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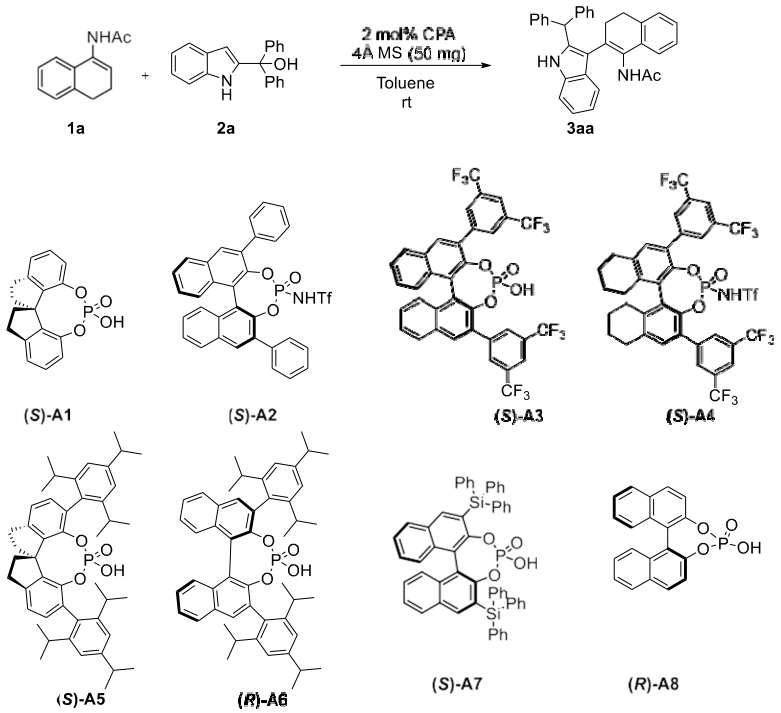
A. General information

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere in anhydrous conditions. All chemicals which are commercially available were used without further purification unless otherwise noted. All the solvents were purified according to the standard procedures. Analytical thin-layer chromatography (TLC) was performed on silica gel plates (GF-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (200-300 mesh). NMR spectra were recorded at ambient temperature in $CDCl_3$ and DMSO on a Bruker AMX 500 (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz) or on a AVANCE III (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm). High resolution mass spectra were obtained on a Agilent 6200 Q-TOF MS and Waters G2-S QTOF. The substrates were prepared by know methods.[1,2]

B. Screening of the CPA



Entry	Acid	Time (h)	Yield (%)[b]	Ee (%)
1	A1	36	15	0
2[c]	A2	72	NR	--
3[c]	A3	72	NR	--
4	A4	36	17	0
5[c]	A5	72	NR	--
6[c]	A6	72	NR	--
7[c]	A7	72	NR	--
8	A8	2	35	0

[a]Unless otherwise noted, the reactions were performed with **1a** (0.20 mmol), **2a** (0.20

mmol) in toluene (2 ml) at room temperature. [b] Isolated yield of the product. [c] The reaction was run at 70 ℃.

C. X-Ray Crystallographic Data of 3aa

Crystallization procedure of 3aa: Single crystals of **3aa** were obtained by slow evaporation of a solution containing **3aa** in the mixture of DCM and *n*-Hexane at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **3aa** are listed in the **Table S1**.

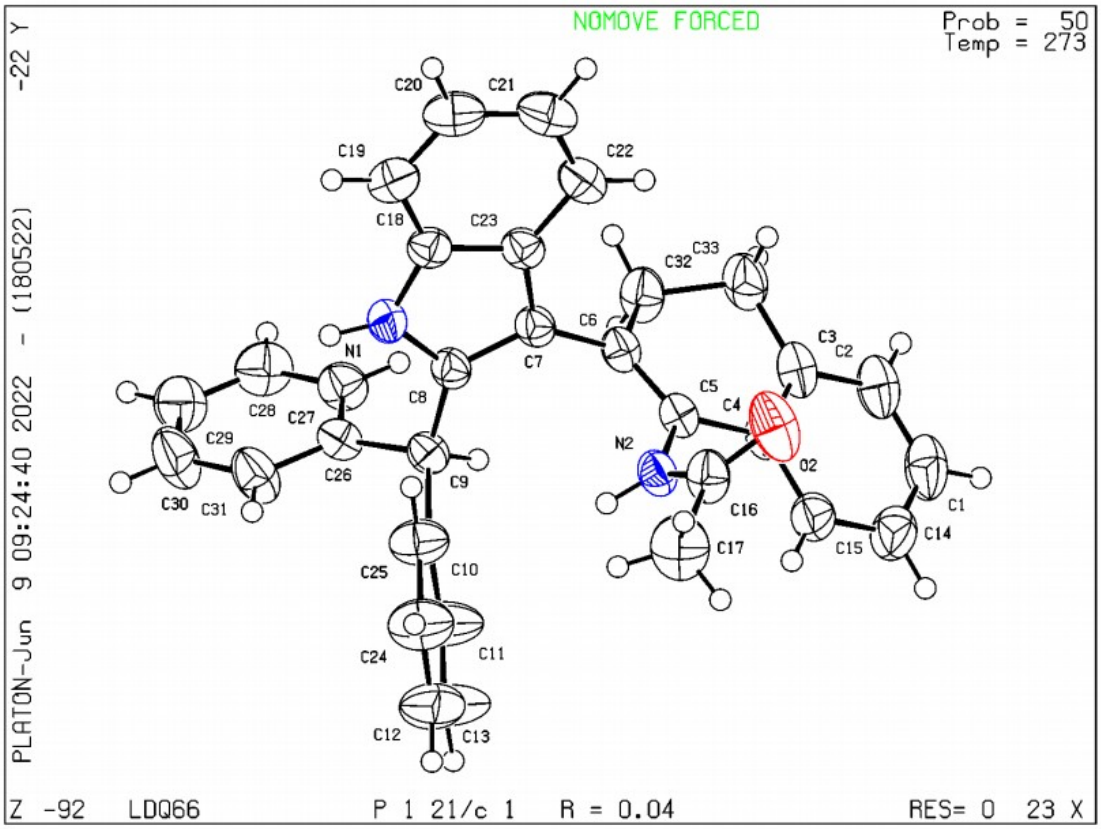


Figure S1. ORTEP view of the compound **3aa** with thermal ellipsoids drawn

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

Bond precision: C-C = 0.0019 A Wavelength=1.54178

Cell: a=8.9311 (1) b=15.3156 (2) c=19.5342 (3)
alpha=90 beta=102.695(1) gamma=90

Temperature: 273 K

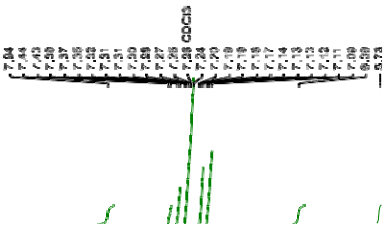
	Calculated	Reported
Volume	2606.67(6)	2606.67(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula:	C_{33} H_{28} N_2O	?
Sum formula:	C_{33} H_{28} N_2O	C_{33} H_{28} N_2O
Mr:	468.57	468.57

Dx, g cm^{-3}:	1.194	1.194
Z:	4	4
Mu (mm^{-1}):	0.558	0.558
F000:	992.0	992.0
F000':	994.68	
h, k, lmax:	11,19,24	11,19,24
Nref:	5662	5651
Tmin, Tmax:	0.921,0.943	0.660,0.940
Tmin':	0.886	

Correction method = # Reported T Limits: Tmin = 0.660 Tmax = 0.940
AbsCorr = MULTI - SCAN

Data completeness = 0.998 Theta (max) = 79.370

R (reflections) = 0.0446 (5033) wR_2(reflections) = 0.1186 (5651)
S = 1.034 Npar= 330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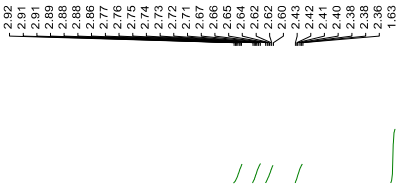

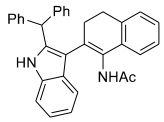
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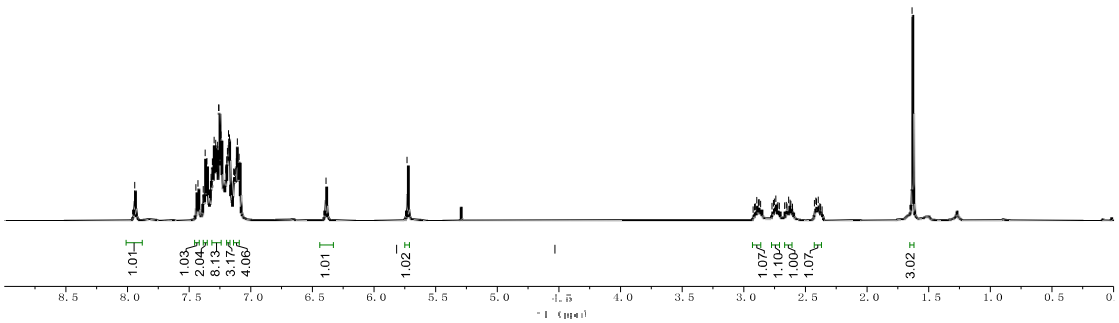
HN
NHAc

3aa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7.0
6.5
6.0
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3.5
3.0
2.5
2.0
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0.5
0


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136.51
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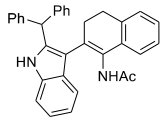
Ph
Ph
HN
NHAc

