Rhodium(III)-catalyzed oxidative alkylation of *N*-aryl-7-azaindoles with cyclopropanols

Jidan Liu,*[a] Jinyuan Jiang,[a] Zhenke Yang,[a] Qiaohai Zeng,[a] Jieying Zheng,[a] Siying Zhang,[a] Liyao Zheng,[a] Shang-Shi Zhang,[b] and Zhao-Qing Liu*[a]

[a]*School of Chemistry and Chemical Engineering/Institute of Clean Energy and Materials/Guangzhou Key Laboratory for Clean Energy and Materials, Guangzhou University, Guangzhou, 510006, P. R. China*

[b]*Center for Drug Research and Development, Guangdong Pharmaceutical University, Guangzhou, 510006, P. R. China*

Supporting information

Table of contents

1. General information and starting materials

N-substituted-7-azaindoles[1] and cyclopropanols[2] were prepared according to the reported procedures. Other reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted. All reactions were carried out using Schlenk techniques or in a nitrogen-filled glovebox. NMR spectra were recorded on the Bruker spectrometer in $CDCl_3$ at room temperature. ^1H NMR (500 MHz or 600 MHz) chemical shifts (δ) were referenced to internal standard TMS (δ = 0.00 ppm), and $^{13}C\{^1H\}$ NMR (126 MHz or 151 MHz) chemical shifts were referenced to internal solvent $CDCl_3$ (δ = 77.16 ppm) and chemical shifts are reported as parts per million (ppm). Resonance patterns are reported with the notations s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), quint (quintet), sext (sextet), and m (multiplet). Coupling constants (*J*) are reported in hertz (Hz). HRMS data were recorded on a JEOL JMS-600 spectrometer with electron spray ionization (ESI) source. The melting points were uncorrected. Products were purified by flash column chromatography on silica gel (200-300 mesh) with freshly distilled ethyl acetate (EA) and petroleum ether (PE).

2. General procedure for the synthesis of 3

To an oven-dried sealed tube charged with *N*-phenyl-7-azaindole **1a** (38.8 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (5 mg, 4 mol %), CsOAc (7.6 mg, 20 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (80 mg, 0.4 mmol) were added 1-benzylcyclopropanol **2a** (44.5 mg, 0.3 mmol) and methanol (1 mL) at room temperature. The reaction mixture was allowed to stir in an oil bath at 50 °C for 4 h. Then the reaction mixture was diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 15:1) to afford 58.5 mg of **3a** in 86% yield.

3. General procedure for the synthesis of 4

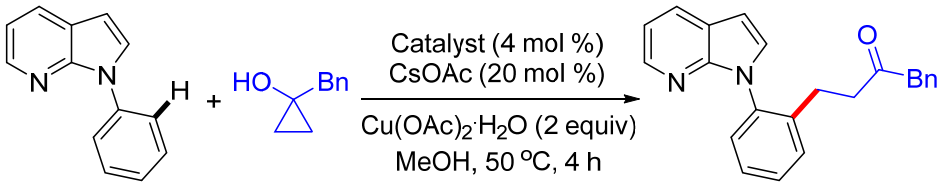
To an oven-dried sealed tube charged with 3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylpropan-1-one **3f** (65.2 mg, 0.2 mmol), and $Cu(OAc)_2$ (109 mg, 0.6 mmol) was added anhydrous toluene (1 mL) at room temperature. The reaction mixture was allowed to stir in an oil bath at 130 °C under N_2 for 2 h. Then the reaction mixture was diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 20:1) to afford the product **4a** as an orange solid (37.4 mg, 58%).

4. Gram-scale synthesis of 3a

To a 100 mL round-bottomed flask charged with *N*-phenyl-7-azaindole **1a** (776 mg, 4 mmol), $[RhCp^*Cl_2]_2$ (99 mg, 4 mol %), CsOAc (154 mg, 20 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (1.6 g, 8 mmol) were added 1-benzylcyclopropanol **2a** (890 mg, 6 mmol) and methanol (20 mL) at room temperature. The reaction mixture was allowed to stir in an oil bath at 50 °C for 12 h. Then the reaction mixture was diluted with EtOAc (60 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 15:1) to afford **3a** (1.02 g, 75%) as a colorless oil.

