SUPPORTING INFORMATION

Alkali-Amide Controlled Selective Synthesis of 7-Azaindole and 7-Azaindoline through Domino Reactions of 2-Fluoro-3-methylpyridine and Aldehydes

Xinyu Xu,[a] Mingjie Ou,[a] Yan-En Wang,[b] Tingzhi Lin,[a] Dan Xiong [a], Fei Xue[b], Patrick J. Walsh[d] and Jianyou Mao*[a]

[a]Technical Institute of Fluorochemistry (TIF), Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Centre for Advanced Materials, Nanjing Tech University, 30 South Puzhu Road, Nanjing 211816 (P.R. China)

[b]Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China

[c]College of Life Sciences, Hebei Agricultural University, Baoding 071001, P. R. China.

[d]Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, USA.

Table of Contents

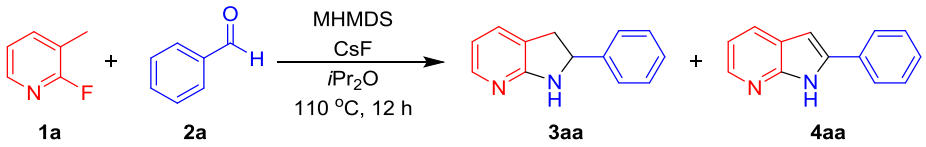
1. General Information

All reactions were performed under an atmosphere of dry argon. Lithium bis(trimethylsilyl)amide (LiHMDS; Aldrich, 97%), Sodium bis(trimethylsilyl)amide (NaHMDS; Aldrich, 95%), Potassium bis(trimethylsilyl)amide (KHMDS; Aldrich, 95%), CsF (Aldrich, 99%). Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, Alfa Aesar, TCI China, Adamas-beta, or J&K.

The progress of the reactions was monitored by thin-layer chromatography using TLC plates and visualized by short-wave ultraviolet light or by treatment with ninhydrin. Flash chromatography was performed with Qingdao Haiyang flash silica gel (200–300 mesh). The NMR spectra were obtained using a Brüker 400 MHz Fourier-transform and a JEOL 400 MHz Fourier-transform NMR spectrometer. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. The infrared spectra were obtained with KBr plates by using a IS10 FT-IR Spectrometer (ThermoFisher Corporation). High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive or negative mode. Melting points were measured using a WRS-1C Melt-Temp apparatus and were uncorrected.

2. Systematic Study of Reaction Conditions

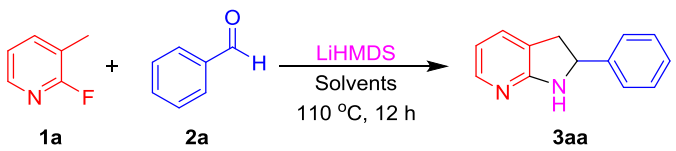
2.1. Screen of the base and additive (Table S1)



entry	bases	additives	1a:2a:base	Solvents/0.1 mL	3aa AY(%)[a]	4aa AY(%)[a]
1	$LiN(SiMe_3)_2$	-	1:1:3	iPr_2O	68	Trace
2	$NaN(SiMe_3)_2$	-	1:1:3	iPr_2O	26	48
3	$KN(SiMe_3)_2$	-	1:1:3	iPr_2O	Trace	74
4	$LiN(SiMe_3)_2$	CsF	1:1:3	iPr_2O	Trace	50
5	$NaN(SiMe_3)_2$	CsF	1:1:3	iPr_2O	16	34
6	$KN(SiMe_3)_2$	CsF	1:1:3	iPr_2O	0	68

[a]Assay yield(AY) determined by ^1H NMR analysis of crude reaction mixture with CH_2Br_2 as an internal stand.

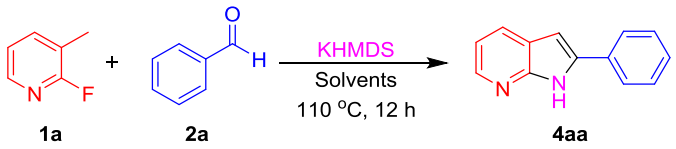
2.2. Screen of the 7-azaindoline (Table S2)



entry	bases	1a:2a:base	solvents	3aa AY(%)[a]
1	$LiN(SiMe_3)_2$	1:1:3	iPr_2O (0.1 mL)	68
2	$LiN(SiMe_3)_2$	1:1:3	iPr_2O (1 mL)	56
3	$LiN(SiMe_3)_2$	1:1:4	iPr_2O (1 mL)	77
4	$LiN(SiMe_3)_2$	1:1:5	iPr_2O (1 mL)	83
5	$LiN(SiMe_3)_2$	1:2:3	iPr_2O (1 mL)	22
6	$LiN(SiMe_3)_2$	1:3:3	iPr_2O (1 mL)	Trace
7	$LiN(SiMe_3)_2$	2:1:3	iPr_2O (1 mL)	59
8	$LiN(SiMe_3)_2$	3:1:3	iPr_2O (1 mL)	68
9	$LiN(SiMe_3)_2$	2:1:4	iPr_2O (1 mL)	72
10	$LiN(SiMe_3)_2$	3:1:4	iPr_2O (1 mL)	92
11	$LiN(SiMe_3)_2$	2:1:3	iPr_2O (0.5 mL)	93
12[b]	$LiN(SiMe_3)_2$	2:1:3	iPr_2O (0.5 mL)	78
13[c]	$LiN(SiMe_3)_2$	2:1:3	iPr_2O (0.5 mL)	43
14[d]	$LiN(SiMe_3)_2$	2:1:3	iPr_2O (0.5 mL)	0
15[e]	$LiN(SiMe_3)_2$	2:1:3	iPr_2O (0.5 mL)	0

[a]Assay yield(AY) determined by chromatography on silica gel. [b]At 90 °C. [c]At 70 °C. [d]At 50 °C. [e]At 25 °C.

2.3. Screen of the 7-azaindole (Table S3)



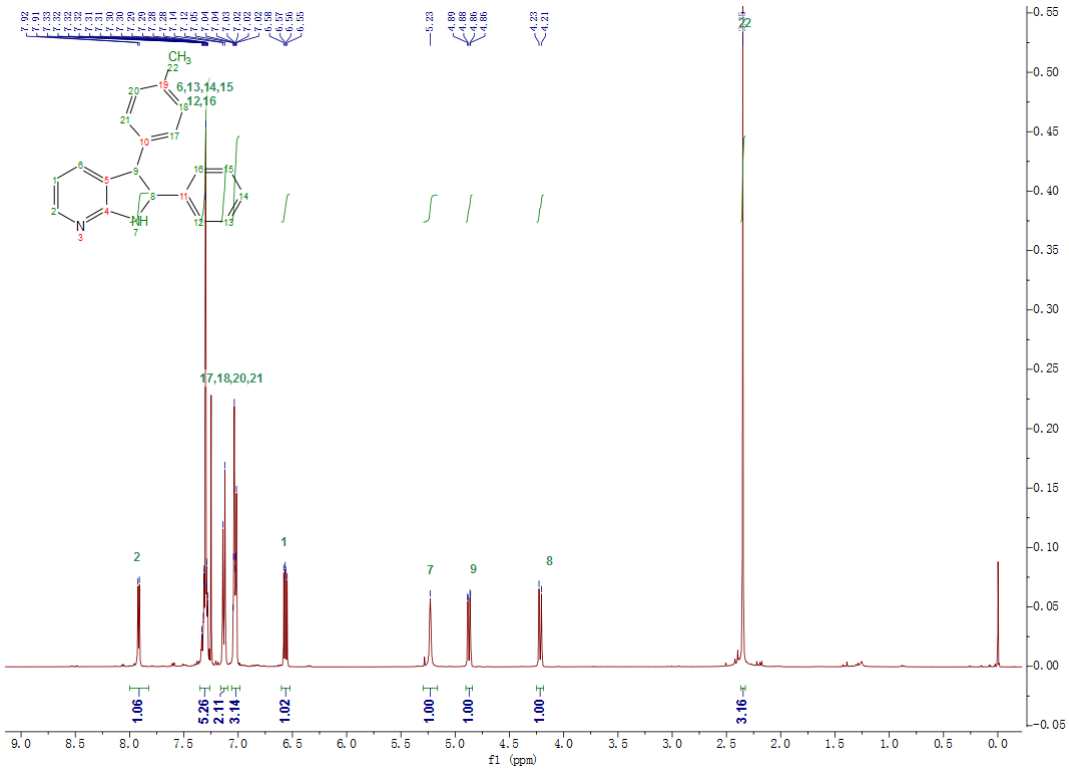
1a 2a 4aa

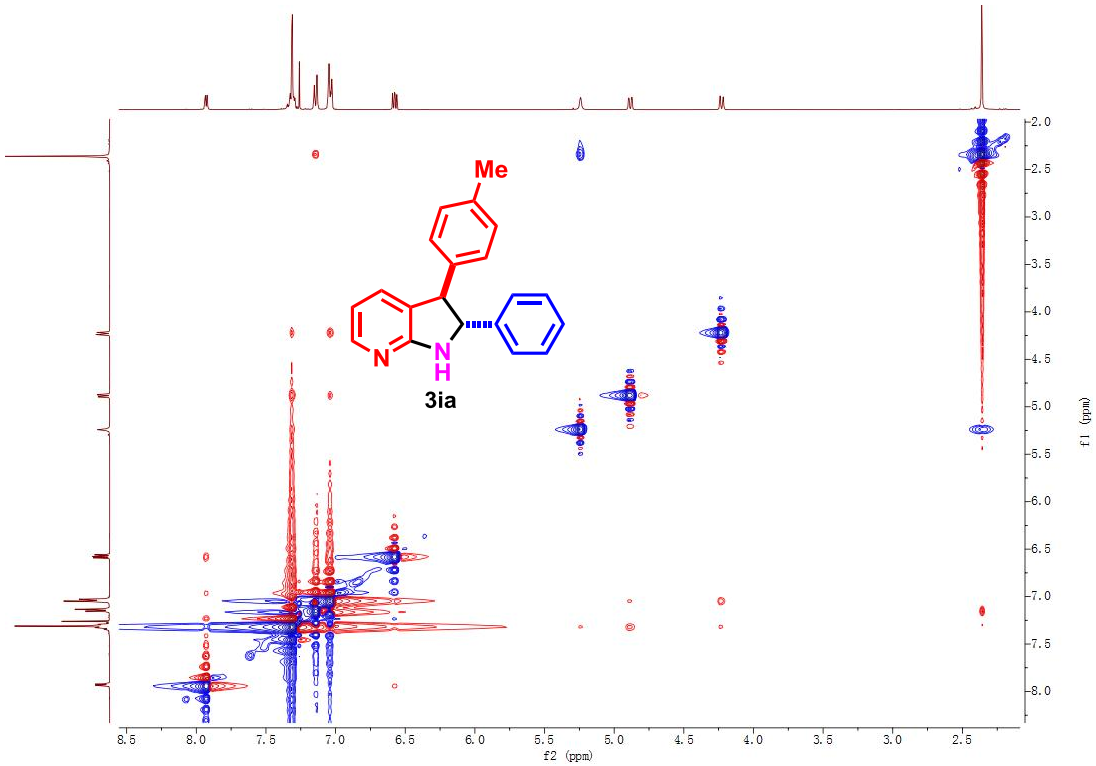
entry	bases	1a:2a:base	solvents	4aa AY(%)[a]
1	$KN(SiMe_3)_2$	1:1:3	iPr_2O (0.1 mL)	82
2[b]	$KN(SiMe_3)_2$	1:1:3	iPr_2O (0.1 mL)	51
3[c]	$KN(SiMe_3)_2$	1:1:3	iPr_2O (0.1 mL)	32
4[d]	$KN(SiMe_3)_2$	1:1:3	iPr_2O (0.1 mL)	0
5[e]	$KN(SiMe_3)_2$	1:1:3	iPr_2O (0.1 mL)	0
6	$KN(SiMe_3)_2$	1:1:3	iPr_2O (0.2 mL)	66
7	$KN(SiMe_3)_2$	1:1:3	iPr_2O (1 mL)	52
8	$KN(SiMe_3)_2$	1:1:3	iPr_2O (0.05 mL)	66

9	$KN(SiMe_3)_2$	1:1:3	neat	40
10	$KN(SiMe_3)_2$	1:2:4	iPr_2O (0.1 mL)	61
11	$KN(SiMe_3)_2$	1:3:5	iPr_2O (0.1 mL)	62
12	$KN(SiMe_3)_2$	1:1:3	CPME (0.1 mL)	75
13	$KN(SiMe_3)_2$	1:1:3	TBME (0.1 mL)	76
14	$KN(SiMe_3)_2$	1:1:3	2-MeTHF (0.1 mL)	56
15	$KN(SiMe_3)_2$	1:1:3	Dioxane (0.1 mL)	Trace
16	$KN(SiMe_3)_2$:$LiN(SiMe_3)_2$=3:2	1:3:5	iPr_2O (1 mL)	86
17[b]	$KN(SiMe_3)_2$:$LiN(SiMe_3)_2$=3:2	1:3:5	iPr_2O (1 mL)	54
18[c]	$KN(SiMe_3)_2$:$LiN(SiMe_3)_2$=3:2	1:3:5	iPr_2O (1 mL)	26
19[d]	$KN(SiMe_3)_2$:$LiN(SiMe_3)_2$=3:2	1:3:5	iPr_2O (1 mL)	Trace
20[e]	$KN(SiMe_3)_2$:$LiN(SiMe_3)_2$=3:2	1:3:5	iPr_2O (1 mL)	0

[a]Assay yield(AY) determined by chromatography on silica gel. [b]At 90 °C. [c]At 70 °C. [d]At 50 °C. [e]At 25 °C.

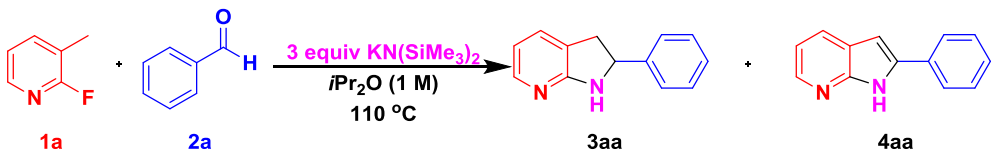
3. NOESY of the compound 3ia





4. Mechanistic Experiments (Figure S1)

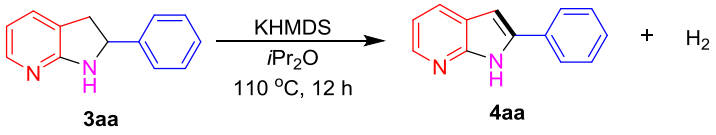
4.1 Time-controlled reactions



1a 2a 3aa 4aa

	15 min	30 min	45 min	1 h	2 h	4 h	6 h	8 h	10 h	12 h
3aa yields:	52%	48%	32%	31%	31%	20%	Trace	Trace	Trace	Trace
	15 min	30 min	45 min	1 h	2 h	4 h	6 h	8 h	10 h	12 h
4aa yields:	26%	36%	40%	46%	56%	66%	76%	80%	82%	84%

4.2 Hydrogen detection



3aa 4aa

Reaction 1:

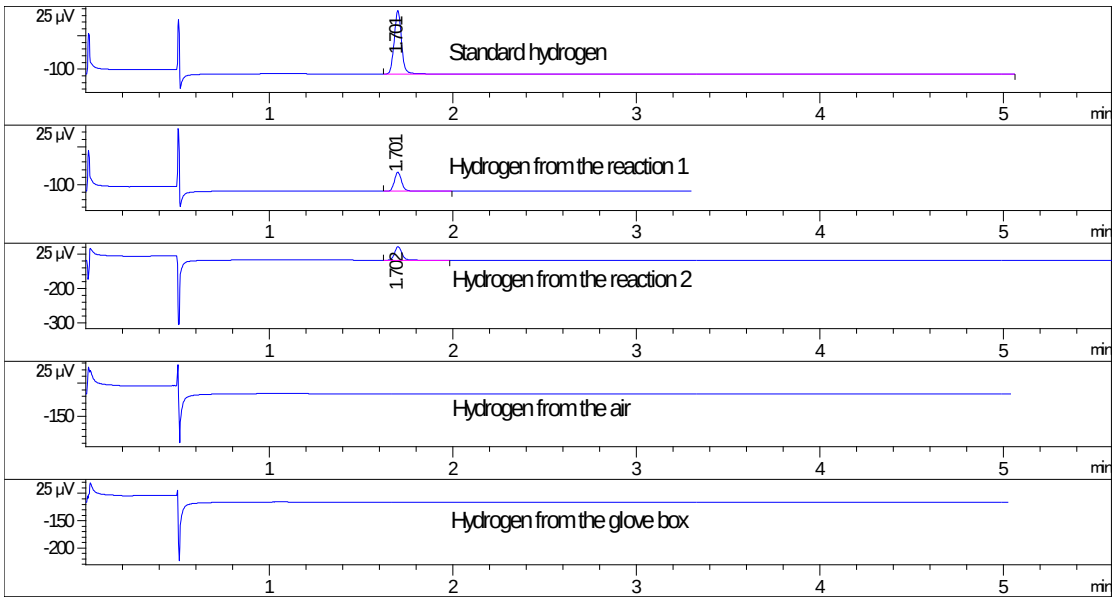
To an oven-dried 10 mL Schlenk tube with a branch equipped with a stir bar under argon atmosphere inside a glove box was added $KN(SiMe_3)_2$ (600.0 mg, 3.0 mmol), 7-azaindoline (196.2 mg, 1.0 mmol) and iPr_2O (1.0 mL). A 10 mL air bag was connected with the Schlenk tube and removed from the glove box. The reaction mixture was heated to 110 °C in an oil bath and stirred for 12 h.

Then, the valve of the air bag was screwed. GC analysis of the gas (shown below) indicated that hydrogen was produced in the procedure of transformation from azaindoline to azaindole. (GC-TCD: Agilent GC 7890B)

Reaction 2:

1a 2a 4aa

To an oven-dried 10 mL Schlenk tube with a branch equipped with a stir bar under argon atmosphere inside a glove box was added $KN(SiMe_3)_2$ (600.0 mg, 3.0 mmol), 2-fluoro-3-methylpyridine (210 μL, 1.0 mmol), benzaldehyde (210 μL, 1.0 mmol) and iPr_2O (1.0 mL). A 10 mL air bag was connected with the Schlenk tube and removed from the glove box. The reaction mixture was heated to 110 °C in an oil bath and stirred for 12 h. Then, the valve of the air bag was screwed. GC analysis of the gas (shown below) indicated that hydrogen was produced in the procedure of the formation of azaindole. (GC-TCD: Agilent GC 7890B)



5. General Procedure

5.1. General Procedure A

To an oven-dried microwave vial equipped with a stir bar under argon atmosphere inside a glove box was added $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), iPr_2O (1.0 mL) and the corresponding 2-fluoro-3-methylpyridine derivative (0.40 mmol) via microliter pipette. Then benzaldehyde derivative (0.20 mmol) was added via microliter pipette. The microwave vial was sealed with a cap and removed from the glove box. The reaction mixture was heated to 110 °C in an oil bath and stirred for 12 h. The sealed vial was cooled to room temperature, opened to air, and then 5 drops of water were added. The reaction mixture was passed through a short pad of silica, washed with an 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 of the azaindolines.

5.2. General Procedure B

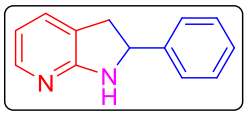
To an oven-dried microwave vial equipped with a stir bar under argon atmosphere inside a glove box

was added $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), iPr_2O (0.2 mL) and 2-fluoro-3-methylpyridine derivative (0.20 mmol) via microliter pipette. Then the corresponding benzaldehyde derivative (0.20 mmol) was added via microliter pipette. The microwave vial was sealed with a cap and removed from the glove box. The reaction mixture was heated to 110 °C in an oil bath and stirred for 12 h. The sealed vial was cooled to room temperature, opened to air, and then 5 drops of water were added. The reaction mixture was passed through a short pad of silica, washed with an 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 of the azaindoles.

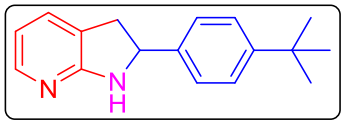
5.3. General Procedure C

To an oven-dried microwave vial equipped with a stir bar under argon atmosphere inside a glove box was added $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (66.8 mg, 0.40 mmol), iPr_2O (1.0 mL) and 2-fluoro-3-methylpyridine derivative (0.20 mmol) was added via microliter pipette. Then the corresponding benzaldehyde derivative (0.60 mmol) was added via microliter pipette. The microwave vial was sealed with a cap and removed from the glove box. The reaction mixture was heated to 110 °C in an oil bath and stirred for 12 h. The sealed vial was cooled to room temperature, opened to air, and then 5 drops of water were added. The reaction mixture was passed through a short pad of silica, washed with an 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 of the azaindoles.

6. Characterization Data for Products

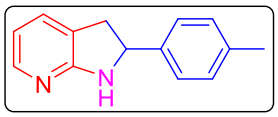


2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3aa) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (36.5 mg, 93% yield) as a light yellow solid. Mp 125 – 126 °C. R_f = 0.50 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 5.4, 1.4 Hz, 1H), 7.44 – 7.19 (m, 6H), 6.54 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.10 (s, 1H), 5.00 (t, *J* = 8.6 Hz, 1H), 3.48 (dd, *J* = 16.3, 9.5 Hz, 1H), 2.94 (dd, *J* = 16.3, 7.8 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.9, 146.2, 144.0, 131.5, 128.7, 127.6, 126.0, 120.9, 113.7, 60.3, 38.0 ppm. IR (neat): 3445, 3201, 2906, 1614, 1591,1491, 1454, 1255, 992, 900, 772, 699 cm^{-1}. HRMS: calcd for $C_{13}H_{13}N_2$ $[M+H]^+$ 197.1079, found 197.1079.

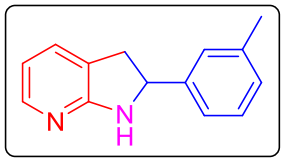


2-(4-(tert-butyl)phenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ab) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-(tert-butyl)benzaldehyde (**2b**) (34 µL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (44.4 mg, 88% yield) as a light yellow solid. Mp 128 – 129 °C. R_f = 0.53 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 5.6 Hz, 1H), 7.30 (d, *J* = 16.4 Hz, 3H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.08 (s, 1H), 6.56 (t, *J* = 6.4 Hz, 1H), 5.07 (t, *J* = 8.8 Hz, 1H), 3.49 (dd, *J* = 16.9,

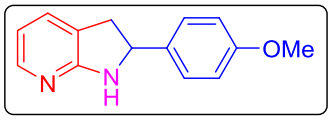
9.9 Hz, 1H), 2.92 (dd, *J* = 16.8, 7.0 Hz, 1H), 1.30 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.2, 150.8, 142.8, 139.8, 133.4, 125.7, 125.4, 124.6, 113.2, 59.9, 37.0, 34.5, 31.3 ppm. IR (neat): 3335, 2962, 2867, 2089, 1628, 1496, 1447, 1268, 1109, 1016, 923, 734 cm^{-1}. HRMS: calcd for $C_{17}H_{21}N_2$ $[M+H]^+$ 253.1705, found 253.1703.



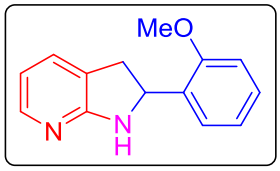
2-(p-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ac) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-methylbenzaldehyde (**2c**) (24 µL, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (27.8 mg, 66% yield) as a white solid. Mp 132 – 133 °C. R_f = 0.57 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 5.1 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.54 (dd, *J* = 7.0, 5.3 Hz, 1H), 5.05 (s, 1H), 4.98 (t, *J* = 8.6 Hz, 1H), 3.46 (dd, *J* = 16.3, 9.4 Hz, 1H), 2.93 (dd, *J* = 16.3, 7.8 Hz, 1H), 2.35 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.9, 146.0, 141.0, 137.3, 131.4, 129.3, 125.9, 121.0, 113.6, 60.0, 37.9, 21.0 ppm. IR (neat): 3443, 3194, 3059, 2897, 1617, 1595, 1445, 1262, 1174, 1021, 907, 814, 767 cm^{-1}. HRMS: calcd for $C_{14}H_{15}N_2$ $[M+H]^+$ 211.1235, found 211.1237.



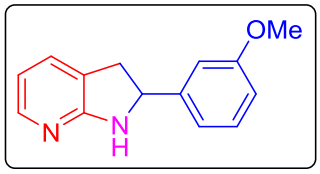
2-(m-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ad) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 3-methylbenzaldehyde (**2d**) (36 µL, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (37.8 mg, 90% yield) as a light yellow solid. Mp 102 – 103 °C. R_f = 0.57 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 5.7 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.18 – 7.07 (m, 3H), 6.56 (dd, *J* = 7.0, 5.7 Hz, 1H), 6.07 (s, 1H), 5.03 (t, *J* = 8.6 Hz, 1H), 3.49 (dd, *J* = 16.6, 9.7 Hz, 1H), 2.93 (dd, *J* = 16.6, 7.5 Hz, 1H), 2.34 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.5, 144.3, 143.3, 138.5, 132.5, 128.7, 128.5, 126.5, 122.9, 113.4, 60.2, 37.5, 21.4 ppm. One resonance was not observed due to overlapping resonances. IR (neat): 3331, 3059, 2919, 1609, 1599, 1489, 1422, 1304, 1183, 901, 769 cm^{-1}. HRMS: calcd for $C_{14}H_{15}N_2$ $[M+H]^+$ 211.1235, found 211.1231.



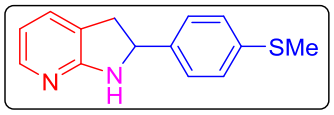
2-(4-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ae) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-methoxybenzaldehyde (**2e**) (25 µL, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (29.4 mg, 65% yield) as a white solid. Mp 136 – 137 °C. R_f = 0.41 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 5.2 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.22 (d, *J* = 7.0 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.53 (dd, *J* = 7.0, 5.4 Hz, 1H), 5.10 (s, 1H), 4.96 (t, *J* = 8.6 Hz, 1H), 3.80 (s, 3H), 3.43 (dd, *J* = 16.3, 9.4 Hz, 1H), 2.91 (dd, *J* = 16.3, 7.9 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.9, 159.0, 146.0, 136.0, 131.4, 127.1, 121.0,114.0, 113.6, 59.9, 55.2, 38.0 ppm. IR (neat): 3424, 3053, 2931, 2060, 1617, 1512, 1414, 1246, 1175, 1033, 952, 817, 775 cm^{-1}. HRMS: calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1184, found 227.1187.



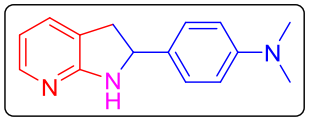
2-(2-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3af) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 2-methoxybenzaldehyde (**2f**) (37 µL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (37.1 mg, 82% yield) as a light yellow solid. Mp 103 – 104 °C. R_f = 0.60 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 5.1 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.28 – 7.16 (m, 2H), 6.98 – 6.85 (m, 2H), 6.50 (dd, *J* = 7.0, 5.4 Hz, 1H), 5.30 (t, *J* = 8.1 Hz, 1H), 5.07 (s, 1H), 3.84 (s, 3H), 3.53 (dd, *J* = 16.3, 9.4 Hz, 1H), 2.85 (dd, *J* = 16.3, 7.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 164.0, 156.5, 145.8, 131.9, 131.4, 128.2, 125.8, 121.4, 120.6, 113.4, 110.2, 55.2, 54.6, 35.6 ppm. IR (neat): 3388, 3211, 3062, 2835, 1614, 1586, 1490, 1463, 1443, 1241, 1050, 935, 800 cm^{-1}. HRMS: calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1184, found 227.1186.



2-(3-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ag) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 3-methoxybenzaldehyde (**2g**) (37 µL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (38.9 mg, 86% yield) as a white solid. Mp 90 – 91 °C. R_f = 0.46 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (dd, *J* = 5.6, 1.3 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.92 – 6.87 (m, 2H), 6.82 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 6.56 (dd, *J* = 7.0, 5.7 Hz, 1H), 6.00 (s, 1H), 5.20 – 4.89 (m, 1H), 3.79 (s, 3H), 3.50 (dd, *J* = 16.6, 9.7 Hz, 1H), 2.94 (dd, *J* = 16.6, 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.5, 159.9, 145.1, 144.5, 132.5, 129.9, 122.7, 118.0, 113.6, 113.1, 111.3, 60.2, 55.3, 37.5 ppm. IR (neat): 3321, 3218, 2959, 2835, 1601, 1489, 1433, 1283, 1167, 1046, 870, 769 cm^{-1}. HRMS: calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1184, found 227.1186.

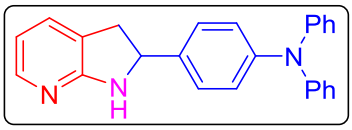


2-(4-(methylthio)phenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ah) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-(methylthio)benzaldehyde (**2h**) (27 µL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (33.0 mg, 68% yield) as a light yellow solid. Mp 139 – 141 °C. R_f = 0.43 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 5.1 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.18 (m, 3H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.15 (s, 1H), 4.96 (t, *J* = 8.6 Hz, 1H), 3.45 (dd, *J* = 16.3, 9.4 Hz, 1H), 2.90 (dd, J = 16.2, 7.9 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.9, 146.1, 140.9, 137.6, 131.5, 126.9, 126.5, 120.8, 113.7, 59.9, 37.9, 15.9 ppm. IR (neat): 3424, 3202, 3078, 2890, 1614, 1590, 1492, 1405, 1260, 1173, 973, 768 cm^{-1}. HRMS: calcd for $C_{14}H_{15}N_2S$ $[M+H]^+$ 243.0956, found 243.0957.

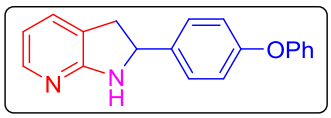


4-(2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-2-yl)-N,N-dimethylanilin e (3ai) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (63 µL, 0.60 mmol), $LiN(SiMe_3)_2$

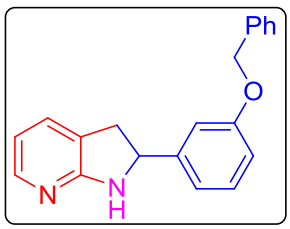
(100.0 mg, 0.60 mmol), 4-(dimethylamino)benzaldehyde (**2i**) (30 mg, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (29.7 mg, 62% yield) as a light yellow solid. Mp 162 – 163 °C. R_f = 0.47 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 5.3 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.77 – 6.67 (m, 2H), 6.53 (dd, *J* = 7.0, 5.4 Hz, 1H), 4.98 – 4.76 (m, 2H), 3.41 (dd, *J* = 16.4, 9.2 Hz, 1H), 2.99 – 2.87 (m, 7H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.9, 150.0, 145.9, 131.6, 131.2, 126.8, 121.3, 113.3, 112.6, 60.0, 40.5, 37.8 ppm. IR (neat): 3394, 3197, 2895, 1878, 1612, 1521, 1441, 1355, 1221, 1046, 8114, 764 cm^{-1}. HRMS: calcd for $C_{15}H_{18}N_3$ $[M+H]^+$ 240.1501, found 240.1505.



4-(2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-2-yl)-N,N-diphenylaniline (3aj) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (63 µL, 0.60 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-(diphenylamino)benzaldehyde (**2j**) (54.7 mg, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (53.1 mg, 73% yield) as a light yellow solid. Mp 224 – 225 °C. R_f = 0.60 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 5.2 Hz, 1H), 7.29 – 7.19 (m, 7H), 7.10 – 6.97 (m, 8H), 6.56 – 6.50 (m, 1H), 5.03 – 4.90 (m, 2H), 3.45 (dd, *J* = 16.3, 9.3 Hz, 1H), 2.97 (dd, *J* = 16.5, 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.9, 147.7, 147.3, 146.1, 137.9, 131.4, 129.2, 126.9, 124.2, 124.0, 122.8, 121.0, 113.7, 60.0, 37.8 ppm. IR (neat): 3429, 3060, 2883, 1613, 1586, 1507, 1441, 1276, 1173, 919, 828, 749 cm^{-1}. HRMS: calcd for $C_{25}H_{22}N_3$ $[M+H]^+$ 364.1814, found 364.1811.

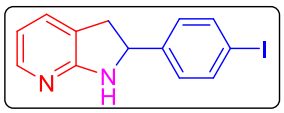


2-(4-phenoxyphenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ak) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-phenoxybenzaldehyde (**2k**) (36 µL, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (41.5 mg, 72% yield) as a light yellow solid. Mp 157 – 158 °C. R_f = 0.49 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 – 7.83 (m 1H), 7.39 – 7.30 (m, 4H), 7.23 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.04 – 6.97 (m, 4H), 6.55 (dd, *J* = 7.1, 5.4 Hz, 1H), 5.14 (s, 1H), 5.00 (t, *J* = 8.6 Hz, 1H), 3.47 (dd, *J* = 16.3, 9.4 Hz, 1H), 2.95 (dd, *J* = 16.3, 7.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.9, 157.1, 156.7, 146.1, 138.8, 131.4, 129.7, 127.4, 123.3, 120.9, 118.9, 118.8, 113.7, 59.8, 37.9 ppm. IR (neat): 3428, 3201, 2897, 1610, 1589, 1504, 1488, 1450, 1235, 1069, 866, 770 cm^{-1}. HRMS: calcd for $C_{19}H_{17}N_2O$ $[M+H]^+$ 289.1341, found 289.1342.

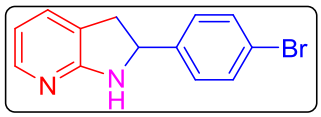


2-(3-(benzyloxy)phenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3al) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 3-(benzyloxy)benzaldehyde (**2l**) (39 µL, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (38.7 mg, 64% yield) as a brown solid. Mp 178 – 179 °C. R_f = 0.58

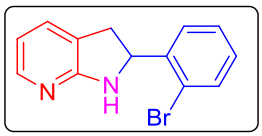
(Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 5.3 Hz, 1H), 7.45 – 7.19 (m, 7H), 7.09 – 7.03 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.54 (dd, *J* = 7.2, 5.2 Hz, 1H), 5.14 (s, 1H), 5.05 (s, 2H), 4.98 (t, *J* = 9.1 Hz, 1H), 3.47 (dd, *J* = 16.3, 9.5 Hz, 1H), 2.94 (dd, *J* = 16.3, 7.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.9, 159.1, 146.1, 145.8, 136.8, 131.5, 129.5, 128.5, 127.9, 127.5, 120.9, 118.5, 113.8, 113.7, 112.3, 69.9, 60.2, 37.8 ppm. IR (neat): 3387, 3202, 3061, 2963, 1611, 1597, 1485, 1438, 1255, 1173, 965, 880, 770 cm^{-1}. HRMS: calcd for $C_{20}H_{19}N_2O$ $[M+H]^+$ 303.1497, found 303.1496.



2-(4-iodophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3am) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (63 μL, 0.60 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-iodobenzaldehyde (**2m**) (46.6 mg, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (41.2 mg, 64% yield) as a brown solid. Mp 177 – 178 °C. R_f = 0.34 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 – 7.84 (m, 1H), 7.71 – 7.63 (m, 2H), 7.25 – 7.21 (m, 1H), 7.18 – 7.12 (m, 2H), 6.56 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.99 – 4.93 (m, 1H), 4.91 (s, 1H), 3.48 (dd, *J* = 16.3, 9.5 Hz, 1H), 2.89 (dd, *J* = 16.3, 7.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.9, 146.3, 143.9, 137.9, 131.8, 128.1, 120.7, 114.1, 93.0, 60.0, 38.0 ppm. IR (neat): 3443, 2900, 1635, 1614, 1594, 1483, 1256, 1056, 818, 775, 601 cm^{-1}. HRMS: calcd for $C_{13}H_{12}N_2I$ $[M+H]^+$ 323.0045, found 323.0041.

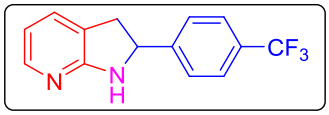


2-(4-bromophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3an) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (63 μL, 0.60 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-bromobenzaldehyde (**2n**) (37.1 mg, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (32.5 mg, 59% yield) as a brown solid. Mp 162 – 163 °C. R_f = 0.51 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 – 7.76 (m, 1H), 7.50 – 7.40 (m, 2H), 7.30 – 7.22 (m, 2H), 7.22 – 7.14 (m, 1H), 6.51 (dd, *J* = 7.1, 5.4 Hz, 1H), 5.36 (s, 1H), 4.95 (t, *J* = 8.7 Hz, 1H), 3.44 (dd, *J* = 16.3, 9.5 Hz, 1H), 2.86 (dd, *J* = 16.3, 8.0 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 164.0, 146.3, 143.3, 131.9, 131.7, 127.9, 121.4, 120.8, 113.9, 59.9, 38.0 ppm. IR (neat): 3431, 3207, 2900, 2861, 1613, 1592, 1487, 1438, 1290, 1151, 1008, 852, 749 cm^{-1}. HRMS: calcd for $C_{13}H_{12}N_2Br$ $[M+H]^+$ 275.0184, found 275.0183.

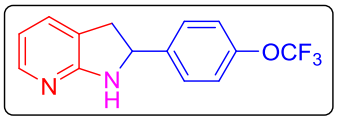


2-(2-bromophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ao) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 μL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 2-bromobenzaldehyde (**2o**) (24 μL, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (34.1 mg, 62% yield) as a light yellow solid. Mp 128 – 130 °C. R_f = 0.66 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (dd, *J* = 5.4, 1.4 Hz, 1H), 7.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.30 (td, *J* = 7.6, 1.3 Hz, 1H), 7.22 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.14 (td, *J* = 7.6, 1.8 Hz, 1H), 6.54 (dd, *J* = 7.1, 5.4 Hz, 1H), 5.41 – 5.29 (m, 2H), 3.71 (dd, *J* = 16.4, 9.9 Hz, 1H), 2.80 (dd, *J* = 16.4, 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.9, 146.1, 143.0, 132.9, 131.7, 128.8, 127.8, 127.2, 122.2, 120.4, 113.8, 59.2, 36.2 ppm. IR (neat): 3428, 2946, 2836, 1613,

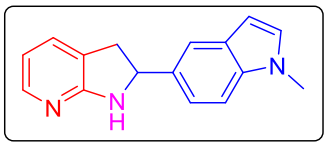
1592, 1485, 1430, 1323, 1170, 1020, 752 cm^{-1}. HRMS: calcd for $C_{13}H_{12}N_2Br$ $[M+H]^+$ 275.0184, found 275.0183.



2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ap) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (63 μL, 0.60 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-(trifluoromethyl)benzaldehyde (**2p**) (28 μL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (24.3 mg, 46% yield) as a white solid. Mp 172 – 174 °C. R_f = 0.47 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.88 – 7.78 (m, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.26 – 7.19 (m, 1H), 6.55 (dd, J = 7.1, 5.3 Hz, 1H), 5.52 (s, 1H), 5.08 (t, J = 8.8 Hz, 1H), 3.52 (dd, J = 16.3, 9.6 Hz, 1H), 2.91 (dd, J = 16.3, 8.0 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.9, 148.1(dd, $J^4_{C\text{-}F}$ = 1.7 Hz), 146.1, 131.6, 129.8(dd, $J^2_{C\text{-}F}$ = 32.5 Hz), 136.3, 125.7 (dd, $J^3_{C\text{-}F}$ = 4.0 Hz), 124.1 (dd, $J^1_{C\text{-}F}$ = 273.3 Hz), 120.5, 113.8, 59.8, 37.8 ppm. ^{19}F NMR (377MHz, $CDCl_3$): -62.3 ppm. IR (neat): 3454, 2895, 2844, 2075, 1924, 1640, 1597, 1447, 1331, 1258, 1109, 835, 780 cm^{-1}. HRMS: calcd for $C_{14}H_{12}N_2F_3$ $[M+H]^+$ 265.0953, found 265.0950.

