Supporting Information

Synthesis of 2-Arylindoles by Rhodium-Catalyzed/Copper-Mediated Annulative Coupling of *N*-Aryl-2-Aminopyridines and Propargyl Alcohols *via* Selective C−H/C−C Activation

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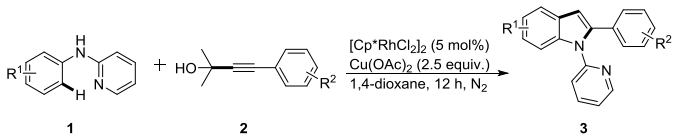
I. General remarks

NMR spectra were obtained on a Bruker AV II-400 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm) or DMSO-d_6 (δ = 2.50. ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm) or DMSO-d_6 (δ = 39.52. ppm). High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). Melting points were determined in open glass capillaries and were uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. *N*-aryl-2-aminopyridines and *tert*-propargl alcohols were prepared according to the literature procedures.[1,2] All the solvents mentioned were dried before used.

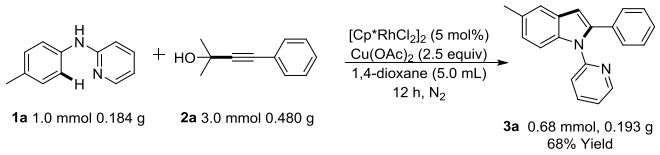
II. General procedures

1. Representative procedures to access 2-arylindole derivatives



A Schlenk tube with a magnetic stir bar was charged with **1** (0.2 mmol), **2** (0.6 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Cu(OAc)_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 12 hours under N_2. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product **3**.

2. A scale-up experiment of **1a**



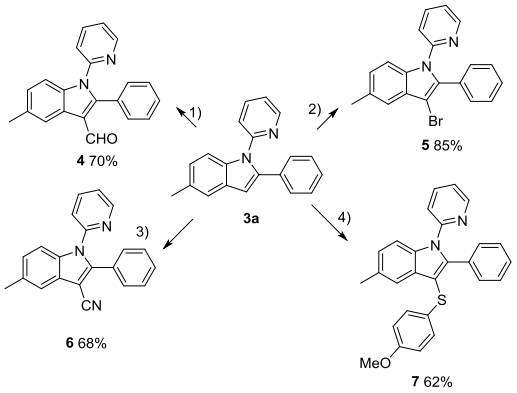
A Schlenk tube with a magnetic stir bar was charged with **1a** (1.0 mmol, 0.184 g), **2a** (3.0 mmol, 0.480 g), $[Cp^*RhCl_2]_2$ (31.0 mg, 0.05 mmol), $Cu(OAc)_2$ (500.0 mg, 2.5 mmol) and 1,4-dioxane (5.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 12 hours under N_2. The reaction solution was then cooled to ambient temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product **3a** (0.68 mmol, 0.193 g) in 68% yield.

III. Product transformations

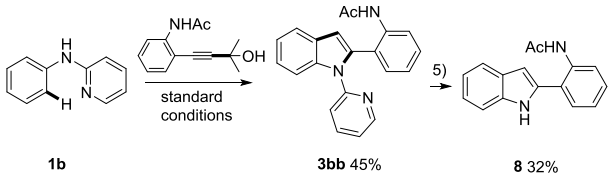
1) To a solution of **3a** (0.2 mmol) in DMF (1.0 mL), $POCl_3$ (0.3 mmol) was added dropwisely and then the mixture was heated at 50 °C under air overnight. The reaction solution was then cooled to room temperature and purified by column chromatography on silica gel to provide the desired product **4** (70% yield).
2) To a solution of **3a** (0.2 mmol) in $CHCl_3$ (3.0 mL), NBS (*N*-bromosuccinimide) (0.2 mmol) was added portionwisely and then the mixture was heated at r.t. under air for 5 h. The reaction solution was concentrated and purified by column chromatography on silica gel to provide the desired product **5** (85% yield).

3) To a solution of **3a** (0.2 mmol) in DMF (2.0 mL), CuI (0.2 mmol) and benzyl cyanide (0.3 mmol) was added and then the mixture was heated at 130 °C under air for 40 h. The reaction solution was then cooled to room temperature, diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product **6** (68% yield).

4) A Schlenk tube with a magnetic stir bar was charged with **3a** (0.2 mmol), $(4\text{-MeOC}_6H_4S)_2$ (0.1 mmol), KIO_3 (0.02 mmol) and glycerol (1.0 mmol). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was stirred at 100 °C for 6 h under air. The reaction solution was then cooled to room temperature and purified by column chromatography on silica gel to provide the desired product **7** (62% yield).

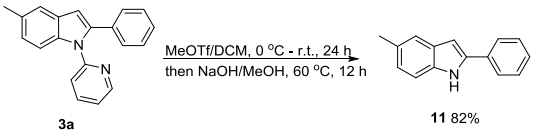


5) **3bb** was obtained in a 45% yield according to the representative procedure. To a solution of **3bb** (0.2 mmol) in DCM (1.0 mL), methyl trifluoromethanesulfonate (0.24 mmol) was added dropwisely at 0 °C and the mixture was stirred for 12 h at r.t.. The solvent was removed under *vacuo*. Then, $Pd(OH)_2/C$ (10 wt.%, 19.2 mg), NH_4HCO_3 (2.0 mmol) and MeOH (2.0 mL) were added and the mixture was stirred at 60 °C for 24 h. After cooled to room temperature, the reaction solution was diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product **8** (32% yield).



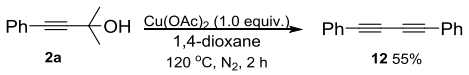
6) Cleavage of the pyridyl directing group of **3a**

To a solution of **3a** (0.2 mmol) in DCM (1.0 mL), methyl trifluoromethanesulfonate (0.24 mmol) was added dropwisely at 0 °C and the mixture was stirred for 24 h at r.t.. The solvent was removed under *vacuo* and the residue was dissolved in MeOH (2 mL). Aqueous NaOH solution (2 M, 1.5 mL) was added and the mixture was stirred at 60 °C for 12 h. After being cooled to ambient temperature, the reaction solution was diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product **11** (82% yield).



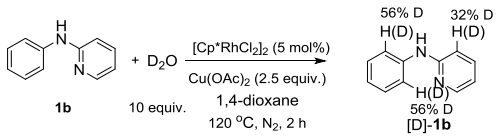
IV. Mechanistic studies

1. Synthesis of compound **12**

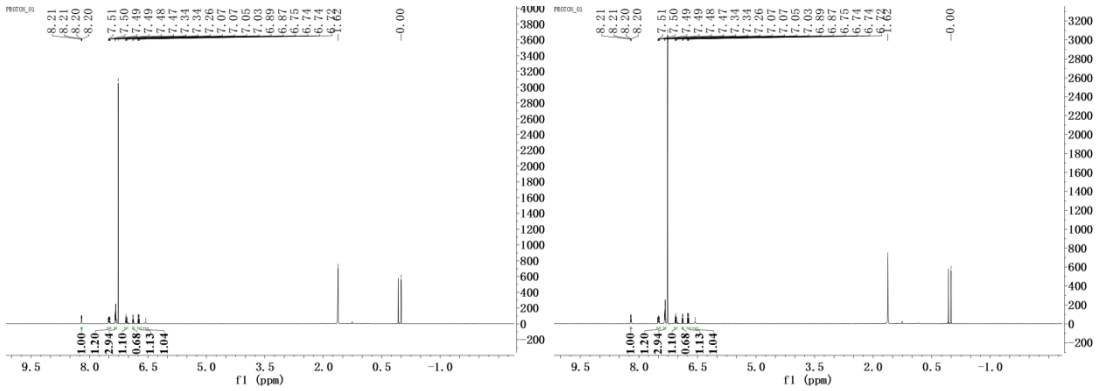


A Schlenk tube with a magnetic stir bar was charged with **2a** (0.2 mmol), $Cu(OAc)_2$ (40.0 mg, 0.2 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 2 hours under N_2. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product **12** in 55% yield.

2. The H/D exchange experiment of **1b**



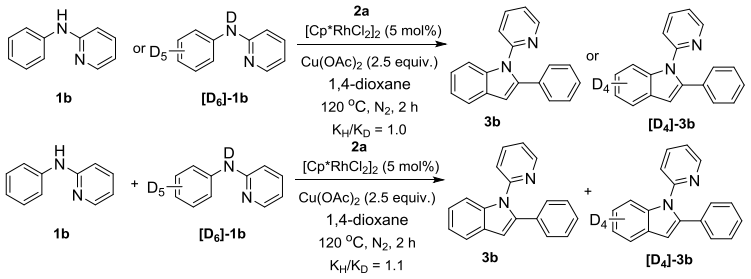
A Schlenk tube with a magnetic stir bar was charged with **1b** (0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Cu(OAc)_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 2 hours under N_2. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide [D]-**1b.** The deuterium incorporation was calculated from ^{1}H-NMR.

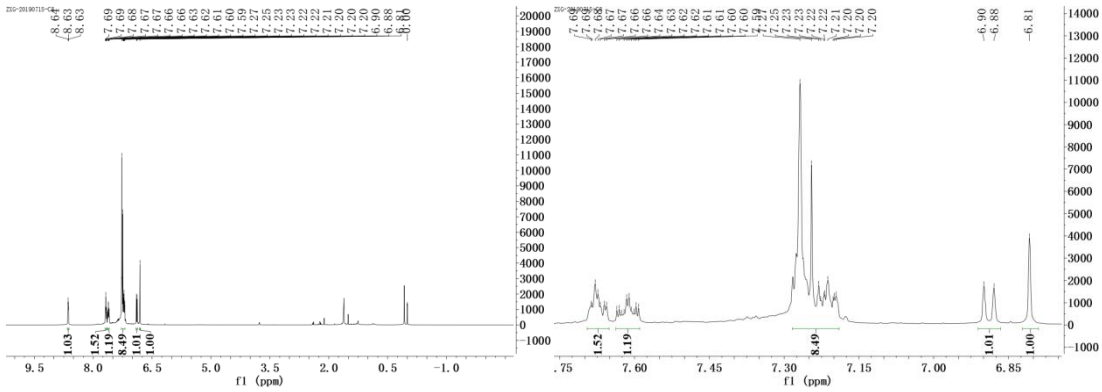


3. KIE experiments

A Schlenk tube with a magnetic stir bar was charged with **1b** or $[D_6]$-**1b** (0.2 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Cu(OAc)_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 2 hours under N_2. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide **3b** (12 mg) or $[D_4]$-**3b** (12 mg) and the KIE value was measured to be 1.0.

A Schlenk tube with a magnetic stir bar was charged with **1b** (0.1 mmol) and $[D_6]$-**1b** (0.1 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Cu(OAc)_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 2 hours under N_2. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide a mixture of **3b** and $[D_4]$-**3b** (10 mg) and the KIE value was measured to be 1.1 according to ^{1}H-NMR.

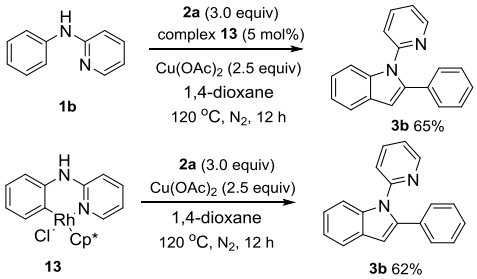




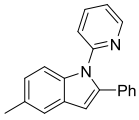
4. Catalytic and stoichiometric reactions by using complex **13**

A Schlenk tube with a magnetic stir bar was charged with **1b** (0.2 mmol), **2a** (0.6 mmol), complex **13** (4.4 mg, 0.01 mmol), $Cu(OAc)_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 12 hours under N_2. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide **3b** in a yield of 65%.

A Schlenk tube with a magnetic stir bar was charged with complex **13** (88 mg, 0.2 mmol), **2a** (0.6 mmol), $Cu(OAc)_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 12 hours under N_2. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH_2Cl_2, filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide **3b** in a yield of 62%.



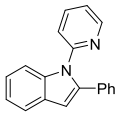
V. Experimental data for the described substances



5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3a)

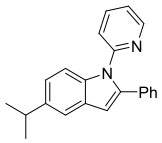
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3a** as a

colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.47 – 7.41 (m, 1H), 7.28 – 7.22 (m, 5H), 7.17 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.85 (dt, *J* = 8.1, 0.9 Hz, 1H), 6.72 (d, *J* = 0.7 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.24, 149.15, 139.97, 137.71, 136.96, 132.84, 130.66, 128.98, 128.69, 128.32, 127.34, 124.60, 121.86, 121.43, 120.29, 111.26, 105.41, 21.47. HRMS (ESI$^+$): calcd for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1392, found 285.1396.



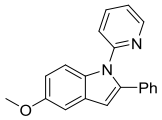
2-phenyl-1-(pyridin-2-yl)-1H-indole (3b)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3b** as a white solid (mp = 130−131 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.8, 1.9, 0.7 Hz, 1H), 7.68 (ddd, *J* = 7.1, 6.0, 1.4 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.29 – 7.19 (m, 8H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 0.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.07, 149.19, 139.96, 138.50, 137.76, 132.69, 128.75, 128.71, 128.32, 127.43, 123.02, 122.03, 121.62, 121.36, 120.57, 111.51, 105.62. HRMS (ESI$^+$): calcd for $C_{19}H_{15}N_2$ $[M+H]^+$ 271.1235, found 271.1238.



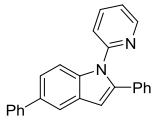
5-isopropyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3c)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3c** as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.51 (d, *J* = 1.4 Hz, 1H), 7.28 – 7.23 (m, 5H), 7.18 (ddd, *J* = 7.4, 4.9, 0.6 Hz, 1H), 7.12 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 3.08 – 2.96 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.21, 149.15, 142.15, 140.01, 137.65, 137.10, 132.88, 128.80, 128.71, 128.30, 127.32, 122.29, 121.81, 121.40, 117.47, 111.35, 105.60, 34.18, 24.60. HRMS (ESI$^+$): calcd for $C_{22}H_{21}N_2$ $[M+H]^+$ 313.1705, found 313.1708.



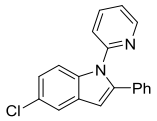
5-methoxy-2-phenyl-1-(pyridin-2-yl)-1H-indole (3d)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3d** as a white solid (mp = 91−92 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.60 (m, 1H), 7.65 – 7.56 (m, 2H), 7.29 – 7.26 (m, 5H), 7.23 – 7.17 (m, 1H), 7.12 (d, *J* = 2.5 Hz, 1H), 6.90 – 6.81 (m, 2H), 6.73 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.24, 152.21, 149.15, 140.45, 137.72, 133.75, 132.78, 129.25, 128.72, 128.35, 127.44, 121.83, 121.44, 112.91, 112.53, 105.56, 102.31, 55.85. HRMS (ESI$^+$): calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1341, found 301.1345.



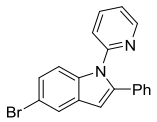
2,5-diphenyl-1-(pyridin-2-yl)-1H-indole (3e)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3e** as a yellowish solid (mp = 130−131 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.62 (m, 1H), 7.88 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.63 (td, *J* = 7.8, 2.0 Hz, 1H), 7.48 (ddd, *J* = 17.6, 9.4, 4.7 Hz, 3H), 7.35 – 7.21 (m, 7H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.00, 149.24, 142.27, 140.61, 138.01, 137.82, 134.83, 132.58, 129.20, 128.76, 128.67, 128.37, 127.55, 127.36, 126.48, 122.80, 121.93, 121.68, 119.03, 111.82, 105.91. HRMS (ESI$^+$): calcd for $C_{25}H_{19}N_2$ $[M+H]^+$ 347.1548, found 347.1550.



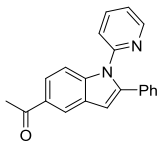
5-chloro-2-phenyl-1-(pyridin-2-yl)-1H-indole (3f)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3f** as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.61 (m, 1H), 7.64 – 7.58 (m, 3H), 7.29 – 7.21 (m, 6H), 7.16 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.67, 149.25, 141.20, 137.90, 136.80, 132.16, 129.72, 128.78, 128.41, 127.81, 126.82, 123.15, 121.95, 121.91, 119.90, 112.72, 104.89. HRMS (ESI$^+$): calcd for $C_{19}H_{14}ClN_2$ $[M+H]^+$ 305.0846, found 305.0849.



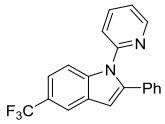
5-bromo-2-phenyl-1-(pyridin-2-yl)-1H-indole (3g)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3g** as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.62 (td, *J* = 7.8, 1.9 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.31 – 7.22 (m, 7H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.63, 149.25, 141.07, 137.90, 137.11, 132.12, 130.35, 128.79, 128.41, 127.82, 125.72, 122.99, 121.96, 121.94, 114.45, 113.14, 104.76. HRMS (ESI$^+$): calcd for $C_{19}H_{14}{}^{79}BrN_2$ $[M+H]^+$ 349.0340, found 349.0343; calcd for $C_{19}H_{14}{}^{81}BrN_2$ $[M+H]^+$ 351.0320, found 351.0311.



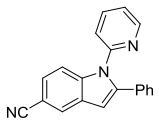
1-(2-phenyl-1-(pyridin-2-yl)-1H-indol-5-yl)ethan-1-one (3h)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) afforded **3h** as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (ddd, *J* = 4.9, 1.8, 0.7 Hz, 1H), 8.34 (d, *J* = 1.4 Hz, 1H), 7.89 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.67 (ddd, *J* = 7.9, 4.3, 2.0 Hz, 2H), 7.31 – 7.26 (m, 6H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.25, 151.34, 149.35, 141.59, 140.86, 138.04, 131.95, 131.14, 128.76, 128.42, 128.22, 127.90, 123.21, 122.54, 122.26, 122.07, 111.40, 106.32, 26.72. HRMS (ESI$^+$): calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$ 313.1341, found 313.1346.



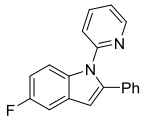
2-phenyl-1-(pyridin-2-yl)-5-(trifluoromethyl)-1H-indole (3i)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3i** as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.73 (dd, *J* = 8.7, 0.6 Hz, 1H), 7.66 (ddd, *J* = 8.0, 7.6, 2.0 Hz, 1H), 7.45 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.28 (tdd, *J* = 4.1, 3.1, 1.6 Hz, 6H), 6.93 – 6.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.55, 149.51, 141.87, 139.77, 138.17, 132.08, 128.99, 128.60, 128.19, 128.12, 126.65 (q, $^{1}J_{C-F}$ = 271 Hz), 123.93 (q, $^{2}J_{C-F}$ = 31 Hz), 122.38, 122.21, 119.73 (q, $^{3}J_{C-F}$ = 4 Hz), 118.34 (q, $^{3}J_{C-F}$ = 4 Hz), 112.01, 105.81. HRMS (ESI^{+}): calcd for $C_{20}H_{14}F_3N_2$ $[M+H]^+$ 339.1109, found 339.1113.



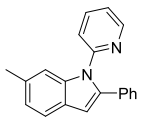
2-phenyl-1-(pyridin-2-yl)-1H-indole-5-carbonitrile (3j)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3j** as a white solid (mp = 155-156 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.63 (m, 1H), 8.01 (d, *J* = 1.0 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.45 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.26 (t, *J* = 2.9 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.84 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.00, 148.42, 141.31, 138.82, 137.16, 130.48, 127.86, 127.52, 127.42, 127.26, 124.86, 124.81, 121.55, 121.13, 119.50, 111.51, 104.22, 103.37. HRMS (ESI^{+}): calcd for $C_{20}H_{14}N_3$ $[M+H]^+$ 296.1188, found 296.1190.



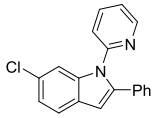
5-fluoro-2-phenyl-1-(pyridin-2-yl)-1H-indole (3k)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3k** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.62 (ddd, *J* = 14.3, 6.6, 3.2 Hz, 2H), 7.32 – 7.21 (m, 7H), 6.96 (td, *J* = 9.1, 2.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.90 (d, $^{1}J_{C-F}$ = 235 Hz), 152.02, 149.35, 141.58, 137.99, 135.12, 132.49, 129.25 (d, $^{3}J_{C-F}$ = 10 Hz), 128.91, 128.54, 127.88, 122.09, 121.91, 112.64 (d, $^{3}J_{C-F}$ = 10 Hz), 111.24 (d, $^{2}J_{C-F}$ = 26 Hz), 105.55 (d, $^{2}J_{C-F}$ = 23 Hz), 105.53 (d, $^{4}J_{C-F}$ = 4 Hz). HRMS (ESI^{+}): calcd for $C_{19}H_{14}FN_2$ $[M+H]^+$ 289.1141, found 289.1143.



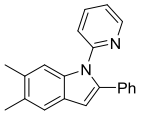
6-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3l)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3l** as a white solid (mp = 144−145 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.60 (td, *J* = 7.7, 2.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.27 – 7.18 (m, 6H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.20, 149.16, 139.36, 138.92, 137.75, 133.02, 132.83, 128.62, 128.29, 127.23, 126.52, 123.05, 122.09, 121.51, 120.21, 111.39, 105.56, 21.98. HRMS (ESI^{+}): calcd for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1392, found 285.1393.



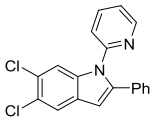
6-chloro-2-phenyl-1-(pyridin-2-yl)-1H-indole (3m)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3m** as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.61 (m, 1H), 7.72 – 7.68 (m, 1H), 7.61 (ddd, *J* = 9.4, 7.8, 1.9 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.21 (m, 6H), 7.16 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.53, 148.26, 139.60, 137.71, 136.89, 131.16, 127.77, 127.66, 127.36, 126.67, 126.18, 120.96, 120.90, 120.87, 120.31, 110.69, 104.33. HRMS (ESI$^+$): calcd for $C_{19}H_{14}ClN_2$ $[M+H]^+$ 305.0846, found 305.0849.



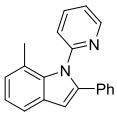
5,6-dimethyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3n)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3n** as a white solid (mp = 105−106 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.59 (td, *J* = 7.8, 1.9 Hz, 1H), 7.48 (s, 1H), 7.41 (s, 1H), 7.27 – 7.17 (m, 6H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 2.35 (d, *J* = 5.6 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 152.40, 149.12, 139.12, 137.66, 137.58, 132.98, 132.21, 130.01, 128.58, 128.26, 127.12, 127.04, 121.90, 121.30, 120.67, 111.83, 105.32, 20.66, 20.08. HRMS (ESI$^+$): calcd for $C_{21}H_{19}N_2$ $[M+H]^+$ 299.1548, found 299.1550.



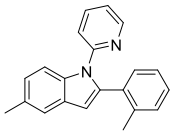
5,6-dichloro-2-phenyl-1-(pyridin-2-yl)-1H-indole (3o)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3o** as a yellowish solid (mp = 144−145 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.64 (m, 1H), 7.83 (s, 1H), 7.72 (s, 1H), 7.66 – 7.60 (m, 1H), 7.32 – 7.23 (m, 6H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 0.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.29, 149.35, 141.77, 138.03, 137.10, 131.77, 128.76, 128.49, 128.28, 128.05, 126.65, 125.17, 122.14, 121.81, 121.34, 113.38, 104.65. HRMS (ESI$^+$): calcd for $C_{19}H_{13}Cl_2N_2$ $[M+H]^+$ 339.0456, found 339.0460.



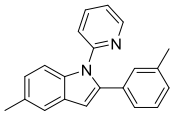
7-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3p)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3p** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.60 (m, 1H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1H), 7.54 (t, *J* = 8.2 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.28 – 7.18 (m, 5H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.75 (s, 1H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.55, 148.66, 141.65, 137.54, 137.40, 132.75, 129.18, 128.97, 128.02, 127.32, 125.31, 125.11, 123.34, 121.81, 120.82, 118.62, 104.23, 19.54. HRMS (ESI$^+$): calcd for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1392, found 285.1395.



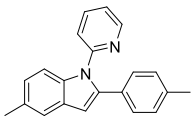
5-methyl-1-(pyridin-2-yl)-2-(o-tolyl)-1H-indole (3q)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3q** as a white solid (mp = 149−150 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.53 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.06 (m, 5H), 6.68 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.58 (s, 1H), 2.47 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.04, 148.82, 138.97, 137.42, 137.37, 135.53, 132.91, 131.02, 130.58, 130.16, 128.86, 128.19, 125.58, 124.37, 120.80, 120.26, 120.06, 111.73, 105.91, 21.44, 20.17. HRMS (ESI$^+$): calcd for $C_{21}H_{19}N_2$ $[M+H]^+$ 299.1548, found 299.1549.



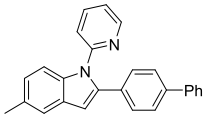
5-methyl-1-(pyridin-2-yl)-2-(m-tolyl)-1H-indole (3r)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3r** as a white solid (mp = 106−107 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.59 (ddd, *J* = 8.4, 7.0, 3.1 Hz, 2H), 7.44 (s, 1H), 7.16 (ddd, *J* = 20.2, 11.3, 6.2 Hz, 3H), 7.08 – 7.02 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 2.46 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.31, 149.07, 140.13, 137.95, 137.61, 136.91, 132.71, 130.59, 129.34, 128.98, 128.10, 128.08, 125.83, 124.47, 121.86, 121.34, 120.21, 111.21, 105.24, 21.42, 21.41. HRMS (ESI$^+$): calcd for $C_{21}H_{19}N_2$ $[M+H]^+$ 299.1548, found 299.1551.



5-methyl-1-(pyridin-2-yl)-2-(p-tolyl)-1H-indole (3s)

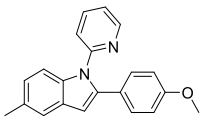
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3s** as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.61 (m, 1H), 7.65 – 7.54 (m, 2H), 7.43 (s, 1H), 7.22 – 7.18 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.08 – 7.01 (m, 3H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 2.45 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.34, 149.08, 140.06, 137.65, 137.17, 136.86, 130.56, 129.92, 129.02, 128.55, 124.36, 121.88, 121.34, 120.13, 111.18, 109.99, 104.91, 21.42, 21.21. HRMS (ESI$^+$): calcd for $C_{21}H_{19}N_2$ $[M+H]^+$ 299.1548, found 299.1549.



2-([1,1'-biphenyl]-4-yl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3t)

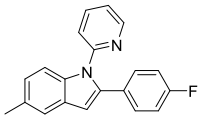
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3t** as a yellowish solid (mp = 155−156 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.61 (m, 1H), 7.64 (td, *J* = 7.7, 1.9 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 3H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.35 – 7.30 (m, 3H), 7.24 – 7.19 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.78 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.26, 149.21, 140.41, 139.92, 139.60, 137.83, 137.08, 131.73, 130.71, 129.00, 128.96, 128.80, 127.41,

126.95, 126.92, 124.66, 121.93, 121.50, 120.28, 111.20, 105.48, 21.45. HRMS (ESI$^+$): calcd for $C_{26}H_{21}N_2$ $[M+H]^+$ 361.1705, found 361.1710.



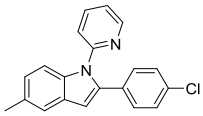
2-(4-methoxyphenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3u)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3u** as a white solid (mp = 101−102 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.9, 1.9, 0.7 Hz, 1H), 7.59 (ddd, *J* = 13.0, 9.5, 5.2 Hz, 2H), 7.42 (s, 1H), 7.22 – 7.15 (m, 3H), 7.02 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 0.5 Hz, 1H), 3.79 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.95, 152.30, 149.07, 139.82, 137.67, 136.72, 130.54, 129.91, 129.03, 125.33, 124.21, 121.89, 121.35, 120.02, 113.78, 111.12, 104.42, 55.22, 21.43. HRMS (ESI$^+$): calcd for $C_{21}H_{19}N_2O$ $[M+H]^+$ 315.1497, found 315.1499.



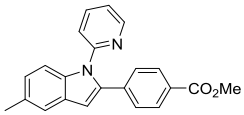
2-(4-fluorophenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3v)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3v** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.24 – 7.19 (m, 3H), 7.05 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.88 (dt, *J* = 8.0, 0.8 Hz, 1H), 6.69 (d, *J* = 0.5 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.26 (d, $^1J_{C-F}$ = 246 Hz), 152.15, 149.38, 139.03, 137.95, 136.95, 130.88, 130.43 (d, $^3J_{C-F}$ = 8 Hz), 129.13 (d, $^4J_{C-F}$ = 3 Hz), 128.97, 124.77, 121.91, 121.69, 120.38, 115.50 (d, $^2J_{C-F}$ = 21 Hz), 111.26, 105.37, 21.56. HRMS (ESI$^+$): calcd for $C_{20}H_{16}FN_2$ $[M+H]^+$ 303.1298, found 303.1302.



2-(4-chlorophenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3w)

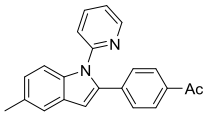
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3w** as a yellowish solid (mp = 111−112 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.24 – 7.16 (m, 5H), 7.05 (dd, *J* = 8.5, 1.3 Hz, 1H), 6.90 (dt, *J* = 8.0, 0.8 Hz, 1H), 6.72 (d, *J* = 0.6 Hz, 1H), 2.46 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.00, 149.35, 138.74, 137.96, 137.07, 133.31, 131.39, 130.86, 129.81, 128.86, 128.58, 124.90, 121.80, 121.68, 120.40, 111.18, 105.70, 21.45. HRMS (ESI$^+$): calcd for $C_{20}H_{16}ClN_2$ $[M+H]^+$ 319.1002, found 319.1005.



methyl 4-(5-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)benzoate (3x)

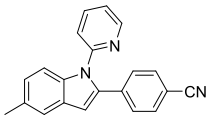
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3x** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.65 (ddd,

J = 8.0, 7.5, 2.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.34 – 7.30 (m, 2H), 7.23 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.93 (dt, *J* = 8.0, 0.9 Hz, 1H), 6.83 (d, *J* = 0.7 Hz, 1H), 3.90 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.83, 151.91, 149.36, 138.74, 137.98, 137.34, 137.28, 130.94, 129.57, 128.77, 128.55, 128.27, 125.26, 121.73, 120.56, 111.16, 106.71, 52.15, 21.42. HRMS (ESI$^+$): calcd for $C_{22}H_{19}N_2O_2$ $[M+H]^+$ 343.1447, found 343.1448.



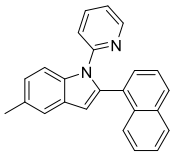
1-(4-(5-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)phenyl)ethan-1-one (3y)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **3y** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.59 (m, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.68 (td, *J* = 7.7, 2.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 0.7 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.08 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.85 (s, 1H), 2.58 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.61, 151.91, 149.40, 138.64, 138.03, 137.44, 135.44, 130.99, 129.92, 128.76, 128.38, 125.35, 121.77, 121.72, 120.58, 111.15, 106.87, 26.61, 21.42. HRMS (ESI$^+$): calcd for $C_{22}H_{19}N_2O$ $[M+H]^+$ 327.1497, found 327.1500.



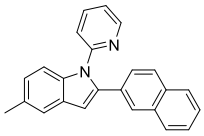
4-(5-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)benzonitrile (3z)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **3z** as a white solid (mp = 104−105 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.55 (m, 1H), 7.73 (td, *J* = 7.7, 1.9 Hz, 1H), 7.53 (dd, *J* = 11.2, 4.5 Hz, 3H), 7.47 (s, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.09 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.62, 149.55, 138.20, 137.82, 137.50, 137.36, 132.06, 131.18, 128.70, 128.63, 125.69, 121.99, 121.56, 120.74, 118.84, 111.08, 110.43, 107.37, 21.40. HRMS (ESI$^+$): calcd for $C_{21}H_{16}N_3$ $[M+H]^+$ 310.1344, found 310.1349.



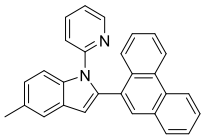
5-methyl-2-(naphthalen-1-yl)-1-(pyridin-2-yl)-1H-indole (3aa)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3aa** as a yellowish solid (mp = 125−126 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.77 (m, 3H), 7.51 (s, 1H), 7.44 – 7.39 (m, 3H), 7.34 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.12 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.98 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 6.78 (s, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.96, 148.75, 137.61, 137.37, 135.92, 133.49, 132.15, 130.77, 130.71, 128.91, 128.87, 128.46, 128.08, 126.40, 126.00, 125.90, 125.08, 124.63, 120.88, 120.35, 120.18, 111.71, 107.35, 21.47. HRMS (ESI$^+$): calcd for $C_{24}H_{19}N_2$ $[M+H]^+$ 335.1548, found 335.1549.



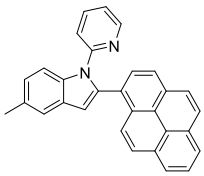
5-methyl-2-(naphthalen-2-yl)-1-(pyridin-2-yl)-1H-indole (3ab)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3ab** as a yellowish solid (mp = 129−130 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.9, 1.9, 0.7 Hz, 1H), 7.81 – 7.68 (m, 4H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.45 (ddd, *J* = 5.9, 4.5, 1.9 Hz, 3H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.18 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 7.07 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 0.5 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.28, 149.18, 139.93, 137.79, 137.10, 133.24, 132.44, 130.74, 130.33, 129.04, 128.08, 127.78, 127.64, 127.50, 126.62, 126.32, 126.15, 124.72, 121.85, 121.42, 120.31, 111.29, 105.93, 21.46. HRMS (ESI$^+$): calcd for $C_{24}H_{19}N_2$ $[M+H]^+$ 335.1548, found 335.1551.



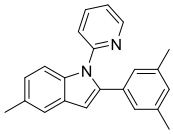
5-methyl-2-(phenanthren-9-yl)-1-(pyridin-2-yl)-1H-indole (3ac)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3ac** as a yellowish solid (mp = 175−176 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 8.2, 3.7 Hz, 2H), 8.47 (ddd, *J* = 4.9, 1.9, 0.7 Hz, 1H), 7.95 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.82 (dd, *J* = 9.6, 5.4 Hz, 3H), 7.65 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.61 – 7.49 (m, 3H), 7.39 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.13 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.91 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 6.83 (s, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.99, 148.74, 137.85, 137.54, 135.92, 131.19, 131.01, 130.74, 130.29, 130.21, 129.88, 129.73, 128.92, 128.88, 127.08, 126.83, 126.81, 126.76, 126.58, 124.72, 122.62, 122.52, 120.89, 120.24, 120.04, 111.79, 107.43, 21.49. HRMS (ESI$^+$): calcd for $C_{28}H_{21}N_2$ $[M+H]^+$ 385.1705, found 385.1708.



