Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Mn(III)-catalyzed arylboronic acids-based cascade reaction via nonclassical organometallic-radical mechanism

Hui-Min Qian [a], Jian-Dong Zhang[a], Shun-Jun Ji*[a] and Xiao-Ping Xu*[ab]

[a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123;[b] Innovation Center for Chemical Science, Soochow University, China

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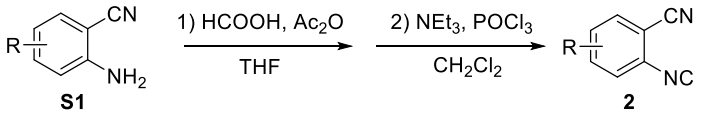
Experimental Procedure

1.General methods

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Melting points were recorded on an electrothermal digital melting point apparatus. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q =quarter and m = multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectroscopy (HRMS) analyses were performed using a commercial apparatus (ESI or EI Source). Crystal was tested by Bruker Apex II D8 Quest Agilent Gemini Atlas.

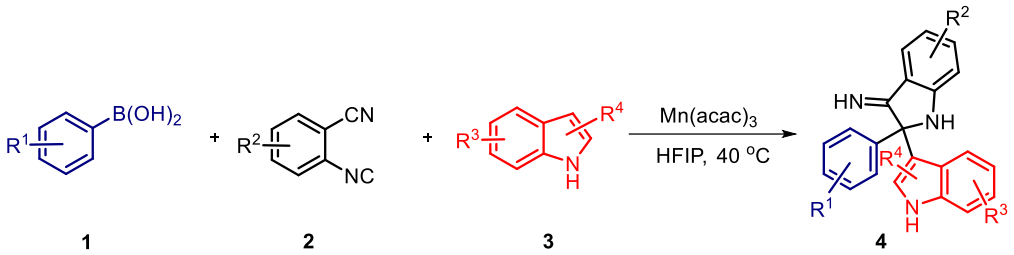
2.Synthesis of the starting materials

2.1 General procedure for the synthesis of substrate 2.



2-Isocyanobenzonitrile were prepared following the literature procedures.[1] To an oven-dried flask equipped with a dropping funnel, **S1** (5 mmol) and THF (15 mL) were cooled to 0 °C. Acetic formic anhydride, which was prepared from the reaction of acetic anhydride (1.2 mL) with formic acid (0.6 mL) at 55 °C for 2 h, was transferred to the dropping funnel and dropped to the solution of **S1** at 0 °C. After the addition was complete, the mixture was warmed to room temperature and stirred for 2 h. Then, the mixture was quenched by saturated aqueous solution of $NaHCO_3$ and extracted with EA three times. The extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give formamide. This formamide was used for the subsequent dehydration without further purification. To an oven-dried flask equipped with a dropping funnel, CH_2Cl_2 (20 mL), NEt_3 (5 mL, 30 mmol) and the whole amount of formamide obtained above were added under Ar atmosphere and cooled to 0 °C. $POCl_3$ (0.6 mL, 6 mmol) was added dropwise, and the mixture was stirred for 2 h at 0 °C after the addition was complete. Then, the mixture was quenched by saturated aqueous solution of Na_2CO_3 and stirred for 0.5 h. The mixture was extracted with CH_2Cl_2 three times, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The compound was purified by column chromatography on silica gel using PE/EA as eluent to give the desired substrate **2**.

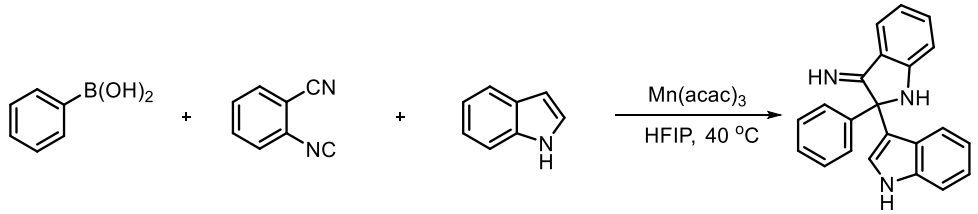
3.Typical procedure for the synthesis of 4



To an 8 mL tube, a mixture of boronic acid **1** (0.6 mmol, 3.0 equiv.), isocyanide **2** (0.2 mmol, 1.0 equiv.), indole **3** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol%), 2 mL HFIP were added. The reaction mixture was stirred at 40 °C for 40 min. The solvent was evaporated under the reduced pressure directly. The product **4** was purified by flash column chromatography with petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 3 : 1) as eluents.

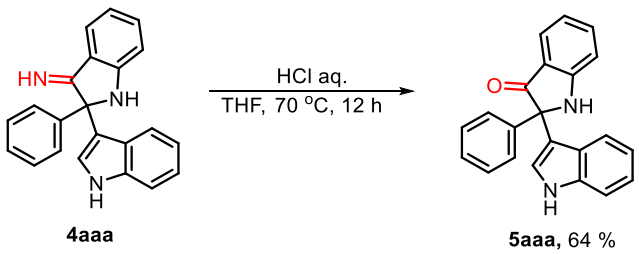
4.Gram-scale synthesis and further transformation

4.1 Gram-scale synthesis



Phenylboronic acid **1a** (12 mmol, 3.0 equiv.), isocyanide **2a** (4 mmol, 1.0 equiv.), indole **3a** (4 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol %) were added in HFIP (40 mL). The reaction mixture was stirred at 40 °C for 1 h. After completion of the reaction, the reaction mixture was concentrated by rotary evaporation under reduced pressure. **4aaa** in the form of yellow solid (1.23 g) was obtained by column chromatography on silica gel using petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 3 : 1) as eluents.

4.2 further transformation

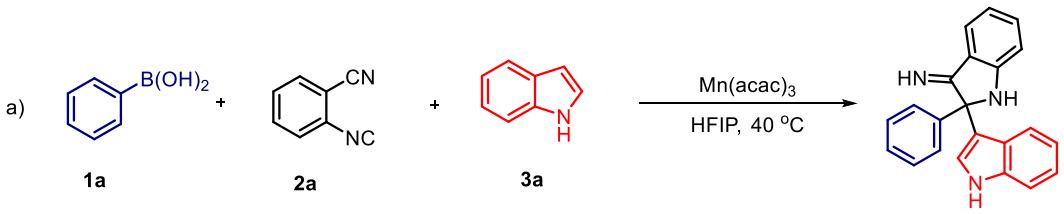


To a solution of the 2-Indolyl-indoline **4aaa** (0.2 mmol, 1.0 equiv.) in THF (1.0 mL) was added HCl (aq. 1mol•L^{-1}, 1 mL). After the reaction was proceeded at 70 °C for 12 h, the reaction mixture was quenched with saturated $NaHCO_3$ solution. By extraction with CH_2Cl_2, the organic layer was washed with brine

and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 6 : 1) to afford the desired product **5aaa** as a yellow solid.

5. Control experiments

5.1 Free radical trapping experiments



1a **2a** **3a**

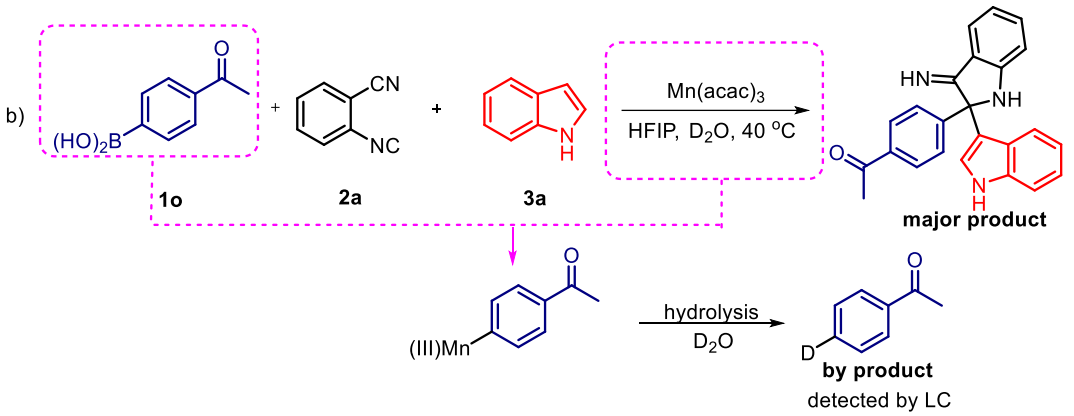
radical trapping agent:	**4aaa**
TEMPO	93%
BHT	73%
1,1-Diphenylethylene	93%
N,*N*-diallyl-4-methylbenzenesulfonamide	90%

To an 8 mL tube, a mixture of boronic acid **1a** (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), indole **3a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol%), TEMPO (0.4 mmol), 2 mL HFIP were added. The reaction mixture was stirred at 40 °C for 40 min. The yield was determined by LC analysis.

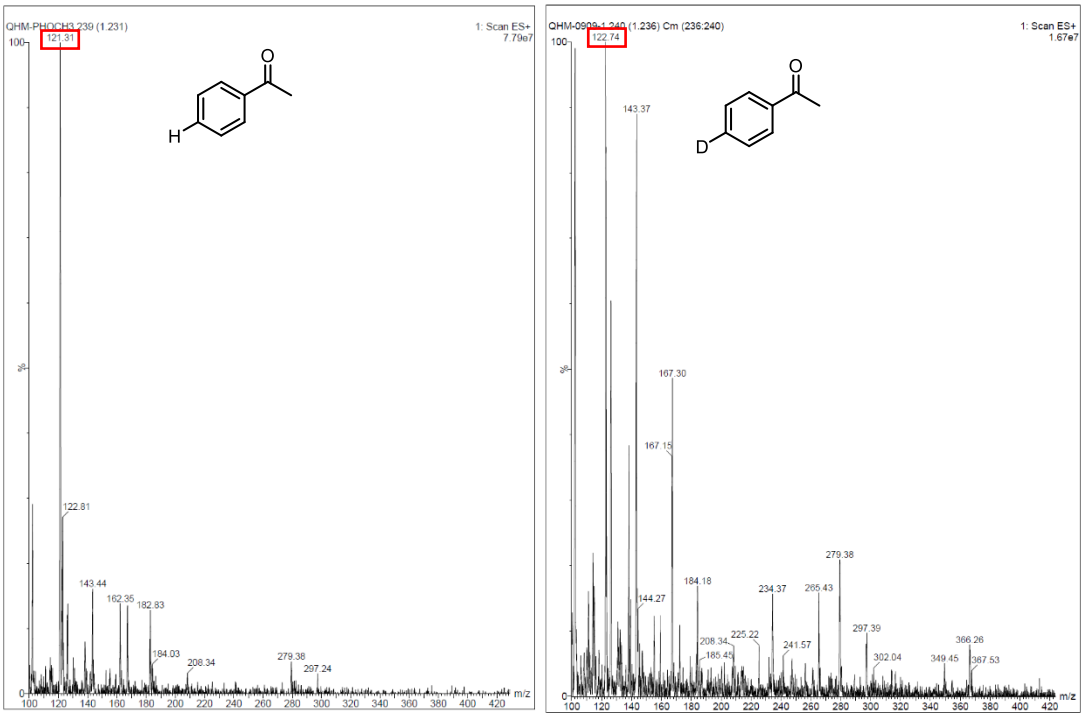
To an 8 mL tube, a mixture of boronic acid **1a** (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), indole **3a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol%), BHT (0.4 mmol), 2 mL HFIP were added. The reaction mixture was stirred at 40 °C for 40 min. The yield was determined by LC analysis.

To an 8 mL tube, a mixture of boronic acid **1a** (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), indole **3a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol%), 1,1-diyldibenzene (0.4 mmol), 2 mL HFIP were added. The reaction mixture was stirred at 40 °C for 40 min. The yield was determined by LC analysis.

To an 8 mL tube, a mixture of boronic acid **1a** (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), indole **3a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol%), N,N-diallyl-4-methylbenzenesulfonamide (0.4 mmol), 2 mL HFIP were added. The reaction mixture was stirred at 40 °C for 40 min. The yield was determined by LC analysis.

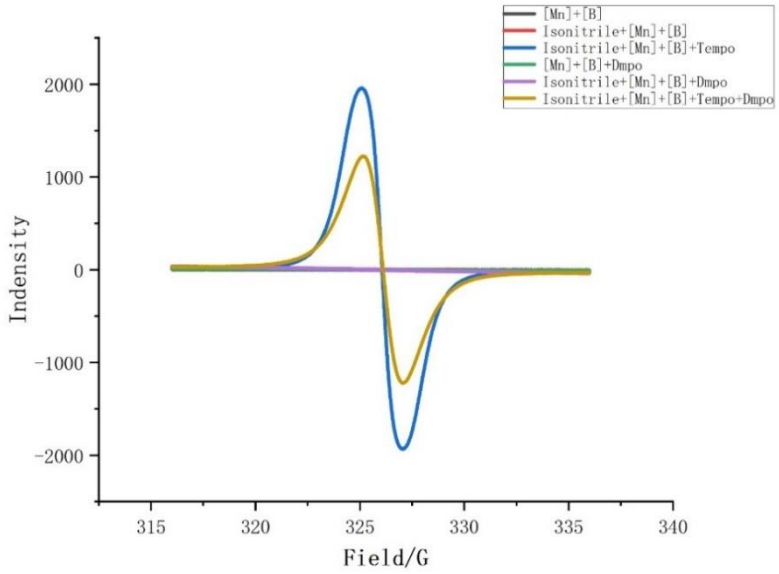


b) Mass spectra of acetophenone and deuterated acetophenone



c) To an 8 mL tube, a mixture of triphenylboroxin (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), indole **3a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol%), 2 mL HFIP were added. The reaction mixture was stirred at 40 ºC for 40 min. The solvent was evaporated under the reduced pressure directly. The product **4aaa** was isolated by flash column chromatography with petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 3 : 1) as eluents.

5.2 Details of the EPR signals



Black line: Phenylboronic acid **1a** (0.6 mmol, 3.0 equiv.), $Mn(acac)_3$ (30 mol %) were added in HFIP (2 mL). The reaction mixture was stirred at 40 ºC for 1 min. Samples were prepared and tested at room temperature, no free radical signals were detected.

Red line: Phenylboronic acid **1a** (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol %) were added in HFIP (2 mL). The reaction mixture was stirred at 40 ºC for 1 min. Samples were prepared and tested at room temperature, no free radical signals were detected.

Blue line: Phenylboronic acid **1a** (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol %), TEMPO (0.4 mmol) were added in HFIP (2 mL). The reaction mixture was stirred at 40 ºC for 1 min. Samples were prepared and tested at room temperature, only the free radical signal of tempo was detected.

Green line: Phenylboronic acid **1a** (0.6 mmol, 3.0 equiv.), $Mn(acac)_3$ (30 mol %),Dmpo (0.4 mmol) were added in HFIP (2 mL). The reaction mixture was stirred at 40 ºC for 1 min. Samples were prepared and tested at room temperature, no free radical signals were detected.

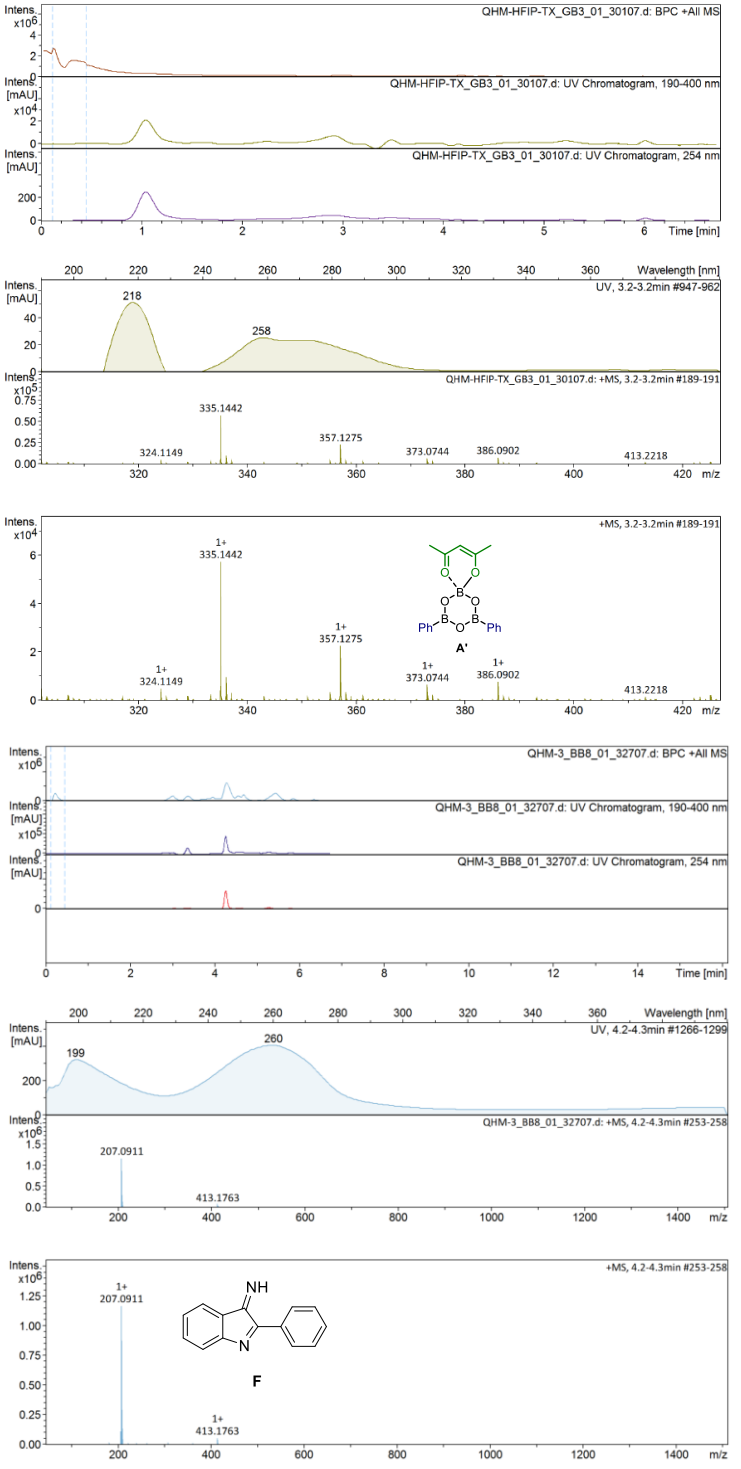
Purple line: Phenylboronic acid **1a** (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol %), Dmpo (0.4 mmol) were added in HFIP (2 mL). The reaction mixture was stirred at 40 ºC for 1 min. Samples were prepared and tested at room temperature, no free radical signals were detected.

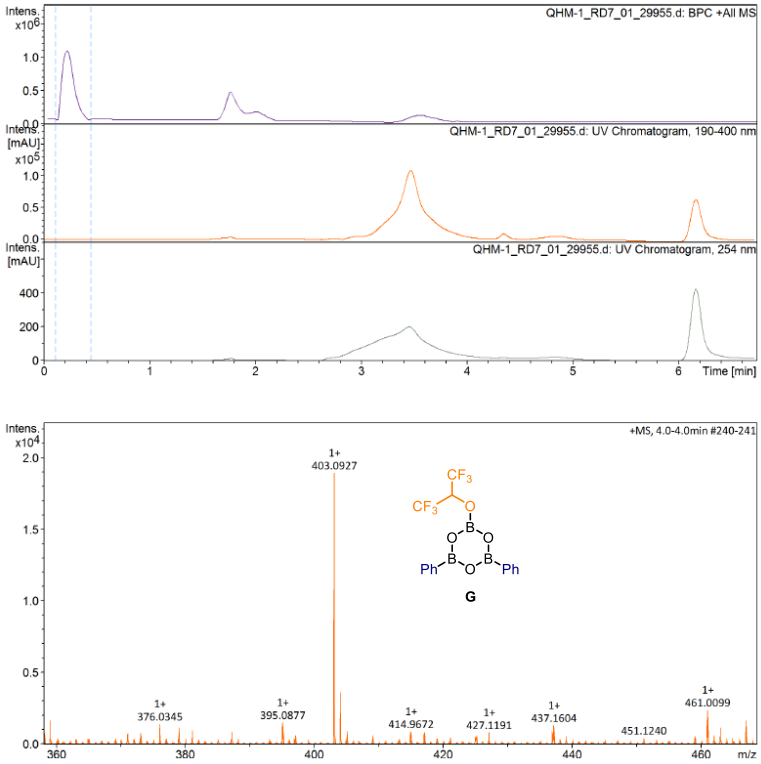
Yellow line: Phenylboronic acid **1a** (0.6 mmol, 3.0 equiv.), isocyanide **2a** (0.2 mmol, 1.0 equiv.), $Mn(acac)_3$ (30 mol %), TEMPO (0.4 mmol), Dmpo (0.4 mmol) were added in HFIP (2 mL). The reaction mixture was stirred at 40 ºC for 1 min. Samples were prepared and tested at room temperature, only the free radical signal of tempo was detected.

5.3 Crystal preparation of triphenylboroxin

To an 8 mL tube, a mixture of boronic acid (1.0 mmol, 1.0 equiv.), $Mn(acac)_3$ (1.0 mmol, 1.0 equiv.), 2 mL HFIP were added. The reaction mix ture was stirred at 40 ºC for 40 min under Ar atmosphere. After that, all volatiles were removed in vacuo. The residue was dissolved in toluene (3.50 mL), and colorless crystals were obtained after standing at about -20 ℃ for two days.

5.4 HRMS details of A', F and G

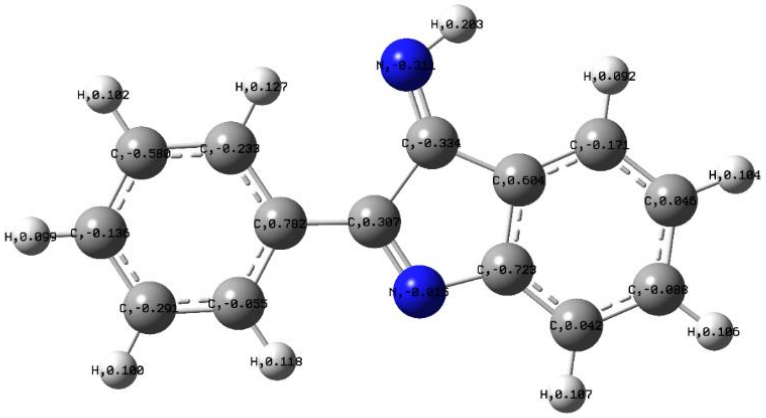




6. DFT details for mechanistic studies

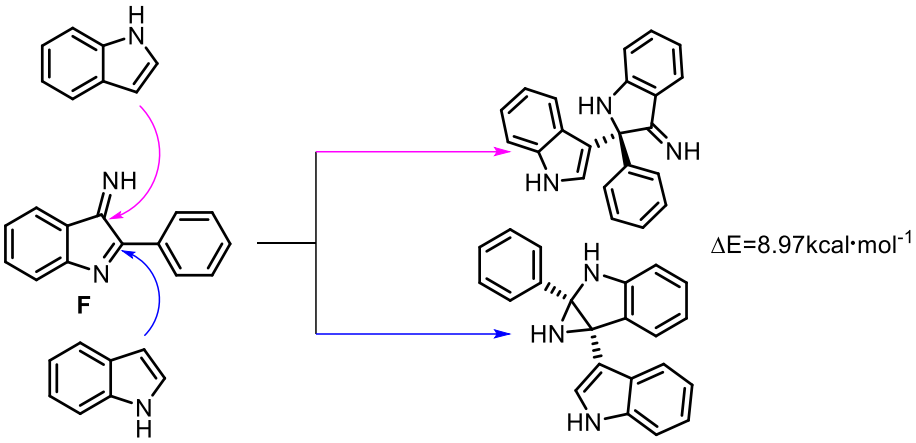
The molecular geometry optimized using the Density Functional Theory (DFT) method of B3LYP with the basis set of 6-31+g(d,p) . All calculations were performed using GAUSSIAN 2016 package[2]. All the optimized stationary points had been identified as minima (zero imaginary frequencies) and transition states (one imaginary frequency), via the vibrational analysis.

6.1 Theoretical interpretation for the regioselective addition of indole



Mulliken charge distribution in the intermediate **F**

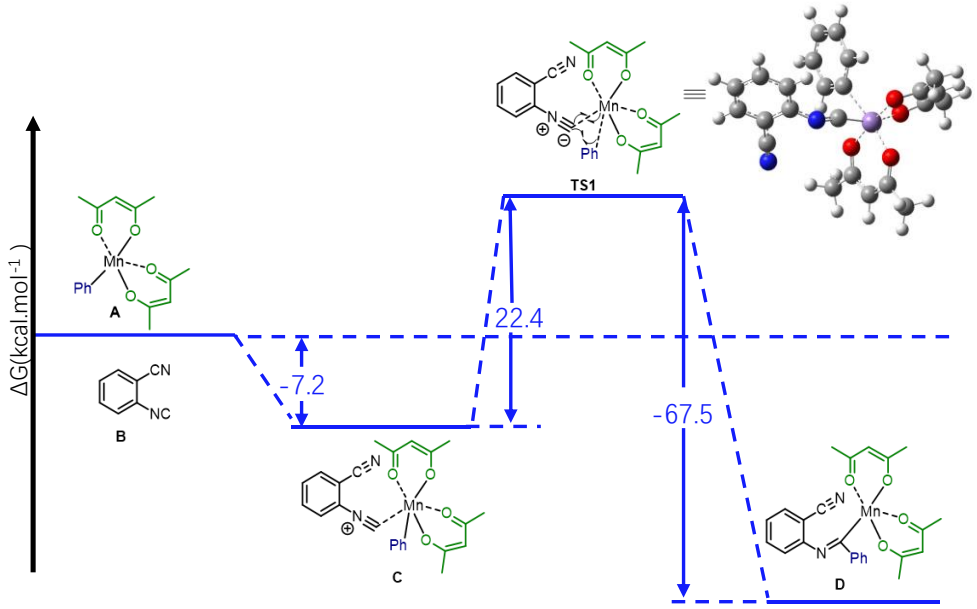
1) According to the DFT calculation on the intermediate **F**, Mulliken charge distribution at the carbon atom of two imine fragments was different. C2 is 0.307, and C3 is -0.334. It seems that C2 is more inclined to be attacked by nucleophiles. It is the first reason why addition of indole to the imine fragments is regioselective.



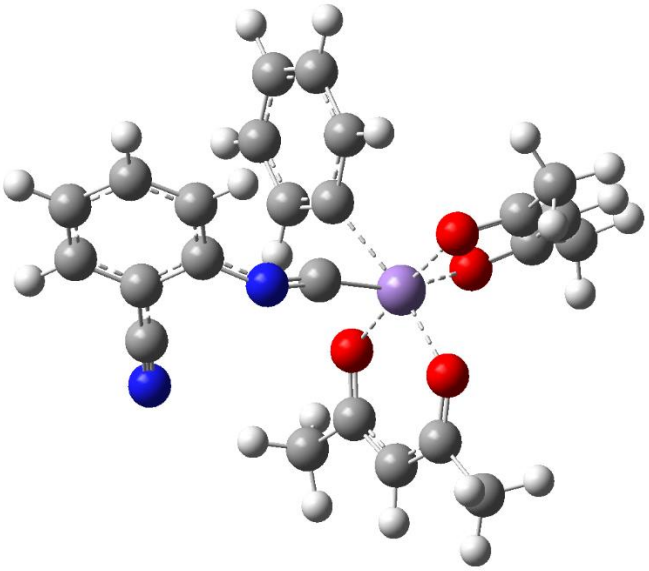
The possible pathways for addition of indole to intermediate **F**

2) Both of the two imine fragments are readily to be attacked by indole. But two pathways give different intermediates. Free energy barrier in the pathway (C2 attacked) is 8.97 kcal•mol^{-1} lower than the other (C3 attacked). It is the second reason why addition of indole to the imine fragments is regioselective.

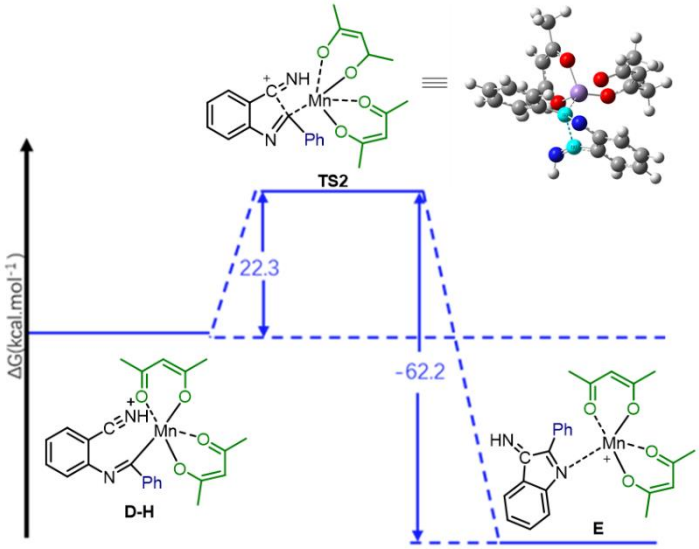
6.2



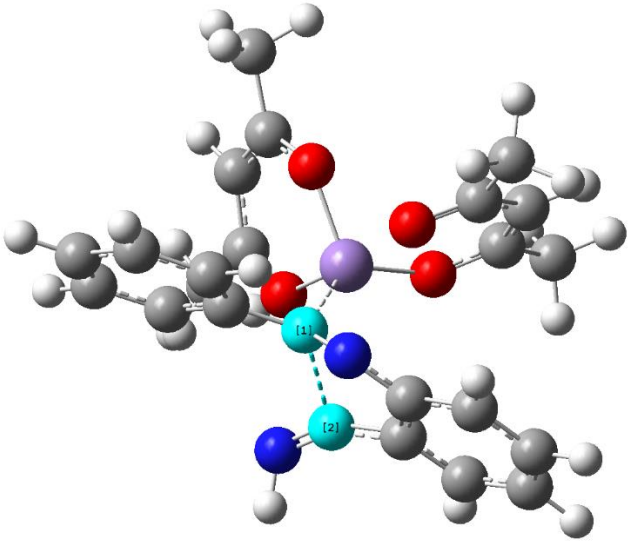
DFT computed energy surface for the process of **A** to **D**



the 3D figure for **TS1**

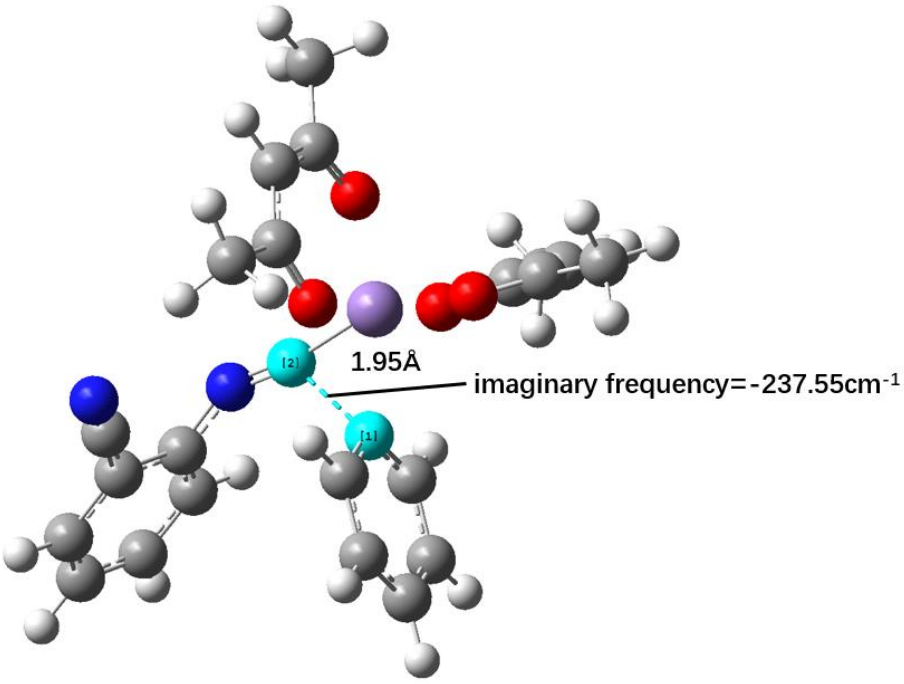


DFT computed energy surface for the process of **D-H** to **E**

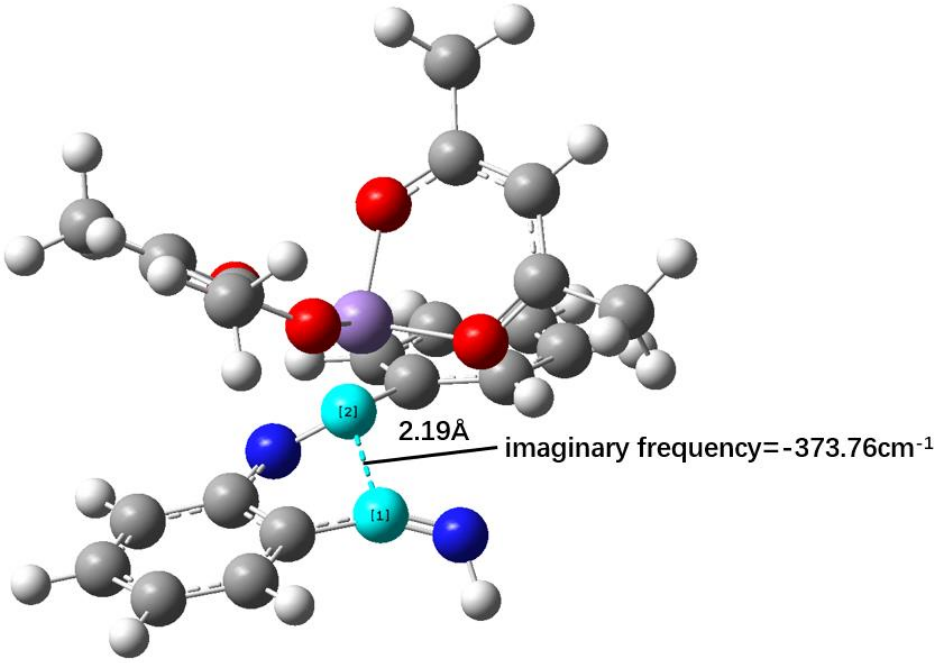


the 3D figure for **TS2**

6.3



The bond lengths and only one imaginary frequency for **TS1**



The bond lengths and only one imaginary frequency for **TS2**

6.4 The free energy for the species in the calculation

Species	Free energy (a.u.)	Species	Free energy (a.u.)
1a	-2186.409577	**2a**	-995.332388
A'	-1108.915969	**A**	-2072.799104
B	-416.652707	**C**	-2489.463315
TS1	-2489.499458	**D**	-2489.53515
D-H	-2489.83894	**TS2**	-2489.803451

E	-2489.902588	**G**	-1552.991739
4aaa	-1012.596395		

6.5 The coordination for the species.

1a				**2a**			
Mn	0.09508700	0.05058200	0.00818600	O	-0.39849800	-1.31572300	-0.00231600
O	1.49174900	-0.23701600	1.33312700	B	-1.35841500	-0.31740900	-0.00235000
O	1.44929200	0.72151800	-1.25530500	O	-0.94066600	1.00274200	-0.00743800
O	-0.15774700	1.79541600	0.79915500	B	0.40343000	1.33519000	-0.00277800
O	-1.27505100	0.40093800	-1.28689700	O	1.33795800	0.31329300	0.00149000
O	0.37778500	-1.67370900	-0.80127600	B	0.95374900	-1.01717100	-0.00107500
O	-1.21123500	-0.64766900	1.23457300	C	0.85336000	2.82215100	-0.00225700
C	2.71165400	0.72477200	-1.12611600	C	2.21983700	3.16562100	0.00097500
C	2.75736300	-0.14965300	1.18696800	C	2.62723500	4.50100200	0.00531300
C	3.48252900	1.24911500	-2.31781500	C	1.66974200	5.52162500	0.00456600
C	3.40531700	0.29336500	0.02411600	C	0.30748000	5.20262300	-0.00135500
C	3.56652200	-0.55095100	2.39979100	C	-0.09350100	3.86507200	-0.00327300
C	-1.20243100	2.51548200	0.70655200	C	2.01722900	-2.15031600	-0.00132800
C	-2.20439100	1.27699900	-1.19012000	C	1.63234300	-3.50579900	-0.00787100
C	-1.24792000	3.71974800	1.61901500	C	2.58564000	-4.52582200	-0.00659300
C	-2.25182300	2.27822700	-0.20775900	C	3.94800200	-4.20630200	-0.00036200
C	-3.26589700	1.20705600	-2.26335700	C	4.35220900	-2.86685900	0.00567500
C	-1.81174400	-1.77096000	1.12740900	C	3.39374900	-1.85109100	0.00596800
C	-0.40897500	-2.67364900	-0.71395300	C	-2.87117200	-0.67139900	0.00071900
C	-2.89434500	-2.02094600	2.15261300	C	-3.30023100	-2.01347000	0.00995900
C	-1.50302200	-2.75521100	0.17109300	C	-4.65859600	-2.33572100	0.01004800
C	-0.07418600	-3.84032000	-1.61498500	C	-5.61672300	-1.31548800	0.00327500
H	3.27376600	0.61435800	-3.18752300	C	-5.21239800	0.02392100	-0.00400100
H	3.12870200	2.25802300	-2.56103100	C	-3.85217600	0.33953500	-0.00643200
H	4.56100200	1.27478800	-2.13959300	H	2.96526100	2.37372500	0.00066500
H	4.48851900	0.34060300	0.02186700	H	3.68653500	4.74797400	0.00729600
H	3.30503600	-1.57684300	2.68579700	H	1.98459700	6.56299400	0.00615700
H	4.64353100	-0.48618100	2.22250700	H	-0.43739900	5.99525600	-0.00331700
H	3.29779500	0.09778200	3.24227900	H	-1.15285300	3.61907600	-0.00445300
H	-0.36958400	4.34882500	1.43192200	H	0.57399600	-3.75608800	-0.01314000
H	-2.15509800	4.31446800	1.48176000	H	2.27060300	-5.56690300	-0.01123200
H	-1.18860000	3.38222600	2.66061000	H	4.69275800	-4.99934200	-0.00069600
H	-3.07819600	2.98049100	-0.23177500	H	5.41099500	-2.61765200	0.01032000
H	-2.79748200	1.36261400	-3.24283700	H	3.70983800	-0.81052700	0.01127200
H	-3.70957300	0.20448900	-2.27275800	H	-2.55656600	-2.80696500	0.01645300
H	-4.05305900	1.95206200	-2.11904200	H	-4.97232600	-3.37719400	0.01716400

H	-2.44791300	-2.01568500	3.15448600	H	-6.67594600	-1.56379900	0.00522700
H	-3.62386200	-1.20327400	2.11950100	H	-5.95664100	0.81716300	-0.00799100
H	-3.40723000	-2.97334400	1.99344700	H	-3.53920800	1.38103400	-0.01475300
H	-2.08000500	-3.67374500	0.18271000				
H	-0.10934200	-3.50781000	-2.65941400				
H	0.95220100	-4.16990400	-1.41485900				
H	-0.75801600	-4.68277200	-1.48042700				
A'				**A**			
O	-0.81747700	-1.23995800	0.00047900	Mn	-0.08803000	-0.14228100	-0.00003100
B	-1.50466700	-0.06031600	0.00021300	O	0.17011300	1.05716400	-1.40180300
O	-0.80859000	1.14361500	0.00000000	O	0.16995400	1.05702600	1.40190400
B	0.57982200	1.16132800	0.00006700	O	2.18478200	-0.02448700	0.00004500
O	1.27229300	-0.01714700	0.00015700	O	0.25190200	-1.95768000	0.00000500
B	0.60043400	-1.27856000	0.00021000	C	0.62475400	2.24916600	1.24637100
C	1.33626000	2.53003000	0.00007300	C	0.62495700	2.24927000	-1.24610800
C	2.74372300	2.57880100	0.00021100	C	0.85020600	3.01460400	2.52647700
C	3.42615600	3.79763800	0.00021300	C	0.87208900	2.85092100	0.00017500
C	2.70788300	4.99881800	0.00007400	C	0.85077400	3.01475000	-2.52612100
C	1.30897300	4.97398900	-0.00006400	C	2.99511200	-0.97192300	0.00016200
C	0.63411900	3.75049000	-0.00006200	C	1.28343400	-2.75899500	0.00022600
C	-3.06786400	-0.04948000	0.00010500	C	4.48045700	-0.65944000	-0.00055800
C	-3.79700400	-1.25434700	0.00028800	C	2.60158200	-2.35356600	0.00036700
C	-5.19386100	-1.25451500	0.00019600	C	0.90573000	-4.21869100	0.00032300
C	-5.89150600	-0.04122400	-0.00008700	C	-2.02784500	-0.21440000	-0.00010400
C	-5.18710500	1.16768600	-0.00027400	C	-2.74936400	-0.29600000	1.20711600
C	-3.78984500	1.15930200	-0.00017700	C	-4.13625000	-0.48425400	1.20994600
H	3.30216200	1.64515400	0.00032000	C	-4.83234700	-0.58170900	-0.00026800
H	4.51417300	3.81459300	0.00032300	C	-4.13608800	-0.48442000	-1.21040500
H	3.23631300	5.95003300	0.00007400	C	-2.74920400	-0.29616400	-1.20741200
H	0.74814100	5.90632800	-0.00017200	H	-0.07874900	3.03631600	3.10825100
H	-0.45335700	3.73277400	-0.00016700	H	1.60120400	2.49213500	3.13167300
H	-3.25406500	-2.19697900	0.00050800	H	1.18605200	4.03819200	2.34239700
H	-5.73974100	-2.19580300	0.00034400	H	1.23136800	3.87421200	0.00024800
H	-6.97967100	-0.03805200	-0.00016000	H	1.60247700	2.49266300	-3.13078100
H	-5.72710900	2.11227500	-0.00049300	H	-0.07780800	3.03587400	-3.10850400
H	-3.24363700	2.09988000	-0.00031900	H	1.18594800	4.03853400	-2.34190500
O	1.06567600	-2.05953100	-1.23373600	H	4.63359600	0.42227900	0.00530200
O	1.06613300	-2.05970100	1.23383000	H	4.96405000	-1.10367000	0.87876600
C	2.05360000	-2.88745500	-1.20433200	H	4.96002900	-1.09293500	-0.88748800

C	2.05396500	-2.88773300	1.20392000
C	2.50684300	-3.39243100	-2.53995700
C	2.63184800	-3.30406900	-0.00033900
C	2.50726800	-3.39341100	2.53926100
H	1.65335000	-3.83002800	-3.07101000
H	2.86208300	-2.54690500	-3.14178700
H	3.30310700	-4.13470500	-2.44858500
H	3.45590900	-4.00595900	-0.00053900
H	2.85966500	-2.54792900	3.14277000
H	1.65433600	-3.83406700	3.06874100
H	3.30539900	-4.13363500	2.44755700

H	3.37659400	-3.11349600	0.00060900
H	0.29009300	-4.43553100	0.88175200
H	0.29083300	-4.43582400	-0.88155500
H	1.78361300	-4.87029900	0.00078200
H	-2.22500300	-0.20690200	2.15820600
H	-4.67490400	-0.54781700	2.15402900
H	-5.91129700	-0.72249400	-0.00033000
H	-4.67461600	-0.54811400	-2.15455100
H	-2.22472100	-0.20719300	-2.15844700

B

C	-2.24525500	-0.84061600	0.00000000
C	-2.33827400	0.55545800	0.00000100
C	-1.18519300	1.33944700	0.00000000
C	0.07455600	0.72760300	-0.00000100
C	0.17840000	-0.68228100	-0.00000100
C	-0.99480300	-1.45568900	0.00000000
C	1.45817700	-1.32592900	-0.00000100
N	2.48267800	-1.87528400	0.00000100
N	1.21295400	1.50995500	0.00000000
C	2.17531300	2.19590400	0.00000000
H	-3.14514700	-1.44917000	0.00000100
H	-3.31210000	1.03765400	0.00000100
H	-1.24113700	2.42351900	0.00000000
H	-0.90856200	-2.53808200	-0.00000100

