

## *Supporting Information*

# **Substituent-controllable regioselective annulation of $\beta$ -enaminones with *N*-sulfonyl triazoles for modular access to imidazoles and pyrroles**

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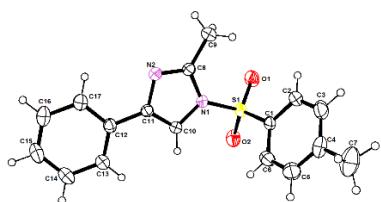
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### 1. X-ray crystallographic data of compound 3a



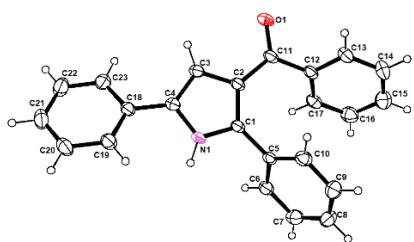
**Figure S1.** ORTEP drawing of compound 3a (30% probability for the thermal ellipsoid).

The purified compound 3a is dissolved in a mixed solvent of ethyl acetate and petroleum ether, and placed in a dark cabinet to slowly evaporate. After several days, a colourless bulk crystal was obtained. The X-ray crystal-structure determinations were obtained on a Bruker Smart CCDC APEX-2 diffractometer (graphite- monochromated Mo  $K\alpha$  radiation,  $\lambda=0.71073$  nm) at 298 K.

**Table S1.** Crystal data and structure refinement for compound 3a.

CCDC number	2260879
Identification code	20191014c
Empirical formula	C17 H16 N2 O2 S
Formula weight	312.38
Temperature	298.15 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Unit cell dimensions	$a = 12.6175(5)$ Å $\alpha = 90^\circ$ . $b = 12.5587(5)$ Å $\beta = 99.2860(10)$ . $c = 10.4154(4)$ Å $\gamma = 90^\circ$ .
Volume	1628.79(11) Å <sup>3</sup>
Z	4
Density (calculated)	1.274 g/cm <sup>3</sup>
$\mu$	0.207 mm <sup>-1</sup>
F(000)	656.0
Crystal size	0.21 × 0.2 × 0.19 mm <sup>3</sup>
2 $\Theta$ range for data collection	5.722 to 55.072°
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -13 ≤ l ≤ 13
Reflections collected	42190
Independent reflections	3738 [R(int) = 0.0258, R(sigma) = 0.0119]
Data / restraints / parameters	3738 / 0 / 201
Goodness-of-fit on F <sup>2</sup>	1.088
Final R indices [I>2sigma(I)]	R <sub>1</sub> = 0.0429, wR <sub>2</sub> = 0.1112
Final R indices (all data)	R <sub>1</sub> = 0.0511, wR <sub>2</sub> = 0.1204
Largest diff. peak and hole	0.21 and -0.43 eÅ <sup>-3</sup>

### 1. X-ray crystallographic data of compound 5a



**Figure S2.** ORTEP drawing of compound **5a** (30% probability for the

The purified compound **5a** is dissolved in a mixed solvent of ethyl acetate and petroleum ether, and placed in a dark cabinet to slowly evaporate. After several days, a colourless bulk crystal was obtained. The X-ray crystal-structure determinations were obtained on a Bruker Smart CCDC APEX-2 diffractometer (graphite- monochromated Mo  $K\alpha$  radiation,  $\lambda=0.71073$  nm) at 298 K.

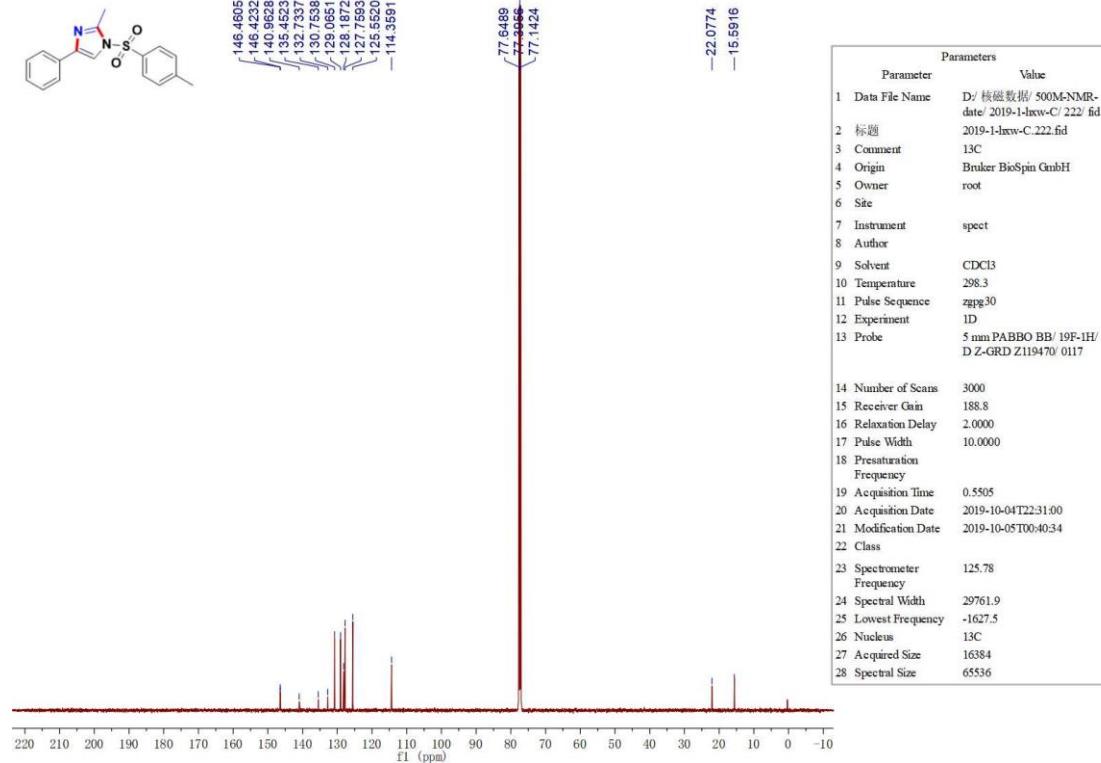
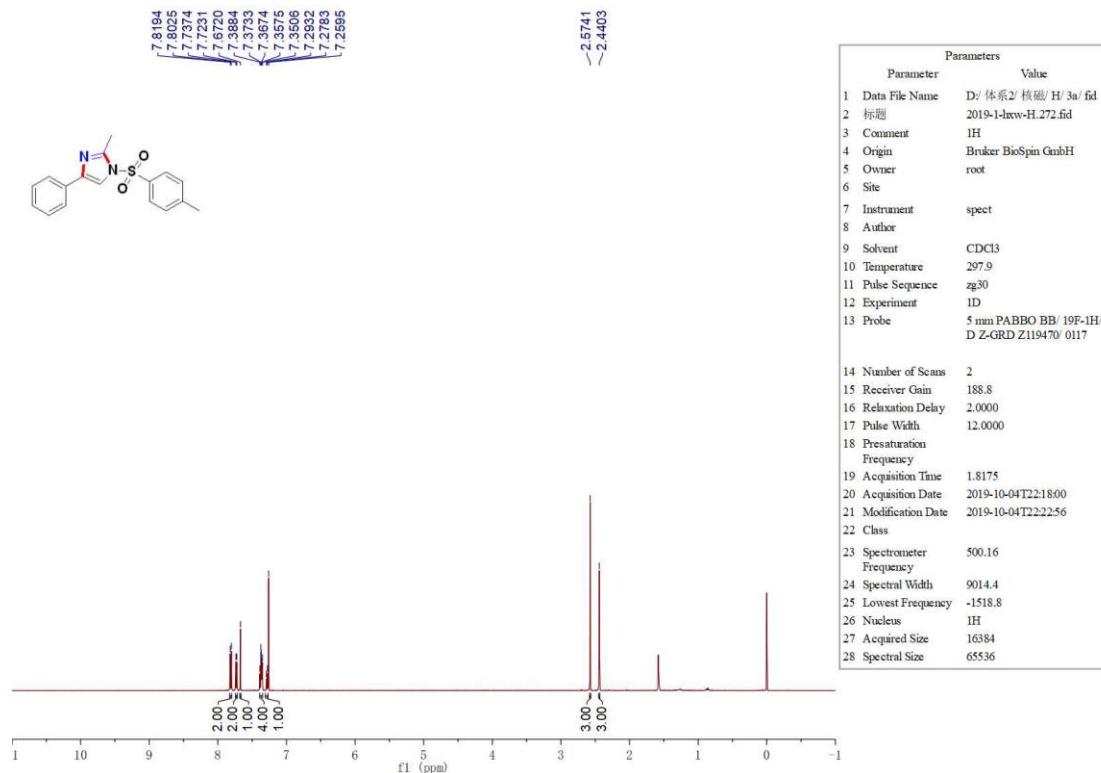
thermal ellipsoid).

**Table S2.** Crystal data and structure refinement for compound **5a**.

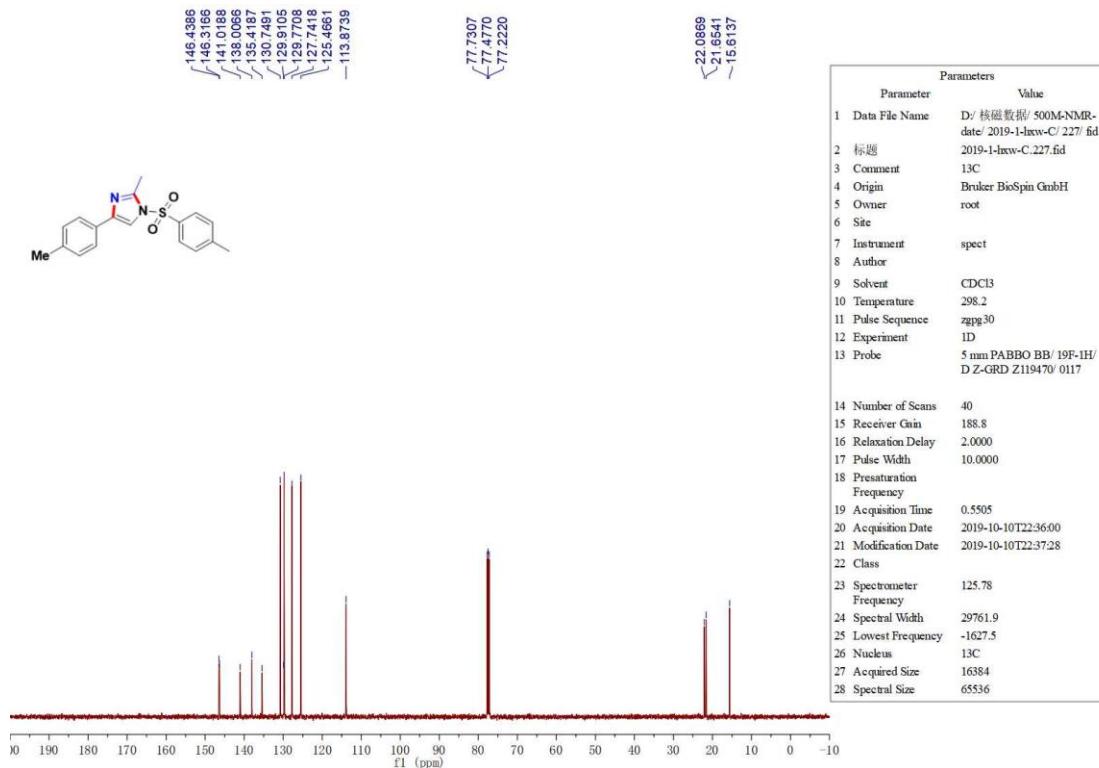
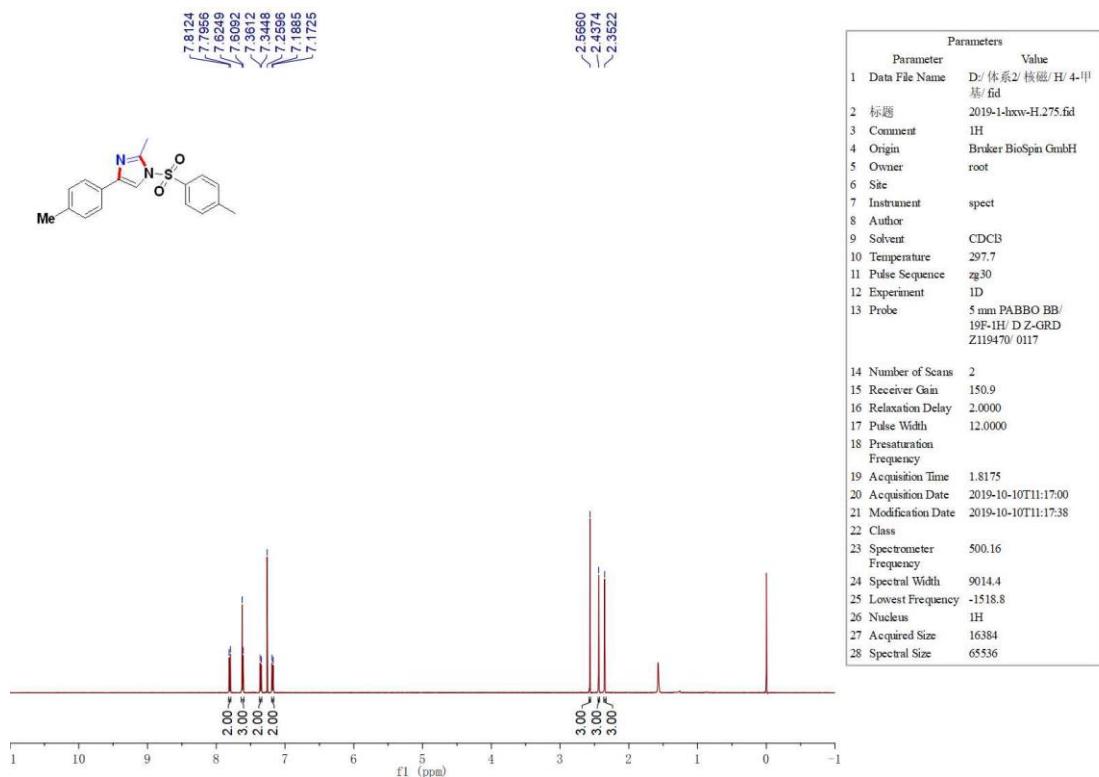
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Identification code	mo_20200109b_0m_a	
Empirical formula	C23 H17 N O	
Formula weight	323.38	
Temperature	298.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 9.9209(10)$ Å	$\alpha = 113.914(4)^\circ$
	$b = 13.3600(16)$ Å	$\beta = 91.364(4)^\circ$
	$c = 14.6495(16)$ Å	$\gamma = 102.145(5)^\circ$
Volume	$1722.3(3)$ Å <sup>3</sup>	
Z	4	
Density (calculated)	1.247 g/cm <sup>3</sup>	
$\mu$	0.076 mm <sup>-1</sup>	
F(000)	680.0	
Crystal size	$0.23 \times 0.21 \times 0.2$ mm <sup>3</sup>	
$2\Theta$ range for data collection	5.84 to 55.168°	
Index ranges	$-12 \leq h \leq 12, -17 \leq k \leq 17, -19 \leq l \leq 19$	
Reflections collected	68223	
Independent reflections	7947 [R(int) = 0.0439, R(sigma) = 0.0241]	
Data / restraints / parameters	7947 / 0 / 451	
Goodness-of-fit on F <sup>2</sup>	1.046	
Final R indices [I>2sigma(I)]	R <sub>1</sub> = 0.0547, wR <sub>2</sub> = 0.1552	
Final R indices (all data)	R <sub>1</sub> = 0.0784, wR <sub>2</sub> = 0.1779	
Largest diff. peak and hole	0.26 and -0.29 eÅ <sup>-3</sup>	

### 3. NMR spectra for all compounds

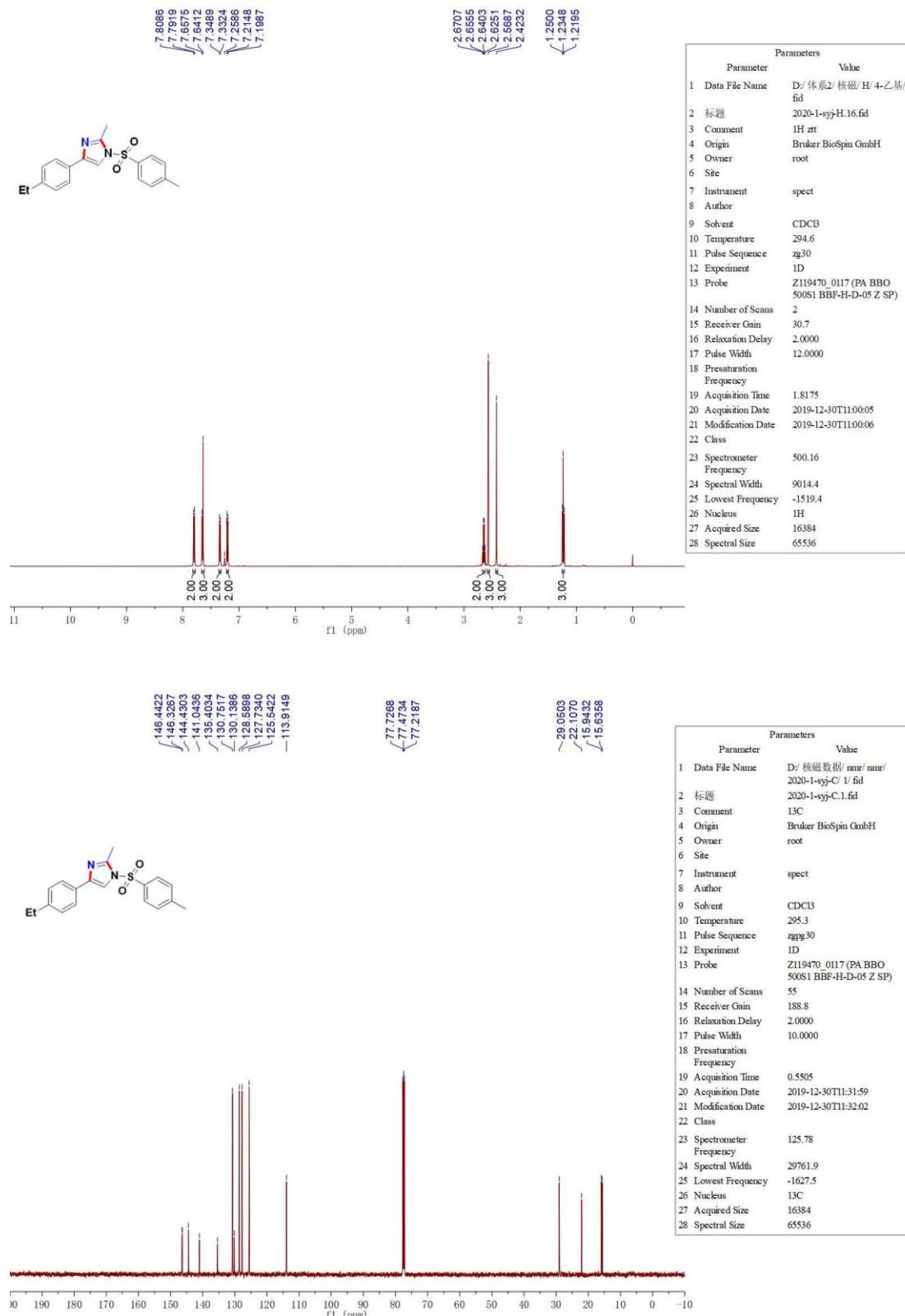
#### 2-Methyl-4-phenyl-1-tosyl-1H-imidazole (3a)



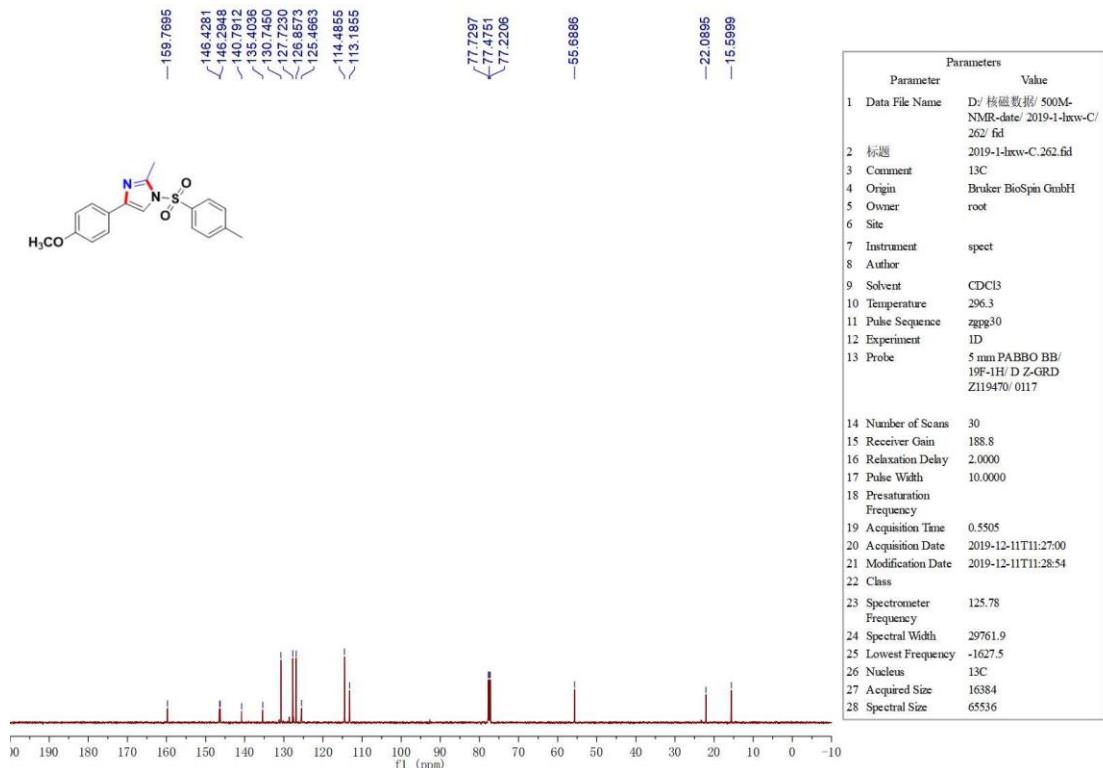
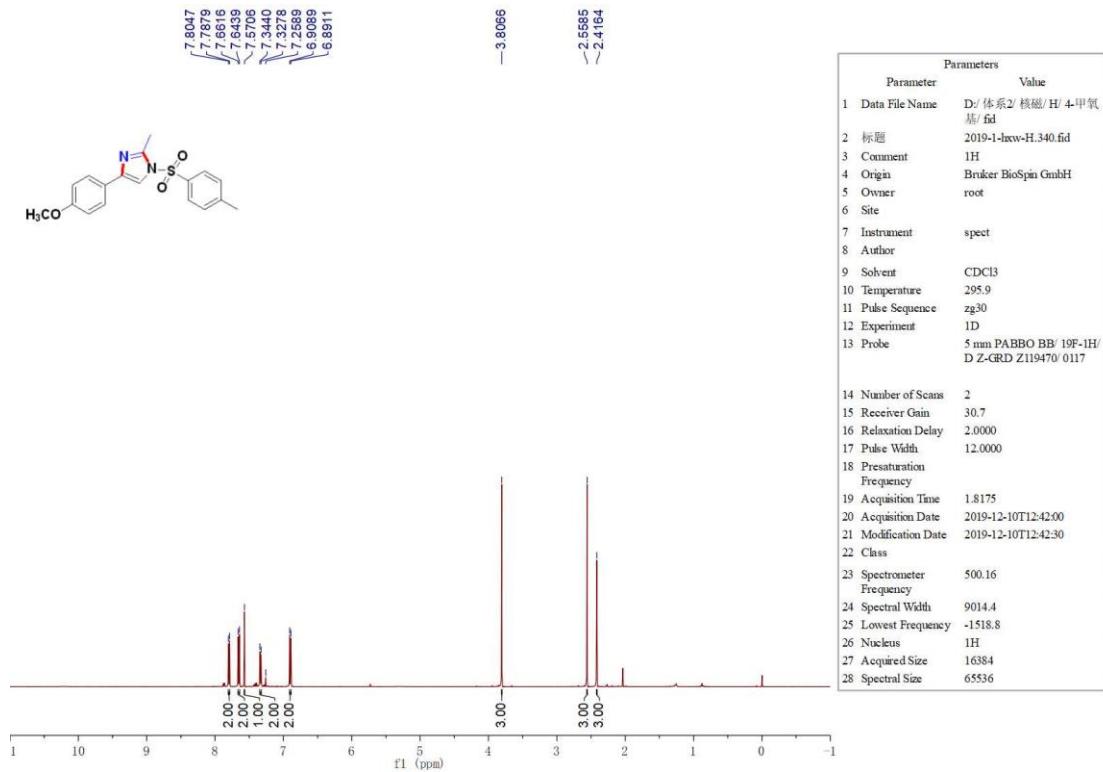
### 2-Methyl-4-(*p*-tolyl)-1-tosyl-1*H*-imidazole (3b)



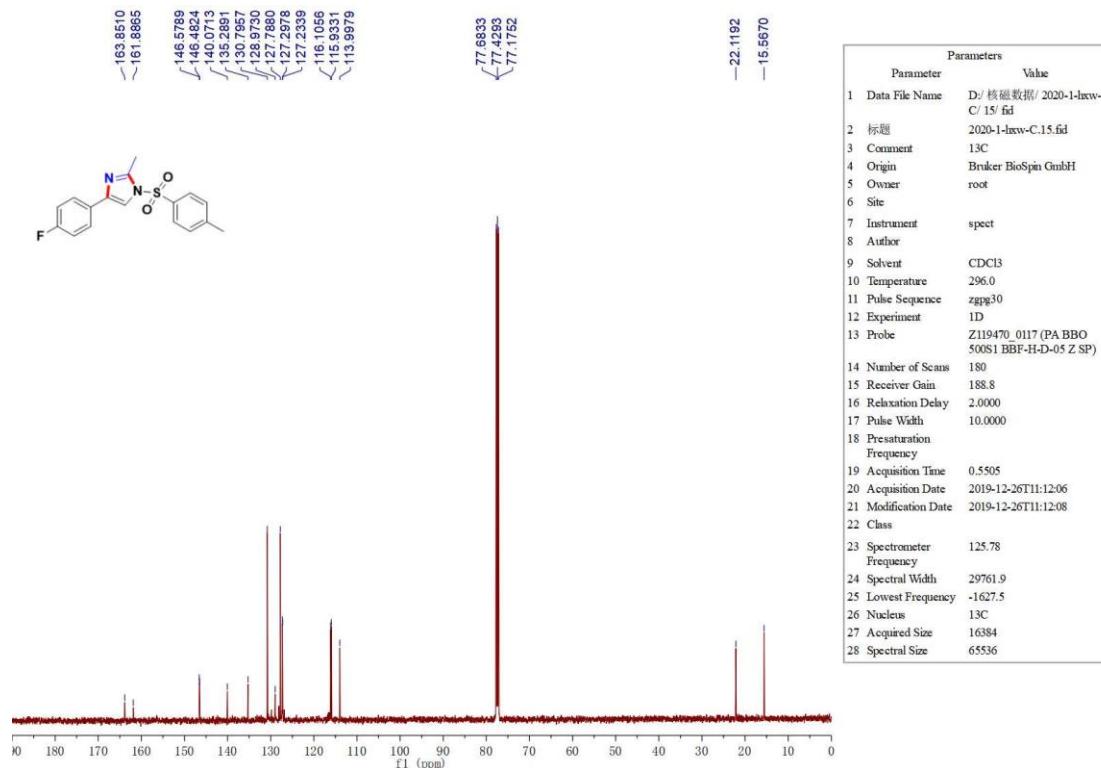
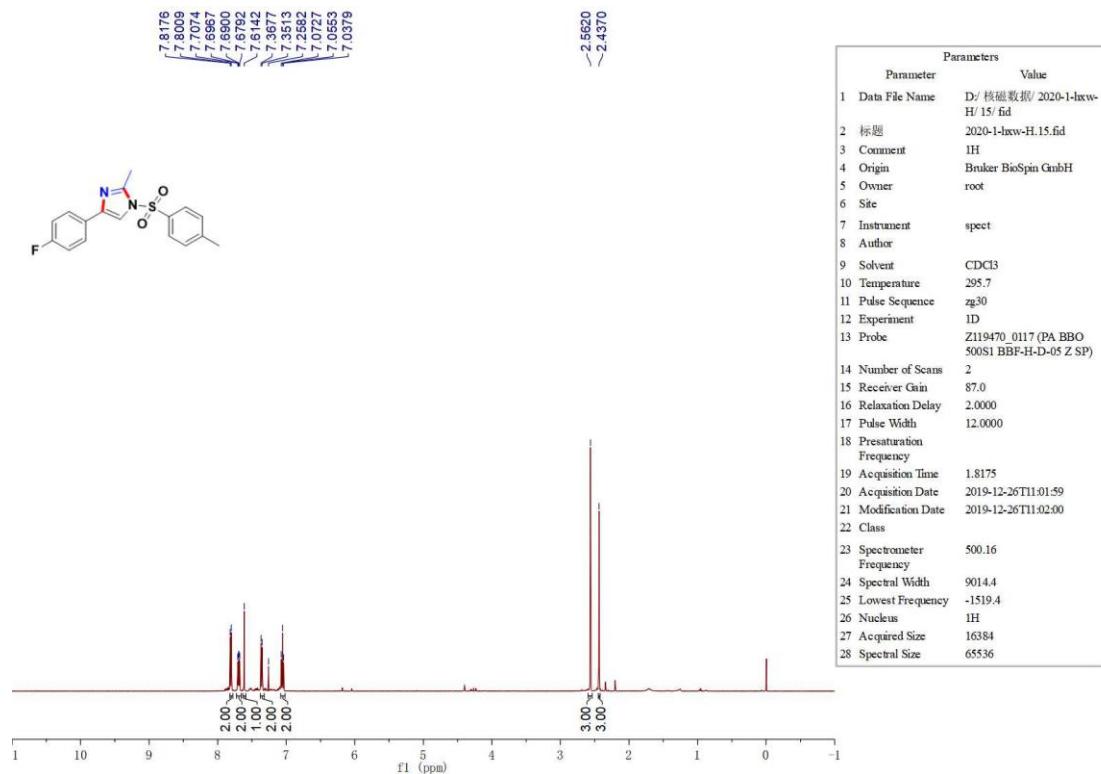
**4-(4-Ethylphenyl)-2-methyl-1-tosyl-1H-imidazole (3c)**



