Electronic Supplementary Information

Selective Construction of Alkaloid Scaffolds by Alcohol-Based Direct and Mild Aerobic Oxidative Pictet–Spengler Reactions

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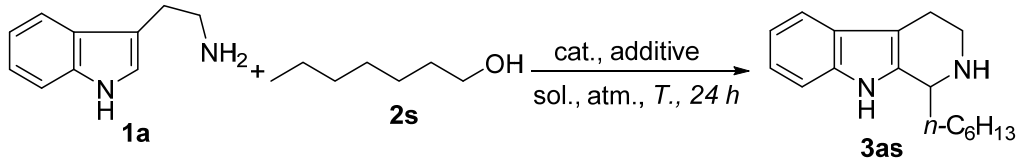
Detailed Condition Screening Tables

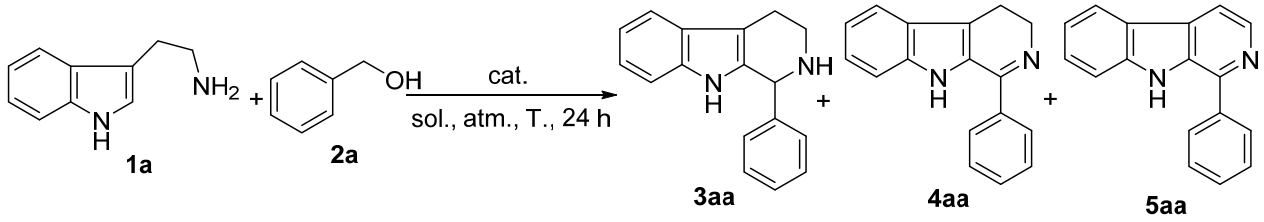
Table S1. Detailed Condition Screening for Aerobic Oxidative PSR of Tryptamine with *n*-Heptanol for THBC Construction.[a]



run	catalyst (mol%)	additive (mol%)	solvent (mL)	atm., *T.*	**3as**%[b]
1	TBN (30) TEMPO (30)	—	AcOH (1)	O_2, 80 °C	—
2	TBN (30) TEMPO (30)	TFA (150)	DCE (1)	O_2, 80 °C	—
3	TBN (100) TEMPO (100)	TFA (150)	DCE (1)	O_2, 80 °C	—
4	$Fe(NO_3)_3$ (20) TEMPO (10)	TFA (150)	DCE (1)	O_2, 80 °C	—
5	TBHP (30)	TFA (150)	DCE (1)	O_2, 80 °C	—
6	$Pd(OAc)_2$ (5)	TFA (150)	DCE (1)	O_2, 80 °C	—
7	CuI (5) TEMPO (10)	Bipy (5)	CH_3CN (1)	air, 80 °C	—
8	$Cu(OAc)_2$ (5) TEMPO (10)	TFA (150)	DCE (1)	air, 80 °C	—
9	$Cu(OAc)_2$ (5) TEMPO (10)	TFA (150)	toluene (1)	air, 100 °C	—
10[c]	$Cu(OAc)_2$ (5) TEMPO (10)	TFA (150)	1-heptanol (1)	air, 100 °C	10
11[c]	$Cu(OAc)_2$ (15) TEMPO (30)	TFA (150)	1-heptanol (1)	O_2, 100 °C	21
12[c]	TBN (30) TEMPO (30)	TFA (150)	1-heptanol (1)	O_2, 100 °C	41
13[c]	***TBN (30) TEMPO (30)***	***TFA (150)***	***1-heptanol (0.5)***	***O_2, 100 °C***	***44***
14[c]	TBN (50) TEMPO (50)	TFA (150)	1-heptanol (1)	O_2, 100 °C	32
15[c]	TBN (100) TEMPO (100)	TFA (150)	1-heptanol (1)	O_2, 100 °C	trace
16[c]	TBN (30) TEMPO (30)	—	1-heptanol (1)	O_2, 100 °C	—
17[c]	TBN (30) TEMPO (30)	—	1-heptanol (0.5), AcOH (0.5)	O_2, 100 °C	trace
18[c]	TBN (30) TEMPO (30)	—	1-heptanol (0.5), TFA (0.5)	O_2, 100 °C	trace

[a] Unless otherwise noted, the mixture of tryptamine **1a** (0.5 mmol), 1-heptanol **2s** (0.6 mmol, 1.2 equiv.), catalysts, and additives in a solvent in a Schlenk tube (100 mL) was sealed under O_2 or air atmosphere and then heated for 24 h. [b] Isolated yields based on **1a**. [c] Excess 1-heptanol was used as both the reactant and solvent.

Table S2. Detailed Condition Screening for Aerobic Oxidative PSR of Tryptamine with Benzyl Alcohol for BC Construction.[a]



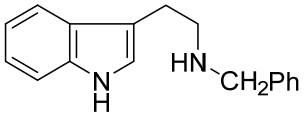
entry	catalyst (mol%)	sol., atm., *T*.	**1a**% (**3:4:5**)[b]	**5aa**%[c]	note
1	TBN (30) TEMPO (30)	AcOH, O_2, 80 °C	100 (88:9:3)	—	82% **3aa** isolated
2	TBN (30) TEMPO (30)	AcOH, O_2, 100 °C	100 (65:23:12)	trace	The reaction got tarred with 54% **3aa** isolated.
3	TBN (30) TEMPO (30)	AcOH, O_2, 130 °C	100 (0:6:94)	69%	The reaction got tarred.
4	TBN (20) TEMPO (20)	AcOH, O_2, 130 °C	100 (0:9:91)	65%	The reaction got tarred.
5	TBN (10) TEMPO (10)	AcOH, O_2, 130 °C	100 (0:7:93)	53%	The reaction got tarred.
6	TBN (50) TEMPO (50)	AcOH, O_2, 80 °C	100 (88:2:10)	Trace	81% **3aa** isolated
7	TBN (80) TEMPO (80)	AcOH, O_2, 80 °C	100 (0:23:77)	65%	-
8	***TBN (100) TEMPO (100)***	***AcOH, O_2, 80 °C***	***100 (0:2:98)***	***85%***	**-**
9	TBN (150) TEMPO (150)	AcOH, O_2, 80 °C	100 (0:2:98)	47%	The reaction got tarred.
10	TBN (200) TEMPO (200)	AcOH, O_2, 80 °C	100 (0:2:98)	Trace	The reaction got tarred.
11	TBN (100) TEMPO (100)	AcOH, O_2, 100 °C	100 (0:1:99)	74%	The reaction got tarred.
12	TBN (100) TEMPO (100)	AcOH, O_2, 120 °C	100 (0:2:98)	54%	The reaction got tarred.

[a] Unless otherwise noted, the mixture of tryptamine **1a** (0.5 mmol, 0.0801g), benzyl alcohol **2a** (0.6 mmol, 1.2 equiv.), TEMPO, TBN, and solvent in a 100 mL Schlenk tube was sealed under O_2 atmosphere and then heated and monitored by TLC/GC-MS. [b] Conversion of **1a** and **3aa**/**4aa**/**5aa** ratios (in parenthesis) were determined by GC-MS. [c] Isolated yields based on **1a**.

Experimental Section

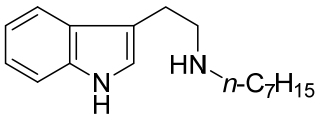
General. Unless otherwise noted, most chemicals were purchased and used without further purification. Substituted tryptamines **1f-1i** were prepared according to the literature methods (*vide infra*). Unless otherwise specified, all reactions were carried out in 100 mL sealed Schlenk tubes under O_2 or air atmosphere and then monitored by TLC and/or GC-MS. The products were purified by column chromatography or PTLC on silica gel using methanol and dichloromethane as the eluent. Unless otherwise noted, ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-III 500 instrument (500 MHz for ^{1}H and 125.4 MHz for ^{13}C NMR spectroscopy) using d_6-DMSO as the solvent. Chemical shifts for ^{1}H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) as the standard. ^{19}F NMR spectra were measured on a Bruker Avance-II 400 instrument (376 MHz for ^{19}F NMR spectroscopy) using d_6-DMSO as the solvent and $CFCl_3$ as the external standard. Mass spectra were measured on a Shimadzu GC-MS-QP2010 Plus spectrometer (EI). High Resolution Mass Spectra (HRMS) were measured on a Bruker micrOTOF-Q II instrument (ESI) at Wenzhou University.

Preparation of some substituted tryptamines 1f-1i.



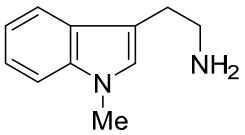
***N*-Benzyltryptamine (1f)** was prepared according to the literature procedure (David, B.; Martin, C.; Vanderwal, C. D. *J. Am. Chem. Soc.* **2009**, *131,* 3472-3473): In a round-bottomed flask, tryptamine (2.50 g, 15.6 mmol), benzaldehyde (1.66 g, 1.59 mL, 15.6 mmol), molecular sieves (5Å), and MeOH (60 mL) were mixed, stirred at room temperature and the reaction was monitored by TLC. Upon full conversion of benzaldehyde (ca. 30 h), solid $NaBH_4$ (590 mg, 15.6 mmol) was added and stirred for more 24 h. The reaction mixture was then filtered through a pad of celite and washed with MeOH (2 x 50 mL). The filtrate was evaporated *in vacuo*. The residue was washed with sat. $NaHCO_3$ (50 mL), H_2O (50 mL), extracted with EtOAc (100 mL), and separated. The organic layer was washed with H_2O (50 mL) and brine (50 mL), and then was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was then purified by column chromatography on silica gel using dichloromethane and methanol as the eluent (10:1), giving **1f** as a brown oil.

^{1}H NMR (500 MHz, d_6-DMSO): δ 10.78 (br s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.33-7.27 (m, 5H), 7.21 (t, J = 7.0 Hz, 1H), 7.12 (s, 1H), 7.05 (t, J = 7.0 Hz, 1H), 6.95 (t, J = 7.0 Hz, 1H), 3.74 (s, 2H), 2.85 (t, J = 6.0 Hz, 2H), 2.79 (t, J = 6.0 Hz, 2H).



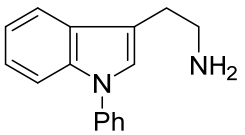
***N*-Heptyltryptamine** (**1g**) was obtained by the same procedure as the above process for **1f** using tryptamine (2.50 g, 15.6 mmol), heptanal (1.79 g, 2.18 mL, 15.6 mmol), and $NaBH_4$ (590 mg, 15.6 mmol) respectively. **1g** was obtained as a brown oil.

^{1}H NMR (500 MHz, d_6-DMSO) δ 10.73 (s, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 2.2 Hz, 1H), 7.07 (dt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 6.96-6.88 (m, 1H), 2.85-2.62 (m, 4H), 2.48-2.4 (m, 2H), 1.45-1.03 (m, 10H), 0.81 (t, J = 6.6 Hz, 3H).



2-(*1*-*N*-Methyl-1H-indol-3-yl)ethan-1-amine (1h) was prepared according to the literature procedure (Lygin, A. V.; Meijere, A. D. *Eur. J. Org. Chem.* **2009**, *2009*, 5138-5141.): to a 60% dispension of sodium hydride (0.88 g, 22 mmol, stored in mineral oil) in anhydrous DMF (60 mL) was added dropwise at room temperature a solution of tryptamine (3.2 g, 20 mmol) in anhydrous DMF (40 mL) within 20 min. The mixture was stirred at room temperature for more 30 min, cooled to 0 °C, and MeI (3.12 g, 1.37 mL, 22 mmol) was then added dropwise. The resulting mixture was stirred at room temperature for more 1 h, and then the solvent was removed *in vacuo*. The residue was washed with water (300 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phase was then dried over Na_2SO_4, and the solvent removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (DCM/MeOH/Et_3N 85 : 10 : 5), giving a brown oil.

^{1}H NMR (500 MHz, d_6-DMSO): δ 7.53 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.14-7.09 (m, 2H), 7.00 (t, J = 7.5 Hz, 1H), 3.71 (s, 3H), 2.84-2.78 (m, 2H), 2.76-2.72 (m, 2H).



2-(*1*-*N*-Phenyl-1H-indol-3-yl)ethan-1-amine(1i) was prepared according to the literature procedure (Antilla, J. C.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 11684-11688): the mixture of CuI (0.095 g, 0.50 mmol), tryptamine (1.60 g, 10 mmol), K_3PO_4 (4.46 g, 21 mmol), iodobenzene (1.34 mL, 12 mmol), 1,2-diaminocyclohexane (320 μL, 2.0 mmol, 20 mol%), and

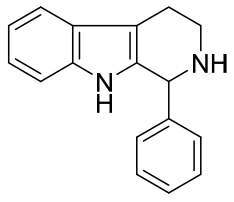
toluene (10 mL) was sealed in a flask under nitrogen and stirred at 110 °C for 24 h. Ethyl acetate (30 mL) was then added and the reaction mixture filtered through a plug of silica gel, concentrated *in vacuo*. The product was purified by flash chromatography on silica gel (DCM : MeOH 50:1), giving a light yellow oil.

^{1}H NMR (500 MHz, d_6-DMSO): δ 7.65 (d, J = 8.0 Hz, 1H), 7.59-7.53 (m, 5H), 7.47 (s, 1H), 7.38-7.35 (m, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 2.89 (t, J = 6.5 Hz, 2H), 2.82 (t, J = 6.5 Hz, 2H).

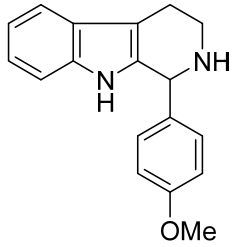
Typical procedure for aerobic oxidative PSR of tryptamines with alcohols for THBC construction (the standard conditions): The mixture of tryptamine **1a** (0.5 mmol, 0.0801g), benzyl alcohol (1.2 equiv., 0.0621 mL), TBN (30 mol%, 0.0176 mL), TEMPO (30 mol%, 0.0234g), and AcOH (0.5 mL) in a 100 mL Schlenk tube was sealed under O_2 and then stirred at the 80 ^{o}C for 24 h. The reaction was then monitored by TLC and/or GC-MS. After completion of the reaction, the reaction mixture was quenched with dichloromethane and aqueous NaOH was added to adjust *p*H to about 8~9. The reaction mixture was then extracted with dichloromethane for three to four times. The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was then purified by column chromatography on silica gel using dichloromethane and methanol as an eluent (10:1), affording tetrahydro-*β*-carboline **3aa** in 82% isolated yield.

Typical alternative conditions (A) for the reactions of aliphatic alcohols: The mixture of tryptamine **1a** (0.5 mmol, 0.0801g), TBN (30 mol%, 0.0176 mL), TEMPO (30 mol%, 0.0234g), TFA (1.5 equiv., 0.0557 mL), and 1-heptanol **2s** (0.5 mL) in a 100 mL Schlenk tube was sealed under O_2 and then stirred at the 100 ^{o}C for 24 h. The reaction mixture was then monitored by TLC and/or GC-MS. After completion of the reaction, the reaction was quenched with dichloromethane and aqueous NaOH was added to adjust pH to about 8~9. The reaction mixture was then extracted with dichloromethane for three to four times. The combined organic layer was then dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by PTLC on silica gel using dichloromethane and methanol as an eluent (10:1), affording tetrahydro-*β*-carboline **3as** in 44% isolated yield.

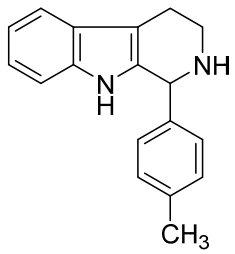
Characterization of THBC products:



1-Phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3aa). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.41 (br s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.36-7.28 (m, 5H), 7.24 (d, J = 8.0 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 5.15 (s, 1H), 3.11-3.06 (m, 1H), 2.98-2.94 (m, 1H), 2.79-2.67 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 143.1, 135.9, 135.3, 128.4, 128.0, 127.1, 126.9, 120.4, 118.1, 117.5, 111.0, 108.3, 56.6, 41.2, 22.2. MS (EI): m/z (%) 248 (100), 216 (85), 202 (9), 170 (57), 144 (10), 108 (16), 77 (3). This compound was known: Pakhare, D. S.; Kusurkar, R. S. *Tetrahedron Lett.* **2015**, *56*, 6012-6015.



1-(4-Methoxyphenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ab). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.44 (br s, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 8.5 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.5 Hz, 2H), 5.12 (s, 1H), 3.73 (s, 3H), 3.11-3.09 (m, 1H), 2.98-2.93 (m, 1H), 2.79-2.66 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 158.6, 135.9, 135.1, 134.5, 129.6, 126.8,120.5, 118.1, 117.5, 113.5, 111.0, 108.0, 55.9, 55.1, 41.1, 21.9. MS (EI): m/z (%) 278 (100), 249 (79), 234 (11), 218 (45), 204 (21), 171 (31), 91 (13), 77 (7). This compound was known: Wang, L.-N.; Shen, S.-L.; Qu, J. *RSC Adv.*, **2014**, *4*, 30733-30741



1-(*p*-Tolyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ac). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.37 (br s, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.17-7.12 (m, 4H), 6.99 (t, J = 7.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 5.04 (s, 1H), 3.09-3.04 (m, 1H), 2.94-2.89 (m, 1H), 2.73-2.63 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 140.1, 136.2, 135.9, 135.5, 128.6, 128.3, 126.8, 120.4, 118.1, 117.4, 110.9, 108.1, 56.3, 41.3, 22.2, 20.7. MS (EI): m/z (%) 262 (M+, 100), 233 (31), 218 (89), 171 (55), 144 (12), 130 (10), 115 (15), 77 (5).This compound was known: Gellis, A.; Dume`tre, A.; Lanzada, G.; Hutter, S.; Ollivier, E.; Vanelle, P.; Azas, N.

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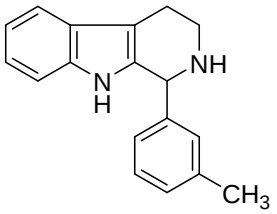
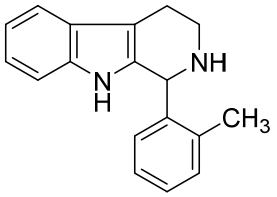
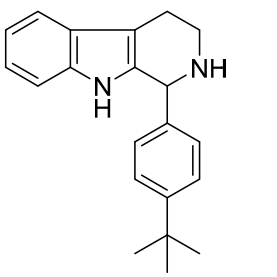


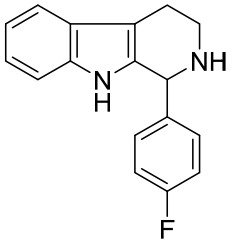
1-(*m*-Tolyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ad). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.40 (br s, 1H), 7.40 (d, J = 9.0 Hz, 1H), 7.23-7.20 (m, 2H), 7.11-7.06 (m, 3H), 6.99 (t, J = 7.0 Hz, 1H), 6.94 (t, J = 7.0 Hz, 1H), 5.05 (s, 1H), 3.10-3.06 (m, 1H), 2.95-2.90 (m, 1H), 2.77-2.63 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): 142.9, 137.1, 135.9, 135.3, 128.9, 127.9, 127.8, 126.8, 125.6, 120.4, 118.1, 117.4, 111.0, 108.1, 56.6, 41.3, 22.2, 21.0. MS (EI): m/z (%) 262 (M+, 100), 233 (38), 218 (78), 171 (54), 144 (13), 130 (12), 115 (20), 108 (18), 91 (9), 77 (7). This compound was known: Gellis, A.; Dume`tre, A.; Lanzada, G.; Hutter, S.; Ollivier, E.; Vanelle, P.; Azas, N. *Biomedicine & Pharmacotherapy*, **2012**, *66*, 339-347.



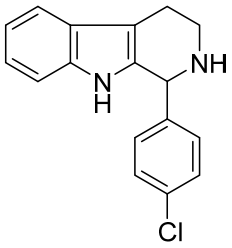
1-(*o*-Tolyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ae). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.46 (br s, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.24 (t, J = 8.5 Hz, 2H), 7.19 (t, J = 7.0 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 5.33 (s, 1H), 3.06-3.01 (m, 1H), 2.97-2.92 (m, 1H), 2.79-2.68 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 140.7, 136.8, 135.9, 135.3, 130.4, 128.6, 127.0, 126.9, 125.3, 120.4, 118.1, 117.4, 110.9, 108.7, 53.5, 40.9, 22.3, 18.8. MS (EI): m/z (%) 262 (M+, 100), 233 (31), 218 (89), 171 (55), 144 (12), 130 (10), 115 (15), 77 (5). This compound was known: Gellis, A.; Dume`tre, A.; Lanzada, G.; Hutter, S.; Ollivier, E.; Vanelle, P.; Azas, N. *Biomedicine & Pharmacotherapy*, **2012**, *66*, 339-347.



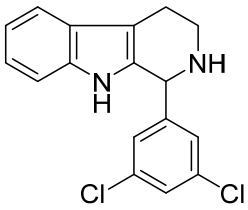
1-(4-*tert*-Butylphenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3af). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.42 (br s, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 7.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 5.05 (s, 1H), 3.08-3.04 (m, 1H), 2.93-2.89 (m, 1H), 2.75-2.63 (m, 2H), 1.27 (s, 9H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 149.4, 140.2, 135.9, 135.4, 128.1, 126.8, 124.8, 120.4, 118.1, 117.4, 110.9, 108.2, 56.2, 41.2, 34.2, 31.2, 22.3. HRMS Calcd for $[C_{21}H_{24}N_2 + H]^+$: 305.2012; found : 305.2002.



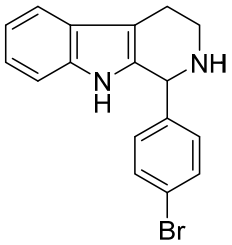
1-(4-Fluorophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ag). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.56 (br s, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.36-7.34 (m, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 8.5 Hz, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 5.24 (s, 1H), 3.25-3.10 (m, 1H), 3.03-2.99 (m, 1H), 2.84-2.71 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 161.4 (d, J = 241.9 Hz), 139.3 (d, J = 3.0 Hz), 135.9, 135.1, 130.2 (d, J = 8.2 Hz), 128.3 (d, J = 7.9 Hz), 126.8, 120.5, 117.9 (d, J = 84.6 Hz), 114.7 (d, J = 20.9 Hz), 111.0, 108.3, 55.8, 41.2, 22.1. ^{19}F NMR (376 MHz, d_6-DMSO): δ -114.5(S, 1F). MS (EI): m/z (%) 266 (M+, 73), 236 (100), 217 (7), 171 (30), 144 (10), 117 (13). This compound was known: Gellis, A.; Dume`tre, A.; Lanzada, G.; Hutter, S.; Ollivier, E.; Vanelle, P.; Azas, N. *Biomedicine & Pharmacotherapy*, **2012**, *66*, 339-347.



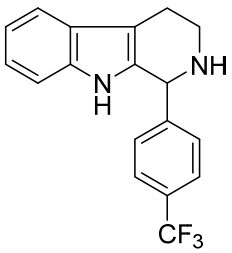
1-(4-Chlorophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ah). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.47 (br s, 1H), 7.43-7.37 (m, 3H), 7.3 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.5 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 5.13 (s, 1H), 3.08-3.03 (m, 1H), 2.98-2.93 (m, 1H), 2.77-2.65 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.0, 135.9, 134.8, 131.7, 130.3, 127.9, 126.8, 120.6, 118.2, 117.5, 111.0, 108.4, 55.8, 41.1, 22.1. MS (EI): m/z (%) 282 (M+, 78), 253 (39), 218 (100), 207 (11), 171 (55), 144 (14), 115 (15), 77 (9). This compound was known: Wang, L.-N.; Shen, S.-L.; Qu, J. *RSC Adv.*, **2014**, *4*, 30733-30741.



1-(3,5-Dichlorophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ai). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.52 (br s, 1H), 7.51 (s, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.33 (s, 2H), 7.26 (d, J = 7.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 5.14 (s, 1H), 3.07-2.93 (m, 2H), 2.78-2.64 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 147.4, 136.0, 133.9, 133.7, 127.1, 126.8, 126.7, 120.8, 118.4, 117.7, 111.1, 108.6, 55.6, 41.2, 21.9. MS (EI): m/z (%) 317 (M+, 77), 287 (32), 252 (45), 217 (79), 171 (100), 144 (15), 108 (21), 77 (6). HRMS Calcd for $[C_{17}H_{14}Cl_2N_2 + Na]^+$: 339.0426; found : 339.0400.

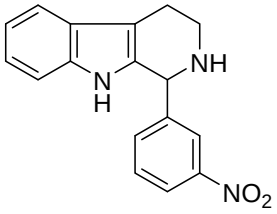


1-(4-Bromophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3aj). Pale yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.46 (br s, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.25-7.22 (m, 3H), 7.02 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 5.12 (s, 1H), 3.08-3.04 (m, 1H), 2.98-2.93 (m, 1H), 2.78-2.65 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.5, 135.9, 134.8, 130.9, 130.6, 128.5, 126.8, 120.6, 120.2, 118.2, 117.5, 111.0, 108.3, 55.9, 41.1, 22.1. MS (EI): m/z (%) 326 (M+, 46), 297 (19), 218 (100), 171 (59), 144 (14), 108 (23), 77 (7). This compound was known: Gellis, A.; Dume`tre, A.; Lanzada, G.; Hutter, S.; Ollivier, E.; Vanelle, P.; Azas, N. *Biomedicine & Pharmacotherapy*, **2012**, *66*, 339-347.

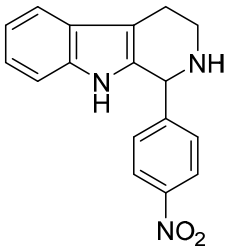


1-(4-Trifluoromethylphenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ak). Yellow solid, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.48(br s, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.02 (t, J = 7.0 Hz, 1H), 6.96 (t, J = 7.0 Hz, 1H),

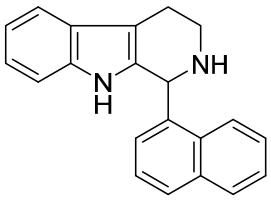
5.18 (s, 1H), 3.05-2.94 (m, 2H), 2.76-2.66 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 147.9, 135.9, 134.5, 129.2, 127.8 (q, J = 47.2 Hz), 126.8 , 124.4 (q, J = 271.1 Hz), 124.9 (q, J = 3.3 Hz), 120.7, 118.3, 117.6, 111.0, 108.5, 56.1, 41.1, 22.1. ^{19}F NMR (376 MHz, d_6-DMSO): δ -60.9 (S, 3F). MS (EI): m/z (%) 316 (100), 297 (11), 287 (54), 218 (95), 171 (60), 144 (15), 130 (6), 115 (12), 77 (5). This compound was known: Gellis, A.; Dume`tre, A.; Lanzada, G.; Hutter, S.; Ollivier, E.; Vanelle, P.; Azas, N. *Biomedicine & Pharmacotherapy*, **2012**, *66*, 339-347.



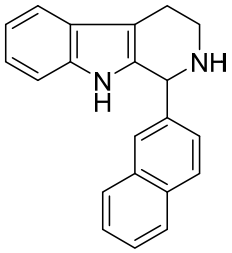
1-(3-Nitrophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3al). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.54 (br s, 1H), 8.18 (d, J = 7.5 Hz, 2H), 7.79 (d, J = 7.5 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 5.29 (s, 1H), 3.09-2.97 (m, 2H), 2.81-2.68 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 147.7, 145.5, 136.0, 135.2, 134.2, 129.6, 126.8, 122.9, 122.2, 120.8, 118.4, 117.7, 111.1, 108.6, 55.7, 41.2, 21.9. MS (EI): m/z (%) 293 (100), 264 (43), 247 (38), 233 (10), 217 (92), 204 (17), 189 (10), 171 (90), 144 (17), 130 (10), 115 (17), 77 (9). This compound was known: Gellis, A.; Dume`tre, A.; Lanzada, G.; Hutter, S.; Ollivier, E.; Vanelle, P.; Azas, N. *Biomedicine & Pharmacotherapy*, **2012**, *66*, 339-347.



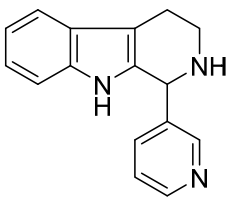
1-(4-Nitrophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3am). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.55 (br s, 1H), 8.22 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 9.0 Hz. 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 5.25 (s, 1H), 3.05-2.96 (m, 2H), 2.79-2.67 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 150.9, 146.7, 136.0, 134.1, 129.7, 126.8, 123.2, 120.8, 118.3, 117.7, 111.1, 108.6, 55.7, 40.9, 22.0. MS (EI): m/z (%) 293 (M+, 100). This compound was known: Wang, L.-N.; Shen, S.-L.; Qu, J. *RSC Adv.*, **2014**, *4*, 30733-30741.



1-(Naphthalen-1-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3an). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.48 (br s, 1H), 8.41-8.39 (m, 1H), 7.95-7.93 (m, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.56-7.45 (m, 3H), 7.40 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.07-6.96 (m, 3H), 5.85 (s, 1H), 3.01-2.97 (m, 2H), 2.83-2.71 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 138.2, 135.9, 135.3, 133.8, 131.6, 128.3, 127.8, 126.9, 126.6, 125.7, 125.4, 125.0, 124.7, 120.4, 118.1, 117.5, 110.9, 108.8, 48.6, 40.9, 22.4. MS (EI): m/z (%) 294 (M+, 100). This compound was known: Huang, Y.-Q.; Song, H,-J.; Liu, Y.-X.; Wang, Q.-M. *Chem. Eur. J.* **2018**, *24*, 2065 - 2069.

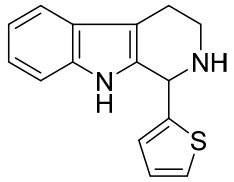


1-(Naphthalen-2-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ao). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.47 (br s, 1H), 7.89-7.85 (m, 3H), 7.77 (s, 1H), 7.49-7.47 (m 3H), 7.45 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 7.0 Hz, 1H), 6.97 (t, J = 7.0 Hz, 1H), 5.29 (s, 1H), 3.18-3.13 (m, 1H), 3.02-2.98 (m, 1H), 2.85-2.69 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 140.7, 136.0, 135.4, 132.8, 132.5, 127.8, 127.6, 127.4, 127.0, 126.9, 126.8, 125.9, 125.7, 120.5, 118.2, 117.6, 111.1, 108.3, 56.9, 41.6, 22.3. MS (EI): m/z (%) 294 (M+, 100), 146 (20), 132 (5), 119 (2). This compound was known: Huang, Y.-Q.; Song, H,-J.; Liu, Y.-X.; Wang, Q.-M. *Chem. Eur. J.* **2018**, *24*, 2065 - 2069.

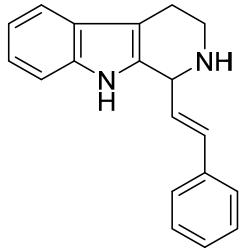


1-(Pyridin-3-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ap). Yellow oil. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.58 (br s, 1H), 8.54 (s, 1H), 8.49 (d, J = 5.0 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.34 (q, J = 5.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 5.16 (s, 1H), 3.07-3.03 (m, 1H), 2.98-2.94 (m, 1H), 2.78 -2.65 (m, 2H). ^{13}C NMR

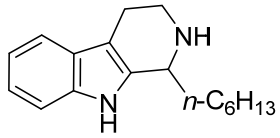
(125.4 MHz, d_6-DMSO): δ 149.7, 148.3, 138.4, 136.0, 135.8, 134.4, 126.8, 123.3, 120.6, 118.2, 117.6, 111.0, 108.5, 54.2, 41.1, 22.0. MS (EI): m/z (%) 249 (M+, 73), 219 (100), 193 (15), 171 (57), 77 (5). This compound was known: Pakhare, D. S.; Kusurkar, R. S. *Tetrahedron Lett.* **2015**, *56*, 6012-6015.



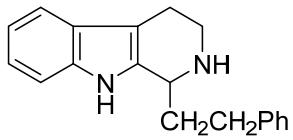
1-(Thiophen-2-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3aq). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.65 (br s, 1H), 7.40 (d, J = 5.5 Hz, 2H), 7.27 (d, J = 8.0 Hz, 1H), 7.04-6.95 (m, 4H), 5.37 (s, 1H), 3.09-2.97 (m, 2H), 2.70-2.61 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 147.8, 135.8, 134.9, 126.7, 126.4, 125.2, 124.9, 120.7, 118.2, 117.6, 111.1, 107.5, 51.6, 40.6, 22.0. MS (EI): m/z (%) 254 (M+, 100) This compound was known: Wang, L.-N.; Shen, S.-L.; Qu, J. *RSC Adv.*, **2014**, *4*, 30733-30741.



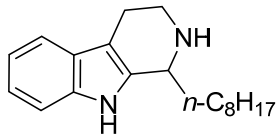
(*E*)-1-(2-Phenylvinyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ar). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.75 (br s, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H), 6.57 (dd, J_1 = 6.5 Hz, J_2 = 16.0 Hz, 1H), 4.68 (d, J = 6.5 Hz, 1H), 3.19-3.14 (m, 1H), 2.98-2.94 (m, 1H), 2.66-2.59 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 136.9, 135.8, 135.1, 130.7, 130.1, 128.5, 127.3, 127.0, 126.3, 120.4, 118.1, 117.4, 110.9, 107.3, 54.3, 41.2, 22.2. MS (EI): m/z (%) 274 (M+, 100), 244 (14), 197 (35), 183 (22), 169 (23), 154 (25), 143 (21), 128 (18), 115 (14), 77 (9). This compound was known: Handy, S.; Wright, M. *Tetrahedron Lett.* **2014**, *55*, 3440-3442.



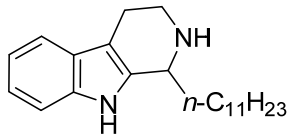
1-Hexyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3as). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.65 (br s, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 3.92-3.90 (m, 1H), 3.16-3.12 (m, 1H), 2.86-2.81 (m, 2H), 2.63-2.52 (m, 2H), 1.92-1.87 (m, 1H), 1.61-1.54 (m, 1H), 1.48-1.40 (m, 2H), 1.34-1.22 (m, 5H), 0.88 (t, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 137.4, 135.6, 127.1, 120.1, 118.0, 117.2, 110.8, 107.1, 52.1, 41.9, 34.1, 31.3, 28.9, 25.3, 22.4, 22.1, 13.9. MS (EI): m/z (%) 256 (M+, 100). This compound was known: Sudžukovic´, N.; Schinnerl, J.; Brecker, L. *Bioorg. Med. Chem.* **2016**, *24*, 588-595.



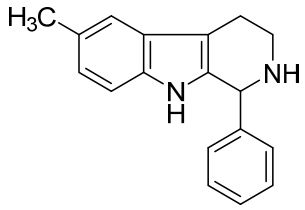
1-(2-Phenylethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3at). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.73 (br s, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.31-7.26 (m, 5H), 7.19-7.16 (m, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 3.97 (d, J = 9.0 Hz, 1H), 3.22-3.18 (m, 1H), 2.88-2.84 (m, 1H), 2.80-2.70 (m, 2H), 2.66-2.56 (m, 2H), 2.26-2.19 (m, 1H), 1.90-1.84 (m, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.4, 137.0, 135.7, 128.3, 128.2, 127.1, 125.6, 120.2, 118.1, 117.3, 110.8, 107.3, 51.7, 41.9, 35.8, 31.5, 22.3. MS (EI): m/z (%) 276 (M+,100). This compound was known: Chauhan, J.; Luthra, T.; Sen, S. *Eur. J. Org. Chem*. **2018**, *2018*, 4776-4786.



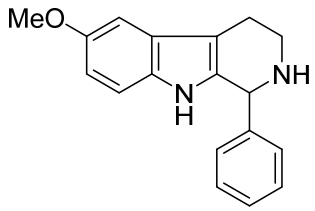
1-Octyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3au). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.94 (br s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 4.33 (d, J = 6.5 Hz, 1H), 3.42-3.38 (m, 1H), 3.14-3.08 (m, 1H), 3.84-3.73 (m, 2H), 2.08-2.01 (m, 1H), 1.76-1.69 (m, 1H), 1.51-1.41 (m, 2H), 1.38-1.20 (m, 11H), 0.87 (t, J = 3.5 Hz, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 135.9, 133.2, 126.3, 121.0, 118.6, 117.6, 111.1, 106.2, 52.3, 41.3, 32.5, 31.2, 28.9, 28.8, 28.6, 24.8, 22.1, 19.8, 13.9. MS (EI): m/z (%) 284 (M+,100). This compound was known: Roszkowski, P.; Wojtasiewicz, K.; Leniewski A.; Maurin, J. K.; Lis, T.; Czarnocki, Z. *Journal of Molecular Catalysis A: Chemical,* **2005**, *232*, 143-149.



1-Undecyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3av). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.94 (br s, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 4.32 (d, J = 7.0 Hz, 1H), 3.42-3.37 (m, 1H), 3.13-3.08 (m, 1H), 2.84-2.72 (m, 2H), 2.08-2.01 (m, 1H), 1.77-1.69 (m, 1H), 1.52-1.10 (m, 17H), 0.86 (t, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 135.9, 133.3, 126.3, 121.0, 118.5, 117.6, 111.1, 106.2, 52.3, 41.3, 32.6, 31.3, 29.0, 28.9, 28.8, 28.7, 24.8, 22.0, 19.9, 13.9. MS (EI): m/z (%) 326 (M+,100). This compound was known: Mirabal-Gallardo, Y.; Soriano, M. D. P. C.; Santos, L. S. *Tetrahedron: Asymmetry*, **2013**, *24*, 440-443.

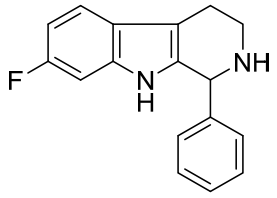


6-Methyl-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ba). White solid, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.45 (br s, 1H), 7.38-7.31 (m, 5H), 7.22 (s, 1H), 7.13 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 5.30 (s, 1H), 3.16-3.11 (m, 1H), 3.07-3.02 (m, 1H), 2.86-2.71 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 140.7, 134.4, 133.3, 128.8, 128.2, 127.8, 126.7, 122.3, 117.3, 110.9, 107.5, 56.2, 40.8, 21.2. MS (EI): m/z (%) 262 (M+, 100), 233 (72), 218 (30), 185 (58), 143 (9), 130 (11), 77 (10). This compound was known: Liu, F.; You, Q.-D. *Synth. Comm.*, **2007**, *37*, 3933-3938.

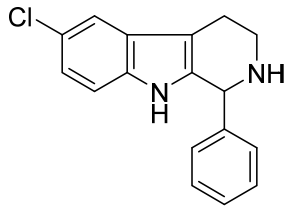


6-Methoxy-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ca). brown solid, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.25 (br s, 1H), 7.34-7.25 (m, 5H), 7.11 (d, J = 8.5 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.65 (dd, J_1 = 2.5 Hz, J_2 = 8.5 Hz, 1H), 5.07 (s, 1H), 3.75 (s, 3H), 3.07-3.03 (m, 1H), 2.95-2.90 (m, 1H), 2.74-2.61 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 152.9, 143.1, 135.9, 131.0, 128.4, 128.0, 127.1, 126.4, 111.6, 110.2, 108.1, 99.9, 56.6, 55.4, 41.2, 22.3. MS (EI): m/z (%)

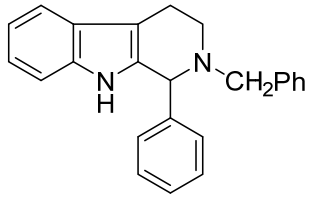
278 (M+, 100), 249 (64), 234 (21), 218 (16), 207 (17), 201 (53), 91 (5). This compound was known: Desroses, M.; Koolmeister, T.; Jacques, S.; Llona, S.; Helleday, T.; Scobie, M. *Tetrahedron Lett*. **2013**, *54*, 3554-3557.



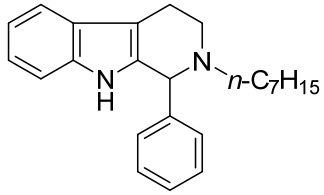
7-Fluoro-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3da). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.54 (br s, 1H), 7.40-7.27 (m, 6H), 6.98 (d, J = 9.0 Hz, 1H), 6.81 (d, J = 9.0 Hz, 1H), 5.06 (s, 1H), 3.08-3.04 (m, 1H), 2.94-2.90 (m, 1H), 2.75-2.63 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 158.5 (d, J = 232.2 Hz), 142.9, 135.9 (d, J = 3.4 Hz), 135.8 (d, J = 12.5 Hz), 128.4, 128.1, 127.2, 123.7, 118.2 (d, J = 10.2 Hz), 108.4, 106.3 (d, J = 24.1 Hz), 97.1 (d, J = 25.5 Hz), 56.5, 41.2, 22.1. ^{19}F NMR (376 MHz, d_6-DMSO): δ -122.3 (S, 1F). MS (EI): m/z (%) 266 (M+, 88), 236 (100), 222 (12), 207 (6), 189 (56), 117 (10), 77 (7). HRMS Calcd for $[C_{17}H_{15}F_1N_2 + H]^+$: 267.1292; found : 267.1284.



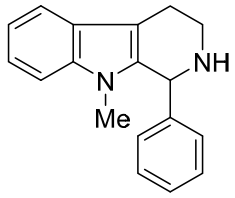
6-Chloro-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ea). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.70 (br s, 1H), 7.48 (s, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.30-7.25 (m, 4H), 7.03 (d, J = 8.5 Hz, 1H), 5.10 (s, 1H), 3.10-3.05 (m, 1H), 2.96-2.91 (m, 1H), 2.77-2.64 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.8, 137.3, 134.4, 128.4, 128.1, 128.0, 127.2, 122.9, 120.3, 116.8, 112.4, 108.3, 56.6, 41.1, 22.0. MS (EI): m/z (%) 283 (M+,46), 282 (100), 253 (84), 217 (87), 207 (87), 191 (11), 176 (14), 108 (32), 77 (16). This compound was known: You, Q.-D. *Synth. Comm.*, **2007**, *37*, 3933-3938.



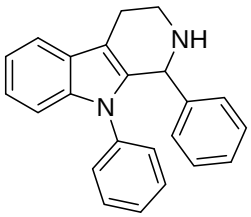
***2-N*-Benzyl-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3fa)**. light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.34 (br s, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.36-7.21 (m, 11H), 7.00 (t, J = 7.5 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 4.74 (s, 1H), 3.72 (d, J = 13.5 Hz, 1H), 3.50 (d, J = 13.5 Hz, 1H), 3.04-2.99 (m, 1H), 2.79-2.69 (m, 2H), 2.65-2.61 (m, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 141.8, 139.4, 136.4, 134.6, 128.8, 128.4, 128.2, 128.2, 127.4, 126.8, 126.5, 120.5, 118.2, 117.6, 111.1, 107.0, 62.6, 57.2, 46.3, 20.2. MS (EI): m/z (%) 338 (M+, 100). This compound was known: Qi, L.; Hou, H.; Ling, F.; Zhong, W. *Org. Biomol. Chem.*, **2018**, *16*, 566-574.



2-*N*-Heptyl-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ga). Slight yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.30 (br s, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.39-7.32 (m, 5H), 7.26 (d, J = 7.5 Hz, 1H), 7.06-6.99 (m, 2H), 4.69 (s, 1H), 3.22-3.18 (m, 1H), 2.84-2.82 (m, 2H), 2.70-2.67 (m, 1H), 2.56-2.52 (m, 1H), 2.44-2.40 (m, 1H), 1.55-1.50 (m, 2H), 1.29-1.22 (m, 8H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.0, 136.3, 135.0, 128.9, 127.9, 127.2, 126.4, 120.4, 118.1, 117.5, 111.0, 107.1, 63.1, 52.9, 46.7, 31.2, 28.4, 26.7, 26.6, 22.0, 20.4, 13.9. HRMS Calcd for $[C_{24}H_{30}N_2 + H]^+$: 347.2487; found : 347.2481.

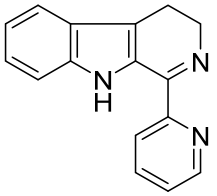


***9-N*-Methyl-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ha)**. light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.51-7.46 (m, 1H), 7.36-7.24 (m, 4H), 7.16-6.99 (m, 4H), 5.19 (s, 1H), 3.22 (s, 3H), 2.90-2.68 (m, 4H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.7, 136.5, 135.8, 128.3, 128.1, 127.1, 126.5, 120.7, 118.4, 117.7, 108.9, 108.7, 54.5, 29.5, 22.2. MS (EI): m/z (%) 262 (M+, 100). This compound was known: Zhang, L.; Wang, Y.; Yao, Z.-J.; Wang, S. Yu, Z.-X. *J. Am. Chem. Soc.* **2015**, *137*, 13290-13300.

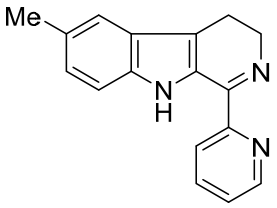


1,9-Diphenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3ia). light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.58 (d, J = 7.0 Hz, 1H), 7.30-7.21 (m, 3H), 7.17-7.13 (m, 1H), 7.12-7.04 (m, 6H), 6.99 (d, J = 7.5 Hz, 1H), 6.91-6.88 (m, 2H), 5.22 (s, 1H), 3.03-2.95 (m, 2H), 2.87-2.80 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 141.6, 137.2, 137.1, 135.8, 129.1, 128.4, 127.5, 127.1, 127.1, 126.8, 126.7, 121.8, 119.5, 118.0, 109.5, 55.2, 21.9. HRMS Calcd for $[C_{23}H_{20}N_2 + H]^+$: 325.1705; found : 325.1712.

Characterization of DHBC products:

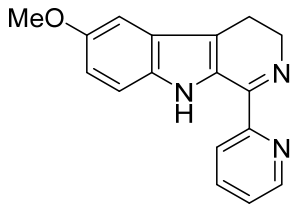


1-(Pyridin-2-yl)-4,9-dihydro-3H-pyrido[3,4-b]indole (4aw). Yellow solid, ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.43(br s, 1H), 8.79 (d, J = 4.0 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.97 (t, J = 8.0 Hz, 1H), 7.62 (dd, J_1 = 8.0 Hz, J_2 = 17.5 Hz, 2H), 7.56 (t, J = 6.0 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 4.03 (t, J = 8.0 Hz, 2H), 2.91 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 155.7, 155.5, 148.3, 137.1, 136.6, 127.3, 124.7, 124.3, 123.7, 120.9, 119.4, 119.3, 116.1, 113.0, 48.4, 18.7. MS (EI): m/z (%) 247 (M+, 83), 246 (100), 219 (19), 191 (4), 169 (3), 143 (4), 115 (7), 77 (7). MS (EI): m/z (%) 247 (M+, 79), 246 (100), 219 (15), 207 (16), 109 (11). HRMS Calcd for $[C_{16}H_{13}N_3 + Na]^+$: 270.1007; found : 270.1022.

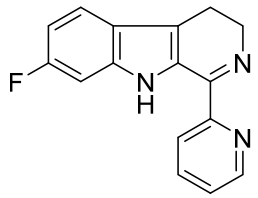


6-Methyl-1-(pyridin-2-yl)-4,9-dihydro-3H-pyrido[3,4-b]indole (4bw). Yellow solid, ^{1}H NMR (400 MHz, d_6-DMSO): δ 11.34 (br s, 1H), 8.80 (d, J = 4.8 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.98 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 6.0 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.39 (s, 1H), 7.07 (d, J = 8.4 Hz, 1H), 4.03 (t, J = 8.4 Hz, 2H), 2.89 (t, J = 8.4 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (125.4 MHz,

d_6-DMSO): δ 155.7, 155.5, 148.3, 137.1, 135.1, 127.8, 127.4, 125.6, 124.7, 124.5, 120.9, 118.7, 115.6, 112.7, 48.4, 21.1, 18.8. MS (EI): m/z (%) 261 (M+, 100), 244 (5), 231 (5), 218 (7). HRMS Calcd for $[C_{17}H_{15}N_3 + H]^+$: 262.1339; found : 262.1341.



6-Methoxy-1-(pyridin-2-yl)-4,9-dihydro-3H-pyrido[3,4-b]indole (4cw). Yellow solid, ^{1}H NMR (400 MHz, d_6-DMSO): δ 11.33 (br s, 1H), 8.80 (d, J = 4.4 Hz, 1H), 8.22 (d, J = 4.0 Hz, 1H), 7.99 (td, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.59 (td, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 2.4 Hz, 1H), 6.90 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 4.04 (t, J = 8.4 Hz, 2H), 3.81 (s, 3H), 2.92 (t, J = 8.4 Hz, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 155.7, 155.5, 153.5, 148.3, 137.1, 131.9, 127.8, 124.7, 124.5, 120.9, 115.7, 114.9, 113.9, 99.9, 55.3, 48.4, 18.8. MS (EI): m/z (%) 277 (M+, 100), 261 (12), 234 (13). HRMS Calcd for $[C_{17}H_{15}N_3O + H]^+$: 278.1288; found : 278.1295.

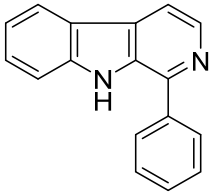


7-Fluoro-1-(pyridin-2-yl)-4,9-dihydro-3H-pyrido[3,4-b]indole (4dw). Yellow solid, ^{1}H NMR (400 MHz, d_6-DMSO): δ 11.56 (br s, 1H), 8.81 (d, J = 4.0 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.99 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.65 (dd. J_1 = 8.8 Hz, J_2 = 5.6 Hz, 1H), 7.59 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 1H), 7.42 (dd, J_1 = 10.4 Hz, J_2 = 2.4 Hz, 1H), 6.96 (td, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 4.04 (t, J = 8.4 Hz, 2H), 2.92 (t, J = 8.4 Hz, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 160.1 (d, J = 236.4 Hz), 155.4, 148.3, 137.2, 136.6 (d, J = 13.0 Hz), 127.9, 124.8, 121.3, 120.9, 120.7 (d, J = 10.4 Hz), 116.5, 108.3 (d, J = 24.9 Hz), 98.7 (d, J = 25.8 Hz), 48.3, 18.6. ^{19}F NMR (376 MHz, d_6-DMSO): δ -117.4 (S, 1F). MS (EI): m/z (%) 265 (M+, 82), 264 (100), 237 (18), 133 (7), 118 (9). HRMS Calcd for $[C_{16}H_{12}F_1N_3 + H]^+$: 266.1088; found : 266.1059.

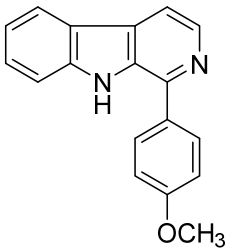
Typical procedure for aerobic oxidative PSR of tryptamines with alcohols for BC construction: The mixture of tryptamine **1a** (0.5 mmol, 0.0801g), benzyl alcohol **2a** (1.2 equiv., 0.0621 mL), TBN (100 mol%, 0.0586 mL), TEMPO (100 mol%, 0.0790g), and AcOH (0.5 mL) in a 100 mL Schlenk

tube was sealed under O_2 and then stirred at the 80 ^oC for 24 h. The reaction was then monitored by TLC and/or GC-MS. After completion of the reaction, the reaction mixture was quenched with dichloromethane and aqueous NaOH was added to adjust *p*H to about 8~9. The mixture was then extracted with dichloromethane for three to four times. The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using dichloromethane and methanol as an eluent (100:1), affording *β*-carboline **5aa** in 85% isolated yield.

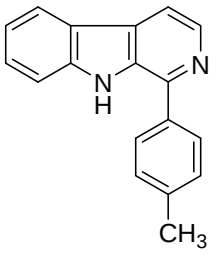
Characterization of BC products:



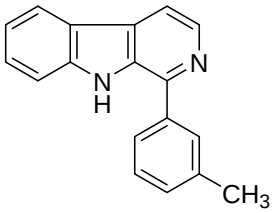
1-Phenyl-9H-pyrido[3,4-b]indole (5aa). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.54 (br s, 1H), 8.48 (d, J = 5.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 5.0 Hz, 1H), 8.06 (d, J = 7.5 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 7.5 Hz, 2H), 7.58-7.52 (m, 2H), 7.28 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.1, 141.1, 138.3, 138.2, 132.9, 129.2, 128.7, 128.5, 128.3, 128.1, 121.5, 120.8, 119.5, 113.8, 112.4. MS (EI): m/z (%) 244 (M+, 100) This compound was known: Pakhare, D. S.; Kusurkar, R. S. *Tetrahedron Lett.* **2015**, *56*, 6012-6015.



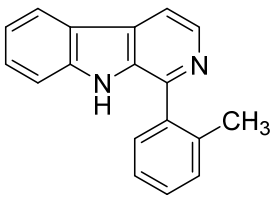
1-(4-Methoxyphenyl)-9H-pyrido[3,4-b]indole (5ab). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.51 (br s, 1H), 8.43 (d, J = 5.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 5.0 Hz, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 159.6, 142.1, 141.0, 138.2, 132.7, 130.9, 129.6, 128.9, 127.9, 121.5, 120.9, 119.4, 114.1, 113.2, 112.4, 55.3. MS (EI): m/z (%) 274 (M+, 100), 259 (13), 231 (21), 115 (17). This compound was known: Kamal, A.; Tangella, Y.; Manasa, K. L.; Sathish, M.; Srinivasulu, V.; Chetna, J.; Alarifi, A. *Org. Biomol. Chem.*, **2015**, *13*, 8652-8662.



1-(*p*-Tolyl)-9H-pyrido[3,4-b]indole (5ac). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.51 (br s, 1H), 8.46 (d, J = 5.0 Hz, 1H), 8.26 (d, J = 7.5 Hz, 1H), 8.10 (d, J = 5.0 Hz, 1H), 7.96 (d, J = 7.5 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 7.5 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.2, 141.0, 138.2, 137.9, 135.6, 132.9, 129.2, 129.0, 128.2, 128.0, 121.5, 120.8, 119.4, 113.6, 112.4, 20.9. MS (EI): m/z (%) 258 (M+, 100), 243 (10), 228(3), 214 (3), 188(3), 140(2) 128(5). This compound was known: Kulkarni, A.; Abid, M.; Huang, X. *Tetrahedron Lett*. **2009**, *50*, 1791-1794.

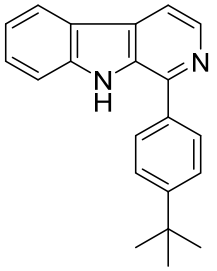


1-(*m*-Tolyl)-9H-pyrido[3,4-b]indole (5ad). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.53 (br s, 1H), 8.47 (d, J = 5.0 Hz, 1H), 8.27 (d, J = 7.5 Hz, 1H), 8.12 (d, J = 5.0 Hz, 1H), 7.86 (s, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.3, 141.0, 138.3, 138.2, 137.8, 133.0, 129.1, 129.0, 128.9, 128.6, 128.1, 125.5, 121.5, 120.8, 119.4, 113.7, 112.4, 21.2. MS (EI): m/z (%) 258 (M+, 100), 243 (13), 128 (21), 121 (14). HRMS Calcd for $[C_{18}H_{14}N_2 + Na]^+$: 281.1049; found : 281.1055.

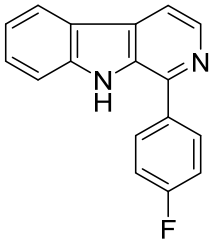


1-(*o*-Tolyl)-9H-pyrido[3,4-b]indole (5ae). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.21 (br s, 1H), 8.44 (d, J = 5.5 Hz, 1H), 8.27 (d, J = 7.5 Hz, 1H), 8.12 (d, J = 5.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.48 (d, 7.5 Hz, 1H), 7.45-7.39 (m, 3H), 7.26 (t, J = 7.5 Hz, 1H), 7.20 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 143.8, 140.9, 137.8, 136.2, 133.8, 130.5, 129.6,

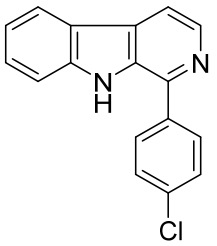
128.3, 128.1, 127.9, 125.8, 121.6, 120.8, 119.3, 113.6,112.2, 19.5. MS (EI): m/z (%) 258 (M+, 100), 243 (11), 128 (26). This compound was known: Horton, W.; Sood, A.; Peerannawar, S.; Kugyela, N.; Kulkarni, A.; Tulsan, R.; Tran, C. D.; Soule, J.; LeVine, H.; Török, B.; Török, M. *Bioorg. Med. Chem. Lett.*, **2017**, *27*, 232-236.



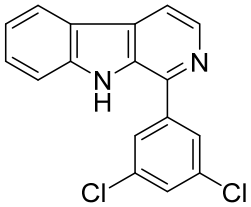
1-(4-*tert*-Butylphenyl)-9H-pyrido[3,4-b]indole (5af). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.54 (br s, 1H), 8.46 (d, J = 5.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 5.0 Hz, 1H), 7.98 (d, J = 8.0, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 150.9, 142.2, 141.1, 138.3, 135.7, 132.9, 129.0, 128.1, 125.4, 121.5, 120.8, 119.4, 113.6, 112.4, 34.4, 31.1. MS (EI): m/z (%) 300 (M+, 100), 269 (12), 257 (9), 243 (14), 207 (4), 128 (33), 115 (8). HRMS Calcd for $[C_{21}H_{20}N_2 + Na]^+$: 323.1519; found : 323.1544.



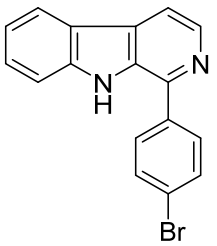
1-(4-Fluorophenyl)-9H-pyrido[3,4-b]indole (5ag). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.57 (br s, 1H), 8.46 (d, J = 5.0 Hz, 1H), 8.28 (d, J = 7.5 Hz, 1H), 8.13 (d, J = 5.0 Hz, 1H), 8.09 (q, J = 6.0 Hz, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 8.5 Hz, 2H), 7.28 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 162.3 (d, J = 244.7 Hz), 141.1 (d, J = 6.5 Hz), 138.3, 134.8 (d, J = 3.0 Hz), 132.9, 130.5 (d, J = 8.4 Hz), 129.2, 128.2, 121.6, 120.8, 119.5, 115.6, 115.4, 113.9, 112.3. ^{19}F NMR (376 MHz, d_6-DMSO): δ -113.3 (S, 1F). MS (EI): m/z (%) 262 (M+, 100), 243 (5), 233(3), 207 (3), 140(5), 131(3) 107(2). This compound was known: Kulkarni, A.; Abid, M.; Huang, X. *Tetrahedron Lett*. **2009**, *50*, 1791-1794.



1-(4-Chlorophenyl)-9H-pyrido[3,4-b]indole (5ah). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.59 (br s, 1H), 8.48 (d, J = 5.0 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 5.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.68-7.66 (m, 3H), 7.58 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 141.1, 140.8, 138.4, 137.1, 133.2, 132.9, 130.1, 129.4, 128.7, 128.2, 121.6, 120.8, 119.6, 114.2, 112.3. MS (EI): m/z (%) 278 (M+, 100), 242 (30), 207 (5), 139 (8), 121 (25), 107 (10). This compound was known: Kamal, A.; Sathish, M.; Prasanthi, A. V. G.; Chetna, J.; Tangella, Y.; Srinivasulu, V.; Shankaraiah, N.; Alarifi, A. *RSC Adv.*, **2015**, *5*, 90121-90126.

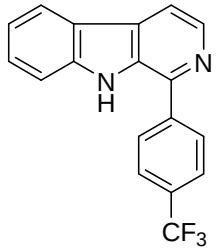


1-(3,5-Dichlorophenyl)-9H-pyrido[3,4-b]indole (5ai). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.74 (br s, 1H), 8.46 (d, J = 5.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 5.0 Hz, 1H), 8.00 (s, 2H), 7.69-7.68 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 141.6, 141.3, 138.8, 138.4, 134.4, 133.1, 129.8, 128.4, 127.8, 126.9, 121.6, 120.7, 119.7, 114.8, 112.4. MS (EI): m/z (%) 313 (M+, 40), 312 (100), 277 (28), 242 (27), 214 (9), 138 (27), 120 (10), 107 (7). HRMS Calcd for $[C_{17}H_{10}Cl_2N_2 + H]^+$: 313.0294; found : 313.0288.

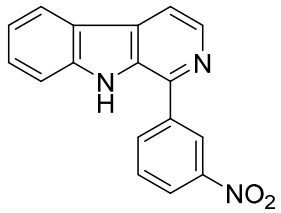


1-(4-Bromophenyl)-9H-pyrido[3,4-b]indole (5aj). a light tan solid, ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.59 (br s, 1H), 8.48 (d, J = 5.5 Hz, 1H), 8.28 (d, J = 7.5 Hz, 1H), 8.15 (d, J = 5.5 Hz, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.5 Hz,

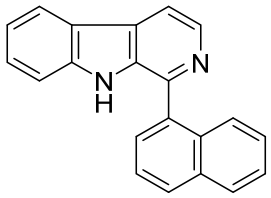
1H), 7.29 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 141.1, 140.9, 138.4, 137.5, 132.9, 131.6, 130.4, 129.4, 128.3, 121.9, 121.6, 120.8, 119.6, 114.2, 112.3. MS (EI): m/z (%) 323 (M+, 100), 242 (68), 214 (15), 207 (11), 162 (8), 140 (11), 122 (63), 108 (22), 94 (9). This compound was known: Durham, S. D.; Sierra, B.; Gomez, M. J.; Tran, J. K.; Anderson, M. O.; Eagon, S. *Tetrahedron Lett.*, **2017**, *58*, 2747-2750.



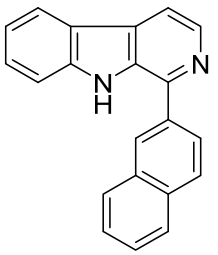
1-(4-Trifluoromethylphenyl)-9H-pyrido[3,4-b]indole (5ak). Light yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.69 (br s, 1H), 8.52 (d, J = 5.5 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 2H), 8.20 (d, J = 5.5 Hz, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.5 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.3, 141.2, 140.4, 138.5, 133.2, 129.6, 129.1, 128.6 (q, J = 47.5 Hz), 128.4, 125.5 (q, J = 3.6 Hz), 124.3 (q, J = 271.4 Hz), 121.6, 120.7, 119.6, 114.6, 112.3. ^{19}F NMR (376 MHz, d_6-DMSO): δ -61.1 (S, 3F). MS (EI): m/z (%) 312 (M+, 100), 291 (13), 242 (15), 146 (10). This compound was known: Kamal, A.; Sathish, M.; Prasanthi, A. V. G.; Chetna, J.; Tangella, Y.; Srinivasulu, V.; Shankaraiah, N.; Alarifi, A. *RSC Adv.*, **2015**, *5*, 90121-90126.



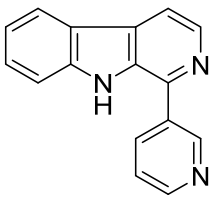
1-(3-Nitrophenyl)-9H-pyrido[3,4-b]indole (5al). yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.76 (br s, 1H), 8.83 (s, 1H), 8.54 (d, J = 5.0 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 5.0 Hz, 1H), 7.92 (t, J = 8.0 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 148.2, 141.2, 139.8, 139.4, 138.6, 134.6, 133.2, 130.3, 129.8, 128.5, 122.9, 121.7, 120.8, 119.7, 114.8, 112.3. MS (EI): m/z (%) 289 (M+, 94), 243 (100), 214 (10), 207 (34), 121 (14). This compound was known: Song, Y.; Wang, J.; Teng, S. F.; Kesuma, D.; Deng, Y.; Duan, J.; Wang, J. H.; Qi, R. Z.; Sim, M. M. *Bioorg. Med. Chem. Lett.*, **2002**, *12*, 1129-1132.



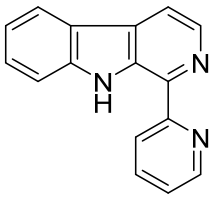
1-(Naphthalen-1-yl)-9H-pyrido[3,4-b]indole (5an). Off white solid, ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.19 (br s, 1H), 8.54 (d, J = 5.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 5.0 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 7.0 Hz, 1H), 7.72 (dd, J_1 = 7.5 Hz, J_2 = 13.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 6.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 6.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.7, 140.9, 137.9, 135.6, 134.6, 133.6, 131.2, 128.6, 128.5, 128.3, 128.1, 127.5, 126.3, 126.0, 125.6, 125.5, 121.7, 120.8, 119.4, 113.9, 112.2. MS (EI): m/z (%) 294 (M+, 100), 264 (10), 253(10), 239 (15), 215 (5), 188 (7), 146(18), 121 (5). This compound was known: Kamal, A.; Tangella, Y.; Manasa, K. L.; Sathish, M.; Srinivasulu, V.; Chetna, J.; Alarifi, A. *Org. Biomol. Chem.*, **2015**, *13*, 8652-8662.



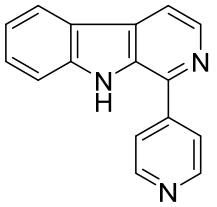
1-(Naphthalen-2-yl)-9H-pyrido[3,4-b]indole (5ao). Brown solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.73 (br s, 1H), 8.61 (s, 1H), 8.54 (d, J = 5.5 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 5.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 2H), 8.04 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.64-7.59 (m, 3H), 7.30 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.0, 141.1, 138.4, 135.7, 133.3, 132.9, 132.8, 129.3, 128.7, 128.2, 128.1, 127.55, 127.5, 126.6, 126.4, 126.3. 121.6, 120.9, 119.5, 113.9, 112.4. MS (EI): m/z (%) 294 (M+, 100), 264 (10), 253(5), 239 (8), 215 (3), 188 (5), 166(3), 146(15), 121 (5). This compound was known: Kulkarni, A.; Abid, M.; Huang, X. *Tetrahedron Lett*. **2009**, *50*, 1791-1794.



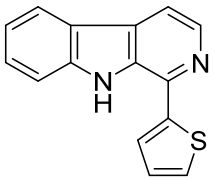
1-(Pyridin-3-yl)-9H-pyrido[3,4-b]indole (5ap). Yellow oil. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.78 (br s, 1H), 9.29 (s, 1H), 8.76 (d, J = 3.0 Hz, 1H), 8.54 (d, J = 5.0 Hz, 1H), 8.45 (d, J = 7.5 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 5.0 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.66 (dd, J_1 = 4.5 Hz, J_2 = 8.0 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 149.3, 149.0, 141.2, 139.3, 138.5, 135.8, 133.9, 133.3, 129.4, 128.3, 123.8, 121.6, 120.7, 119.6, 114.4, 112.4. MS (EI): m/z (%) 245 (M+, 100), 219 (11), 207 (8), 140 (9), 122 (13), 109 (9), 95 (4). This compound was known: Pakhare, D. S.; Kusurkar, R. S. *Tetrahedron Lett.* **2015**, *56*, 6012-6015.



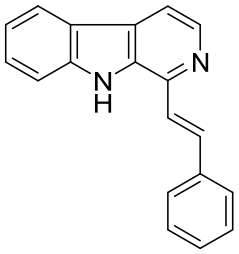
1-(Pyridin-2-yl)-9H-pyrido[3,4-b]indole (5aw). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.98 (br s, 1H), 8.91 (d, J = 5.0 Hz, 1H), 8.66 (d, J = 8.0 Hz, 1H), 8.52 (d, J = 5.0 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 5.0 Hz, 1H), 8.05 (t, J = 7.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 6.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 157.1, 148.7, 140.9, 138.1, 137.7, 137.2, 133.5, 129.9, 128.3, 123.3, 121.6, 120.8, 120.3, 119.5, 115.6, 112.8. MS (EI): m/z (%) 245 (M+, 100), 217 (10), 207 (7), 108 (5). This compound was known: Pakhare, D. S.; Kusurkar, R. S. *Tetrahedron Lett.* **2015**, *56*, 6012-6015.



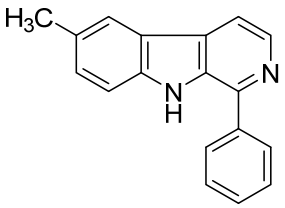
1-(Pyridin-4-yl)-9H-pyrido[3,4-b]indolev (5ax). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.70 (br s, 1H), 8.82 (d, J = 5.0 Hz, 2H), 8.54 (d, J = 5.0 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 5.0 Hz, 1H), 8.05 (d, J = 5.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 150.1, 145.3, 141.2, 139.1, 138.6, 133.3, 129.8, 128.5, 122.7, 121.6, 120.6, 119.8, 115.2, 112.4. MS (EI): m/z (%) 245 (M+, 100), 217 (14), 207 (25), 109 (11). HRMS Calcd for $[C_{16}H_{11}N_3 + H]^+$: 246.1026; found : 246.1035.



1-(Thiophen-2-yl)-9H-pyrido[3,4-b]indole (5aq). Brown solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.53 (br s, 1H), 8.38 (d, J = 5.0 Hz, 1H), 8.27 (d, J = 7.5 Hz, 1H), 8.14 (d, J = 3.5 Hz, 1H), 8.10 (d, J = 5.0 Hz, 1H), 7.77-7.74 (m, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 3.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 143.6, 141.2, 138.0, 136.5, 130.8, 129.7, 128.4, 128.3, 128.0, 125.7, 121.5, 120.7, 119.9, 113.9, 112.6. MS (EI): m/z (%) 250 (M+, 100), 205 (28), 125 (7), 103 (14). This compound was known: Huang, Y.-Q.; Song, H, -J.; Liu, Y.-X.; Wang, Q.-M. *Chem. Eur. J.* **2018**, *24*, 2065-2069.

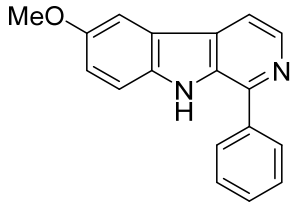


(*E*)-1-(2-Phenylvinyl)-9H-pyrido[3,4-b]indole (5ar). yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.92 (br s, 1H), 8.40 (d, J = 5.0 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.06-8.03 (m, 2H), 7.91 (d, J = 15.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 140.5, 139.0, 138.3, 136.8, 134.1, 131.5, 128.8, 128.5, 128.2, 127.0, 123.3, 121.8, 120.9, 119.4, 113.7, 111.8. MS (EI): m/z (%) 270 (M+, 100). This compound was known: Cao, R.; Yi, W.; Wu, Q.; Guan, X.; Feng, M.; Ma, C.; Chen, Z.; Song, H.; Peng, W. *Bioorg. Med. Chem. Lett.*, **2008**, *18*, 6558-6561.

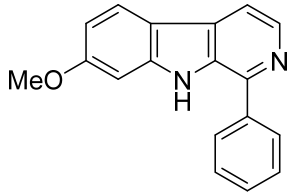


6-Methyl-1-phenyl-9H-pyrido[3,4-b]indole (5ba). yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.41 (br s, 1H), 8.44 (d, J = 5.0 Hz, 1H), 8.07-8.03 (m, 4H), 7.61 (t, J = 7.5 Hz, 2H), 7.56-7.51 (m, 2H), 7.38 (d, J = 8.5 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.0, 139.4, 138.4,

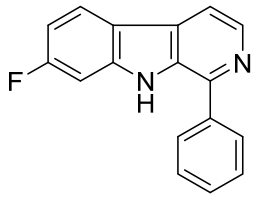
138.1, 133.2, 129.6, 128.9, 128.6, 128.4, 128.3, 128.2, 121.0, 120.9, 113.7, 112.1, 21.0. MS (EI): m/z (%) 258 (M+, 100), 242 (6), 227 (2), 179 (5), 152 (4), 128 (24), 77 (3). This compound was known: Kulkarni, A.; Abid, M.; Huang, X. *Tetrahedron Lett*. **2009**, *50*, 1791-1794.



6-Methoxy-1-phenyl-9H-pyrido[3,4-b]indole (5ca). a crystalline solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.38 (br s, 1H), 8.45 (d, J = 5.0 Hz, 1H), 8.11 (d, J = 5.5 Hz, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 2.5 Hz, 1H), 7.64-7.59 (m, 3H), 7.53 (t, J = 7.5 Hz, 1H), 7.23 (dd, J_1 = 2.5 Hz, J_2 = 8.5 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 153.5, 142.2, 138.5, 137.7, 135.9, 133.5, 129.0, 128.6, 128.4, 128.3, 121.1, 118.2, 113.9, 113.2, 103.3, 55.6. MS (EI): m/z (%) 274 (M+, 86), 259 (100), 231 (25), 203 (3), 176 (3), 153 (4), 137 (7), 115 (21). This compound was known: Kulkarni, A.; Abid, M.; Huang, X. *Tetrahedron Lett*. **2009**, *50*, 1791-1794.

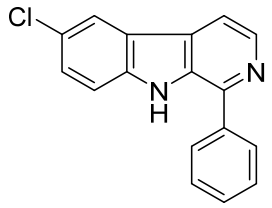


7-Methoxy-1-phenyl-9H-pyrido[3,4-b]indole (5ja). a dark yellow crystalline solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.43 (br s, 1H), 8.42 (d, J = 5.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.04-7.98 (m, 3H), 7.62 (t, J = 7.5 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.12 (s, 1H), 6.89 (dd, J_1 = 2.5 Hz, J_2 = 9.0 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 160.2, 142.7, 141.4, 138.6, 138.5, 133.1, 129.4, 128.6, 128.3, 128.2, 122.4, 114.5, 113.1, 109.3, 95.1, 55.2. MS (EI): m/z (%) 274 (M+, 100), 259 (4), 245 (6), 231 (45), 207 (22), 136 (7), 115 (16), 77 (4). This compound was known: Eagon, s.; Anderson, M. O. *Eur. J. Org. Chem.*, **2014**, *2014*, 1653-1665.

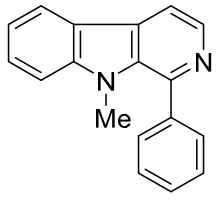


7-Fluoro-1-phenyl-9H-pyrido[3,4-b]indole (5da). White solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ

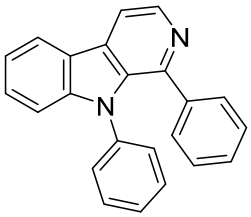
11.66 (br s, 1H), 8.48 (d, J = 5.0 Hz, 1H), 8.30 (dd, J_1 = 6.0 Hz, J_2 = 9.0 Hz, 1H), 8.10 (d, J = 5.0 Hz, 1H), 8.02 (d, J = 7.0 Hz, 2H), 7.62 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.0 Hz, 1H), 7.36 (dd, J_1 = 2.0 Hz, J_2 = 9.5 Hz, 1H), 7.21 (td, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 162.5 (d, J = 241.3 Hz), 142.1, 141.8 (d, J = 13.3 Hz), 138.6, 138.2, 133.6 (d, J = 1.9 Hz), 128.9, 128.7, 128.5, 128.3, 123.3 (d, J = 10.9 Hz), 117.6, 113.6, 107.9(d, J = 24.6 Hz), 98.4 (d, J = 26.1 Hz). ^{19}F NMR (376 MHz, d_6-DMSO): δ -111.8 (S, 1F). MS (EI): m/z (%) 262 (M+, 100), 236 (4), 207 (14), 189 (2), 158 (6), 130 (24), 116 (5), 77 (3). This compound was known: Song, Y.; Wang, J.; Teng, S. F.; Kesuma, D.; Deng, Y.; Duan, J.; Wang, J. H.; Qi, R. Z.; Sim, M. M. *Bioorg. Med. Chem. Lett.*, **2002**, *12*, 1129-1132.



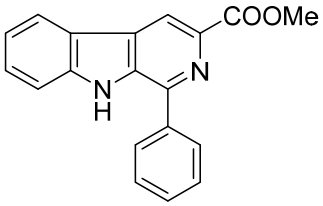
6-Chloro-1-phenyl-9H-pyrido[3,4-b]indole (5ea). a light brown solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.67 (br s, 1H), 8.49 (d, J = 5.0 Hz, 1H), 8.41 (d, J = 2.0 Hz, 1H), 8.18 (d, J = 5.0 Hz, 1H), 8.03 (d, J = 7.0 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.63 (t, J = 7.0 Hz, 1H), 7.58-7.52 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 142.6, 139.5, 138.6, 138.1, 133.5, 128.7, 128.6, 128.3, 128.0, 123.8, 122.1, 121.1, 114.1, 113.9. MS (EI): m/z (%) 279 (M+, 38), 278 (100), 266 (3), 252 (7), 242 (22), 217 (2), 207 (57), 190 (8), 176 (5), 121 (18), 107 (9), 77 (6). This compound was known: Durham, S. D.; Sierra, B.; Gomez, M. J.; Tran, J. K.; Anderson, M. O.; Eagon, S. *Tetrahedron Lett.*, **2017**, *58*, 2747-2750.



9-*N*-Methyl-1-phenyl-9H-pyrido[3,4-b]indole (5ha). yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.42 (d, J = 5.0 Hz, 1H), 8.32 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 5.0 Hz, 1H), 7.64-7.62 (m, 4H), 7.57-7.52 (m, 3H), 7.34-7.30 (m, 1H), 3.44 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 143.7, 142.2, 139.6, 137.9, 134.3, 129.6, 129.2, 128.4, 128.2, 127.9, 121.5, 120.4, 119.7, 113.7, 110.4, 32.7. MS (EI): m/z (%) 258 (M+, 100). This compound was known: Wang, Z.-X.; Xiang, J.-C.; Cheng, Y.; Ma, J.-T.; Wu, Y.-D.; Wu, A.-X. *J. Org. Chem*. **2018**, *83*, 12247-12254.



1,9-Diphenyl-9H-pyrido[3,4-b]indole (5ia). yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (d, J = 5.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 5.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.38-7.35 (m, 2H), 7.22-7.20 (m, 2H), 7.15-7.12 (m, 3H), 7.09-7.00 (m, 5H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.0, 142.3, 139.2, 138.2, 137.2, 133.7, 130.3, 128.8, 128.7, 127.4, 127.2, 127.0, 126.9, 126.5, 121.8, 121.0, 120.8, 113.7, 110.7. HRMS Calcd for $[C_{17}H_{15}F_1N_2 + H]^+$: 267.1292; found : 267.1284.

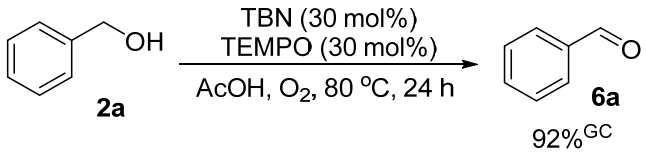


Methyl 1-phenyl-9H-pyrido[3,4-b]indole-3-carboxylate (5ka). Yellow solid. ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.97 (br s, 1H), 8.95 (s, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.67-7.57 (m, 4H), 7.34 (t, J = 7.5 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 166.0, 142.1, 141.5, 137.5, 136.7, 134.6, 129.1, 128.9, 128.8, 128.6, 128.5, 122.0, 121.1, 120.4, 116.6, 112.7, 52.0. MS (EI): m/z (%) 302 (M+, 100). This compound was known: Z.-X. Wang, J.-C. Xiang, Y. Cheng, J.-T. Ma, Y.-D. Wu, A.-X. Wu, *J. Org. Chem*. **2018**, *83*, 12247-12254.

Detailed procedure for synthesis of *β*-carboline by decarboxylative PSR of tryptophan with benzyl alcohol. The mixture of tryptophan (0.5 mmol, 0.1021g), benzyl alcohol **2a** (1.2 equiv., 0.0621 mL), TBN (100 mol%, 0.0586 mL), TEMPO (100 mol%, 0.0790g), and AcOH (2.0 mL) in a 100 mL Schlenk tube was sealed under O_2 and then stirred at 80 ^{o}C for 24 h. The reaction was then monitored by TLC and/or GC-MS. The reaction mixture was then quenched with dichloromethane and aqueous NaOH was added to adjust *p*H to about 8~9. The mixture was then extracted with dichloromethane for three to four times. The combined organic layer was dried over Na_2SO_4 and solvent evaporated *in vacuo*. The residue was purified by column chromatography on silica gel using dichloromethane and methanol as an eluent (100:1), affording *β*-carboline **5aa** in 52% isolated yield. See the proceeding section for characterization data of **5aa**.

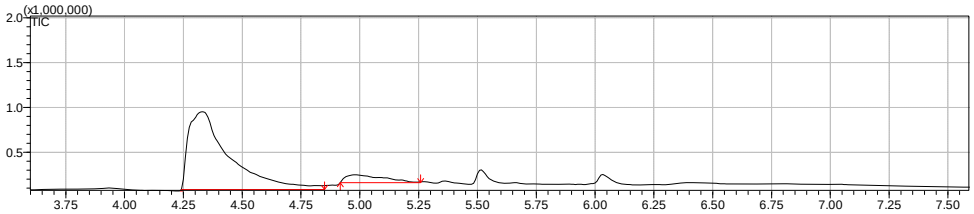
Control Reactions for Mechanistic Studies

1. TBN/TEMPO-catalyzed aerobic oxidation of alcohol under O_2 (eq. 3 in the main text).



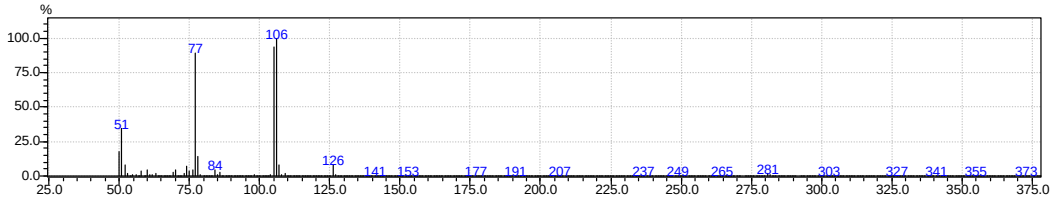
Experimental Procedure: The mixture of benzyl alcohol (0.6 mmol, 1.2 equiv., 0.0621 mL), TBN (30 mol%, 0.0176 mL), and TEMPO (30 mol%, 0.0234g) in AcOH (0.5 mL) in a 100 mL Schlenk tube was sealed under O_2 and stirred at 80 °C for 24 h. The reaction was then monitored by TLC and/or GC-MS, which revealed that large amount of benzaldehyde (**6a**) was generated in ca. 92% GC yield..

GC Spectra:

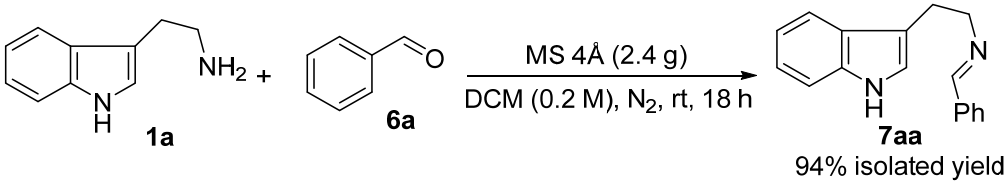


MS Spectra:

4.342 min, m/z = 106, PhCHO (**6a**)



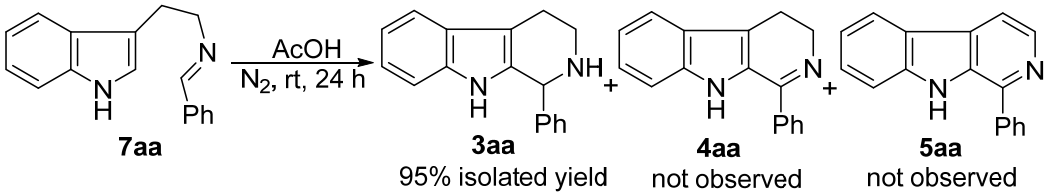
2. Condensation of tryptamine (1a) with benzaldehyde (6a) under N_2 at room temperature in DCM (eq. 4 in the main text).



Experimental Procedure: According to the literature procedure (Youn, S. W. *J. Org. Chem*. **2006**, *71*, 2521-2523), the mixture of tryptamine **1a** (5 mmol, 0.8010g), benzaldehyde **6a** (5.25 mmol, 1.05 equiv. 0.5336 mL), and 4A Molecular sieve (2.4 g, 480 mg / 1 mmol) in DCM (25 mL, 0.2 M) in a 100 mL Schlenk tube was sealed under N_2 and stirred at the room temperature for 18 h. The mixture

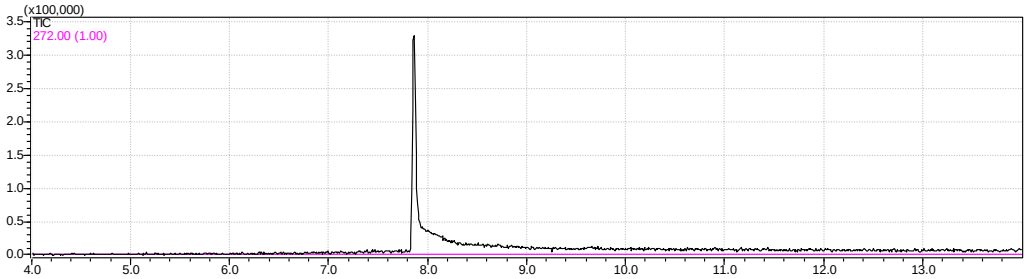
was monitored by TLC and/or GC-MS and then purified by column chromatography on silica gel using dichloromethane and methanol as the eluent (10:1), affording (*E*)-N-(2-(1H-indol-3-yl)ethyl)-1-phenylmethanimine (**7aa**) in 94% isolated yield.

3. Cyclization of 7aa under N_2 at room temperature in AcOH (eq. 5 in the main text).



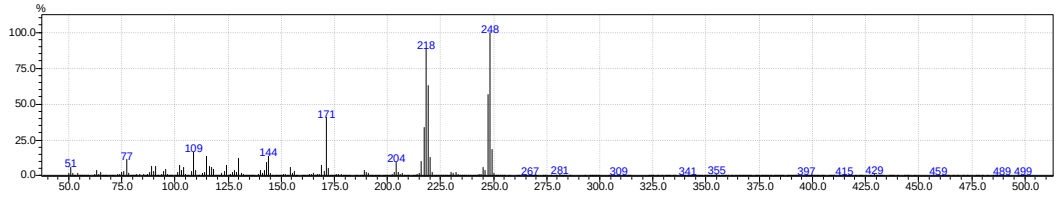
Experimental Procedure: The solution of imine **7aa** (0.5 mmol, 0.1240g) in AcOH (0.5 mL) in a 100 mL Schlenk tube was sealed under N_2 and stirred at room temperature for 24 h. The reaction was then monitored by TLC and/or GC-MS, which revealed that **3aa** was generated as the major product and obtained in 95% isolated yield by column chromatography. In contrast, no **4aa** and **5aa** were observed under the present conditions. This result indicates that the intermediate **7aa** obtained under neutral conditions (see control reaction 2 as above) also tends to undergo cyclization reaction under the acidic conditions in AcOH to afford cyclic product **3aa**.

GC Spectra:

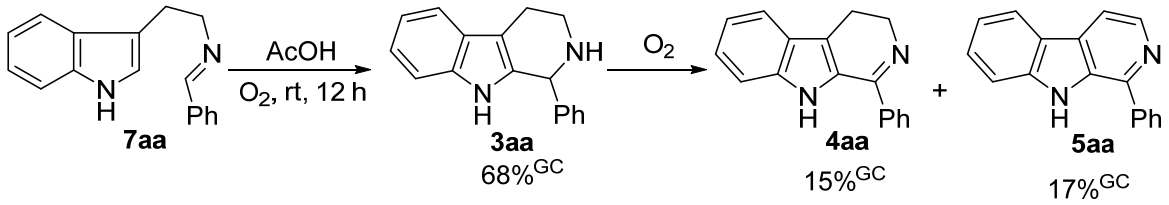


MS Spectra:

7.900 min, m/z = 248, **3aa**

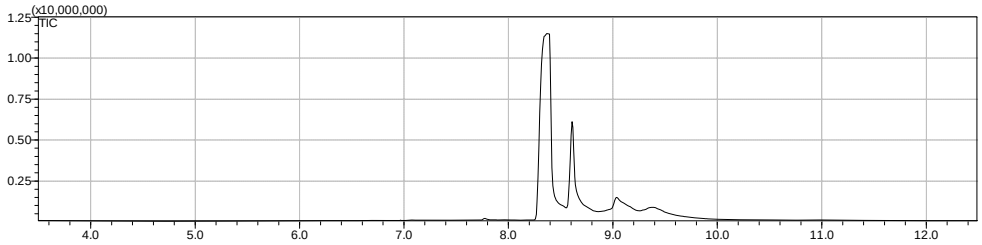


4. Cyclization of 7aa under O_2 at room temperature in AcOH.



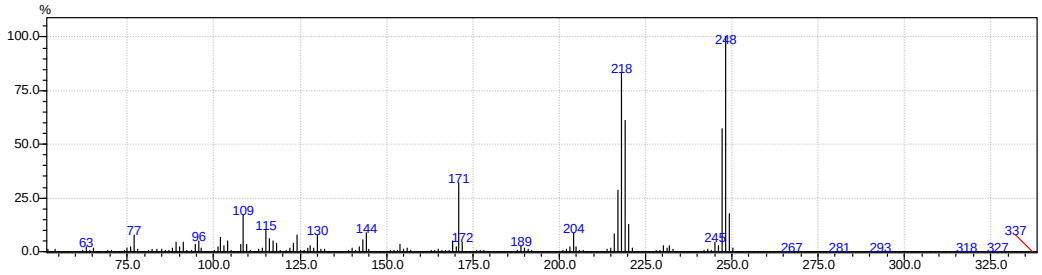
Experimental Procedure: The solution of imine **7aa** (0.5 mmol, 0.1240g) in AcOH (0.5 mL) in a 100 mL Schlenk tube was sealed under O_2 and stirred at room temperature for 12 h. The reaction was then monitored by TLC and/or GC-MS, which revealed that, in addition to the formation of **3aa**, **4aa** and **5aa** were also generated in low yields under the present conditions. In comparison with the reaction under N_2 (see control reaction 4 as above), this result indicates that **4aa** and **5aa** are most possibly generated via the oxidation of **3aa** by O_2.

GC Spectra:

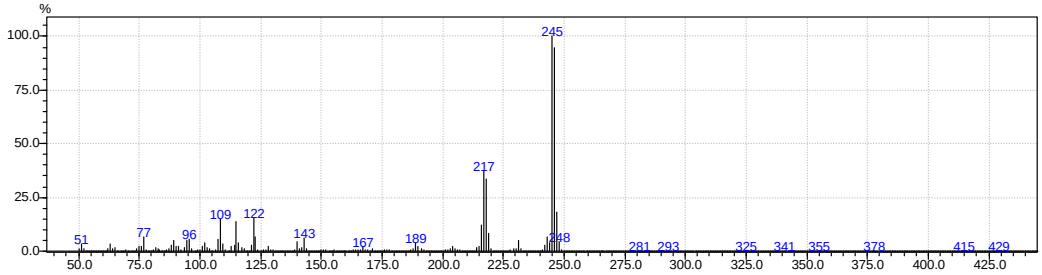


MS Spectra:

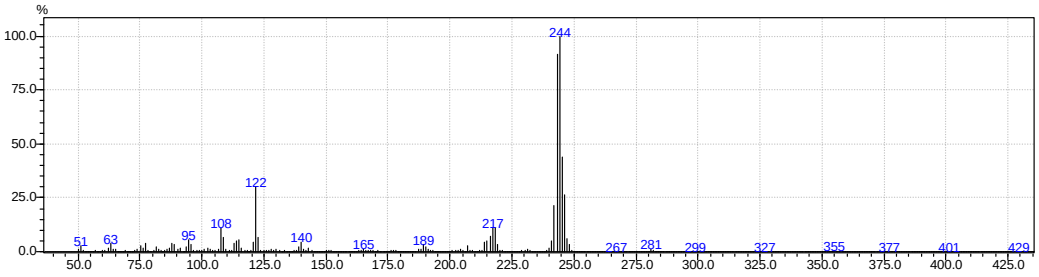
8.367 min, m/z = 248, **3aa**



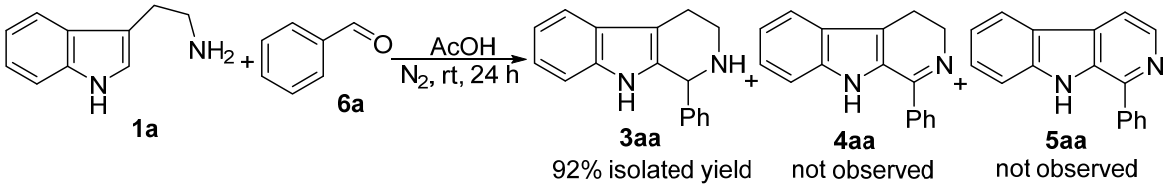
8.608 min, m/z = 246, **4aa**



9.042 min, m/z = 244, **5aa**

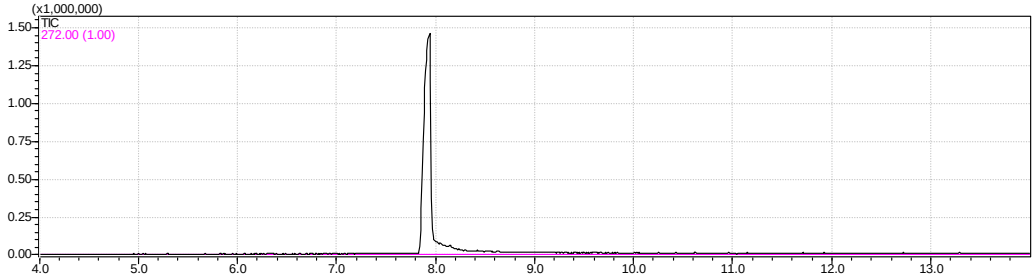


5. Cyclocondensation of tryptamine (1a) with benzaldehyde (6a) under N_2 at room temperature in AcOH (eq. 6 in the main text).



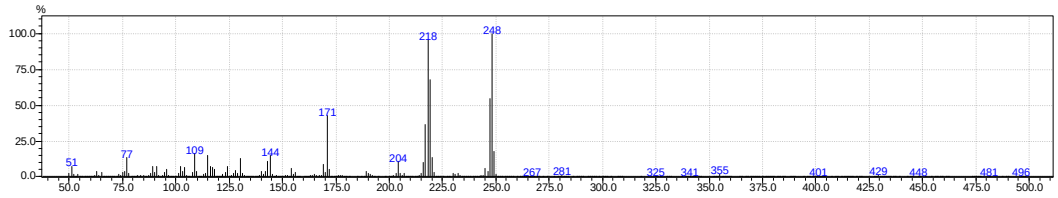
Experimental Procedure: The mixture of tryptamine **1a** (0.5 mmol, 0.8010g) and benzaldehyde (1.05 equiv. 0.0534 mL) in AcOH (0.5 mL) in a 100 mL Schlenk tube was sealed under N_2 and stirred at room temperature for 24 h. The reaction was then monitored by TLC and/or GC-MS, which revealed that **3aa** was generated as the major product and obtained in 92% isolated yield by column chromatography. In contrast, no **4aa** and **5aa** were observed under the present conditions. This result indicates that, under acidic conditions such as in AcOH, the mixture of **1a** and **6a** tends to undergo cyclocondensation reaction to afford cyclic product **3aa** rather than the usual condensation reaction in neutral solvents to give imine intermediate **7aa** (see control reaction 2 as above).

GC Spectra:

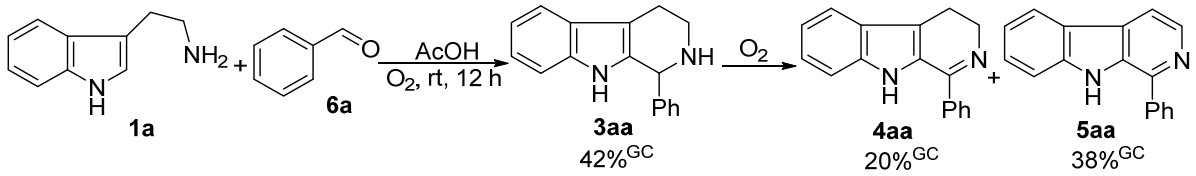


MS Spectra:

7.900 min, m/z = 248, **3aa**

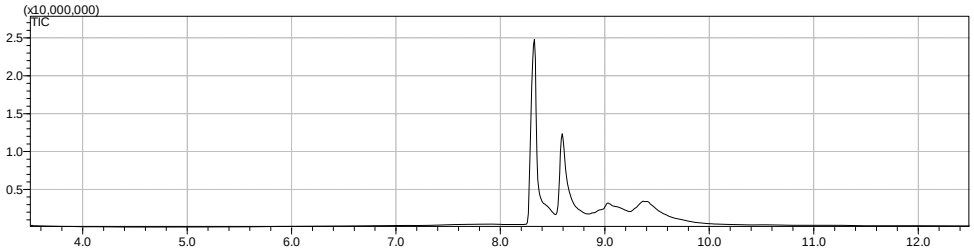


6. Cyclocondensation of tryptamine (1a) with benzaldehyde (6a) under O_2 at room temperature in AcOH.



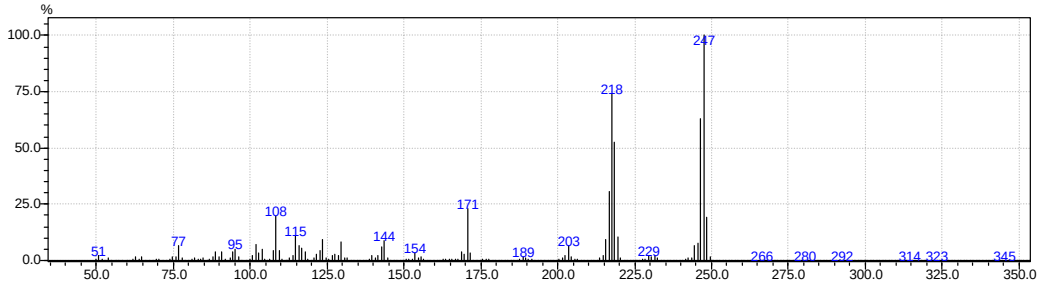
Experimental Procedure: The mixture of tryptamine **1a** (0.5 mmol, 0.8010g) and benzaldehyde **6a** (1.05 equiv. 0.0534 mL) in AcOH (0.5 mL) in a 100 mL Schlenk tube was sealed under O_2 and stirred at the room temperature for 12 h. The reaction was then monitored by TLC and/or GC-MS, which revealed that, in addition to the formation of **3aa**, **4aa** and **5aa** were also generated under the present conditions. In comparison with the reaction under N_2 (see control reaction 3 as above), this result indicates that **4aa** and **5aa** are most possibly generated via the oxidation of **3aa** by O_2.

GC Spectra:

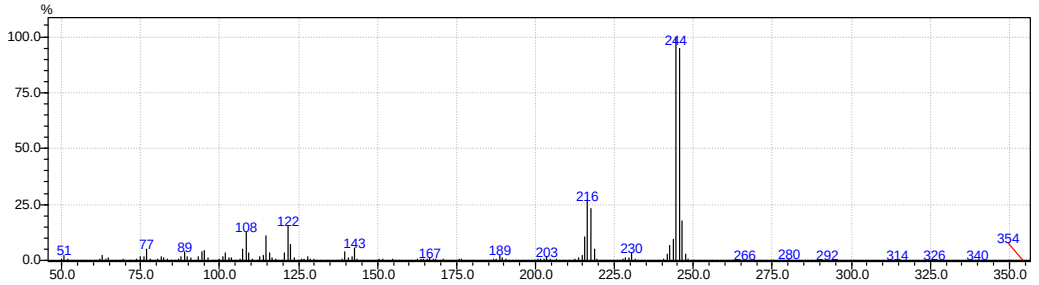


MS Spectra:

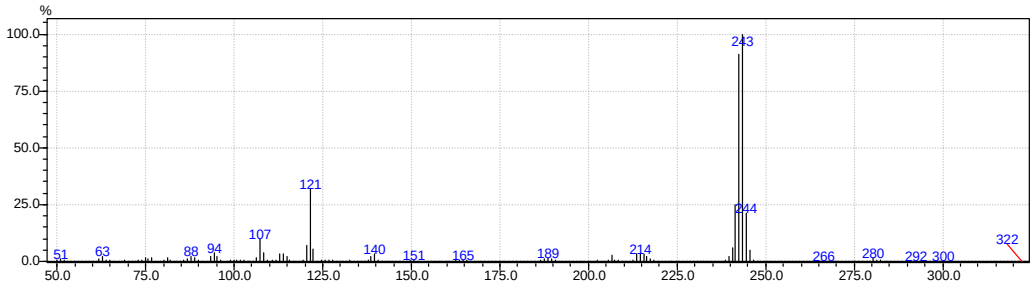
8.317 min, m/z = 248, **3aa**



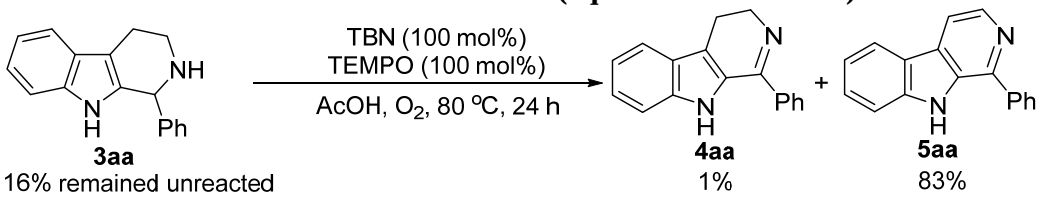
8.617 min, m/z = 246, **4aa**



9.408 min, m/z = 244, **5aa**



7. Oxidation of 3aa under the standard conditions (eq. 7 in the main text)



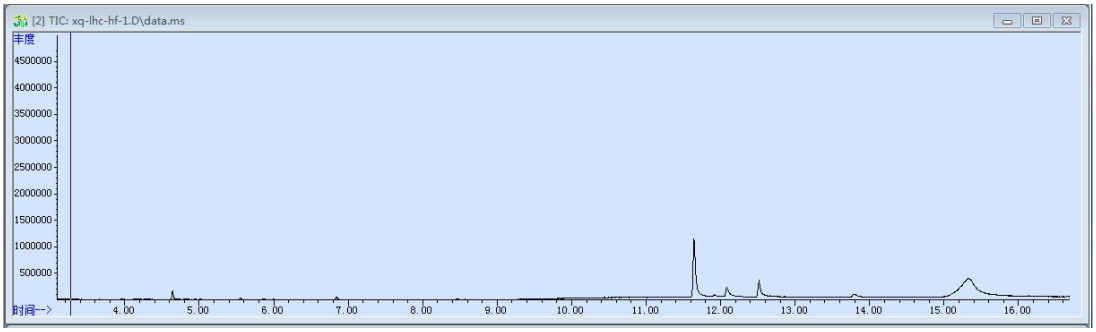
3aa
16% remained unreacted

4aa
1%

5aa
83%

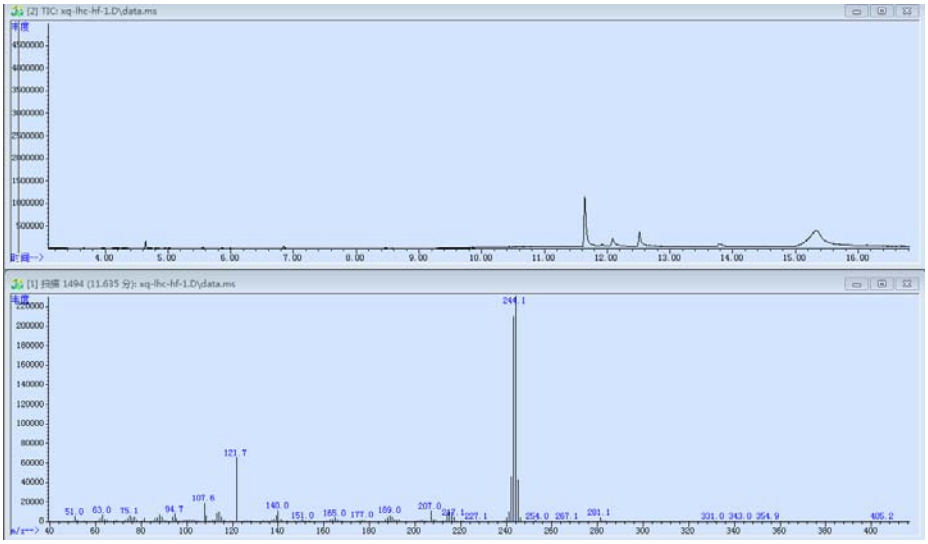
Experimental Procedure (the standard conditions for BC construction, Table 3 in the main text): The prepared tetrahydro-*β*-carboline **3aa** (0.5 mmol, 0.1280g) was mixed with TEMPO (0.0781g, 100 mol%) and TBN (0.0587 mL, 100 mol%) in AcOH (0.5 mL) in a 100 mL Schlenk tube. The mixture was then sealed under O_2, stirred at 80 °C for 24 h, and monitored by GC-MS. The result showed that the ratio of **3aa**/**4aa**/**5aa** is 16/1/83, revealing that dihydro-*β*-carbolines (although low yields in this case) and *β*-carbolines are indeed the oxidation products of the tetrahydro-*β*-carbolines. Please see the GC-MS Spectra and analysis below.

GC Spectra:

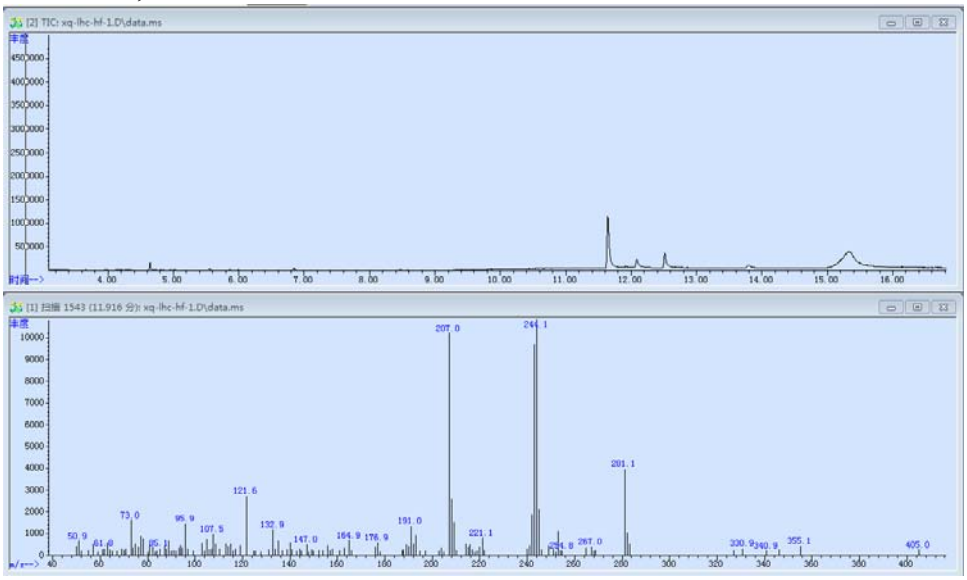


MS Spectra:

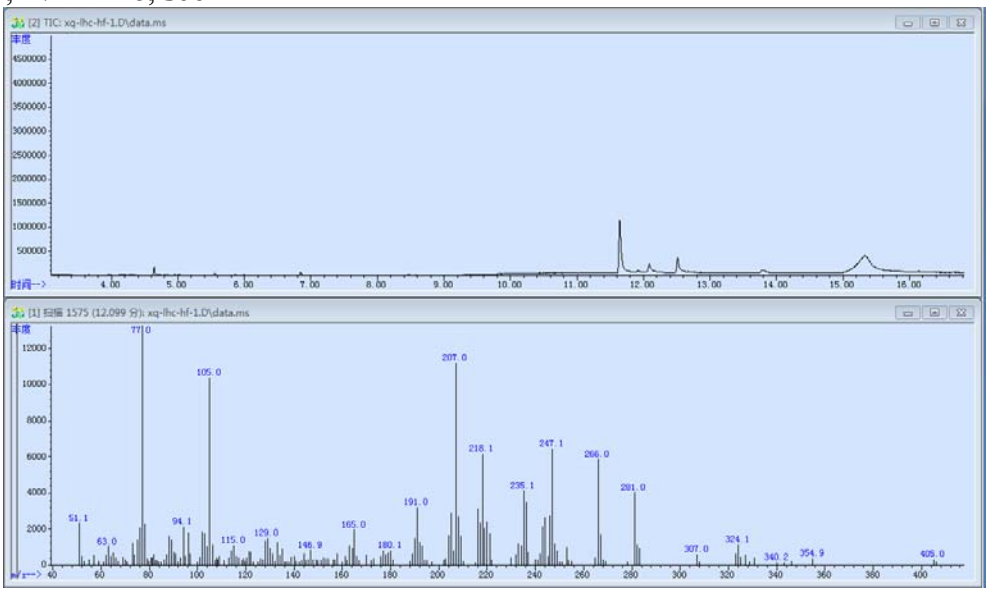
11.635 min, m/z = 244, **5aa**



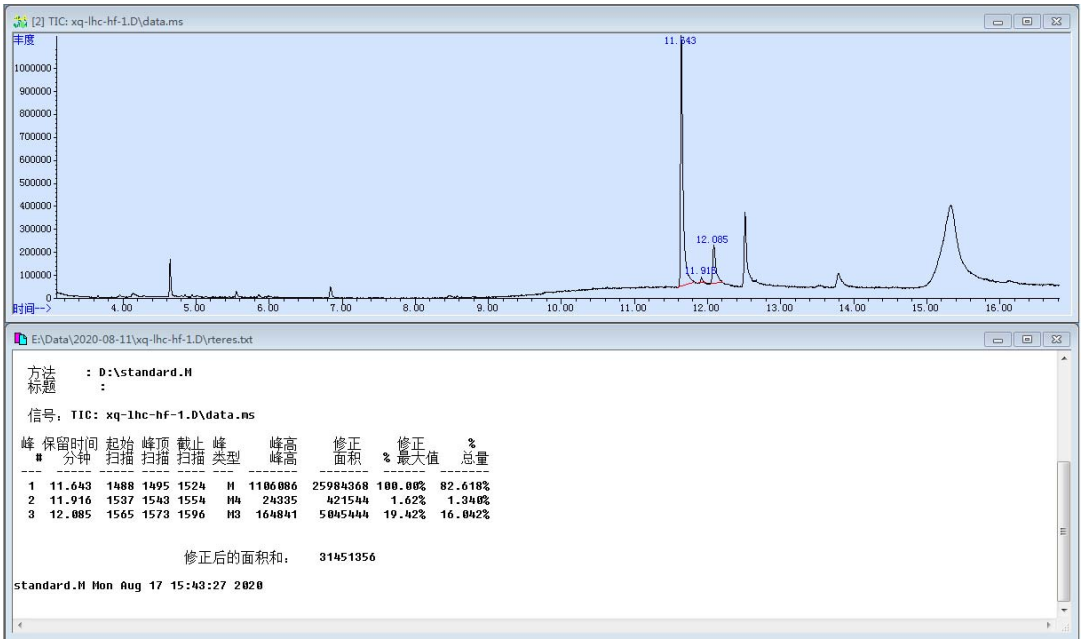
11.916 min, m/z = 246, **4aa**



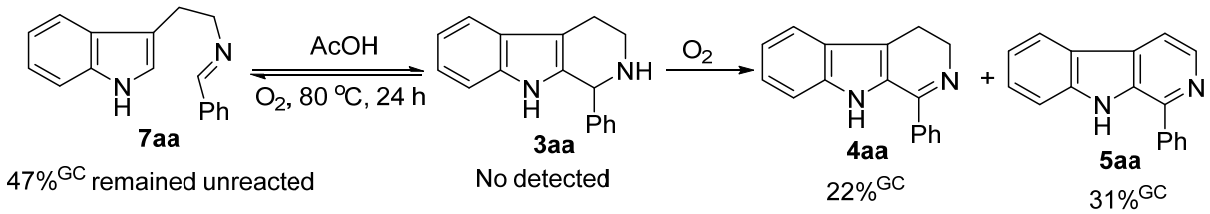
12.099 min, m/z = 248, **3aa**



3aa:**4aa**:**5aa** = 16:1:83

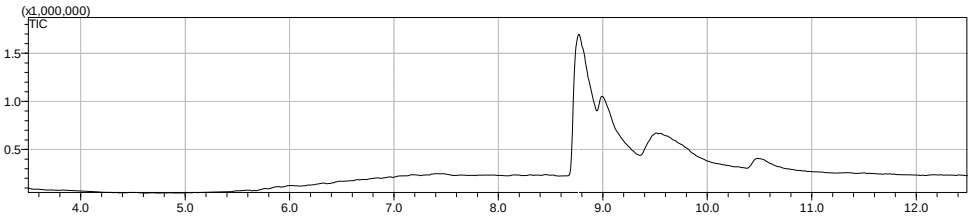


8. Cyclization of 7aa under O_2 at 80 ^oC in AcOH (eq. 8 in the main text).



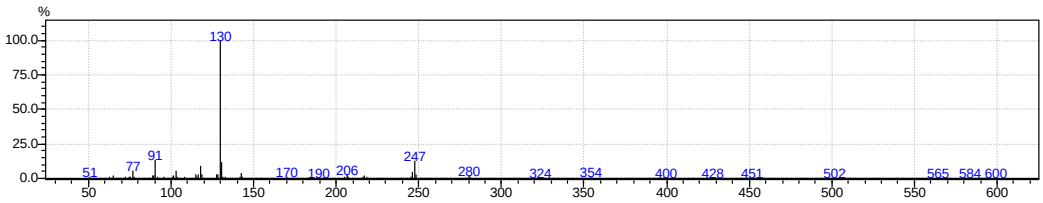
Experimental Procedure: The solution of imine **7aa** (0.5 mmol, 0.1240g) in AcOH (0.5 mL) in a 100 mL Schlenk tube was sealed under O_2 and then stirred at 80 ^oC for 24 h. The reaction was then monitored by TLC and/or GC-MS, which revealed that, in addition to the formation of **4aa** and **5aa**, considerable amounts of **7aa** remained unreacted. This result indicates that conversion of **7aa** to **3aa** is most likely an equilibrium, so that at higher temperatures such as at 80 ^oC and without the facilitation of cyclization reagents, **3aa** tends to convert back to **7aa**.

GC Spectra:

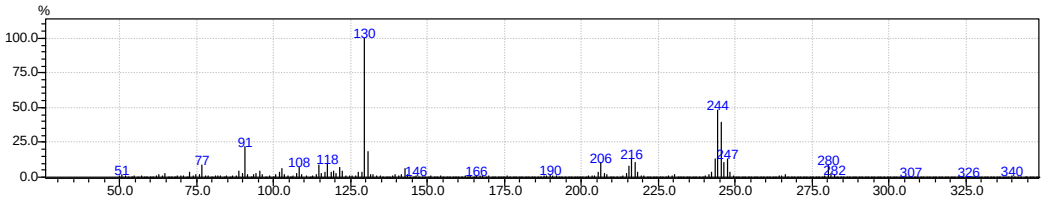


MS Spectra:

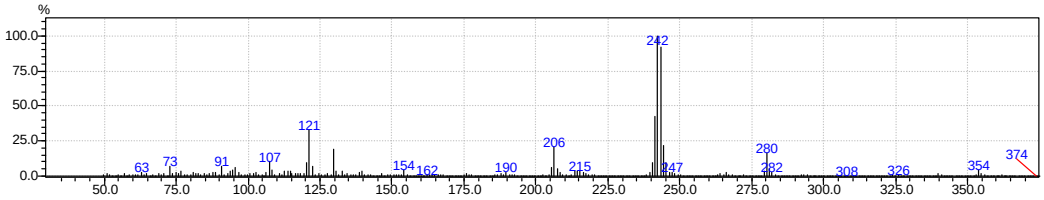
8.792 min, m/z = 248, **7aa**



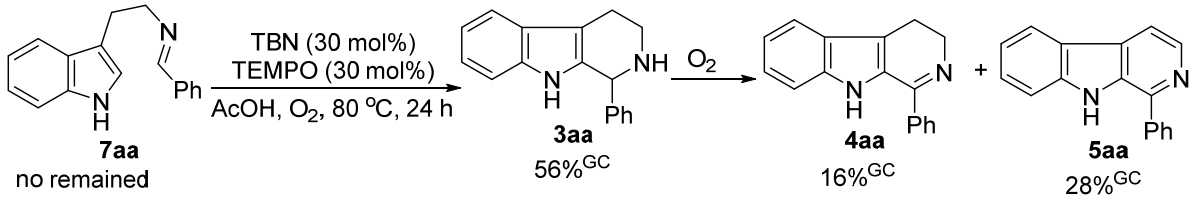
9.017 min, m/z = 246, **4aa**



9.525 min, m/z = 244, **5aa**

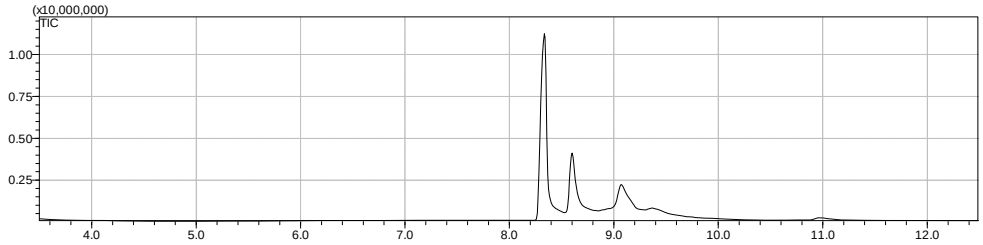


9. Cyclization of 7aa under O_2 at 80 ^oC in AcOH in the presence of TBN/TEMPO (eq. 9 in the main text).



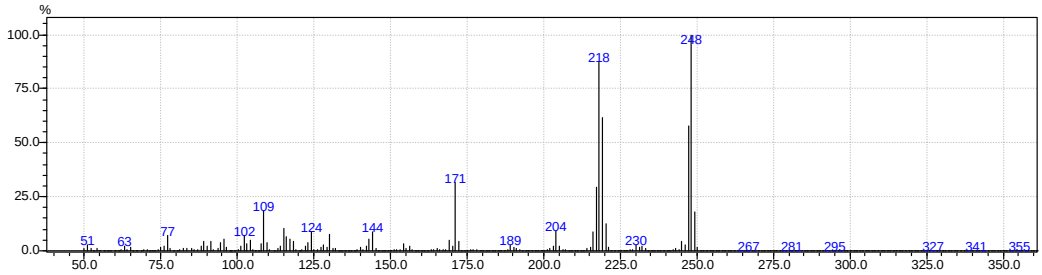
Experimental Procedure: The mixture of imine **7aa** (0.5 mmol, 0.1240g), TBN (30 mol%, 0.0176 mL), and TEMPO (30 mol%, 0.0234g) in AcOH (0.5 mL) in a 100 mL Schlenk tube was sealed under O_2 and stirred at the 80 ^oC for 24 h. The reaction was then monitored by TLC and/or GC-MS, which revealed that, quite different to the above reaction (control reaction 7) without the addition of TBN/TEMPO, in addition to the formation of **4aa** and **5aa**, large amounts of **3aa** was also generated under the present conditions. This result indicates that, although the conversion of **7aa** to **3aa** is an equilibrium reaction, ***the presence of TBN/TEMPO can greatly facilitate the cyclization of 7aa to 3aa***, thus promoting the whole reaction go forward to finally consume **7aa** completely and afford large amounts of **3aa**, **4aa** and **5aa** under the present conditions.

GC spectra:

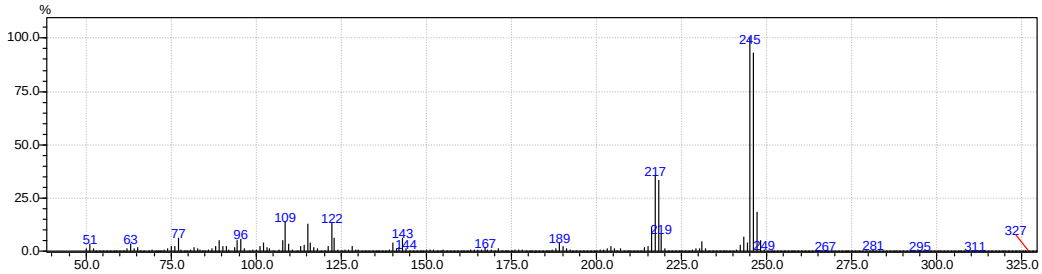


MS Spectra:

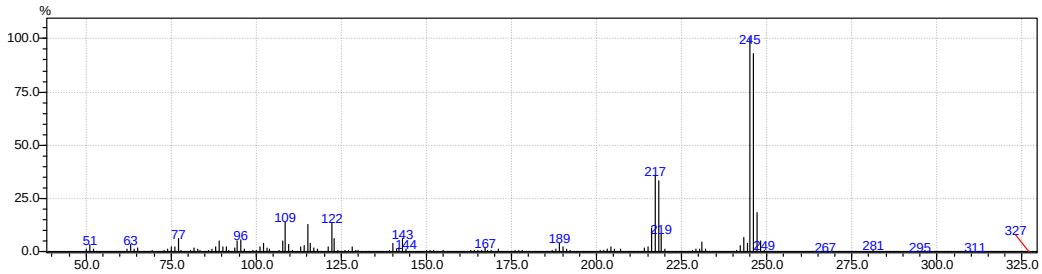
8.325 min, m/z = 248, **3aa**



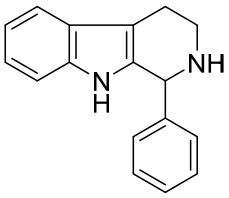
8.600 min, m/z = 246, **4aa**



9.075 min, m/z = 244, **5aa**

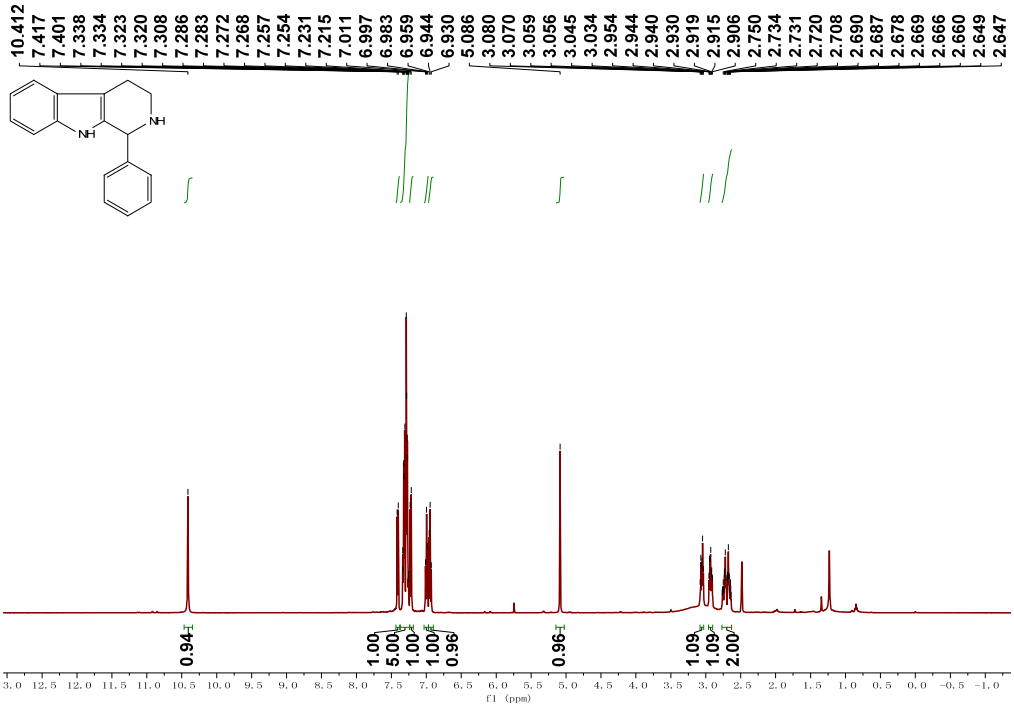


^{1}H, ^{13}C, and ^{19}F NMR of the Products

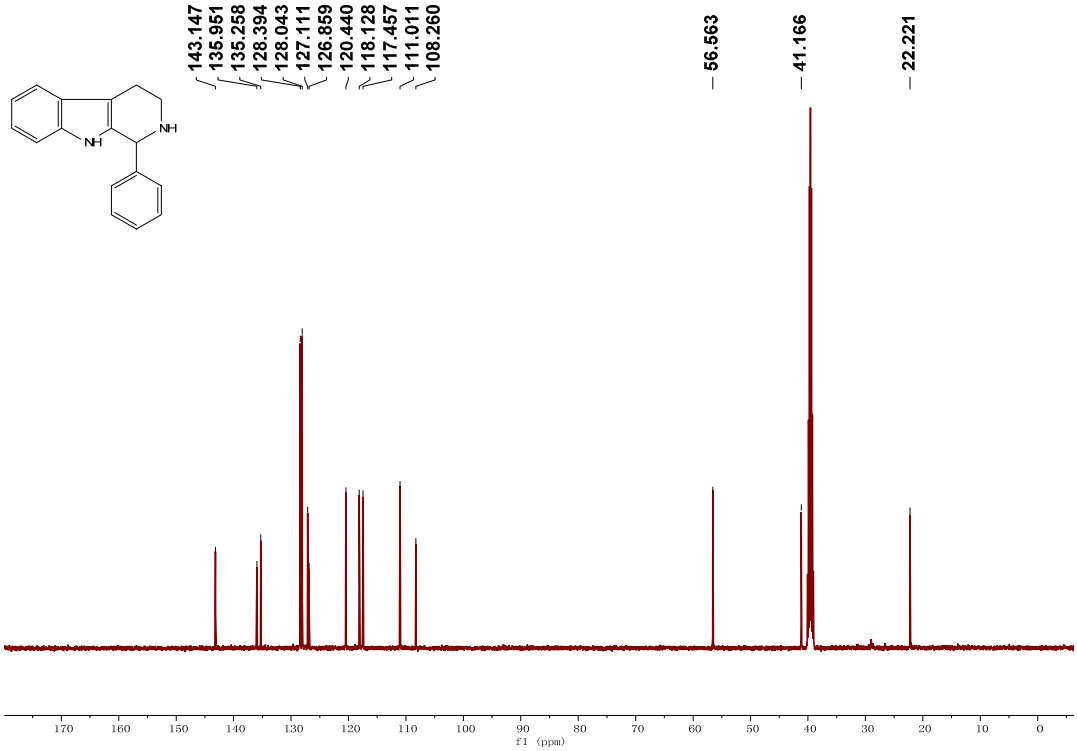


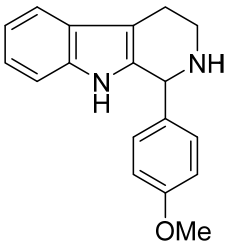
3aa

^{1}H NMR



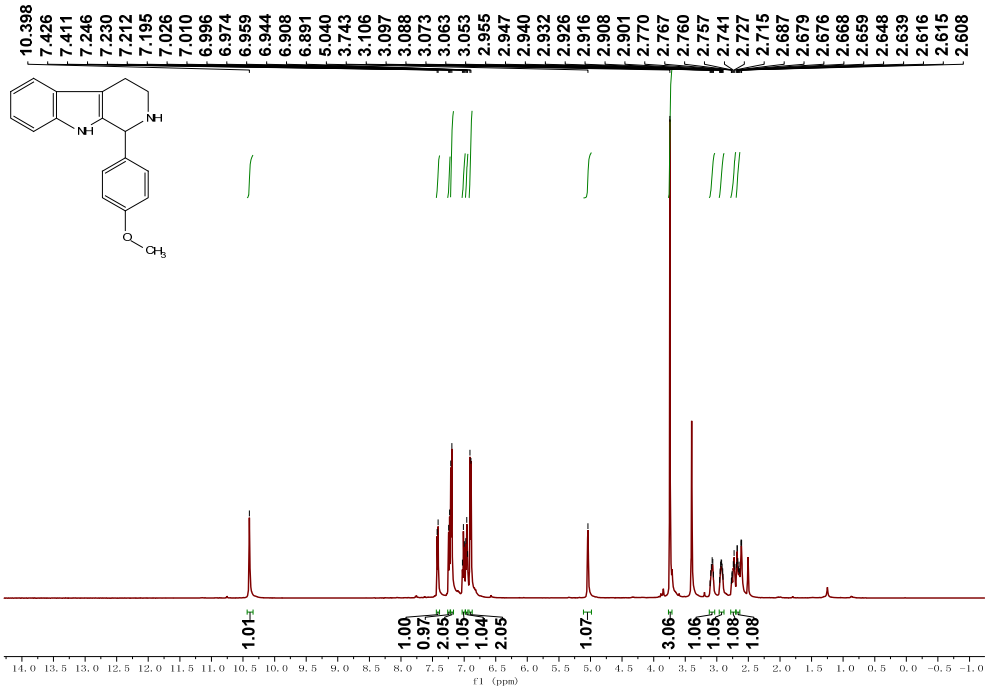
^{13}C NMR



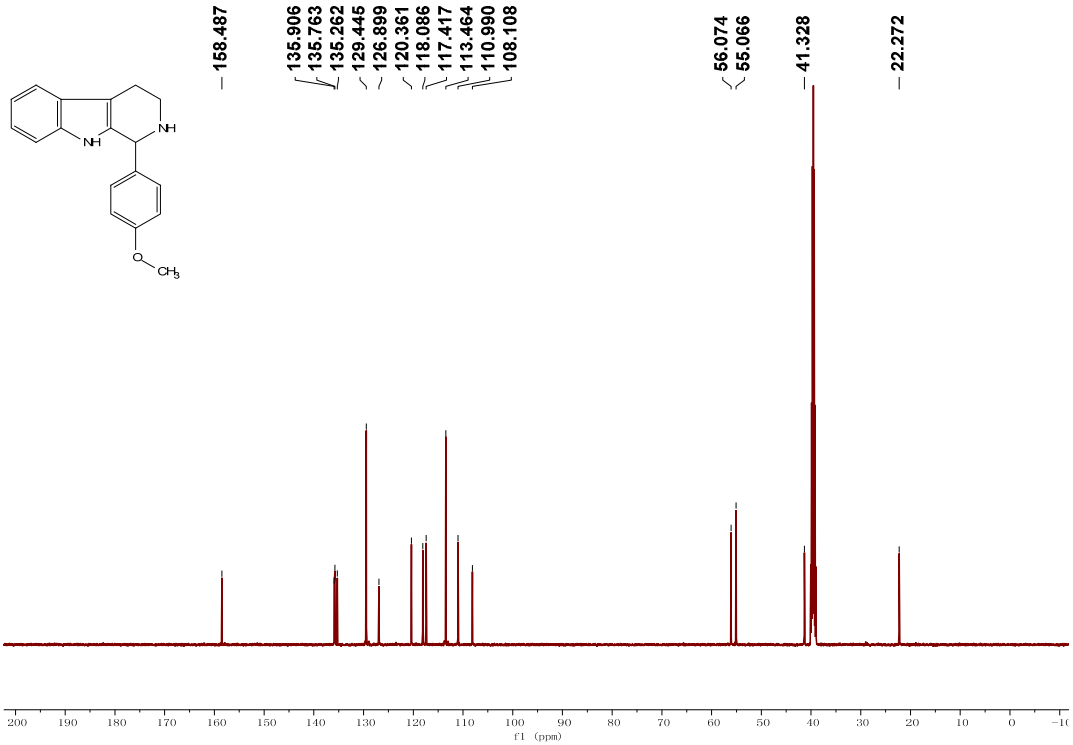


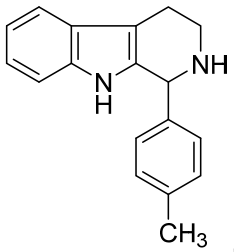
3ab

^{1}H NMR



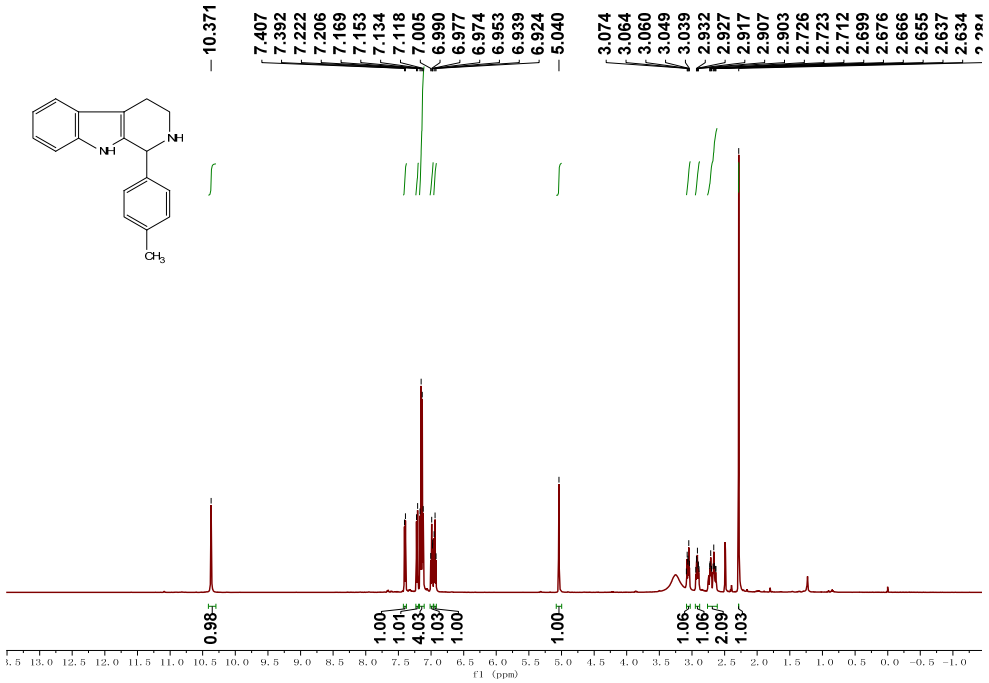
^{13}C NMR



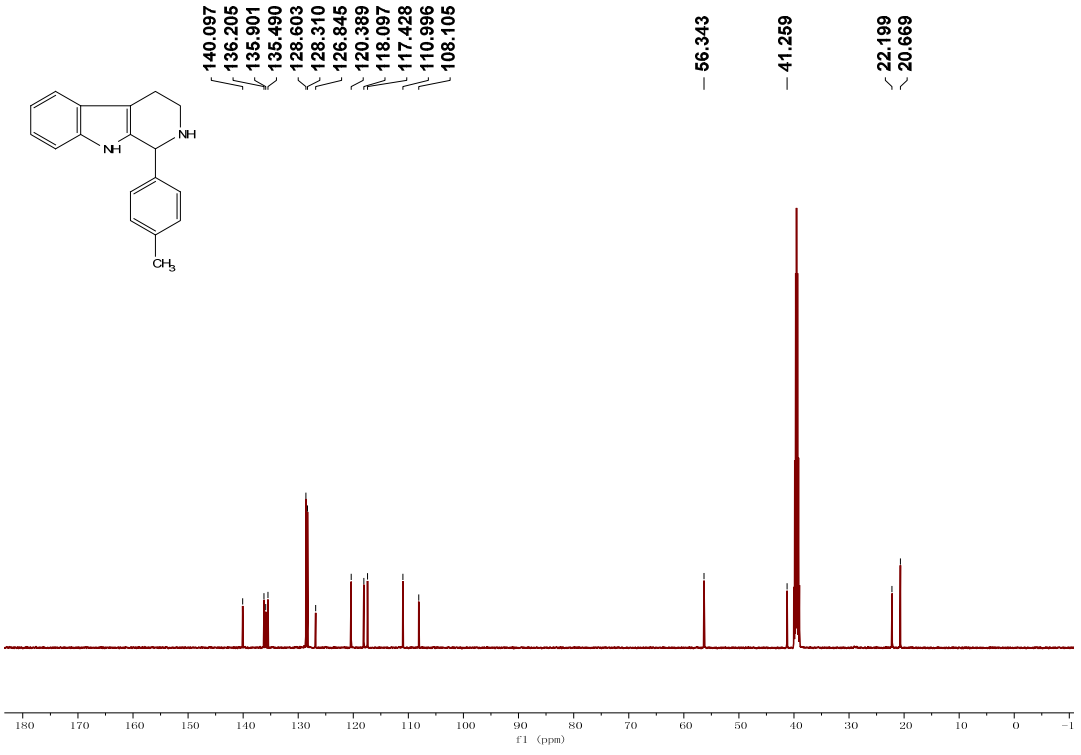


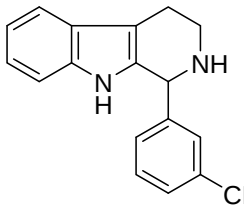
3ac

^{1}H NMR



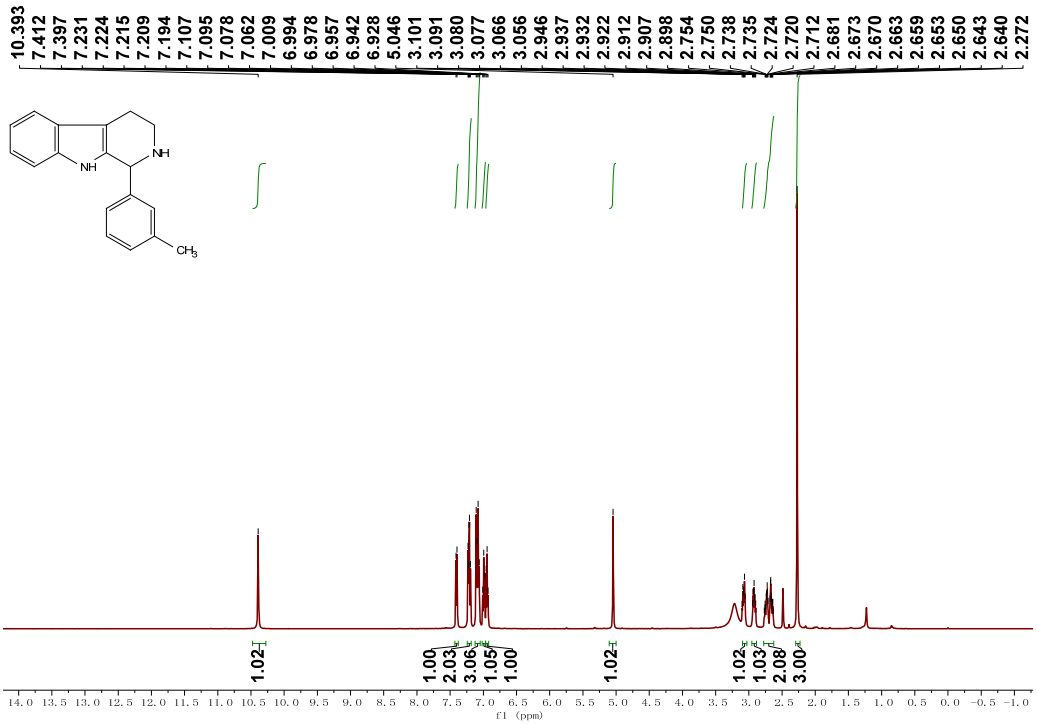
^{13}C NMR



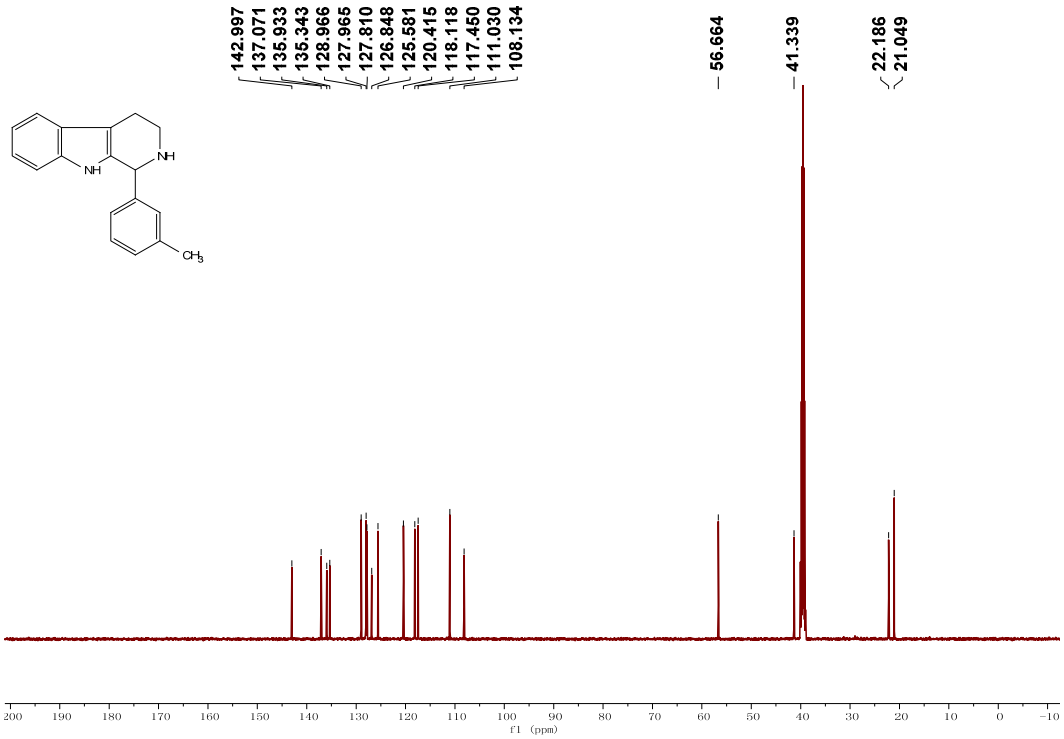


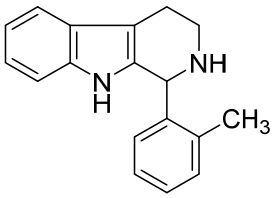
3ad

^{1}H NMR



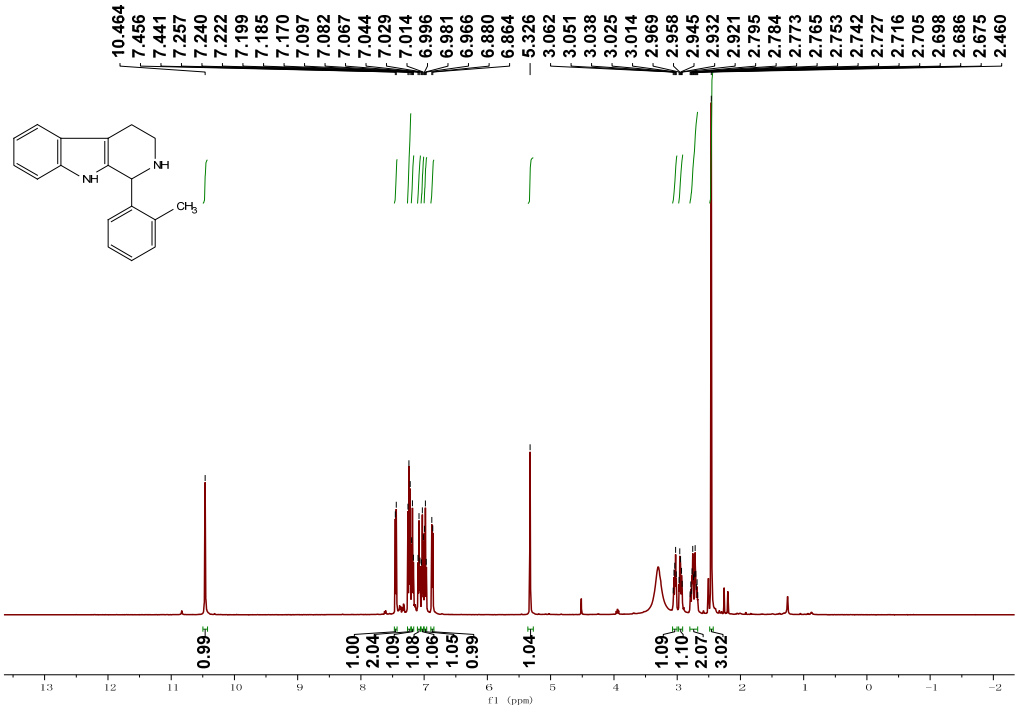
^{13}C NMR



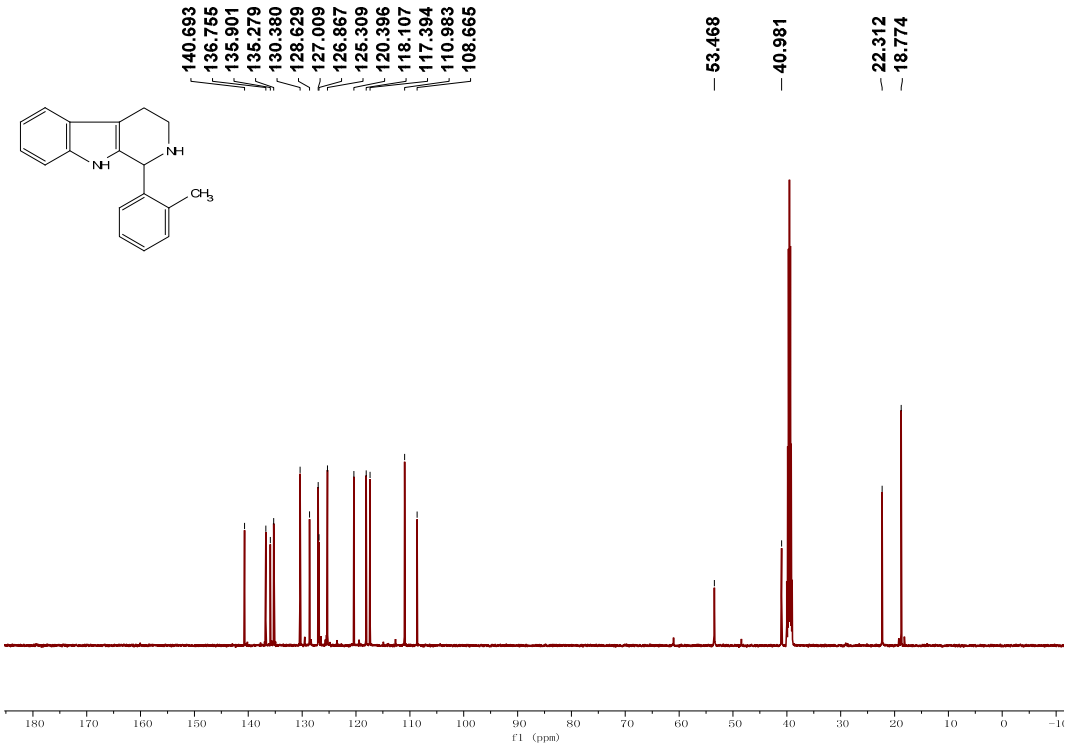


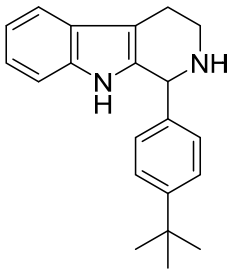
3ae

^{1}H NMR



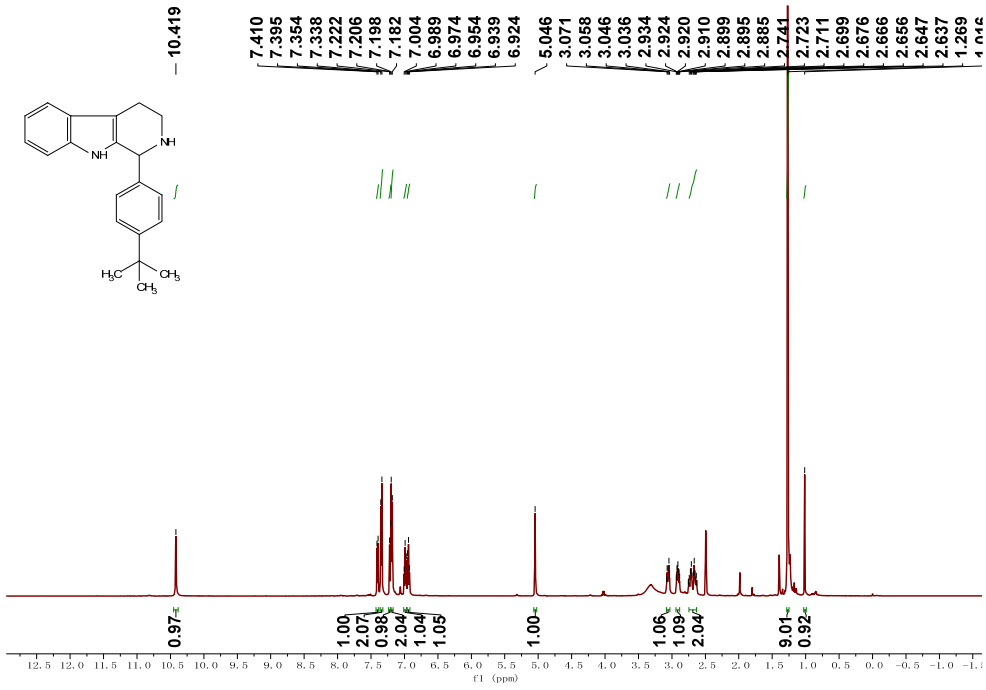
^{13}C NMR



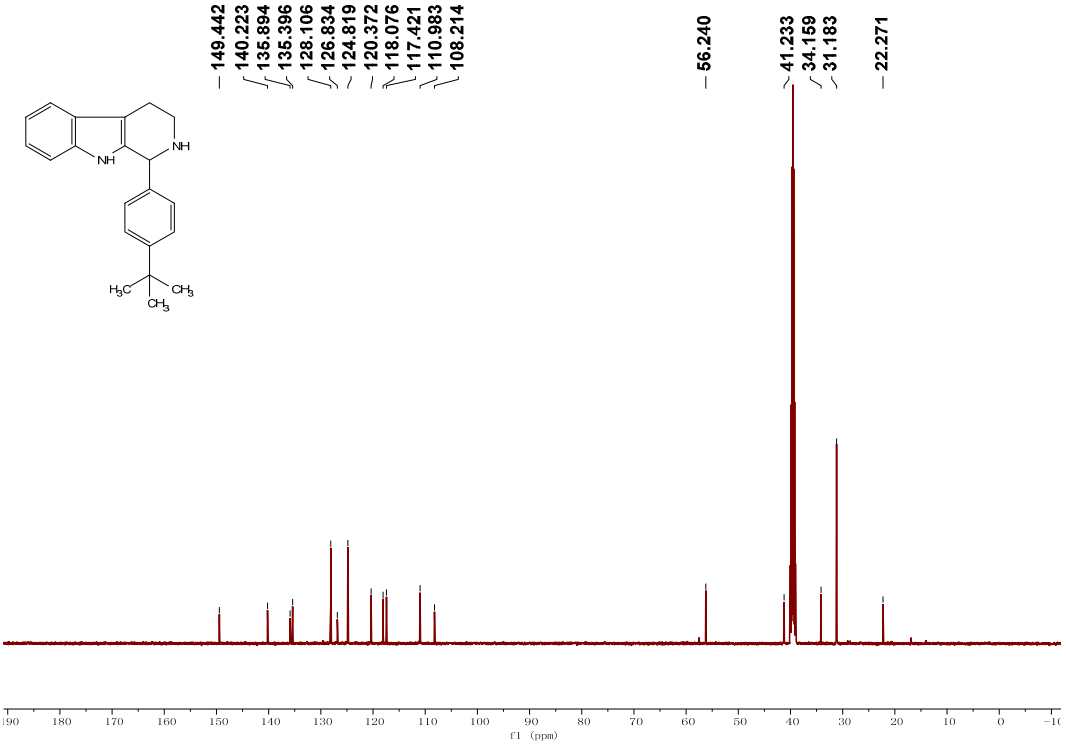


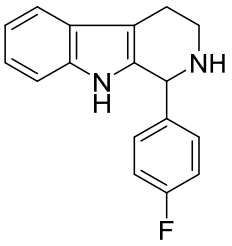
3af

^{1}H NMR



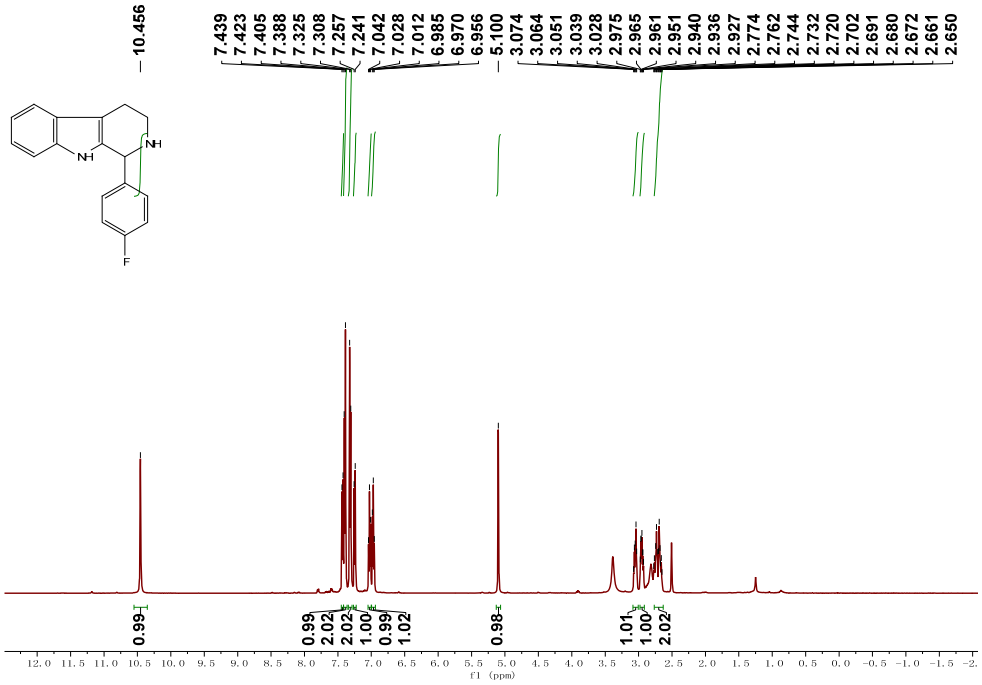
^{13}C NMR



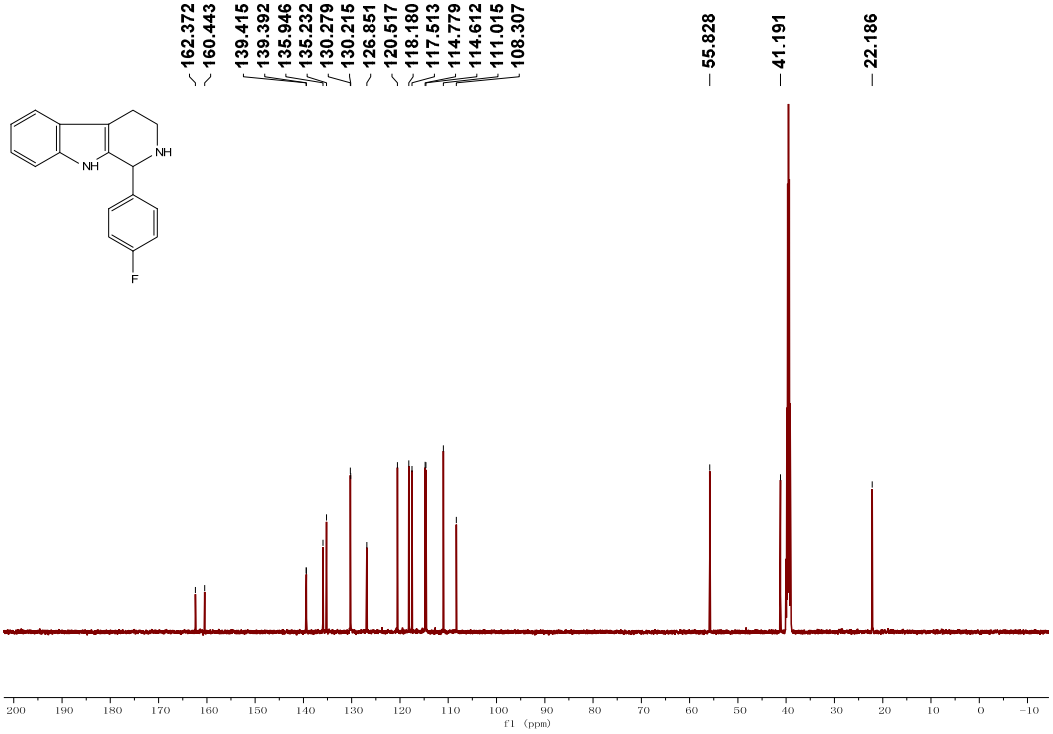


3ag

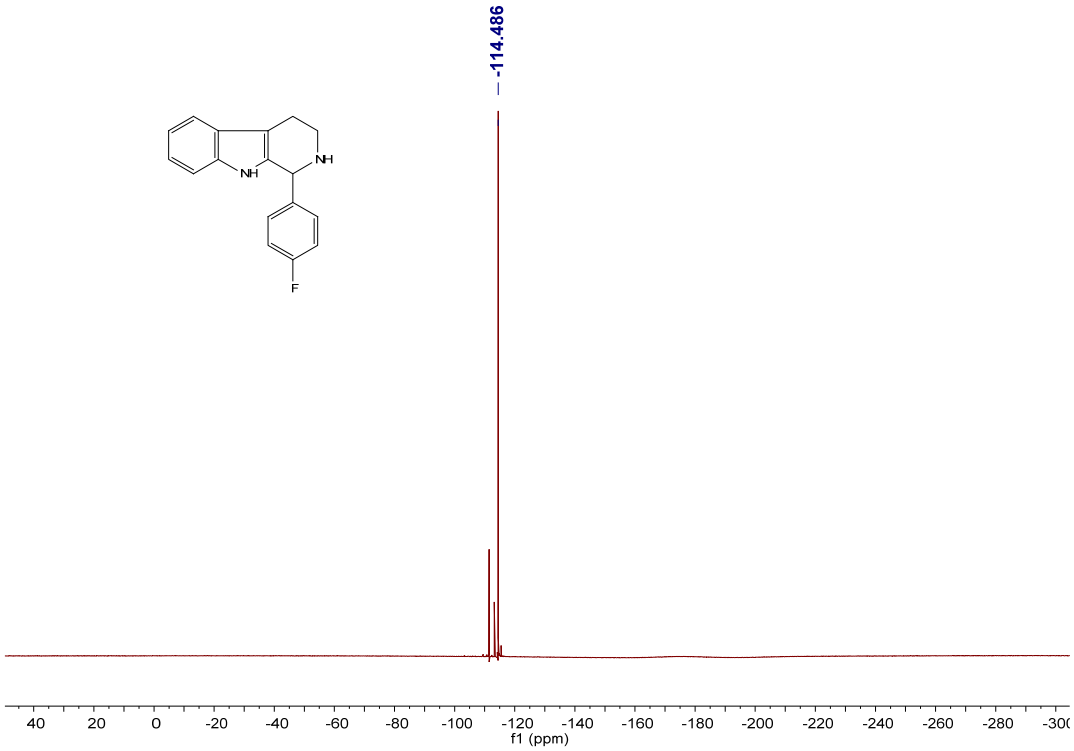
^{1}H NMR

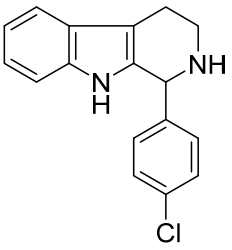


^{13}C NMR



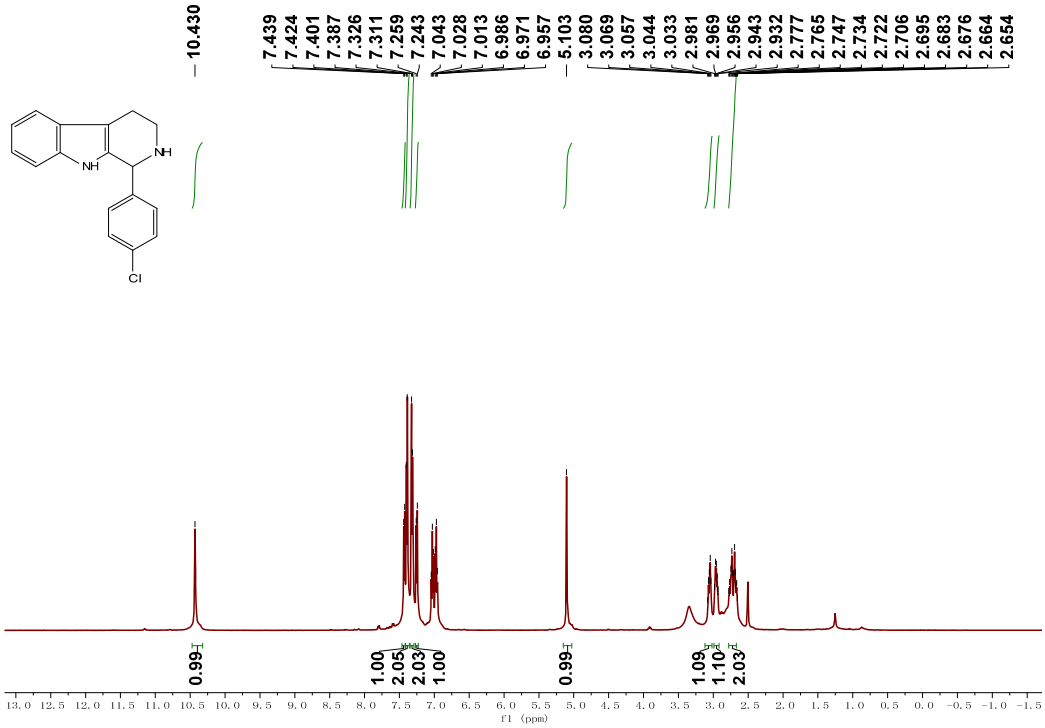
^{19}F NMR


-114.486
NH
NH
F
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

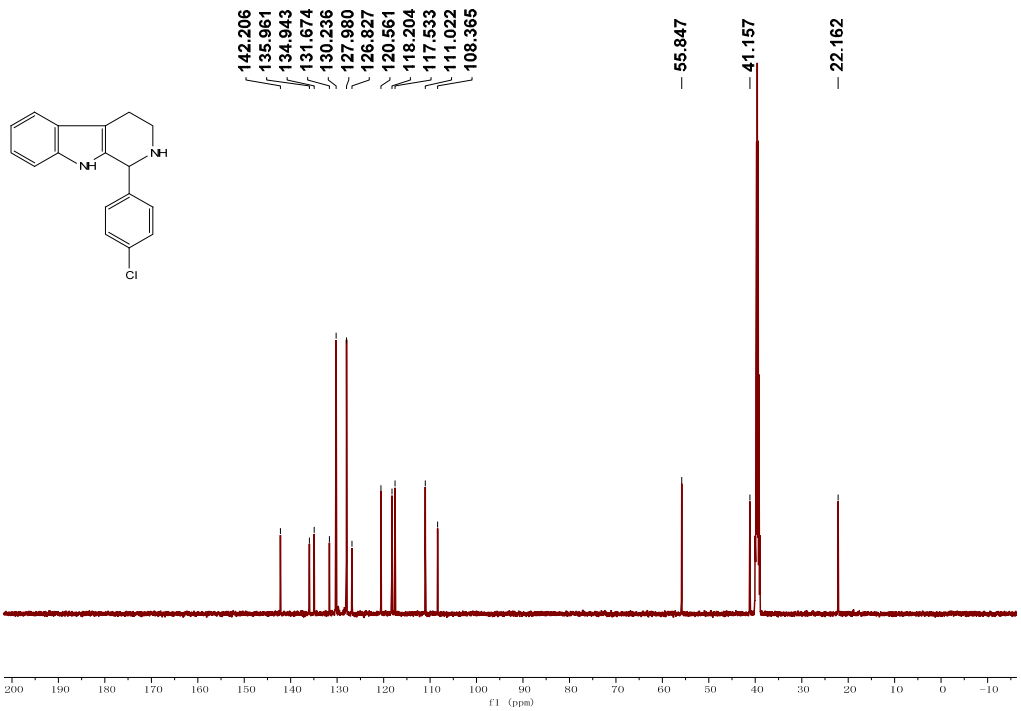


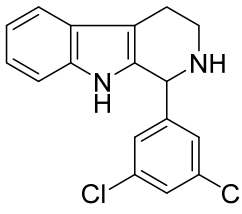
3ah

^{1}H NMR



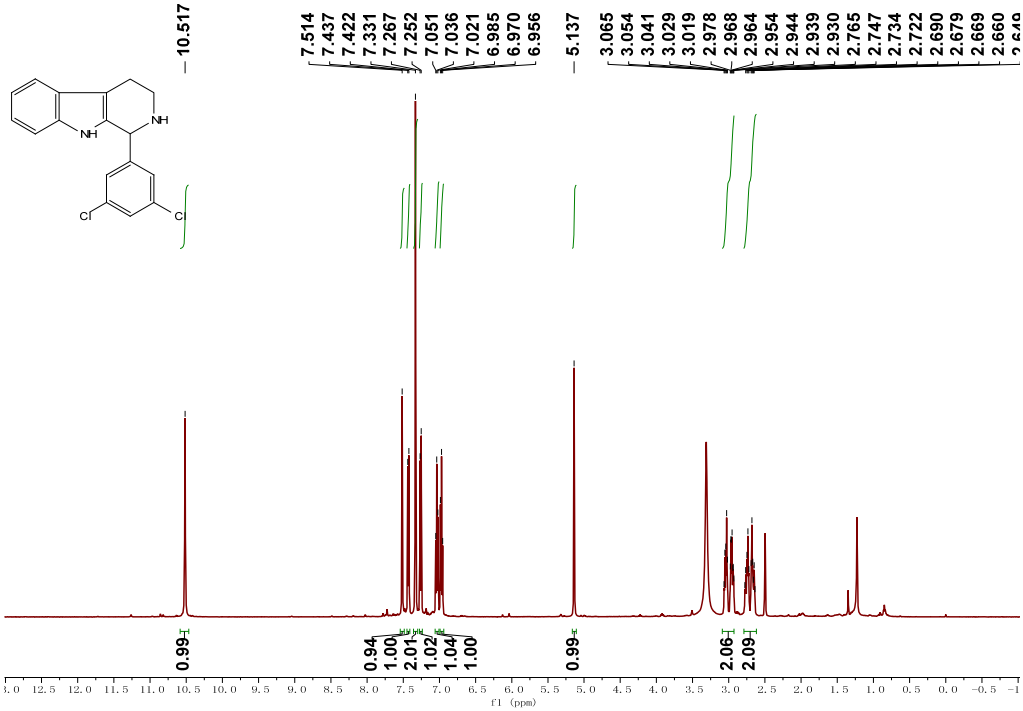
^{13}C NMR



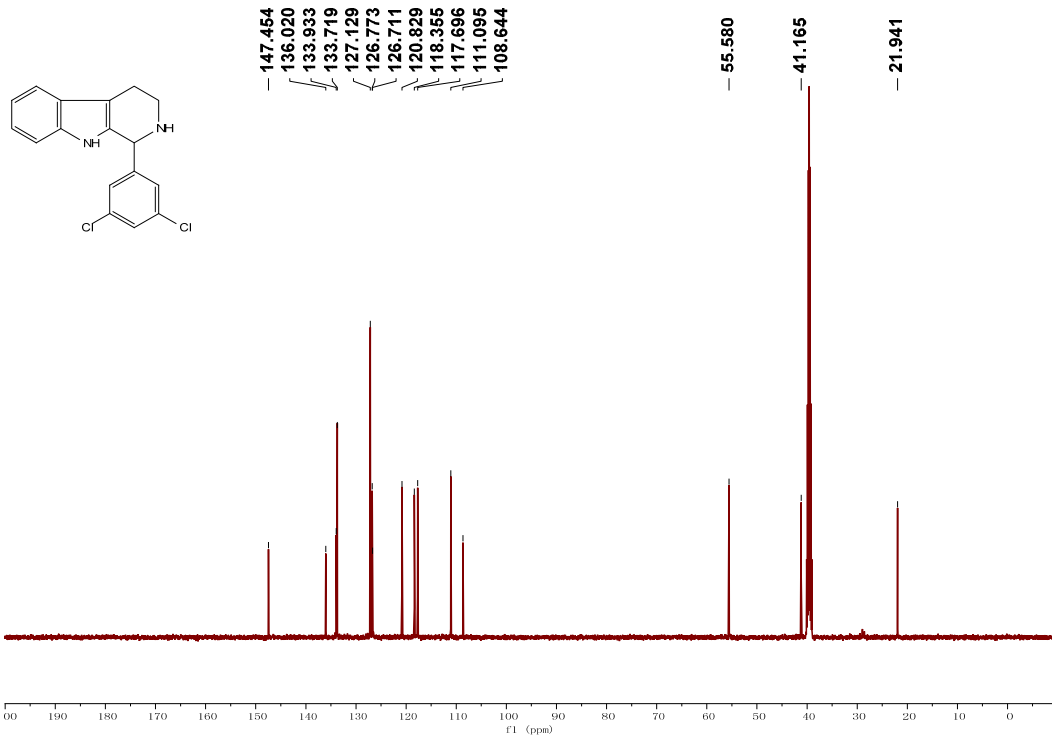


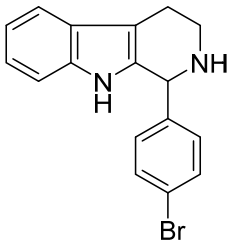
3ai

^{1}H NMR



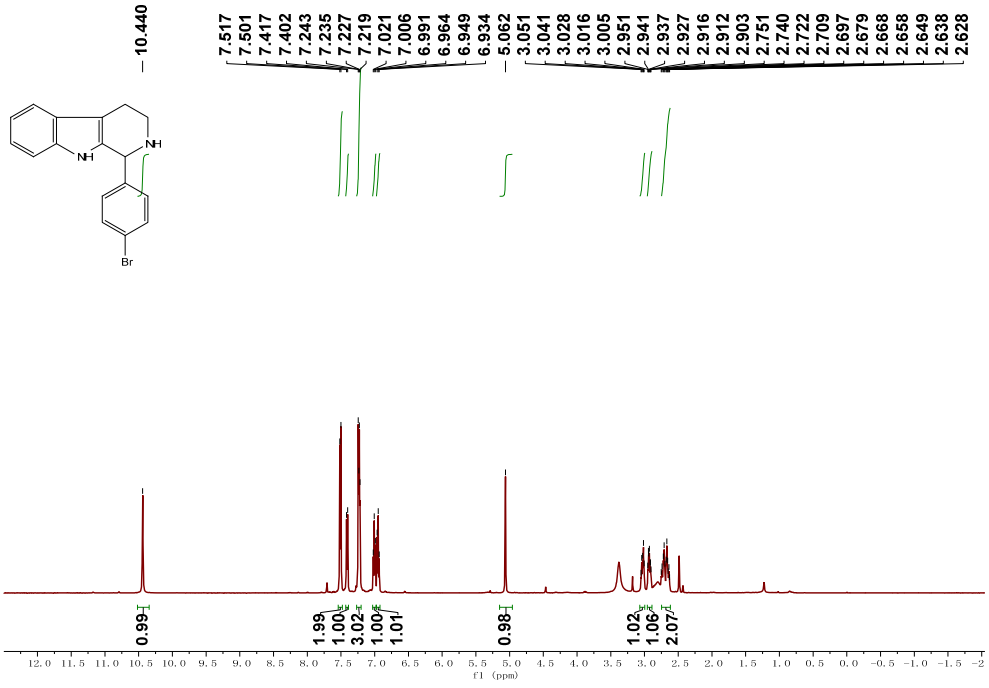
^{13}C NMR



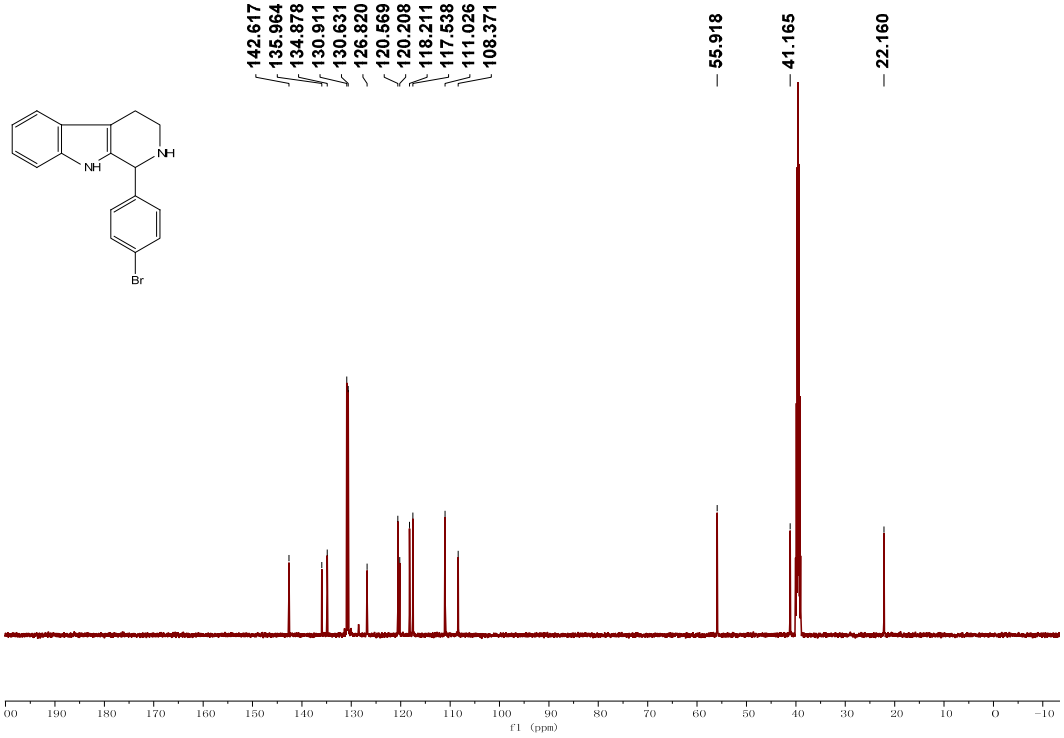


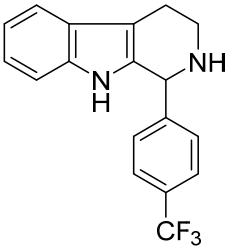
3aj

^{1}H NMR



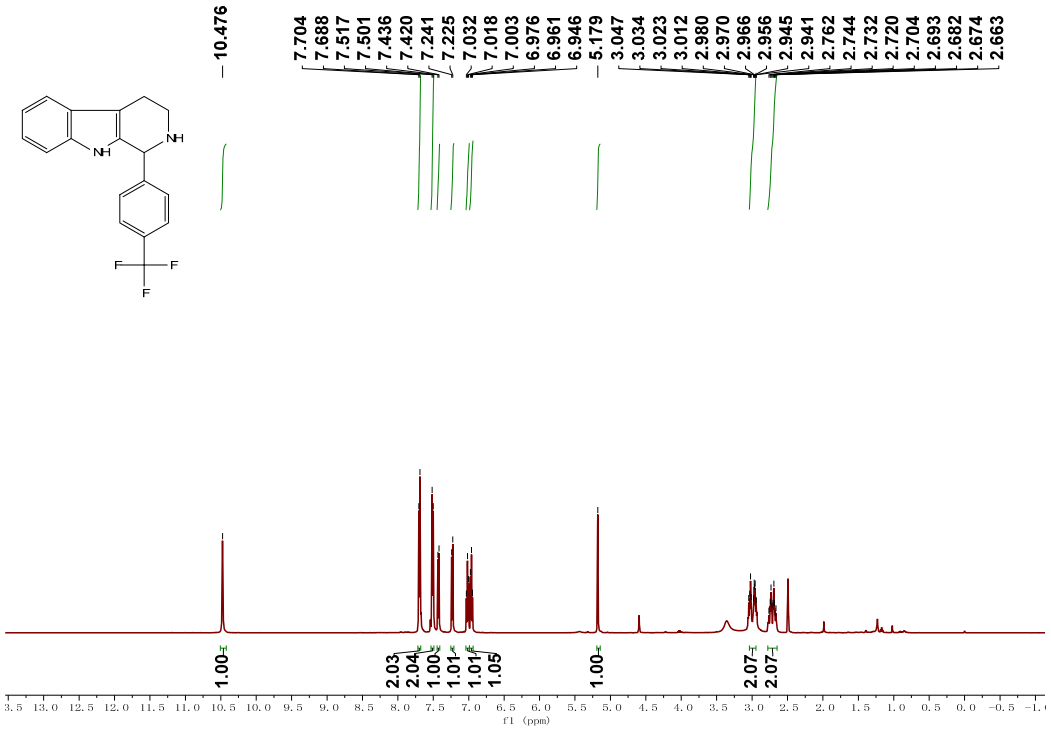
^{13}C NMR



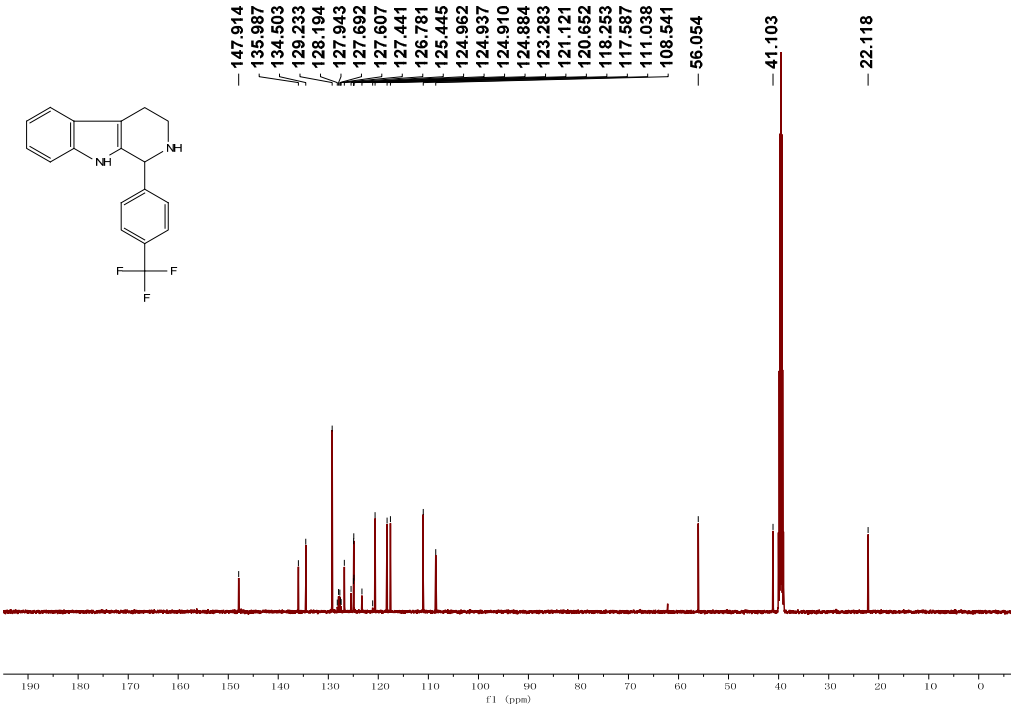


3ak

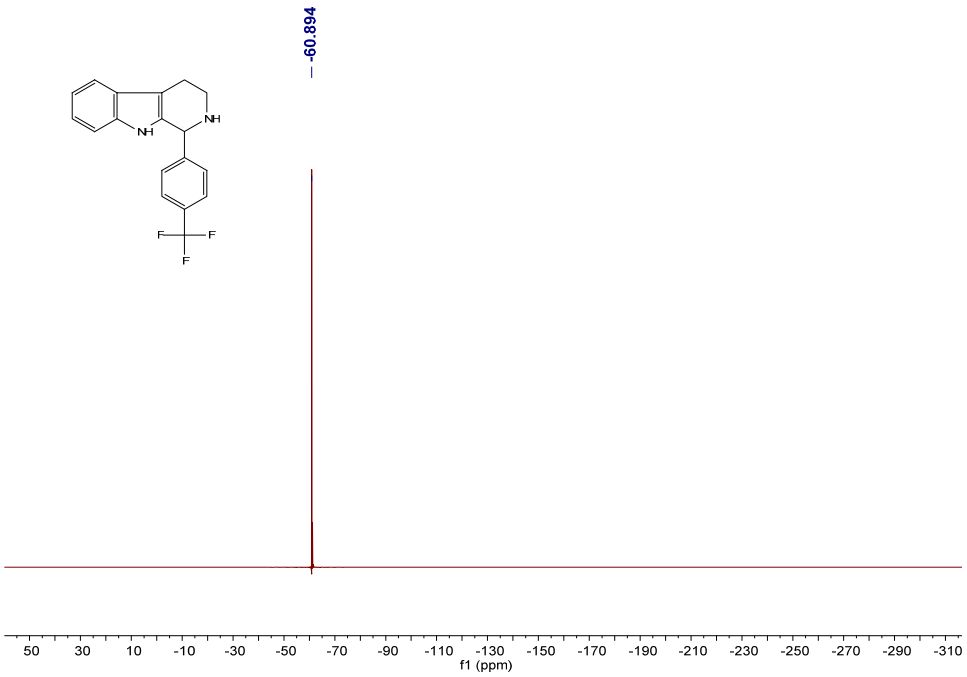
^{1}H NMR



^{13}C NMR



^{19}F NMR


-60.894
NH
NH
F
F
F
50
30
10
-10
-30
-50
-70
-90
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-130
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-170
-190
-210
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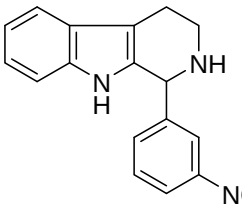
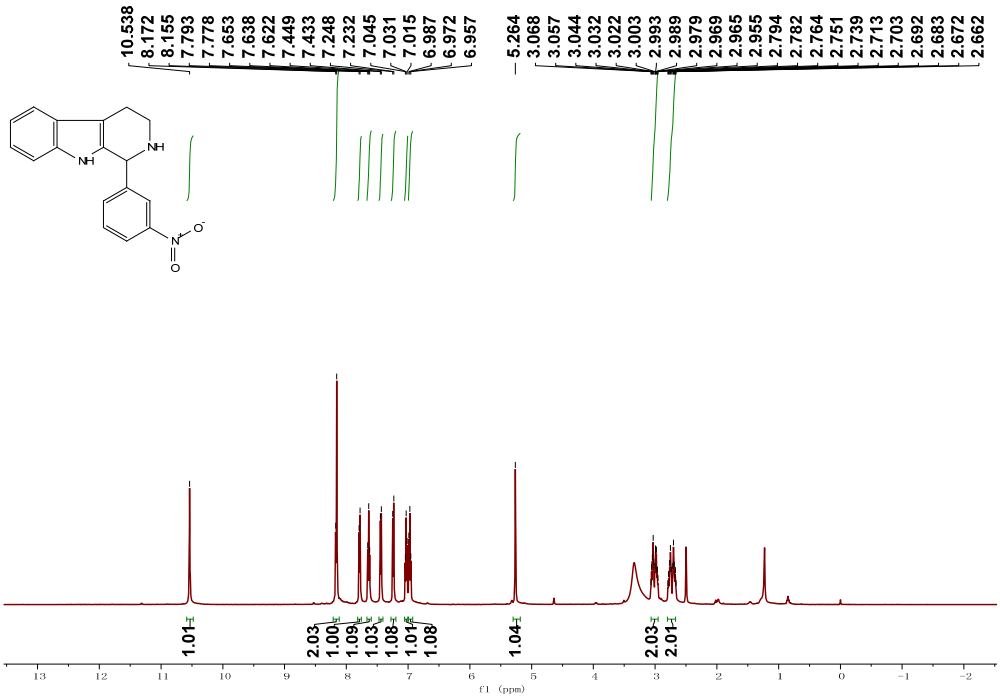
-250
-270
-290
-310
f1 (ppm)

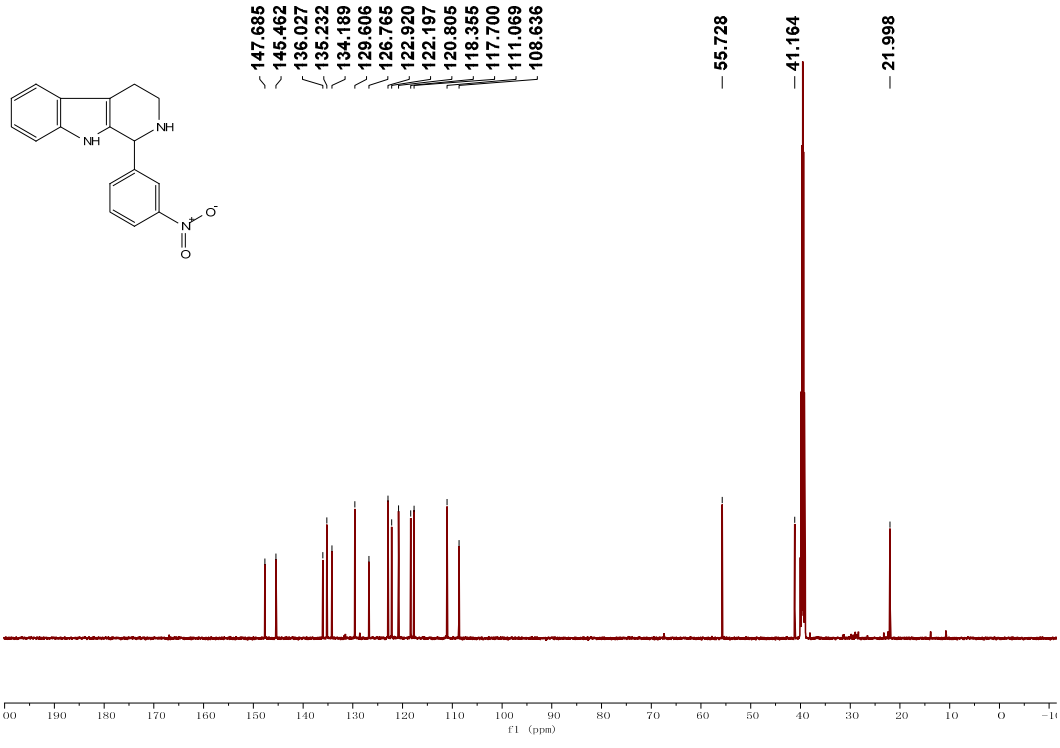


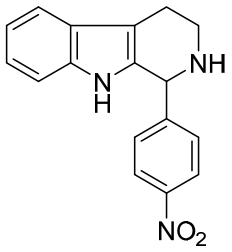
3al

^{1}H NMR



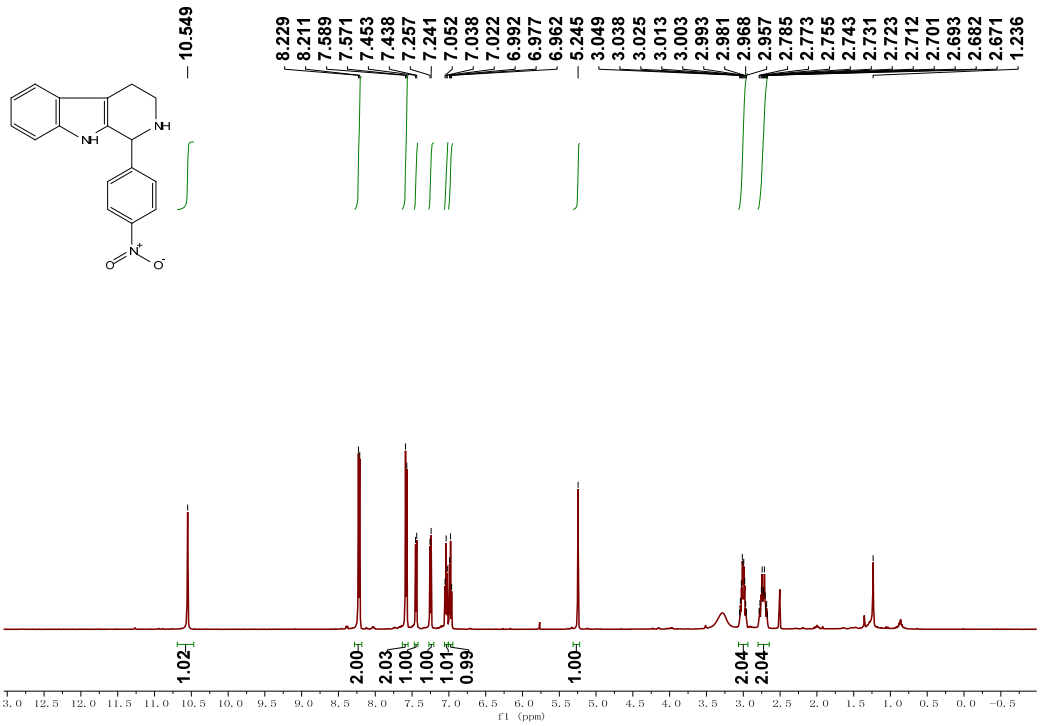
^{13}C NMR



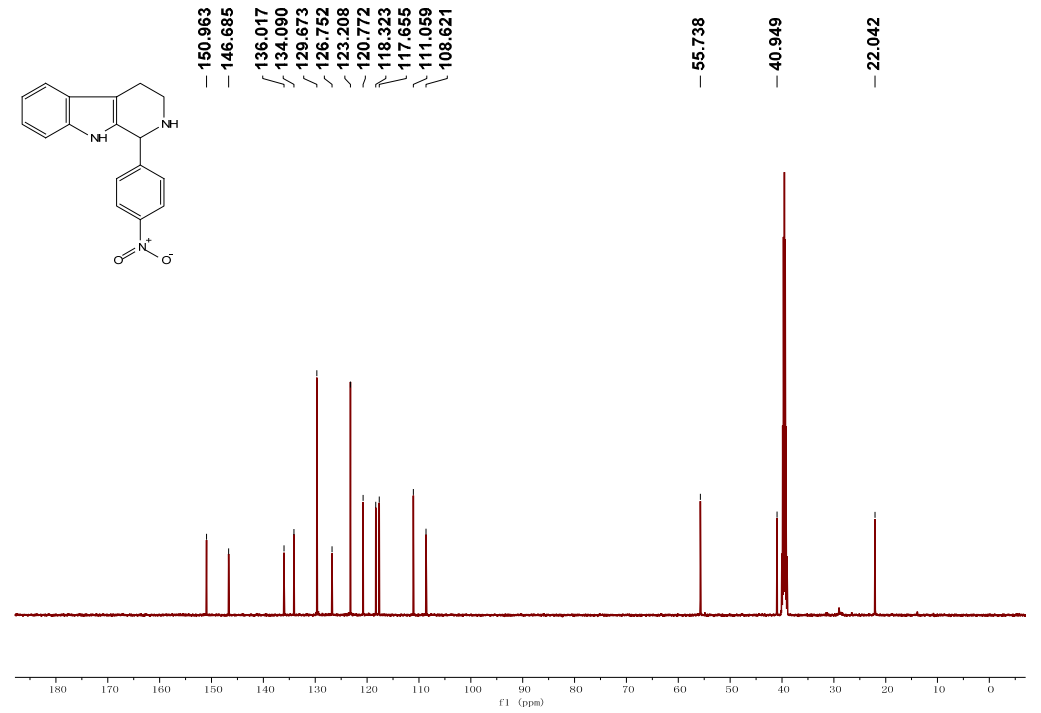


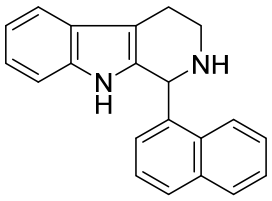
3am

^{1}H NMR



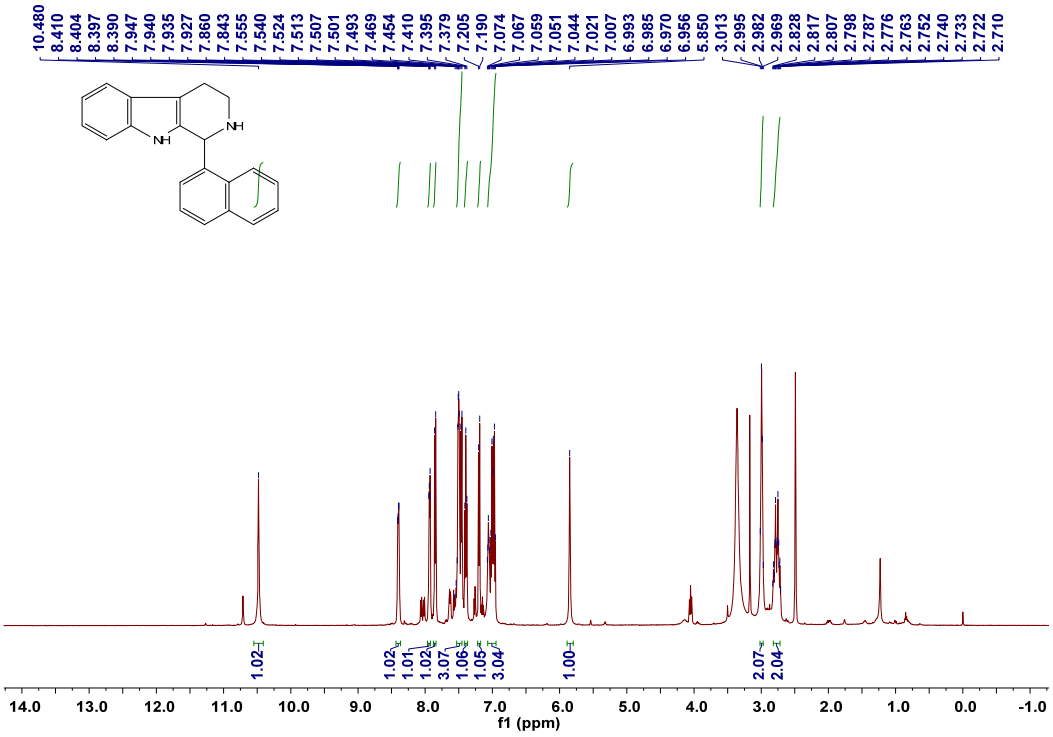
^{13}C NMR



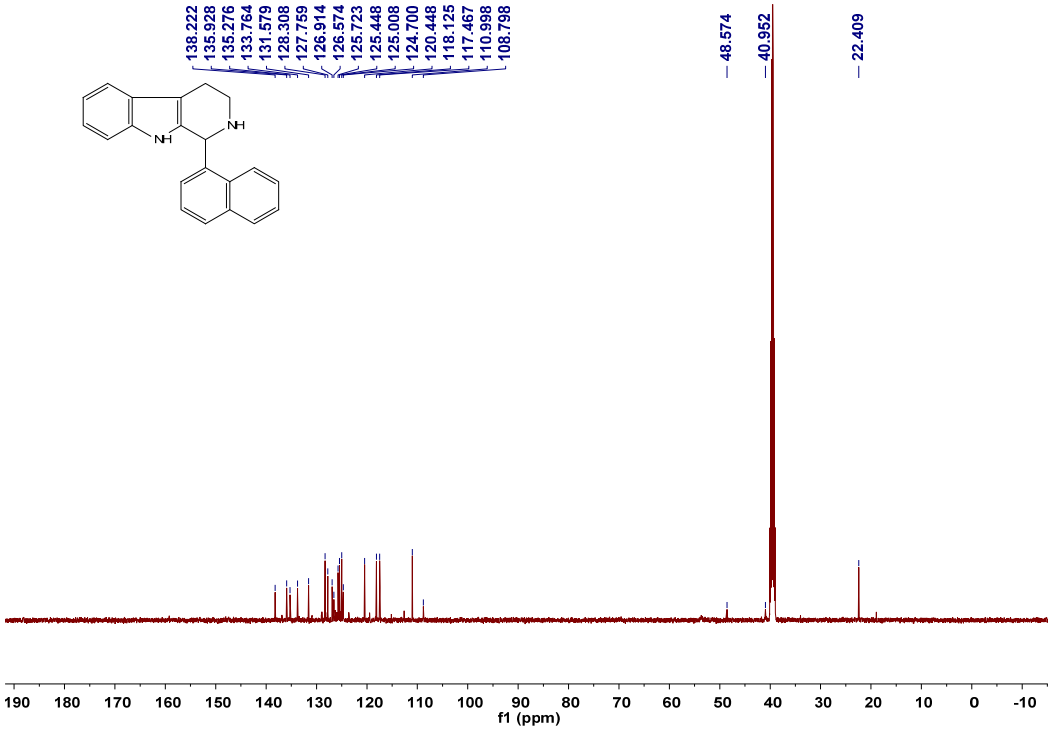


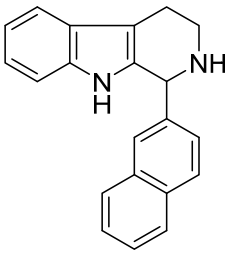
3an

^{1}H NMR



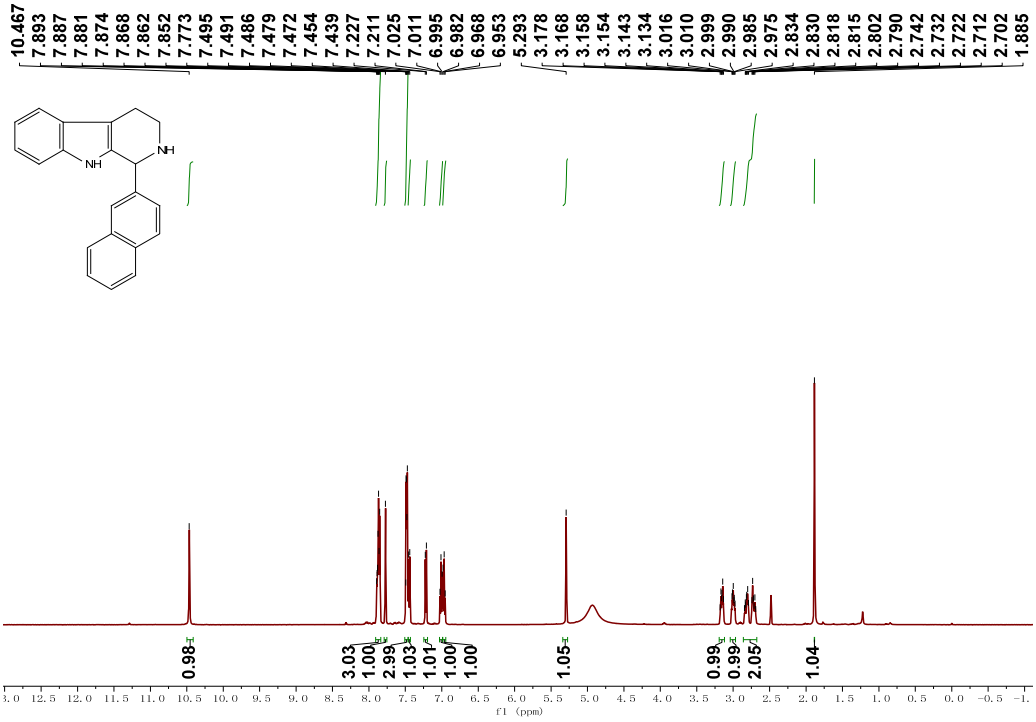
^{13}C NMR



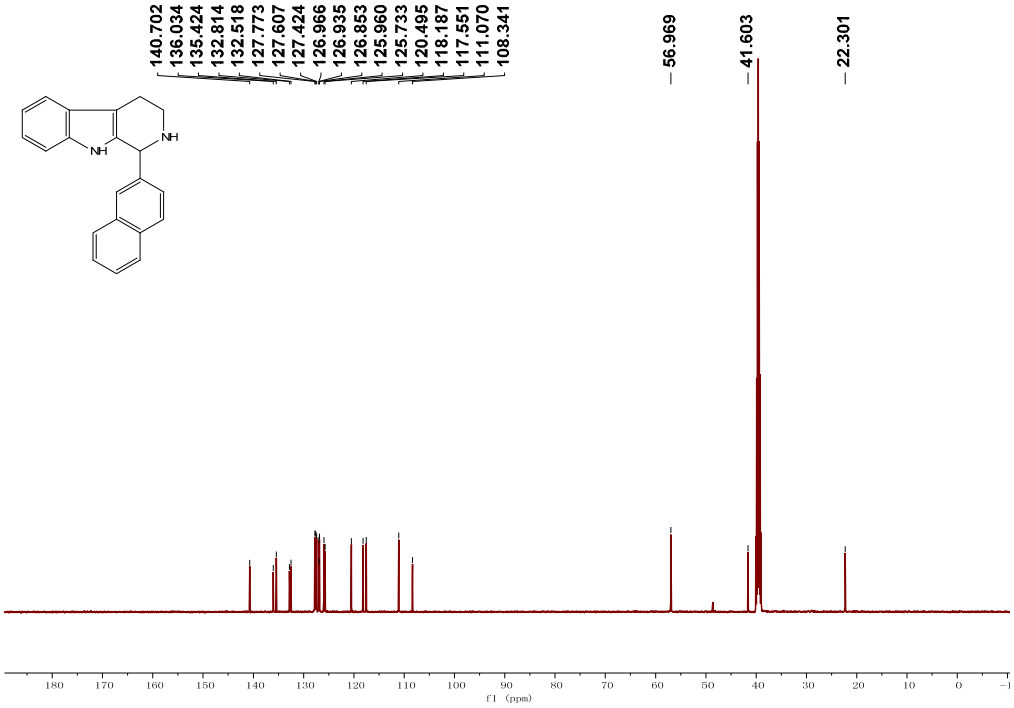


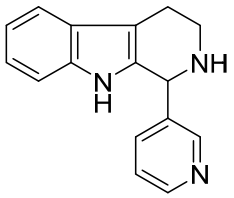
3ao

^{1}H NMR



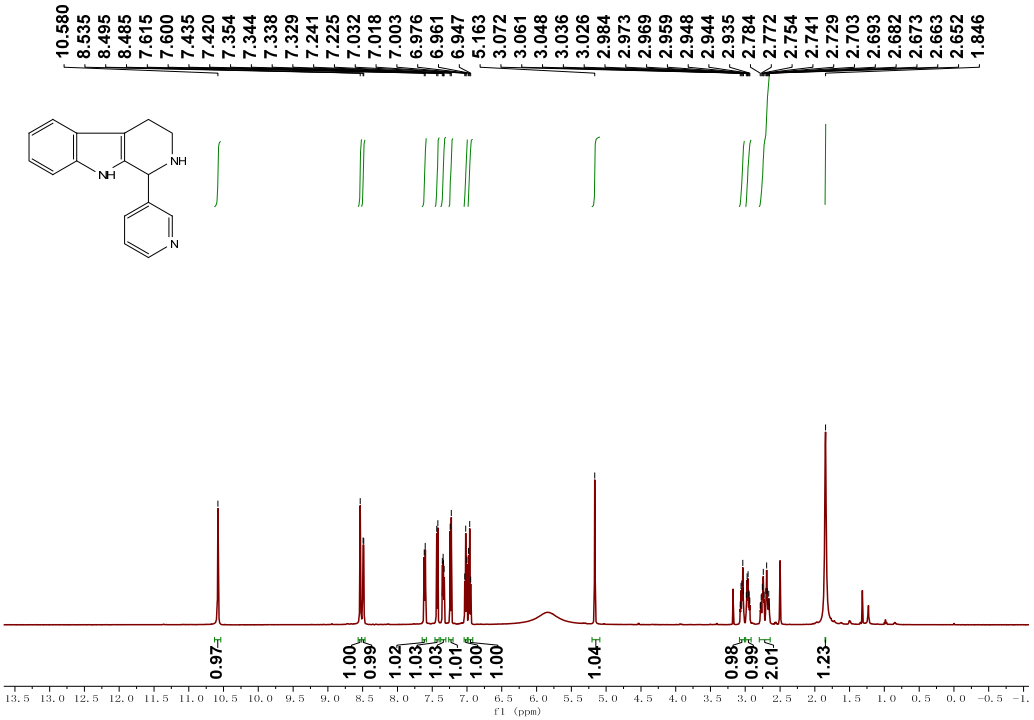
^{13}C NMR



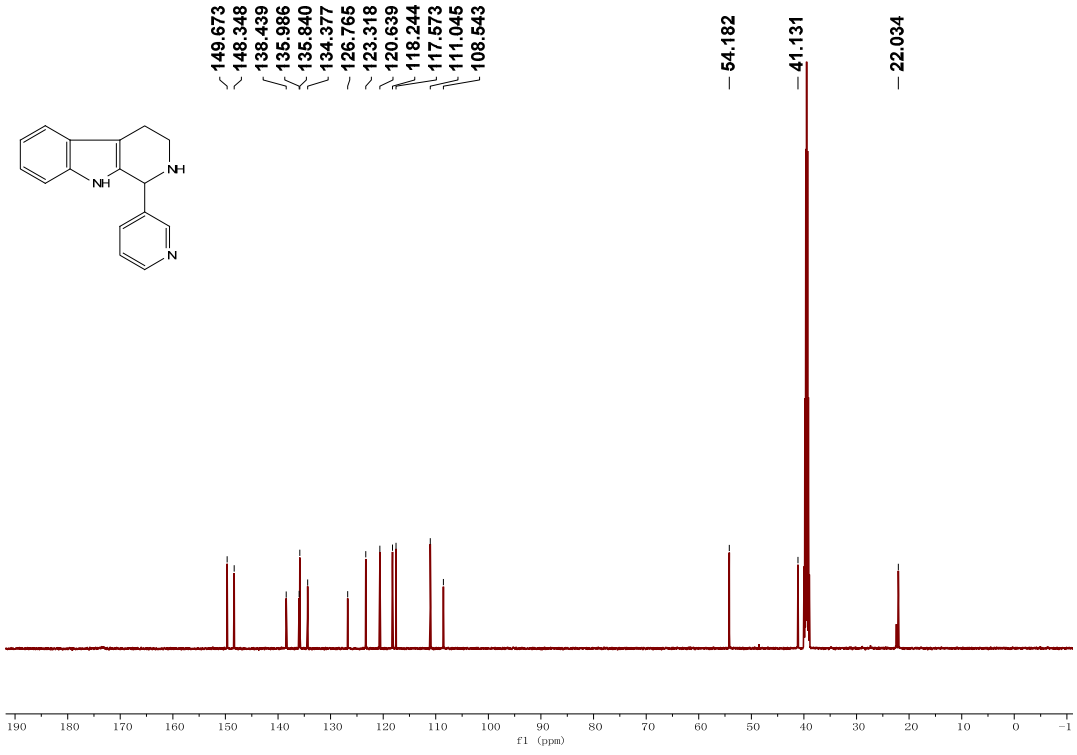


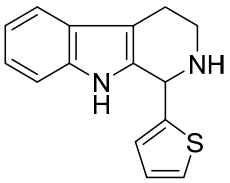
3ap

^{1}H NMR



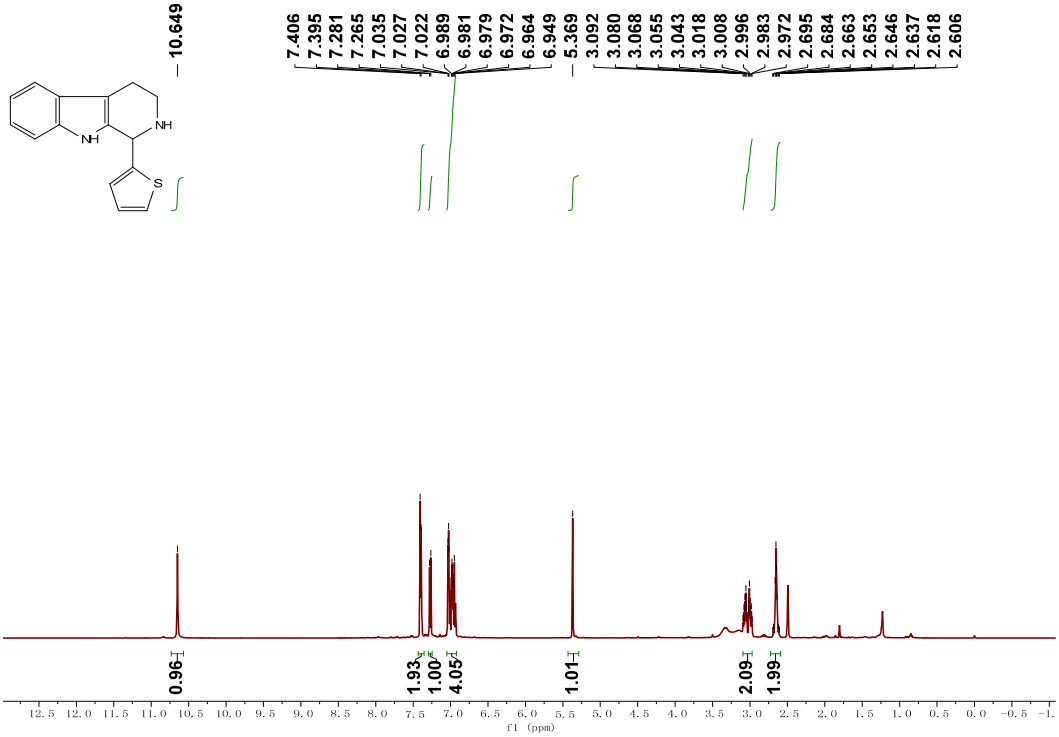
^{13}C NMR



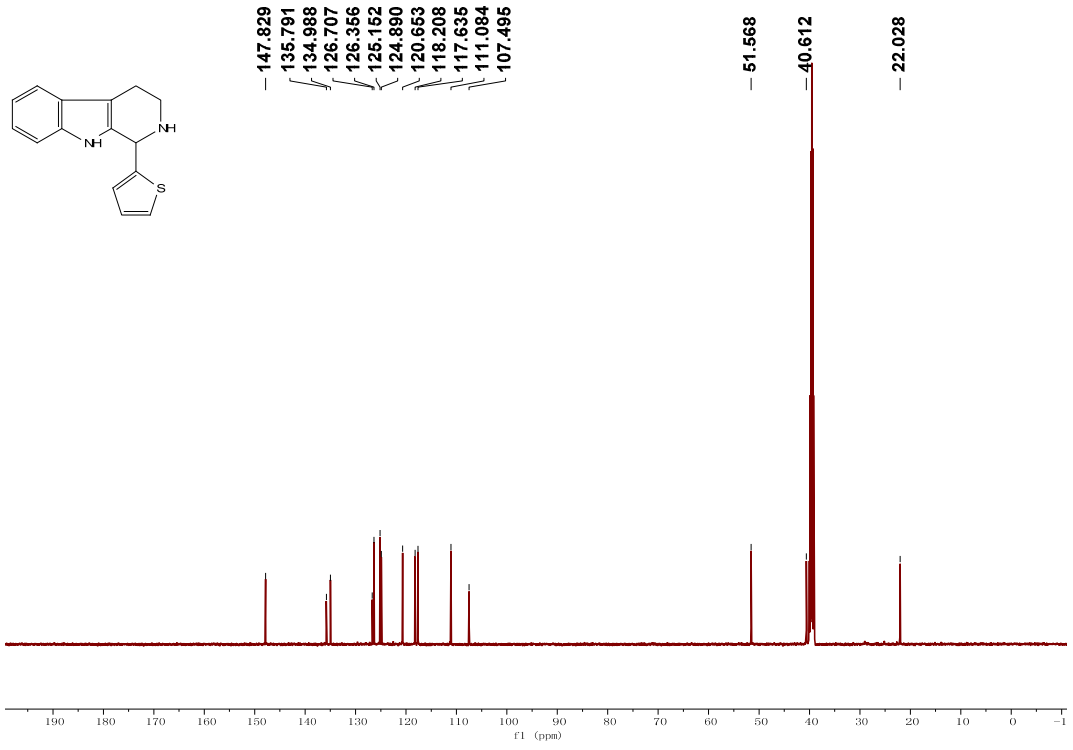


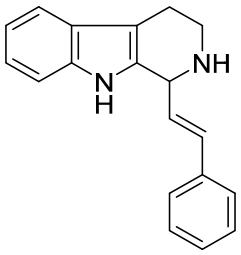
3aq

^{1}H NMR



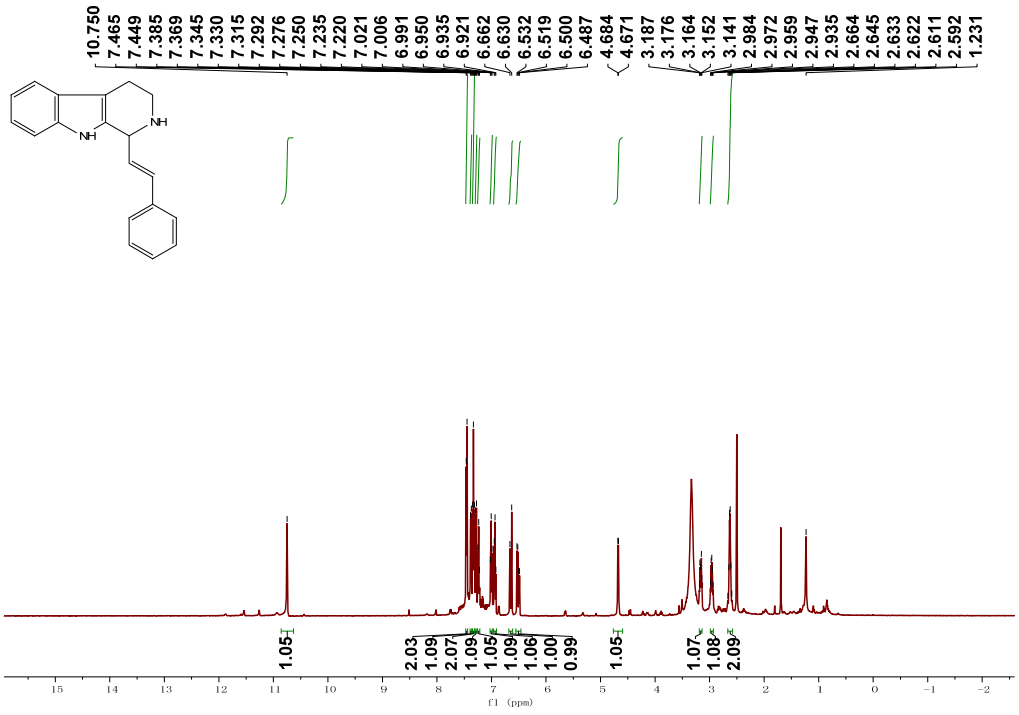
^{13}C NMR



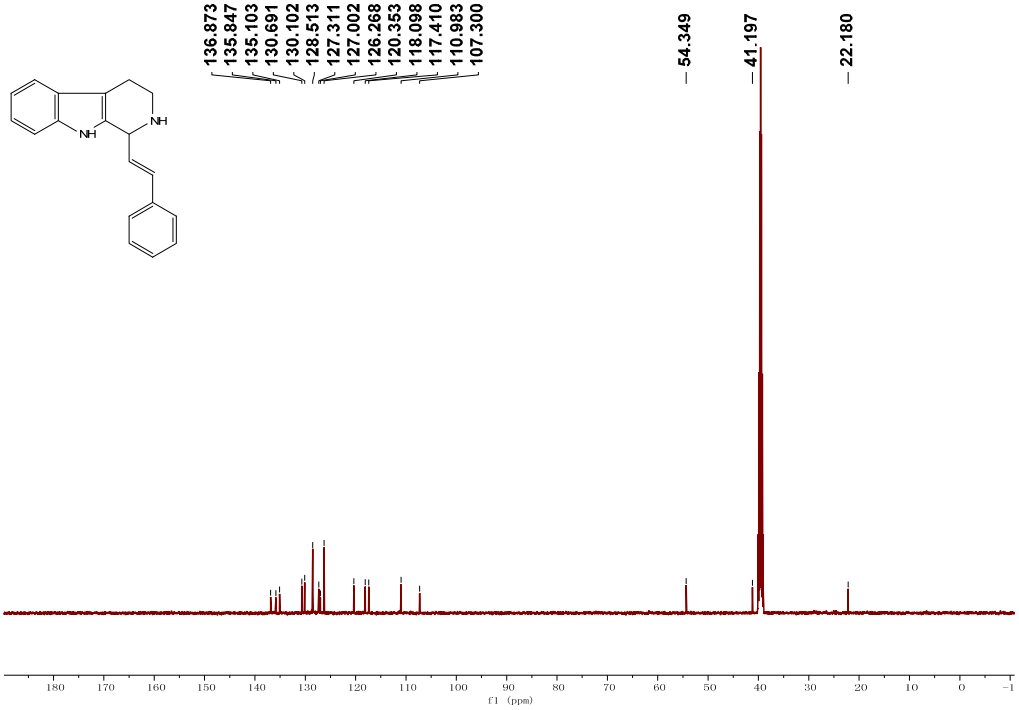


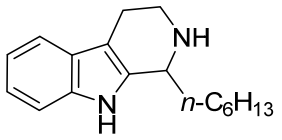
3ar

^{1}H NMR



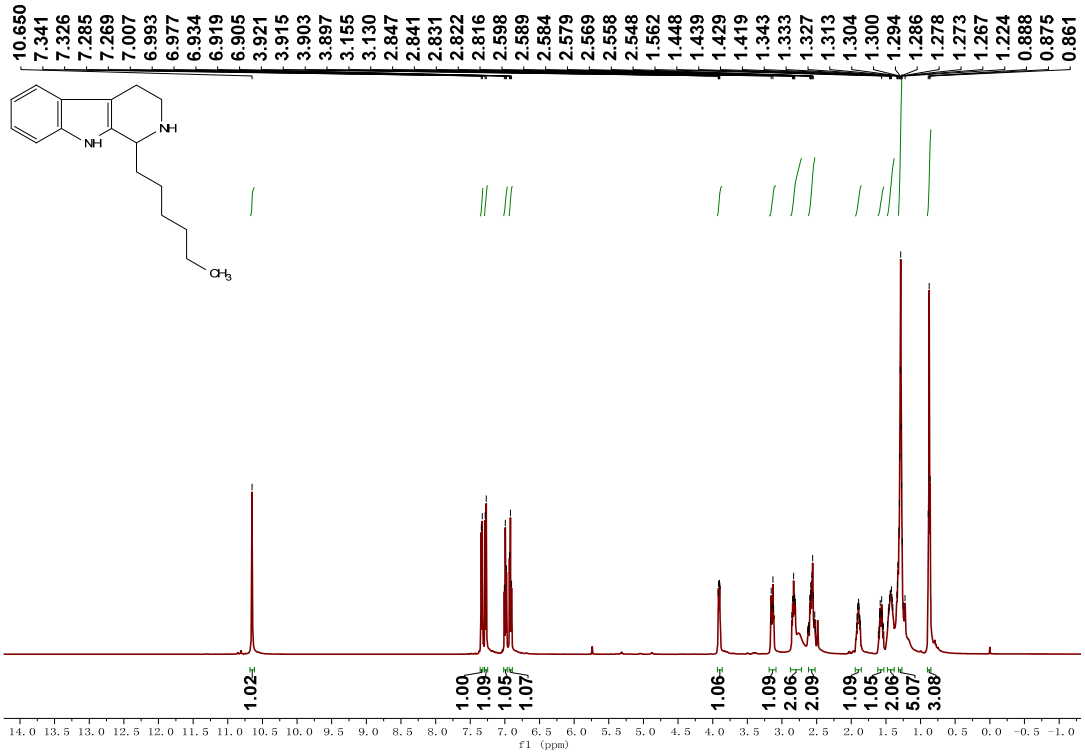
^{13}C NMR



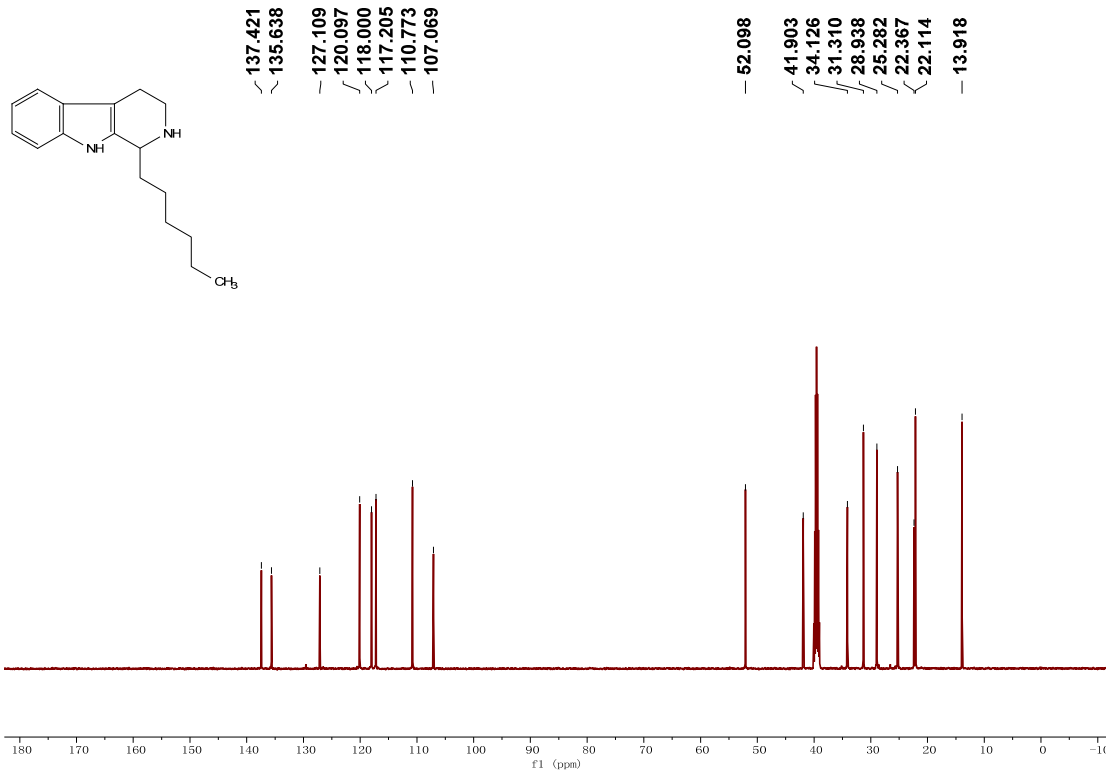


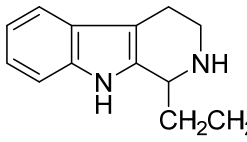
3as

^{1}H NMR



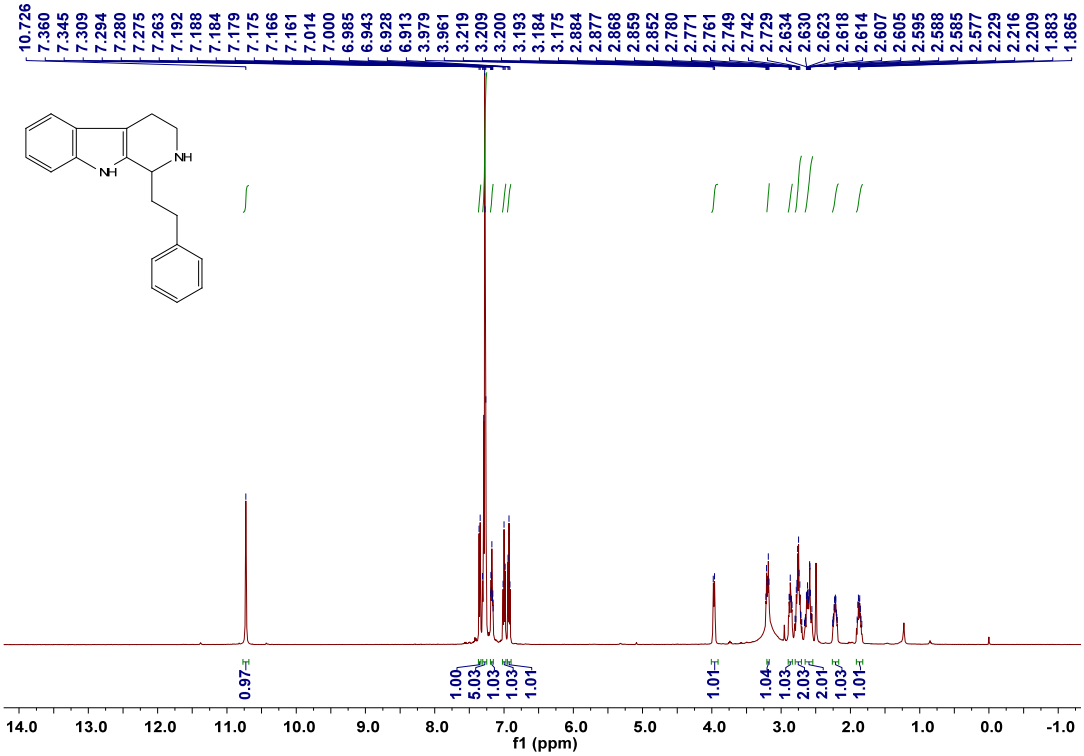
^{13}C NMR



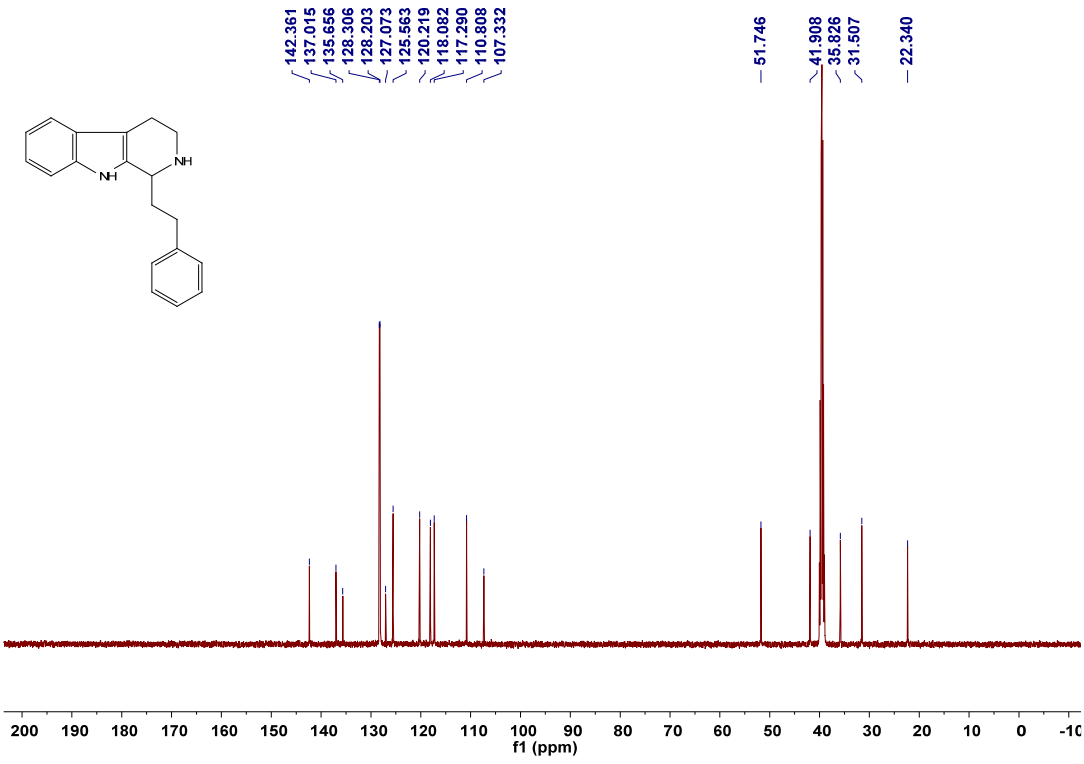


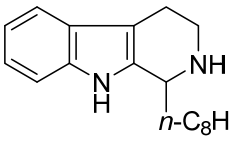
3at

^{1}H NMR



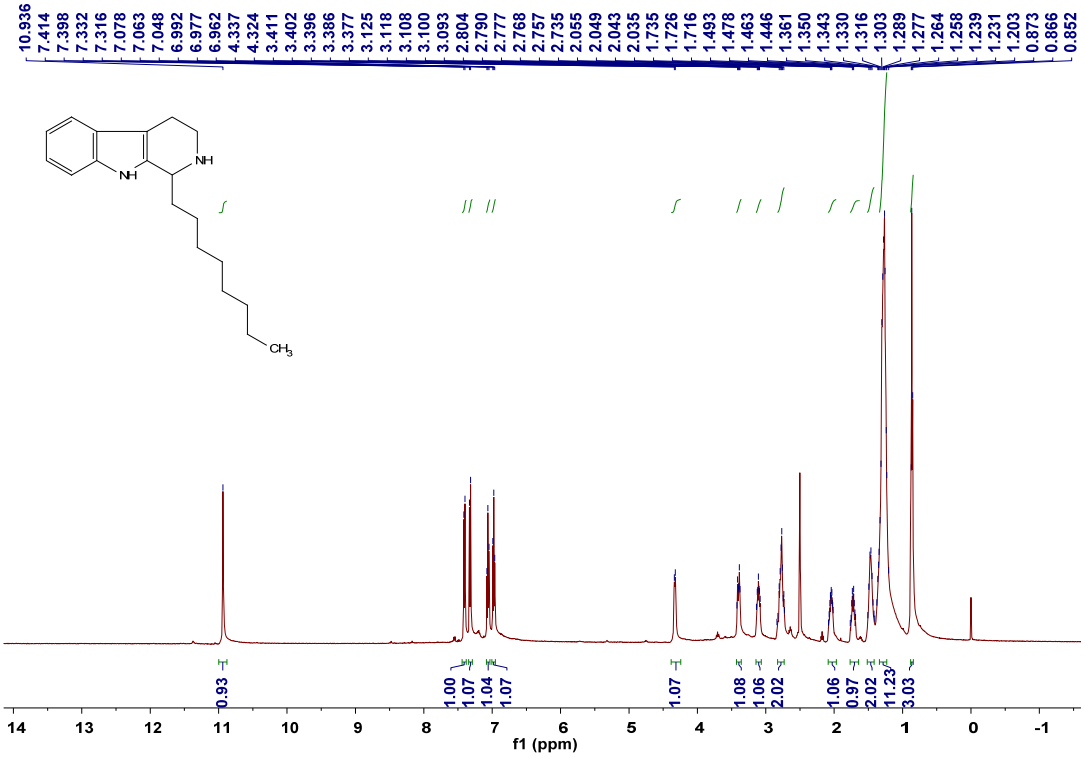
^{13}C NMR



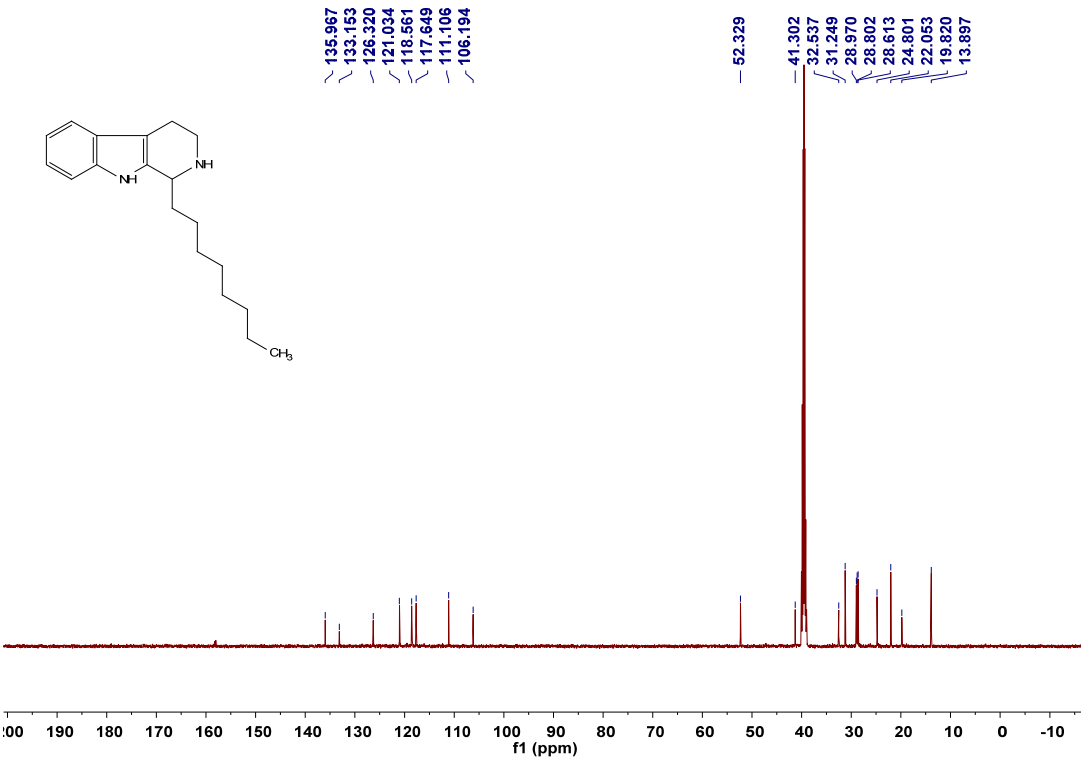


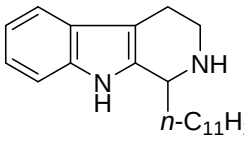
3au

^{1}H NMR



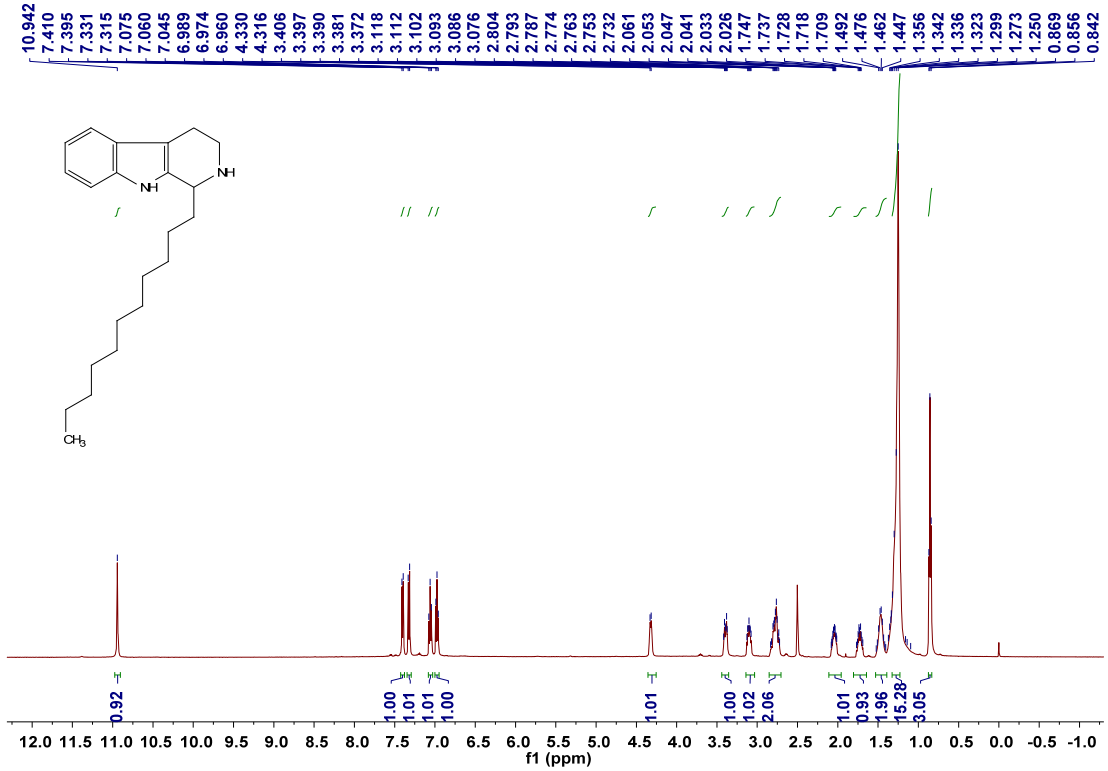
^{13}C NMR



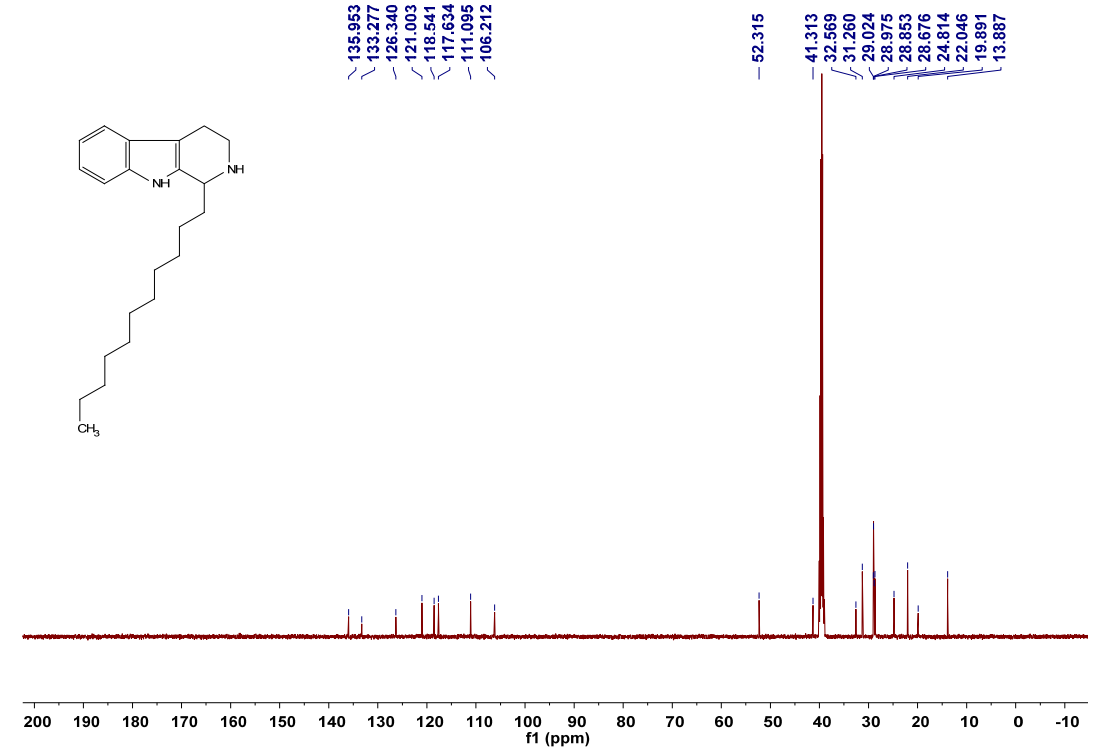


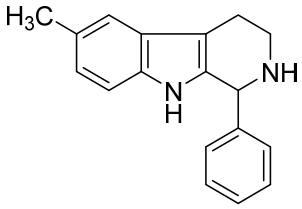
3av

^{1}H NMR



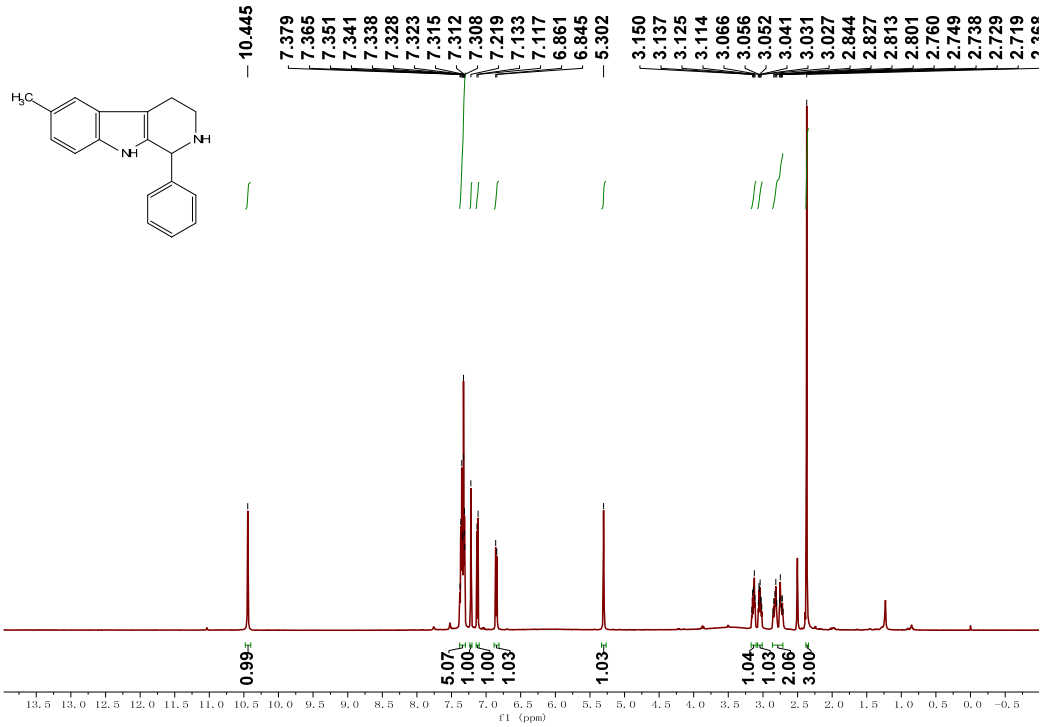
^{13}C NMR



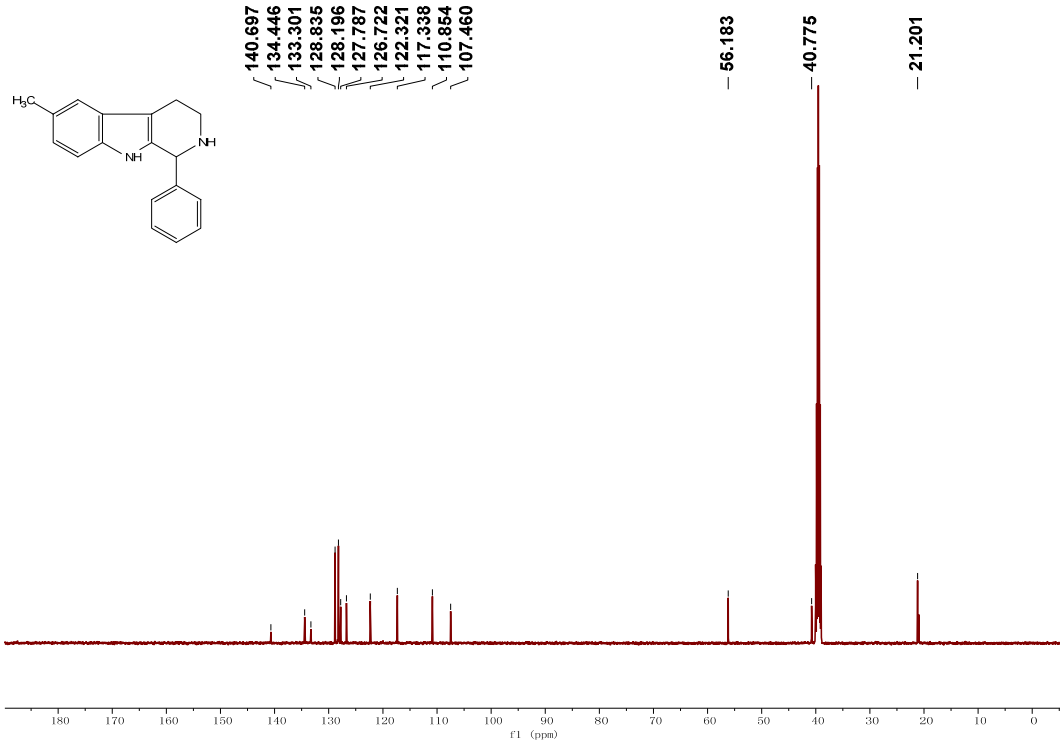


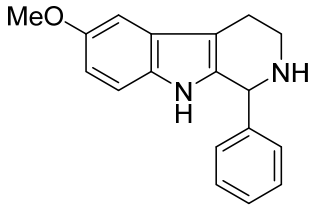
3ba

^{1}H NMR



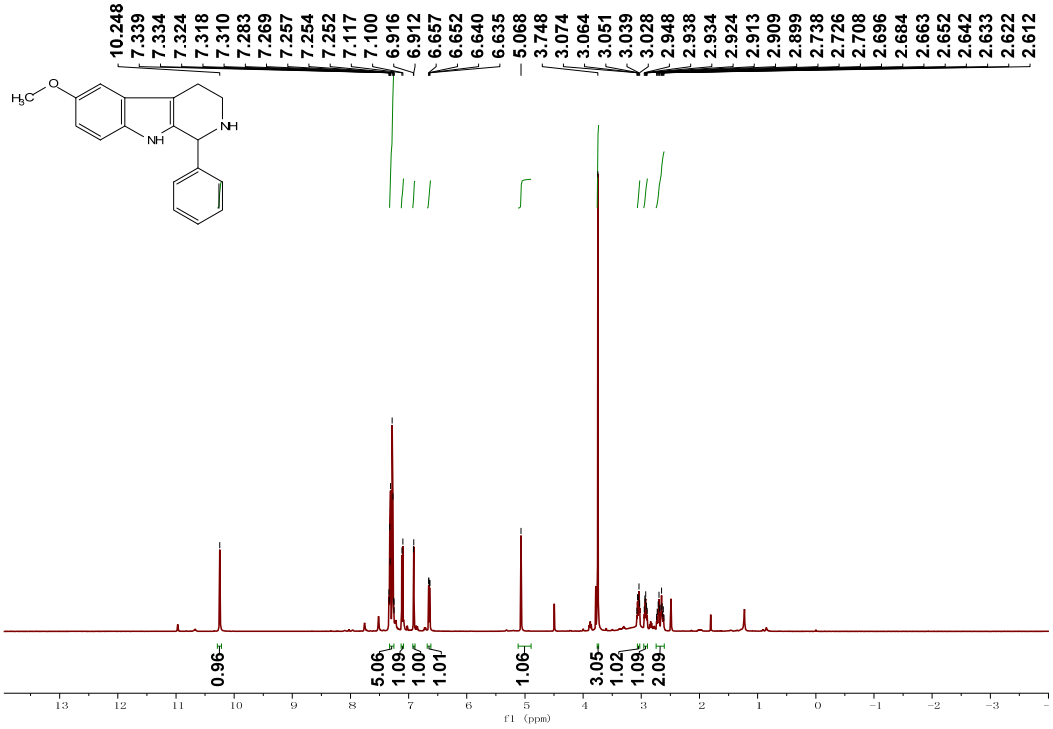
^{13}C NMR



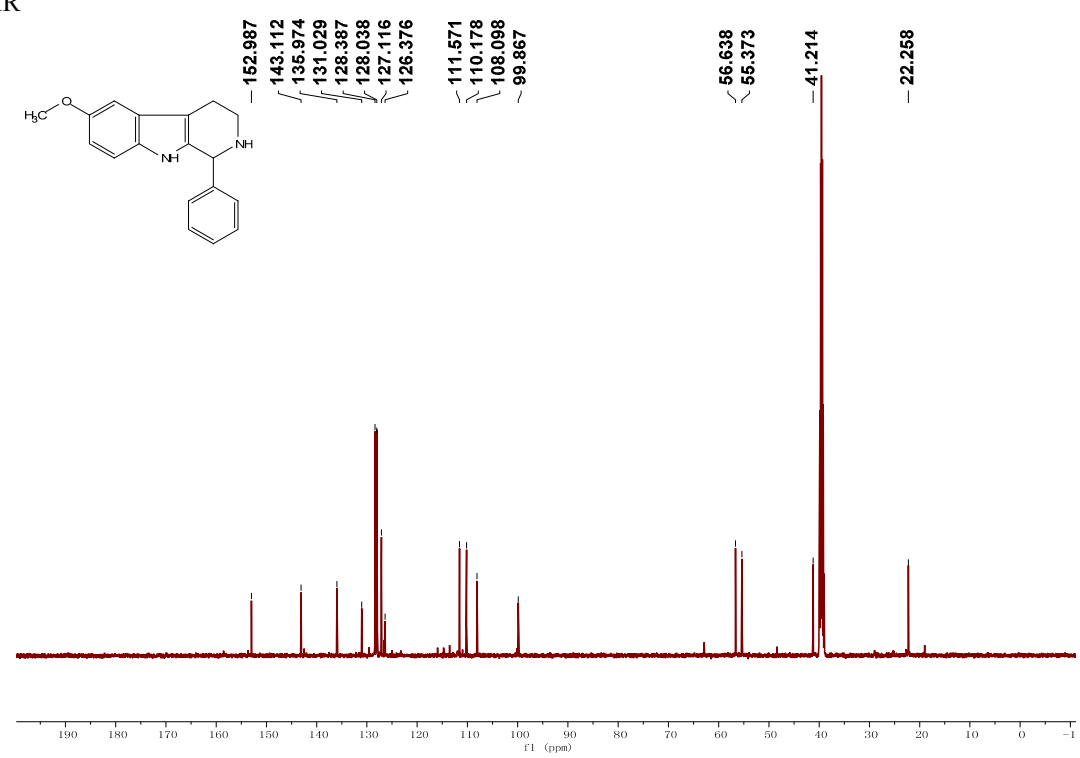


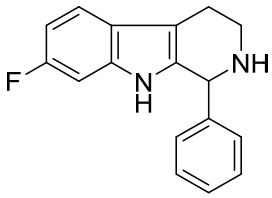
3ca

^{1}H NMR



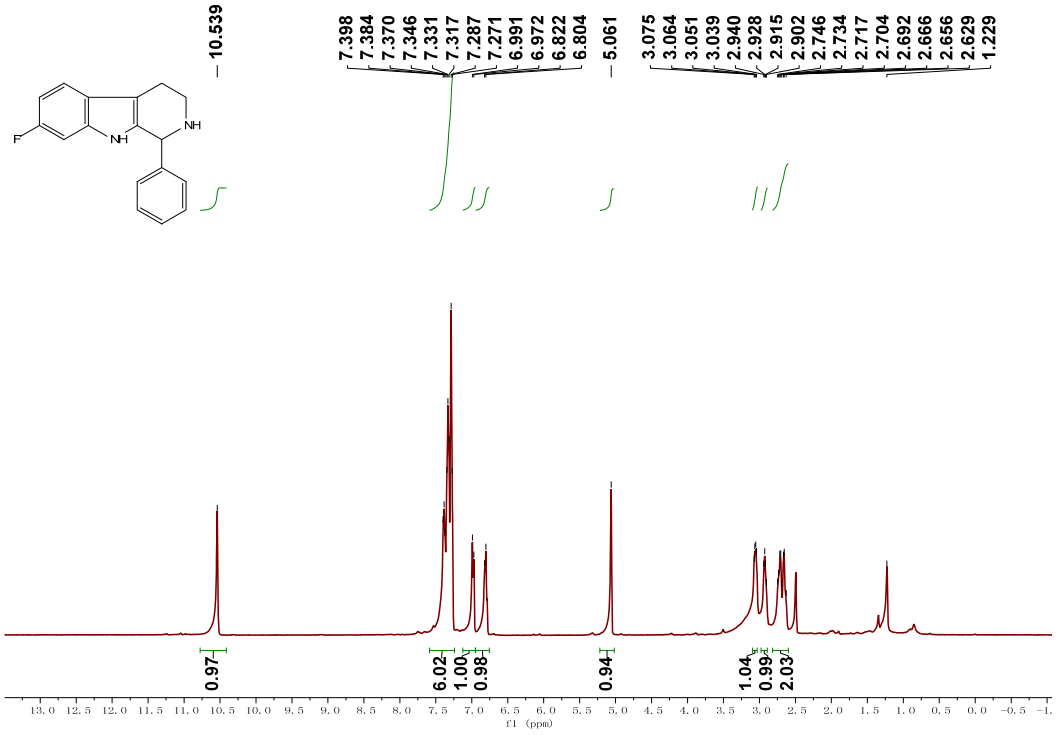
^{13}C NMR



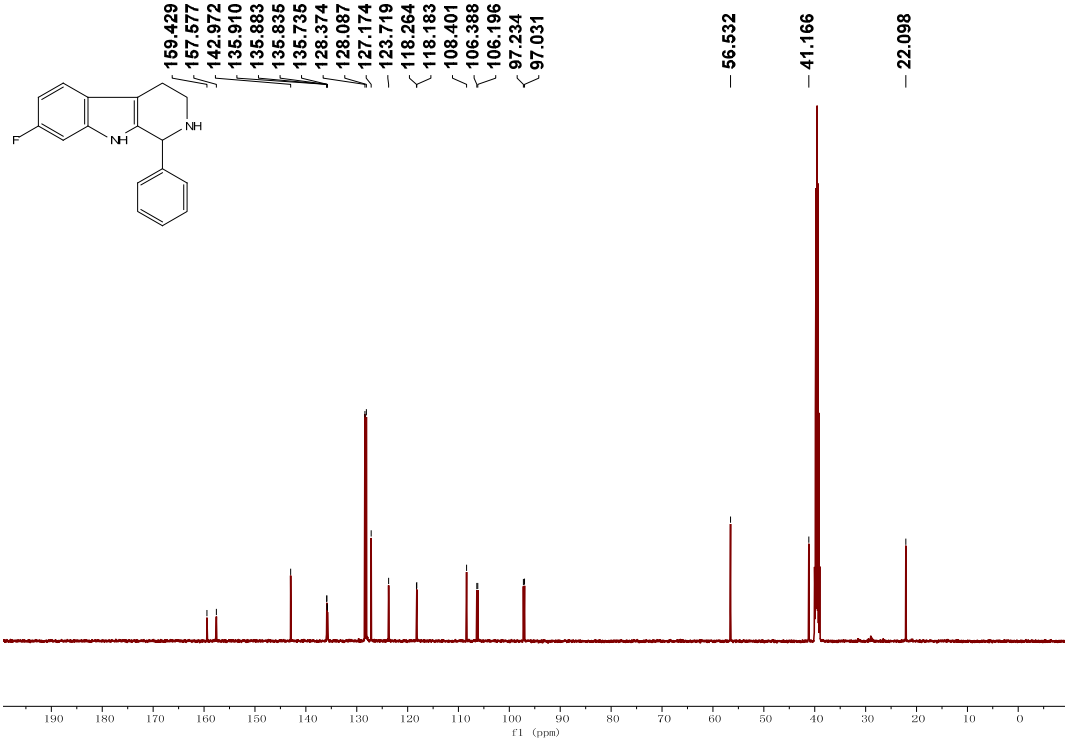


3da

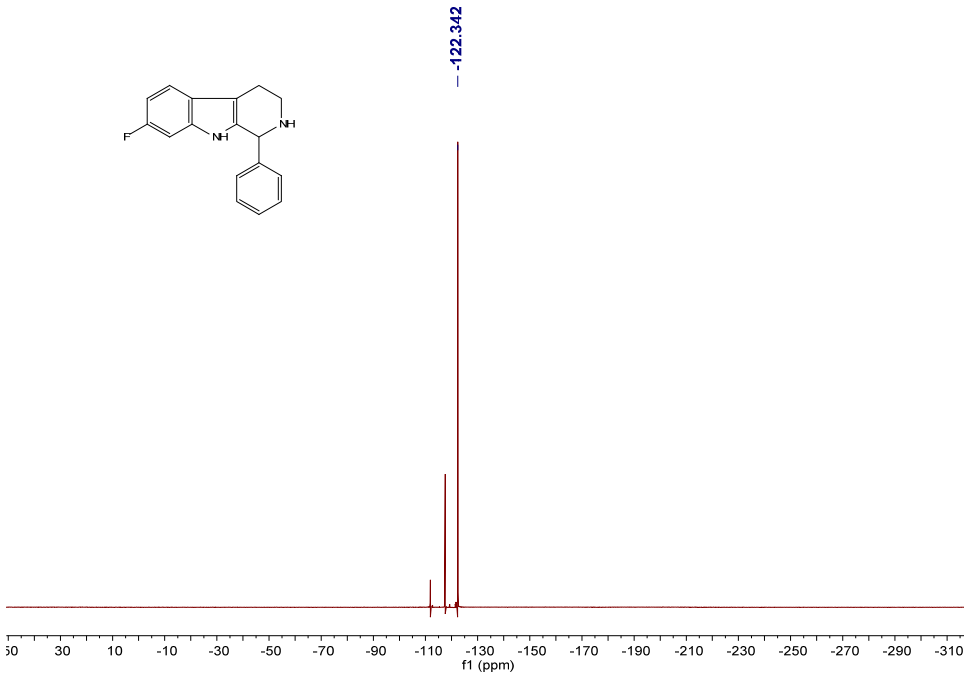
^{1}H NMR

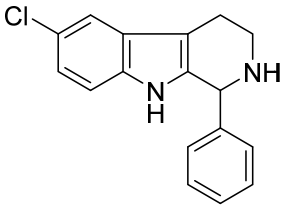


^{13}C NMR



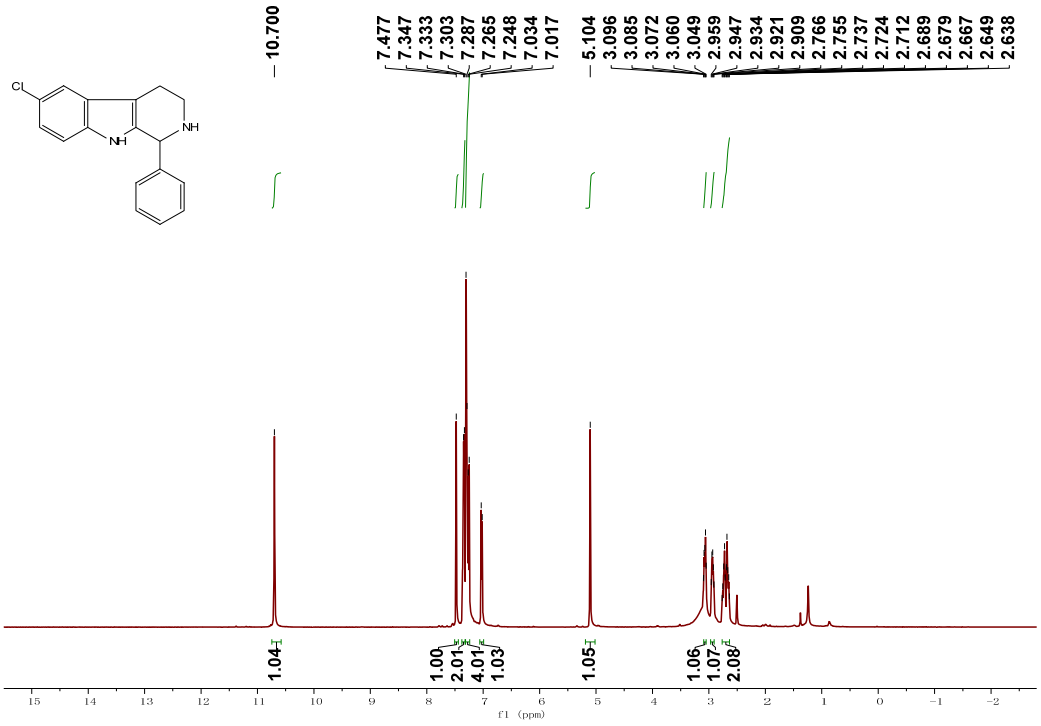
^{19}F NMR


-122.342
F
NH
NH
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290 -310
f1 (ppm)

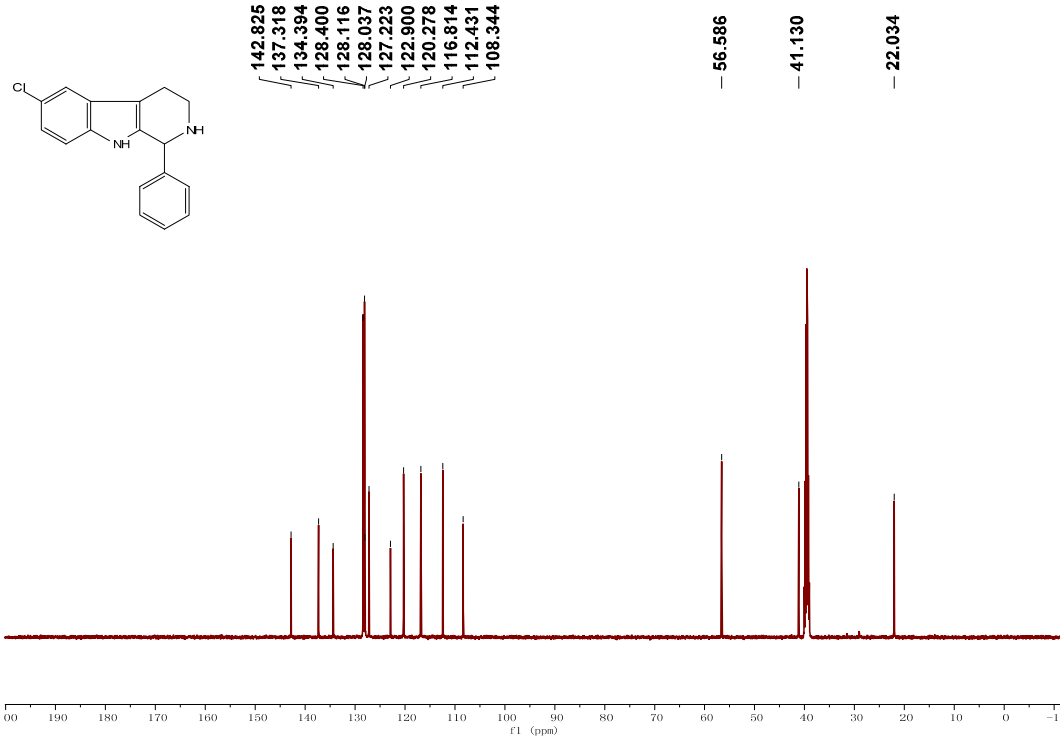


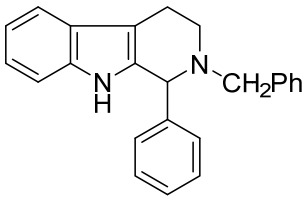
3ea

^{1}H NMR



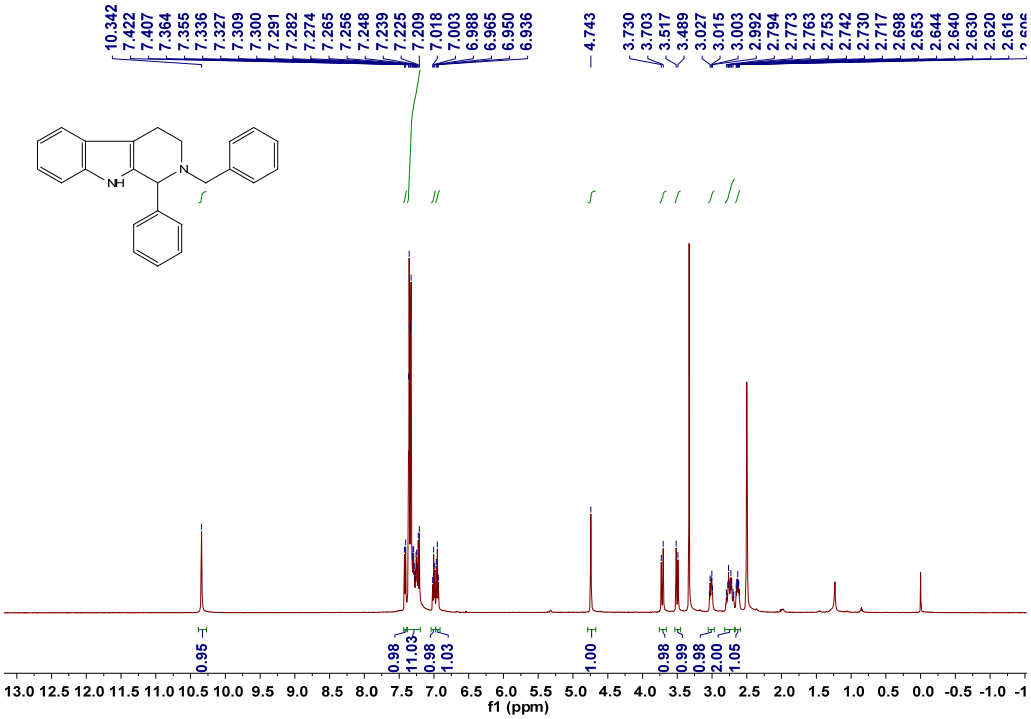
^{13}C NMR



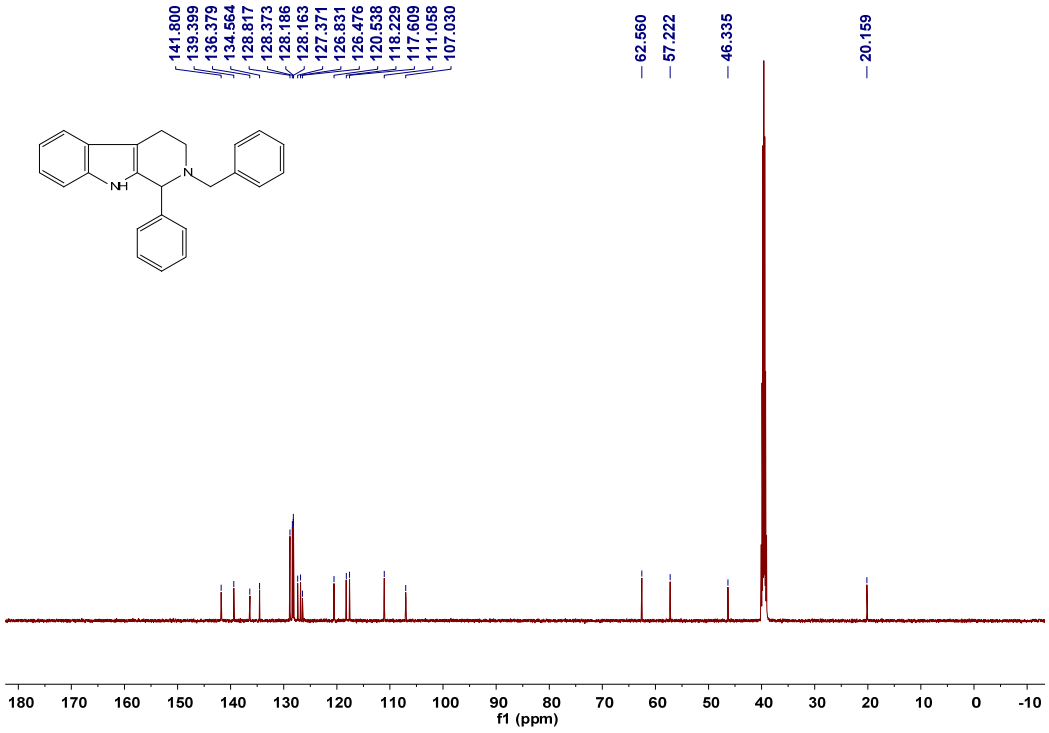


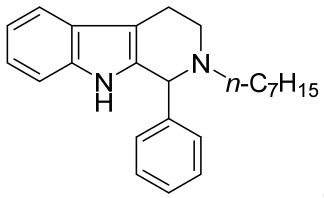
3fa

^{1}H NMR



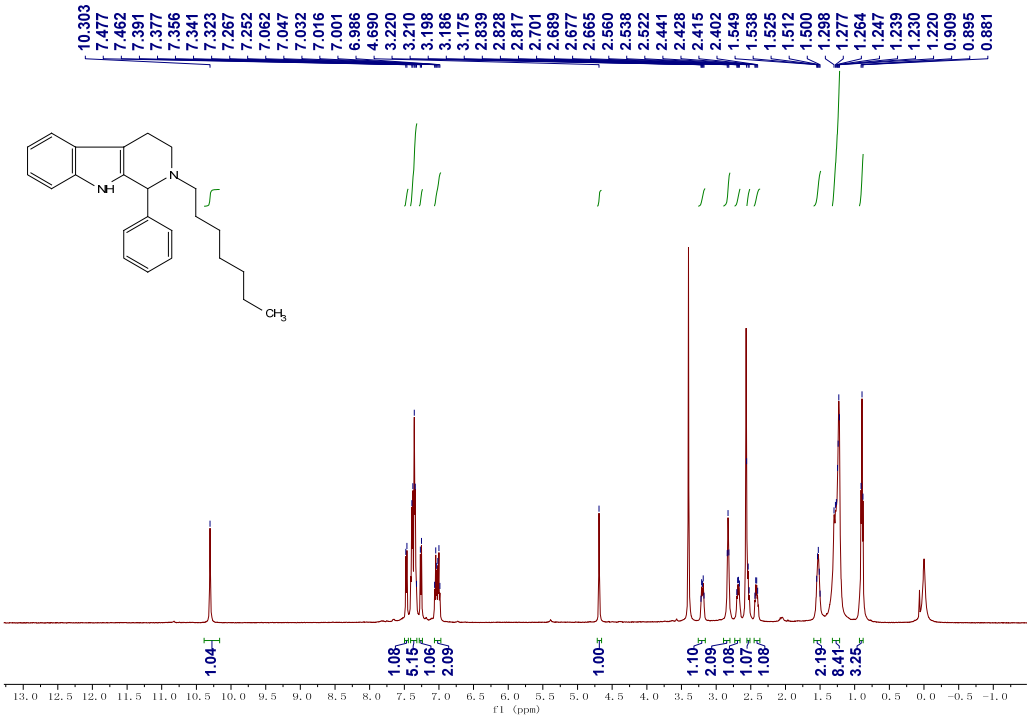
^{13}C NMR



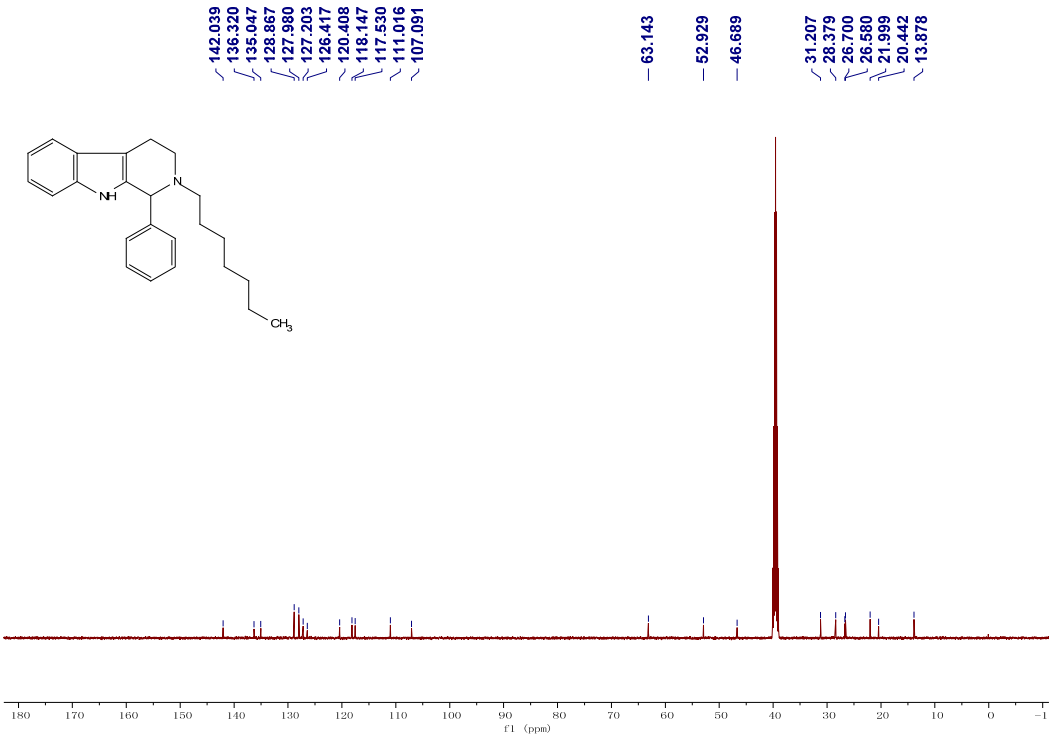


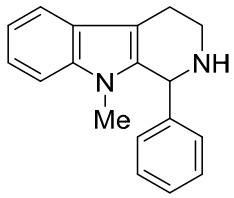
3ga

^{1}H NMR



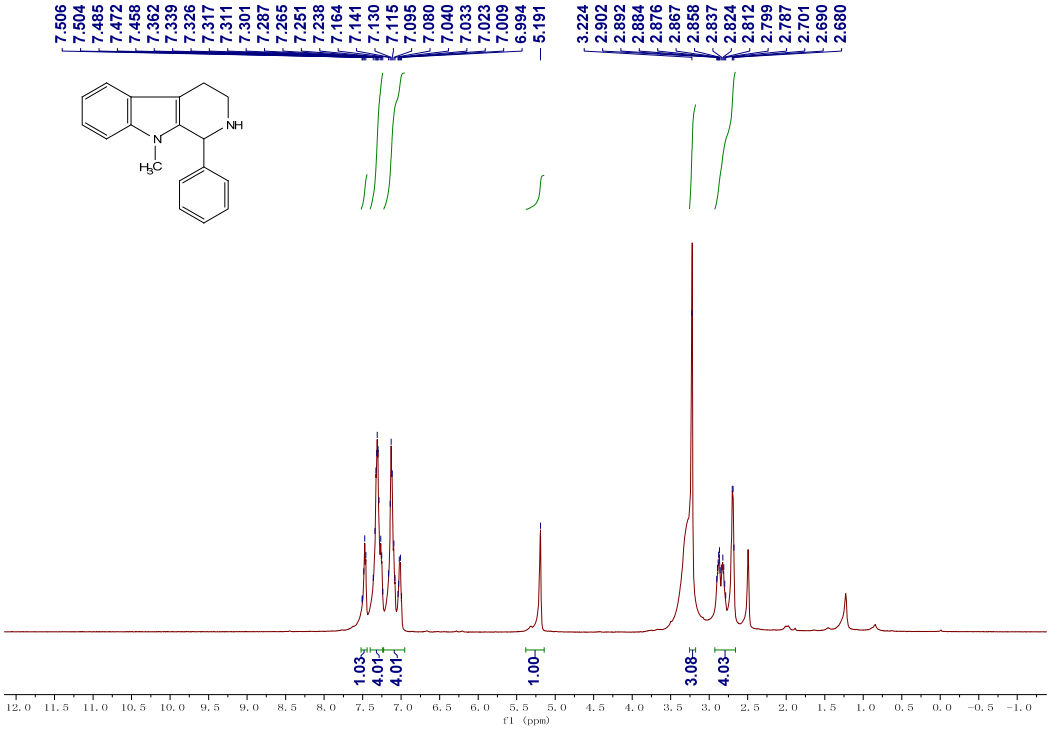
^{13}C NMR





3ha

^{1}H NMR



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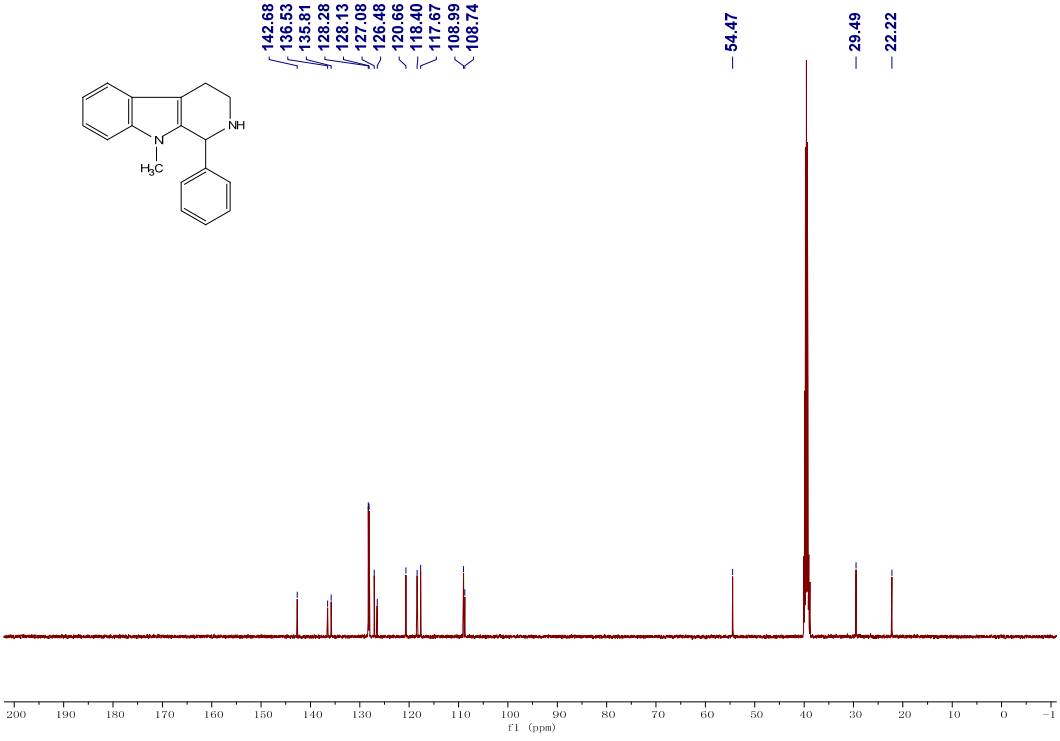

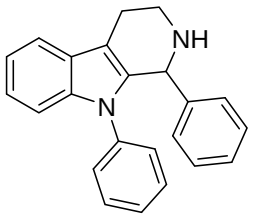

3ia

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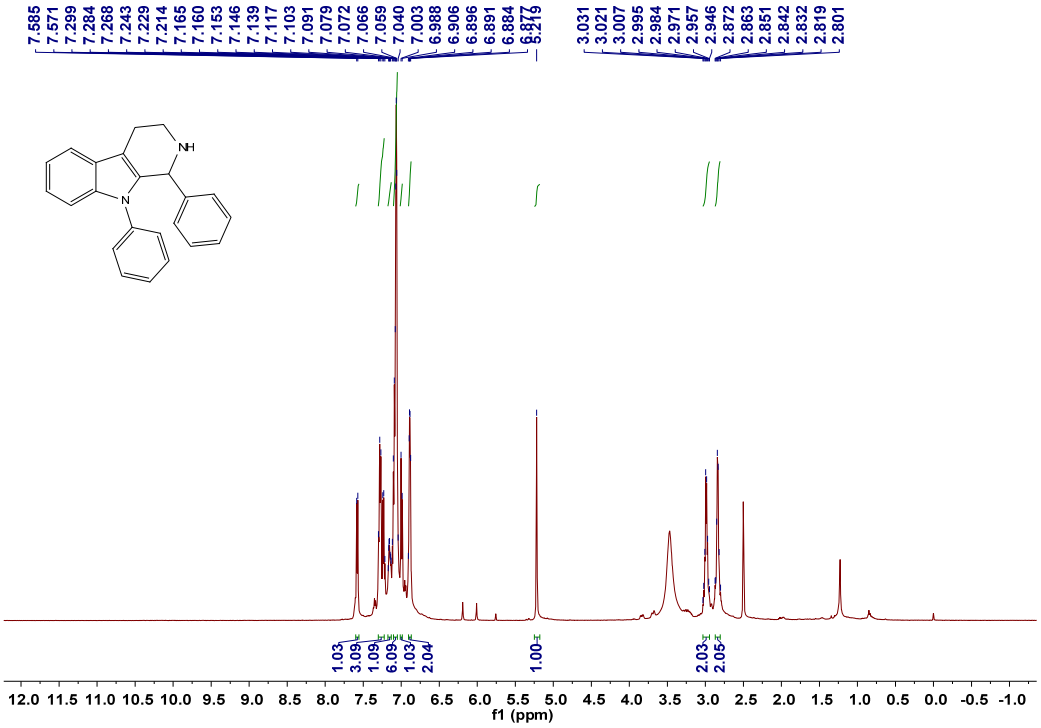

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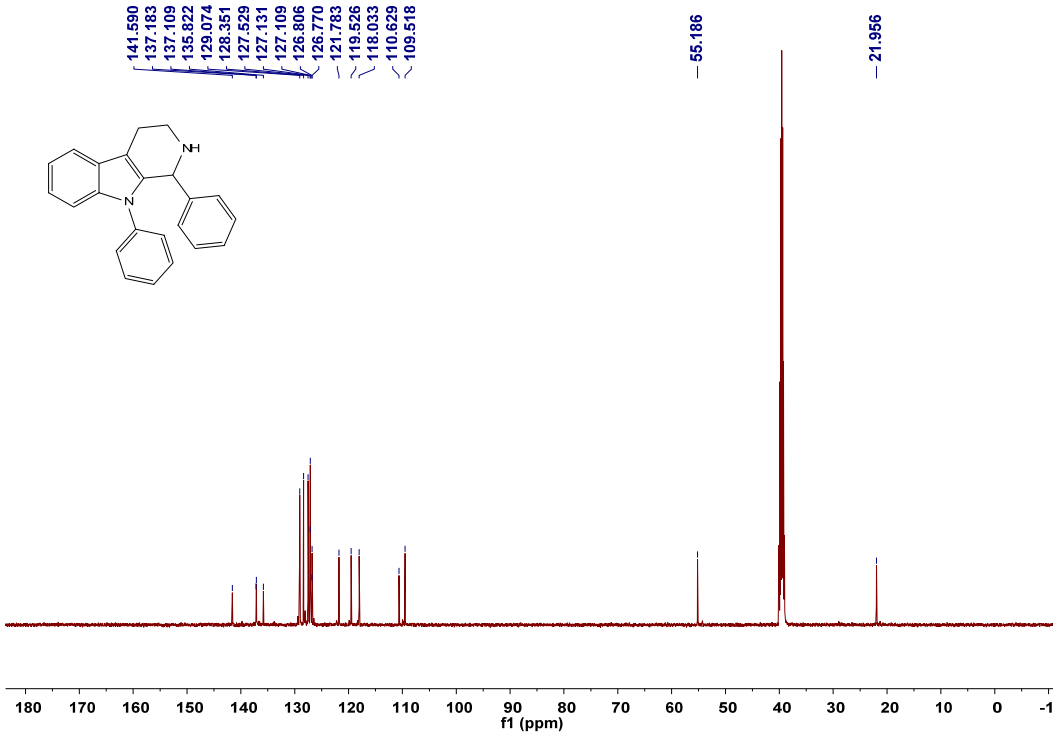
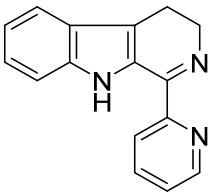
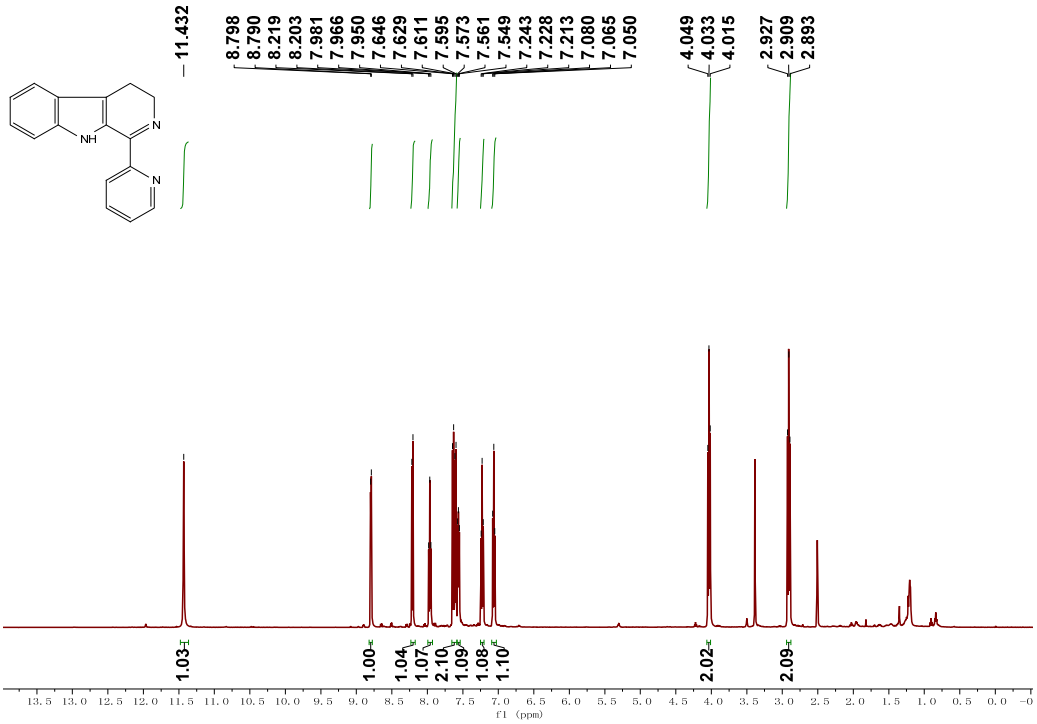


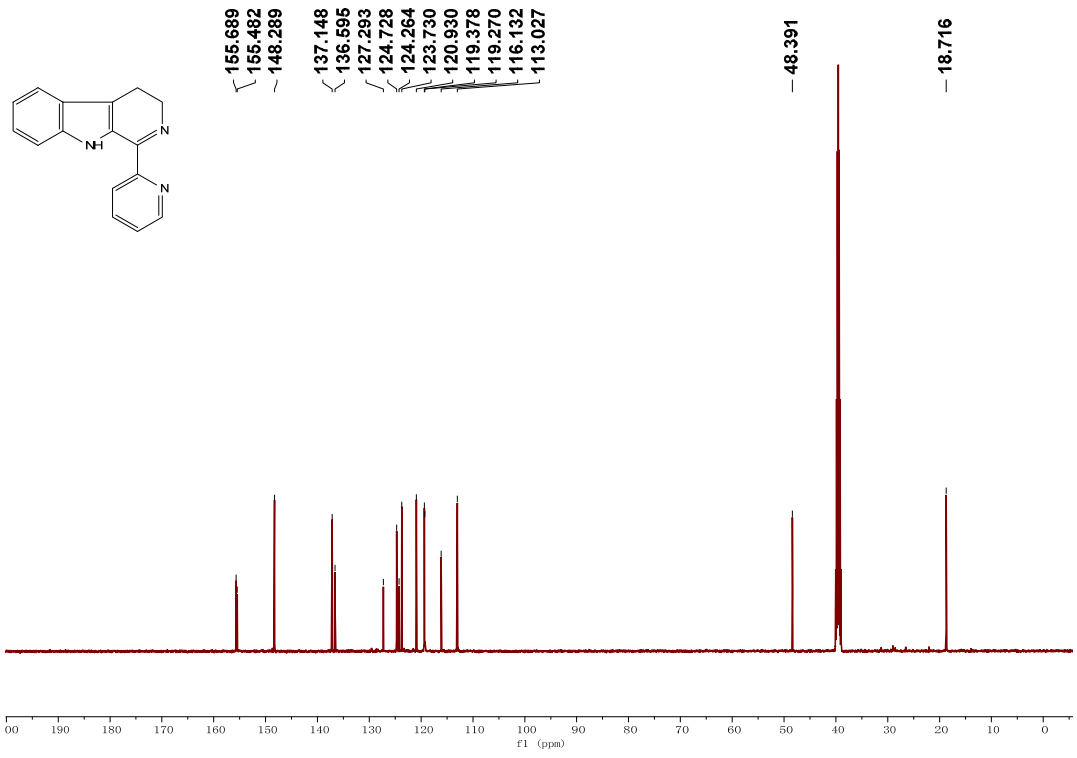


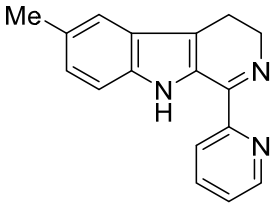
4aw

^{1}H NMR



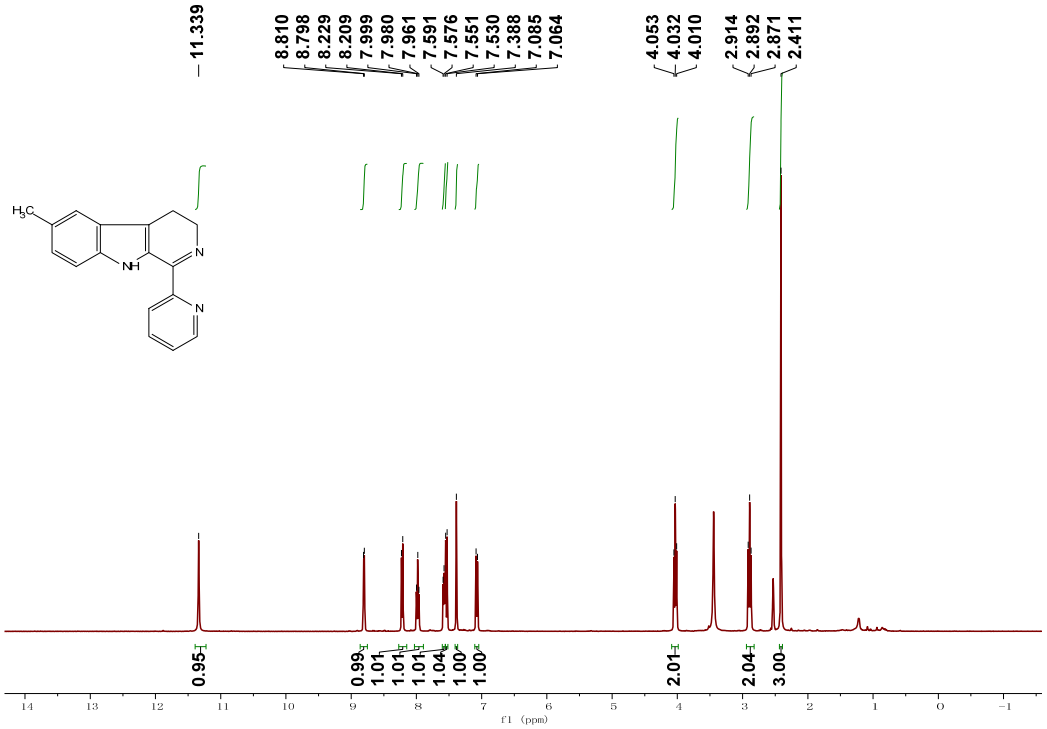
^{13}C NMR



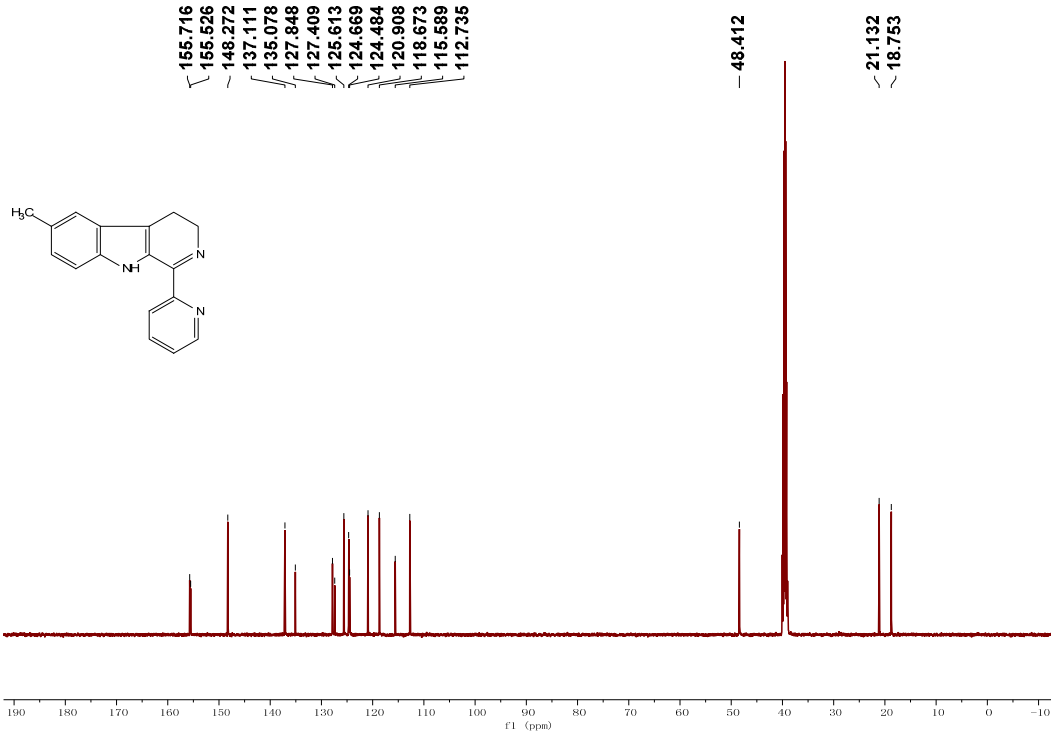


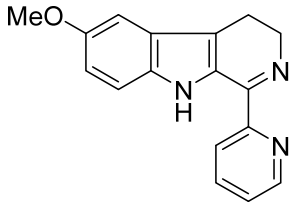
4bw

^{1}H NMR



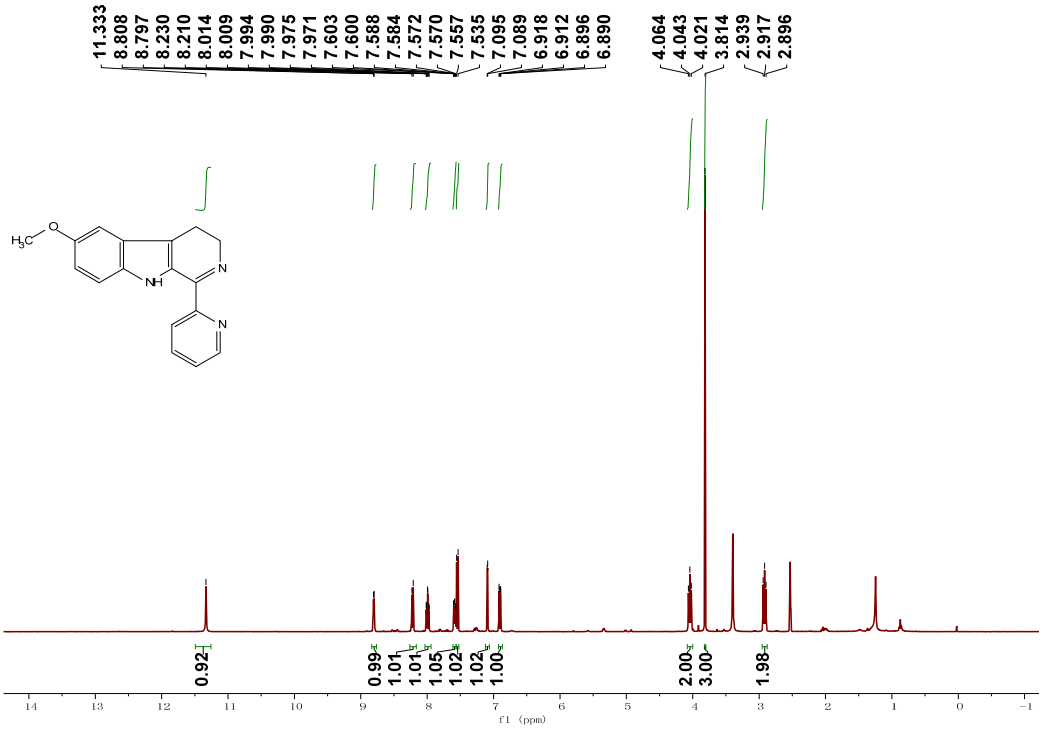
^{13}C NMR



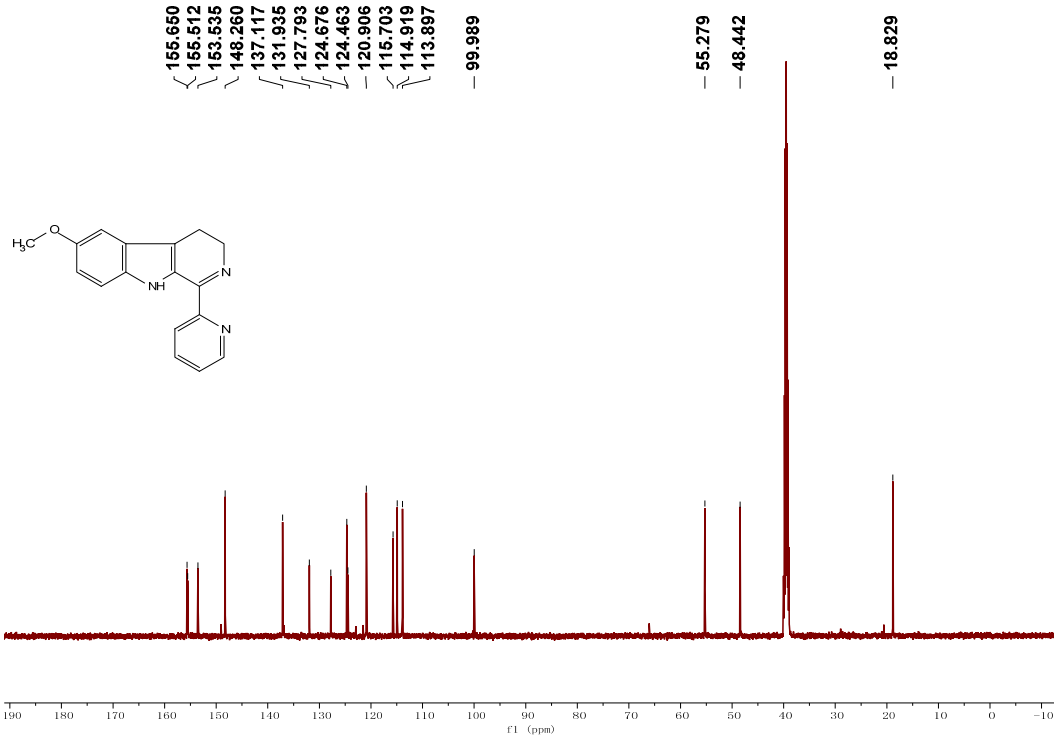


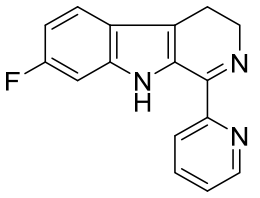
4cw

^{1}H NMR



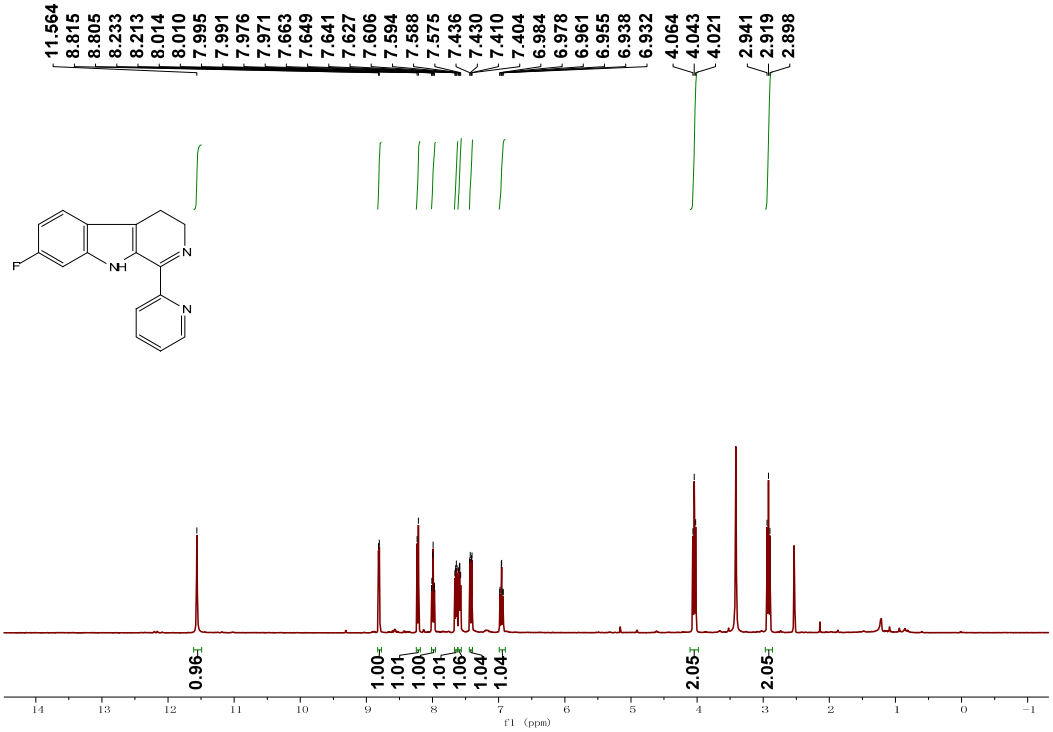
^{13}C NMR



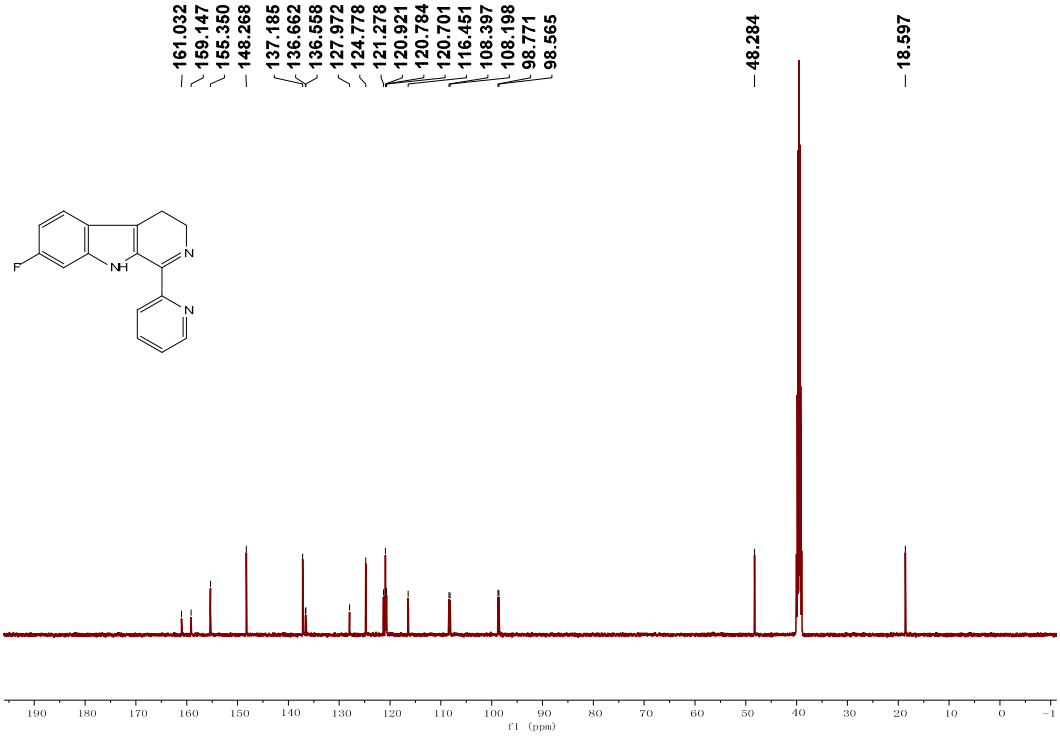


4dw

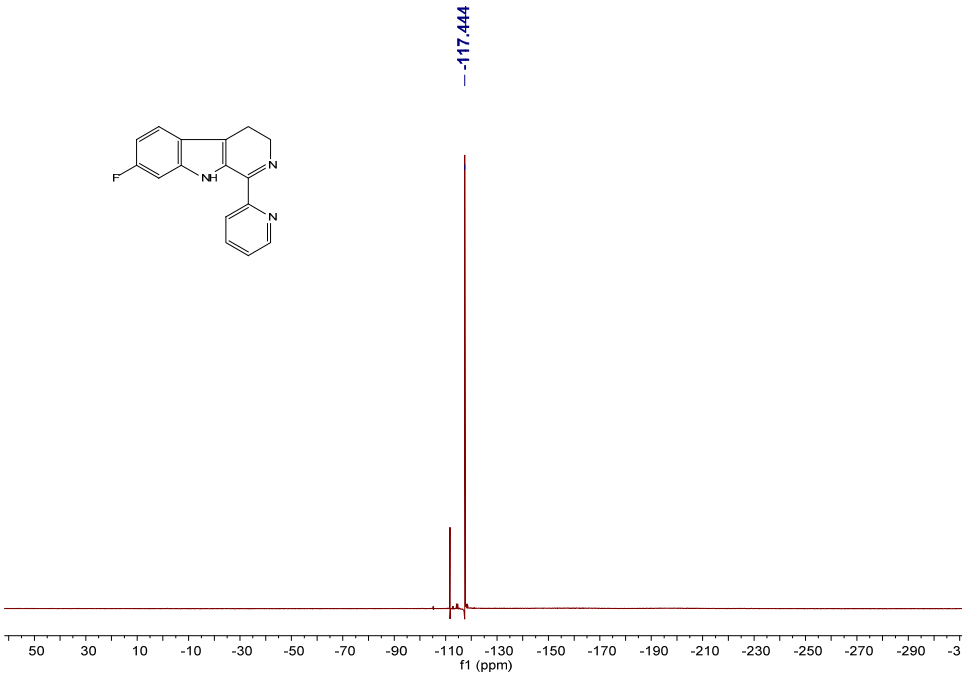
^{1}H NMR



^{13}C NMR



^{19}F NMR


-117.444
F
NH
N
N
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
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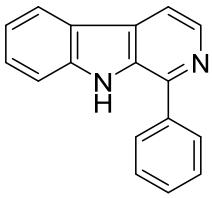
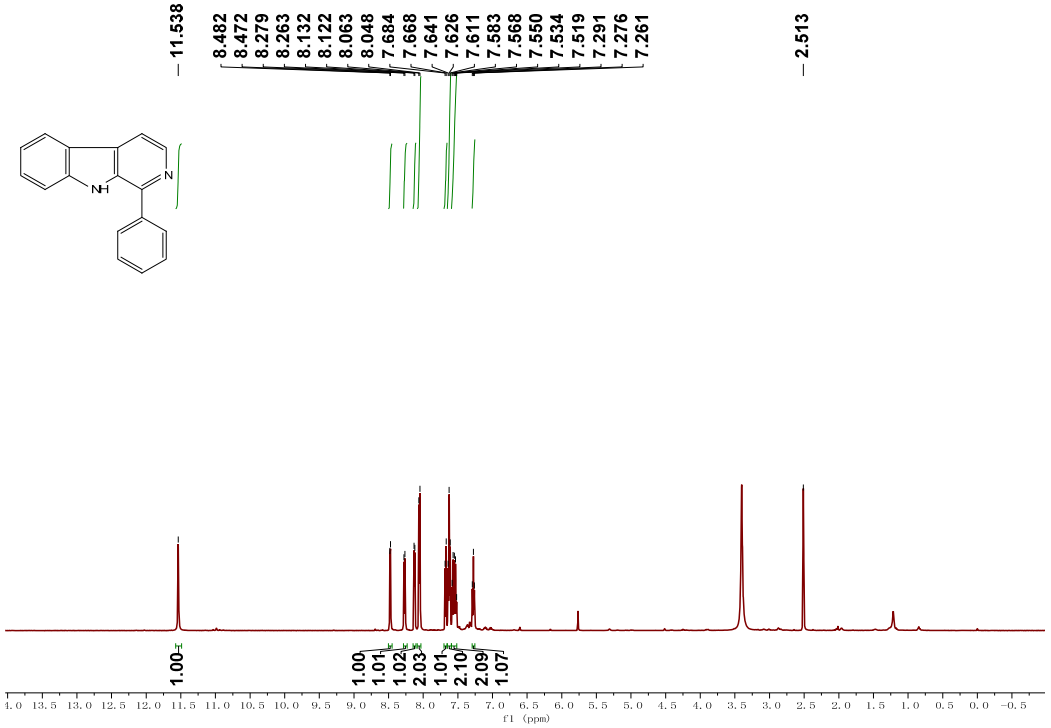
-250
-270
-290
-3
f1 (ppm)

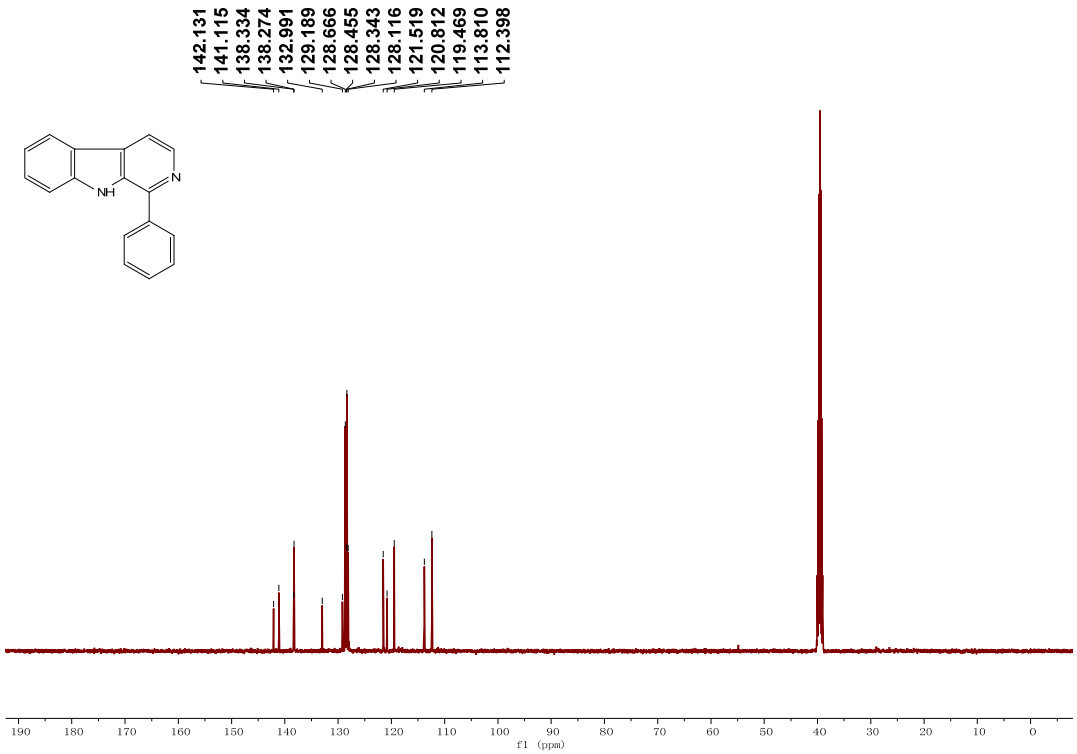


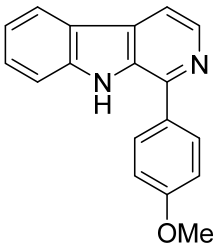
5aa

^{1}H NMR



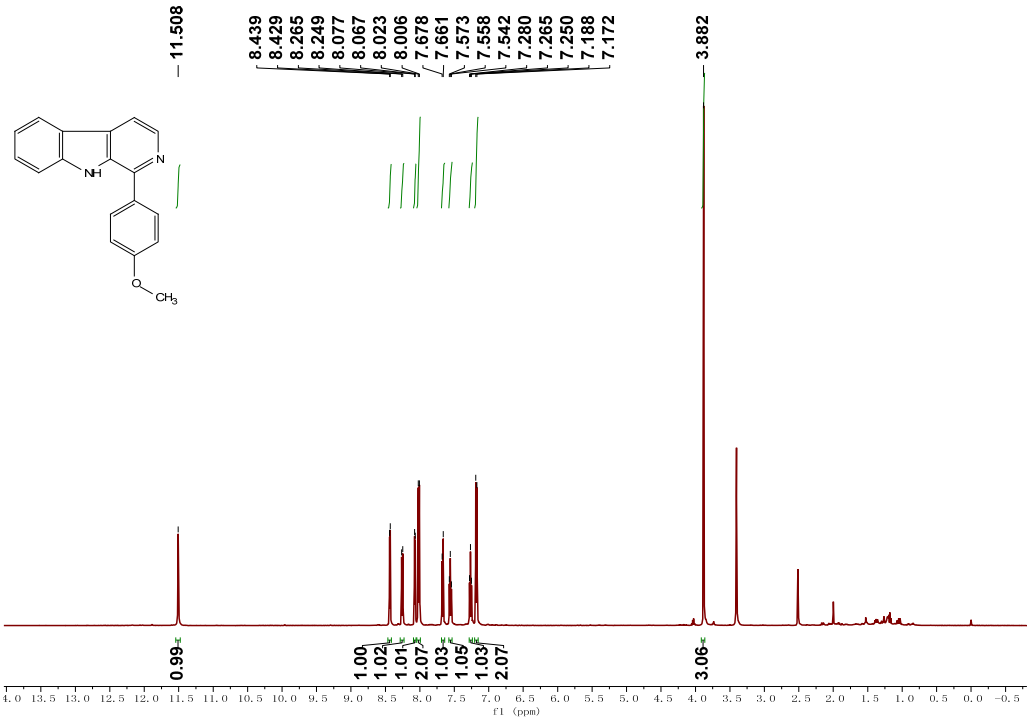
^{13}C NMR



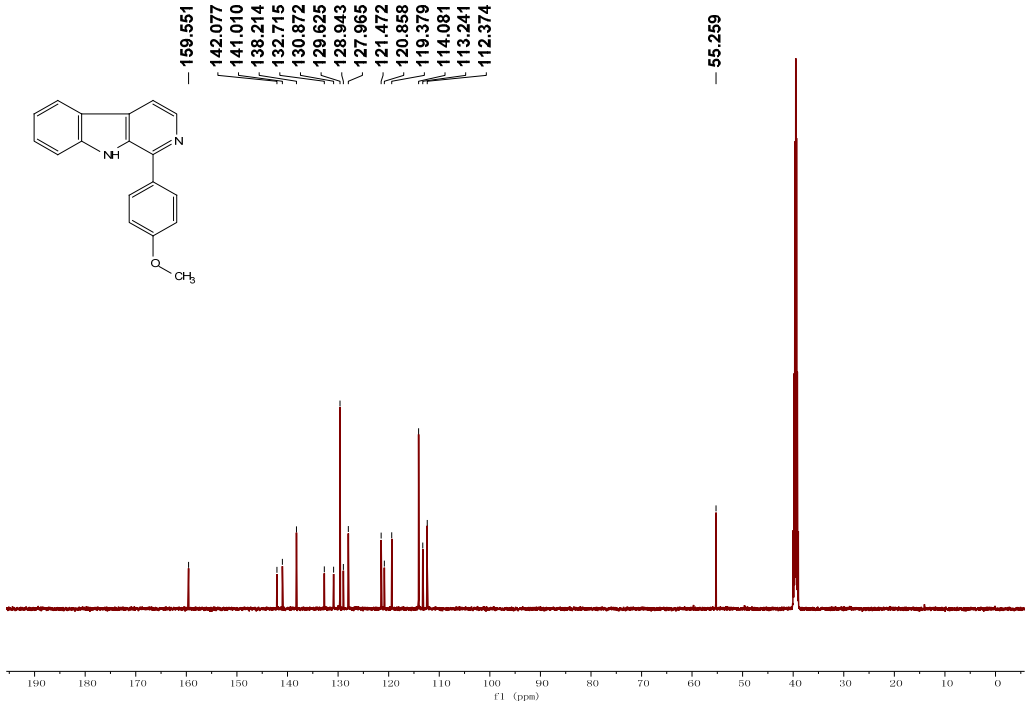


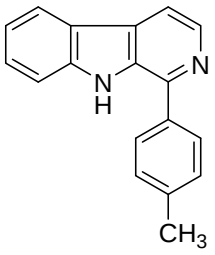
5ab

^{1}H NMR



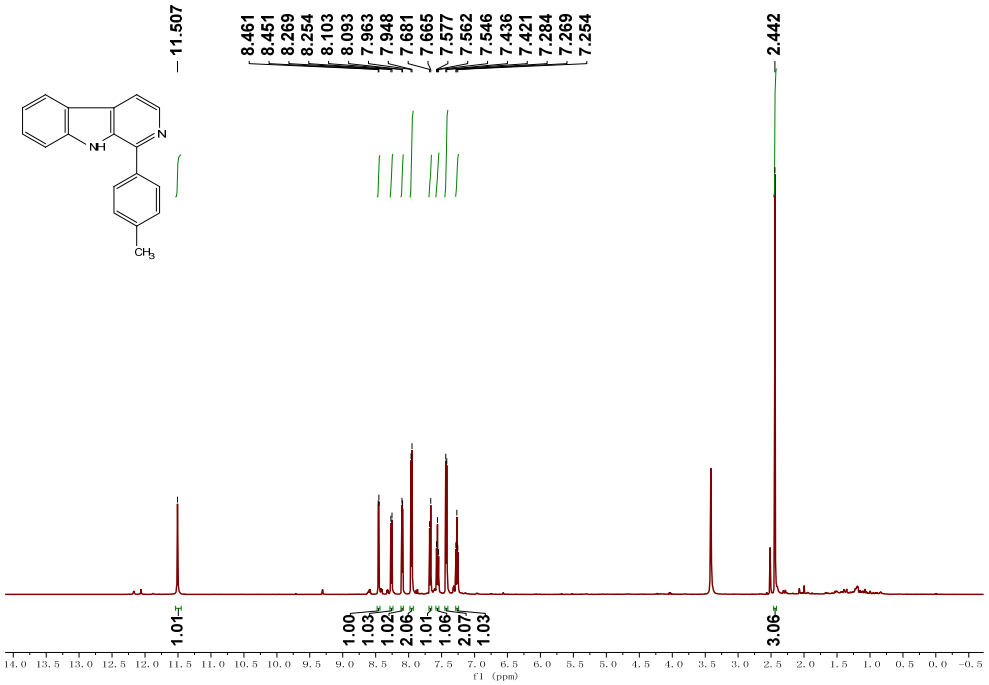
^{13}C NMR



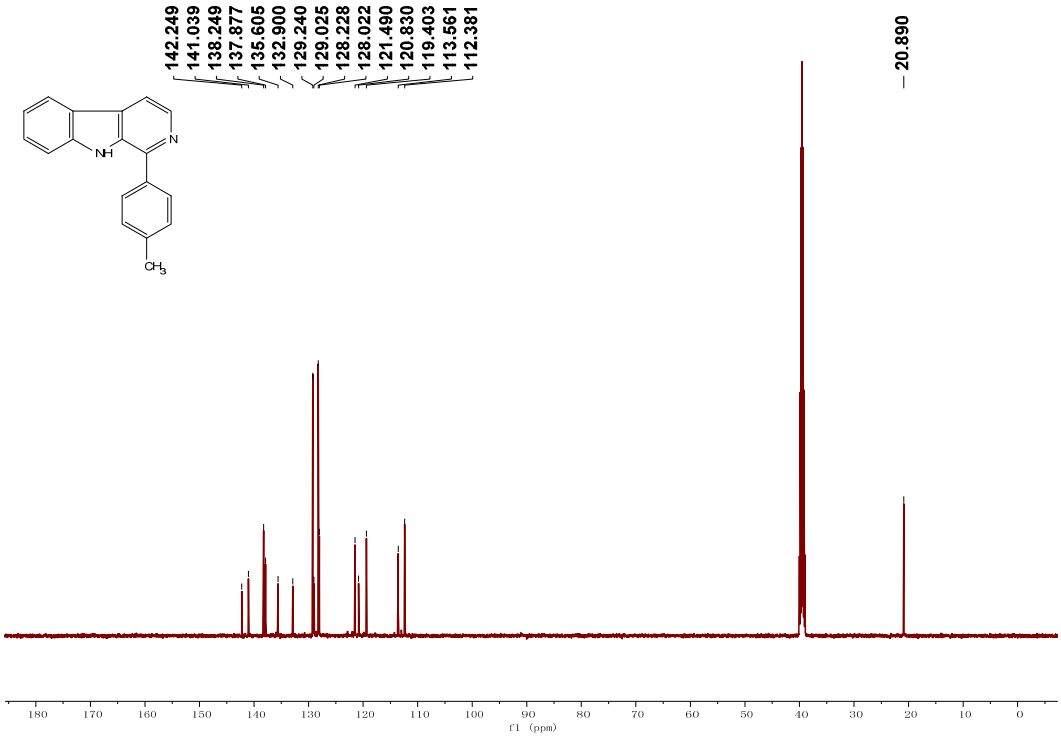


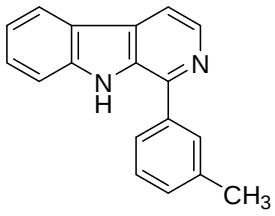
5ac

^{1}H NMR



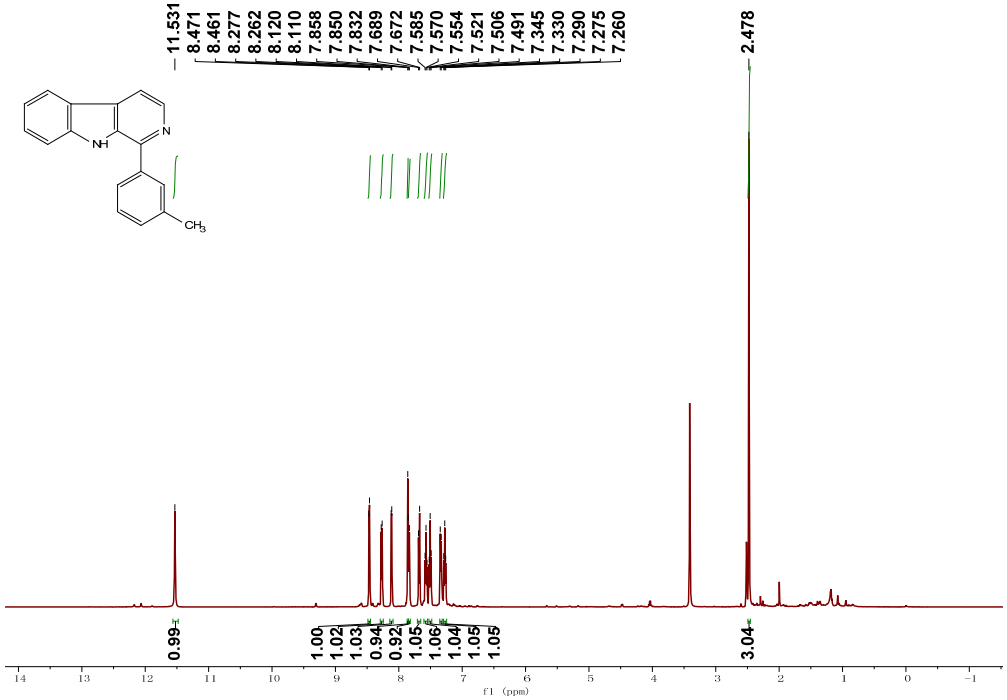
^{13}C NMR



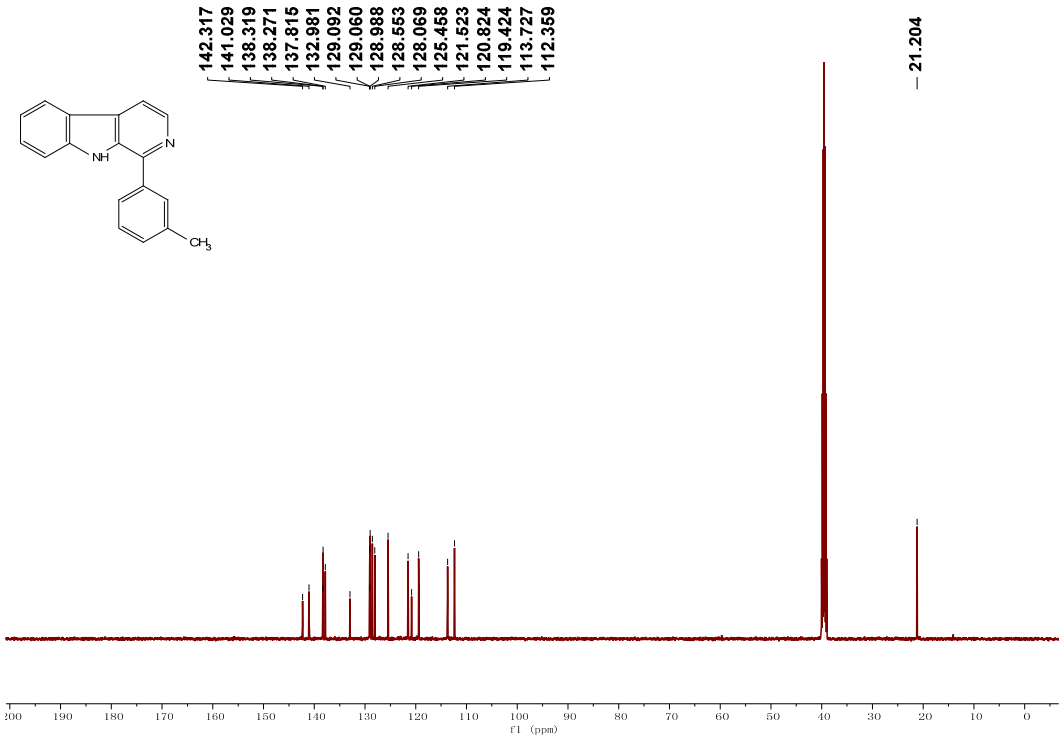


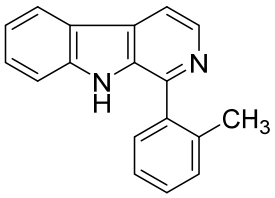
5ad

^{1}H NMR



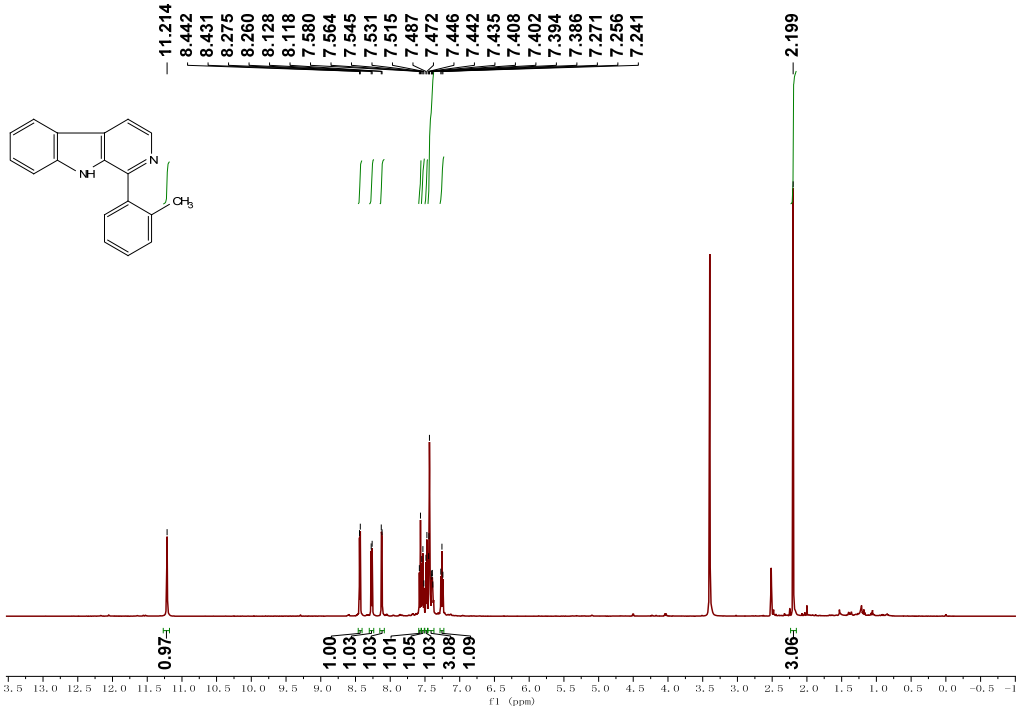
^{13}C NMR



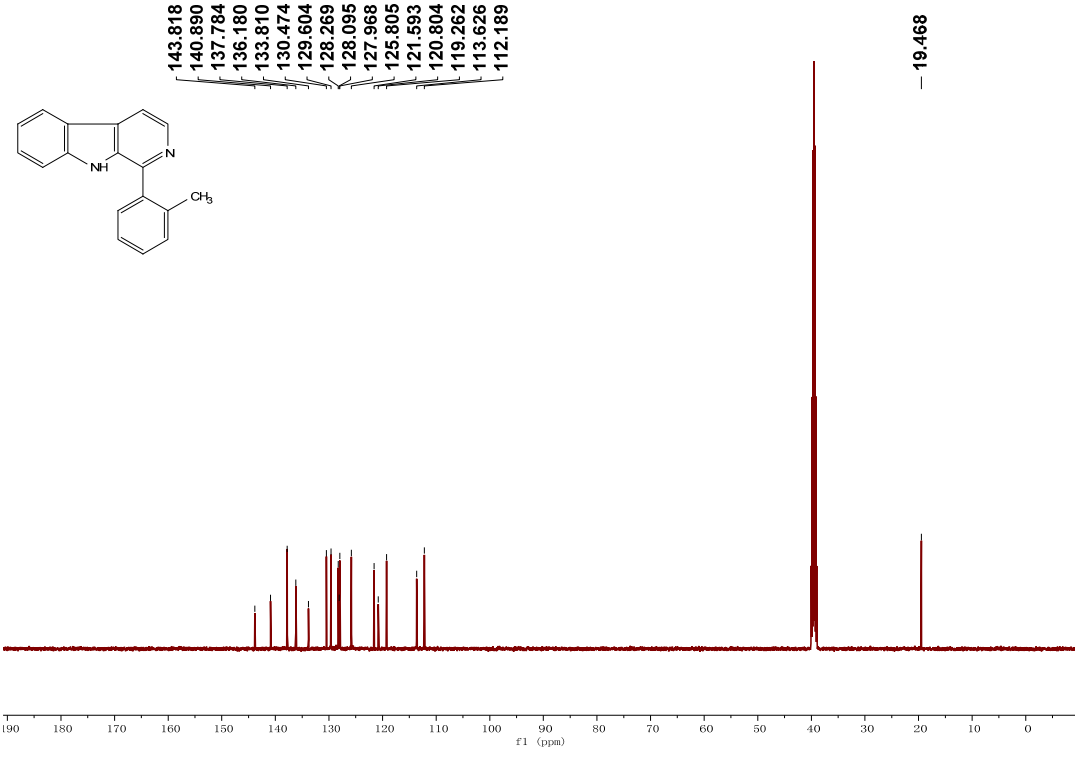


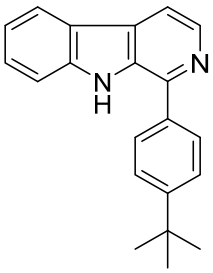
5ae

^{1}H NMR



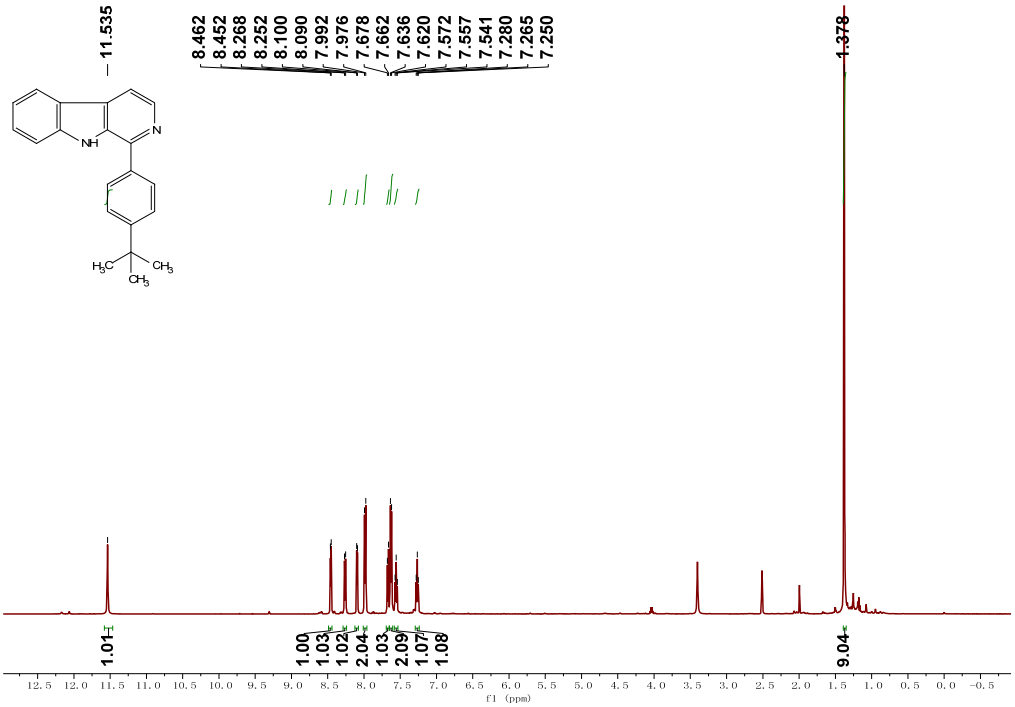
^{13}C NMR



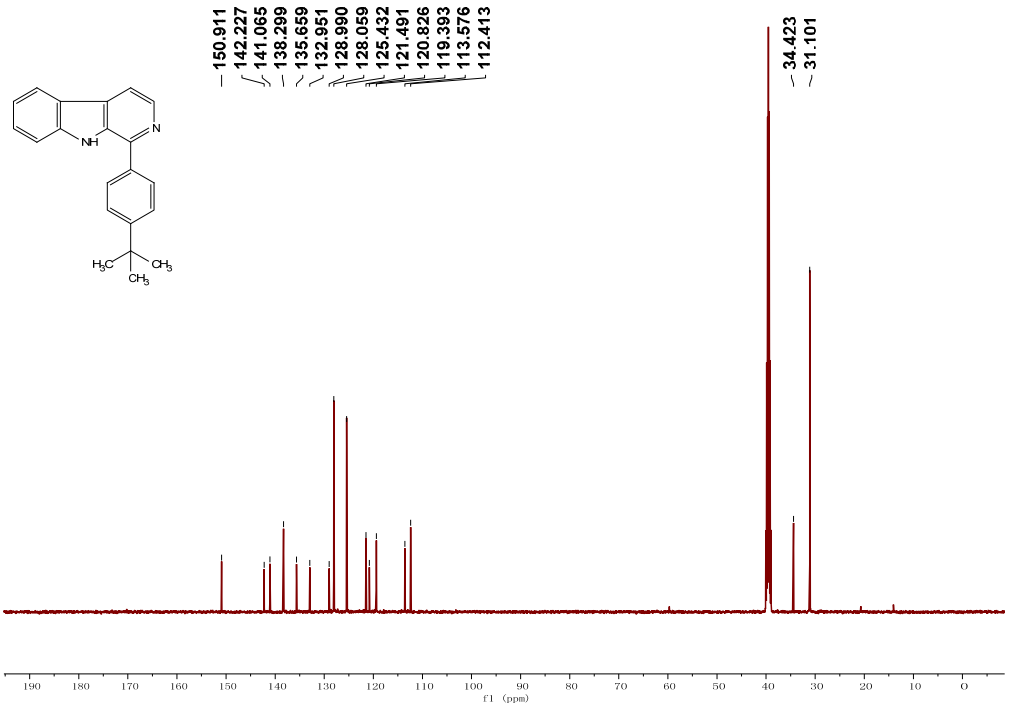


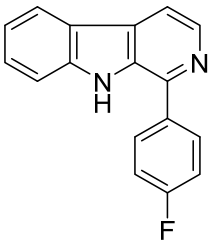
5af

^{1}H NMR



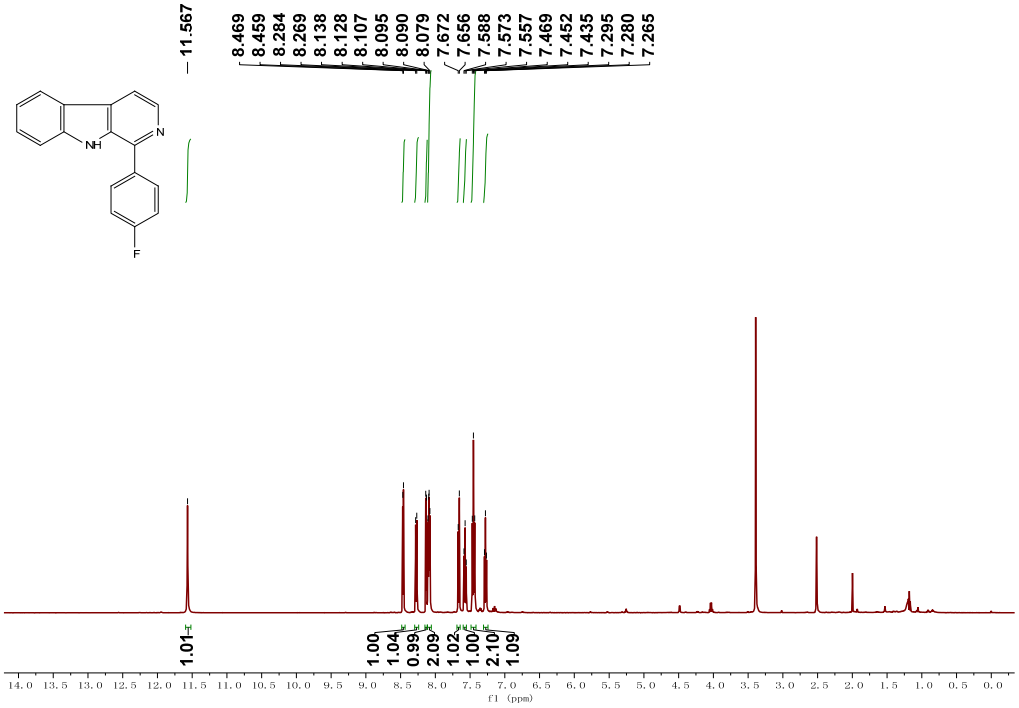
^{13}C NMR



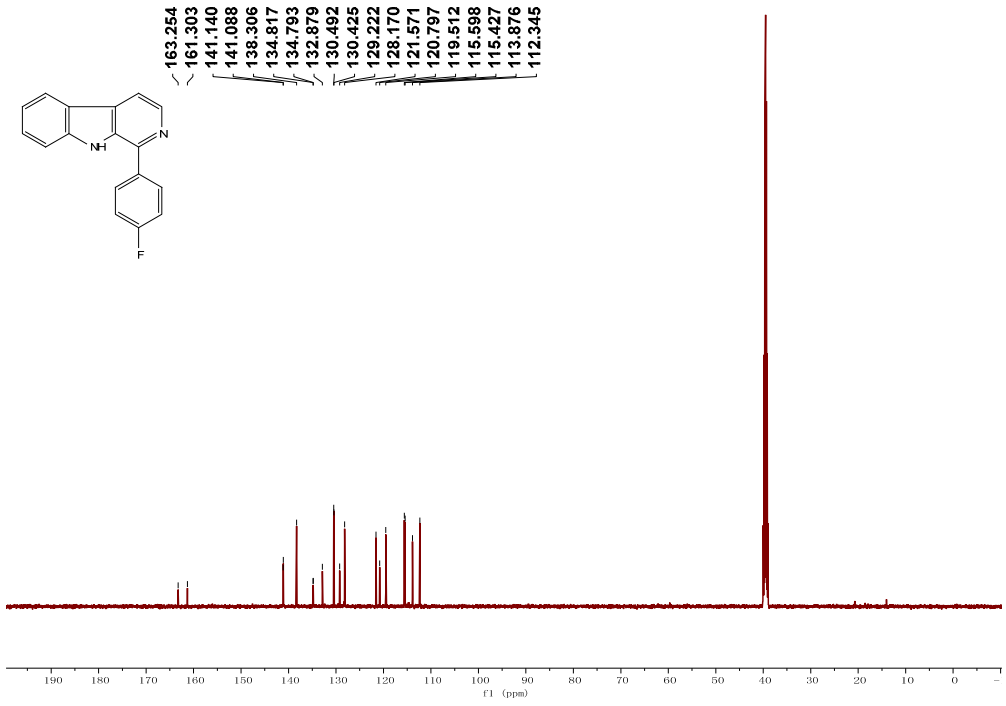


5ag

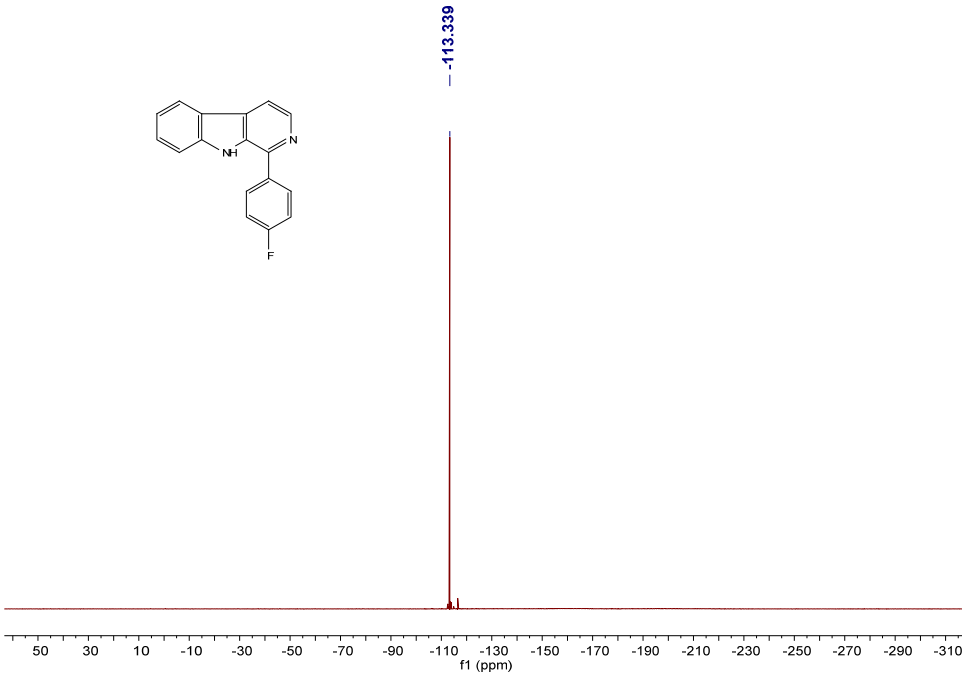
^{1}H NMR

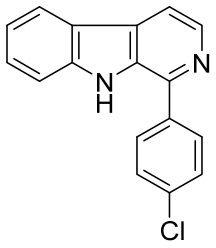


^{13}C NMR



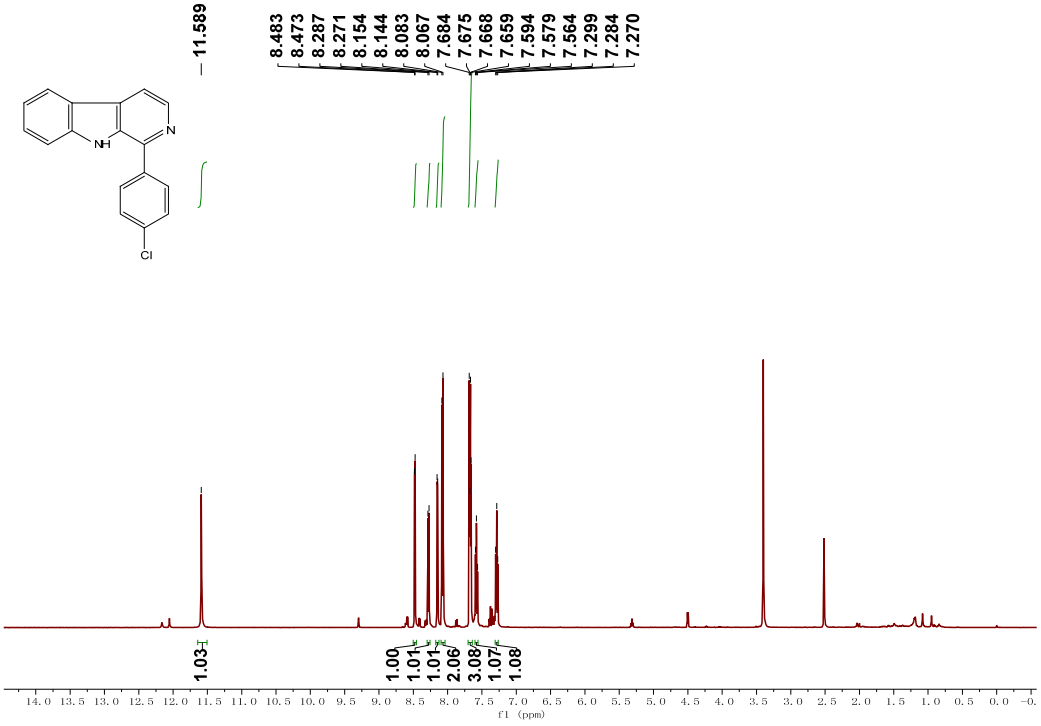
^{19}F NMR


-113.339
NH
N
F
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290 -310
f1 (ppm)

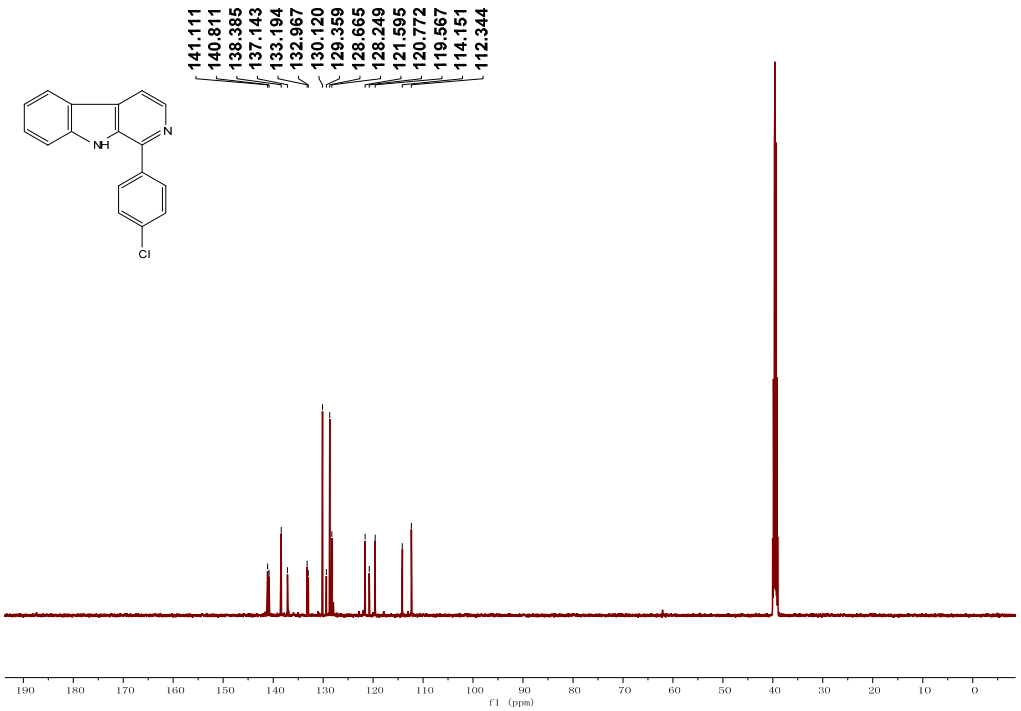


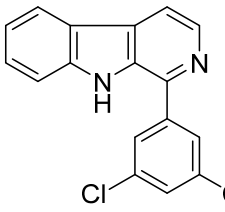
5ah

^{1}H NMR



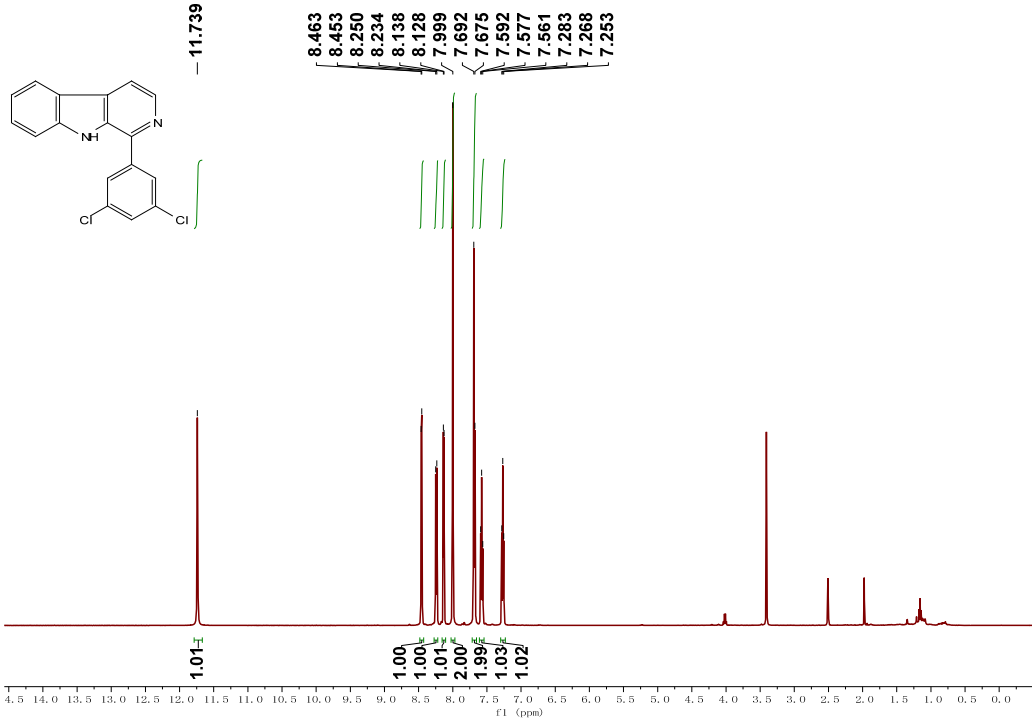
^{13}C NMR



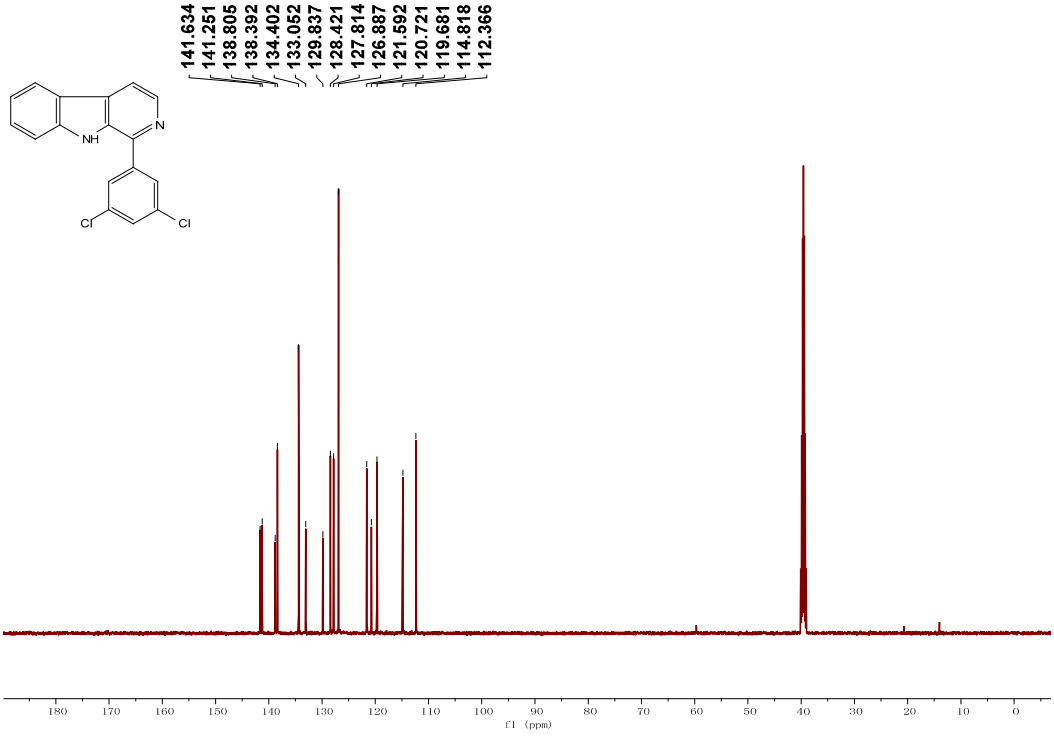


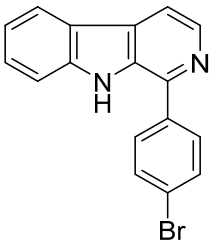
5ai

^{1}H NMR



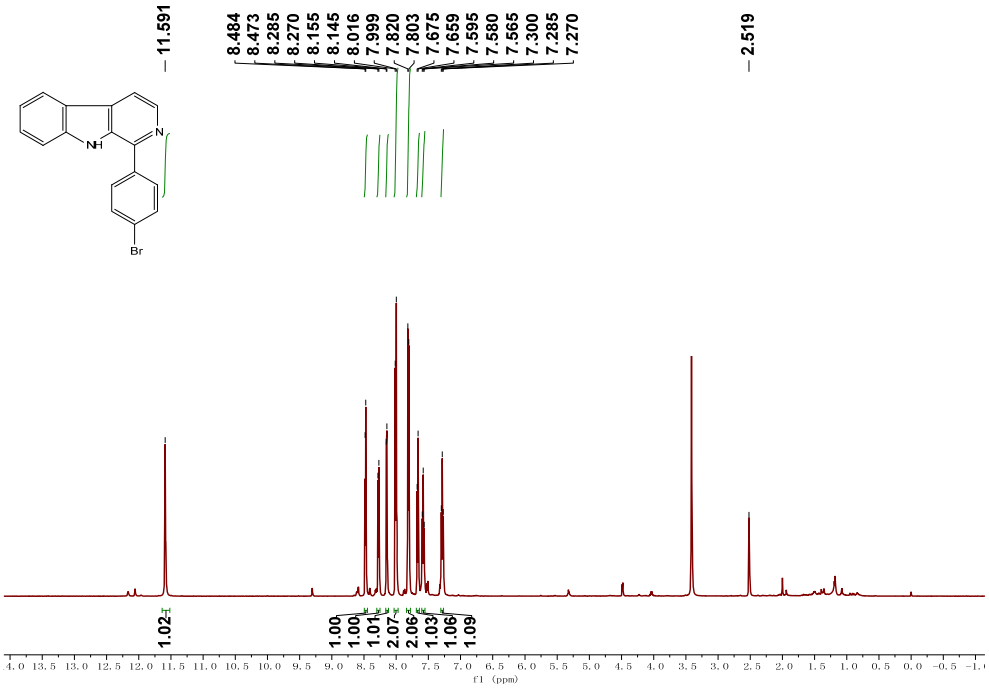
^{13}C NMR



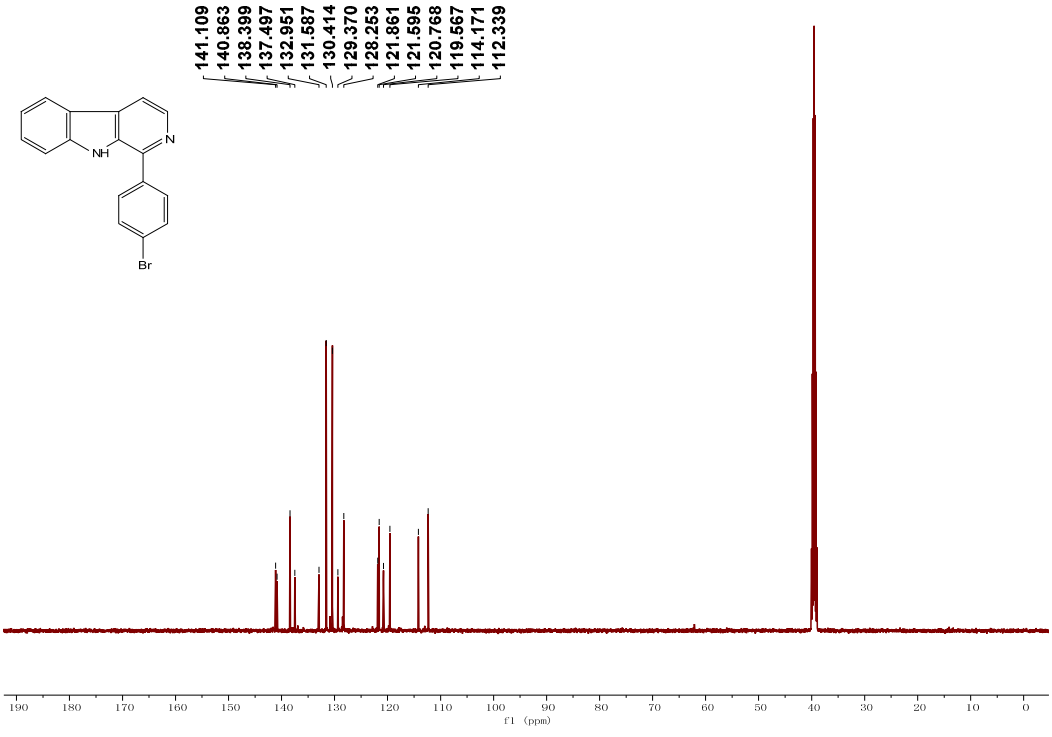


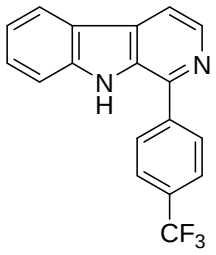
5aj

^{1}H NMR



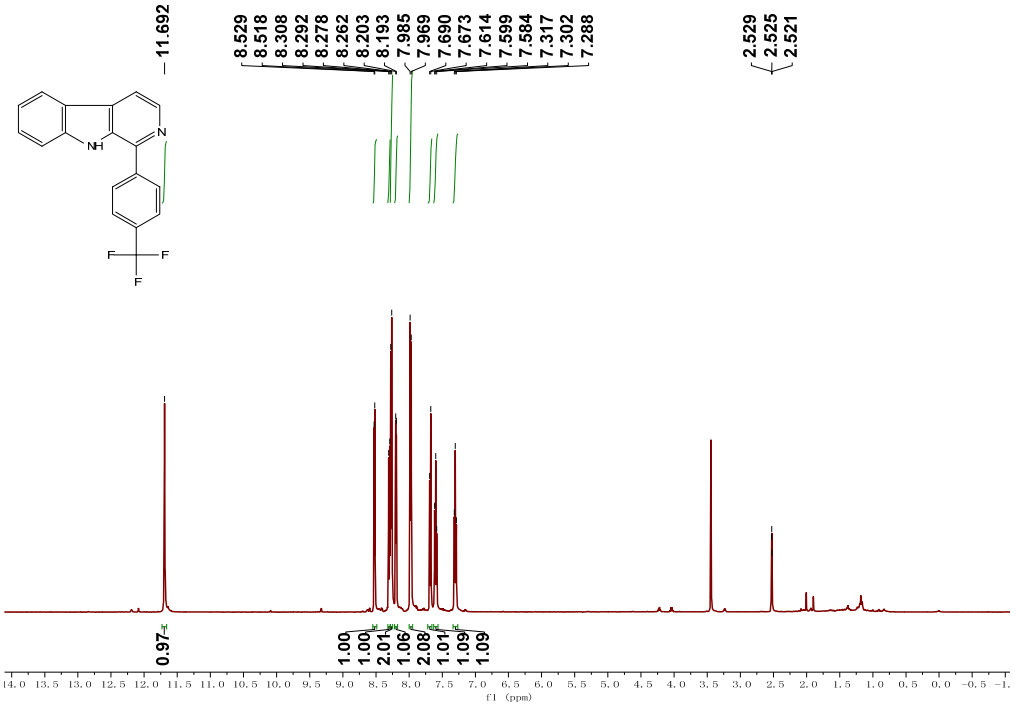
^{13}C NMR



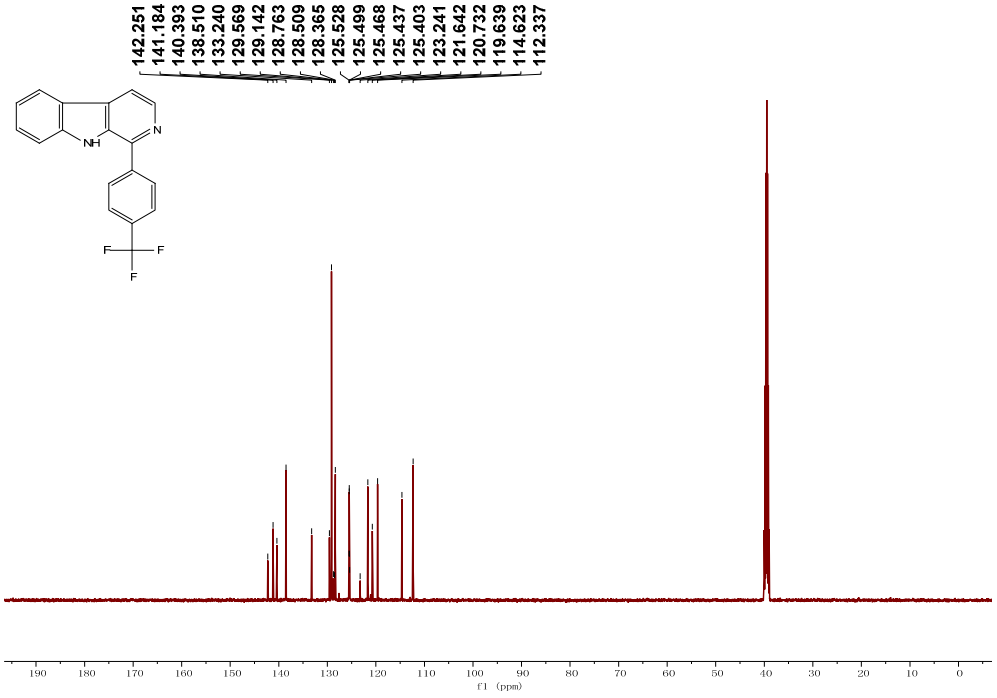


5ak

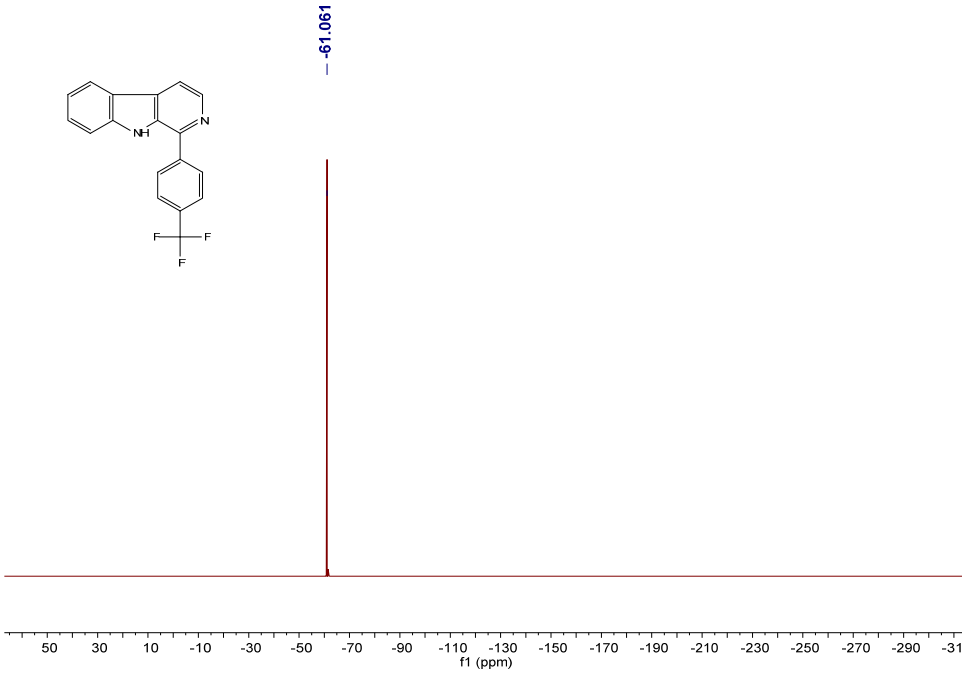
^{1}H NMR

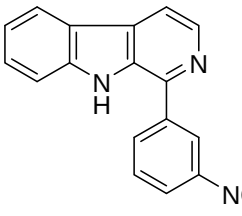


^{13}C NMR



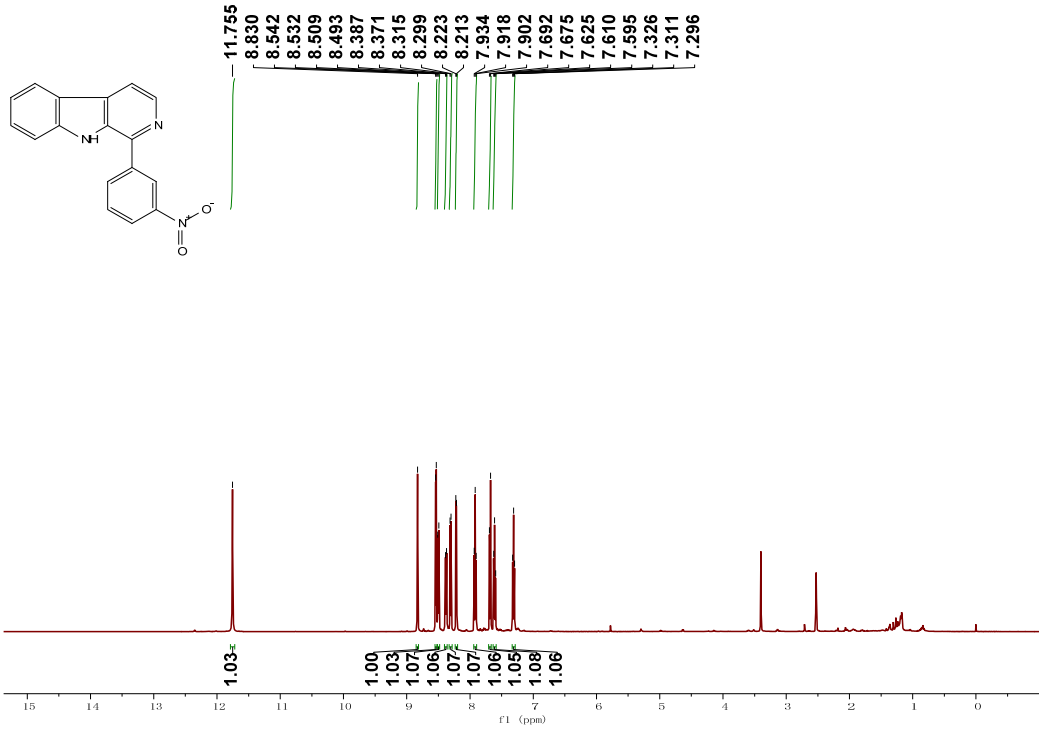
^{19}F NMR


-61.061
NH
N
F
F
F
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290 -31
f1 (ppm)

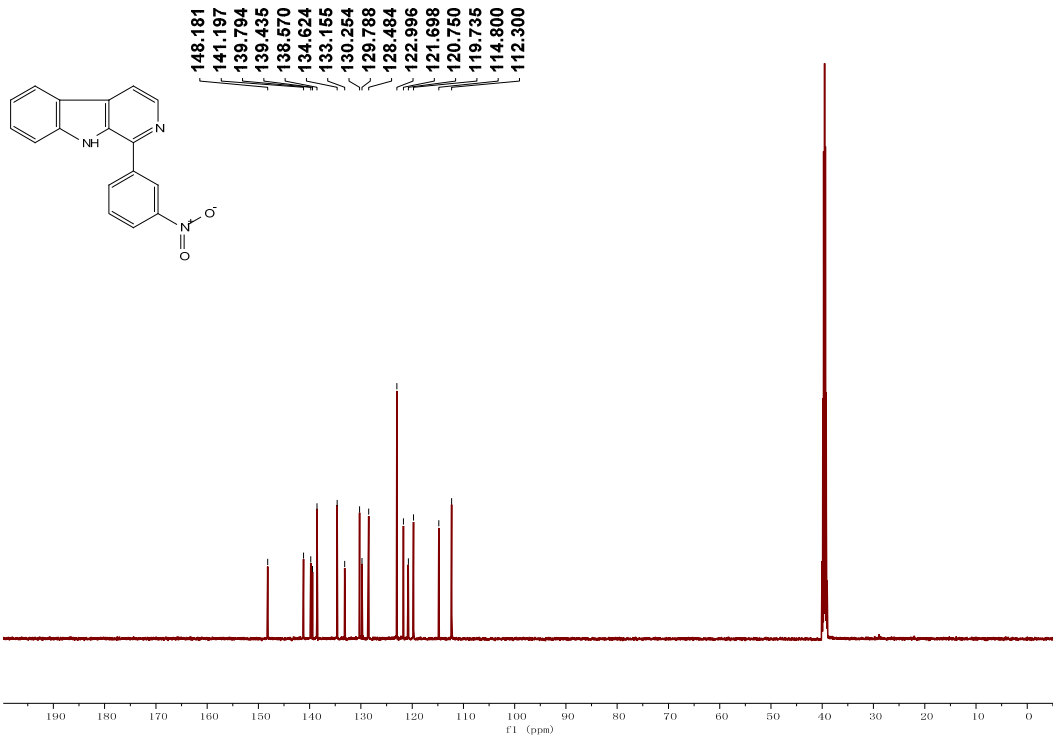


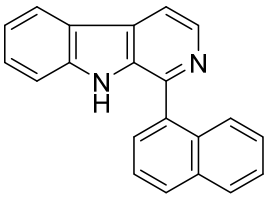
5al

^{1}H NMR



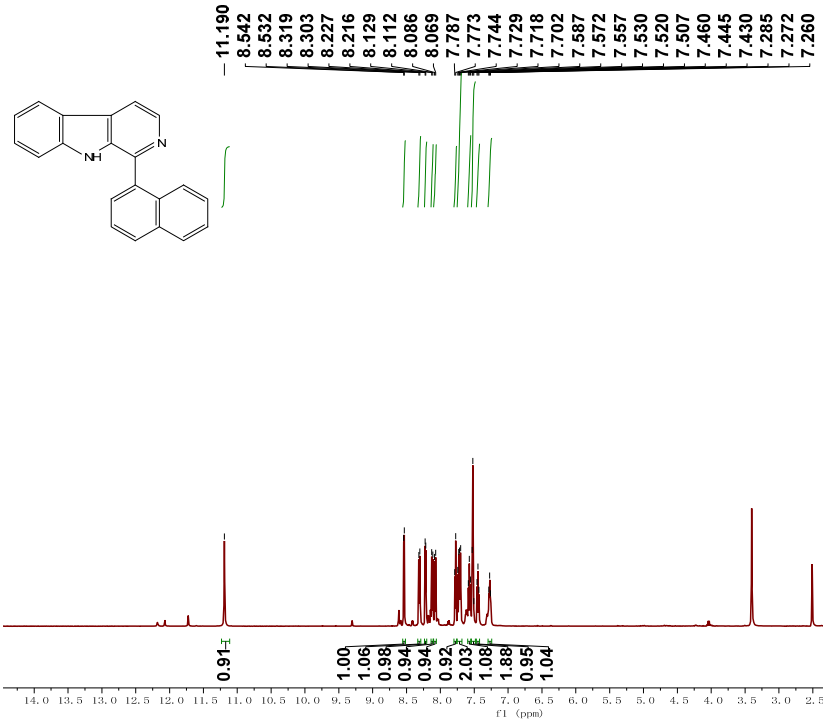
^{13}C NMR



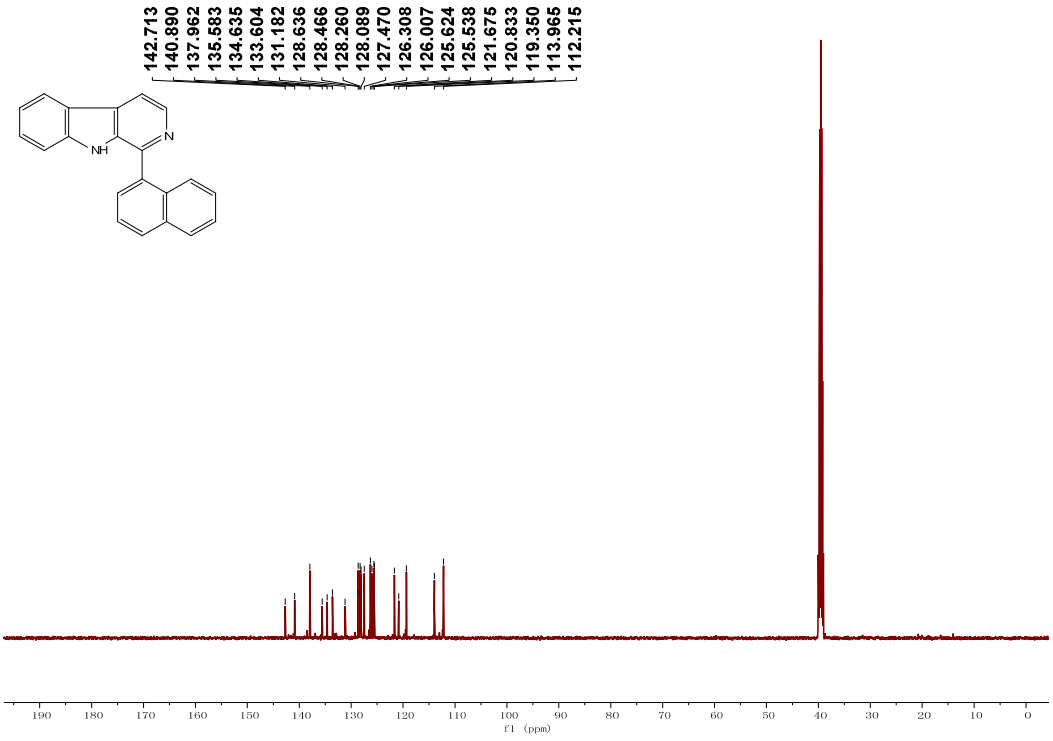


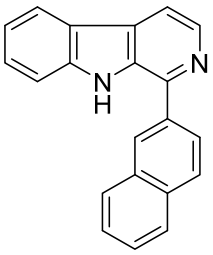
5an

^{1}H NMR



^{13}C NMR





5ao

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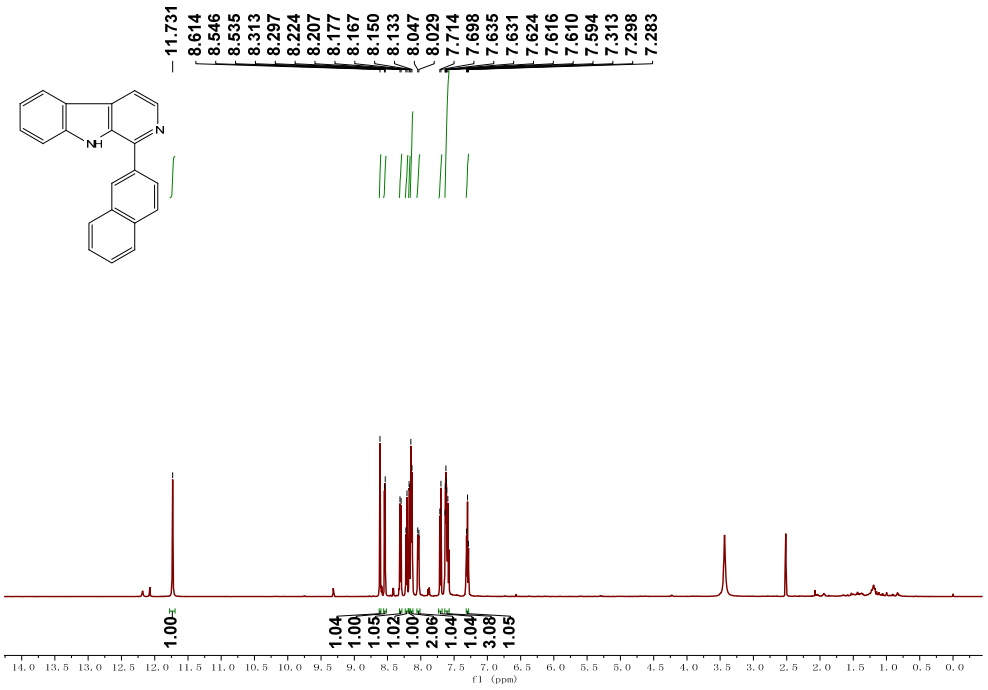
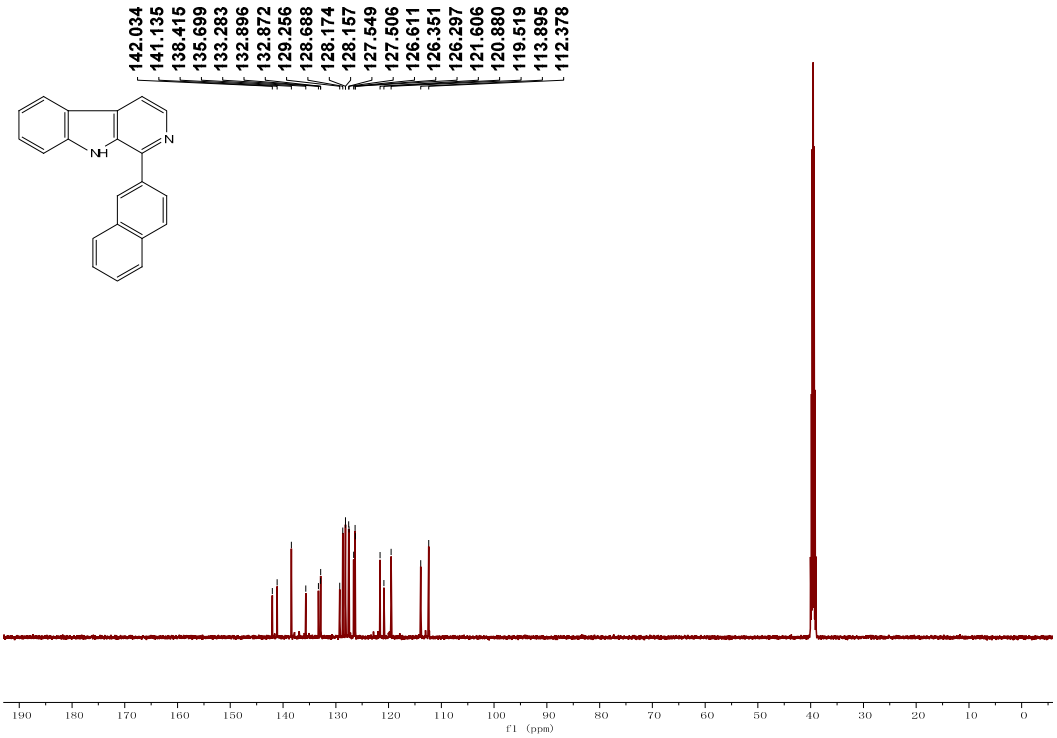
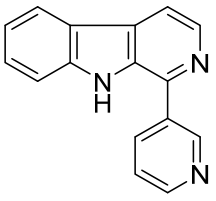


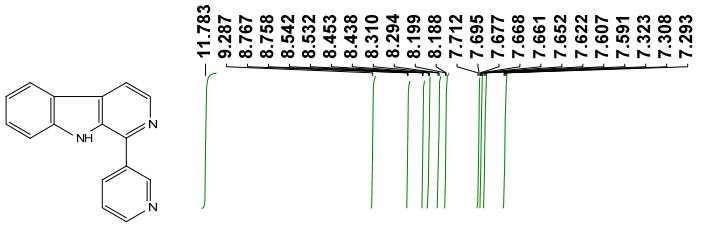
^{13}C NMR

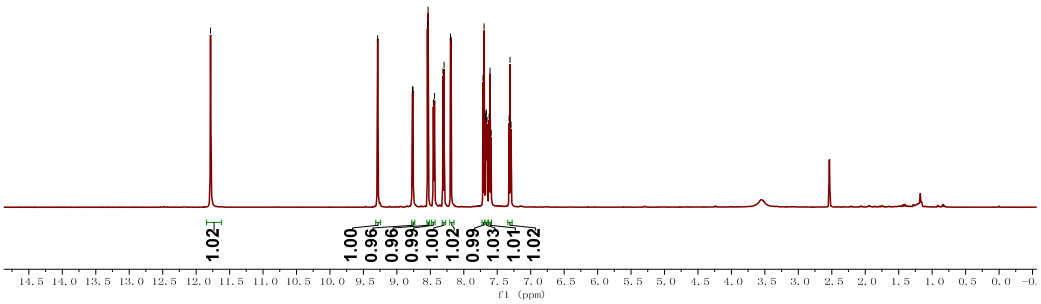




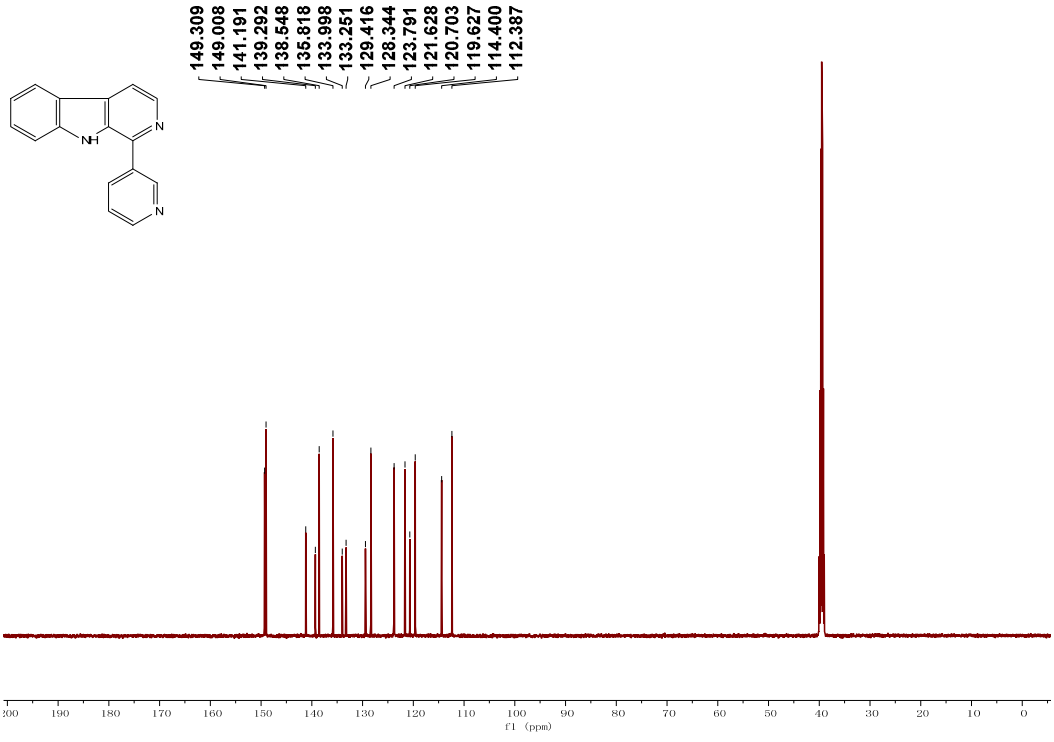
5ap

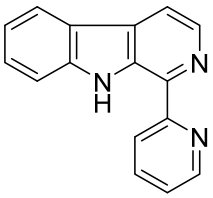
^{1}H NMR





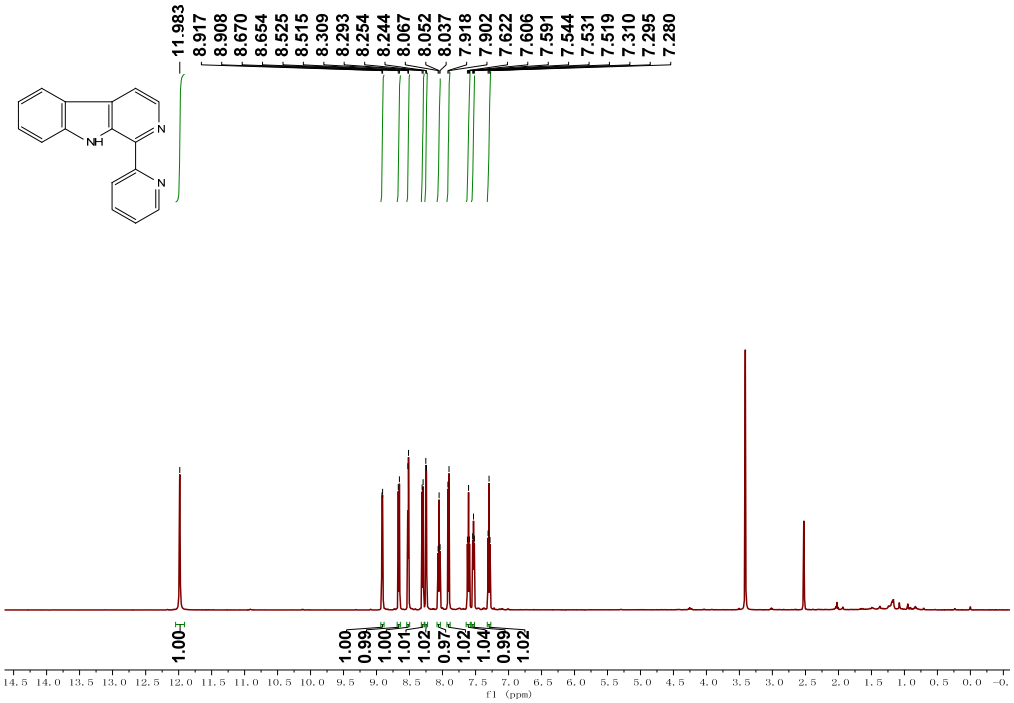
^{13}C NMR



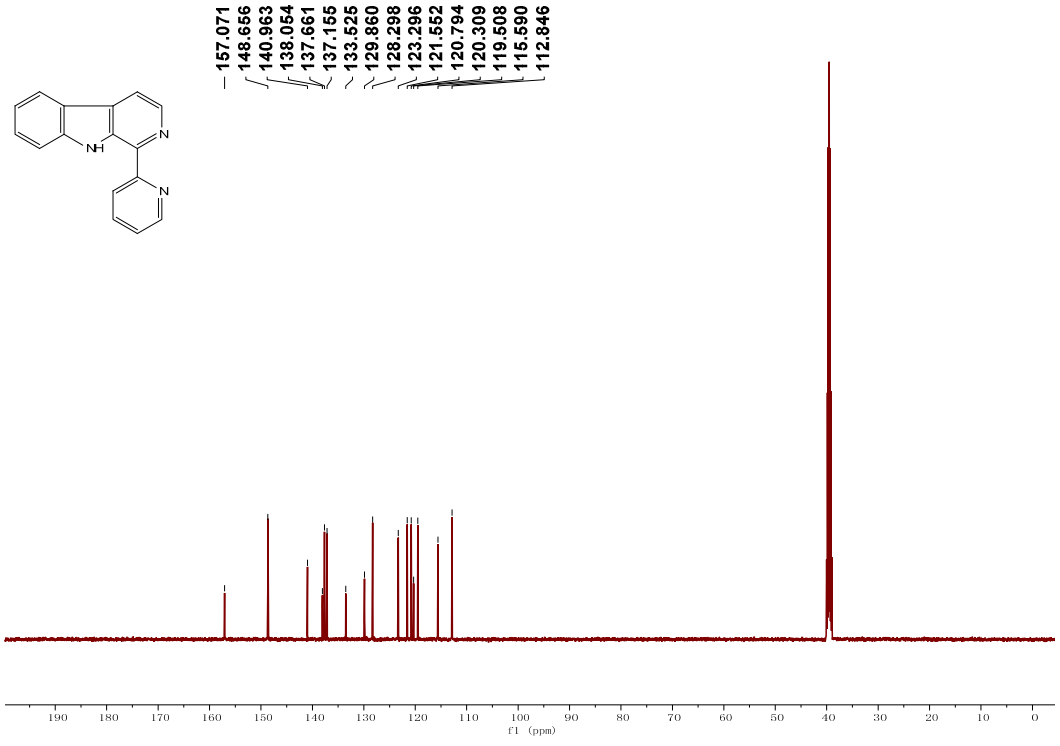


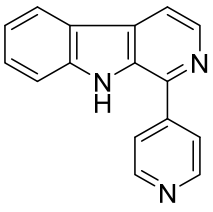
5aw

^{1}H NMR



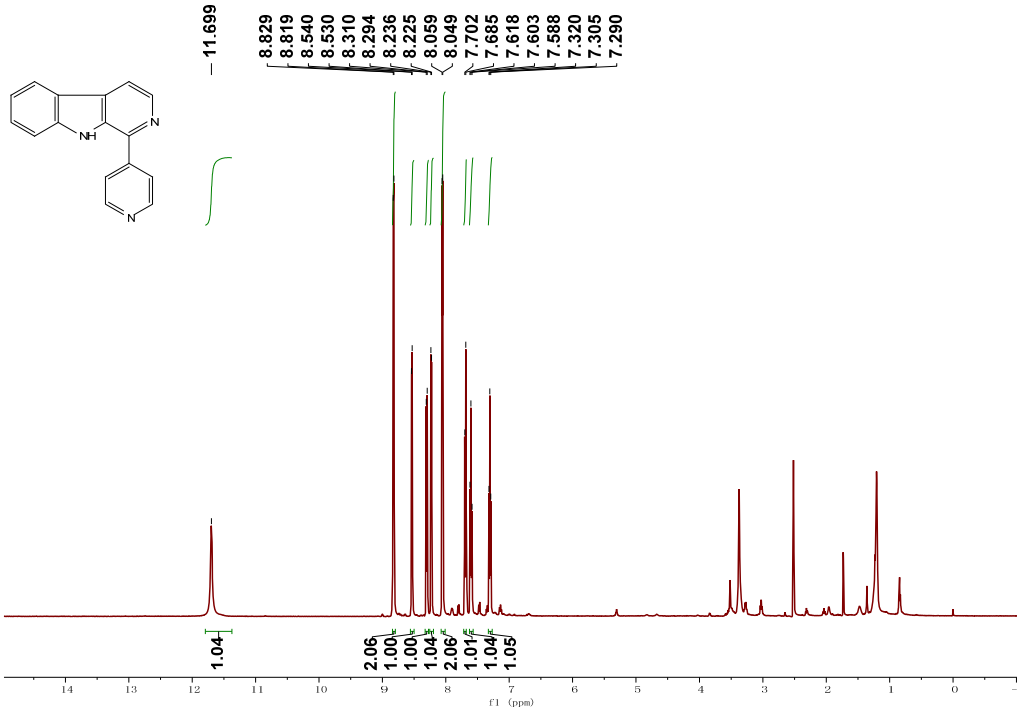
^{13}C NMR



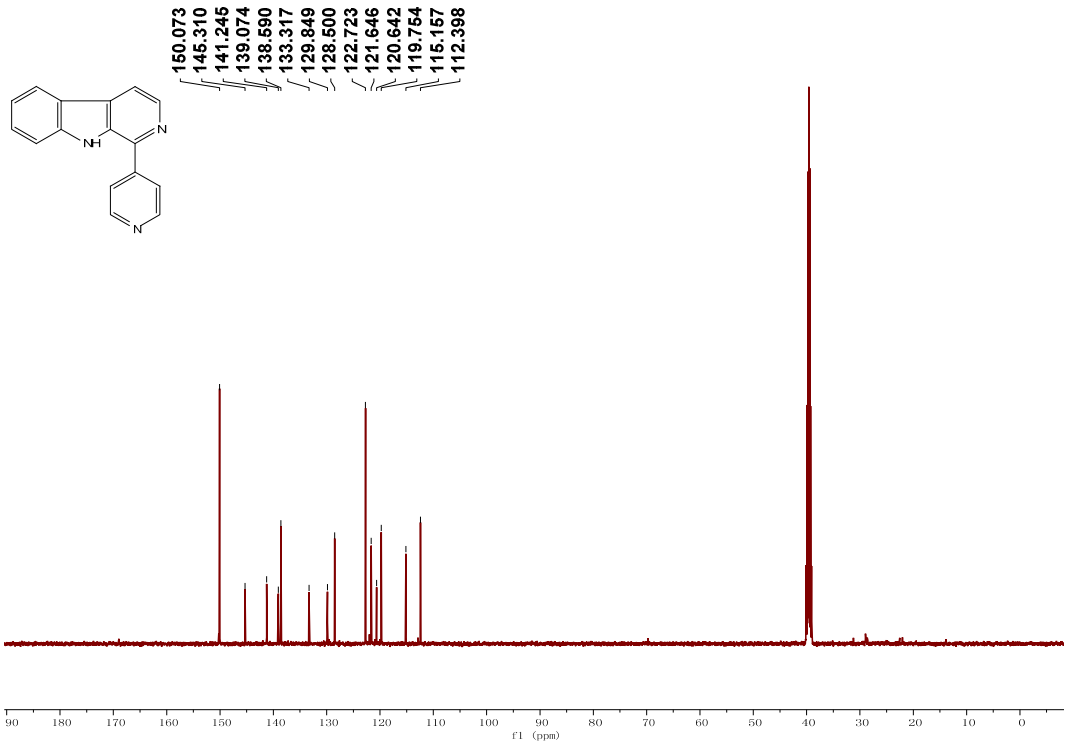


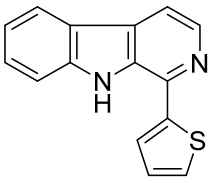
5ax

^{1}H NMR



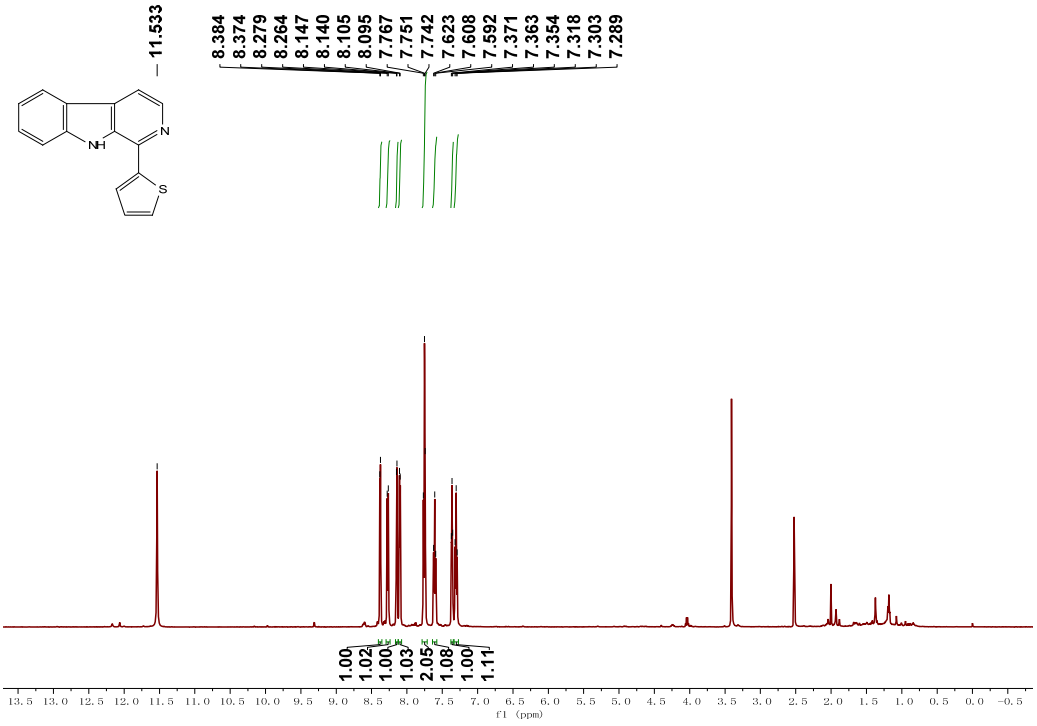
^{13}C NMR



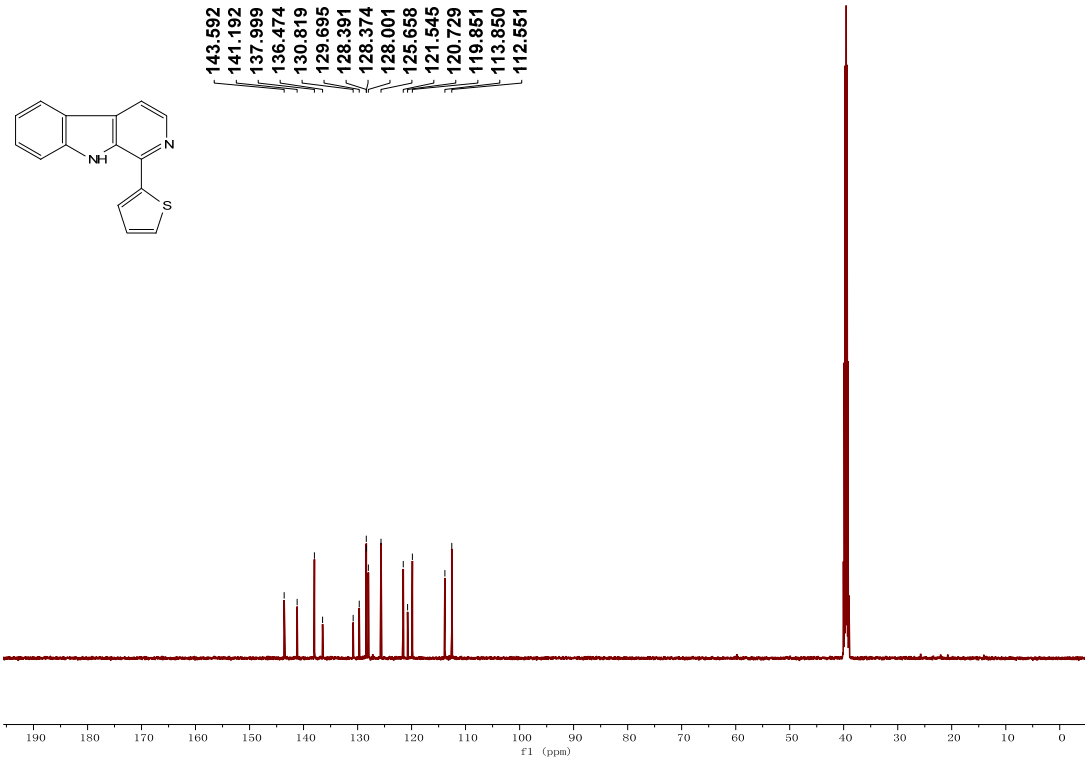


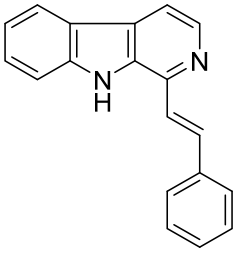
5aq

^{1}H NMR



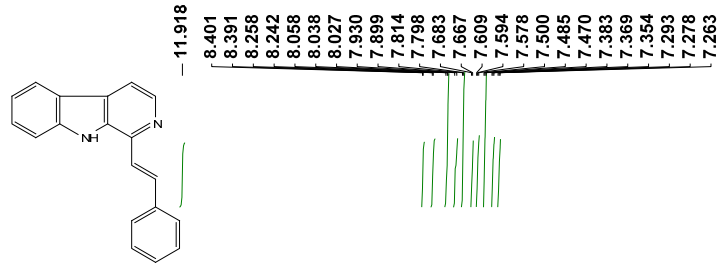
^{13}C NMR

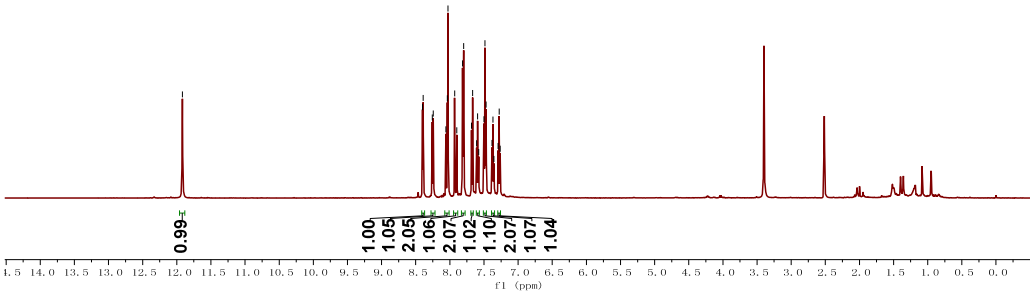




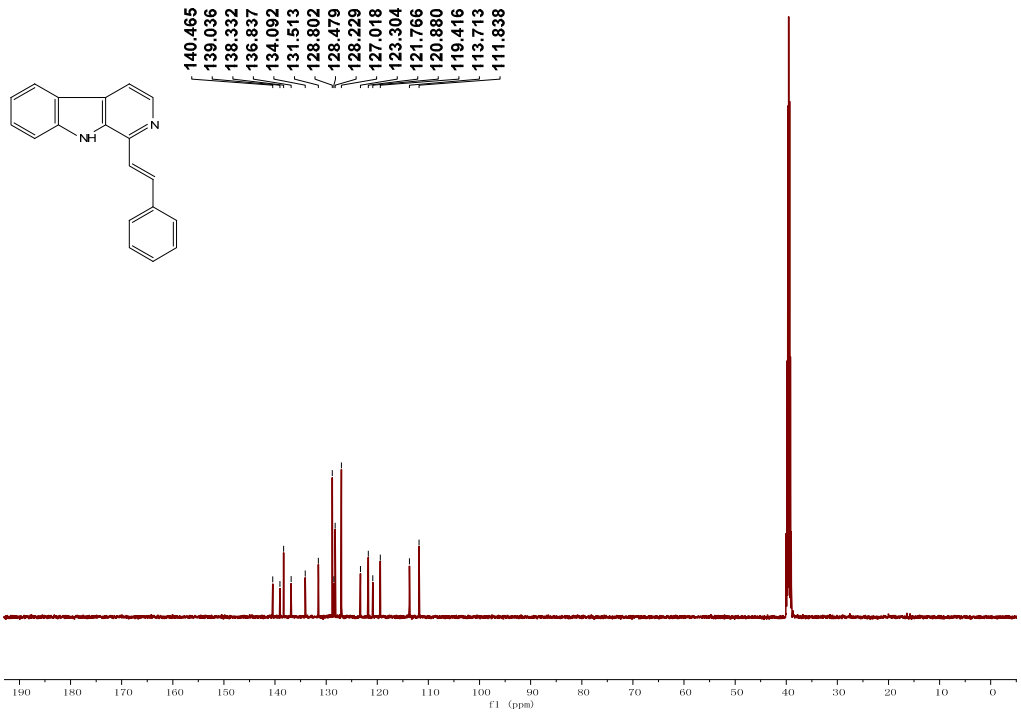
5ar

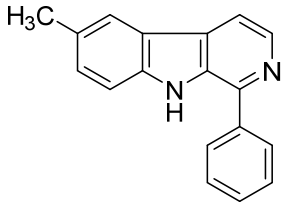
^{1}H NMR





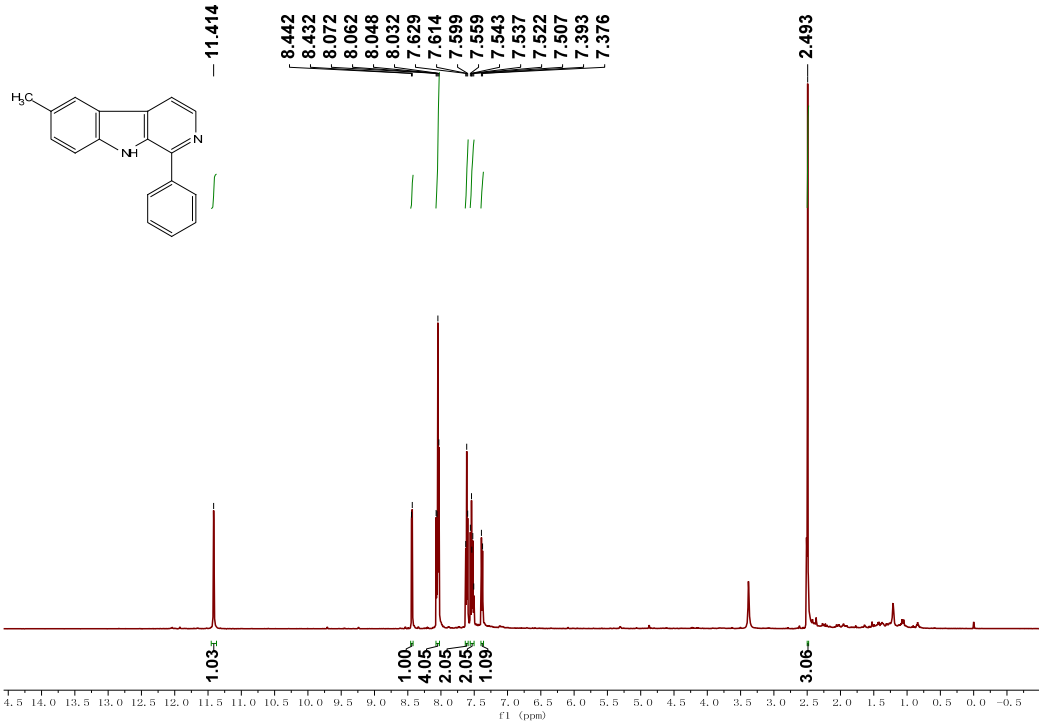
^{13}C NMR



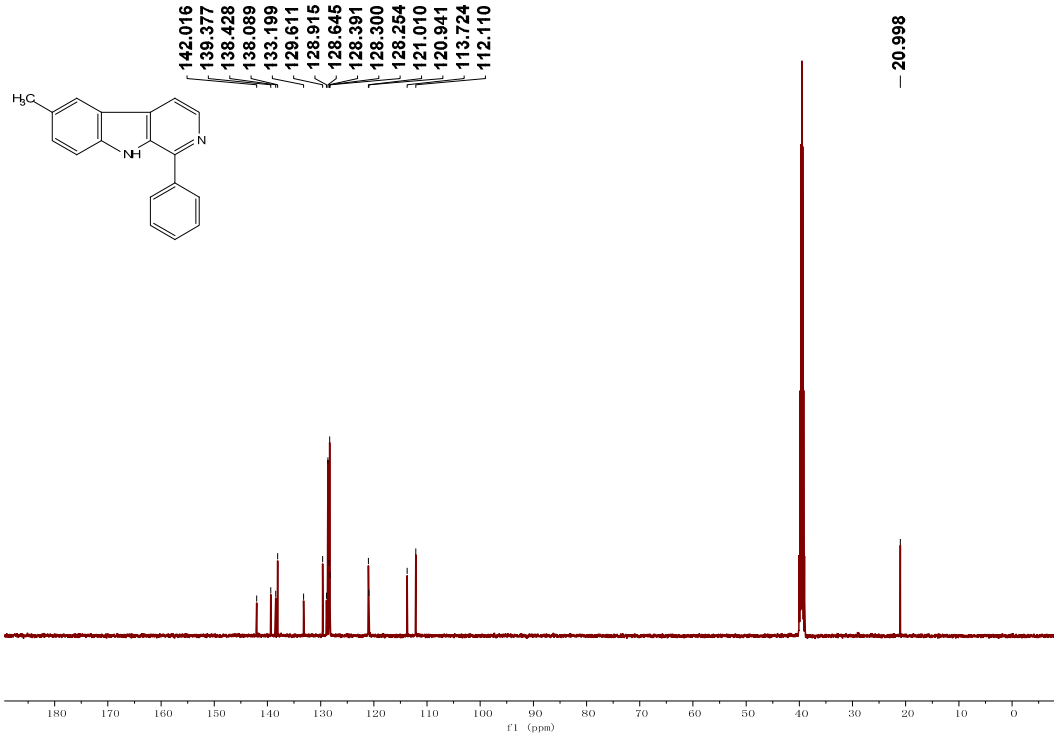


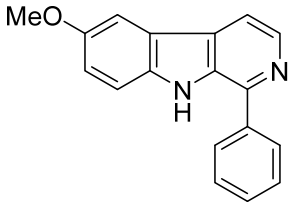
5ba

^{1}H NMR



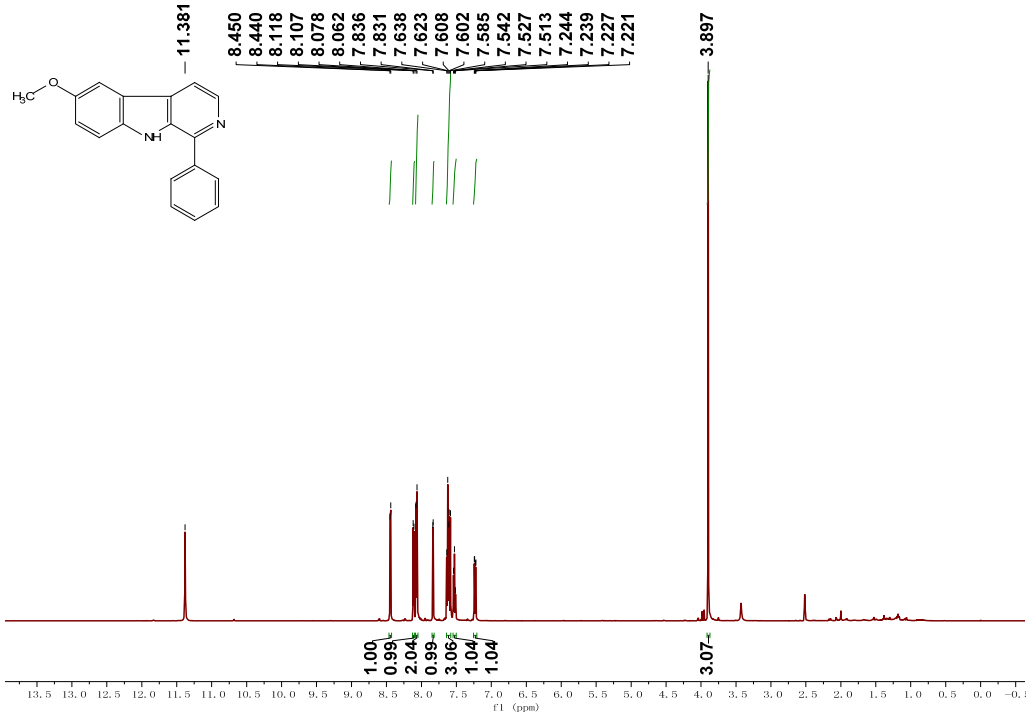
^{13}C NMR



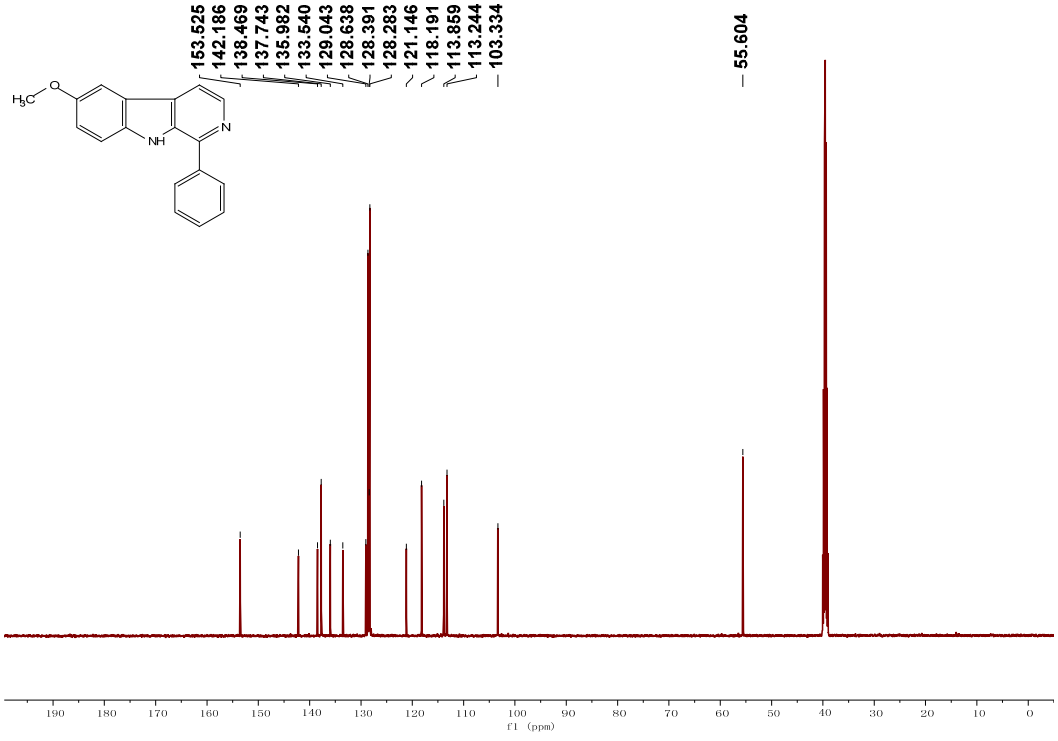


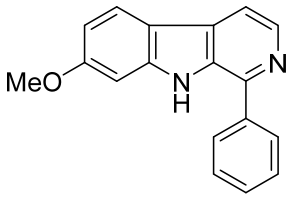
5ca

^{1}H NMR



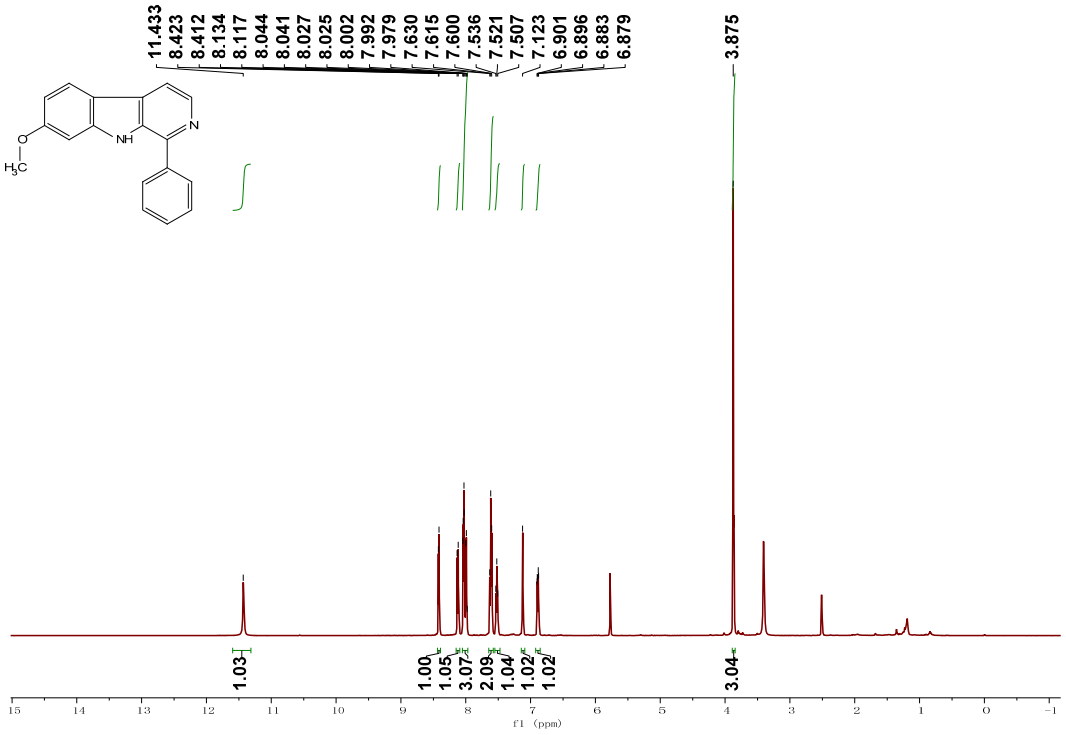
^{13}C NMR



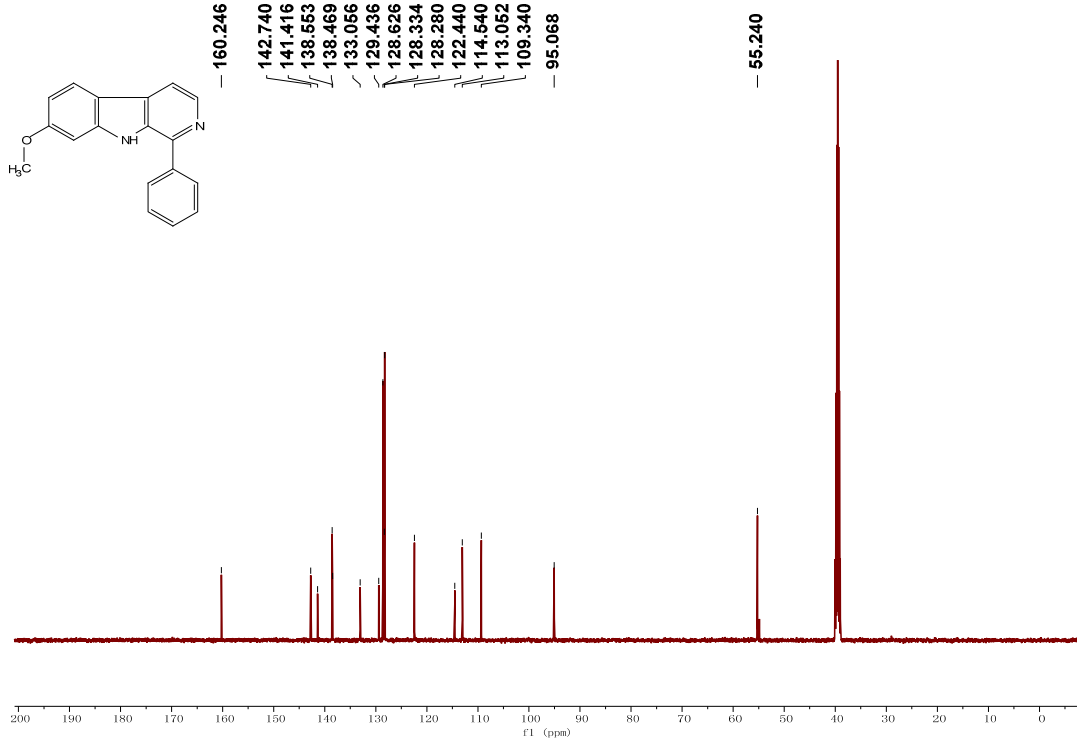


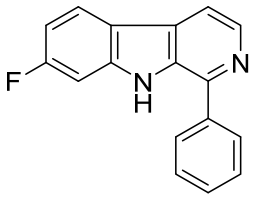
5ja

^{1}H NMR



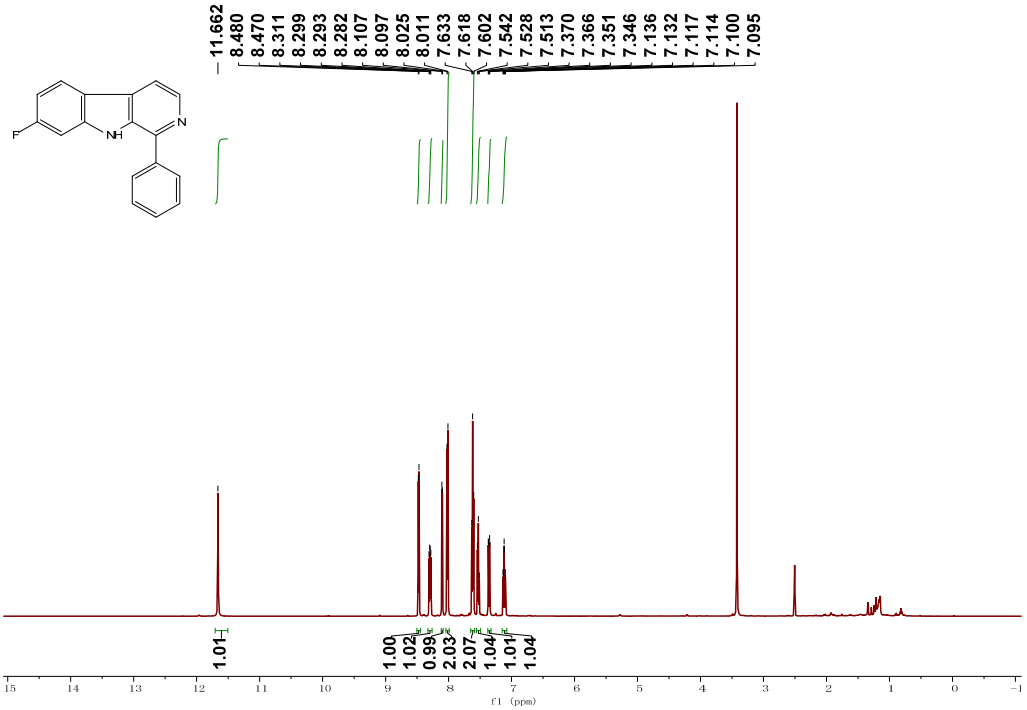
^{13}C NMR



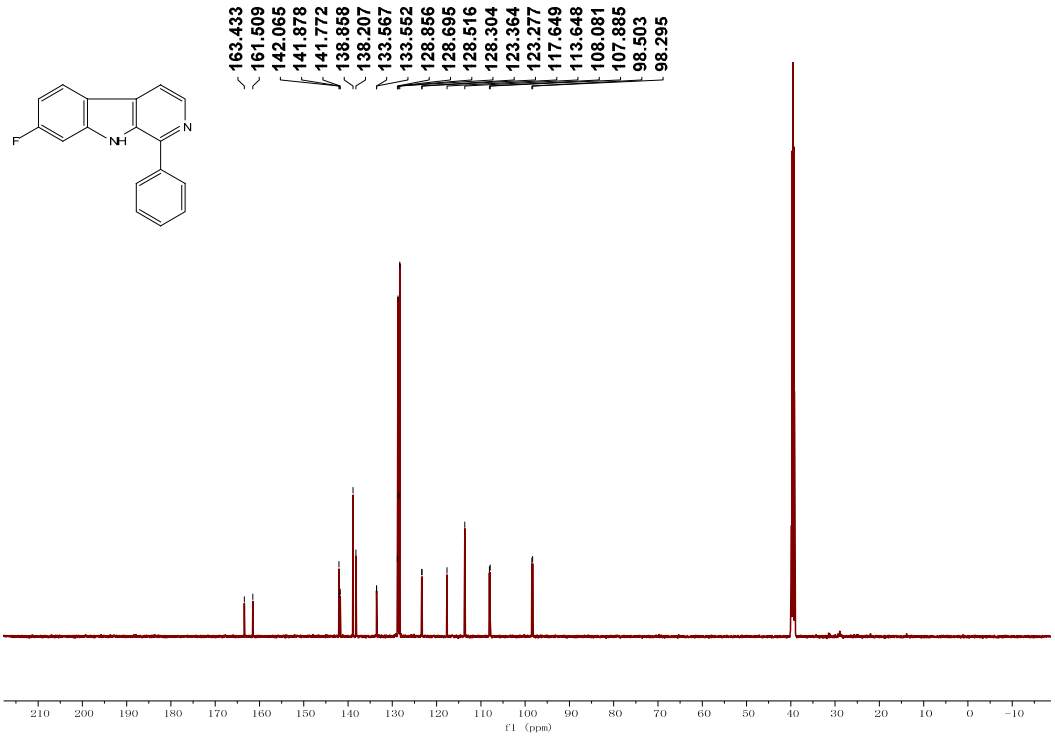


5da

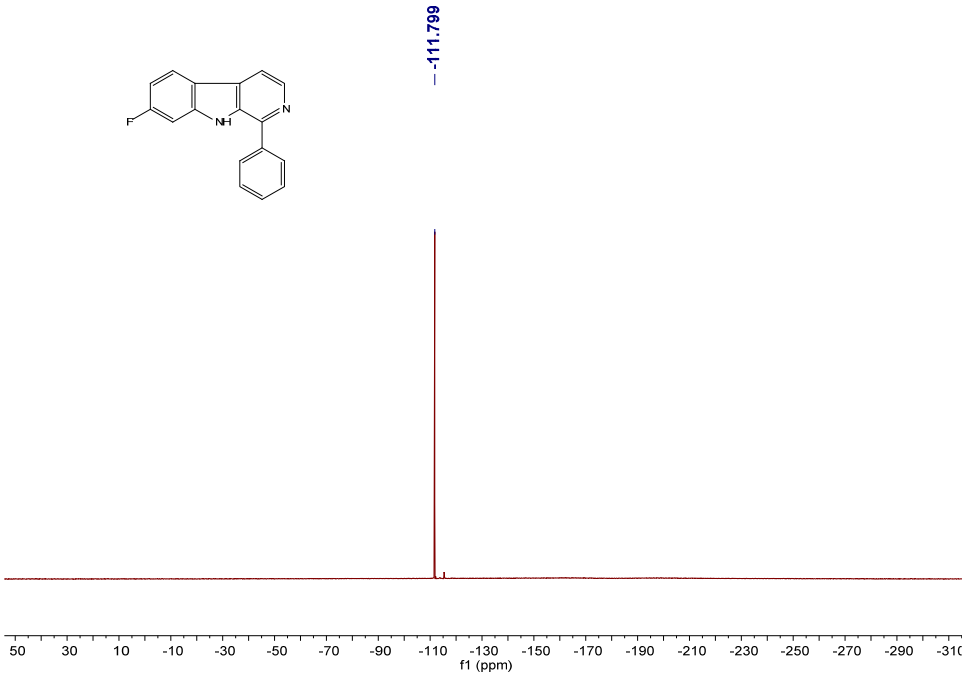
^{1}H NMR

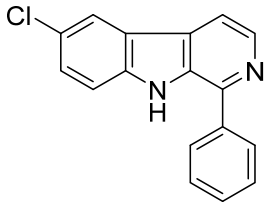


^{13}C NMR



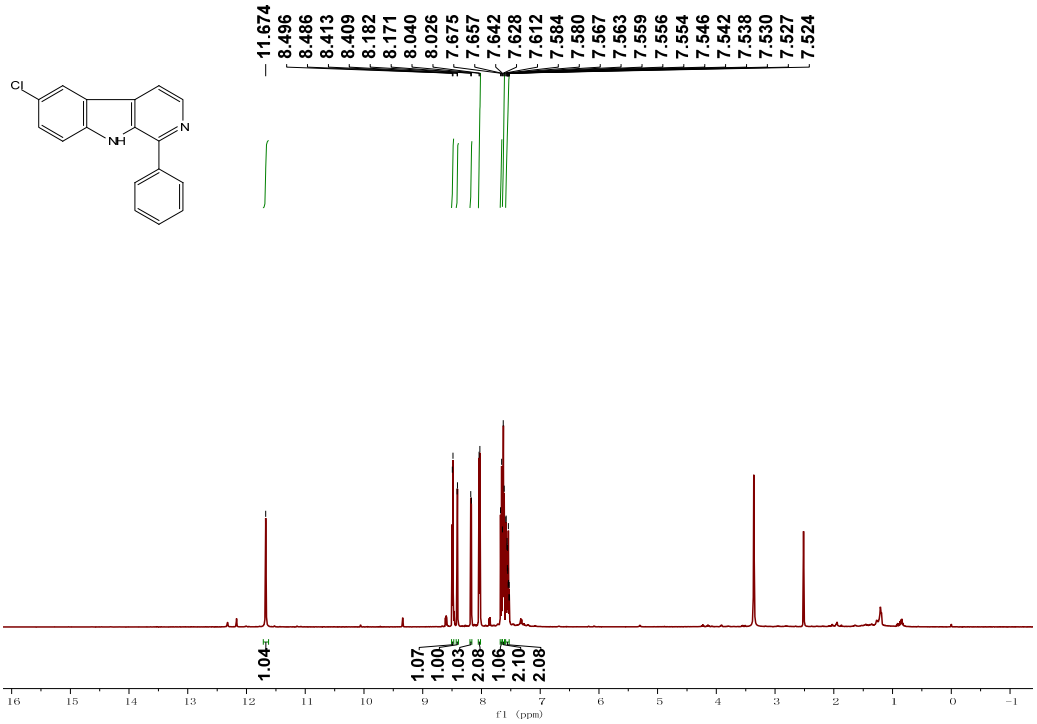
^{19}F NMR


-111.799
F
NH
N
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

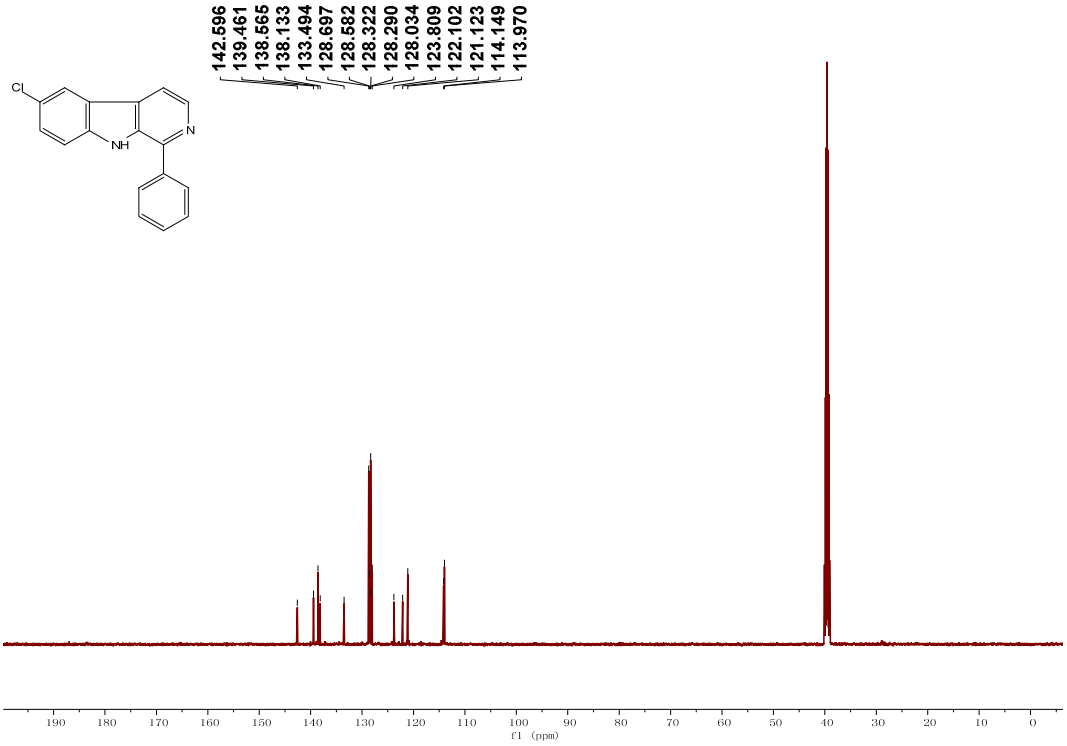


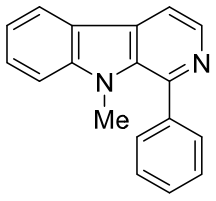
5ea

^{1}H NMR



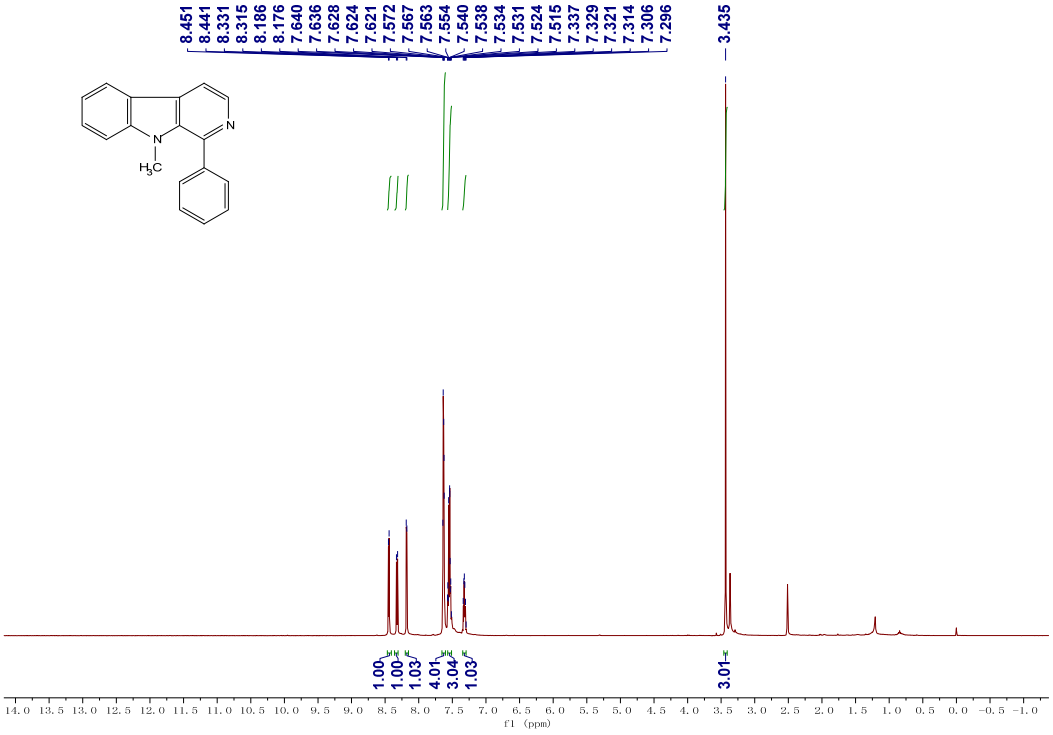
^{13}C NMR



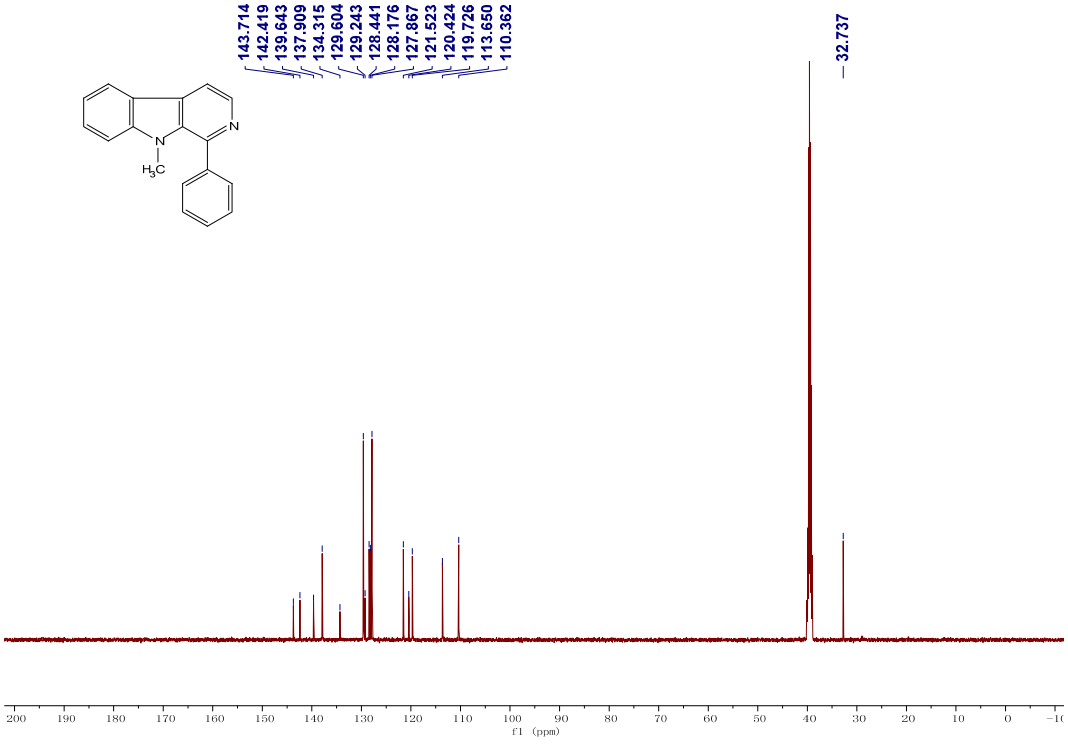


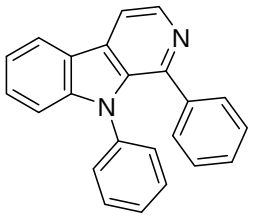
5ha

^{1}H NMR



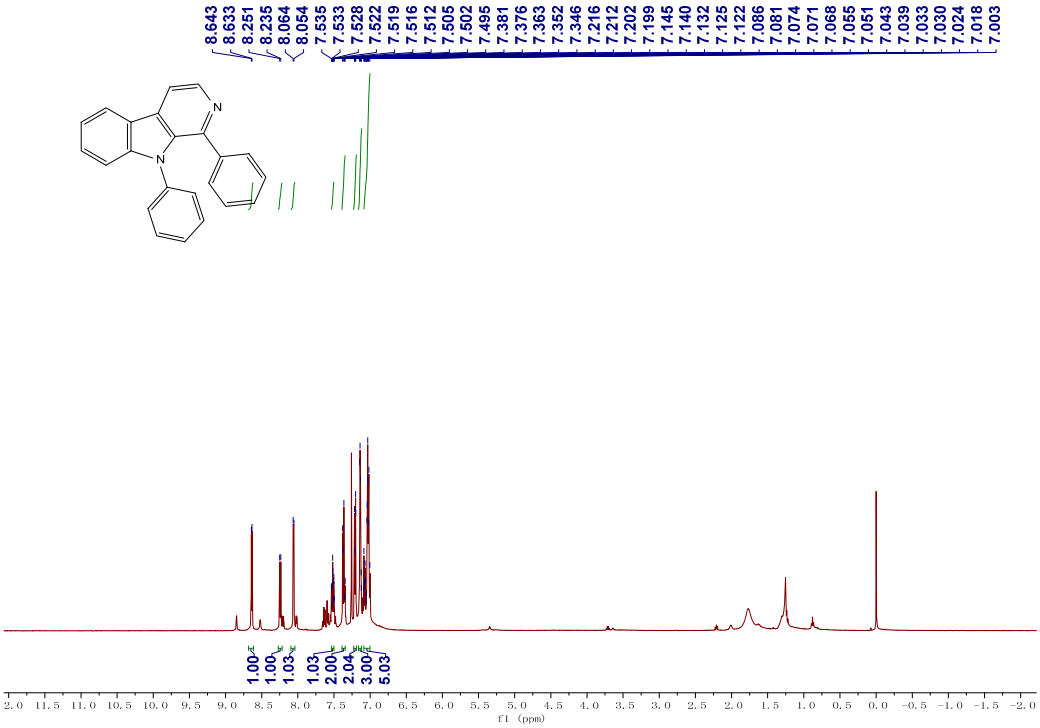
^{13}C NMR



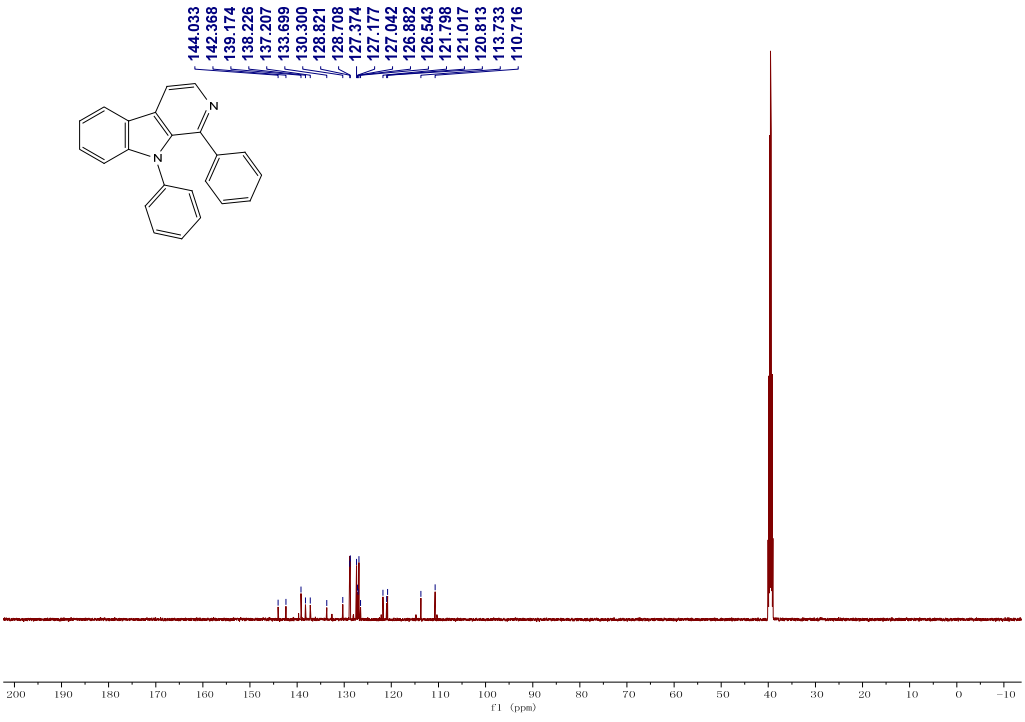


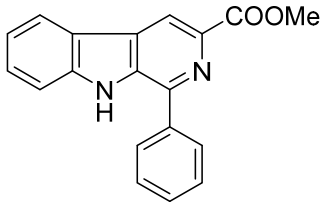
5ia

^{1}H NMR



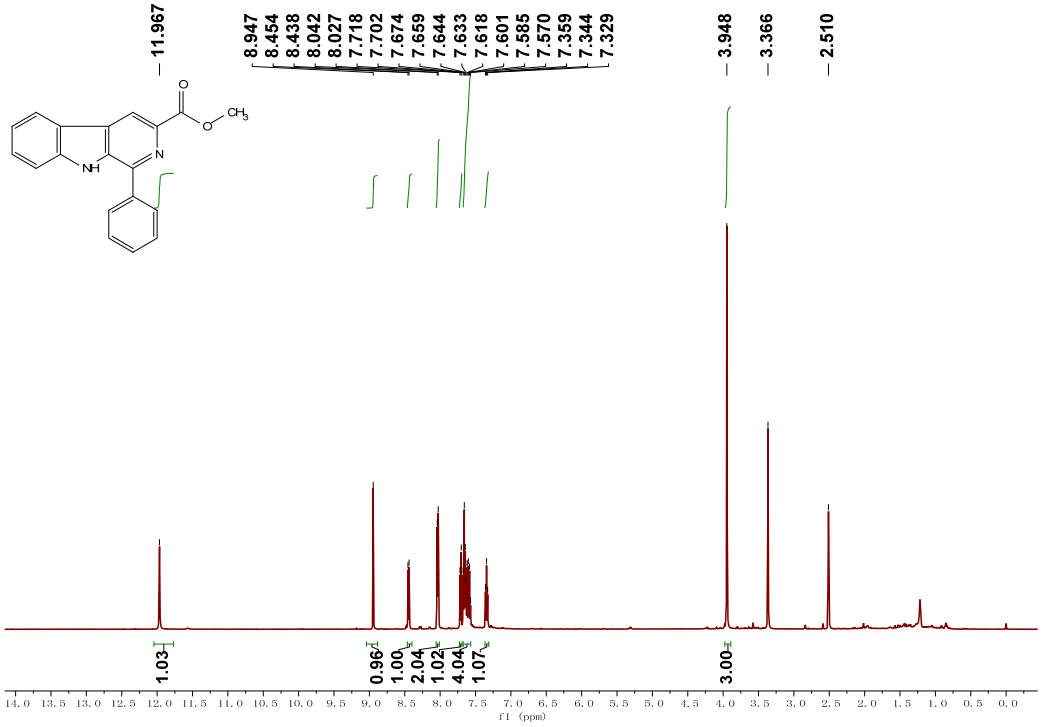
^{13}C NMR





5ka

^{1}H NMR



^{13}C NMR