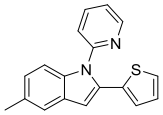
5-methyl-2-(pyren-1-yl)-1-(pyridin-2-yl)-1H-indole (3ad)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3ad** as a yellowish solid (mp = 183−184 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 8.02 (ddd, *J* = 29.2, 26.2, 13.0 Hz, 8H), 7.84 (d, *J* = 14.5 Hz, 1H), 7.55 (s, 1H), 7.14 (s, 2H), 6.91 (s, 2H), 6.60 – 6.53 (m, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.98, 148.82, 137.99, 137.40, 136.15, 131.29, 130.98, 130.87, 130.85, 129.73, 129.05, 128.70, 127.98, 127.90, 127.82, 127.31, 126.10, 125.30, 125.18, 125.16, 124.75, 124.58, 124.38, 120.86, 120.60, 120.23, 111.77, 108.09, 21.51. HRMS (ESI$^+$): calcd for $C_{30}H_{21}N_2$ $[M+H]^+$ 409.1705, found 409.1709.



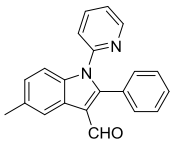
2-(3,5-dimethylphenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3ae)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3ae** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.59 (m, 1H), 7.63 – 7.56 (m, 2H), 7.43 (s, 1H), 7.19 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.87 (dd, *J* = 5.4, 2.6 Hz, 4H), 6.70 (s, 1H), 2.46 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.37, 149.01, 140.27, 137.73, 137.55, 136.87, 132.60, 130.53, 129.05, 128.99, 126.52, 124.38, 121.89, 121.28, 120.17, 111.21, 105.12, 21.43, 21.27. HRMS (ESI$^+$): calcd for $C_{22}H_{21}N_2$ $[M+H]^+$ 313.1705, found 313.1710.



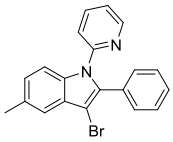
5-methyl-1-(pyridin-2-yl)-2-(thiophen-2-yl)-1H-indole (3af)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **3af** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.63 (m, 1H), 7.77 – 7.68 (m, 1H), 7.45 – 7.36 (m, 2H), 7.32 – 7.20 (m, 2H), 7.14 – 7.00 (m, 2H), 6.92 (td, *J* = 4.8, 2.2 Hz, 1H), 6.80 – 6.71 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.70, 149.33, 137.96, 136.99, 134.50, 133.17, 130.67, 128.59, 127.28, 126.41, 125.60, 124.77, 122.30, 122.21, 120.18, 110.84, 105.30, 21.43. HRMS (ESI$^+$): calcd for $C_{18}H_{15}N_2S$ $[M+H]^+$ 291.0956, found 291.0959.



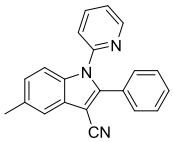
5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole-3-carbaldehyde (4)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **4** as a white solid (mp = 175–176 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.62 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.30 (s, 1H), 7.66 (td, *J* = 7.8, 1.9 Hz, 1H), 7.43 – 7.33 (m, 6H), 7.29 (ddd, *J* = 7.5, 4.9, 0.9 Hz, 1H), 7.16 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.68, 150.35, 149.84, 149.53, 138.15, 135.74, 133.68, 131.04, 129.37, 128.93, 128.40, 126.24, 125.59, 122.92, 122.22, 121.86, 116.59, 111.09, 21.50. HRMS (ESI$^+$): calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$ 313.1341, found 313.1342.



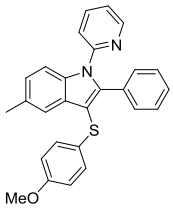
3-bromo-5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (5)

Purification by column chromatography on silica gel (petroleum ether/dichloromethane = 5/1, v/v) afforded **5** as a white solid (mp = 134–135 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 4.9, 1.9, 0.7 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.46 – 7.43 (m, 1H), 7.39 – 7.28 (m, 5H), 7.16 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 7.11 (dd, *J* = 8.5, 1.3 Hz, 1H), 6.76 (dt, *J* = 8.1, 0.8 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.61, 148.02, 136.70, 135.06, 134.13, 130.50, 129.70, 129.42, 127.19, 127.14, 127.04, 124.83, 120.58, 120.54, 118.06, 110.49, 93.73, 20.40. HRMS (ESI$^+$): calcd for $C_{20}H_{16}BrN_2$ $[M+H]^+$ 363.0497, found 363.0499.



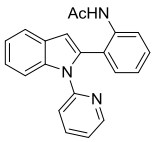
5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole-3-carbonitrile (6)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **6** as a white solid (mp = 142−143 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.9, 1.8, 0.7 Hz, 1H), 7.67 (td, *J* = 7.8, 1.9 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.29 (m, 6H), 7.15 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.47, 149.63, 146.38, 138.38, 135.35, 133.09, 129.63, 129.46, 129.06, 128.94, 128.79, 127.99, 127.21, 126.49, 123.10, 122.23, 119.21, 116.38, 111.93, 88.14, 21.47. HRMS (ESI$^+$): calcd for $C_{21}H_{16}N_3$ $[M+H]^+$ 310.1344, found 310.1349.



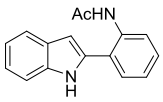
3-((4-methoxyphenyl)thio)-5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (7)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded **7** as a white solid (mp = 177−178 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.47 (d, *J* = 0.7 Hz, 1H), 7.30 – 7.25 (m, 5H), 7.20 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 7.12 – 7.04 (m, 3H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.75 – 6.70 (m, 2H), 3.72 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.58, 151.73, 149.14, 143.62, 137.80, 135.88, 131.62, 130.85, 130.73, 130.46, 129.62, 128.16, 128.08, 127.98, 125.57, 121.94, 121.84, 119.54, 114.52, 111.48, 104.92, 55.33, 21.51. HRMS (ESI$^+$): calcd for $C_{27}H_{23}N_2OS$ $[M+H]^+$ 423.1531, found 423.1534.



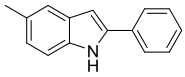
N-(2-(1-(pyridin-2-yl)-1H-indol-2-yl)phenyl)acetamide (**3bb**)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1, v/v) afforded **3bb** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 3.7 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.70 (dd, *J* = 11.1, 9.6 Hz, 3H), 7.60 (td, *J* = 7.8, 1.8 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.25 (s, 1H), 7.21 (ddd, *J* = 7.5, 4.9, 0.9 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.33, 151.25, 149.05, 138.21, 137.75, 136.35, 135.61, 131.23, 129.52, 128.49, 123.96, 123.48, 122.95, 122.15, 121.70, 121.62, 120.78, 120.60, 111.84, 106.88, 24.70. HRMS (ESI$^+$): calcd for $C_{21}H_{18}N_3O$ $[M+H]^+$ 328.1450, found 328.1456.



N-(2-(1H-indol-2-yl)phenyl)acetamide (8)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **8** as a white solid (mp = 131–132 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 7.85 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 8.3 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.28 – 7.24 (m, 1H), 7.22 – 7.15 (m, 2H), 6.65 (s, 1H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.88, 136.63, 135.33, 134.13, 129.34, 129.23, 128.70, 124.49, 123.41, 122.79, 121.86, 120.73, 120.53, 111.18, 102.44, 24.78. HRMS (ESI$^+$): calcd for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1184, found 251.1180.

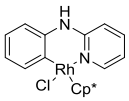


5-methyl-2-phenyl-1H-indole (11)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **11** as a brown solid (mp = 216–217 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.64 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.33 – 7.26 (m, 2H), 7.02 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.75 (dd, *J* = 2.1, 0.8 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.91, 134.13, 131.49, 128.52, 128.44, 127.95, 126.54, 124.03, 122.95, 119.27, 109.51, 98.51, 20.44. HRMS (ESI$^+$): calcd for $C_{15}H_{14}N$ $[M+H]^+$ 208.1126, found 208.1129.

1,4-diphenylbuta-1,3-diyne (12)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **11** as a white solid (mp = 85–86 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 4H), 7.40 – 7.31 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.52, 129.23, 128.46, 121.80, 81.56, 73.91. GC-MS: m/z = 202. Its characterization is in accordance with the literature (*J. Org. Chem.* **2019**, *84*, 4413).



Compound 13

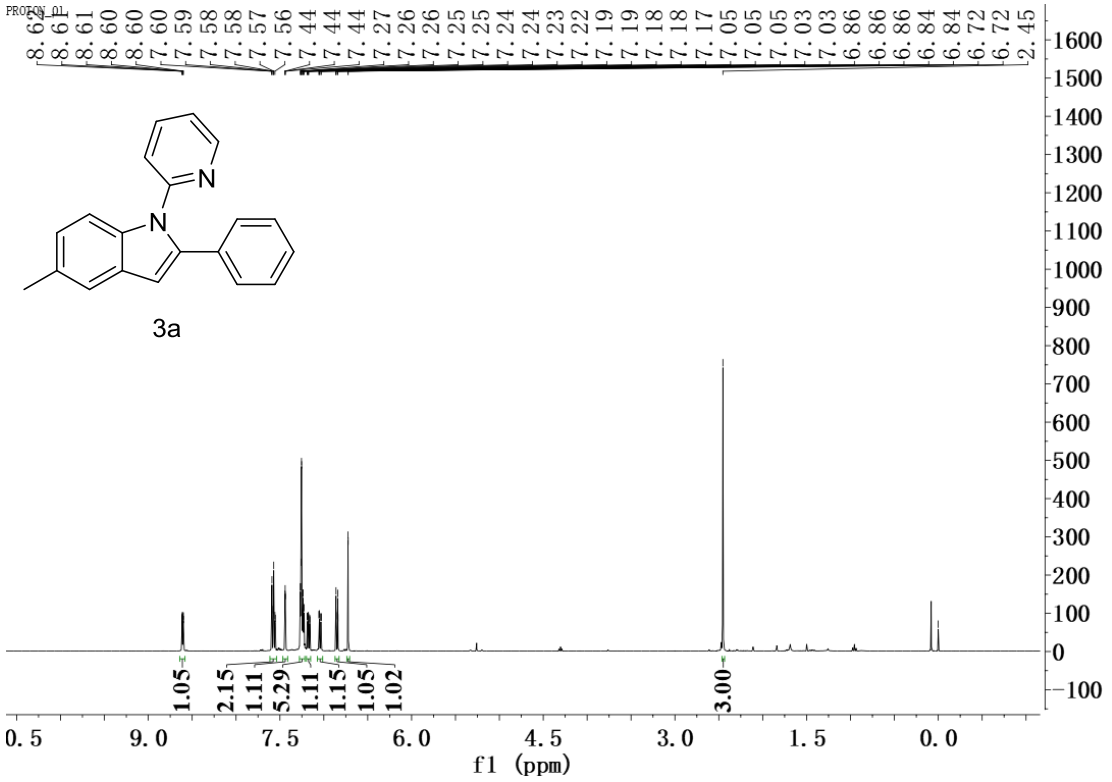
13 was recrystalized form dichloromethane as a reddish brown solid (mp = 285–286 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.77 (s, 1H), 7.50 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.24 (s, 1H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.79 – 6.71 (m, 1H), 1.56 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.53, 151.94, 138.83, 138.19, 128.70, 122.78, 119.70, 114.59, 109.20, 98.96, 93.56, 93.47, 7.93. HRMS (ESI$^+$): calcd for $C_{21}H_{24}ClN_2NaRh$ $[M+Na]^+$ 465.0581, found 465.0585.

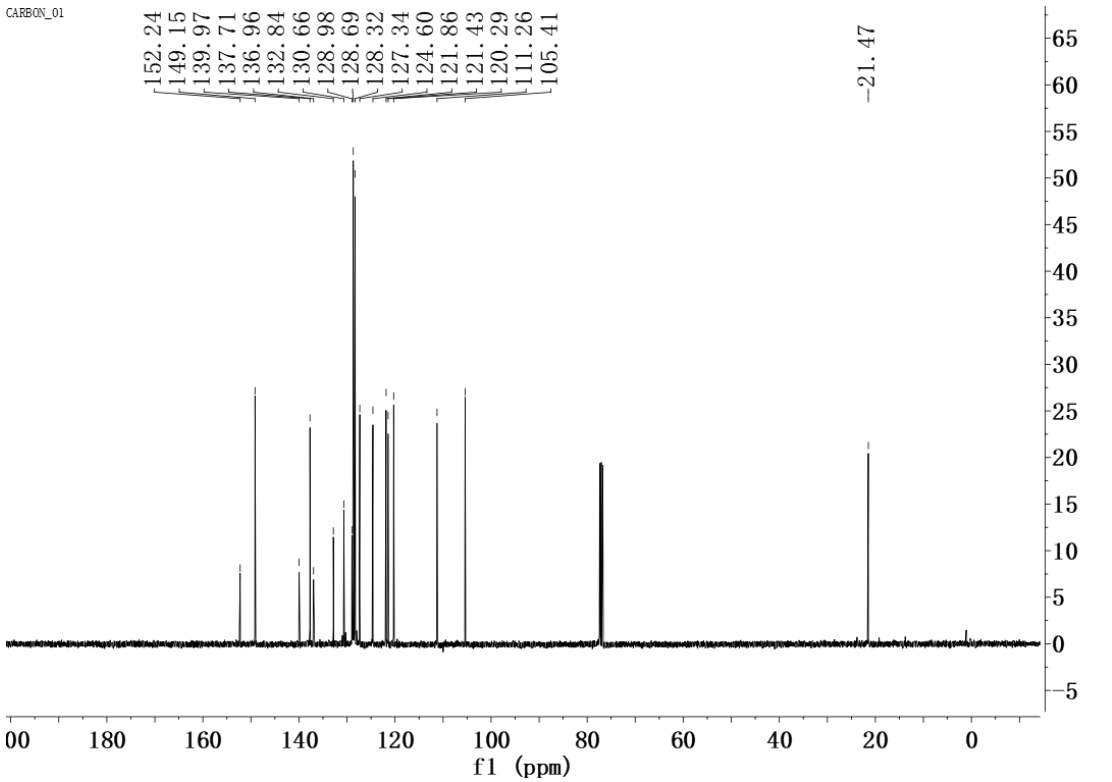
VII. References

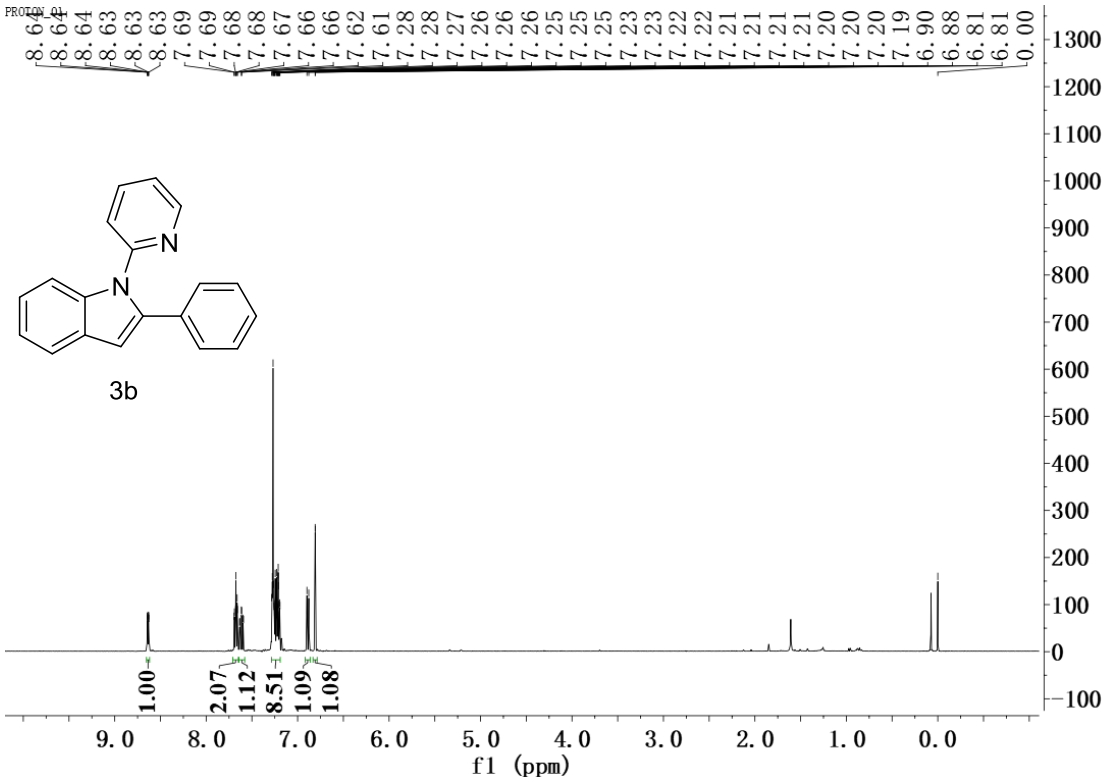
1 (a) Huang, X.; S. Xu, S.; Tan, Q.; Gao, M.; Li, M.; Xu, B. *Chem. Commun.* **2014**, *50*, 1465. (b) Ackermann, L.; Lygin, A. V. *Org. Lett.* **2012**, *14*, 764. (c) Grasa, G.; Viciu, M.; Huang, J.; Nolan, S. *J. Org. Chem.* **2001**, *66*, 7729.

2 (a) Li, Y.; Zou, H.; Gong, J.; Xiang, J.; Luo, T.; Quan, J.; Wang, G.; Yang, Z. *Org. Lett*. **2007**, *9*, 4057. (b) Hussain, M. K.; Ansari, M. I.; Kant, R.; Hajela, K. *Org. Lett*. **2014**, *16*, 560. (c) Arsenyan, P.; Rubina, K.; Vasiljeva, J.; Belyakov, S. *Tetrahedron Lett.* **2013**, *54*, 6524.

VIII. Copies of ^{1}H and ^{13}C spectra



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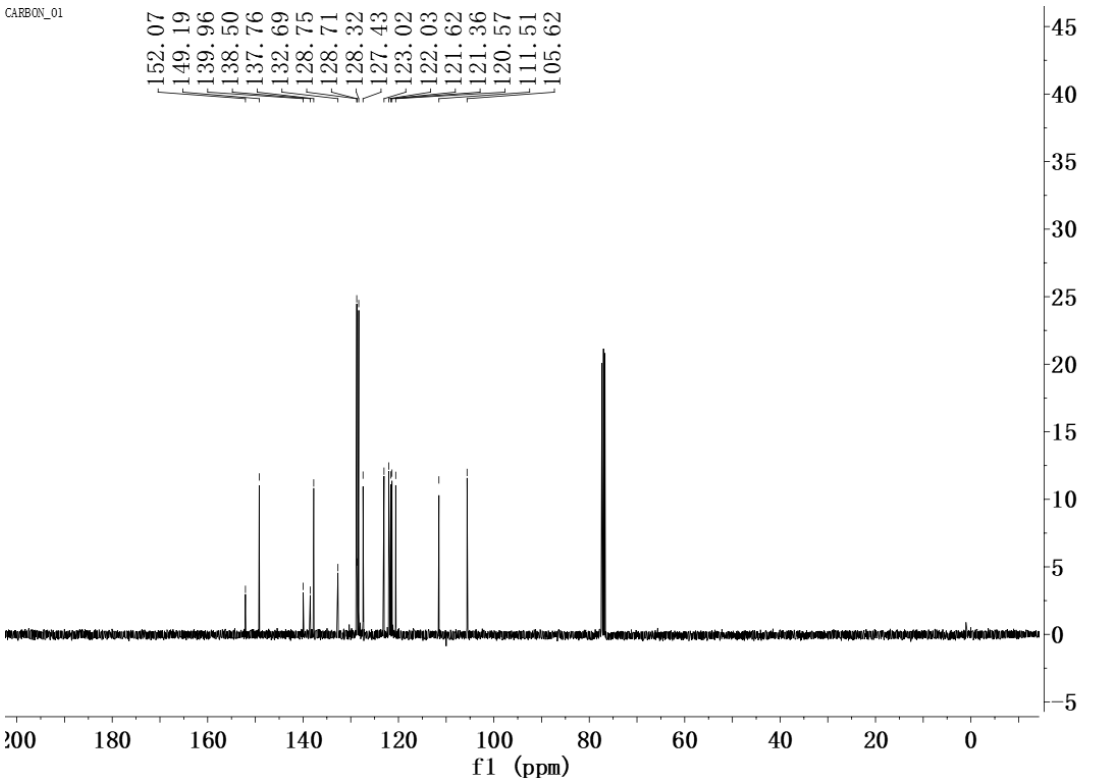
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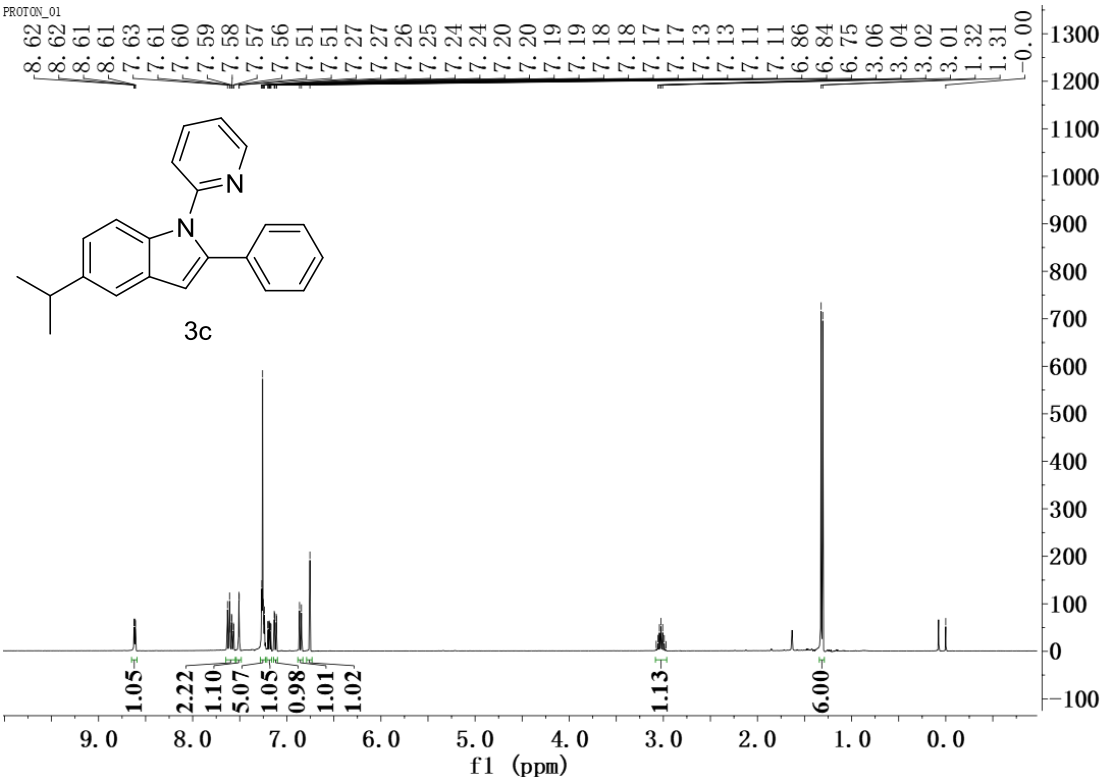
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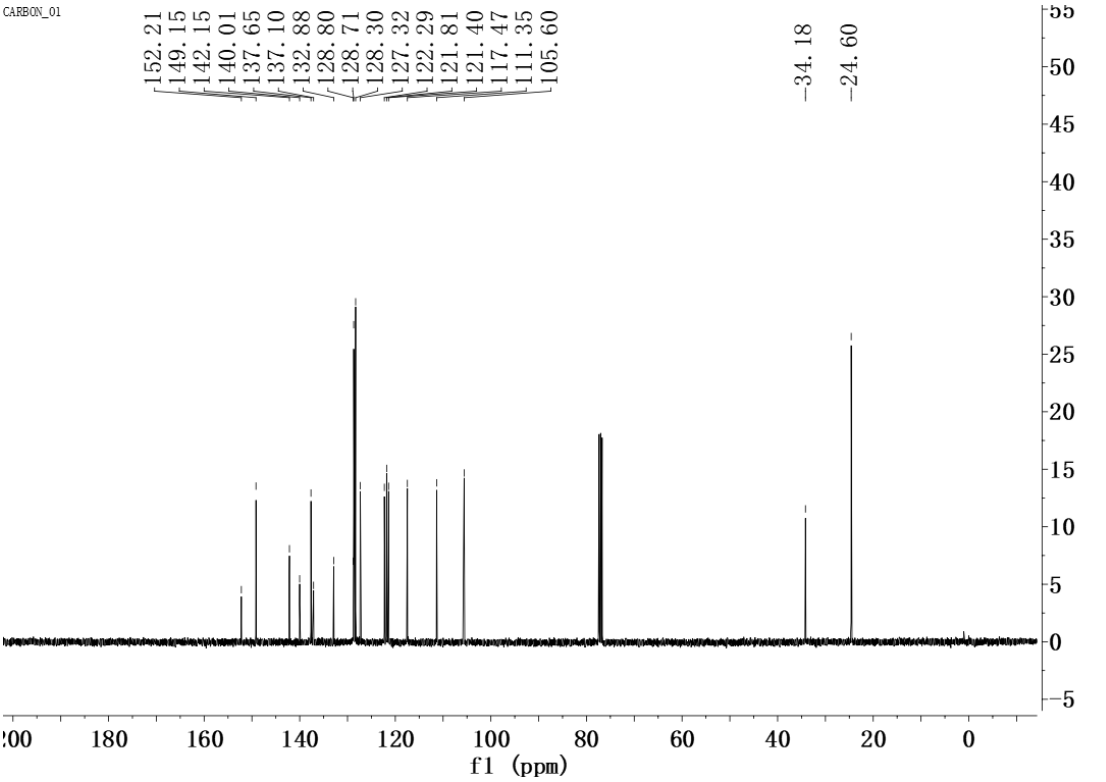
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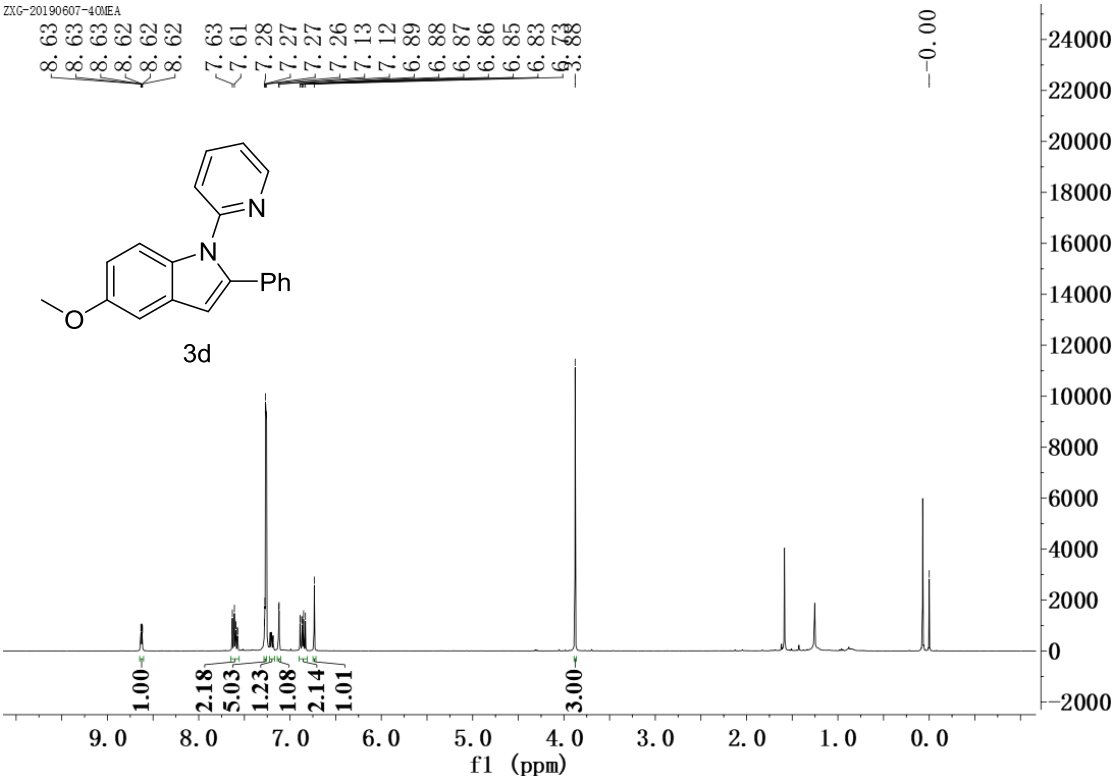
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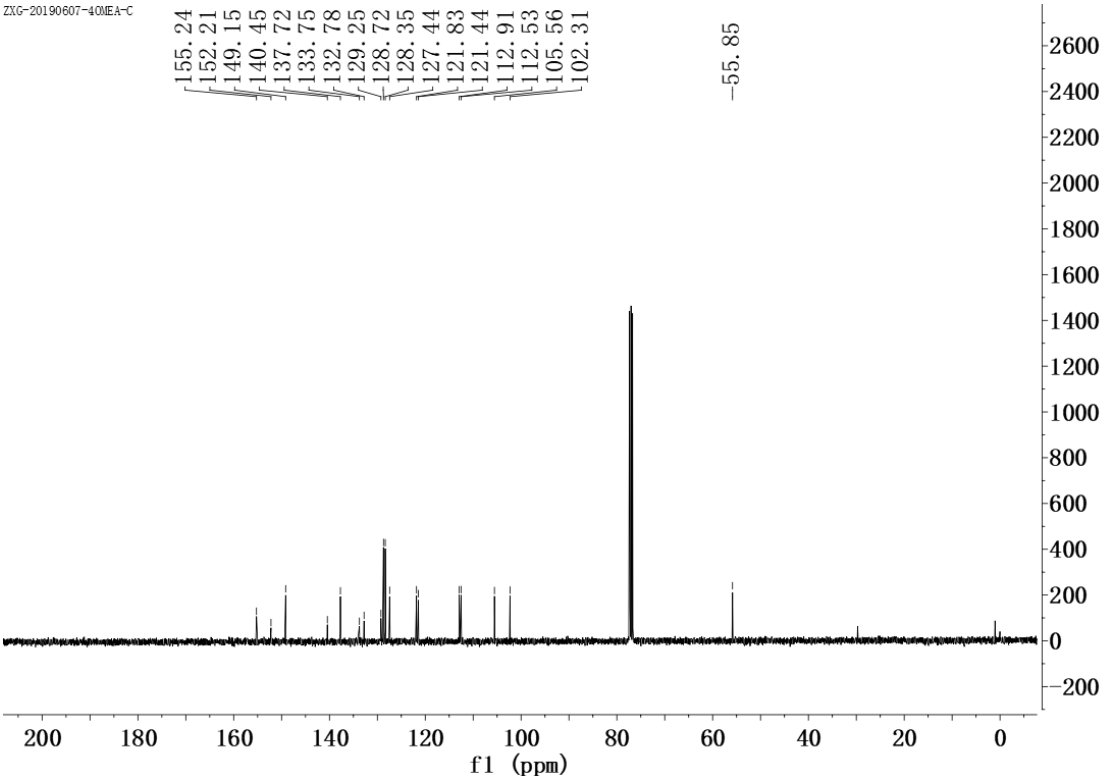
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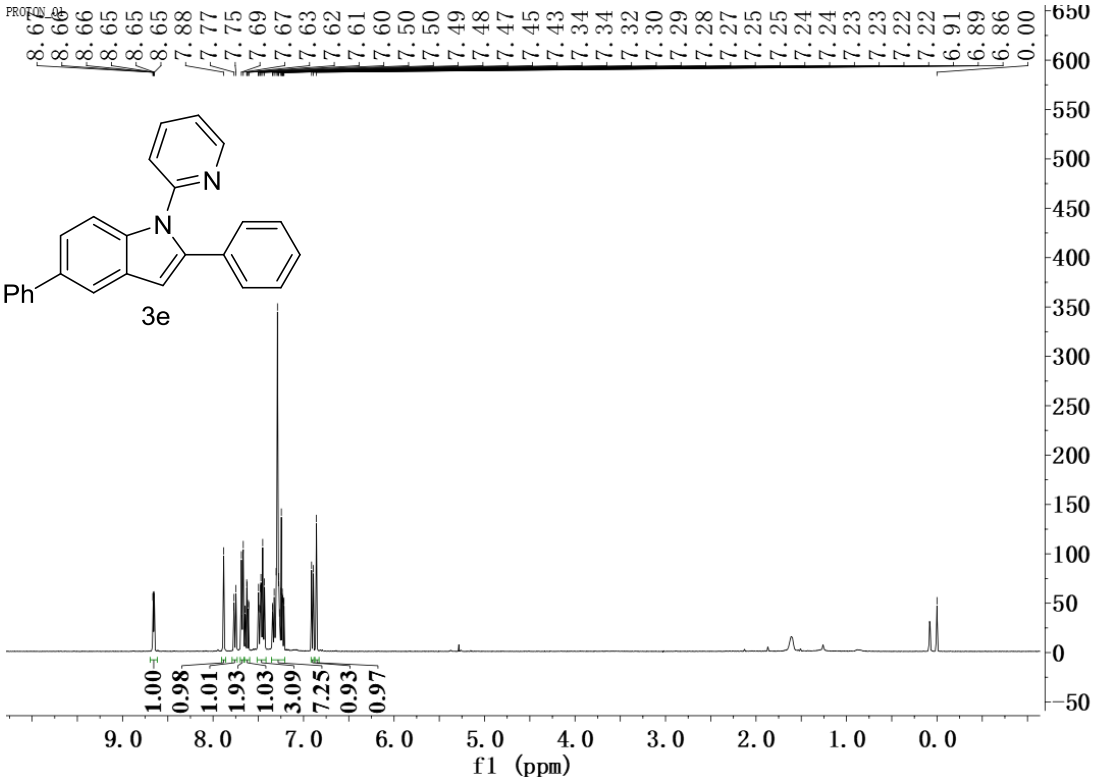
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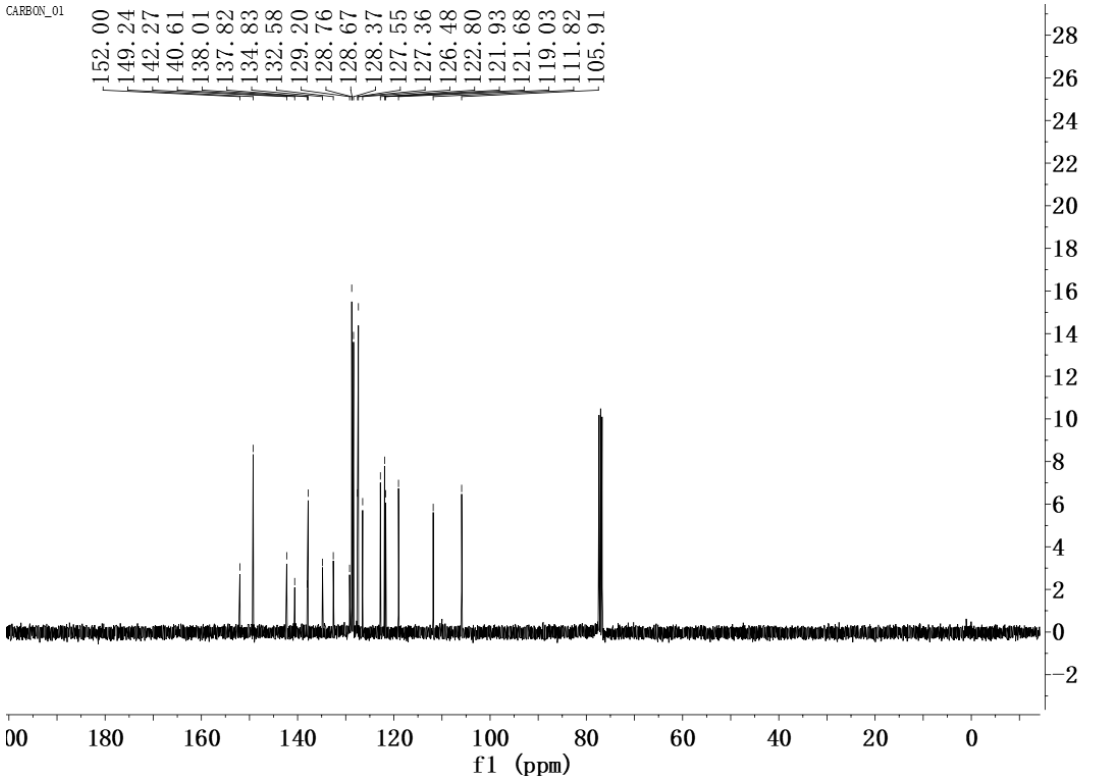
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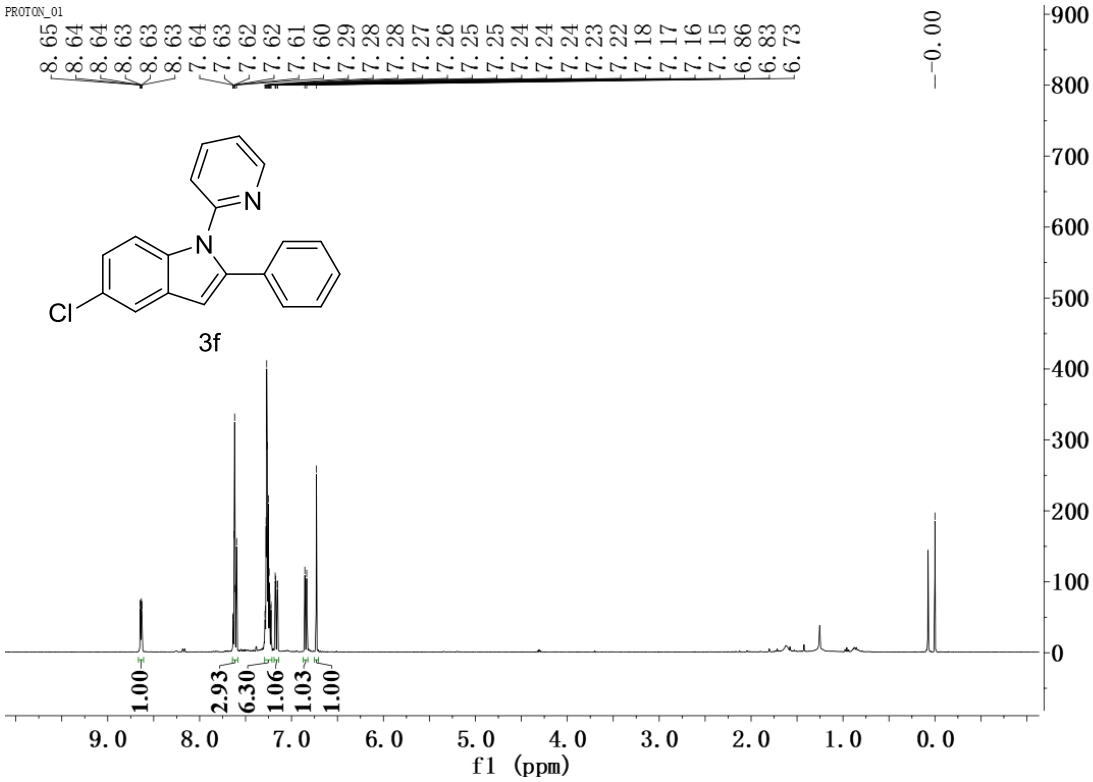
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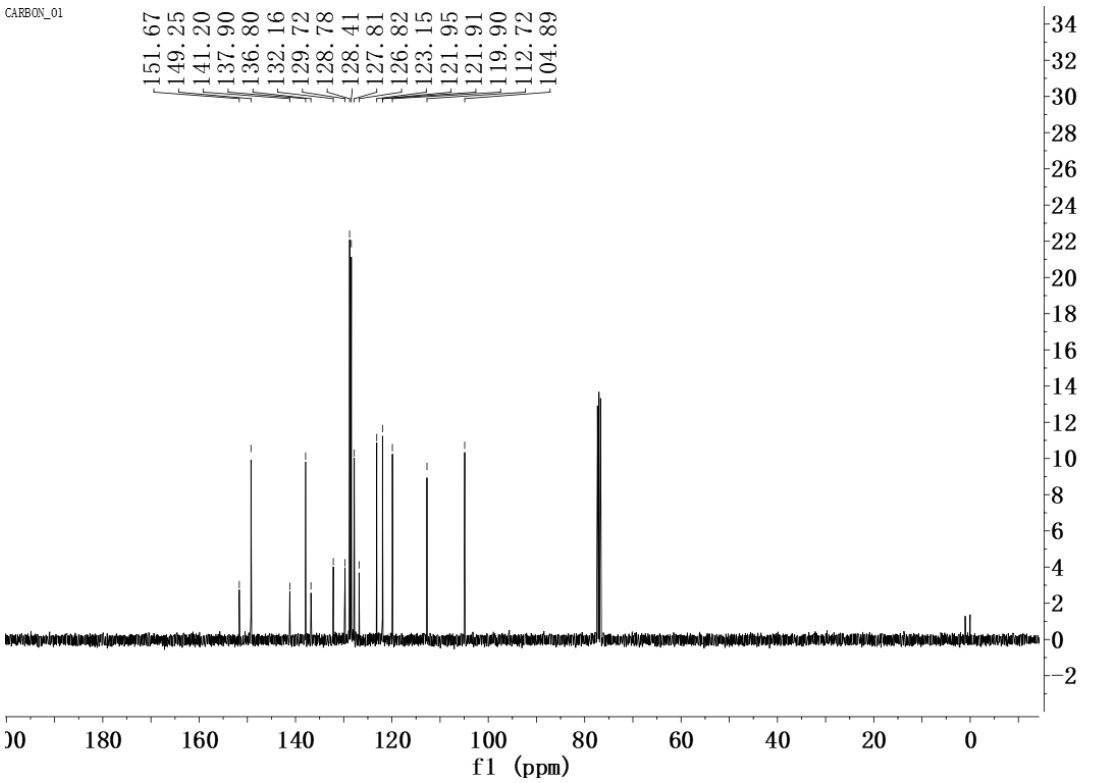
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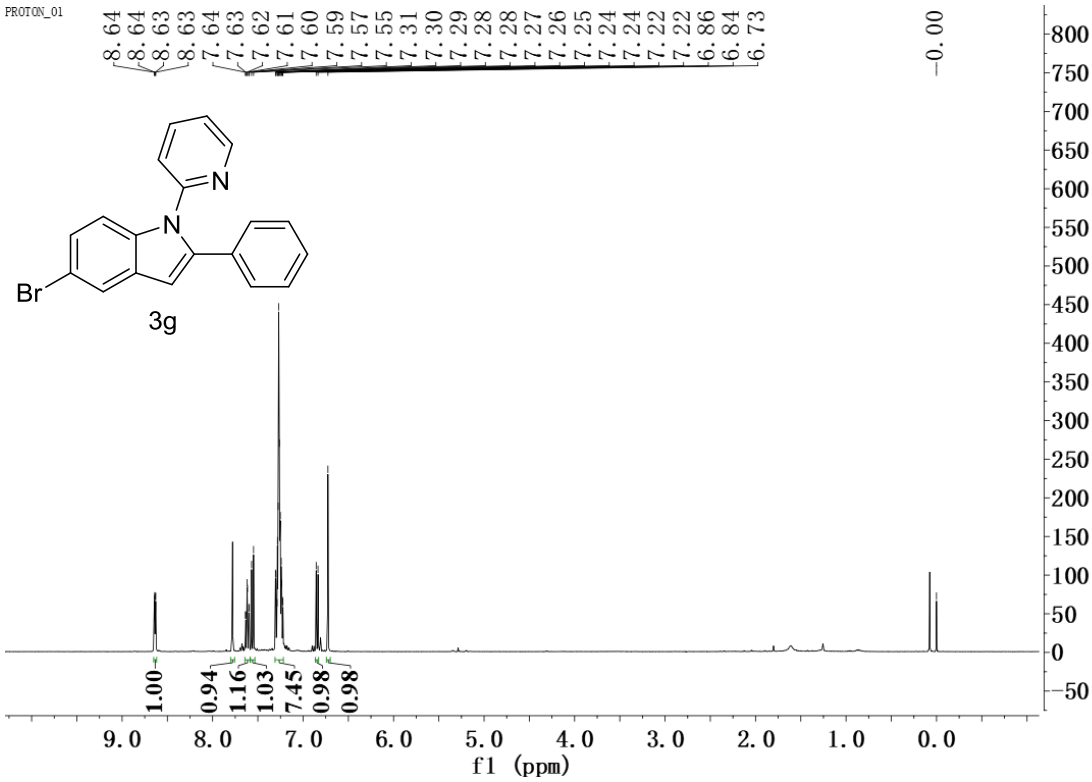
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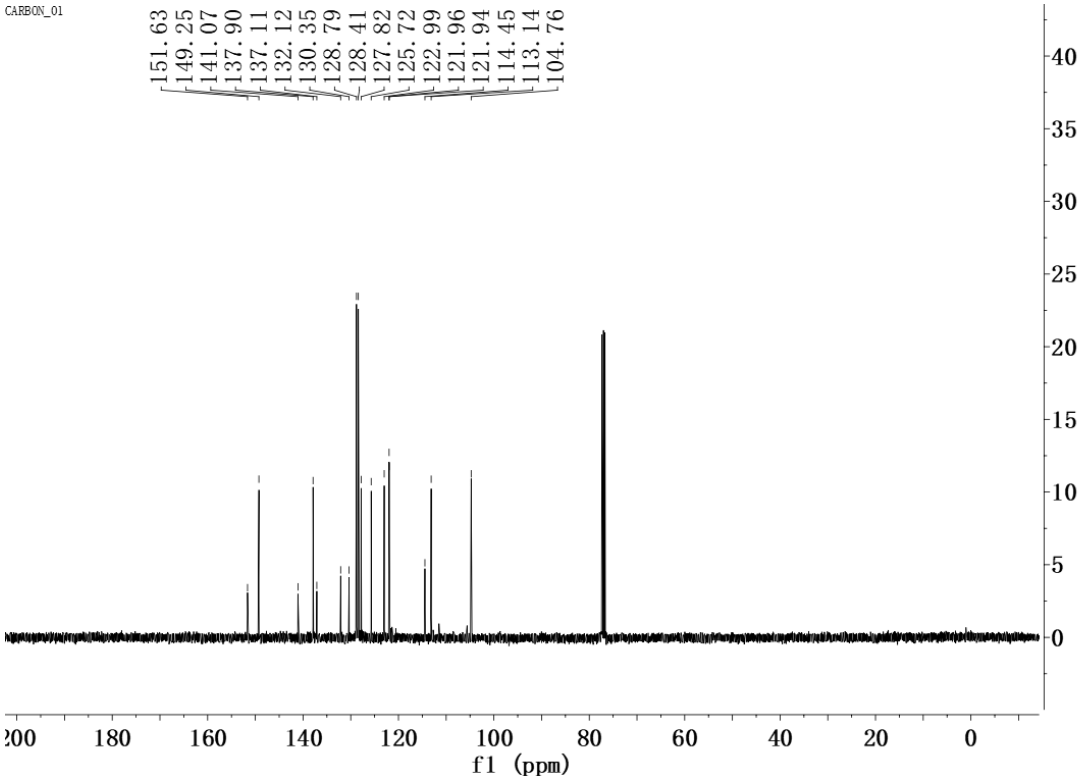
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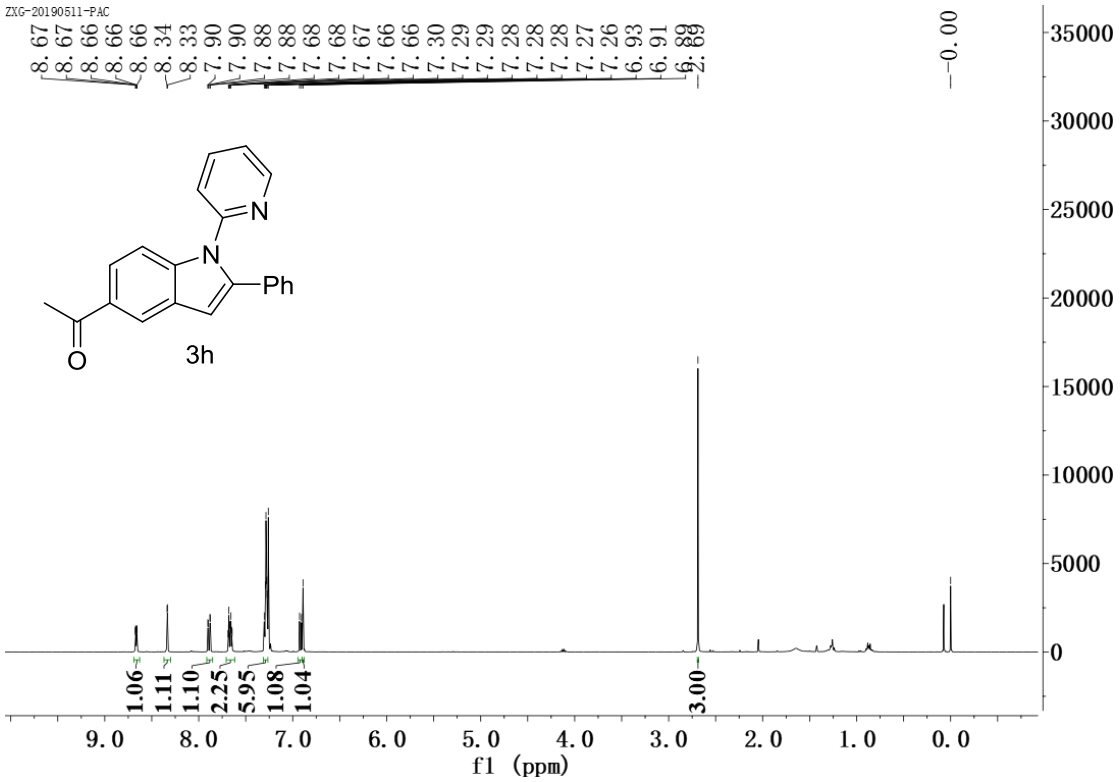
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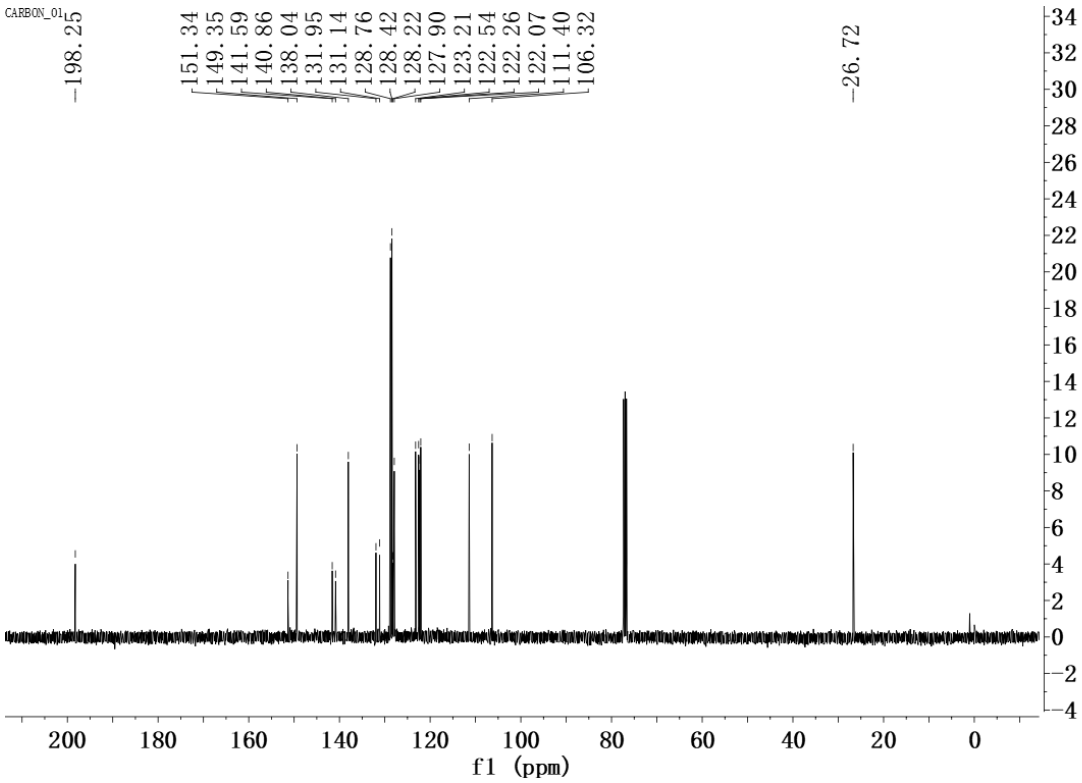
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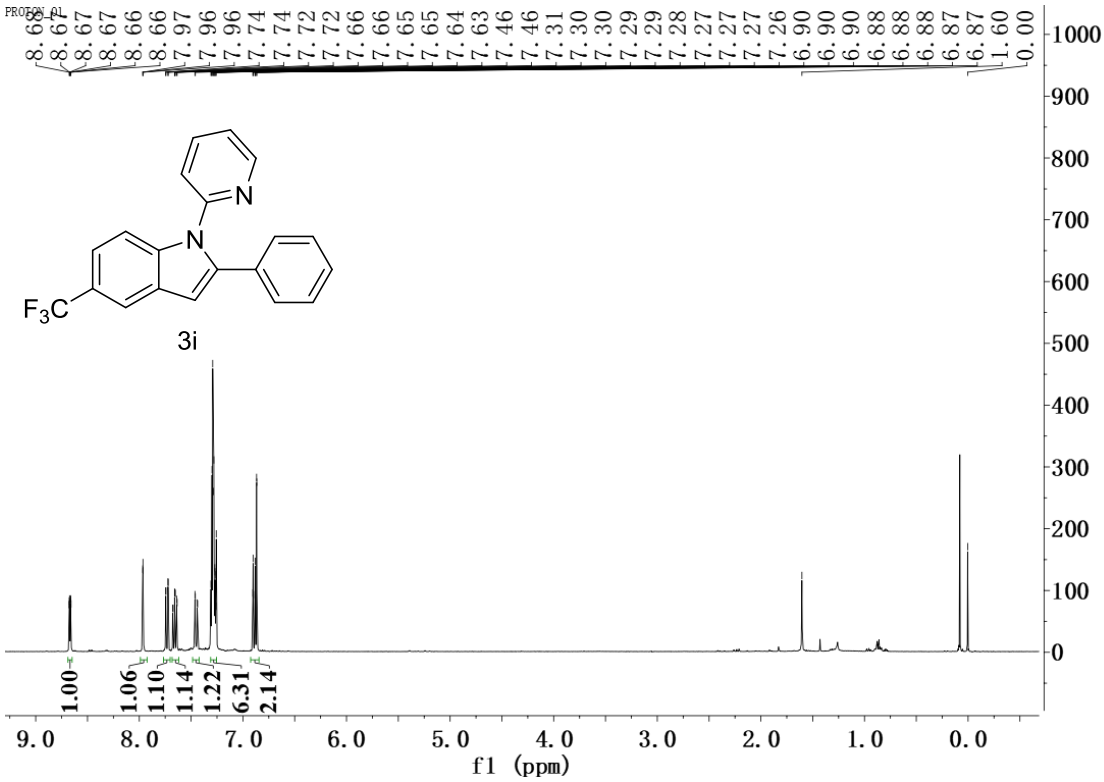
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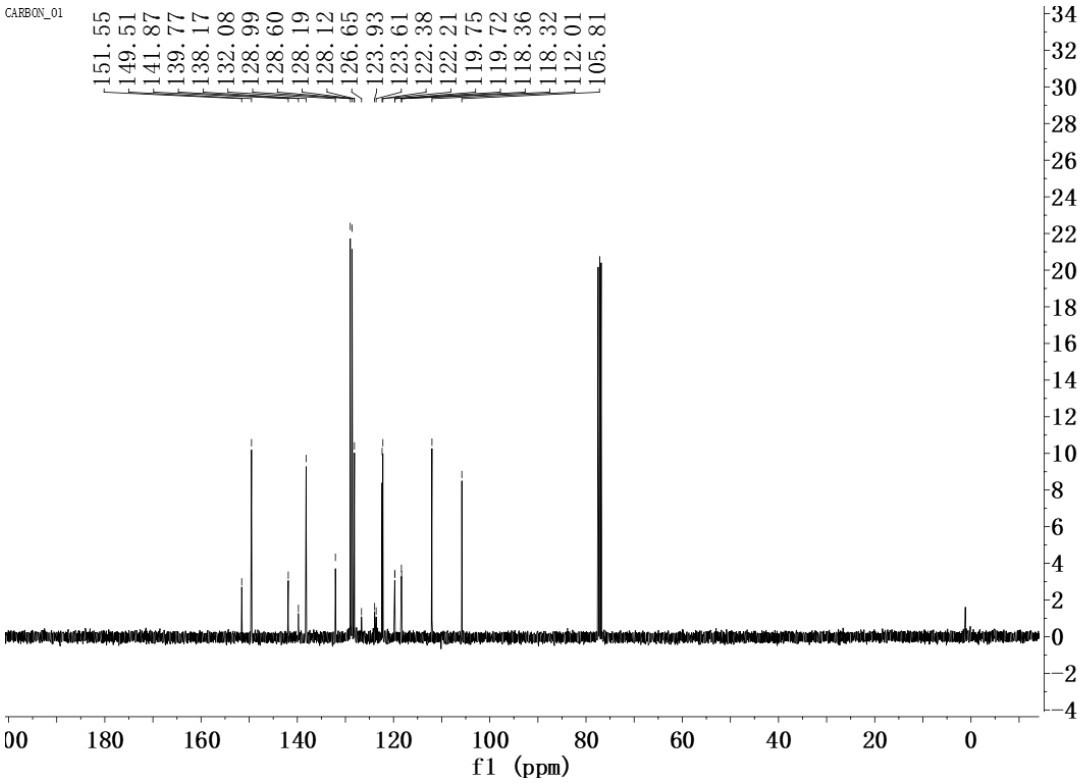
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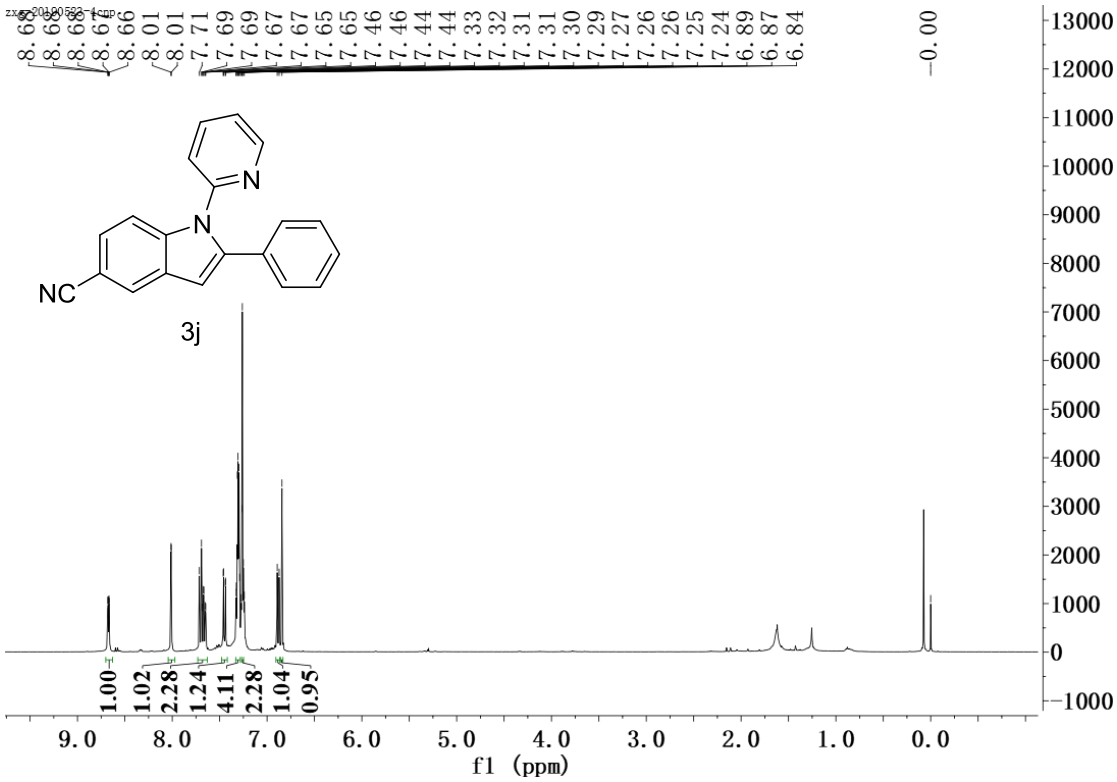
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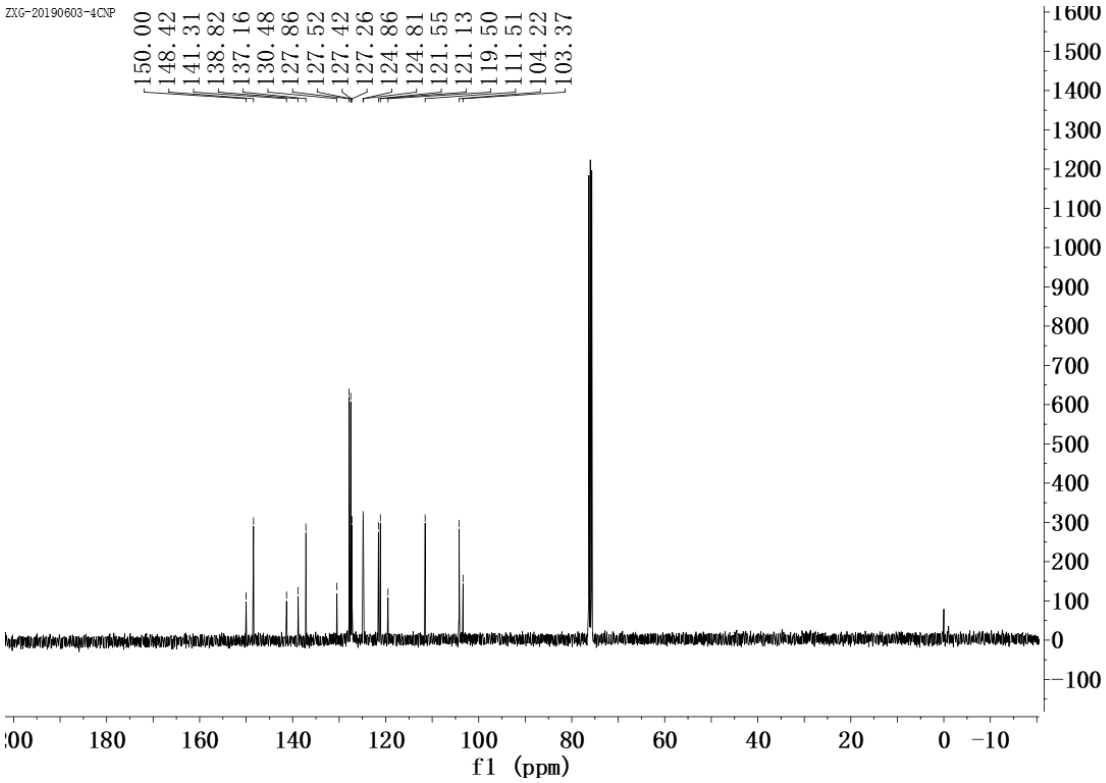
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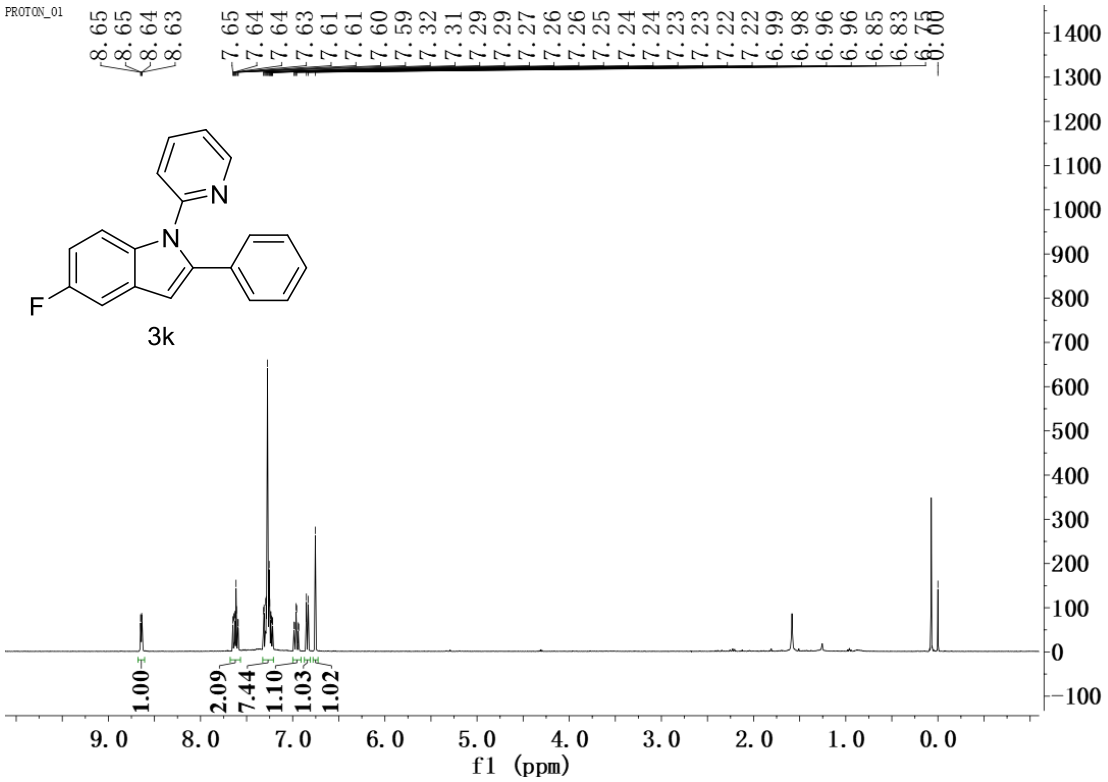
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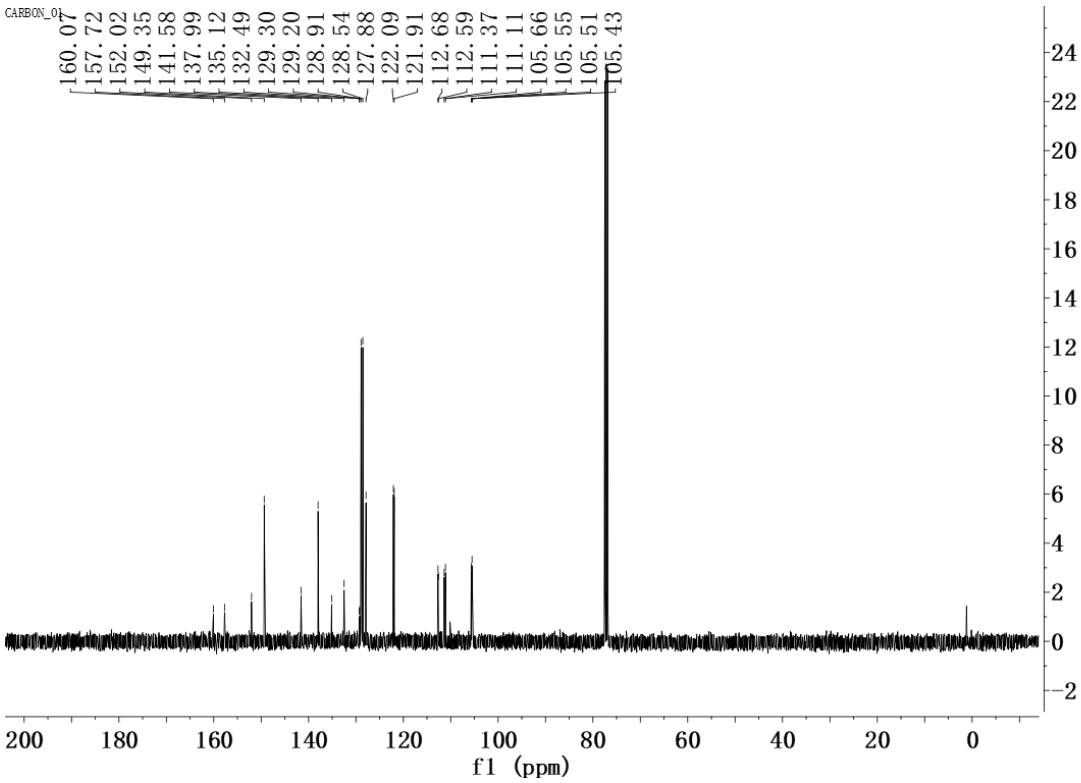
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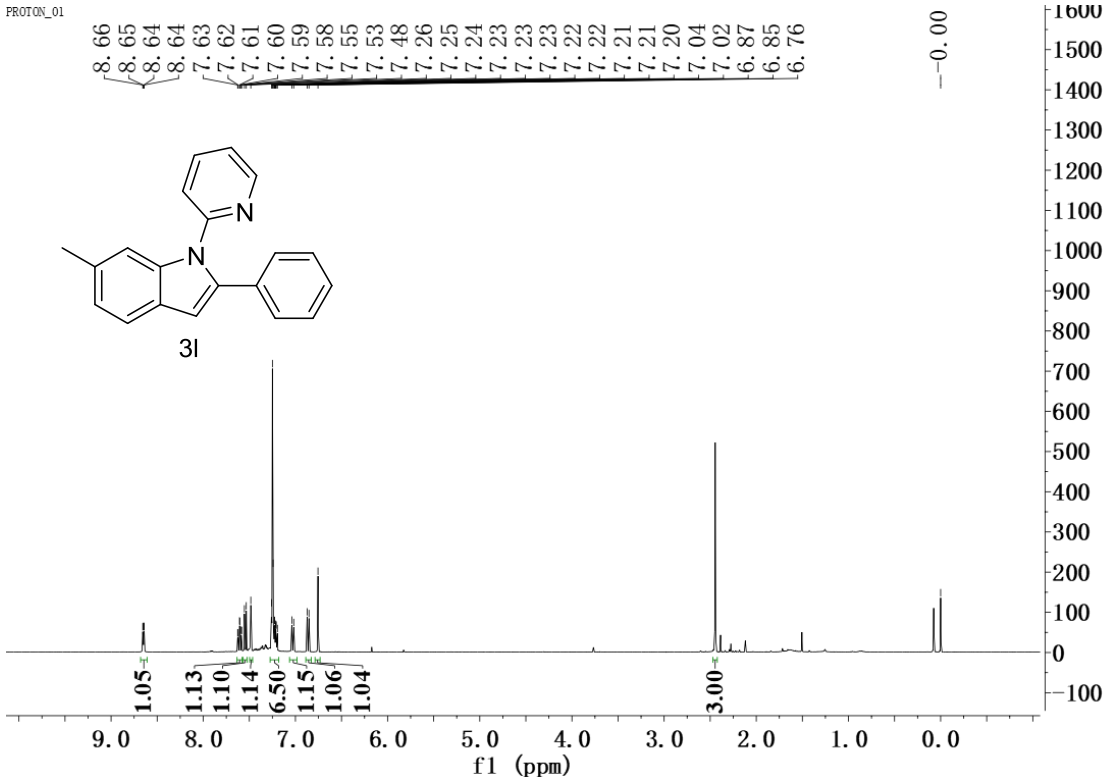
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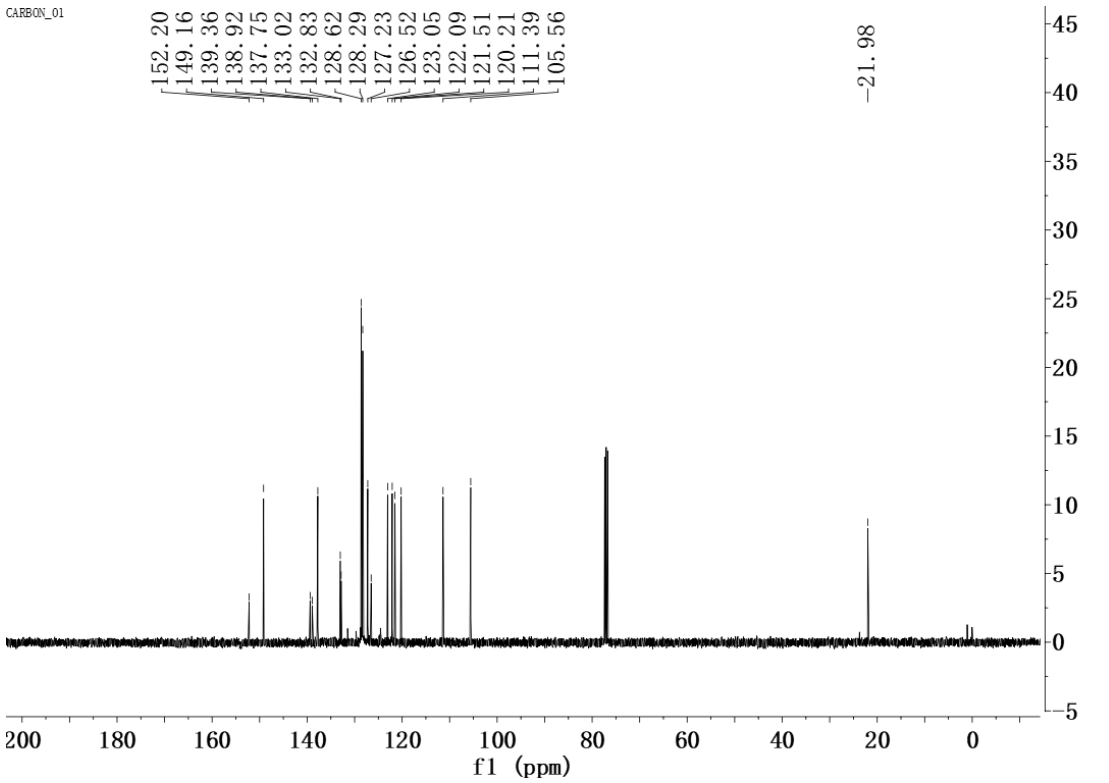
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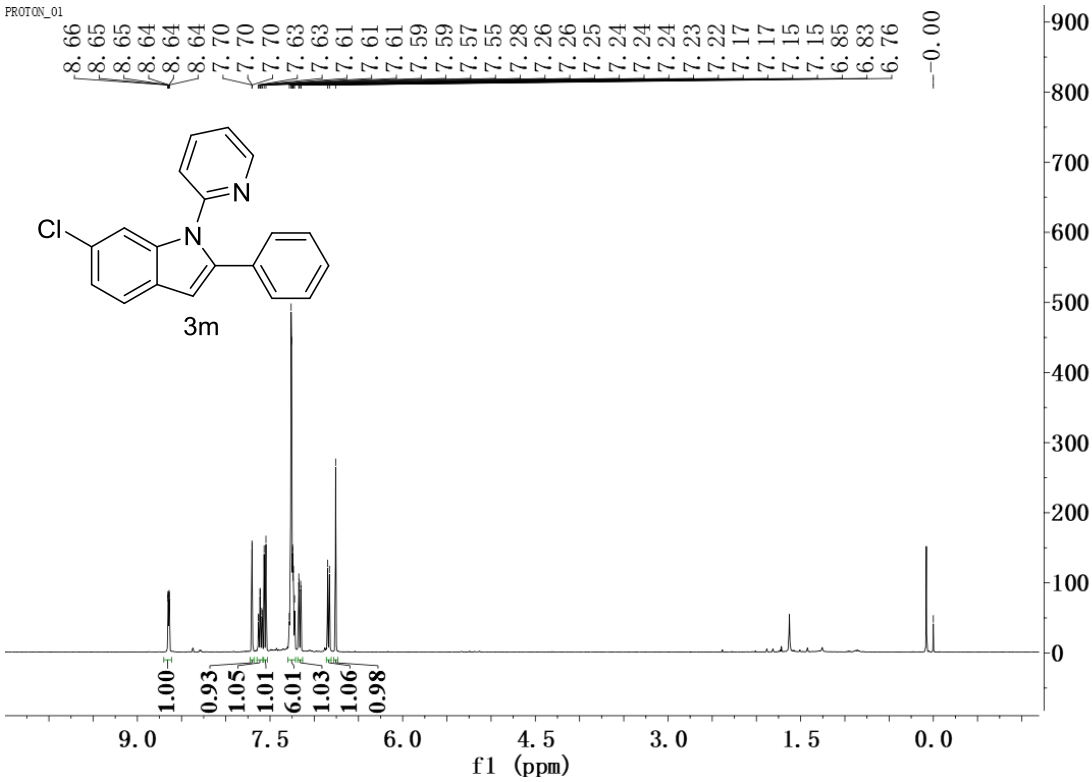
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7.22
7.17
7.17
7.15
7.15
6.85
6.83
6.76
-0.00
Cl
N
N
3m
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1.05
1.01
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3.0
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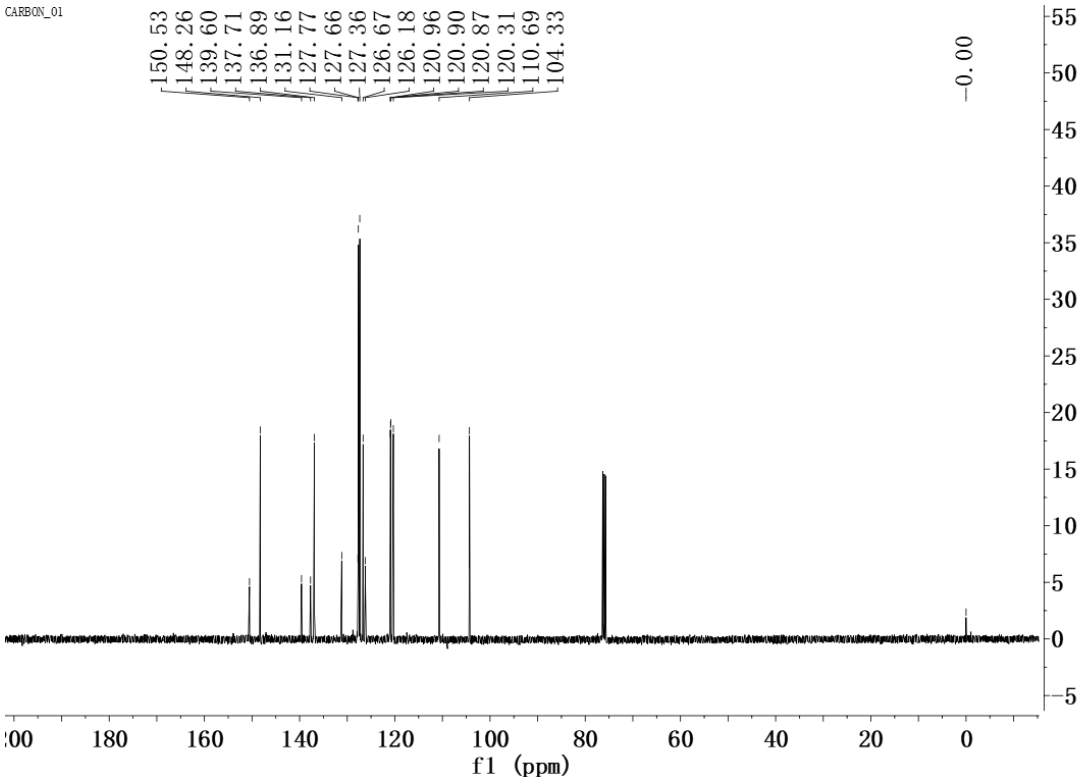
f1 (ppm)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120.96
120.90
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140
120
100
80
60
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20
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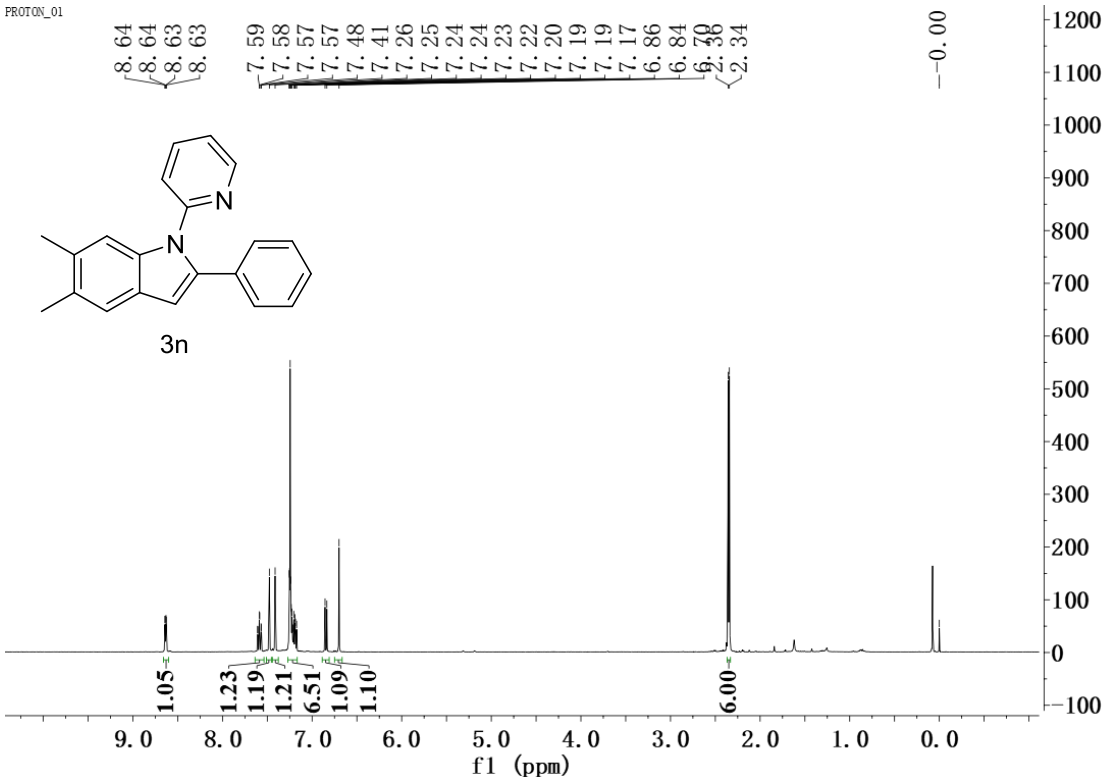
f1 (ppm)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7.25
7.24
7.24
7.23
7.22
7.20
7.19
7.19
7.17
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6.84
2.34
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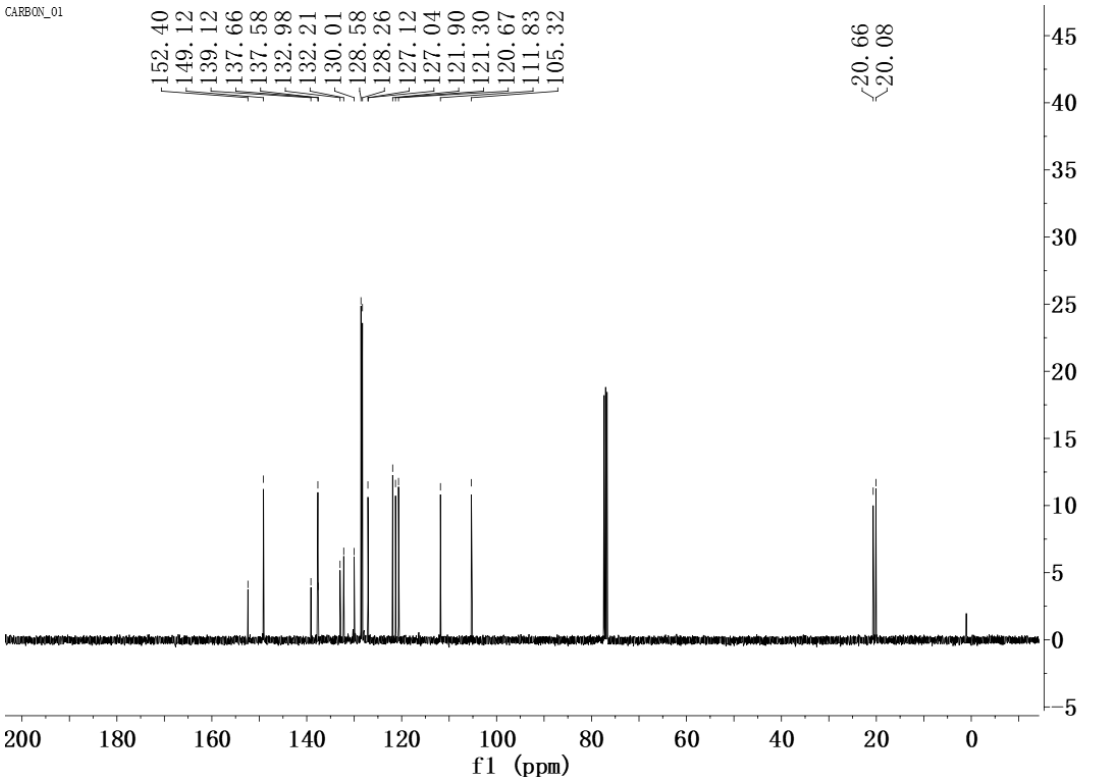
6.00
f1 (ppm)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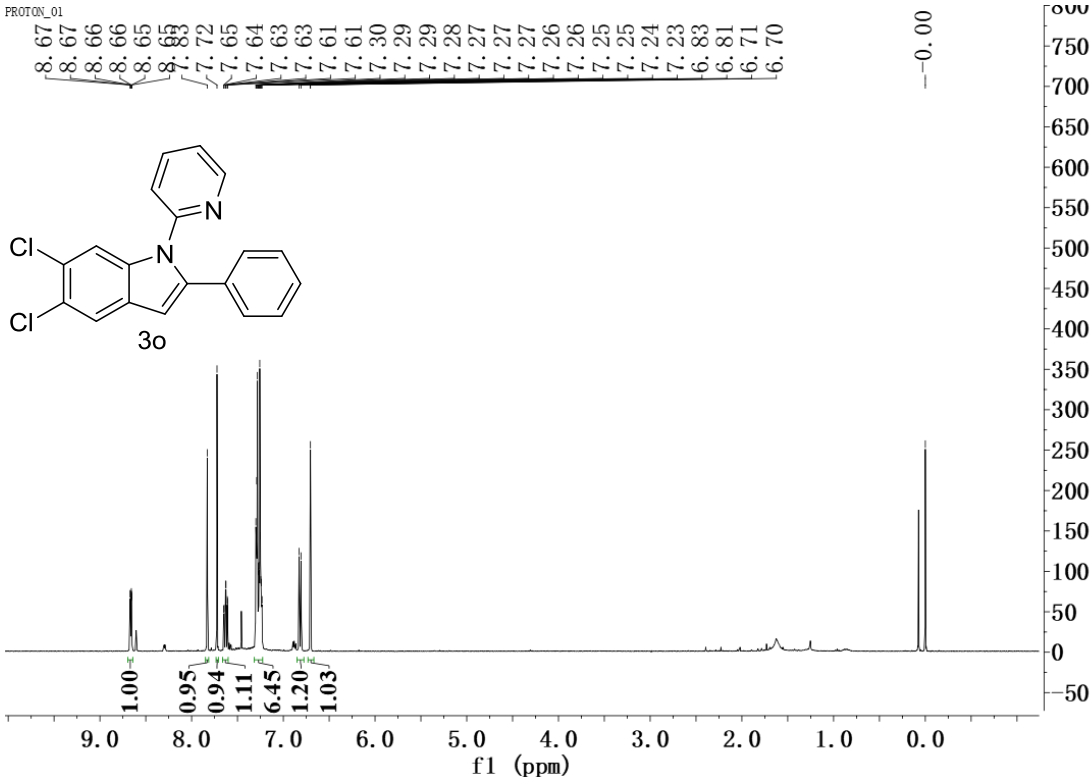
20.08
f1 (ppm)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7.64
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7.63
7.61
7.61
7.30
7.29
7.29
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.23
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6.81
6.71
6.70
0.00
Cl
Cl
N
N
3o
1.00
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0.94
1.11
6.45
1.20
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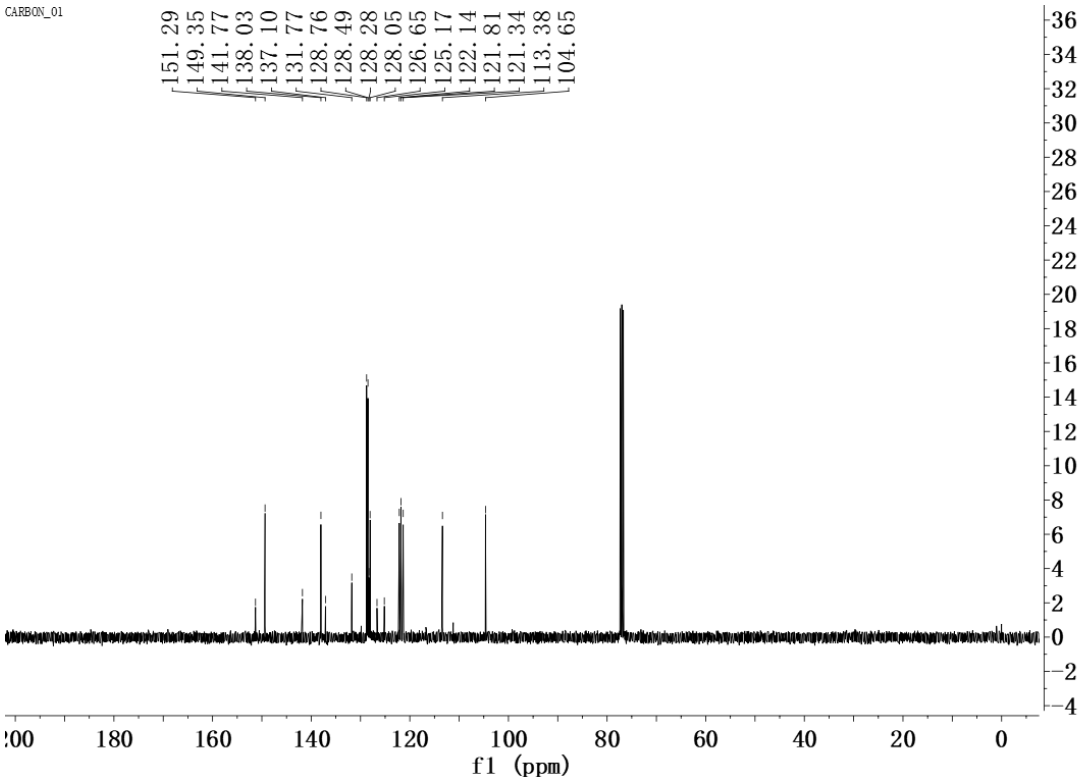
f1 (ppm)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125.17
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140
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100
80
60
40
20
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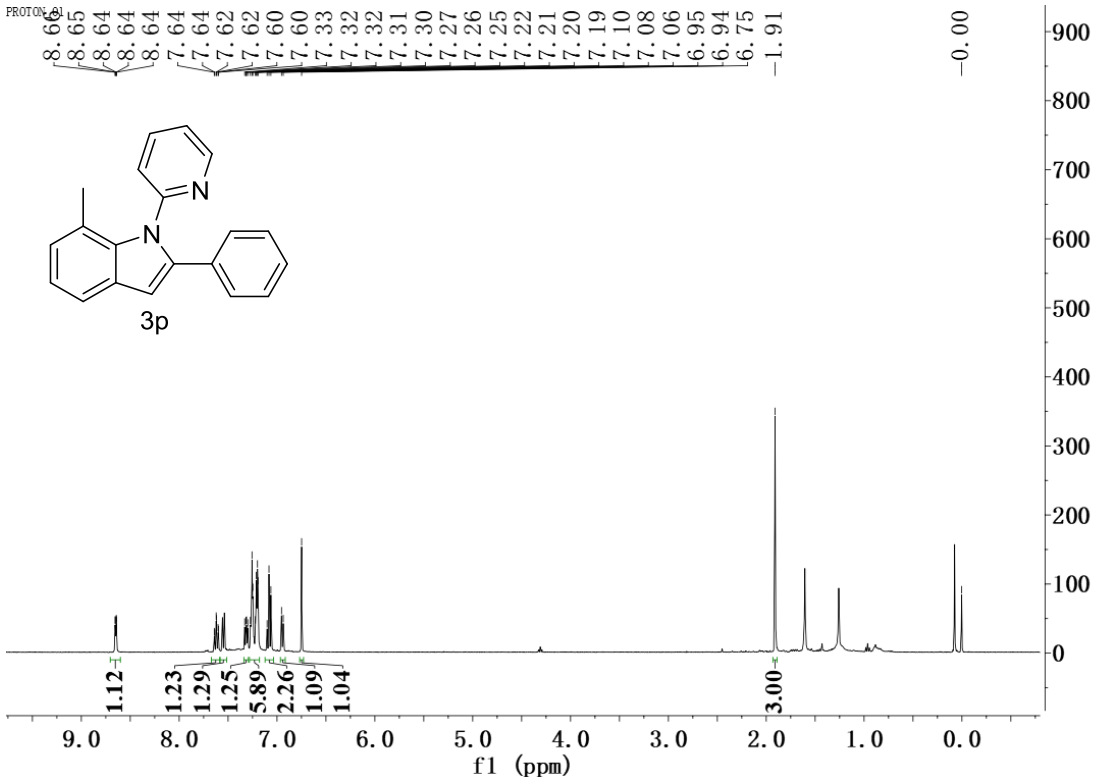
f1 (ppm)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7.60
7.60
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7.32
7.31
7.30
7.27
7.26
7.25
7.22
7.21
7.20
7.19
7.10
7.08
7.06
6.95
6.94
6.75
1.91
0.00
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1.23
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1.25
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1.09
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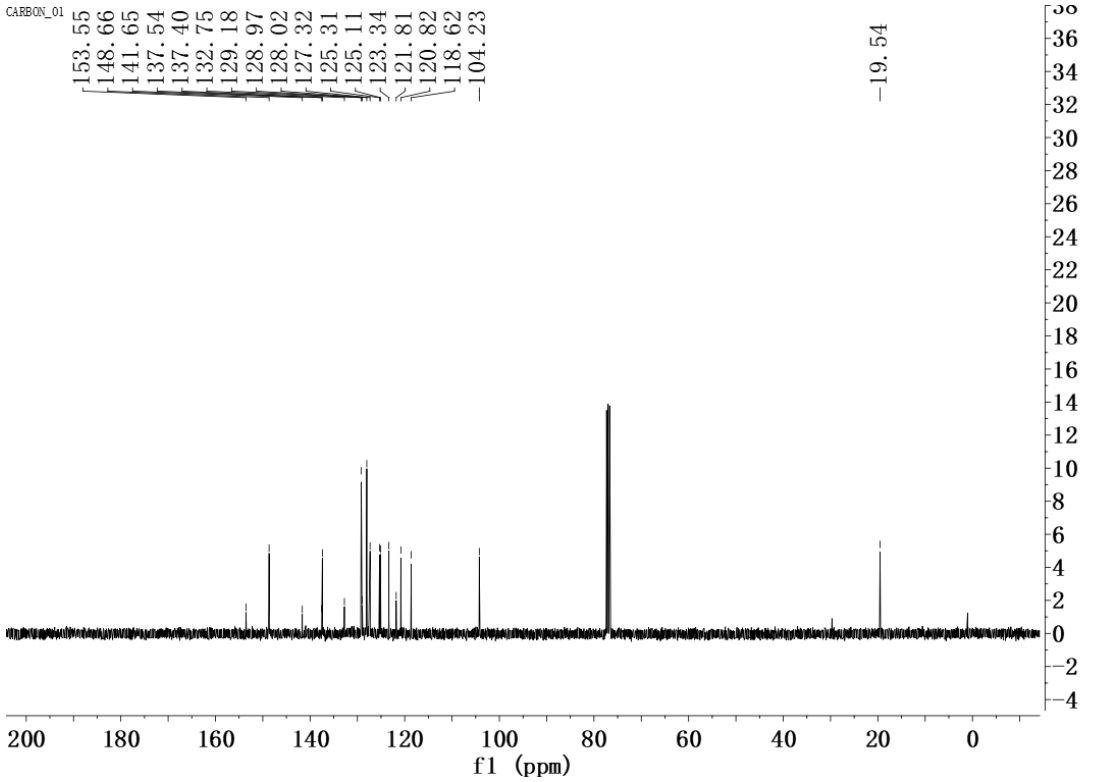
3.00
f1 (ppm)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123.34
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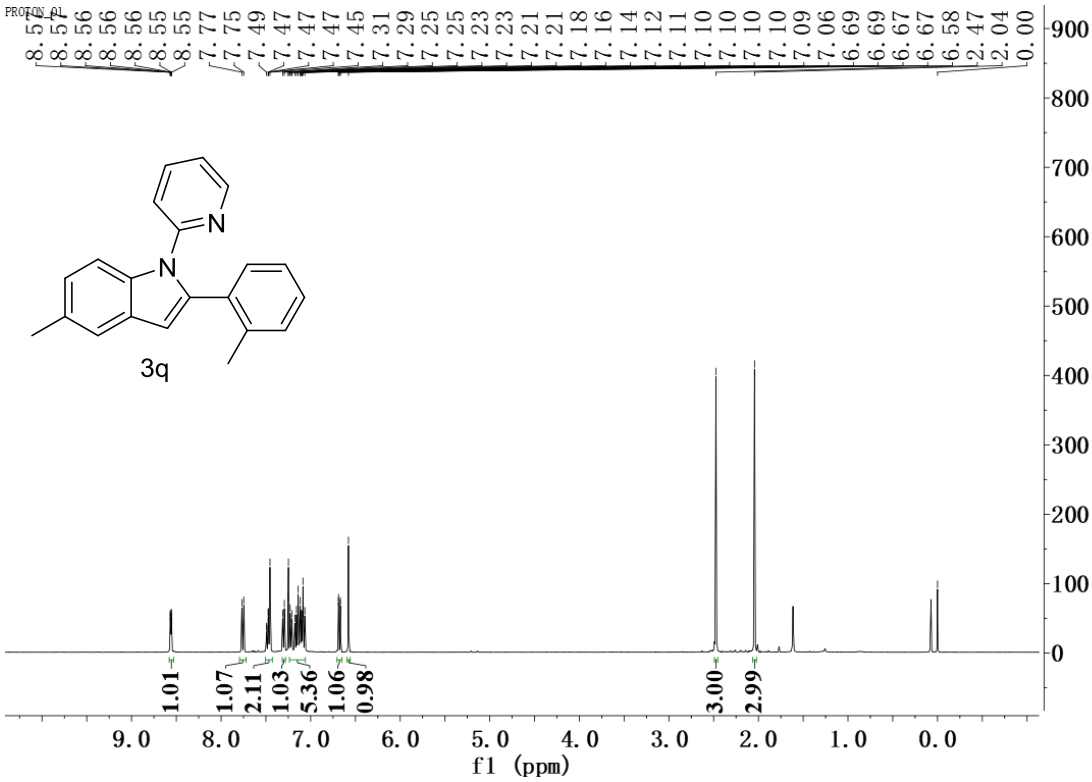
19.54
f1 (ppm)


PROTON_01
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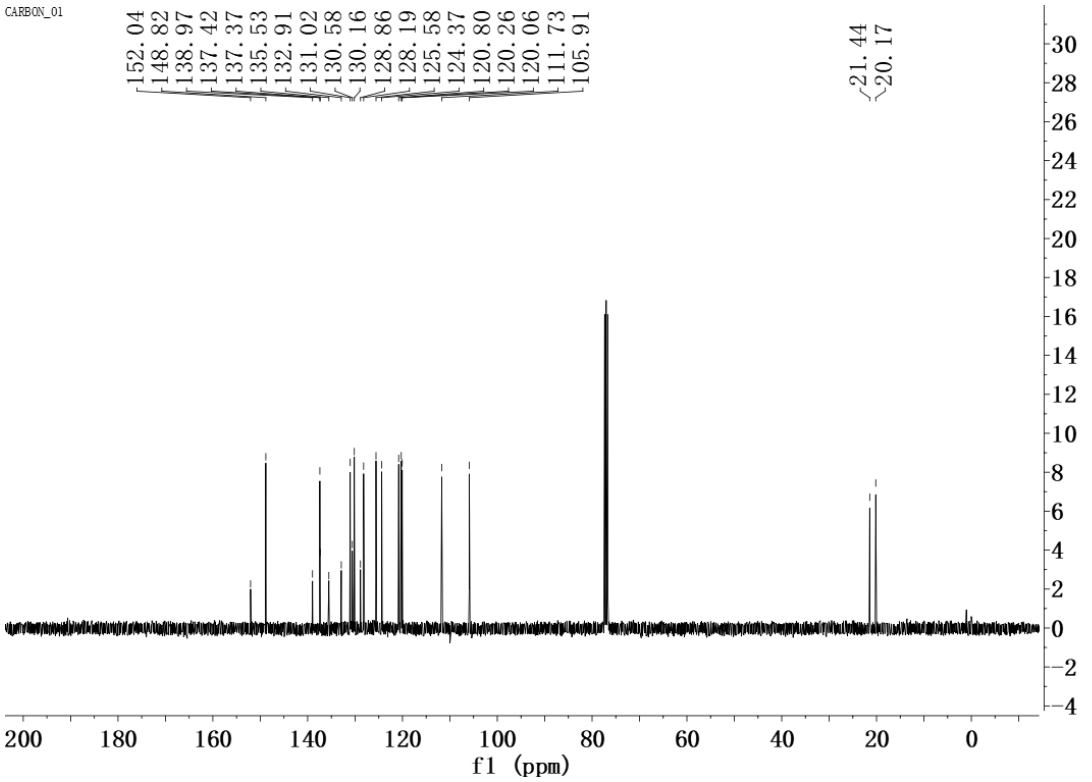
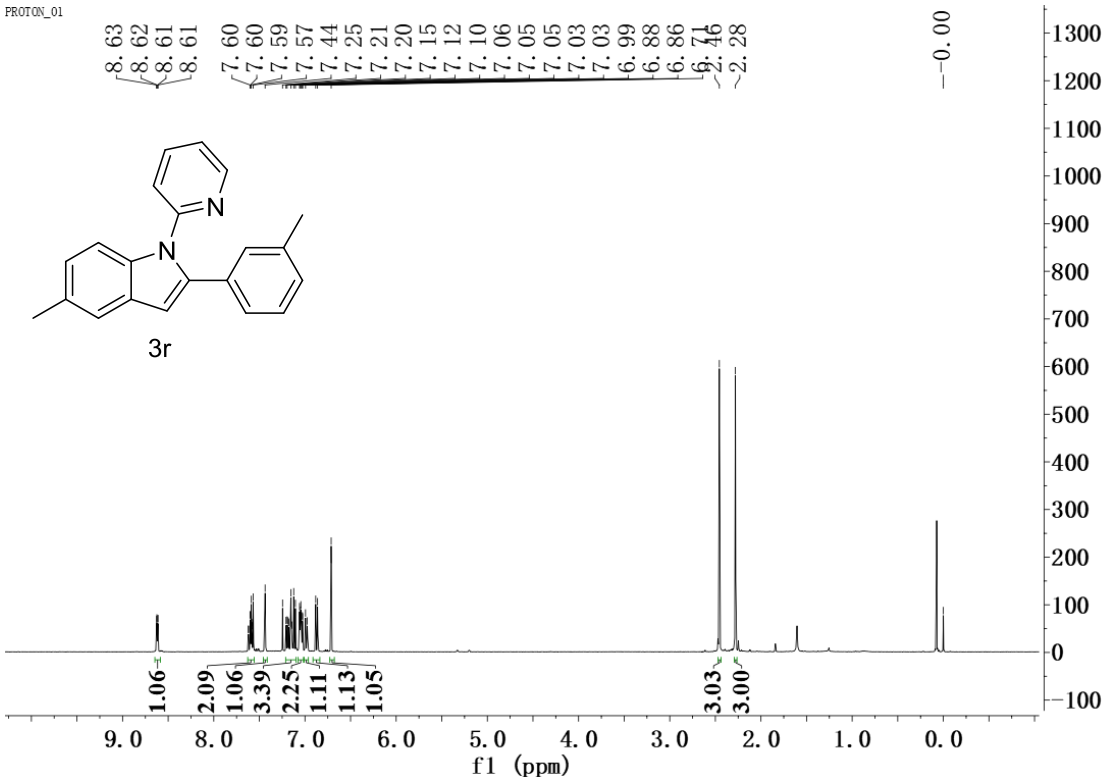
1.07
2.11
1.03
5.36
1.06
0.98
3.00
2.99
f1 (ppm)


CARBON_01
152.04 148.82 138.97 137.42 137.37 135.53 132.91 131.02 130.58 130.16 128.86 128.19 125.58 124.37 120.80 120.26 120.06 111.73 105.91
21.44 20.17
f1 (ppm)


PROTON_01
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7.25
7.21
7.20
7.15
7.12
7.10
7.06
7.05
7.05
7.03
7.03
6.99
6.88
6.86
6.71
2.46
2.28
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N
N
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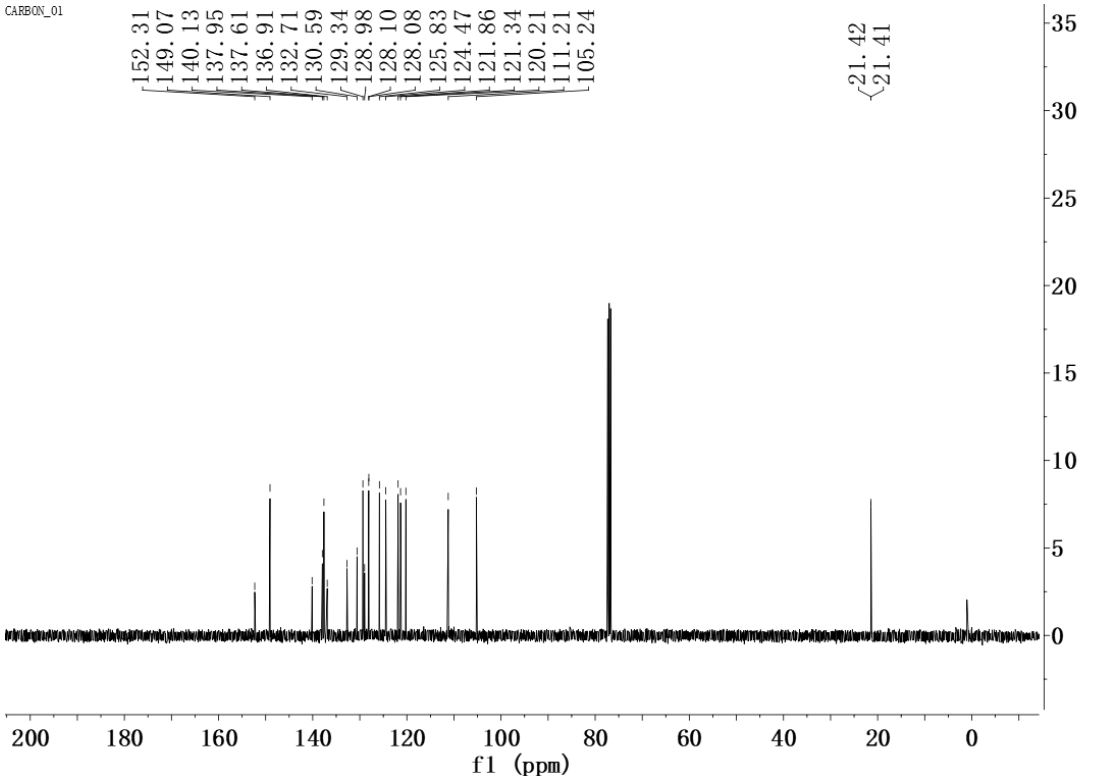
1.06
3.39
2.25
1.11
1.13
1.05
3.03
3.00
f1 (ppm)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129.34
128.98
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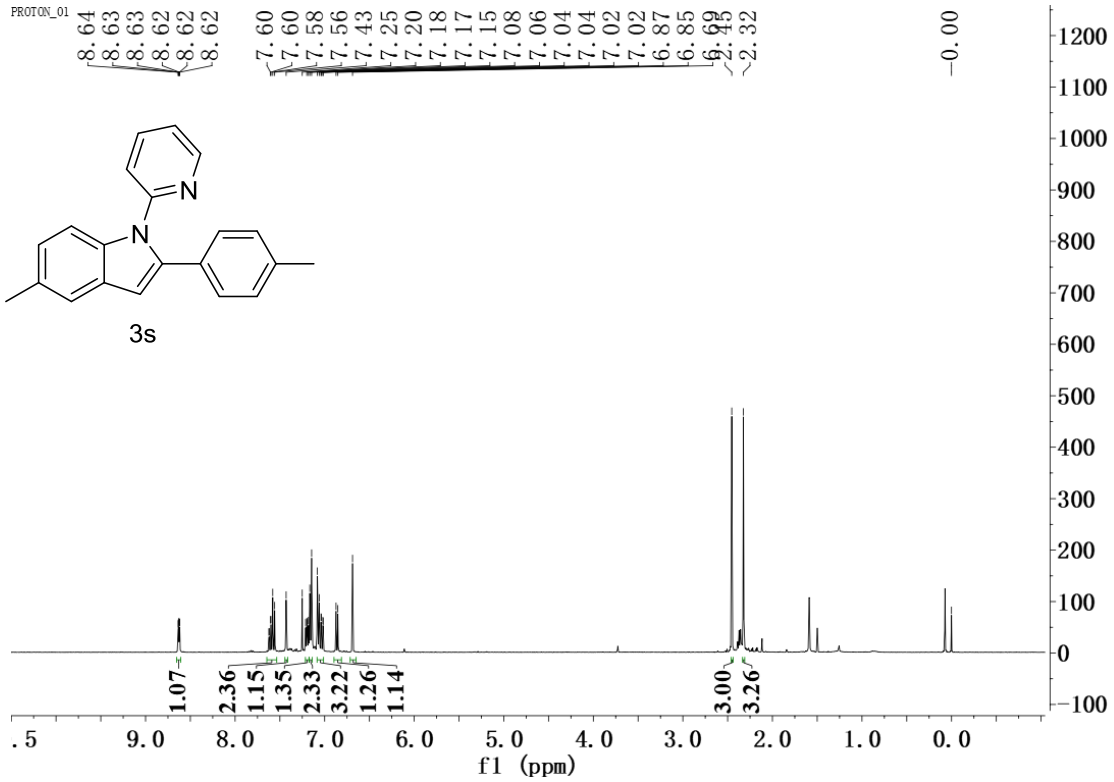
111.21
105.24
21.42
21.41
f1 (ppm)


PROTON_01
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7.20
7.18
7.17
7.15
7.08
7.06
7.04
7.04
7.02
7.02
6.87
6.85
2.32
0.00
N
N
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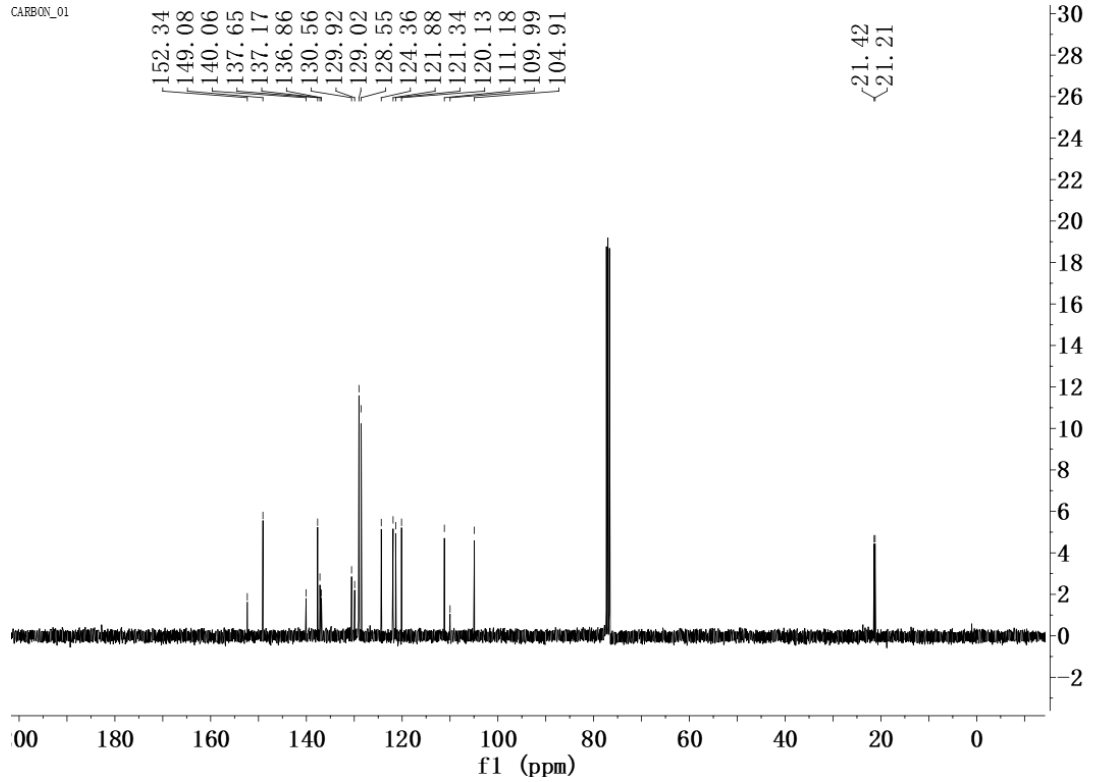
1.15
1.35
2.33
3.22
1.26
1.14
3.00
3.26
f1 (ppm)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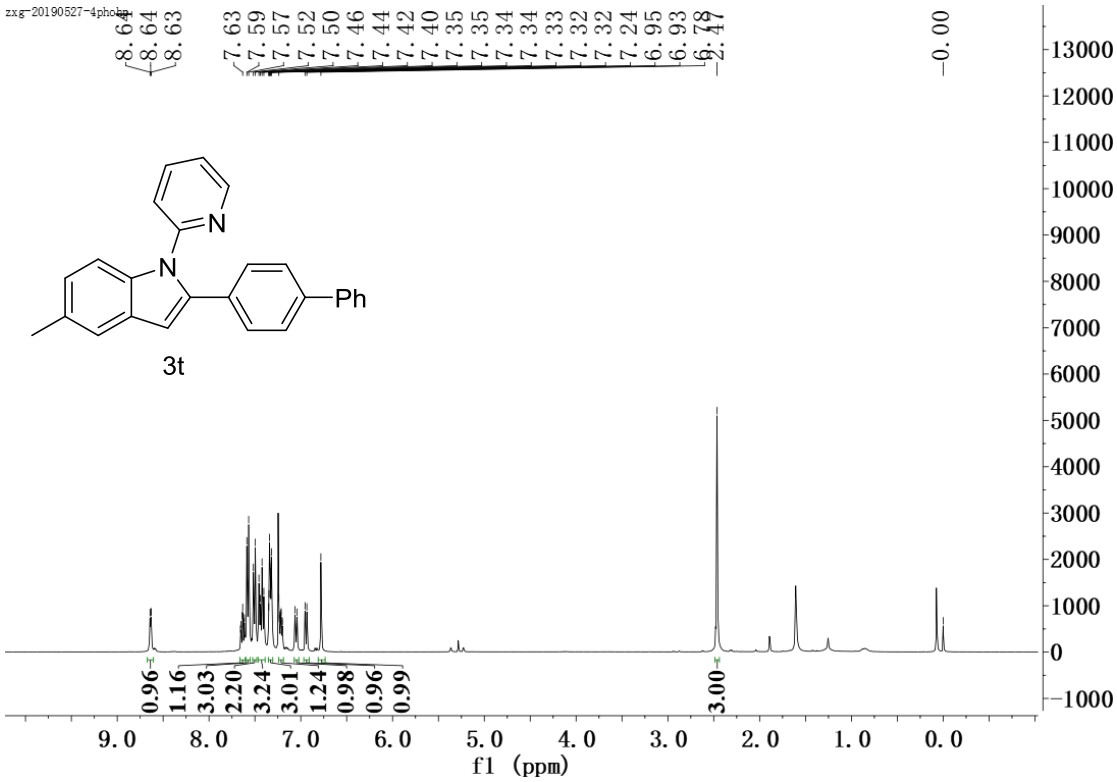
104.91
21.42
21.21
f1 (ppm)


zxg-20190527-4phobp
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7.50
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7.44
7.42
7.40
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.24
6.95
6.93
6.78
6.77
2.47
-0.00
N
N
Ph
3t
0.96
1.16
3.03
2.20
3.24
3.01
1.24
0.98
0.96
0.99
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7.0
6.0
5.0
4.0
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2.0
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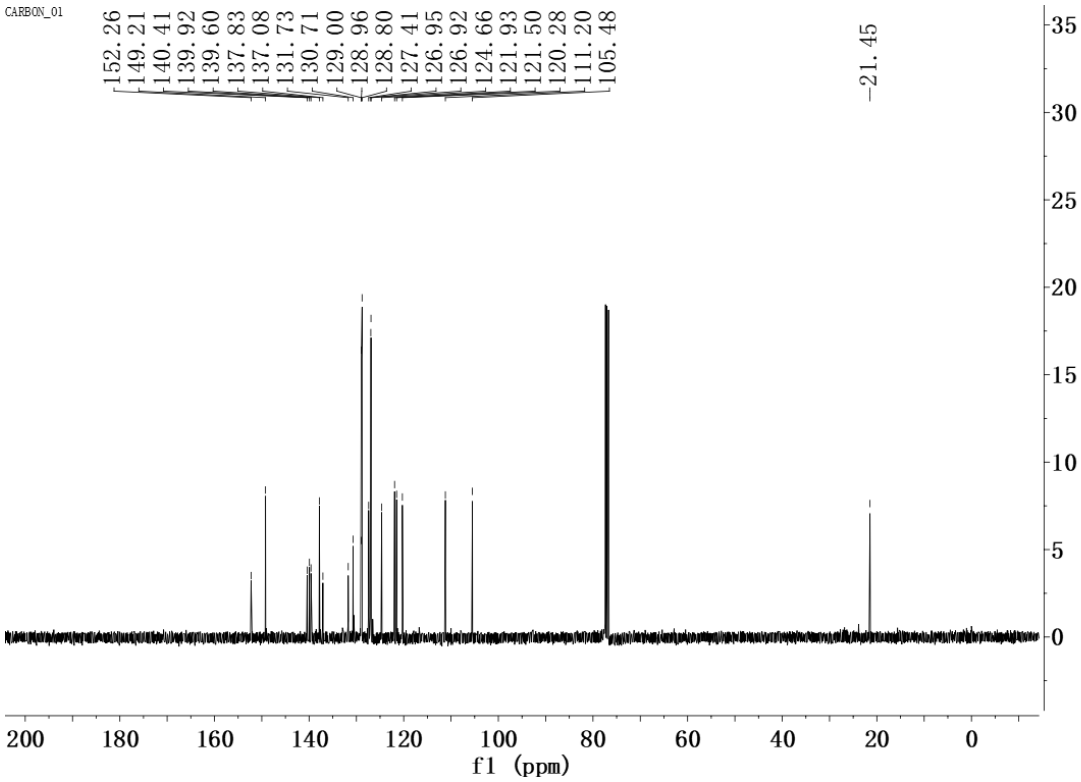
f1 (ppm)


CARBON_01
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137.08
131.73
130.71
129.00
128.96
128.80
127.41
126.95
126.92
124.66
121.93
121.50
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140
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100
80
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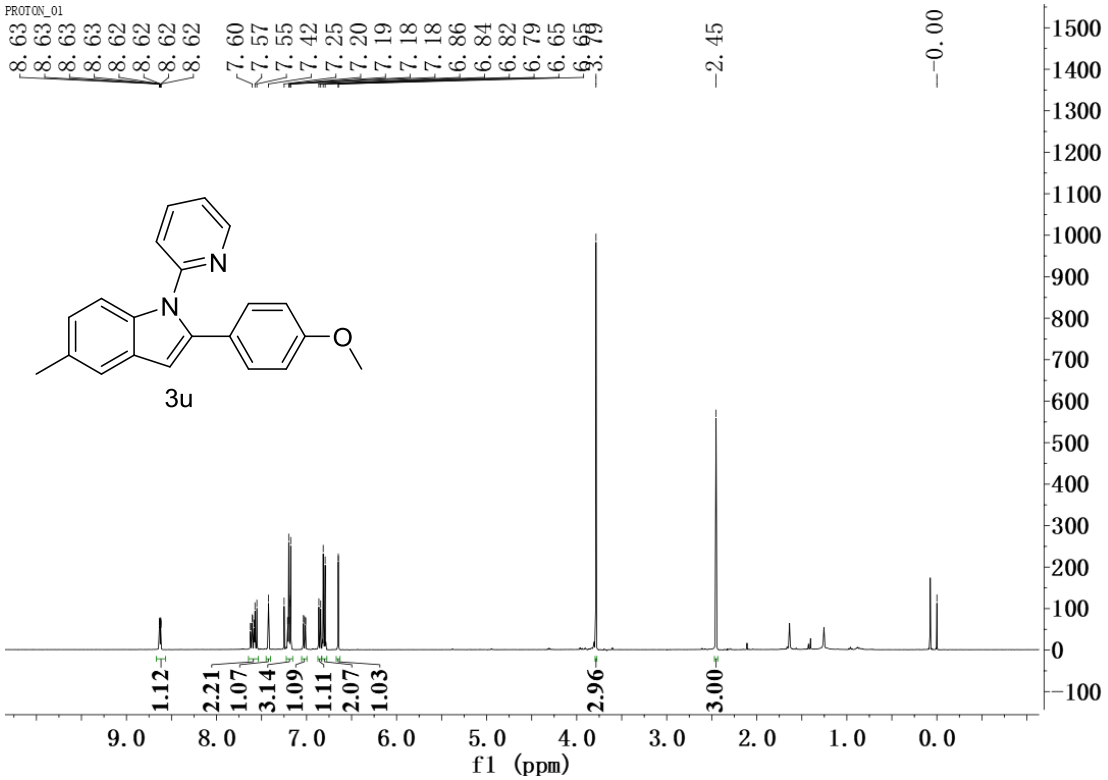
40
20
0
f1 (ppm)


PROTON_01
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7.42
7.25
7.20
7.19
7.18
7.18
6.86
6.84
6.82
6.79
6.65
6.65
3.79
2.45
-0.00
N
N
O
3u
1.12
2.21
1.07
3.14
1.09
1.11
2.07
1.03
2.96
3.00
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6.0
5.0
4.0
3.0
2.0
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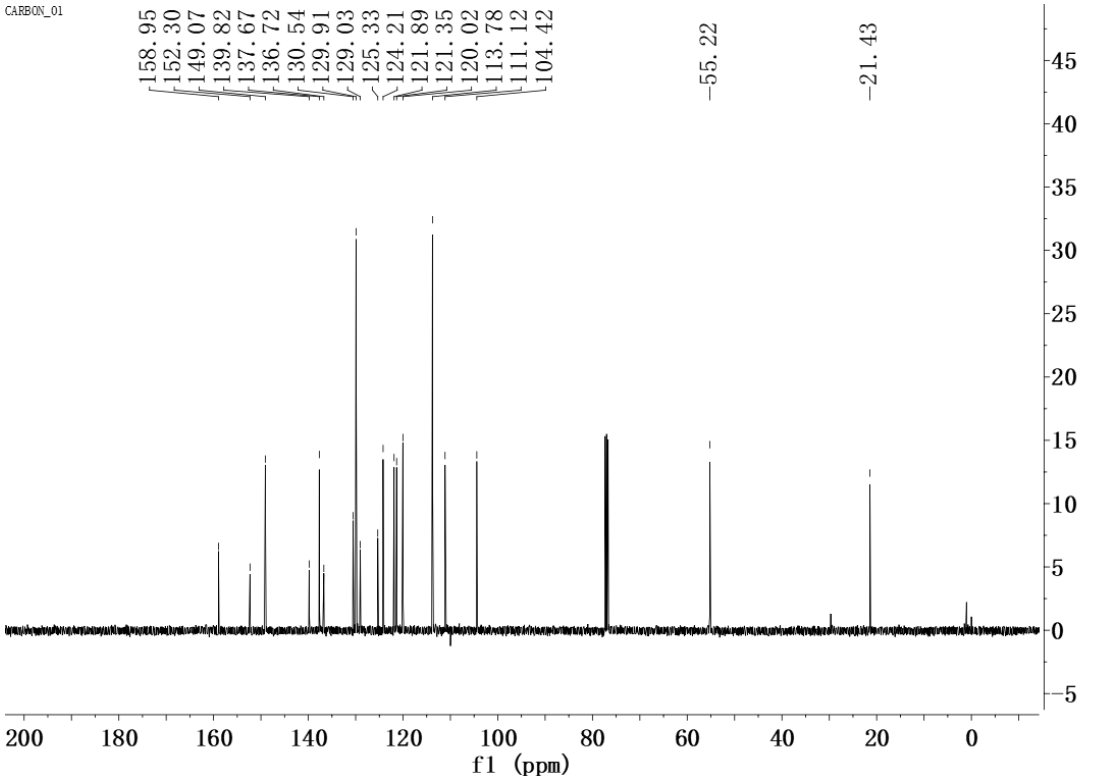
0.0
f1 (ppm)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121.35
120.02
113.78
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21.43
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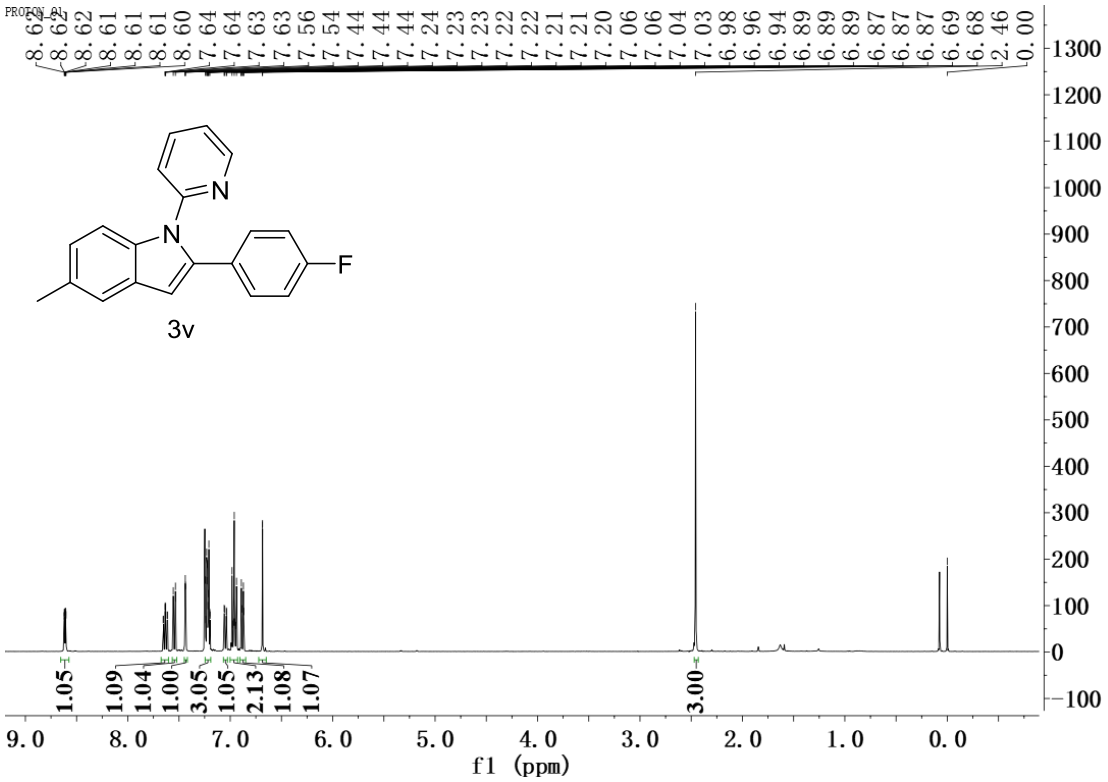
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


PROTON_01
8.62 8.62 8.62 8.61 8.61 8.61 8.60 7.64 7.64 7.63 7.63 7.56 7.54 7.44 7.44 7.44 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.06 7.06 7.04 7.03 6.98 6.96 6.94 6.89 6.89 6.89 6.87 6.87 6.87 6.69 6.68 2.46 0.00
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N
F
3v
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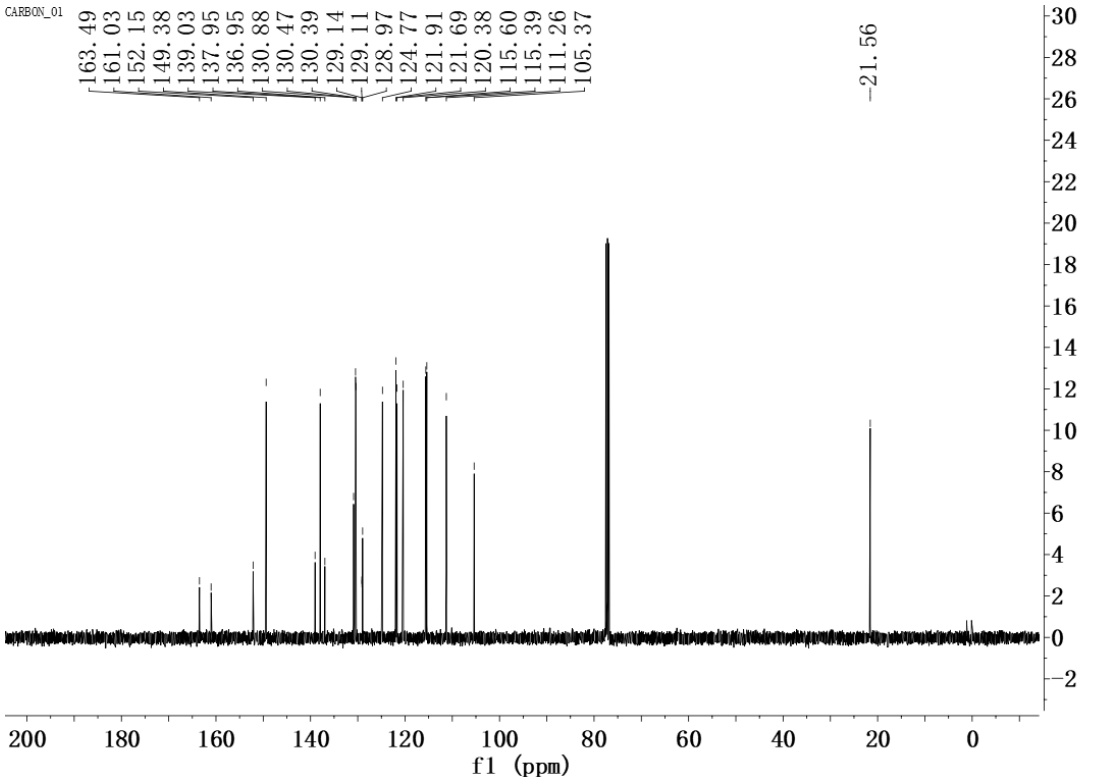
f1 (ppm)


CARBON_01
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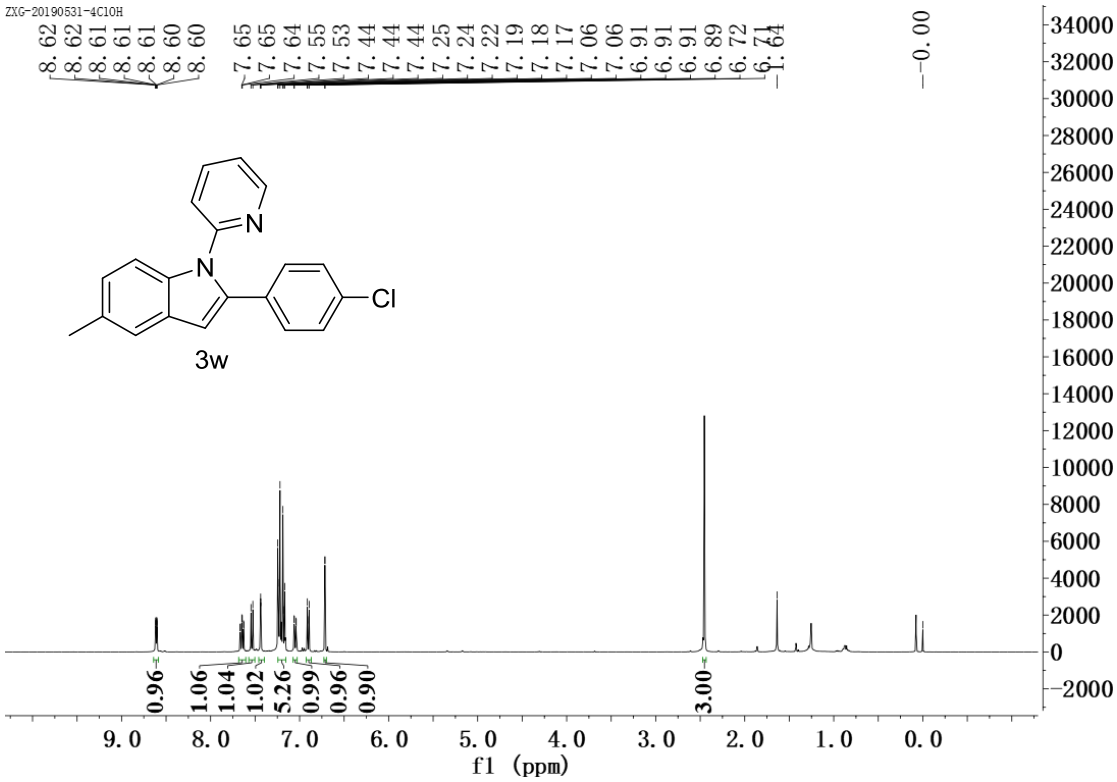
21.56
f1 (ppm)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7.55
7.53
7.44
7.44
7.44
7.25
7.24
7.22
7.19
7.18
7.17
7.06
7.06
6.91
6.91
6.89
6.72
6.71
1.64
-0.00
N
N
Cl
3w
0.96
1.06
1.04
1.02
5.26
0.99
0.96
0.90
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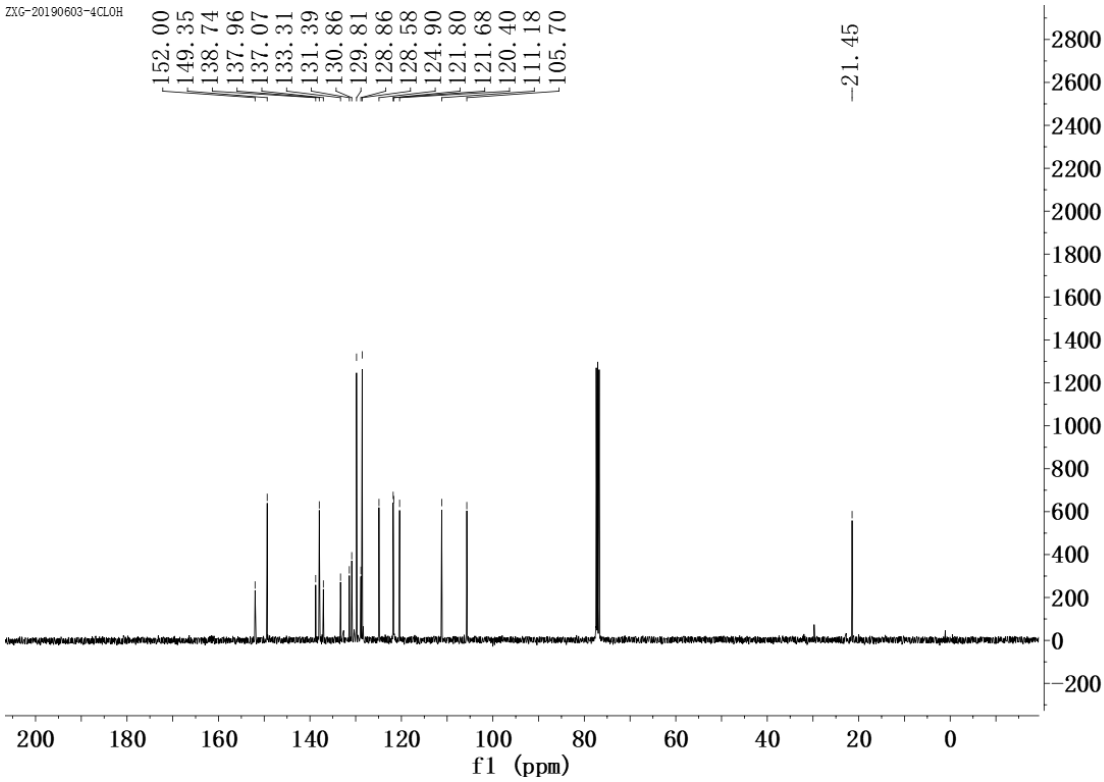
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


ZXG-20190603-4ClOH
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121.80
121.68
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-21.45
200
180
160
140
120
100
80
60
40
20
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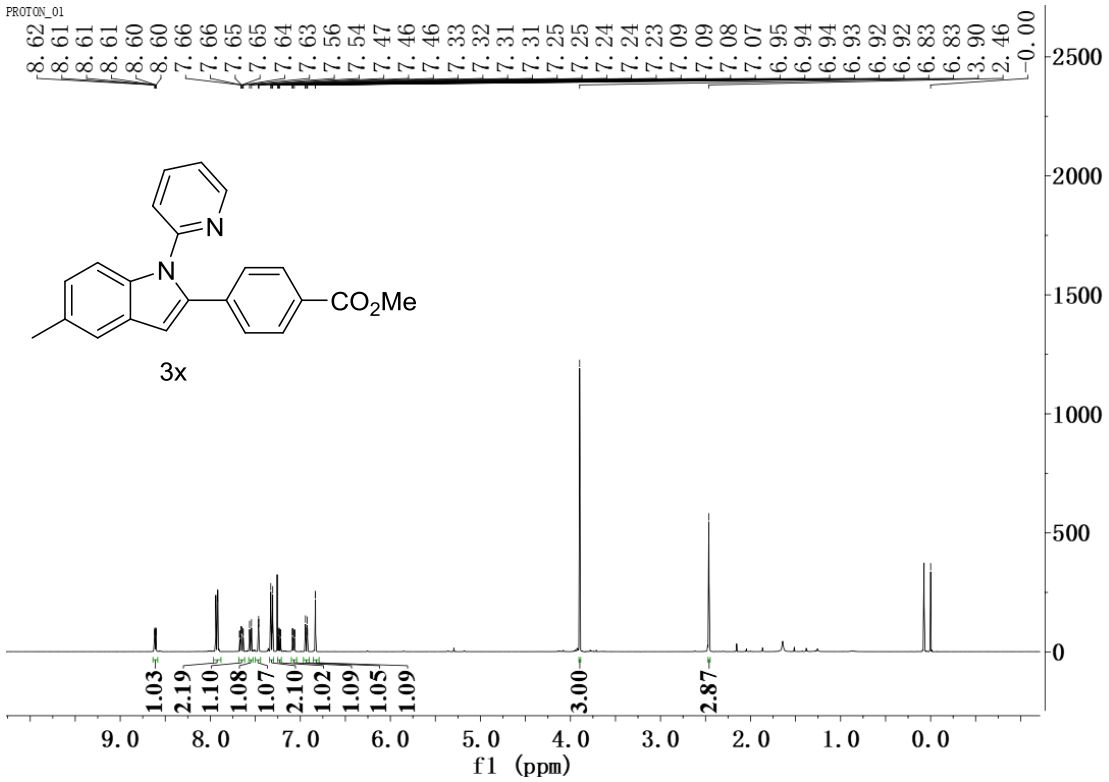
f1 (ppm)


PROTON_01
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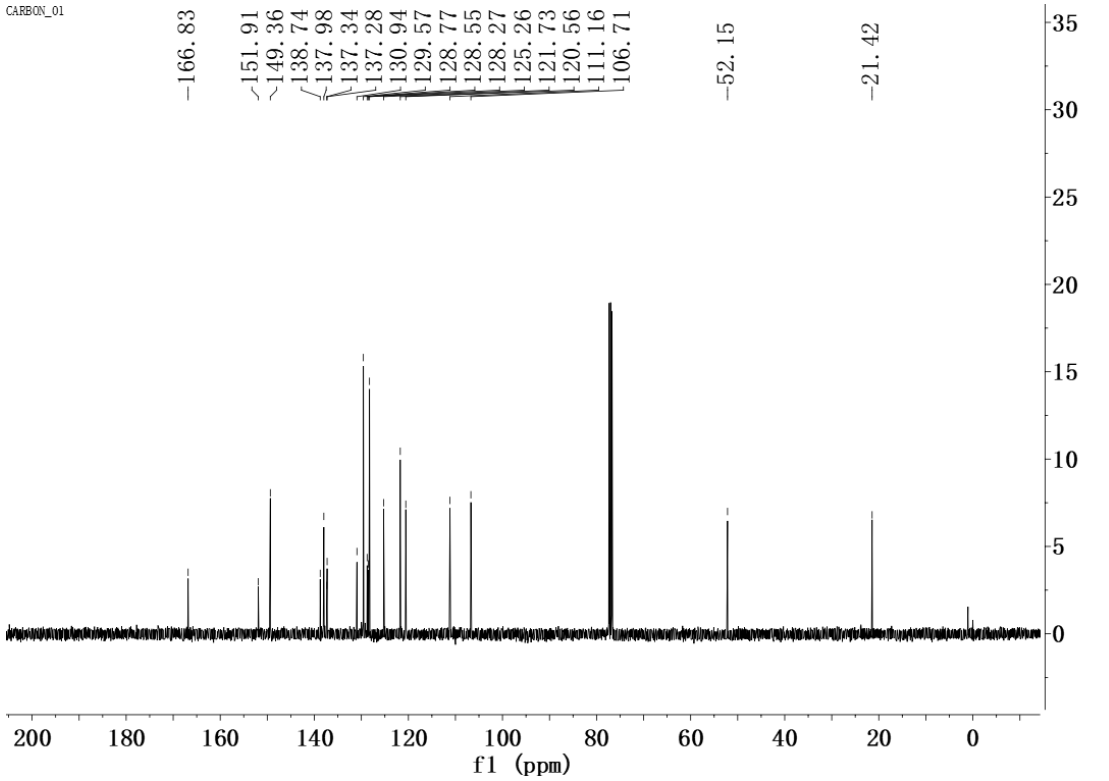
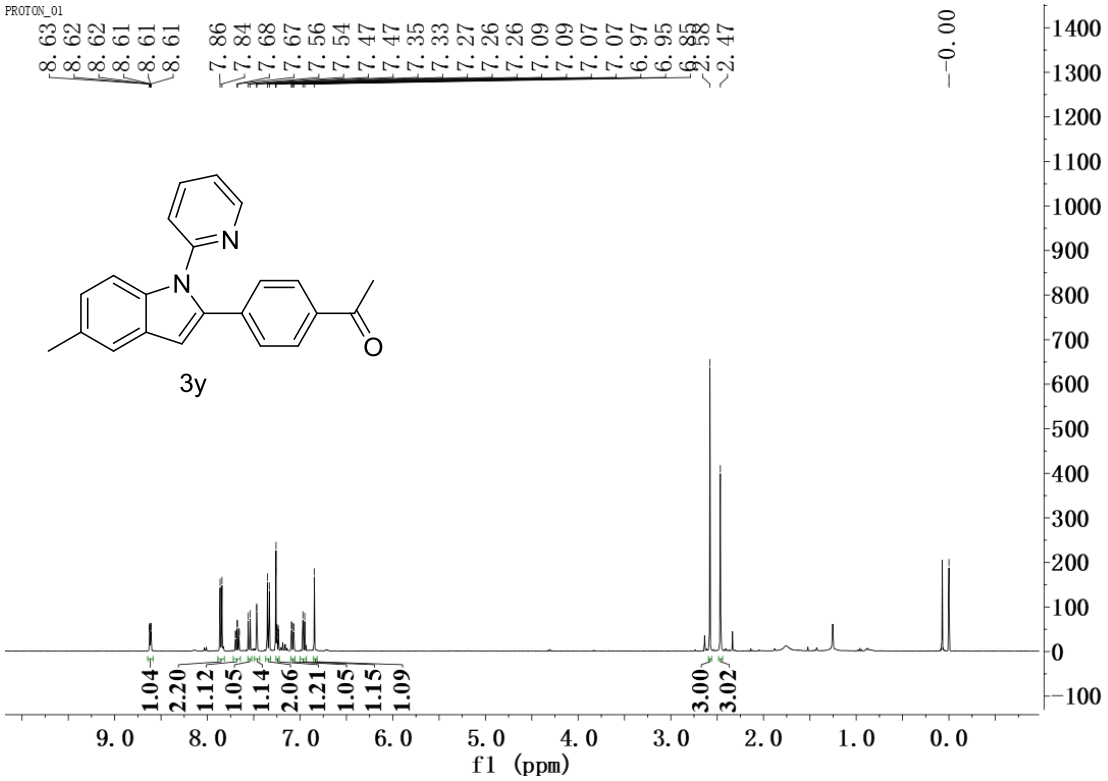
N
CO2Me
3x
1.03 2.19 1.10 1.08 1.07 2.10 1.02 1.09 1.05 1.09 3.00 2.87
f1 (ppm)


CARBON_01
166.83 151.91 149.36 138.74 137.98 137.34 137.28 130.94 129.57 128.77 128.55 128.27 125.26 121.73 120.56 111.16 106.71 52.15 21.42
f1 (ppm)


PROTON_01
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8.62
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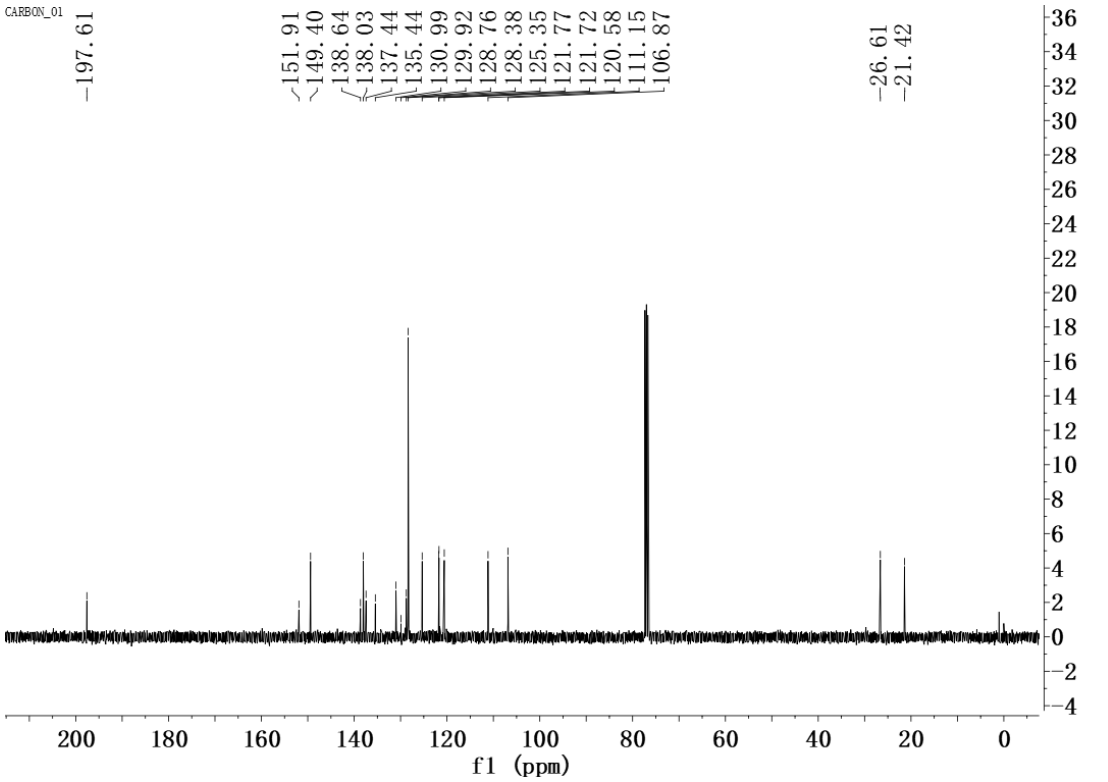
8.61
7.86
7.84
7.68
7.67
7.56
7.54
7.47
7.47
7.35
7.33
7.27
7.26
7.26
7.09
7.09
7.07
7.07
6.97
6.95
6.85
6.58
2.58
2.47
-0.00
N
N
O
3y
1.04
2.20
1.12
1.05
1.14
2.06
1.21
1.05
1.15
1.09
3.00
3.02
f1 (ppm)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135.44
130.99
129.92
128.76
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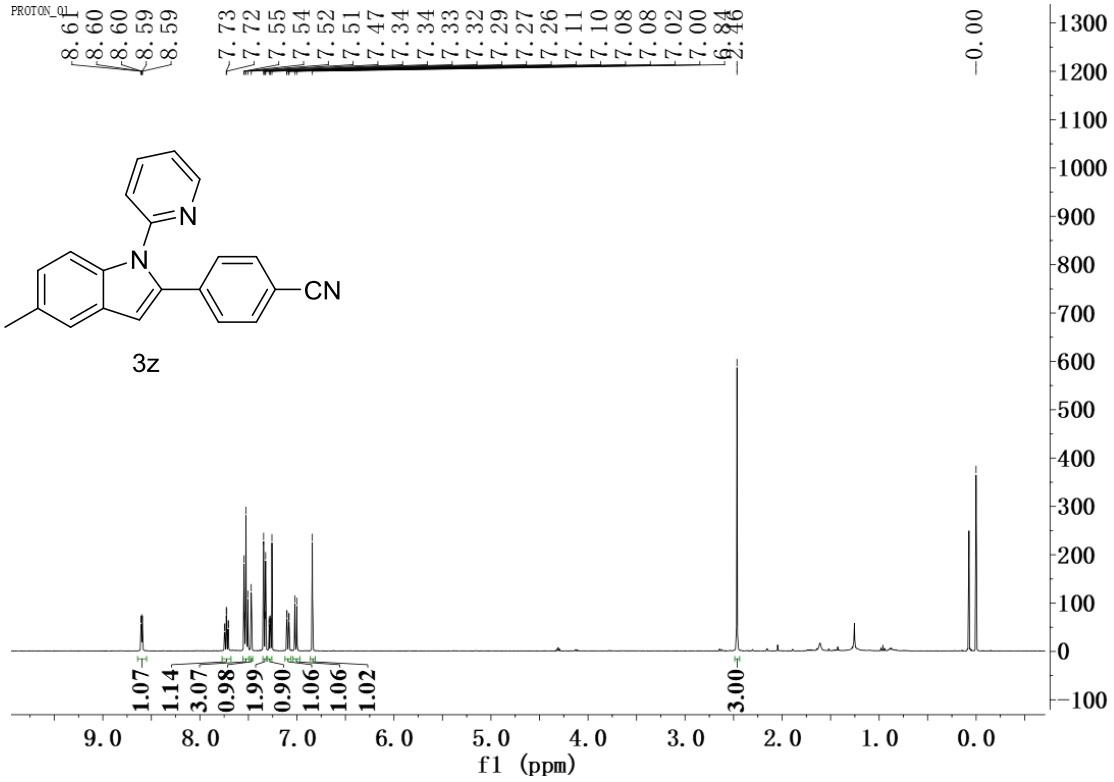
111.15
106.87
26.61
21.42
f1 (ppm)


PROTON_01
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8.60
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8.59
7.73
7.72
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7.54
7.52
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7.33
7.32
7.29
7.27
7.26
7.11
7.10
7.08
7.08
7.02
7.00
6.84
6.46
2.46
-0.00
N
N
CN
3z
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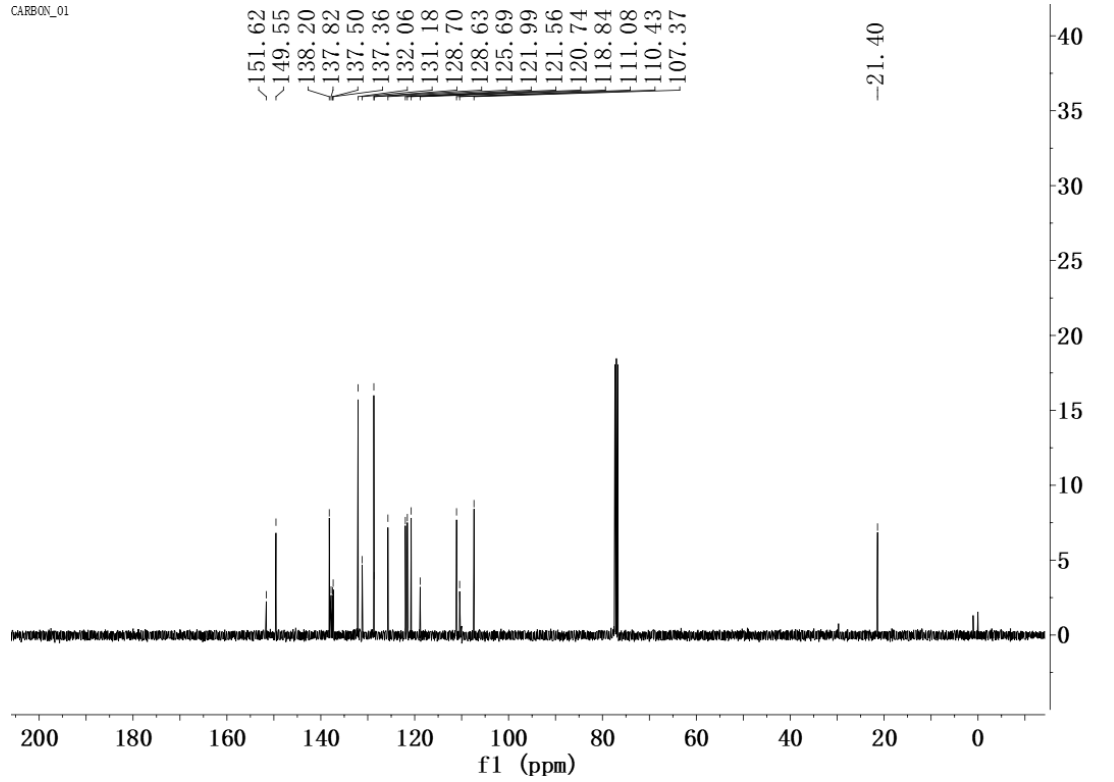
1.14
3.07
0.98
1.99
0.90
1.06
1.06
1.02
3.00
f1 (ppm)


CARBON_01
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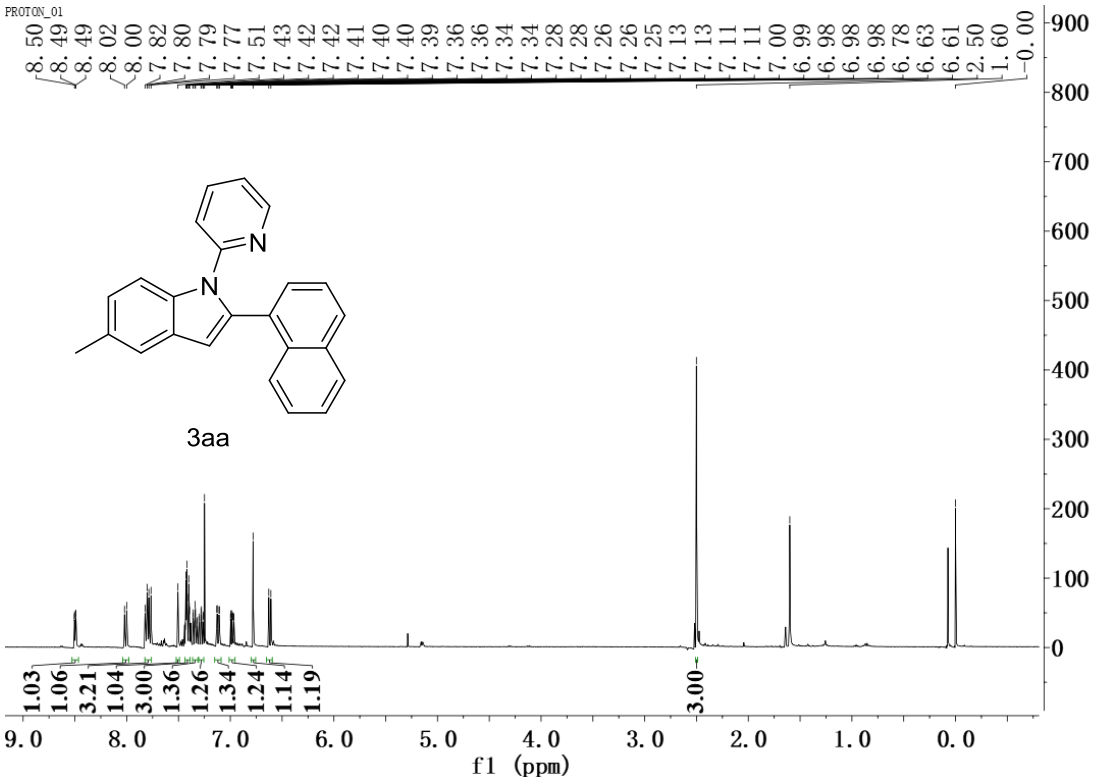
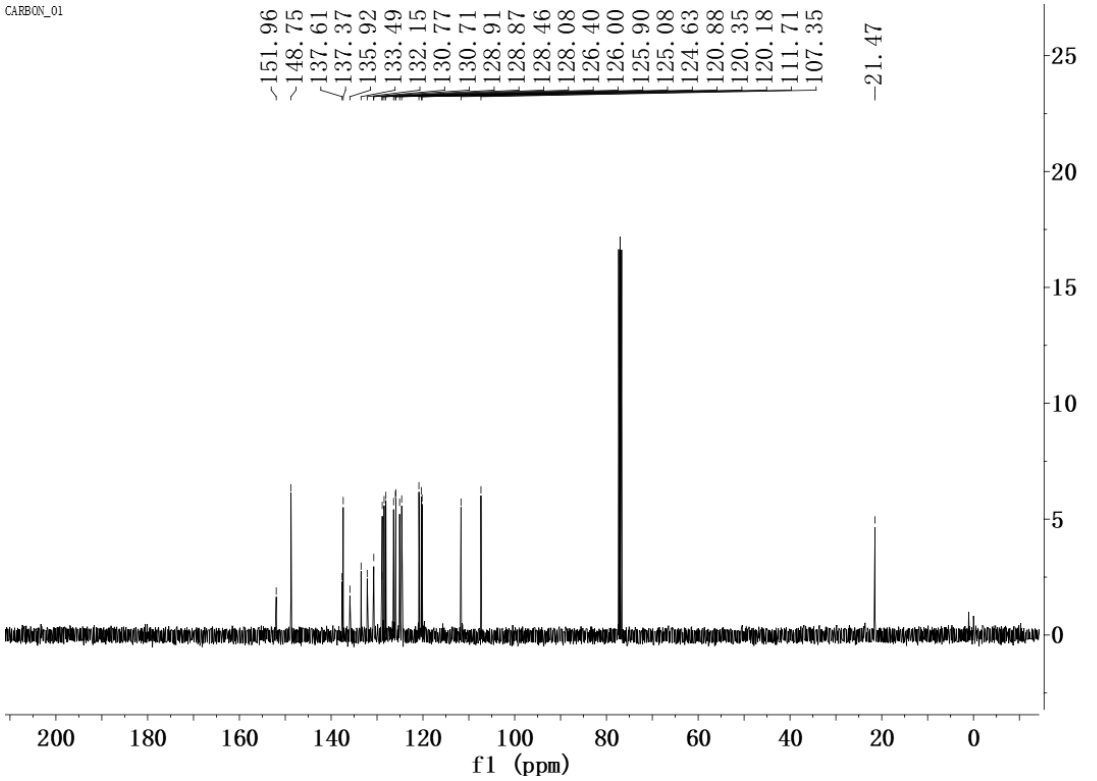
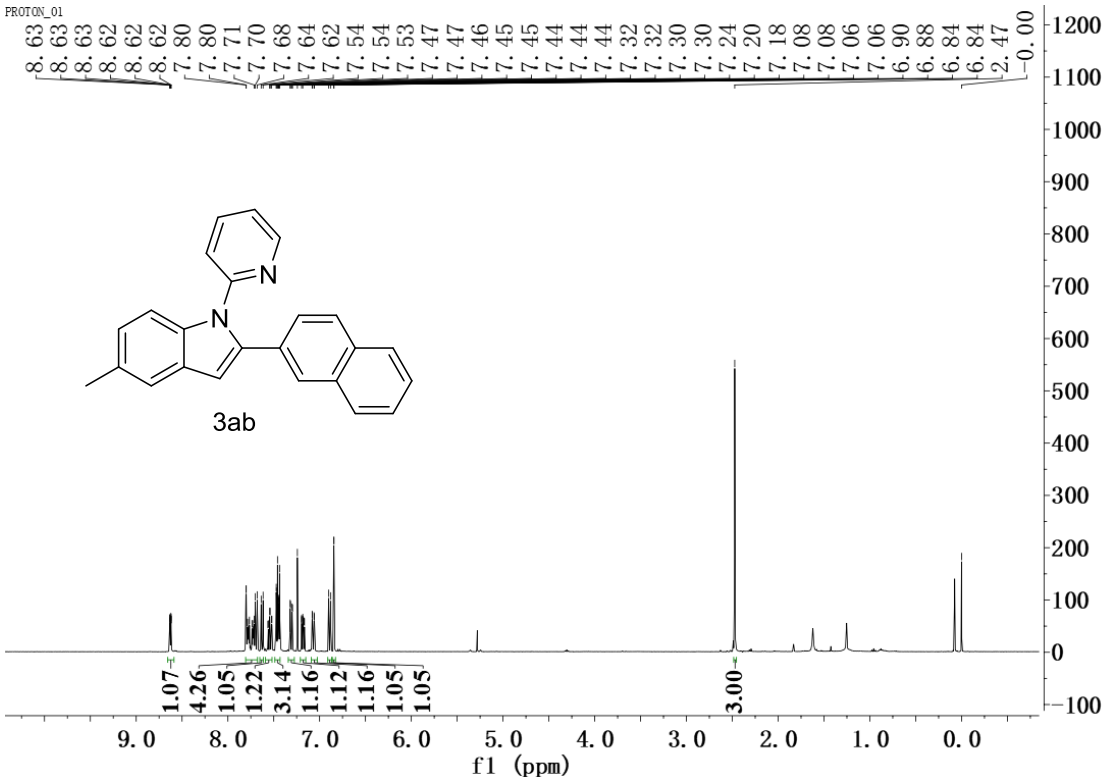
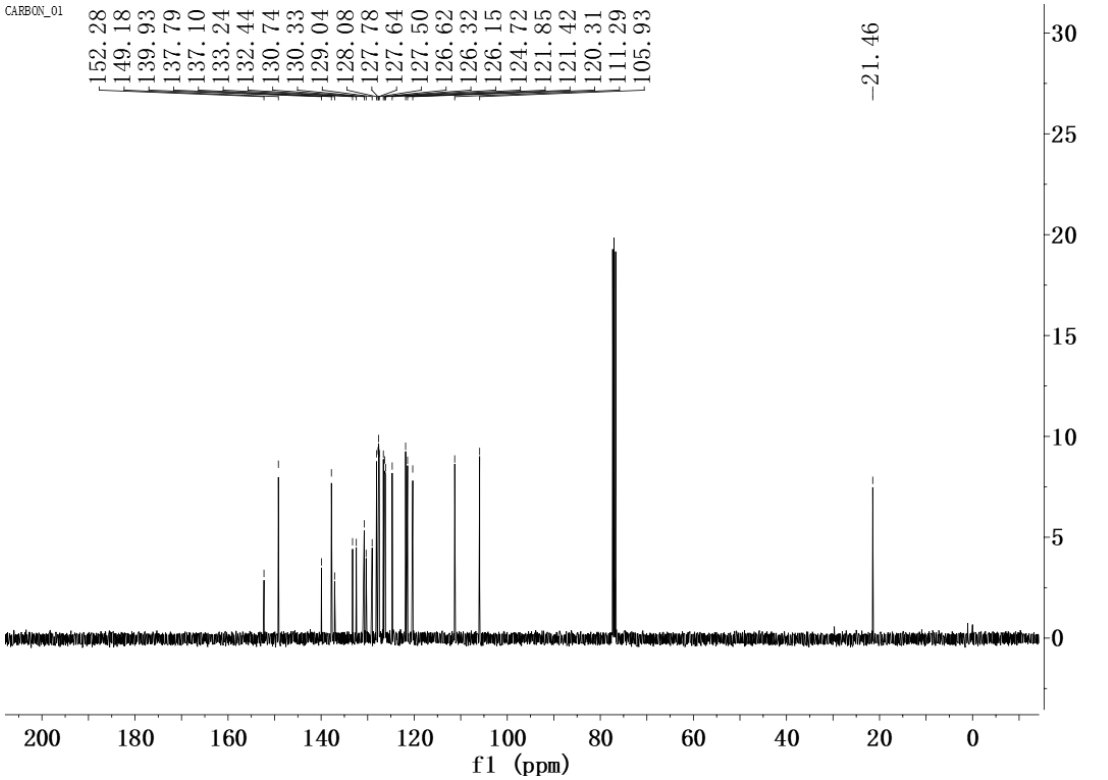
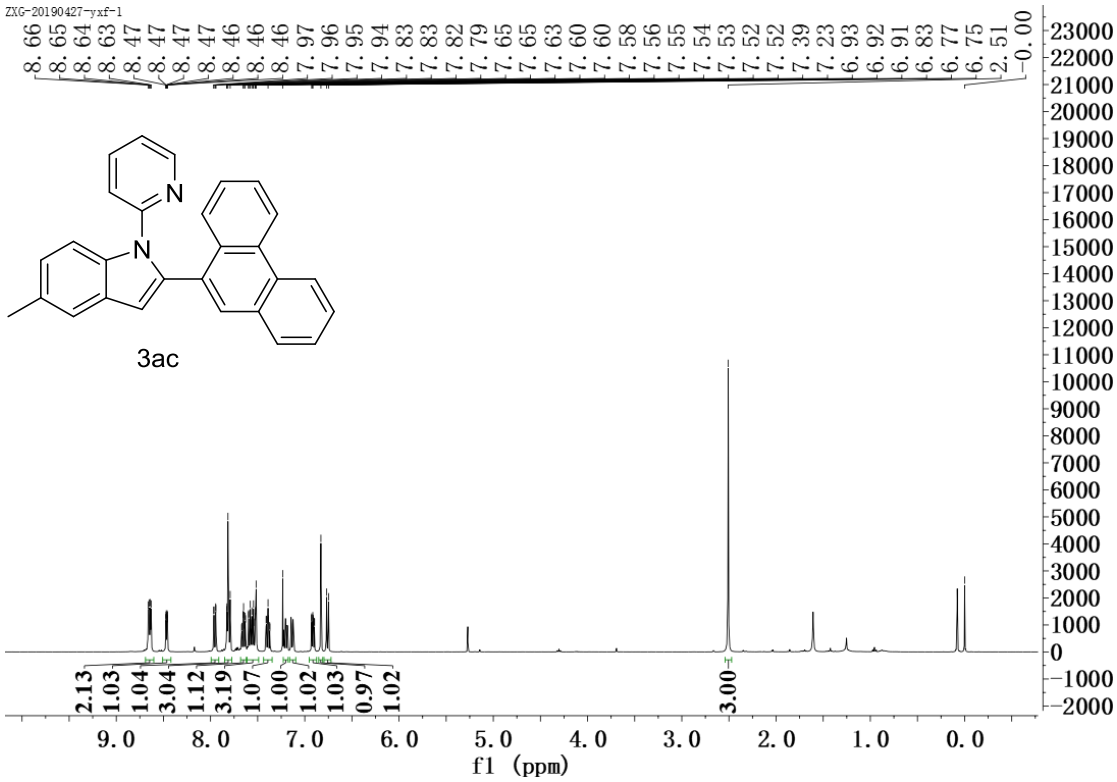
132.06
131.18
128.70
128.63
125.69
121.99
121.56
120.74
118.84
111.08
110.43
107.37
-21.40
f1 (ppm)

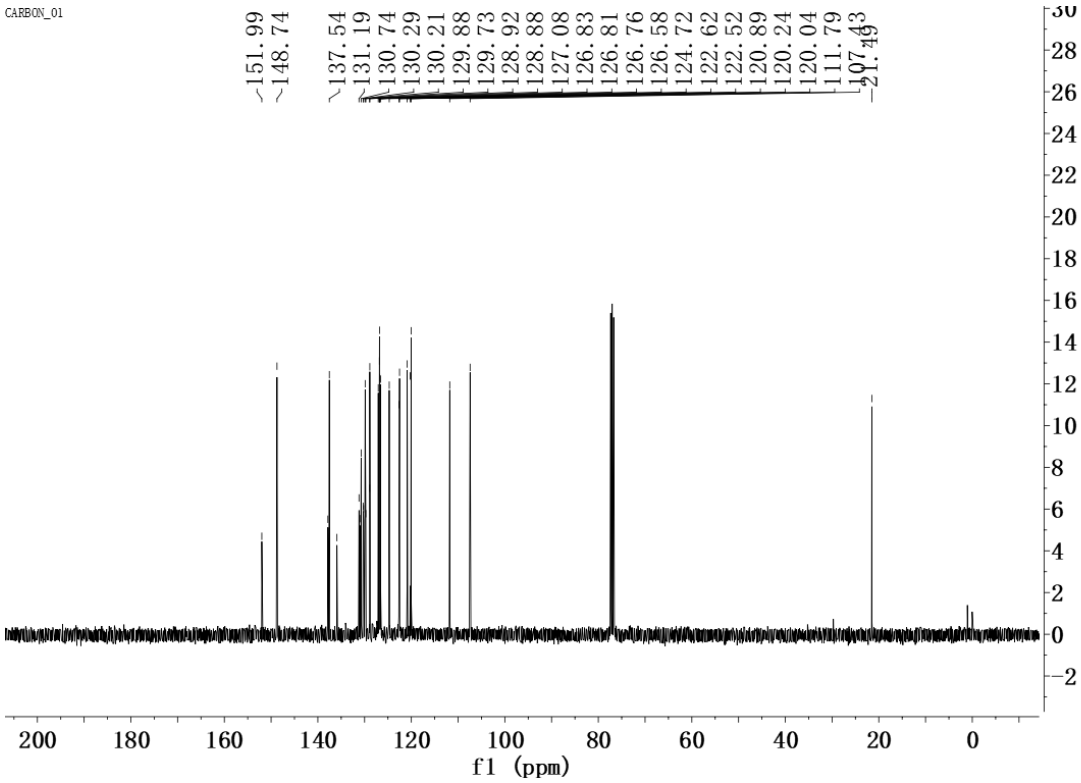

PROTON_01
8.50 8.49 8.49 8.02 8.00 7.82 7.80 7.79 7.77 7.51 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.36 7.36 7.34 7.34 7.28 7.28 7.26 7.26 7.25 7.13 7.13 7.11 7.11 7.00 6.99 6.98 6.98 6.98 6.78 6.63 6.61 2.50 1.60 0.00
N
N
3aa
1.03 1.06 3.21 1.04 3.00 1.36 1.26 1.34 1.24 1.14 1.19
3.00
f1 (ppm)

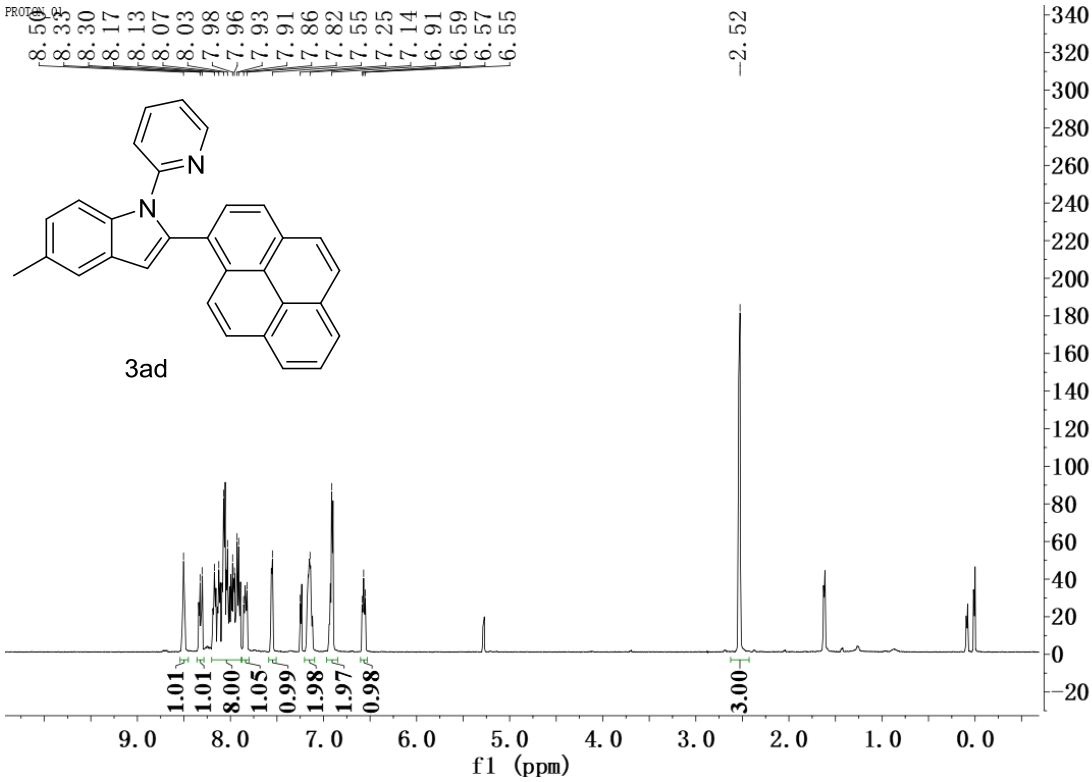

CARBON_01
151.96 148.75 137.61 137.37 135.92 133.49 132.15 130.77 130.71 128.91 128.87 128.46 128.08 126.40 126.00 125.90 125.08 124.63 120.88 120.35 120.18 111.71 107.35
21.47
f1 (ppm)

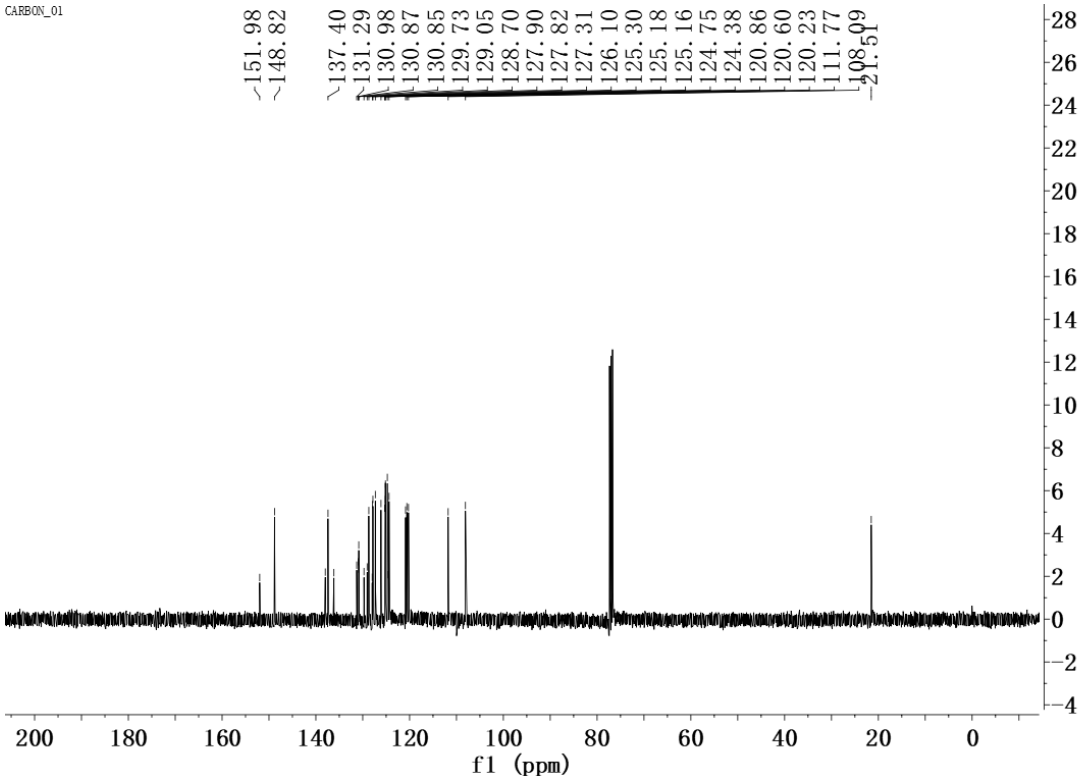

PROTON_01
8.63 8.63 8.63 8.62 8.62 8.62 7.80 7.80 7.71 7.70 7.68 7.64 7.62 7.54 7.54 7.53 7.47 7.47 7.46 7.45 7.45 7.44 7.44 7.44 7.32 7.32 7.30 7.30 7.24 7.20 7.18 7.08 7.08 7.06 7.06 6.90 6.88 6.84 6.84 2.47 -0.00
N
N
3ab
1.07 4.26 1.05 1.22 3.14 1.16 1.12 1.16 1.05 1.05
3.00
f1 (ppm)

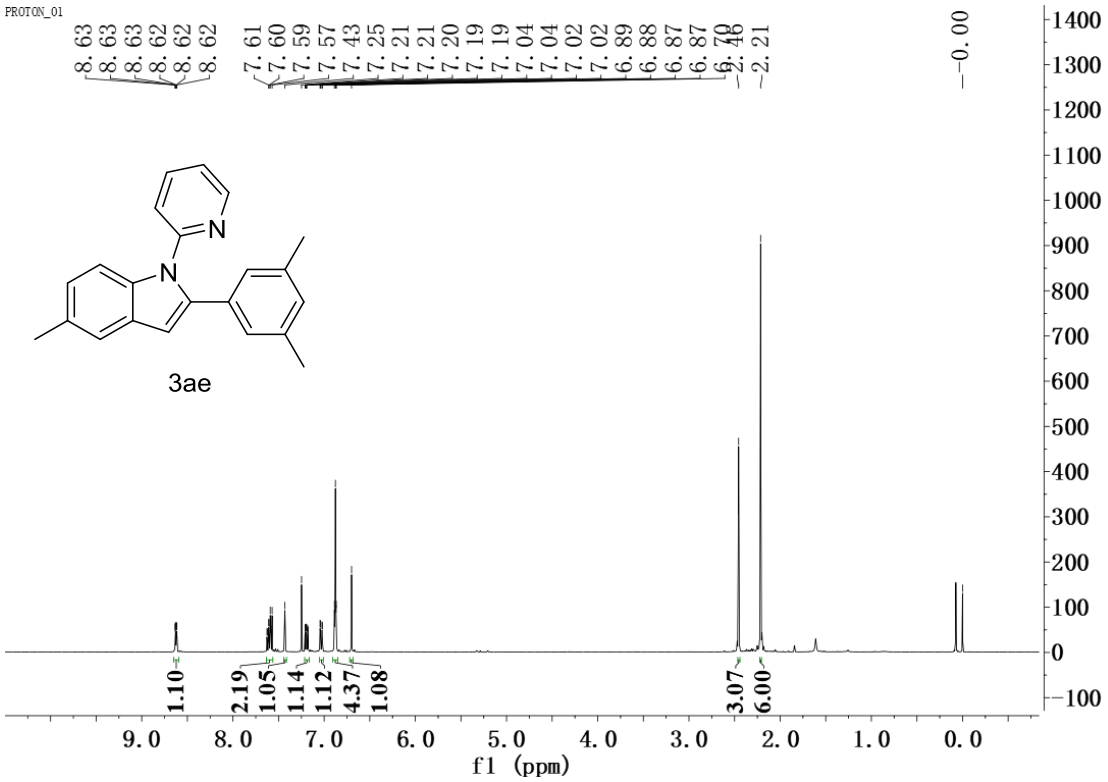

CARBON_01
152.28 149.18 139.93 137.79 137.10 133.24 132.44 130.74 130.33 129.04 128.08 127.78 127.64 127.50 126.62 126.32 126.15 124.72 121.85 121.42 120.31 111.29 105.93
-21.46
f1 (ppm)

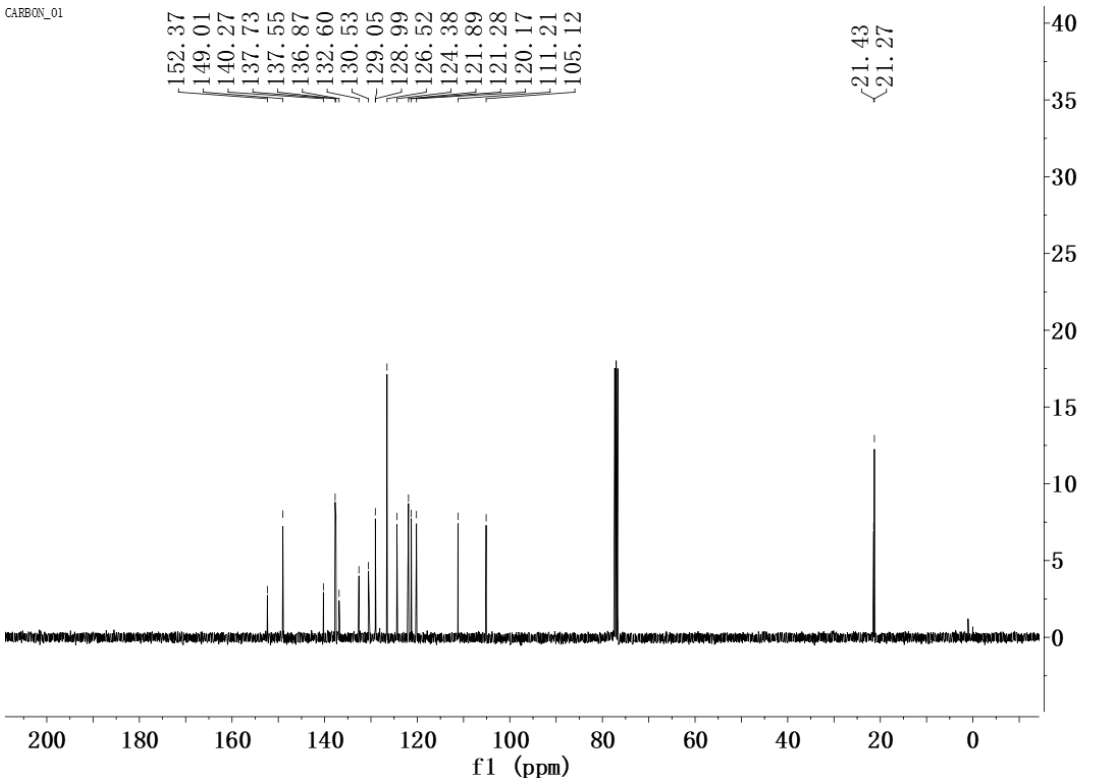

ZXG-20190427-yxf-1
8.66 8.65 8.64 8.63 8.47 8.47 8.47 8.47 8.46 8.46 8.46 7.97 7.96 7.95 7.94 7.83 7.83 7.82 7.79 7.65 7.65 7.63 7.60 7.60 7.58 7.56 7.55 7.54 7.53 7.52 7.52 7.39 7.23 6.93 6.92 6.91 6.83 6.77 6.75 2.51 -0.00
N
N
3ac
2.13 1.03 1.04 3.04 1.12 3.19 1.07 1.00 1.02 1.03 0.97 1.02
3.00
f1 (ppm)


CARBON_01
151.99 148.74 137.54 131.19 130.74 130.29 130.21 129.88 129.73 128.92 128.88 127.08 126.83 126.81 126.76 126.58 124.72 122.62 122.52 120.89 120.24 120.04 111.79 107.43 21.49
f1 (ppm)


PROTON_01
8.50
8.33
8.30
8.17
8.13
8.07
8.03
7.98
7.96
7.93
7.91
7.86
7.82
7.55
7.25
7.14
6.91
6.59
6.57
6.55
2.52
N
N
3ad
1.01
1.01
8.00
1.05
0.99
1.98
1.97
0.98
3.00
f1 (ppm)


CARBON_01
151.98
148.82
137.40
131.29
130.98
130.87
130.85
129.73
129.05
128.70
127.90
127.82
127.31
126.10
125.30
125.18
125.16
124.75
124.38
120.86
120.60
120.23
111.77
108.09
21.51
f1 (ppm)


PROTON_01
8.63
8.63
8.63
8.62
8.62
8.62
7.61
7.60
7.59
7.57
7.43
7.25
7.21
7.21
7.20
7.19
7.19
7.04
7.04
7.02
7.02
6.89
6.88
6.87
6.87
2.46
2.21
-0.00
N
N
3ae
1.10
2.19
1.05
1.14
1.12
4.37
1.08
3.07
6.00
f1 (ppm)


CARBON_01
152.37
149.01
140.27
137.73
137.55
136.87
132.60
130.53
129.05
128.99
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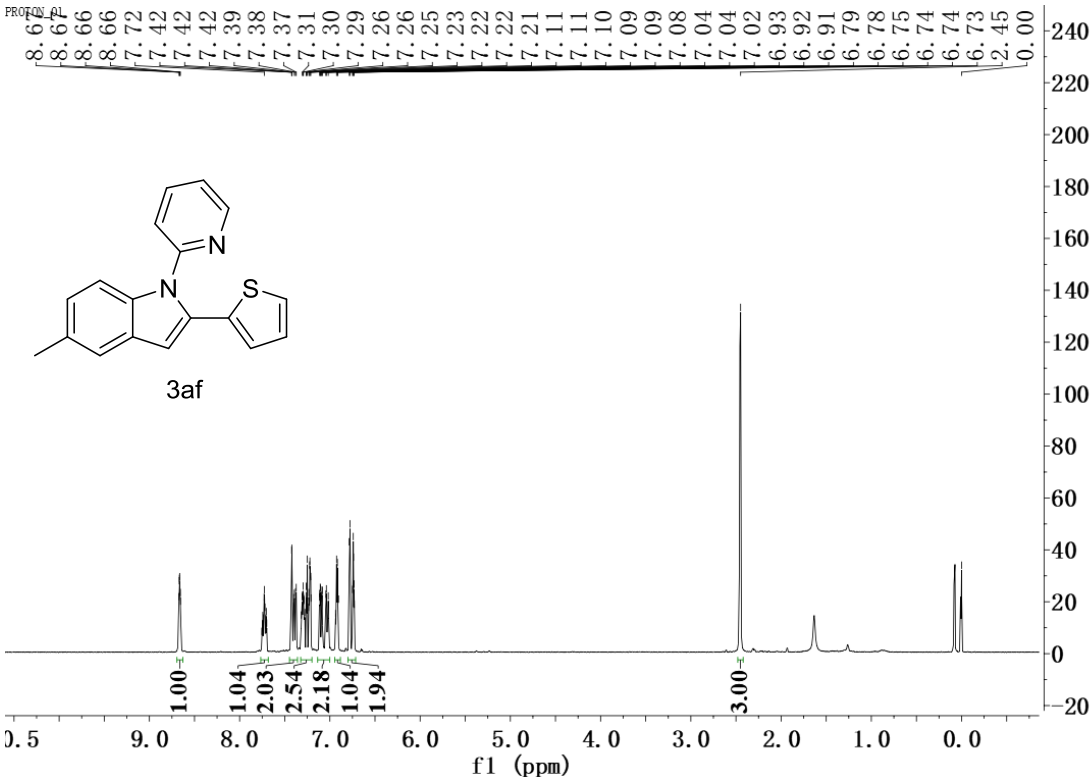
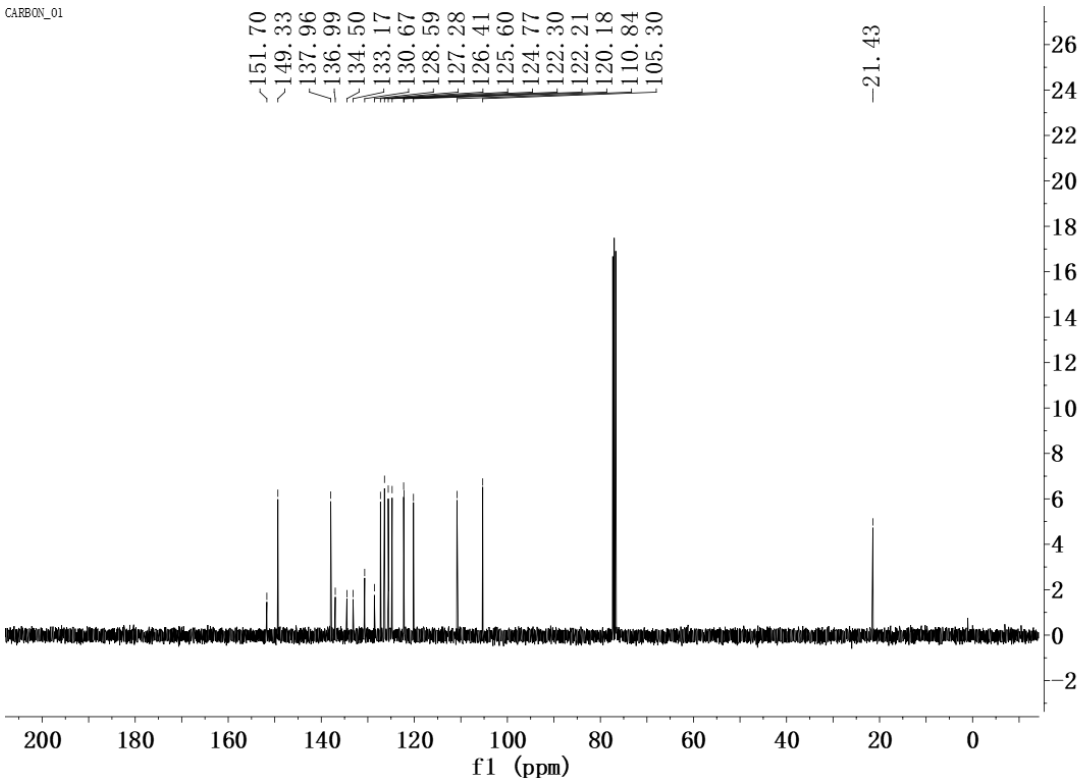
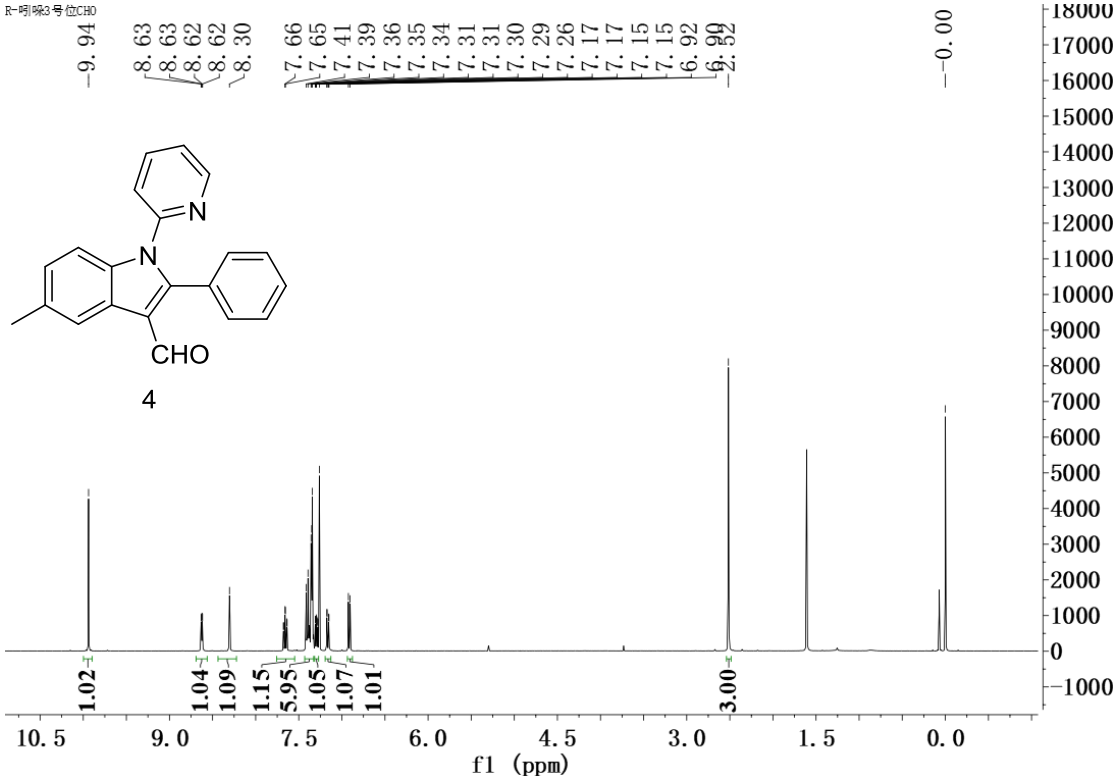
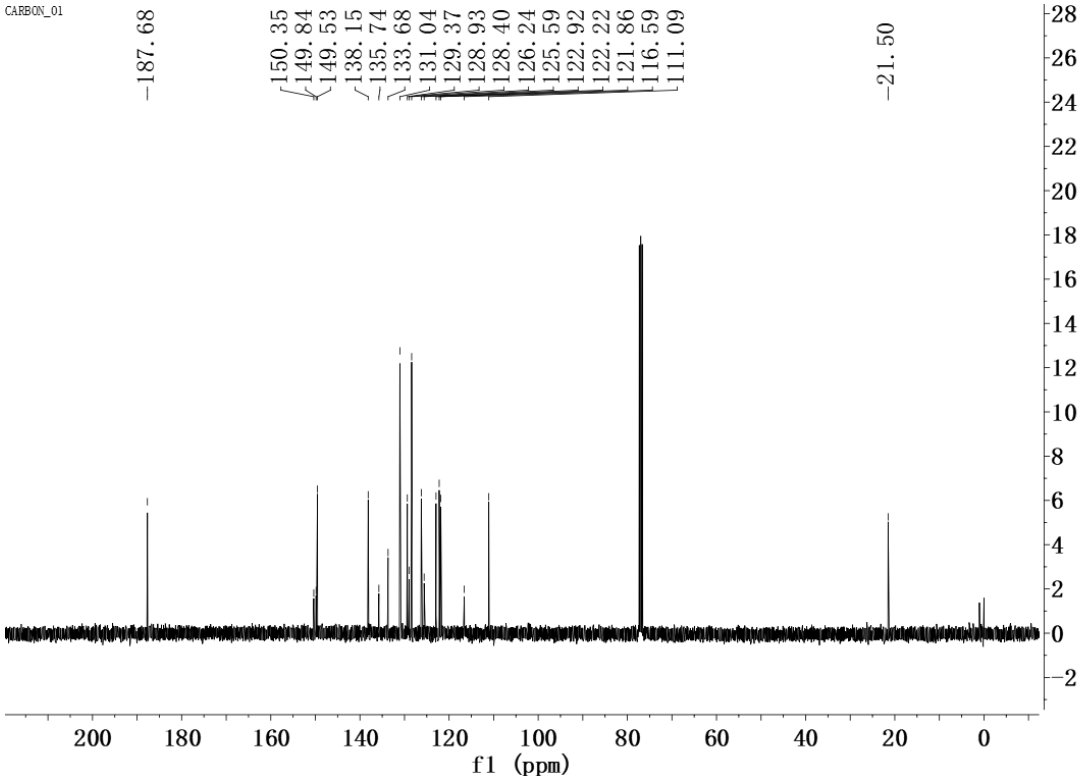
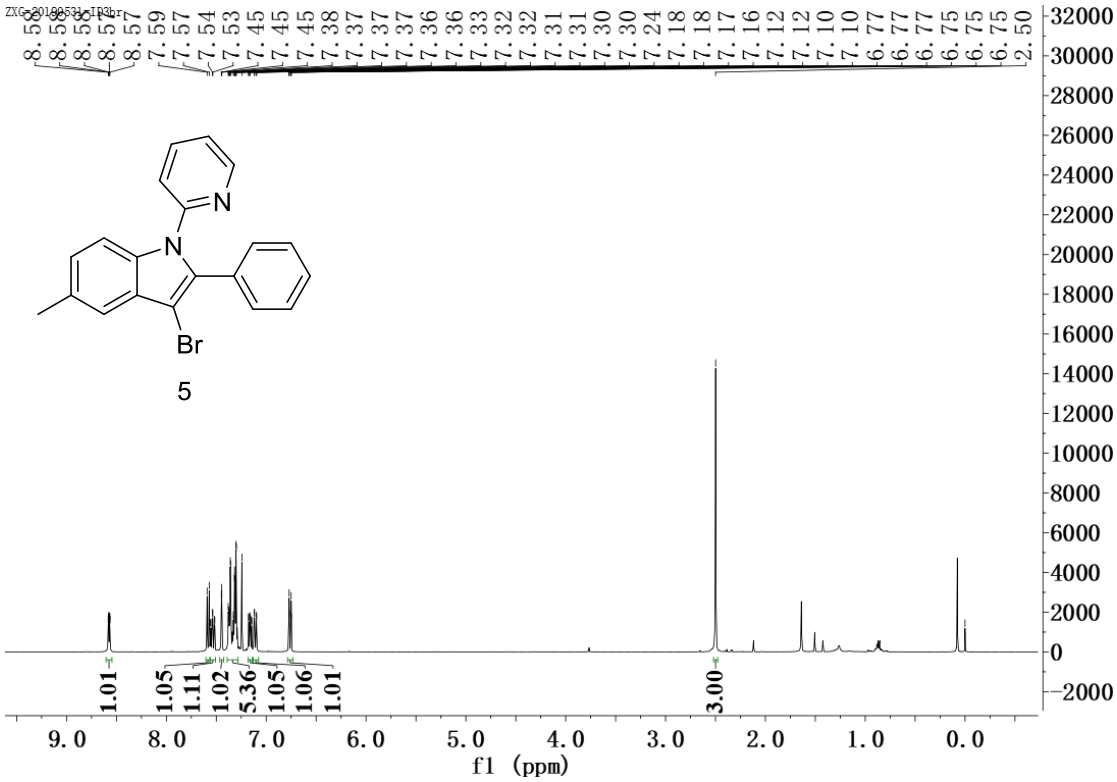
124.38
121.89
121.28
120.17
111.21
105.12
21.43
21.27
f1 (ppm)

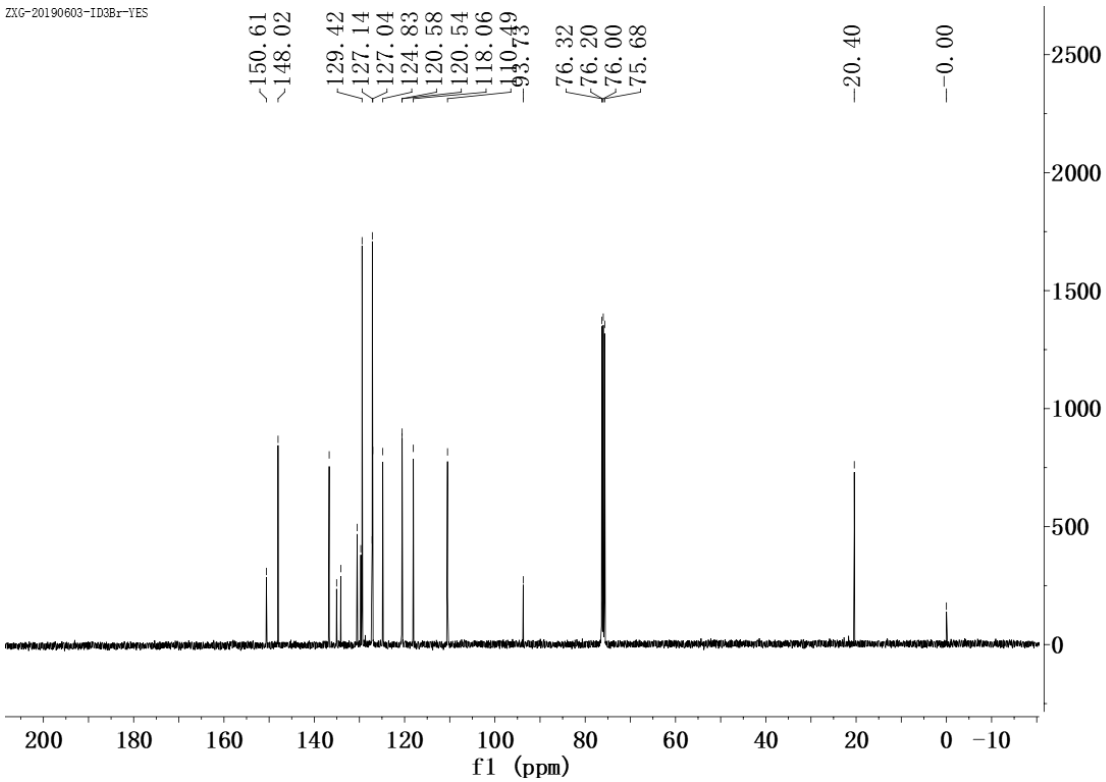

PROTON_01
8.67
8.67
8.66
8.66
7.72
7.42
7.42
7.42
7.39
7.38
7.37
7.31
7.30
7.29
7.26
7.26
7.25
7.23
7.22
7.22
7.21
7.11
7.11
7.10
7.09
7.09
7.08
7.04
7.04
7.02
6.93
6.92
6.91
6.79
6.78
6.75
6.74
6.74
6.73
2.45
0.00
N
N
S
3af
1.00
1.04
2.03
2.54
2.18
1.04
1.94
3.00
f1 (ppm)

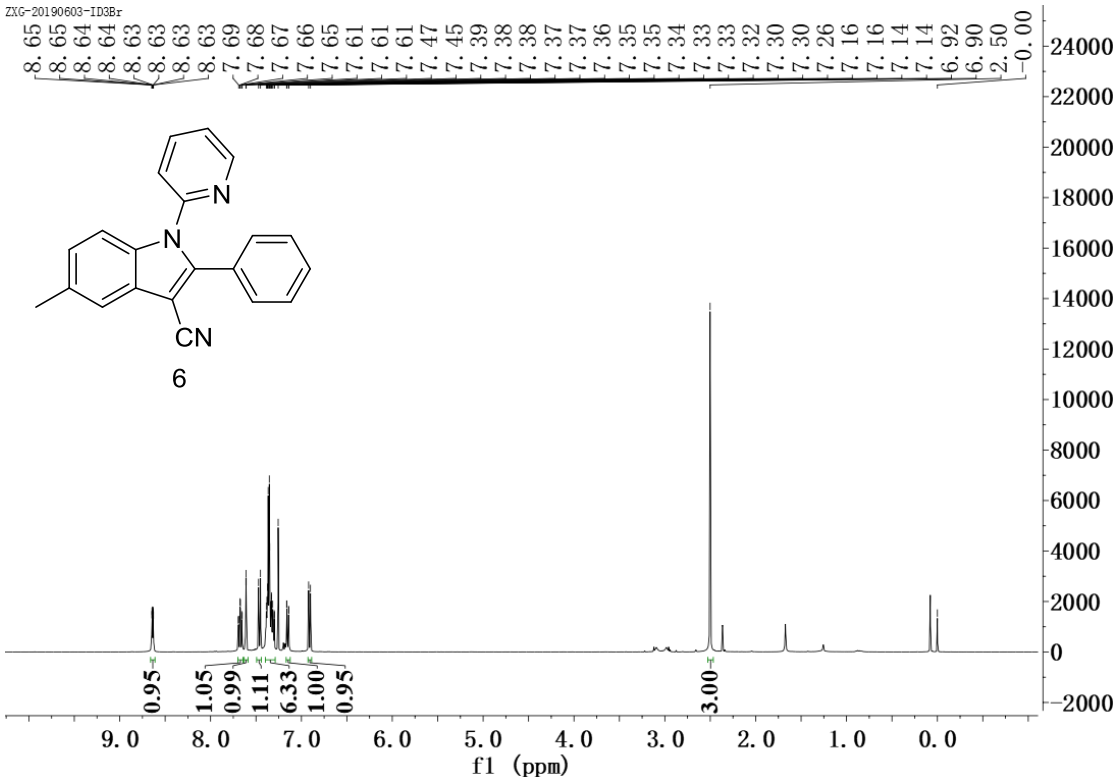

CARBON_01
151.70
149.33
137.96
136.99
134.50
133.17
130.67
128.59
127.28
126.41
125.60
124.77
122.30
122.21
120.18
110.84
105.30
21.43
f1 (ppm)

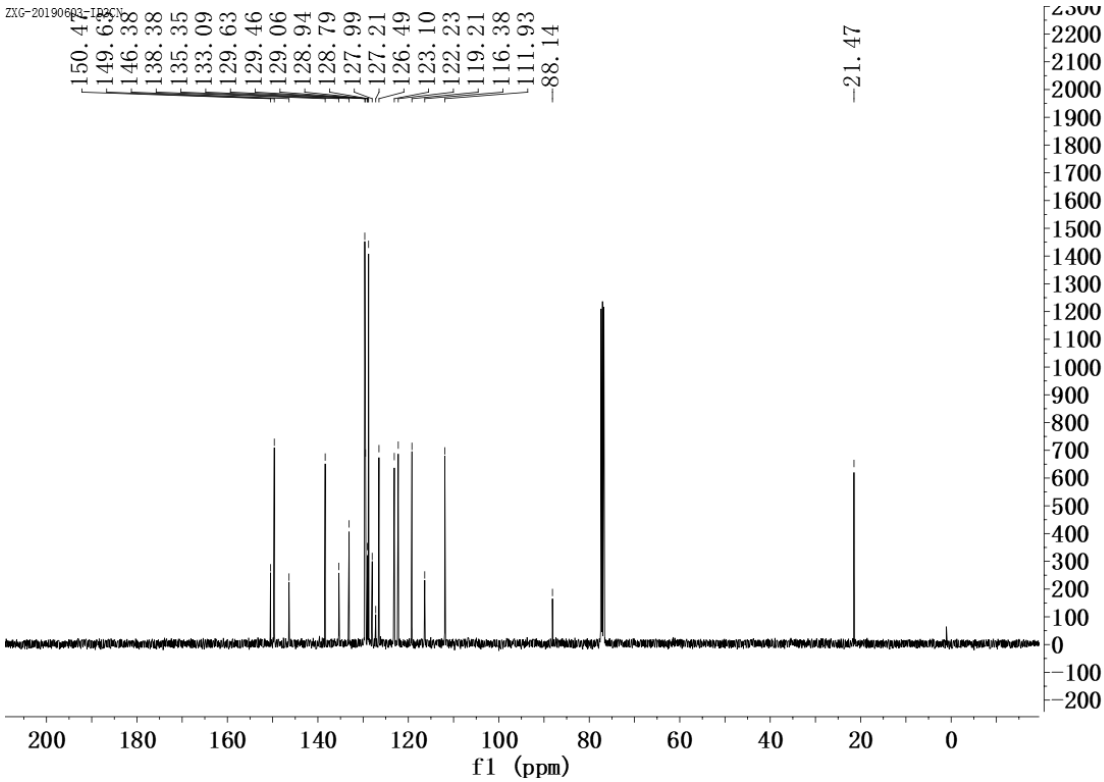

R-吲哚3号位CHO
9.94
8.63
8.63
8.62
8.62
8.30
7.66
7.65
7.41
7.39
7.36
7.35
7.34
7.31
7.31
7.30
7.29
7.26
7.17
7.17
7.15
7.15
6.92
6.90
6.89
2.32
0.00
N
N
CHO
4
1.02
1.04
1.09
1.15
5.95
1.05
1.07
1.01
3.00
10.5
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

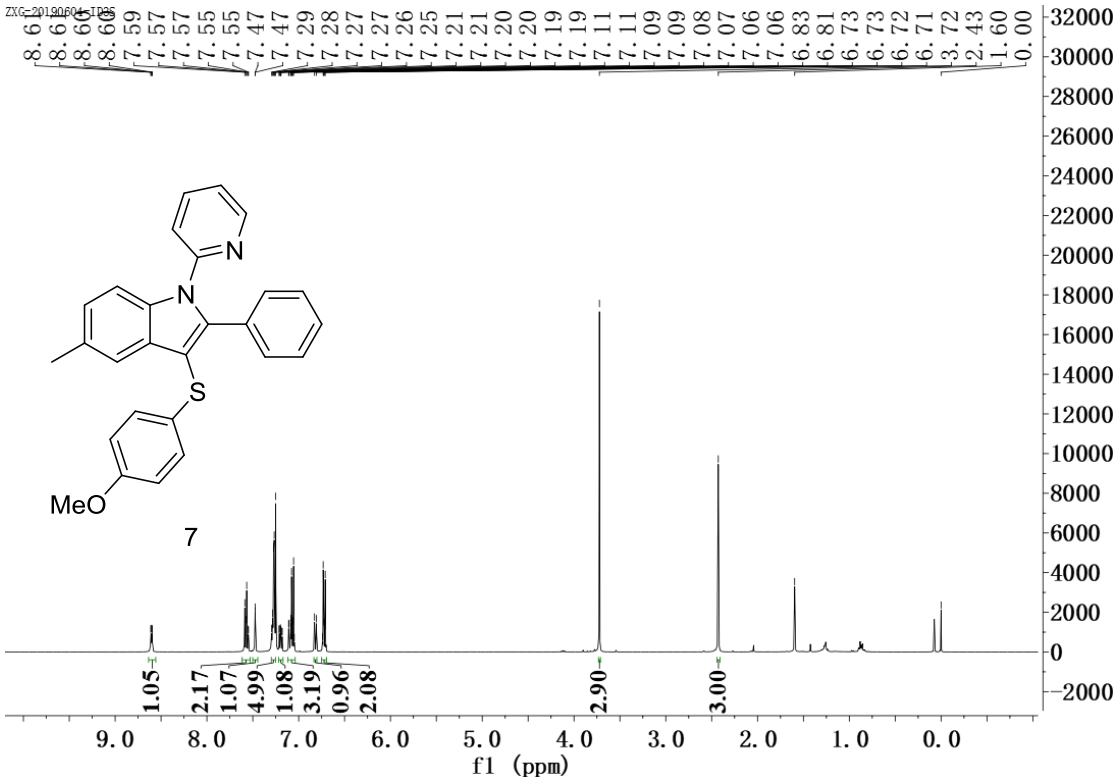

CARBON_01
187.68
150.35
149.84
149.53
138.15
135.74
133.68
131.04
129.37
128.93
128.40
126.24
125.59
122.92
122.22
121.86
116.59
111.09
21.50
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