C

Mn	-0.98292600	-0.05639500	-0.04715000
O	-2.92456500	-0.07189600	0.03831700
O	-1.05231200	0.34510400	-1.93325100
O	-0.80992200	-1.98203100	-0.37499800
O	-1.07067400	-0.54973700	1.90468600
C	-2.08371200	0.37509500	-2.69571800
C	-3.76442000	0.02408500	-0.91391100
C	-1.78453400	0.62282400	-4.15655400
C	-3.40825100	0.21620400	-2.26430200
C	-5.22001600	-0.06899100	-0.51625000
C	-1.01152800	-2.99787800	0.37751700
C	-1.26122600	-1.68171800	2.44133200
C	-0.90640300	-4.33767700	-0.31125000
C	-1.27273000	-2.91260800	1.74905300
C	-1.45496200	-1.66754900	3.94382000
C	-0.64671100	1.81567400	0.65453100
C	-0.95789800	2.24849800	1.95538300
C	-0.91096300	3.60431200	2.29854200
C	-0.53797000	4.56476000	1.35160700
C	-0.20761900	4.15358500	0.05724700
C	-0.24566400	2.79433300	-0.28022900
H	-1.25912000	1.57961800	-4.26378300
H	-1.11111300	-0.16011200	-4.52561200
H	-2.68950900	0.63964000	-4.76992600
H	-4.20013100	0.27821800	-3.00297400
H	-5.38880900	-1.00723600	0.02522500

				H	-5.45742100	0.75023700	0.17333400
				H	-5.89252300	-0.02010200	-1.37713000
				H	0.13127700	-4.49113200	-0.63349800
				H	-1.20323400	-5.16145200	0.34407400
				H	-1.53283400	-4.33893600	-1.21053500
				H	-1.40936800	-3.82834000	2.31335600
				H	-0.59319200	-1.18246400	4.41743700
				H	-2.34078200	-1.06791800	4.18657400
				H	-1.57693700	-2.67194100	4.35860300
				H	-1.24448000	1.51553700	2.70234200
				H	-1.16840600	3.91127600	3.31122300
				H	-0.50194600	5.61851200	1.62066000
				H	0.08331200	4.88767900	-0.69293800
				H	0.01471500	2.49835700	-1.29410500
				C	6.22662200	0.55114900	-0.27249700
				C	5.37697300	1.65361300	-0.11964000
				C	3.99397200	1.48432700	-0.09632900
				C	3.44551100	0.19977300	-0.23007000
				C	4.29766700	-0.91995200	-0.38440800
				C	5.68948500	-0.72792800	-0.40300400
				C	3.75320500	-2.23833200	-0.51621500
				N	3.33529200	-3.31817000	-0.62400700
				N	2.08399900	0.03510600	-0.21029400
				C	0.90488900	0.01671000	-0.15917500
				H	7.30420000	0.68801600	-0.28877000
				H	5.79325700	2.65213800	-0.01524900
				H	3.32219500	2.32856600	0.02607700
				H	6.33645600	-1.59219900	-0.52044700
TS1				**D**			
Mn	1.10411700	0.07364800	-0.09983900	Mn	0.25150900	0.75950100	0.82543600
O	2.65637300	-0.40487200	1.06362700	O	0.27971900	2.48877500	-0.02753500
O	1.60905800	-1.35434200	-1.36437800	O	-1.61909700	0.94976200	1.11482000
O	2.05985900	1.29860400	-1.28187600	O	2.10632900	0.93339700	1.17360500
O	0.73521400	1.55127900	1.13015100	O	0.21485600	-0.83767000	1.87396400
C	2.73922100	-1.95008700	-1.41863700	C	-2.38756700	1.96281600	0.91484700
C	3.64174600	-1.14670300	0.75354200	C	-0.66268400	3.33828600	-0.18589700
C	2.93950000	-2.81318800	-2.64512800	C	-3.78407800	1.82291600	1.46479300
C	3.75141000	-1.87902300	-0.44738800	C	-1.98369200	3.13237600	0.25699200

C	4.74615300	-1.22783900	1.78438000	C	-0.27121500	4.62425900	-0.87352700
C	2.23996900	2.56059000	-1.14308600	C	2.90963600	0.13734800	1.79656000
C	1.05171200	2.77954700	1.01967900	C	1.16589600	-1.48045900	2.43637400
C	3.01233700	3.21824600	-2.26344700	C	4.34461500	0.59645000	1.84356600
C	1.78008100	3.32190700	-0.06076900	C	2.51162100	-1.05665400	2.40184600
C	0.57088700	3.67468100	2.13625500	C	0.76878700	-2.73629900	3.16668800
C	-0.37166100	-1.16010900	0.78938500	H	-4.24702200	0.91768100	1.05679500
C	-0.89106700	-0.76935600	2.03923600	H	-3.72972100	1.69802200	2.55347300
C	-1.50306900	-1.70632200	2.87639400	H	-4.40793000	2.69076900	1.23424100
C	-1.62627600	-3.03994200	2.47170500	H	-2.70973300	3.92474100	0.11299400
C	-1.13820100	-3.43398400	1.22075700	H	0.07443700	4.40306300	-1.89095500
C	-0.52321800	-2.50032400	0.38259100	H	-1.10043100	5.33477600	-0.92533800
H	2.14619400	-3.56911900	-2.69347100	H	0.56862700	5.08317500	-0.33864800
H	2.84483500	-2.18775600	-3.54097000	H	4.39260300	1.60387700	2.27402800
H	3.91237600	-3.31186500	-2.65196300	H	4.97518200	-0.07903100	2.42756900
H	4.65217800	-2.46073600	-0.60958500	H	4.73368800	0.66104000	0.82000100
H	5.11626600	-0.21778800	1.99667500	H	3.25905600	-1.66070700	2.90350300
H	4.33241000	-1.62251000	2.72034900	H	-0.07021500	-2.51823700	3.83741800
H	5.57765600	-1.86030900	1.46171800	H	0.41808000	-3.47595800	2.43595700
H	2.48238000	3.05611000	-3.20987400	H	1.59878500	-3.15653200	3.74104400
H	3.14714400	4.29122700	-2.10290100	C	-4.74060700	-1.53095000	-0.97528500
H	3.99405500	2.73836400	-2.35645900	C	-4.28129700	-0.37495800	-1.62447300
H	1.98783100	4.38594100	-0.05404100	C	-2.91948400	-0.12189400	-1.75409300
H	-0.52394900	3.73873000	2.08920600	C	-1.96400400	-1.01751300	-1.23052100
H	0.83645800	3.22906700	3.10154500	C	-2.43331800	-2.19844900	-0.59511500
H	0.99156500	4.68161400	2.06892400	C	-3.81449600	-2.43638300	-0.46697400
H	-0.79453000	0.26420100	2.35777400	C	-1.50628300	-3.17689400	-0.11552000
H	-1.88379400	-1.39355100	3.84662200	N	-0.77633200	-4.00250600	0.26010200
H	-2.10414600	-3.76687000	3.12490300	N	-0.62398400	-0.83978500	-1.49016300
H	-1.23516100	-4.46901000	0.89869800	H	-5.80494400	-1.72750700	-0.88178800
H	-0.14403800	-2.80856800	-0.58780300	H	-4.99521500	0.33374600	-2.03882800
C	-5.89302400	-0.38782800	-1.03020700	H	-2.56589200	0.76596600	-2.27016900
C	-5.03944600	-1.21790700	-1.76829000	H	-4.14350700	-3.34609800	0.02787800
C	-3.66536900	-0.98937200	-1.78672800	C	1.68213300	-0.35915000	-1.58218100
C	-3.11630100	0.07530100	-1.05300300	C	2.10976100	-1.61363300	-2.05185800
C	-3.97784600	0.92332700	-0.31203400	C	2.50208100	0.76342000	-1.77914900
C	-5.36216800	0.67709400	-0.30699500	C	3.33656300	-1.74172700	-2.70596100
C	-3.44552800	2.02500400	0.43220900	H	1.47423500	-2.48105400	-1.89655300
N	-3.03252500	2.92590000	1.04165400	C	3.71535900	0.63539800	-2.45980300
N	-1.76469400	0.32540900	-1.09514200	H	2.18132800	1.73008300	-1.40488100

C	-0.65716300	0.11109400	-0.65729200	C	4.13972000	-0.61623200	-2.91886700
H	-6.96408100	-0.56872500	-1.02168100	H	3.66119400	-2.71926300	-3.05539600
H	-5.44782300	-2.05075700	-2.33536200	H	4.33267300	1.51531500	-2.62811900
H	-2.99813400	-1.62451400	-2.36116900	H	5.09060200	-0.71398700	-3.43808700
H	-6.00817300	1.33226800	0.27030400	C	0.34157900	-0.24365600	-0.92251700
D-H				**TS2**			
Mn	0.48165300	0.73020400	0.28976500	Mn	-0.16072700	0.62868400	-0.07861700
O	1.01013400	1.18604600	-1.64220400	O	0.83163400	0.36733600	1.69964300
O	-0.87383800	1.96792500	0.12785200	O	1.14206900	1.80899300	-0.54727500
O	2.21731900	1.30584700	0.60977800	O	-1.39101000	1.39860100	1.06303500
O	0.14290000	0.22795600	2.07756200	O	-1.16985500	0.97905700	-1.64329600
C	-1.17441100	2.84578400	-0.80033900	C	2.06653600	2.43862900	0.15377300
C	0.56056600	2.09661000	-2.38449700	C	1.71689700	1.10400700	2.19615500
C	-2.30724700	3.76000400	-0.42158900	C	2.78934900	3.49845000	-0.62877100
C	-0.52205000	2.95353600	-2.01164000	C	2.35378100	2.16603700	1.47045800
C	1.22669800	2.29570800	-3.72407500	C	2.13277500	0.84619800	3.62224600
C	2.74614300	1.47156500	1.78714900	C	-2.43130700	2.09475600	0.70765900
C	0.88140100	0.48634100	3.09484300	C	-2.18788700	1.75077500	-1.73257700
C	4.11832500	2.08949300	1.76309100	C	-3.21188900	2.65723900	1.86415600
C	2.14138300	1.11037300	2.99474100	C	-2.82956700	2.31817800	-0.61163600
C	0.33001400	0.07079700	4.43282900	C	-2.69819200	2.00756000	-3.12544700
H	-3.18789500	3.16563900	-0.15104100	H	3.25767100	3.04964900	-1.51301900
H	-2.02503500	4.33723600	0.46756100	H	2.06929000	4.24280300	-0.98967000
H	-2.56481500	4.44884700	-1.22959400	H	3.55396900	3.99657500	-0.02829300
H	-0.83974200	3.72179000	-2.70831800	H	3.12304400	2.74639800	1.96853200
H	1.78089300	1.39770900	-4.00680500	H	1.68260100	-0.07940700	3.98650500
H	0.50089100	2.55495800	-4.50177500	H	3.22404700	0.79947700	3.71309300
H	1.93680300	3.13042800	-3.64641300	H	1.79280100	1.67927900	4.25204900
H	4.06863000	3.06554200	1.26580600	H	-2.55605800	3.28714700	2.47666700
H	4.53248000	2.21464100	2.76593700	H	-4.07248300	3.24259700	1.53320200
H	4.79252600	1.46049100	1.16949600	H	-3.55603400	1.83418000	2.50176200
H	2.69352700	1.29097500	3.91008800	H	-3.70537800	2.93421900	-0.78078400
H	-0.60371800	0.61389700	4.62384000	H	-3.59843400	2.62598600	-3.12955000
H	0.08563900	-0.99749900	4.41279600	H	-1.91567000	2.50737100	-3.70923300
H	1.03008300	0.26672400	5.24800300	H	-2.90962700	1.05321000	-3.62169400
C	-5.07120700	-0.50137700	-0.40025400	C	4.45844000	-1.36323600	-1.35378700
C	-4.23257600	-0.05733500	-1.46861300	C	4.47706000	-1.89861200	-0.04186400
C	-2.88619500	-0.32876100	-1.50676700	C	3.30582600	-2.20842900	0.63316200
C	-2.25730400	-1.07392700	-0.45837000	C	2.07407700	-1.95639700	-0.00292500

C	-3.12261100	-1.52995900	0.62556000	C	2.06311300	-1.47927400	-1.34487300
C	-4.53188300	-1.22302300	0.62681200	C	3.25967600	-1.13869500	-2.01257100
C	-2.60030000	-2.28132600	1.63319300	C	0.76057100	-1.39125400	-1.89589000
N	-2.13846500	-2.84691600	2.57673300	N	-0.02931800	-1.50163300	-2.81341000
N	-0.98699800	-1.42492200	-0.50774300	N	0.85294100	-2.16727200	0.56566700
H	-6.13121100	-0.26833500	-0.41039800	H	5.39723100	-1.16267000	-1.86250900
H	-4.67567100	0.51706700	-2.27895800	H	5.43471600	-2.07004000	0.44294500
H	-2.26615900	0.01227000	-2.32967000	H	3.31325500	-2.61165200	1.64120400
H	-5.14372600	-1.57735700	1.45120800	H	3.23816900	-0.76178600	-3.03112100
C	1.30123400	-1.96909100	-0.95128100	C	-1.53375700	-1.95230300	0.33691700
C	1.00505600	-3.31642700	-1.25046800	C	-1.81607000	-2.67384700	1.51775700
C	2.62388800	-1.50947900	-1.09190400	C	-2.57408800	-1.68542400	-0.57368900
C	2.00821300	-4.18062800	-1.67693900	C	-3.11122100	-3.11374000	1.77453300
H	-0.01645800	-3.67227200	-1.14424700	H	-1.01346800	-2.87285600	2.22090200
C	3.62610200	-2.38033700	-1.52338000	C	-3.86485600	-2.15135200	-0.31767000
H	2.85397900	-0.46964700	-0.88621200	H	-2.35944900	-1.15265600	-1.49295200
C	3.32292400	-3.71332700	-1.81367100	C	-4.13877100	-2.85784800	0.85678200
H	1.77189400	-5.21685200	-1.90497300	H	-3.32132900	-3.66380400	2.68822500
H	4.64401200	-2.01682100	-1.63731900	H	-4.65716100	-1.96387000	-1.03782300
H	4.10619500	-4.38929200	-2.14768500	H	-5.14706400	-3.21108500	1.05729600
C	0.23859300	-1.04879800	-0.50659000	C	-0.14960200	-1.49493400	0.09176600
H	-2.02684800	-3.84305900	2.75066800	H	0.21009500	-2.01463000	-3.66496600

E-H				**G**			
Mn	0.87863500	-0.43691400	0.29020600	O	-0.80549900	-1.40707400	-0.00019900
O	1.02128900	-0.42560000	-1.75698800	B	-2.06706700	-0.82561400	0.00006400
O	2.69094900	-0.40705600	0.32392200	O	-2.14782000	0.55890500	0.00017200
O	0.25726800	-2.15233700	0.02757400	B	-1.02897800	1.36843100	-0.00005000
O	0.56912200	-0.41505400	2.13030700	O	0.22386400	0.75360300	-0.00020600
C	3.62203800	-0.64086000	-0.58842800	B	0.31221100	-0.61930300	-0.00020100
C	2.03854500	-0.61400600	-2.47085900	O	1.53264500	-1.24941400	-0.00002500
C	5.00617100	-0.73487100	-0.01580700	C	2.73371900	-0.53036000	-0.00016200
C	3.35782100	-0.76856700	-1.92954600	C	-1.15060100	2.91300200	-0.00024200
C	1.85733900	-0.66432300	-3.96533400	C	-0.00665200	3.73595700	-0.00005900
C	-0.01984900	-2.99869700	0.97765600	C	-0.12016600	5.12716800	-0.00004000
C	0.24339600	-1.41717900	2.86830500	C	-1.38665200	5.72229100	-0.00014000
C	-0.36528200	-4.37696100	0.48568700	C	-2.53592900	4.92398600	-0.00036500
C	-0.02784600	-2.69503300	2.34247800	C	-2.41619900	3.53327900	-0.00042700
C	0.14948200	-1.14087800	4.34221100	C	-3.34059100	-1.70643300	0.00013100

H	5.25113900	0.19332000	0.51460800
H	5.04366900	-1.54550700	0.72208100
H	5.75308500	-0.91621800	-0.79182900
H	4.18224300	-0.94443200	-2.61185400
H	0.82004900	-0.45473400	-4.23324900
H	2.52073900	0.05764700	-4.45630600
H	2.13604600	-1.65957600	-4.33558300
H	0.45156000	-4.75895900	-0.13757700
H	-0.55144700	-5.07124300	1.30772900
H	-1.25819000	-4.31879000	-0.14837100
H	-0.29152300	-3.48594300	3.03521400
H	1.11508700	-0.76776200	4.70375600
H	-0.58797900	-0.34857700	4.51786500
H	-0.13233000	-2.02920200	4.91130000
C	0.64466500	5.07490300	0.56643400
C	1.67881400	4.13429000	0.61217000
C	1.43458700	2.76565500	0.40699000
C	0.12293400	2.38203900	0.15926500
C	-0.92065500	3.31666400	0.11251600
C	-0.67431200	4.67037000	0.31383400
C	-2.14652800	2.55123500	-0.17401500
N	-3.36107700	2.88922400	-0.36477000
N	-0.38300900	1.05133300	-0.06807200
H	0.86520100	6.12624400	0.72722800
H	2.69484000	4.46567300	0.80898900
H	2.25076200	2.05040500	0.44735900
H	-1.47822700	5.40228000	0.27889500
C	-2.56987900	-0.01239400	-0.57404000
C	-2.17884500	-1.01732700	-1.48296800
C	-3.86082400	-0.05919800	-0.00366400
C	-3.06426300	-2.04219600	-1.81208300
H	-1.19993000	-0.96876600	-1.94614800
C	-4.72632200	-1.10490800	-0.31780400
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C	-4.33464800	-2.09328200	-1.22735200
H	-2.76691400	-2.79634900	-2.53649800
H	-5.71288300	-1.14029400	0.13627100
H	-5.02150200	-2.89498800	-1.48730100
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C	-4.38794300	-3.91149700	0.00016500
C	-5.65398600	-3.31526700	0.00006400
C	-5.77253300	-1.92079500	0.00004500
C	-4.62485800	-1.12620900	0.00005500
F	4.64602000	-0.15443800	1.37861600
C	3.50256600	-0.86267300	1.29678300
F	3.80760800	-2.16261300	1.41165800
F	2.73769600	-0.52428200	2.35732300
F	3.80730700	-2.16387500	-1.41075700
C	3.50282000	-0.86368400	-1.29668300
F	4.64675900	-0.15606200	-1.37834800
F	2.73868200	-0.52546500	-2.35762800
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H	0.97965500	3.27787800	0.00016400
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4aaa

C	0.08077900	4.48001700	-0.89056300
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C	0.34241900	2.09658600	-0.78406200
C	0.40739400	2.17471300	0.62030800
C	0.33019000	3.40944100	1.27132800
N	0.49332000	0.79175300	-1.22755300
C	0.59343300	-0.15144200	-0.08030900
C	0.48016200	0.80571300	1.15306700
N	0.44463100	0.36367000	2.35044300
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C	-0.41357200	-2.51489400	-0.35670500
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C	-4.02553700	-2.24800100	-0.19338500
C	-4.76347500	-1.08457500	0.00614300
C	-4.12275400	0.16200700	0.17335100
C	-2.73559800	0.27025100	0.14594200
C	0.17170200	4.56889500	0.51081900
C	1.97592100	-0.84439400	-0.06941500
C	2.35968500	-1.63534100	1.02723800
C	3.59615000	-2.28424200	1.03681100
C	4.47360000	-2.15498600	-0.04594900
C	4.10224100	-1.36504600	-1.13514100
C	2.86264400	-0.71383700	-1.14551900
H	-0.05244600	5.38878800	-1.47351800
H	0.10504000	3.20220600	-2.63929200
H	0.38272900	3.46540300	2.35734600
H	-0.06509200	0.48389900	-2.01306200
H	0.39253800	1.13422300	3.02222400
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H	-2.26427800	1.23922500	0.28353500
H	0.11299200	5.53887600	0.99687600

H	1.69292500	-1.72141100	1.87957800	
H	3.87651500	-2.88872300	1.89682200	
H	5.43694600	-2.65995700	-0.03562100	
H	4.77626700	-1.24751200	-1.98096200	
H	2.58488600	-0.09088000	-1.98961200	

7. References

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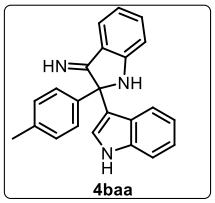
[2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian*16, Gaussian, Inc., Wallingford, CT, **2016**.

8. Analytical and spectral data of substrates

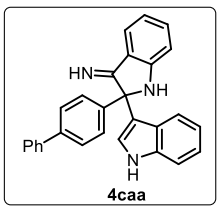
2-(12-(1H-indol-3-yl)-2-(p-tolyl)indolin-3-imine (4baa)



4baa

97% yield (66 mg). Yellow solid, mp: 135.7 – 136.4 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.22 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.15 – 7.10 (m, 3H), 7.07 (d, *J* = 2.2 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.02 (s, 1H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 182.0, 155. 9, 138.7, 137.5, 137.4, 134.6, 129.4, 126.8, 125.5, 124.3, 124.1, 122.5, 121.5, 120.0, 119.9, 119.6, 117.3, 112.2, 111.7, 71.5, 21.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3^+$, m/z: 338.1652, found: 338.1646. **IR (thin film)**: ν_{max} 3418, 1615, 1471, 1313, 1148, 1109, 744cm^{-1}.

2-([1,1'-biphenyl]-4-yl)-2-(1H-indol-3-yl)indolin-3-imine (4caa)

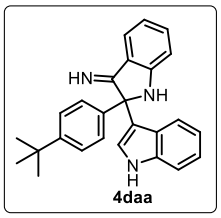


4caa

60% yield (48 mg). Yellow solid, mp: 133.9 – 134.7 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.43 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.52 (m, 6H), 7.44 – 7.28 (m, 5H), 7.20 – 7.15 (m, 2H), 7.08 (d, *J* = 2.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.07 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.6, 155.7, 141.0, 140.7, 140.5, 137.4,

134.5, 128.8, 127.4, 127.4, 127.3, 127.1, 125.4, 124.3, 123.8, 122.6, 121.8, 120.1, 120.1, 119.7, 117.4, 112.2, 111.7, 71.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{22}N_3^+$, m/z: 400.1808, found: 400.1812. **IR (thin film)**: ν_{max} 3391, 1614, 1471, 1312, 1148, 1007, 744cm^{-1}.

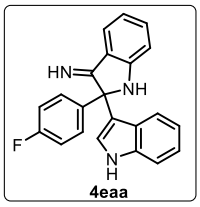
2-(4-(tert-butyl)phenyl)-2-(1H-indol-3-yl)indolin-3-imine (4daa)



4daa

76% yield (58 mg). Yellow solid, mp: 134.4 – 135.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.66 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.32 (m, 6H), 7.19 (t, *J* = 8.1 Hz, 2H), 7.04 – 6.98 (m, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.09 (s, 1H), 1.32 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 182.0, 155.8, 150.6, 138.7, 137.4, 134.5, 126.5, 125.6, 125.5, 124.4, 123.9, 122.5, 121.7, 120.1, 119.9, 119.6, 117.4, 112.1, 111.7, 71.5, 34.5, 31.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{26}N_3^+$, m/z: 380.2121, found: 380.2123. **IR (thin film)**: ν_{max} 3407, 2960, 1614, 1470, 1312, 1246, 1149, 744cm^{-1}.

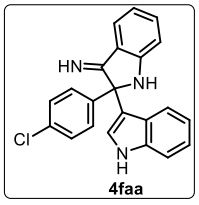
2-(4-fluorophenyl)-2-(1H-indol-3-yl)indolin-3-imine (4eaa)



4eaa

77% yield (53 mg). Yellow solid, mp: 113.6 – 115.1 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.51 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.35 (m, 4H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.11 – 7.04 (m, 2H), 7.03 – 6.95 (m, 3H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.06 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 178.1, 162.6 (d, $J_{(C-F)}$ = 247.4 Hz), 155.9, 137.5, 134.9, 129.8, 128.9 (d, $J_{(C-F)}$ = 8.2 Hz), 126.6, 125.3, 124.3, 124.1, 122.8, 120.0 (d, $J_{(C-F)}$ = 11.5 Hz), 119.9, 117.1, 115.6 (d, $J_{(C-F)}$ = 21.5 Hz), 112.5, 112.0, 71.1, one C missing. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -108.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}FN_3^+$, m/z: 342.1401, found: 342.1410. **IR (thin film)**: ν_{max} 3406, 1614, 1504, 1470, 1312, 1224, 1155, 1013, 745cm^{-1}.

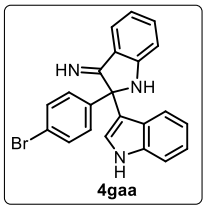
2-(4-chlorophenyl)-2-(1H-indol-3-yl)indolin-3-imine (4faa)



4faa

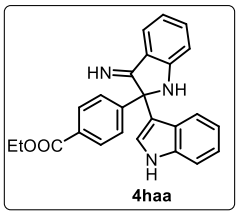
79% yield (57 mg). Yellow solid, mp: 194.9 – 195.7 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.42 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.34 (m, 4H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.12 – 7.04 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.01 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.9, 155.6, 140.6, 137.4, 134.6, 133.7, 128.7, 128.5, 125.2, 124.2, 123.8, 122.7, 121.4, 120.1, 120.0, 119.8, 117.0, 112.4, 111.8, 70.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}ClN_3^+$, m/z: 358.1106, found: 358.1119. **IR (thin film)**: ν_{max} 3384, 2922, 1613, 1469, 1313, 1246, 1092, 1013, 743cm^{-1}.

2-(4-bromophenyl)-2-(1H-indol-3-yl)indolin-3-imine (4gaa)



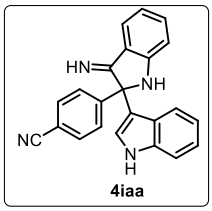
76% yield (61 mg). Yellow solid, mp: 202.8 – 203.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.43 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.33 (m, 6H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.04 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 5.01 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.2, 167.4, 155.6, 137.4, 134.6, 131.7, 128.8, 125.2, 124.2, 123.8, 122.7, 122.0, 120.2, 119.9, 119.8, 117.0, 112.4, 111.8, 102.9, 71.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0586. **IR (thin film)**: ν_{max} 3381, 2924, 1614, 1471, 1313, 1149, 1010, 745cm^{-1}.

ethyl 4-(3-imino-2-(1H-indol-3-yl)indolin-2-yl)benzoate (4haa)



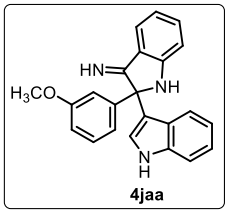
46% yield (37 mg). Yellow solid, mp: 115.6 – 116.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.77 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.15 (t, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.3 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 1H), 5.09 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 214.8, 181.2, 166.5, 155.7, 147.0, 137.4, 134.7, 129.9, 127.0, 125.2, 124.3, 123.8, 122.7, 121.4, 120.1, 119.9, 119.7, 116.8, 112.4, 111.9, 71.3, 61.0, 14.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{22}N_3O_2^+$, m/z: 396.1707, found: 396.1723. **IR (thin film)**: ν_{max} 3368, 1703, 1608, 1471, 1277, 1106, 1020, 744cm^{-1}.

4-(3-imino-2-(1H-indol-3-yl)indolin-2-yl)benzonitrile (4iaa)



43% yield (30 mg). Yellow solid, mp: 165.4 – 165.9 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.56 (s, 1H), 7.68 – 7.61 (m, 3H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.23 – 7.16 (m, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.00 (d, *J* = 3.9 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.05 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 180.8, 155.5, 147.7, 137.4, 134.8, 132.4, 127.9, 124.9, 124.3, 123.6, 122.9, 121.2, 120.3, 120.2, 119.4, 118.9, 116.4, 112.7, 112.0, 111.5, 70.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{17}N_4^+$, m/z: 349.1448, found: 349.1463. **IR (thin film)**: ν_{max} 3391, 2228, 1612, 1470, 1312, 1245, 1147, 745cm^{-1}.

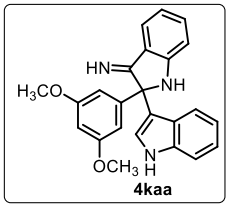
2-(1H-indol-3-yl)-2-(3-methoxyphenyl)indolin-3-imine (4jaa)



88% yield (63 mg). Yellow solid, mp: 120.6 – 121.3 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.07 (s, 1H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.11 (s, 1H), 7.03 – 6.97 (m, 2H), 6.91 – 6.86 (m, 3H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.39 (s, 1H), 3.72 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 182.1, 160.0, 158.9, 156.8, 142.7, 137.4, 135.7, 130.0, 128.6, 125.3, 124.5, 122.5, 120.0, 119.9, 119.8, 119.4, 116.1, 113.2, 112.9, 112.3, 112.0, 72.0, 55.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3O^+$, m/z: 354.1601, found:

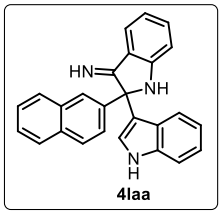
354.1612. **IR (thin film)**: ν_{max} 3380, 1609, 1471, 1312, 1246, 1039, 745cm^{-1}.

2-(3,5-dimethoxyphenyl)-2-(1H-indol-3-yl)indolin-3-imine (4kaa)



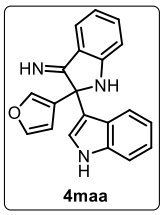
90% yield (69 mg). Yellow solid, mp: 124.4 – 125.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.83 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.22 – 7.13 (m, 2H), 7.04 – 6.97 (m, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 2.2 Hz, 2H), 6.43 (t, *J* = 2.2 Hz, 1H), 5.08 (s, 1H), 3.71 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.3, 161.0, 155.8, 144.3, 137.4, 134.5, 133.7, 125.4, 124.3, 124.0, 122.5, 121.6, 119.9, 119.9, 119.7, 117.0, 112.3, 111.8, 105.4, 99.3, 71.7, 55.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{22}N_3O_2^+$, m/z: 384.1707, found: 384.1722. **IR (thin film)**: ν_{max} 3409, 1605, 1470, 1312, 1203, 1152, 1045, 744cm^{-1}.

2-(1H-indol-3-yl)-2-(naphthalen-2-yl)indolin-3-imine (4laa)



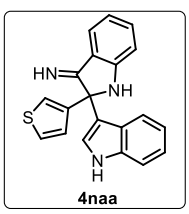
91% yield (68 mg). Yellow solid, mp: 143.7 – 144.5 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.53 (s, 1H), 7.93 (s, 1H), 7.84 – 7.75 (m, 3H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 9.7 Hz, 1H), 7.52 – 7.33 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.07 (m, 2H), 7.00 – 6.79 (m, 3H), 5.17 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.7, 156.0, 139.2, 137.5, 134.8, 133.4, 133.1, 128.7, 128.5, 127.7, 126.3, 126.2, 126.0, 125.6, 125.2, 124.5, 124.1, 122.7, 120.2, 120.1, 119.9, 117.3, 112.4, 111.9, 71.9 one C missing. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{20}N_3^+$, m/z: 374.1652, found: 374.1660. **IR (thin film)**: ν_{max} 3405, 2923, 1613, 1469, 1311, 1148, 1048, 742cm^{-1}.

2-(furan-3-yl)-2-(1H-indol-3-yl)indolin-3-imine (4maa)



91% yield (57 mg). Yellow solid, mp: 146.3 – 147.4 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.89 (s, 1H), 8.05 (s, 1H), 7.63 (s, 1H), 7.49 – 7.43 (m, 1H), 7.39 (s, 1H), 7.35 – 7.27 (m, 1H), 7.21 (s, 1H), 7.17 – 7.10 (m, 1H), 7.03 – 6.96 (m, 1H), 6.93 – 6.84 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.55 (s, 1H), 6.37 (s, 1H), 5.41 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 182.6, 157.2, 151.1, 144.3, 142.6, 141.0, 137.3, 137.1, 126.6, 125.0, 124.8, 122.9, 120.3, 120.2, 119.6, 113.5, 112.4, 112.1, 67.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{16}N_3O^+$, m/z: 314.1288, found: 314.1280. **IR (thin film)**: ν_{max} 3227, 2919, 1611, 1470, 1313, 1149, 1023, 744cm^{-1}.

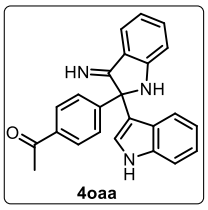
2-(1H-indol-3-yl)-2-(thiophen-3-yl)indolin-3-imine (4naa)



94% yield (62 mg). Yellow solid, mp: 133.6 – 134.5 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.92 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 –7.20 (m, 2H), 7.19 – 7.15 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 4.8 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.32 (s, 1H), 5.08 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.7, 155.5, 143.4, 137.4, 134.7, 126.9, 126.6, 125.5, 124.2, 123.9, 122.9, 122.5, 121.7, 120.0, 119.7, 117.2, 112.2, 111.9, 69.5, one

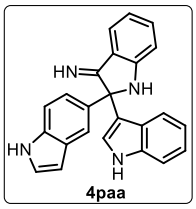
C missing. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{16}N_3S^+$, m/z: 330.1059, found: 330.1072. **IR (thin film)**: ν_{max} 3391, 1613, 1414, 1312, 1246, 1148, 744cm^{-1}.

1-(4-(3-imino-2-(1H-indol-3-yl)indolin-2-yl)phenyl)ethan-1-one (4oaa)



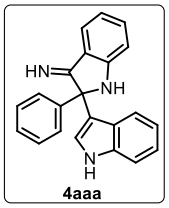
92% yield (68 mg). Yellow solid, mp: 151.6 – 153.3 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.84 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.06 – 7.01 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 5.16 (s, 1H), 2.55 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 198.1, 181.4, 155.9, 147.4, 137.5, 136.5, 135.0, 128.8, 127.3, 125.2, 124.4, 124.0, 122.8, 121.2, 120.2, 120.1, 119.7, 116.7, 112.6, 112.0, 71.4, 26.8. **HRMS (ESI)** calcd for $[M+H]^+C_{24}H_{20}N_3O^+$, m/z: 366.1601, found: 366.1612. **IR (thin film)**: ν_{max} 3381, 1745, 1640, 1480, 1241, 769 cm^{-1}.

[3,2':2',5''-terindolin]-3'-imine (4paa)



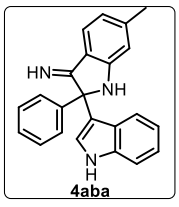
86% yield (63 mg). Yellow solid, mp: 160.6 – 162.9 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.04 (s, 1H), 10.98 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.48 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.26 (m, 4H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.98 (s, 1H), 6.83 – 6.76 (m, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.36 (s, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 181.5, 137.6, 137.5, 135.5, 135.4, 134.3, 133.7, 127.7, 126.3, 126.0, 125.8, 124.9, 124.7, 123.8, 121.6, 121.0, 118.8, 118.2, 117.2, 112.0, 111.5, 110.8, 101.8 one C missing. **HRMS (ESI)** calcd for $[M+H]^+C_{24}H_{19}N_4^+$, m/z: 363.1604, found: 363.1609. **IR (thin film)**: ν_{max} 3377, 1622, 1445, 1136, 702 cm^{-1}.

2-(1H-indol-3-yl)-2-phenylindolin-3-imine (4aaa)



97% yield (63 mg). Yellow solid, mp: 121.5 – 123.2 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.59 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.42 (m, 2H), 7.38 – 7.24 (m, 5H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.05 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.8, 155.8, 141.8, 137.4, 134.5, 128.7, 127.8, 126.9, 125.4, 124.3, 123.9, 122.5, 121.6, 120.0, 119.9, 119.7, 117.3, 112.2, 111.8, 71.6. **HRMS (ESI)** calcd for $[M+H]^+C_{22}H_{18}N_3^+$, m/z: 324.1495, found: 324.1503. **IR (thin film)**: ν_{max} 3371, 1735, 1609. 1471, 1235, 751 cm^{-1}.

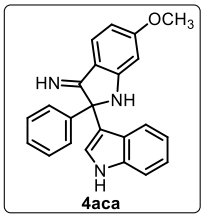
2-(1H-indol-3-yl)-6-methyl-2-phenylindolin-3-imine (4aba)



97% yield (80 mg). Yellow solid, mp: 193.8 – 195.7 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.02 (s, 1H), 9.53 (s, 1H), 7.56 – 7.44 (m, 4H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.05 (t, *J* = 7.3 Hz, 2H), 6.97 (s, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.63 (s, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 180.0, 155.8, 144.1, 143.0, 137.1, 128.0, 127.0, 126.7,

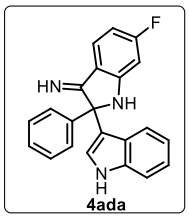
125.6, 124.6, 123.1, 121.2, 120.3, 118.5, 118.4, 118.1, 111.6, 110.6, 70.6, 21.82 one C missing. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3^+$, m/z: 338.1652, found: 338.1646. **IR (thin film)**: ν_{max} 3377, 1613, 1325, 1251, 1117, 703 cm^{-1}.

2-(1H-indol-3-yl)-6-methoxy-2-phenylindolin-3-imine (4aca)



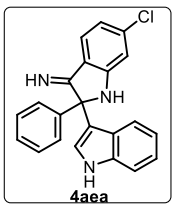
95% yield (67 mg). Yellow solid, mp: 149.9 – 150.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.49 (s, 1H), 10.69 (s, 1H), 9.13 (s, 1H), 8.02 (d, *J* = 8.9 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.43 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.39 (d, *J* = 2.1 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 180.6, 169.1, 161.6, 140.1, 137.4, 129.0, 128.7, 128.1, 127.2, 125.9, 125.7, 122.0, 120.0, 119.4, 113.4, 112.5, 110.5, 93.0, 72.6, 56.3 one C missing. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3O^+$, m/z: 354.1601, found: 354.1613. **IR (thin film)**: ν_{max} 3392, 1607, 1453, 1320, 1283, 1204, 740 cm^{-1}.

6-fluoro-2-(1H-indol-3-yl)-2-phenylindolin-3-imine (4ada)



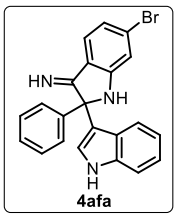
91% yield (62 mg). Yellow solid, mp: 123.3 – 123.8 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.06 (s, 1H), 9.81 (s, 1H), 7.91 (s, 1H), 7.67 – 7.62 (m, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.25 (m, 3H), 7.10 – 6.97 (m, 3H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.54 – 6.46 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.4, 168.8 (d, $J_{(C-F)}$ = 252.5 Hz), 158.4, 140.3, 137.5, 131.1, 129.5, 128.3, 127.1 (d, $J_{(C-F)}$ = 14.4 Hz), 126.7, 125.2, 124.8, 122.5, 119.8 (d, $J_{(C-F)}$ = 27.6 Hz), 115.7 (d, $J_{(C-F)}$ = 8.7 Hz), 112.2, 108.2 (d, $J_{(C-F)}$ = 24.4 Hz), 98.6 (d, $J_{(C-F)}$ = 31.1 Hz), 72.7 one C missing.**^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -106.5. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}FN_3^+$, m/z: 342.1401, found: 342.1408. **IR (thin film)**: ν_{max} 3735, 1622, 1458, 1287, 1148, 743cm^{-1}.

6-chloro-2-(1H-indol-3-yl)-2-phenylindolin-3-imine (4aea)



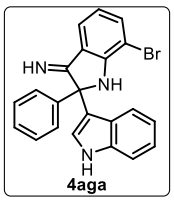
94% yield (67 mg). Yellow solid, mp: 134.4 – 135.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.10 (s, 1H), 9.91 (s, 1H), 7.89 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 6.5 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.25 (m, 3H), 7.12 – 6.99 (m, 3H), 6.91 – 6.81 (m, 2H), 6.72 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.3, 156.8, 141.6, 140.7, 137.5, 128.9, 128.2, 126.5, 125.5, 125.2, 124.6, 122.6, 120.3, 120.0, 119.7, 118.9, 115.8, 112.1, 112.0, 72.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}ClN_3^+$, m/z: 358.1106, found: 358.1109. **IR (thin film)**: ν_{max} 3377, 1606, 1445, 1262, 1066, 702cm^{-1}.

6-bromo-2-(1H-indol-3-yl)-2-phenylindolin-3-imine (4afa)



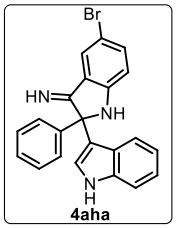
92% yield (74 mg). Yellow solid, mp: 125.1 – 125.8 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.07 (s, 1H), 9.72 (s, 1H), 7.85 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.38 (s, 1H), 7.37 – 7.25 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.03 – 6.96 (m, 3H), 6.84 (t, *J* = 7.9 Hz, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.9, 157.4, 140.0, 137.4, 129.5, 129.0, 128.4, 126.7, 126.1, 125.1, 124.7, 123.2, 122.6, 120.0, 119.8, 119.6, 115.7, 115.1, 112.2, 72.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0605. **IR (thin film)**: ν_{max} 3408, 1604, 1445, 1311, 1044, 905, 743cm^{-1}.

7-bromo-2-(1H-indol-3-yl)-2-phenylindolin-3-imine (4aga)



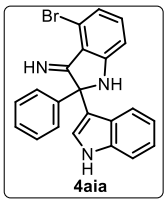
86% yield (69 mg). Yellow solid, mp: 208.4 – 208.9 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.07 (s, 1H), 10.06 (s, 1H), 7.71 – 7.52 (m, 5H), 7.45 – 7.27 (m, 4H), 7.14 – 7.03 (m, 2H), 6.91 – 6.83 (m, 2H), 6.68 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 182.2, 154.1, 140.6, 137.5, 129.0, 128.3, 126.9, 125.3, 124.7, 124.1, 123.7, 122.7, 121.9, 120.9, 120.2, 119.8, 115.9, 112.1, 105.7, 72.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0596. **IR (thin film)**: ν_{max} 3238, 1603, 1475, 1440, 1300, 1110, 1027, 746cm^{-1}.

5-bromo-2-(1H-indol-3-yl)-2-phenylindolin-3-imine (4aha)



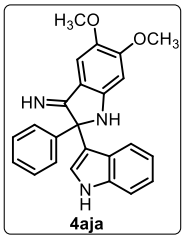
91% yield (73 mg). Yellow solid, mp: 179.2 – 180.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.04 (s, 1H), 9.83 (s, 1H), 7.77 (s, 1H), 7.50 (s, 2H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.24 (m, 4H), 7.10 – 6.94 (m, 3H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 180.8, 154.7, 141.1, 137.5, 128.9, 128.2, 128.1, 126.8, 125.3, 124.7, 124.5, 123.1, 122.6, 120.0, 119.8, 116.4, 113.8, 112.1, 111.6, 72.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0610. **IR (thin film)**: ν_{max} 3373, 1638, 1604, 1469, 1157, 1012, 744cm^{-1}.

4-bromo-2-(1H-indol-3-yl)-2-phenylindolin-3-imine (4aia)



87% yield (69 mg). Yellow solid, mp: 121.5 – 122.4 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.97 (s, 1H), 10.35 (s, 1H), 7.92 (s, 1H), 7.42 (s, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.15 (m, 3H), 7.10 (t, *J* = 7.9 Hz, 1H), 7.01 – 6.88 (m, 3H), 6.77 – 6.71 (m, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 179.9, 164.2, 157.9, 143.1, 137.5, 135.5, 128.5, 127.7, 127.2, 125.9, 125.2, 121.7, 120.6, 119.3, 119.0, 117.4, 112.2, 110.3, 71.1 one C missing. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0603. **IR (thin film)**: ν_{max} 3407, 1600, 1473, 1306, 1199, 1136, 904, 741cm^{-1}.

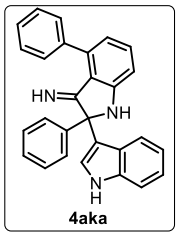
2-(1H-indol-3-yl)-5,6-dimethoxy-2-phenylindolin-3-imine (4aja)



4aja

94% yield (72 mg). Yellow solid, mp: 149.3 – 149.9 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.20 (s, 1H), 9.43 (s, 1H), 7.84 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.25 (m, 4H), 7.08 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 11.4 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.47 (s, 1H), 3.83 (s, 3H), 3.73 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 185.1, 162.5, 159.4, 148.4, 147.1, 142.3, 133.4, 132.7, 131.9, 130.7, 130.0, 126.6, 125.2, 123.9, 120.7, 117.0, 114.2, 110.6, 99.2, 76.6, 61.2, 61.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{22}BrN_3O_2^+$, m/z: 384.1707, found: 384.1726. **IR (thin film)**: ν_{max} 3096, 1632, 1489, 1437, 1283, 1228, 1203, 1118, 1006, 746cm^{-1}.