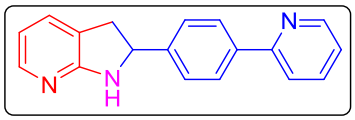


2-(4-(trifluoromethoxy)phenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3aq) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (63 μL, 0.60 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-(trifluoromethoxy)benzaldehyde (**2q**) (29 μL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (40.4 mg, 72% yield) as a red-brown solid. Mp 132 – 133 °C R_f = 0.59 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 5.2 Hz, 1H), 7.43 (d, J = 8.6 Hz, 2H), 7.27 – 7.16 (m, 3H), 6.56 (dd, J = 7.1, 5.3 Hz, 1H), 5.15 (s, 1H), 5.03 (t, J = 8.7 Hz, 1H), 3.49 (dd, J = 16.3, 9.5 Hz, 1H), 2.91 (dd, J = 16.3, 8.0 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 164.0, 148.6(dd, $J^2_{C\text{-}F}$ = 2.1 Hz), 146.3, 142.9, 131.7, 127.5, 121.3(dd, $J^3_{C\text{-}F}$ = 1.2 Hz), 120.8, 120.5(dd, $J^1_{C\text{-}F}$ = 258.3 Hz), 114.0, 59.8, 38.0 ppm. ^{19}F NMR (377MHz, $CDCl_3$): -57.8 ppm. IR (neat): 3412, 3192, 2892, 2838, 1613, 1592, 1506, 1418, 1037, 920, 847, 750 cm^{-1}. HRMS: calcd for $C_{14}H_{12}N_2F_3O$ $[M+H]^+$ 281.0902, found 281.0900.

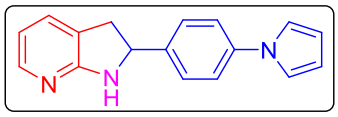


2-(1-methyl-1H-indol-5-yl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ar) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 μL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 1-methyl-1H-indole-5-carbaldehyde (**2r**) (32 mg, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (32.9 mg, 66% yield) as a light yellow solid. Mp 190 – 192 °C. R_f = 0.39 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J = 5.3 Hz, 1H), 7.63 (s, 1H), 7.39 – 7.13 (m, 3H), 7.05 (d, J = 3.1 Hz, 1H), 6.64 – 6.48 (m, 1H), 6.45 (d, J = 3.1 Hz, 1H), 5.22 – 4.94 (m, 2H), 3.77 (s, 3H), 3.48 (dd, J = 16.3, 9.4 Hz, 1H), 3.00 (dd, J = 16.3, 7.7 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 164.2, 146.1, 136.4, 135.1, 131.5, 129.6, 128.6, 121.5, 119.9, 118.3, 113.6, 109.7, 101.0, 61.0, 38.5, 33.2 ppm. IR

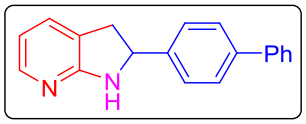
(neat): 3449, 3081, 1602, 1578, 1540, 1507, 1441, 1359, 1340, 1224, 755, 493 cm^{-1}. HRMS: calcd for $C_{16}H_{16}N_3$ $[M+H]^+$ 250.1344, found 250.1340.



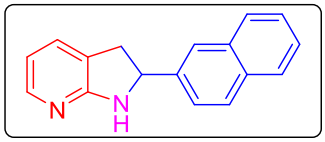
2-(4-(pyridin-2-yl)phenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3as) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-(pyridin-2-yl)benzaldehyde (**2s**) (39.8 mg, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (38.8 mg, 71% yield) as a light yellow solid. Mp 168 – 169 °C. R_f = 0.19 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 – 8.64 (m, 1H), 8.00 – 7.92 (m, 2H), 7.88 – 7.81 (m, 1H), 7.76 – 7.66 (m, 2H), 7.53 – 7.45 (m, 2H), 7.24 – 7.15 (m, 2H), 6.52 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.50 (s, 1H), 5.05 (t, *J* = 8.7 Hz, 1H), 3.49 (dd, *J* = 16.3, 9.4 Hz, 1H), 2.94 (dd, *J* = 16.3, 7.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 164.0, 156.9, 149.6, 146.0, 144.8, 138.6, 136.7, 131.4, 127.1, 126.3, 122.0, 120.8, 120.3, 113.5, 60.0, 37.8 ppm. IR (neat): 3436, 2894, 2840, 1615, 1590, 1507, 1434, 1258, 1175, 1055, 755, 721 cm^{-1}. HRMS: calcd for $C_{18}H_{16}N_3$ $[M+H]^+$ 274.1344, found 274.1340.



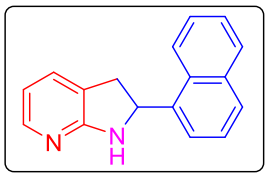
2-(4-(1H-pyrrol-1-yl)phenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3at) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 4-(1H-pyrrol-1-yl)benzaldehyde (**2t**) (34.4 mg, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (40.2 mg, 77% yield) as a gray solid. Mp 193 – 194 °C. R_f = 0.40 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 5.1 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.20 (m, 1H), 7.09 (t, *J* = 2.1 Hz, 2H), 6.57 (dd, *J* = 7.1, 5.4 Hz, 1H), 6.36 (t, *J* = 2.2 Hz, 2H), 5.18 (s, 1H), 5.04 (t, *J* = 8.3 Hz, 1H), 3.51 (dd, *J* = 16.3, 9.4 Hz, 1H), 2.96 (dd, *J* = 16.3, 7.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.9, 146.2, 141.4, 140.1, 131.6, 127.2, 120.7, 120.6, 119.2, 113.8, 110.4, 59.8, 38.0 ppm. IR (neat): 3444, 2901, 1899, 1616, 1593, 1523, 1429, 1273, 1118, 1075, 827, 719 cm^{-1}. HRMS: calcd for $C_{17}H_{16}N_3$ $[M+H]^+$ 262.1344, found 262.1348.



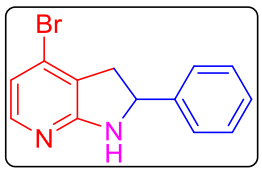
2-([1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3au) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), [1,1'-biphenyl]-4-carbaldehyde (**2u**) (36.6 mg, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (45.2 mg, 83% yield) as a light yellow solid. Mp 171 – 173 °C. R_f = 0.49 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 5.3 Hz, 1H), 7.64 – 7.16 (m, 10H), 6.54 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.25 (s, 1H), 5.04 (t, *J* = 8.7 Hz, 1H), 3.49 (dd, *J* = 16.3, 9.5 Hz, 1H), 2.97 (dd, *J* = 16.3, 7.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 164.0, 146.1, 143.1, 140.6, 140.5, 131.5, 128.7, 127.4, 127.3, 127.0, 126.4, 120.9, 113.7, 60.0, 37.9 ppm. IR (neat): 3429, 2955, 1909, 1613, 1592, 1443, 1407, 1275, 1004, 834, 757 cm^{-1}. HRMS: calcd for $C_{19}H_{17}N_2$ $[M+H]^+$ 273.1392, found 273.1390.



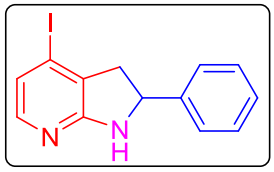
2-(naphthalen-2-yl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3av) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 μL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.6 mmol), 2-naphthaldehyde (**2v**) (31.4 mg, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (38.9 mg, 79% yield) as a light yellow solid. Mp 154 – 155 °C. R_f = 0.48 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 5.3 Hz, 1H), 7.87 – 7.76 (m, 4H), 7.53 – 7.42 (m, 3H), 7.32 – 7.21 (m, 1H), 6.57 (dd, *J* = 7.0, 5.5 Hz, 1H), 5.55 (s, 1H), 5.19 (t, *J* = 8.6 Hz, 1H), 3.56 (dd, *J* = 16.4, 9.6 Hz, 1H), 3.01 (dd, *J* = 16.4, 7.7 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 164.0, 146.1, 141.3, 133.2, 132.9, 131.5, 128.6, 127.8, 127.7, 126.3, 125.8, 124.5, 124.2, 120.9, 113.7, 60.3, 37.8 ppm. IR (neat): 3440, 2906, 2071, 1614, 1485, 1444, 1342, 1255, 1056, 819, 764 cm^{-1}. HRMS: calcd for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1235, found 247.1235.



2-(naphthalen-1-yl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3aw) The reaction was performed following the General Procedure A with 2-fluoro-3-methylpyridine (**1a**) (42 μL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), 1-naphthaldehyde (**2w**) (28 μL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (35.5 mg, 72% yield) as a brown solid. Mp 114 –116 °C. R_f = 0.51 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.04 – 7.95 (m, 1H), 7.96 – 7.87 (m, 1H), 7.90 – 7.81 (m, 1H), 7.83 – 7.72 (m, 2H), 7.62 – 7.48 (m, 2H), 7.50 – 7.40 (m, 1H), 7.19 (dd, *J* = 7.0, 1.5 Hz, 1H), 6.52 (dd, *J* = 7.0, 5.3 Hz, 1H), 5.82 – 5.69 (m, 2H), 3.74 (dd, *J* = 16.3, 9.8 Hz, 1H), 2.96 (dd, *J* = 16.3, 7.3 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 164.0, 146.0, 139.4, 133.9, 131.6, 130.2, 128.9, 127.7, 126.1, 125.6, 125.5, 122.8, 122.4, 120.8, 113.3, 56.7, 37.0 ppm. IR (neat): 3396, 3207, 3006, 2907, 1612, 1593, 1485, 1443, 1261, 1011, 894, 799 cm^{-1}.HRMS: calcd for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1235, found 247.1240.

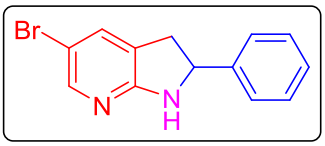


4-bromo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ba) The reaction was performed following the General Procedure A with 4-bromo-2-fluoro-3-methylpyridine (**1b**) (48 μL, 0.40 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 μL, 0.20 mmol) and iPr_2O (0.4 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (36.9 mg, 67% yield) as a brown solid. Mp 112 – 113 °C. R_f = 0.38 (Petroleum ether : EtOAc = 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.71 – 7.62 (m, 1H), 7.44 – 7.28 (m, 5H), 6.69 (d, *J* = 5.8 Hz, 1H), 5.28 (s, 1H), 5.16 – 4.93 (m, 1H), 3.52 (dd, *J* = 16.9, 9.8 Hz, 1H), 2.96 (dd, *J* = 17.9, 7.5 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 164.0, 147.2, 143.6, 129.0, 128.5, 127.9, 126.0, 122.2, 117.0, 59.3, 38.9 ppm. IR (neat): 3416, 3195, 3032, 2890, 1610, 1578, 1490, 1457, 1360, 1269, 1085, 942, 775 cm^{-1}. HRMS: calcd for $C_{13}H_{12}N_2Br$ $[M+H]^+$ 275.0184, found 275.0179.

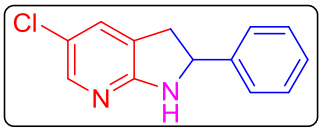


4-iodo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ca) The reaction was performed following the General Procedure A with 2-fluoro-4-iodo-3-methylpyridine (**1c**) (50 μL, 0.40 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 μL, 0.20 mmol) and iPr_2O

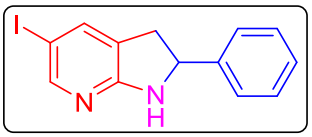
(0.4 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (45.1 mg, 70% yield) as a brown solid. Mp 148 –149 °C. R_f = 0.41 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 5.7 Hz, 1H), 7.41 – 7.27 (m, 5H), 6.87 (d, *J* = 5.7 Hz, 1H), 5.41 (s, 1H), 5.12 – 4.96 (m, 1H), 3.44 (dd, *J* = 16.9, 9.8 Hz, 1H), 2.91 (dd, *J* = 16.9, 7.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 162.3, 146.5, 143.5, 128.8, 127.8, 127.1, 125.9, 122.3, 102.7, 58.5, 42.2 ppm. IR (neat): 3129, 3029, 2881, 1619, 1599, 1481, 1361, 1243, 1167, 935, 775 cm^{-1}. HRMS: calcd for $C_{13}H_{12}N_2I$ $[M+H]^+$ 323.0045, found 323.0044.



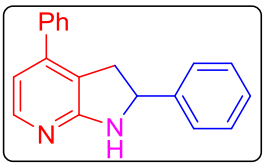
5-bromo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3da) The reaction was performed following the General Procedure A with 5-bromo-2-fluoro-3-methylpyridine (**1d**) (114 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (34.1 mg, 62% yield) as a brown solid. Mp 130 – 131 °C. R_f = 0.59 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 – 7.83 (m, 1H), 7.39 – 7.35 (m, 4H), 7.33 – 7.27 (m, 2H), 5.31 (s, 1H), 5.09 – 4.98 (m, 1H), 3.49 (dd, *J* = 16.6, 9.5 Hz, 1H), 2.95 (dd, *J* = 16.6, 7.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 162.6, 146.4, 143.4, 134.2, 128.8, 127.8, 125.9, 123.3, 108.1, 60.7, 37.6 ppm. IR (neat): 3173, 3087, 3045, 2901, 1607, 1581, 1488, 1359, 1288, 1141, 908, 743 cm^{-1}. HRMS: calcd for $C_{13}H_{12}N_2Br$ $[M+H]^+$ 275.0184, found 275.0187.



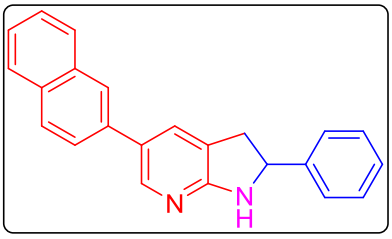
5-chloro-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ea) The reaction was performed following the General Procedure A with 5-chloro-2-fluoro-3-methylpyridine (**1e**) (69 µL, 0.60 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (30.0 mg, 65% yield) as a brown solid. Mp 126 – 127 °C. R_f = 0.58 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 – 7.77 (m, 1H), 7.39 – 7.28 (m, 5H), 7.21 – 7.16 (m, 1H), 5.11 (s, 1H), 5.08 – 4.99 (m, 1H), 3.49 (dd, *J* = 16.6, 9.5 Hz, 1H), 2.96 (dd, *J* = 16.6, 7.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 162.5, 144.3, 143.6, 131.9, 128.9, 127.9, 126.0, 122.9, 120.9, 60.9, 37.3 ppm. IR (neat): 3179, 3151, 3048, 2877, 1609, 1583, 1454, 1360, 1265, 1144, 932, 755 cm^{-1}. HRMS: calcd for $C_{13}H_{12}N_2Cl$ $[M+H]^+$ 231.0689, found 231.0687.



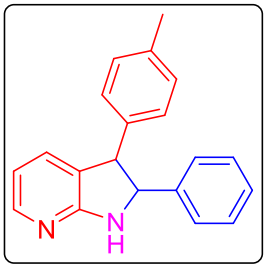
5-iodo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3fa) The reaction was performed following the General Procedure A with 2-fluoro-5-iodo-3-methylpyridine (**1f**) (94.8 mg, 0.40 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and *i*Pr_2O (0.4 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (43.2 mg, 67% yield) as a brown solid. Mp 137 – 138 °C. R_f = 0.59 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 – 7.98 (m, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.27 (m, 5H), 5.14 (s, 1H), 5.07 – 4.98 (m, 1H), 3.48 (dd, *J* = 16.6, 9.6 Hz, 1H), 2.95 (dd, *J* = 16.6, 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 162.8, 151.7, 143.4, 139.1, 128.8, 127.9, 125.9, 124.0, 77.6, 60.5, 37.6 ppm. IR (neat): 3199, 3029, 2849, 1602, 1577, 1481, 1452, 1355, 1248, 1050, 898, 760 cm^{-1}. HRMS: calcd for $C_{13}H_{12}N_2I$ $[M+H]^+$ 323.0045, found 323.0044.



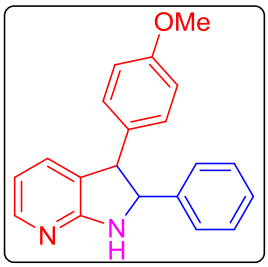
2,4-diphenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ga) The reaction was performed following the General Procedure A with 2-fluoro-3-methyl-4-phenylpyridine (**1g**) (68 µL, 0.40 mmol), $LiN(SiMe_3)_2$ (100.0 mg, 0.60 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (33.2 mg, 61% yield) as a brown solid. Mp 143 – 144 °C. R_f = 0.64 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 4.9 Hz, 1H), 7.48 – 7.26 (m, 10H), 6.67 (dd, *J* = 5.6, 1.0 Hz, 1H), 5.14 (s, 1H), 5.01 (t, J = 8.7 Hz, 1H), 3.59 (dd, *J* = 16.4, 9.3 Hz, 1H), 3.11 (dd, *J* = 16.4, 8.1 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 164.6, 146.6, 144.6, 143.9, 138.3, 128.7, 128.6, 128.2, 127.8, 127.6, 126.0, 118.1, 113.8, 60.5, 38.3 ppm. IR (neat): 3190, 3059, 3027, 2893, 1609, 1596, 1498, 1431, 1359, 1072, 945, 760 cm^{-1}. HRMS: calcd for $C_{19}H_{17}N_2$ $[M+H]^+$ 273.1392, found 273.1390.



5-(naphthalen-2-yl)-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ha) The reaction was performed following the General Procedure A with 2-fluoro-3-methyl-5-(naphthalen-2-yl)pyridine (**1h**) (142.4 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (41.9 mg, 65% yield) as a light yellow solid. Mp 177 – 178 °C. R_f = 0.63 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.29 – 8.24 (m, 1H), 7.94 (d, *J* = 1.8 Hz, 1H), 7.93 – 7.83 (m, 3H), 7.67 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.41 – 7.29 (m, 3H), 5.23 – 4.95 (m, 2H), 3.60 (dd, *J* = 16.4, 9.5 Hz, 1H), 3.06 (dd, *J* = 16.4, 7.6 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.4, 145.1, 143.9, 136.3, 133.7, 132.3, 130.8, 128.8, 128.5, 127.9, 127.7, 127.6, 127.4, 126.3, 126.0, 125.6, 125.0, 124.5, 121.4, 60.6, 37.9 ppm. IR (neat): 3189, 3051, 1617, 1591, 1490, 1436, 1355, 1250, 1136, 889, 741 cm^{-1}. HRMS: calcd for $C_{23}H_{19}N_2$ $[M+H]^+$ 323.1548, found 323.1547.

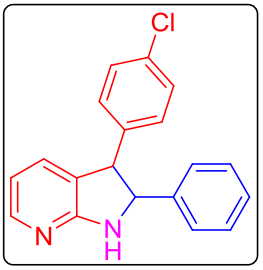


2-phenyl-3-(p-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ia) The reaction was performed following the General Procedure A with 2-fluoro-3-(4-methylbenzyl)pyridine (**1i**) (120.7 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (54.4 mg, 95% yield) as a brown solid. Mp 189 – 190 °C. R_f = 0.51 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.97 – 7.91 (m, 1H), 7.37 – 7.28 (m, 5H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 – 7.01 (m, 3H), 6.58 (dd, *J* = 7.2, 5.3 Hz, 1H), 5.15 (s, 1H), 4.89 (dd, *J* = 8.8, 2.2 Hz, 1H), 4.23 (d, *J* = 8.8 Hz, 1H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.5, 146.9, 142.6, 138.5, 137.0, 132.3, 129.5, 128.7, 128.6, 127.9, 126.5, 124.8, 114.3, 70.8, 57.0, 21.2 ppm. IR (neat): 3158, 3059, 3028, 2918, 1612, 1593, 1491, 1440, 1360, 1060, 905, 775 cm^{-1}. HRMS: calcd for $C_{20}H_{19}N_2$ $[M+H]^+$ 287.1548, found 287.1546.

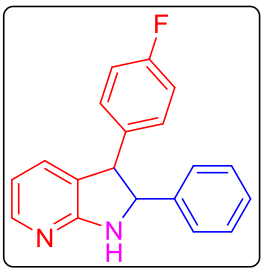


3-(4-methoxyphenyl)-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ja) The reaction was performed following the General Procedure A

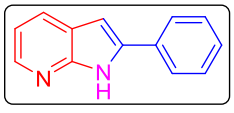
with 2-fluoro-3-(4-methoxybenzyl)pyridine (**1j**) (130.3 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 μL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (58.7 mg, 97% yield) as a white solid. Mp 138 – 139 °C. R_f = 0.49 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 – 7.88 (m, 1H), 7.38 – 7.27 (m, 5H), 7.11 – 7.01 (m, 3H), 6.91 – 6.83 (m, 2H), 6.58 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.25 (s, 1H), 4.86 (dd, *J* = 9.0, 2.3 Hz, 1H), 4.21 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.3, 158.7, 146.7, 142.3, 133.3, 132.0, 129.6, 128.5, 127.7, 126.4, 124.7, 114.1, 114.0, 70.9, 56.5, 55.2 ppm. IR (neat): 3161, 3059, 2835, 1612, 1512, 1487, 1454, 1249, 1177, 1033, 766 cm^{-1}. HRMS: calcd for $C_{20}H_{19}N_2O$ $[M+H]^+$ 303.1497, found 303.1492.



3-(4-chlorophenyl)-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3ka) The reaction was performed following the General Procedure A with 3-(4-chlorobenzyl)-2-fluoropyridine (**1k**) (133.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 μL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (60.1 mg, 98% yield) as a brown solid. Mp 211 – 212 °C. R_f = 0.50 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 – 7.97 (m, 1H), 7.36 – 7.28 (m, 5H), 7.25 – 7.19 (m, 2H), 7.12 – 7.03 (m, 3H), 6.64 (dd, *J* = 7.1, 5.6 Hz, 1H), 6.05 (s, 1H), 4.90 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.23 (d, *J* = 7.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.3, 147.1, 141.9, 139.8, 133.1, 132.1, 129.9, 128.9, 128.7, 128.0, 126.4, 123.9, 114.3, 70.8, 56.8 ppm. IR (neat): 3159, 3060, 2850, 1611, 1490, 1439, 1359, 1260, 1089, 861, 776 cm^{-1}. HRMS: calcd for $C_{19}H_{16}N_2Cl$ $[M+H]^+$ 307.1002, found 307.1006.

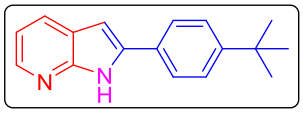


3-(4-fluorophenyl)-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3la) The reaction was performed following the General Procedure A with 2-fluoro-3-(4-fluorobenzyl)pyridine (**1l**) (123.1 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (133.4 mg, 0.80 mmol), benzaldehyde (**2a**) (21 μL, 0.20 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (57.5 mg, 99% yield) as a light yellow solid. Mp 193 – 194 °C. R_f = 0.51 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 – 7.92 (m, 1H), 7.36 – 7.26 (m, 5H), 7.16 – 7.05 (m, 2H), 7.06 – 6.99 (m, 3H), 6.60 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.07 (s, 1H), 4.83 (dd, *J* = 8.9, 2.3 Hz, 1H), 4.25 (d, *J* = 9.0 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 162.0(d, $J^1_{C\text{-}F}$ = 246.8 Hz), 160.8, 146.9, 142.0, 137.0(d, $J^4_{C\text{-}F}$ = 3.1 Hz), 132.1, 130.1(d, $J^3_{C\text{-}F}$ = 8.0 Hz), 128.6, 127.9, 126.4, 124.2, 115.6(d, $J^2_{C\text{-}F}$ = 21.4 Hz), 114.2, 70.9, 56.6 ppm. ^{19}F NMR (377MHz, $CDCl_3$): -115.2 ppm. IR (neat): 3206, 3061, 2915, 1612, 1508, 1491, 1441, 1360, 1223, 1158, 842, 767 cm^{-1}. HRMS: calcd for $C_{19}H_{16}N_2F$ $[M+H]^+$ 291.1298, found 291.1300.

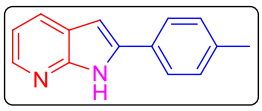


2-phenyl-1H-pyrrolo[2,3-b]pyridine (4aa) The reaction was performed following the General Procedure B with 2-fluoro-3-methylpyridine (**1a**) (21 μL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), benzaldehyde (**2a**) (21 μL, 0.20 mmol) and iPr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (31.9 mg, 82% yield) as a light yellow solid. Mp 195 – 196 °C. R_f = 0.41 (Petroleum ether : EtOAc = 3:1).

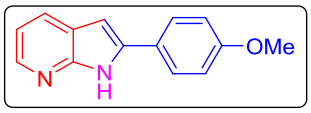
^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.16 (s, 1H), 8.21 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.03 – 7.86 (m, 3H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.07 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ: 150.1, 143.3, 138.6, 132.0, 129.4, 128.5, 128.3, 125.8, 121.4, 116.5, 97.5 ppm. IR (neat): 3438, 3029, 2988, 1639, 1587, 1456, 1330, 1280, 1073, 902, 752 cm^{-1}. HRMS: calcd for $C_{13}H_{11}N_2$ $[M+H]^+$ 195.0922, found 195.0925.



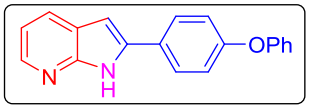
2-(4-(tert-butyl)phenyl)-1H-pyrrolo[2,3-b]pyridine (4ab) The reaction was performed following the General Procedure B with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), 4-(tert-butyl)benzaldehyde (**2b**) (34 µL, 0.20 mmol) and *i*Pr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (35.5 mg, 71% yield) as a white solid. Mp 209 – 211 °C R_f = 0.53 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.98 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.64 – 7.52 (m, 2H), 7.15 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.79 (d, *J* = 1.2 Hz, 1H), 1.44 (s, 9H) ppm. One resonance was not observed due to the deuterated solvent.^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 151.5, 150.1, 142.0, 139.8, 129.7, 128.6, 126.0, 125.7, 122.6, 116.1, 97.0, 34.9, 31.4 ppm. IR (neat): 3160, 2902, 2867, 1588, 1505, 1440, 1420, 1359, 1280, 1112, 915, 764 cm^{-1}. HRMS: calcd for $C_{17}H_{19}N_2$ $[M+H]^+$ 251.1548, found 251.1548.



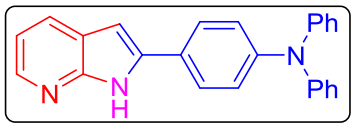
2-(p-tolyl)-1H-pyrrolo[2,3-b]pyridine (4ac) The reaction was performed following the General Procedure C with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (66.8 mg, 0.40 mmol), 4-methylbenzaldehyde (**2c**) (72 µL, 0.60 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (27.5 mg, 66% yield) as a white solid. Mp 235 – 236 °C. R_f = 0.38 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.24 (s, 1H), 8.36 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.07 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.22 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 2.50 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ: 149.7, 142.6, 138.5, 137.6, 129.6, 128.9, 127.8, 125.4, 121.2, 116.1, 96.6, 20.9 ppm. IR (neat): 3141, 3084, 2982, 2924, 1605, 1587, 1491, 1434, 1277, 1122, 912, 819 cm^{-1}. HRMS: calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1079, found 209.1077



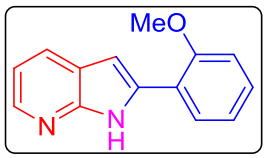
2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4ae) The reaction was performed following the General Procedure C with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (66.8 mg, 0.40 mmol), 4-methoxybenzaldehyde (**2e**) (75 µL, 0.60 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (22.4 mg, 50% yield) as a white solid. Mp 209 – 210 °C. R_f = 0.24 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.15 – 6.99 (m, 3H), 6.67 (s, 1H), 3.89 (s, 3H) ppm. One resonance was not observed due to the deuterated solvent.^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 159.9, 150.1, 141.6, 139.8, 128.4, 127.4, 125.3, 122.7, 116.1, 114.6, 96.2, 55.5 ppm. IR (neat): 3155, 2934, 1614, 1587, 1546, 1492, 1441, 1385, 1278, 1183, 1030, 913, 800 cm^{-1}. HRMS: calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$ 225.1028, found 225.1026.



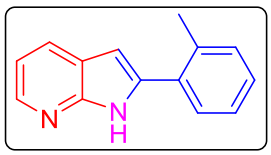
2-(4-phenoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4ak) The reaction was performed following the General Procedure C with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (66.8 mg, 0.40 mmol), 4-phenoxybenzaldehyde (**2k**) (108 µL, 0.60 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (40.7 mg, 71% yield) as a white solid. Mp 215 – 217 °C R_f = 0.34 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.07 (s, 1H), 8.15 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.87 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44 – 7.34 (m, 2H), 7.19 – 7.10 (m, 1H), 7.08 – 6.99 (m, 5H), 6.82 (d, *J* = 2.1 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ: 157.2, 156.8, 150.2, 143.1, 138.3, 130.7, 128.1, 127.7, 127.5, 124.3, 121.5, 119.5, 119.4, 116.5, 97.1 ppm. IR (neat): 3132, 3019, 1613, 1587, 1543, 1487, 1439, 1281, 1235, 1163, 913, 767 cm^{-1}. HRMS: calcd for $C_{19}H_{15}N_2O$ $[M+H]^+$ 287.1184, found 287.1185.



N,N-diphenyl-4-(1H-pyrrolo[2,3-b]pyridin-2-yl)aniline (4aj) The reaction was performed following the General Procedure B with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), 4-(diphenylamino)benzaldehyde (**2j**) (164.1 mg, 0.60 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (36.9 mg, 51% yield) as a brown solid. Mp 219 – 220 °C. R_f = 0.47 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.72 (s, 1H), 8.22 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.90 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.32 – 7.26 (m, 4H), 7.23 – 7.12 (m, 6H), 7.10 – 7.03 (m, 3H), 6.68 (s, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 149.8, 148.1, 147.5, 142.0, 139.3, 129.5, 128.4, 126.6, 125.9, 124.8, 123.5, 123.4, 122.5, 116.3, 96.6 ppm. IR (neat): 3132, 3033, 2922, 1589, 1492, 1419, 1329, 1275, 1112, 914, 753 cm^{-1}. HRMS: calcd for $C_{25}H_{20}N_3$ $[M+H]^+$ 362.1657, found 362.1659.

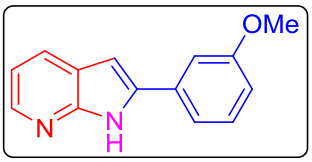


2-(2-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4af) The reaction was performed following the General Procedure C with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (66.8 mg, 0.40 mmol), 2-methoxybenzaldehyde (**2f**) (111 µL, 0.60 mmol) and iPr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (34.1 mg, 76% yield) as a white solid. Mp 103 – 104 °C. R_f = 0.41 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.49 (s, 1H), 8.31 – 8.22 (m, 1H), 7.87 (dd, *J* = 21.5, 7.8 Hz, 2H), 7.37 – 7.28 (m, 1H), 7.13 – 6.98 (m, 3H), 6.90 – 6.78 (m, 1H), 3.97 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.1, 148.7, 143.0, 136.3, 129.4, 128.3, 128.1, 121.5, 120.7, 120.1, 116.2, 112.0, 98.2, 55.8 ppm. IR (neat): 3135, 3076, 2967, 2834, 1599, 1588, 1492, 1464, 1428, 1329, 1282, 1025, 808, 751 cm^{-1}. HRMS: calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$ 225.1028, found 225.1027.

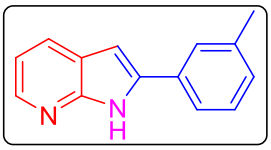


2-(o-tolyl)-1H-pyrrolo[2,3-b]pyridine (4ax) The reaction was performed following the General Procedure B with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), 3-methylbenzaldehyde (**2x**) (36 µL, 0.20 mmol) and iPr_2O

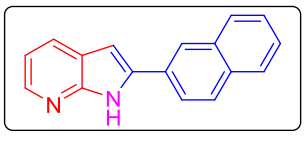
(0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (21.2 mg, 51% yield) as a brown solid. Mp 151 – 152 °C. R_f = 0.50 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.30 (s, 1H), 8.10 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.75 – 7.65 (m, 1H), 7.43 – 7.32 (m, 3H), 7.06 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 2.56 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 149.2, 142.0, 138.9, 136.4, 132.6, 131.3, 129.6, 128.6, 128.3, 126.3, 121.8, 115.9, 100.6, 21.3 ppm. IR (neat): 3131, 3070, 2908, 2825, 1610, 1588, 1489, 1410, 1328, 1116, 1035, 915, 755 cm^{-1}. HRMS: calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1079, found 209.1077.



2-(3-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4ag) The reaction was performed following the General Procedure C with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (66.8 mg, 0.40 mmol), 3-methoxybenzaldehyde (**2g**) (111 µL, 0.60 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (33.2 mg, 74% yield) as a white solid. Mp 169 – 170 °C. R_f = 0.435(Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.34 (s, 1H), 8.41 – 8.24 (m, 1H), 7.95 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 – 7.38 (m, 3H), 7.15 – 7.05 (m, 1H), 6.98 – 6.90 (m, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 3.89 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 160.3, 150.1, 142.4, 139.6, 134.0, 130.2, 128.9, 122.4, 118.6, 116.2, 113.5, 112.0, 97.7, 55.5 ppm. IR (neat): 3138, 3082, 2917, 2833, 1602, 1588, 1541, 1488, 1279, 1046, 873, 765 cm^{-1}. HRMS: calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$ 225.1028, found 225.1024.

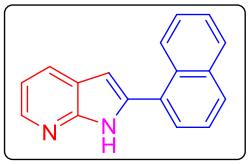


2-(m-tolyl)-1H-pyrrolo[2,3-b]pyridine (4ad) The reaction was performed following the General Procedure C with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (66.8 mg, 0.40 mmol), 3-methylbenzaldehyde (**2d**) (108 µL, 0.60 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (37.9 mg, 91% yield) as a white solid. Mp 147 – 148 °C. R_f = 0.50 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.38 (s, 1H), 8.30 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.44 – 7.37 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.77 (d, *J* = 1.8 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 149.9, 142.2, 139.6, 138.7, 132.3, 129.1, 129.0, 128.6, 126.5, 123.0, 122.3, 116.1, 97.3, 21.6 ppm. IR (neat): 3138, 3028, 2917, 1608, 1589, 1539, 1435, 1401, 1327, 1279, 917, 763 cm^{-1}. HRMS: calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1079, found 209.1076.



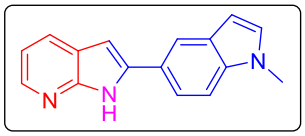
2-(naphthalen-2-yl)-1H-pyrrolo[2,3-b]pyridine (4av) The reaction was performed following the General Procedure C with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), $LiN(SiMe_3)_2$ (66.8 mg, 0.40 mmol), 2-naphthaldehyde (**2v**) (94.2 mg, 0.60 mmol) and *i*Pr_2O (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (38.6 mg, 79% yield) as a brown solid. Mp 218 – 219 °C. R_f = 0.35 (Petroleum ether : EtOAc = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.28 (s, 1H), 8.51 (d, *J* = 1.6 Hz, 1H), 8.23 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.08 (dd, *J* = 8.6, 1.8 Hz,

1H), 8.01 – 7.91 (m, 4H), 7.59 – 7.48 (m, 2H), 7.15 – 7.02 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ: 150.4, 143.6, 138.7, 133.7, 133.1, 129.5, 129.0, 128.6, 128.4, 128.2, 127.3, 126.9, 124.3, 124.2, 121.5, 116.6, 98.5 ppm. IR (neat): 3152, 3050, 2833, 1603, 1588, 1442, 1385, 1278, 948, 858, 763 cm^{-1}. HRMS: calcd for $C_{17}H_{13}N_2$ $[M+H]^+$ 245.1079, found 245.1076.

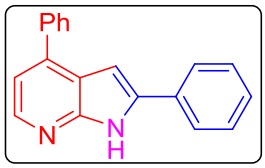


2-(naphthalen-1-yl)-1H-pyrrolo[2,3-b]pyridine (4aw) The reaction was performed following the General Procedure B with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), 1-naphthaldehyde (**2w**) (28 µL, 0.20 mmol) and iPr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the desired product (26.4 mg, 54% yield) as a white solid. Mp 192 – 193 °C. R_f = 0.45 (Petroleum ether : EtOAc = 3:1). ^1H NMR (400 MHz, DMSO-d_6) δ: 12.11 (s, 1H), 8.32 – 8.18 (m, 2H), 8.08 – 7.94 (m, 3H), 7.69 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.64 – 7.49 (m, 3H), 7.09 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.70 (d, *J* = 2.0 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ: 149.6, 143.3, 137.7, 134.0, 131.3, 130.8, 129.1, 129.0, 128.5, 128.2, 127.4, 126.7, 126.0, 125.9, 121.1, 116.5, 101.6 ppm. IR (neat): 3131, 2917, 1603, 1584, 1491, 1425, 1350, 1279, 1104, 912, 757 cm^{-1}. HRMS: calcd for $C_{17}H_{13}N_2$ $[M+H]^+$ 245.1079, found 245.1079.

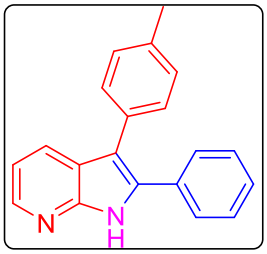
.



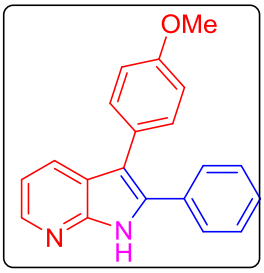
2-(1-methyl-1H-indol-5-yl)-1H-pyrrolo[2,3-b]pyridine (4ar) The reaction was performed following the General Procedure B with 2-fluoro-3-methylpyridine (**1a**) (21 µL, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), 1-methyl-1H-indole-5-carbaldehyde (**2r**) (32 mg, 0.20 mmol) and iPr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (19.8 mg, 40% yield) as a brown solid. Mp 259 – 261 °C. R_f = 0.18 (Petroleum ether : EtOAc = 3:1). ^1H NMR (400 MHz, DMSO-d_6) δ: 12.01 (s, 1H), 8.21 – 8.11 (m, 2H), 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.75 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 3.1 Hz, 1H), 7.02 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 6.49 (d, *J* = 3.1 Hz, 1H), 3.82 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ: 149.6, 141.8, 140.2, 136.3, 130.6, 128.2, 126.9, 122.8, 121.3, 119.3, 117.4, 115.7, 110.2, 100.9, 95.4, 32.6 ppm. IR (neat): 3449, 3081, 1602, 1578, 1540, 1507, 1441, 1359, 1340, 1224, 755, 493 cm^{-1}. IR (neat): 3130, 2918, 2849, 1663, 1603, 1587, 1478, 1421, 1381, 1276, 1245, 1081, 798 cm^{-1}. HRMS: calcd for $C_{16}H_{14}N_3$ $[M+H]^+$ 248.1188, found 248.1186.



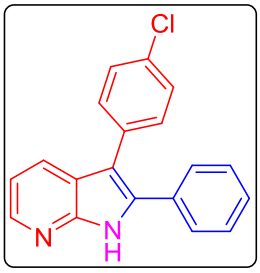
2,4-diphenyl-1H-pyrrolo[2,3-b]pyridine (4ga) The reaction was performed following the General Procedure B with 2-fluoro-3-methyl-4-phenylpyridine (**1g**) (37.5 mg, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and iPr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (28.1 mg, 52% yield) as a brown solid. Mp 234 – 235 °C. R_f = 0.64 (Petroleum ether : EtOAc = 1:1). ^1H NMR (400 MHz, DMSO-d_6) δ: 12.28 (s, 1H), 8.25 (d, *J* = 5.0 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.84 – 7.77 (m, 2H), 7.58 – 7.50 (m, 2H), 7.49 – 7.39 (m, 3H), 7.35 – 7.27 (m, 1H), 7.16 (d, *J* = 4.8 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ: 150.9, 143.8, 140.5, 139.3, 138.8, 132.0, 129.6, 129.4, 129.0, 128.8, 128.6, 126.0, 119.1, 115.3, 96.9 ppm. IR (neat): 3051, 2917, 1654, 1586, 1482, 1455, 1385, 1248, 1026, 857, 751 cm^{-1}. HRMS: calcd for $C_{19}H_{15}N_2$ $[M+H]^+$ 271.1235, found 271.1236.



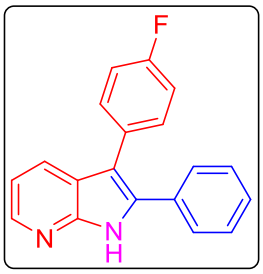
2-phenyl-3-(p-tolyl)-1H-pyrrolo[2,3-b]pyridine (4ia) The reaction was performed following the General Procedure B with 2-fluoro-3-(4-methylbenzyl)pyridine (**1i**) (40.2 mg, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and iPr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (30.1 mg, 53% yield) as a light yellow solid. Mp 257 – 258 °C. R_f = 0.53 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.05 (s, 1H), 8.22 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.80 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.37 – 7.22 (m, 4H), 7.18 – 7.14 (m, 3H), 7.06 (dd, *J* = 7.9, 4.7 Hz, 1H), 2.29 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ: 149.0, 143.8, 136.1, 134.8, 132.3, 131.8, 130.0, 129.9, 129.1, 129.0, 128.5, 127.3, 120.9, 116.8, 112.2, 21.3 ppm. IR (neat): 3141, 3085, 2917, 2849, 1652, 1600, 1581, 1515, 1482, 1248, 925, 770 cm^{-1}. HRMS: calcd for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1392, found 285.1391.