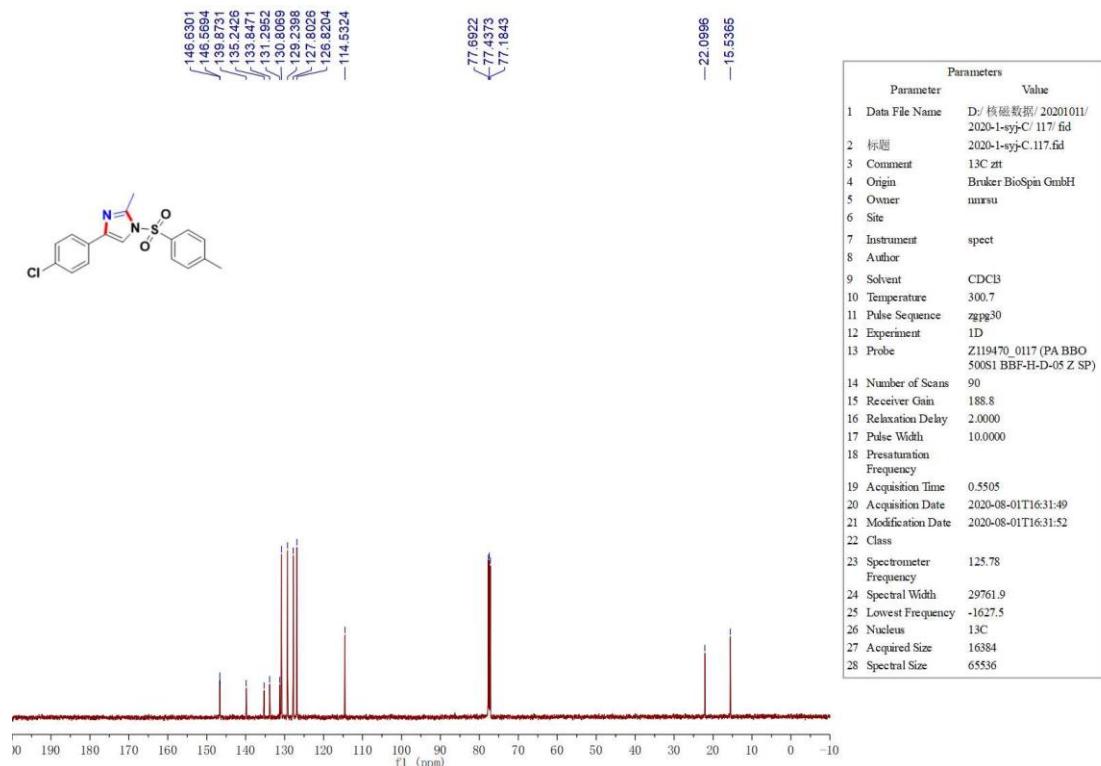
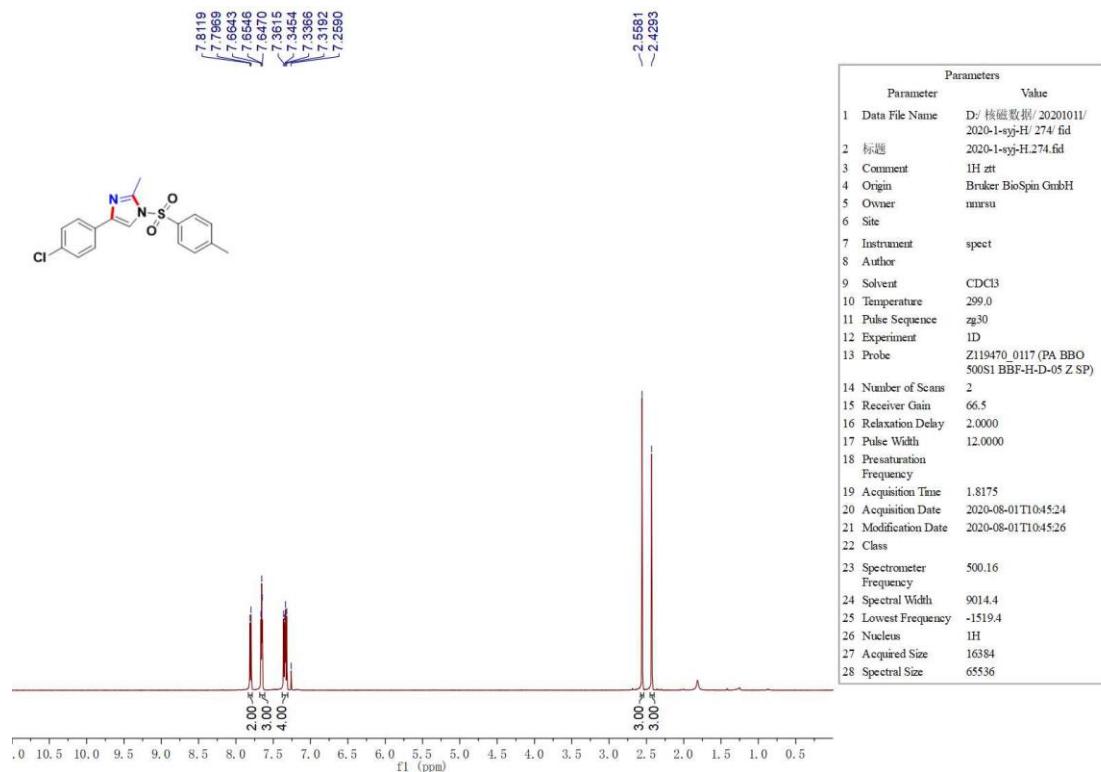
**4-(4-Methoxyphenyl)-2-methyl-1-tosyl-1H-imidazole (3d)**



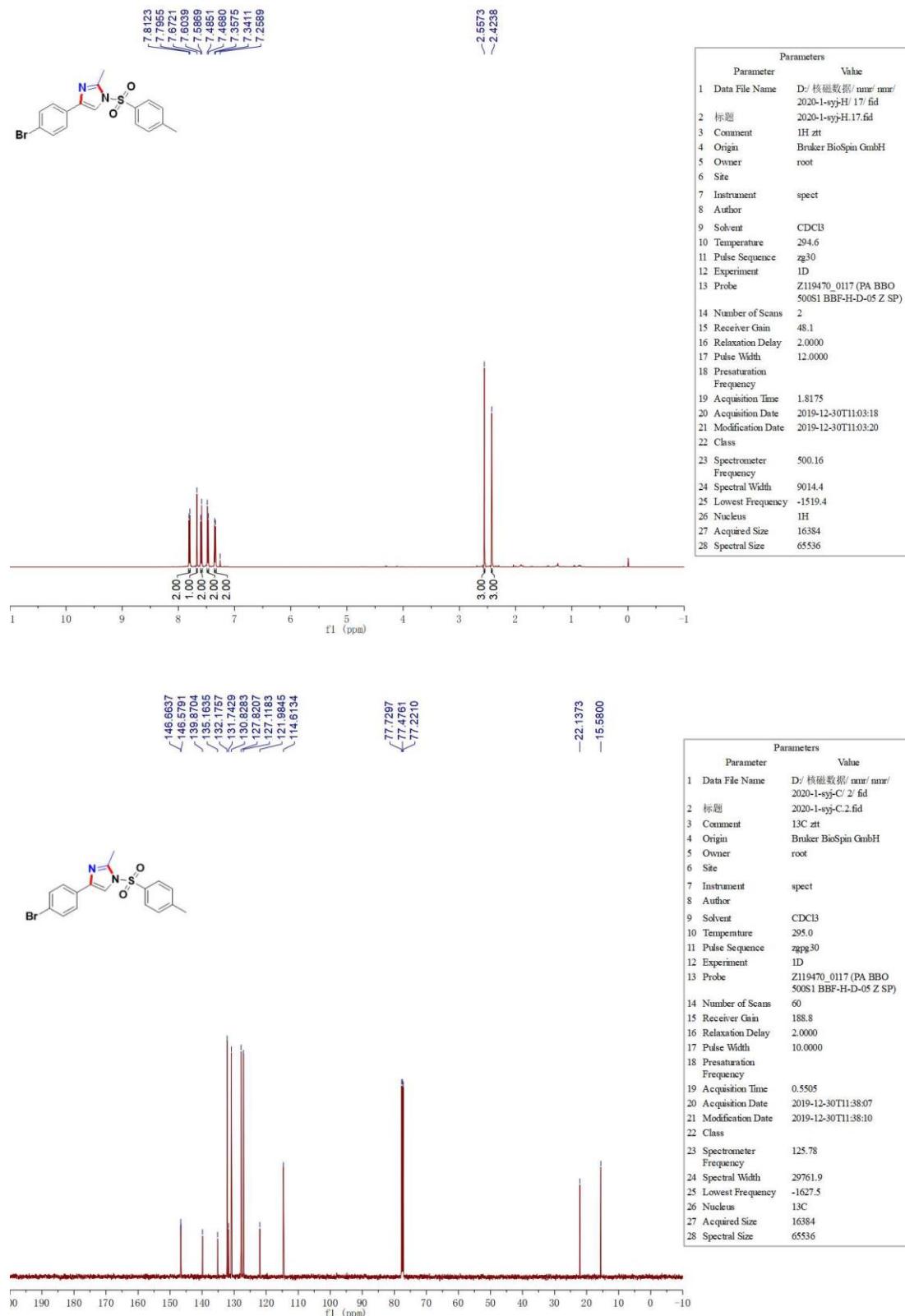
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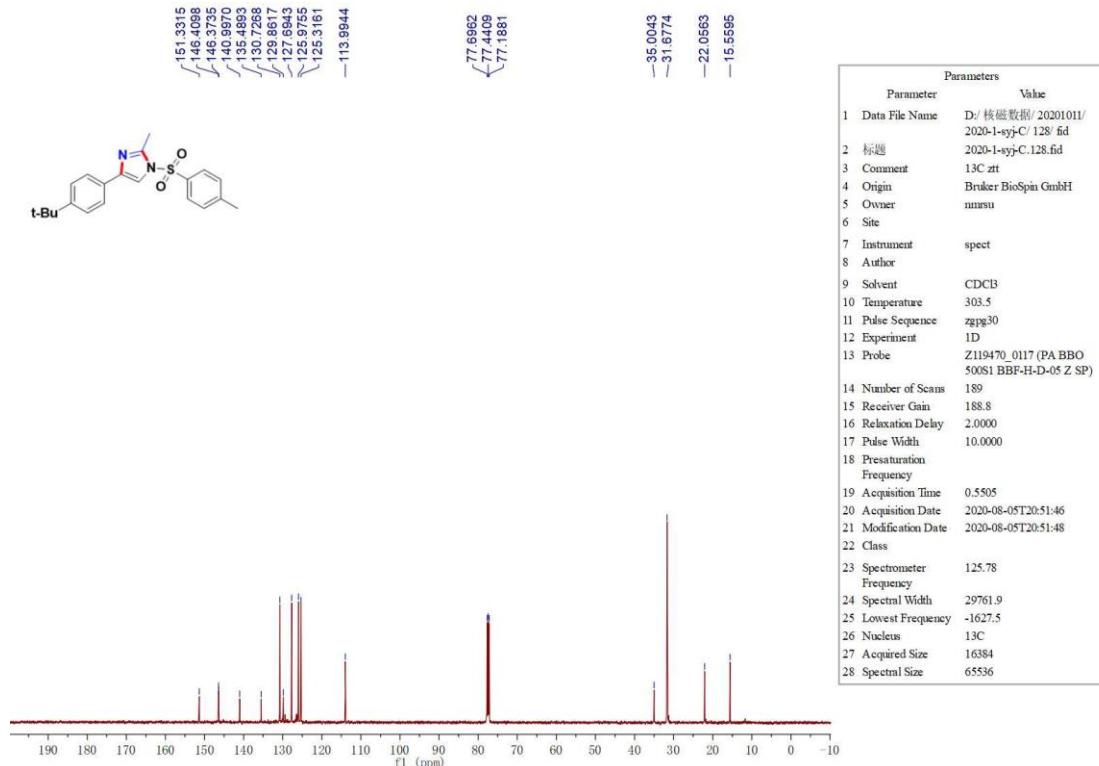
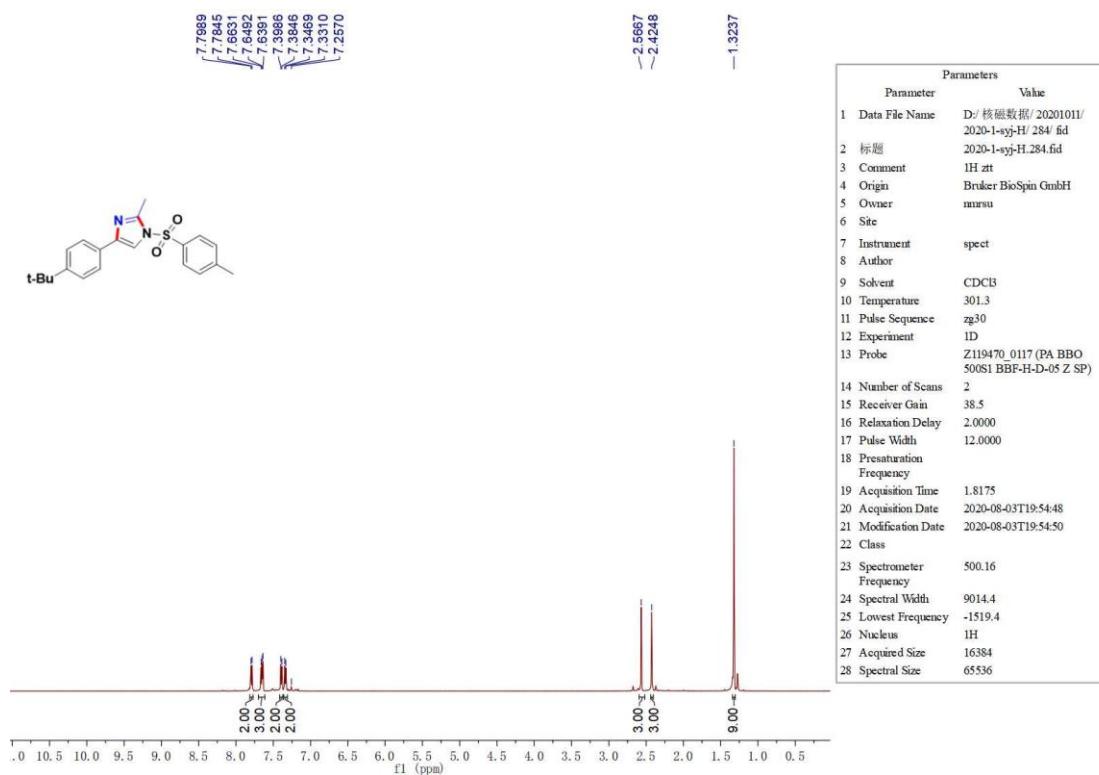
**4-(4-Chlorophenyl)-2-methyl-1-tosyl-1H-imidazole (3f)**



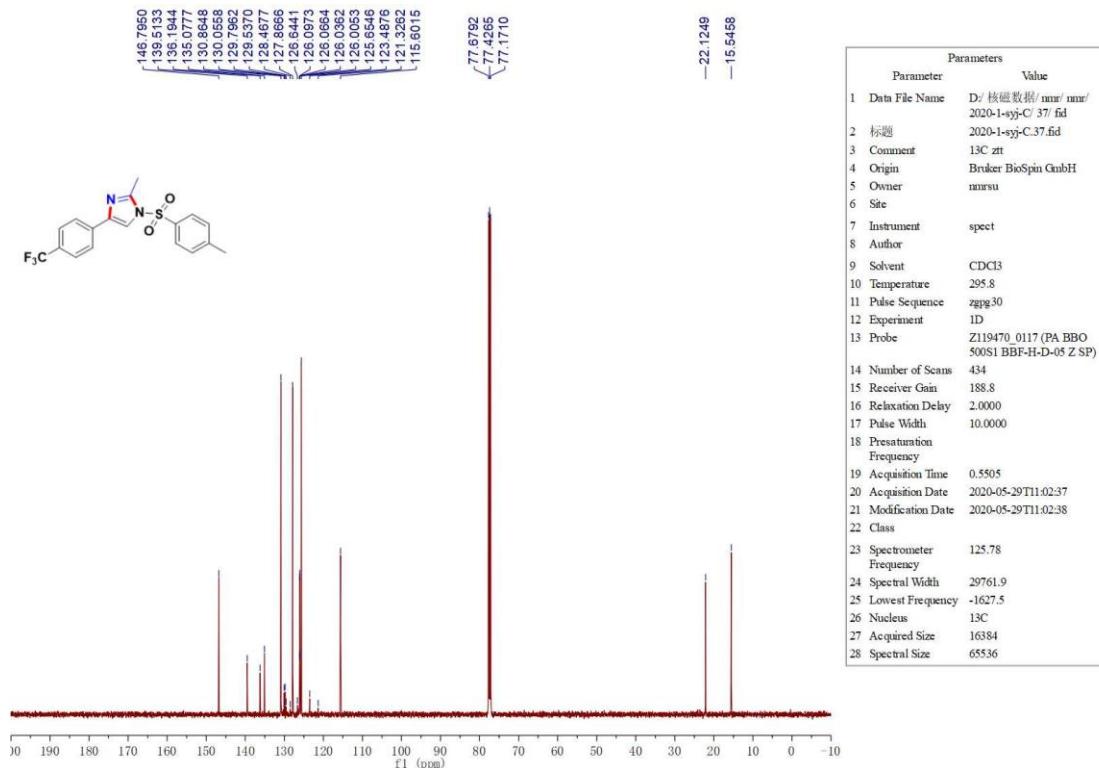
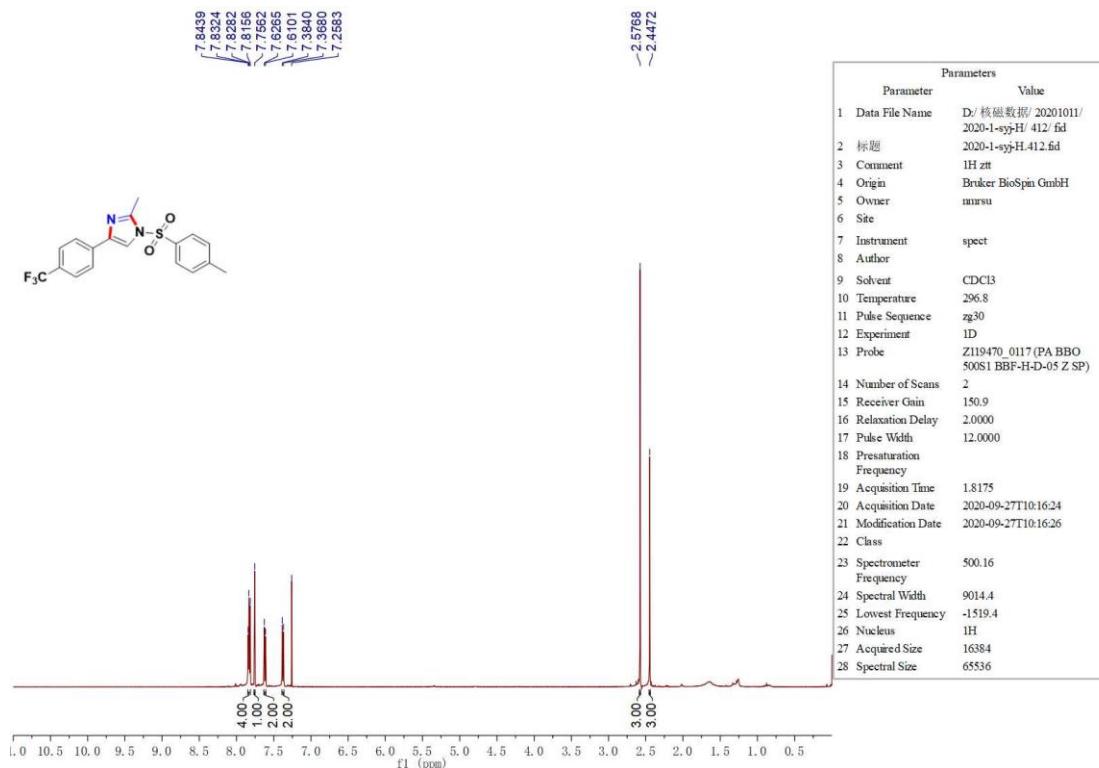
**4-(4-Bromophenyl)-2-methyl-1-tosyl-1*H*-imidazole (3g)**



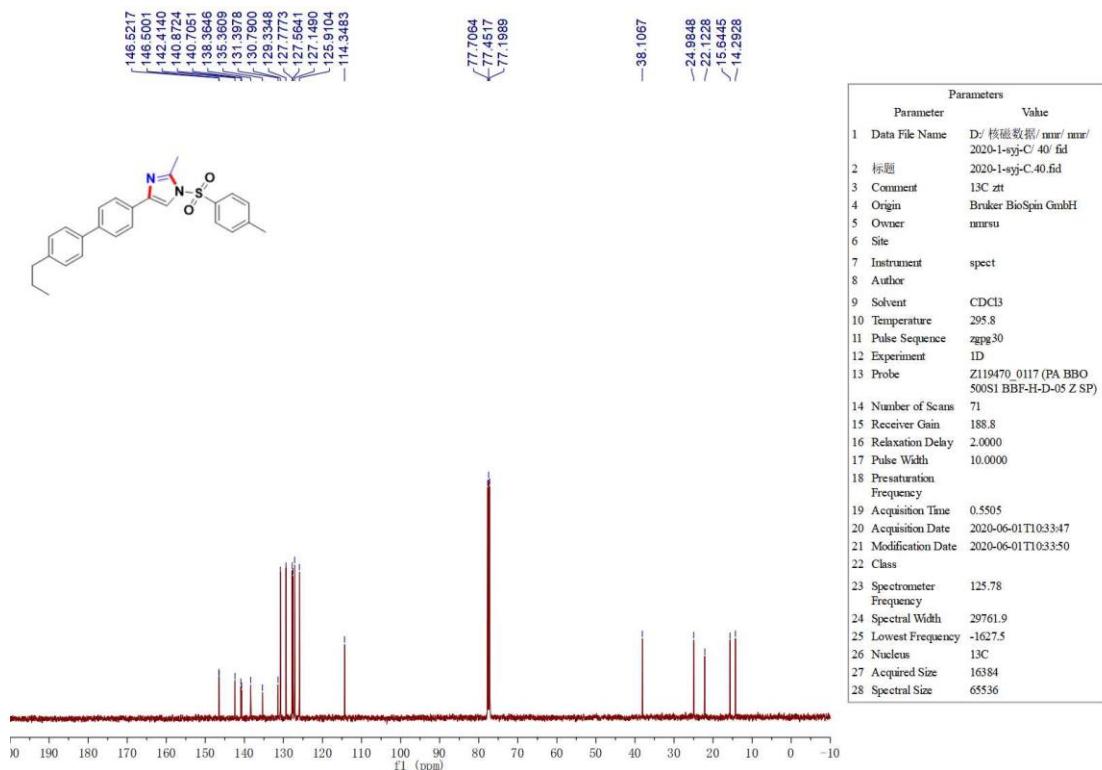
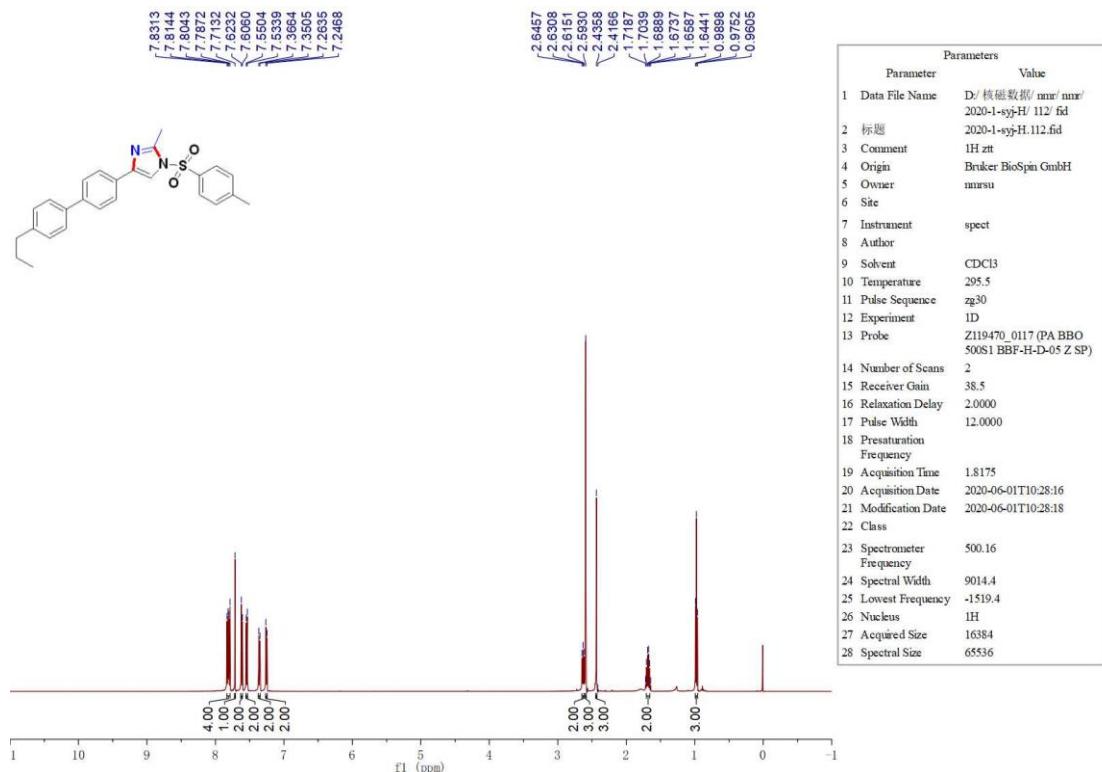
**4-(4-(*tert*-Butyl)phenyl)-2-methyl-1-tosyl-1*H*-imidazole (3h)**