3aa

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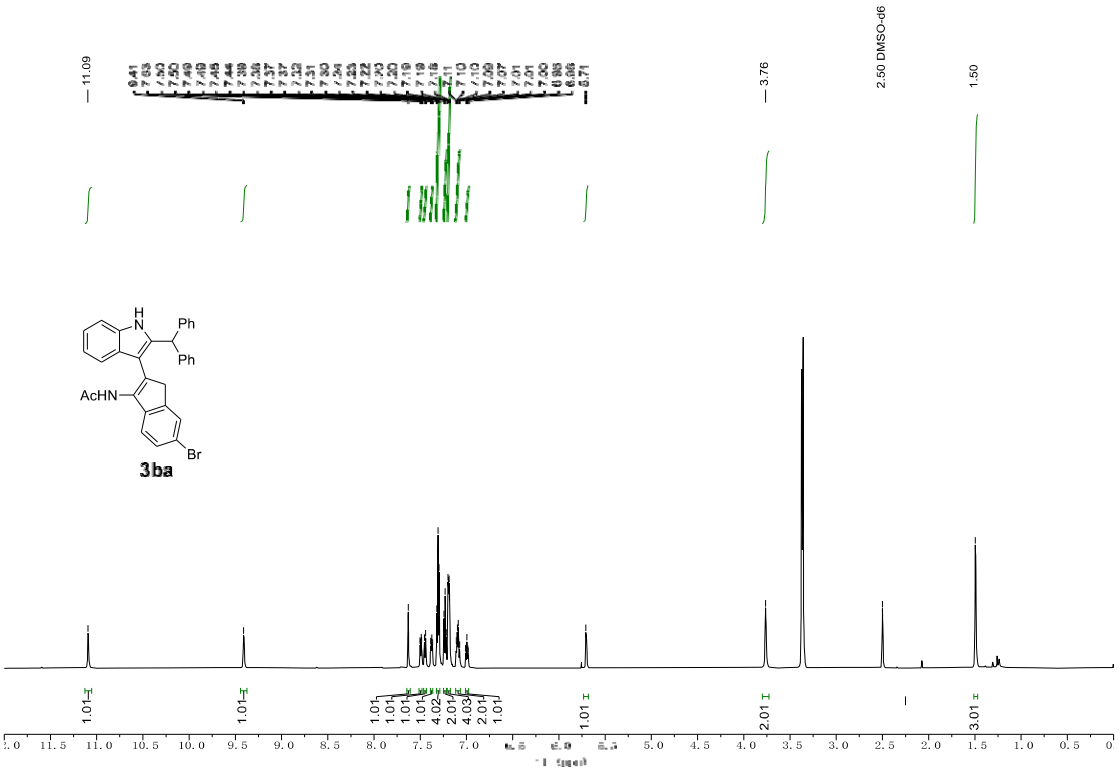
20
10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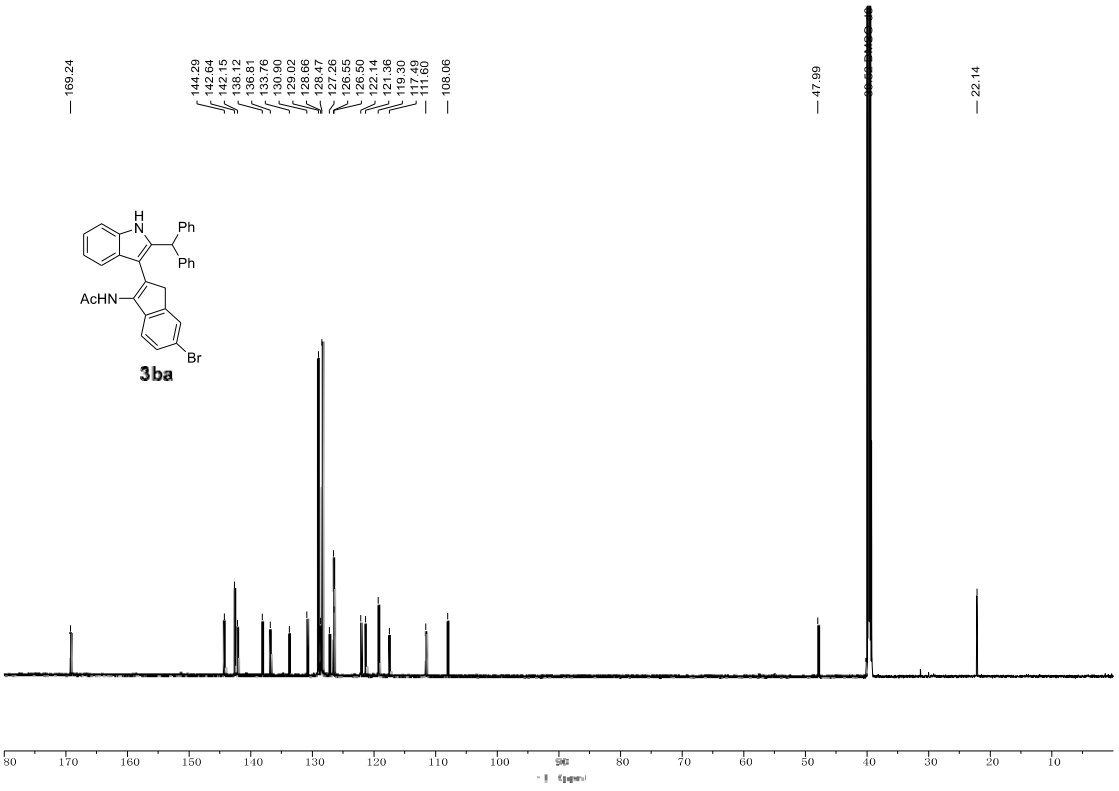
3.01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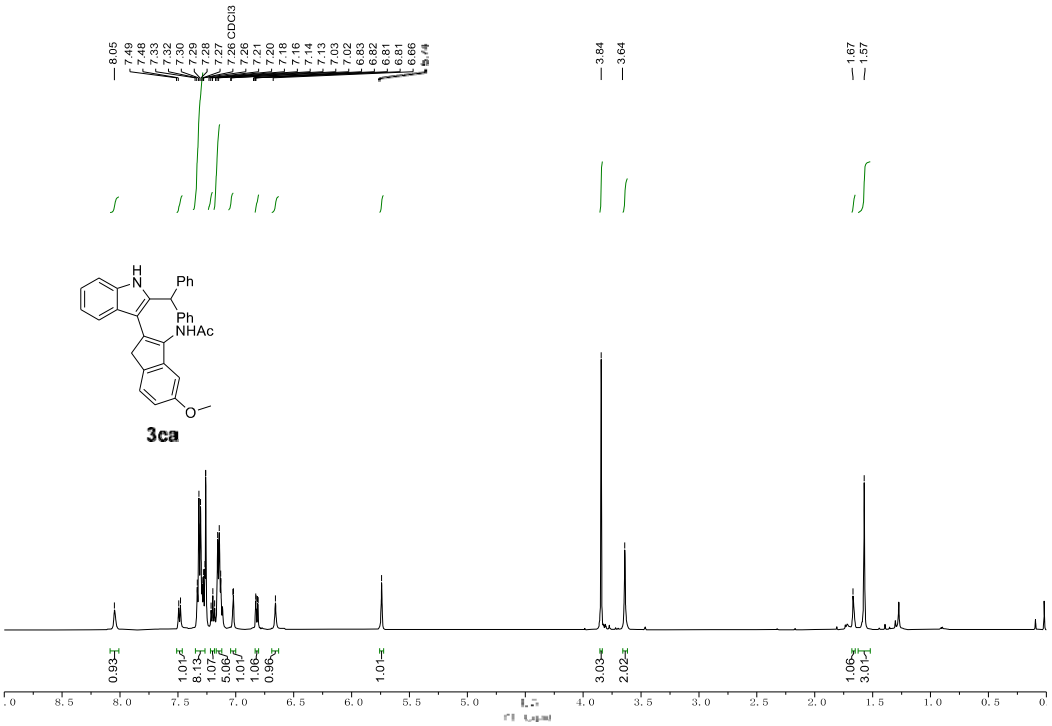
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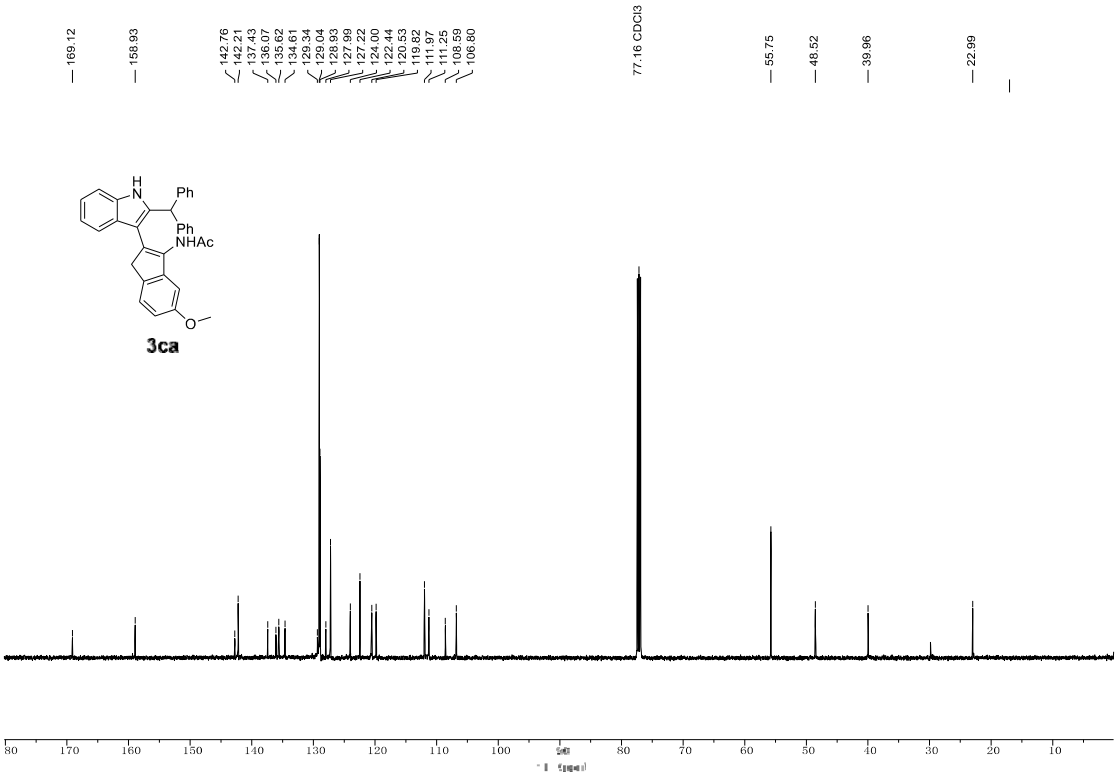
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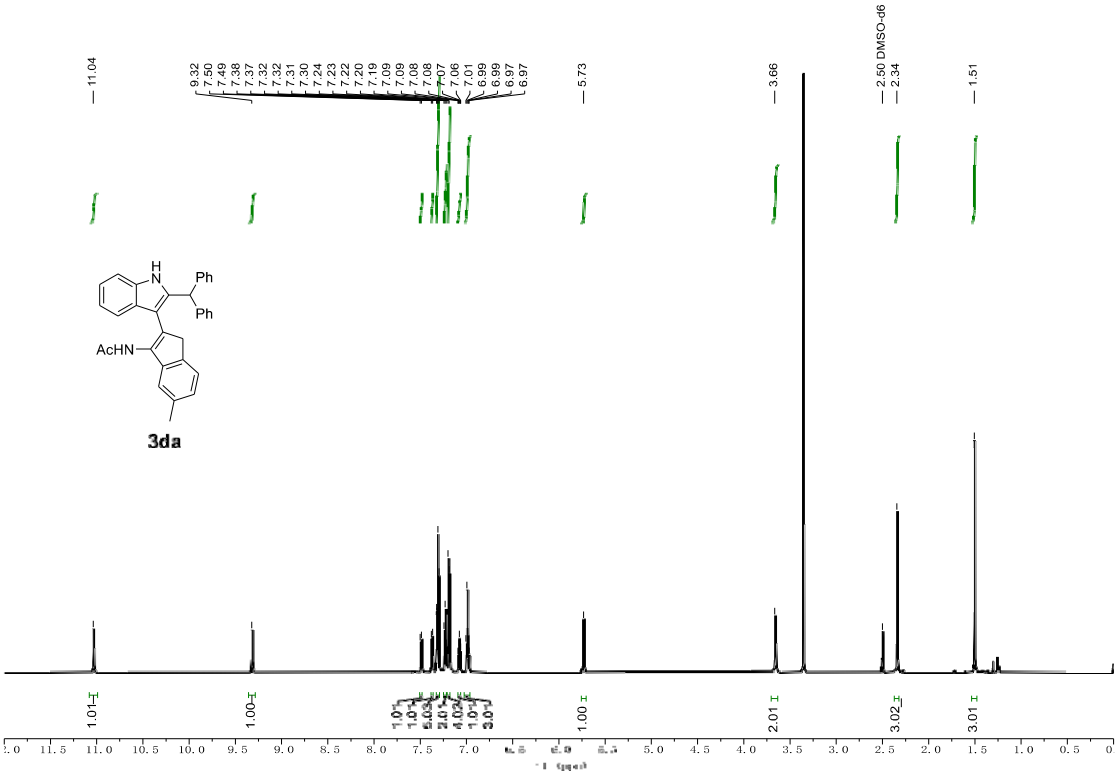
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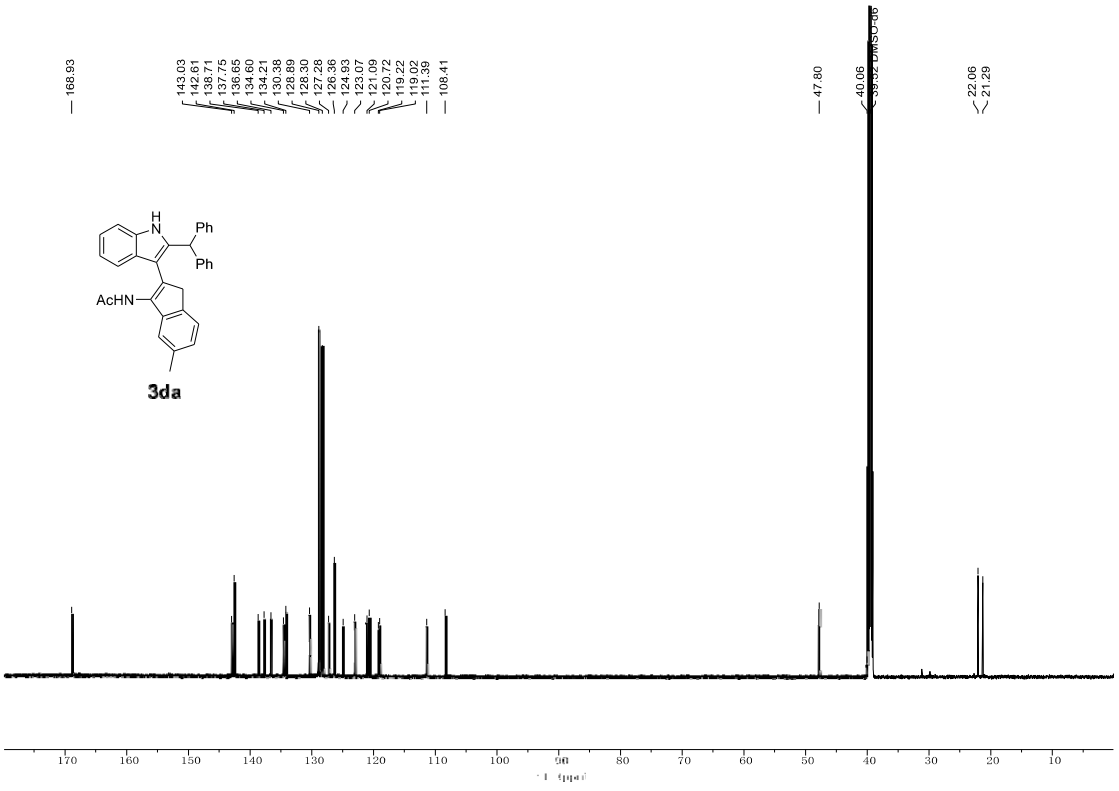
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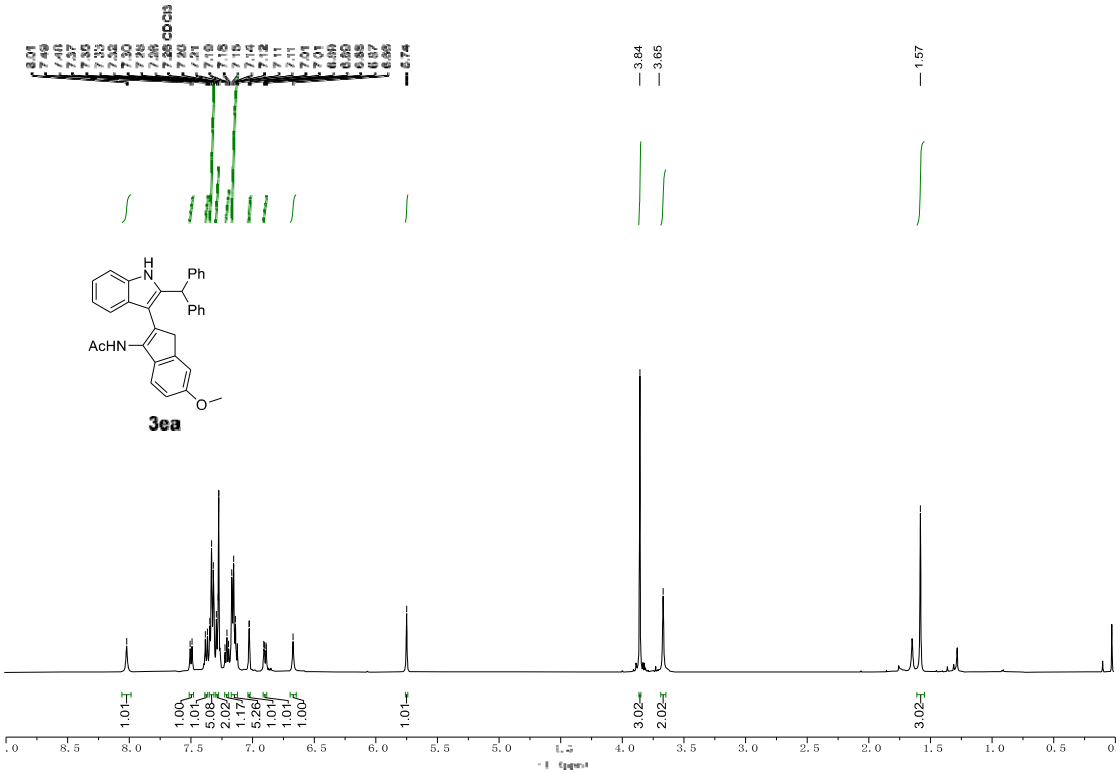
