Supporting Information

Chelation-assisted Rh(III)-catalyzed C2-selective oxidative C–H/C–H cross-coupling of indoles/pyrroles with heteroarenes

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I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz or a Varian Inova 400 MHz spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$, TMS or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; TMS: δ = 0.00 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). X-Ray single-crystal diffraction data were collected on an Oxford Xcalibur E X-ray single crystal diffractometer. Melting points were determined with XRC-1 and are uncorrected. Absorption spectra were detected on a HITACHI U-2910 absorption spectrophotometer. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer.

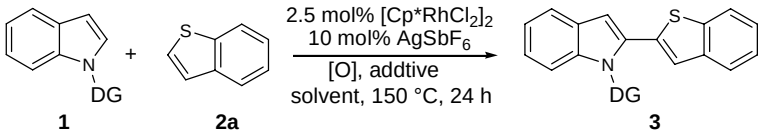
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $RhCl_3 \cdot 3H_2O$ were purchased from Shaanxi Kaida Chemical Engineering (China) CO., Ltd. $AgSbF_6$ was purchased from Alfa Aesar. Ag_2CO_3 was purchased from Tianjin Yin Li Da Chemical Engineering (China) CO., Ltd. $Cu(OAc)_2 \cdot H_2O$ was purchased from Shanghai Kefeng Chemical Reagent (China) CO., Ltd. $[Cp^*RhCl_2]_2$,[1] indole derivatives,[2] pyrrole derivatives,[3] diketopyrrolopyrrole derivatives,[4] ethyl 5-methyloxazole-4-carboxylate,[5] and *N*-heteroarene *N*-oxides[6] were prepared according to the literature procedures. All solvents were purified and dried according to standard methods prior to use.

II. Optimization of the oxidative cross-coupling of *N*-substituted indole with benzothiophene

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $[Cp^*RhCl_2]_2$ (3.9 mg, 6.25 μmol, 2.5 mol%), $AgSbF_6$ (8.6 mg, 25.0 μmol, 10 mol%) , *N*-substituted indole (0.25 mmol), benzothiophene (0.75 mmol, 3.0 equiv) and oxidant (0.50 mmol, 2.0 equiv) in solvent (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under an N_2 atmosphere, and then heated at 120-150 °C in a

pre-heated oil bath for the indicated time. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated, and the resulting residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 10/1-8/1 v/v) to provide the desired product **3a**.

Table S1 Optimization of the reaction conditions[a,b]



Entry	DG	Additive	Oxidant	Solvent	Yield (%)
1	Pym	PivOH/CsOPiv(20 mol %)	$Cu(OAc)_2$	DCE	52
2	Pym	PivOH/CsOAc (20 mol %)	$Cu(OAc)_2$	DCE	48
3	Pym	PivOH	$Cu(OAc)_2$	DCE	68
4[c]	Pym	PivOH	$Cu(OAc)_2$	DCE	28
5	Pym	-	$Cu(OAc)_2$	DCE	33
6	Pym	HOAc	$Cu(OAc)_2$	DCE	43
7	Pym	2,4,6-trimethylbenzoic acid	$Cu(OAc)_2$	DCE	55
8	Pym	PivOH	Ag_2CO_3	DCE	70
9	Pym	PivOH	AgOAc	DCE	49
10	Pym	PivOH	AgF	DCE	58
11	Pym	PivOH	Ag_2CO_3	DMF	86
12	Pym	PivOH	Ag_2CO_3	DMSO	-
13	Pym	PivOH	Ag_2CO_3	toluene	52
14	Pym	PivOH	Ag_2CO_3	*t*-amylOH	25
15	Pym	PivOH	Ag_2CO_3	1,4-dioxane	38
16[d]	Pym	PivOH	Ag_2CO_3	DMF	65
17[e]	Pym	PivOH	Ag_2CO_3	DMF	51
18	Bn	PivOH	Ag_2CO_3	DMF	-
19	$(CH_3)_2NCO$	PivOH	Ag_2CO_3	DMF	-
20	Ts	PivOH	Ag_2CO_3	DMF	-
21	Piv	PivOH	Ag_2CO_3	DMF	-
22	H	PivOH	Ag_2CO_3	DMF	-
23	Py	PivOH	Ag_2CO_3	DMF	83

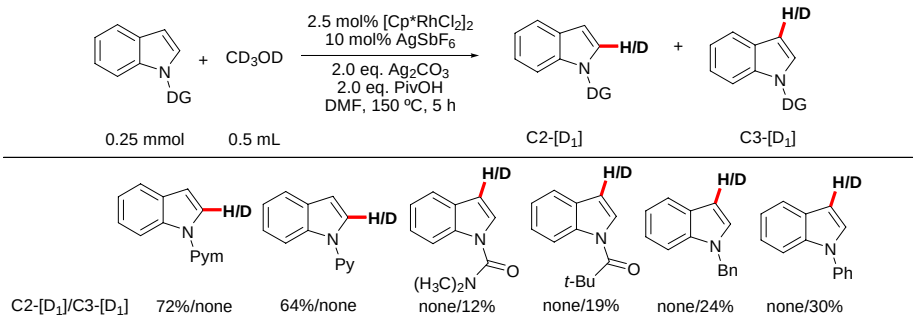
[a] Reactions were carried out using $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), additive (0.50 mmol, 2.0 equiv), indole (0.25 mmol), benzothiophene (0.75 mmol, 3.0 equiv) and solvent (1.0 mL) at 150 °C for 24 hours under an N_2 atmosphere. [b] Yield of isolated product. [c] 120 °C. [d] Without $AgSbF_6$. [e] Benzothiophene (0.375 mmol, 1.5 equiv). DMF = dimethyl formamide, DCE = 1,2-dichloroethane, DMSO = dimethyl sulfoxide, Pym = 2-pyrimidyl, Bn = benzyl, Ts = tosyl, Piv

= pivaloyl, Py = 2-pyridinyl.

III. General procedure for the cross-coupling of indoles or pyrroles with heteroarenes

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $[Cp^*RhCl_2]_2$ (3.9 mg, 6.25 μmol, 2.5 mol%), $AgSbF_6$ (8.6 mg, 25.0 μmol, 10 mol%), indole or pyrrole derivative (0.25 mmol), heteroarene (0.75 mmol, 3.0 equiv), PivOH (0.50 mmol, 2.0 equiv), and Ag_2CO_3 (0.50 mmol, 2.0 equiv) in DMF or 1,4-dioxane (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under an N_2 atmosphere, and then heated at 120-150 °C in a pre-heated oil bath for the indicated time. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

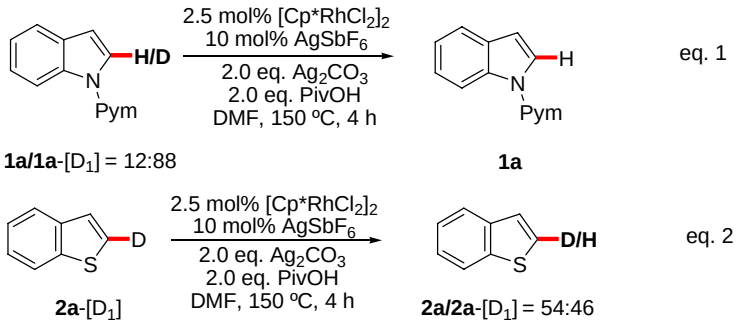
IV. Deuterium labeling experiments of *N*-substituted indoles



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $[Cp^*RhCl_2]_2$ (3.9 mg, 6.25 μmol, 2.5 mol%), $AgSbF_6$ (8.6 mg, 25.0 μmol, 10 mol%), *N*-substituted indoles (0.25 mmol), PivOH (0.50 mmol, 2.0 equiv), and Ag_2CO_3 (0.50 mmol, 2.0 equiv) in DMF (1.0 mL) and CD_3OD (0.5 mL). The reaction mixture was stirred for 10 min at room temperature under an N_2 atmosphere, and then heated at 150 °C in a pre-heated oil bath for 5 h. The reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with

sat. NH_4Cl solution, and dried over anhydrous Na_2SO_4. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. The deuterium incorporation was calculated from ^1H NMR analysis.

V. The H/D exchange experiments for each coupling partner (1a and 2a)



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $[Cp^*RhCl_2]_2$ (3.9 mg, 6.25 μmol, 2.5 mol%), $AgSbF_6$ (8.6 mg, 25.0 μmol, 10 mol%), 2-deuterio-1-(pyrimidin-2-yl)-1*H*-indole (0.25 mmol) or 2-deuterio-benzothiophene (0.25 mmol), PivOH (0.50 mmol, 2.0 equiv), and Ag_2CO_3 (0.50 mmol, 2.0 equiv) in DMF (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under an N_2 atmosphere, and then heated at 150 °C in a pre-heated oil bath for 4 h. The reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH_4Cl solution, and dried over anhydrous Na_2SO_4. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. The deuterium incorporation was calculated from ^1H NMR analysis.

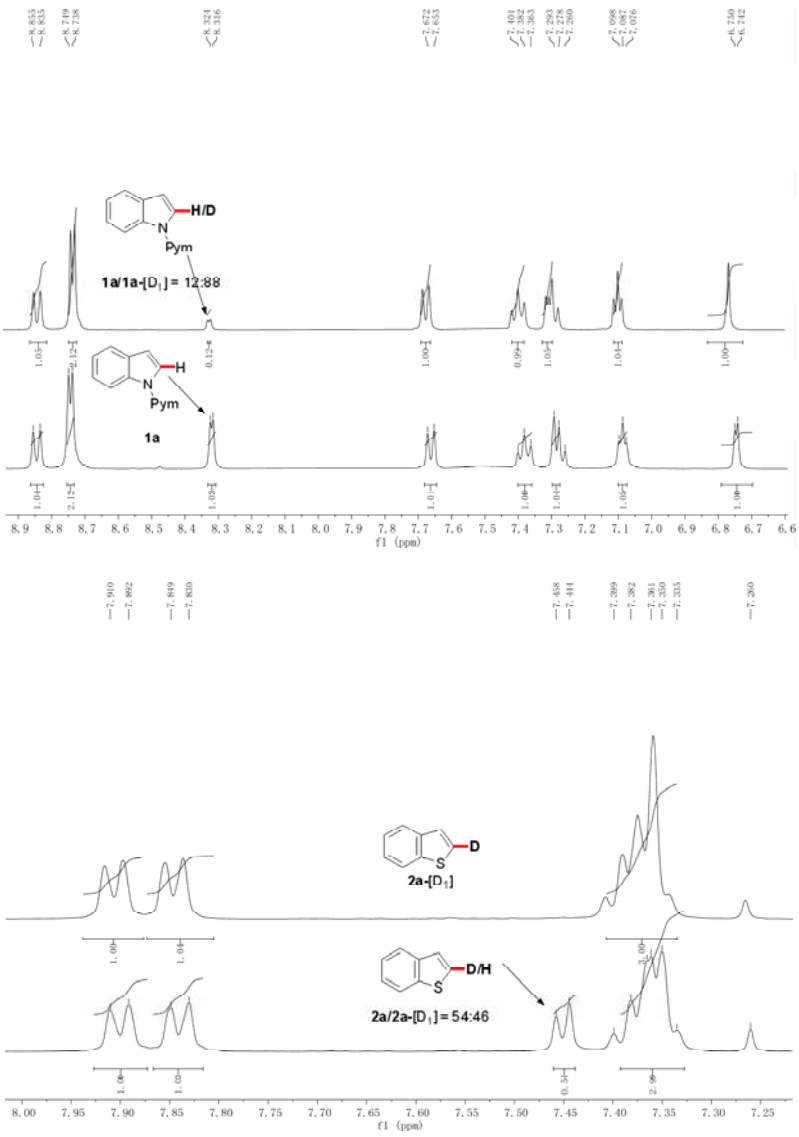
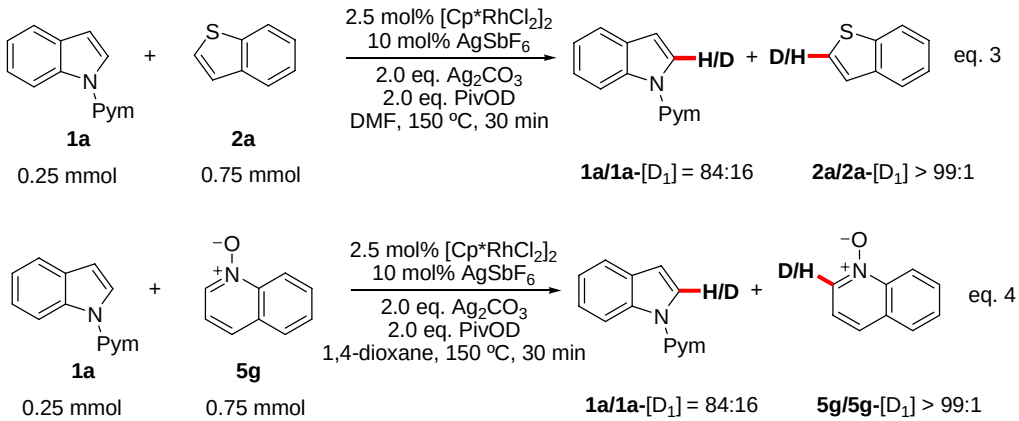


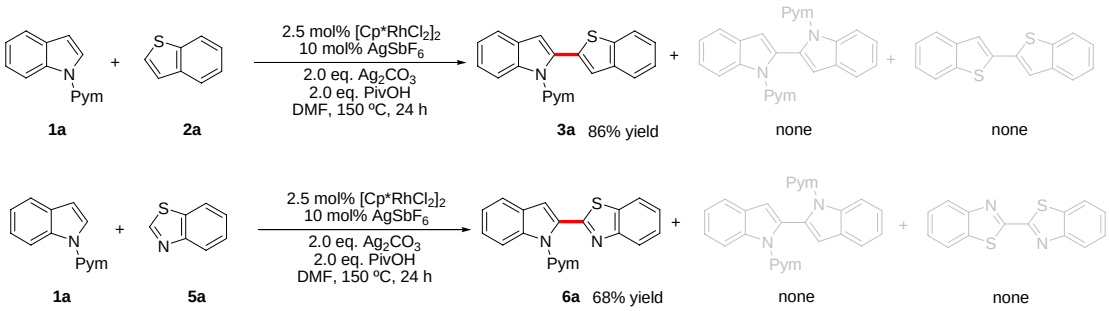
Fig. S1 Copies of ^{1}H NMR spectra of H/D exchange experiments.

VI. The competitive H/D exchange experiments for cross-couplings of 1a with 2a or 5g



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $[Cp^*RhCl_2]_2$ (3.9 mg, 6.25 μmol, 2.5 mol%), $AgSbF_6$ (8.6 mg, 25.0 μmol, 10 mol%), heteroarene **1a**, heteroarene **2a** or **5g**, PivOD (0.50 mmol, 2.0 equiv), and Ag_2CO_3 (0.50 mmol, 2.0 equiv) in DMF or 1,4-dioxane (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under an N_2 atmosphere, and then heated at 150 °C in a pre-heated oil bath for 30 min. The reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH_4Cl solution, and dried over anhydrous Na_2SO_4. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. The deuterium incorporation was calculated from ^1H NMR analysis.

VII. Investigation of ^1H NMR spectra of reaction mixtures of cross-couplings of 1a with 2a or 5a



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $[Cp^*RhCl_2]_2$ (3.9 mg, 6.25 μmol, 2.5 mol%), $AgSbF_6$ (8.6 mg, 25.0 μmol, 10 mol%), 1-(pyrimidin-2-yl)-1*H*-indole (**1a**, 0.25 mmol), benzothiophene (**2a**, 0.75 mmol) or benzothiazole (**5a**, 0.75 mmol), PivOH (0.50 mmol, 2.0 equiv), and Ag_2CO_3 (0.50 mmol, 2.0 equiv) in DMF (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under an N_2 atmosphere, and then heated at 150 °C in a pre-heated oil bath for 24 h. The reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH_4Cl solution, and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. The ^1H NMR spectrum of the resulting mixture did not indicated any homo-coupling products of **1a, 2a** and **5a** except the cross-coupling products **3a** and **6a** as well as the

remained starting materials.

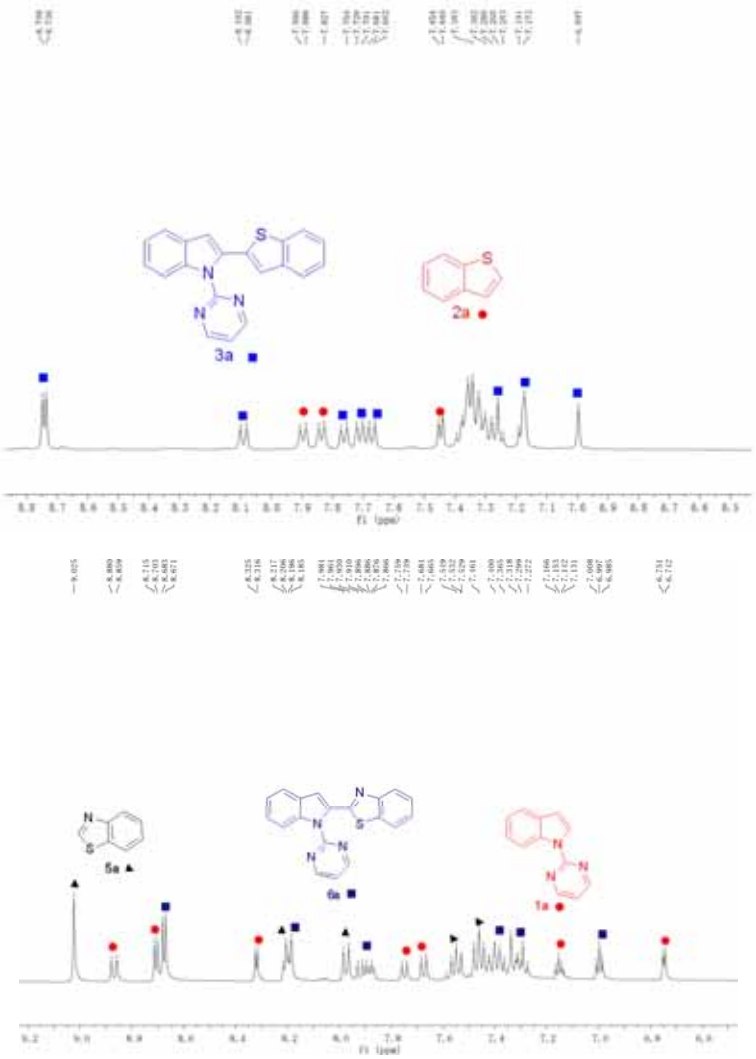
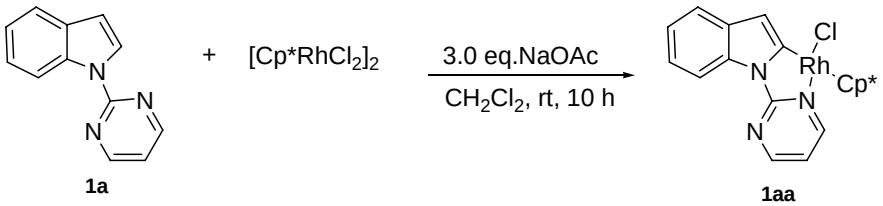


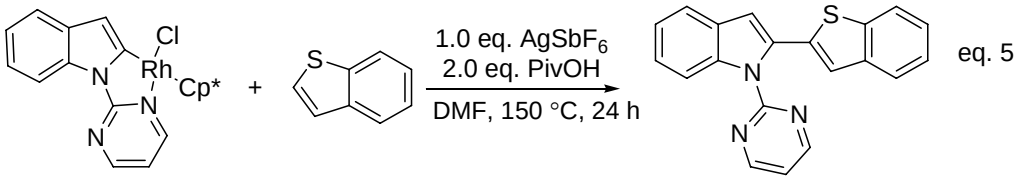
Fig. S2 Copies of ^{1}H NMR spectra of reaction mixtures of **1a** with **2a** or **5a**.

VIII. Procedure for the synthesis of cyclometalated Rh(III) complex 1aa



$[Cp^*RhCl_2]_2$ (309.0 mg, 0.50 mmol), 1-(pyrimidin-2-yl)-1*H*-indole (243.8 mg, 1.25 mmol), and sodium acetate (3.0 equiv) in CH_2Cl_2 (5 mL) was stirred for 10 h at room temperature. The solution was filtered through Celite and evaporated to dryness. The product was crystallized from CH_2Cl_2/hexane to give **1aa** (510.0 mg, 54%) as orange crystals.[7]

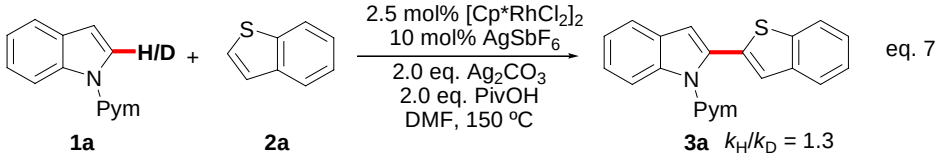
IX. Procedure for the cross-coupling of cyclometalated Rh(III) complex 1aa with benzothiophene 2a



1aa, 0.25 mmol **2a**, 0.75 mmol **3a**, 72%

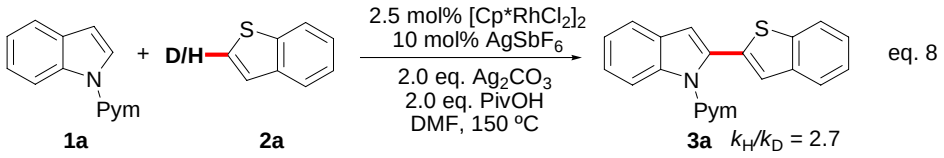
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with the Rh(III) complex **1aa** (118.0 mg, 0.25 mmol), benzothiophene (100.5 mg, 0.75 mmol), $AgSbF_6$ (86 mg, 1.0 equiv), and PivOH (0.50 mmol, 2.0 equiv) in DMF (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under an N_2 atmosphere, and then heated at 150 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product (**3a**, 59 mg) in 72% yield.

X. Kinetic isotope experiments



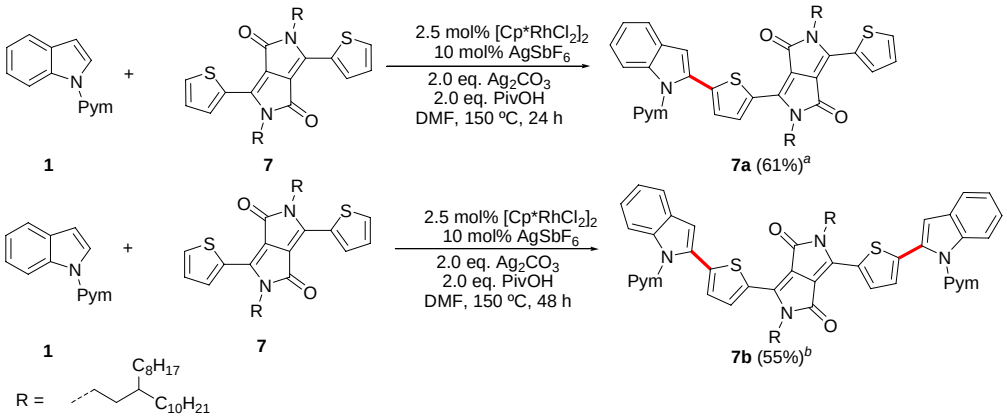
1a **2a** **3a** k_H/k_D = 1.3

Two sets of reactions were carried out in a parallel manner. In each case benzothiophene was allowed to react with 1-(pyrimidin-2-yl)-1*H*-indole and 2-deuterio-1-(pyrimidin-2-yl)-1*H*-indole, respectively. The sealed tubes were screw capped and heated to 150 °C (oil bath). After being stirred for 4 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH_4Cl solution, and dried over anhydrous Na_2SO_4. The yield of **3a** was determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard.



Two sets of reactions were carried out in a parallel manner. In each case 1-(pyrimidin-2-yl)-1*H*-indole was allowed to react with benzothiophene and 2-deuterio-benzothiophene, respectively. The sealed tubes were screw capped and heated to 150 °C (oil bath). After being stirred for 4 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH_4Cl solution, and dried over anhydrous Na_2SO_4. The yield of **3a** was determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard.

XI. Synthesis of 7a and 7b



Scheme S1 [a] Reaction conditions: $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Ag_2CO_3 (2.0 equiv), PivOH (2.0 equiv), 1-(pyrimidin-2-yl)-1*H*-indole **1** (0.25 mmol), diketopyrrolopyrrole derivative **7** (0.75 mmol) at 150 °C for 24 h under an N_2 atmosphere. Isolated yields based on **1**. [b] 1-(pyrimidin-2-yl)-1*H*-indole **1** (0.75 mmol), diketopyrrolopyrrole derivative **7** (0.25 mmol) at 150 °C for 48 h under an N_2 atmosphere. Isolated yield based on **7**.

XII. Absorption and fluorescence emission spectroscopy of 7a and 7b

UV/vis spectra were measured on a HITACHI U-2910 with a slit width of 1.0 nm. Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system (slit width: 1.0 nm). To reduce the fluctuation in the excitation intensity during measurement, the lamp was kept on for 1 h prior to the experiment. The path

length was 1 cm with a cell volume of 3.0 mL.

Table S2 Optical properties of DPP **7a** and **7b** in dichloromethane

Compound	λ_{abs} (nm)[a]	ε_{max} (M^{-1} cm^{-1})[a]	λ_{em} (nm)[a]	Φ_f (%)[a,b]
7a	570	36800	617	21
7b	605	58800	652	28

[a] UV/vis absorption and fluorescence spectra of **7a** and **7b** in dichloromethane (1×10^{-5} M).

[b] Absolute quantum yield determined with a calibrated integrating sphere system.

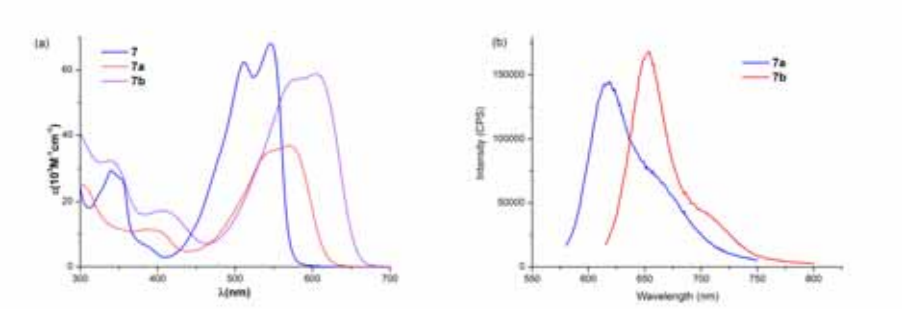
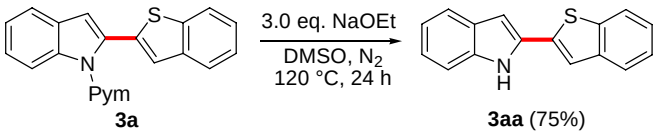


Fig. S3 (a) UV spectra of **7**, **7a** and **7b** in CH_2Cl_2 (1×10^{-5} M). (b) Emission spectra of **7a** and **7b** in CH_2Cl_2 (1×10^{-5} M).

XIII. General procedure for removal of 2-pyrimidyl group from indole nucleus



eq. 9

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (**3a**, 163 mg, 0.50 mmol), NaOEt (102 mg, 1.5 mmol) and DMSO (1.0 mL) under N_2. The reaction mixture was stirred for 10 min at room temperature, and then heated at 120 °C for 24 h. The reaction mixture was then cooled to ambient temperature, and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4. Concentration in vacuo followed by purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) gave 2-(benzothiophen-2-yl)-1*H*-indole (**3aa**, 94 mg) in 75% yield.

XIV. Procedure for the synthesis of 3a on gram scale

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with

$[Cp^*RhCl_2]_2$ (154.5 mg, 250.0 μmol, 2.5 mol%), $AgSbF_6$ (343.6 mg, 1.0 mmol, 10 mol%), 1-(pyrimidin-2-yl)-1*H*-indole (10.0 mmol), benzothiophene (30.0 mmol, 3.0 equiv), PivOH (20.0 mmol, 2.0 equiv) and Ag_2CO_3 (20.0 mmol, 2.0 equiv) in DMF (10.0 mL). The reaction mixture was stirred for 10 min at room temperature under an N_2 atmosphere, and then heated at 150 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to ambient temperature, diluted with 50 mL of CH_2Cl_2, filtered through a celite pad and washed with 50 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1-8/1, v/v) to provide 2-(benzothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (**3a**, 2.64 g) in 81% yield.

XV. ORTEP diagram of compound 3a

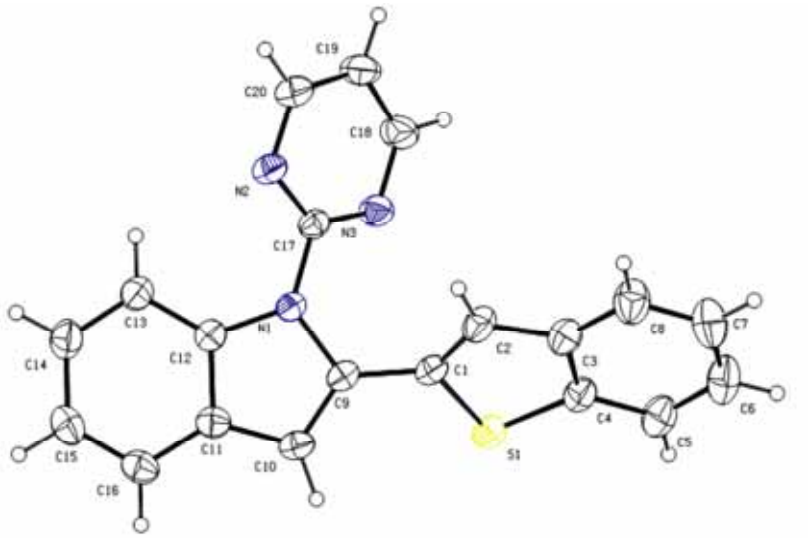
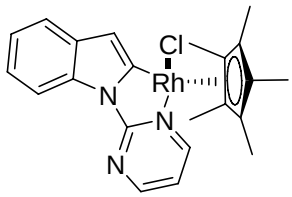


Fig. S4 ORTEP diagram of **3a**. Thermal ellipsoids are shown at the 50% probability level.

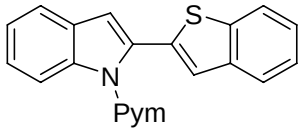
XVI. Experimental data for the described substances



***rac*-(T-4)-Chloro(η^5-pentamethylcyclopentadienyl)(1-(pyrimidin-2-yl-κN),**

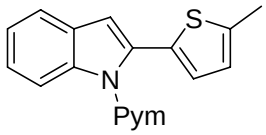
1*H*-indole-$\kappa C^{2'}$)rhodium(III) (1aa)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (s, 15H), 6.63 (s, 1H), 6.88 (t, J = 4.4 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 8.43 (d, J = 7.6 Hz, 1H), 8.60 (d, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6 ($CpMe_5$), 96.7 (5 C, $^1J_{Rh\text{-}C}$ = 6.5, $CpMe_5$), 110.9, 113.6, 114.5, 118.1, 120.6, 122.6, 135.2, 136.5, 158.9, 159.5, 159.8, 163.6 ($^1J_{Rh\text{-}C}$ = 32) ppm.



2-(Benzothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3a)

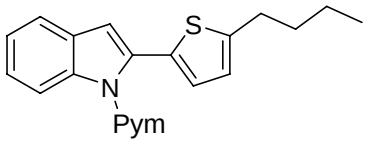
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (70 mg, 86%). M.p.: 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 (s, 1H), 7.09-7.12 (m, 2H), 7.18-7.20 (m, 1H), 7.22-7.27 (m, 3H), 7.58 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 8.67 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.2, 112.9, 118.3, 121.0, 122.1, 122.5, 122.7, 123.8, 124.4, 124.5, 129.0, 133.5, 135.9, 138.5, 139.9, 140.3, 157.9, 158.6 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{14}N_3S$ $[M+H]^+$ 328.0908, found 328.0908.



2-(5-Methylthiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3b)

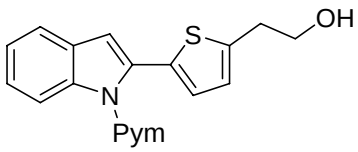
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (45 mg, 63%). M.p.: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ =

2.45 (s, 3H), 6.62 (s, 1H), 6.69 (s, 1H), 6.79 (s, 1H), 7.17-7.20 (m, 1H), 7.21-7.22 (m, 1H), 7.25-7.26 (m, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.76 (d, J =4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4, 108.2, 112.6, 118.2, 120.7, 122.2, 123.7, 125.4, 126.5, 129.1, 133.0, 134.0, 138.1, 140.6, 158.0, 158.5 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{14}N_3S$ $[M+H]^+$ 292.0908, found 292.0909.



2-(5-Butylthiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3c)

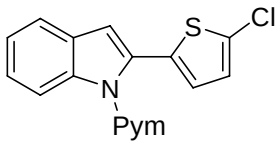
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as yellow oil (48 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.4 Hz, 3H), 1.33-1.42 (m, 2H), 1.59-1.67 (m, 2H), 2.74 (t, J = 7.6 Hz, 2H), 6.63 (d, J = 3.2 Hz, 1H), 6.71 (d, J = 3.2 Hz, 1H), 6.80 (s, 1H), 7.18-7.20 (m, 1H), 7.22 (ds, 1H), 7.25-7.26 (m, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.75 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.3, 29.9, 33.8, 108.1, 112.6, 118.2, 120.7, 122.2, 123.7, 124.2, 126.3, 129.2, 132.7, 134.1, 138.1, 146.7, 158.0, 158.5 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{20}N_3S$ $[M+H]^+$ 334.1378, found 334.1376.



2-(5-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)thiophen-2-yl)ethanol (3d)

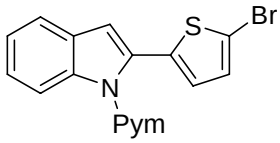
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as yellow oil (51 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (s, 1H), 3.01 (t, J = 6.2 Hz, 2H), 3.84 (s, 2H), 6.74 (s, 2H), 6.82 (s, 1H), 7.19-7.22 (m, 1H), 7.23-7.28 (m,

2H), 7.61 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 8.76 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.6, 63.5, 108.5, 112.6, 118.3, 120.7, 122.3, 123.9, 125.8, 126.6, 129.1, 133.6, 134.0, 138.1, 141.5, 157.9, 158.5 ppm. HRMS (ESI^+): calcd for $C_{18}H_{16}N_3OS$ $[M+H]^+$ 322.1014, found 322.1009.



2-(5-Chlorothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3e)

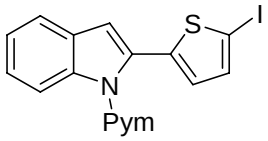
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 120 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (62 mg, 80%). M.p.: 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82 (d, J = 4.0 Hz, 1H), 6.88 (d, J = 4.0 Hz, 1H), 6.91 (s, 1H), 7.25 (t, J = 4.8 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.83 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.5, 113.0, 118.3, 120.9, 122.5, 124.3, 126.1, 126.2, 128.8, 130.4, 132.6, 134.2, 138.1, 157.6, 158.5 ppm. HRMS (ESI^+): calcd for $C_{16}H_{11}ClN_3S$ $[M+H]^+$ 312.0362, found 312.0359.



2-(5-Bromothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3f)

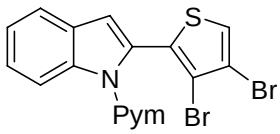
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 120 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (69 mg, 78%). M.p.: 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (d, J = 4.0 Hz, 1H), 6.83 (s, 1H), 6.92 (d, J = 3.6 Hz, 1H), 7.17 (t, J = 5.0 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 8.03

(d, J = 8.4 Hz, 1H), 8.75 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.5, 112.7, 113.0, 118.3, 120.9, 122.5, 124.3, 127.1, 128.9, 129.9, 132.5, 137.1, 138.1, 157.7, 158.5 ppm. HRMS (ESI^+): calcd for $C_{16}H_{11}BrN_3S$ $[M+H]^+$ 355.9857, found 355.9860.



2-(5-Iodothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3g)

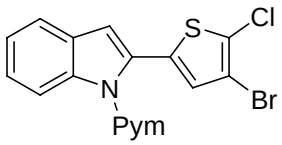
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 120 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as yellow oil (59 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64 (d, J = 3.6 Hz, 1H), 6.83 (s, 1H), 7.12 (d, J = 3.6 Hz, 1H), 7.18-7.21 (m, 1H), 7.23-7.31 (m, 2H), 7.62 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 8.76 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.9, 109.5, 113.0, 118.3, 120.9, 122.5, 124.3, 128.3, 128.9, 132.4, 137.0, 138.1, 141.6, 157.7, 158.5 ppm. HRMS (ESI^+): calcd for $C_{16}H_{11}IN_3S$ $[M+H]^+$ 403.9718, found 403.9715.



2-(3,4-Dibromothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3h)

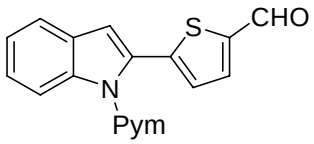
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 120 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (82 mg, 75%). M.p.: 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (s, 1H), 7.08 (t, J = 4.6 Hz, 1H), 7.23-7.24 (m, 1H), 7.31-7.35 (m, 2H), 7.63 (d, J = 7.6 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.63 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.8, 113.8, 114.0, 114.3, 117.7, 121.2, 122.6, 123.1, 124.8, 128.6,

130.1, 133.1, 137.6, 157.6, 158.3 ppm. HRMS (ESI^+): calcd for $C_{16}H_{10}Br_2N_3S$ $[M+H]^+$ 435.8942, found 435.8943.



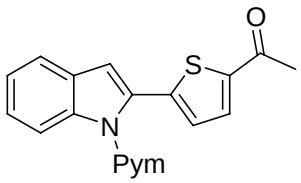
2-(4-Bromo-5-chlorothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3i)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 120 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (74 mg, 76%). M.p.: 114-116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 1H), 6.85 (s, 1H), 7.20 (t, J = 5.0 Hz, 1H), 7.24-7.26 (m, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.77 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.2, 110.4, 113.3, 118.3, 121.1, 122.7, 124.7, 127.0, 128.5, 128.7, 131.5, 134.0, 138.1, 157.4, 158.5 ppm. HRMS (ESI^+): calcd for $C_{16}H_{10}BrClN_3S$ $[M+H]^+$ 389.9467, found 389.9467.



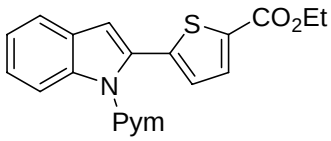
5-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)thiophene-2-carbaldehyde (3j)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 120 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 5/1-2/1, v/v) afforded the desired product as a yellow solid (52 mg, 68%). M.p.: 176-178 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.02-7.04 (m, 2H), 7.21-7.23 (m, 1H), 7.26 (d, J = 7.6 Hz 1H), 7.32-7.36 (t, J = 7.8 Hz 1H), 7.63-7.67 (m, 2H), 8.09 (d, J = 8.4 Hz, 1H), 8.75 (d, J = 4.8 Hz, 2H), 9.86 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.2, 113.2, 118.5, 121.3, 122.8, 125.1, 127.1, 128.7, 132.2, 136.5, 138.8, 143.0, 145.8, 157.5, 158.6, 182.9 ppm. HRMS (ESI^+): calcd for $C_{17}H_{11}N_3NaOS$ $[M+Na]^+$ 328.0521, found 328.0521.



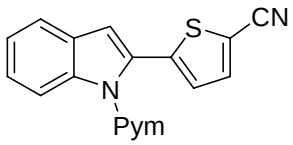
1-(5-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)thiophen-2-yl)ethanone (3k)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 5/1-2/1, v/v) afforded the desired product as a yellow solid (56 mg, 70%). M.p.: 222-224 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.56 (s, 3H), 6.96-6.97 (m, 1H), 7.00 (s, 1H), 7.23-7.26 (m, 1H), 7.28-7.30 (m, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.58-7.59 (m, 1H), 7.67 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.77-8.79 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.7, 110.6, 113.1, 118.4, 121.2, 122.7, 124.9, 127.0, 128.8, 132.5, 132.6, 138.6, 143.8, 144.2, 157.6, 158.6, 190.6 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{14}N_3OS$ $[M+H]^+$ 320.0858, found 320.0854.



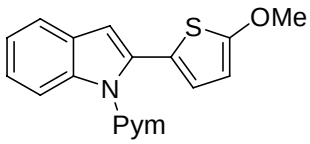
Ethyl 5-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)thiophene-2-carboxylate (3l)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 5/1-2/1, v/v) afforded the desired product as yellow oil (57 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ =1.32 (t, J = 7.2 Hz, 3H), 4.28 (q, J = 7.2 Hz, 2H), 6.83 (d, J = 4.0 Hz, 1H), 6.91 (s, 1H), 7.16 (t, J = 4.8 Hz, 1H), 7.22-7.24 (m, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.61-7.63 (m, 2H), 8.04 (d, J = 8.4 Hz, 1H), 8.71 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 61.3, 110.4, 113.1, 118.4, 121.1, 122.7, 124.7, 126.9, 128.9, 132.5, 133.2(8), 133.3, 138.5, 142.5, 157.7, 158.6, 162.4 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{16}N_3O_2S$ $[M+H]^+$ 350.0963, found 350.0962.



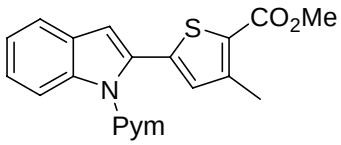
5-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)thiophene-2-carbonitrile (3m)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (69 mg, 85%). M.p.: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (d, J = 4.0 Hz, 1H), 6.97 (s, 1H), 7.22 (t, J = 4.8 Hz, 1H), 7.24-7.29 (m, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 3.6 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.75 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.2, 111.5, 113.4, 114.5, 118.4, 121.3, 122.9, 125.2, 126.6, 128.6, 131.0, 137.3, 138.5, 143.3, 157.4, 158.6 ppm. HRMS (ESI^+): calcd for $C_{17}H_{10}N_4NaS$ $[M+Na]^+$ 325.0524, found 325.0528.



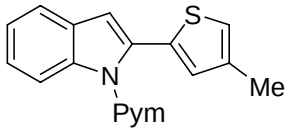
2-(5-Methoxythiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3n)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 120 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (58 mg, 75%). M.p.: 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3H), 6.09 (d, J = 3.6 Hz, 1H), 6.59 (d, J = 4.0 Hz, 1H), 6.77 (s, 1H), 7.19-7.22 (m, 2H), 7.25 (d, J = 4.0 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.78 (t, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.3, 103.9, 108.2, 112.6, 118.2, 120.6, 121.5, 122.3, 123.7, 124.5, 129.1, 134.1, 138.0, 158.0, 158.5, 167.1 ppm. HRMS (ESI^+): calcd for $C_{17}H_{14}N_3OS$ $[M+H]^+$ 308.0858, found 308.0848.



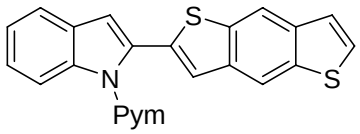
Methyl 3-Methyl-5-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)thiophene-2-carboxylate (3o)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 5/1-2/1, v/v) afforded the desired product as a yellow solid (57 mg, 65%). M.p.: 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3H), 3.83 (s, 3H), 6.76 (s, 1H), 6.92 (s, 1H), 7.19 (t, J = 5.0 Hz, 1H), 7.24 (m, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.76 (d, J =4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2, 51.8, 110.2, 113.0, 118.4, 121.1, 122.6, 124.6, 126.2, 128.9, 130.7, 132.7, 138.5, 139.9, 146.3, 157.7, 158.6, 163.3 ppm. HRMS (ESI^+): calcd for $C_{19}H_{16}N_3O_2S$ $[M+H]^+$ 350.0963, found 350.0963.



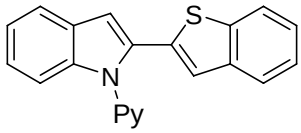
2-(4-Methylthiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3p)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (50 mg, 69%). M.p.: 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09 (s, 3H), 6.65 (s, 1H), 6.70-6.71 (m, 2H), 7.04 (t, J = 5.0 Hz, 1H), 7.08-7.15 (m, 2H), 7.48 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 8.62 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9, 108.5, 112.6, 118.2, 120.7, 121.4, 122.3, 123.8, 128.8, 129.1, 133.9, 135.2, 137.6, 138.2, 157.9, 158.5 ppm. HRMS (ESI^+): calcd for $C_{17}H_{14}N_3S$ $[M+H]^+$ 292.0908, found 292.0906.



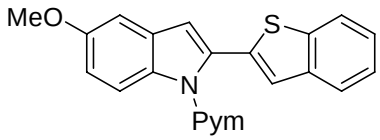
2-(Benzodithiophene-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3q)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (86 mg, 90%). M.p.: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 (s, 1H), 7.05-7.08 (m, 2H), 7.13-7.17 (m, 2H), 7.19-7.23 (m, 1H), 7.33 (d, J = 5.6 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 8.0 Hz, 2H), 8.06 (s, 1H), 8.62 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.3, 112.9, 116.4, 117.0, 118.3, 121.1, 121.7, 122.6, 123.1, 124.5, 127.2, 129.1, 133.6, 136.3, 137.3, 137.5, 137.6, 137.8, 138.6, 157.9, 158.6 ppm. HRMS (ESI^+): calcd for $C_{22}H_{14}N_3S_2$ $[M+H]^+$ 384.0629, found 384.0627.



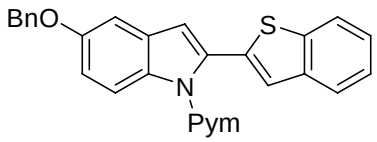
2-(Benzothiophen-2-yl)-1-(pyridin-2-yl)-1*H*-indole (3r)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (68 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (s, 1H), 6.99 (s, 1H), 7.18-7.24 (m, 3H), 7.26-7.30 (m, 2H), 7.31-7.34 (m, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.72 (t, J = 7.4 Hz, 2H), 8.69-8.70 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.1, 111.4, 120.9, 121.7, 122.1, 122.6, 122.7, 122.8, 123.8, 123.8(1), 124.6, 128.4, 133.2, 134.6, 138.4, 139.1, 139.9, 140.0, 149.6, 151.6 ppm. HRMS (ESI^+): calcd for $C_{21}H_{15}N_2S$ $[M+H]^+$ 327.0956, found 327.0956.