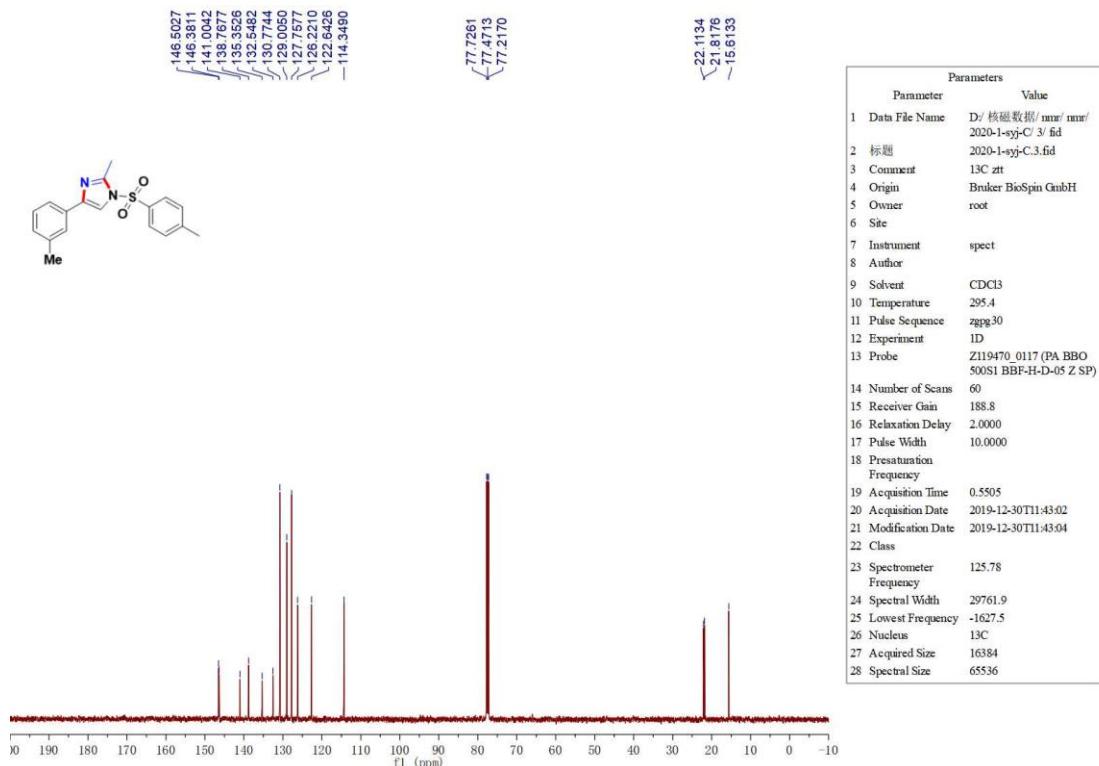
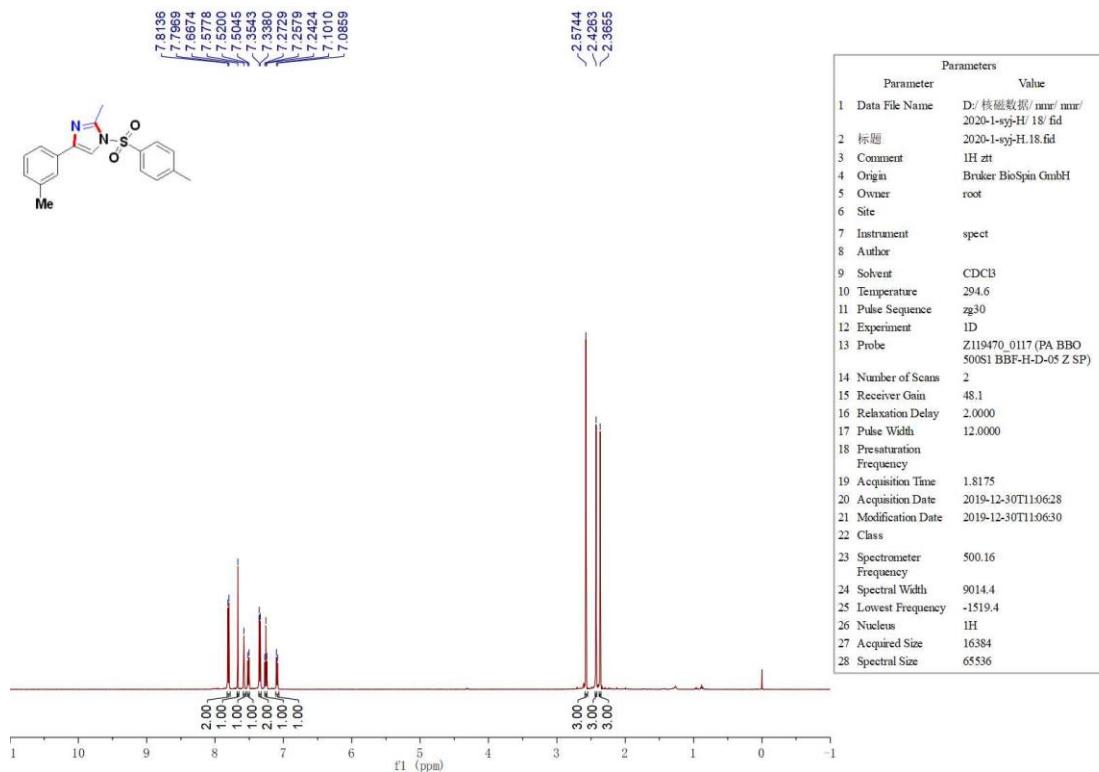
**2-Methyl-1-tosyl-4-(4-(trifluoromethyl)phenyl)-1*H*-imidazole (3i)**



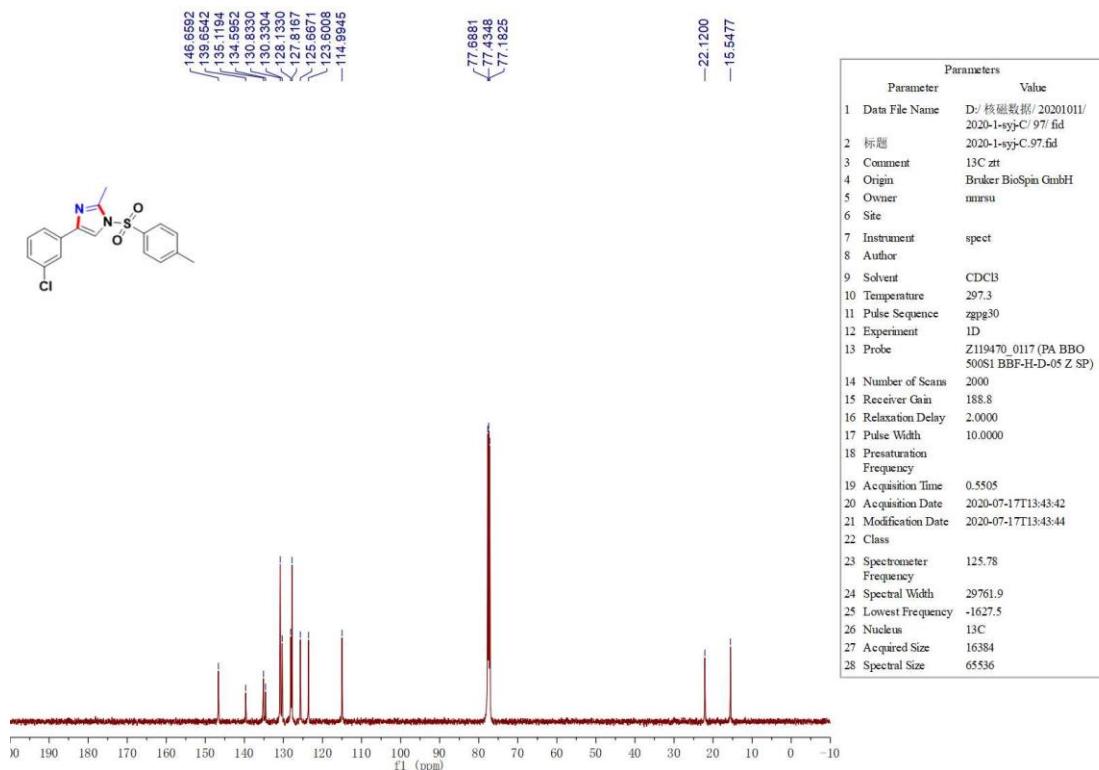
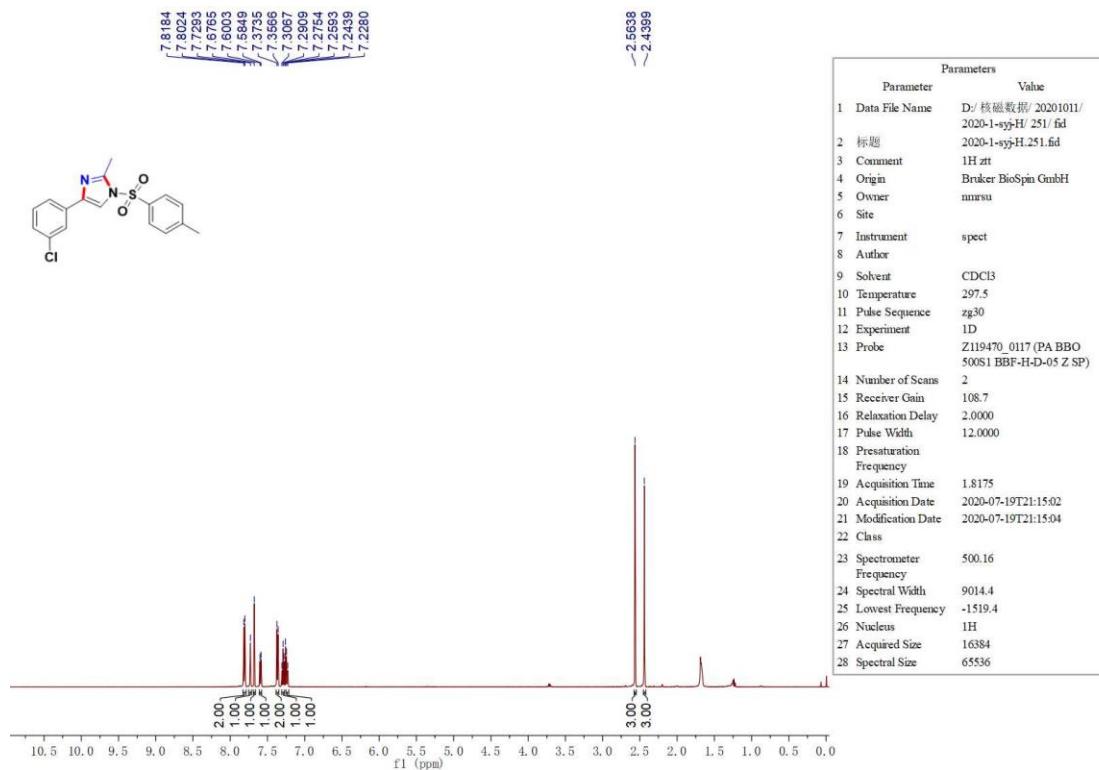
**2-Methyl-4-(4'-propyl-[1,1'-biphenyl]-4-yl)-1-tosyl-1*H*-imidazole (3j)**



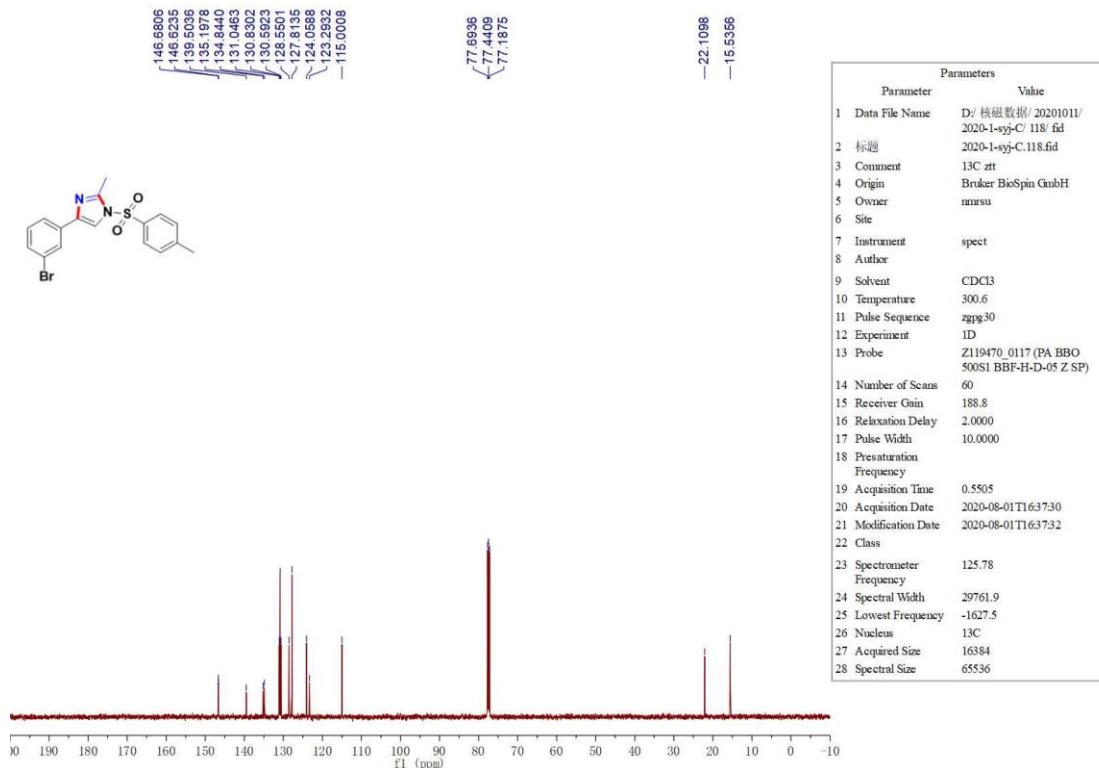
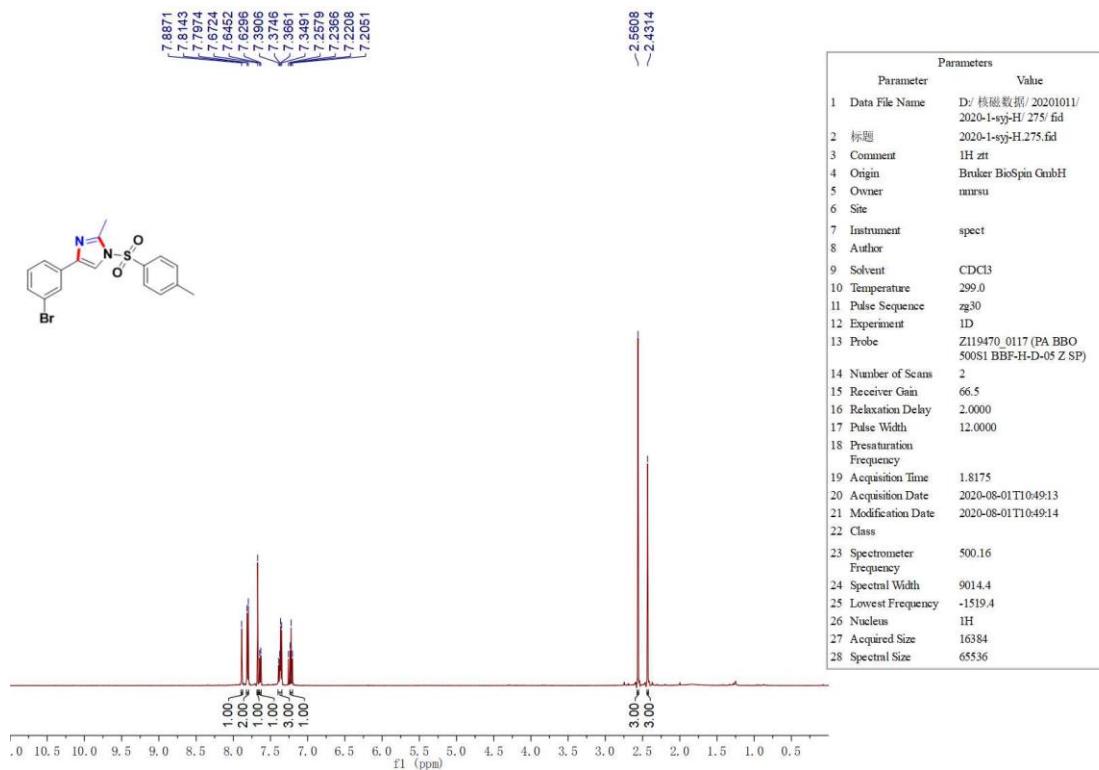
### 2-Methyl-4-(*m*-tolyl)-1-tosyl-1*H*-imidazole (3k)



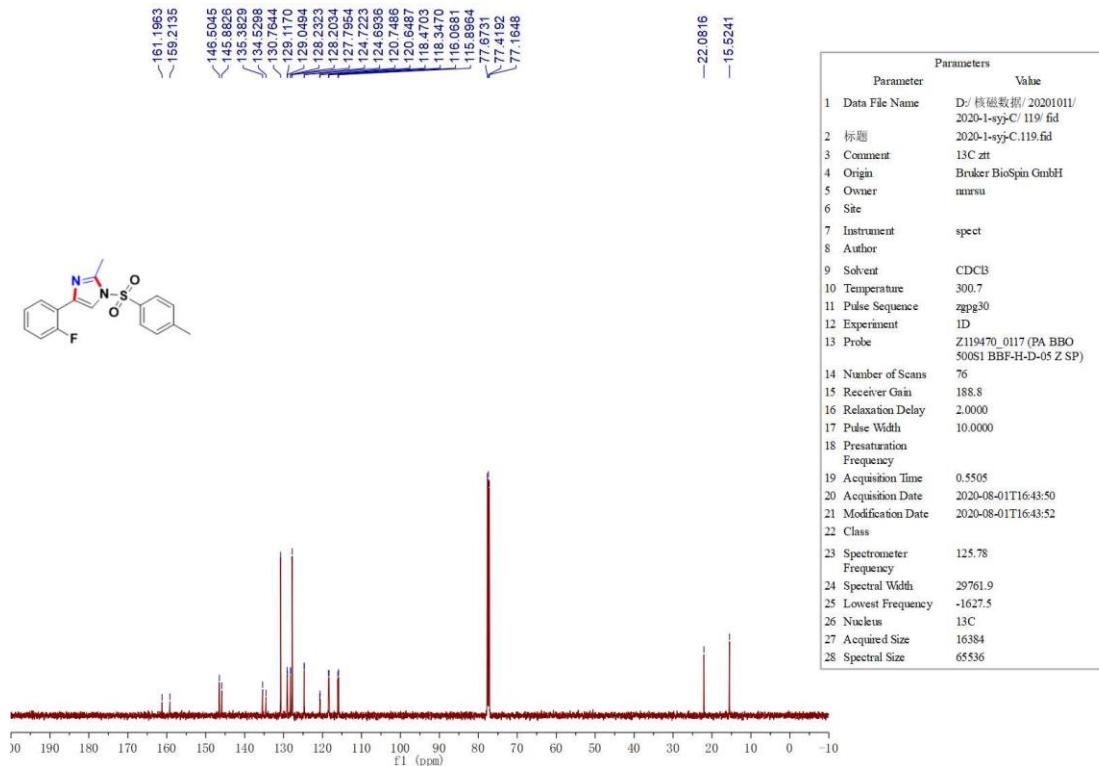
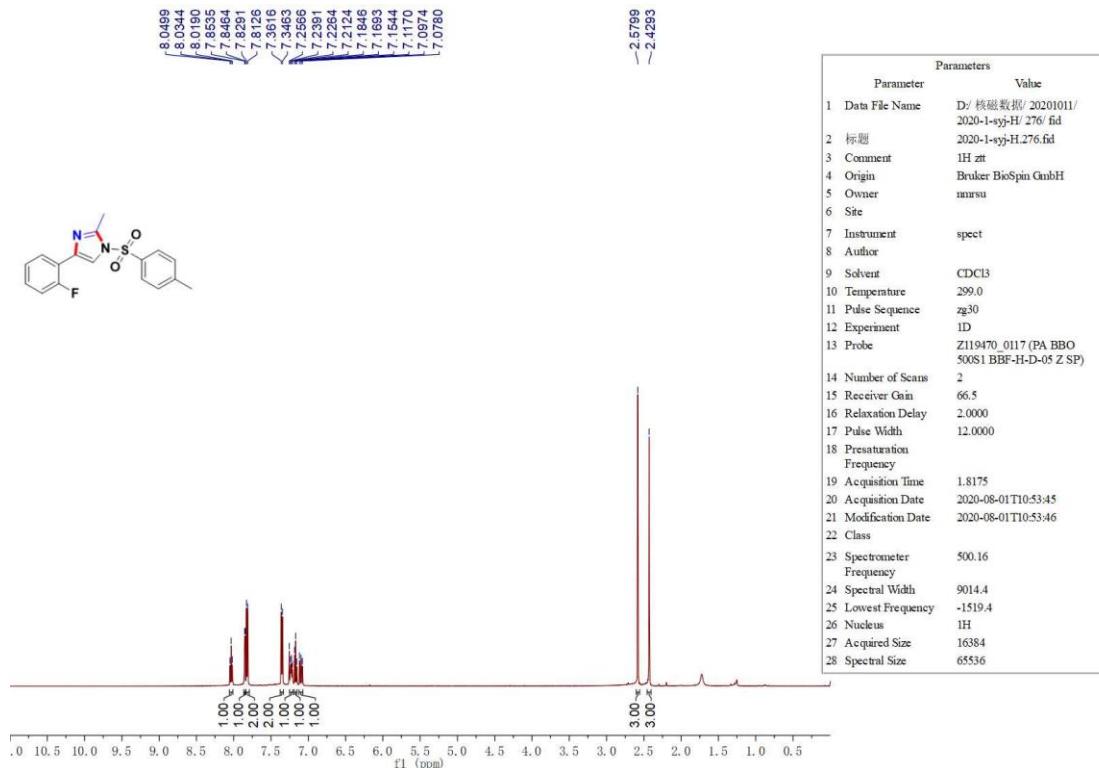
**4-(3-Chlorophenyl)-2-methyl-1-tosyl-1*H*-imidazole (3l)**



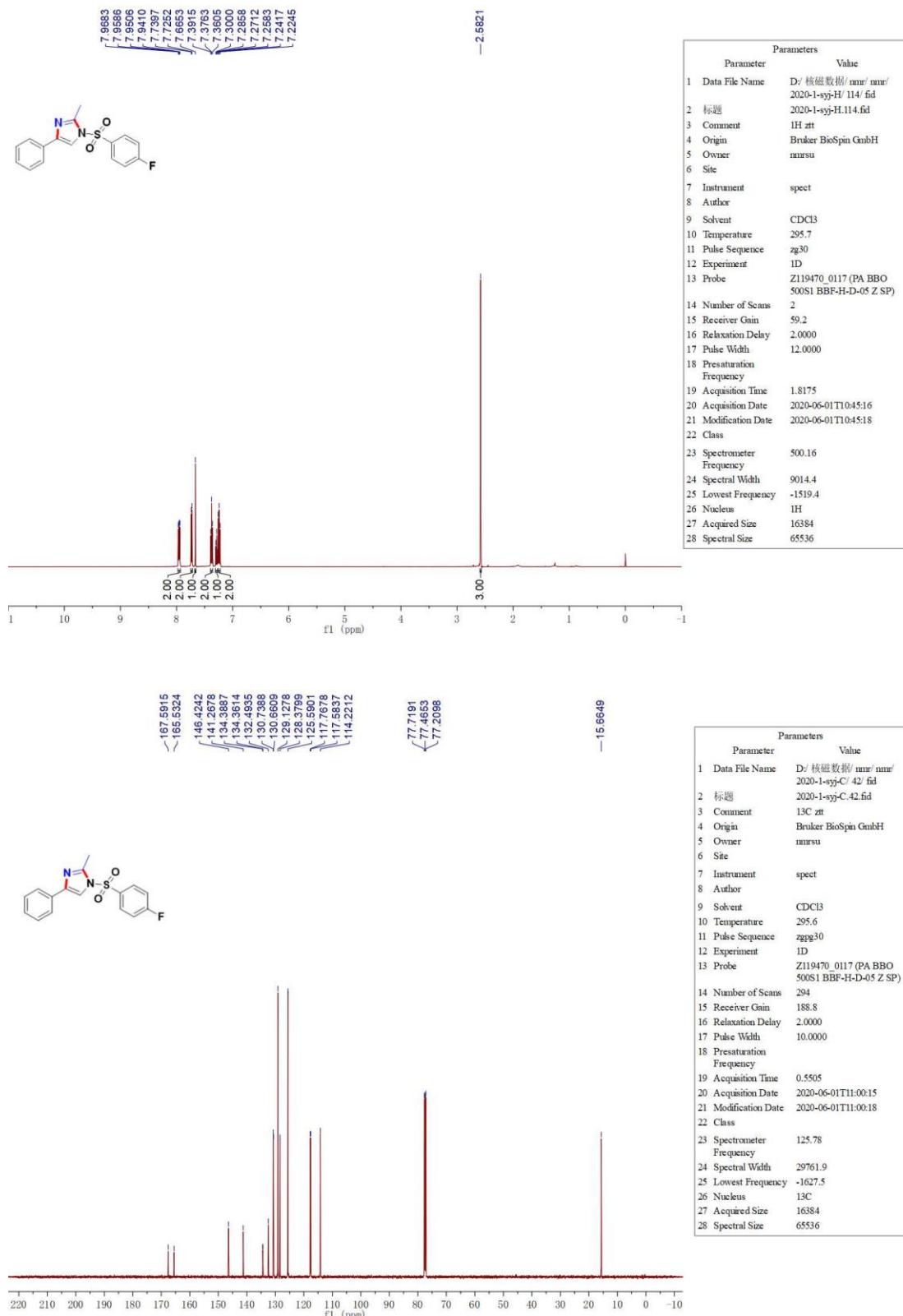
**4-(3-Bromophenyl)-2-methyl-1-tosyl-1*H*-imidazole (3m)**