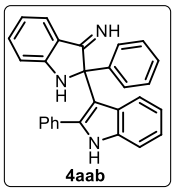
2-(1H-indol-3-yl)-2,4-diphenylindolin-3-imine (4aka)



4aka

81% yield (65 mg). Yellow solid, mp: 103.2 – 104.8 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.28 (s, 1H), 7.51 – 7.43 (m, 2H), 7.40 – 7.34 (m, 3H), 7.32 (d, *J* = 5.0 Hz, 1H), 7.30 (d, *J* = 4.5 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.18 (s, 1H), 7.10 – 7.02 (m, 2H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 7.2 Hz, 1H), 5.09 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.2, 156.1, 142.7, 141.6, 138.5, 137.4, 133.8, 128.8, 128.8, 128.4, 128.2, 127.6, 127.2, 125.7, 124.6, 122.4, 121.6, 120.1, 120.0, 118.4, 116.6, 111.8, 111.4, 70.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{22}N_3^+$, m/z: 400.1808, found: 400.1826. **IR (thin film)**: ν_{max} 2919, 1591, 1447, 1332, 1300, 1245, 1080, 904cm^{-1}.

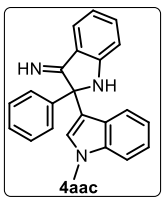
2-phenyl-2-(2-phenyl-1H-indol-3-yl)indolin-3-imine (4aab)



4aab

50% yield (40 mg). Yellow solid, mp: 128.7 – 129.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.32 (s, 1H), 7.45 – 7.40 (m, 3H), 7.32 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.21 – 7.17 (m, 3H), 7.13 – 7.10 (m, 1H), 7.09 (s, 1H), 7.07 (s, 1H), 7.06 – 7.03 (m, 2H), 6.92 – 6.88 (m, 2H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 4.84 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.2, 154.8, 143.0, 137.2, 135.7, 134.1, 133.4, 129.8, 128.5, 128.1, 127.5, 127.4, 127.3, 126.9, 123.8, 122.6, 122.3, 121.3, 120.0, 119.4, 113.5, 111.6, 110.9, 72.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{22}N_3^+$, m/z: 400.1808, found: 400.1823. **IR (thin film)**: ν_{max} 3388, 1613, 1470, 1310, 1147, 1027, 743cm^{-1}.

2-(1-methyl-1H-indol-3-yl)-2-phenylindolin-3-imine (4aac)

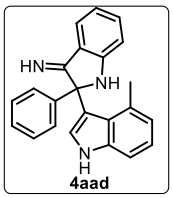


4aac

76% yield (52 mg). Yellow solid, mp: 222.9 – 223.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 (d, *J* = 6.4 Hz, 1H), 7.48 (d, *J* = 6.3 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.01 (s, 1H), 3.73 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.5, 155.7, 141.9, 138.2, 134.4, 128.8, 128.6, 127.7, 126.9, 125.9, 123.9, 122.2, 121.8, 120.1, 119.6, 119.6, 116.0, 112.2, 109.8, 71.5, 32.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3^+$, m/z: 338.1652, found: 338.1645. **IR (thin film)**: ν_{max} 3369,

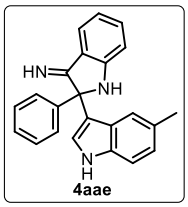
1641, 1606, 1469, 1307, 1227, 1152, 1028, 748cm^{-1}.

2-(4-methyl-1H-indol-3-yl)-2-phenylindolin-3-imine (4aad)



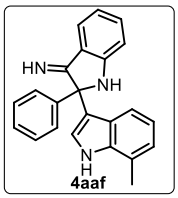
43% yield (29 mg). Yellow solid, mp: 127.4 – 128.6 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.03 (s, 1H), 9.19 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.41 – 7.11 (m, 7H), 7.02 (s, 1H), 6.96 – 6.82 (m, 3H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.0 Hz, 1H), 1.85 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 181.5, 156.4, 145.8, 141.7, 138.7, 134.3, 130.4, 128.7, 127.4, 126.7, 126.2, 124.8, 123.8, 122.0, 121.6, 118.4, 116.5, 112.5, 110.0, 71.7, 21.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3^+$, m/z: 338.1652, found: 338.1668. **IR (thin film)**: ν_{max} 3311, 1610, 1471, 1314, 1151, 1025, 750cm^{-1}.

2-(5-methyl-1H-indol-3-yl)-2-phenylindolin-3-imine (4aae)



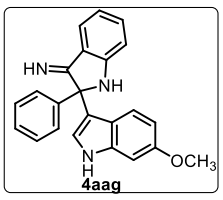
61% yield (42 mg). Yellow solid, mp: 155.2 – 156.4 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.45 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.38 – 7.28 (m, 4H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.00 – 6.97 (m, 2H), 6.89 – 6.85 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.07 (s, 1H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.9, 156.1, 141.9, 135.9, 134.6, 129.4, 128.8, 127.8, 127.0, 125.7, 124.5, 124.3, 124.1, 121.7, 119.8, 119.6, 116.6, 112.4, 111.6, 71.7, 21.6. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3^+$, m/z: 338.1652, found: 338.1652. **IR (thin film)**: ν_{max} 3387, 1605, 1470, 1446, 1335, 1249, 1036, 733cm^{-1}.

2-(7-methyl-1H-indol-3-yl)-2-phenylindolin-3-imine (4aaf)



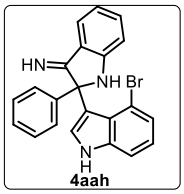
71% yield (48 mg). Yellow solid, mp: 128.1 – 128.7 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.94 (s, 1H), 9.35 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 3H), 7.29 – 7.15 (m, 4H), 6.89 (s, 1H), 6.80 (t, *J* = 6.3 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 180.7, 156.0, 143.5, 137.1, 134.4, 128.5, 127.5, 127.2, 125.7, 124.6, 123.8, 122.2, 121.2, 119.2, 118.4, 118.1, 117.4, 114.1, 111.0, 70.7, 17.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3^+$, m/z: 338.1652, found: 338.1657. **IR (thin film)**: ν_{max} 3243, 2924, 1613, 1471, 1312, 1147, 1024, 748cm^{-1}.

2-(6-methoxy-1H-indol-3-yl)-2-phenylindolin-3-imine (4aag)



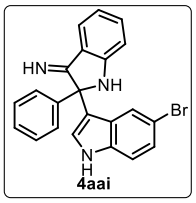
63% yield (45 mg). Yellow solid, mp: 164.4 – 165.3 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.40 (s, 1H), 7.75 (d, *J* = 6.9 Hz, 1H), 7.44 (s, 2H), 7.39 – 7.23 (m, 4H), 7.07 (s, 1H), 7.00 – 6.86 (m, 4H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.06 (s, 1H), 2.45 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.9, 156.0, 141.9, 137.1, 134.7, 128.8, 128.8, 127.9, 127.0, 125.1, 124.1, 124.0, 123.2, 121.2, 120.4, 119.8, 117.9, 117.8, 112.3, 71.8, 16.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3O^+$, m/z: 354.1601, found: 354.1599. **IR (thin film)**: ν_{max} 3247, 2927, 1613, 1470, 1311, 1148, 1105, 1026, 747cm^{-1}.

2-(4-bromo-1H-indol-3-yl)-2-phenylindolin-3-imine (4aah)



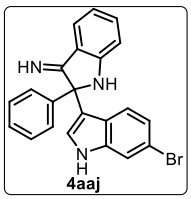
45% yield (36 mg). Yellow solid, mp: 135.4 – 136.7 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.53 (s, 1H), 9.67 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.21 (m, 5H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.90 (s, 1H), 6.75 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 180.9, 156.0, 145.6, 139.8, 134.3, 129.8, 128.6, 128.2, 127.1, 126.6, 124.6, 124.4, 123.7, 123.2, 118.1, 115.7, 113.2, 112.2, 112.0, 71.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0587. **IR (thin film)**: ν_{max} 3411, 2923, 1614, 1472, 1316, 1023, 758cm^{-1}.

2-(5-bromo-1H-indol-3-yl)-2-phenylindolin-3-imine (4aai)



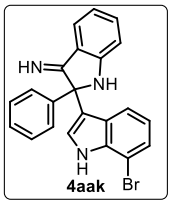
83% yield (67 mg). Yellow solid, mp: 144.6 – 147.3 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.26 (s, 1H), 9.64 (s, 1H), 7.68 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.23 – 7.16 (m, 2H), 7.11 (s, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 180.6, 155.9, 143.2, 136.3, 134.5, 128.6, 127.8, 127.7, 127.1, 126.5, 124.2, 123.9, 122.9, 120.4, 117.6, 117.5, 114.2, 111.6, 110.9, 70.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0589. **IR (thin film)**: ν_{max} 3204, 1612, 1470, 1316, 1148, 1103, 1051, 751cm^{-1}.

2-(6-bromo-1H-indol-3-yl)-2-phenylindolin-3-imine (4aaj)



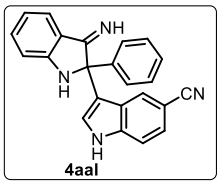
74% yield (60 mg). Yellow solid, mp: 142.1 – 142.8 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.15 (s, 1H), 9.91 (s, 1H), 7.65 – 7.54 (m, 3H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.23 (m, 4H), 7.03 (s, 1H), 6.98 (s, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.7, 155.8, 141.5, 136.1, 135.0, 128.8, 128.1, 127.0, 126.8, 125.1, 125.0, 124.3, 121.4, 121.3, 119.9, 119.4, 118.8, 112.2, 105.4, 83.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0592. **IR (thin film)**: ν_{max} 3144, 1613, 1470, 1310, 1147, 1049, 748cm^{-1}.

2-(7-bromo-1H-indol-3-yl)-2-phenylindolin-3-imine (4aak)



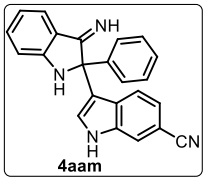
60% yield (49 mg). Yellow solid, mp: 198.3 – 199.1 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.30 (s, 1H), 9.82 (s, 1H), 7.64 (s, 2H), 7.52 (s, 2H), 7.38 – 7.24 (m, 5H), 7.09 (s, 2H), 6.88 – 6.77 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 181.7, 155.8, 141.5, 136.1, 135.0, 128.8, 128.1, 127.0, 126.8, 125.1, 125.0, 124.3, 121.4, 121.3, 120.0, 119.4, 118.8, 112.2, 105.4, 83.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{17}BrN_3^+$, m/z: 402.0600, found: 402.0593. **IR (thin film)**: ν_{max} 3240, 1638, 1611, 1470, 1309, 1174, 1150, 752cm^{-1}.

3-(3-imino-2-phenylindolin-2-yl)-1H-indole-5-carbonitrile (4aal)



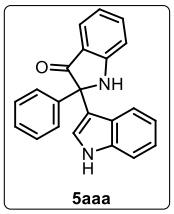
80% yield (56 mg). Yellow solid, mp: 132.8 – 134.2 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ δ 11.63 (s, 1H), 7.88 – 7.72 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.46 – 7.42 (m, 2H), 7.41 – 7.38 (m, 1H), 7.36 – 7.30 (m, 4H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 180.0, 139.0, 138.8, 134.3, 134.1, 130.1, 128.2, 127.4, 127.1, 126.9, 126.6, 125.9, 125.4, 123.9, 123.6, 120.8, 117.3, 113.1, 110.5, 100.6, 69.5. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{17}N_4^+$, m/z: 349.1448, found: 349.1446. **IR (thin film)**: ν_{max} 3211, 2217, 1612, 1470, 1315, 1147, 1023, 756cm^{-1}.

3-(3-imino-2-phenylindolin-2-yl)-1H-indole-6-carbonitrile (4aam)



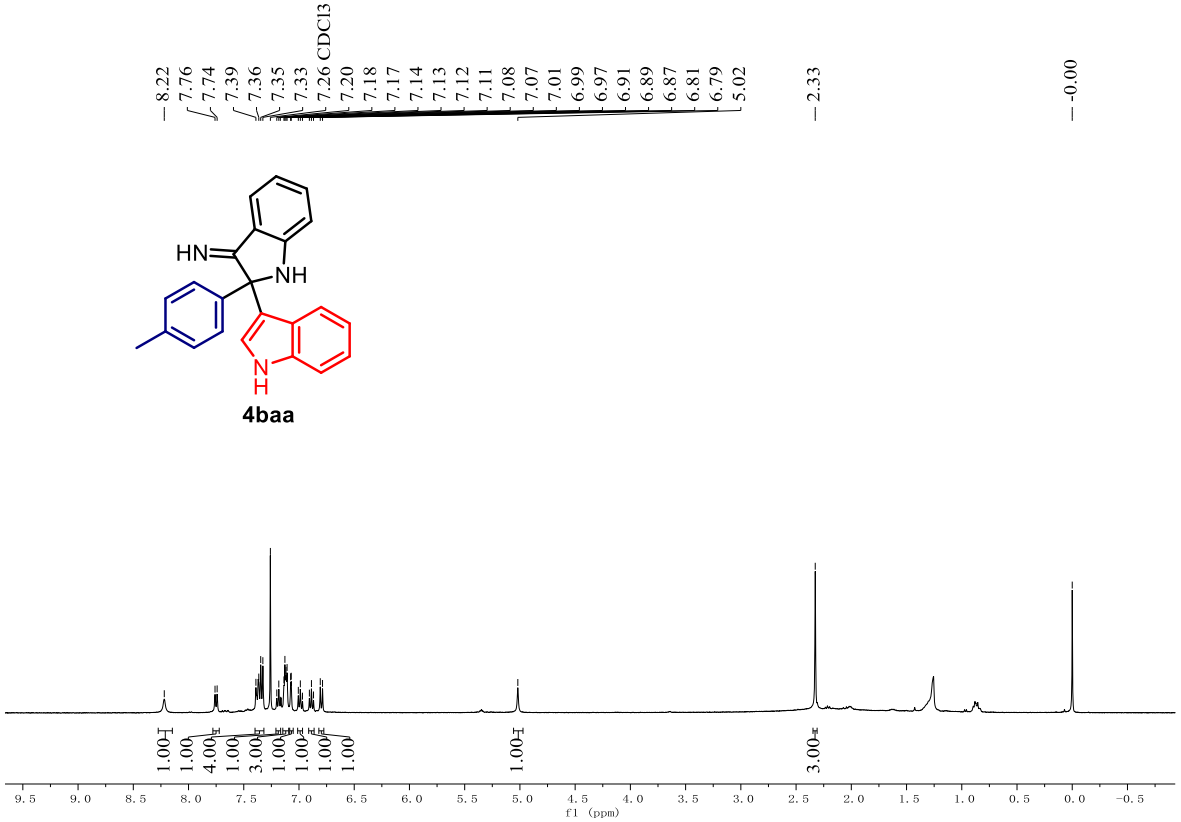
78% yield (55 mg). Yellow solid, mp: 135.6 – 136.3 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H N MR (400 MHz, DMSO-*d*$_6$)** δ 11.66 (s, 1H), 10.00 (s, 1H),7.93 (s, 1H), 7.82 (d, *J* = 6.7 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.26 – 7.15 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 180.7, 156.0, 141.9, 136.0, 135.8, 134.1, 130.1, 129.1, 129.0, 128.4, 127.4, 126.7, 123.9, 121.3, 120.5, 118.9, 117.7, 116.8, 110.8, 102.9, 69.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{17}N_4^+$, m/z: 349.1448, found: 349.1448. **IR (thin film)**: ν_{max} 3248, 2219, 1614, 1441, 1343, 1266, 1005, 730m^{-1}.

2-(1H-indol-3-yl)-2-phenylindolin-3-one (5aaa)

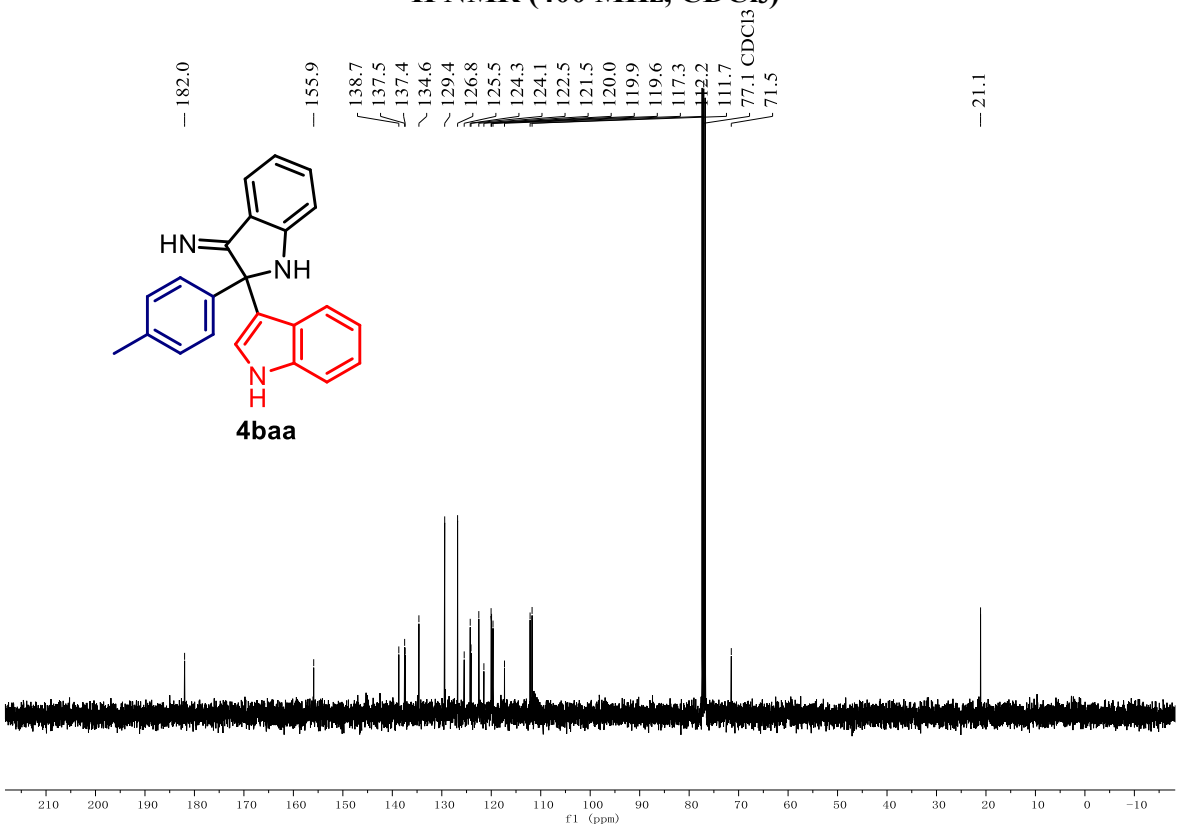


64% yield (42 mg). Yellow solid, mp: 182.4 – 183.7 ºC, petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 1 : 1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.35 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.13 – 7.06 (m, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 2H), 5.41 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 201.1, 160.7, 139.6, 137.7, 137.0, 128.5, 127.8, 126.9, 125.6, 125.6, 124.0, 122.5, 120.0, 119.8, 119.6, 119.5, 115.3, 113.0, 111.9, 71.5. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{22}H_{16}N_2ONa^+$, m/z: 347.1155, found: 347.1150. **IR (thin film)**: ν_{max} 3295, 1685, 1611, 1482, 1465, 1323, 749cm^{-1}.

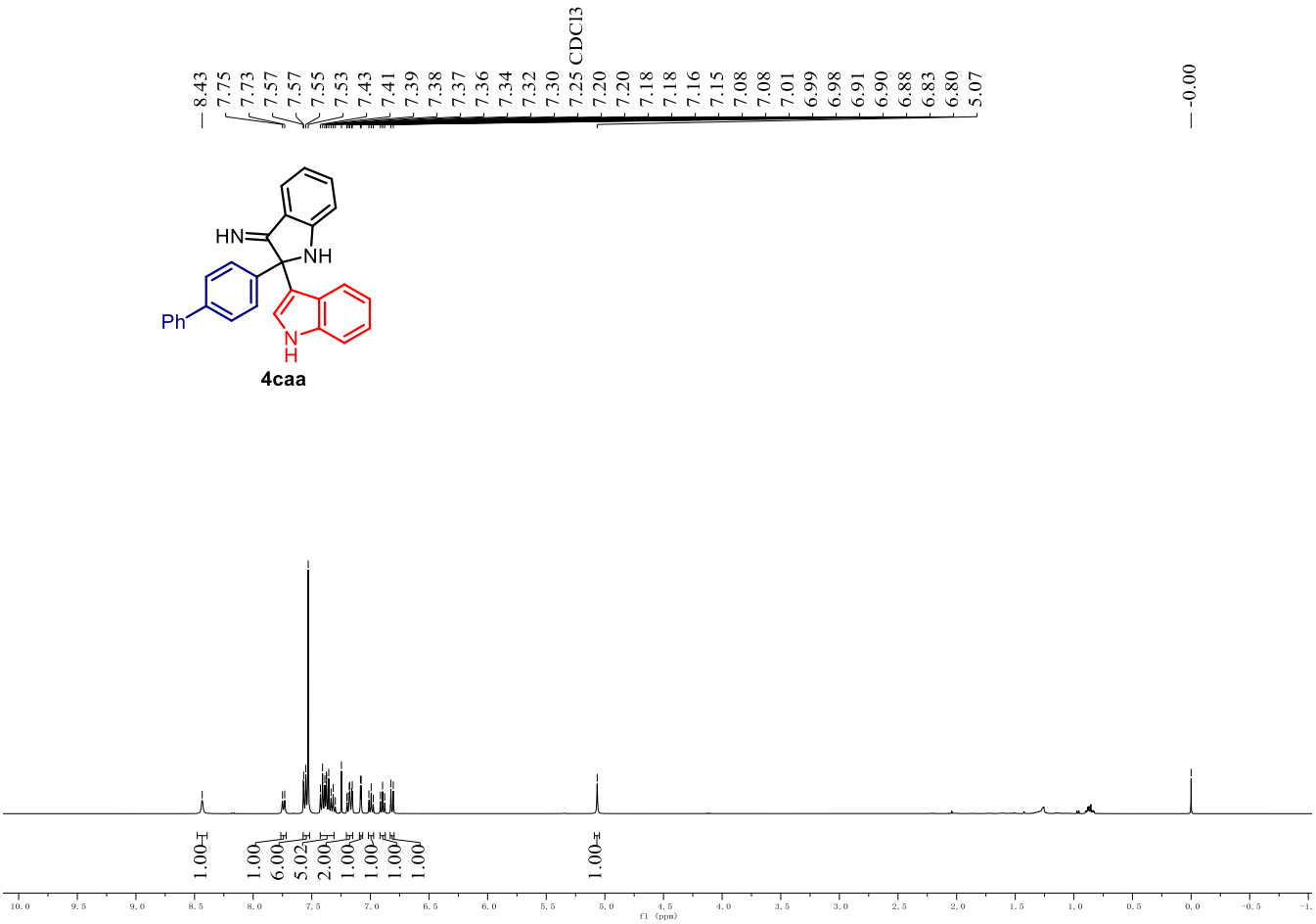
9. The ^{1}H, ^{13}C, ^{19}F NMR spectra of all products



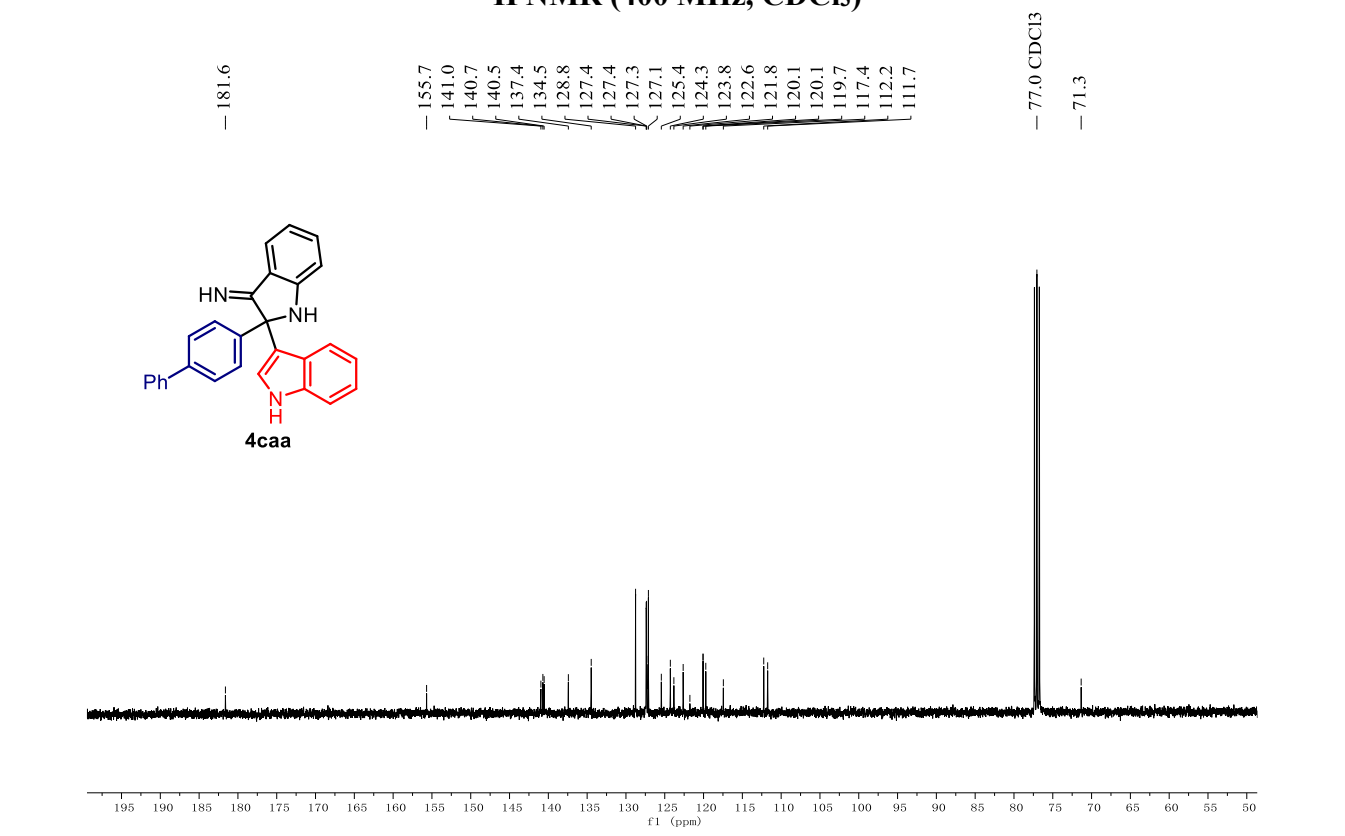
^{1}H NMR (400 MHz, $CDCl_3$)



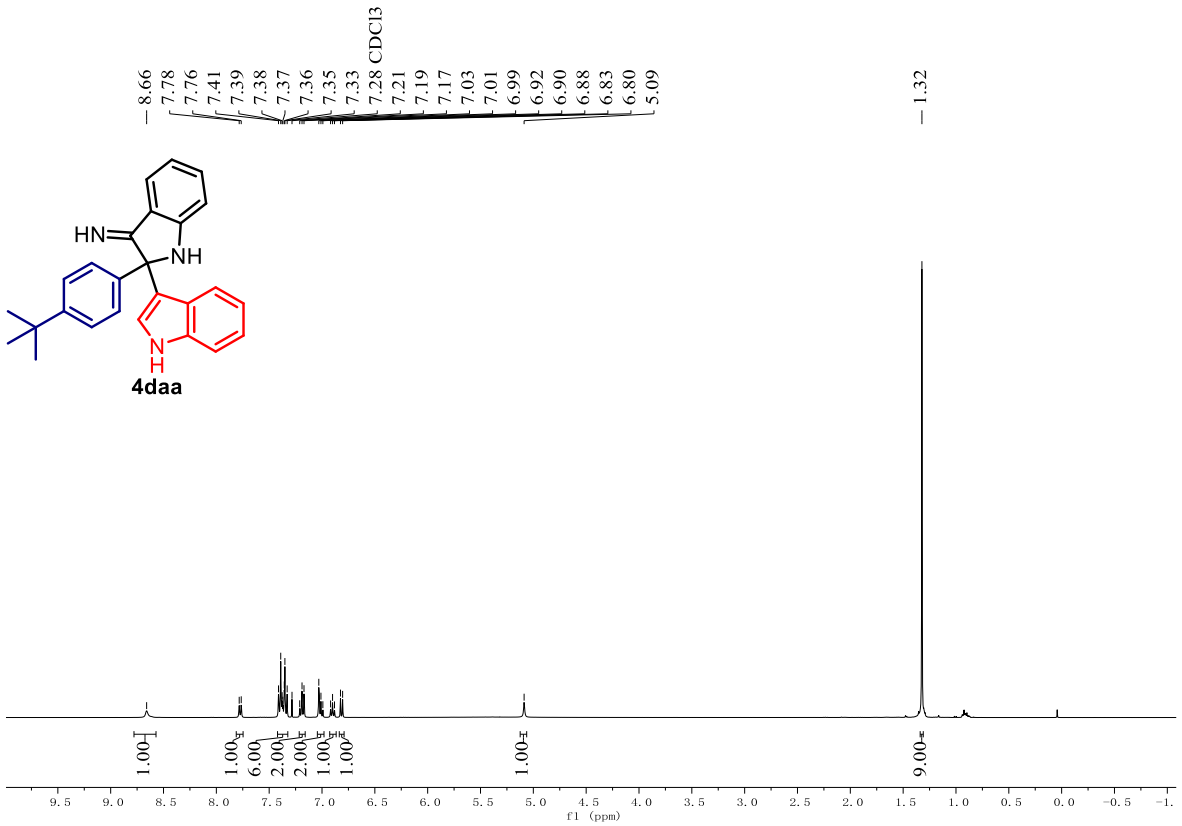
^{13}C NMR (100 MHz, $CDCl_3$)



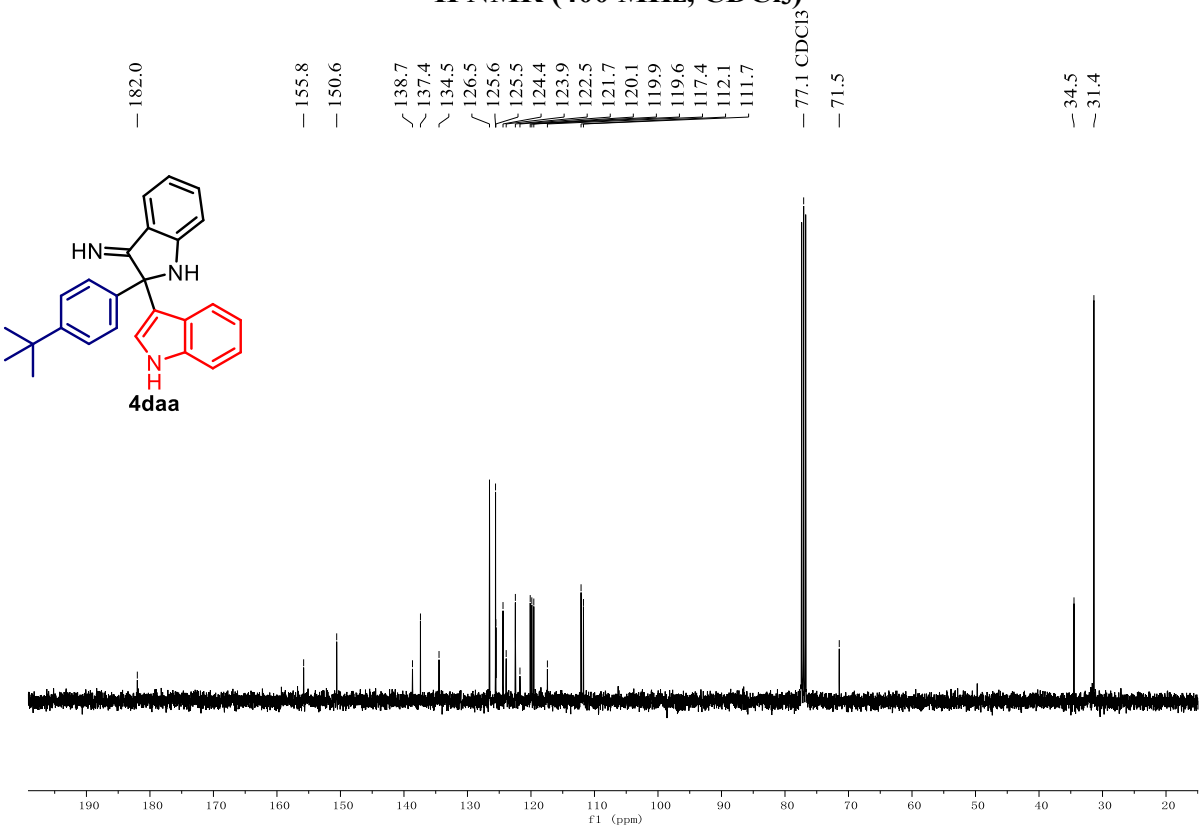
^{1}H NMR (400 MHz, $CDCl_3$)



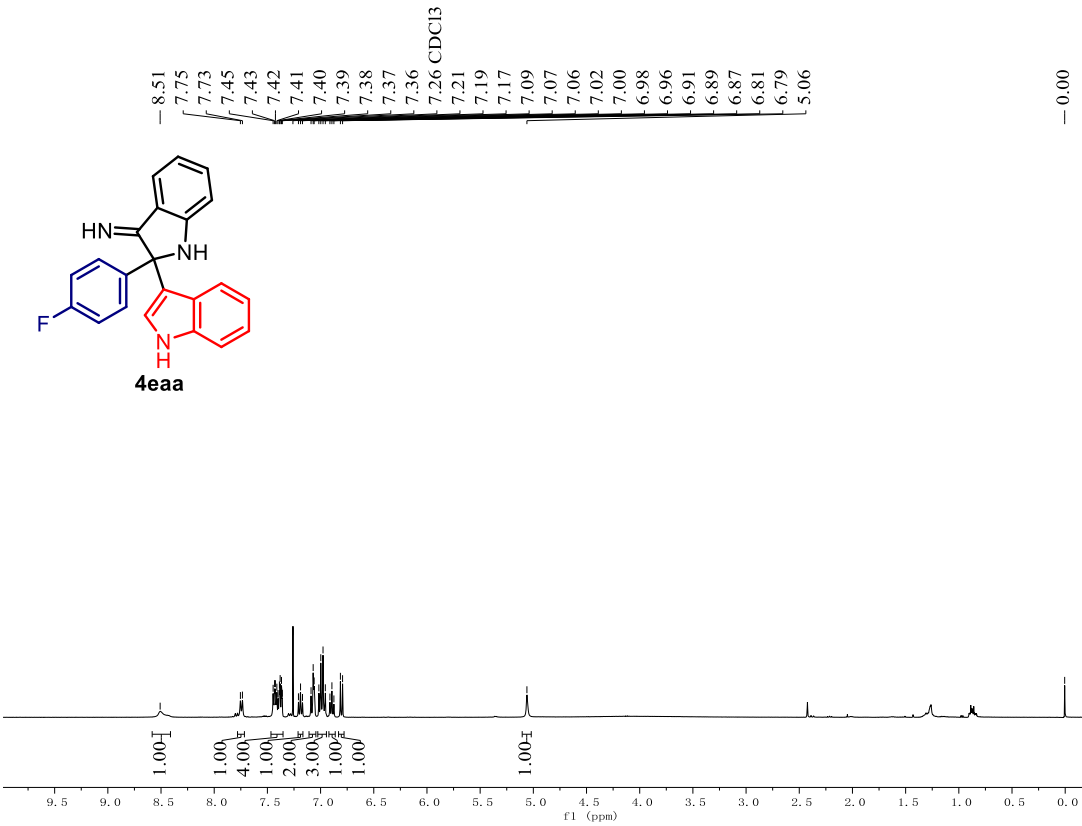
^{13}C NMR (100 MHz, $CDCl_3$)



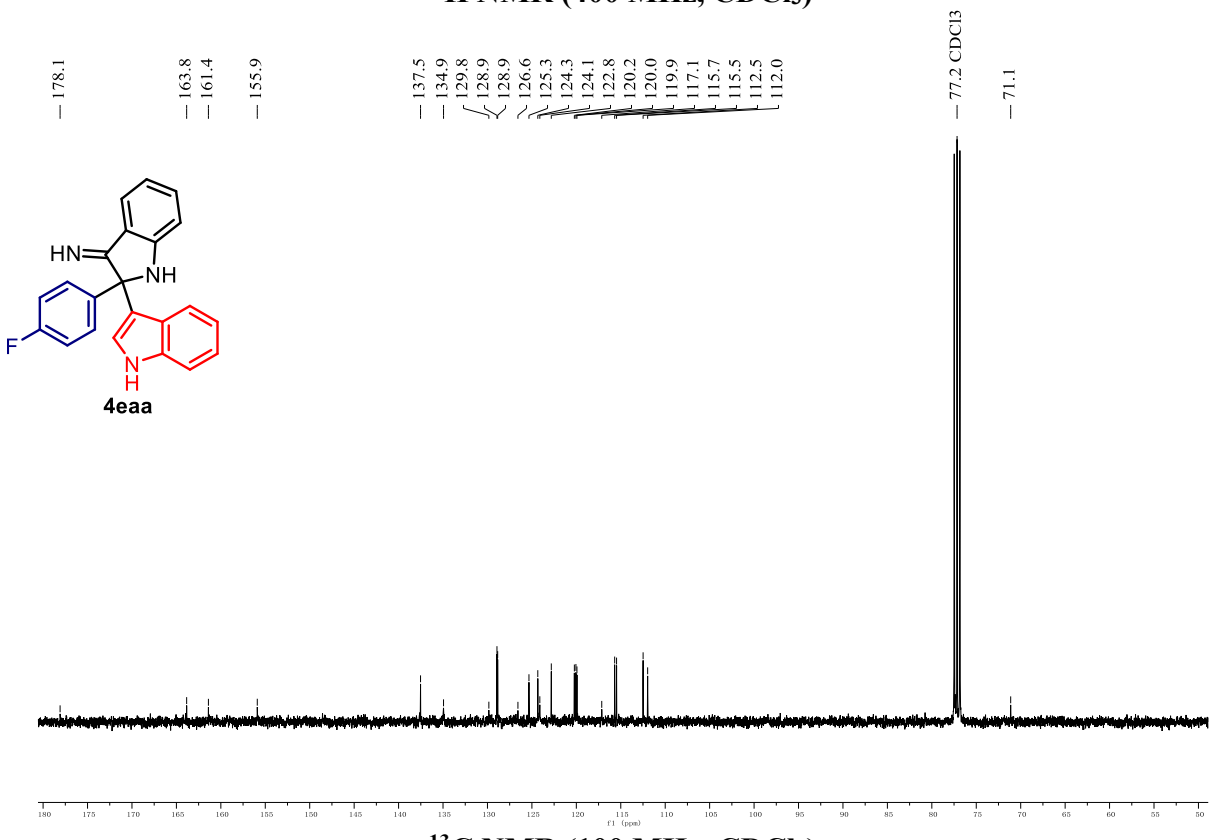
^{1}H NMR (400 MHz, $CDCl_3$)



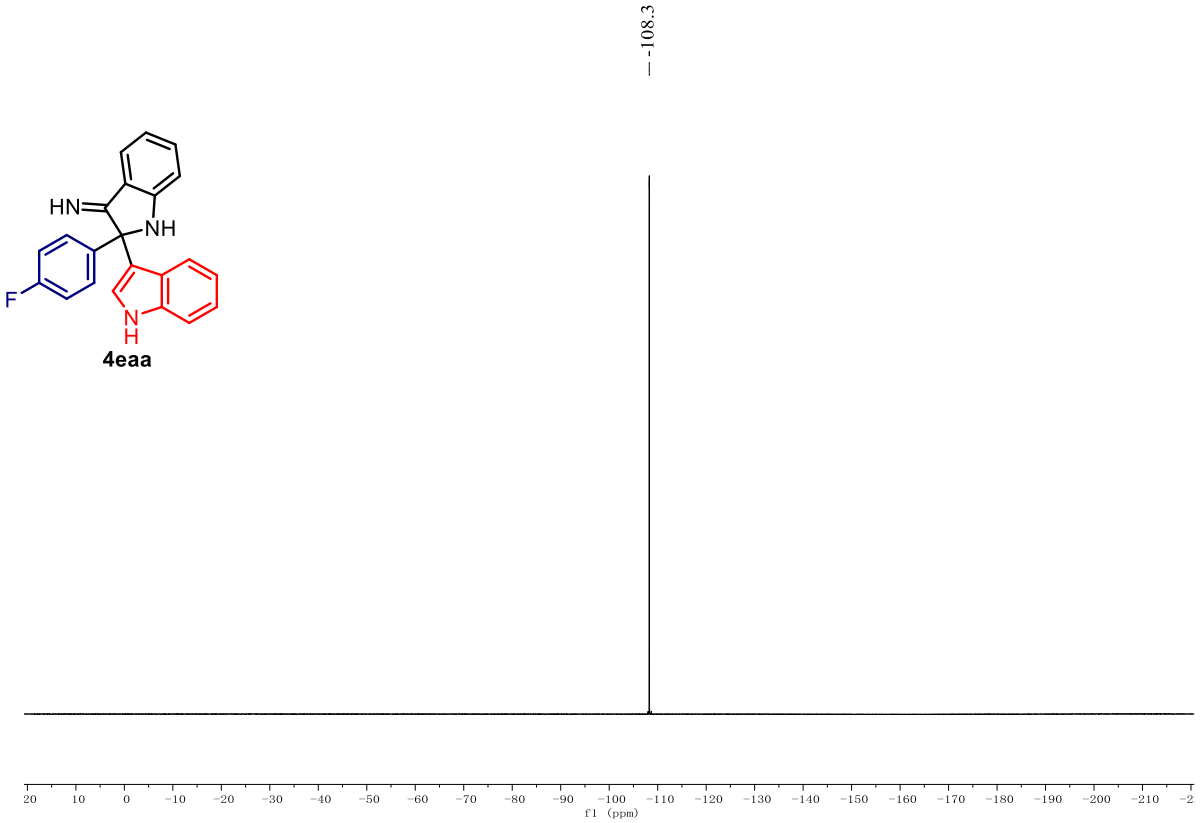
^{13}C NMR (100 MHz, $CDCl_3$)



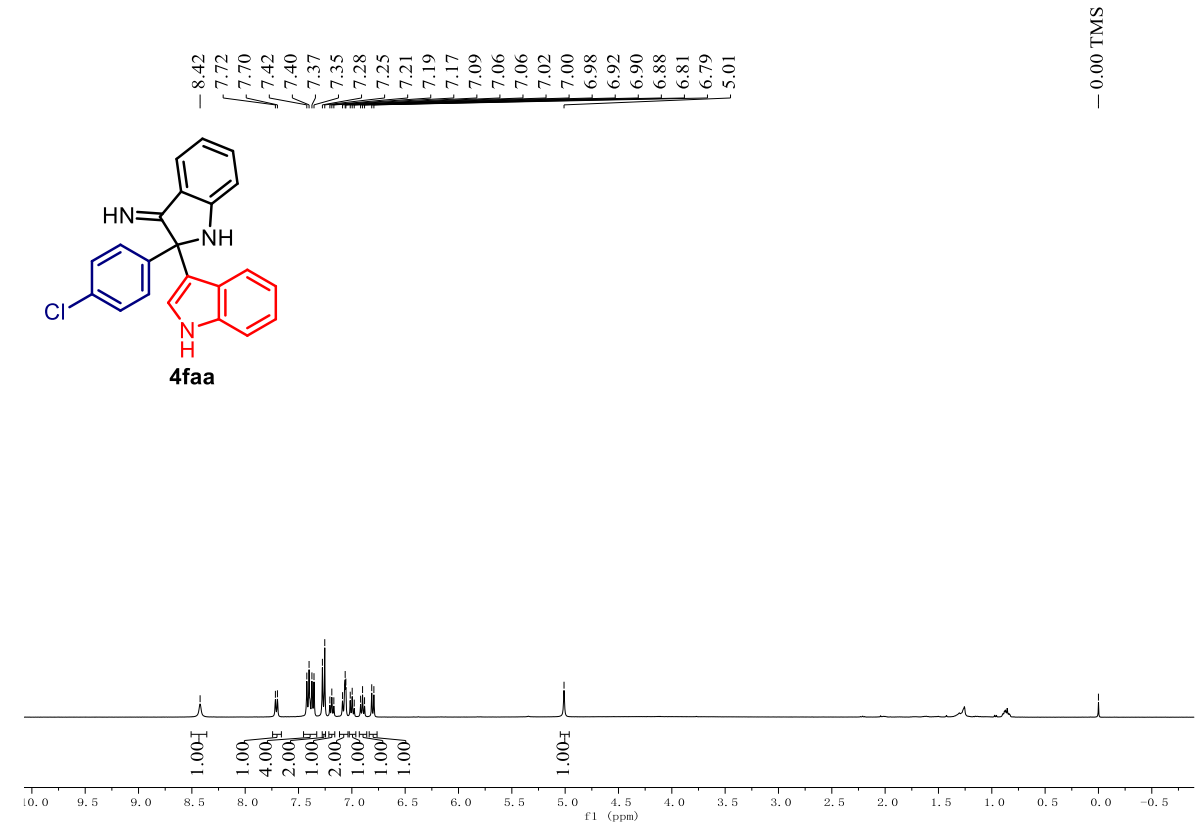
^{1}H NMR (400 MHz, $CDCl_3$)



