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Supporting Information for

Lewis Acid-Catalyzed Regioselective Substitution of 2-Indolylmethanols with Pyrroles

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[c] *School of Petrochemical Engineering, Changzhou University, Changzhou, 213164, China*
[d] *School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China*

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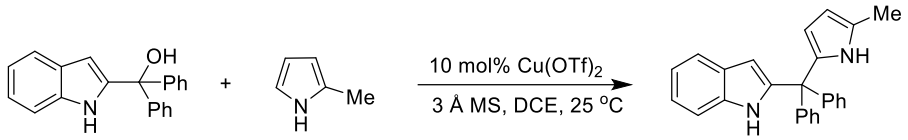
1. Procedure for Gram-scale reaction



1a 3 mmol | **2a** 3.6 mmol | **3aa** 96% yield (1.03g)

2-indolylmethanol **1a** (3 mmol), pyrrole **2a** (3.6 mmol), $Cu(OTf)_2$ (0.3 mmol) and 3 Å MS (3.0 g) were added to a reaction tube. Then, DCE (30 mL) was added to the reaction mixture, which was stirred at 25 °C for 12 h. After the completion of the reaction which was indicated by TLC, the mixture was directly purified by silica gel column chromatography to afford pure product **3aa**.

2. Biological evaluation of selected compounds 3

Procedure for determination of Hep G2 cell viability by Cell Counting Kit-8 (CCK8) assay:

Human liver cancer cell lines (Hep G2) were seeded in 96-well plates at the density of $5*10^4$ cells per well with 100 μL of complete culture medium. After adhesion for 24 hours, the medium was changed to DMEM supplemented without FBS, and the selected products **3** were added to the medium with final concentrations ranging from 6.25 μg/mL to 200 μg/mL. The cells were then cultured for another 24 h. Cells that did not exposed to products **3** were used as controls, and the wells to which only culture medium was added served as blanks. At the end of compounds stimulation, the supernatant was removed, and 100 μL of DMEM containing 10 μL of CCK8 was added to each well for another 1 h at 37 °C. The culture plates were then shaken for 5s and the optical density (OD) values were read at 450 nm. Then, the IC_{50} values of tested products **3** to Hep G2 cell line were calculated by GraphPad software.

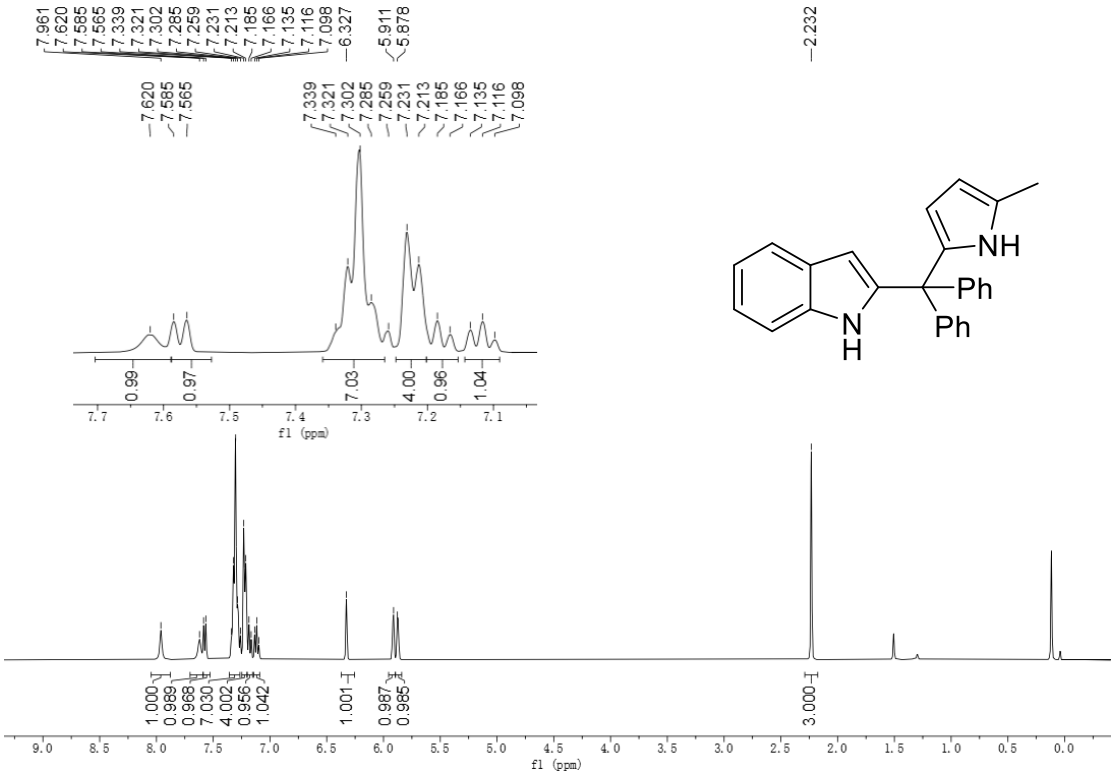
Table S1. Cytotoxicity of selected products **3** on Hep G2 cancer cell line

Compound	Viability rate of Hep G2 cancer cell line (%)						IC_{50} (μg/mL)[a]
	6.25 (μg/mL)	12.5 (μg/mL)	25 (μg/mL)	50 (μg/mL)	100 (μg/mL)	200 (μg/mL)	
3da	84.75±6.91	68.96±6.65	26.88±2.20	11.72±2.76	5.15±0.66	4.20±0.38	16.8
3ea	62.23±6.19	24.94±1.00	13.86±1.74	6.25±0.15	4.08±0.24	2.25±0.17	7.8
3ha	74.63±3.48	55.08±4.47	30.38±1.63	17.21±1.17	8.59±0.50	5.38±0.53	14.2
3pa	59.45±3.11	35.83±1.81	27.95±0.28	13.71±1.17	9.36±0.81	8.17±0.90	8.3
3ac	93.05±8.24	82.10±6.57	47.41±6.24	41.39±5.06	38.14±6.51	37.07±6.20	17.0
3ae	72.90±7.87	10.68±1.22	2.87±0.50	1.45±0.24	1.26±0.20	1.05±0.20	7.80

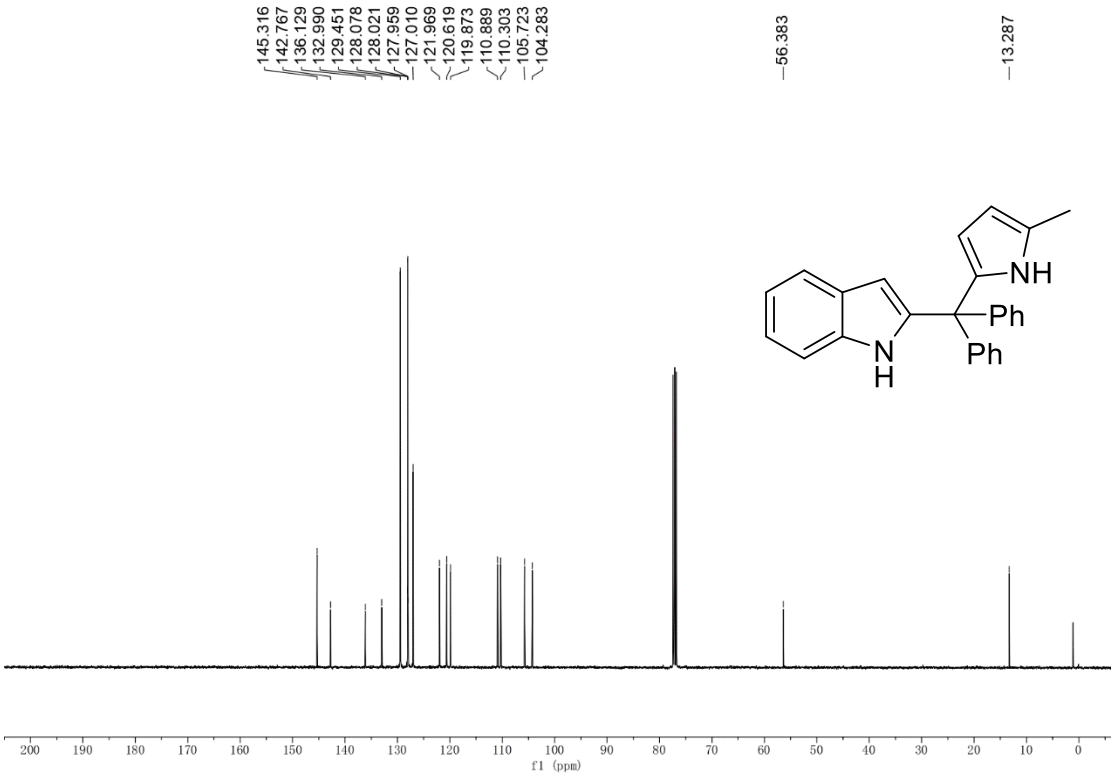
[a]The IC_{50} value corresponded to the compound concentration causing 50% mortality in cancer cells.

3. NMR spectra of products 3, 5 and 7

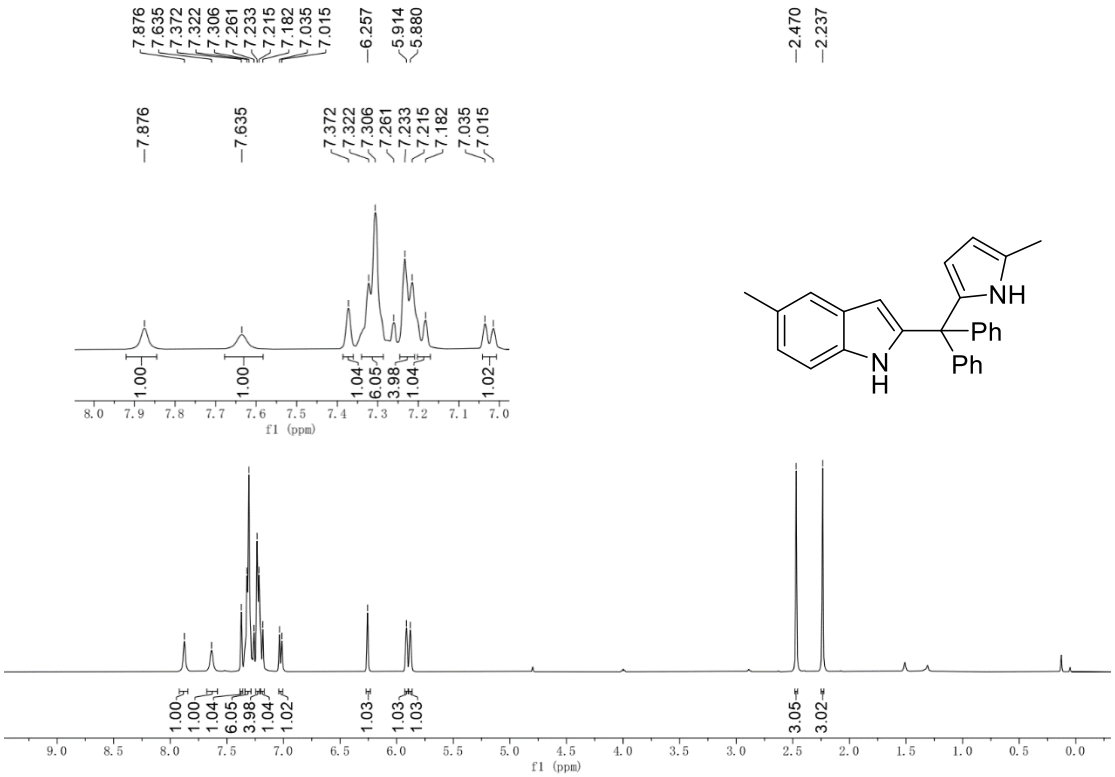
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa**:



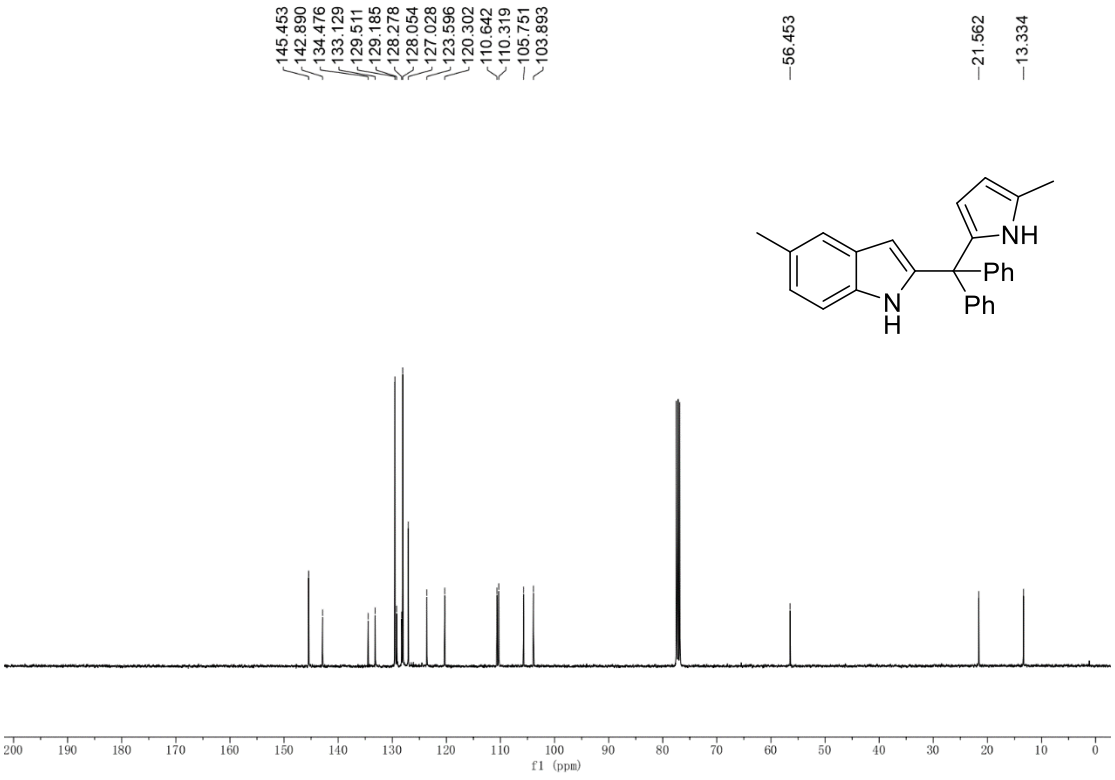
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3aa**:



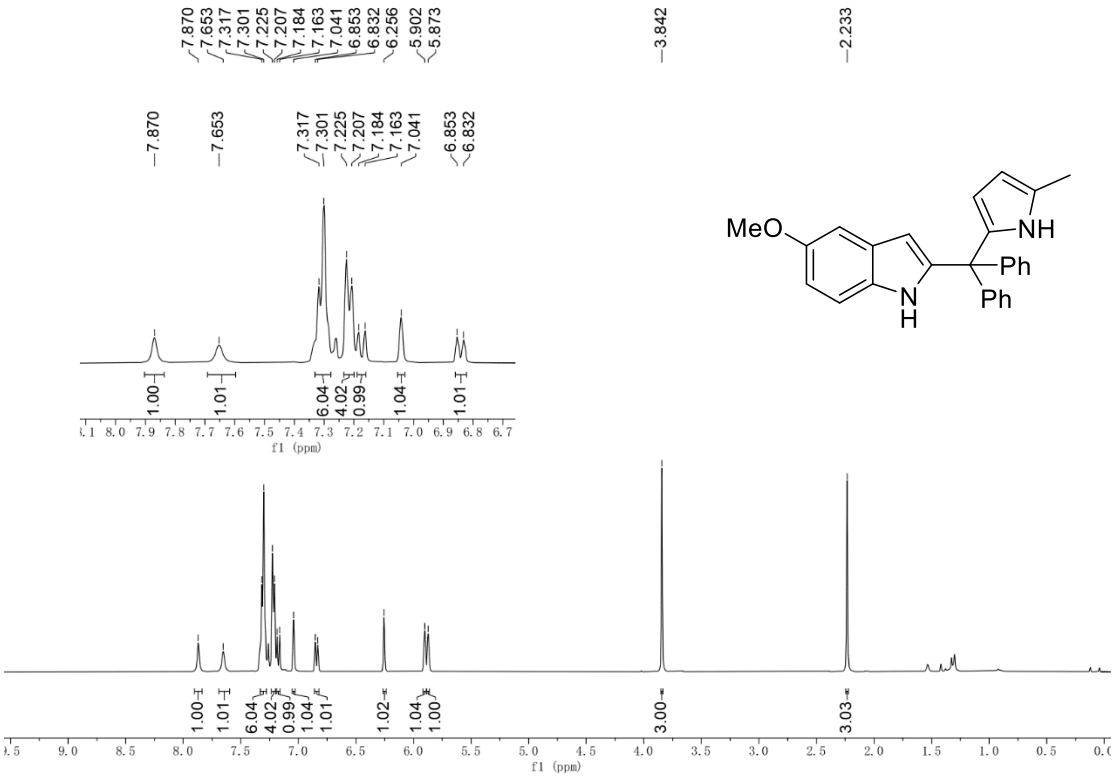
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ba**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ba**:



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ca**:



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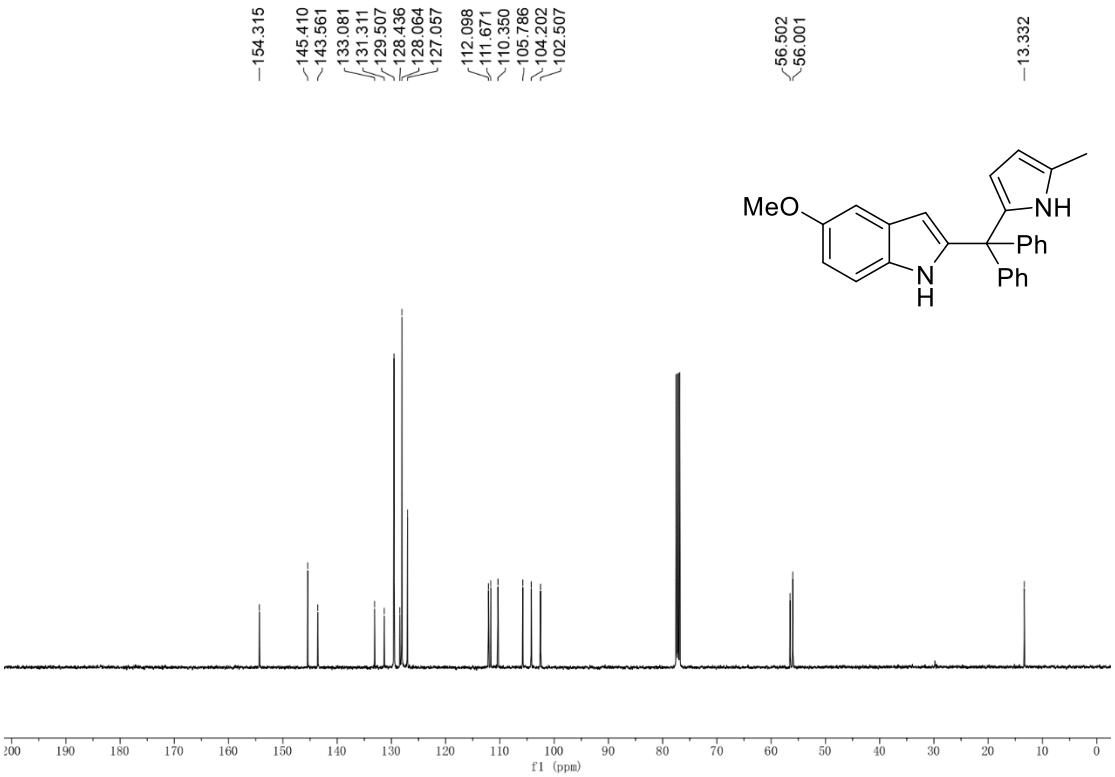
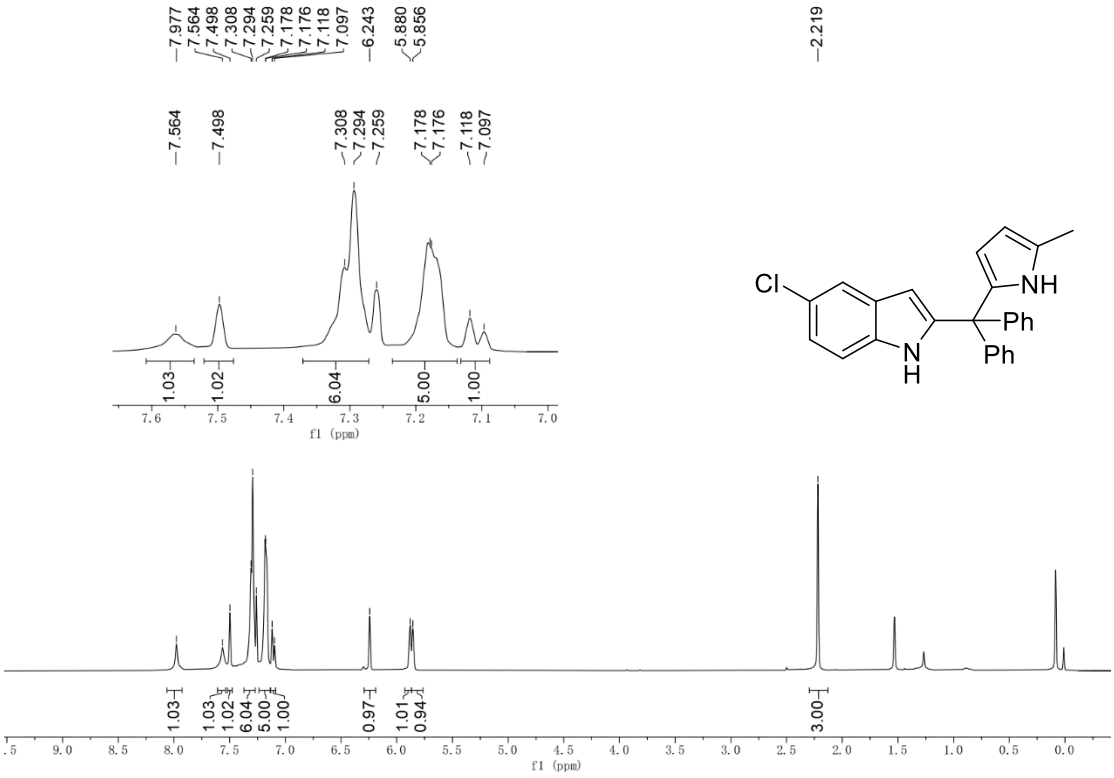
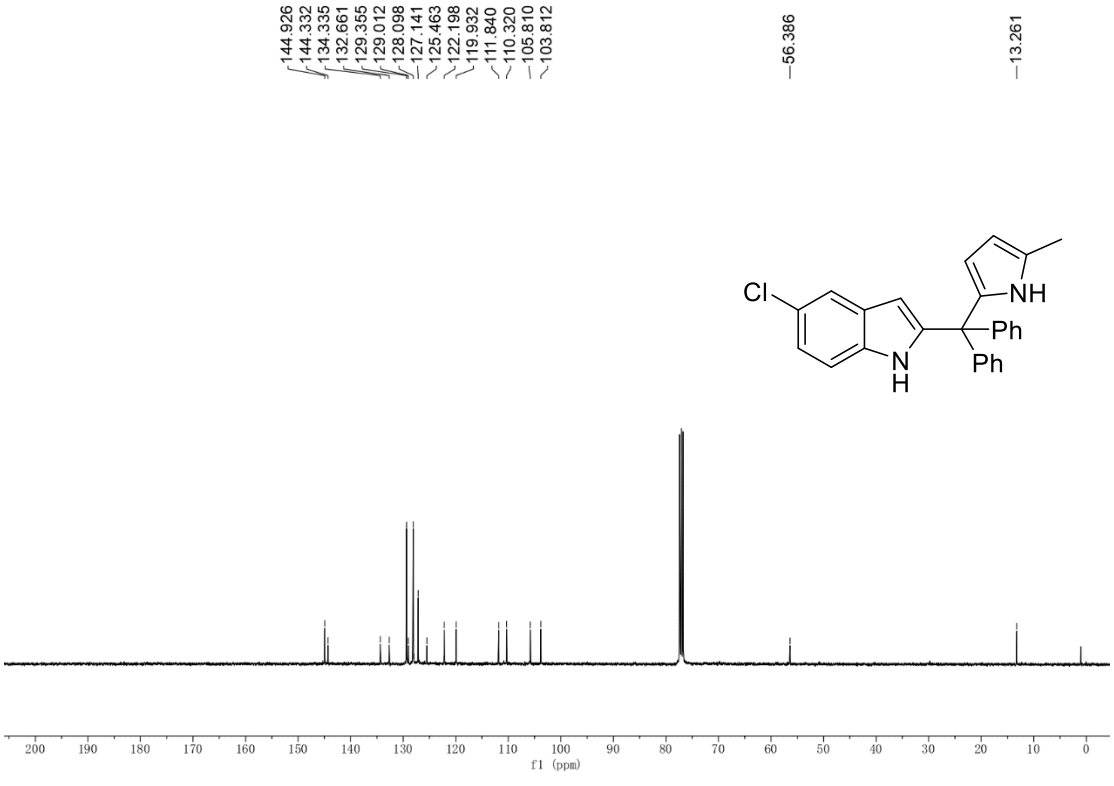


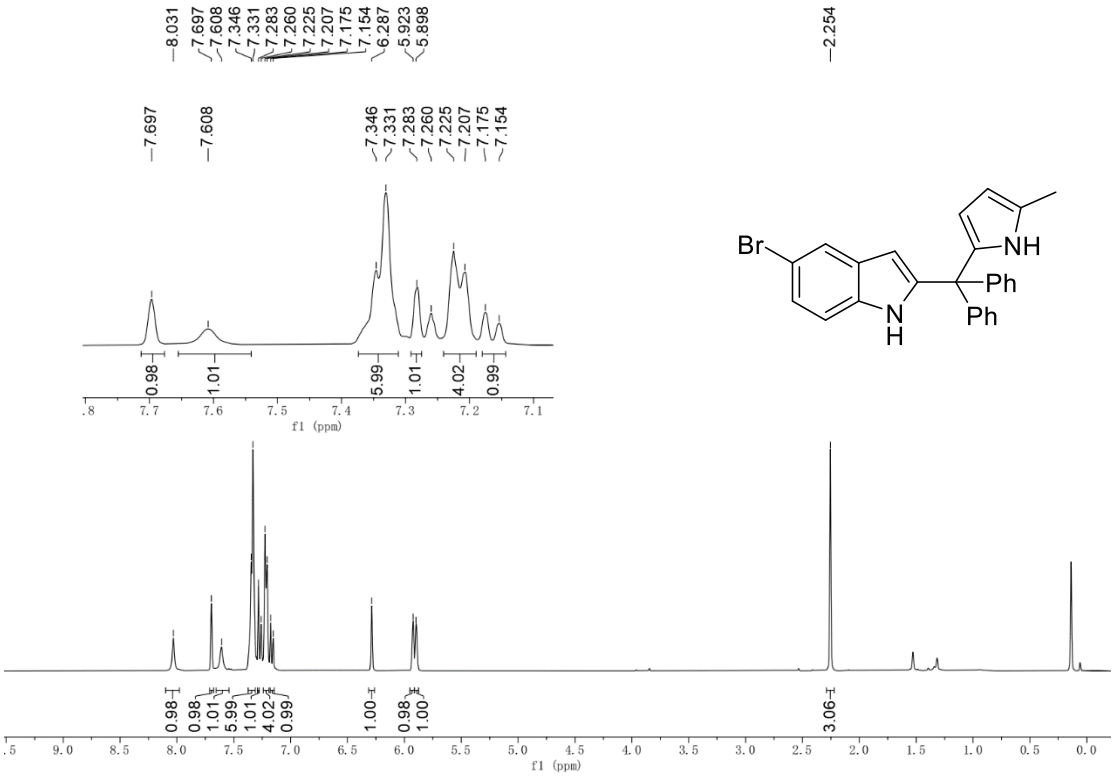
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3da**:



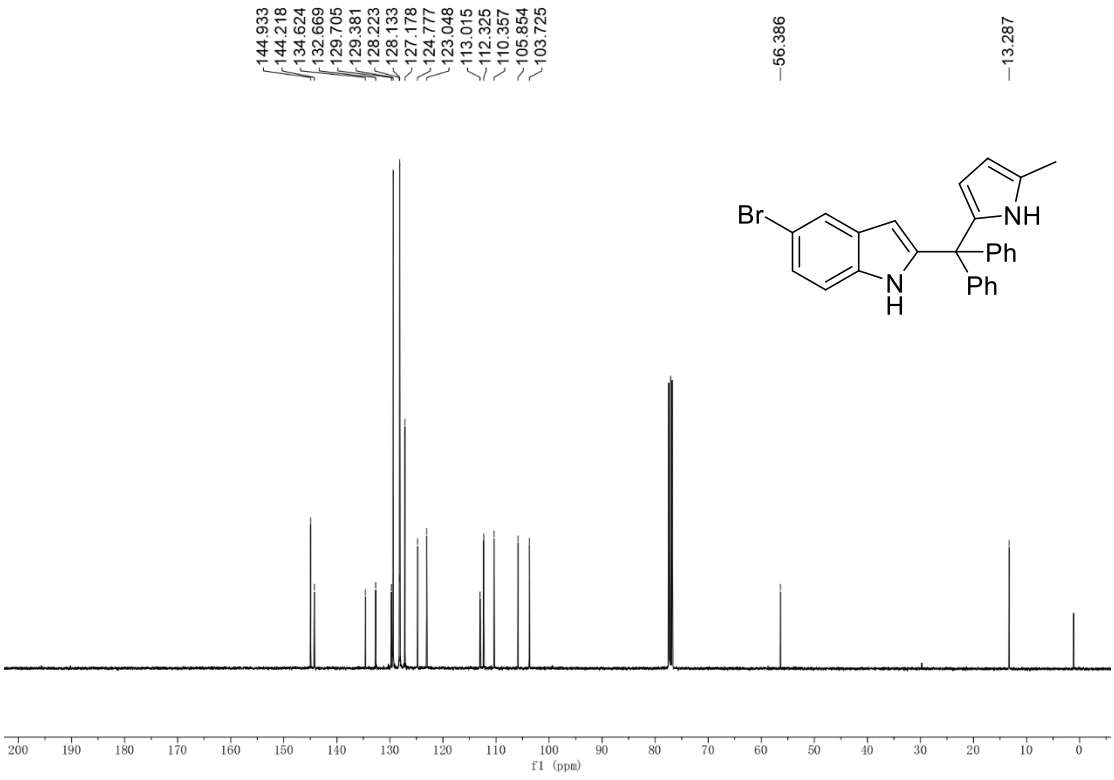
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3da**:



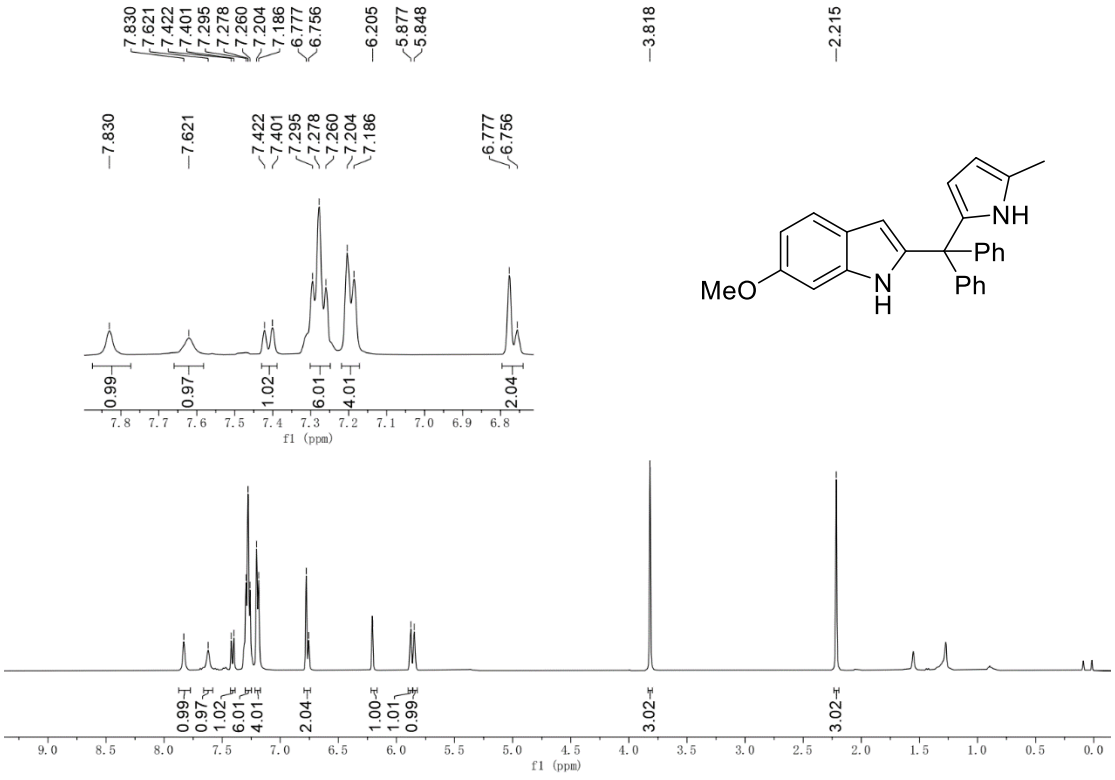
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ea**:



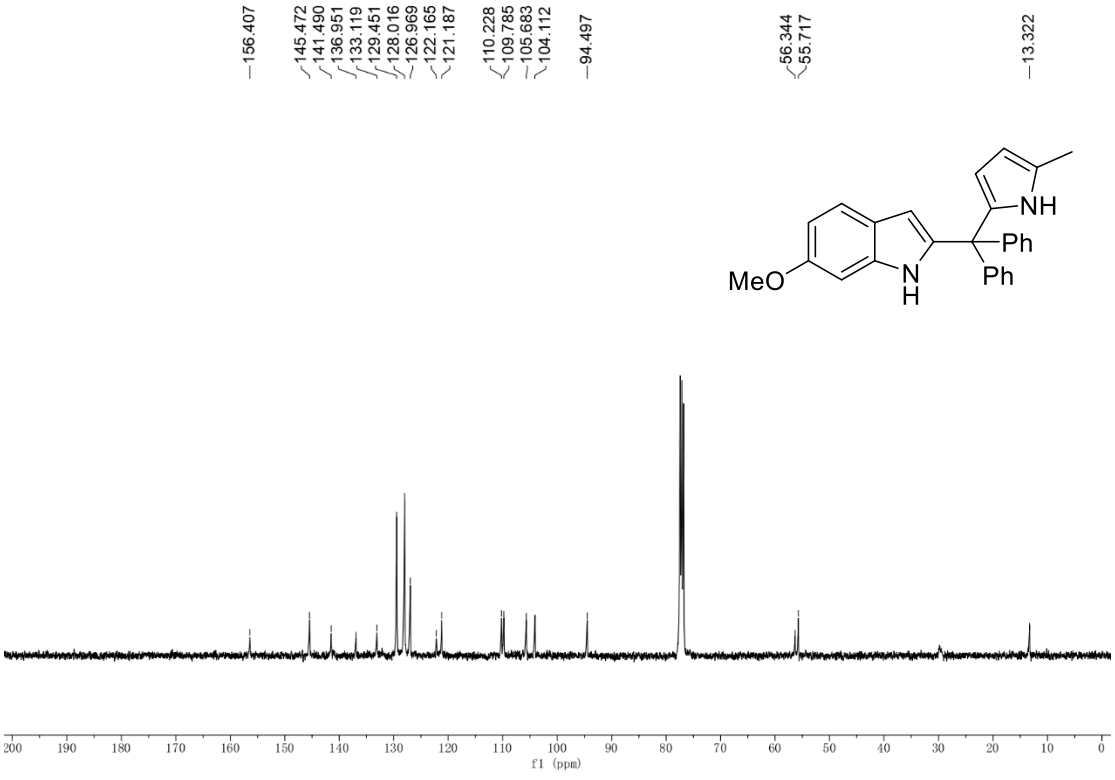
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ea**:



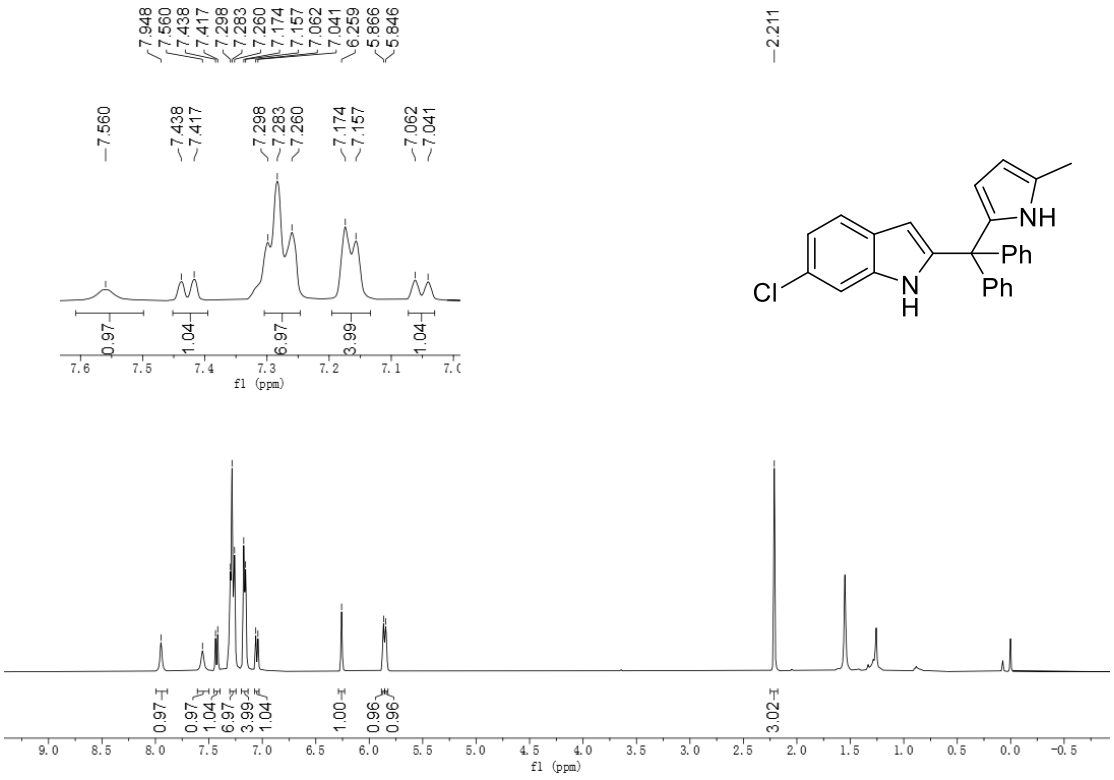
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3fa**:



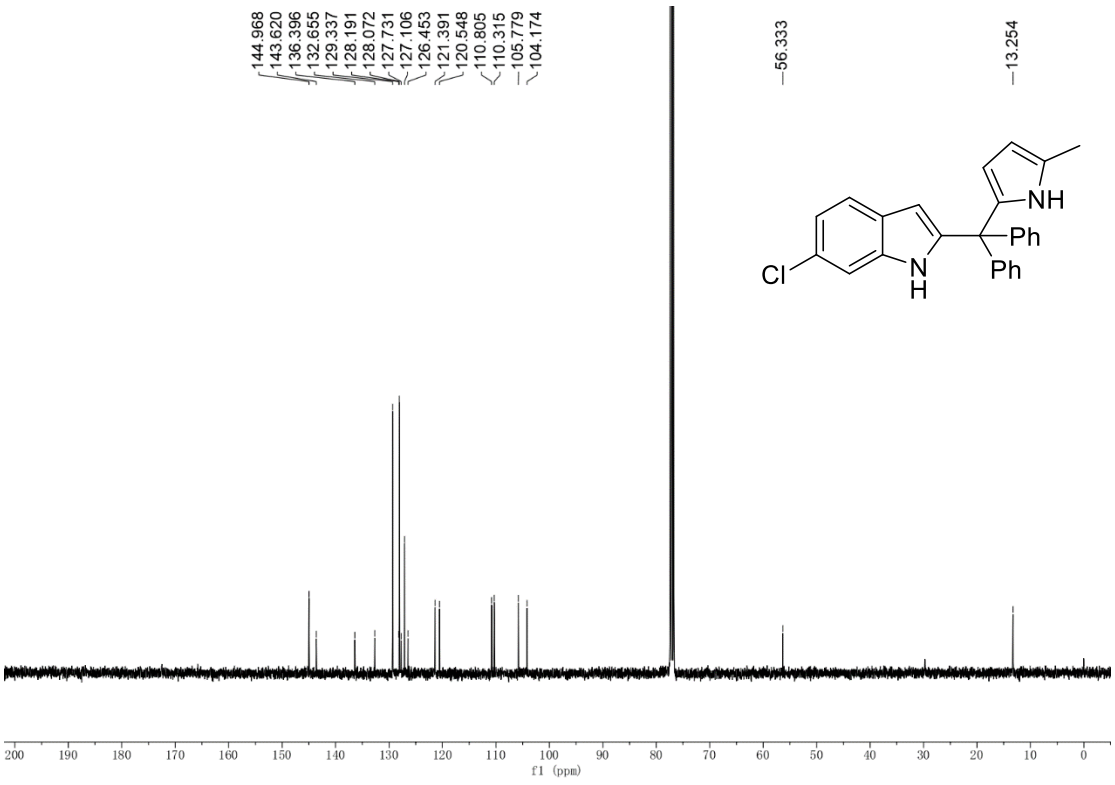
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3fa**:



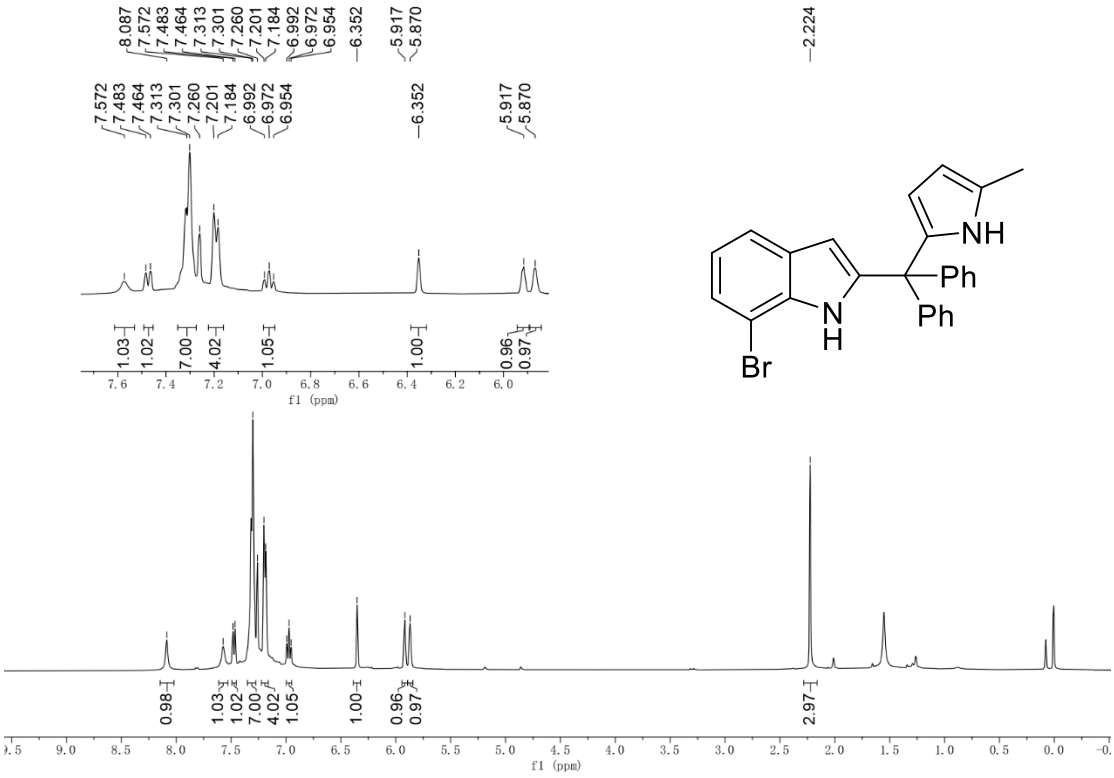
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ga**:



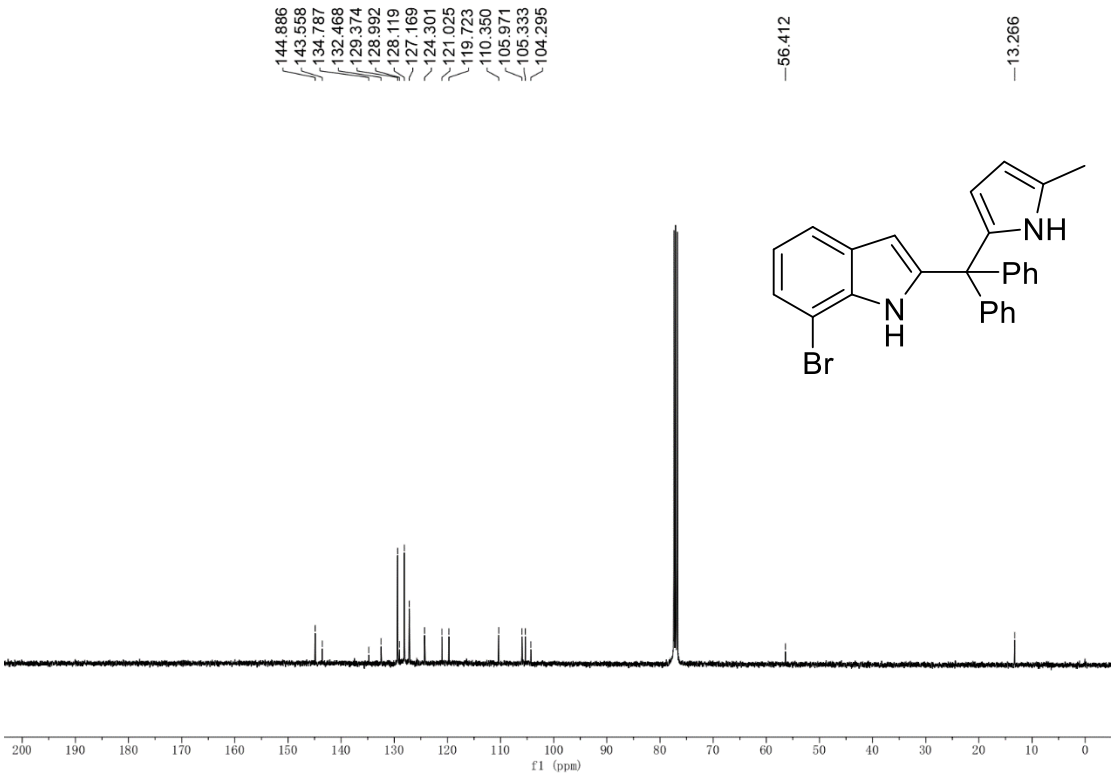
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ga**:



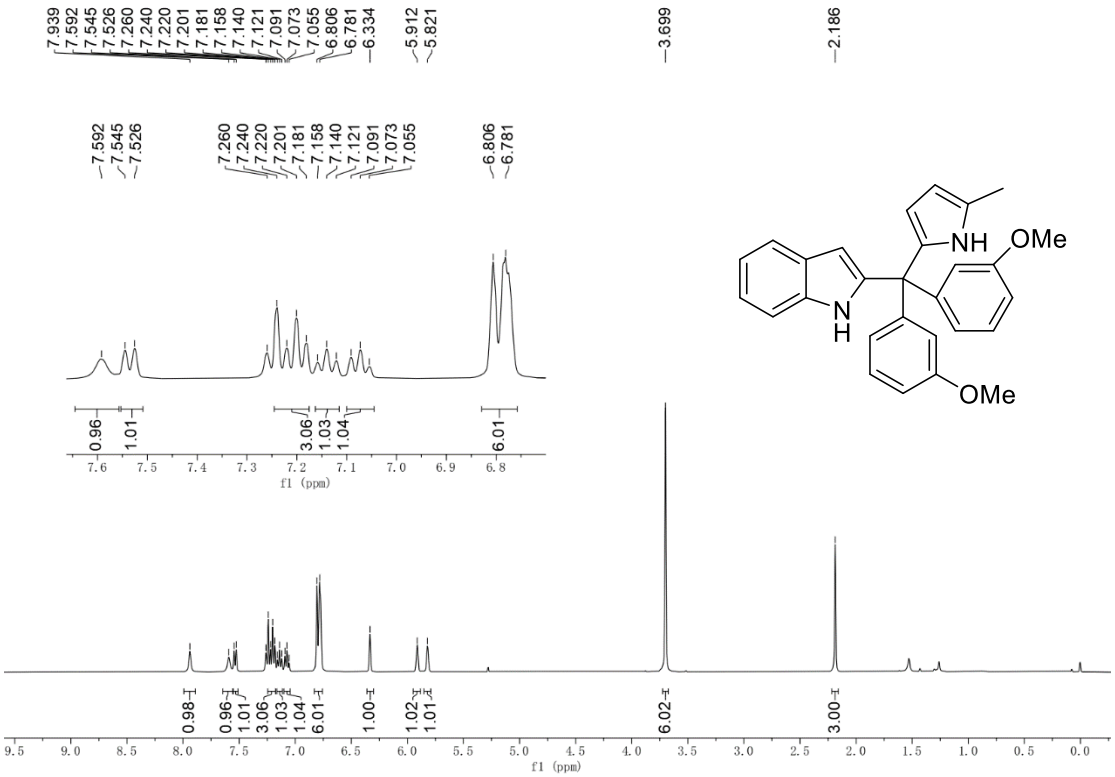
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ha**:



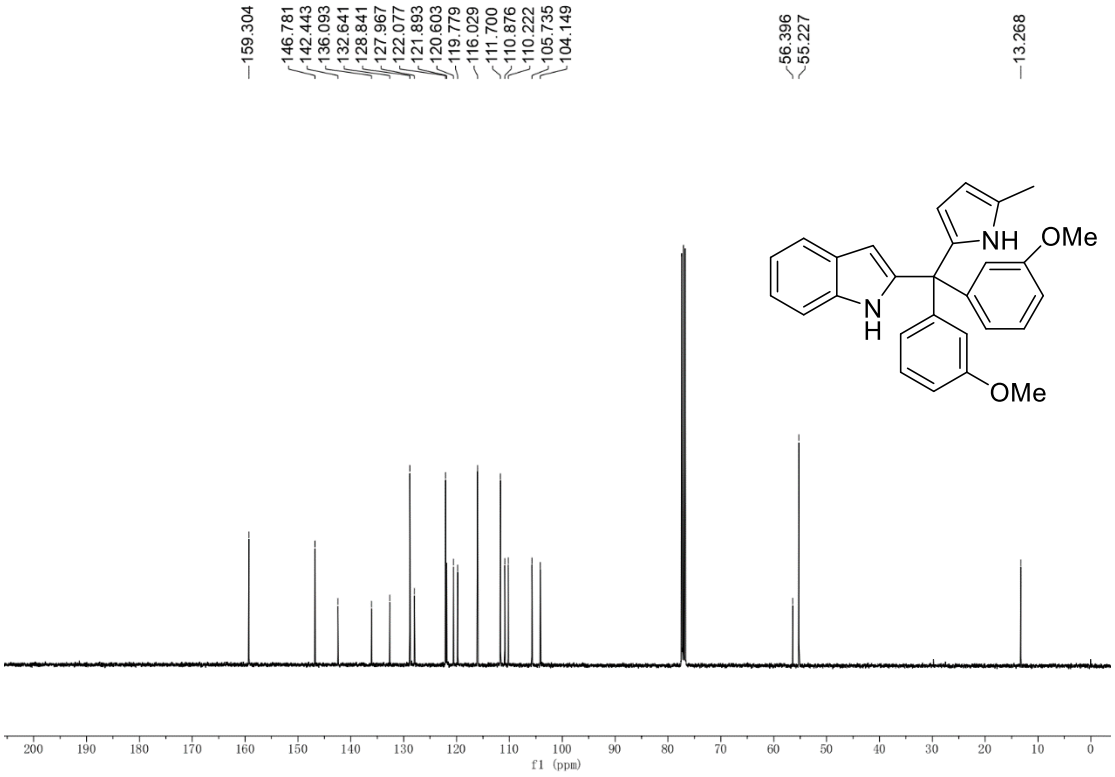
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ha**:



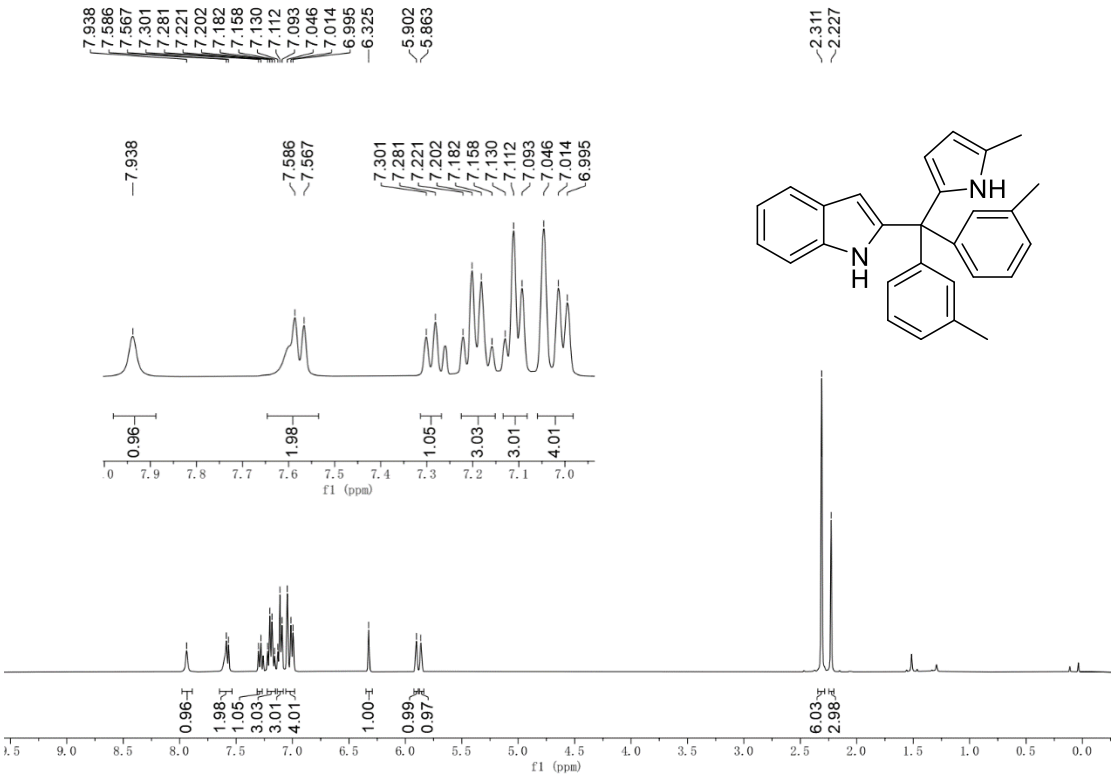
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ia:**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ia:**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ja:**