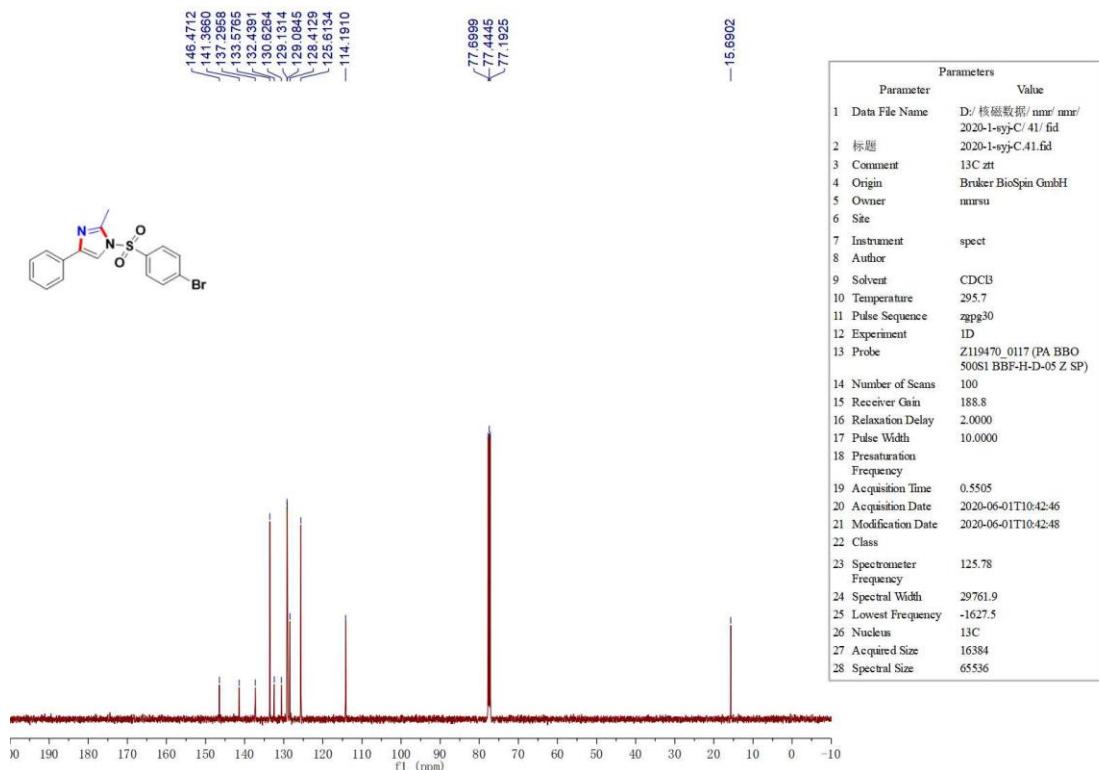
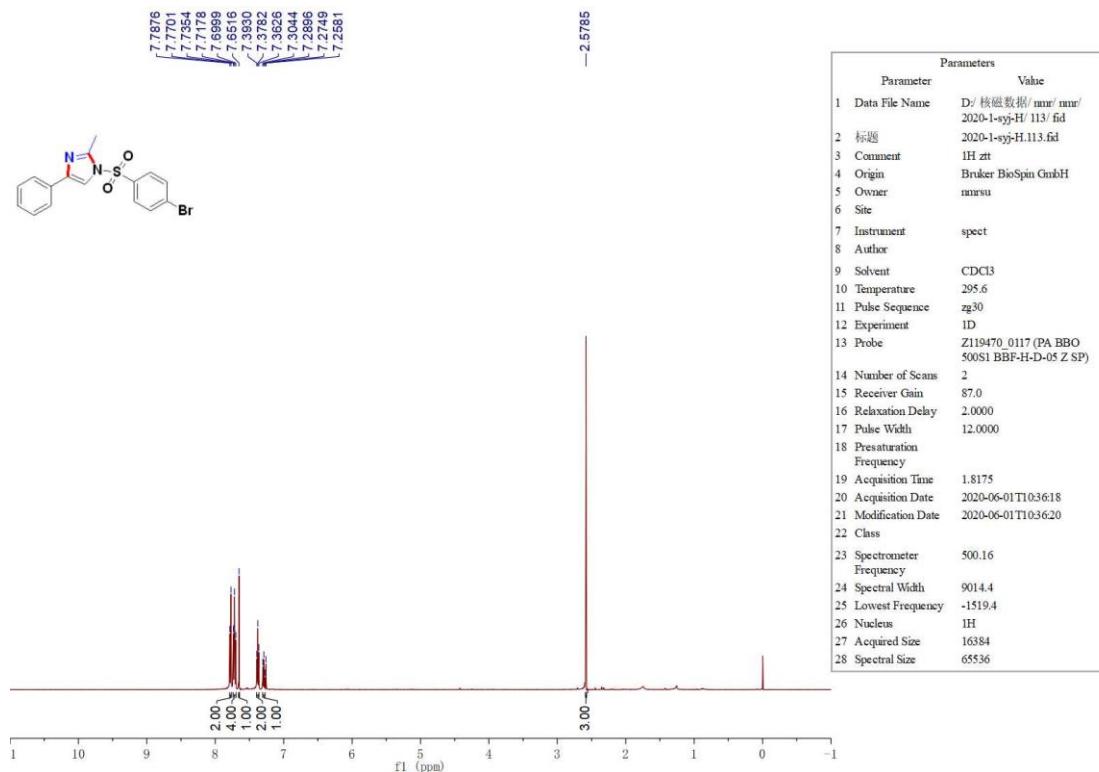
**4-(2-Fluorophenyl)-2-methyl-1-tosyl-1H-imidazole (3n)**



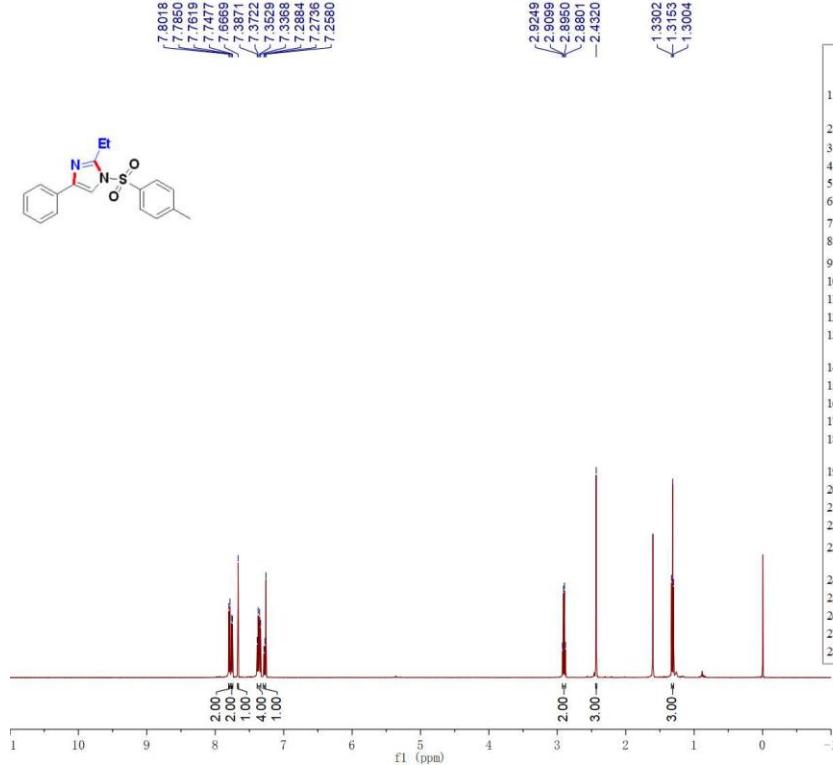
**1-((4-Fluorophenyl)sulfonyl)-2-methyl-4-phenyl-1*H*-imidazole (3o)**



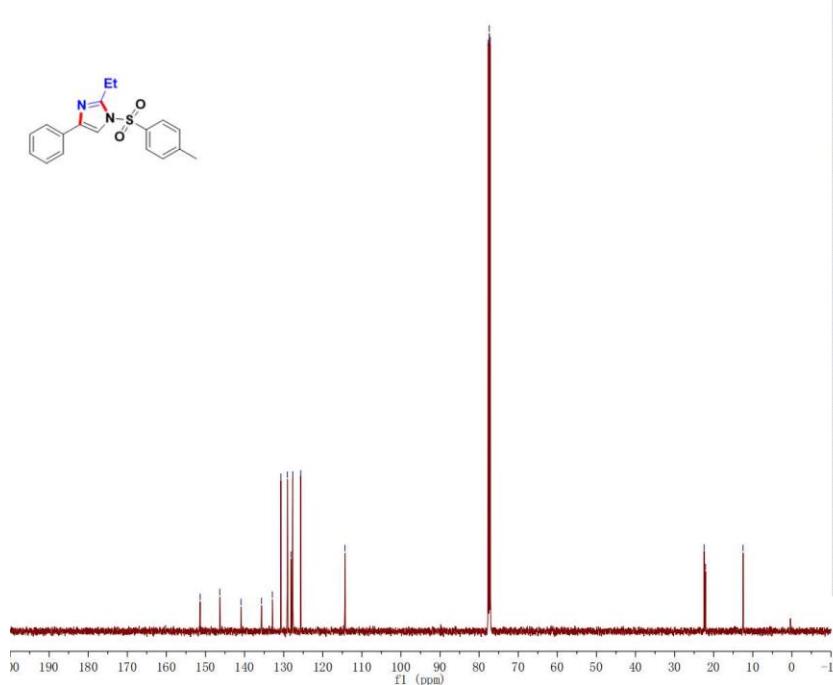
**1-((4-Bromophenyl)sulfonyl)-2-methyl-4-phenyl-1*H*-imidazole (3p)**



### 2-Ethyl-4-phenyl-1-tosyl-1*H*-imidazole (3q)

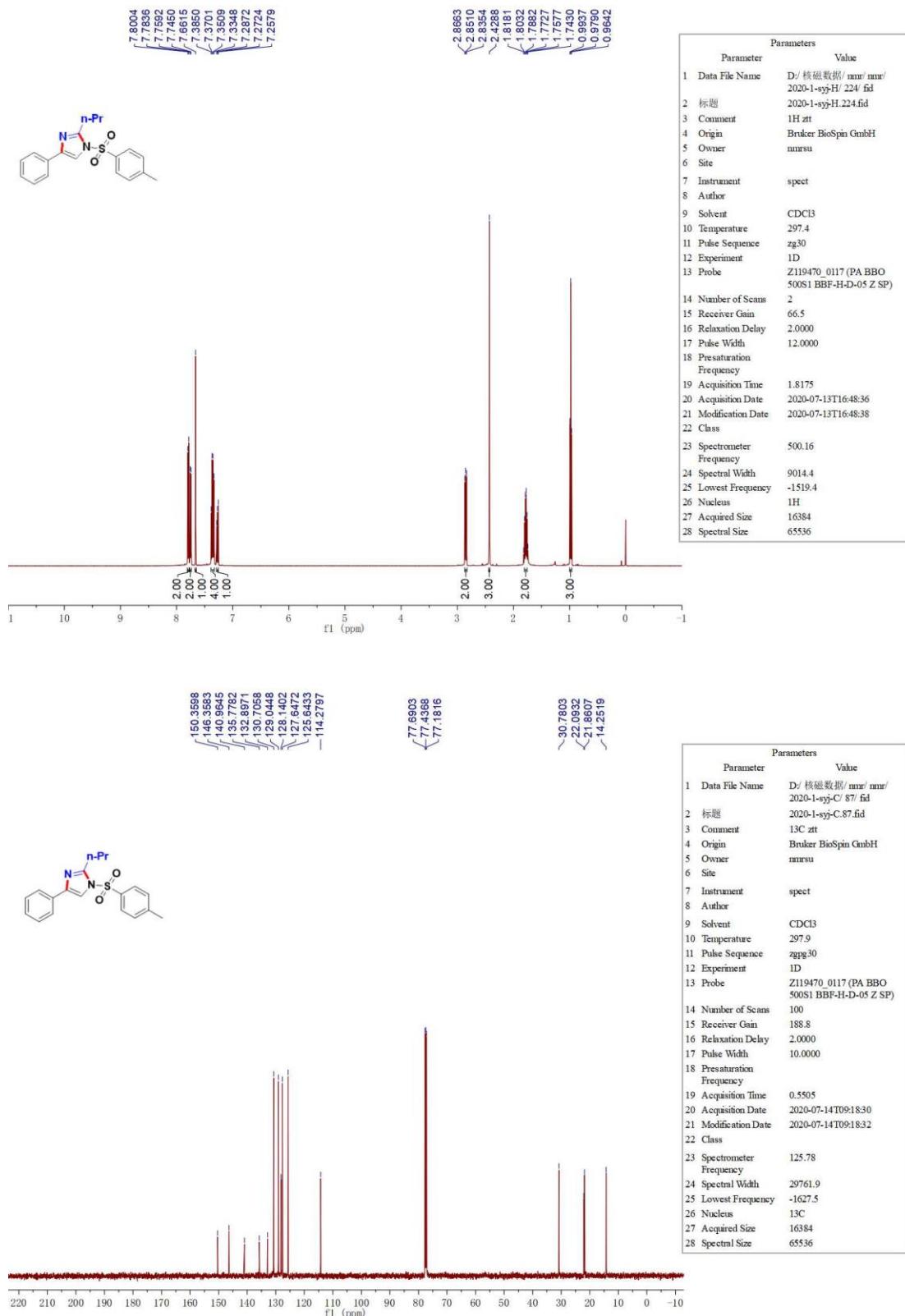


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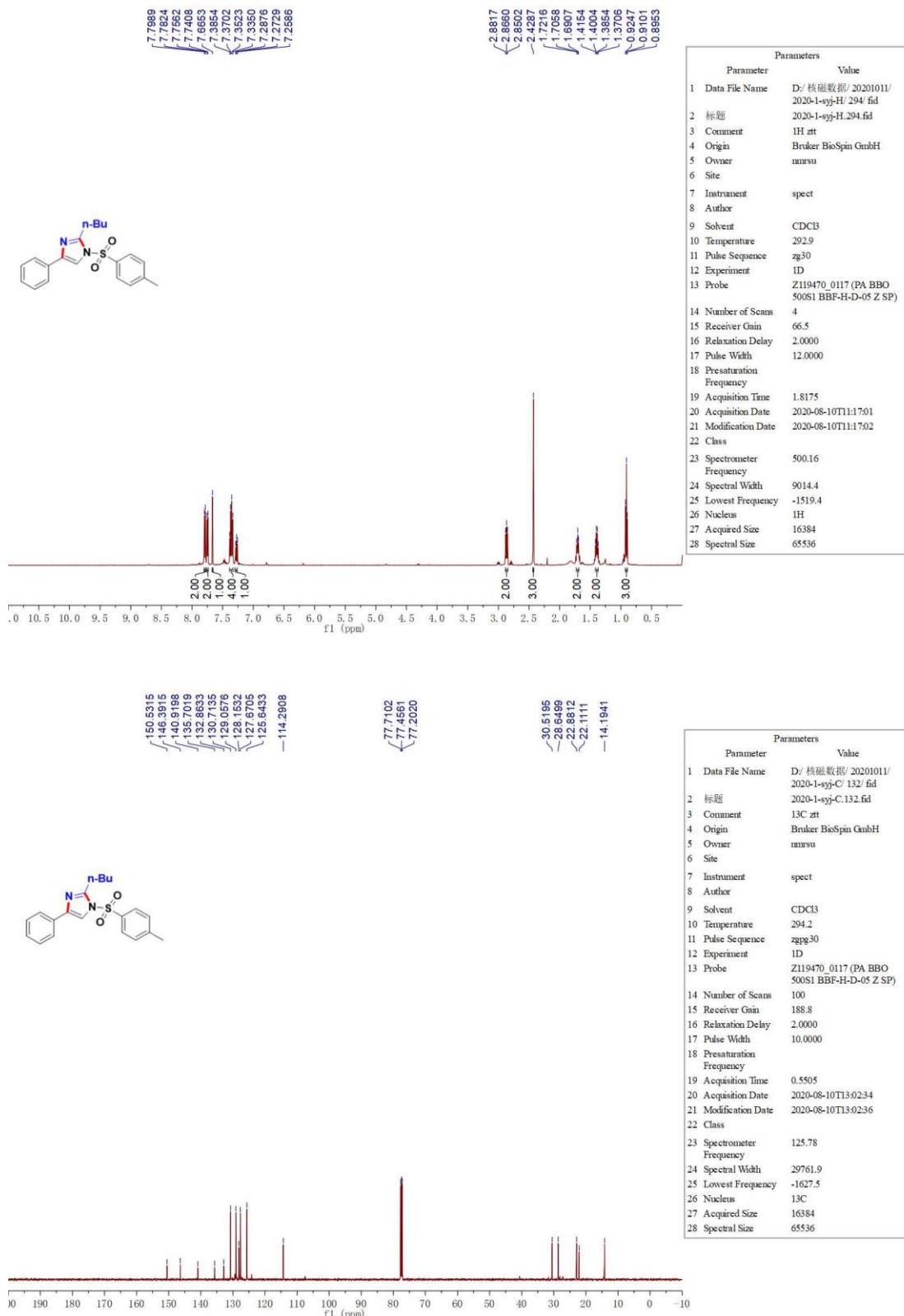


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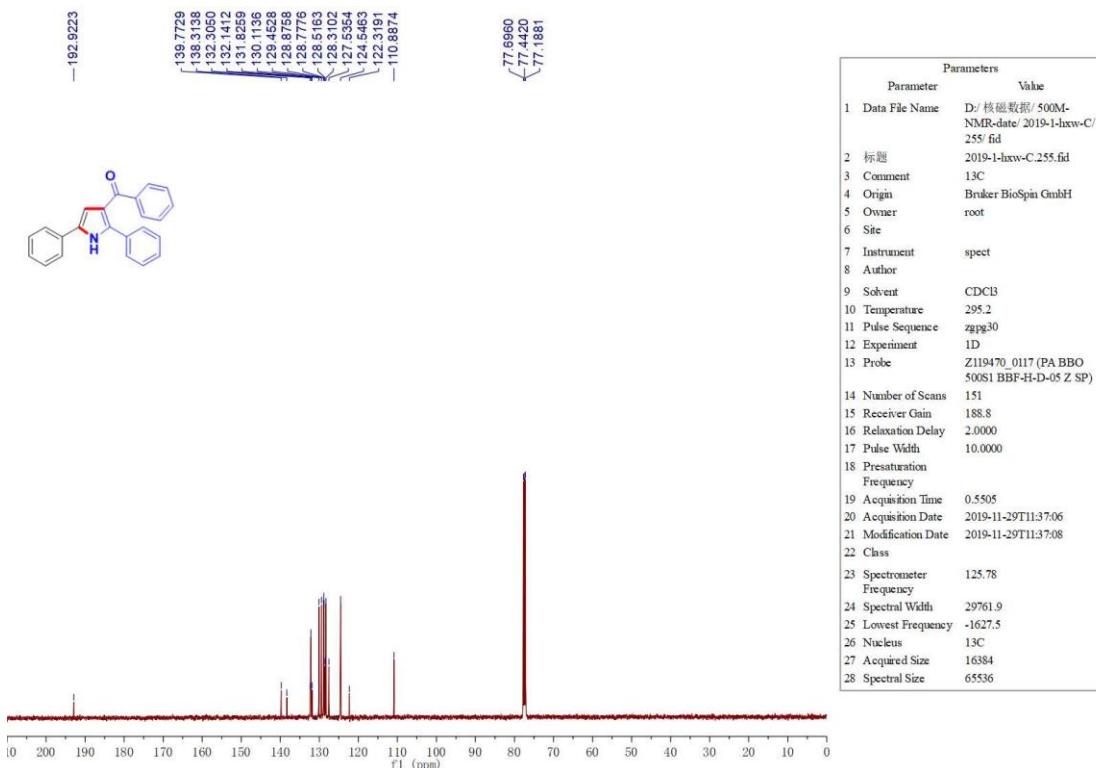
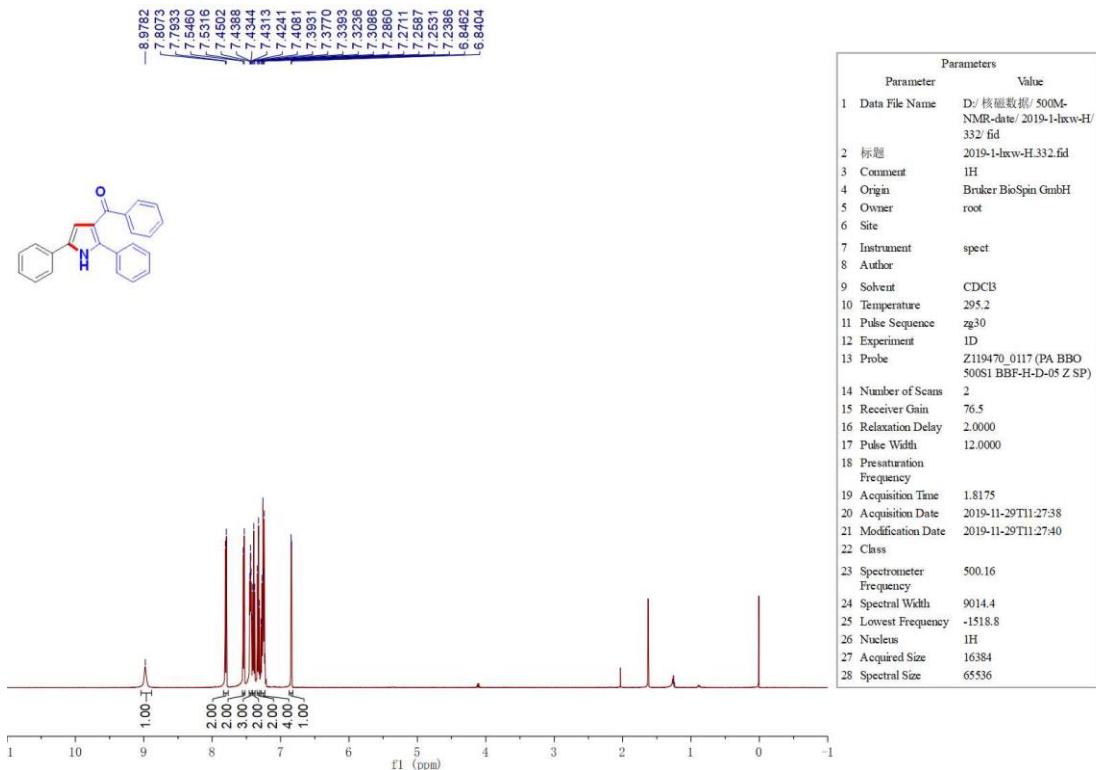
### 4-Phenyl-2-propyl-1-tosyl-1H-imidazole (3r)



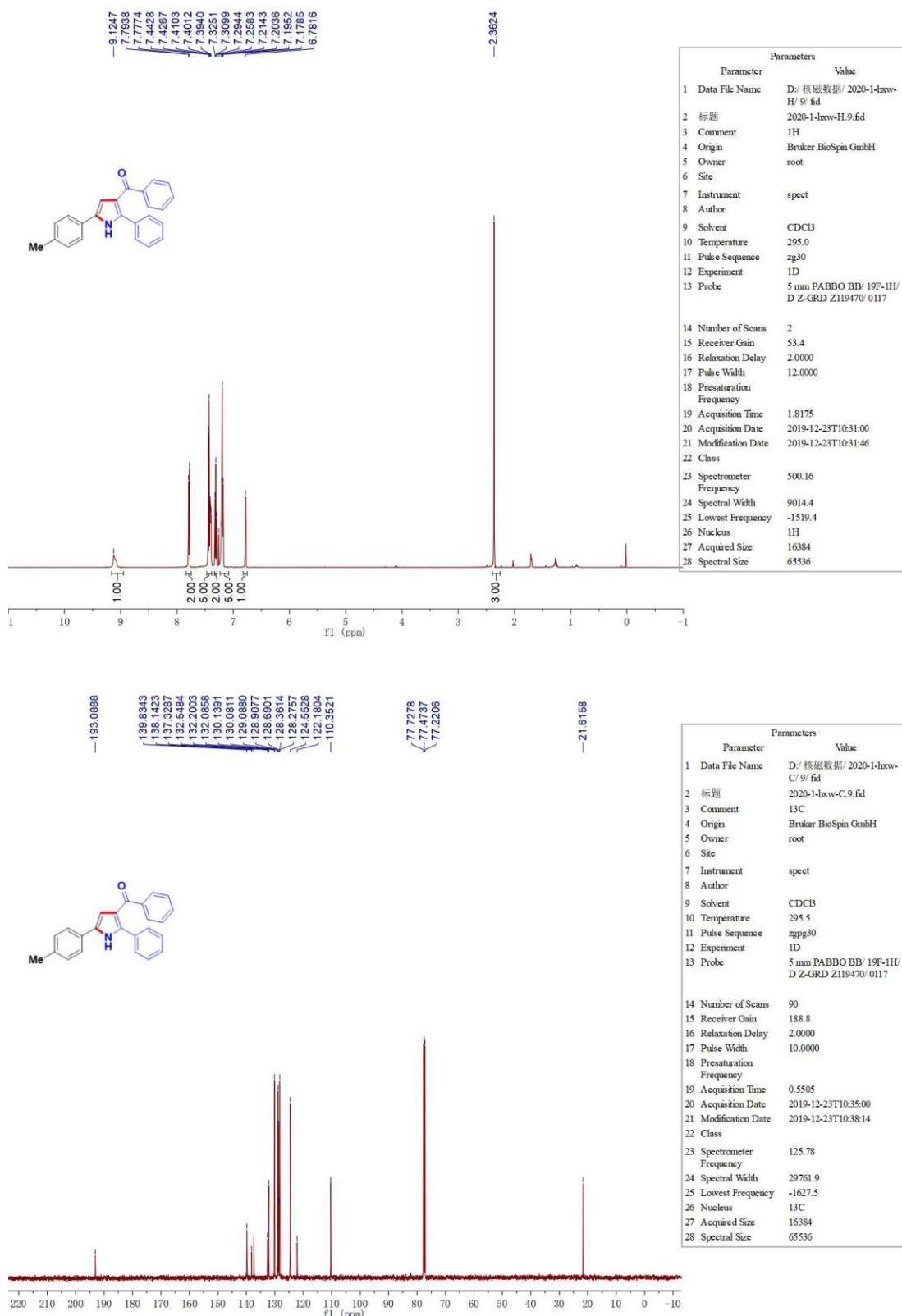
**2-Butyl-4-phenyl-1-tosyl-1H-imidazole (3s)**



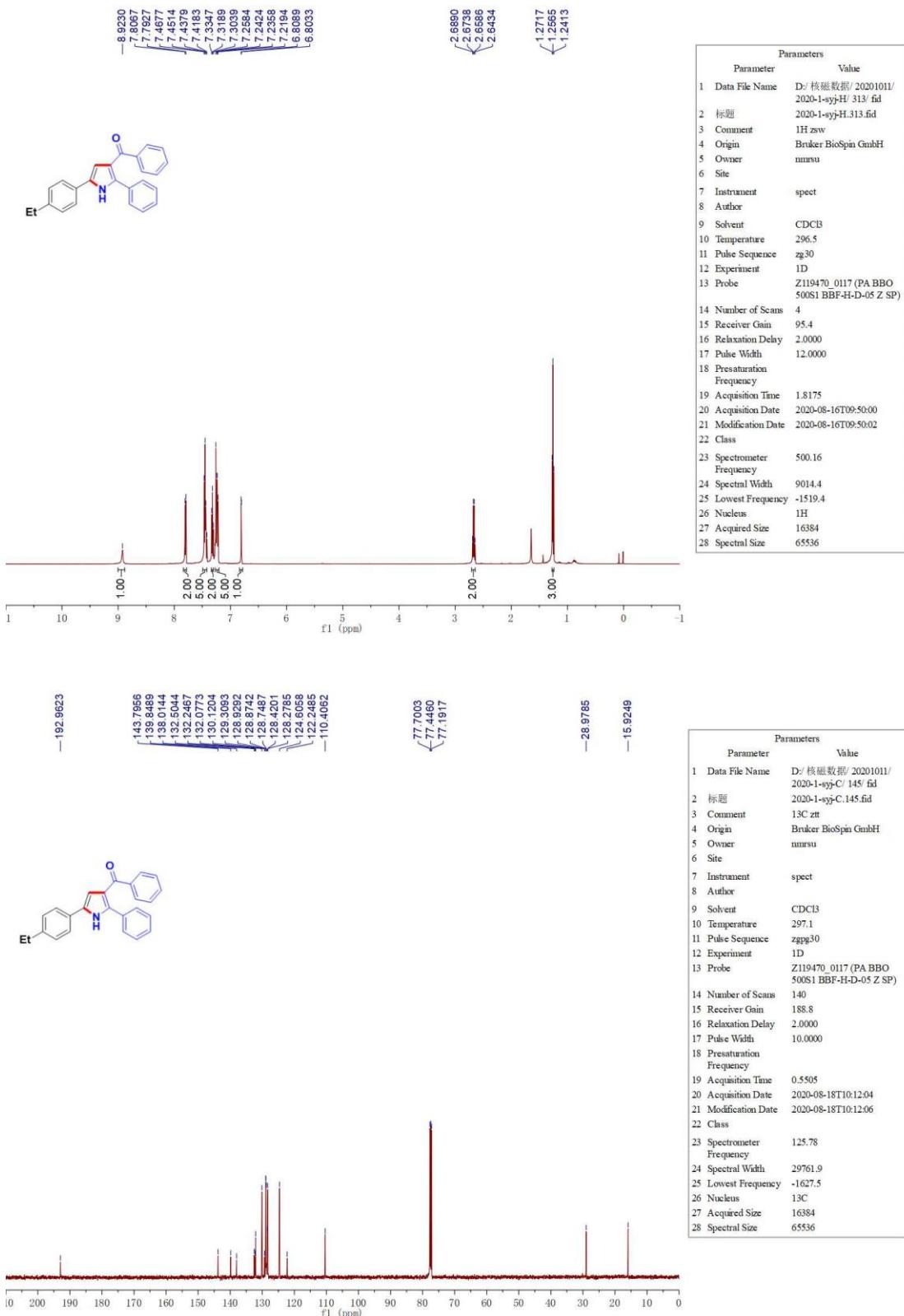
**(2,5-Diphenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (5a)**