5. Optimization of reaction conditions

Table S1. Screening of other metal catalyst[a]



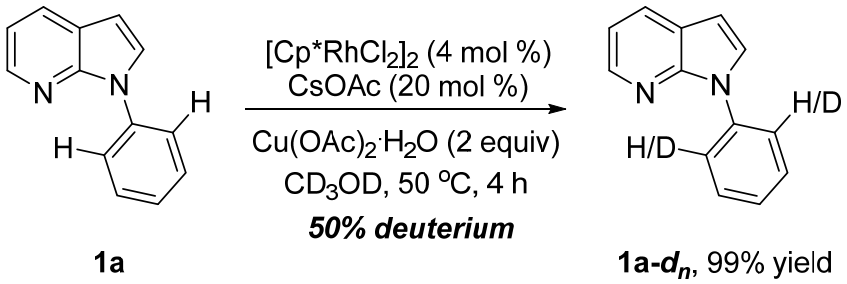
1a **2a** **3a**

entry	catalyst	yield (%)[b]
1	$[Ru(p\text{-cymene})Cl_2]_2$	6
2	$CoCp^*(CO)I_2$	trace
3	$[IrCp^*Cl_2]_2$	3
4	$Pd(OAc)_2$	0
5	$PdCl_2$	0
6	$CoCl_2$	0
7	$Co(OAc)_2{\cdot}4H_2O$	0
8	$NiCl_2$	0
9	$Ni(OAc)_2$	0

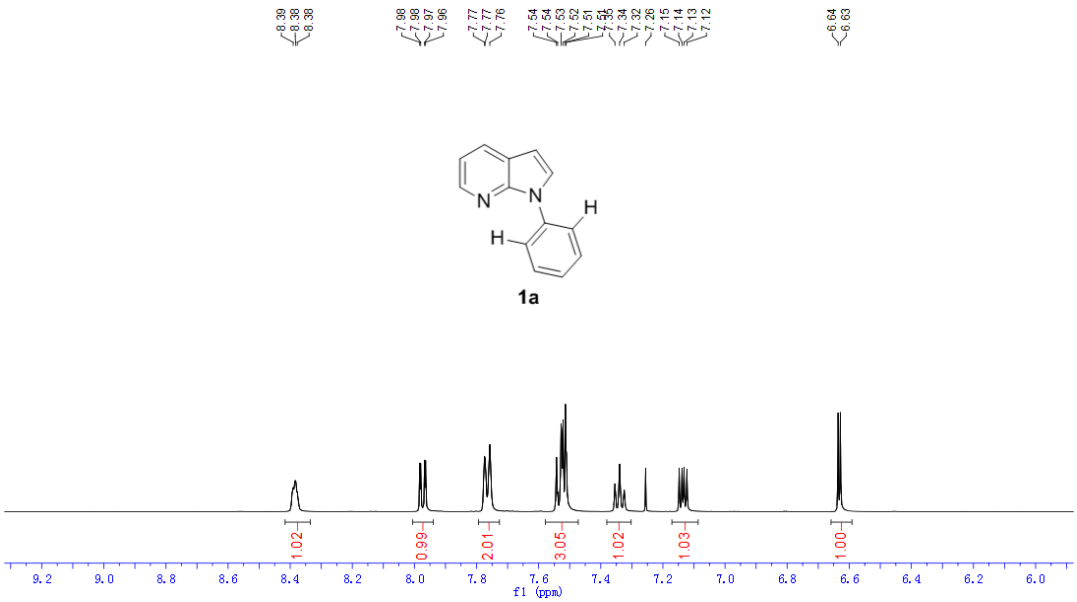
[a]Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (4 mol %), CsOAc (20 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (2 equiv) in MeOH (1 mL) in a sealed tube at 50 °C under N_2 for 4 h. [b]Isolated yield.