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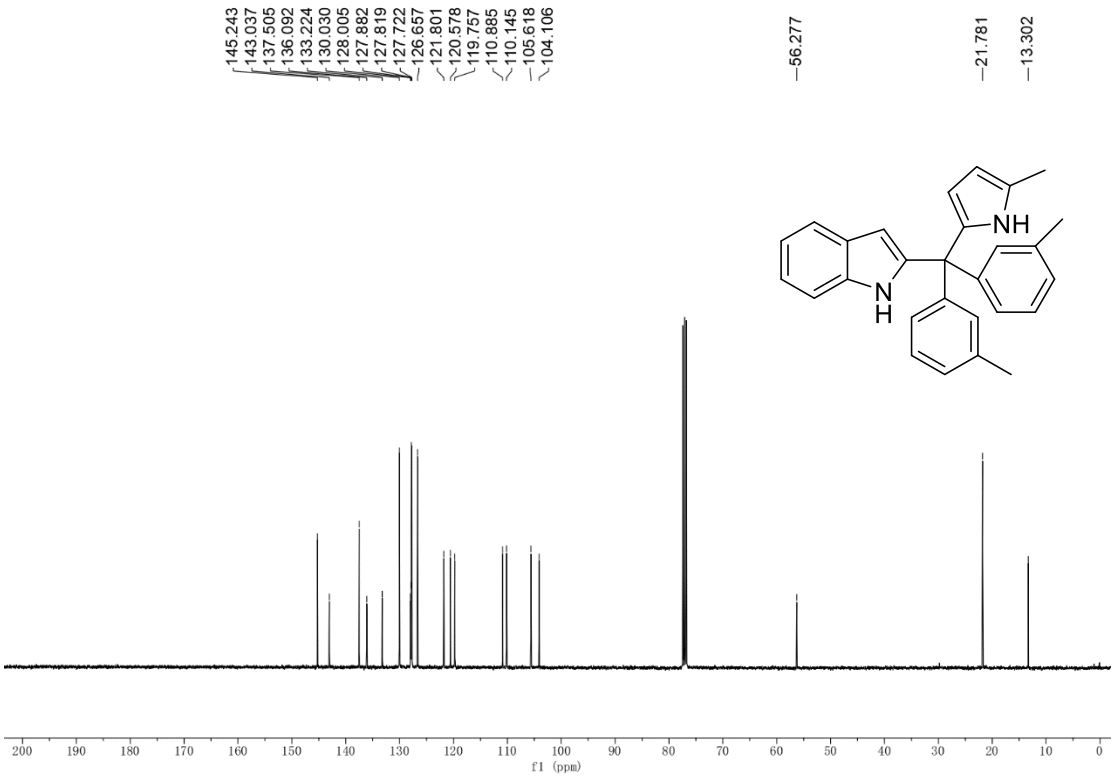
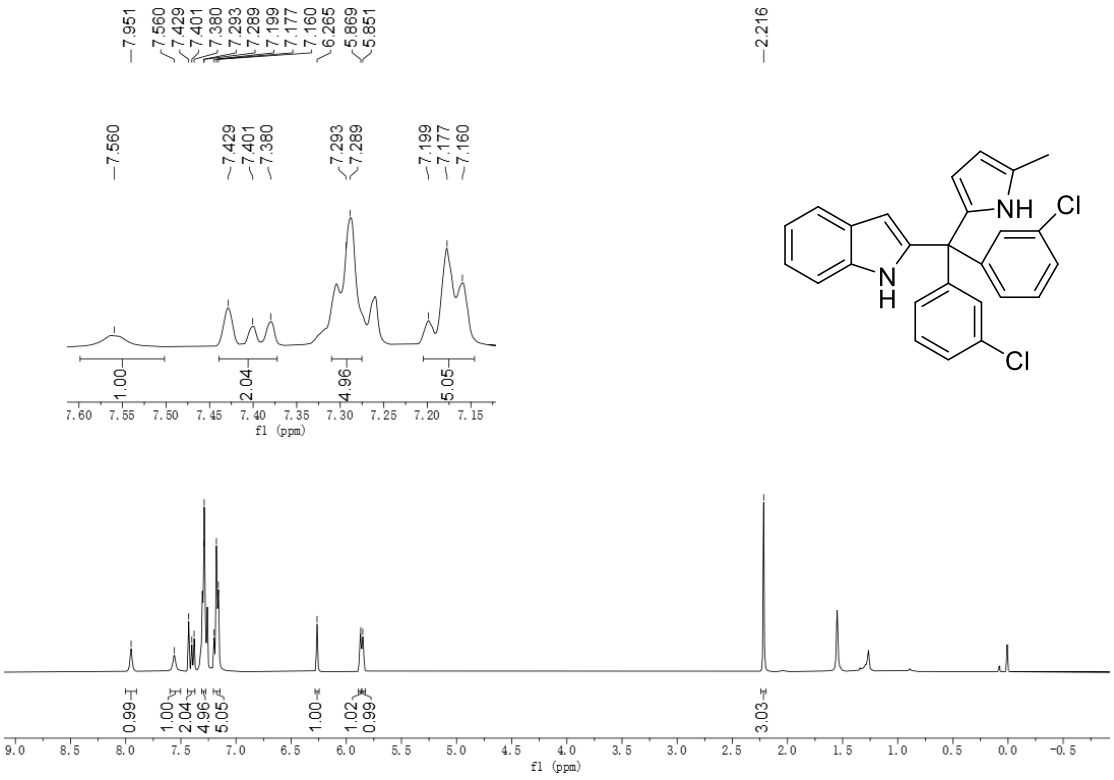


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ka:**



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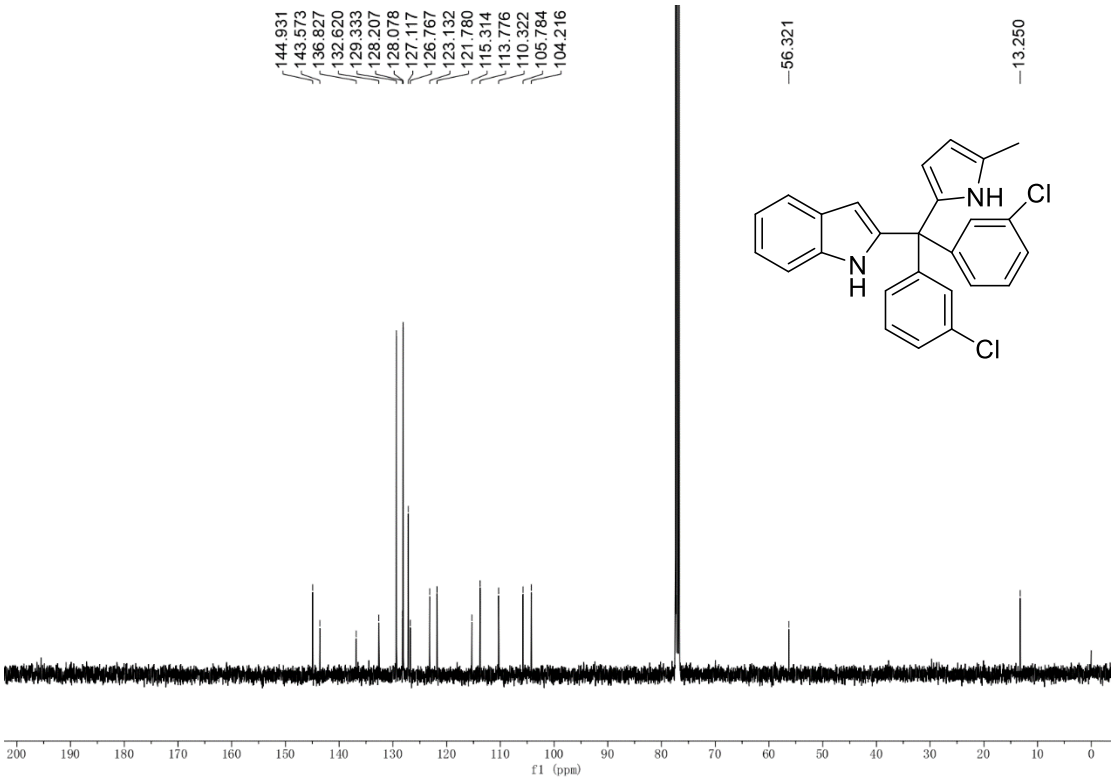
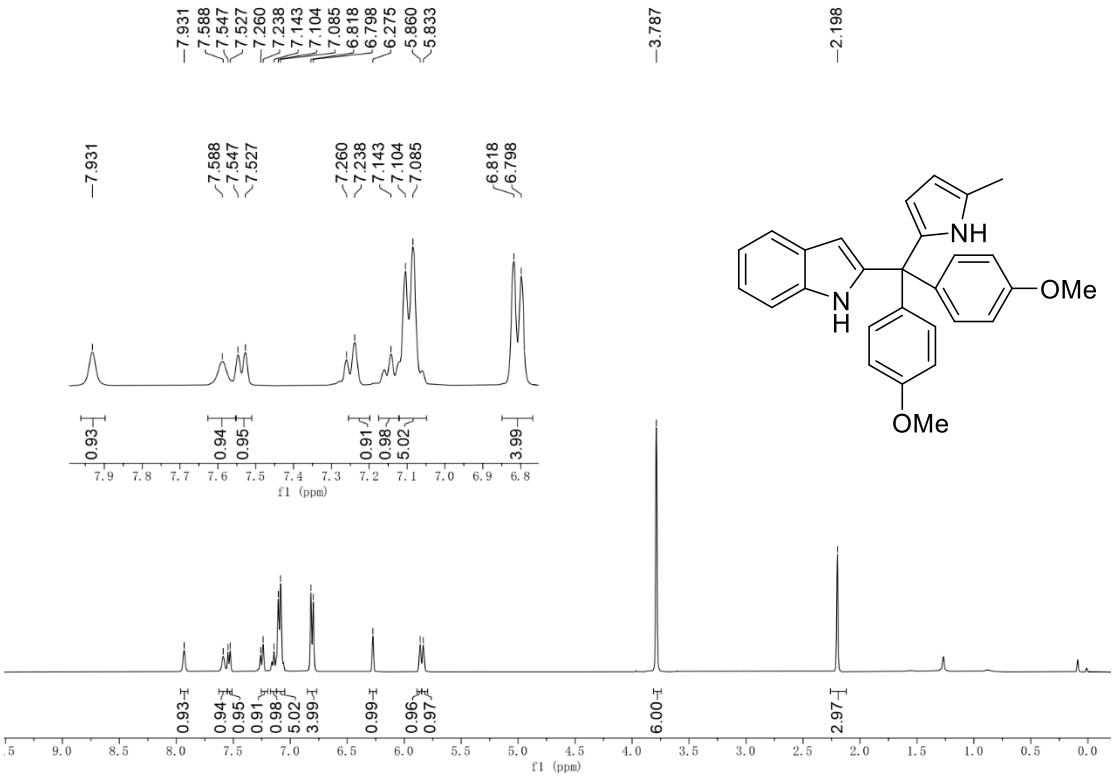
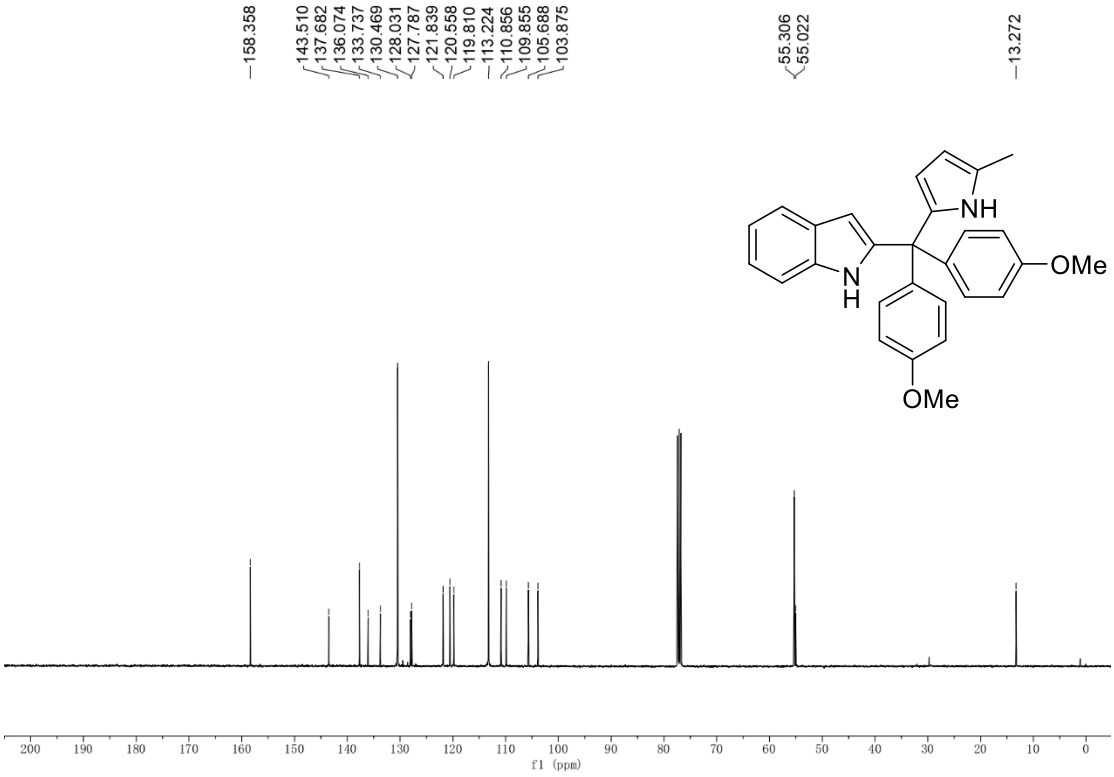


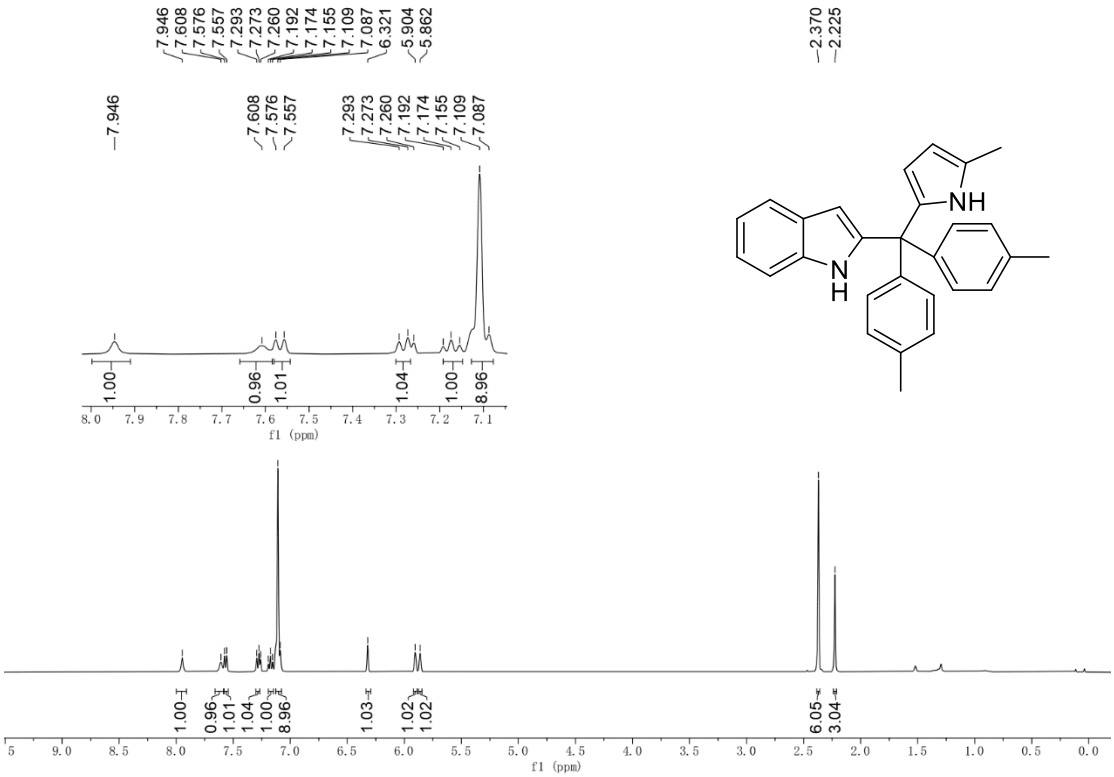
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3la**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3la**:



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ma**:



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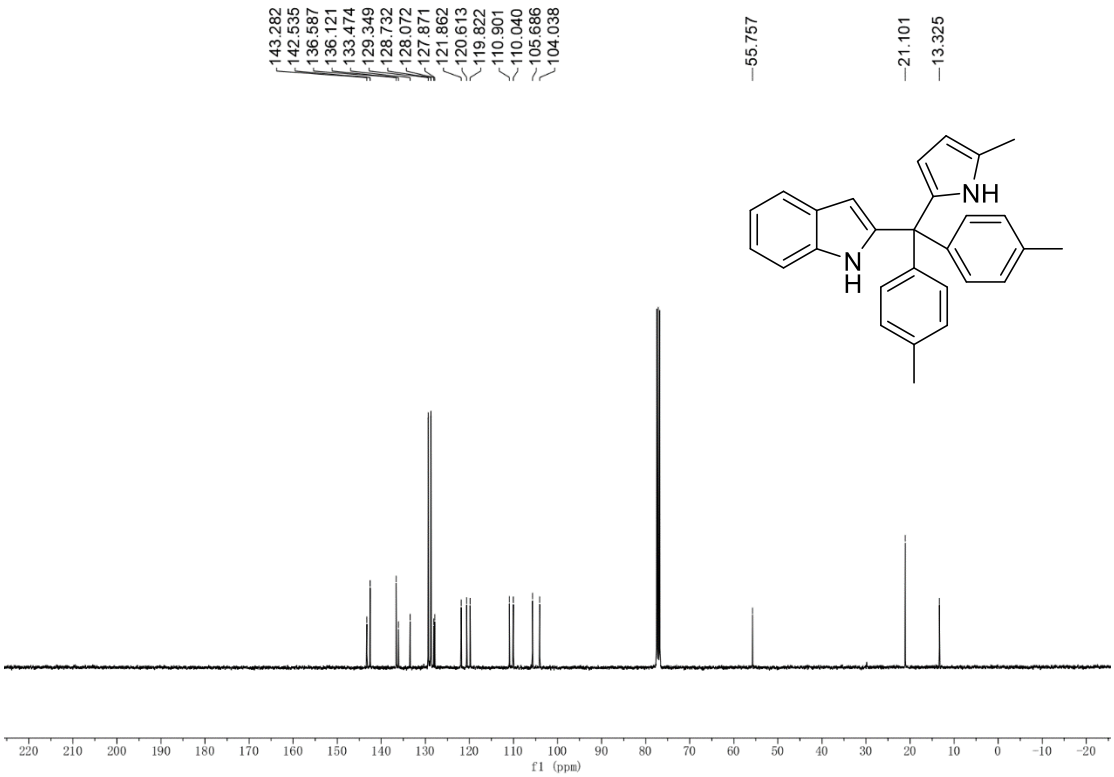
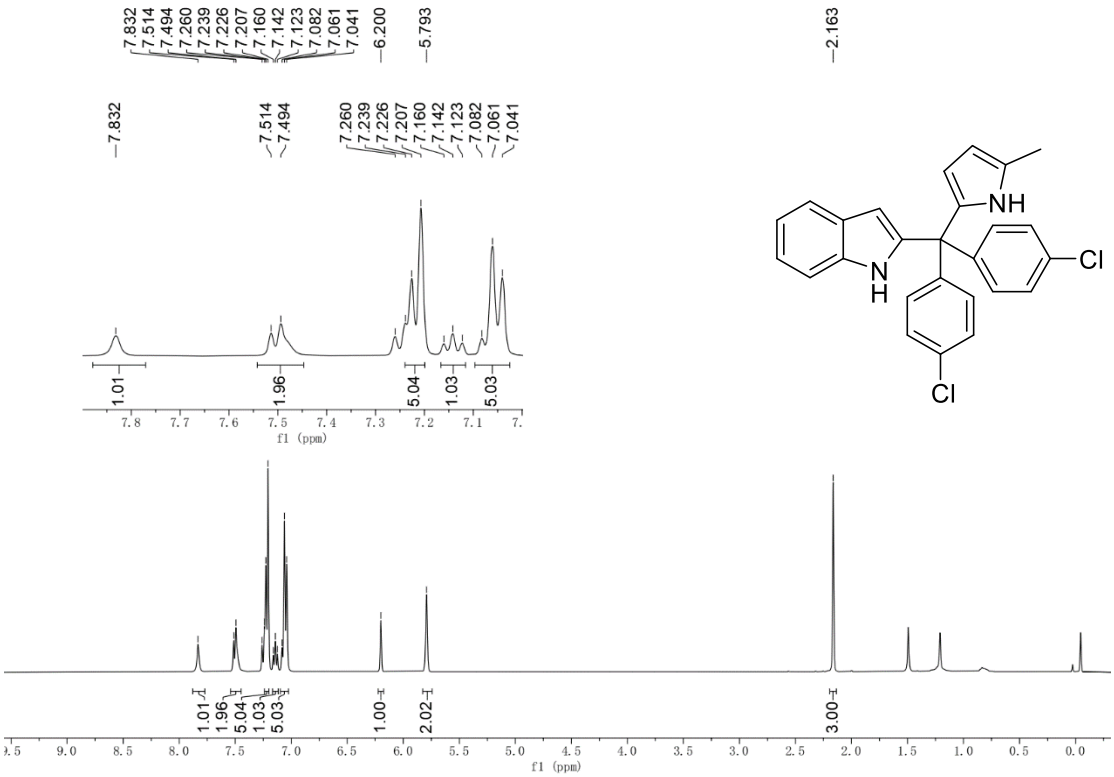


