Supporting Information

A combination of polarity reversal, Diels-Alder cycloaddition and skeletal remodeling to access pyridine fused nitrones

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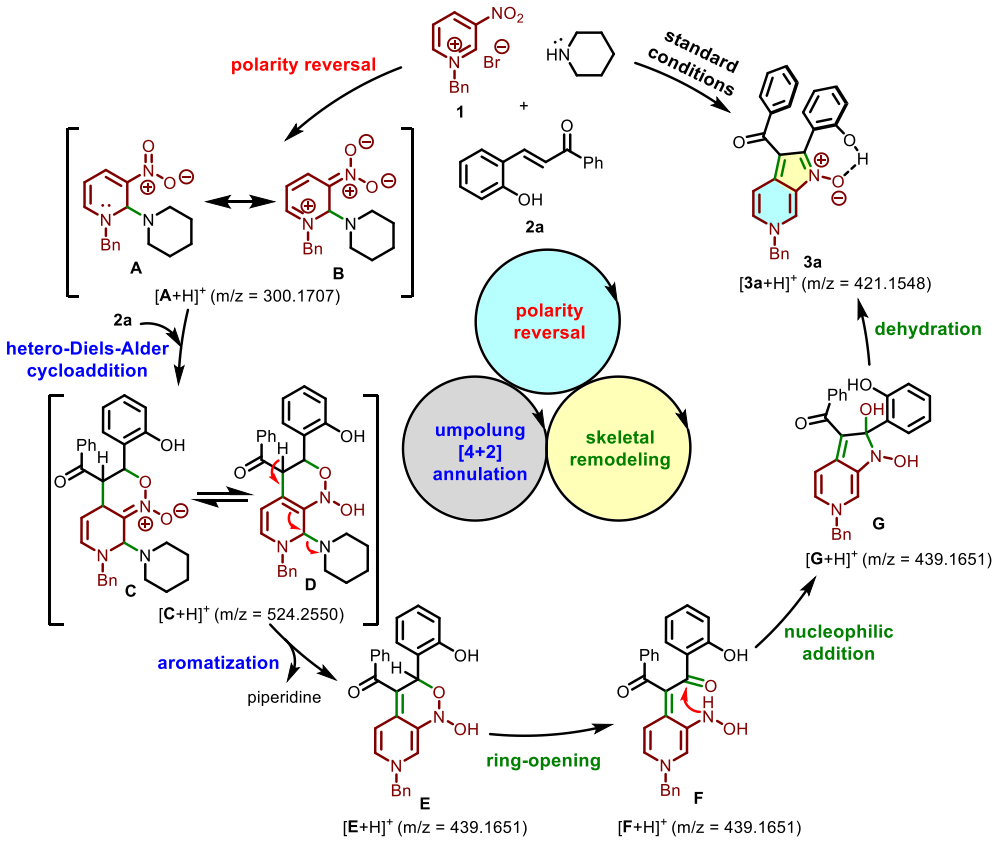
1. General methods

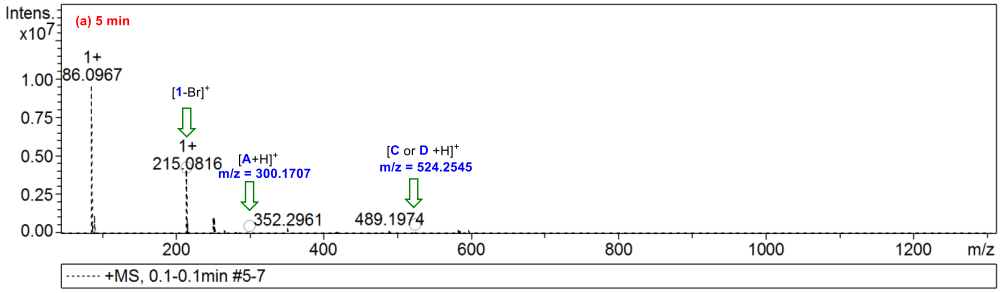
NMR spectra were recorded with tetramethylsilane as the internal standard. For compounds **3d**, **3f**, **3i**, **3r**, **4, 5** and **7**, ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). For other products, ^{1}H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz (Bruker Avance). For compounds **3c** and **3m**, ^{19}F NMR spectra were recorded at 376 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification.

2. Mechanistic studies

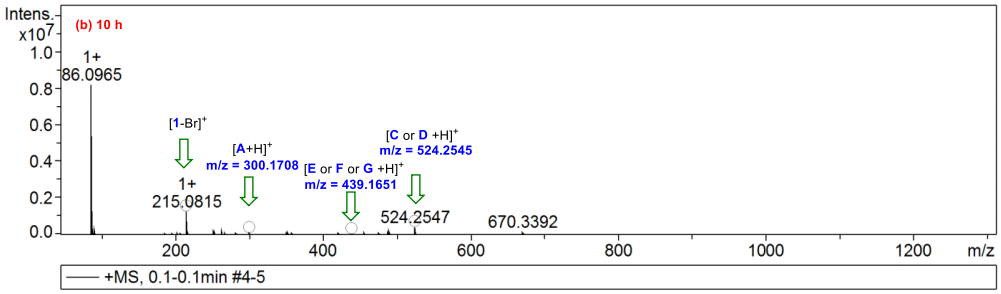
Based on the experimental results, a tentative reaction mechanism was proposed to explain the uncommon reaction pathway (Scheme S1, taking the formation of **3a** as an example). This reaction commenced with a dearomative nucleophilic addition between pyridinium salt **1** and piperidine to inverse the polarity of **1** from strong electron-poor substrate to electron-rich π-extended species **A**. The intermediate **A** had a resonance structure of **B**. The D-π-A structural character of **A** rendered it a good diene to participate in normal Diels-Alder cycloaddition with *o*-hydroxychalcone **2a** to produce intermediate **C**. The intermediate **C** was easily isomerized into **D** with more conjugated structure with the help of piperidine. Then, piperidine was squeezed out from **D** driven by aromatization, leading to intermediate **E**. **E** was not stable and a ring-opening proceeded subsequently through a 1,5-hydride shift process to give **F**. Followed by an intramolecular nucleophilic addition and dehydration, the desired product **3a** was delivered in the end.



Scheme S1 Proposed mechanism



Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	Score	rdb	N-Rule	e¯ Conf
215.0816	1	C12H11N2O2	C12H10N2O2	215.0815	M+H	-0.6	1+	0.5	100.00	9.0	ok	even
300.1707	1	C17H22N3O2	C17H21N3O2	300.1707	M+H	-0.2	1+	13.4	100.00	9.0	ok	even
524.2545	1	C32H34N3O4	C32H33N3O4	524.2544	M+H	-0.3	1+	9.6	100.00	18.0	ok	even



Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	Score	rdb	N-Rule	e¯ Conf
215.0815	1	C12H11N2O2	C12H10N2O2	215.0815	M+H	-0.1	1+	0.4	100.00	9.0	ok	even
300.1708	1	C17H22N3O2	C17H21N3O2	300.1707	M+H	-0.5	1+	31.3	100.00	9.0	ok	even
439.1651	1	C27H23N2O4	C27H22N2O4	439.1652	M+H	0.4	1+	n.a.	100.00	18.0	ok	even
524.2547	1	C32H34N3O4	C32H33N3O4	524.2544	M+H	-0.5	1+	2.0	100.00	18.0	ok	even

Figure S1 (a) Full HRMS spectra of the model reaction for 5 min; (b) Full HRMS spectra of the

model reaction for 10 h.

To get some evidences, we tried to detect the intermediate of the crude reaction mixture among **1**, **2a** and piperidine under optimized conditions by HRMS analysis. As shown in Figure S1, after the reaction proceeded for 5 min, we could obtain the signal peaks of intermediates **A**, **C** and **D**. After the reaction proceeded for 10 h, we also detected the signal peaks of intermediates **E**, **F** and **G**.

(a) The relative Gibbs free energies (Δ*G*) of the transition states and the addition products with Br⁻ absent or present, and the Laplacian of the electron density at the bond (3,-1) critical point ($\nabla^2\rho_{BCP}$) for each transition state.

			C2	C4	C6
Δ*G* (kcal/mol)	Br⁻ absent	TS	8.9	9.8	10.4
		Pro	2.4	-2.0	-1.6
	Br⁻ present	TS	6.3	9.0	8.8
		Pro	-2.3	-5.7	-0.8
$\nabla^2\rho_{BCP}$ (a.u.)		N–H···Br	0.052	0.047	0.041
		LP···π	0.042	0.043	0.049

(b) The optimized geometries and NCI analysis for transition state corresponding to addition at the C2, C4 and C6 position, respectively.

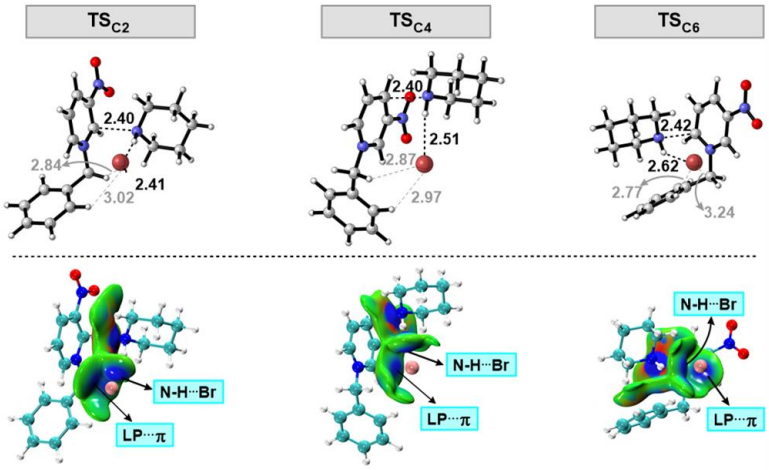


Figure S2 The DFT computational results

In order to get deeper insights into the regioselectivity for the amine addition on C2, C4 or C6 of the 3-nitropyridinium, the Gibbs free energy barriers were calculated by using the density functional theory (DFT) method. As shown in Figure S2a, the selectivity is poor when the Br– anion is not involved during the addition process because the barriers for reaction at the C2, C4 and C6 position are similar. Instead, presence of Br– could not only lower the reaction barrier, but also induce the distinctive C2-selectivity. Although the C4 addition product is more stable than the

C2 or C6 addition product (well consistent with experimental results [1-3]), the barrier via TS_{C2} is more than 2.5 kcal/mol lower than that corresponding to reactions at the other two positions. In addition, the barrier for the reverse reaction via TS_{C4} is 14.7 kcal/mol, indicating an equilibrium process. The noncovalent interaction (NCI) combined with the atoms in molecules (AIM) analyses afford useful information for understanding the origin. As illustrated in Figure S2b, the NCI maps indicate that it should be the N–H…Br interaction between the piperidine and the bromine anion and the LP…π interaction between the bromine anion and the pyridinium that exert profound influence onto the stability of the transition states. The AIM analysis show that the value of $\nabla^2\rho_{BCP}$ (Laplacian of the electron density at the bond (3,-1) critical point) of these two interactions corresponds quantitatively well with the relative barriers of reactions at distinctive positions. In particular, the $\nabla^2\rho_{BCP}$ value indicates the most and least significant N–H…Br interaction in TS_{C2} and TS_{C6}, respectively, and contrarily the strongest and weakest LP…π interaction in TS_{C6} and TS_{C2}, respectively. As a result, discrepancy of the noncovalent interaction between the bromine anion and the other two reagents brings about the regioselectivity.

DFT calculations

2.1 Method

The density functional theory (DFT)[4] calculations were performed by using the *Gaussian 09* program.[5] The geometric structures of all involved transition states were optimized by using the M06-2X[6] density functional, combined with the 6-31+G(d,p)[7] basis set . The solvent effects of *i*-PrOH were simulated by the SMD model.[8] The harmonic frequency calculations were conducted at the same level to corroborate each transition state has one and only one imaginary frequency and other structures have no imaginary frequency. The atoms in molecules (AIM)[9] and the non-covalent interaction (NCI) analysis was conducted to clarify the origin of regioselectivity, which was plotted by VMD[10] (version 1.9.3) and Multiwfn[11] (version 3.6) programs. The key optimized geometries involved in the reaction were illustrated using the CYLview program.[12]

2.2 Energies of all the optimized structures.

Table S1. Calculated Energies and Imaginary Frequency of the Transition State.

Geometry	ZPE[1]	*G*(thermo)[2]	*E*[3]	*G*[4]	Imaginary Frequency

1.00000	0.21596	0.16254	-3295.09713	-3295.15056	
piperidine	0.16012	0.12737	-251.64670	-251.67945	
1-noBr	0.21637	0.17098	-723.11238	-723.15777	
TS_{C2}	0.37755	0.31287	-3546.75527	-3546.81994	-78.0*i*
Pro_{C2}	0.38051	0.31956	-3546.77265	-3546.83360	
TS_{C4}	0.37762	0.31382	-3546.75190	-3546.81570	-133.7*i*
Pro_{C4}	0.38135	0.32074	-3546.77853	-3546.83914	
TS_{C6}	0.37788	0.31704	-3546.75515	-3546.81598	-83.8*i*
Pro_{C6}	0.38160	0.32206	-3546.77170	-3546.83124	
TSC2-noBr:	0.37748	0.32020	-974.76576	-974.82305	-119.9*i*
Pro_{C2}-noBr:	0.38141	0.32474	-974.77678	-974.83345	
TSC4-noBr:	0.37748	0.31910	-974.76325	-974.82163	-133.5*i*
Pro_{C4}-noBr:	0.38171	0.32485	-974.78348	-974.84035	
TSC6-noBr:	0.37744	0.32084	-974.76404	-974.82064	-143.6*i*
Pro_{C6}-noBr:	0.38150	0.32586	-974.78412	-974.83975	

[1]Zero-point Energies. [2]Thermal corrections to Gibbs free energies. [3]ZPE plus electronic energies. [4]*G*(thermo) plus electronic energies.

References

1 R. E. Lyle and G. J. Gauthier, *Tetrahedron Lett.* 1965, **6**, 4615-4621.

2 G. Bertuzzi, A. Sinisi, L. Caruana, A. Mazzanti, M. Fochi and L. Bernardi, *ACS Catal.* 2016, **6**, 6473-6477.

3 G. Bertuzzi, A. Sinisi, D. Pecorari, L. Caruana, A. Mazzanti, L. Bernardi and M. Fochi, *Org. Lett.* 2017, **19**, 834-837.

4 W. Kohn and L. J. Sham, *Phys. Rev.* 1965, **140**, A1133-A1138.

5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,

H. Nakai, T. Vreven, J. A. Montgomery, J. E. P. Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, **2010**.

6 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215-241.

7 J. D. Dill and J. A. Pople, *J. Chem. Phys.* 1975, **62**, 2921-2923.

8 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378-6396.

9 R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford, 1994.

10 W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graphics* 1996, **14**, 33-38.

11 T. Lu and F. Chen, *J. Comput. Chem.* 2012, **33**, 580-592.

12 L. C. Y., *CYLview, 1.0b, Université de Sherbrooke* http://www.cylview.org, 2009.

2.3 Cartesian coordination of all the optimized structures

1

0 1

O	–1.22505800	–0.75038900	–2.49395600
O	–3.13599500	–1.61967200	–1.99251400
N	–0.11185600	–0.51389900	1.34269000
N	–2.04165500	–1.17122700	–1.69334300
C	2.55604100	0.94065100	–0.22201400
C	3.55976300	0.71426400	–1.16471200
C	4.25873500	–0.49221200	–1.16701300
C	3.94917300	–1.48011000	–0.22959200
C	2.94870400	–1.25557800	0.71302600
C	2.24888100	–0.04447100	0.72064700
C	1.15310300	0.18212400	1.72546500
C	–0.47099300	–0.54881200	0.05073000
C	–1.68912900	–1.12751800	–0.27956300
C	–2.58419900	–1.55667200	0.67970800
C	–2.20311300	–1.42798400	2.01543800
C	–0.96718500	–0.89297100	2.31580700

H	3.79551200	1.48124400	–1.89631700
H	5.04146700	–0.66556900	–1.89958400
H	4.49155600	–2.42081800	–0.22942500
H	2.70737000	–2.02082200	1.44737900
H	1.42525700	–0.20280500	2.70876000
H	0.88896800	1.24183600	1.79582900
H	0.24172800	–0.22693100	–0.69454900
H	–3.54355000	–1.97677400	0.39870100
H	–2.85898800	–1.73548800	2.81989400
H	–0.61545200	–0.76960800	3.33403900
H	1.99648600	1.87343500	–0.22400800
Br	–1.14760100	2.23184000	–0.00462700

piperidine

0 1

C	0.73545000	–1.21677800	0.20491900
C	–0.72727100	–1.25147400	–0.22819500
C	–1.45305600	0.01421800	0.23564800
C	–0.70255200	1.26538600	–0.22825500
C	0.75917500	1.20217400	0.20499900
H	–2.48474600	0.02432800	–0.13297000
H	–0.77163700	–1.32268500	–1.32289000
H	–1.21136300	–2.14572000	0.17971500
H	0.78014400	–1.24625800	1.30955800
H	1.26921800	–2.09527600	–0.17040300
H	–0.74551900	1.33740900	–1.32299100
H	–1.16889100	2.16899900	0.17960900
H	1.31002200	2.07005200	–0.17036400
H	0.80465900	1.23066700	1.30962800
H	–1.50488400	0.01473700	1.33372600
N	1.38381000	–0.01349300	–0.32379300
H	2.36585900	–0.02295600	–0.06076500

1–noBr

1 1

O	–2.43103400	–2.34145000	–0.40389600
O	–3.93436100	–1.37682400	0.80792300
N	–0.30841400	1.05855700	–0.73435000
N	–2.90688700	–1.37356800	0.15931200
C	2.53800400	–0.91388500	–0.96321000
C	3.47429400	–1.57713400	–0.16817700
C	3.91013700	–0.99975500	1.02280900
C	3.41377900	0.24477500	1.41924200
C	2.48417000	0.90967300	0.62419100
C	2.04249200	0.33034700	–0.57048800
C	1.02034000	1.03993500	–1.42233300

C	–0.98196200	–0.09799200	–0.62400600
C	–2.18375700	–0.09987800	0.05006800
C	–2.71319400	1.05100700	0.61887300
C	–1.98407700	2.22509100	0.48155800
C	–0.78058700	2.20330700	–0.20283500
H	3.85914700	–2.54322700	–0.48045900
H	4.63756400	–1.51550800	1.64255600
H	3.75539900	0.69722100	2.34524900
H	2.09790900	1.88049600	0.92962700
H	1.28534900	2.08196600	–1.60328800
H	0.87115800	0.53534300	–2.37849600
H	–0.54314900	–0.98512300	–1.06829100
H	–3.66023100	1.02422600	1.14666300
H	–2.33878800	3.15893800	0.89927300
H	–0.16717400	3.08588300	–0.34140400
H	2.19524900	–1.36189700	–1.89252800

TS_{C2}

0 1

O	2.67819900	2.80603500	–1.18516500
O	3.01550800	3.53052400	0.81957500
N	–0.69869800	0.91916700	–0.13974700
N	2.36582800	2.90799400	–0.00686300
C	–3.66400000	1.30647200	–1.20704400
C	–5.04016300	1.33277200	–0.99488700
C	–5.69194500	0.19979800	–0.50202900
C	–4.96317700	–0.95394300	–0.21692400
C	–3.58254900	–0.97934900	–0.42186200
C	–2.92999500	0.14995400	–0.92188300
C	–1.44346000	0.12631000	–1.15751700
C	0.46084100	1.49581100	–0.51893100
C	1.16048000	2.23858800	0.43144200
C	0.78171400	2.26396500	1.76408200
C	–0.35208300	1.54908600	2.13057200
C	–1.06209100	0.86385300	1.15961100
H	–5.60567000	2.23217300	–1.21997700
H	–6.76586400	0.21839500	–0.34094800
H	–5.46695000	–1.83493500	0.16976900
H	–3.00274500	–1.86674900	–0.17834100
H	–1.05102000	–0.89376000	–1.09587300
H	–1.19054200	0.56336800	–2.12502900
H	0.67388000	1.54839000	–1.57736700
H	1.35804800	2.82860700	2.48898800
H	–0.68662100	1.51011600	3.15904400
H	–1.96987000	0.31945800	1.38196100
H	–3.15469000	2.18425700	–1.59918800

C	2.05669400	–1.04593200	–1.92224200
C	2.80100800	–2.38326800	–1.85959900
C	4.10948000	–2.23079600	–1.07987600
C	3.84797100	–1.62190100	0.30043900
C	3.06960800	–0.31006000	0.16436600
H	4.61242900	–3.19902600	–0.98156500
H	2.15733600	–3.11922000	–1.35866200
H	2.99266400	–2.75054600	–2.87445700
H	2.64087400	–0.32046900	–2.50675800
H	1.08745400	–1.16294600	–2.42023000
H	3.25483300	–2.32067900	0.90551900
H	4.78891400	–1.44095900	0.83271400
H	2.81987200	0.09534700	1.15268500
H	3.69348800	0.43211400	–0.35470500
H	4.78792400	–1.57241500	–1.64102300
N	1.82841800	–0.47422100	–0.59407800
H	1.20445700	–1.09070000	–0.05945200
Br	–0.41562000	–2.18660100	1.35617500

Pro$_{C2}$

0 1

O	2.90130900	2.59331800	–1.15539300
O	2.94625200	3.72244300	0.69286300
N	–0.56017600	0.81136800	–0.12519600
N	2.45946000	2.83911400	–0.02182000
C	–3.56266300	1.49669400	–1.03581100
C	–4.92299800	1.58184700	–0.74713700
C	–5.60978000	0.45741000	–0.28391700
C	–4.93175700	–0.74828200	–0.10755000
C	–3.56799100	–0.83225600	–0.39204400
C	–2.87897000	0.28861400	–0.86211200
C	–1.40807100	0.20124700	–1.17378600
C	0.81716100	1.06047900	–0.47907000
C	1.38950600	2.06648400	0.45065300
C	0.93882200	2.18211000	1.74794500
C	–0.17266400	1.43952200	2.14902300
C	–0.92353300	0.81405800	1.16299300
H	–5.44870000	2.52165200	–0.88825900
H	–6.67110500	0.52206400	–0.06235700
H	–5.46240800	–1.62359700	0.25554700
H	–3.02683100	–1.76258600	–0.23486600
H	–1.11560900	–0.84901000	–1.29393300
H	–1.18116200	0.73866500	–2.09954400
H	0.87152100	1.39849400	–1.51450100
H	1.44274400	2.85666800	2.43293200
H	–0.52936600	1.44381800	3.16958300

H	–1.89156400	0.38038500	1.38638100
H	–3.02621100	2.36947000	–1.40180000
C	1.87193100	–0.75585300	–1.86872900
C	2.43433800	–2.16863700	–1.87898400
C	3.69791900	–2.25169600	–1.02515700
C	3.39173300	–1.77107300	0.39181700
C	2.79821500	–0.36587300	0.40021400
H	4.07377100	–3.27884400	–1.00072700
H	1.67466600	–2.86288100	–1.49842600
H	2.63892300	–2.43949300	–2.91916000
H	2.58727100	–0.03505000	–2.27956100
H	0.94214000	–0.68906700	–2.43796800
H	2.68405600	–2.45653400	0.87248500
H	4.29694400	–1.74520200	1.00611600
H	2.49026400	–0.08179500	1.40762400
H	3.51291000	0.36641600	0.01143700
H	4.48191800	–1.62488000	–1.47023800
N	1.57295400	–0.31051000	–0.46829100
H	0.90299600	–1.00982500	–0.03100900
Br	–0.32858600	–2.34895800	1.08307200

TS_{C4}

0 1

O	0.48117600	1.81842700	2.27674600
O	–1.27521800	2.88831100	1.62283400
N	1.22225400	0.45433600	–1.42281900
N	–0.31769000	2.15871100	1.41582500
C	3.49970600	–1.30104500	0.37668300
C	4.53488100	–1.20596900	1.30694700
C	5.51839900	–0.22768700	1.16260900
C	5.46374600	0.66298900	0.08875700
C	4.43298600	0.56658000	–0.84406600
C	3.44832300	–0.41703700	–0.70544200
C	2.32732400	–0.50873100	–1.70406300
C	0.96515200	0.85425500	–0.17351200
C	–0.12132000	1.67318500	0.06576700
C	–1.07456500	1.94731100	–0.91696000
C	–0.76280500	1.50750100	–2.22062400
C	0.36349700	0.75891800	–2.43353300
H	4.57189300	–1.89582700	2.14489100
H	6.32425800	–0.15590100	1.88720500
H	6.22745900	1.42660500	–0.02506200
H	4.39107000	1.25486400	–1.68534700
H	2.67662500	–0.27840100	–2.71177400
H	1.86353100	–1.49923200	–1.68597300
H	1.65360900	0.56909500	0.61082100

H	–1.87790200	2.64712600	–0.73303100
H	–1.40953100	1.74349400	–3.05637300
H	0.63772000	0.38465700	–3.41366500
H	2.71570200	–2.04597800	0.49314300
C	–3.09794300	0.27883700	1.12407700
C	–4.00726500	–0.90778400	1.45337300
C	–5.24397100	–0.90105400	0.55051100
C	–4.83425300	–0.85293400	–0.92424200
C	–3.89029600	0.32682100	–1.17973500
H	–5.86674600	–1.78110500	0.74582700
H	–3.43574800	–1.83282800	1.29723600
H	–4.29526300	–0.87159900	2.51066700
H	–3.60583800	1.22069100	1.37529100
H	–2.17525600	0.22151100	1.71327800
H	–4.31705200	–1.78454100	–1.19219200
H	–5.71497400	–0.77053000	–1.57168400
H	–3.53063100	0.31854300	–2.21531900
H	–4.43259800	1.27109400	–1.02496400
H	–5.85630700	–0.01777400	0.78310900
N	–2.73152200	0.32436800	–0.29157200
H	–2.12393900	–0.47743500	–0.48629100
Br	–0.24024600	–1.98249300	0.19926400

Pro$_{C4}$

0 1

O	–0.72901200	3.09312800	–1.25032200
O	1.34025000	3.43625100	–0.73608300
N	–1.11757500	0.21794700	1.47830300
N	0.28773600	2.80173100	–0.60920800
C	–3.08785100	–1.02815800	–0.75939900
C	–4.04873700	–0.86443200	–1.75444500
C	–5.23245400	–0.17411300	–1.48351900
C	–5.45189800	0.35621800	–0.21309900
C	–4.49087400	0.19153600	0.78584300
C	–3.31147100	–0.50768600	0.52196400
C	–2.28271800	–0.68877400	1.60556400
C	–0.93670700	1.05922100	0.46358300
C	0.25879200	1.72475700	0.30093900
C	1.49052300	1.34092400	1.04610700
C	1.05614300	0.73048000	2.34974600
C	–0.14334200	0.14562700	2.47399600
H	–3.87478400	–1.27510800	–2.74490900
H	–5.98064600	–0.05140700	–2.26128200
H	–6.36967300	0.89540800	0.00244900
H	–4.66025500	0.60205600	1.77844200
H	–2.72547800	–0.50923100	2.58923200

H	–1.87392800	–1.70385200	1.57628200
H	–1.76774200	1.23491400	–0.20861100
H	2.16022000	2.19187900	1.19242600
H	1.73320800	0.73223000	3.19551600
H	–0.45150500	–0.37419100	3.37505300
H	–2.16101800	–1.56285400	–0.95897800
C	2.65471500	0.74531900	–1.13143000
C	3.42414700	–0.33911000	–1.87463200
C	4.70033100	–0.72121400	–1.12939300
C	4.34676800	–1.14986800	0.29241400
C	3.56149200	–0.06710700	1.02074100
H	5.21937400	–1.53046900	–1.65176700
H	2.77924500	–1.21808800	–1.99045400
H	3.64734100	0.04317000	–2.87547000
H	3.23501600	1.66931700	–1.05013000
H	1.71020500	0.95363300	–1.63787800
H	3.74777400	–2.06867200	0.26662800
H	5.24488800	–1.36036600	0.88096800
H	3.25075500	–0.41528300	2.00641000
H	4.15084200	0.85012300	1.13386300
H	5.38222300	0.13907200	–1.09685700
N	2.32655200	0.30824500	0.26325900
H	1.71866300	–0.55462100	0.16851500
Br	0.44220600	–2.19256800	–0.25184500

TS_{C6}

0 1

O	4.31623100	–1.04296600	0.76131300
O	4.87276200	0.28577500	–0.84600500
N	0.60452600	–1.50907500	–0.69164000
N	4.07452100	–0.44561900	–0.27609900
C	–2.67039600	–2.44806200	–0.90274400
C	–4.01955800	–2.10424200	–0.80724200
C	–4.46865900	–1.33783000	0.26810500
C	–3.56471900	–0.90989800	1.24246500
C	–2.21502400	–1.24318400	1.14205000
C	–1.76036600	–2.01753300	0.06789800
C	–0.31914500	–2.45768600	0.00336700
C	1.83885400	–1.35786100	–0.17809400
C	2.76101800	–0.59856700	–0.86356300
C	2.44428800	0.02113400	–2.07819600
C	1.15996200	–0.11865900	–2.55126300
C	0.21496400	–0.81686500	–1.78679100
H	–4.71915600	–2.44625300	–1.56409500
H	–5.52034900	–1.07892200	0.34964200
H	–3.91130400	–0.31586300	2.08331800

H	–1.50227600	–0.90248800	1.89066700
H	0.08357400	–2.57273300	1.01059900
H	–0.23276100	–3.40933500	–0.52738400
H	2.08712000	–1.90453100	0.72041400
H	3.19642300	0.58234500	–2.62156900
H	0.84304700	0.34291900	–3.47817500
H	–0.78481200	–1.01410300	–2.15129600
H	–2.32437800	–3.06910300	–1.72621500
C	0.09521800	2.24759900	–0.75391100
C	–0.43391800	3.43473200	0.05498200
C	–1.86117900	3.78929600	–0.37219100
C	–2.76816800	2.55629800	–0.31296400
C	–2.15270100	1.40180200	–1.10863300
H	–2.26249900	4.59073700	0.25801900
H	–0.41794800	3.15581600	1.11724300
H	0.23398000	4.29542200	–0.06888100
H	0.19662900	2.52966400	–1.81305900
H	1.08244900	1.94562100	–0.38985500
H	–2.88892900	2.23702900	0.73240200
H	–3.76763500	2.78703200	–0.70035900
H	–2.76343800	0.49654700	–1.02486800
H	–2.10992900	1.67079600	–2.17460100
H	–1.84492100	4.17156600	–1.40302000
N	–0.79165800	1.08948800	–0.67865900
H	–0.77328200	0.74401200	0.28447600
Br	0.96268300	0.31528400	2.20055100