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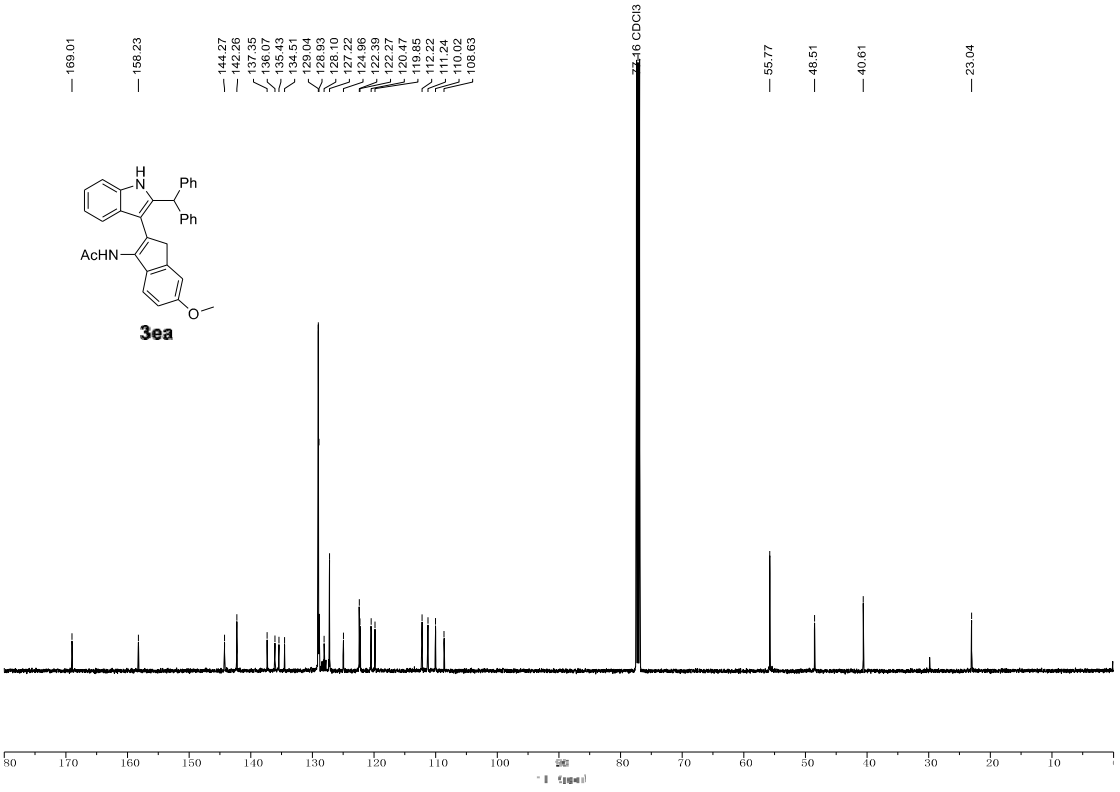
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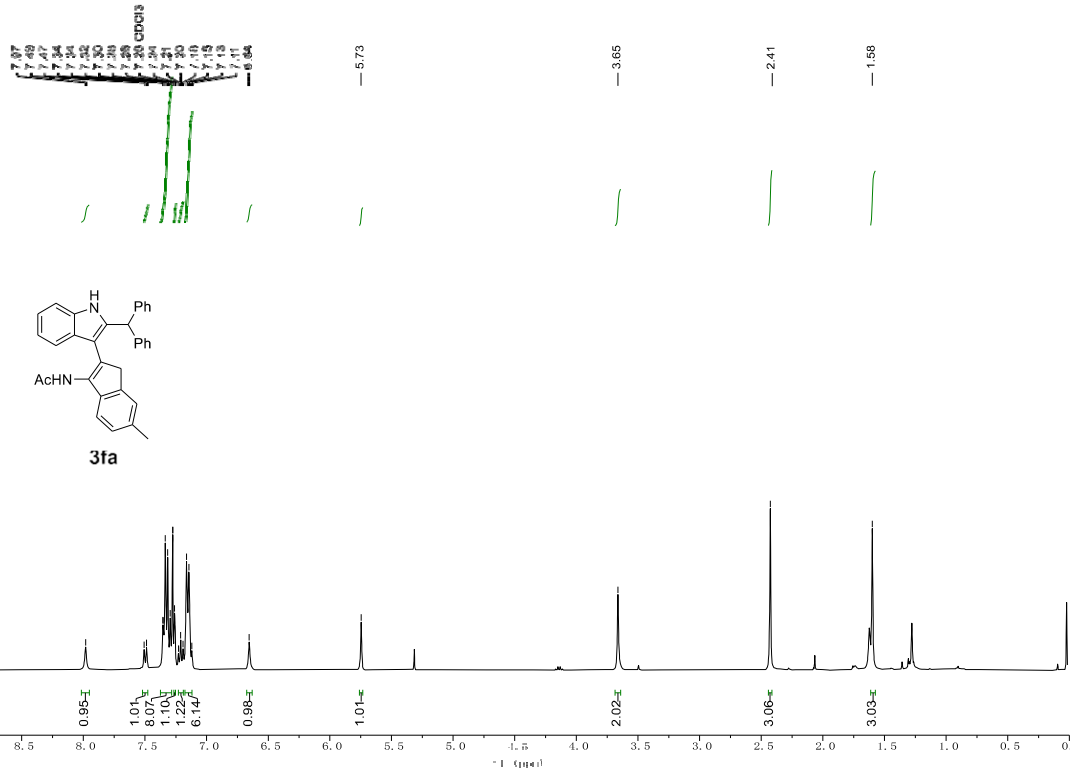
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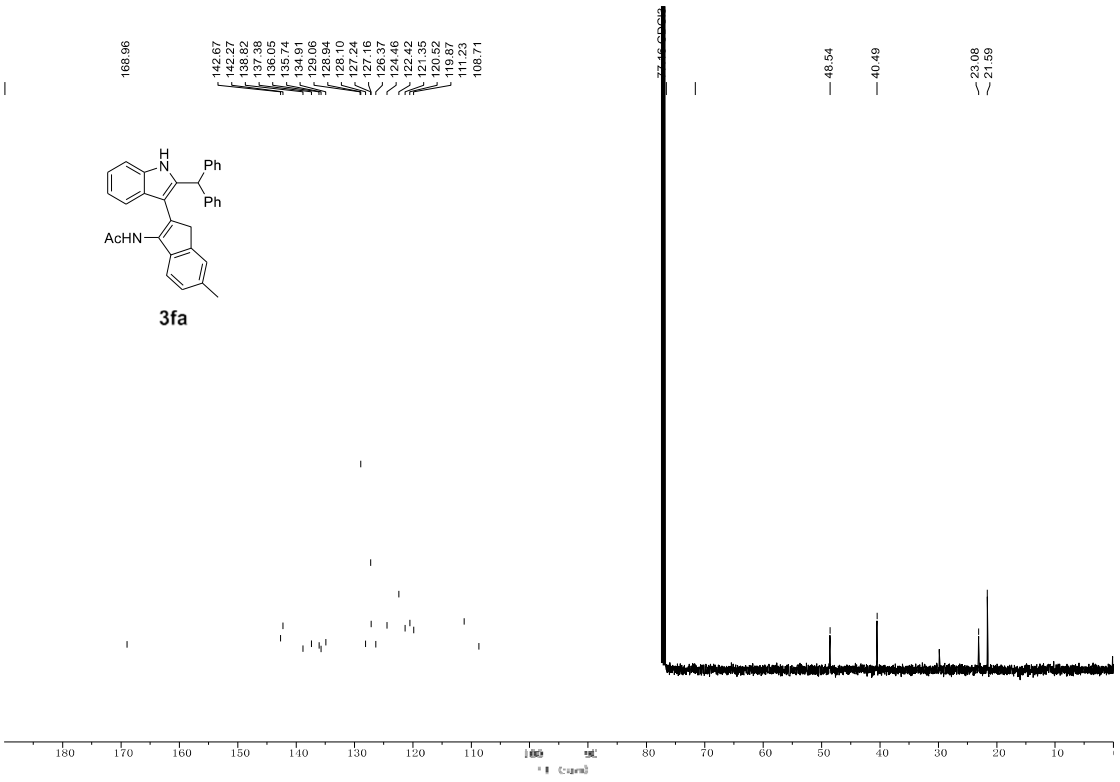
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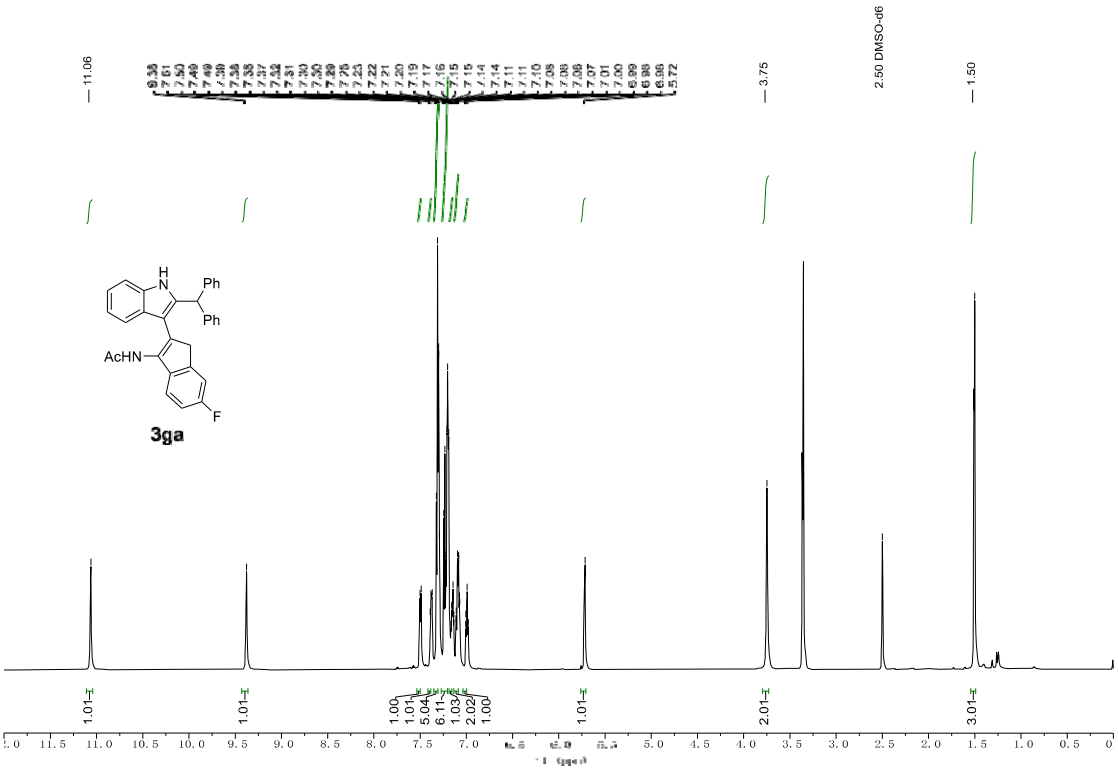
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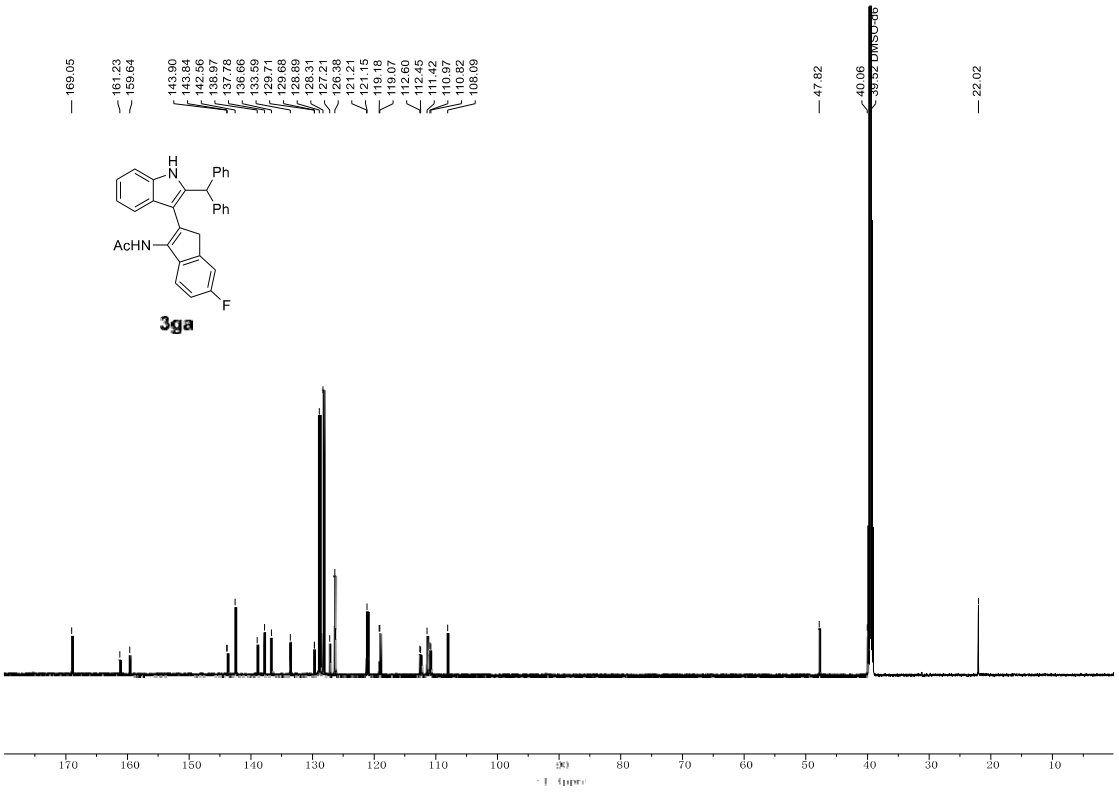
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Ph
F
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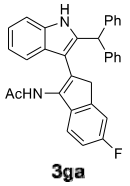
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Ph
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F

