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Supporting Information

Rhodium (III)-Catalyzed Regioselective Oxidative Annulation of Anilines and Allylbenzenes via C(sp^3)−H/C(sp^2)−H Bond Cleavage

Yunqi Liu, Yudong Yang, Chunxia Wang, Zhishuo Wang, and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P. R. China.

*E-mail: jsyou@scu.edu.cn

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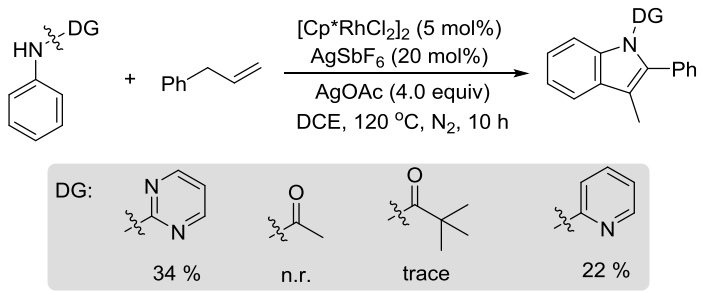
I. General remarks

NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were recorded relative to $CDCl_3$ (δ_H = 7.26 ppm) or DMSO-d_6 (δ_H = 2.50 ppm) as the internal reference. The ^{13}C NMR (100 MHz) chemical shifts were recorded using $CDCl_3$ as the internal standard (δ_C = 77.16 ppm). GC-MS analysis was performed with GCMS-QP2010 SE. High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). MALDI-TOF mass spectrum was obtained with a Bruker Autoflex III smartbeam MALDI-TOF spectrometer. Melting points were detected by a micromelting point apparatus SGWX-4/4A/4B and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. *N*-phenylpyrimidin-2-amines,[1] allylbenzenes,[2] and $[Cp^*RhCl_2]_2$[3] were prepared according to the literatures. $[Cp^*Rh(MeCN)_3][SbF_6]_2$ was prepared[4] and recrystallized for two times. The solvents were purified and dried using an Innovative Technology PS-MD-5 Solvent Purification System. Dichloroethane (DCE) was dried by refluxing over CaH_2.

II. Screening of directing groups

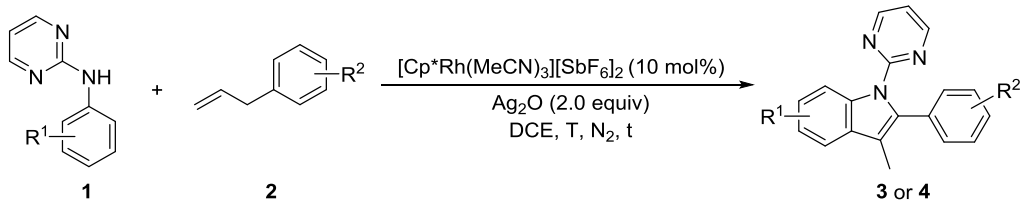


Scheme S1. General procedure for the screening of directing group.

An oven-dried Schlenk tube with a magnetic stir bar was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, 16.6 mg), Ag_2O (0.4 mmol, 92.7 mg), amine (0.2 mmol) and DCE (1.0 mL) under an N_2 atmosphere. Then allylbenzene **2** (0.3 mmol) was added. The resulting mixture was stirred at room temperature for 5 min and then stirred at the indicated temperature for appropriate time. Next, the

mixture was filtered through a celite pad and washed with dichloromethane (10 mL). Then NMR yields were obtained with CH_2Br_2 as internal standard.

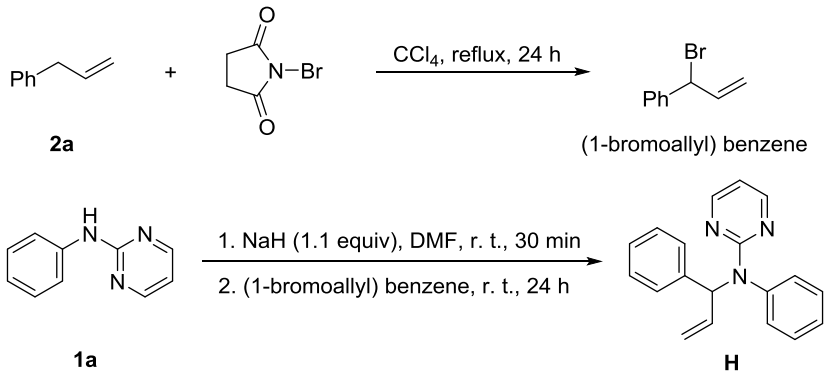
III. General procedure for rhodium (III)-catalyzed regioselective allylic annulation of anilines and allylbenzenes



Scheme S2. General procedure for the annulation of anilines **1** with allylbenzenes **2**.

An oven-dried Schlenk tube with a magnetic stir bar was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, 16.6 mg), Ag_2O (0.4 mmol, 92.7 mg), *N*-phenylpyrimidin-2-amine **1** (0.2 mmol) and DCE (1.0 mL) under an N_2 atmosphere. Then allylbenzene **2** (0.3 mmol) was added. The resulting mixture was stirred at room temperature for 5 min and then stirred at the indicated temperature for appropriate time. Next, the mixture was filtered through a celite pad and washed with dichloromethane (10-20 mL). The collected filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the target product **3** or **4**.

IV. Synthesis and characterization of *N*-phenyl-*N*-(1-phenylallyl)pyrimidin-2-amine H



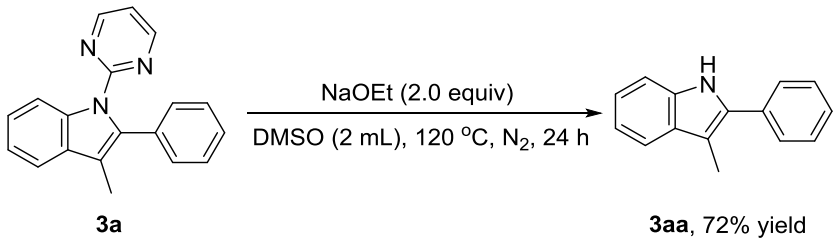
Scheme S3. General procedure for the synthesis of *N*-phenyl-*N*-(1-phenylallyl)pyrimidin-2-amine **H**.

Under a 200W lamp, a mixture of allylbenzene **2a** (6 mmol, 795 μL) and *N*-bromosuccinimide (9 mmol, 1.06 g) in CCl_4 (30 mL) was refluxed for 24 h. Then the mixture was cooled to room temperature

and filtered. The collected filtrate was evaporated. The resulting crude product (1-bromoallyl) benzene (863 mg, 73% yield) was storaged under an N_2 atomesphere without further purification.

N-phenylpyrimidin-2-amine **1a** (5 mmol, 855 mg) was dissolved in dry DMF (10 mL) in ice bath, and then NaH (5.5 mmol, 220 mg, 60% dispersion in mineral oil) was added. After stiring for 30 min, a solution of the above prepared (1-bromoallyl) benzene in CCl_4 (5 mL) was added dropwise. The resulting mixture was stirred at room temperature for 24 h. Then water (20 mL) was added. The organic layer was extracted by ethyl acetate (3 x 20 mL) and dried over anhydrous magnesium sulfate. After the solvent was evaporated under reduced pressure, the crude product was purified by silica column to give the target product *N*-phenyl-*N*-(1-phenylallyl)pyrimidin-2-amine **H** as a white solid (933.9 mg, 65% yield based on *N*-phenylpyrimidin-2-amine), mp 74-76 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.37 (d, *J* = 4.8 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.36 – 7.34 (m, 4H), 7.31 – 7.26 (m, 3H), 7.25 – 7.20 (m, 1H), 6.60 (t, *J* = 4.8 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.43 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.77 (d, *J* = 4.6 Hz, 2H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 161.7, 157.9, 144.4, 137.1, 132.0, 129.4, 128.6, 127.52, 127.46, 126.5, 126.4, 125.7, 111.1, 53.1 ppm. HRMS (ESI^+): calcd for $C_{19}H_{18}N_3$ $[M+H]^+$, 288.1495, found 288.1489.

V. Removal of the directing group



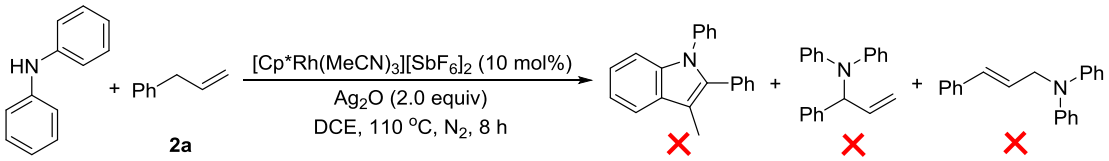
3a **3aa**, 72% yield

Scheme S4. Procedure for the removal of the directing group.

A dry Schlenk tube with a magnetic stir bar was charged with **3a** (0.2 mmol, 57.1 mg), NaOEt (0.4 mmol, 27.2 mg) and DMSO (2.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 120 ^{o}C for 24 h. After the mixture was cooled to room temperature, water (10 mL) was added. The organic layer was extracted by ethyl acetate (3 x 10 mL) and then dried over anhydrous magnesium sulfate.

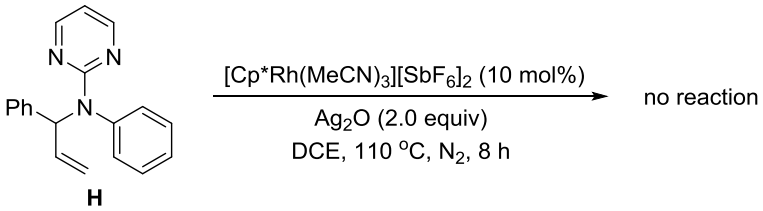
After the solvent was evaporated under reduced pressure, the crude product was purified by silica column to give the target product **3aa** as a white solid (29.8 mg, 72% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.01 (s, 1H), 7.64 – 7.62 (m, 1H), 7.61 – 7.59 (m, 2H), 7.52 – 7.47 (m, 2H), 7.39 – 7.37 (m, 2H), 7.25 – 7. 21 (m, 1H), 7.19 – 7.15 (m, 1H), 2.49 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 135.9, 134.1, 133.5, 130.1, 128.9, 127.9, 127.4, 122.4, 119.7, 119.1, 110.8, 108.8, 9.8 ppm.

VI. Procedures for control experiments



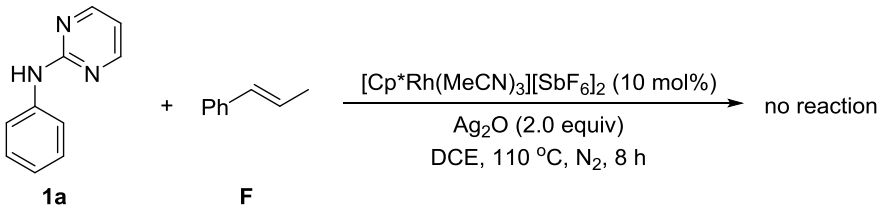
Scheme S5. Procedure for the reaction of diphenylamine and **2a**.

An oven-dried schlenk tube with a magnetic stir bar was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, 16.6 mg), Ag_2O (0.4 mmol, 92.7 mg), diphenylamine (0.2 mmol, 33.9 mg) and DCE (1.0 mL) under an N_2 atmosphere. Then allylbenzene **2a** (0.3 mmol, 40 μL) was added. The resulting mixture was stirred at room temperature for 5 min and then stirred at 110 °C for 8 h. After the mixture was cooled to room temperature, it was detected by thin layer chromatography (TLC) and GC-MS.



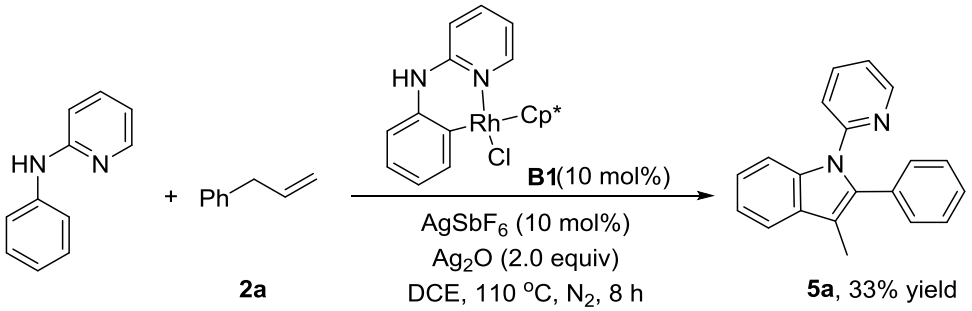
Scheme S6. Procedure for the intramolecular annulation of *N*-phenyl-*N*-(1-phenylallyl)pyrimidin-2-amine **H**.

An oven-dried schlenk tube with a magnetic stir bar was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, 16.6 mg), Ag_2O (0.4 mmol, 92.7 mg), *N*-phenyl-*N*-(1-phenylallyl)pyrimidin-2-amine **H** (0.2 mmol, 57.5 mg) and DCE (1.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at room temperature for 5 min and then stirred at 110 °C for 8 h. After the mixture was cooled to room temperature, it was detected by thin layer chromatography (TLC) and GC-MS.



Scheme S7. Procedure for the reaction of **1a** and (*E*)-prop-1-en-1-ylbenzene **F**.

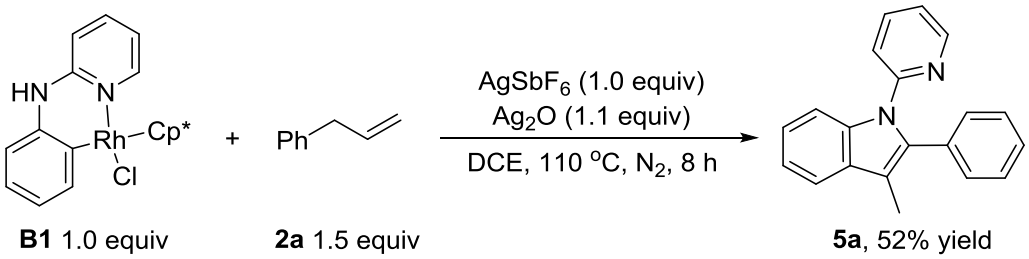
An oven-dried schlenk tube with a magnetic stir bar was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, 16.6 mg), Ag_2O (0.4 mmol, 92.7 mg), *N*-phenylpyrimidin-2-amine **1a** (0.2 mmol, 34.2 mg) and DCE (1.0 mL) under an N_2 atmosphere. Then (*E*)-prop-1-en-1-ylbenzene **F** (0.3 mmol, 39 μL) was added. The resulting mixture was stirred at room temperature for 5 min and then stirred at 110 °C for 8 h. After the mixture was cooled to room temperature, it was detected by thin layer chromatography (TLC) and GC-MS.



Scheme S8. Procedure for the reaction of *N*-phenylpyridin-2-amine and **2a**.

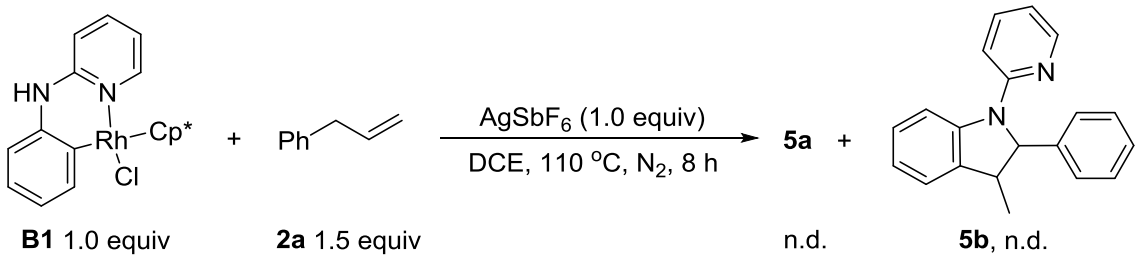
An oven-dried Schlenk tube with a magnetic stir bar was charged with cyclometallated Rh^{III} complex **B1** (0.02 mmol, 8.9 mg), $AgSbF_6$ (0.02 mmol, 6.9 mg), Ag_2O (0.4 mmol, 92.7 mg), *N*-phenylpyridin-2-amine (0.2 mmol, 34.1 mg) and DCE (1.0 mL) under an N_2 atmosphere. Then allylbenzene **2a** (0.3 mmol, 40 μL) was added. The resulting mixture was stirred at room temperature for 5 min and then stirred at 110 °C for 8 h. When the mixture was cooled to room temperature, it was diluted with dichloromethane (5 mL), filtered through a celite pad and washed with dichloromethane (10 mL). The collected filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the target product 3-methyl-2-phenyl-1-(pyridin-2-yl)-1*H*-indole **5a** as a white solid (18.7 mg, 33% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.58 (d, *J* = 4.8 Hz, 1H),

7.78 – 7.75 (m, 1H), 7.67 – 7.64 (m, 1H), 7.55 – 7.50 (m, 1H), 7.34 – 7.27 (m, 5H), 7.25 – 7.24 (m, 2H), 7.15 – 7.12 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 152.4, 149.0, 137.6, 137.4, 135.8, 132.5, 130.4, 129.8, 128.3, 127.3, 123.4, 121.6, 121.03, 120.98, 119.0, 112.8, 111.6, 9.7 ppm.



Scheme S9. Procedure for the reaction of **B1** and **2a** with oxidant.

An oven-dried Schlenk tube with a magnetic stir bar was charged with cyclometallated Rh^{III} complex **B1** (0.2 mmol, 88.6 mg), $AgSbF_6$ (0.2 mmol, 68.7 mg), Ag_2O (0.22 mmol, 61.0 mg) and DCE (1.0 mL) under an N_2 atmosphere. Then allylbenzene **2a** (0.3 mmol, 40 μL) was added. The resulting mixture was stirred at room temperature for 5 min and then stirred at 110 °C for 8 h. When the mixture was cooled to room temperature, it was diluted with dichloromethane (5 mL), filtered through a celite pad and washed with dichloromethane (10 mL). The collected filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the target product **5a** as a white solid (29.6 mg, 52% yield).

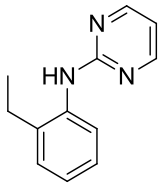


Scheme S10. Procedure for the reaction of **B1** and **2a** without oxidant.

An oven-dried Schlenk tube with a magnetic stir bar was charged with cyclometallated Rh^{III} complex **B1** (0.2 mmol, 88.6 mg), $AgSbF_6$ (0.2 mmol, 68.7 mg) and DCE (1.0 mL) under an N_2 atmosphere. Then allylbenzene **2a** (0.3 mmol, 40 μL) was added. The resulting mixture was stirred at room temperature

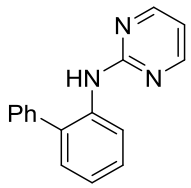
for 5 min and then stirred at 110 °C for 8 h. After the mixture was cooled to room temperature, it was detected by thin layer chromatography (TLC) and GC-MS.

VII. Characterization of 1f, 1h and 1k



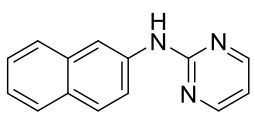
***N*-(2-Ethylphenyl)pyrimidin-2-amine** (**1f**)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) afforded the desired product **1f** as a white solid, mp 91-93 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.38 (d, *J* = 4.8 Hz, 2H), 7.88 – 7.86 (m, 1H), 7.28 – 7.24 (m, 2H), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 6.92 (s, 1H), 6.68 (t, *J* = 4.8 Hz, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 161.1, 158.3, 136.6, 135.7, 128.9, 126.7, 124.7, 123.4, 112.4, 24.7, 14.2 ppm. HRMS (ESI^+): calcd for $C_{12}H_{14}N_3$ $[M+H]^+$, 200.1182, found 200.1178.



***N*-([1,1'-Biphenyl]-2-yl)pyrimidin-2-amine** (**1h**)

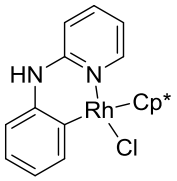
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1, v/v) afforded the desired product **1h** as a white solid, mp 88-90 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.41 – 8.37 (m, 3H), 7.49 – 7.36 (m, 6H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.12 (m, 2H), 6.69 (t, *J* = 4.8 Hz, 1H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 160.2, 158.1, 138.8, 136.3, 132.4, 130.5, 129.6, 129.1, 128.3, 127.9, 123.0, 120.6, 112.7 ppm. HRMS (ESI^+): calcd for $C_{16}H_{14}N_3$ $[M+H]^+$, 248.1182, found 248.1179.



***N*-(Naphthalen-2-yl)pyrimidin-2-amine** (**1k**)

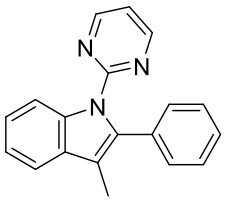
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1, v/v) afforded the desired product **1h** as a white solid, mp 143-144 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.49 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 2.0 Hz, 1H), 7.78 – 7.82 (m, 4H), 7.60 – 7.58 (m,, 1H), 7.48 – 7.44 (m, 1H), 7.39 – 7.36 (m, 1H), 6.76 (td, *J* = 4.8, 1.6 Hz, 1H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 160.4, 158.2, 137.1, 134.3, 130.0, 128.8, 127.7, 127.5, 126.5, 124.4, 120.7, 115.4, 112.8 ppm. HRMS (ESI^+): calcd for $C_{14}H_{12}N_3$ $[M+H]^+$, 222.1026, found 222.1024.

VIII. Synthesis and characterization of cyclometallated Rh (III) complex B1



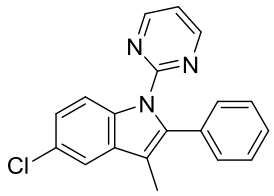
The cyclometallated Rh (III) complex **B1** was prepared by the liteature.[5] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 10.15 (s, 1H), 8.77 (s, 1H), 7.51 – 7.47 (m, 1H), 7.39 – 7.34 (m, 2H), 7.23 (s, 1H), 7.12 – 7.09 (m, 2H), 6.76 – 6.72 (m, 1H), 1.55 (s, 15H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.6, 153.0, 140.0, 139.3, 129.8, 123.9, 120.8, 115.7, 110.3, 94.7, 94.6, 9.1 ppm.

IX. Characterization of product 3 and 4



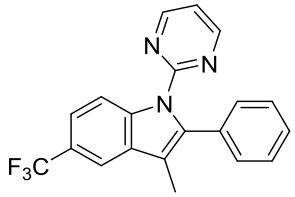
3-Methyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3a)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **3a** as a white solid (38.8 mg, 68% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.59 (d, *J* = 4.8 Hz, 2H), 8.21 – 8.19 (m, 1H), 7.65 – 7.62 (m, 1H), 7.37 – 7.30 (m, 4H), 7.29 – 7.26 (m, 3H), 7.02 (t, *J* = 4.8 Hz, 1H), 2.38 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.2, 158.1, 137.0, 136.0, 133.8, 130.6, 129.7, 128.0, 126.9, 123.9, 121.8, 119.1, 117.1, 115.1, 112.9, 9.6 ppm. HRMS (ESI^+): calcd for $C_{19}H_{16}N_3$ $[M+H]^+$, 286.1339, found 286.1337.



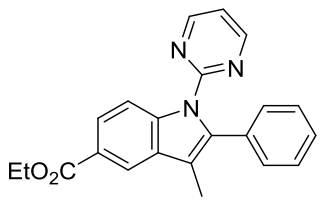
5-Chloro-3-methyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3b)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **3b** as a white solid (42.9 mg, 67% yield), mp 40-42 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.58 (d, *J* = 4.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.27 – 7.26 (m, 2H), 7.25 – 7.24 (m, 1H), 7.04 (t, *J* = 4.8 Hz, 1H), 2.32 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.1, 157.9, 137.3, 135.3, 133.3, 131.8, 129.7, 128.1, 127.3, 127.2, 123.9, 118.6, 117.4, 114.5, 114.2, 9.5 ppm. HRMS (ESI^+): calcd for $C_{19}H_{15}{}^{35}ClN_3$ $[M+H]^+$, 320.0949, found 320.0946; calcd for $C_{19}H_{15}{}^{37}ClN_3$ $[M+H]^+$, 322.0920, found 322.0914.



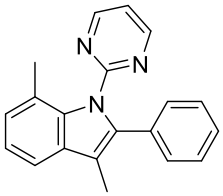
3-Methyl-2-phenyl-1-(pyrimidin-2-yl)-5-(trifluoromethyl)-1*H*-indole (3c)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) afforded **3c** as a white solid (38.9 mg, 55% yield), mp 90-92 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.62 (d, *J* = 4.8 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 1H), 7.91 – 7.89 (m, 1H), 7.55 – 7.52 (m, 1H), 7.38 – 7.31 (m, 3H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.25 (t, *J* = 1.6 Hz, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 2.39 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.3, 157.8, 138.3, 137.7, 133.1, 130.1, 129.7, 128.2, 127.4, 125.3 (d, *J* = 271.7 Hz), 124.0 (d, *J* = 32.0 Hz), 120.5 (q, *J* = 3.0 Hz), 117.8, 116.6 (q, *J* = 4.0 Hz), 115.1, 113.2, 9.5 ppm. HRMS (ESI^+): calcd for $C_{20}H_{15}F_3N_3$ $[M+H]^+$, 354.1213, found 354.1204.



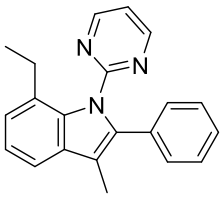
Ethyl 3-methyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-indole-5-carboxylate (3d)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) afforded **3d** as a white solid (62.9 mg, 88% yield), mp 125-127 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.62 (d, *J* = 4.8 Hz, 2H), 8.37 (dd, *J* = 2.0, 0.8 Hz, 1H), 8.14 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.01 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.26 (s, overlapped, 1H), 7.24 (t, *J* = 1.6 Hz, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 167.6, 158.3, 157.9, 139.6, 137.2, 133.2, 130.3, 129.7, 128.1, 127.2, 125.2, 124.0, 121.6, 117.7, 115.6, 112.5, 60.9, 14.6, 9.6 ppm. HRMS (ESI^+): calcd for $C_{22}H_{19}N_3NaO_2$ $[M+Na]^+$, 380.1369, found 380.1363.



3,7-Dimethyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3e)

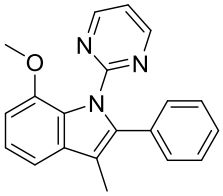
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **3e** as a white solid (38.9 mg, 65% yield), mp 175-177 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.69 (d, *J* = 4.8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.27 (m, 5H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 2.38 (s, 3H), 2.01 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 159.8, 158.0, 137.8, 136.6, 132.3, 130.4, 130.3, 128.0, 127.3, 125.8, 121.6, 121.0, 119.3, 117.1, 112.3, 19.8, 9.6 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3$ $[M+H]^+$, 300.1495, found 300.1489.



7-Ethyl-3-methyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3f)

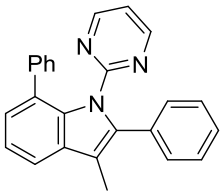
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **3f** as a white solid (38.2 mg, 61% yield), mp 86-88 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.67 (d, *J* = 4.8 Hz, 2H), 7.51 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.26 – 7.19 (m, 6H), 7.17 (d, *J* = 4.8 Hz, 1H), 7.09 – 7.07 (m,

1H), 2.37 (q, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 160.4, 158.1, 138.1, 135.9, 132.3, 130.6, 130.4, 128.1, 127.8, 127.1, 123.7, 121.1, 119.2, 117.0, 112.4, 25.7, 14.4, 9.6 ppm. HRMS (ESI^+): calcd for $C_{21}H_{20}N_3$ $[M+H]^+$, 314.1652, found 314.1649.



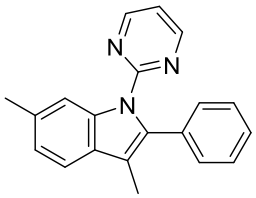
7-Methoxy-3-methyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3g)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **3g** as a light yellow solid (40.4 mg, 64% yield), mp 101-103 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.66 (d, *J* = 4.8 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.26 – 7.22 (m, 2H), 7.16 – 7.15 (m, 1H), 7.14 – 7.12 (m, 1H), 6.71 (dd, *J* = 7.6, 0.8 Hz, 1H), 3.64 (s, 3H), 2.35 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 159.8, 157.7, 147.0, 137.6, 132.1, 131.7, 130.4, 128.0, 127.33, 127.28, 121.2, 119.1, 112.3, 112.1, 105.0, 55.9, 9.8 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3O$ $[M+H]^+$, 316.1444, found 316.1435.



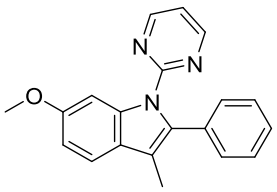
3-Methyl-2,7-diphenyl-1-(pyrimidin-2-yl)-1*H*-indole (3h)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **3h** as a white solid (41.9 mg, 58% yield), mp 153-155 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.11 (d, *J* = 4.8 Hz, 2H), 7.68 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.22 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.11 – 7.08 (m, 2H), 7.02 – 7.00 (m, 3H), 6.73 (t, *J* = 4.8 Hz, 1H), 2.37 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 157.8, 157.1, 140.8, 137.5, 134.0, 132.4, 131.0, 130.6, 128.2, 127.9, 127.7, 127.4, 127.1, 125.72, 125.67, 121.0, 118.4, 117.9, 112.4, 9.6 ppm. HRMS (ESI^+): calcd for $C_{25}H_{20}N_3$ $[M+H]^+$, 362.1652, found 362.1648.



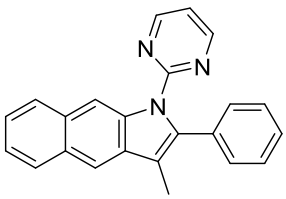
3,6-Dimethyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3i)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **3i** as a white solid (34.7 mg, 58% yield), mp 99-101 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.68 (d, *J* = 4.8 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.22 (m, 5H), 7.17 (t, *J* = 4.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 1.98 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 159.9, 158.1, 137.8, 136.6, 132.4, 130.5, 130.4, 128.0, 127.3, 125.9, 121.7, 121.0, 119.3, 117.2, 112.3, 19.8, 9.6 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3$ $[M+H]^+$, 300.1495, found 300.1489.



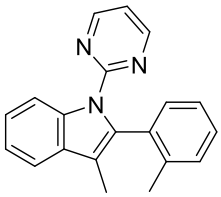
6-Methoxy-3-methyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3j)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1, v/v) afforded **3j** as a white solid (45.4 mg, 72% yield), mp 157-159 ^{o}C. **^{1}H NMR** (DMSO-d_6, 400 MHz): δ = 8.72 (d, *J* = 4.8 Hz, 2H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.27 – 7.24 (m, 1H), 7.16 – 7.14 (m, 2H), 6.90 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.79 (s, 3H), 2.27 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.3, 158.0, 157.8, 138.0, 134.8, 134.1, 129.5, 128.0, 126.6, 125.0, 119.6, 116.9, 115.2, 110.8, 97.5, 55.9, 9.7 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3O$ $[M+H]^+$, 316.1444, found 316.1435.