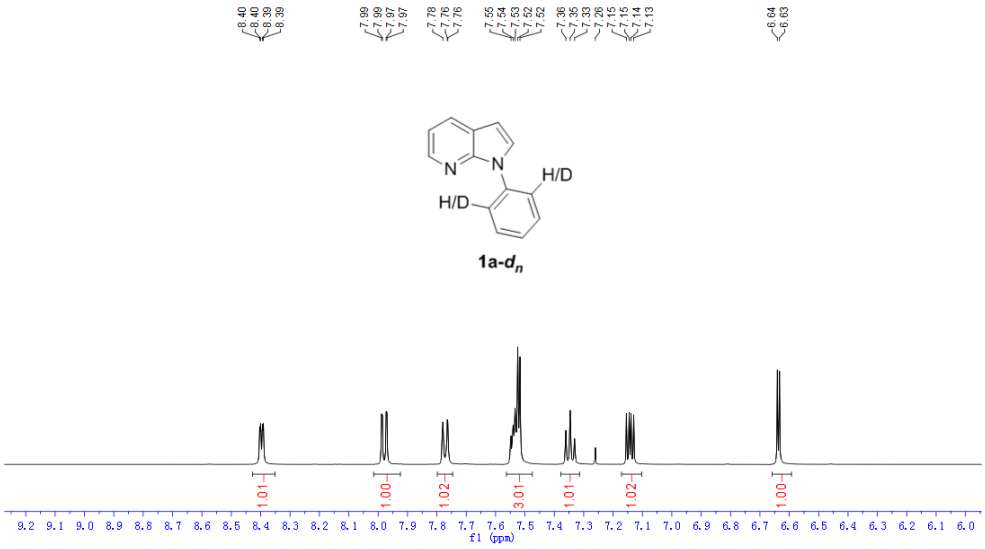
6. Preliminary mechanism studies

(a) *H/D exchange experiment*

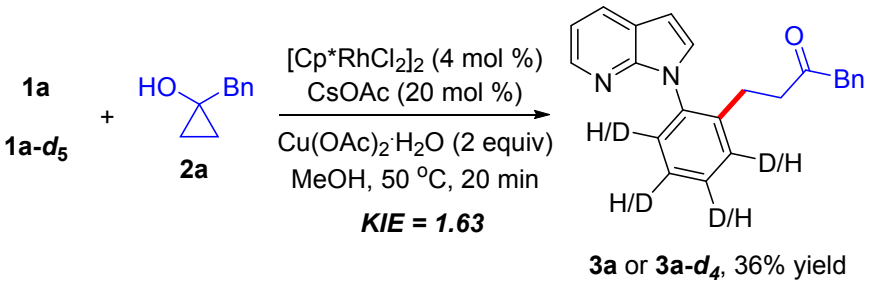


(a) H/D exchange experiment: To an oven-dried sealed tube charged with *N*-phenyl-7-azaindole **1a** (38.8 mg, 0.2 mmol), [RhCp*Cl_2]$_2$ (5 mg, 4 mol %), CsOAc (7.6 mg, 20 mol %), and Cu(OAc)$_2$·H_2O (80 mg, 0.4 mmol) were added 1-benzylcyclopropanol **2a** (44.5 mg, 0.3 mmol) and methanol-D_4 (1 mL) at room temperature. The reaction mixture was allowed to stir in an oil bath at 50 °C for 4 h. Then the reaction mixture was diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 15:1) to afford **deutrio-1a** in 99% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, J = 4.7, 1.5 Hz, 1H), 7.98 (dd, J = 7.8, 1.6 Hz, 1H), 7.80-7.75 (m, 1H), 7.56-7.47 (m, 3H), 7.36-7.33 (m, 1H), 7.14 (dd, J = 7.8, 4.7 Hz, 1H), 6.64 (d, J = 3.6 Hz, 1H).