3ga

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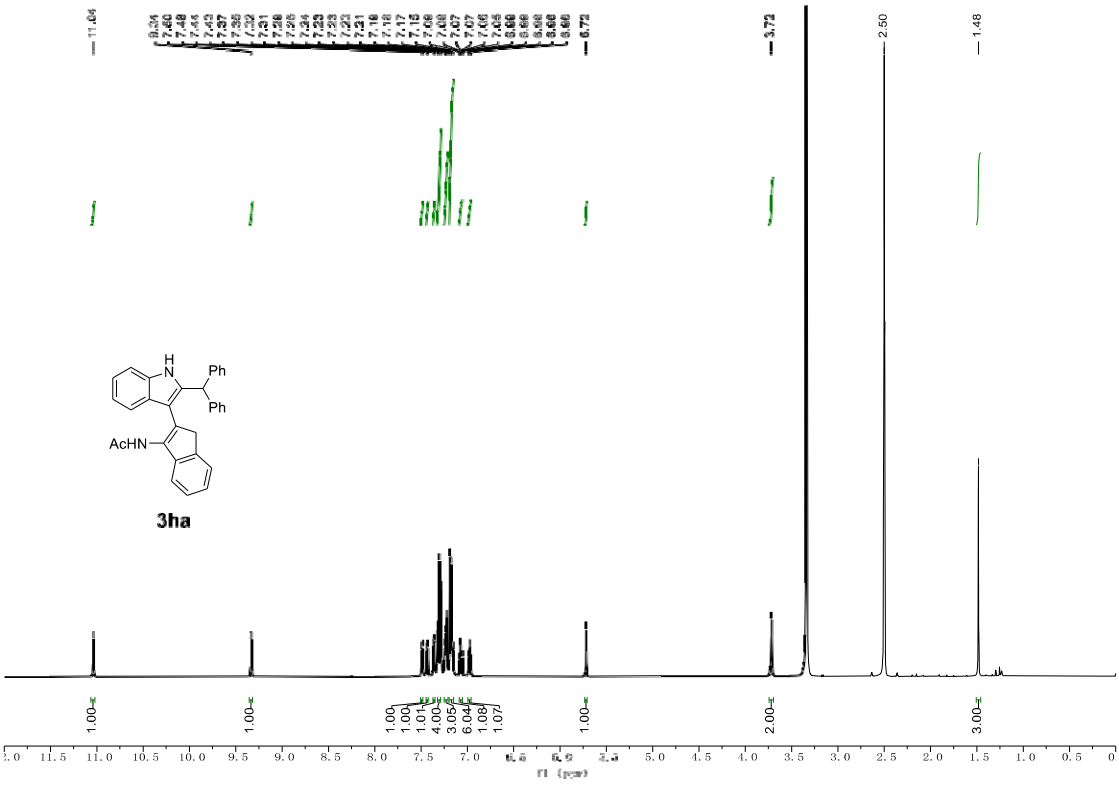
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H
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Ph
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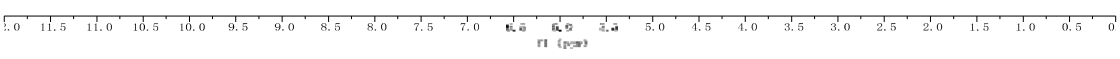
3ha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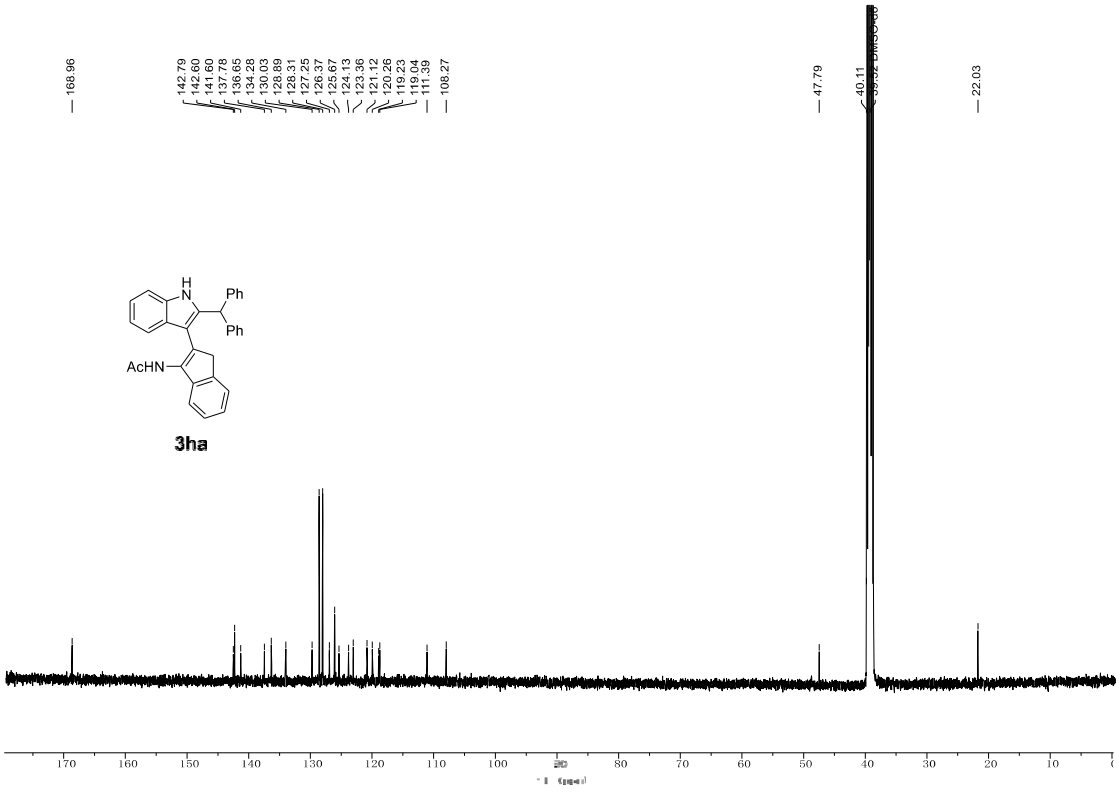
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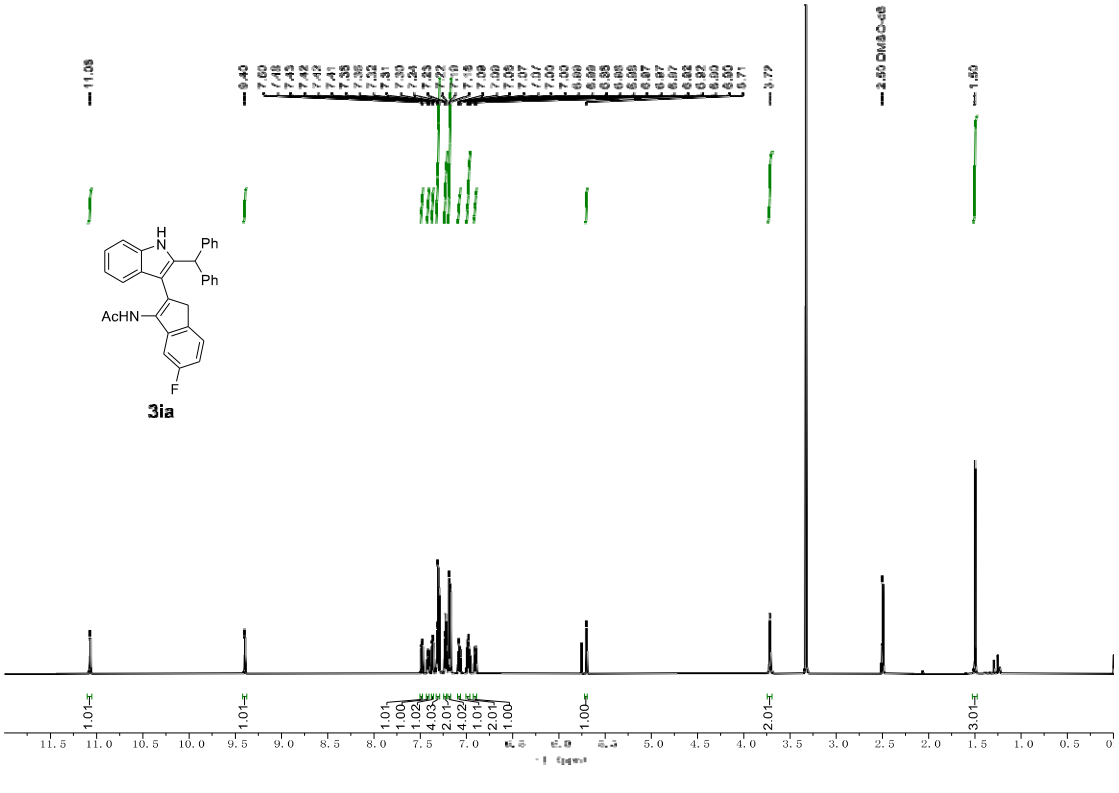
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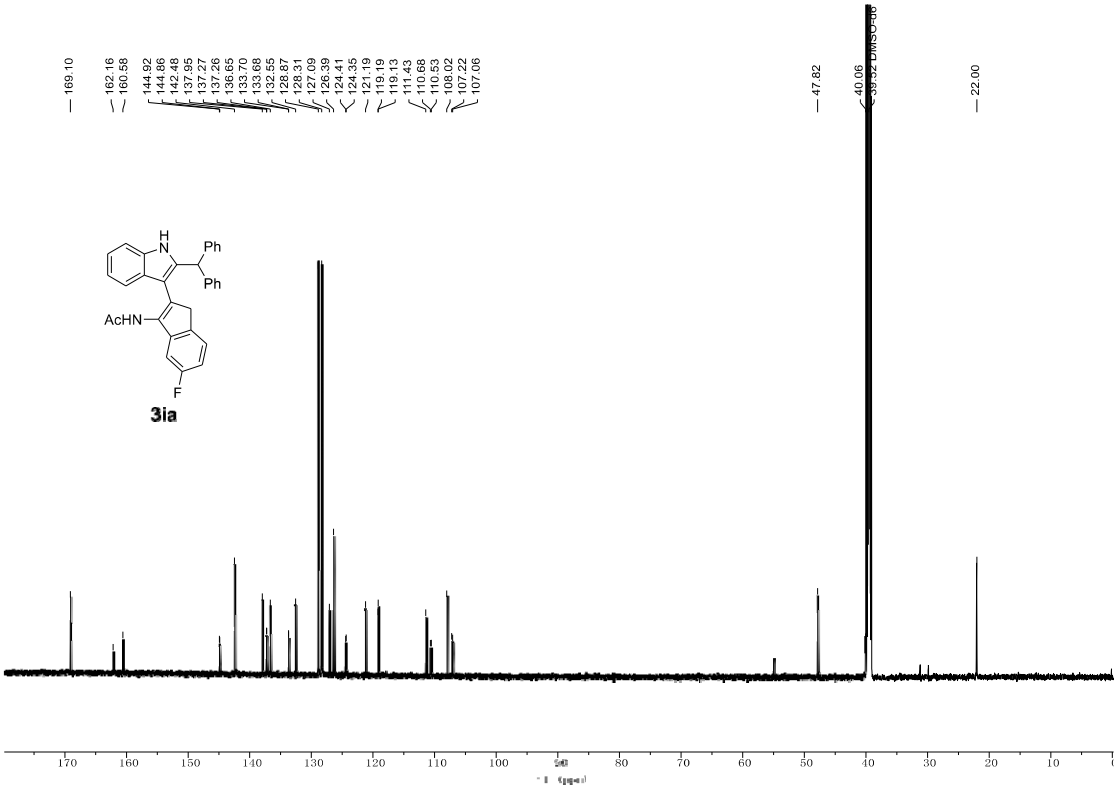
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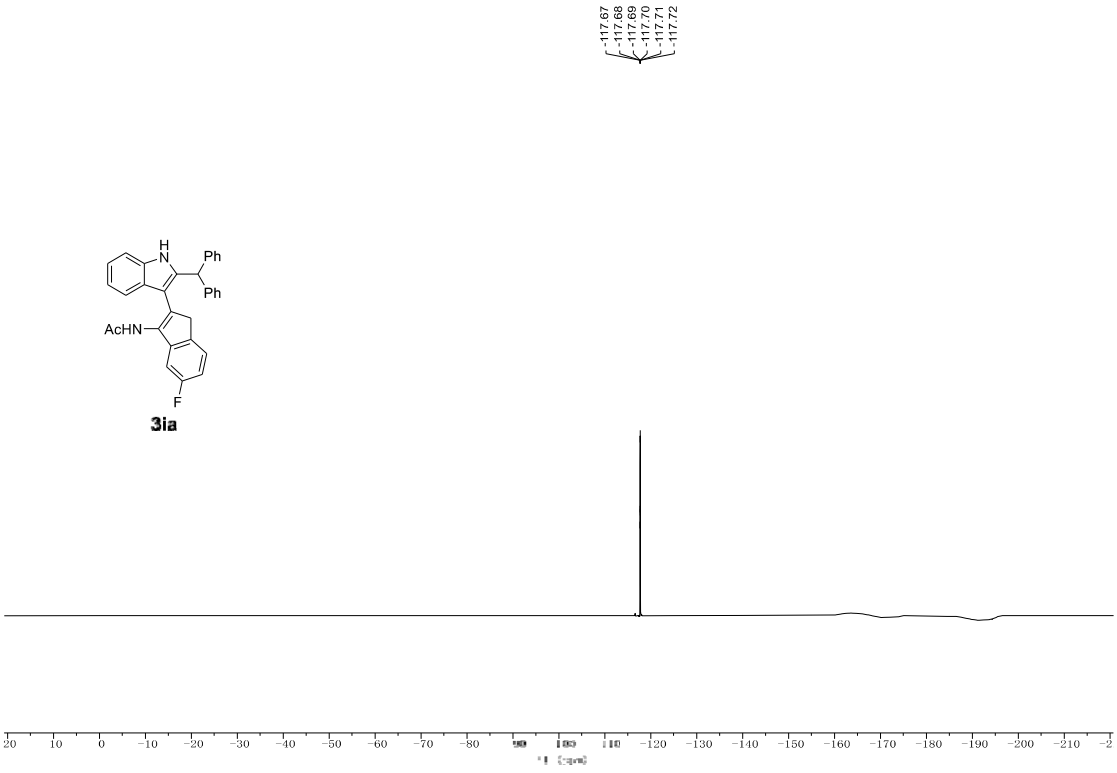
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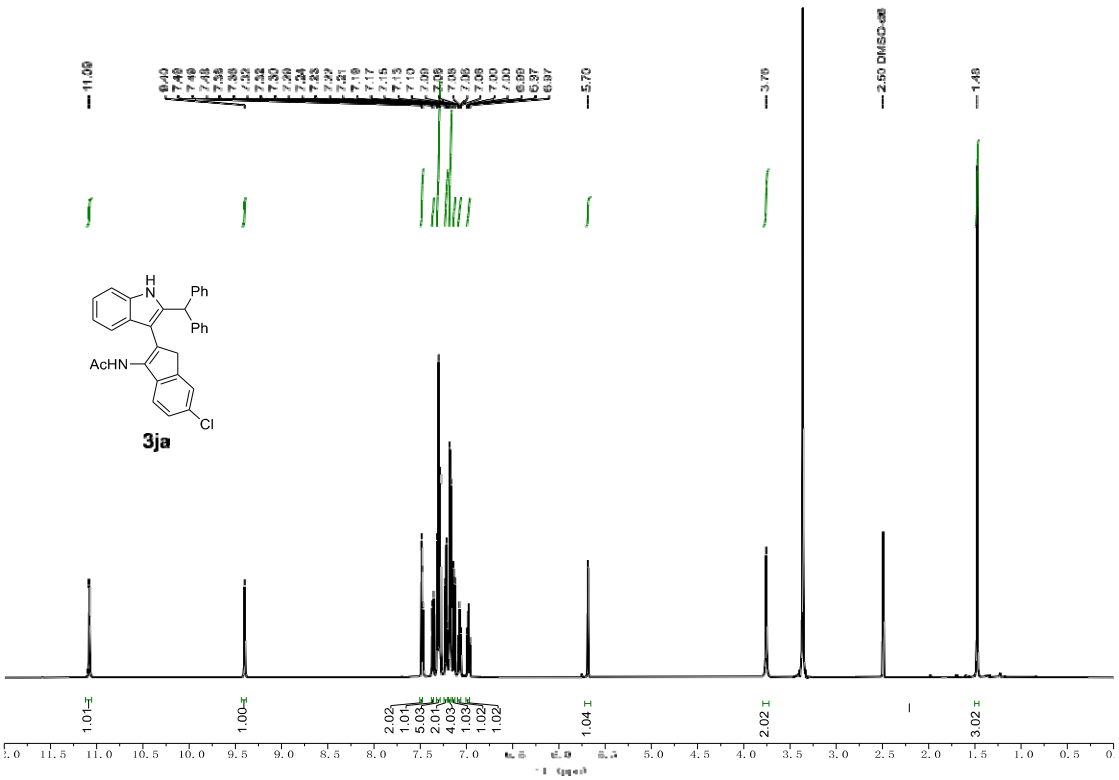
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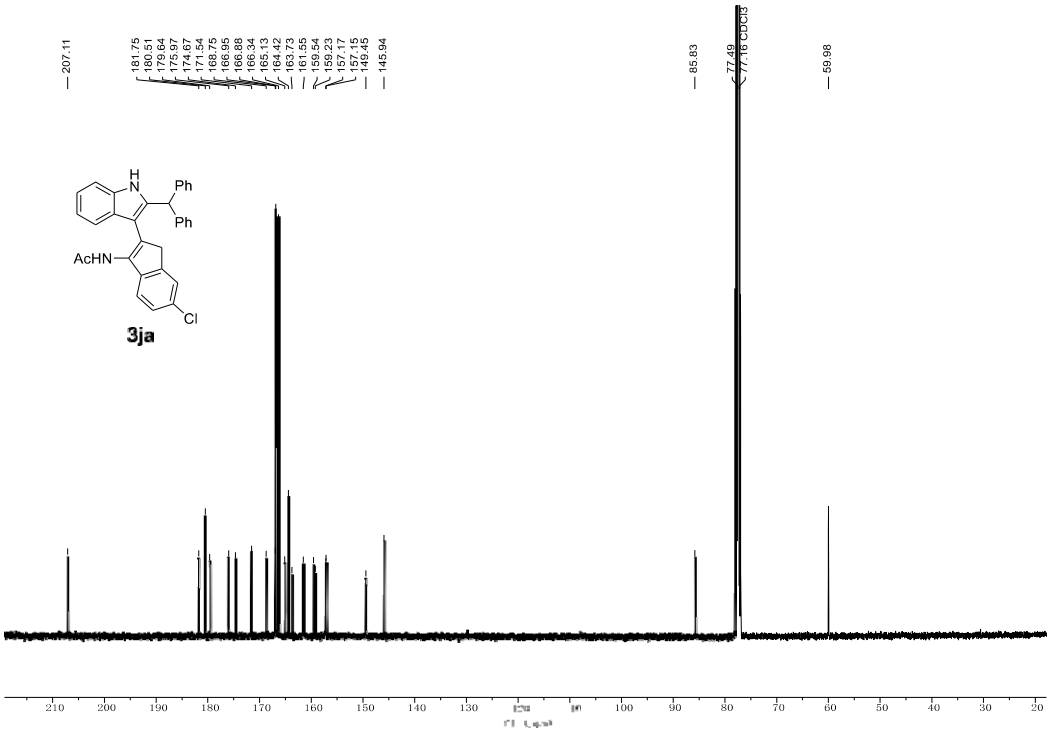
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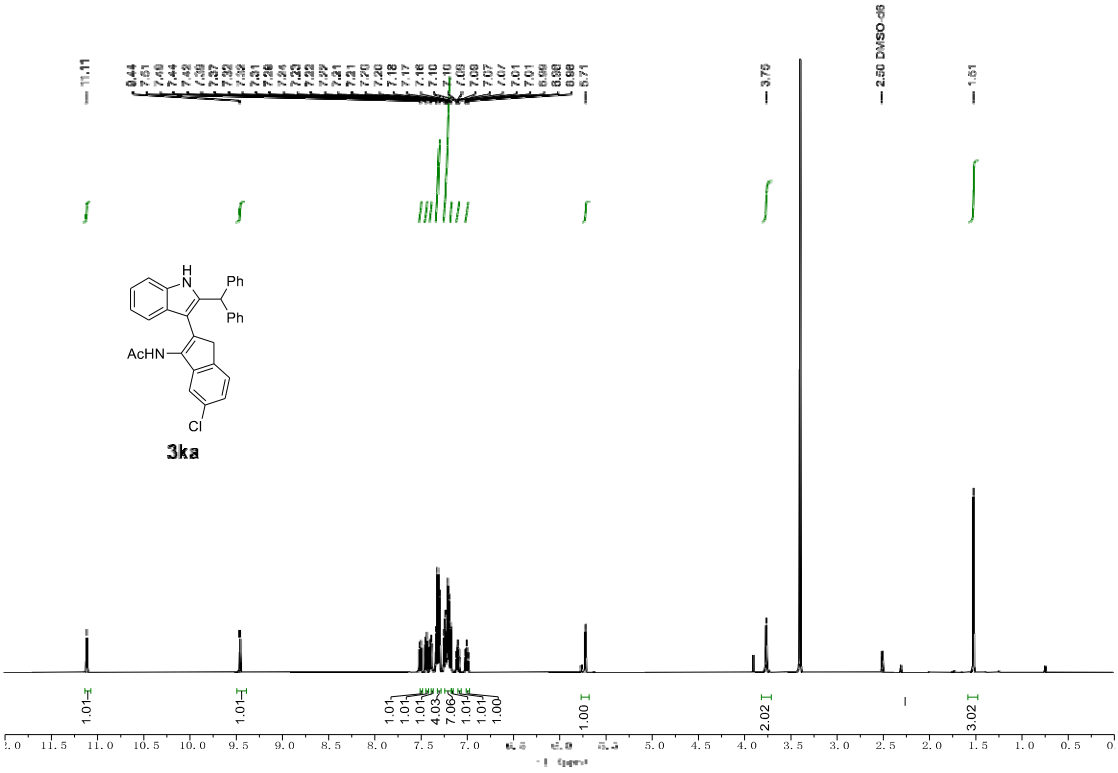
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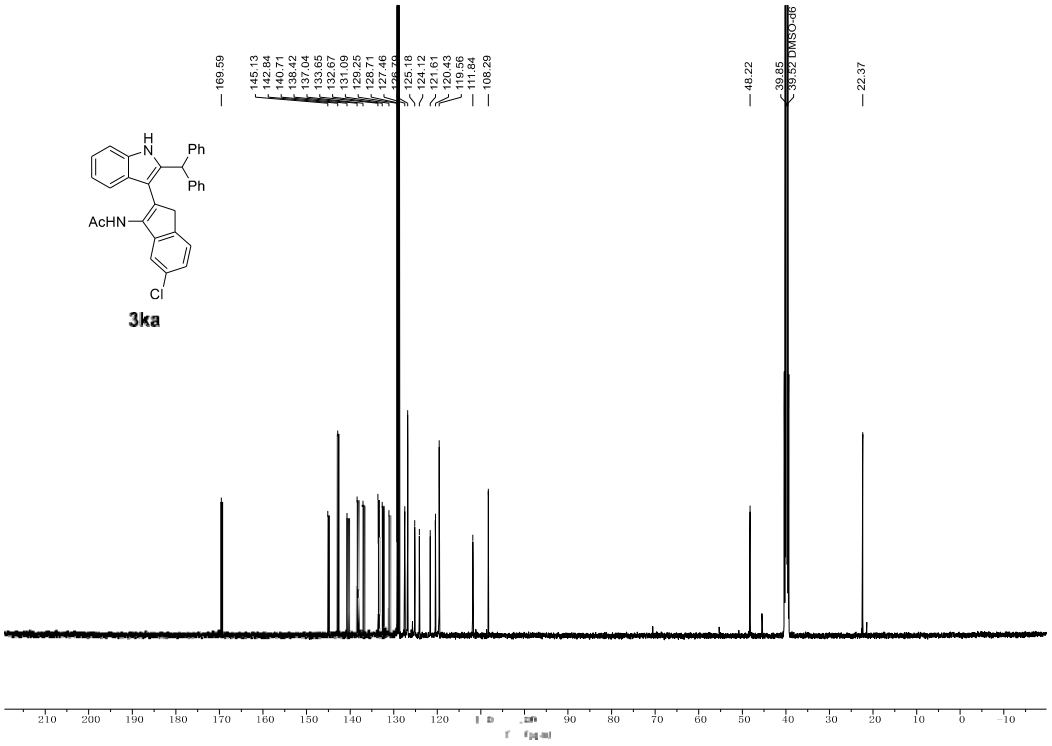
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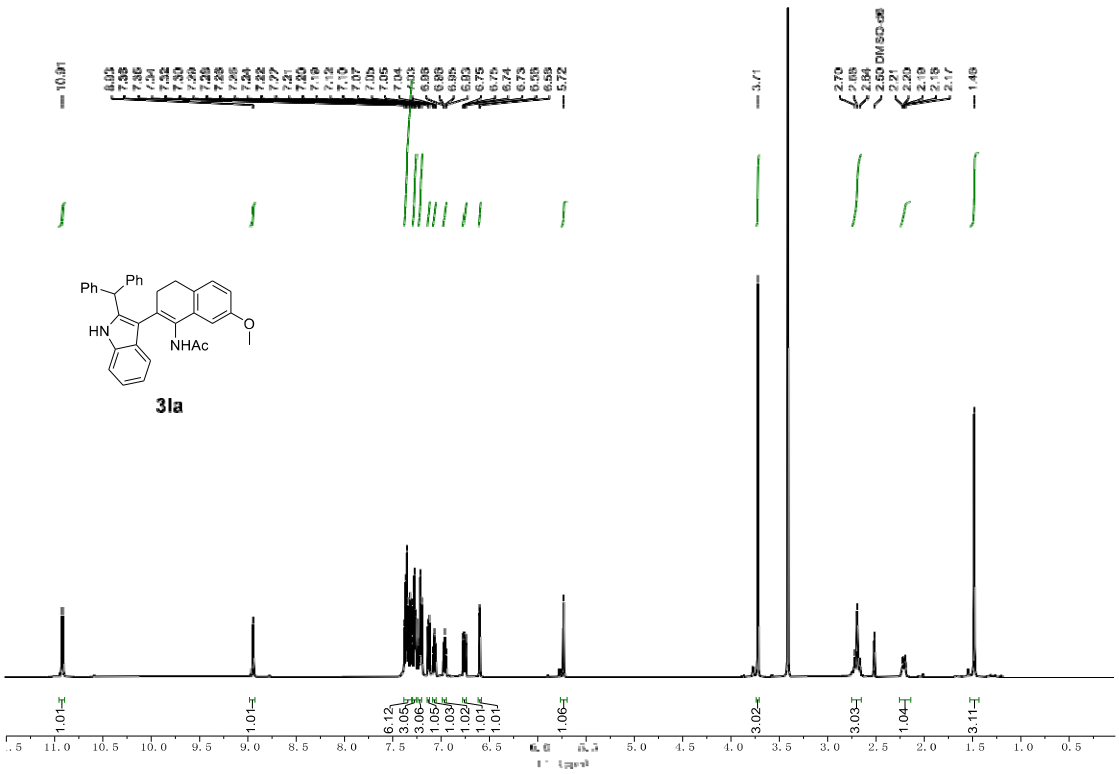