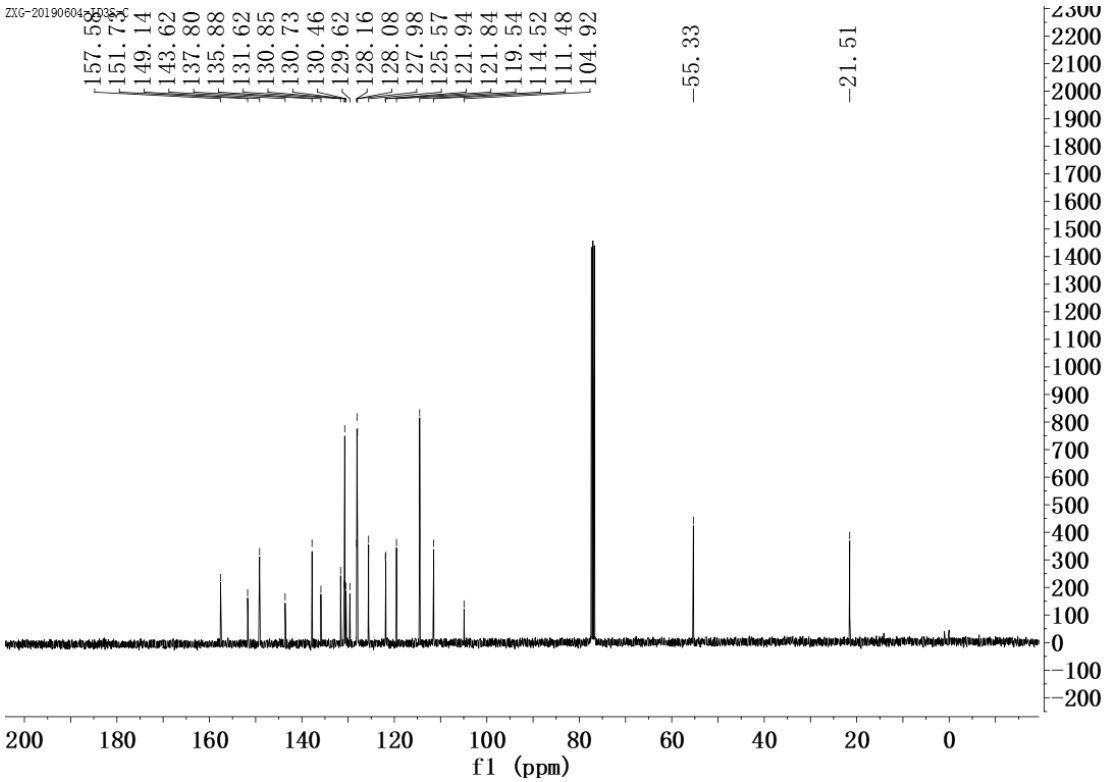

ZXG-20190531-ID3br
8.58 8.58 8.58 8.57 8.57 7.59 7.57 7.54 7.53 7.45 7.45 7.45 7.38 7.37 7.37 7.37 7.36 7.36 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.24 7.18 7.18 7.17 7.16 7.12 7.12 7.10 7.10 6.77 6.77 6.77 6.75 6.75 6.75 2.50
N
N
Br
5
1.01 1.05 1.11 1.02 5.36 1.05 1.06 1.01 3.00
f1 (ppm)

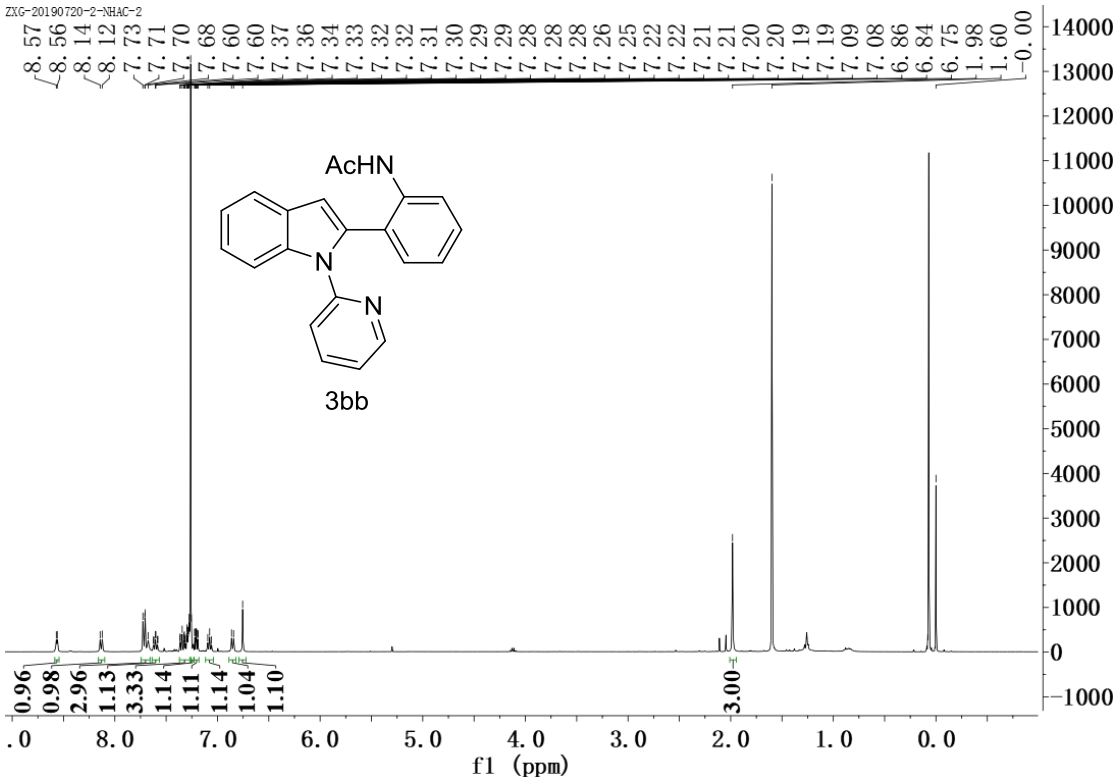

ZXG-20190603-ID3Br-YES
150.61 148.02 129.42 127.14 127.04 124.83 120.58 120.54 118.06 110.49 93.73 76.32 76.20 76.00 75.68 20.40 -0.00
f1 (ppm)

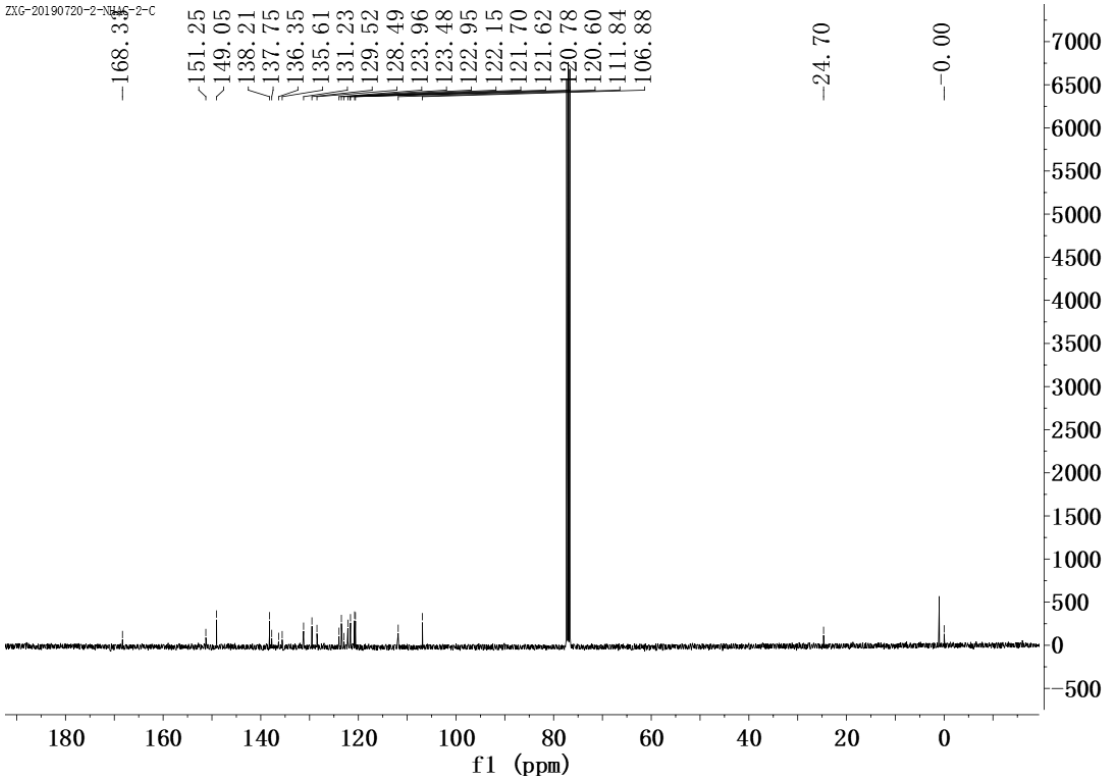

ZXG-20190603-ID3Br
8.65 8.65 8.64 8.64 8.63 8.63 8.63 8.63 7.69 7.68 7.67 7.66 7.65 7.61 7.61 7.61 7.47 7.45 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.30 7.30 7.26 7.16 7.16 7.14 7.14 6.92 6.90 2.50 -0.00
N
N
CN
6
0.95 1.05 0.99 1.11 6.33 1.00 0.95 3.00
f1 (ppm)

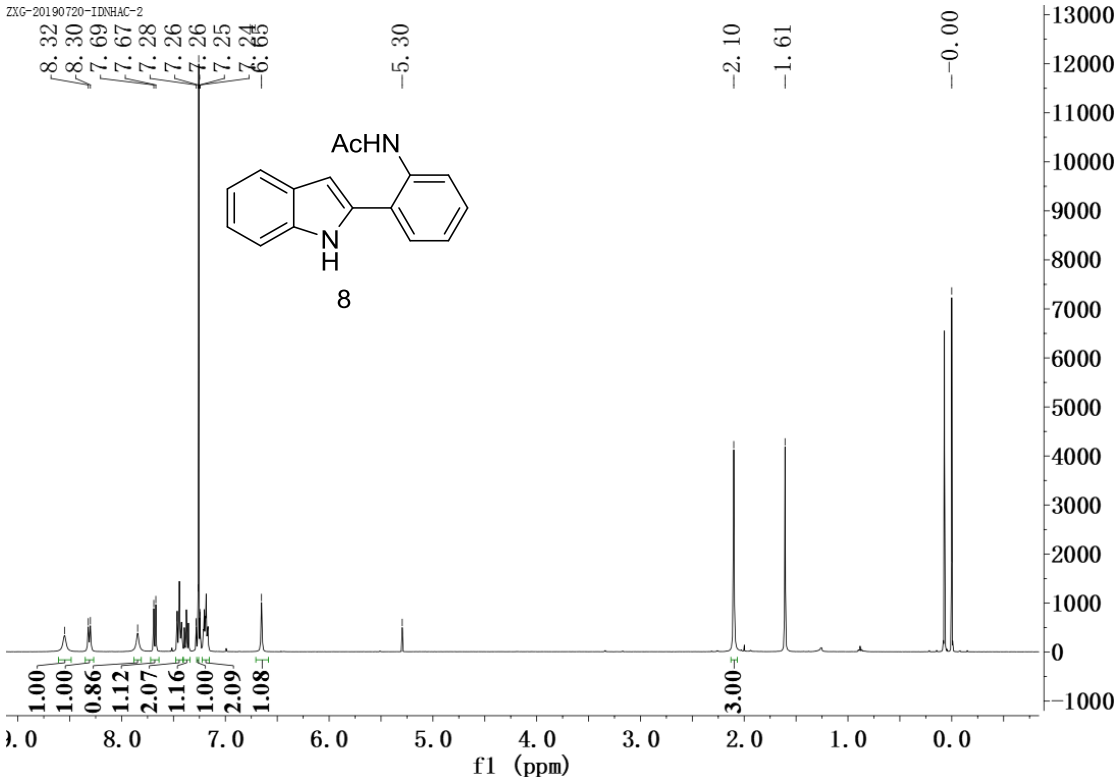

ZXG-20190603-ID3CN
150.47 149.63 146.38 138.38 135.35 133.09 129.63 129.46 129.06 128.94 128.79 127.99 127.21 126.49 123.10 122.23 119.21 116.38 111.93 88.14
21.47
f1 (ppm)

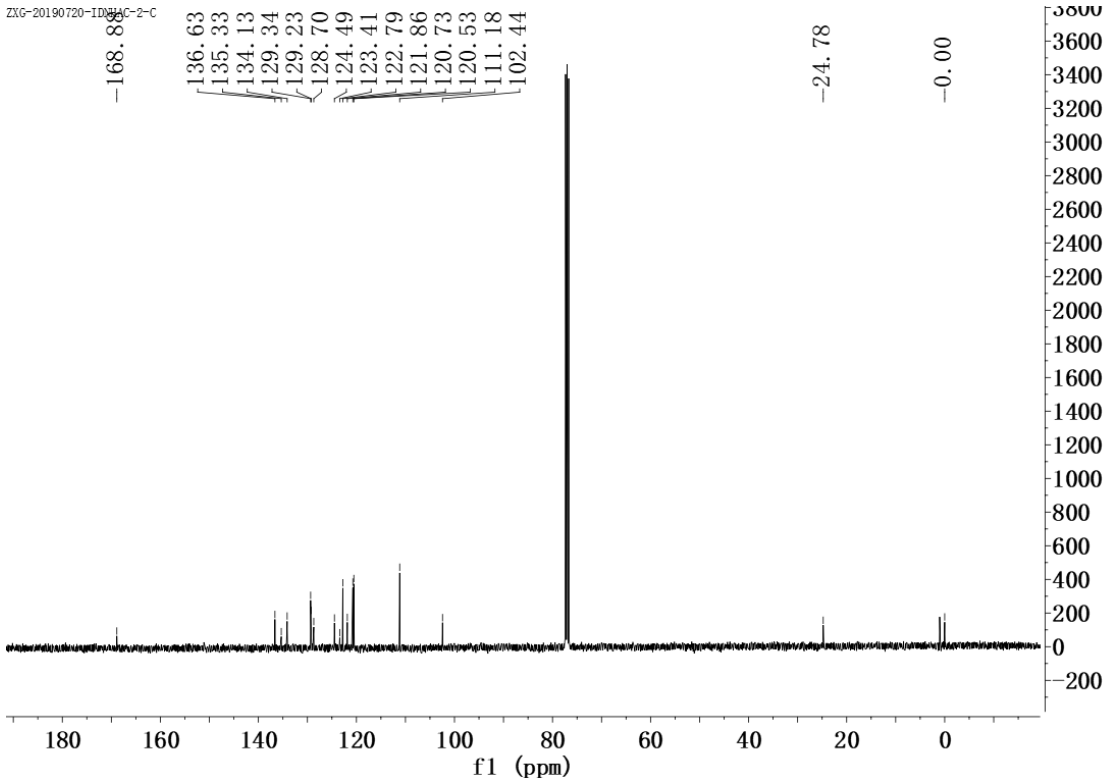

ZXG-20190604-T035
8.61 8.61 8.60 8.60 7.59 7.57 7.57 7.55 7.55 7.47 7.47 7.29 7.28 7.27 7.27 7.26 7.25 7.21 7.21 7.20 7.20 7.19 7.19 7.11 7.11 7.09 7.09 7.08 7.07 7.06 7.06 6.83 6.81 6.73 6.73 6.72 6.71 3.72 2.43 1.60 0.00
N
N
S
MeO
7
1.05 2.17 1.07 4.99 1.08 3.19 0.96 2.08 2.90 3.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

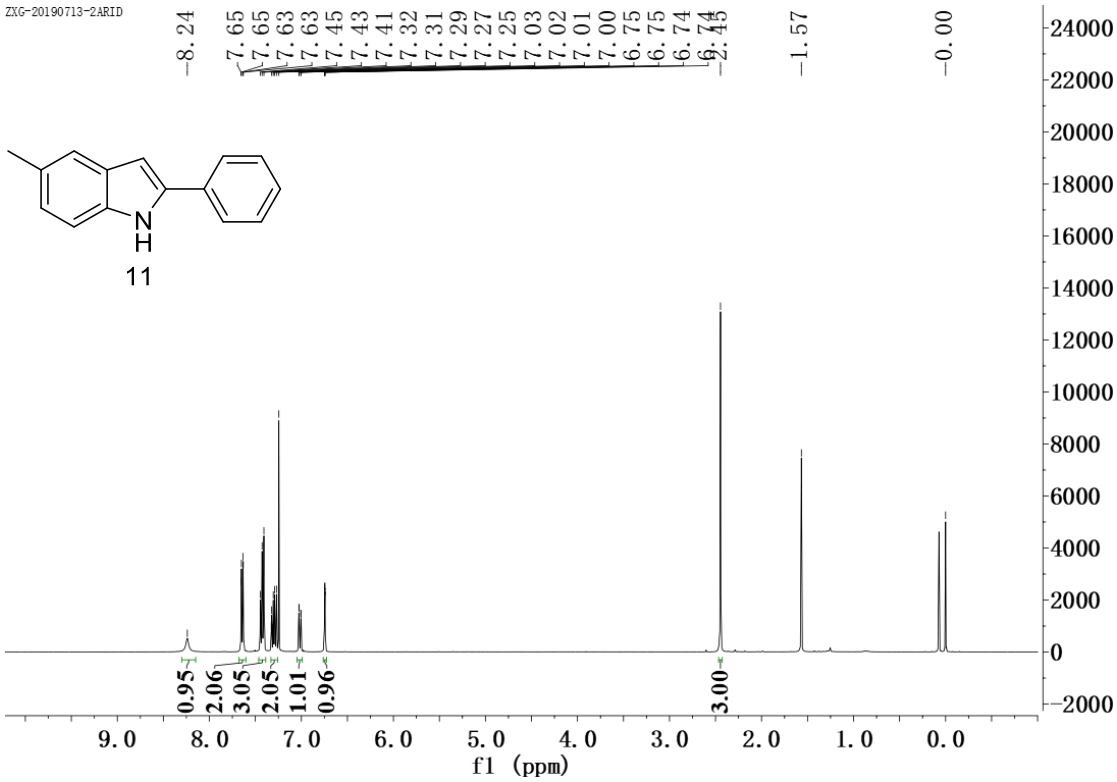

ZXG-20190604-T035-C
157.58 151.73 149.14 143.62 137.80 135.88 131.62 130.85 130.73 130.46 129.62 128.16 128.08 127.98 125.57 121.94 121.84 119.54 114.52 111.48 104.92
55.33
21.51
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

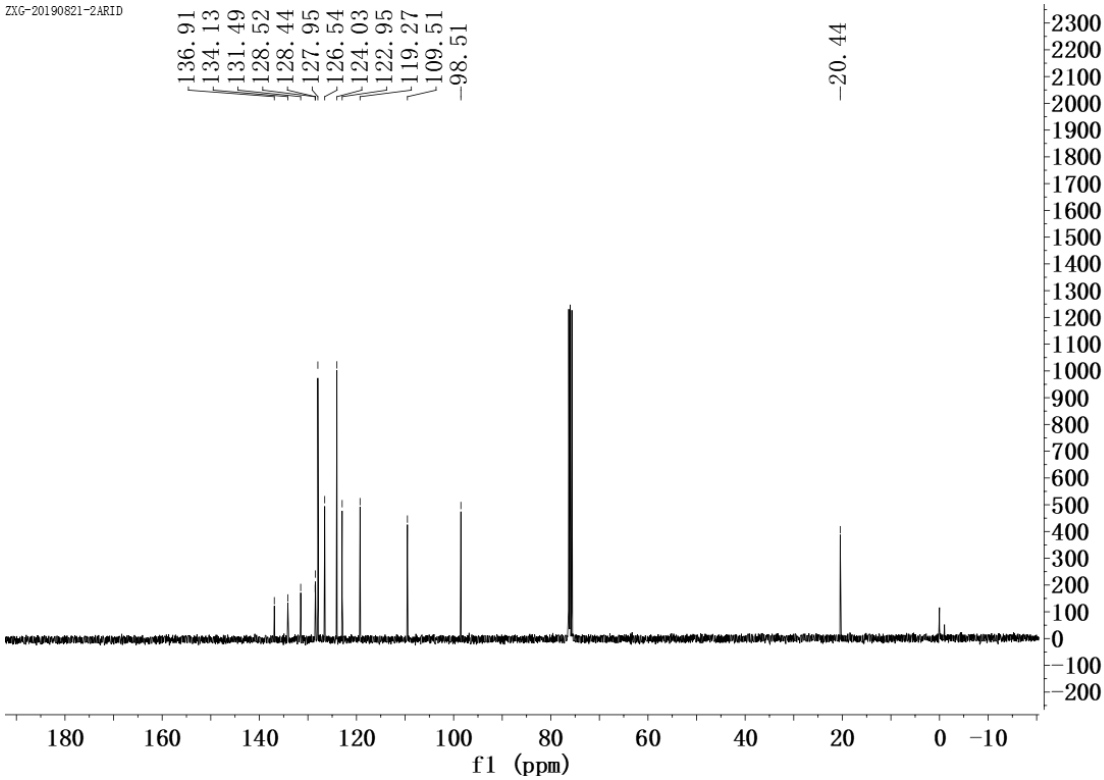

ZXG-20190720-2-NHAC-2
AcHN
N
N
3bb
f1 (ppm)

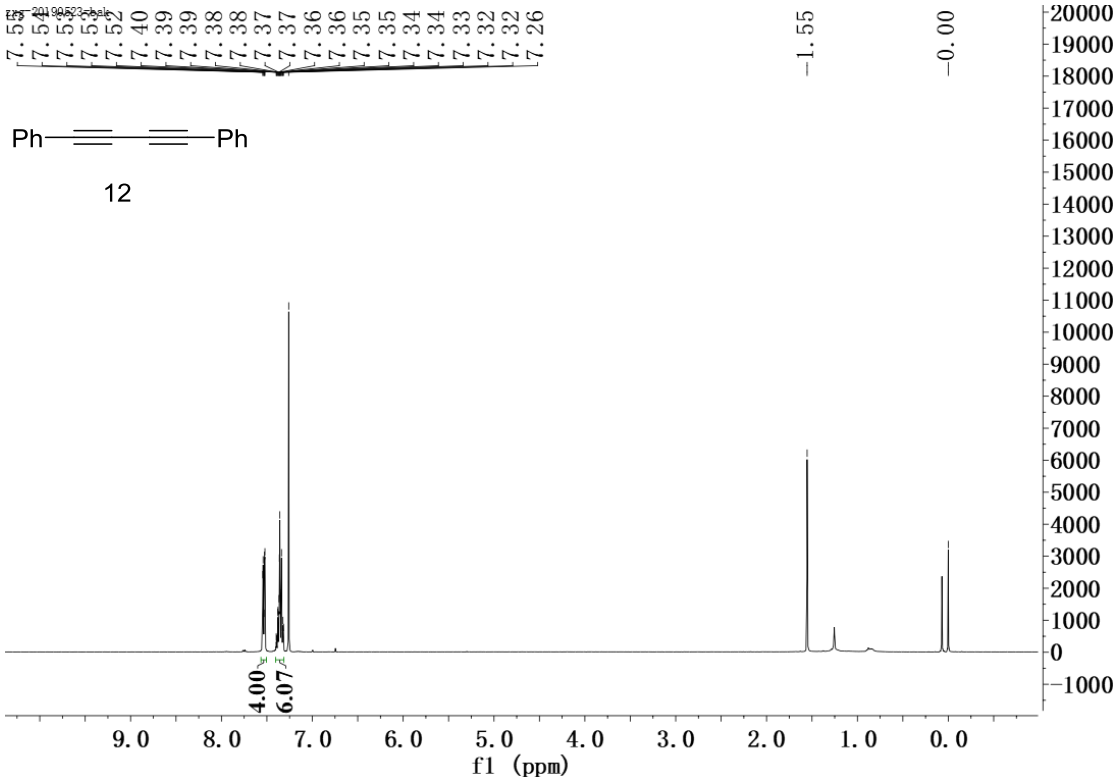

ZXG-20190720-2-NHAC-2-C
f1 (ppm)

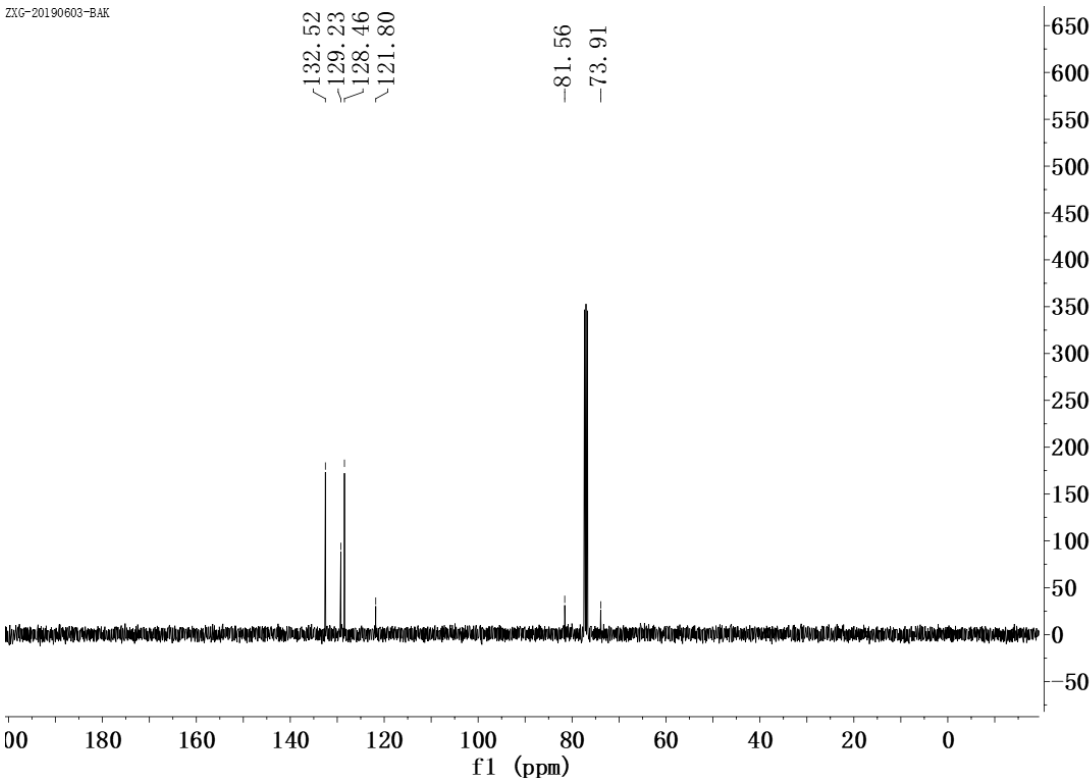

ZXG-20190720-IDNHAC-2
8.32
8.30
7.69
7.67
7.28
7.26
7.26
7.25
7.24
6.65
5.30
2.10
1.61
0.00
AcHN
N
H
8
1.00
1.00
0.86
1.12
2.07
1.16
1.00
2.09
1.08
3.00
f1 (ppm)

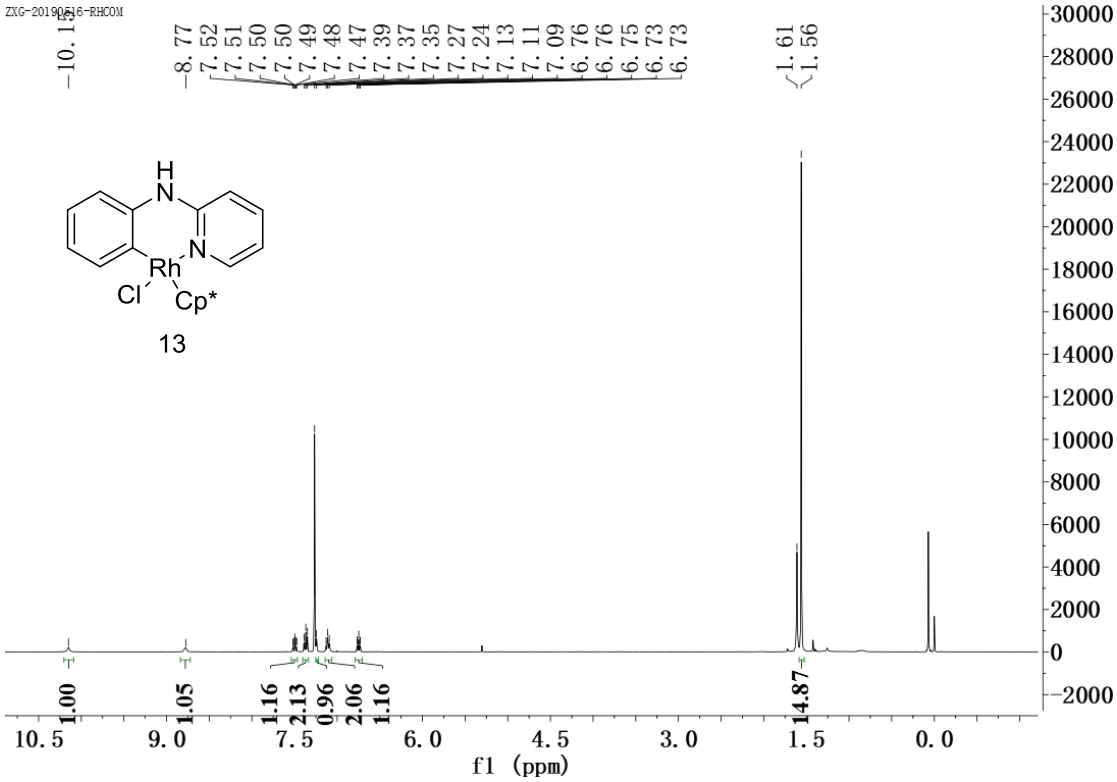

ZXG-20190720-IDNHAC-2-C
168.86
136.63
135.33
134.13
129.34
129.23
128.70
124.49
123.41
122.79
121.86
120.73
120.53
111.18
102.44
24.78
0.00
f1 (ppm)

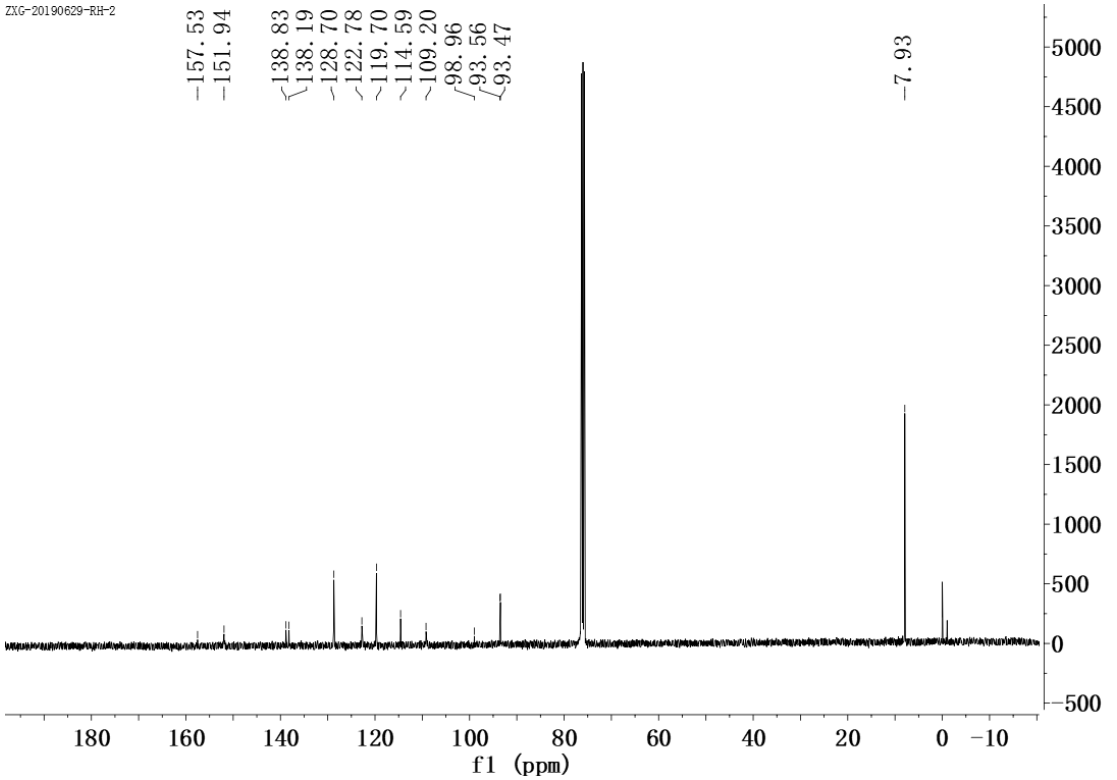

ZXG-20190713-2ARID
8.24
7.65
7.65
7.63
7.63
7.45
7.43
7.41
7.32
7.31
7.29
7.27
7.25
7.03
7.02
7.01
7.00
6.75
6.75
6.74
6.74
2.45
1.57
0.00
N
H
11
0.95
2.06
3.05
2.05
1.01
0.96
3.00
f1 (ppm)


ZXG-20190821-2ARID
136.91
134.13
131.49
128.52
128.44
127.95
126.54
124.03
122.95
119.27
109.51
98.51
20.44
f1 (ppm)


7.55
7.54
7.53
7.52
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.26
-1.55
-0.00
Ph
Ph
12
4.00
6.07
f1 (ppm)


ZXG-20190603-BAK
132.52
129.23
128.46
121.80
81.56
73.91
f1 (ppm)


ZXG-20190516-RHCOM
10.13
8.77
7.52
7.51
7.50
7.50
7.49
7.48
7.47
7.39
7.37
7.35
7.27
7.24
7.13
7.11
7.09
6.76
6.76
6.75
6.73
6.73
1.61
1.56
H
N
N
Rh
Cl
Cp*
13
1.00
1.05
1.16
2.13
0.96
2.06
1.16
14.87
f1 (ppm)


ZXG-20190629-RH-2
157.53
151.94
138.83
138.19
128.70
122.78
119.70
114.59
109.20
98.96
93.56
93.47
7.93
f1 (ppm)