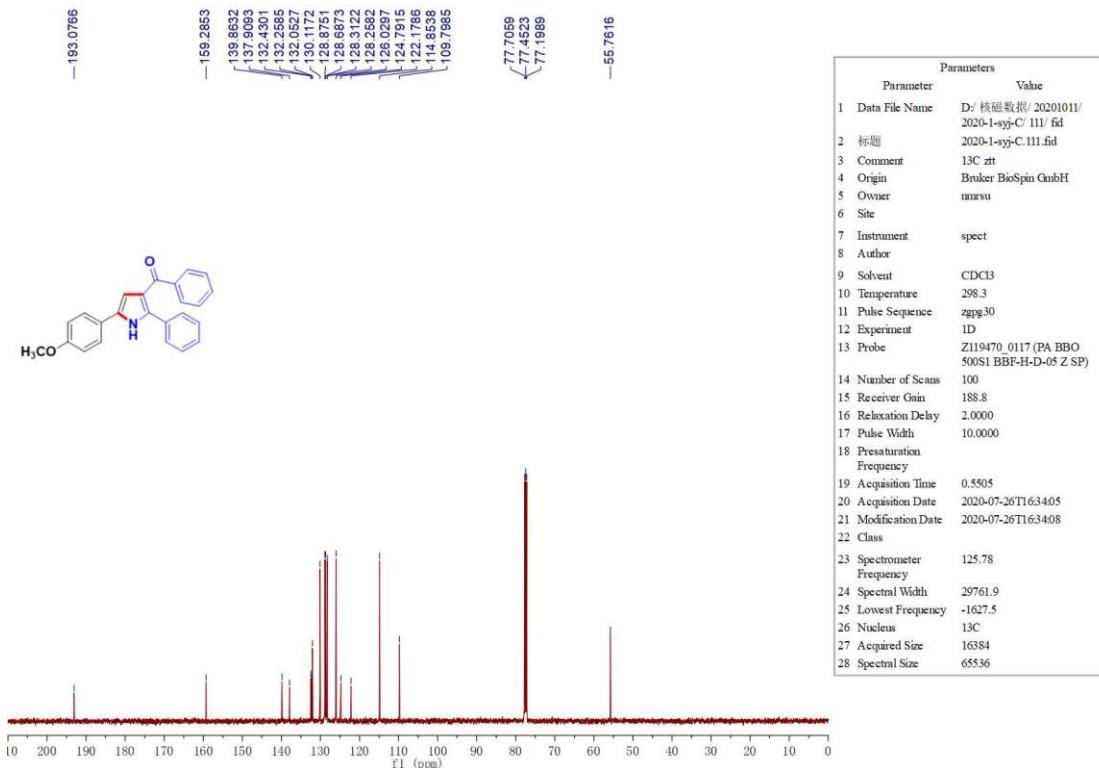
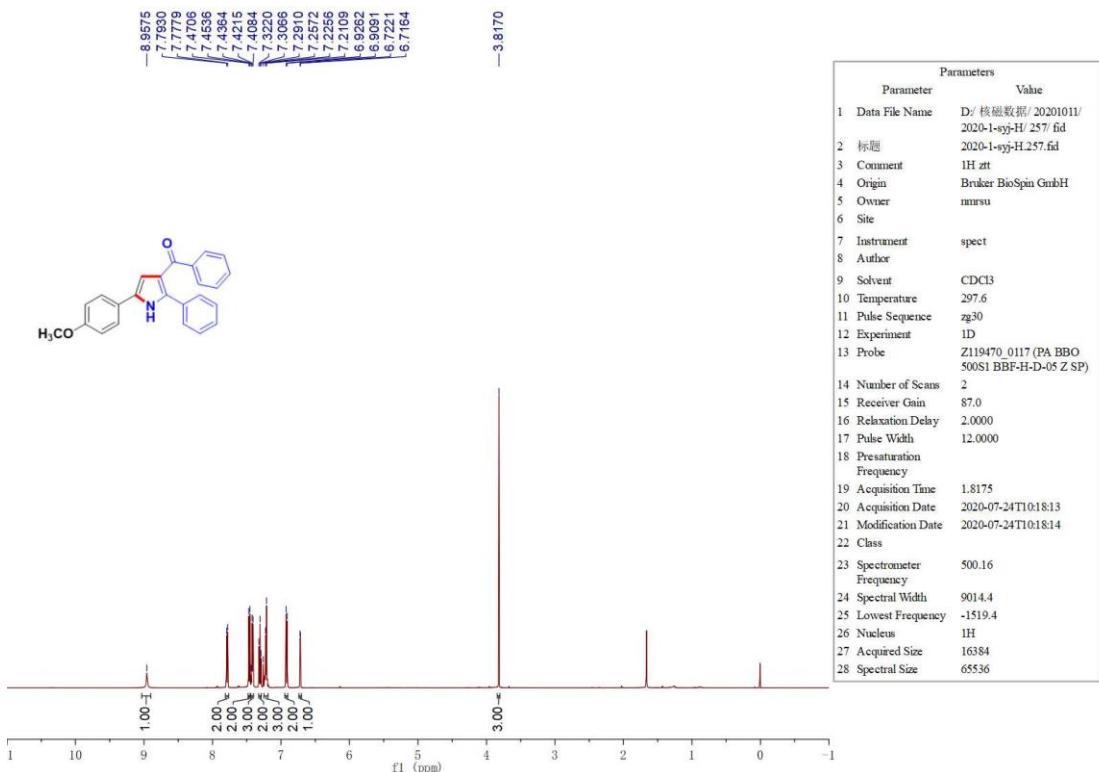
**Phenyl(2-phenyl-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)methanone (5b)**



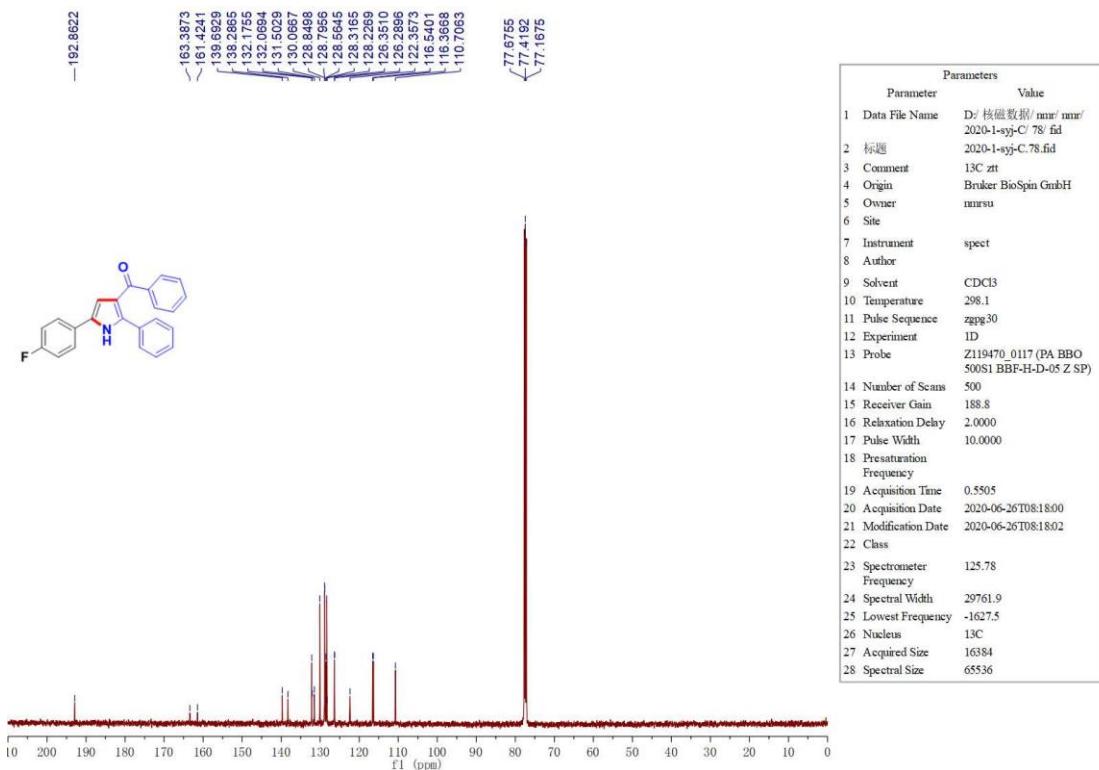
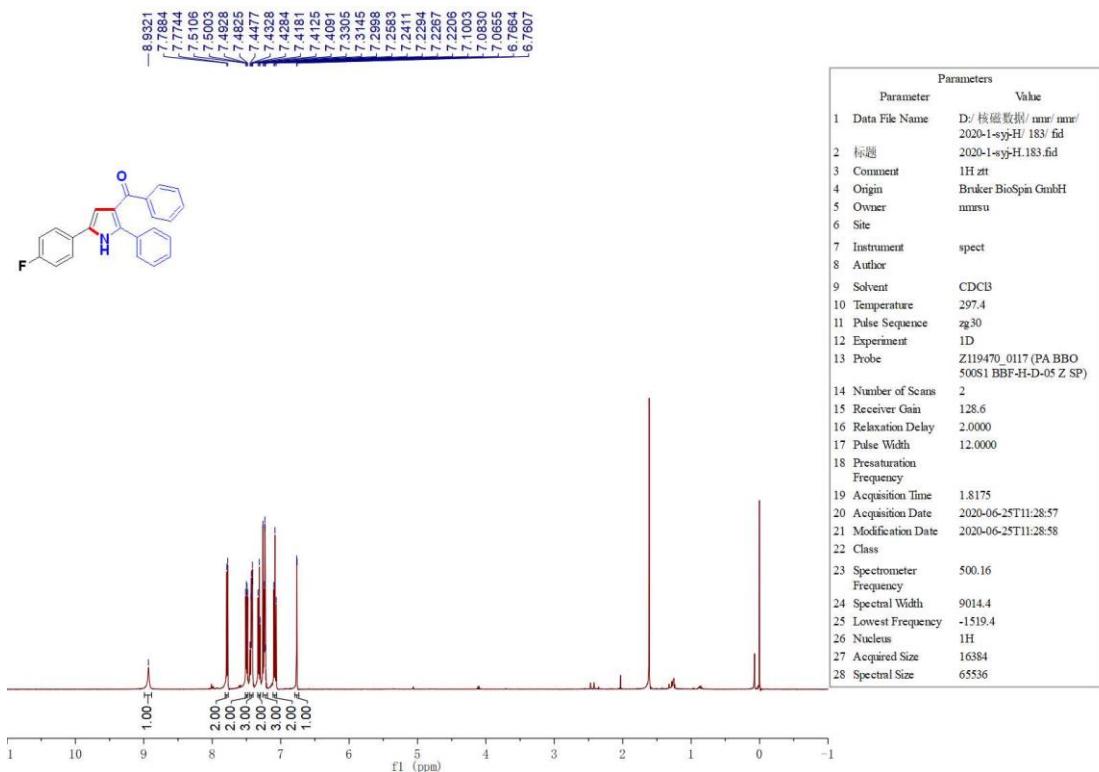
**(5-(4-Ethylphenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (5c)**



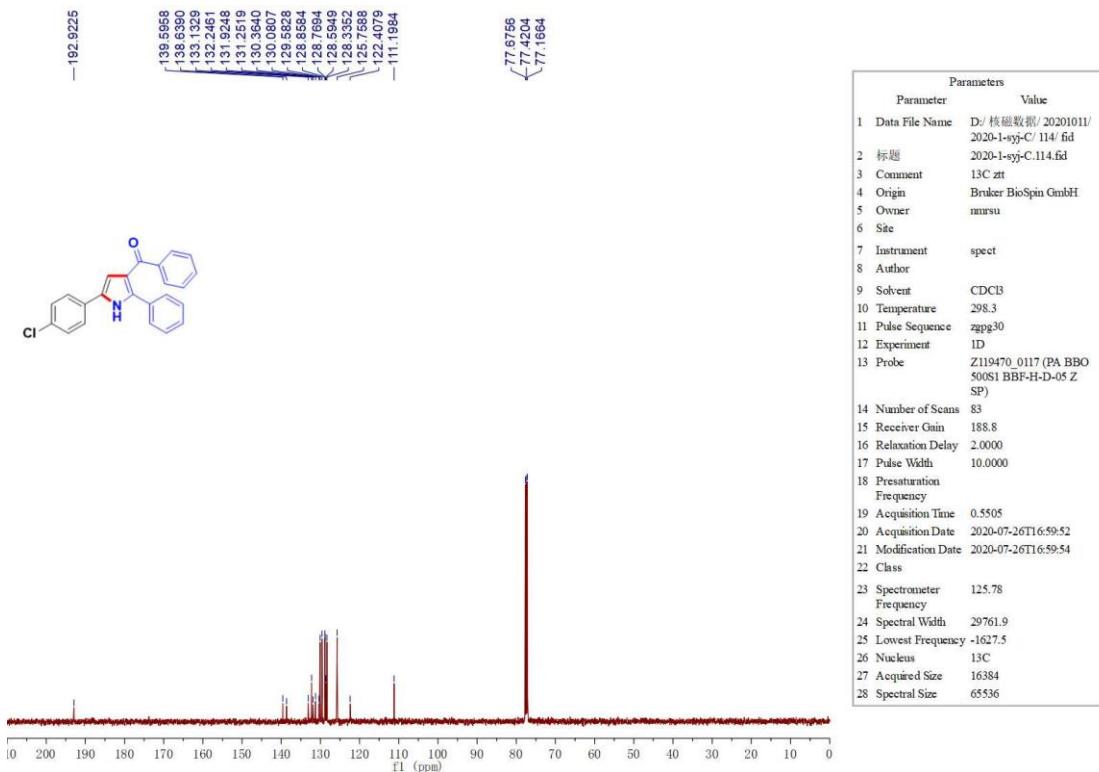
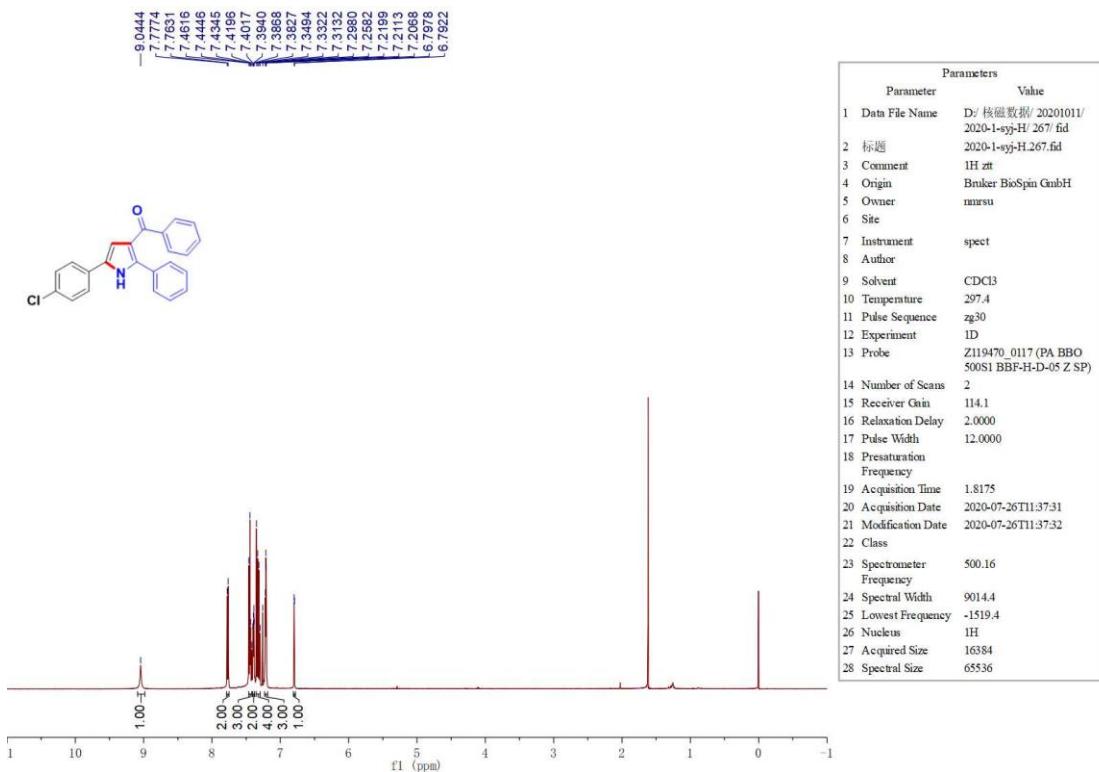
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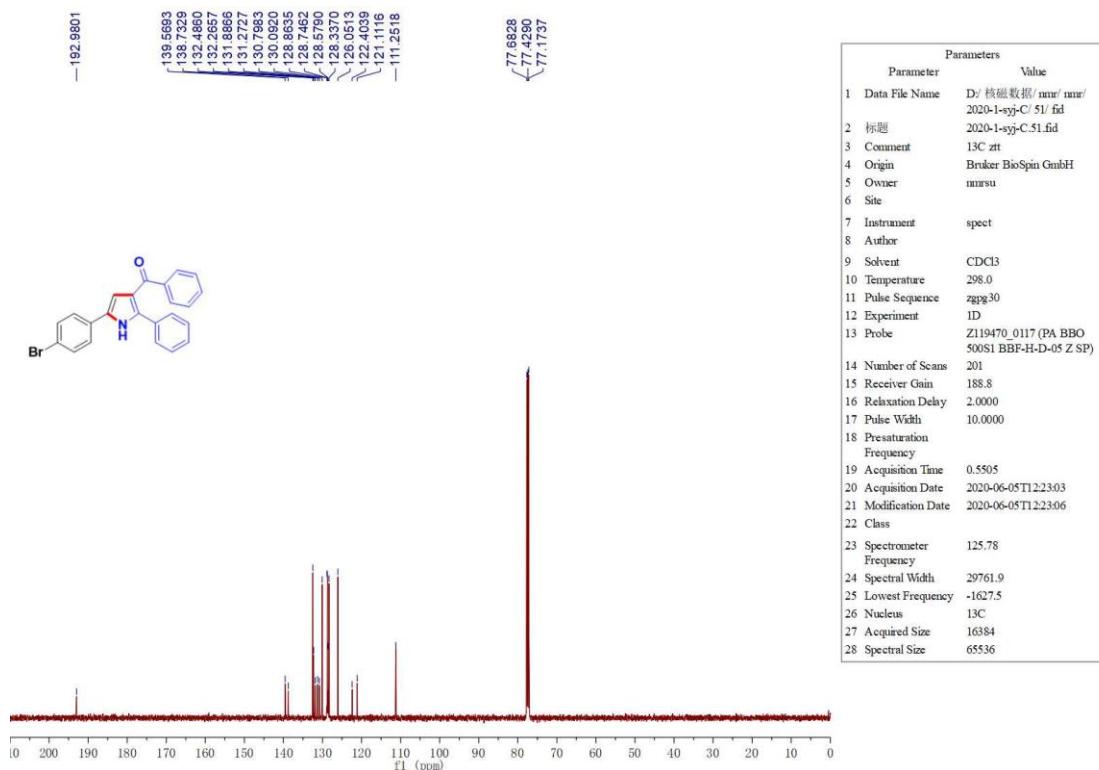
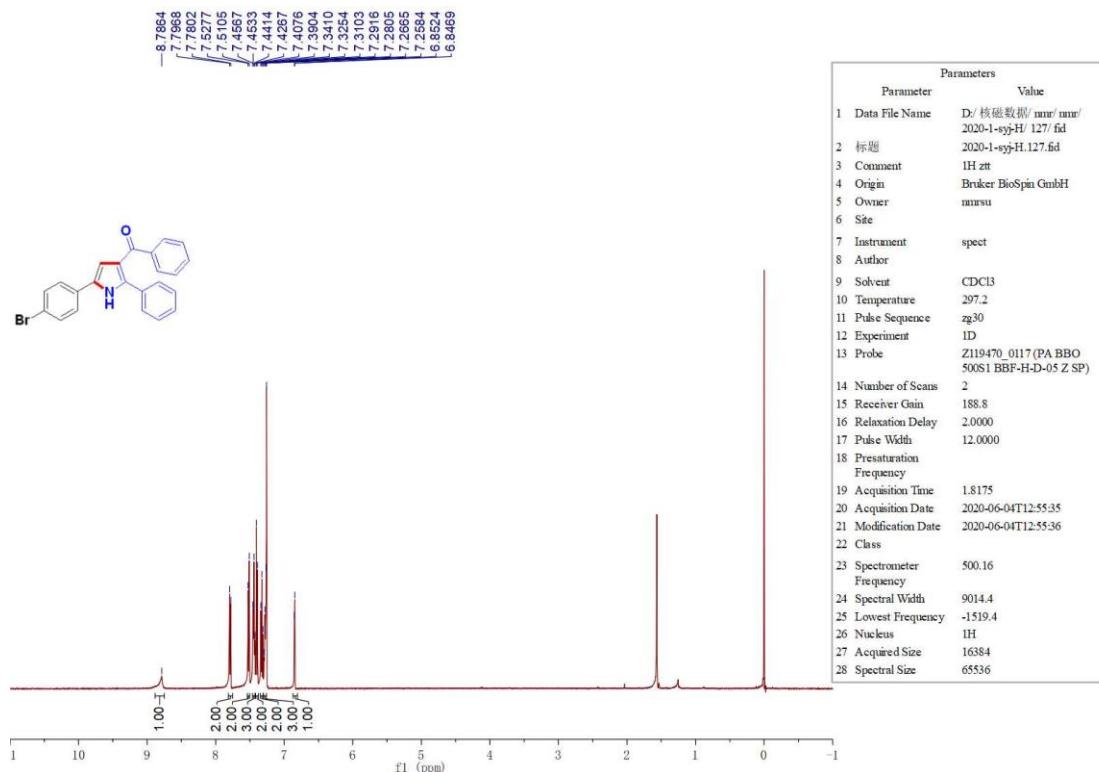
**(5-(4-Fluorophenyl)-2-phenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (5e)**



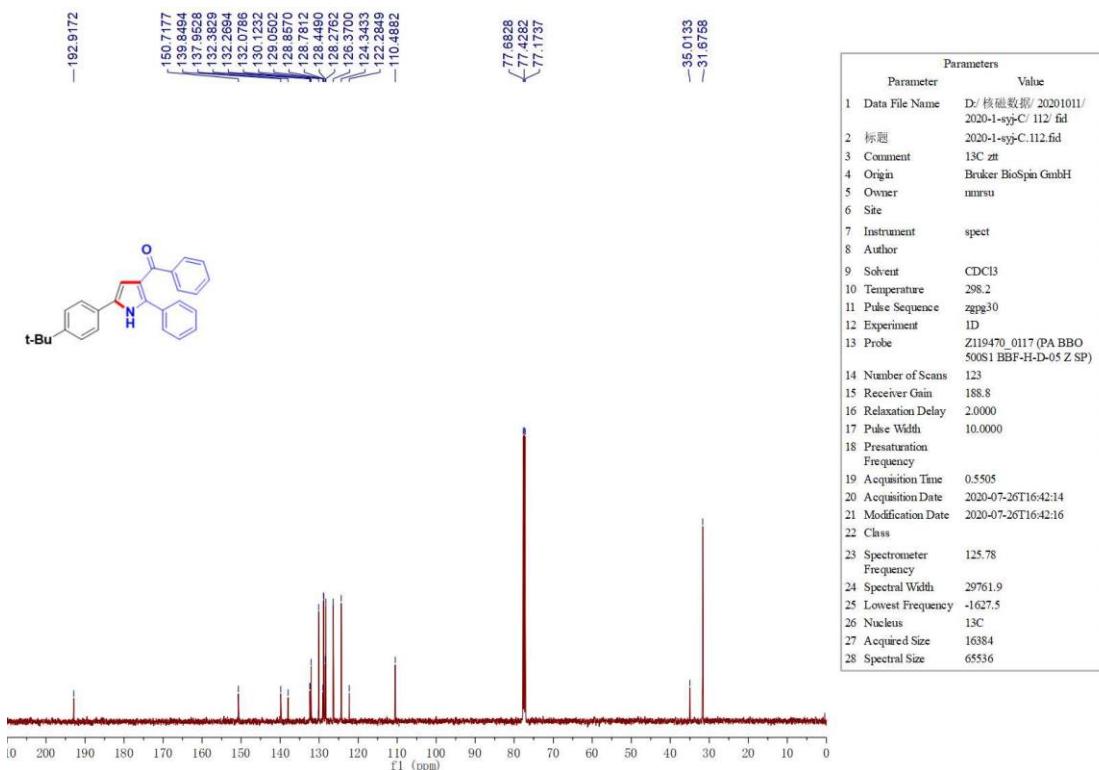
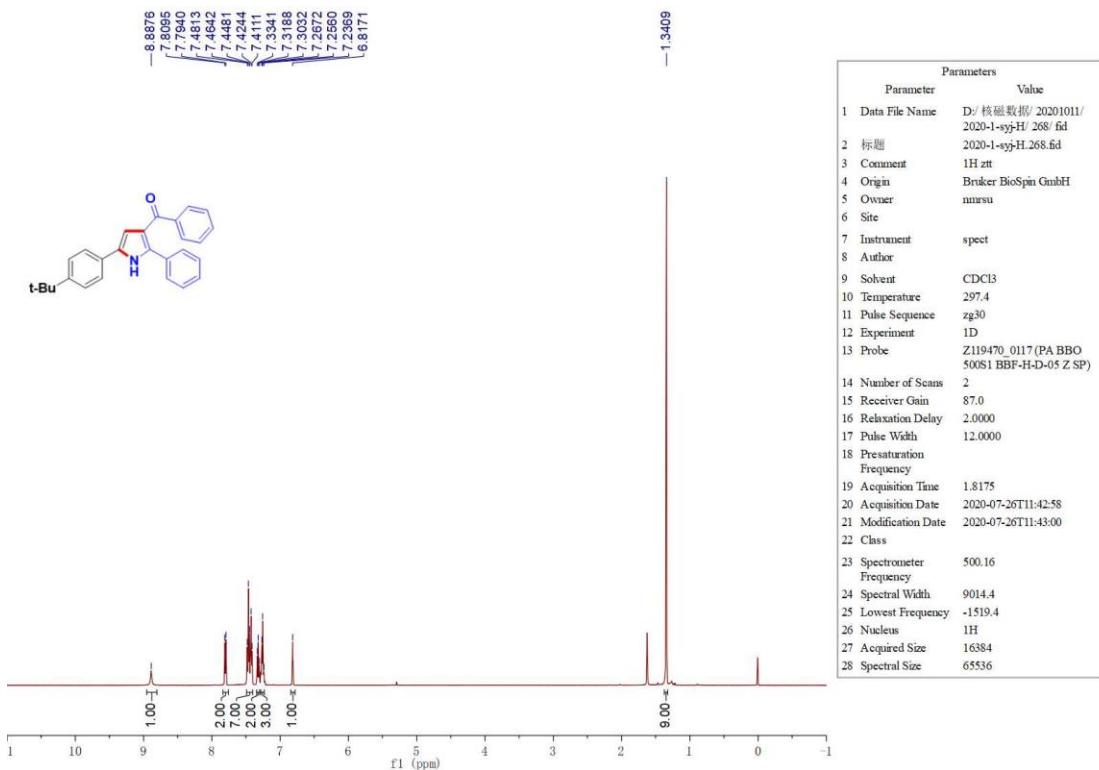
**(5-(4-Chlorophenyl)-2-phenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (5f)**