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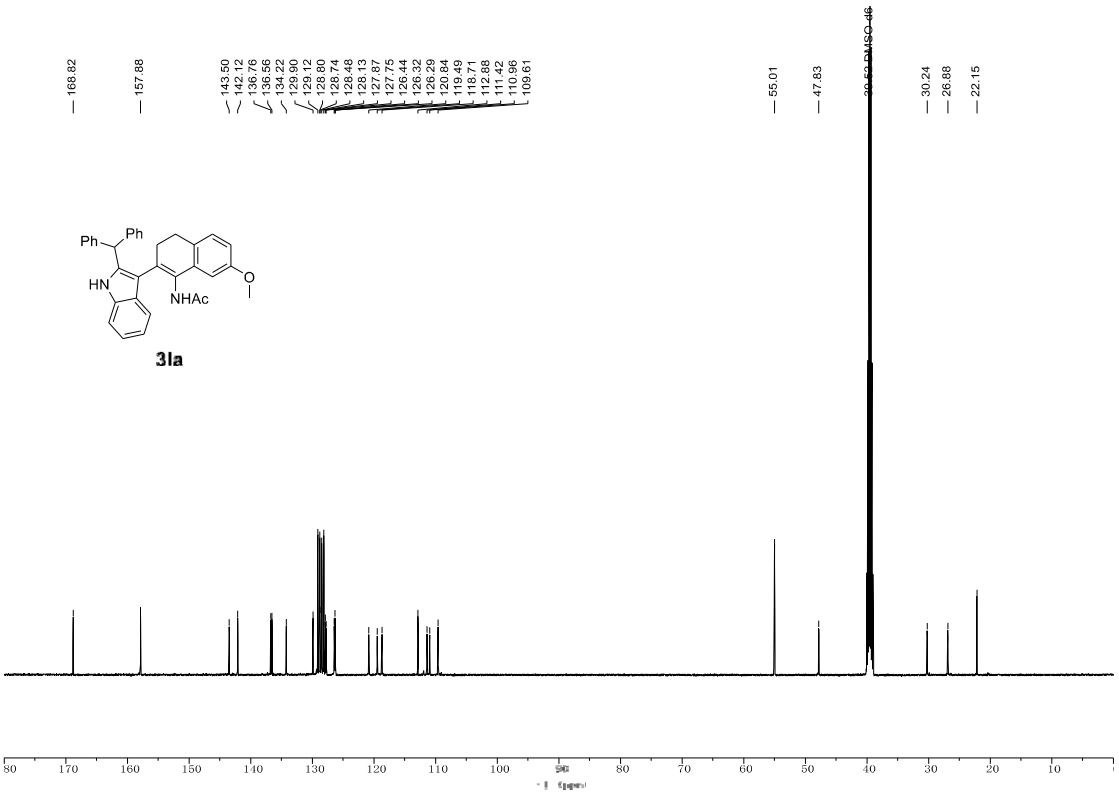

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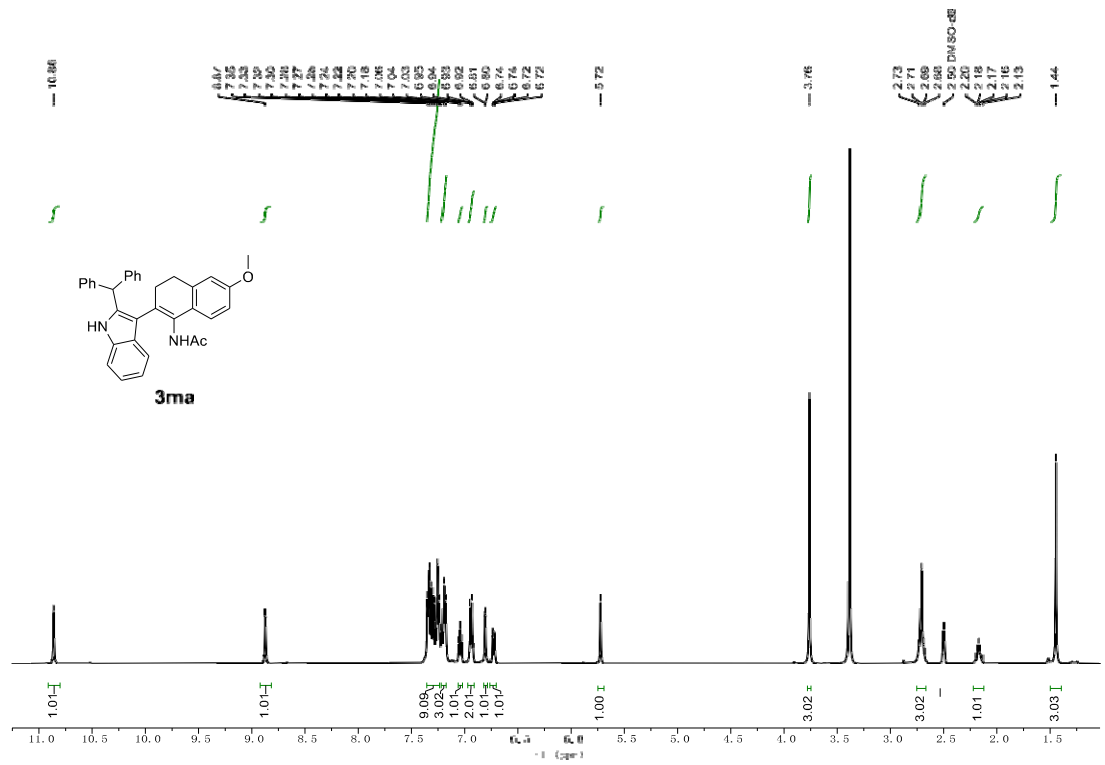
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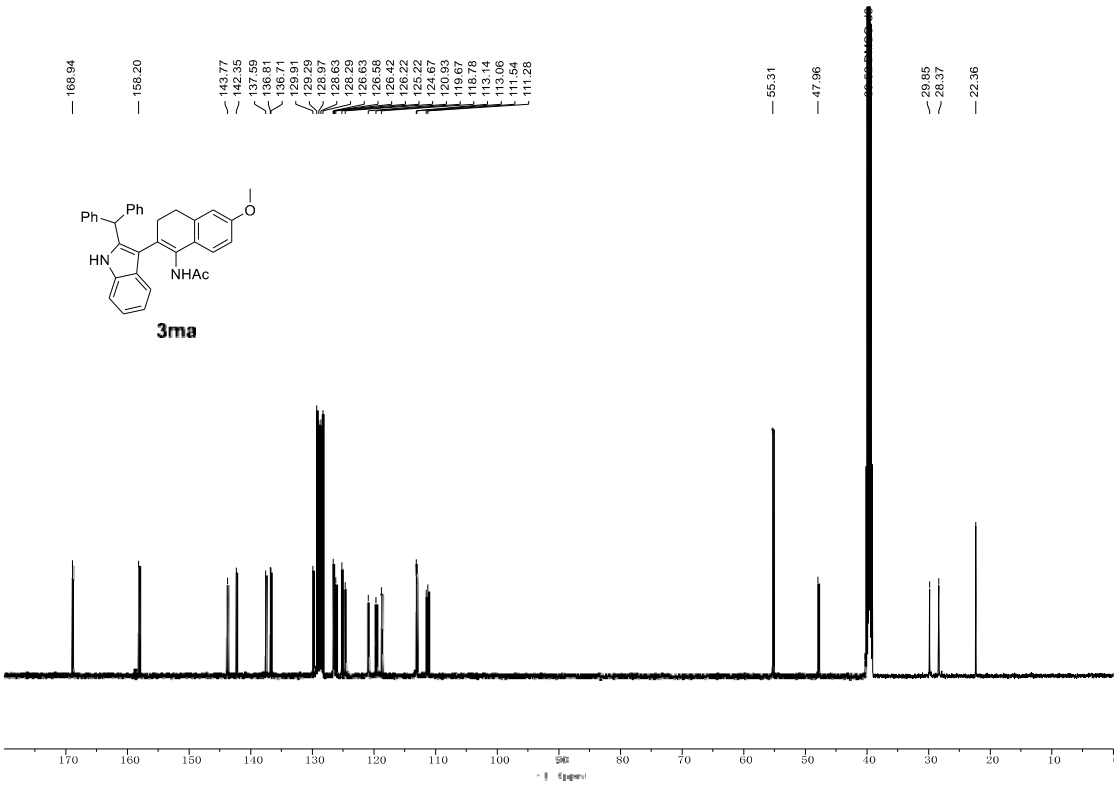
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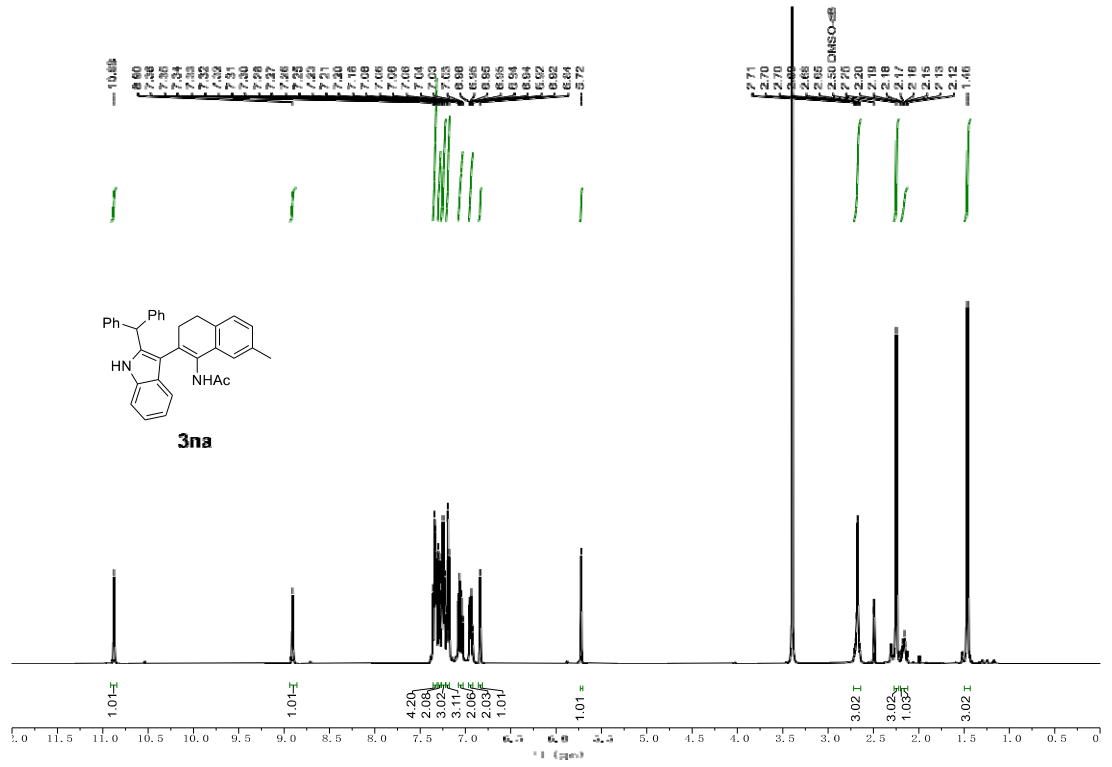
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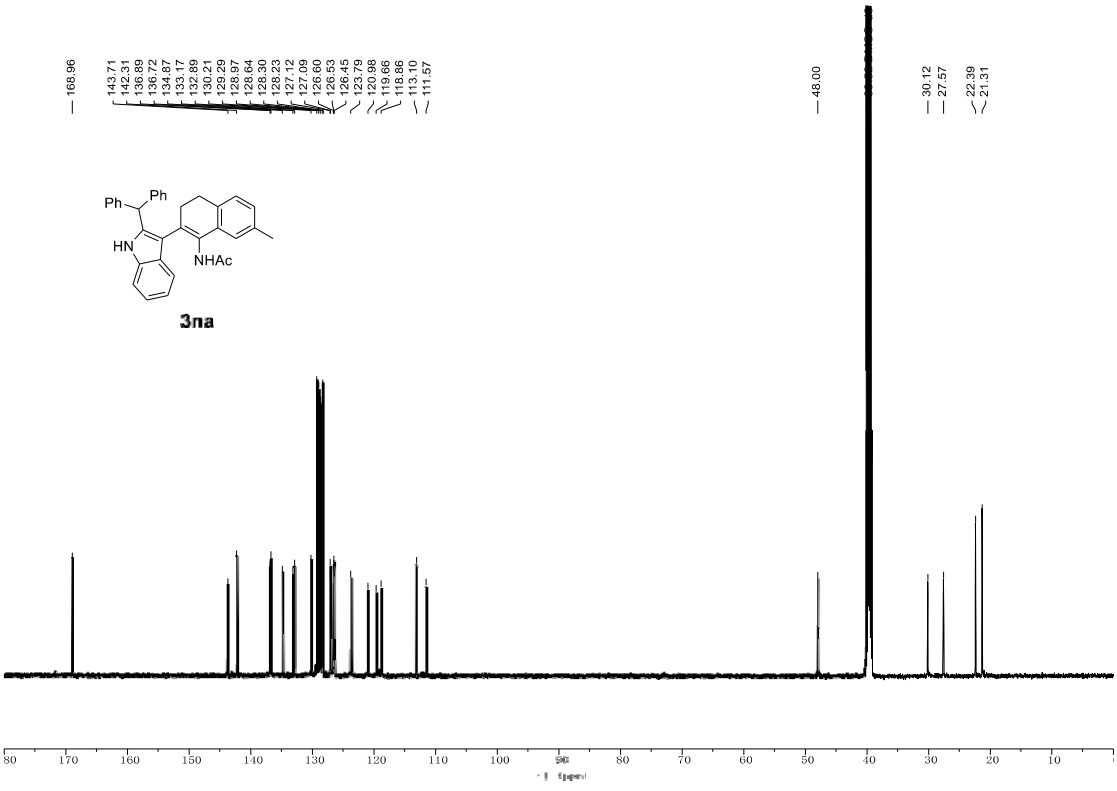
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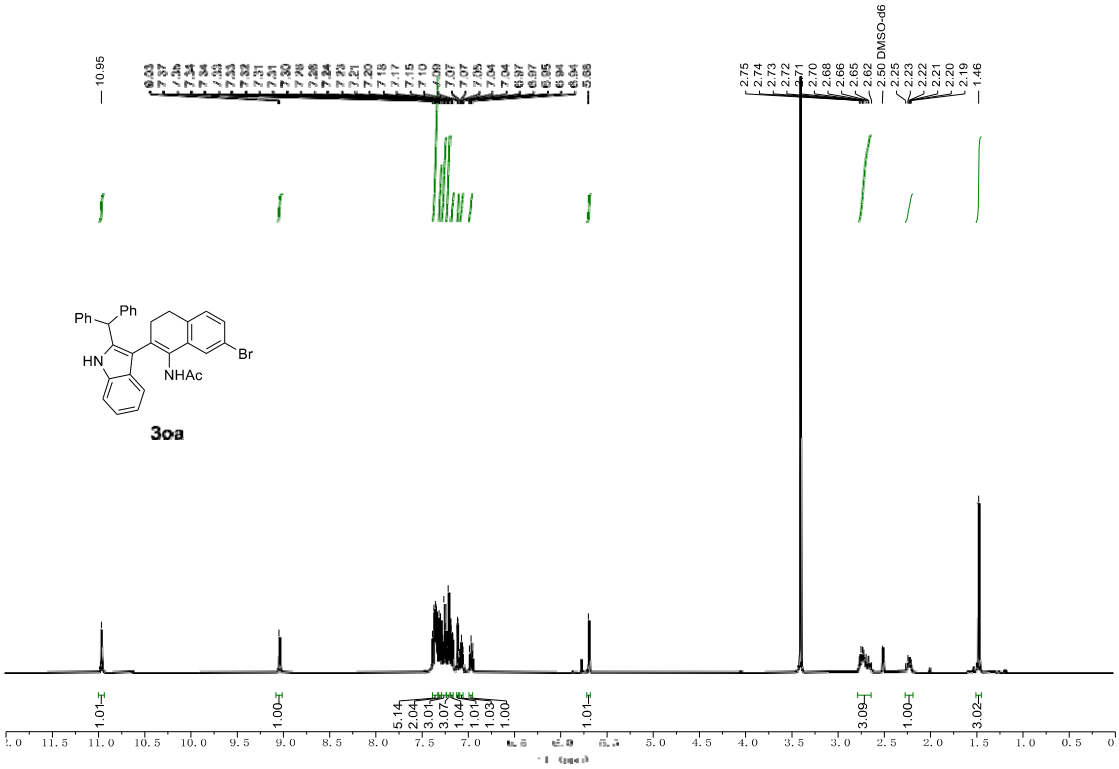
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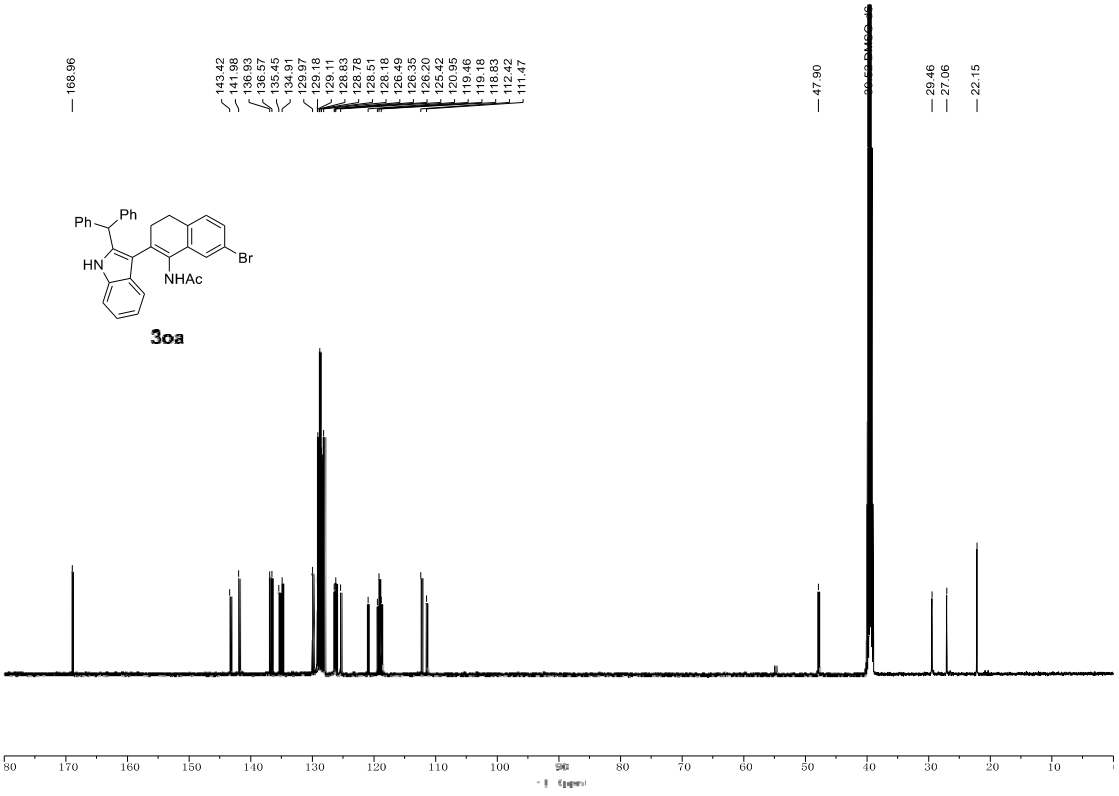
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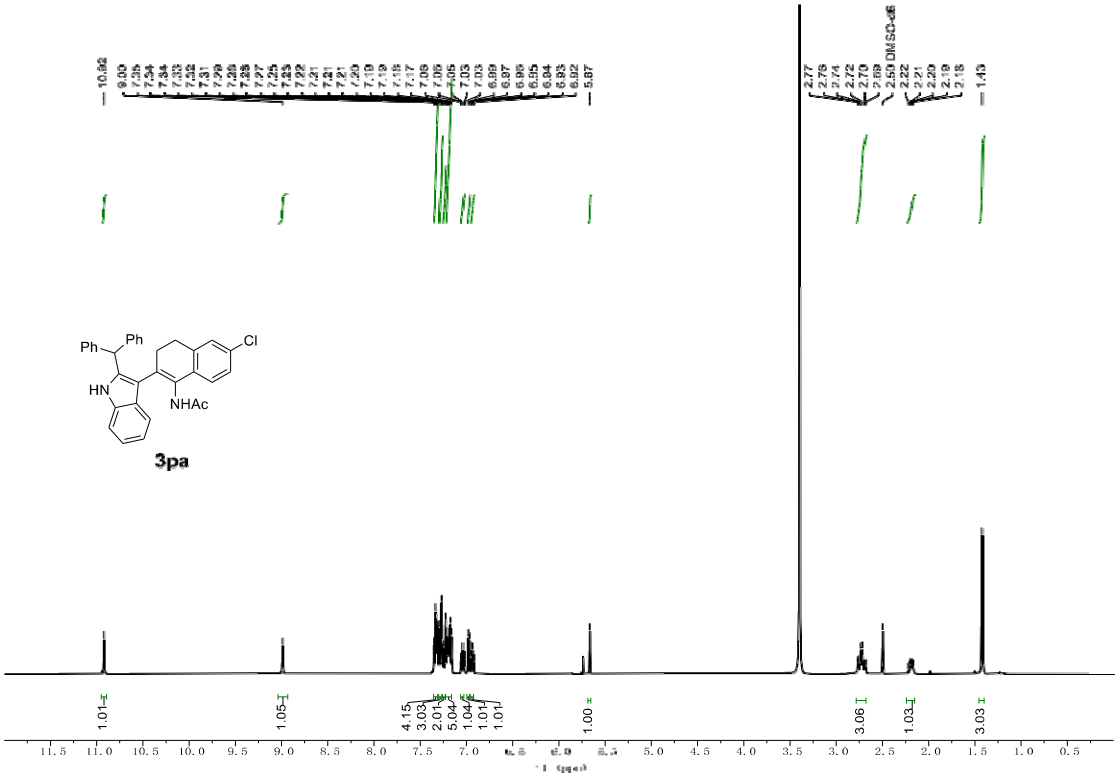
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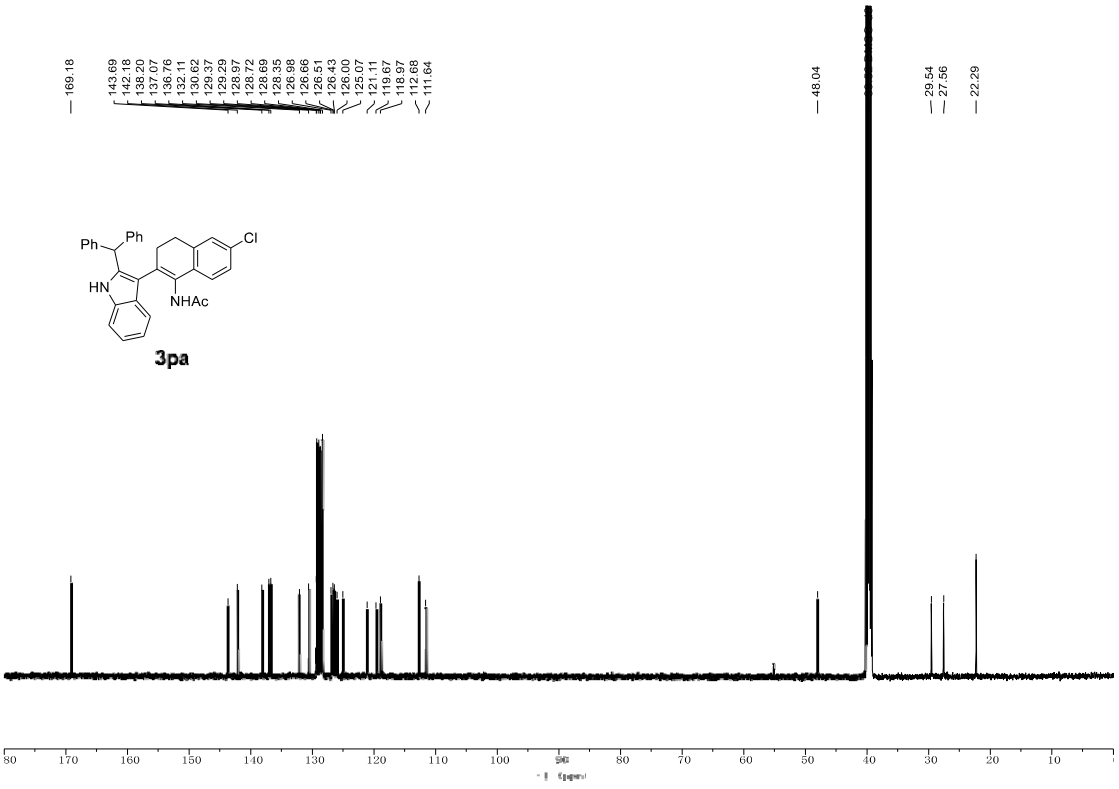