Pro$_{C6}$

0 1

O	4.32414400	–1.10217000	0.94740100
O	4.98521200	–0.34831800	–0.96754400
N	0.52047200	–1.37305600	–0.32322700
N	4.09088500	–0.74307600	–0.21126300
C	–2.65405200	–2.44475100	–0.72359200
C	–3.99817000	–2.10599900	–0.87432300
C	–4.58404400	–1.17913700	–0.01030200
C	–3.82361200	–0.60167000	1.00696000
C	–2.47597200	–0.93342900	1.15196000
C	–1.88091700	–1.85724200	0.28440000
C	–0.42807300	–2.23838900	0.43119100
C	1.78456200	–1.32526200	0.09656900
C	2.76842300	–0.76759700	–0.69386300
C	2.46300400	–0.39954000	–2.05138000
C	1.17423000	–0.34430600	–2.42822500
C	0.08739800	–0.54035900	–1.42007000
H	–4.58752800	–2.56787100	–1.66079600

H	–5.63198600	–0.91695800	–0.12312700
H	–4.27792000	0.11226500	1.68809200
H	–1.87653600	–0.47640300	1.93639100
H	–0.12456600	–2.17224300	1.47920900
H	–0.28192800	–3.26494700	0.08266000
H	2.01473800	–1.81238100	1.03778000
H	3.27129000	–0.22263800	–2.75223200
H	0.88175100	–0.13571800	–3.45092700
H	–0.79375200	–0.98647700	–1.87892600
H	–2.19928700	–3.17396700	–1.39053700
C	0.51918300	1.97515100	–0.95970000
C	–0.05395800	3.21698800	–0.28816900
C	–1.42182700	3.58816500	–0.85564700
C	–2.36191200	2.38975400	–0.74437100
C	–1.77299500	1.16730300	–1.43010900
H	–1.83442200	4.44624900	–0.31682400
H	–0.12429300	3.03115000	0.78946800
H	0.66827700	4.02645300	–0.43452200
H	0.68744300	2.14264300	–2.02611700
H	1.45139200	1.66709700	–0.48405300
H	–2.54463100	2.15135500	0.31260000
H	–3.33399700	2.59643600	–1.20245100
H	–2.42146100	0.29582400	–1.32090500
H	–1.59874900	1.34782900	–2.49677300
H	–1.32414100	3.87812700	–1.91010700
N	–0.43862300	0.81872500	–0.83848000
H	–0.52821600	0.66894200	0.19069800
Br	0.59362700	0.69865400	2.30729600

TS_{C2}–noBr

1 1

O	–1.15348700	–0.70062900	–2.40507700
O	–1.63507800	–2.78929300	–2.14476700
N	0.75238000	–0.51795800	1.12102600
N	–1.14702800	–1.73917100	–1.76104400
C	2.87043700	1.81031100	–0.36468200
C	4.00307900	1.89457200	–1.17683400
C	5.03203800	0.96547100	–1.03638700
C	4.93256300	–0.04753400	–0.07907700
C	3.80534800	–0.12866800	0.73380100
C	2.76823200	0.79967600	0.59233000
C	1.54306700	0.69179100	1.46672000
C	0.06363400	–0.50452200	–0.04486600
C	–0.52732300	–1.70982700	–0.44906100
C	–0.58072700	–2.81497500	0.37489000
C	0.02744000	–2.72794200	1.62936800

C	0.69876000	–1.57140100	1.96567800
H	4.07761100	2.68431400	–1.91838700
H	5.91247100	1.02969700	–1.66882500
H	5.73528200	–0.76993900	0.03451900
H	3.72673200	–0.91429200	1.48289400
H	1.80844900	0.60494200	2.52118000
H	0.88537300	1.55532900	1.33718800
H	0.26764700	0.30097900	–0.73888700
H	–1.07661900	–3.72189700	0.04525600
H	0.01020200	–3.55743300	2.32430400
H	1.23164000	–1.45902400	2.90293800
H	2.06695200	2.53497400	–0.47175000
C	–1.89997400	1.93624400	–0.36596700
C	–3.11981400	2.79235000	–0.02300000
C	–4.38724800	1.93466800	–0.00419500
C	–4.21376700	0.74086100	0.93737000
C	–2.95982100	–0.05595100	0.56923300
H	–5.25170500	2.53565700	0.29704600
H	–2.96939000	3.25192800	0.96345600
H	–3.20928500	3.60568200	–0.75151800
H	–1.99081700	1.54765300	–1.38827900
H	–0.97779600	2.52495700	–0.31610700
H	–4.11855100	1.09626400	1.97236000
H	–5.08702300	0.08081700	0.89841000
H	–2.78825600	–0.87443100	1.27625700
H	–3.09471600	–0.49842900	–0.42809900
H	–4.58878200	1.56656200	–1.01971400
N	–1.75563700	0.77966600	0.52848700
H	–1.54444200	1.10655500	1.47330400

Pro$_{C2}$–noBr

1 1

O	–1.03029700	0.84326200	2.36568900
O	–1.28745800	2.97588000	2.09836200
N	0.45761500	0.39975500	–1.36275200
N	–1.01476500	1.85885100	1.65920700
C	2.95133300	–1.91210000	–0.06658400
C	4.03540100	–1.93006100	0.81282700
C	4.70803500	–0.74721400	1.11471500
C	4.29713100	0.45382900	0.53228500
C	3.21926600	0.47059700	–0.35018400
C	2.54185700	–0.71475800	–0.65560500
C	1.38365600	–0.71071100	–1.63042900
C	–0.28401400	0.33336600	–0.13128100
C	–0.69094900	1.69570100	0.29370800
C	–0.76729400	2.75169700	–0.57799100

C	–0.34359900	2.58826200	–1.90540000
C	0.32593900	1.42415800	–2.22185800
H	4.34671500	–2.86612500	1.26681300
H	5.54685000	–0.75810200	1.80435500
H	4.81740800	1.37802100	0.76599900
H	2.90207400	1.40962200	–0.79926900
H	1.73384100	–0.59324900	–2.65857000
H	0.83664800	–1.65762700	–1.56961300
H	0.31699100	–0.16644200	0.63317300
H	–1.12673400	3.71133500	–0.22004800
H	–0.41355200	3.38655900	–2.63087000
H	0.83855300	1.29983500	–3.17115300
H	2.42092700	–2.83338500	–0.29651500
C	–1.38355900	–1.84799000	0.56504200
C	–2.43268400	–2.88845400	0.21059300
C	–3.83798100	–2.29121200	0.26077800
C	–3.91815000	–1.06310500	–0.64441500
C	–2.85771300	–0.03211700	–0.28201800
H	–4.57602700	–3.03596300	–0.05004300
H	–2.22663700	–3.28226400	–0.79339400
H	–2.32917300	–3.72002100	0.91358800
H	–1.51229200	–1.46302500	1.58015100
H	–0.36680200	–2.23245400	0.45420800
H	–3.79049500	–1.35828400	–1.69389400
H	–4.89303900	–0.57413200	–0.56151700
H	–2.86406200	0.81250200	–0.97276400
H	–2.99264100	0.32622100	0.74240900
H	–4.07654000	–2.00262100	1.29222400
N	–1.49192300	–0.65904400	–0.35068100
H	–1.38651600	–1.00981200	–1.31317700

TS_{C4}–noBr

1 1

O	–0.39660000	2.82283600	0.84480900
O	–1.79661400	2.68912200	–0.79256500
N	1.08260600	–0.83373200	0.05450200
N	–0.88904500	2.24439200	–0.11142200
C	4.03222600	0.24702500	1.36731800
C	5.24242700	0.85596900	1.03280600
C	5.92285400	0.46698900	–0.12006900
C	5.39523800	–0.53537200	–0.93689800
C	4.18887300	–1.14569100	–0.60113500
C	3.49985100	–0.75358300	0.55152200
C	2.17648700	–1.38977000	0.89866600
C	0.59655500	0.38066900	0.34492800

C	–0.37163100	0.93139600	–0.46393300
C	–0.91943400	0.24546400	–1.55697000
C	–0.32242400	–0.99531600	–1.86243900
C	0.64093900	–1.51557200	–1.03864400
H	5.65263600	1.63039300	1.67390100
H	6.86503800	0.93979400	–0.38071200
H	5.92714400	–0.84503000	–1.83144200
H	3.78304500	–1.93143700	–1.23429500
H	2.18692300	–2.46622300	0.72433500
H	1.90351300	–1.20126100	1.93843500
H	1.00439800	0.89226900	1.21046900
H	–1.56833900	0.75232200	–2.25750000
H	–0.63516500	–1.55889100	–2.73279100
H	1.10841300	–2.47648000	–1.22063200
H	3.50233000	0.54565600	2.26835600
C	–2.67297500	–0.88457000	0.72209500
C	–3.85196400	–1.58411500	1.40344300
C	–5.10704700	–0.70979600	1.33369900
C	–5.39721400	–0.29087900	–0.11001300
C	–4.16542400	0.37301200	–0.73039200
H	–5.96513500	–1.24136200	1.75869900
H	–4.03771300	–2.53997300	0.89514500
H	–3.59308900	–1.81268000	2.44327100
H	–2.41222400	0.02513300	1.28360200
H	–1.78710500	–1.53231400	0.70635600
H	–5.66569100	–1.17403700	–0.70580900
H	–6.24595300	0.40093800	–0.15169800
H	–4.33793100	0.62950800	–1.78045700
H	–3.93745400	1.30310400	–0.19441800
H	–4.95210700	0.19041900	1.94454100
N	–2.97419200	–0.48053700	–0.65035200
H	–3.10944100	–1.31153500	–1.22831100

Pro$_{C4}$–noBr

1 1

O	–0.88388000	3.03261500	1.28307400
O	–2.17134100	2.82823500	–0.43748000
N	1.01940500	–0.38720300	0.46672800
N	–1.29949000	2.39132100	0.31556600
C	3.76057200	0.77515500	0.09446700
C	4.97306400	1.05257500	–0.53207100
C	5.92557200	0.04346100	–0.69300700
C	5.65773500	–1.24276300	–0.22839800
C	4.43966000	–1.52113000	0.39493000
C	3.48831300	–0.51419700	0.56479900
C	2.18094000	–0.81599700	1.26386700

C	0.30213300	0.69090100	0.80215300
C	–0.75415500	1.11226100	0.03260000
C	–1.28811100	0.31703700	–1.10612200
C	–0.23204400	–0.64715100	–1.55826700
C	0.79915200	–0.98809200	–0.77402400
H	5.17678600	2.05629700	–0.89323800
H	6.87059400	0.26065100	–1.18205600
H	6.39206700	–2.03281900	–0.35491900
H	4.22728600	–2.52643700	0.75048300
H	2.08560100	–1.88819800	1.45273900
H	2.11725000	–0.29617900	2.22262300
H	0.61161400	1.24240900	1.68350100
H	–1.62802900	0.95293100	–1.92669800
H	–0.32946600	–1.09715200	–2.54009200
H	1.54360900	–1.71984200	–1.06875500
H	3.02258100	1.56558300	0.21651000
C	–2.40195700	–1.32631300	0.51206500
C	–3.59918100	–2.25321700	0.67604600
C	–4.90950100	–1.46803100	0.70967100
C	–5.02383600	–0.58328300	–0.53096700
C	–3.81271500	0.32721500	–0.66974800
H	–5.75920700	–2.15444600	0.76459200
H	–3.61237000	–2.97467400	–0.15111300
H	–3.45506500	–2.82154200	1.59946400
H	–2.32545900	–0.62371100	1.34659100
H	–1.47103200	–1.88911200	0.41959300
H	–5.11383200	–1.20509200	–1.43118600
H	–5.91384600	0.05090900	–0.48433600
H	–3.84801900	0.92756500	–1.58040600
H	–3.71512900	0.98964900	0.19345000
H	–4.93631500	–0.84030400	1.60953600
N	–2.55631500	–0.49822400	–0.73134200
H	–2.67689300	–1.15513100	–1.51565600

TS_{C6}–noBr

1 1

O	–4.36355300	–1.08703100	–1.53994300
O	–5.06993800	0.52620700	–0.29384800
N	–0.90454500	–1.33253500	0.51149700
N	–4.22780800	–0.29306100	–0.62162800
C	2.44918900	–2.32760300	0.89893500
C	3.76459900	–2.00022400	0.56336200
C	4.04855700	–1.45604900	–0.68760600
C	3.01926600	–1.25676100	–1.61230000
C	1.71087100	–1.60203500	–1.28349600
C	1.41700500	–2.12498800	–0.01932600

C	0.00324000	–2.50378600	0.33957300
C	–2.06454600	–1.29243700	–0.17054100
C	–2.98409400	–0.31719700	0.12956300
C	–2.77461300	0.58853500	1.18462700
C	–1.56774300	0.54457100	1.83381700
C	–0.57165900	–0.34827900	1.39069900
H	4.56212200	–2.16357700	1.28186100
H	5.06952300	–1.19258900	–0.94769200
H	3.23965300	–0.84200700	–2.59154000
H	0.90992500	–1.46154300	–2.00748100
H	–0.44685400	–3.12266300	–0.43769000
H	–0.02276800	–3.05403600	1.28282000
H	–2.24241300	–2.06622900	–0.90784000
H	–3.55354500	1.28694100	1.46940400
H	–1.34025000	1.21417400	2.65415200
H	0.34363000	–0.50583200	1.94980100
H	2.22365000	–2.74600500	1.87680200
C	–0.11710800	2.34419300	–0.15514600
C	0.68978700	3.39436200	–0.92295400
C	2.00973700	3.69007400	–0.20777900
C	2.78814300	2.39485000	0.03187300
C	1.92040200	1.37451800	0.77013800
H	2.61030100	4.39569100	–0.79138400
H	0.89432200	3.01676800	–1.93388600
H	0.08935400	4.30444000	–1.02996100
H	–0.41680500	2.75192900	0.82008000
H	–1.03182400	2.07933000	–0.69596000
H	3.09730800	1.96534000	–0.93142900
H	3.69905900	2.58503600	0.61043900
H	2.44509000	0.42068800	0.88241900
H	1.68331600	1.74651200	1.77738300
H	1.79854500	4.16935100	0.75836200
N	0.64576200	1.11936000	0.09185800
H	0.81653100	0.63806300	–0.79104000

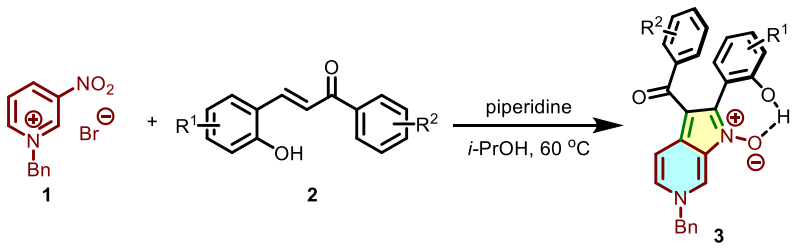
Pro$_{C6}$–noBr

1 1

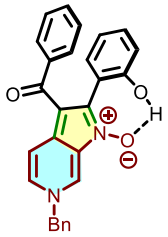
O	–4.06191200	–1.54545900	–1.36590400
O	–4.95157900	0.28873800	–0.65177800
N	–0.76753600	–0.97523800	0.87302700
N	–4.02148200	–0.51801900	–0.68386400
C	2.64616100	–1.60549400	1.21080800
C	3.86148500	–1.38774800	0.55654500
C	3.93234800	–1.48267800	–0.83230300
C	2.78975900	–1.80566900	–1.56946300
C	1.57834700	–2.02279400	–0.91767200
C	1.49773500	–1.91573900	0.47630100

C	0.16276400	–2.08478000	1.16557100
C	–1.88204700	–1.19251000	0.16522300
C	–2.86747500	–0.23851600	0.08589700
C	–2.79788600	0.93094000	0.92289800
C	–1.66681300	1.18036400	1.60301700
C	–0.44946300	0.33433800	1.40304800
H	4.74897600	–1.14431500	1.13302400
H	4.87587600	–1.31111500	–1.34178500
H	2.84471600	–1.88750500	–2.65093500
H	0.68649200	–2.27054000	–1.49004100
H	–0.32882300	–3.00482400	0.84371700
H	0.29341700	–2.12642500	2.25095400
H	–1.99236300	–2.16864400	–0.29575000
H	–3.67798100	1.55277400	1.04275300
H	–1.60089000	1.99277400	2.31713700
H	0.11944100	0.20573700	2.32873500
H	2.58678500	–1.52768200	2.29395200
C	0.09612200	1.25623000	–0.94025000
C	1.23755600	1.81595800	–1.77969800
C	1.78924100	3.11117500	–1.18613000
C	2.20302700	2.88905600	0.26790000
C	1.04493200	2.33277500	1.08244200
H	2.64372600	3.45943300	–1.77311300
H	2.03442500	1.06270600	–1.84460800
H	0.85828400	1.97416600	–2.79333800
H	–0.74905300	1.94827200	–0.89012900
H	–0.23980600	0.29181000	–1.32572600
H	3.04800800	2.18933600	0.31904900
H	2.52422600	3.82345700	0.73683900
H	1.33178500	2.11286100	2.11345700
H	0.19345200	3.01833400	1.07959500
H	1.01956200	3.89213200	–1.23052100
N	0.56708800	1.04480500	0.46953200
H	1.38643800	0.42075100	0.42251400

3. Experimental data for the formation of 3

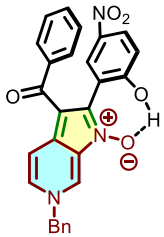


General procedure: To a 5.0 mL vial were successively added pyridinium salts **1** (0.2 mmol), *ortho*-hydroxychalcones **2** (0.70 mmol, 3.5 equiv.) and 1.0 mL of *i*-PrOH. And then, piperidine (149.0 mg, 1.75 mmol) was added by syringe. The resulting mixture was stirred at 60 ^{o}C, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate or dichloromethane/methanol) to afford the corresponding products **3**.



3-Benzoyl-6-benzyl-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3a**)

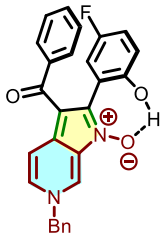
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 1:10); 69.1 mg, 82% yield; reaction time = 24 h; mp 147.3-148.0 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.59 (br, 1H), 9.14 (s, 1H), 7.95 (d, *J* = 6.0 Hz, 1H), 7.56 (d, *J* = 6.0 Hz, 1H), 7.49 (d, *J* = 6.0 Hz, 2H), 7.36-7.29 (m, 4H), 7.21-7.12 (m, 5H), 6.96 (d, *J* = 6.0 Hz, 1H), 6.84 (d, *J* = 6.0 Hz, 1H), 6.36 (t, *J* = 6.0 Hz, 1H), 5.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 159.5, 151.4, 138.6, 133.9, 133.5, 132.1, 131.7, 130.6, 130.4, 130.0, 129.5, 129.5, 129.2, 128.4, 128.1, 127.9, 119.9, 118.4, 117.1, 116.5, 108.0, 63.2. IR (KBr) ν 3413, 1622, 1454, 748 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{21}N_2O_3$ $[M+H]^+$: 421.1547, found: 421.1571.



3-Benzoyl-6-benzyl-2-(2-hydroxy-5-nitrophenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3b**)

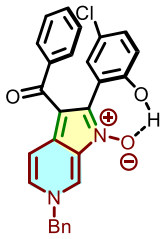
Yellow solid obtained by column chromatography (dichloromethane/methanol = 120:1 to 80:1); 39.2 mg, 42% yield; reaction time = 72 h; mp 280.9-281.6 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.72 (s, 1H), 8.41 (d, *J* = 6.0 Hz, 1H), 8.02 (d, *J* = 6.0 Hz, 1H), 7.95 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.75 (d, *J* = 3.0 Hz, 1H), 7.55 (d, *J* = 6.0 Hz, 2H), 7.43-7.41 (m, 5H), 7.34 (d, *J* = 6.0 Hz, 1H), 7.19 (t, *J* = 6.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 1H), 5.83 (s, 2H), the proton of phenolic hydroxyl

group was missing; ^{13}C NMR (75 MHz, DMSO-d_6) δ 189.8, 168.4, 147.8, 138.5, 136.9, 135.6, 133.2, 131.8, 130.6, 130.4, 130.0, 129.2, 129.0, 128.9, 128.7, 128.5, 128.0, 127.1, 120.6, 116.8, 116.4, 107.4, 62.0. IR (KBr) ν 3424, 3042, 1624, 1486, 1333, 749 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}N_3O_5$ [M+H]$^+$: 466.1397, found: 466.1395.



3-Benzoyl-6-benzyl-2-(5-fluoro-2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3c**)

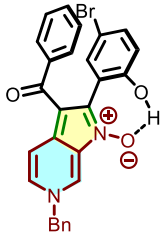
Yellow solid obtained by column chromatography (dichloromethane/methanol = 120:1 to 70:1); 68.9 mg, 79% yield; reaction time = 72 h; mp 208.7-209.4 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.72 (s, 1H), 9.62 (s, 1H), 8.29 (d, J = 6.0 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.53-7.37 (m, 8H), 7.28 (t, J = 6.0 Hz, 2H), 7.06-6.99 (m, 1H), 6.83 (dd, J_1 = 9.0 Hz, J_2 = 6.0 Hz, 1H), 6.70 (dd, J_1 = 12.0 Hz, J_2 = 6.0 Hz, 1H), 5.78 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 189.3, 155.9, 154.2 (d, J = 232.5 Hz, 1C), 148.3 (d, J = 2.3 Hz, 1C), 139.2, 135.7, 132.6, 131.8, 129.9, 129.7, 129.5, 129.2, 128.9, 128.8, 128.4, 128.1, 120.5 (d, J = 8.3 Hz, 1C), 118.7 (d, J = 2.3 Hz, 1C), 118.4 (d, J = 3.0 Hz, 1C), 117.9 (d, J = 8.3 Hz, 1C), 116.2, 106.8, 61.7; ^{19}F NMR (376 MHz, DMSO-d_6) δ -127.4. IR (KBr) ν 3427, 3048, 1627, 1464, 1133 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}FN_2O_3$ [M+H]$^+$: 439.1452, found: 439.1452.



3-Benzoyl-6-benzyl-2-(5-chloro-2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3d**)

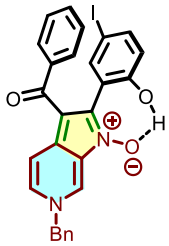
Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 80:1); 56.4 mg, 62% yield; reaction time = 72 h; mp 234.7-235.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.26 (s, 1H), 9.62 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.53-7.40 (m, 8H), 7.28 (t, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 1H), 6.89 (s, 1H), 6.83 (d, J = 8.0 Hz, 1H), 5.78 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.4, 158.8, 148.1, 139.1, 135.6, 132.6, 132.4, 131.8,

131.2, 129.9, 129.8, 129.4, 129.1, 128.9, 128.6, 128.4, 128.1, 121.2, 121.2, 118.6, 116.2, 106.8, 61.7. IR (KBr) ν 3046, 1622, 1450, 1129 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}ClN_2O_3$ $[M+H]^+$: 455.1157, found: 455.1157.



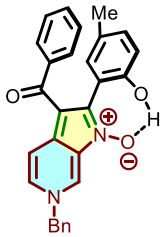
3-Benzoyl-6-benzyl-2-(5-bromo-2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3e**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 120:1 to 80:1); 55.7 mg, 56% yield; reaction time = 72 h; mp 229.8-231.3 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 14.32 (br, 1H), 9.63 (s, 1H), 8.31 (d, *J* = 6.0 Hz, 1H), 7.85 (d, *J* = 6.0 Hz, 1H), 7.52 (d, *J* = 6.0 Hz, 2H), 7.46-7.40 (m, 6H), 7.30-7.25 (m, 3H), 6.99 (d, *J* = 3.0 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 1H), 5.78 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 189.6, 159.2, 148.1, 139.1, 135.7, 135.4, 134.1, 132.8, 131.9, 129.9, 129.9, 129.4, 129.2, 129.0, 128.7, 128.5, 128.2, 121.7, 119.2, 116.3, 108.7, 106.9, 61.8. IR (KBr) ν 3429, 3030, 1623, 1451, 746 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}BrN_2O_3$ $[M+H]^+$: 499.0652, found: 499.0651.



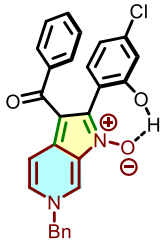
3-Benzoyl-6-benzyl-2-(2-hydroxy-5-iodophenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3f**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 120:1 to 80:1); 65.9 mg, 60% yield; reaction time = 72 h; mp 115.8-116.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.86 (br, 1H), 9.19 (s, 1H), 8.26 (d, *J* = 4.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.43-7.42 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28-7.20 (m, 4H), 7.05 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 159.7, 149.9, 142.2, 140.4, 138.5, 133.2, 131.8, 130.9, 130.6, 130.1, 129.8, 129.7, 128.9, 128.6, 128.2, 128.1, 122.1, 119.4, 117.2, 108.3, 79.3, 63.5. IR (KBr) ν 3423, 2931, 1626, 1451 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}IN_2O_3$ $[M+H]^+$: 547.0513, found: 547.0524.



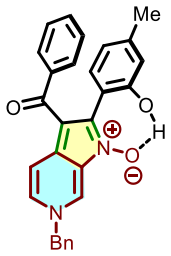
3-Benzoyl-6-benzyl-2-(2-hydroxy-5-methylphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3g**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 120:1 to 90:1); 35.3 mg, 41% yield; reaction time = 72 h; mp 233.7-234.8 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.30 (s, 1H), 9.27 (s, 1H), 8.14 (d, *J* = 6.0 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 6.0 Hz, 2H), 7.39-7.37 (m, 3H), 7.32-7.22 (m, 3H), 7.16 (t, *J* = 9.0 Hz, 2H), 6.93 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.87 (d, *J* = 6.0 Hz, 1H), 6.59 (s, 1H), 5.49 (s, 2H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 157.2, 151.5, 138.8, 134.2, 133.5, 132.8, 131.4, 130.8, 130.4, 130.2, 129.5, 129.4, 128.9, 128.4, 128.1, 127.7, 127.5, 119.5, 116.6, 108.0, 63.2, 19.8, one carbon missing in the aromatic region. IR (KBr) ν 3424, 3044, 1626, 1461, 1230 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{23}N_2O_3$ $[M+H]^+$: 435.1703, found: 435.1702.



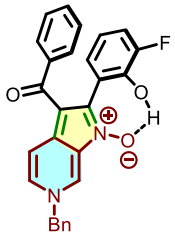
3-Benzoyl-6-benzyl-2-(4-chloro-2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3h**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 120:1 to 50:1); 61.6 mg, 68% yield; reaction time = 72 h; mp 205.7-206.9 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 14.88 (br, 1H), 9.62 (s, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 6.0 Hz, 1H), 7.53-7.37 (m, 8H), 7.29 (t, *J* = 6.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.88 (d, *J* = 6.0 Hz, 1H), 6.44 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 1H), 5.78 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.4, 161.0, 148.7, 139.0, 136.2, 135.6, 134.6, 132.5, 131.9, 129.8, 129.6, 129.2, 129.1, 128.9, 128.3, 128.1, 119.2, 117.6, 116.3, 115.9, 106.8, 61.7, one carbon missing in the aromatic region. IR (KBr) ν 3424, 1625, 1401, 1225 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}ClN_2O_3$ $[M+H]^+$: 455.1157, found: 455.1182.



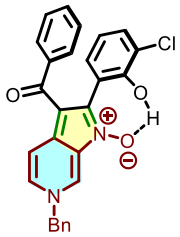
3-Benzoyl-6-benzyl-2-(2-hydroxy-4-methylphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3i**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 120:1 to 50:1); 56.5 mg, 65% yield; reaction time = 72 h; mp 169.0-169.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.56 (br, 1H), 8.98 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 4.0 Hz, 2H), 7.44-7.42 (m, 3H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.28-7.27 (m, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 6.82 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 5.47 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 159.5, 151.5, 142.8, 138.8, 133.6, 131.6, 130.5, 130.3, 130.0, 129.4, 129.4, 129.3, 128.1, 127.9, 120.3, 119.6, 116.1, 114.2, 107.8, 63.1, 21.3, two carbons missing in the aromatic region. IR (KBr) ν 3423, 2379, 1624, 1484 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{23}N_2O_3$ $[M+H]^+$: 435.1703, found: 435.1716.



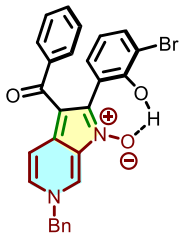
3-Benzoyl-6-benzyl-2-(3-fluoro-2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3j**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 50:1); 45.6 mg, 52% yield; reaction time = 72 h; mp 254.9-255.6 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 14.87 (br, 1H), 9.66 (s, 1H), 8.31 (d, *J* = 6.0 Hz, 1H), 7.81 (d, *J* = 6.0 Hz, 1H), 7.54-7.35 (m, 8H), 7.27 (t, *J* = 6.0 Hz, 2H), 7.09 (t, *J* = 9.0 Hz, 1H), 6.72 (d, *J* = 6.0 Hz, 1H), 6.37-6.30 (m, 1H), 5.79 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.4, 153.3 (d, *J* = 238.0 Hz, 1C), 148.8, 148.8, 148.6, 138.9, 135.6, 132.6, 132.0, 129.8, 129.2, 129.1, 128.9, 128.8 (d, *J* = 3.0 Hz, 1C), 128.4, 128.1, 119.7 (d, *J* = 3.0 Hz, 1C), 117.2, 117.0, 117.0, 116.1, 106.8, 61.7; ^{19}F NMR (376 MHz, DMSO-d_6) δ -135.5. IR (KBr) ν 3406, 3070, 1632, 1479, 1402, 1114 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}FN_2O_3$ $[M+H]^+$: 439.1452, found: 439.1440.