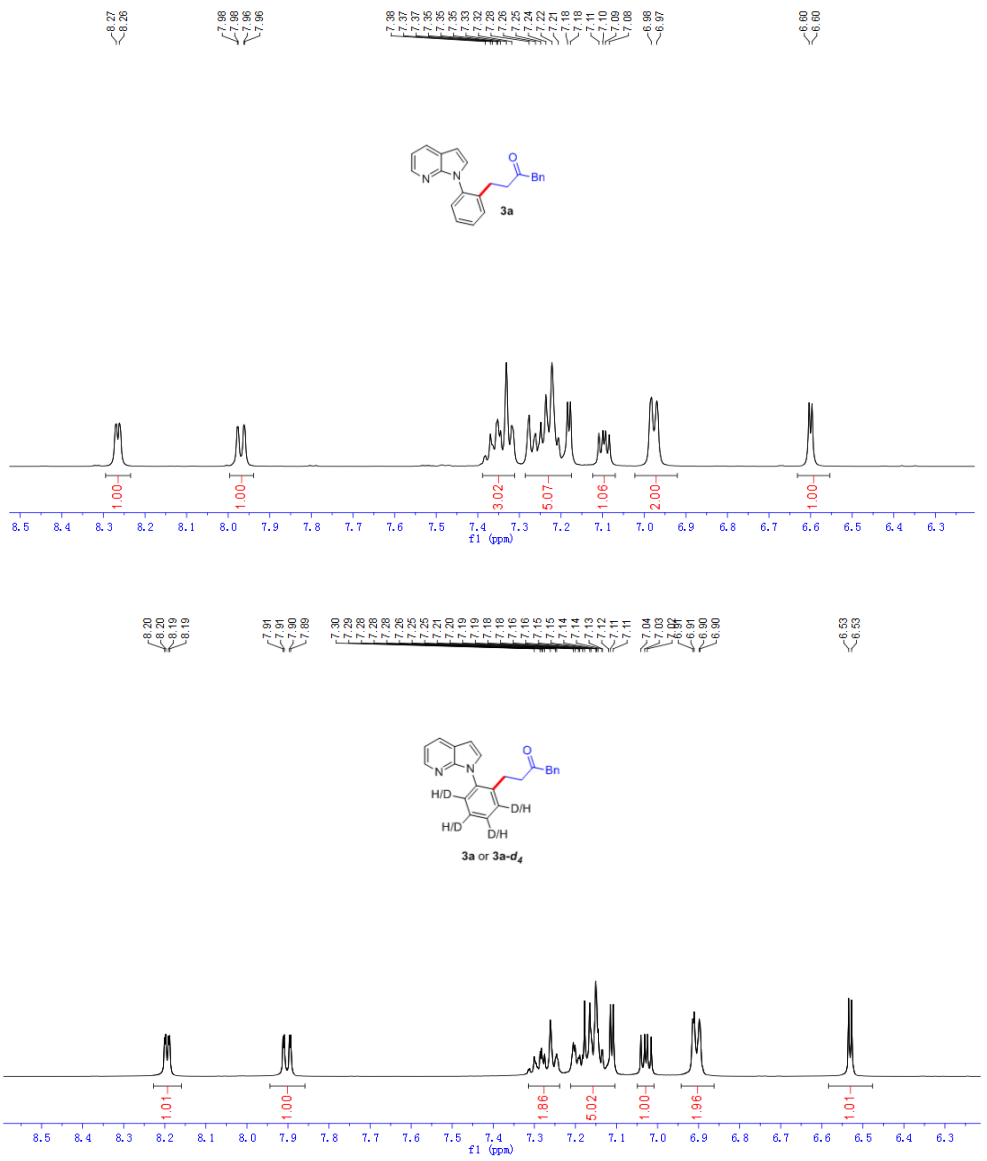


(b) ***Intermolecular competition experiment***

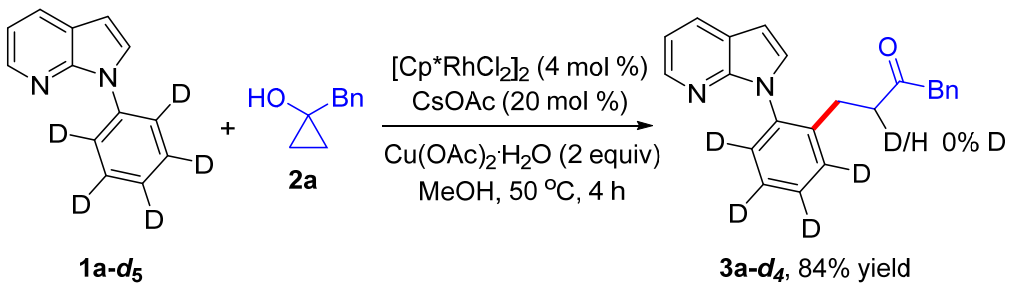


3a or **3a-*d*$_4$**, 36% yield

(b) Intermolecular competition experiment: To an oven-dried sealed tube charged with the mixture of *N*-phenyl-7-azaindole **1a** (19.4 mg, 0.1 mmol), **1a-d$_5$** (19.9 mg, 0.1 mmol), $[RhCp^*Cl_2]_2$ (5 mg, 4 mol %), CsOAc (7.6 mg, 20 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (80 mg, 0.4 mmol) were added 1-benzylcyclopropanol **2a** (44.5 mg, 0.3 mmol) and methanol (1 mL) at room temperature. The reaction mixture was allowed to stir in an oil bath at 50 °C for 20 min. Then the reaction mixture was diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 15:1) to afford **deutrio-3a** in 36% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, J = 4.7, 1.5 Hz, 1H), 7.90 (dd, J = 7.8, 1.5 Hz, 1H), 7.31-7.24 (m, 1.86H), 7.21-7.10 (m, 5H), 7.03 (dd, J = 7.8, 4.7 Hz, 1H), 6.90 (dd, J = 7.6, 1.5 Hz, 2H), 6.53 (d, J = 3.5 Hz, 1H), 3.35 (s, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.43 (t, J = 7.6 Hz, 2H).

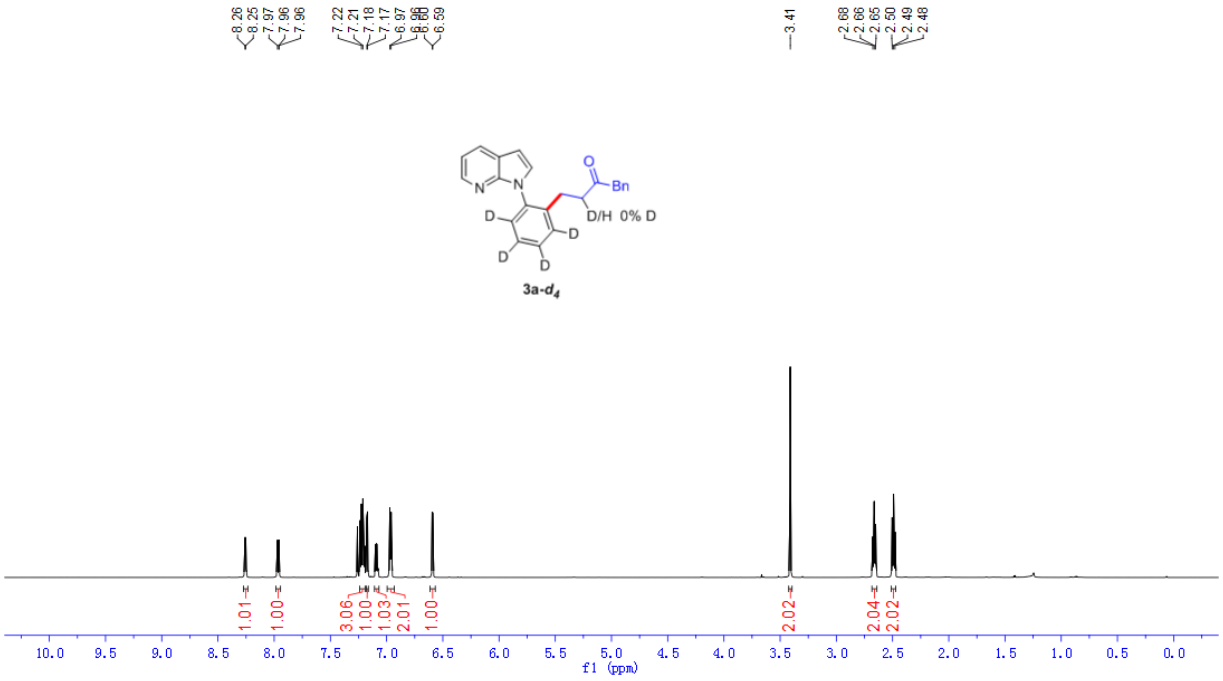


(c) ***Deuterium incorporation experiment***



1a-*d*$_5$ **3a-*d*$_4$**, 84% yield

(c) Deuterium incorporation experiment: To an oven-dried sealed tube charged with **1a-d$_5$** (39.8 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (5 mg, 4 mol %), CsOAc (7.6 mg, 20 mol %), and Cu(OAc)$_2$·H$_2$O (80 mg, 0.4 mmol) were added 1-benzylcyclopropanol **2a** (44.5 mg, 0.3 mmol) and methanol (1 mL) at room temperature. The reaction mixture was allowed to stir in an oil bath at 50 °C for 4 h. Then the reaction mixture was diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 15:1) to afford **3a-d$_4$** in 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 4.6 Hz, 1H), 7.99-7.94 (m, 1H), 7.24-7.19 (m, 3H), 7.18-7.17 (m, 1H), 7.09 (dd, J = 7.8, 4.7 Hz, 1H), 6.97 (d, J = 6.8 Hz, 2H), 6.59 (d, J = 3.5 Hz, 1H), 3.41 (s, 2H), 2.66 (t, J = 7.6 Hz, 2H), 2.49 (t, J = 7.6 Hz, 2H).



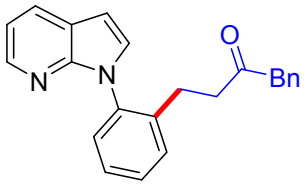
Reference

1. G. Qian, X. Hong, B. Liu, H. Mao and B. Xu, *Org. Lett*., 2014, **16**, 5294.

2. (*a*) J. Liu, E. Xu, J. Jiang, Z. Huang, L. Zheng and Z.-Q. Liu, *Chem. Commun*., 2020, **56**, 2202; (*b*) X.-P. He, Y.-J. Shu, J.-J. Dai, W.-M. Zhang, Y.-S. Feng and H.-J. Xu, *Org. Biomol. Chem*., 2015, **13**, 7159; (*c*) Y. Li, Z. Ye, T. M. Bellman, T. Chi and M. Dai, *Org. Lett*., 2015, **17**, 2186.

7. Characterization data of products