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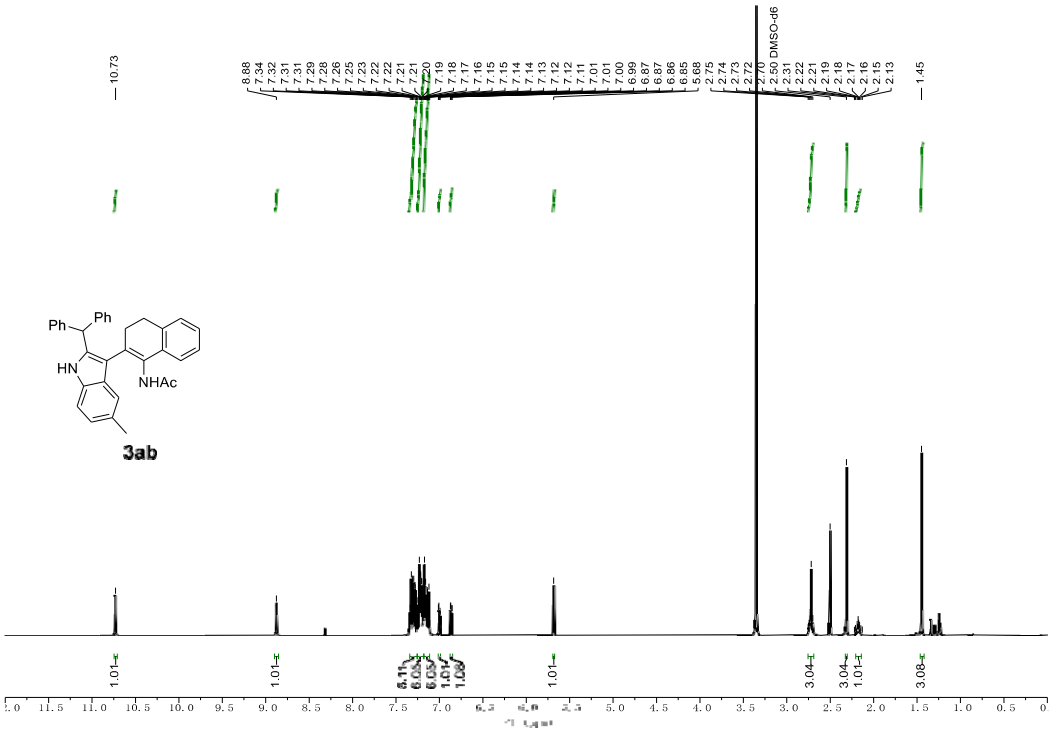
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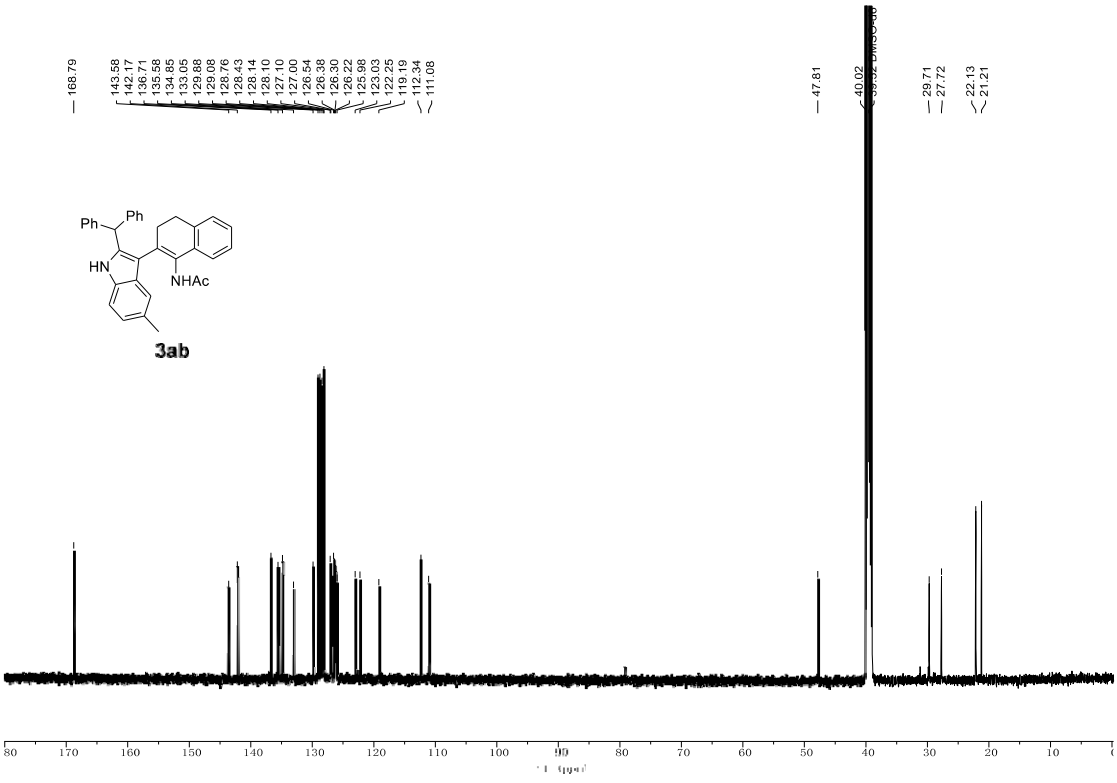
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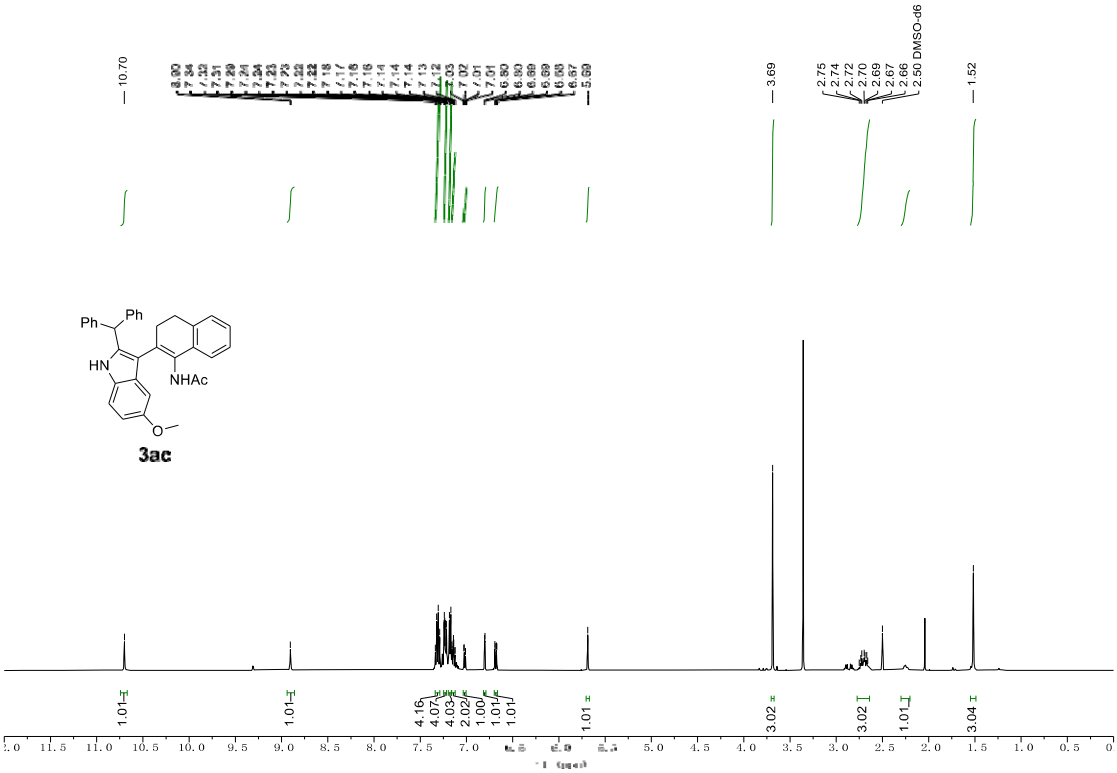
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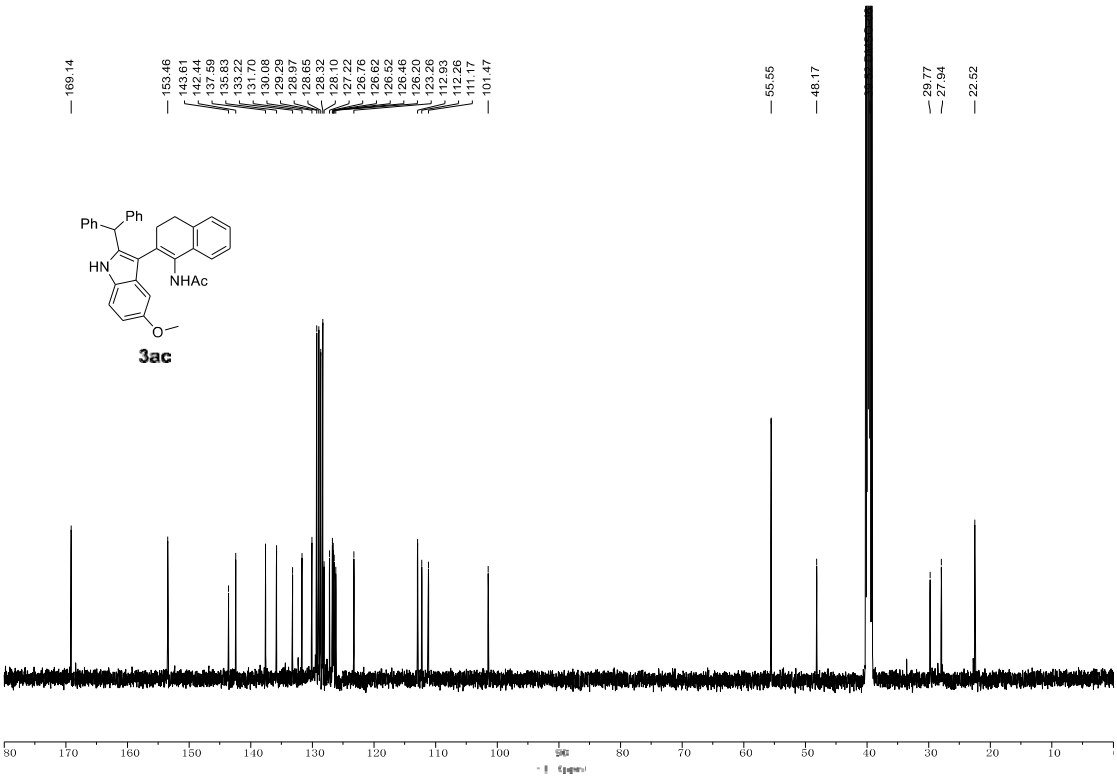
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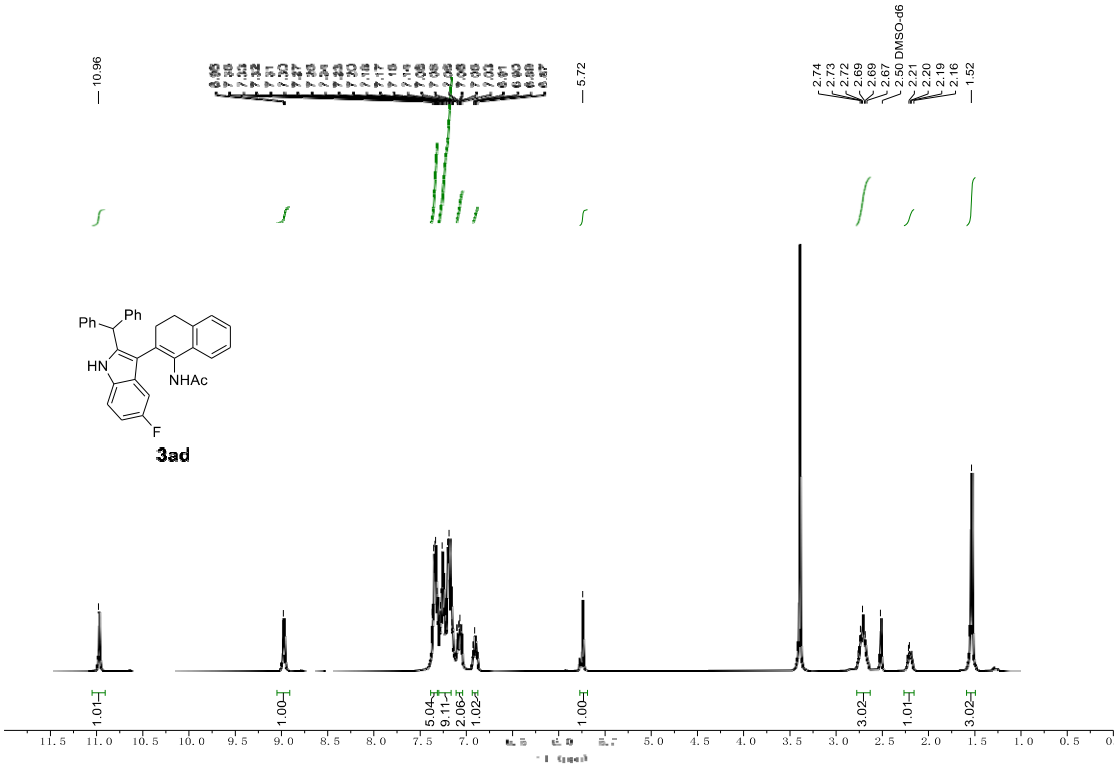
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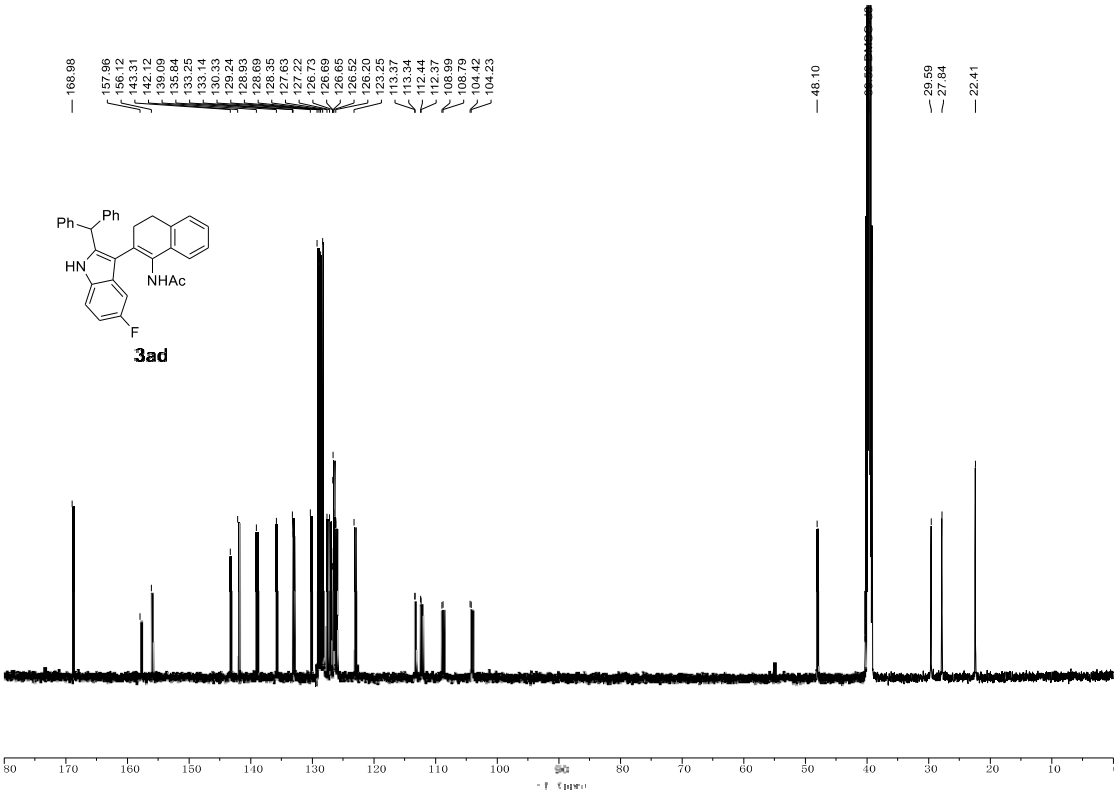
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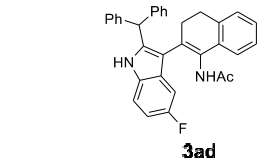
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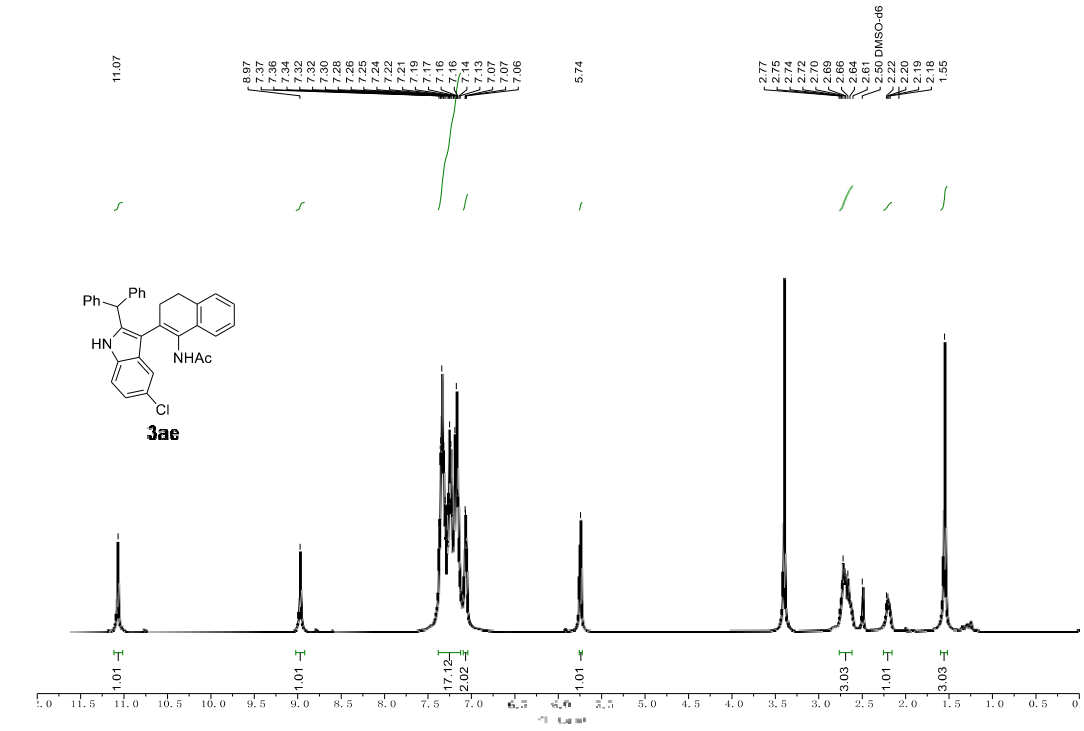
