Base Promoted Tandem Synthesis of 2-Azaaryl indoline

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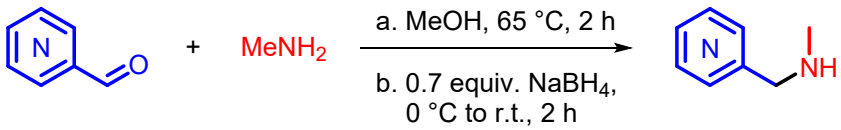
General Information:

All reactions were carried out under dry nitrogen. Anhydrous cyclopentyl methyl ether (CPME), 1,4-dioxane, dichloromethane, toluene, dimethoxyethane, THF, DMSO, DMF and acetonitrile were purchased from Sigma-Aldrich and directly used without further purification. Unless otherwise stated, reagents were commercially available and used as purchased. Chemicals were purchased from SigmaAldrich, Acros Organics, Alfa Aesar, TCI or Matrix Scientific. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 µm precoated 60 Å silica gel plates and visualized by short-wave ultraviolet light as well as by treatment with iodine. Flash chromatography was performed with silica gel (230– 400 mesh, Silicycle). The NMR spectra were obtained using a Bruker 500 MHz Fourier transform NMR spectrometer. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 100 Series FTIR spectrometer. High resolution mass spectrometry (HRMS) data were obtained on a Waters LCTOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus.

General Procedure A: Synthesis of 2-Azaarylmethyl Amine

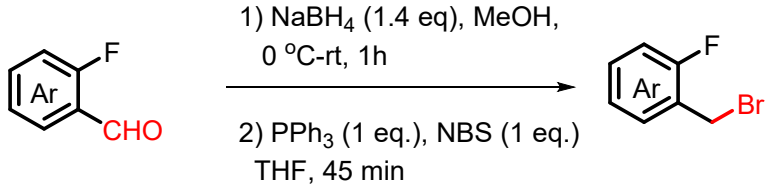


1.0 equiv. 1.5 equiv.

A flame-dried two-neck flask (250 mL) equipped with a reflux condenser and a stirring bar was charged with aldehyde (10 mmol, 1 equiv.) in methanol (10 mL) under air at room temperature. A solution of methanamine (0.78 g, 15 mmol, 1.5 equiv.) in methanol (60% w/w) was added by syringe over 5 min at room temperature, then the flask was sealed with septum and one empty balloon with needle was attached by piercing the septum on the top of condenser. The reaction mixture was heated to 65 °C in an oil bath and stirred for 2 h. After the period, the reaction flask was cooled to 0 °C and $NaBH_4$ (0.27 g, 7.0 mmol, 0.7 equiv.) was added in portions over 15 min. After the addition, the reaction mixture was warmed to room temperature and stirred for 2 h.

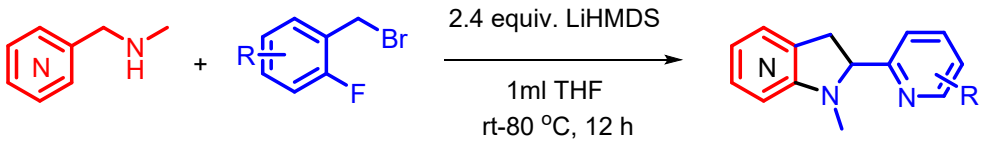
Next, 1 mL water was added to quench the reaction and the solution was concentrated *in vacuo* to remove methanol. To the resulting residue was added 50 mL CH_2Cl_2 to give a homogeneous solution. This solution was added to a separatory funnel and rinsed with brine (3 × 20 mL). The organic phase was collected, dried with Na_2SO_4 for 1 h, filtered and the filtrate was collected and concentrated under reduced pressure. The resulting residue was purified by chromatography.

General Procedure B: Synthesis of 2-fluoro benzyl bromides



A flame-dried two-neck flask (250 mL) with a stirring bar was charged with aldehyde (10 mmol, 1 equiv.) in methanol (10 mL) under air at room temperature. $NaBH_4$ (0.10 g, 2.8 mmol) was added and the resulting mixture was stirred at room temperature for 1 h. Next, 1 mL water was added to quench the reaction and the solution was concentrated *in vacuo* to remove methanol. To the resulting residue was added 50 mL CH_2Cl_2 to give a homogeneous solution. This solution was transfered to a separatory funnel and rinsed with brine (3 × 20 mL). The organic phase was collected, dried with Na_2SO_4 for 1 h, filtered and the filtrate was collected and concentrated under reduced pressure. The resulting residue was dissolved in 10 mL THF, and PPh_3 (0.52 g, 2 mmol) and NBS (0.36 g, 2 mmol) were added at 0 °C, after addition the mixture was warmed to room temperature for 45 min, and then quenched by 10 ml $Na_2S_2O_3$. To the resulting residue was added 50 mL Et_2O to give a homogeneous solution. This solution was transfered to a separatory funnel and rinsed with brine (3 × 20 mL). The organic phase was collected, dried with Na_2SO_4 for 1 h, filtered and the filtrate was collected and concentrated under reduced pressure. The resulting residue was purified by chromatography.

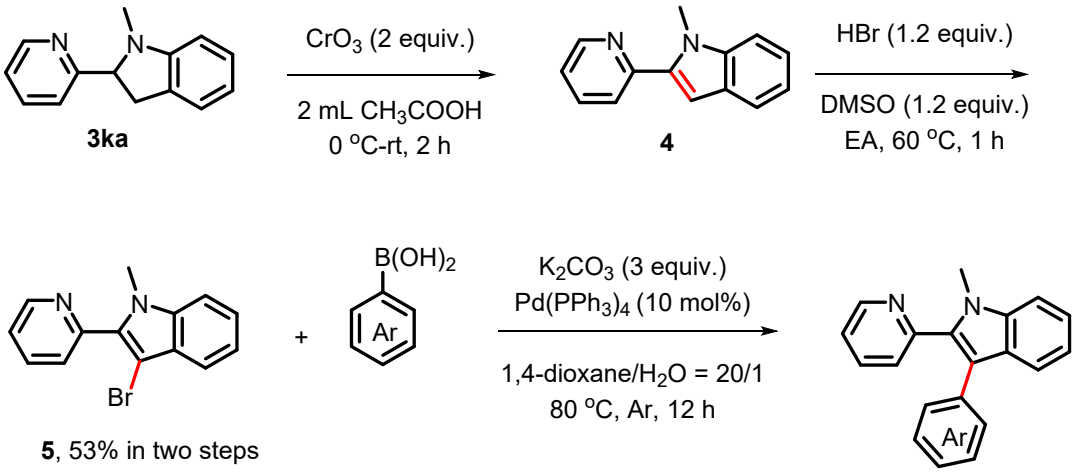
General Procedure C: Synthesis of 2-azaaryl indoline



To an oven dried scintillation vial equipped with a stir bar under an nitrogen atmosphere in the glove box were added azaarylmethylamine (0.24 mmol, 1.2 equiv.), anhydrous tetrahydrofuran

(2 mL), $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol, 2.4 equiv.) and then the corresponding 2-fluoro benzyl bromides (0.20 mmol, 1.0 equiv.) at room temperature. The scintillation vial was sealed with cap containing a septum and removed from the glove box. The reaction mixture was heated to 80 °C and stirred for 12 h. The scintillation vial was cooled to room temperature, the reaction mixture was passed through a short pad of silica, washed with additional 6 mL of ethyl acetate (3 × 2 mL), and the combined solutions were concentrated *in vacuo*. The crude material was loaded onto a column of silica gel for purification under the conditions below, to afford the desired product.

General Procedure D: Synthesis of 2-azaaryl indole



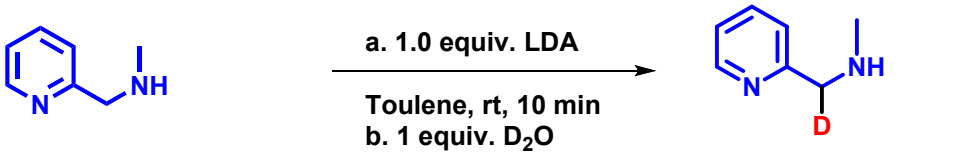
Step 1: A flame-dried two-neck flask (250 mL) equipped with a stirring bar was charged with 2-pyridyl indoline **3ka** (2.10 g, 10 mmol, 1 equiv.) in acetic acid (2 mL) under air at 0 °C. Then CrO_3 (1.98 g, 20 mmol, 2 equiv.) was added to the mixture in portions. After addition, the mixture was warmed to room temperature and stirred for 8h. Next, 10 mL water was added to dilute the mixture. To the resulting residue 50 mL CH_2Cl_2 was added to give out a homogeneous solution. This solution was added to a separatory funnel and rinsed with brine (3 × 20 mL). The organic phase was collected, dried with Na_2SO_4 for 1 h, filtered and the filtrate was collected and concentrated under reduced pressure. The resulting residue was used in next step without further purification.

Step 2: The mixture of step 1 was dissolved in EA (50 mL), then hydrobromic acid (0.96 g, 12 mmol, 1.2 equiv.) and DMSO (0.94 g, 12 mmol, 1.2 equiv.) was added dropwise at room temperature. Reaction progress was monitored by TLC while the reaction mixture was stirred for 5 h at 60 °C for 1h. Upon reaction completion, the mixture was cooled to room temperature and

poured into an ice-cold solution of aq. ammonia (0.5%) and aq. $Na_2S_2O_3$ (0.1%). After 50 mL CH_2Cl_2 was added to give out a homogeneous solution. The resulting mixture was transfered to a separatory funnel and rinsed with brine (3 × 20 mL). The organic phase was collected, dried with Na_2SO_4 for 1 h, filtered and the filtrate was collected and concentrated under reduced pressure. The crude material was loaded onto a column of silica gel (20:1 petroleum ether: ethyl acetate as eluent) to give out the target product **5** with 53% yield in two steps.

Step 3: A flame-dried two-neck flask (250 mL) equipped with a stirring bar and condenser was charged with bromide **5** (0.1 g, 0.35 mmol, 1 equiv.), K_2CO_3 (0.15 g, 1.05 mmol, 3 equiv.), $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol, 0.1 equiv.) and corresponding aryl boric acid (0.7 mmol, 2 equiv.) in 1,4-dioxane and water (20/1) under Ar at rt. Then the mixture was heated to 80 °C and stirred at that temperature for 12h. After that the mixture was cooled to room temperature and 50 mL CH_2Cl_2 was added to give out a homogeneous solution. The resulting mixture was transfered to a separatory funnel and rinsed with brine (3 × 20 mL). The organic phase was collected, dried with Na_2SO_4 for 1 h, filtered and the filtrate was collected and concentrated under reduced pressure. The crude material was loaded onto a column of silica gel for purification under the conditions below, to afford the desired product.

Synthesis of deuterated N-methyl-1-(pyridin-2-yl)methanamine

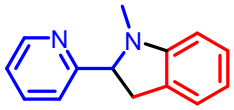


1a 1.0 equiv. **5aa 98% yield, 72% D**

To an oven dried scintillation vial equipped with a stir bar under an nitrogen atmosphere in the glove box were added azaarylmethylamine (0.2 mmol, 1.0 equiv.), anhydrous tetrahydrofuran (2 mL), and lithium diisopropyl amide (LDA) (.2 mL, 0.2 mmol, 1.0 equiv.) at room temperature. The scintillation vial was sealed with cap containing a septum and removed from the glove box. The reaction mixture was stirred for 10 min at room temperature. Then the cap was removed and 3.6 uL D_2O was added to quench the mixture.The reaction mixture was passed through a short pad of silica, washed with additional 6 mL of ethyl acetate (3 × 2 mL), and the combined solutions were concentrated *in vacuo*. The crude material was loaded onto a column of silica gel for purification via silica gel chromatography (2:1 petroleum ether: ethyl acetate as eluent) to give out

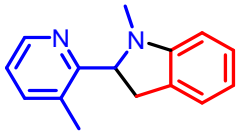
D-1a (23.4 mg, 98%, 72% D) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 4.9, 1.4 Hz, 1H), 7.76 (td, J = 7.7, 1.8 Hz, 1H), 7.58 – 7.47 (m, 1H), 7.34 – 7.21 (m, 2H), 6.47 (s, 3H), 4.39 – 4.10 (m, 1H), 2.72 (s, 3H).

1-methyl-2-(pyridin-2yl)-2,3-indoline (3aa)



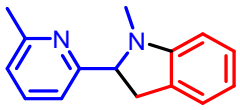
The compound was prepared according to procedure C with **1a** (29.3 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3aa** (31.1 mg, 74%) as light yellow solid. m.p. 65-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61-8.60 (m, 1H), 7.71 (td, J = 7.7, 1.8 Hz, 1H), 7.54 (dt, J = 7.9, 1.1 Hz, 1H), 7.22 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 7.08 (dd, J = 7.2, 1.4 Hz, 1H), 6.73 (td, J = 7.4, 1.0 Hz, 1H), 6.56 (d, J = 7.8 Hz, 1H), 4.57 (dd, J = 10.9, 9.1 Hz, 1H), 3.47 (dd, J = 15.7, 9.2 Hz, 1H), 2.99 (ddt, J = 15.6, 10.9, 1.2 Hz, 1H), 2.69 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.5, 153.2, 149.4, 137.0, 128.4, 127.7, 124.2, 122.5, 121.1, 118.4, 107.5, 73.4, 38.0, 34.9. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{15}N_2$ 211.1230; Found 211.1232.

1-methyl-2-(3-methylpyridin-2yl)-2,3-indoline (3ba)



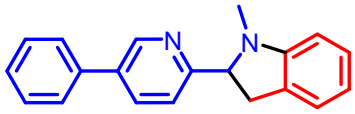
The compound was prepared according to procedure C with **1b** (32.6 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ba** (29.3 mg, 65%) as light yellow solid . m.p. 64-65 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, J = 4.8, 1.7 Hz, 1H), 7.48 (ddd, J = 7.6, 1.8, 0.8 Hz, 1H), 7.17 – 7.05 (m, 3H), 6.71 (td, J = 7.4, 1.0 Hz, 1H), 6.54 (d, J = 7.8 Hz, 1H), 4.76 (dd, J = 11.6, 9.0 Hz, 1H), 3.33 (dd, J = 15.4, 9.0 Hz, 1H), 3.13 (ddt, J = 15.4, 11.7, 1.2 Hz, 1H), 2.66 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.4, 153.1, 147.3, 138.7, 132.0, 128.3, 127.6, 124.0, 122.3, 118.1, 107.7, 71.0, 35.8, 34.8, 18.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2$ 225.1386; Found 225.1382.

1-methyl-2-(6-methylpyridin-2yl)-2,3-indoline (3ca)



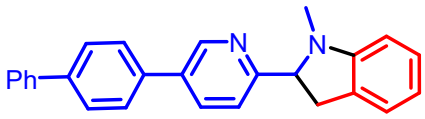
The compound was prepared according to procedure C with **1c** (32.6 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ca** (30.6 mg, 68%) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, J = 7.7 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.07 (dd, J = 7.5, 2.5 Hz, 2H), 6.72 (td, J = 7.4, 1.0 Hz, 1H), 6.55 (d, J = 7.8 Hz, 1H), 4.53 (dd, J = 10.9, 9.2 Hz, 1H), 3.48 (dd, J = 15.7, 9.2 Hz, 1H), 3.01 – 2.87 (m, 1H), 2.69 (s, 3H), 2.58 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1, 157.9, 153.3, 137.2, 128.5, 127.7, 124.2, 122.1, 118.2, 117.8, 107.3, 73.5, 38.1, 34.8, 24.6. HRMS (ESI-TOF) m/z: [M+H]+ Calcd for $C_{15}H_{17}N_2$ 225.1386; Found 225.1381.

1-methyl-2-(5-phenylpyridin-2yl)-2,3-indoline (3da)



The compound was prepared according to procedure C with **1d** (47.5 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3da** (35.0 mg, 61%) as light yellow solid . m.p. 56-57 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 – 8.79 (m, 1H), 7.92 (dd, J = 8.1, 2.4 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.55 – 7.47 (m, 2H), 7.46 – 7.38 (m, 1H), 7.17 (t, J = 7.7 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.76 (td, J = 7.4, 1.0 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 4.63 (dd, J = 11.0, 9.1 Hz, 1H), 3.51 (dd, J = 15.7, 9.1 Hz, 1H), 3.04 (dd, J = 15.8, 11.0 Hz, 1H), 2.74 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 153.2, 147.8, 137.7, 135.6, 135.4, 129.2, 128.4, 128.1, 127.8, 127.2, 124.2, 121.1, 118.4, 107.5, 73.2, 38.0, 34.9. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2$ 287.1543; Found 287.1538.

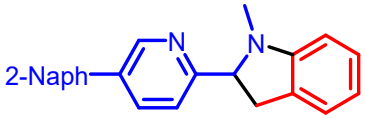
1-methyl-2-(5-(4-phenyl)phenylpyridin-2yl)-2,3-indoline (3ea)



The compound was prepared according to procedure C with **1e** (65.8 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude

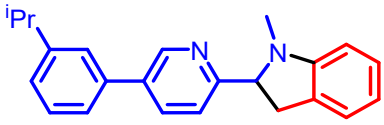
material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ea** (58.8 mg, 81%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 – 8.70 (m, 1H), 7.97 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.81 (dd, *J* = 1.9, 1.0 Hz, 1H), 7.71 – 7.62 (m, 4H), 7.62 – 7.54 (m, 2H), 7.49 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.45 – 7.37 (m, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.83 – 6.71 (m, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 4.65 (dd, *J* = 10.7, 8.9 Hz, 1H), 3.52 (dd, *J* = 15.7, 9.2 Hz, 1H), 3.06 (ddd, *J* = 15.5, 10.9, 1.3 Hz, 1H), 2.75 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5, 153.2, 147.9, 142.2, 140.8, 135.6, 129.6, 129.0, 128.4, 127.8, 127.7, 127.3, 127.0, 126.1, 126.1, 124.2, 121.1, 118.5, 107.5, 73.2, 38.1, 35.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{23}N_2$ 363,1856; Found 363.1853.

1-methyl-2-(5-(naphthalen-2-yl)pyridin-2yl)-2,3-indoline (3fa)



The compound was prepared according to procedure C with **1f** (59.5 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3fa** (30.3 mg, 45%) as light yellow solid . m.p. 66-67 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 2.4, 0.9 Hz, 1H), 8.10 – 8.01 (m, 2H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.74 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.66 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.60 – 7.47 (m, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.14 – 7.09 (m, 1H), 6.77 (td, *J* = 7.4, 1.0 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 4.66 (dd, *J* = 10.9, 9.2 Hz, 1H), 3.53 (dd, *J* = 15.7, 9.2 Hz, 1H), 3.07 (ddt, *J* = 15.7, 11.1, 1.2 Hz, 1H), 2.76 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.3, 153.2, 148.0, 135.7, 135.5, 135.0, 133.6, 132.9, 129.0, 128.4, 128.3, 127.8, 126.7, 126.5, 126.1, 125.1, 124.2, 121.1, 118.5, 107.5, 73.2, 38.1, 35.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{21}N_2$ 337.1699; Found 337.1692.

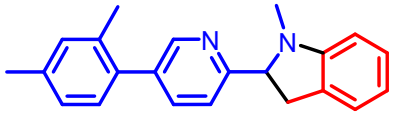
1-methyl-2-(5-(3-isopropyl)phenylpyridin-2yl)-2,3-indoline (3ga)



The compound was prepared according to procedure C with **1g** (39.4 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent)

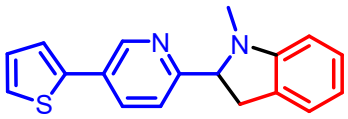
to give **3ga** (41.5 mg, 63%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.8 (dd, *J* = 2.3, 0.8 Hz, 1H), 7.9 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.6 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.5 (q, *J* = 1.5 Hz, 1H), 7.4 – 7.4 (m, 2H), 7.3 (td, *J* = 4.6, 1.8 Hz, 1H), 7.2 (t, *J* = 7.7 Hz, 1H), 7.1 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.8 (td, *J* = 7.4, 1.0 Hz, 1H), 6.6 (d, *J* = 7.7 Hz, 1H), 4.6 (dd, *J* = 11.0, 9.2 Hz, 1H), 3.5 (dd, *J* = 15.7, 9.1 Hz, 1H), 3.1 – 3.0 (m, 2H), 2.7 (s, 3H), 1.3 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1, 153.2, 149.8, 147.9, 137.8, 135.9, 135.5, 129.1, 128.5, 127.8, 126.2, 125.4, 124.7, 124.2, 121.0, 118.4, 107.5, 73.2, 38.1, 34.9, 34.3, 24.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2$ 329.2012; Found 329.2011.

1-methyl-2-(5-(2,4-dimethyl)phenylpyridin-2yl)-2,3-indoline (3ha)



The compound was prepared according to procedure C with **1h** (54.2 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ha** (41.0 mg, 65%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.2 Hz, 1H), 7.69 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.59 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.22 – 7.07 (m, 5H), 6.75 (td, *J* = 7.4, 1.0 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.63 (dd, *J* = 10.9, 9.2 Hz, 1H), 3.52 (dd, *J* = 15.7, 9.1 Hz, 1H), 3.07 (dd, *J* = 15.6, 10.9 Hz, 1H), 2.75 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.7, 153.2, 149.4, 137.8, 137.5, 136.4, 135.6, 132.5, 130.7, 130.6, 128.8, 128.5, 127.8, 124.2, 120.4, 118.4, 107.5, 73.2, 38.0, 35.0, 20.9, 20.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$ 315.1856; Found 318.1850.

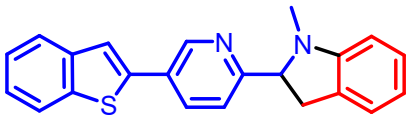
1-methyl-2-(5-(thiophen-2-yl)pyridin-2-yl)-2,3-indoline (3ia)



The compound was prepared according to procedure C with **1i** (49.0 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ia** (24.0 mg, 41%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.3 Hz, 1H), 7.88 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.15 – 7.10 (m, 2H),

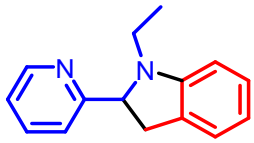
7.09 – 7.06 (m, 1H), 6.79 – 6.69 (m, 1H), 6.55 (d, J = 7.8 Hz, 1H), 4.56 (dd, J = 10.9, 9.1 Hz, 1H), 3.46 (dd, J = 15.7, 9.2 Hz, 1H), 2.99 (dd, J = 15.7, 10.9 Hz, 1H), 2.69 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 153.1, 146.5, 140.4, 134.2, 129.4, 128.3, 128.3, 127.8, 125.9, 124.2, 124.2, 121.1, 118.5, 107.5, 73.1, 38.0, 34.9. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2S$ 293.1107; Found 293.1099.

2-(5-(benzo[b]thiophen-2-yl)pyridin-2-yl)-1-methylindoline (3ja)



The compound was prepared according to procedure C with **1i** (60.5 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ja** (54.0 mg, 79%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 2.3 Hz, 1H), 7.99 (dd, J = 8.2, 2.4 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.63 – 7.60 (m, 2H), 7.42 – 7.34 (m, 2H), 7.20 – 7.16 (m, 2H), 6.78 – 6.74 (m, 1H), 6.60 (d, J = 7.8 Hz, 1H), 4.61 (dd, J = 9.2, 9.1 Hz, 1H), 3.50 (dd, J = 15.7, 9.2 Hz, 1H), 3.03 (dd, J = 15.7, 10.9 Hz, 1H), 2.73 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.2, 153.1, 146.9, 140.4, 140.2, 139.7, 134.7, 129.3, 128.3, 127.8, 124.90, 124.87, 124.2, 124.0, 122.4, 121.2, 120.6, 107.6, 73.1, 38.0, 34.9. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2S$ 343.1263; Found 343.1260.

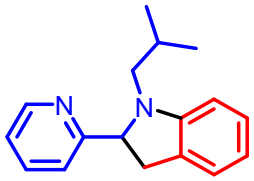
1-ethyl-2-(pyridin-2yl)-2,3-indoline (3ka)



The compound was prepared according to procedure C with **1k** (32.6 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ka** (39.2 mg, 87%) as light yellow solid. m.p. 30-31 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.69 (td, J = 7.7, 1.8 Hz, 1H), 7.54 (dt, J = 7.9, 1.1 Hz, 1H), 7.21 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 7.12 (t, J = 7.7 Hz, 1H), 7.05 (dd, J = 7.2, 1.3 Hz, 1H), 6.69 (td, J = 7.4, 1.0 Hz, 1H), 6.53 (d, J = 7.7 Hz, 1H), 4.86 (t, J = 9.8 Hz, 1H), 3.50 (dd, J = 15.8, 9.6 Hz, 1H), 3.30 (dq, J = 14.4, 7.2 Hz, 1H), 3.13 – 2.90 (m, 2H), 1.05 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100

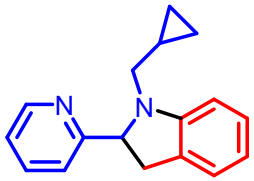
MHz, $CDCl_3$) δ 163.3, 151.7, 149.2, 136.9, 128.3, 127.7, 124.3, 122.4, 121.2, 117.7, 107.1, 69.4, 41.0, 38.2, 10.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2$ 225.1386; Found 225.1380.

1-ethyl-2-(pyridin-2yl)-2,3-indoline (3la)



The compound was prepared according to procedure C with **1l** (38.9 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3la** (35.9 mg, 71%) as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.21 – 7.19 (m, 1H), 7.17 – 7.10 (m, 1H), 7.08 – 7.02 (m, 1H), 6.67 – 6.63 (m, 1H), 6.47 (d, *J* = 7.7, 1H), 4.83 (d, *J* = 7.9 Hz, 1H), 3.56 (dd, *J* = 15.9, 9.6 Hz, 1H), 3.03 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.95 – 2.90 (m, 1H), 2.82 – 2.76 (m, 1H), 1.80 – 1.77 (m, 1h), 0.87 (d, *J* = 3.8 Hz, 3H), 0.77 (d, *J* = 3.8 Hz, 3H) $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 152.8, 149.2, 136.7, 127.6, 127.5, 124.3, 122.5, 121.4, 117.1, 106.1, 71.1, 56.2, 38.0, 27.55, 20.70, 20.54. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{21}N_2$ 253.1699; Found 253.1704.

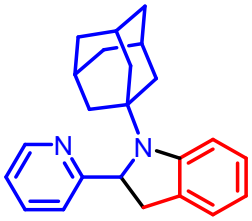
1-(cyclopropylmethyl)-2-(pyridin-2-yl)indoline (3ma)



The compound was prepared according to procedure C with **1m** (38.4 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ma** (32.5 mg, 65%) as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.9, 1H), 7.72 – 7.68 (m, 1H), 7.57 (d, *J* = 9.96 Hz, 1H), 7.28 (d, *J* = 1.9 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.17 – 7.07 (m, 1H), 6.73 – 6.72 (m, 1H), 6.71 – 6.6.61 (m, 1H), 5.07 (t, *J* = 10.1 Hz, 1H), 3.55 (dd, *J* = 15.7, 9.5 Hz, 1H), 3.32 (dd, *J* = 7.2, 1.8 Hz, 1H), 3.29 (dd, *J* = 7.2, 1.8 Hz, 1H), 2.72 – 2.67 (m, 1H), 0.92 – 0.90 (m, 1H), 0.48 – 0.46 (m, 1H), 0.33 – 0.31 (m, 1H), 0.09 – 0.06 (m, 1H),

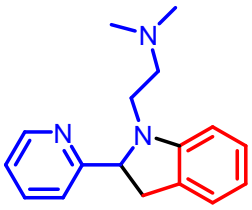
0.05 – -0.07 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 152.2, 149.2, 136.8, 128.1, 127.7, 124.3, 122.4, 121.4, 117.8, 107.2, 70.0, 51.8.0, 38.4, 8.1, 4.9, 2.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}N_2$ 251.1543; Found 251.1540.

1-((1s,3s)-adamantan-1-yl)-2-(pyridin-2-yl)indoline (3na)



The compound was prepared according to procedure C with **1n** (57.6 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3na** (52.8 mg, 80%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (ddd, *J* = 4.9, 2.7, 1,4 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.45 – 7.42 (m, 1H), 7.11 – 7.10 (m, 1H), 7.10 – 7.01 (m, 1H), 6.99 – 6.96 (m, 2H), 6.68 – 6.64 (m, 1H), 5.17 (dd, *J* = 10.6, 3.1 Hz, 1H), 3.65 – 3.58 (m, 1H), 2.78 (dd, *J* = 16.08 3.2 Hz, 1H), 2.06 – 1.99 (m, 9H), 1.65 – 1.60 (m, 6H), $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 149.7, 148.8, 136.7, 130.5, 126.6, 124.8, 121.7, 120.7, 117.9, 112.8, 63.9, 56.4, 41.0, 38.2, 36.5, 29.8 HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{27}N_2$ 331.2169; Found 331.2168.

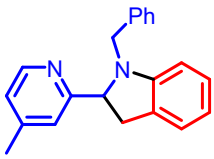
1-(cyclopropylmethyl)-2-(pyridin-2-yl)indoline (3oa)



The compound was prepared according to procedure C with **1o** (42.5 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3oa** (34.7 mg, 65%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.49 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.23 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.05 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.69 (td, *J* = 7.4, 1.0 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 4.86 (t, *J* = 9.8 Hz, 1H), 3.50 (dd, *J* = 15.8, 9.6 Hz, 1H), 3.30 (dd, *J*

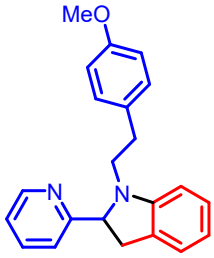
= 14.4, 7.2 Hz, 1H), 3.14 – 3.11 (m, 1H), 3.02 – 2.96 (m, 1H), 2.48 (t, *J* = 4.6 Hz, 1H), 2.32 (dd, *J* = 10.2, 4.8 Hz, 1H), 2.18 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 151.8, 149.2, 136.9, 128.3, 127.7, 124.3, 122.6, 121.3, 117.8, 106.6, 70.5, 55.7, 45.8, 45.4, 38.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{22}N_2$ 268.1808; Found 268.1804.

1-benzyl-2-(4-methylpyridin-2yl)-2,3-indoline (3pa)



The compound was prepared according to procedure C with **1p** (50.4 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3pa** (40.3 mg, 67%) as light yellow solid . m.p. 55-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.1 Hz, 1H), 7.46 – 7.32 (m, 2H), 7.27 (s, 2H), 7.24 – 7.18 (m, 1H), 7.11 – 7.04 (m, 2H), 7.00 (dd, *J* = 5.1, 1.7 Hz, 1H), 6.72 (td, *J* = 7.4, 1.0 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 4.85 (t, *J* = 9.8 Hz, 1H), 4.38 (d, *J* = 15.8 Hz, 1H), 4.14 (d, *J* = 15.8 Hz, 1H), 3.84 – 3.62 (m, 1H), 3.53 (dd, *J* = 15.9, 9.5 Hz, 1H), 3.08 (dd, *J* = 15.9, 10.2 Hz, 1H), 2.30 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.4, 152.3, 149.0, 148.0, 138.3, 128.8, 128.4, 128.3, 128.2, 127.7, 126.9, 124.3, 123.5, 122.3, 118.2, 107.6, 70.8, 52.0, 38.1, 21.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{21}N_2$301.1699; Found 301.1695.

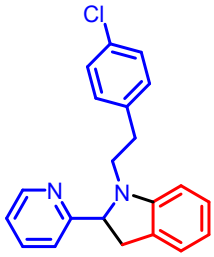
1-benzyl-2-(4-methylpyridin-2yl)-2,3-indoline (3qa)



The compound was prepared according to procedure C with **1q** (60.9 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3qa** (45.7 mg, 69%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 3.5, 1.2 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.19 – 7.18 (m, 2H),

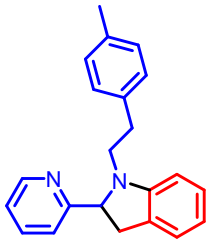
7.17 – 7.13 (m, 1H), 7.08 – 7.00 (m, 1H), 6.99 – 6.77 (m, 2H), 6.72 – 6.68 (m, 1H), 6.56 (d, J = 6.6 Hz, 1H), 4.88 (t, J = 8.8 Hz, 1H), 3.77 (s, 3H), 3.51 (dd, J = 15.8, 9.6 Hz, 1H), 3.39 – 3.35 (m, 1H), 3.18 – 3.14 (m, 1H), 2.98 (dd, J = 15.9, 9.6 Hz, 1H), 2.77 – 2.68 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 158.0, 151.6, 149.2, 137.0, 131.7, 129.7, 128.2, 127.8, 124.4, 122.5, 121.3, 117.8, 113.9, 106.8, 70.0, 55.3, 49.2, 38.1, 31.4. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$ 331.1805; Found 331.1809.

1-benzyl-2-(4-methylpyridin-2yl)-2,3-indoline (3ra)



The compound was prepared according to procedure C with **1r** (61.9 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ra** (38.2 mg, 55%) as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 3.5, 1.2 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.39 – 7.37 (m, 1H), 7.23 – 7.16 (m, 4H), 7.14 – 7.12 (m, 1H), 7.09 – 7.00 (m, 2H), 6.74 – 6.70 (m, 1H), 6.55 (d, J = 7.8 Hz, 1H), 4.84 (t, J = 9.6 Hz, 1H), 3.54 – 3.52 (m, 1H), 3.50 – 3.39 (m, 1H), 3.19 – 3.17 (m, 1H), 2.98 (d, J = 9.6 Hz, 1H), 2.77 – 2.73 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 151.4, 149.2, 138.2, 137.0, 131.9, 130.1, 128.6, 128.2, 127.8, 124.4, 122.5, 121.3, 118.0, 106.8, 70.2, 49.0, 38.1, 31.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{20}ClN_2$ 348.1393; Found 348.1391.

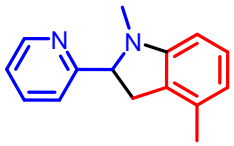
(S)-1-(4-methylphenethyl)-2-(pyridin-2yl)-2,3-indoline (3sa)



The compound was prepared according to procedure C with **1s** (54.2 mg, 0.24 mmol), **2a** (37.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent)

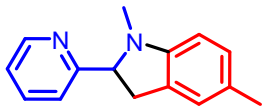
to give **3na** (38.5 mg, 61%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 5.2, 1.7 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.11 (m, 2H), 7.11 – 7.04 (m, 3H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.91 (t, *J* = 9.6 Hz, 1H), 3.53 (dd, *J* = 15.9, 9.6 Hz, 1H), 3.42 (ddd, *J* = 14.3, 10.5, 5.6 Hz, 1H), 3.17 (ddd, *J* = 14.3, 10.4, 5.7 Hz, 1H), 3.01 (dd, *J* = 15.8, 9.6 Hz, 1H), 2.76 (dddd, *J* = 29.2, 13.2, 10.4, 5.6 Hz, 2H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.0, 151.5, 149.3, 136.9, 136.6, 135.7, 129.2, 128.6, 128.2, 127.8, 124.4, 122.5, 121.3, 117.8, 106.8, 70.0, 49.1, 38.1, 31.7, 21.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$ 315.1856; Found 315.1855

1,4-dimethyl-2-(pyridin-2yl)-2,3-indoline (3ab)



The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2b** (40.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ab** (24.8 mg, 55%) as light yellow solid . m.p. 61-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.55 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.22 (ddd, *J* = 7.5, 4.9, 1.3 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 4.56 (dd, *J* = 10.8, 9.4 Hz, 1H), 3.45 (dd, *J* = 15.7, 9.4 Hz, 1H), 2.89 (s, 1H), 2.69 (s, 3H), 2.19 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7, 153.0, 149.3, 137.0, 133.8, 127.9, 126.9, 122.5, 121.0, 119.8, 105.0, 73.1, 36.8, 35.1, 18.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2$ 225.1386; Found 225.1382.

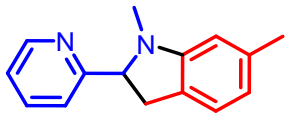
1,5-dimethyl-2-(pyridin-2yl)-2,3-indoline (3ac)



The compound was prepared according to procedure B with **1a** (29.3mg, 0.24 mmol), **2c** (40.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ac** (27.5 mg, 61%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.74 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.25 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.04 – 6.90 (m, 2H), 6.51 (d, *J* = 7.8 Hz, 1H), 4.52 (dd, *J* = 11.2, 9.0 Hz, 1H), 3.44 (dd, *J* =

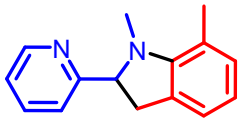
15.6, 9.0 Hz, 1H), 2.97 (ddt, *J* = 15.6, 11.3, 1.2 Hz, 1H), 2.69 (s, 3H), 2.30 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5, 151.1, 149.3, 137.0, 128.7, 127.9, 125.1, 122.5, 121.1, 107.6, 73.9, 38.1, 35.4, 20.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2$ 225.1386; Found 225.1387.

1,6-dimethyl-2-(pyridin-2yl)-2,3-indoline (3ad)



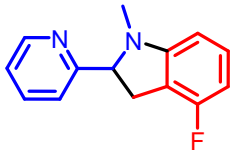
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2d** (40.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ad** (26.1 mg, 58%) as white solid . m.p. 45-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.22 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.55 (ddd, *J* = 7.3, 1.5, 0.8 Hz, 1H), 6.40 (d, *J* = 1.4 Hz, 1H), 4.55 (dd, *J* = 10.9, 9.1 Hz, 1H), 3.43 (dd, *J* = 15.5, 9.1 Hz, 1H), 2.92 (ddt, *J* = 15.6, 10.9, 1.2 Hz, 1H), 2.68 (s, 3H), 2.33 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.6, 153.4, 149.3, 137.6, 137.0, 125.5, 123.9, 122.5, 121.0, 119.0, 108.5, 73.7, 37.7, 34.9, 21.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2$ 225.1386; Found 225.1382.

1,7-dimethyl-2-(pyridin-2yl)-2,3-indoline (3ae)



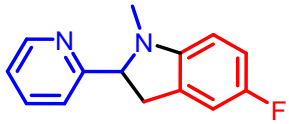
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2e** (40.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ae** (28.4 mg, 63%) as light yellow solid . m.p. 33-34 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.62 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.21 (ddd, *J* = 7.4, 4.9, 1.3 Hz, 1H), 6.93 (dd, *J* = 13.8, 7.3 Hz, 2H), 6.71 (t, *J* = 7.4 Hz, 1H), 4.48 (dd, *J* = 10.9, 9.5 Hz, 1H), 3.53 (dd, *J* = 15.7, 9.5 Hz, 1H), 2.90 (s, 4H), 2.43 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 151.3, 149.3, 137.0, 131.1, 129.2, 122.4, 122.2, 121.1, 120.3, 119.7, 74.2, 39.2, 37.9, 19.7. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2$ 225.1386; Found 225.1381.

4-fluoro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3af)



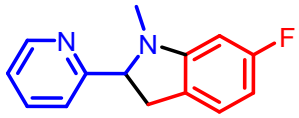
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2f** (41.4 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3af** (24.7 mg, 54%) as white solid . m.p. 73-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.6 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.7 (td, J = 7.7, 1.9 Hz, 1H), 7.5 (dt, J = 7.9, 1.2 Hz, 1H), 7.2 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 7.1 (td, J = 8.1, 5.8 Hz, 1H), 6.5 – 6.4 (m, 1H), 6.3 (d, J = 7.8 Hz, 1H), 4.6 (dd, J = 10.4, 9.4 Hz, 1H), 3.6 (dd, J = 15.9, 9.5 Hz, 1H), 3.0 (dd, J = 16.0, 10.5 Hz, 1H), 2.7 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7, 159.2 (J = 244.7), 155.7 (J = 9.3), 149.5, 137.0, 129.5 (J = 8.6 Hz), 122.7, 121.2, 113.4 (J = 21.4 Hz), 105.6 (J = 21.0 Hz), 103.1 (J = 2.9 Hz), 73.24, 34.62, 34.02. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.89. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}FN_2$ 229.1136; Found 229.1133.

5-fluoro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3ag)



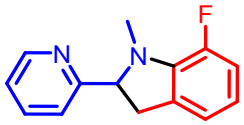
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2g** (41.4 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ag** (20.2 mg, 44%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.72 (td, J = 7.7, 1.8 Hz, 1H), 7.52 (dt, J = 7.9, 1.2 Hz, 1H), 7.23 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 6.88 – 6.75 (m, 2H), 6.46 – 6.37 (m, 1H), 4.52 (dd, J = 11.2, 9.0 Hz, 1H), 3.40 (dd, J = 15.9, 9.0 Hz, 1H), 2.98 (ddd, J = 15.9, 11.1, 1.3 Hz, 1H), 2.65 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 149.5, 137.0, 130.0 (J = 8.0 Hz), 122.6, 121.2, 113.3 (J = 22.0 Hz), 111.9 (J = 24.0 Hz), 107.5 (J = 8.0 Hz), 74.0, 37.7, 35.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.88. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}FN_2$ 229.1136; Found 229.1134.

6-fluoro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3ah)



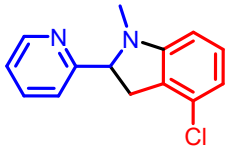
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2h** (41.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ah** (24.3 mg, 53%) as light yellow solid . m.p. 50-51 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.47 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.23 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.94 (ddt, *J* = 8.0, 5.6, 1.2 Hz, 1H), 6.36 (ddd, *J* = 10.0, 8.0, 2.4 Hz, 1H), 6.22 (dd, *J* = 10.2, 2.4 Hz, 1H), 4.64 (dd, *J* = 10.5, 9.2 Hz, 1H), 3.47 – 3.36 (m, 1H), 2.94 (ddt, *J* = 15.5, 10.4, 1.7 Hz, 1H), 2.67 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 154.7 (*J* = 11.5 Hz), 149.5, 137.0, 124.3 (*J* = 10.6 Hz), 123.5 (*J* = 2.5 Hz), 122.7, 121.1, 103.8 (*J* = 22.4 Hz), 95.3 (*J* = 26.8 Hz), 73.7, 37.2, 34.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.46. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}FN_2$ 229.1136; Found 229.1145.

7-fluoro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3ai)



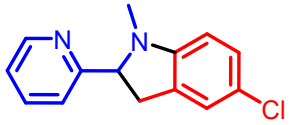
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2i** (41.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ai** (31.0 mg, 68%) as light yellow solid . m.p. 50-51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.58 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.23 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 6.90 – 6.81 (m, 2H), 6.67 (ddd, *J* = 8.3, 7.2, 4.3 Hz, 1H), 4.55 (dd, *J* = 11.3, 9.4 Hz, 1H), 3.52 (dd, *J* = 15.9, 9.4 Hz, 1H), 3.00 (dd, *J* = 15.9, 11.3 Hz, 1H), 2.89 (d, *J* = 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 149.5, 149.4 (*J* = 239 Hz), 139.5 (*J* = 8.5 Hz), 137.1, 132.1 (*J* = 5.4 Hz) , 122.6, 121.2, 120.0 (*J* = 2.9 Hz), 119.6 (*J* = 6.0 Hz), 115.5 (*J* = 19.6 Hz), 38.5, 37.4, 37.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.58. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}FN_2$ 229.1136; Found 229.1128.

4-chloro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3aj)



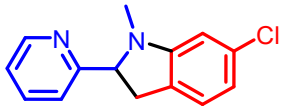
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2j** (44.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3aj** (27.9 mg, 57%) as light yellow solid . m.p. 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.47 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.29 – 7.19 (m, 1H), 7.06 (td, *J* = 7.9, 0.8 Hz, 1H), 6.67 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 4.63 (t, *J* = 9.9 Hz, 1H), 3.55 (dd, *J* = 16.4, 9.6 Hz, 1H), 2.99 (ddd, *J* = 16.3, 10.4, 1.1 Hz, 1H), 2.68 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.8, 154.3, 149.5, 137.0, 130.2, 129.2, 126.4, 122.7, 121.2, 118.2, 105.3, 72.4, 37.0, 34.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}ClN_2$ 245.0840; Found 245.0837.

5-chloro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3ak)



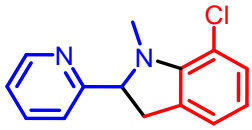
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2k** (44.6 mg, 0.20 mmol) and LiN(SiMe3)2 (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ak** (24.0 mg, 49%) as light yellow solid . m.p. 60-61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.23 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.08 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.02 (dt, *J* = 2.2, 1.1 Hz, 1H), 6.43 (d, *J* = 8.3 Hz, 1H), 4.57 (dd, *J* = 10.7, 9.1 Hz, 1H), 3.42 (dd, *J* = 15.9, 9.2 Hz, 1H), 3.04 – 2.92 (m, 1H), 2.66 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7, 151.8, 149.5, 137.0, 130.2, 127.4, 124.4, 122.9, 122.7, 121.2, 108.0, 73.3, 37.5, 34.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}ClN_2$ 245.0840; Found 245.0848.

6-chloro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3al)



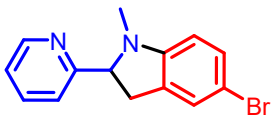
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2l** (44.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3al** (28.9 mg, 59%) as a yellow oil .^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 5.0, 1.9, 1.0 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.28 – 7.19 (m, 1H), 6.94 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.66 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.47 (d, *J* = 1.9 Hz, 1H), 4.63 (dd, *J* = 10.4, 9.3 Hz, 1H), 3.42 (dd, *J* = 15.8, 9.3 Hz, 1H), 2.94 (ddd, *J* = 15.9, 10.3, 1.4 Hz, 1H), 2.67 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.8, 154.3, 149.5, 137.1, 133.4, 126.8, 124.7, 122.7, 121.1, 117.8, 107.5, 73.3, 37.3, 34.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}ClN_2$ 245.0840; Found 245.0831.

7-chloro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3am)



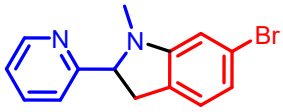
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2m** (44.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3am** (30.9 mg, 63%) as light yellow solid . m.p. 42-43 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.23 (ddt, *J* = 8.0, 4.3, 1.6 Hz, 2H), 7.15 (dt, *J* = 2.2, 1.2 Hz, 1H), 6.39 (d, *J* = 8.3 Hz, 1H), 4.57 (dd, *J* = 10.7, 9.2 Hz, 1H), 3.43 (dd, *J* = 15.9, 9.2 Hz, 1H), 2.99 (ddt, *J* = 16.0, 10.7, 1.2 Hz, 1H), 2.66 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4, 149.4, 148.3, 137.1, 131.7, 129.9, 122.7, 122.6, 121.0, 120.1, 115.5, 73.8, 38.0, 37.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}ClN_2$ 245.0840; Found 245.0834.

4-bromo -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3an)



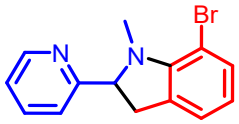
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2n** (53.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3an** (31.8 mg, 55%) as light yellow solid . m.p. 62-63°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.47 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.23 (ddt, *J* = 8.0, 4.3, 1.6 Hz, 2H), 7.15 (dt, *J* = 2.2, 1.2 Hz, 1H), 6.39 (d, *J* = 8.3 Hz, 1H), 4.57 (dd, *J* = 10.7, 9.2 Hz, 1H), 3.43 (dd, *J* = 15.9, 9.2 Hz, 1H), 2.99 (ddt, *J* = 16.0, 10.7, 1.2 Hz, 1H), 2.66 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7, 152.2, 149.5, 137.0, 130.7, 130.3, 127.1, 122.7, 121.2, 109.9, 108.6, 73.2, 37.5, 34.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}BrN_2$ 289.0335; Found 289.0340.

6-bromo -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3ao)



The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2o** (53.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ao** (25.4 mg, 44%) as light yellow solid . m.p. 62-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, J = 4.85, 1.84, 0.94 Hz, 1H), 7.71 (td, J = 7.69, 1.83 Hz, 1H), 7.45 (dt, J = 7.86, 1.07 Hz, 1H), 7.23 (ddd, J = 7.59, 4.88, 1.20 Hz, 1H), 6.90-6.79 (m, 2H), 6.62 (d, J = 1.79 Hz, 1H), 4.62 (dd, J = 10.31, 9.31 Hz, 1H), 3.41 (dd, J = 15.90, 9.32 Hz, 1H), 2.92 (ddd, J = 15.95, 10.31, 1.34 Hz, 1H), 2.66 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7, 154.5, 149.5, 137.1, 127.4, 125.2, 122.7, 121.4, 121.0, 120.7, 110.2, 73.1, 37.3, 34.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}BrN_2$ 289.0335; Found 289.0333.

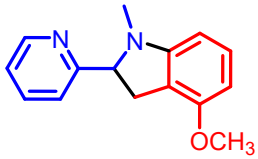
7-bromo -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3ap)



The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2p** (53.6 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ap** (36.9 mg, 64%) as a yellow oil .^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.9, 1.8,

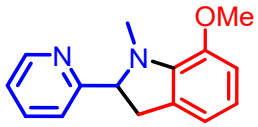
1.0 Hz, 1H), 7.71 (td, *J* = 7.6, 1.8 Hz, 1H), 7.57 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.33 – 7.14 (m, 2H), 6.98 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.60 (dd, *J* = 8.1, 7.1 Hz, 1H), 4.59 (t, *J* = 10.0 Hz, 1H), 3.56 (ddt, *J* = 16.0, 9.8, 0.9 Hz, 1H), 3.08 (s, 3H), 2.92 (ddt, *J* = 16.0, 10.1, 1.2 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.6, 149.7, 149.4, 137.1, 133.1, 132.0, 123.3, 122.5, 121.0, 120.5, 103.1, 73.8, 38.4, 37.4. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}BrN_2$ 289.0335; Found 289.0329.

4-methoxy -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3aq)



The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2q** (43.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3aq** (30.4 mg, 63%) as light yellow solid . m.p. 87-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dt, *J* = 4.8, 1.3 Hz, 1H), 7.70 (td, *J* = 7.7, 1.8 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.21 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.34 (d, *J* = 8.3 Hz, 1H), 6.25 (d, *J* = 7.8 Hz, 1H), 4.57 (t, *J* = 10.1 Hz, 1H), 3.80 (s, 3H), 3.51 (dd, *J* = 15.9, 9.6 Hz, 1H), 2.86 (dd, *J* = 15.9, 10.6 Hz, 1H), 2.68 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.6, 155.9, 154.8, 149.3, 137.0, 129.1, 122.5, 121.1, 114.3, 101.9, 101.3, 73.5, 55.3, 35.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2O$ 241.1335; Found 241.1330.

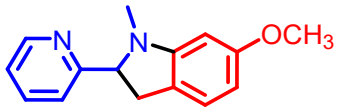
7-methoxy -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3as)



The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2s** (43.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3as** (31.8mg, 66%) as a white solid. m.p. 73-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 5.0, 1.8, 1.0 Hz, 1H), 7.71 (td, *J* = 7.6, 1.8 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.23 – 7.17 (m, 1H), 6.80 – 6.71 (m, 3H), 4.47 (dd, *J* = 11.5, 9.5 Hz, 1H), 3.84 (s, 3H), 3.53 (dd, *J* = 15.7, 9.5 Hz, 1H), 3.03 – 2.83 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 149.3, 146.6, 141.3, 137.1,

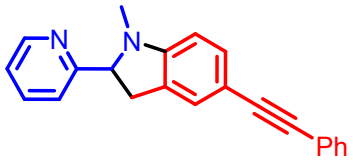
130.4, 122.5, 121.2, 120.3, 117.4, 111.6, 74.6, 55.9, 38.7, 38.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2O$ 241.1335; Found 241.1329.

6-methoxy -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3ar)



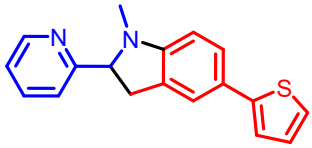
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2r** (43.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ar** (28.9 mg, 60%) as a white solid. m.p. 73-74 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.70 (td, *J* = 7.7, 1.8 Hz, 1H), 7.51 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.22 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.95 (dt, *J* = 7.9, 1.2 Hz, 1H), 6.25 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.14 (d, *J* = 2.3 Hz, 1H), 4.59 (dd, *J* = 10.5, 9.2 Hz, 1H), 3.80 (s, 3H), 3.40 (dd, *J* = 15.3, 9.2 Hz, 1H), 2.91 (ddd, *J* = 15.3, 10.5, 1.3 Hz, 1H), 2.67 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.4, 160.5, 154.5, 149.3, 137.0, 124.2, 122.5, 121.0, 120.7, 102.1, 95.1, 73.8, 55.5, 37.3, 34.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2O$ 241.1335; Found 241.1329.

1-methyl-5-(phenylethynyl)-2-(pyridin-2-yl)- 2,3-indoline (3at)



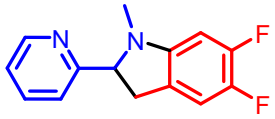
The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2s** (57.8 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3as** (30.5 mg, 49%) as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.71 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.50 (t, *J* = 1.9 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.37 – 7.31 (m, 3H), 7.31 – 7.28 (m, 1H), 7.26 – 7.21 (m, 2H), 6.47 (d, *J* = 8.1 Hz, 1H), 4.67 (t, *J* = 9.7 Hz, 1H), 3.49 (dd, *J* = 15.9, 9.4 Hz, 1H), 3.01 (ddt, *J* = 15.8, 10.1, 1.1 Hz, 1H), 2.72 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.9, 153.1, 149.5, 137.1, 132.1, 131.3, 128.4, 128.3, 127.5, 127.4, 124.2, 122.7, 121.1, 112.1, 106.6, 90.8, 87.1, 72.7, 37.4, 34.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2$ 311.1543; Found 311.1544.

1-methyl-2-(pyridin-2-yl)-5-(thiophen-2-yl)- 2,3-indoline (3au)



The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2t** (54.2 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3ar** (35.7 mg, 61%) as light yellow solid. m.p. 94-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.50 (m, 1H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.42 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.28 – 7.18 (m, 1H), 7.18 – 7.12 (m, 2H), 7.03 (dd, *J* = 4.8, 3.9 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 4.63 (dd, *J* = 10.6, 9.2 Hz, 1H), 3.51 (dd, *J* = 15.8, 9.2 Hz, 1H), 3.12 – 2.95 (m, 1H), 2.72 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.1, 152.8, 149.5, 145.6, 137.1, 129.1, 127.9, 125.9, 125.1, 122.8, 122.7, 122.2, 121.1, 121.1, 107.3, 73.2, 37.7, 34.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2S$ 293.1107; Found 293.1102.

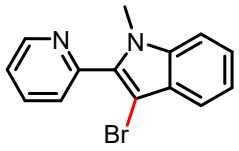
5,6-difluoro -1-methyl-2-(pyridin-2-yl)- 2,3-indoline (3av)



The compound was prepared according to procedure B with **1a** (29.3 mg, 0.24 mmol), **2u** (45.0 mg, 0.20 mmol) and $LiN(SiMe_3)_2$ (80.2 mg, 0.48 mmol) in tetrahydrofuran (2 mL). The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **3as** (31.2 mg, 63%) as light yellow solid. m.p. 63-64°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.23 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.93 – 6.73 (m, 1H), 6.29 (dd, *J* = 11.2, 6.5 Hz, 1H), 4.56 (dd, *J* = 10.9, 9.1 Hz, 1H), 3.37 (dd, *J* = 15.7, 9.1 Hz, 1H), 2.99-2.91 (m, 1H), 2.63 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 150.3 (dd, J = 241.3, 13.8 Hz), 149.6, 149.5, 143.7 (dd, J = 234.6, 13.6 Hz), 137.0, 123.2 (dd, J = 5.9, 2.9 Hz), 122.8, 121.2, 113.1 (J = 20.0 Hz), 96.7 (J =

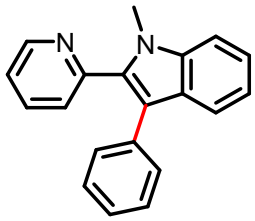
21.9 Hz), 73.7, 37.1, 35.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.96, -152.1187. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{13}F_2N_2$ 247.1041; Found 247.1147.

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



The compound was prepared according to procedure D. The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **5** (1.5 g, 53%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.9 Hz, 1H), 7.88 – 7.82 (m, *2*H), 7.65 (d, *J* = 7.9, Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.1, 149.6, 137.4, 136.3, 135.8, 127.1, 126.7, 123.6, 122.7, 120.6, 119.8, 110.0, 91.4, 32.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{12}BrN_2$ 287.0178; Found 287.0175.

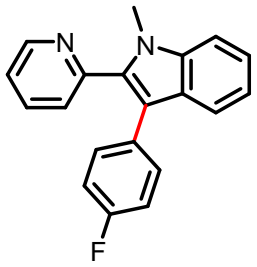
1-methyl-3-phenyl-2-(pyridin-2-yl)-1H-indole (6)



A flame-dried two-neck flask (250 mL) equipped with a stirring bar was charged with bromide **5** (0.1 g, 0.35 mmol, 1 equiv.), K_2CO_3 (0.15 g, 1.05 mmol, 3 equiv.), $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol, 0.1 equiv.) and phenyl boric acid (0.85 g, 0.7 mmol, 2 equiv.) in 1,4-dioxane and water (20/1) under Ar with stirring at rt. The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **6** (56.2 mg, 62%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (ddd, *J* = 2.8, 1.9, 0.9 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.55 – 7.51 (m, 1H), 7.47 – 7.44 (m, 1H), 7.35 – 7.24 (m, 5H), 7.23 – 7.16 (m, 4H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR

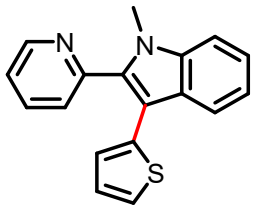
(100 MHz, $CDCl_3$) δ 151.8, 149.5, 137.9, 136.0, 135.7, 135.1, 130.2, 128.4, 127.2, 126.9, 126.1, 122.9, 122.1, 120.2, 119.9, 117.0, 109.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{17}BrN_2$ 285.1386; Found 285.1380.

3-(4-fluorophenyl)-1-methyl-2-(pyridin-2-yl)-1H-indole (7)



A flame-dried two-neck flask (250 mL) equipped with a stirring bar was charged with bromide **5** (0.1 g, 0.35 mmol, 1 equiv.), K_2CO_3 (0.15 g, 1.05 mmol, 3 equiv.), $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol, 0.1 equiv.) and phenyl boric acid (0.85 g, 0.7 mmol, 2 equiv.) in 1,4-dioxane and water (20/1) under Ar with stirring at rt. The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **7** (68.9 mg, 65%) as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 – 8.77 (m, 1H), 7.69 (d, J = 7.96 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.45 (d, J = 8.24 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.29 – 7.22 (m, 3H), 7.21 – 7.14 (m, 2H), 7.04 – 7.00 (m, 3H), 3.88 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.5, (d, J = 246.4 Hz), 151.6, 149.6, 137.8, 136.1, 135.7, 131.6 (d, J = 7.8 Hz), 131.0 (d, J = 2.9 Hz), 127.1, 126.9, 123.0, 122.2, 120.3, 119.7, 115.9, 115.6 (d, J = 21.0 Hz), 109.9, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.7. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{16}FN_2$ 303.1292; Found 303.1287.

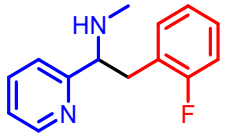
1-methyl-2-(pyridin-2-yl)-3-(thiophen-2-yl)-1H-indole (8)



A flame-dried two-neck flask (250 mL) equipped with a stirring bar was charged with bromide **5** (0.1 g, 0.35 mmol, 1 equiv.), K_2CO_3 (0.15 g, 1.05 mmol, 3 equiv.), $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol, 0.1 equiv.) and phenyl boric acid (0.85 g, 0.7 mmol, 2 equiv.) in 1,4-dioxane and water (20/1) under Ar with stirring at rt. The crude material was purified via silica gel chromatography (20:1 petroleum ether: ethyl acetate as eluent) to give **8** (40.1 mg, 45%) as light yellow oil. ^1H NMR

(400 MHz, $CDCl_3$) δ 8.45 (ddd, *J* = 2.8, 1.9, 1.0 Hz, 1H), 7.89 – 7.87 (m, 1H), 7.68 – 7.63 (m, 1H), 7.46 – 7.23 (m, 6H), 7.03 (dd, *J* = 5.2, 3.5 Hz, 1H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.4, 149.6, 137.6, 136.6, 136.2, 127.2, 127.0, 126.0, 124.4, 123.1, 122.6, 120.5, 120.1, 109.8, 109.6, 31.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{15}N_2$ 291.0950; Found 291.0945.

N-methyl- α -(2-fluorobenzyl bromide)-2-pyridinemethanamine (4aa)



This compound was purified by column chromatography (MeOH/DCM = 1:20, R_f =0.3) to afford as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.84, 1.78, 0.90 Hz, 1H), 7.55 (td, *J* = 7.67, 1.84 Hz, 1H), 7.18 – 7.11 (m, 2H), 7.09 (dt, *J* = 7.76, 1.10 Hz, 1H), 7.01 – 6.92 (m, 3H), 3.91 (t, *J* = 7.12 Hz, 1H), 3.16 – 2.96 (m, 2H), 2.27 (s, 3H), 1.98 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.2, 161.4 (d, *J* = 246.3 Hz), 149.6, 136.2, 131.7 (d, *J* = 5.0 Hz), 128.1 (d, *J* = 8.0 Hz), 125.6 (d, *J* = 15.3 Hz), 123.8 (d, *J* = 3.6 Hz), 122.4 (d, *J* = 36.8 Hz), 115.2 (d, *J* = 21.9 Hz), 66.2, 36.5, 34.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{16}FN_2$ 231.1292; Found 231.1284.

NMR Data

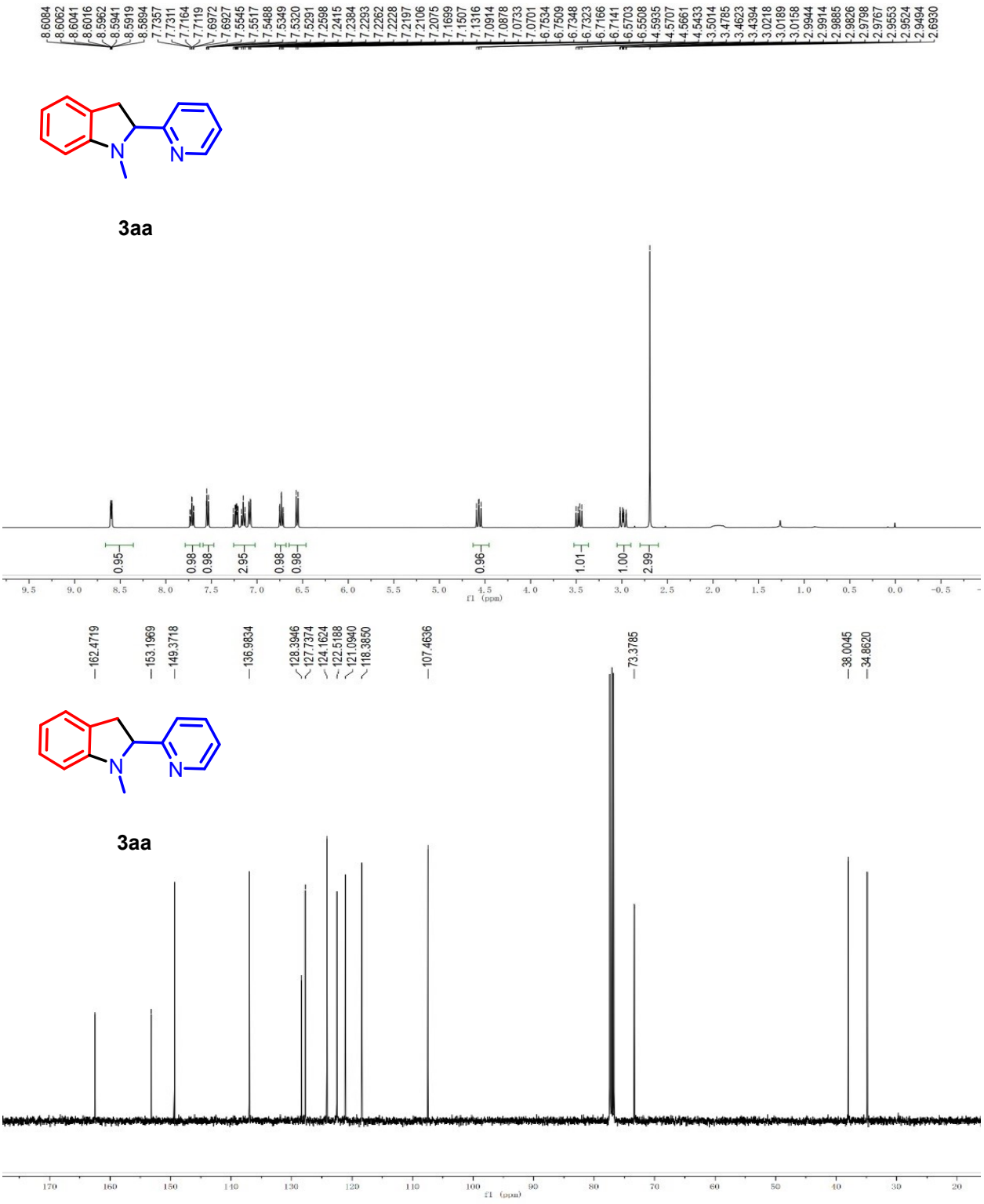


Figure S1. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3aa in $CDCl_3$

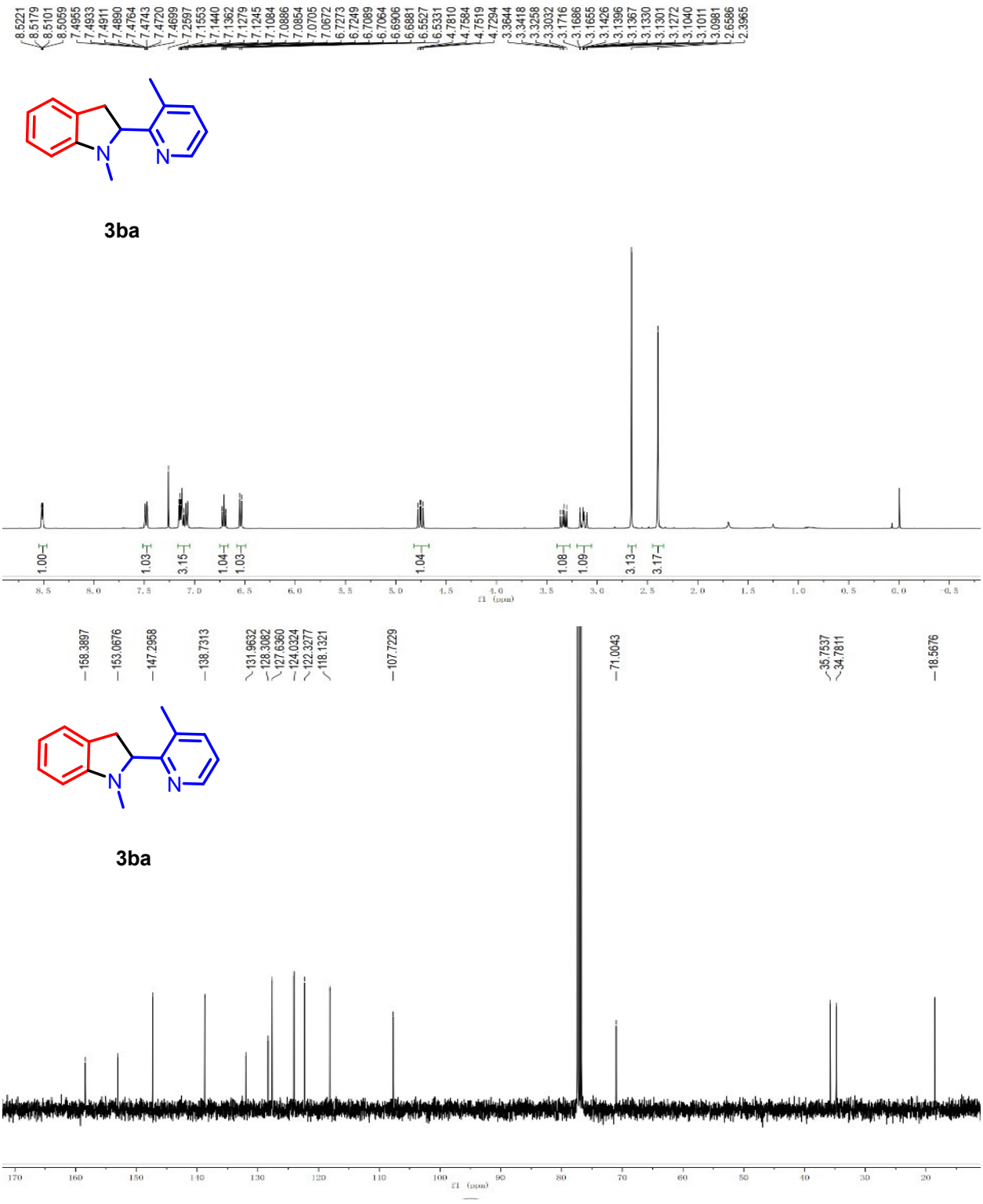


Figure S2. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ba in $CDCl_3$

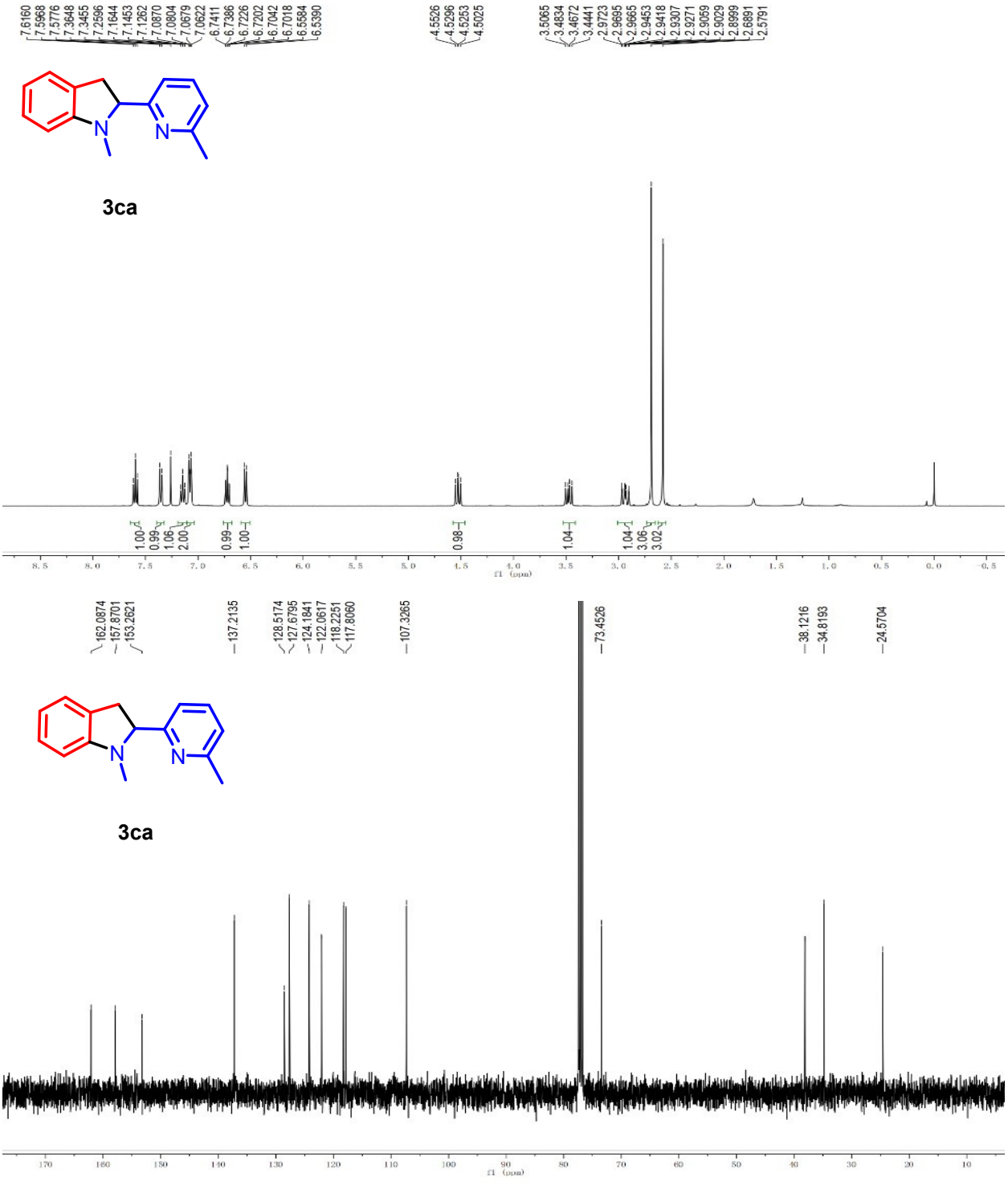


Figure S3. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ca in $CDCl_3$

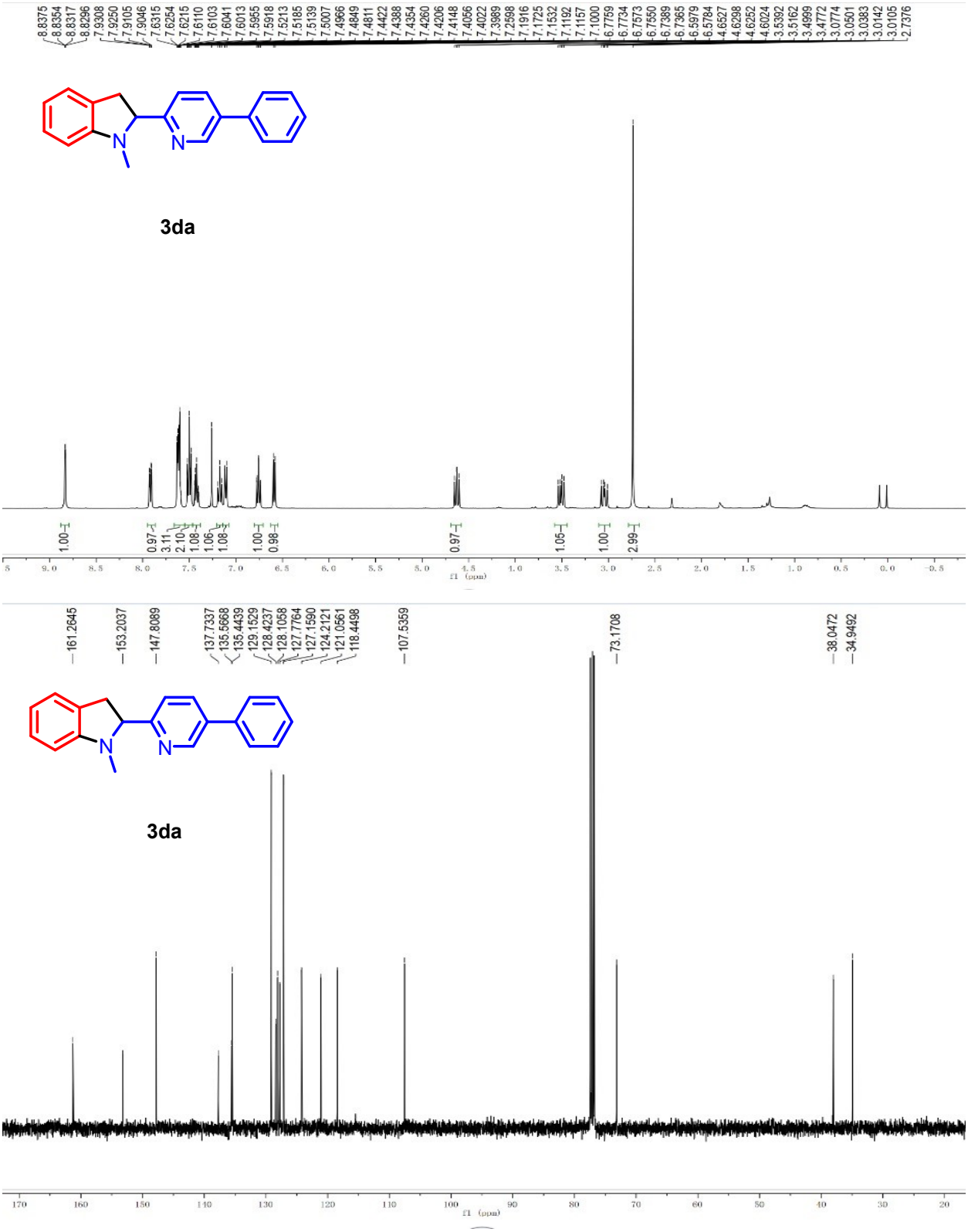


Figure S4. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3da in $CDCl_3$

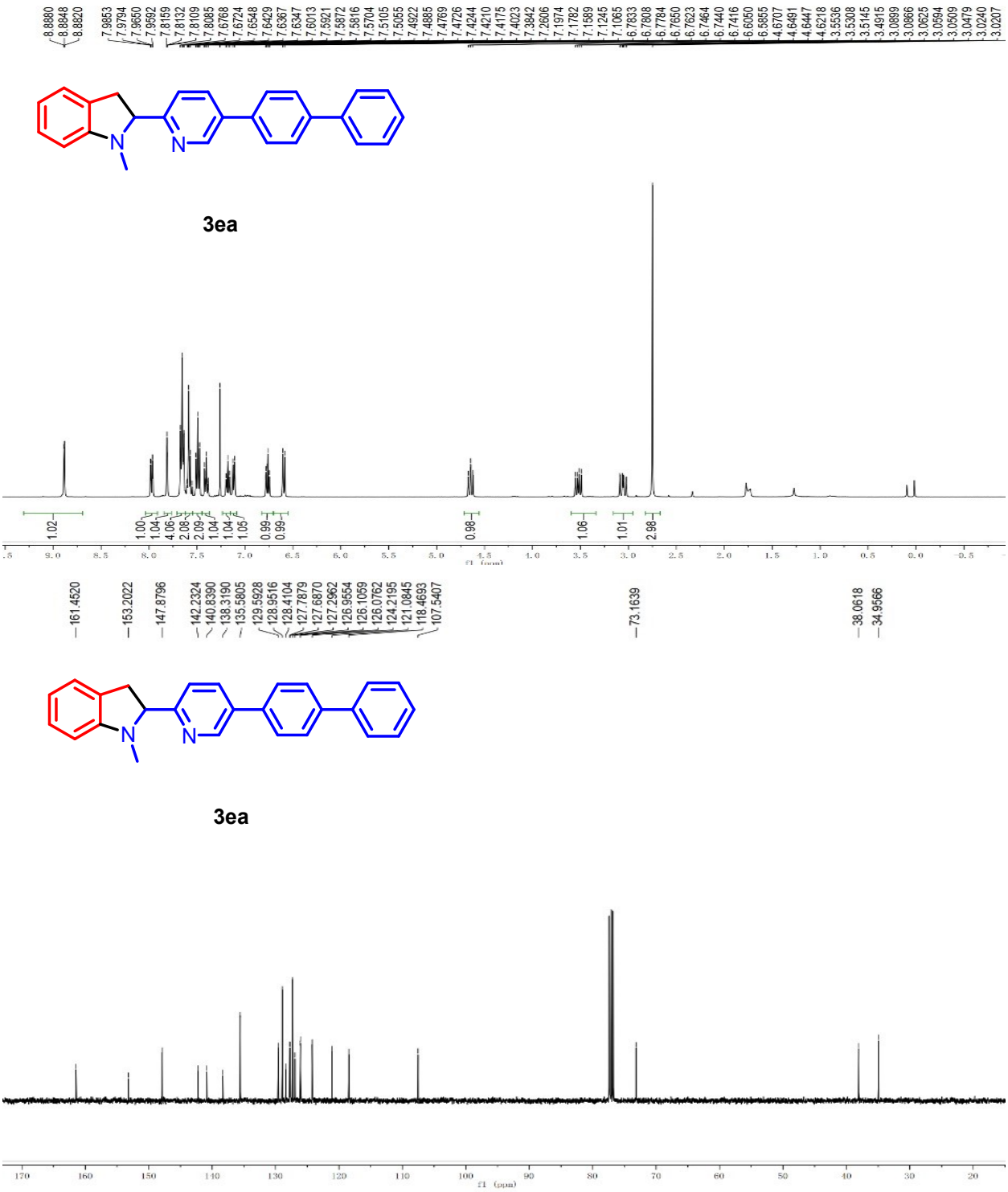


Figure S5. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ea in $CDCl_3$

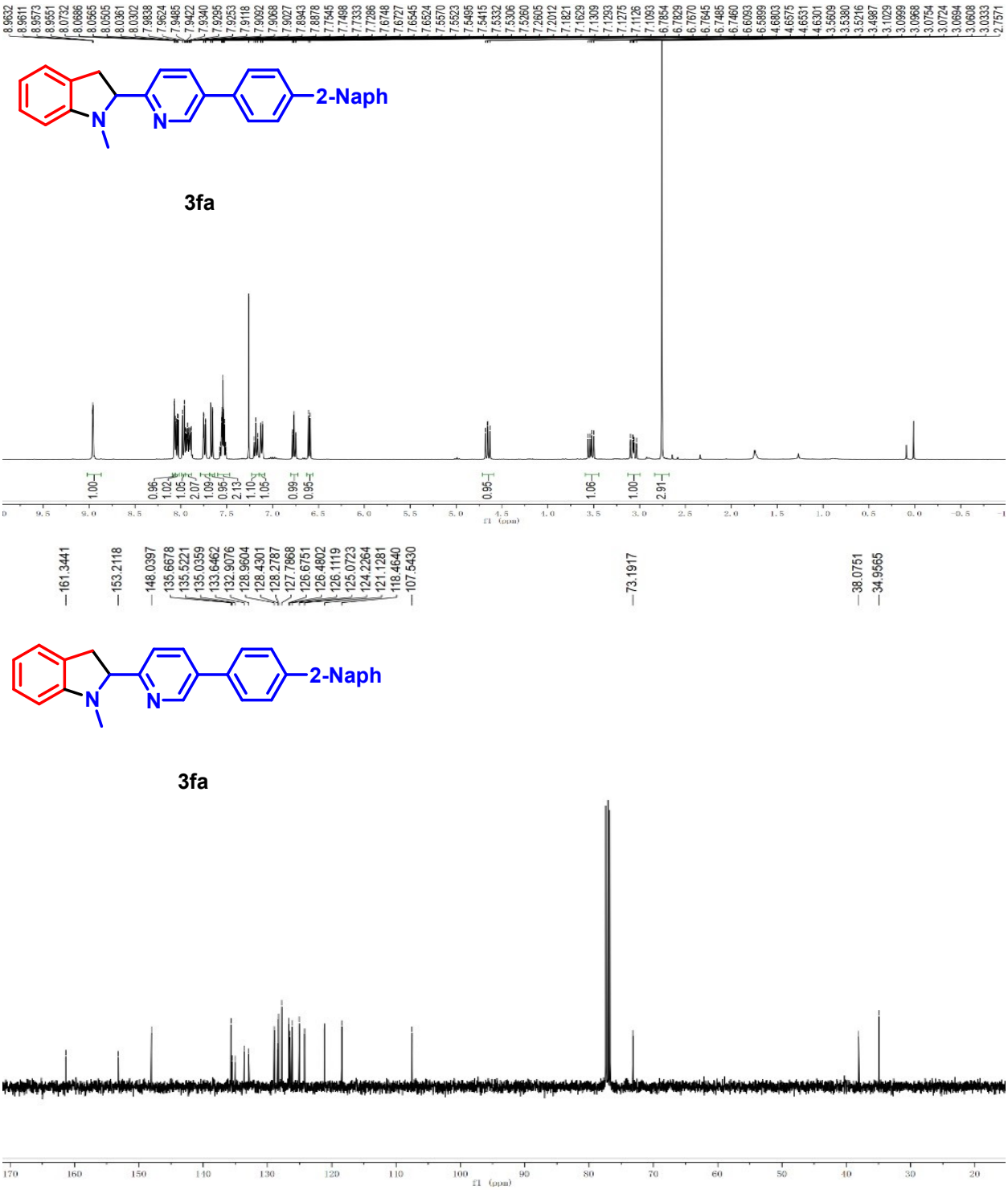


Figure S6. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3fa in $CDCl_3$

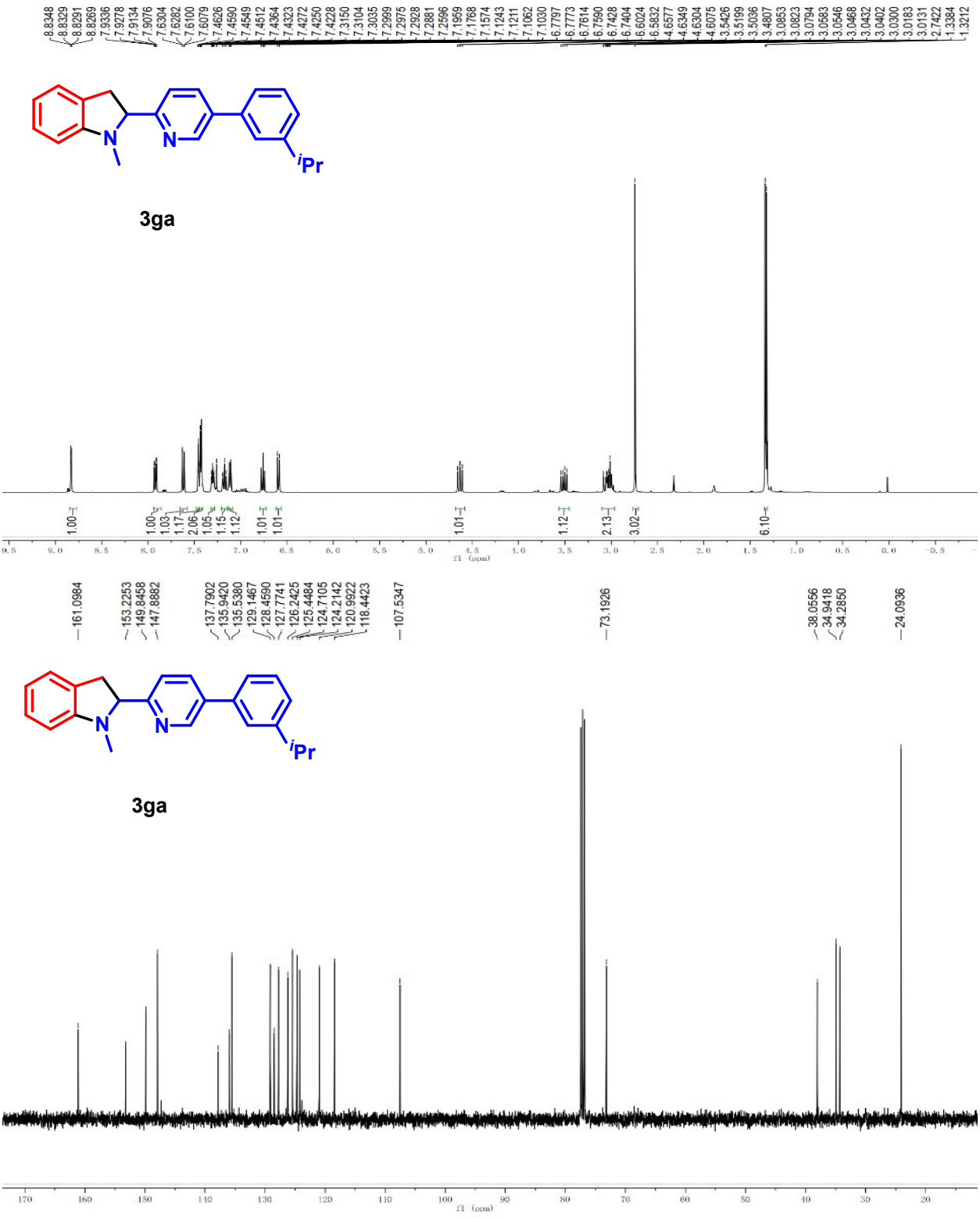


Figure S7. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ga in $CDCl_3$

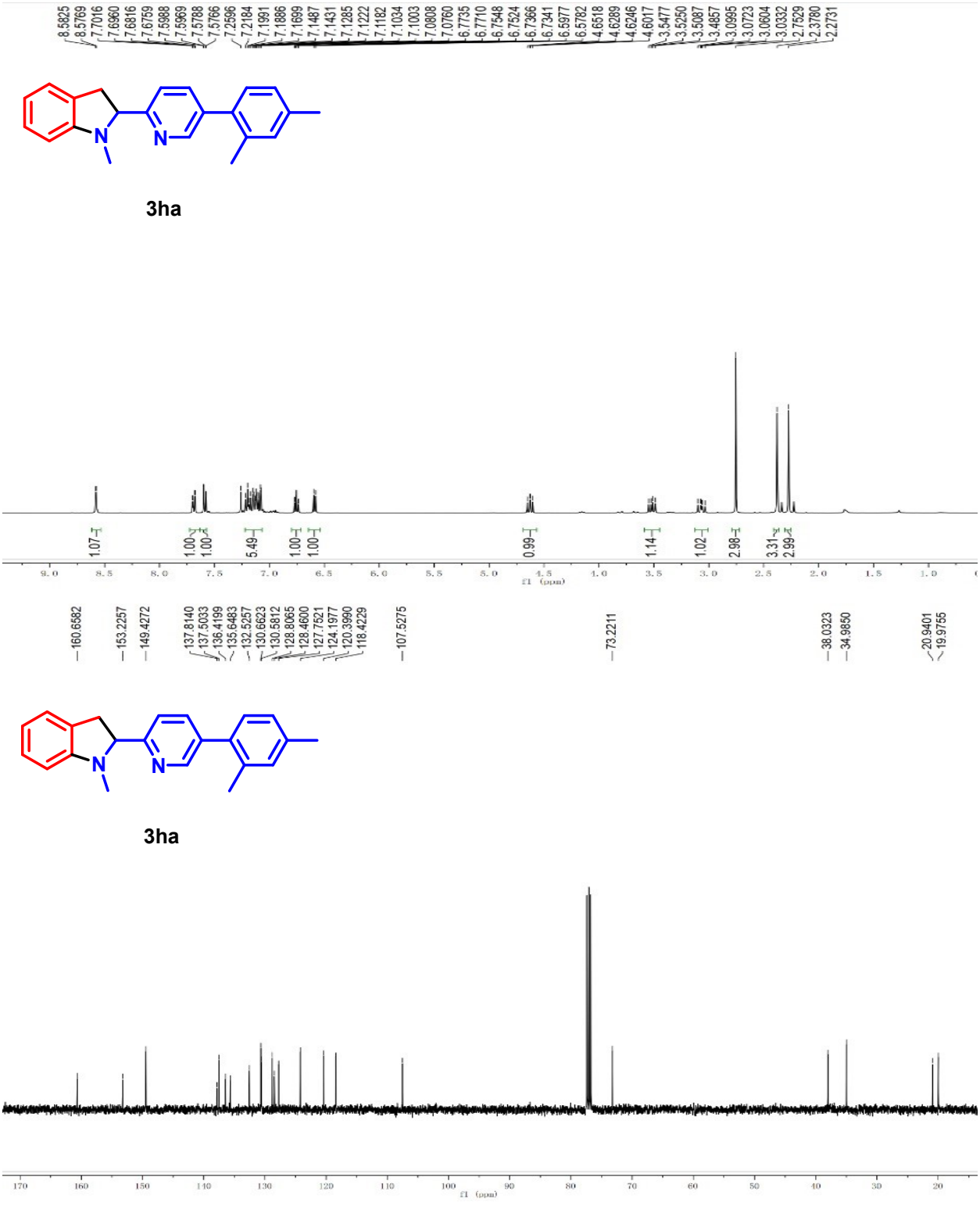


Figure S8. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ha in $CDCl_3$

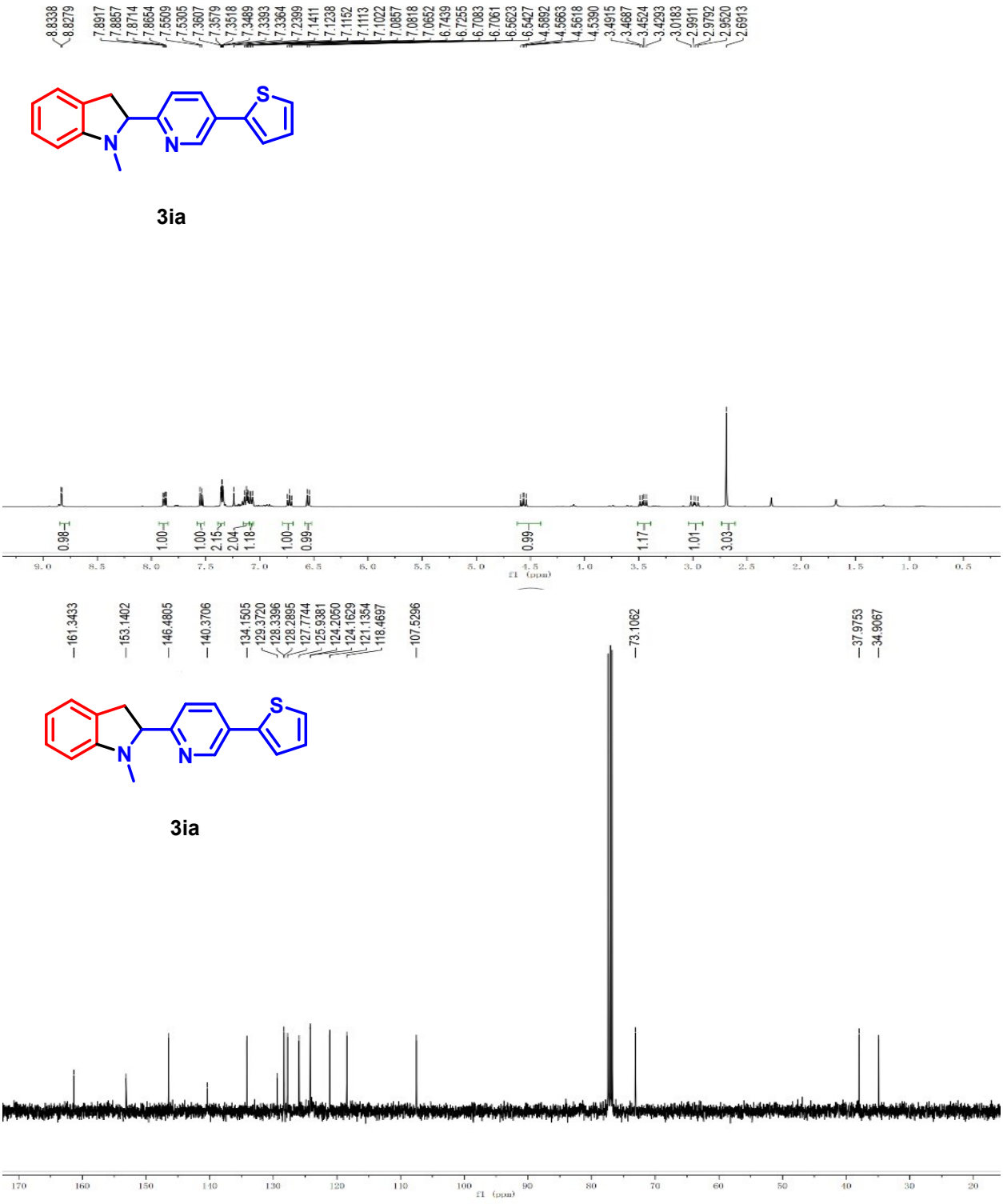


Figure S9. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ia in $CDCl_3$

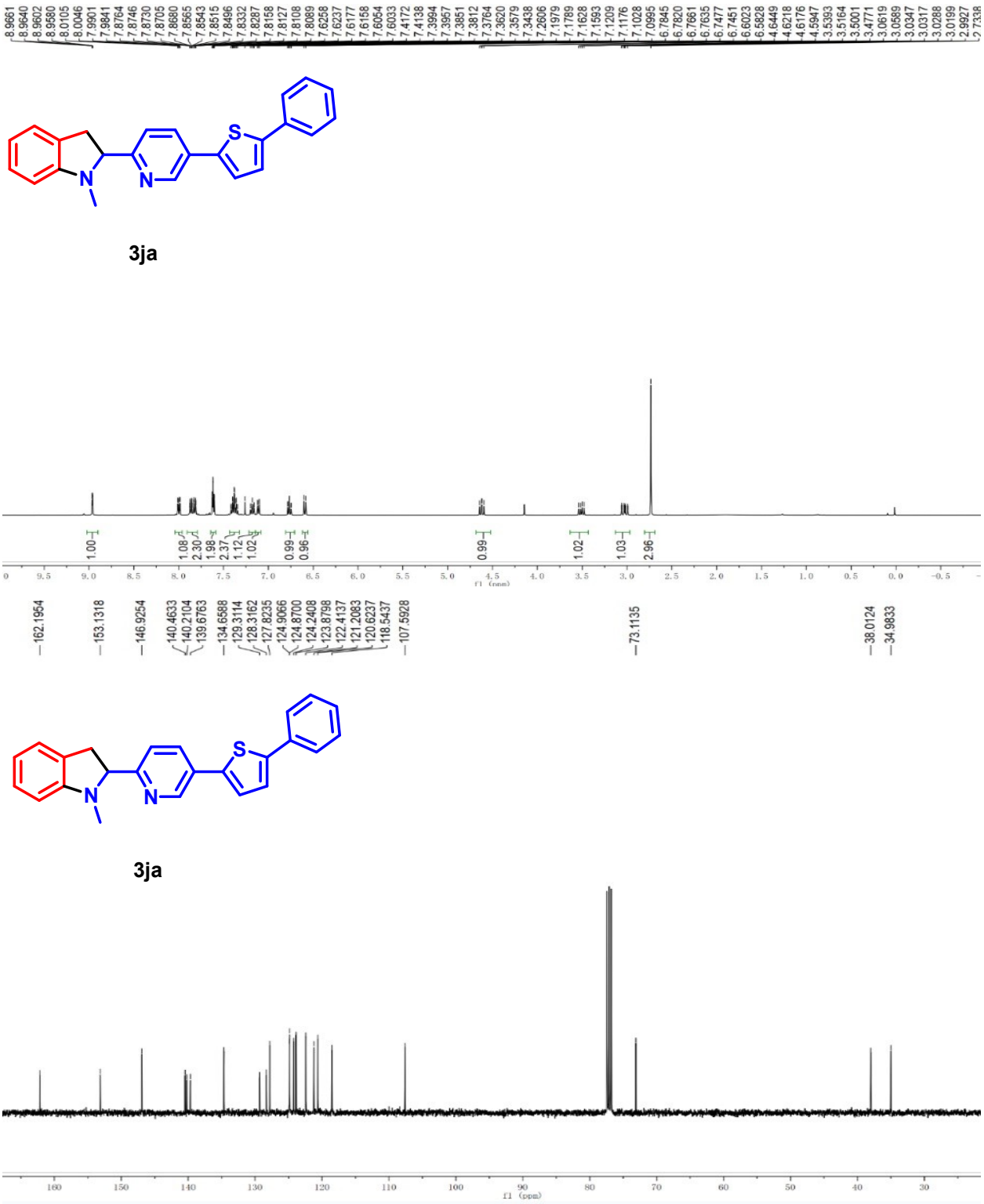


Figure S10. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ga in $CDCl_3$

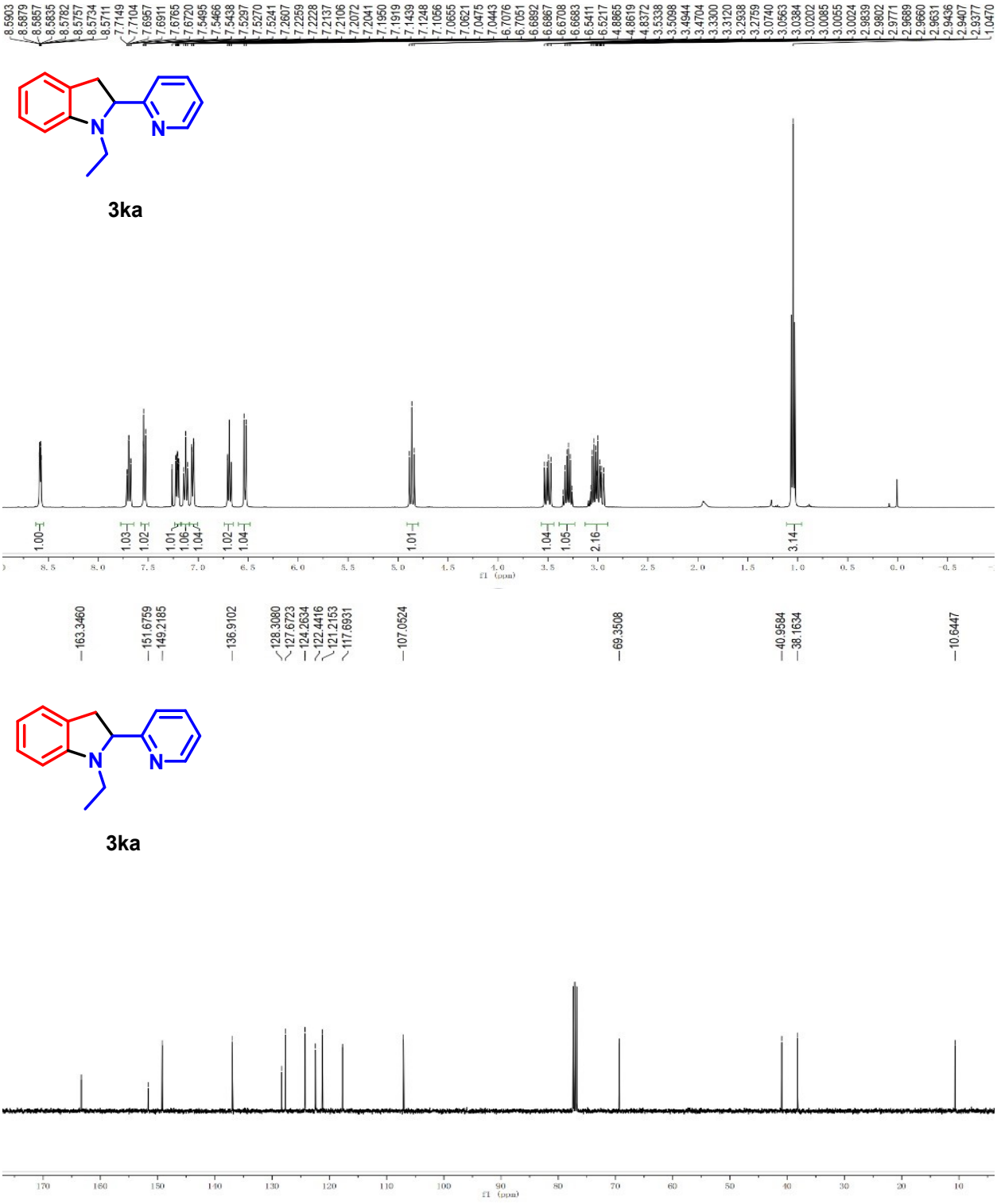
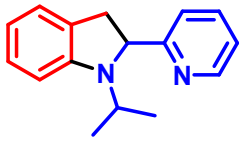
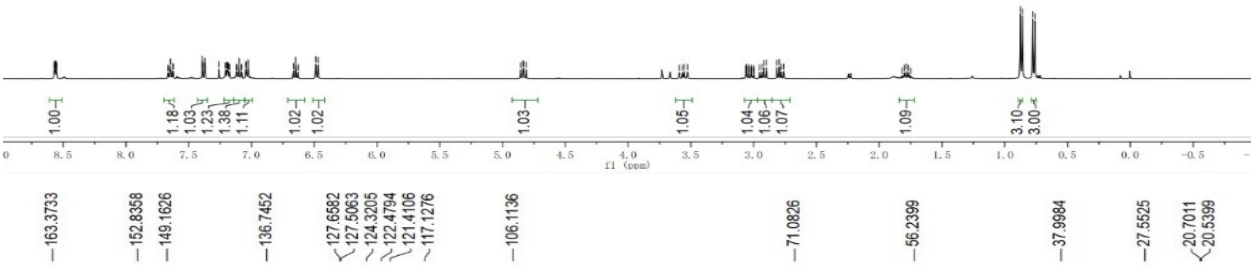
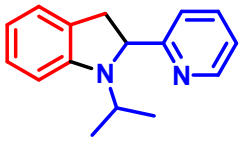


Figure S11. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ka in $CDCl_3$



3la





3la

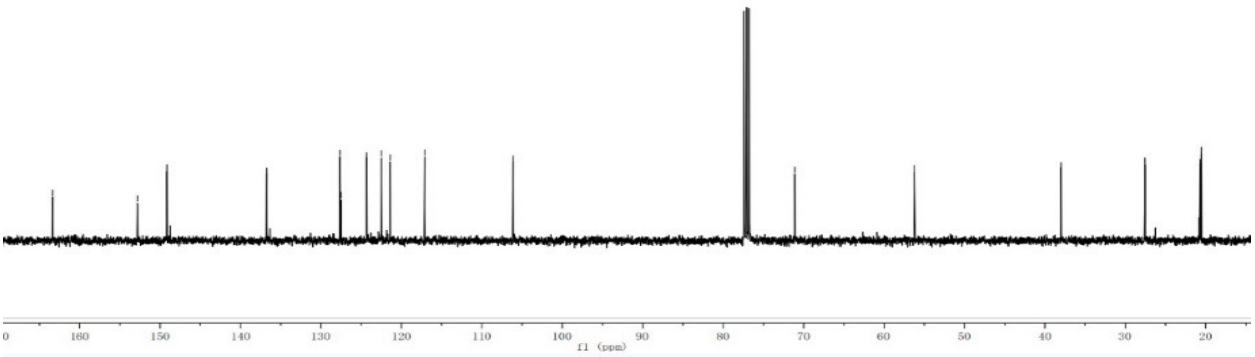


Figure S12. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3la in $CDCl_3$

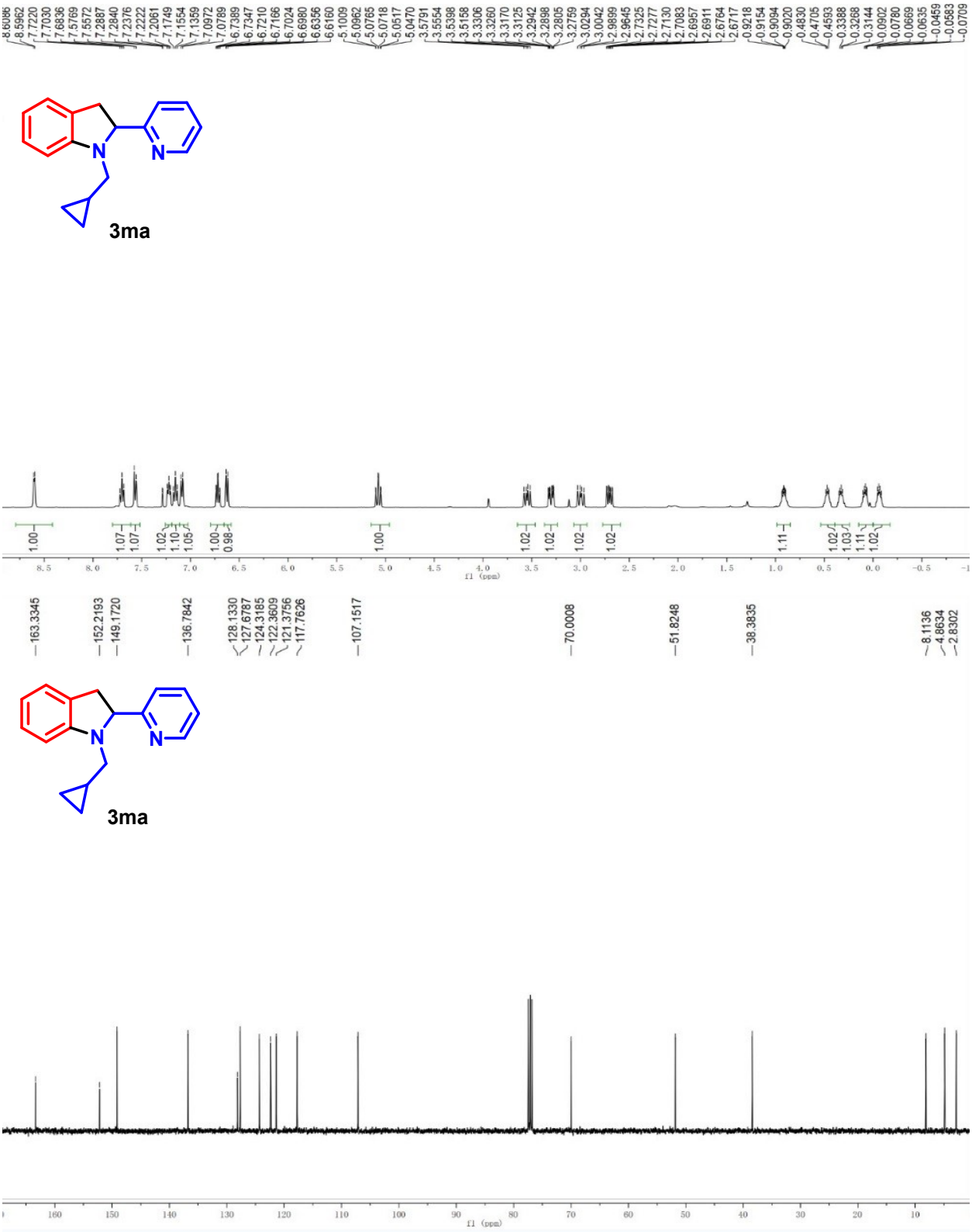


Figure S13. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ma in $CDCl_3$

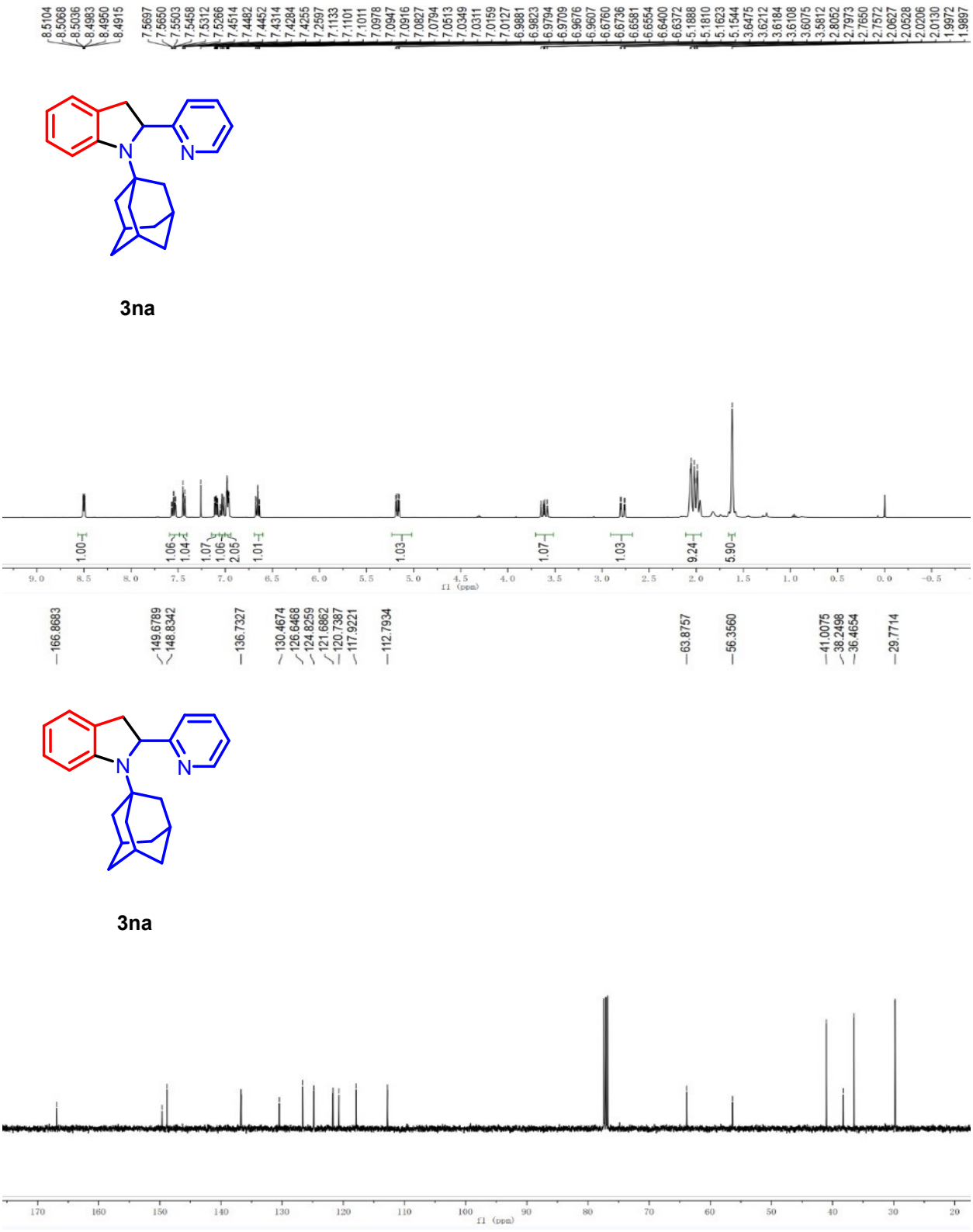


Figure S14. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3na in $CDCl_3$

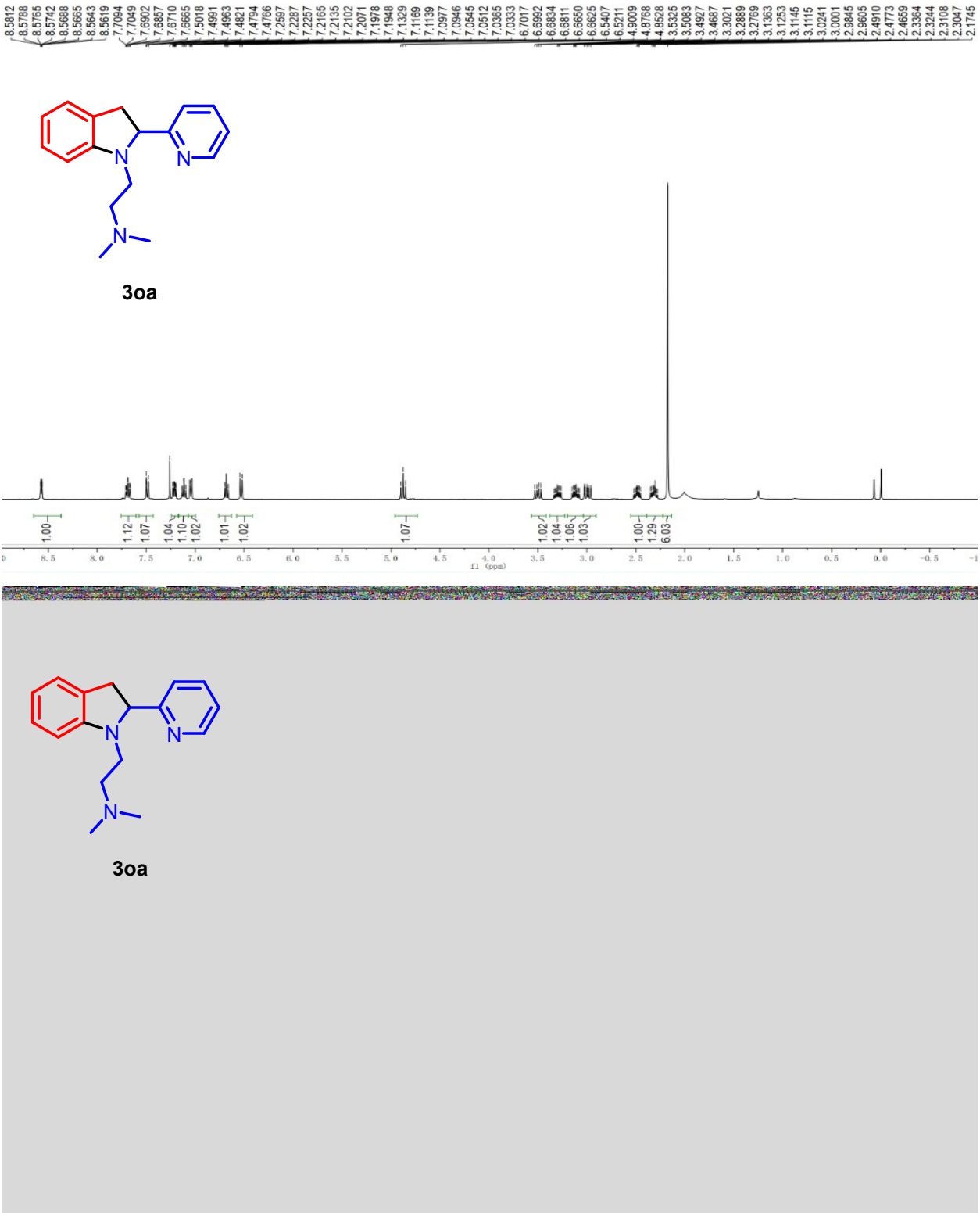


Figure S15. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3oa in $CDCl_3$

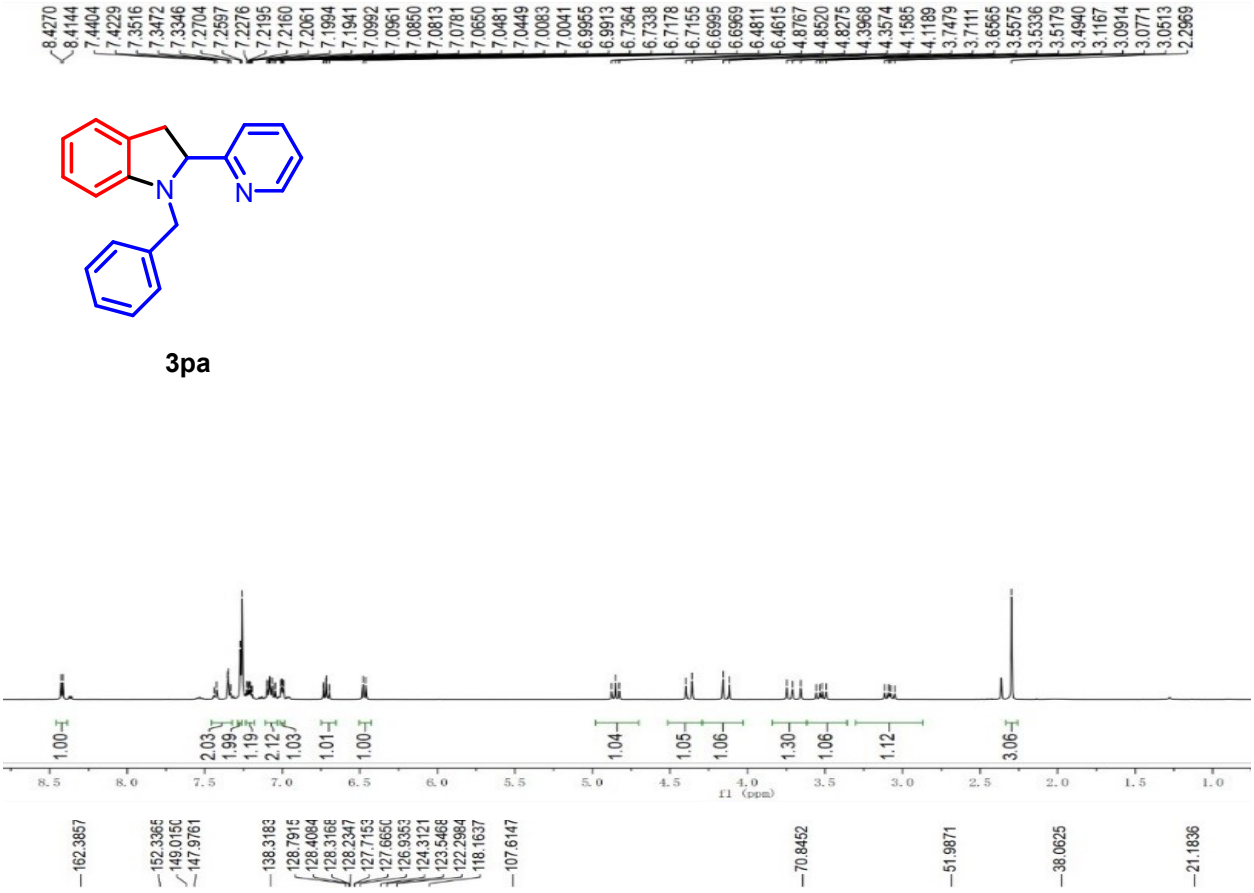


Figure S16. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3pa in $CDCl_3$

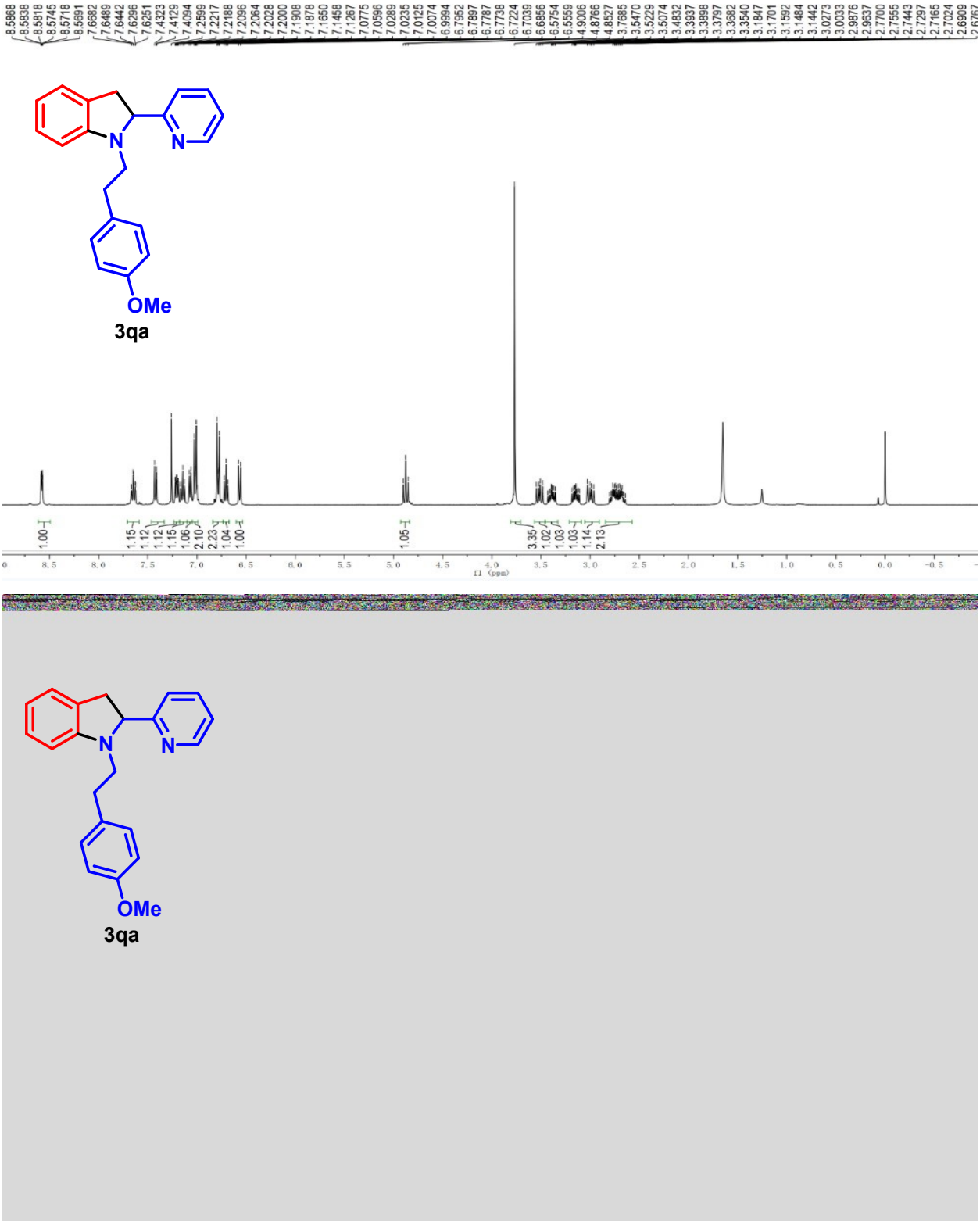


Figure S17. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3qa in $CDCl_3$

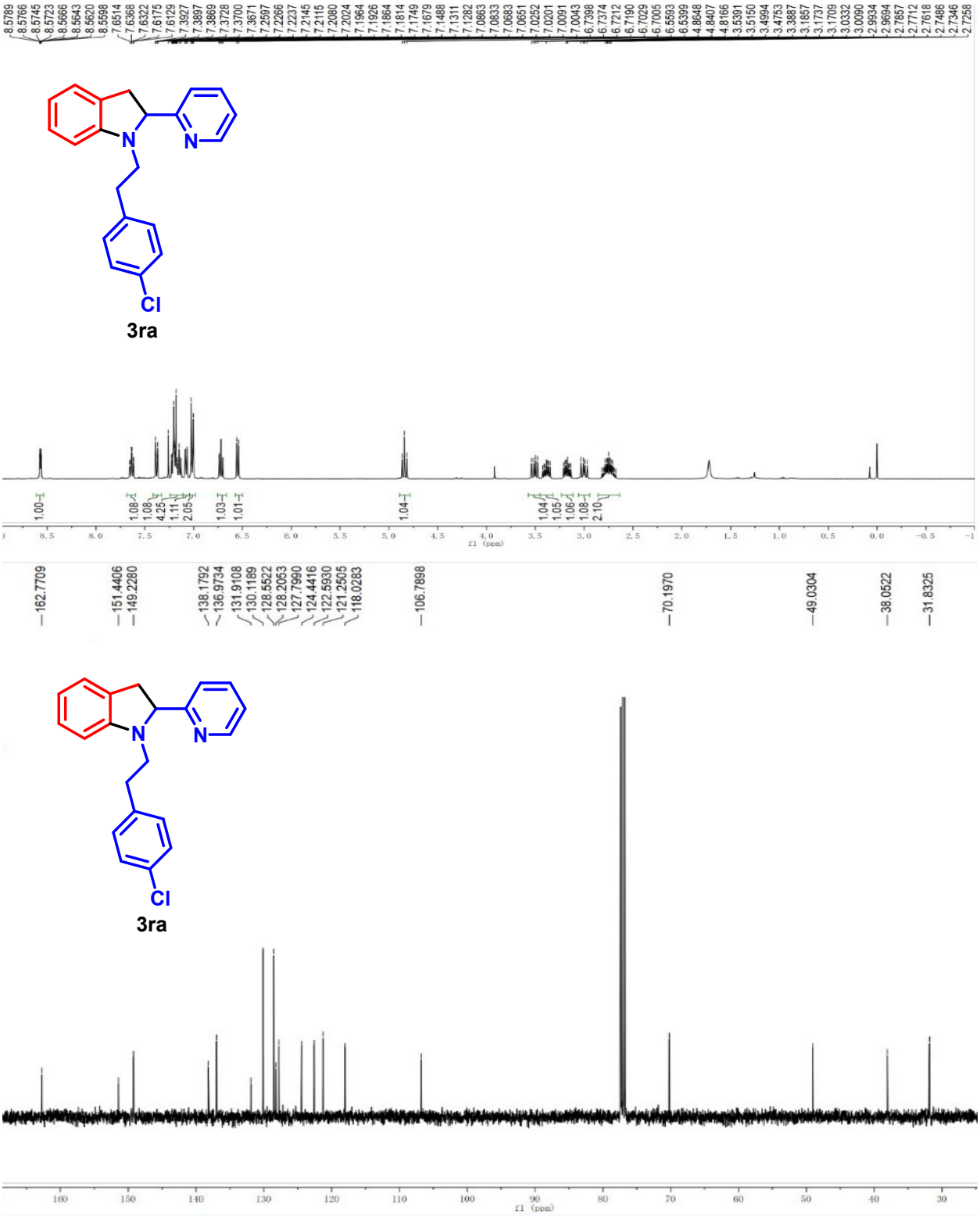


Figure S18. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ra in $CDCl_3$

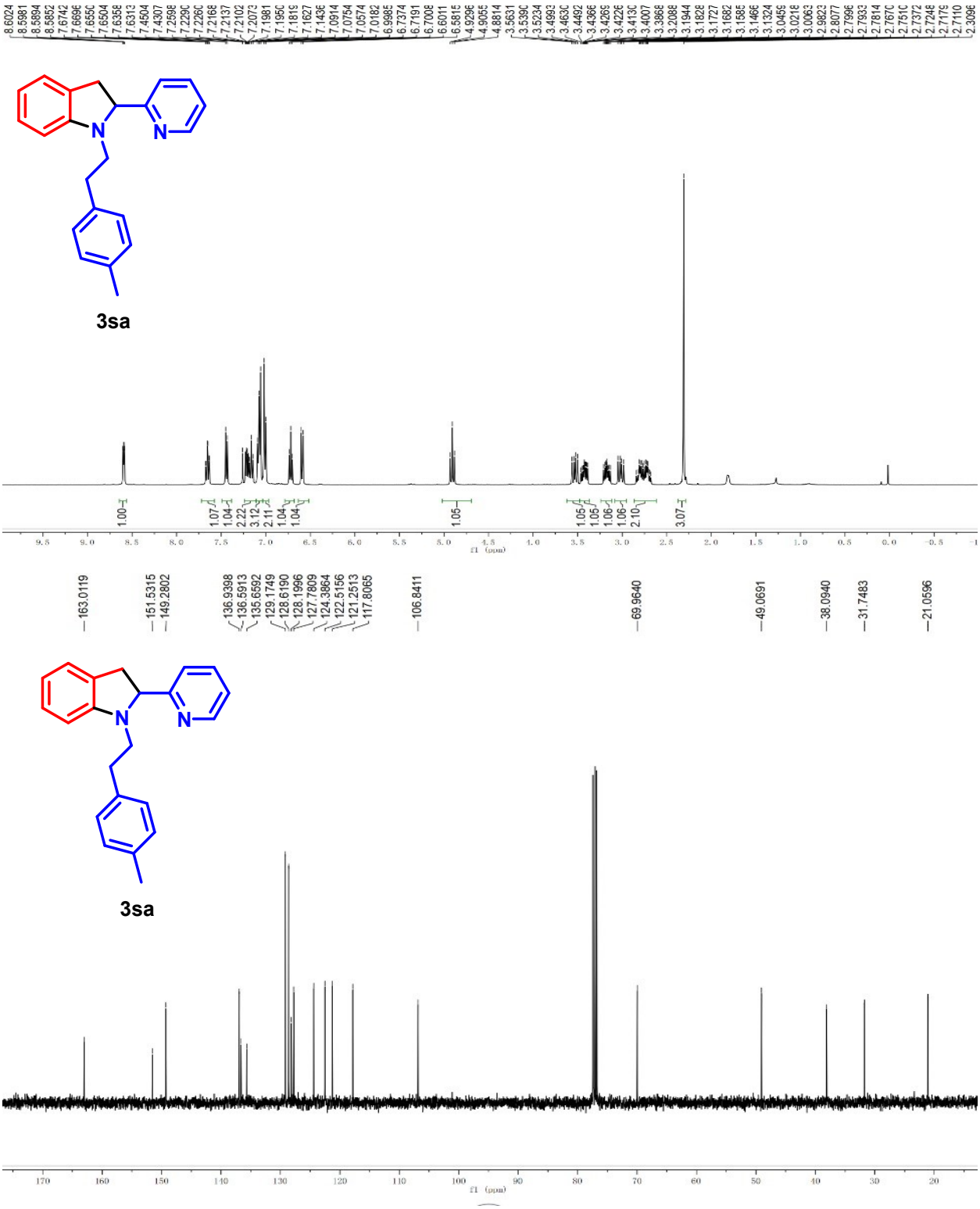


Figure S19. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3sa in $CDCl_3$

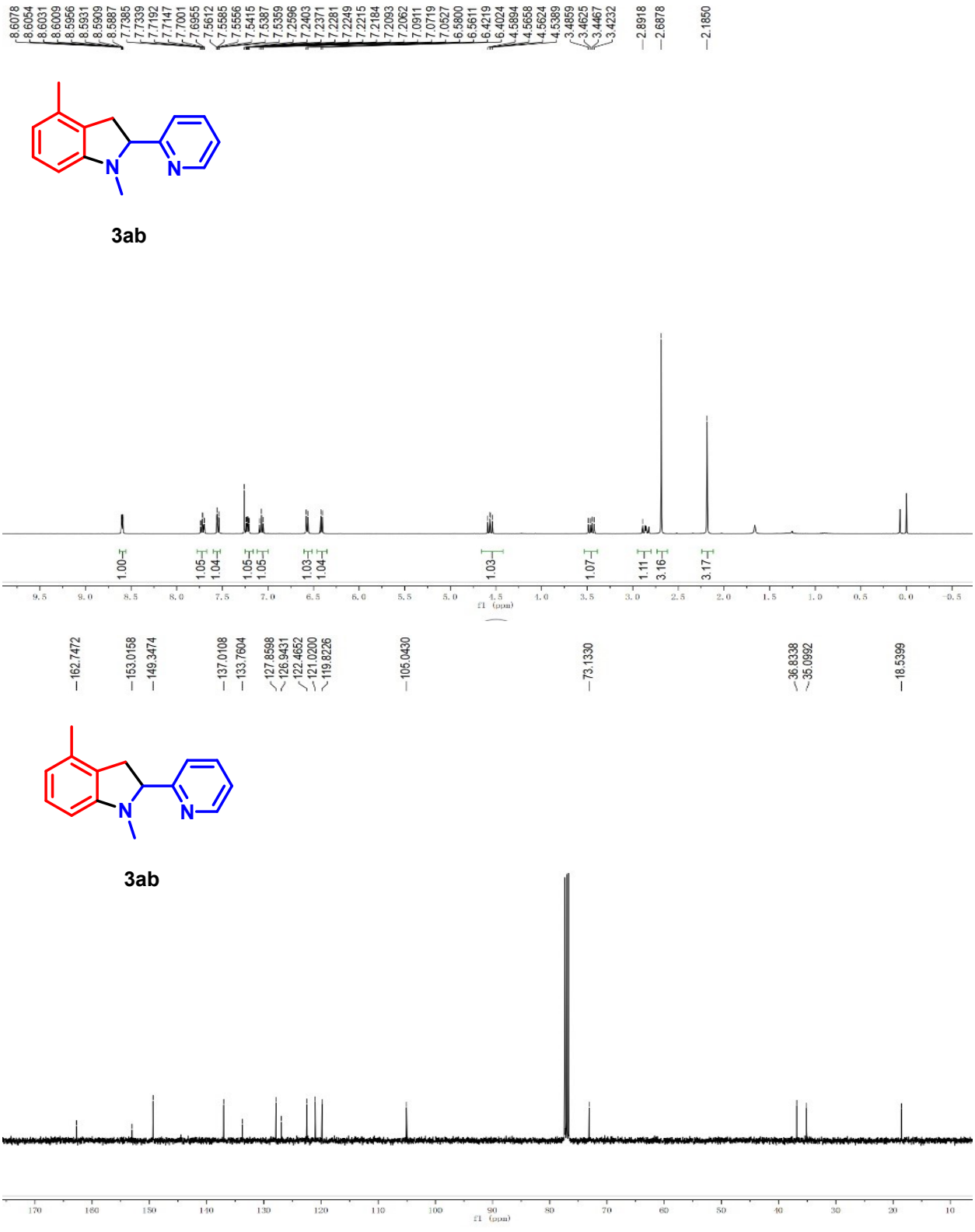


Figure S20. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ab in $CDCl_3$

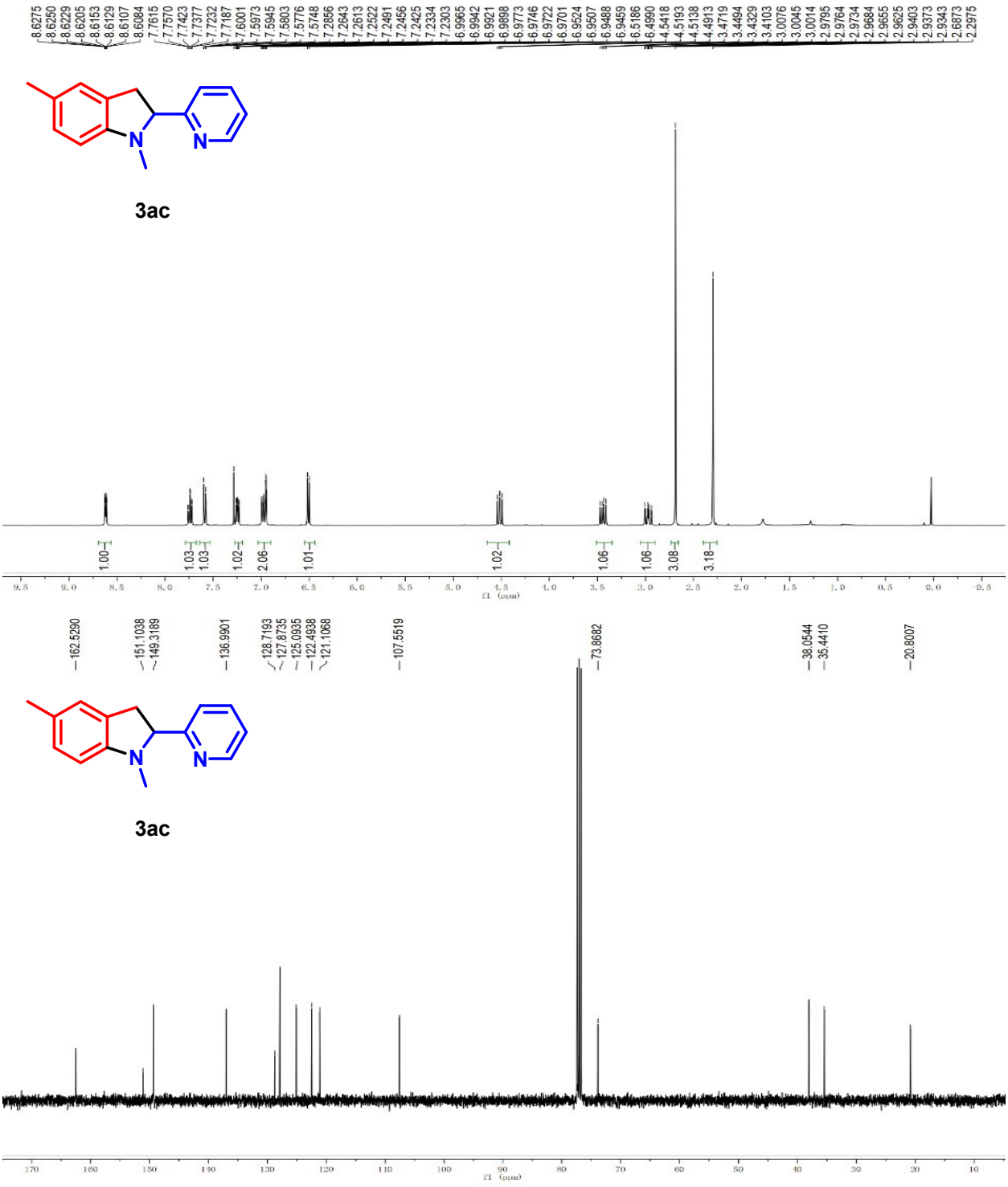


Figure S21. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ac in $CDCl_3$

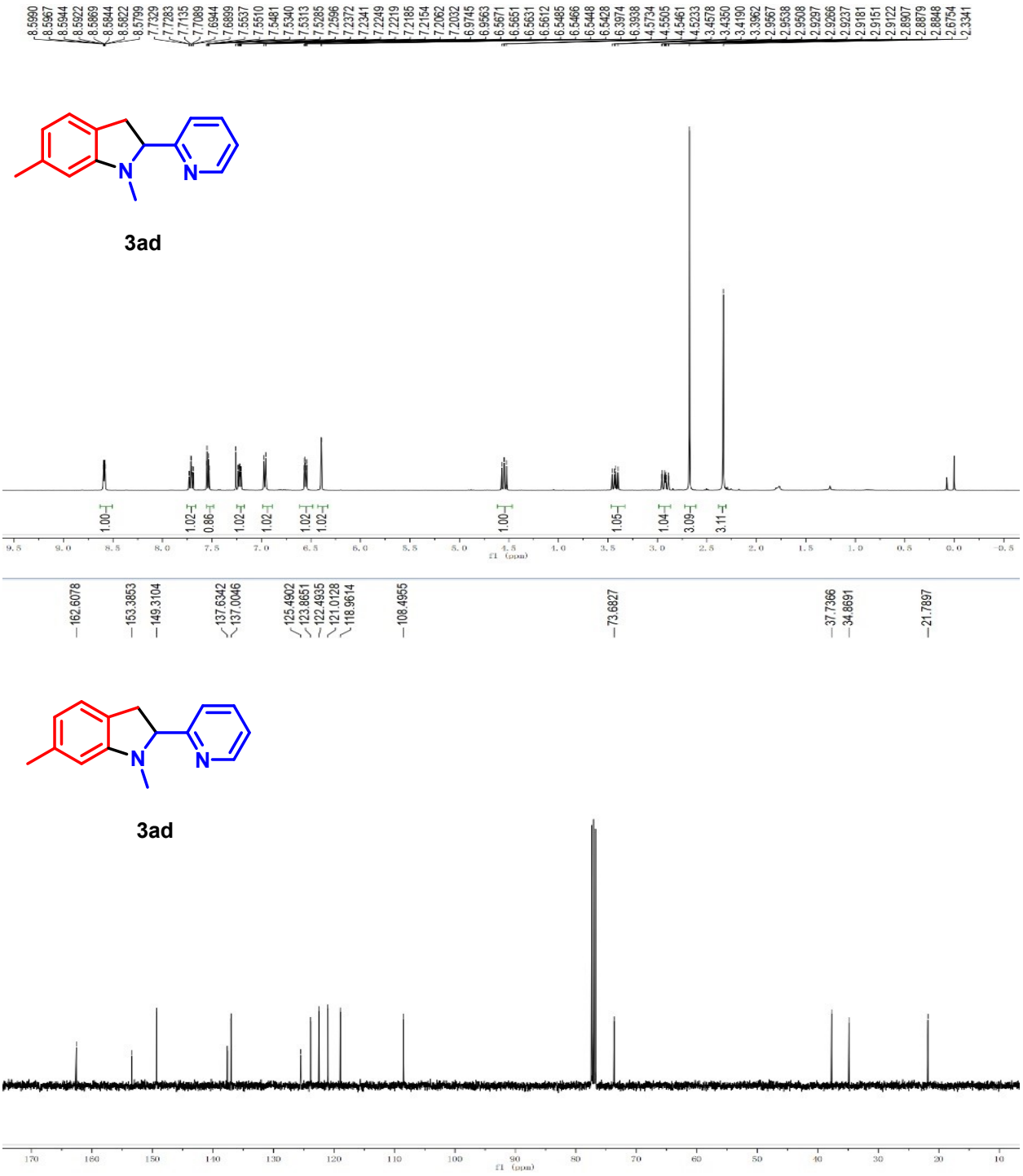


Figure S22. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ad in $CDCl_3$

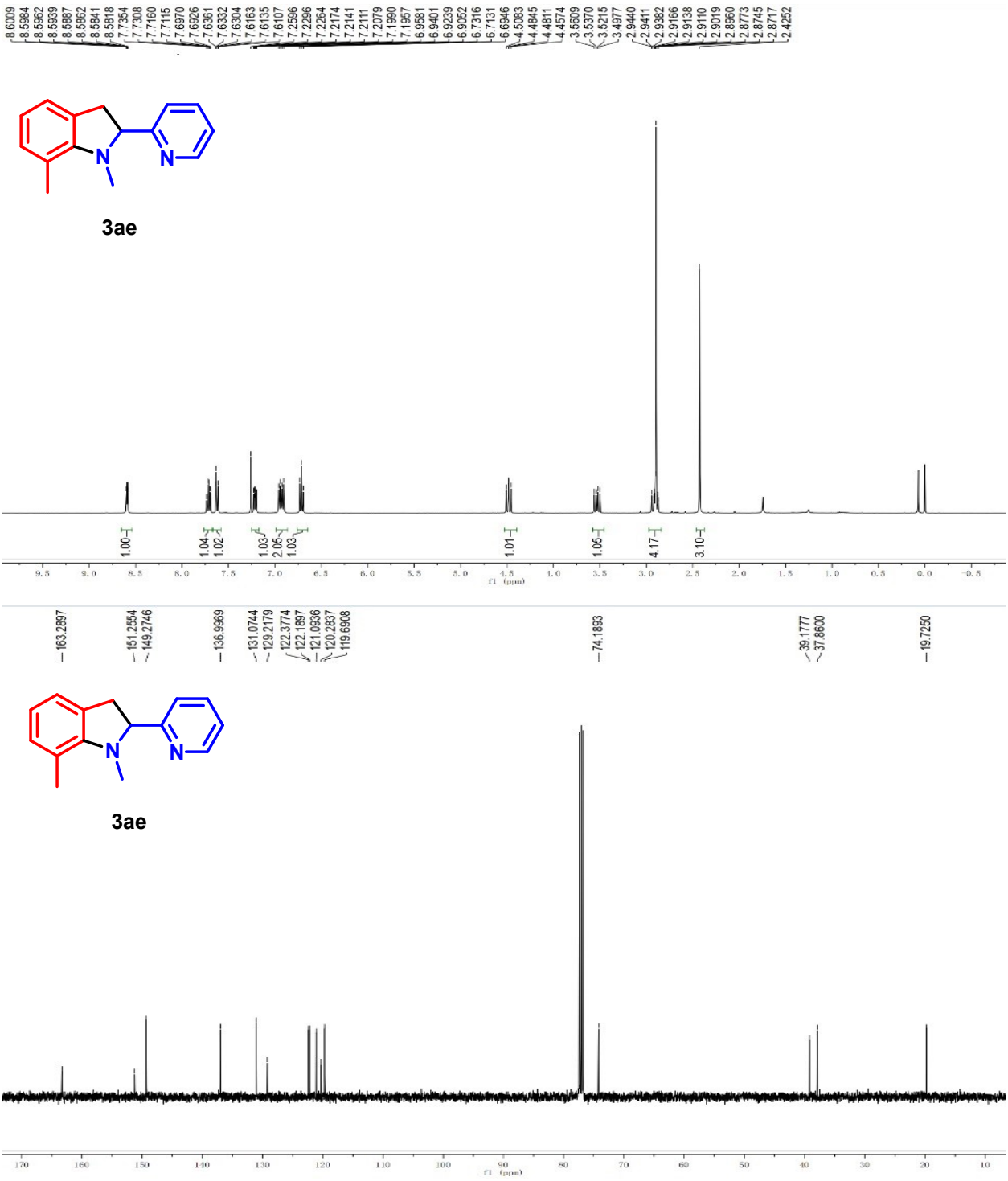
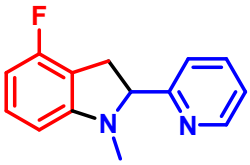
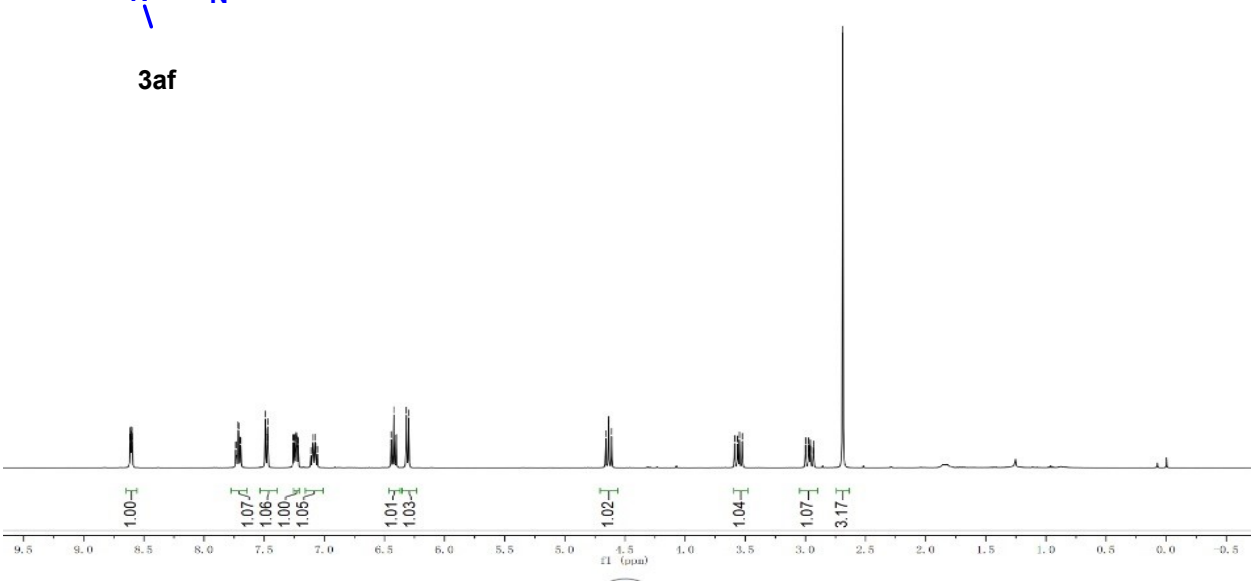
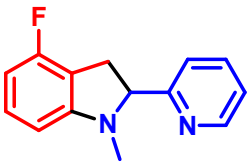


Figure S23. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ae in $CDCl_3$

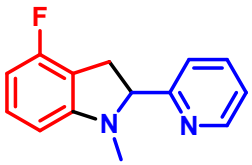


3af



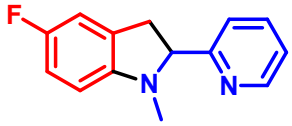


3af

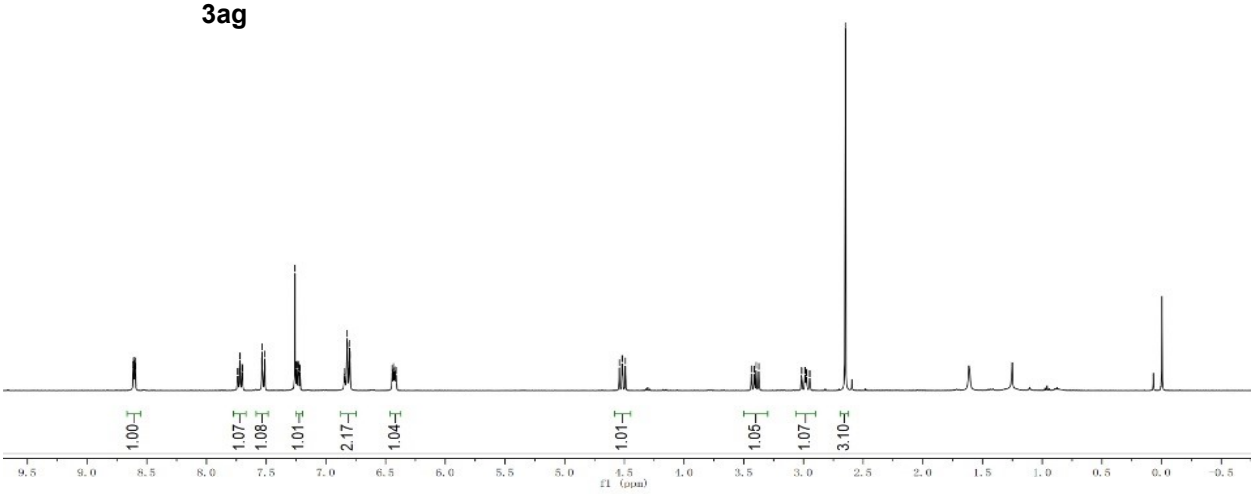


3af

Figure S24. ^{1}H NMR (400 MHz) ^{13}C {101 MHz} and ^{19}F NMR (376 MHZ) NMR spectra of 3af in $CDCl_3$



3ag



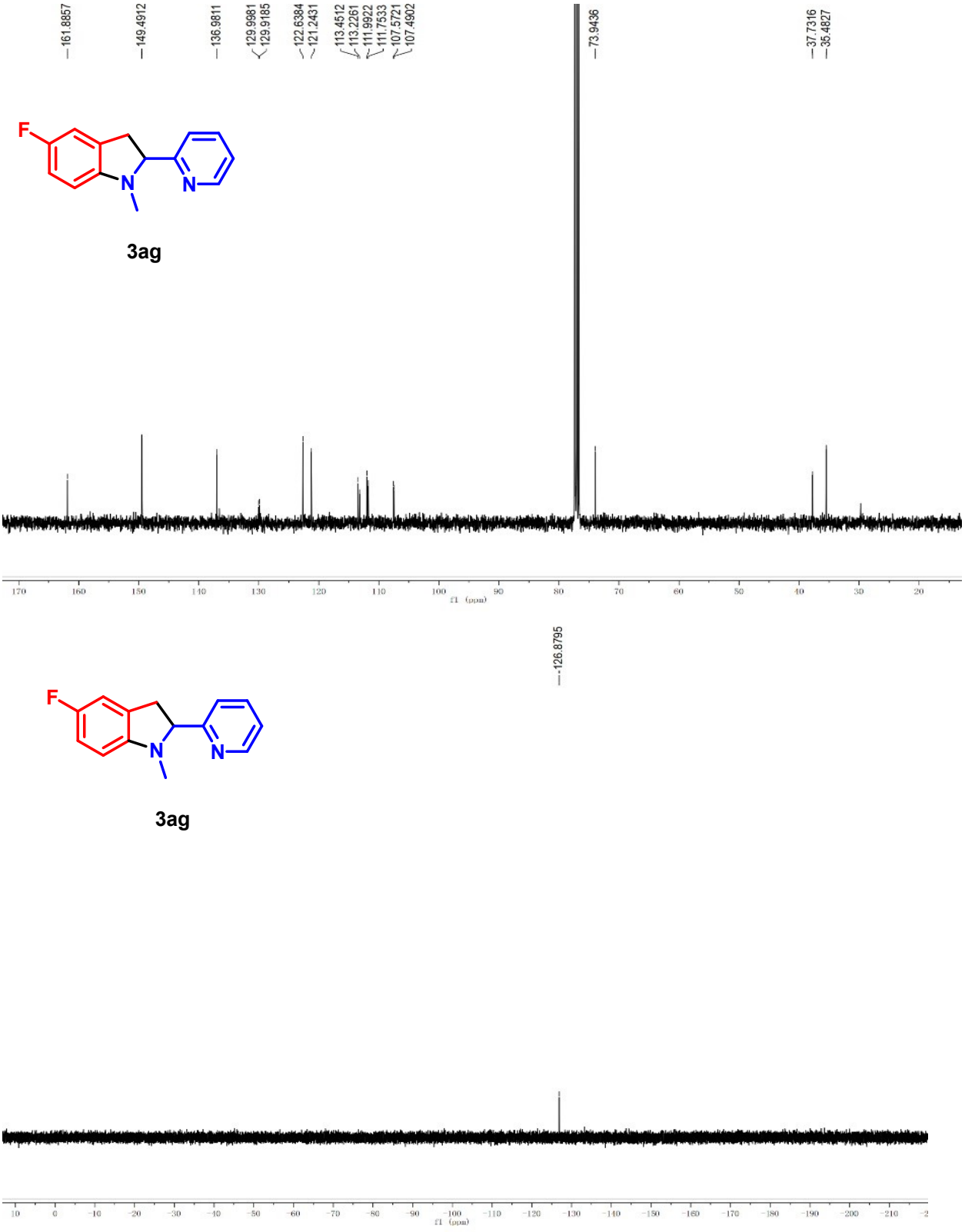


Figure S25. ^{1}H NMR (400 MHz) ^{13}C {101 MHz} and ^{19}F NMR (376 MHZ) NMR spectra of 3ag in $CDCl_3$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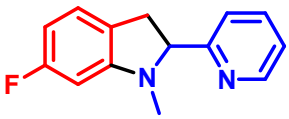
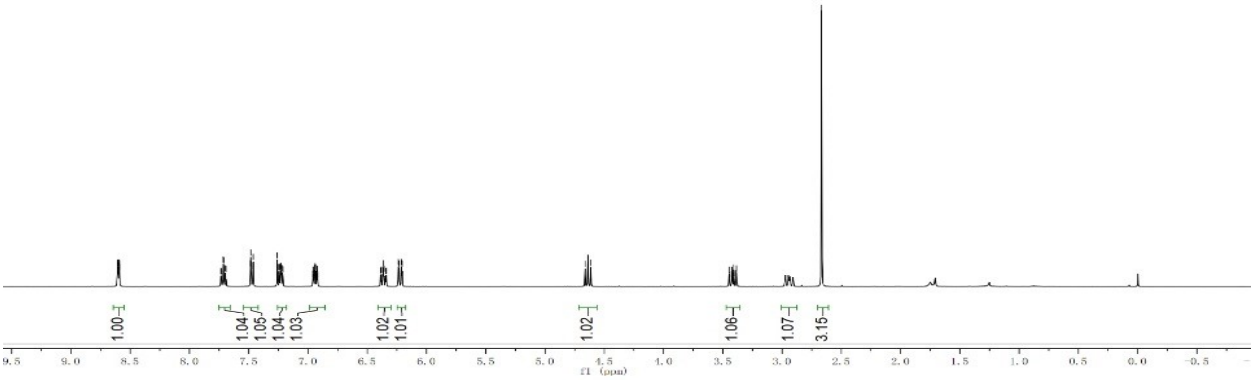


3ah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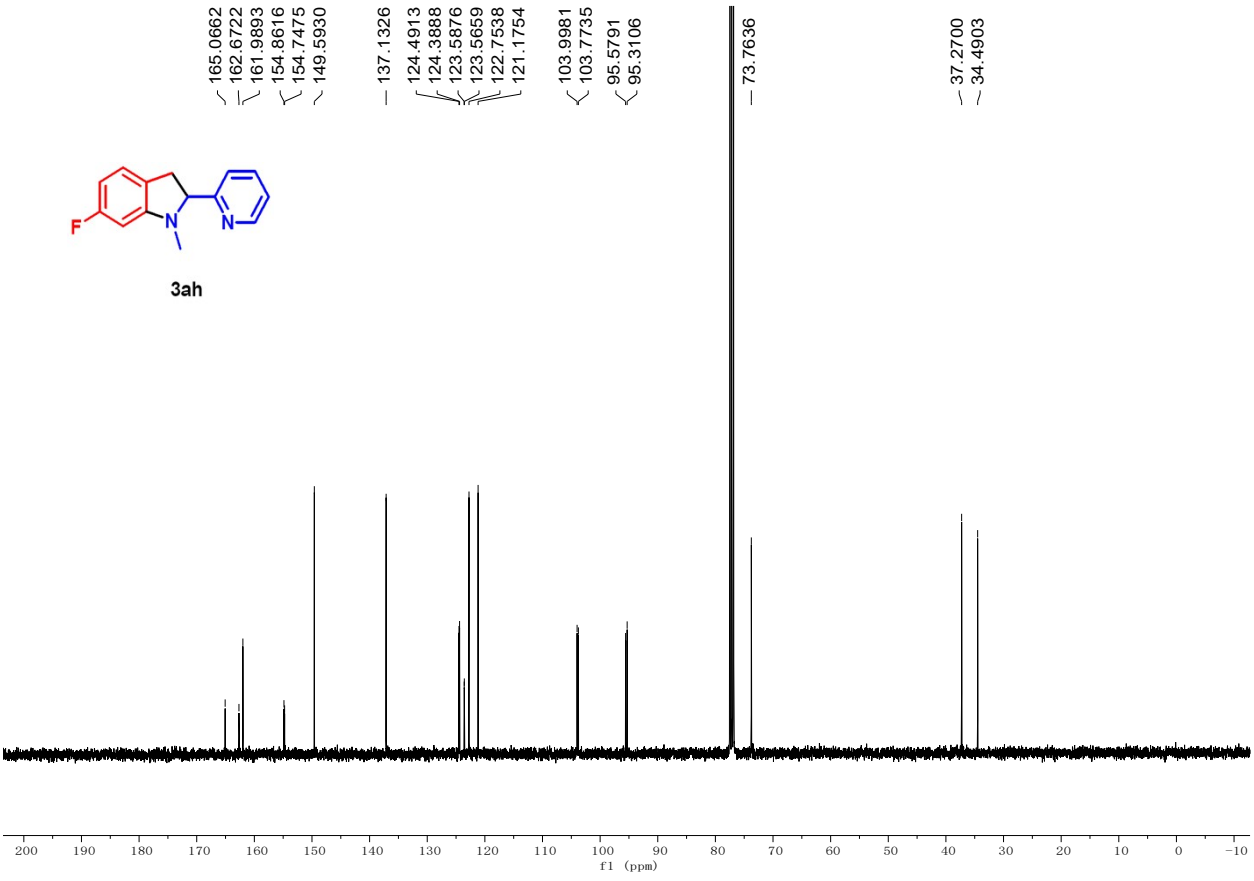
1.05
1.04
1.03
1.02
1.01
1.02
1.06
1.07
3.15
f1 (ppm)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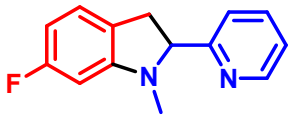
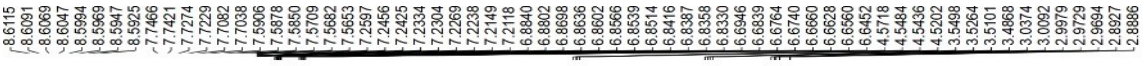
37.2700
34.4903
f1 (ppm)

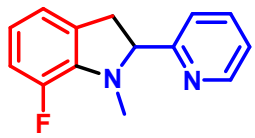
3ah



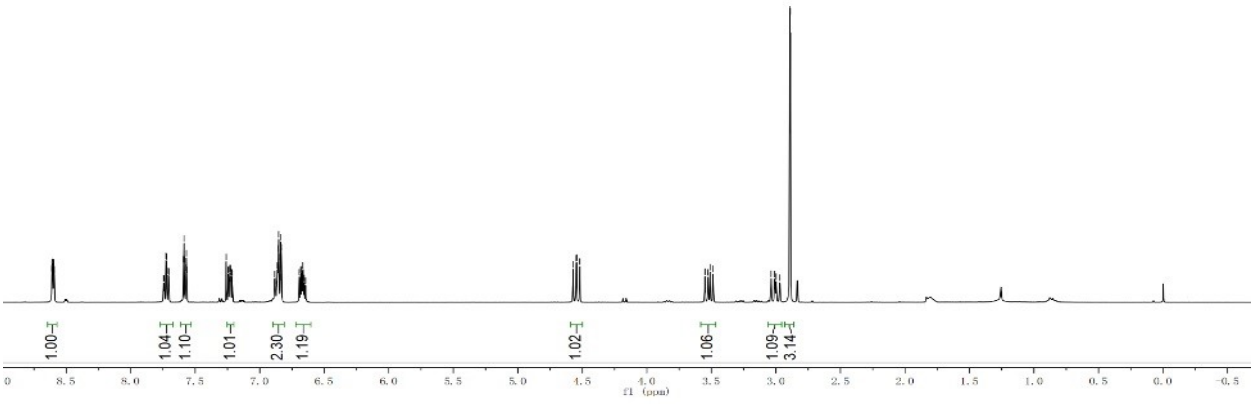
3ah

Figure S26. ^{1}H NMR (400 MHz) ^{13}C {101 MHz} and ^{19}F NMR (376 MHZ) NMR spectra of 3ah in $CDCl_3$





3ai



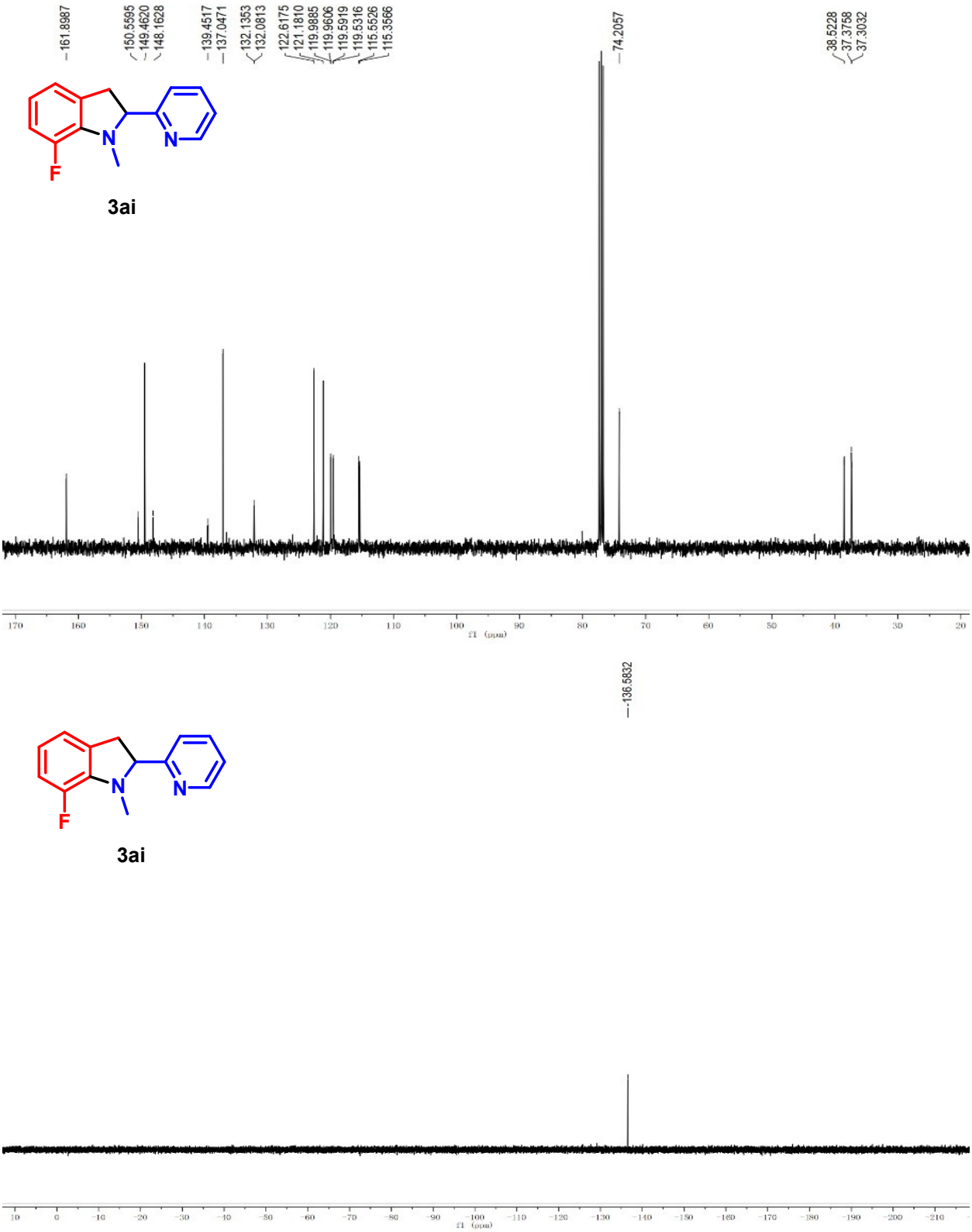


Figure S27. ^{1}H NMR (400 MHz) ^{13}C {101 MHz} and ^{19}F NMR (376 MHZ) NMR spectra of 3ai in $CDCl_3$

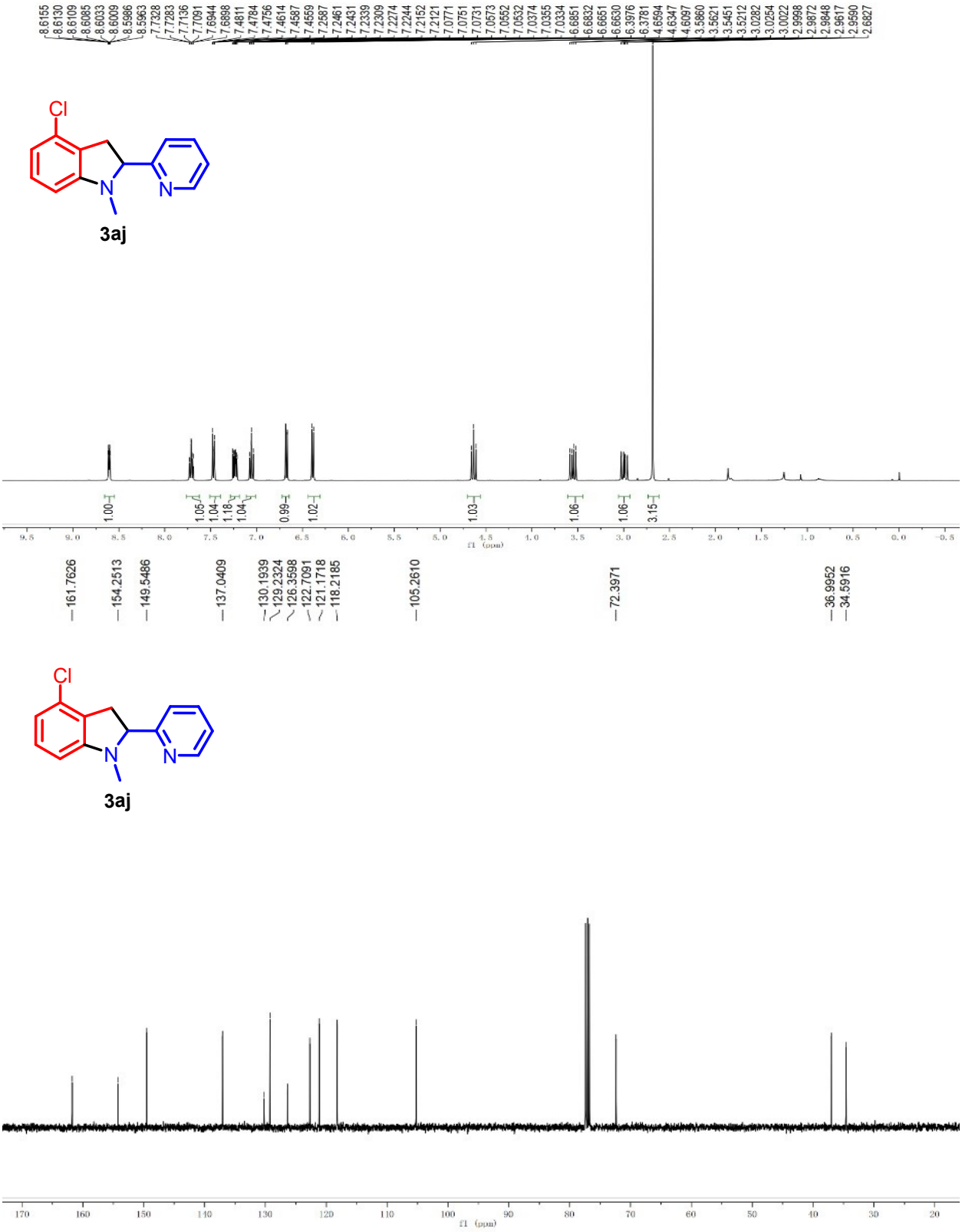


Figure S28. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3aj in $CDCl_3$

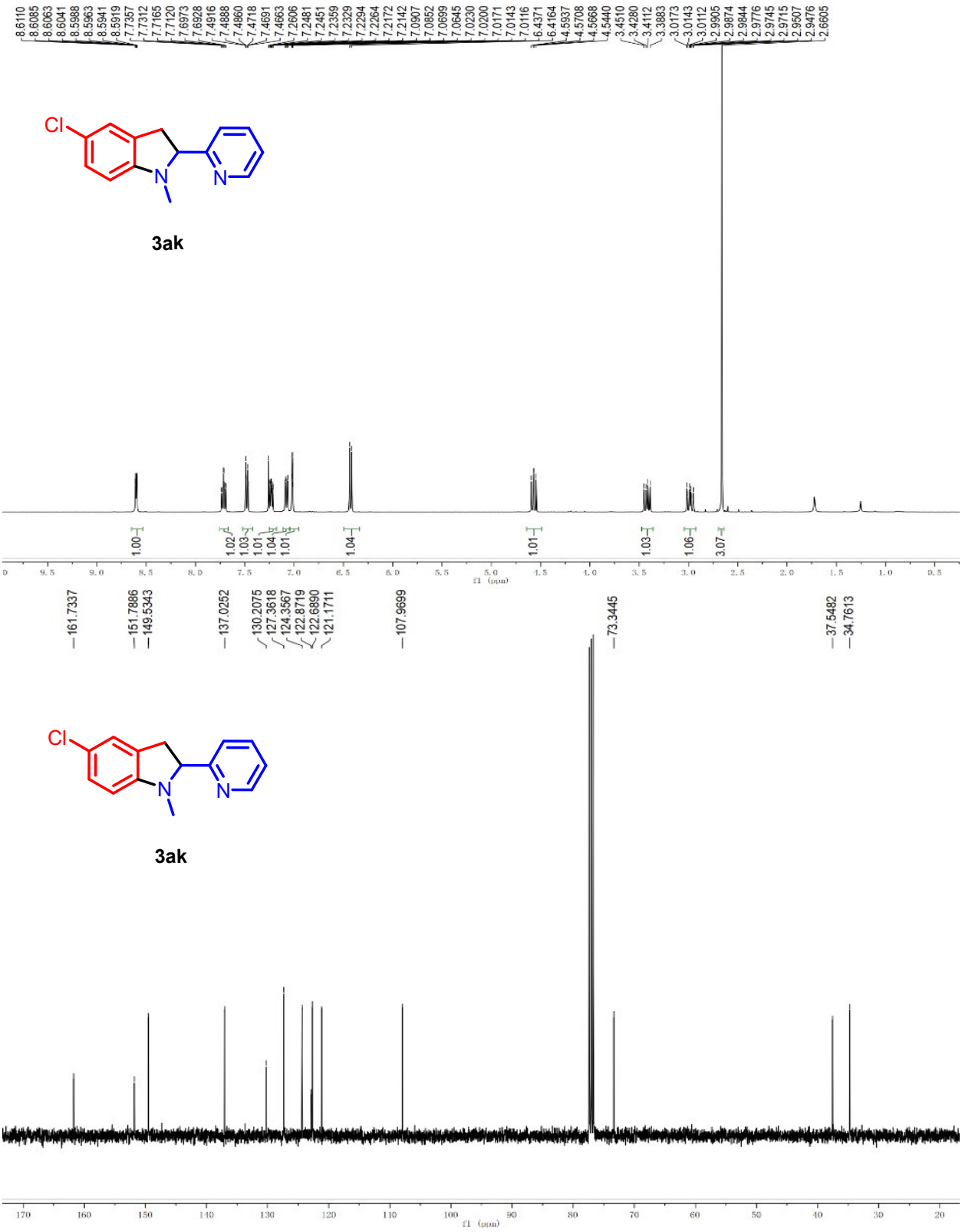


Figure S29. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ak in $CDCl_3$

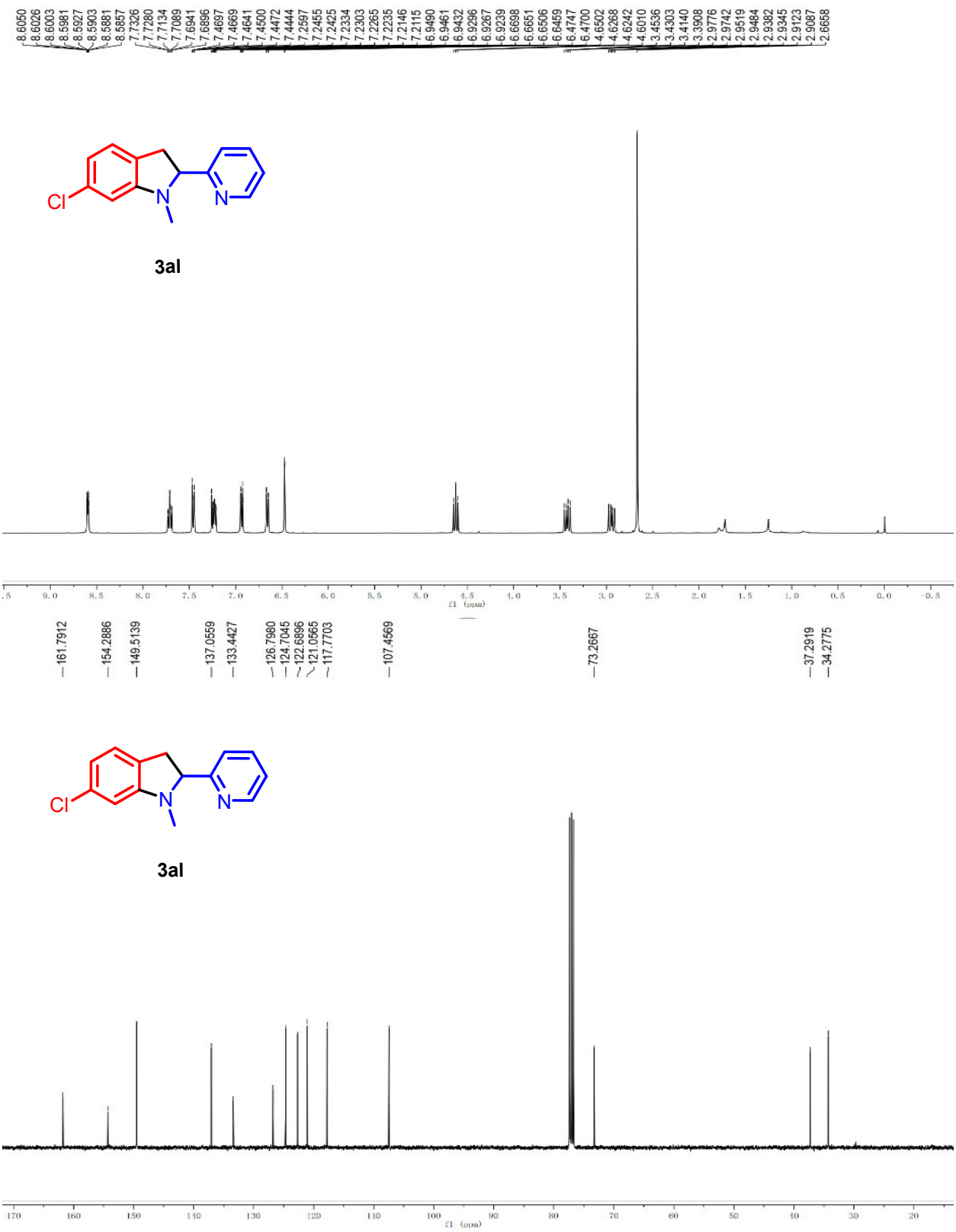


Figure S30. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3al in $CDCl_3$

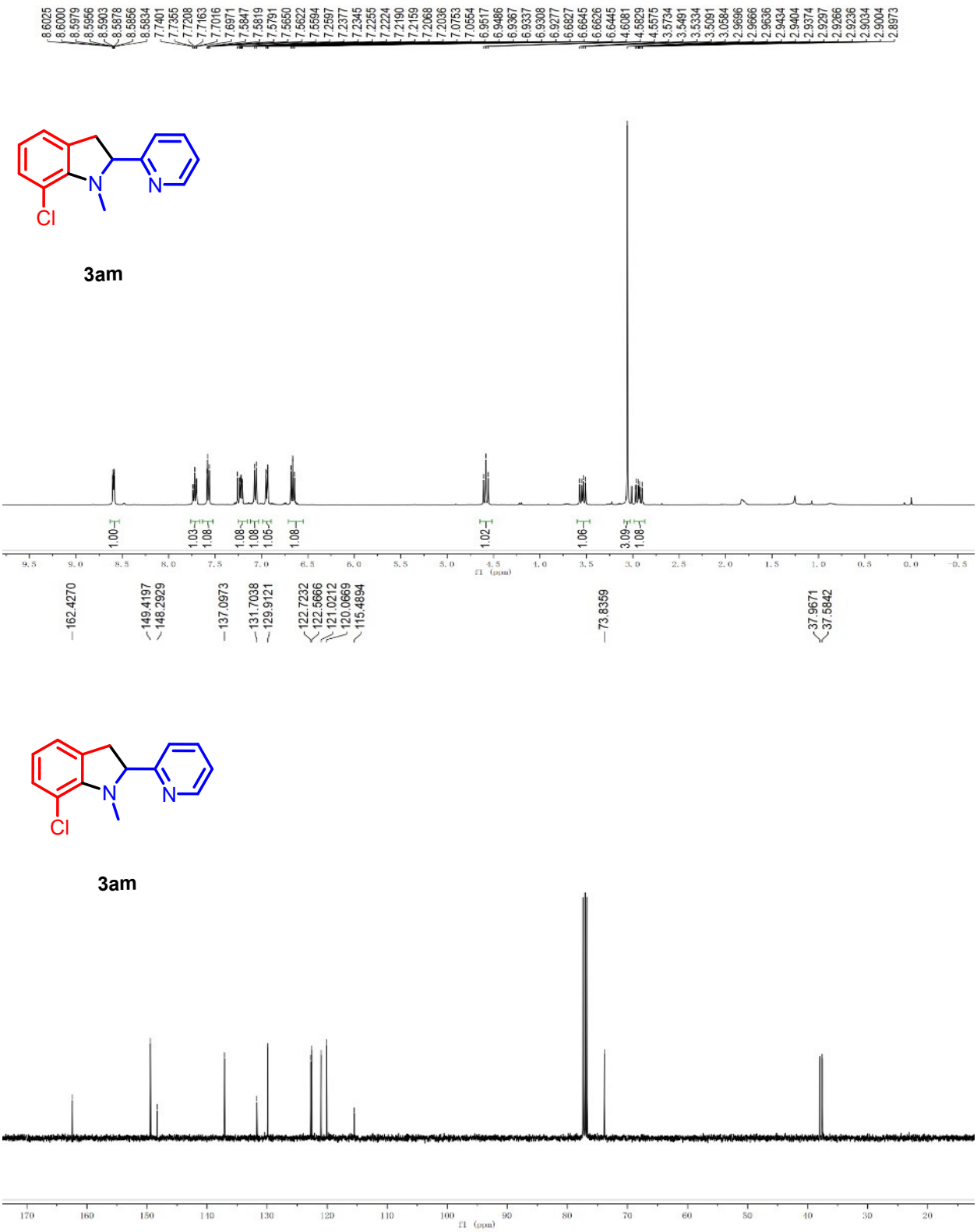


Figure S31. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3am in $CDCl_3$

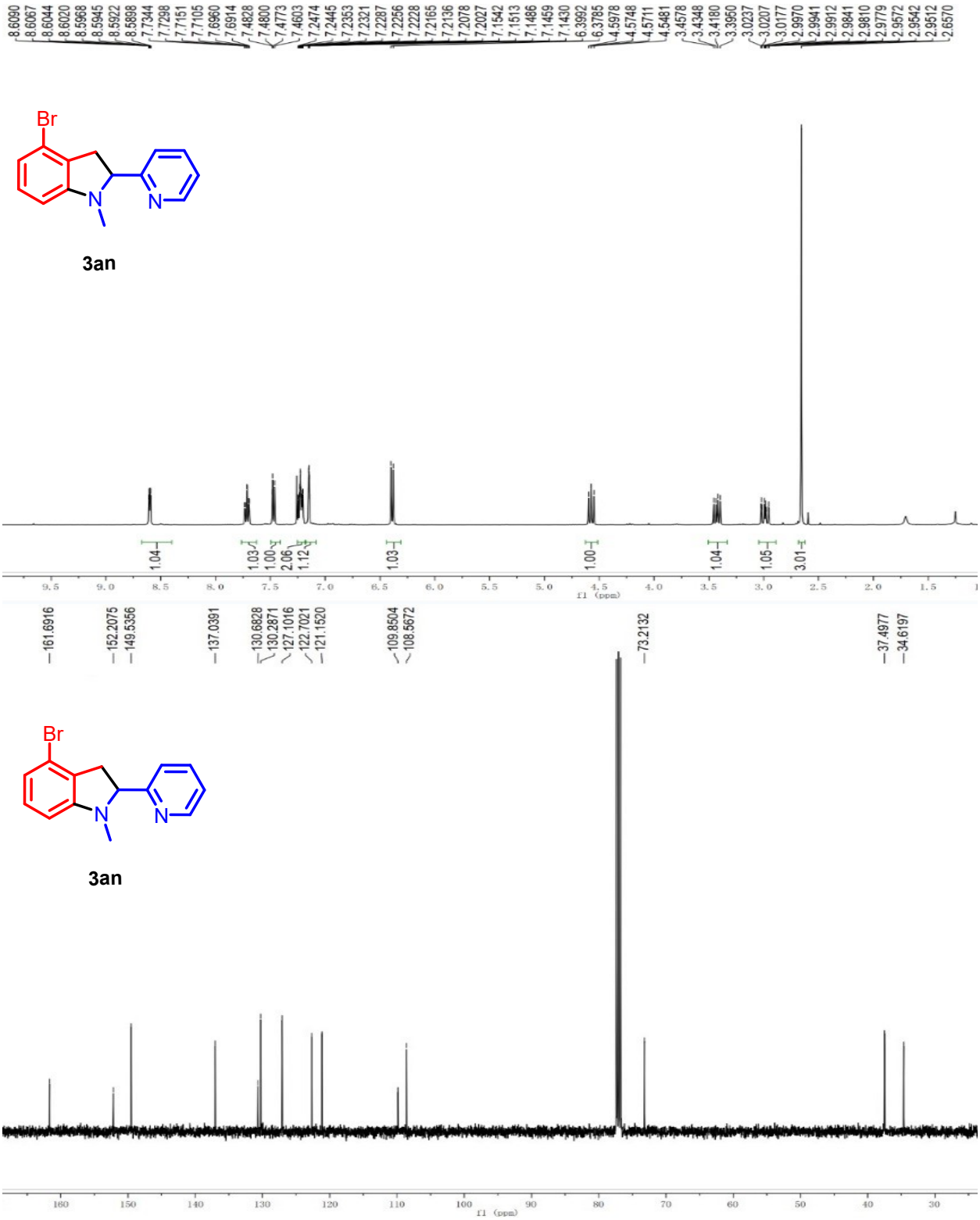


Figure S32. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3an in $CDCl_3$

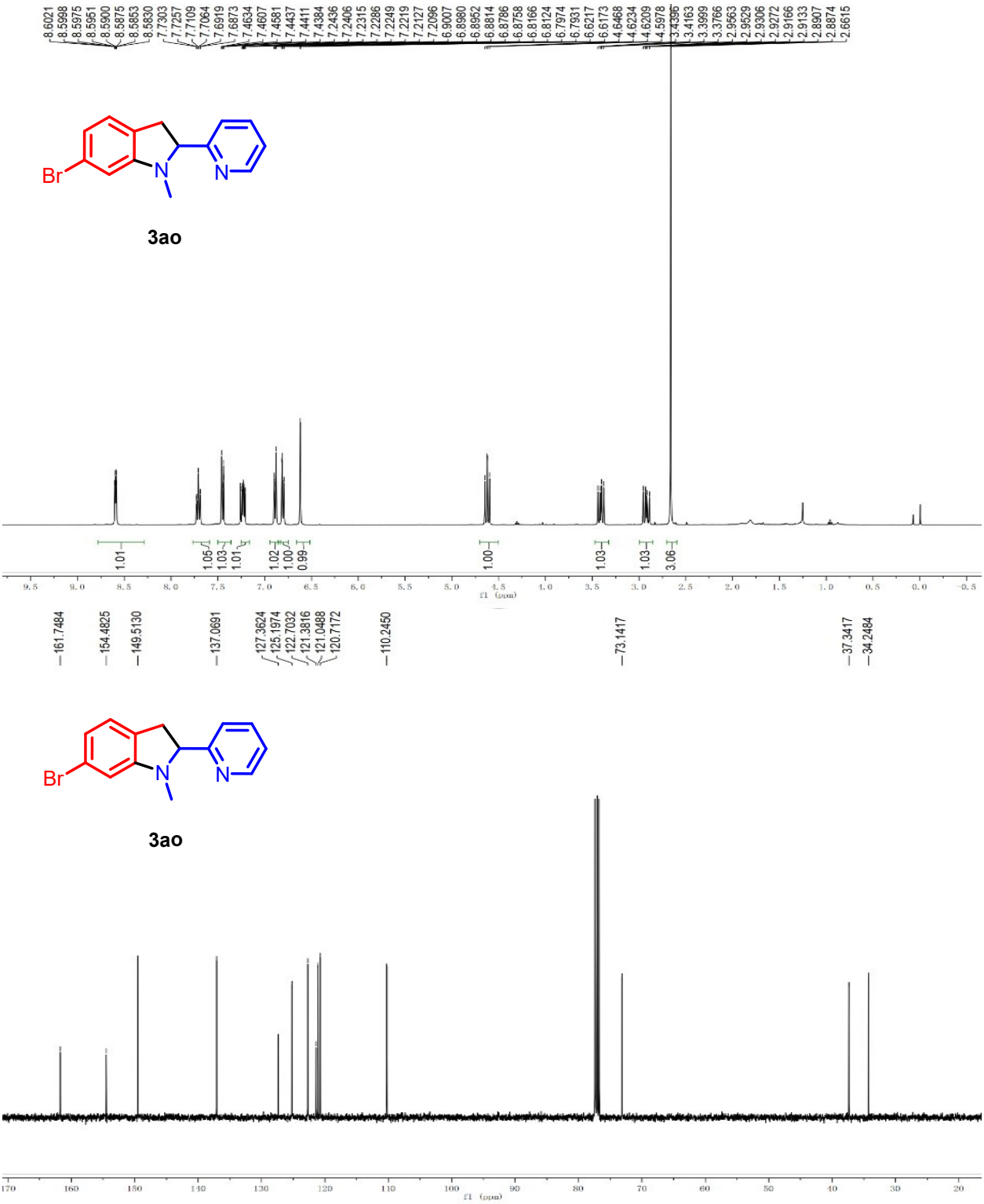


Figure S33. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ao in $CDCl_3$

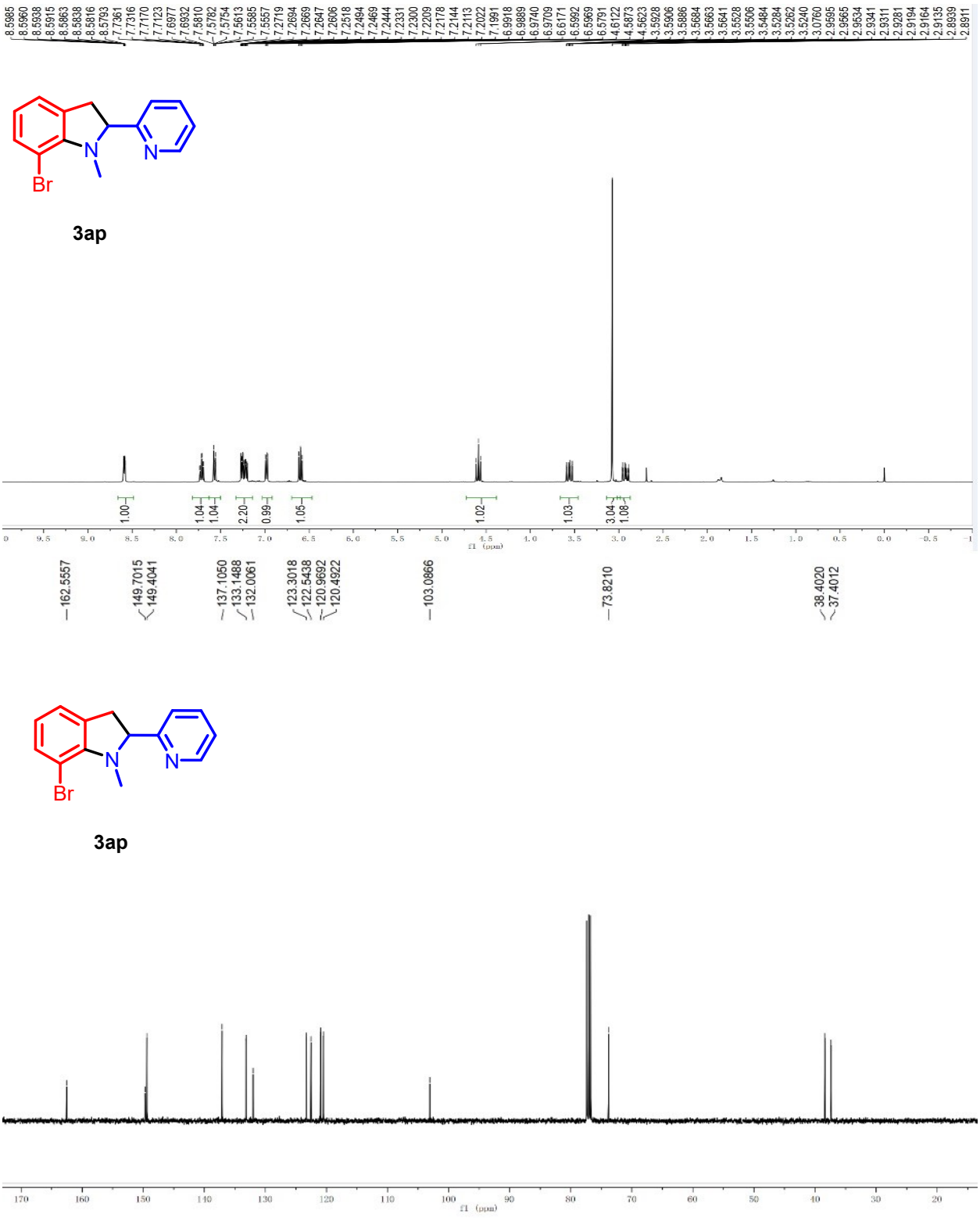
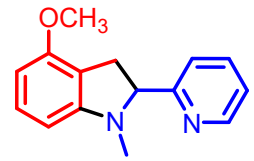
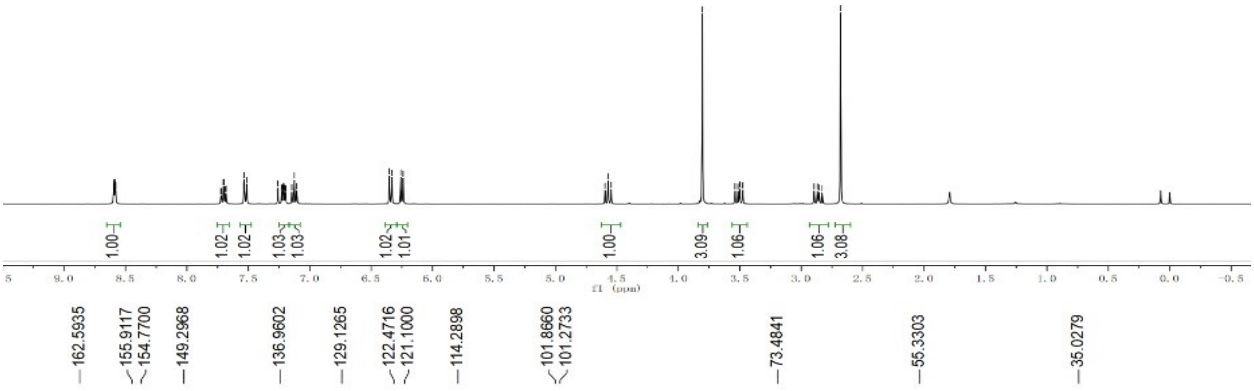
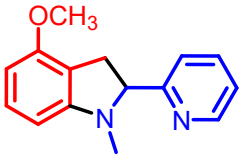


Figure S34. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ap in $CDCl_3$



3aq





3aq

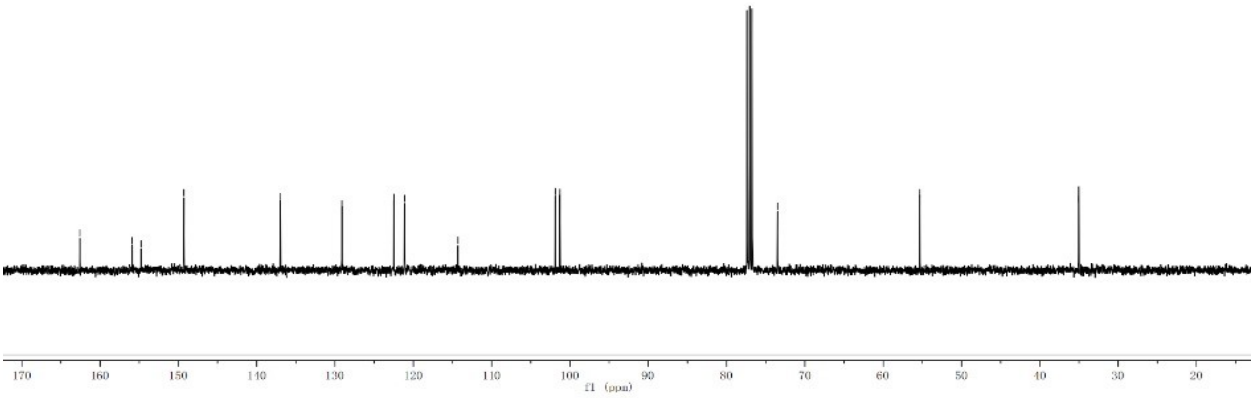


Figure S35. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3aq in $CDCl_3$

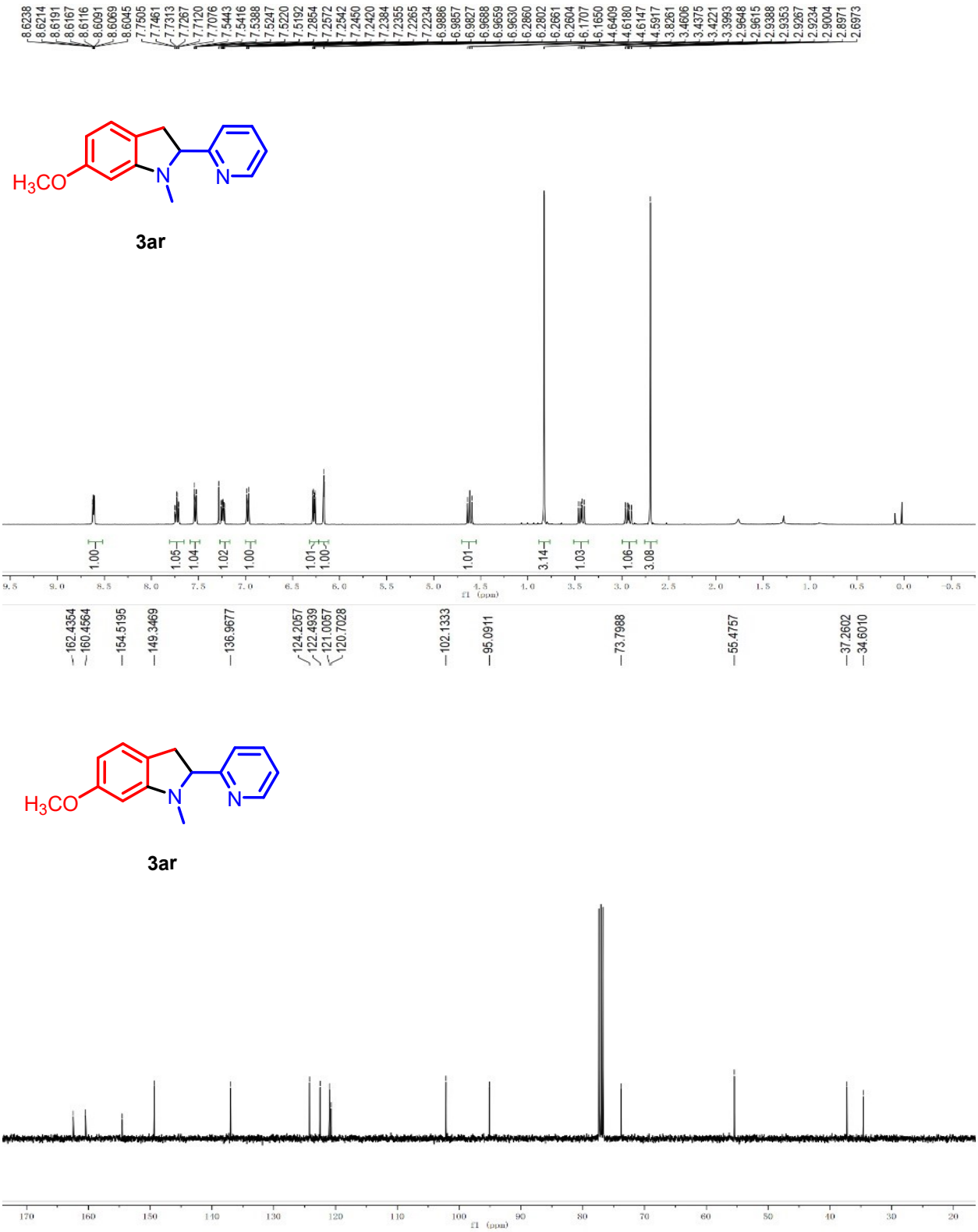


Figure S36. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3ar in $CDCl_3$

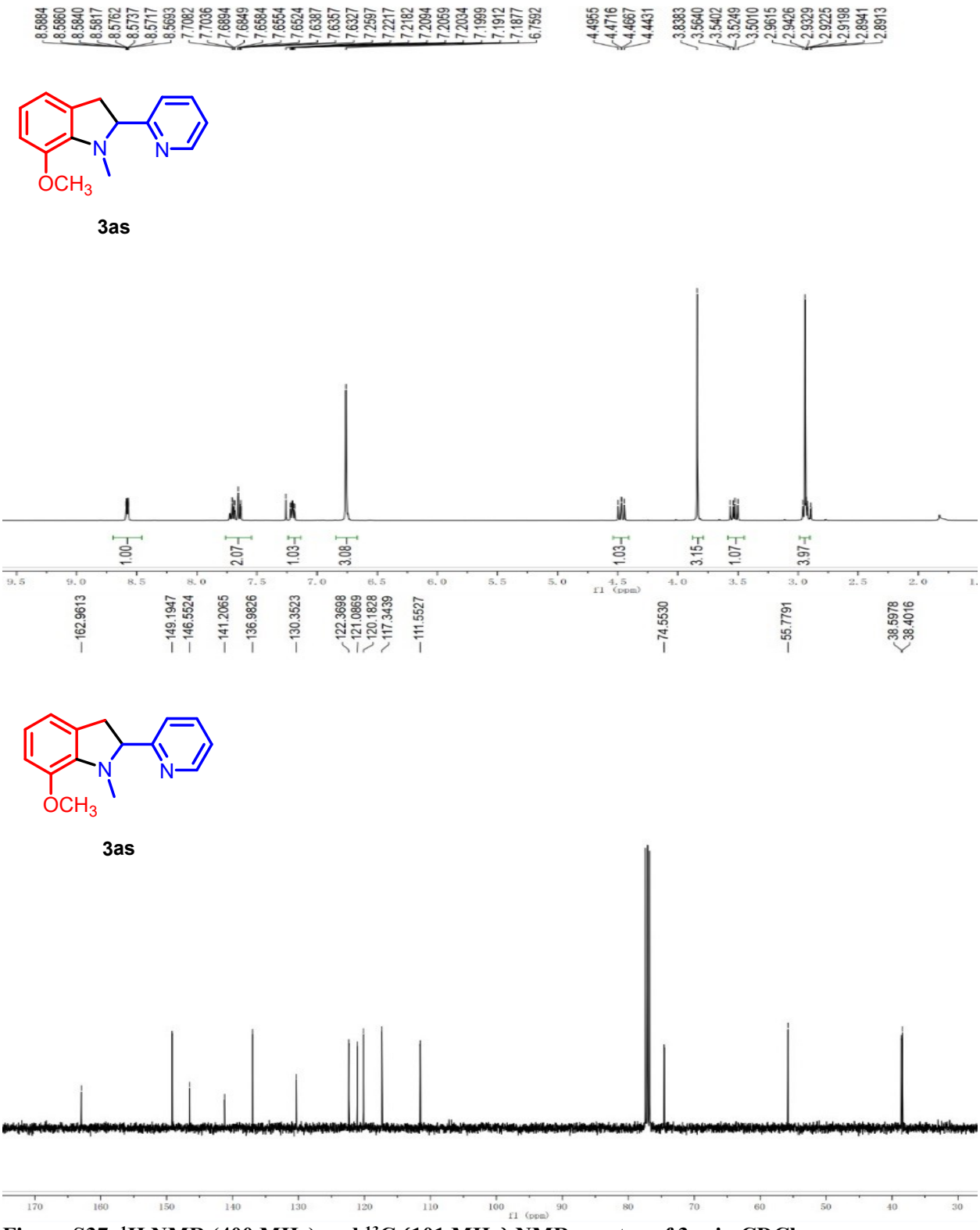


Figure S37. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3as in $CDCl_3$

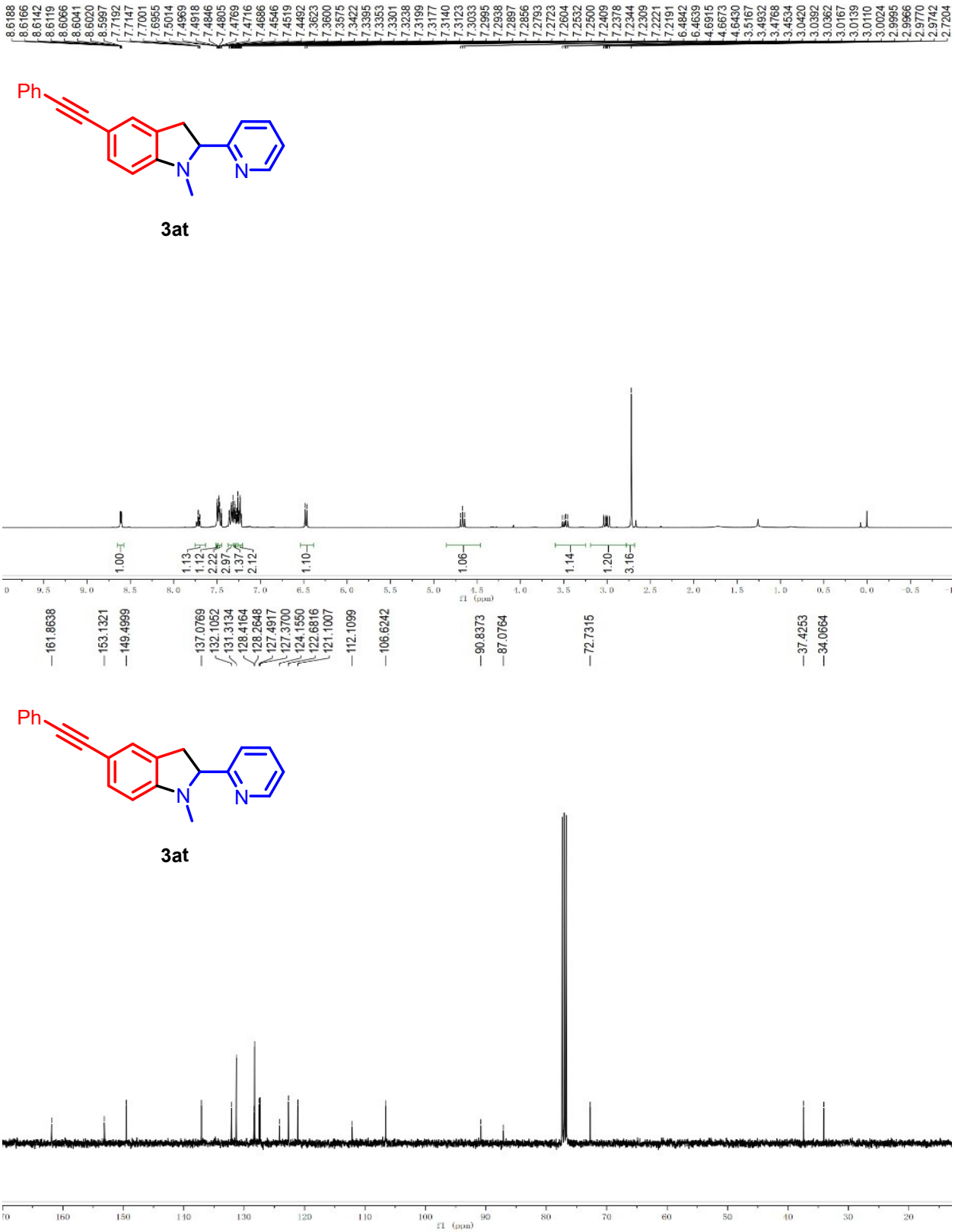


Figure S38. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3at in $CDCl_3$

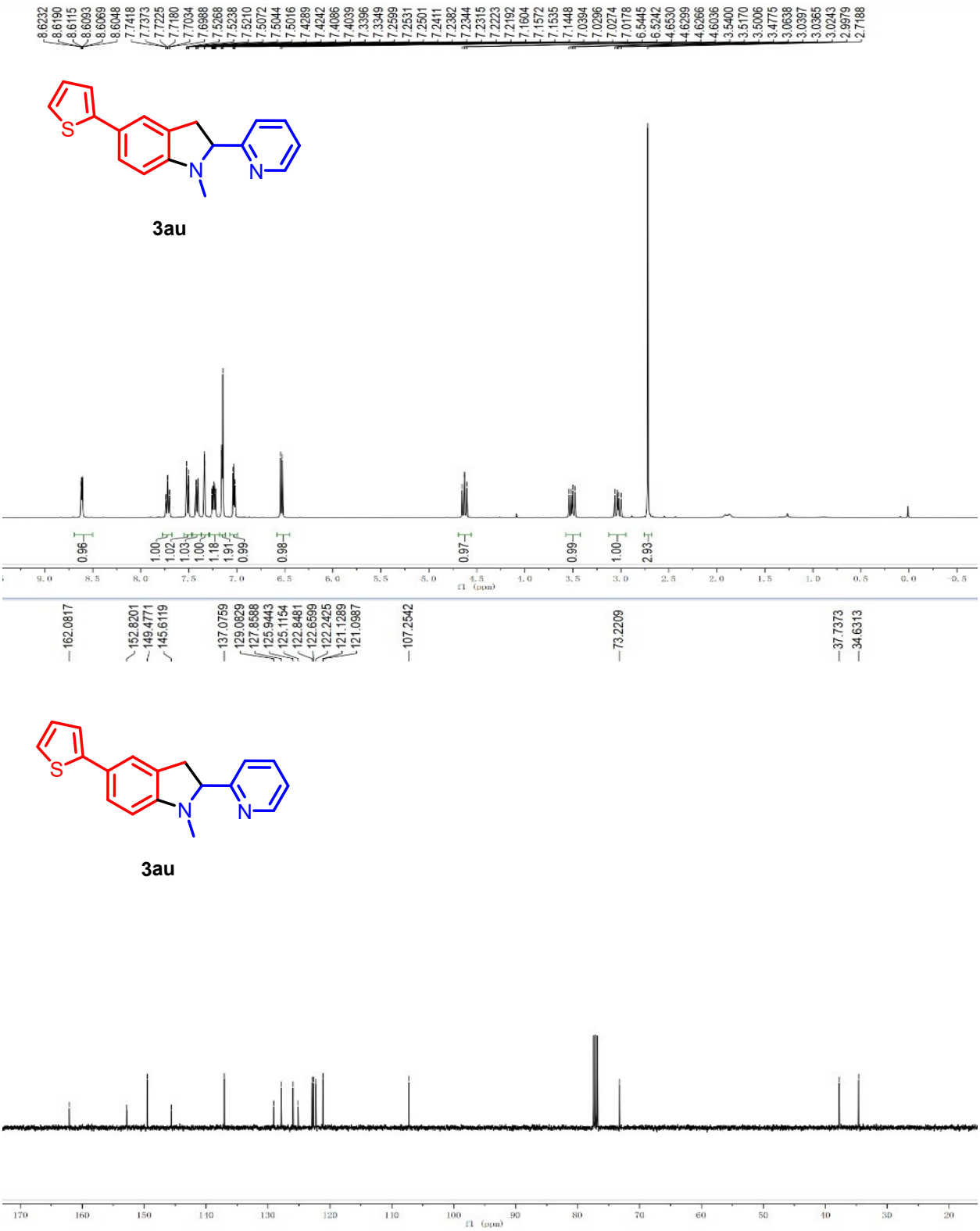
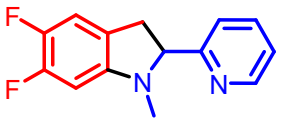
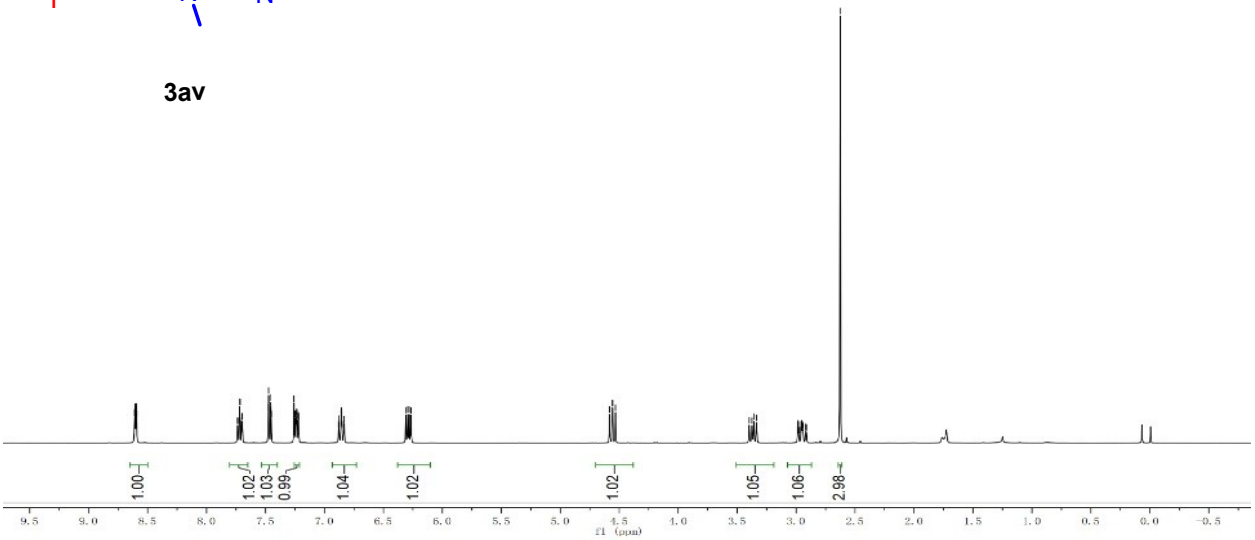
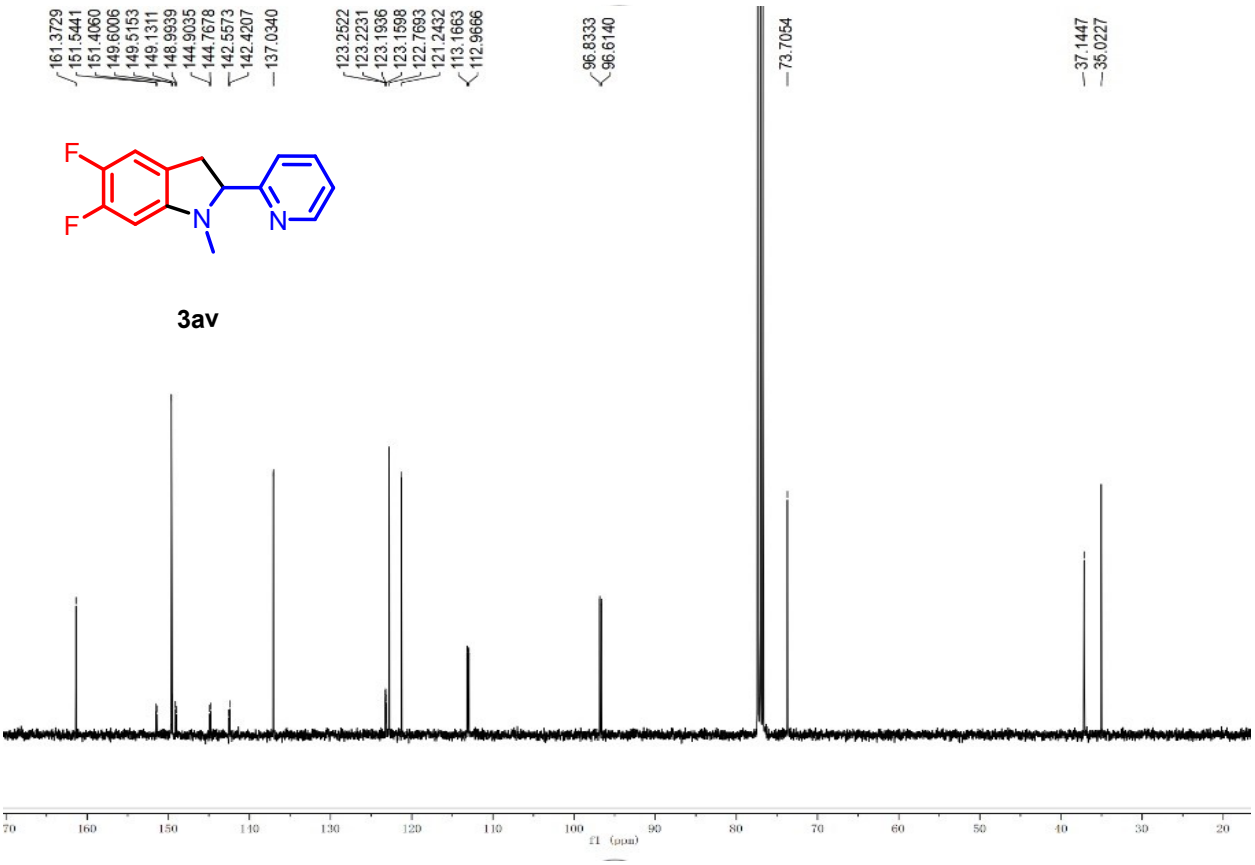


Figure S39. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 3au in $CDCl_3$



3av





3av

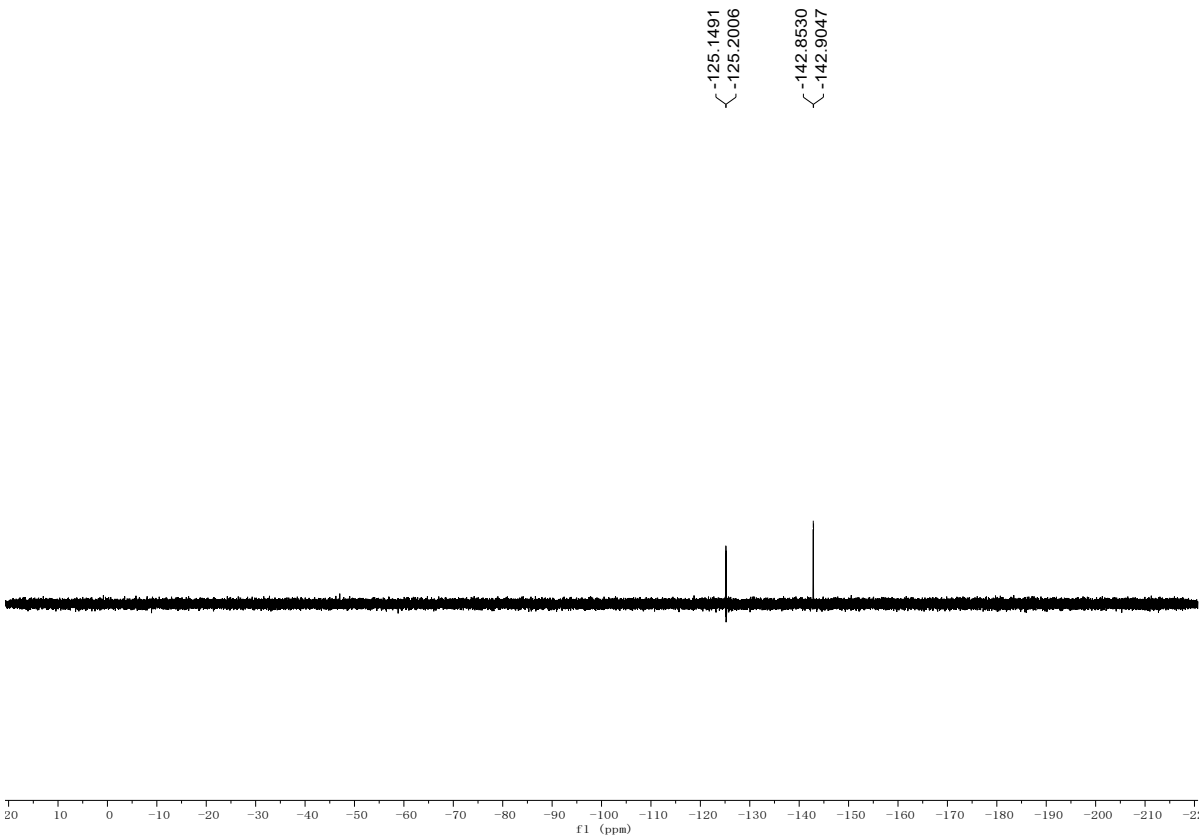


Figure S40. ^{1}H NMR (400 MHz) ^{13}C {101 MHz} and ^{19}F NMR (376 MHZ) NMR spectra of 3av in $CDCl_3$

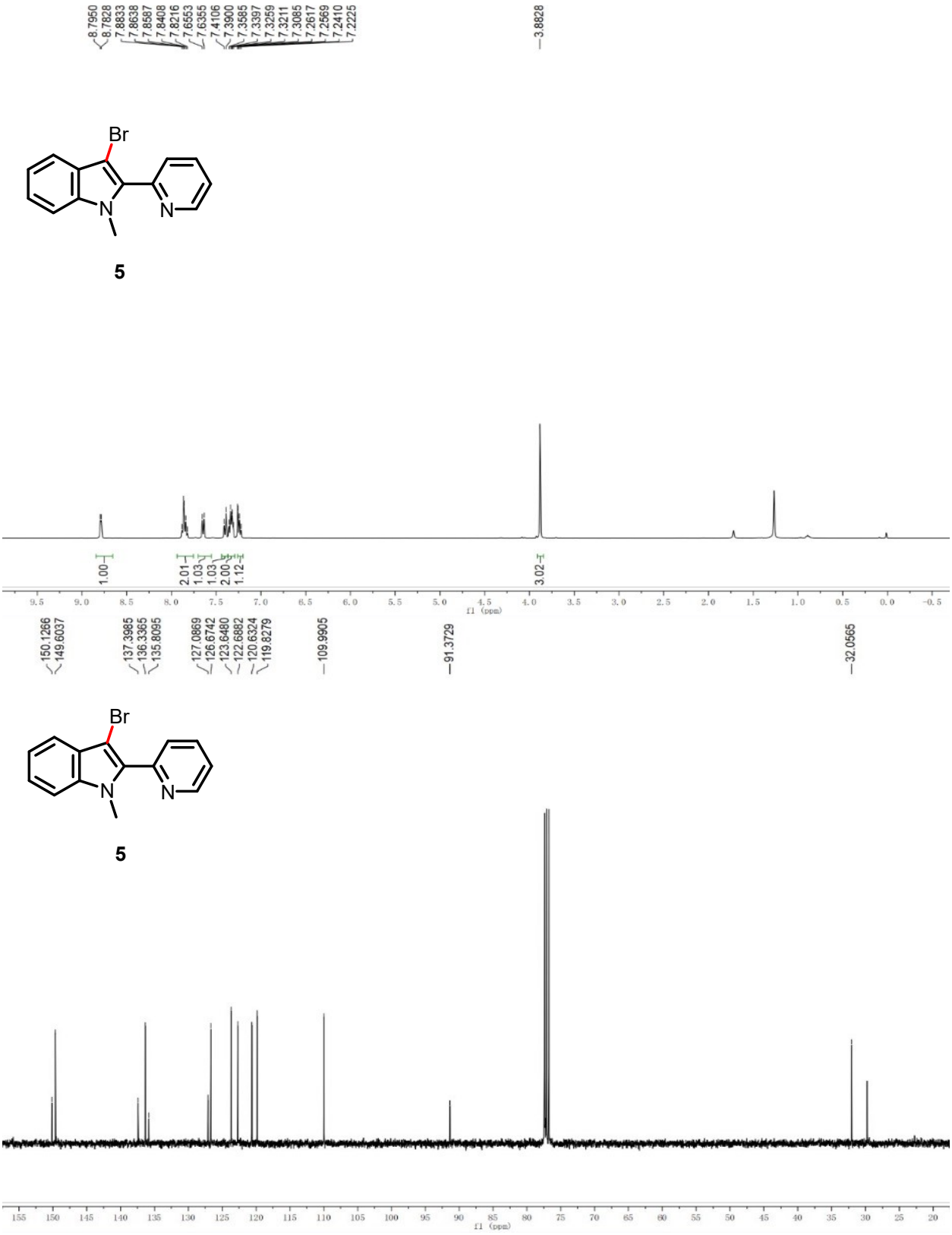


Figure S41. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 5 in $CDCl_3$

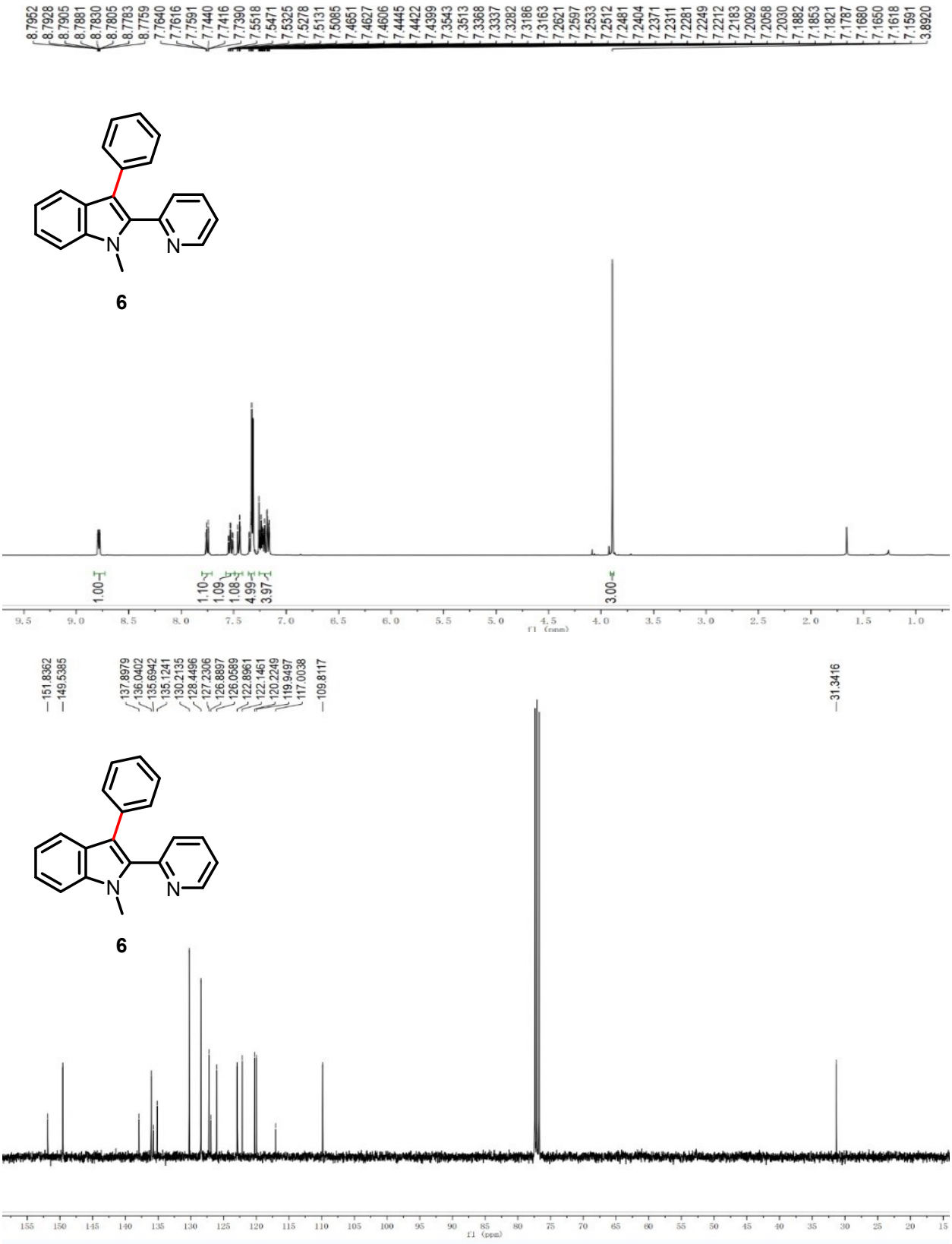
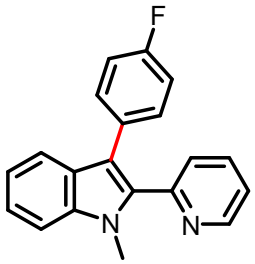
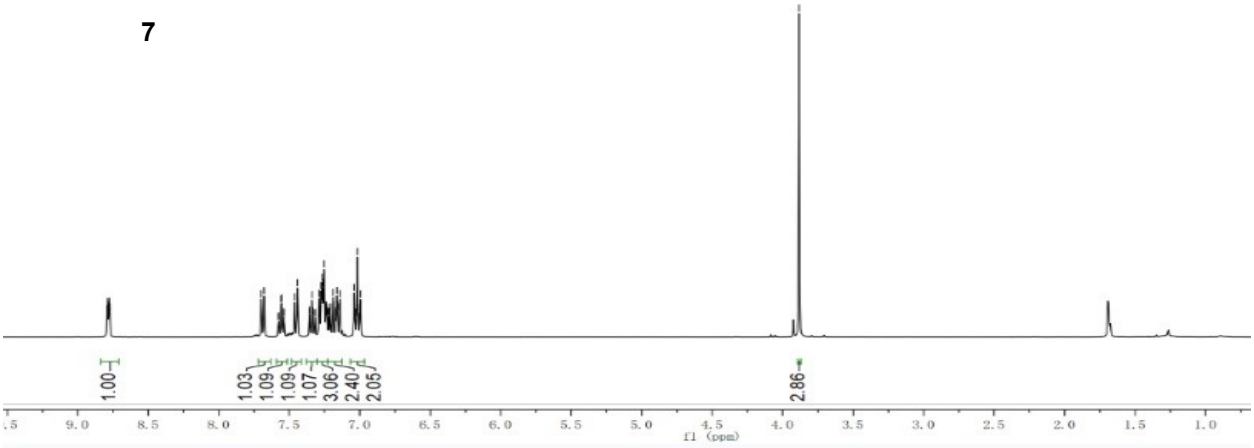


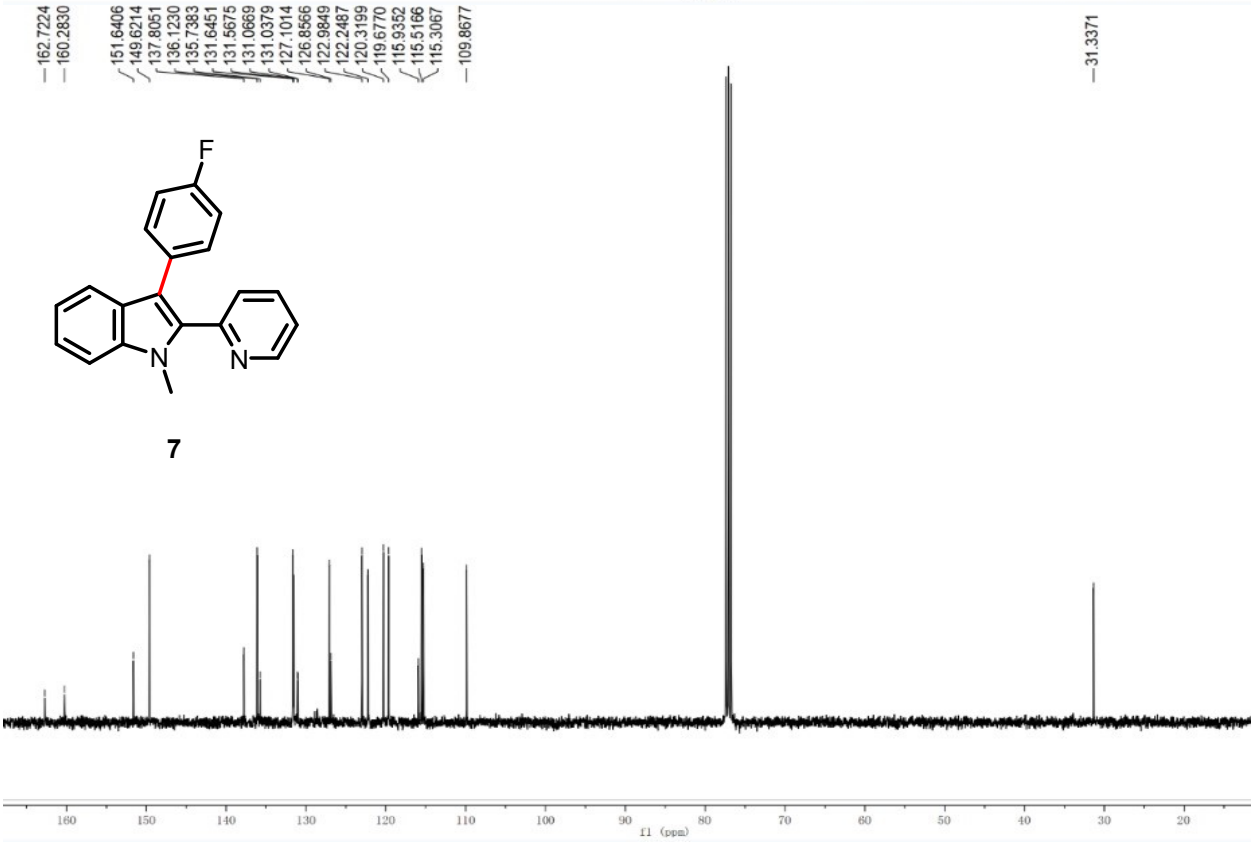
Figure S42. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 6 in $CDCl_3$


8.7917
8.7886
8.7854
8.7795
8.7764
8.7730
7.6987
7.6788
7.5783
7.5737
7.5591
7.5544
7.5397
7.5351
7.4622
7.4416
7.3578
7.3549
7.3403
7.3372
7.3339
7.3197
7.3167
7.2886
7.2837
7.2744
7.2671
7.2604
7.2531
7.2417
7.2389
7.2348
7.2319
7.2227
7.2197
7.2099
7.2073
7.1901
7.1869
7.1724
7.1699
7.1620
7.1587
7.1453
7.1422
7.1390
7.0390
7.0340
7.0234
7.0171
7.0117
7.0006
6.9953
3.8828


F
N
N

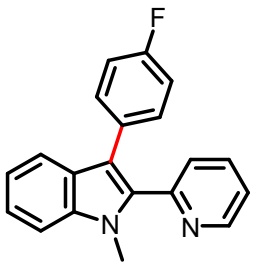
7


1.00
1.03
1.09
1.09
1.07
3.06
2.40
2.05
2.86
f1 (ppm)


162.7224
160.2830
151.6406
149.6214
137.8051
136.1230
135.7383
131.6451
131.5675
131.0669
131.0379
127.1014
126.8566
122.9849
122.2487
120.3199
119.6770
115.9352
115.5166
115.3067
109.8677
31.3371
f1 (ppm)

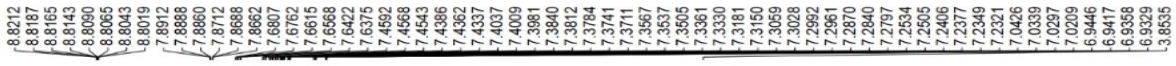
F
N
N

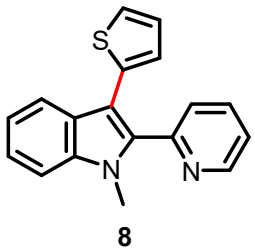
7



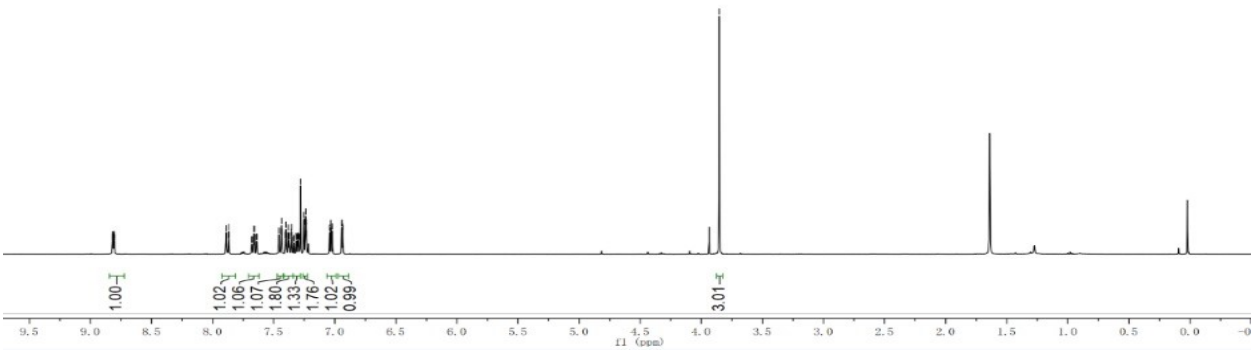
7

Figure S43. ^{1}H NMR (400 MHz) ^{13}C {101 MHz} and ^{19}F NMR (376 MHZ) NMR spectra NMR spectra of 7 in $CDCl_3$





8



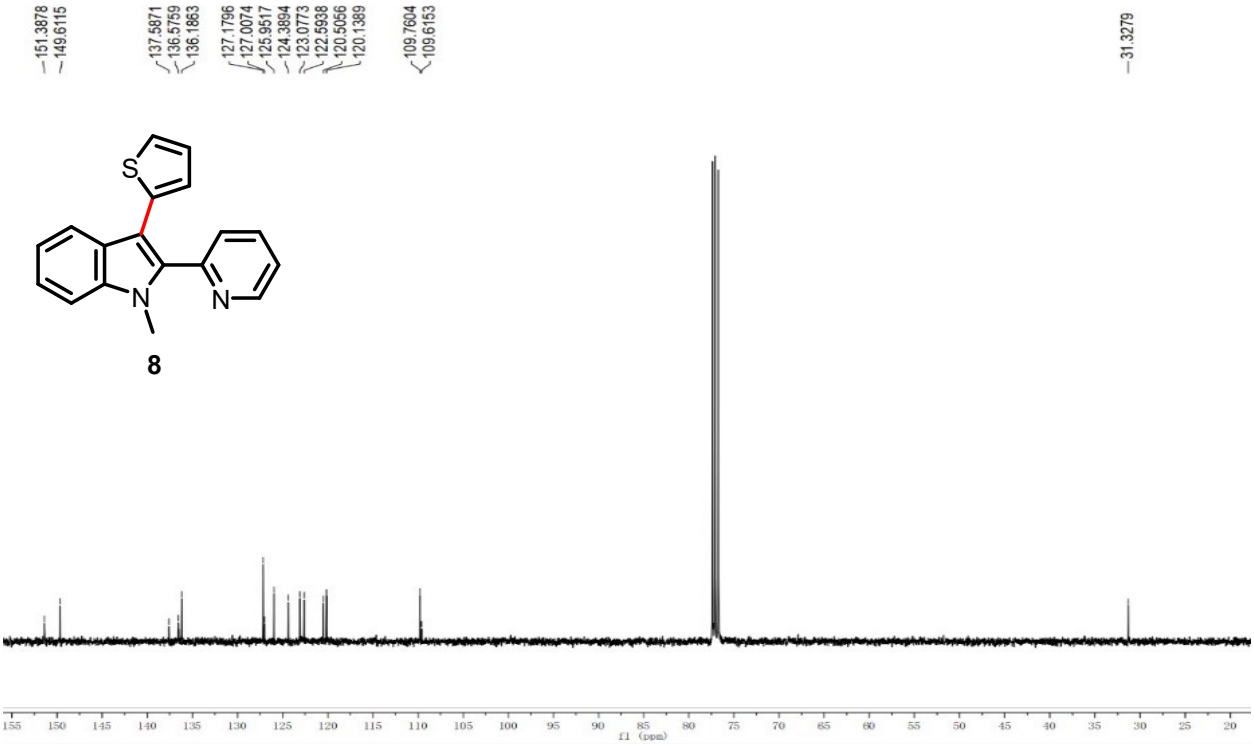
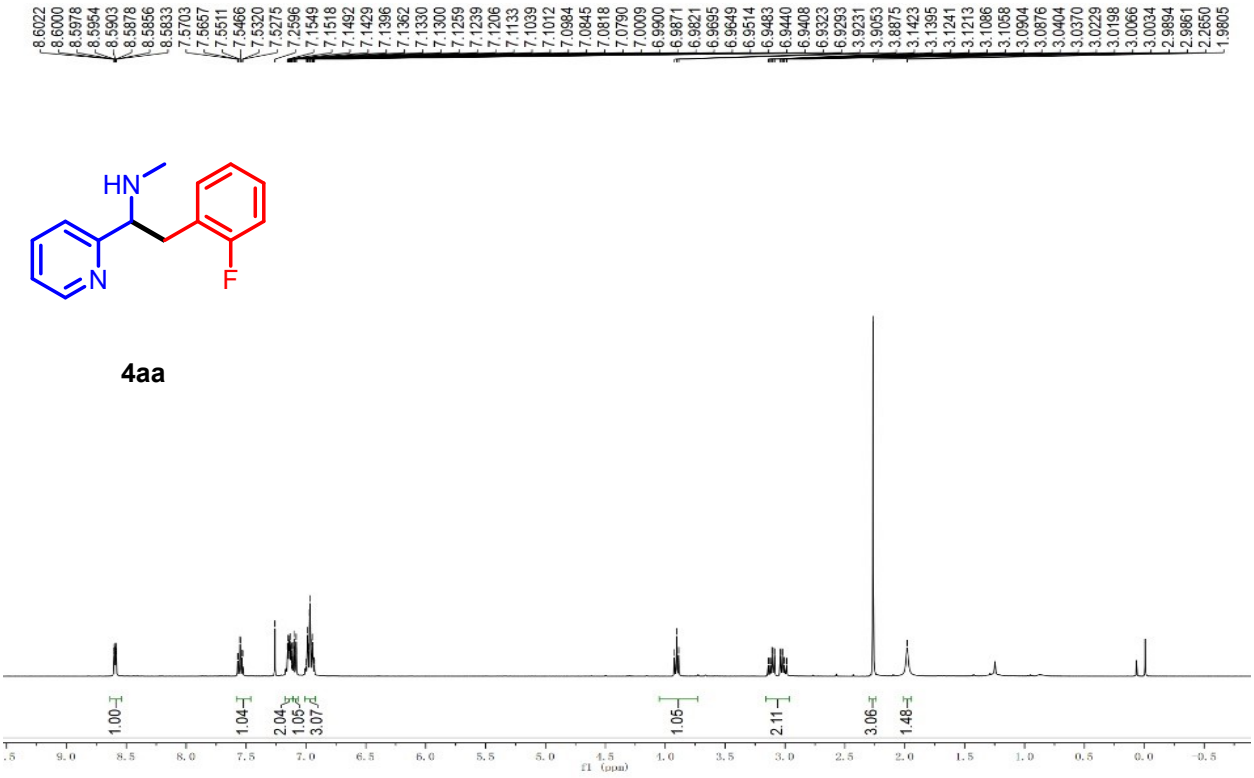


Figure S44. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 8 in $CDCl_3$



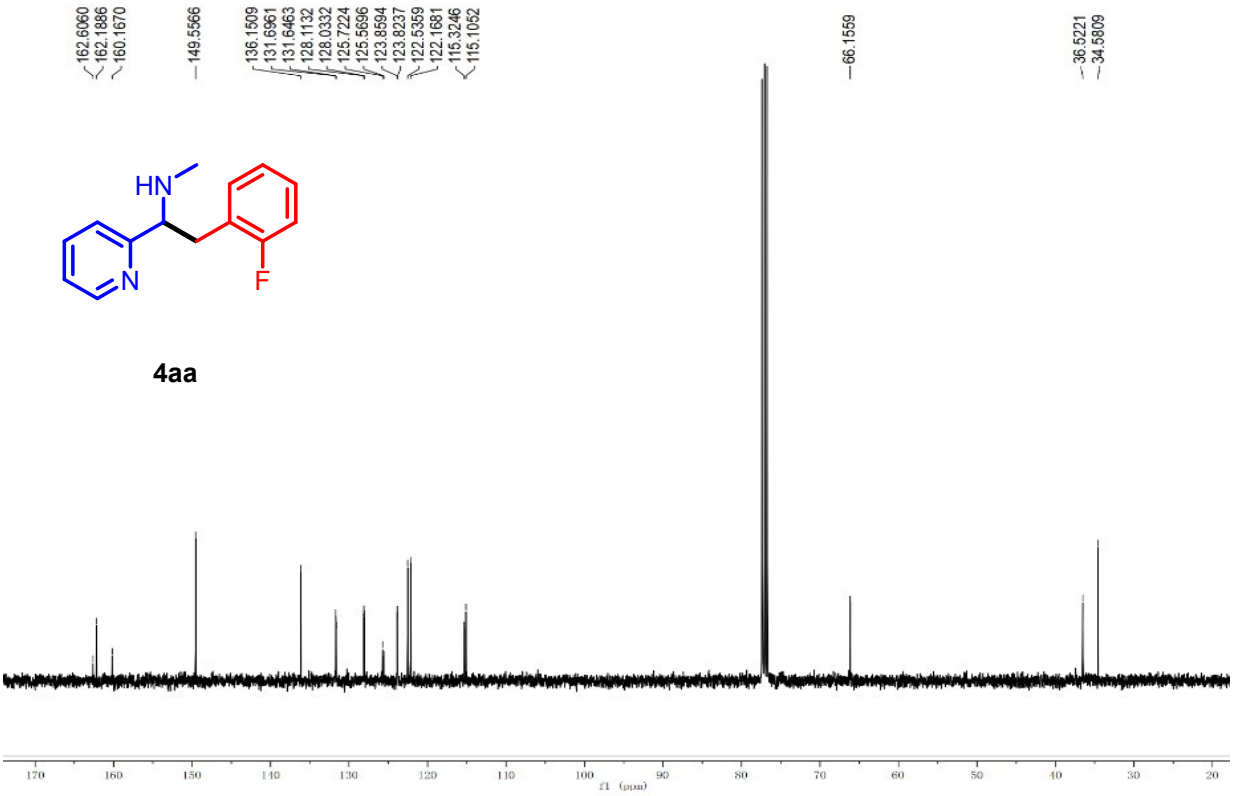


Figure S45. ^{1}H NMR (400 MHz) and ^{13}C {101 MHz} NMR spectra of 4aa in $CDCl_3$

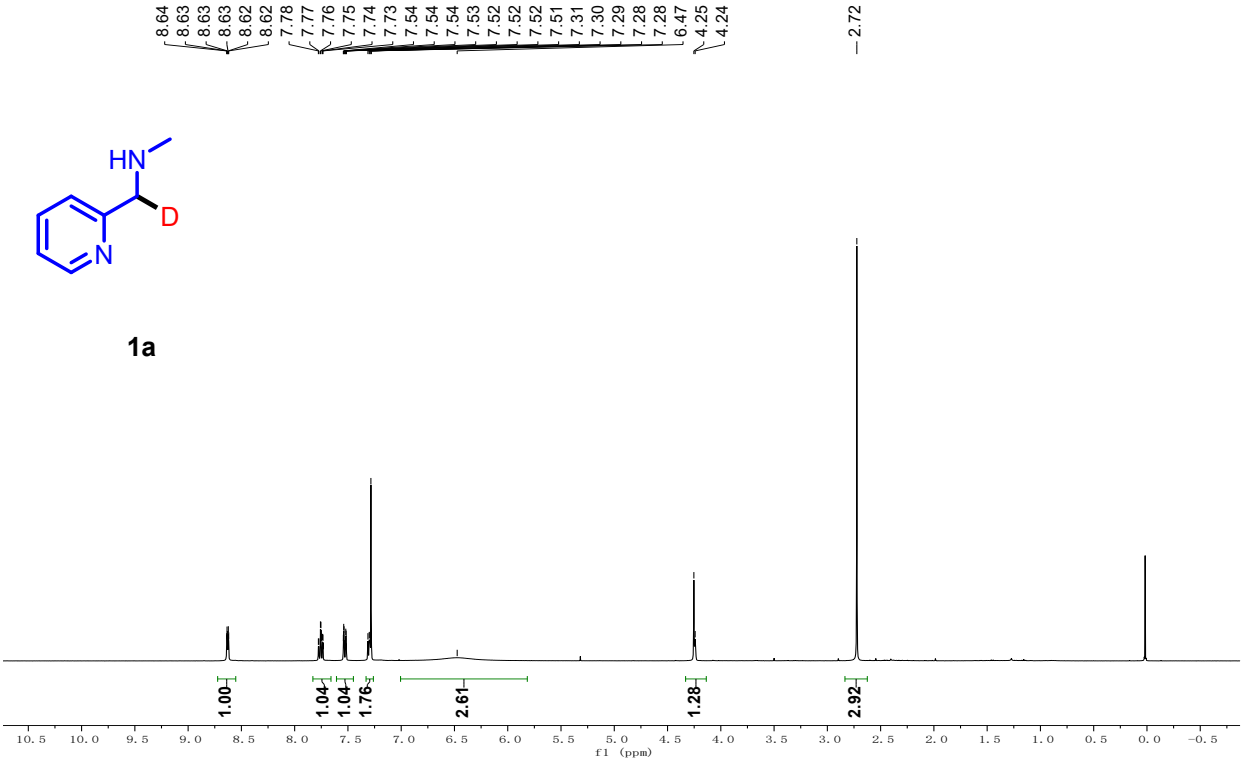


Figure S46. ^{1}H NMR (400 MHz) of D-1a in $CDCl_3$