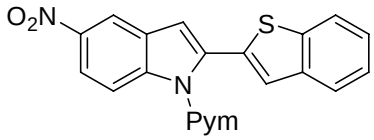
2-(Benzothiophen-2-yl)-5-methoxy-1-(pyrimidin-2-yl)-1*H*-indole (4a)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a off white solid (77 mg, 86%). M.p.: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 6.92 (s, 1H), 6.95-6.97 (m, 1H), 7.11-7.15 (m, 2H), 7.18 (s, 1H), 7.28-7.34 (m, 2H), 7.70 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 6.8 Hz, 1H), 8.70 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.9, 102.8, 110.2, 113.9, 114.1, 118.0, 122.1, 122.6, 123.8, 124.4, 124.4(4), 129.7, 133.5, 134.0, 136.1, 139.9, 140.3, 155.9, 157.9, 158.5 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{16}N_3OS$ $[M+H]^+$ 358.1014, found 358.1011.



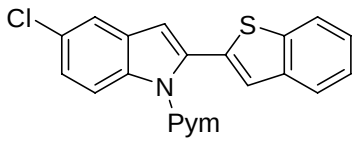
2-(Benzothiophen-2-yl)-5-(benzyloxy)-1-(pyrimidin-2-yl)-1*H*-indole (4b)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (98 mg, 90%). M.p.: 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.16 (s, 2H), 6.91 (s, 1H), 7.03-7.06 (m, 1H), 7.12 (t, J = 4.8 Hz, 1H), 7.18-7.19 (m, 2H), 7.28-7.36 (m, 3H), 7.39 (t, J = 7.0 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 8.05 (d, J =9.2 Hz, 1H), 8.70 (d, J = 4.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.8, 104.4, 110.2, 114.1, 114.7, 118.0, 122.1, 122.6, 123.8, 124.4, 124.4(4), 127.7, 128.0, 128.7, 129.7, 133.7, 134.0, 136.1, 137.5, 139.9, 140.3, 155.1, 157.9, 158.5 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{20}N_3OS$ $[M+H]^+$ 434.1327, found 434.1326.



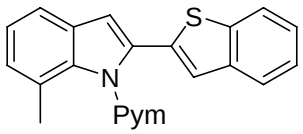
2-(Benzothiophen-2-yl)-5-nitro-1-(pyrimidin-2-yl)-1*H*-indole (4c)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 2/1-1/1, v/v) afforded the desired product as a yellow solid (63 mg, 68%). M.p.: 146-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (s, 1H), 7.20 (s, 1H), 7.29-7.38 (m, 3H), 7.72 (d, J = 7.2 Hz, 1H), 7.76 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H), 8.58 (s, 1H), 8.79 (d, J = 4.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.2, 113.1, 117.6, 119.4, 119.4(2), 122.2, 123.9, 124.1, 124.8, 125.0, 128.4, 134.1, 136.8, 139.6, 140.5, 141.0, 143.6, 157.1, 158.9 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{13}N_4O_2S$ $[M+H]^+$ 373.0759, found 373.0757.



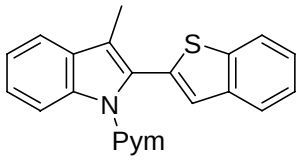
2-(Benzothiophen-2-yl)-5-chloro-1-(pyrimidin-2-yl)-1*H*-indole (4d)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (68 mg, 75%). M.p.: 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 (s, 1H), 7.18 (s, 1H), 7.20 (t, J = 4.8 Hz, 1H), 7.25-7.26 (d, J = 7.6 Hz, 1H), 7.29-7.36 (m, 2H), 7.62 (s, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 8.01 (d, J =8.8 Hz, 1H), 8.73 (d, J =4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.3, 114.2, 118.5, 120.4, 122.2, 123.2, 123.9, 124.5, 124.6, 124.6(2), 128.0, 130.1, 134.9, 135.3, 136.8, 139.8, 140.4, 157.6, 158.6 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{13}ClN_3S$ $[M+H]^+$ 362.0519, found 362.0523.



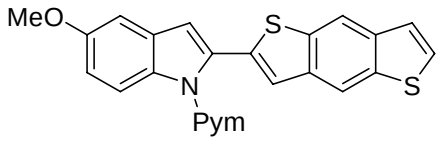
2-(Benzothiophen-2-yl)-7-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4e)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as red oil (72 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 3H), 6.92 (s, 1H), 6.94-6.97 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 7.20-7.26 (m, 2H), 7.33 (t, J = 4.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 6.8 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 8.80 (d, J =4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 107.1, 119.2, 120.7, 121.8, 122.0, 122.9, 123.7, 124.5, 126.3, 129.0, 131.1, 134.6, 134.6(5), 138.3, 140.0, 140.1, 158.6, 159.8 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{16}N_3S$ $[M+H]^+$ 342.1065, found 342.1067.



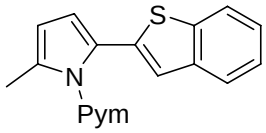
2-(Benzothiophen-2-yl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4f)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (68 mg, 80%). M.p.: 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3H), 7.04 (t, J = 4.8 Hz, 1H), 7.28-7.39 (m, 5H), 7.64 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.9, 113.2, 117.4, 118.1, 119.4, 122.1, 122.1(2), 123.8, 124.1(6), 124.2, 124.3, 124.7, 129.2, 130.2, 135.7, 137.5, 139.8, 140.9, 158.0, 158.3 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{16}N_3S$ $[M+H]^+$ 342.1065, found 342.1067.



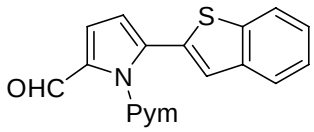
2-(Benzodithiophene-2-yl)-5-methoxy-1-(pyrimidin-2-yl)-1*H*-indole (4g)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a yellow solid (89 mg, 86%). M.p.: 216-218 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 6.95 (s, 1H), 6.97 (s, 1H), 7.11 (s, 1H), 7.14-7.17 (m, 2H), 7.32 (d, J = 5.6 Hz, 1H), 7.44 (d, J = 5.2 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 8.18 (s, 2H), 8.70 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.9, 102.8, 110.3, 114.0(8), 114.1, 116.4, 117.0, 118.0, 121.6, 123.1, 127.1, 129.7, 133.6, 134.1, 136.5, 137.3, 137.5, 137.6, 137.9, 156.0, 157.9, 158.5 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{16}N_3OS_2$ $[M+H]^+$ 414.0735, found 414.0741.



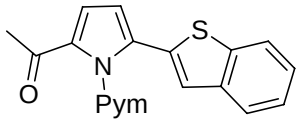
2-(2-(Benzothiophen-2-yl)-5-methyl-1*H*-pyrrol-1-yl)pyrimidine (4h)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column chromatography (petroleum ether/acetone = 10/1, v/v) afforded the desired product as yellow oil (40 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3H), 6.09 (d, J = 2.8 Hz, 1H), 6.49 (d, J = 3.2 Hz, 1H), 6.75 (s, 1H), 7.18-7.25 (m, 3H), 7.55 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 8.75 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 109.6, 112.9, 119.5, 120.1, 122.0, 123.2, 123.7, 124.3, 127.4, 133.5, 136.3, 139.5, 140.3, 158.2, 158.8 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{13}N_3NaS$ $[M+Na]^+$ 314.0728, found 314.0730.



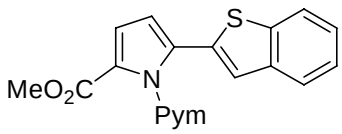
5-(Benzothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-pyrrole-2-carbaldehyde (4i)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column chromatography (petroleum ether/acetone = 8/1-6/1, v/v) afforded the desired product as a yellow solid (38 mg, 50%). M.p.: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.72 (d, J = 4.0 Hz, 1H), 7.03 (s, 1H), 7.16 (d, J = 4.0 Hz, 1H), 7.28-7.32 (m, 2H), 7.45 (t, J = 4.8 Hz, 1H), 7.63-7.65 (m, 1H), 7.69-7.71 (m, 1H), 8.86 (d, J = 4.8 Hz, 2H), 9.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.9, 121.3, 122.1, 123.0, 123.8, 124.0, 124.8, 125.1, 132.3, 134.9, 136.1, 137.9, 139.6, 140.2, 159.1, 178.6 ppm. HRMS (ESI^+): calcd for $C_{17}H_{11}N_3NaOS$ $[M+Na]^+$ 328.0521, found 328.0518.



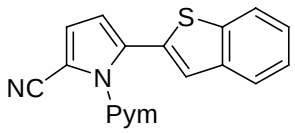
1-(5-(Benzothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-pyrrol-2-yl)ethanone (4j)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column chromatography (petroleum ether/acetone = 8/1-6/1, v/v) afforded the desired product as a yellow solid (62 mg, 78%). M.p.: 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 6.64 (d, J = 4.0 Hz, 1H), 6.95 (s, 1H), 7.11 (d, J = 4.0 Hz, 1H), 7.24-7.28 (m, 2H), 7.42 (t, J = 4.8 Hz, 1H), 7.59-7.61 (m, 1H), 7.67-7.69 (m, 1H), 8.84 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 111.9, 119.6, 121.1, 122.0, 123.2, 123.9, 124.7, 124.9, 132.7, 134.2, 135.1, 139.7, 140.0, 158.8(6), 158.9, 187.1 ppm. HRMS (ESI^+): calcd for $C_{18}H_{14}N_3OS$ $[M+H]^+$ 320.0858, found 320.0854.



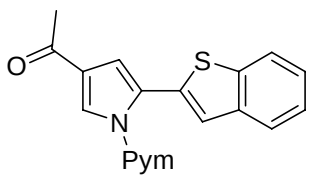
Methyl 5-(Benzothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-pyrrole-2-carboxylate (4k)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column chromatography (petroleum ether/acetone = 8/1-6/1, v/v) afforded the desired product as a yellow solid (62 mg, 74%). M.p.: 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3H), 6.62 (d, J = 4.0 Hz, 1H), 6.94 (s, 1H), 7.12 (d, J = 4.0 Hz, 1H), 7.24-7.30 (m, 2H), 7.43 (t, J = 4.8 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H)), 8.87 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.6, 111.8, 118.3, 121.2, 122.0, 122.8, 123.8, 124.6, 124.7, 126.0, 133.1, 134.1, 139.7, 139.9, 158.4, 158.9, 161.0 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{14}N_3O_2S$ $[M+H]^+$ 336.0807, found 336.0880.



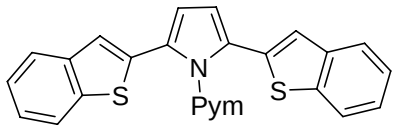
5-(Benzothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-pyrrole-2-carbonitrile (4l)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column chromatography (petroleum ether/acetone = 10/1-8/1, v/v) afforded the desired product as a yellow solid (39 mg, 51%). M.p.: 178-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.60 (d, J = 4.0 Hz, 1H), 7.08 (d, J = 4.0 Hz, 1H), 7.12 (s, 1H), 7.29-7.34 (m, 2H), 7.35 (t, J = 4.4 Hz, 1H), 7.68-7.70 (m, 1H), 7.72 (d, J = 8.0 Hz, 1H), 8.79 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 100.1, 102.9, 113.6, 114.1, 120.7, 122.2, 123.0, 124.0, 124.1, 124.8, 125.0, 127.6, 132.9, 133.0, 139.6, 159.1 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{11}N_4S$ $[M+H]^+$ 303.0704, found 303.0708.



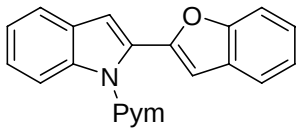
1-(5-(Benzothiophen-2-yl)-1-(pyrimidin-2-yl)-1*H*-pyrrol-3-yl)ethanone (4m)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column chromatography (petroleum ether/acetone = 4/1-2/1, v/v) afforded the desired product as a yellow solid (45 mg, 56%). M.p.: 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 6.90 (d, J = 1.6 Hz, 1H), 7.12-7.16 (m, 1H), 7.19 (s, 1H), 7.21-7.31 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 8.20 (d, J = 2.0 Hz, 1H), 8.57 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.3, 115.2, 119.3, 122.1, 123.7, 123.8, 124.4, 124.5, 127.2, 128.5, 128.7, 135.0, 139.6, 140.6, 156.7, 158.7, 193.4 ppm. HRMS (ESI^+): calcd for $C_{18}H_{14}N_3OS$ $[M+H]^+$ 320.0858, found 320.0854.



2-(2,5-Di(benzothiophen-2-yl)-1*H*-pyrrol-1-yl)pyrimidine (4n)

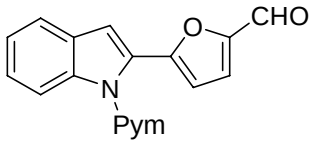
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1, v/v) afforded the desired product as a yellow solid (54 mg, 53%). M.p: 202-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.69 (s, 2H), 6.88 (s, 2H), 7.22-7.29 (m, 4H), 7.36 (t, J = 4.8 Hz, 1H), 7.59 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 7.6 Hz, 2H), 8.81 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.8, 121.0, 121.4, 122.0, 123.5, 124.2, 124.5, 130.8, 134.5, 139.7, 140.1, 158.2, 159.1 ppm. HRMS (ESI^+): calcd for $C_{24}H_{16}N_3S_2$ $[M+H]^+$ 410.0786, found 410.0782.



2-(Benzofuran-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (4o)

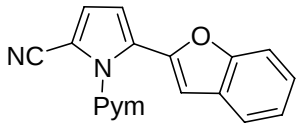
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column

chromatography (petroleum ether/EtOAc = 10/1-8/1, v/v) afforded the desired product as a red solid (53 mg, 68%). M.p.: 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 1H), 7.13 (s, 1H), 7.17-7.18 (m, 1H), 7.22-7.24 (m, 3H), 7.32-7.36 (m, 2H), 7.54-7.58 (m, 1H), 7.68 (d, J = 7.6 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 104.6, 110.2, 111.1, 113.5, 118.0, 121.1, 121.3, 122.6, 123.0, 124.3, 124.7, 129.0, 129.0(2), 130.0, 138.3, 149.9, 155.0, 158.0, 158.4 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{14}N_3O$ $[M+H]^+$ 312.1137, found 312.1139.



5-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)furan-2-carbaldehyde (4p)

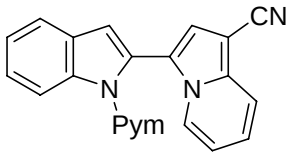
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 5/1-2/1, v/v) afforded the desired product as a yellow solid (46 mg, 64%). M.p.: 116-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.52 (d, J = 3.6 Hz, 1H), 7.09 (s, 1H), 7.13 (t, J = 4.8 Hz, 1H), 7.18-7.22 (m, 2H), 7.27 (t, J = 7.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.66 (d, J = 4.8 Hz, 2H), 9.45 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 103.9, 108.2, 112.6, 118.2, 120.6, 121.5, 122.2, 123.6, 124.5, 129.1, 134.1, 138.0, 158.0, 158.5, 167.2 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{11}N_3NaO_2$ $[M+Na]^+$ 312.0749, found 312.0753.



5-(Benzofuran-2-yl)-1-(pyrimidin-2-yl)-1*H*-pyrrole-2-carbonitrile (4q)

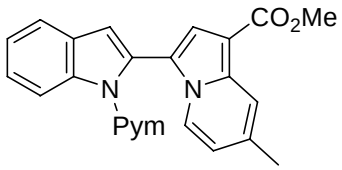
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column

chromatography (petroleum ether/acetone = 8/1-6/1, v/v) afforded the desired product as a yellow solid (43 mg, 61%). M.p.: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (s, 1H), 6.74 (d, J = 4.0 Hz, 1H), 7.08 (d, J = 4.0 Hz, 1H), 7.19-7.27 (m, 3H), 7.35 (t, J = 4.8 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 8.78 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 105.6, 107.1, 111.2, 113.4, 113.8, 120.5, 121.4, 123.2, 123.3, 125.0, 128.4, 129.4, 147.4, 154.8, 156.0, 159.0 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{11}N_4O$ $[M+H]^+$ 287.0933, found 287.0929.



3-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)indolizine-1-carbonitrile (4r)

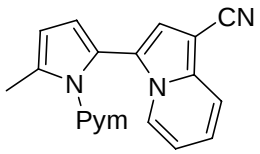
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 6/1-4/1, v/v) afforded the desired product as a yellow solid (69 mg, 82%). M.p.: 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62-6.66 (m, 1H), 6.91 (s, 1H), 6.97-7.01 (m, 2H), 7.07-7.10 (m, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.67-7.71 (m, 2H), 7.85 (d, J = 7.2 Hz, 1H), 8.42 (d, J = 4.8 Hz, 2H), 8.48 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 81.6, 112.6, 112.8, 114.9, 117.2, 117.4, 117.7, 118.4, 119.6, 121.1, 122.6, 122.8, 124.9, 125.4, 127.7, 128.9, 137.3, 138.1, 157.5, 158.2 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{14}N_5$ $[M+H]^+$ 336.1249, found 336.1248.



Methyl 7-Methyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)indolizine-1-carboxylate (4s)

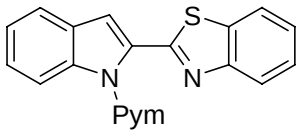
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column

chromatography (petroleum ether/EtOAc = 10/1-6/1, v/v) afforded the desired product as a yellow solid (57 mg, 60%). M.p.: 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 3.88 (s, 3H), 6.42-6.44 (m, 1H), 6.88 (s, 1H), 6.95 (t, J = 4.8 Hz, 1H), 7.18 (s, 1H), 7.26-7.31 (m, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.68-7.73 (m, 2H), 8.03 (s, 1H), 8.43-8.45 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 50.9, 102.0, 111.9, 114.6, 115.0, 117.3, 117.8, 118.1, 118.5, 121.0, 122.6, 124.5, 129.2, 129.3, 133.7, 136.9, 137.3, 157.7, 158.2, 165.7 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{19}N_4O_2$ $[M+H]^+$ 383.1508, found 383.1512.



3-(5-Methyl-1-(pyrimidin-2-yl)-1*H*-pyrrol-2-yl)indolizine-1-carbonitrile (4t)

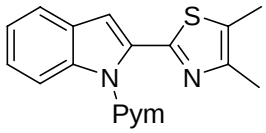
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 8/1-6/1, v/v) afforded the desired product as a yellow solid (46 mg, 62%). M.p.: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3H), 6.17 (d, J = 3.2 Hz, 1H), 6.41 (d, J = 3.2 Hz, 1H), 6.64 (t, J = 6.8 Hz, 1H), 6.74 (s, 1H), 7.02-7.07 (m, 2H), 7.58 (d, J = 8.8 Hz, 1H), 7.98 (d, J = 7.2 Hz, 1H), 8.46 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6, 110.0, 112.5, 114.8, 115.7, 117.4, 117.6, 118.3, 118.7, 119.7, 121.2, 122.4, 125.4, 133.2, 137.8, 157.5, 158.3 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{13}N_5Na$ $[M+Na]^+$ 322.1069, found 322.1068.



2-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)benzothiazole (6a)

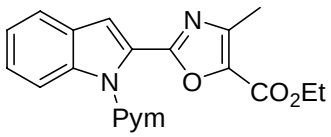
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column

chromatography (petroleum ether/EtOAc = 8/1-6/1, v/v) afforded the desired product as a yellow solid (56 mg, 68%). M.p.: 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, J = 4.6 Hz, 1H), 7.25-7.29 (m, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.39-7.44 (m, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 4.8 Hz, 2H) ppm.. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.6, 113.4, 118.3, 121.5, 121.8, 122.7, 123.4, 125.2, 125.6, 126.2, 128.6, 132.8, 135.5, 139.0, 153.7, 157.9, 158.4, 160.3 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{13}N_4S$ $[M+H]^+$ 329.0861, found 329.0862.



2-(4,5-Dimethylthiazol-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (6b)

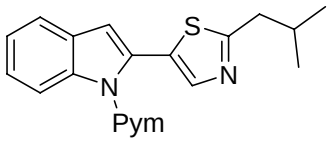
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 8/1-6/1, v/v) afforded the desired product as a yellow solid (50 mg, 65%). M.p.: 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 2.35 (s, 3H), 7.07 (s, 1H), 7.17 (t, J = 4.8 Hz, 1H), 7.21-7.26 (m, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 14.9, 110.1, 113.1, 118.2, 121.4, 122.4, 124.7, 127.0, 128.7, 132.9, 138.5, 148.8, 155.4, 158.0, 158.3 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{15}N_4S$ $[M+H]^+$ 307.1017, found 307.1014.



Ethyl 4-Methyl-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)oxazole-5-carboxylate (6c)

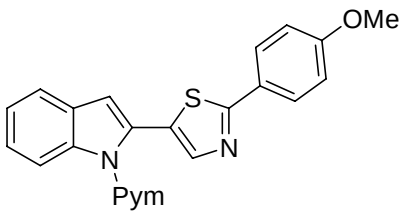
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 8/1-6/1, v/v) afforded the desired product

as a yellow solid (68 mg, 78%). M.p.: 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.2 Hz, 3H), 2.51 (s, 3H), 4.29 (q, J = 7.2 Hz, 2H), 7.17 (t, J = 4.8 Hz, 1H), 7.28-7.30 (t, J = 7.6 Hz, 1H), 7.38-7.42 (m, 2H), 7.70 (d, J = 7.6 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.71 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.4, 61.0, 113.6, 114.0, 118.1, 122.1, 122.9, 126.0, 126.1, 128.4, 137.3, 138.6, 146.9, 157.3, 157.6, 158.2, 158.8 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{17}N_4O_3$ $[M+H]^+$ 349.1301, found 349.1295.



2-(2-Isobutylthiazol-5-yl)-1-(pyrimidin-2-yl)-1*H*-indole (6d)

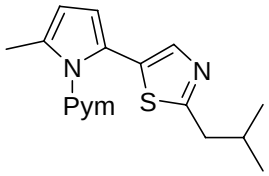
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 8/1-6/1, v/v) afforded the desired product as yellow oil (54 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, J = 6.8 Hz, 6H), 1.99-2.13 (m, 1H), 2.84 (d, J = 7.2 Hz, 2H), 6.88 (s, 1H), 7.17 (t, J = 4.8 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.28-7.33 (m, 1H), 7.56 (s, 1H), 7.62 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.73 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.4, 29.9, 42.5, 110.2, 113.2, 118.2, 120.9, 122.5, 124.3, 128.9, 129.8, 130.2, 138.1, 141.0, 157.9, 158.4, 171.0 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{19}N_4S$ $[M+H]^+$ 335.1330, found 335.1327.



2-(4-Methoxyphenyl)-5-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)thiazole (6e)

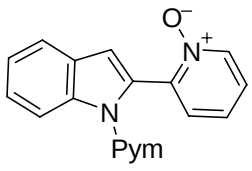
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column

chromatography (petroleum ether/EtOAc = 8/1-6/1, v/v) afforded the desired product as a yellow solid (65 mg, 68%). M.p.: 134- 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3H), 6.96-6.98 (m, 3H), 7.20 (t, J = 4.8 Hz, 1H), 7.28-7.30 (m, 1H), 7.31-7.36 (m, 1H), 7.60-7.68 (m, 2H), 7.87 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 7.6 Hz, 1H), 8.78 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 110.4, 113.2, 118.2, 120.9, 122.6, 124.4, 126.6, 128.0, 128.1, 128.9, 129.6, 130.1, 138.2, 142.2, 157.6, 158.5, 161.3, 168.3 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{17}N_4OS$ $[M+H]^+$ 385.1123, found 385.1121.



2-(2-(2-Isobutylthiazol-5-yl)-5-methyl-1*H*-pyrrol-1-yl)pyrimidine (6f)

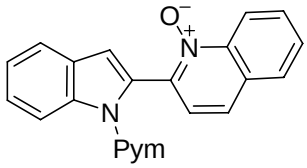
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 8/1-6/1, v/v) afforded the desired product as yellow oil (47 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (d, J = 6.8 Hz, 6H), 1.99-2.06 (m, 1H), 2.31 (s, 3H), 2.74 (d, J = 7.2 Hz, 2H), 6.06 (d, J = 3.2 Hz, 1H), 6.36 (d, J = 3.2 Hz, 1H), 7.19 (s, 1H), 7.25-7.27 (m, 1H), 8.74 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 22.4, 29.8, 42.4, 109.5, 112.8, 119.4, 123.7, 130.0, 133.0, 139.1, 157.8, 158.6, 169.2 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{18}N_4NaS$ $[M+Na]^+$ 321.1150, found 321.1147.



2-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)-pyridine *N*-oxide (6g)

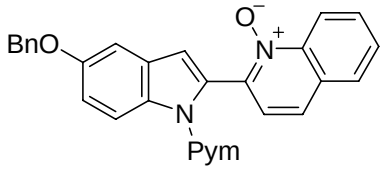
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column

chromatography (CH_2Cl_2/Acetone/MeOH = 30/1/1, v/v) afforded the desired product as a yellow solid (38 mg, 53%). M.p.: 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (s, 1H), 7.06 (t, J = 4.8 Hz, 1H), 7.24-7.31 (m, 2H), 7.38-7.41 (m, 2H), 7.67 (d, J = 7.6 Hz, 2H), 8.17 (d, J = 4.8 Hz, 1H), 8.55-8.57 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.6, 114.9, 117.5, 121.3, 122.3, 125.0, 125.2, 126.3, 127.4, 128.7, 131.2, 137.3, 139.5, 145.5, 157.9, 158.0 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{13}N_4O$ $[M+H]^+$ 289.1089, found 289.1093.



2-(1-(Pyrimidin-2-yl)-indol-yl)-quinoline *N*-oxide (6h)

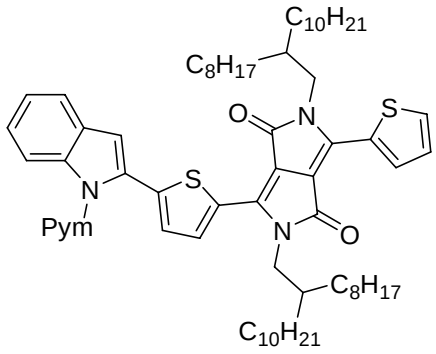
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column chromatography (CH_2Cl_2/EtOAc = 4/1, v/v) afforded the desired product as a yellow solid (46 mg, 54%). M.p.: 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98-7.01 (m, 2H), 7.25-7.28 (m, 1H), 7.38 (t, J = 4.0 Hz, 1H), 7.61-7.63 (m, 1H), 7.66-7.70 (m, 3H), 7.76 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.47 (d, J = 4.0 Hz, 2H), 8.52-8.58 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.5, 114.6, 117.2, 119.7, 121.1, 122.0, 123.3, 124.8, 124.9, 128.0, 128.2, 128.7, 129.7, 130.1, 132.3, 137.2, 140.9, 141.6, 157.7, 157.8 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{15}N_4O$ $[M+H]^+$ 339.1246, found 339.1240.



2-(1-(Pyrimidin-2-yl)-5-(benzyloxy)-indol-yl)-quinoline *N*-oxide (6i)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 36 h. Purification via silica gel column

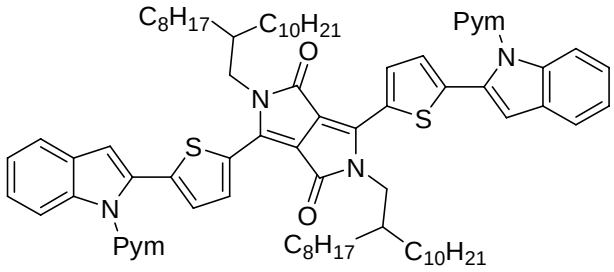
chromatography (CH_2Cl_2/EtOAc = 4/1, v/v) afforded the desired product as a yellow solid (58 mg, 52%). M.p.: 209-211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.15 (s, 2H), 6.96 (t, *J* = 4.8 Hz, 2H), 7.10 (dd, *J* = 9.2 Hz, 2.4Hz, 1H), 7.19 (d, *J* = 2.0 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.61-7.66 (m, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 4.8 Hz, 2H), 8.49 (d, *J* = 9.2 Hz, 1H), 8.53 (d, *J* = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.7, 104.5, 111.7, 115.5, 116.0, 117.1, 119.9, 123.5, 125.4, 127.7, 128.0, 128.1, 128.4, 128.7, 129.5, 129.8, 130.4, 132.5, 132.6, 137.5, 141.5, 141.7, 154.8, 157.8(6), 157.9 ppm. HRMS (ESI$^+$): calcd for $C_{28}H_{21}N_4O_2$ $[M+H]^+$ 445.1665, found 445.1656.



2,5-Bis(2-octyldodecyl)-3-(5-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (7a)

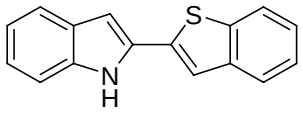
Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 24 h. Purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 1/1, v/v) afforded the desired product as purple oil (160 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83-0.88 (m, 12H), 1.22-1.29 (m, 66H), 3.97 (d, *J* = 7.6 Hz, 2H), 4.01 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 4.0 Hz, 1H), 7.01 (s, 1H), 7.21-7.27 (m, 3H), 7.30-7.35 (m, 1H), 7.60 (d, *J* = 4.8 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 4.8 Hz, 2H), 8.85 (d, *J* = 3.2 Hz, 1H), 8.97 (d, *J* = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.8, 22.8(3), 29.4, 29.4(6), 29.5, 29.6, 29.7, 29.7(8), 29.7(9), 29.8, 30.2, 30.2(5), 31.4, 32.0, 32.1, 37.9, 38.0, 46.4, 46.5, 108.0, 108.3, 110.6, 113.1, 118.4, 121.2, 122.8, 124.9, 127.7, 128.5, 129.0, 130.1, 130.4, 132.3, 135.2, 136.5, 138.8, 139.9, 140.6,

141.3, 157.8, 158.2, 158.6, 161.8, 161.9 ppm. HRMS (ESI^+): calcd for $C_{66}H_{96}N_5O_2S_2$ $[M+H]^+$ 1054.7005, found 1054.7012.



2,5-Bis(2-octyldodecyl)-3,6-bis(5-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)thiophen-2-yl) pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (7b)

Following the general procedure, the reaction mixture was stirred for 10 min at room temperature, and then heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 1/1, v/v) afforded the desired product as blue oil (171 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83-0.88 (m, 12H), 1.23-1.26 (m, 66H), 3.98 (d, J = 7.6 Hz, 4H), 6.95 (d, J = 4.4 Hz, 2H), 7.01 (s, 2H), 7.21-7.28 (m, 4H), 7.31 (t, J = 7.6 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 8.78 (d, J = 4.8 Hz, 4H), 8.96 (d, J = 4.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.8, 22.83, 26.4, 29.4(6), 29.5, 29.7, 29.8, 29.8(3), 30.2(6), 30.2(8), 31.3, 31.4, 32.0, 32.1, 38.0, 46.5, 108.2, 110.6, 113.0, 118.4, 121.2, 122.8, 127.7, 132.3, 136.3, 138.8, 140.0, 141.1, 157.8, 158.6, 161.8 ppm. HRMS (ESI^+): calcd for $C_{78}H_{103}N_8O_2S_2$ $[M+H]^+$ 1247.7645, found 1247.7648.



2-(Benzothiophen-2-yl)-1*H*-indole (3aa)

M.p.: 214-216 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.82 (s, 1H), 7.01 (t, J = 7.4Hz, 1H), 7.14 (t, J = 7.4Hz, 1H), 7.33-7.41 (m, 3H), 7.55 (d, J = 8.0 Hz, 1H), 7.82 (s, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 11.79 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 100.8, 111.3, 119.3, 119.7, 120.3, 122.4, 122.4(3), 123.6, 124.6, 124.9, 128.3, 131.9, 135.4, 137.2, 138.2, 140.1 ppm. HRMS (ESI^+):

calcd for $C_{16}H_{12}NS$ $[M+H]^+$ 250.0690, found 250.0691.

XVII. References

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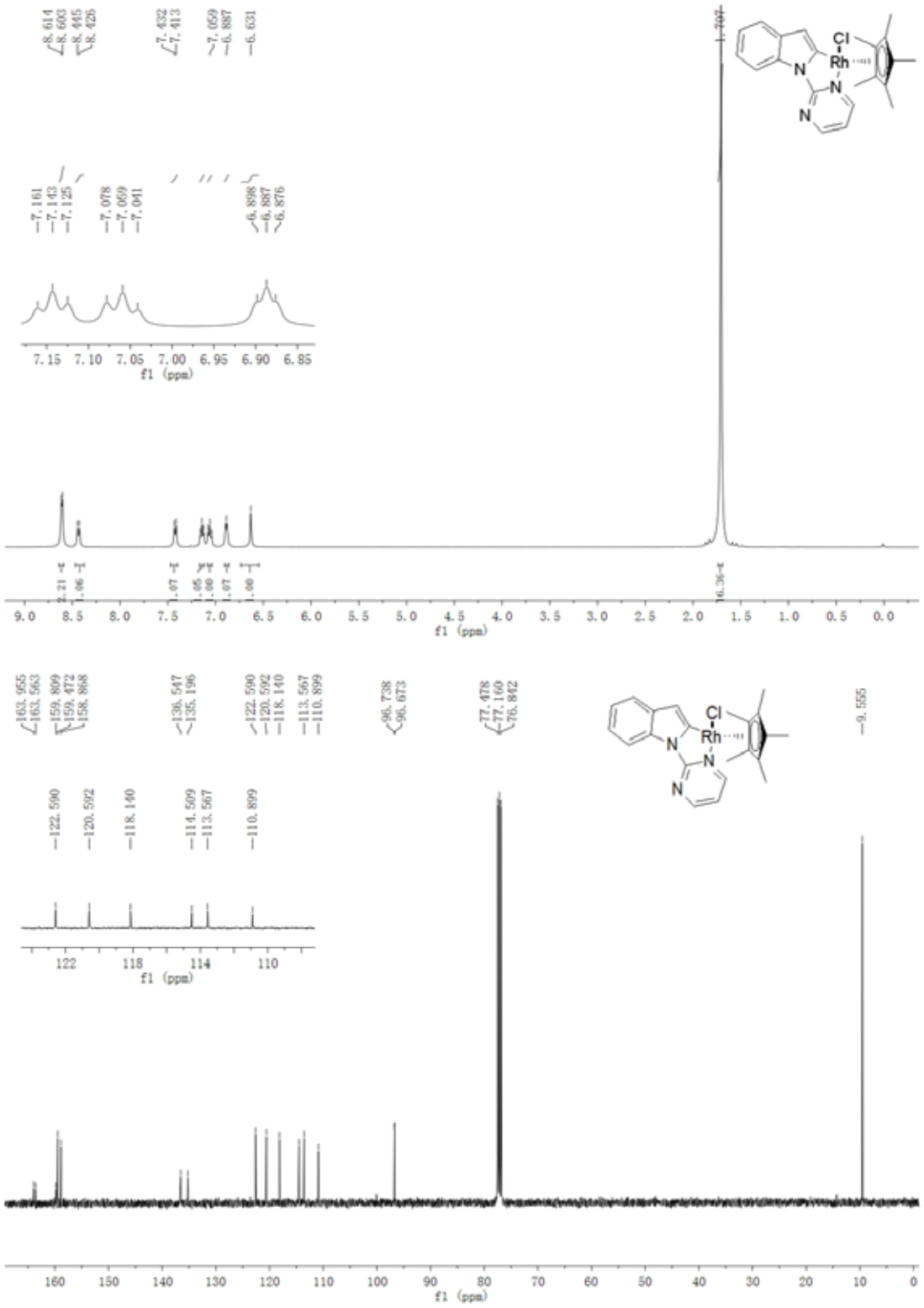
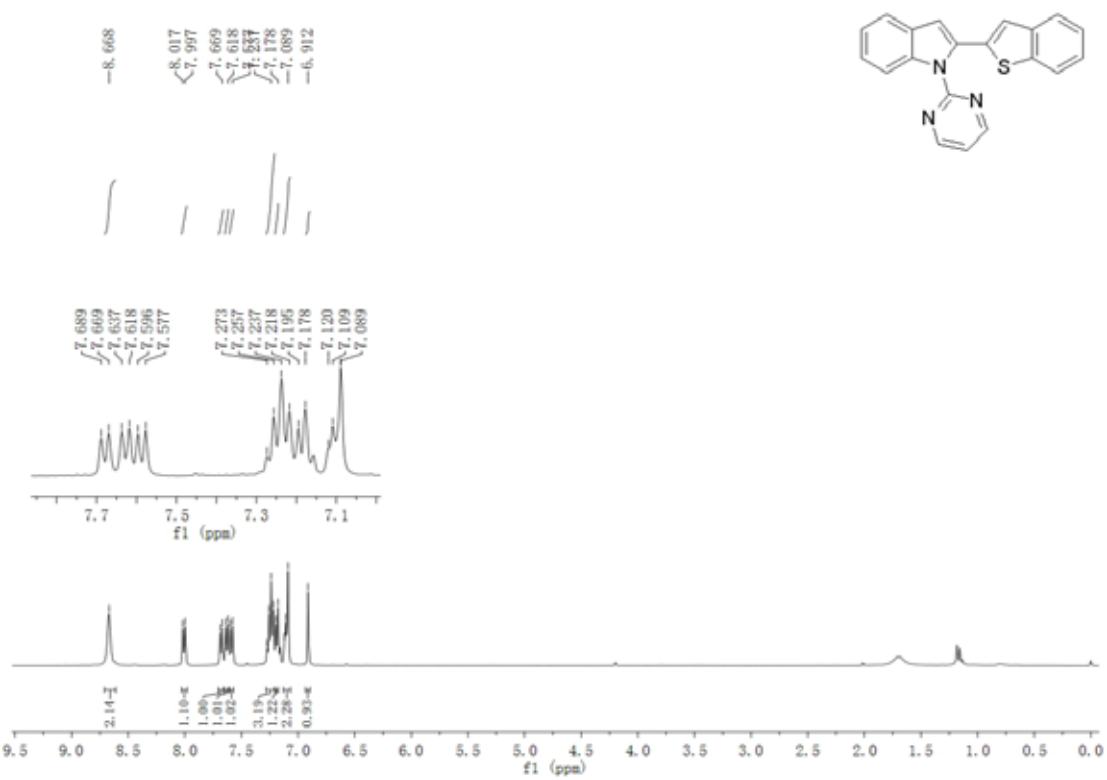
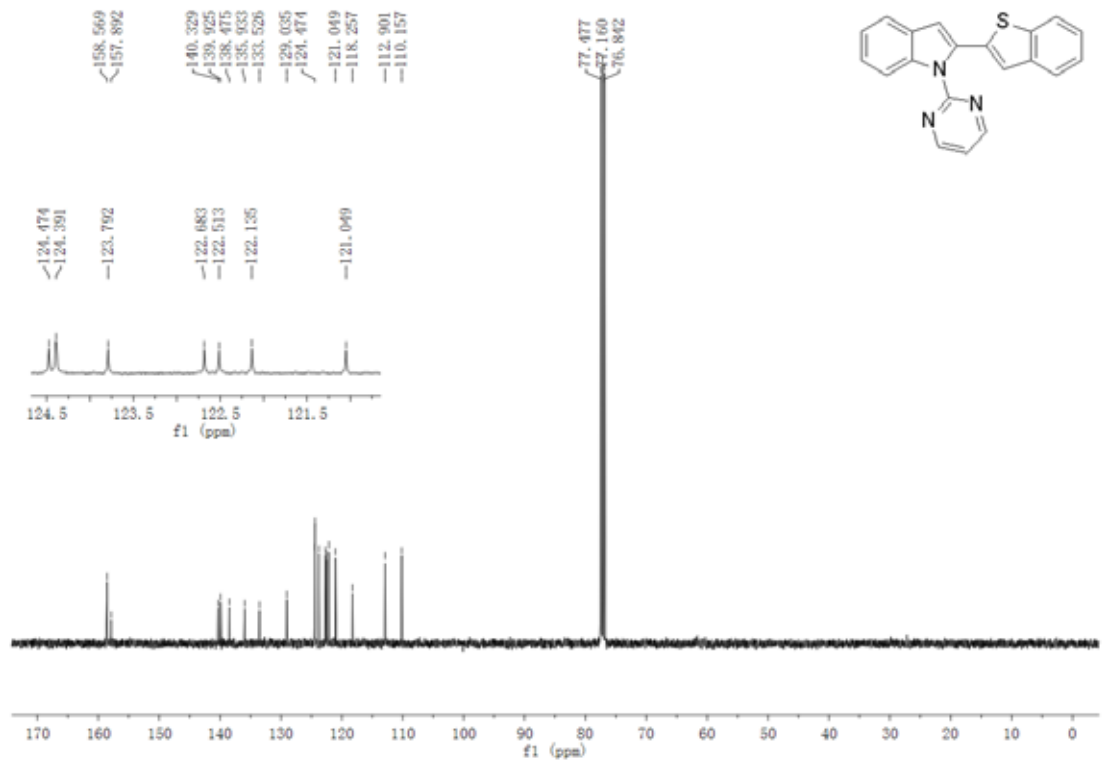
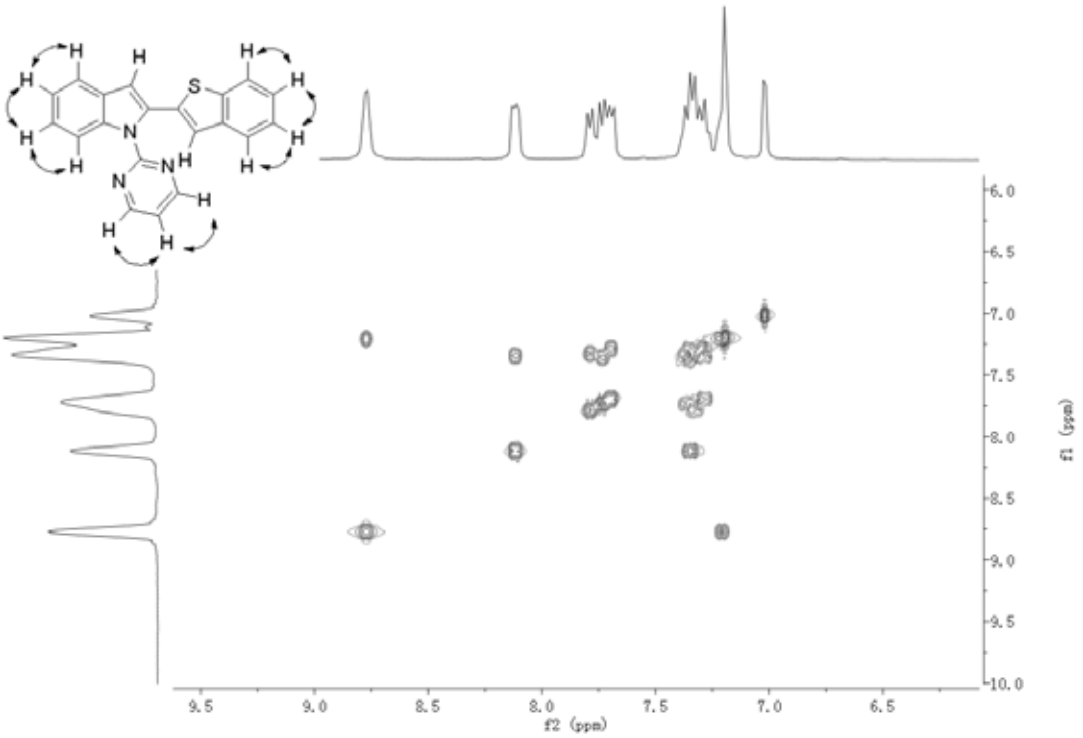
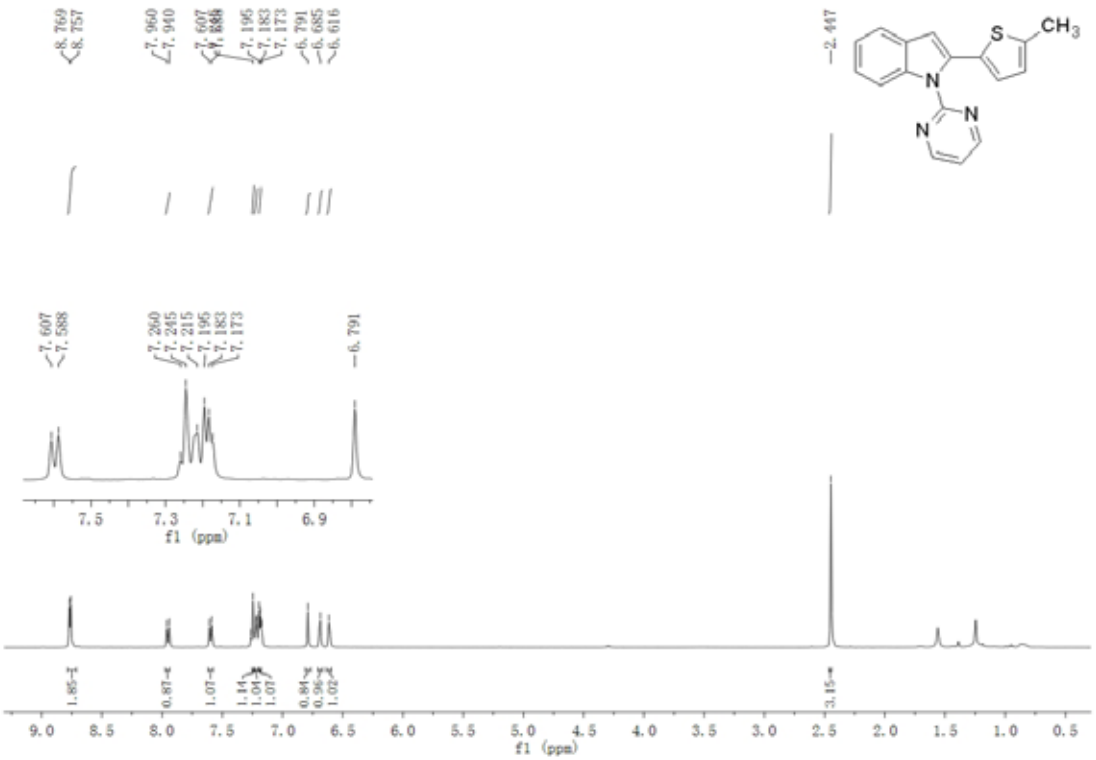
XVIII. Copies of ^{1}H, ^{13}C and ^{1}H-^{1}H COSY NMR spectra