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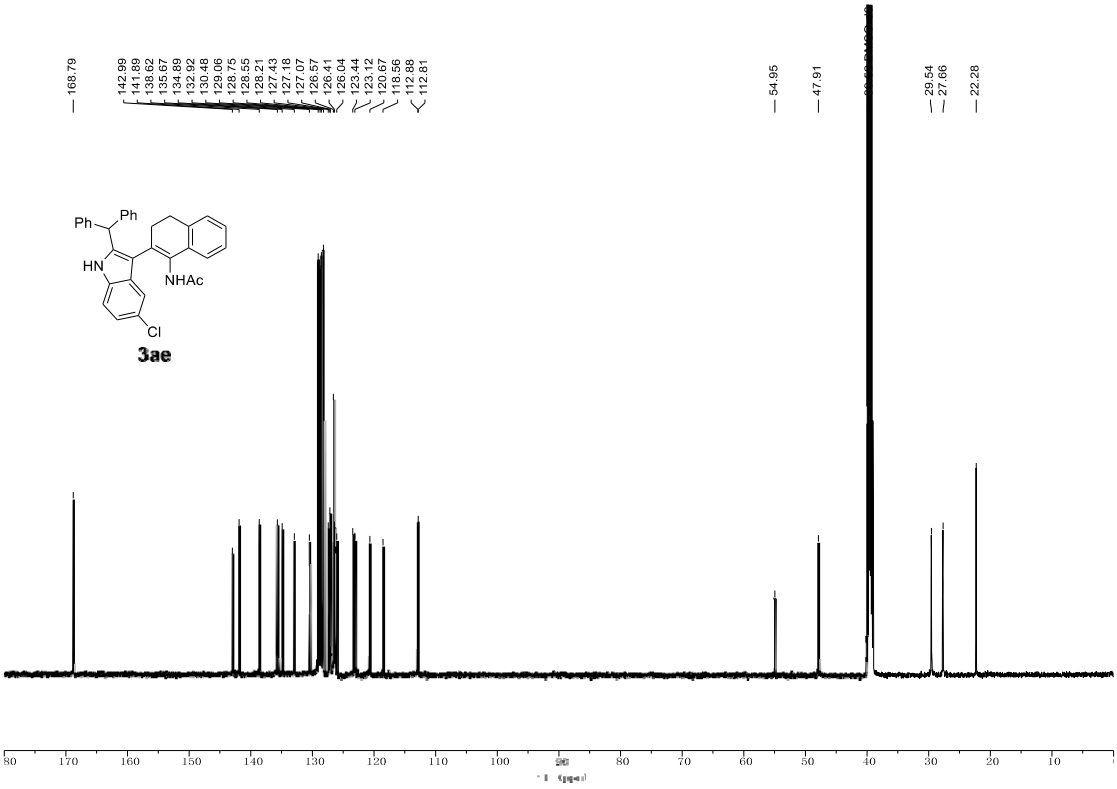
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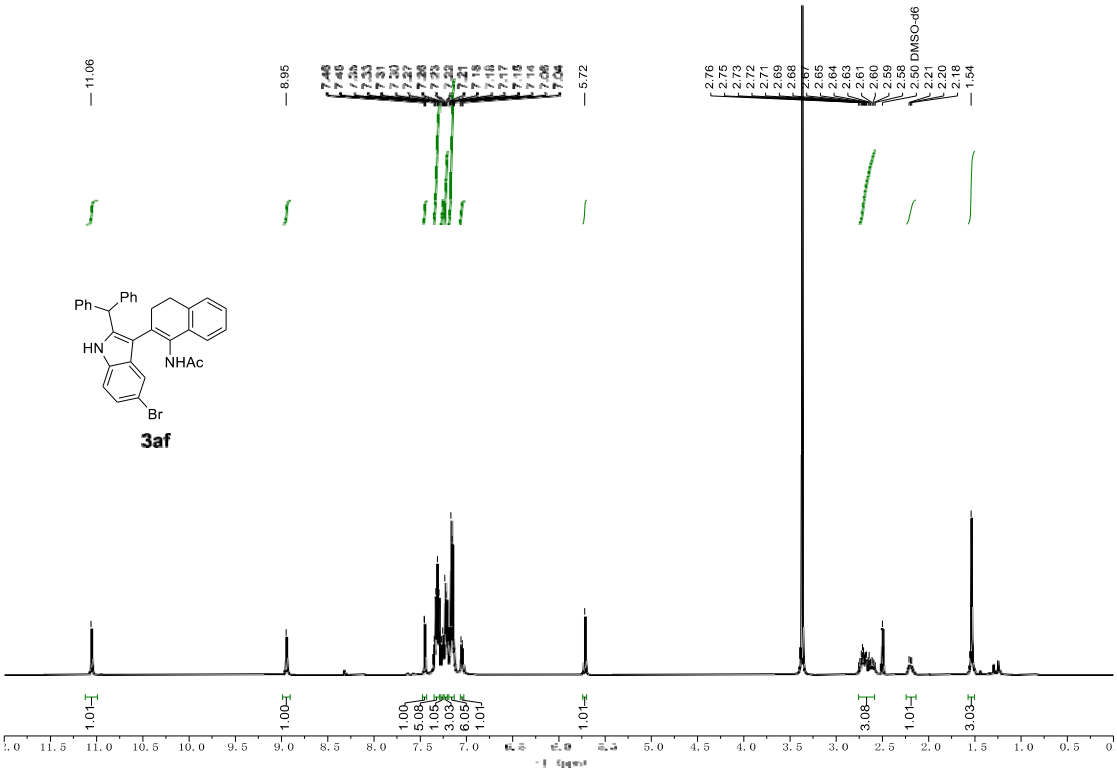
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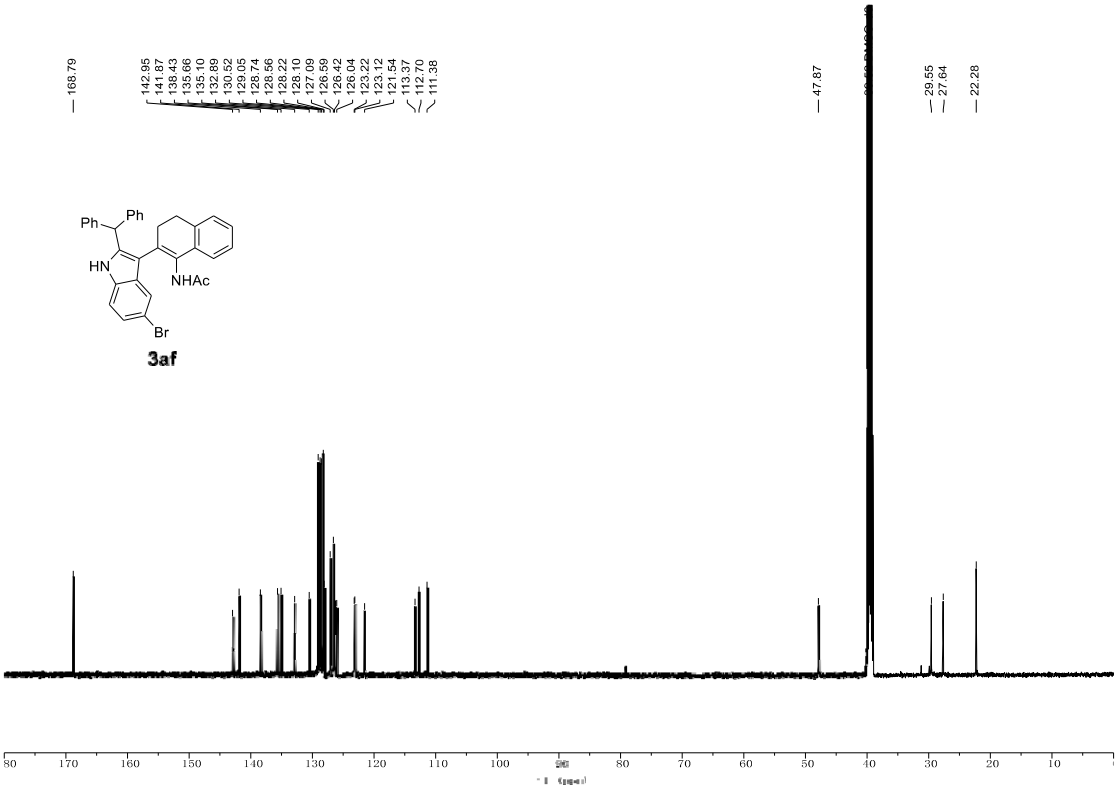
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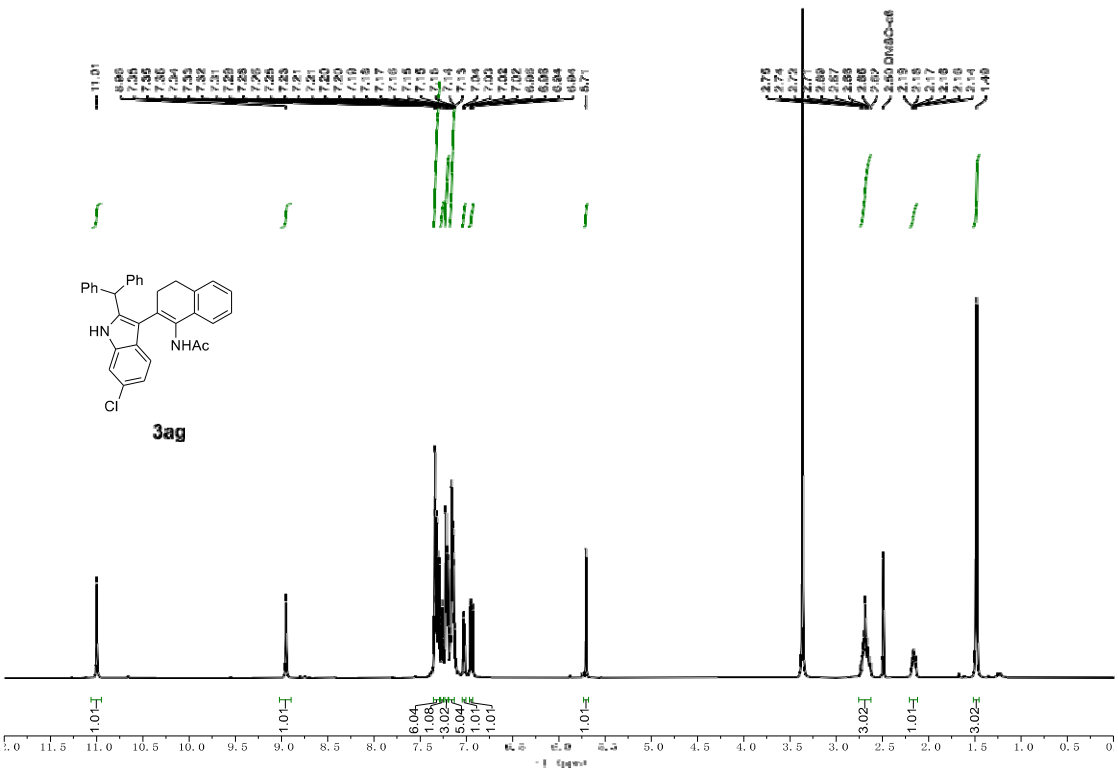
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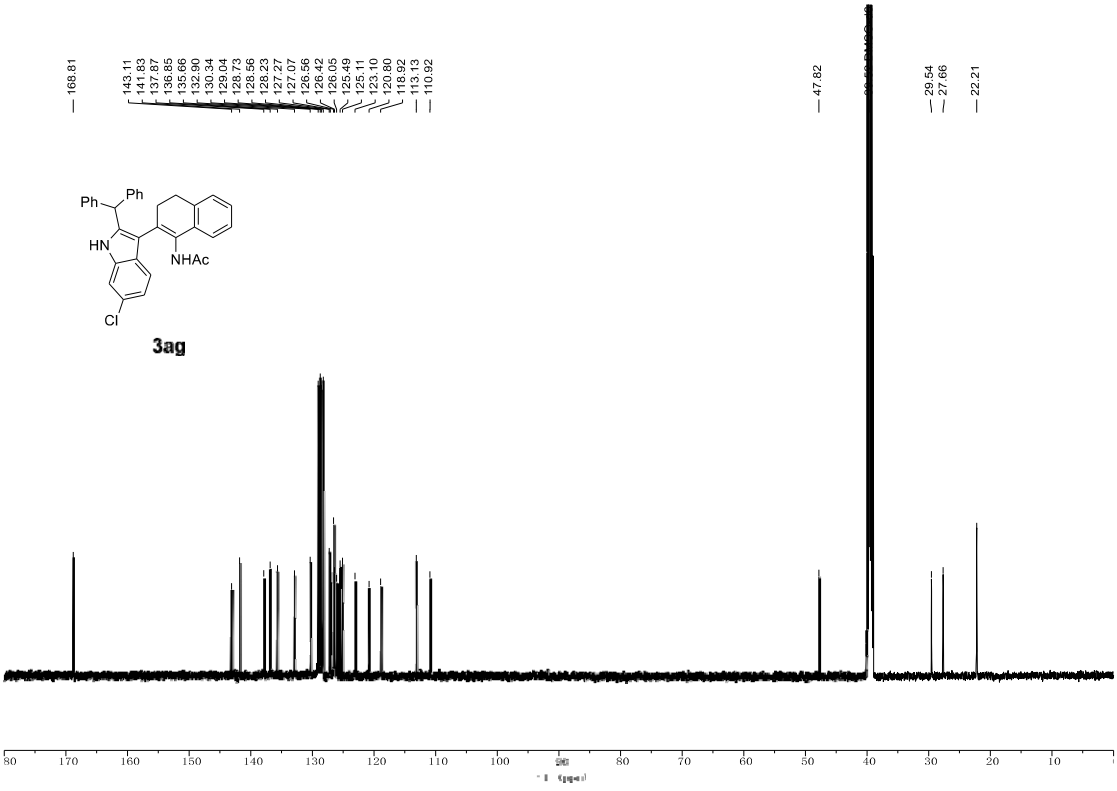
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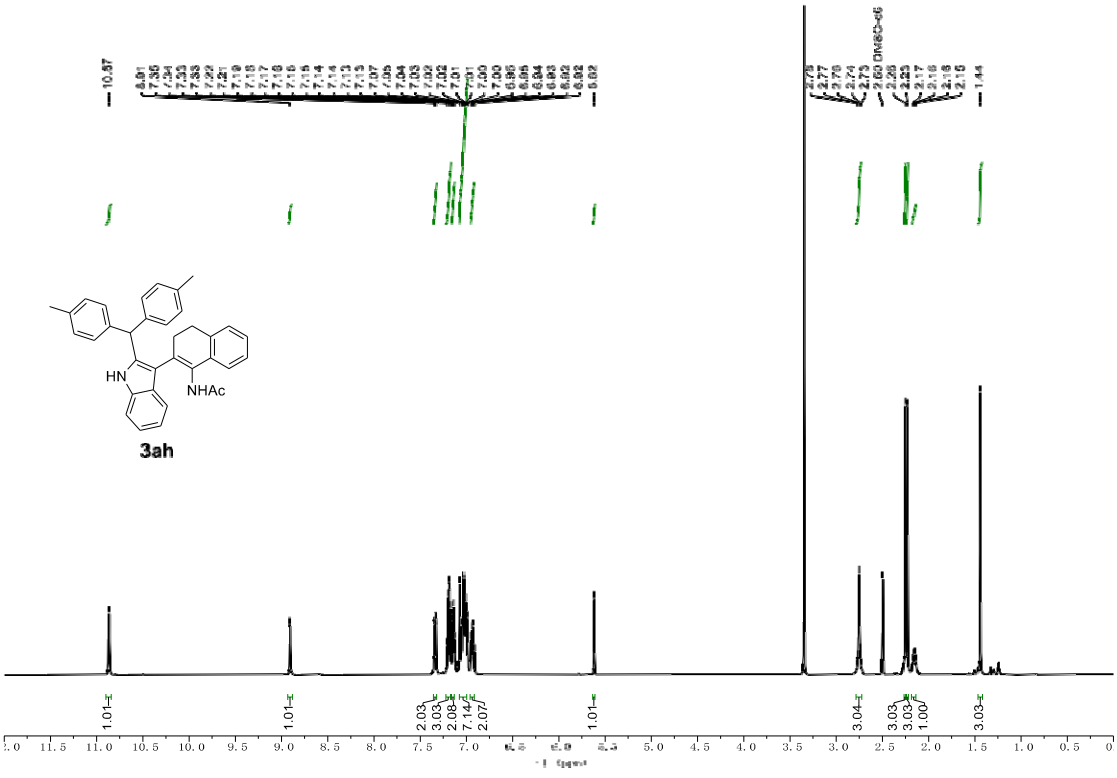
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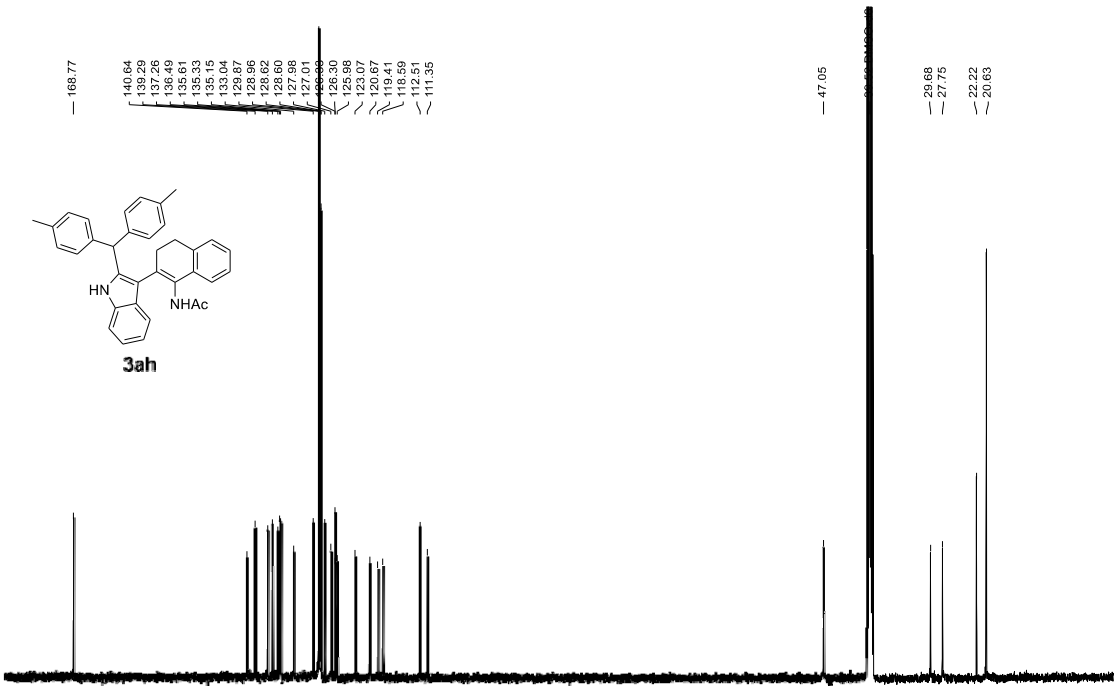
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