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3na**:



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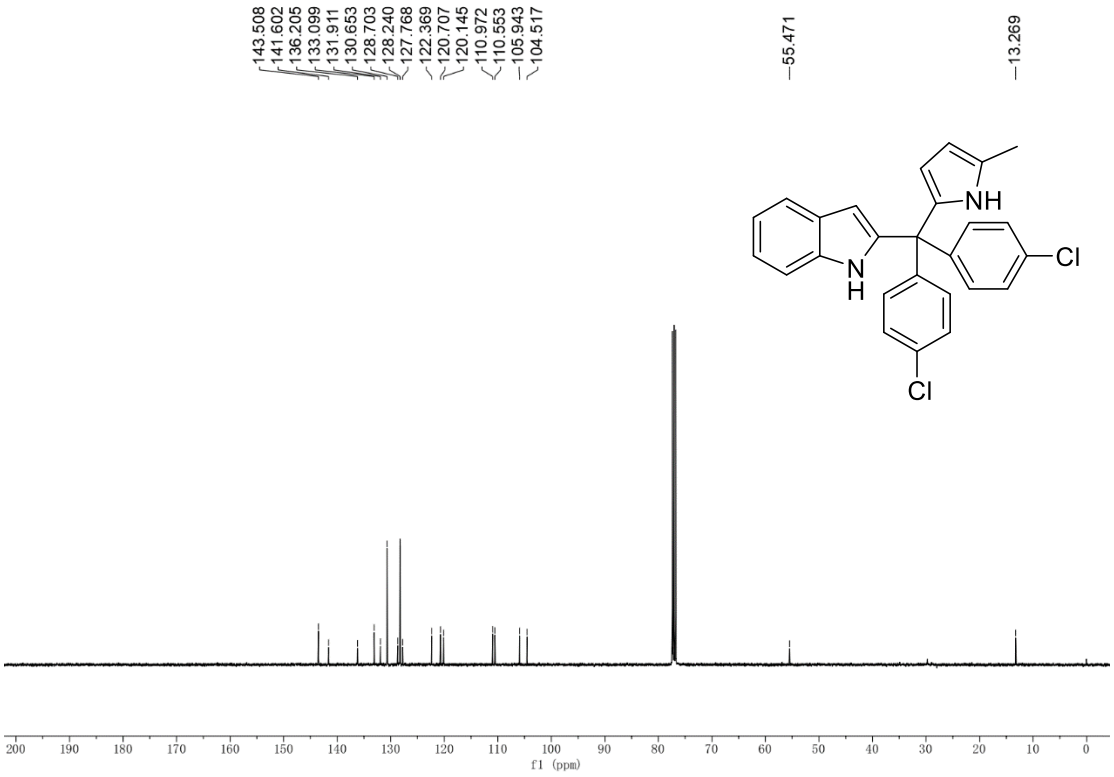
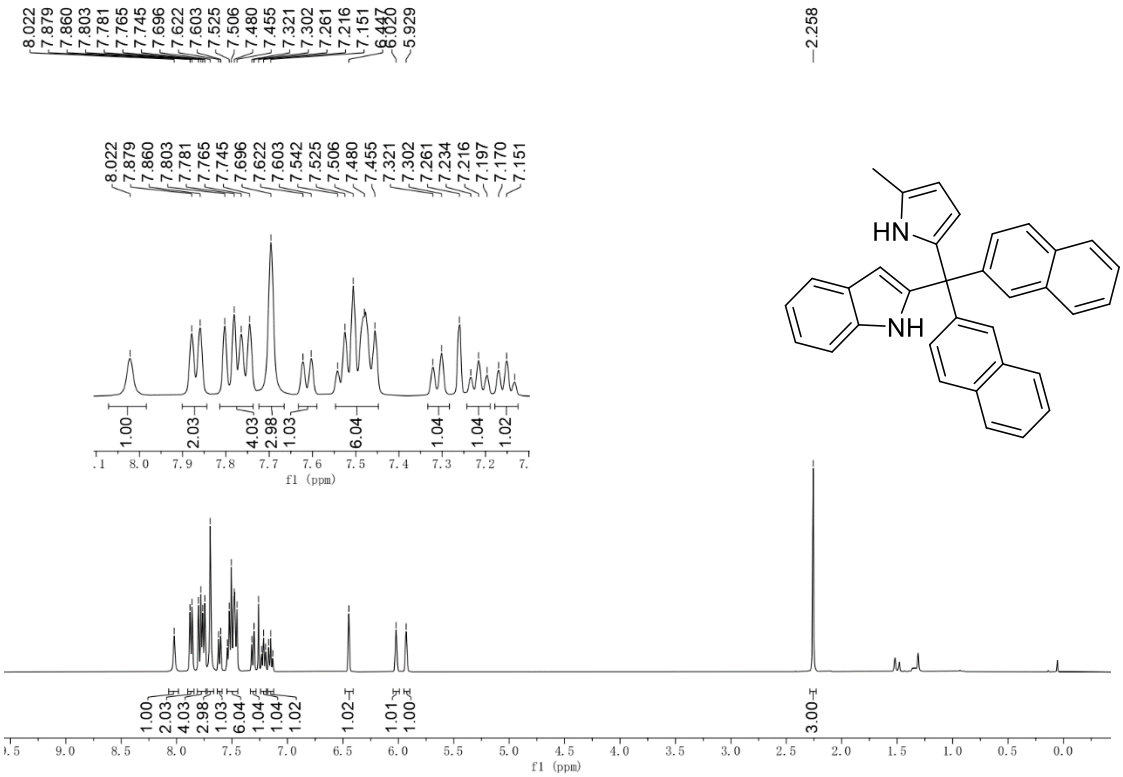


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3oa**:



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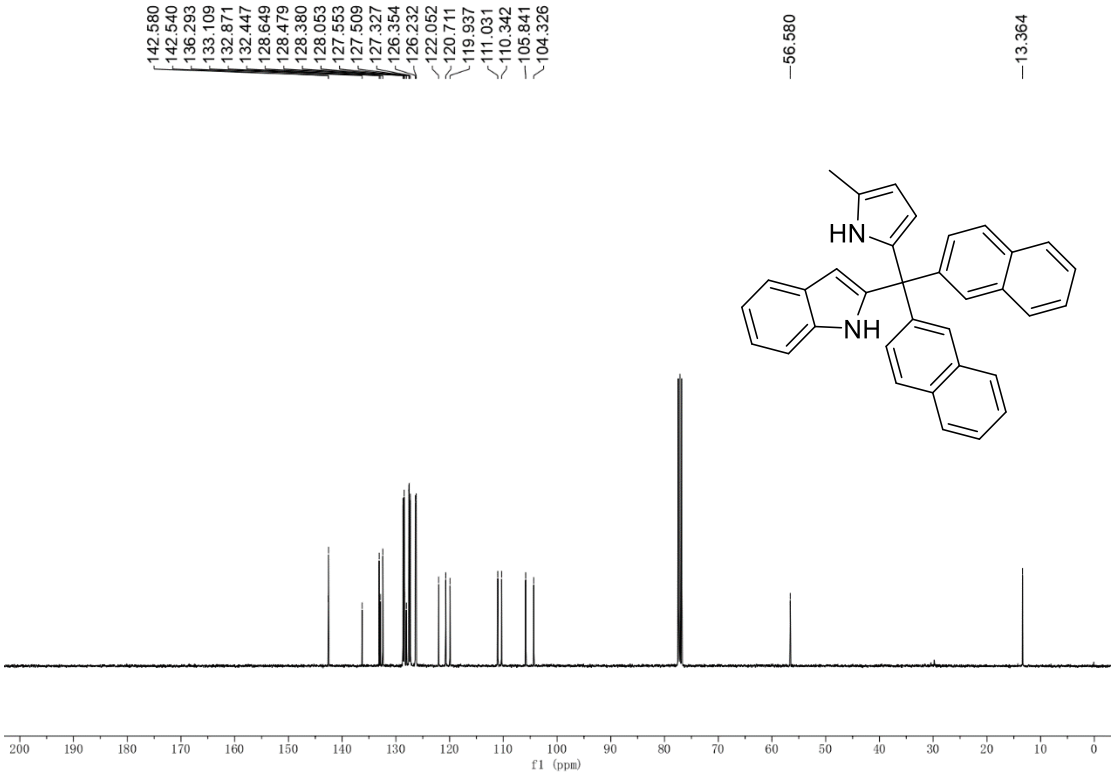
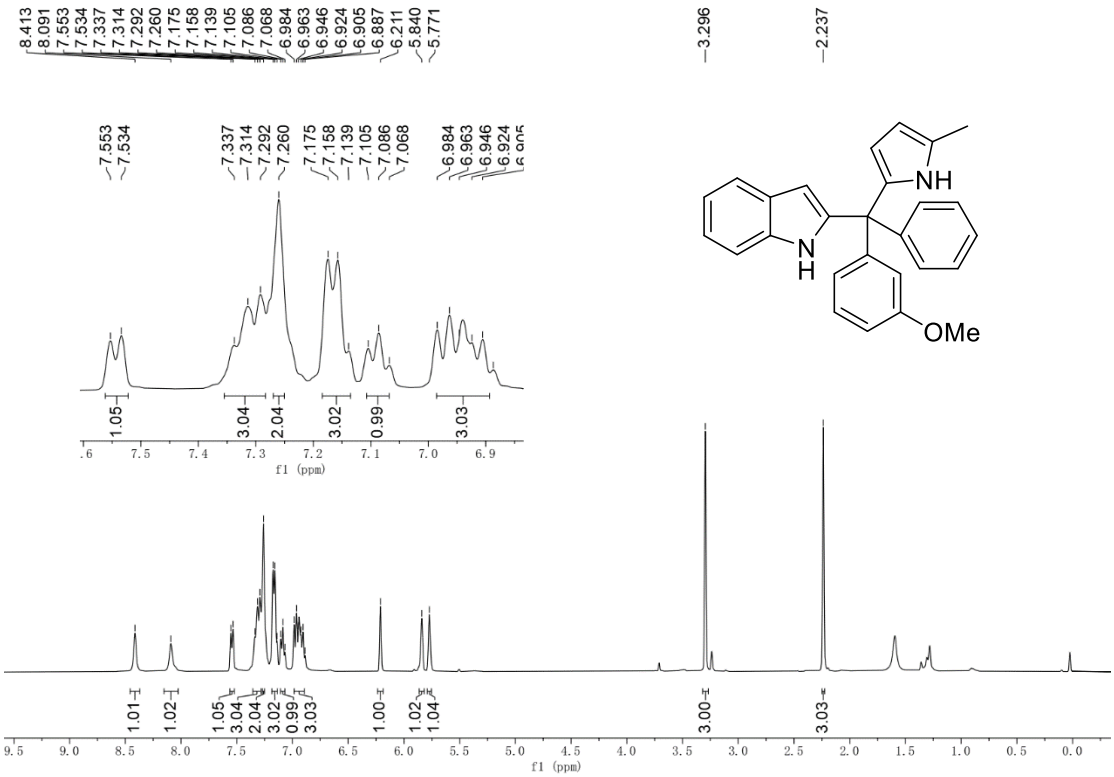


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3pa**:



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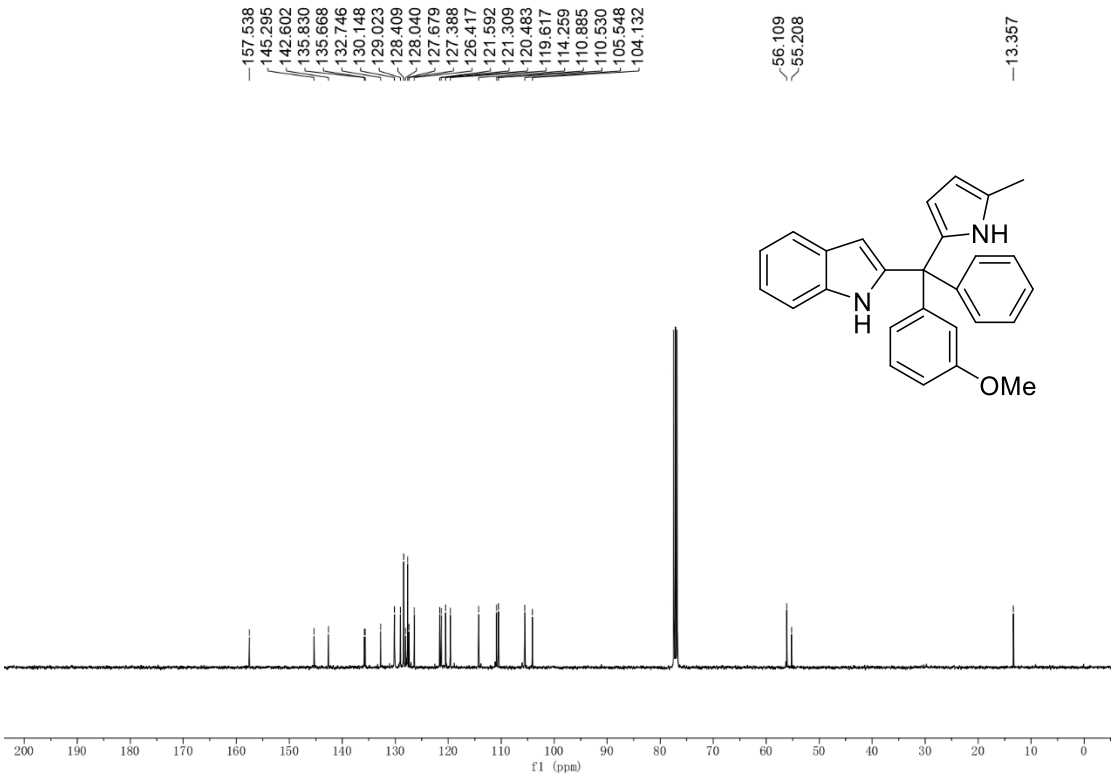
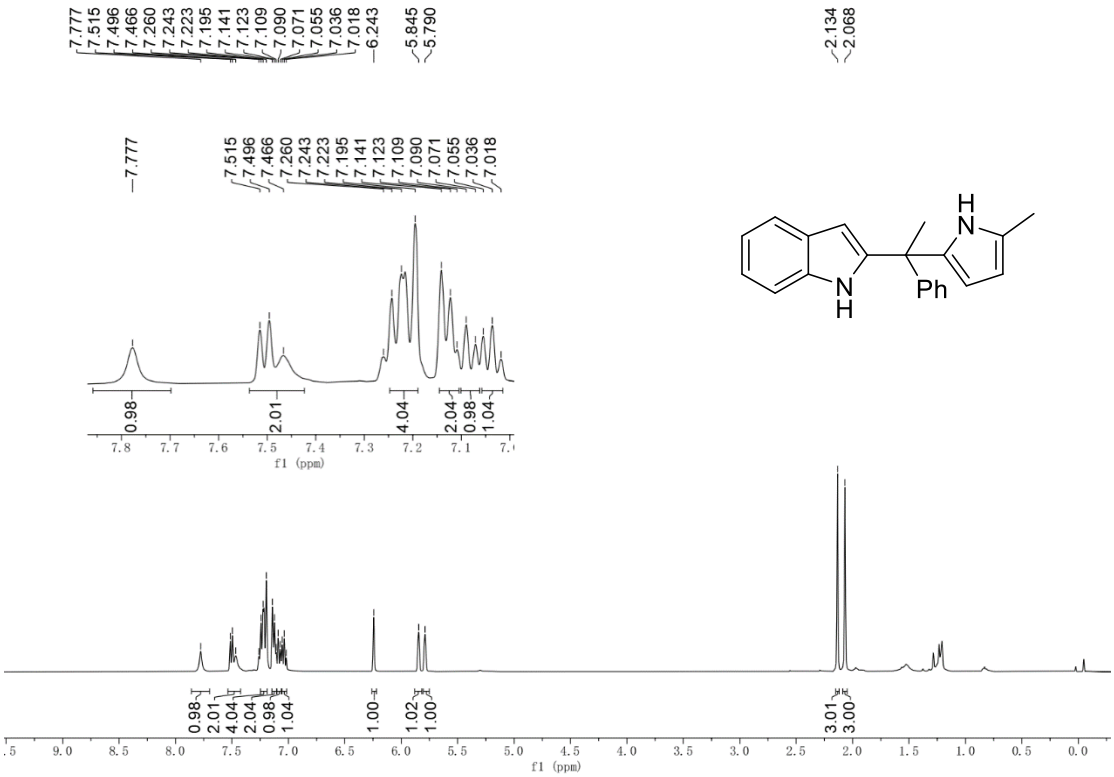


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3qa**:



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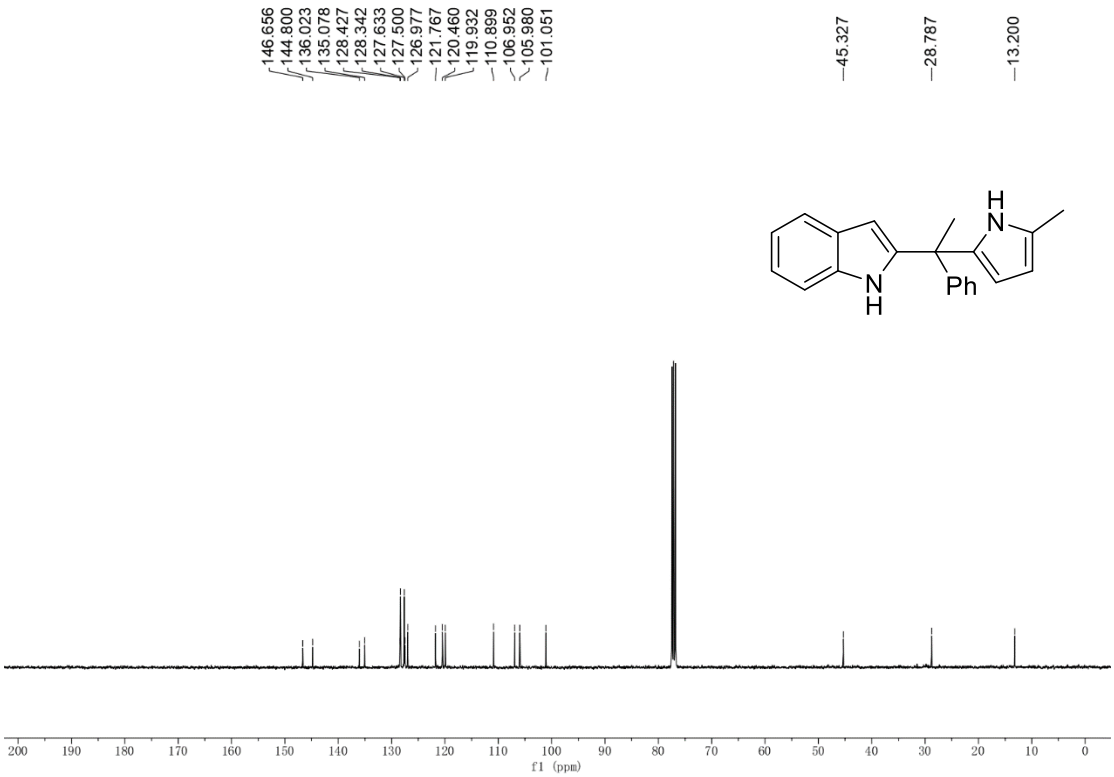
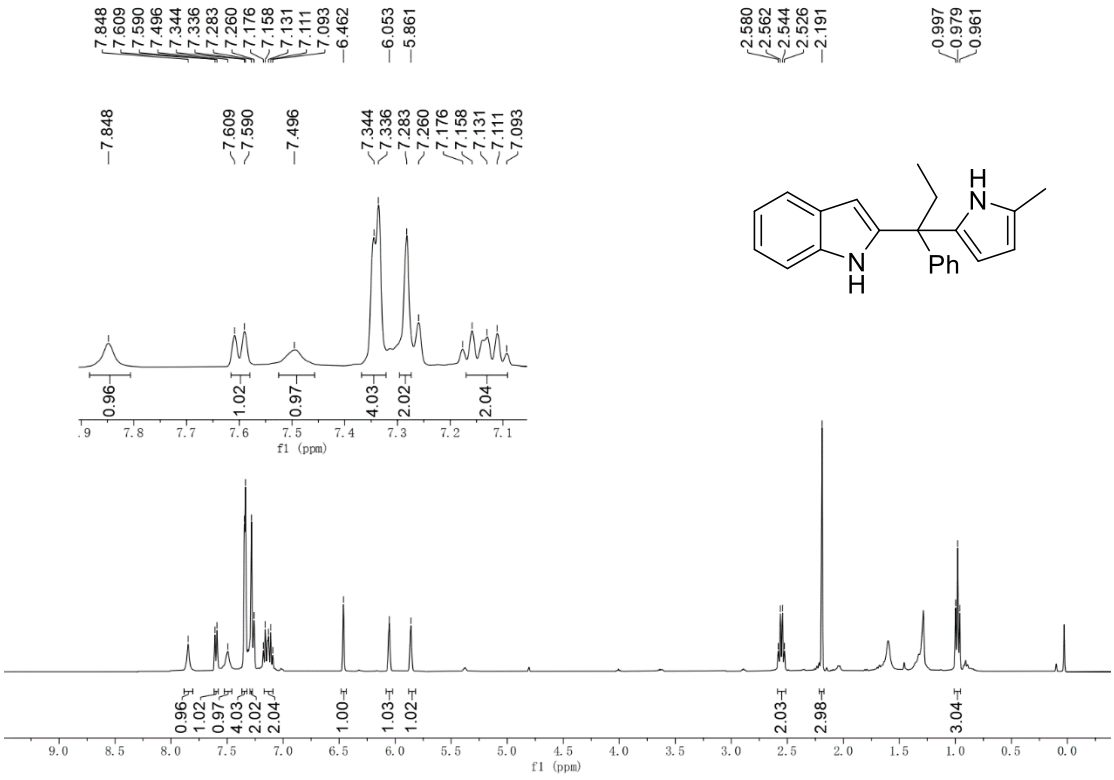
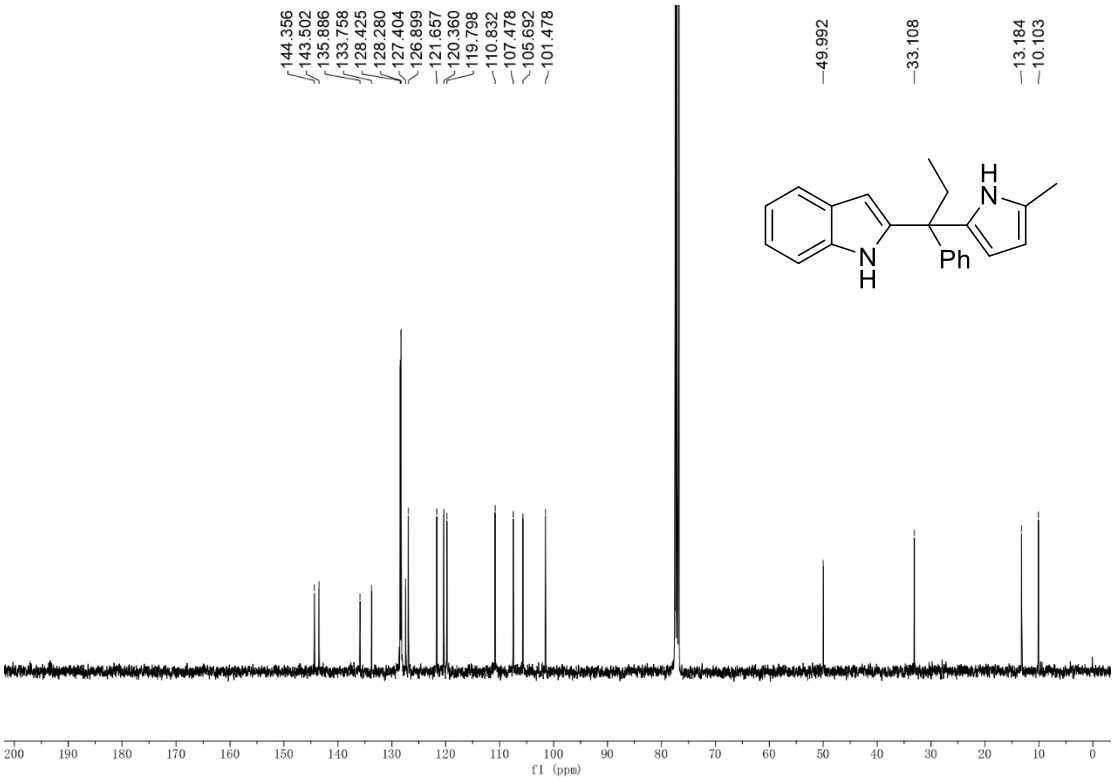


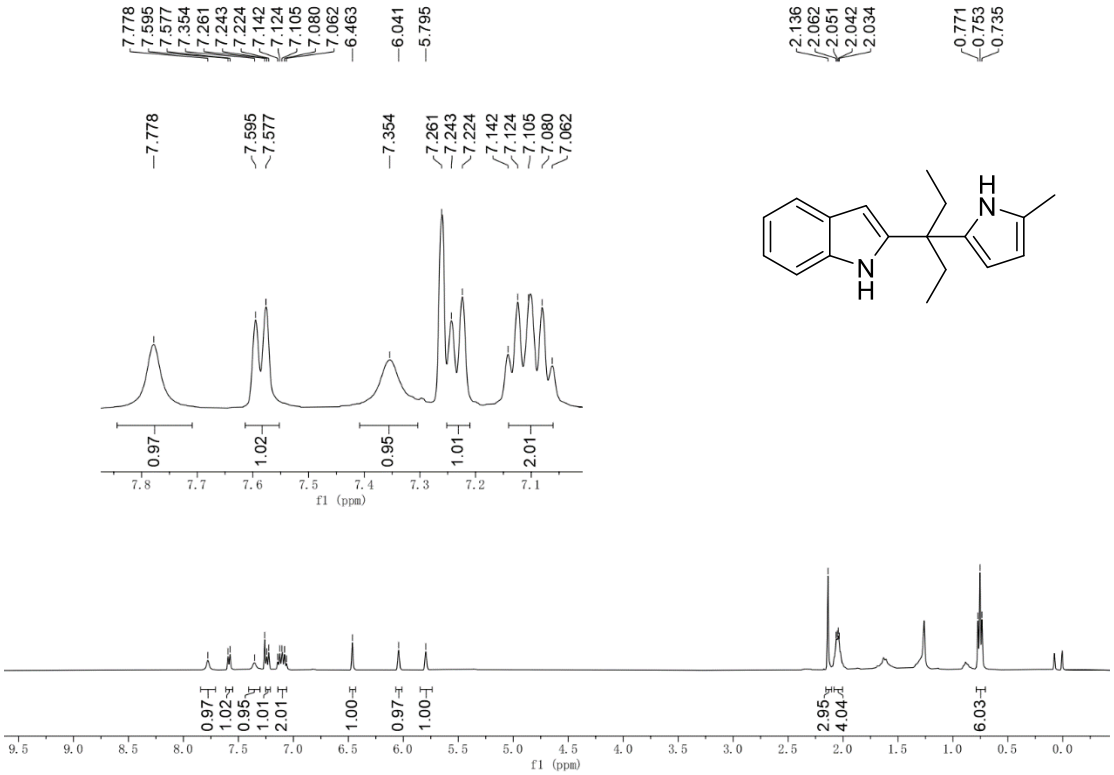
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ra**:



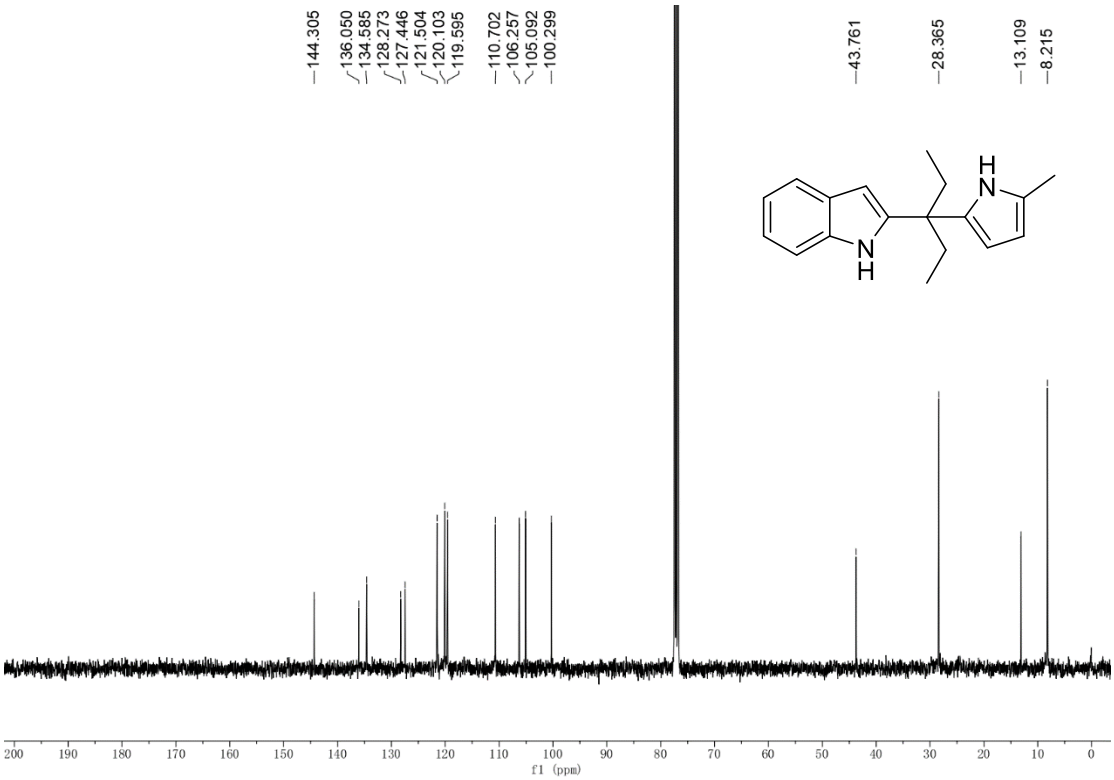
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ra**:



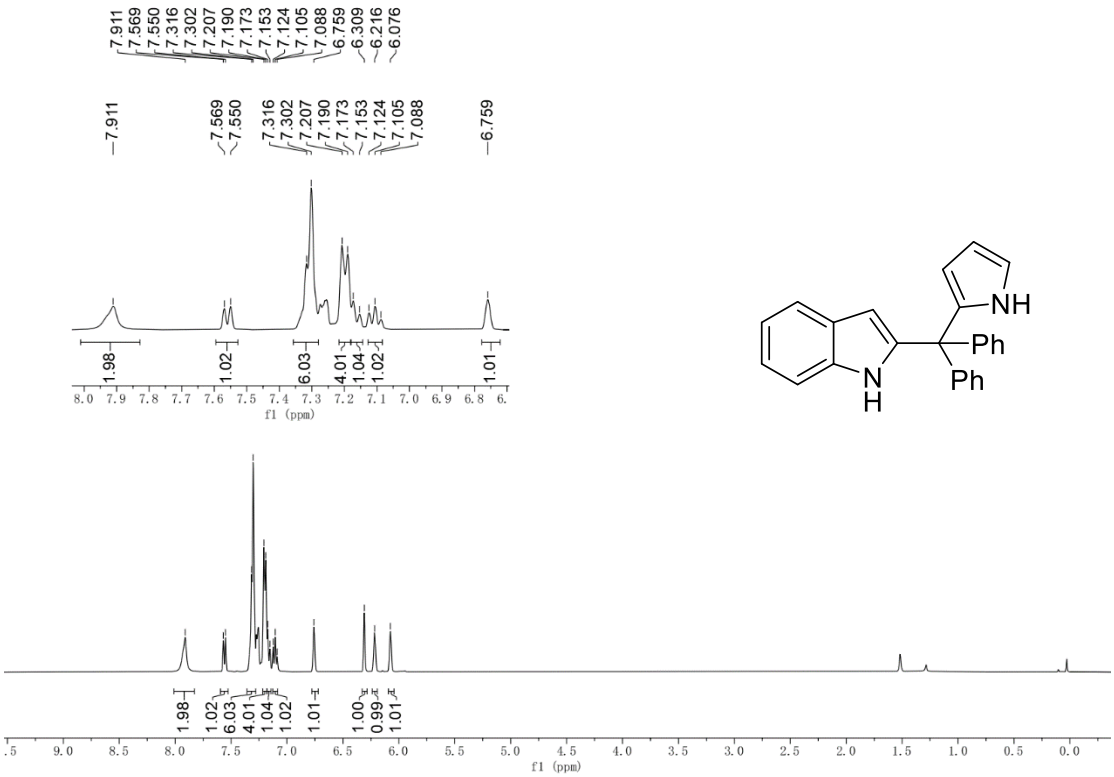
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3sa**:



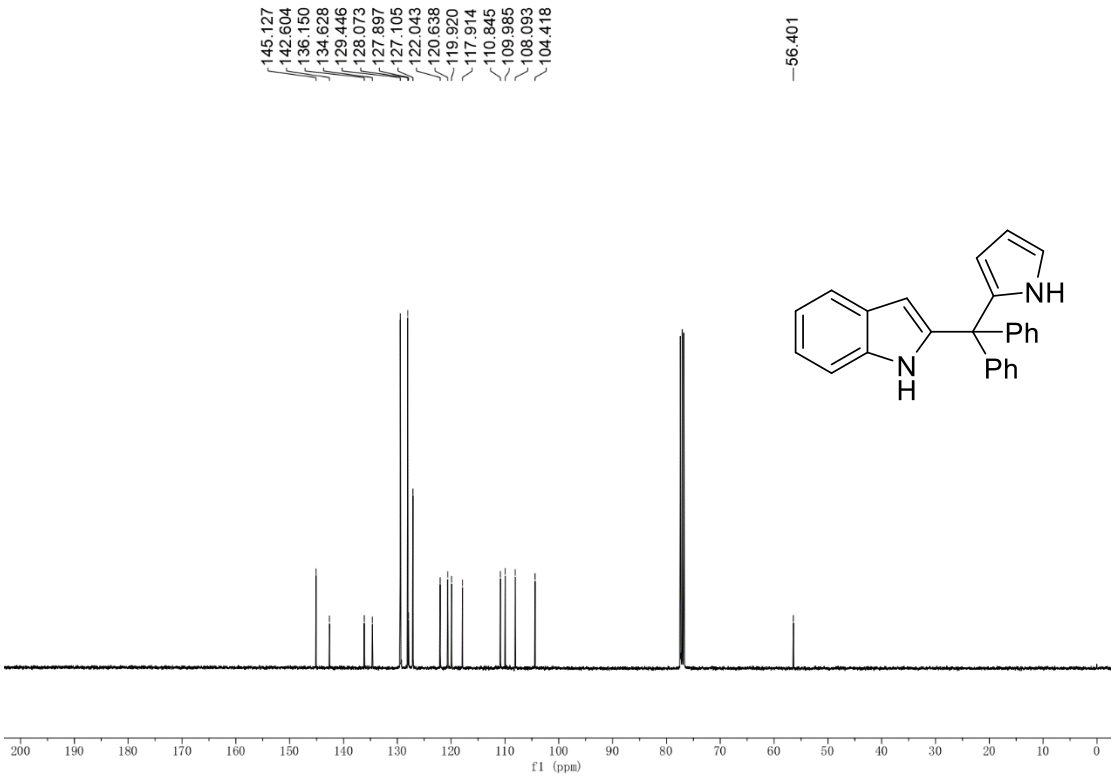
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3sa**:



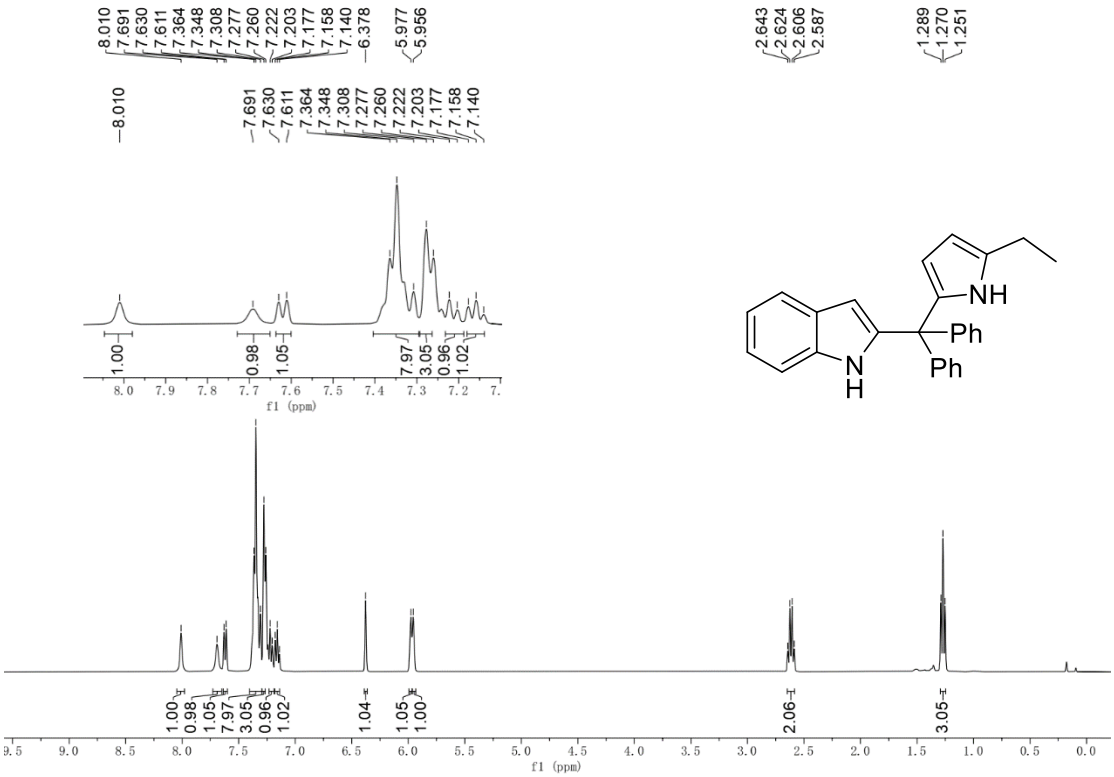
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ab:**



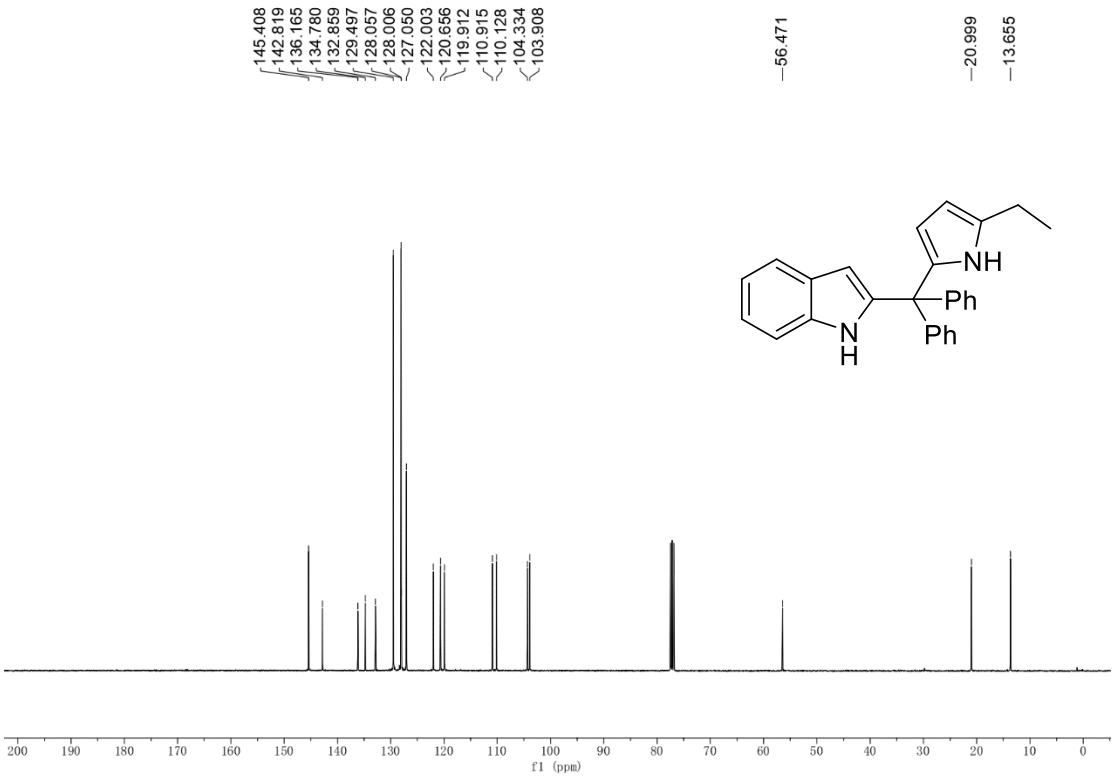
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ab:**



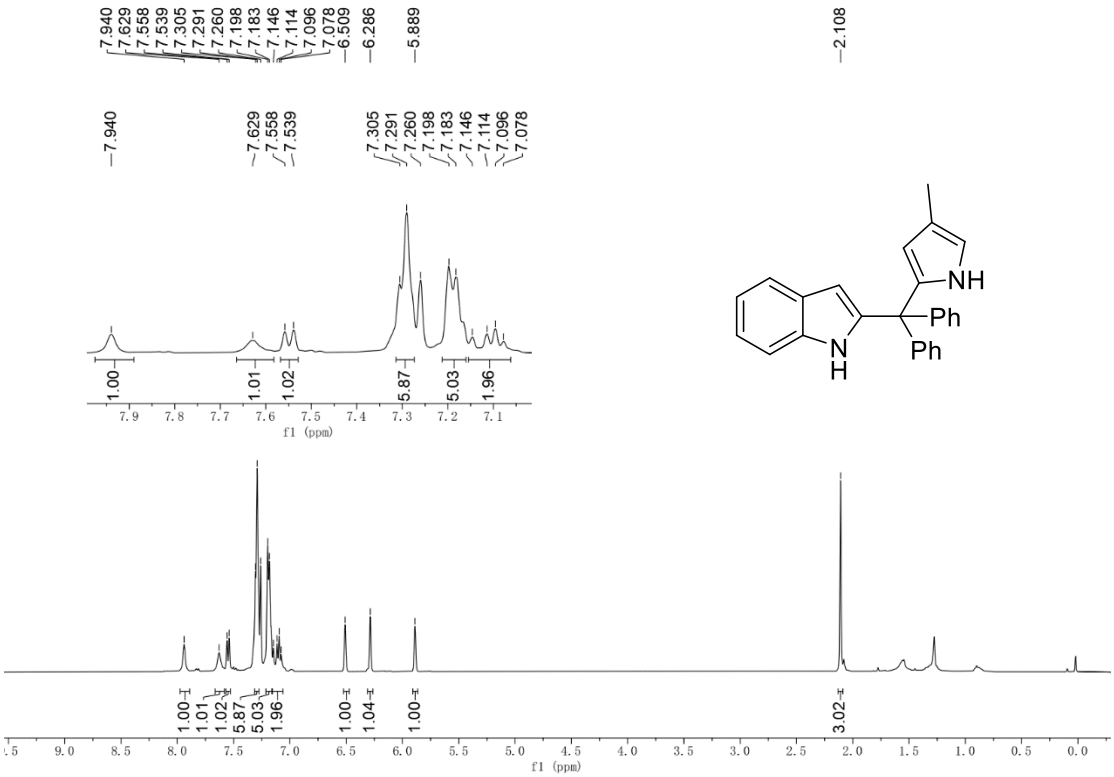
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ac:**



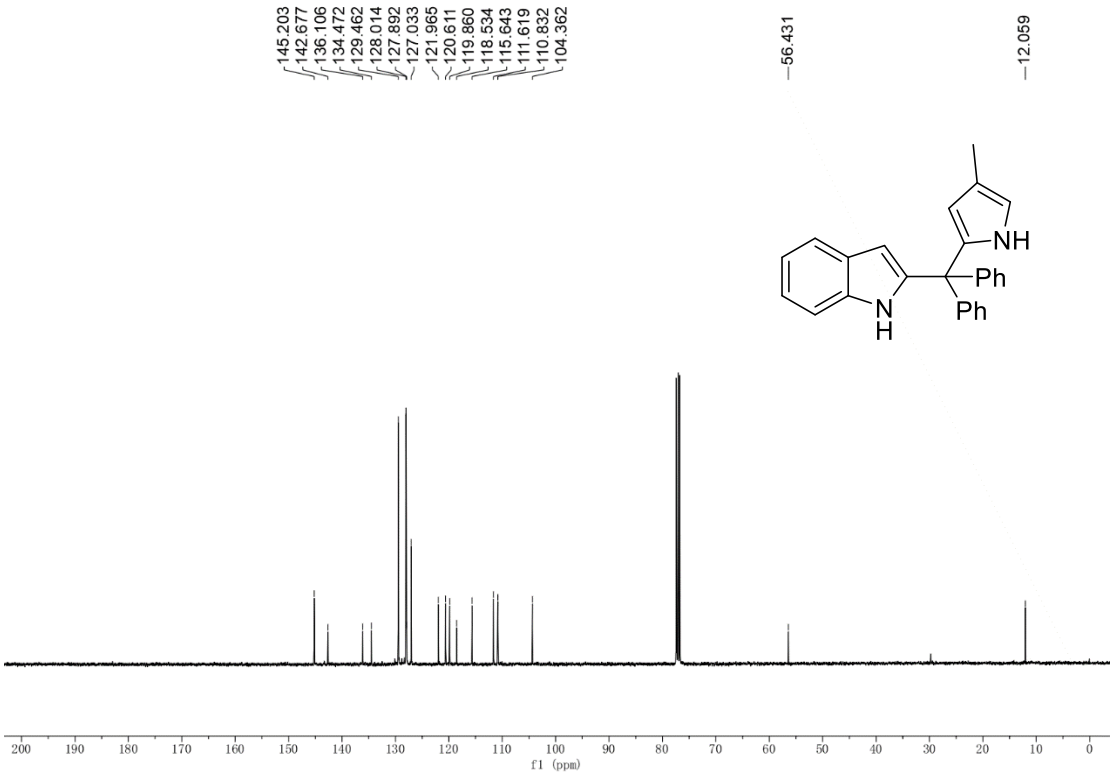
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ac:**



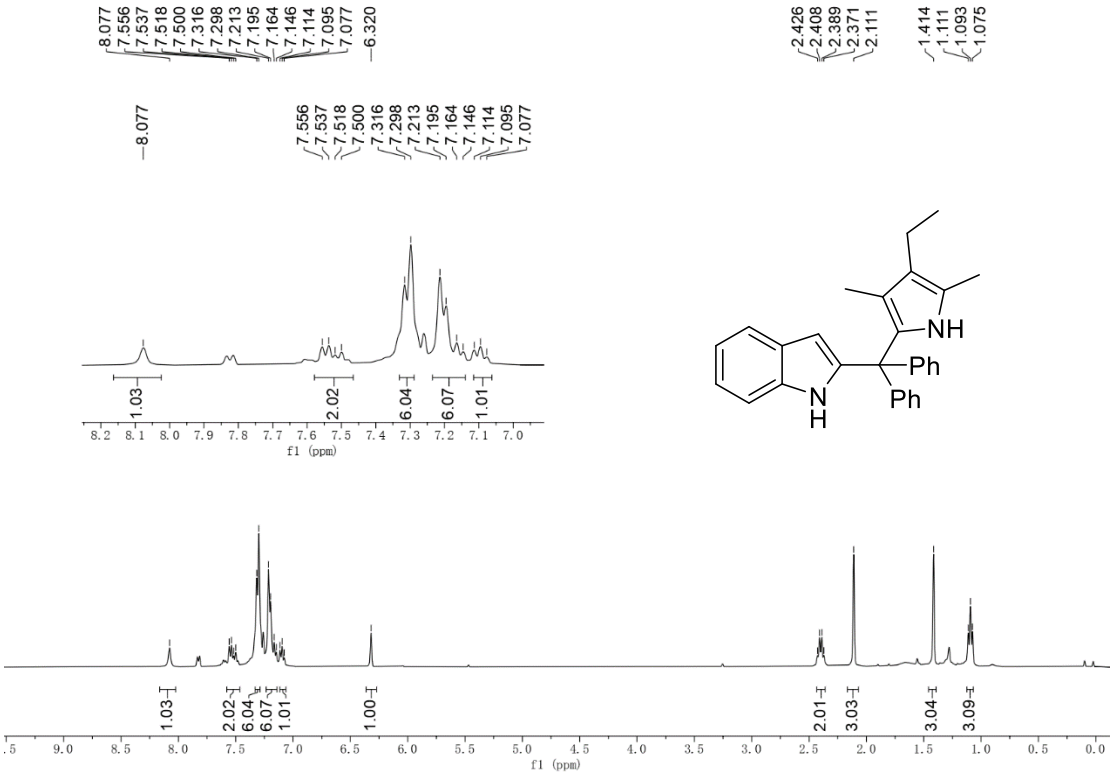
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ad:**



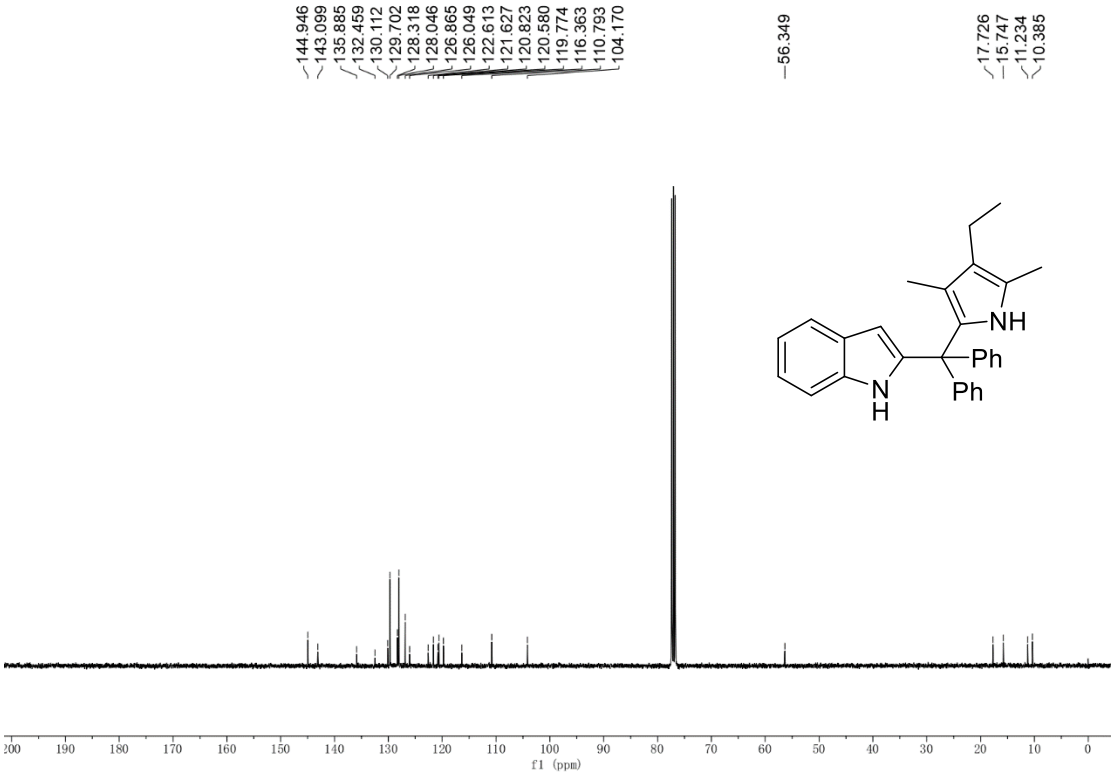
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ad:**



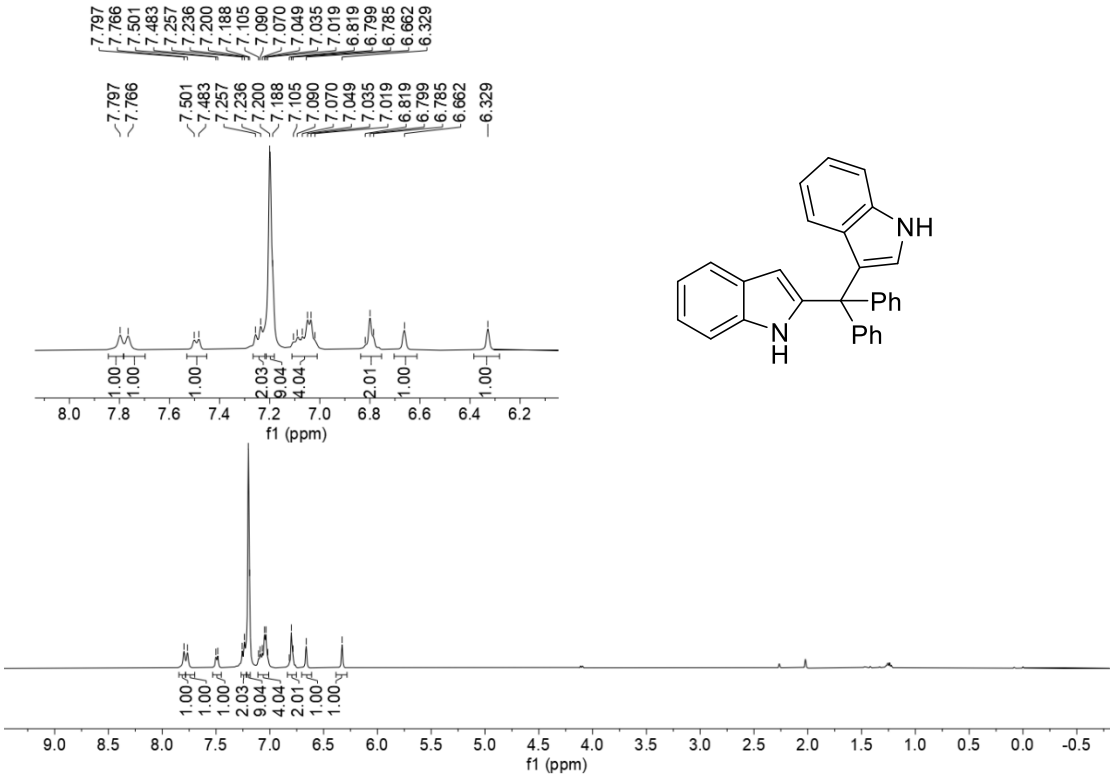
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ae**:



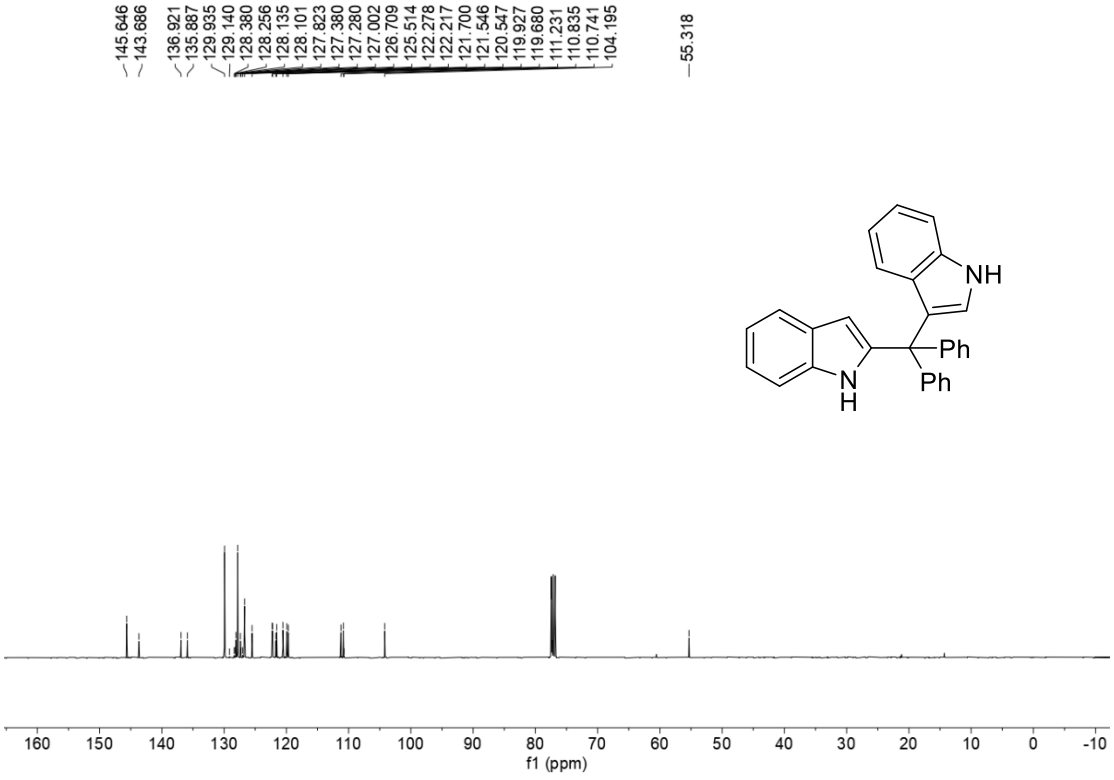
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ae**:



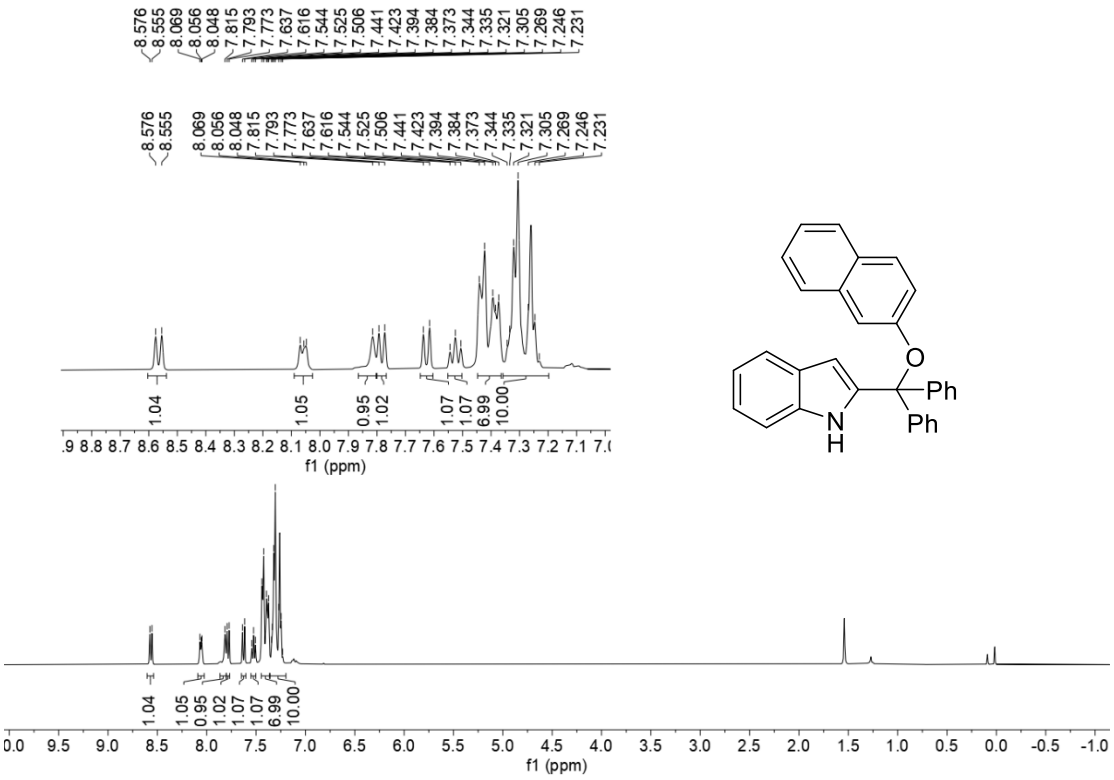
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3af**:



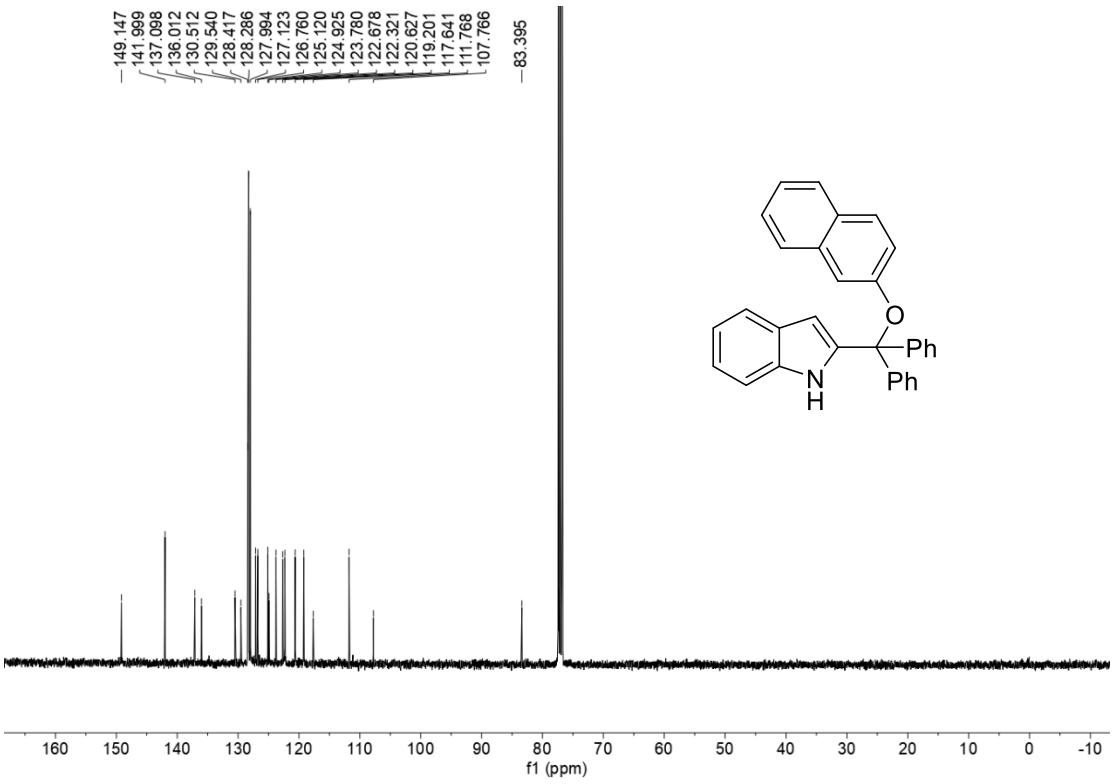
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3af**:



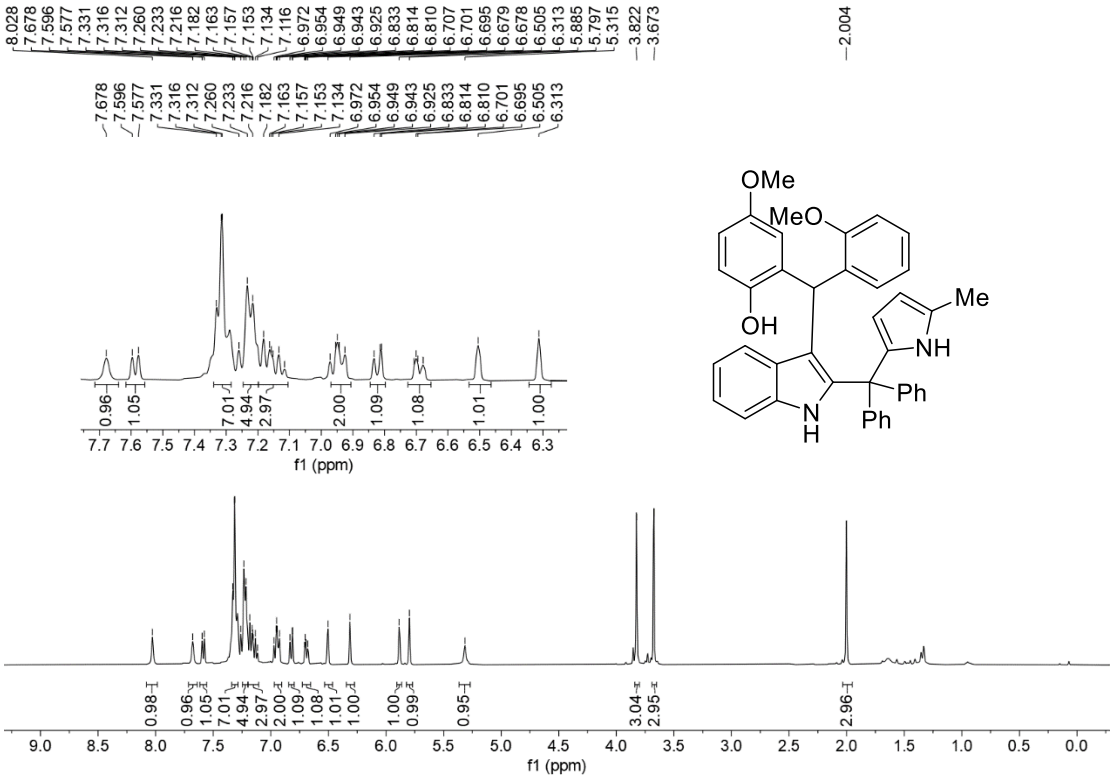
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ag**:



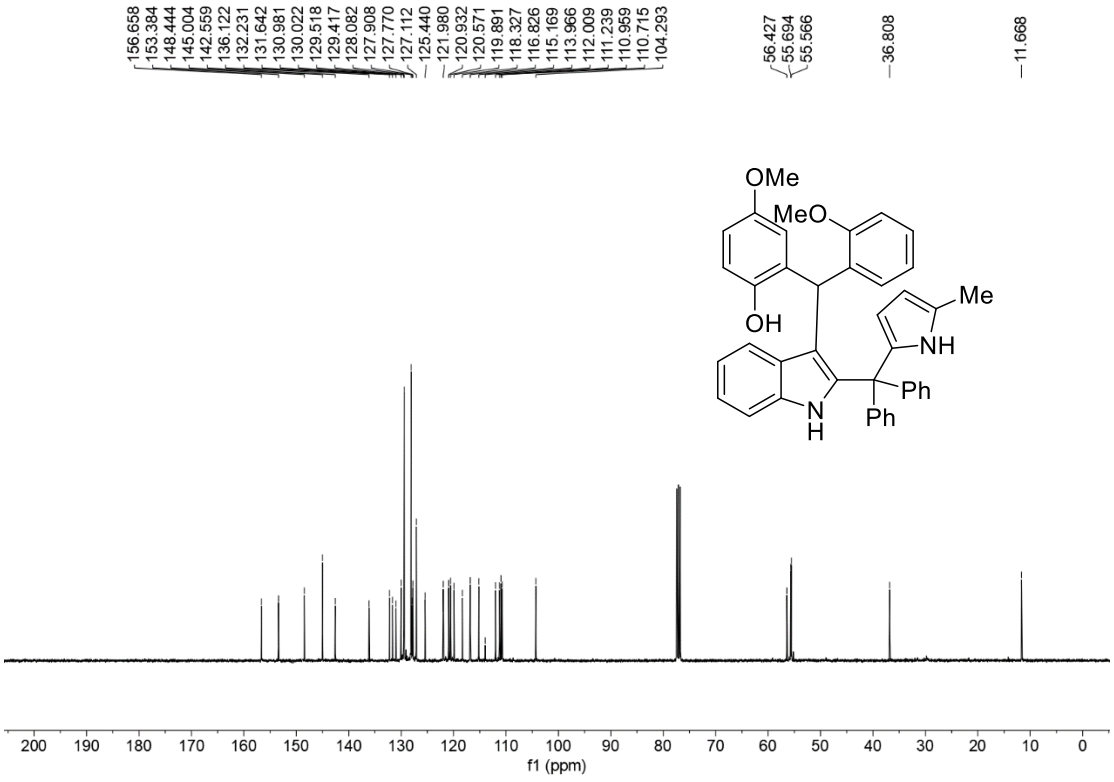
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ag**:



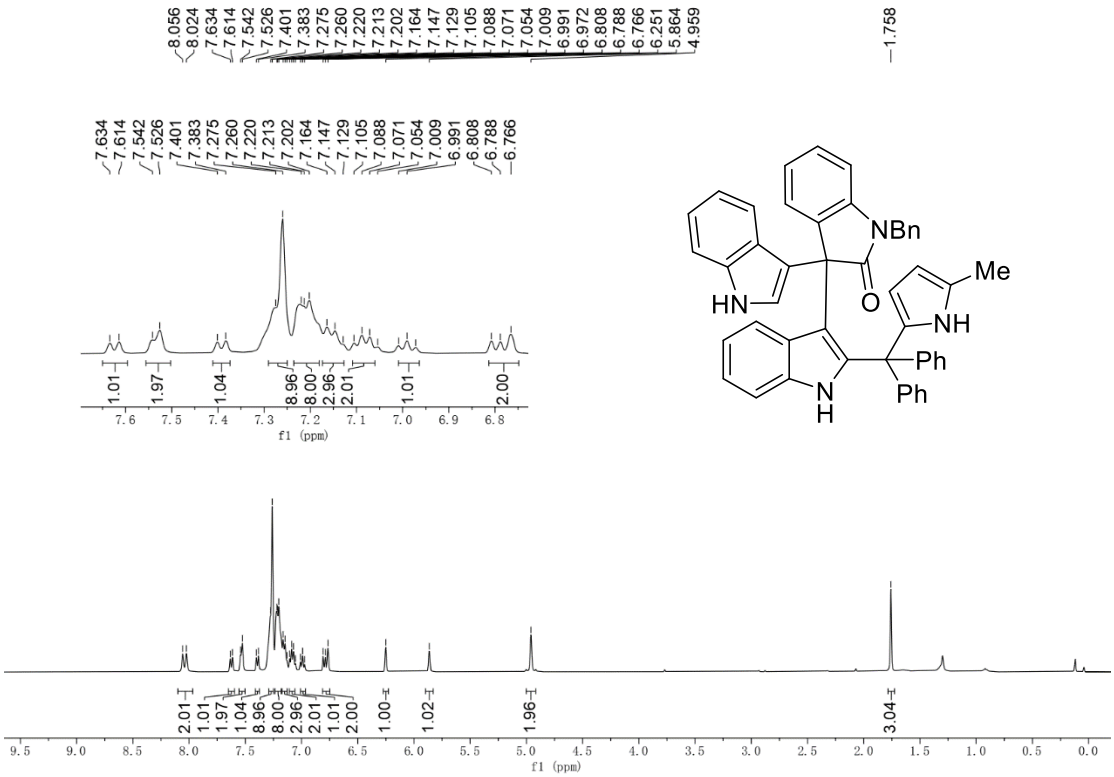
^{1}H NMR (400 MHz, $CDCl_3$) of compound **(5)**:



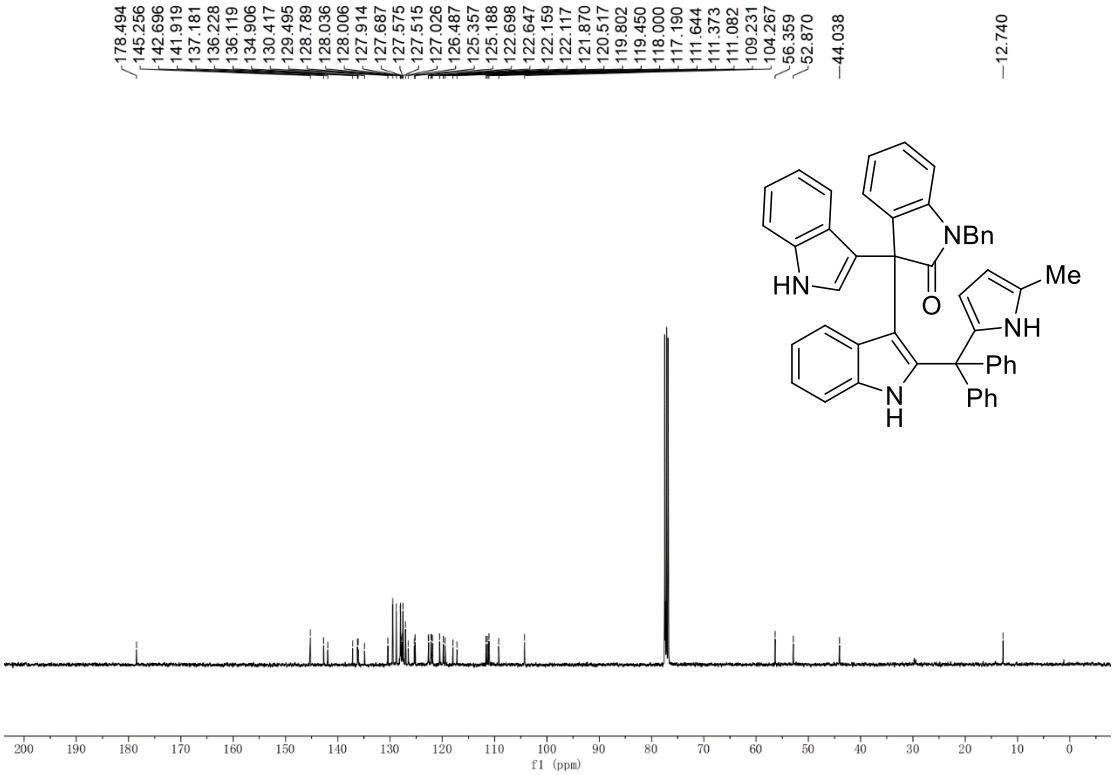
^{13}C NMR (100 MHz, $CDCl_3$) of compound (**5**):



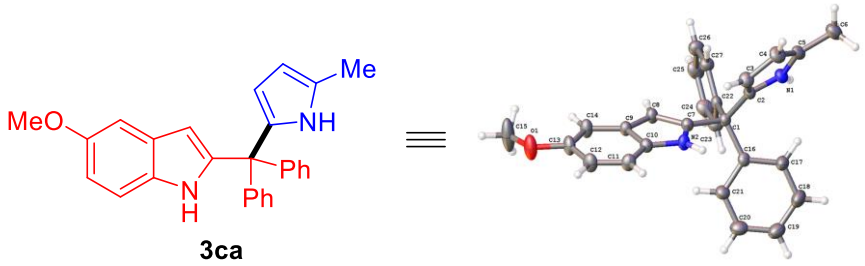
^{1}H NMR (400 MHz, $CDCl_3$) of compound **(7)**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound (**7**):



4. X-ray single crystal data for product 3ca



3ca

Empirical formula	$C_{27}H_{24}N_2O$	
Formula weight	392.48	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.4546(7) Å	a= 90°.
	b = 17.7571(13) Å	b= 99.501(2)°.
	c = 11.7155(10) Å	g = 90°.
Volume	2145.1(3) $Å^3$	
Z	4	
Density (calculated)	1.215 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	832	
Crystal size	0.12 x 0.07 x 0.07 mm^3	
Theta range for data collection	2.284 to 27.595°.	
Index ranges	-13<=h<=13, -23<=k<=23, -12<=l<=15	
Reflections collected	21156	
Independent reflections	4937 [R(int) = 0.1306]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4348	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4937 / 0 / 273	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0888, wR2 = 0.1687	
R indices (all data)	R1 = 0.1992, wR2 = 0.2153	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.193 and -0.214 $e.Å^{-3}$	