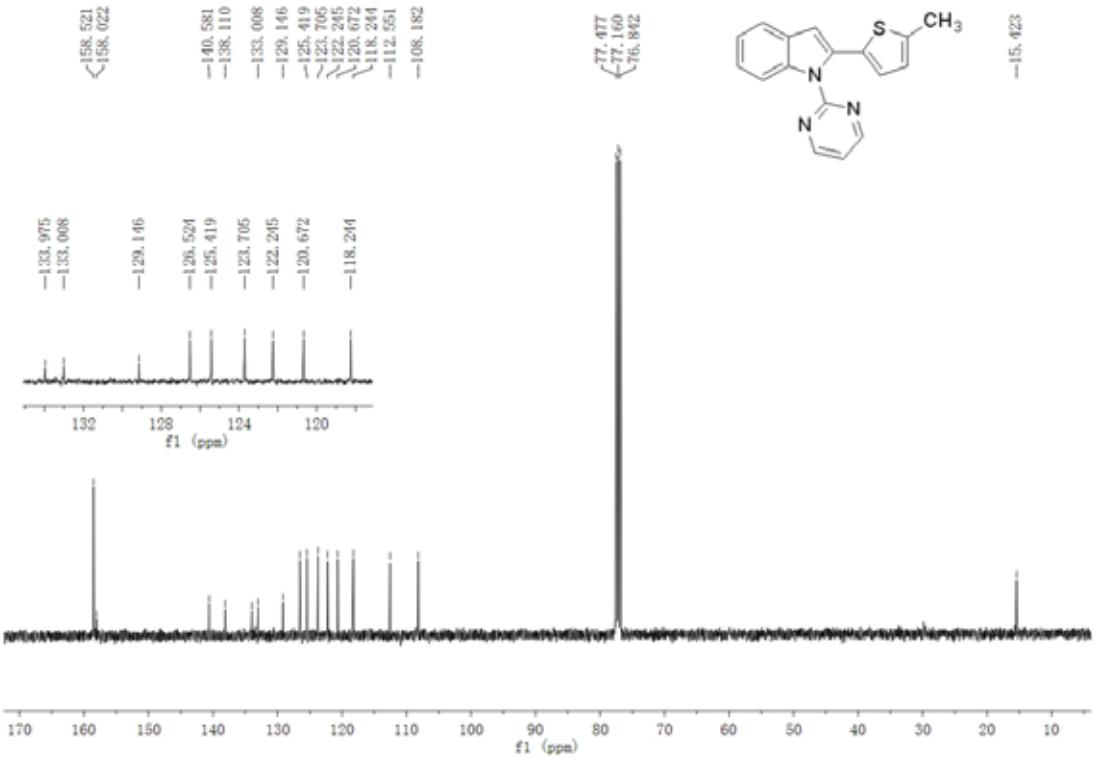


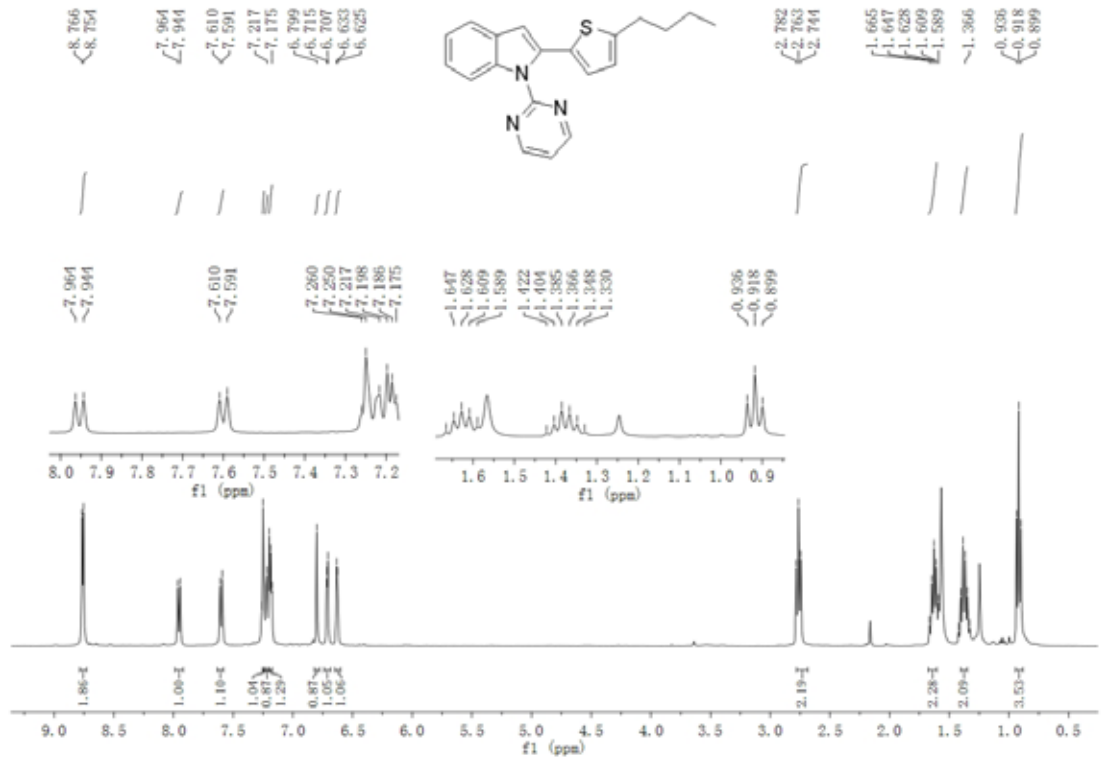








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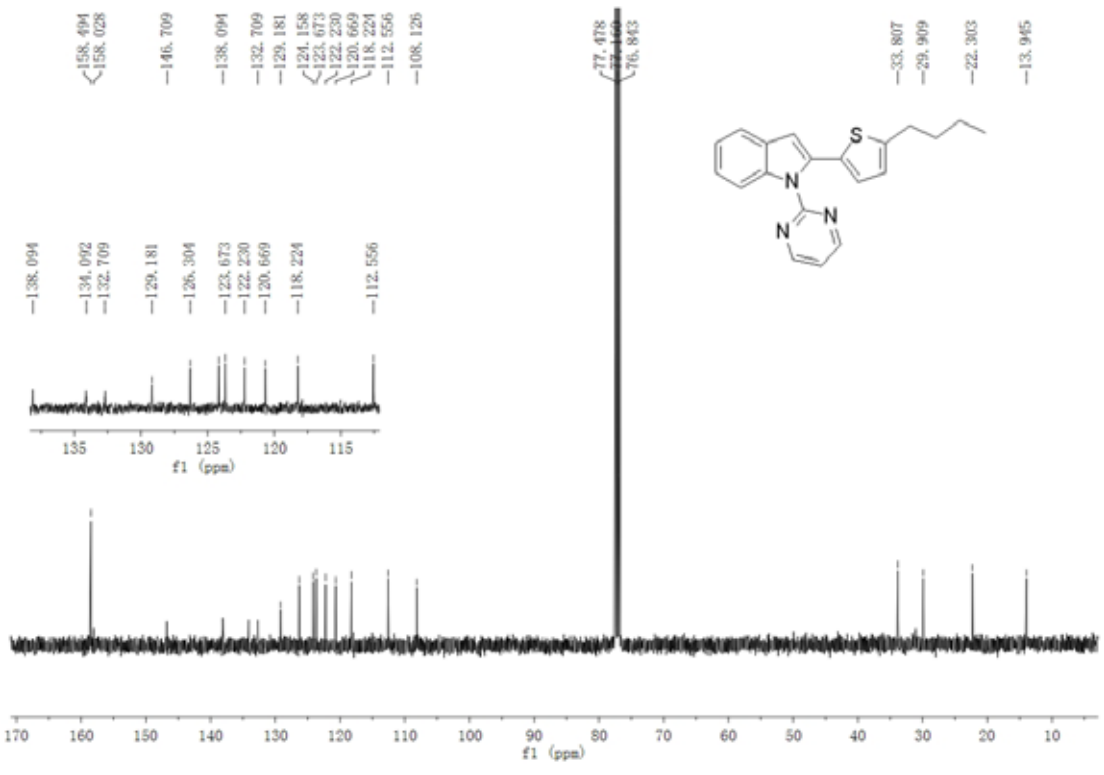
7.964
7.944
7.610
7.591
7.217
7.175
6.799
6.715
6.707
6.633
6.625
2.782
2.763
2.744
1.665
1.647
1.628
1.609
1.589
1.366
0.936
0.918
0.899
S
N
N
N
f1 (ppm)
f1 (ppm)
f1 (ppm)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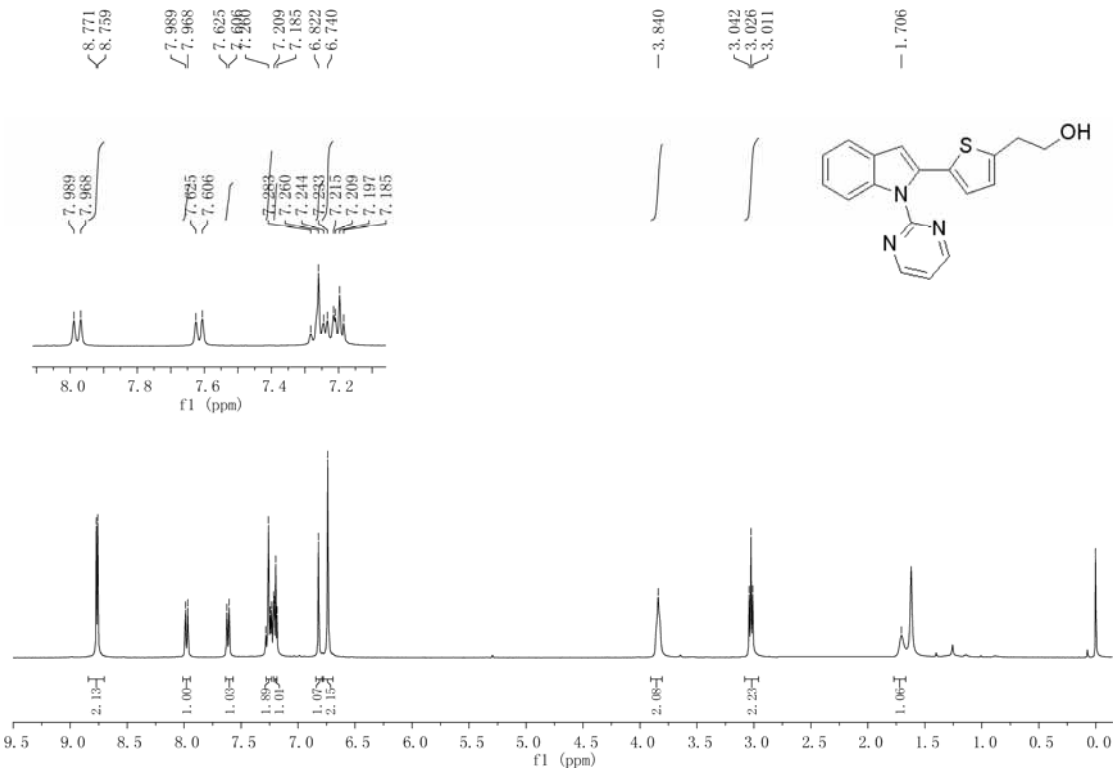
158.028
146.709
138.094
132.709
129.181
124.158
123.673
122.230
120.669
118.224
112.556
108.126
77.478
77.166
76.843
33.807
29.909
22.303
13.945
S
N
N
N
f1 (ppm)
f1 (ppm)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7.989
7.968
7.625
7.606
7.209
7.185
6.822
6.740
3.840
3.042
3.026
3.011
1.706
OH
S
N
N
N
f1 (ppm)
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1.00
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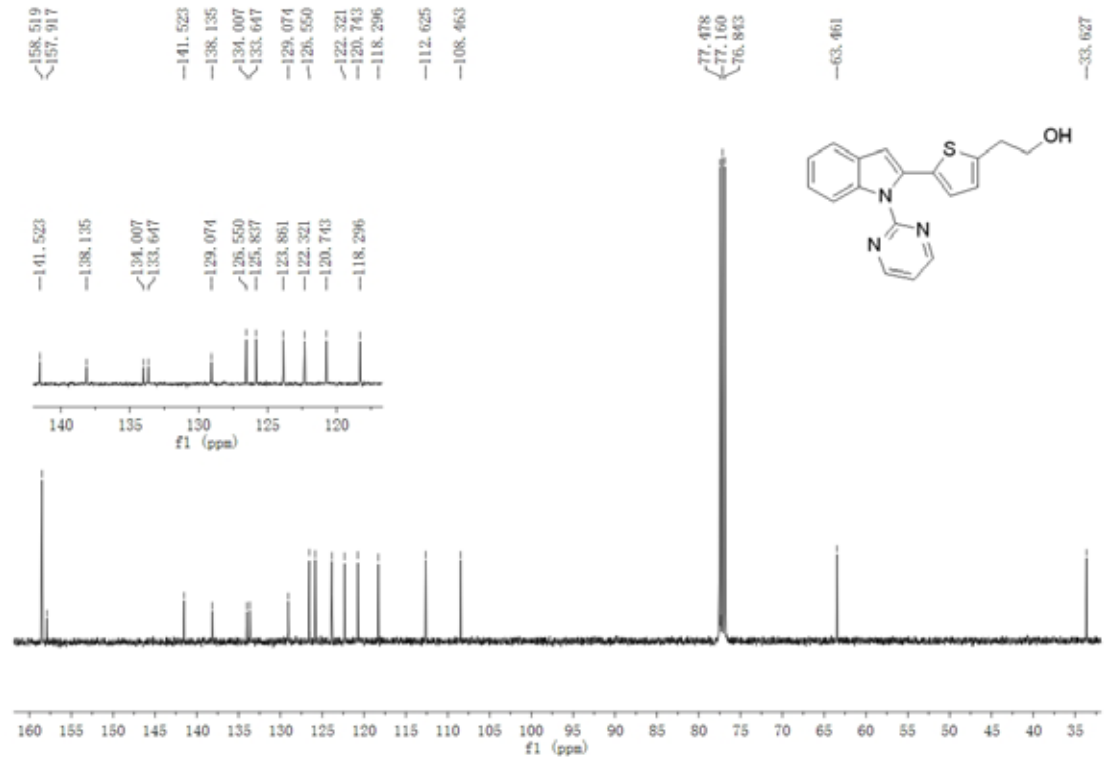
1.89
1.01
1.07
2.15
2.08
2.23
1.06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77.478
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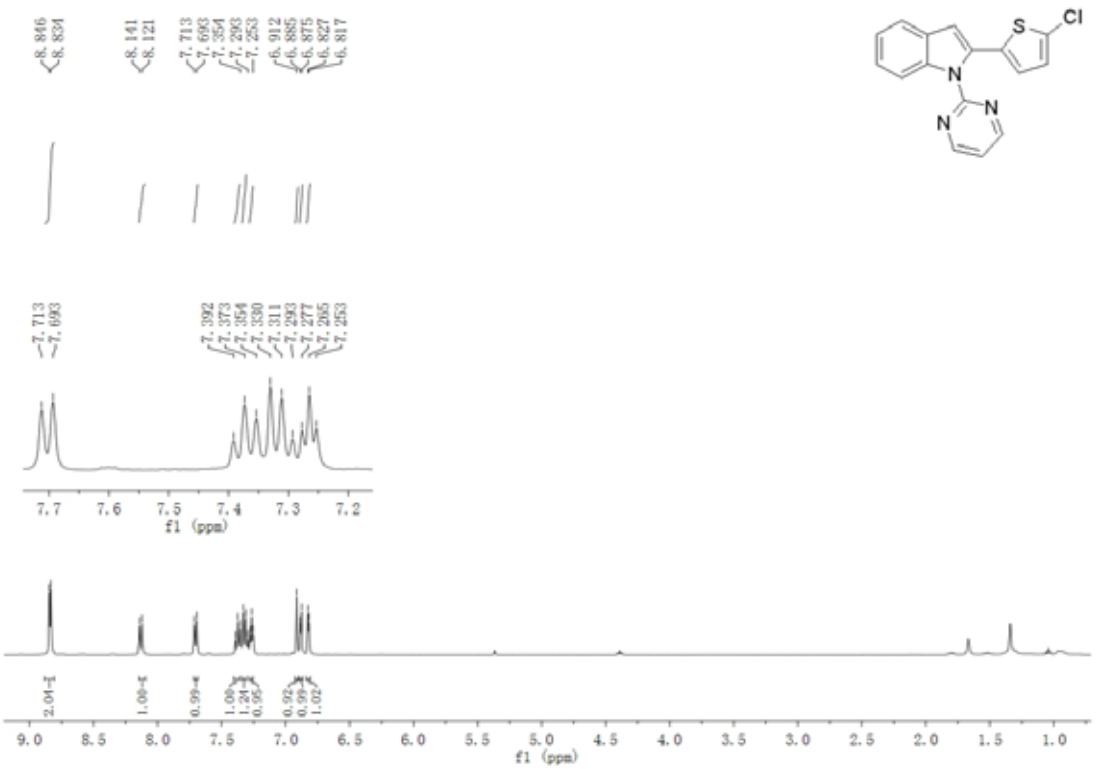
76.843
63.461
33.627
OH
S
N
N
N
f1 (ppm)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6.827
6.817
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Cl
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N
N
7.713
7.693
7.392
7.373
7.354
7.330
7.311
7.293
7.277
7.265
7.253
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
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1.00
0.99
1.08
1.24
0.95
0.92
0.99
1.02
9.0
8.5
8.0
7.5
7.0
6.5
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3.5
3.0
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2.0
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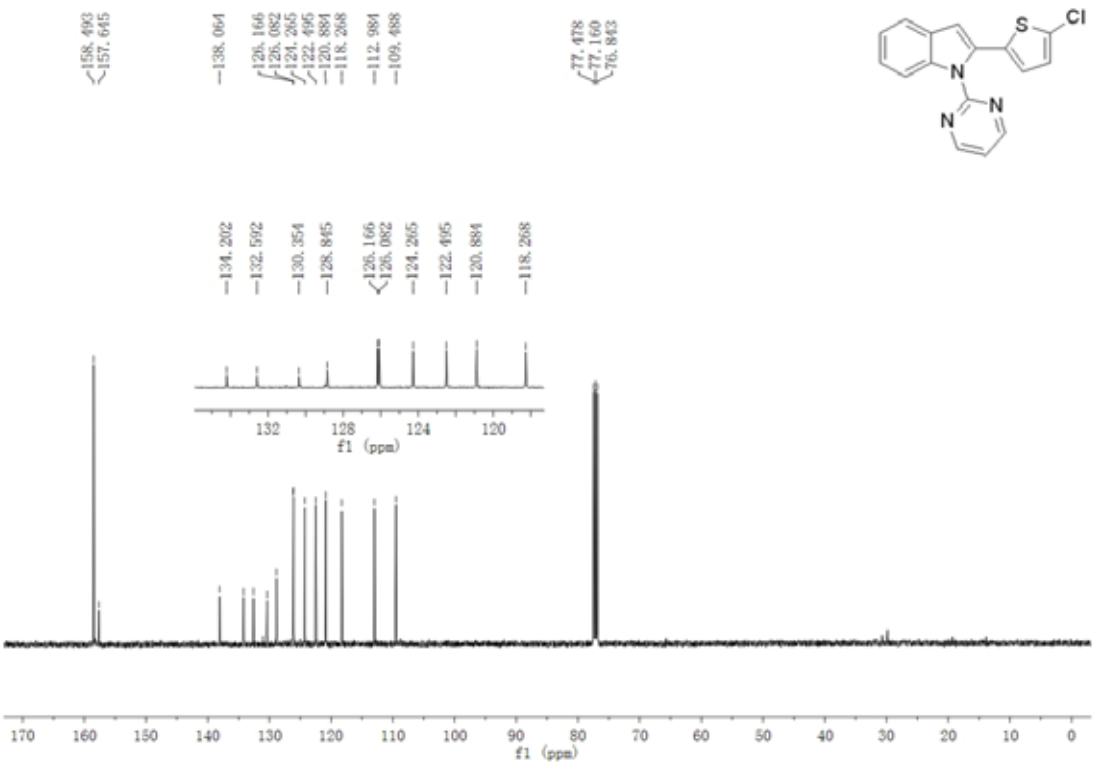
1.0
f1 (ppm)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77.160
76.843
S
Cl
N
N
N
134.202
132.592
130.354
128.845
126.166
126.082
124.265
122.495
120.884
118.268
132
128
124
120
f1 (ppm)
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150
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130
120
110
100
90
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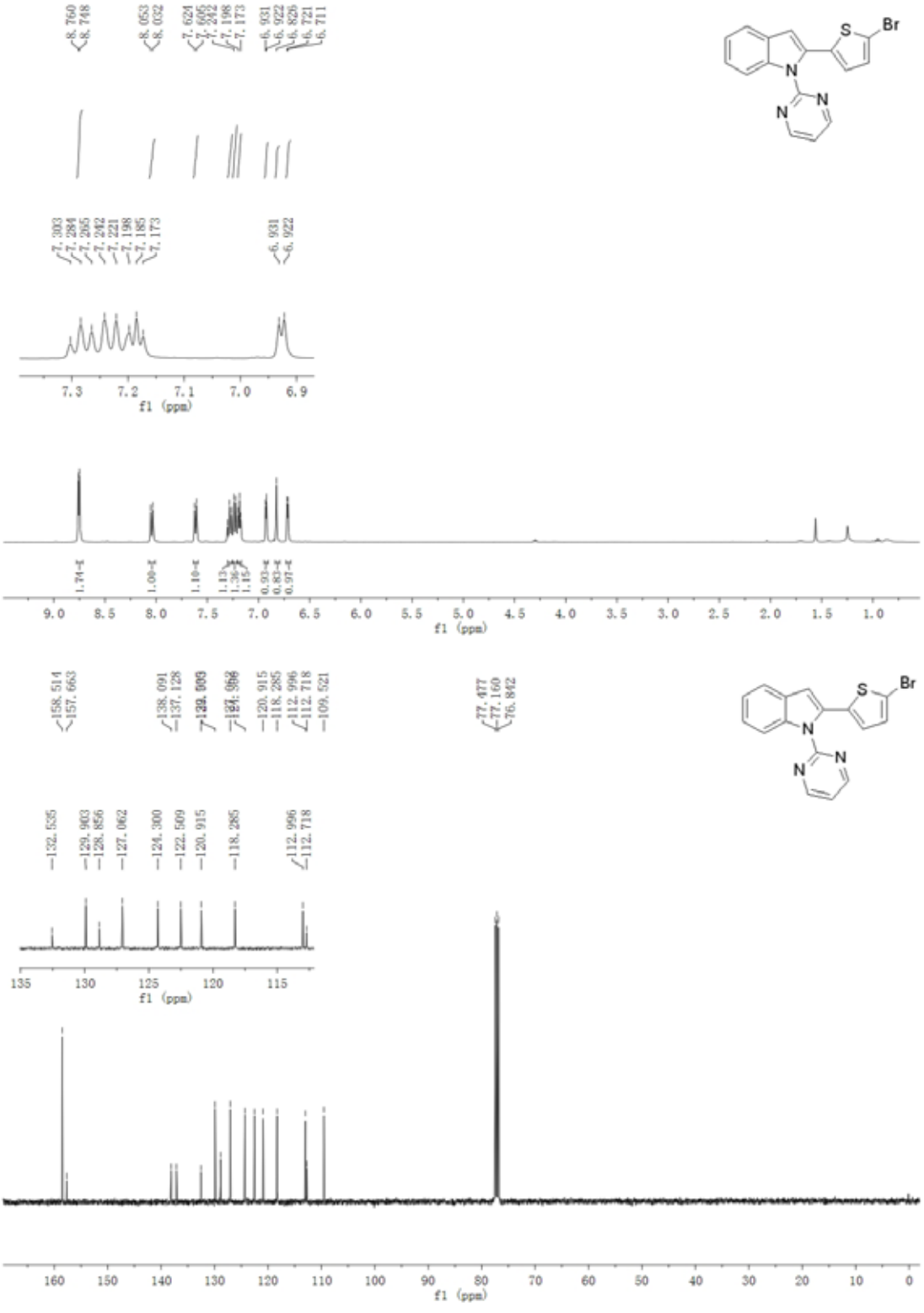
60
50
40
30
20
10
0
f1 (ppm)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6.922
6.825
6.721
6.711
Br
S
N
N
N
7.303
7.284
7.265
7.242
7.221
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7.185
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6.931
6.922
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
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1.00
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1.13
1.36
1.15
0.93
0.83
0.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
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118.285
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S
N
N
N
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112.996
112.718
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130
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120
115
f1 (ppm)
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130
120
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50
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30
20
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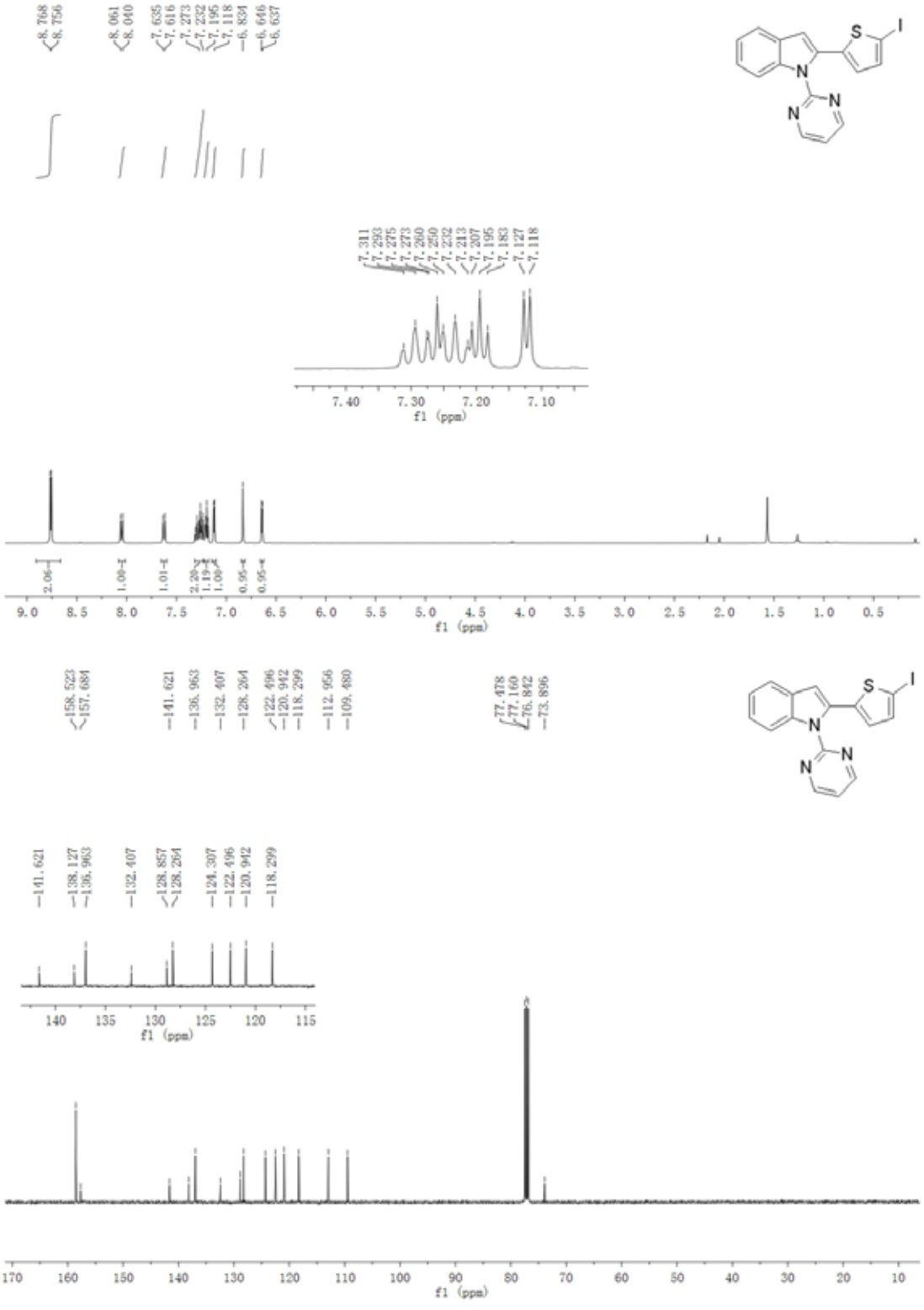
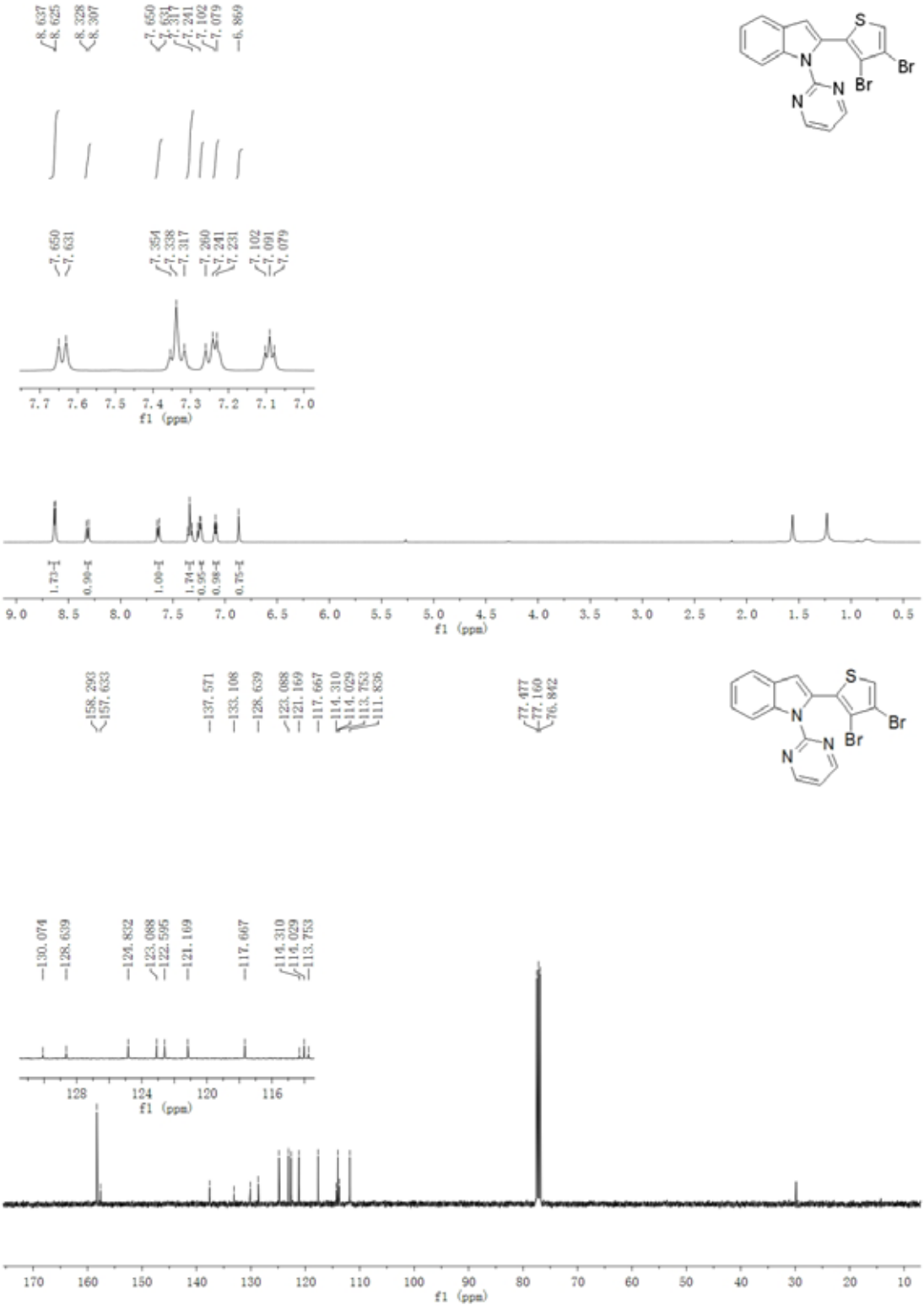
0
f1 (ppm)

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N
Br
N
N
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7.231
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7.091
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Br
N
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Br
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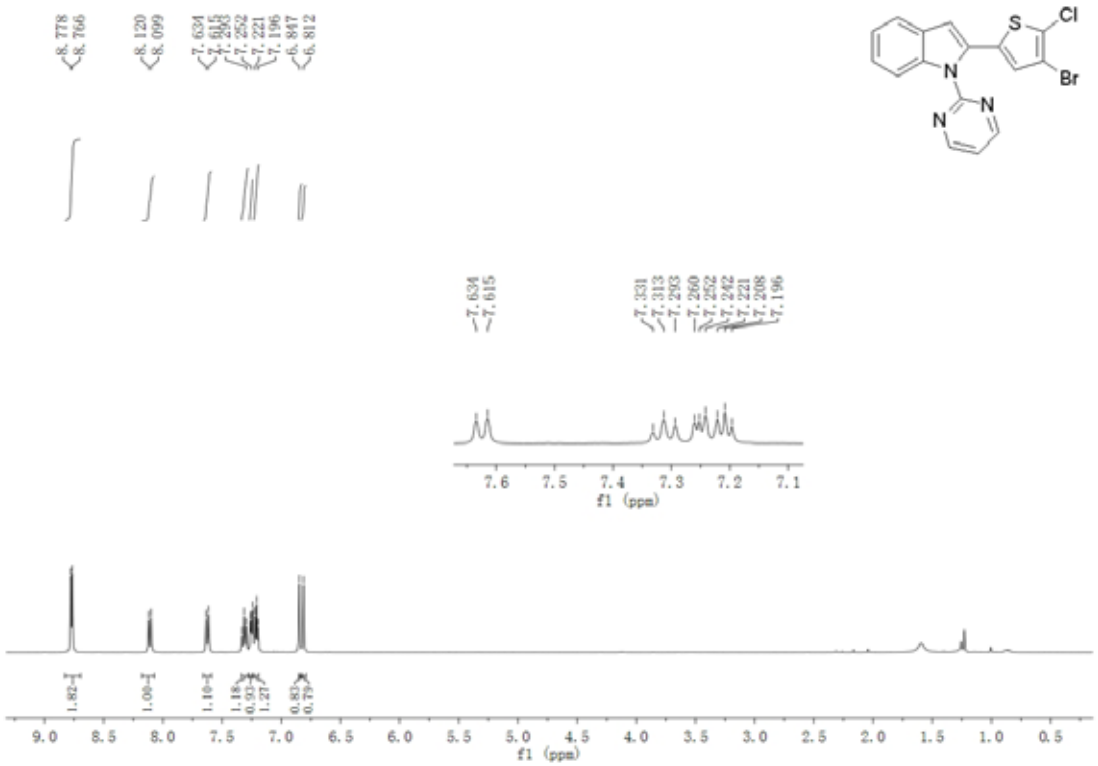
114.029
113.753
f1 (ppm)
f1 (ppm)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Cl
S
Br
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N
N
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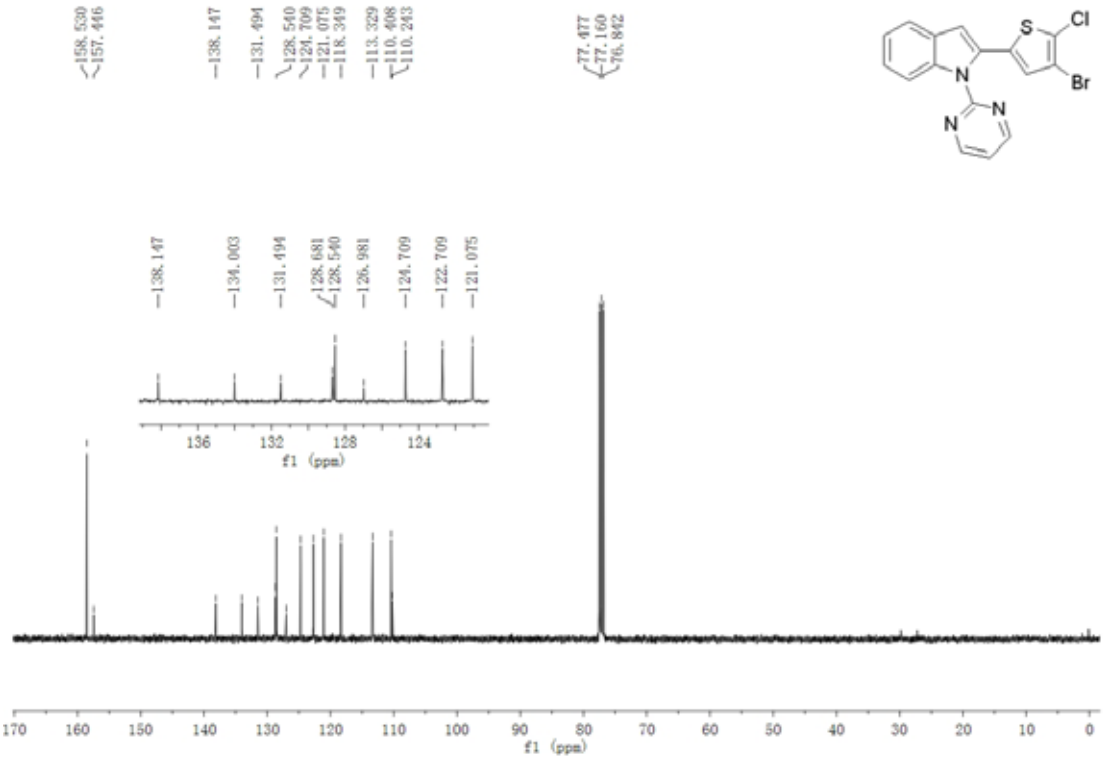
0.79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Cl
S
Br
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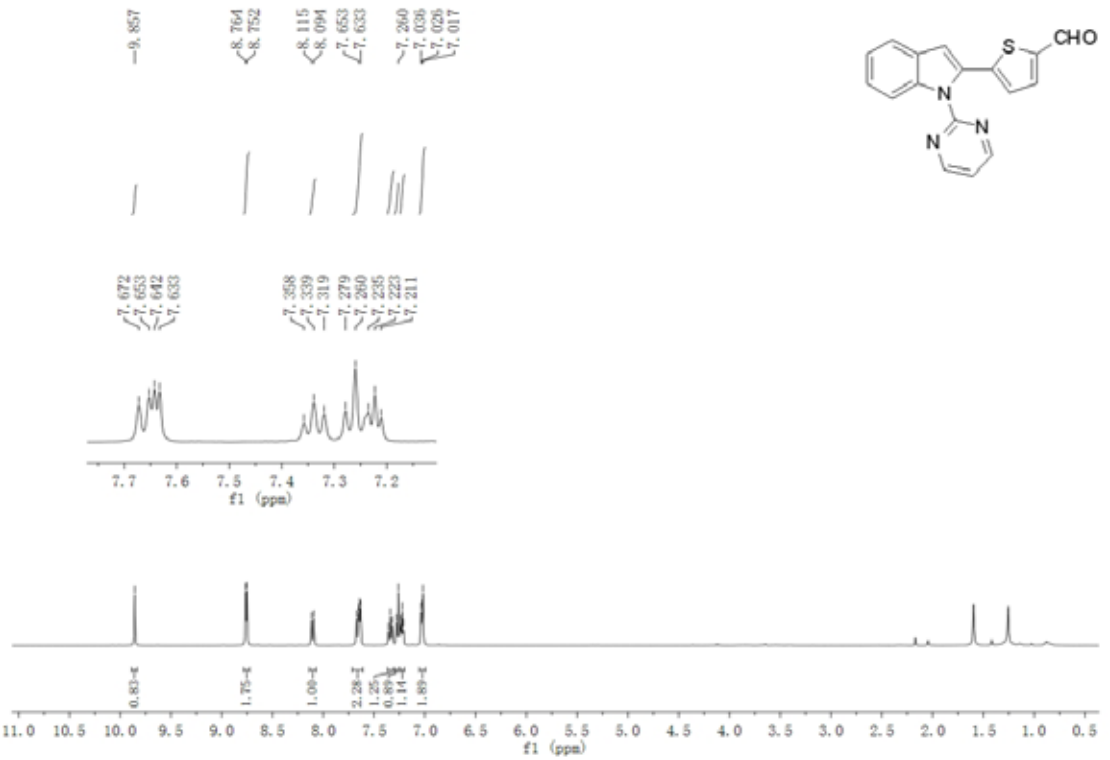
N
N
f1 (ppm)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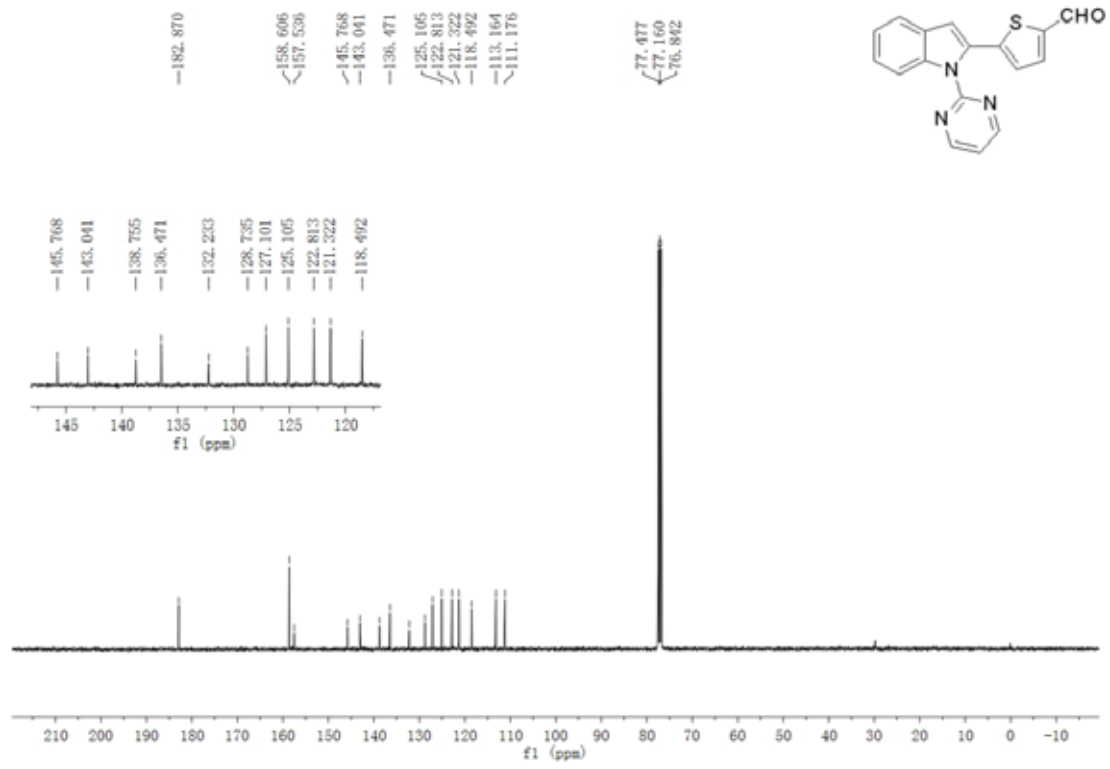
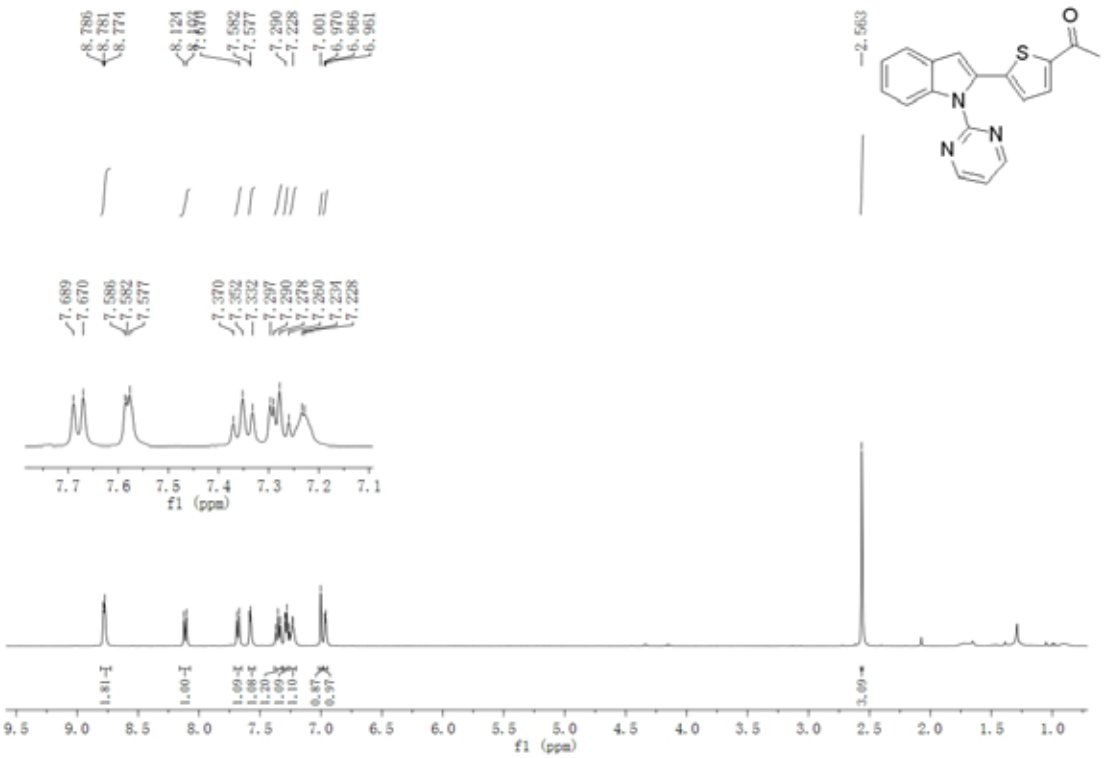
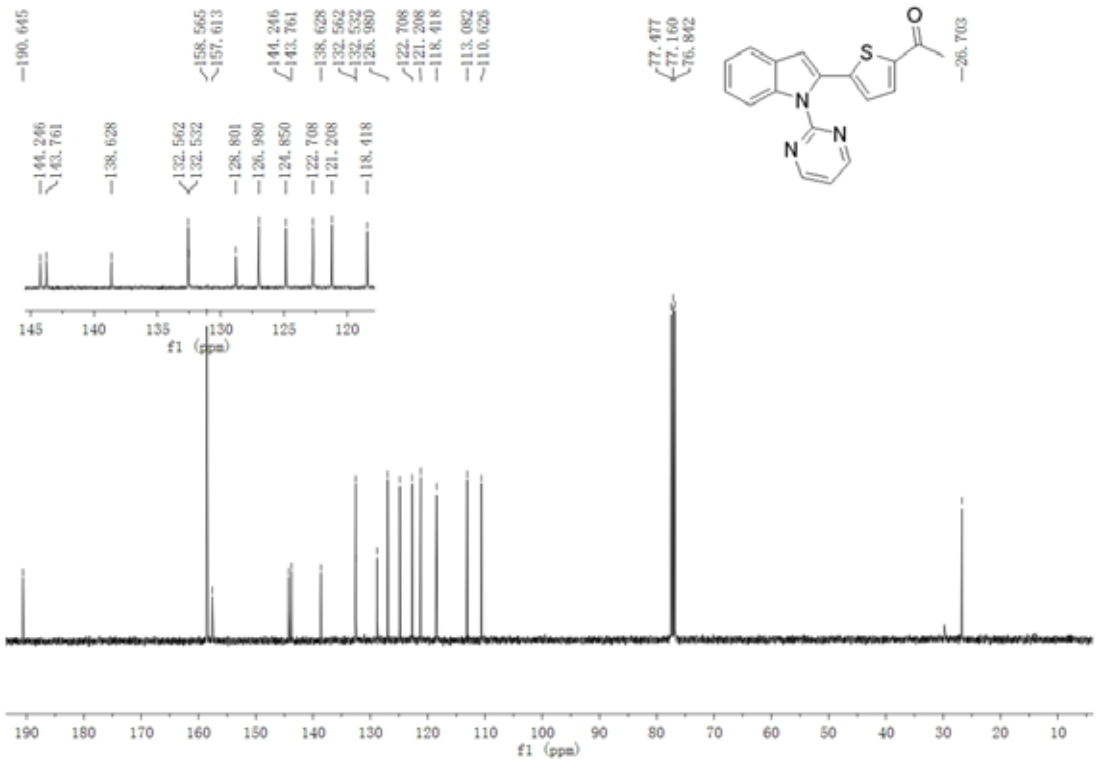
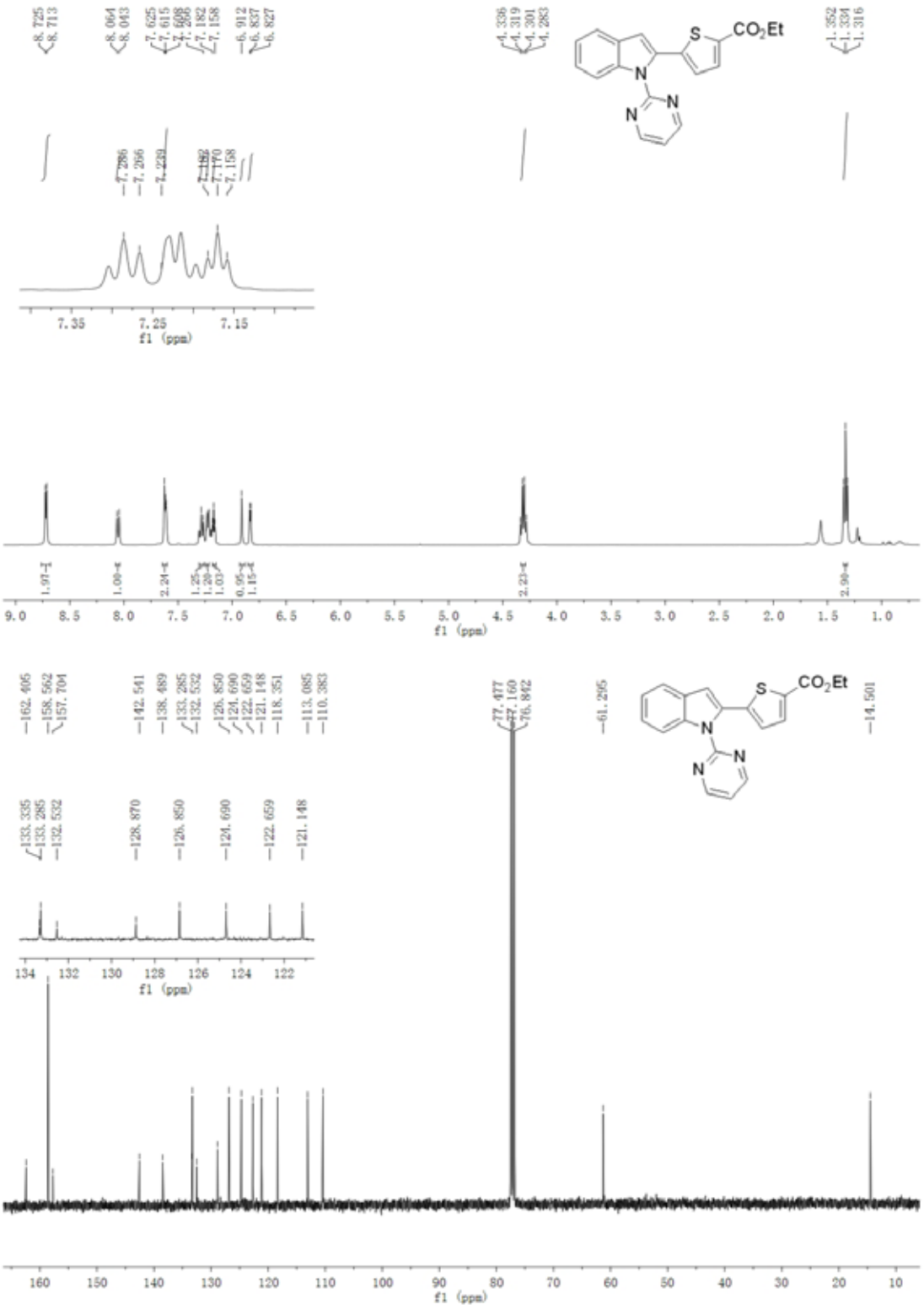
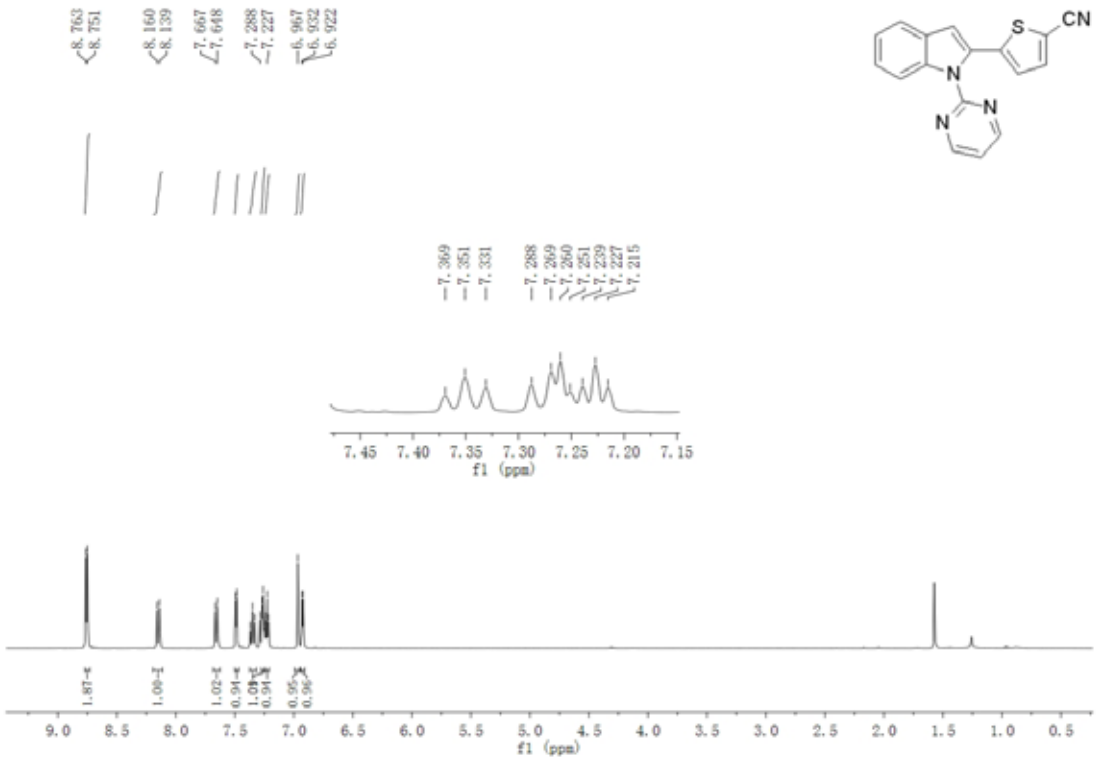
7.036
7.026
7.017
7.672
7.653
7.642
7.633
7.358
7.339
7.319
7.279
7.260
7.235
7.223
7.211
S
CHO
N
N
N
f1 (ppm)
0.83
1.75
1.00
2.28
1.25
0.89
1.14
1.89