3-(4-methoxyphenyl)-2-phenyl-1H-pyrrolo[2,3-b]pyridine (4ja) The reaction was performed following the General Procedure B with 2-fluoro-3-(4-methoxybenzyl)pyridine (**1j**) (43.4 mg, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and iPr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (34.2 mg, 57% yield) as a white solid. Mp 241 – 243 °C. R_f = 0.52 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.04 (s, 1H), 8.22 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.79 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.36 – 7.18 (m, 5H), 7.06 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.97 – 6.91 (m, 2H), 3.75 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ: 158.4, 149.0, 143.8, 134.6, 132.4, 131.3, 129.0, 128.9, 128.4, 127.2, 126.9, 121.1, 116.7, 114.8, 112.0, 55.6 ppm. IR (neat): 3085, 3030, 2916, 2848, 1610, 1582, 1514, 1438, 1382, 1179, 924, 770 cm^{-1}. HRMS: calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1341, found 301.1343.



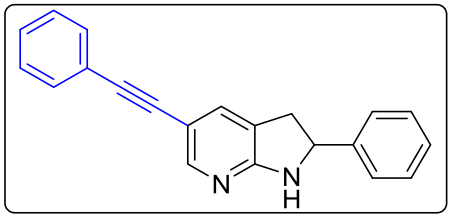
3-(4-chlorophenyl)-2-phenyl-1H-pyrrolo[2,3-b]pyridine (4ka) The reaction was performed following the General Procedure B with 3-(4-chlorobenzyl)-2-fluoropyridine (**1k**) (44.3 mg, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), benzaldehyde (**2a**) (21 µL, 0.20 mmol) and iPr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (39.0 mg, 64% yield) as a white solid. Mp 246 – 248 °C. R_f = 0.54 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.11 (s, 1H), 8.24 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.84 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.46 – 7.22 (m, 9H), 7.08 (dd, *J* = 8.0, 4.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ: 149.0, 143.9, 135.0, 134.8, 132.2, 130.1, 129.3, 129.1, 129.0, 128.6, 127.3, 127.0, 120.8, 116.9, 112.3 ppm. IR (neat): 3135, 3083, 2916, 2848, 1597, 1508, 1410, 1283, 1089, 926, 771 cm^{-1}. HRMS: calcd for $C_{19}H_{14}N_2Cl$ $[M+H]^+$ 305.0846, found 305.0846.



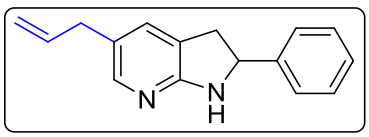
3-(4-fluorophenyl)-2-phenyl-1H-pyrrolo[2,3-b]pyridine (4la) The reaction was performed following the General Procedure B with

2-fluoro-3-(4-fluorobenzyl)pyridine (**1l**) (41 mg, 0.20 mmol), $KN(SiMe_3)_2$ (120.0 mg, 0.60 mmol), benzaldehyde (**2a**) (21 μL, 0.20 mmol) and iPr_2O (0.2 mL). The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 3:1) to give the desired product (38.6 mg, 67% yield) as a white solid. Mp 284 – 285 °C. R_f = 0.53 (Petroleum ether : EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.16 (s, 1H), 8.25 (dd, *J* = 4.4, 1.2 Hz, 1H), 7.81 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.37 – 7.16 (m, 7H), 7.11 – 7.05 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ: 149.0, 144.0, 135.2, 134.9(d, $J^2_{C\text{-}F}$ = 17.2 Hz), 132.2, 132.0, 131.2(d, $J^3_{C\text{-}F}$ = 4.0 Hz), 129.7(d, $J^1_{C\text{-}F}$ = 85.9 Hz), 129.1(d, $J^3_{C\text{-}F}$ = 4.0 Hz), 128.6, 127.2, 120.8(d, $J^4_{C\text{-}F}$ = 2.0 Hz), 116.9,116.2(d, $J^2_{C\text{-}F}$ = 21.2 Hz), 111.2 ppm. ^{19}F NMR (377MHz, $CDCl_3$): -116.0 ppm. IR (neat): 3138, 3084, 3034, 2916, 1598, 1579, 1514, 1411, 1381, 1286, 1222, 1072, 925, 779 cm^{-1}. HRMS: calcd for $C_{19}H_{14}N_2F$ $[M+H]^+$ 289.1141, found 289.1139.

Further Transformation of 5-bromo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine

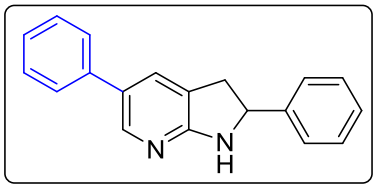


2-phenyl-5-(phenylethynyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (5) To an oven-dried vial equipped with a stir bar under an argon atmosphere was added 5-bromo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine **(3da)** (55.0 mg, 0.2 mmol), phenylacetylene (33 μL, 0.3 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol%), XPhos (8.7 mg, 7.5 mol%), K_3PO_4 (127.4 mg, 0.6 mmol) and acetonitrile (0.6 mL). The microwave vial was sealed with a cap and removed from the glove box. The reaction mixture was stirred at the 80 °C in an oil bath for 12 h. The sealed vial was cooled to room temperature, opened to air, and then 2 drops water was added. The reaction mixture was passed through a short pad of silica gel, rinsed with an addition 6 mL of ethyl acetate (3 × 2 mL), and the combined solutions were concentrated in vacuo. The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the product (53.0 mg, 90% yield) as a light yellow solid. Mp 154 – 158 °C. R_f = 0.5 (Petroleum ether : EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 1.9 Hz, 1H), 7.49 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.42 – 7.35 (m, 4H), 7.35 – 7.28 (m, 5H), 5.87 (s, 1H), 5.05 (t, *J* = 8.5 Hz, 1H), 3.49 (dd, *J* = 16.5, 9.6 Hz, 1H), 2.95 (dd, *J* = 16.5, 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.3, 150.1, 143.8, 133.9, 131.4, 129.0, 128.5, 128.0,127.9, 126.1, 123.7, 121.0, 109.3, 89.4, 89.0, 60.4, 37.6 ppm. IR (neat): 3388, 3183, 3139, 2918, 2849, 2206, 1620, 1595, 1492, 1441, 1355, 1253, 911, 753, 698 cm^{-1}. HRMS: calcd for $C_{21}H_{16}N_2$ $[M+H]^+$ 297.1392, found 297.1393.

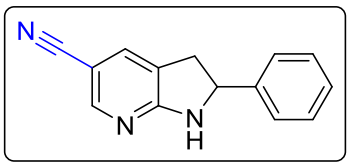


5-allyl-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (6) To an oven-dried vial equipped with a stir bar under an argon atmosphere was added 5-bromo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine **(3da)** (55.0 mg, 0.2 mmol), allyltributylstannane (68 μL, 0.22 mmol), $Pd(PPh_3)_4$ (23.0 mg, 10 mol%), LiCl (17.0 mg, 0.4 mmol), and THF (1.0 mL). The microwave vial was sealed with a cap and removed from the glove box. The reaction mixture was stirred at the 110 °C in an oil bath for 12 h. The sealed vial was cooled to room temperature, opened to air, and then 2 drops water was added. The reaction mixture was passed through a short pad of silica gel, rinsed with an addition 6 mL of ethyl acetate (3 × 2 mL), and the combined solutions were concentrated in vacuo. The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the product (42.0

mg, 89% yield) as a white solid. Mp 119 – 121 °C. R_f = 0.5 (Petroleum ether : EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 1H), 7.41 – 7.30 (m, 4H), 7.30 – 7.23 (m, 1H), 7.08 (s, 1H), 6.10 – 5.66 (m, 1H), 5.10 – 4.90 (m, 4H), 3.44 (dd, *J* = 16.3, 9.3 Hz, 1H), 3.21 (d, *J* = 6.6 Hz, 2H), 2.91 (dd, *J* = 16.3, 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 162.4, 143.2, 142.0, 136.7, 134.7, 129.0, 127.9, 127.0, 125.9, 125.1, 116.7, 60.7, 37.3, 36.6 ppm. IR (neat): 3726, 2704, 2625, 2594, 2917, 2849, 1578, 1542, 1385, 751 cm^{-1}. HRMS: calcd for $C_{16}H_{16}N_2$ $[M+H]^+$ 237.1392, found 237.1392.



2,5-diphenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (7) To an oven-dried vial equipped with a stir bar under an argon atmosphere was added 5-bromo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine **(3da)** (55.0 mg, 0.2 mmol), phenylboronic acid (42.6 mg, 0.35 mmol), K_3PO_4 (85.0 mg, 0.4 mmol) and toluene (0.6 mL). To the mixture was added 30 µL of a catalyst solution composed of $Pd(OAc)_2$ (2.2 mg, 5 mol%), XPhos (5.7 mg, 5.0 mol%) and THF (200 µL). The microwave vial was sealed with a cap and removed from the glove box. The reaction mixture was stirred at the 110 °C in an oil bath for 12 h. The sealed vial was cooled to room temperature, opened to air, and then 2 drops water was added. The reaction mixture was passed through a short pad of silica gel, rinsed with an addition 6 mL of ethyl acetate (3 × 2 mL), and the combined solutions were concentrated in vacuo. The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the product (45.0 mg, 83% yield) as a white solid. Mp 162 – 163 °C. R_f = 0.5 (Petroleum ether : EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 2.1 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.45 – 7.33 (m, 6H), 7.33 – 7.27 (m, 2H), 5.29 (s, 1H), 5.07 (t, *J* = 8.4 Hz, 1H), 3.55 (dd, *J* = 16.4, 9.5 Hz, 1H), 3.01 (dd, *J* = 16.4, 7.7 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.5, 144.7, 144.1, 139.1, 130.8, 129.0, 128.9, 127.8, 127.5, 126.8, 126.5, 126.2, 121.5, 60.7, 38.0 ppm. IR (neat): 2955, 2917, 2849, 1622, 1579, 1542, 1472, 1417, 1274, 1124, 754, 697 cm^{-1}. HRMS: calcd for $C_{19}H_{16}N_2$ $[M+H]^+$ 273.1392, found 273.1396.



2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine-5-carbonitrile (8) To an oven-dried vial equipped with a stir bar under an argon atmosphere was added 5-bromo-2-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine **(3da)** (55.0 mg, 0.2 mmol), $Zn(CN)_2$ (13.2 mg, 56 mol%), $Pd(TFA)_2$ (2.8 mg, 4.3 mol%), 2-(Di-tert-butylphosphino)-1, 1'-binaphtyl (6.0 mg, 8.8 mol%), zinc flakes (2.4 mg, 19 mol%) and DMA (720 µL). The microwave vial was sealed with a cap and removed from the glove box. The reaction mixture was stirred at the 110 °C in an oil bath for 12 h. The sealed vial was cooled to room temperature, opened to air, and then 2 drops water was added. The reaction mixture was passed through a short pad of silica gel, rinsed with an addition 6 mL of ethyl acetate (3 × 2 mL), and the combined solutions were concentrated in vacuo. The crude product was purified by chromatography on silica gel (eluted with Petroleum ether : EtOAc = 5:1) to give the product (38.0 mg, 86% yield) as a light brown solid. Mp 161 – 163 °C. R_f = 0.5 (Petroleum ether : EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 2.0 Hz, 1H), 7.40 – 7.30 (m, 5H), 7.27 (d, *J* = 1.8 Hz, 1H), 6.88 (s, 1H), 5.11 (dd, *J* = 9.9, 7.0 Hz, 1H), 3.54 (dd, *J* = 17.1, 9.9 Hz, 1H), 2.97 (dd, *J* = 17.1, 7.0 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 165.4, 152.4, 142.8, 132.5, 129.2, 128.3, 125.9, 122.0, 119.0, 97.4, 60.1, 39.0 ppm.

IR (neat): 3726, 3594, 2917, 2849, 2216, 1622, 1578, 1490, 1275, 1261, 764, 750 cm^{-1}. HRMS: calcd for $C_{14}H_{11}N_3$ $[M+H]^+$ 222.1031, found 222.1034.

7. NMR Spectra

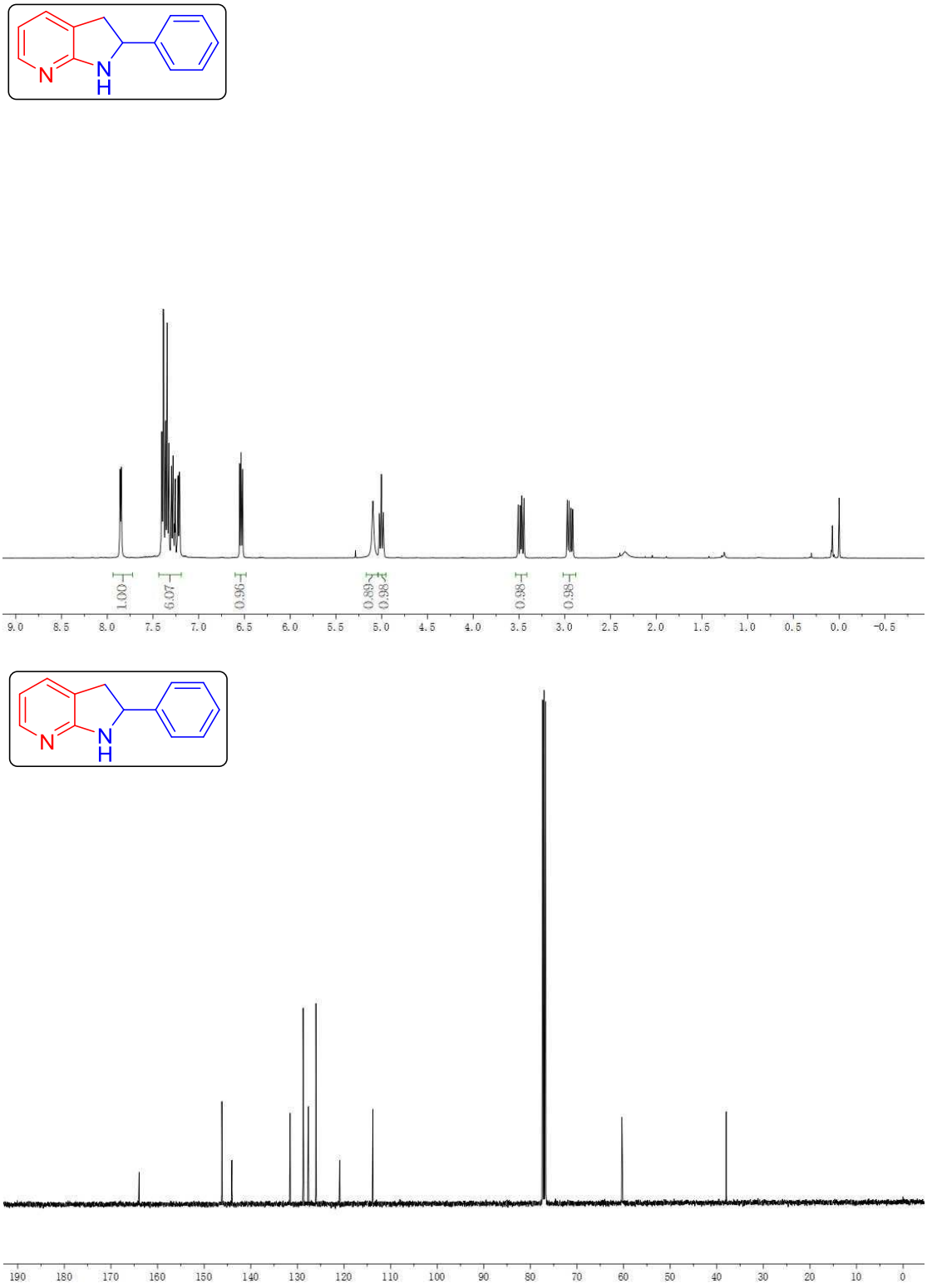


Figure S1. ^{1}H (400 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra of **3aa** in $CDCl_3$.