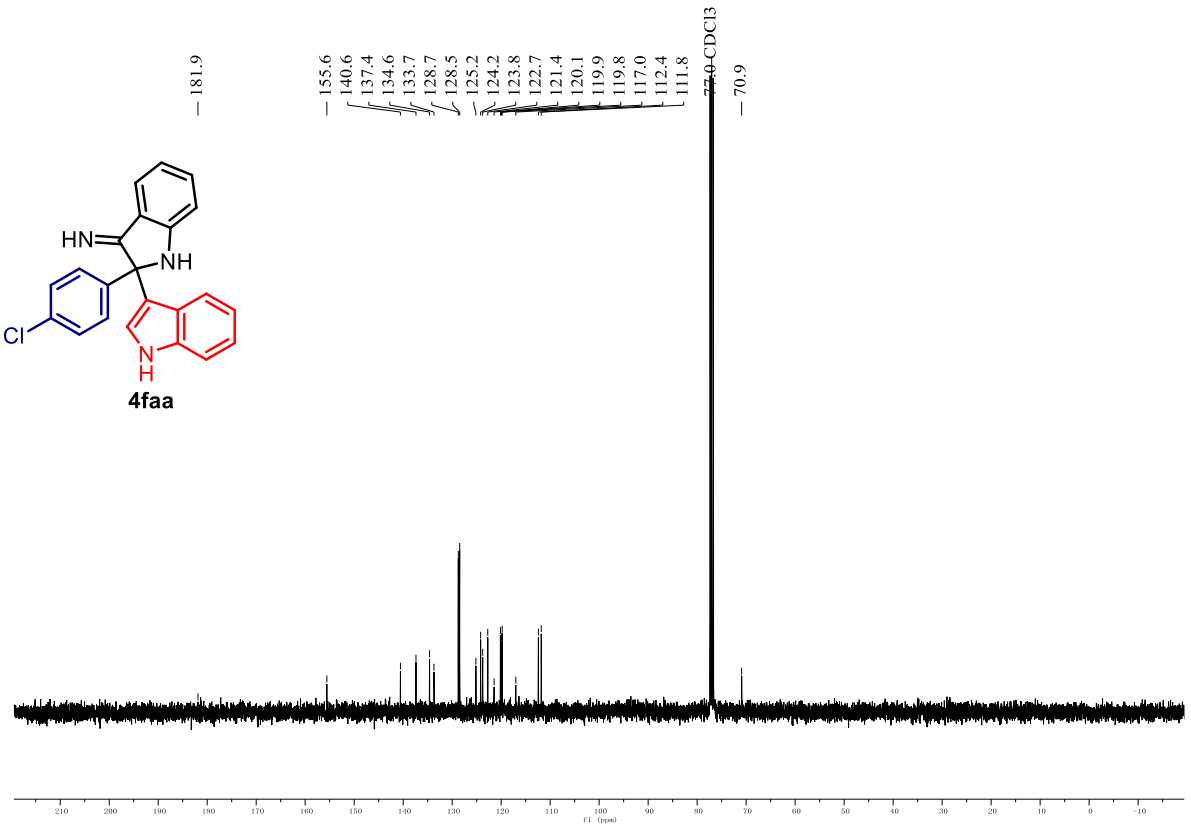
^{13}C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

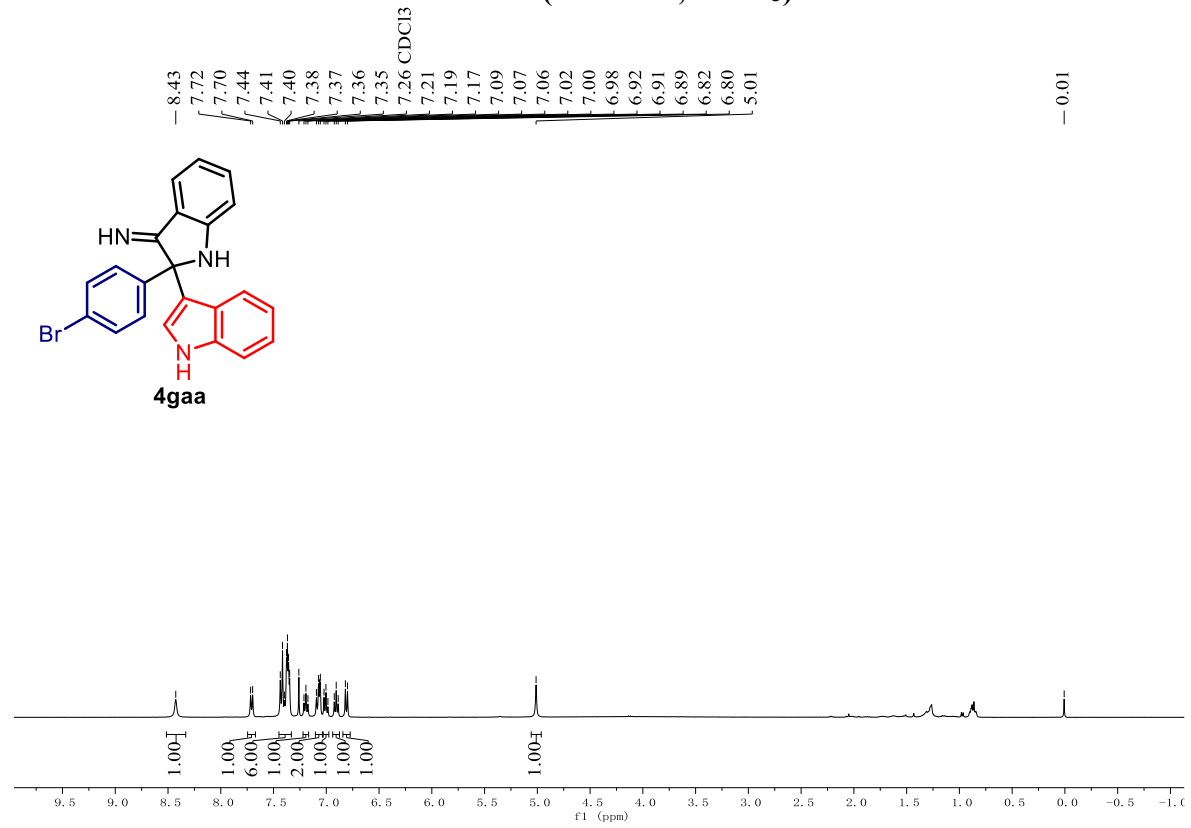


^{1}H NMR (400 MHz, $CDCl_3$)



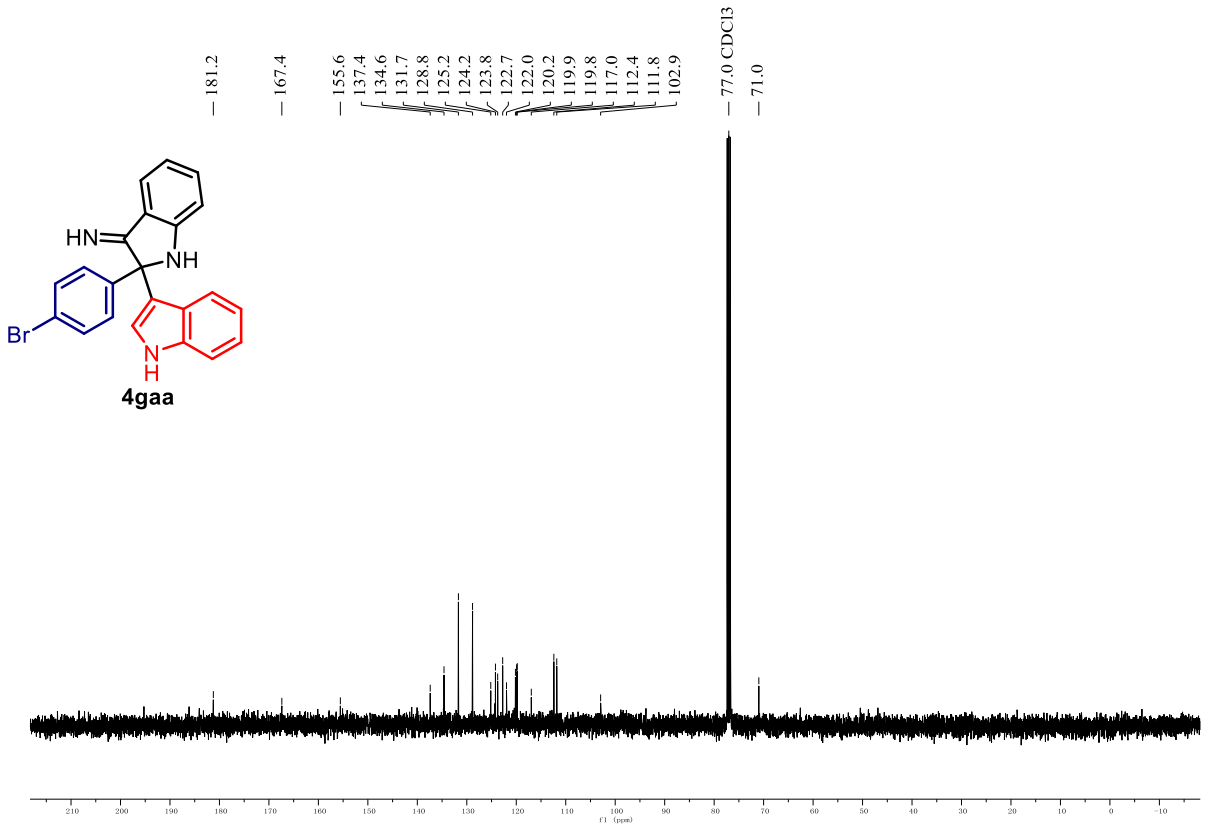
4faa

^{13}C NMR (100 MHz, $CDCl_3$)



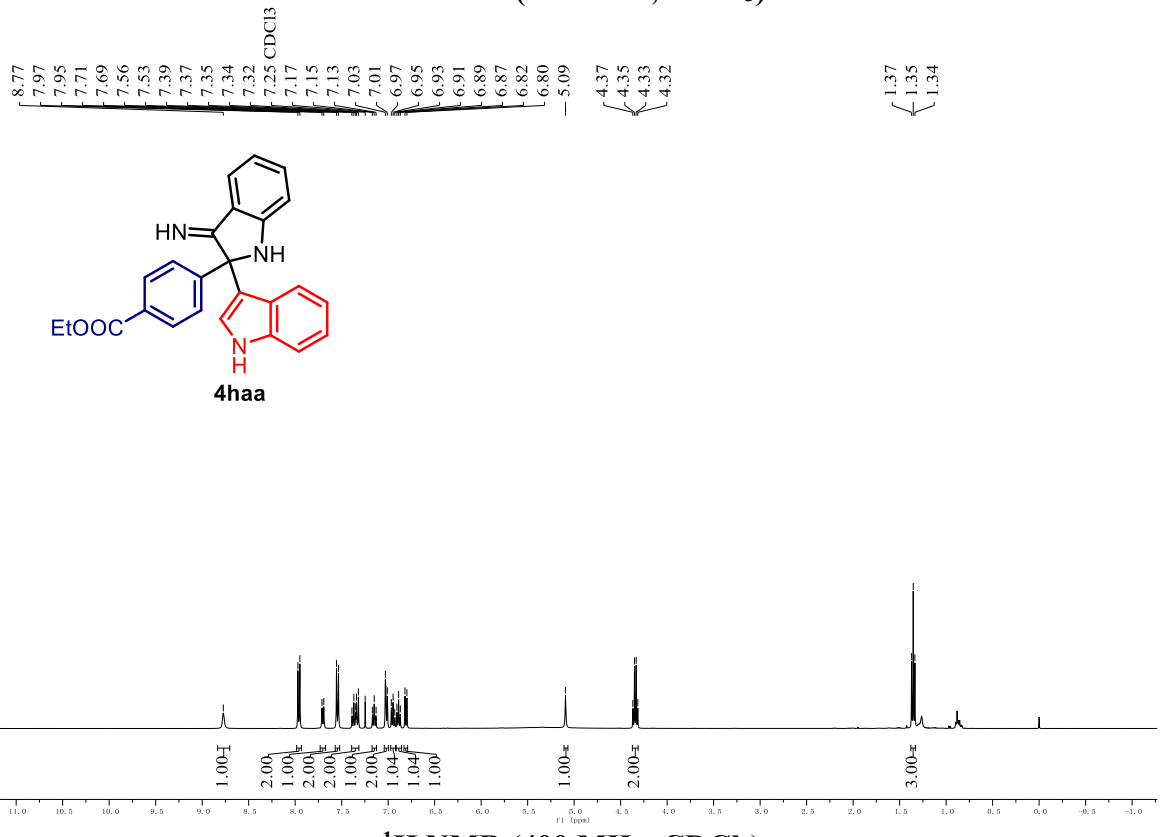
4gaa

^{1}H NMR (400 MHz, $CDCl_3$)



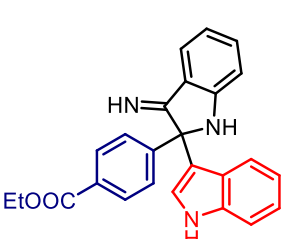
4gaa

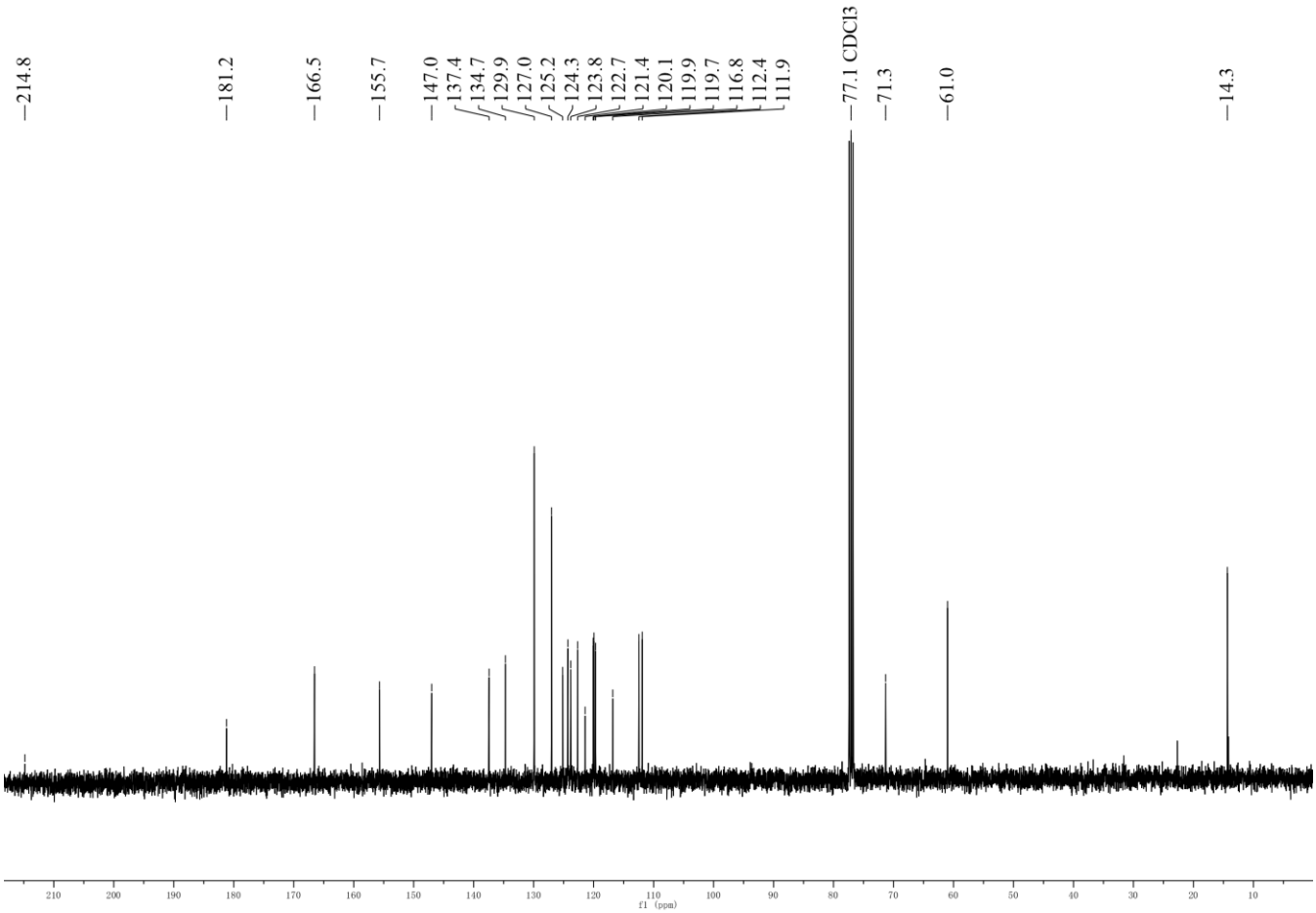
^{13}C NMR (100 MHz, $CDCl_3$)



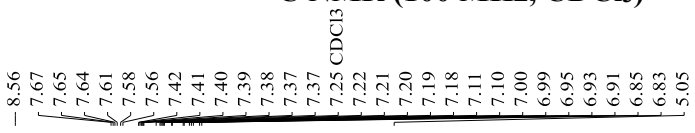
4haa

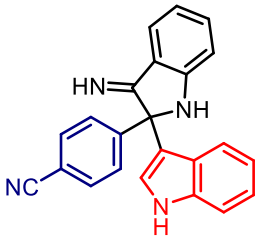
^{1}H NMR (400 MHz, $CDCl_3$)



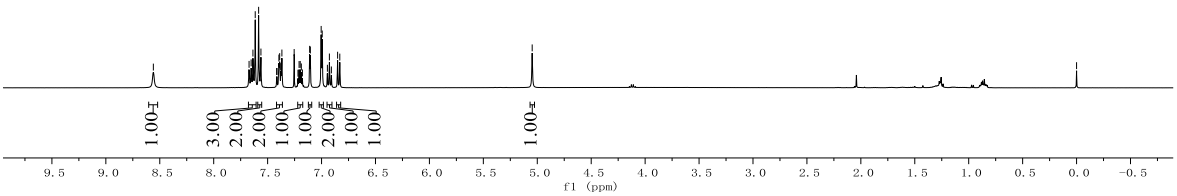


^{13}C NMR (100 MHz, $CDCl_3$)

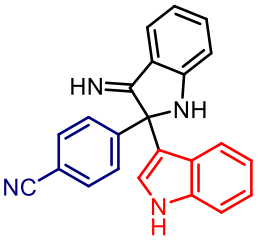




4iaa

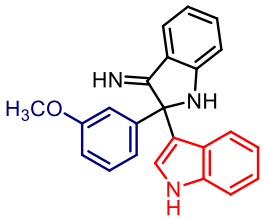


^{1}H NMR (400 MHz, $CDCl_3$)

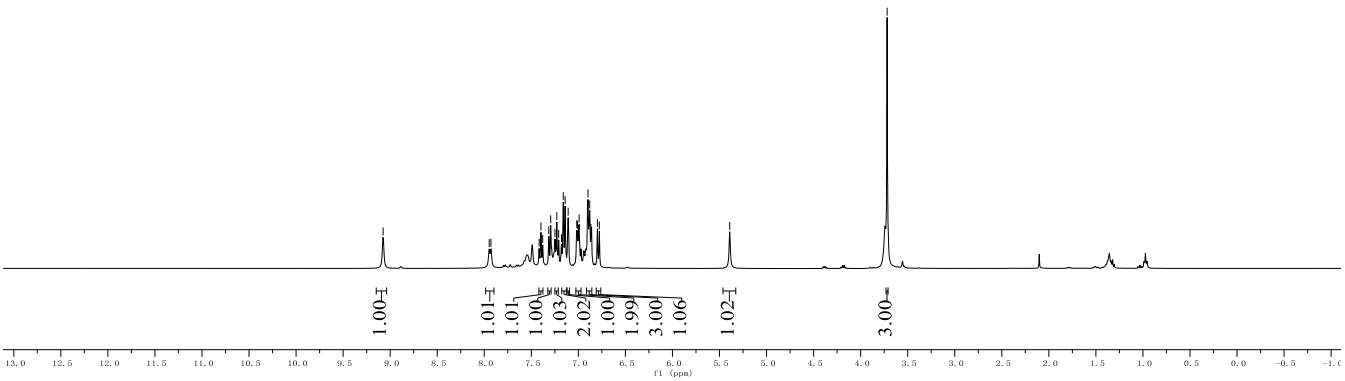


4iaa

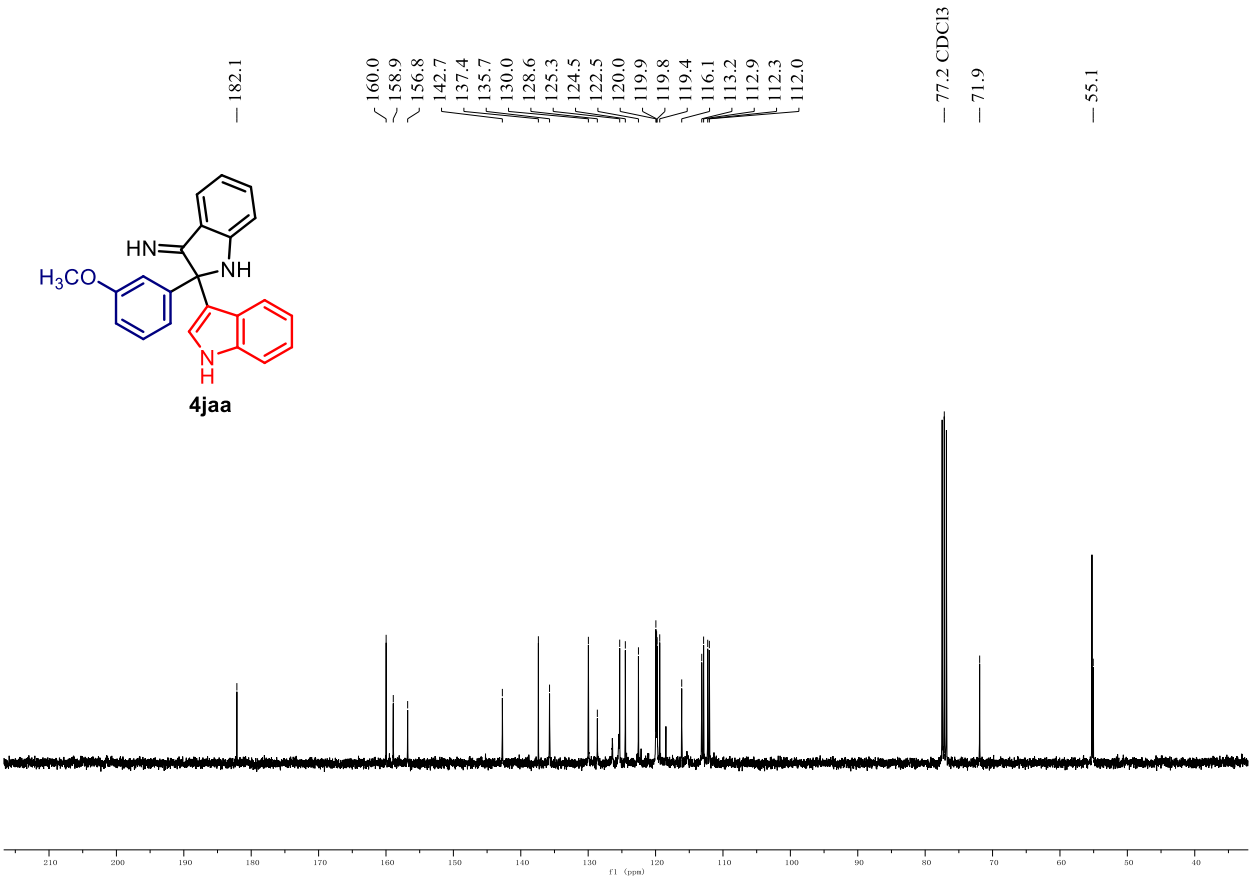
^{13}C NMR (100 MHz, $CDCl_3$)



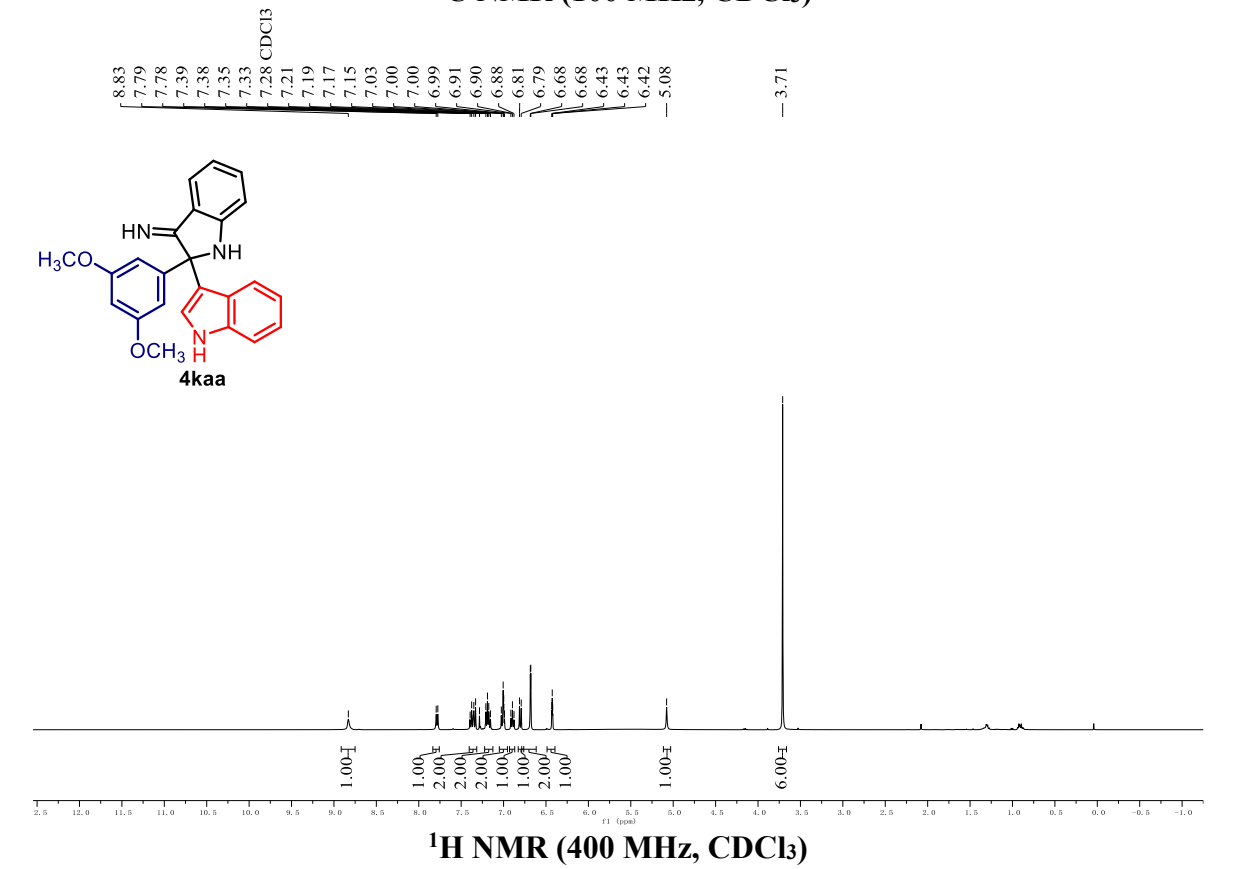
4jaa



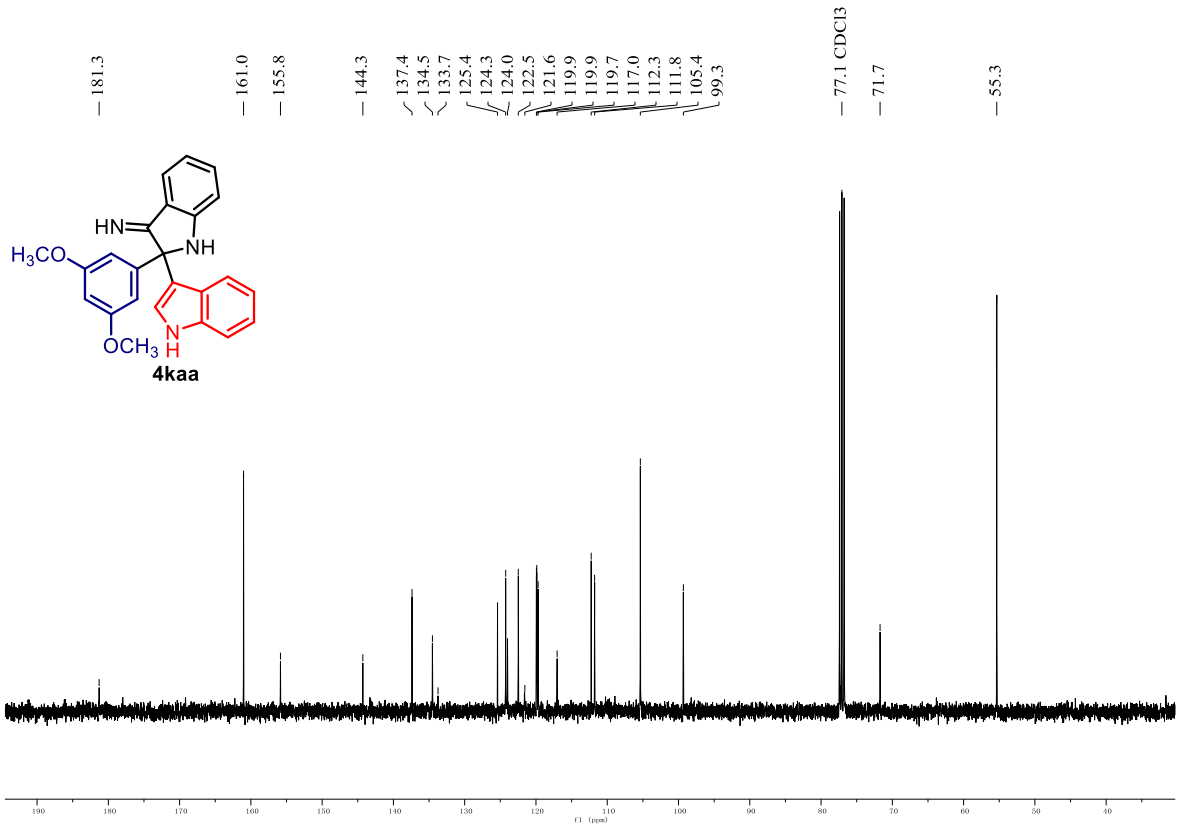
^{1}H NMR (400 MHz, $CDCl_3$)



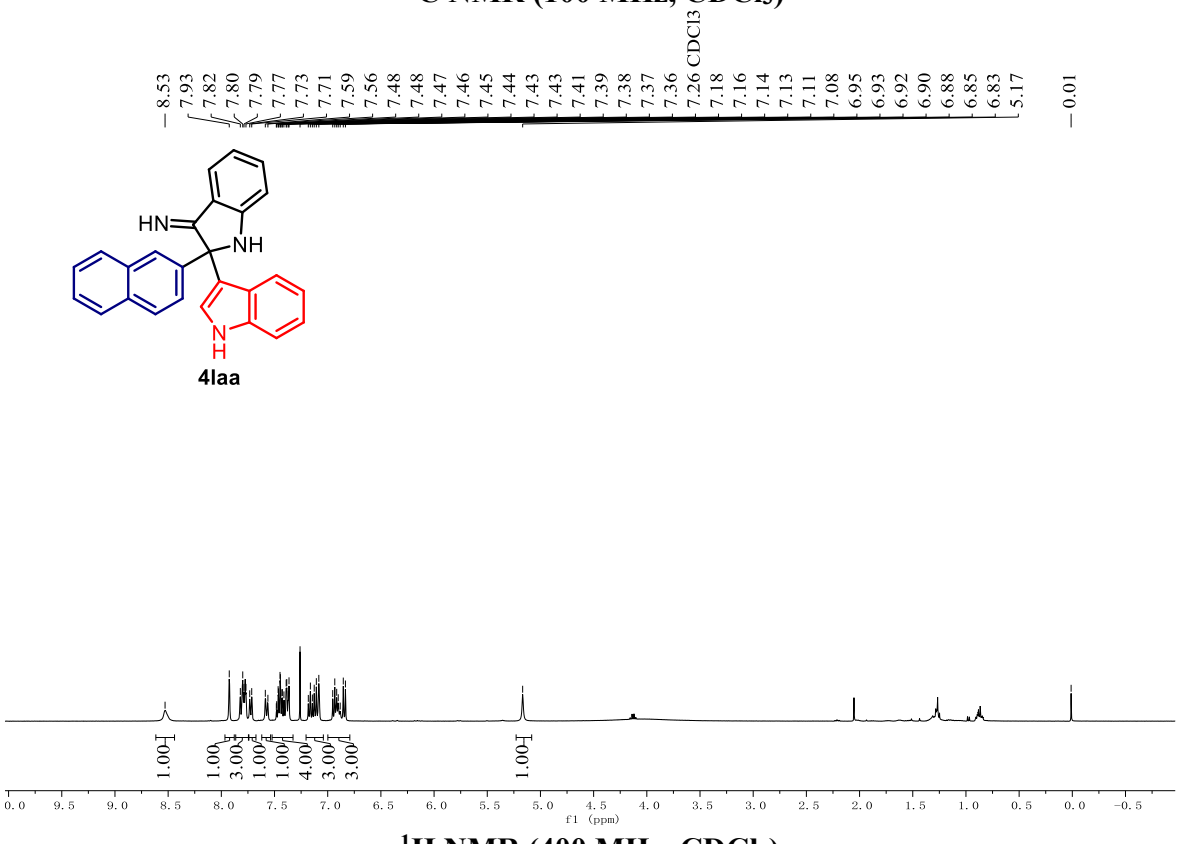
^{13}C NMR (100 MHz, CDCl$_3$)



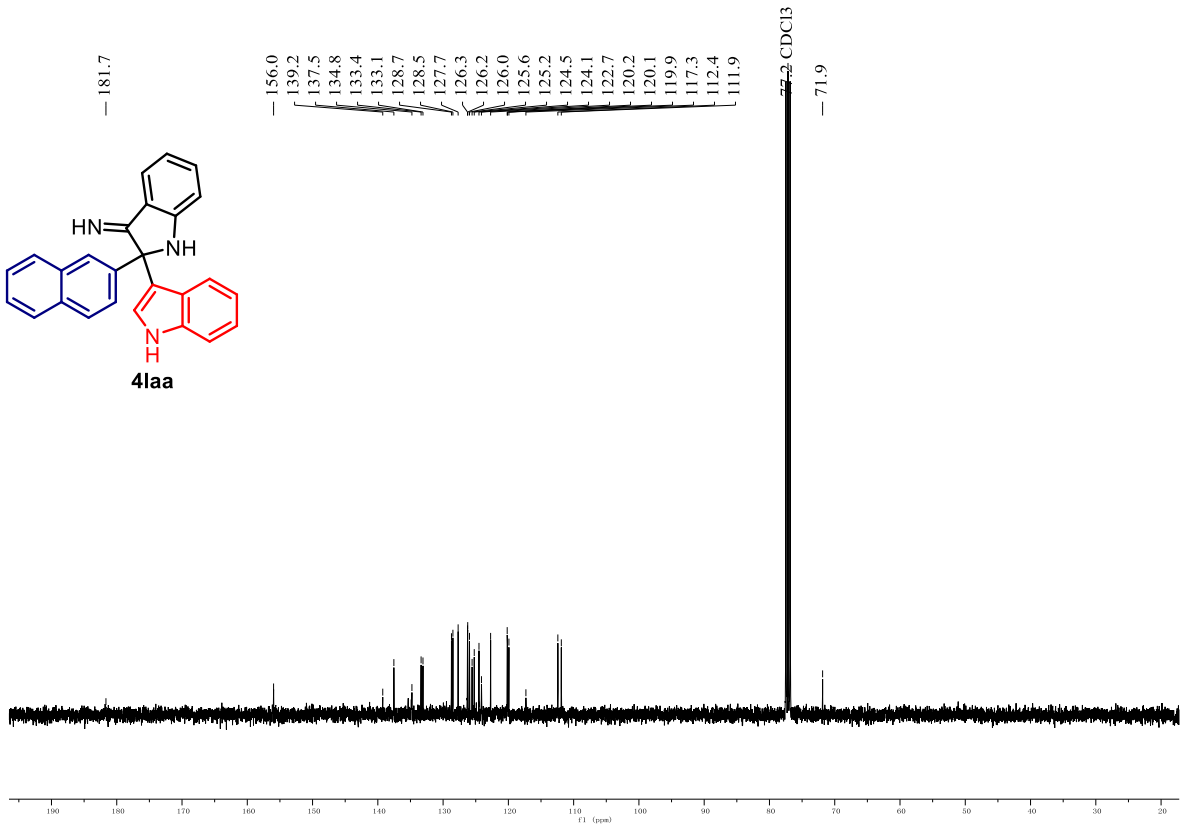
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

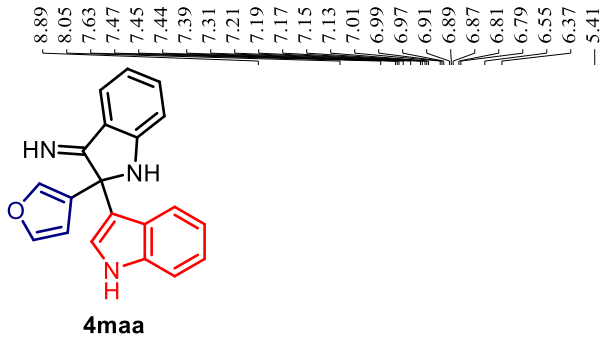


^{1}H NMR (400 MHz, $CDCl_3$)

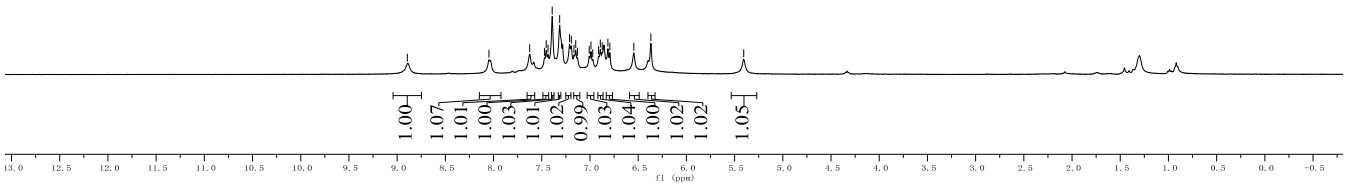


4laa

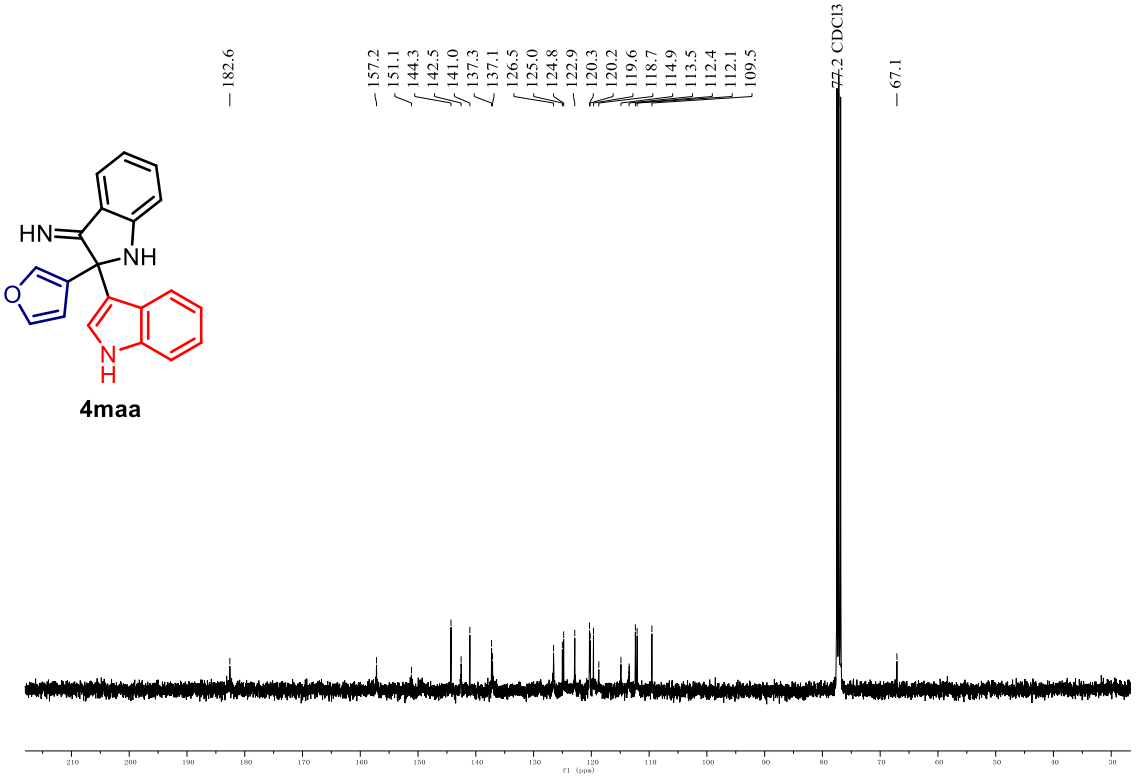
^{13}C NMR (100 MHz, $CDCl_3$)



4maa

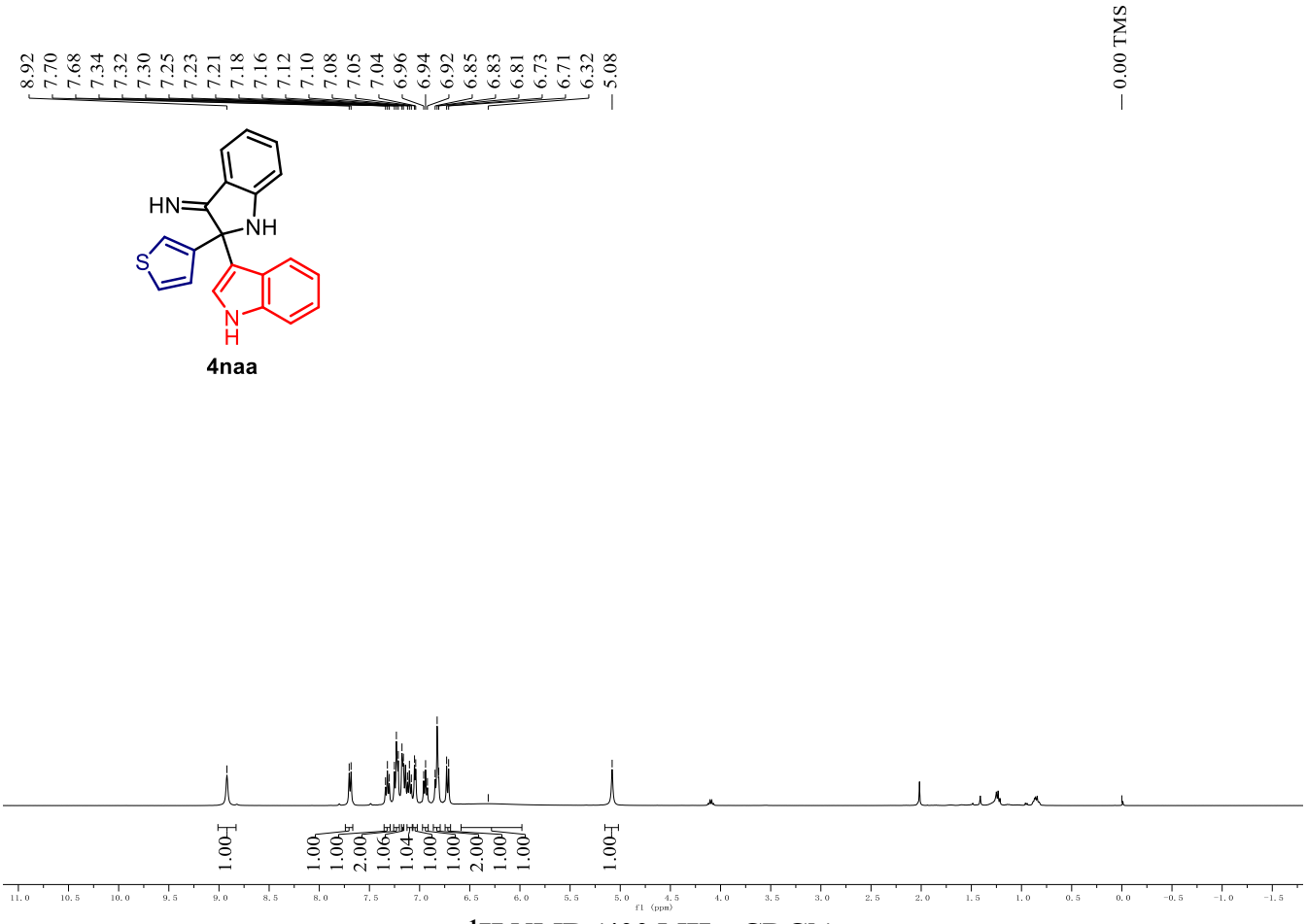


^{1}H NMR (400 MHz, $CDCl_3$)