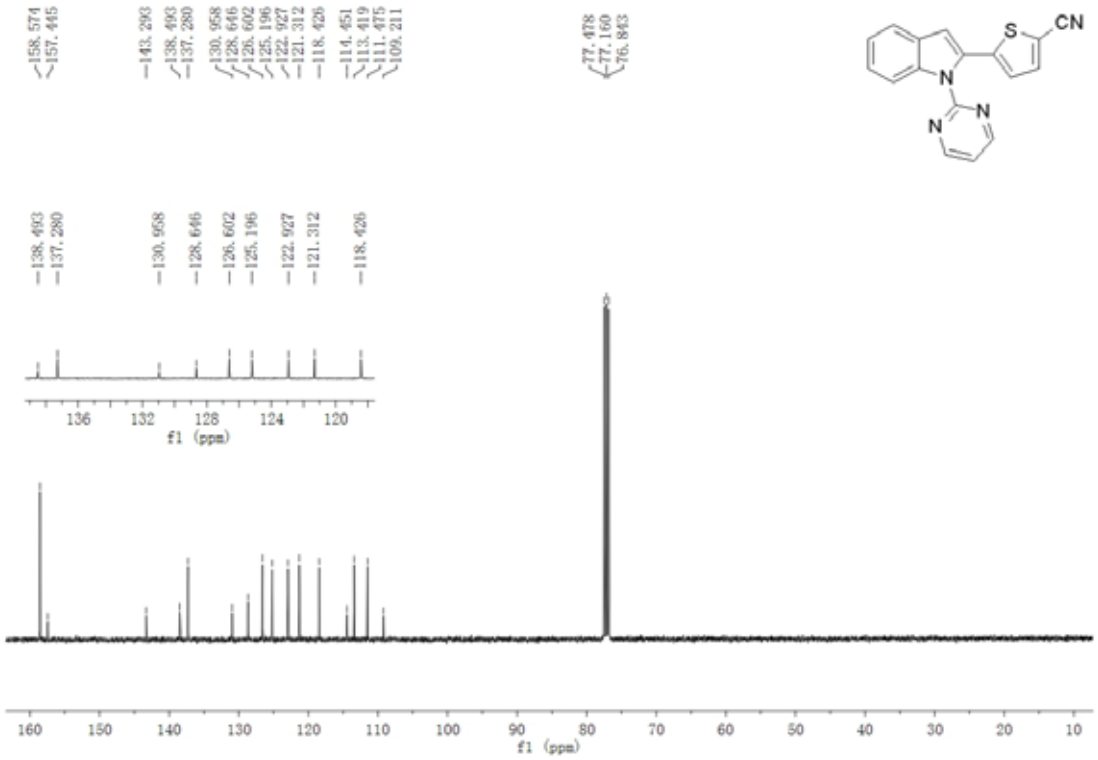

182.870
158.606
157.536
145.768
143.041
136.471
125.105
122.813
121.322
118.492
113.164
111.176
77.477
77.160
76.842
S
CHO
N
N
N
145.768
143.041
138.755
136.471
132.233
128.735
127.101
125.105
122.813
121.322
118.492
f1 (ppm)

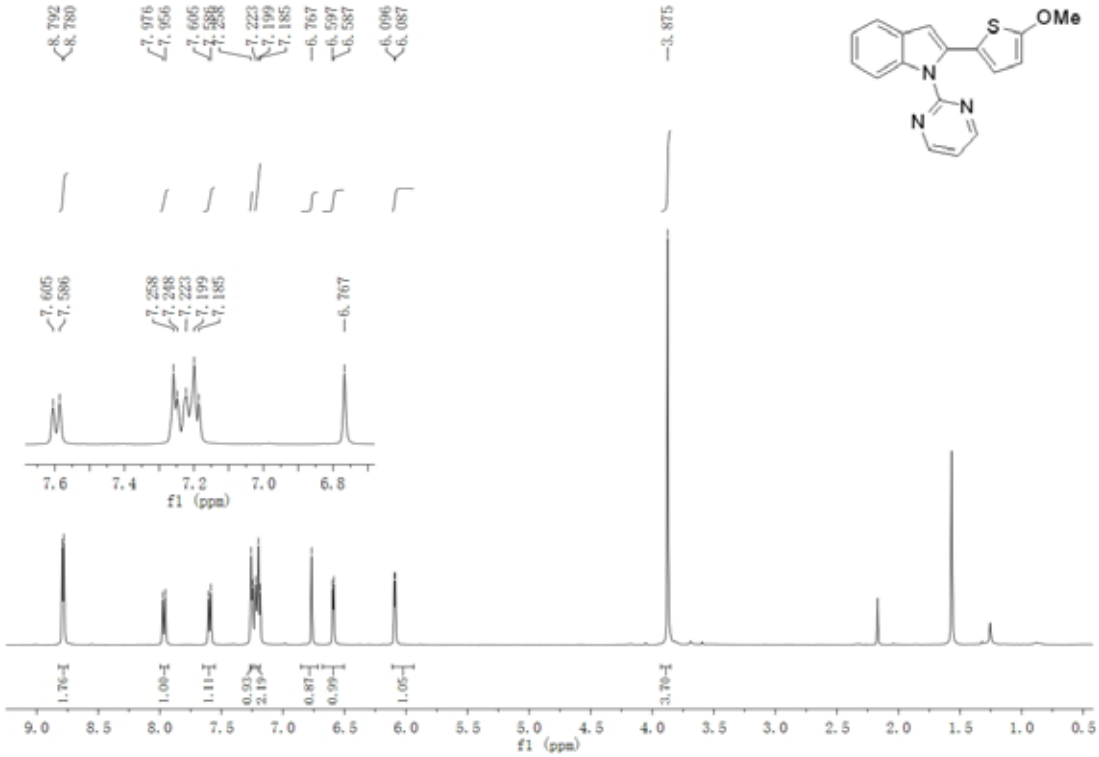


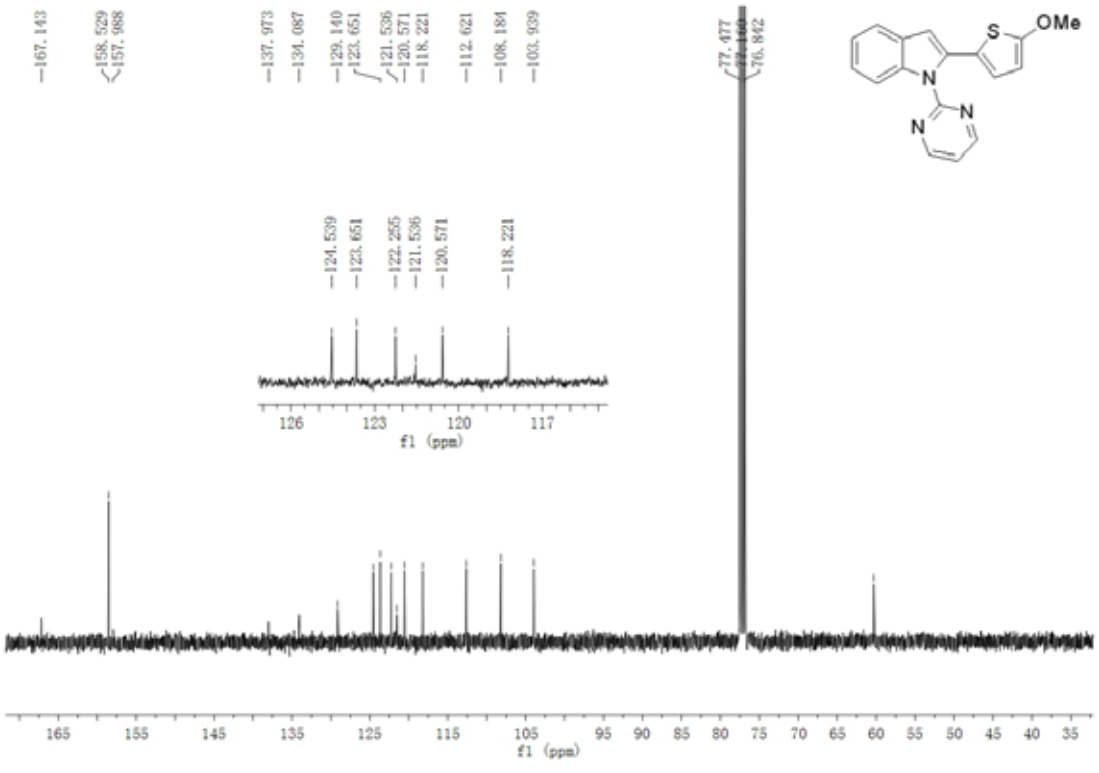


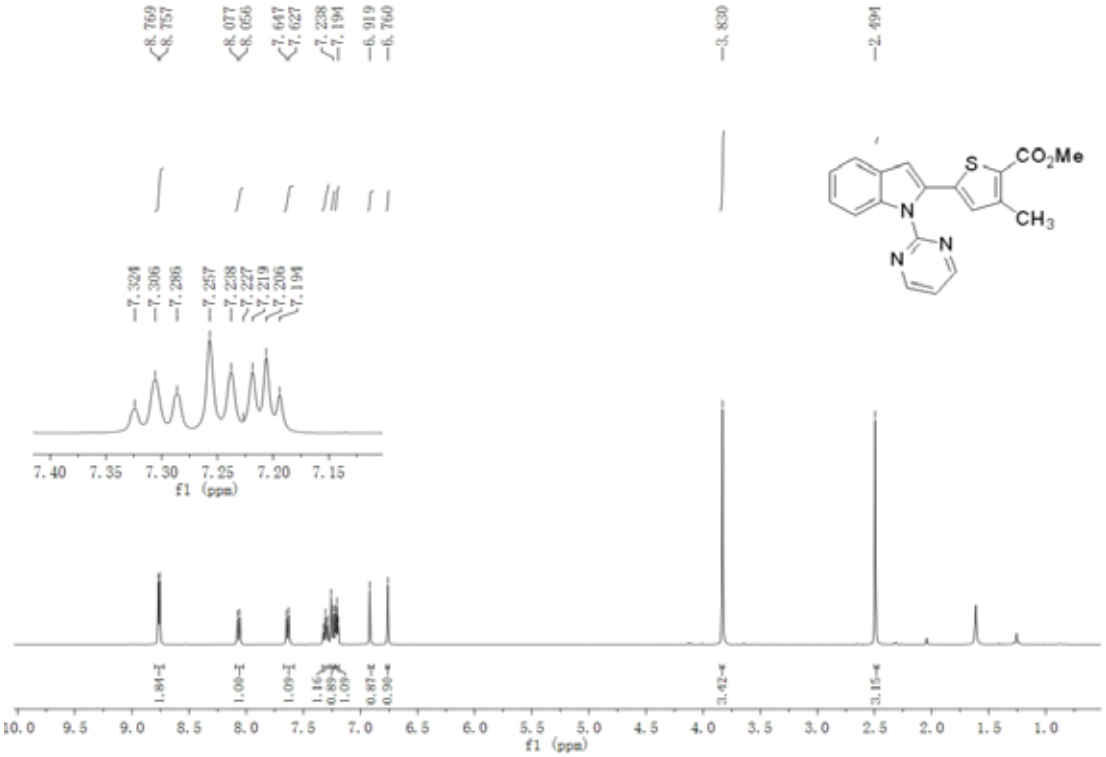

8.725
8.713
8.064
8.043
7.625
7.615
7.608
7.266
7.182
7.158
6.912
6.837
6.827
4.336
4.319
4.301
4.283
1.352
1.334
1.316
CO2Et
S
N
N
N
7.286
7.266
7.239
7.192
7.170
7.158
7.35
7.25
7.15
f1 (ppm)
1.97
1.00
2.24
1.25
1.28
1.03
0.95
1.15
2.23
2.90
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
162.405
158.562
157.704
142.541
138.489
133.285
132.532
126.850
124.690
122.659
121.148
118.351
113.085
110.383
77.477
77.160
76.842
61.295
14.501
CO2Et
S
N
N
N
133.335
133.285
132.532
128.870
126.850
124.690
122.659
121.148
134
132
130
128
126
124
122
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

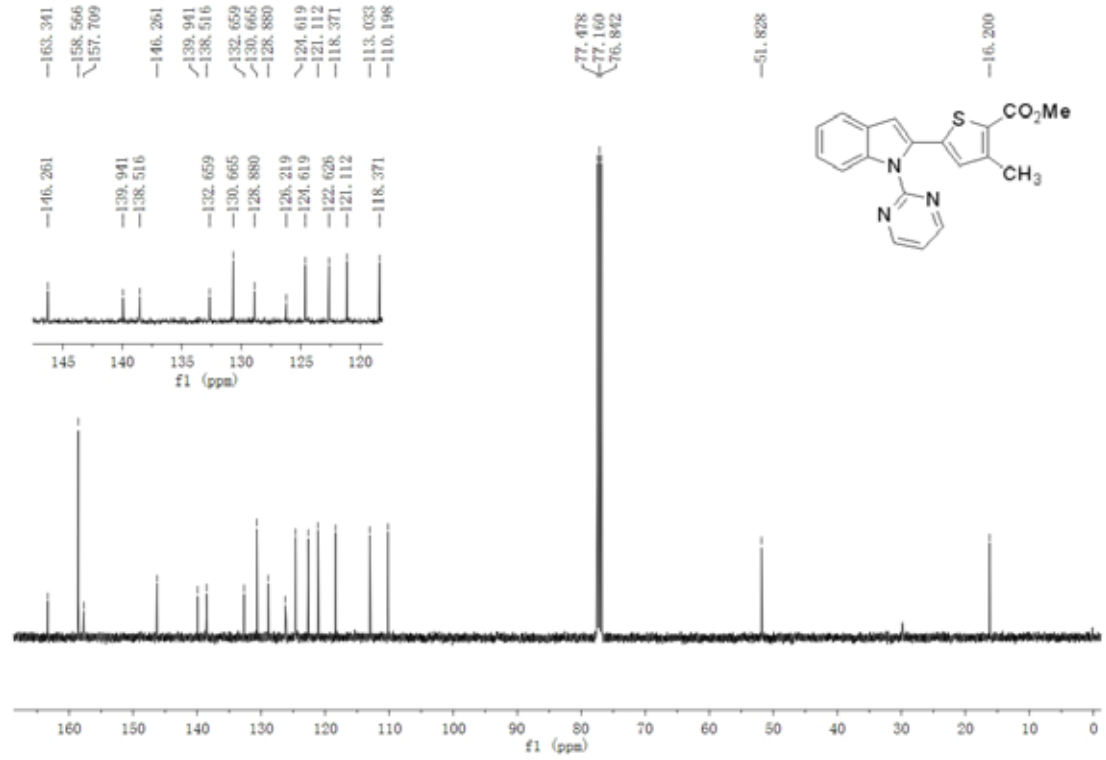

8.763
8.751
8.160
8.139
7.667
7.648
7.288
7.227
6.967
6.932
6.922
CN
S
N
N
N
7.369
7.351
7.331
7.288
7.269
7.260
7.251
7.239
7.227
7.215
7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
1.87
1.00
1.02
0.94
1.05
0.94
0.95
0.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

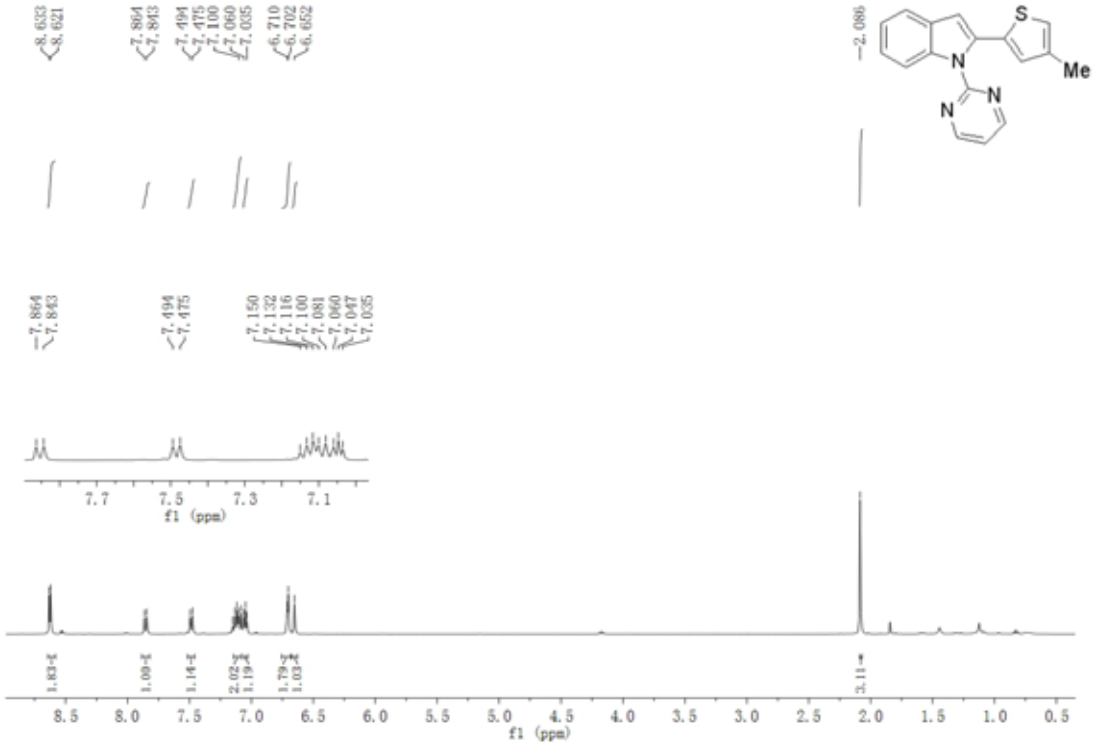

158.574
157.445
143.293
138.493
137.280
130.958
128.646
126.602
125.196
122.927
121.312
118.426
114.451
113.419
111.475
109.211
77.478
77.160
76.843
CN
S
N
N
N
138.493
137.280
130.958
128.646
126.602
125.196
122.927
121.312
118.426
136 132 128 124 120
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

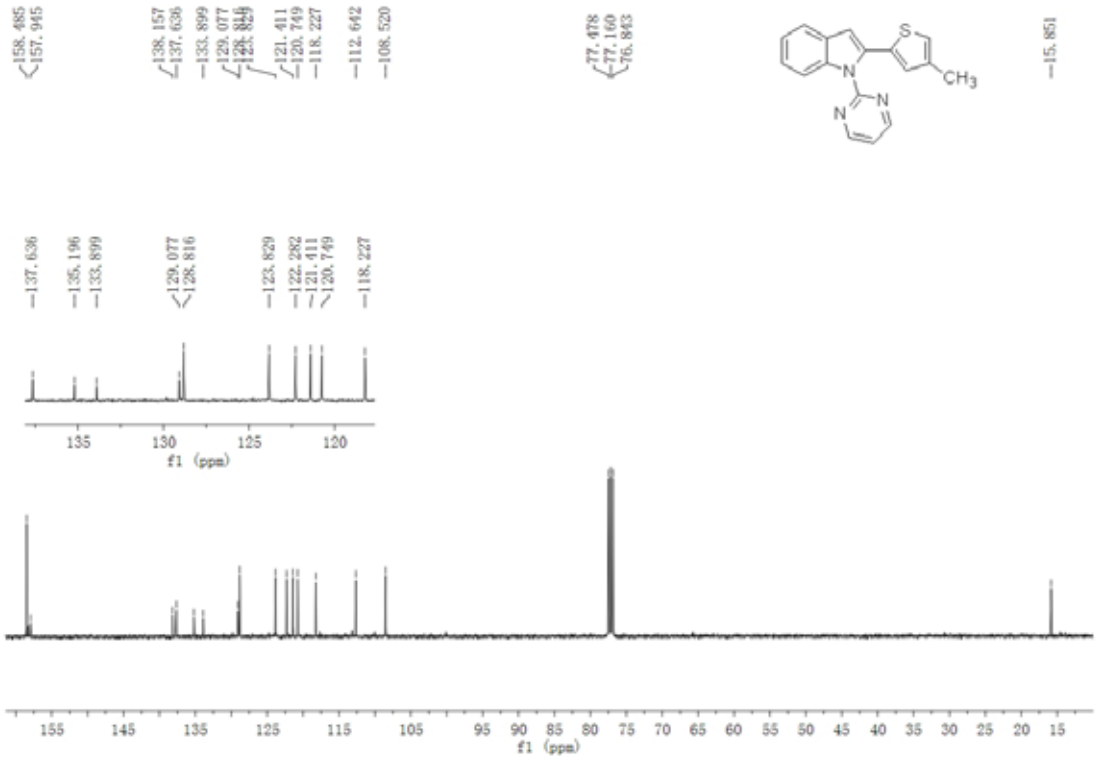

8.792
8.780
7.976
7.956
7.605
7.586
7.258
7.248
7.223
7.199
7.185
6.767
6.597
6.587
6.096
6.087
3.875
OMe
S
N
N
N
f1 (ppm)
1.76
1.00
1.11
0.93
2.19
0.87
0.99
1.05
3.70

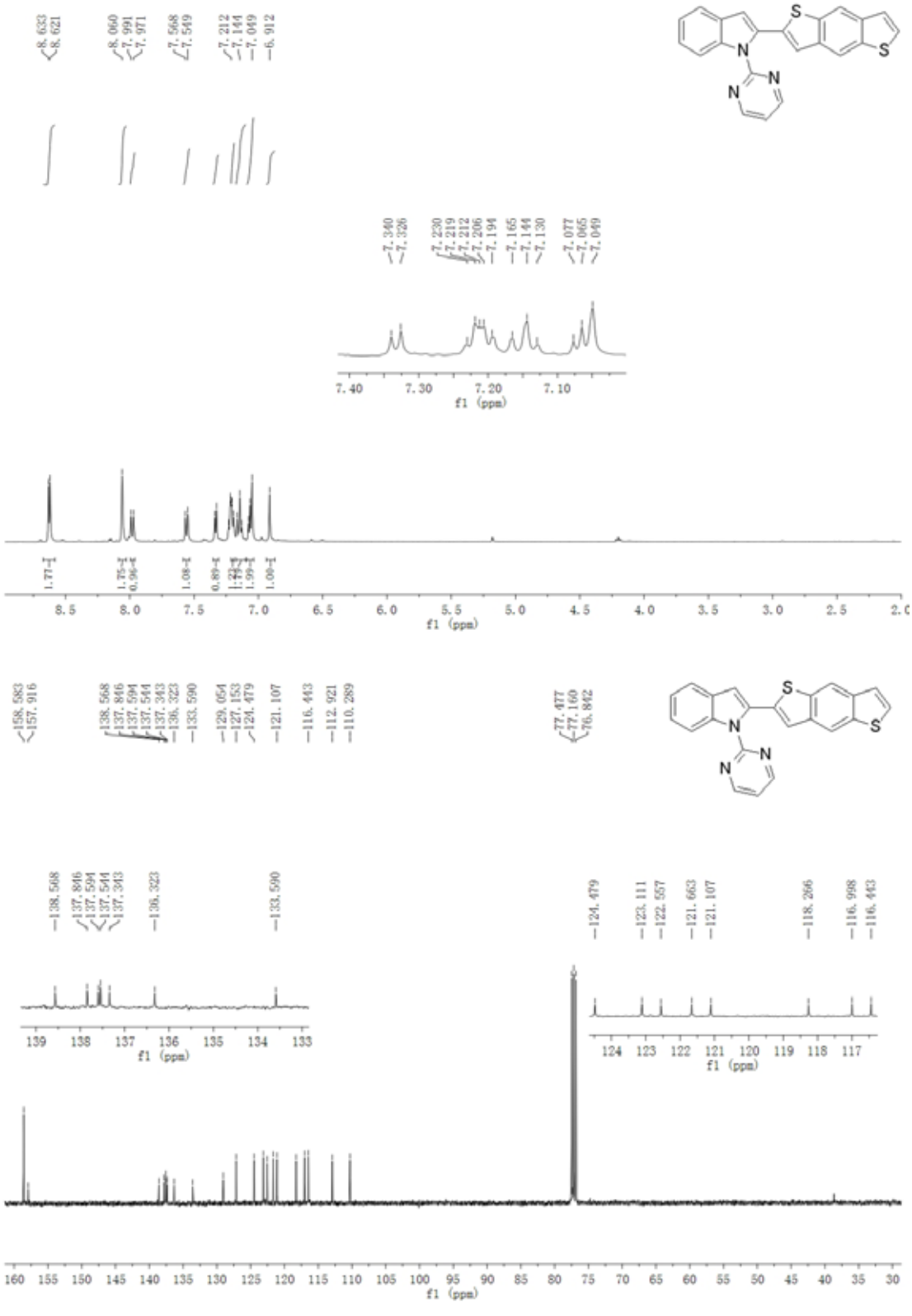

167.143
158.529
157.988
137.973
134.087
129.140
123.651
121.536
120.571
118.221
112.621
108.184
103.939
77.477
77.160
76.842
124.539
123.651
122.295
121.536
120.571
118.221
OMe
S
N
N
N
f1 (ppm)

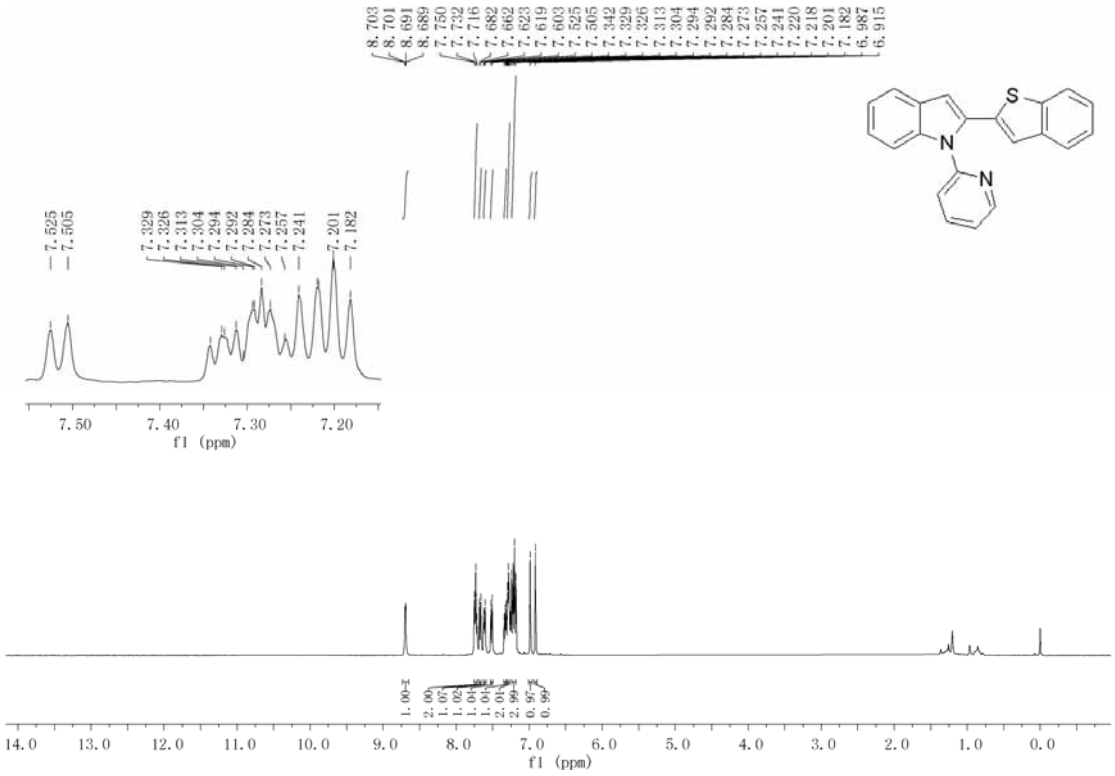

8.769
8.757
8.077
8.056
7.647
7.627
7.238
7.194
6.919
6.760
3.830
2.494
7.324
7.306
7.286
7.257
7.238
7.227
7.219
7.206
7.194
CO2Me
S
N
N
N
CH3
1.84
1.00
1.09
1.16
0.89
1.09
0.87
0.90
3.42
3.15
f1 (ppm)

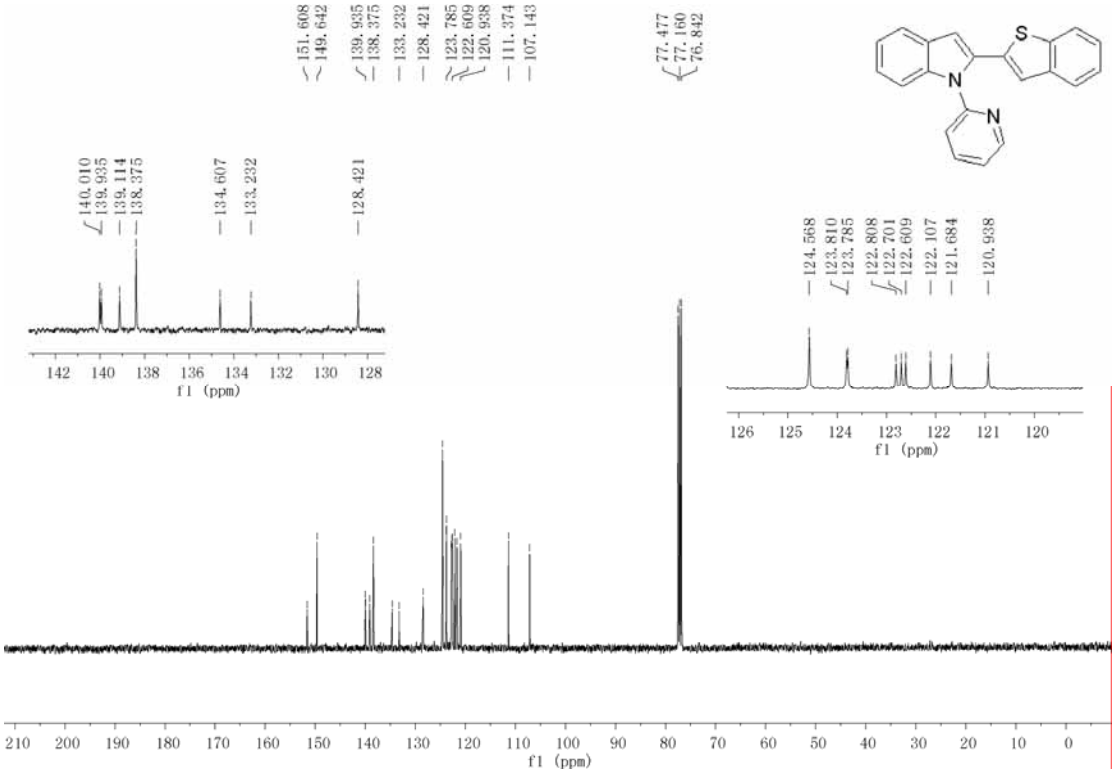

163.341
158.566
157.709
146.261
139.941
138.516
132.659
130.665
128.880
124.619
121.112
118.371
113.033
110.198
77.478
77.160
76.842
51.828
16.200
CO2Me
S
N
N
N
CH3
f1 (ppm)

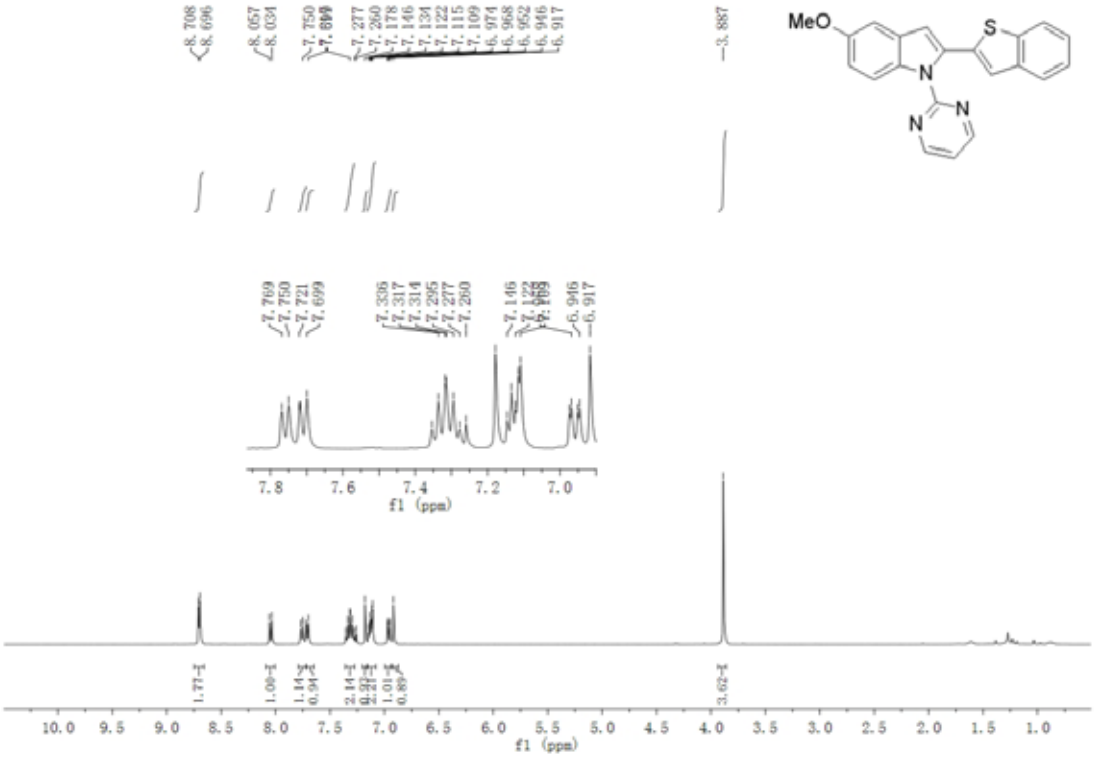


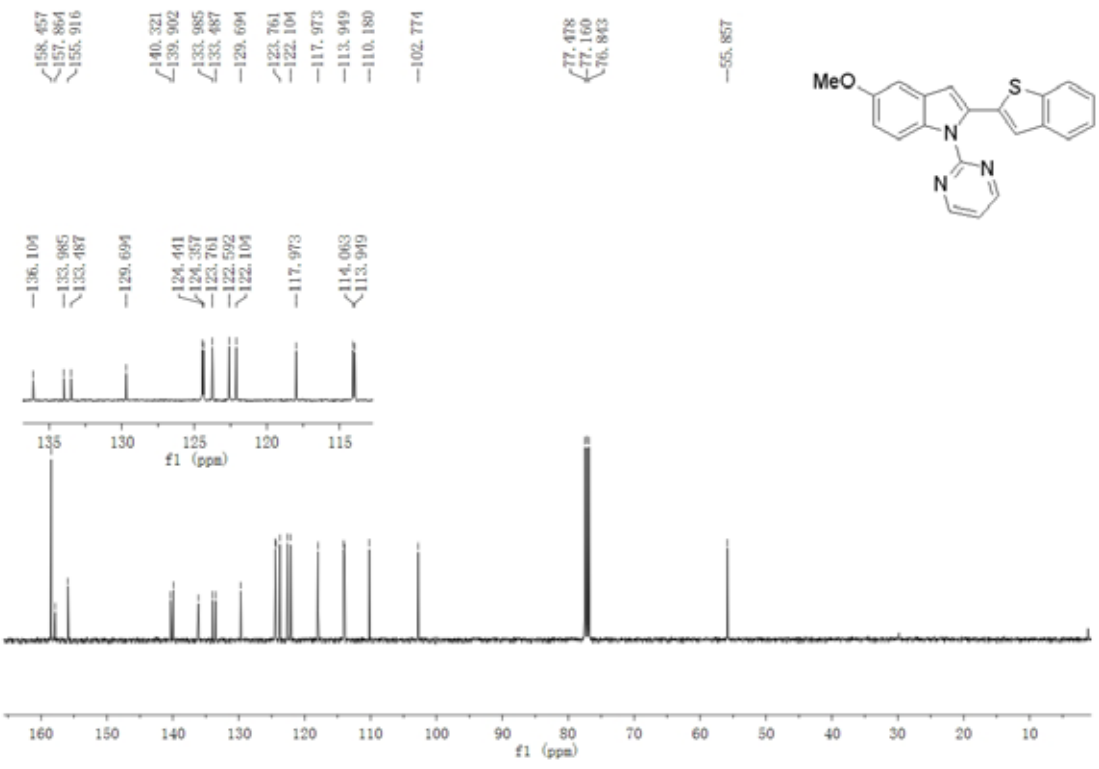


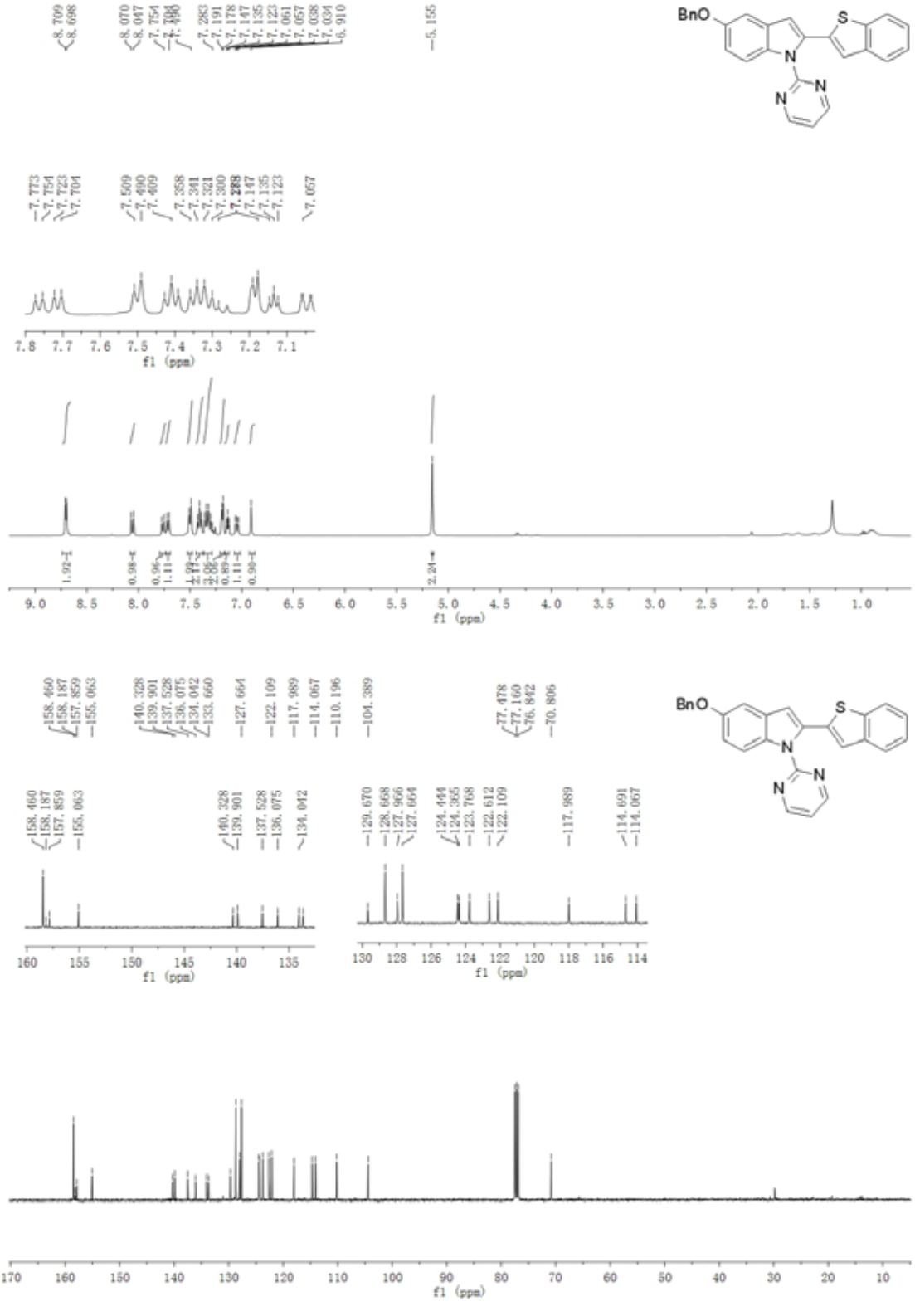

8.633
8.621
8.060
7.991
7.971
7.568
7.549
7.212
7.144
7.049
6.912
7.340
7.326
7.230
7.219
7.212
7.206
7.194
7.165
7.144
7.130
7.077
7.065
7.049
f1 (ppm)
1.77
1.75
0.96
1.08
0.89
1.99
1.00
f1 (ppm)
158.583
157.916
138.568
137.846
137.594
137.544
137.343
136.323
133.590
129.054
127.153
124.479
121.107
116.443
112.921
110.289
77.477
77.160
76.842
f1 (ppm)
f1 (ppm)
f1 (ppm)