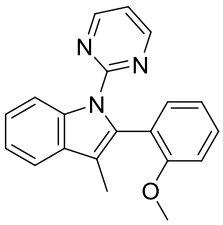
3-Methyl-2-phenyl-1-(pyrimidin-2-yl)-1*H*-benzo[f]indole (3k)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **3k** as a white solid (37.6 mg, 56% yield), mp 123-125 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.75 (s, 1H), 8.62 (d, *J* = 4.8 Hz, 2H), 8.07 (s, 1H), 8.01 – 7.98 (m, 2H), 7.44 – 7.40 (m, 2H), 7.39 – 7.31 (m, 5H), 7.01 (t, *J* = 4.8 Hz, 1H), 2.48 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.5, 158.0, 139.0, 137.2, 133.9, 132.2, 131.7, 130.1, 129.5, 128.4, 128.09, 128.07, 127.1, 124.3, 123.7, 116.63, 116.61, 115.3, 109.3, 9.9 ppm. HRMS (ESI^+): calcd for $C_{23}H_{18}N_3$ $[M+H]^+$, 336.1495, found 336.1492.



3-Methyl-1-(pyrimidin-2-yl)-2-(*o*-tolyl)-1*H*-indole (4a)

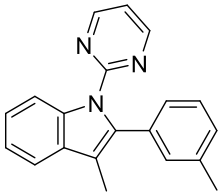
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4a** as a white solid (31.7 mg, 53% yield), mp 132-134 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.50 (d, *J* = 4.8 Hz, 2H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.37 – 7.33 (m, 1H), 7.31 – 7.26 (m, 1H), 7.24 – 7.17 (m, 4H), 6.96 – 6.93 (m, 1H), 2.18 (s, 3H), 2.05 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.2, 157.92, 157.88, 138.1, 136.3, 135.9, 134.0, 130.7, 130.5, 129.5, 127.7, 125.2, 123.6, 121.7, 118.8, 116.7, 114.8, 113.7, 20.2, 9.3 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3$ $[M+H]^+$, 300.1495, found 300.1489.



2-(2-Methoxyphenyl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4b)

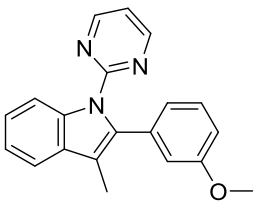
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1, v/v) afforded **4b** as a white solid (30.3 mg, 48% yield), mp 108-110 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.55 (d, *J* = 4.8 Hz, 2H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6, 1H), 7.42 (dd, *J* = 3.6, 2.0 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 4.8 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 3.37

(s, 3H), 2.32 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.3, 157.7, 156.8, 136.3, 133.0, 131.6, 130.5, 129.0, 123.6, 123.1, 121.4, 120.6, 118.9, 116.7, 114.9, 113.2, 110.4, 55.0, 9.7 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3O$ $[M+H]^+$, 316.1444, found 316.1435.



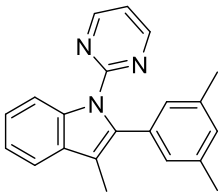
3-Methyl-1-(pyrimidin-2-yl)-2-(*m*-tolyl)-1*H*-indole (4c)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4c** as a light yellow solid (37.1 mg, 62% yield), mp 41-43 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.60 (d, *J* = 5.2 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.14 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.04 – 7.01 (m, 2H), 2.38 (s, 3H), 2.34 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.3, 158.1, 137.6, 137.0, 136.0, 133.6, 130.7, 130.3, 127.9, 127.7, 126.9, 123.8, 121.8, 119.0, 117.1, 115.0, 112.8, 21.7, 9.7 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3$ $[M+H]^+$, 300.1495, found 300.1489.



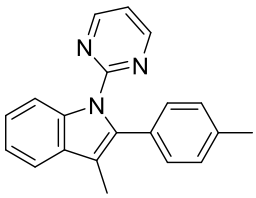
2-(3-Methoxyphenyl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4d)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4d** as a light yellow solid (41.0 mg, 65% yield), mp 55-57 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.61 (d, *J* = 4.8 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.02 (t, *J* = 4.8 Hz, 1H), 6.87 – 6.83 (m, 3H), 3.74 (s, 3H), 2.39 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 159.2, 158.2, 158.1, 137.1, 135.7, 135.1, 130.6, 129.0, 123.9, 122.3, 121.8, 119.1, 117.1, 115.2, 115.1, 112.8, 112.6, 55.3, 9.7 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3O$ $[M+H]^+$, 316.1444, found 316.1435.



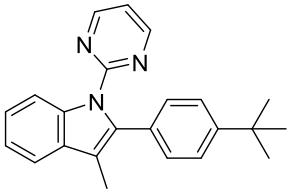
2-(3,5-Dimethylphenyl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4e)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4e** as a white solid (35.1 mg, 56% yield), mp 47-49 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.62 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.03 (t, *J* = 4.8 Hz, 1H), 6.92 (s, 1H), 6.89 (s, 2H), 2.38 (s, 3H), 2.28 (s, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.3, 158.1, 137.4, 137.0, 136.1, 133.4, 130.7, 128.6, 127.5, 123.7, 121.7, 119.0, 117.0, 114.8, 112.7, 21.5, 9.8 ppm. HRMS (ESI^+): calcd for $C_{21}H_{20}N_3$ $[M+H]^+$, 314.1652, found 314.1649.



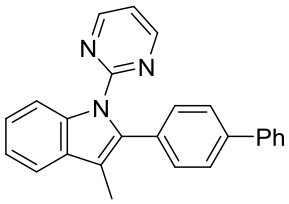
3-Methyl-1-(pyrimidin-2-yl)-2-(*p*-tolyl)-1*H*-indole (4f)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4f** as a white solid (37.7 mg, 63% yield), mp 121-123 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.60 (d, *J* = 4.8 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.34 – 7.27 (m, 2H), 7.18 – 7.14 (m, 4H), 7.02 (t, *J* = 4.8 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.3, 158.1, 137.0, 136.6, 136.0, 130.8, 130.7, 129.6, 128.8, 123.7, 121.8, 119.0, 117.1, 114.7, 112.8, 21.4, 9.7 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}N_3$ $[M+H]^+$, 300.1495, found 300.1489.



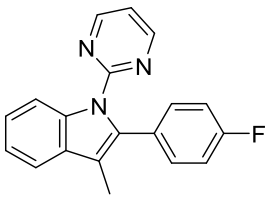
2-(4-(*tert*-Butyl)phenyl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4g)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4g** as a light yellow solid (41.7 mg, 61% yield), mp 111-113 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.60 (d, *J* = 4.8 Hz, 2H), 8.19 – 8.16 (m, 1H), 7.65 – 7.63 (m, 1H), 7.37 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.22 – 7.19 (m, 2H), 7.02 (t, *J* = 4.8 Hz, 1H), 2.40 (s, 3H), 1.35 (s, 9H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.3, 158.1, 149.7, 137.0, 136.0, 130.7, 130.6, 129.3, 125.0, 123.7, 121.7, 119.0, 117.1, 114.7, 112.8, 34.7, 31.5, 9.8 ppm. HRMS (ESI^+): calcd for $C_{23}H_{24}N_3$ $[M+H]^+$, 342.1965, found 342.1963.



2-([1,1'-Biphenyl]-4-yl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4h)

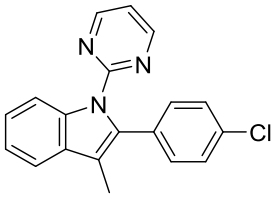
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4h** as a white solid (42.7 mg, 59% yield), mp 93-95 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.60 (d, *J* = 4.8 Hz, 2H), 8.22 – 8.20 (m, 1H), 7.66 – 7.63 (m, 3H), 7.60 – 7.58 (m, 2H), 7.46 – 7.42 (m, 2H), 7.38 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 7.04 (t, *J* = 4.8 Hz, 1H), 2.42 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.3, 158.2, 140.8, 139.4, 137.1, 135.6, 132.8, 130.7, 130.1, 128.9, 127.4, 127.1, 126.7, 124.0, 121.9, 119.1, 117.1, 115.4, 112.9, 9.8 ppm. HRMS (ESI^+): calcd for $C_{25}H_{20}N_3$ $[M+H]^+$, 362.1652, found 362.1648.



2-(4-Fluorophenyl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4i)

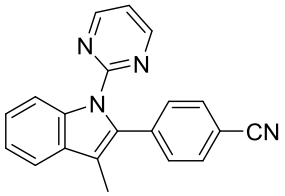
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4i** as a white solid (31.6 mg, 52% yield), mp 149-151 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.60 (d, *J* = 4.8 Hz, 2H), 8.22 – 8.20 (m, 1H), 7.64 – 7.62 (m, 1H), 7.35 – 7.28 (m, 2H), 7.26 – 7.22 (m, 2H), 7.06 – 7.02 (m, 3H), 2.34 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 161.9 (d, *J* = 244.0 Hz), 158.1, 137.0,

135.0, 131.4 (d, *J* = 8.0 Hz), 130.5, 130.0 (d, *J* = 3.0 Hz), 124.0, 121.9, 119.0, 117.1, 115.2, 115.1 (d, *J* = 21.5 Hz), 113.1, 9.6 ppm. HRMS (ESI^+): calcd for $C_{19}H_{15}FN_3$ $[M+H]^+$, 304.1245, found 304.1243.



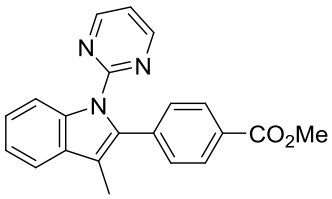
2-(4-Chlorophenyl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4j)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4j** as a white solid (35.2 mg, 55% yield), mp 61-63 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.59 (d, *J* = 4.8 Hz, 2H), 8.25 – 8.22 (m, 1H), 7.65 – 7.62 (m, 1H), 7.36 – 7.31 (m, 3H), 7.30 – 7.27 (m, 1H), 7.22 – 7.19 (m, 2H), 7.03 (t, *J* = 4.8 Hz, 1H), 2.35 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.1, 158.0, 137.0, 134.7, 132.8, 132.5, 131.0, 130.5, 128.3, 124.2, 122.0, 119.1, 117.1, 115.6, 113.1, 9.6 ppm. HRMS (ESI^+): calcd for $C_{19}H_{15}{}^{35}ClN_3$ $[M+H]^+$, 320.0949, found 320.0946; calcd for $C_{19}H_{15}{}^{37}ClN_3$ $[M+H]^+$, 322.0920, found 322.0916.



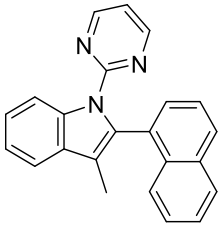
4-(3-Methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)benzonitrile (4k)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1, v/v) afforded **4k** as a light yellow solid (39.1 mg, 63% yield), mp 155-157 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.57 (d, *J* = 4.8 Hz, 2H), 8.32 – 8.29 (m, 1H), 7.66 – 7.61 (m, 3H), 7.39 – 7.35 (m, 3H), 7.33 – 7.29 (m, 1H), 7.05 (t, *J* = 4.8 Hz, 1H), 2.36 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.1, 157.9, 139.1, 137.4, 134.0, 131.8, 130.4, 130.2, 124.9, 122.3, 119.4, 119.2, 117.2, 117.1, 113.6, 110.2, 9.6 ppm. HRMS (ESI^+): calcd for $C_{20}H_{15}N_4$ $[M+H]^+$, 311.1291, found 311.1288.



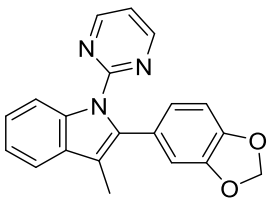
Methyl 4-(3-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)benzoate (4l)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1, v/v) afforded **4l** as a light yellow solid (39.8 mg, 58% yield), mp 56-58 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.57 (d, *J* = 4.8 Hz, 2H), 8.27 – 8.24 (m, 1H), 8.01 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.65 – 7.63 (m, 1H), 7.37 – 7.32 (m, 3H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 7.02 (t, *J* = 4.8 Hz, 1H), 3.93 (s, 3H), 2.38 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 167.2, 158.11, 158.06, 138.8, 137.3, 134.8, 130.5, 129.6, 129.3, 128.3, 124.5, 122.1, 119.3, 117.1, 116.5, 113.2, 52.3, 9.7 ppm. HRMS (ESI^+): calcd for $C_{21}H_{18}N_3O_2$ $[M+H]^+$, 344.1394, found 344.1392.



3-Methyl-2-(naphthalen-1-yl)-1-(pyrimidin-2-yl)-1*H*-indole (4m)

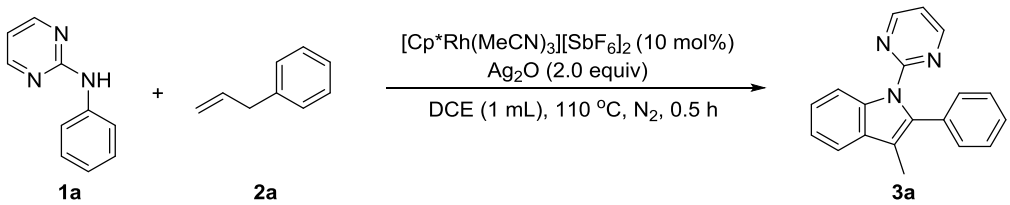
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1, v/v) afforded **4m** as a white solid (48.3 mg, 72% yield), mp 102-104 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ) = 8.41 – 8.38 (m, 1H), 8.33 – 8.31 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.66 (m, 2H), 7.54 – 7.48 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.32 (m, 1H), 7.30 – 7.26 (m, 1H), 6.79 (td, *J* = 4.8, 0.8 Hz, 1H), 2.21 (d, *J* = 0.4 Hz, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 157.8, 157.7, 136.5, 134.5, 133.4, 132.9, 132.0, 130.6, 128.5, 128.2, 128.0, 126.2, 126.0, 125.6, 125.3, 123.9, 121.9, 119.0, 116.6, 116.2, 113.7, 9.6 ppm. HRMS (ESI^+): calcd for $C_{23}H_{18}N_3$ $[M+H]^+$, 336.1495, found 336.1492.



2-(Benzo[*d*][1,3]dioxol-5-yl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (4n)

Purification by column chromatoraphy on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) afforded **4n** as a white solid (40.8 mg, 62% yield), mp 98-100 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.62 (dd, *J* = 4.8, 0.8 Hz, 2H), 8.17 – 8.14 (m, 1H), 7.61 – 7.59 (m, 1H), 7.32 – 7.24 (m, 2H), 7.03 (td, *J* = 4.8, 0.8 Hz, 1H), 6.81 – 6.78 (m, 1H), 6.75 – 6.72 (m, 2H), 5.98 (s, 2H), 2.35 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.2, 158.1, 147.3, 146.6, 136.9, 135.6, 130.5, 127.6, 123.8, 123.5, 121.8, 119.0, 117.1, 114.8, 112.9, 110.2, 108.1, 101.1, 9.7 ppm. HRMS (ESI^+): calcd for $C_{20}H_{16}N_3O_2$ $[M+H]^+$, 330.1237, found 330.1233.

X. MALDI-TOF-MASS analysis of intermediate B or C



An oven-dried Schlenk tube with a magnetic stir bar was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, 16.6 mg), Ag_2O (0.4 mmol, 92.7 mg), *N*-phenylpyrimidin-2-amine **1a** (0.2 mmol, 34.2 mg) and DCE (1.0 mL) under an N_2 atmosphere. Then allylbenzene **2a** (0.3 mmol, 40 μL) was added. The resulting mixture was stirred at room temperature for 5 min and then stirred at 110 °C for 0.5 h. Then the MALDI-TOF-MASS analysis of the resultant solution was immediately performed.

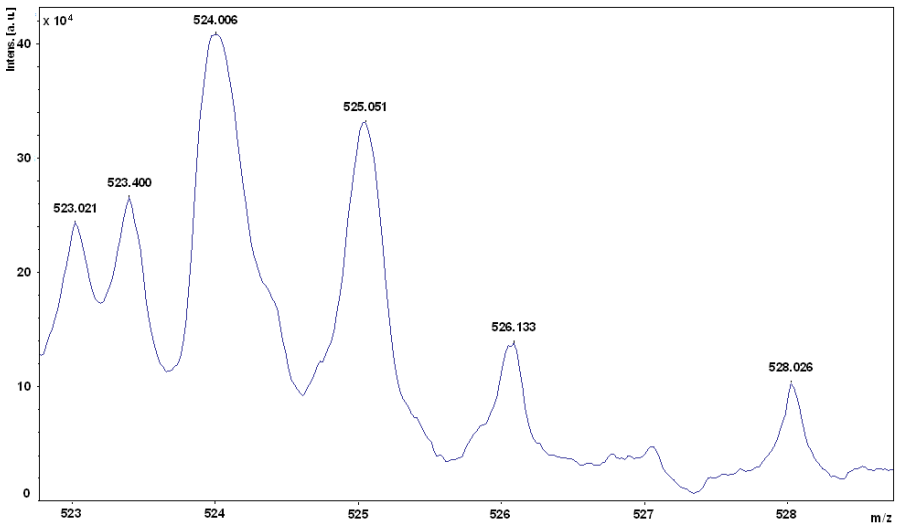


Figure S1. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) of intermediate **B** or **C** (calcd. mass 525.165, found 525.051).

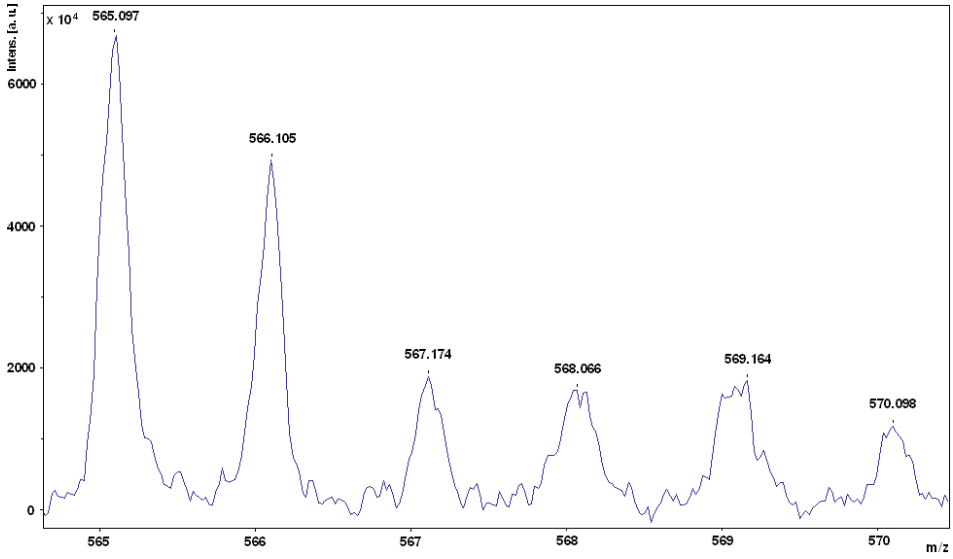
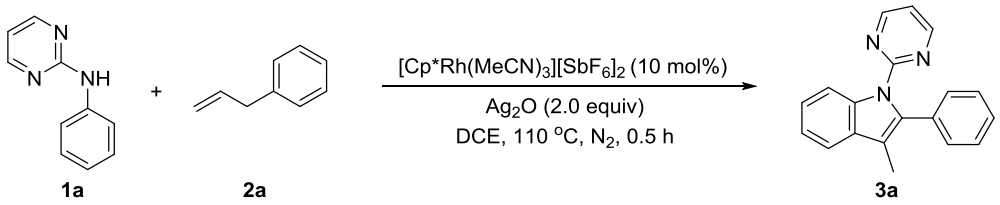


Figure S2. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) of intermediate **B** or **C** ([**M**+CH_3CN] calcd. mass 566.192 , found 566.105).

XI. ESI-HRMS analysis of intermediate A



An oven-dried Schlenk tube with a magnetic stir bar was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, 16.6 mg), Ag_2O (0.4 mmol, 92.7 mg), *N*-phenylpyrimidin-2-amine **1a** (0.2 mmol, 34.2 mg) and DCE (1.0 mL) under an N_2 atmosphere. Then allylbenzene **2a** (0.3 mmol, 40 μL) was added. The resulting mixture was stirred at room temperature for 5 min and then stirred at 110 °C for 0.5 h. Then the HRMS analysis of the resultant solution was subsequently performed.

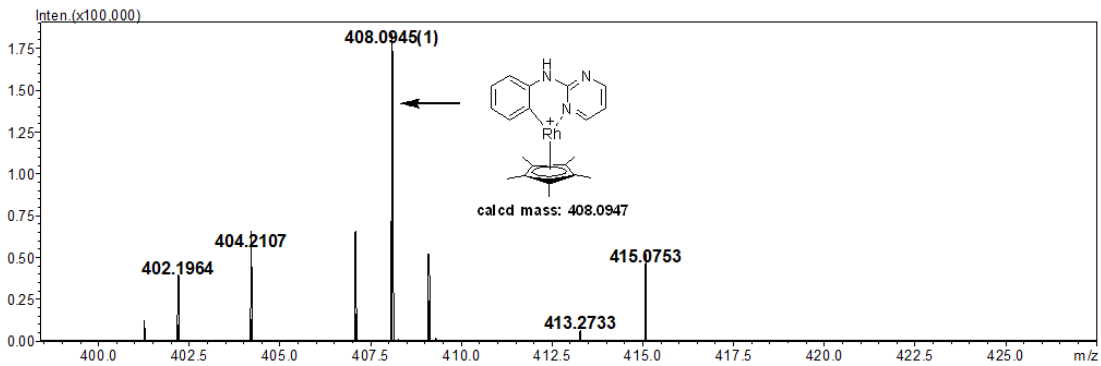


Figure S3. HRMS (ESI^+) spectrum of intermediate **A**, calcd. 408.0947, found 408.0945.

XII. References

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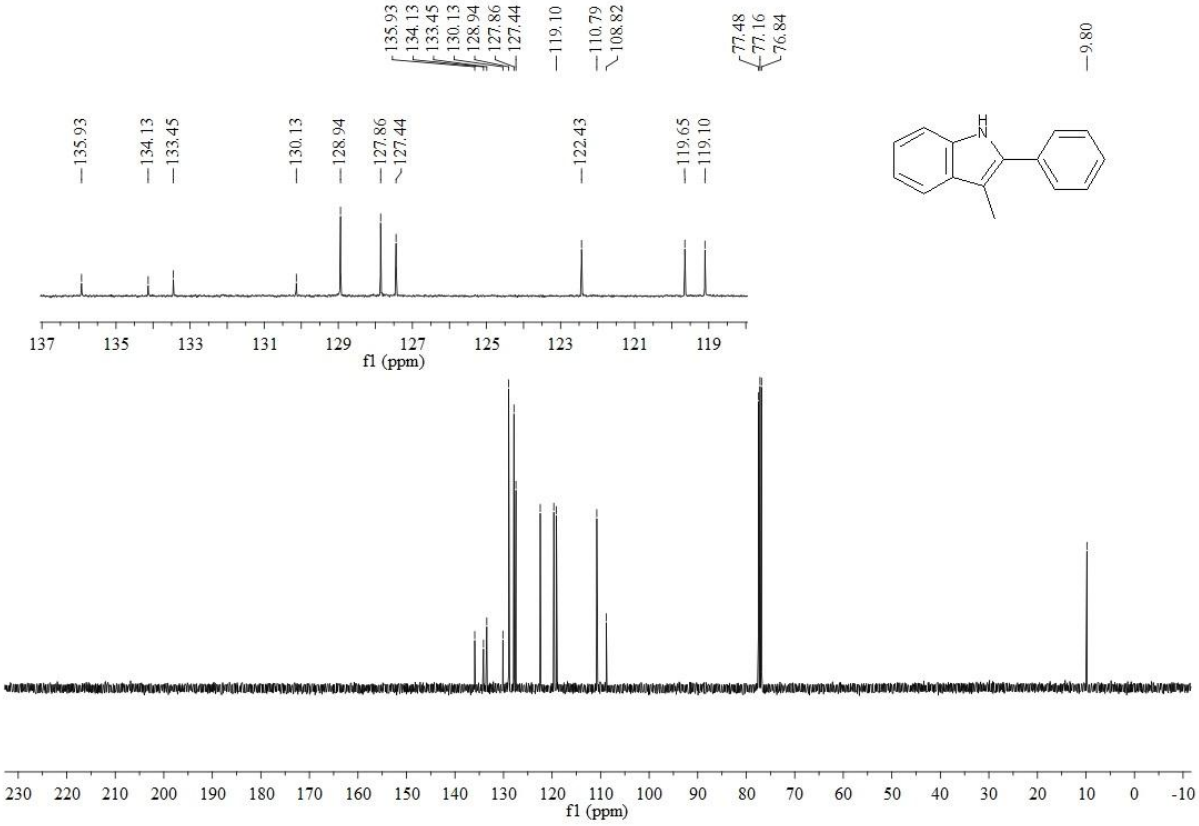
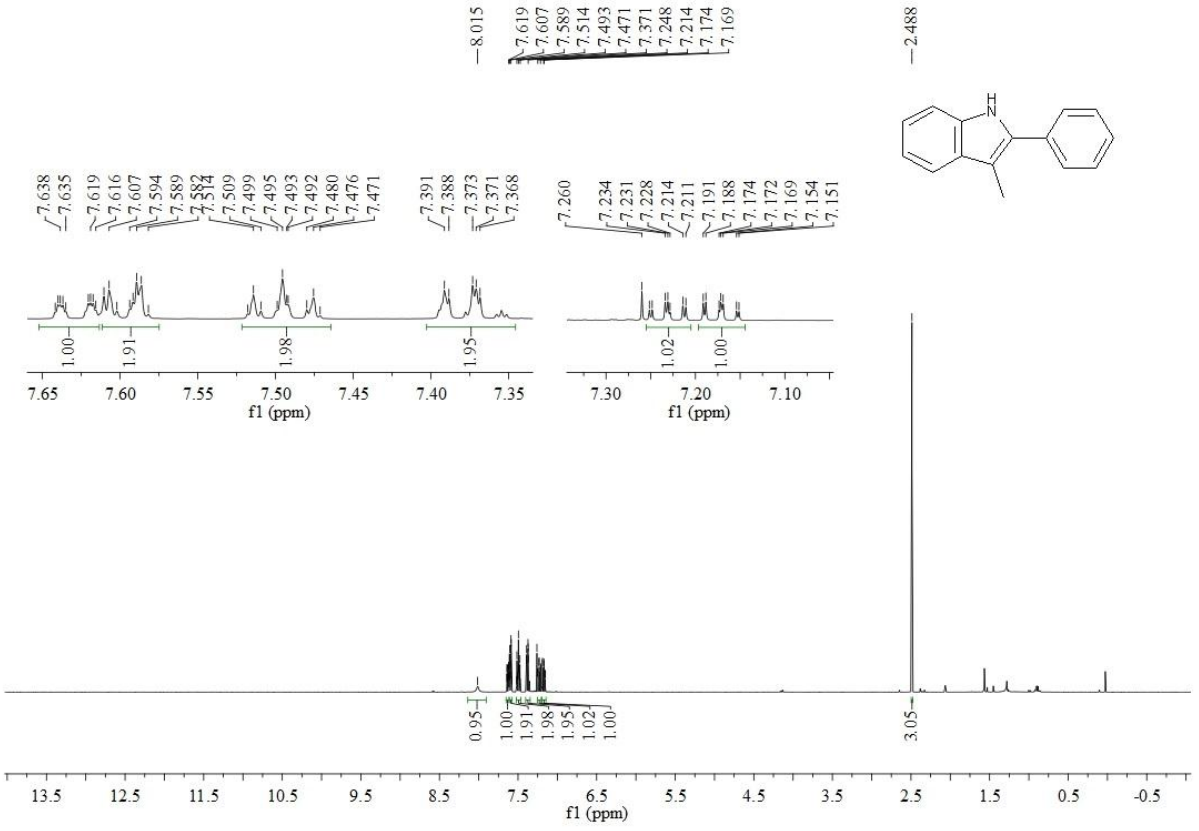
XIII. Copies of NMR spectra

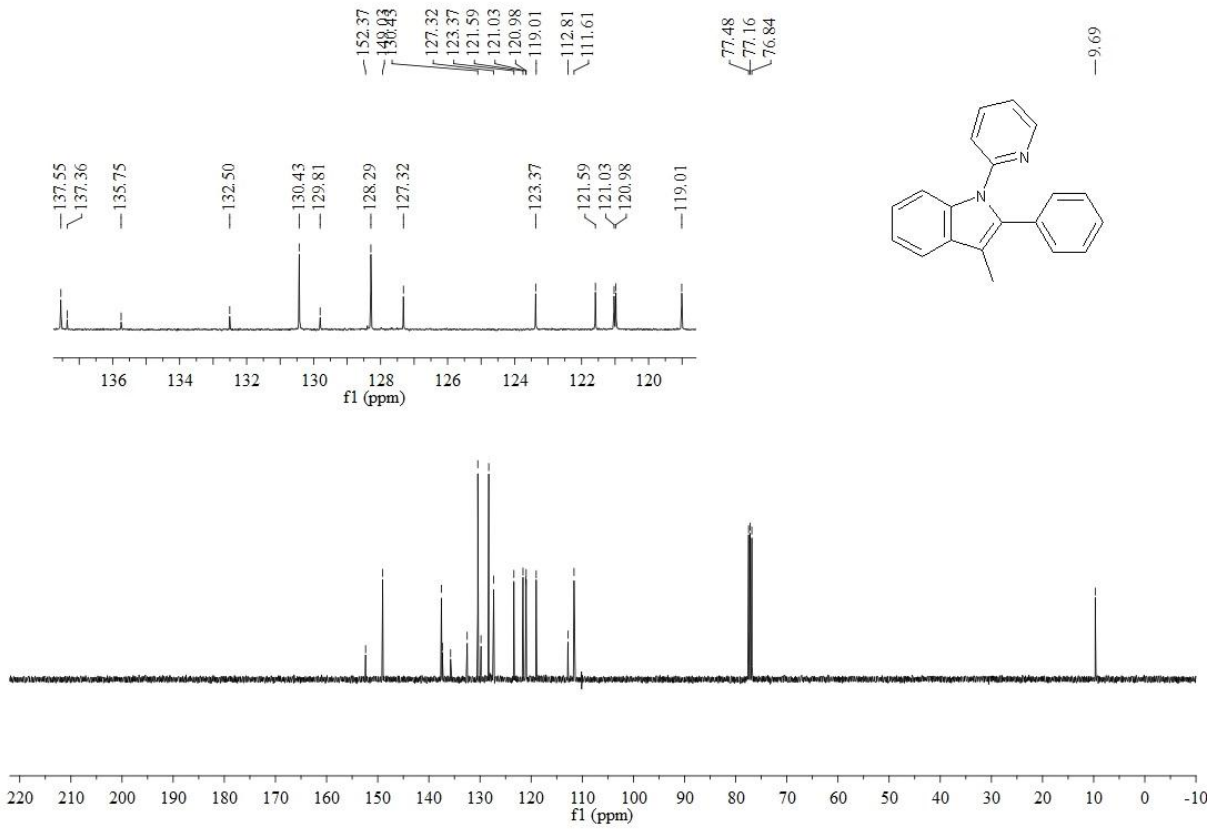
^{13}C NMR spectra of **3aa**:



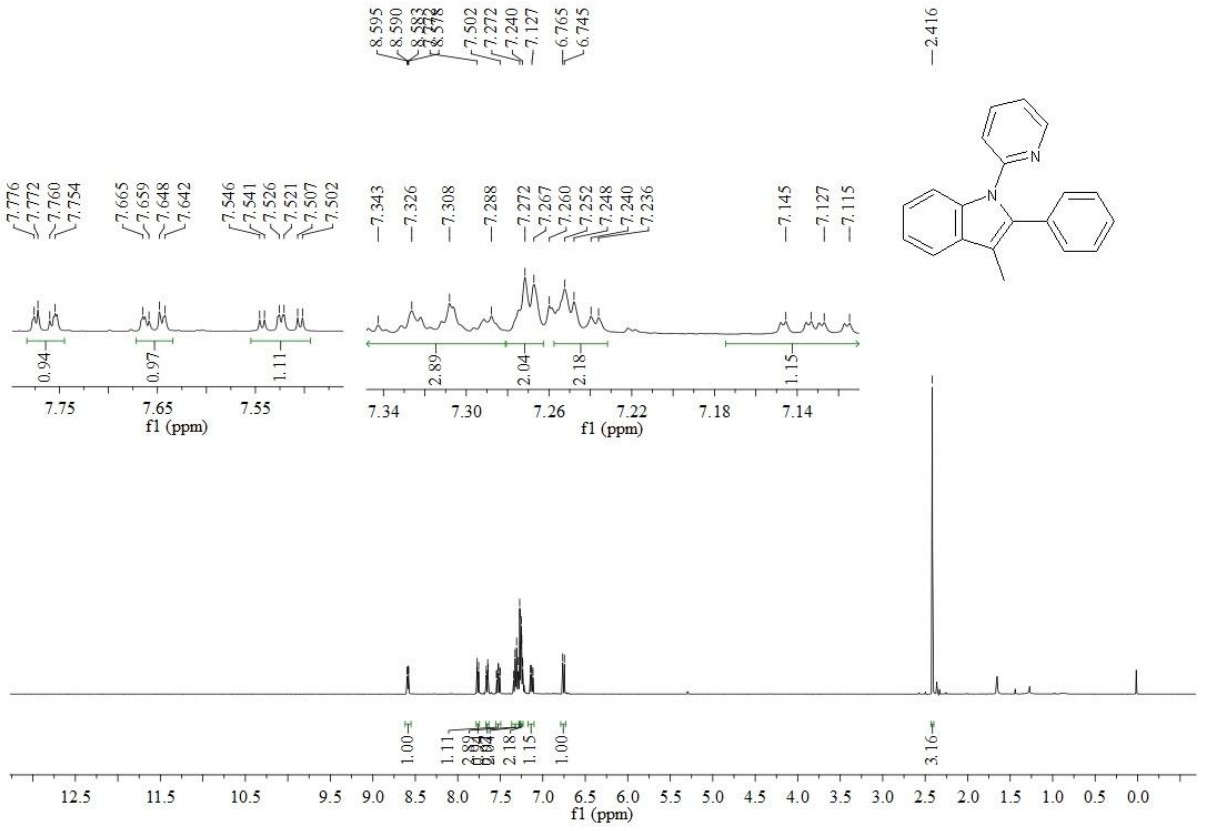
^{1}H NMR spectra of **3aa**:



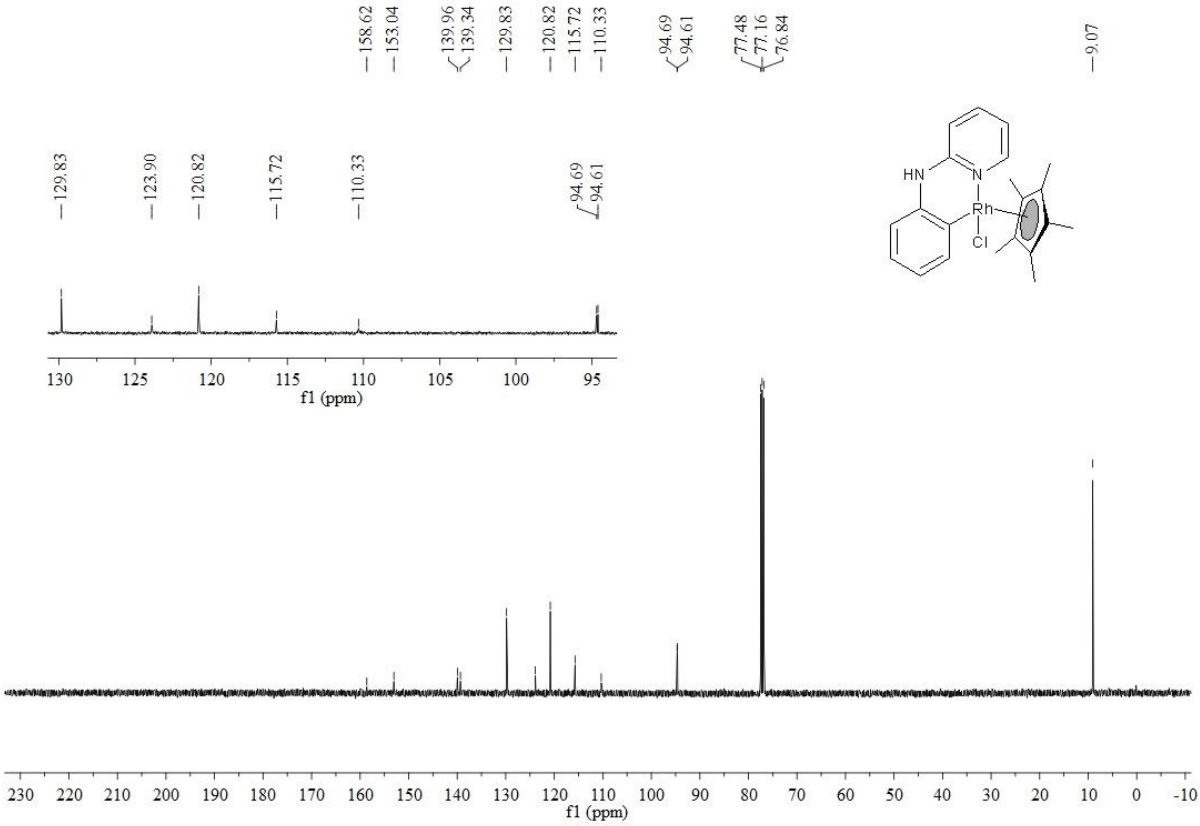
^{13}C NMR spectra of **5a**:



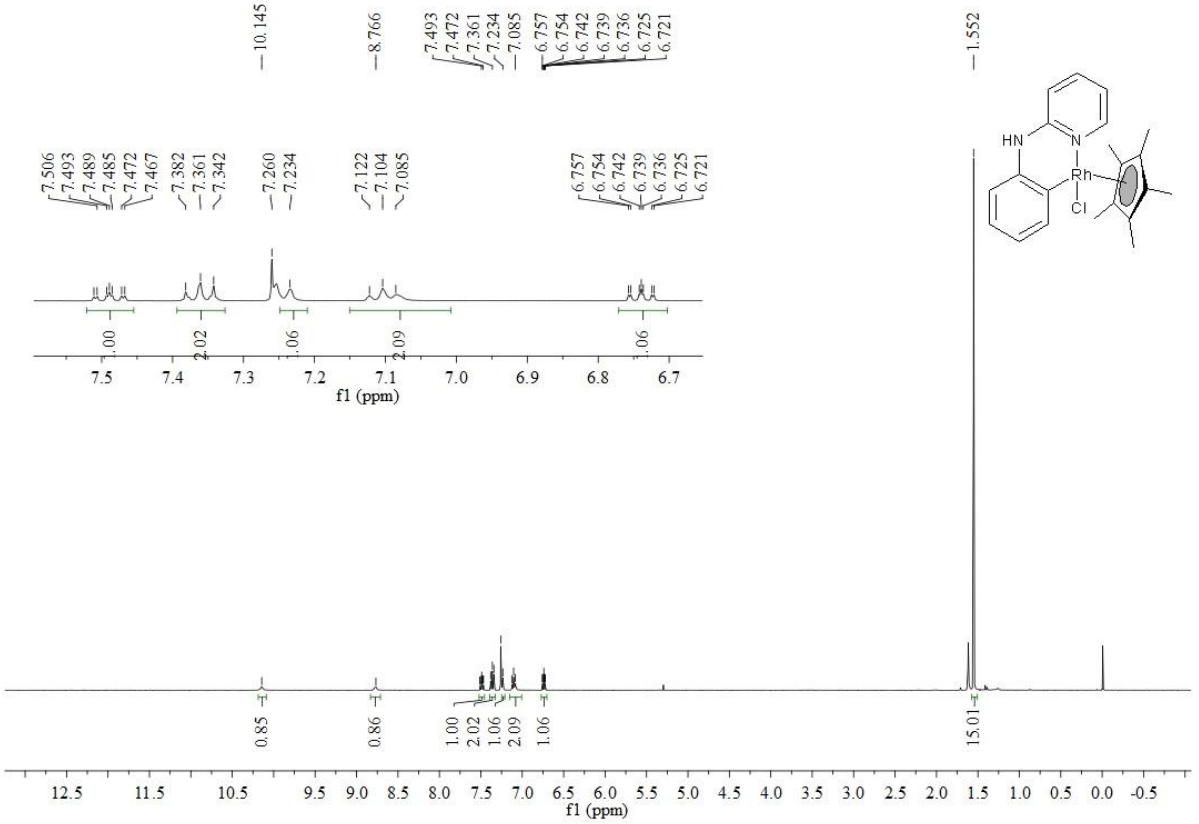
^{1}H NMR spectra of **5a**:



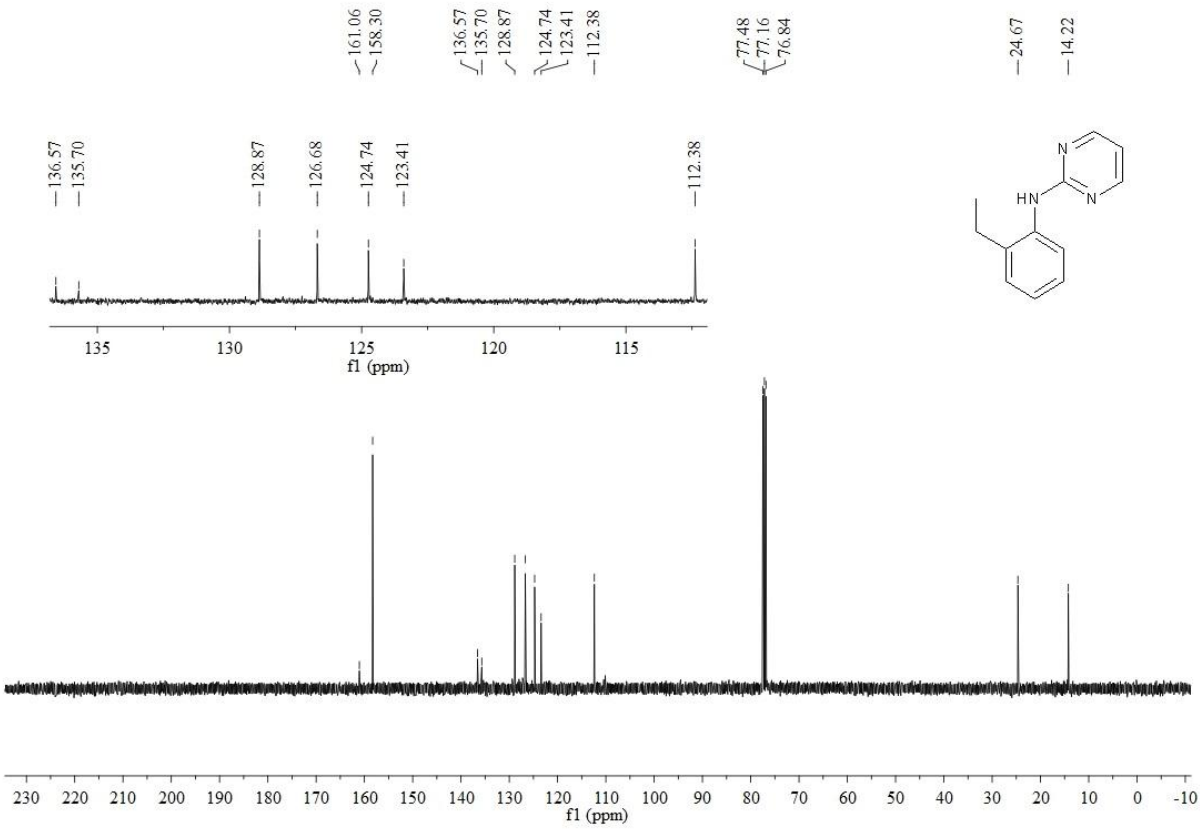
^{13}C NMR spectra of cyclometallated Rh^{III} complex **B1**:



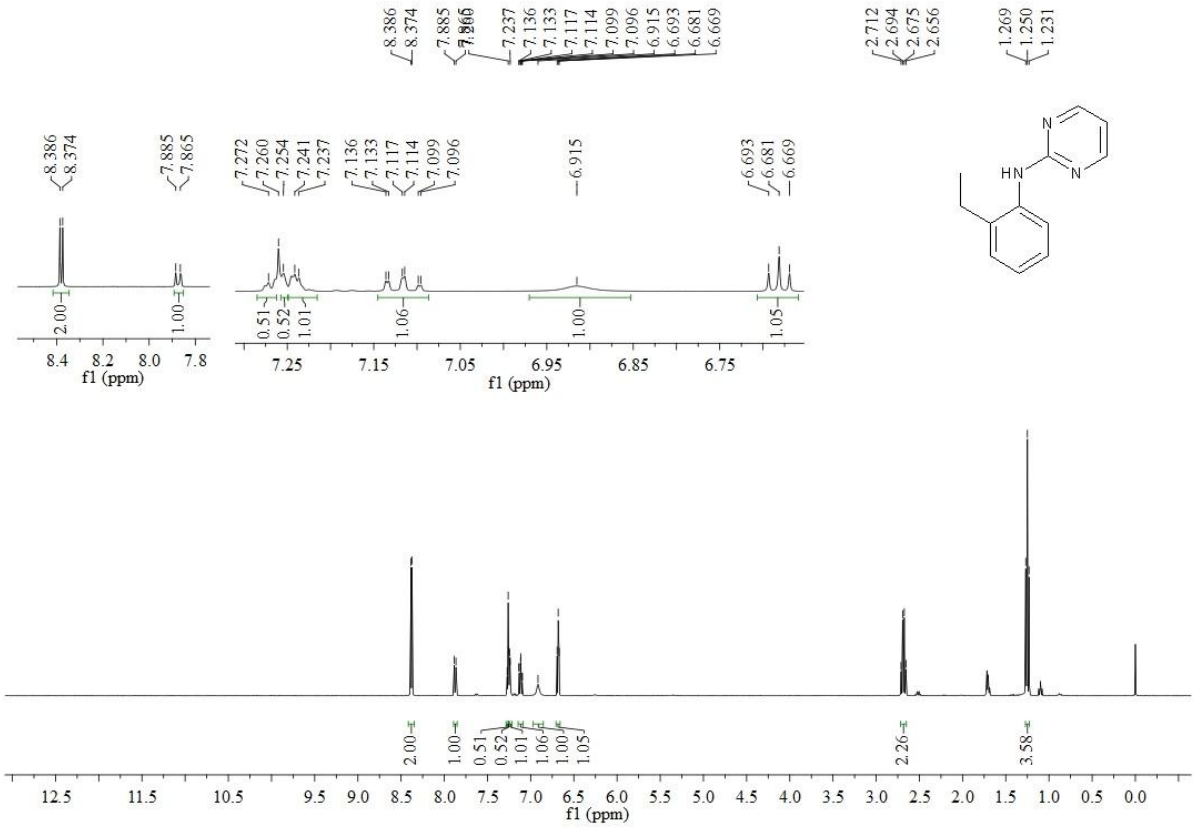
^{1}H NMR spectra of cyclometallated Rh^{III} complex **B1**:



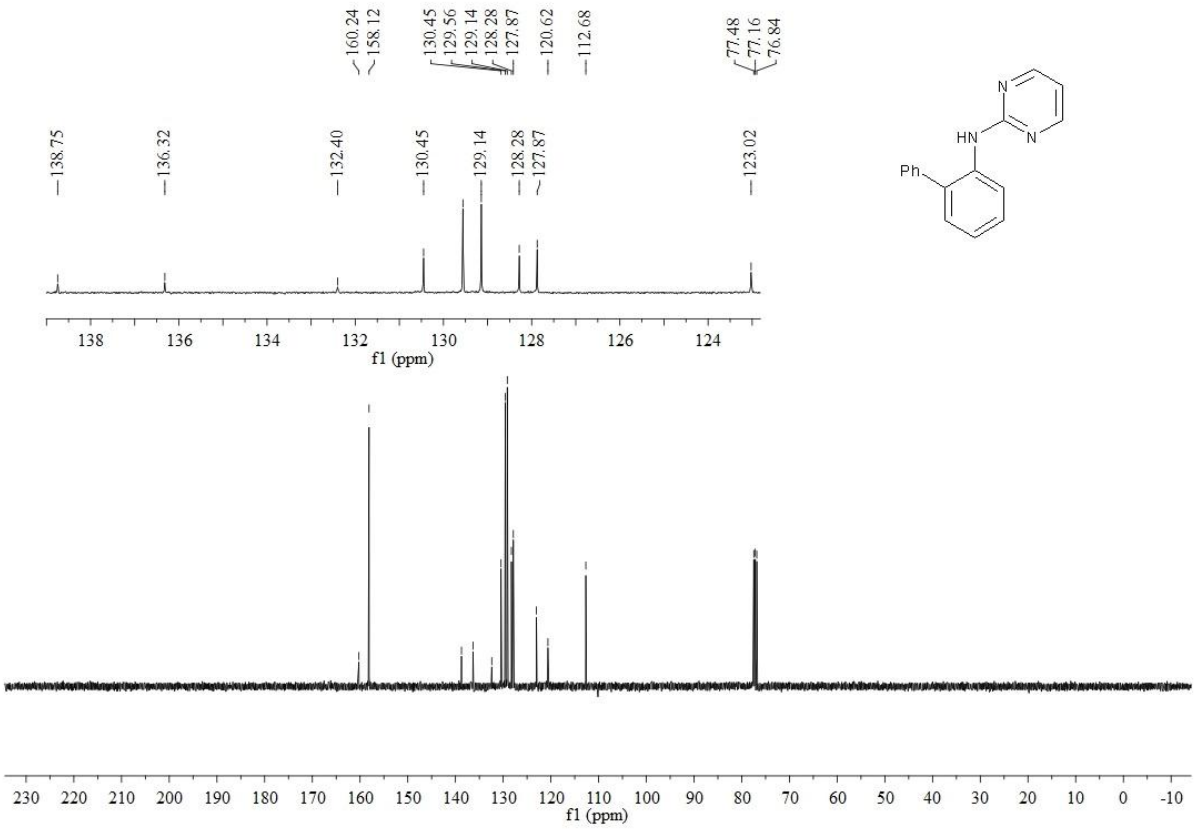
^{13}C NMR spectra of **1f**:



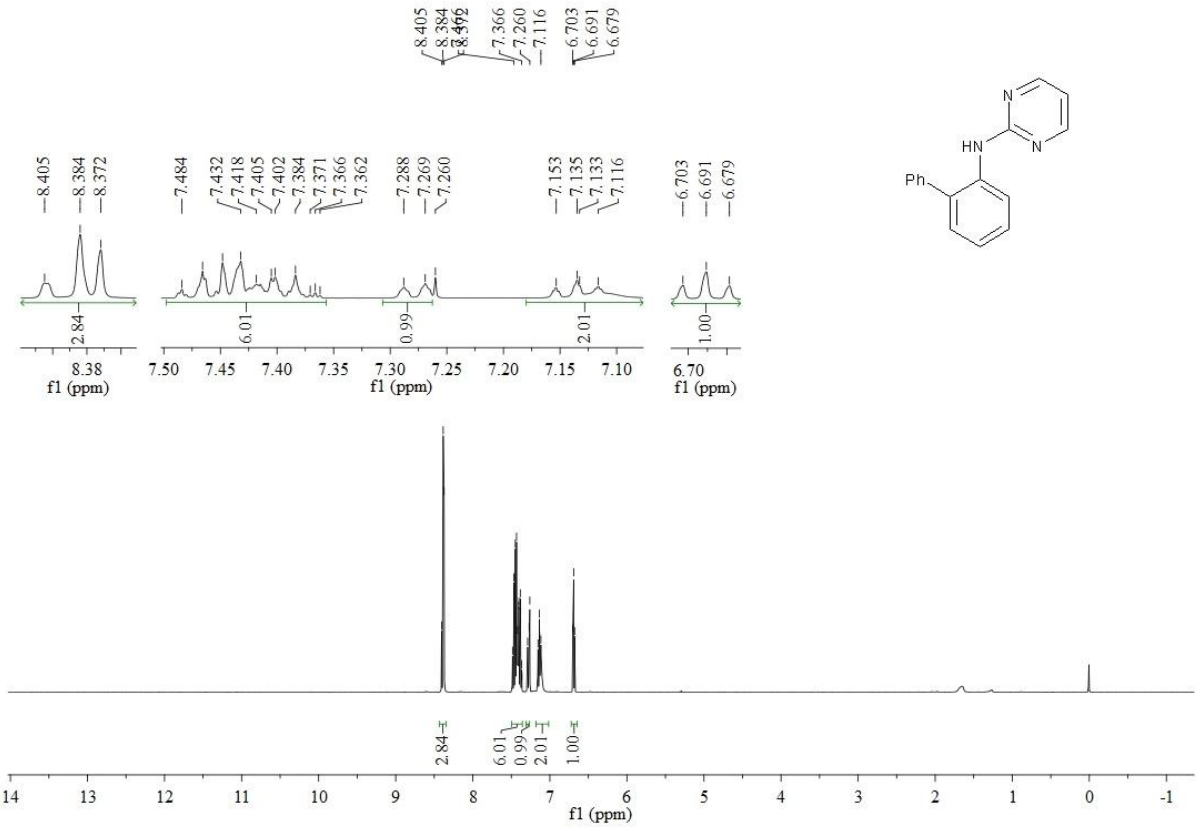
^{1}H NMR spectra of **1f**:



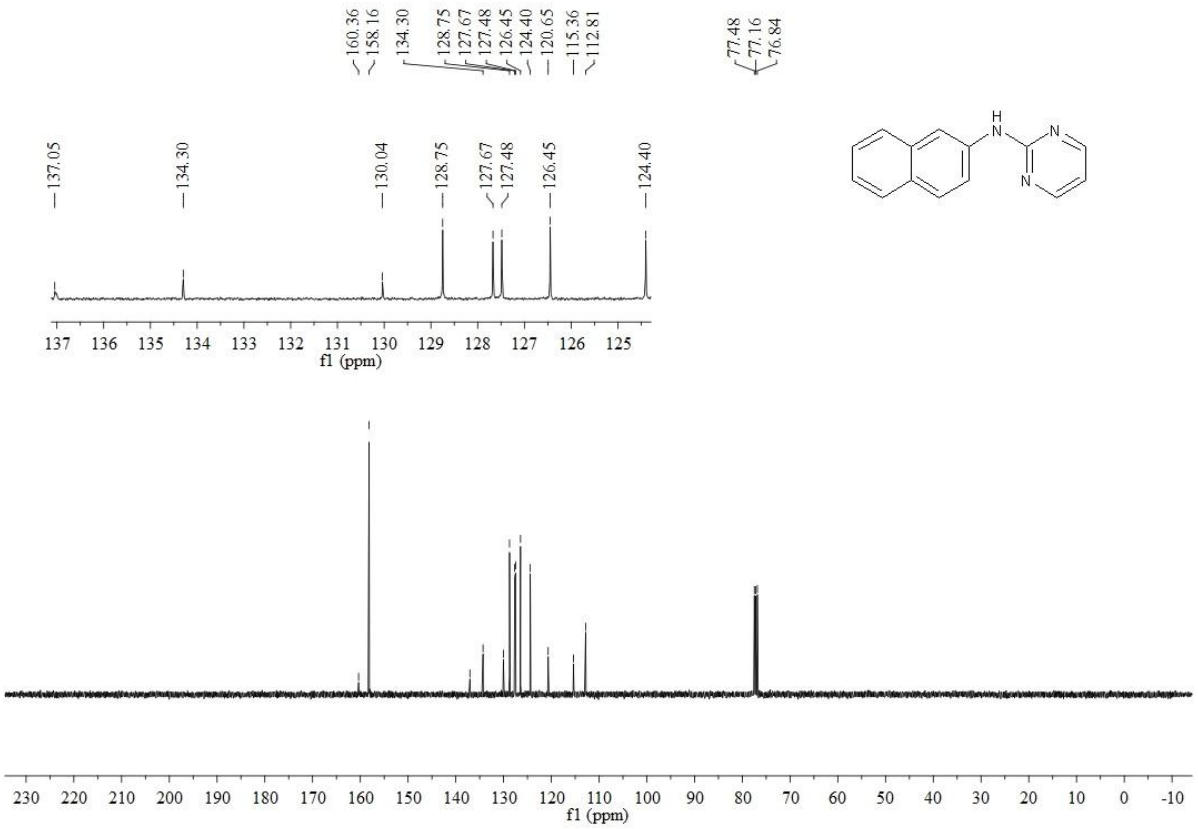
^{13}C NMR spectra of **1h**:



^{1}H NMR spectra of **1h**:



^{13}C NMR spectra of **1k**:



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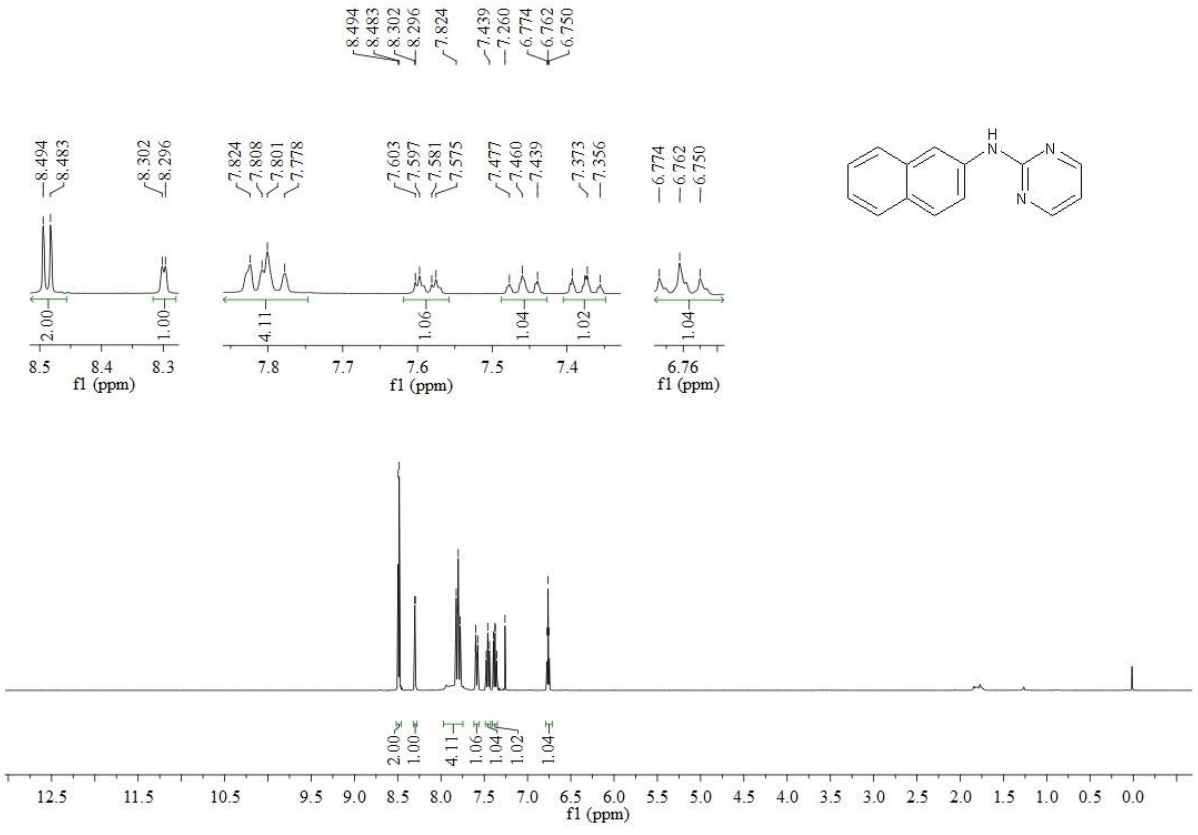
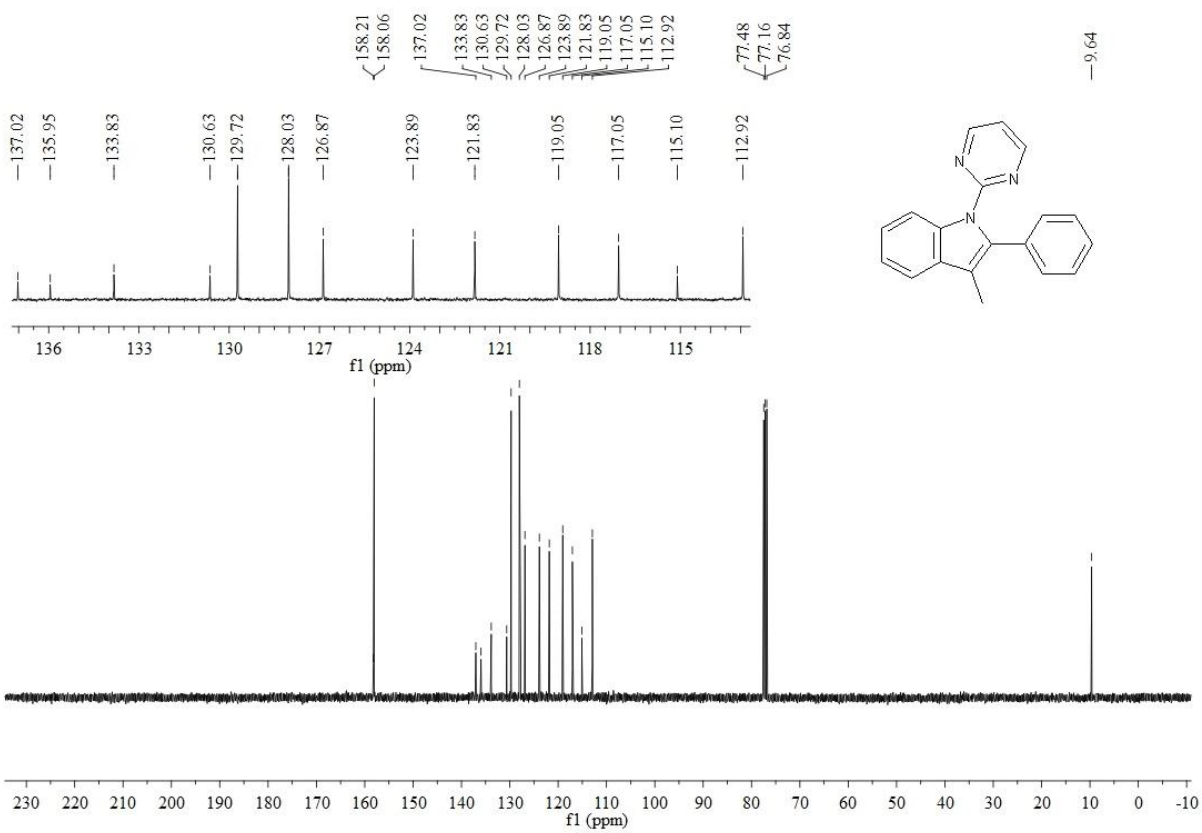
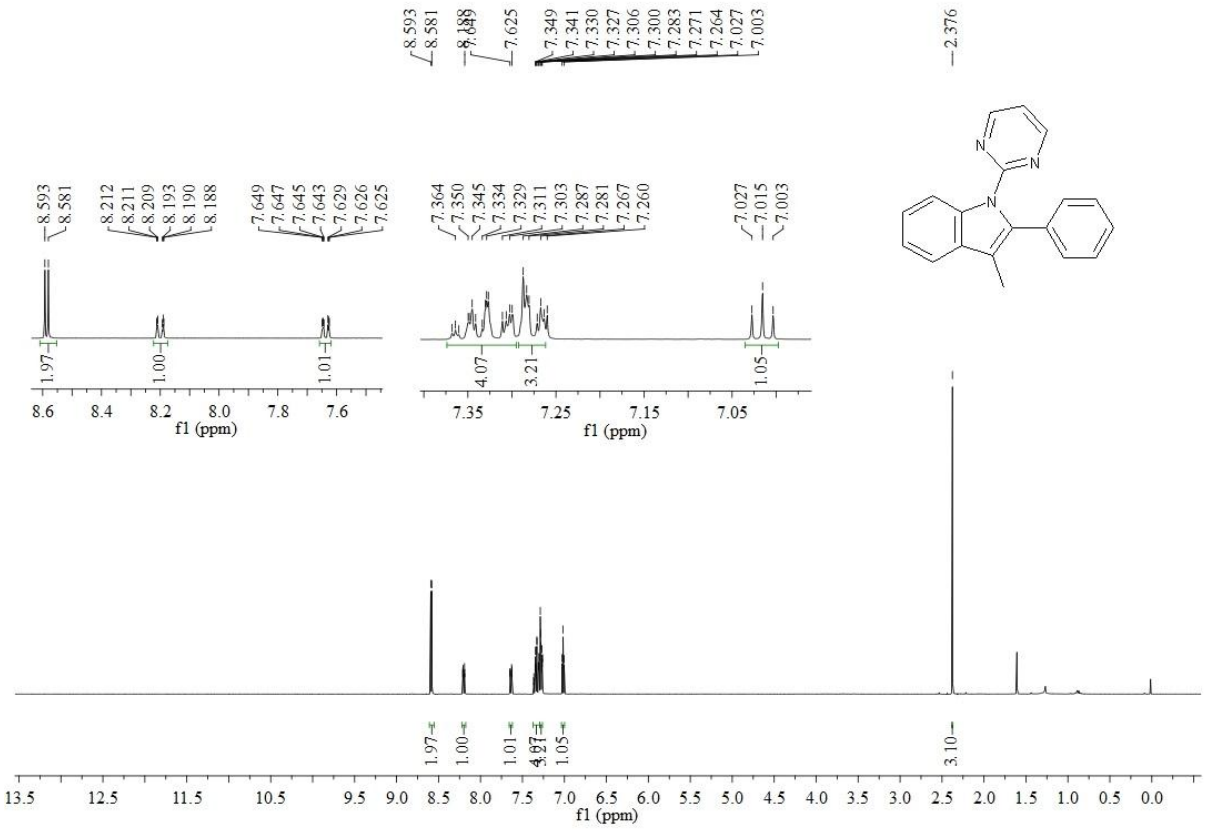