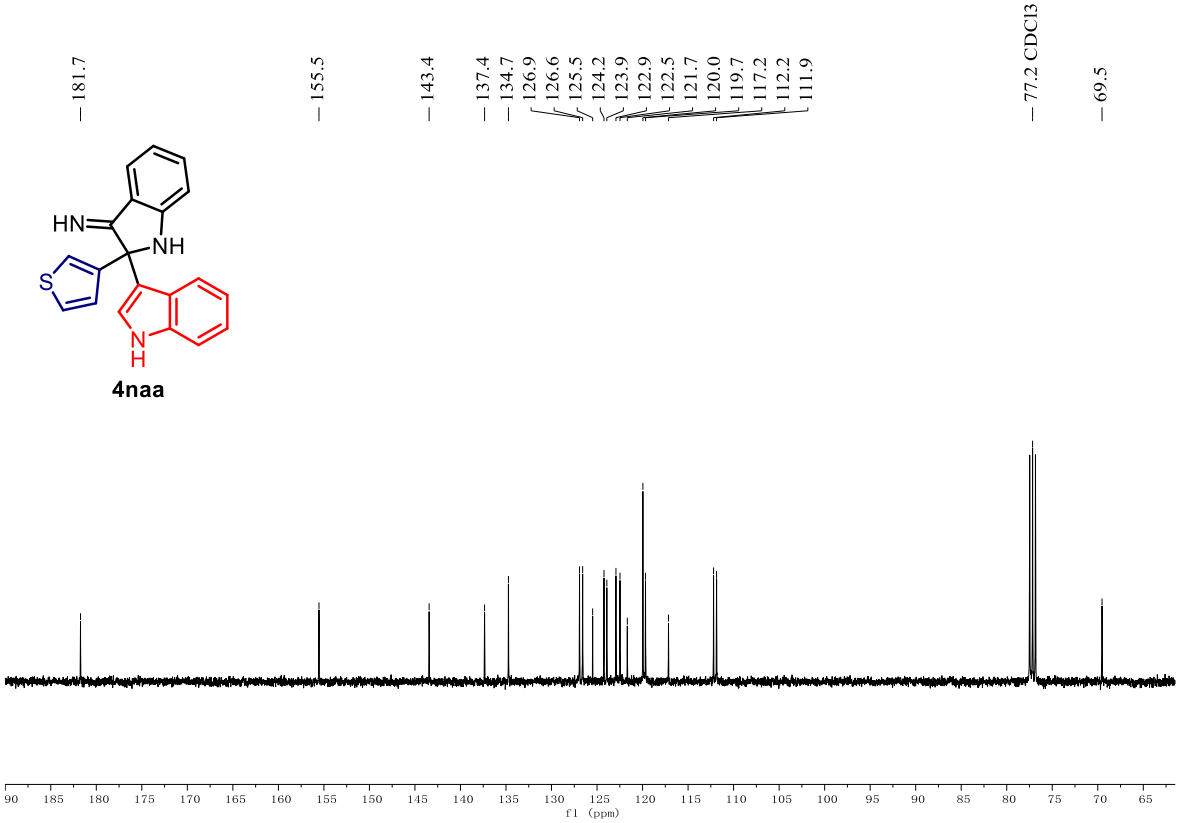
4maa

^{13}C NMR (100 MHz, CDCl$_3$)



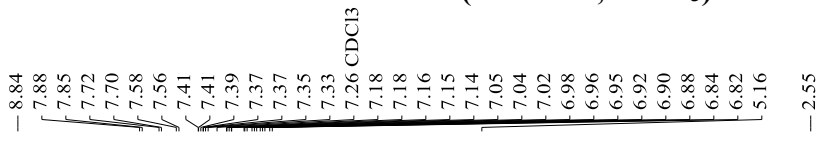
4naa

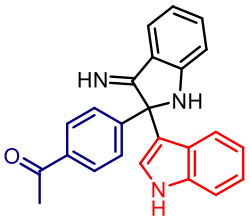
^{1}H NMR (400 MHz, CDCl$_3$)



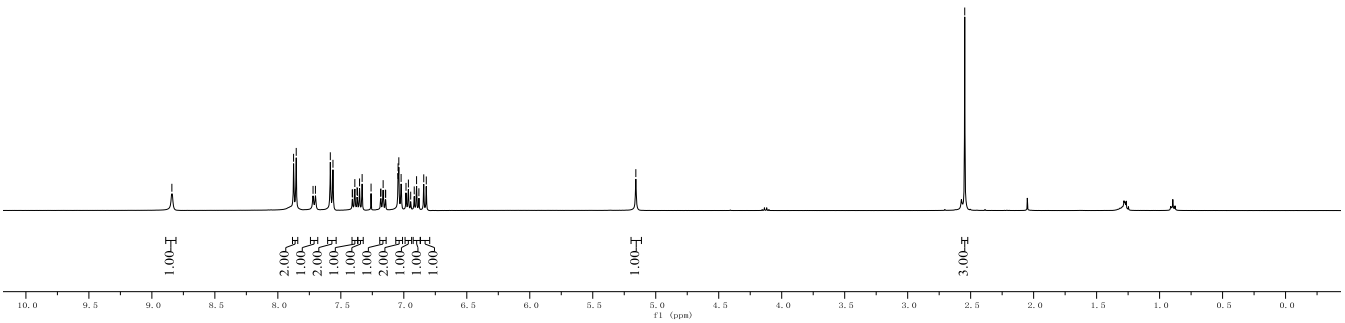
4naa

^{13}C NMR (100 MHz, $CDCl_3$)

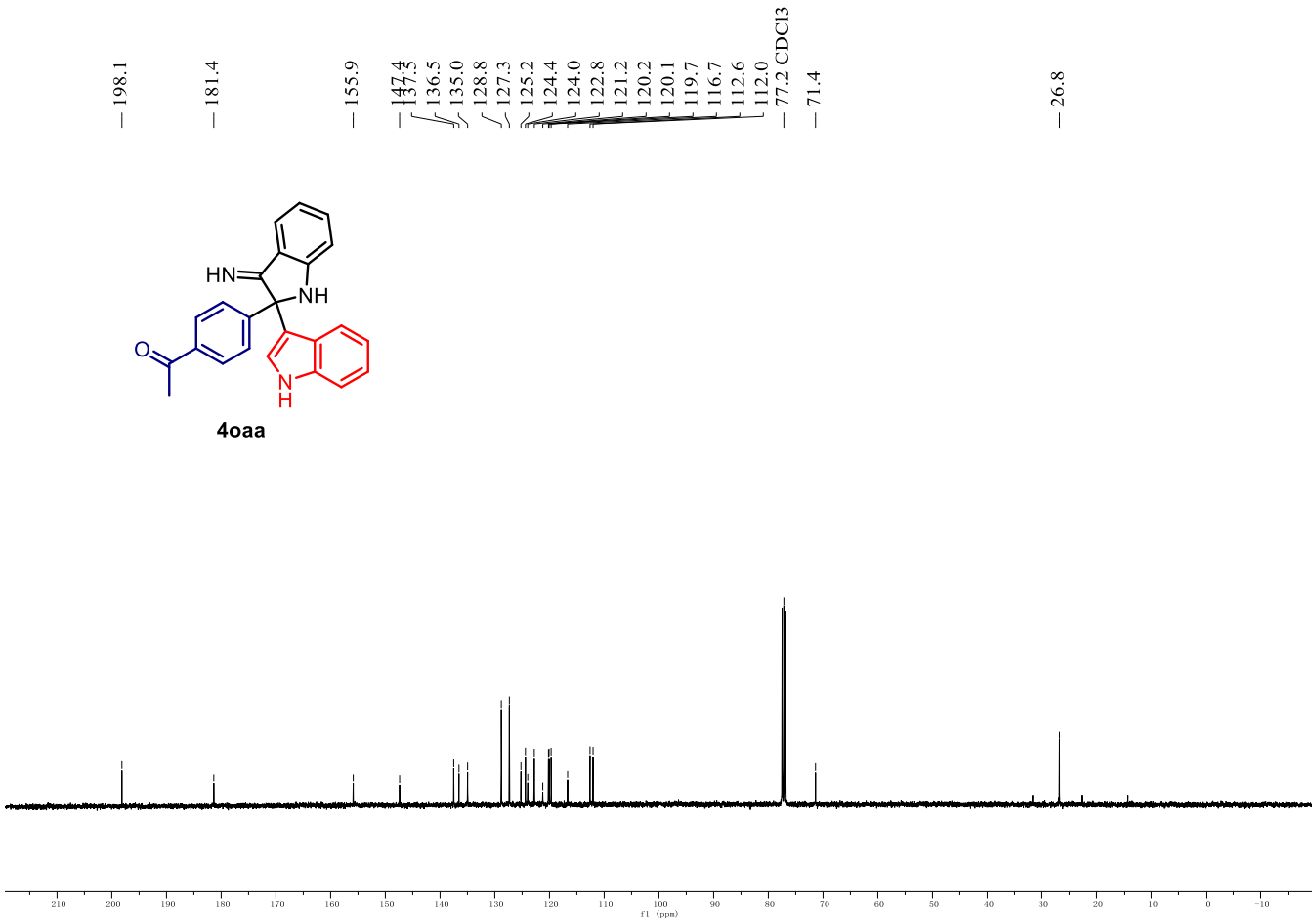




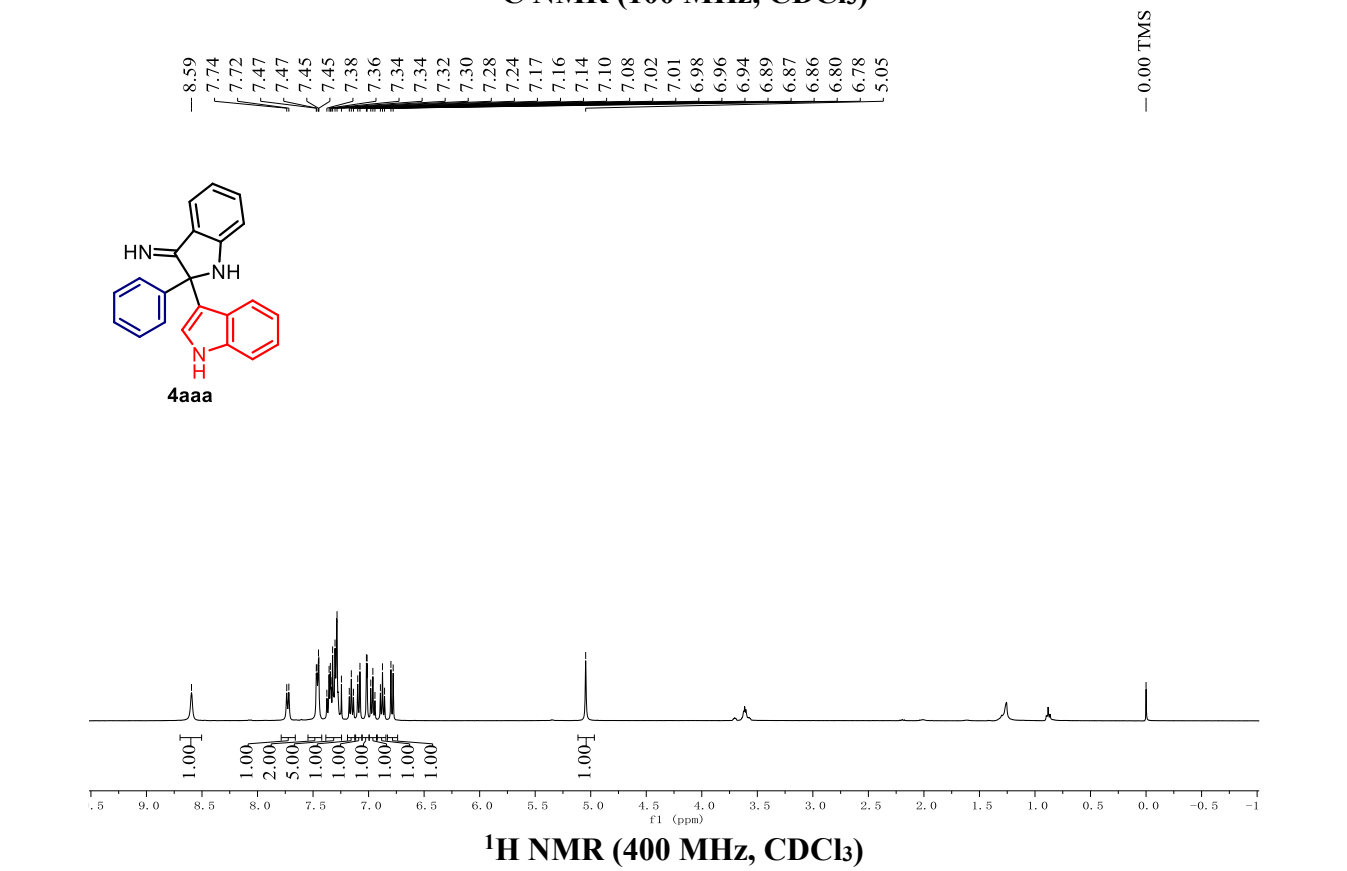
4oaa



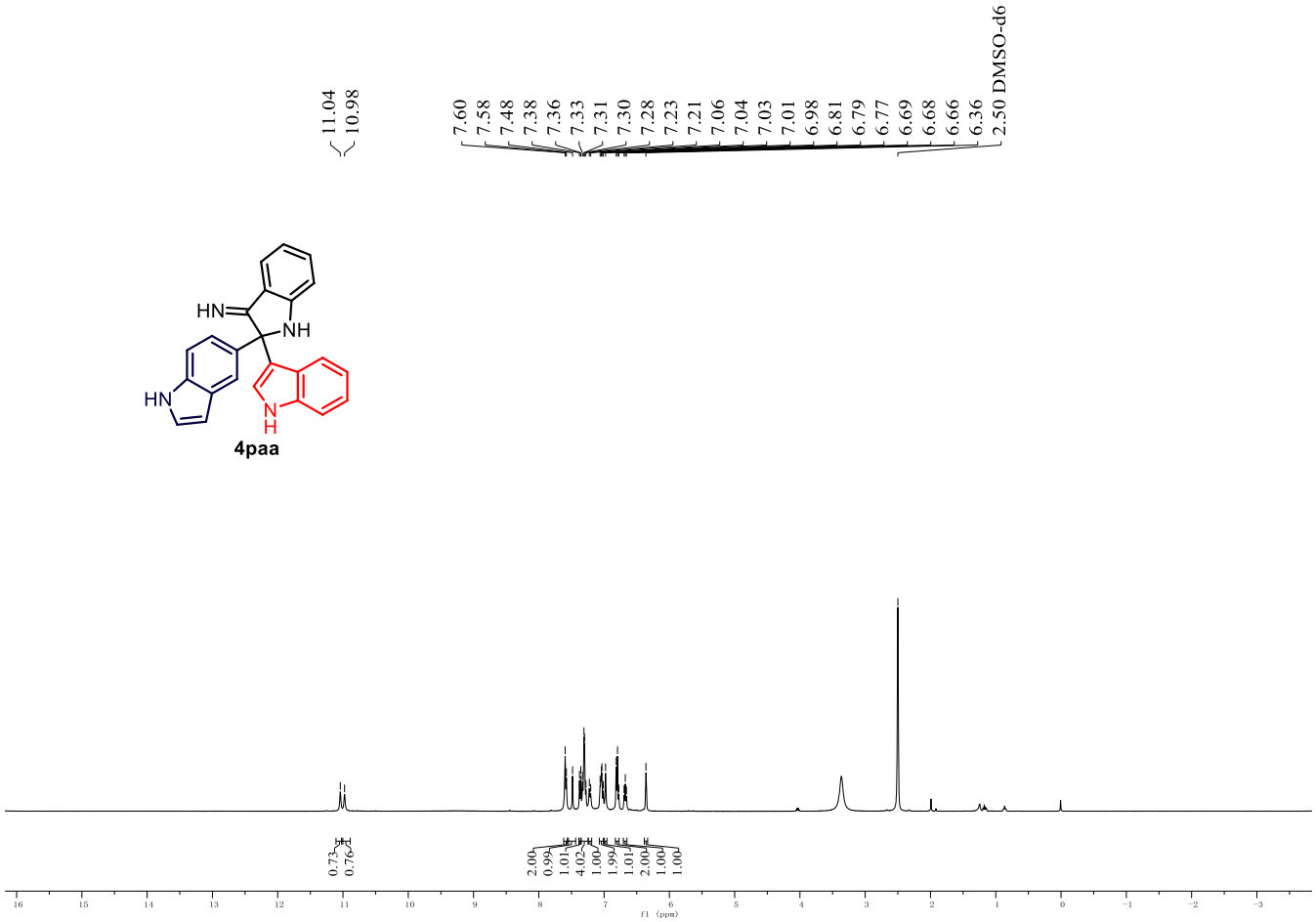
^{1}H NMR (400 MHz, $CDCl_3$)



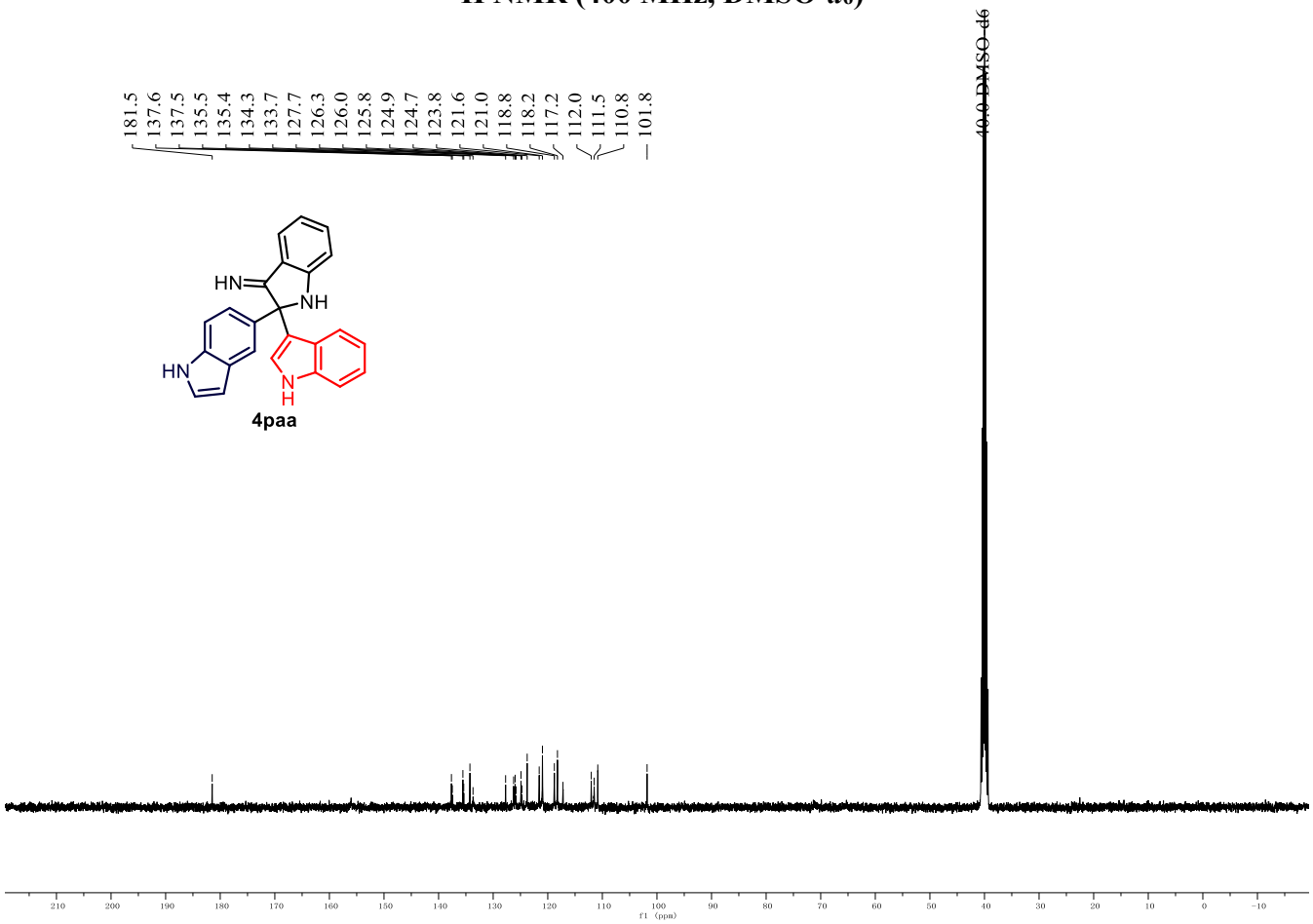
^{13}C NMR (100 MHz, CDCl$_3$)



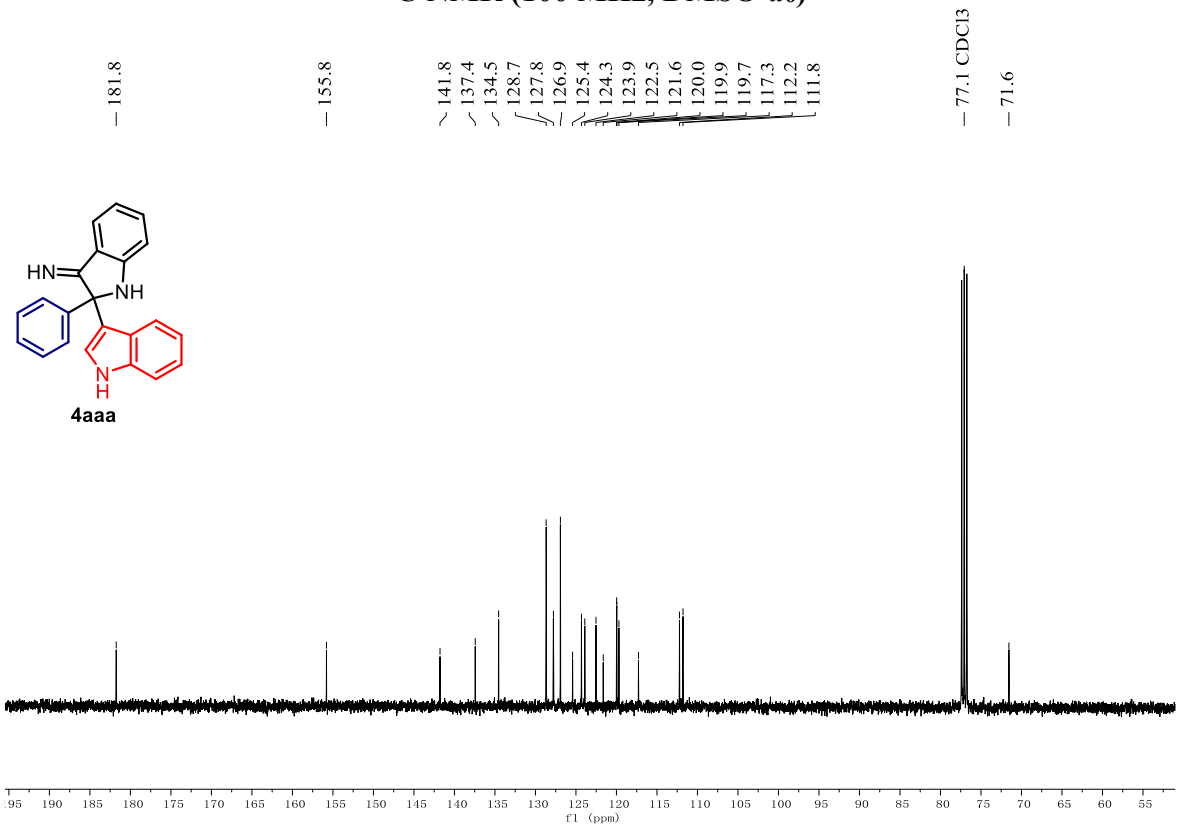
^{1}H NMR (400 MHz, CDCl$_3$)



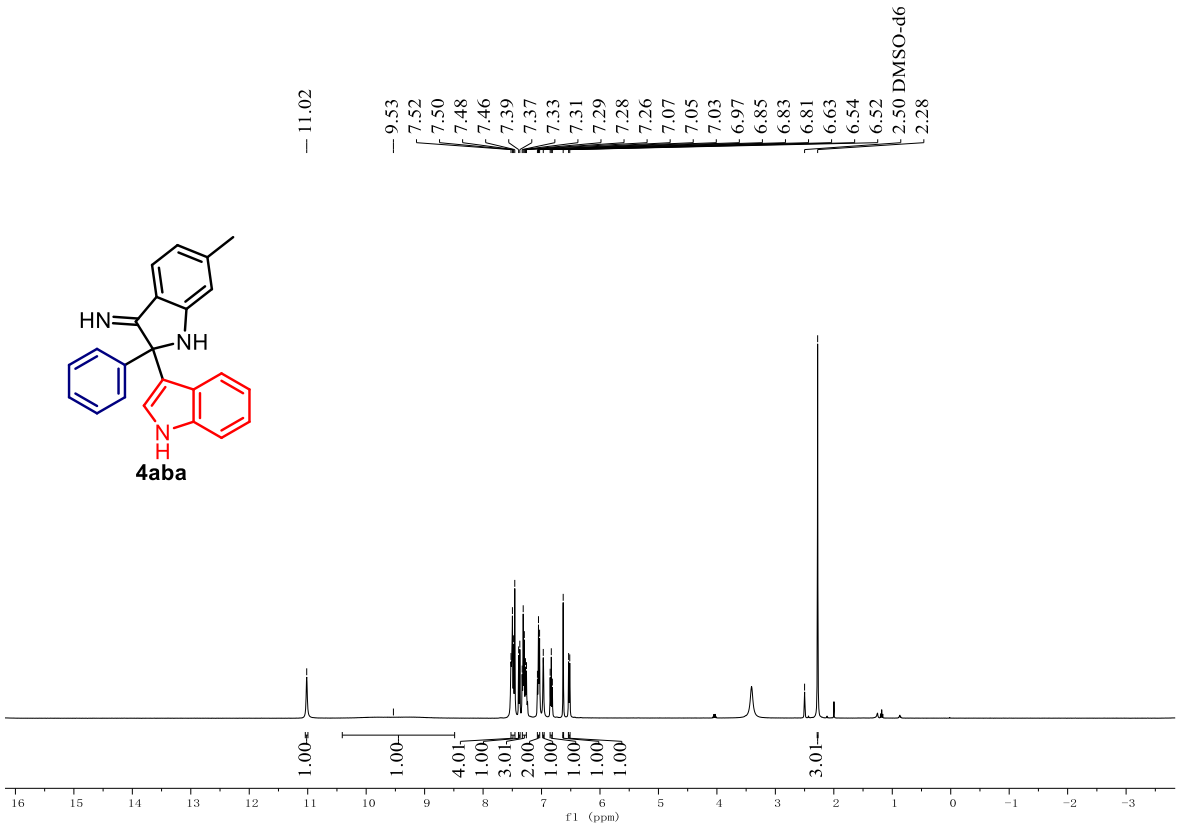
^{1}H NMR (400 MHz, DMSO-d_6)



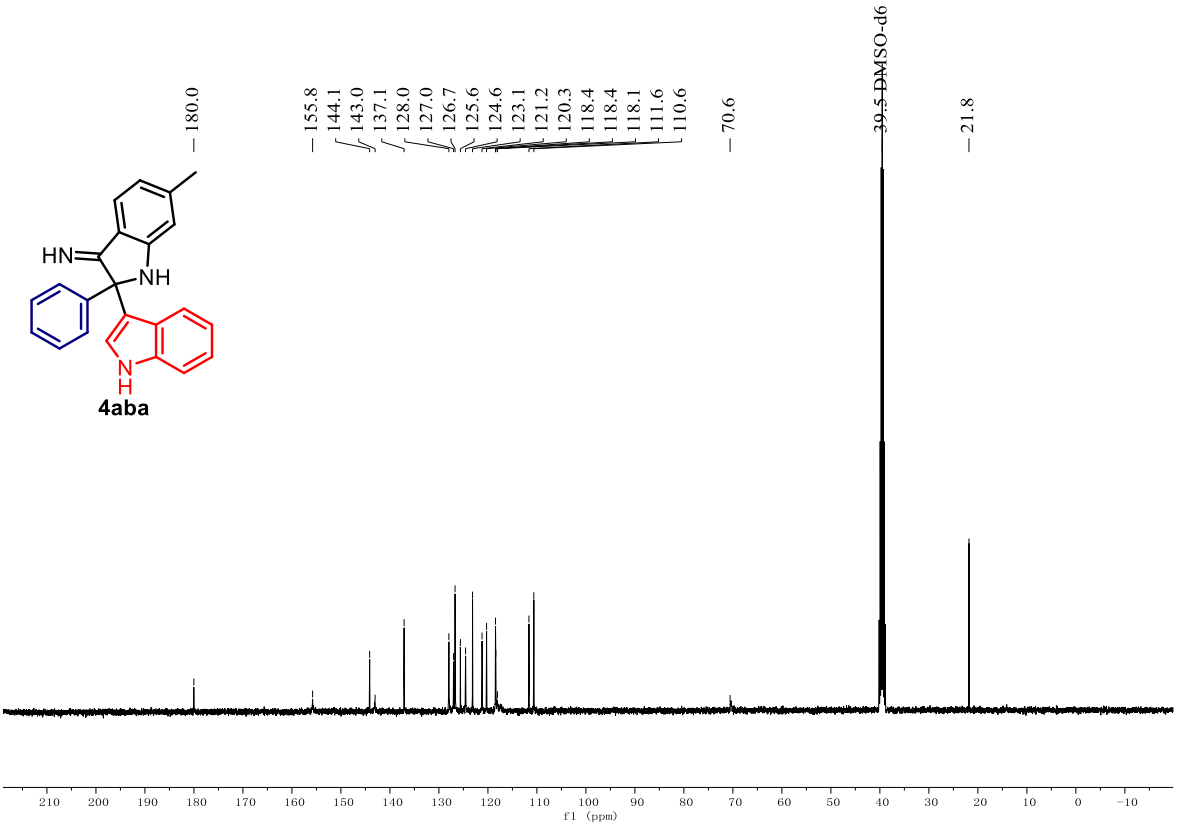
^{13}C NMR (100 MHz, DMSO-*d*$_6$)



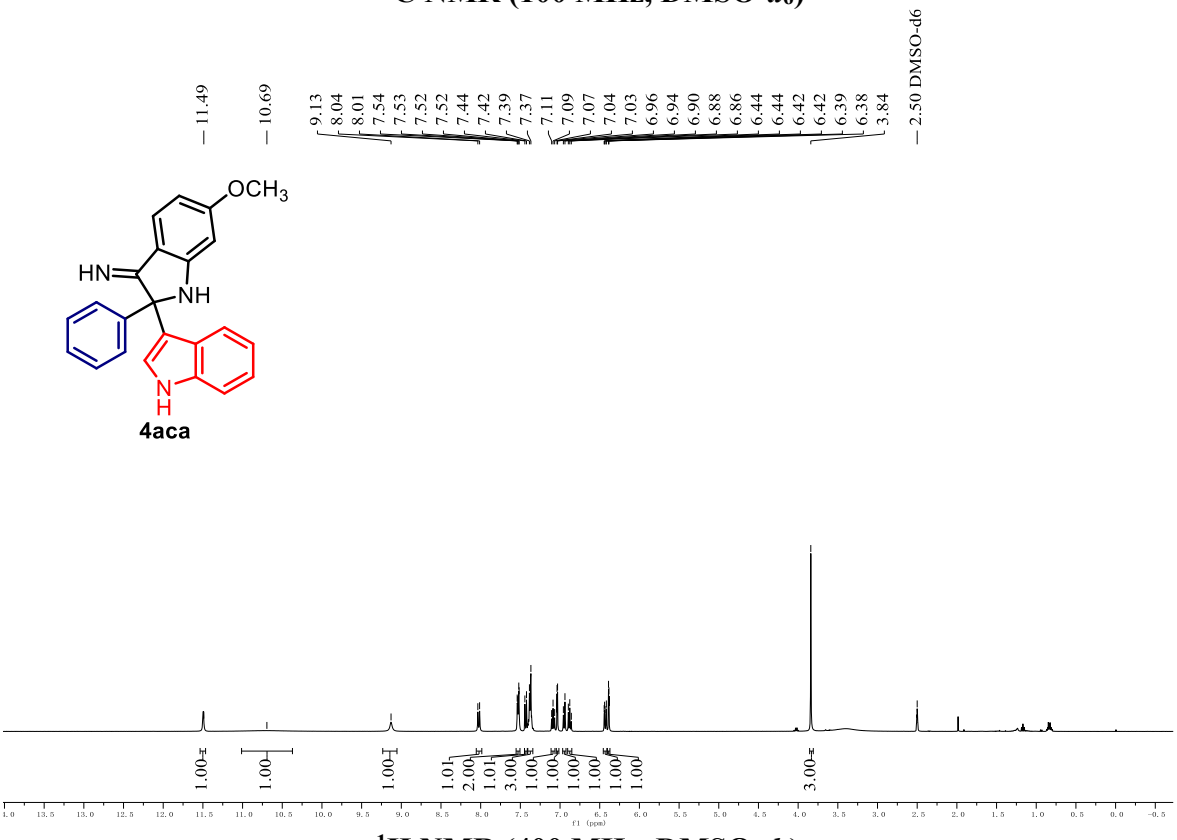
^{13}C NMR (100 MHz, CDCl$_3$)



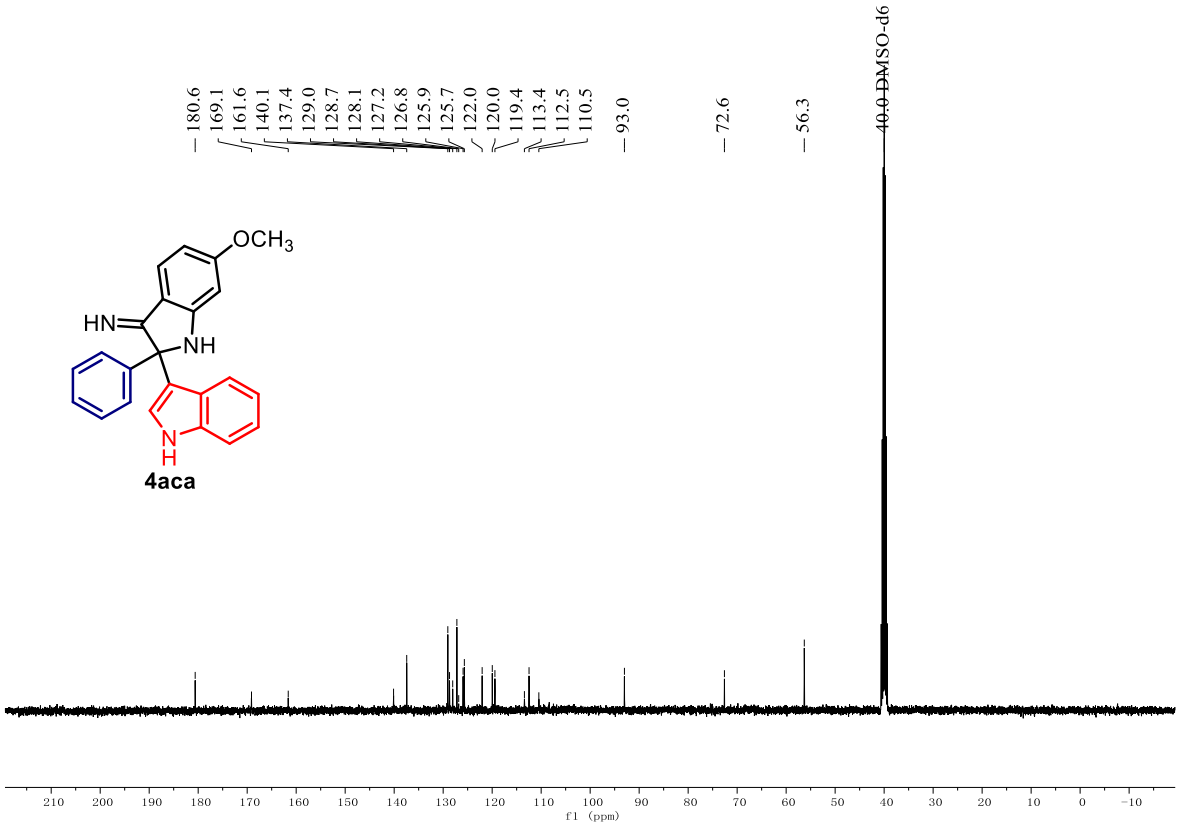
^{1}H NMR (400 MHz, DMSO-*d*$_6$)



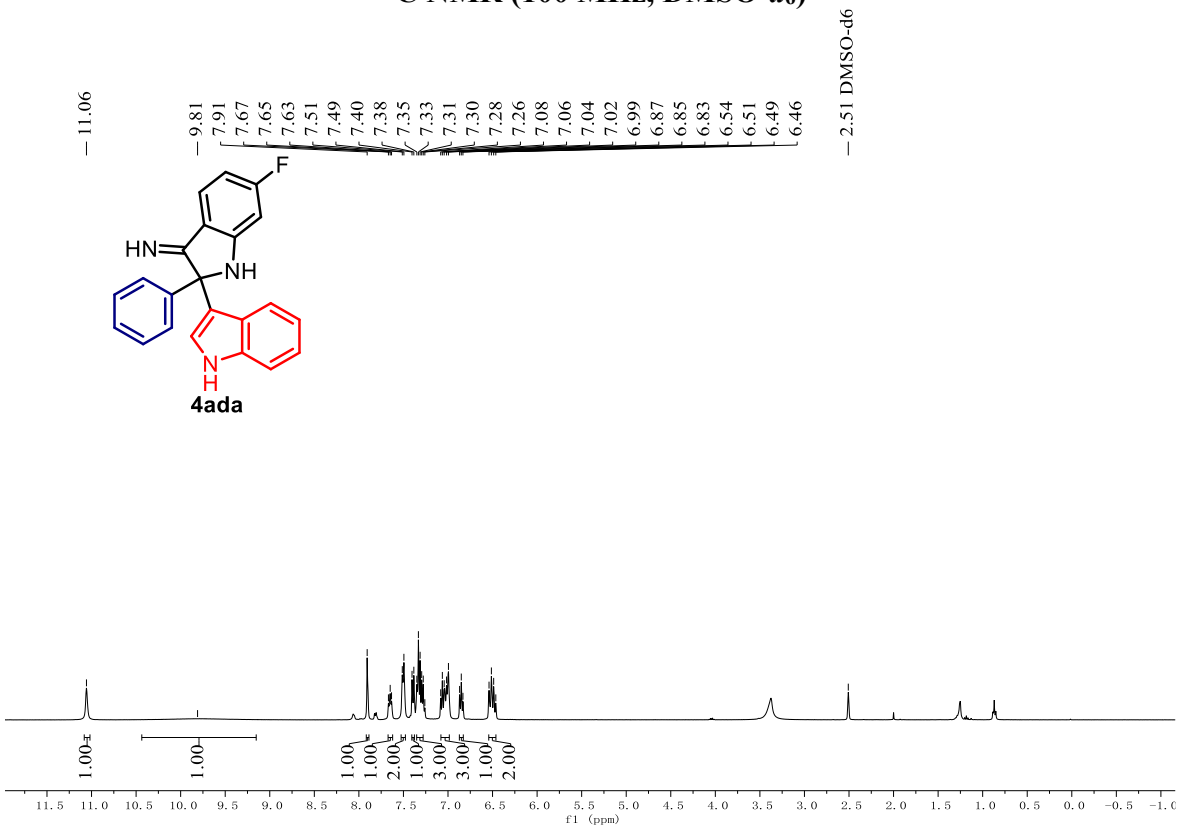
^{13}C NMR (100 MHz, DMSO-*d*$_6$)



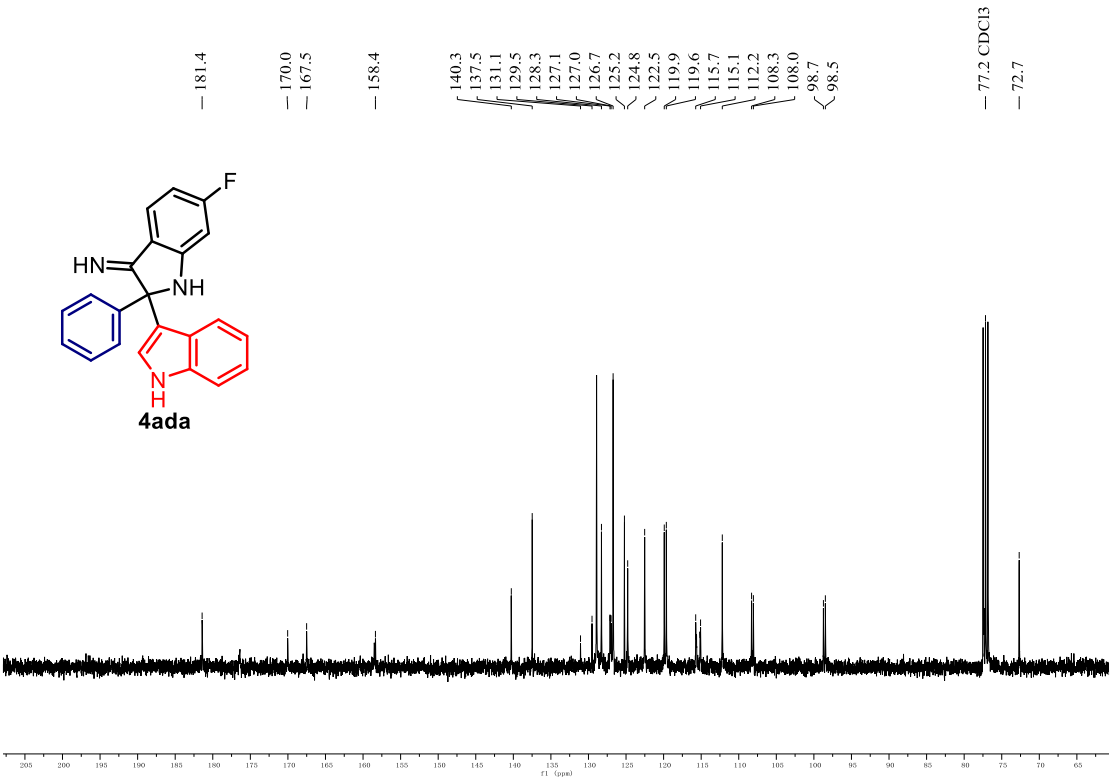
^{1}H NMR (400 MHz, DMSO-*d*$_6$)



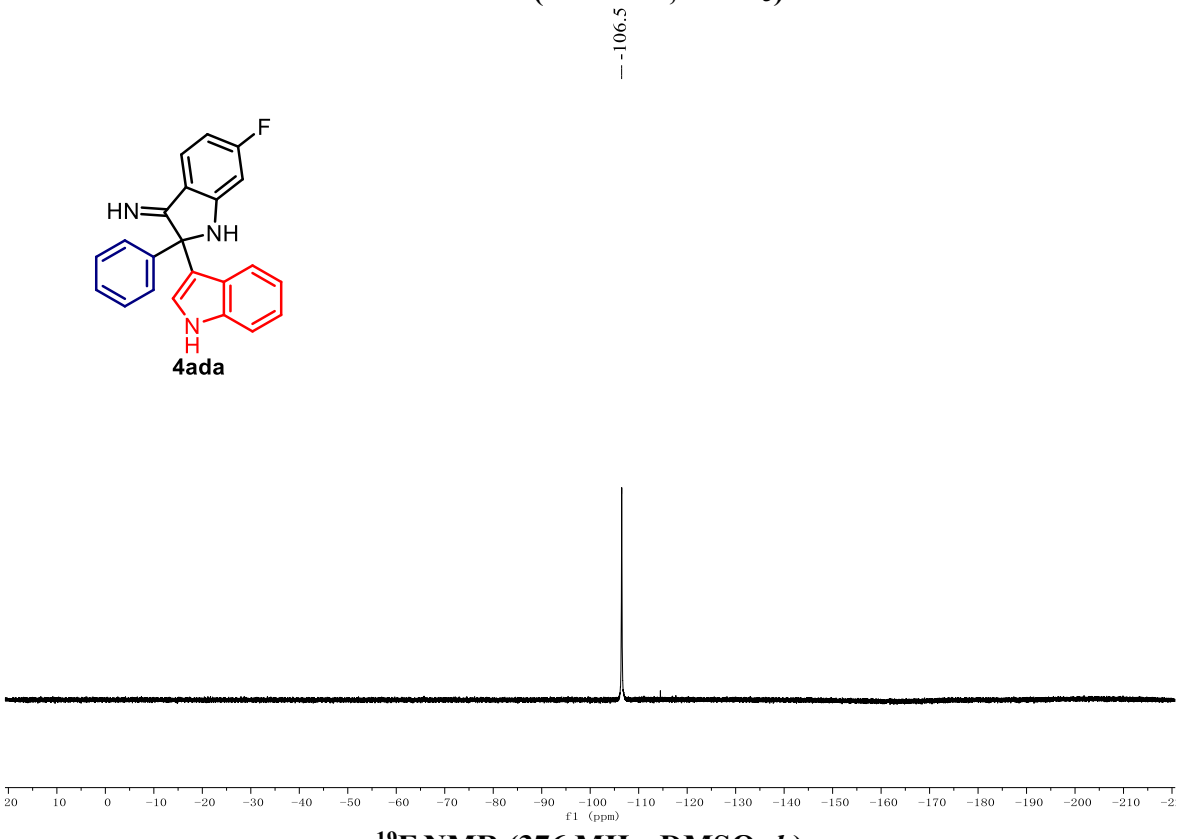
^{13}C NMR (100 MHz, DMSO-*d*$_6$)



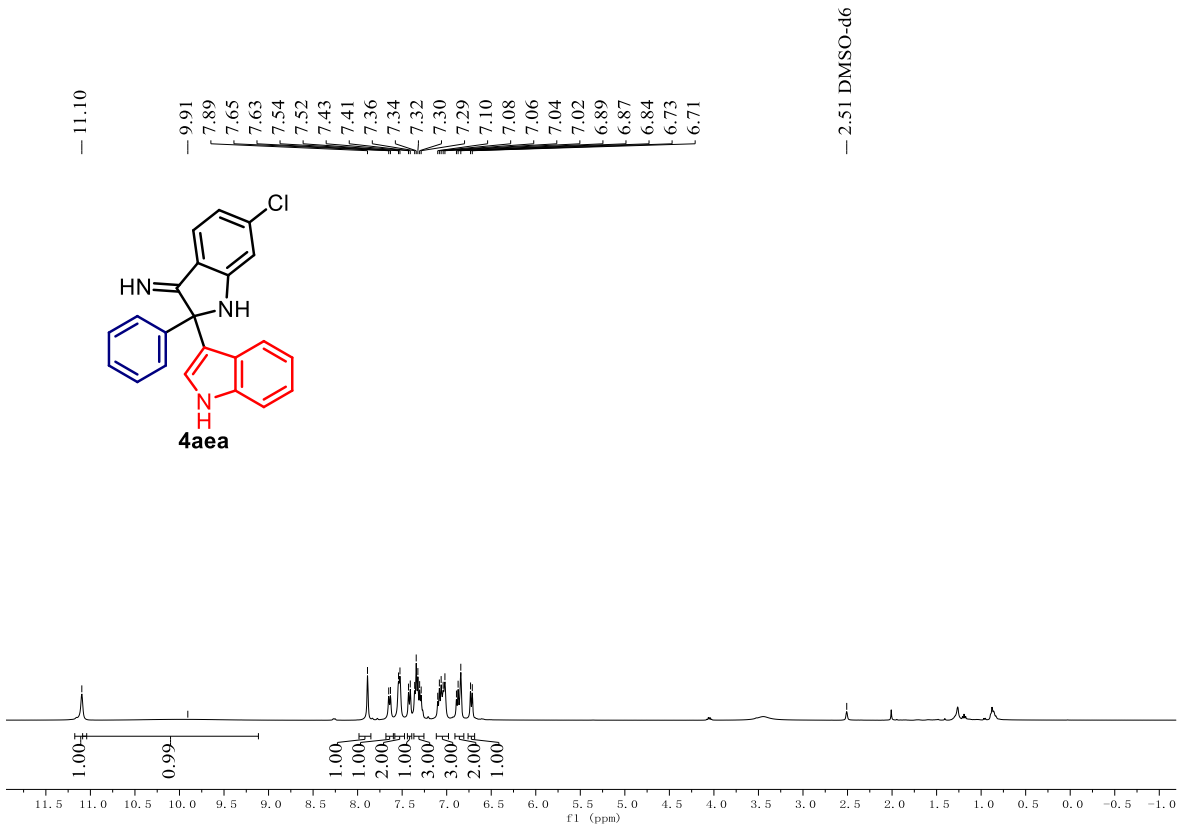
^{1}H NMR (400 MHz, DMSO-*d*$_6$)



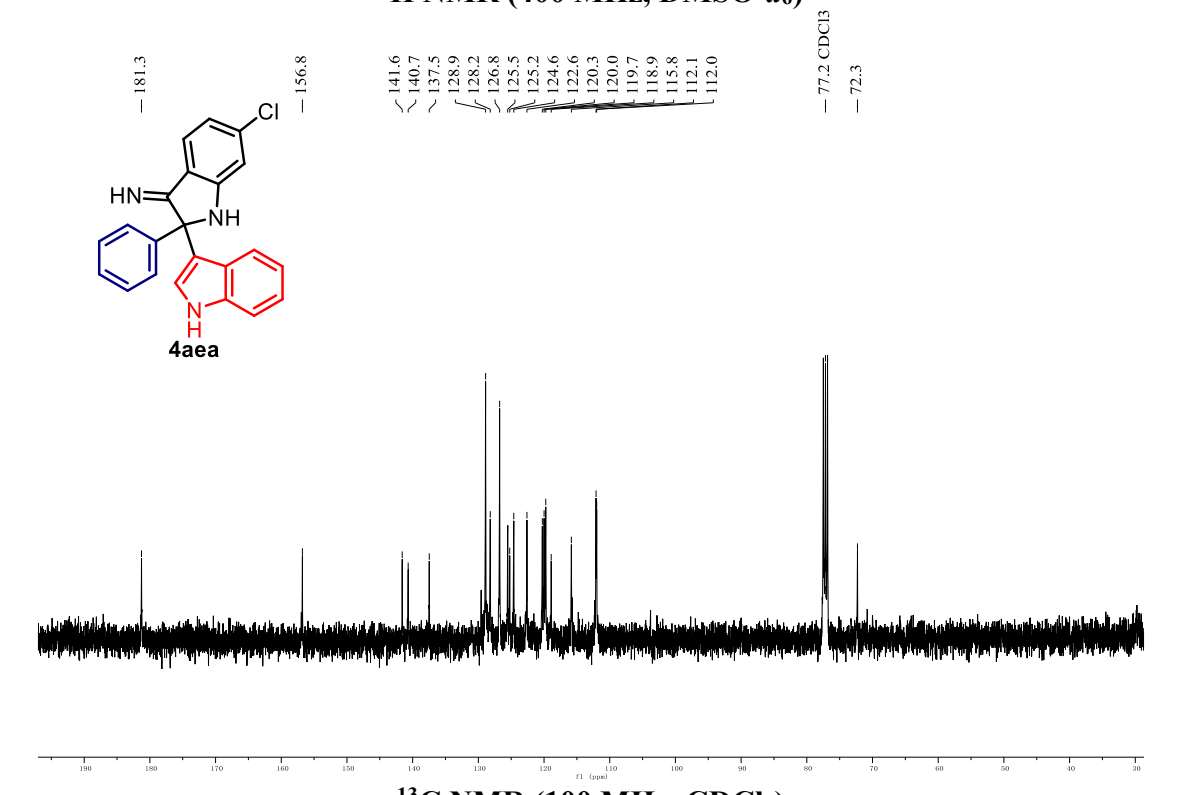
^{13}C NMR (100 MHz, $CDCl_3$)



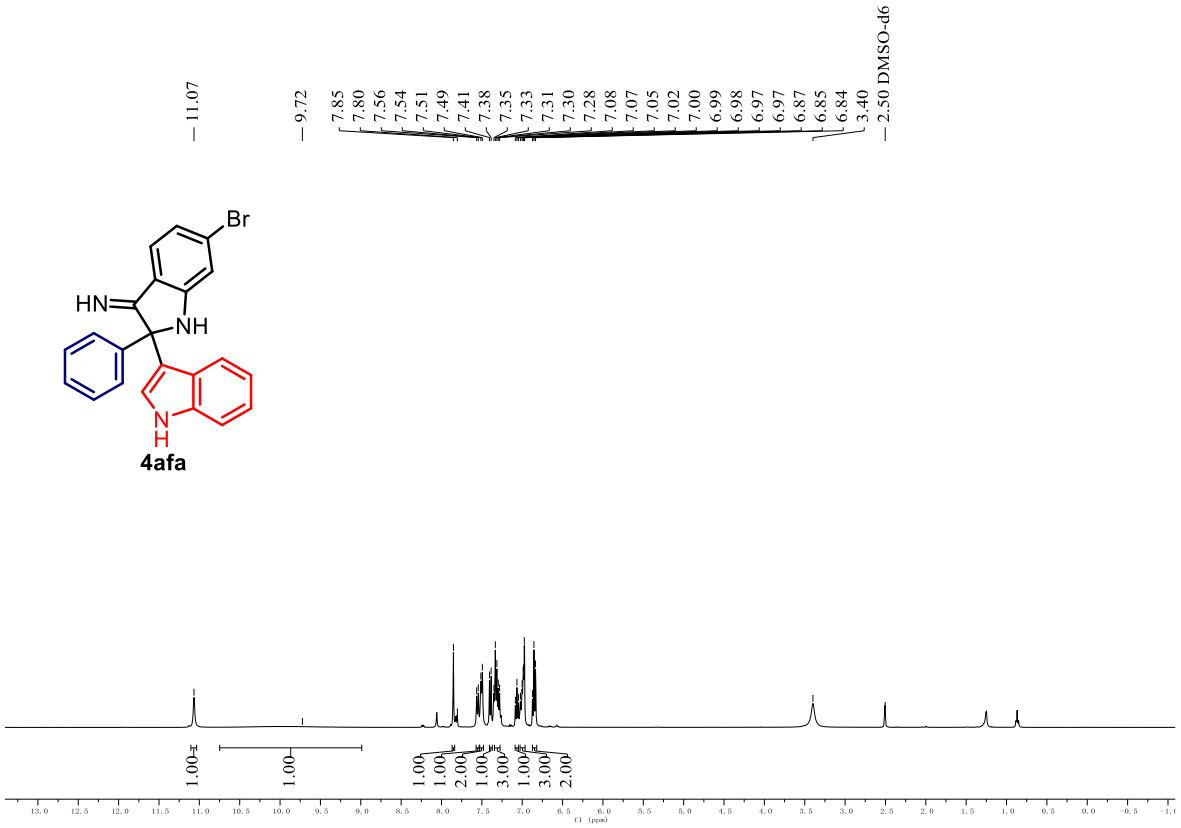
^{19}F NMR (376 MHz, DMSO-d_6)



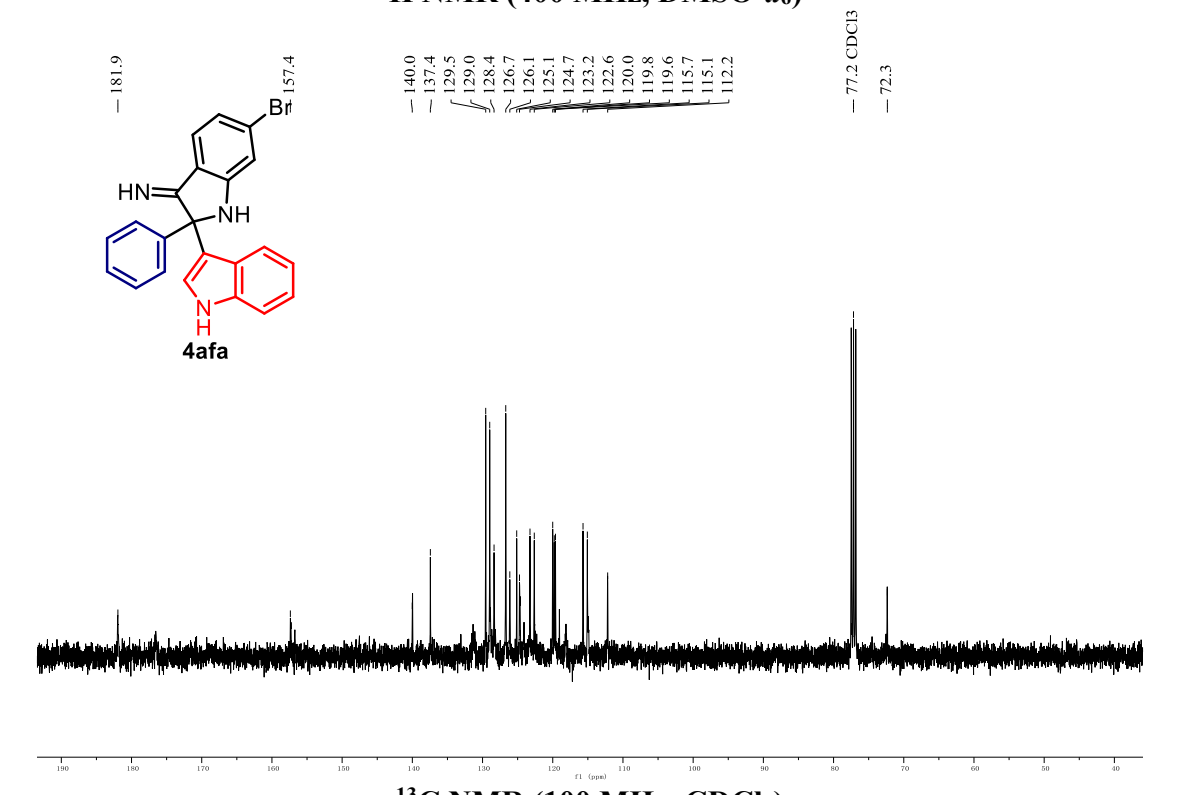
^{1}H NMR (400 MHz, DMSO-d_6)



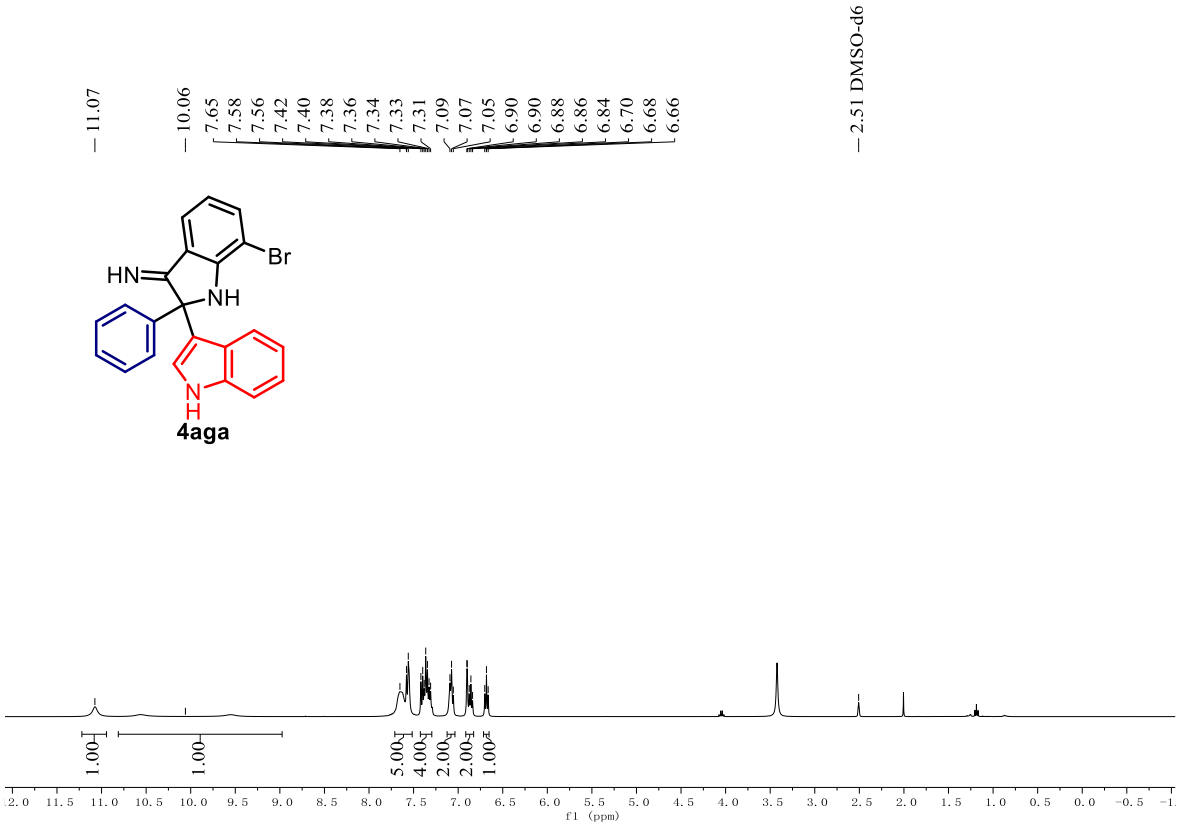
^{13}C NMR (100 MHz, $CDCl_3$)



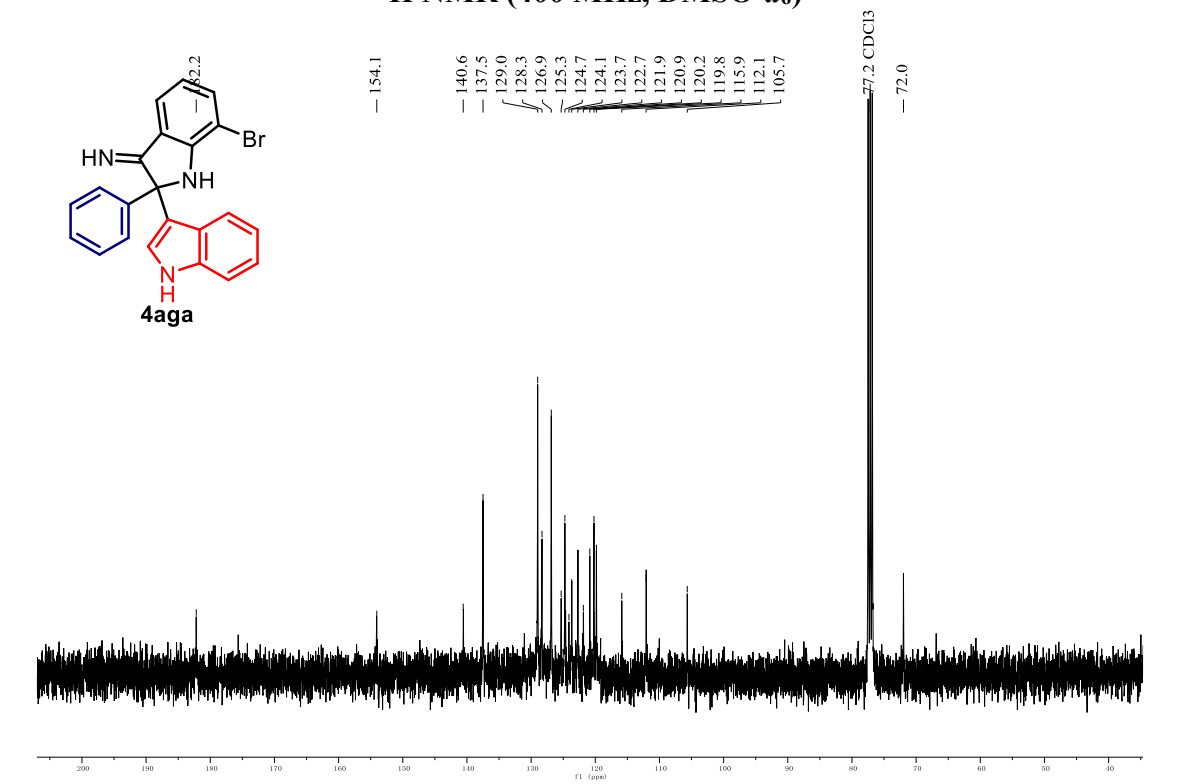
^{1}H NMR (400 MHz, DMSO-d_6)



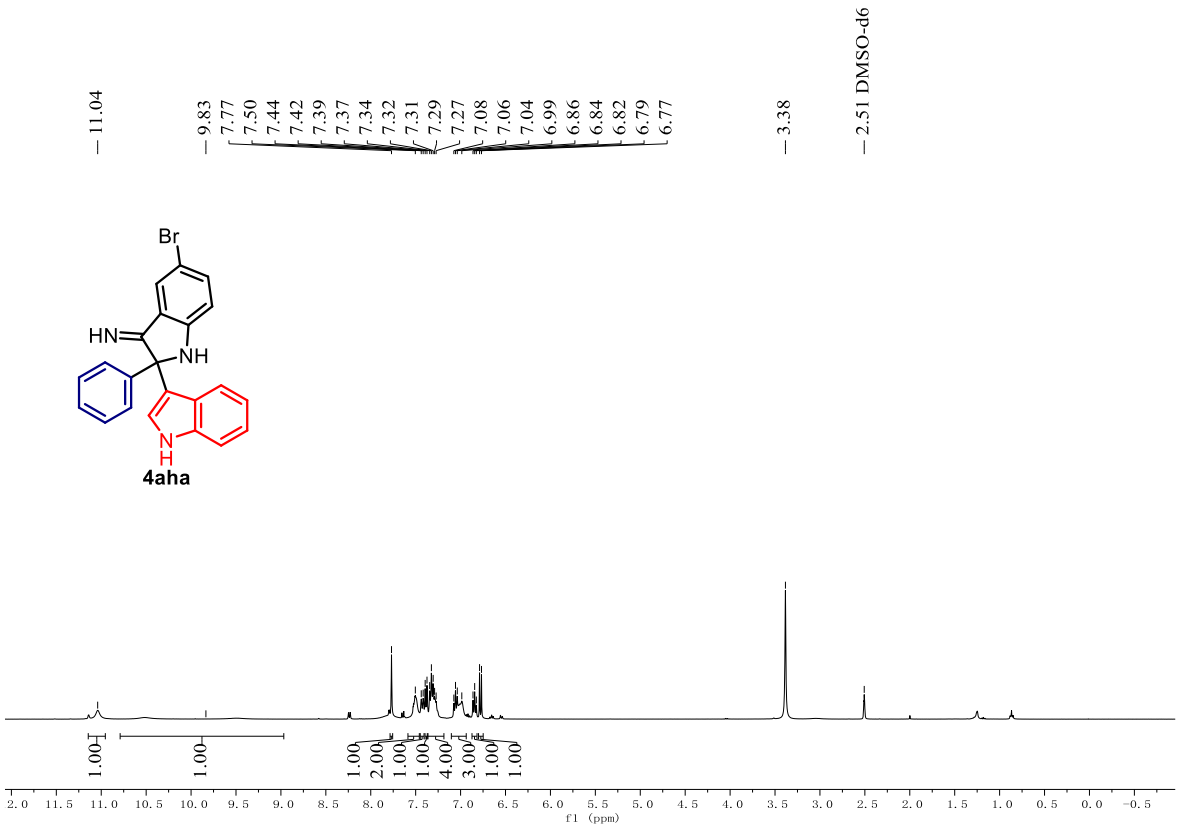
^{13}C NMR (100 MHz, $CDCl_3$)



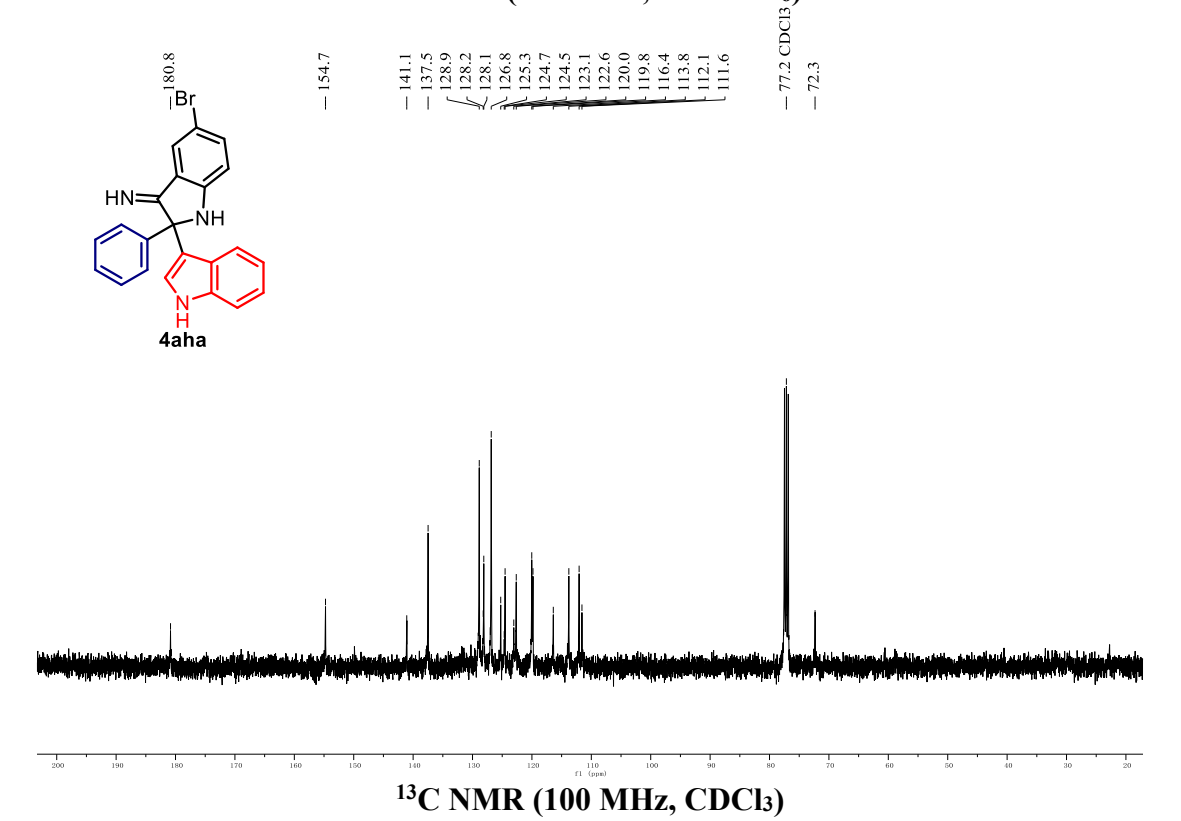
^{1}H NMR (400 MHz, DMSO-d_6)



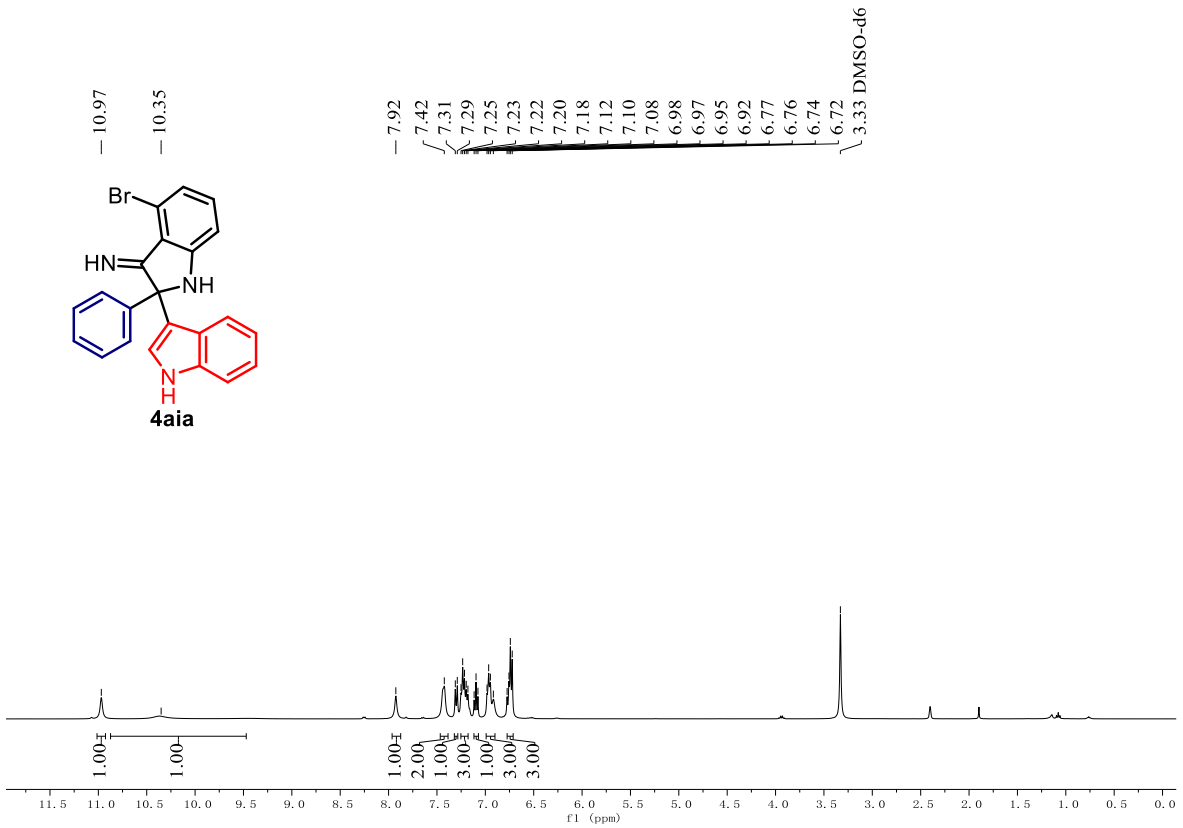
^{13}C NMR (100 MHz, $CDCl_3$)



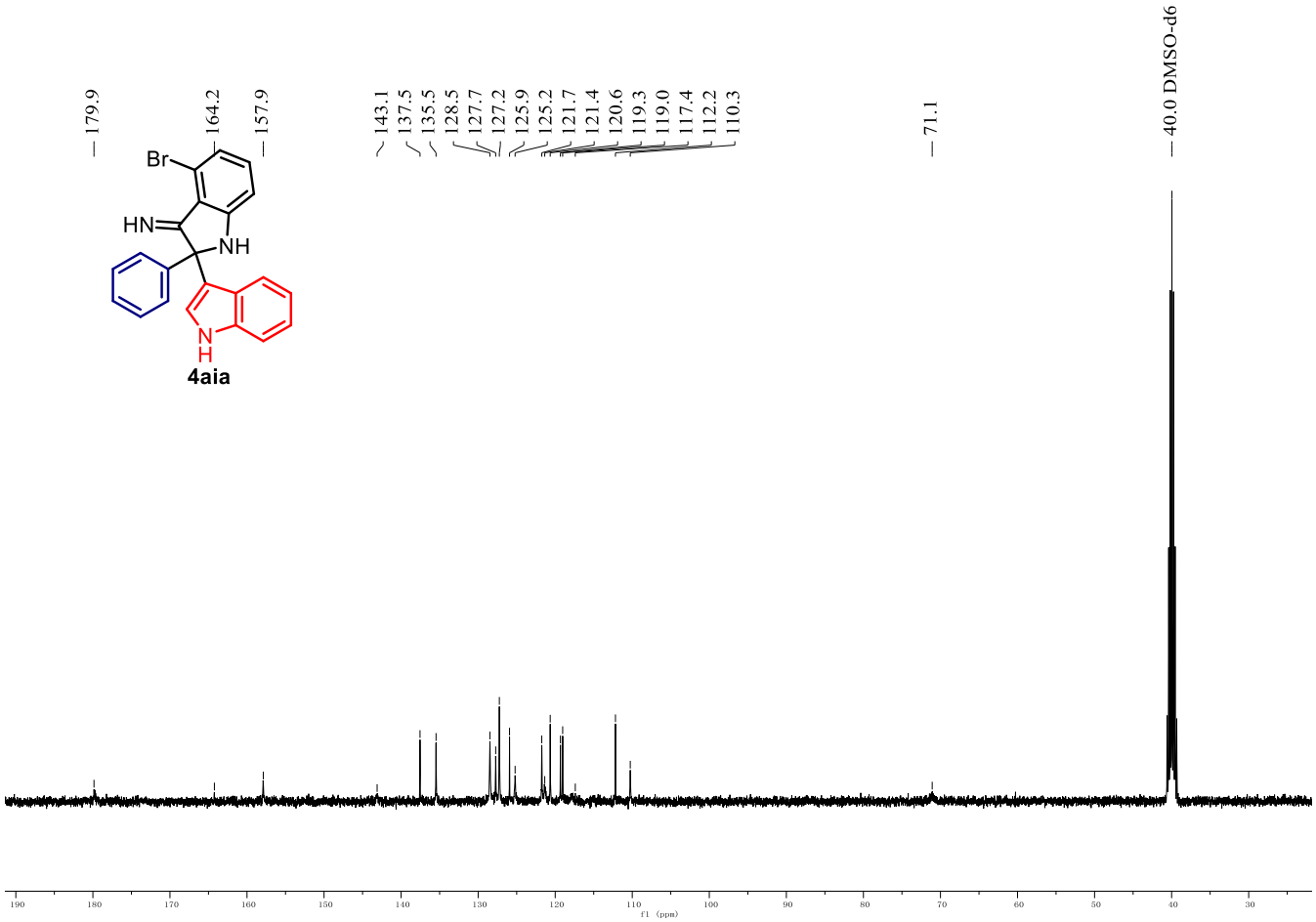
^{1}H NMR (400 MHz, DMSO-d_6)



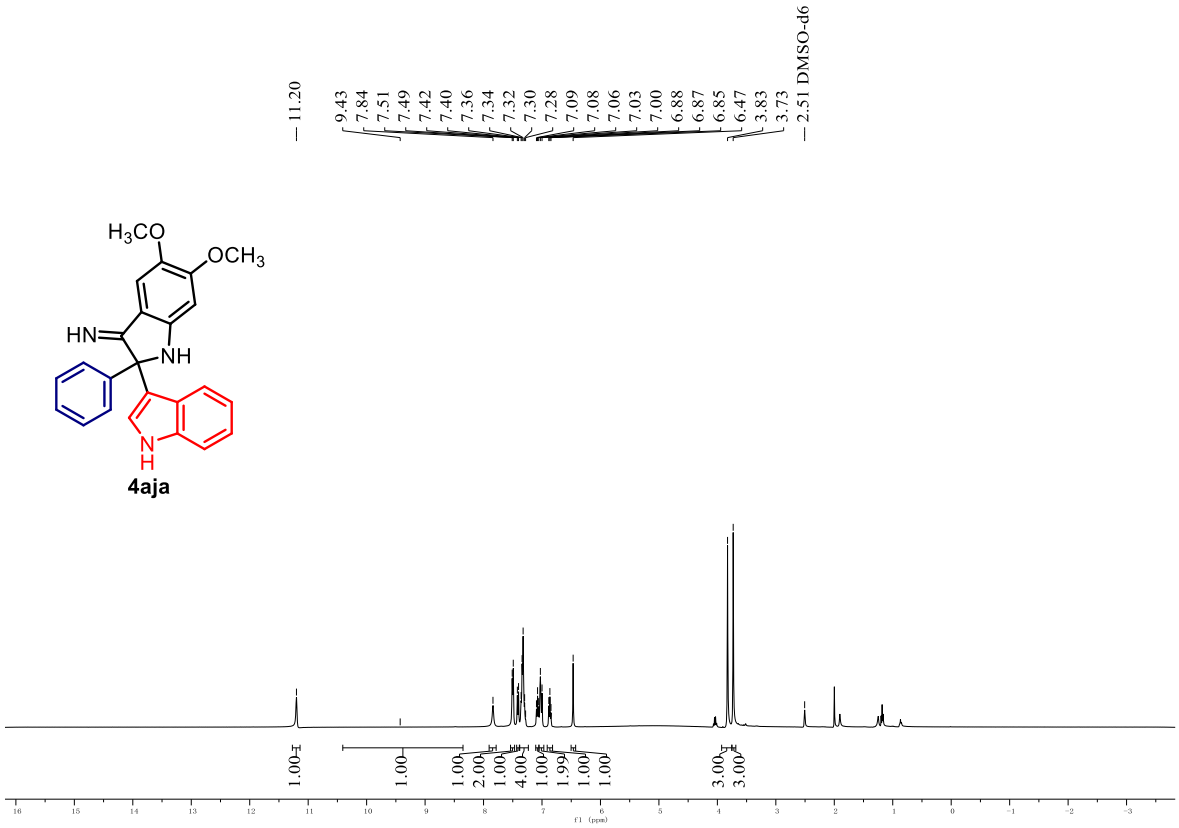
^{13}C NMR (100 MHz, $CDCl_3$)



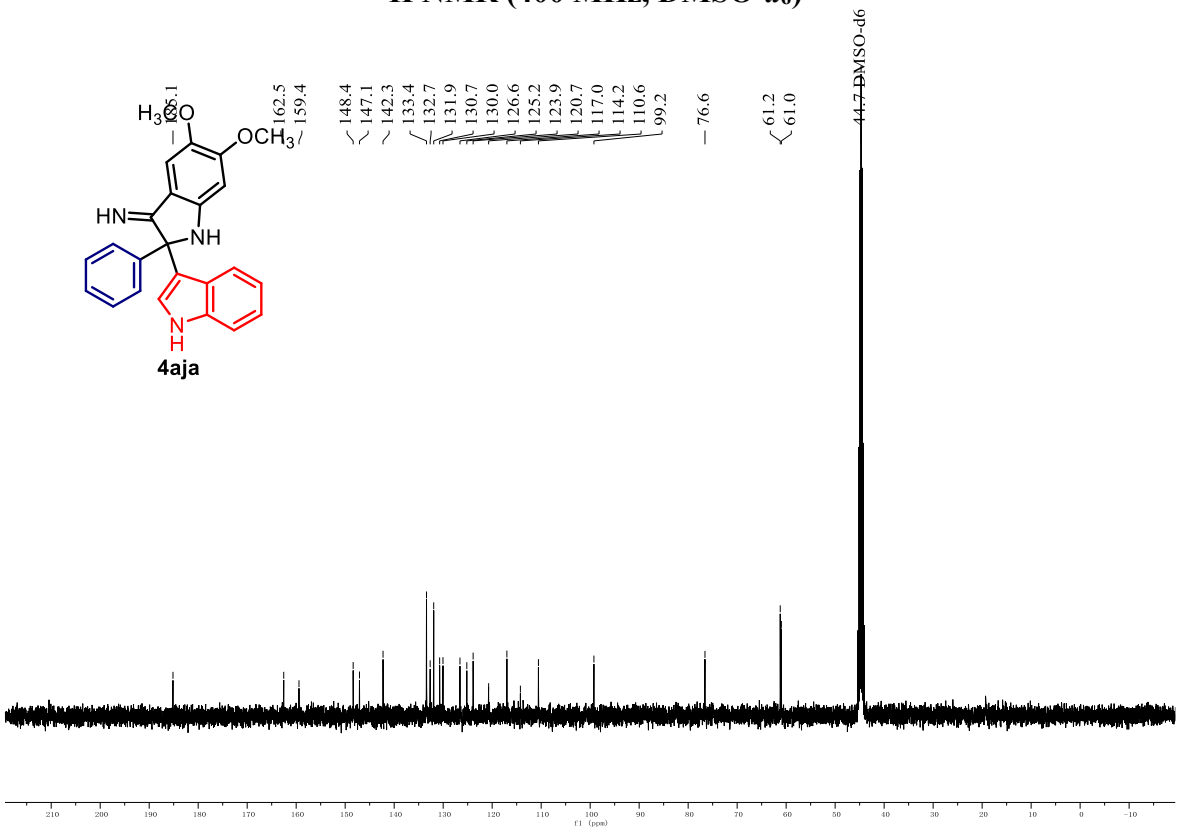
^{1}H NMR (400 MHz, DMSO-d_6)



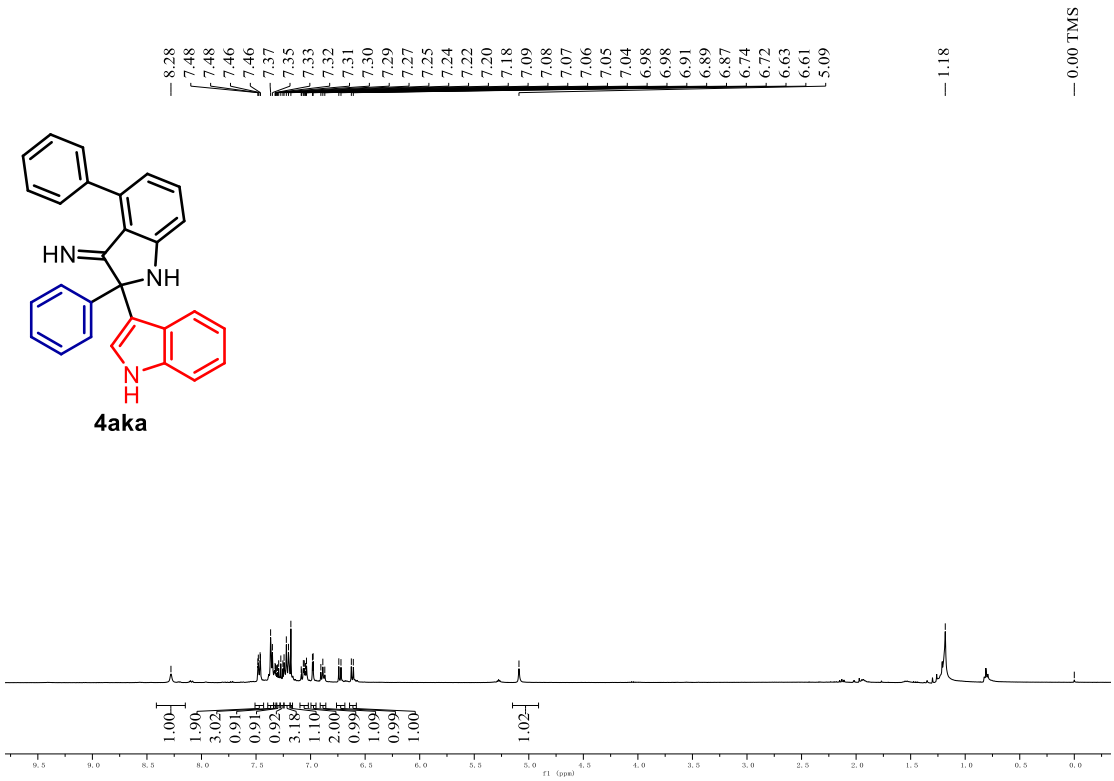
^{13}C NMR (100 MHz, DMSO-d_6)



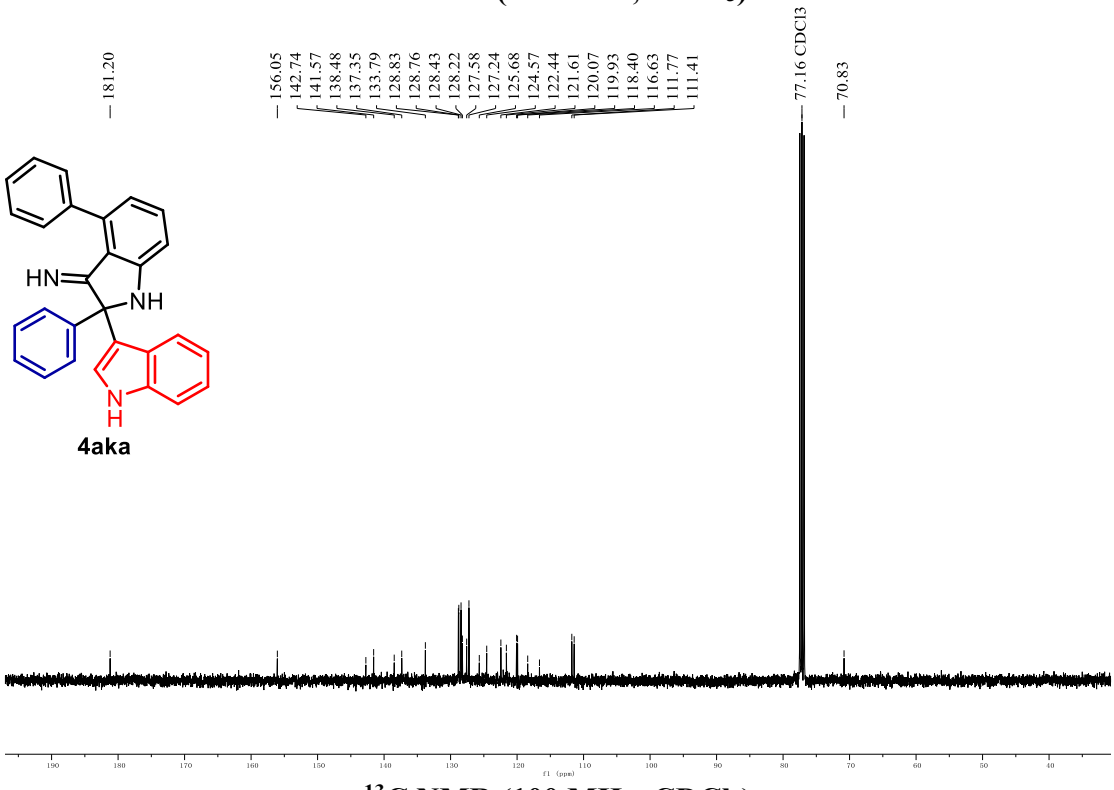
^{1}H NMR (400 MHz, DMSO-*d*$_6$)



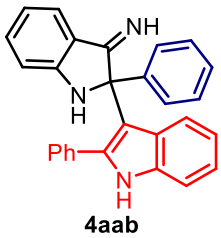
^{13}C NMR (100 MHz, DMSO-*d*$_6$)

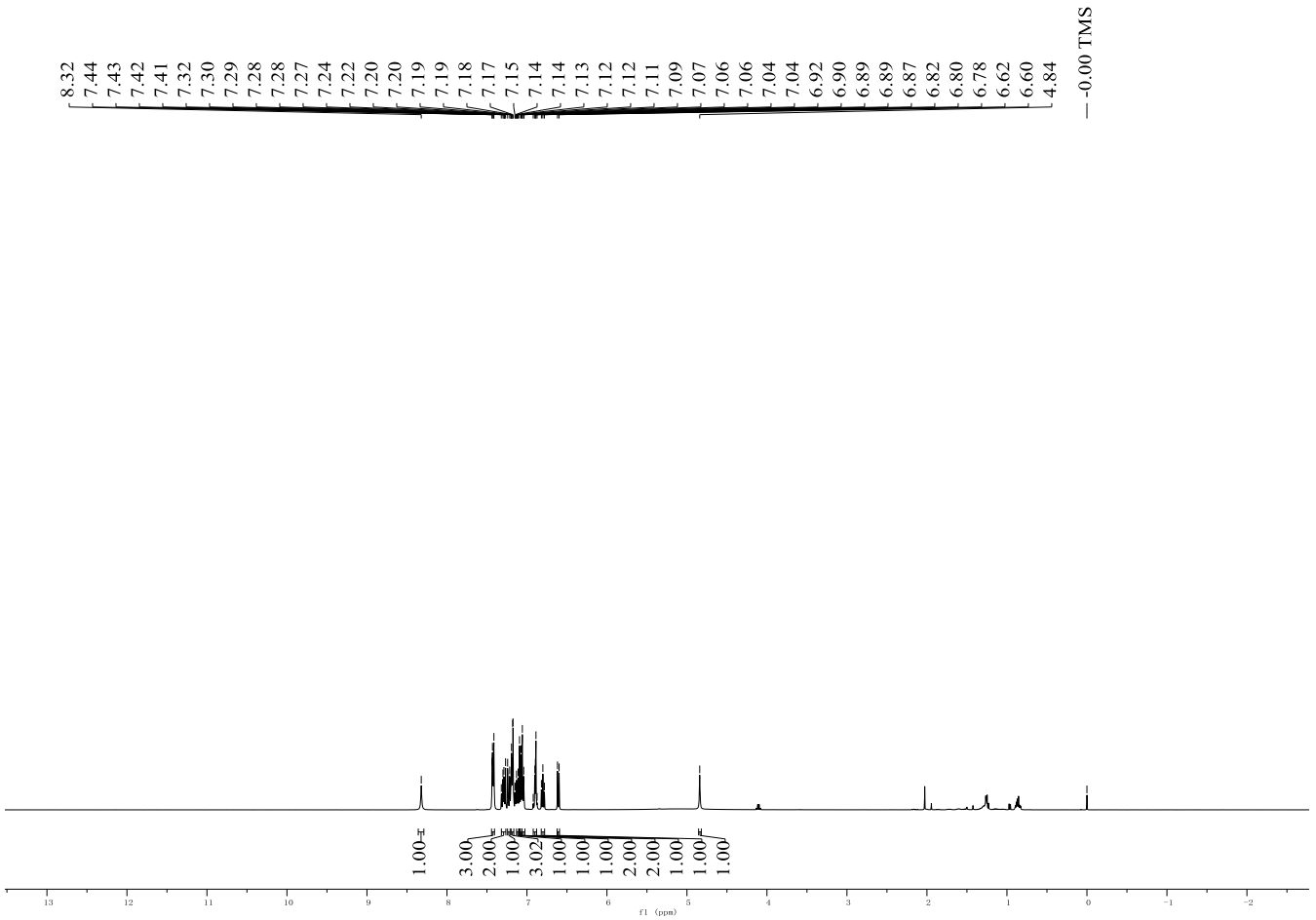


^{1}H NMR (400 MHz, $CDCl_3$)

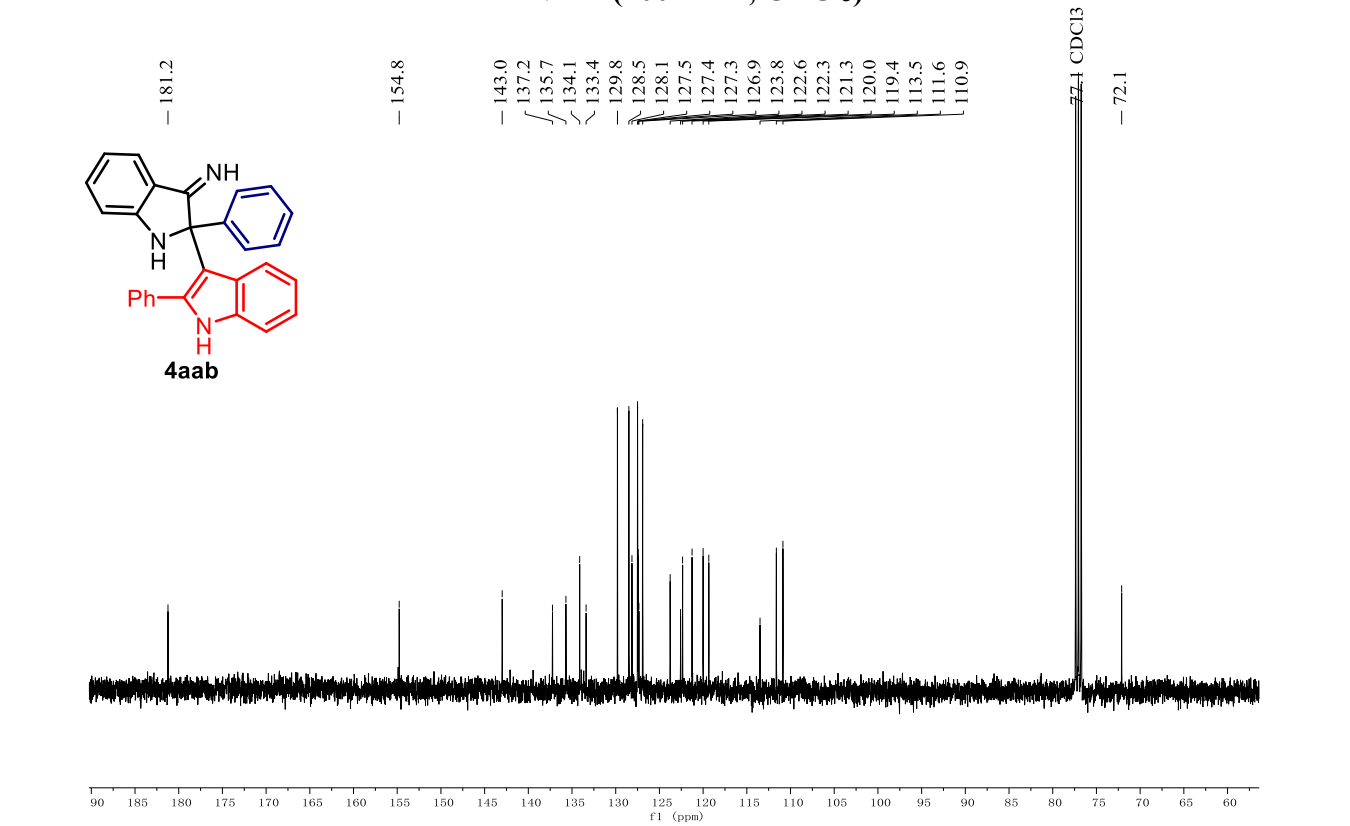


^{13}C NMR (100 MHz, $CDCl_3$)

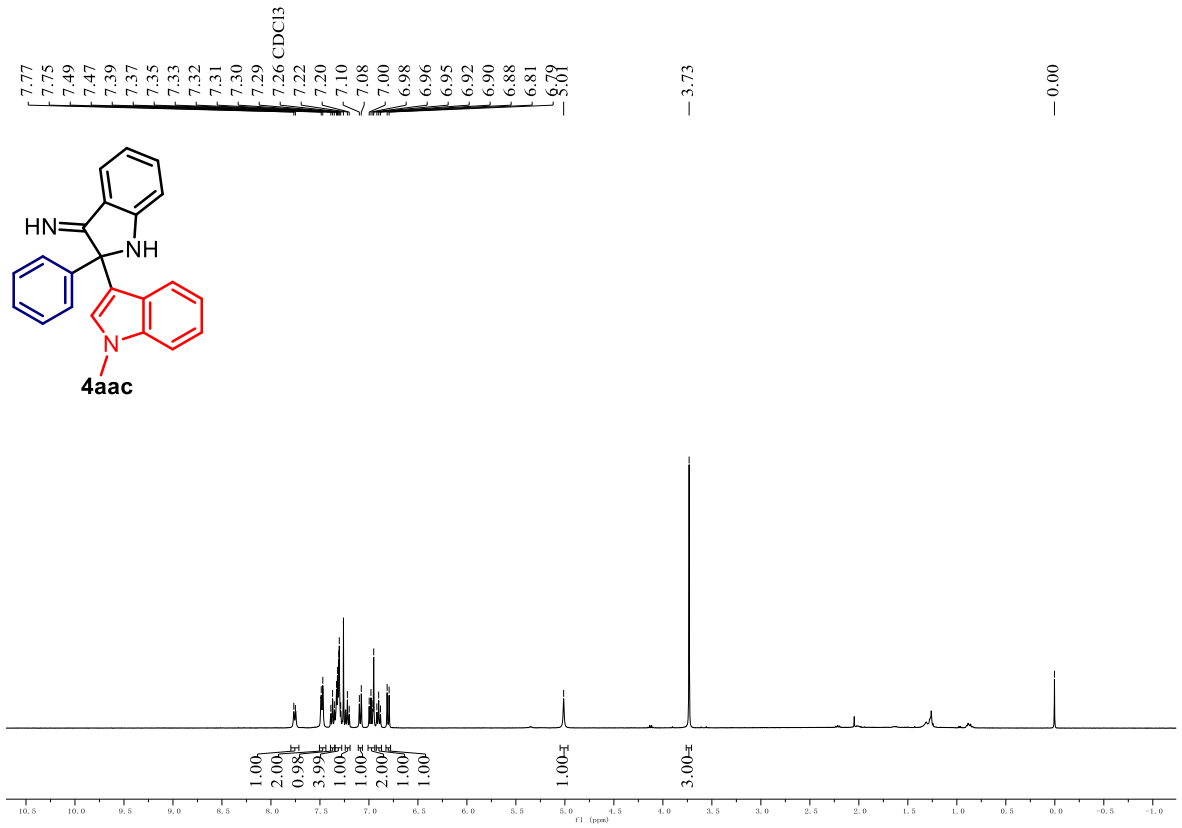




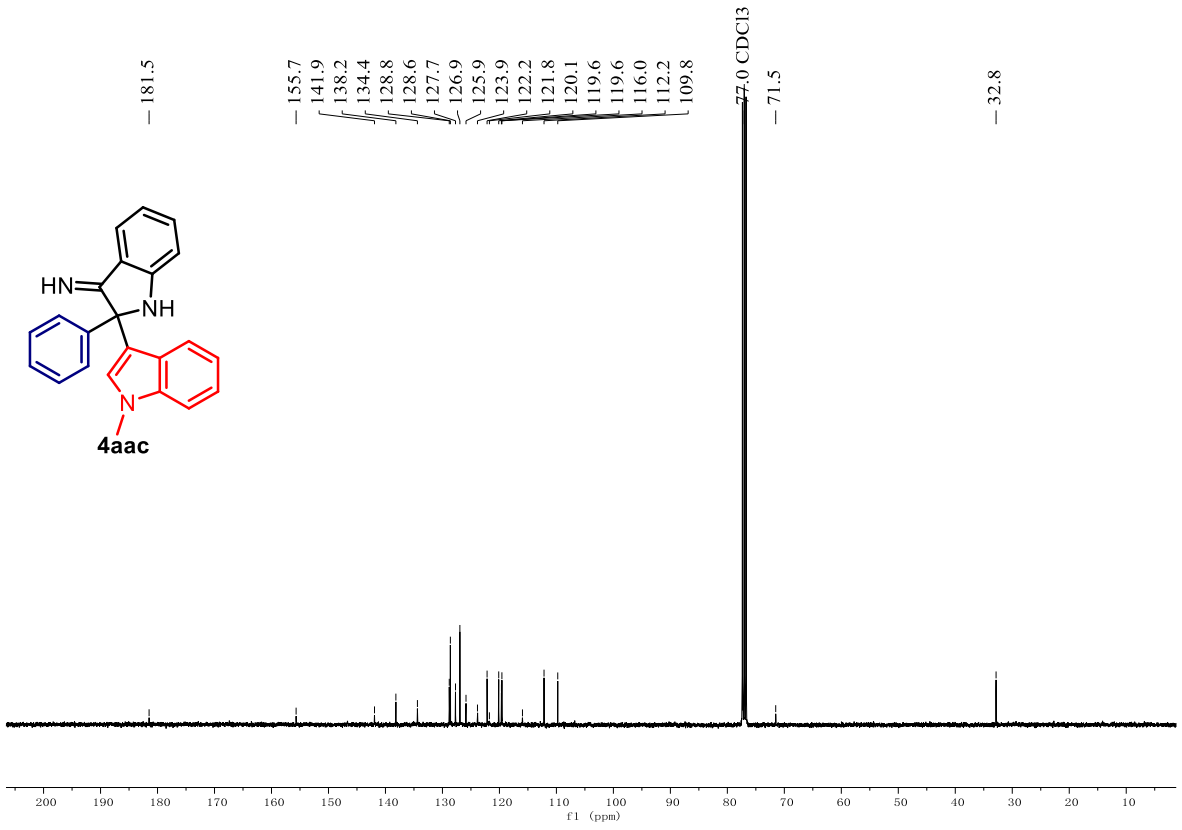
^{1}H NMR (400 MHz, $CDCl_3$)



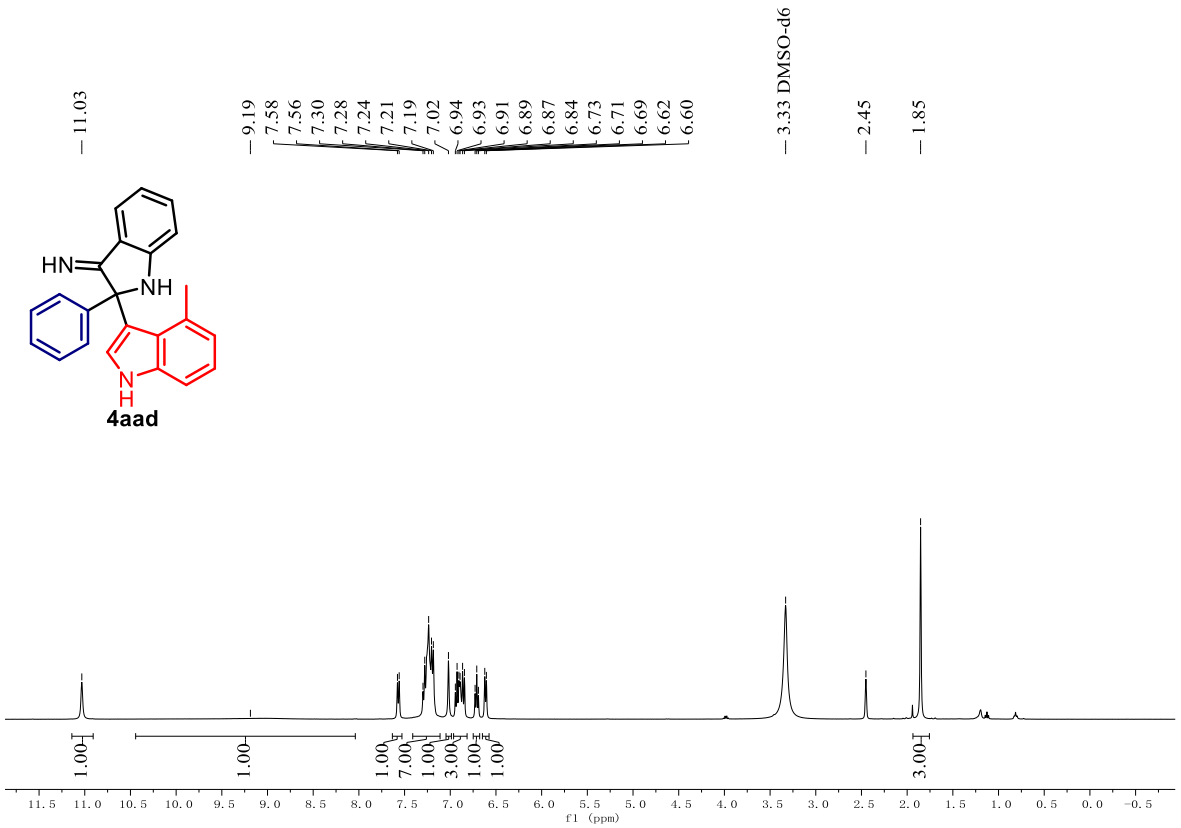
^{13}C NMR (100 MHz, $CDCl_3$)



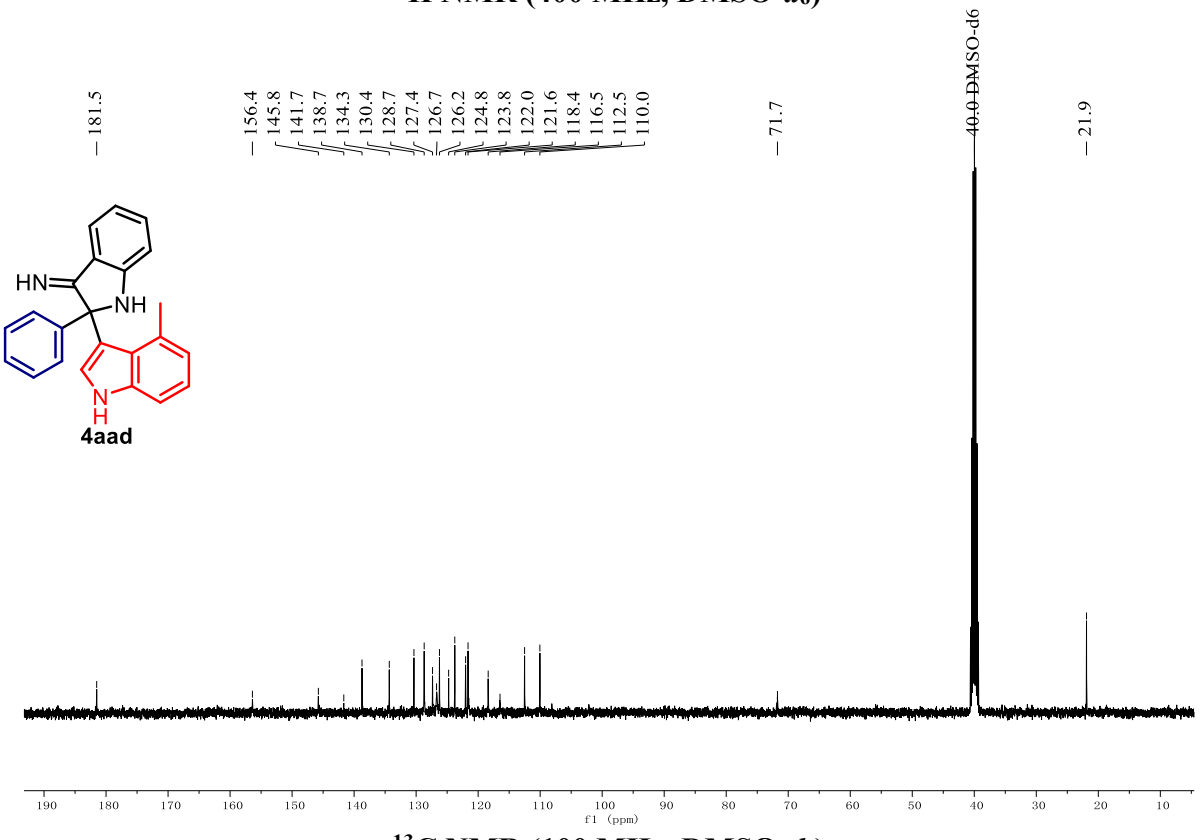
^{1}H NMR (400 MHz, $CDCl_3$)



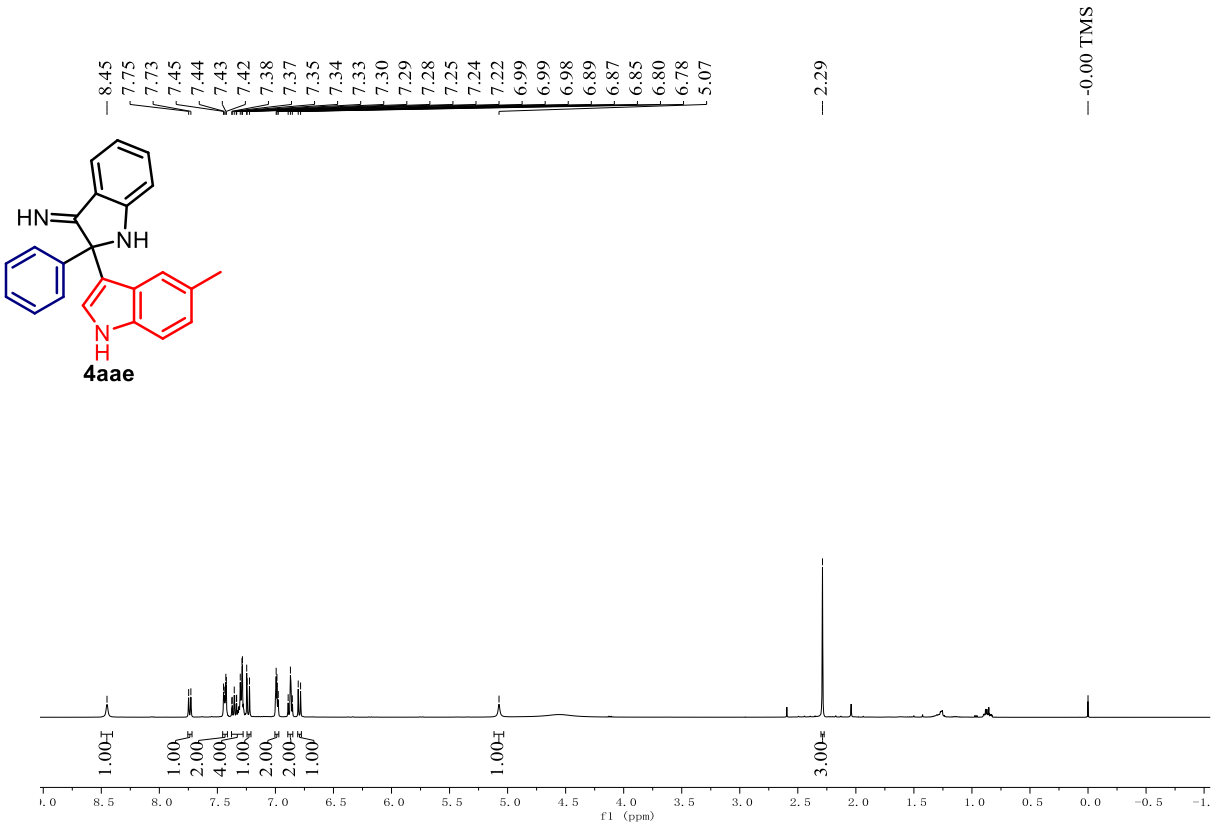
^{13}C NMR (100 MHz, $CDCl_3$)



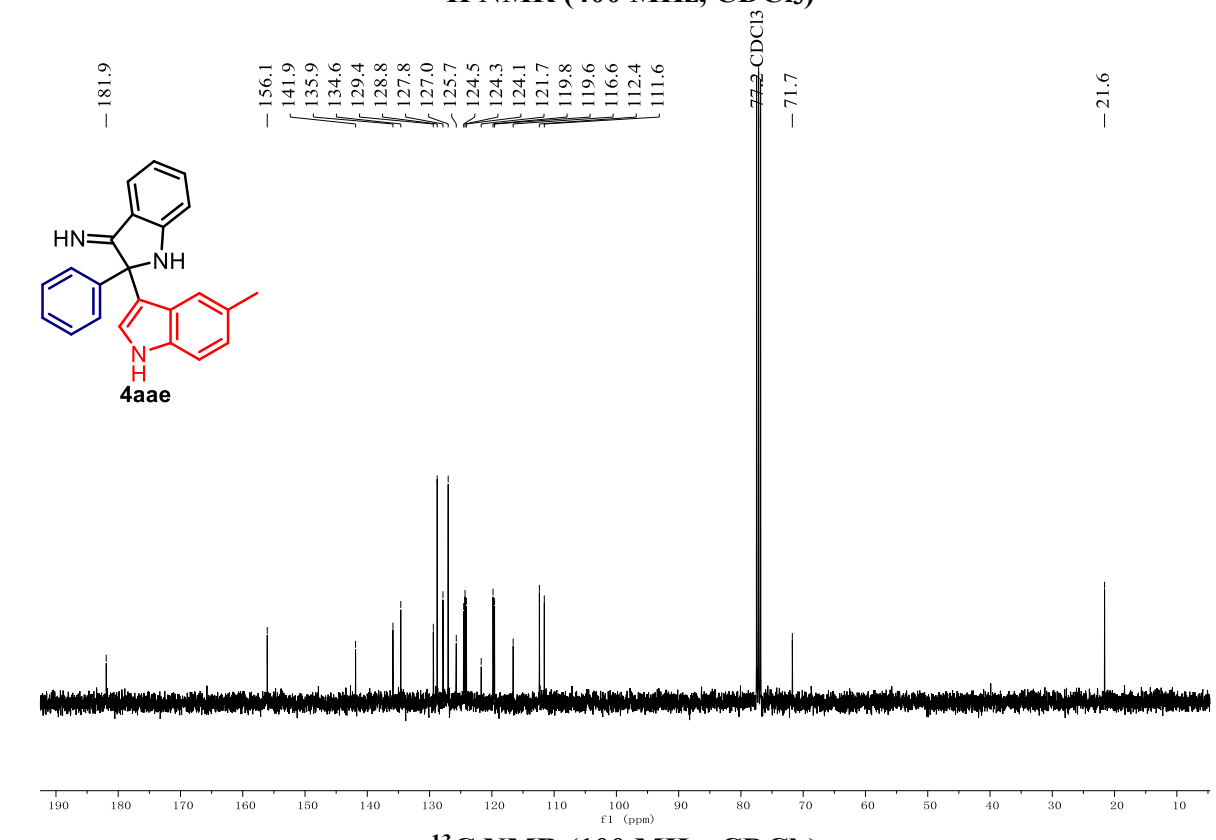
^{1}H NMR (400 MHz, DMSO-d_6)



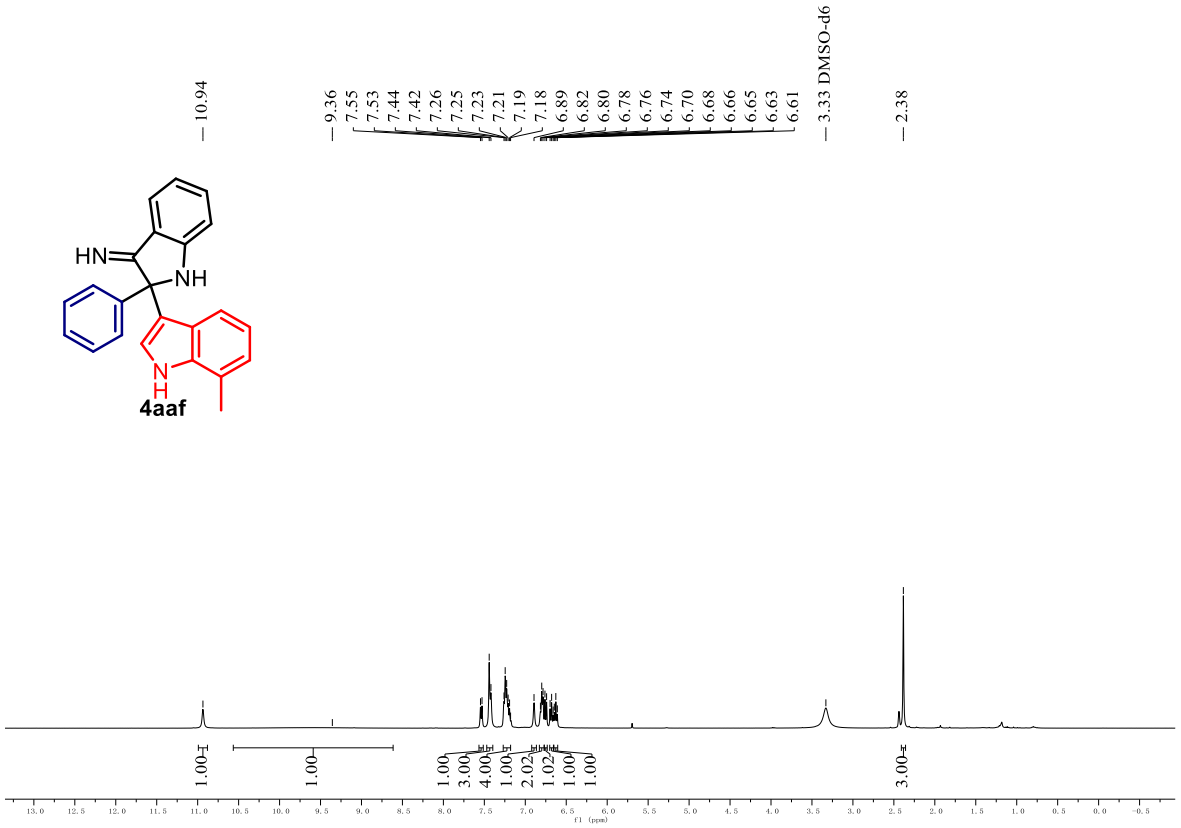
^{13}C NMR (100 MHz, DMSO-d_6)



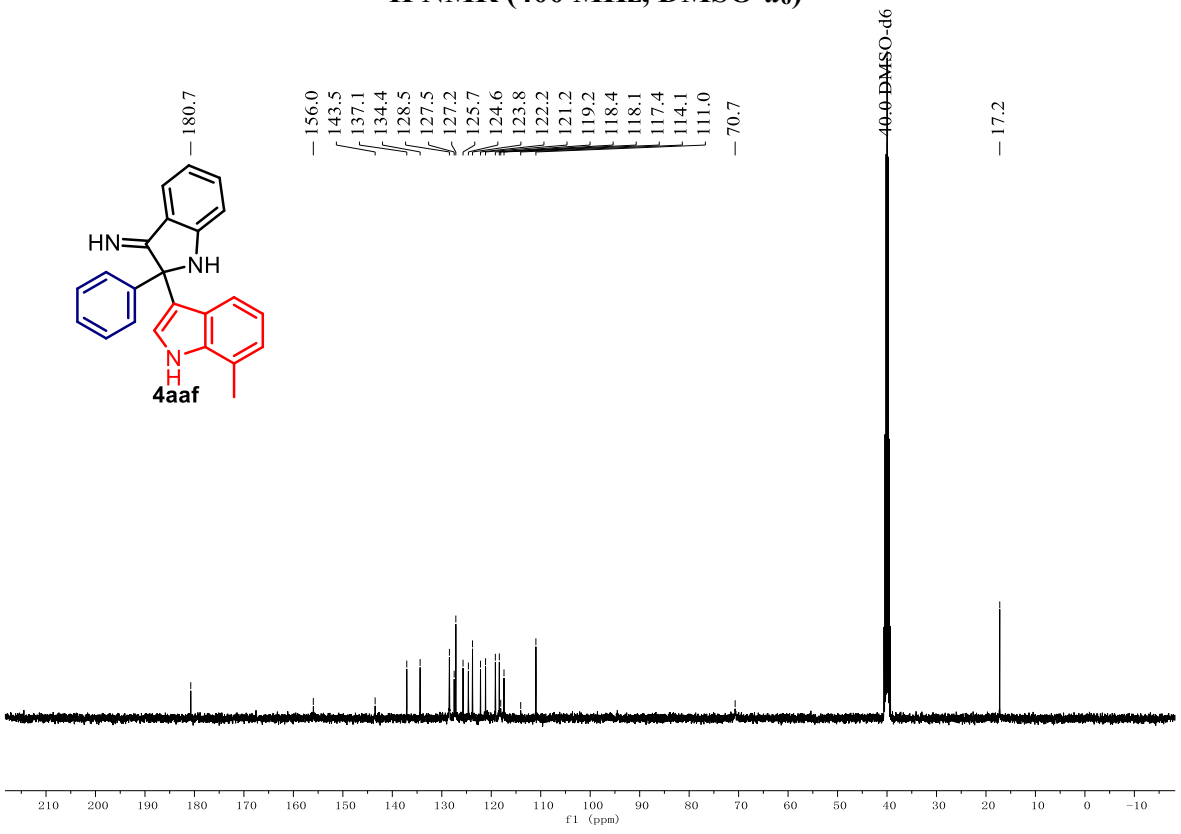
^{1}H NMR (400 MHz, $CDCl_3$)



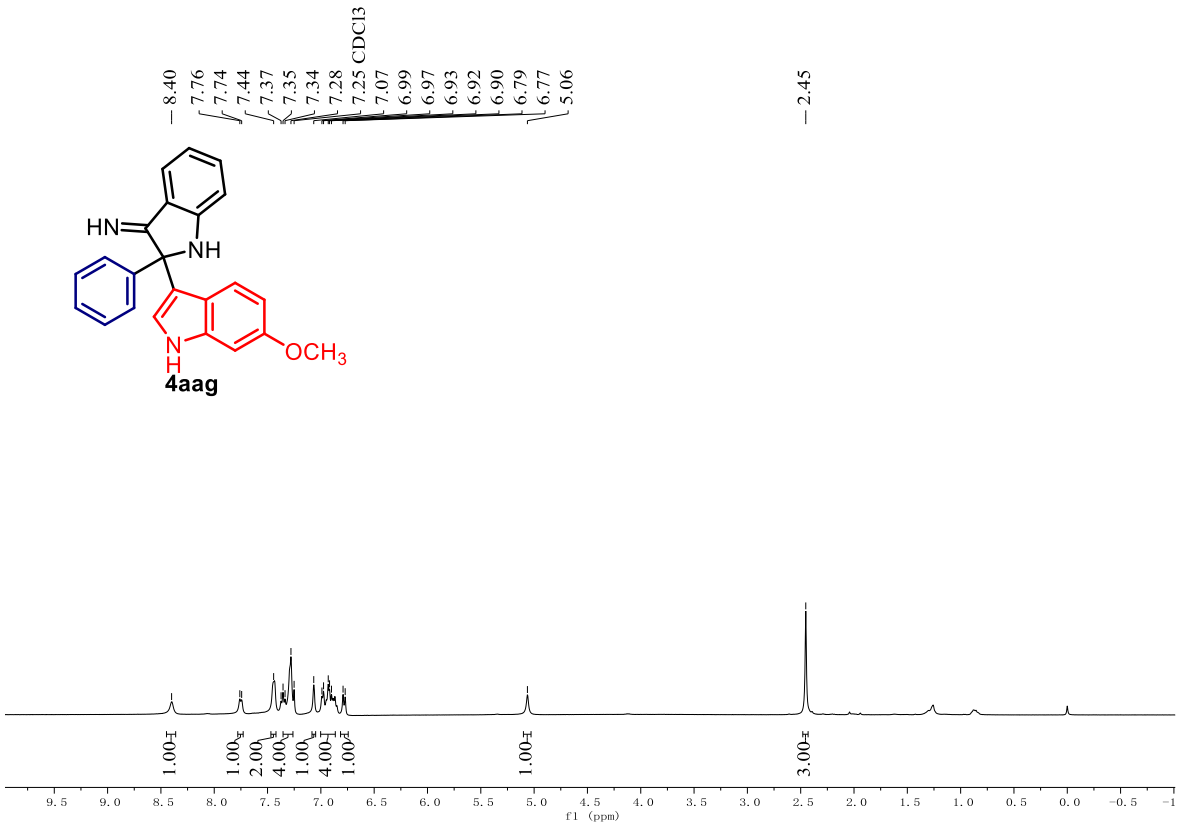
^{13}C NMR (100 MHz, $CDCl_3$)



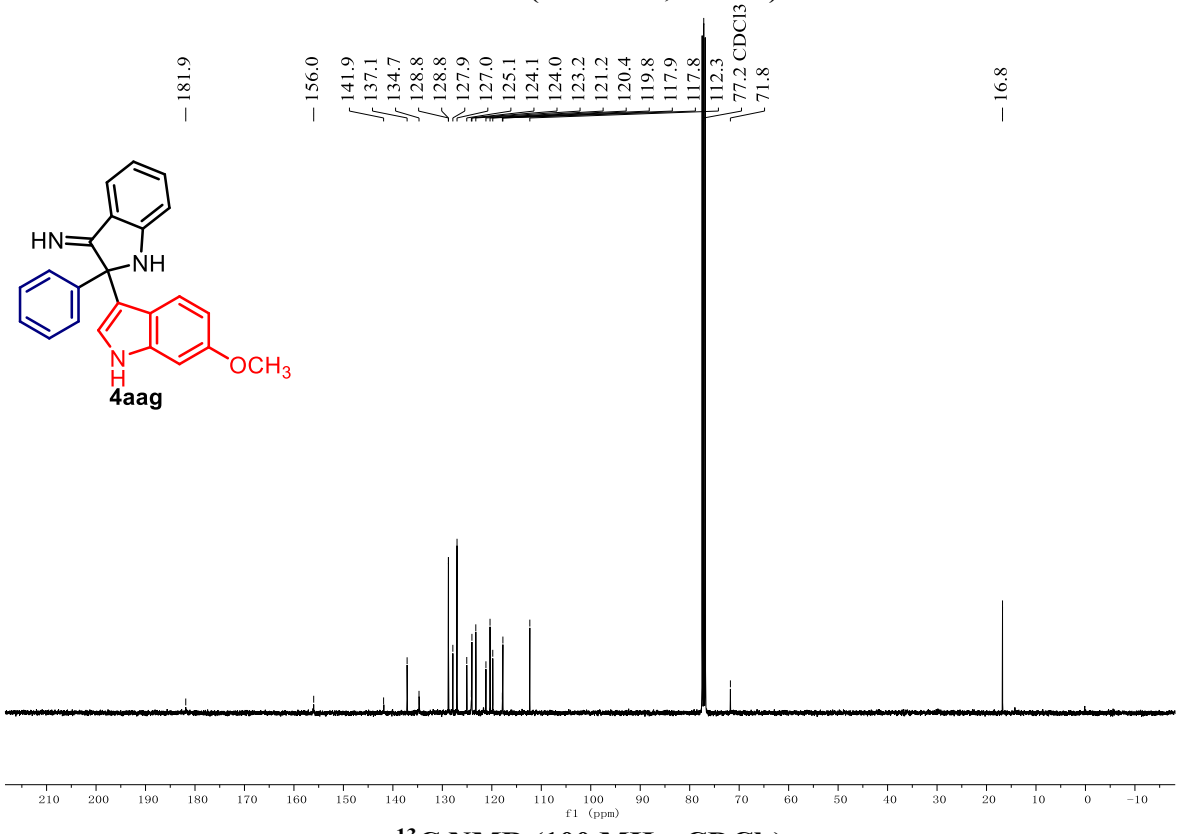
^{1}H NMR (400 MHz, DMSO-*d*$_6$)



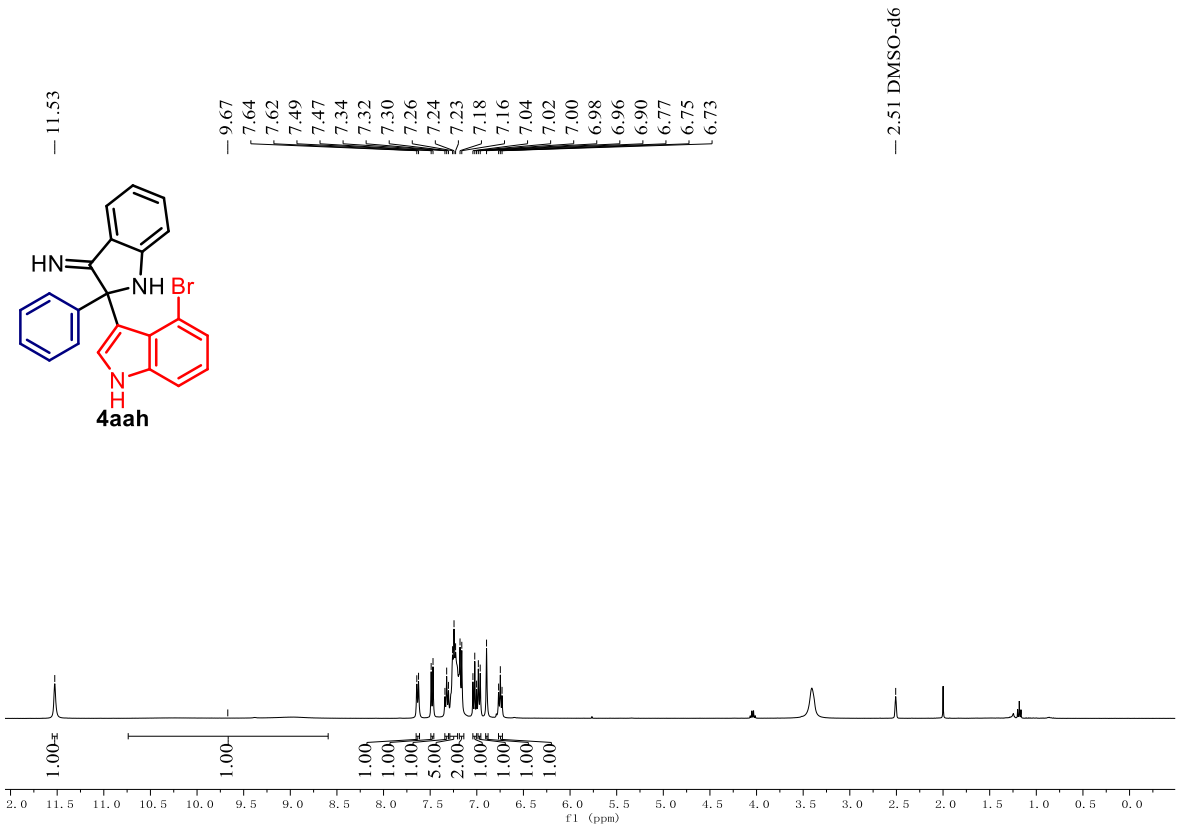
^{13}C NMR (100 MHz, DMSO-*d*$_6$)



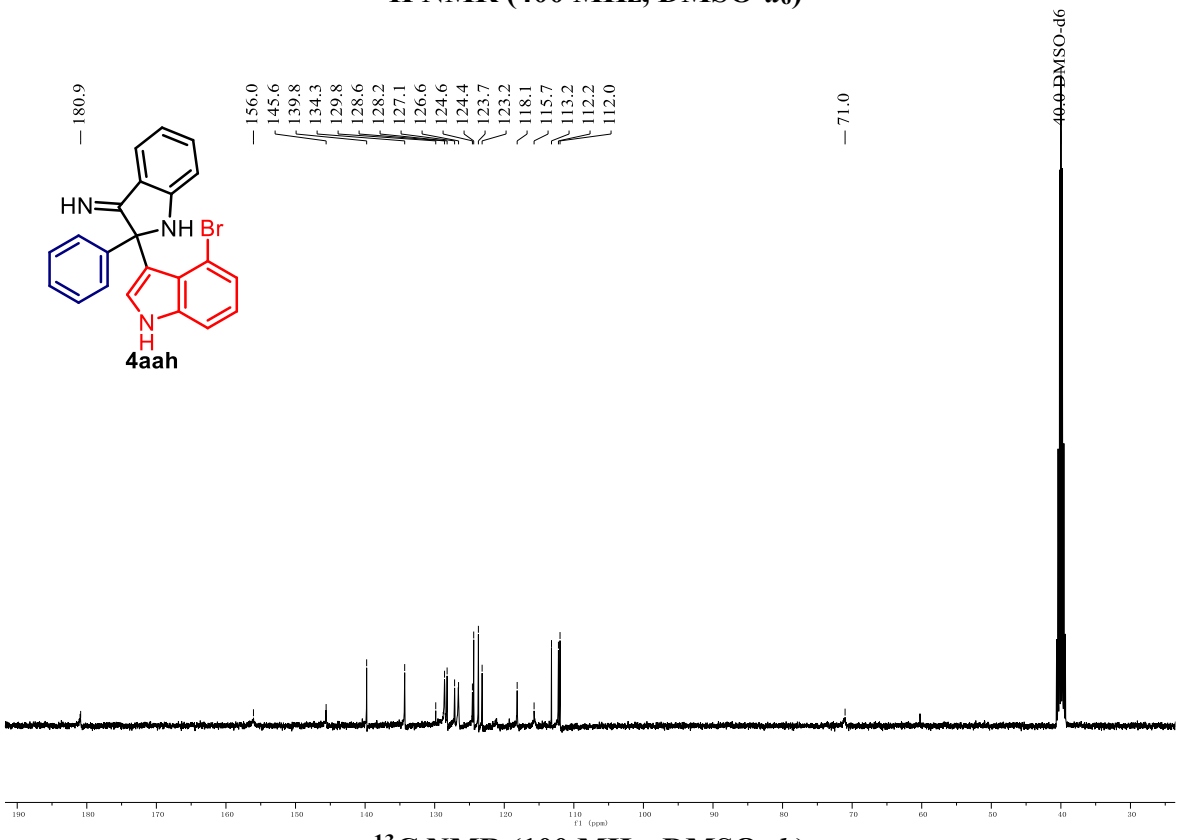
^{1}H NMR (400 MHz, $CDCl_3$)



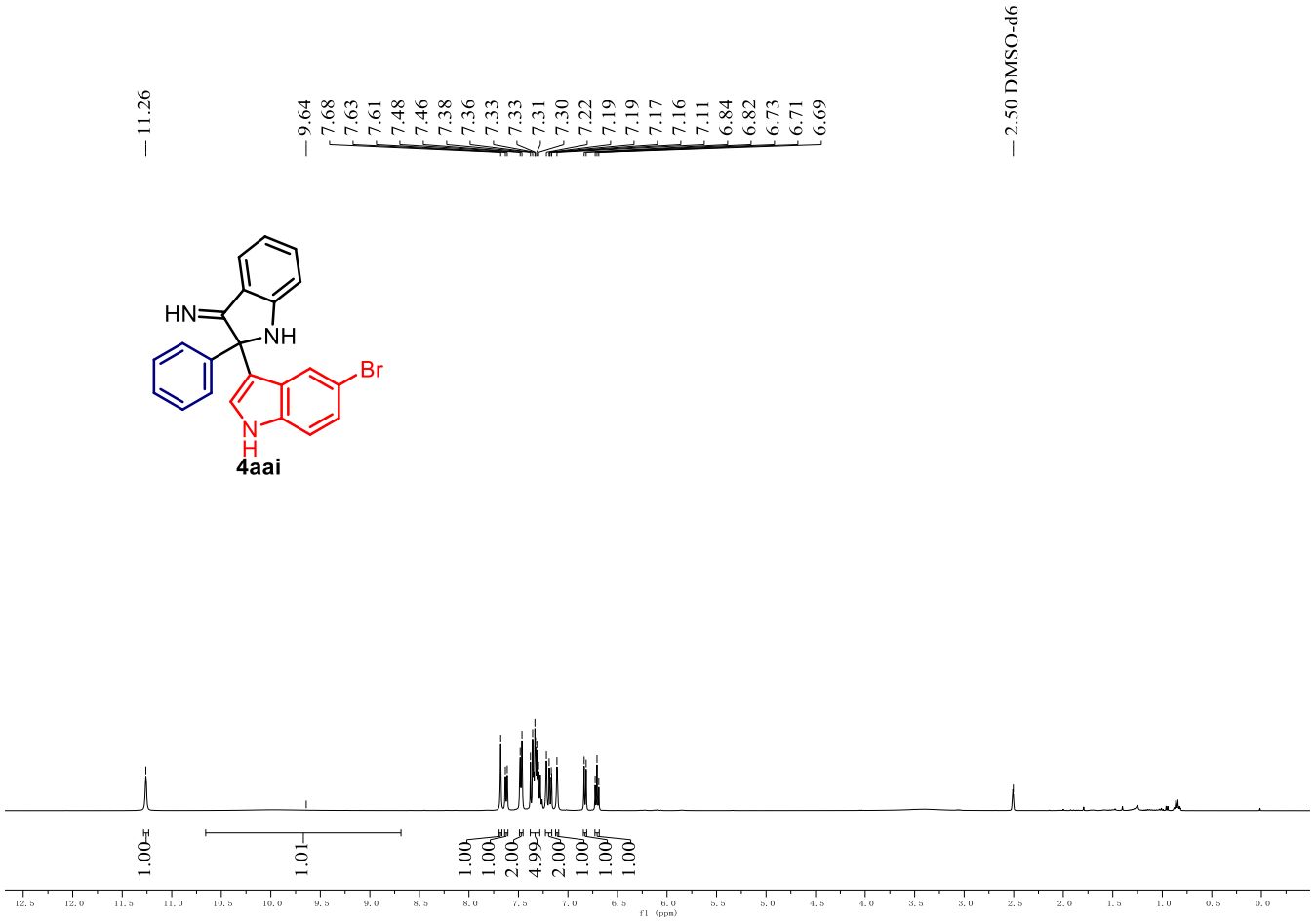
^{13}C NMR (100 MHz, $CDCl_3$)



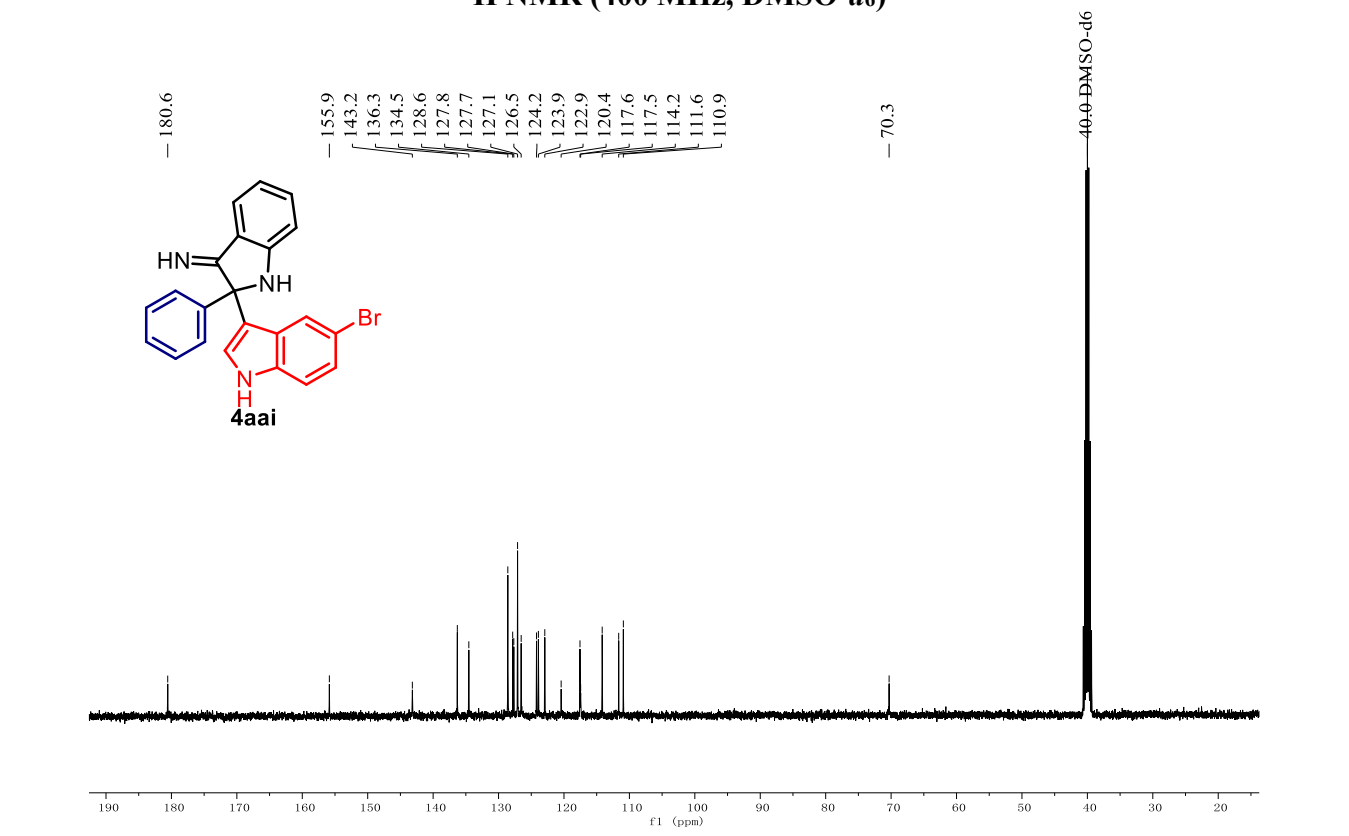
^{1}H NMR (400 MHz, DMSO-*d*$_6$)



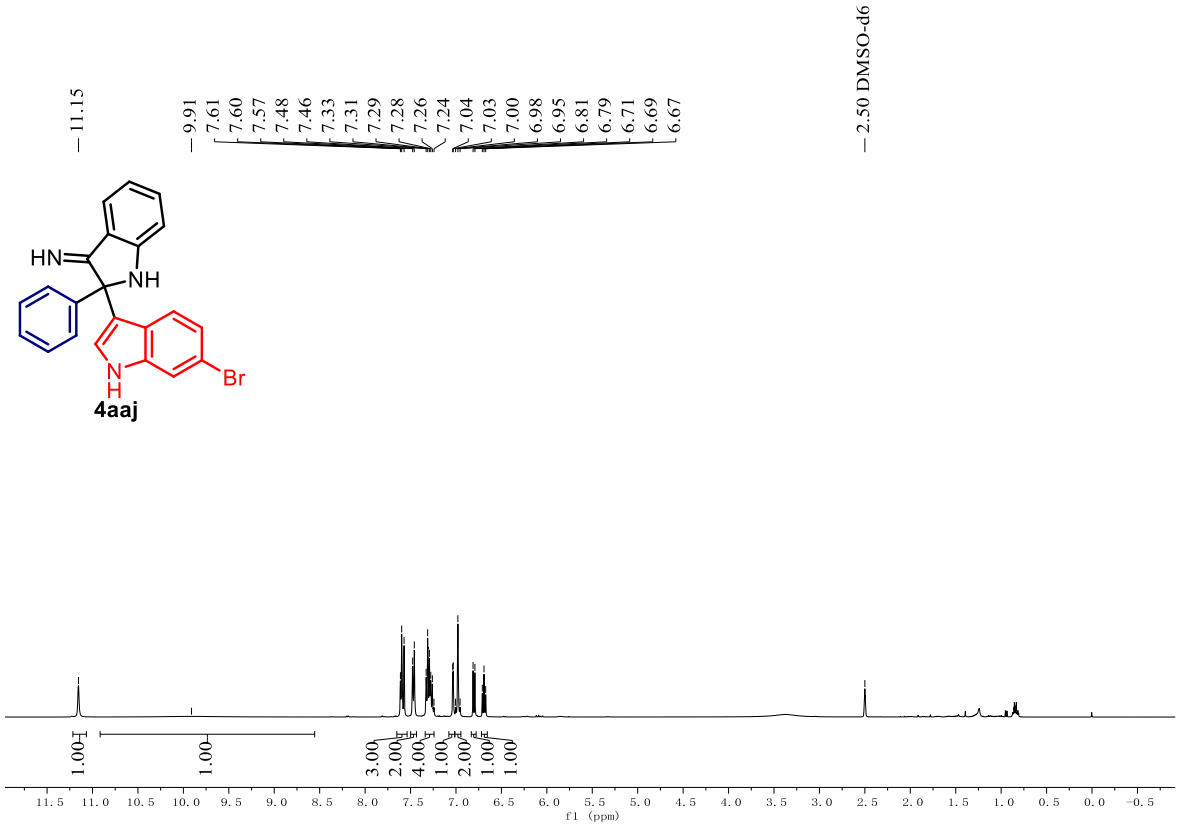
^{13}C NMR (100 MHz, DMSO-*d*$_6$)



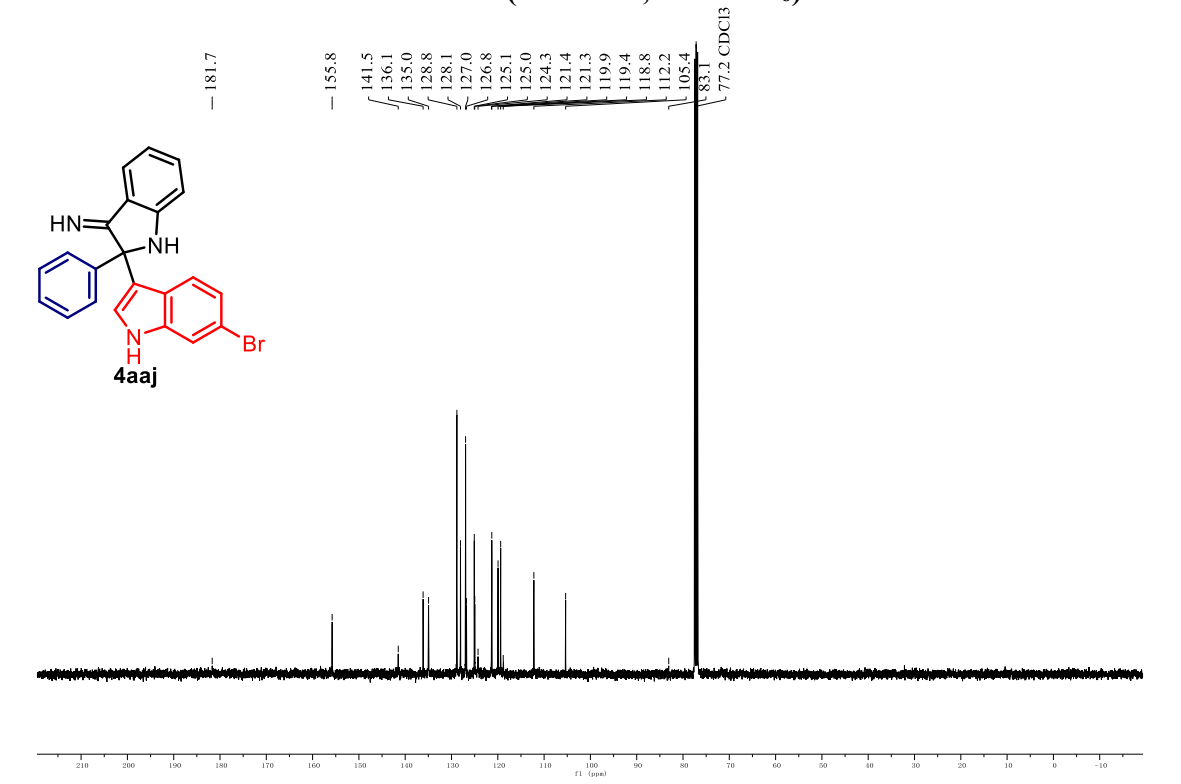
^{1}H NMR (400 MHz, DMSO-*d*$_6$)



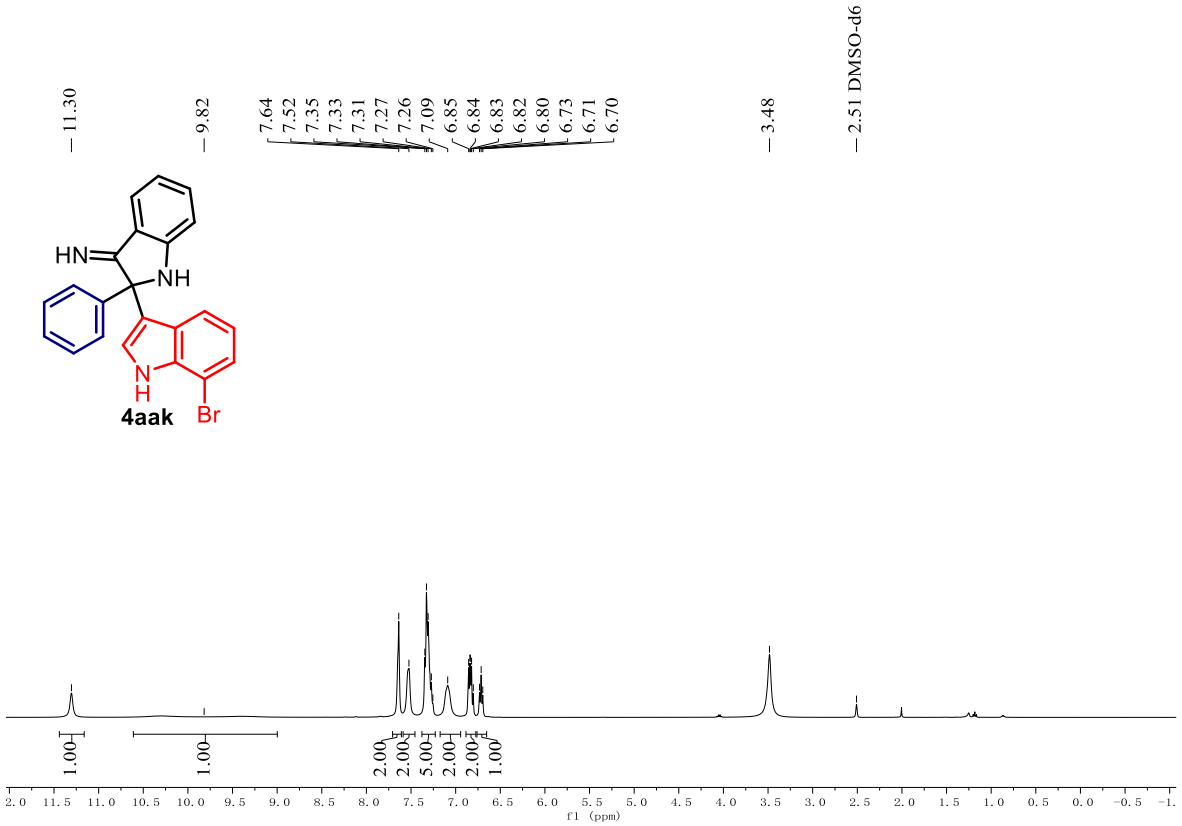
^{13}C NMR (100 MHz, DMSO-*d*$_6$)



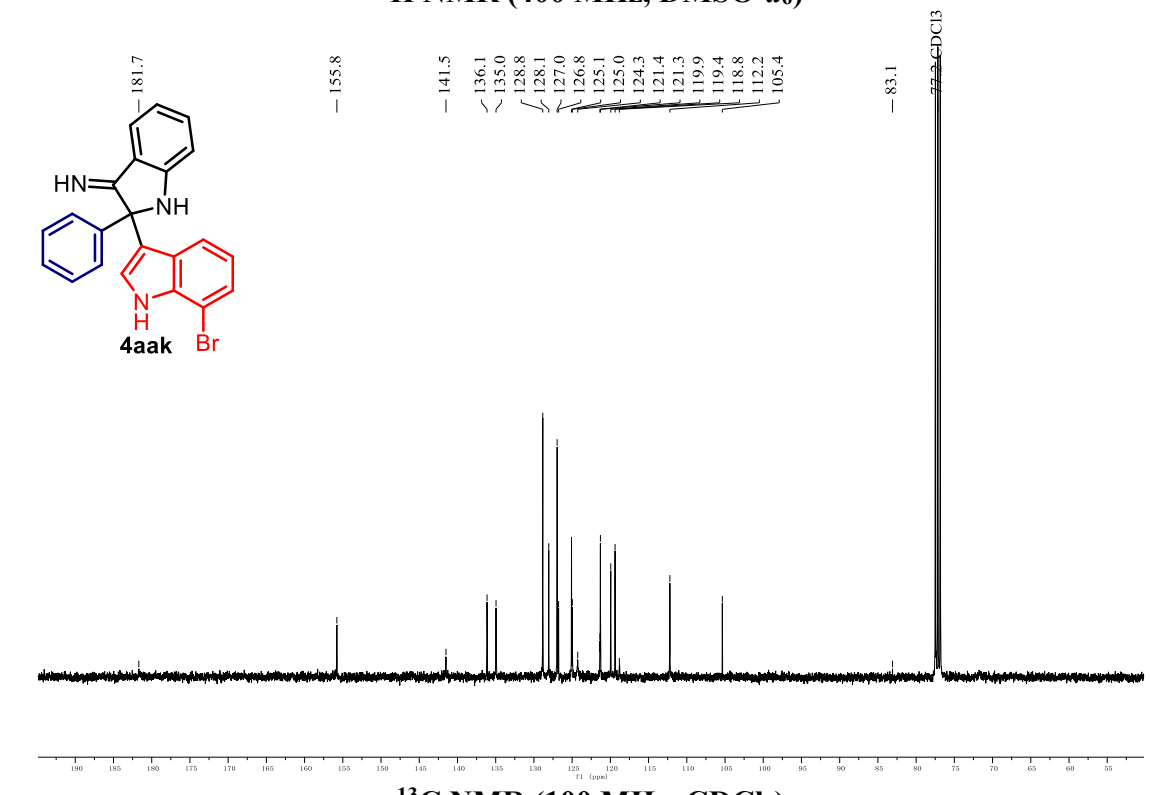
^{1}H NMR (400 MHz, DMSO-d_6)



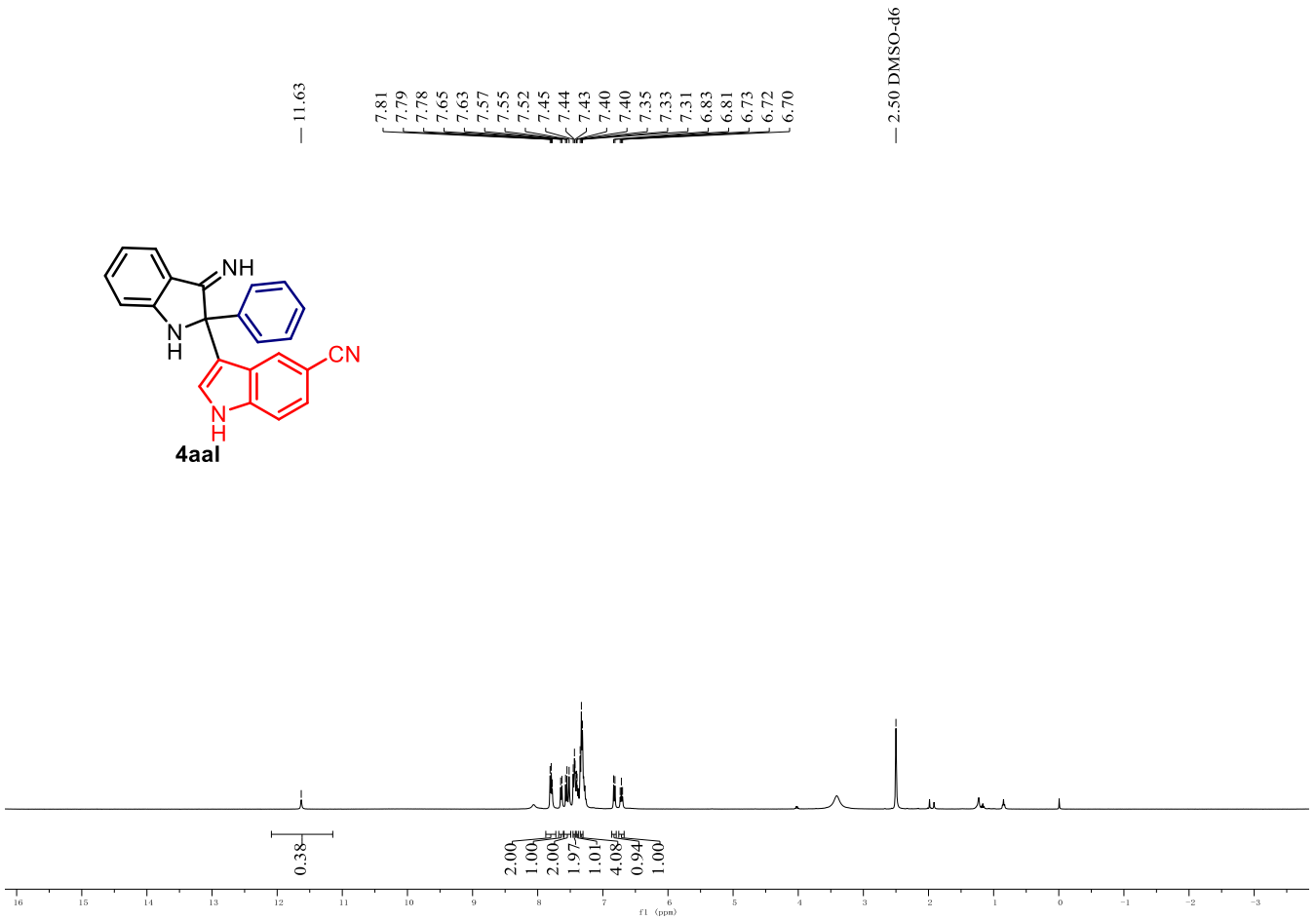
^{13}C NMR (100 MHz, $CDCl_3$)



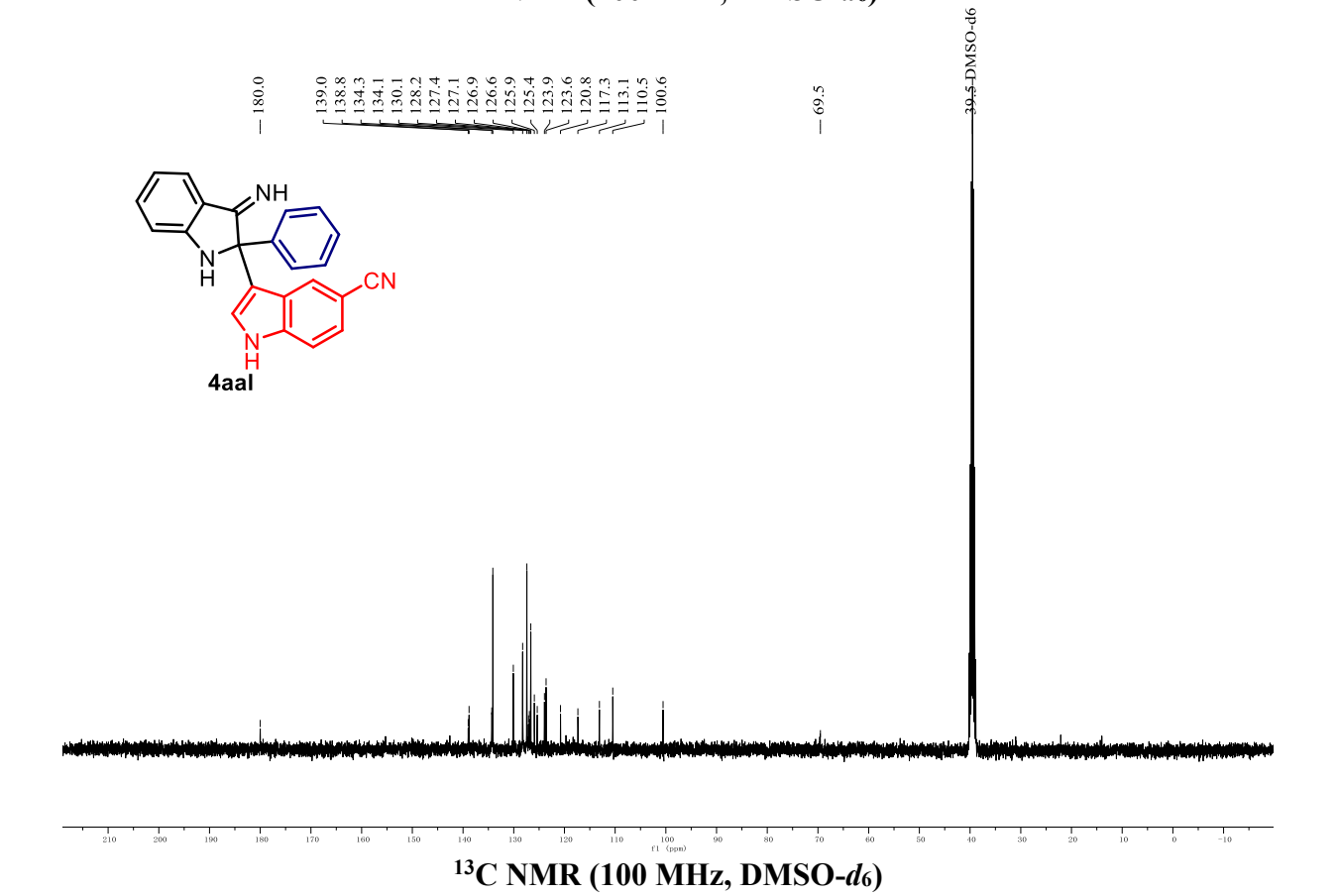
^{1}H NMR (400 MHz, DMSO-d_6)



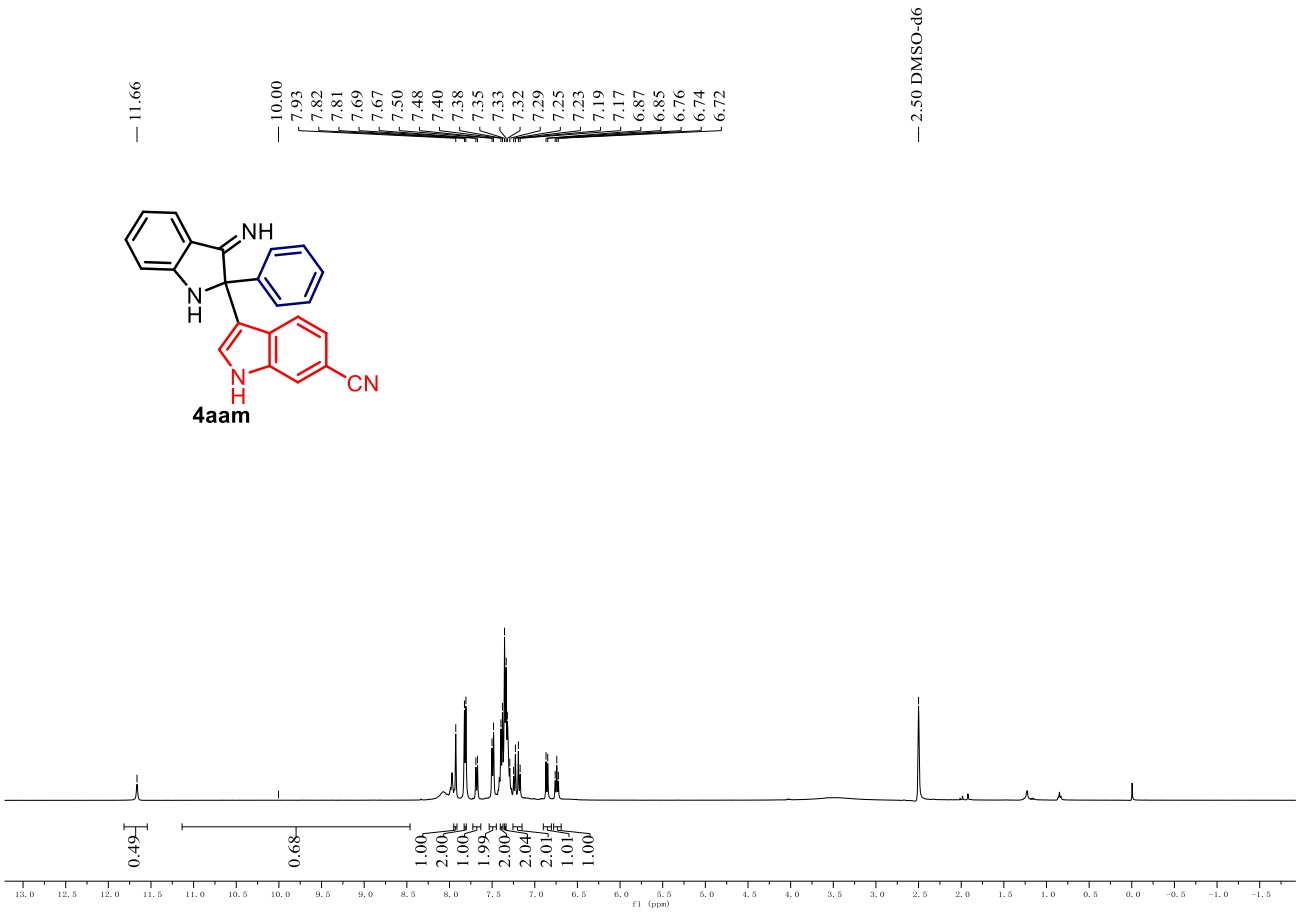
^{13}C NMR (100 MHz, $CDCl_3$)



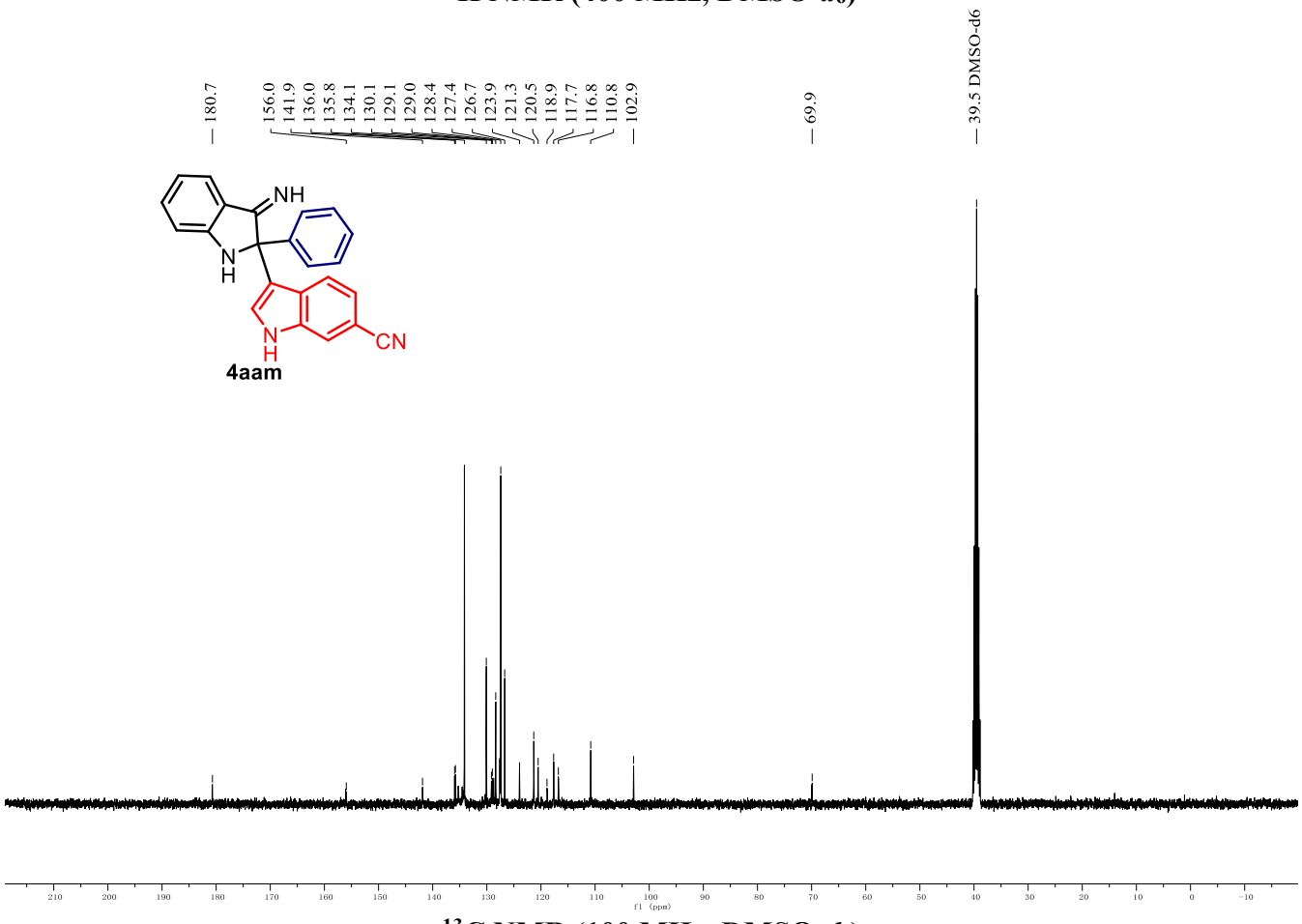
^{1}H NMR (400 MHz, DMSO-*d*$_6$)



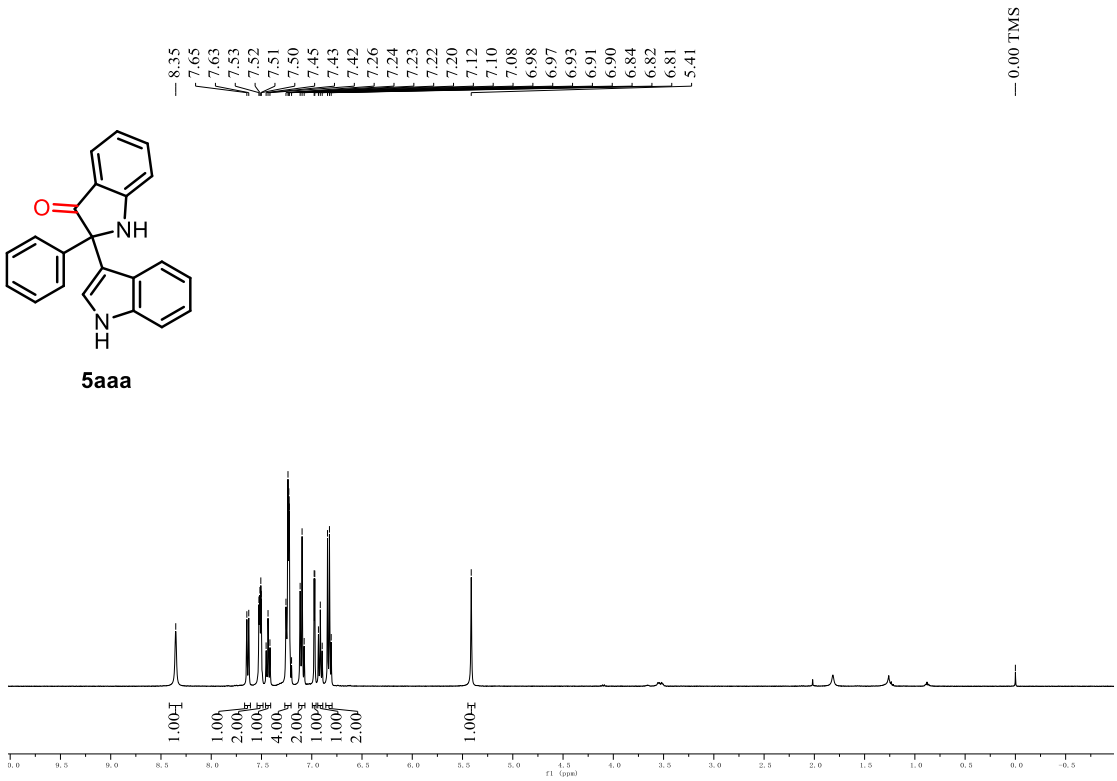
^{13}C NMR (100 MHz, DMSO-*d*$_6$)



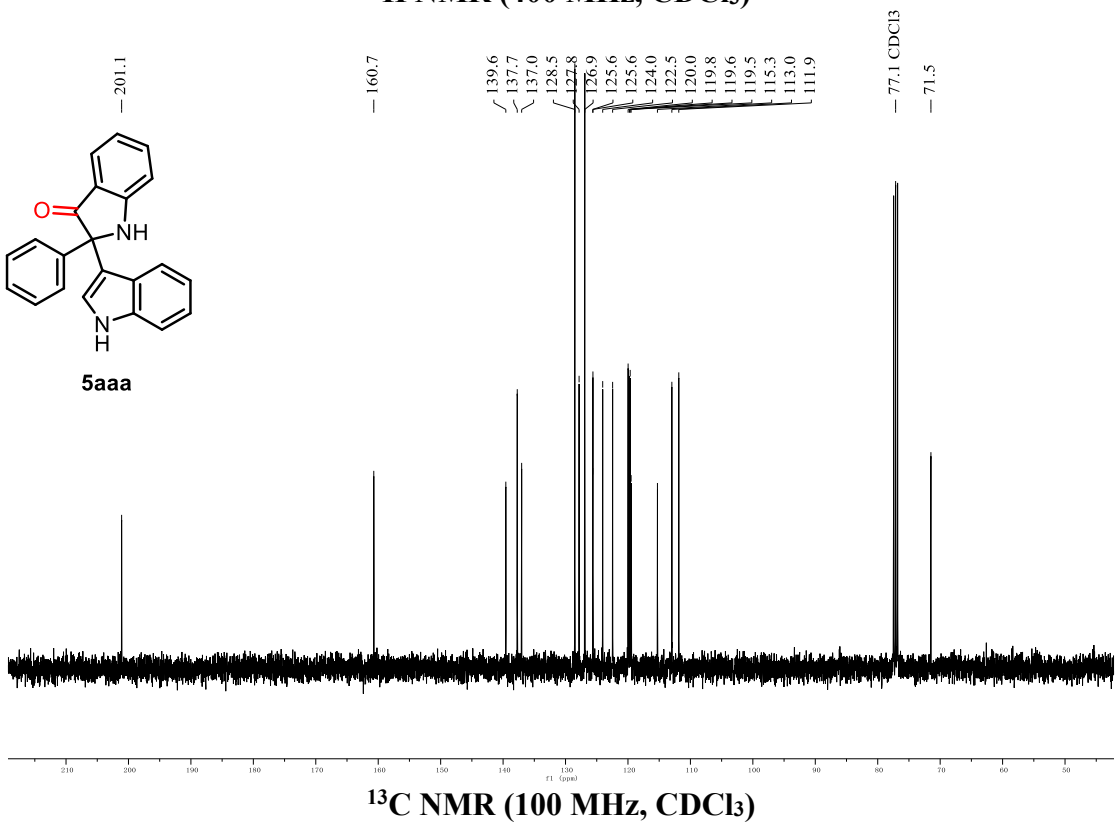
^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)



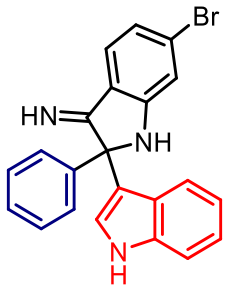
^{1}H NMR (400 MHz, $CDCl_3$)



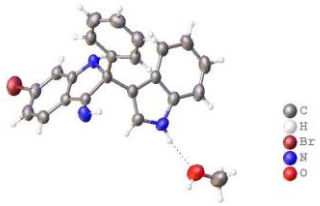
^{13}C NMR (100 MHz, $CDCl_3$)

10.Crystal data and structure refinement for 4afa.

Compound **4afa**: (The crystal structure of compound **4afa** has been deposited at the Cambridge Crystallographic Data Centre (**CCDC** 2282839). The data is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.)



4afa



crystal structure of **4afa**

Crystal data and structure refinement for **4afa**.

Empirical formula	$C_{22}H_{16}N_3Br$	
Formula weight	434.33	
Temperature/K	293.9	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1 -P 1	
Unit cell dimensions	a = 8.7011(6) Å	α = 104.625 °
	b = 10.4405(8) Å	β = 103.707 °
	c = 12.2214(10) Å	γ = 102.923 °
Volume/$Å^3$	995.09(14)	
Z	2	
Density (calculated) g/cm^3	1.450	
Absorption coefficient/mm^{-1}	2.084	
F(000)	444	
Crystal size/mm^3	0.5 × 0.3× 0.15	
Theta range for data collection/°	1.812 to 30.394	
Index ranges	-11 ≤ h ≤ 12, -10 ≤ k ≤ 14, -17 ≤ l ≤ 12	
Reflections collected	2668	
Absorption correction	Multi-scan	
Data / restranits / parameters	5157/1/253	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R_1 = 0.0607, wR_2 = 0.1274	
Final R indices [all data]	R_1 = 0.1350, wR_2 = 0.1598	