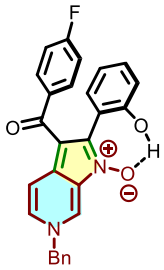
3-Benzoyl-6-benzyl-2-(3-chloro-2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3k**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 90:1); 38.2 mg, 42% yield; reaction time = 72 h; mp 275.9-276.6 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.68 (s, 1H), 8.31 (d, J = 6.0 Hz, 1H), 7.79 (d, J = 6.0 Hz, 1H), 7.54-7.25 (m, 11H), 6.89 (d, J = 6.0 Hz, 1H), 6.36 (t, J = 6.0 Hz, 1H), 5.79 (s, 2H), the proton of phenolic hydroxyl group was missing; ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.5, 156.0, 148.9, 138.9, 135.7, 132.6, 132.5, 132.0, 131.4, 129.8, 129.1, 129.1, 128.9, 128.4, 128.1, 128.0, 127.6, 123.5, 118.8, 117.7, 116.1, 107.0, 61.7. IR (KBr) ν 3421, 3075, 1609, 1406, 1223, 741 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}ClN_2O_3$ $[M+H]^+$: 455.1157, found: 455.1145.



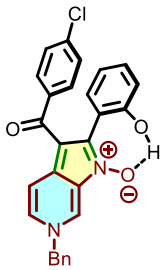
3-Benzoyl-6-benzyl-2-(3-bromo-2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3l**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 50:1); 40.0 mg, 40% yield; reaction time = 72 h; mp 274.6-275.5 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.67 (s, 1H), 8.31 (d, J = 6.0 Hz, 1H), 7.78 (d, J = 6.0 Hz, 1H), 7.54-7.36 (m, 9H), 7.28 (t, J = 6.0 Hz, 2H), 6.93 (d, J = 9.0 Hz, 1H), 6.31 (t, J = 9.0 Hz, 1H), 5.79 (s, 2H), the proton of phenolic hydroxyl group was missing; ^{13}C NMR (75 MHz, DMSO-d_6) δ 189.5, 156.7, 148.9, 138.9, 135.7, 134.6, 133.3, 132.7, 132.1, 129.8, 129.1, 129.1, 128.9, 128.4, 128.2, 118.5, 118.3, 116.1, 113.9, 107.0, 61.7, two carbons missing in the aromatic region. IR (KBr) ν 3072, 1623, 1404, 1325, 739 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}BrN_2O_3$ $[M+H]^+$: 499.0652, found: 499.0651.



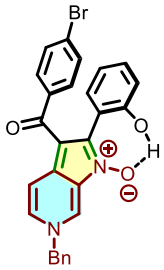
6-Benzyl-3-(4-fluorobenzoyl)-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3m**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 1:5); 50.4 mg, 58% yield; reaction time = 20 h; mp 266.1-266.8 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.54 (s, 1H), 9.10 (s, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 7.64 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 1H), 7.52-7.47 (m, 2H), 7.41-7.39 (m, 3H), 7.25-7.14 (m, 2H), 7.17 (t, *J* = 9.0 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.82-6.77 (m, 3H), 6.38 (t, *J* = 6.0 Hz, 1H), 5.46 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 164.7 (d, *J* = 252.0 Hz, 1C), 159.6, 151.5, 134.7 (d, *J* = 3.0 Hz, 1C), 133.9, 133.3, 132.3, 131.8, 131.7, 130.8, 130.3, 130.3, 129.8, 129.6, 128.2, 128.1, 120.1, 118.5, 116.9 (d, *J* = 19.5 Hz, 1C), 114.9 (d, *J* = 20.9 Hz, 1C), 108.0, 63.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.78 to -106.85 (m, 1F). IR (KBr) ν 3410, 2922, 1600, 1454, 759 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}FN_2O_3$ $[M+H]^+$: 439.1452, found: 439.1453.



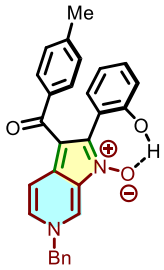
6-Benzyl-3-(4-chlorobenzoyl)-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3n**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 70:1); 68.6 mg, 75% yield; reaction time = 24 h; mp 263.4-264.1 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.93 (s, 1H), 9.59 (s, 1H), 8.30 (d, *J* = 6.0 Hz, 1H), 7.86 (d, *J* = 6.0 Hz, 1H), 7.52 (d, *J* = 6.0 Hz, 2H), 7.46-7.36 (m, 5H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.19 (t, *J* = 6.0 Hz, 1H), 6.87 (d, *J* = 6.0 Hz, 2H), 6.41 (t, *J* = 6.0 Hz, 1H), 5.78 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 188.1, 159.7, 149.7, 137.8, 136.4, 135.7, 133.7, 132.6, 131.7, 130.6, 129.8, 129.6, 129.5, 129.1, 128.9, 128.3, 128.0, 119.5, 117.8, 117.2, 115.9, 106.4, 61.6. IR (KBr) ν 3422, 2378, 1622, 1456, 762 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}ClN_2O_3$ $[M+H]^+$: 455.1157, found: 455.1157.



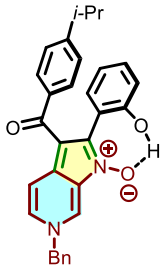
6-Benzyl-3-(4-bromobenzoyl)-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3o**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 1:5); 64.1 mg, 64% yield; reaction time = 20 h; mp 249.2-250.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.47 (br, 1H), 9.10 (s, 1H), 8.11 (d, *J* = 6.0 Hz, 1H), 7.64 (d, *J* = 6.0 Hz, 1H), 7.40-7.39 (m, 3H), 7.34 (d, *J* = 9.0 Hz, 2H), 7.24-7.16 (m, 5H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.78 (d, *J* = 6.0 Hz, 1H), 6.38 (t, *J* = 6.0 Hz, 1H), 5.46 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 159.6, 151.5, 137.4, 133.9, 133.2, 132.3, 131.1, 130.9, 130.8, 130.5, 130.3, 129.8, 129.6, 128.3, 128.1, 126.5, 120.1, 118.5, 116.9, 116.8, 107.9, 63.5. IR (KBr) ν 3400, 3081, 1597, 1455, 759 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}BrN_2O_3$ $[M+H]^+$: 499.0652, found: 499.0652.



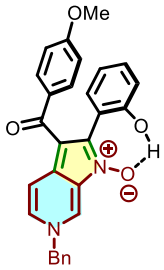
6-Benzyl-2-(2-hydroxyphenyl)-3-(4-methylbenzoyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3p**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 200:1 to 50:1); 44.2 mg, 51% yield; reaction time = 46 h; mp 210.7-211.8 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.62 (s, 1H), 8.99 (s, 1H), 8.10 (d, *J* = 6.0 Hz, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.47-7.45 (m, 5H), 7.30 (s, 2H), 7.20 (t, *J* = 9.0 Hz, 1H), 7.05-6.97 (m, 3H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.42 (t, *J* = 9.0 Hz, 1H), 5.52 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 159.5, 151.4, 142.5, 135.9, 133.9, 133.5, 132.0, 130.4, 130.1, 129.9, 129.6, 129.5, 129.5, 128.6, 128.1, 120.0, 118.4, 117.2, 116.4, 108.3, 63.3, 21.5, one carbon missing in the aromatic region. IR (KBr) ν 3426, 2925, 1625, 1451 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{23}N_2O_3$ $[M+H]^+$: 435.1703, found: 435.1702.



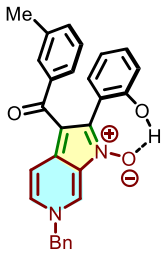
6-Benzyl-2-(2-hydroxyphenyl)-3-(4-isopropylbenzoyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3q**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 100:1 to 70:1); 44.3 mg, 48% yield; reaction time = 72 h; mp 66.2-68.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.48 (s, 1H), 9.02 (s, 1H), 8.17 (d, *J* = 6.0 Hz, 1H), 7.68 (d, *J* = 6.0 Hz, 1H), 7.46-7.44 (m, 5H), 7.31 (s, 2H), 7.15 (t, *J* = 9.0 Hz, 1H), 7.03-7.00 (m, 3H), 6.85 (d, *J* = 6.0 Hz, 1H), 6.35 (t, *J* = 9.0 Hz, 1H), 5.52 (s, 2H), 2.89-2.80 (m, 1H), 1.19 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 159.5, 153.1, 151.6, 136.3, 133.9, 133.5, 131.9, 130.5, 130.2, 130.0, 129.6, 129.5, 129.5, 128.2, 128.1, 125.9, 119.8, 118.3, 117.2, 116.6, 108.4, 63.3, 34.1, 23.6. IR (KBr) ν 3424, 2928, 1605, 1453, 1256, 751 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{27}N_2O_3$ $[M+H]^+$: 463.2016, found: 463.2016.



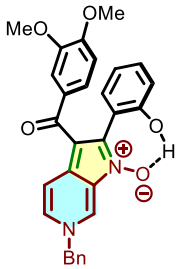
6-Benzyl-2-(2-hydroxyphenyl)-3-(4-methoxybenzoyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3r**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 1:6); 48.5 mg, 54% yield; reaction time = 72 h; mp 256.0-257.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.11 (s, 1H), 9.54 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 4H), 7.44-7.36 (m, 3H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.48 (t, *J* = 8.0 Hz, 1H), 5.76 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.2, 162.3, 159.7, 149.4, 135.8, 133.3, 131.8, 131.6, 131.4, 131.3, 129.4, 129.1, 129.0, 128.9, 128.3, 119.7, 117.9, 117.5, 115.6, 113.4, 107.0, 61.5, 55.4, one carbon missing in the aromatic region. IR (KBr) ν 3412, 2927, 1600, 1453, 1253, 762 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{23}N_2O_4$ $[M+H]^+$: 451.1652, found: 451.1675.



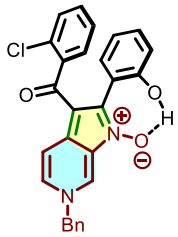
6-Benzyl-2-(2-hydroxyphenyl)-3-(3-methylbenzoyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3s**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 80:1); 41.2 mg, 47% yield; reaction time = 72 h; mp 130.5-131.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.55 (s, 1H), 9.10 (s, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 6.0 Hz, 1H), 7.44-7.31 (m, 7H), 7.18-7.01 (m, 4H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.40 (t, *J* = 9.0 Hz, 1H), 5.51 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 159.6, 151.6, 138.4, 137.6, 133.7, 133.5, 132.5, 132.1, 130.6, 130.2, 130.1, 129.6, 129.5, 128.2, 128.1, 127.8, 126.4, 119.8, 118.4, 117.3, 116.6, 108.3, 63.3, 21.0, one carbon missing in the aromatic region. IR (KBr) ν 3423, 2926, 1627, 1454, 756 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{23}N_2O_3$ $[M+H]^+$: 435.1703, found: 435.1702.



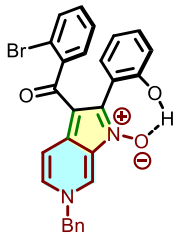
6-Benzyl-3-(3,4-dimethoxybenzoyl)-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3t**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 100:1 to 50:1); 30.7 mg, 33% yield; reaction time = 72 h; mp 204.4-205.3 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.72 (s, 1H), 9.10 (s, 1H), 8.13 (d, *J* = 6.0 Hz, 1H), 7.67 (d, *J* = 6.0 Hz, 1H), 7.44 (s, 3H), 7.30-7.29 (m, 3H), 7.20 (t, *J* = 6.0 Hz, 1H), 7.07 (s, 1H), 7.02 (d, *J* = 6.0 Hz, 1H), 6.93 (d, *J* = 6.0 Hz, 1H), 6.67 (d, *J* = 9.0 Hz, 1H), 6.46 (t, *J* = 6.0 Hz, 1H), 5.51 (s, 2H), 3.86 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 159.5, 152.2, 151.3, 148.1, 133.8, 133.4, 132.3, 131.0, 130.4, 130.1, 129.9, 129.7, 129.6, 128.1, 128.0, 123.9, 120.0, 118.6, 117.5, 116.7, 111.9, 109.9, 108.5, 63.4, 55.9, 55.7. IR (KBr) ν 3431, 2379, 1627, 1456, 1270, 761 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{25}N_2O_5$ $[M+H]^+$: 481.1758, found: 481.1758.



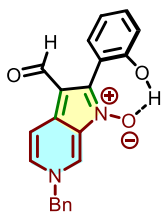
6-Benzyl-3-(2-chlorobenzoyl)-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3u**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 70:1); 62.4 mg, 69% yield; reaction time = 60 h; mp 251.7-252.9 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.42 (s, 1H), 9.58 (s, 1H), 8.32 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 1H), 7.55-7.50 (m, 3H), 7.45-7.38 (m, 3H), 7.32-7.29 (m, 3H), 7.27-7.16 (m, 3H), 6.82 (d, J = 6.0 Hz, 1H), 6.50 (t, J = 6.0 Hz, 1H), 5.76 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 186.6, 159.4, 150.1, 139.9, 135.5, 133.5, 133.4, 131.8, 131.3, 130.5, 130.3, 130.1, 129.7, 129.6, 129.5, 129.1, 128.9, 128.4, 127.1, 119.4, 117.5, 116.9, 115.7, 106.8, 61.7. IR (KBr) ν 3430, 2378, 1627, 1458, 759 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}ClN_2O_3$ $[M+H]^+$: 455.1157, found: 455.1161.



6-Benzyl-3-(2-bromobenzoyl)-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3v**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 70:1); 67.1 mg, 67% yield; reaction time = 48 h; mp 219.0-220.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.09 (s, 1H), 9.15 (s, 1H), 8.01 (d, J = 6.0 Hz, 1H), 7.64 (d, J = 6.0 Hz, 1H), 7.43-7.32 (m, 4H), 7.22 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 2H), 7.16-7.02 (m, 5H), 6.90 (d, J = 9.0 Hz, 1H), 6.46 (t, J = 6.0 Hz, 1H), 5.43 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.0, 159.4, 152.1, 141.0, 133.8, 133.3, 132.1, 131.5, 131.2, 131.0, 130.8, 129.9, 129.7, 129.6, 128.4, 128.2, 126.9, 120.7, 119.9, 118.3, 117.0, 116.7, 108.0, 63.4, one carbon missing in the aromatic region. IR (KBr) ν 3423, 2378, 1623, 1456, 758 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}BrN_2O_3$ $[M+H]^+$: 499.0652, found: 499.0647.

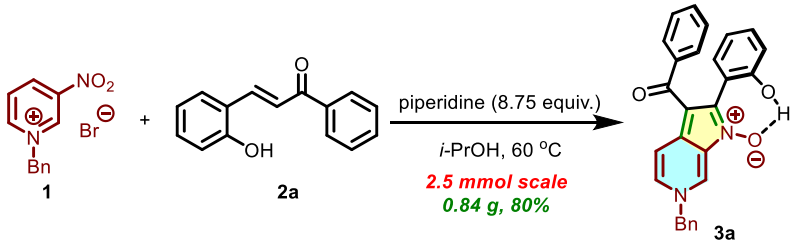


6-Benzyl-3-formyl-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**3w**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 120:1 to 90:1); 21.3 mg, 31% yield; reaction time = 72 h; mp 186.5-187.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.61 (s, 1H), 9.97 (s, 1H), 9.16 (s, 1H), 8.52 (d, *J* = 6.0 Hz, 1H), 7.81 (d, *J* = 6.0 Hz, 1H), 7.51 (d, *J* = 3.0 Hz, 2H), 7.44 (s, 3H), 7.30 (s, 2H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.03 (t, *J* = 6.0 Hz, 1H), 5.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 160.5, 153.3, 133.1, 133.1, 131.7, 131.2, 129.9, 129.7, 129.7, 128.3, 128.1, 121.0, 119.3, 117.5, 116.1, 108.6, 63.7, one carbon missing in the aromatic region. IR (KBr) ν 3411, 3061, 1633, 1456, 1123, 759 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{17}N_2O_3$ $[M+H]^+$: 345.1234, found: 345.1248.

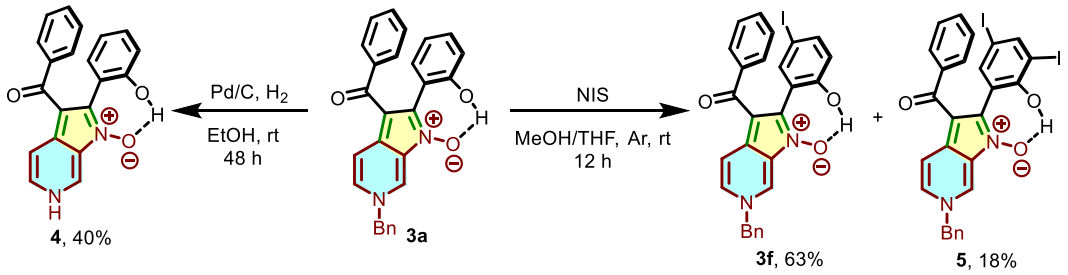
4. Methodology application

4.1 Scalable preparation of 3a



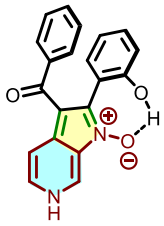
General procedure for scalable preparation of 3a: To a solution of *N*-benzyl pyrridinium salt **1a** (0.56 g, 2.5 mmol) and *ortho*-hydroxychalcone **2a** (2.58 g, 8.75 mmol) in *i*-PrOH (12.5 mL) was added piperidine (1.86 g, 21.88 mmol) successively. After being stirred at 60 °C for 48 h, the mixture was concentrated in vacuum. The residue was purified via flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding product **3a** as yellow solid in 80% yield (0.84 g).

4.2 Chemical conversions of 3a



General procedure for the preparation of 4: To a solution of **3a** (63.1 mg, 0.15 mmol) in EtOH (1.0 mL) was added Pd/C (31.9 mg). Hydrogenation was carried out under hydrogen

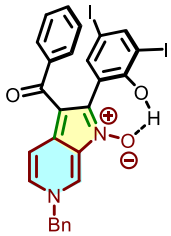
atmosphere at room temperature under atmospheric pressure for 48 h. Then, the reaction mixture was filtered and the filtrate was concentrated in vacuo. Purification of the residue by flash column chromatography afforded the desired product **4** (19.7 mg, 40% yield).



3-Benzoyl-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**4**)

Yellow solid obtained by column chromatography (dichloromethane/methanol = 100:1 to 20:1); 19.7 mg, 40% yield; reaction time = 48 h; mp 129.6-130.8 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (s, 1H), 8.21 (d, *J* = 4.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 9.0 Hz, 2H), 7.14-7.07 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 8.0 Hz, 1H), the protons of N-H and O-H were missing; ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.2, 157.5, 145.3, 139.3, 135.5, 132.7, 131.3, 131.1, 129.9, 129.8, 129.2, 128.7, 127.6, 118.0, 117.2, 116.5, 114.8, 107.4. IR (KBr) ν 3439, 1616, 1459, 1022, 758 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{15}N_2O_3$ $[M+H]^+$: 331.1077, found: 331.1087.

General procedure for the formation of 3f and 5: Under Ar atmosphere, to a solution of **3a** (63.1 mg, 0.15 mmol) in 2.0 mL of combined MeOH and THF (v/v = 1:1), NIS (33.8 mg, 0.15 mmol) was added. The resulting mixture was stirred at room temperature for 12 h, and then purified by silica gel column chromatography (dichloromethane/methanol = 35:1) to afford **3f** and **5** in 63% and 18% yields, respectively.

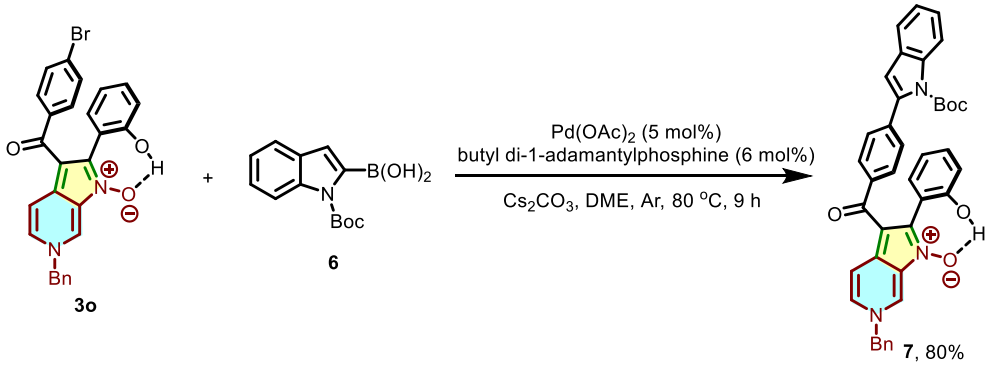


3-Benzoyl-6-benzyl-2-(2-hydroxy-3,5-diiodophenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**5**)

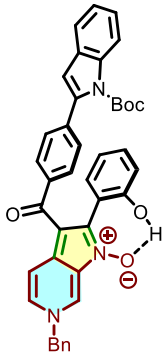
Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 110:1); 17.8 mg,18% yield; reaction time = 12 h; mp 81.4-82.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.09 (br, 1H), 9.23 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H),

7.48-7.43 (m, 5H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.31-7.22 (m, 4H), 7.03 (d, *J* = 4.0 Hz, 1H), 5.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 159.2, 149.1, 148.1, 142.6, 138.3, 133.1, 132.1, 131.0, 130.8, 129.8, 129.7, 129.6, 128.9, 128.8, 128.3, 128.2, 118.1, 117.5, 108.5, 91.5, 78.6, 63.8. IR (KBr) ν 3300, 2926, 1704, 1635, 1184 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{19}I_2N_2O_3$ $[M+H]^+$: 672.9480, found: 672.9485.

4.3 Chemical conversions of 3o



General procedure for the formation of 7: Under nitrogen atmosphere, compound **3o** (74.9 mg, 0.15 mmol), 2-indolylboronic acid **6** (58.7 mg, 0.225 mmol, 1.5 equiv), Cs_2CO_3 (97.8 mg, 0.30 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried Schlenk tube, followed by addition of 1.5 mL of DME. The resulting mixture was stirred at 80 °C for 9 h, and then the reaction mixture was directly subjected to silica gel column chromatography (dichloromethane/methanol as eluent) to afford **7** as a yellow solid in 80% yield.



6-Benzyl-3-(4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)benzoyl)-2-(2-hydroxyphenyl)-6*H*-pyrrolo[2,3-*c*]pyridine 1-oxide (**7**)

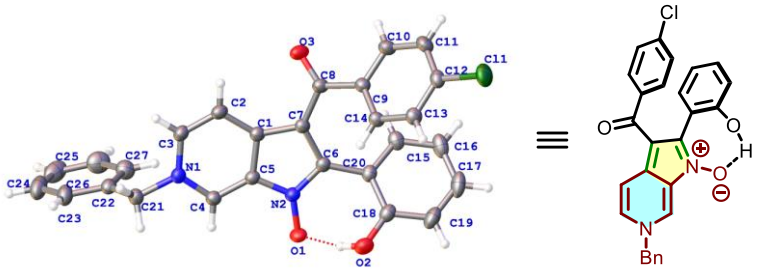
Yellow solid obtained by column chromatography (dichloromethane/methanol = 150:1 to 90:1); 76.2 mg, 80% yield; reaction time = 9 h; mp 70.1-70.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.68 (s,

1H), 9.25 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.59-7.57 (m, 4H), 7.38 (s, 4H), 7.29-7.19 (m, 6H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 6.44 (t, *J* = 8.0 Hz, 1H), 5.44 (s, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 159.6, 151.3, 149.9, 139.5, 137.9, 137.6, 137.4, 133.8, 133.5, 132.0, 130.4, 130.3, 130.1, 129.5, 129.4, 129.0, 128.9, 128.5, 128.1, 127.9, 124.6, 123.0, 120.6, 120.0, 118.5, 117.3, 116.5, 115.2, 110.8, 108.1, 83.8, 63.2, 27.6. IR (KBr) ν 2916, 2855, 1735, 1622, 1455, 1151 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{34}N_3O_5$ $[M+H]^+$: 636.2493, found: 636.2499.

5. Crystal structures

5.1 Crystal structure of 3n

Preparation of the single crystals of **3n**: 22.0 mg of pure compound **3n** was dissolved in the combined solvents of dichloromethane and methanol (4 mL, v/v = 1:3) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about two days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **3n**. The data were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 292.99(10) K during data collection.



3n (CCDC 2130473)

Table S2 Crystal data and structure refinement for **3n.**

Identification code	**3n**
Empirical formula	$C_{27}H_{19}ClN_2O_3$
Formula weight	454.89
Temperature/K	292.99(10)
Crystal system	monoclinic

Space group	$P2_1/c$
a/Å	11.7534(3)
b/Å	13.7503(4)
c/Å	13.8861(4)
α/°	90
β/°	101.298(3)
γ/°	90
Volume/Å^3	2200.68(11)
Z	4
ρ_{calc}g/cm^3	1.373
μ/mm^{-1}	1.806
F(000)	944.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.67 to 147.278
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 16, -17 ≤ l ≤ 15
Reflections collected	8758
Independent reflections	4315 [R_{int} = 0.0288, R_{sigma} = 0.0363]
Data/restraints/parameters	4315/0/300
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1321
Final R indexes [all data]	R_1 = 0.0566, wR_2 = 0.1427
Largest diff. peak/hole / e Å^{-3}	0.27/-0.49

5.2 Crystal structure of 5

Preparation of the single crystals of **5**: 22.0 mg of pure compound **5** was dissolved in 0.5 mL of chloroform at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about two days, several small particles were observed at the bottom of the bottle. The crystals were chosen

and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **5**. The data were collected on a Bruker APEX-II CCD diffractometer. The crystal was kept at 150.0 K during data collection.

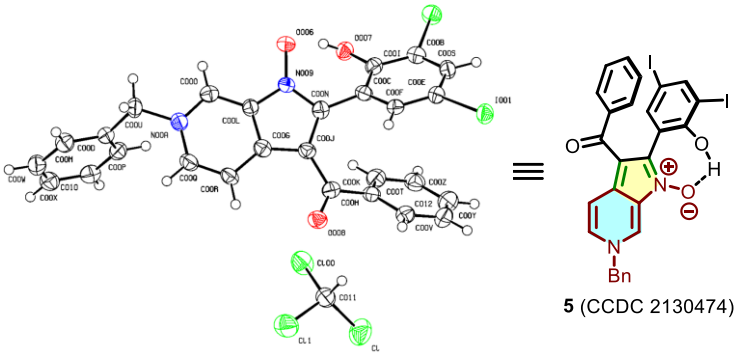


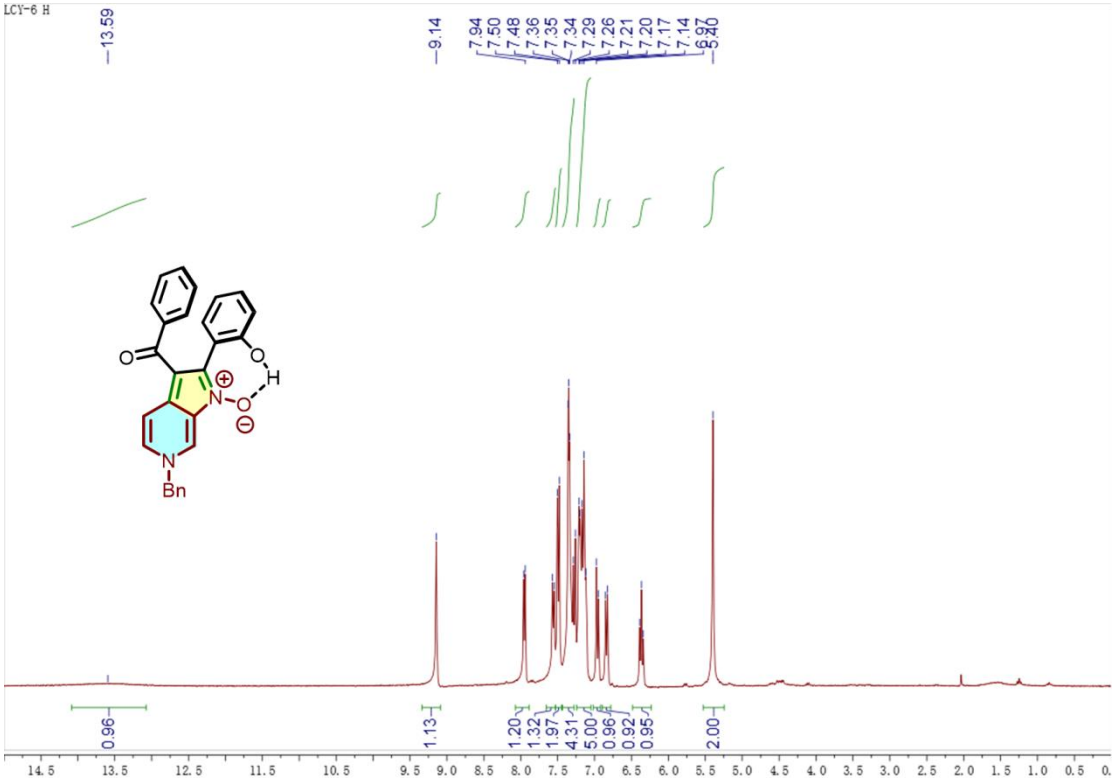
Table S3 Crystal data and structure refinement for **5**.

Identification code	**5**
Empirical formula	$C_{28}H_{19}Cl_3I_2N_2O_3$
Formula weight	791.60
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	9.8911(5)
b/Å	11.6189(5)
c/Å	12.7499(7)
α/°	94.433(2)
β/°	101.832(2)
γ/°	98.841(2)
Volume/Å3	1408.10(12)
Z	2
ρ calcg/cm3	1.867
μ /mm-1	2.552
F(000)	764.0

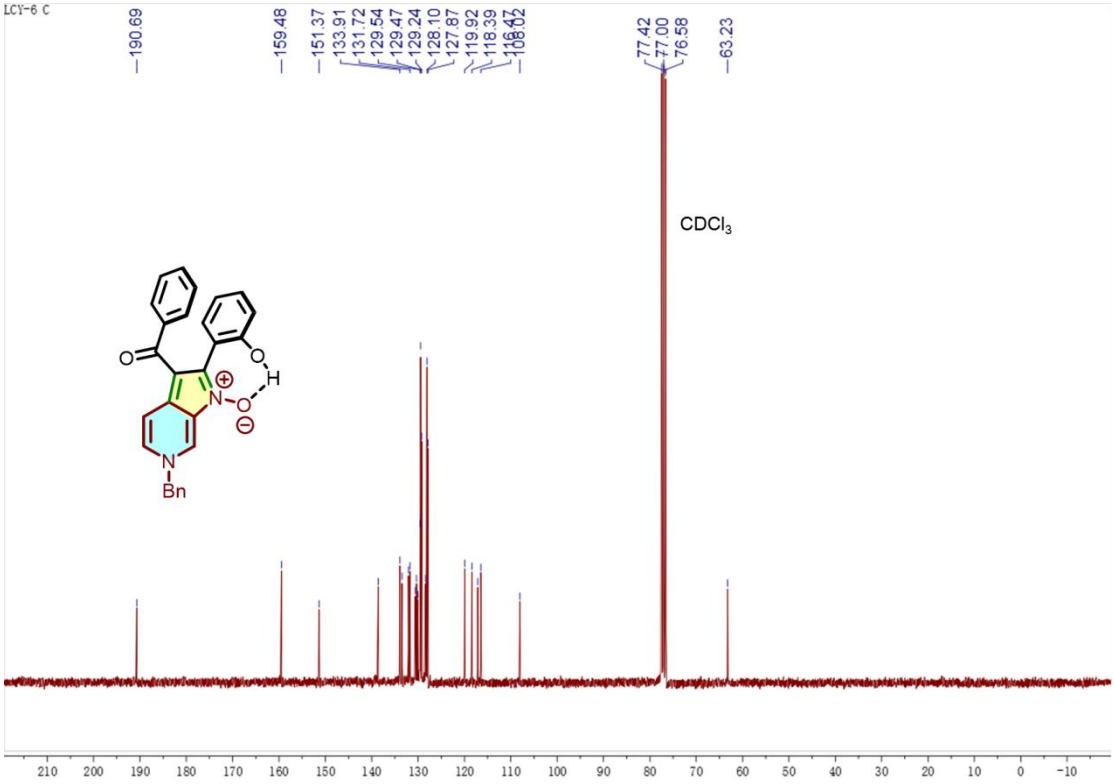
Crystal size/mm3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.272 to 52.95
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	34449
Independent reflections	5812 [Rint = 0.0698, Rsigma = 0.0482]
Data/restraints/parameters	5812/0/344
Goodness-of-fit on F2	1.073
Final R indexes [I>=2σ (I)]	R1 = 0.0389, wR2 = 0.0778
Final R indexes [all data]	R1 = 0.0595, wR2 = 0.0900
Largest diff. peak/hole / e Å-3	0.57/-0.54

6. NMR spectra

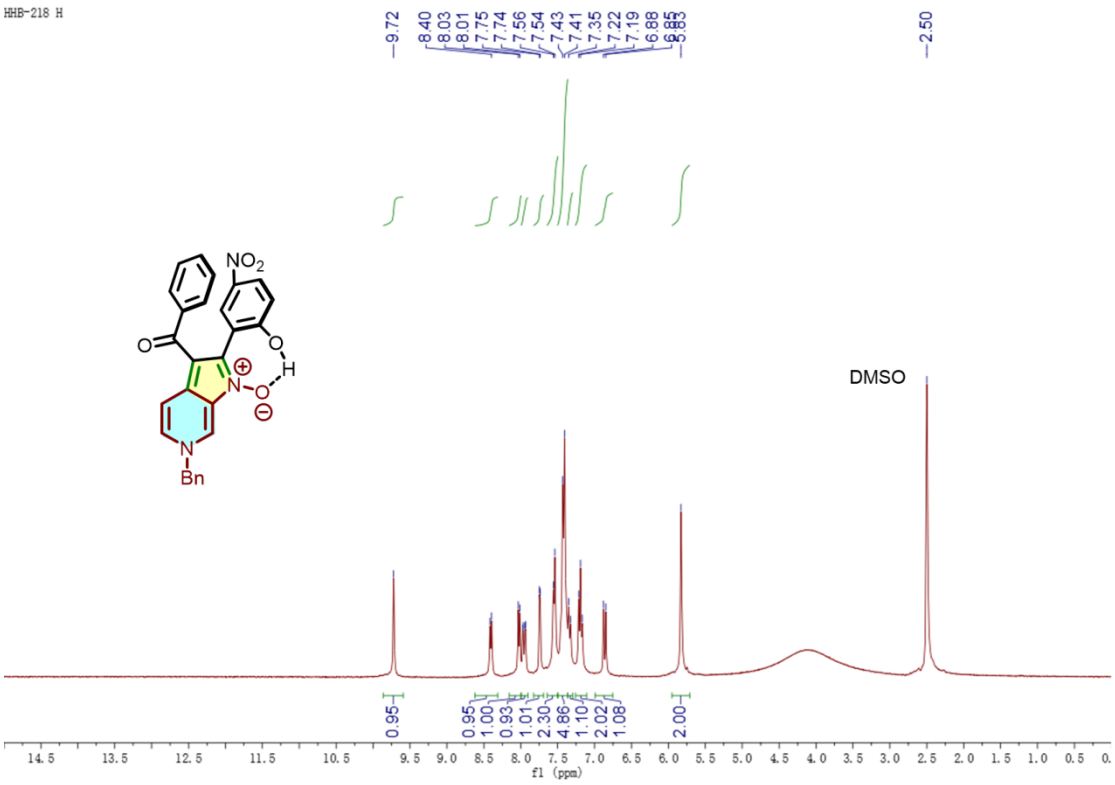
^{1}H NMR spectrum of **3a** (300 MHz, $CDCl_3$)



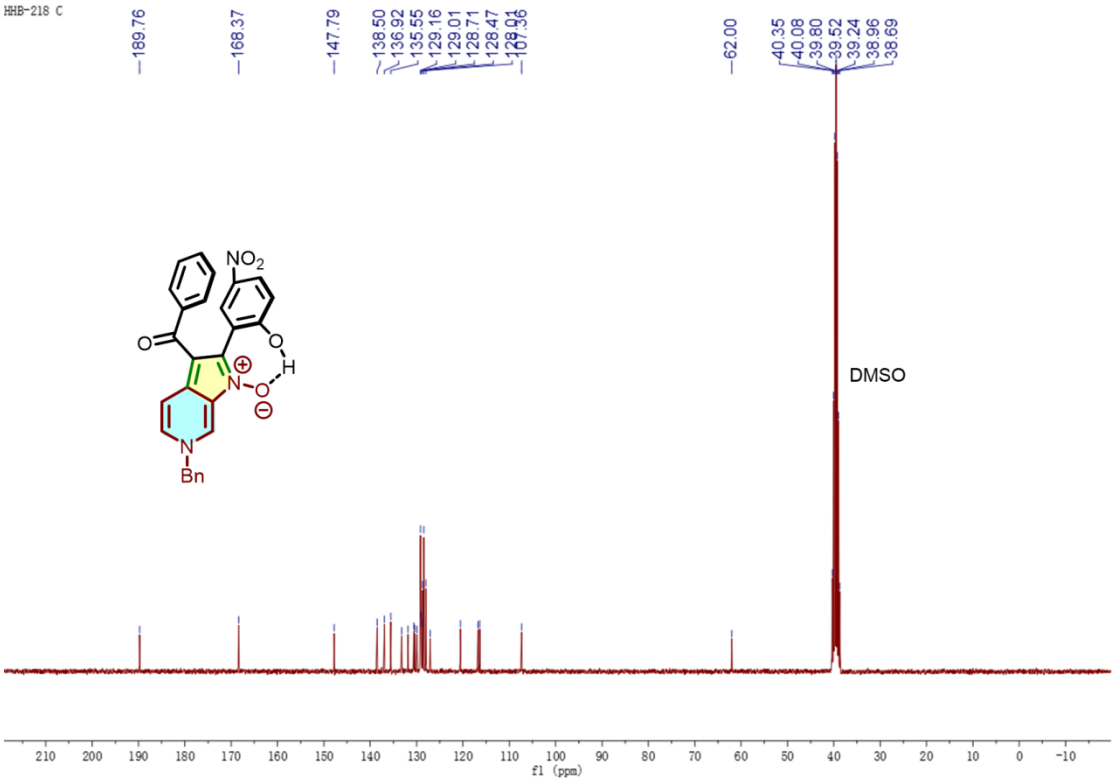
^{13}C NMR spectrum of **3a** (75 MHz, $CDCl_3$)



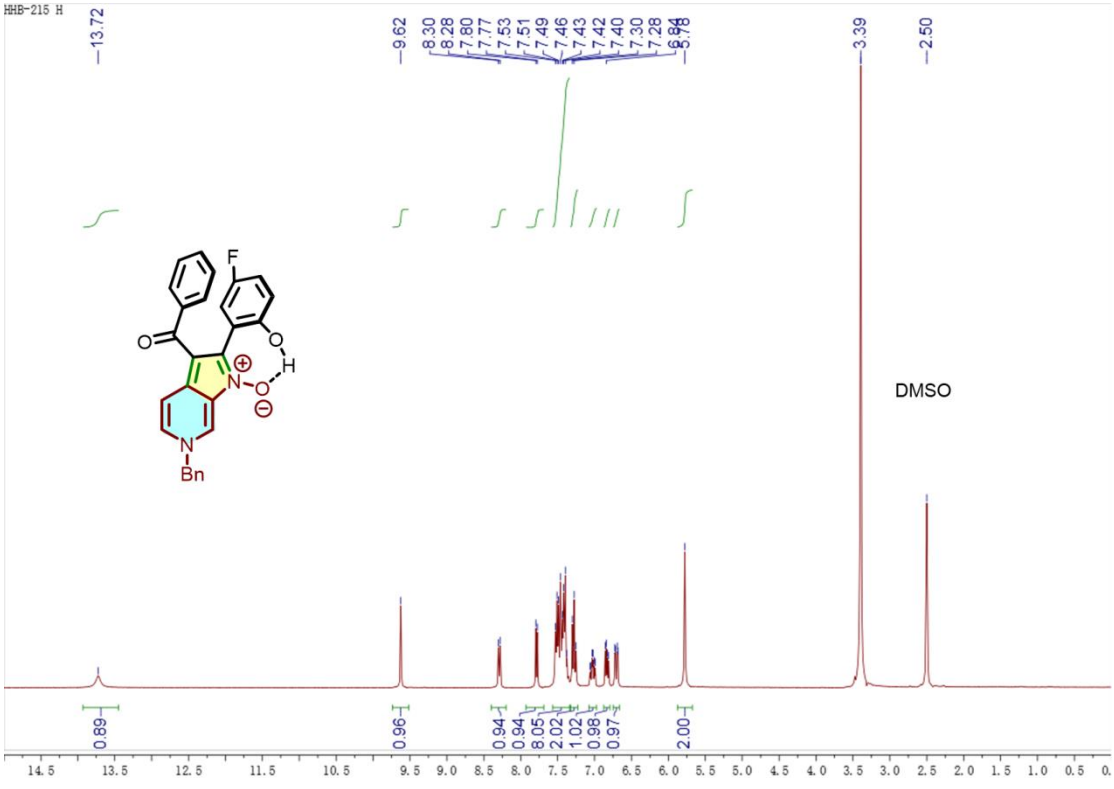
^{1}H NMR spectrum of **3b** (300 MHz, DMSO-d_6)



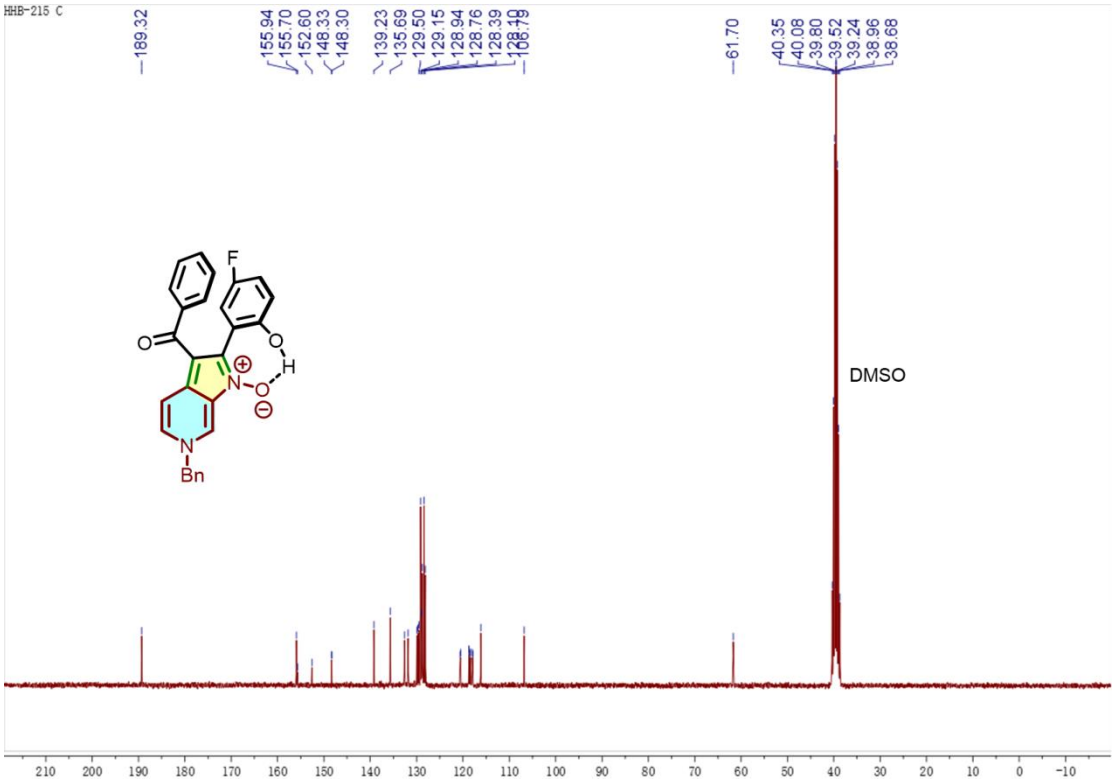
^{13}C NMR spectrum of **3b** (75 MHz, DMSO-d_6)



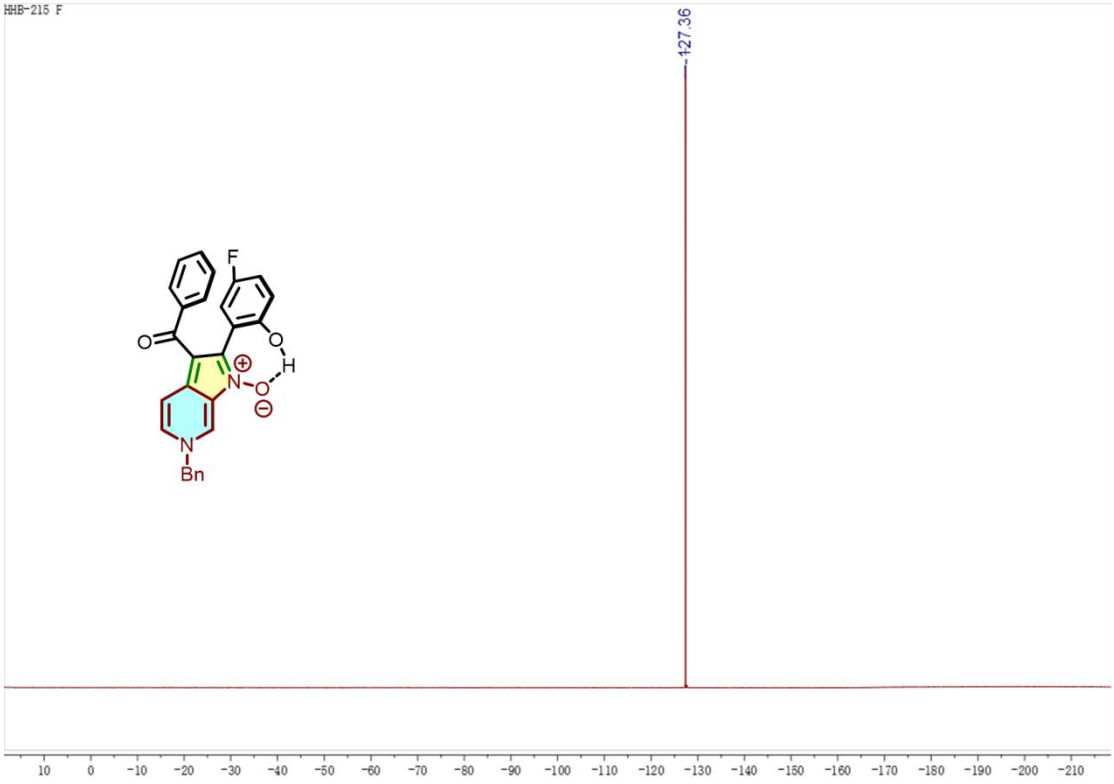
^{1}H NMR spectrum of **3c** (300 MHz, DMSO-d_6)



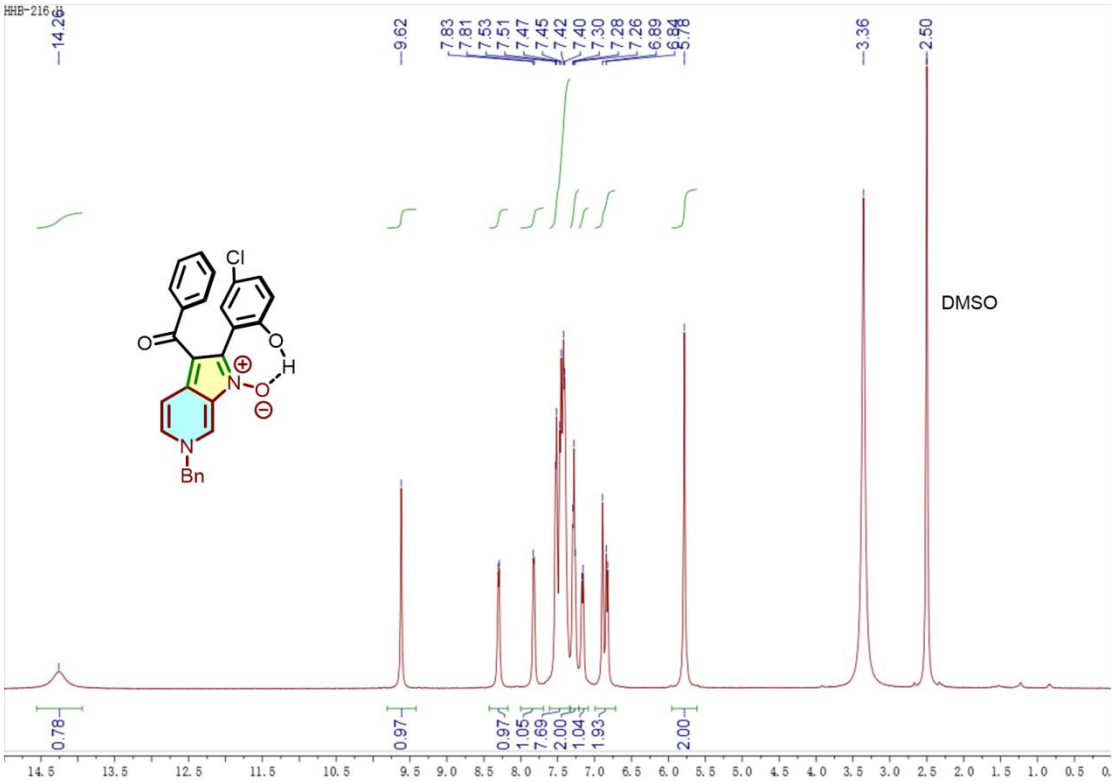
^{13}C NMR spectrum of **3c** (75 MHz, DMSO-d_6)



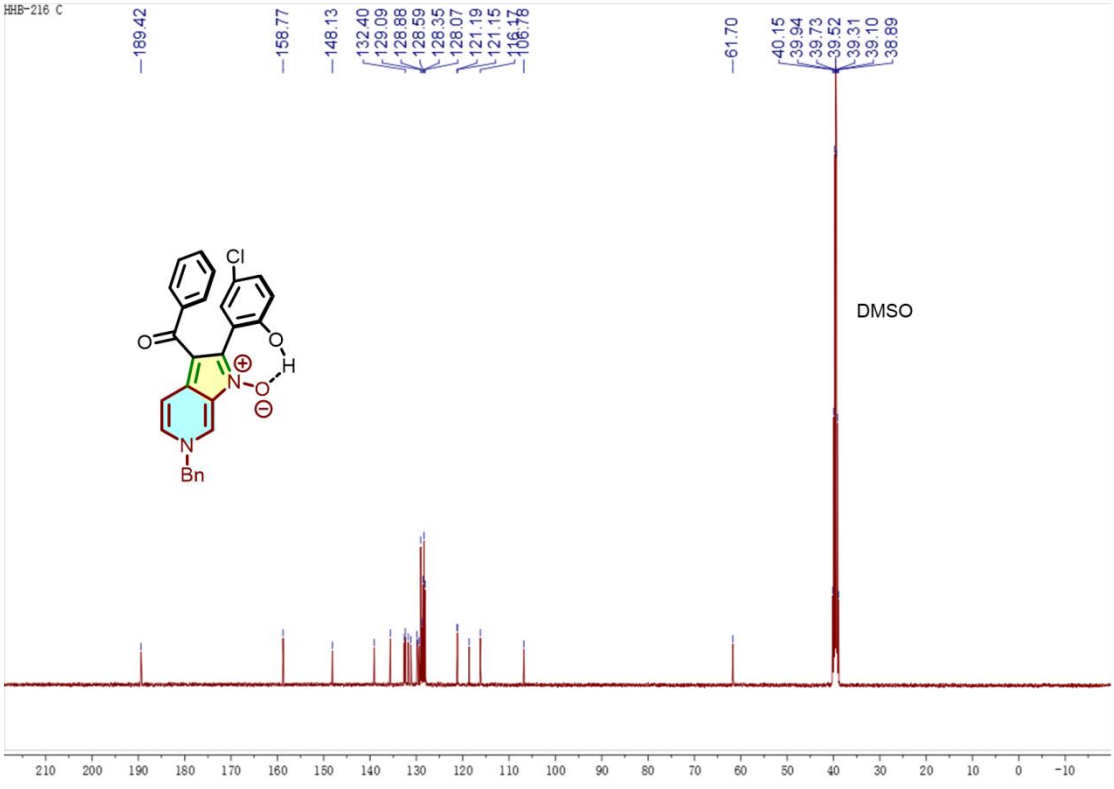
^{19}F NMR spectrum of **3c** (376 MHz, DMSO-d_6)



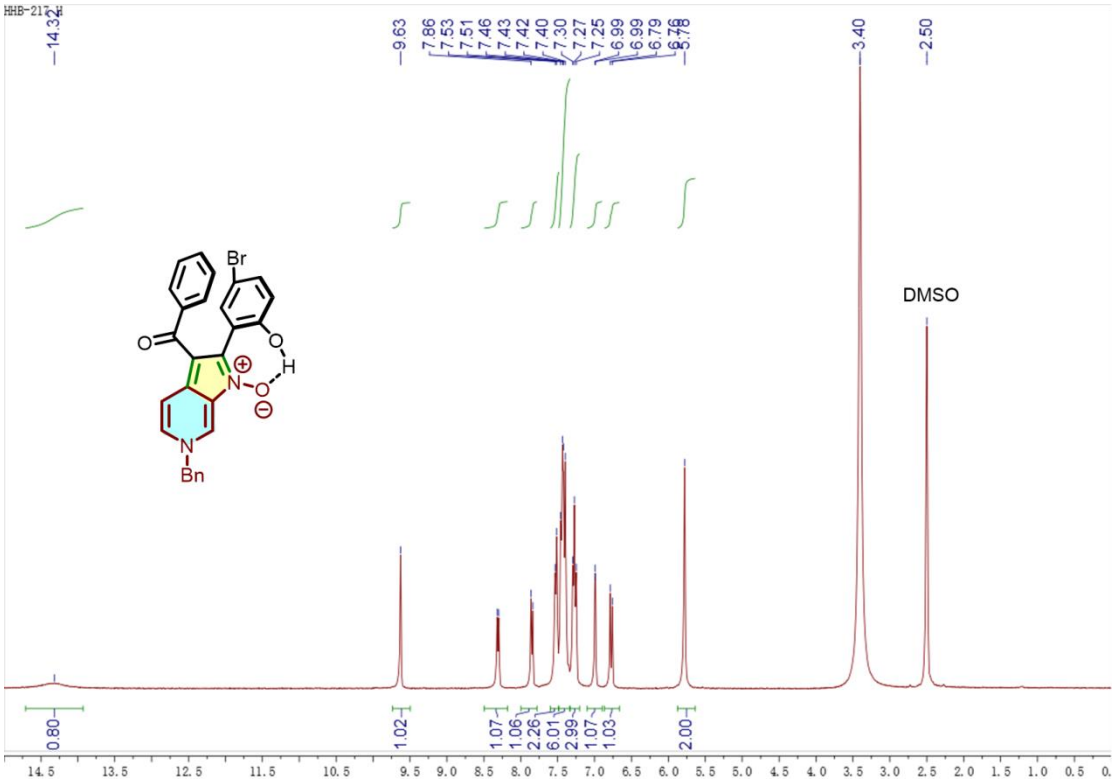
^{1}H NMR spectrum of **3d** (400 MHz, DMSO-d_6)



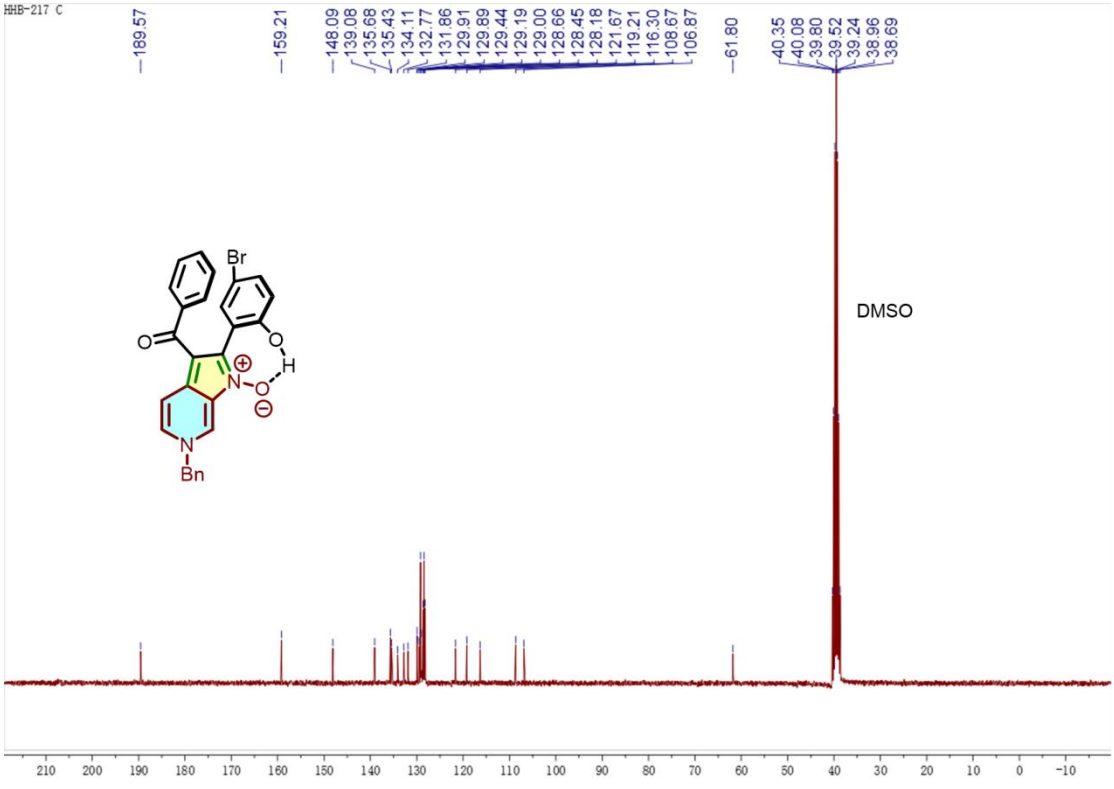
^{13}C NMR spectrum of **3d** (100 MHz, DMSO-d_6)



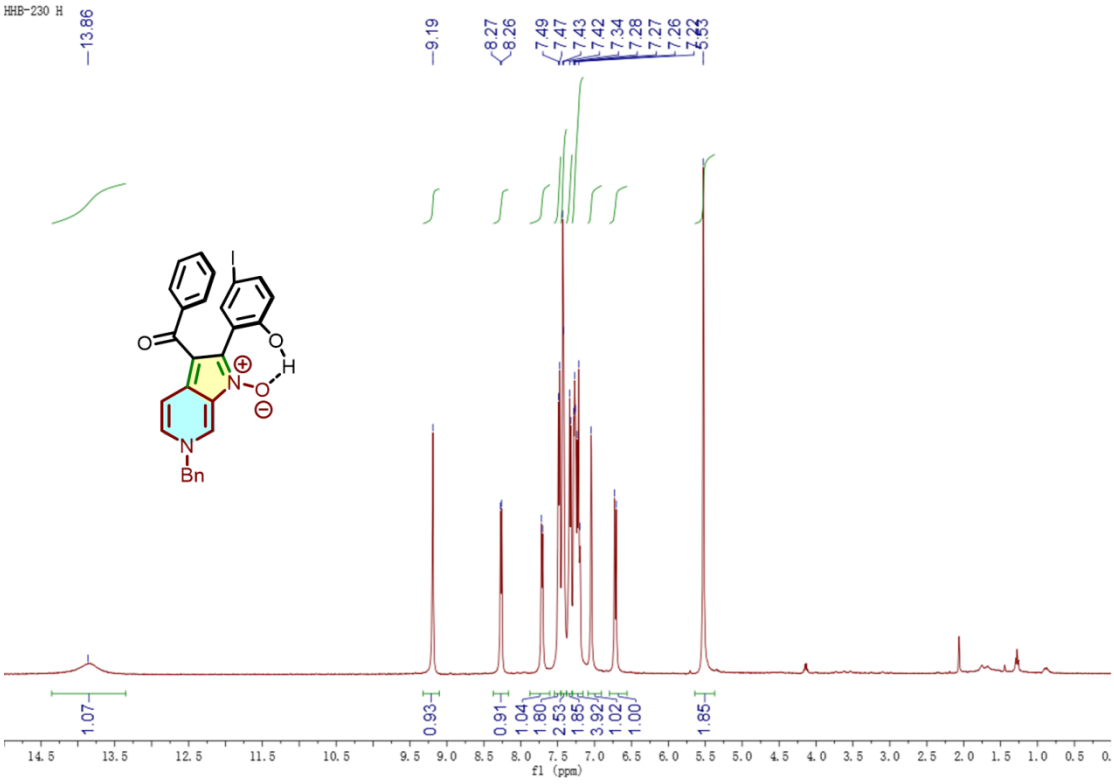
^{1}H NMR spectrum of **3e** (300 MHz, DMSO-d_6)



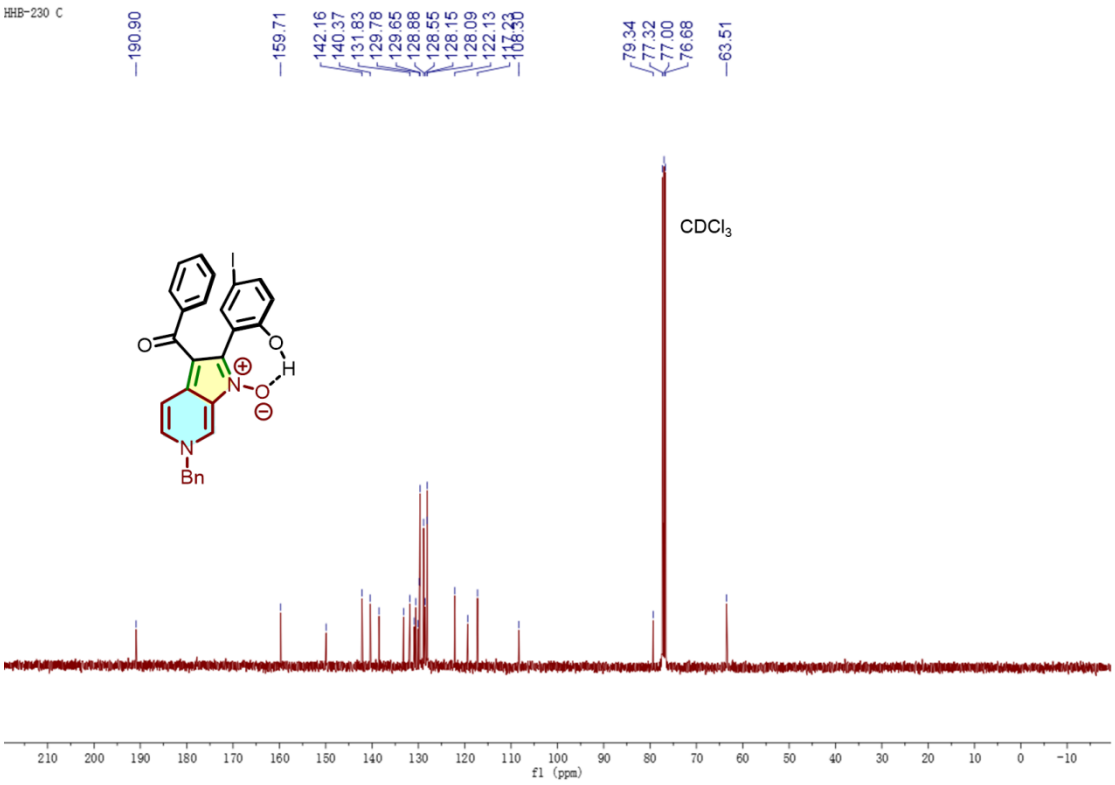
^{13}C NMR spectrum of **3e** (75 MHz, DMSO-d_6)



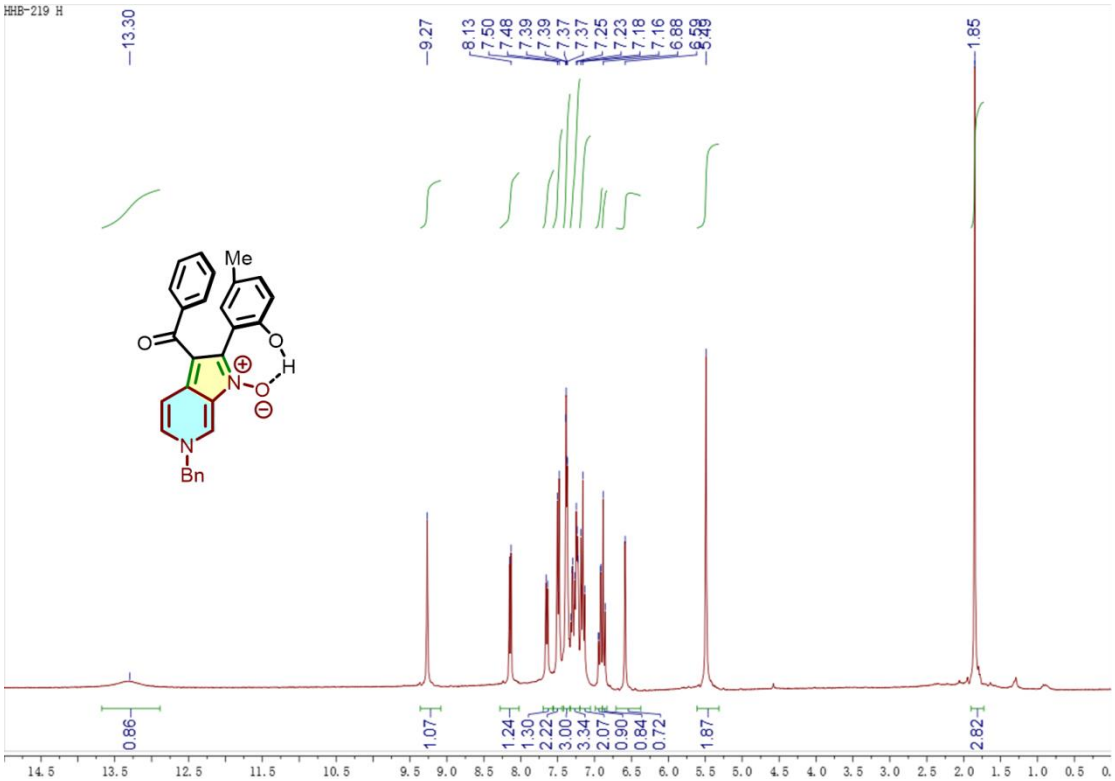
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



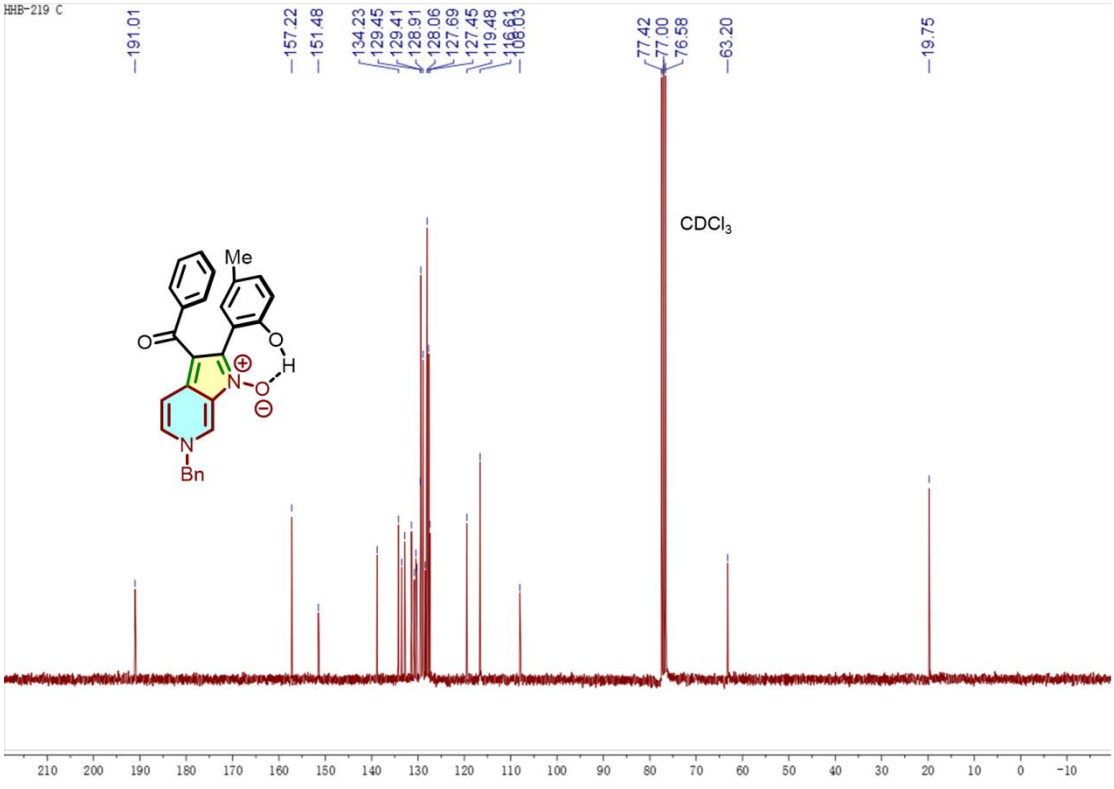
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



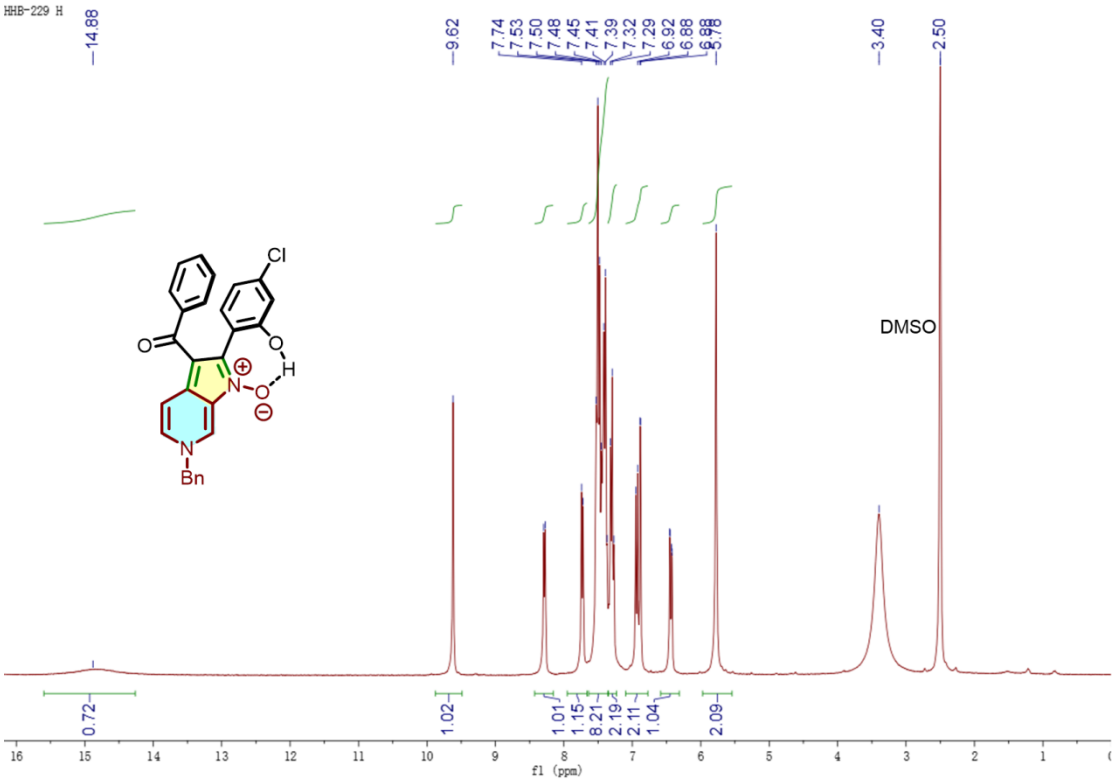
^{1}H NMR spectrum of **3g** (300 MHz, $CDCl_3$)



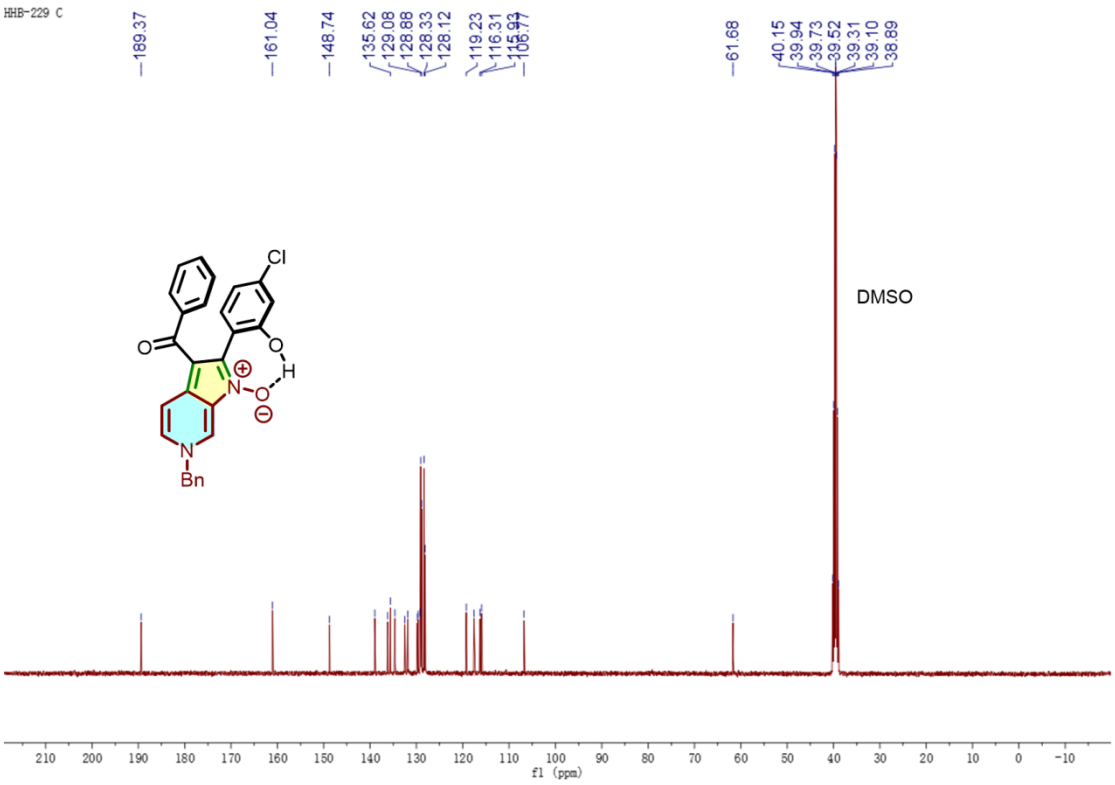
^{13}C NMR spectrum of **3g** (75 MHz, $CDCl_3$)



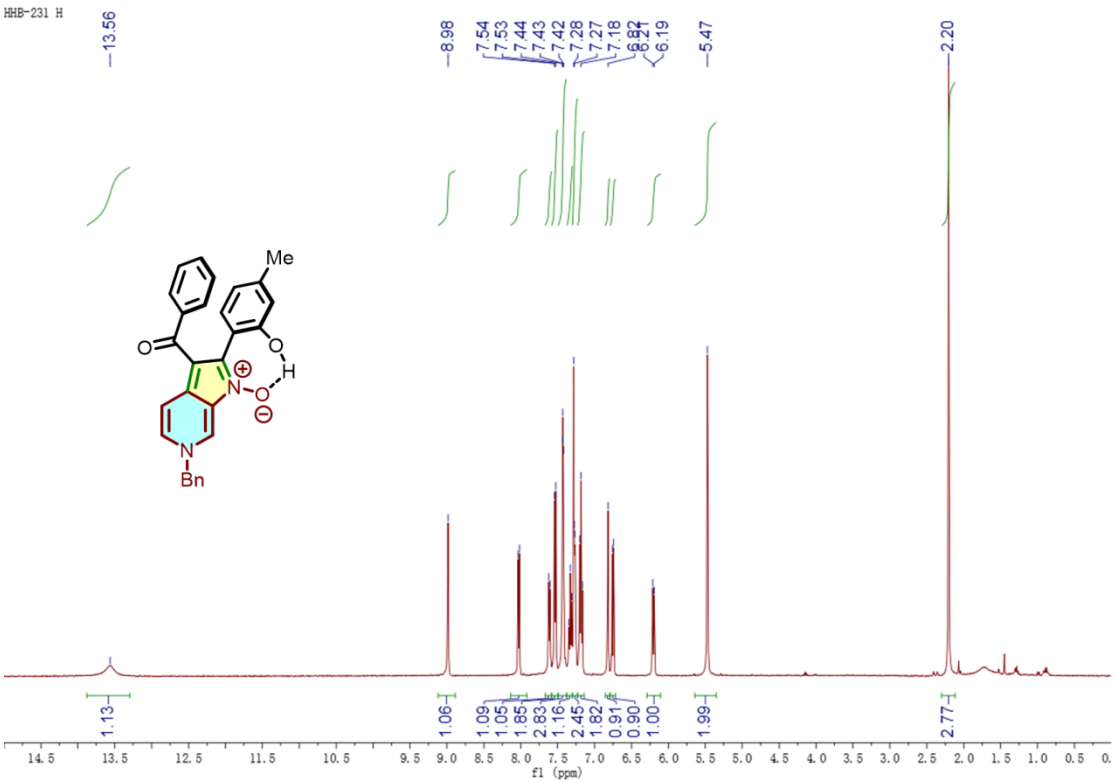
^{1}H NMR spectrum of **3h** (300 MHz, DMSO-d_6)



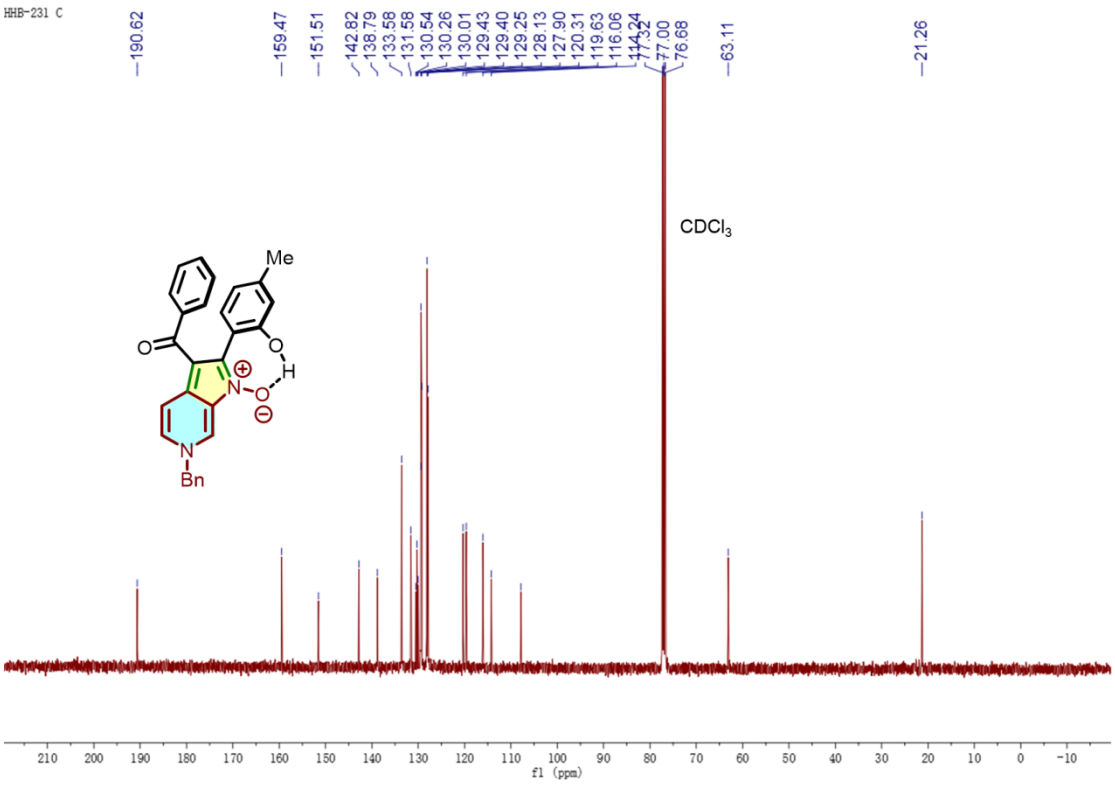
^{13}C NMR spectrum of **3h** (100 MHz, DMSO-d_6)



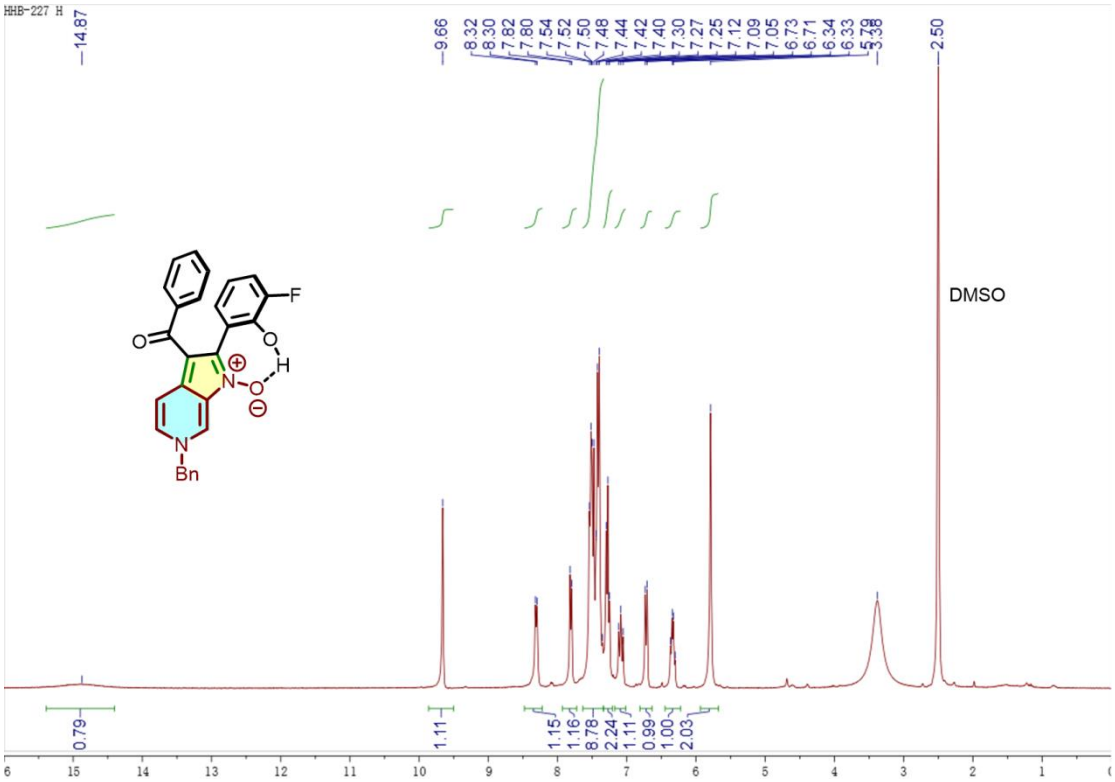
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



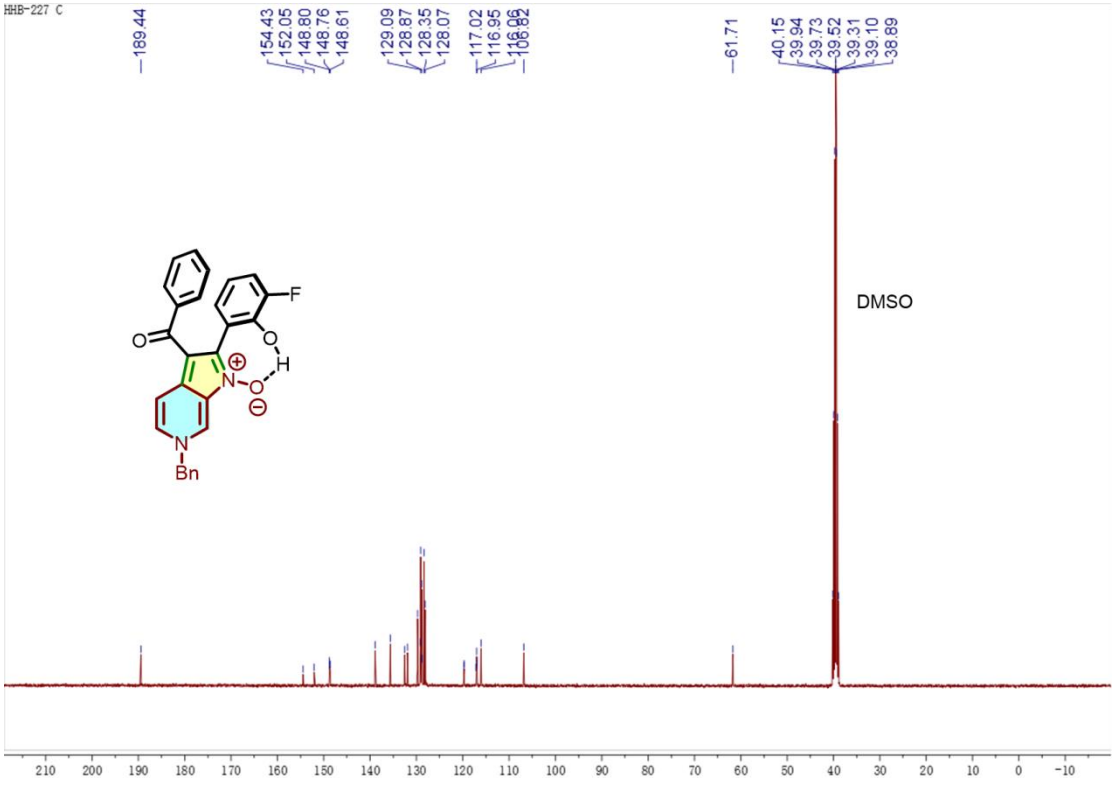
^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$)



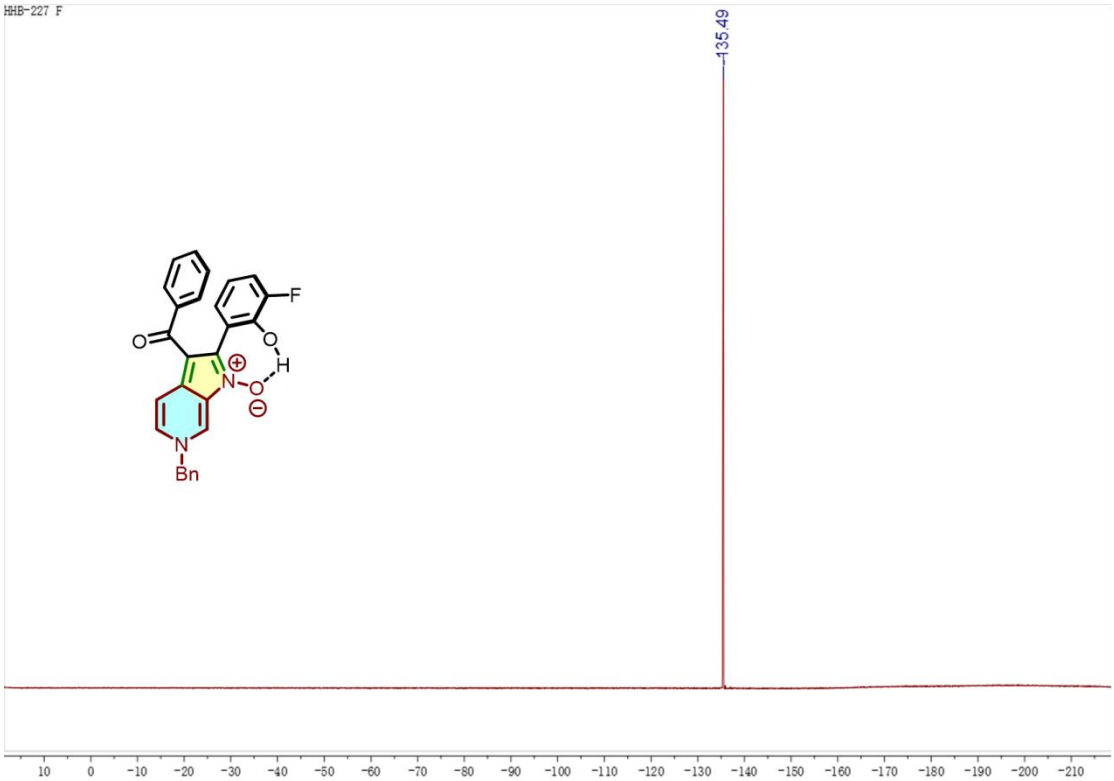
^{1}H NMR spectrum of **3j** (300 MHz, DMSO-d_6)