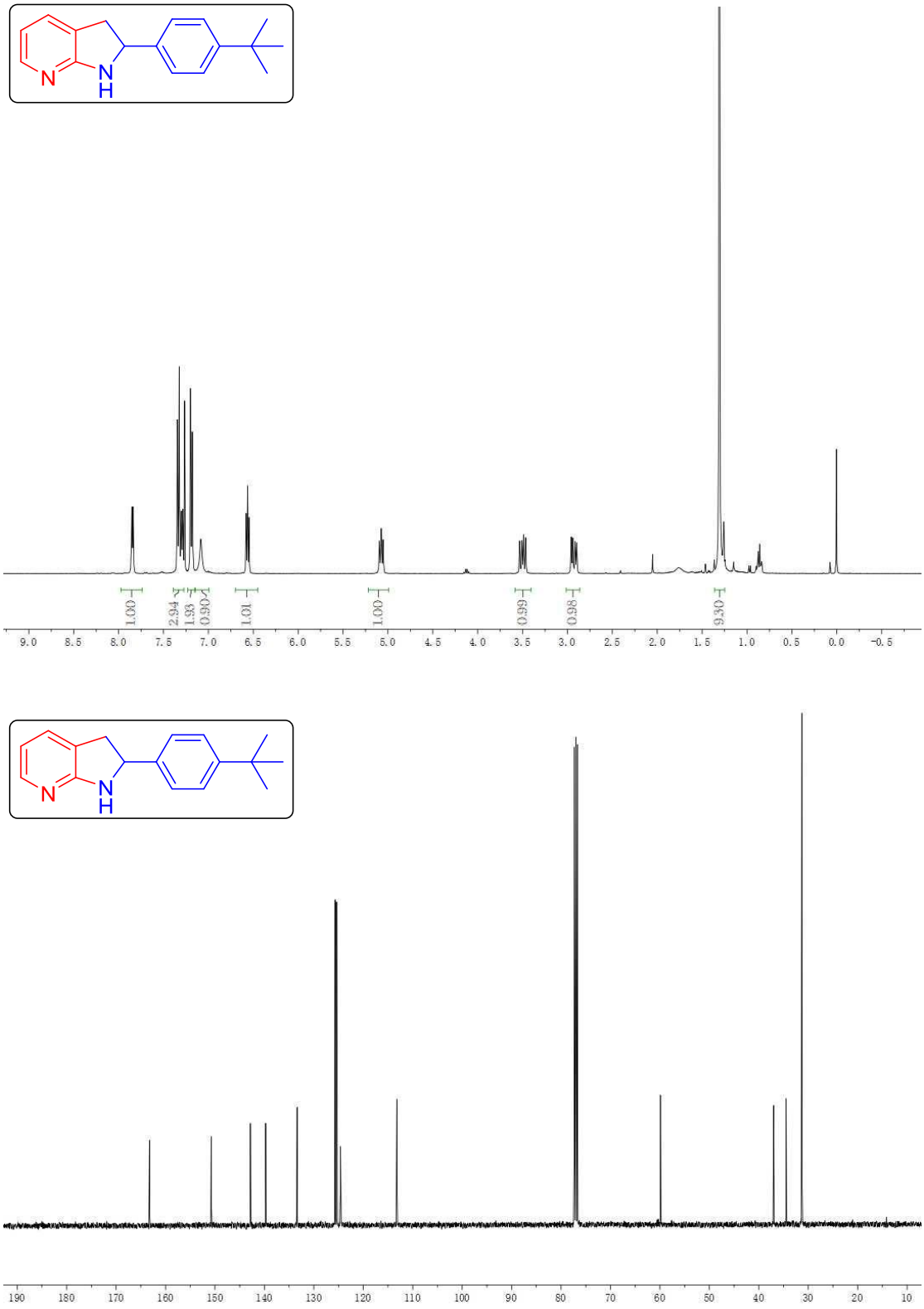


Figure S2. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ab** in $CDCl_3$

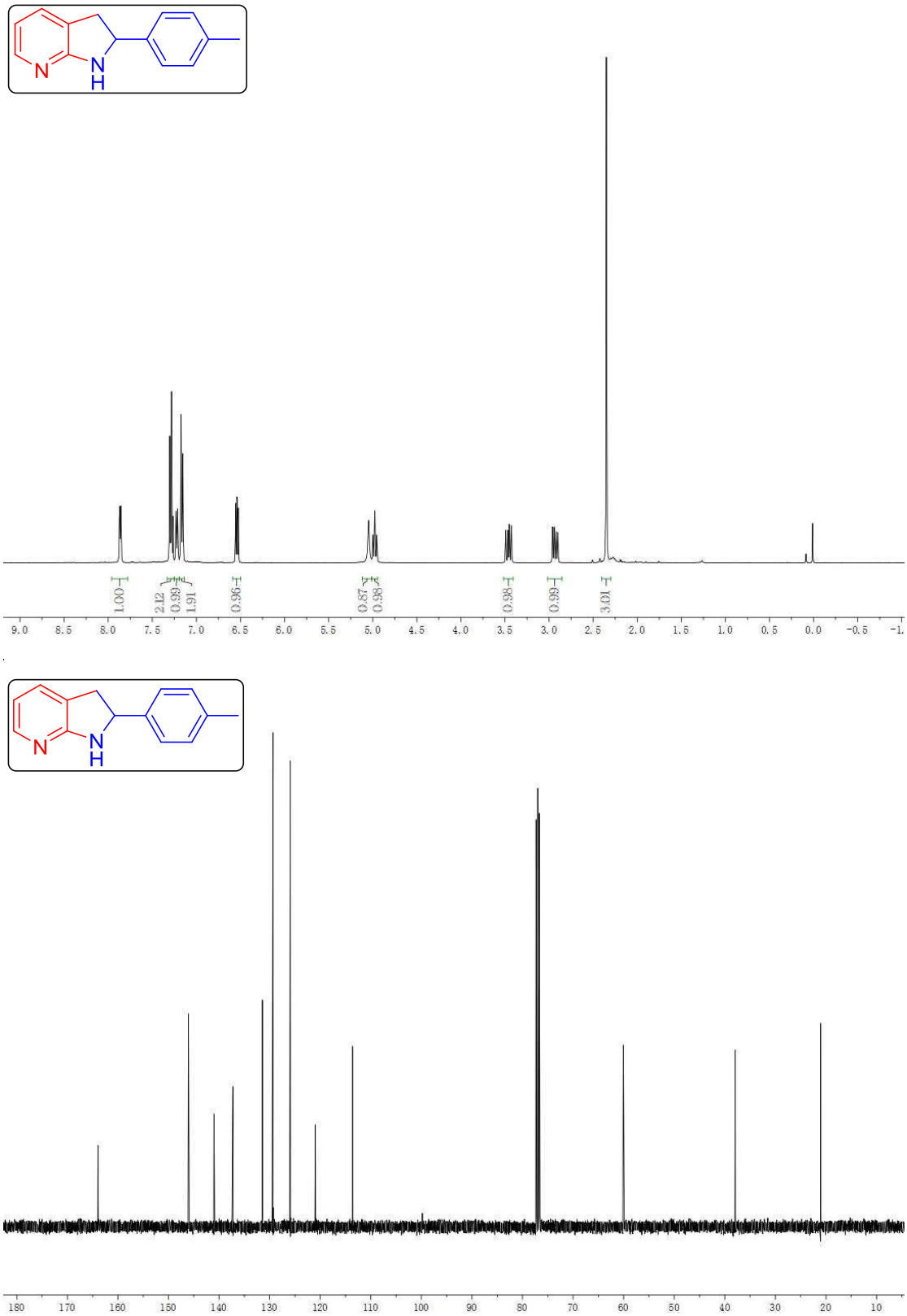


Figure S3. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ac** in $CDCl_3$

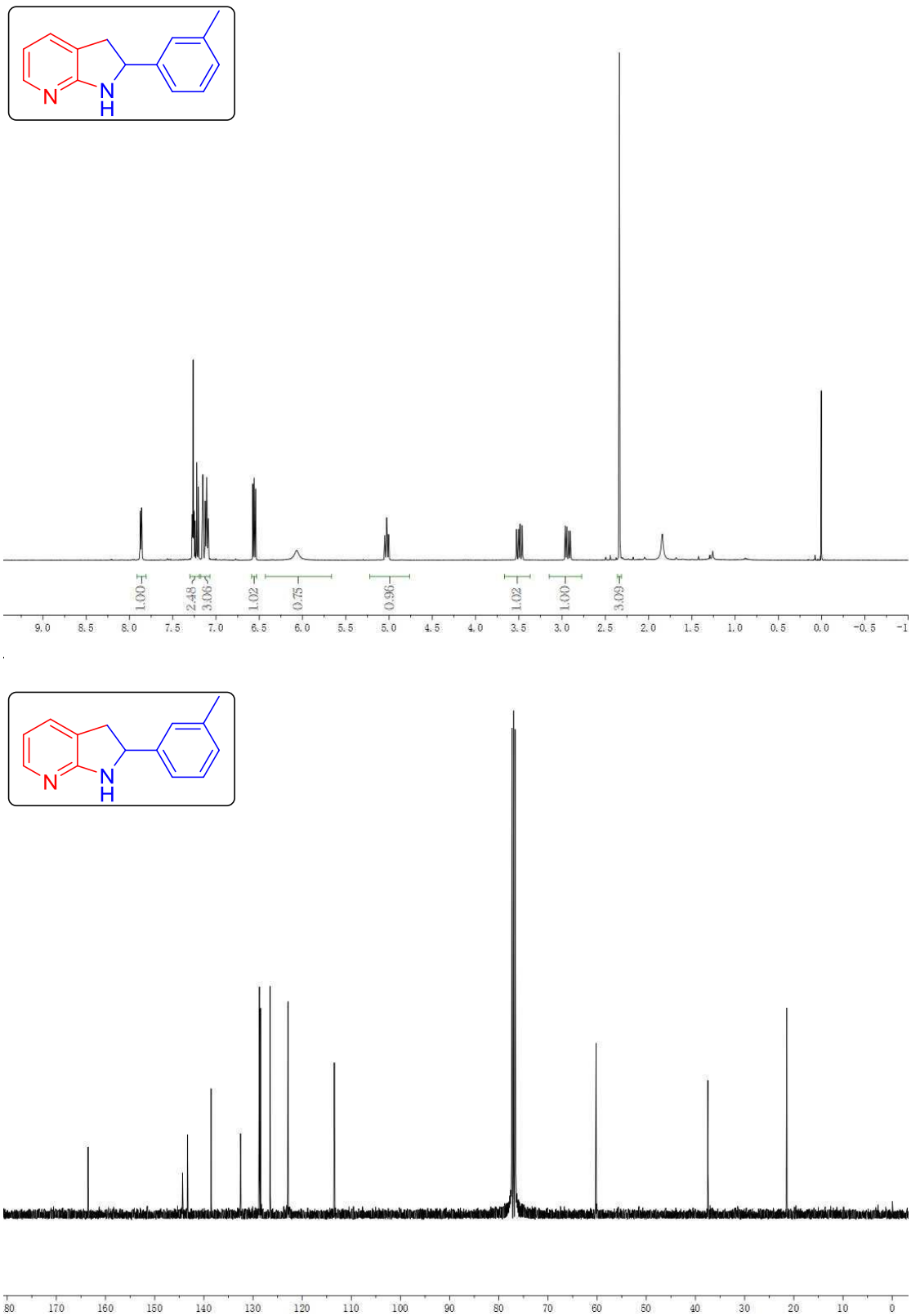


Figure S4. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ad** in $CDCl_3$

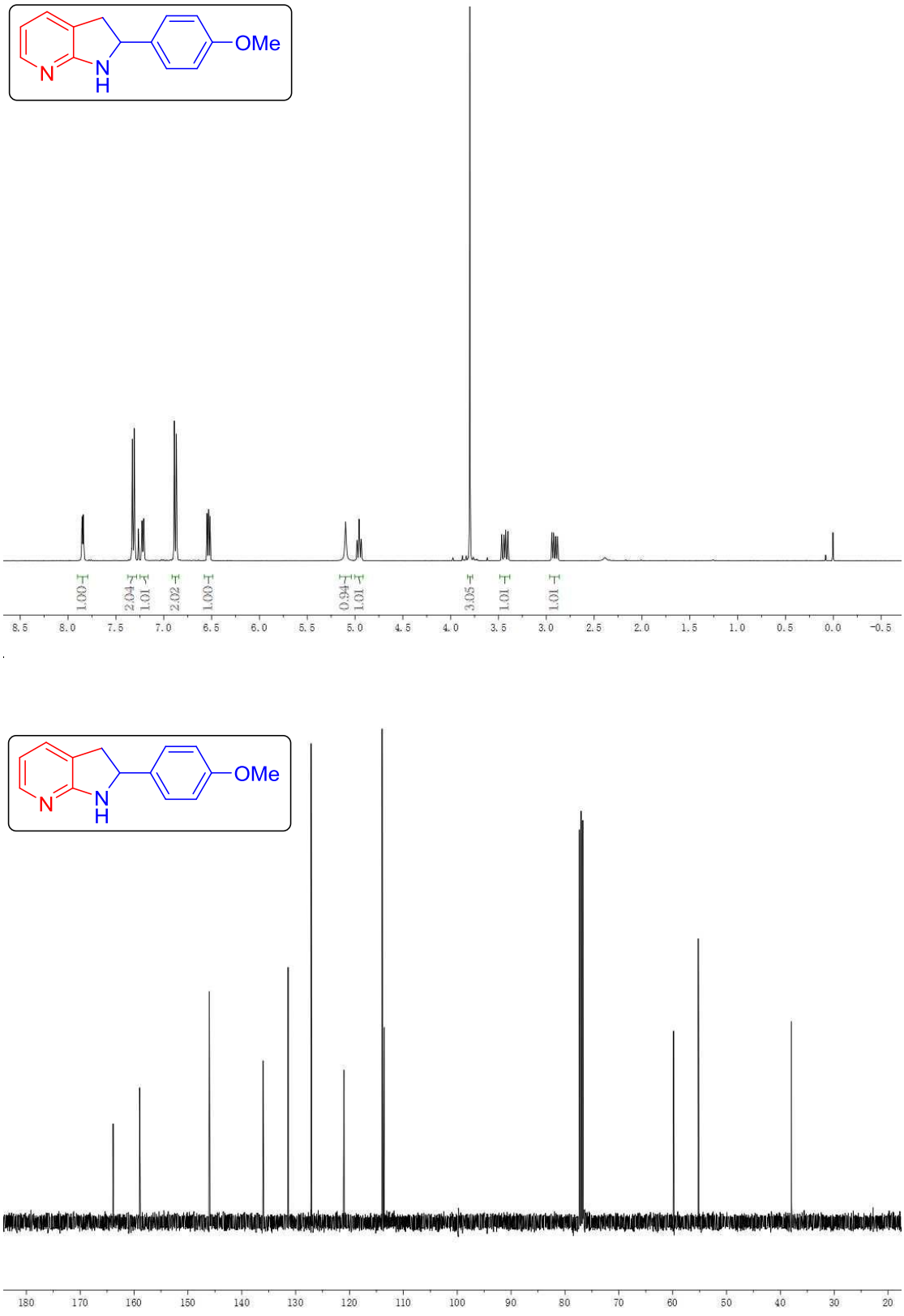


Figure S5. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ae** in $CDCl_3$

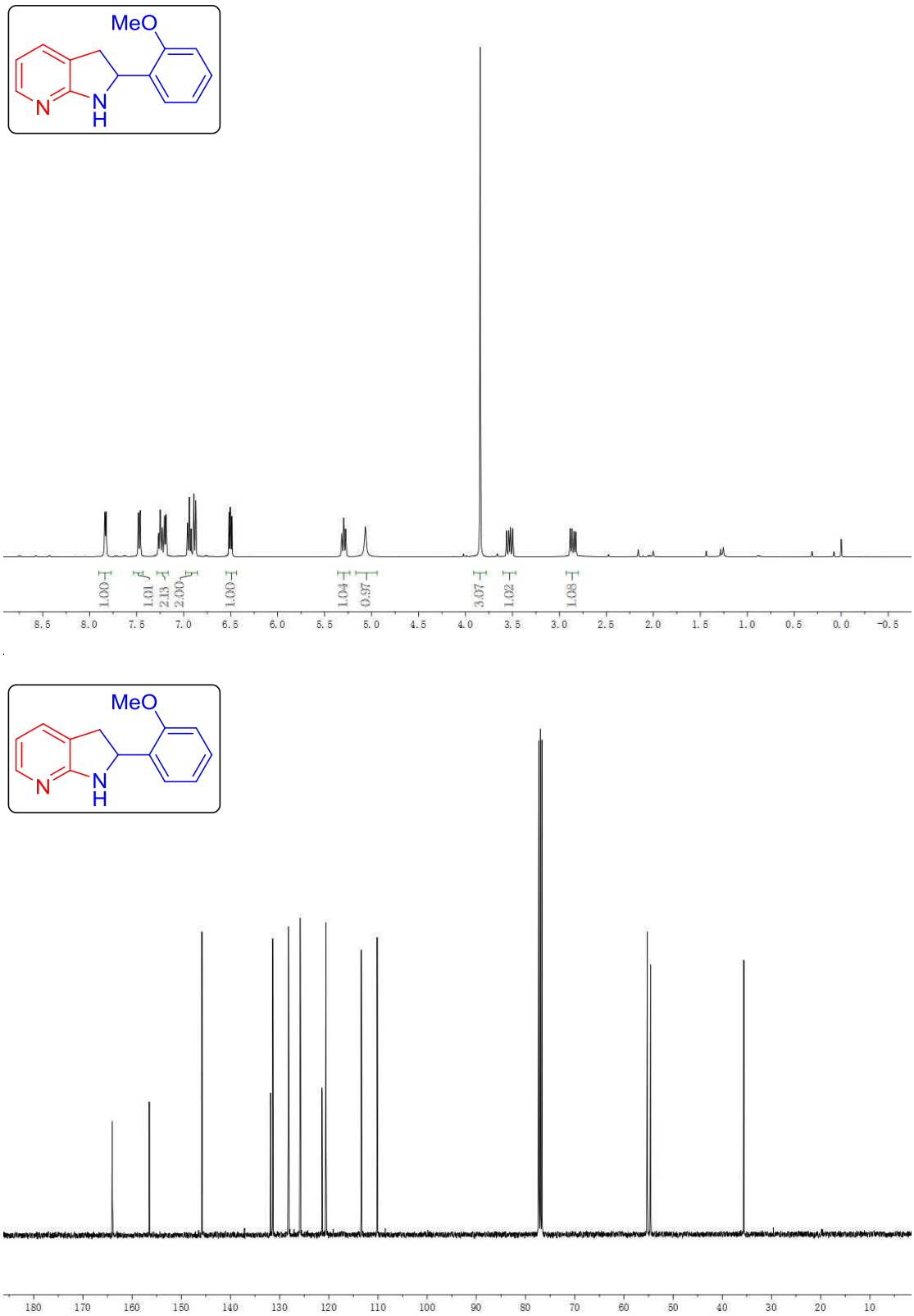


Figure S6. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3af** in $CDCl_3$

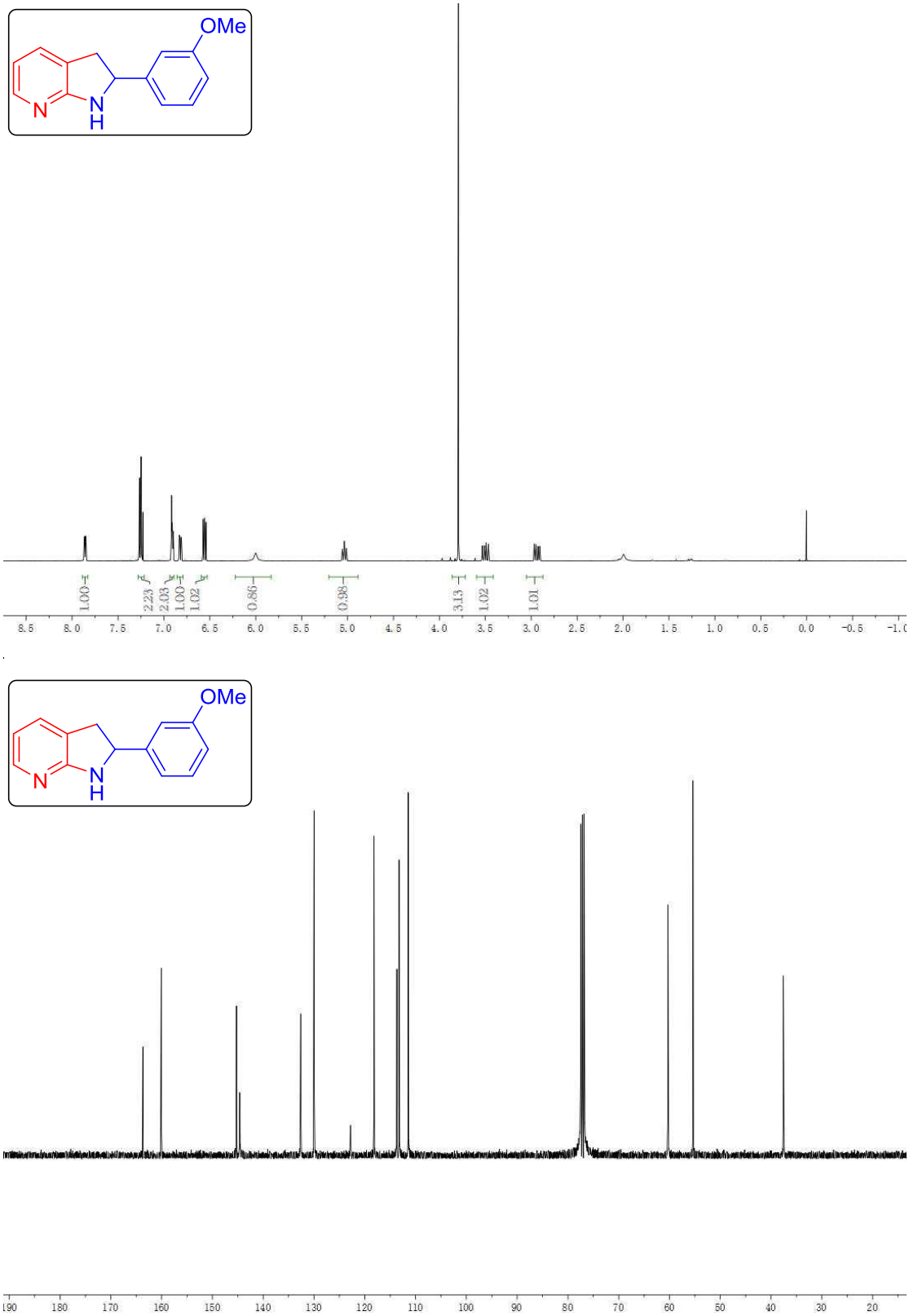


Figure S7. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ag** in $CDCl_3$

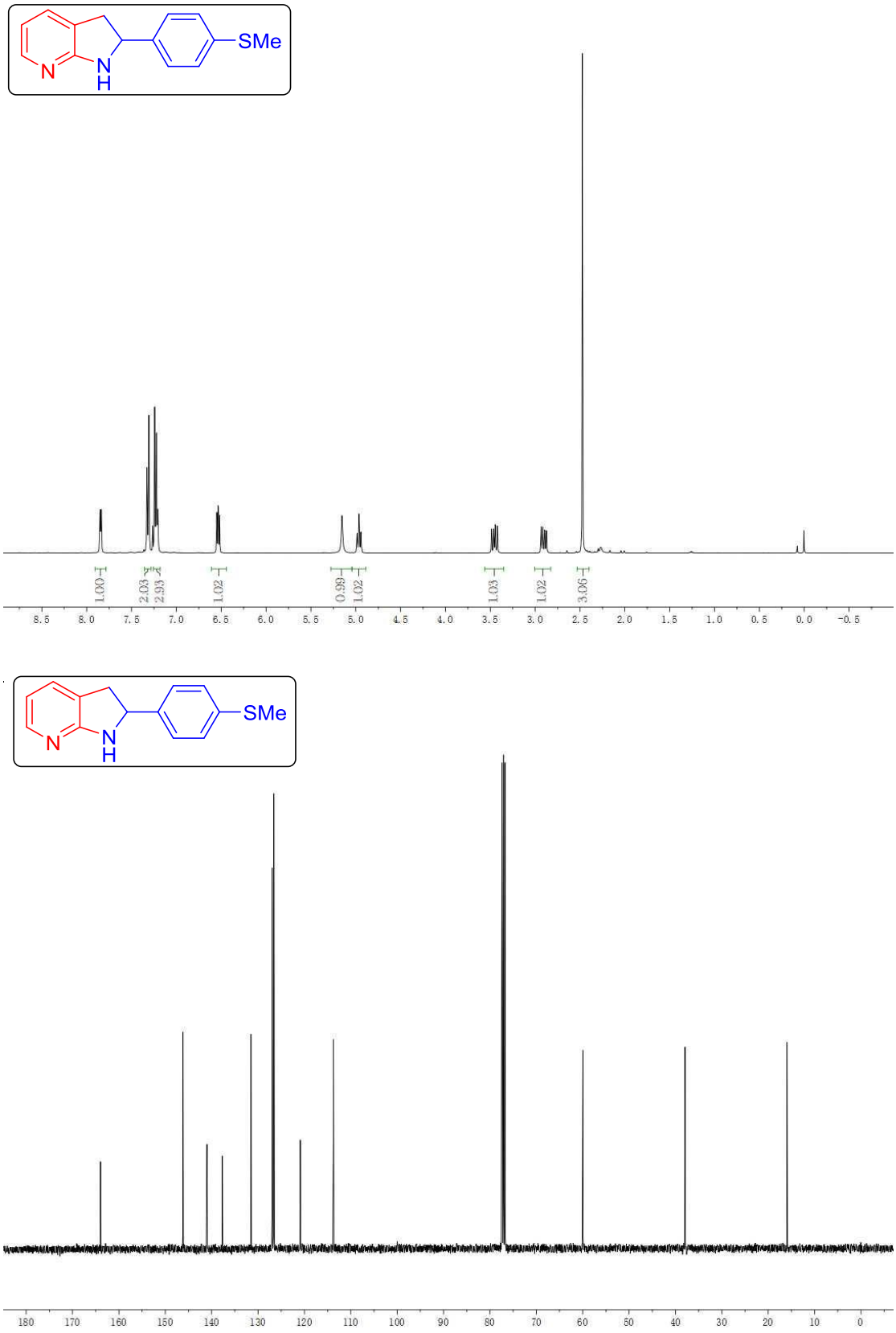


Figure S8. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ah** in $CDCl_3$

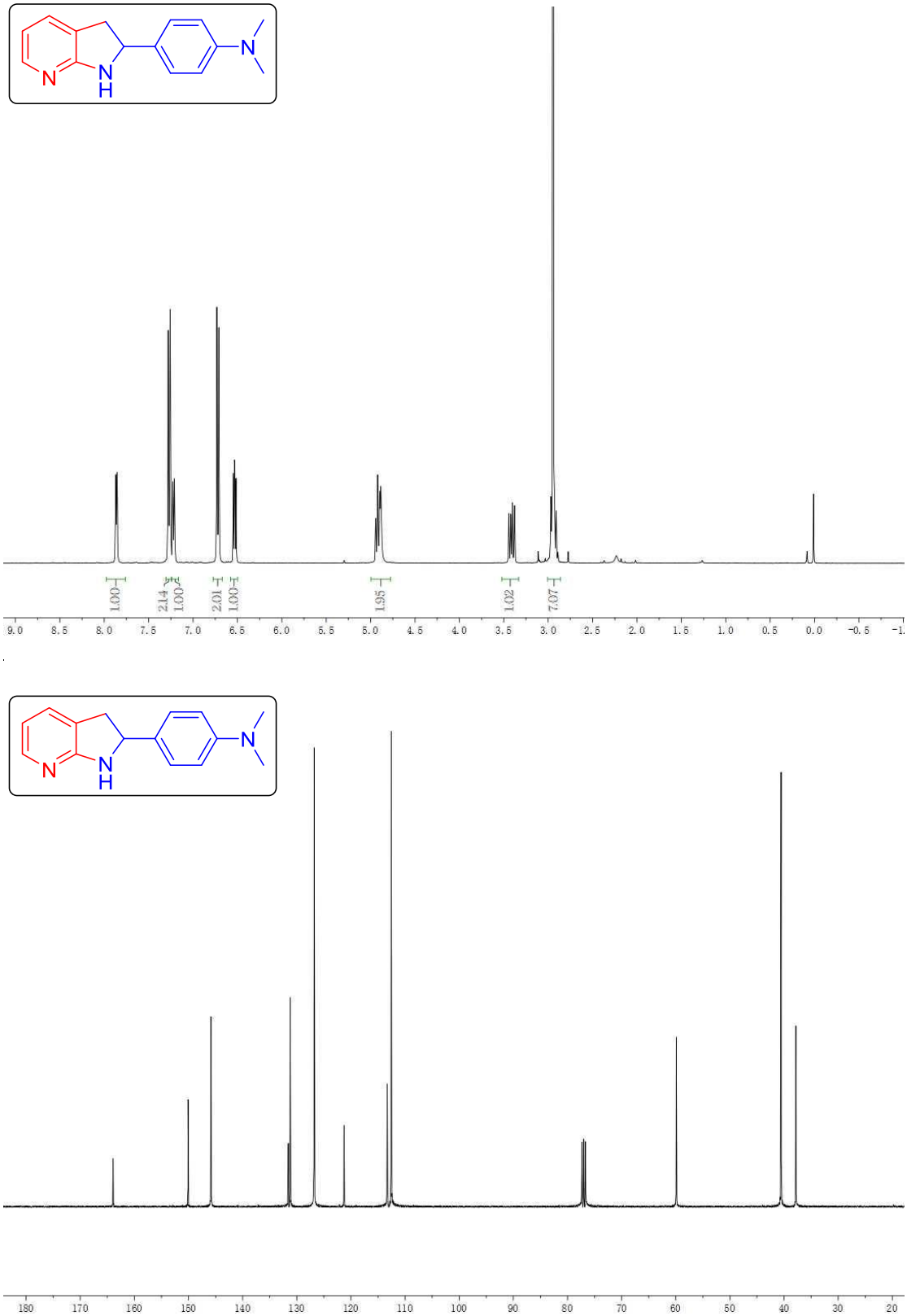


Figure S9. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ai** in $CDCl_3$

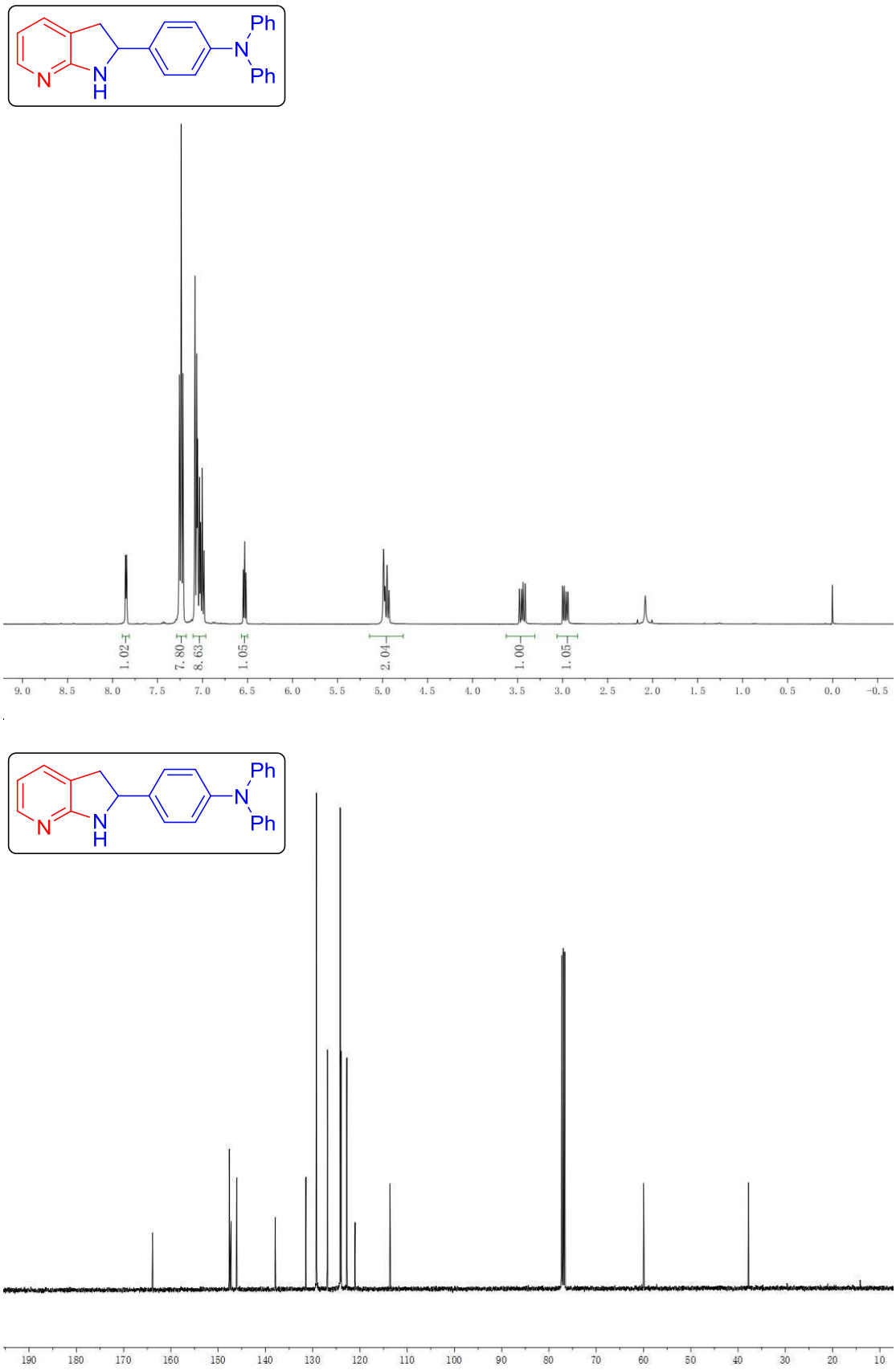


Figure S10. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3aj** in $CDCl_3$

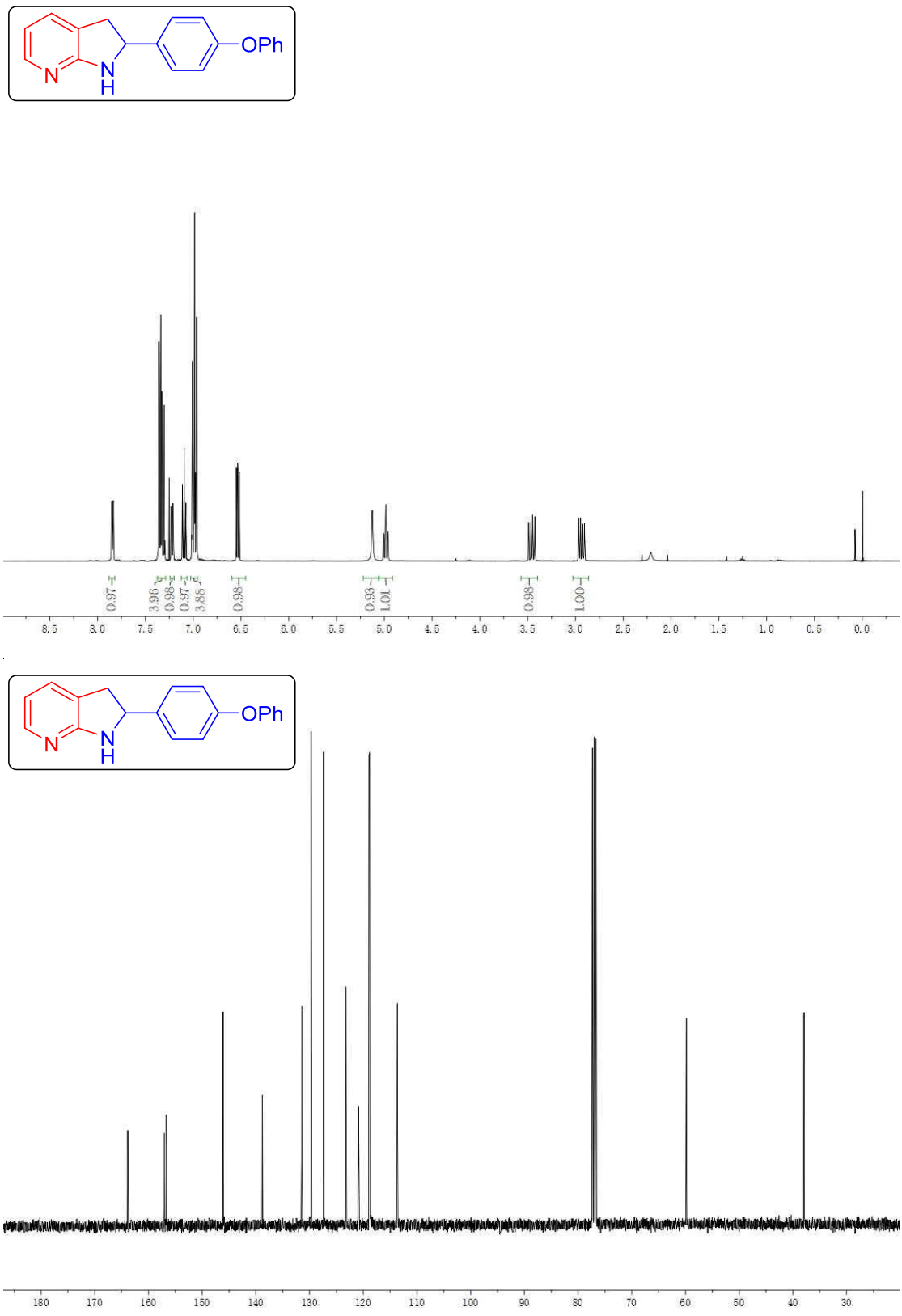


Figure S11. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ak** in $CDCl_3$

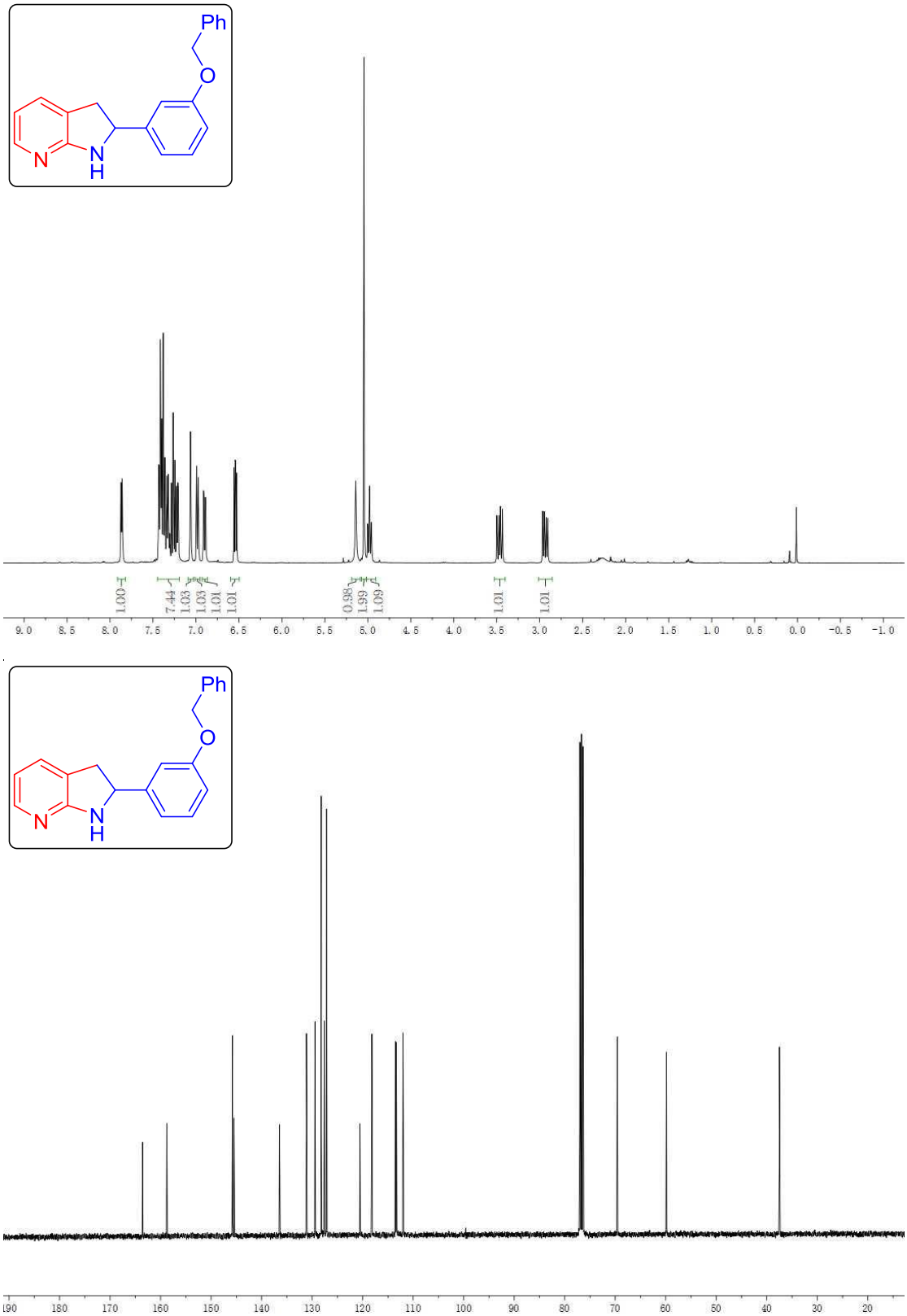


Figure S12. ^{1}H (400 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra of **3al** in $CDCl_3$

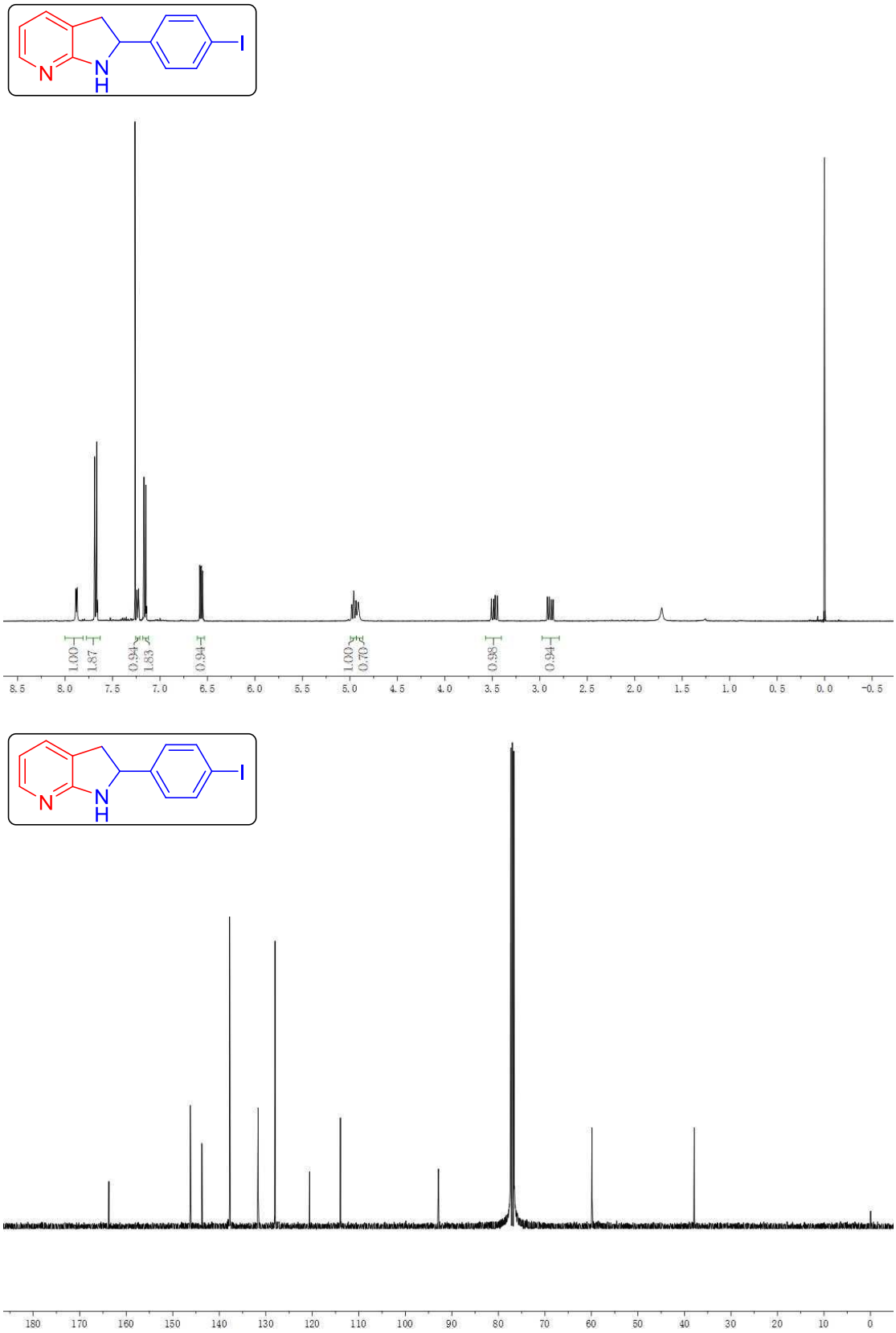


Figure S13. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3am** in $CDCl_3$

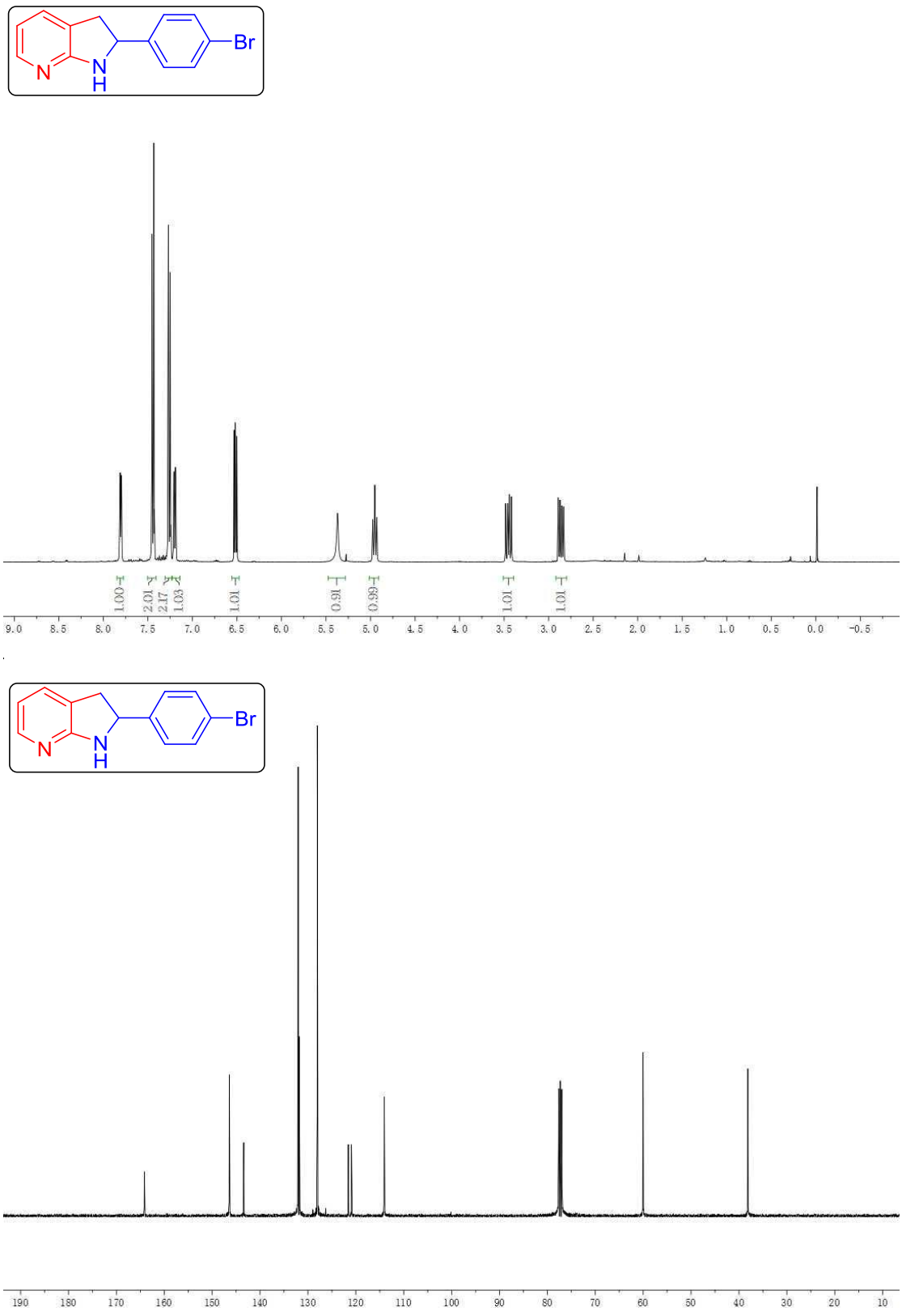


Figure S14. ^{1}H (400 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra of **3an** in $CDCl_3$

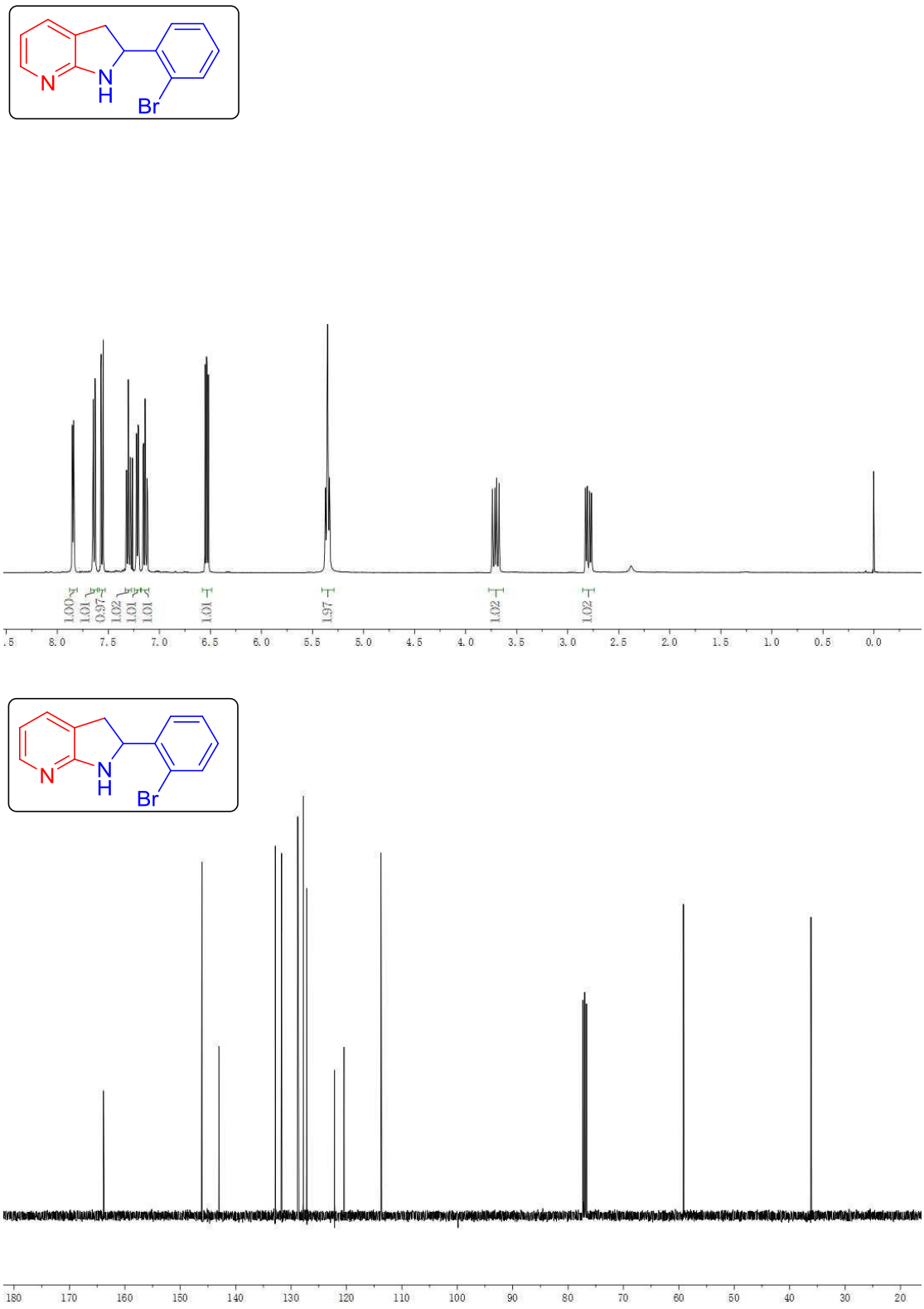
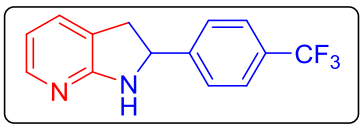
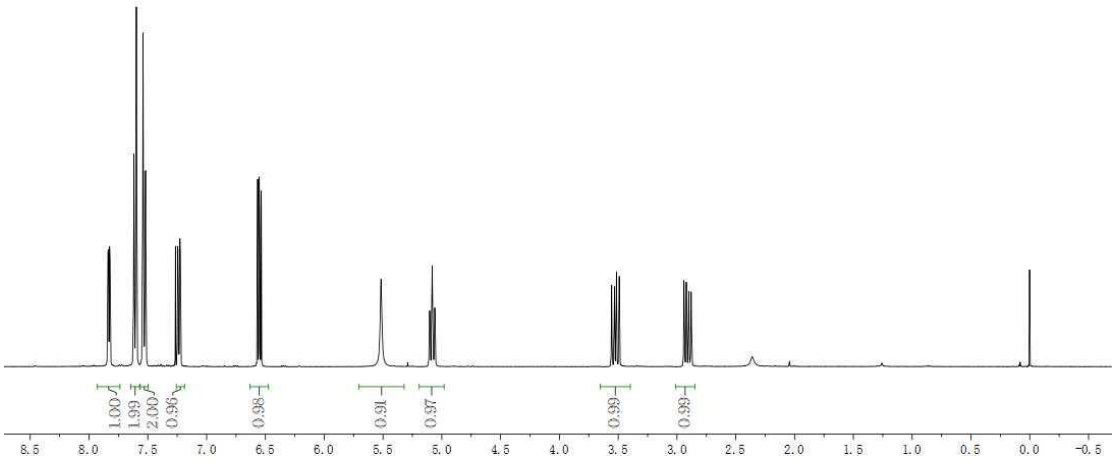
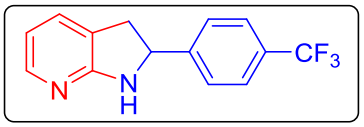
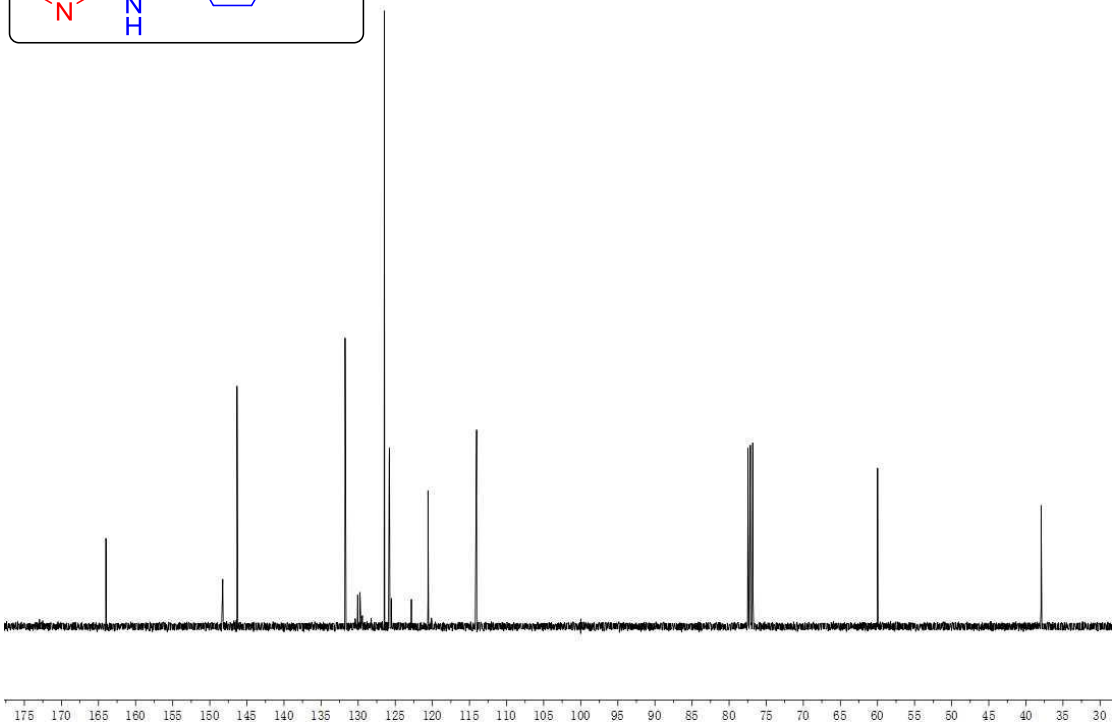


Figure S15. ^{1}H (400 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra of **3ao** in $CDCl_3$


CF3
N
N
H


1.00
1.99
2.00
0.96
0.98
0.91
0.97
0.99
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


CF3
N
N
H


175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30

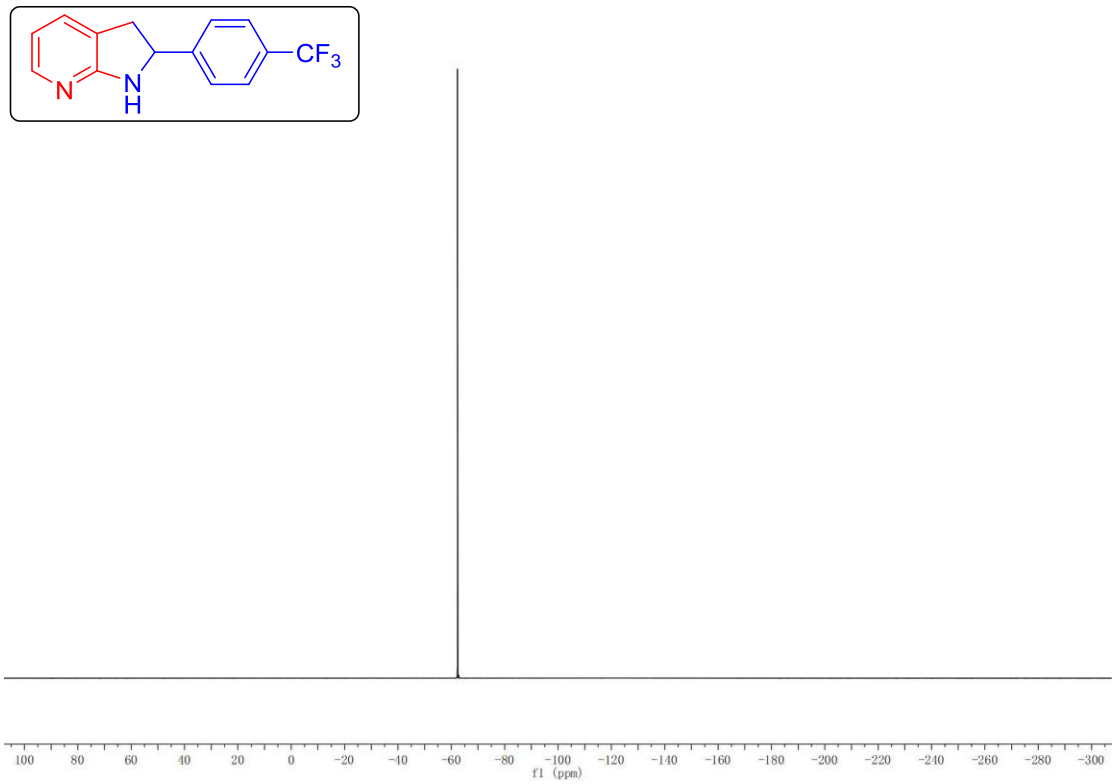
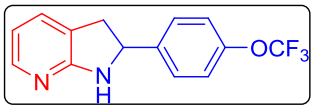
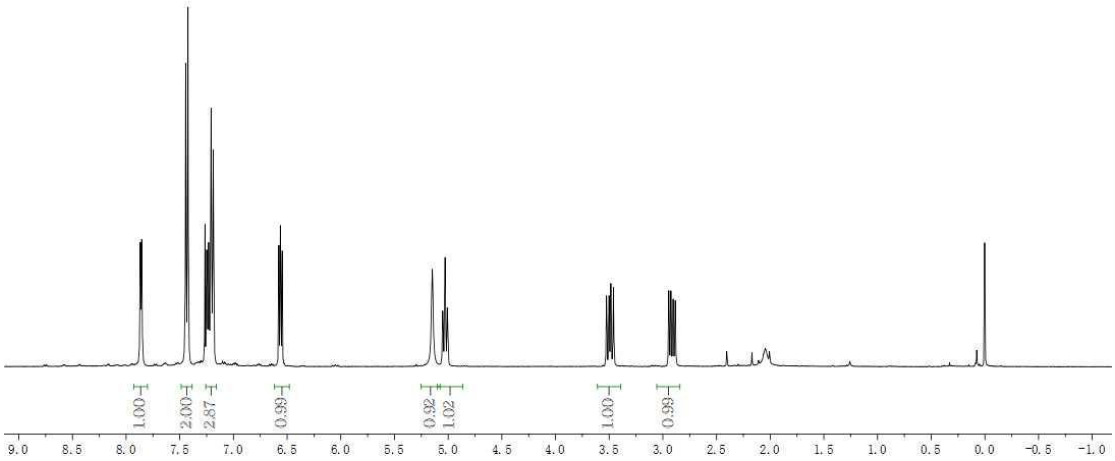
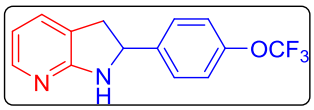
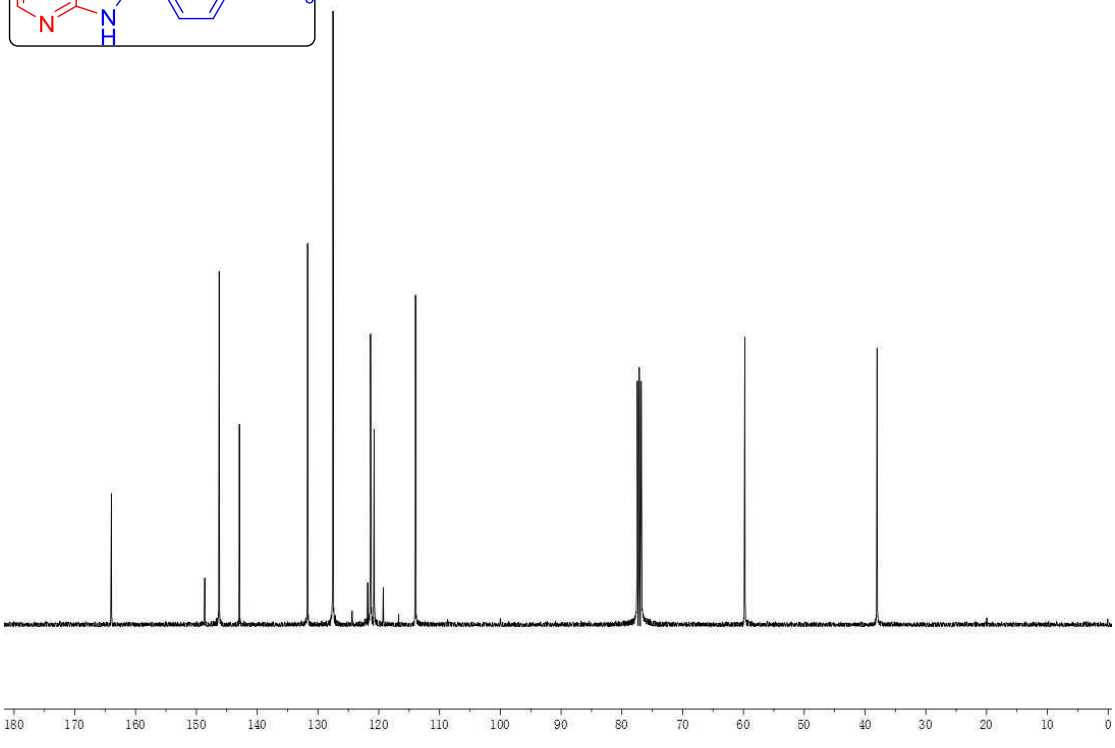