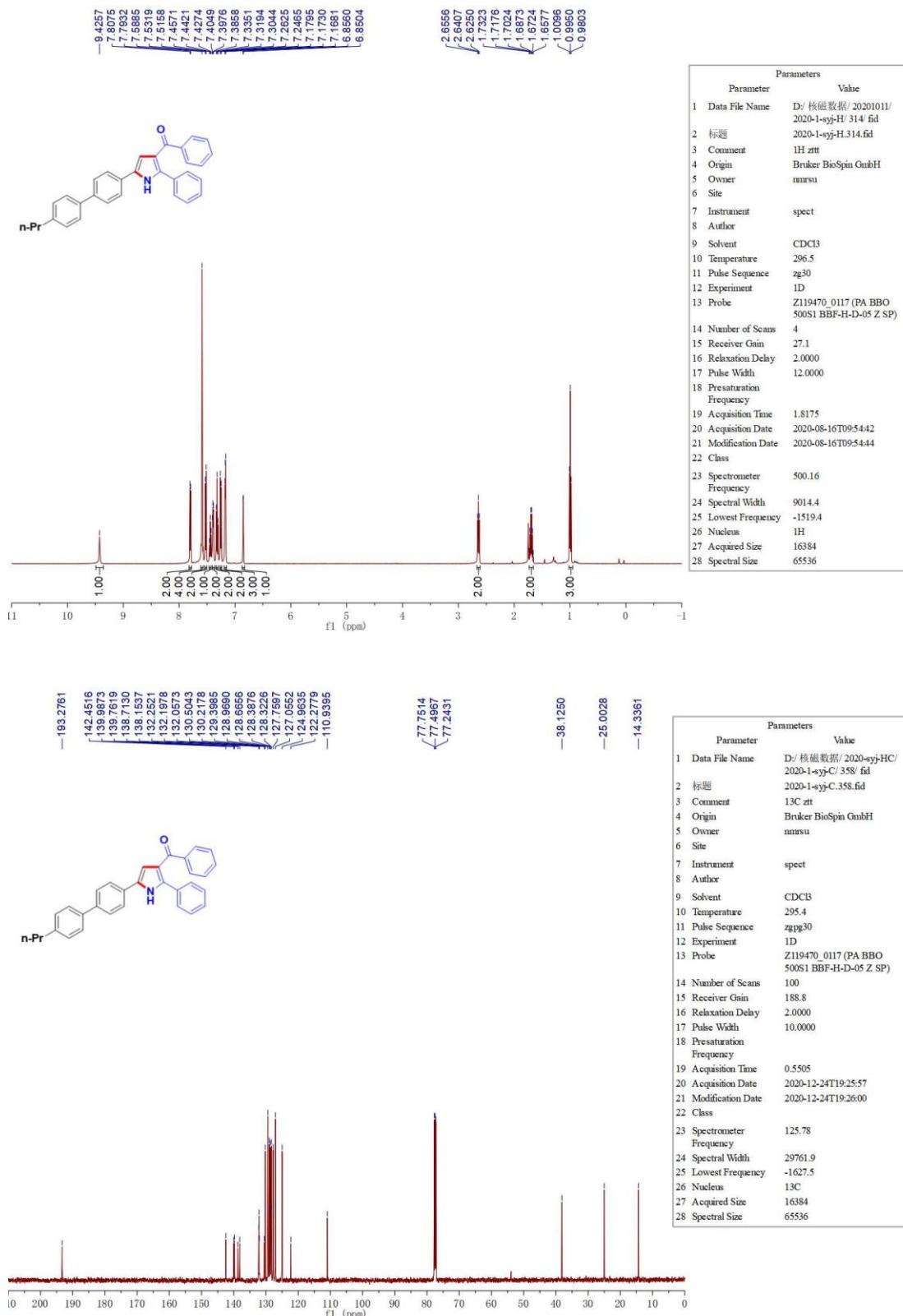
**(5-(4-Bromophenyl)-2-phenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (5g)**



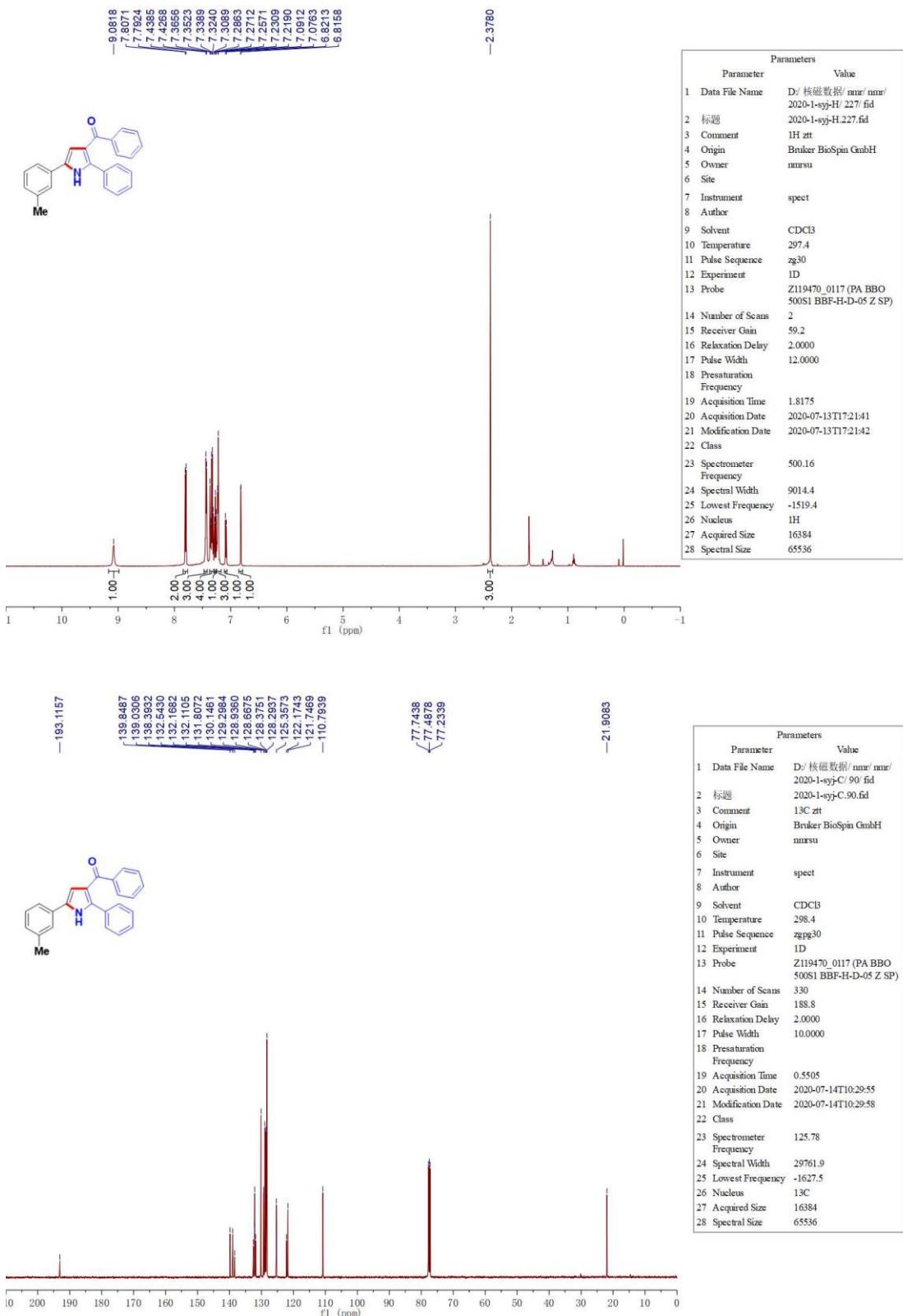
(5-(4-(*tert*-Butyl)phenyl)-2-phenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (**5h**)



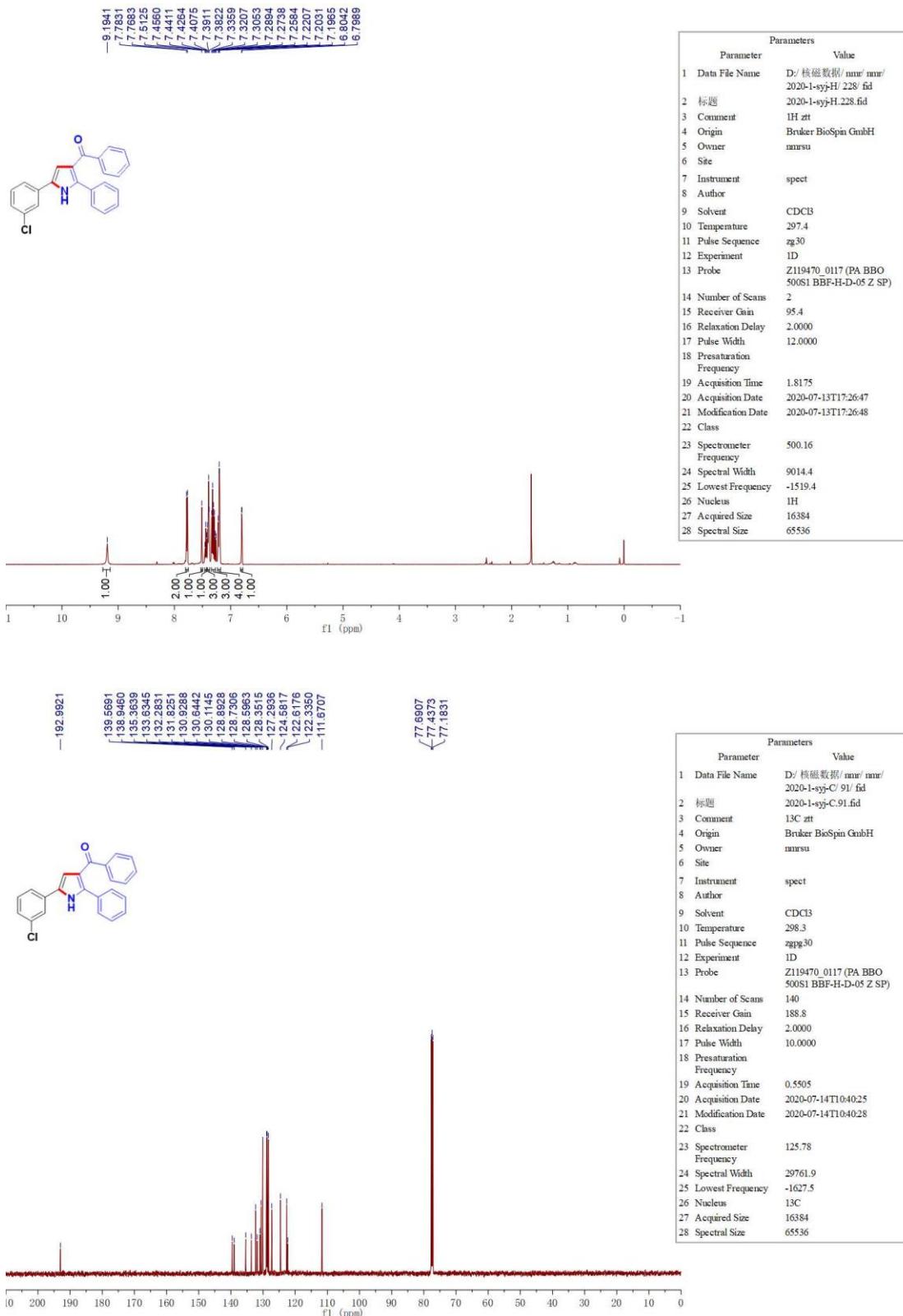
**Phenyl(2-phenyl-5-(4'-propyl-[1,1'-biphenyl]-4-yl)-1H-pyrrol-3-yl)methanone (5i)**



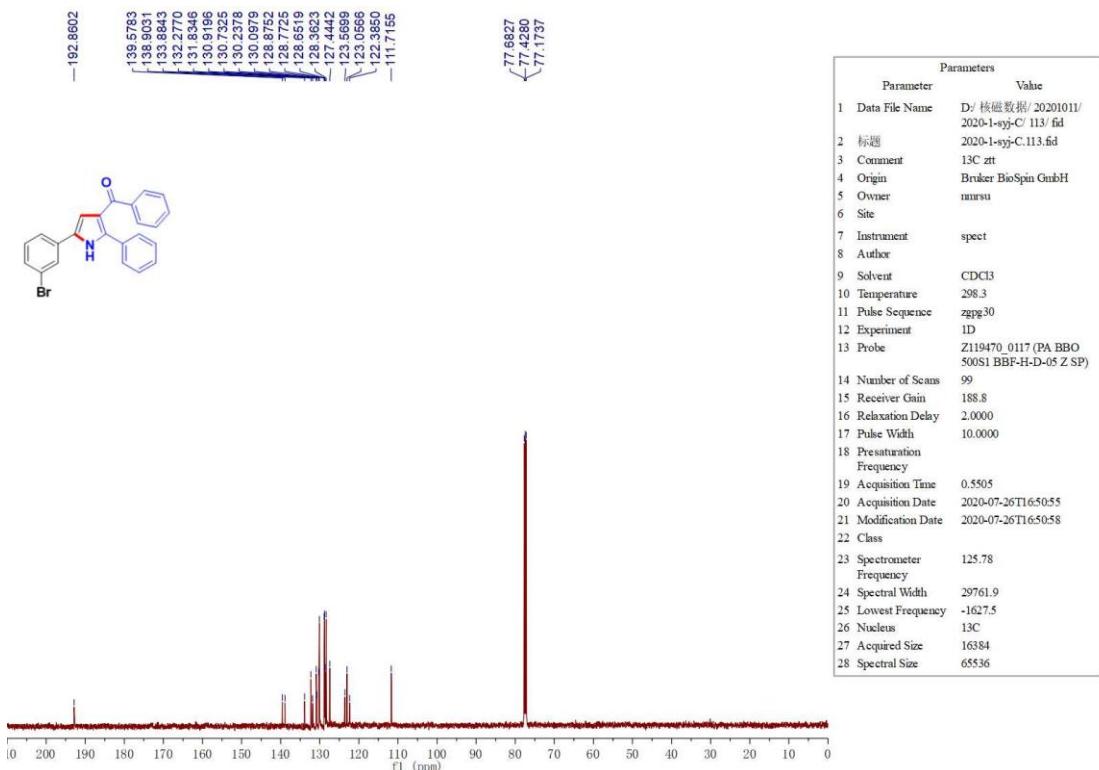
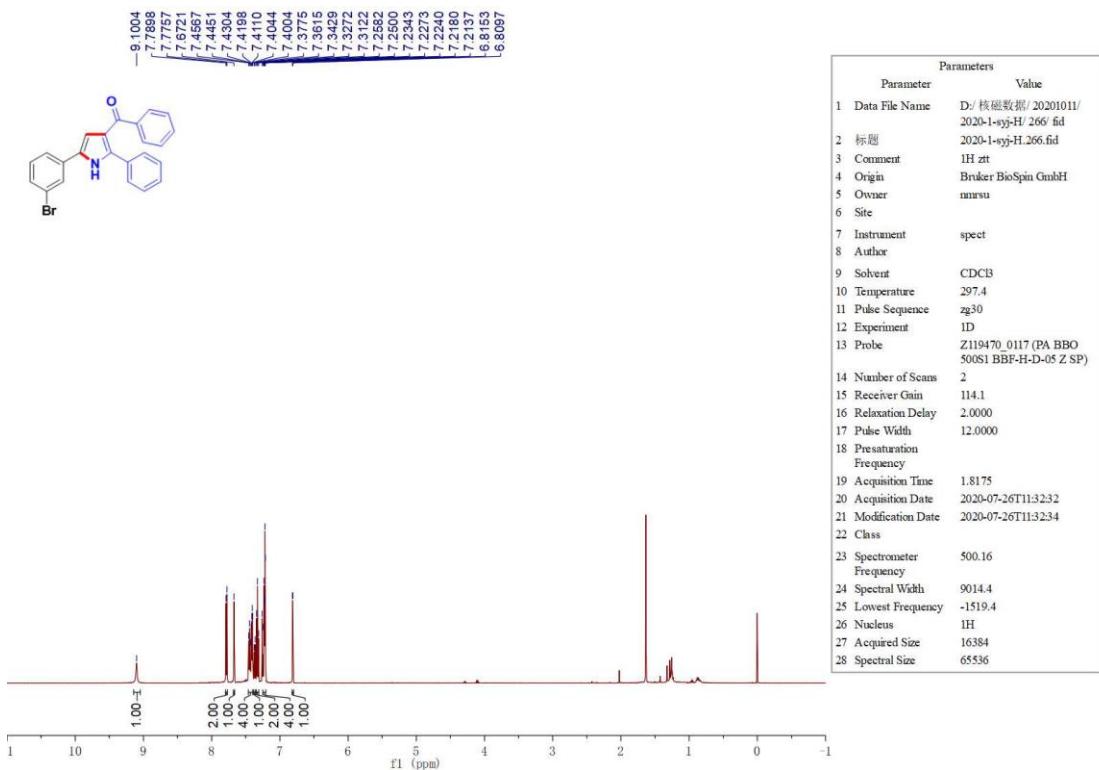
**Phenyl(2-phenyl-5-(*m*-tolyl)-1*H*-pyrrol-3-yl)methanone (5j)**



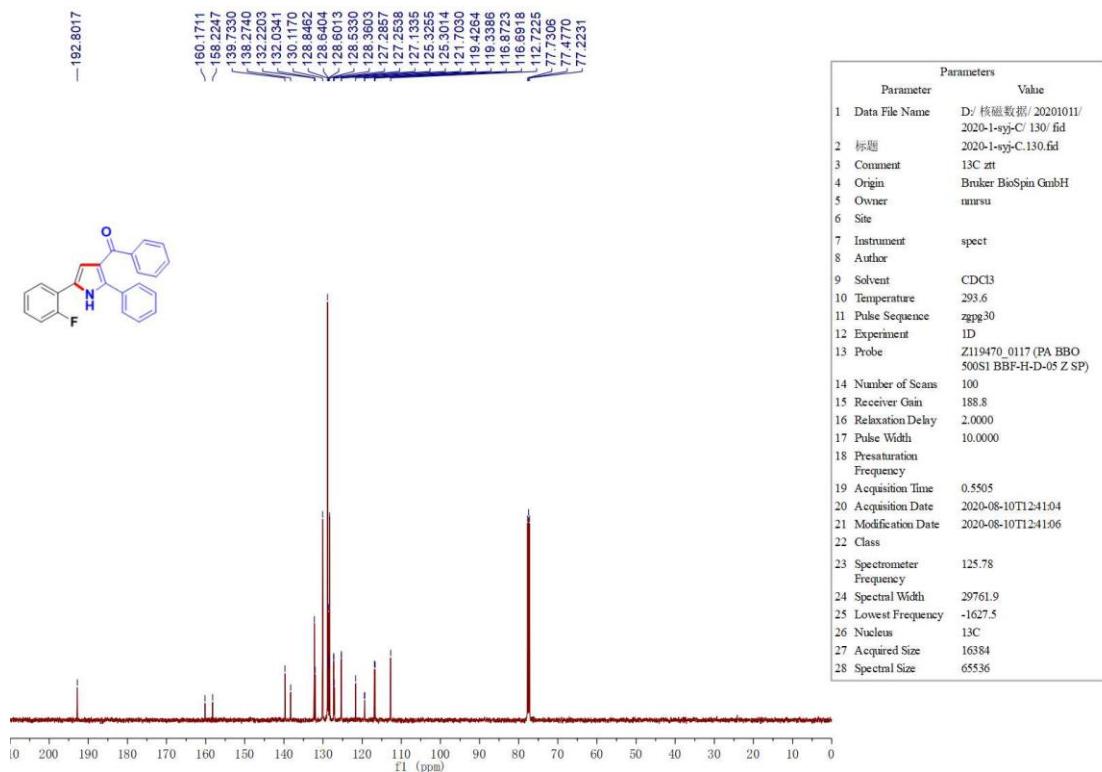
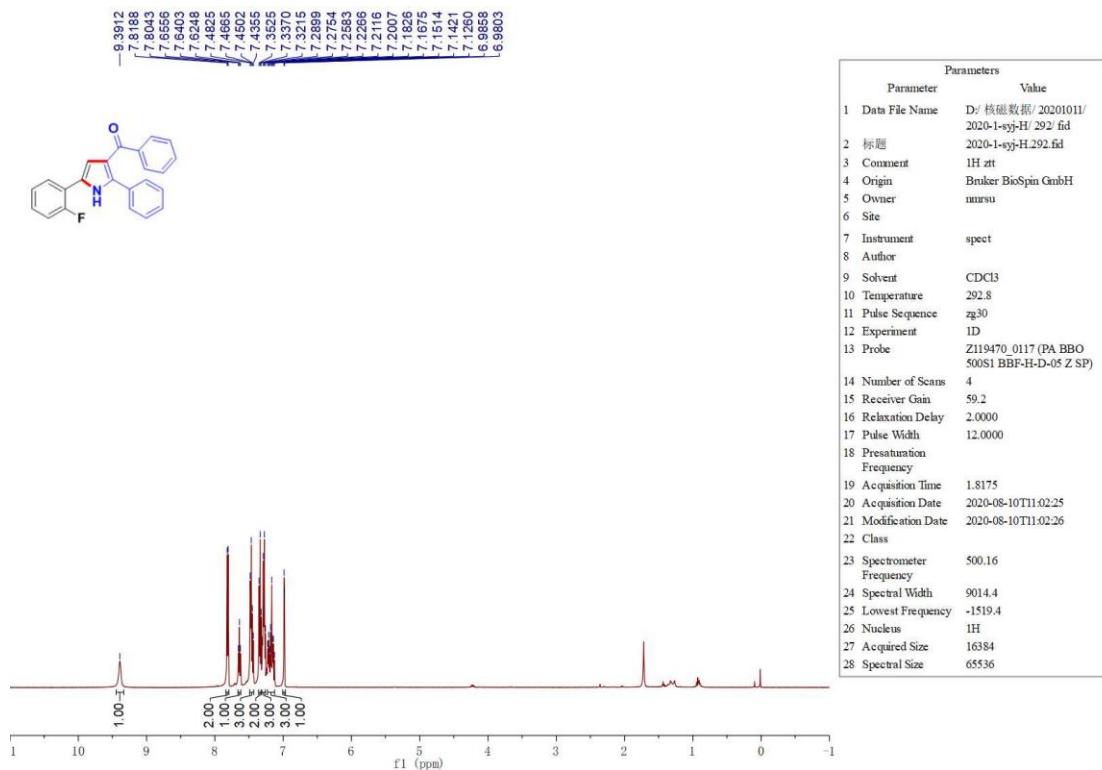
**(5-(3-Chlorophenyl)-2-phenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (5k)**



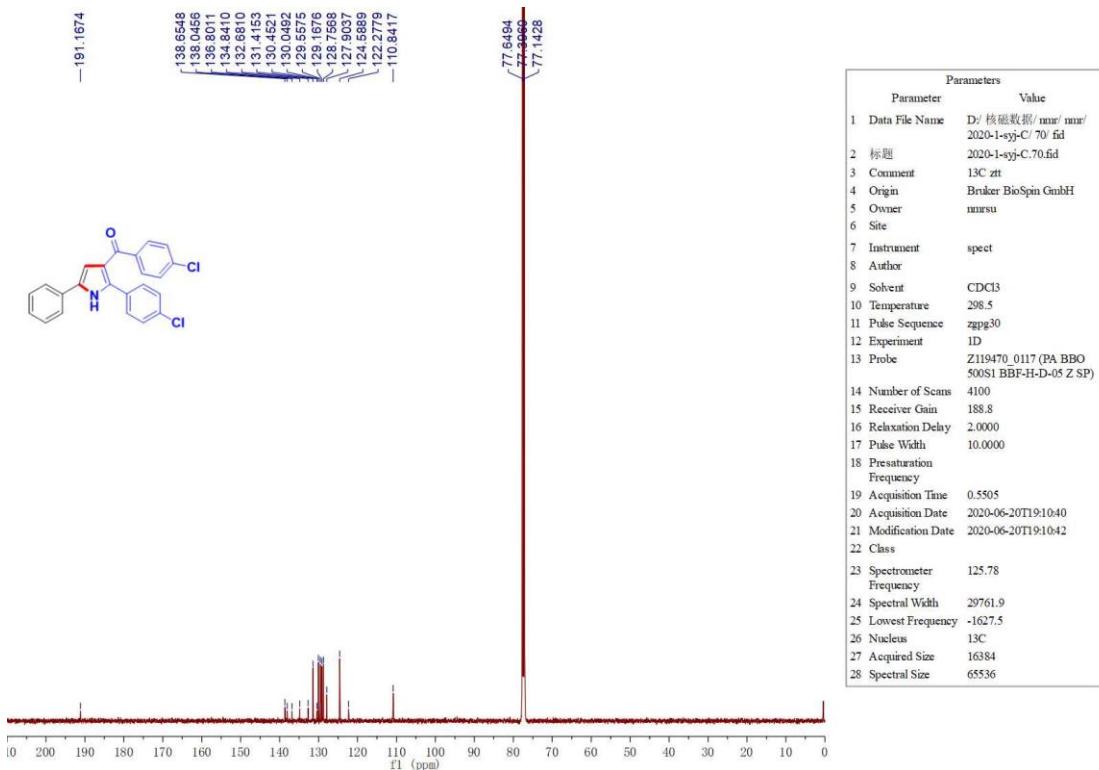
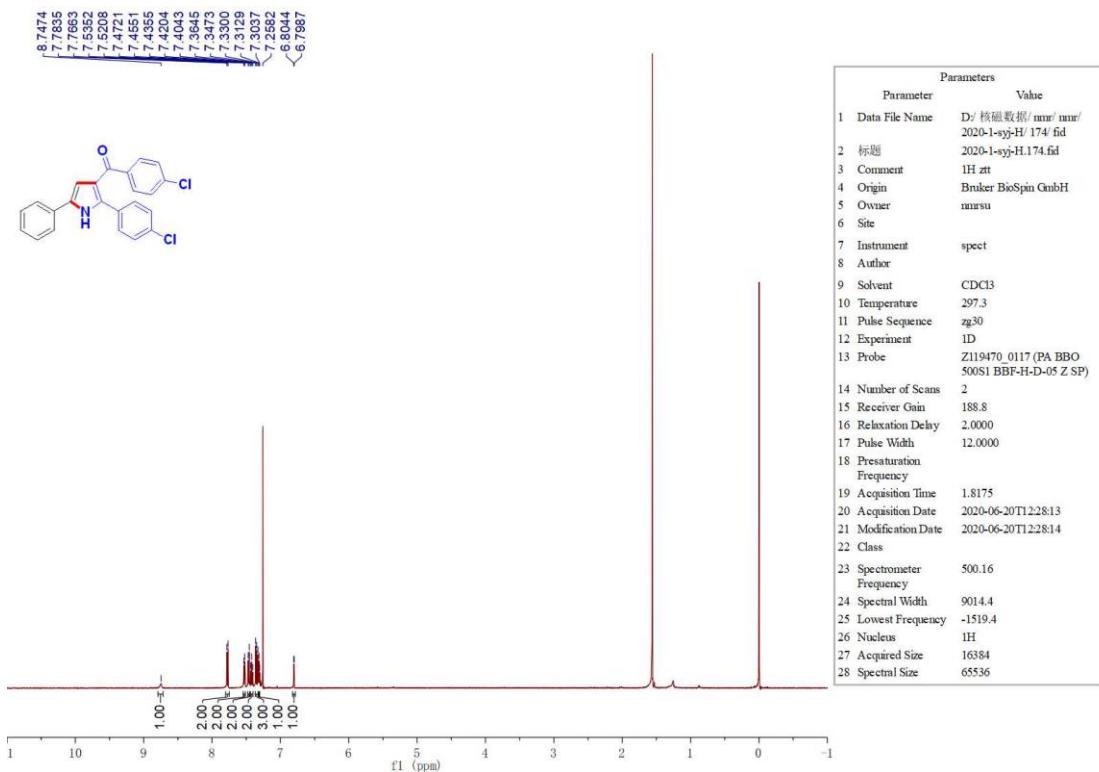
(5-(3-Bromophenyl)-2-phenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (5l)



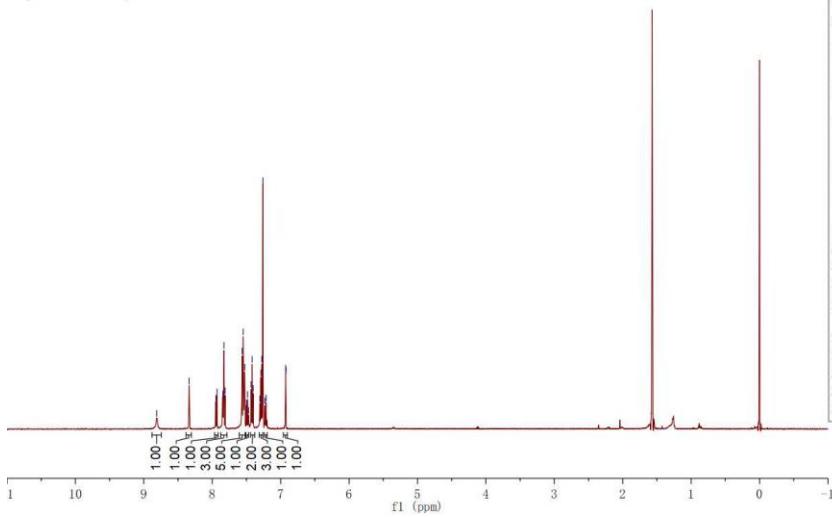
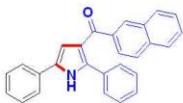
**(5-(2-Fluorophenyl)-2-phenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (5m)**



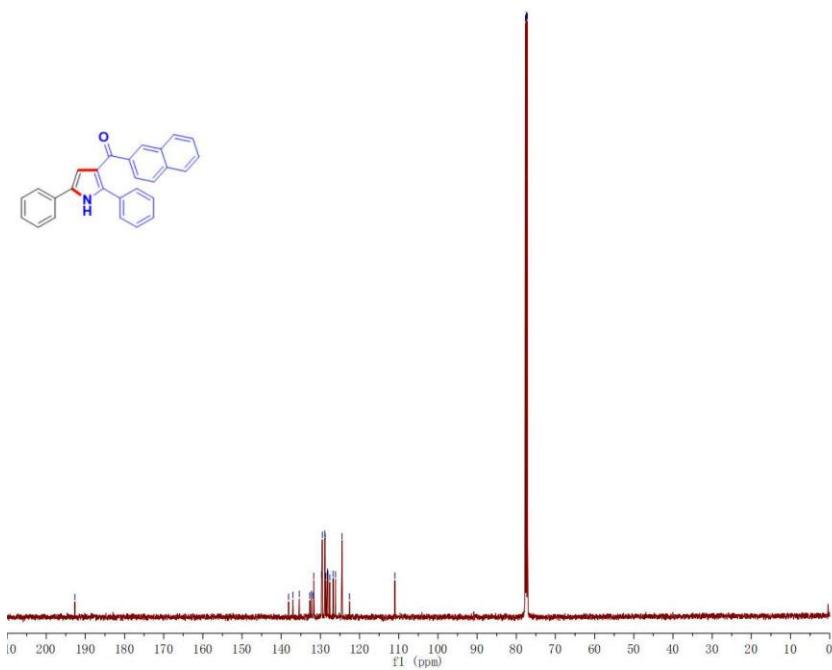
**(4-Chlorophenyl)(2-(4-chlorophenyl)-5-phenyl-1*H*-pyrrol-3-yl) methanone (5n)**



### (2,5-Diphenyl-1*H*-pyrrol-3-yl) (naphthalen-2-yl) methanone (5o)

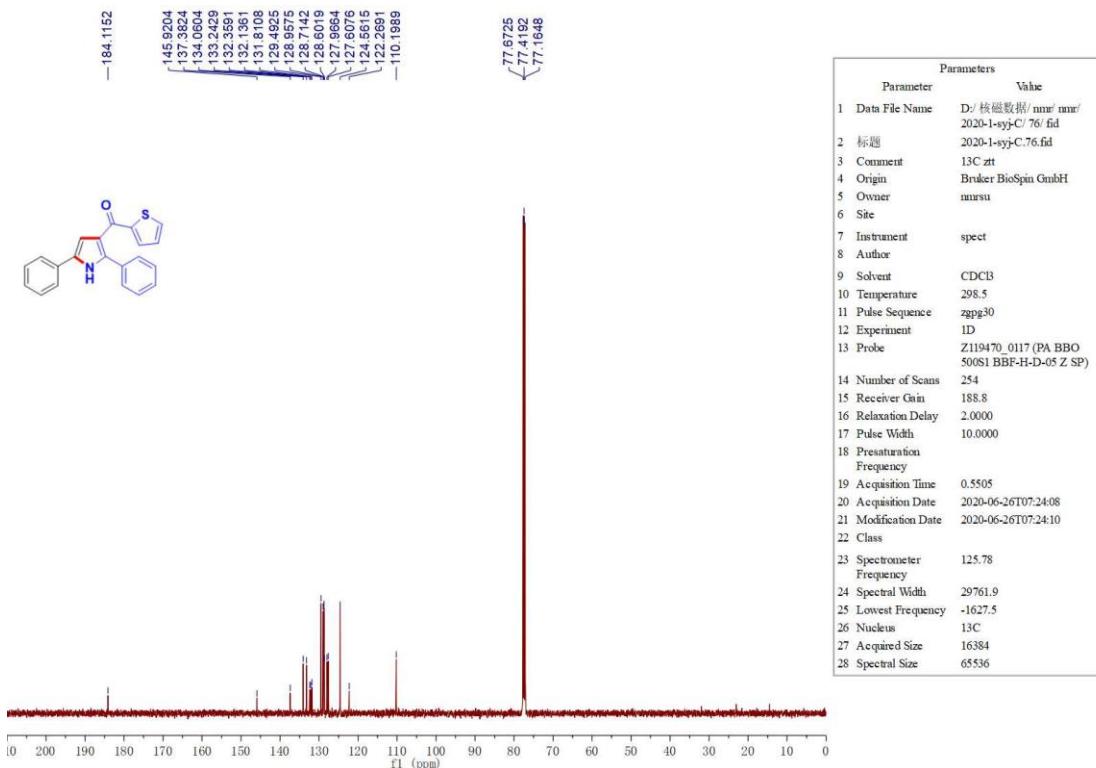
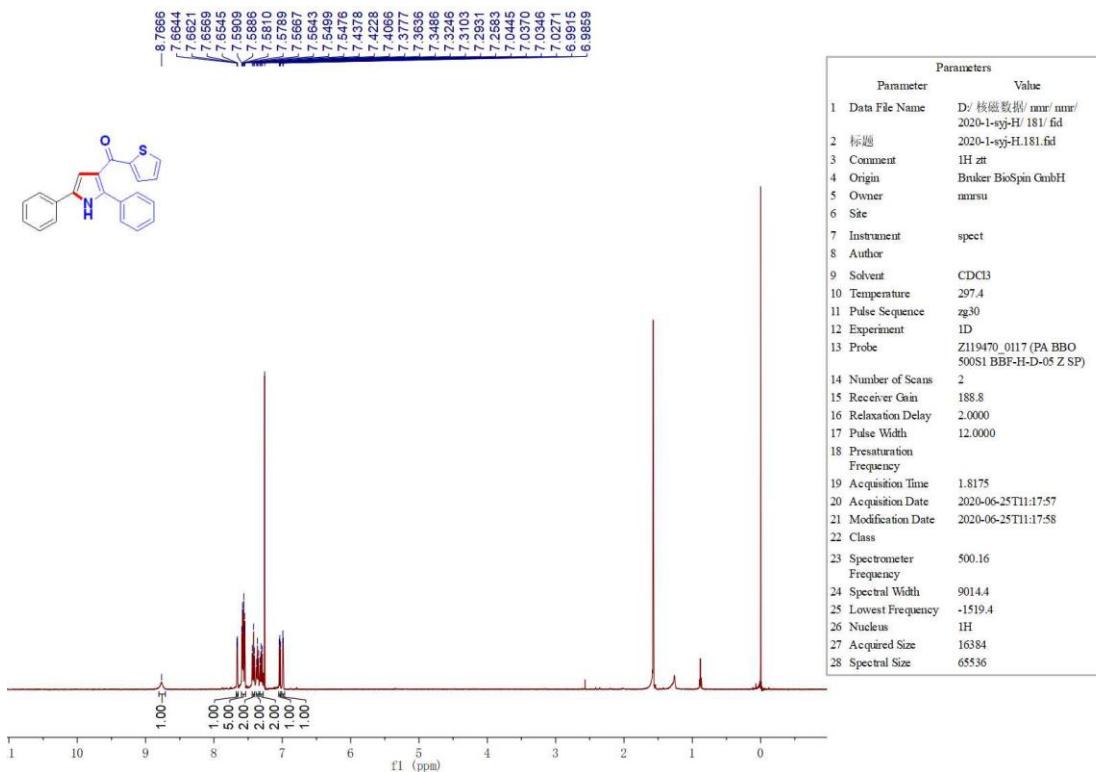


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2 标题	2020-1-sjyH.182.fid
3 Comment	1H zht
4 Origin	Bruker BioSpin GmbH
5 Owner	nmrusr
6 Site	
7 Instrument	spec
8 Author	
9 Solvent	CDCl3
10 Temperature	297.4
11 Pulse Sequence	zg30
12 Experiment	1D
13 Probe	Z119470_0117(PA BBO 500S1 BBF-H-D-05 Z SP)
14 Number of Scans	2
15 Receiver Gain	188.8
16 Relaxation Delay	2.0000
17 Pulse Width	12.0000
18 Presaturation Frequency	
19 Acquisition Time	1.8175
20 Acquisition Date	2020-06-25T11:24:49
21 Modification Date	2020-06-25T11:24:50
22 Class	
23 Spectrometer Frequency	500.16
24 Spectral Width	9014.4
25 Lowest Frequency	-1519.4
26 Nucleus	1H
27 Acquired Size	16384
28 Spectral Size	65536

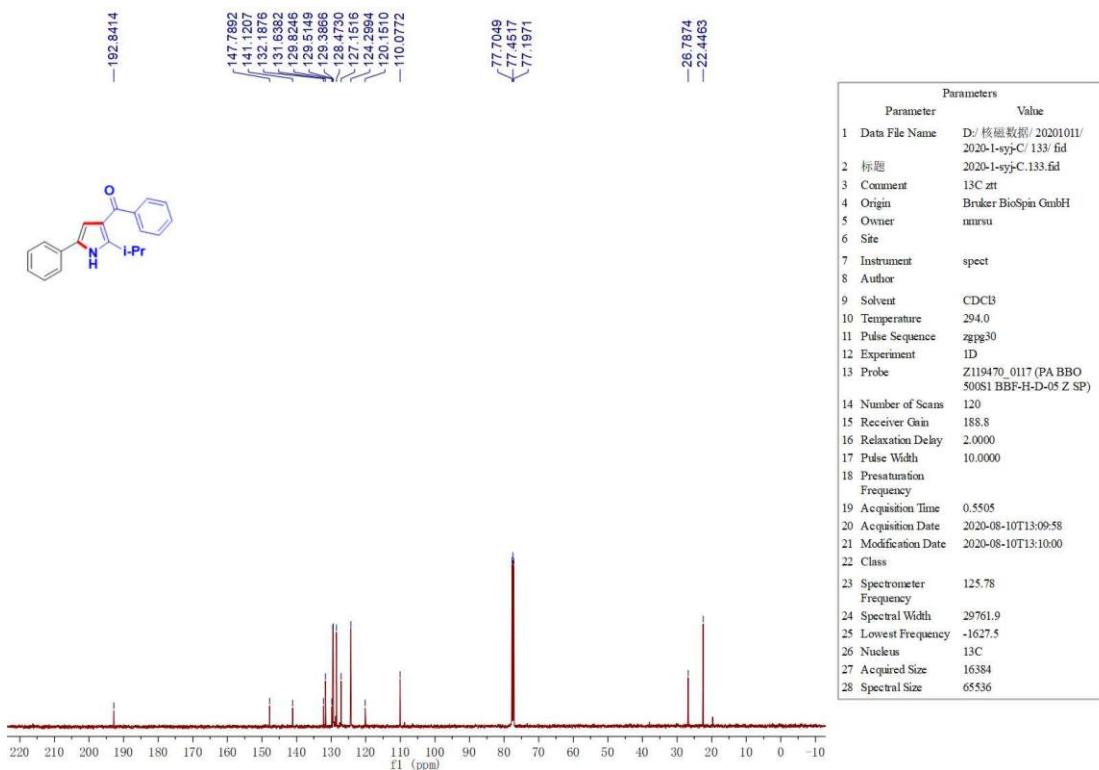
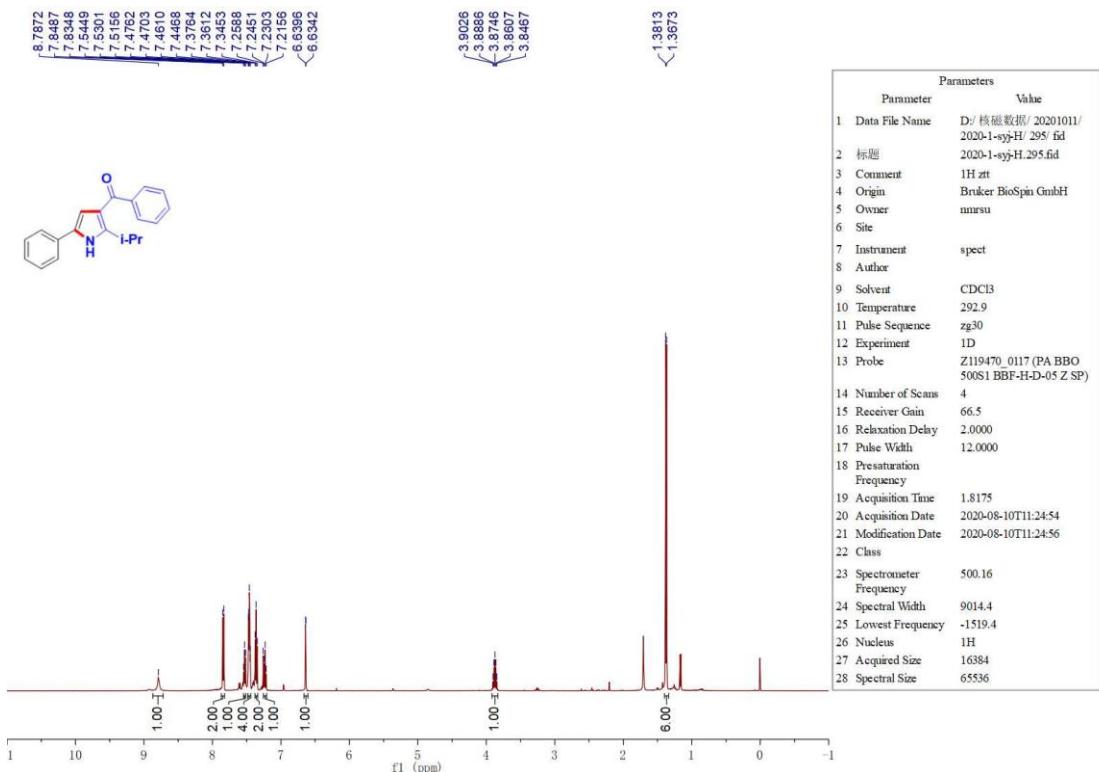


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Parameter	Value
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2 标题	2020-1-sy5C-77.fid
3 Comment	13C ztt
4 Origin	Bruker BioSpin GmbH
5 Owner	nmsu
6 Site	
7 Instrument	spect
8 Author	
9 Solvent	CDCB
10 Temperature	298.2
11 Pulse Sequence	zgpp30
12 Experiment	1D
13 Probe	Z119470_0117 (PA BBO 500S1 BBF-H-D-05 Z SP)
14 Number of Scans	600
15 Receiver Gain	188.8
16 Relaxation Delay	2.0000
17 Pulse Width	10.0000
18 Presaturation Frequency	
19 Acquisition Time	0.5505
20 Acquisition Date	2020-06-26T07:52:58
21 Modification Date	2020-06-26T07:53:00
22 Class	
23 Spectrometer Frequency	125.78
24 Spectral Width	29761.9
25 Lowest Frequency	-1627.5
26 Nucleus	13C
27 Acquired Size	16384
28 Spectral Size	65536

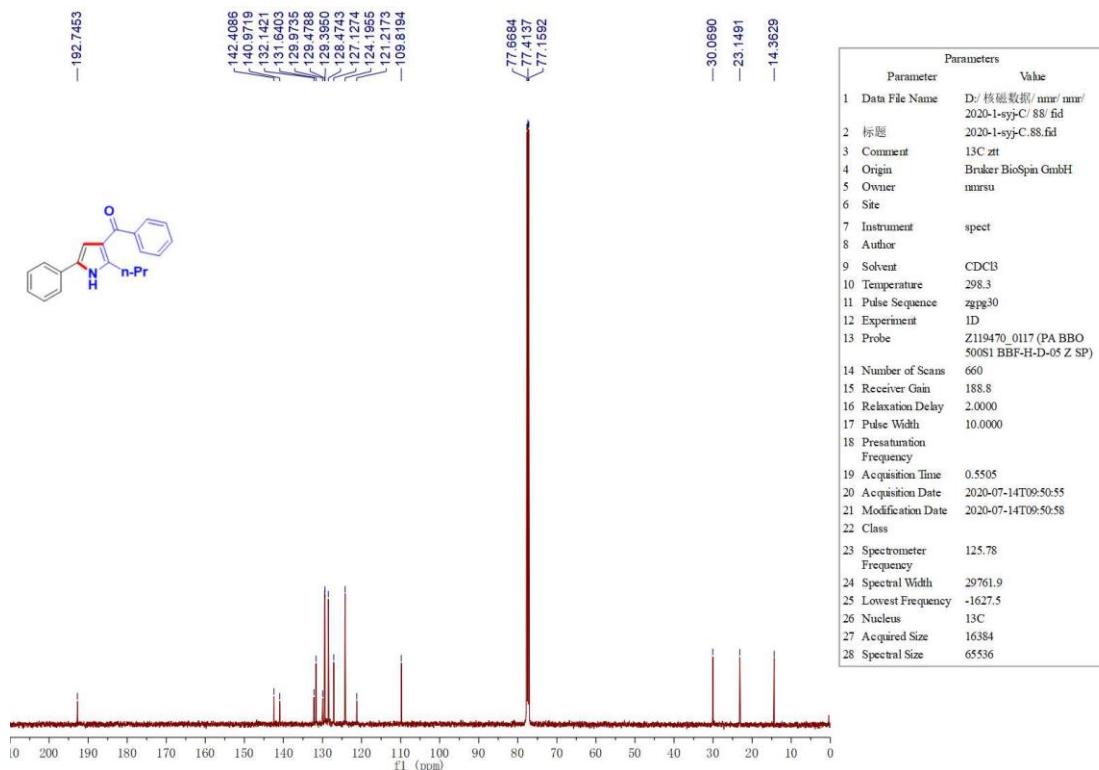
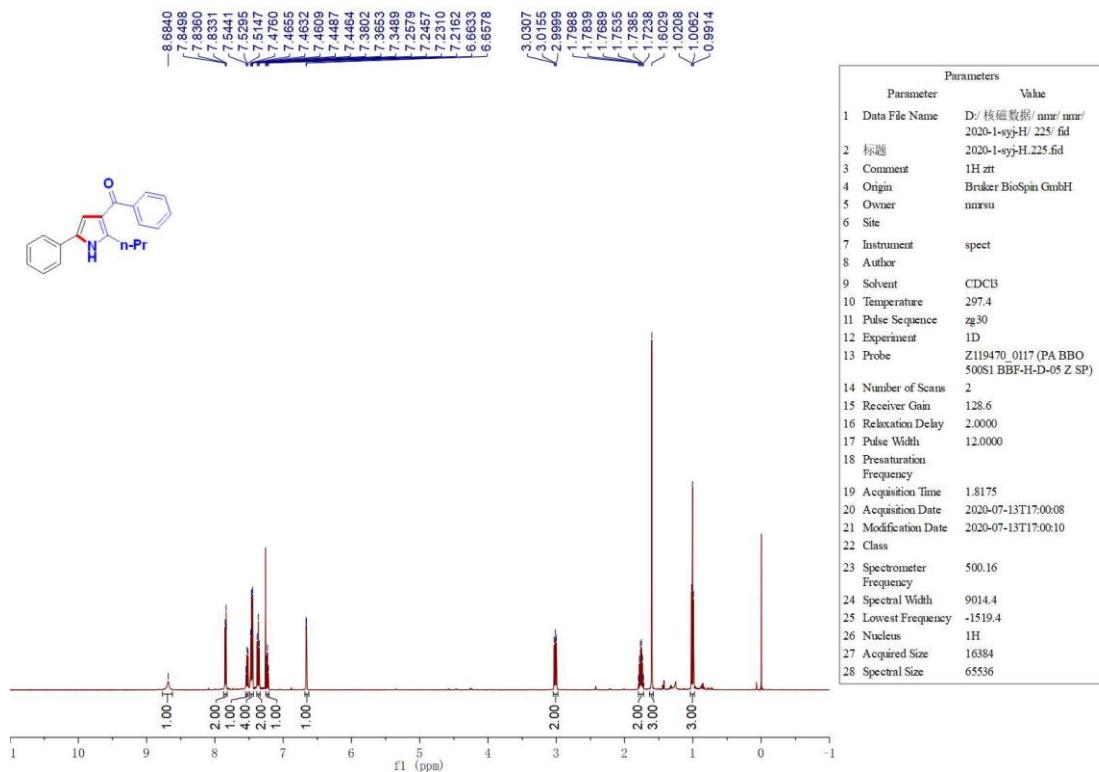
**(2,5-Diphenyl-1*H*-pyrrol-3-yl) (thiophen-2-yl) methanone (5p)**



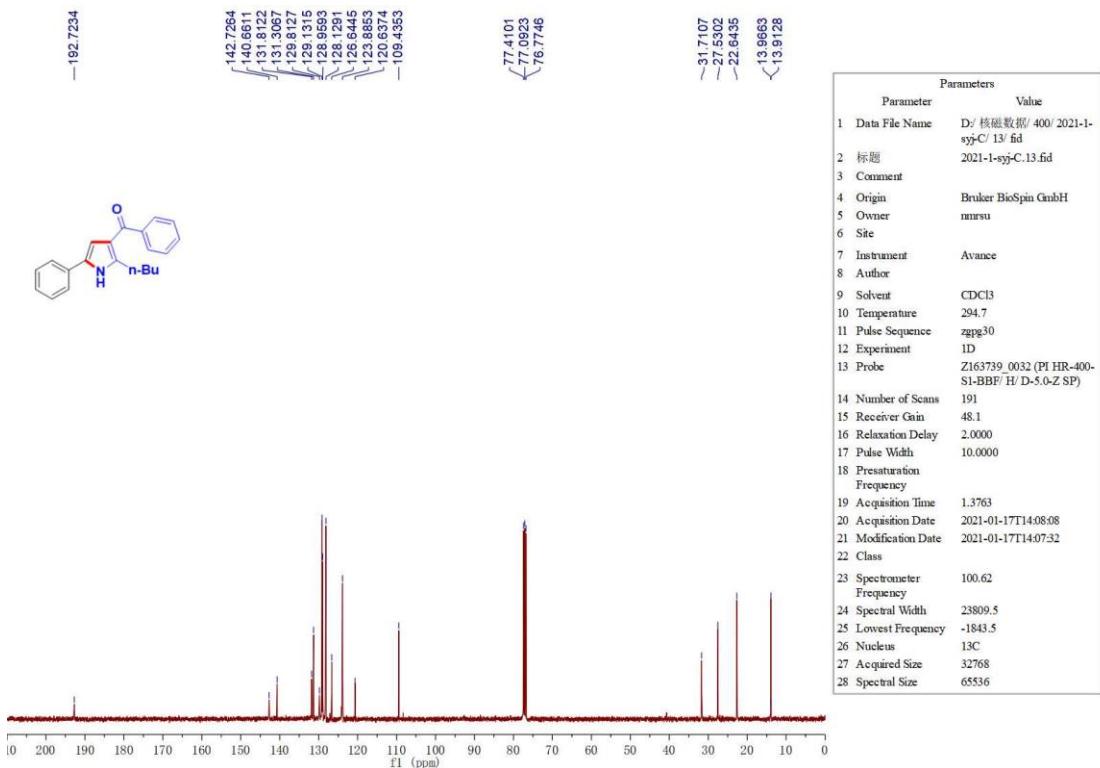
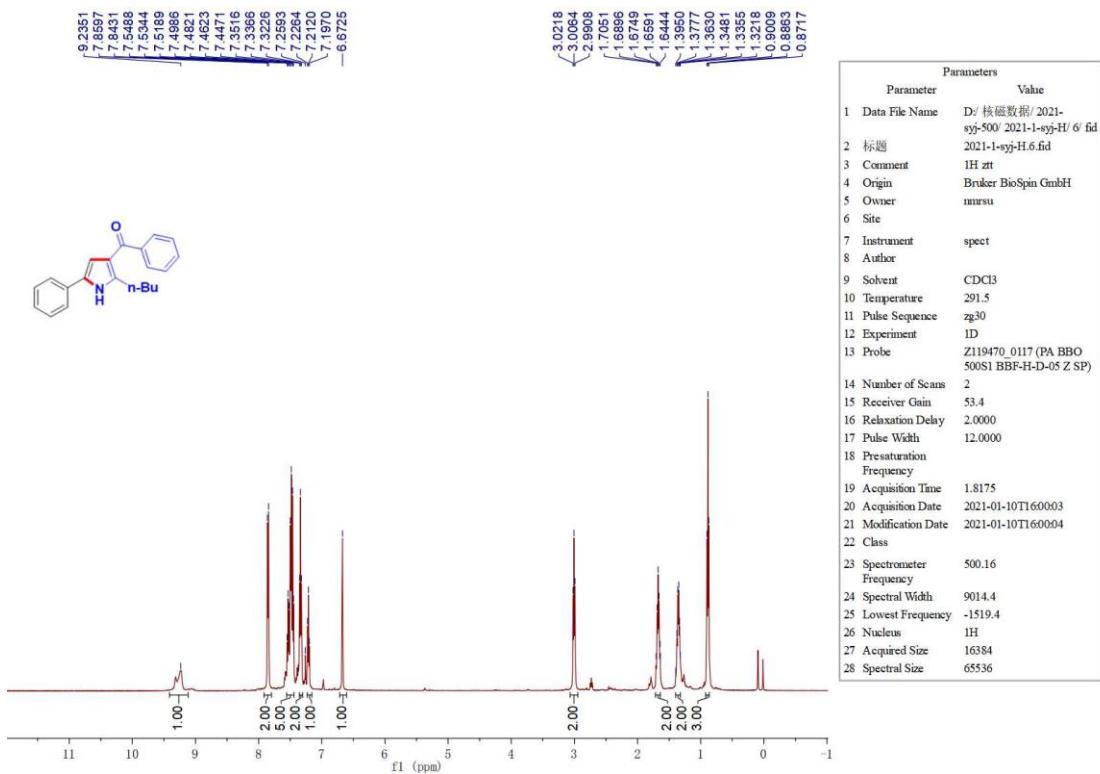
### (2-Isopropyl-5-phenyl-1*H*-pyrrol-3-yl) (phenyl)methanone (5q)