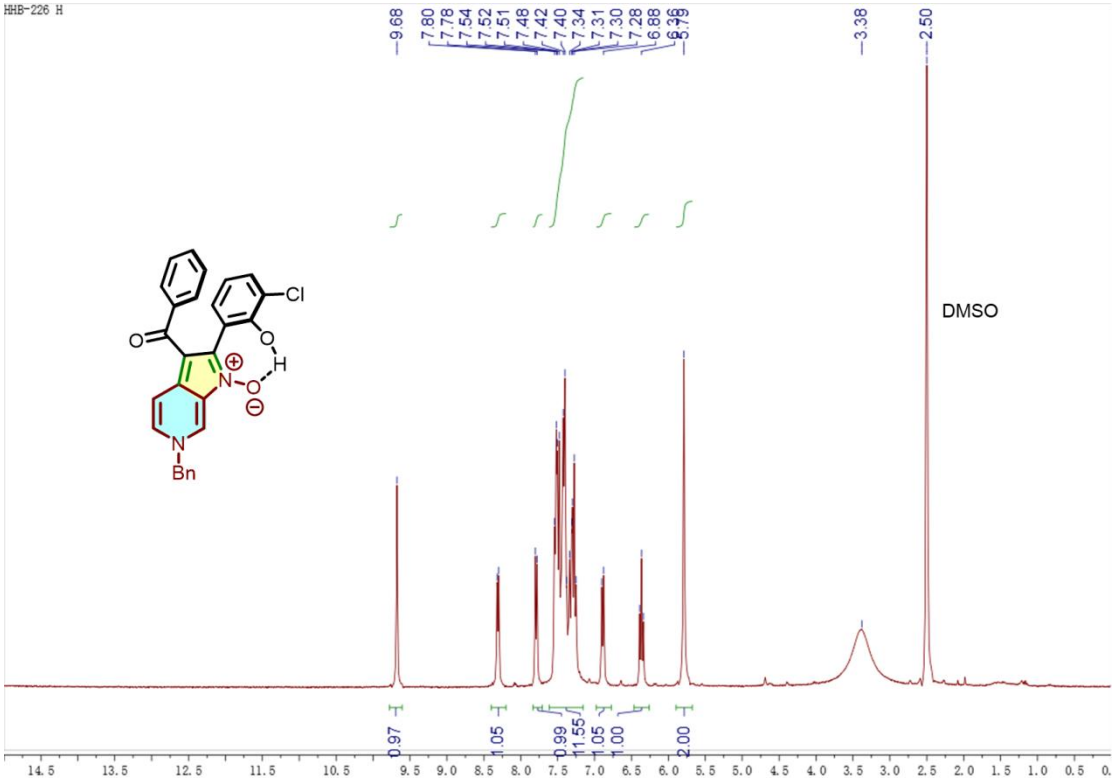
^{13}C NMR spectrum of **3j** (100 MHz, DMSO-d_6)



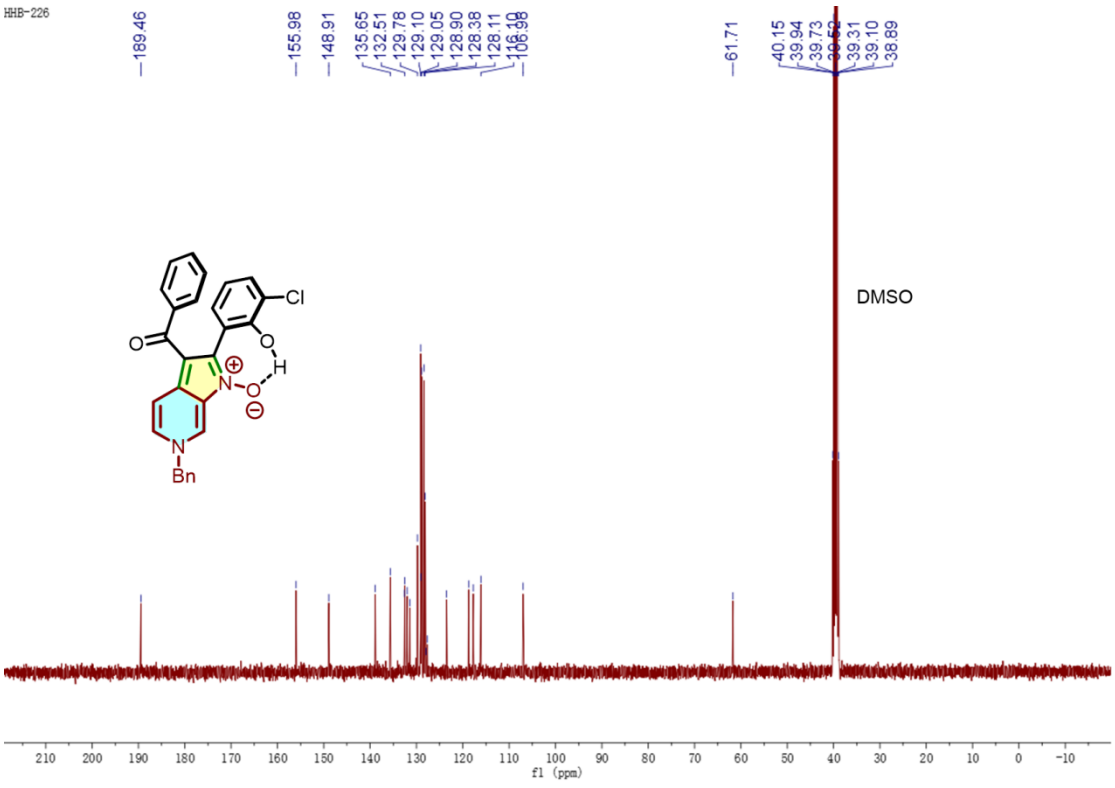
^{19}F NMR spectrum of **3j** (376 MHz, DMSO-d_6)



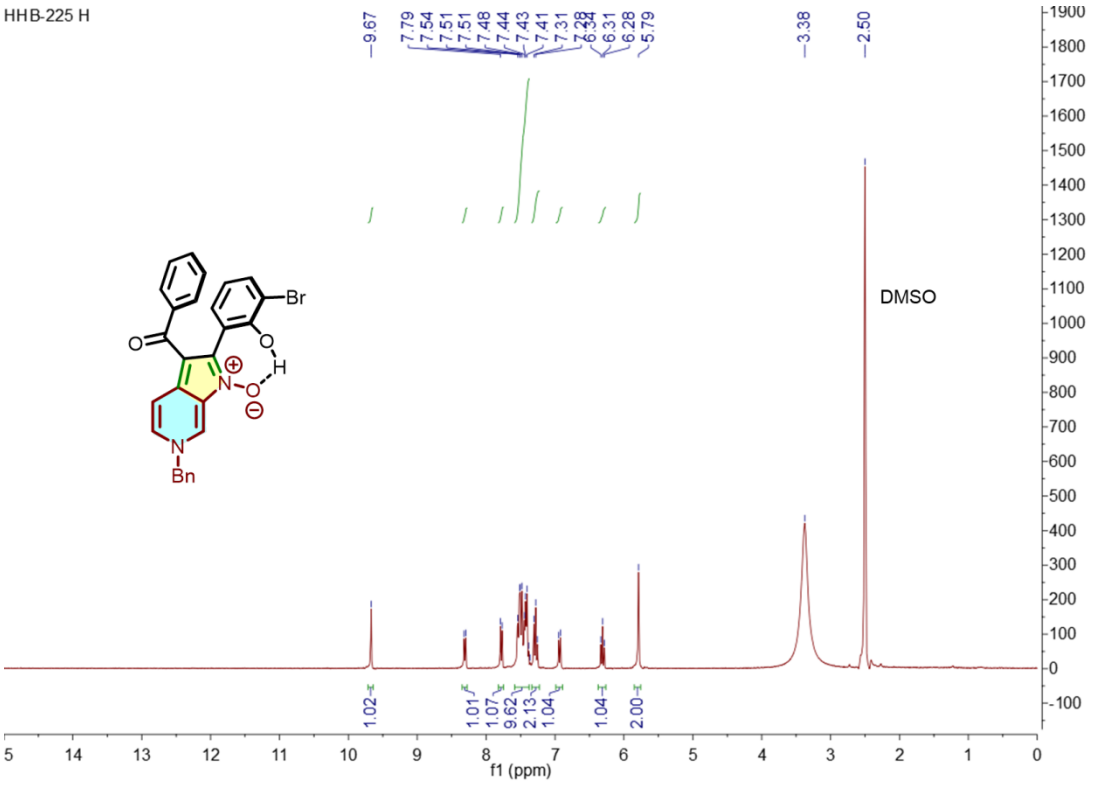
^{1}H NMR spectrum of **3k** (300 MHz, DMSO-d_6)



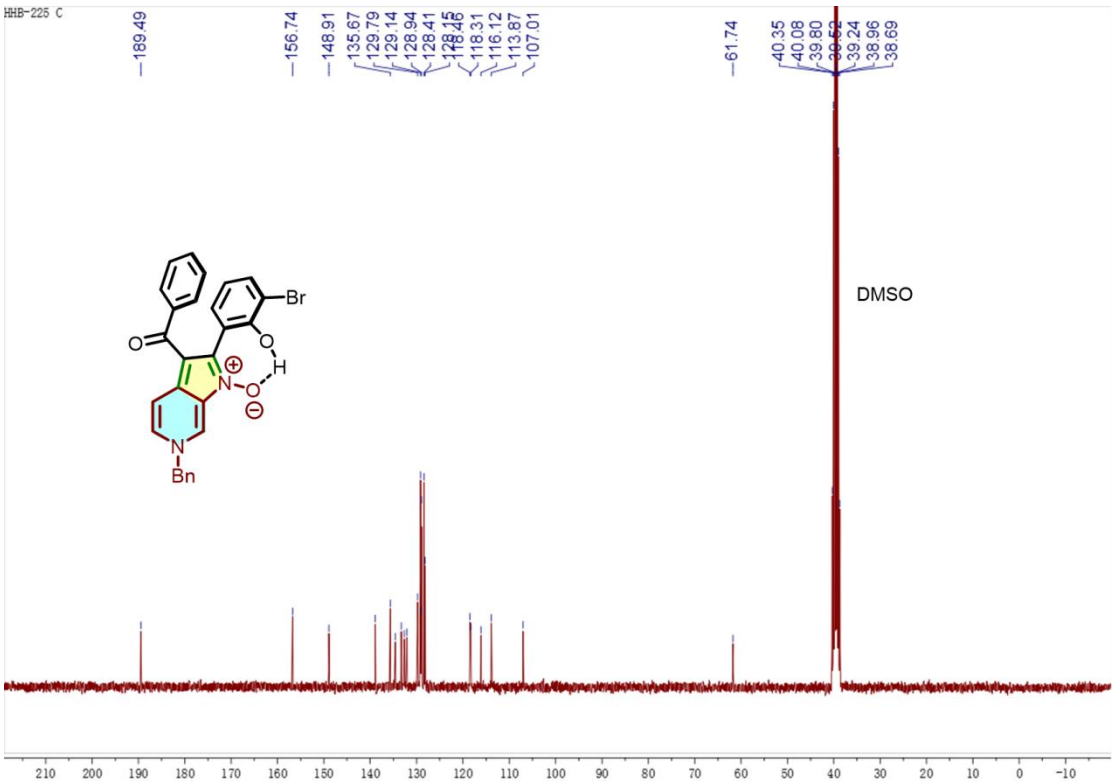
^{13}C NMR spectrum of **3k** (100 MHz, DMSO-d_6)



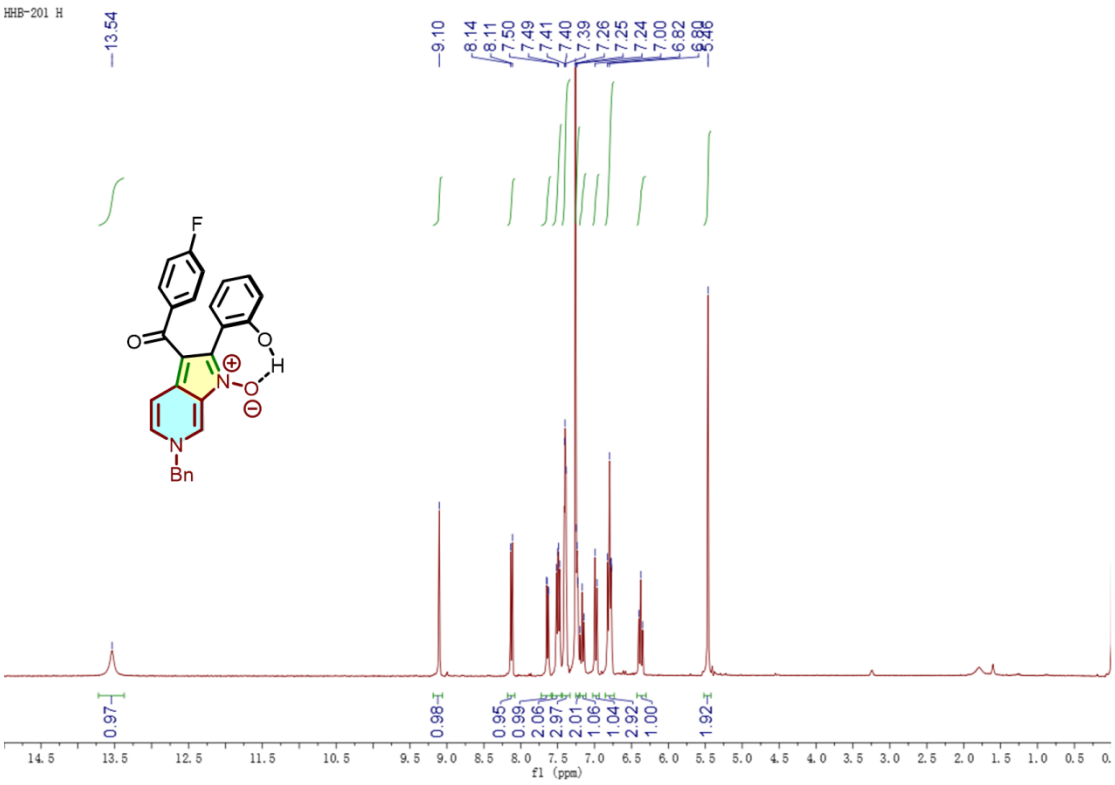
^{1}H NMR spectrum of **3l** (300 MHz, DMSO-d_6)



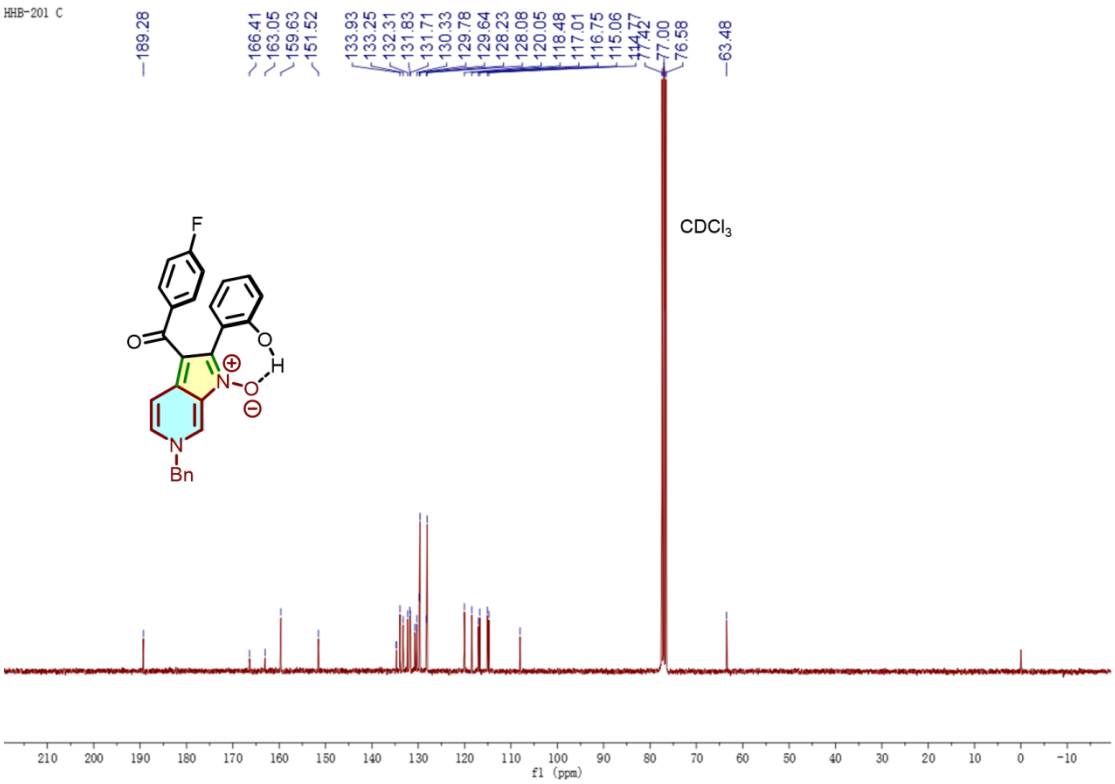
^{13}C NMR spectrum of **3l** (75 MHz, DMSO-d_6)



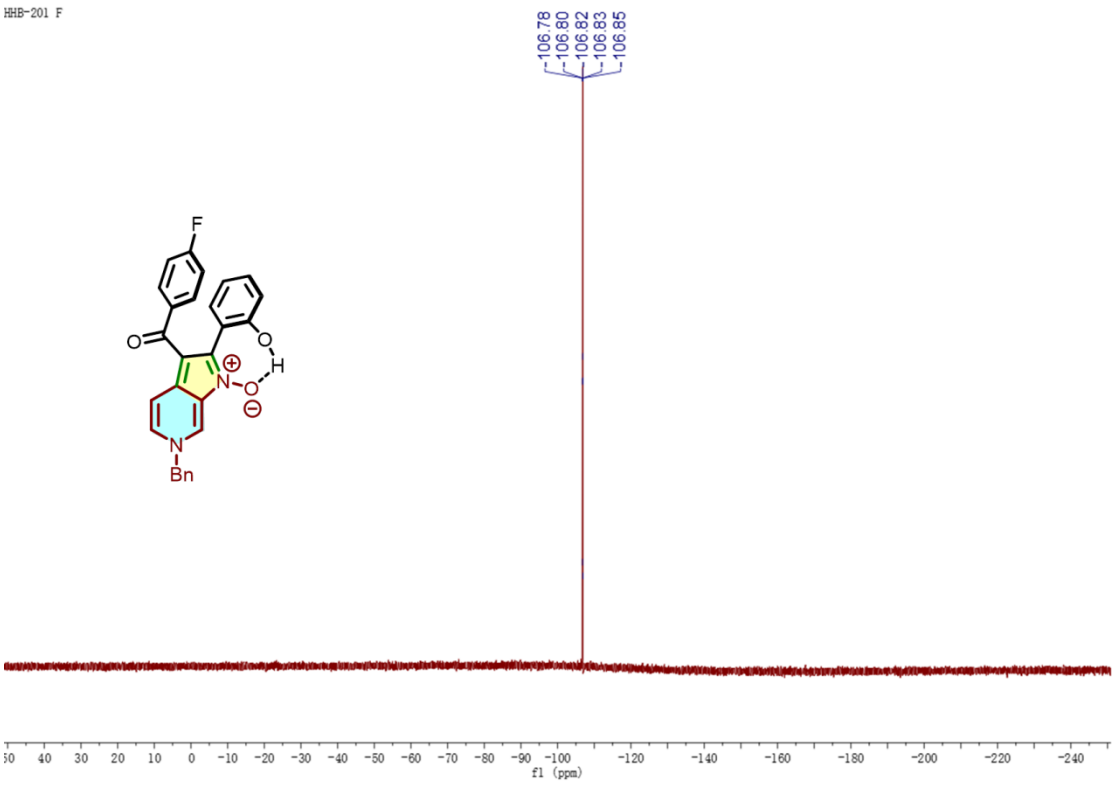
^{1}H NMR spectrum of **3m** (300 MHz, $CDCl_3$)



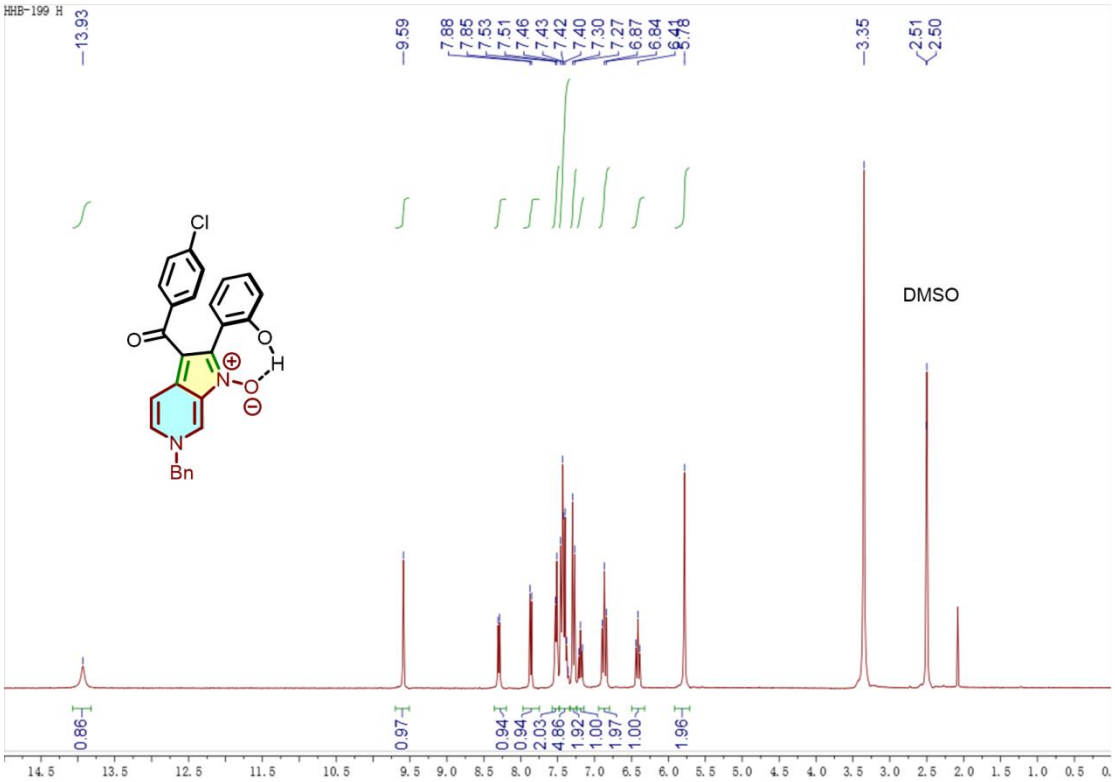
^{13}C NMR spectrum of **3m** (75 MHz, $CDCl_3$)



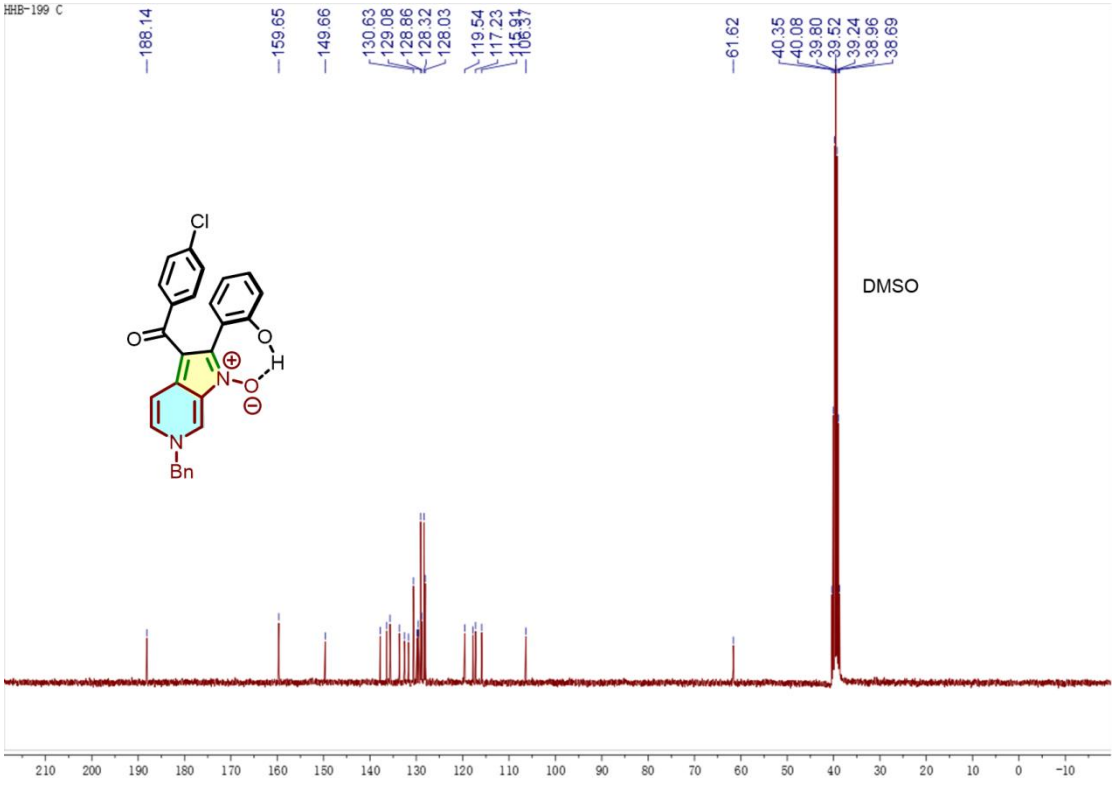
^{19}F NMR spectrum of **3m** (376 MHz, $CDCl_3$)



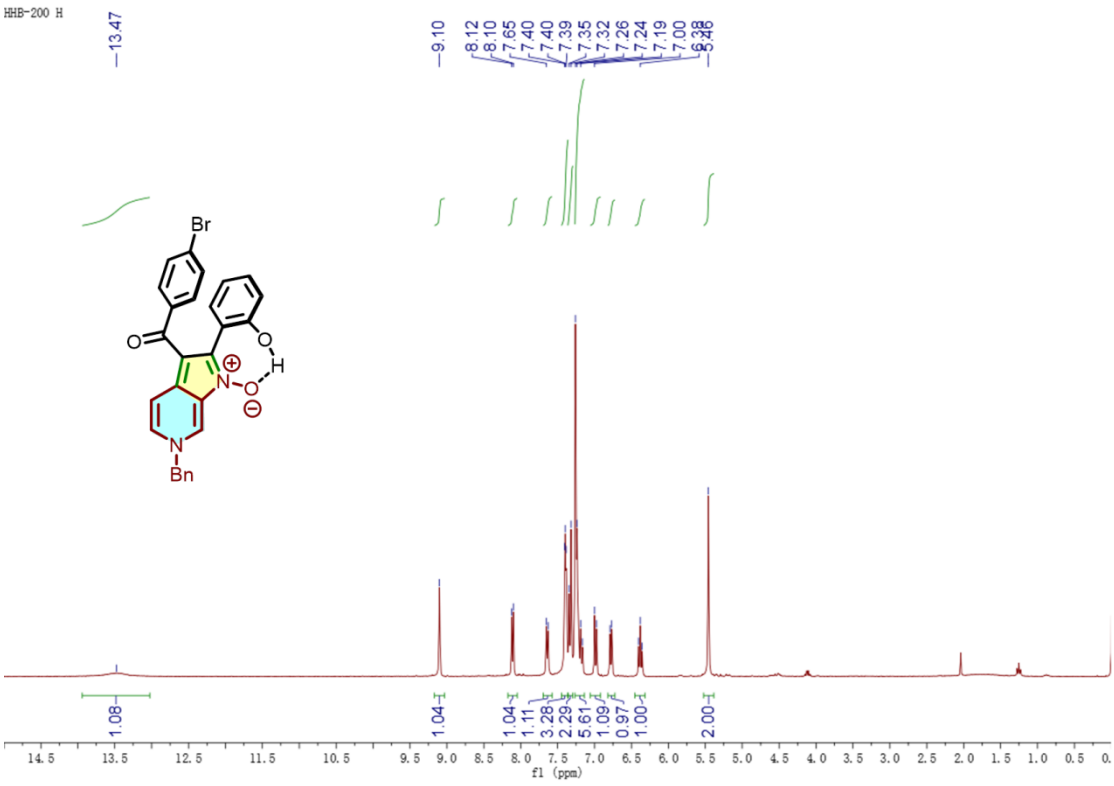
^{1}H NMR spectrum of **3n** (300 MHz, DMSO-d_6)



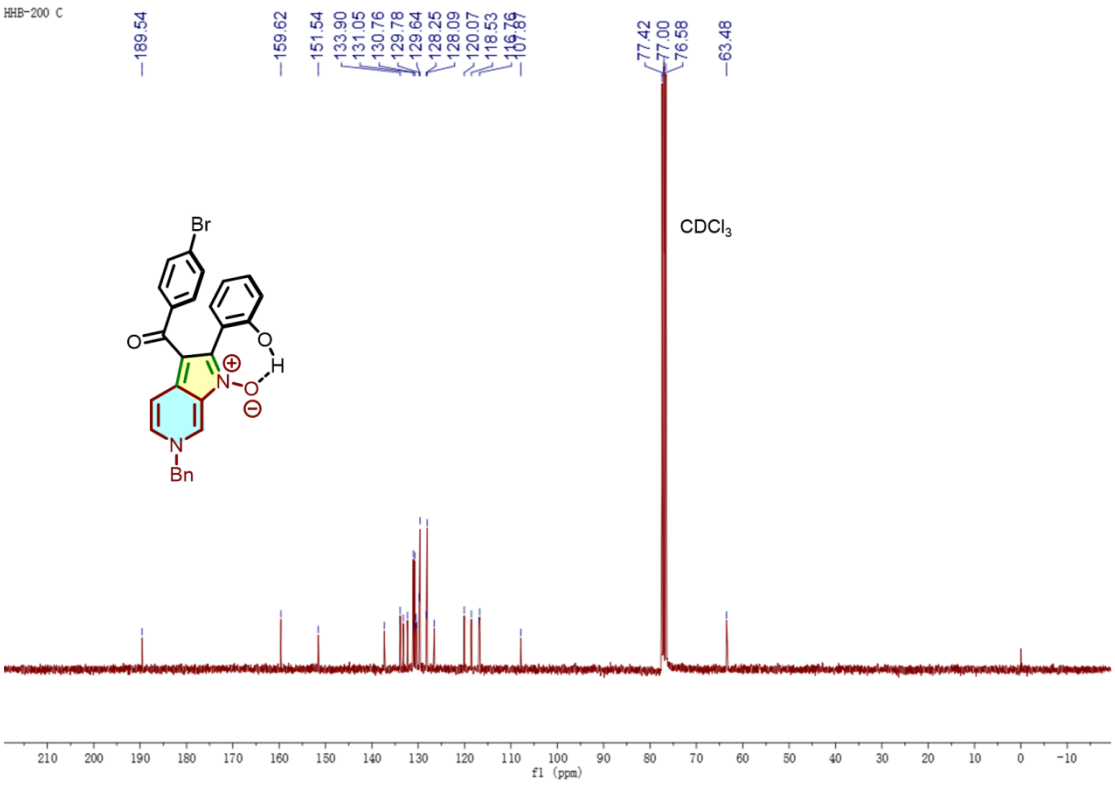
^{13}C NMR spectrum of **3n** (75 MHz, DMSO-d_6)