Figure S16. ^{1}H (400 MHz), ^{13}C $\{^{1}H\}$ (101 MHz) and ^{19}F (377 MHz) NMR spectra of **3ap** in $CDCl_3$


OCF3
N
H


1.00
2.00
2.87
0.99
0.92
1.02
1.00
0.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


OCF3
N
H


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

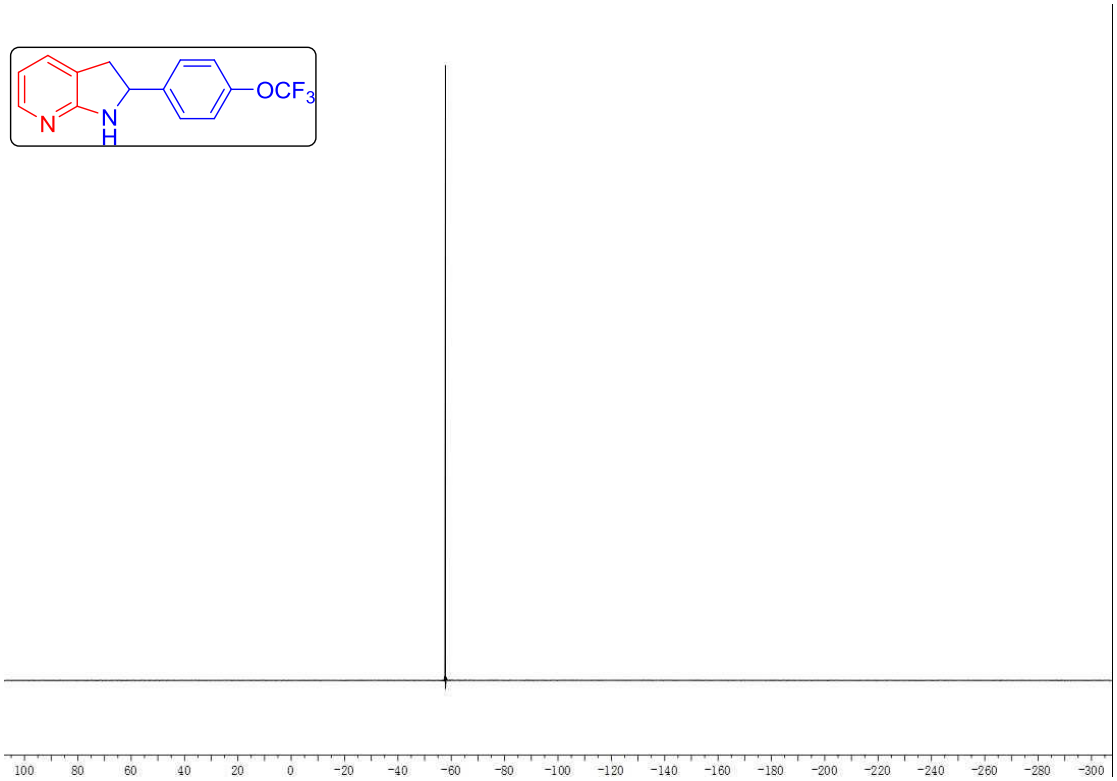


Figure S17. ^{1}H (400 MHz), ^{13}C $\{^{1}H\}$ (101 MHz) and ^{19}F (377 MHz) NMR spectra of **3aq** in $CDCl_3$

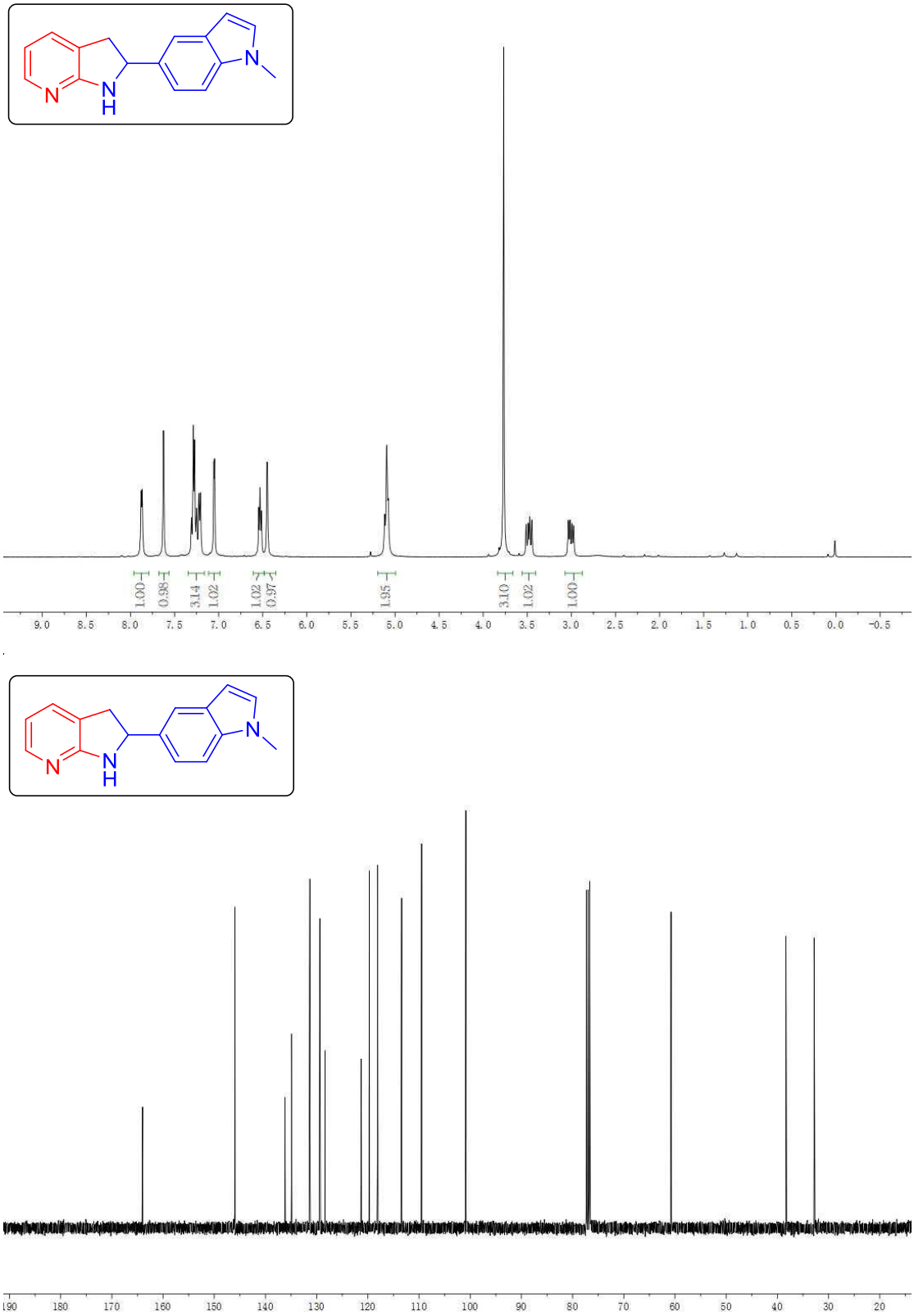


Figure S18. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ar** in $CDCl_3$

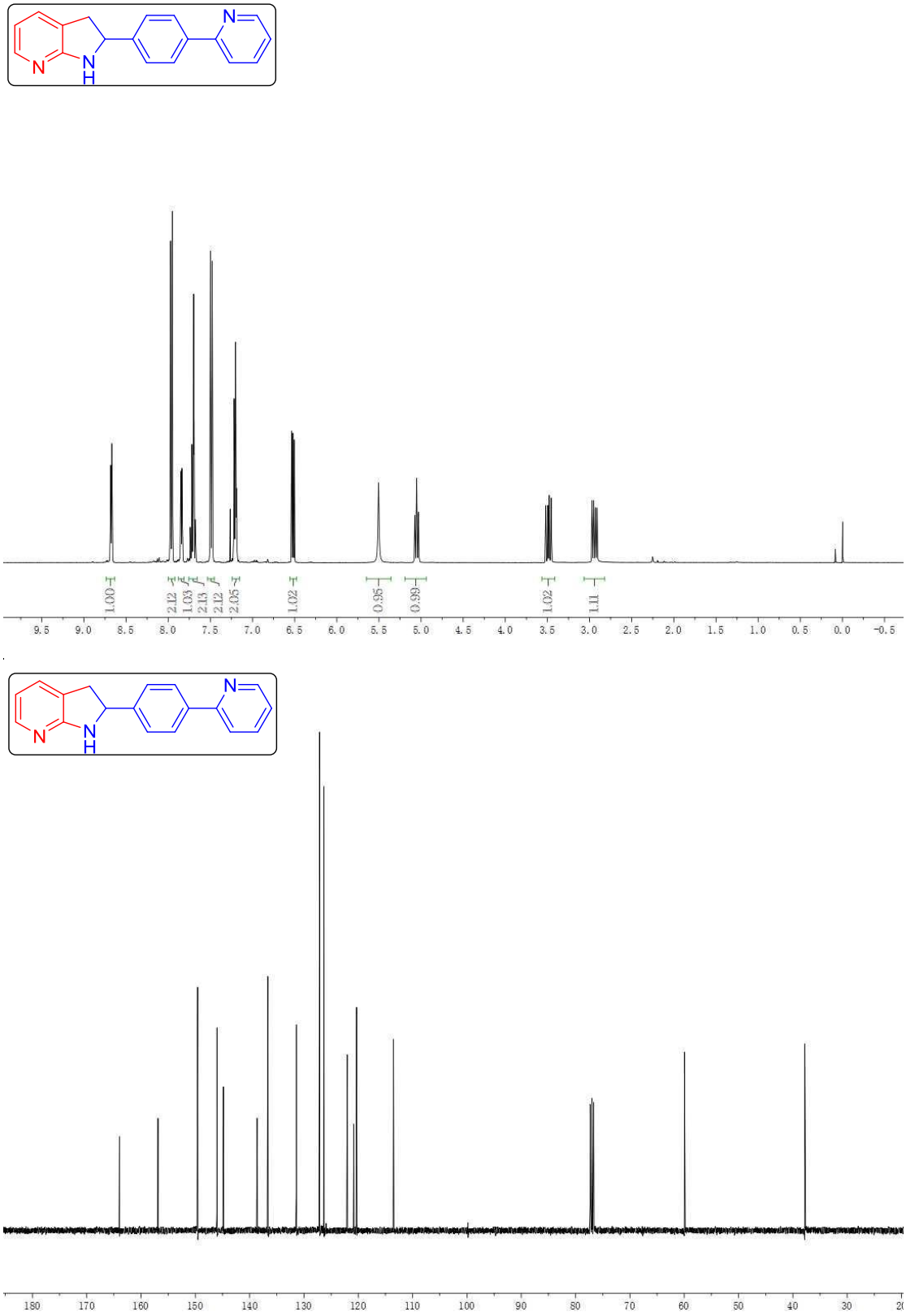


Figure S19. ^{1}H (400 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra of **3as** in $CDCl_3$

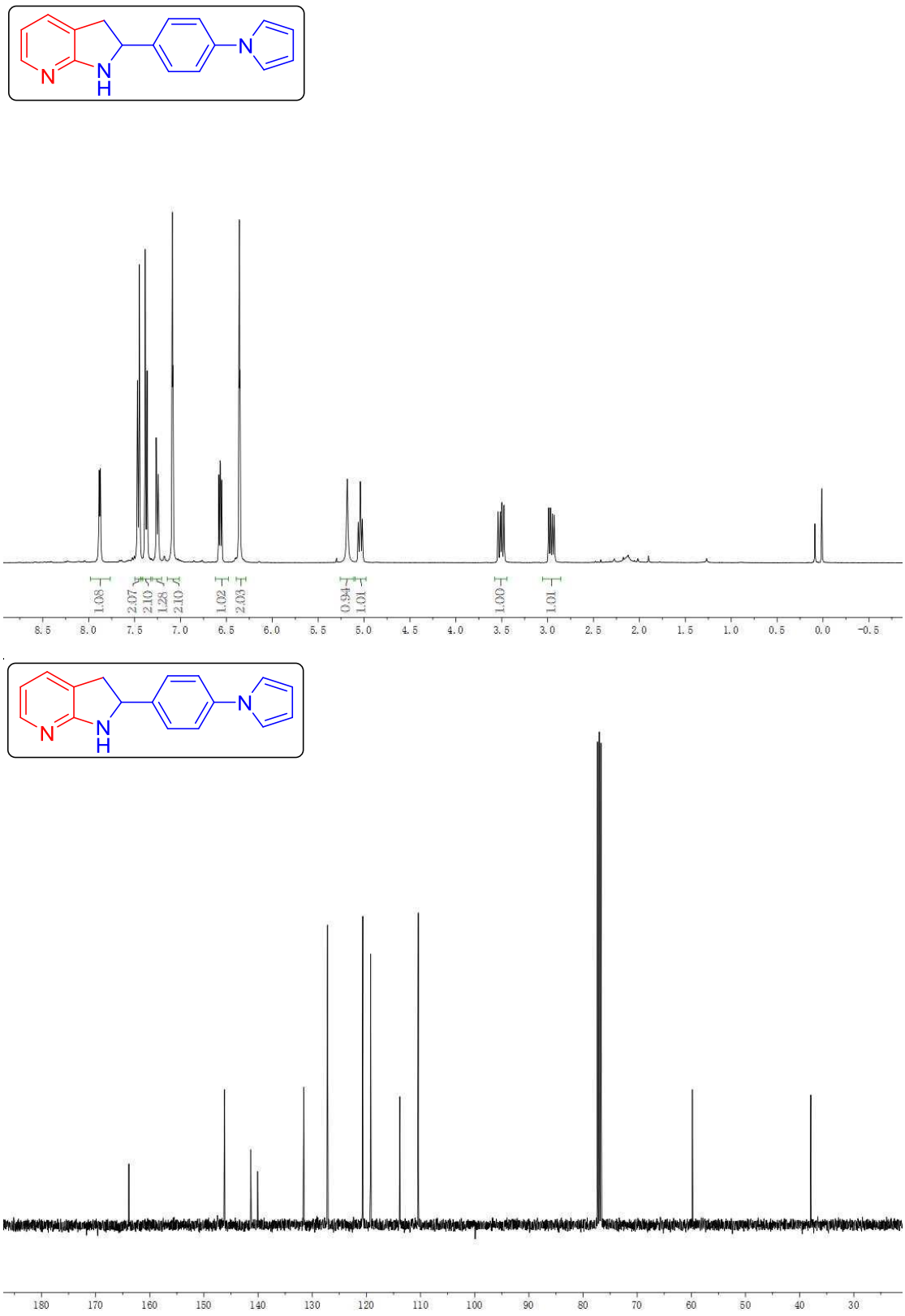


Figure S20. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3at** in $CDCl_3$

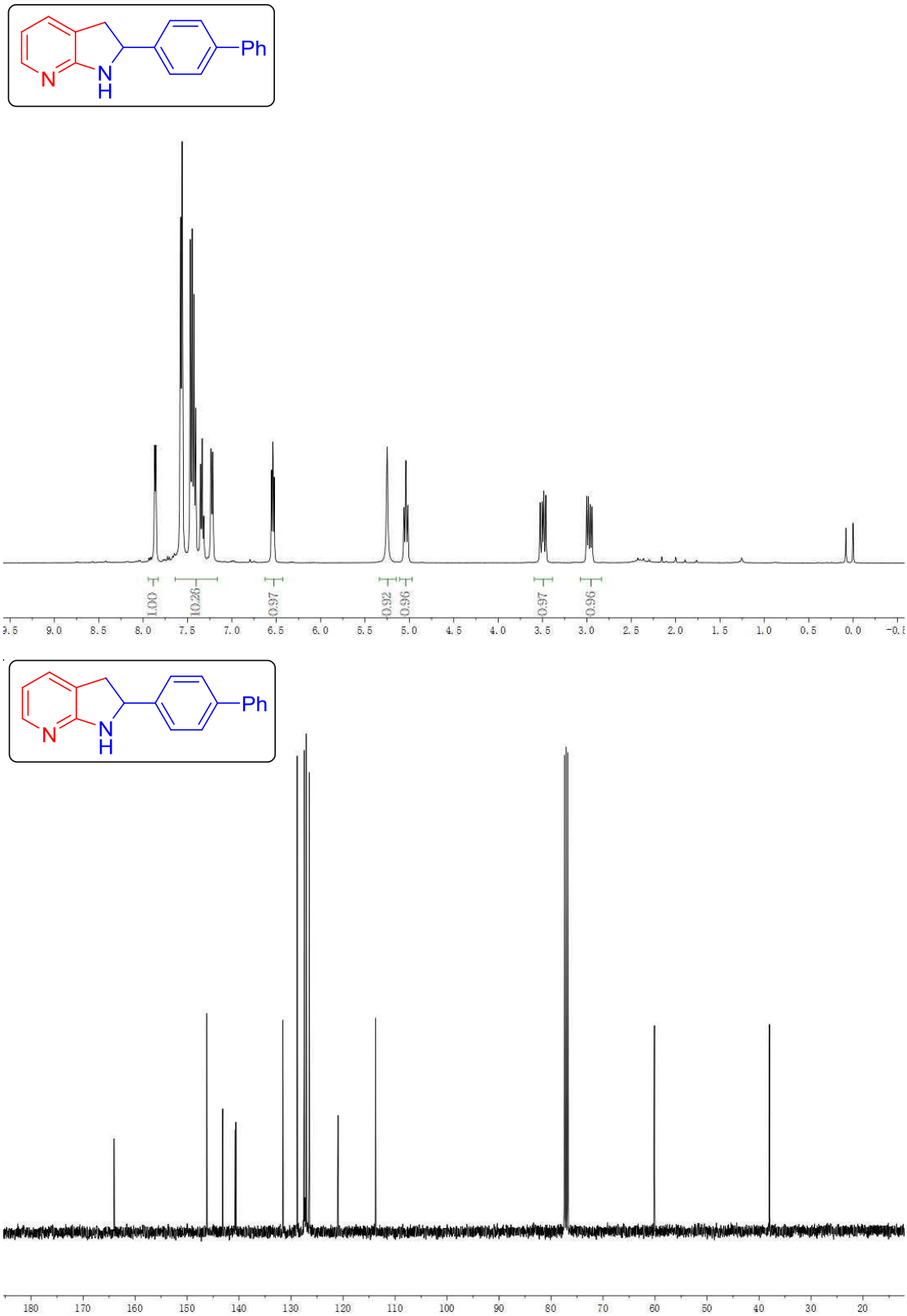


Figure S21. ^{1}H (400 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra of **3au** in $CDCl_3$

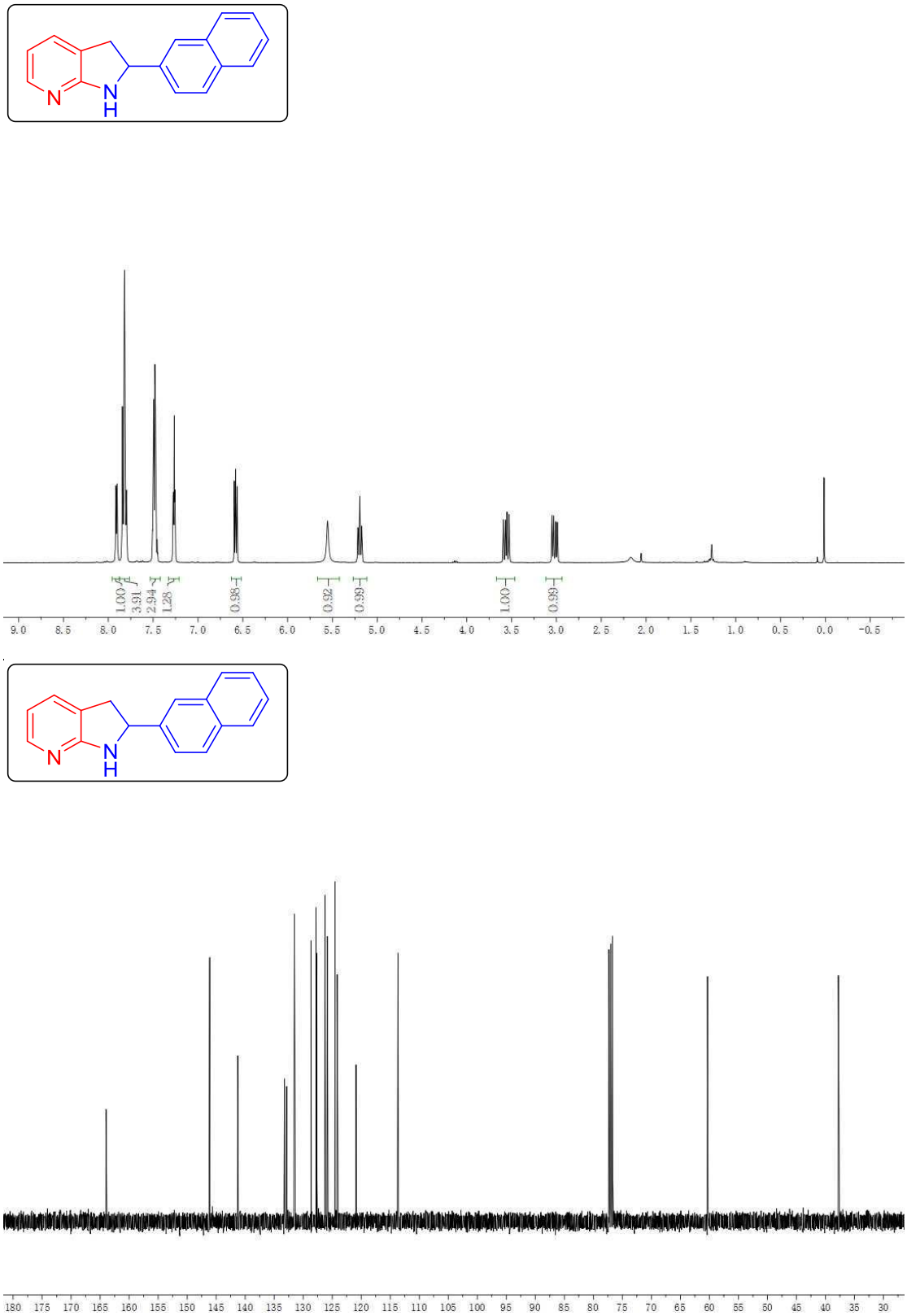


Figure S22. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3av** in $CDCl_3$

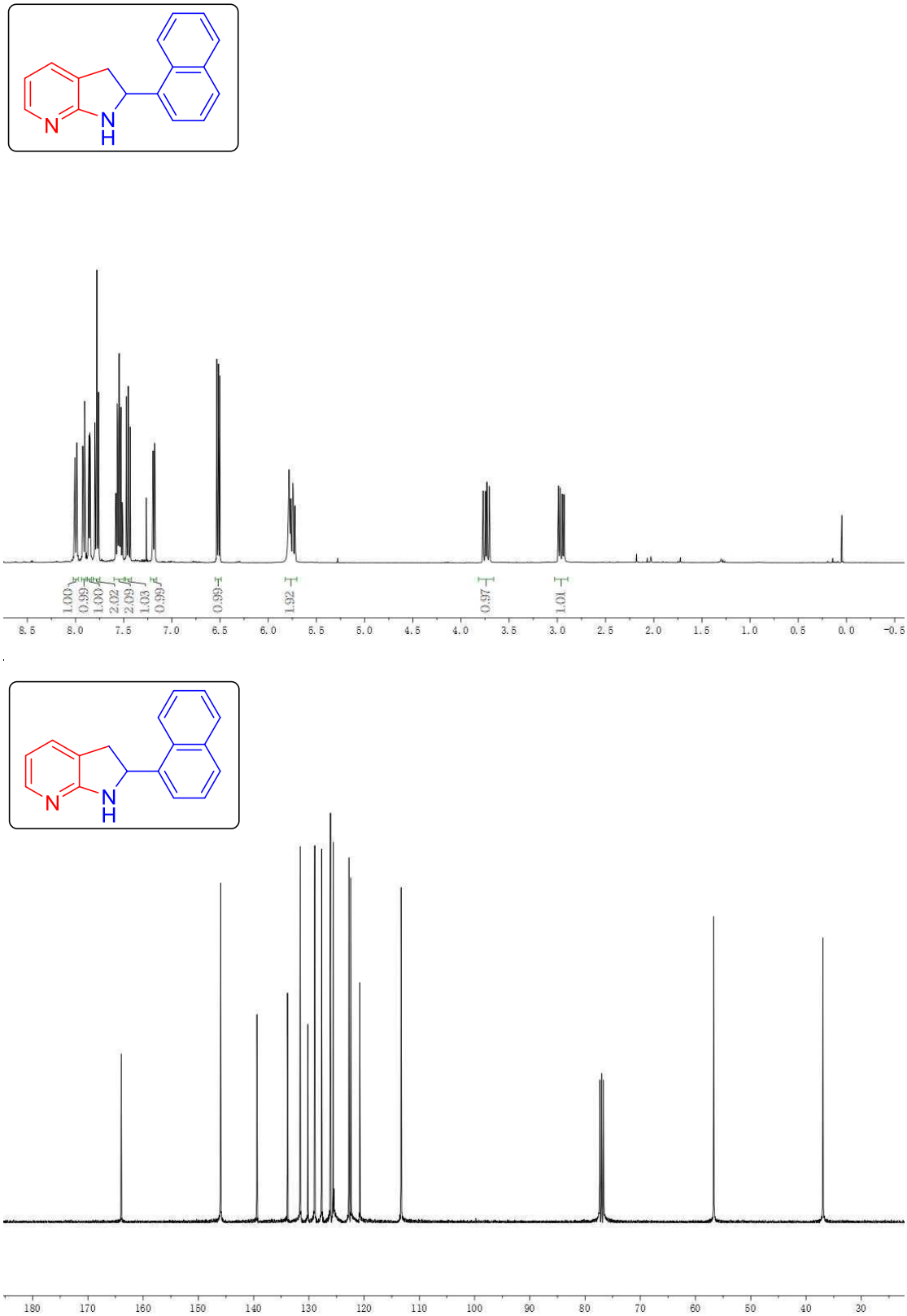


Figure S23. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3aw** in $CDCl_3$

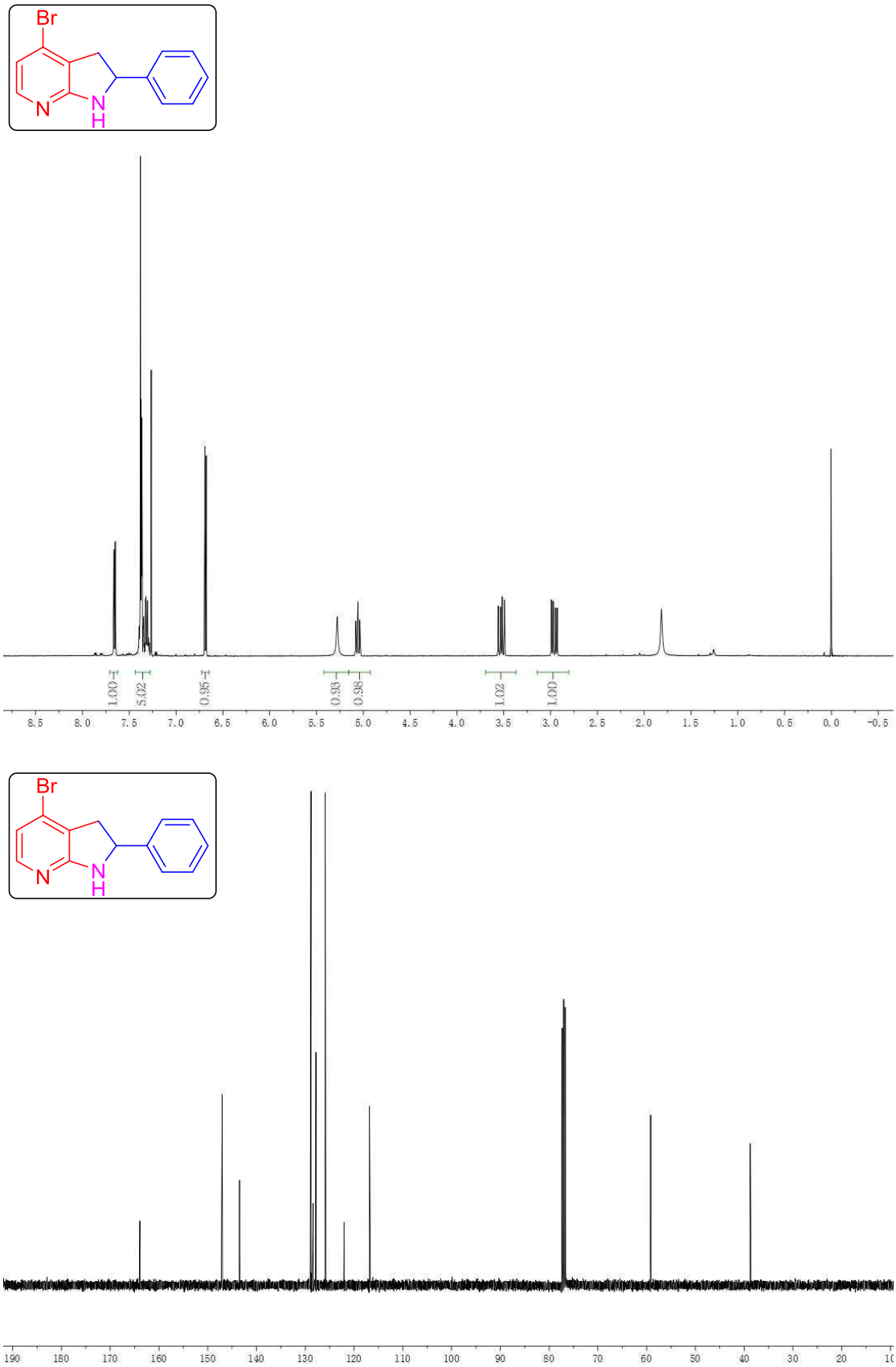


Figure S24. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ba** in $CDCl_3$

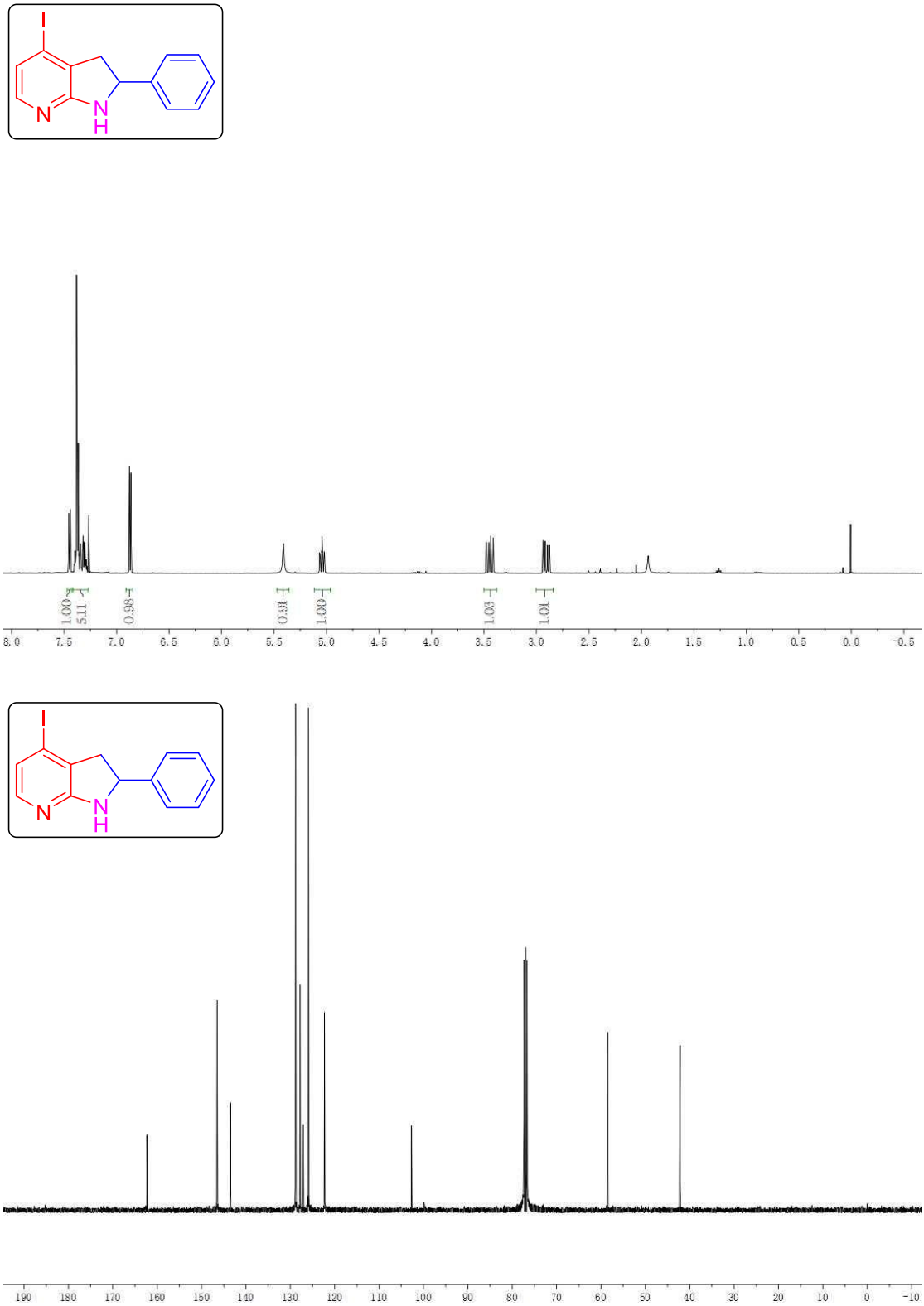


Figure S25. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ca** in $CDCl_3$

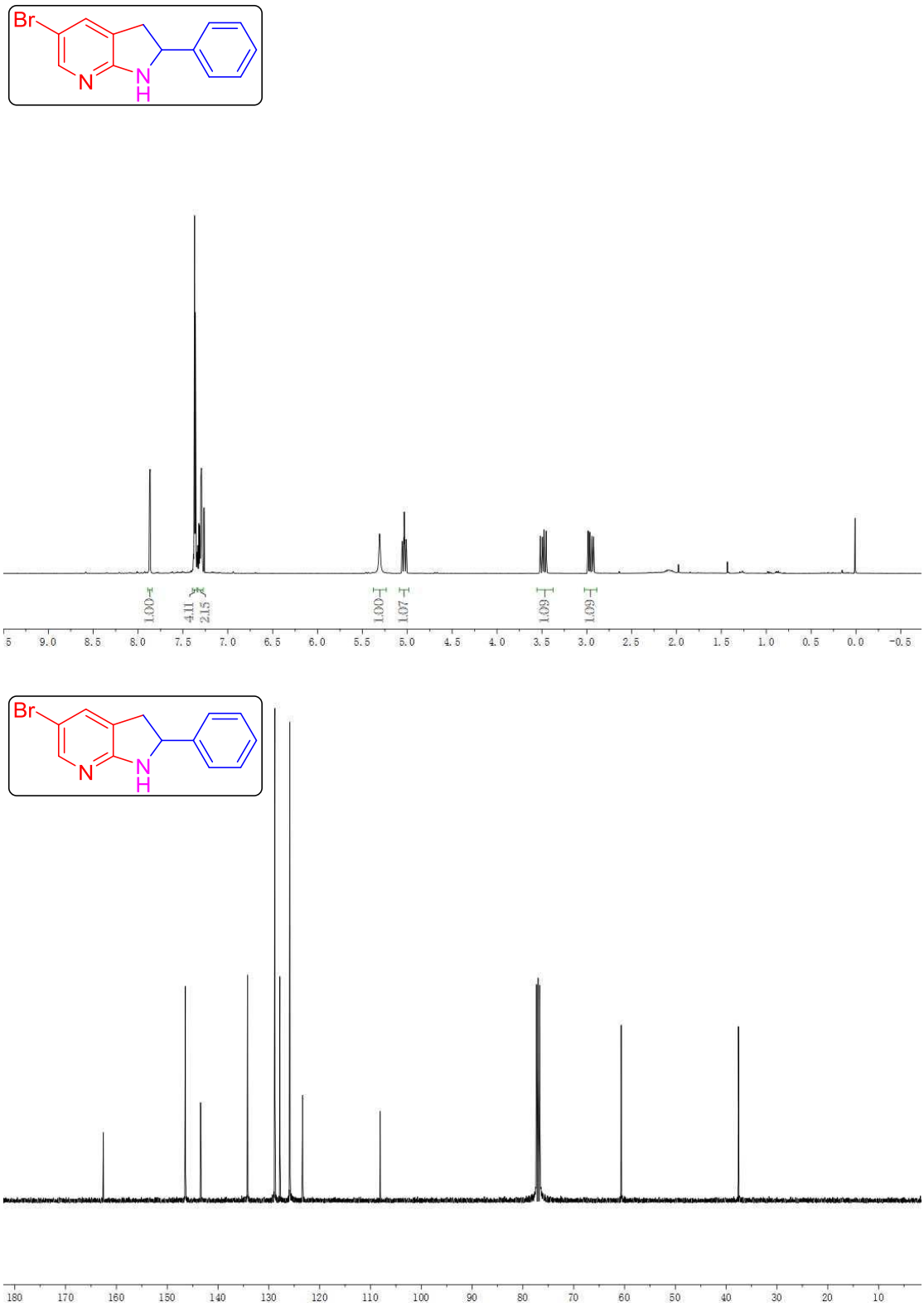


Figure S26. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3da** in $CDCl_3$

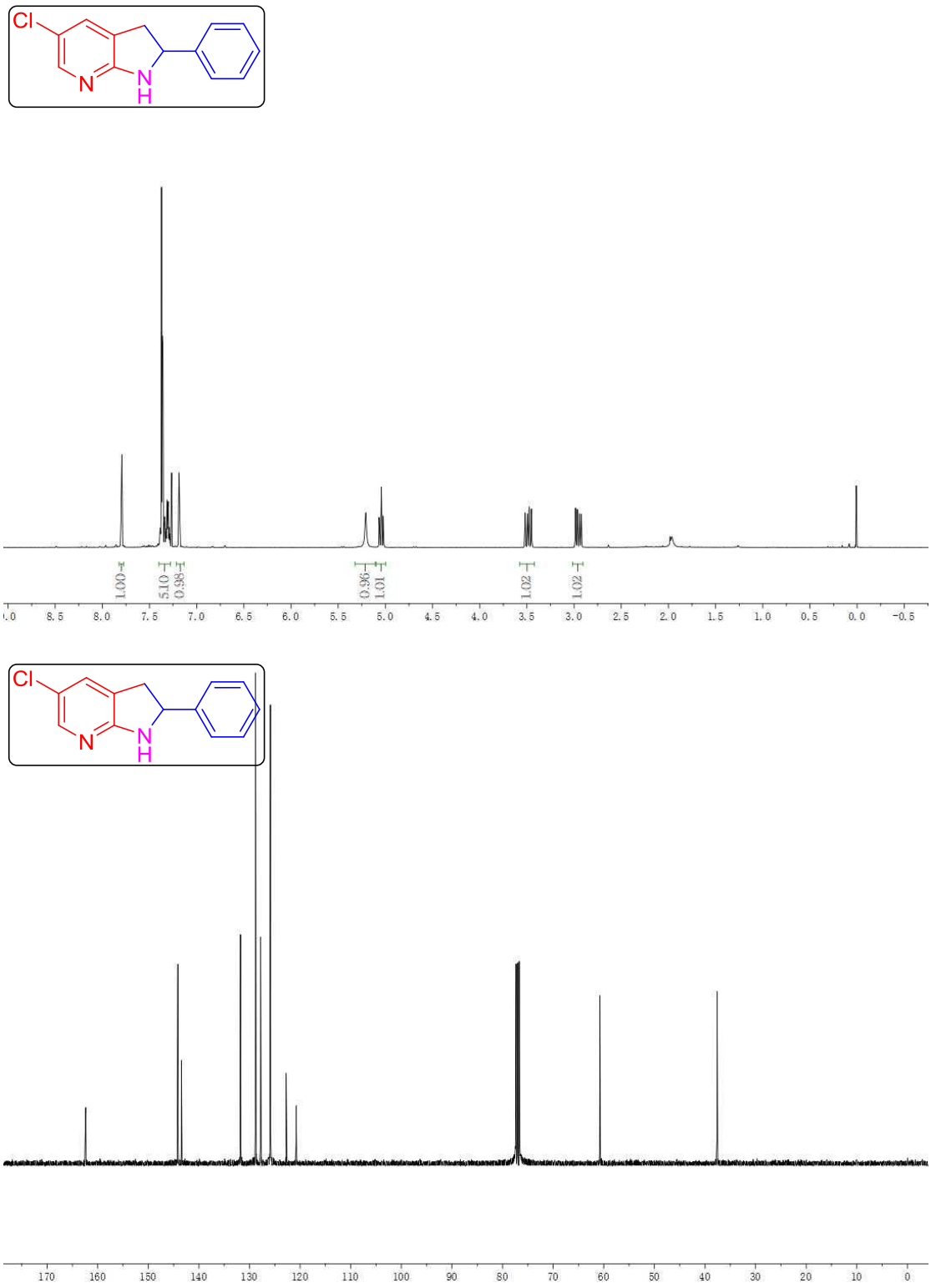


Figure S27. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ea** in $CDCl_3$

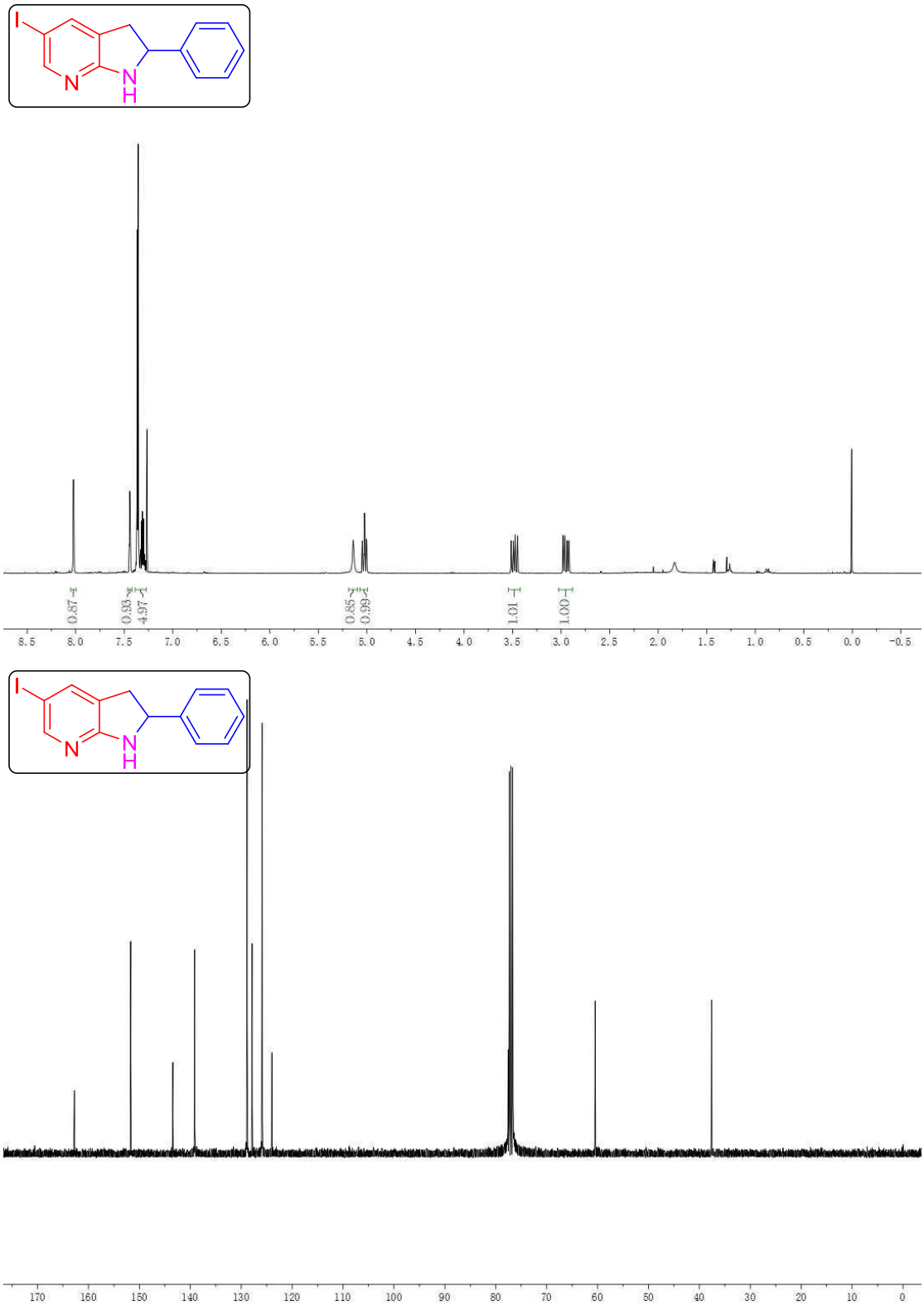


Figure S28. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3fa** in $CDCl_3$

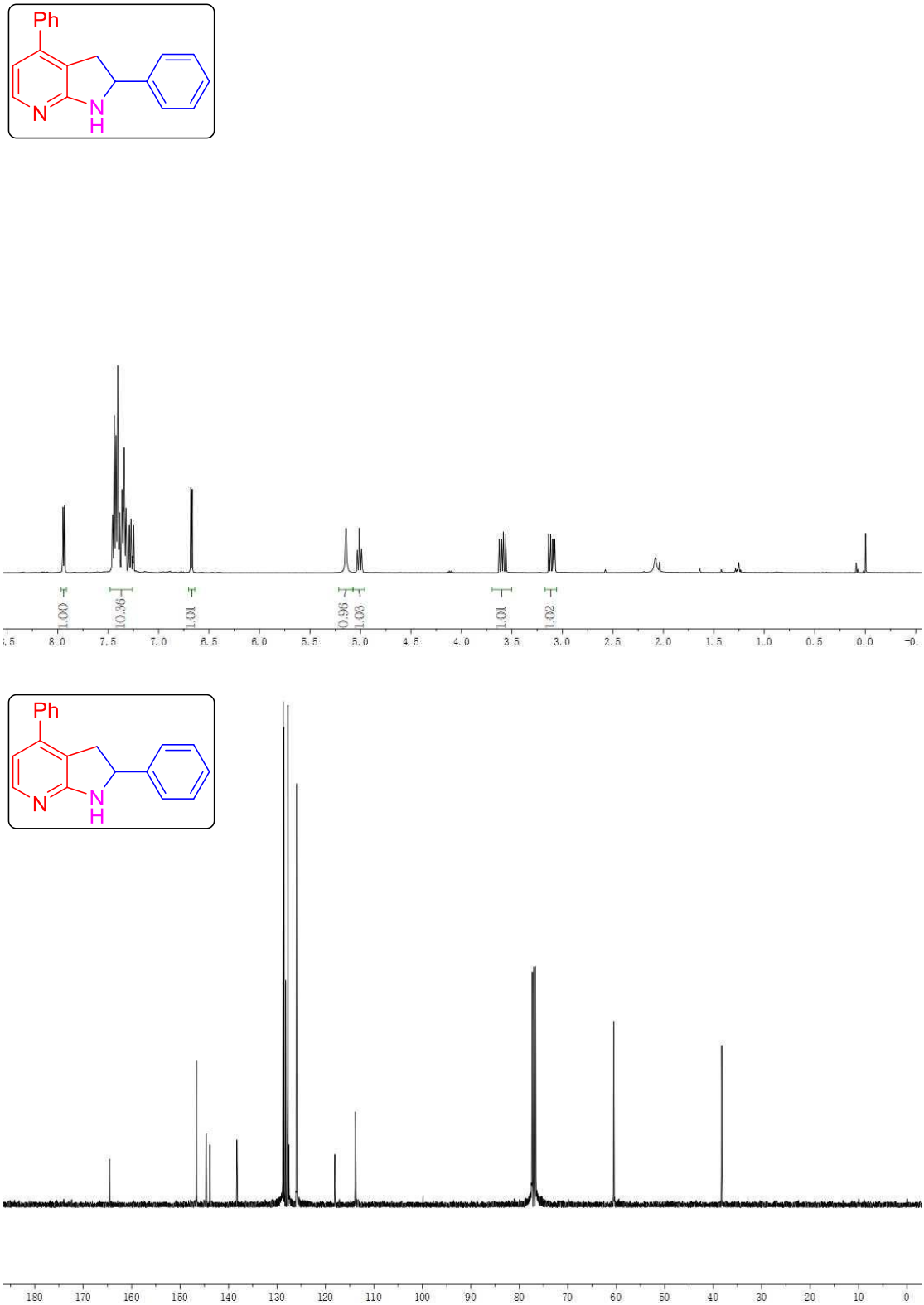


Figure S29. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ga** in $CDCl_3$

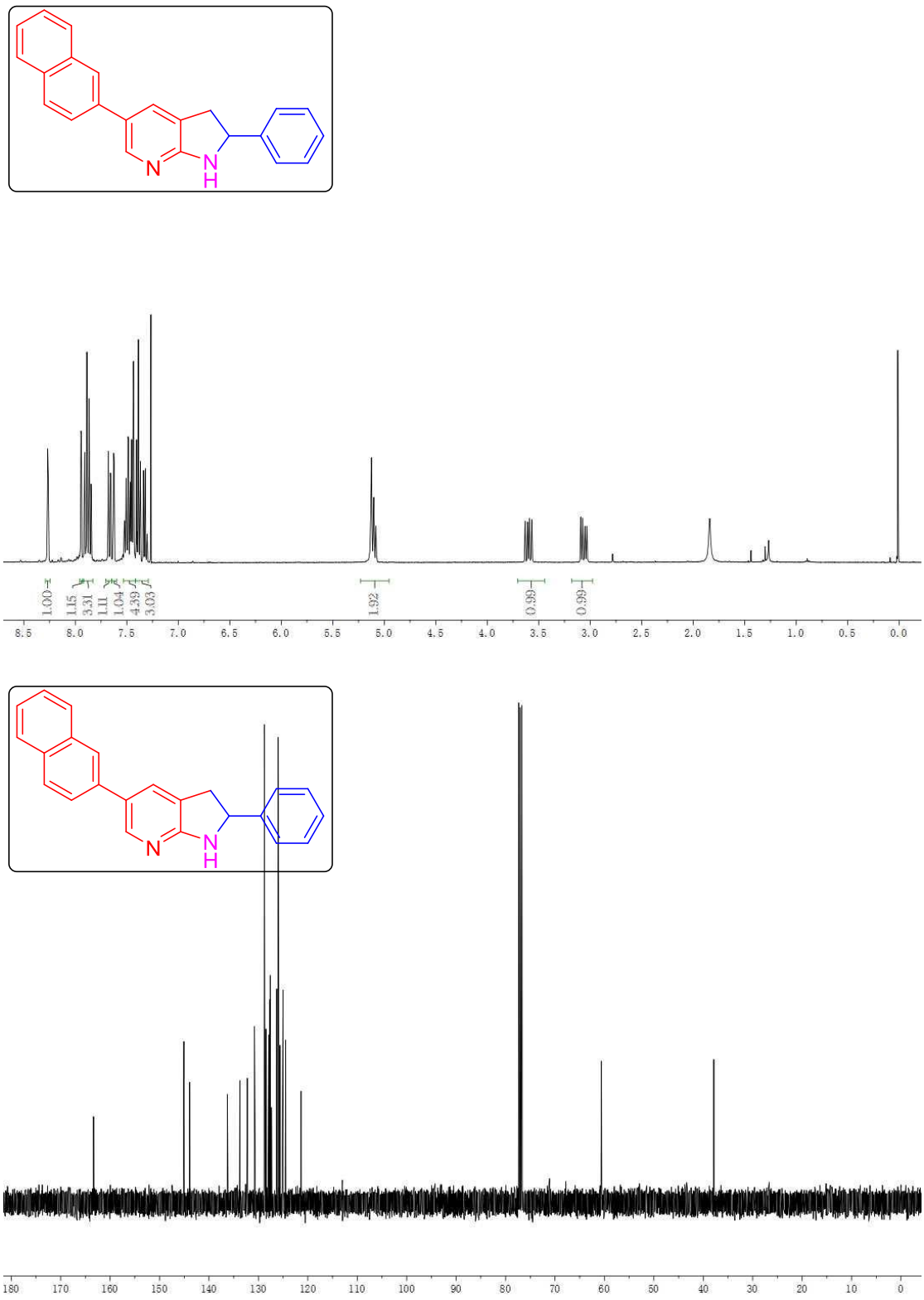


Figure S30. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ha** in $CDCl_3$

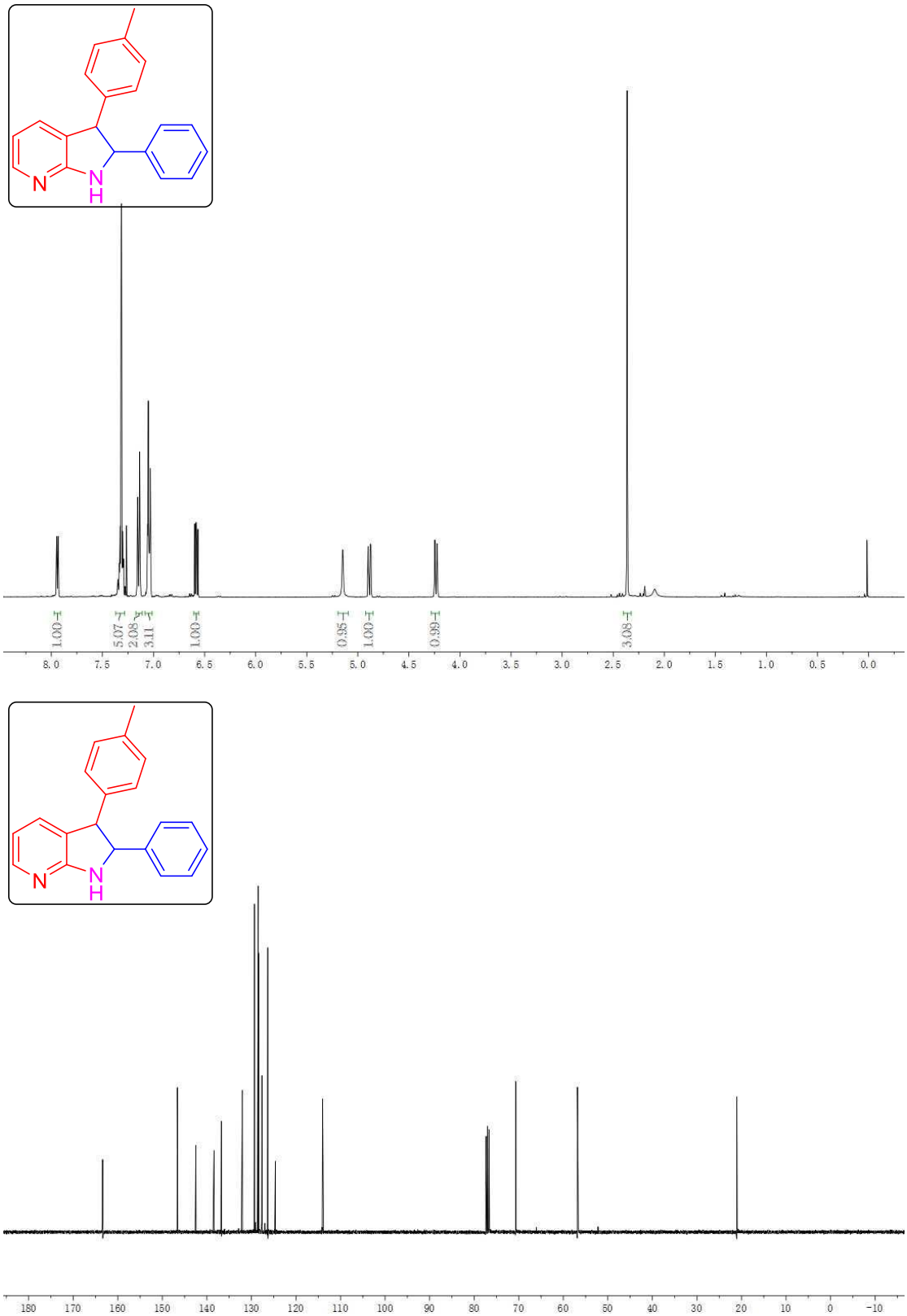


Figure S31. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ia** in $CDCl_3$

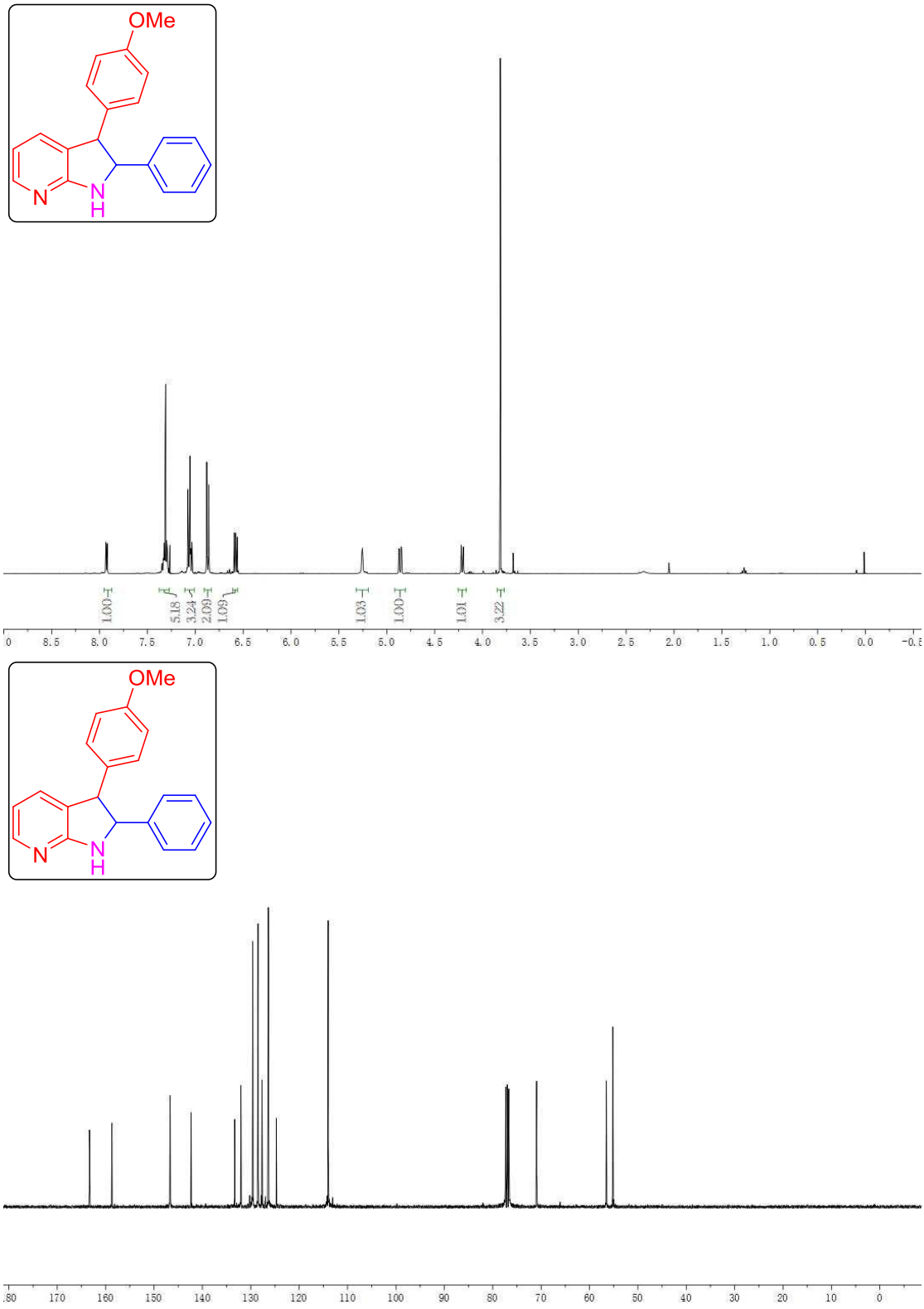


Figure S32. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ja** in $CDCl_3$

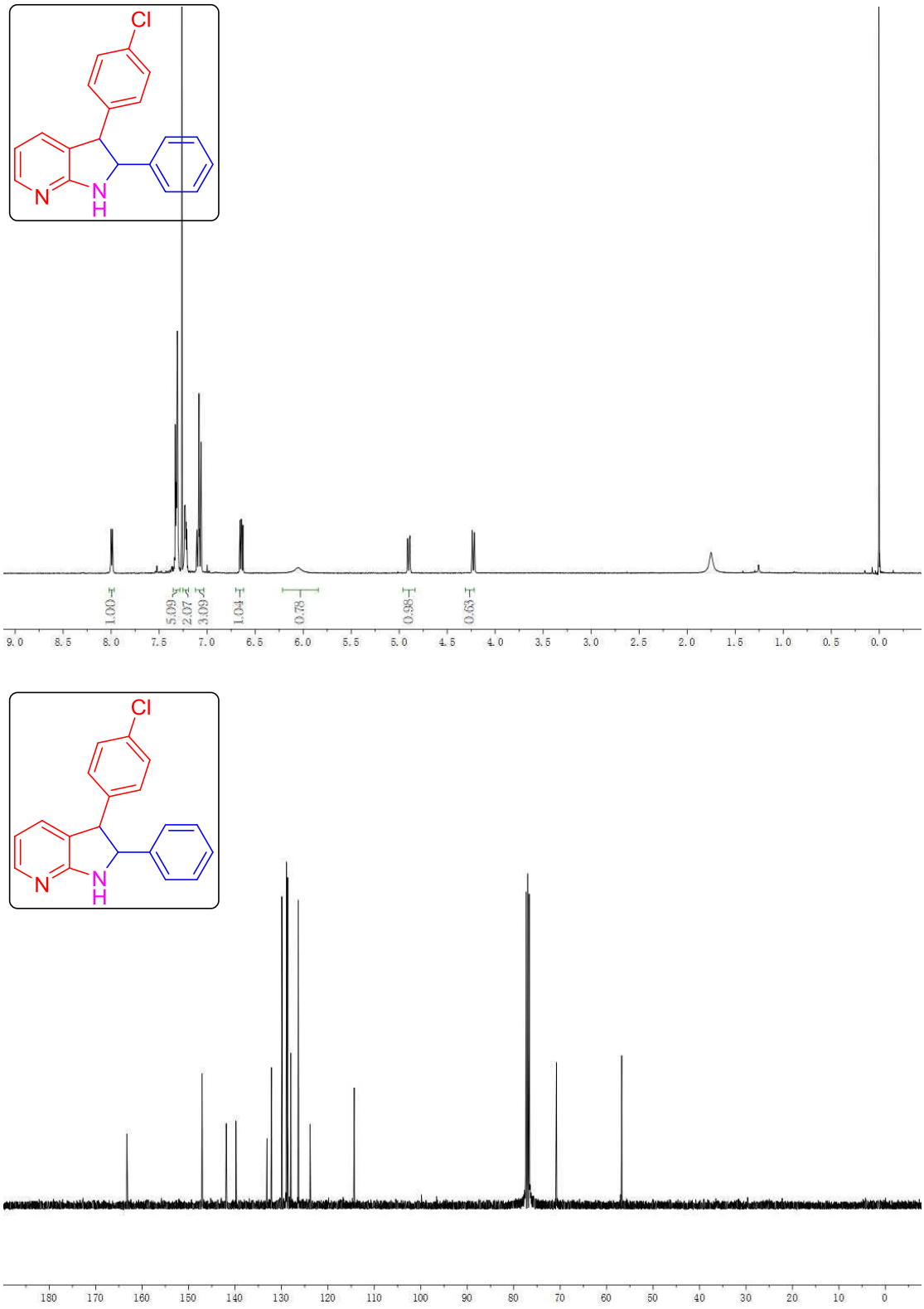
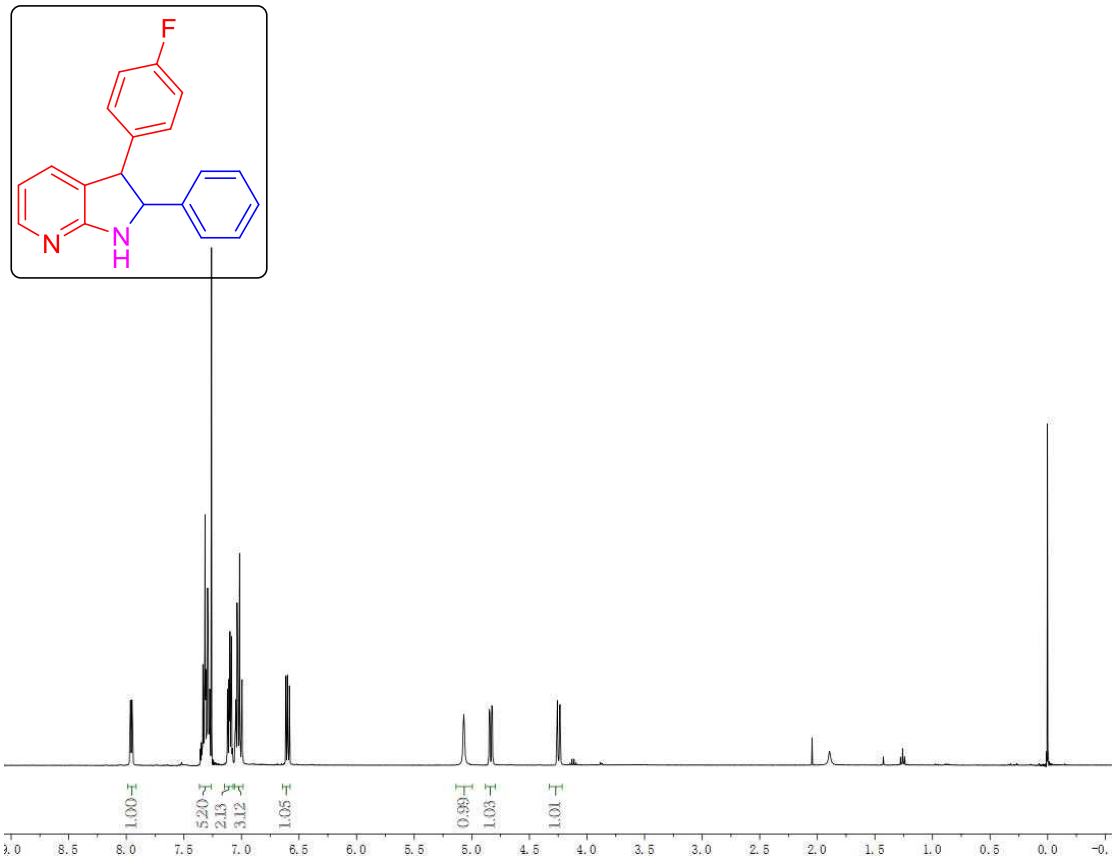
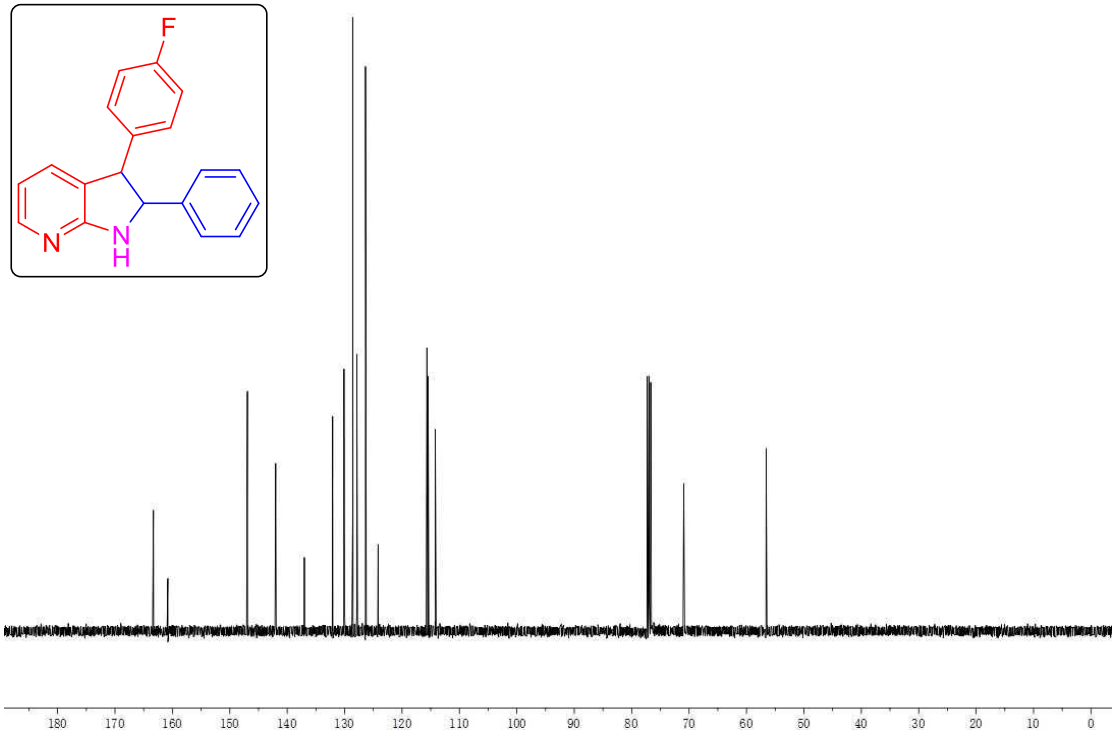


Figure S33. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **3ka** in $CDCl_3$


F
N
H
1.00
5.20
2.13
3.12
1.05
0.99
1.03
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


F
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

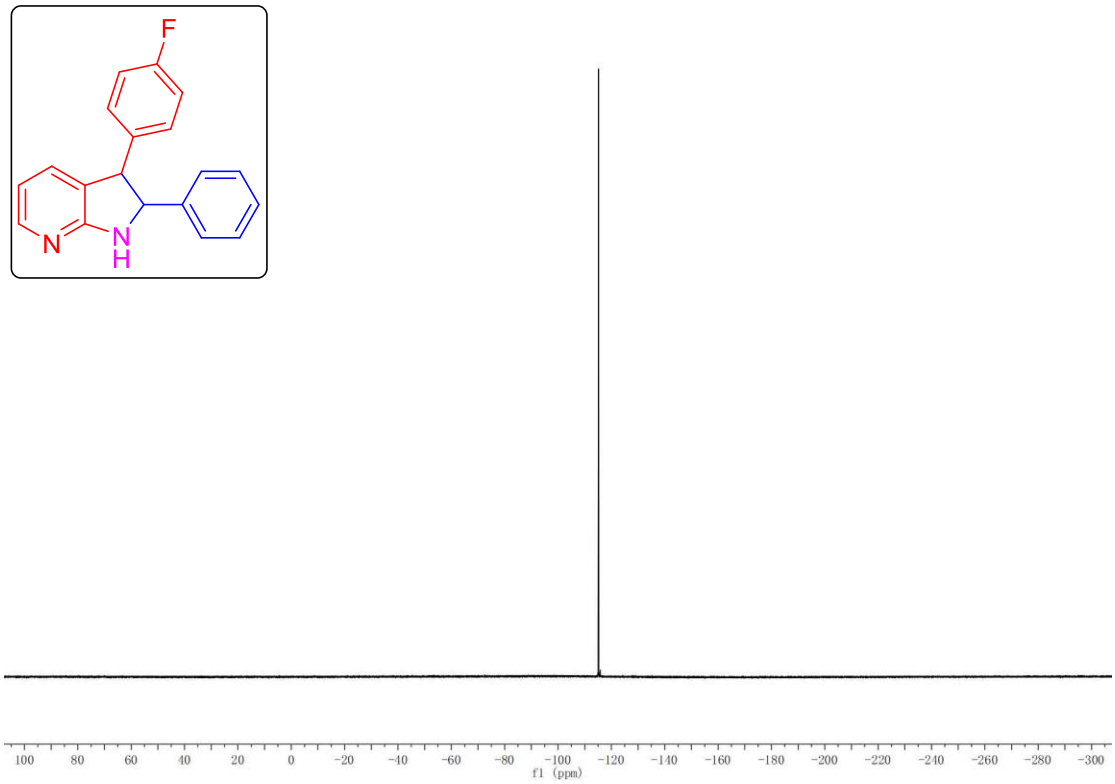


Figure S34. ^{1}H (400 MHz), ^{13}C {^{1}H} (101 MHz) and ^{19}F (377 MHz) NMR spectra of **3la** in $CDCl_3$

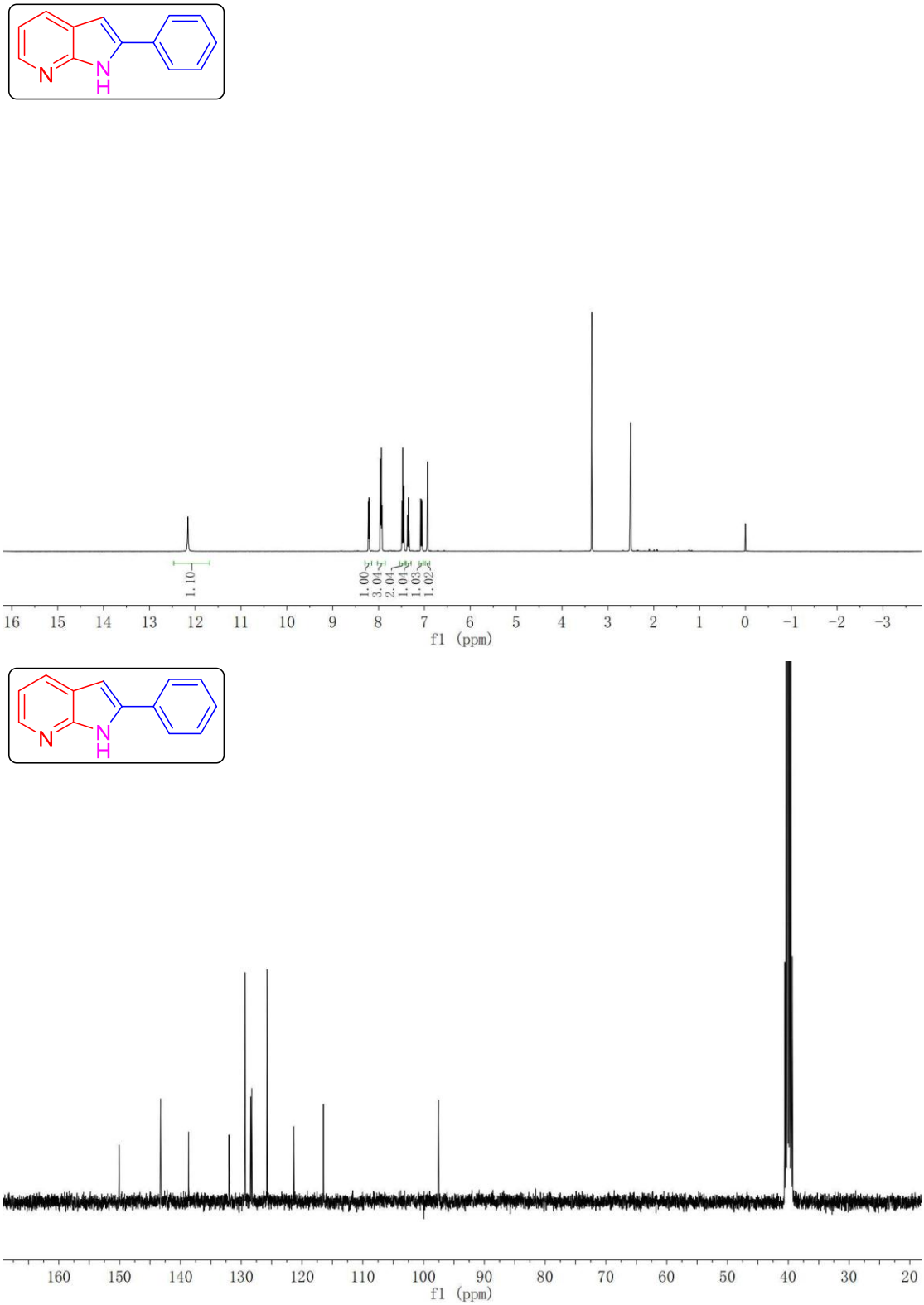


Figure S35. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4aa** in DMSO-d_6.

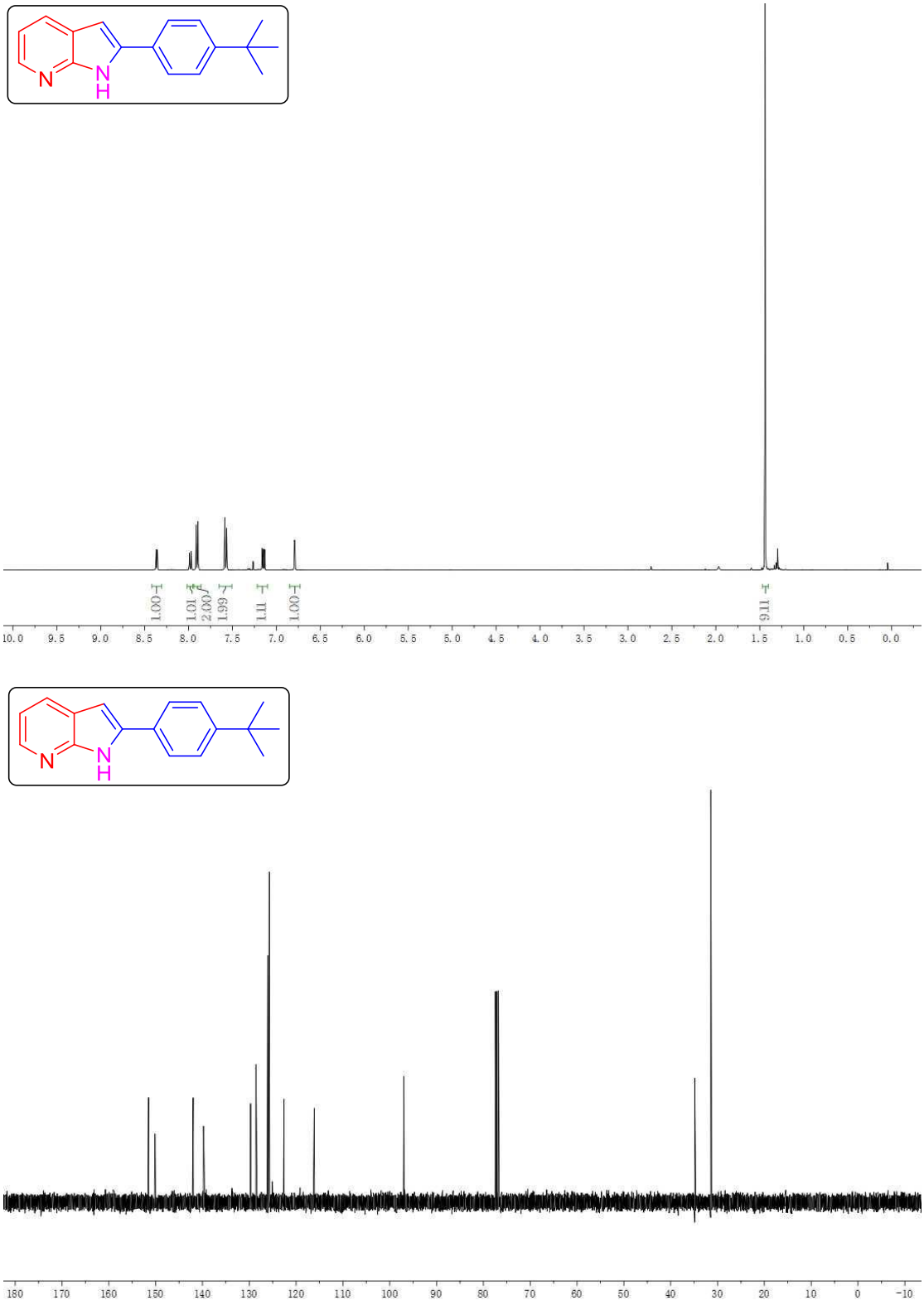


Figure S36. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ab** in $CDCl_3$

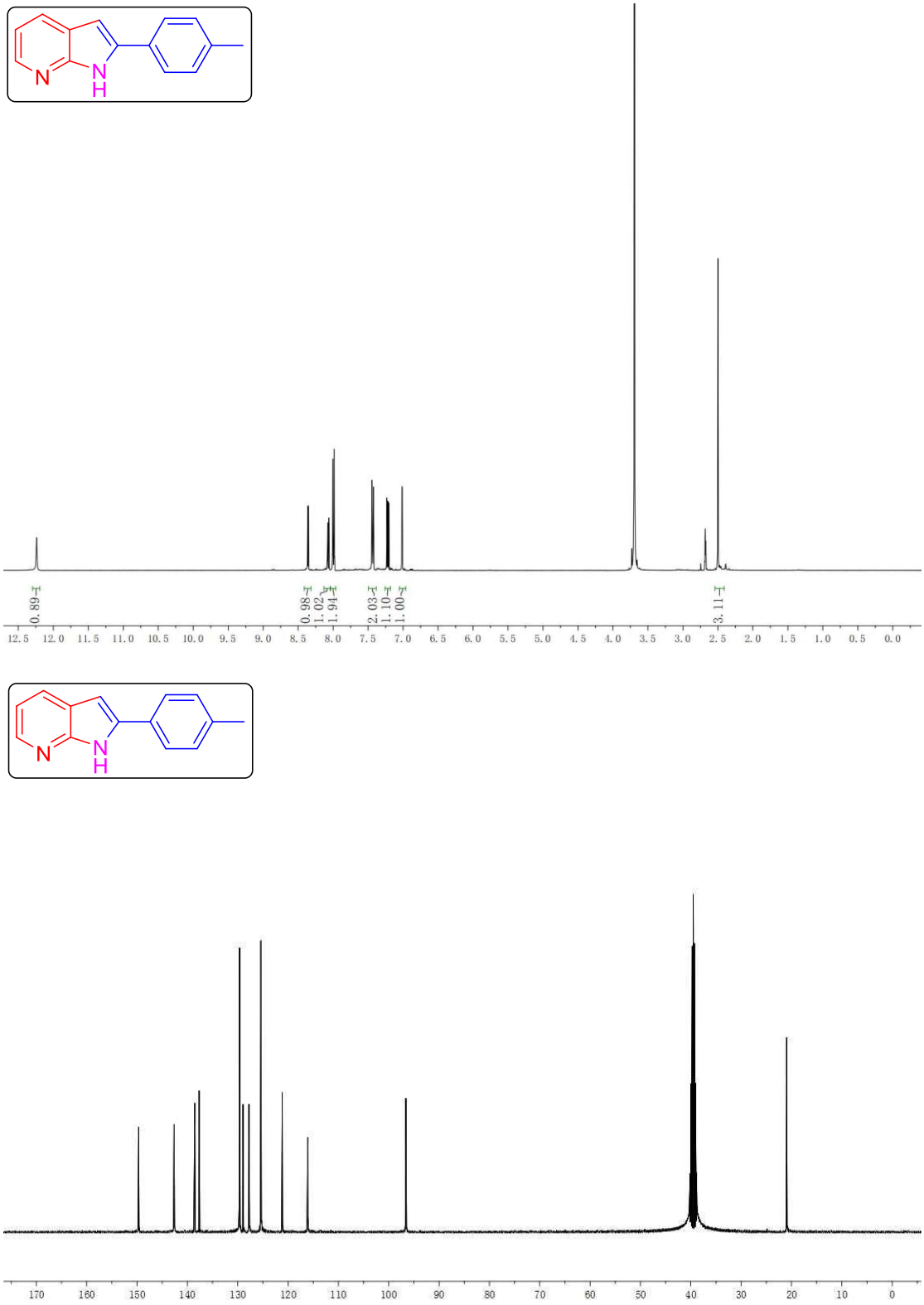


Figure S37. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ac** in DMSO-d_6

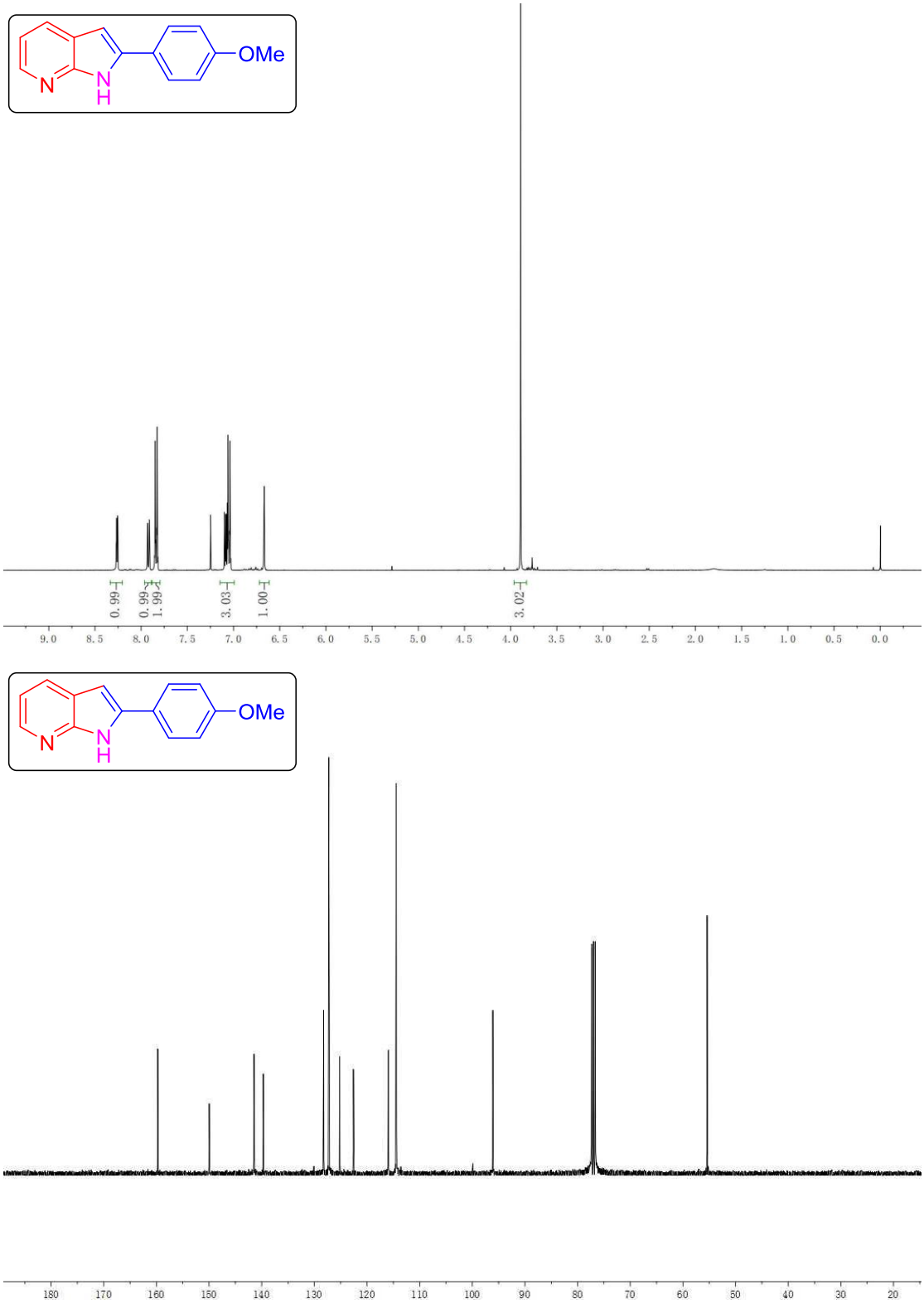


Figure S38. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ae** in $CDCl_3$

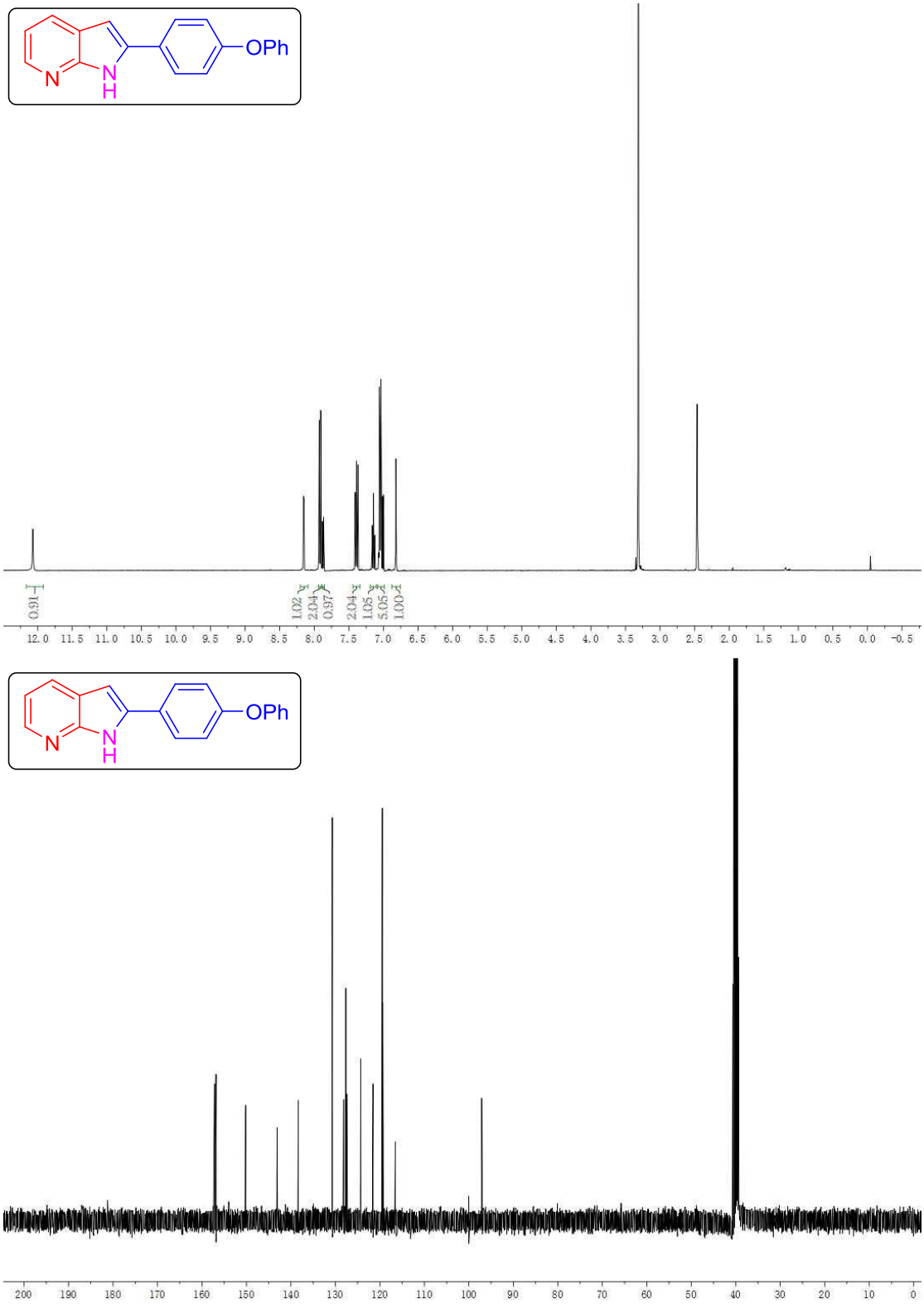


Figure S39. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ak** in DMSO-d_6

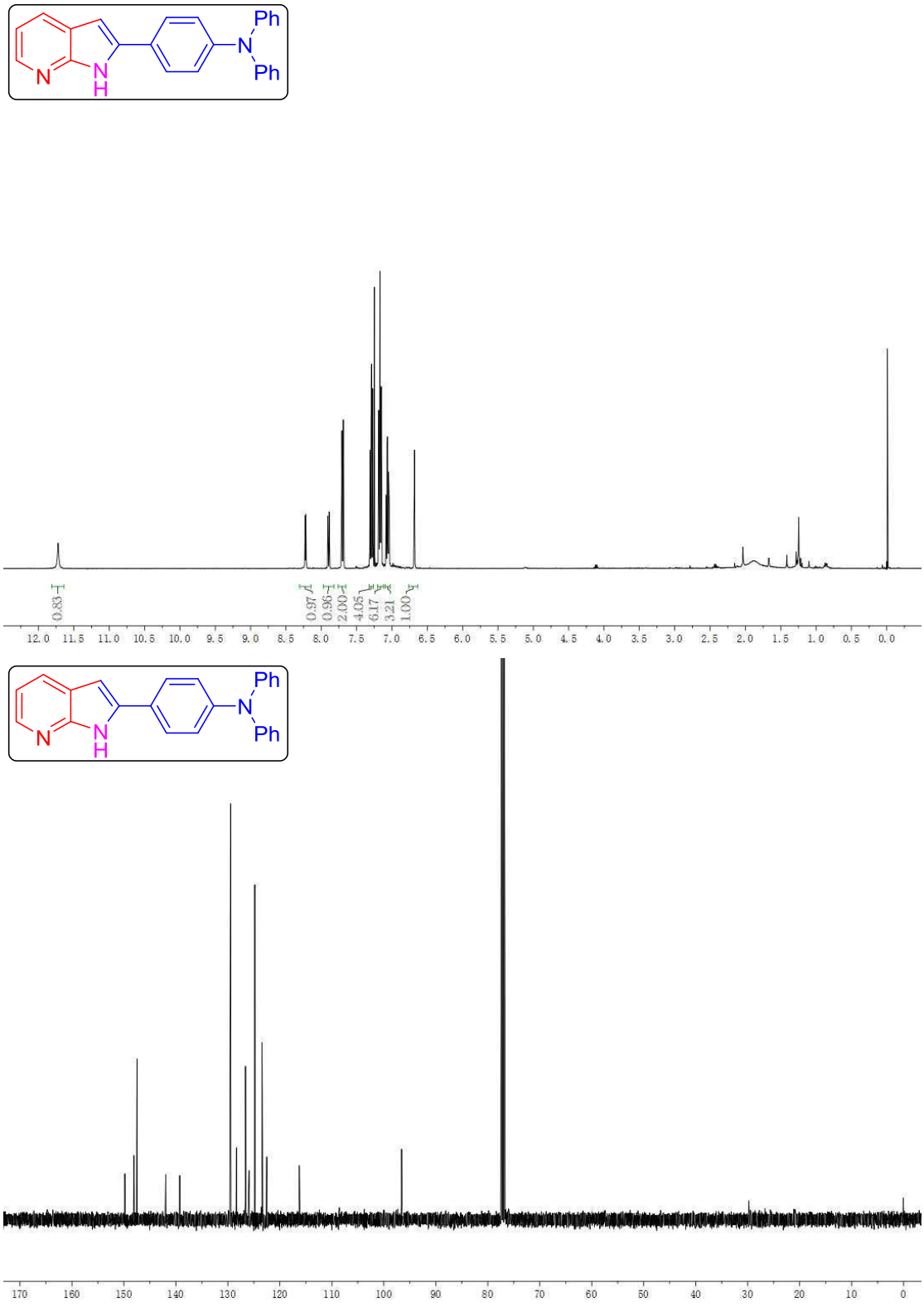


Figure S40. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4aj** in $CDCl_3$

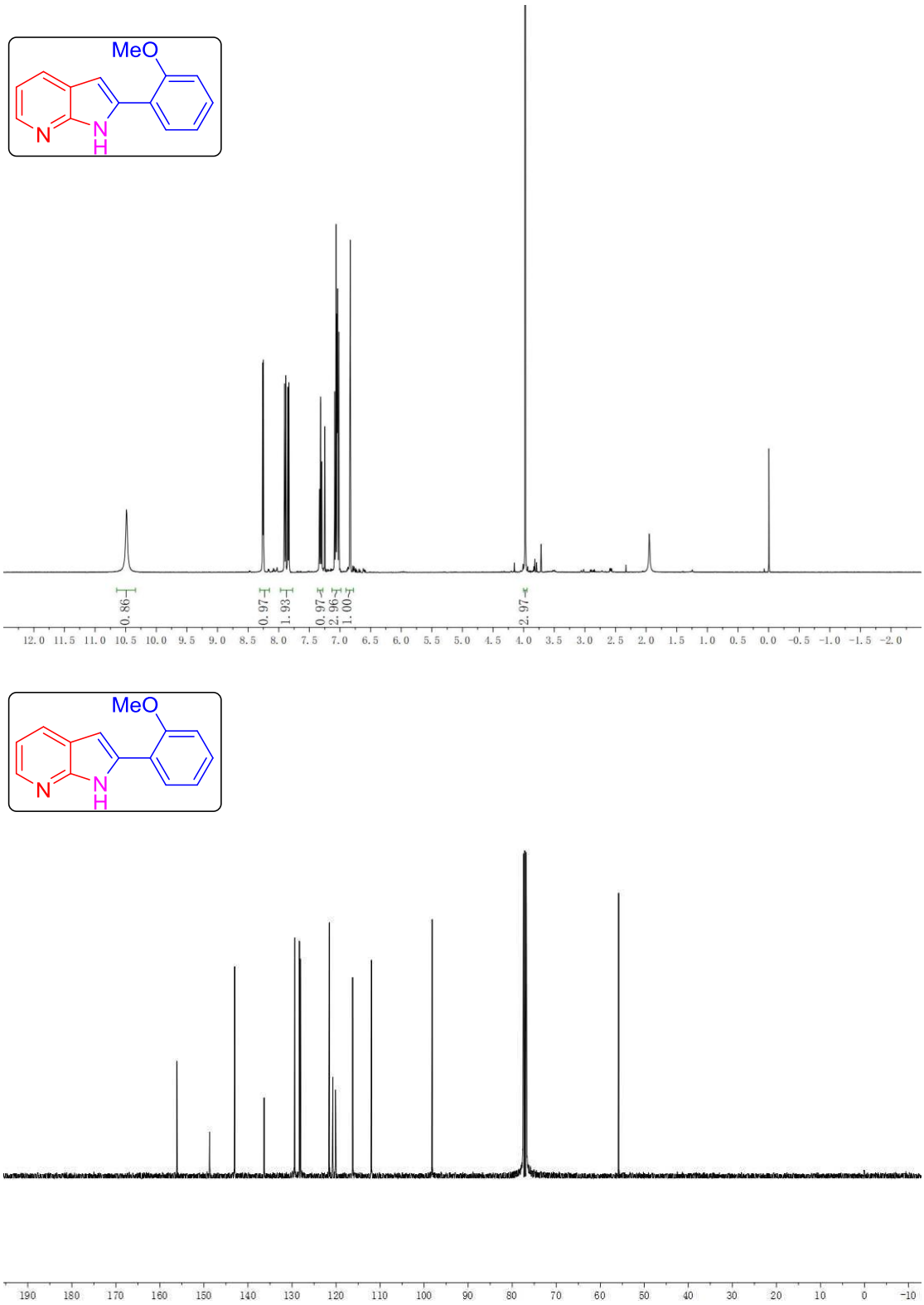


Figure S41. ^{1}H (400 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra of **4af** in $CDCl_3$

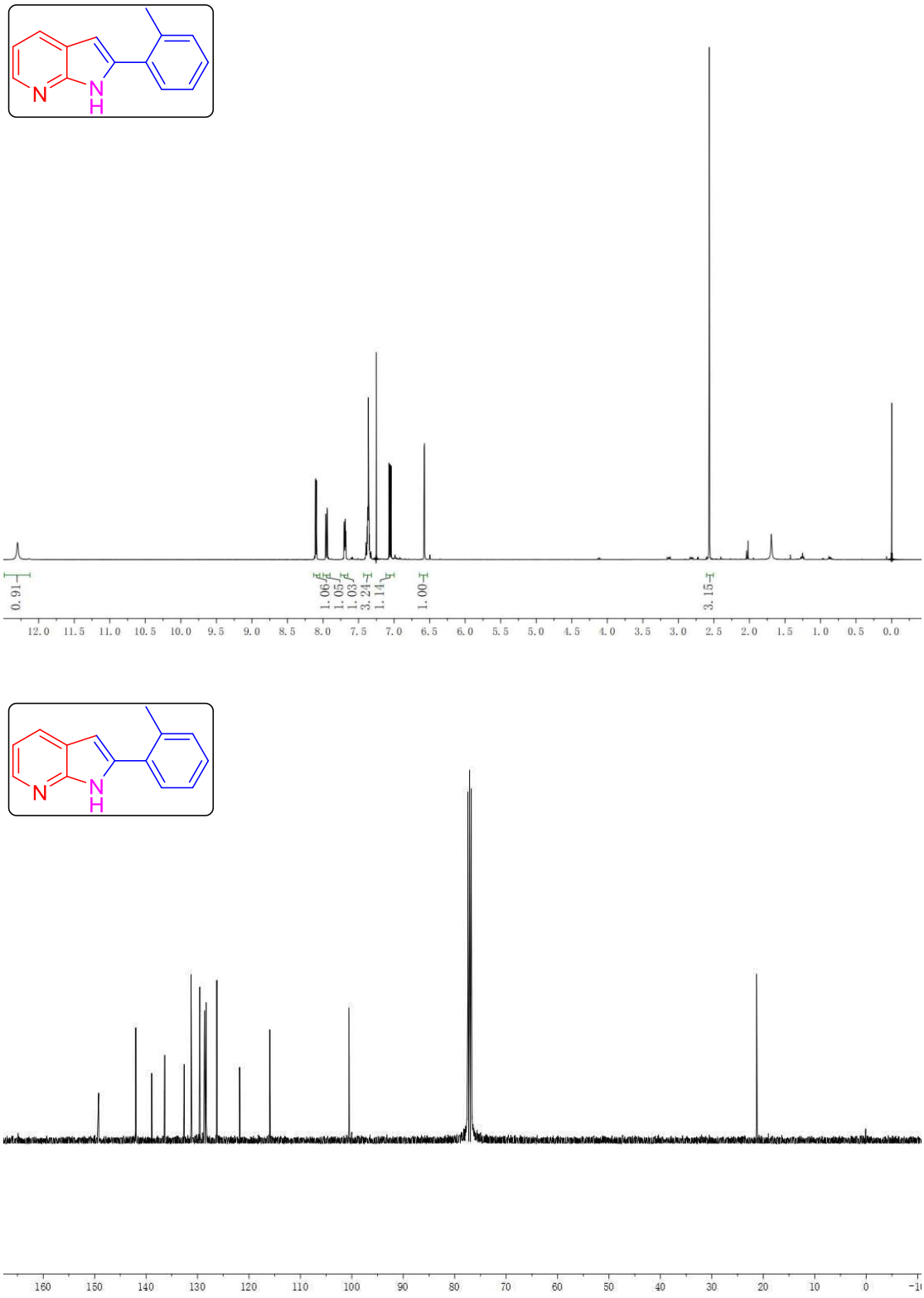


Figure S42. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ax** in $CDCl_3$

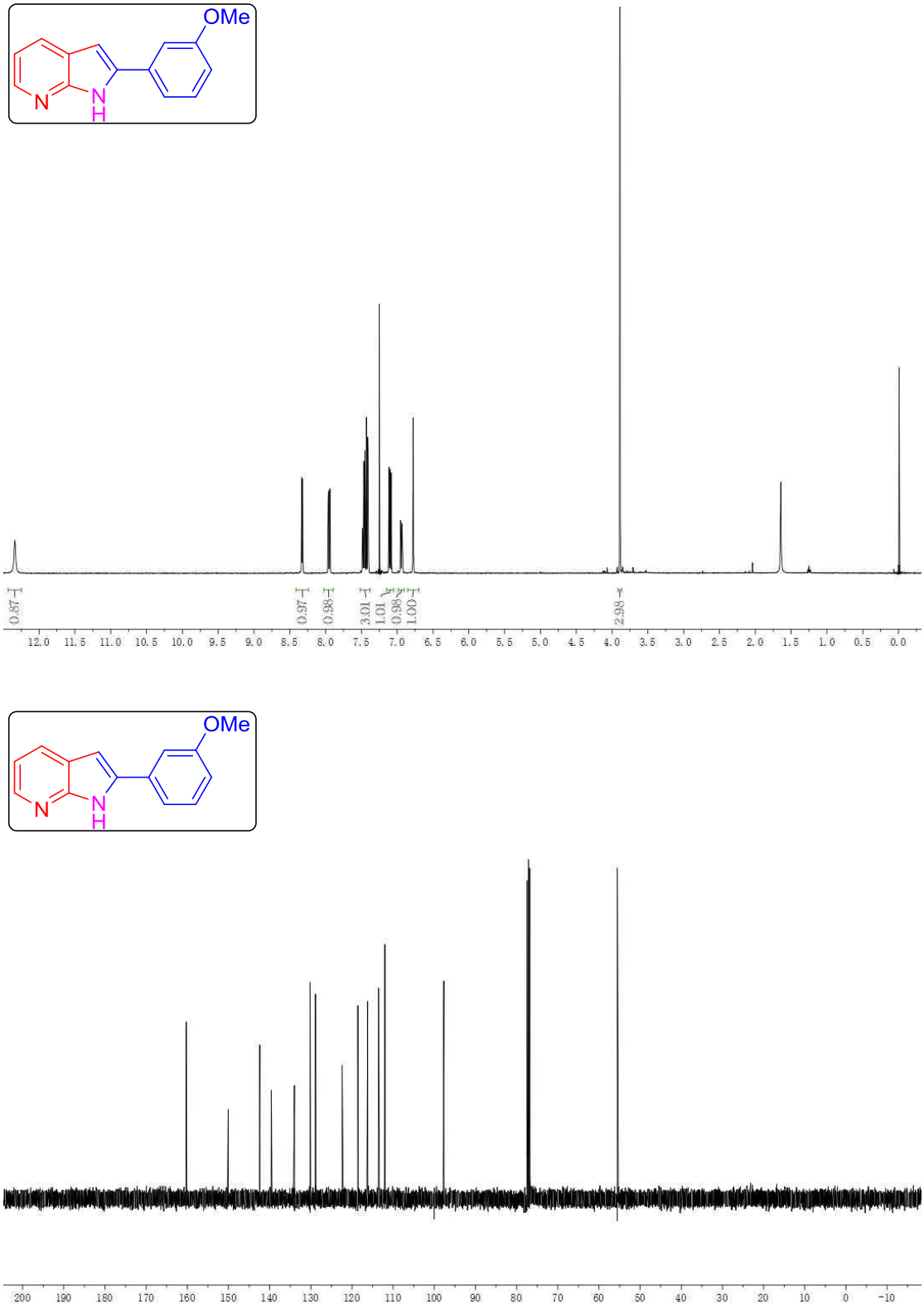


Figure S43. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ag** in $CDCl_3$

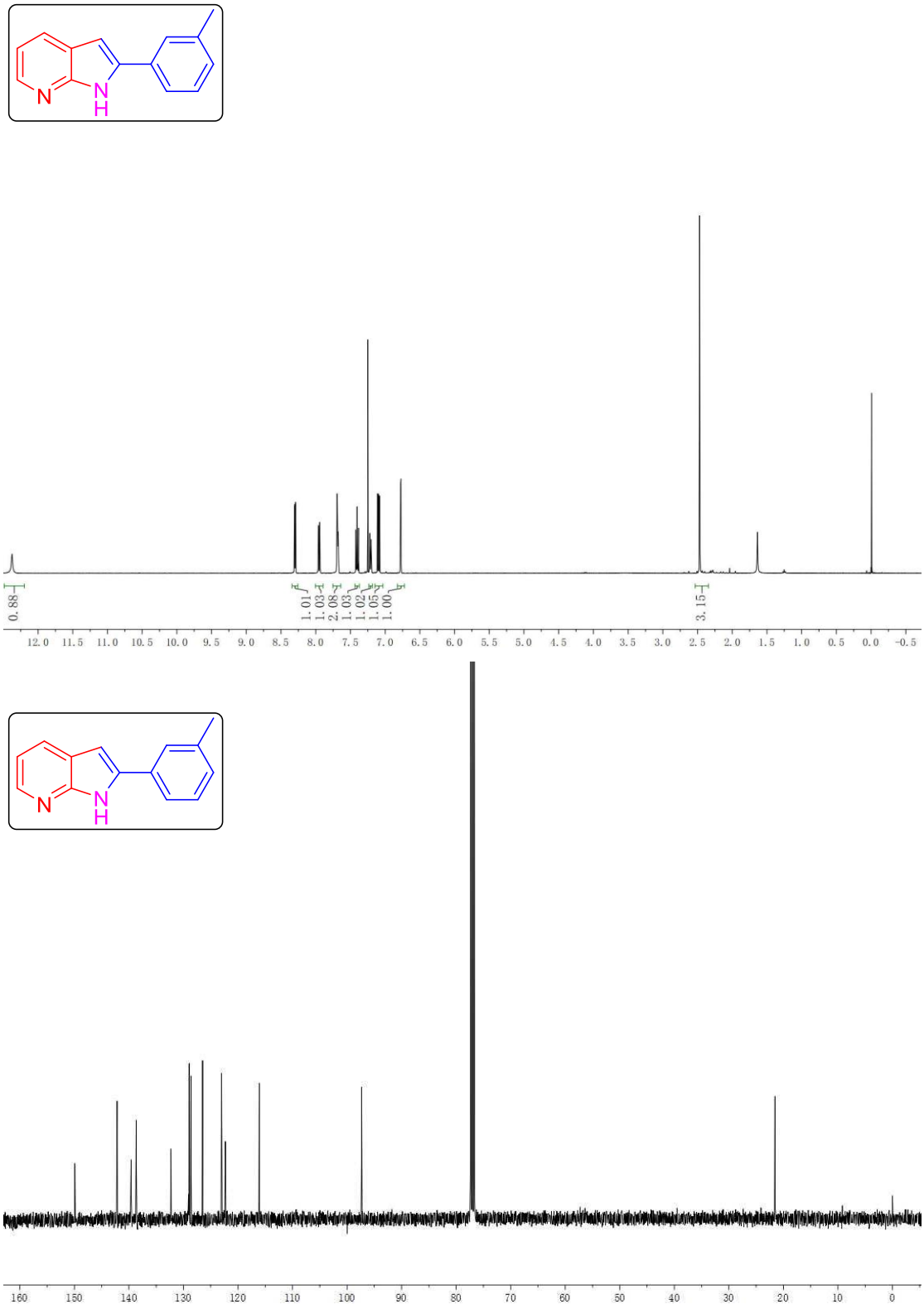


Figure S44. ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR spectra of **4ad** in $CDCl_3$

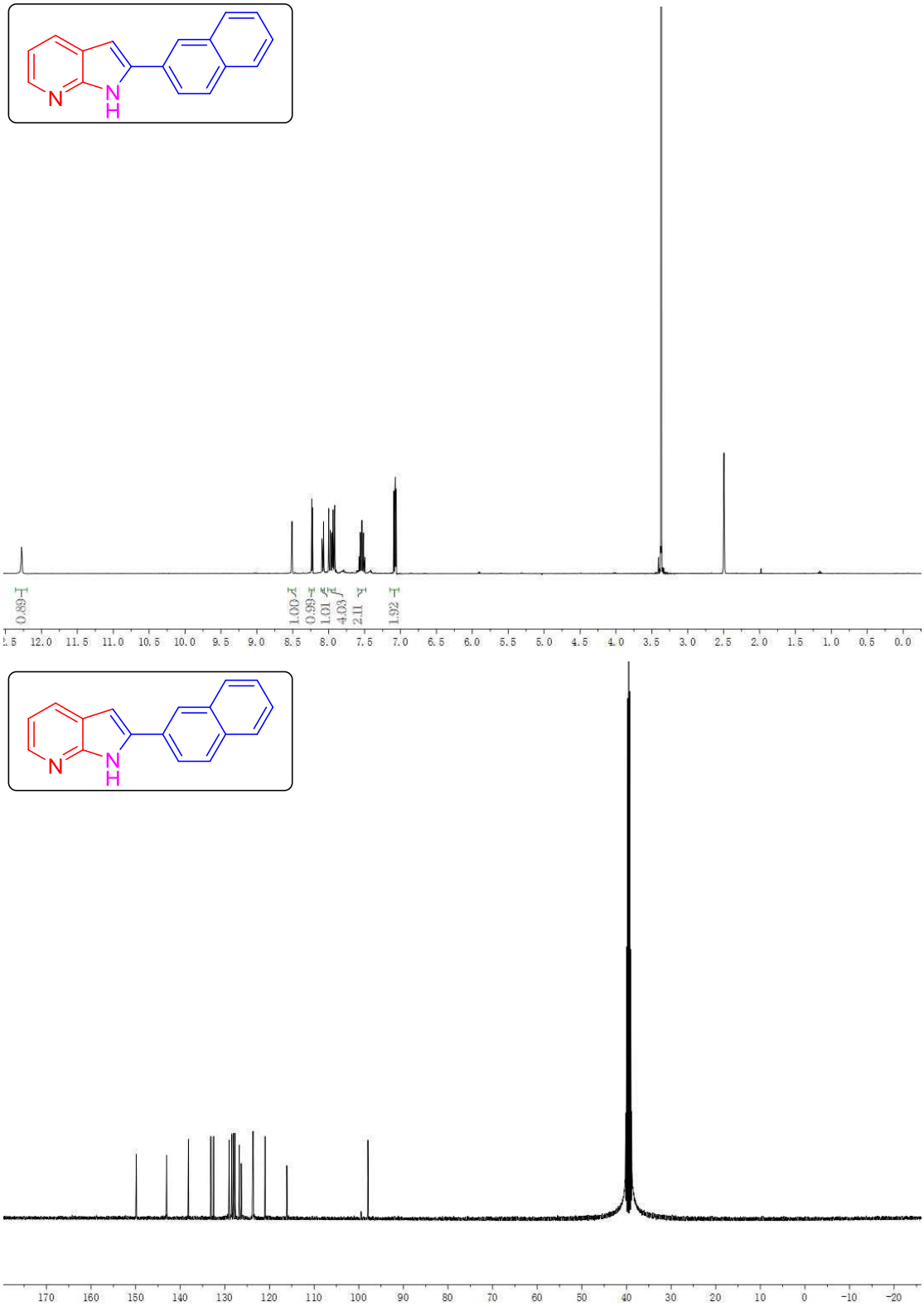


Figure S45. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4av** in DMSO-d_6

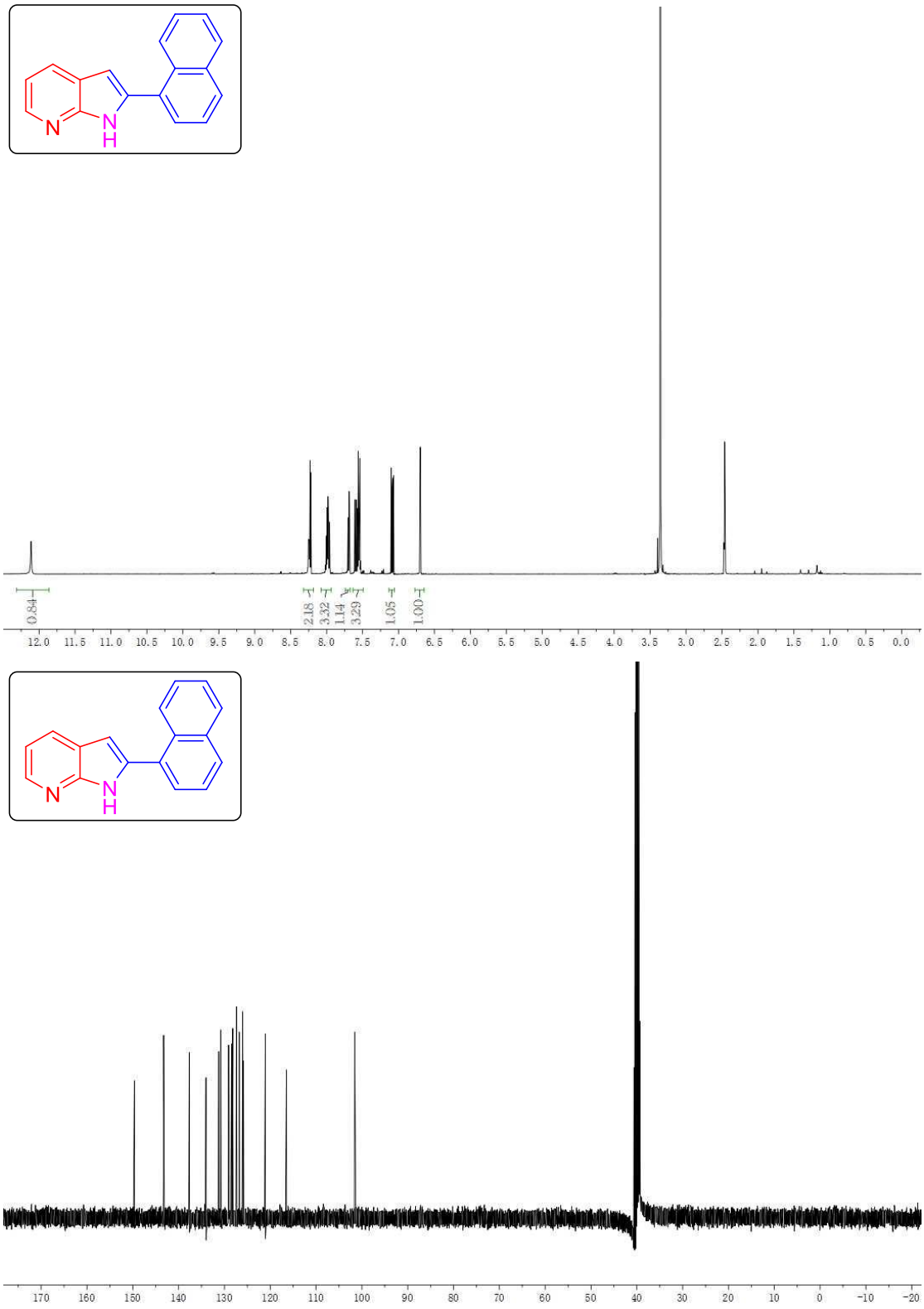


Figure S46. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4aw** in DMSO-d_6