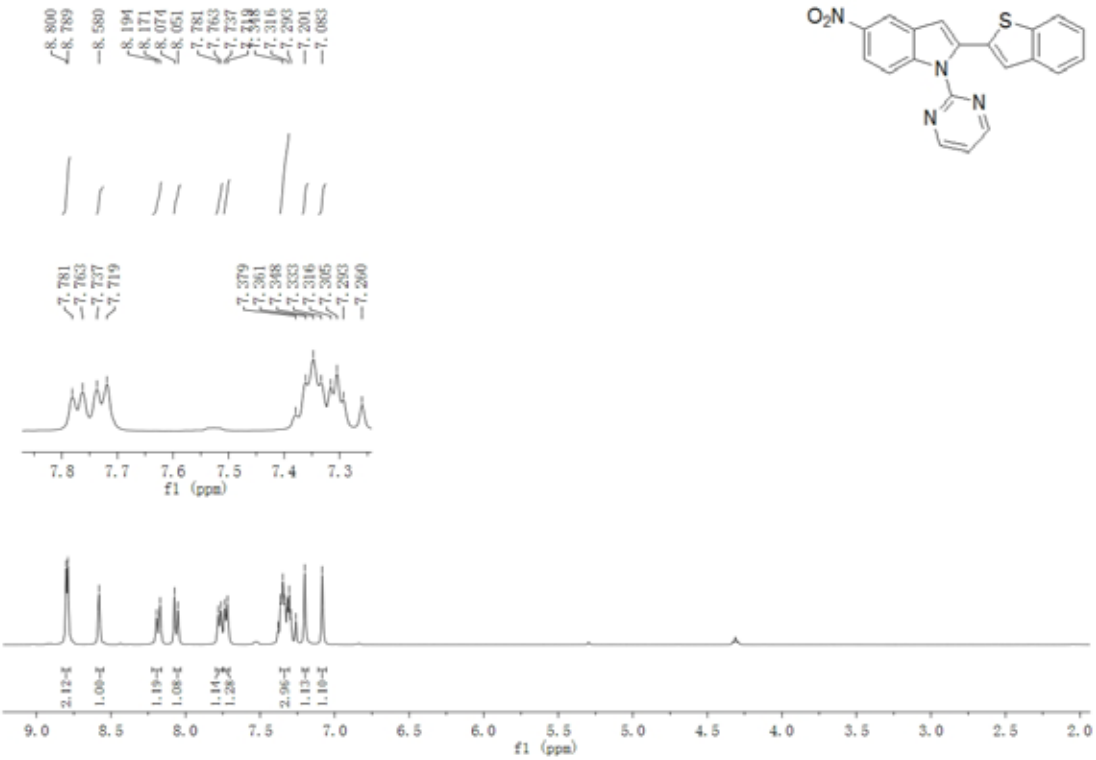

8.703
8.701
8.691
8.689
7.750
7.732
7.716
7.682
7.662
7.623
7.619
7.603
7.525
7.505
7.342
7.329
7.326
7.313
7.304
7.294
7.292
7.284
7.273
7.257
7.241
7.220
7.218
7.201
7.182
6.987
6.915
7.625
7.505
7.329
7.326
7.313
7.304
7.294
7.292
7.284
7.273
7.257
7.241
7.201
7.182
7.50
7.40
7.30
7.20
f1 (ppm)
S
N
N
1.00
2.00
1.07
1.02
1.04
1.04
2.01
2.99
0.97
0.99
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

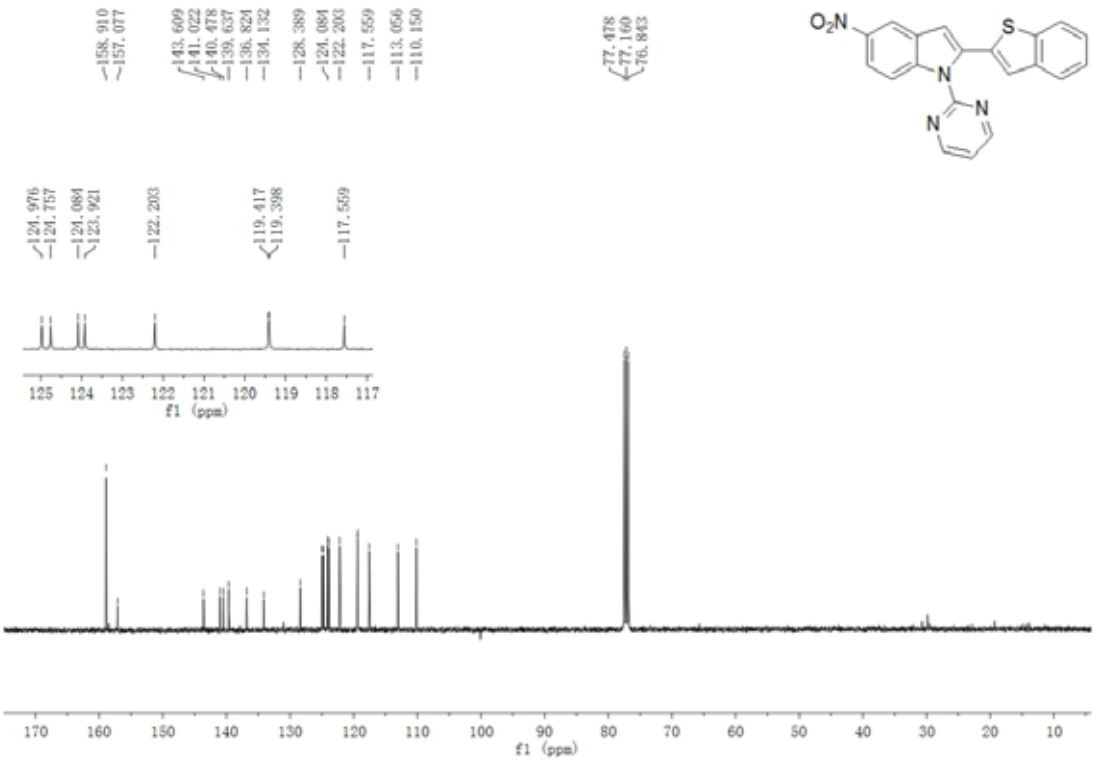

151.608
149.642
139.935
138.375
133.232
128.421
123.785
122.609
120.938
111.374
107.143
77.477
77.160
76.842
140.010
139.935
139.114
138.375
134.607
133.232
128.421
142
140
138
136
134
132
130
128
f1 (ppm)
124.568
123.810
123.785
122.808
122.701
122.609
122.107
121.684
120.938
126
125
124
123
122
121
120
f1 (ppm)
S
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

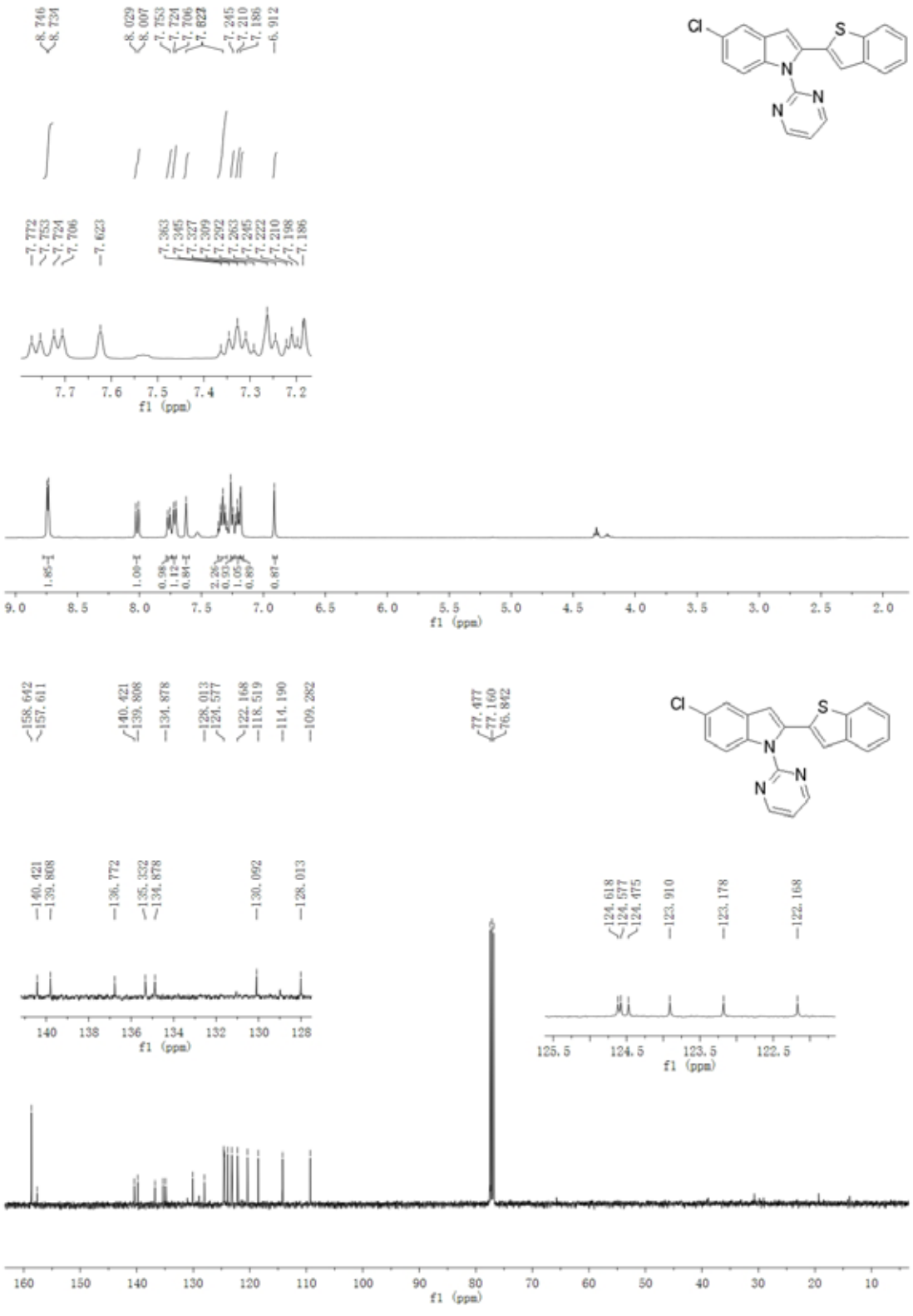

MeO
S
N
N
N
f1 (ppm)

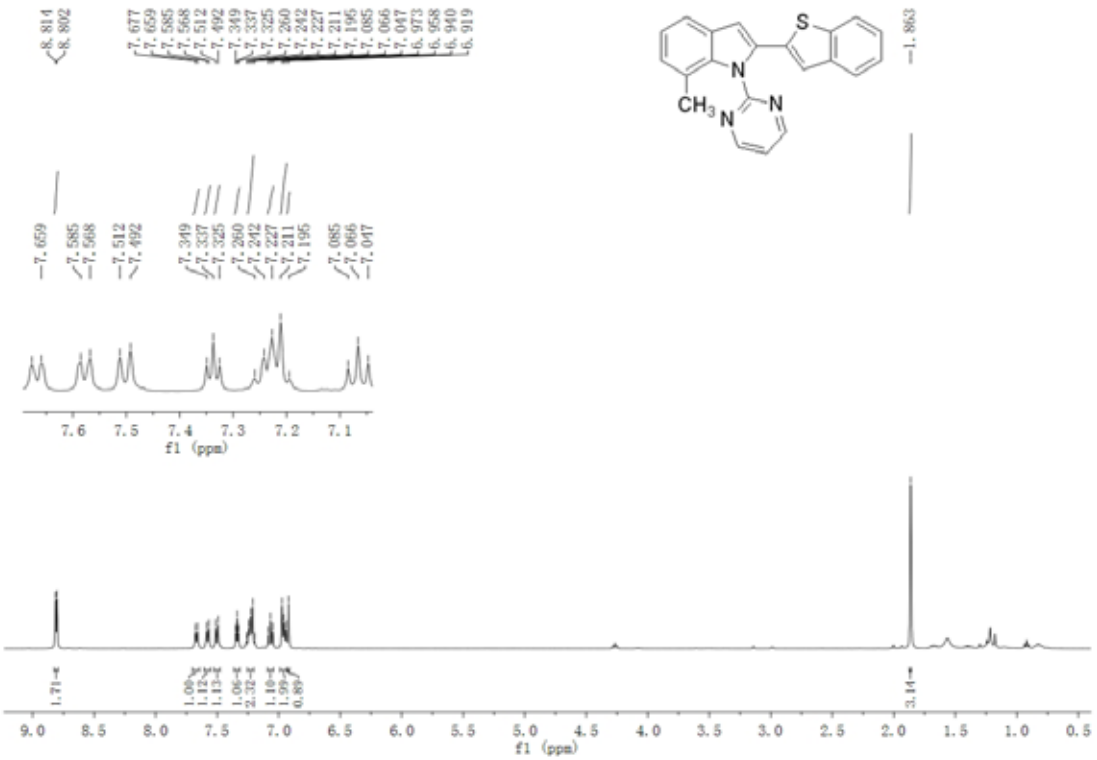

MeO
S
N
N
N
f1 (ppm)

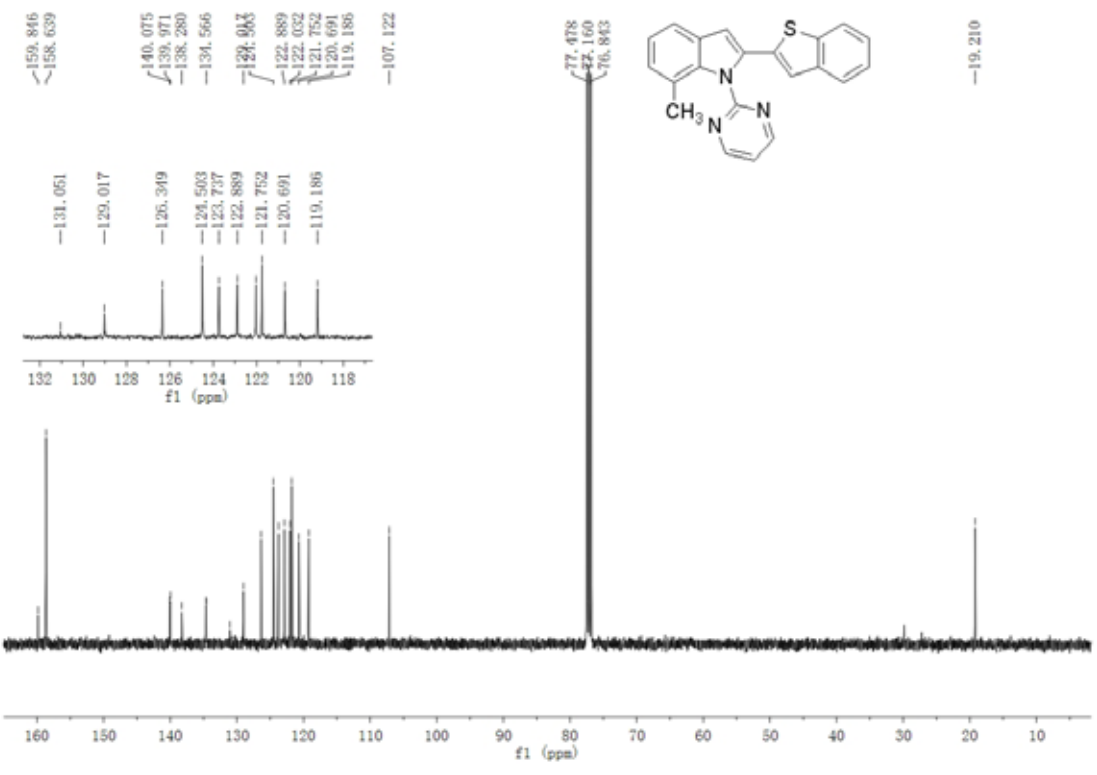

BnO
S
N
N
N
f1 (ppm)
BnO
S
N
N
N
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)

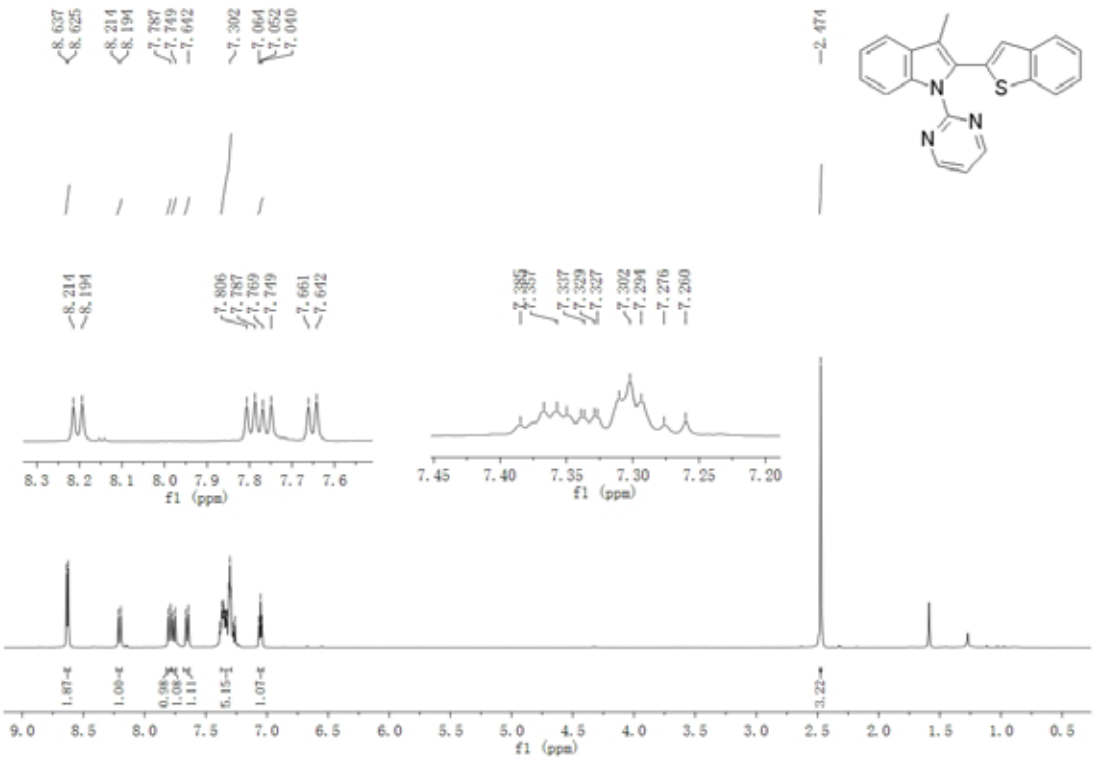

8.800
8.789
8.580
8.194
8.171
8.074
8.051
7.781
7.763
7.737
7.719
7.379
7.361
7.348
7.333
7.316
7.305
7.293
7.260
7.201
7.083
O2N
S
N
N
N
f1 (ppm)

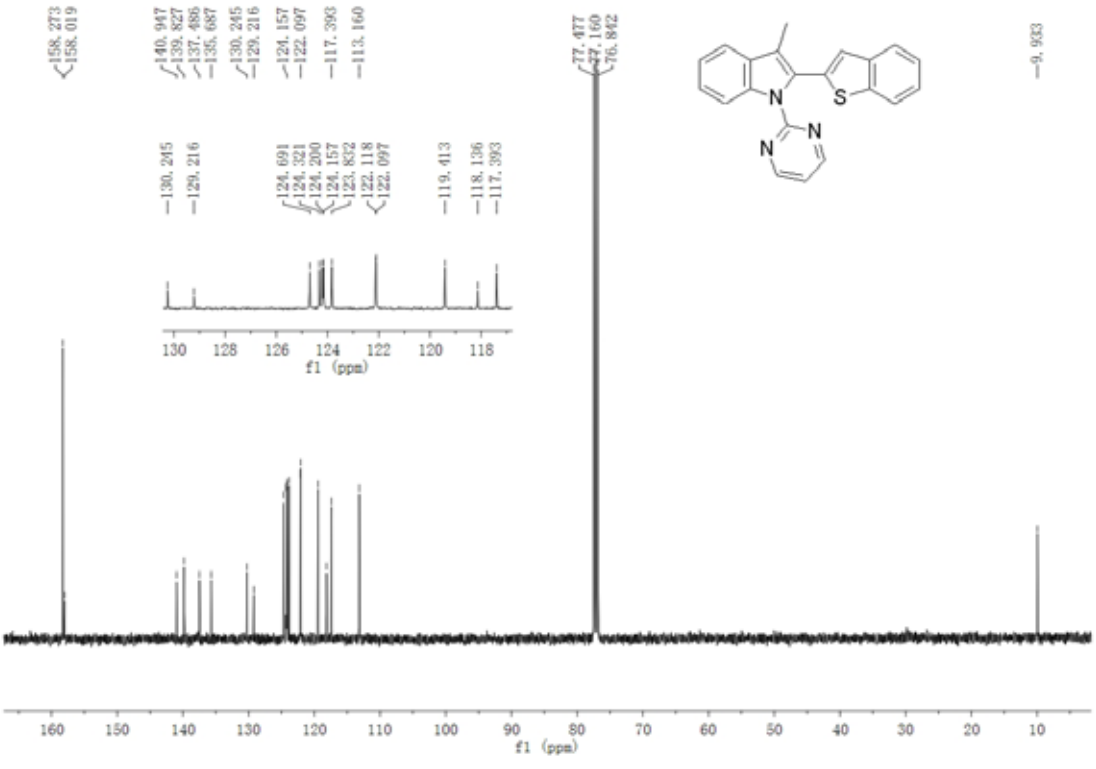

158.910
157.077
143.609
141.022
140.478
139.637
136.824
134.132
128.389
124.084
122.203
117.559
113.056
110.150
77.478
77.160
76.843
O2N
S
N
N
N
121.976
121.757
121.084
120.921
122.203
119.417
119.398
117.559
f1 (ppm)

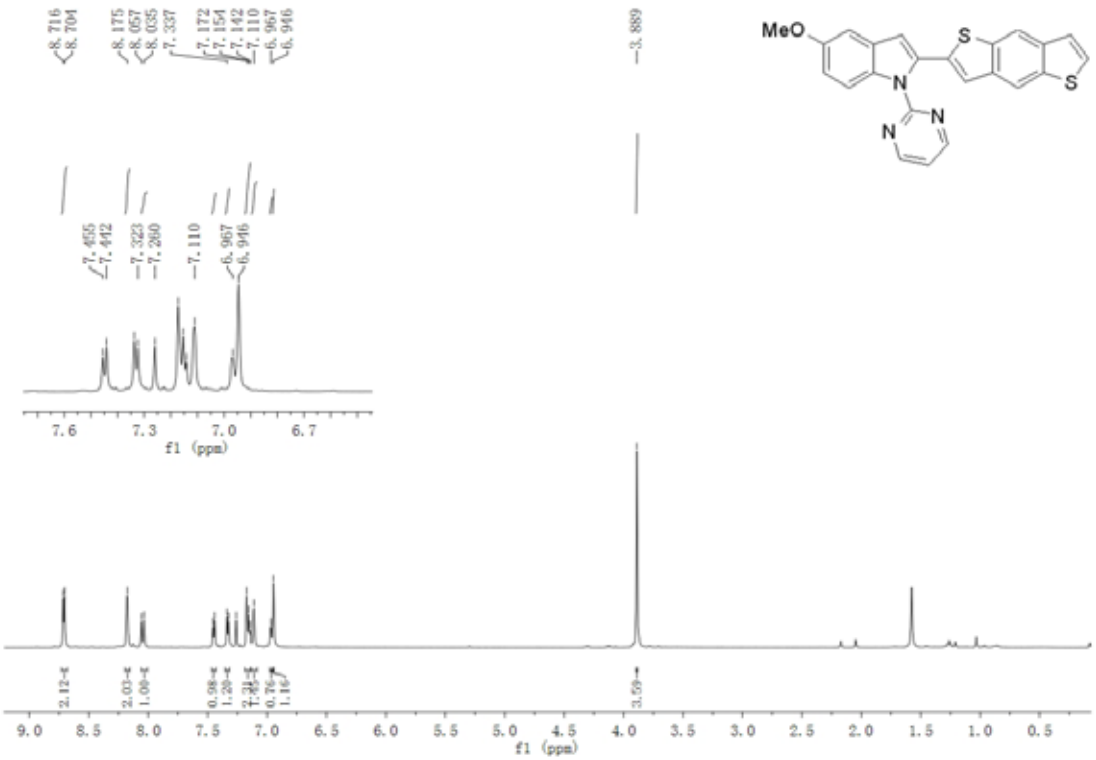

8.746
8.734
8.029
8.007
7.753
7.724
7.706
7.623
7.245
7.210
7.186
6.912
Cl
S
N
N
N
7.772
7.753
7.724
7.706
7.623
7.363
7.345
7.327
7.309
7.292
7.263
7.245
7.222
7.210
7.198
7.186
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
1.85
1.00
0.98
1.12
0.84
2.25
0.93
1.05
0.89
0.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)
158.642
157.611
140.421
139.808
134.878
128.013
124.577
122.168
118.519
114.190
109.282
77.477
77.160
76.842
Cl
S
N
N
N
140.421
139.808
136.772
135.332
134.878
130.092
128.013
140
138
136
134
132
130
128
f1 (ppm)
124.618
124.577
124.475
123.910
123.178
122.168
125.5
124.5
123.5
122.5
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

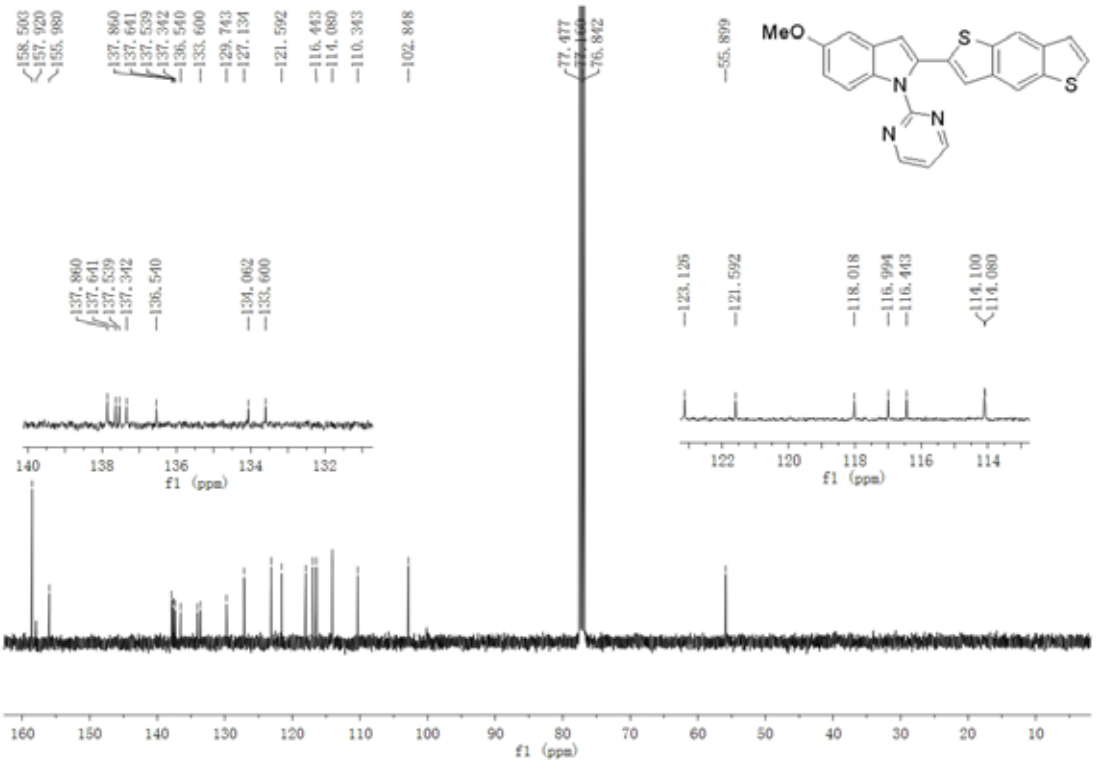

8.814
8.802
7.677
7.659
7.585
7.568
7.512
7.492
7.349
7.337
7.325
7.260
7.242
7.227
7.211
7.195
7.085
7.066
7.047
6.973
6.958
6.940
6.919
1.863
S
N
CH3
N
N
f1 (ppm)

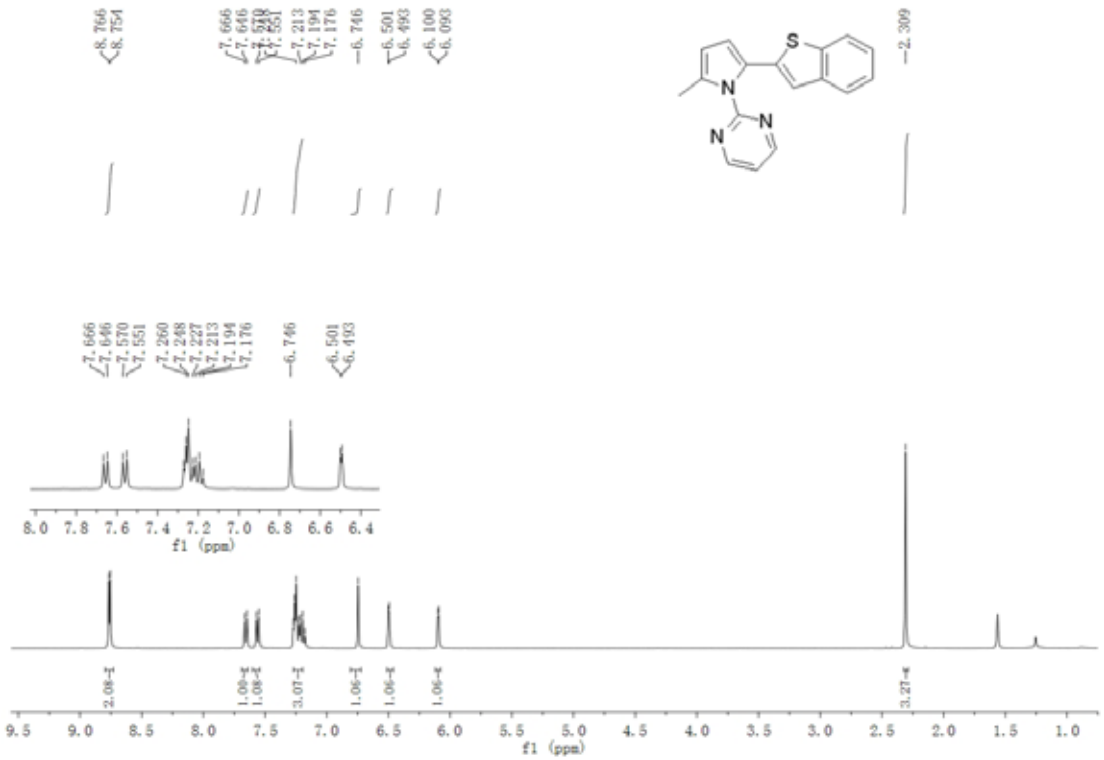

159.846
158.639
140.075
139.971
138.280
134.566
122.889
122.032
121.752
120.691
119.186
107.122
77.478
77.160
76.843
19.210
131.051
129.017
126.349
124.503
123.737
122.889
121.752
120.691
119.186
S
N
CH3
N
N
f1 (ppm)

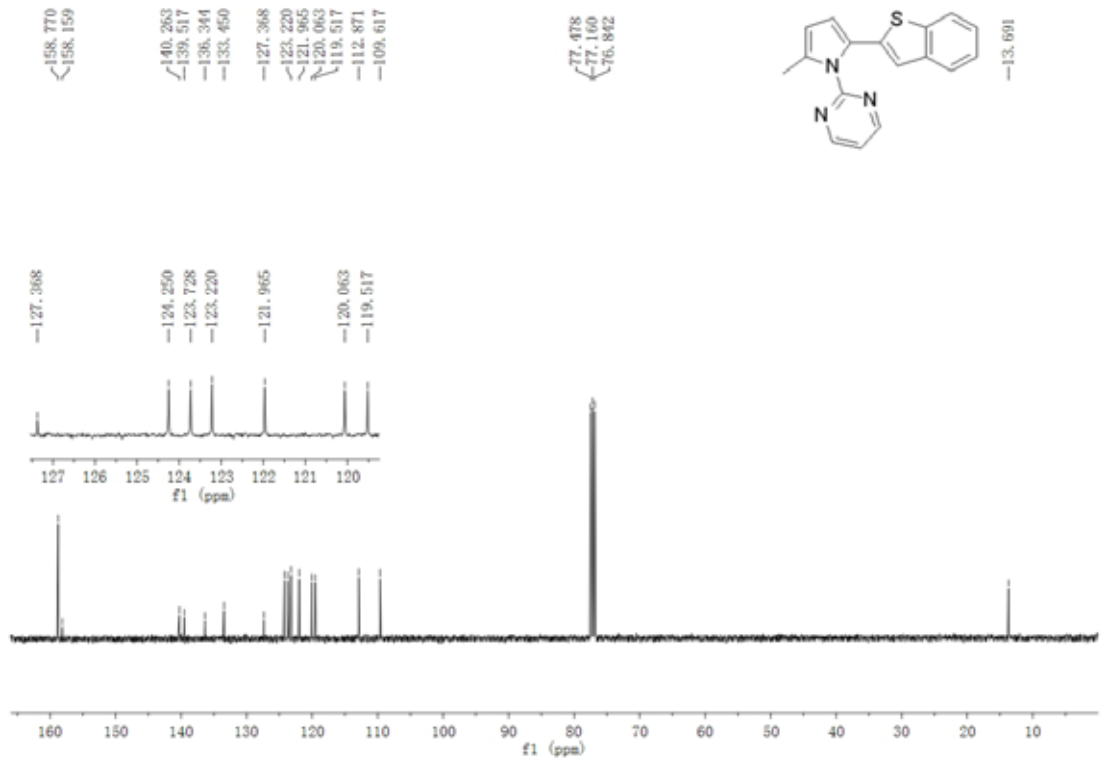

8.637
8.625
8.214
8.194
7.787
7.749
7.642
7.302
7.064
7.052
7.040
2.474
N
S
N
N
8.214
8.194
7.806
7.787
7.769
7.749
7.661
7.642
7.385
7.357
7.337
7.329
7.327
7.302
7.294
7.276
7.260
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6
f1 (ppm)
7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
1.87
1.00
0.98
1.08
1.11
5.15
1.07
3.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

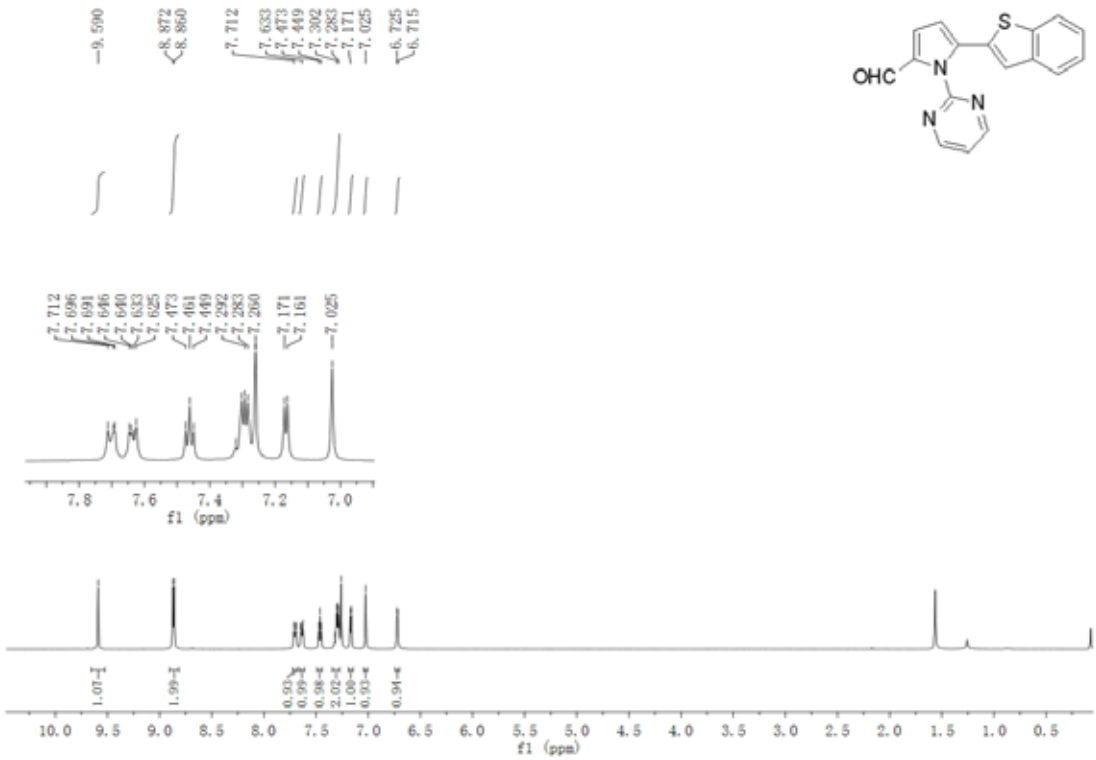

158.273
158.019
140.947
139.827
137.486
135.687
130.245
129.216
124.157
122.097
117.393
113.160
77.477
77.160
76.842
9.933
N
S
N
N
130.245
129.216
124.691
124.321
124.200
124.157
123.852
122.118
122.097
119.413
118.136
117.393
130 128 126 124 122 120 118
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

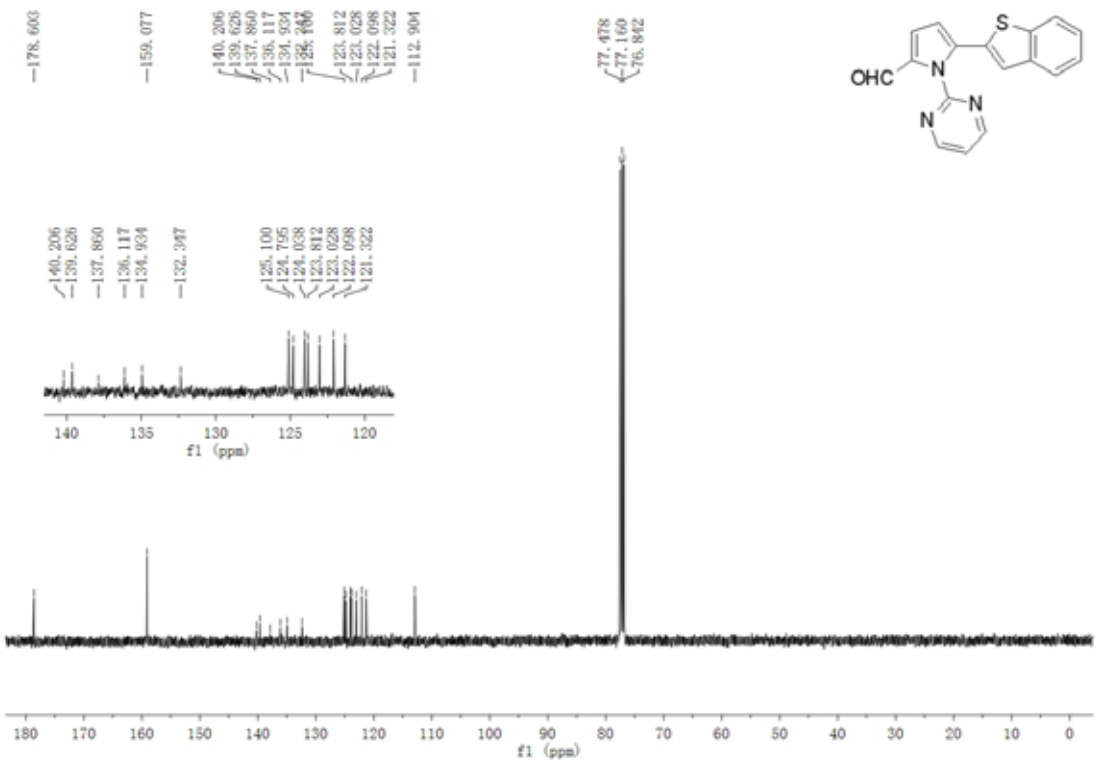

MeO
S
S
N
N
N
f1 (ppm)

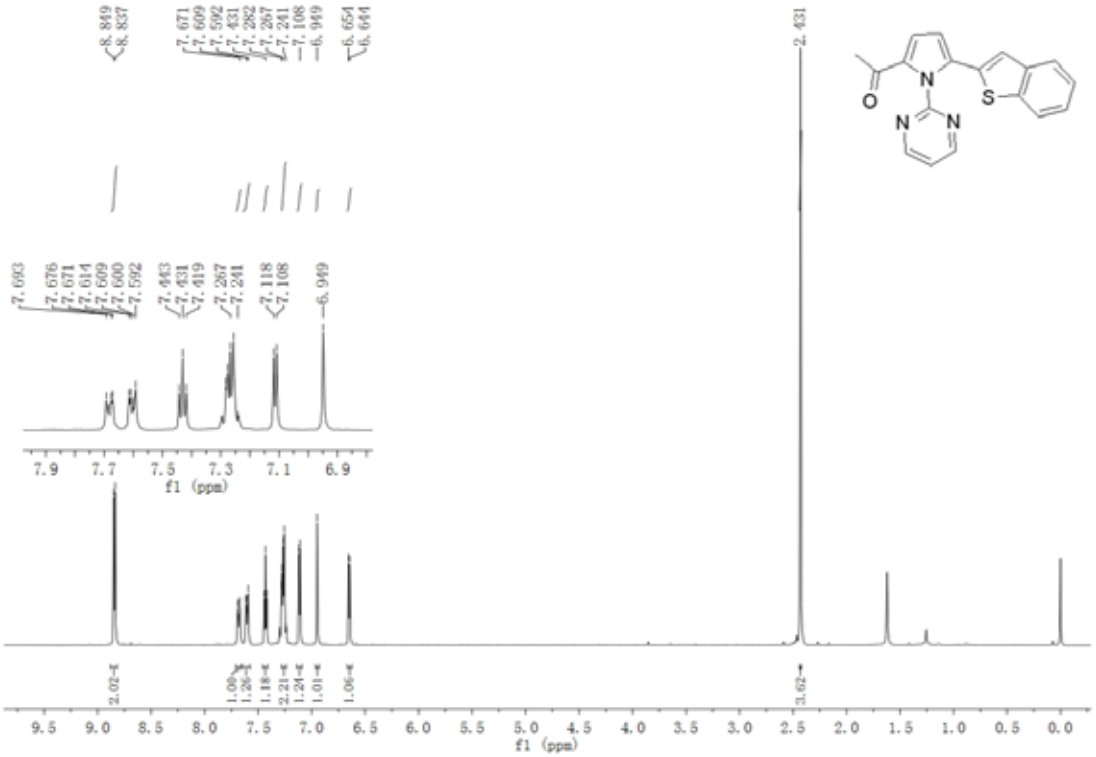

MeO
S
S
N
N
N
f1 (ppm)
f1 (ppm)
f1 (ppm)

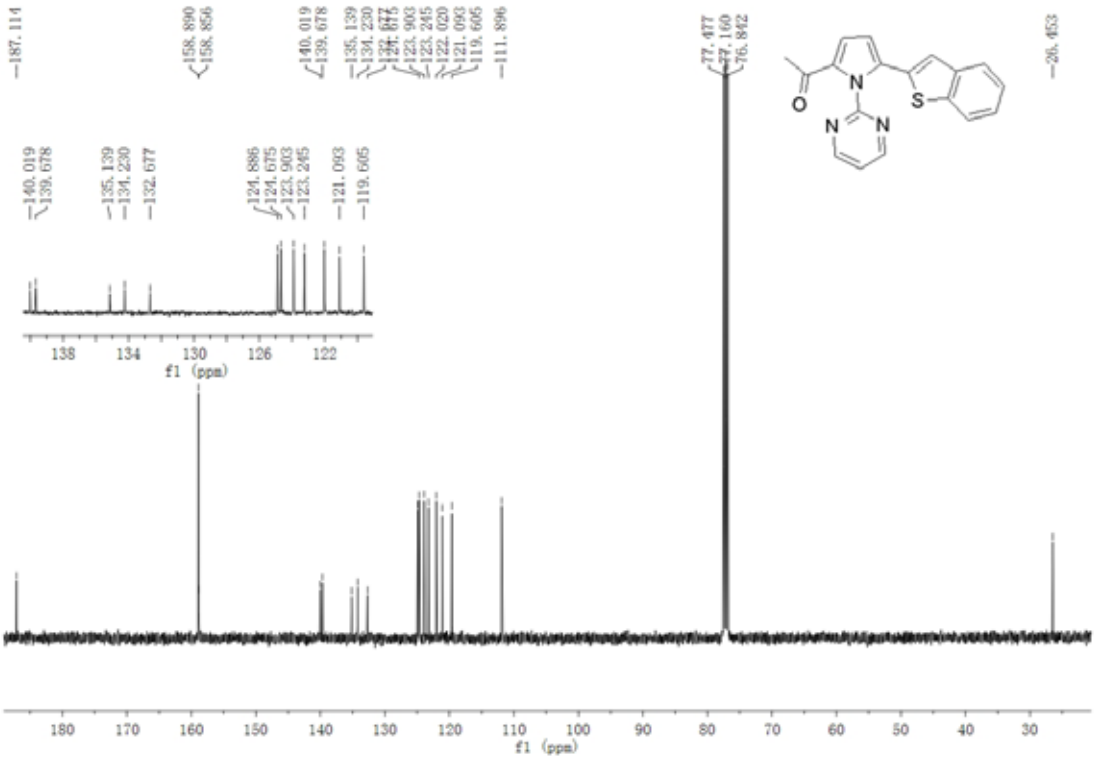

8.766
8.754
7.666
7.646
7.570
7.551
7.260
7.248
7.227
7.213
7.194
7.176
6.746
6.501
6.493
6.100
6.093
2.309
S
N
N
f1 (ppm)
2.08
1.00
1.08
3.07
1.06
1.06
1.06
3.27