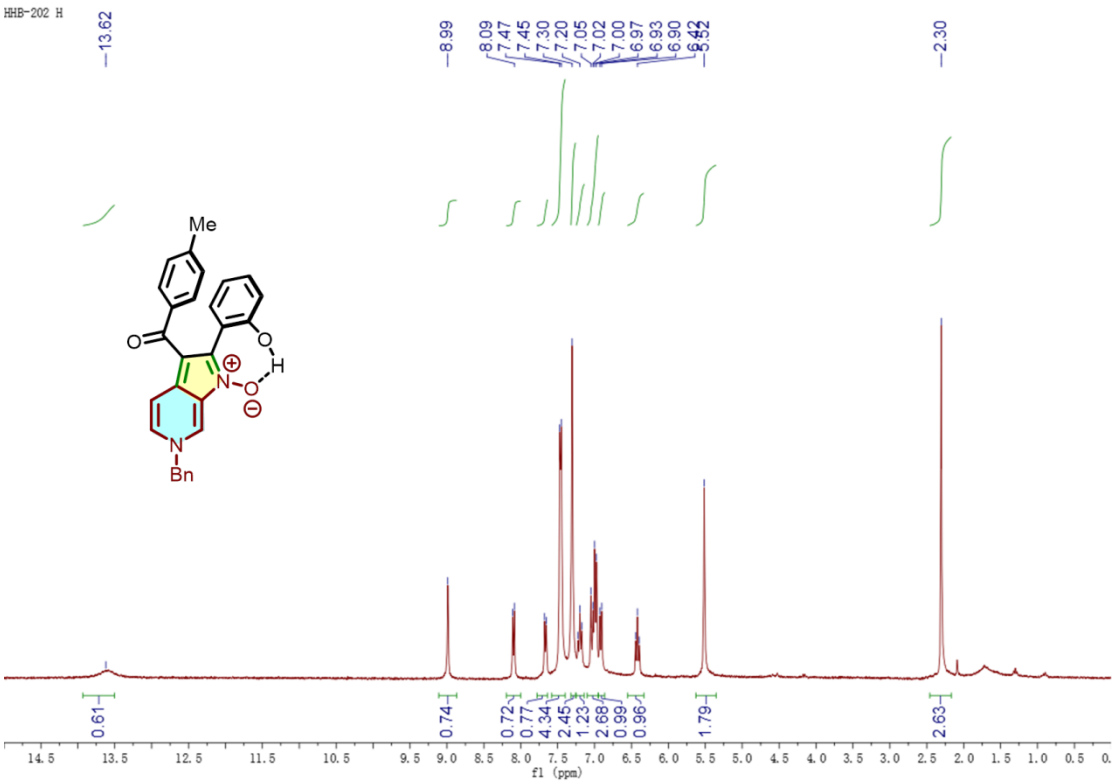
^{1}H NMR spectrum of **3o** (300 MHz, $CDCl_3$)



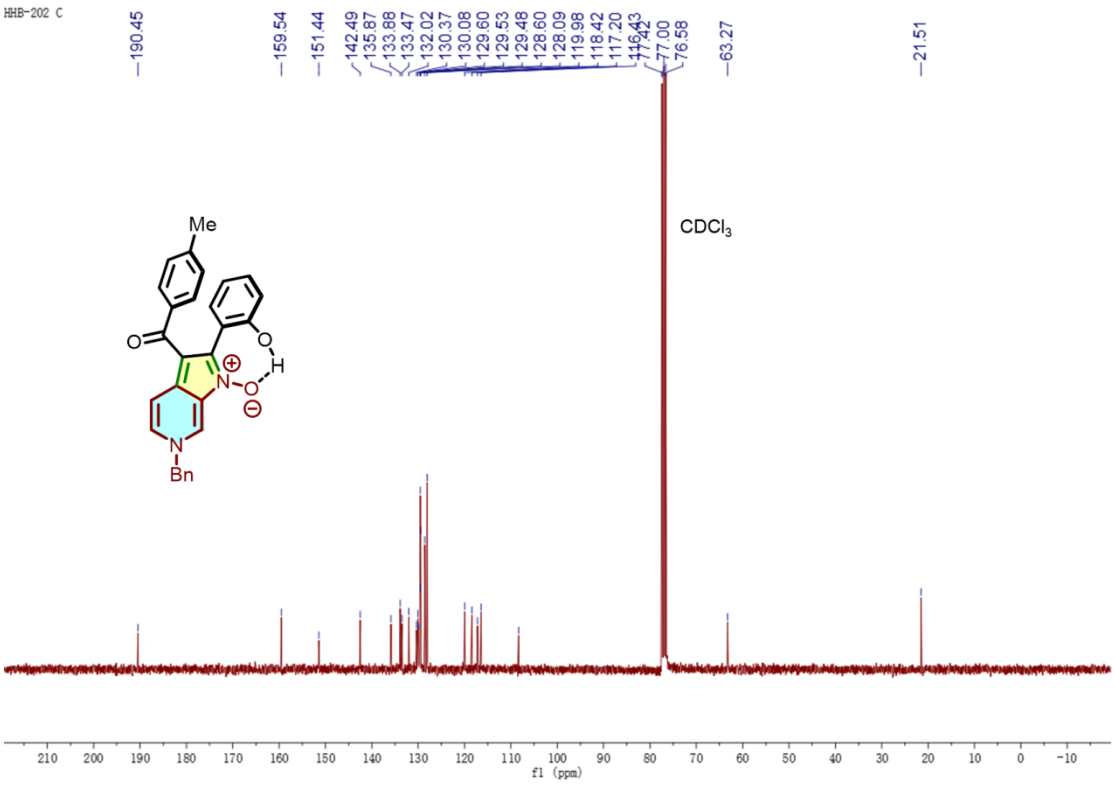
^{13}C NMR spectrum of **3o** (75 MHz, $CDCl_3$)



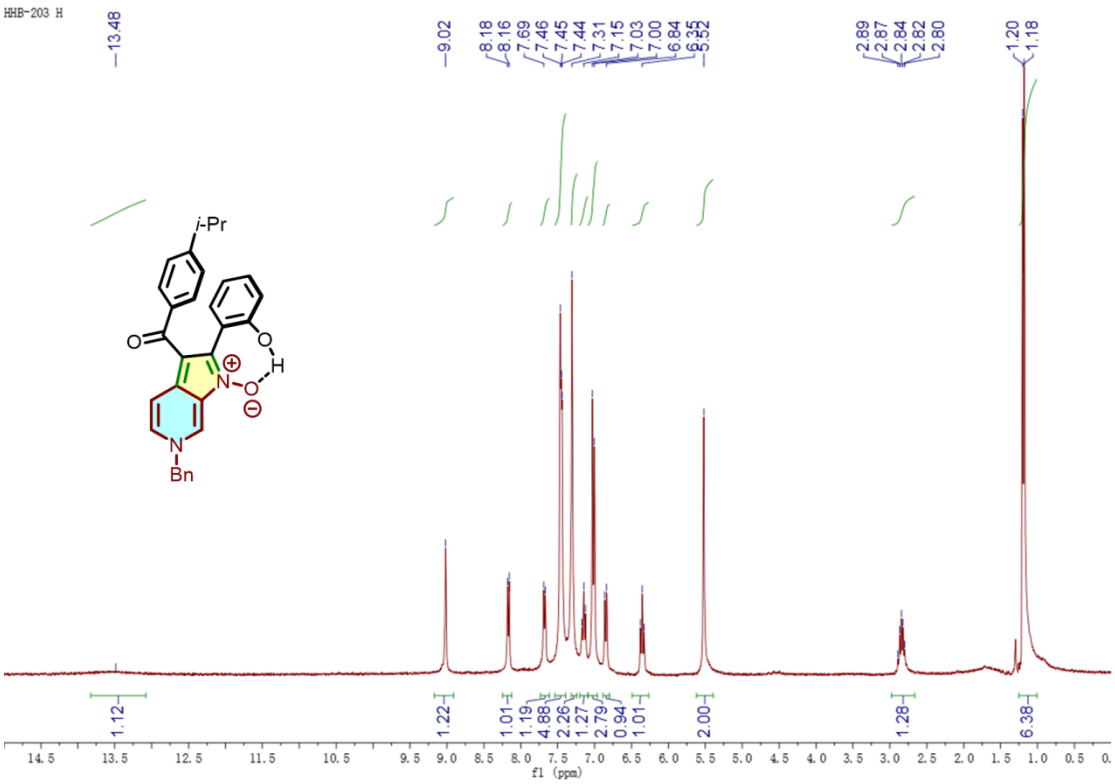
^{1}H NMR spectrum of **3p** (300 MHz, $CDCl_3$)



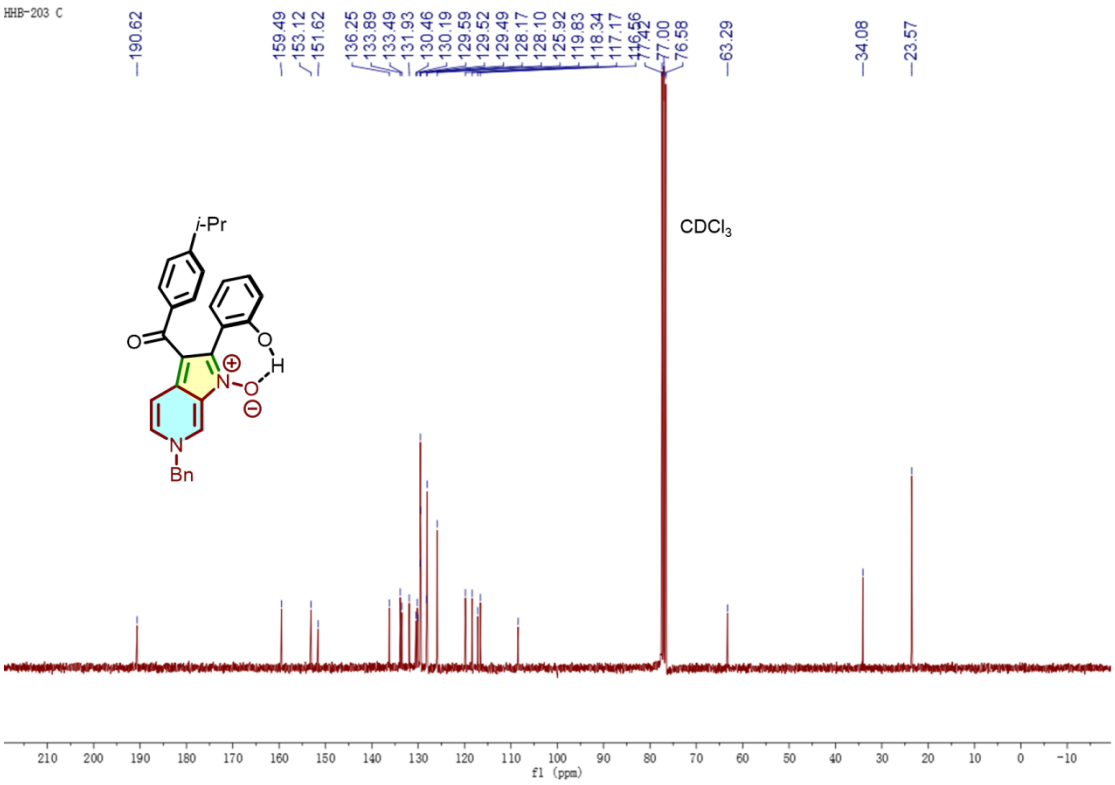
^{13}C NMR spectrum of **3p** (75 MHz, $CDCl_3$)



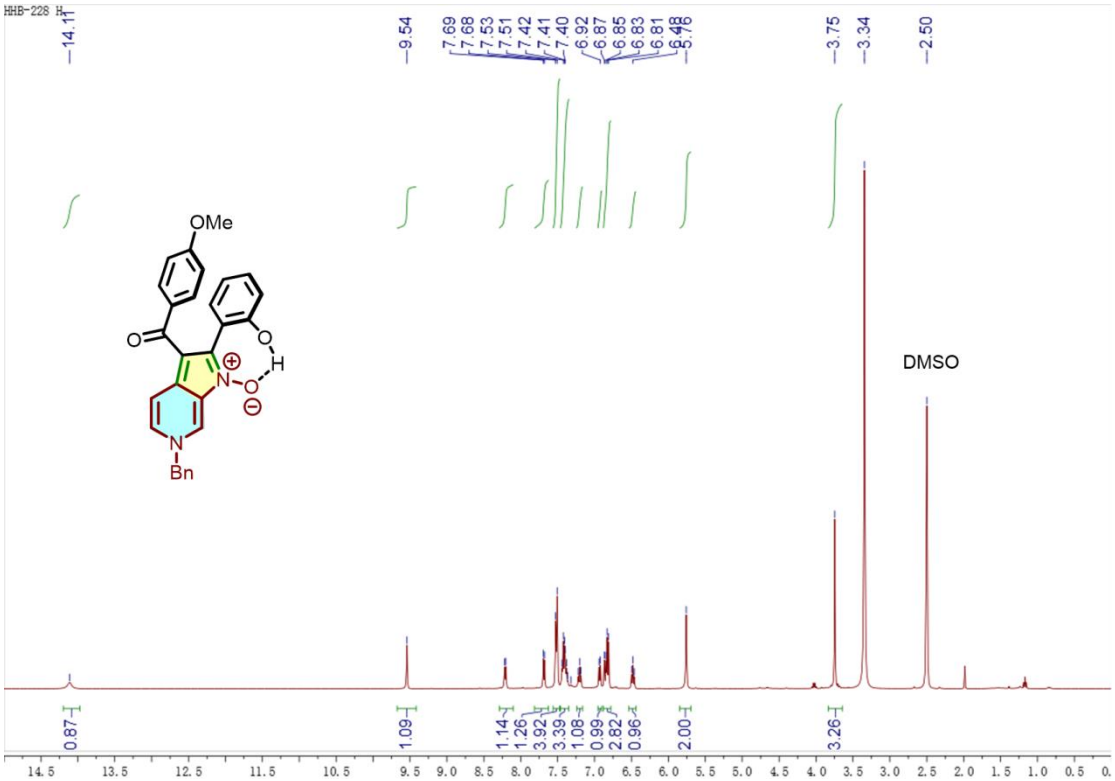
^{1}H NMR spectrum of **3q** (300 MHz, $CDCl_3$)



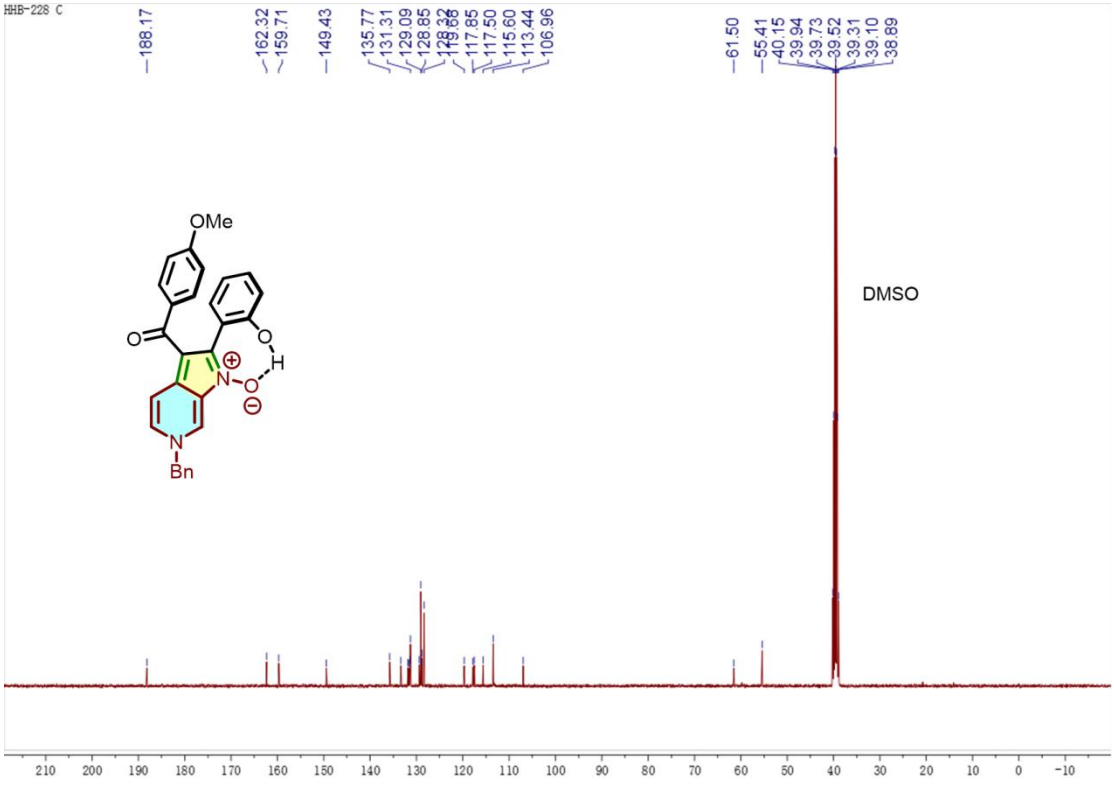
^{13}C NMR spectrum of **3q** (75 MHz, $CDCl_3$)



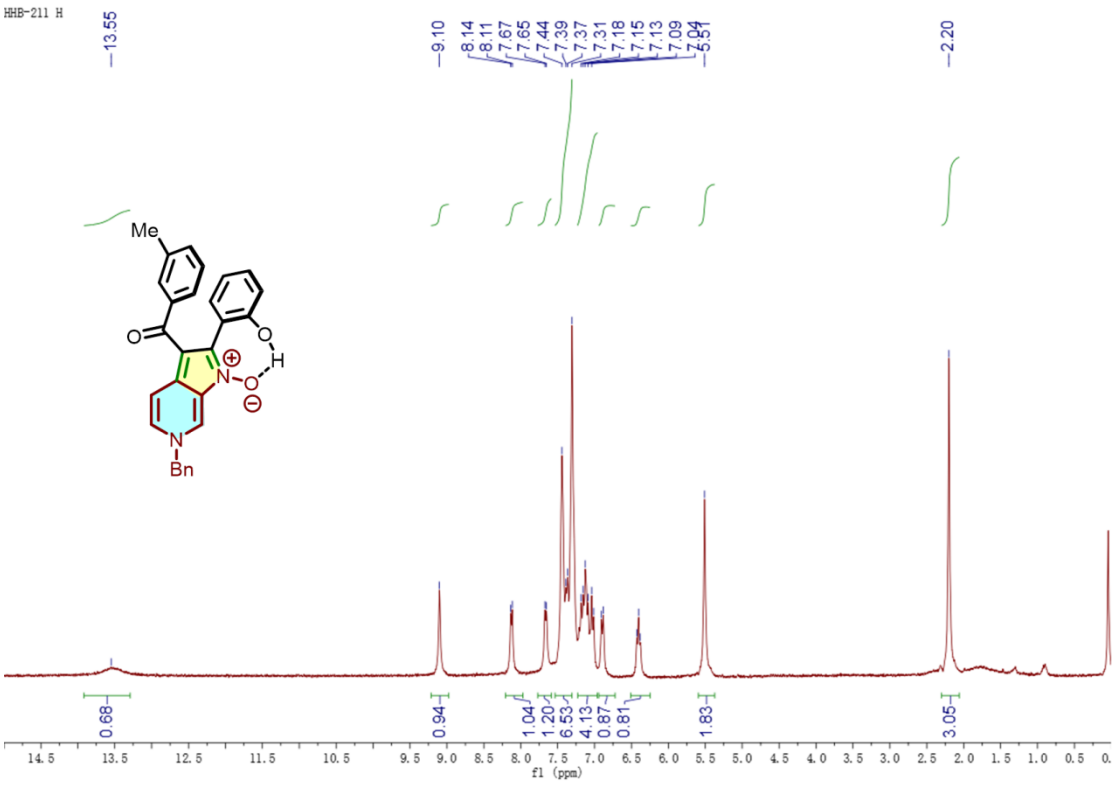
^{1}H NMR spectrum of **3r** (400 MHz, DMSO-d_6)



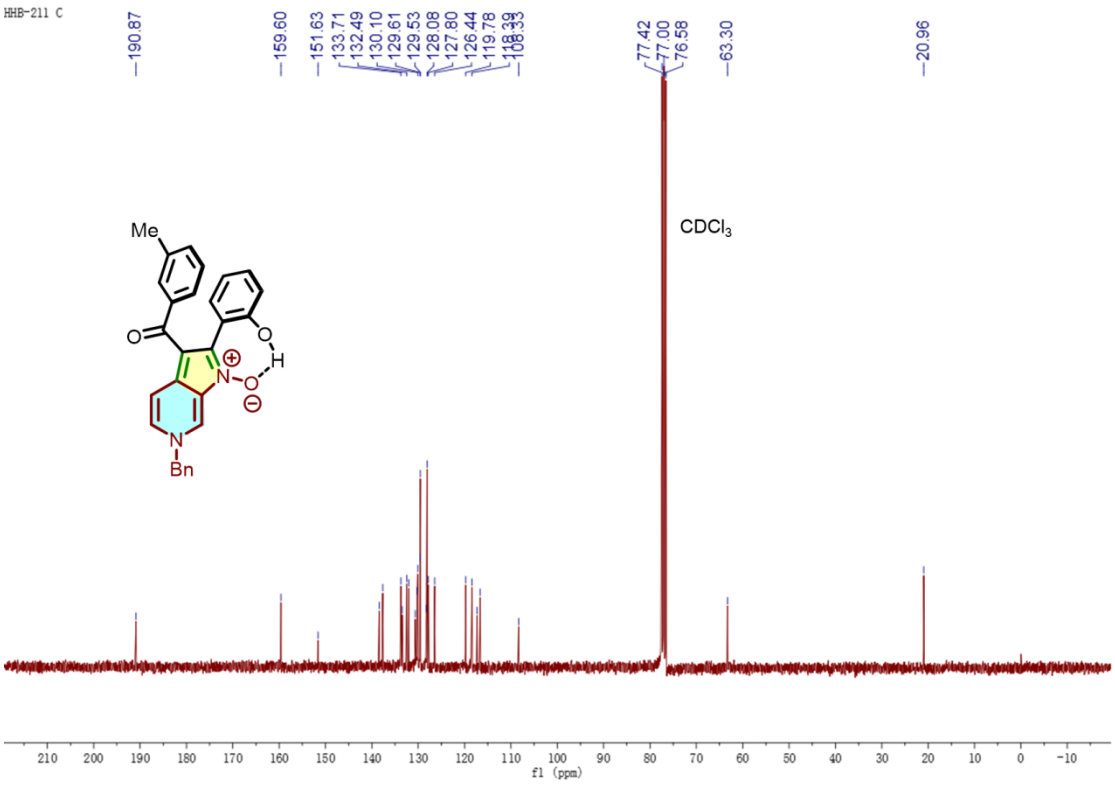
^{13}C NMR spectrum of **3r** (100 MHz, DMSO-d_6)



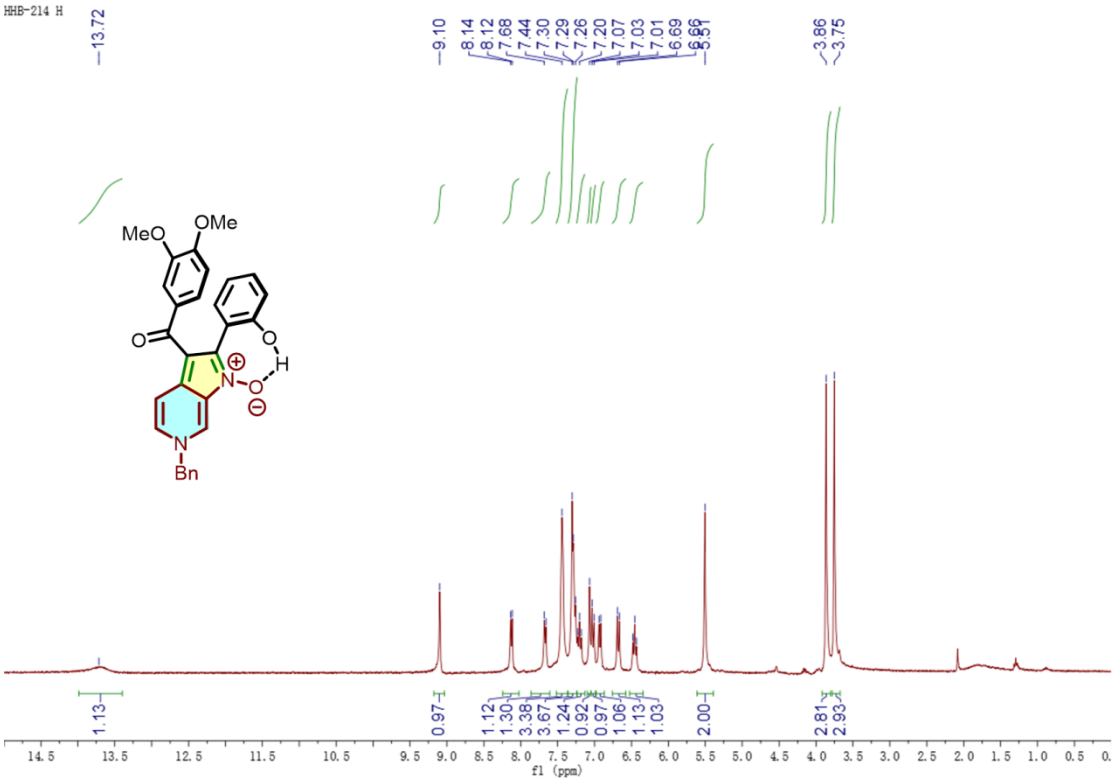
^{1}H NMR spectrum of **3s** (300 MHz, $CDCl_3$)



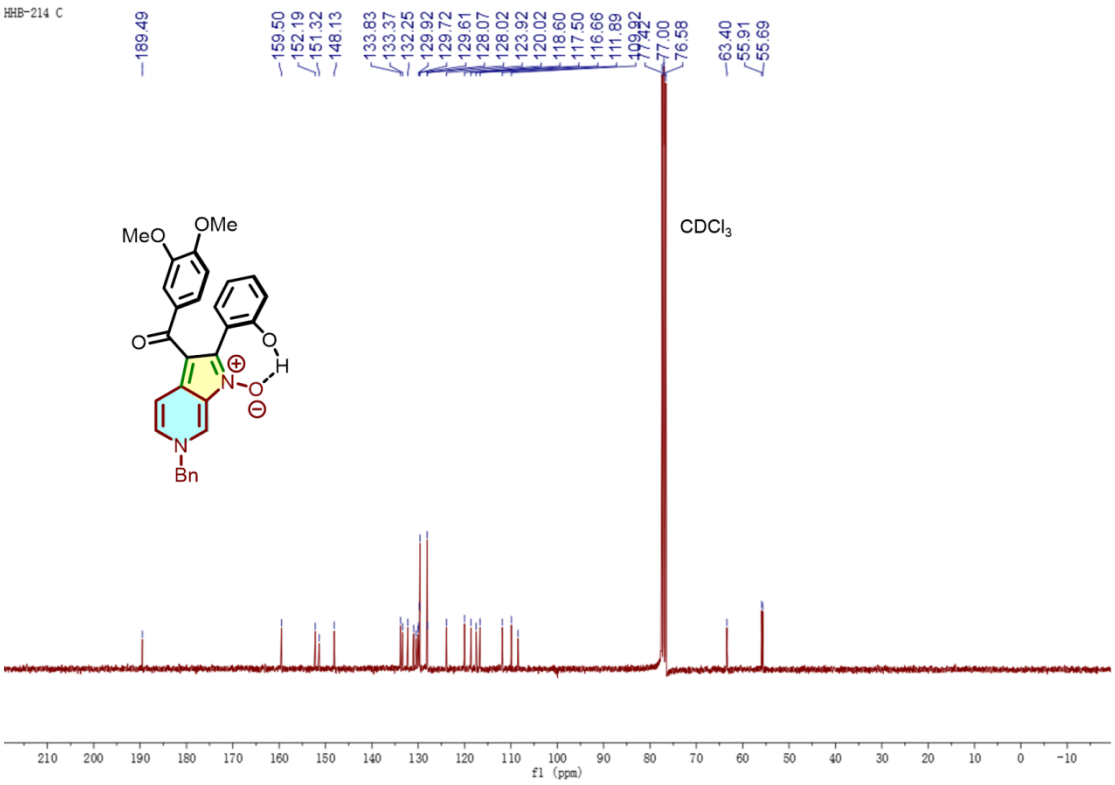
^{13}C NMR spectrum of **3s** (75 MHz, $CDCl_3$)



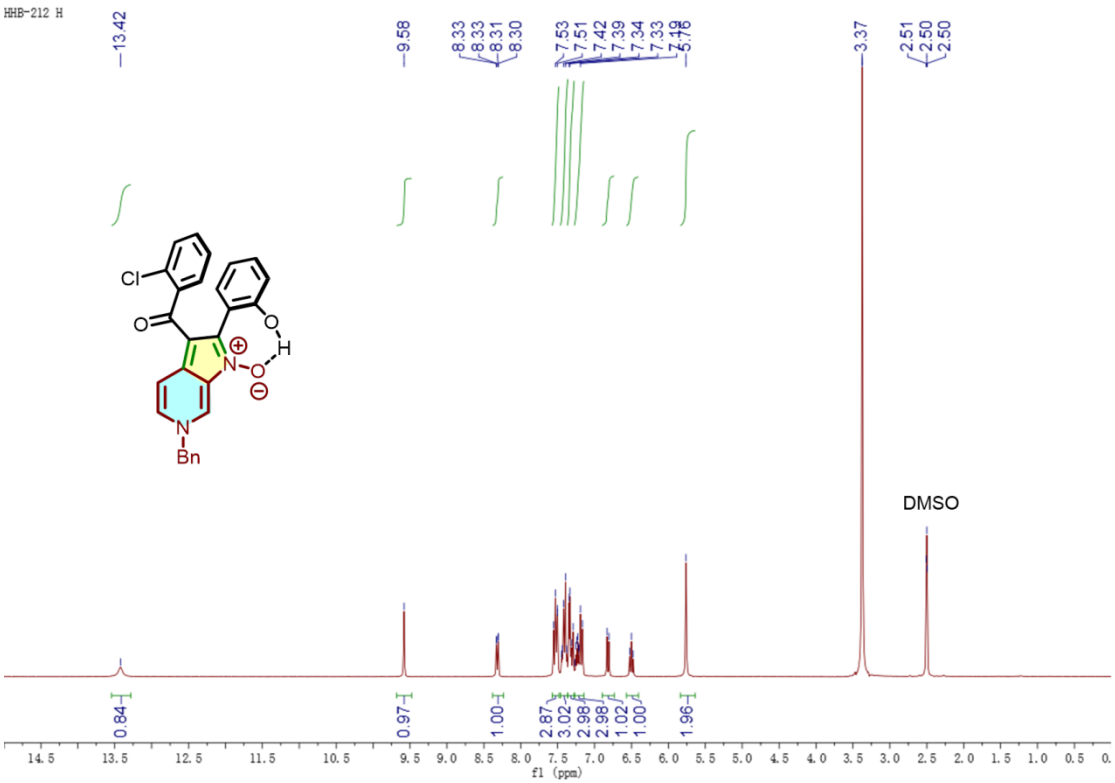
^{1}H NMR spectrum of **3t** (300 MHz, $CDCl_3$)



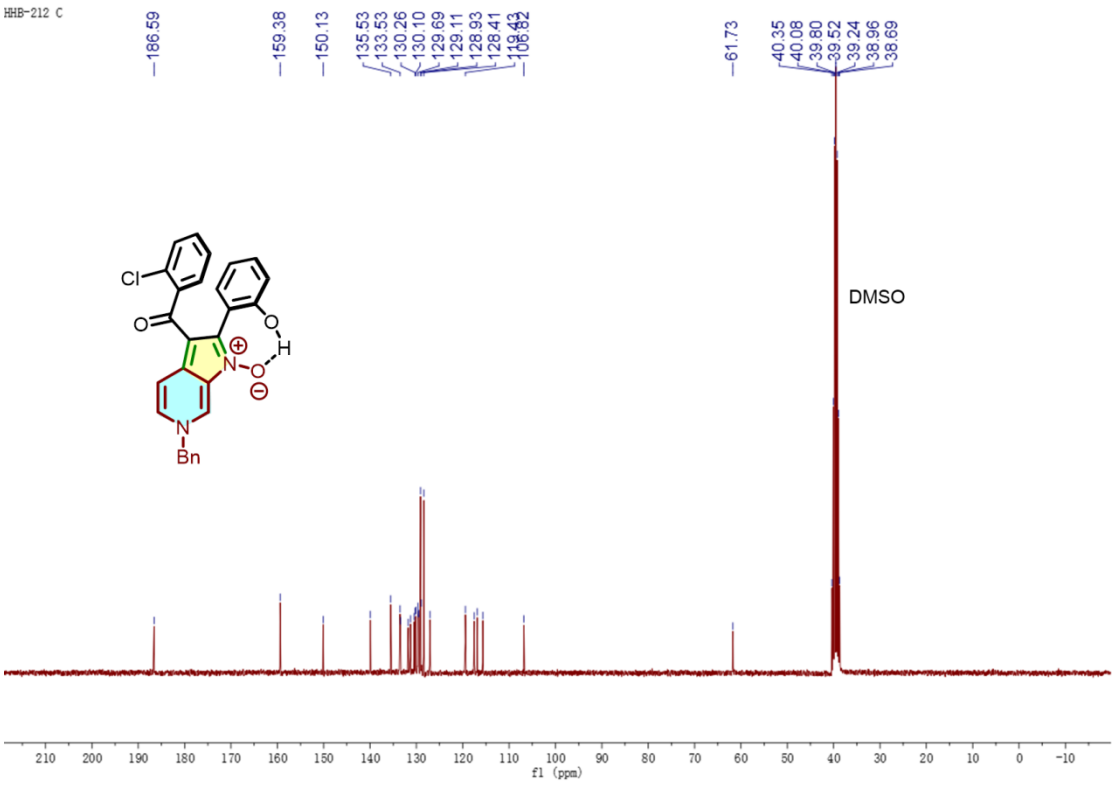
^{13}C NMR spectrum of **3t** (75 MHz, $CDCl_3$)



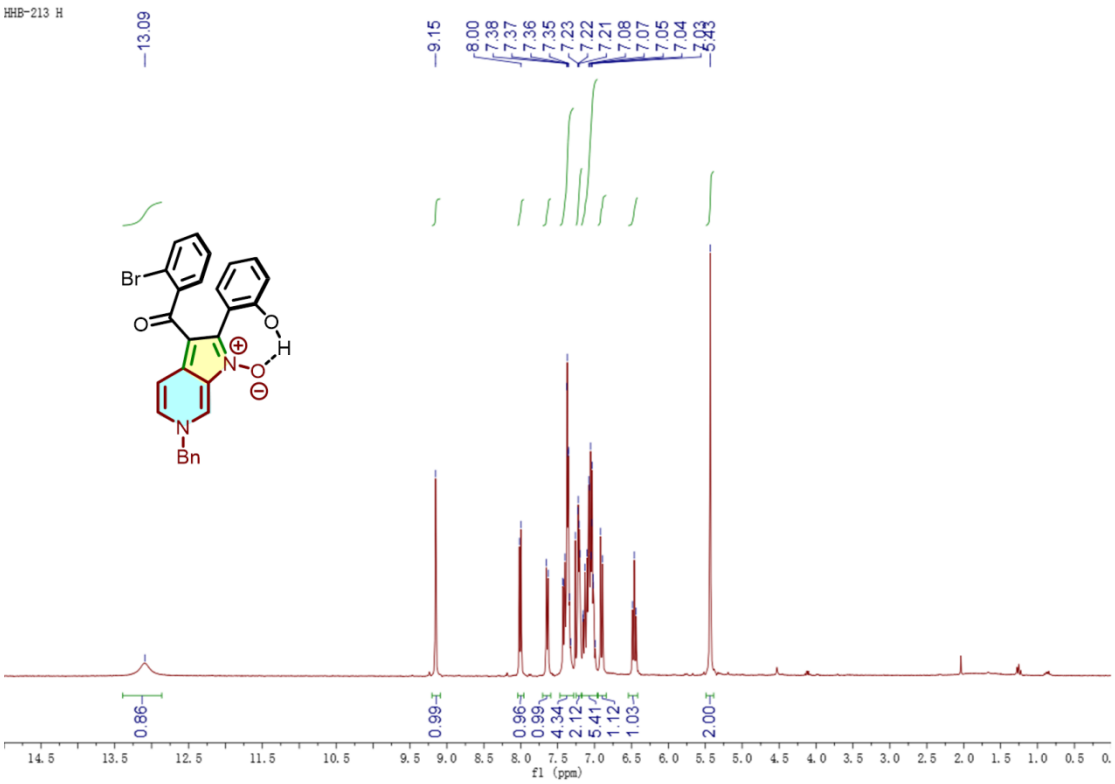
^{1}H NMR spectrum of **3u** (300 MHz, DMSO-d_6)



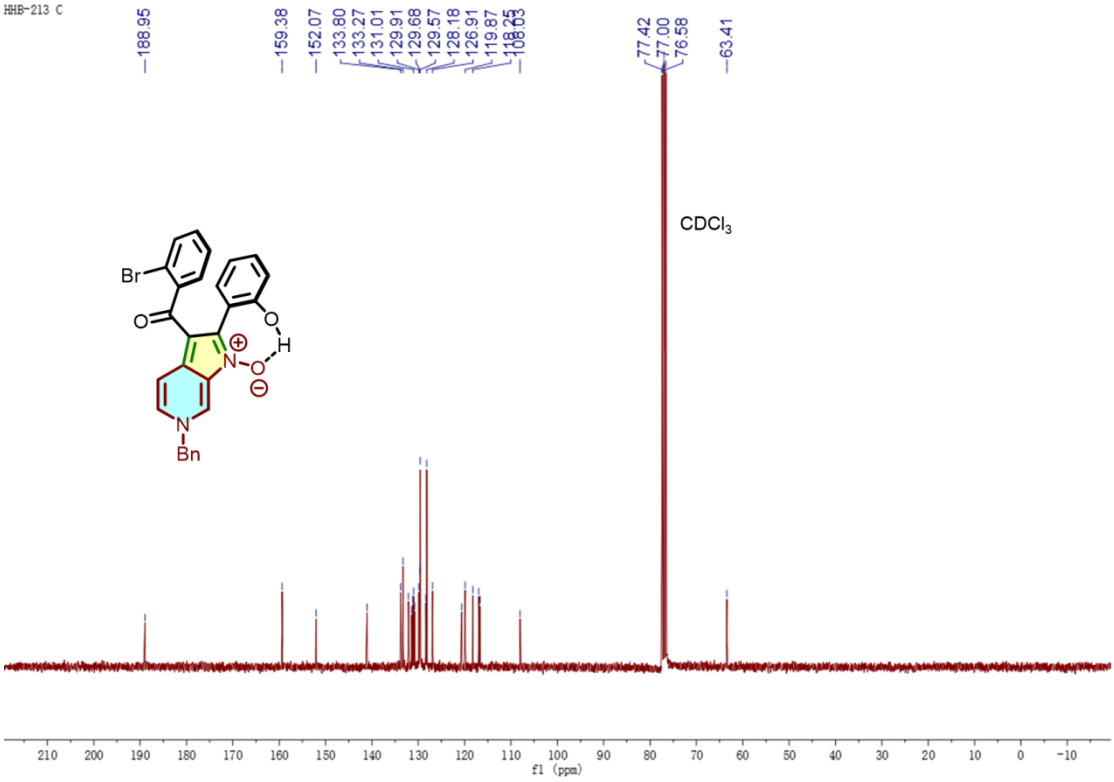
^{13}C NMR spectrum of **3u** (75 MHz, DMSO-d_6)



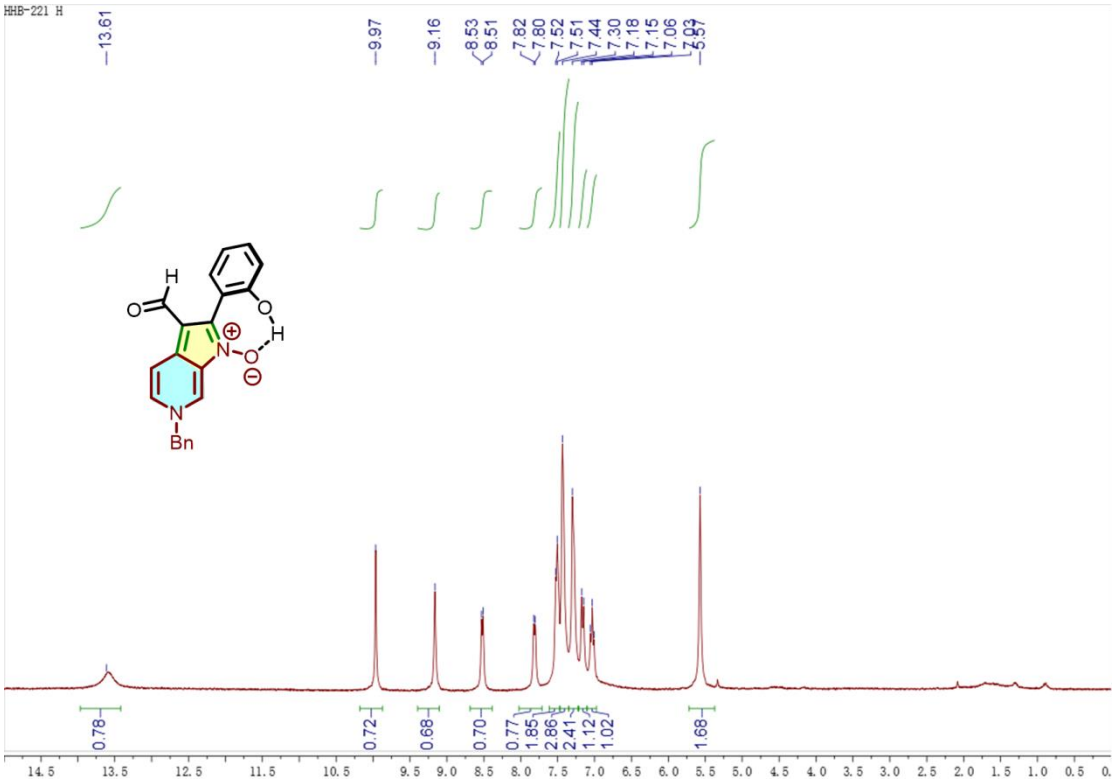
^{1}H NMR spectrum of **3v** (300 MHz, $CDCl_3$)



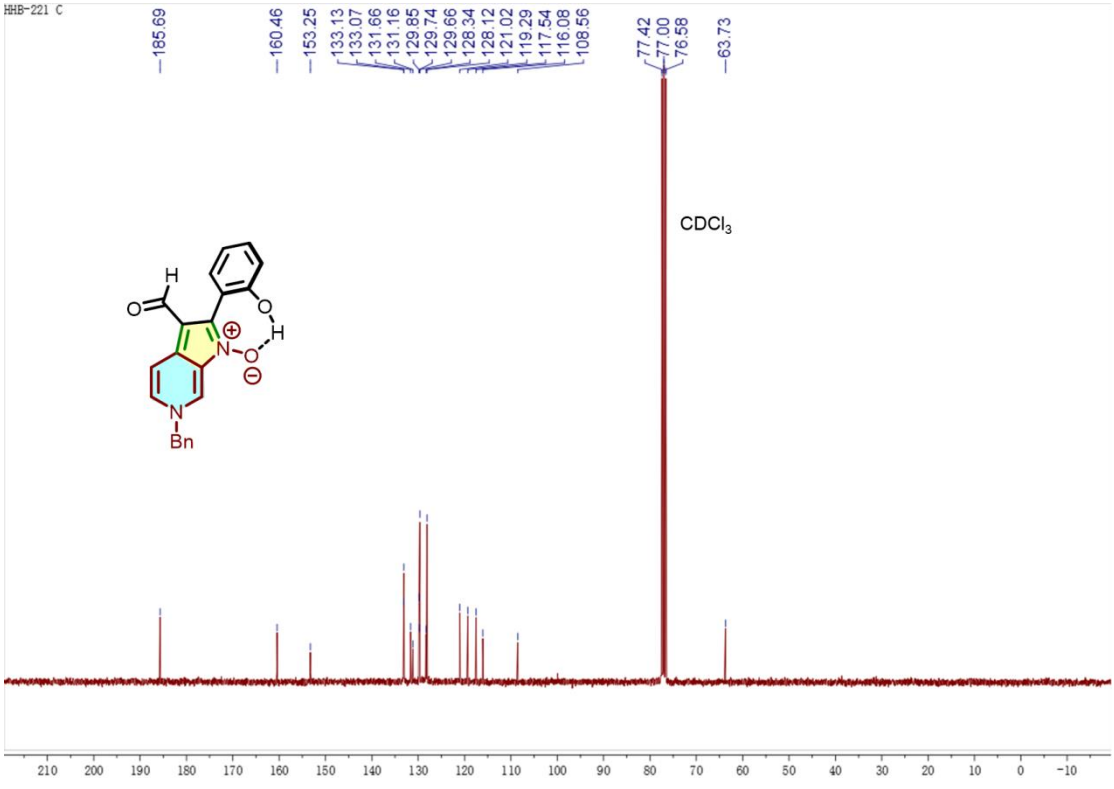
^{13}C NMR spectrum of **3v** (75 MHz, $CDCl_3$)



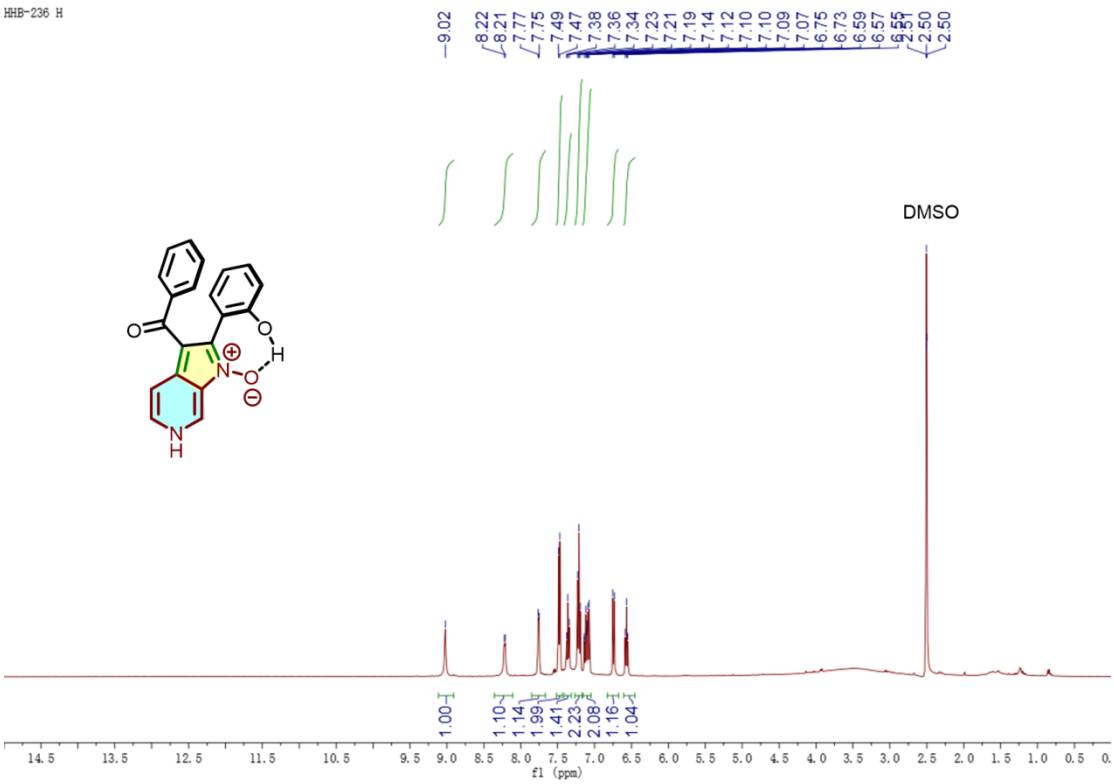
^{1}H NMR spectrum of **3w** (300 MHz, $CDCl_3$)



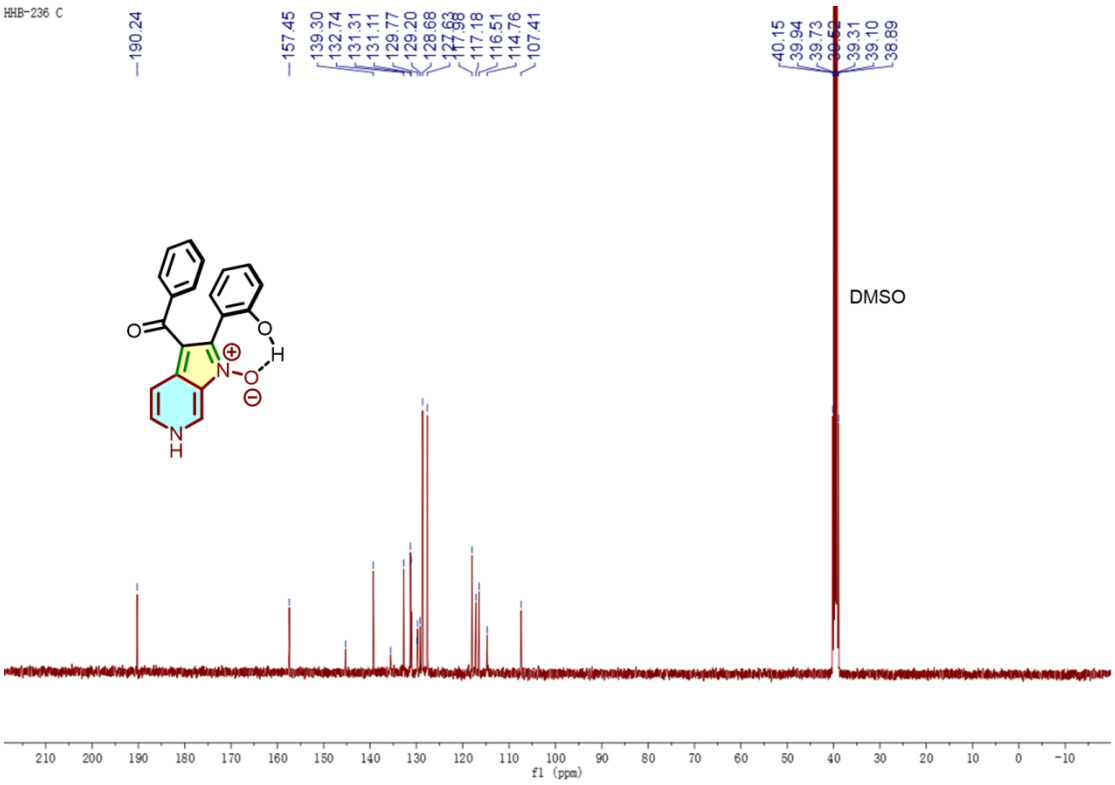
^{13}C NMR spectrum of **3w** (75 MHz, $CDCl_3$)



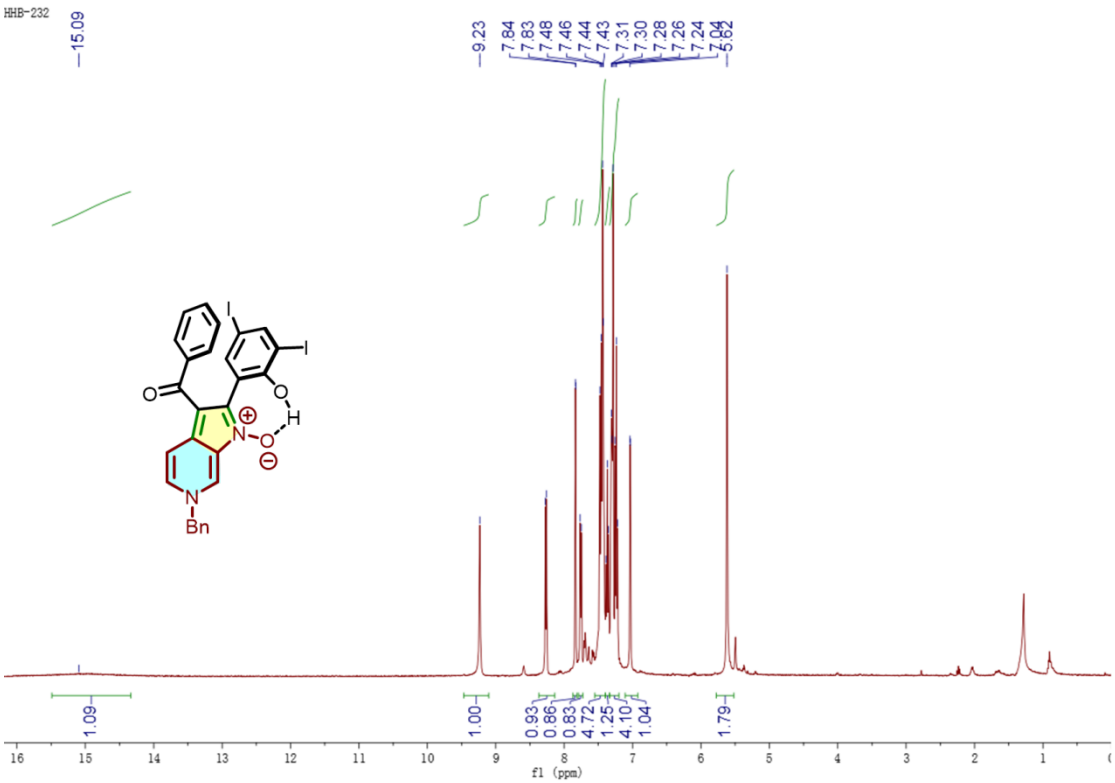
^{1}H NMR spectrum of **4** (400 MHz, DMSO-d_6)



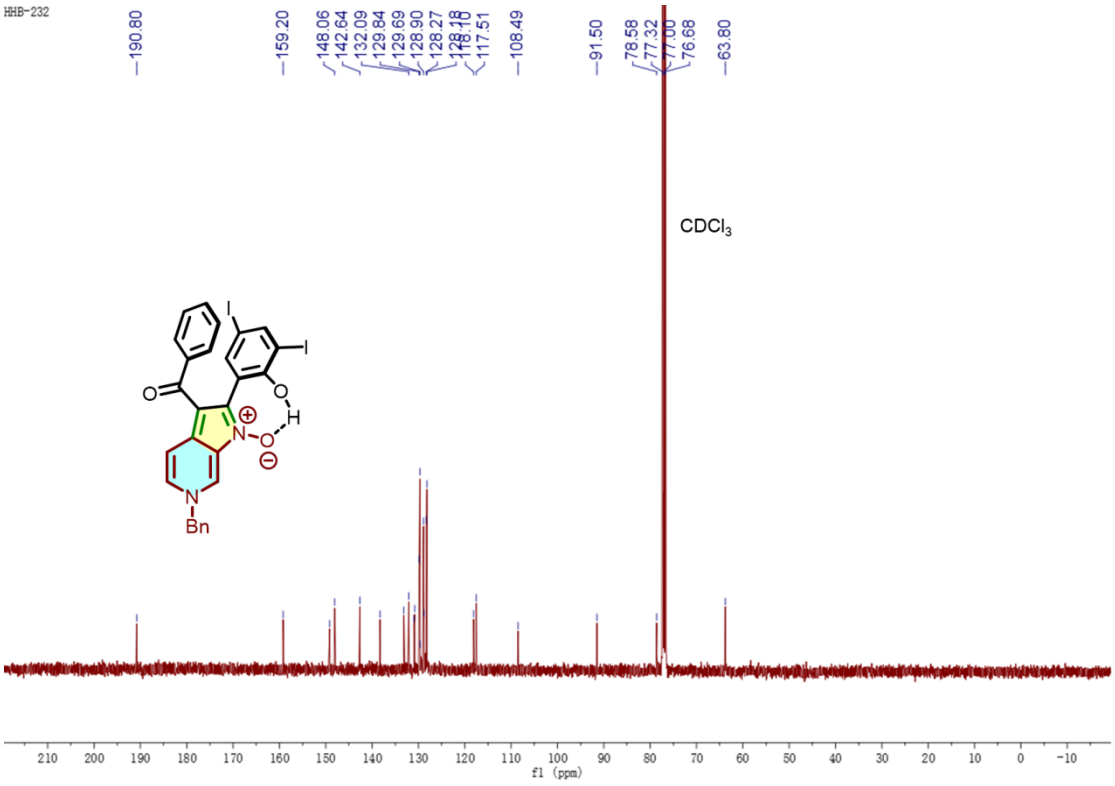
^{13}C NMR spectrum of **4** (100 MHz, DMSO-d_6)



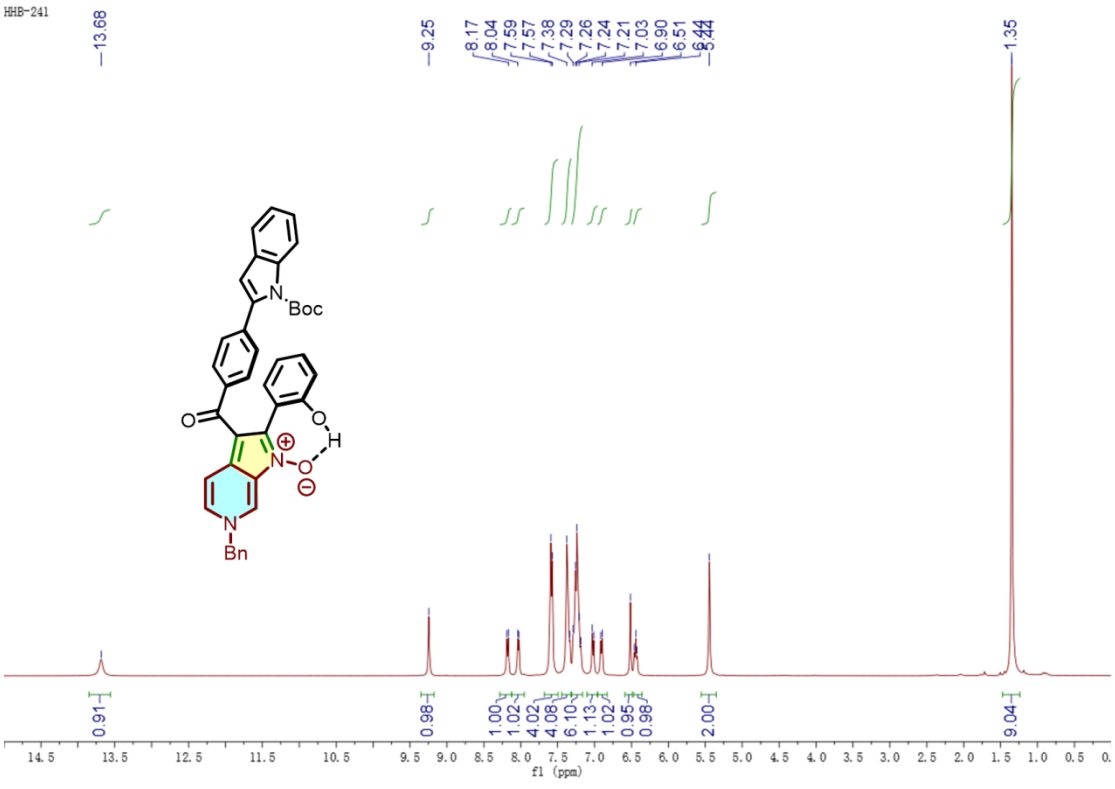
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)



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



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



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