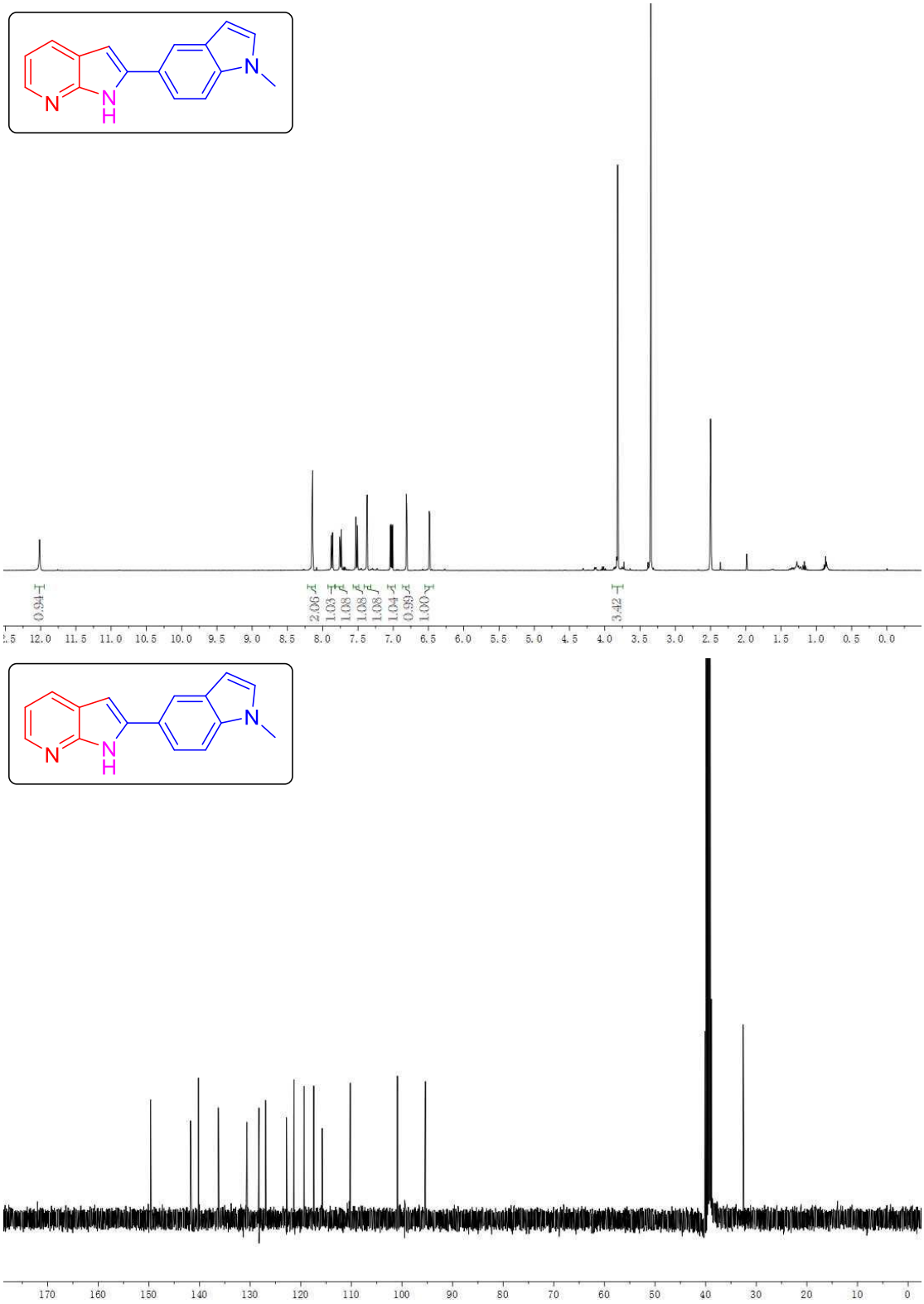


Figure S47. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ar** in DMSO-d_6

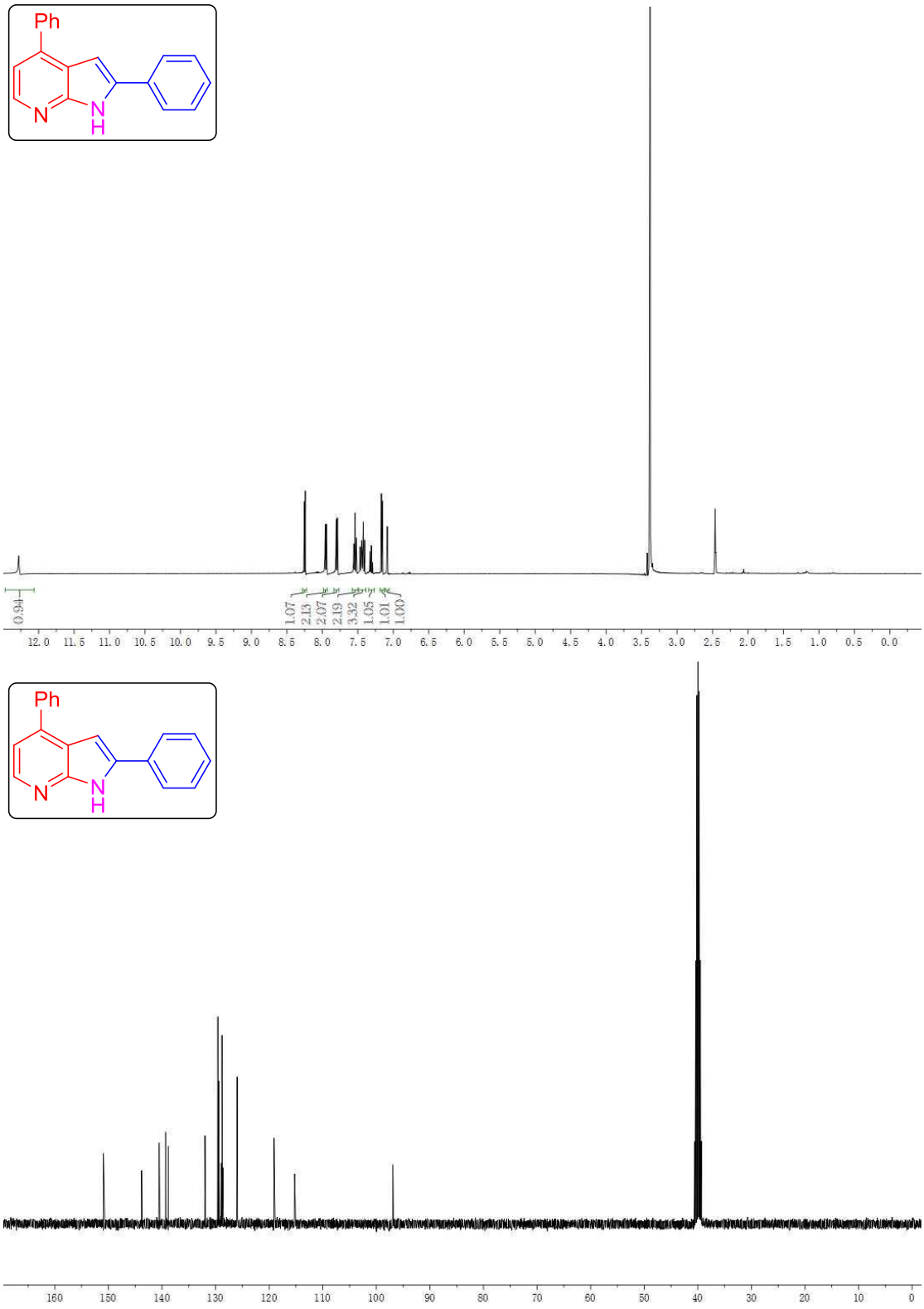


Figure S48. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ga** in DMSO-d_6

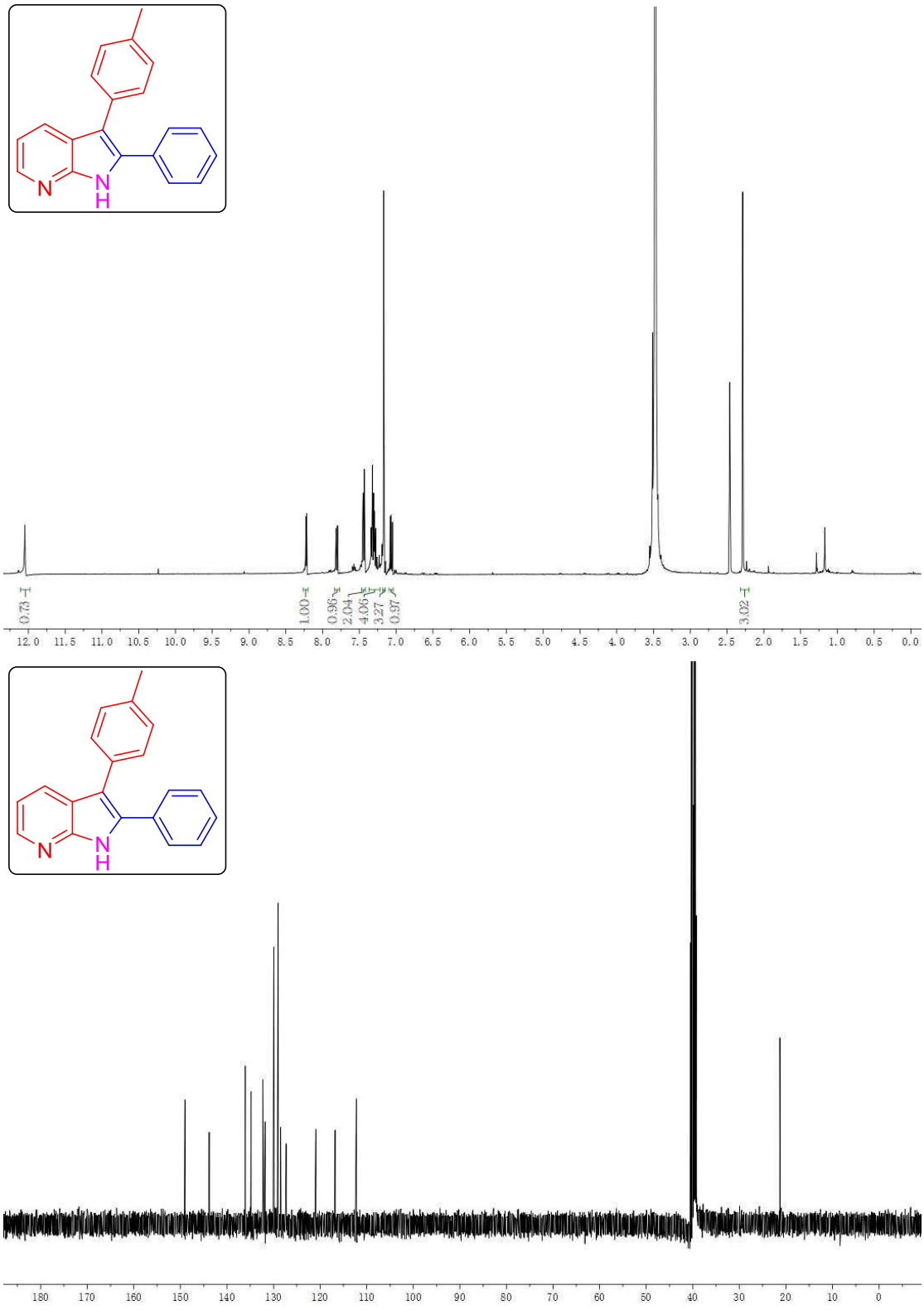


Figure S49. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ia** in DMSO-d_6

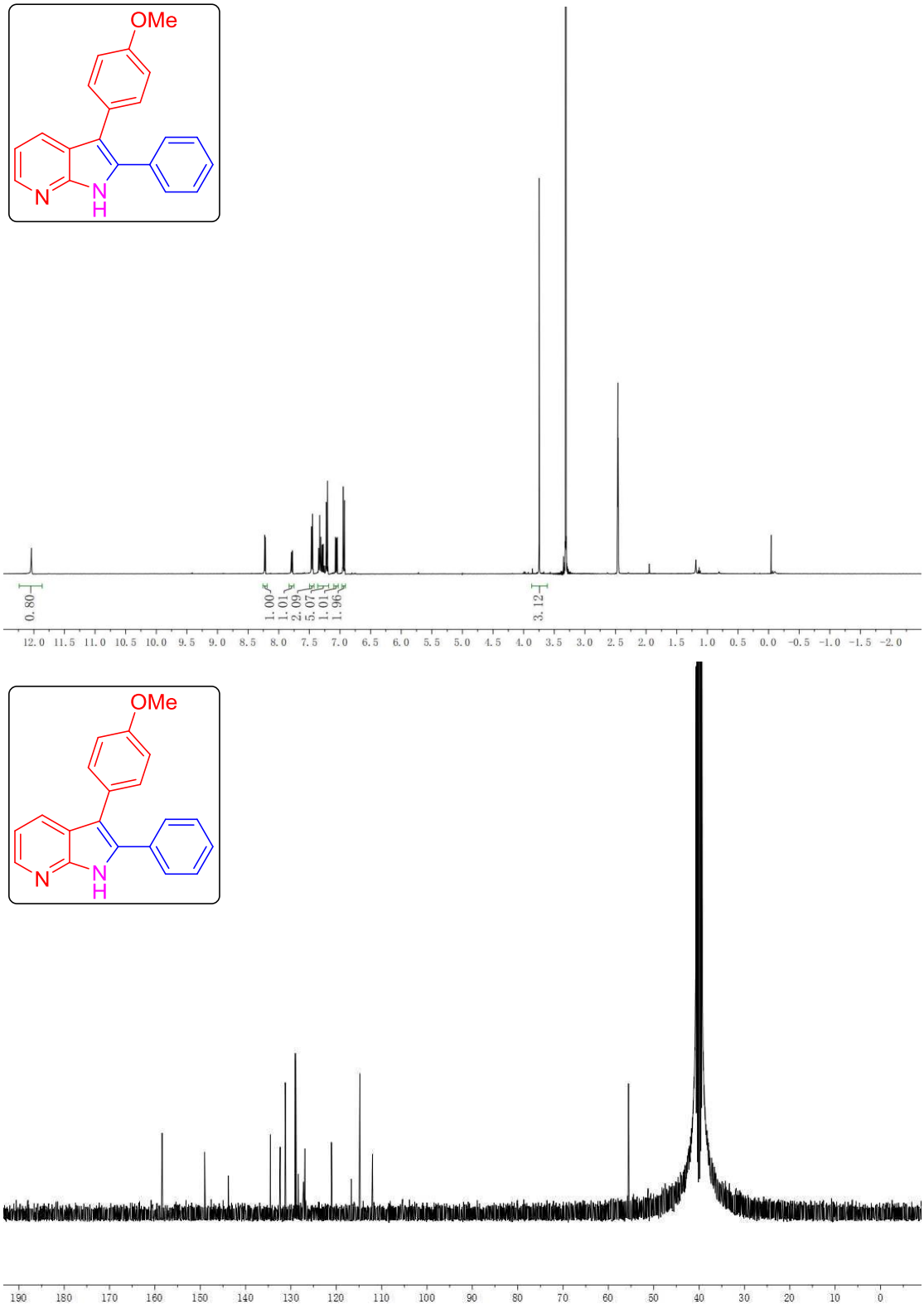


Figure S50. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **4ja** in DMSO-d_6

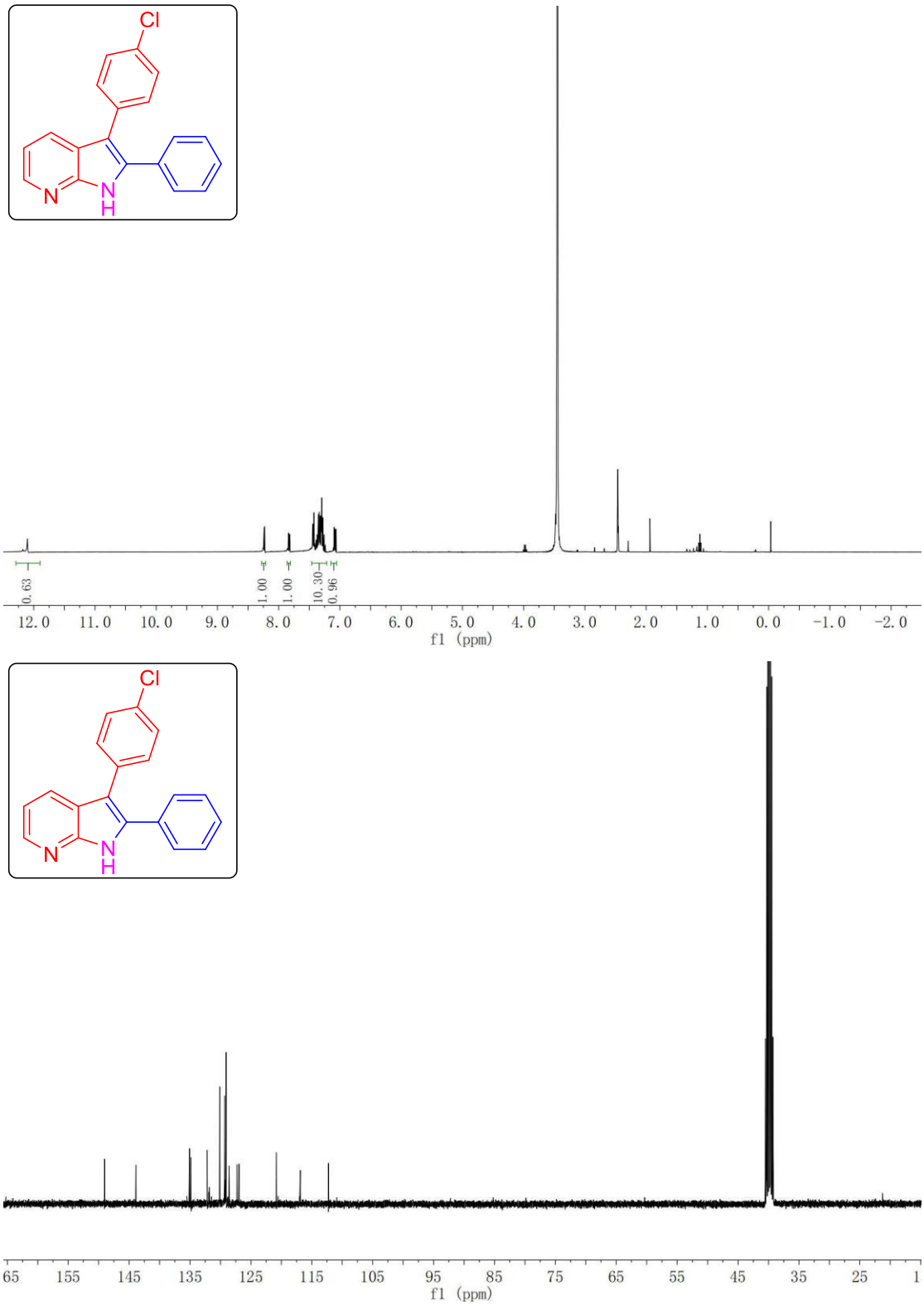
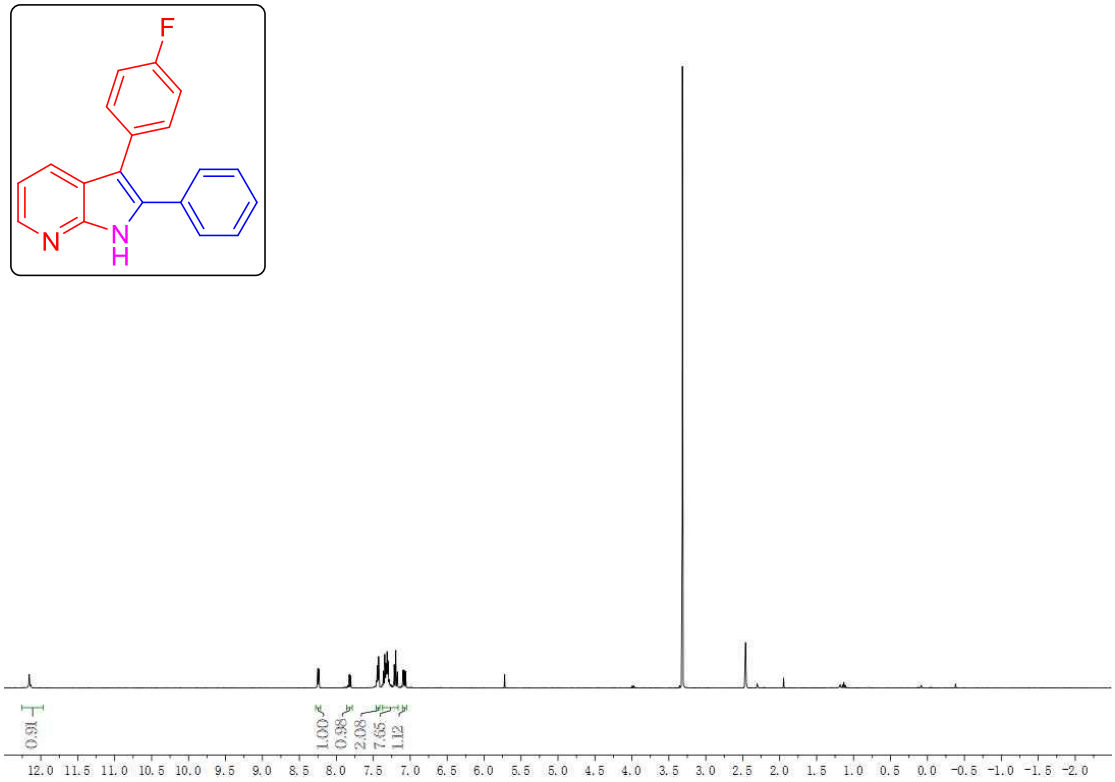
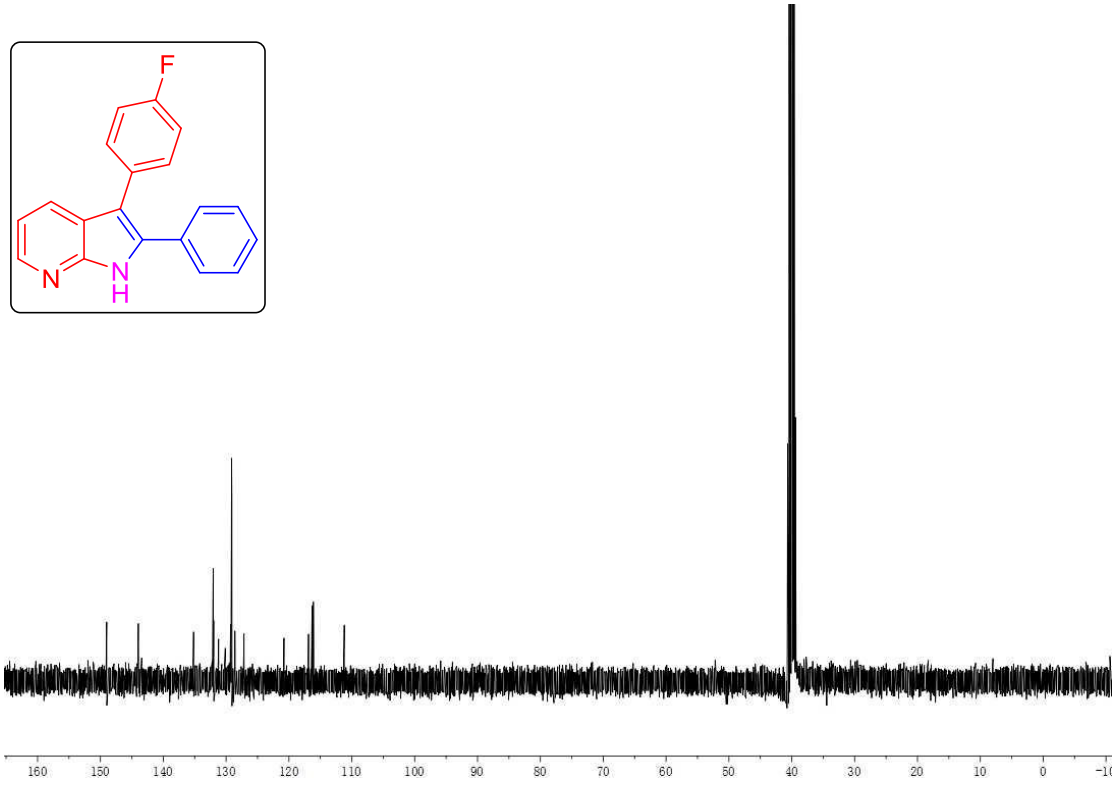


Figure S51. ^{1}H (400 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra of **4ka** in DMSO-d_6


F
N
H
0.91
1.00
0.98
2.08
7.65
1.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0


F
N
H
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

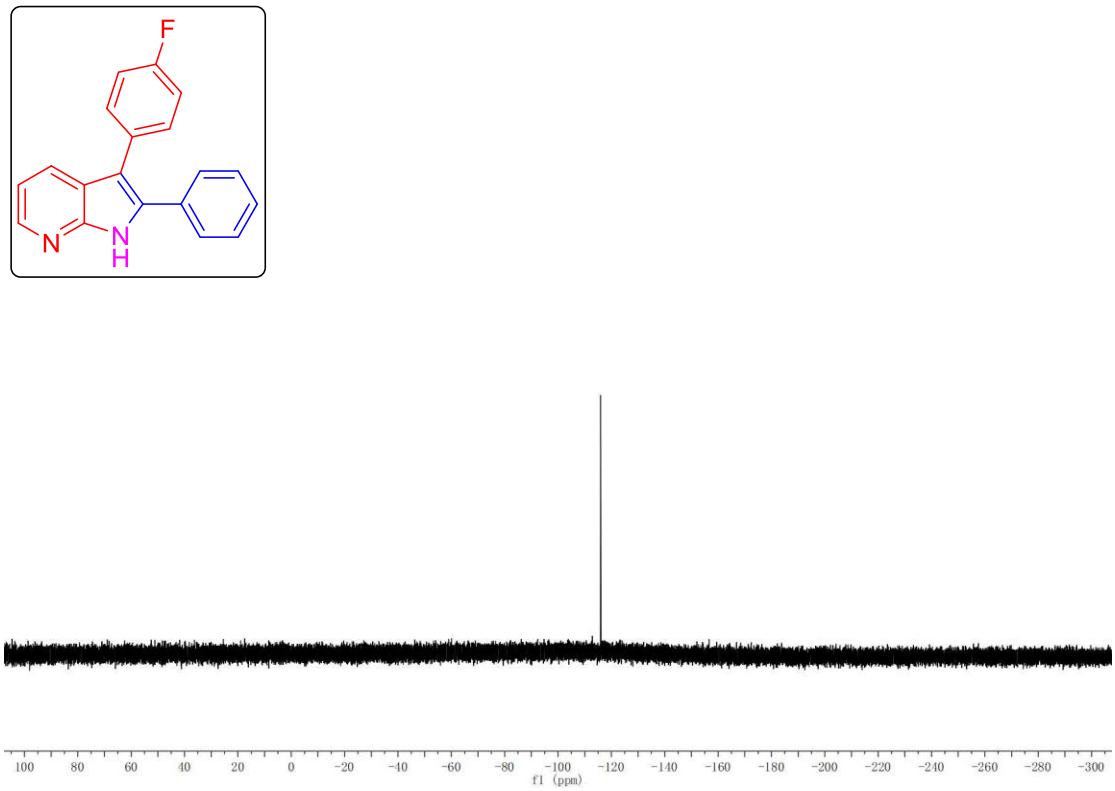


Figure S52. ^{1}H (400 MHz), ^{13}C {^{1}H} (101 MHz) and ^{19}F (377 MHz) NMR spectra of **4la** in DMSO-d_6

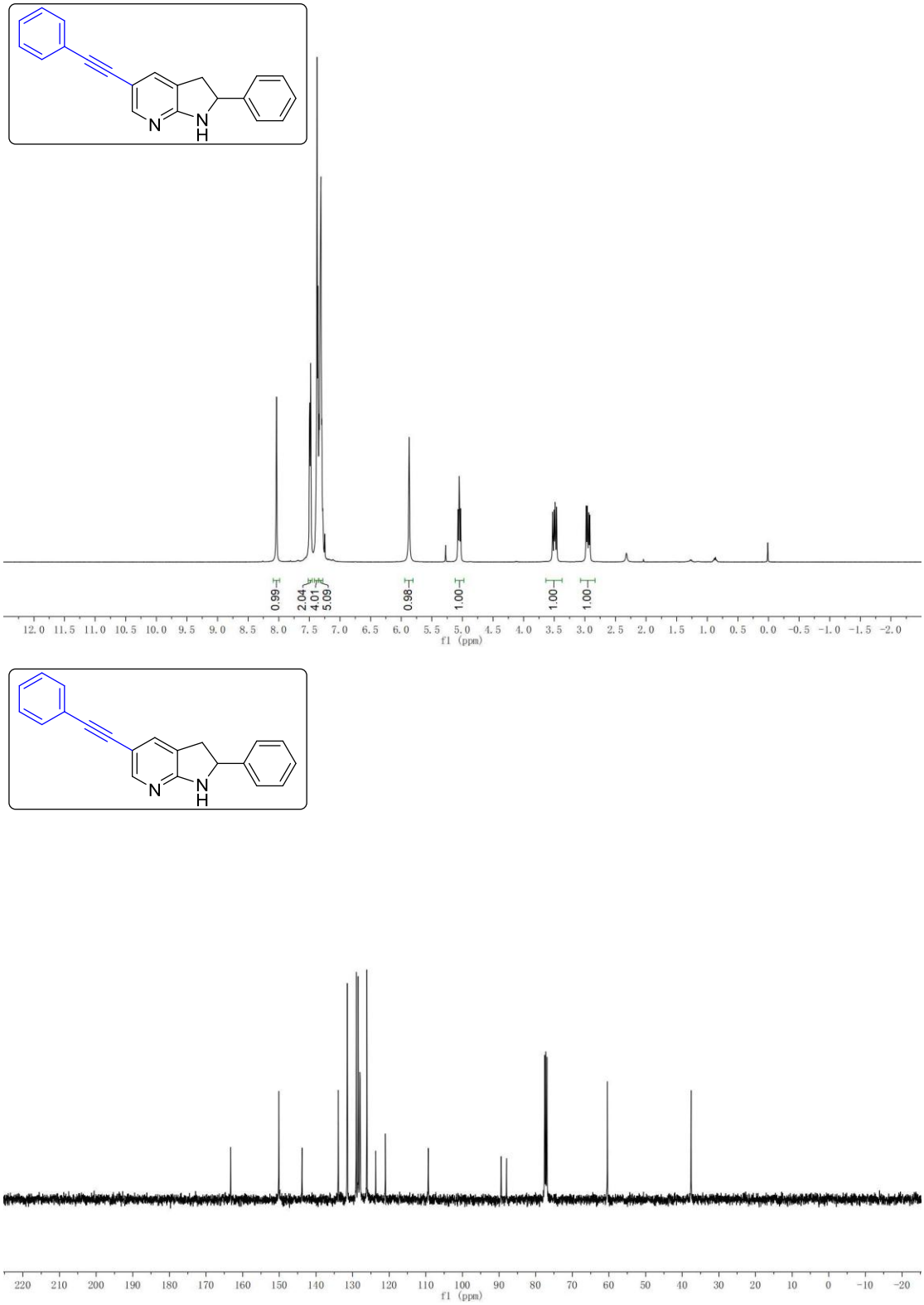


Figure S53. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **5** in $CDCl_3$

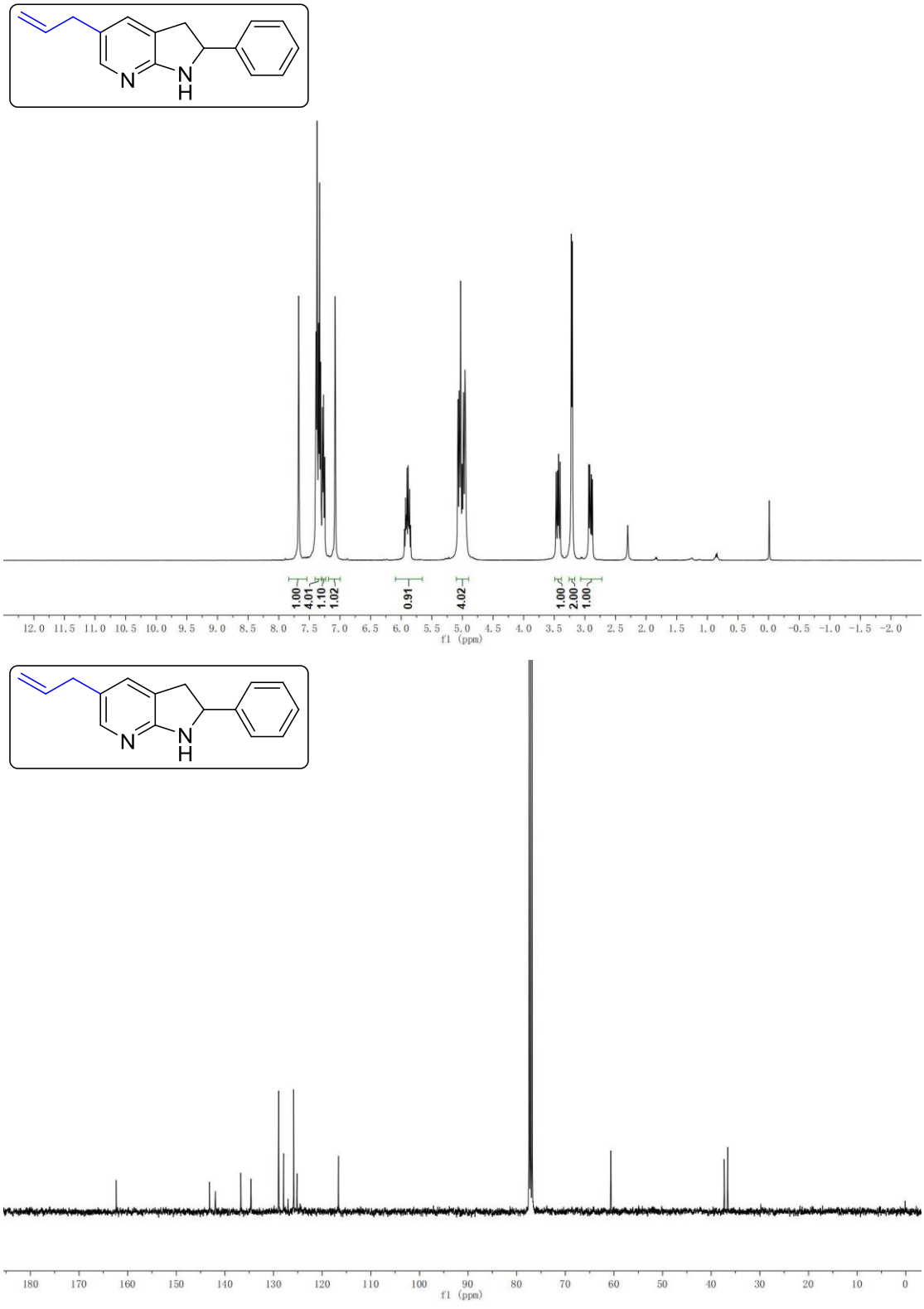


Figure S54. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **6** in $CDCl_3$

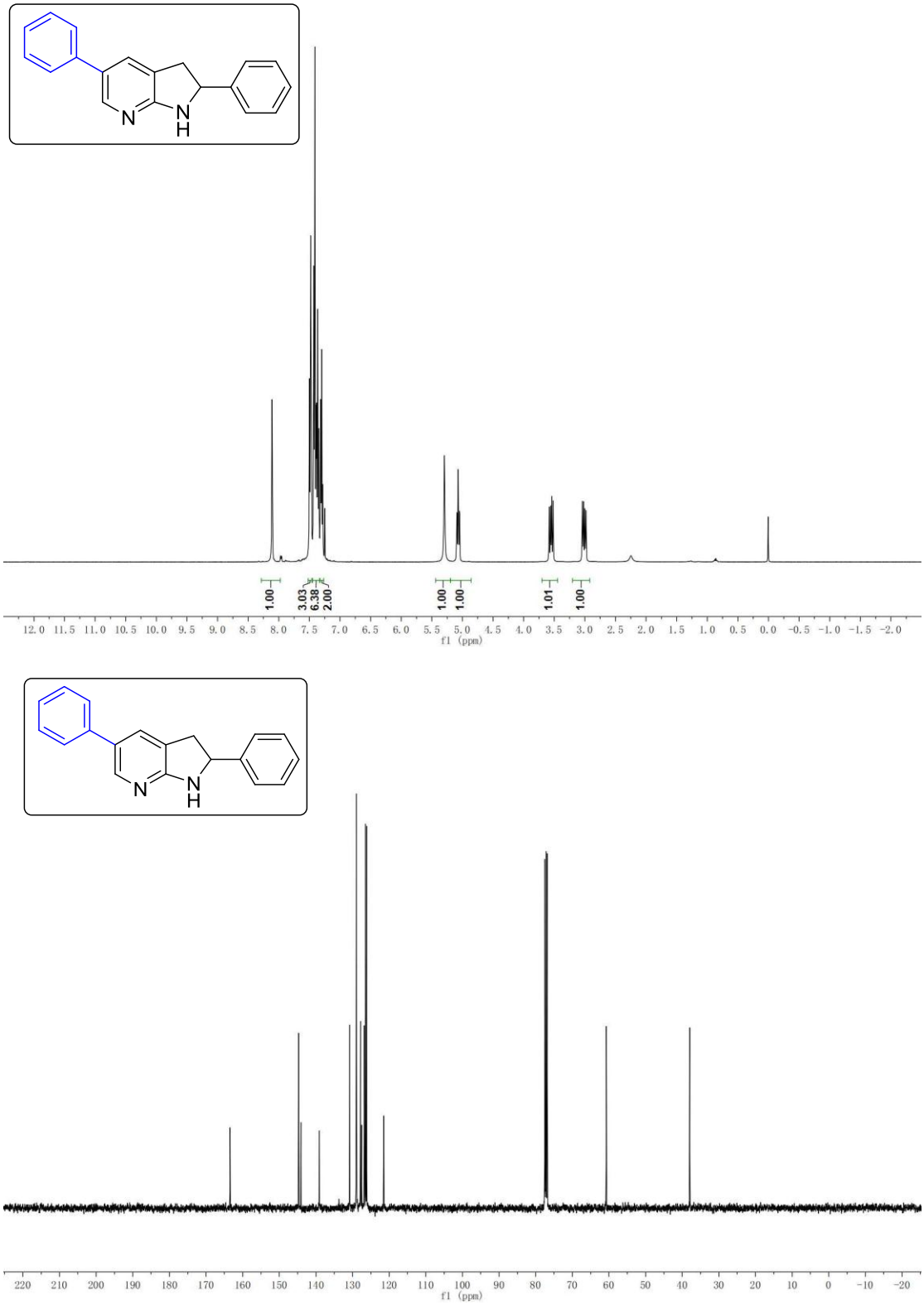


Figure S55. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **7** in $CDCl_3$

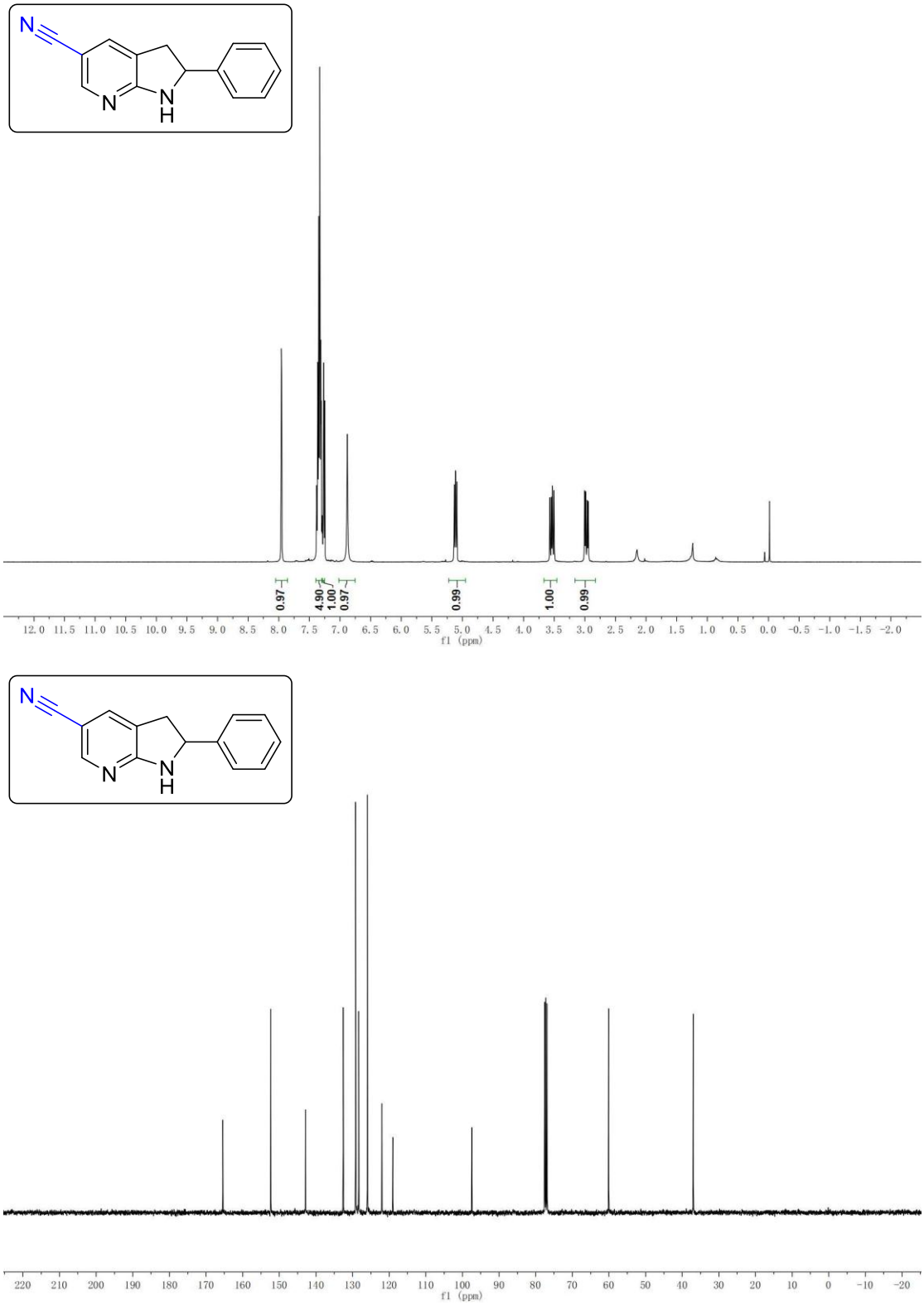


Figure S56. ^{1}H (400 MHz) and ^{13}C $\{^{1}H\}$ (101 MHz) NMR spectra of **8** in $CDCl_3$