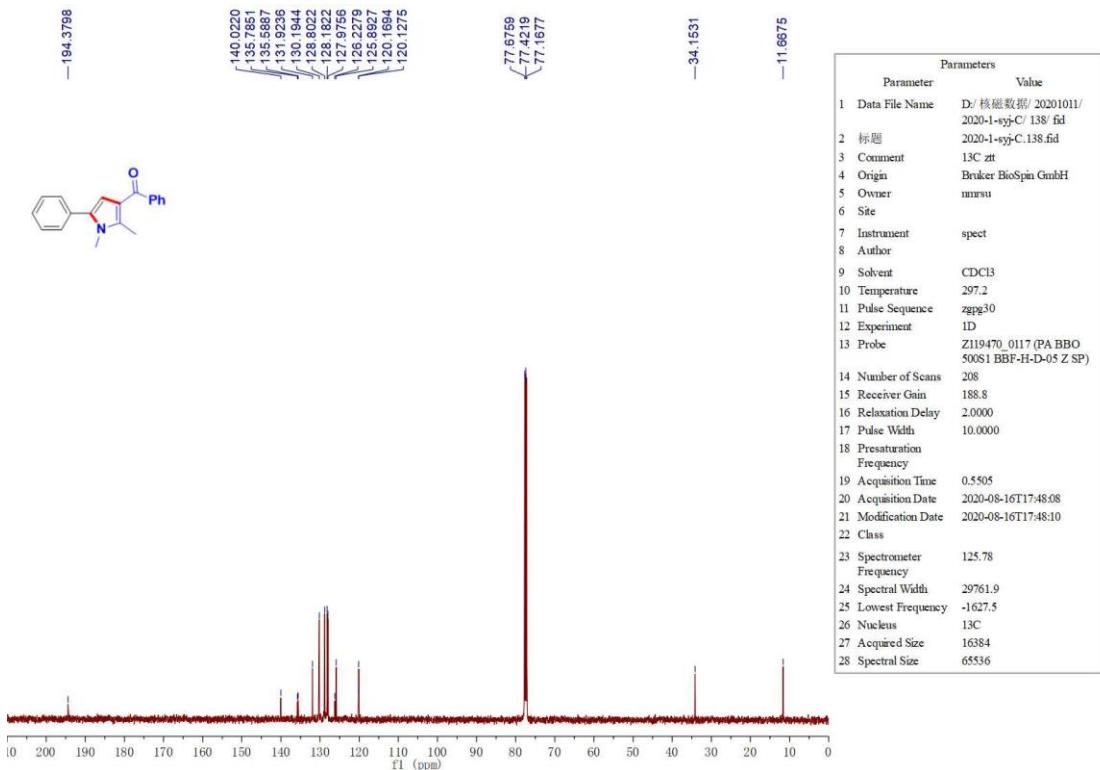
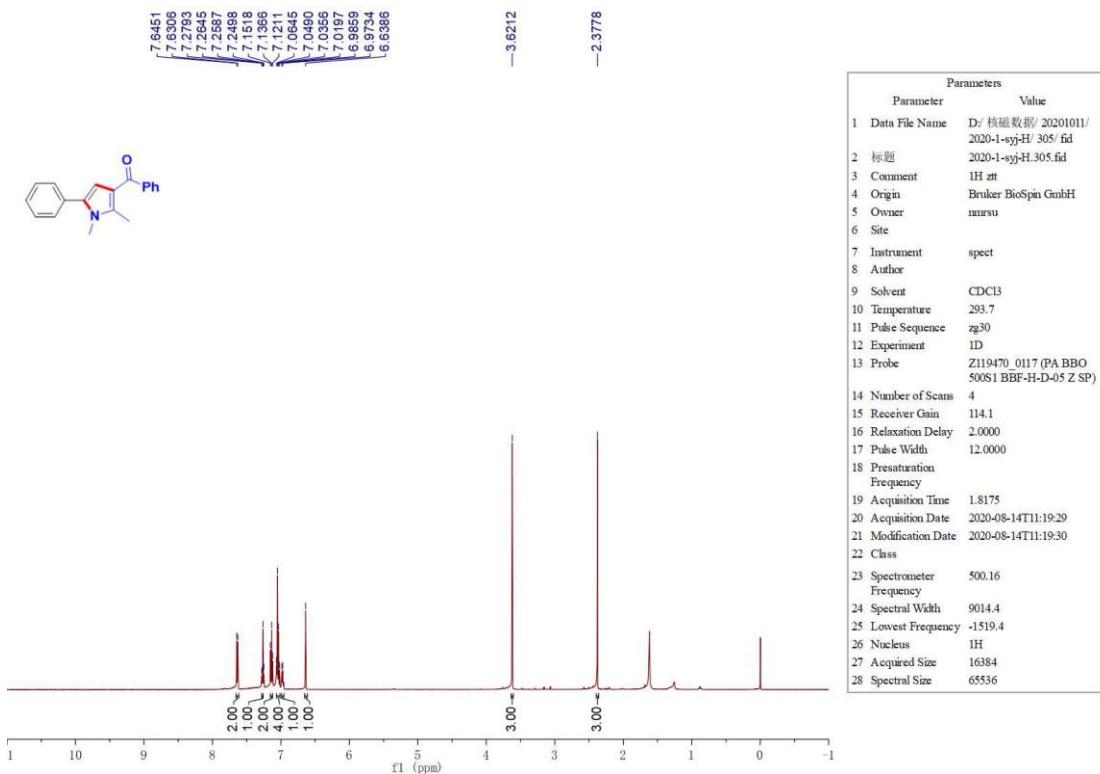
**Phenyl(5-phenyl-2-propyl-1*H*-pyrrol-3-yl) methanone (5r)**



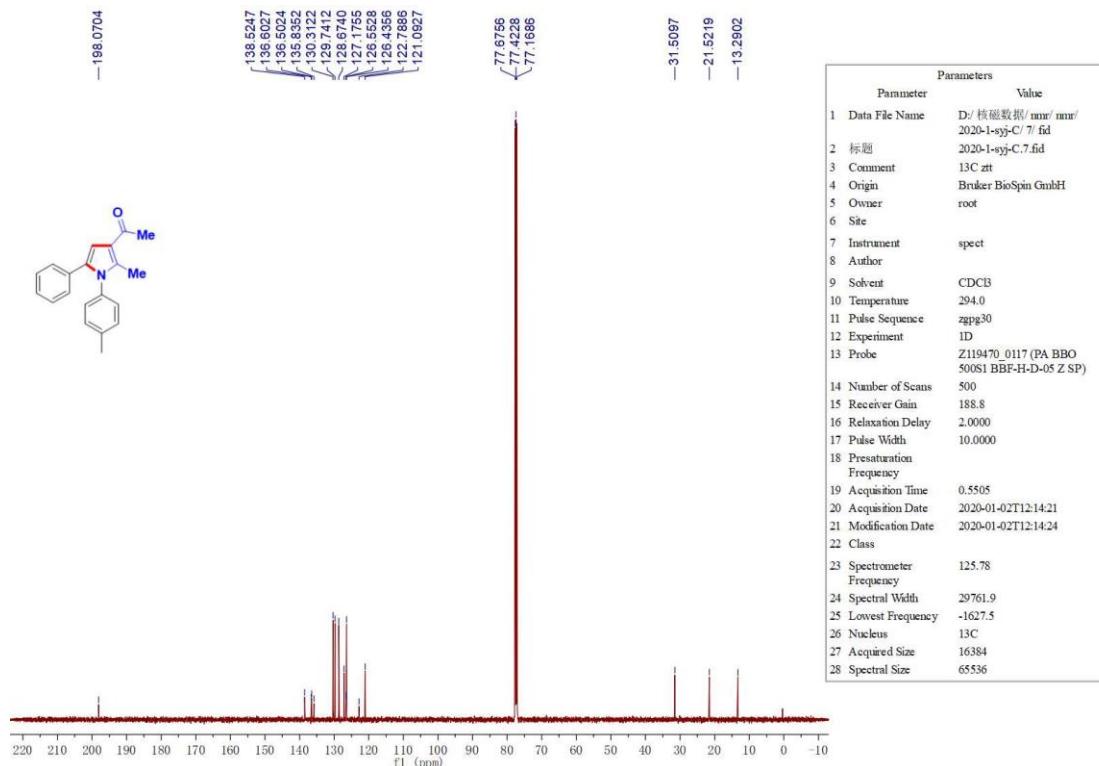
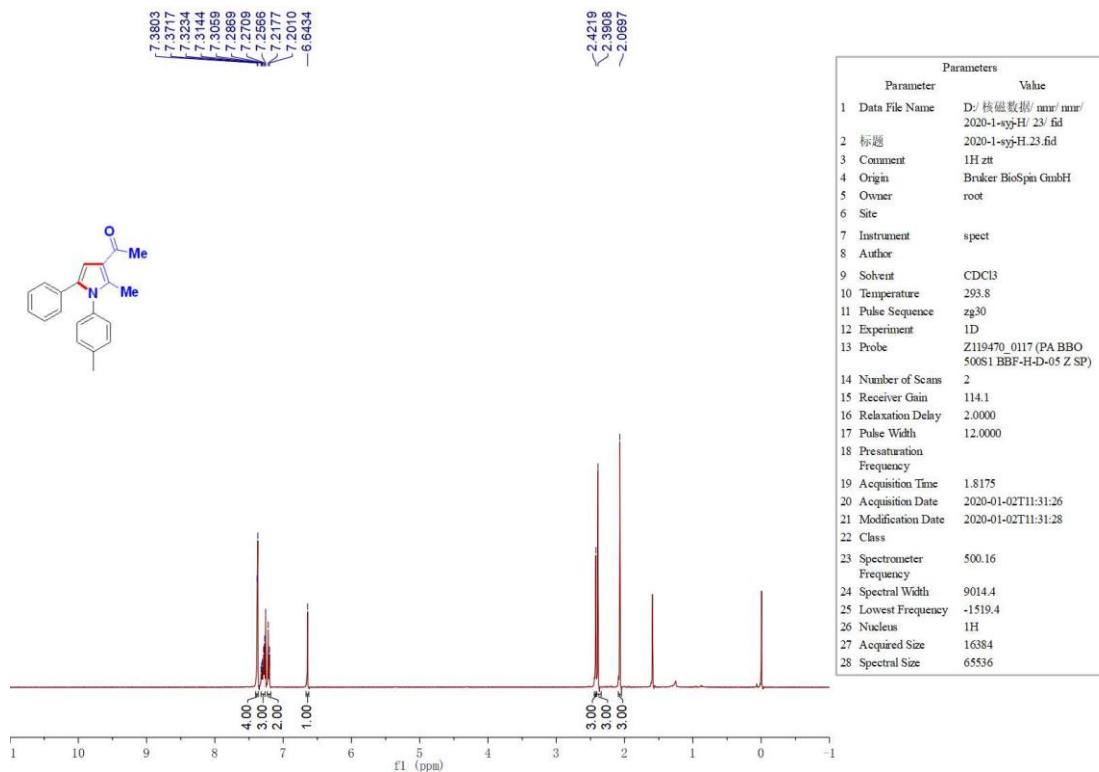
**(2-Butyl-5-phenyl-1*H*-pyrrol-3-yl) (phenyl)methanone (5s)**



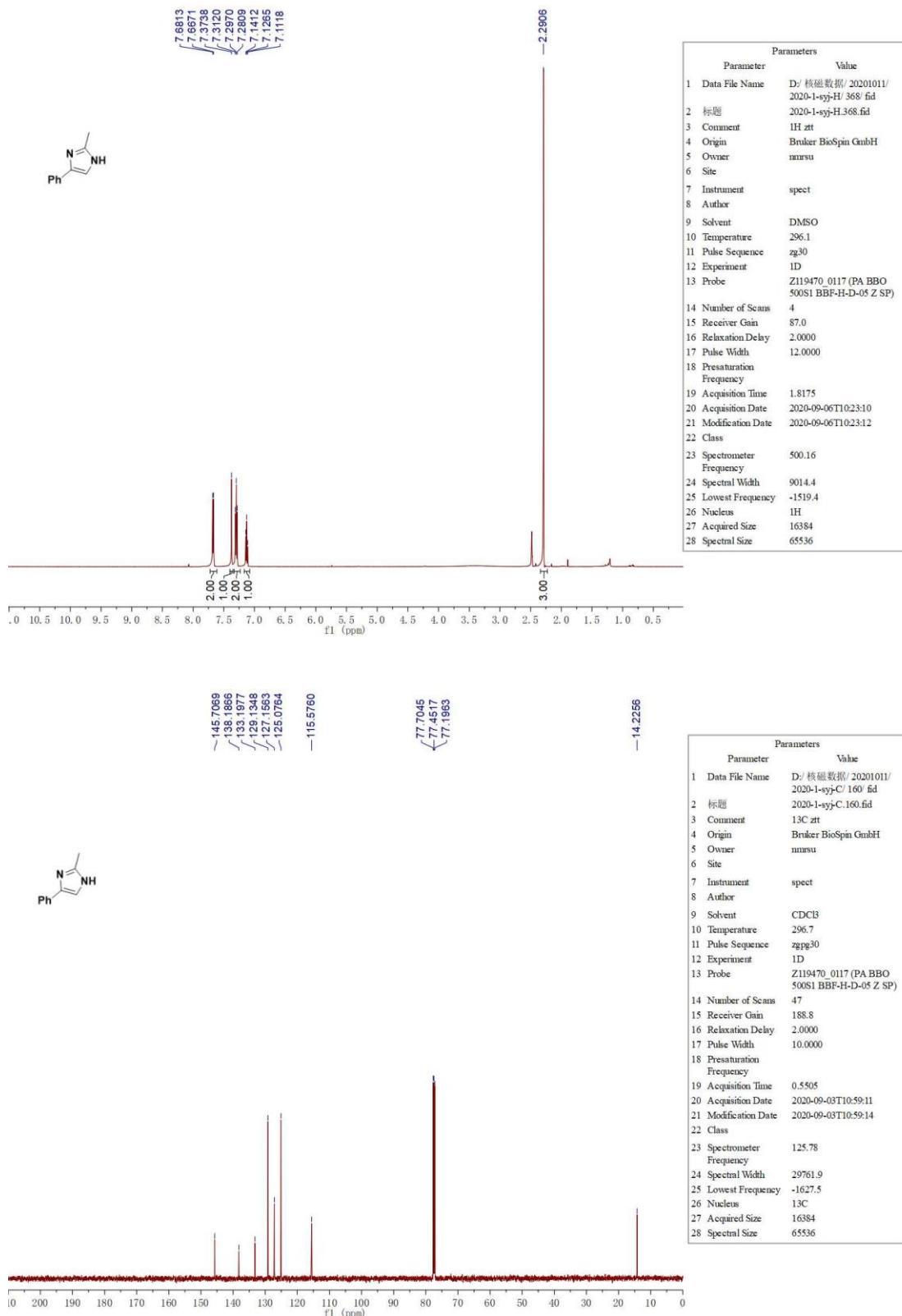
**(1,2-Dimethyl-5-phenyl-1*H*-pyrrol-3-yl) (phenyl)methanone (7a)**



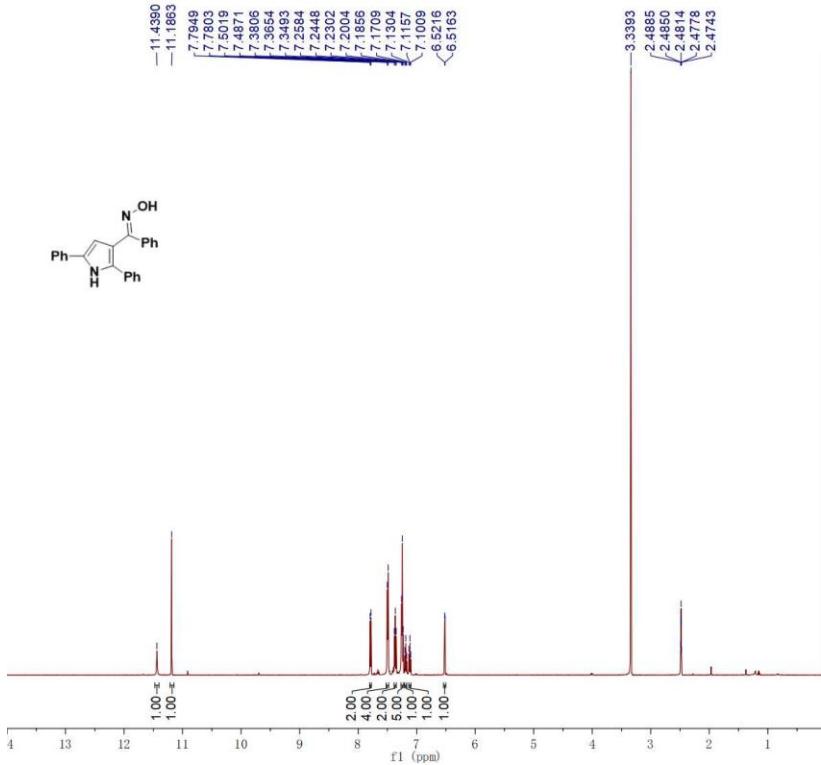
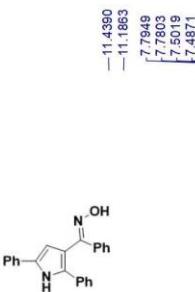
**1-(2-Methyl-5-phenyl-1-(*p*-tolyl)-1*H*-pyrrol-3-yl) ethan-1-one (7b)**



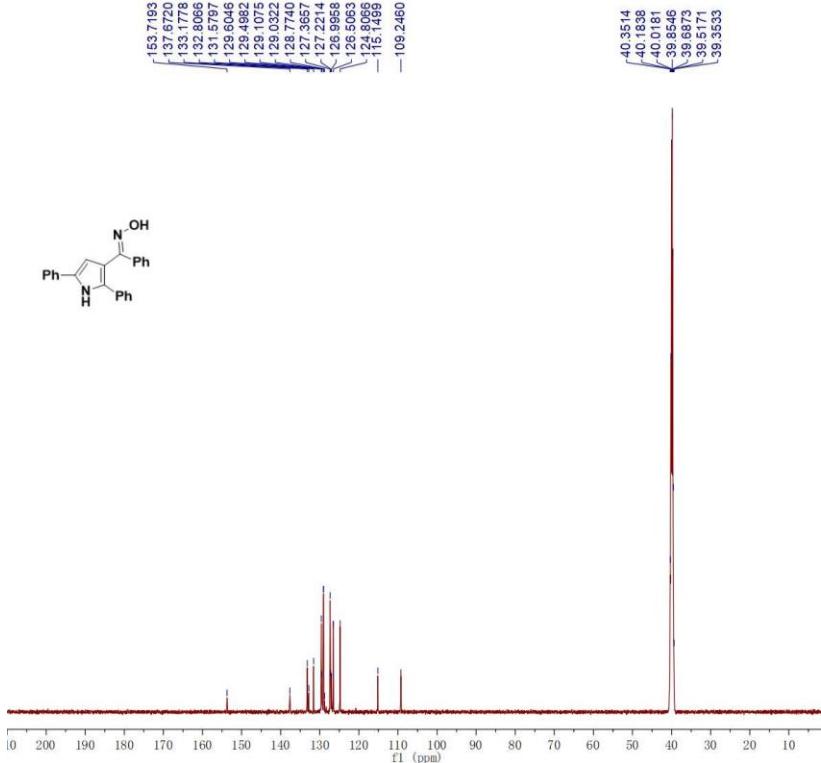
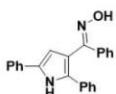
## 2-Methyl-4-phenyl-1*H*-imidazole (8)



**(E)-(2,5-Diphenyl-1*H*-pyrrol-3-yl) (phenyl)methanone oxime (9)**

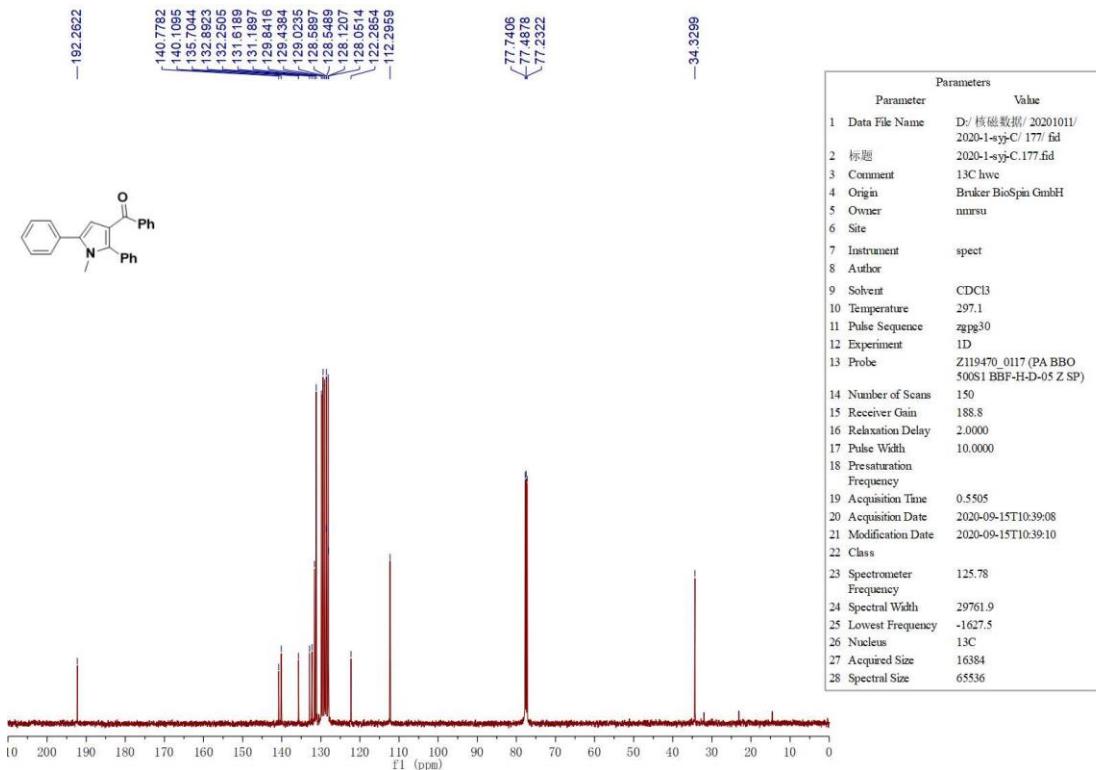
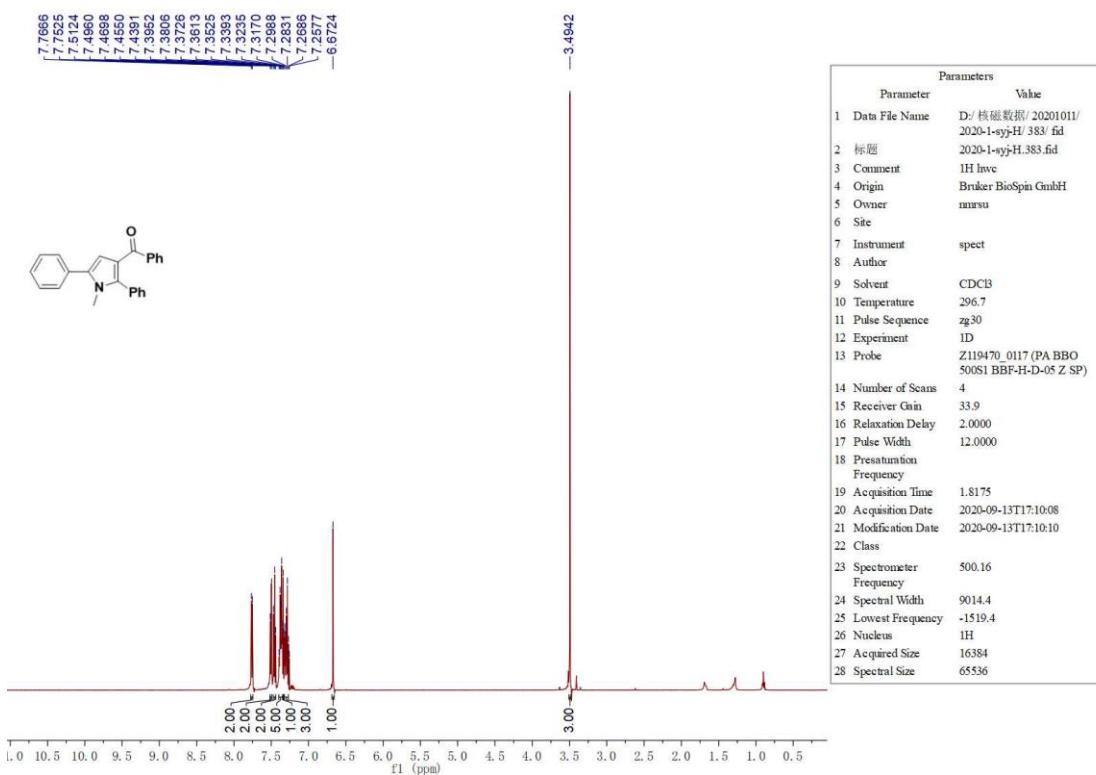


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2 标题	2020-1-sysh-367.fid
3 Comment	1H ztt
4 Origin	Bruker BioSpin GmbH
5 Owner	nmrsu
6 Site	
7 Instrument	spect
8 Author	
9 Solvent	DMSO
10 Temperature	296.1
11 Pulse Sequence	zg30
12 Experiment	1D
13 Probe	Z119470_0117 (PA BBO 500S1 BBF-H-D-05 Z SP)
14 Number of Scans	4
15 Receiver Gain	87.0
16 Relaxation Delay	2.0000
17 Pulse Width	12.0000
18 Presaturation Frequency	
19 Acquisition Time	1.8175
20 Acquisition Date	2020-09-06T10:18:44
21 Modification Date	2020-09-06T10:18:46
22 Class	
23 Spectrometer Frequency	500.16
24 Spectral Width	9014.4
25 Lowest Frequency	-1519.4
26 Nucleus	1H
27 Acquired Size	16384
28 Spectral Size	65536



Parameters	
Parameter	Value
1 Data File Name	D:/ 核磁数据/20201011/2020-1-sjy-C-166.fid
2 标题	2020-1-sjy-C-166.fid
3 Comment	13C ztt
4 Origin	Bruker BioSpin GmbH
5 Owner	nmrsu
6 Site	
7 Instrument	spect
8 Author	
9 Solvent	DMSO
10 Temperature	296.7
11 Pulse Sequence	zgpg30
12 Experiment	ID
13 Probe	Z119470_0117 (PA BBO 500S1 BBF-H-D-05 Z SP)
14 Number of Scans	1105
15 Receiver Gain	188.8
16 Relaxation Delay	2.0000
17 Pulse Width	10.0000
18 Presaturation Frequency	
19 Acquisition Time	0.5505
20 Acquisition Date	2020-09-07T17:17:40
21 Modification Date	2020-09-07T17:17:42
22 Class	
23 Spectrometer Frequency	125.78
24 Spectral Width	29761.9
25 Lowest Frequency	-1627.5
26 Nucleus	13C
27 Acquired Size	16384
28 Spectral Size	65536

**(1-Methyl-2,5-diphenyl-1*H*-pyrrol-3-yl) (phenyl)methanone (10)**



#### 4. GC-MS spectra for mechanistic investigations