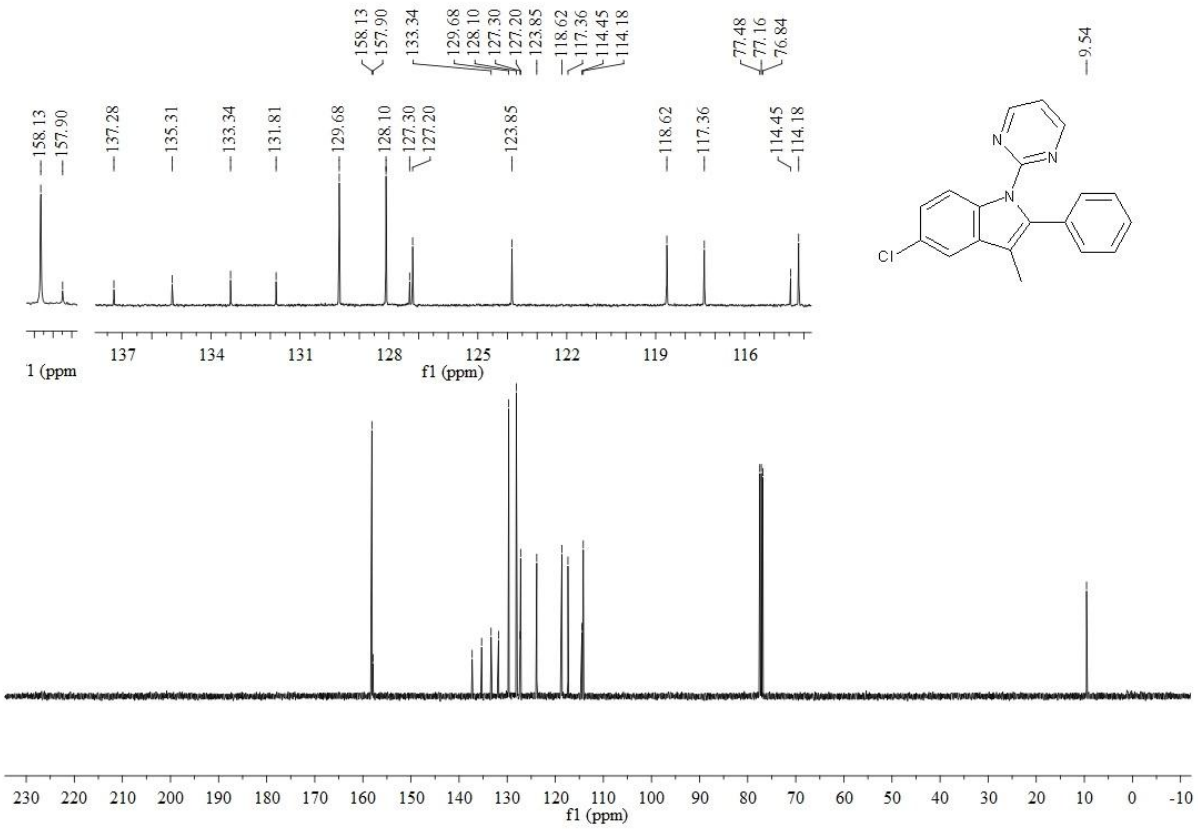
^{13}C NMR spectra of **3a**:



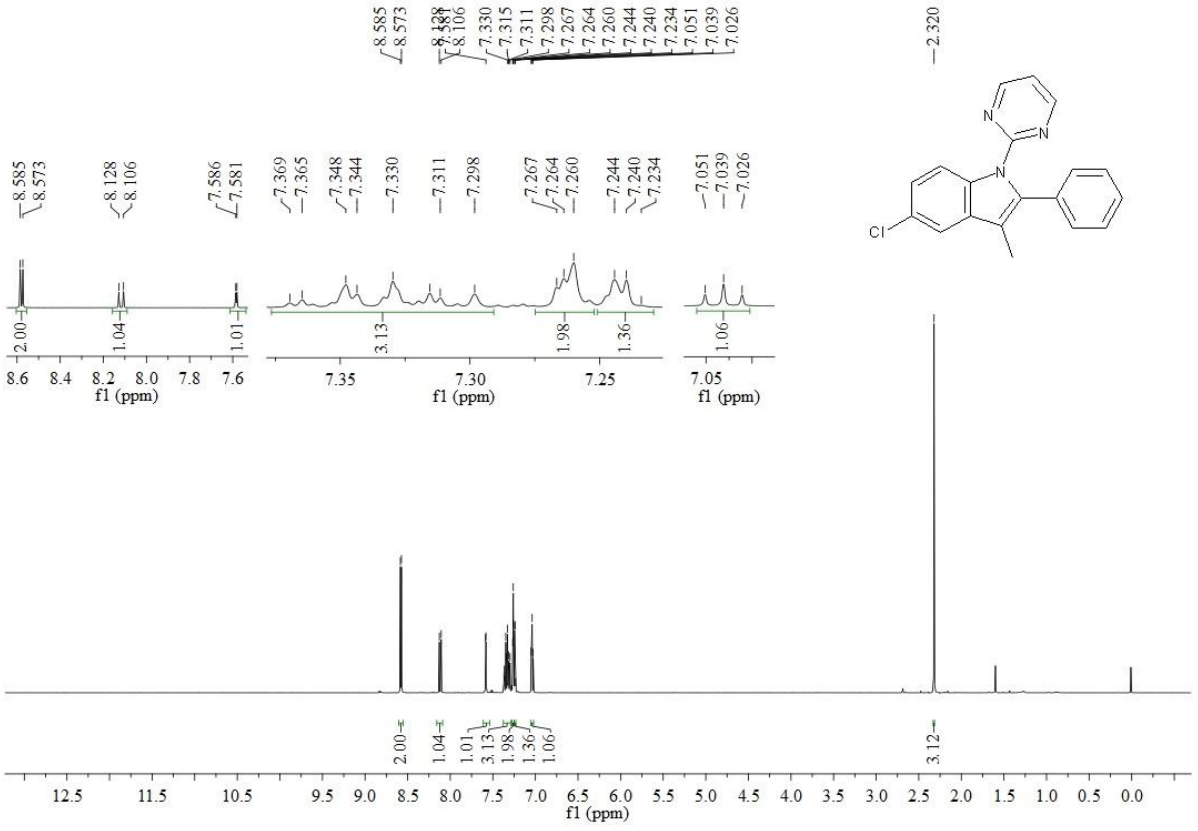
^{1}H NMR spectra of **3a**:



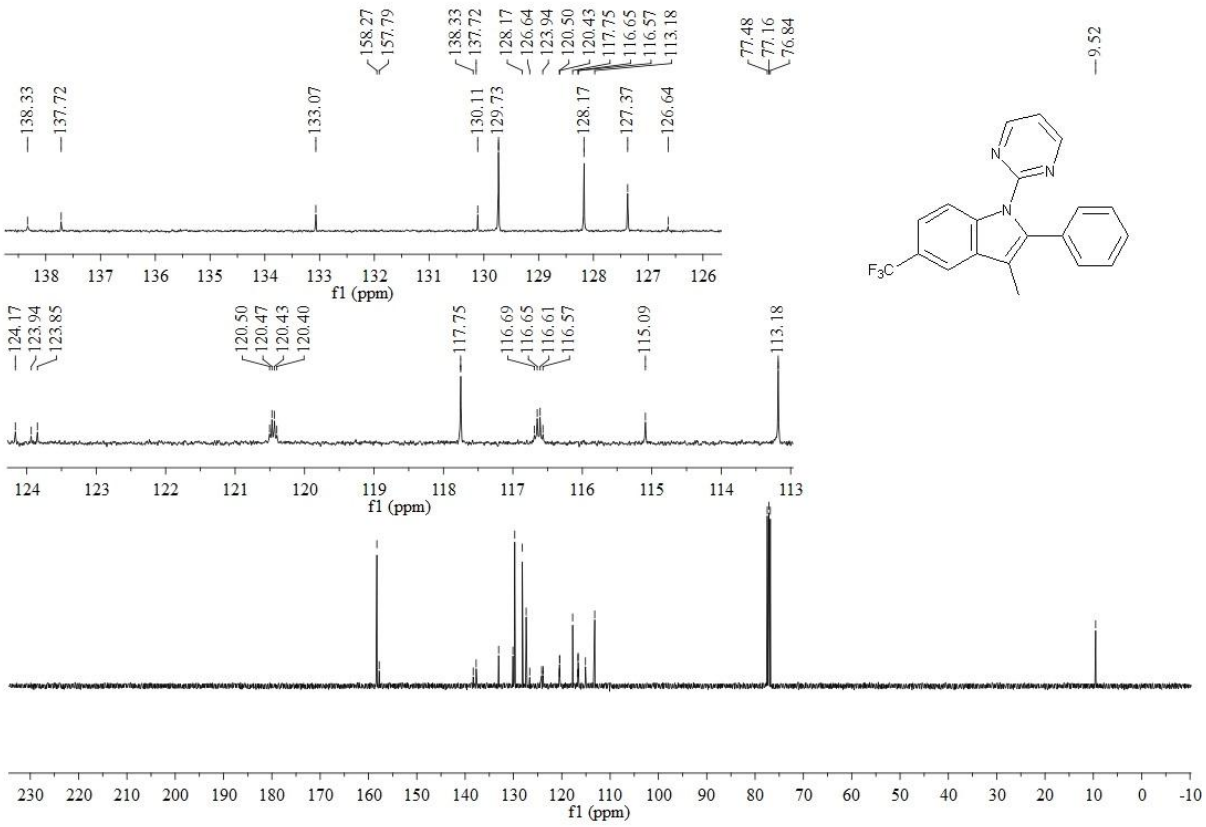
^{13}C NMR spectra of **3b**:



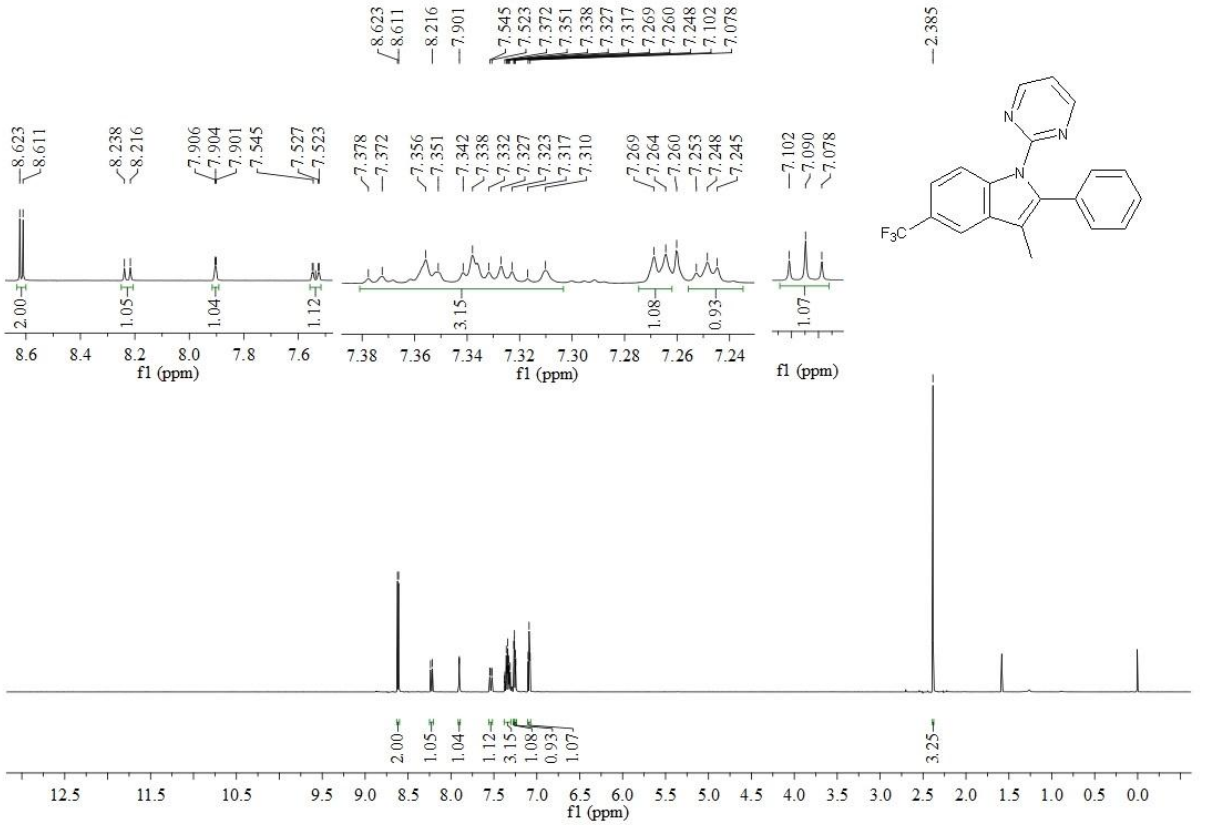
^{1}H NMR spectra of **3b**:



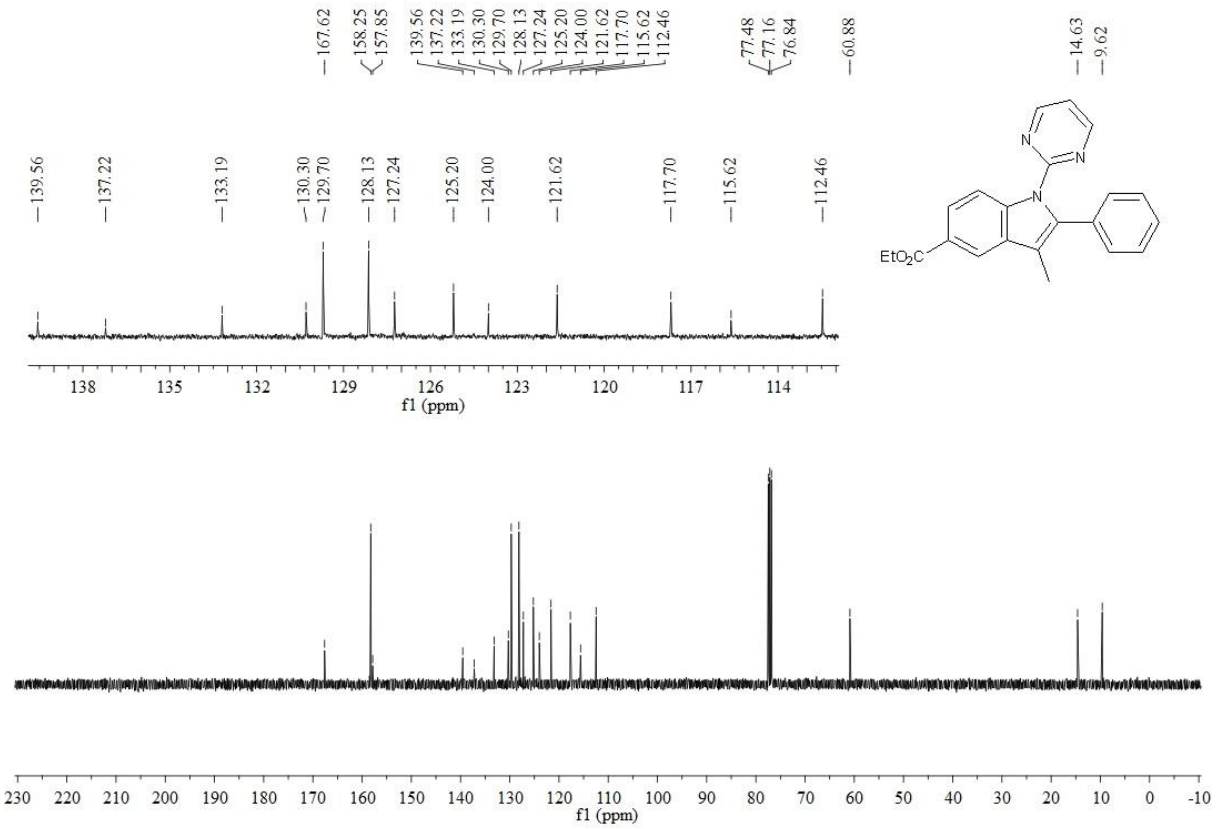
^{13}C NMR spectra of **3c**:



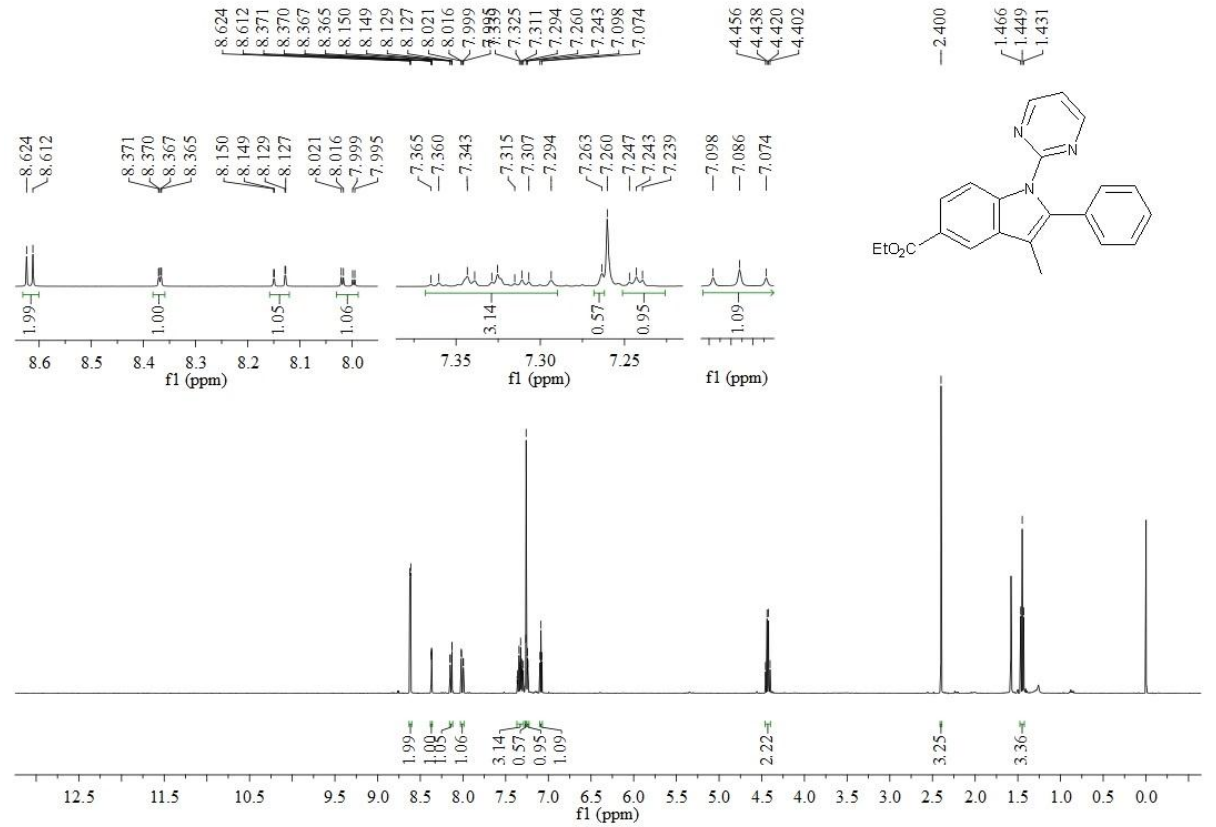
^{1}H NMR spectra of **3c**:



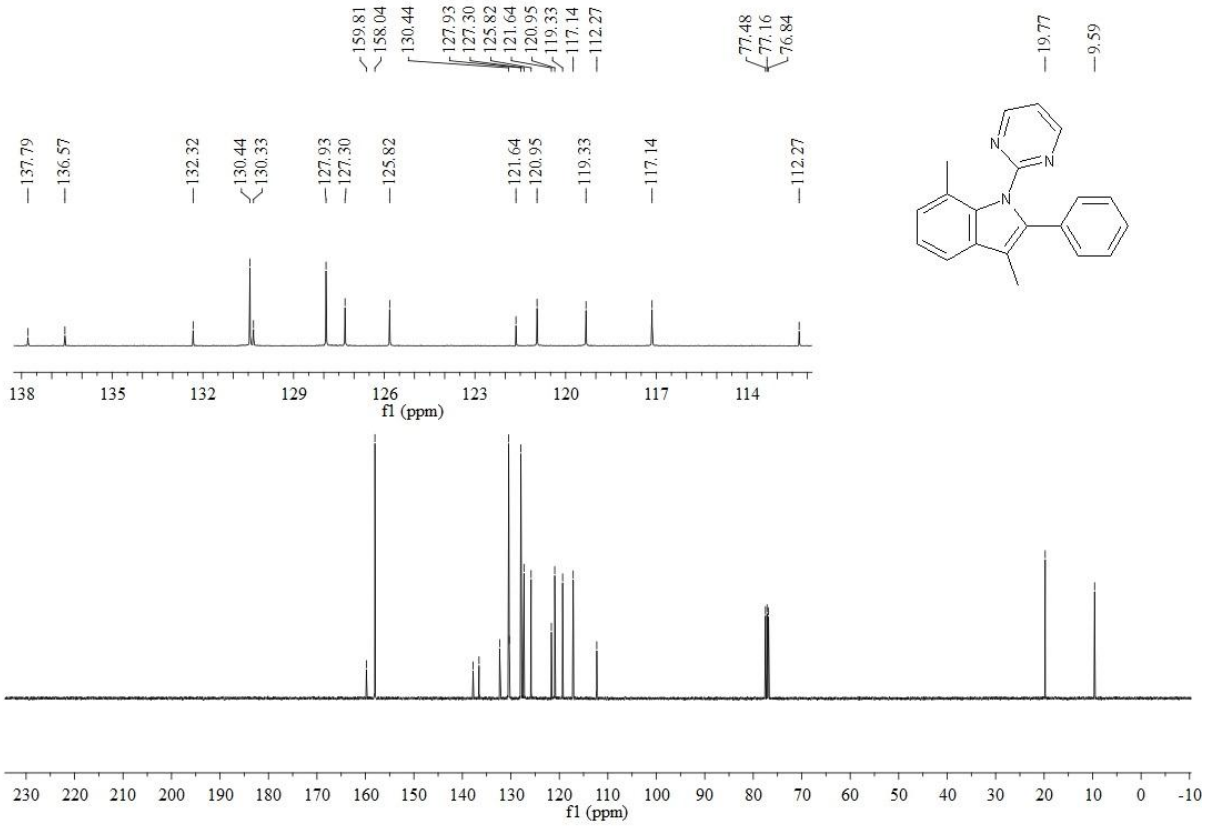
^{13}C NMR spectra of **3d**:



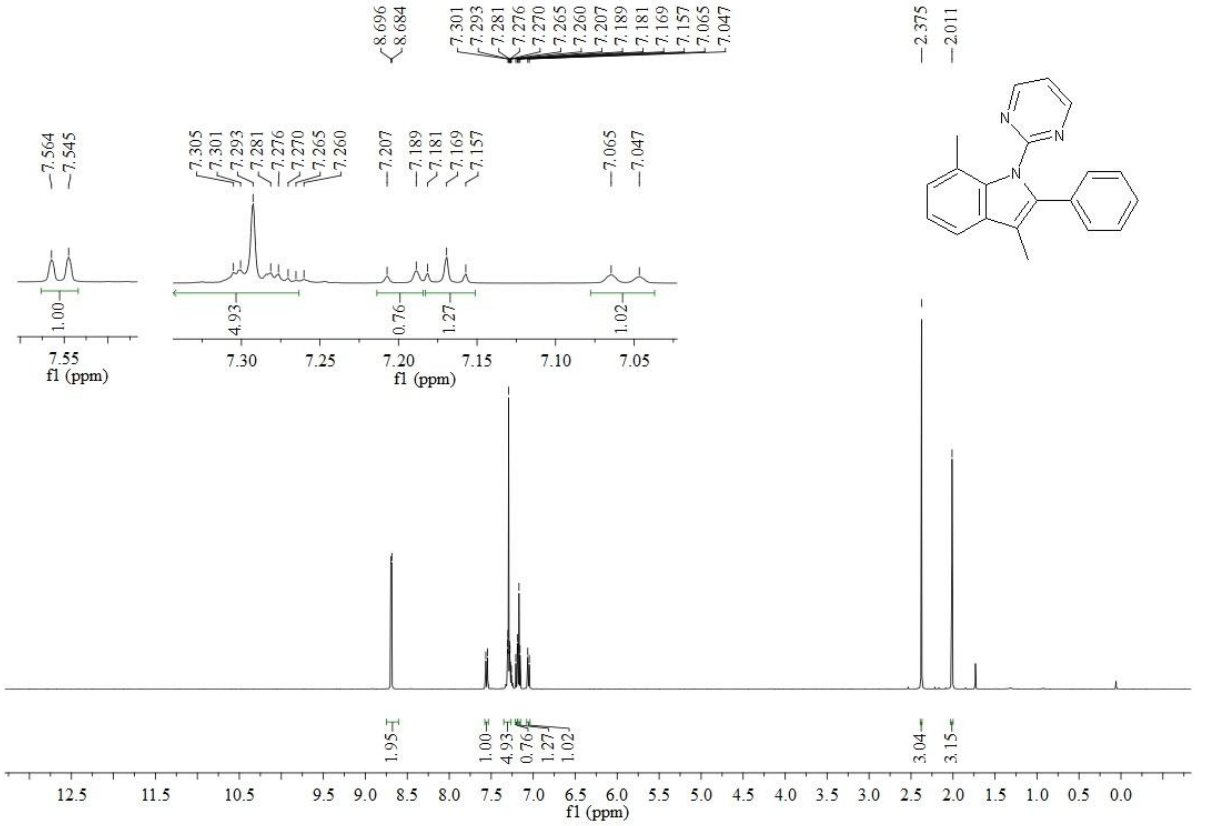
^{1}H NMR spectra of **3d**:



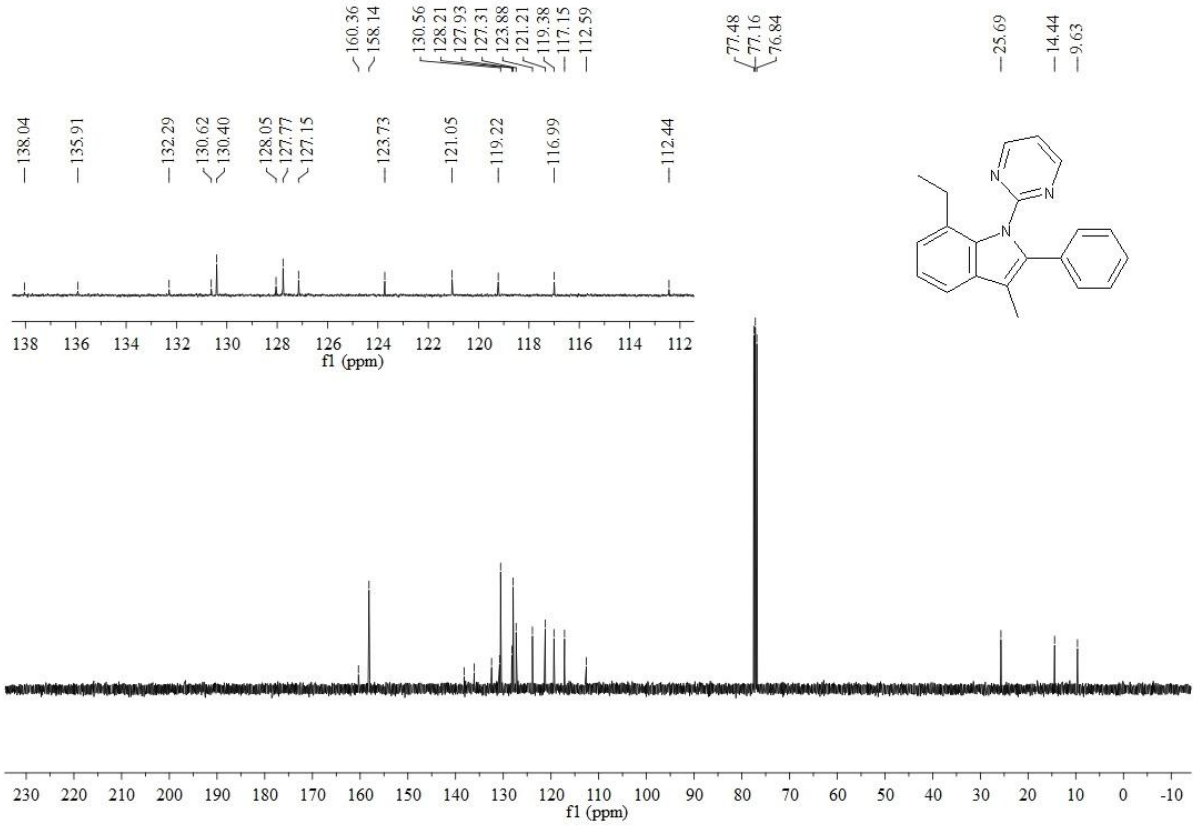
^{13}C NMR spectra of **3e**:



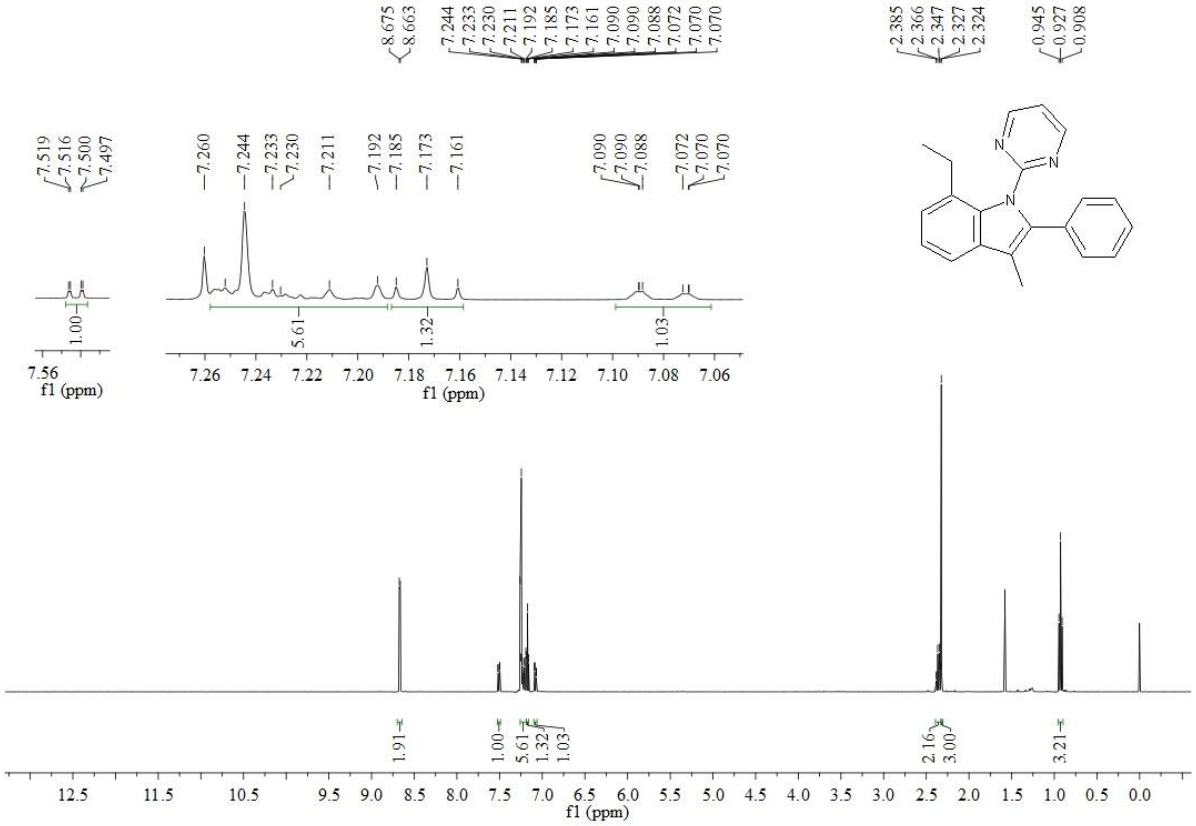
^{1}H NMR spectra of **3e**:



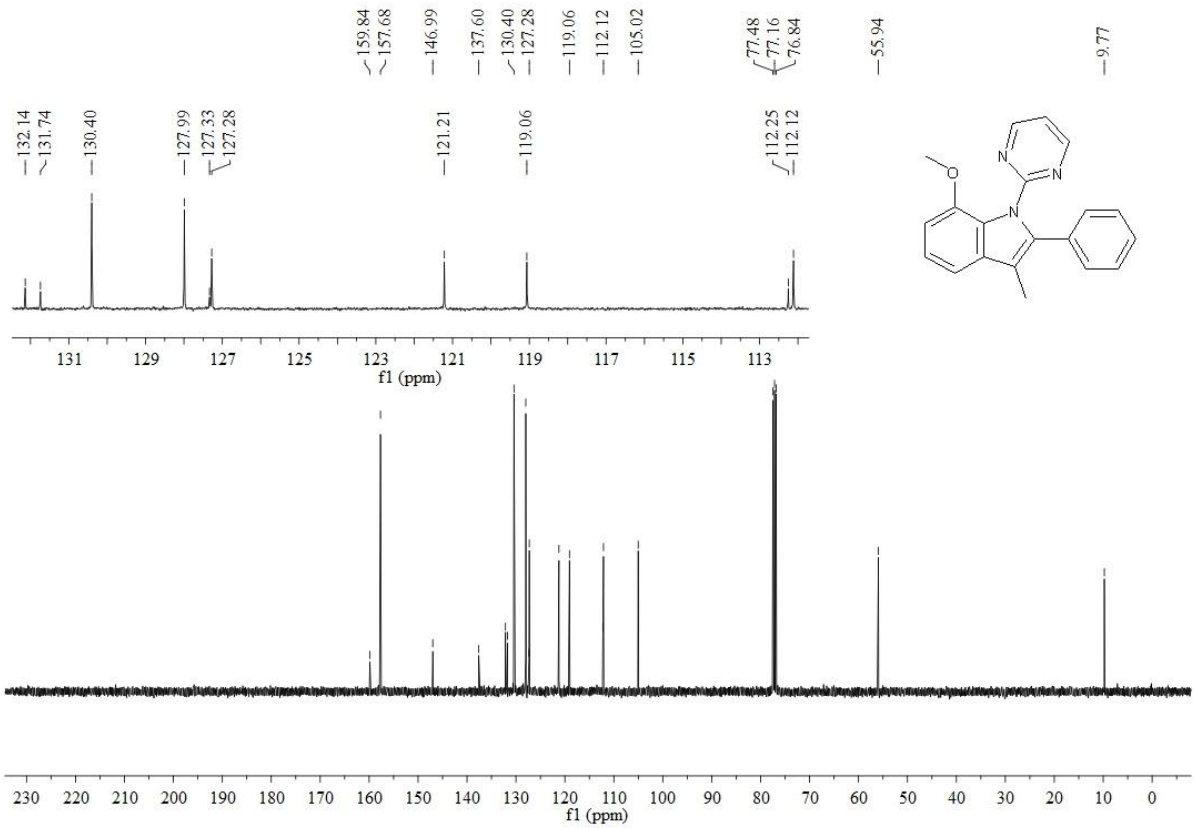
^{13}C NMR spectra of **3f**:



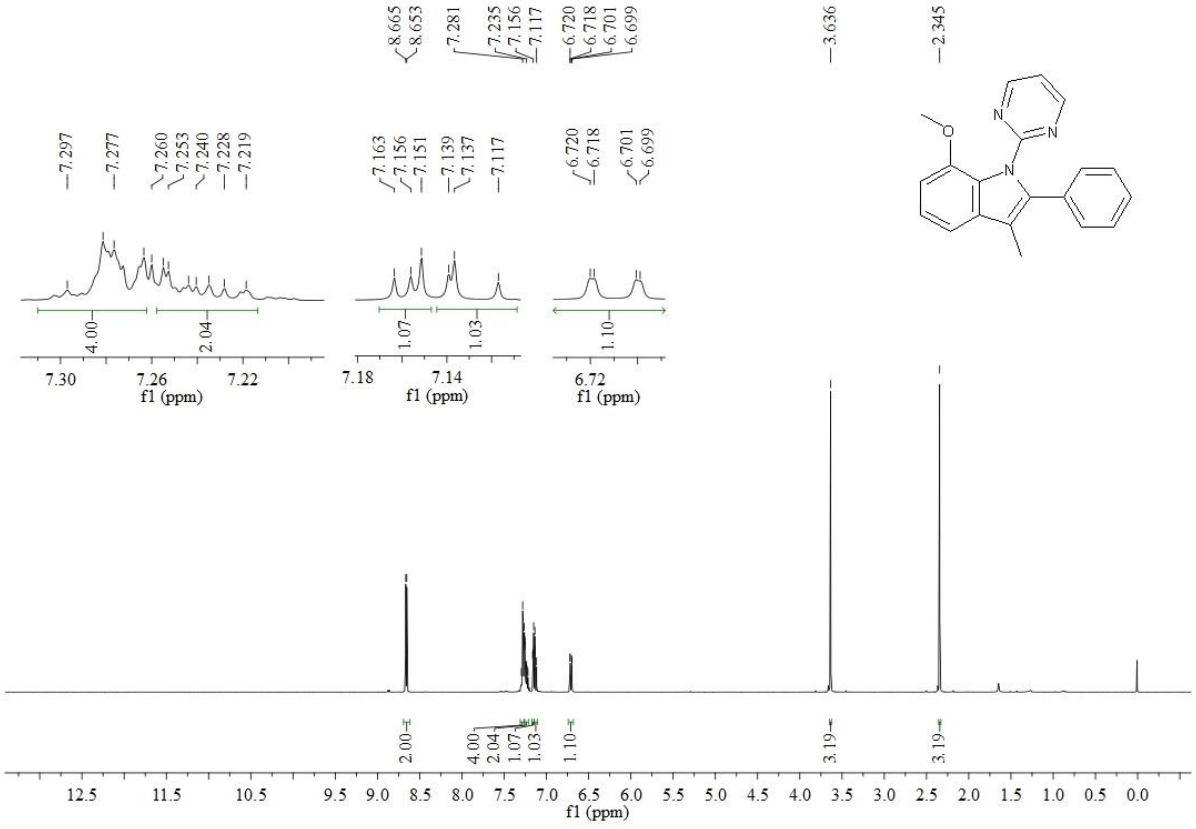
^{1}H NMR spectra of **3f**:



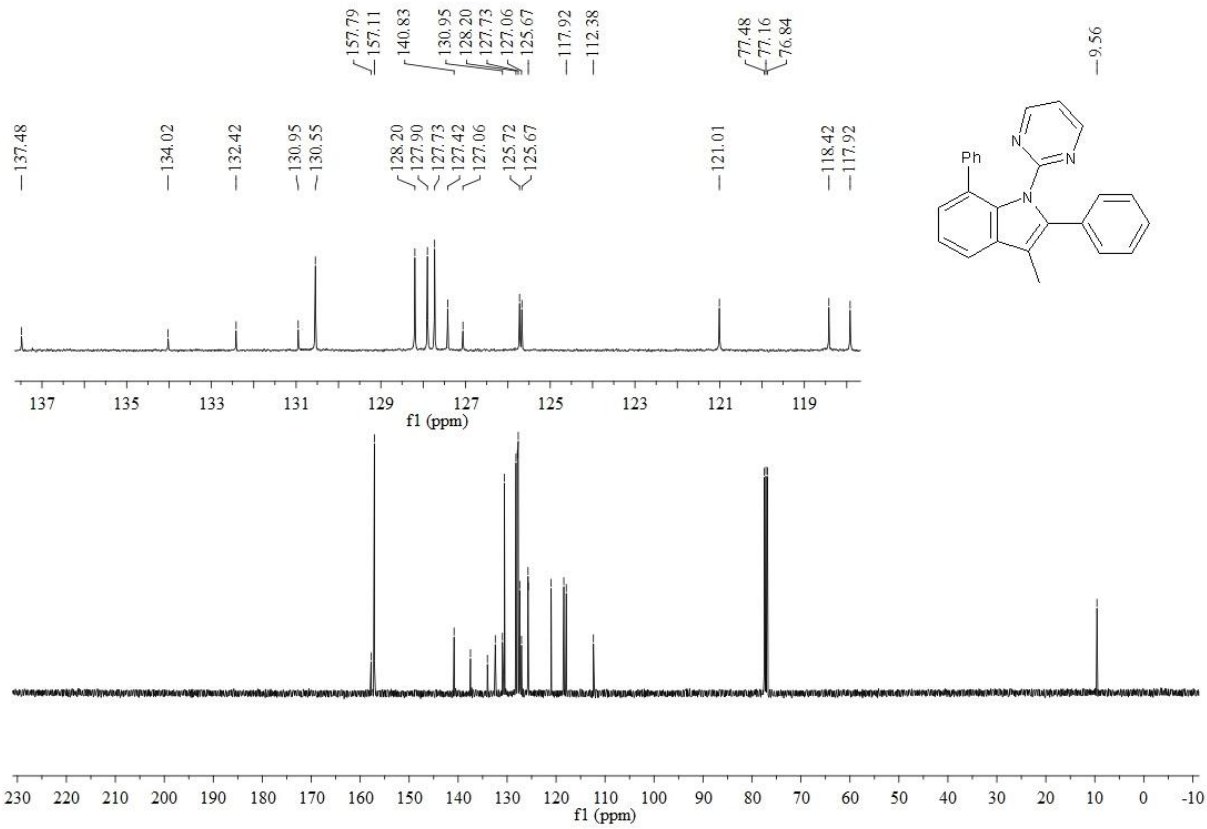
^{13}C NMR spectra of **3g**:



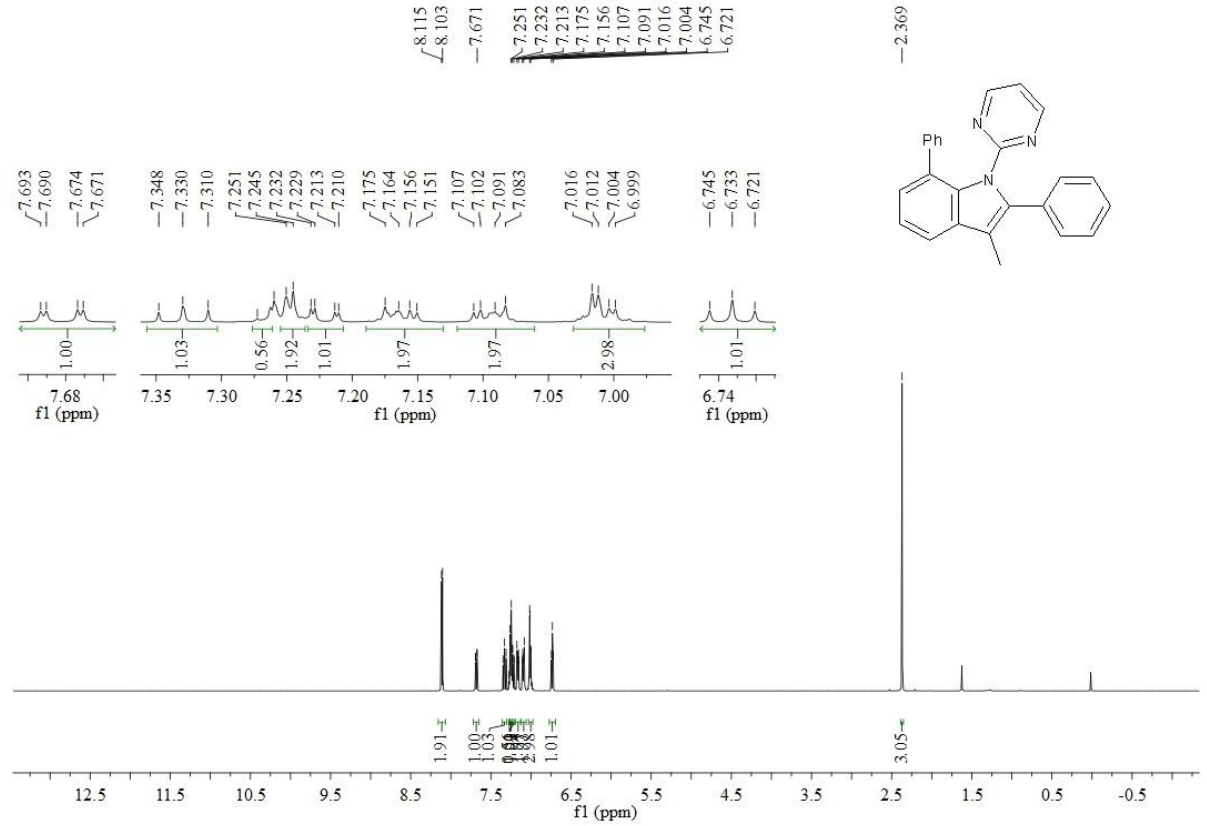
^{1}H NMR spectra of **3g**:



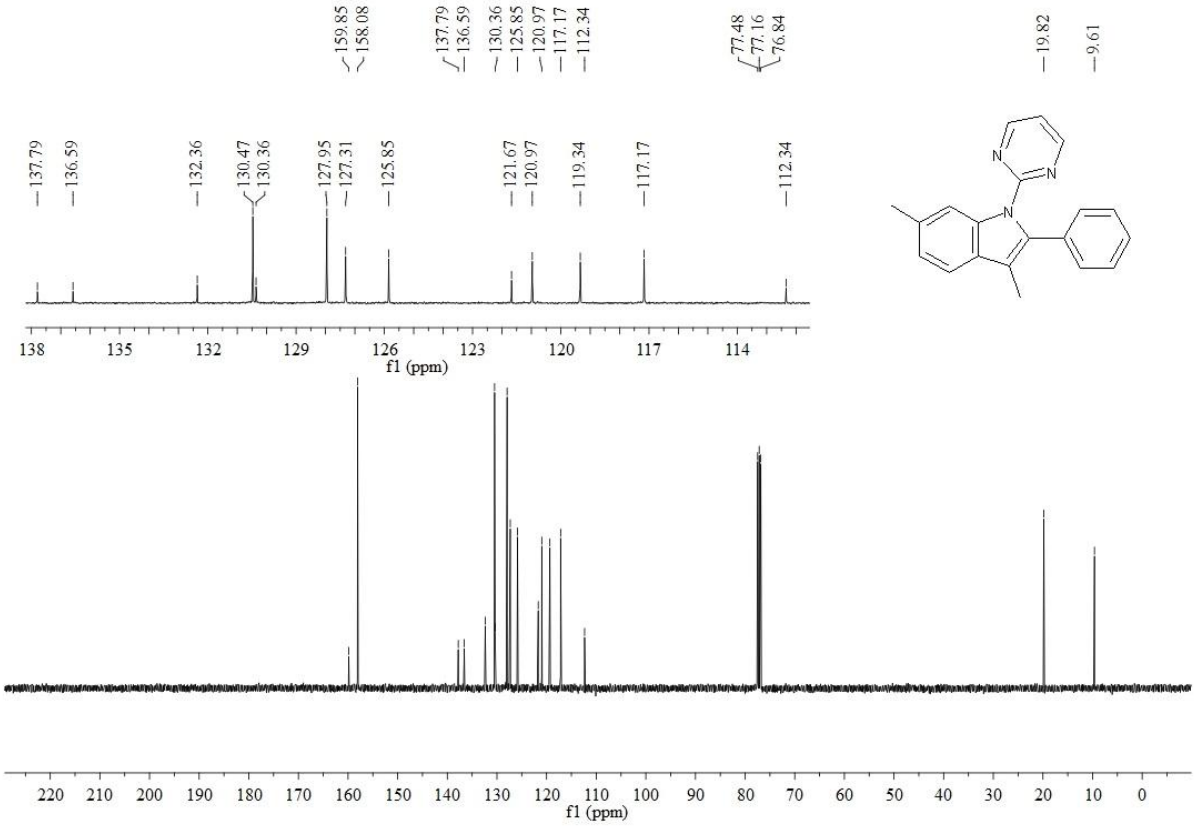
^{13}C NMR spectra of **3h**:



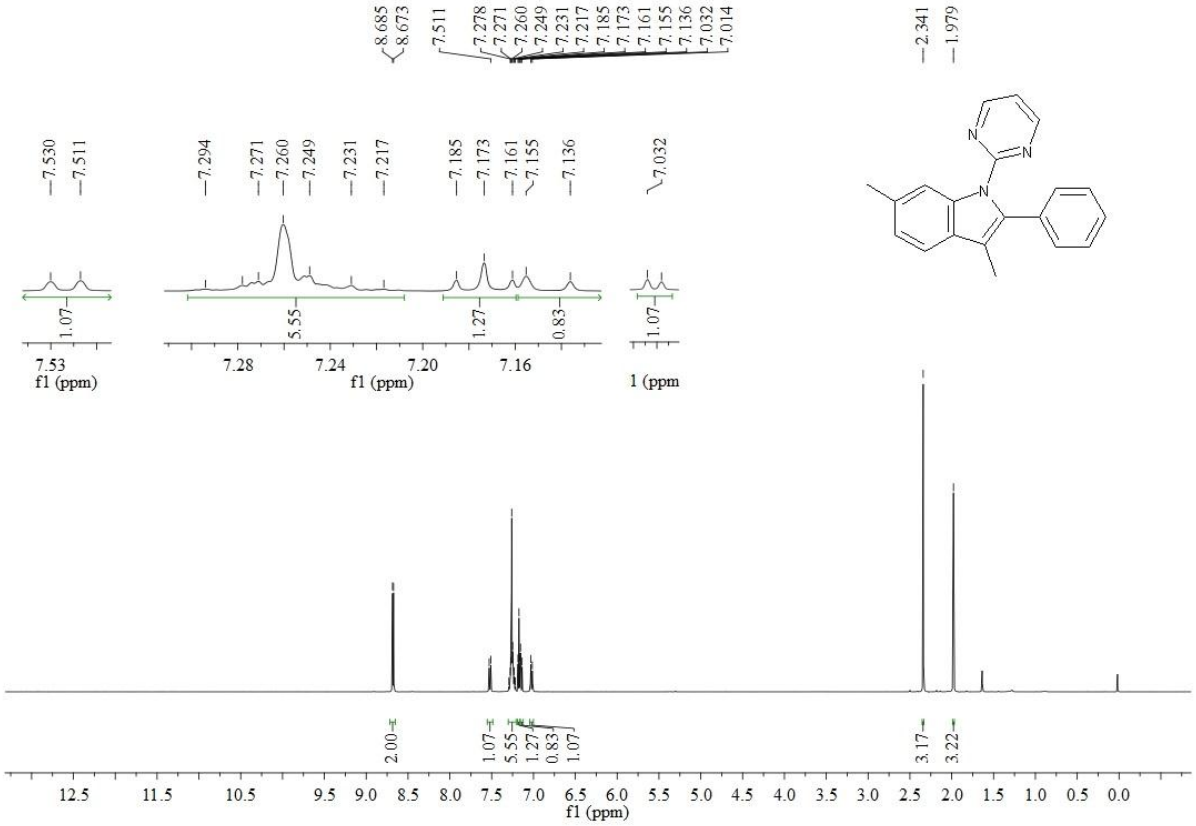
^{1}H NMR spectra of **3h**:



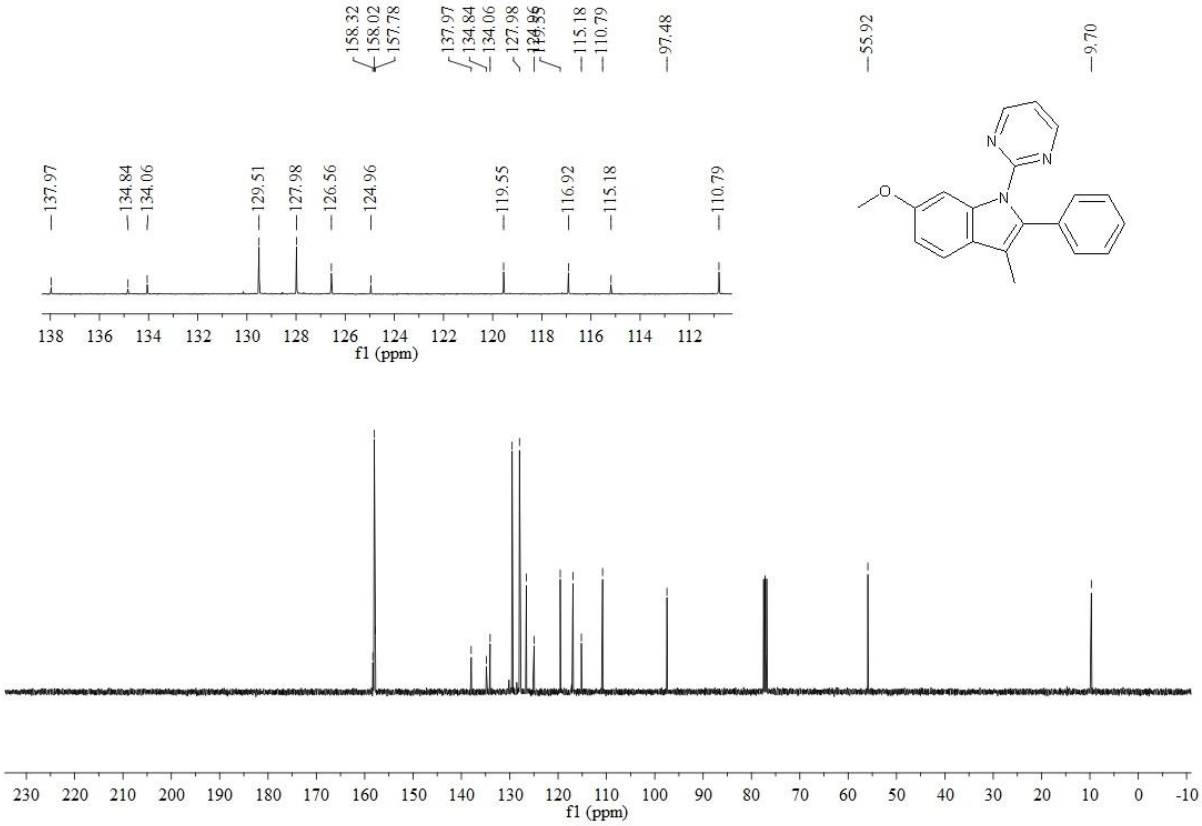
^{13}C NMR spectra of **3i**:



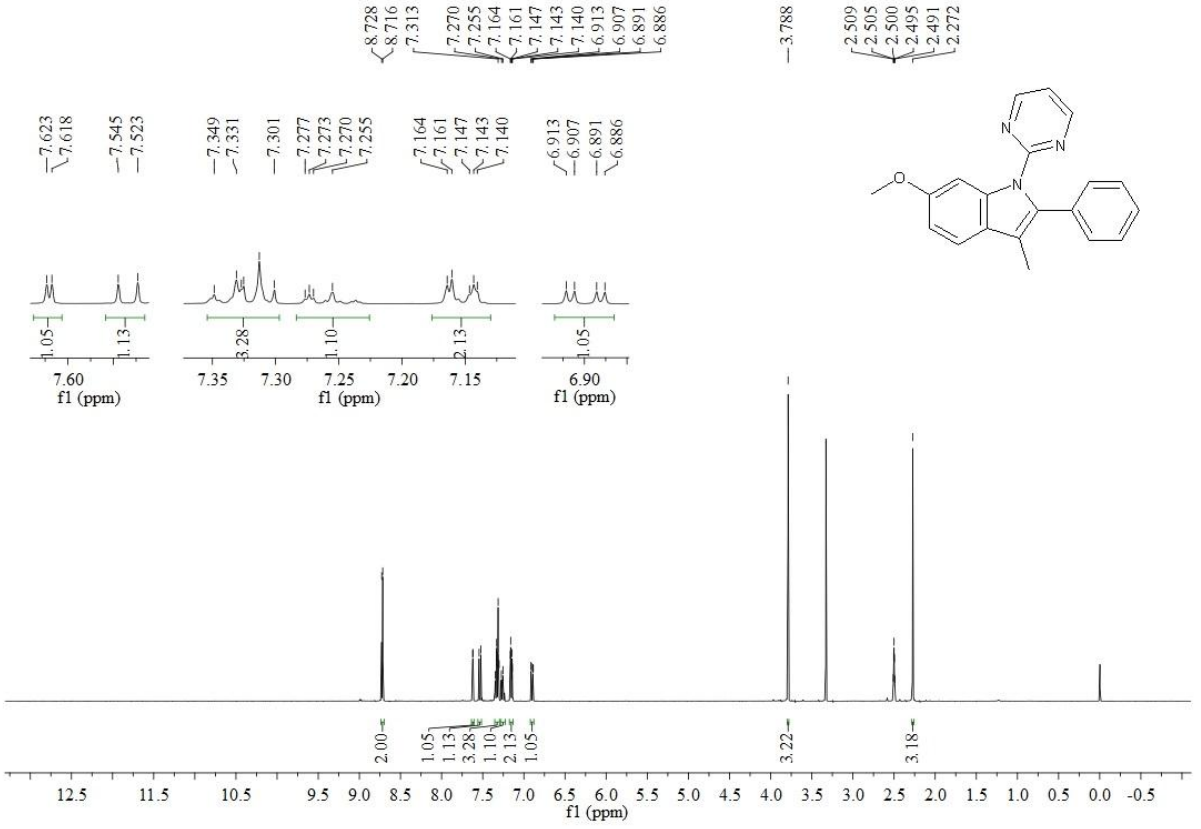
^{1}H NMR spectra of **3i**:



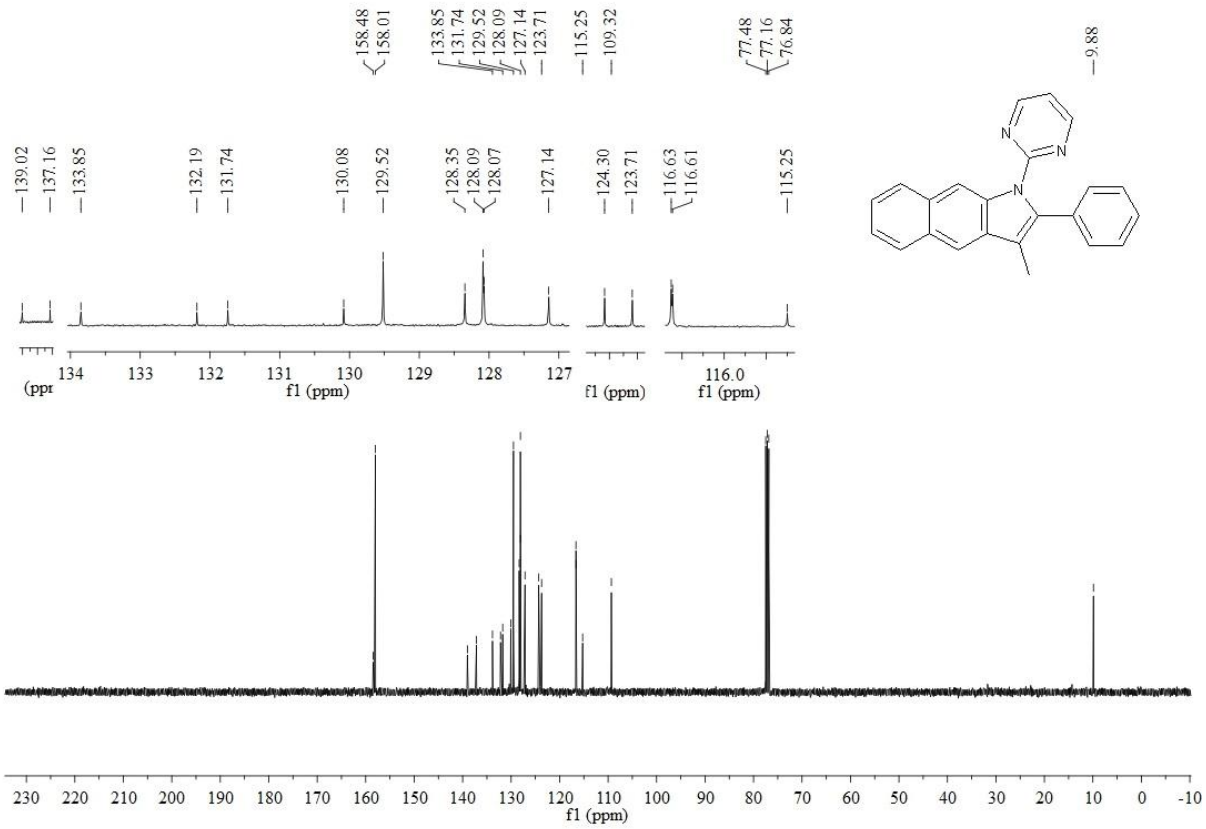
^{13}C NMR spectra of **3j**:



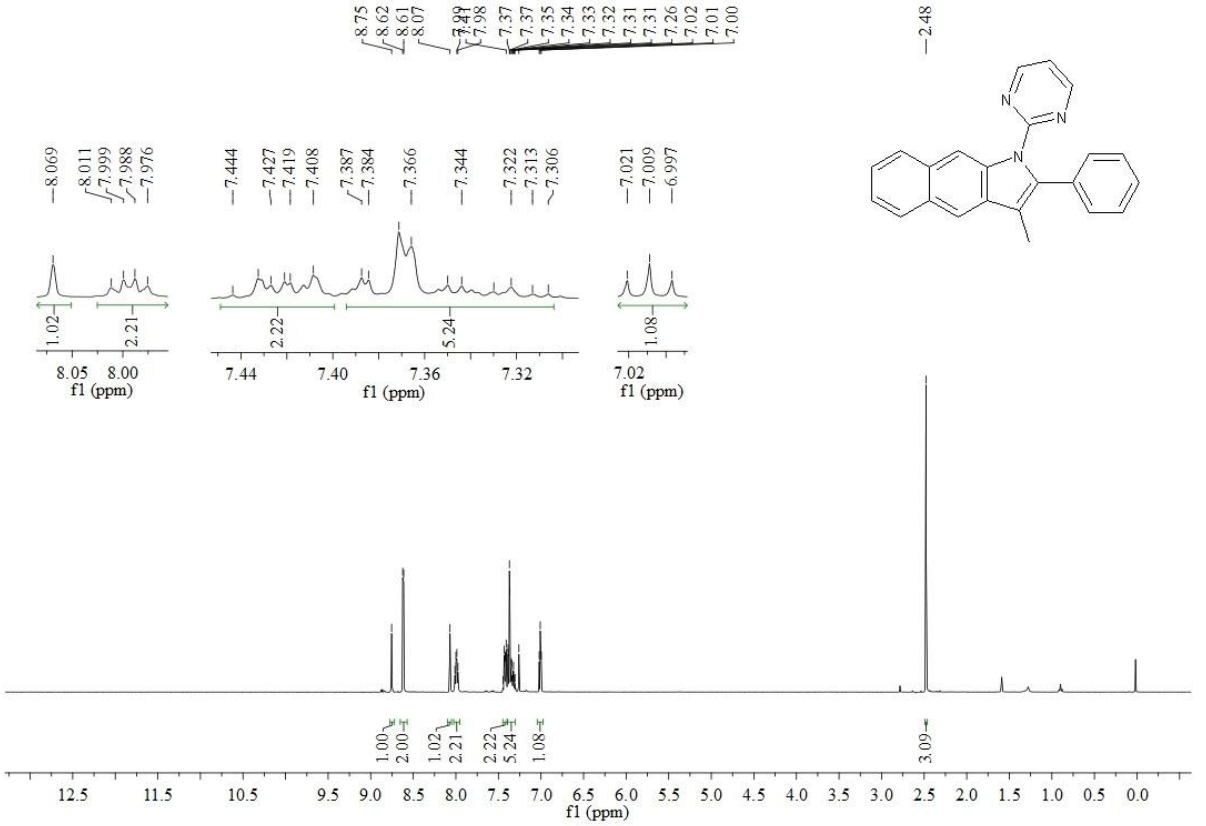
^{1}H NMR spectra of **3j**:



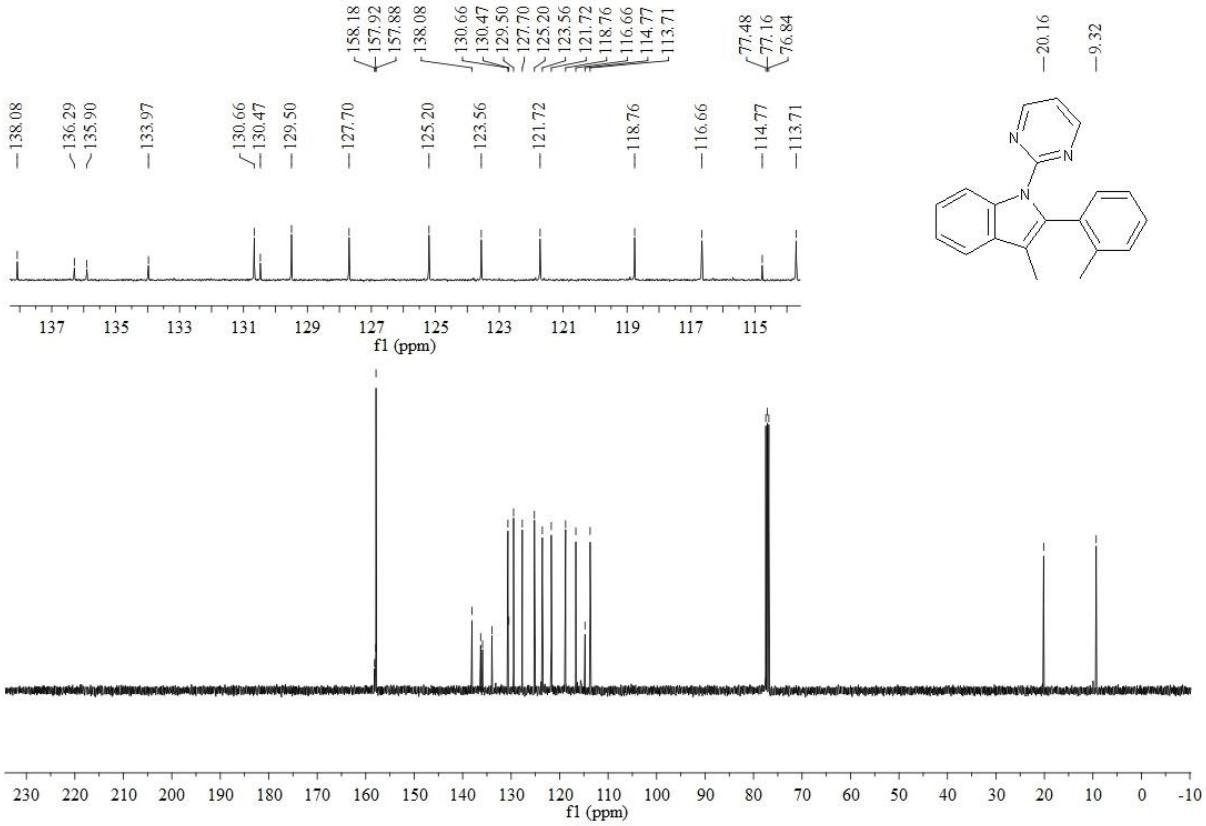
^{13}C NMR spectra of **3k**:



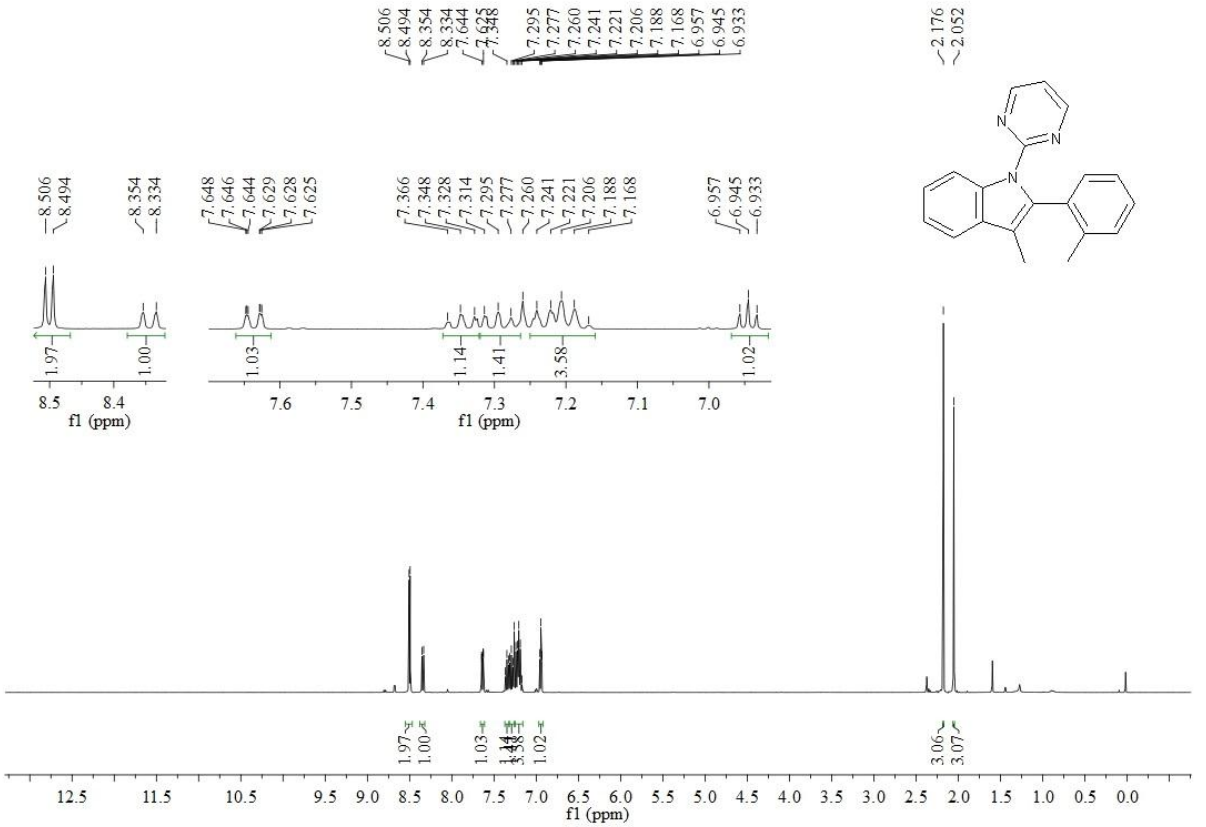
^{1}H NMR spectra of **3k**:



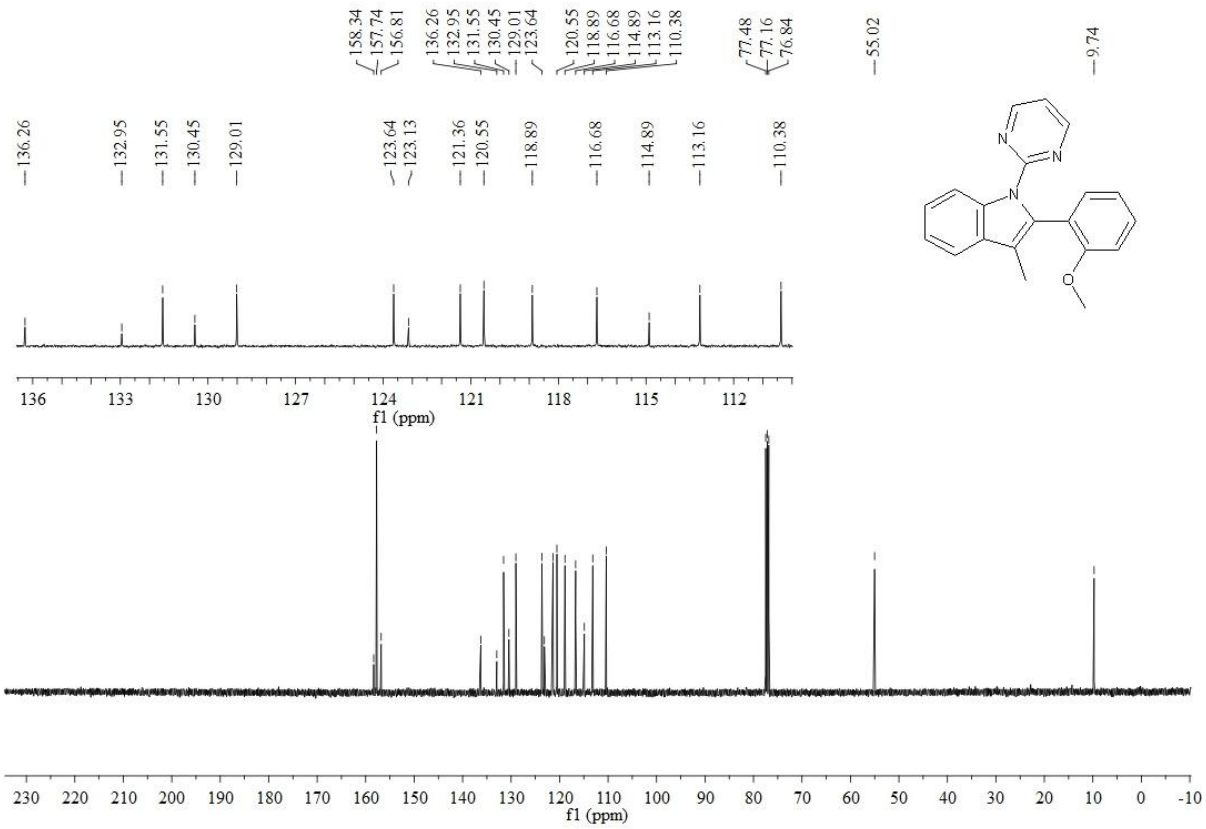
^{13}C NMR spectra of **4a**:



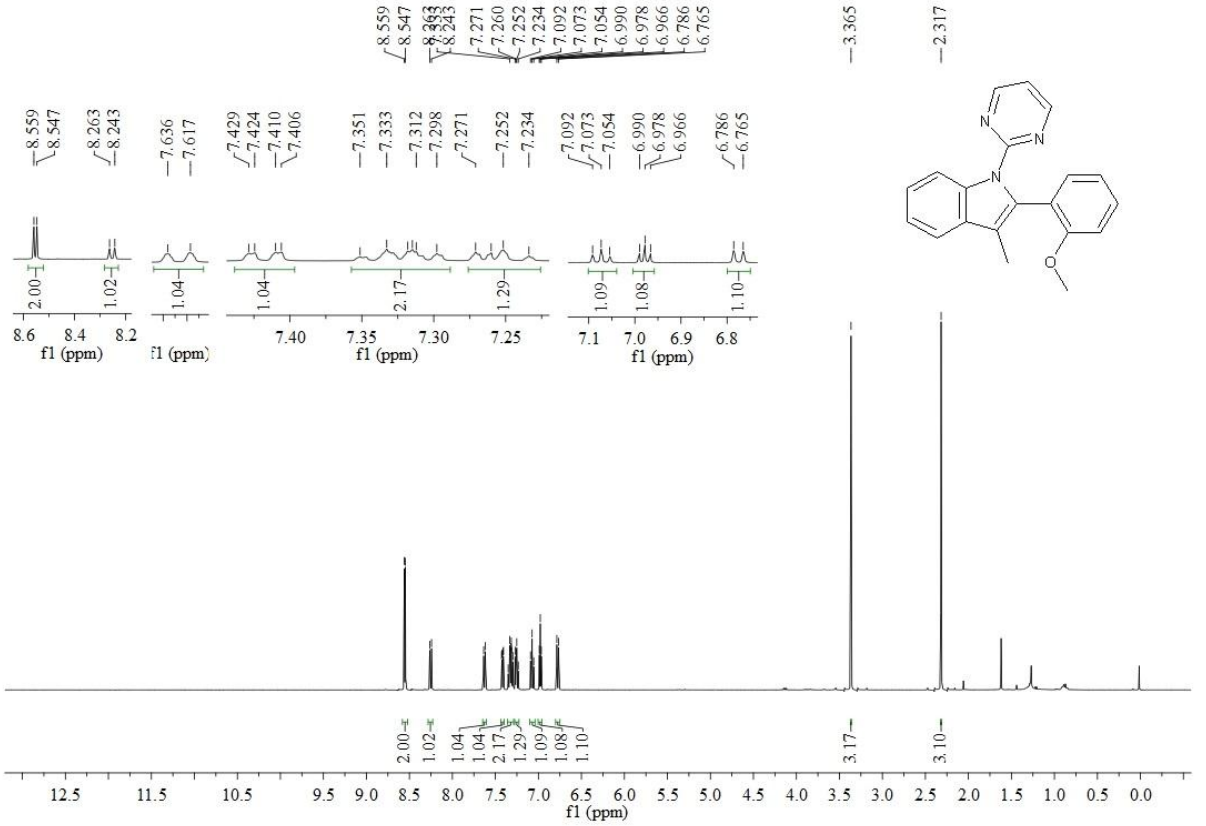
^{1}H NMR spectra of **4a**:



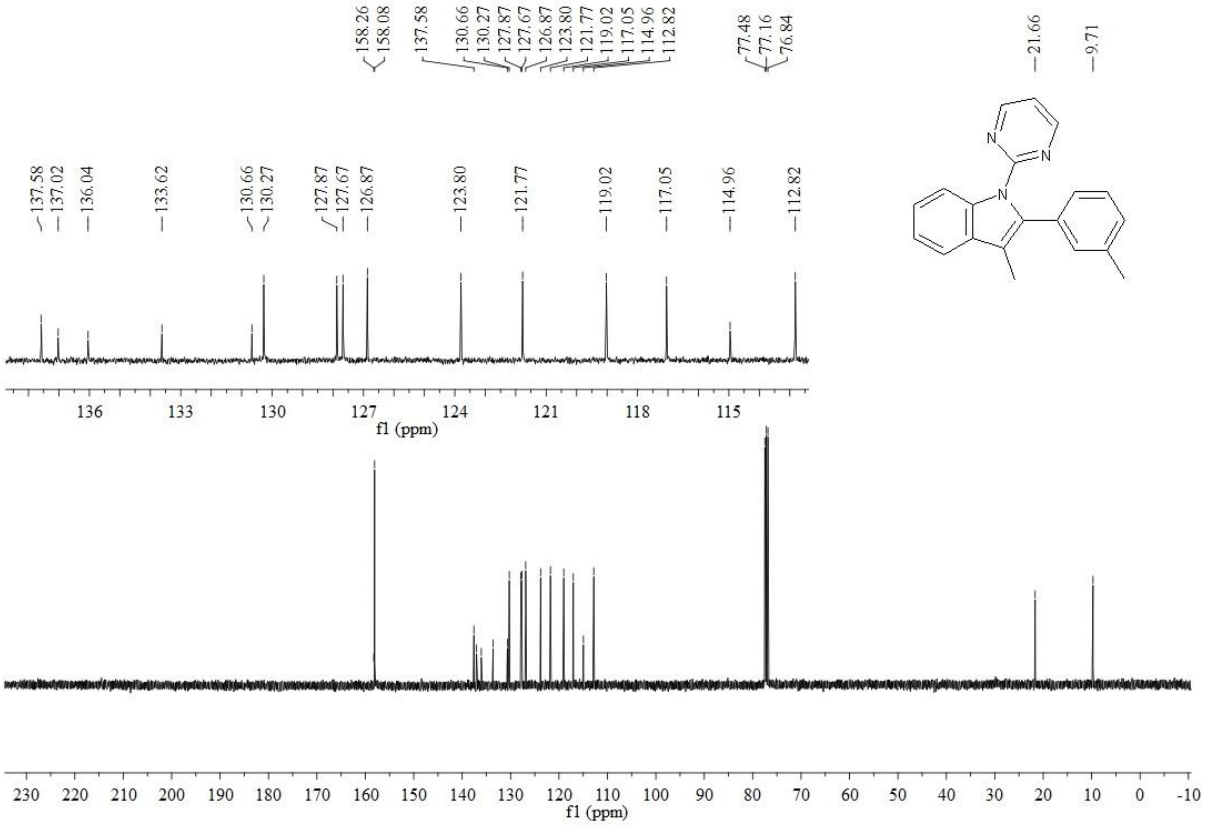
^{13}C NMR spectra of **4b**:



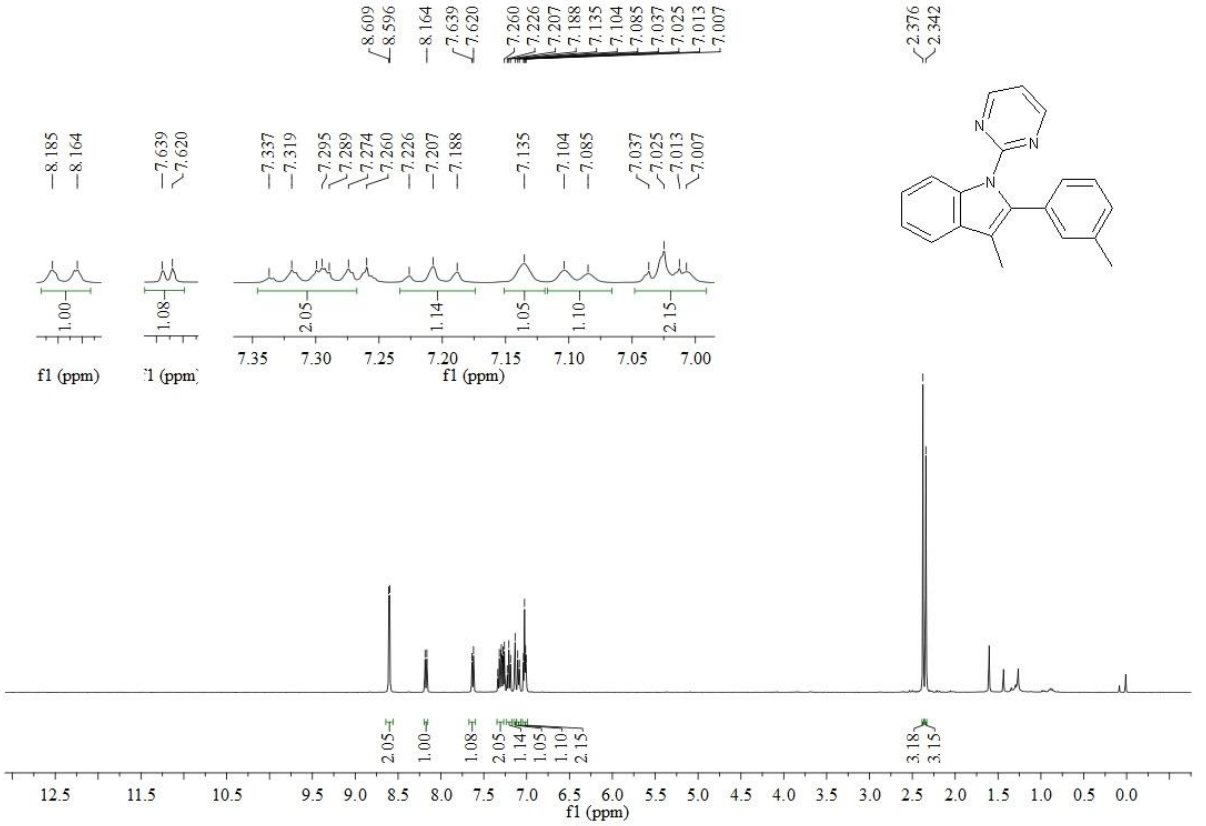
^{1}H NMR spectra of **4b**:



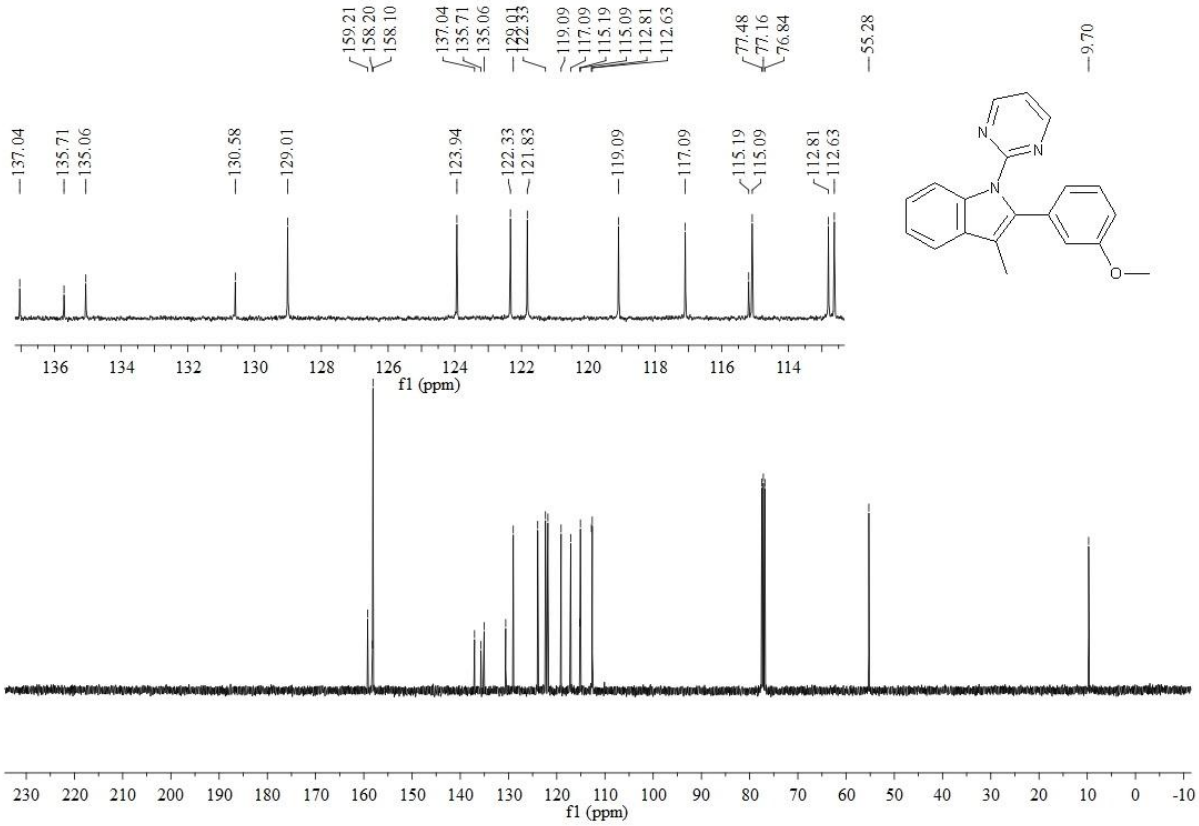
^{13}C NMR spectra of **4c**:



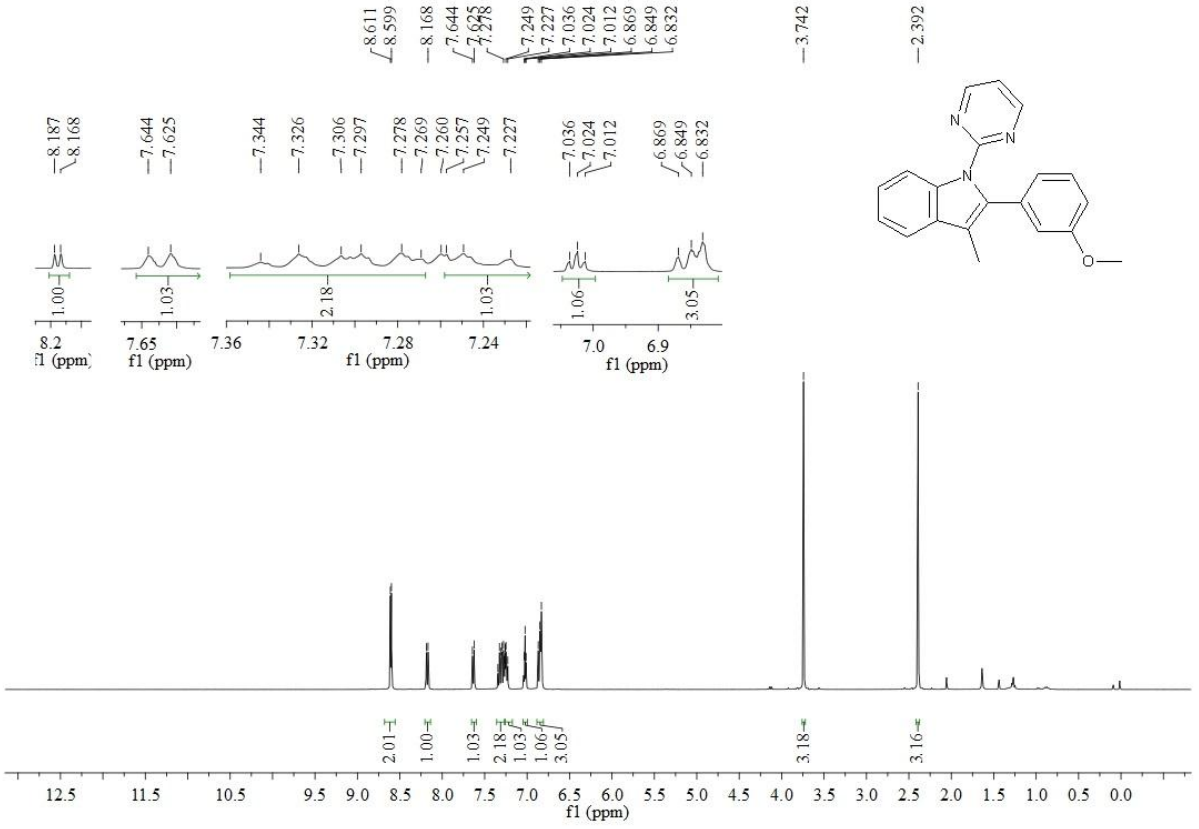
^{1}H NMR spectra of **4c**:



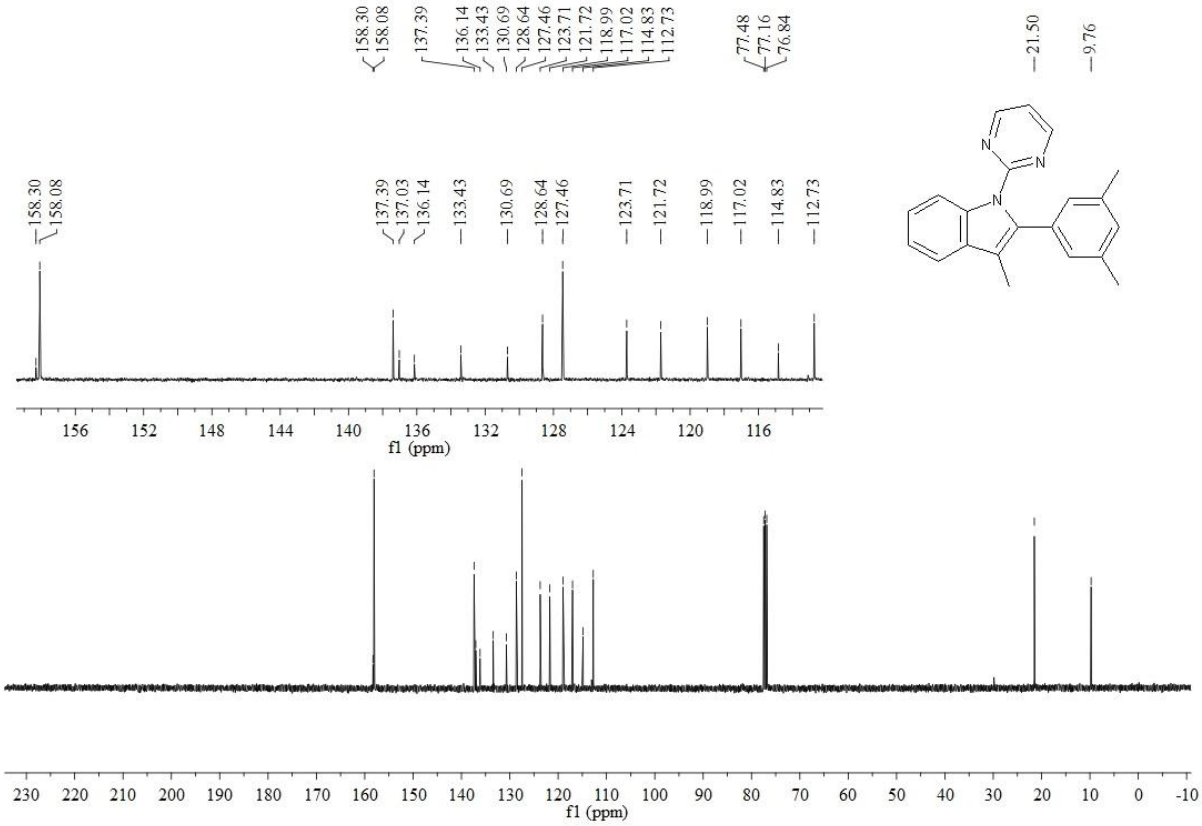
^{13}C NMR spectra of **4d**:



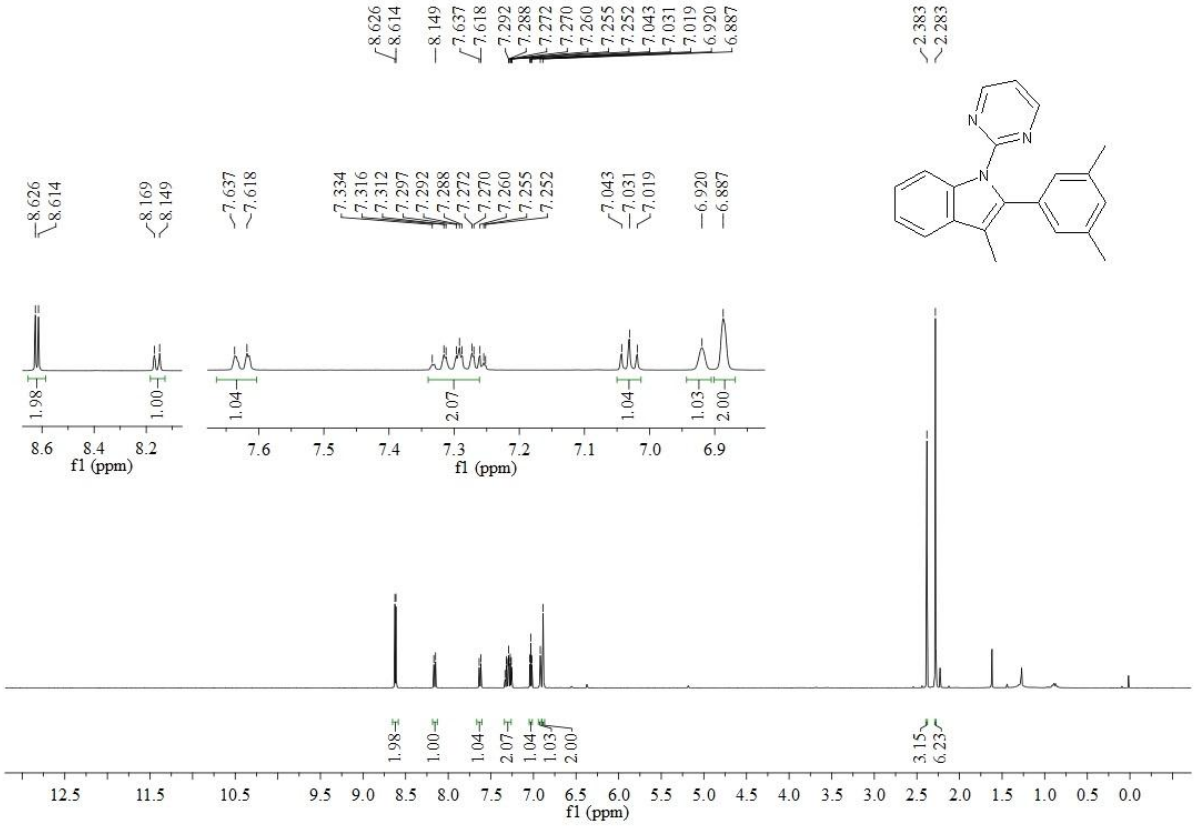
^{1}H NMR spectra of **4d**:



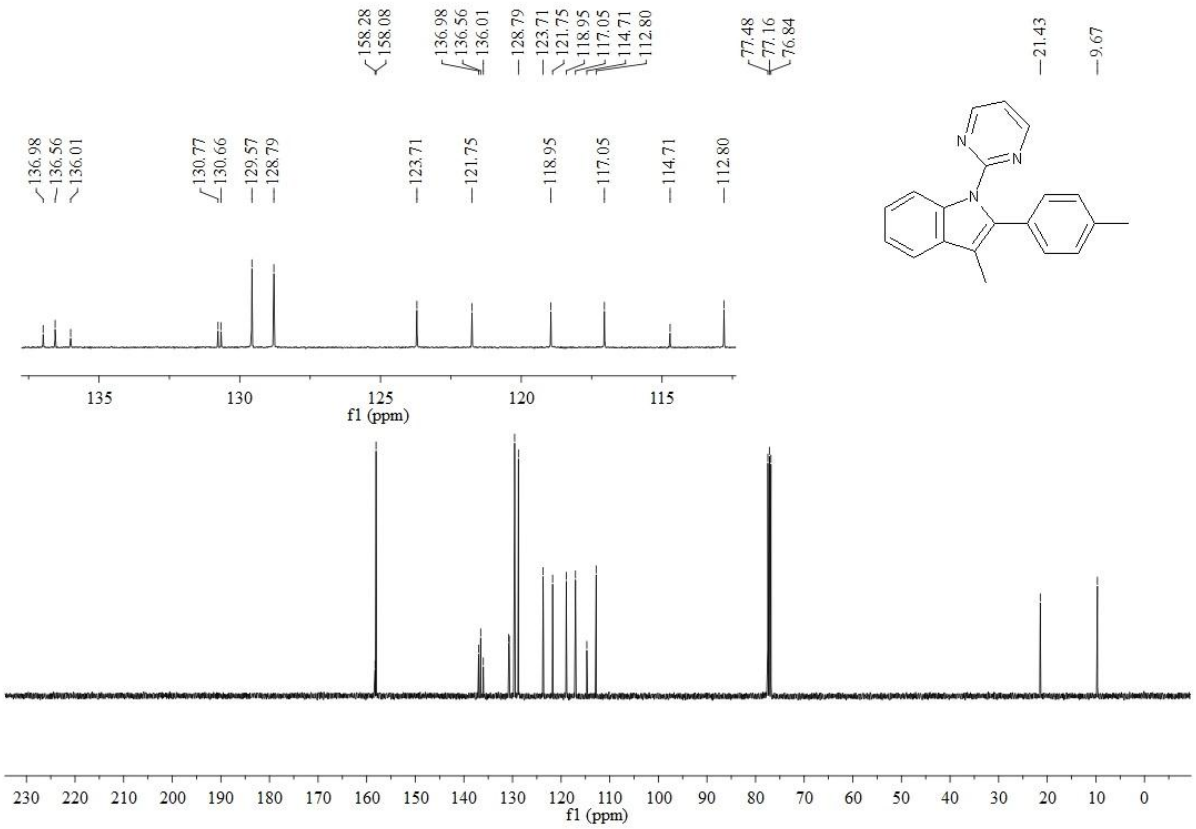
^{13}C NMR spectra of **4e**:



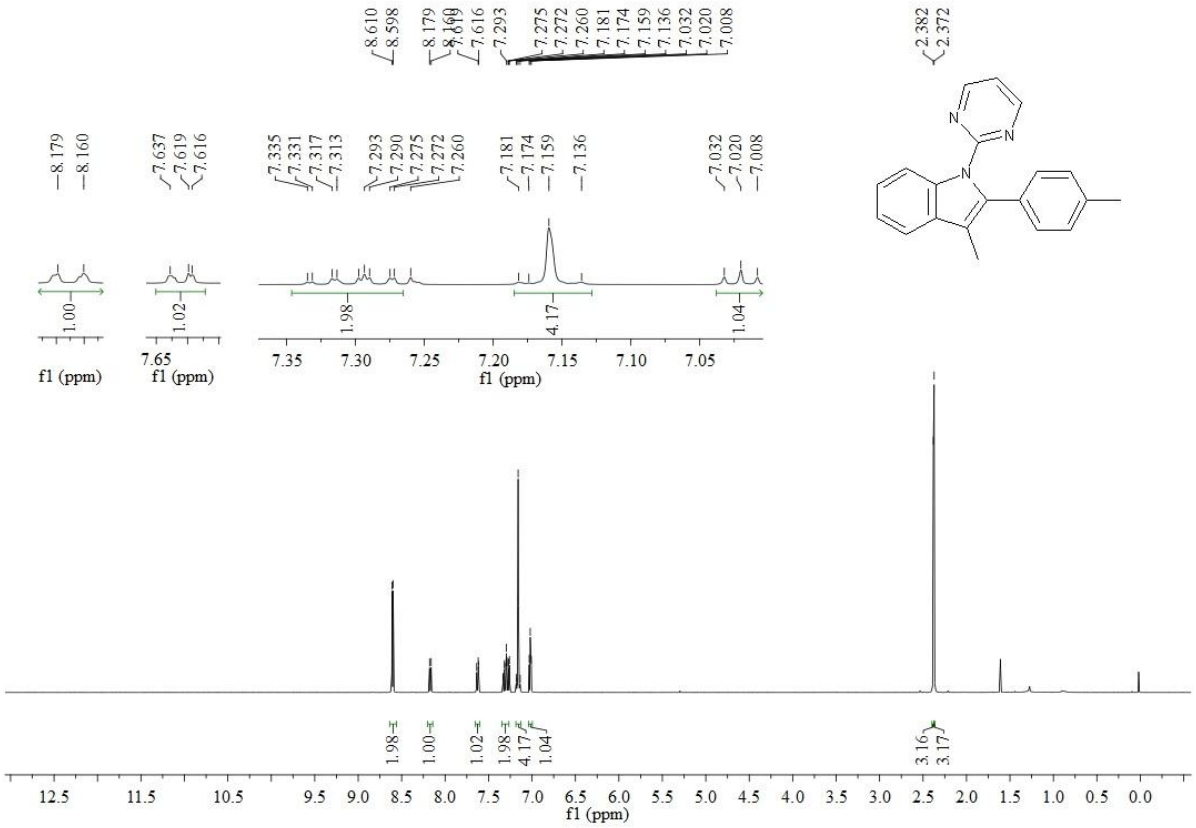
^{1}H NMR spectra of **4e**:



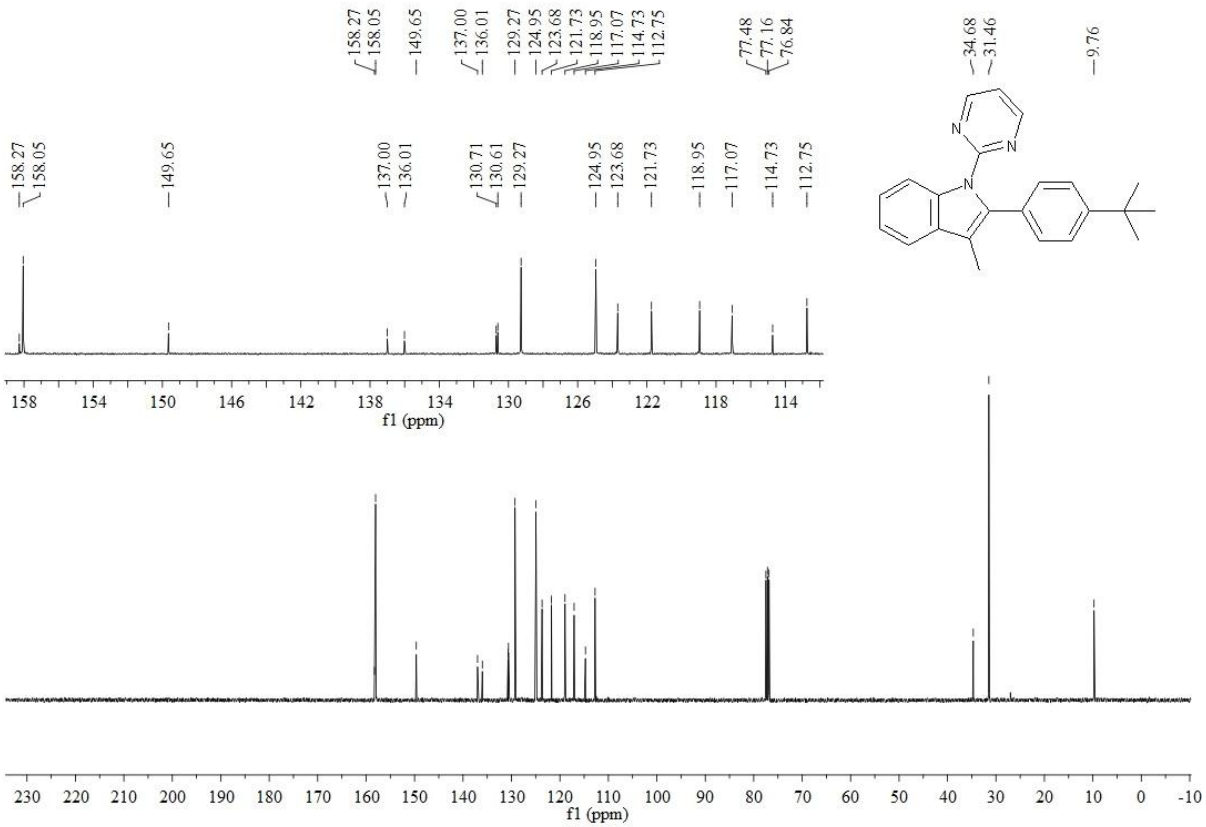
^{13}C NMR spectra of **4f**:



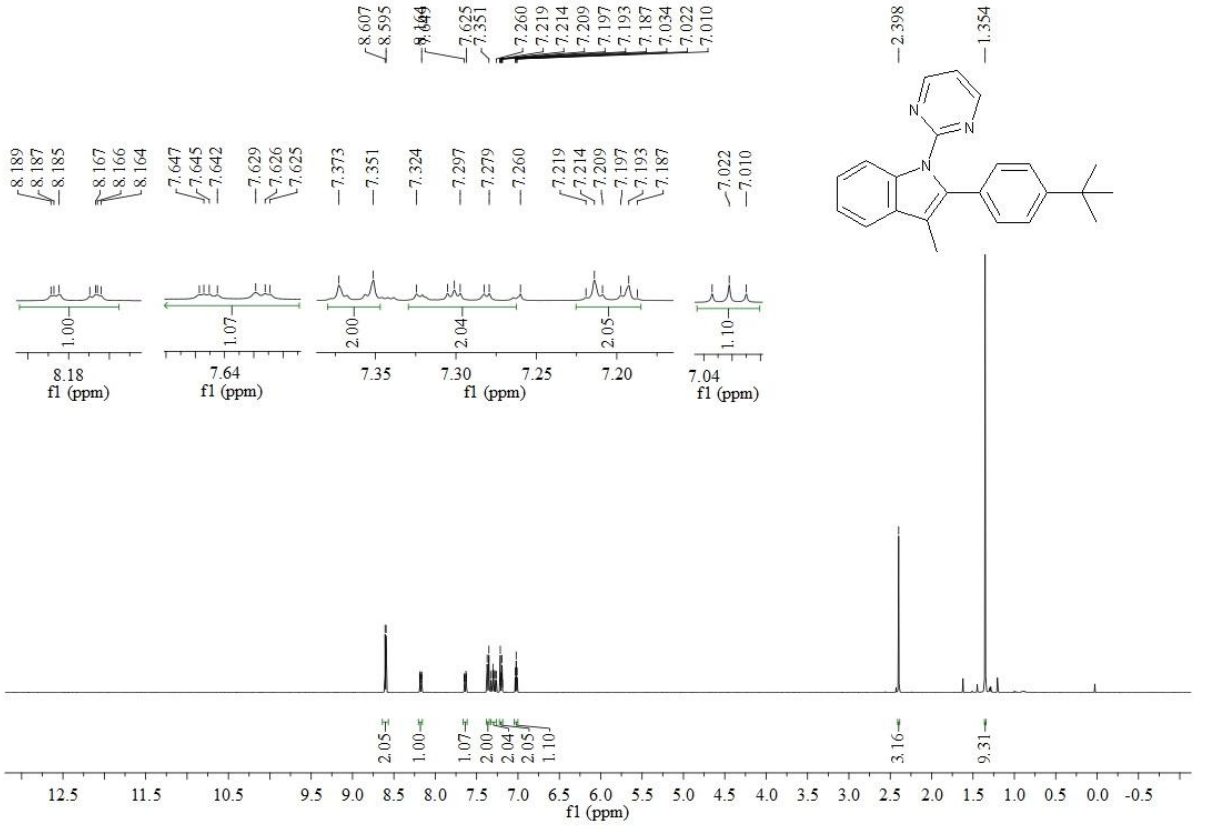
^{1}H NMR spectra of **4f**:



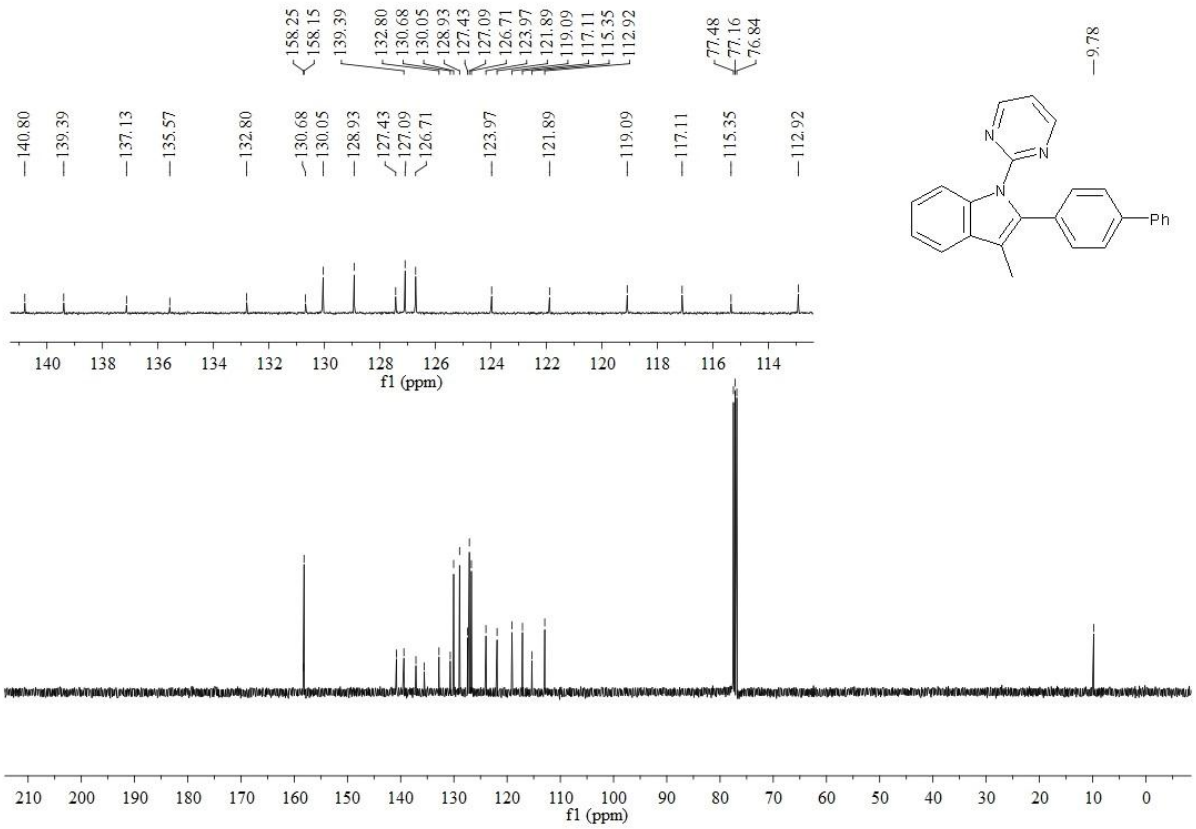
^{13}C NMR spectra of **4g**:



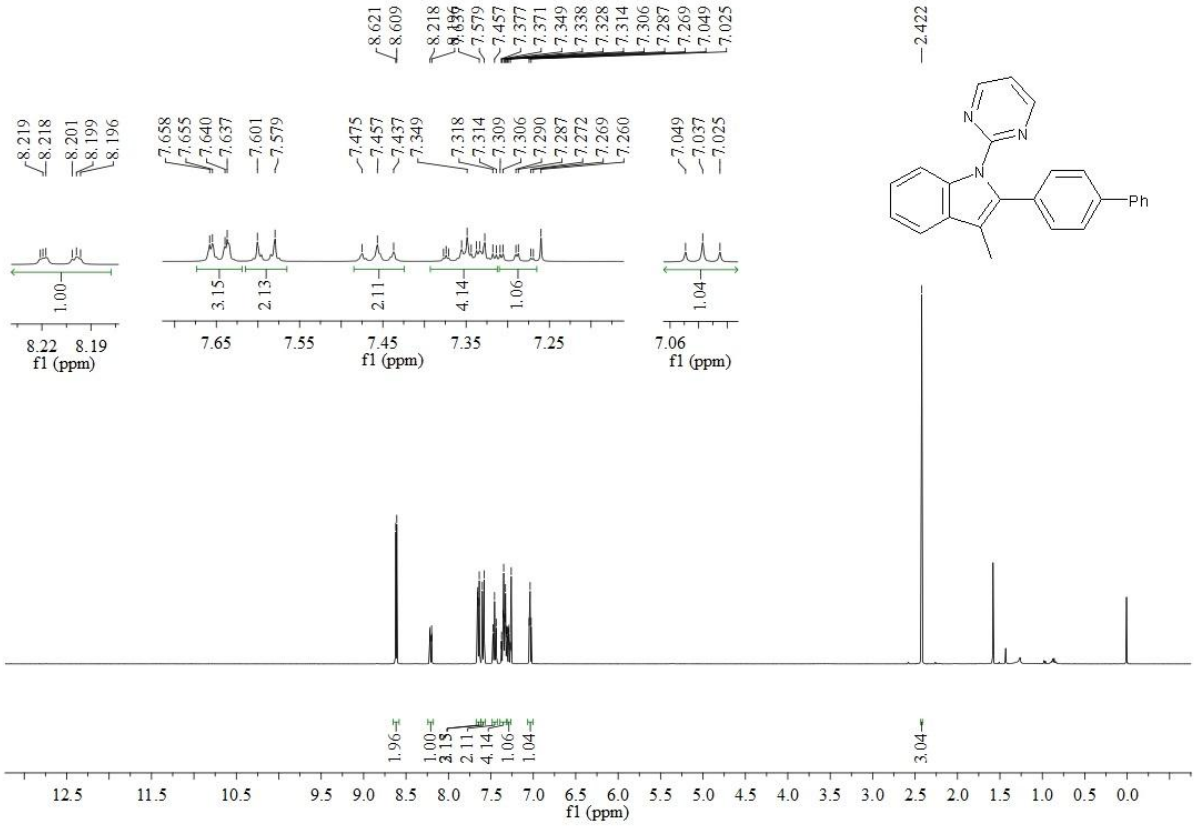
^{1}H NMR spectra of **4g**:



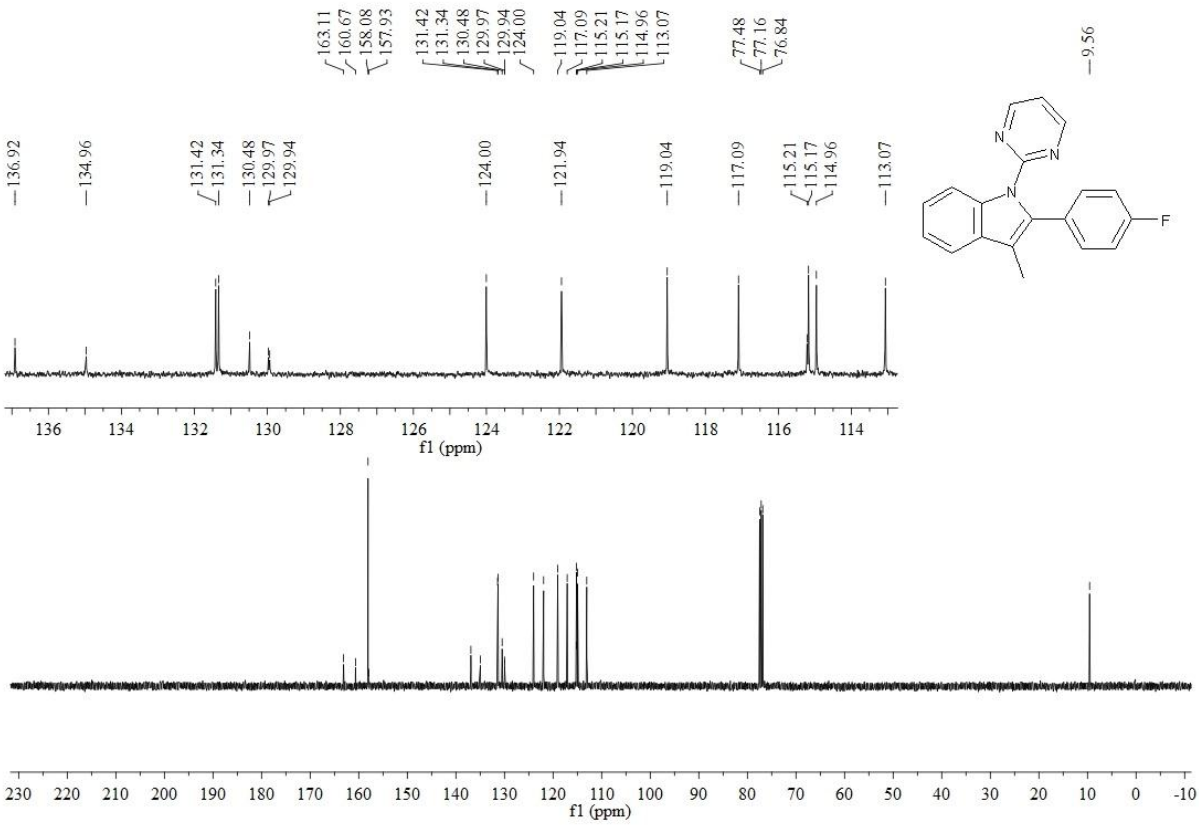
^{13}C NMR spectra of **4h**:



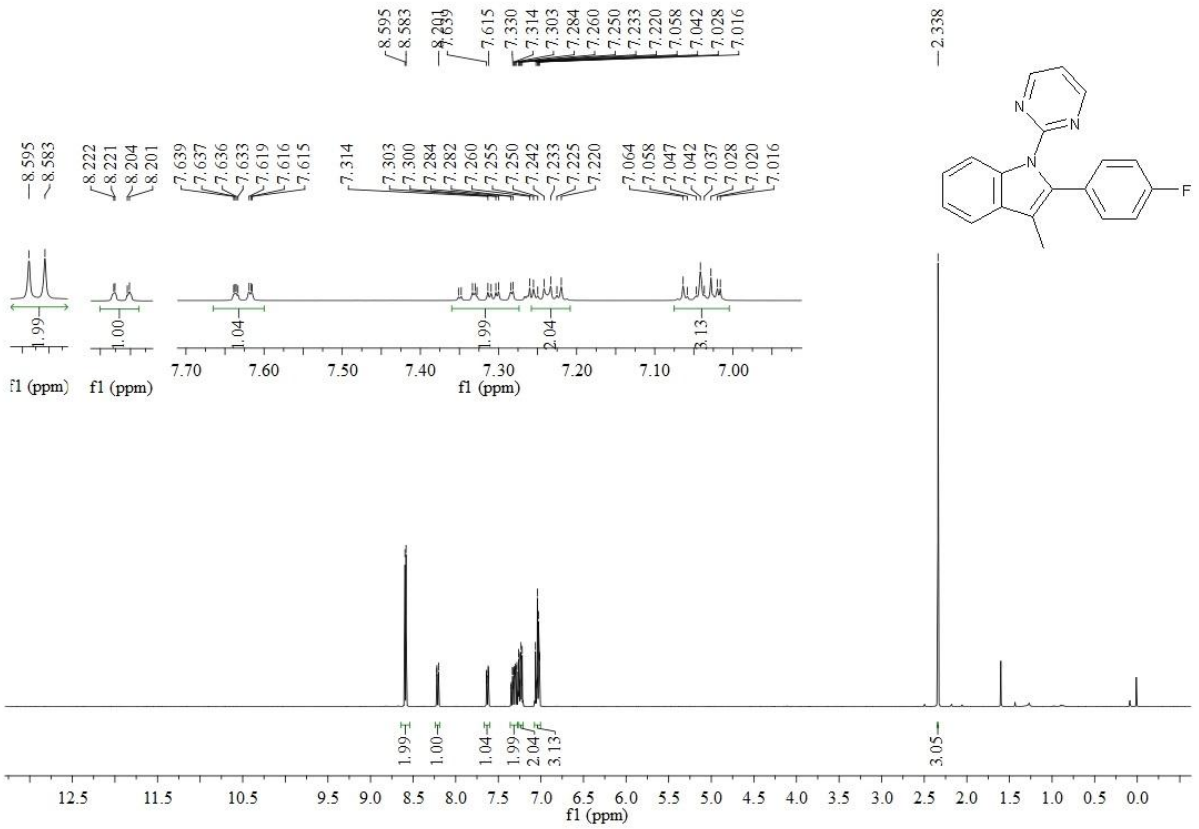
^{1}H NMR spectra of **4h**:



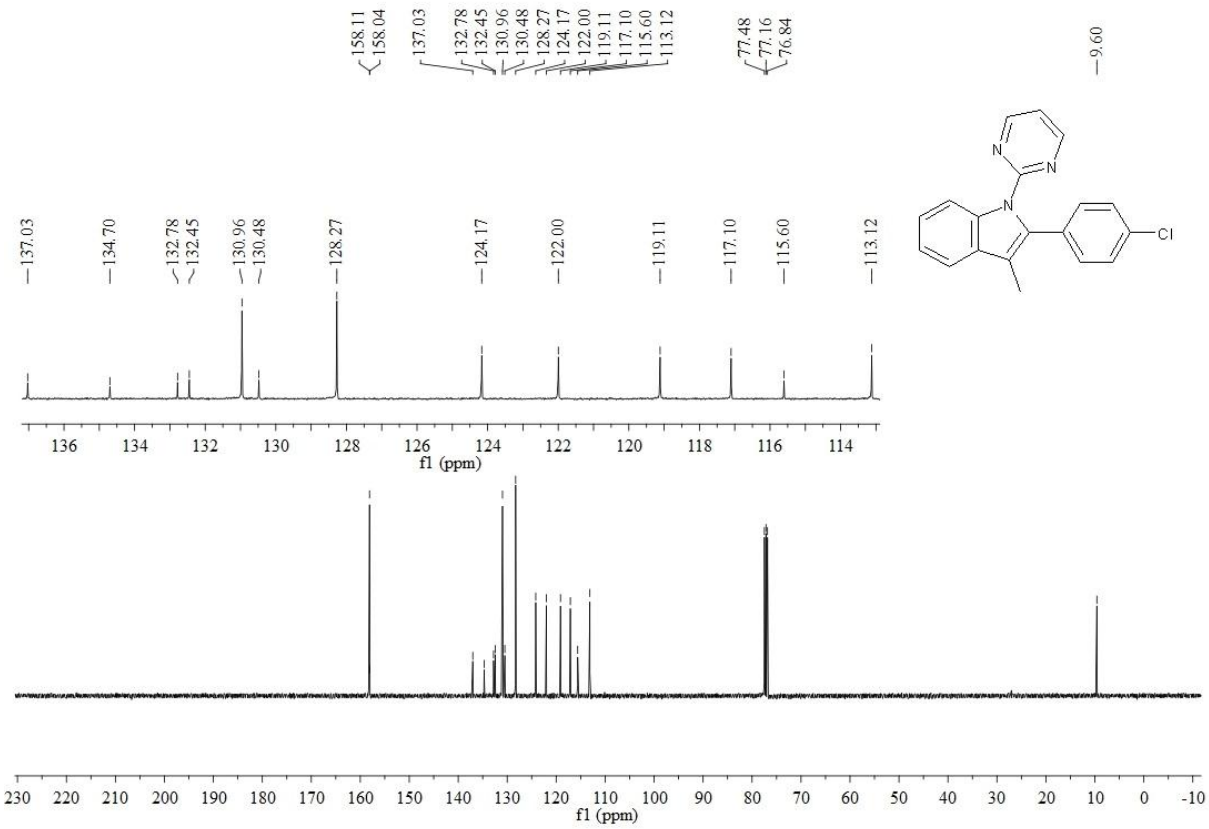
^{13}C NMR spectra of **4i**:



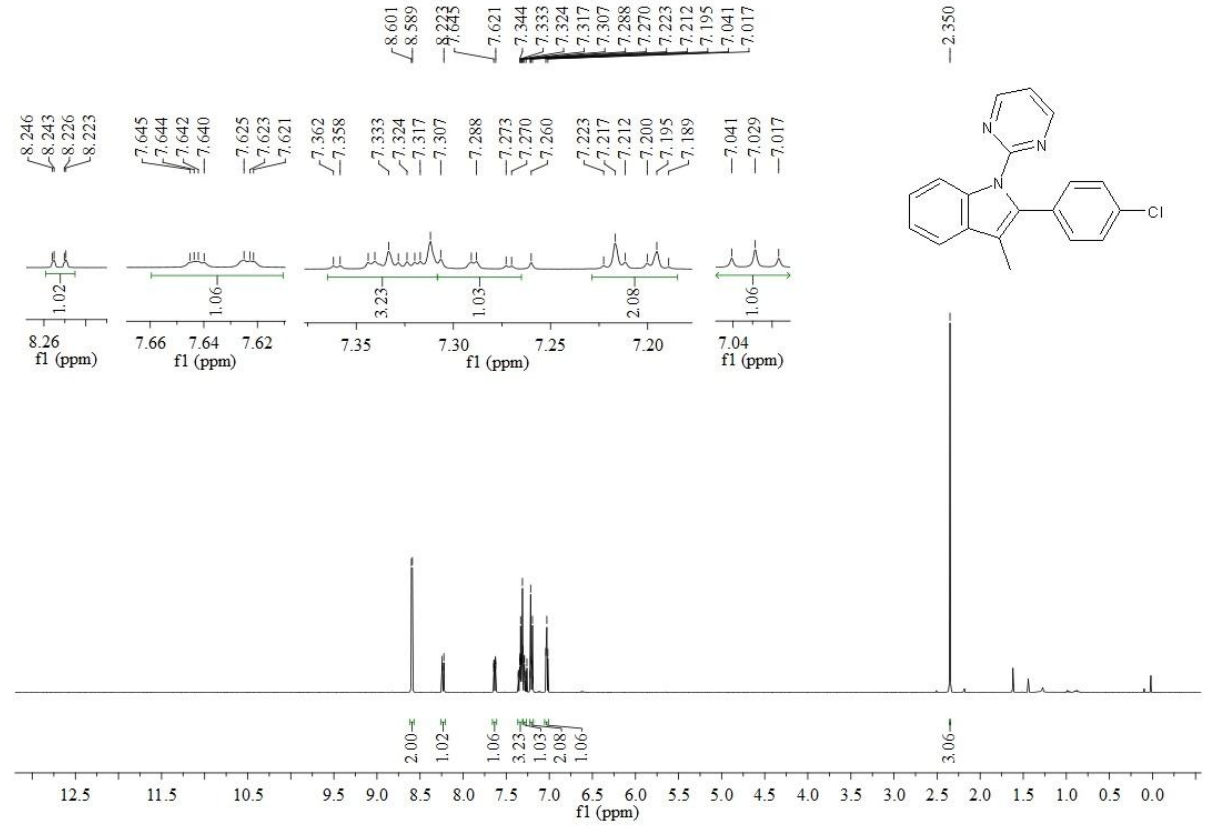
^{1}H NMR spectra of **4i**:



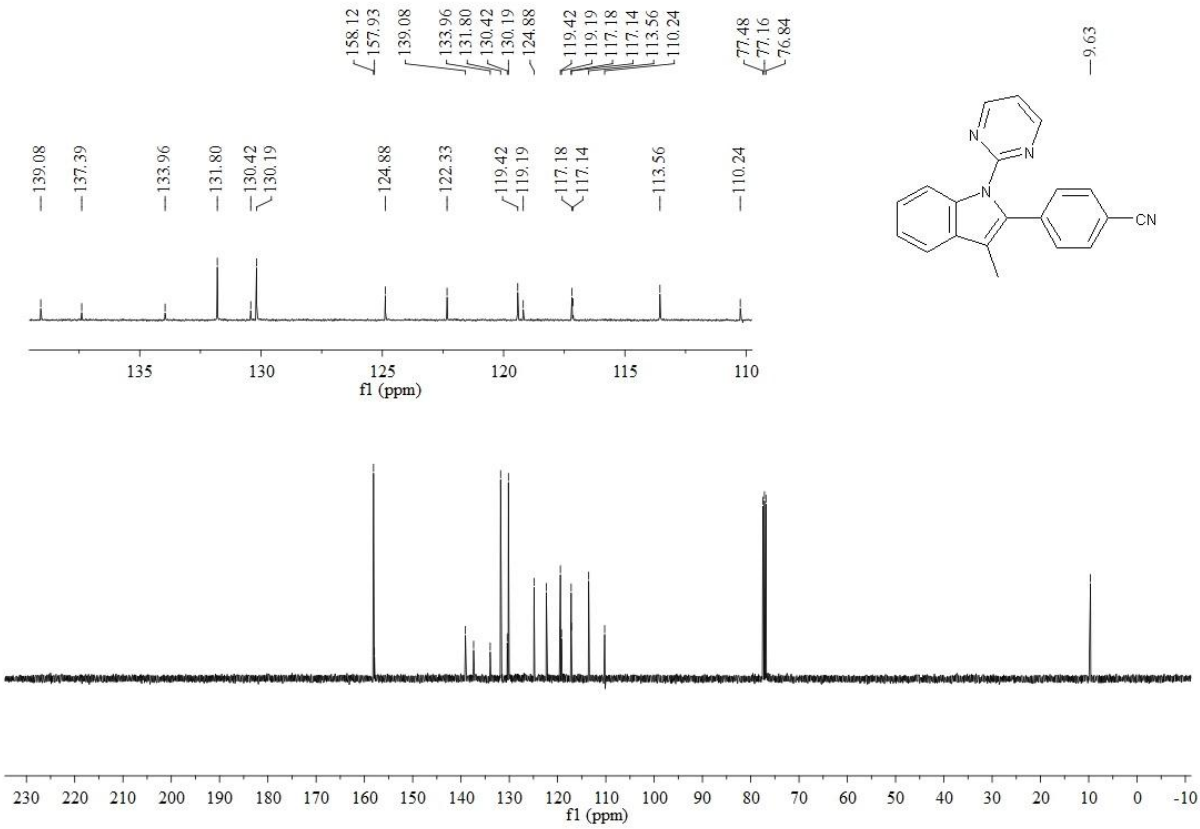
^{13}C NMR spectra of **4j**:



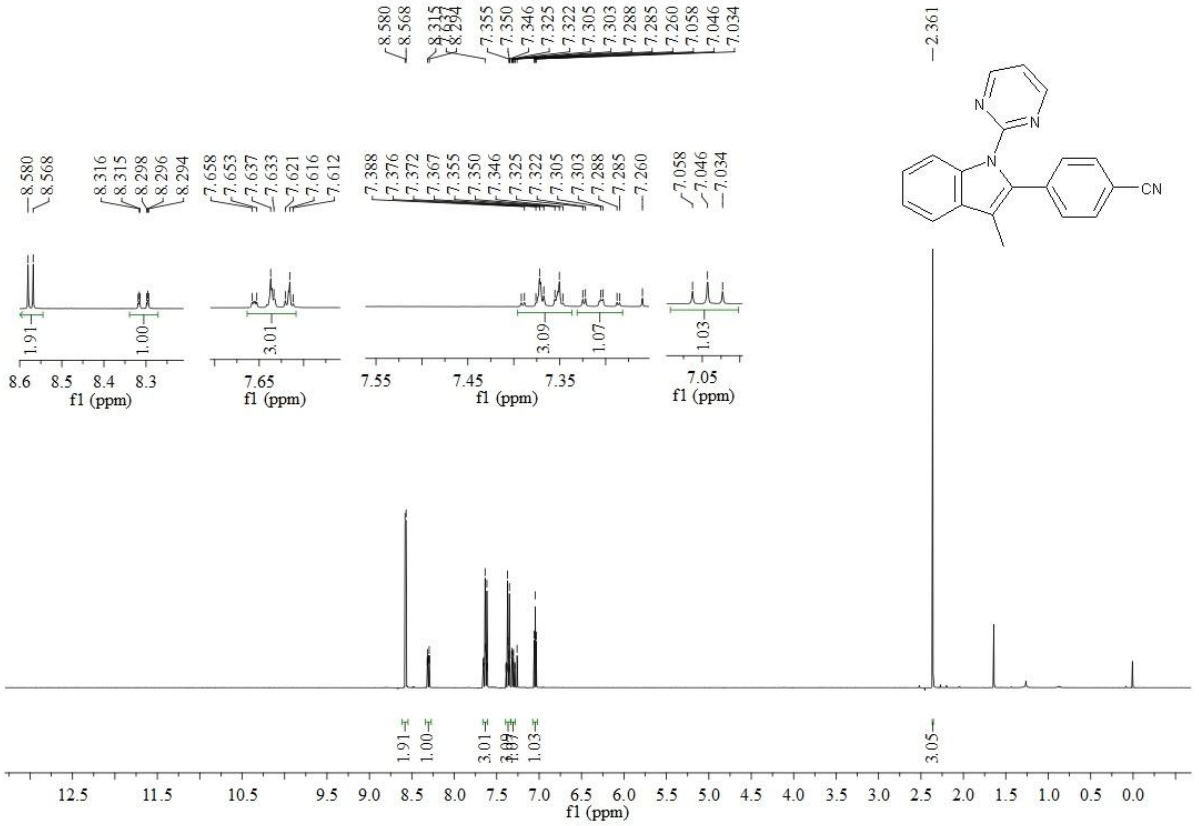
^{1}H NMR spectra of **4j**:



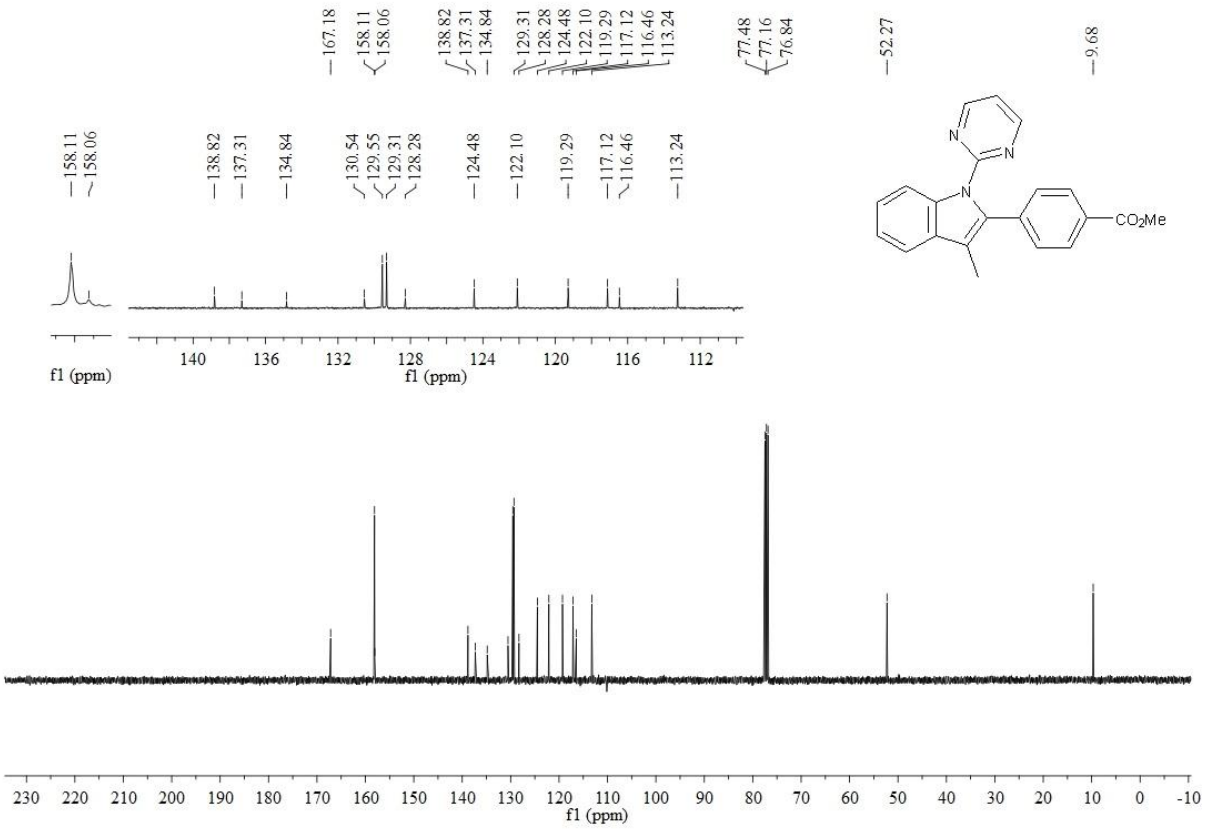
^{13}C NMR spectra of **4k**:



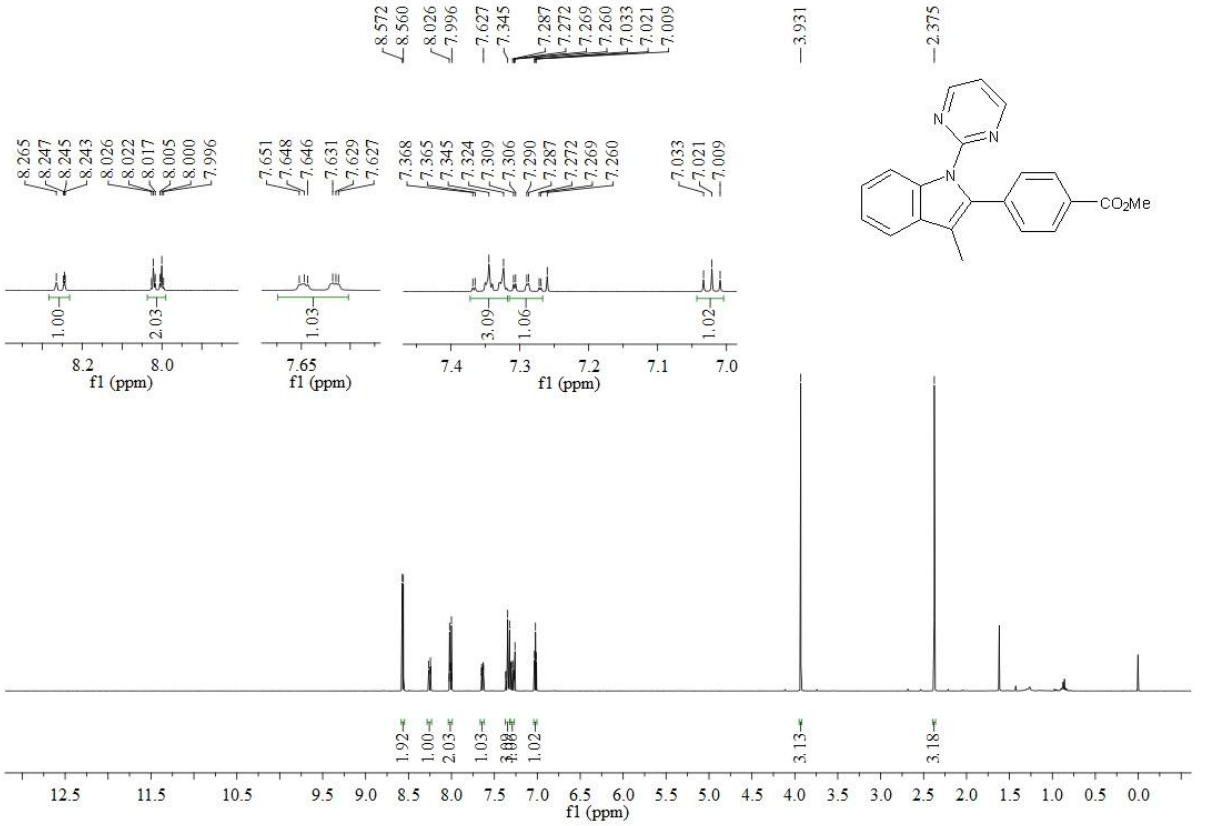
^{1}H NMR spectra of **4k**:



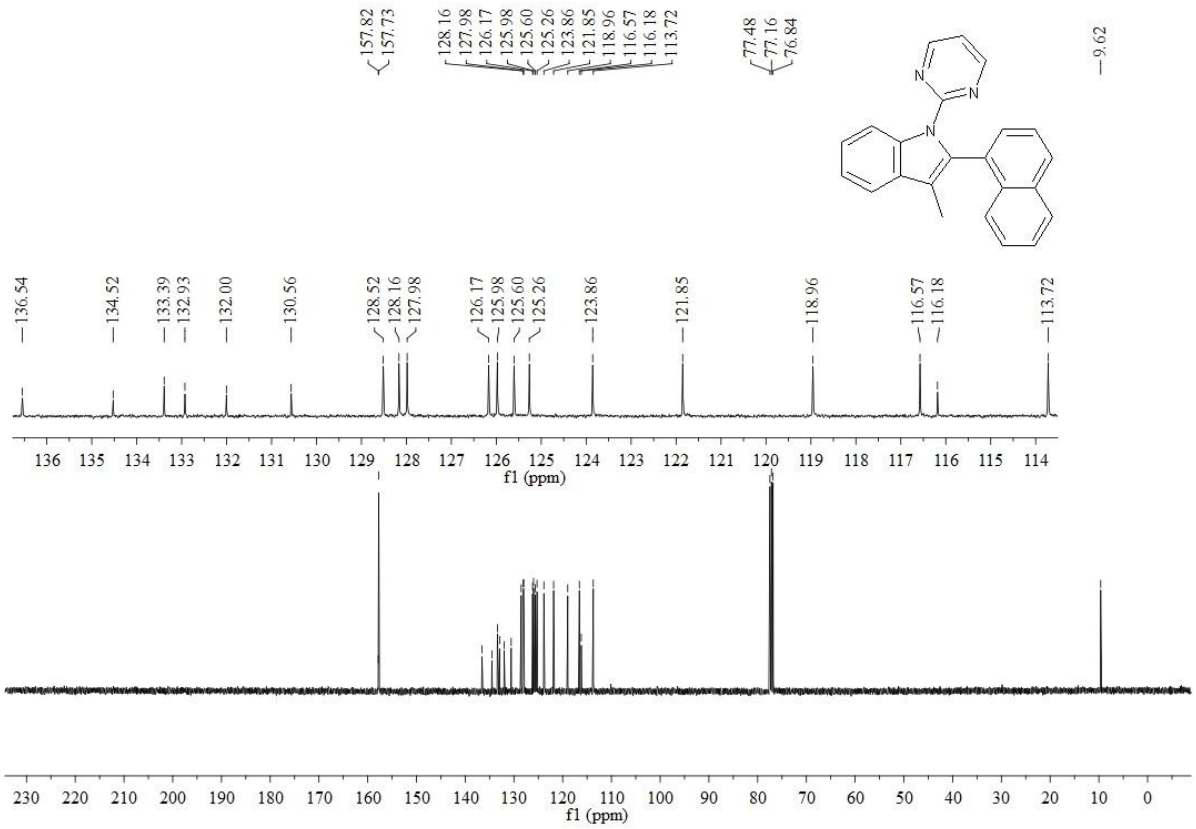
^{13}C NMR spectra of **4l**:



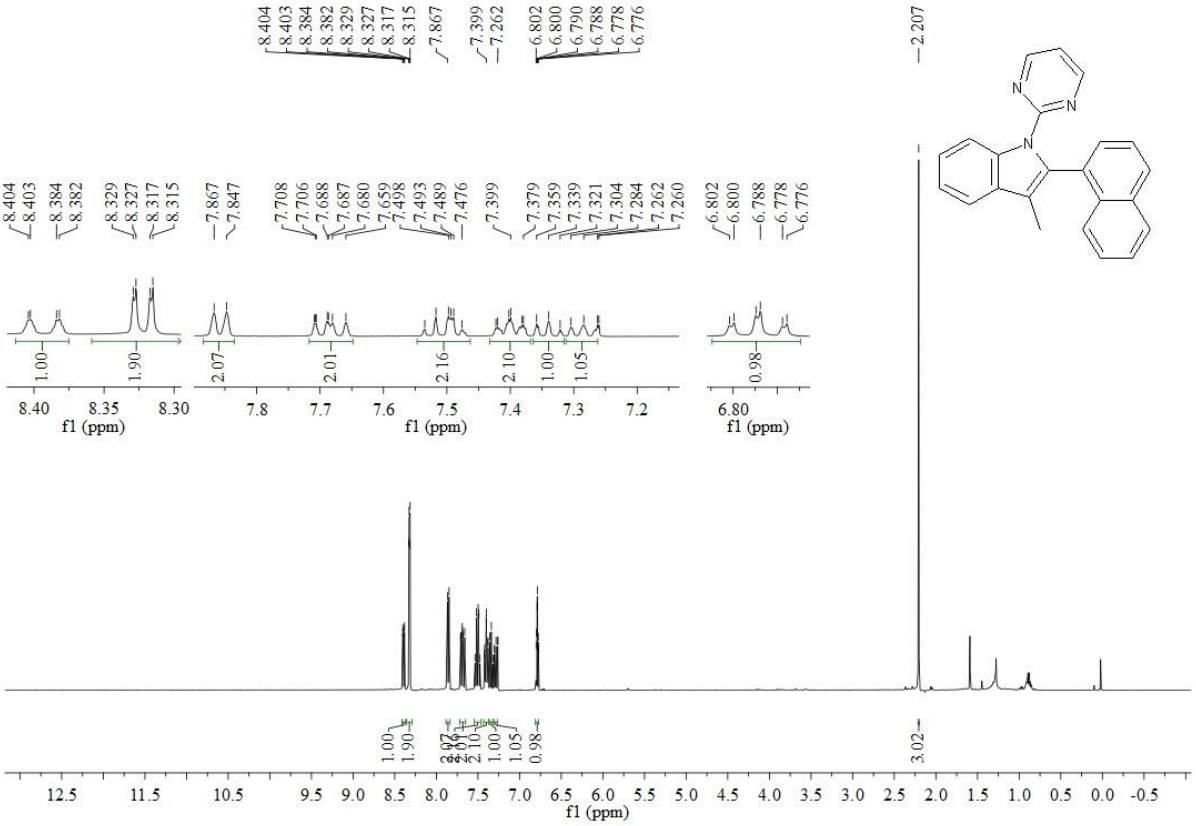
^{1}H NMR spectra of **4l**:



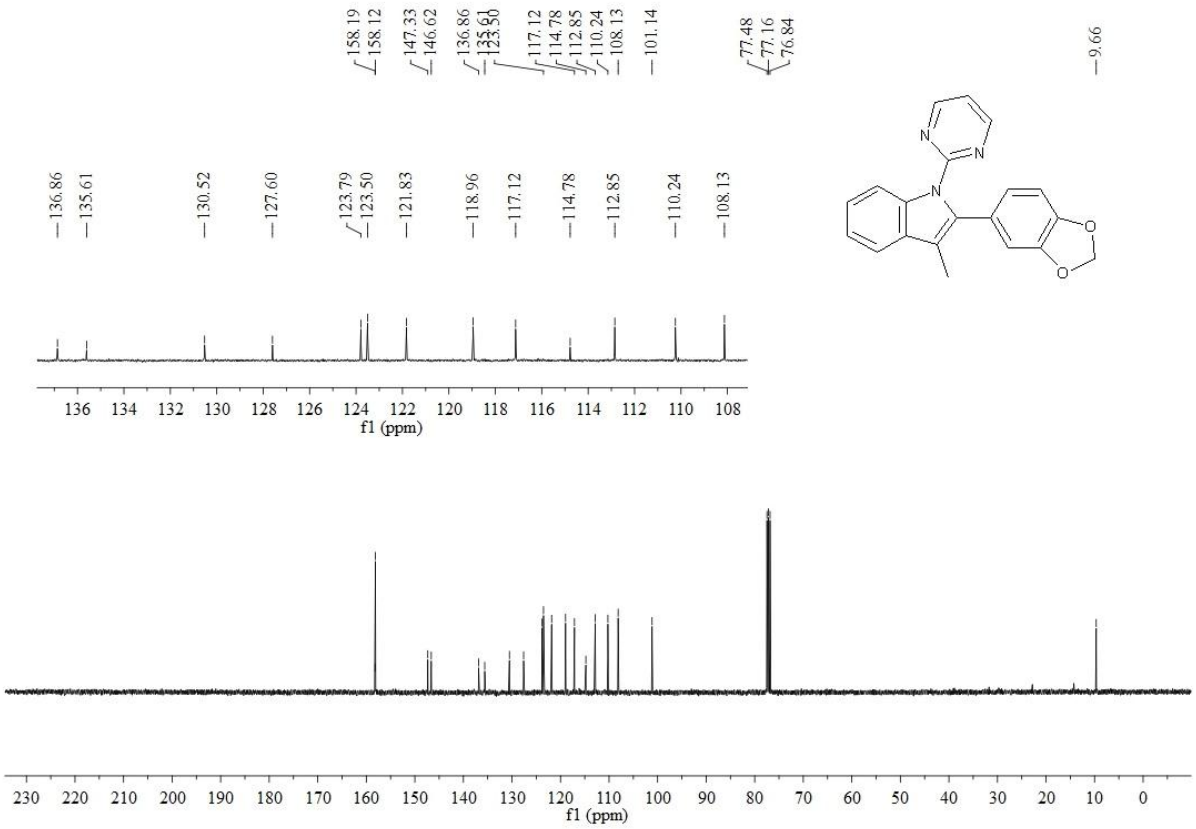
^{13}C NMR spectra of **4m**:



^{1}H NMR spectra of **4m**:



^{13}C NMR spectra of **4n**:



^{1}H NMR spectra of **4n**: