Supporting Information

Palladium-catalyzed Heck cyclization/carbonylation with formates: synthesis of azaindoline-3-acetates and furoazaindolines

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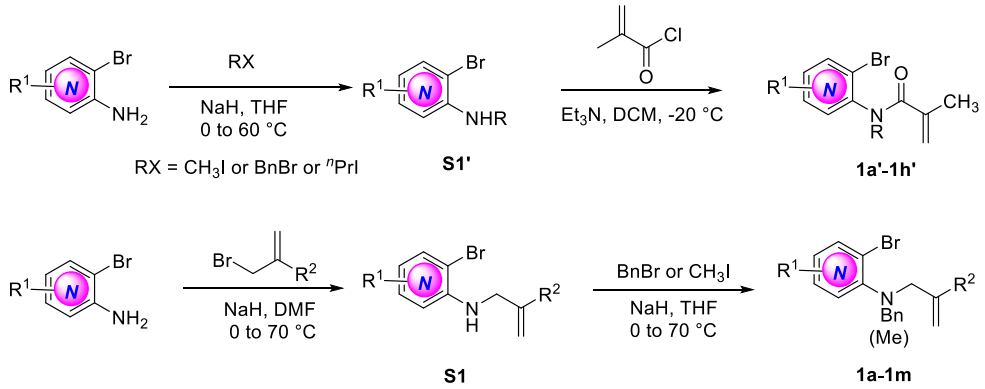
1. General considerations

All materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used. ^{1}H NMR spectra were recorded on a Bruker advance III 400 MHz in $CDCl_3$ [^{1}H NMR: $CD(H)Cl_3$ (7.26 ppm)] and ^{13}C NMR spectra were recorded on 101 MHz in $CDCl_3$ [^{13}C NMR: $CD(H)Cl_3$ (77.00 ppm)]. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR is reported in terms of chemical shift (δ, ppm). High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II.

2. Preparation of substrates

Synthesis of aminopyridine 1



For compounds **1a'-1h':**

Step1:

Sodium hydride (60% in oil, 1.2 equiv.) was added to a solution of the substrate (1 equiv.) in THF (0.4 M) at 0 ˚C. After 30 min at 40 ˚C, Cool the mixture to 0 ˚C, CH_3I (2.0 equiv.) or BnBr (1.2 equiv.) or ^{n}PrI (2.0 equiv.) was added dropwise and the solution was then heated at 60˚C for 4 h. When the reaction was completed, the reaction was cooled to rt, and water was carefully added to the solution. The reaction was diluted with water. The organic was extracted with ethyl acetate for three times. The combined organic layers were washed with brine, dried with sodium sulfate, concentrated and the crude residue was purified by flash column chromatography with EtOAc/petroleum ether 1:10 (v/v) to afford compound **S1'**.

Step2:

To a suspension of **S1'** (1.0 equiv) in DCM (0.5 M with respect to **S1'**) was added Et_3N (2.0 equiv) dropwise at -20 ℃. The reaction mixture was stirred at -20 ℃ for 30 minutes. After adding additional 1.2 equivalent of methacryloyl chloride in DCM (2 M) dropwise, the resulting mixture was allowed to stir at room temperature overnight. The solution was extracted with DCM and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with EtOAc/petroleum ether (1:10~2:1) to afford compounds **1a'-1h'**.

For compounds **1a-1m:**[1]

Step1:

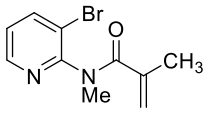
Sodium hydride (60% in oil, 1.2 equiv.) was added to a solution of the substrate (1 equiv.) in DMF (0.1 M) at 0 ˚C. After 30 min, 3-bromo propene (1.2 equiv.) was added and the solution was then heated at 70˚C. Reaction progress was monitored by TLC (3-16 h). Once complete, the reaction was cooled to rt, and water was carefully added to the solution. The reaction was diluted with water. The organic was extracted with ethyl acetate for three times. The combined organic layers were washed with brine, dried with sodium sulfate, concentrated and the crude residue was purified by flash column chromatography with EtOAc/petroleum ether 1:10 (v/v) to afford compound **S1**.

Step 2:

Sodium hydride (60% in oil, 1.2 equiv.) was added to a solution of the compound **S1** (1 equiv.) in THF (0.4 M) at 0 ˚C. After 30 min, BnBr (1.2 equiv.) or CH_3I (2.0 equiv.) was added dropwise and the solution was then heated at 70˚C. Reaction progress was monitored by TLC (3-16 h). Once complete, the reaction was cooled to rt, and water was carefully added to the solution. The reaction was diluted with water. The organic was extracted with ethyl acetate for three times. The combined organic layers were washed with brine, dried with sodium sulfate, concentrated and the crude residue was purified by flash column chromatography with EtOAc/petroleum ether 1:10~1:20 (v/v) to afford compounds **1a**-**1m**.

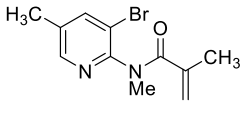
Synthesis of formate 2

According to the known literature,[2] Formic acid (25 mmol, 5.0 equiv) was added to acetic anhydride (20 mmol, 4.0 equiv.) at rt. The mixture was stirred at 60 ℃ for 1 h and cooled to rt. The resulting solution was poured to the flask containing phenol (5 mmol) and AcONa (2.5 mmol, 0.5 equiv). The mixture was stirred for 4 h in water bath and then diluted with toluene 10 mL), washed with H_2O (10 mL) three times, dried over $MgSO_4$, filtered, and concentrated to afford the desired formate **2**. This product was used for carbonylation reaction without further purification.



1a'

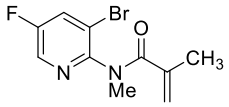
***N*-(3-bromopyridin-2-yl)-*N*-methylmethacrylamide (1a'):** 74% yield (for the last step); white solid; mp = 107-109 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.97 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.16 (dd, *J* = 8.0, 4.7 Hz, 1H), 4.97 (d, *J* = 26.3 Hz, 2H), 3.32 (s, 3H), 1.95 (t, *J* = 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 155.2, 147.8, 142.4, 140.6, 123.9, 119.0, 118.5, 34.8, 19.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{12}N_2OBr$ 255.0128; found: 255.0134.



1b'

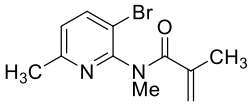
***N*-(3-bromo-5-methylpyridin-2-yl)-*N*-methylmethacrylamide (1b'):** 79% yield (for the last step); pale yellow solid; mp = 132-134 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28-8.13 (m, 1H), 7.81-7.66 (m, 1H), 4.91 (q, *J* = 18.2, 15.5 Hz, 2H), 3.33-3.12 (m, 3H), 2.40-2.24 (m, 3H), 1.99-1.79 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 152.5, 148.1, 142.5, 140.5, 134.3, 118.3,

118.2, 34.6, 19.8, 17.3. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{14}N_2OBr$ 269.0284; found: 269.0287.



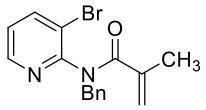
1c'

***N*-(3-bromo-5-fluoropyridin-2-yl)-*N*-methylmethacrylamide (1c'):** 66% yield (for the last step); yellow solid; mp = 136-138 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36-8.26 (m, 1H), 7.74 (ddd, *J* = 6.8, 4.2, 2.5 Hz, 1H), 4.97 (d, *J* = 41.2 Hz, 2H), 3.28 (d, *J* = 7.9 Hz, 3H), 1.93 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 158.5, 155.9, 140.6, 135.8 (d, *J* = 90.2 Hz), 129.3 (dd, *J* = 82.7 Hz), 118.7 (d, *J* = 15 Hz), 118.5, 34.8, 19.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -125.18. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{11}N_2OBrF$ 273.0033; found: 273.0021.



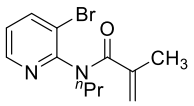
1d'

***N*-(3-bromo-6-methylpyridin-2-yl)-*N*-methylmethacrylamide (1d'):** 51% yield (for the last step); pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.74 (m, 1H), 7.04-6.93 (m, 1H), 4.95 (d, *J* = 16.2 Hz, 2H), 3.37-3.24 (m, 3H), 2.55-2.44 (m, 3H), 1.94 (d, *J* = 4.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 157.5, 154.1, 142.3, 140.7, 123.8, 118.1, 115.4, 34.7, 23.5, 19.9. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{14}N_2OBr$ 269.0284; found: 269.0271.



1e'

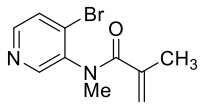
***N*-benzyl-*N*-(3-bromopyridin-2-yl)methacrylamide (1e'):** 78% yield (for the last step); yellow solid; mp = 171-173 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (ddt, *J* = 5.2, 3.4, 1.7 Hz, 1H), 7.82 (ddt, *J* = 7.5, 3.5, 1.7 Hz, 1H), 7.31 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.21 (tdd, *J* = 9.1, 4.5, 2.5 Hz, 3H), 7.03 (dp, *J* = 6.6, 2.2 Hz, 1H), 5.10 (s, 2H), 4.99 (d, *J* = 43.6 Hz, 2H), 2.01-1.92 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 147.6, 142.2, 140.6, 136.4, 128.7, 128.1, 127.2, 123.4, 120.1, 51.4, 19.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}N_2OBr$ 331.0441; found: 331.0441.



1f'

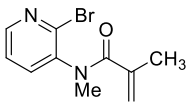
***N*-(3-bromopyridin-2-yl)-*N*-propylmethacrylamide (1f'):** 72% yield (for the last step); white solid; mp = 125-127 ℃;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (dq, *J* = 3.9, 1.8 Hz, 1H), 7.93 (dq, *J* = 7.9, 1.6 Hz, 1H), 7.12 (dd, *J* = 7.9, 4.6 Hz, 1H), 4.93 (d, *J* = 45.6 Hz, 2H), 3.80 (d, *J* = 87.1 Hz, 2H), 1.96 (d, *J* = 2.7 Hz, 3H), 1.62 (h, *J* = 7.4 Hz, 2H), 0.90 (tt, *J* = 7.5, 2.3 Hz, 3H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 171.3, 147.7, 142.3, 140.9, 123.6, 120.1, 118.6, 49.9, 21.0, 20.0, 11.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{16}N_2OBr$ 283.0441; found: 283.0447.



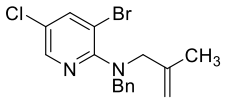
1g'

***N*-(4-bromopyridin-3-yl)-*N*-methylmethacrylamide (1g'):** 81% yield (for the last step); pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52-8.31 (m, 2H), 7.43 (td, *J* = 5.0, 2.4 Hz, 1H), 4.99 (d, *J* = 33.7 Hz, 2H), 3.28 (dd, *J* = 6.2, 3.2 Hz, 3H), 1.84 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 150.2, 150.1, 149.2, 149.0, 141.8, 139.6, 128.3, 125.0, 36.2, 19.9. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{12}N_2OBr$ 255.0128; found: 255.0122.



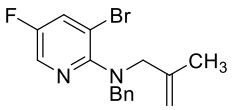
1h'

***N*-(2-bromopyridin-3-yl)-*N*-methylmethacrylamide (1h'):** 58% yield (for the last step); pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42-8.30 (m, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.35 (td, *J* = 8.3, 7.8, 4.3 Hz, 1H), 5.27-4.84 (m, 2H), 3.37-3.19 (m, 3H), 1.85 (d, *J* = 10.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 148.6, 142.5, 139.5, 137.9, 123.4, 36.2, 19.9. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{12}N_2OBr$ 255.0128; found: 255.0126.



1d

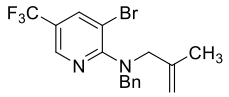
***N*-benzyl-3-bromo-5-chloro-*N*-(2-methylallyl)pyridin-2-amine (1d):** 70% yield (for the last step); pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dq, *J* = 4.4, 2.1 Hz, 1H), 7.78 (q, *J* = 2.0, 1.6 Hz, 1H), 7.33-7.18 (m, 5H), 4.94-4.85 (m, 2H), 4.52 (dd, *J* = 5.6, 2.8 Hz, 2H), 3.85 (d, *J* = 5.9 Hz, 2H), 1.73-1.63 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.6, 144.6, 142.0, 141.6, 138.5, 128.2, 127.9, 126.9, 123.9, 112.8, 112.8, 112.1, 56.3, 53.9, 20.7. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}N_2ClBr$ 351.0258; found: 351.0255.



1e

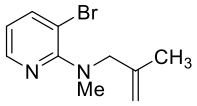
***N*-benzyl-3-bromo-5-fluoro-*N*-(2-methylallyl)pyridin-2-amine (1e):** 79% yield (for the last step); pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (t, *J* = 3.1 Hz, 1H), 7.58 (dt, *J* = 7.2, 2.0 Hz, 1H), 7.33-7.14 (m, 5H), 4.91 (d, *J* = 5.0 Hz, 1H), 4.87-4.80 (m, 1H), 4.42 (dd, *J* = 5.0, 2.3 Hz, 2H), 3.76 (d, *J* = 4.6 Hz, 2H), 1.74-1.65 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0 (d, *J* = 7.5 Hz), 153.2, 142.2, 138.6, 133.4 (d, *J* = 86.5 Hz), 129.6 (d, *J* = 82.7 Hz), 128.1(d, *J* = 41.4 Hz),

126.8, 113.2, 113.1, 112.8, 112.8, 56.8, 54.5, 20.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -134.25. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}N_2FBr$ 335.0554; found: 335.0562.



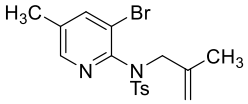
1f

***N*-benzyl-3-bromo-*N*-(2-methylallyl)-5-(trifluoromethyl)pyridin-2-amine (1f):** 66% yield (for the last step); pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43-8.36 (m, 1H), 7.94 (d, *J* = 2.2 Hz, 1H), 7.34-7.19 (m, 5H), 4.95-4.84 (m, 2H), 4.73 (s, 2H), 4.04 (s, 2H), 1.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 143.4, 143.3, 141.4, 140.0, 140.0, 138.1, 128.4, 127.8, 127.0, 119.5 (dd, *J* = 248.2, 48.9 Hz), 112.7, 108.3, 55.6, 53.3, 20.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.27. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}N_2F_3Br$ 385.0522; found: 385.0526.



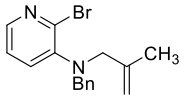
1g

3-bromo-*N*-methyl-*N*-(2-methylallyl)pyridin-2-amine (1g): 81% yield (for the last step); colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dq, *J* = 4.6, 1.4 Hz, 1H), 7.65 (dq, *J* = 7.7, 1.7 Hz, 1H), 6.58 (ddt, *J* = 7.5, 4.1, 1.9 Hz, 1H), 4.95-4.80 (m, 2H), 3.79 (s, 2H), 2.79 (d, *J* = 1.3 Hz, 3H), 1.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 145.9, 142.4, 142.1, 117.2, 112.3, 111.0, 59.4, 38.6, 20.2. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{14}N_2Br$ 241.0335; found: 241.0341.



1i

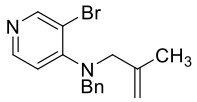
***N*-(3-bromo-5-methylpyridin-2-yl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (1i):** 65% yield (for the last step); yellow solid; mp = 194-196 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.1 Hz, 1H), 7.81 (q, *J* = 2.5 Hz, 1H), 7.65 (dt, *J* = 8.4, 1.5 Hz, 2H), 7.29 (dd, *J* = 8.1, 2.5 Hz, 2H), 4.71-4.60 (m, 2H), 4.01 (s, 2H), 2.47-2.41 (m, 3H), 2.32 (dd, *J* = 4.2, 2.1 Hz, 3H), 1.81 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.7, 147.5, 143.7, 142.8, 139.5, 135.2, 134.6, 134.6, 129.3, 128.5, 122.8, 115.5, 56.0, 21.5, 20.5, 17.5. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{20}N_2O_2BrS$ 395.0423; found: 395.0427.



1k

***N*-benzyl-2-bromo-*N*-(2-methylallyl)pyridin-3-amine (1k):** 70% yield (for the last step); pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dq, *J* = 3.0, 1.8 Hz, 1H), 7.31-7.17 (m, 6H), 7.06 (dt, *J* = 7.7, 3.8 Hz, 1H), 4.97-4.84 (m, 2H), 4.22 (t, *J* = 2.4 Hz, 2H), 3.55 (s, 2H), 1.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 143.6, 141.3, 140.9, 136.9, 131.5, 128.3, 128.1, 128.0, 127.0,

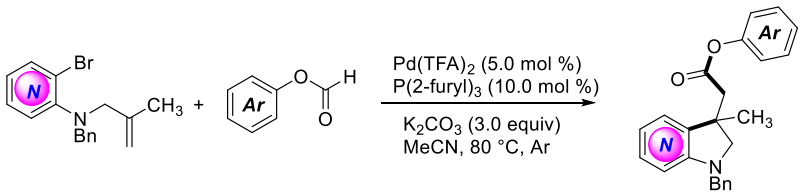
122.3, 113.9, 57.7, 56.5, 20.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{18}N_2Br$ 317.0648; found: 317.0651.



1l

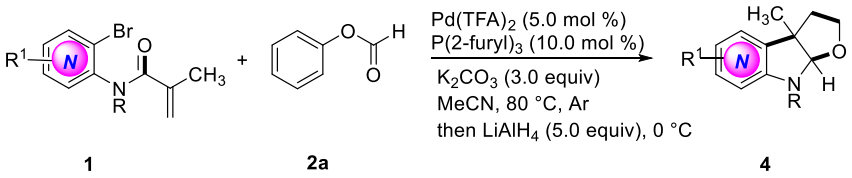
***N*-benzyl-3-bromo-*N*-(2-methylallyl)pyridin-4-amine (1l):** 75% yield (for the last step); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.20 (d, *J* = 5.4 Hz, 1H), 7.33-7.18 (m, 5H), 6.75 (d, *J* = 5.5 Hz, 1H), 4.98-4.87 (m, 2H), 4.46 (s, 2H), 3.72 (s, 2H), 1.69 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 153.5, 148.3, 140.6, 137.0, 128.3, 127.8, 127.2, 116.7, 114.1, 113.6, 56.6, 55.0, 20.3. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{18}N_2Br$ 317.0648; found: 317.0656.

3. Experiment procedure



1 **2** **3**

1 (0.2 mmol), **2** (0.4 mmol), $Pd(TFA)_2$ (5 mol%), $P(2\text{-furyl})_3$ (10 mol%) and K_2CO_3 (0.6 mmol) were added to a sealed tube, MeCN (2.0 mL) were added via syringe. The mixture was stirred at room temperature for 10 min firstly, and then was stirred in an oil bath at 80 ℃ about for 16 h until completion (monitored by TLC). After cooling at room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified through silica gel chromatography (petroleum ether/EtOAc = 20:1~5:1) to afford the coresponding products **3**.

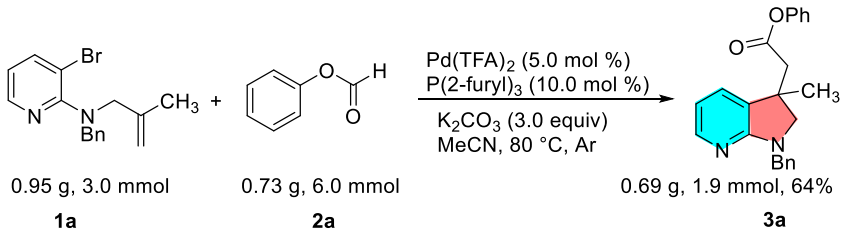


1 **2a** **4**

1 (0.2 mmol), **2a** (0.4 mmol), $Pd(TFA)_2$ (5 mol%), $P(2\text{-furyl})_3$ (10 mol%) and K_2CO_3 (0.6 mmol) were added to a sealed tube, MeCN (2.0 mL) were added via syringe. The mixture was stirred at room temperature for 10 min firstly, and then was stirred in an oil bath at 80 ℃ about for 16 h until completion (monitored by TLC). After cooling at room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate and evaporated under vacuum. The crude product was used in the following step without further purification. To a solution of crude product in THF (4.0 mL) at 0 ℃ was added $LiAlH_4$ (38 mg, 1.0 mmol) in small portions under nitrogen atmosphere. The reaction mixture was stirred at 0 ℃ about for 30 min, and then the reaction was quenched with the addition of brine and diluted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under

reduced pressure. The resulting residue was purified by flash column chromatography (petroleum ether/EtOAc = 20:1~5:1) to provide furoazaindolines **4**.

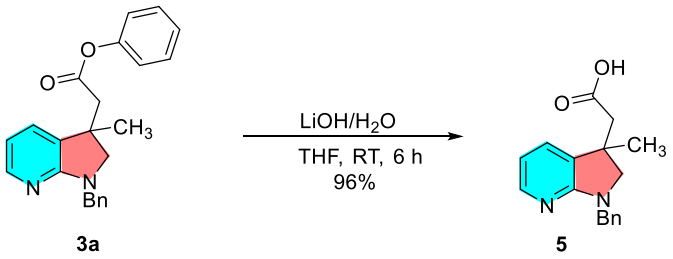
4. Gram-scale reaction of 3a



0.95 g, 3.0 mmol — **1a**; 0.73 g, 6.0 mmol — **2a**; 0.69 g, 1.9 mmol, 64% — **3a**

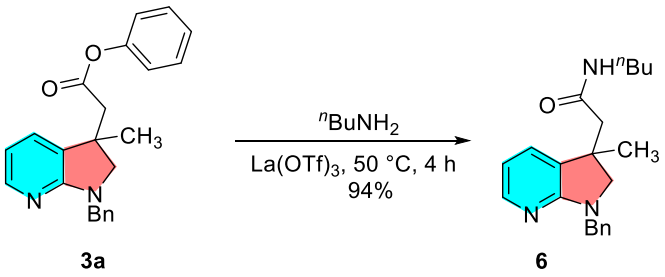
1a (3.0 mmol, 0.95 g), **2a** (6.0 mmol, 0.73 g), $Pd(TFA)_2$ (5 mol%), $P(2\text{-furyl})_3$ (10 mol%), and K_2CO_3 (9.0 mmol) were added to a sealed tube, MeCN (30 mL) were added via syringe. The mixture was stirred at room temperature for 10 min firstly, and then was stirred in an oil bath at 80 ℃ about for 16 h until completion (monitored by TLC). After cooling at room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified through silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford the coresponding product **3a** in 64% yield.

5. Further transformation experiments



3a → **5**

To a solution of **3a** (0.2 mmol) in THF (3.0 mL) and water (0.50 mL) at 0 ℃ were added 30% H_2O_2 (0.29 mL) and LiOH (0.4 mmol). The reaction mixture was stirred for 6 h, quenched with $Na_2S_2O_3$ and $NaHCO_3$, stirred for another 15 min, acidified with 20% HCl, extracted with EtOAc (3×5 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash chromatography (petroleum ether/EtOAc = 2:1) to give acid **5** with 96% yield.

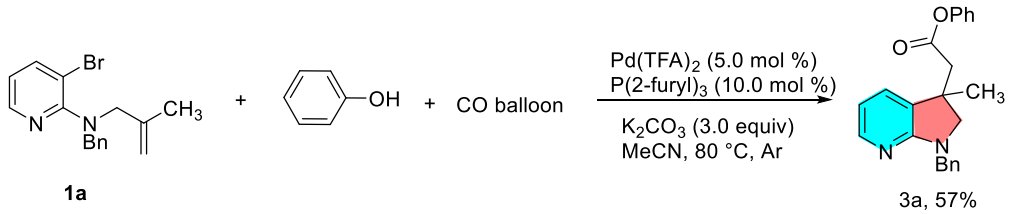


3a → **6**

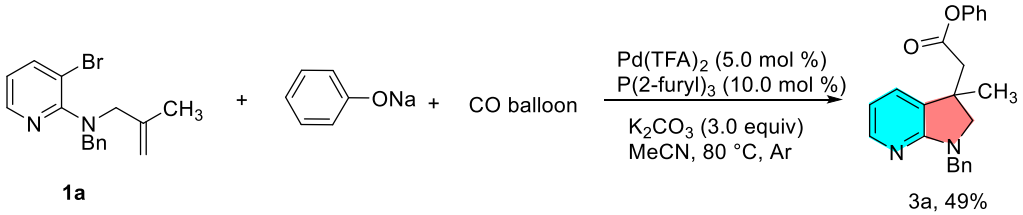
To a solution of **3a** (0.2 mmol) in 1 mL $^nBuNH_2$ was added $La(OTf)_3$ (6 mg, 5 mol%). The reaction mixture was stirred at 50 ℃ for 4 h. After cooling at room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate and concentrated under reduced

pressure. The residue was purified through silica gel chromatography (petroleum ether/EtOAc = 5:1) to give amide **6** with 94% yield.

6. Mechanistic studies

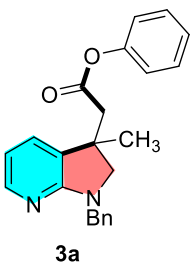


1a (0.2 mmol), phenol (0.4 mmol), $Pd(TFA)_2$ (5 mol%), $P(2\text{-furyl})_3$ (10 mol%) and K_2CO_3 (0.6 mmol) were added to a sealed tube, MeCN (2.0 mL) were added via syringe. Then expelled the air of the system and the sealed tube was then connected with a balloon containing CO. The mixture was stirred at room temperature for 10 min firstly, and then was stirred in an oil bath at 80 ℃ about for 16 h until completion (monitored by TLC). After cooling at room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified through silica gel chromatography (petroleum ether/EtOAc = 10:1) to afford the product **3a** with 57% yield.

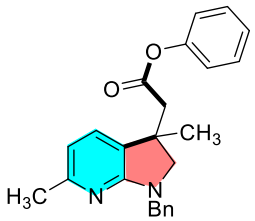


1a (0.2 mmol), sodium phenolate (0.4 mmol), $Pd(TFA)_2$ (5 mol%), $P(2\text{-furyl})_3$ (10 mol%) and K_2CO_3 (0.6 mmol) were added to a sealed tube, MeCN (2.0 mL) were added via syringe. Then expelled the air of the system and the sealed tube was then connected with a balloon containing CO. The mixture was stirred at room temperature for 10 min firstly, and then was stirred in an oil bath at 80 ℃ about for 16 h until completion (monitored by TLC). After cooling at room temperature, the mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified through silica gel chromatography (petroleum ether/EtOAc = 10:1) to afford the product **3a** with 49% yield.

7. Spectra data of products

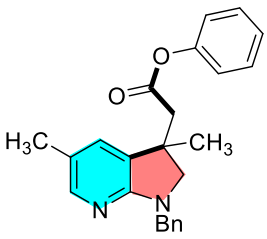


phenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3a): 52 mg; 73% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 5.4, 1.6 Hz, 1H), 7.39-7.18 (m, 9H), 6.98-6.88 (m, 2H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.62 (d, *J* = 3.3 Hz, 2H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.22 (d, *J* = 9.6 Hz, 1H), 2.82 (d, *J* = 3.7 Hz, 2H), 1.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 161.5, 150.3, 146.9, 137.7, 129.8, 129.4, 128.9, 128.5, 128.1, 127.1, 125.9, 121.4, 112.6, 61.6, 48.9, 44.3, 40.4, 25.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_2$ 359.1754; found: 359.1759.



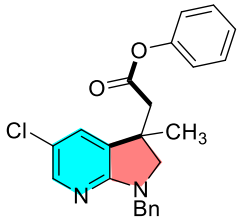
3b

phenyl-2-(1-benzyl-3,6-dimethyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3b): 51 mg; 69% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.17 (m, 9H), 6.97-6.92 (m, 2H), 6.39 (d, *J* = 7.3 Hz, 1H), 4.62 (s, 2H), 3.50 (d, *J* = 9.6 Hz, 1H), 3.17 (d, *J* = 9.5 Hz, 1H), 2.86-2.74 (m, 2H), 2.41 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 161.5, 156.0, 150.3, 138.0, 130.0, 129.4, 128.4, 128.1, 127.0, 125.8, 125.6, 121.5, 111.6, 61.9, 49.1, 44.3, 40.1, 25.7, 24.3. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_2$ 373.1911; found: 373.1918.



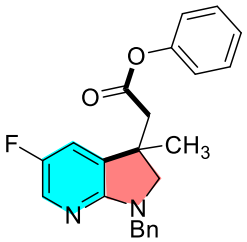
3c

phenyl-2-(1-benzyl-3,5-dimethyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3c): 43 mg; 58% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.36-7.19 (m, 8H), 7.13 (d, *J* = 2.0 Hz, 1H), 6.97-6.90 (m, 2H), 4.58 (s, 2H), 3.51 (d, *J* = 9.5 Hz, 1H), 3.18 (d, *J* = 9.5 Hz, 1H), 2.88-2.75 (m, 2H), 2.19 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 160.0, 150.3, 146.1, 137.9, 131.3, 129.4, 128.8, 128.4, 128.1, 127.1, 125.9, 121.6, 121.4, 62.1, 49.4, 44.2, 40.3, 25.5, 17.9. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_2$ 373.1911; found: 373.1916.



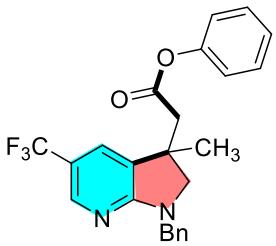
3d

phenyl-2-(1-benzyl-5-chloro-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3d): 42 mg; 54% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.2 Hz, 1H), 7.38-7.19 (m, 10H), 6.95 (dd, *J* = 7.5, 1.4 Hz, 2H), 4.63-4.53 (m, 2H), 3.56 (d, *J* = 9.7 Hz, 1H), 3.25 (d, *J* = 9.7 Hz, 1H), 2.81 (d, *J* = 3.3 Hz, 2H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 159.9, 150.2, 145.1, 137.2, 130.4, 130.2, 129.4, 128.5, 128.0, 127.3, 126.0, 121.4, 119.7, 61.8, 48.9, 44.0, 40.3, 25.7. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}N_2O_2Cl$ 393.1364; found: 393.1370.



3e

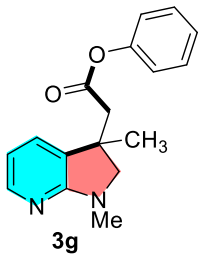
phenyl-2-(1-benzyl-5-fluoro-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3e): 46 mg; 61% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 2.2 Hz, 1H), 7.36-7.19 (m, 8H), 7.11 (dd, *J* = 7.9, 2.7 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 4.56 (s, 2H), 3.53 (d, *J* = 9.5 Hz, 1H), 3.23 (d, *J* = 9.5 Hz, 1H), 2.88-2.76 (m, 2H), 1.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 158.3, 154.2 (d, *J* = 241.8 Hz), 150.2, 137.5, 132.8 (d, *J* = 26.3 Hz), 130.2 (d, *J* = 8.7 Hz), 129.4, 128.5, 128.1, 127.2, 126.0, 121.4, 119.4 (d, *J* = 45.7 Hz), 62.4, 49.5, 43.9, 40.2, 25.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.92. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}N_2O_2F$ 377.1660; found: 377.1669.



3f

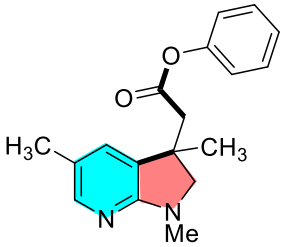
phenyl-2-(1-benzyl-3-methyl-5-(trifluoromethyl)-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl) acetate (3f): 56 mg; 66% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 2.2, 1.2 Hz, 1H), 7.39-7.18 (m, 9H), 6.98-6.91 (m, 2H), 4.76-4.58 (m, 2H), 3.67 (d, *J* = 10.0 Hz, 1H),

3.33 (d, *J* = 9.9 Hz, 1H), 2.84 (d, *J* = 1.5 Hz, 2H), 1.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 162.9, 150.2, 145.7(dd, *J* = 9.5, 4.7 Hz), 136.8, 129.4, 129.1, 128.6, 128.0, 127.5, 126.2, (d, *J* = 3.4 Hz), 121.3, 115.2 (dd, *J* = 65.2, 32.7 Hz), 61.2, 48.3, 44.1, 40.1, 26.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.66. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}N_2O_2F_3$ 427.1628; found: 427.1637.



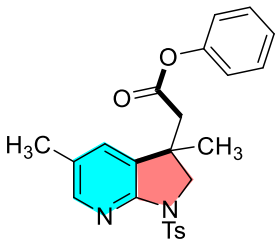
3g

phenyl-2-(1,3-dimethyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3g): 45 mg; 80% yield; colorless oil oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.28-7.19 (m, 2H), 7.02-6.95 (m, 2H), 6.49 (dd, *J* = 7.1, 5.3 Hz, 1H), 3.65 (d, *J* = 9.4 Hz, 1H), 3.29 (d, *J* = 9.4 Hz, 1H), 2.96 (s, 3H), 2.84 (d, *J* = 1.1 Hz, 2H), 1.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 162.1, 150.3, 146.9, 129.4, 129.3, 129.1, 125.9, 121.4, 112.3, 64.4, 44.2, 40.4, 32.2, 25.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2O_2$ 283.1441; found: 283.1447.



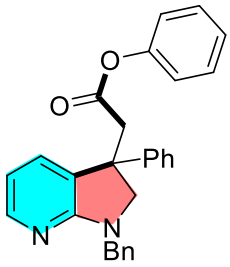
3h

phenyl-2-(1,3,5-trimethyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3h): 42 mg; 72% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.74 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.27-7.20 (m, 1H), 7.09 (d, *J* = 2.1 Hz, 1H), 7.03-6.96 (m, 2H), 3.61 (d, *J* = 9.3 Hz, 1H), 3.24 (d, *J* = 9.3 Hz, 1H), 2.92 (s, 3H), 2.88-2.78 (m, 2H), 2.17 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 160.8, 150.3, 146.1, 130.9, 129.4, 129.1, 125.9, 121.4, 121.3, 65.0, 44.1, 40.3, 32.7, 25.2, 17.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{21}N_2O_2$ 297.1598; found: 297.1604.



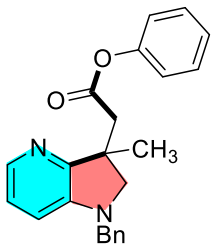
3i

phenyl-2-(3,5-dimethyl-1-tosyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3i): 56 mg; 64% yield; white solid; mp = 201-203 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-7.94 (m, 3H), 7.40-7.30 (m, 2H), 7.27-7.19 (m, 4H), 6.93-6.83 (m, 2H), 4.17 (d, *J* = 10.2 Hz, 1H), 3.82 (d, *J* = 10.2 Hz, 1H), 2.90-2.72 (m, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 153.0, 150.1, 147.7, 144.1, 134.7, 132.7, 130.1, 129.4, 129.3, 128.1, 127.6, 126.0, 121.3, 60.5, 43.8, 40.0, 25.6, 21.5, 18.0. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_4S$ 437.1530; found: 437.1536.



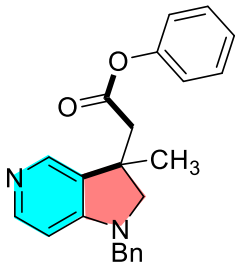
3j

phenyl-2-(1-benzyl-3-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3j): 44 mg; 53% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.40 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.34-7.21 (m, 14H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.77-6.72 (m, 2H), 6.58 (dd, *J* = 7.2, 5.2 Hz, 1H), 4.65 (s, 2H), 3.81-3.70 (m, 2H), 3.42-3.24 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 161.8, 150.2, 147.4, 144.3, 137.5, 132.6, 129.3, 128.7, 128.5, 128.2, 127.2, 127.0, 125.9, 125.9, 121.3, 112.9, 63.3, 49.2, 48.2, 43.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{25}N_2O_2$ 421.1911; found: 421.1917.



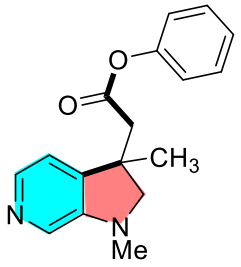
3k

phenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[3,2-b]pyridin-3-yl)acetate (3k): 29 mg; 41% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.82 (m, 1H), 7.38-7.25 (m, 7H), 7.23-7.17 (m, 1H), 7.01-6.91 (m, 3H), 6.69-6.63 (m, 1H), 4.37-4.23 (m, 2H), 3.67 (d, *J* = 9.5 Hz, 1H), 3.34 (dd, *J* = 9.5, 1.2 Hz, 1H), 3.06-2.92 (m, 2H), 1.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 156.8, 150.5, 144.8, 138.0, 137.2, 129.3, 128.6, 127.7, 127.4, 125.7, 122.5, 121.5, 112.4, 63.4, 52.5, 43.0, 42.7, 24.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_2$ 359.1754; found: 359.1759.



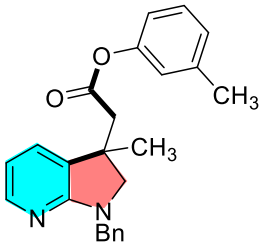
3l

phenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[3,2-c]pyridin-3-yl)acetate (3l): 54 mg; 76% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21-8.13 (m, 2H), 7.37-7.17 (m, 9H), 6.98-6.93 (m, 2H), 6.39 (d, *J* = 5.5 Hz, 1H), 4.40-4.31 (m, 2H), 3.71 (d, *J* = 9.8 Hz, 1H), 3.34 (d, *J* = 9.8 Hz, 1H), 2.89 (d, *J* = 2.6 Hz, 2H), 1.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 156.0, 150.2, 149.8, 142.7, 136.5, 131.2, 129.3, 128.6, 127.5, 127.4, 125.8, 121.3, 101.6, 64.1, 50.4, 44.2, 41.5, 26.1. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_2$ 359.1754; found: 359.1760.



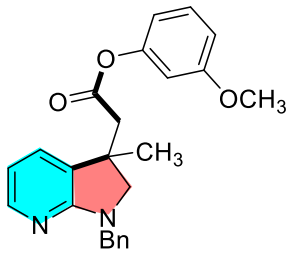
3m

phenyl-2-(1,3-dimethyl-2,3-dihydro-1H-pyrrolo[2,3-c]pyridin-3-yl)acetate (3m): 35 mg; 63% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 4.9 Hz, 1H), 7.90 (s, 1H), 7.41-7.34 (m, 2H), 7.25-7.20 (m, 1H), 7.09 (d, *J* = 4.9 Hz, 1H), 7.03-6.96 (m, 2H), 3.60 (d, *J* = 9.4 Hz, 1H), 3.26 (d, *J* = 9.3 Hz, 1H), 2.86 (d, *J* = 12.5 Hz, 5H), 1.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 150.2, 148.7, 139.6, 129.5, 126.0, 121.4, 118.0, 67.2, 43.1, 42.9, 35.0, 24.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2O_2$ 283.1441; found: 283.1446.



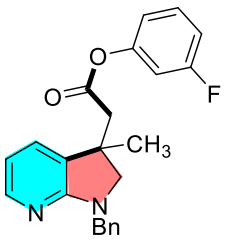
3n

***m*-tolyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3n):** 50 mg; 67% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 5.4, 1.6 Hz, 1H), 7.31-7.19 (m, 7H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 2H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.67-4.57 (m, 2H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.22 (d, *J* = 9.6 Hz, 1H), 2.81 (d, *J* = 3.8 Hz, 2H), 2.33 (s, 3H), 1.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 161.5, 150.2, 146.9, 139.6, 137.7, 129.8, 129.1, 128.9, 128.5, 128.1, 127.1, 126.7, 122.0, 118.4, 112.6, 61.6, 48.9, 44.2, 40.4, 25.8, 21.2. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_2$ 373.1911; found: 373.1918.



3o

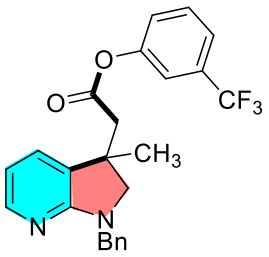
3-methoxyphenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3o): 48 mg; 62% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 5.4, 1.6 Hz, 1H), 7.31-7.21 (m, 7H), 6.76 (ddd, *J* = 8.4, 2.5, 0.9 Hz, 1H), 6.57-6.51 (m, 2H), 6.46 (t, *J* = 2.3 Hz, 1H), 4.68-4.56 (m, 2H), 3.76 (s, 3H), 3.56 (d, *J* = 9.7 Hz, 1H), 3.22 (d, *J* = 9.5 Hz, 1H), 2.81 (d, *J* = 2.5 Hz, 2H), 1.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 161.5, 160.4, 151.2, 146.9, 137.6, 129.8, 129.8, 128.9, 128.5, 128.0, 127.1, 113.6, 112.6, 111.8, 107.4, 61.6, 55.4, 48.9, 44.3, 40.4, 25.9. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_3$ 389.1860; found: 389.1867.



3p

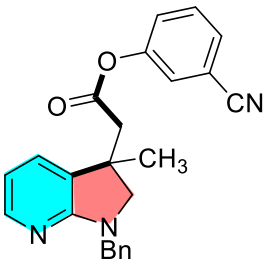
3-fluorophenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3p): 44 mg; 59% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.34-7.23 (m, 7H), 6.92 (tdd, *J* = 8.4, 2.5, 1.0 Hz, 1H), 6.76-6.68 (m, 2H), 6.54 (dd, *J* = 7.1, 5.3

Hz, 1H), 4.61 (d, *J* = 1.1 Hz, 2H), 3.53 (d, *J* = 9.6 Hz, 1H), 3.21 (d, *J* = 9.6 Hz, 1H), 2.81 (d, *J* = 3.3 Hz, 2H), 1.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 164.0, 161.5 (d, *J* = 6.1 Hz), 151.1 (d, *J* = 11.1 Hz), 147.0, 137.6, 130.2 (d, *J* = 9.4 Hz), 129.8, 128.6, 128.5, 128.1, 127.2, 117.3 (d, *J* = 3.4 Hz), 112.9 (d, *J* = 21.2 Hz),, 112.6, 109.6 (d, *J* = 25.3 Hz), 61.5, 49.0, 44.2, 40.4, 25.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.87. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}N_2O_2F$ 377.1660; found: 377.1669.



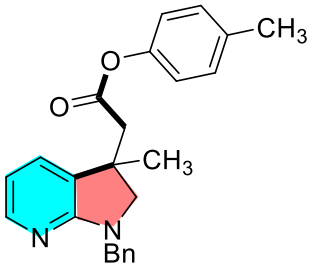
3q

3-(trifluoromethyl)phenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3q): 47 mg; 55% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.51-7.43 (m, 2H), 7.32-7.21 (m, 7H), 7.11 (dt, *J* = 7.0, 2.4 Hz, 1H), 6.54 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.68-4.56 (m, 2H), 3.54 (d, *J* = 9.6 Hz, 1H), 3.22 (d, *J* = 9.6 Hz, 1H), 2.84 (d, *J* = 2.4 Hz, 2H), 1.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 161.5, 150.3, 147.0, 137.6, 131.9 (dd, *J* = 57.6, 35.4 Hz), 130.0, 129.8, 128.6, 128.5, 128.1, 127.2, 125.1, 122.7 (d, *J* = 4.1 Hz), 118.8, (d, *J* = 3.8 Hz), 112.6, 61.5, 48.9, 44.3, 40.4, 25.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.66. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}N_2O_2F_3$ 427.1628; found: 427.1639.



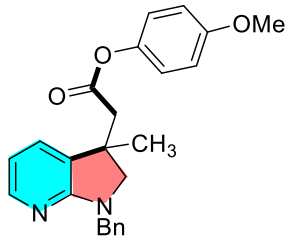
3r

3-cyanophenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3r): 39 mg; 51% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 5.4, 1.6 Hz, 1H), 7.53-7.42 (m, 2H), 7.33-7.22 (m, 7H), 7.15 (ddd, *J* = 8.3, 2.4, 1.2 Hz, 1H), 6.55 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.69-4.54 (m, 2H), 3.52 (d, *J* = 9.6 Hz, 1H), 3.22 (d, *J* = 9.6 Hz, 1H), 2.83 (d, *J* = 2.0 Hz, 2H), 1.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 161.5, 150.3, 147.1, 137.5, 130.4, 129.8, 129.6, 128.5, 128.5, 128.1, 127.3, 126.5, 125.3, 117.7, 113.4, 112.7, 61.5, 49.0, 44.3, 40.4, 25.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}N_3O_2$ 384.1707; found: 384.1715.



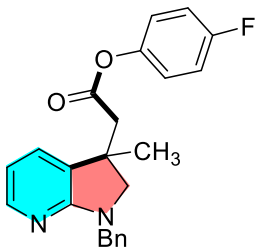
3s

***p*-tolyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3s):** 52 mg; 70% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.34-7.23 (m, 6H), 7.17-7.09 (m, 2H), 6.84-6.77 (m, 2H), 6.52 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.68-4.56 (m, 2H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.21 (d, *J* = 9.6 Hz, 1H), 2.88-2.76 (m, 2H), 2.32 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 161.5, 148.0, 146.9, 137.7, 135.6, 129.9, 129.8, 128.9, 128.5, 128.1, 127.1, 121.1, 112.6, 61.6, 48.9, 44.3, 40.4, 25.8, 20.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_2$ 373.1911; found: 373.1918.



3t

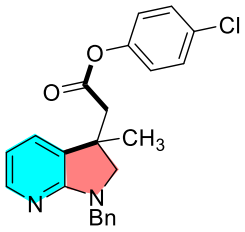
4-methoxyphenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3t): 53 mg; 69% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.32-7.23 (m, 6H), 6.84 (s, 4H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.67-4.55 (m, 2H), 3.77 (s, 3H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.21 (d, *J* = 9.6 Hz, 1H), 2.80 (d, *J* = 3.6 Hz, 2H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 161.5, 157.2, 146.9, 143.8, 137.7, 129.8, 128.9, 128.4, 128.1, 127.1, 122.2, 114.4, 112.6, 61.6, 55.5, 48.9, 44.2, 40.4, 25.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_3$ 389.1860; found: 389.1866.



3u

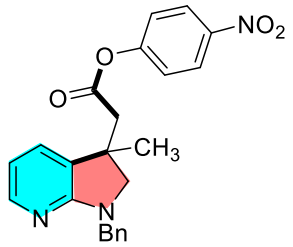
4-fluorophenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3u): 44 mg; 58% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 5.3, 1.6 Hz, 1H),

7.32-7.23 (m, 6H), 7.06-6.98 (m, 2H), 6.90-6.84 (m, 2H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.61 (s, 2H), 3.54 (d, *J* = 9.6 Hz, 1H), 3.21 (d, *J* = 9.6 Hz, 1H), 2.81 (d, *J* = 2.6 Hz, 2H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 161.5, 159.0, 147.0, 146.1 (d, *J* = 3.0 Hz), 137.7, 129.8, 128.7, 128.5, 128.1, 127.2, 122.8 (d, *J* = 9.1 Hz), 116.0 (d, *J* = 23.6 Hz), 112.6, 61.5, 49.0, 44.3, 40.4, 25.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.75. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}N_2O_2F$ 377.1660; found: 377.1662.



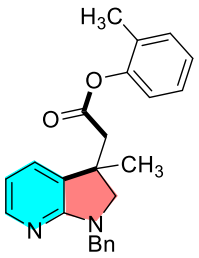
3v

4-chlorophenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3v): 47 mg; 60% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.34-7.23 (m, 8H), 6.92-6.81 (m, 2H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.61 (s, 2H), 3.53 (d, *J* = 9.5 Hz, 1H), 3.21 (d, *J* = 9.6 Hz, 1H), 2.81 (d, *J* = 2.5 Hz, 2H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 161.5, 148.7, 147.0, 137.6, 131.3, 129.8, 129.4, 128.6, 128.5, 128.1, 127.2, 122.8, 112.6, 61.5, 49.0, 44.3, 40.4, 25.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}N_2O_2Cl$ 393.1364; found: 393.1372.



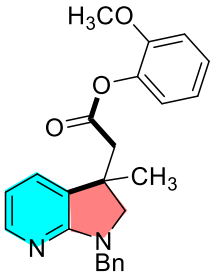
3w

4-nitrophenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3w): 35 mg; 44% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27-8.20 (m, 2H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.95 (dd, *J* = 5.4, 1.6 Hz, 1H), 7.34-7.24 (m, 6H), 7.14-7.06 (m, 2H), 6.83 (d, *J* = 9.1 Hz, 1H), 6.58 (dd, *J* = 7.1, 5.4 Hz, 1H), 4.68-4.55 (m, 2H), 3.58 (d, *J* = 9.7 Hz, 1H), 3.27 (d, *J* = 9.7 Hz, 1H), 2.87 (s, 2H), 1.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 161.1, 154.9, 146.2, 145.4, 137.1, 130.3, 129.1, 128.6, 128.0, 127.4, 126.1, 125.2, 122.3, 115.7, 112.8, 61.5, 49.1, 44.4, 40.4, 26.0. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}N_3O_4$ 404.1605; found: 404.1618.



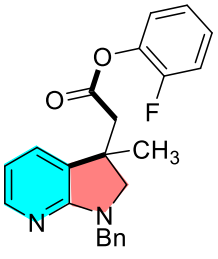
3x

***o*-tolyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3x):** 57 mg; 76% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.33-7.09 (m, 9H), 6.84 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.52 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.68-4.57 (m, 2H), 3.57 (d, *J* = 9.6 Hz, 1H), 3.23 (d, *J* = 9.6 Hz, 1H), 2.87 (d, *J* = 1.4 Hz, 2H), 2.05 (s, 3H), 1.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 161.5, 149.0, 146.9, 137.7, 131.1, 129.9, 129.7, 128.9, 128.4, 128.0, 127.1, 126.9, 126.1, 121.7, 112.6, 61.5, 48.9, 43.8, 40.2, 25.9, 16.2. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_2$ 373.1911; found: 373.1921.



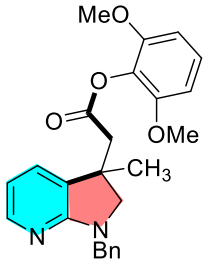
3y

2-methoxyphenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3y): 50 mg; 65% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 5.4, 1.4 Hz, 1H), 7.34-7.15 (m, 7H), 6.92 (dd, *J* = 8.1, 6.4 Hz, 3H), 6.52 (ddd, *J* = 6.7, 5.2, 1.1 Hz, 1H), 4.73-4.52 (m, 2H), 3.72 (d, *J* = 1.2 Hz, 3H), 3.61-3.55 (m, 1H), 3.23 (dd, *J* = 9.6, 1.2 Hz, 1H), 2.91-2.81 (m, 2H), 1.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9, 161.2, 150.9, 146.4, 139.4, 137.7, 129.8, 129.5, 128.4, 128.0, 127.1, 126.9, 122.6, 120.7, 112.5, 112.3, 61.6, 55.6, 49.0, 43.7, 40.3, 25.6. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_3$ 389.1860; found: 389.1870.



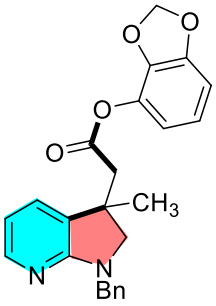
3z

2-fluorophenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3z): 43 mg; 57% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 5.4, 1.6 Hz, 1H), 7.32-7.07 (m, 9H), 6.98 (td, *J* = 7.8, 1.8 Hz, 1H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.69-4.55 (m, 2H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.23 (d, *J* = 9.6 Hz, 1H), 2.93-2.81 (m, 2H), 1.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 161.5, 154.0 (d, *J* = 250.2 Hz), 147.0, 137.7 (t, *J* = 6.1 Hz), 129.7, 128.9, 128.5, 128.1, 127.2 (d, *J* = 7.1 Hz), 127.1, 124.5 (d, *J* = 4.1 Hz), 123.6, 116.6 (d, *J* = 18.6 Hz), 112.6, 61.6, 48.9, 43.8, 40.3, 25.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.98. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}N_2O_2F$ 377.1660; found: 377.1668.



3aa

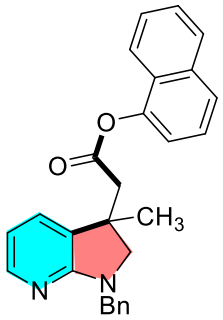
2,6-dimethoxyphenyl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3aa): 52 mg; 62% yield; yellow solid; mp = 173-175 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.35-7.21 (m, 6H), 7.11 (t, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 6.51 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.72 (d, *J* = 15.1 Hz, 1H), 4.53 (d, *J* = 15.1 Hz, 1H), 3.73 (s, 6H), 3.59 (d, *J* = 9.6 Hz, 1H), 3.25 (d, *J* = 9.7 Hz, 1H), 2.97-2.85 (m, 2H), 1.49 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 161.4, 152.1, 146.7, 137.9, 129.6, 129.6, 128.4, 128.0, 127.0, 126.3, 112.6, 104.7, 61.7, 55.9, 48.9, 43.5, 40.3, 25.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{27}N_2O_4$ 419.1965; found: 419.1970.



3ab

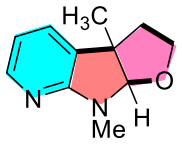
benzo[d][1,3]dioxol-4-yl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3ab): 55 mg; 68% yield; white solid; mp = 156-158 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.33-7.23 (m, 6H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 6.36 (dd, *J* = 8.4, 2.3 Hz, 1H), 5.95 (s, 2H), 4.61 (d, *J* = 1.5 Hz, 2H), 3.53 (d, *J* = 9.6 Hz, 1H), 3.20 (d, *J* = 9.6 Hz, 1H), 2.78 (d, *J* = 3.8 Hz, 2H), 1.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 161.5, 147.9, 147.0, 145.4, 144.5, 137.7, 129.8, 128.7, 128.5, 128.1,

127.1, 113.8, 112.6, 107.9, 103.6, 101.7, 61.6, 48.9, 44.2, 40.4, 25.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_4$ 403.1652; found: 403.1654.



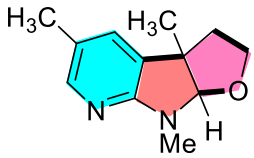
3ac

naphthalen-1-yl-2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3ac): 51 mg; 63% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.84 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.64-7.59 (m, 1H), 7.52-7.39 (m, 3H), 7.34-7.21 (m, 6H), 7.08 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.55 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.63 (d, *J* = 2.4 Hz, 2H), 3.62 (d, *J* = 9.5 Hz, 1H), 3.26 (d, *J* = 9.6 Hz, 1H), 3.02 (d, *J* = 2.5 Hz, 2H), 1.53 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 161.5, 147.0, 146.3, 137.7, 134.6, 129.9, 128.8, 128.5, 128.1, 128.0, 127.1, 126.6, 126.5, 126.4, 126.1, 125.3, 121.0, 117.9, 112.7, 61.6, 49.0, 44.1, 40.4, 26.0. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{25}N_2O_2$ 409.1911; found: 409.1914.



4a

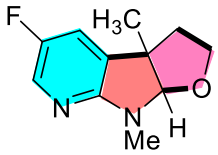
3a,8-dimethyl-3,3a,8,8a-tetrahydro-2H-furo[3',2':4,5]pyrrolo[2,3-b]pyridine (4a): 23 mg; 61% yield; colorless oil; **^{1}H NMR** (400 MHz, CDCl3) δ 7.95 – 7.87 (m, 1H), 7.18 (dd, *J* = 7.0, 1.6 Hz, 1H), 6.49 (dd, *J* = 7.0, 5.3 Hz, 1H), 5.13 (s, 1H), 3.97 (ddd, *J* = 8.9, 5.8, 2.7 Hz, 1H), 3.50 – 3.41 (m, 1H), 3.07 (s, 3H), 2.05 (dd, *J* = 9.7, 6.4 Hz, 2H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 160.91, 146.55, 129.23, 128.33, 112.48, 102.32, 66.82, 50.08, 41.57, 28.54, 24.64. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{15}N_2O$ 191.1179; found: 191.1181.



4b

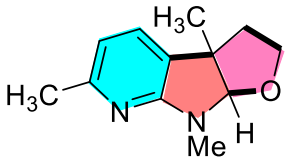
3a,5,8-trimethyl-3,3a,8,8a-tetrahydro-2H-furo[3',2':4,5]pyrrolo[2,3-b]pyridine (4b): 21 mg; 52% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 1.5 Hz, 1H), 7.04 (d, *J* = 2.0 Hz,

1H), 5.11 (s, 1H), 3.96 (ddd, *J* = 8.8, 6.1, 2.6 Hz, 1H), 3.52-3.38 (m, 1H), 3.04 (s, 3H), 2.17 (s, 3H), 2.08-2.00 (m, 2H), 1.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 145.5, 130.8, 128.1, 121.2, 102.6, 66.7, 49.9, 41.4, 28.6, 24.5, 17.7. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{17}N_2O$ 205.1335; found: 205.1340.



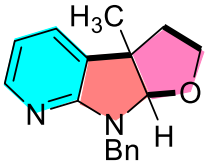
4c

5-fluoro-3a,8-dimethyl-3,3a,8,8a-tetrahydro-2H-furo[3',2':4,5]pyrrolo[2,3-b]pyridine (4c): 19 mg; 47% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 2.3 Hz, 1H), 7.01 (dd, *J* = 7.7, 2.7 Hz, 1H), 5.15 (s, 1H), 4.05-3.94 (m, 1H), 3.53-3.41 (m, 1H), 3.03 (s, 3H), 2.11-2.03 (m, 2H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.6, 155.4, 153.0, 132.2 (d, *J* = 26.3 Hz), 129.7 (d, *J* = 4.3 Hz), 118.8 (d, *J* = 23.2 Hz), 103.0, 66.8, 49.9, 49.9, 41.4, 28.8, 24.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.66. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{14}N_2OF$ 209.1085; found: 209.1087.



4d

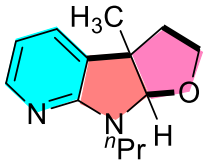
3a,6,8-trimethyl-3,3a,8,8a-tetrahydro-2H-furo[3',2':4,5]pyrrolo[2,3-b]pyridine (4d): 23 mg; 56% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.1 Hz, 1H), 6.34 (d, *J* = 7.1 Hz, 1H), 5.10 (s, 1H), 3.95 (ddd, *J* = 8.7, 5.5, 3.0 Hz, 1H), 3.45 (td, *J* = 9.6, 8.9, 6.8 Hz, 1H), 3.06 (s, 3H), 2.38 (s, 3H), 2.06-1.99 (m, 2H), 1.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 155.5, 129.4, 124.9, 111.2, 102.5, 66.7, 49.7, 41.5, 28.5, 24.7, 24.1. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{17}N_2O$ 205.1335; found: 205.1339.



4e

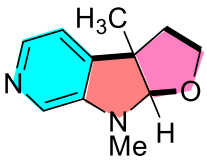
8-benzyl-3a-methyl-3,3a,8,8a-tetrahydro-2H-furo[3',2':4,5]pyrrolo[2,3-b]pyridine (4e): 35 mg; 66% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 5.4, 1.6 Hz, 1H), 7.35-7.20 (m, 6H), 6.53 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.06 (d, *J* = 15.2 Hz, 2H), 4.41 (d, *J* = 15.4 Hz,

1H), 3.94 (ddd, *J* = 8.7, 7.0, 1.5 Hz, 1H), 3.48 (ddd, *J* = 11.1, 8.9, 5.2 Hz, 1H), 2.12-1.95 (m, 2H), 1.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 146.5, 137.9, 129.6, 128.3, 127.8, 126.9, 112.9, 99.7, 66.8, 50.0, 44.9, 41.6, 24.6. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2O$ 267.1492; found: 267.1500.



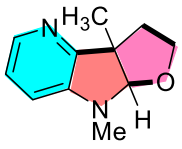
4f

3a-methyl-8-propyl-3,3a,8,8a-tetrahydro-2H-furo[3',2':4,5]pyrrolo[2,3-b]pyridine (4f): 30 mg; 69% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.17 (dd, *J* = 7.1, 1.6 Hz, 1H), 6.47 (dd, *J* = 7.0, 5.3 Hz, 1H), 5.21 (s, 1H), 3.95 (ddd, *J* = 8.7, 6.3, 2.3 Hz, 1H), 3.53-3.39 (m, 3H), 2.11-2.01 (m, 2H), 1.82-1.61 (m, 2H), 1.45 (s, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 146.4, 129.2, 128.2, 112.3, 101.1, 66.5, 50.0, 44.0, 41.6, 24.8, 21.2, 11.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{19}N_2O$ 219.1492; found: 219.1499.



4g

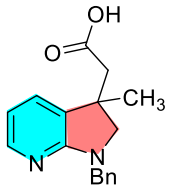
3a,8-dimethyl-3,3a,8,8a-tetrahydro-2H-furo[3',2':4,5]pyrrolo[2,3-c]pyridine (4g): 16 mg; 41% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 4.6 Hz, 1H), 7.74 (s, 1H), 6.99 (d, *J* = 4.6 Hz, 1H), 5.09 (s, 1H), 3.98 (ddd, *J* = 8.8, 6.8, 2.0 Hz, 1H), 3.43 (ddd, *J* = 10.8, 8.9, 5.6 Hz, 1H), 2.96 (s, 3H), 2.15-2.05 (m, 2H), 1.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.7, 143.2, 139.7, 126.6, 117.7, 104.5, 67.2, 53.4, 52.6, 41.1, 30.6, 23.9. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{15}N_2O$ 191.1179; found: 191.1183.



4h

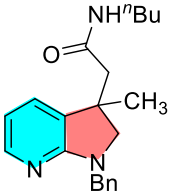
3a,8-dimethyl-3,3a,8,8a-tetrahydro-2H-furo[3',2':4,5]pyrrolo[3,2-b]pyridine (4h): 14 mg; 36% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.95 (dd, *J* = 7.9, 5.0 Hz, 1H), 6.54 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.11 (s, 1H), 3.98 (ddd, *J* = 9.0, 7.5, 1.5 Hz, 1H), 3.42 (ddd, *J* = 11.3, 8.8, 5.2 Hz, 1H), 2.93 (s, 3H), 2.39 (ddd, *J* = 12.1, 5.2, 1.5 Hz, 1H), 2.06 (td, *J*

= 11.8, 7.5 Hz, 1H), 1.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.4, 144.4, 137.7, 122.4, 109.8, 103.1, 67.3, 52.9, 39.9, 30.5, 22.6. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{15}N_2O$ 191.1179; found: 191.1184.



5

2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetic acid (5): 54 mg; 96% yield; white solid; mp = 143-145 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.87 (dd, *J* = 5.6, 1.5 Hz, 1H), 7.32-7.15 (m, 6H), 6.44 (dd, *J* = 7.0, 5.6 Hz, 1H), 4.62 (d, *J* = 15.2 Hz, 1H), 4.42 (d, *J* = 15.3 Hz, 1H), 3.52 (d, *J* = 9.8 Hz, 1H), 3.17 (d, *J* = 9.8 Hz, 1H), 2.56 (d, *J* = 3.3 Hz, 2H), 1.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 160.0, 144.0, 137.2, 131.3, 130.3, 128.5, 127.9, 127.2, 112.3, 61.7, 49.0, 44.5, 40.0, 26.0. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2O_2$ 283.1441; found: 283.1448.



6

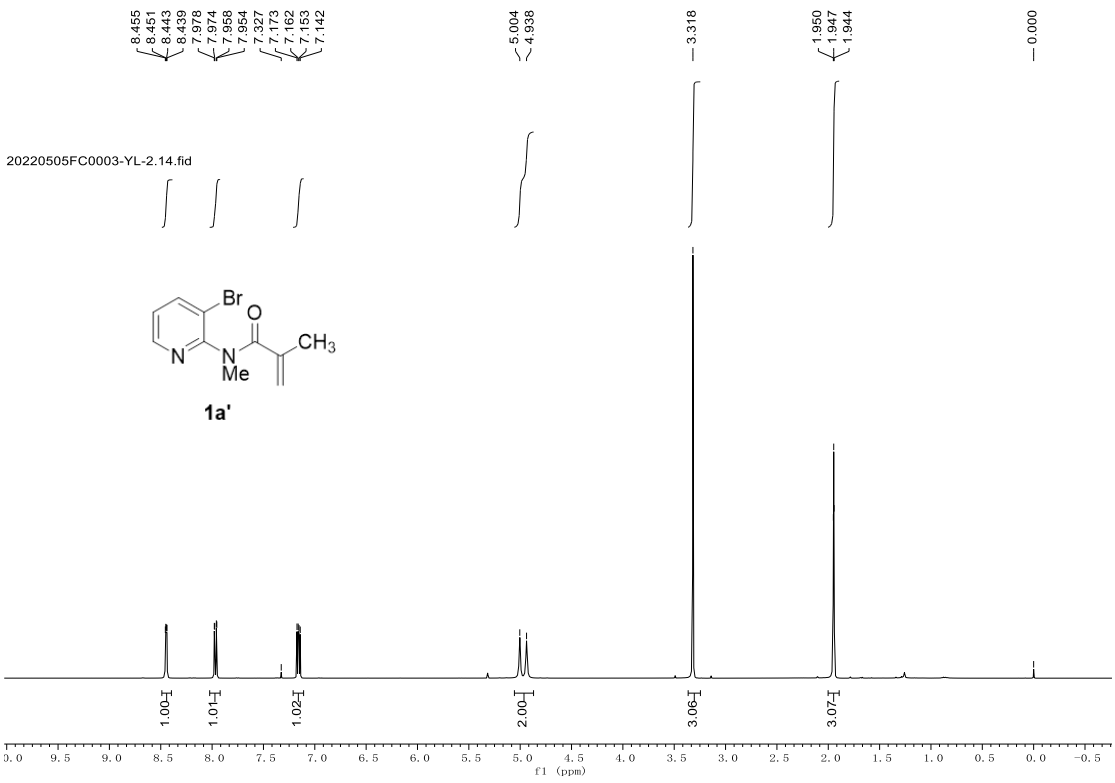
2-(1-benzyl-3-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)-*N*-butylacetamide (6): 63 mg; 94% yield; pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.4, 1.5 Hz, 1H), 7.33-7.21 (m, 5H), 7.15 (dd, *J* = 7.0, 1.6 Hz, 1H), 6.48 (dd, *J* = 7.0, 5.3 Hz, 1H), 5.66 (d, *J* = 5.5 Hz, 1H), 4.64-4.50 (m, 2H), 3.50 (d, *J* = 9.6 Hz, 1H), 3.19-3.06 (m, 3H), 2.37 (d, *J* = 2.0 Hz, 2H), 1.35 (d, *J* = 21.8 Hz, 5H), 1.28-1.15 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 161.4, 146.6, 137.7, 129.6, 129.3, 128.3, 127.9, 127.0, 112.3, 61.6, 48.8, 46.4, 40.5, 39.0, 31.4, 25.5, 19.9, 13.6. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{28}N_3O$ 338.2227; found: 338.2232.

8. References

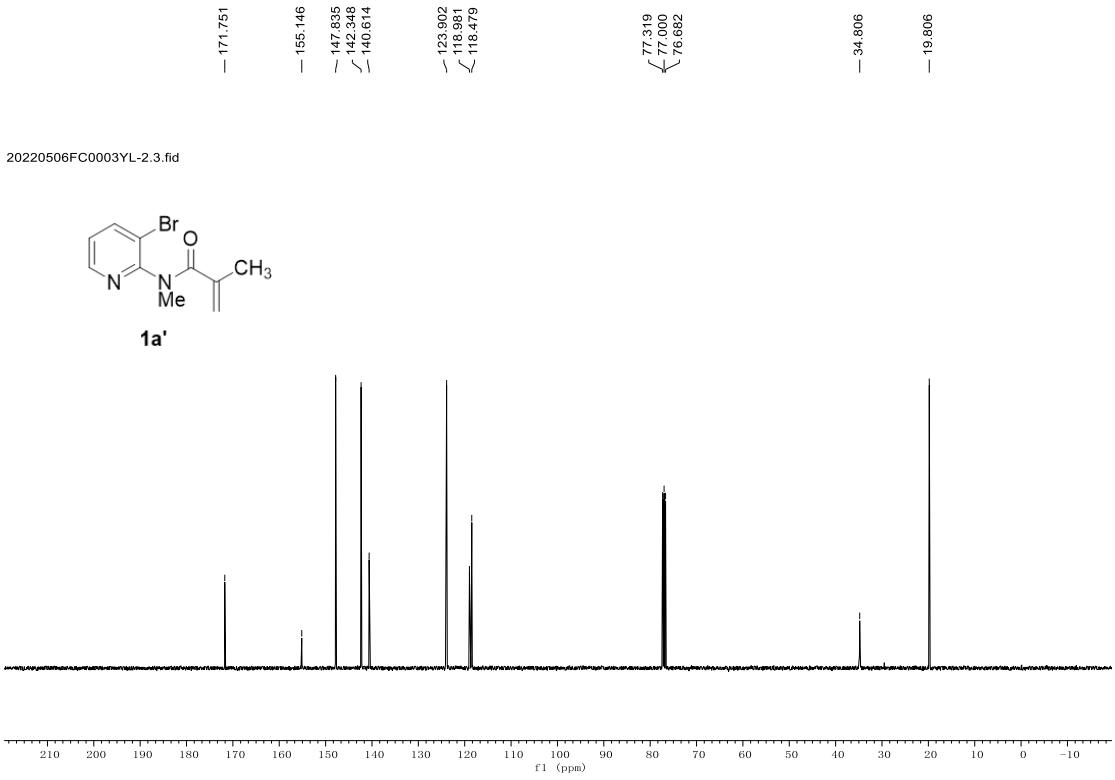
(1) (a) D T. T. Schempp, B. E. Daniels, S. T. Staben and C. E. Stivala, *Org. Lett.*, 2017, **19**, 3616; (b) Y. Ping, K. Wang, Q. Pan, Z. Ding, Z. Zhou, Y. Guo and W. Kong, *ACS Catal.*, 2019, **9**, 7335.
(2) T. Ueda, H. Konishi and K. Manabe, *Org. Lett.*, 2012, **14**, 5370.

9. NMR spectra of the substrates

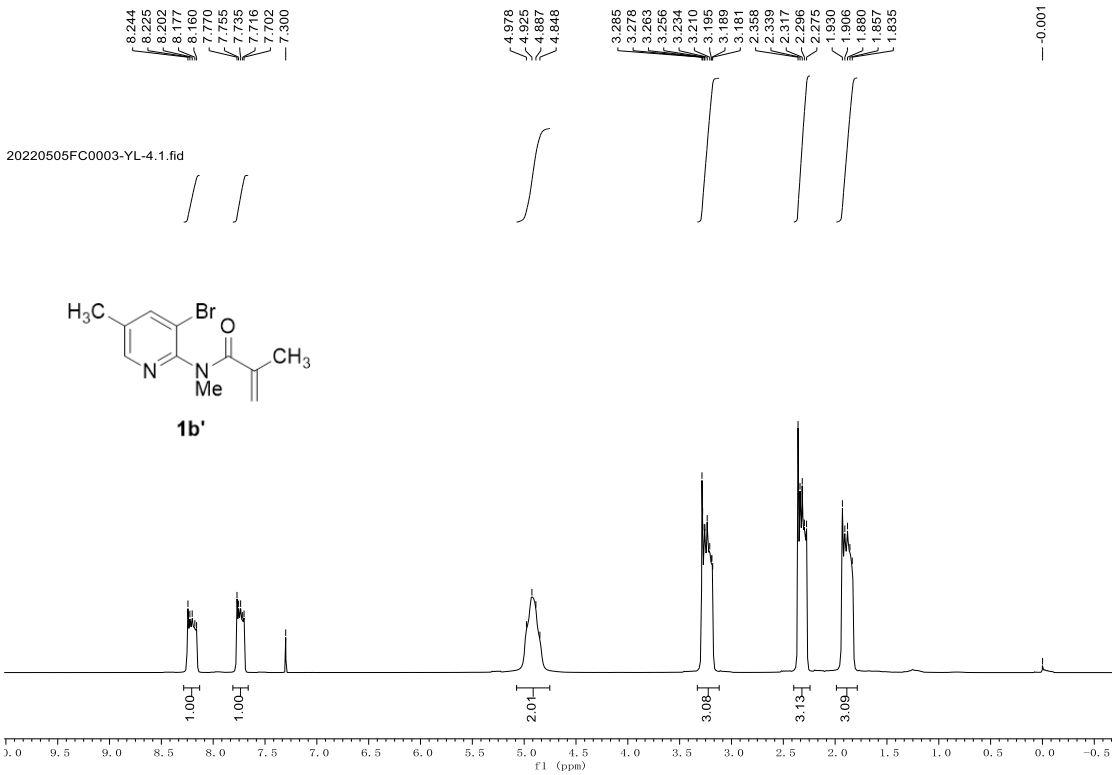
(**1a'**, ^{1}H NMR, $CDCl_3$, 400 MHz)



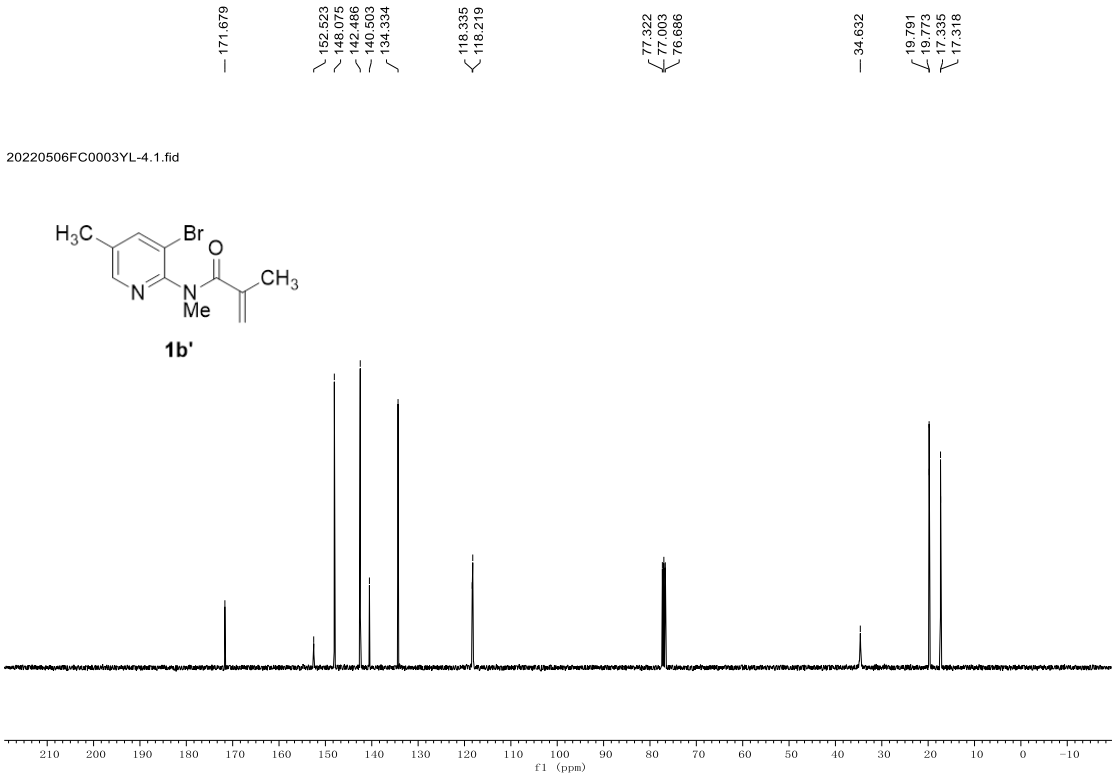
(**1a'**, ^{13}C NMR, $CDCl_3$, 101 MHz)



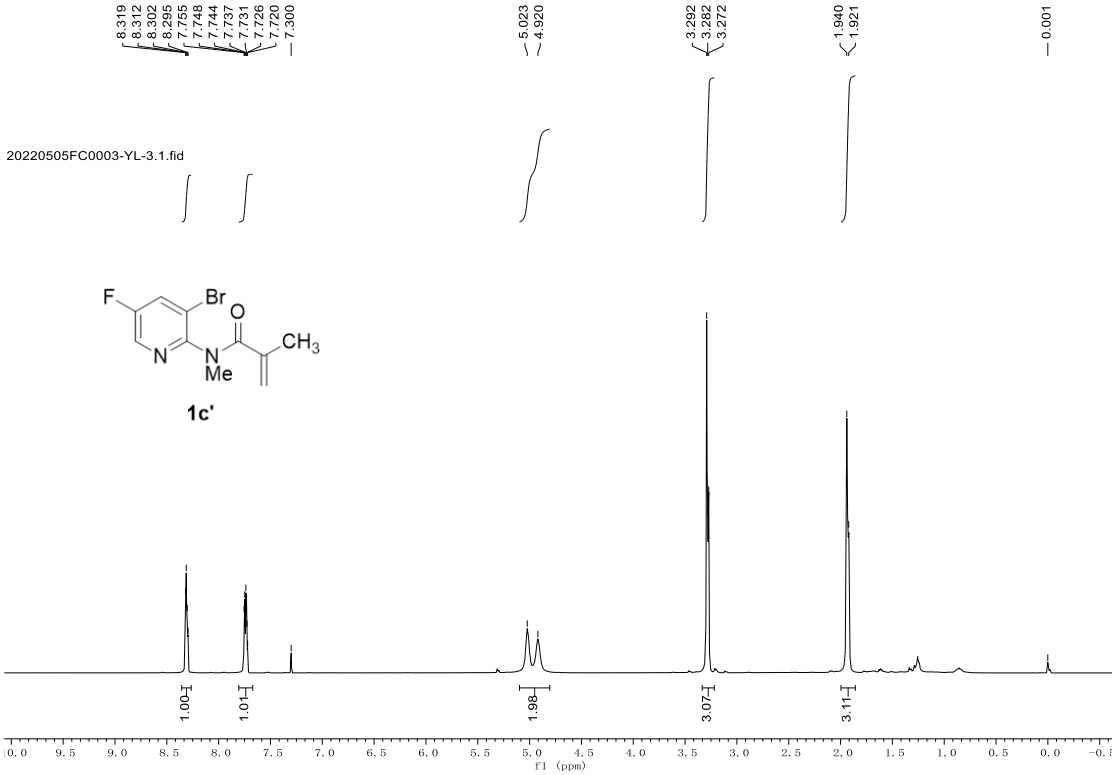
(**1b'**, ^{1}H NMR, $CDCl_3$, 400 MHz)



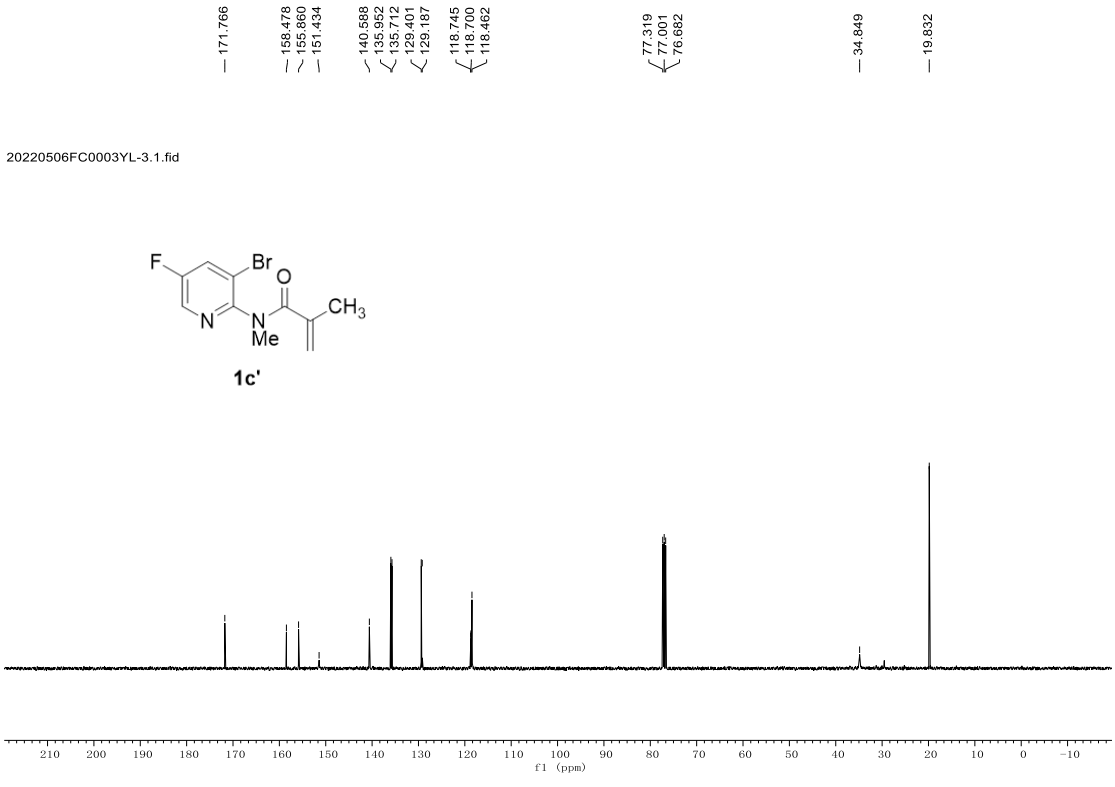
(**1b'**, ^{13}C NMR, $CDCl_3$, 101 MHz)



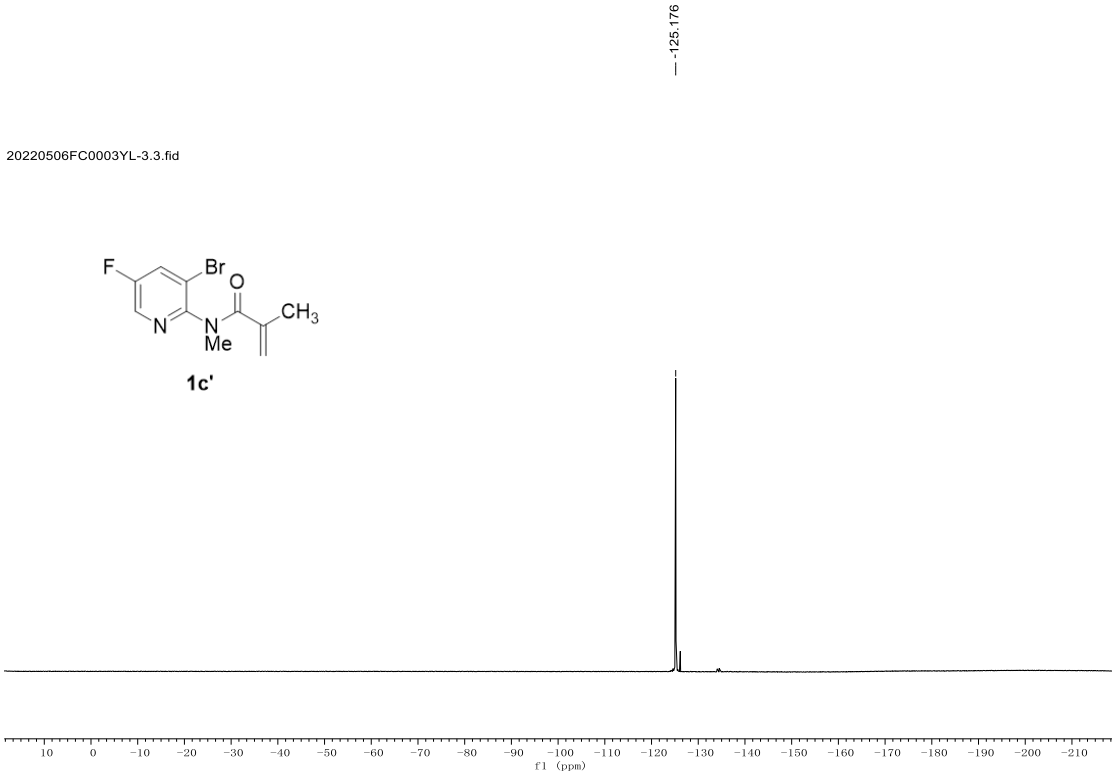
(**1c'**, ^{1}H NMR, $CDCl_3$, 400 MHz)



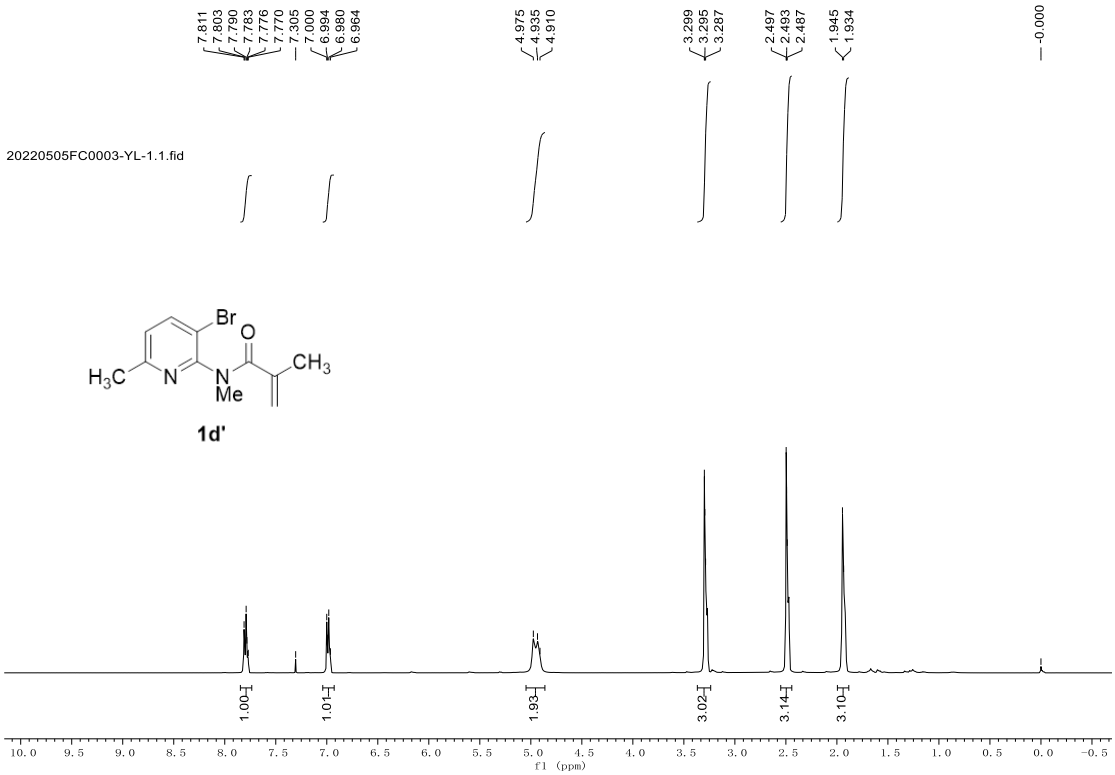
(**1c'**, ^{13}C NMR, $CDCl_3$, 101 MHz)



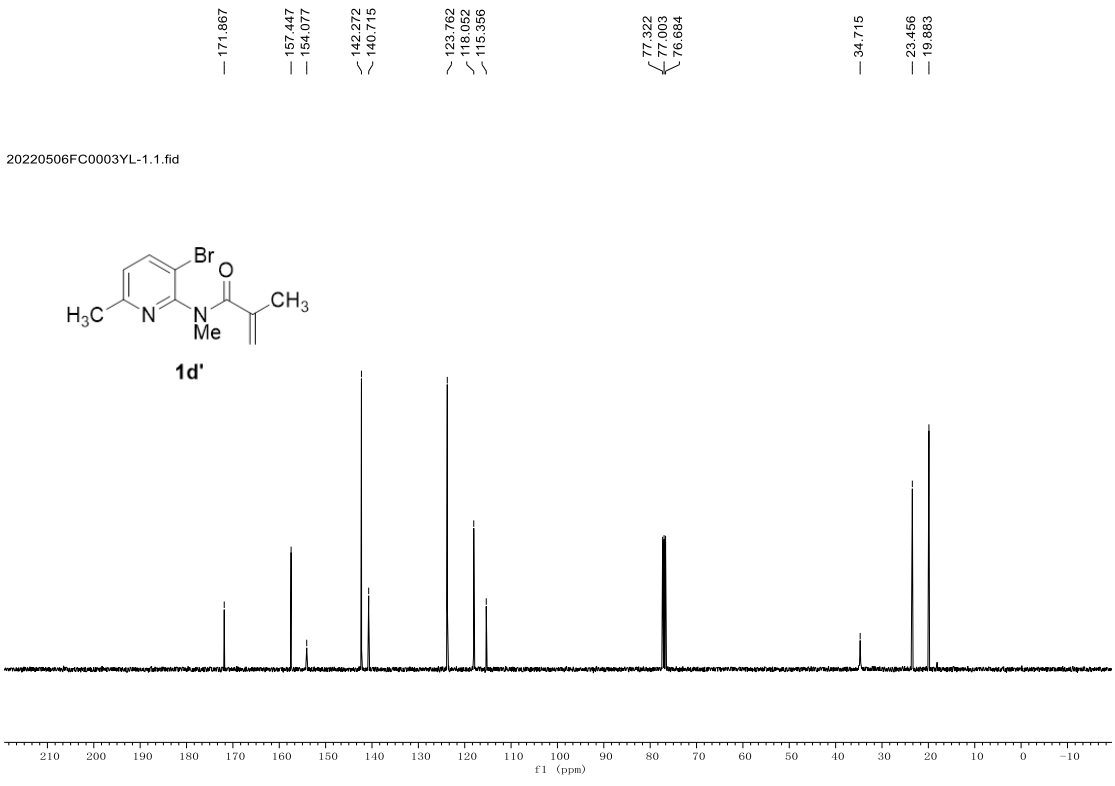
(**1c'**, ^{19}F NMR, $CDCl_3$, 376 MHz)



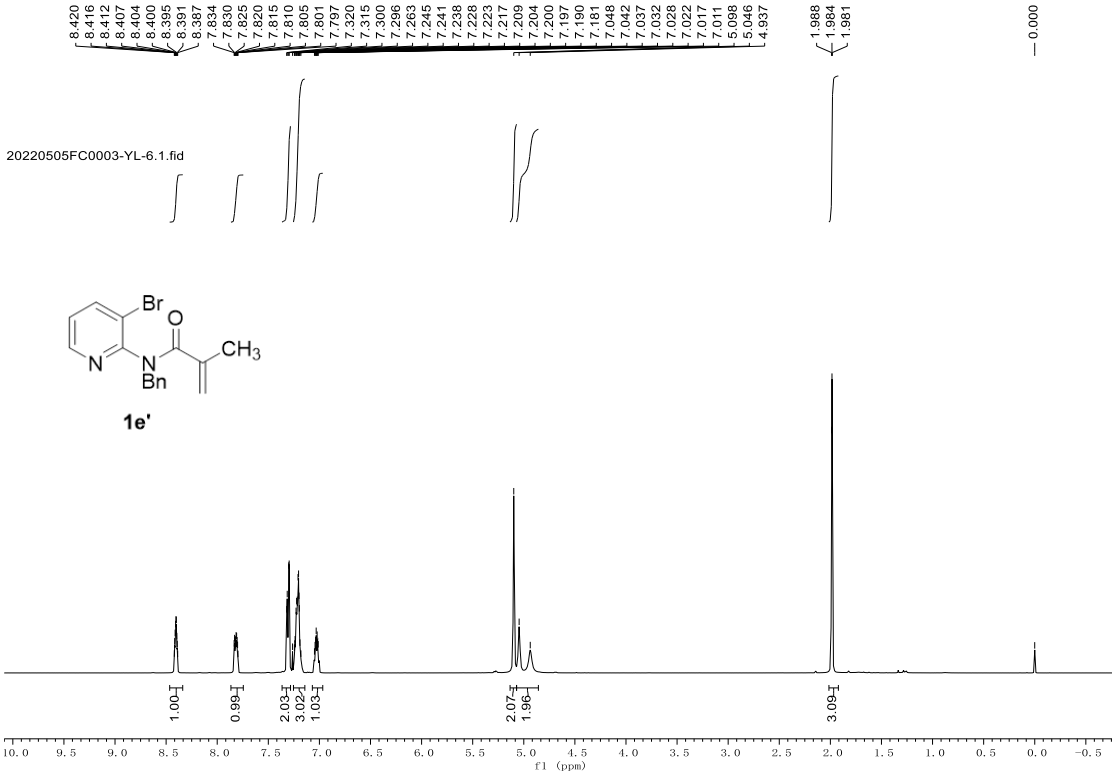
(**1d'**, ^{1}H NMR, $CDCl_3$, 400 MHz)



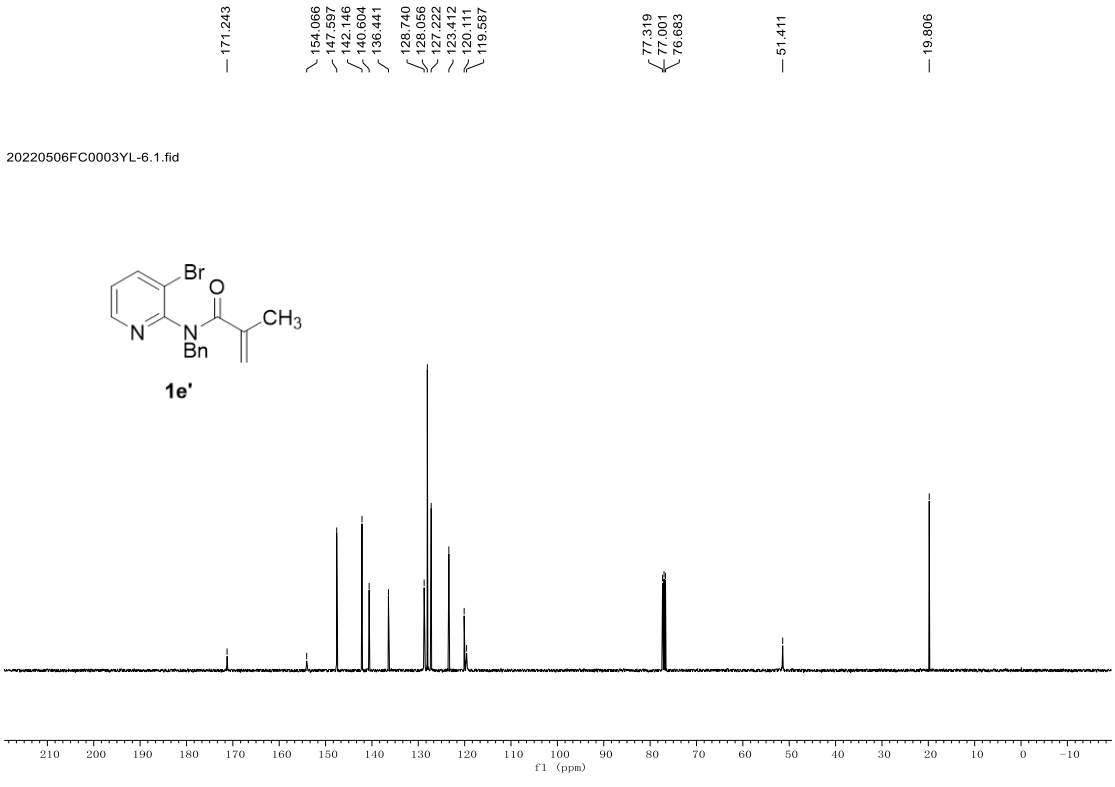
(**1d'**, ^{13}C NMR, $CDCl_3$, 101 MHz)



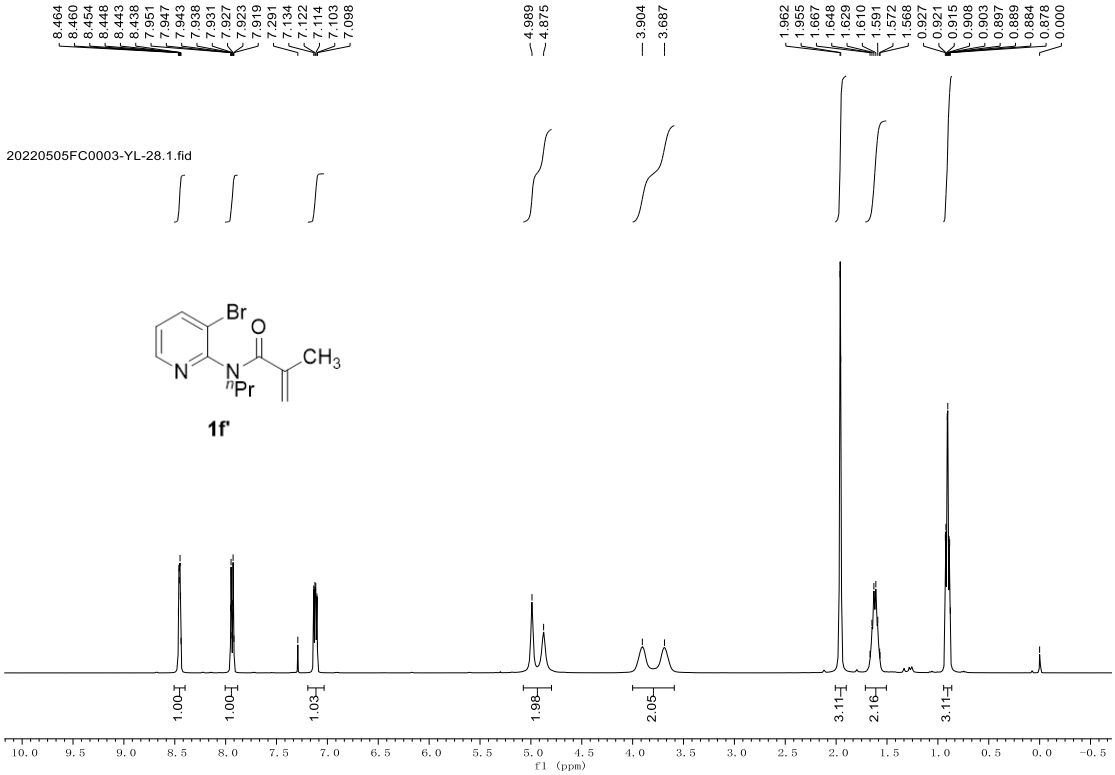
(**1e'**, ^{1}H NMR, $CDCl_3$, 400 MHz)



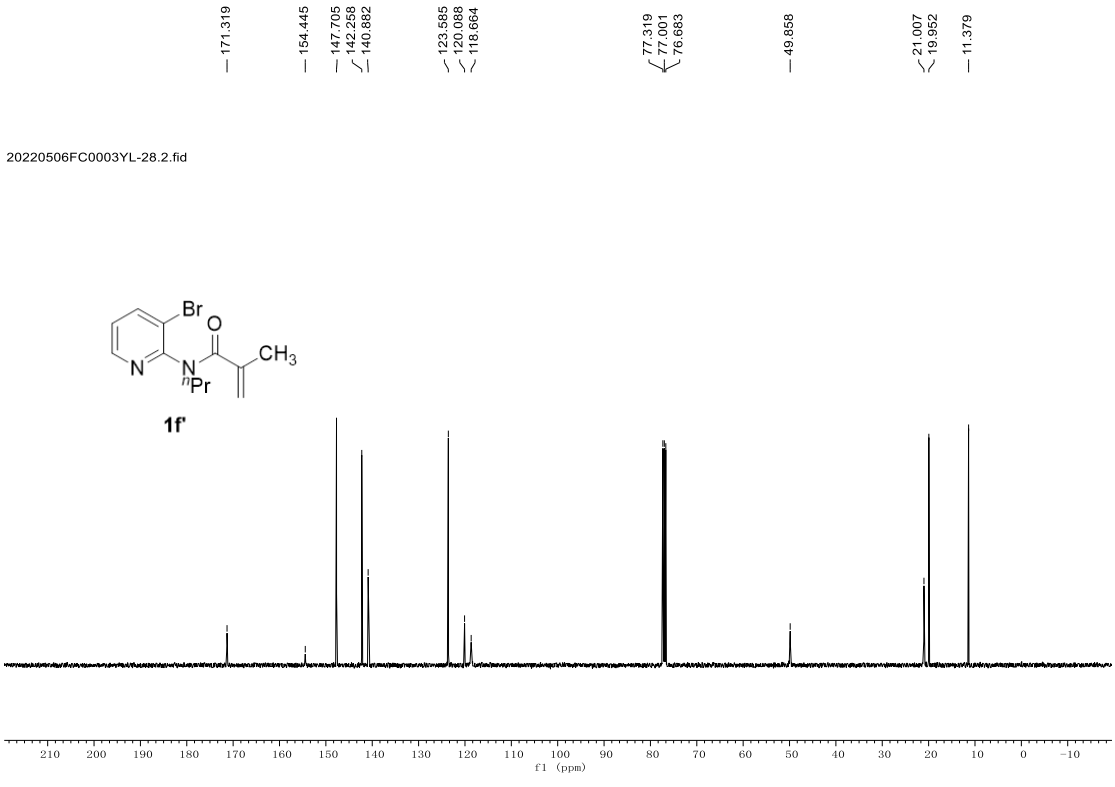
(**1e'**, ^{13}C NMR, $CDCl_3$, 101 MHz)



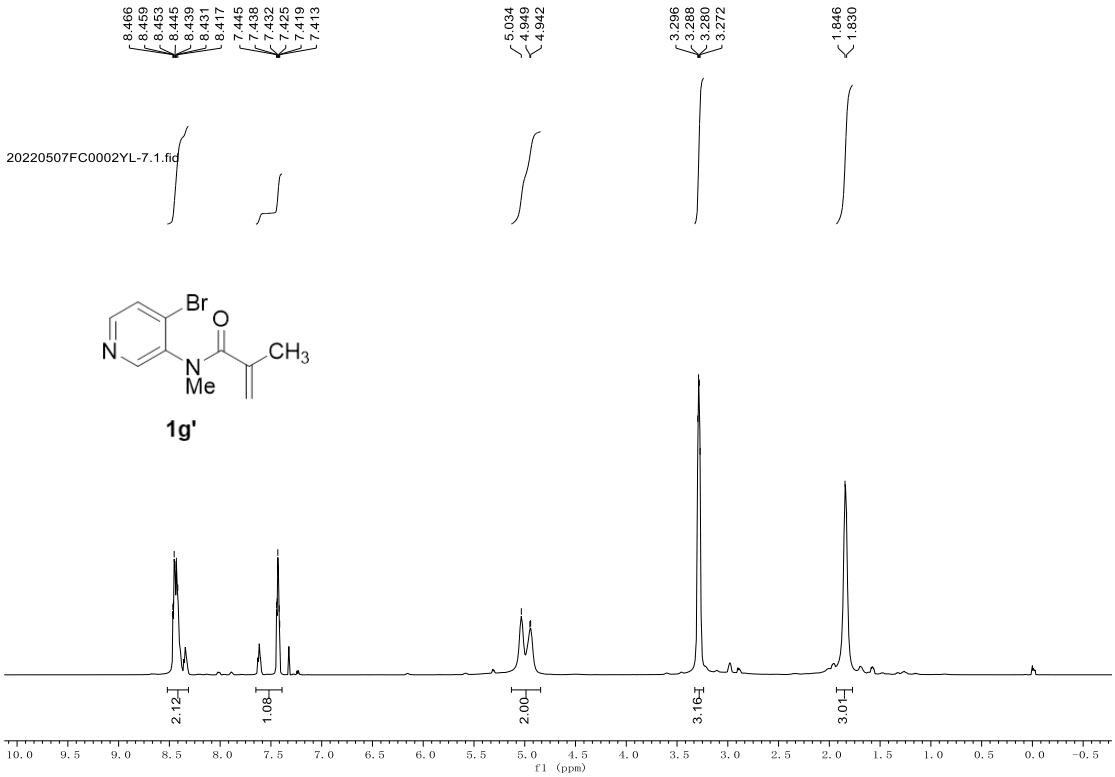
(**1f'**, ^{1}H NMR, $CDCl_3$, 400 MHz)



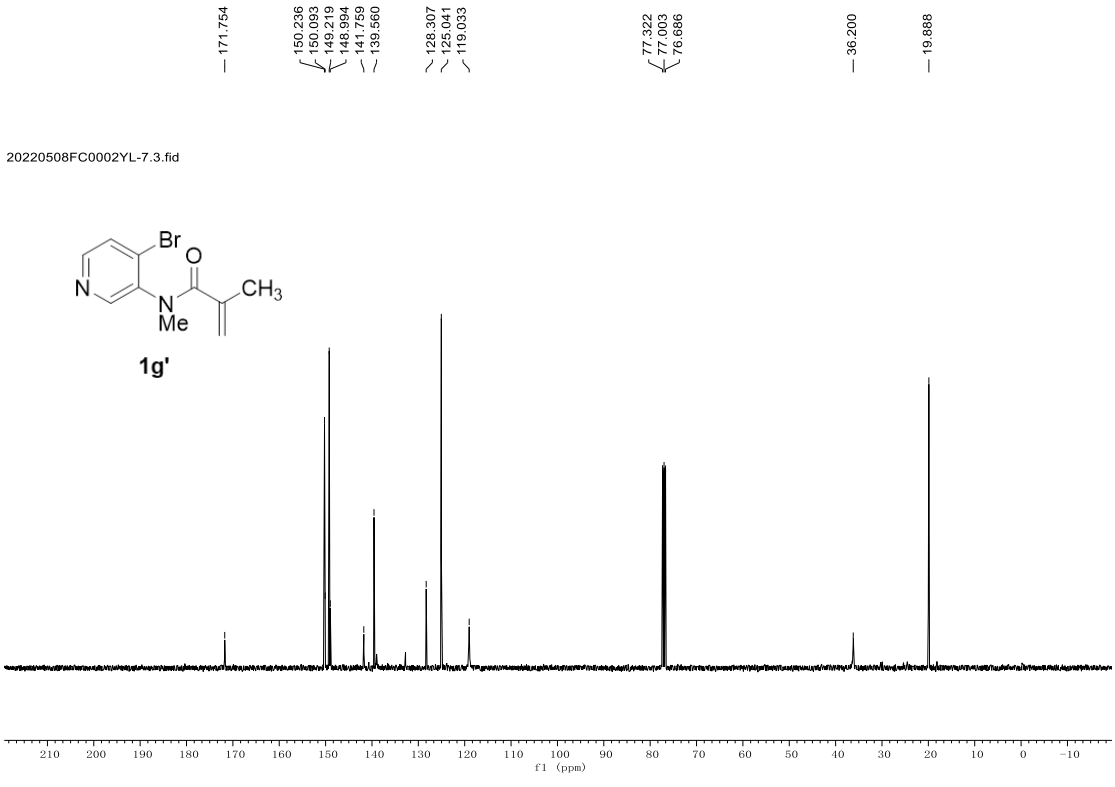
(**1f'**, ^{13}C NMR, $CDCl_3$, 101 MHz)



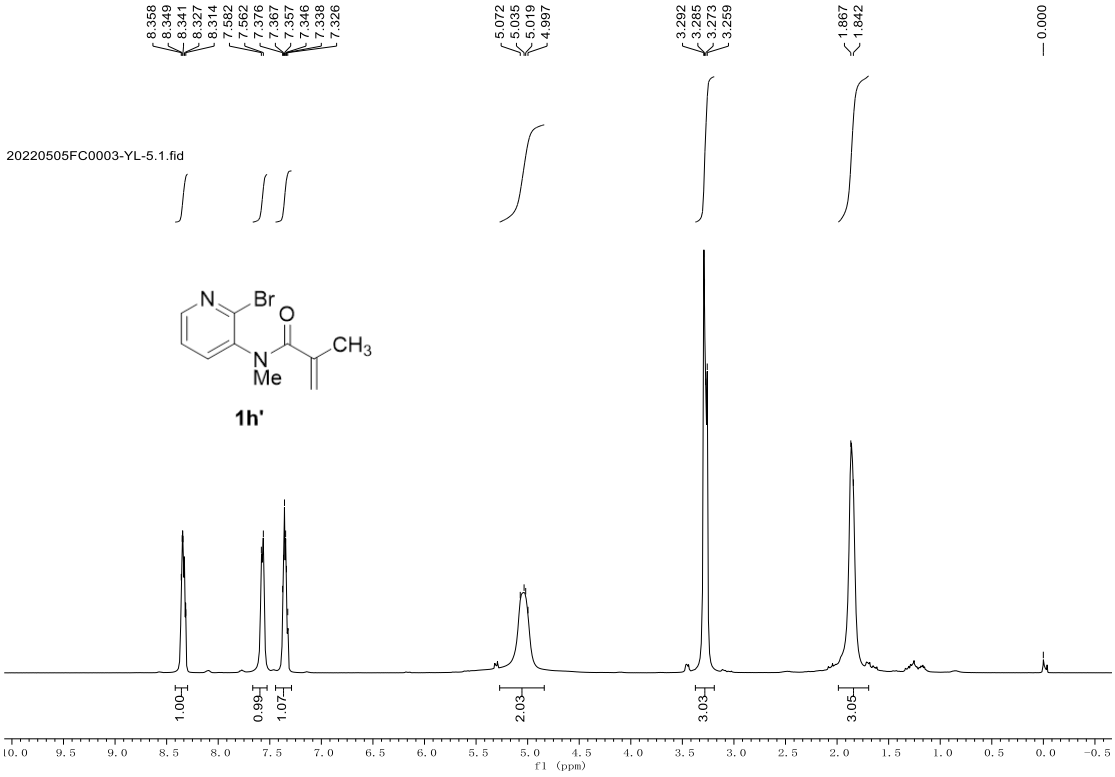
(**1g'**, ^{1}H NMR, $CDCl_3$, 400 MHz)



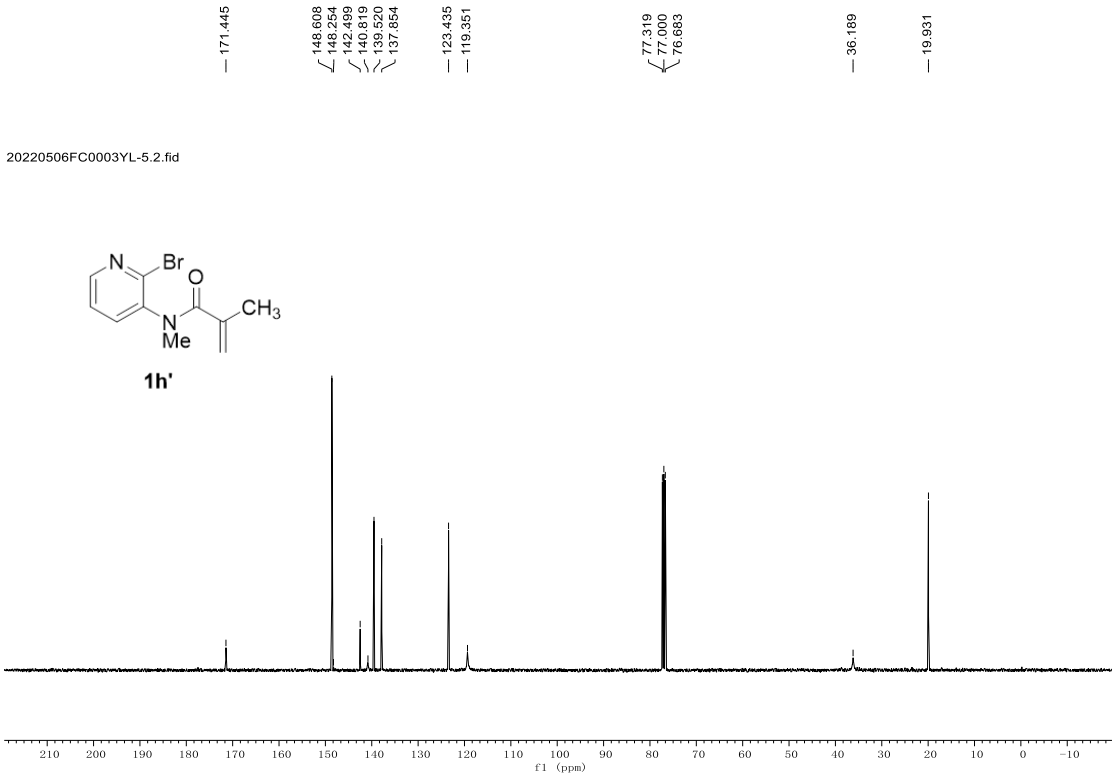
(**1g'**, ^{13}C NMR, $CDCl_3$, 101 MHz)



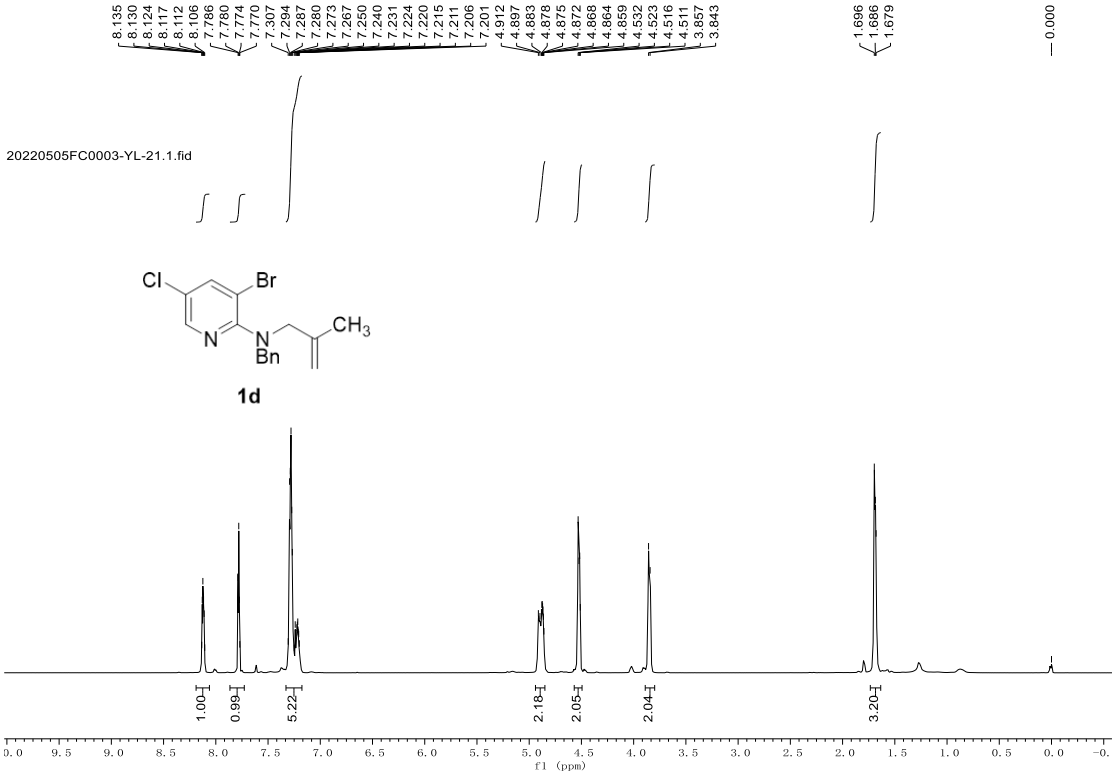
(**1h'**, ^{1}H NMR, $CDCl_3$, 400 MHz)



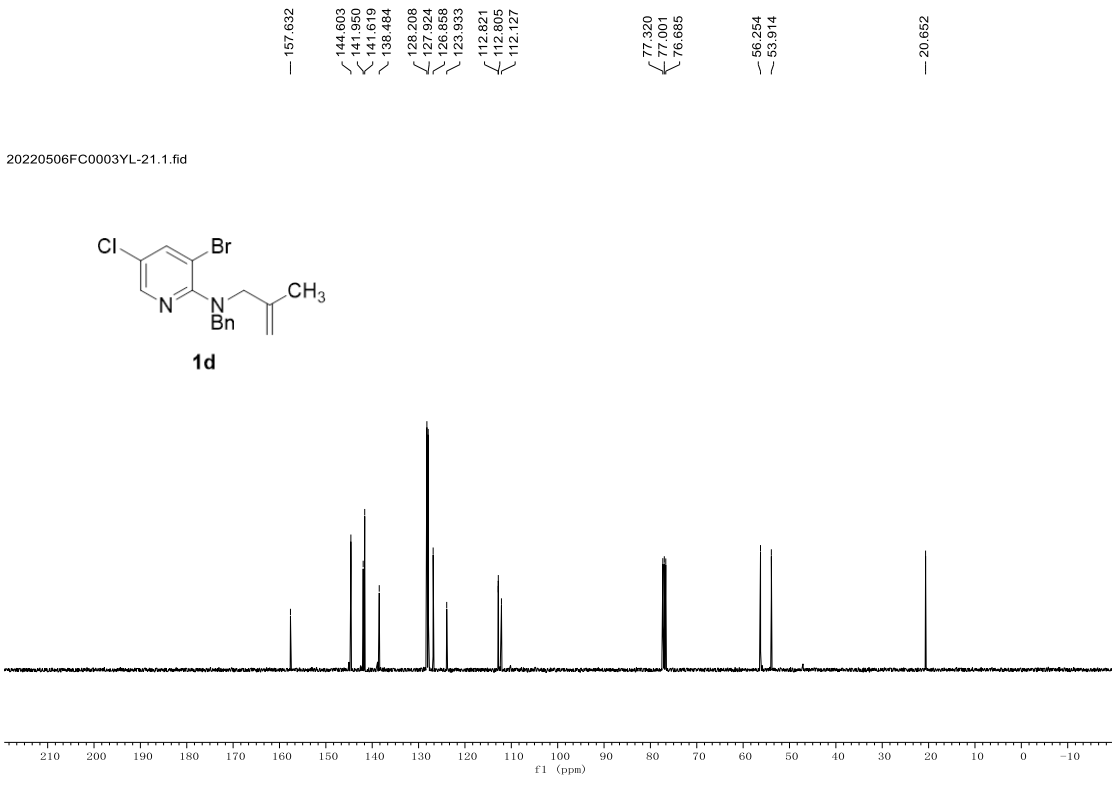
(**1h'**, ^{13}C NMR, $CDCl_3$, 101 MHz)



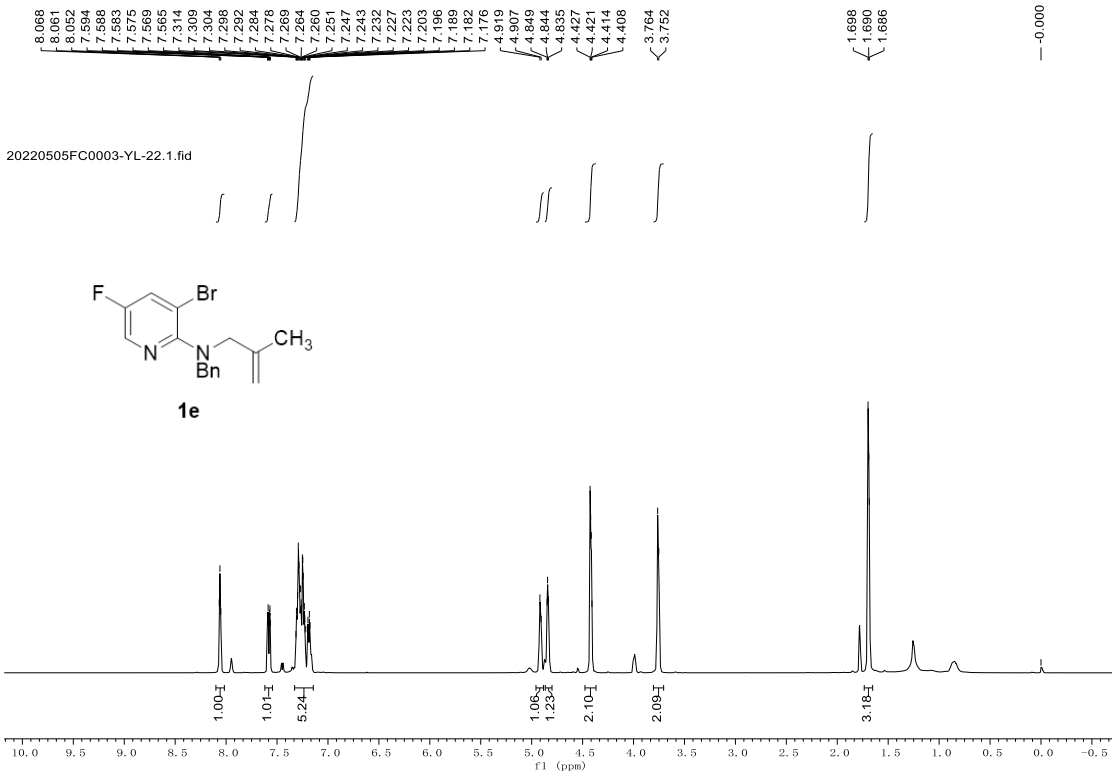
(**1d**, ^{1}H NMR, $CDCl_3$, 400 MHz)



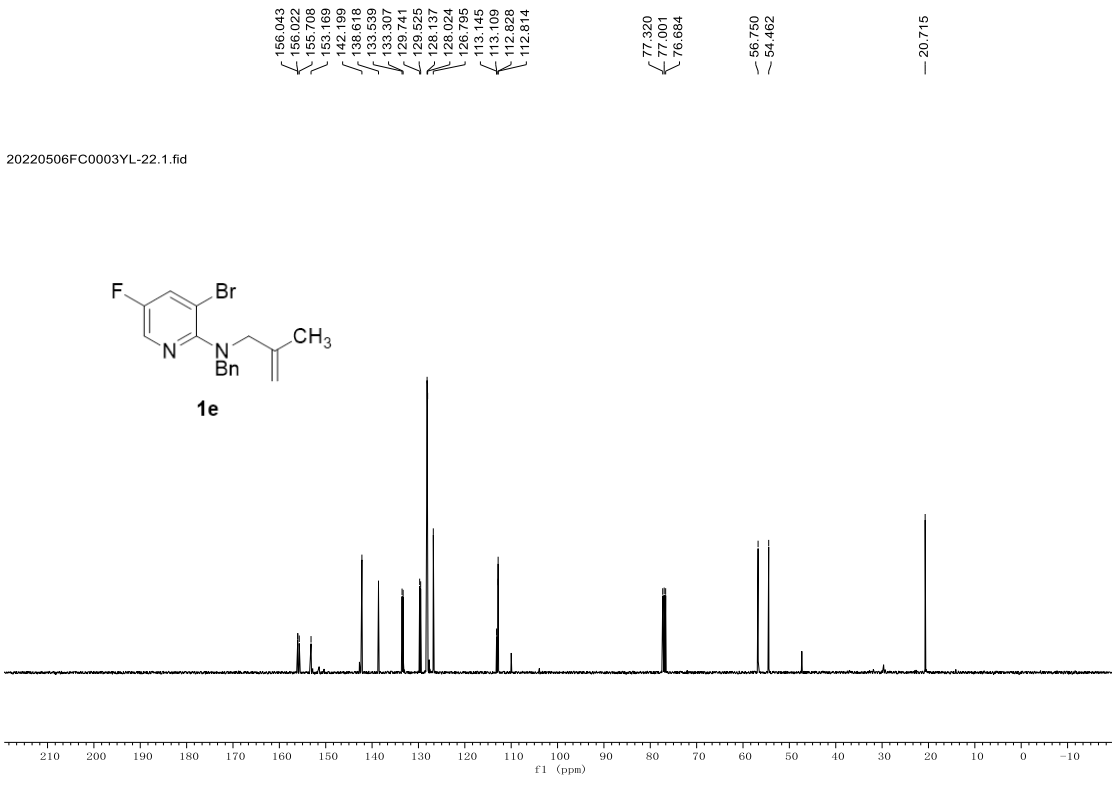
(**1d**, ^{13}C NMR, $CDCl_3$, 101 MHz)



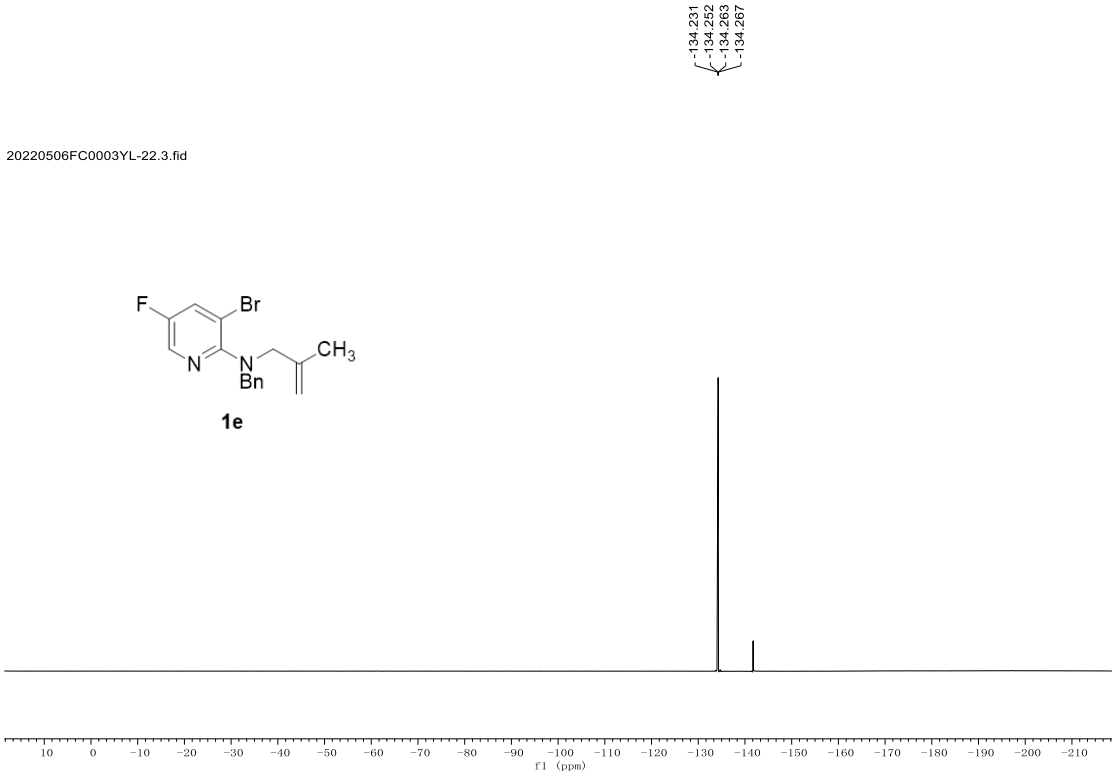
(**1e**, ^{1}H NMR, $CDCl_3$, 400 MHz)



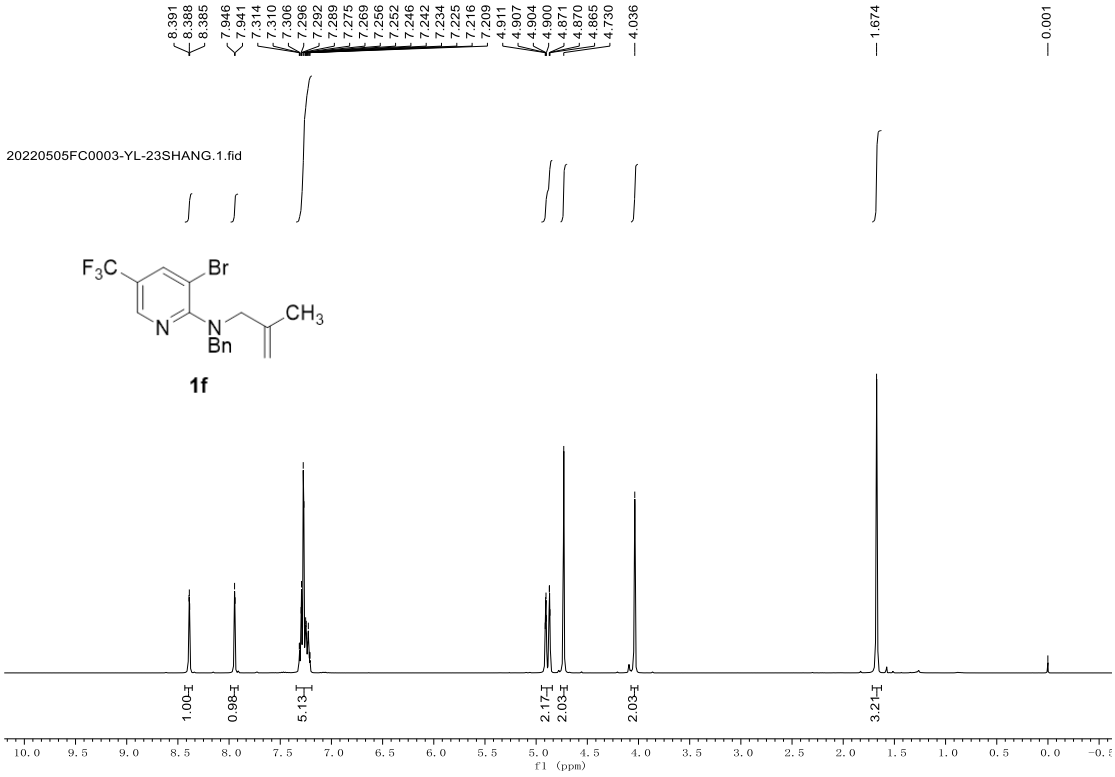
(**1e**, ^{13}C NMR, $CDCl_3$, 101 MHz)



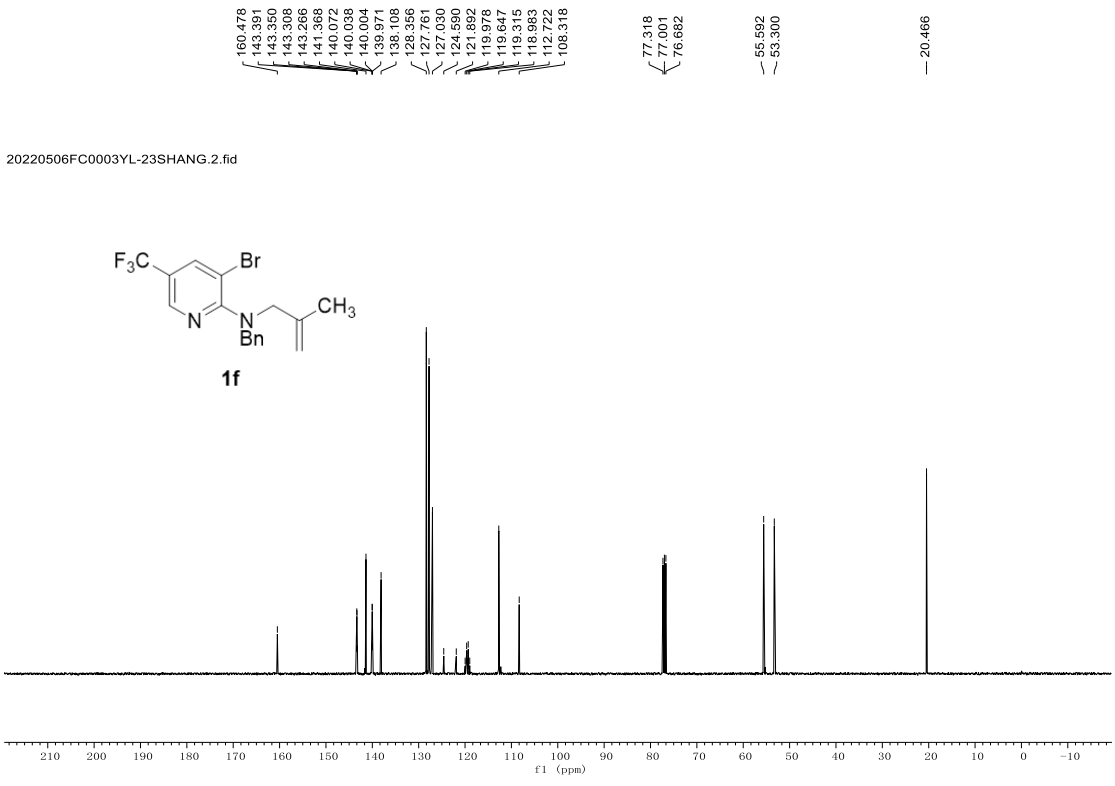
(**1e**, ^{19}F NMR, $CDCl_3$, 376 MHz)



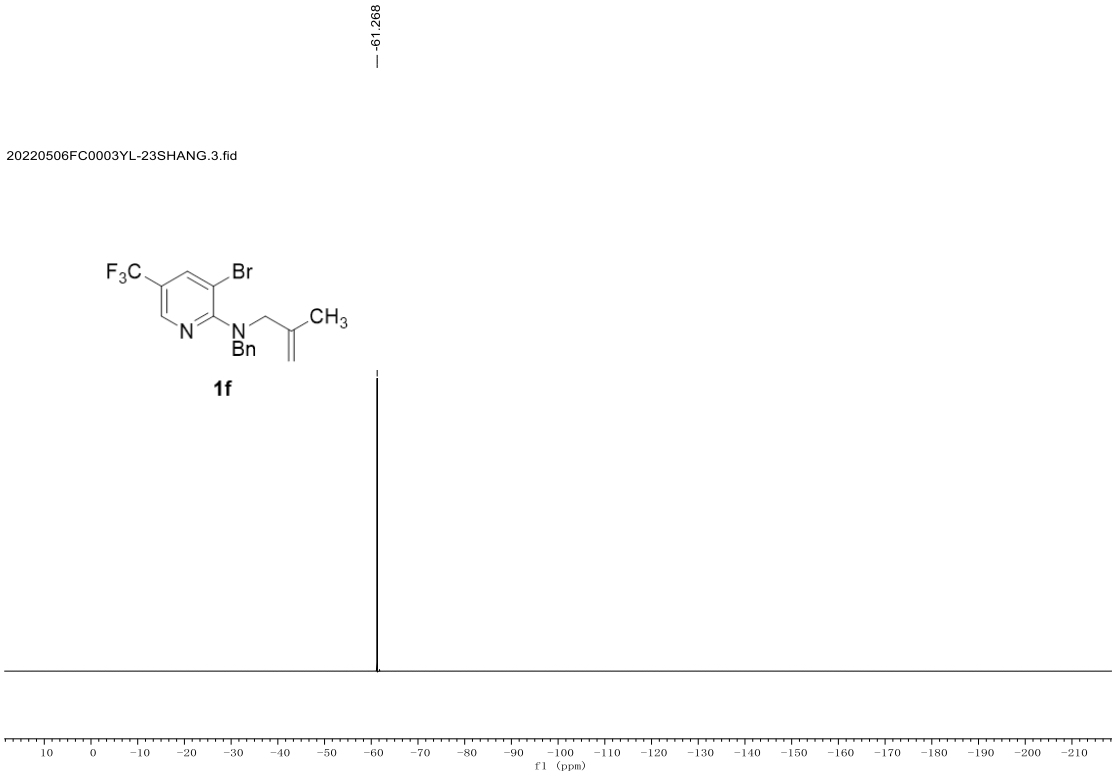
(**1f**, ^{1}H NMR, $CDCl_3$, 400 MHz)



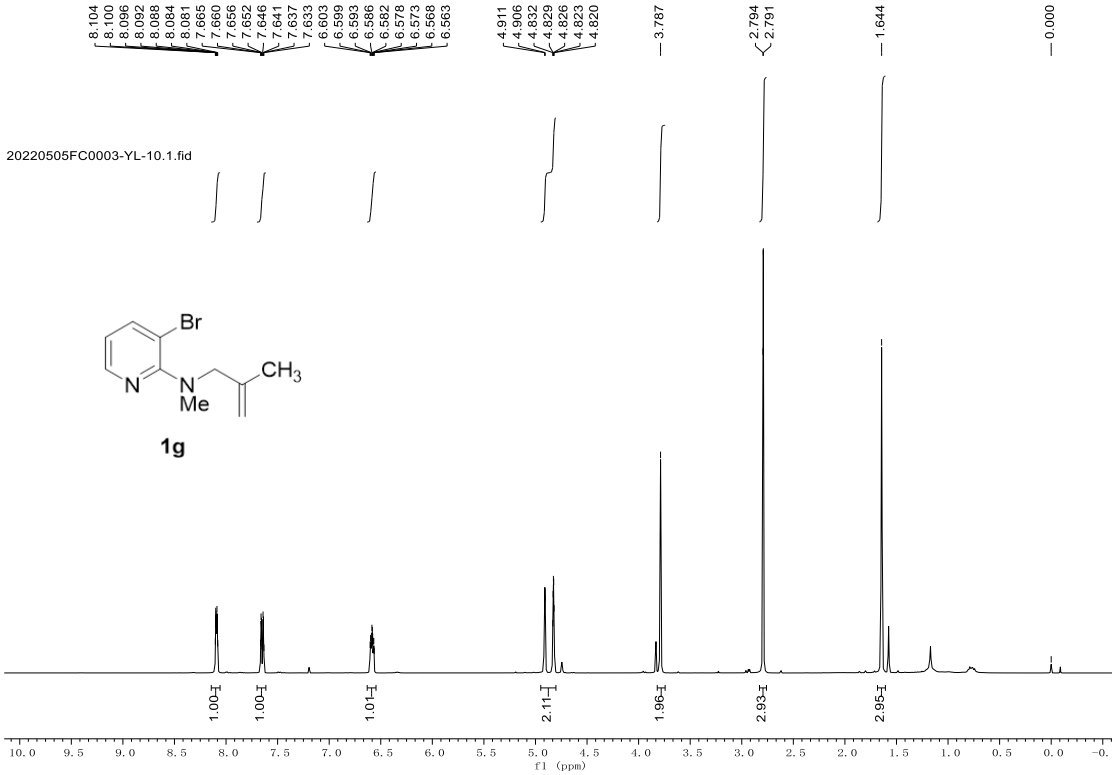
(**1f**, ^{13}C NMR, $CDCl_3$, 101 MHz)



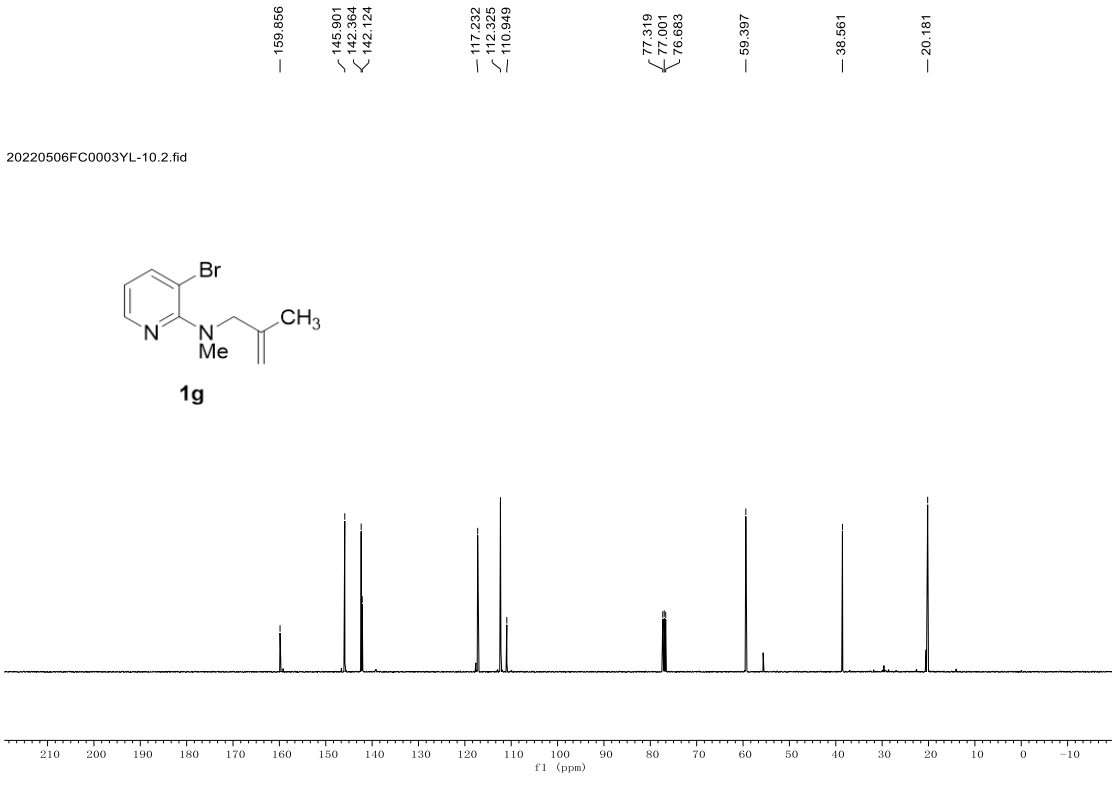
(**1f**, ^{19}F NMR, $CDCl_3$, 376 MHz)



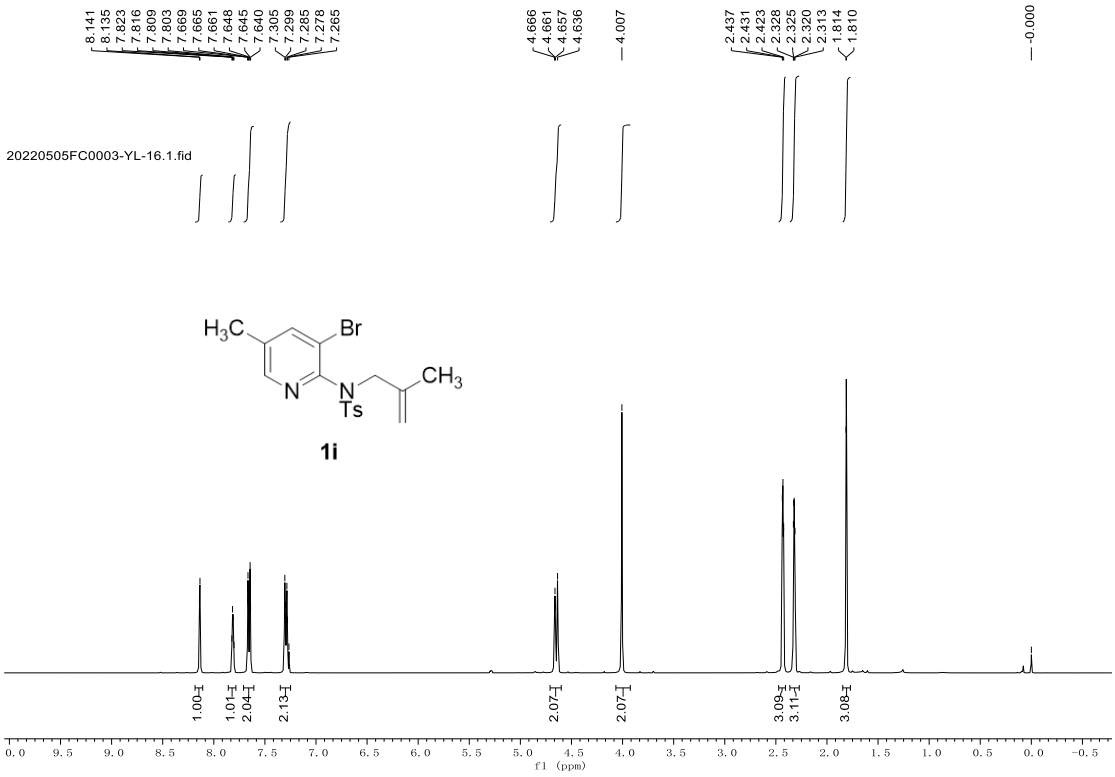
(**1g**, ^{1}H NMR, $CDCl_3$, 400 MHz)



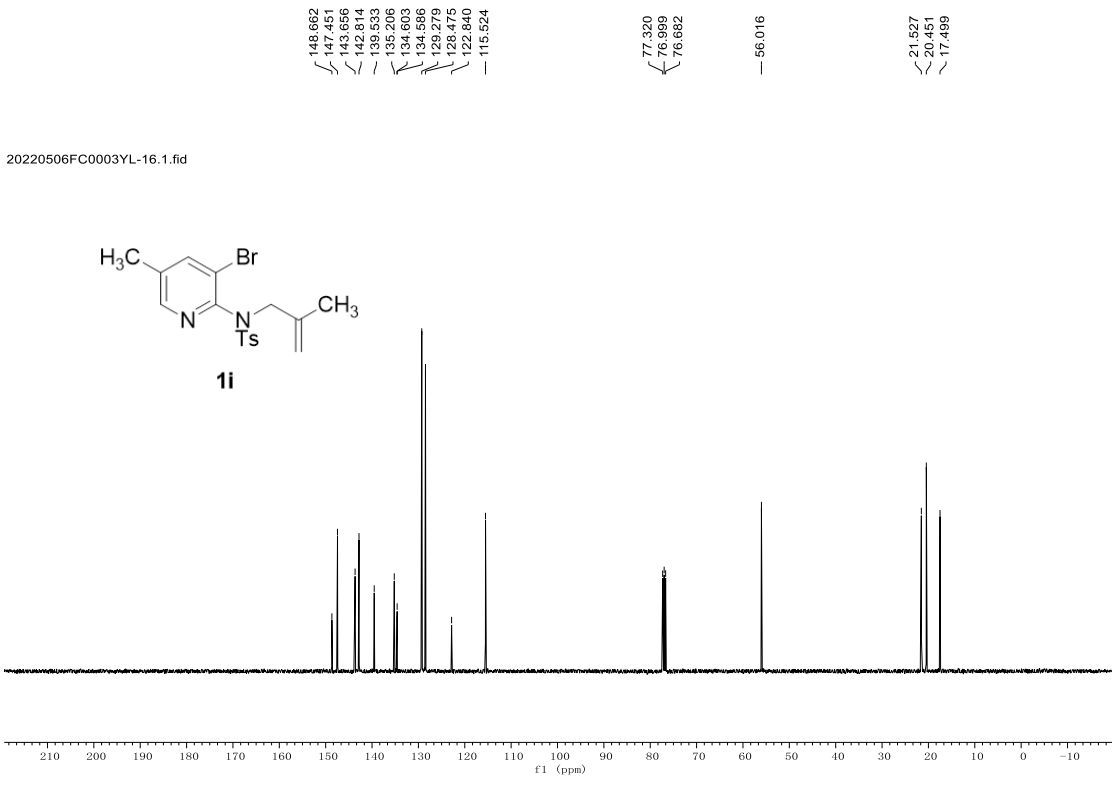
(**1g**, ^{13}C NMR, $CDCl_3$, 101 MHz)



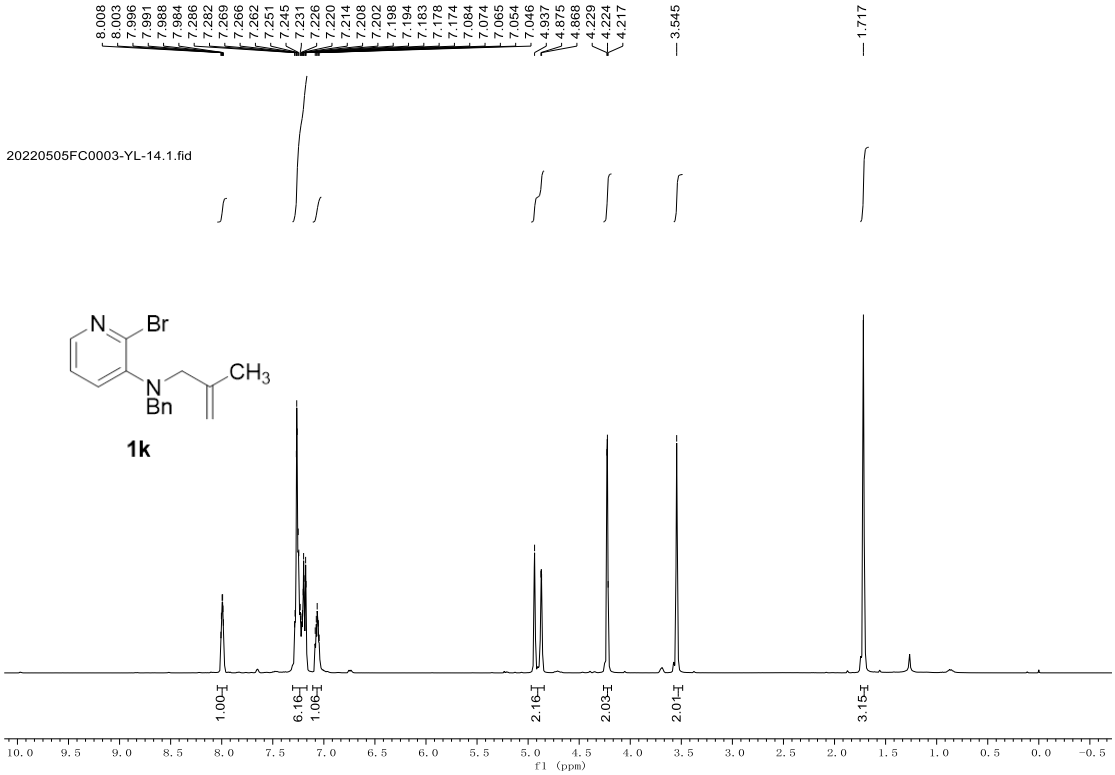
(**1i**, ^{1}H NMR, $CDCl_3$, 400 MHz)



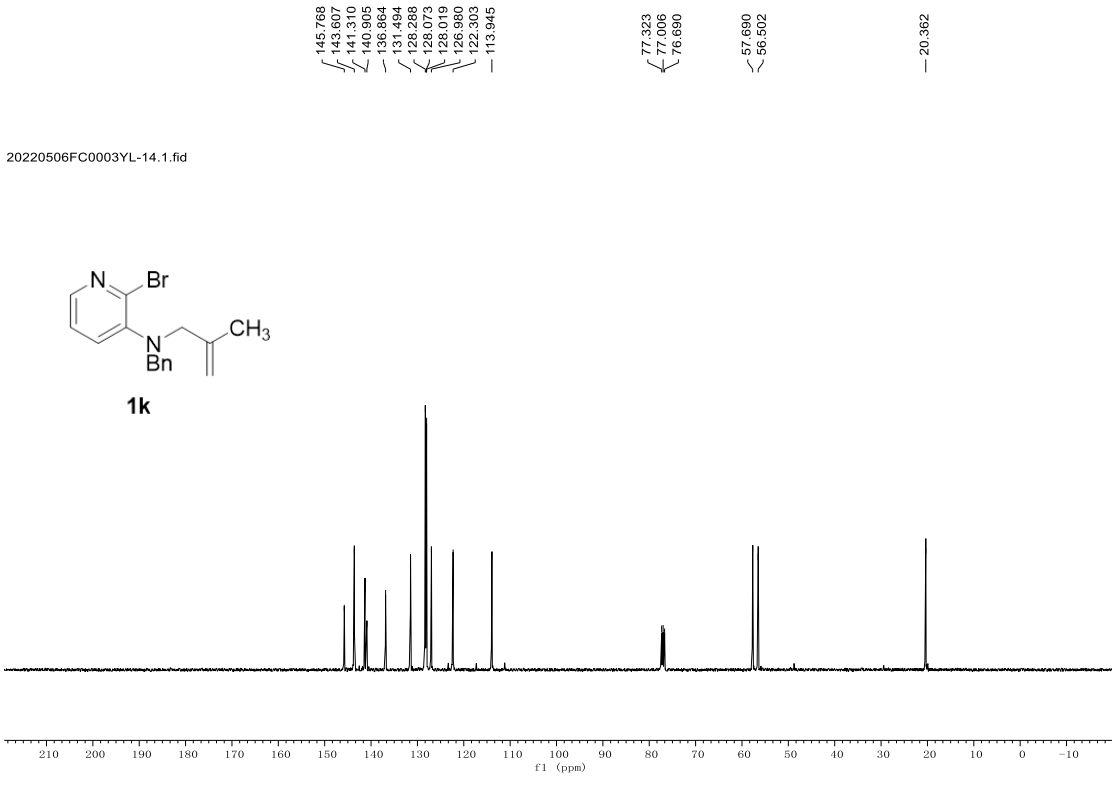
(**1i**, ^{13}C NMR, $CDCl_3$, 101 MHz)



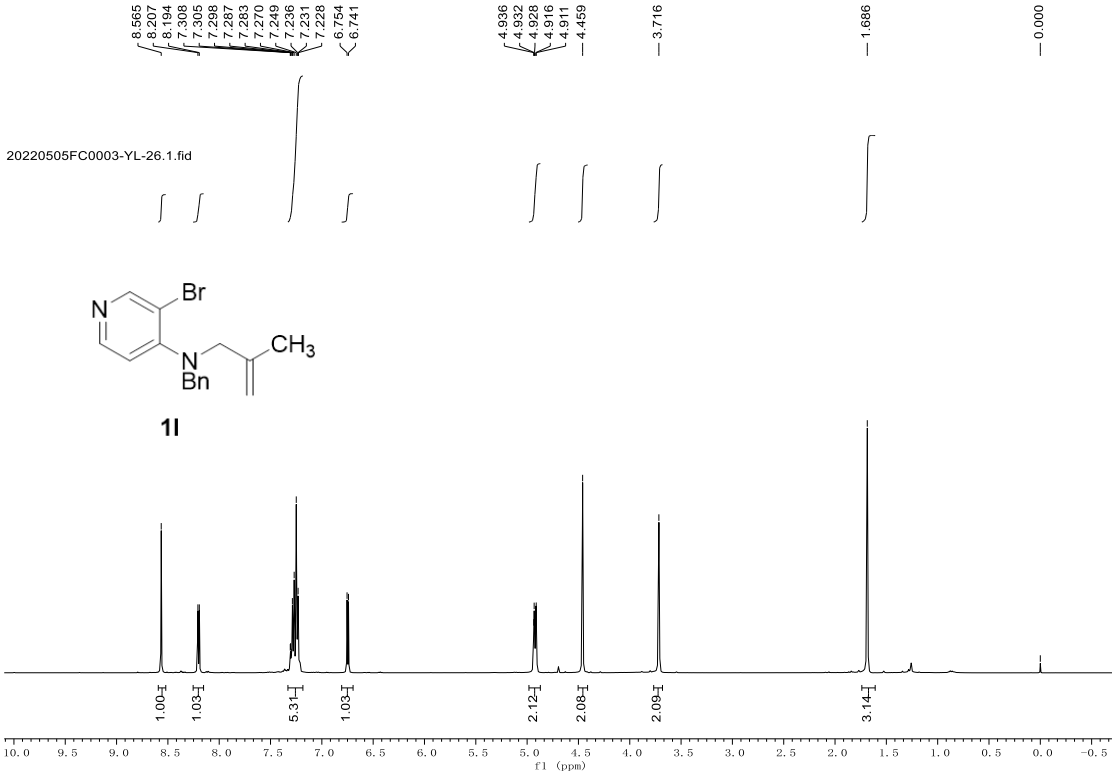
(**1k**, ^{1}H NMR, $CDCl_3$, 400 MHz)



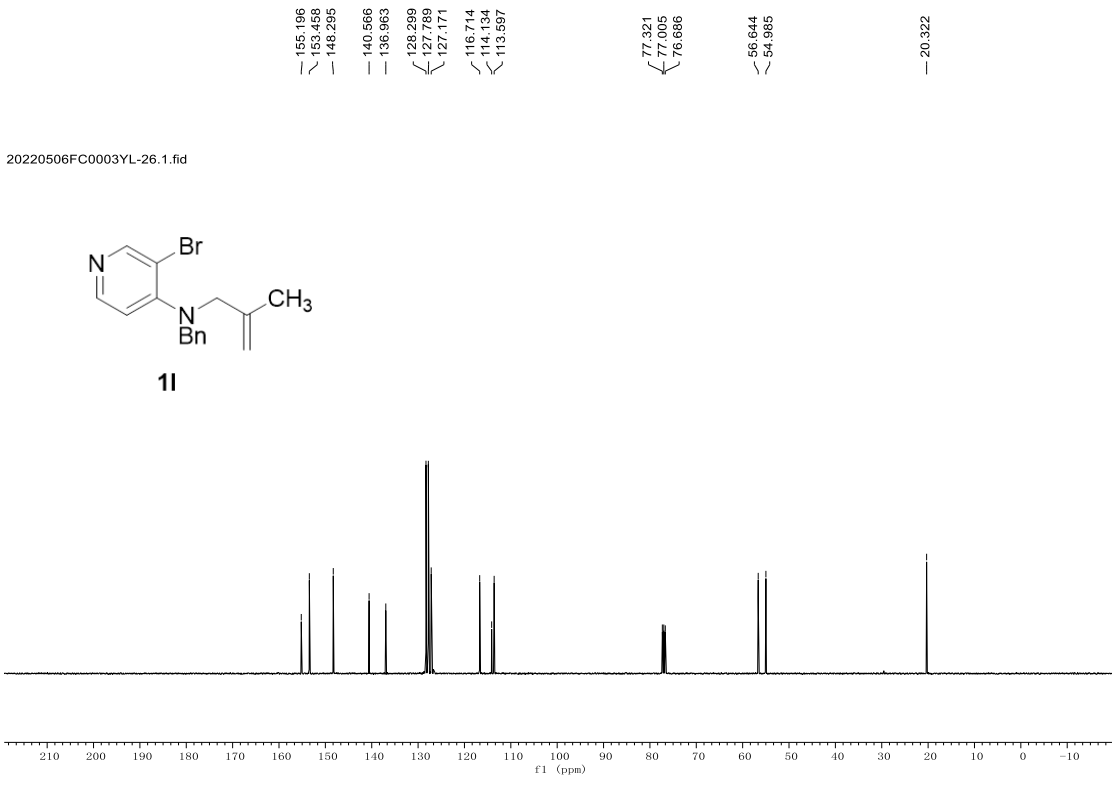
(**1k**, ^{13}C NMR, $CDCl_3$, 101 MHz)



(**1l**, ^{1}H NMR, $CDCl_3$, 400 MHz)

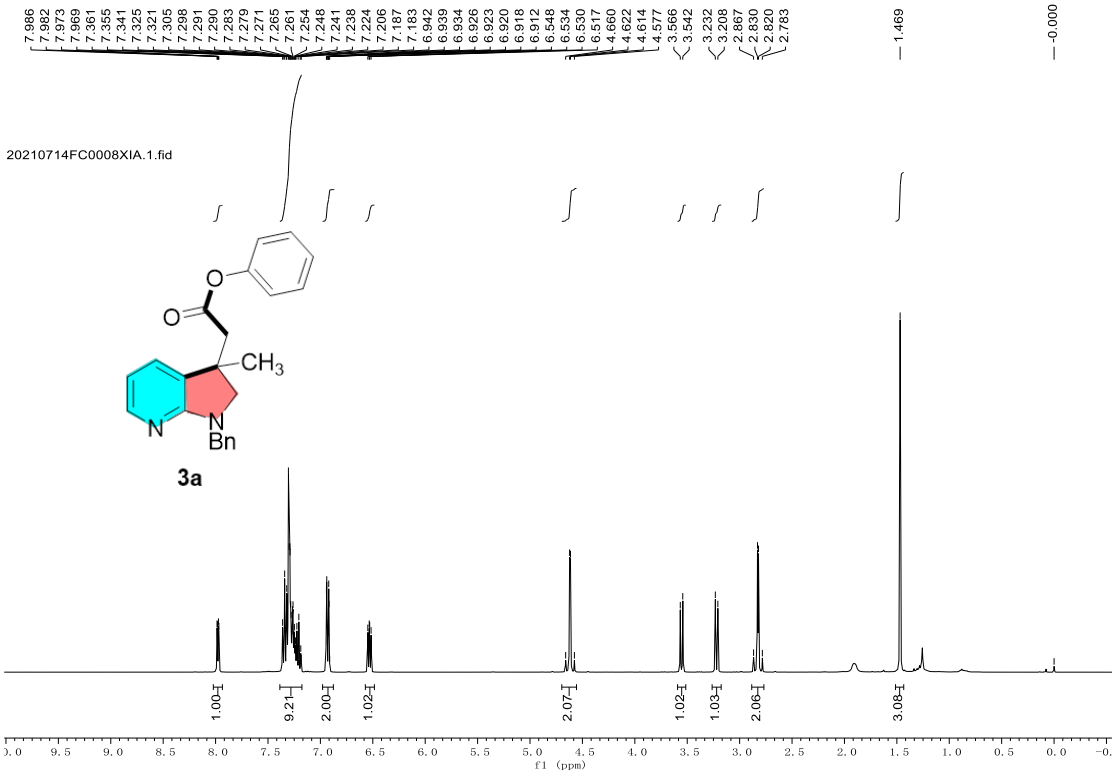


(**1l**, ^{13}C NMR, $CDCl_3$, 101 MHz)

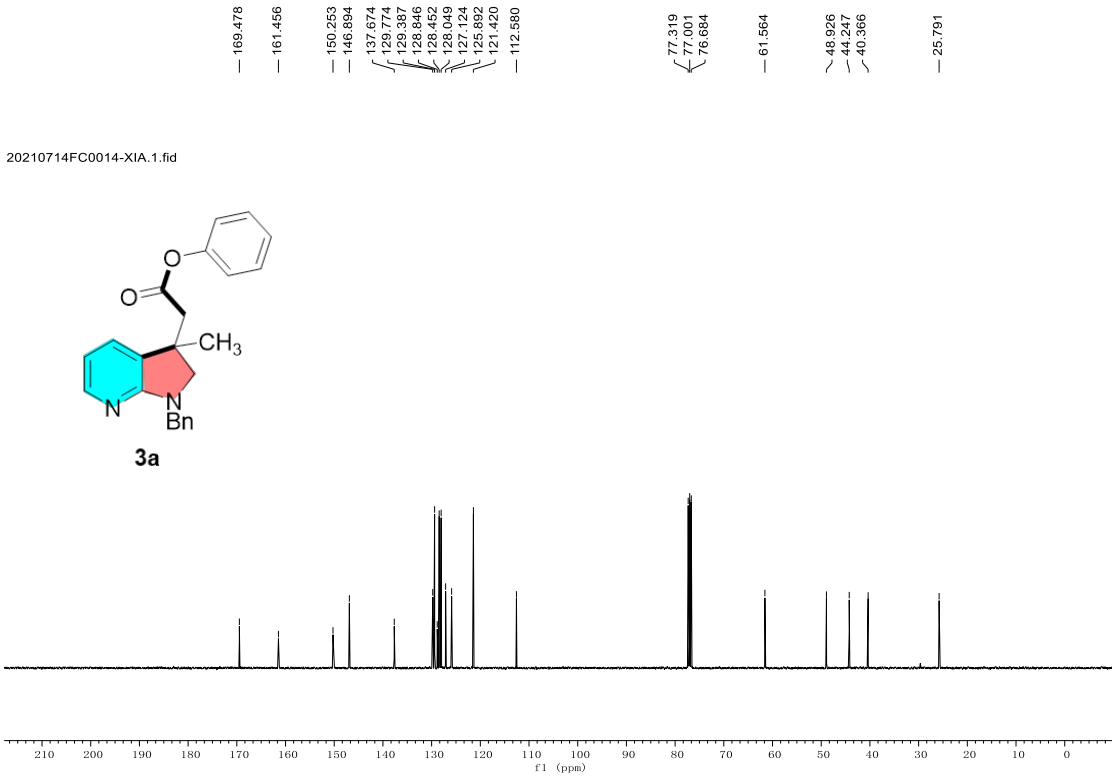


10. NMR spectra of products

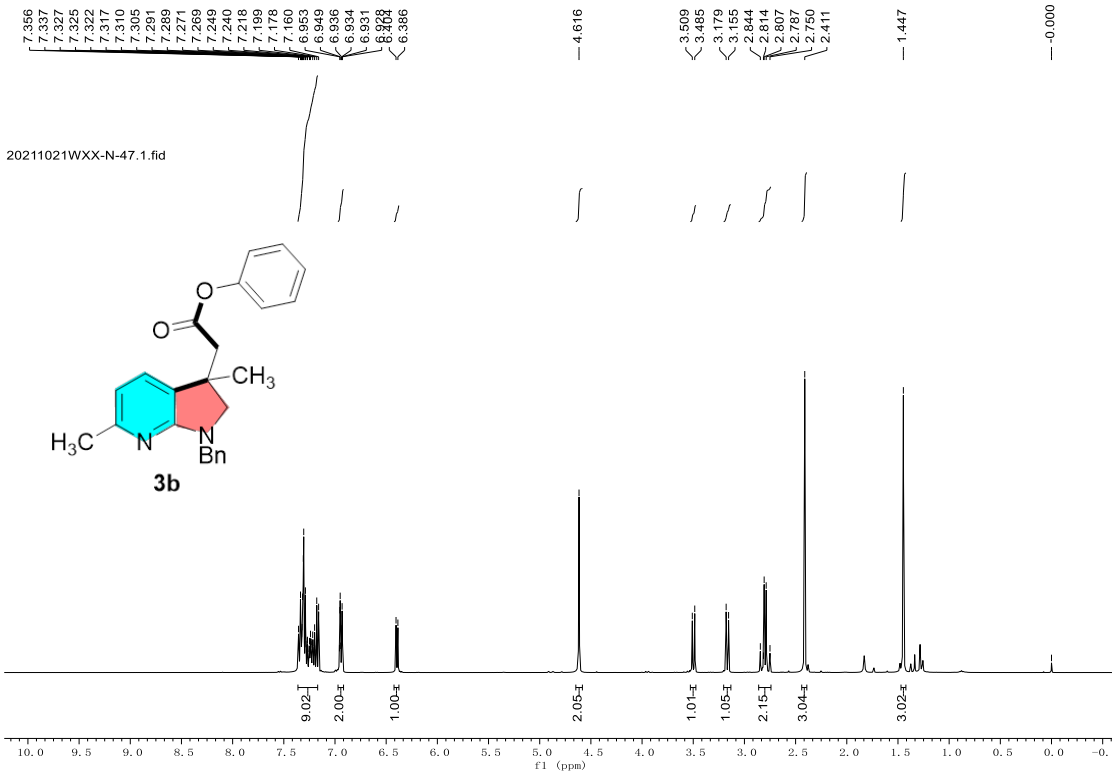
(**3a**, ^{1}H NMR, $CDCl_3$, 400 MHz)



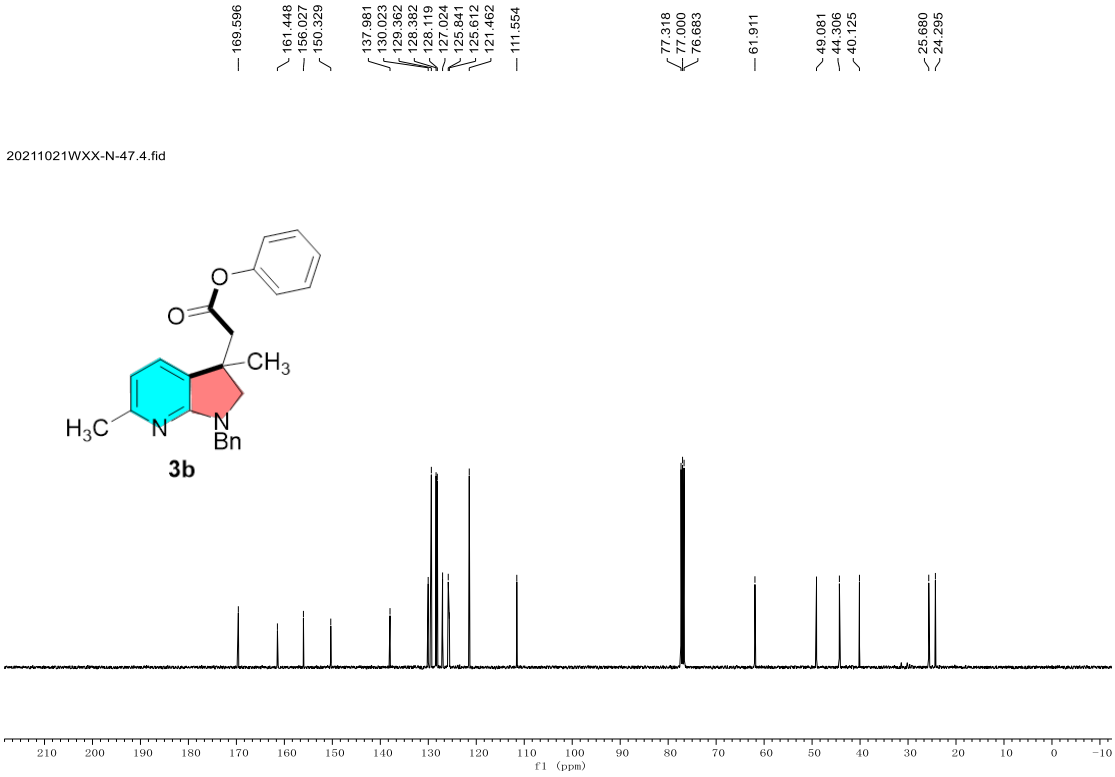
(**3a**, ^{13}C NMR, $CDCl_3$, 101 MHz)



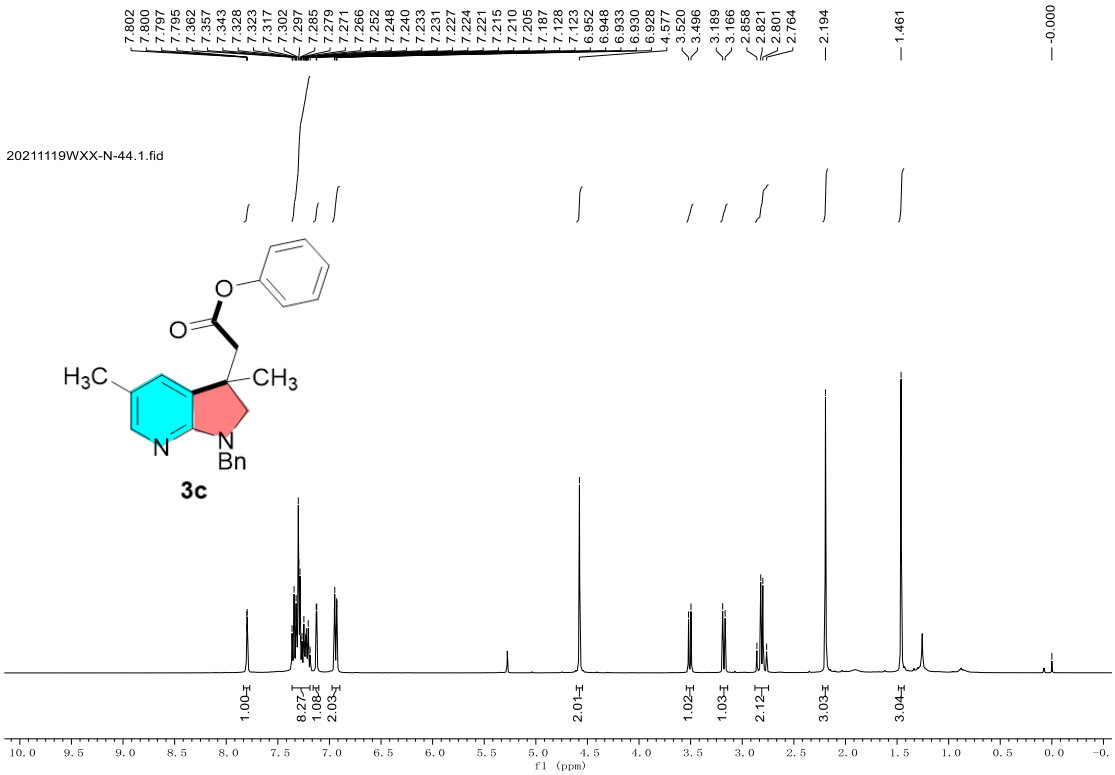
(**3b**, ^{1}H NMR, $CDCl_3$, 400 MHz)



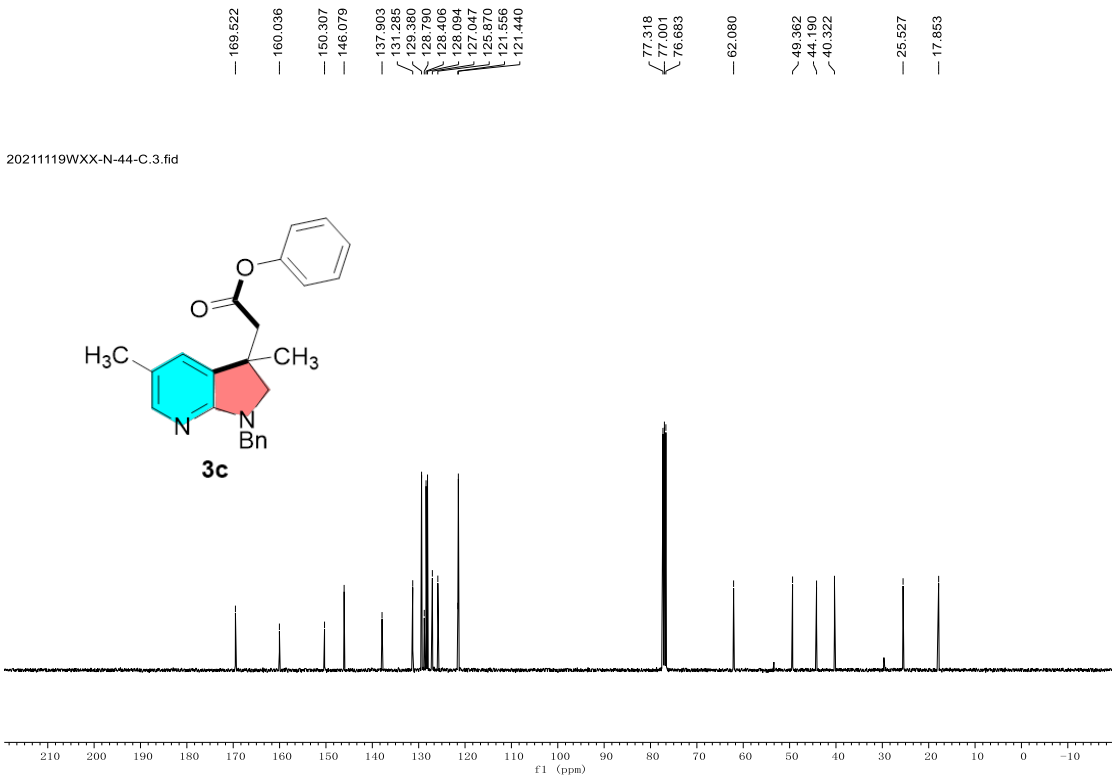
(**3b**, ^{13}C NMR, $CDCl_3$, 101 MHz)



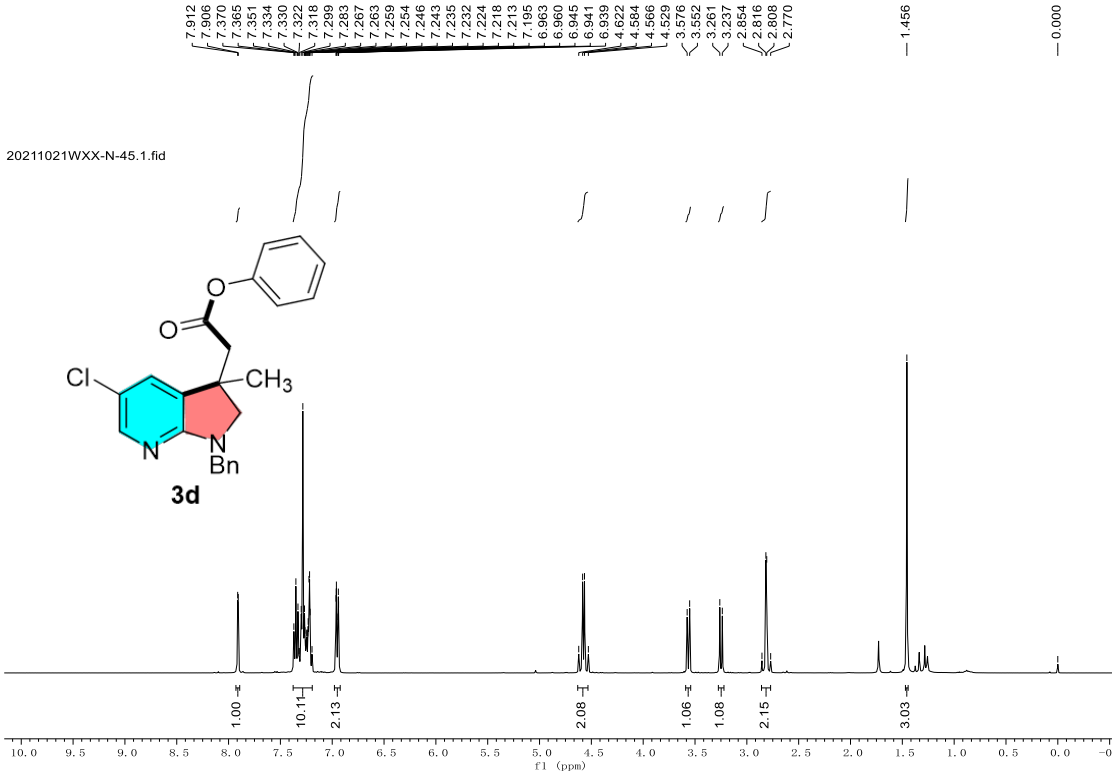
(**3c**, ^{1}H NMR, $CDCl_3$, 400 MHz)



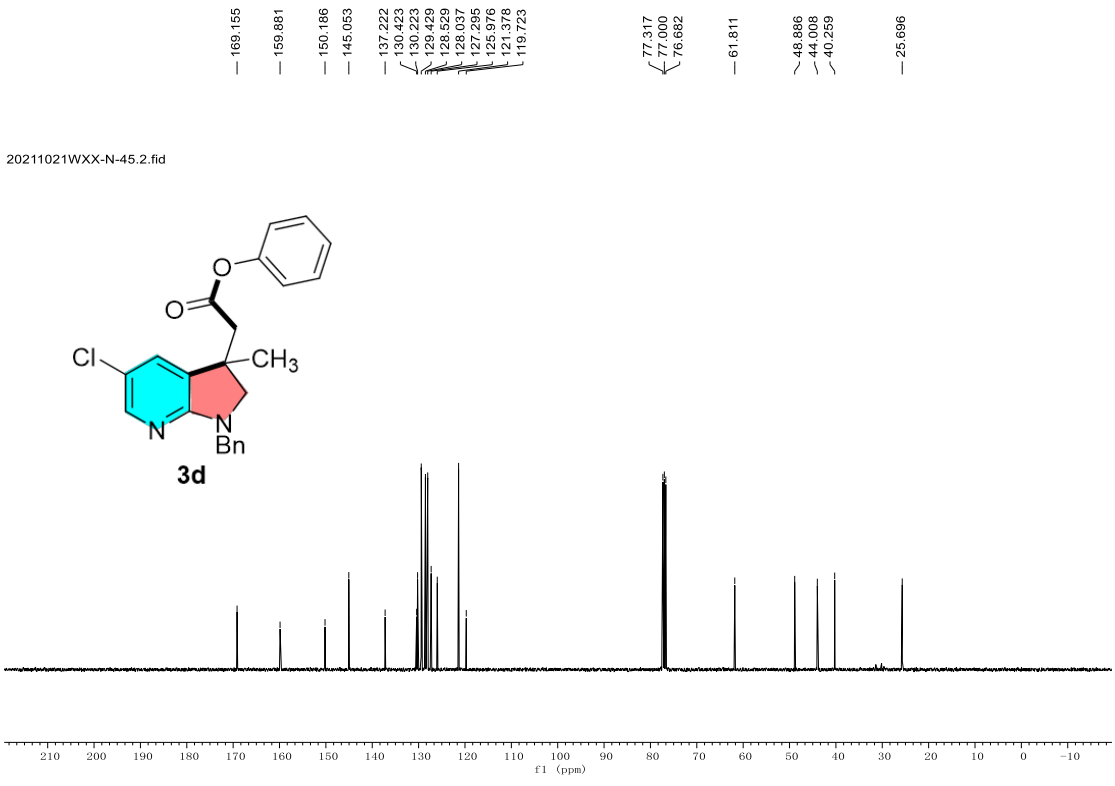
(**3c**, ^{13}C NMR, $CDCl_3$, 101 MHz)



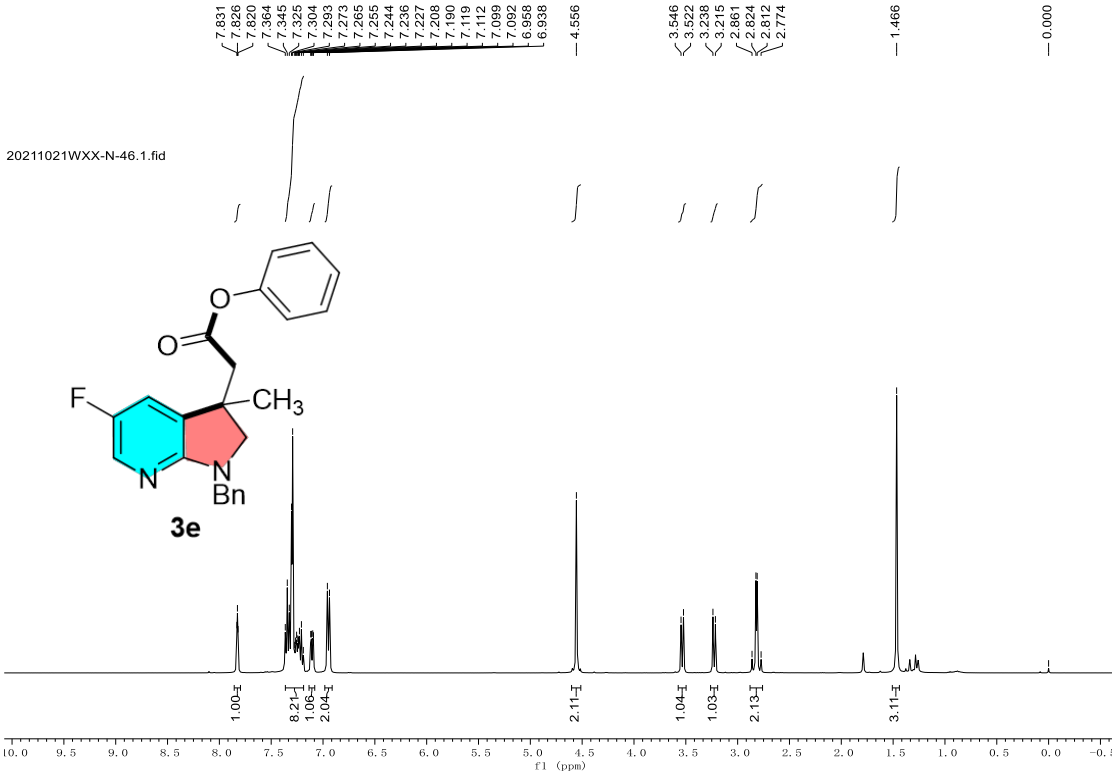
(**3d**, ^{1}H NMR, $CDCl_3$, 400 MHz)



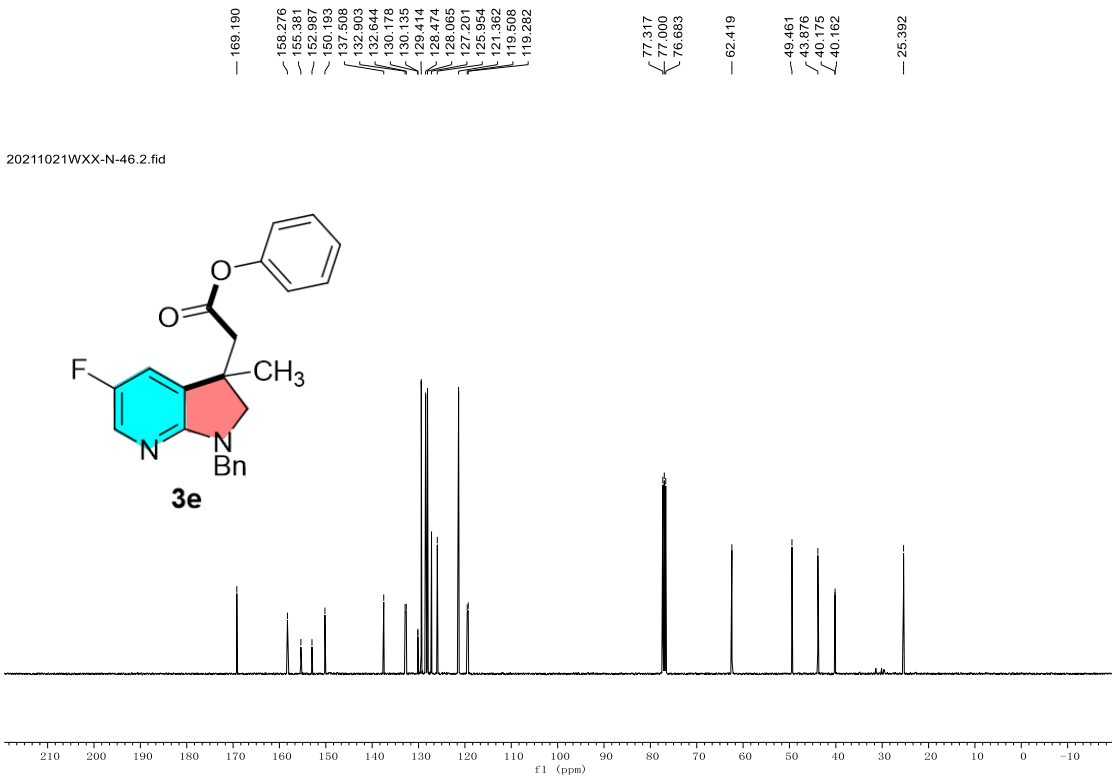
(**3d**, ^{13}C NMR, $CDCl_3$, 101 MHz)



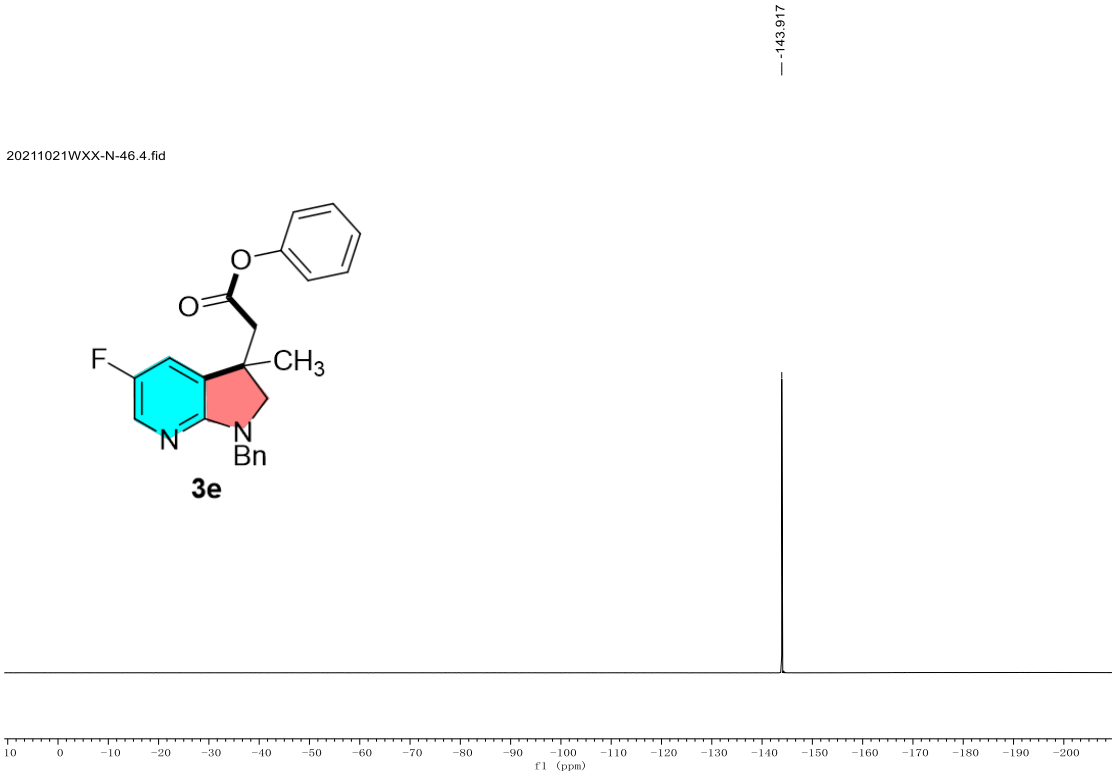
(**3e**, ^{1}H NMR, $CDCl_3$, 400 MHz)



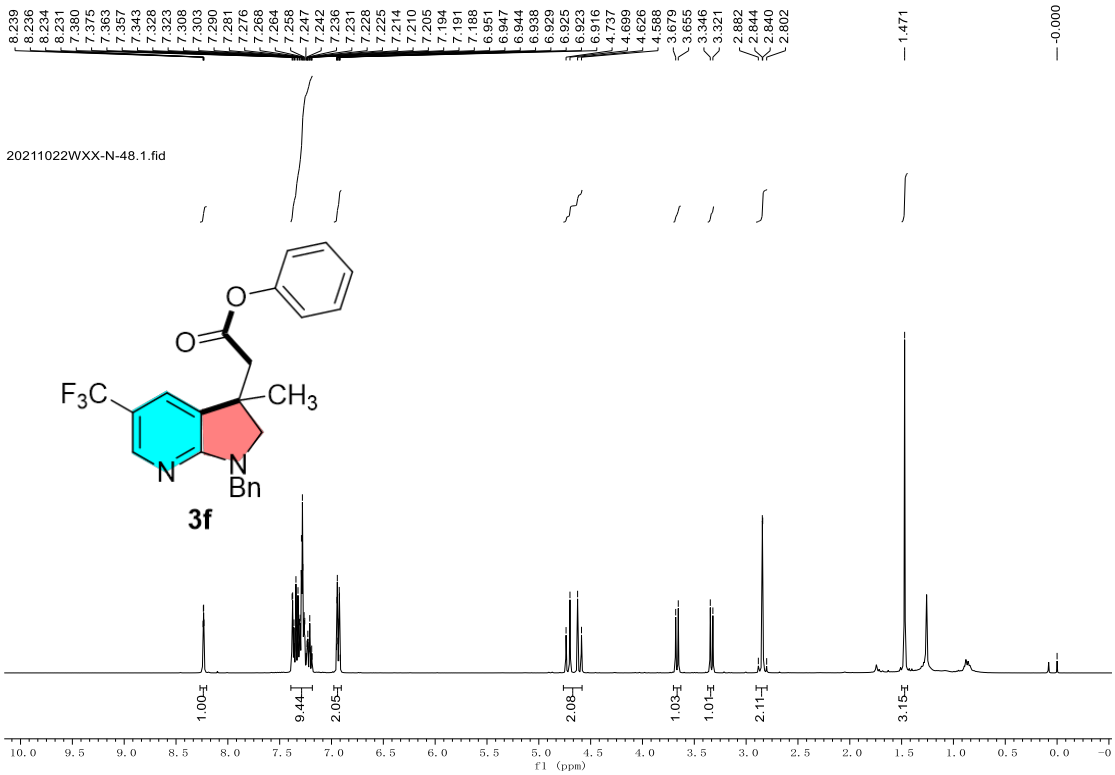
(**3e**, ^{13}C NMR, $CDCl_3$, 101 MHz)



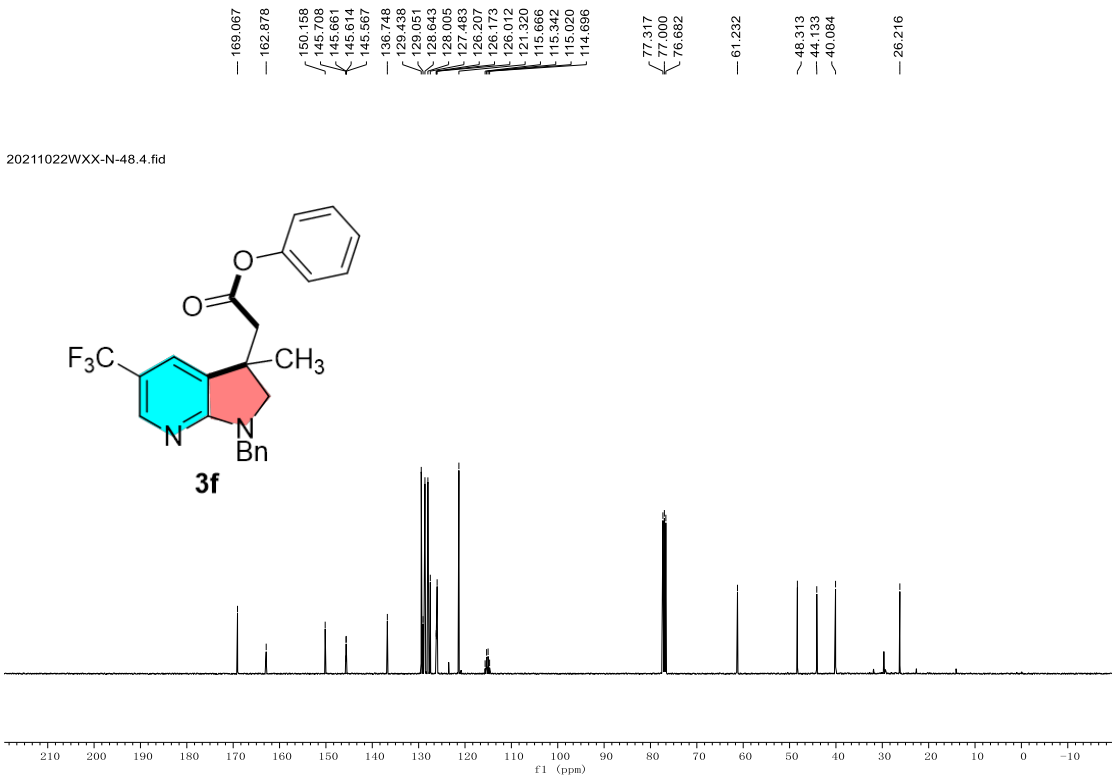
(**3e**, ^{19}F NMR, $CDCl_3$, 376 MHz)



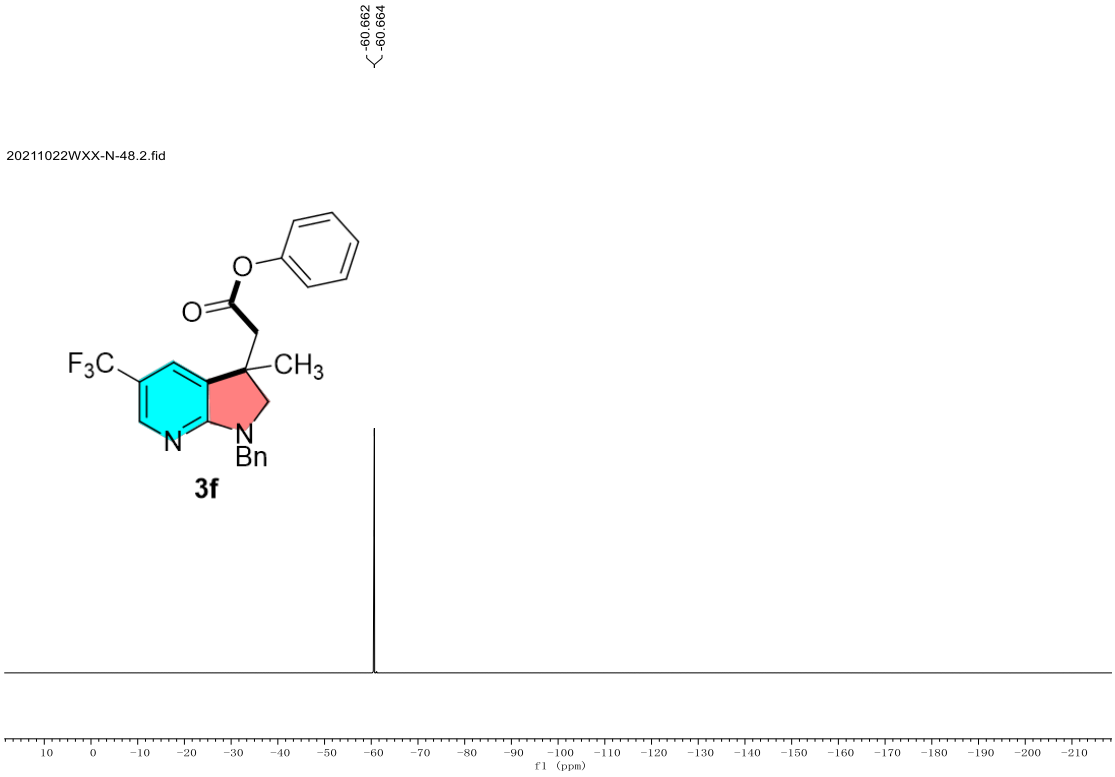
(**3f**, ^{1}H NMR, $CDCl_3$, 400 MHz)



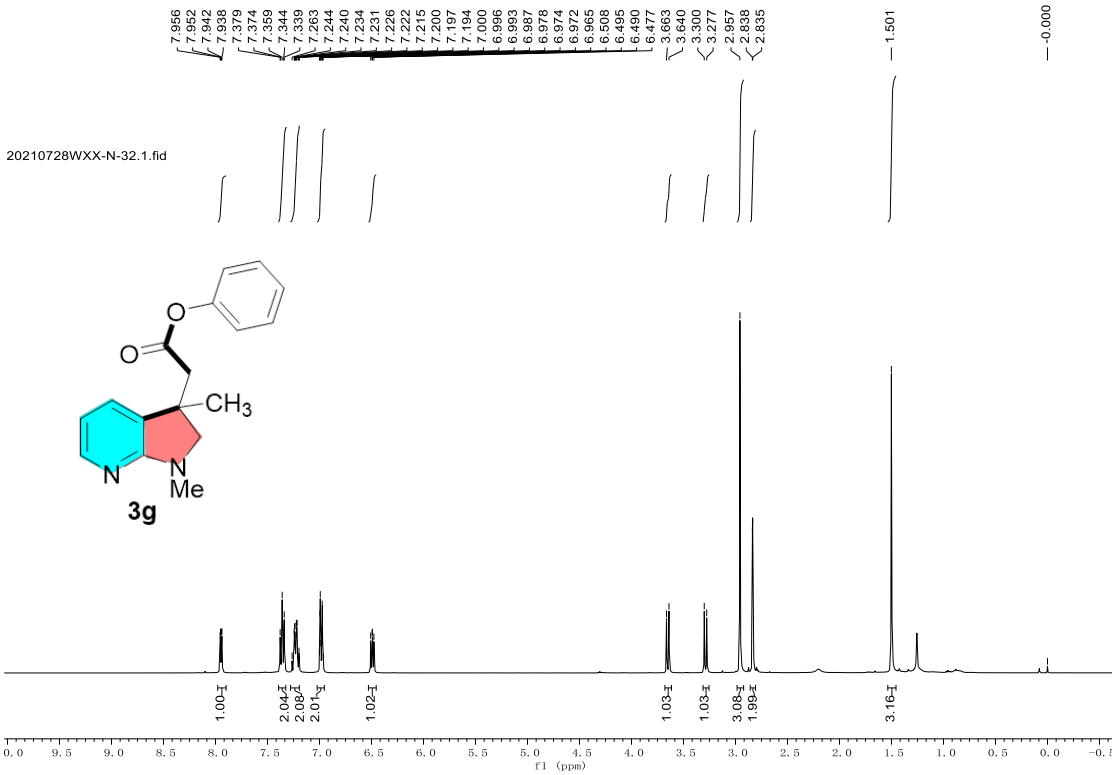
(**3f**, ^{13}C NMR, $CDCl_3$, 101 MHz)



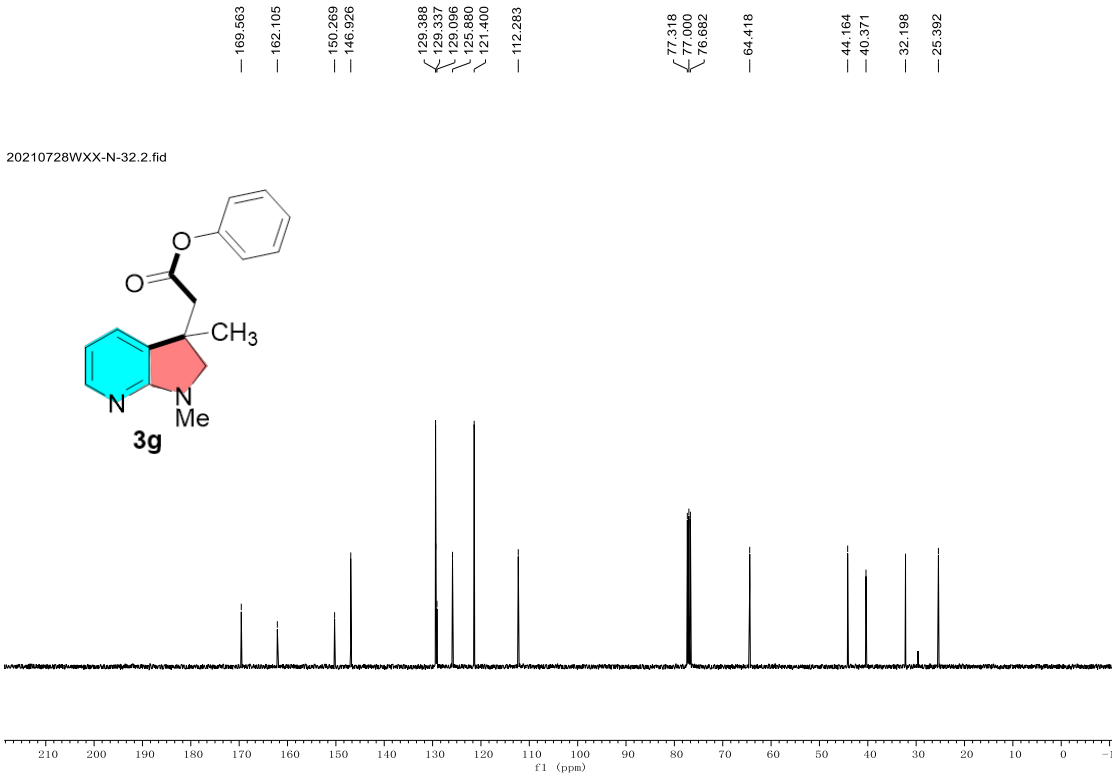
(**3f**, ^{19}F NMR, $CDCl_3$, 376 MHz)



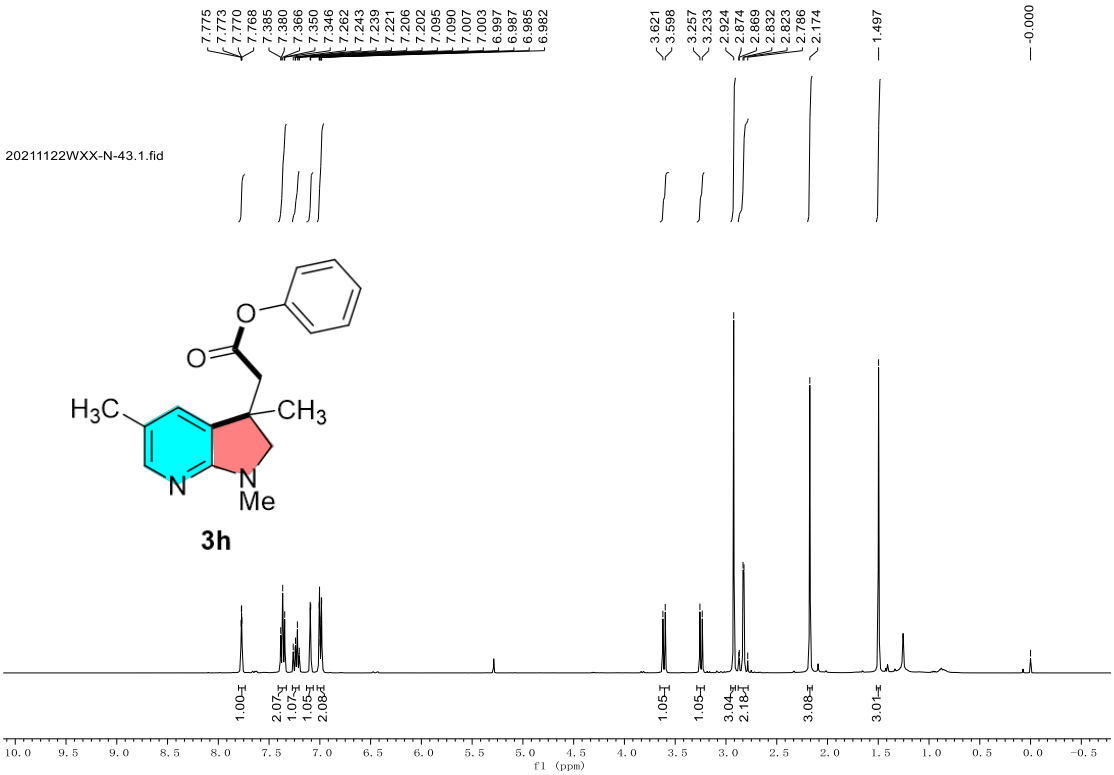
(**3g**, ^{1}H NMR, $CDCl_3$, 400 MHz)



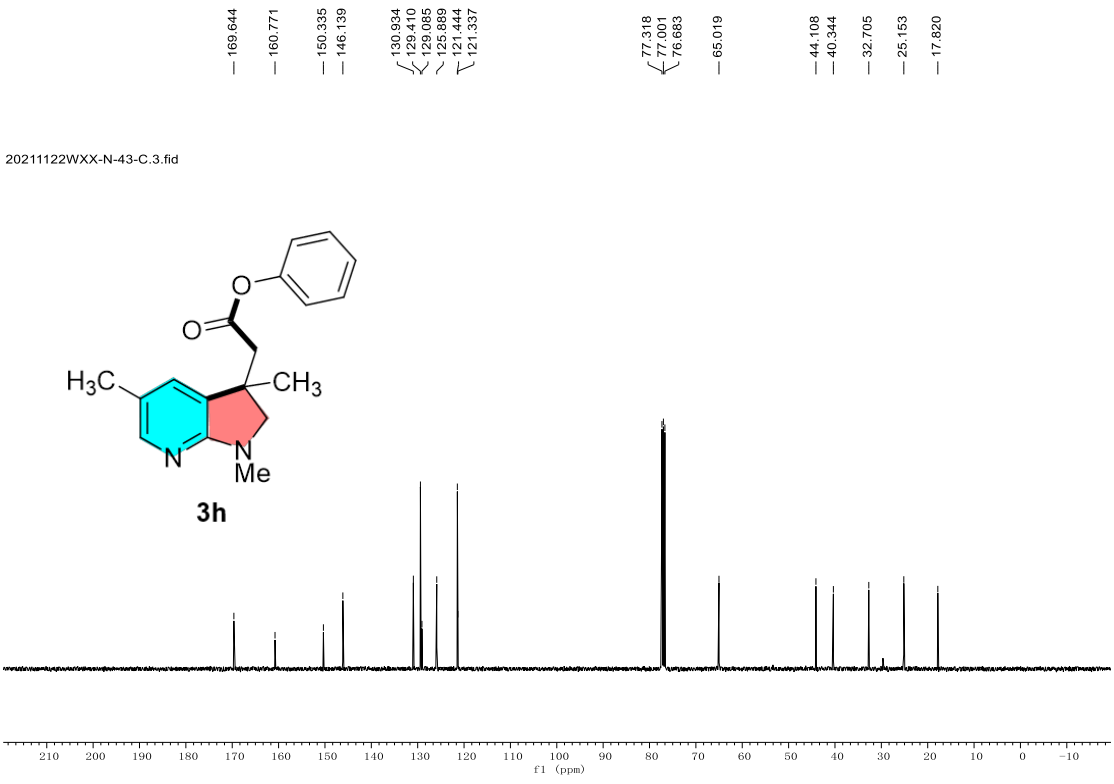
(**3g**, ^{13}C NMR, $CDCl_3$, 101 MHz)



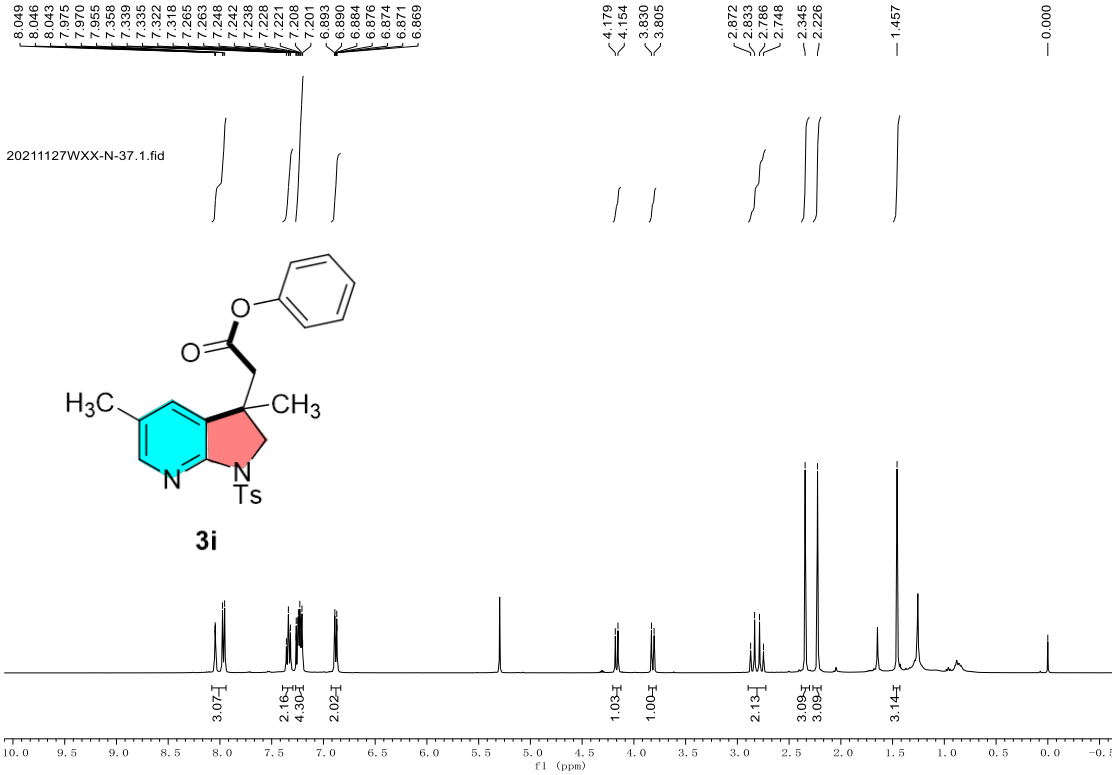
(**3h**, ^{1}H NMR, $CDCl_3$, 400 MHz)



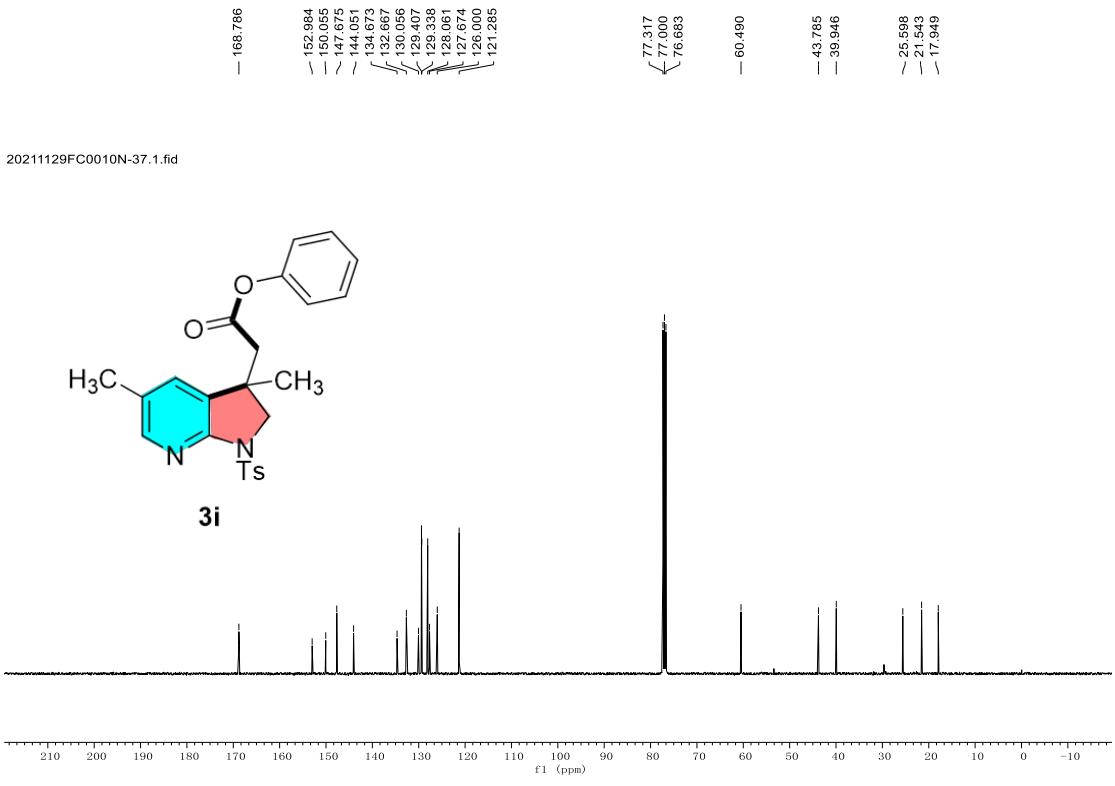
(**3h**, ^{13}C NMR, $CDCl_3$, 101 MHz)



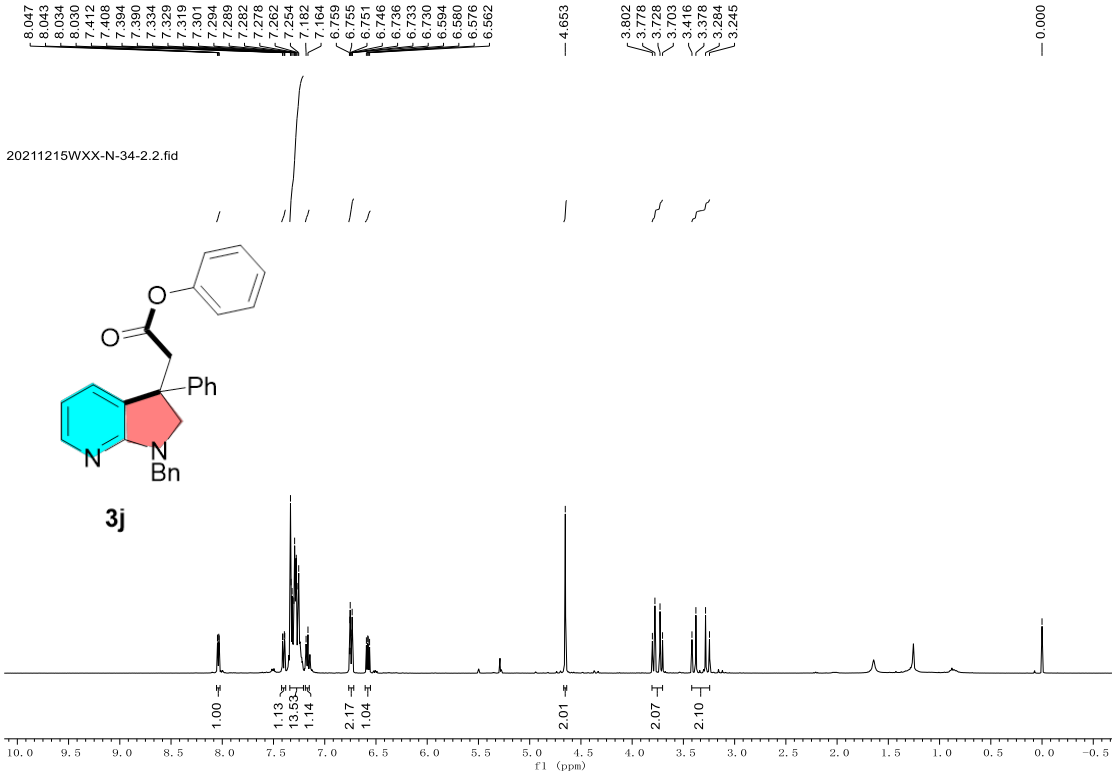
(**3i**, ^{1}H NMR, $CDCl_3$, 400 MHz)



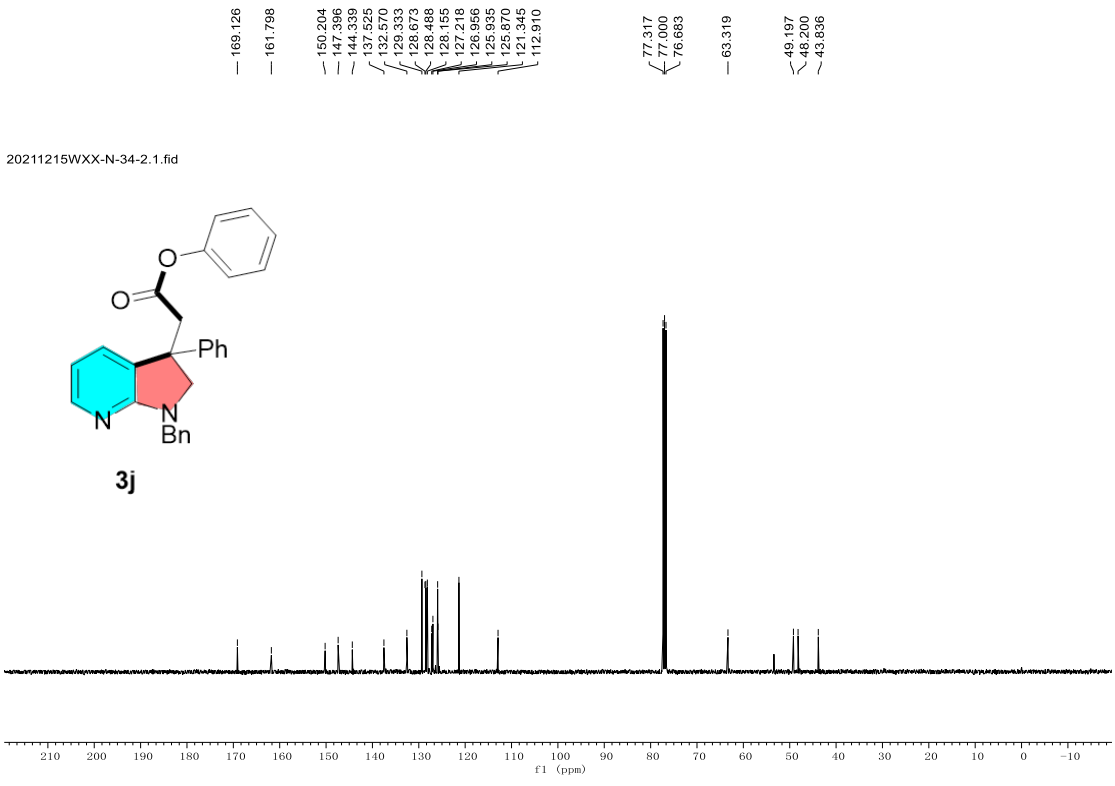
(**3i**, ^{13}C NMR, $CDCl_3$, 101 MHz)



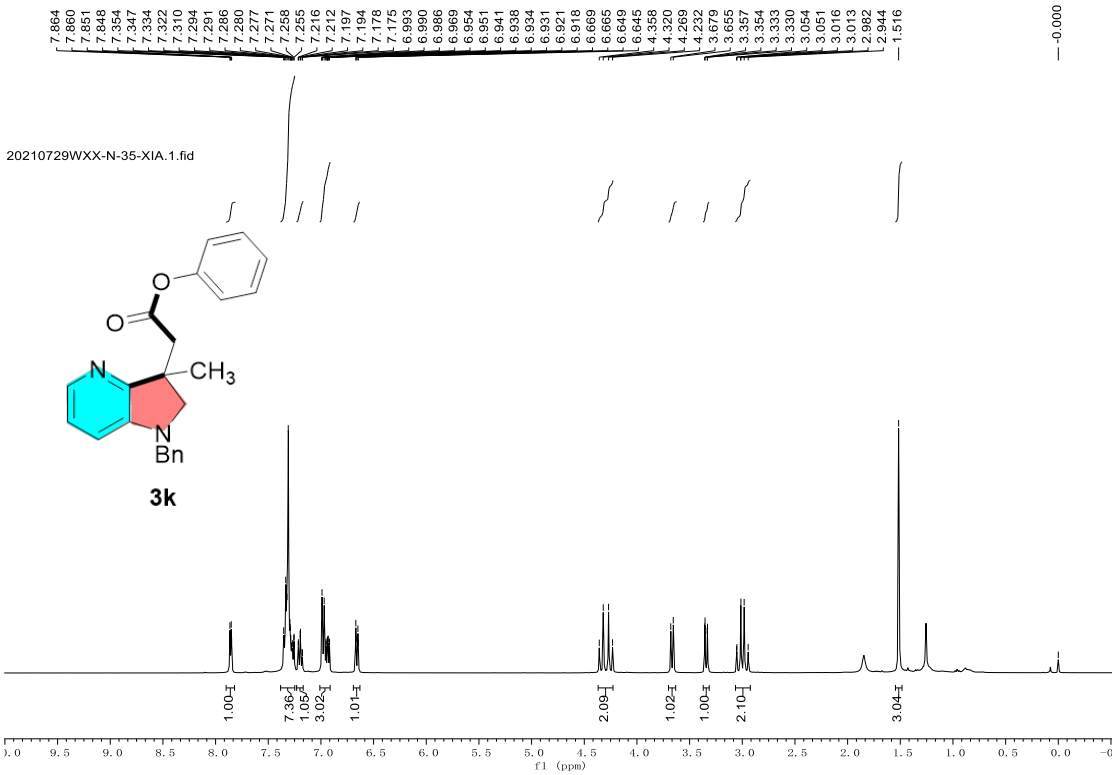
(**3j**, ^{1}H NMR, $CDCl_3$, 400 MHz)



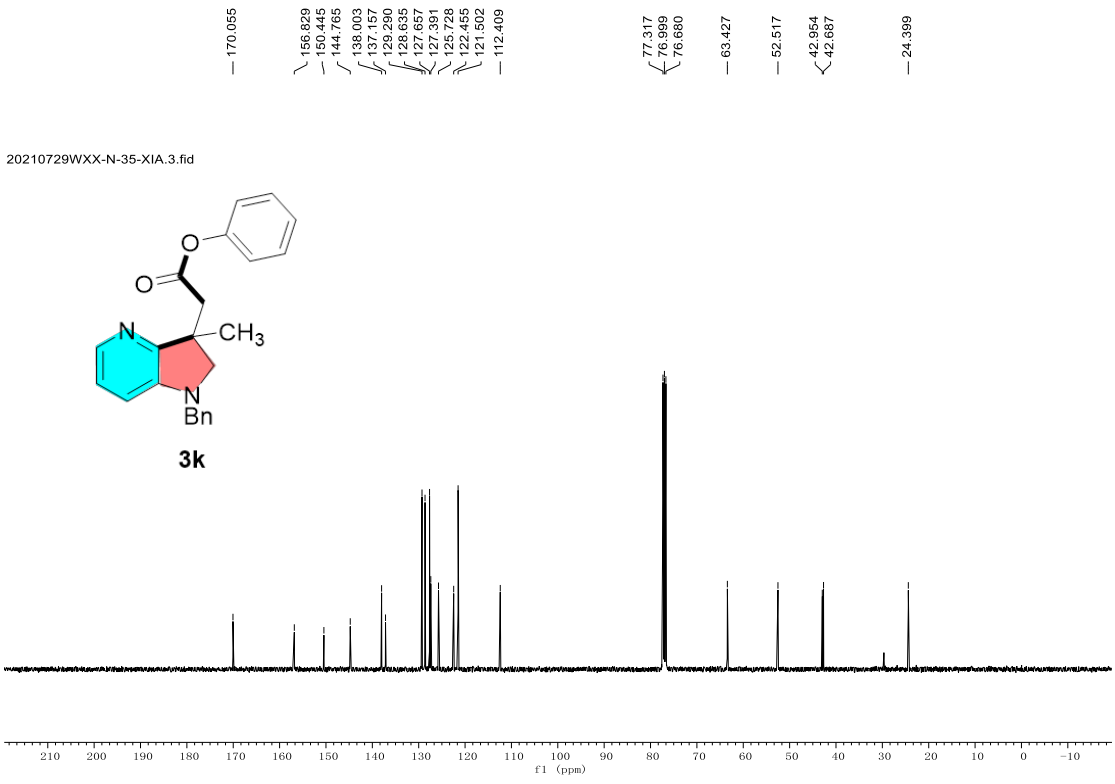
(**3j**, ^{13}C NMR, $CDCl_3$, 101 MHz)



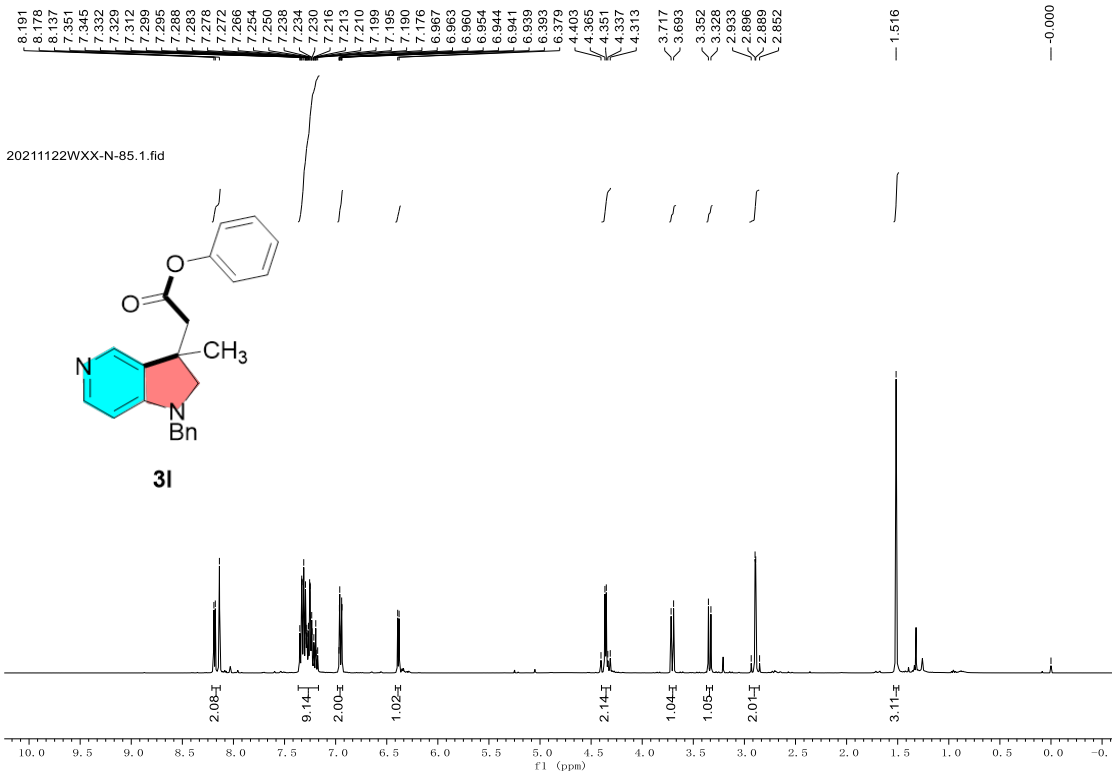
(**3k**, ^{1}H NMR, $CDCl_3$, 400 MHz)



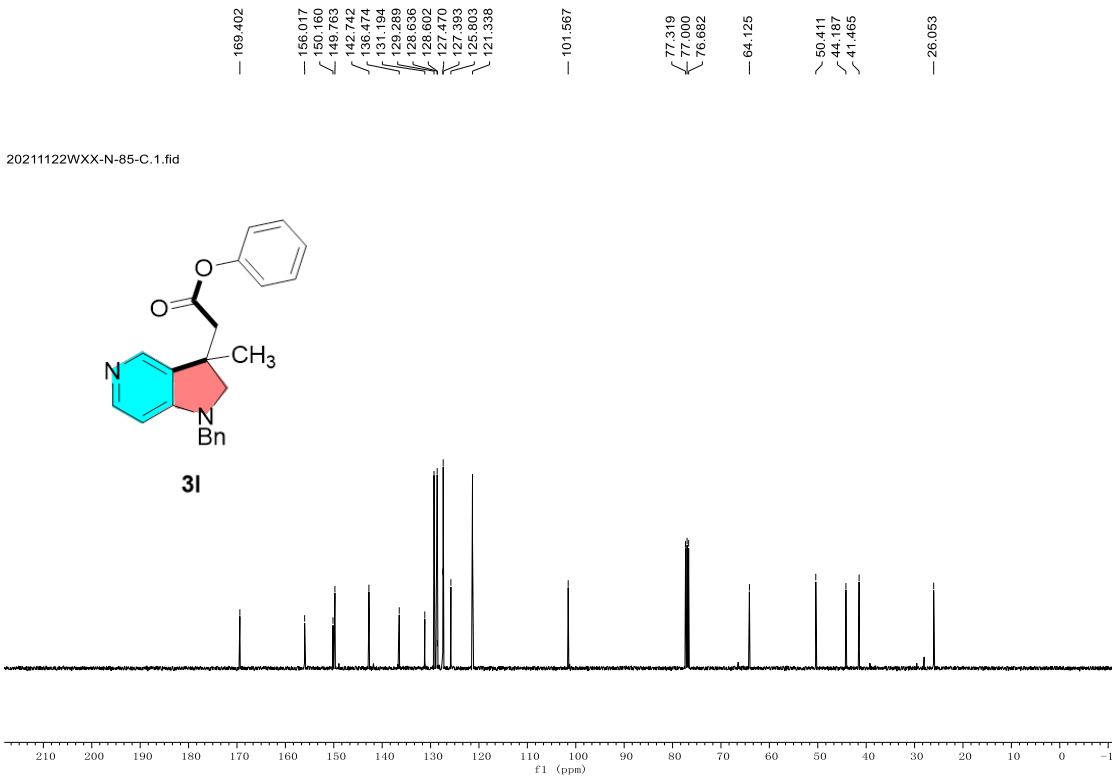
(**3k**, ^{13}C NMR, $CDCl_3$, 101 MHz)



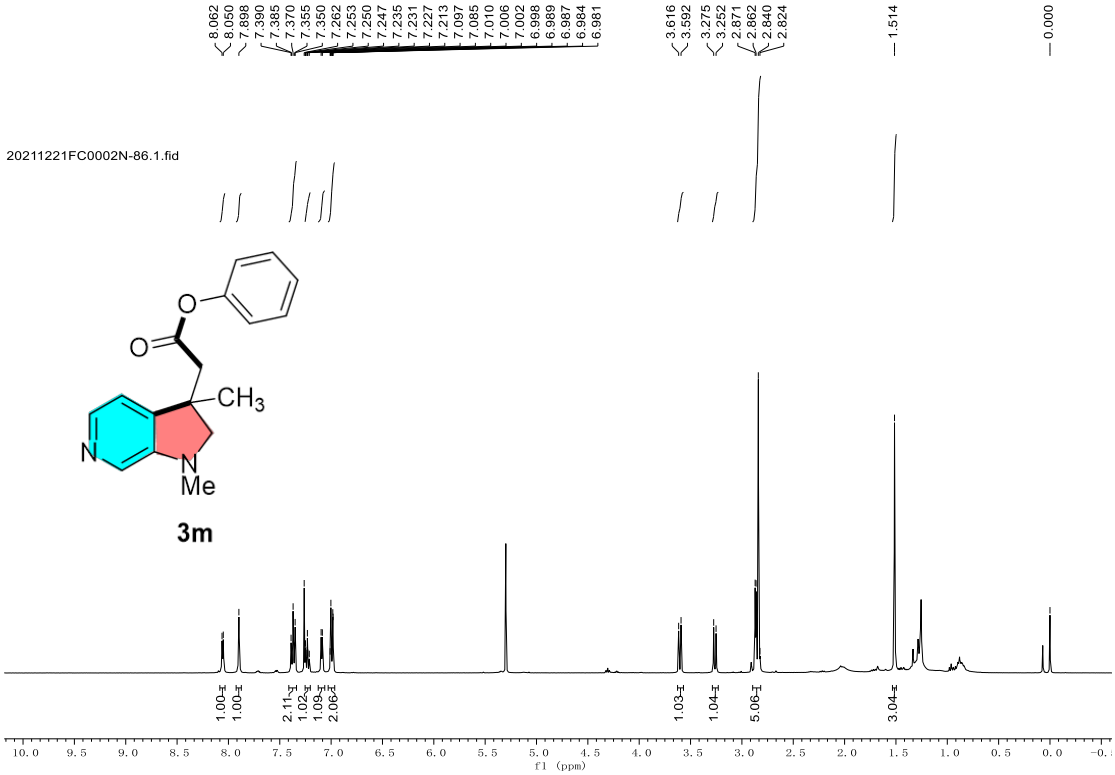
(**3l**, ^{1}H NMR, $CDCl_3$, 400 MHz)



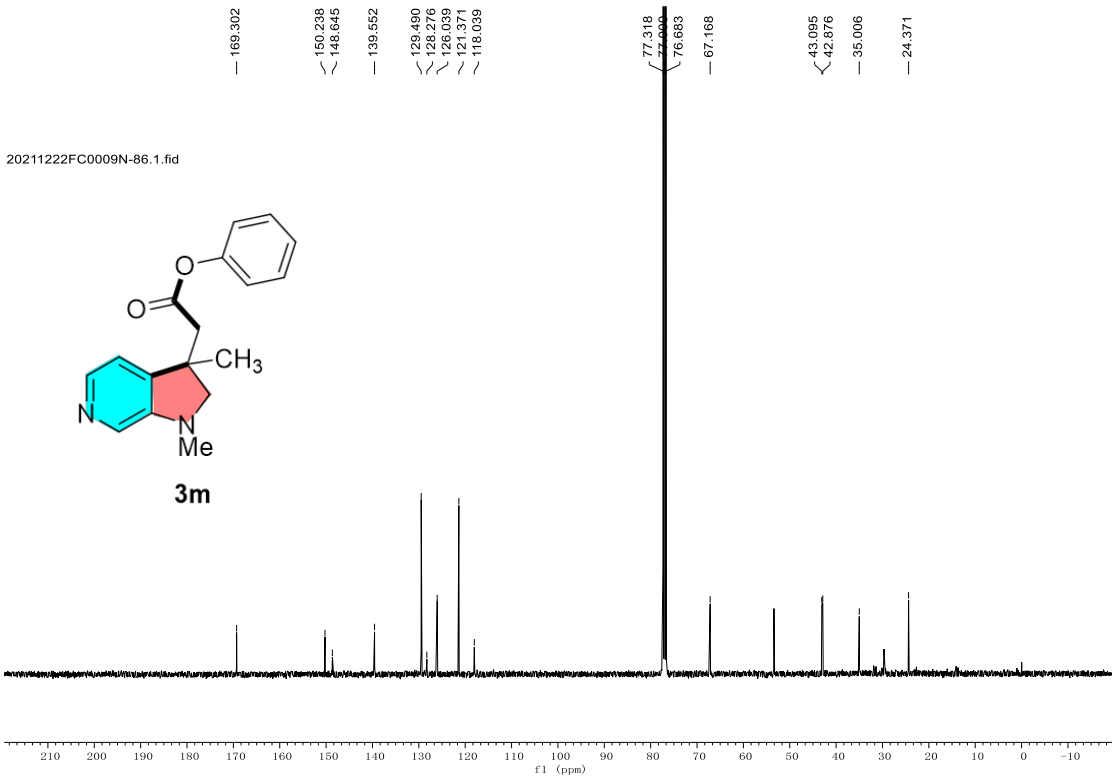
(**3l**, ^{13}C NMR, $CDCl_3$, 101 MHz)



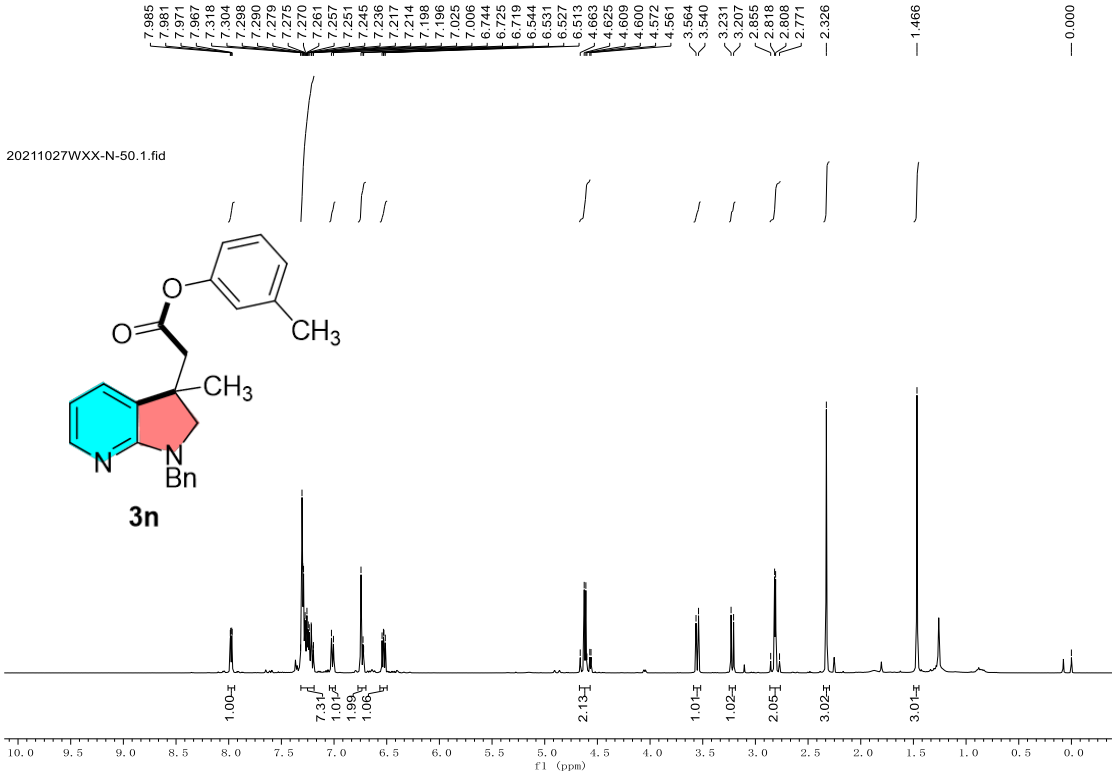
(**3m**, ^{1}H NMR, $CDCl_3$, 400 MHz)



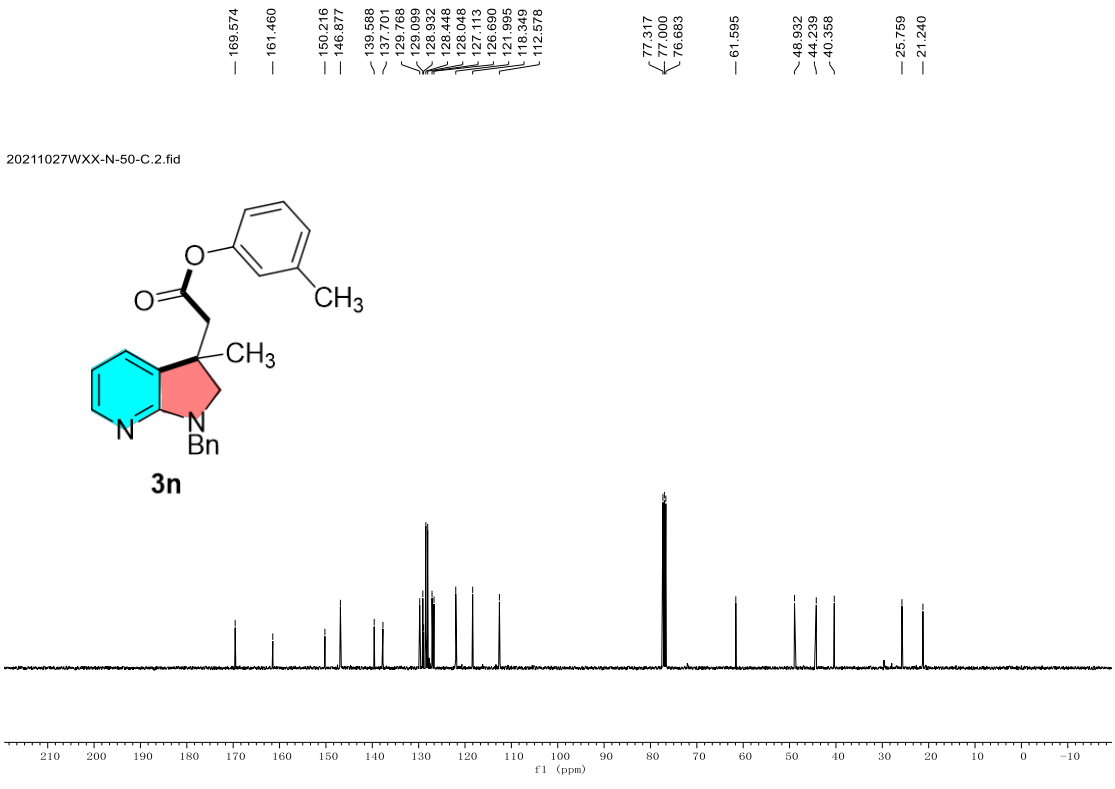
(**3m**, ^{13}C NMR, $CDCl_3$, 101 MHz)



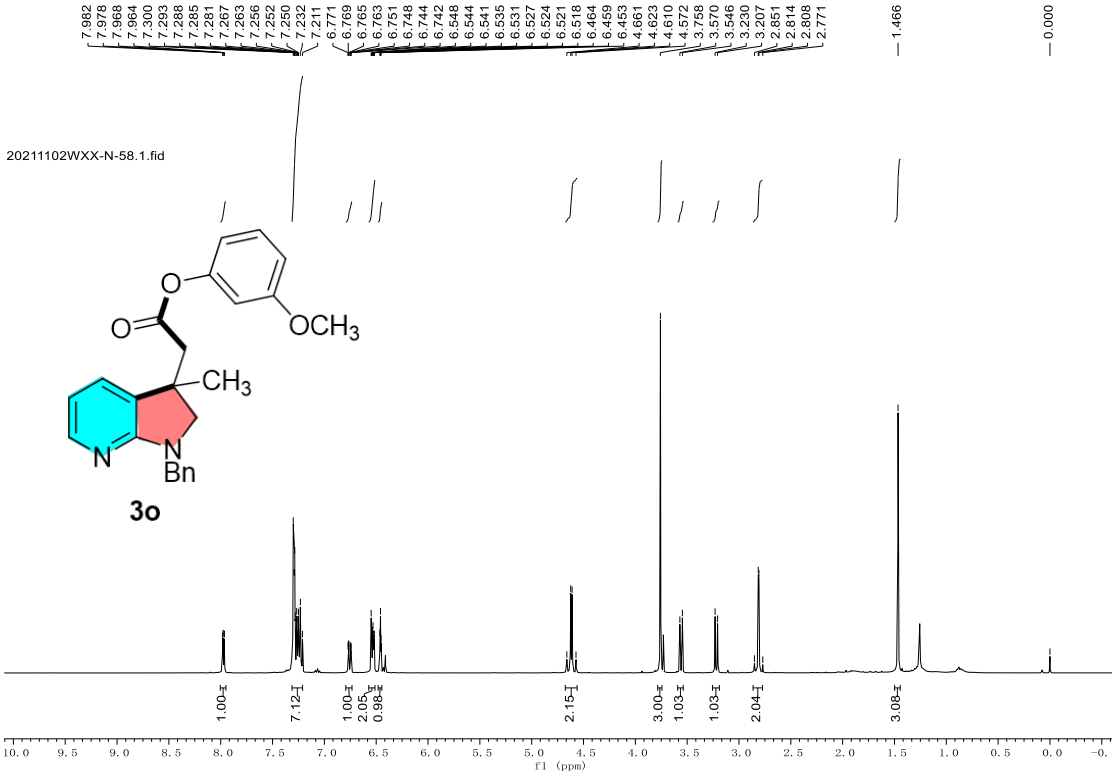
(**3n**, ^{1}H NMR, $CDCl_3$, 400 MHz)



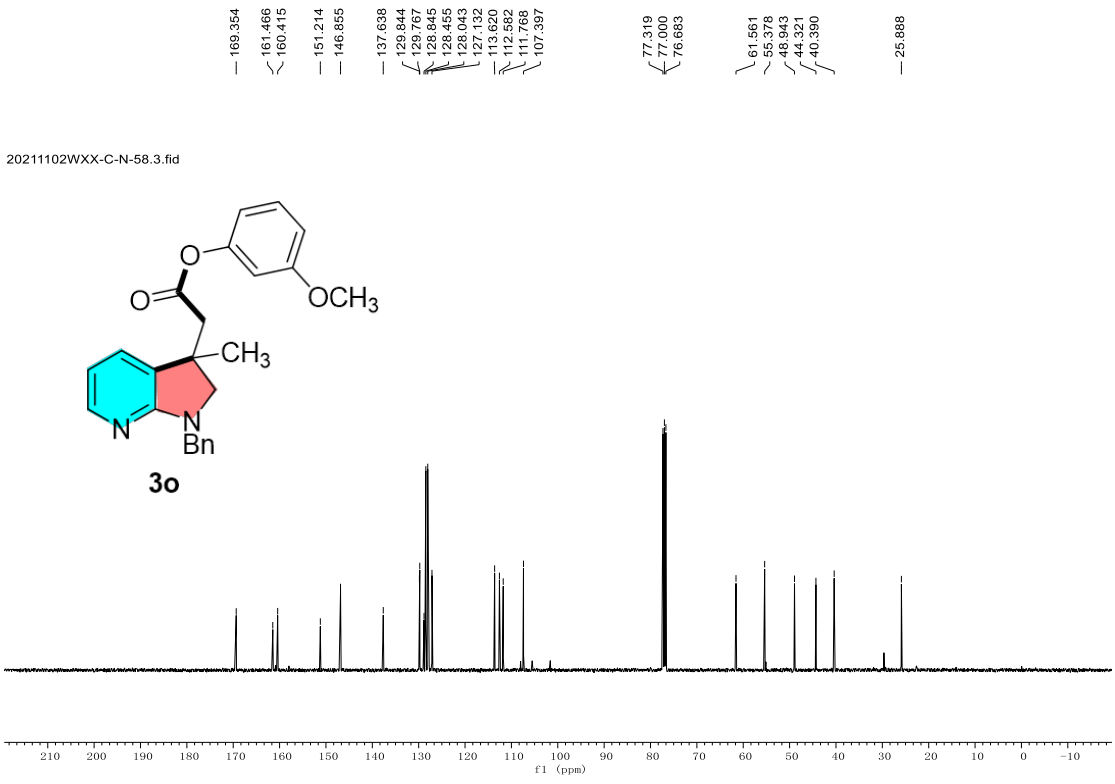
(**3n**, ^{13}C NMR, $CDCl_3$, 101 MHz)



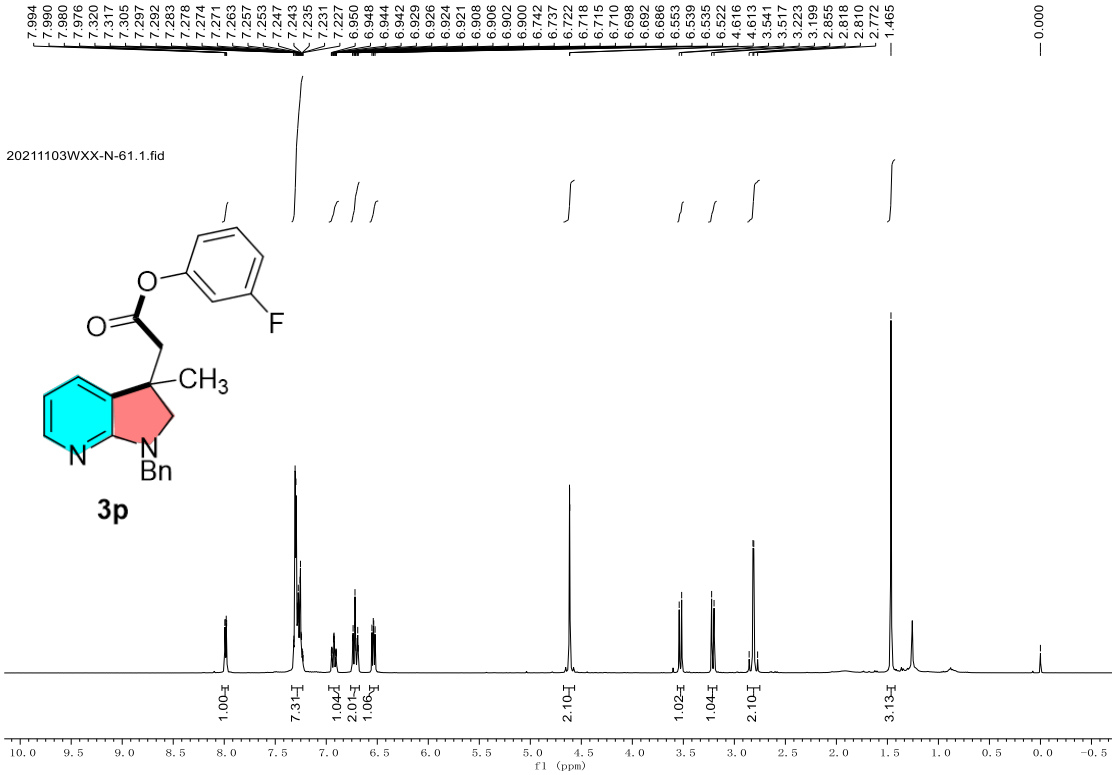
(**3o**, ^{1}H NMR, $CDCl_3$, 400 MHz)



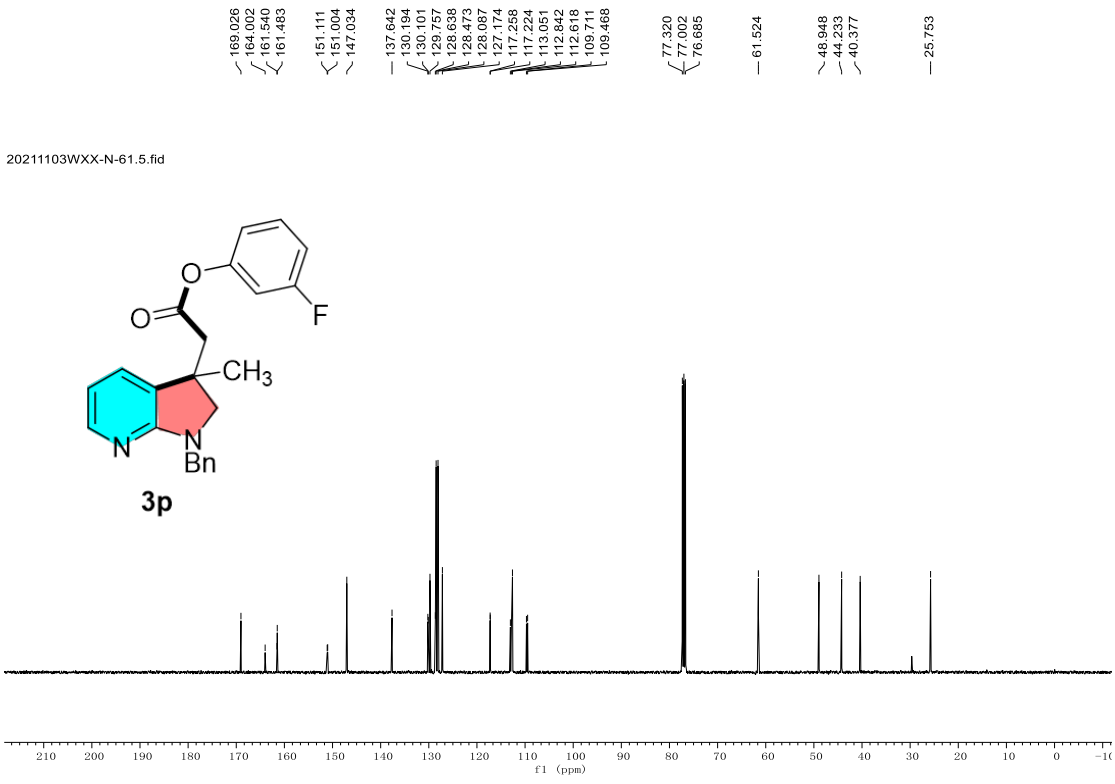
(**3o**, ^{13}C NMR, $CDCl_3$, 101 MHz)



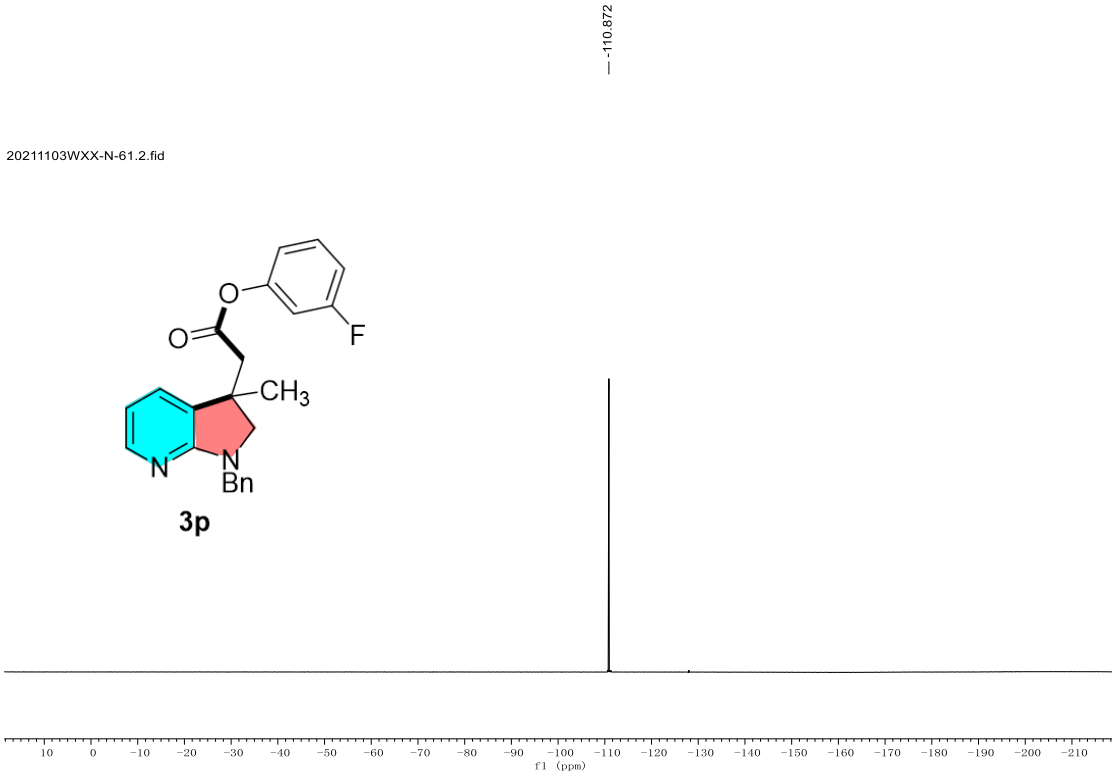
(**3p**, ^{1}H NMR, $CDCl_3$, 400 MHz)



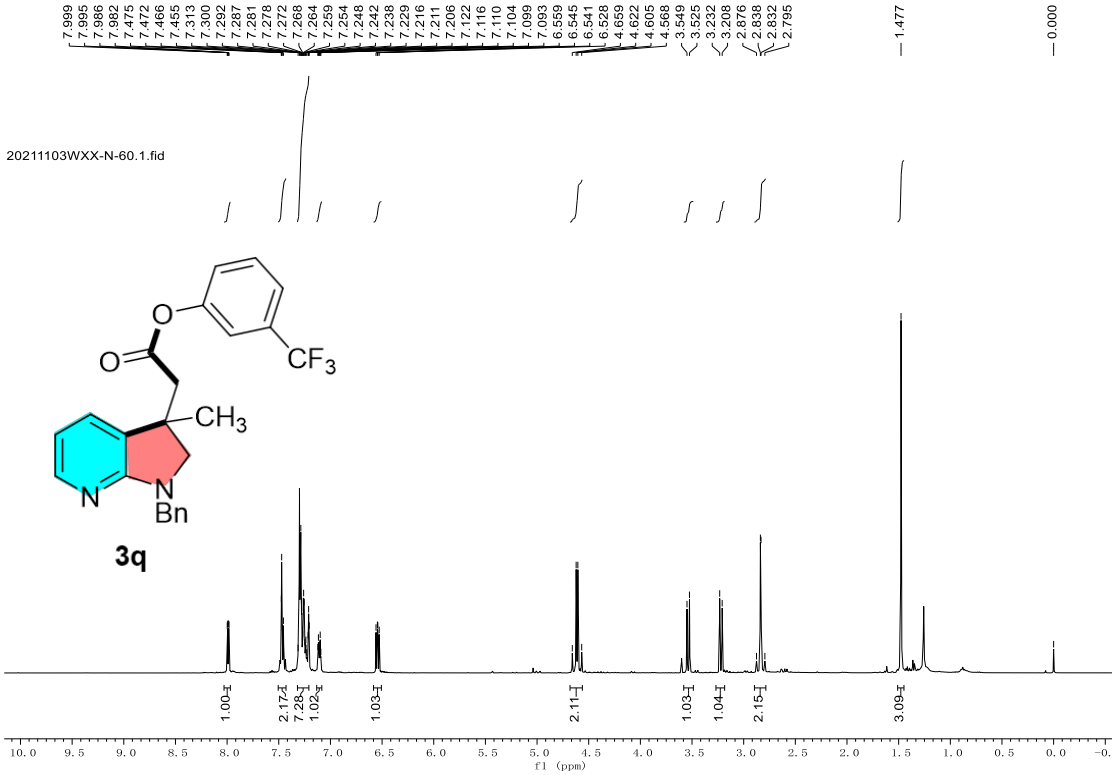
(**3p**, ^{13}C NMR, $CDCl_3$, 101 MHz)



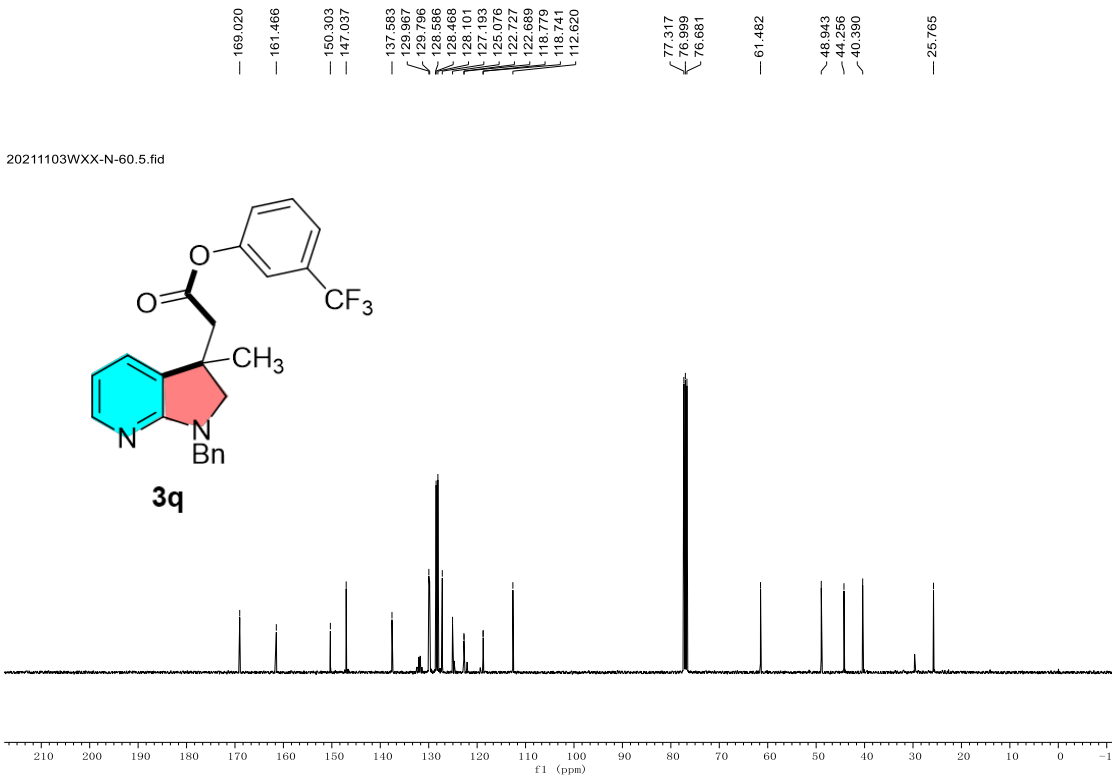
(**3p**, ^{19}F NMR, $CDCl_3$, 376 MHz)



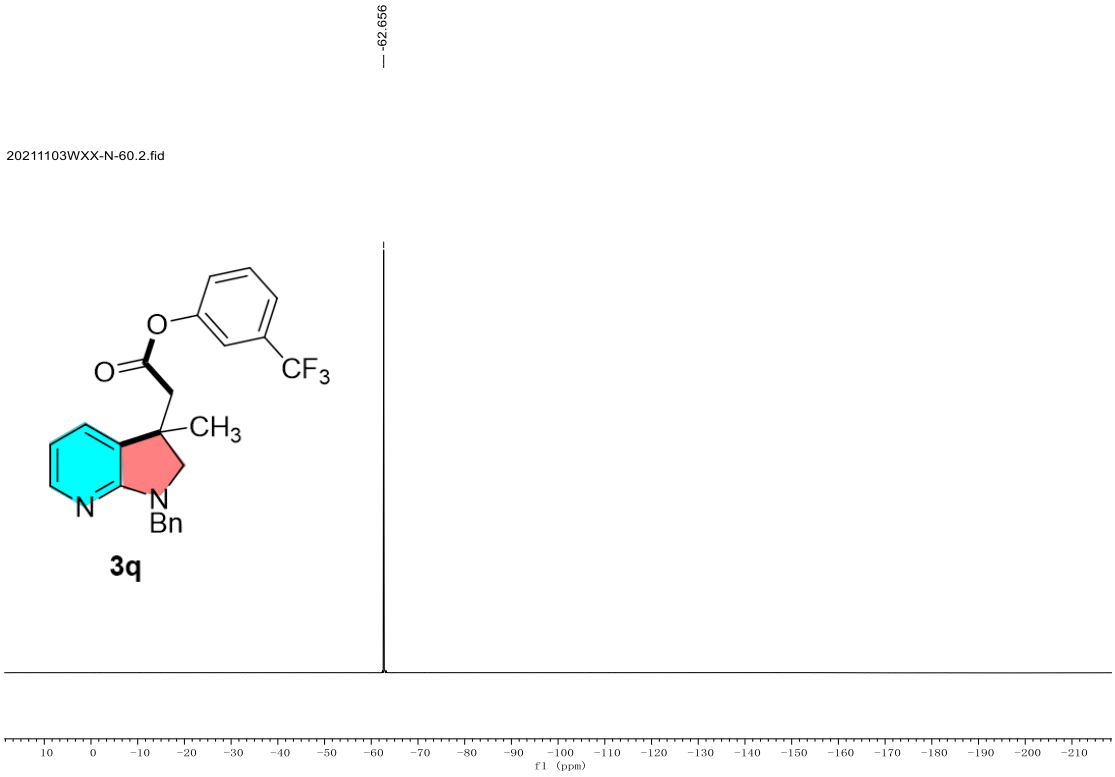
(**3q**, ^{1}H NMR, $CDCl_3$, 400 MHz)



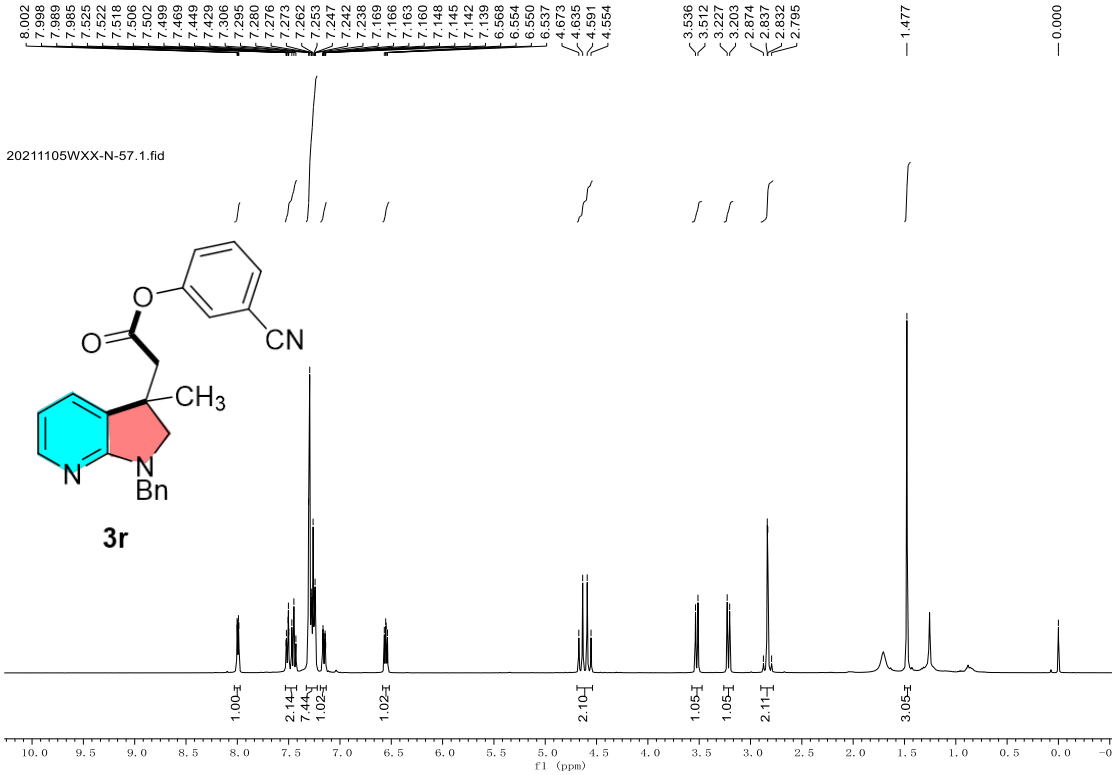
(**3q**, ^{13}C NMR, $CDCl_3$, 101 MHz)



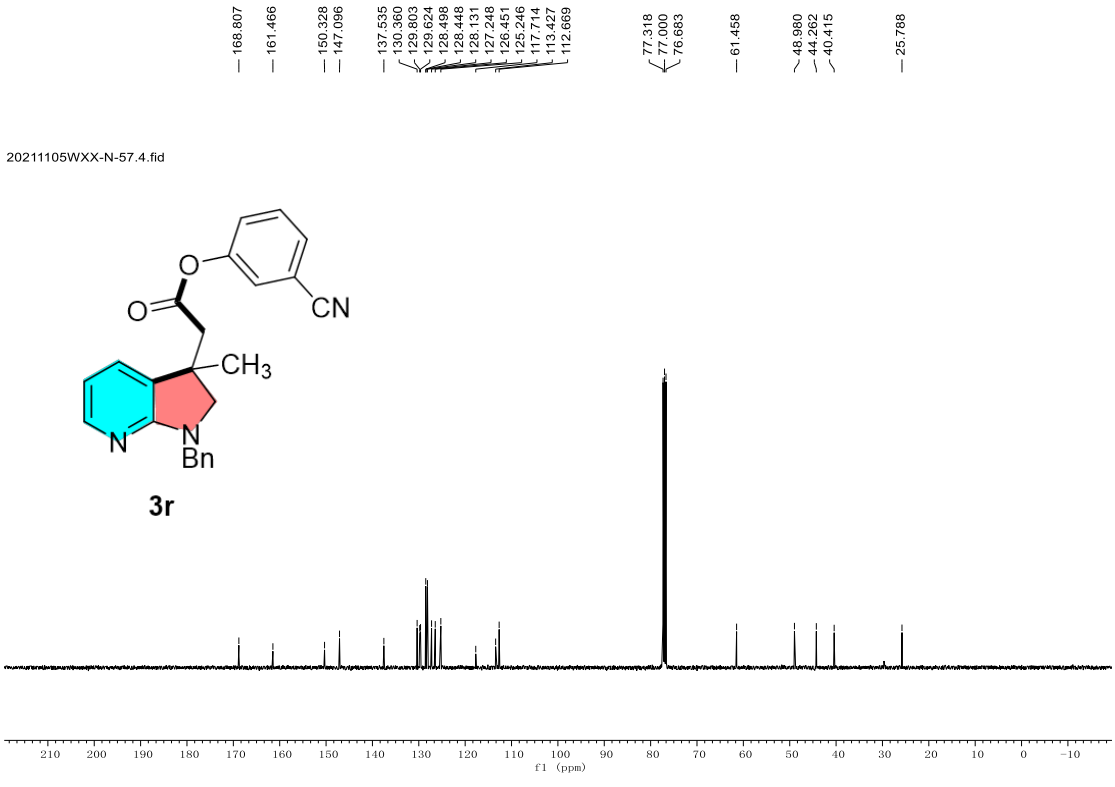
(**3q**, ^{19}F NMR, $CDCl_3$, 376 MHz)



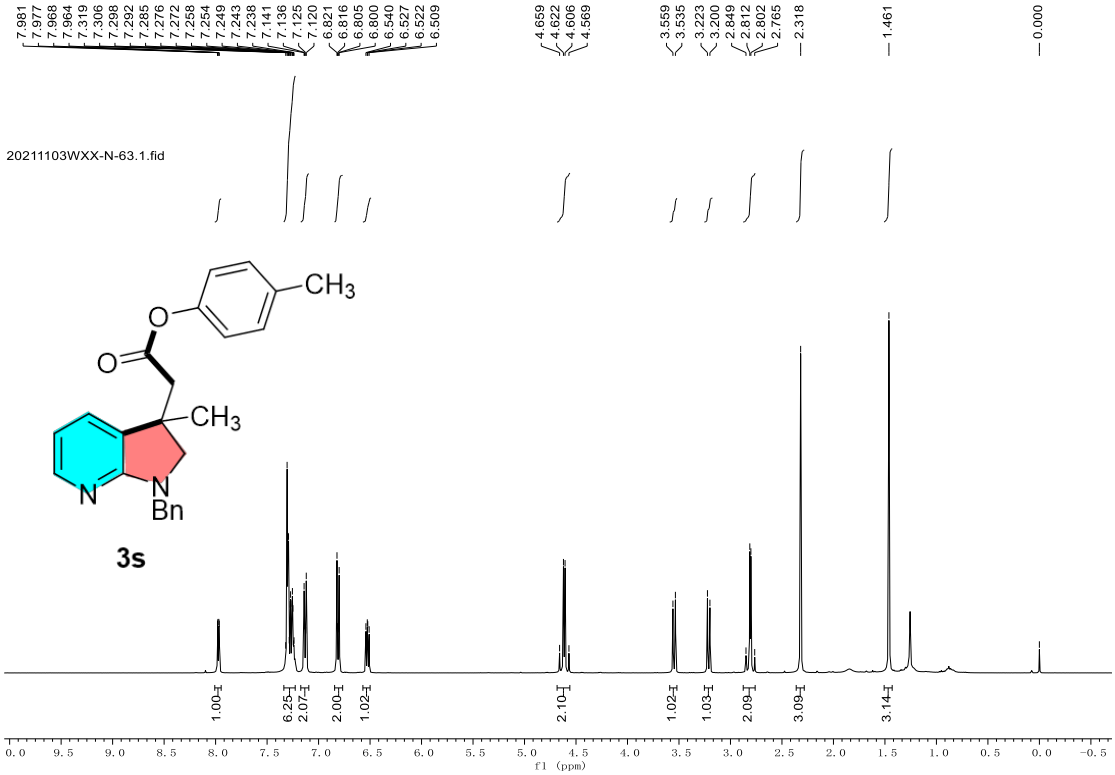
(**3r**, ^{1}H NMR, $CDCl_3$, 400 MHz)



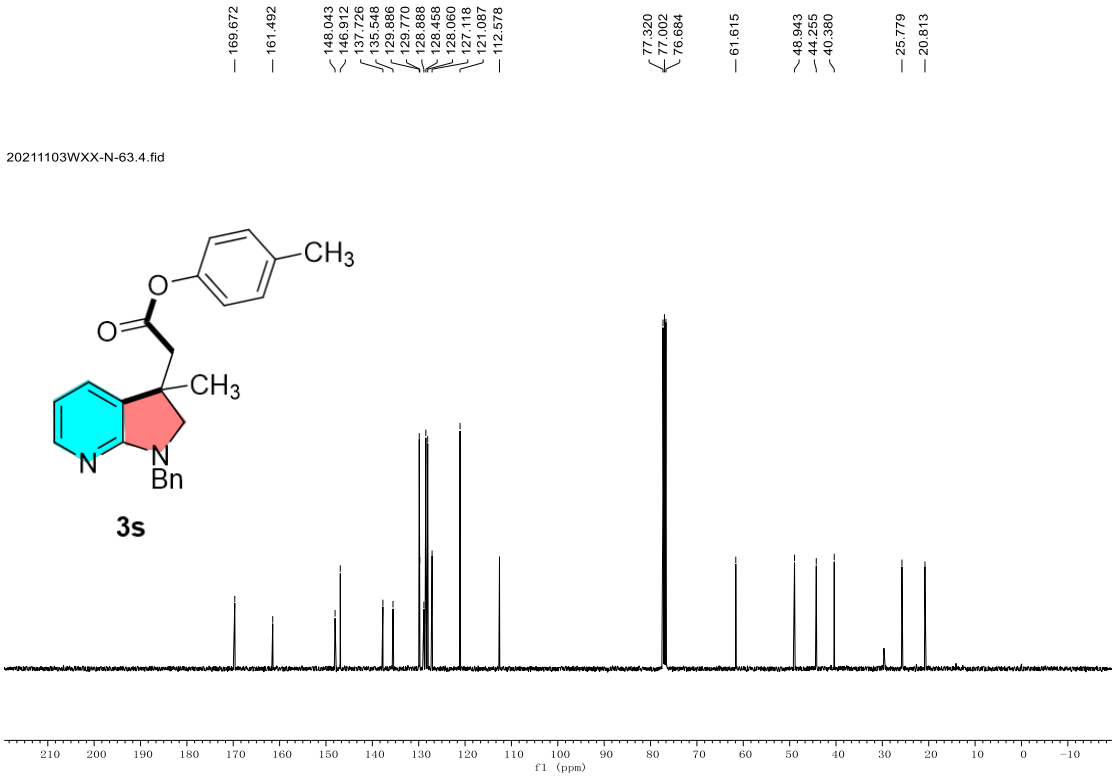
(**3r**, ^{13}C NMR, $CDCl_3$, 101 MHz)



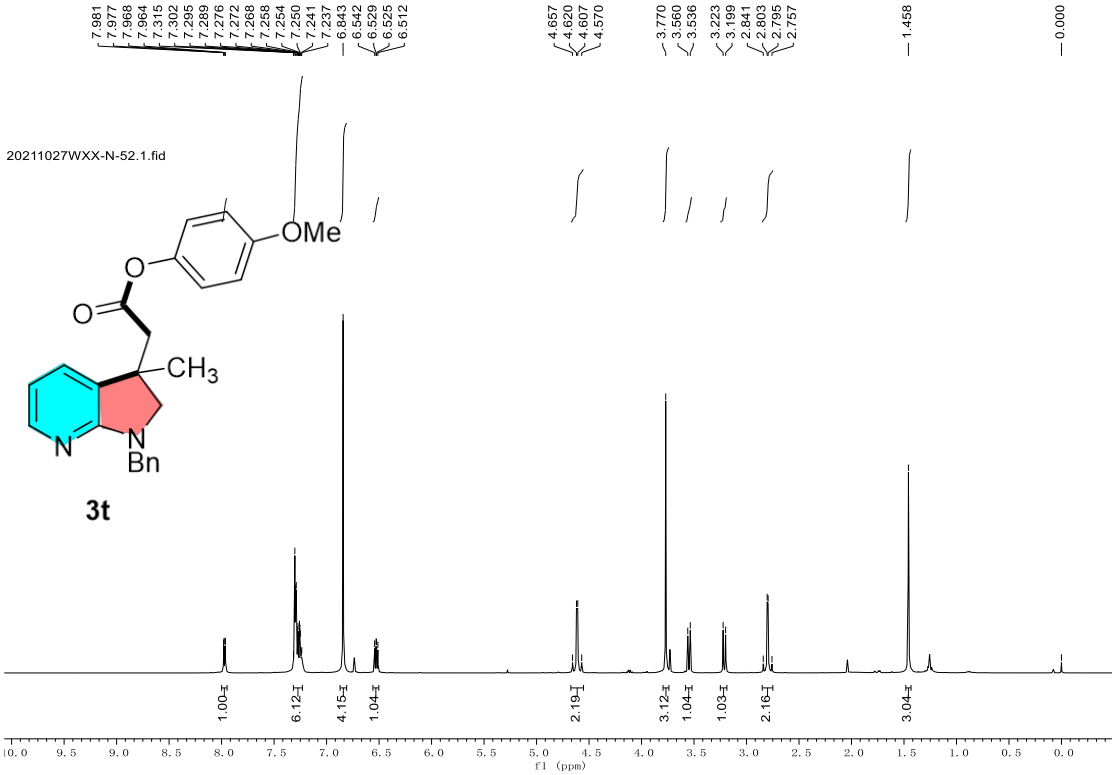
(**3s**, ^{1}H NMR, $CDCl_3$, 400 MHz)



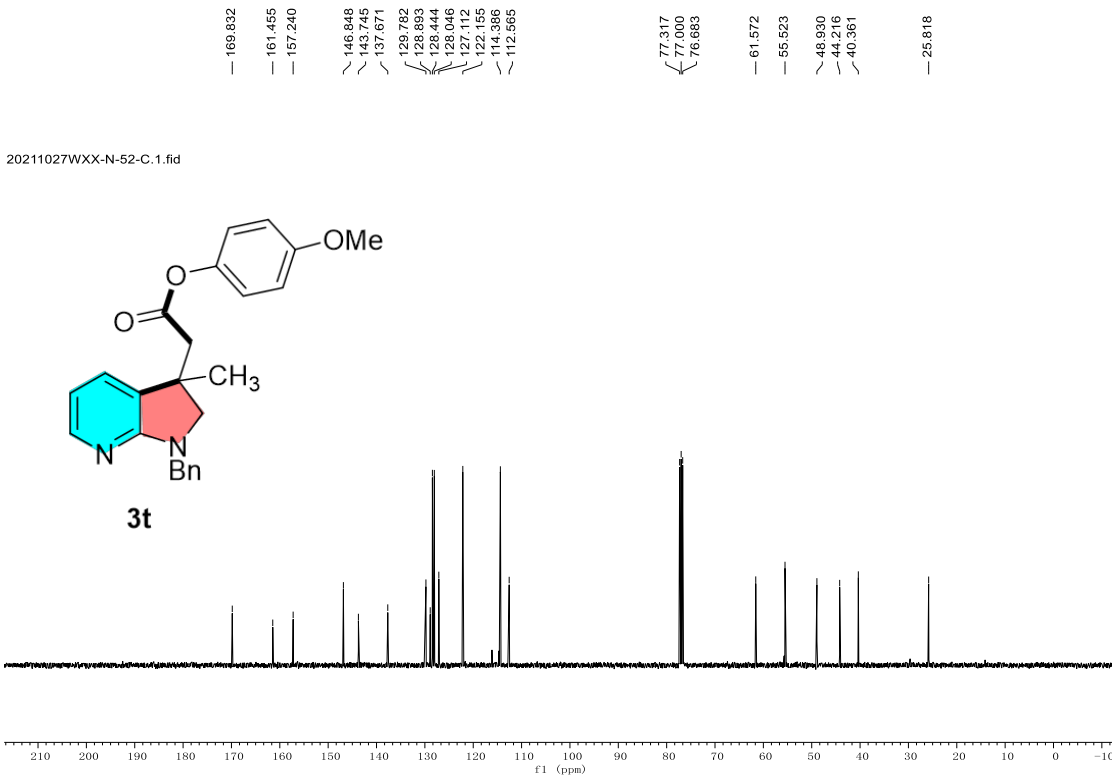
(**3s**, ^{13}C NMR, $CDCl_3$, 101 MHz)



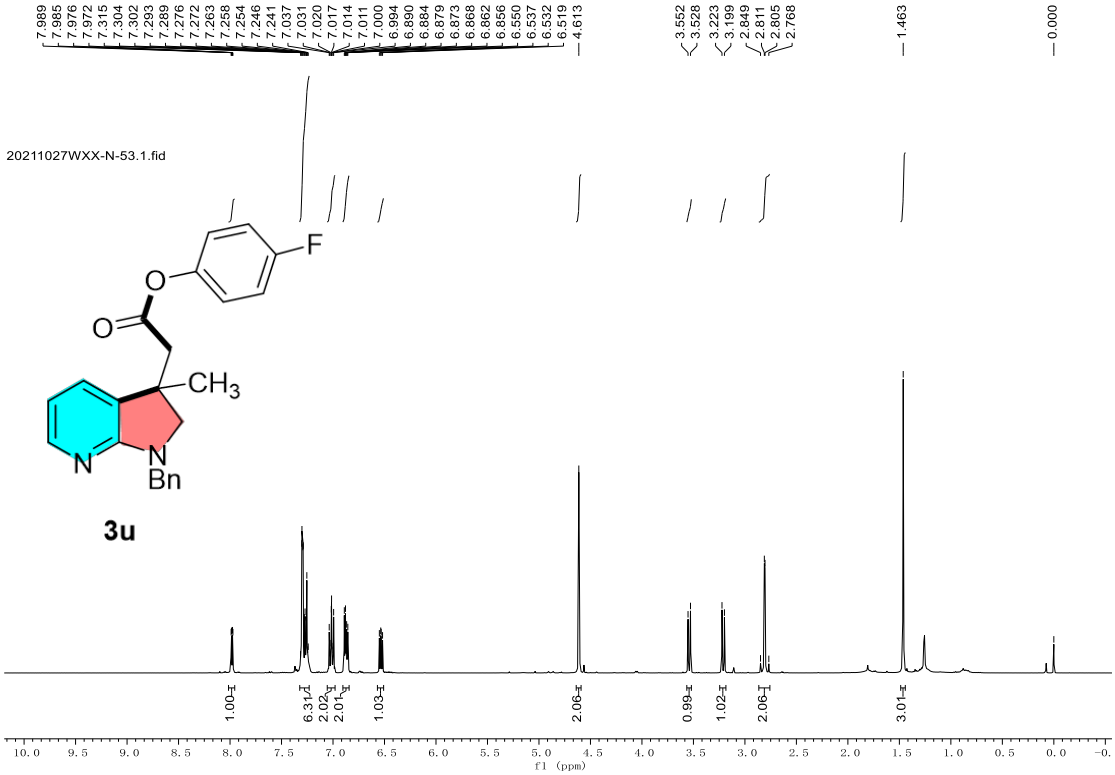
(**3t**, ^{1}H NMR, $CDCl_3$, 400 MHz)



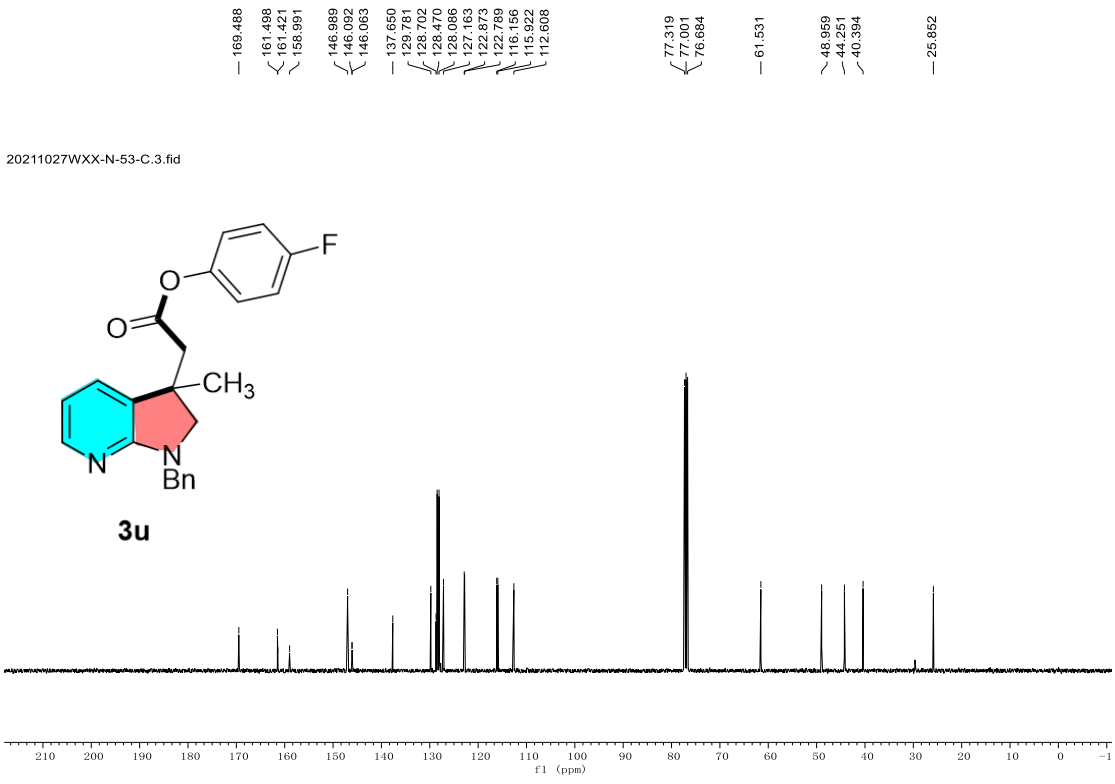
(**3t**, ^{13}C NMR, $CDCl_3$, 101 MHz)



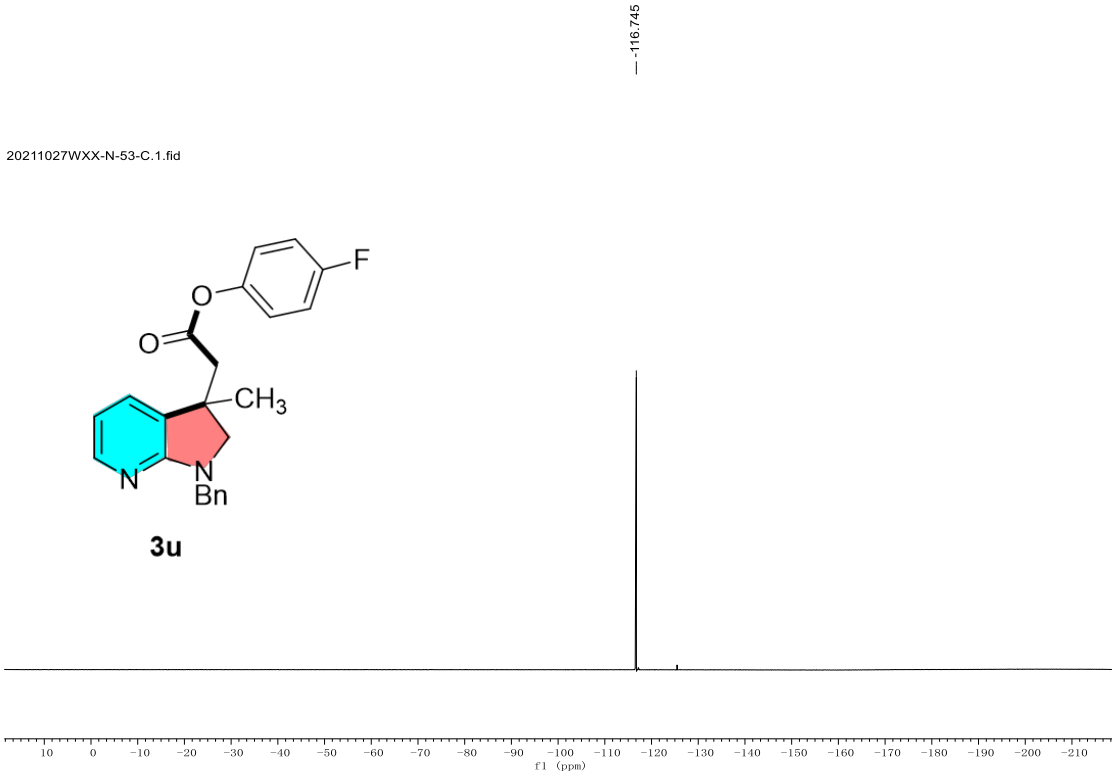
(**3u**, ^{1}H NMR, $CDCl_3$, 400 MHz)



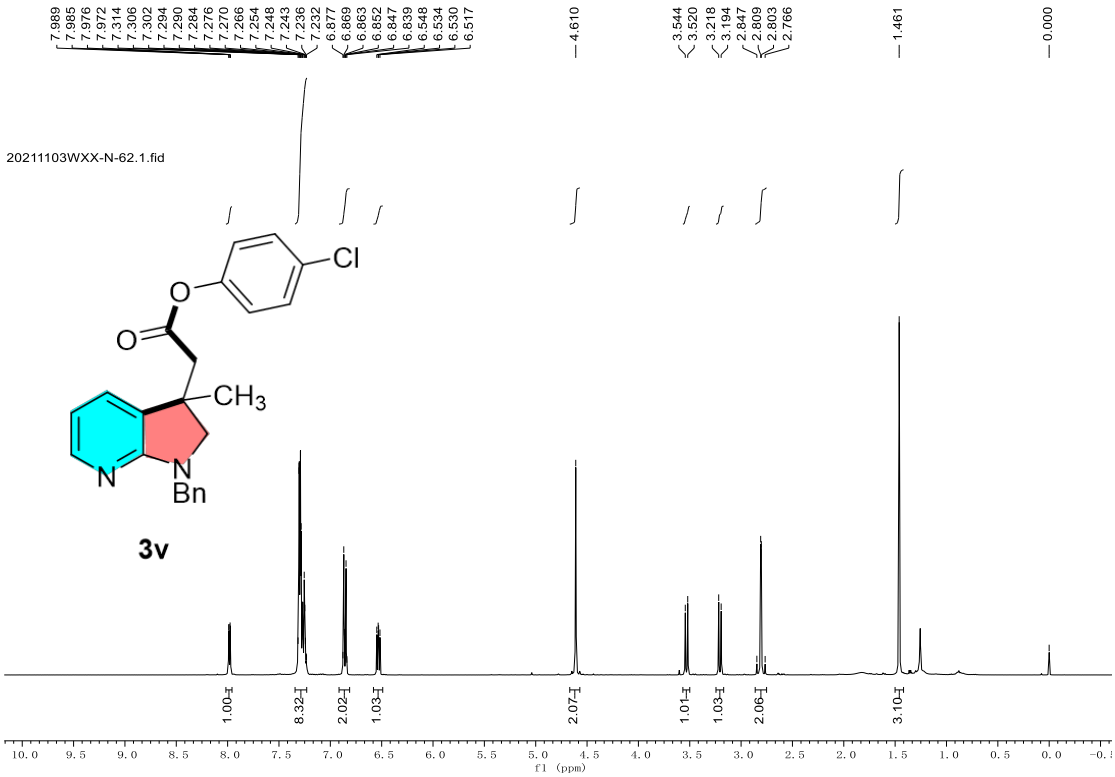
(**3u**, ^{13}C NMR, $CDCl_3$, 101 MHz)



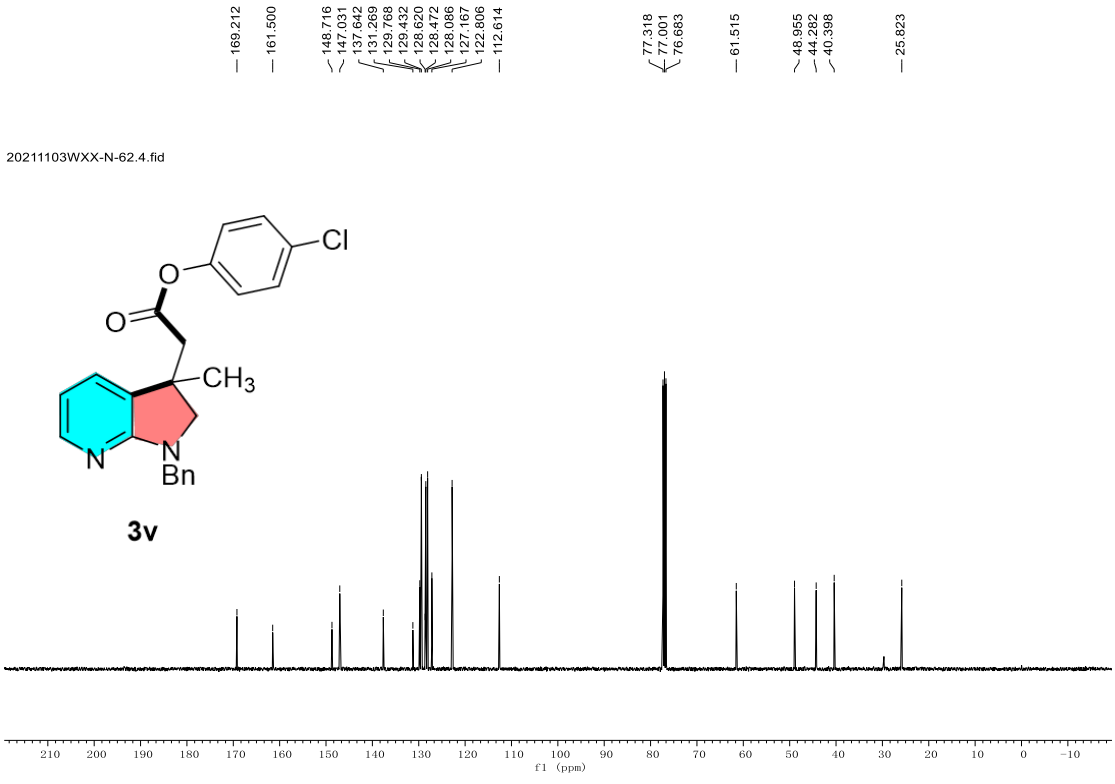
(**3u**, ^{19}F NMR, $CDCl_3$, 376 MHz)



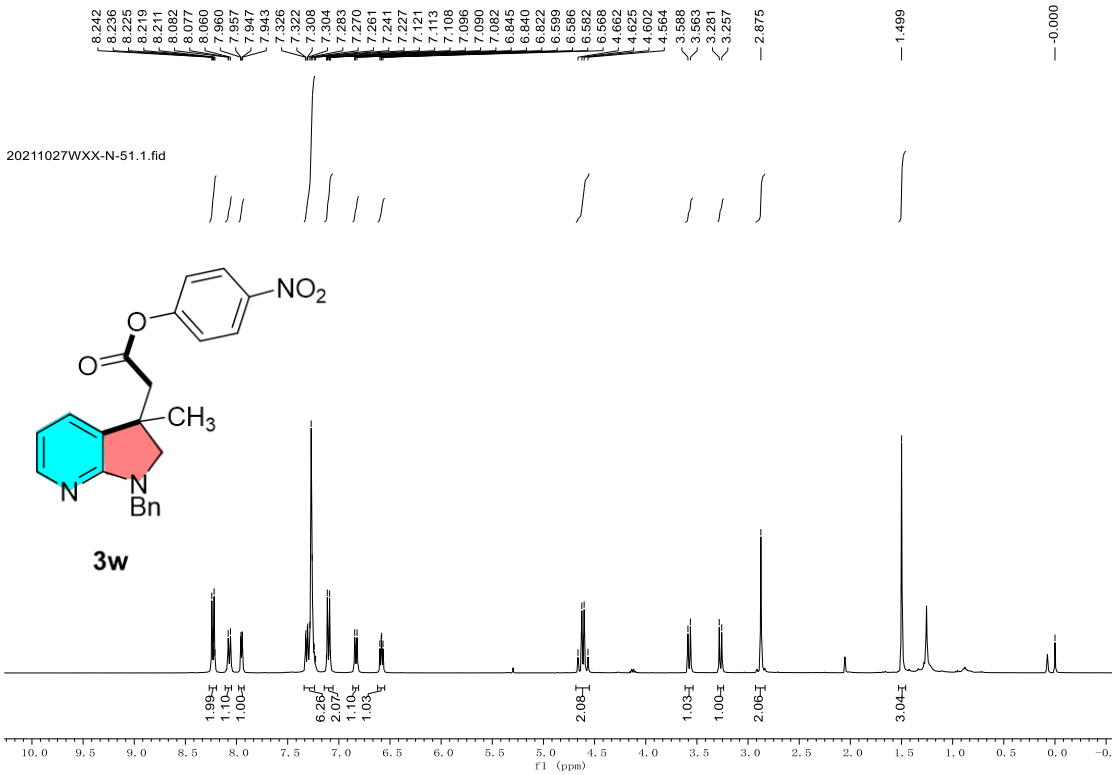
(**3v**, ^{1}H NMR, $CDCl_3$, 400 MHz)



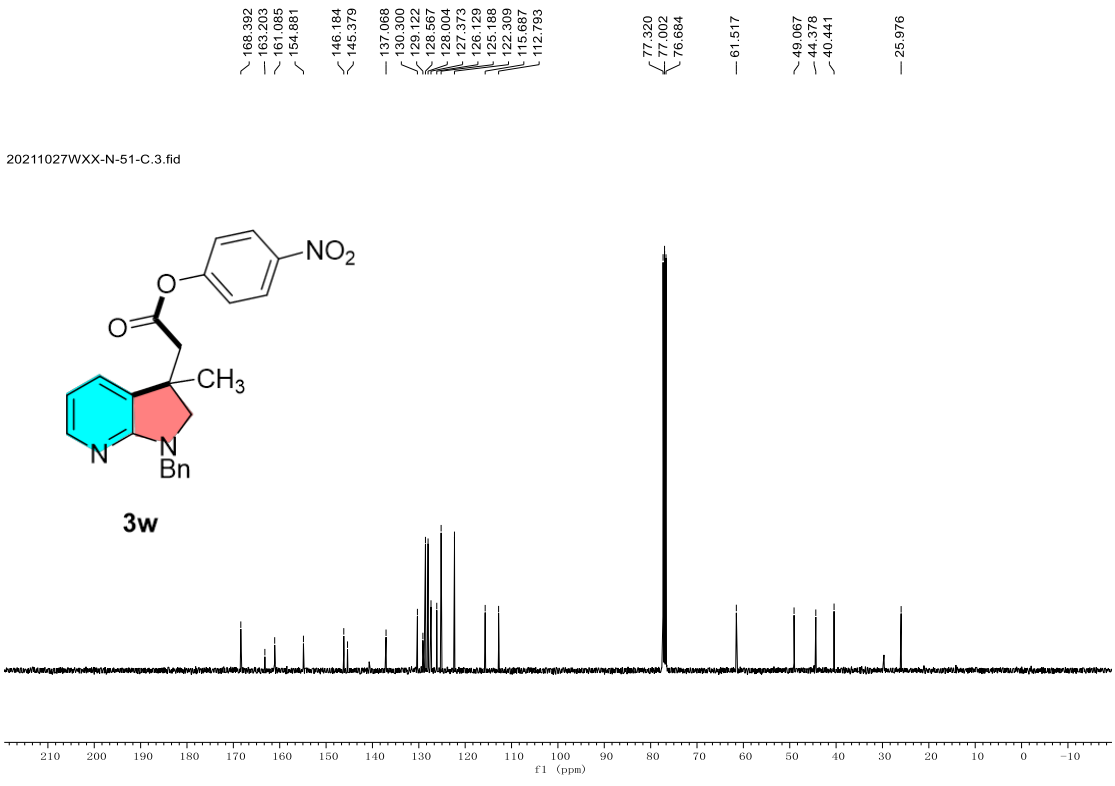
(**3v**, ^{13}C NMR, $CDCl_3$, 101 MHz)



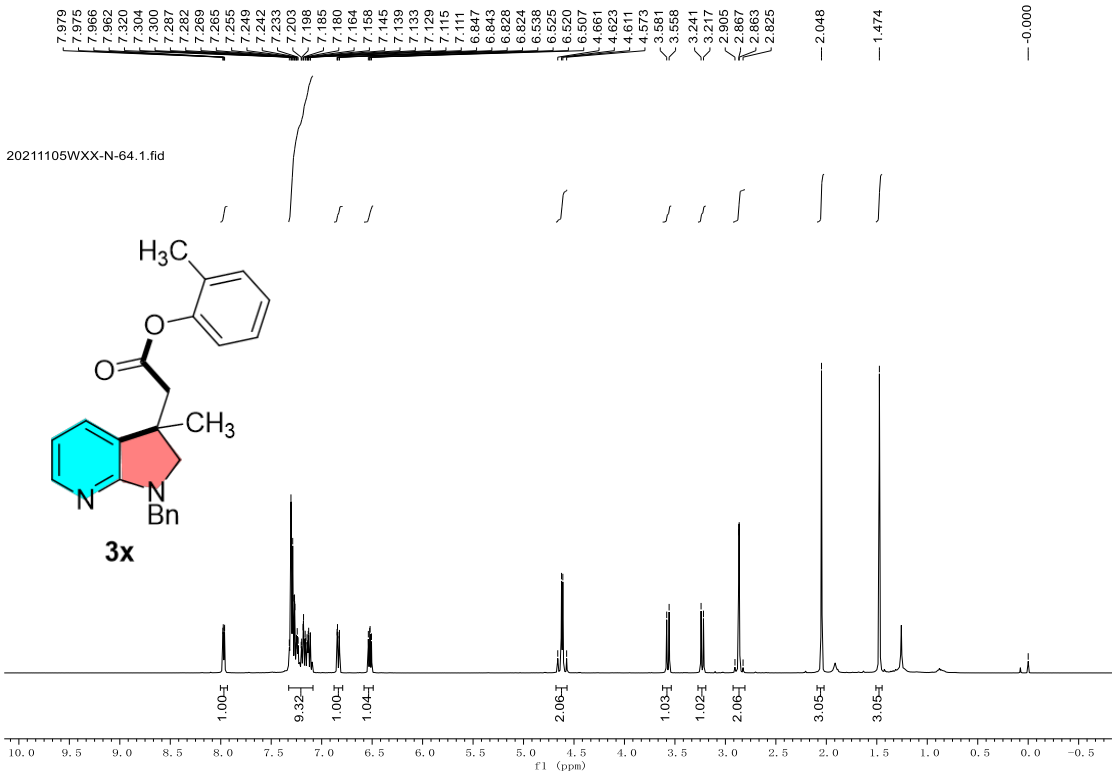
(**3w**, ^{1}H NMR, $CDCl_3$, 400 MHz)



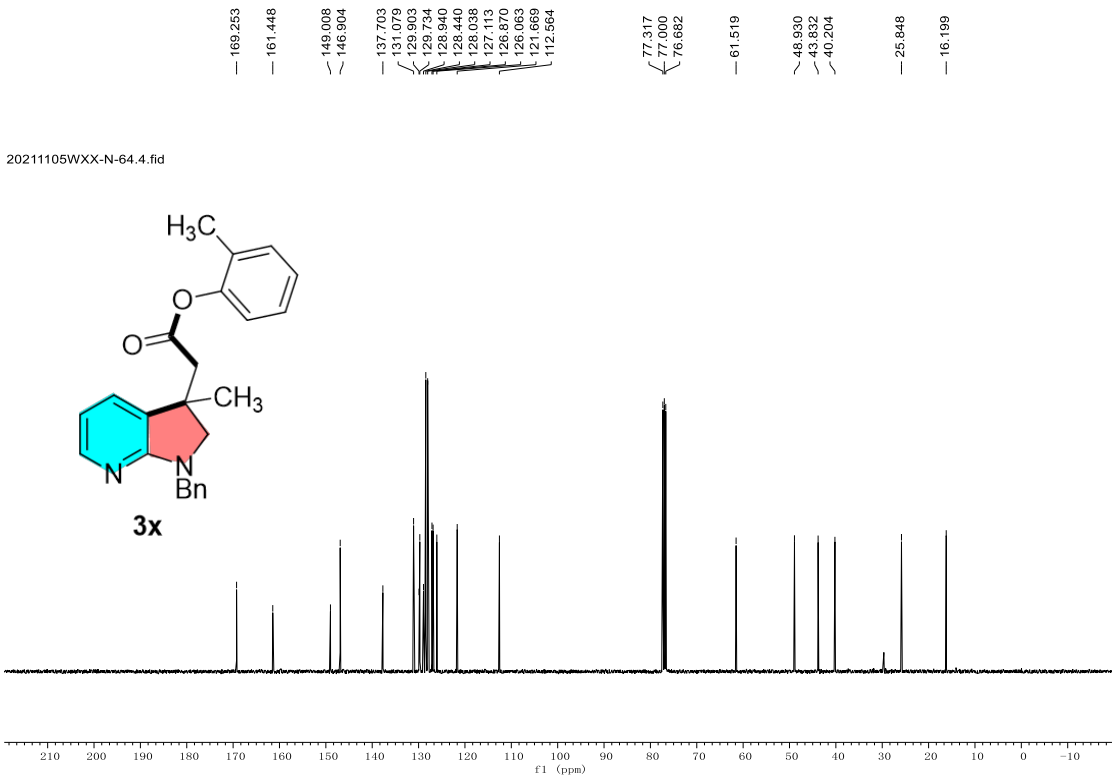
(**3w**, ^{13}C NMR, $CDCl_3$, 101 MHz)



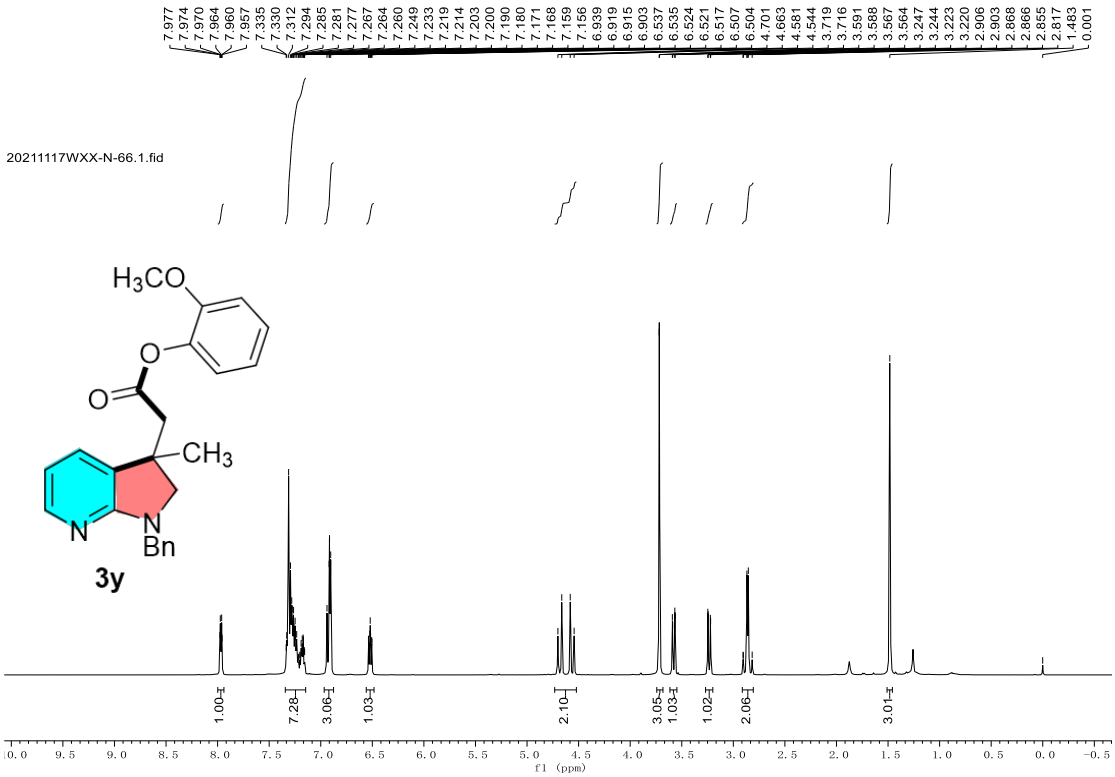
(**3x**, ^{1}H NMR, $CDCl_3$, 400 MHz)



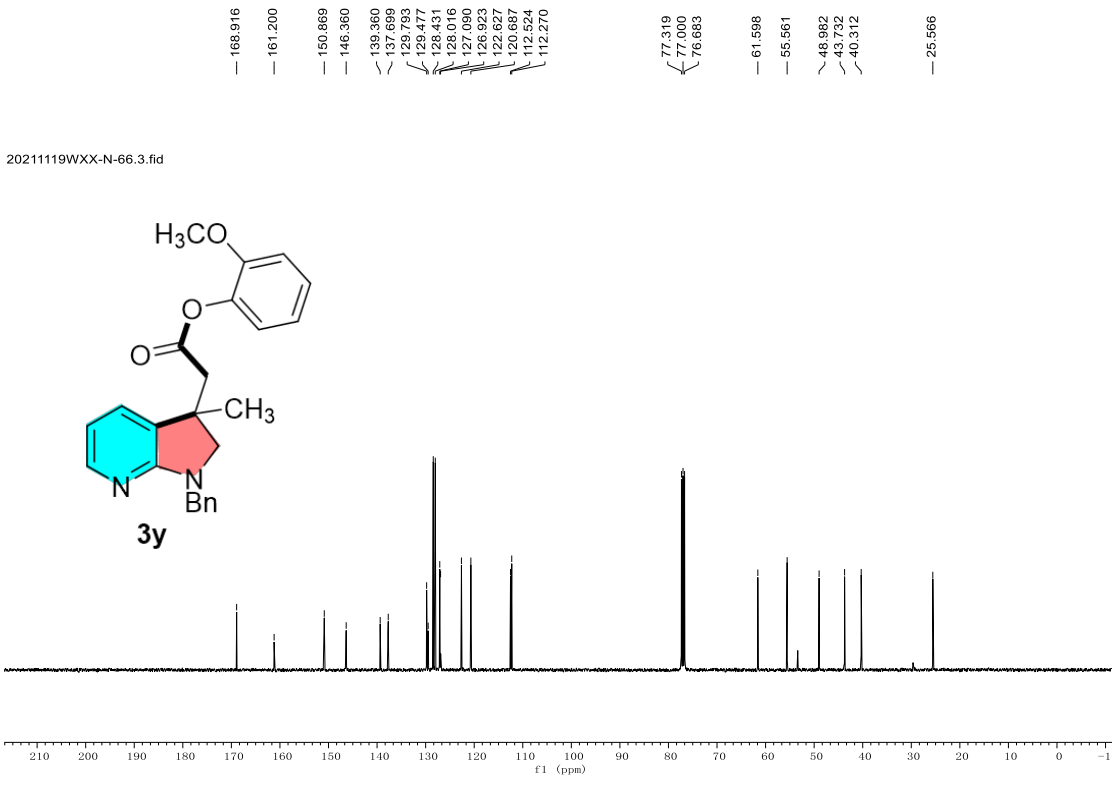
(**3x**, ^{13}C NMR, $CDCl_3$, 101 MHz)



(**3y**, ^{1}H NMR, $CDCl_3$, 400 MHz)



(**3y**, ^{13}C NMR, $CDCl_3$, 101 MHz)



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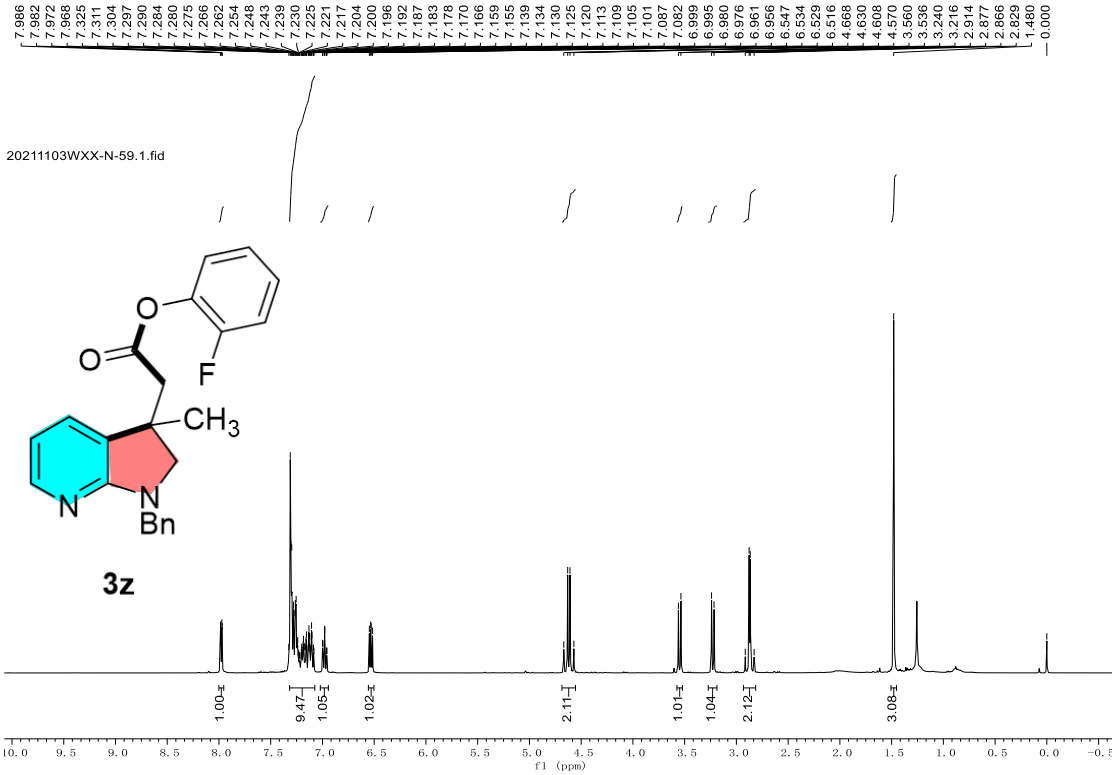
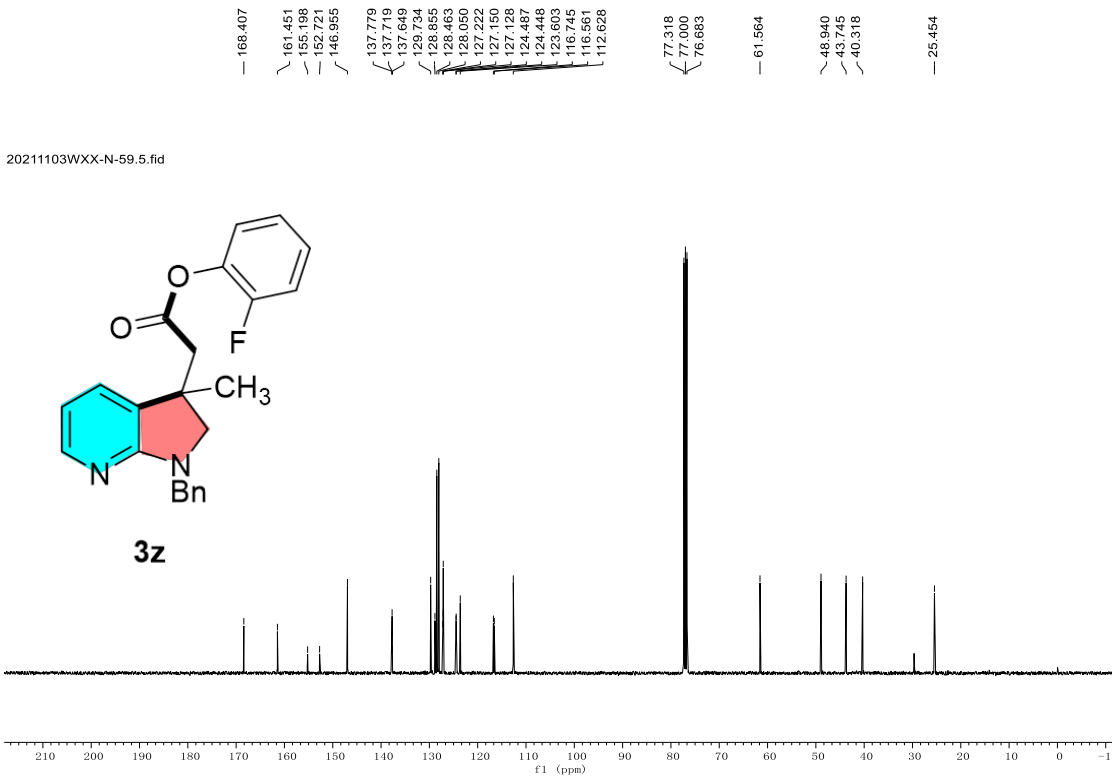
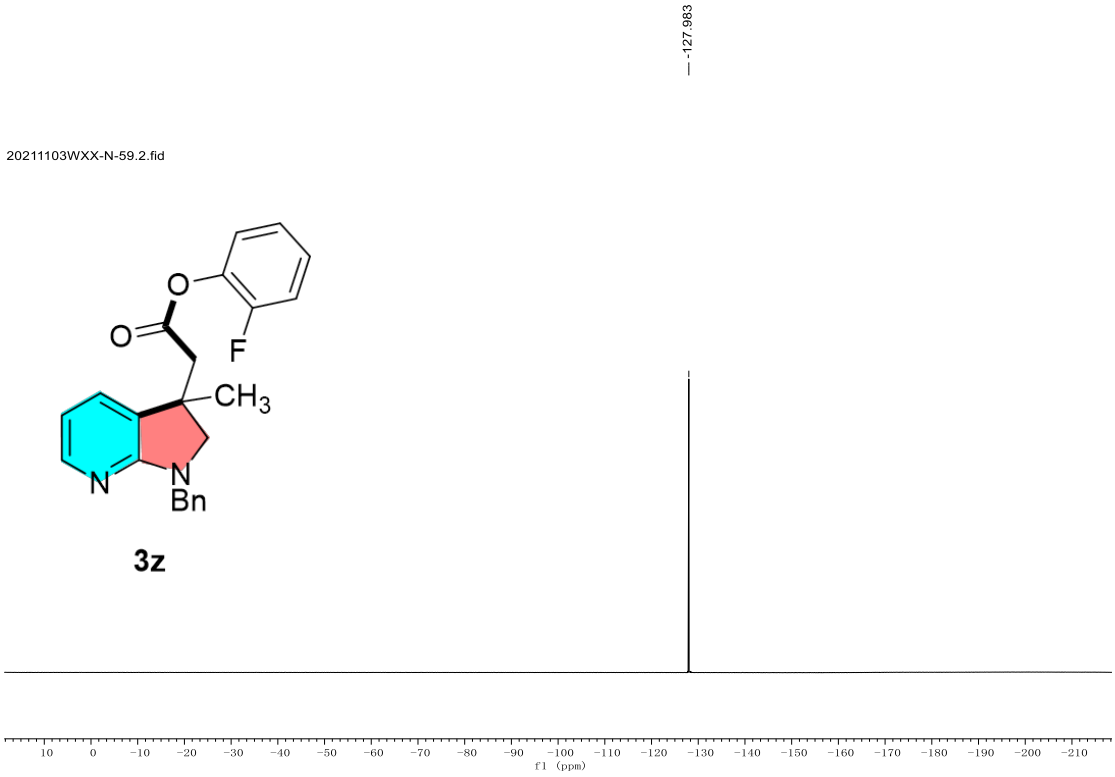


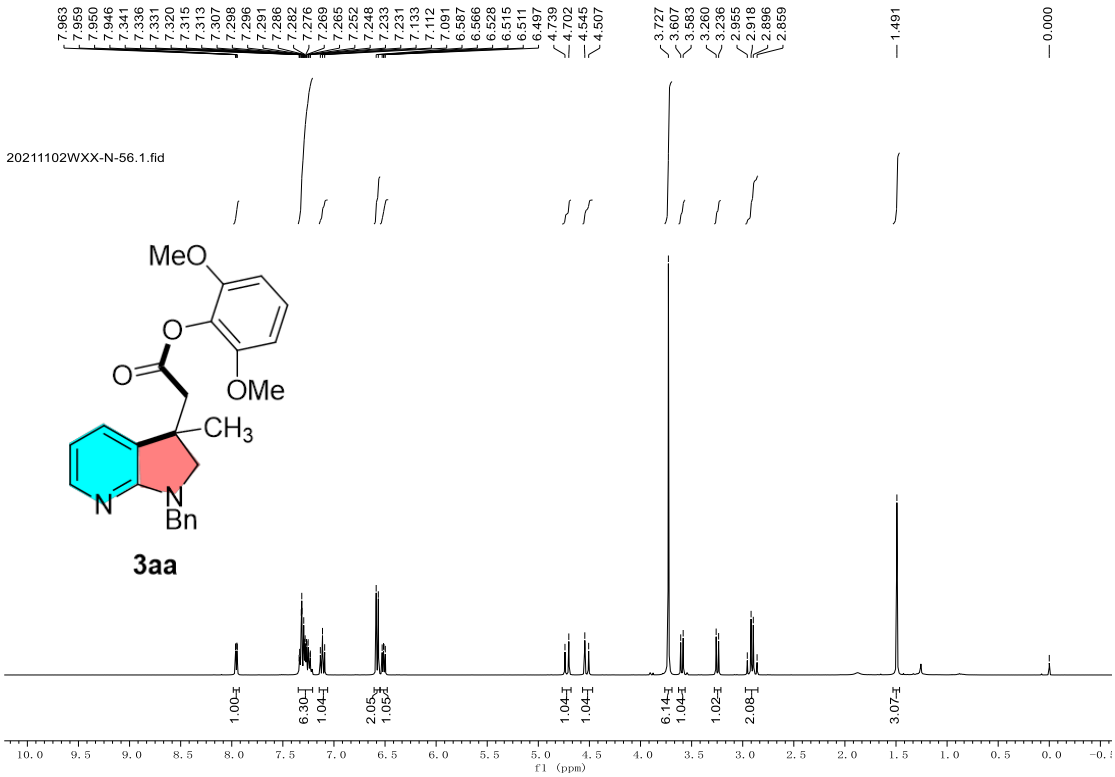
(**3z**, ^{13}C NMR, $CDCl_3$, 101 MHz)



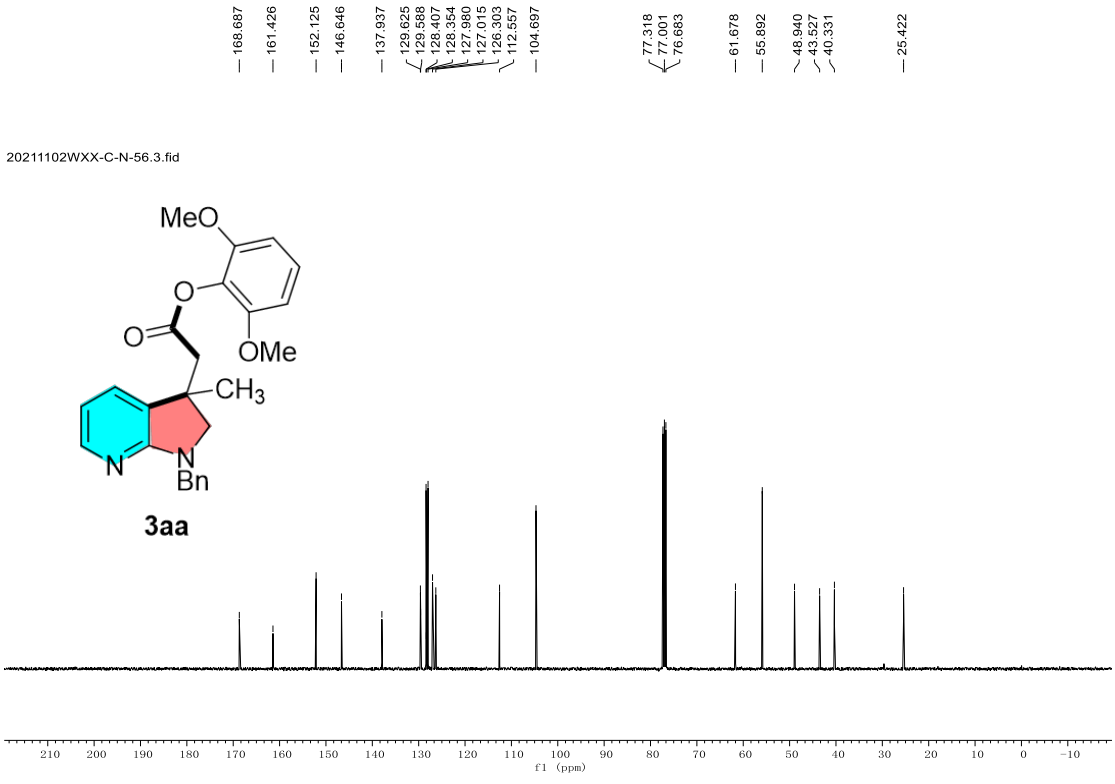
(**3z**, ^{19}F NMR, $CDCl_3$, 376 MHz)



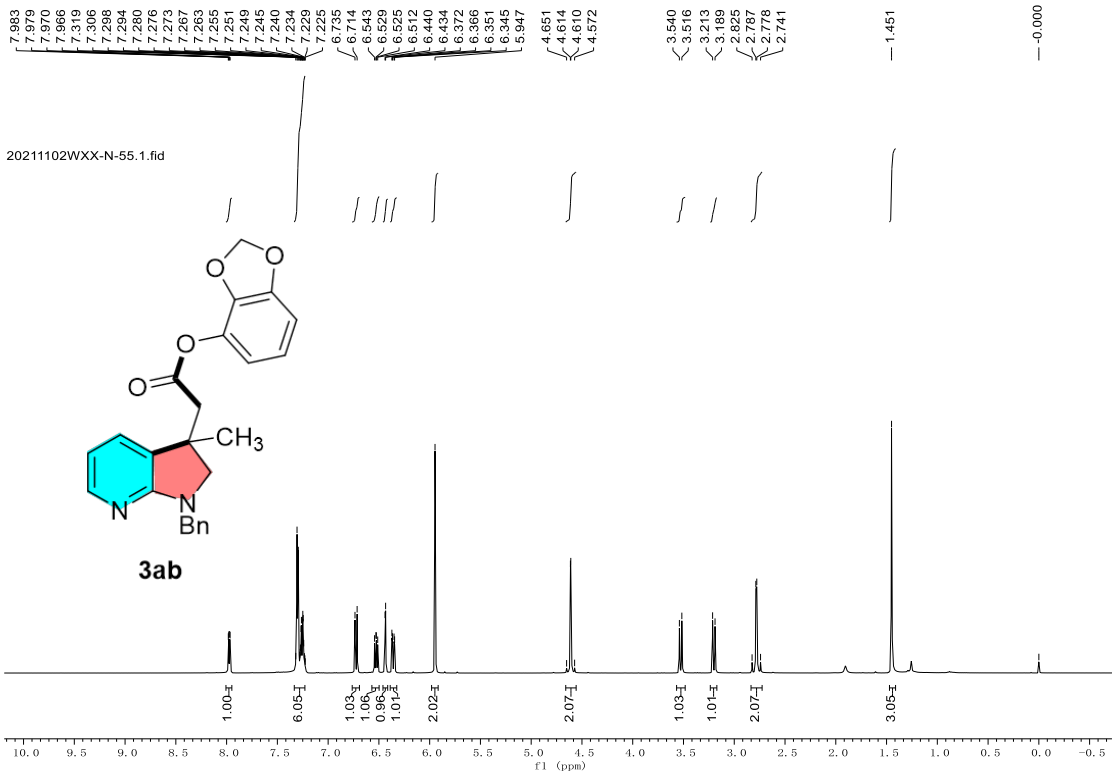
(**3aa**, ^{1}H NMR, $CDCl_3$, 400 MHz)



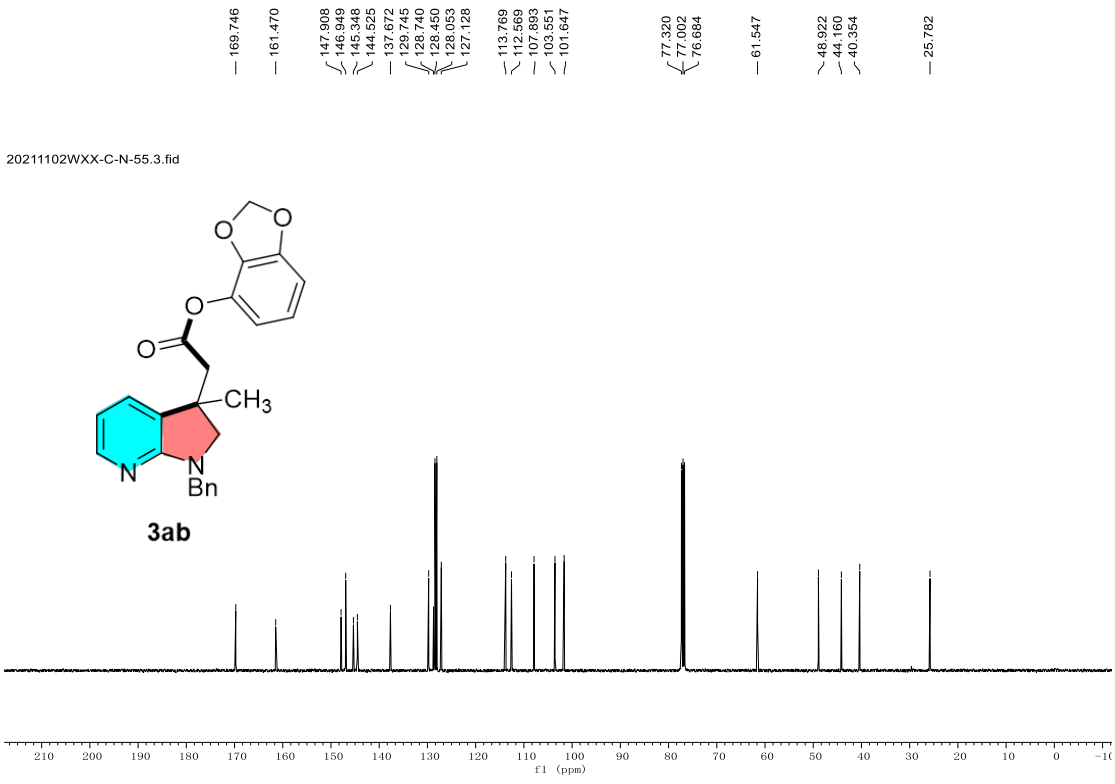
(**3aa**, ^{13}C NMR, $CDCl_3$, 101 MHz)



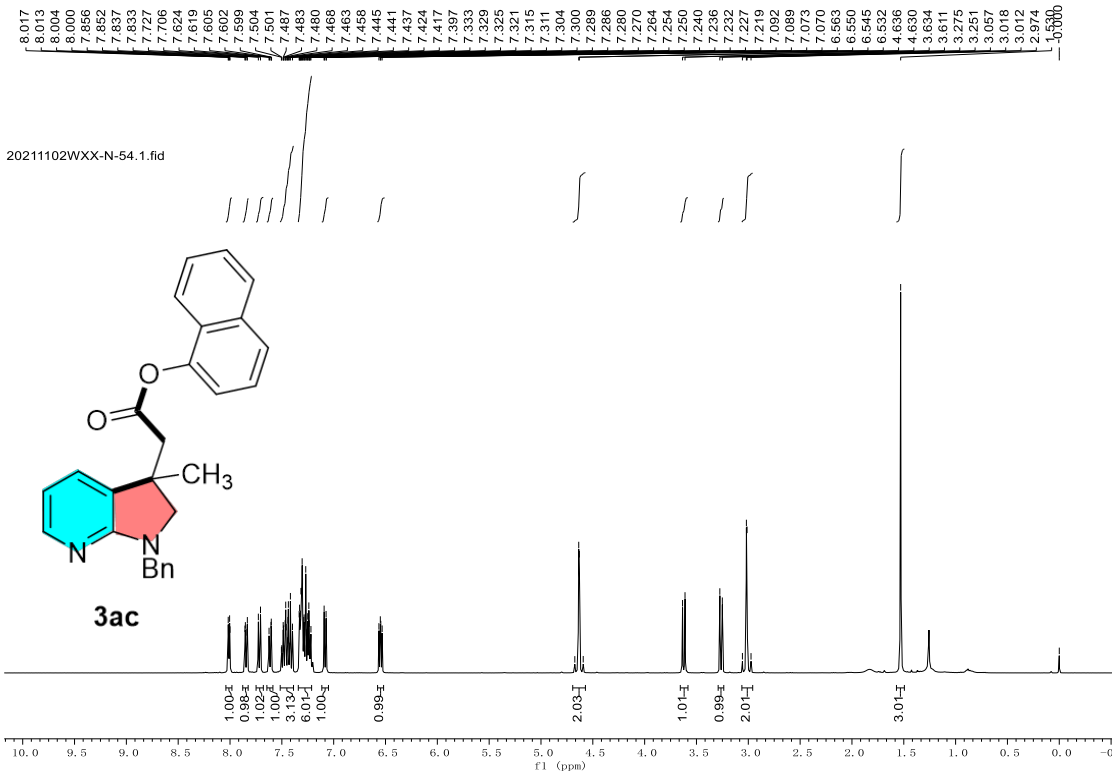
(**3ab**, ^{1}H NMR, $CDCl_3$, 400 MHz)



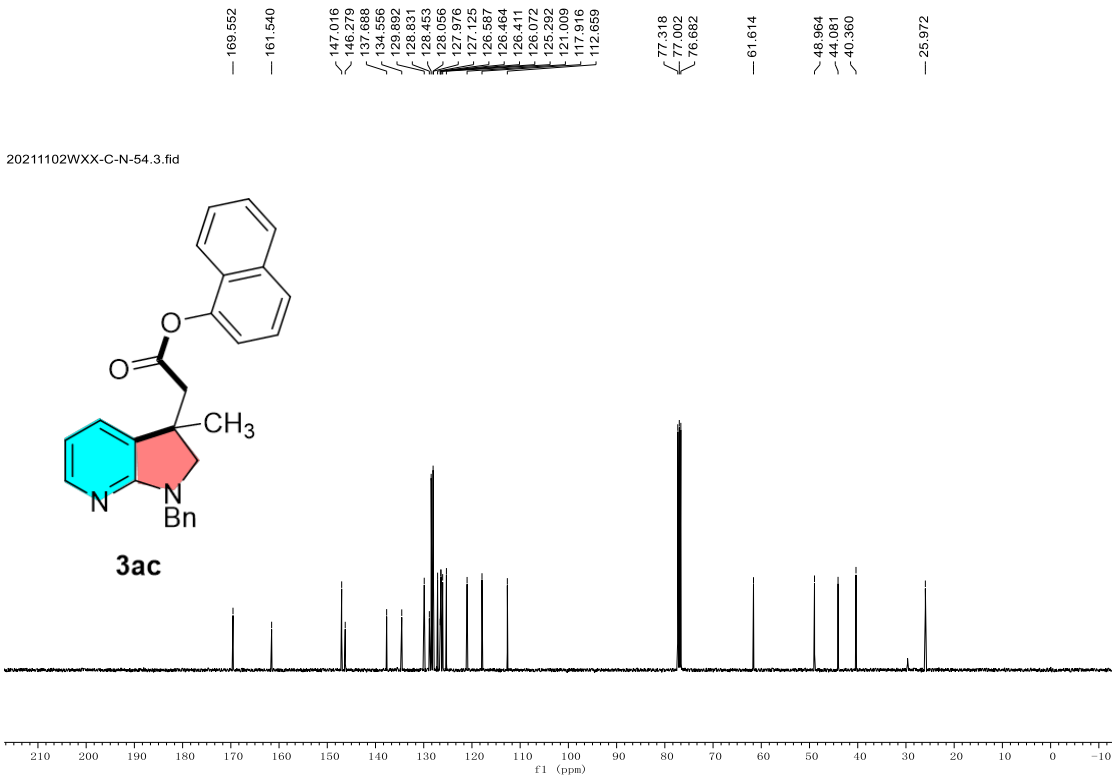
(**3ab**, ^{13}C NMR, $CDCl_3$, 101 MHz)



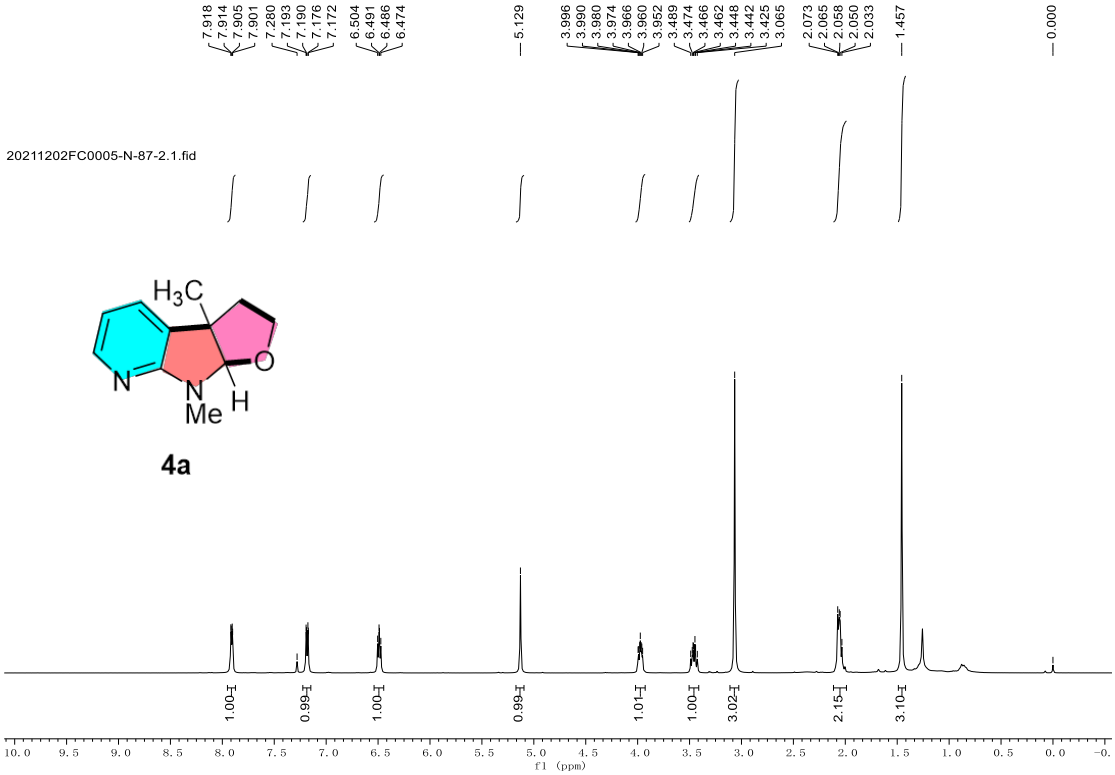
(**3ac**, ^{1}H NMR, $CDCl_3$, 400 MHz)



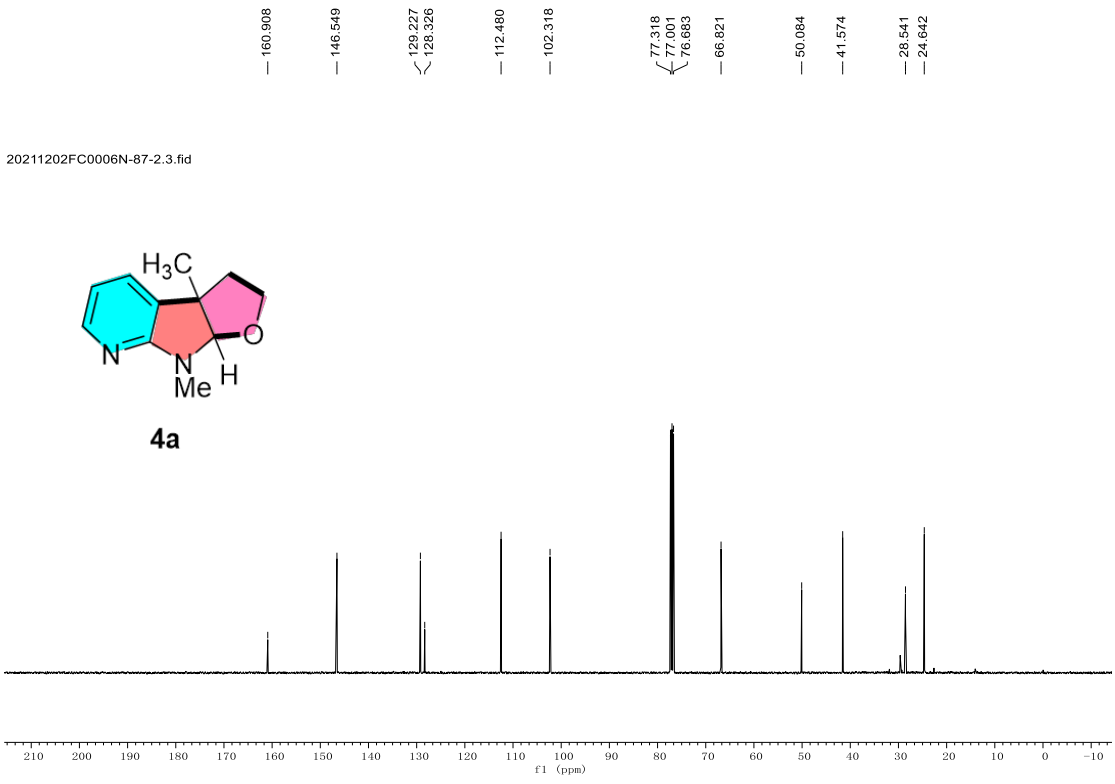
(**3ac**, ^{13}C NMR, $CDCl_3$, 101 MHz)



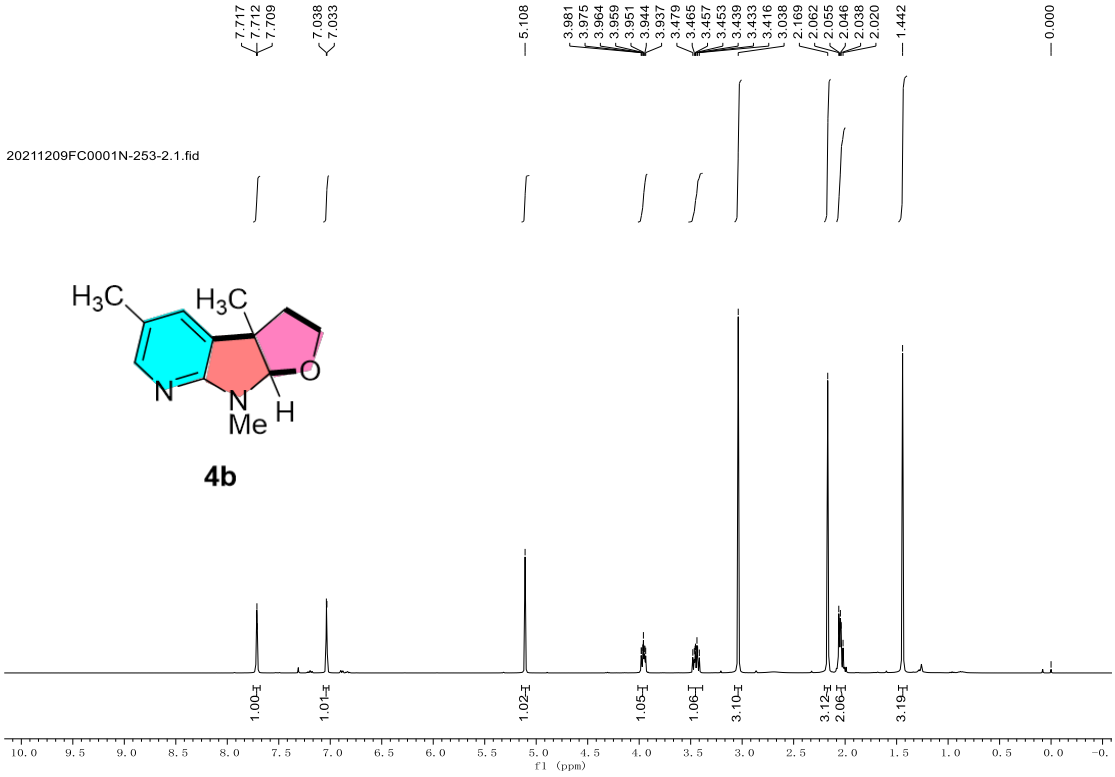
(**4a**, ^{1}H NMR, $CDCl_3$, 400 MHz)



(**4a**, ^{13}C NMR, $CDCl_3$, 101 MHz)

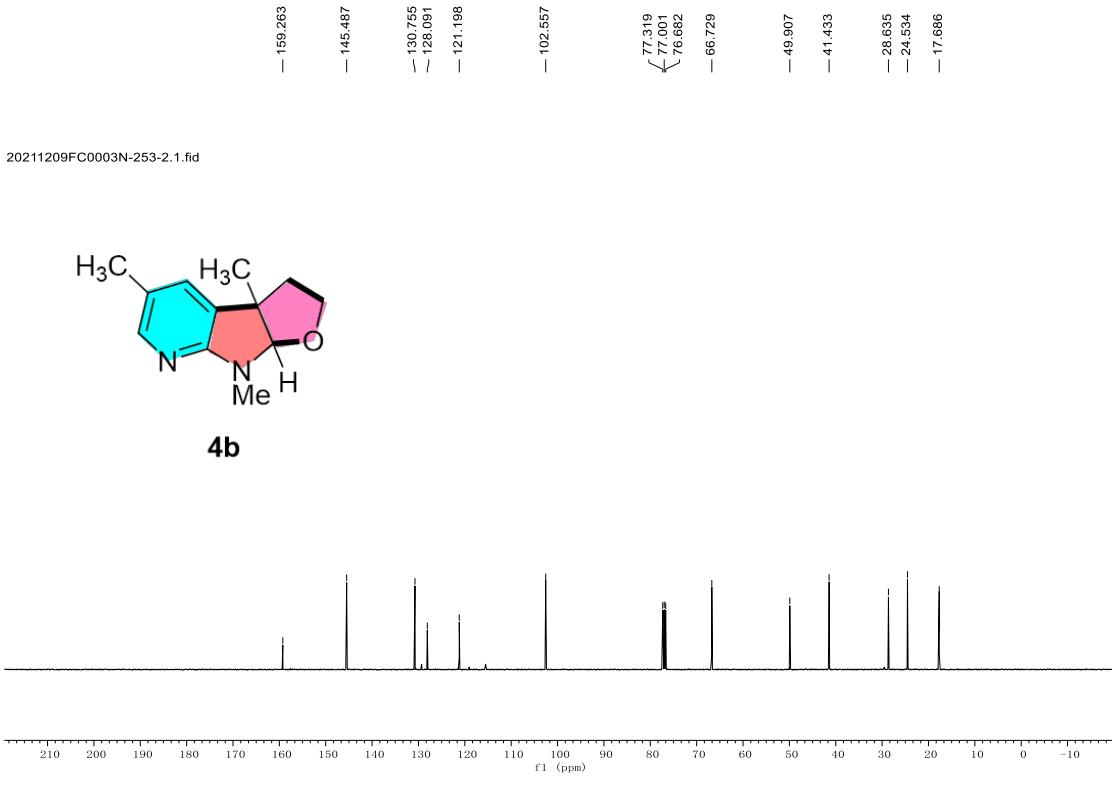


(**4b**, ^{1}H NMR, $CDCl_3$, 400 MHz)



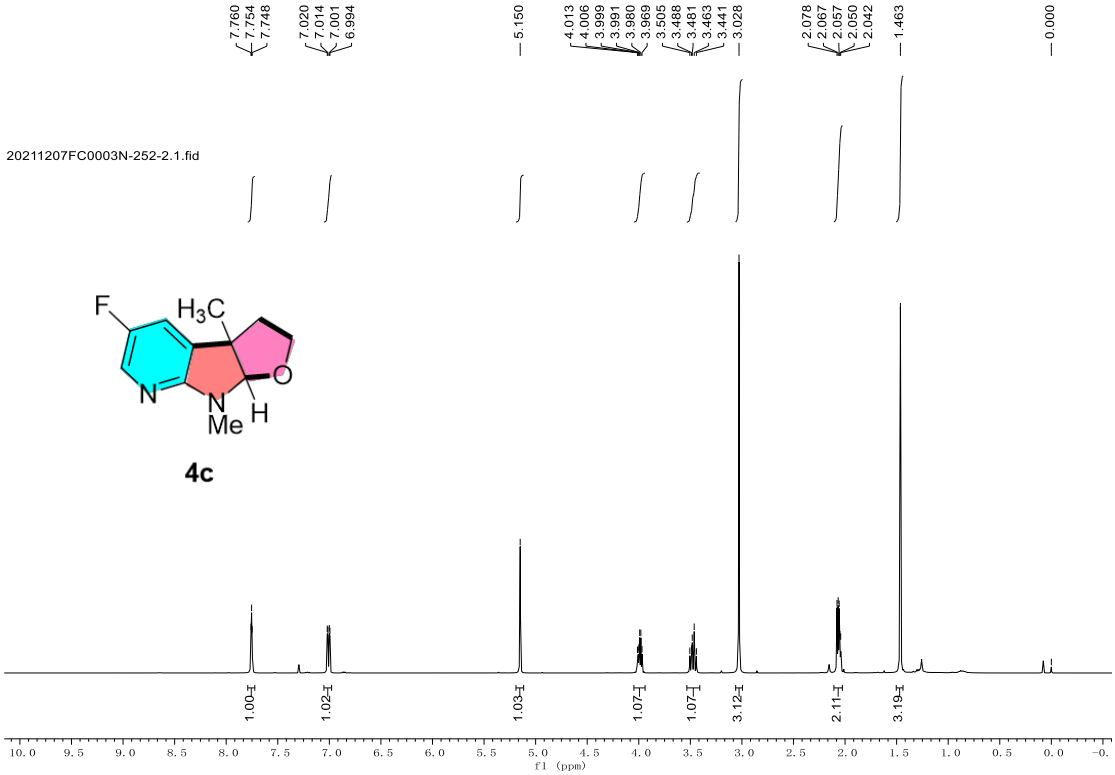
4b

(**4b**, ^{13}C NMR, $CDCl_3$, 101 MHz)

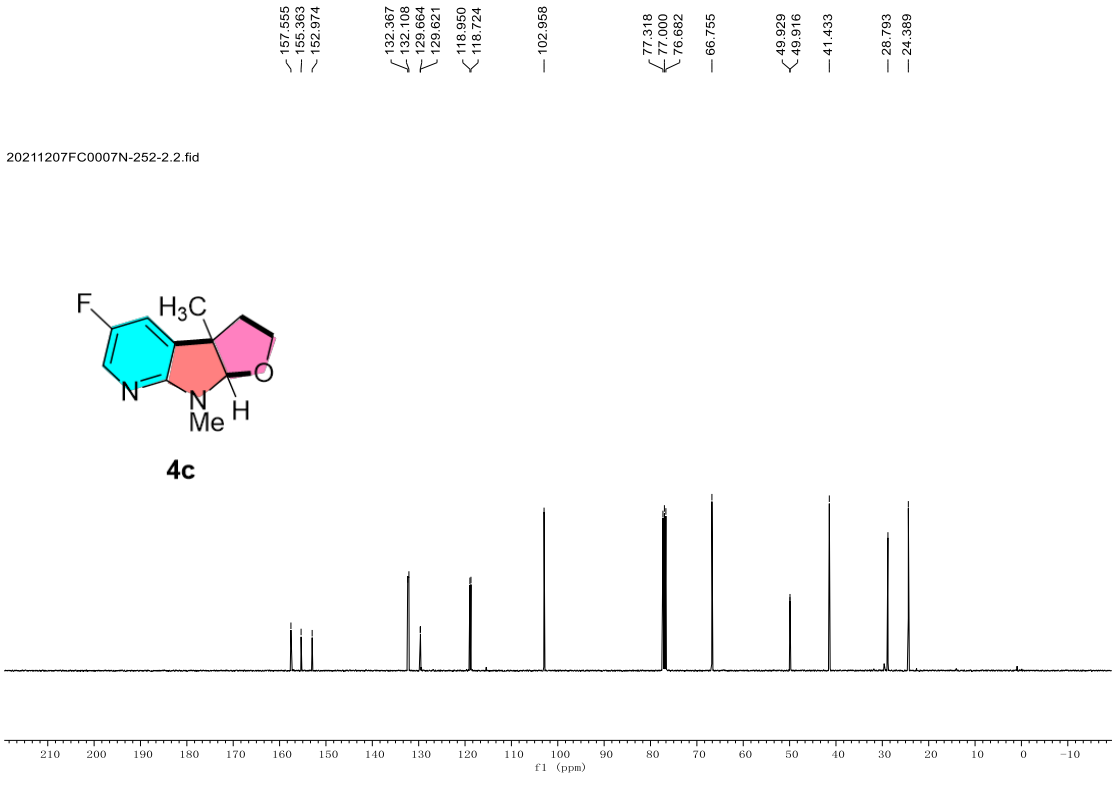


4b

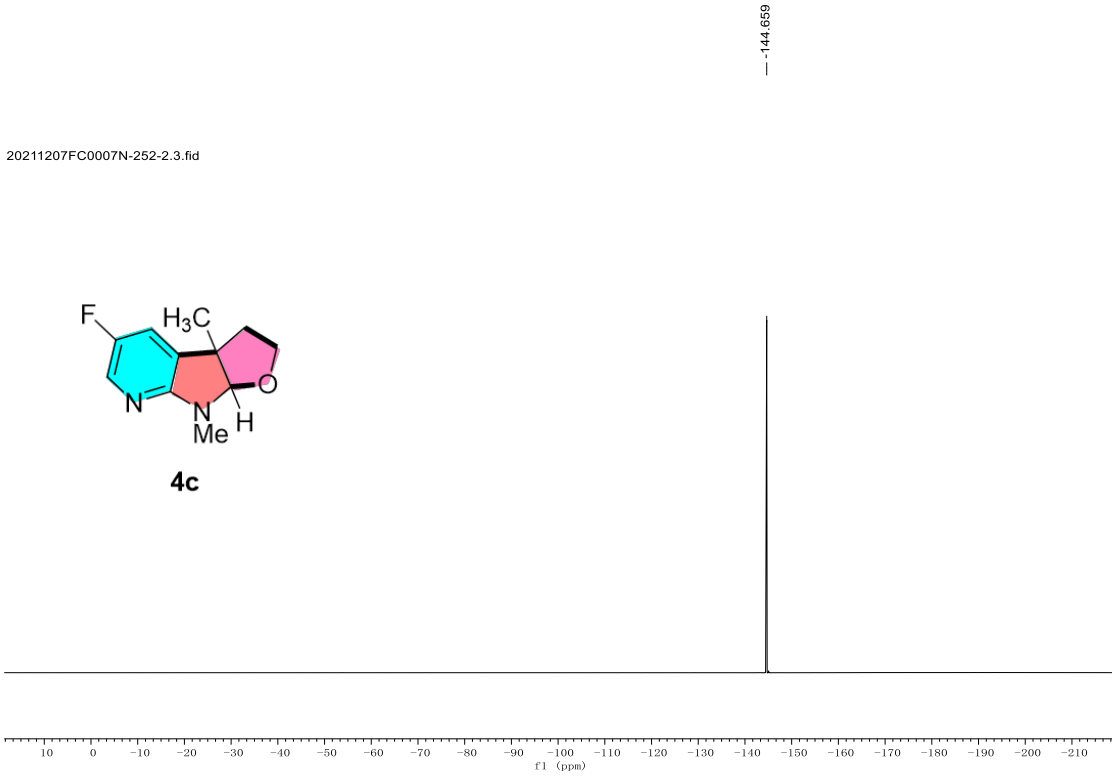
(**4c**, ^{1}H NMR, $CDCl_3$, 400 MHz)



(**4c**, ^{13}C NMR, $CDCl_3$, 101 MHz)

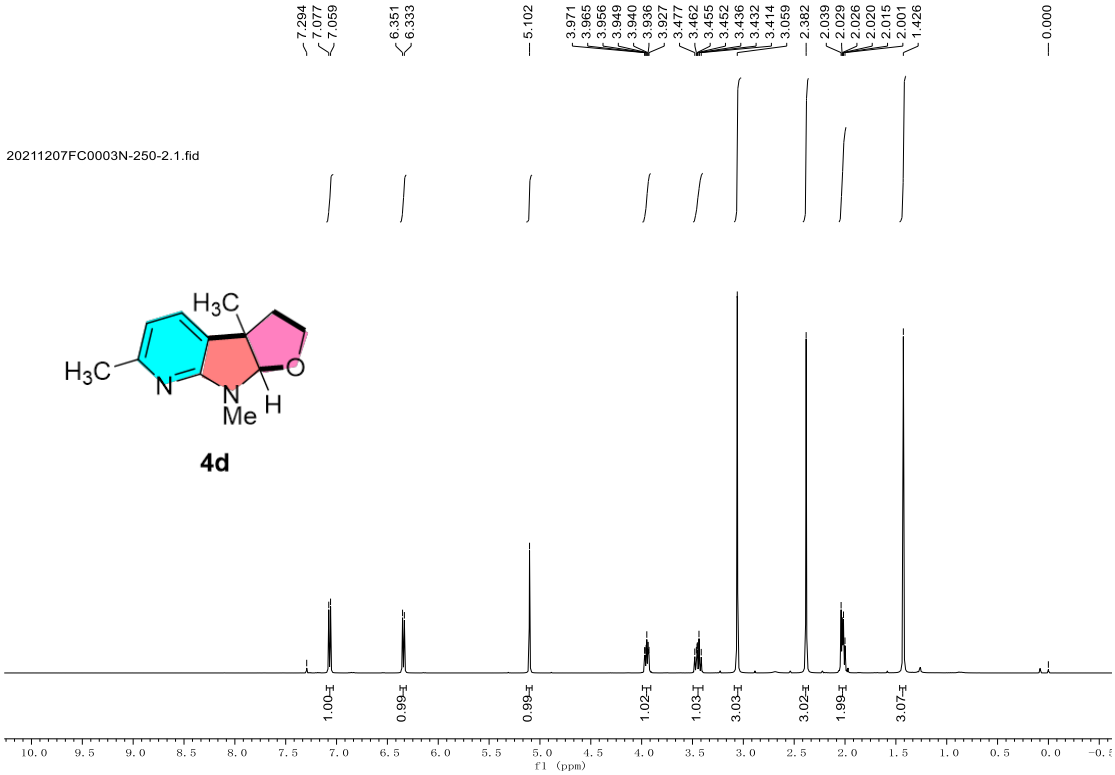


(**4c**, ^{19}F NMR, $CDCl_3$, 376 MHz)



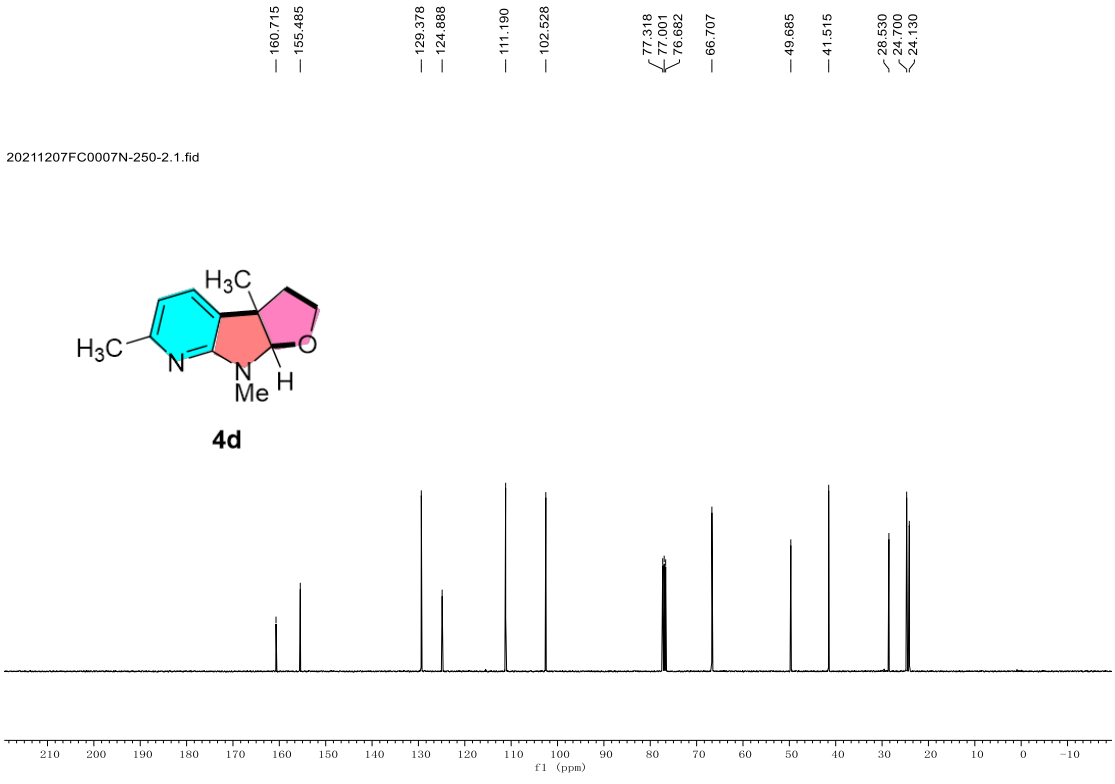
4c

(**4d**, ^{1}H NMR, $CDCl_3$, 400 MHz)



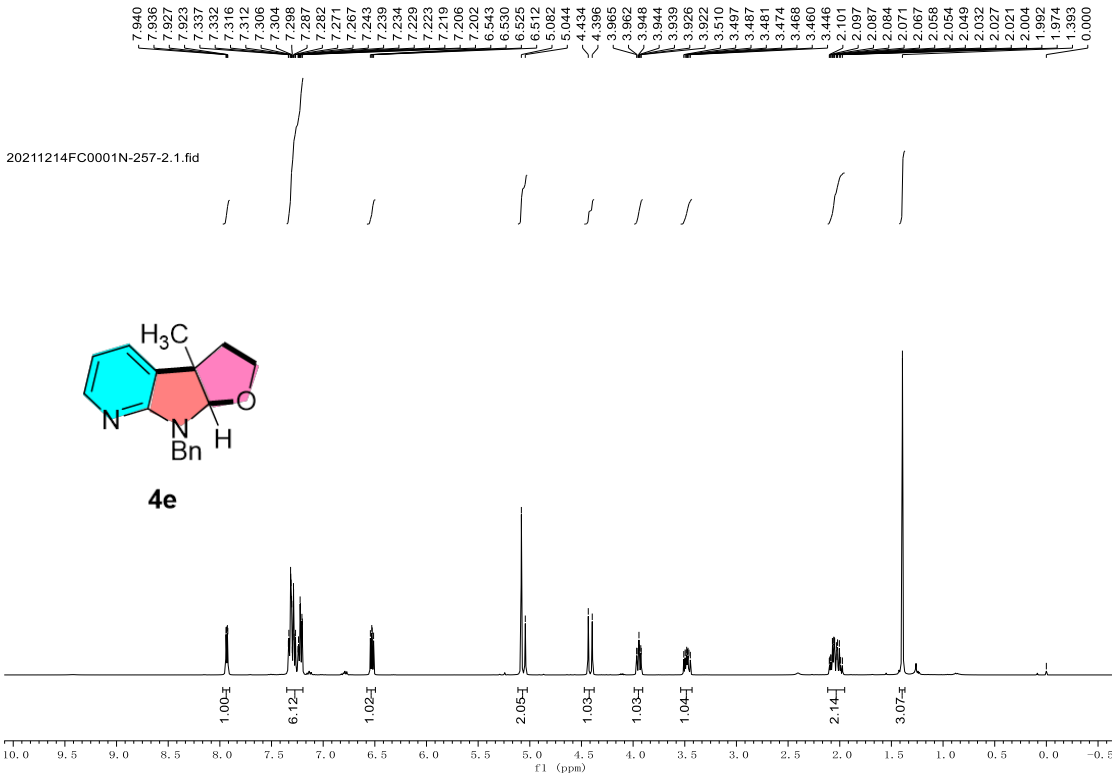
4d

(**4d**, ^{13}C NMR, $CDCl_3$, 101 MHz)

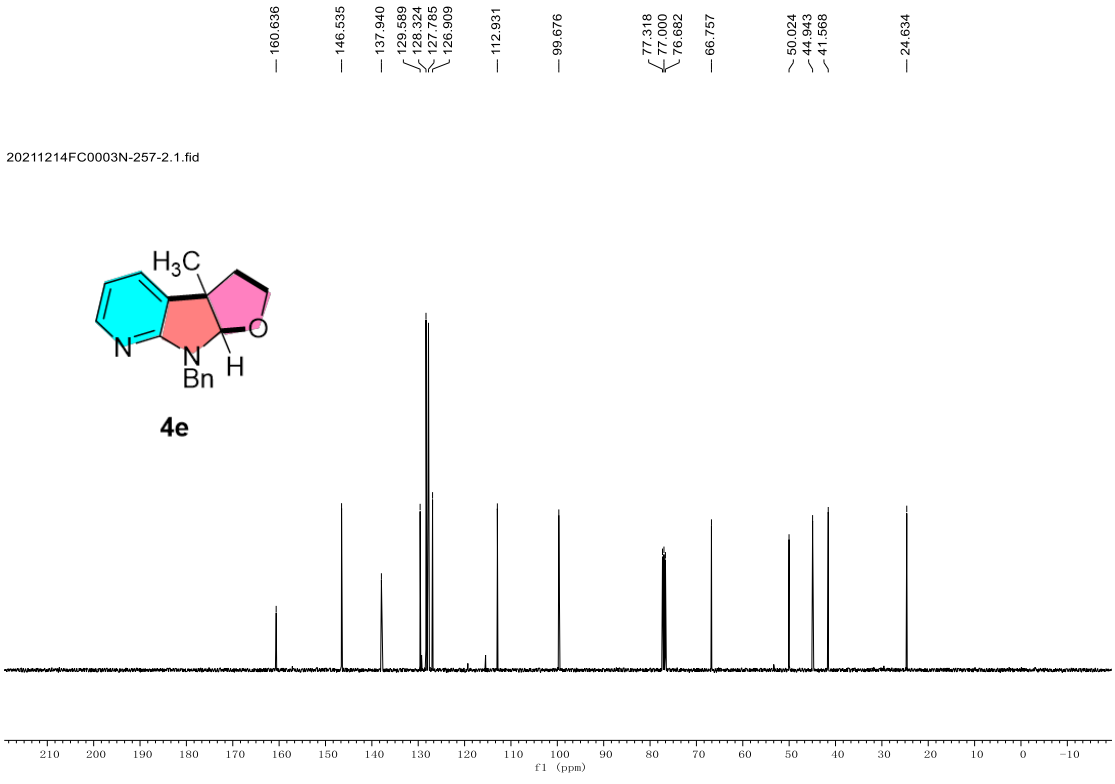


4d

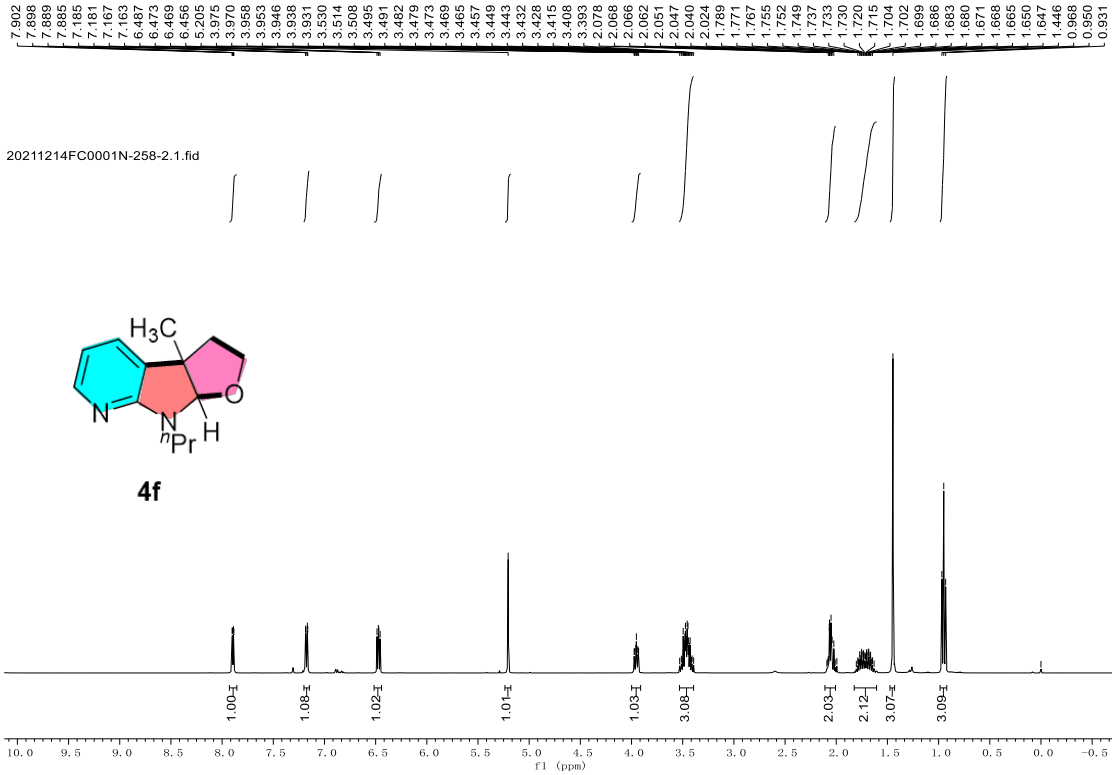
(**4e**, ^{1}H NMR, $CDCl_3$, 400 MHz)



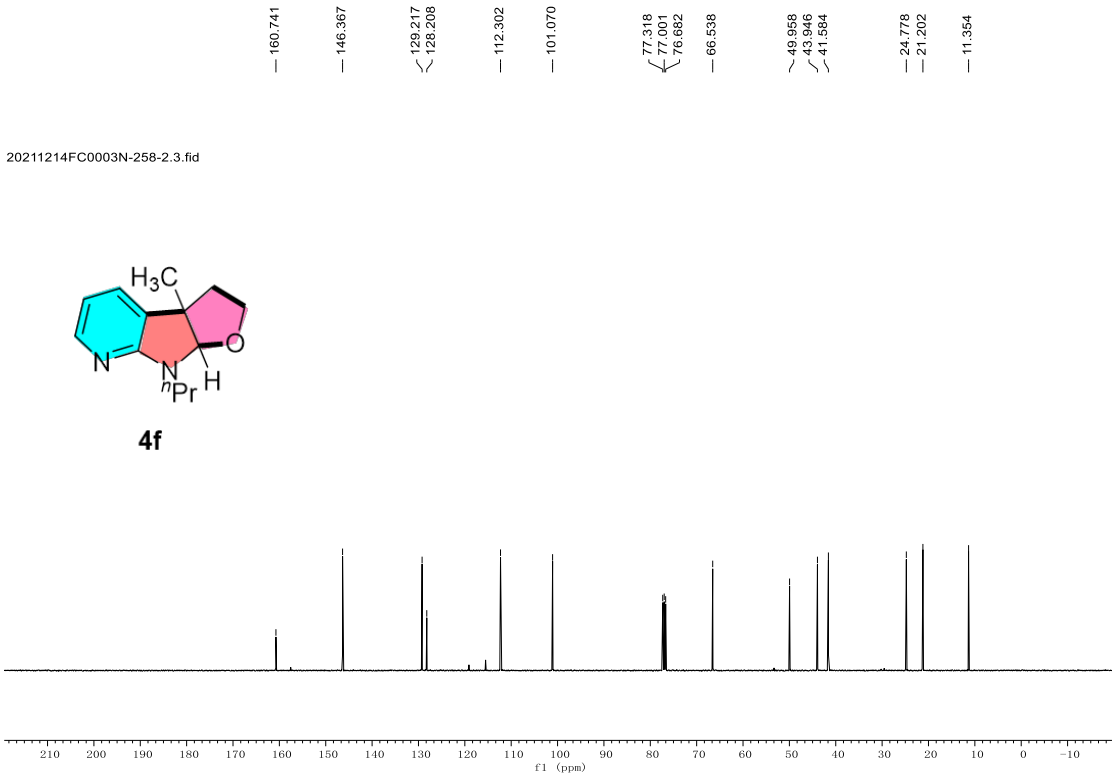
(**4e**, ^{13}C NMR, $CDCl_3$, 101 MHz)



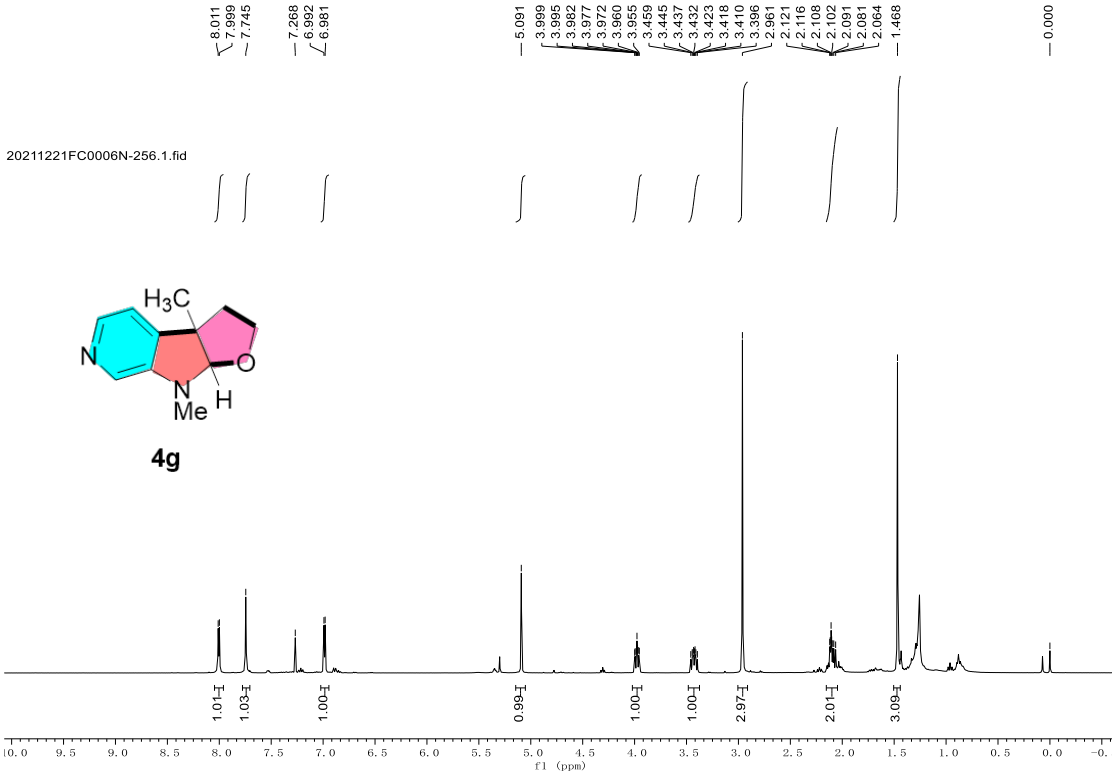
(**4f**, ^{1}H NMR, $CDCl_3$, 400 MHz)



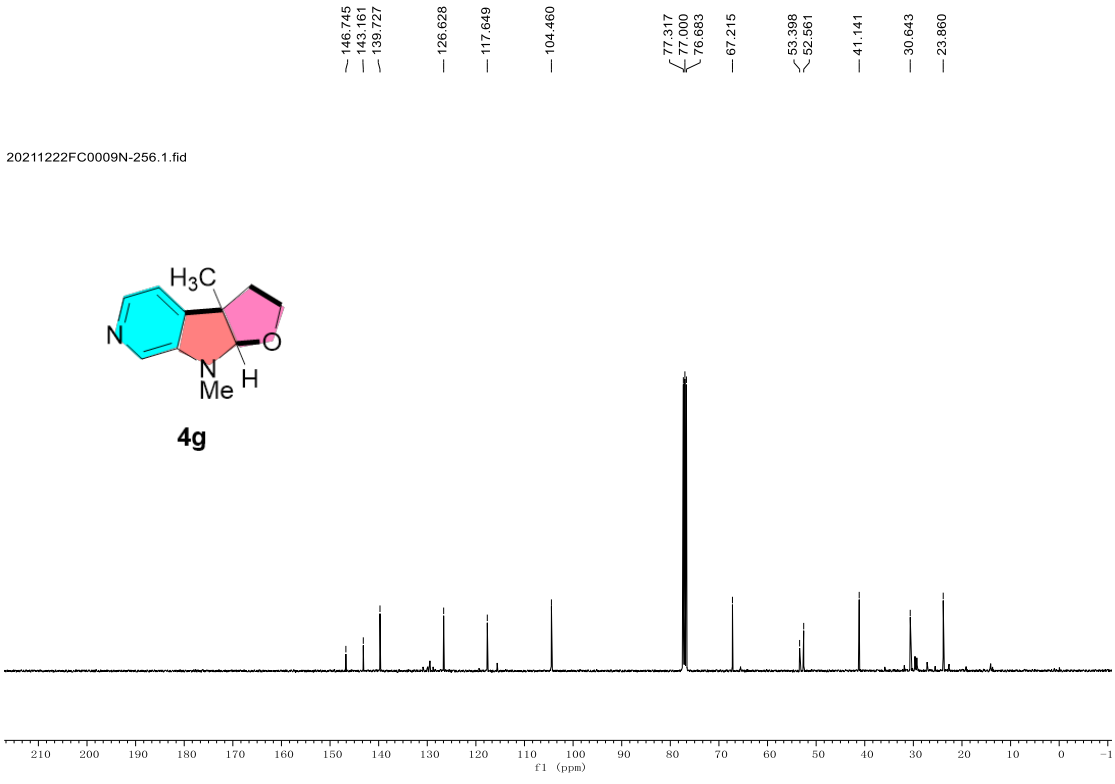
(**4f**, ^{13}C NMR, $CDCl_3$, 101 MHz)



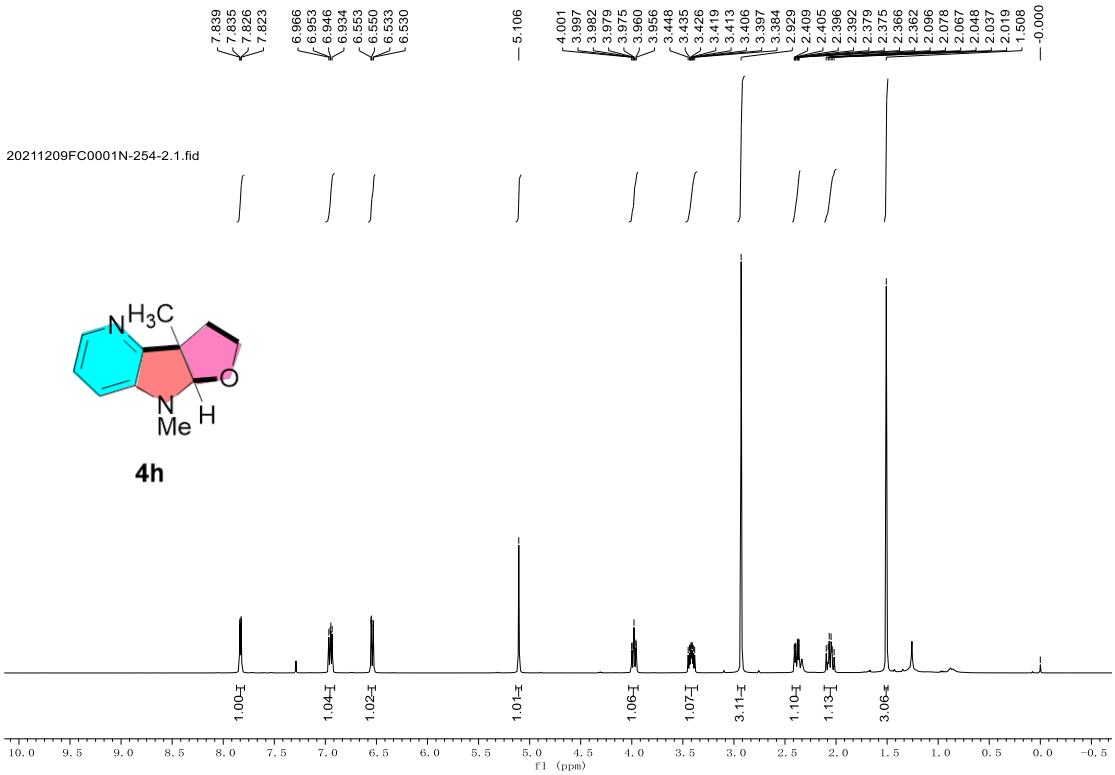
(**4g**, ^{1}H NMR, $CDCl_3$, 400 MHz)



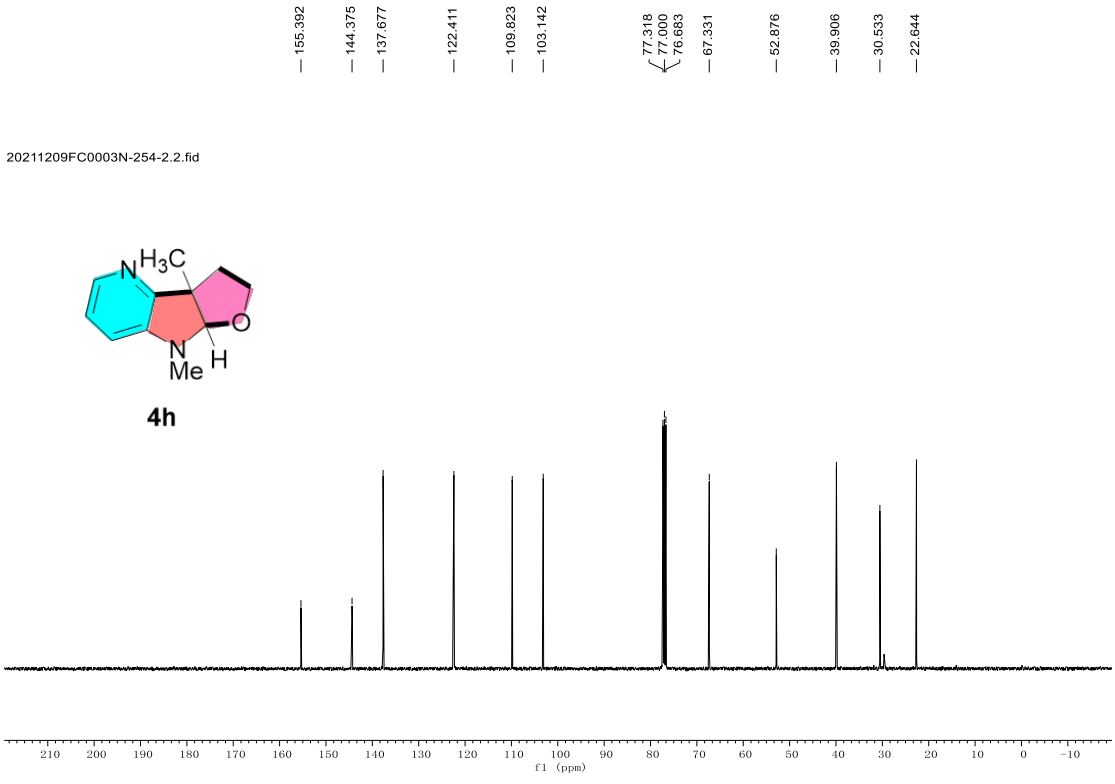
(**4g**, ^{13}C NMR, $CDCl_3$, 101 MHz)



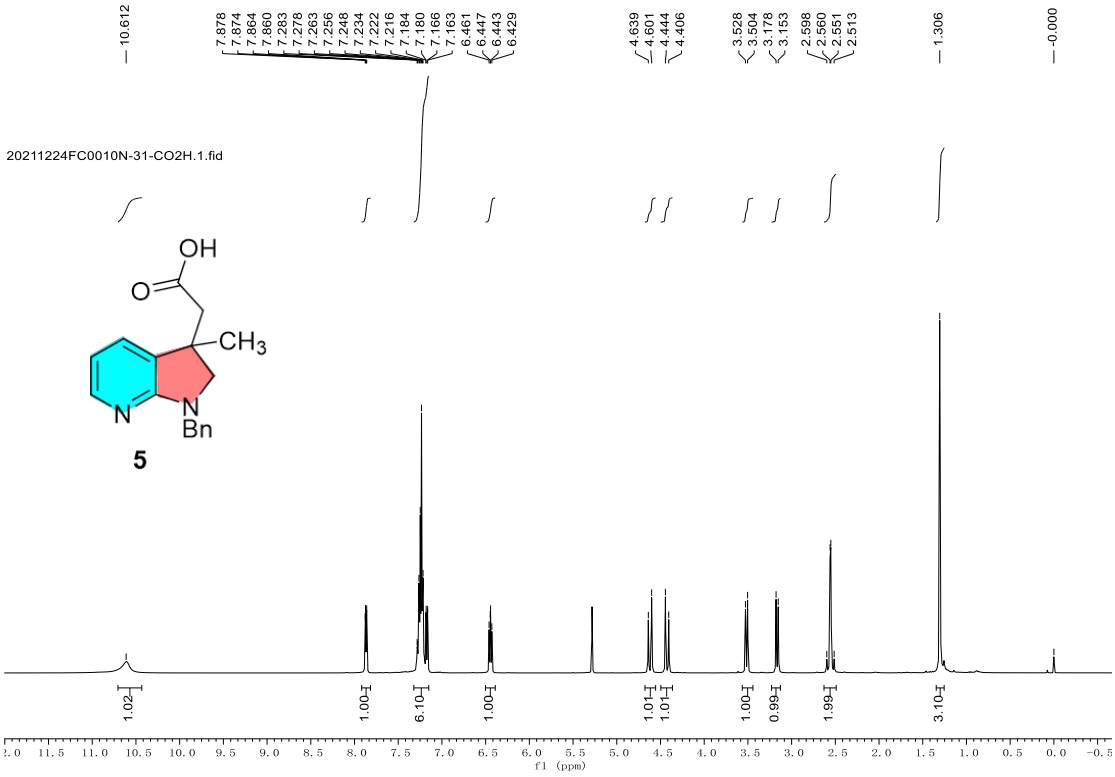
(**4h**, ^{1}H NMR, $CDCl_3$, 400 MHz)



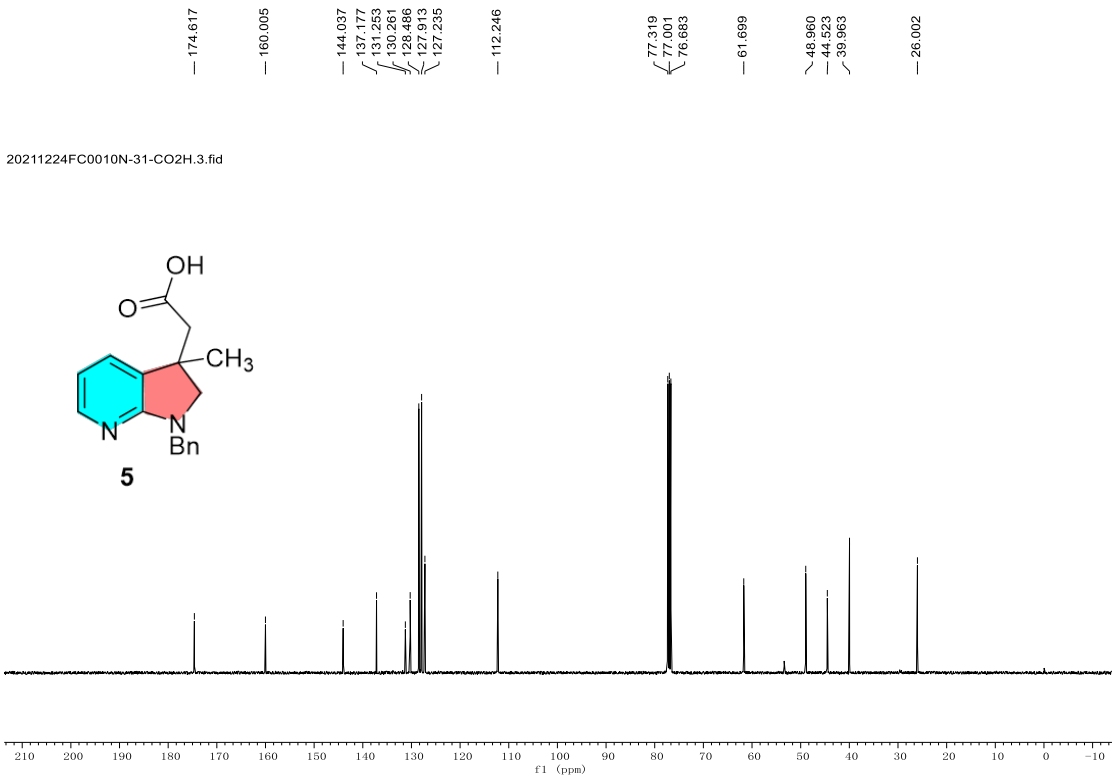
(**4h**, ^{13}C NMR, $CDCl_3$, 101 MHz)



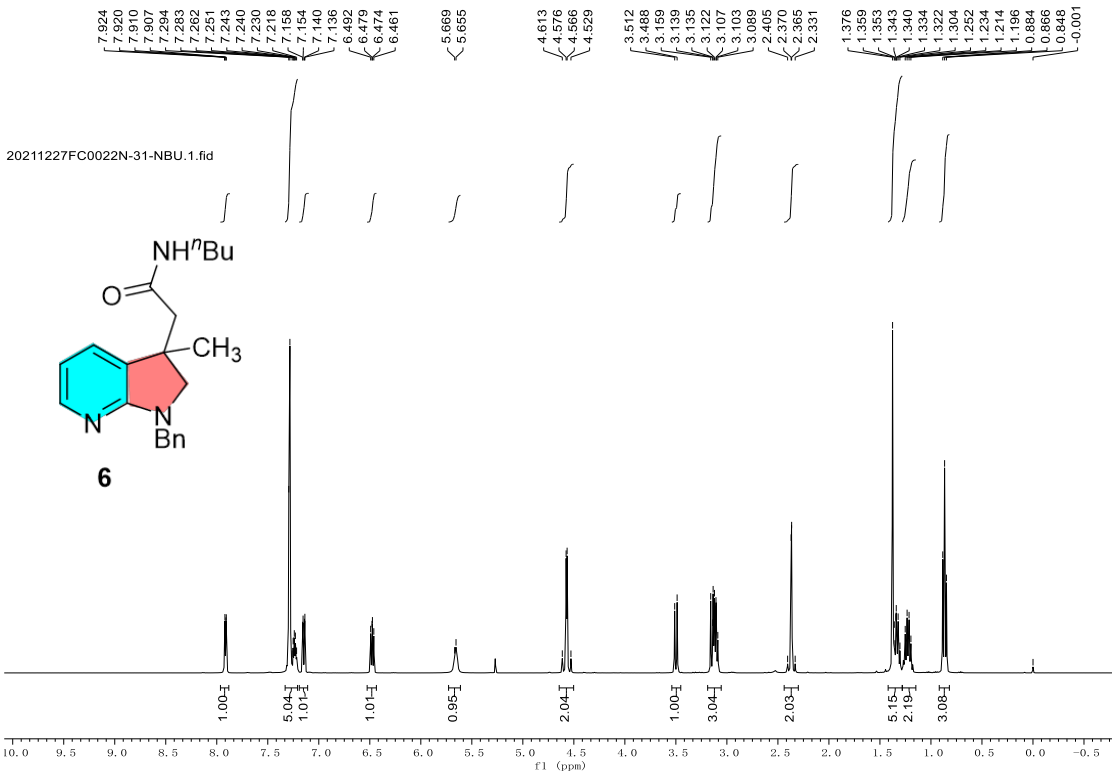
(**5**, ^{1}H NMR, $CDCl_3$, 400 MHz)



(**5**, ^{13}C NMR, $CDCl_3$, 101 MHz)



(**6**, ^{1}H NMR, $CDCl_3$, 400 MHz)



(**6**, ^{13}C NMR, $CDCl_3$, 101 MHz)