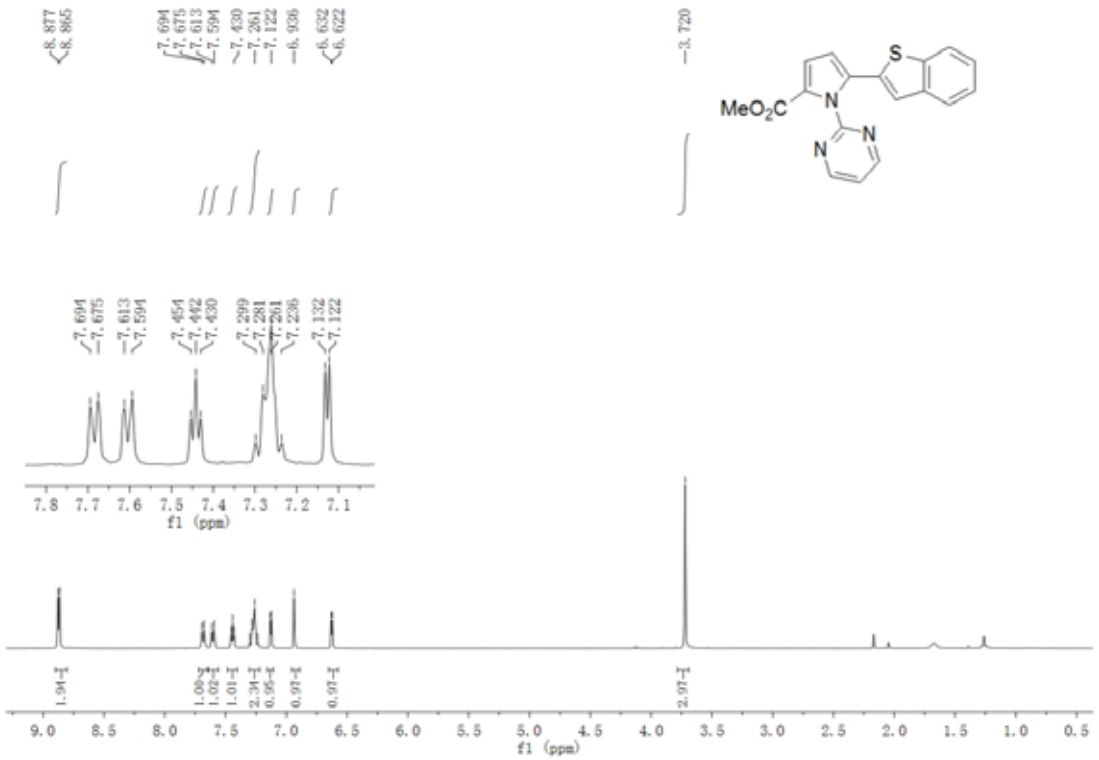

158.770
158.159
140.263
139.517
136.344
133.450
127.368
123.220
121.965
120.063
119.517
112.871
109.617
77.478
77.160
76.842
13.691
S
N
N
f1 (ppm)

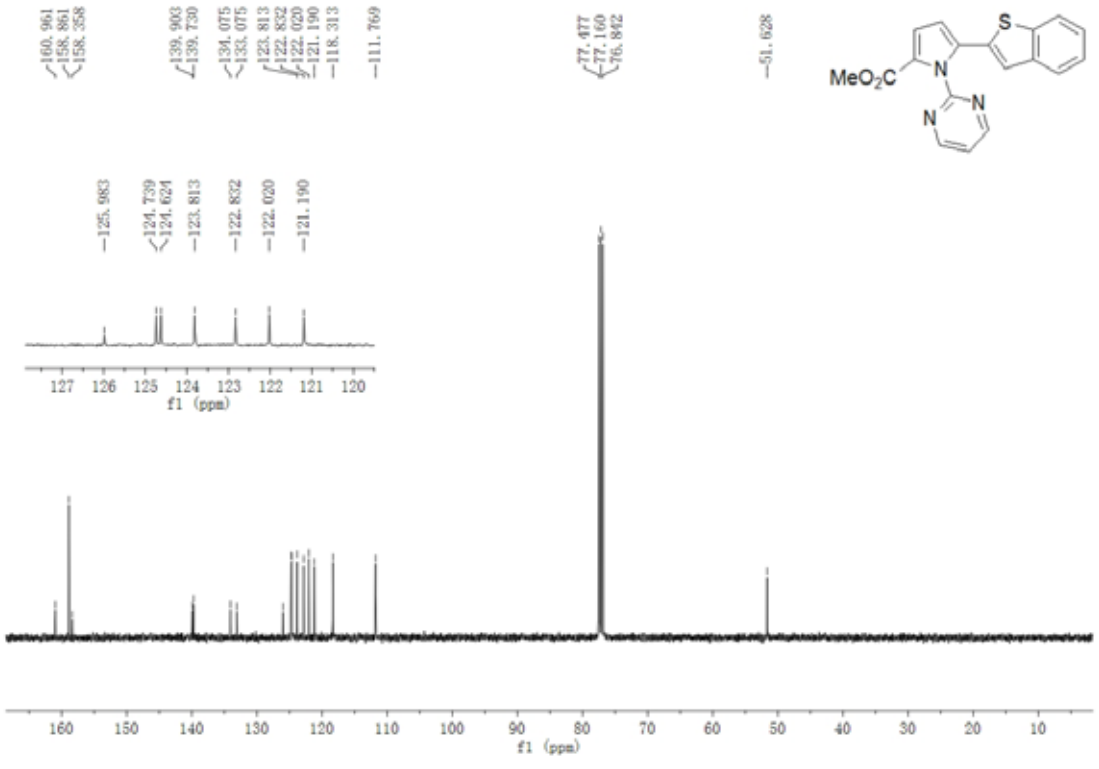

9.590
8.872
8.860
7.712
7.633
7.473
7.449
7.302
7.283
7.171
7.025
6.725
6.715
OHC
S
N
N
N
f1 (ppm)
1.07
1.99
0.93
0.99
0.98
2.02
1.00
0.93
0.94

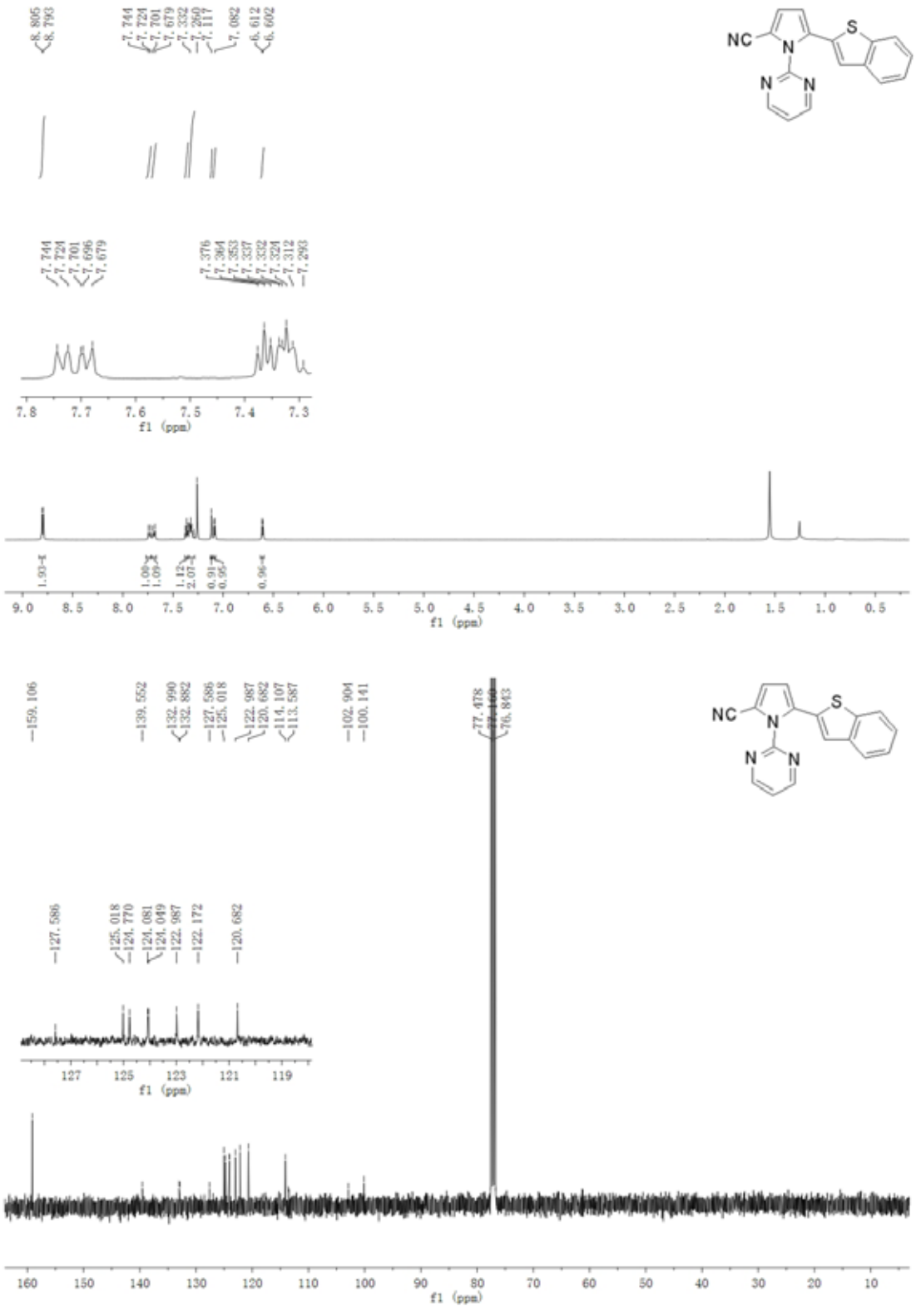

178.603
159.077
140.206
139.626
137.860
136.117
134.934
132.347
125.100
124.795
124.038
123.812
123.028
122.098
121.322
112.904
77.478
77.160
76.842
OHC
S
N
N
N
f1 (ppm)

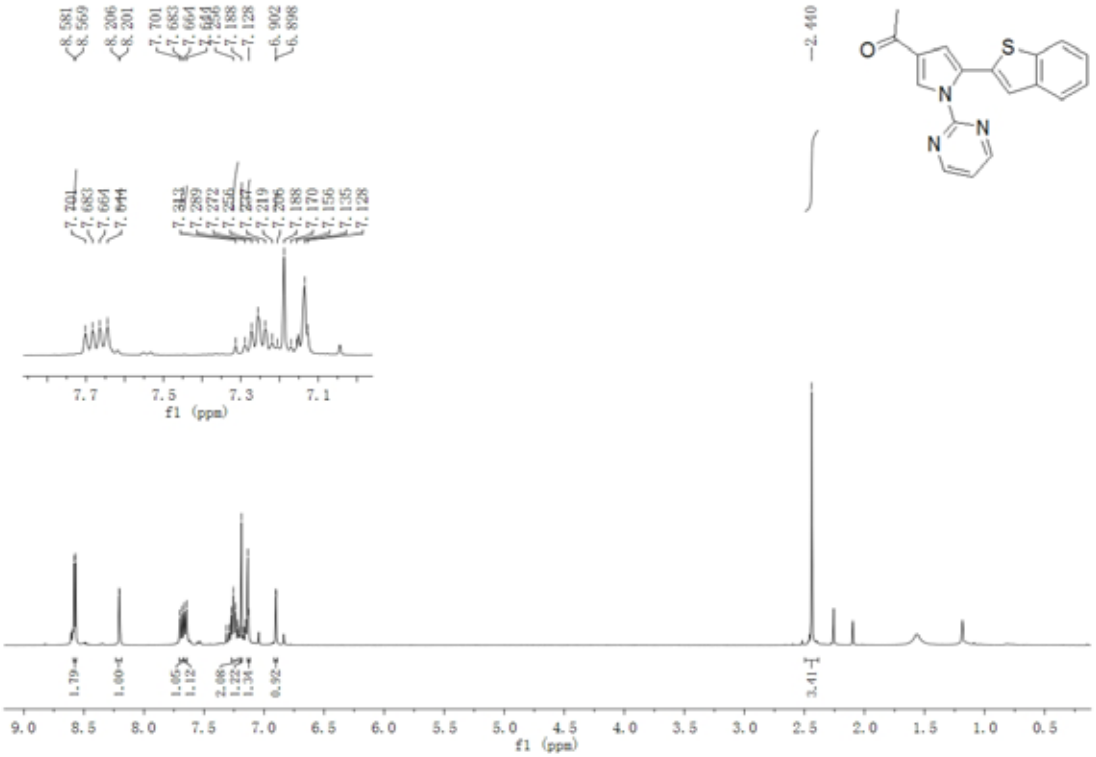

8.849
8.837
7.671
7.609
7.592
7.431
7.282
7.267
7.241
7.108
6.949
6.654
6.644
2.431
O
N
S
N
N
7.693
7.676
7.671
7.614
7.609
7.600
7.592
7.463
7.431
7.419
7.267
7.241
7.118
7.108
6.949
7.9
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
2.02
1.08
1.26
1.18
2.21
1.24
1.01
1.06
3.62
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

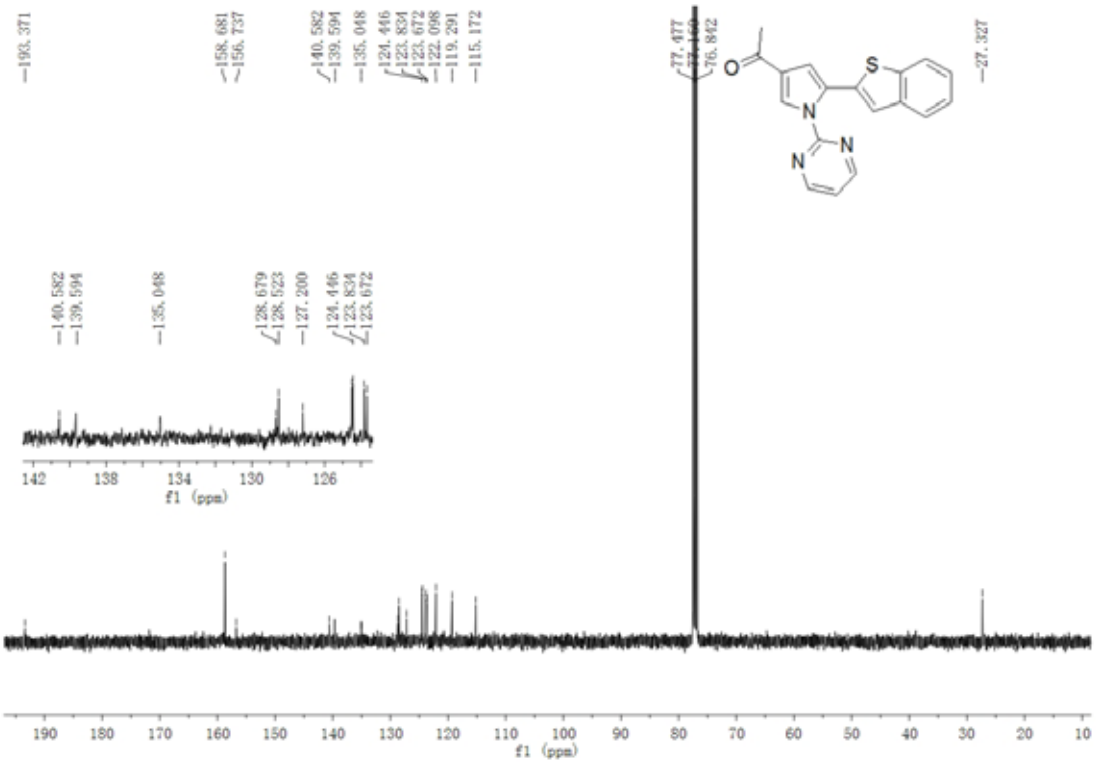

187.114
158.890
158.856
140.019
139.678
135.139
134.230
132.677
124.886
124.675
123.903
123.245
122.020
121.093
119.605
111.896
77.477
77.160
76.842
26.453
O
N
S
N
N
140.019
139.678
135.139
134.230
132.677
124.886
124.675
123.903
123.245
121.093
119.605
138
134
130
126
122
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

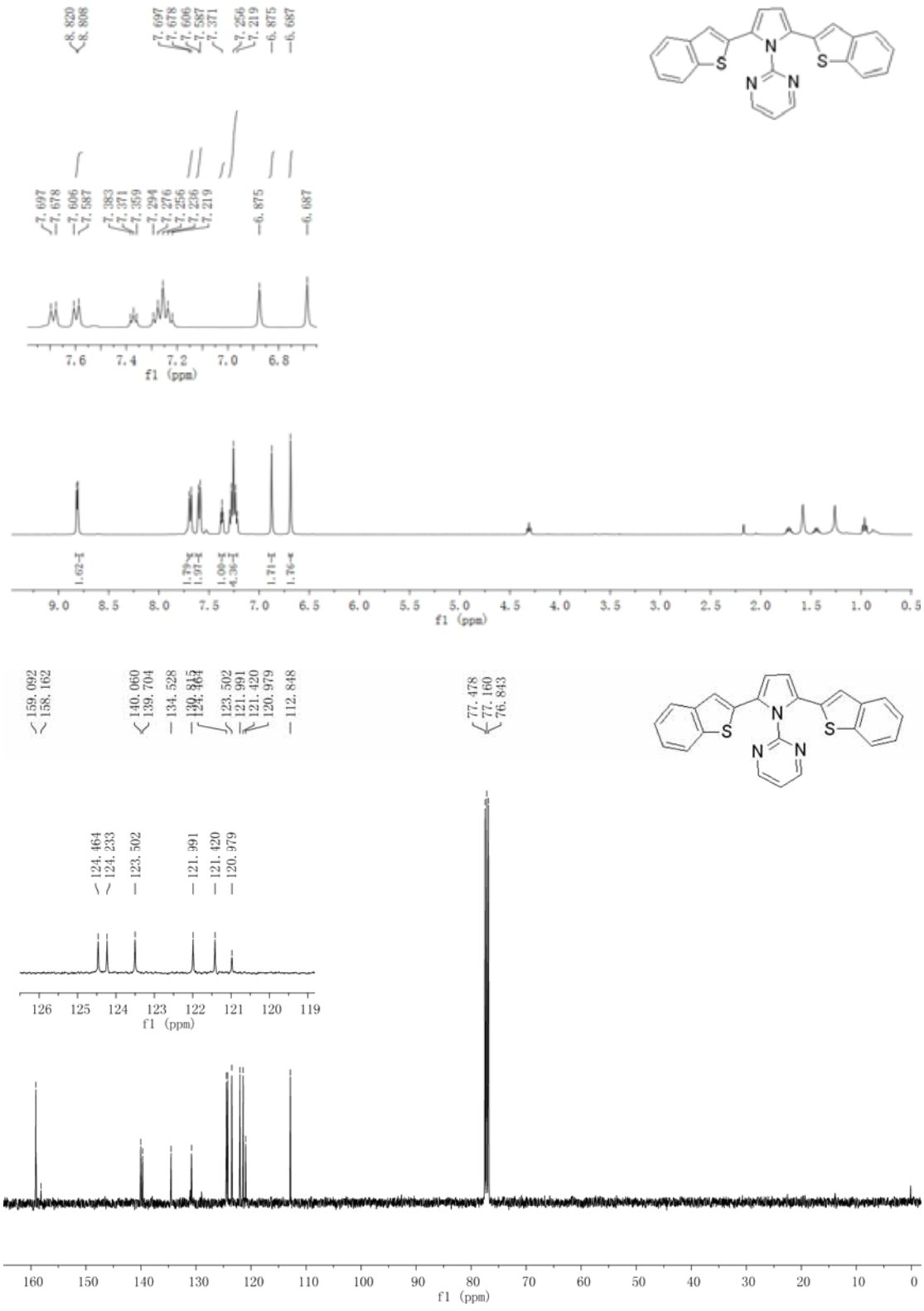

8.877
8.865
7.694
7.675
7.613
7.594
7.430
7.261
7.122
6.936
6.632
6.622
3.720
MeO2C
S
N
N
N
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.94
1.00
1.02
1.01
2.34
0.95
0.97
0.97
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

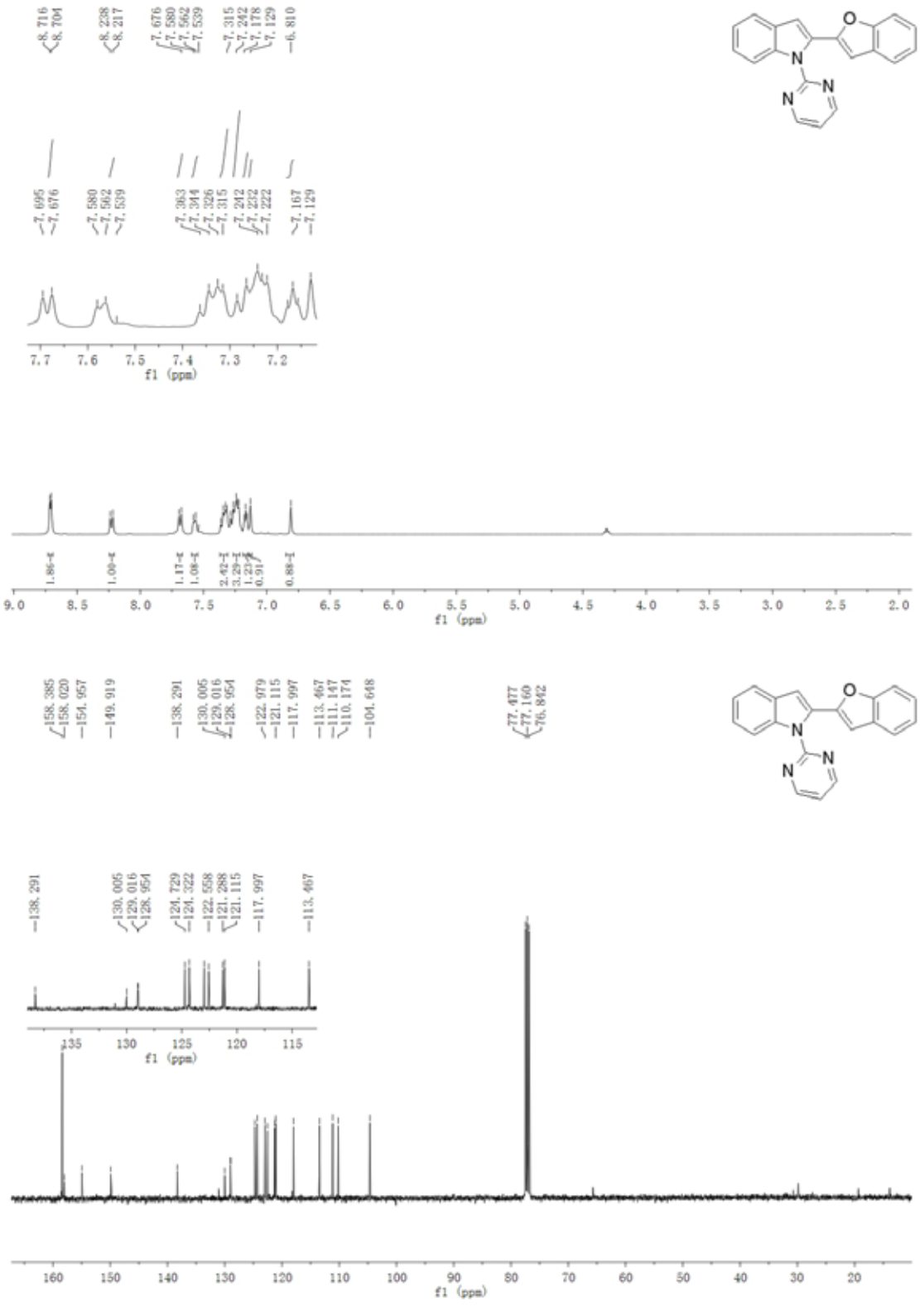

160.961
158.861
158.358
139.903
139.730
134.075
133.075
123.813
122.832
122.020
121.190
118.313
111.769
77.477
77.160
76.842
51.628
MeO2C
S
N
N
N
125.983
124.739
124.624
123.813
122.832
122.020
121.190
127 126 125 124 123 122 121 120
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

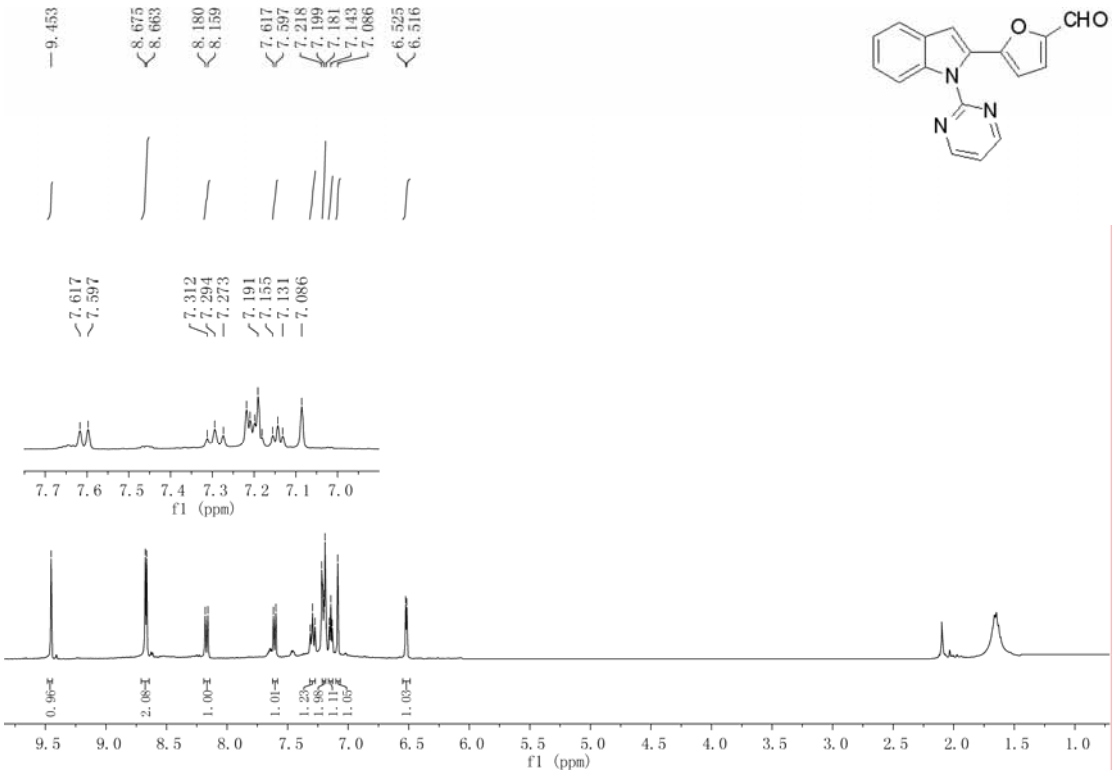


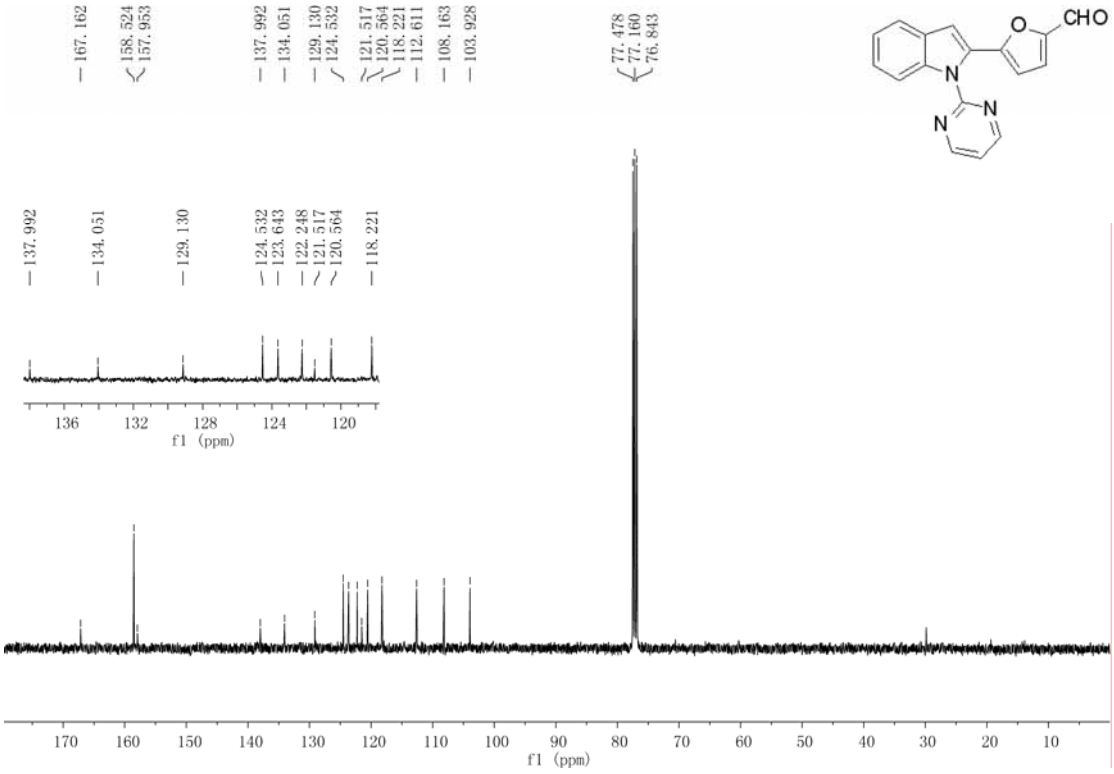

8.581
8.569
8.206
8.201
7.701
7.683
7.664
7.644
7.188
7.128
6.902
6.898
2.440
O
S
N
N
N
7.7
7.5
7.3
7.1
f1 (ppm)
1.79
1.60
1.05
1.12
2.66
1.22
1.34
0.92
3.41
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

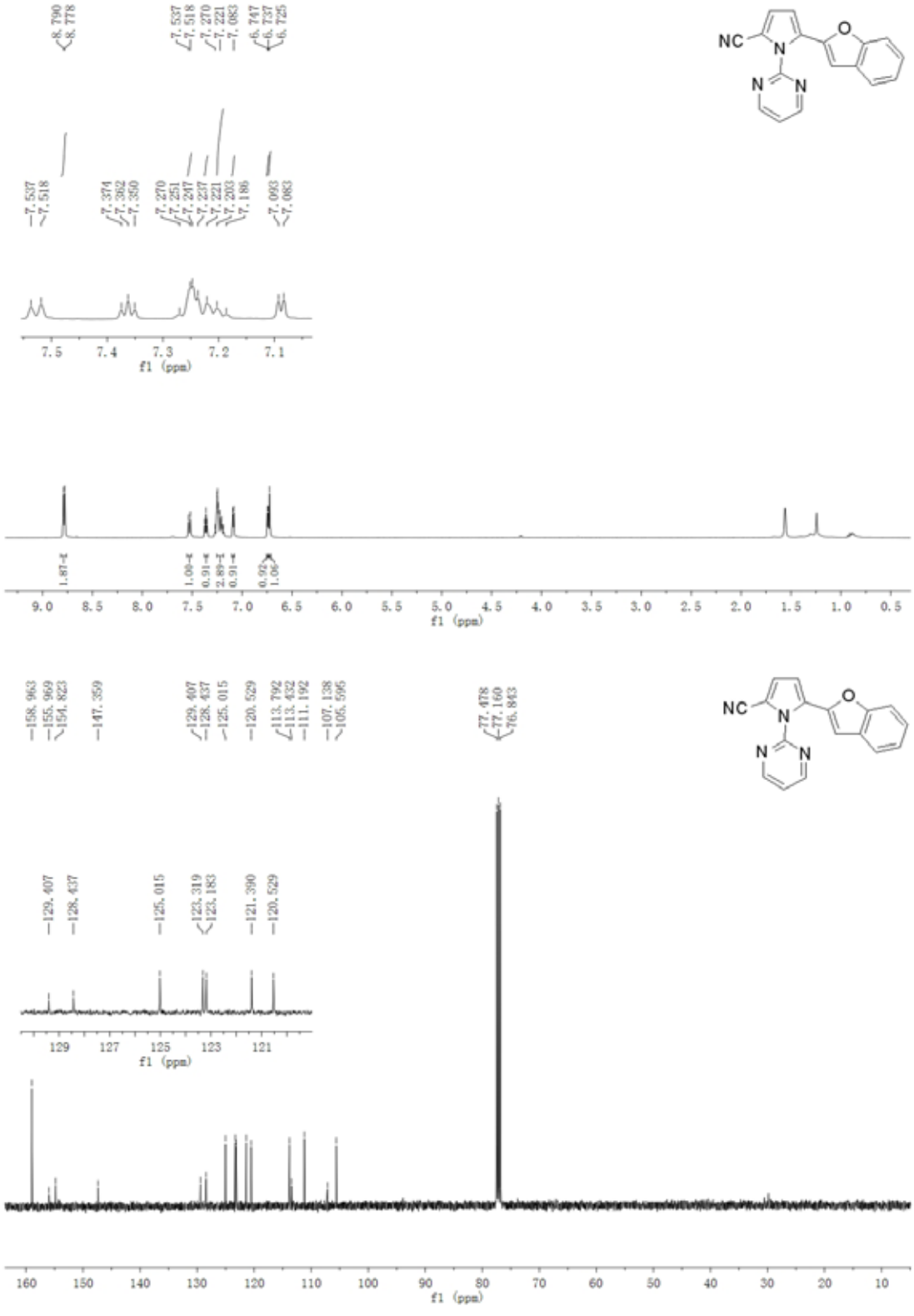

193.371
158.681
156.737
140.582
139.594
135.048
124.446
123.834
123.672
122.098
119.291
115.172
77.477
77.160
76.842
27.327
O
S
N
N
N
140.582
139.594
135.048
128.679
128.523
127.200
124.446
123.834
123.672
142
138
134
130
126
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

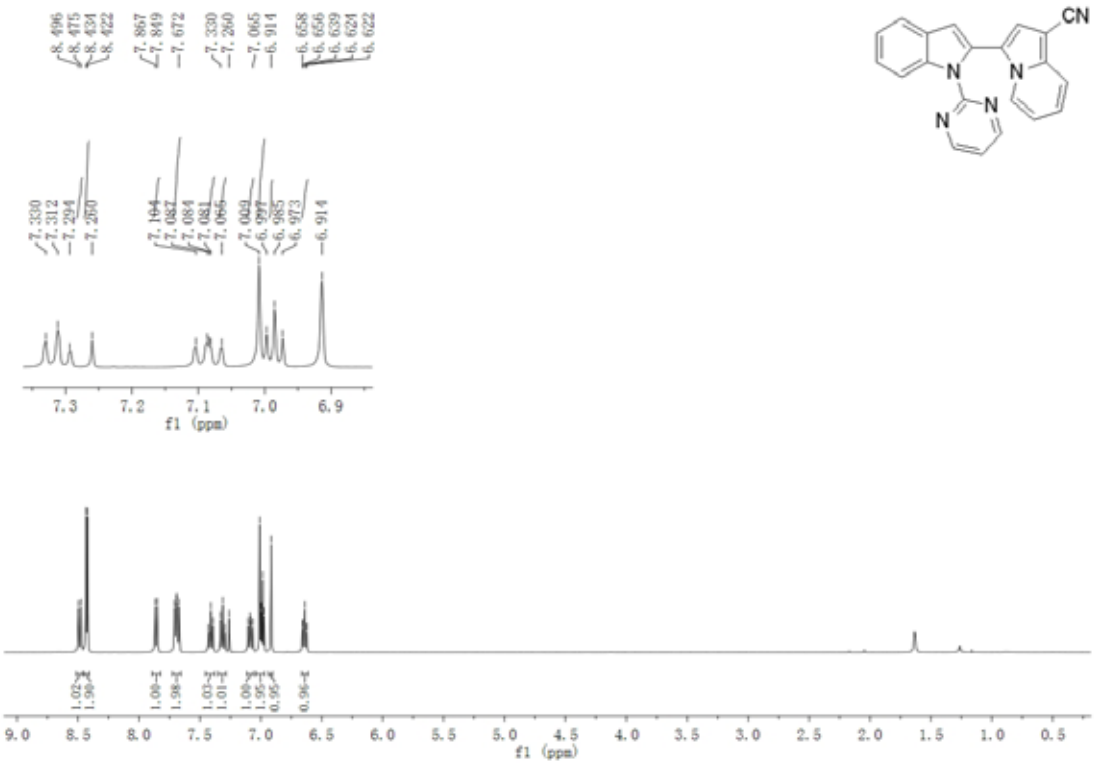

8.820
8.808
7.697
7.678
7.606
7.587
7.371
7.256
7.219
6.875
6.687
f1 (ppm)
159.092
158.162
140.060
139.704
134.528
123.502
121.991
121.420
120.979
112.848
77.478
77.160
76.843
124.464
124.233
123.502
121.991
121.420
120.979
f1 (ppm)
f1 (ppm)

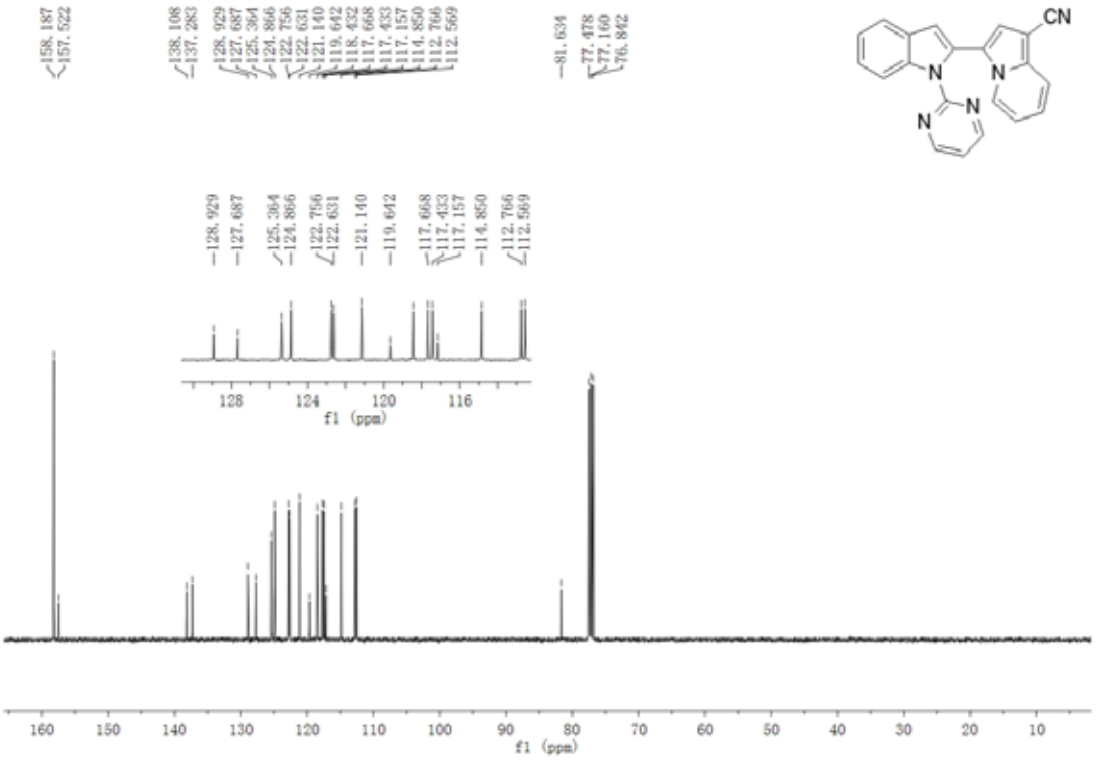

8.716
8.704
8.238
8.217
7.676
7.580
7.562
7.539
7.315
7.242
7.178
7.129
6.810
7.695
7.676
7.580
7.562
7.539
7.363
7.344
7.326
7.315
7.242
7.232
7.222
7.167
7.129
f1 (ppm)
1.86
1.00
1.17
1.08
2.42
3.29
1.23
0.91
0.88
f1 (ppm)
158.385
158.020
154.957
149.919
138.291
130.005
129.016
128.954
122.979
121.115
117.997
113.467
111.147
110.174
104.648
77.477
77.160
76.842
138.291
130.005
129.016
128.954
124.729
124.322
122.558
121.288
121.115
117.997
113.467
f1 (ppm)
f1 (ppm)

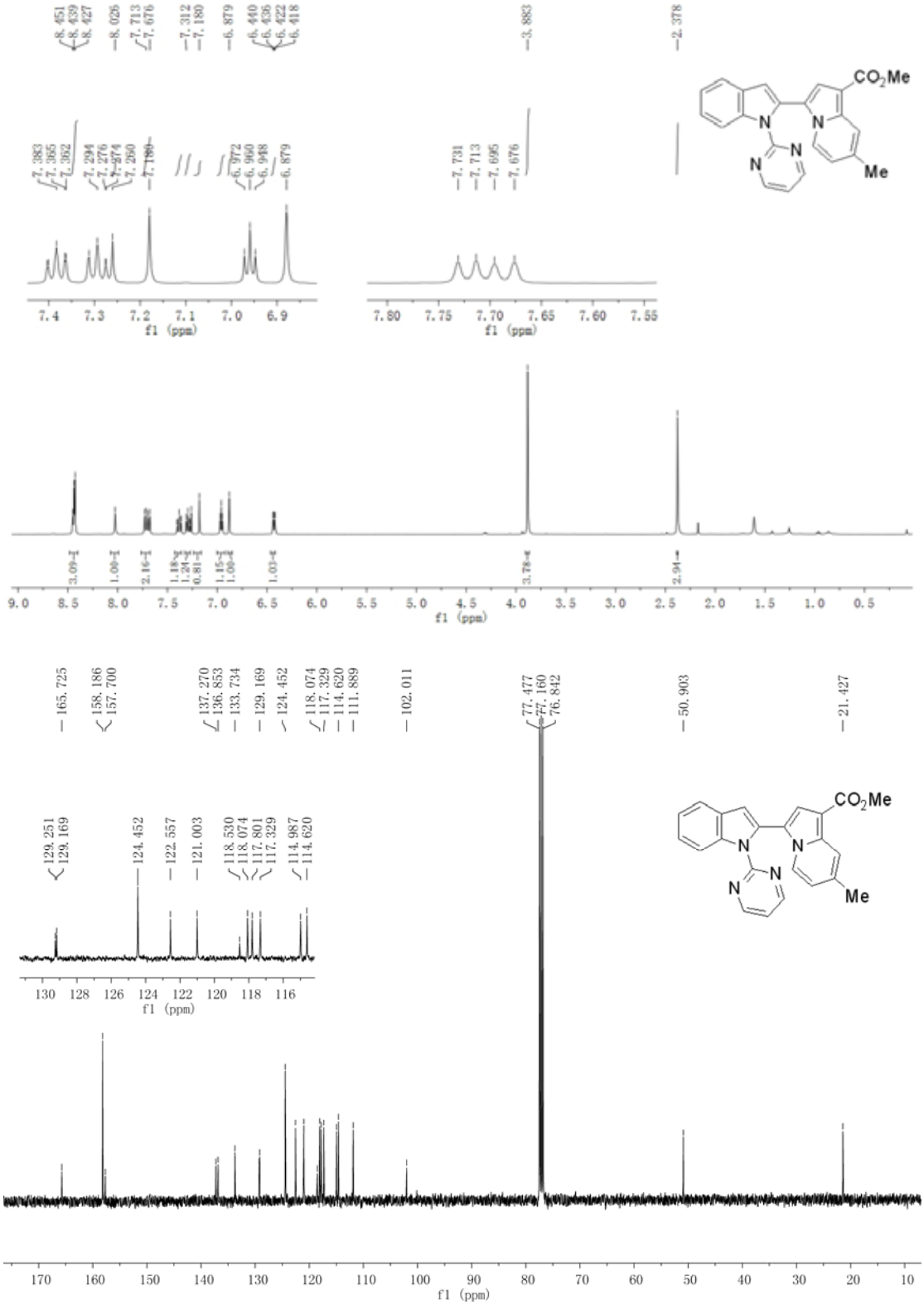

9.453
8.675
8.663
8.180
8.159
7.617
7.597
7.218
7.199
7.181
7.143
7.086
6.525
6.516
CHO
O
N
N
N
7.617
7.597
7.312
7.294
7.273
7.191
7.155
7.131
7.086
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
0.96
2.08
1.00
1.01
1.23
1.98
1.11
1.05
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

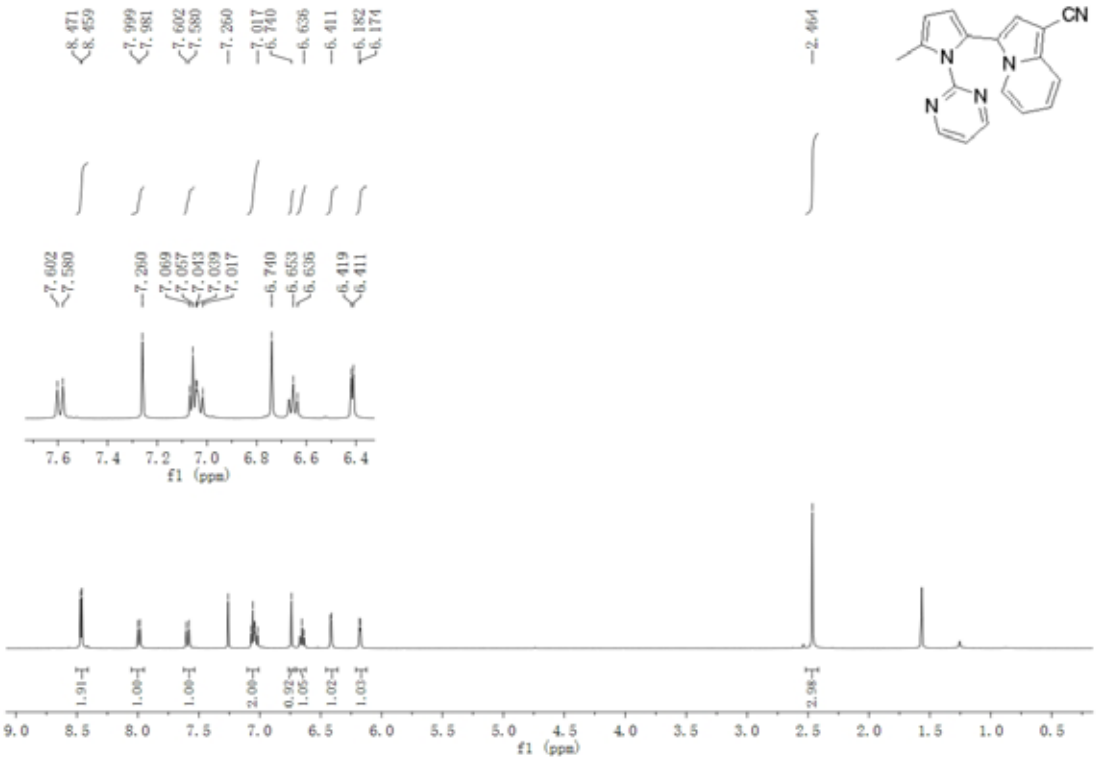

167.162
158.524
157.953
137.992
134.051
129.130
124.532
121.517
120.564
118.221
112.611
108.163
103.928
77.478
77.160
76.843
CHO
O
N
N
N
137.992
134.051
129.130
124.532
123.643
122.248
121.517
120.564
118.221
136 132 128 124 120
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

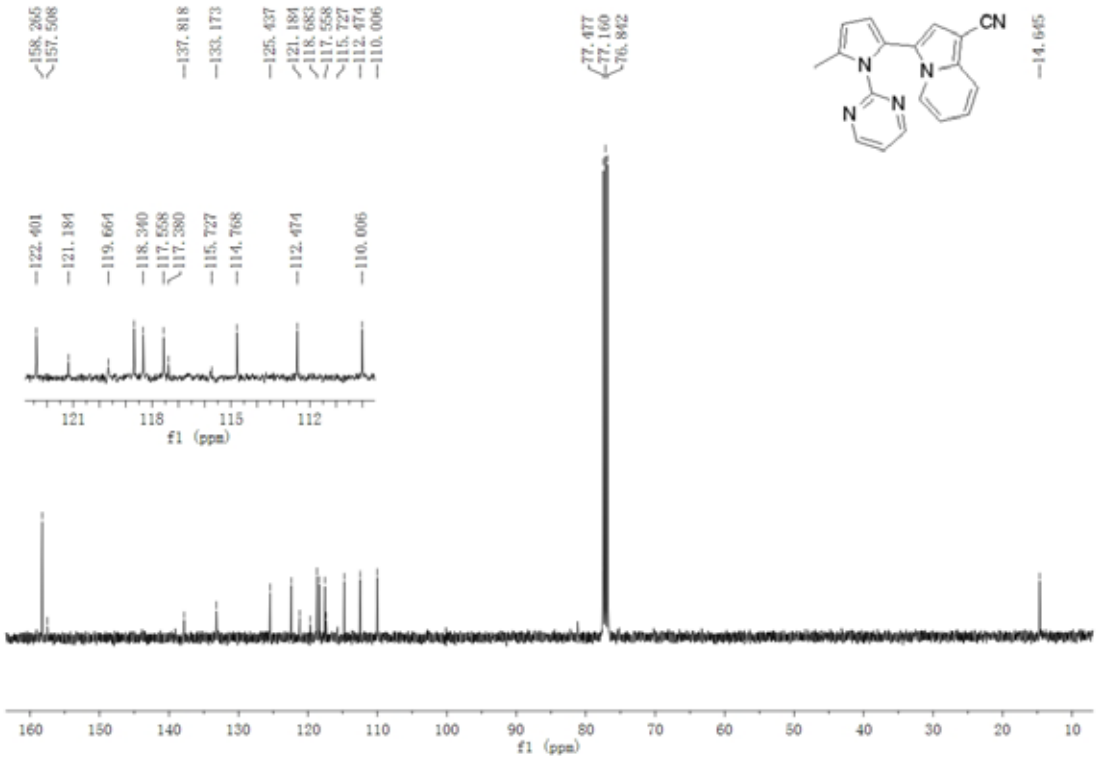

8.790
8.778
7.537
7.518
7.270
7.221
7.083
6.747
6.737
6.725
NC
O
N
N
N
7.374
7.362
7.350
7.270
7.251
7.247
7.237
7.221
7.203
7.186
7.093
7.083
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
1.87
1.00
0.91
2.89
0.91
0.92
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
158.963
155.969
154.823
147.359
129.407
128.437
125.015
120.529
113.792
113.432
111.192
107.138
105.595
77.478
77.160
76.843
NC
O
N
N
N
129.407
128.437
125.015
123.319
123.183
121.390
120.529
129
127
125
123
121
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

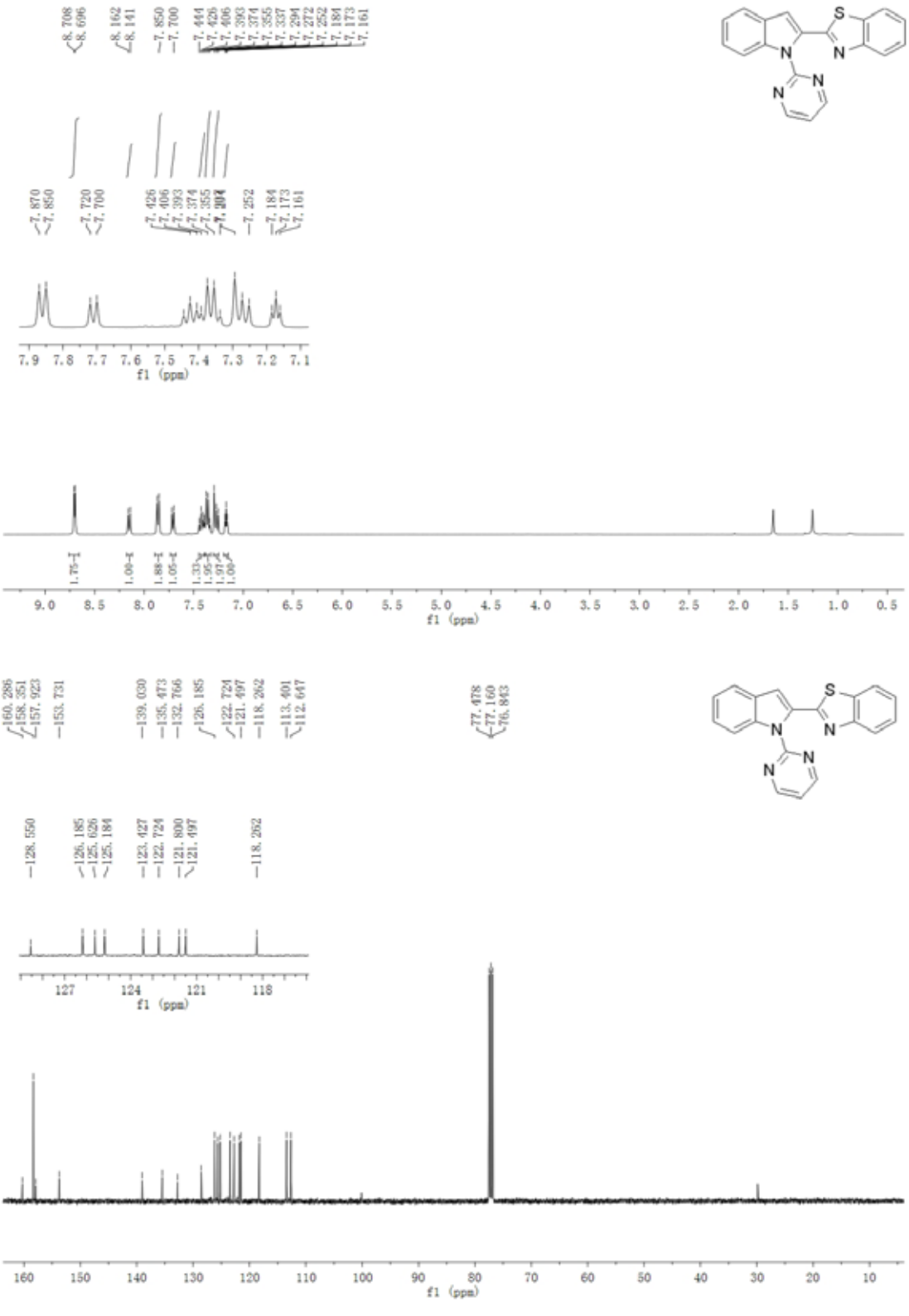

8.496
8.475
8.434
8.422
7.867
7.849
7.672
7.330
7.260
7.065
6.914
6.658
6.656
6.639
6.621
6.622
CN
N
N
N
7.330
7.312
7.294
7.260
7.184
7.082
7.084
7.081
7.065
7.049
6.997
6.985
6.973
6.914
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
1.02
1.98
1.00
1.98
1.03
1.01
1.08
1.95
0.95
0.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

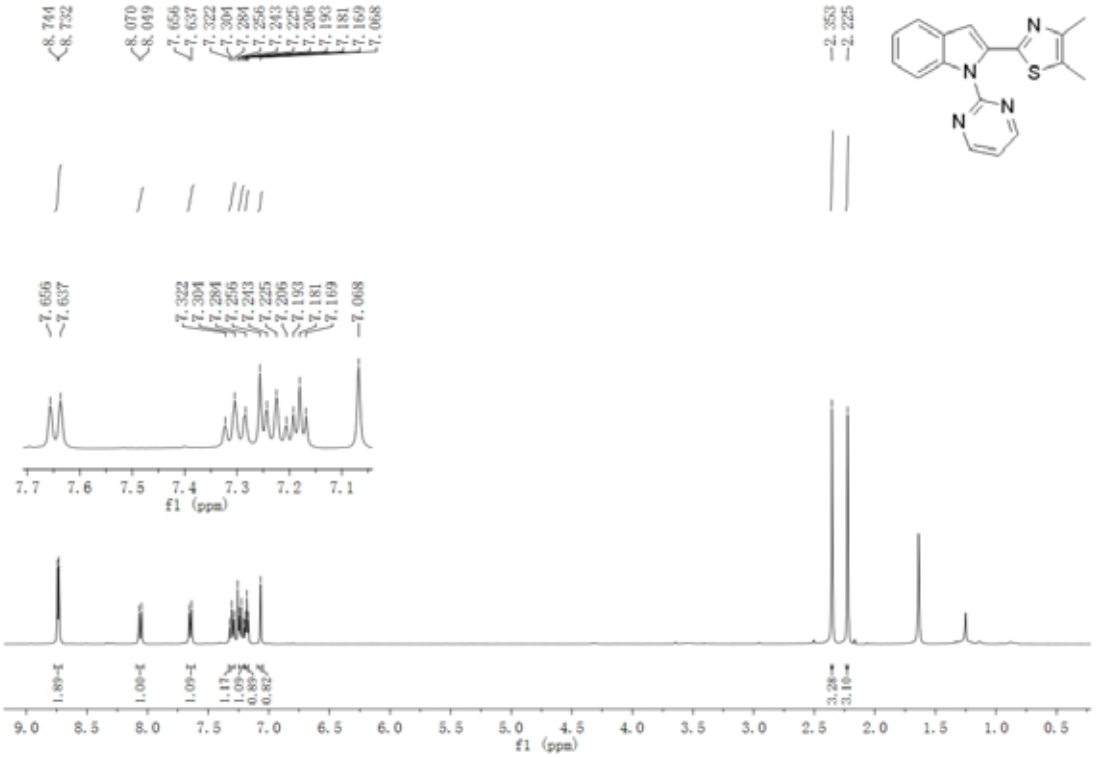

158.187
157.522
138.108
137.283
128.929
127.687
125.384
124.866
122.756
122.631
121.140
119.642
118.432
117.668
117.433
117.157
114.850
112.766
112.569
81.634
77.478
77.160
76.842
CN
N
N
N
128.929
127.687
125.384
124.866
122.756
122.631
121.140
119.642
117.668
117.433
117.157
114.850
112.766
112.569
128
124
120
116
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

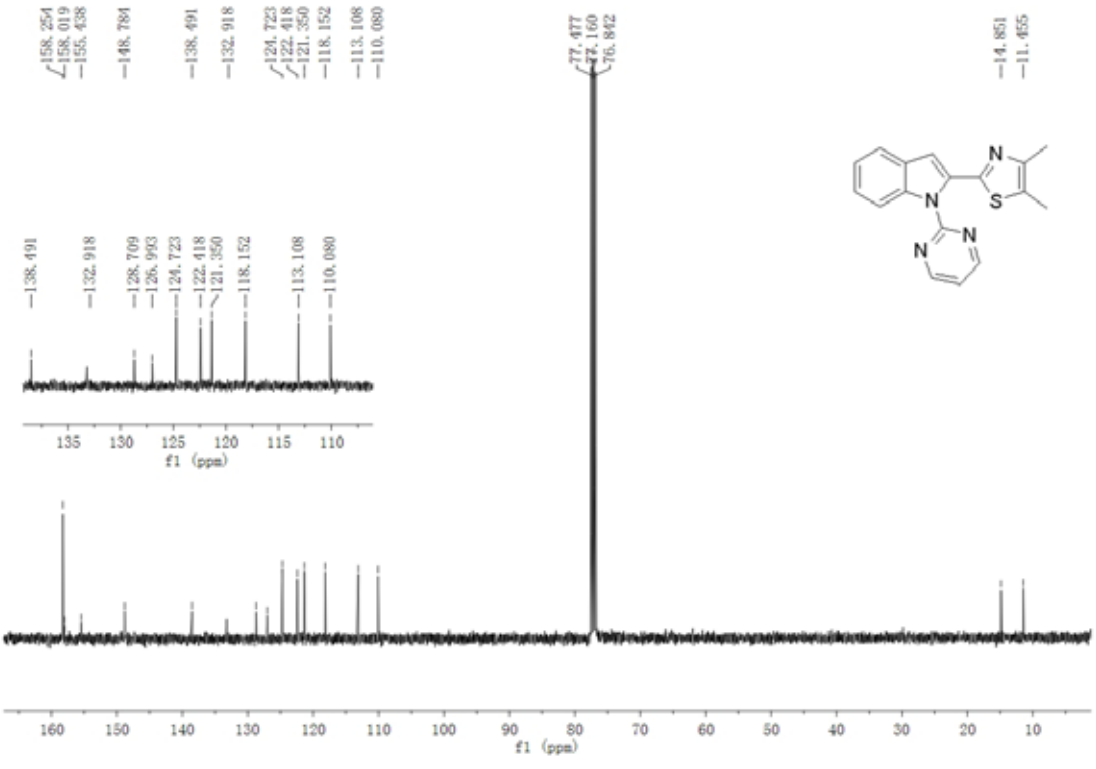

8.451
8.439
8.427
8.026
7.713
7.676
7.312
7.180
6.879
6.440
6.436
6.422
6.418
3.883
2.378
CO2Me
Me
f1 (ppm)
165.725
158.186
157.700
137.270
136.853
133.734
129.169
124.452
118.074
117.329
114.620
111.889
102.011
77.477
77.160
76.842
50.903
21.427
129.251
129.169
124.452
122.557
121.003
118.530
118.074
117.801
117.329
114.987
114.620

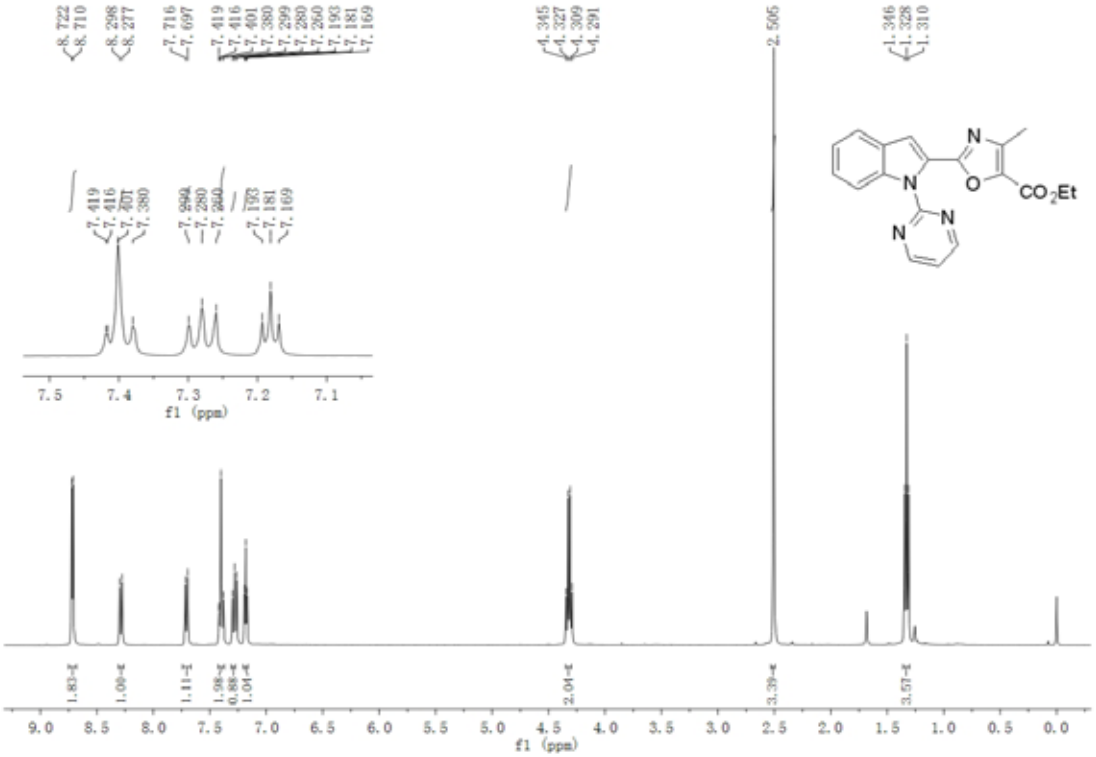

8.471
8.459
7.999
7.981
7.602
7.580
7.260
7.017
6.740
6.636
6.411
6.182
6.174
2.464
CN
N
N
N
7.602
7.580
7.260
7.069
7.057
7.043
7.039
7.017
6.740
6.653
6.636
6.419
6.411
7.6
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
1.91
1.00
1.00
2.00
0.92
1.05
1.02
1.03
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

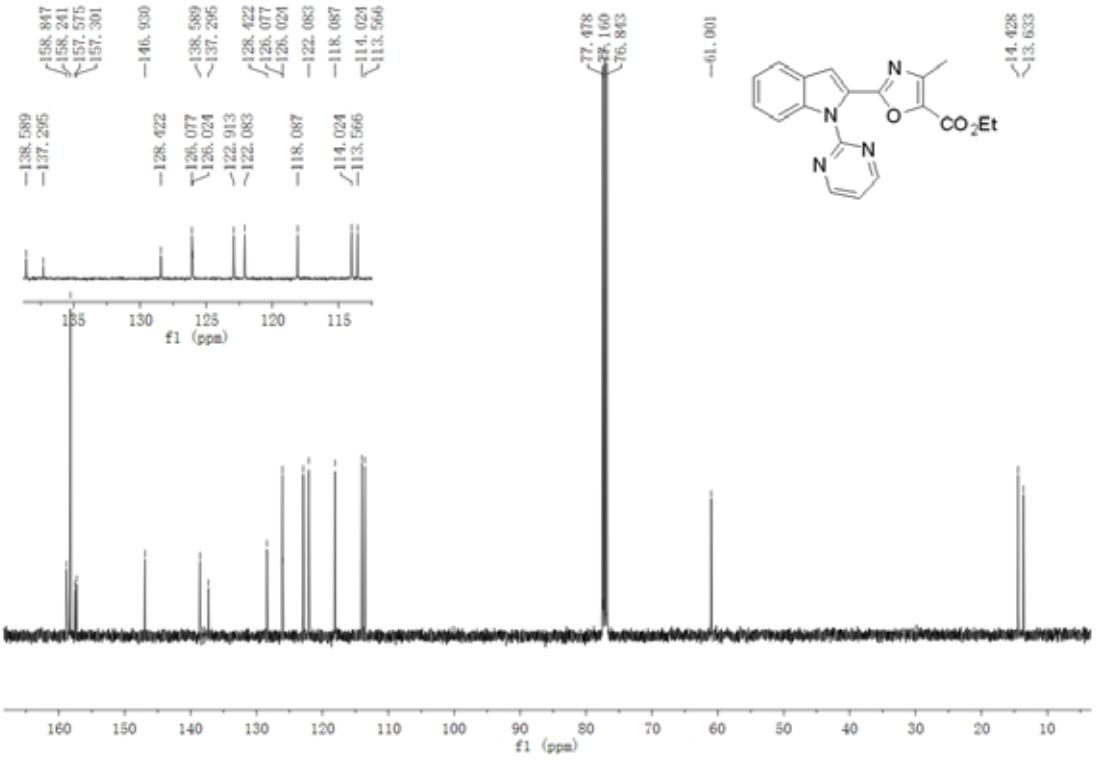

158.265
157.508
137.818
133.173
125.437
121.184
118.683
117.558
115.727
112.474
110.006
77.477
77.160
76.842
14.645
CN
N
N
N
122.401
121.184
119.664
118.340
117.558
117.380
115.727
114.768
112.474
110.006
121
118
115
112
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

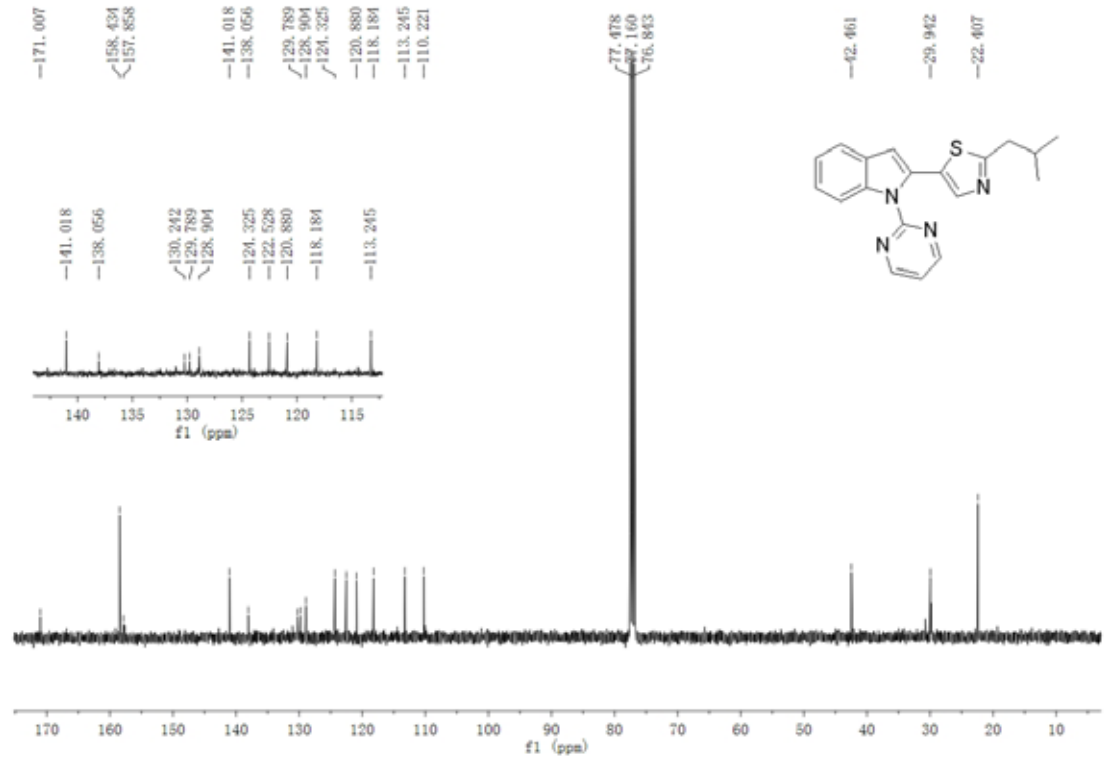

8.708
8.696
8.162
8.141
7.850
7.700
7.444
7.426
7.406
7.393
7.374
7.355
7.337
7.294
7.272
7.252
7.184
7.173
7.161
S
N
N
N
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
160.286
158.351
157.923
153.731
139.030
135.473
132.766
126.185
122.724
121.497
118.262
113.401
112.647
77.478
77.160
76.843
128.550
126.185
125.626
125.184
123.427
122.724
121.800
121.497
118.262
127 124 121 118
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

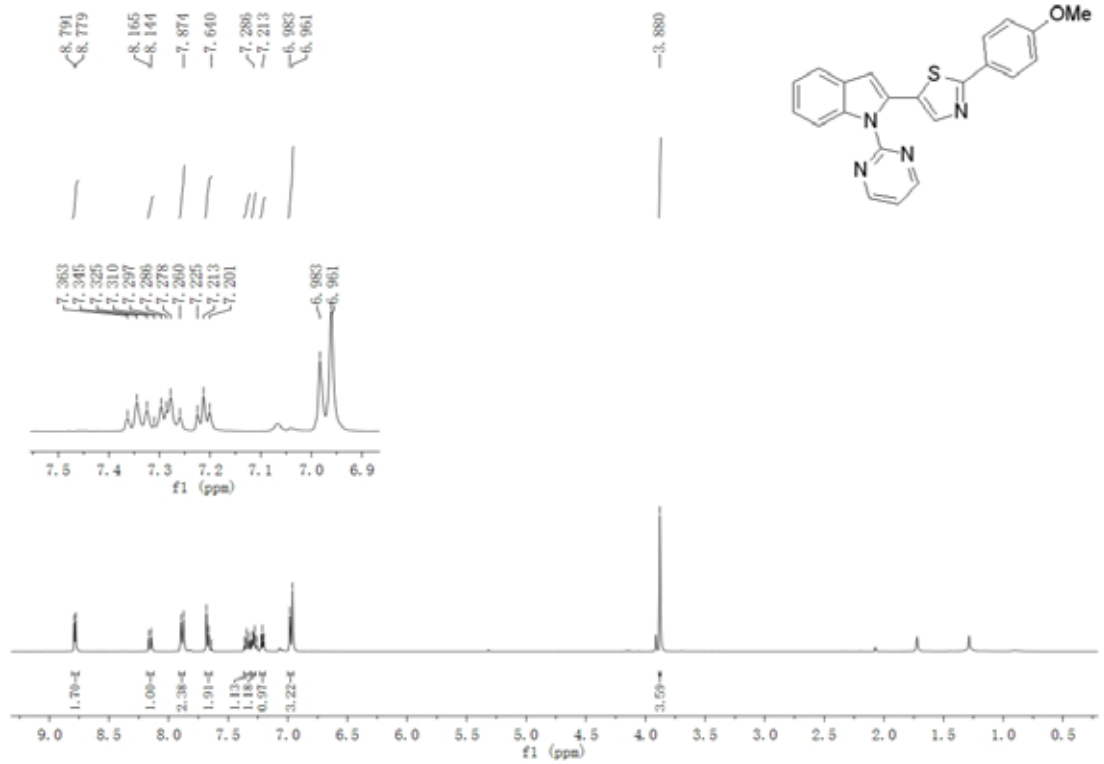

8.744
8.732
8.070
8.049
7.656
7.637
7.322
7.304
7.284
7.256
7.243
7.225
7.206
7.193
7.181
7.169
7.068
2.353
2.225
f1 (ppm)
1.89
1.00
1.09
1.17
1.09
0.89
0.82
3.28
3.10

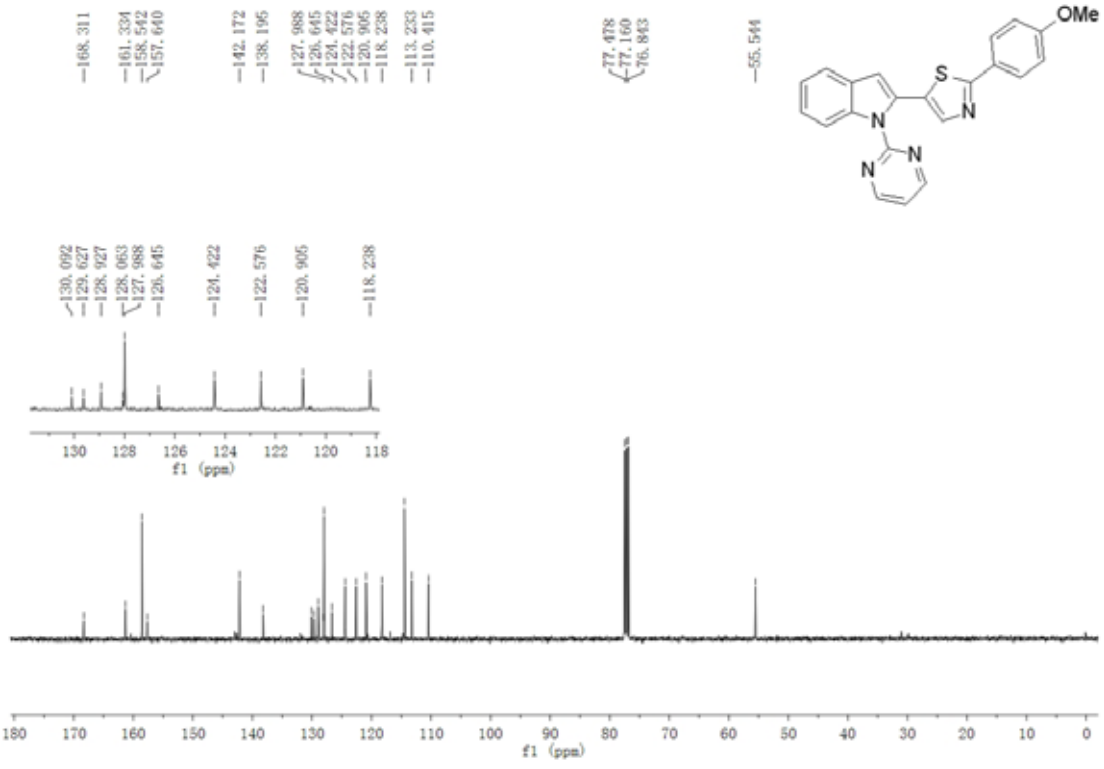

158.254
158.019
155.438
148.784
138.491
132.918
124.723
122.418
121.350
118.152
113.108
110.080
77.477
77.160
76.842
14.851
11.455
f1 (ppm)

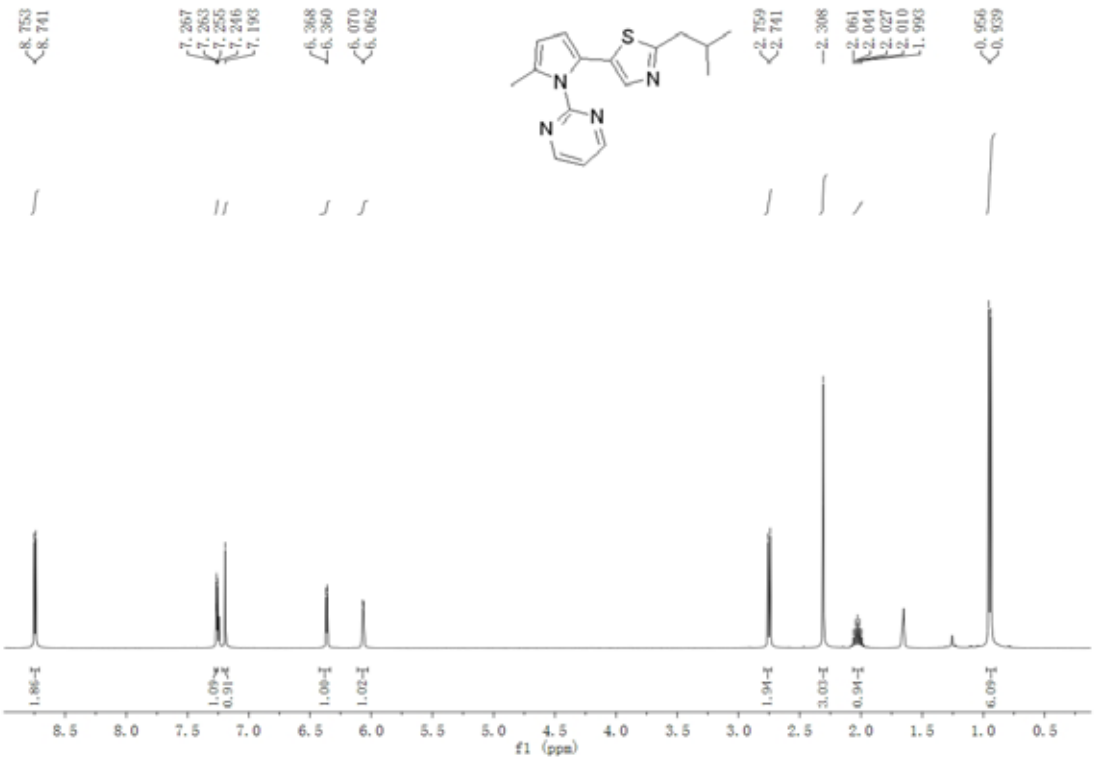


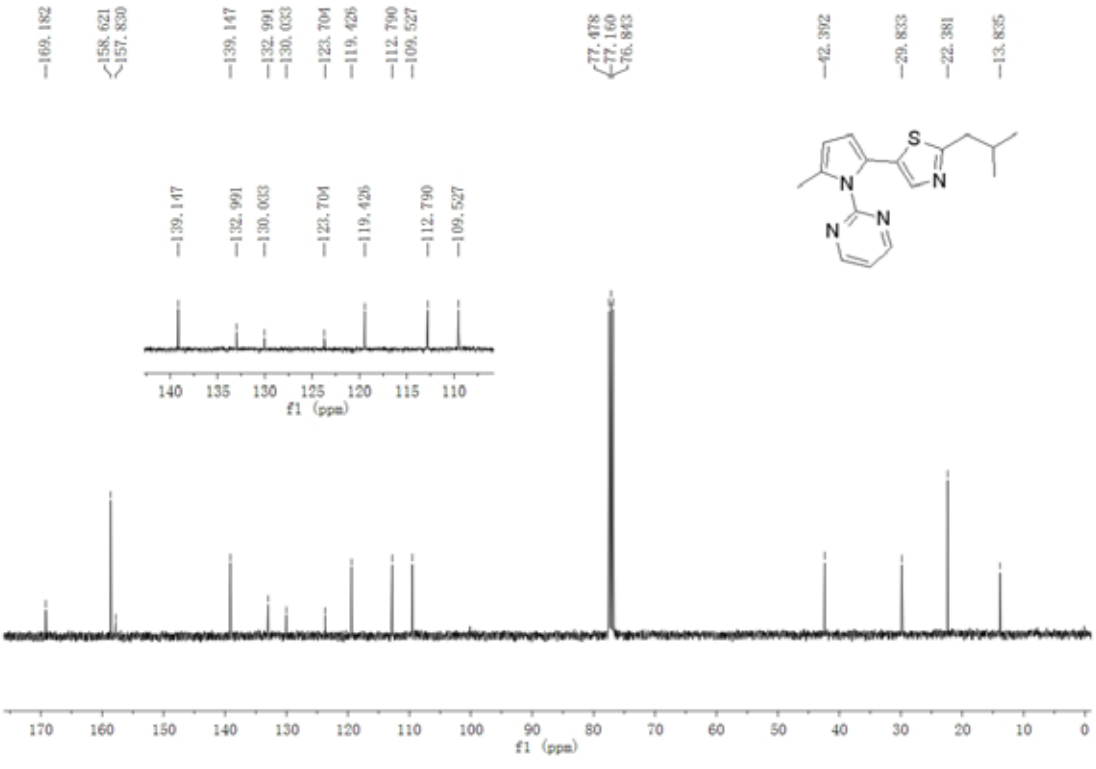


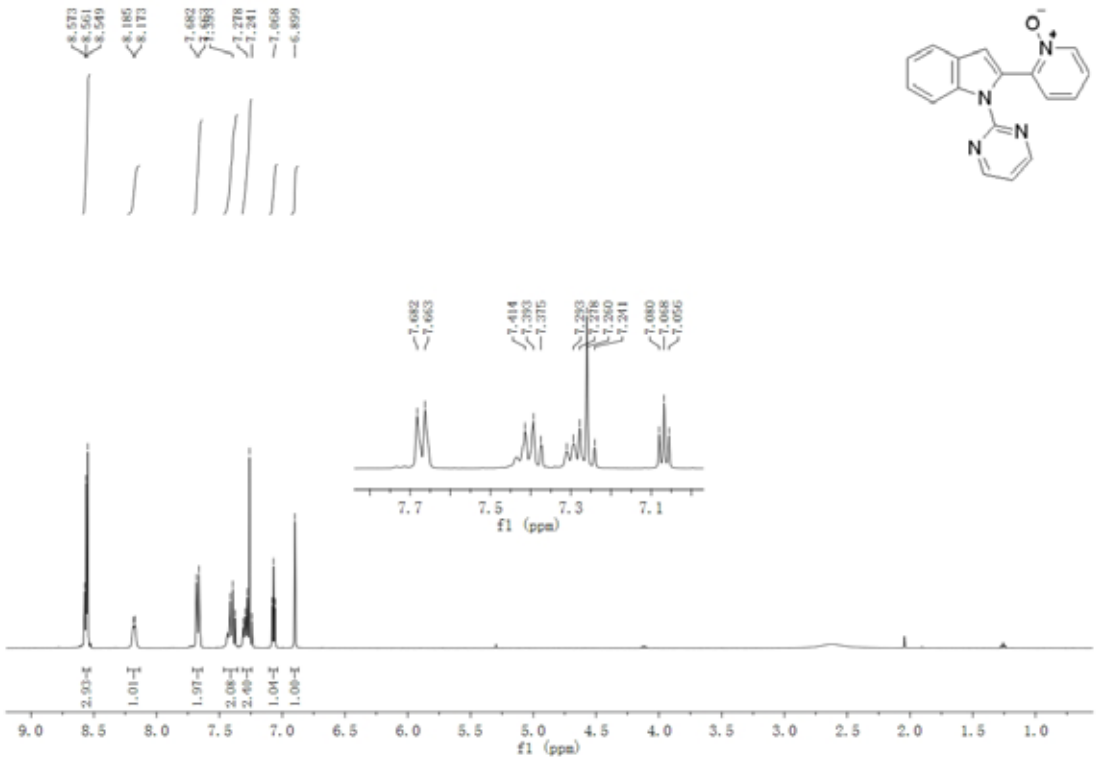


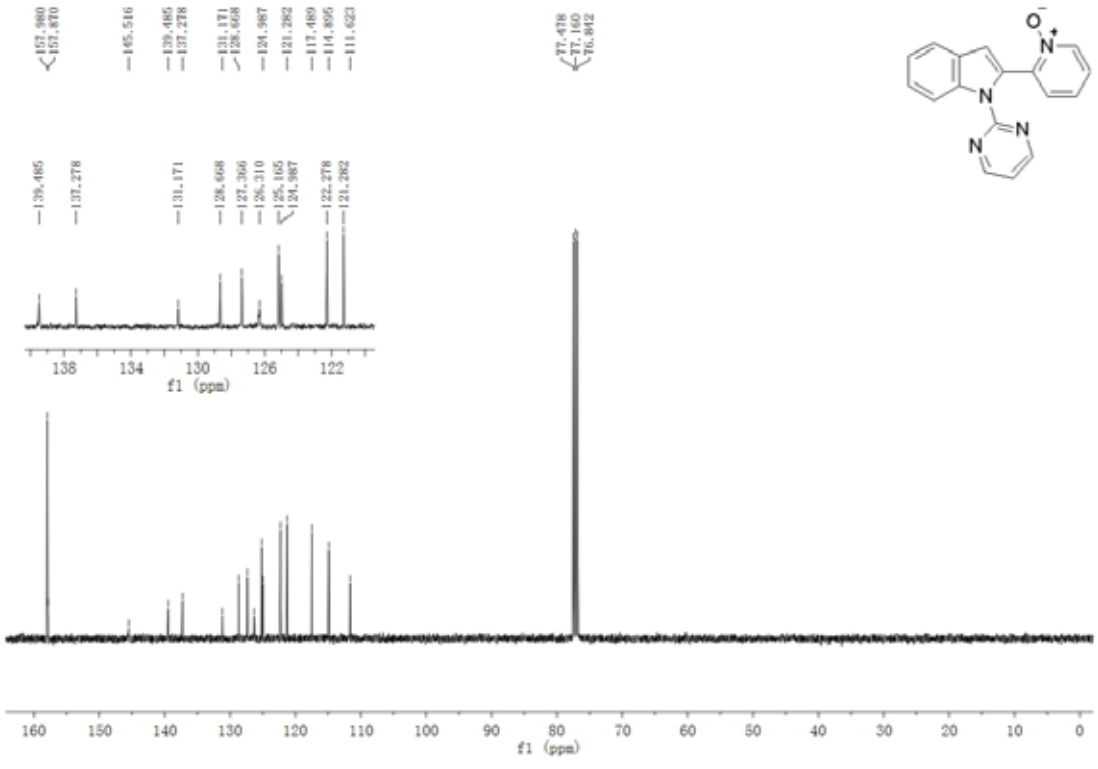

OMe
S
N
N
N
N
f1 (ppm)

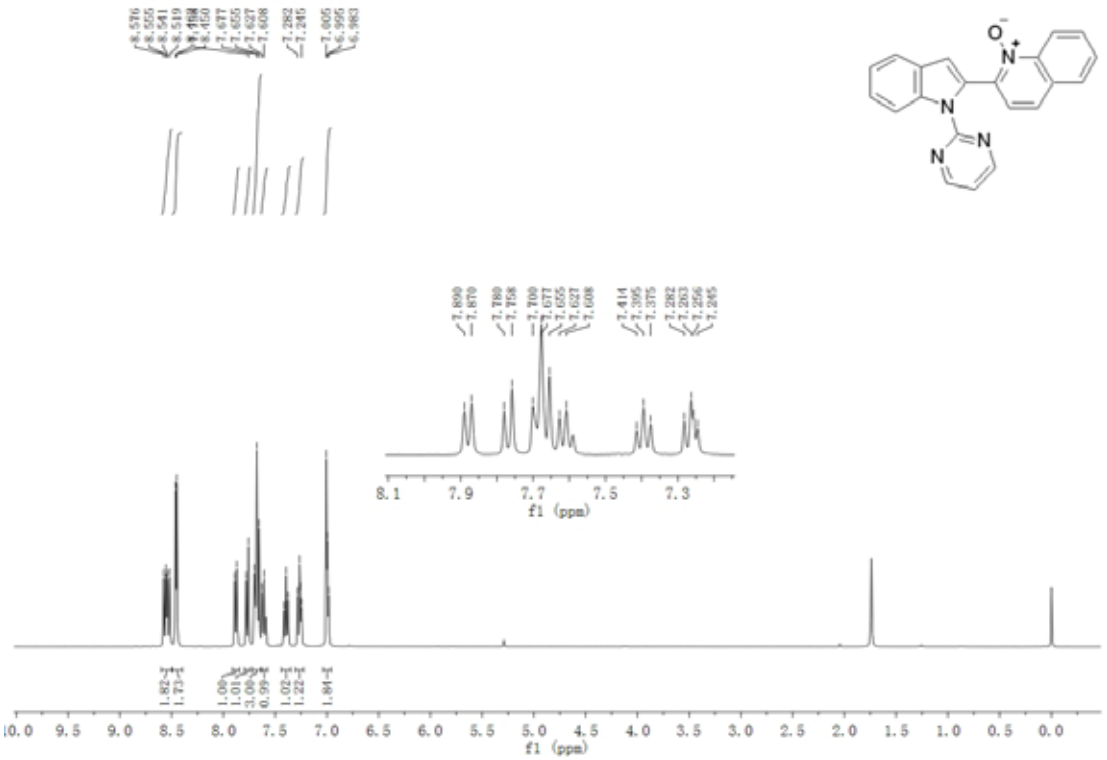

OMe
S
N
N
N
N
f1 (ppm)

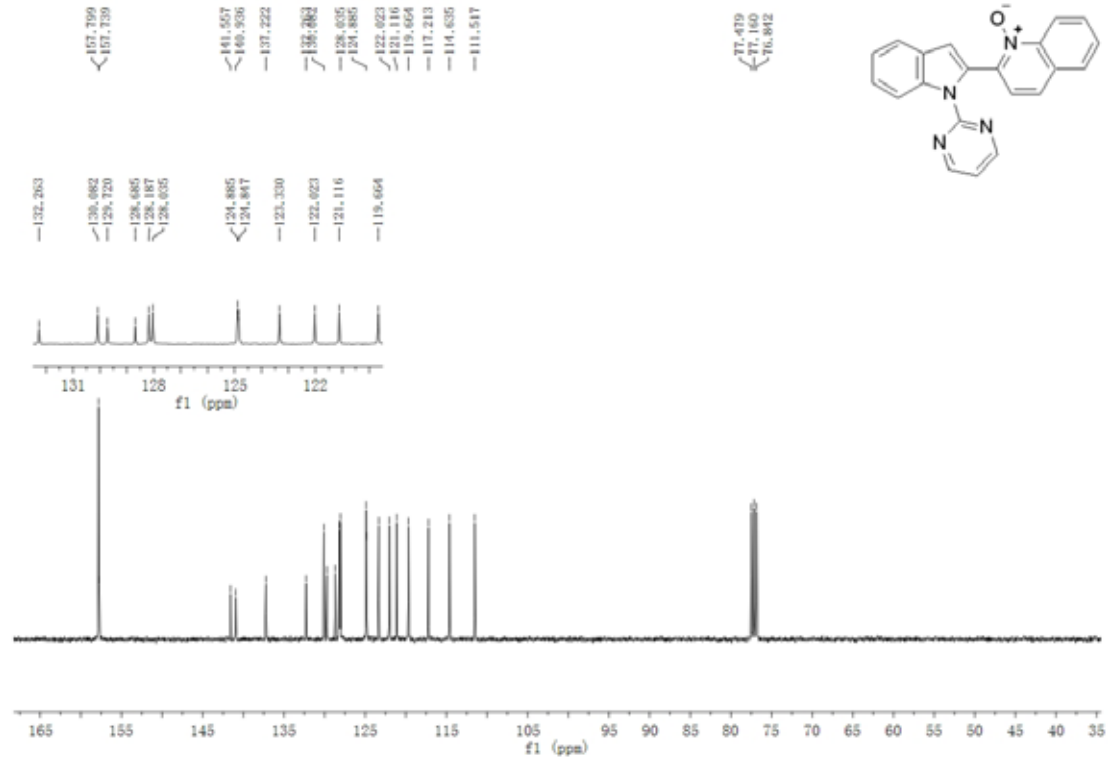

8.753
8.741
7.267
7.263
7.255
7.246
7.193
6.368
6.360
6.070
6.062
2.759
2.741
2.308
2.061
2.044
2.027
2.010
1.993
0.956
0.939
1.86
1.09
0.91
1.00
1.02
1.94
3.03
0.94
6.09
f1 (ppm)

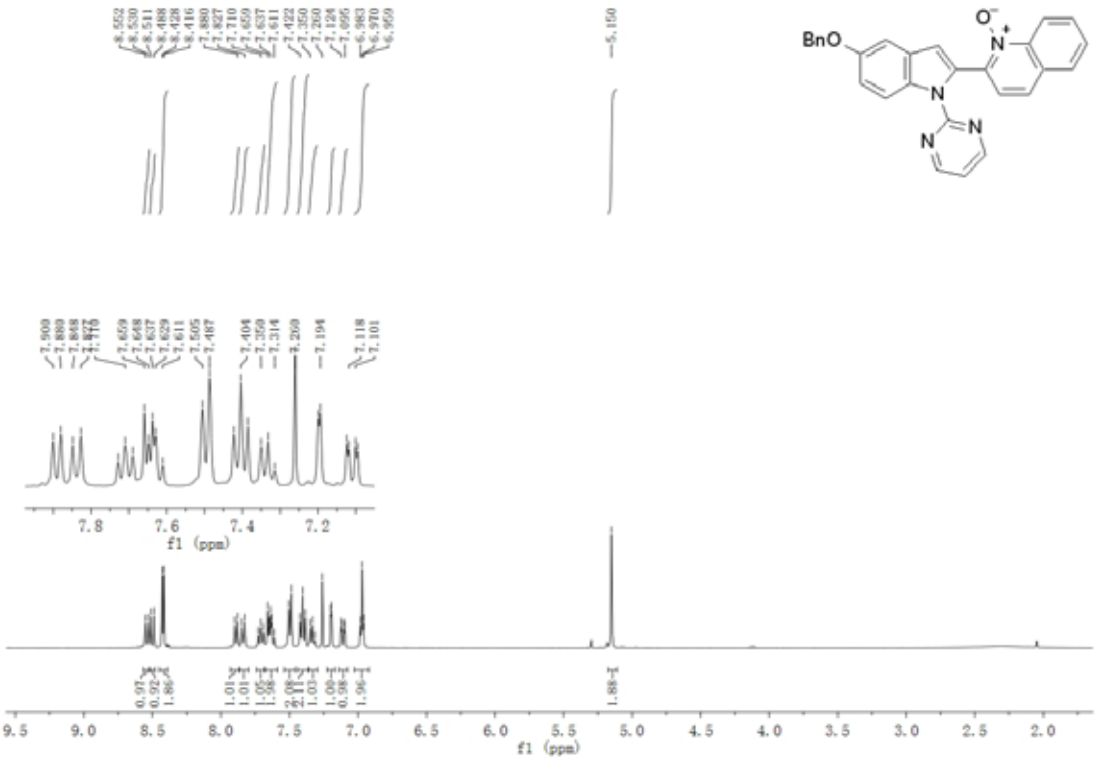

169.182
158.621
157.830
139.147
132.991
130.033
123.704
119.426
112.790
109.527
77.478
77.160
76.843
62.392
29.833
22.381
13.835
f1 (ppm)

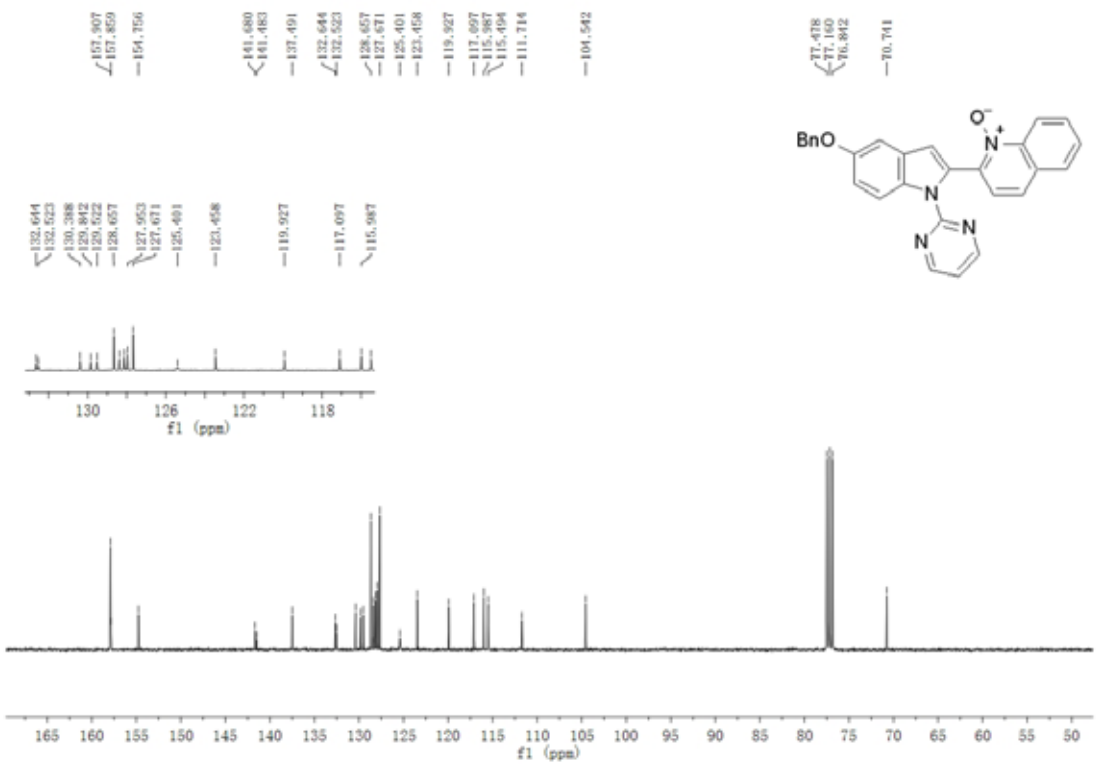

8.573
8.561
8.549
8.185
8.173
7.682
7.663
7.414
7.393
7.375
7.278
7.241
7.080
7.068
7.056
6.899
2.93
1.01
1.97
2.08
2.40
1.04
1.00
f1 (ppm)

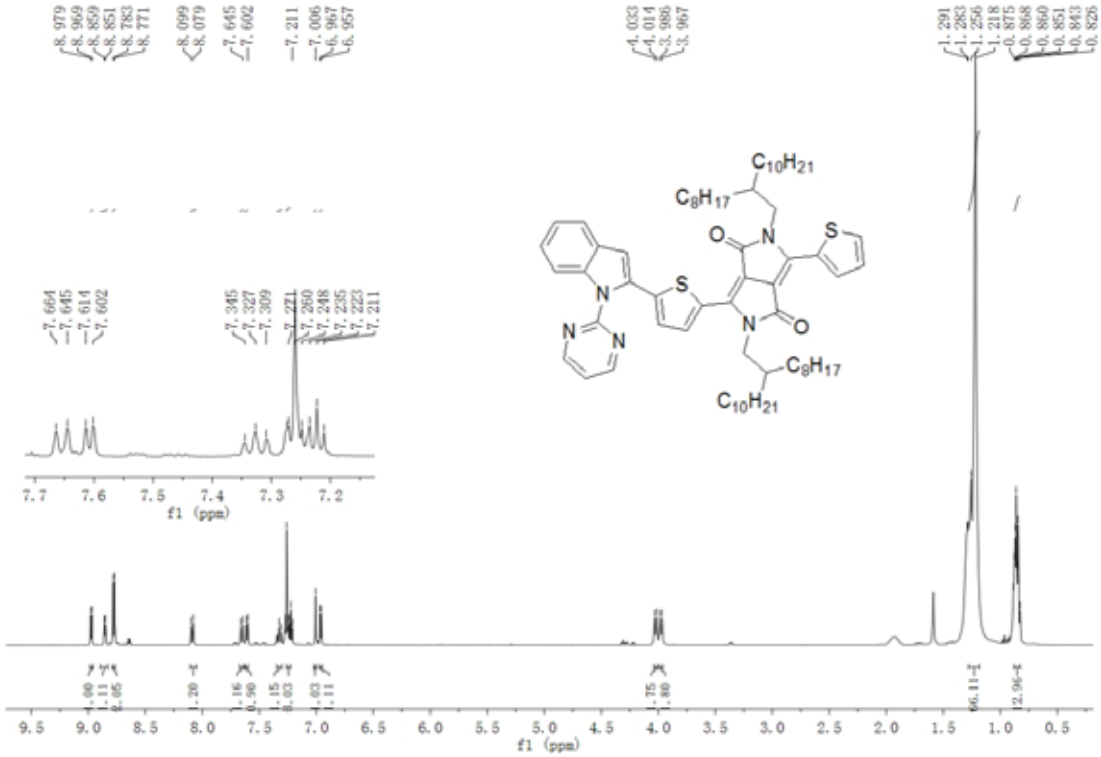

157.980
157.870
145.516
139.485
137.278
131.171
128.668
124.987
121.282
117.489
114.895
111.623
77.478
77.160
76.842
f1 (ppm)

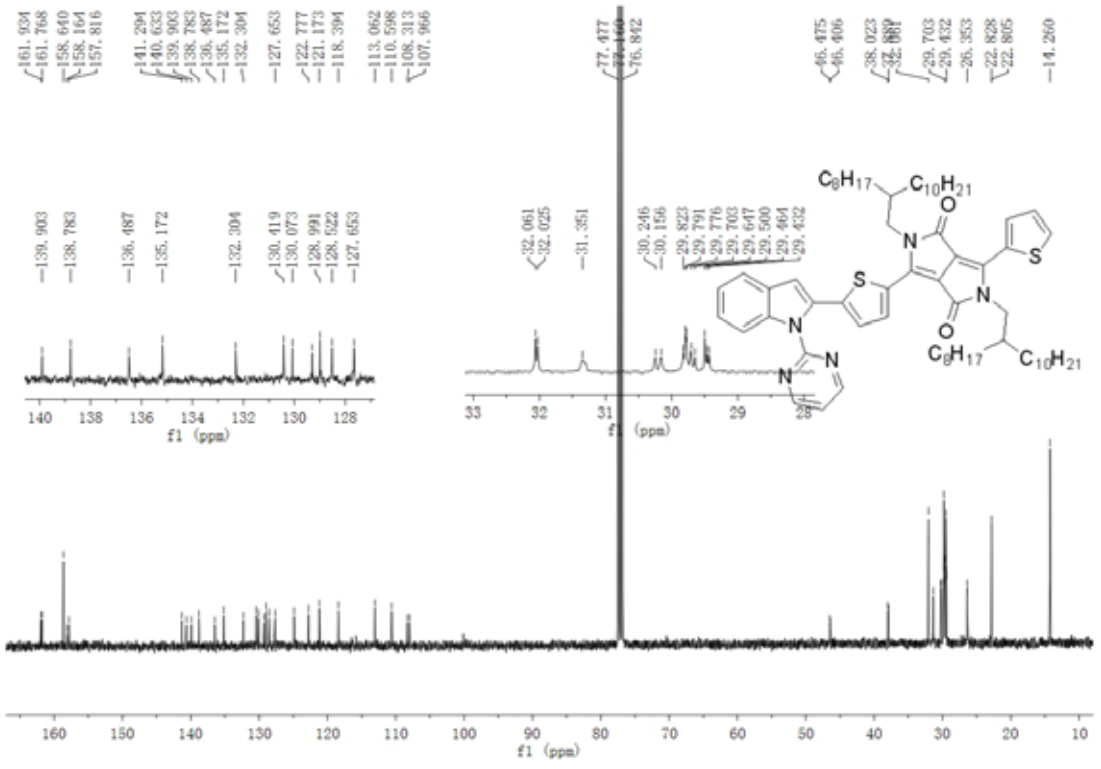

f1 (ppm)

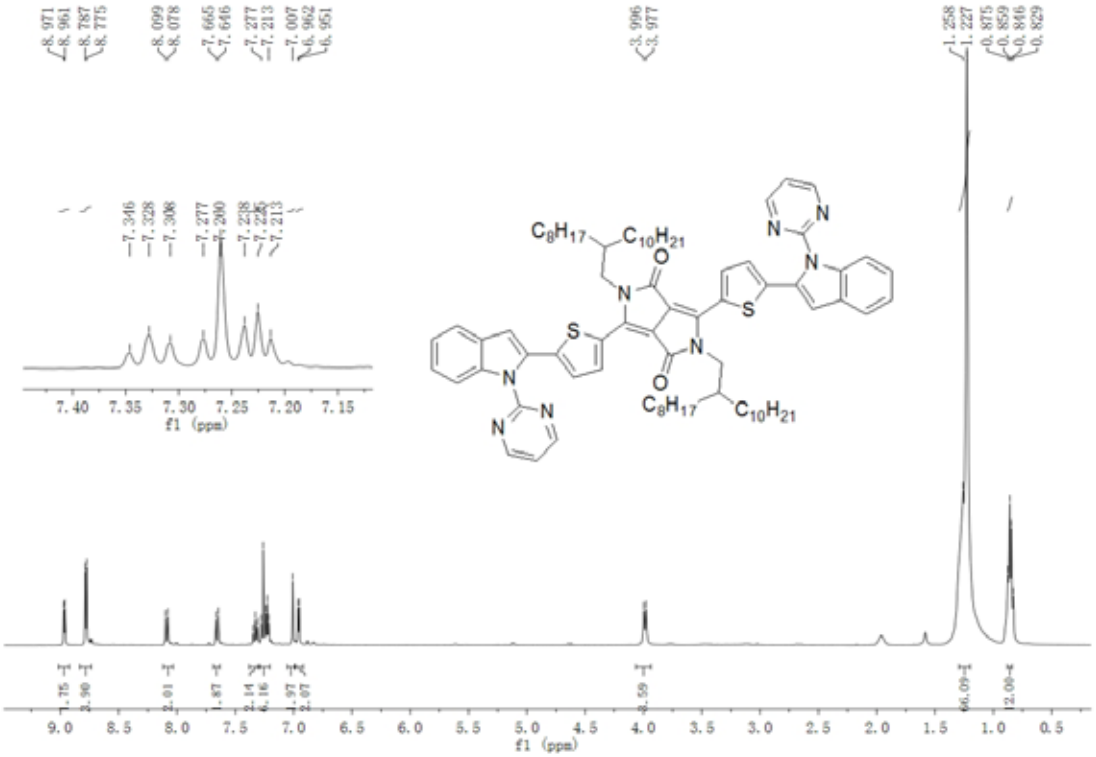

f1 (ppm)

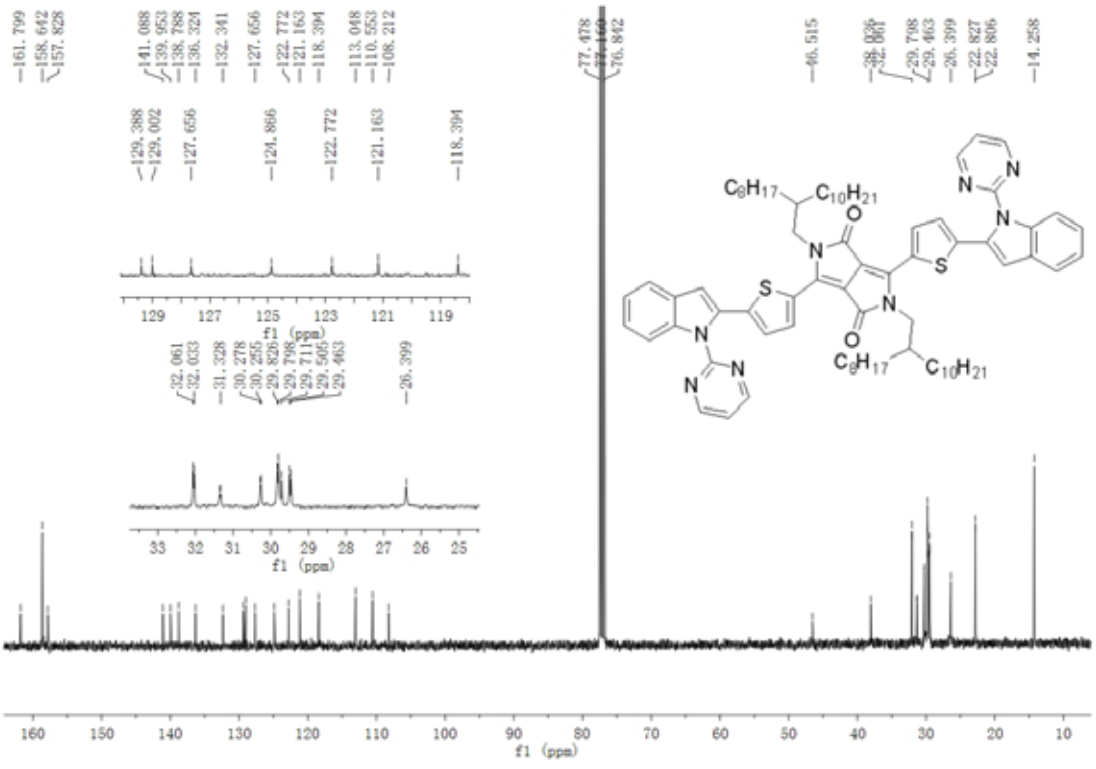

BnO
O
N
N
N
f1 (ppm)

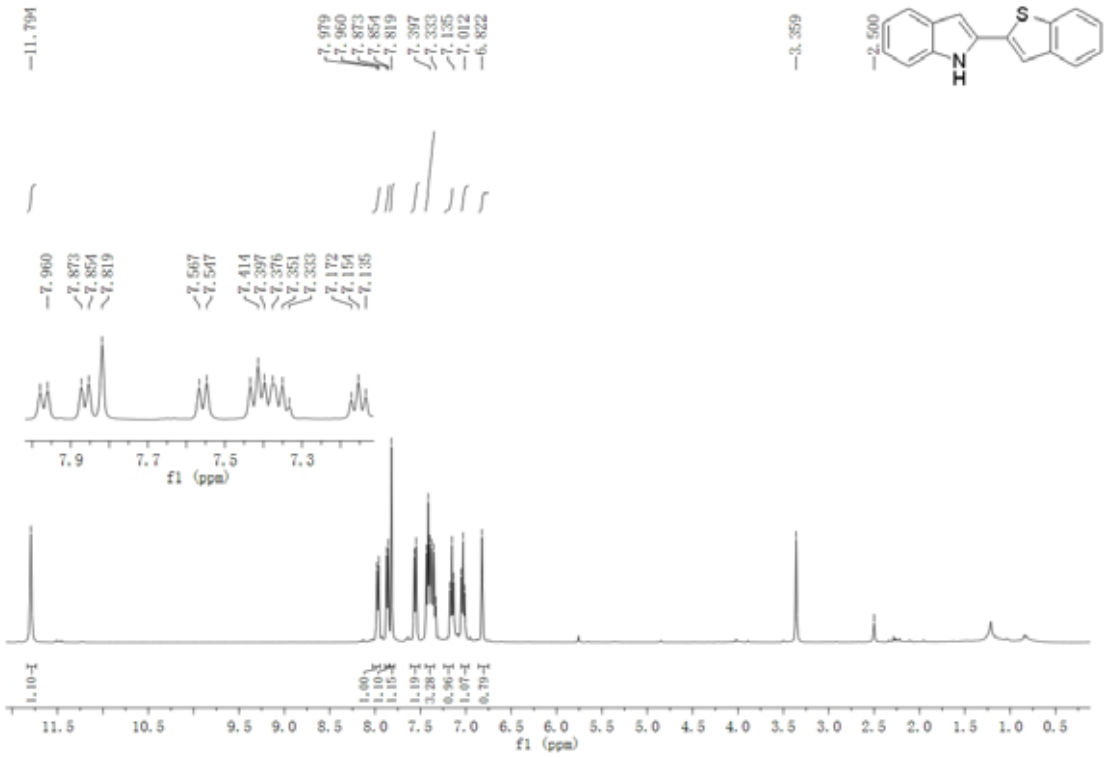

BnO
O
N
N
N
f1 (ppm)

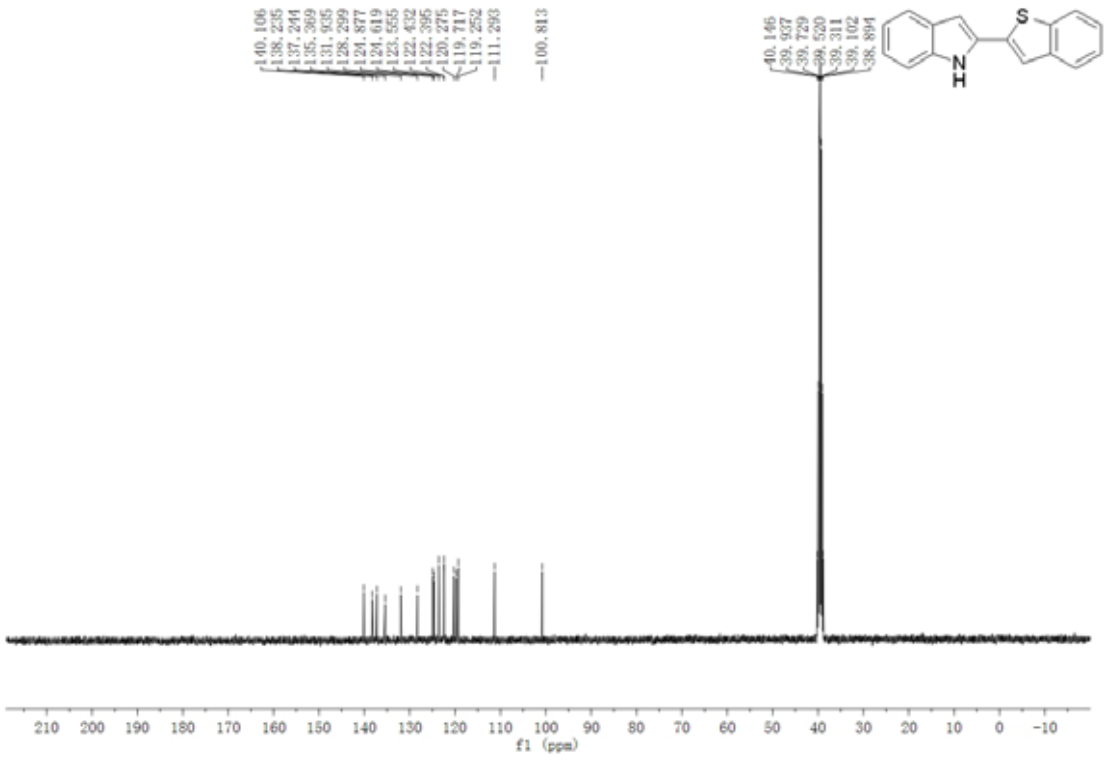

f1 (ppm)

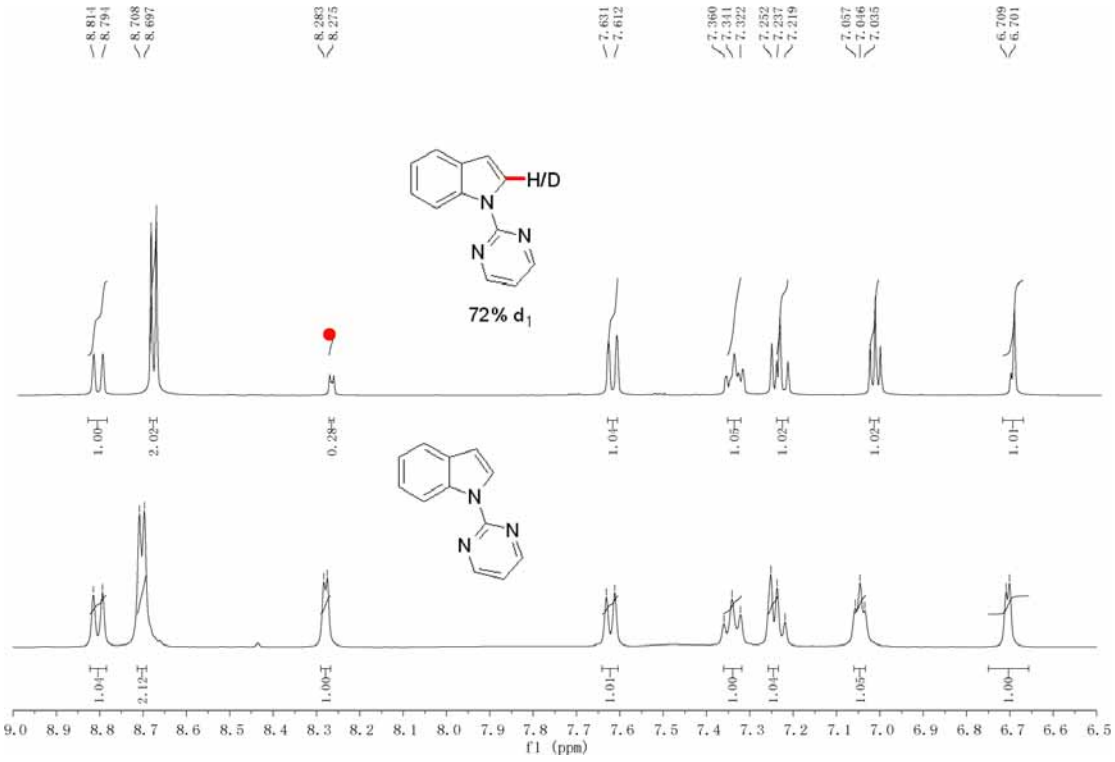

f1 (ppm)

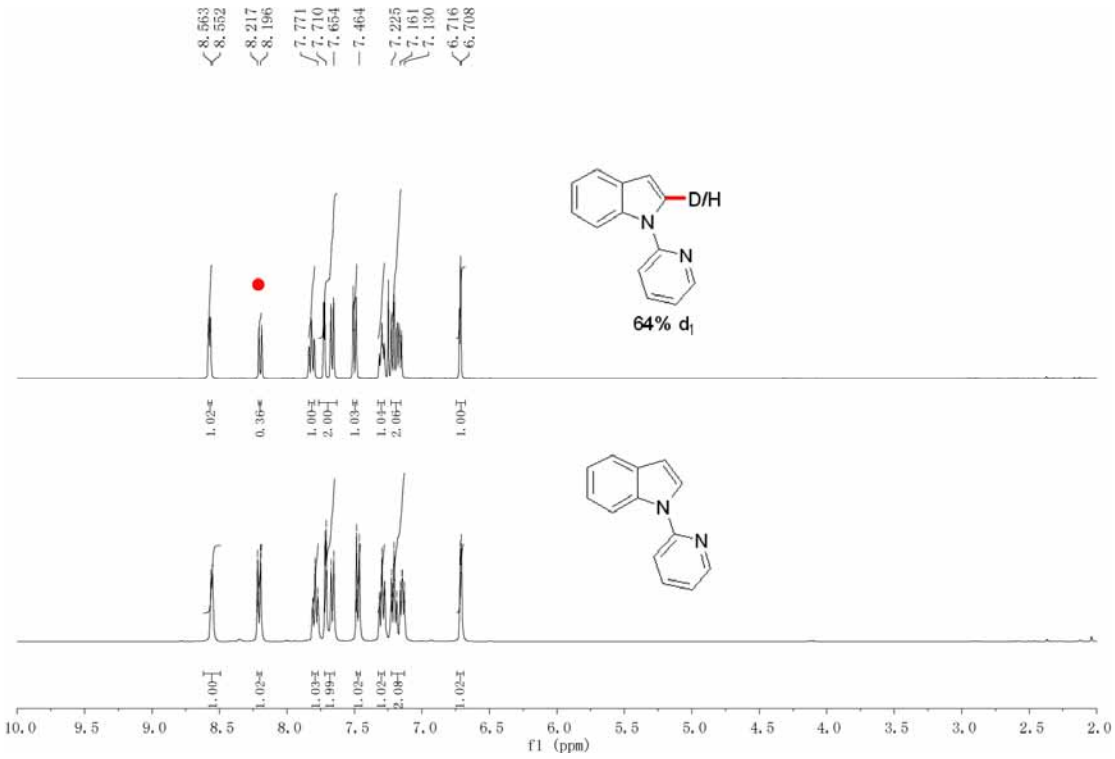


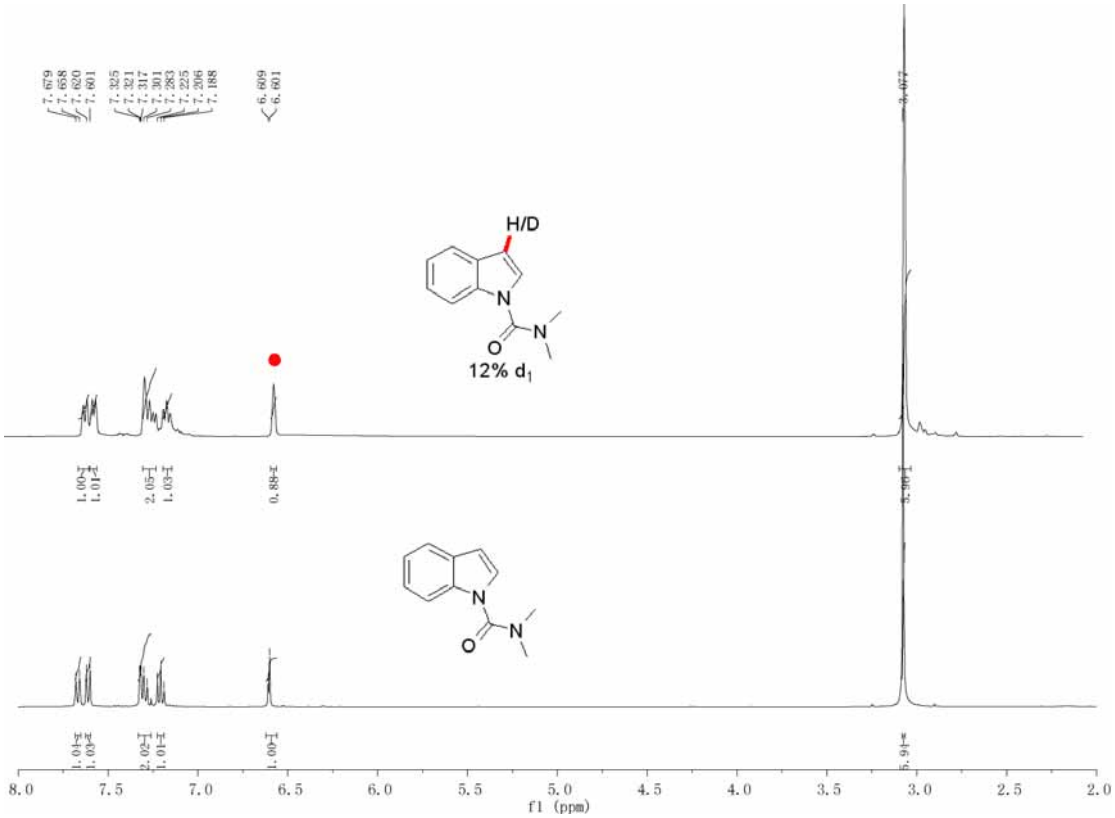


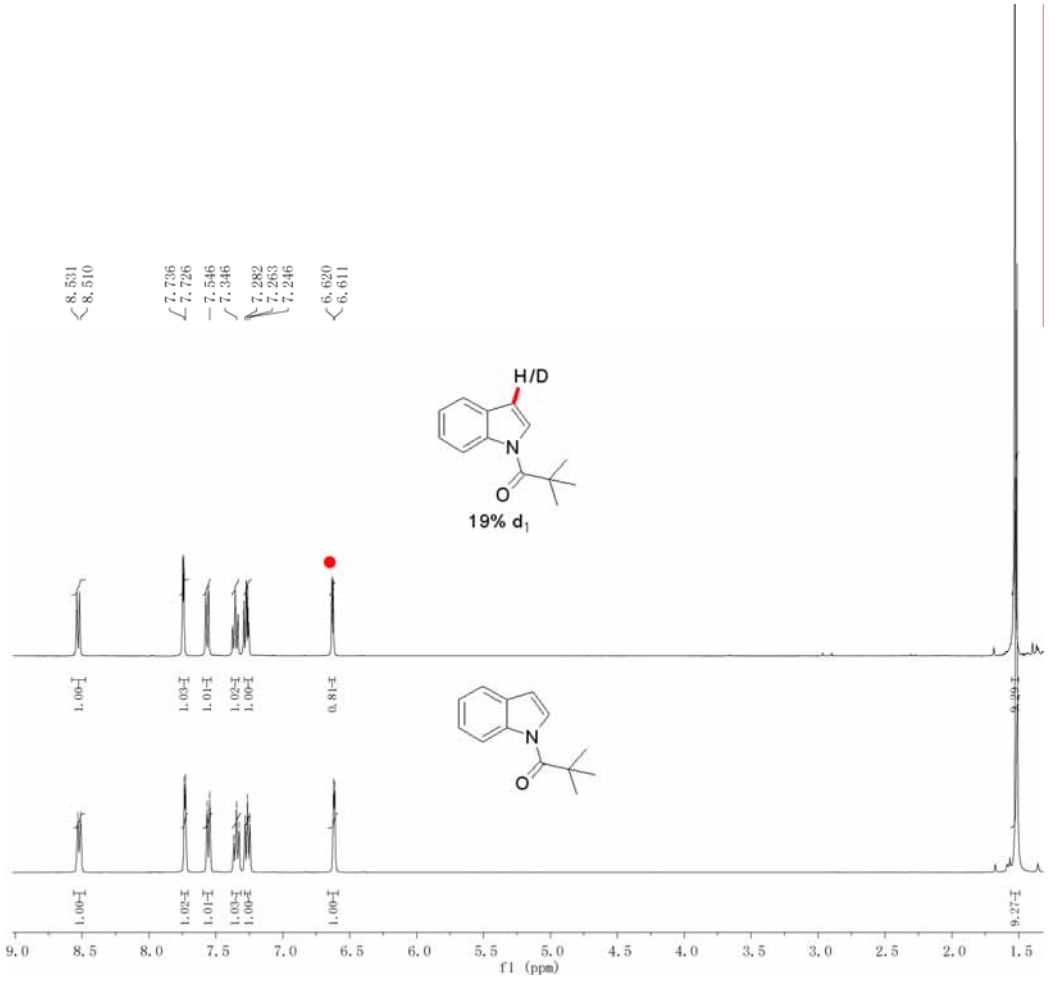


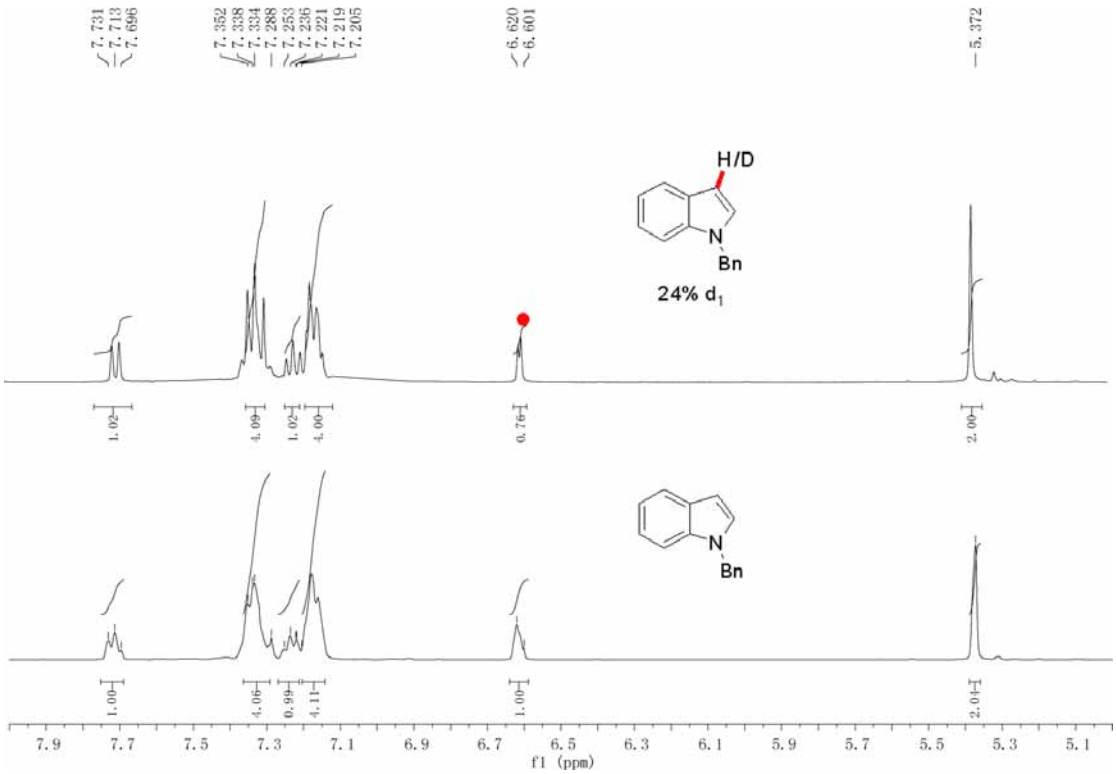


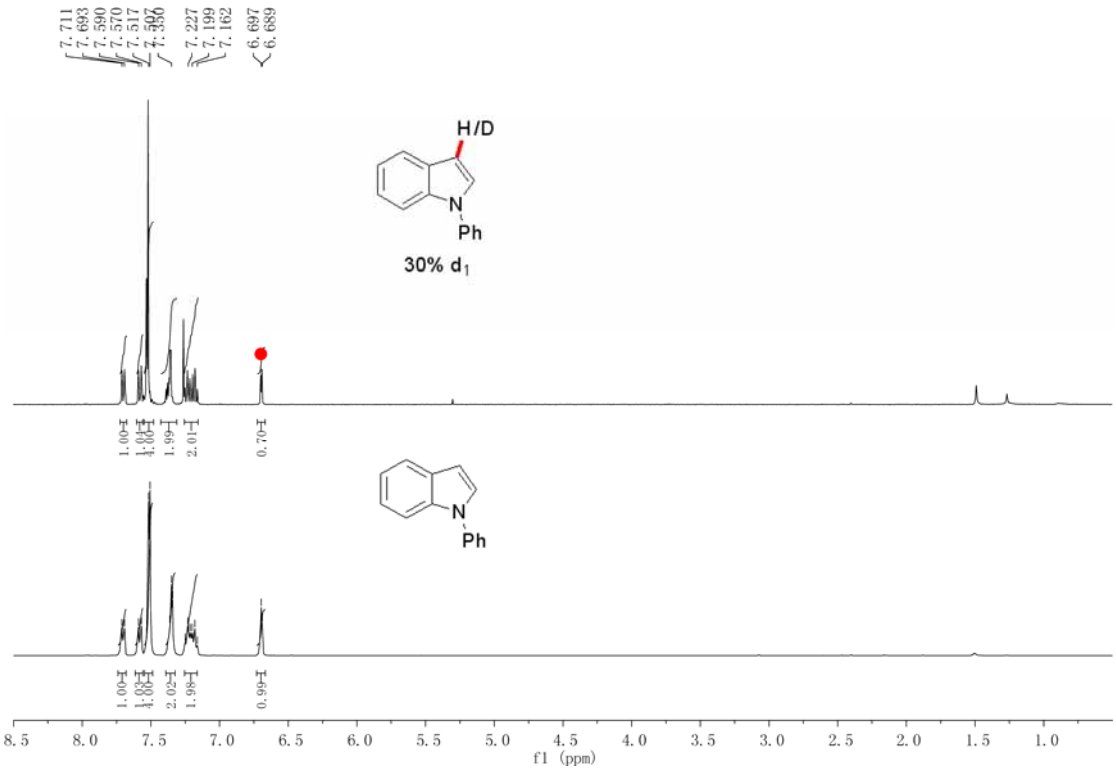

8.814
8.794
8.708
8.697
8.283
8.275
7.631
7.612
7.360
7.341
7.322
7.252
7.237
7.219
7.057
7.046
7.035
6.709
6.701
H/D
72% d1
1.00
2.02
0.28
1.04
1.05
1.02
1.02
1.01
1.04
2.12
1.00
1.01
1.00
1.04
1.05
1.00
f1 (ppm)

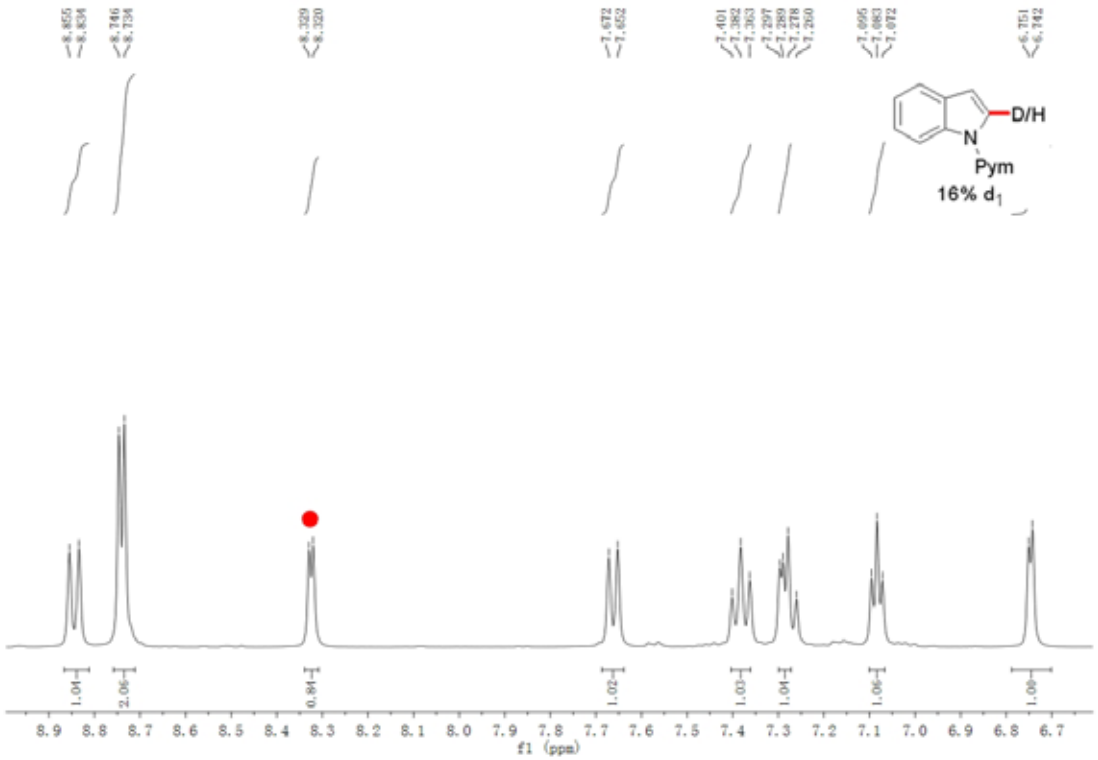

8.563
8.552
8.217
8.196
7.771
7.710
7.654
7.464
7.225
7.161
7.130
6.716
6.708
D/H
64% d1
1.02
0.36
1.00
2.00
1.03
1.04
2.06
1.00
1.00
1.02
1.03
1.99
1.02
1.02
2.08
1.02
f1 (ppm)

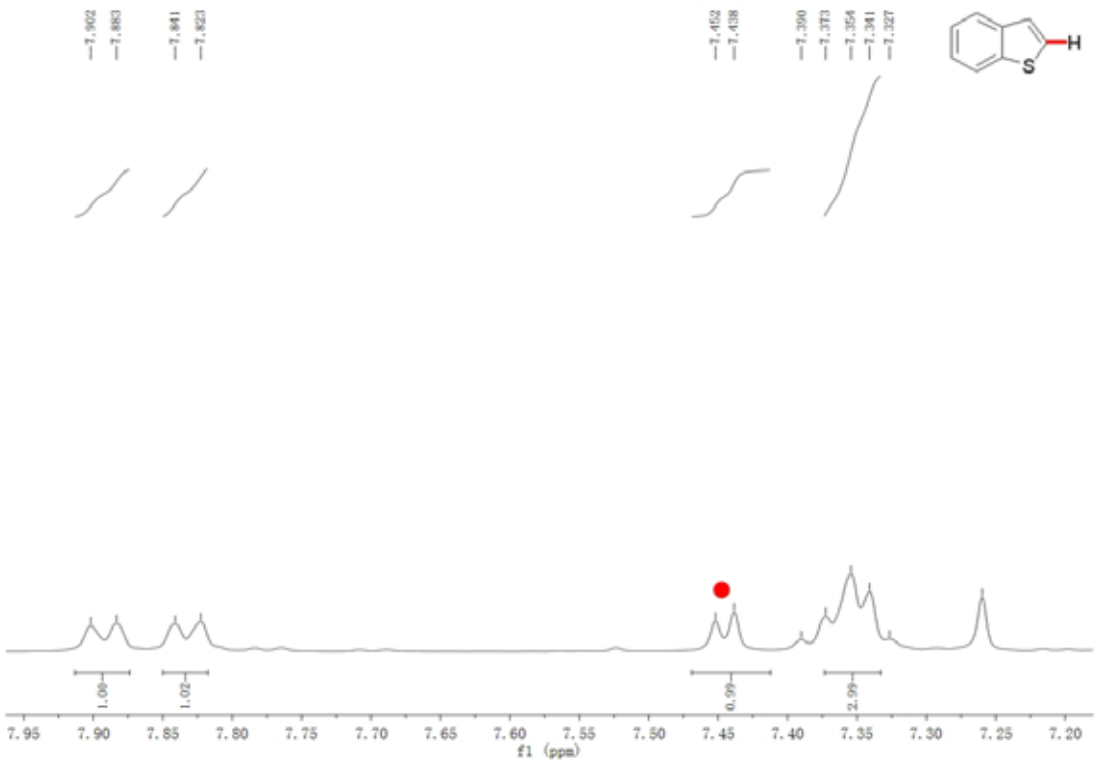

H/D
12% d1
f1 (ppm)


H/D
19% d1
f1 (ppm)


7.731
7.713
7.696
7.352
7.338
7.334
7.288
7.253
7.236
7.221
7.219
7.205
6.620
6.601
5.372
H/D
N
Bn
24% d1
1.02
4.09
1.02
4.00
0.76
2.00
N
Bn
1.00
4.06
0.99
4.11
1.00
2.04
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
f1 (ppm)


7.711
7.693
7.590
7.570
7.517
7.227
7.199
7.162
6.697
6.689
H/D
N
Ph
30% d1
1.00
4.04
4.00
1.99
2.01
0.70
N
Ph
1.00
4.03
4.00
2.02
1.98
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


8.855
8.834
8.746
8.734
8.329
8.320
7.672
7.652
7.401
7.382
7.363
7.297
7.289
7.278
7.260
7.095
7.083
7.072
6.751
6.742
D/H
N
Pym
16% d1
1.04
2.06
0.84
1.02
1.03
1.04
1.06
1.08
f1 (ppm)


7.902
7.883
7.841
7.823
7.452
7.438
7.390
7.373
7.354
7.341
7.327
H
S
1.08
1.02
0.99
2.99
f1 (ppm)