4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3a)



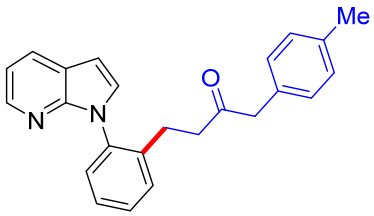
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 86% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 3.6 Hz, 1H), 7.97 (dd, J = 7.8, 0.9 Hz, 1H), 7.39-7.31 (m, 3H), 7.28-7.18 (m, 5H), 7.10 (dd, J = 7.8, 4.7 Hz, 1H), 6.98 (d, J = 6.4 Hz, 2H), 6.60 (d, J = 3.4 Hz, 1H), 3.42 (s, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.50 (t, J = 7.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.2, 148.6, 143.8, 139.1, 137.0, 134.1, 130.4, 129.5, 129.4, 129.2, 129.0, 128.8, 127.5, 127.0, 120.6, 116.4, 101.2, 50.1, 42.3, 25.9 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{23}H_{21}N_2O$ $[M + H]^+$ 341.1648, found 341.1645.

4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-(*p*-tolyl)butan-2-one (3b)



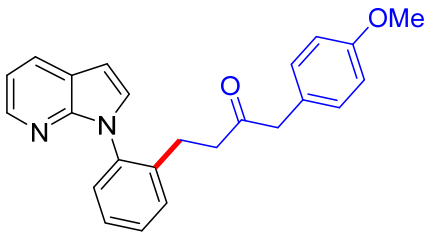
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 88% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (dd, J = 4.7, 1.4 Hz, 1H), 7.97 (dd, J = 7.8, 1.5 Hz, 1H), 7.38-7.31 (m, 3H), 7.29-7.26 (m, 1H), 7.19 (d, J = 3.5 Hz, 1H), 7.10 (dd, J = 7.8, 4.7 Hz, 1H), 7.04 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H), 6.60 (d, J = 3.5 Hz, 1H), 3.38 (s, 2H), 2.66 (t, J = 7.7 Hz, 2H), 2.48 (t, J = 7.7 Hz, 2H), 2.31 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.5, 148.6, 143.9, 139.1, 137.0, 136.6, 131.0, 130.4, 129.5, 129.5, 129.3, 129.2, 129.0, 127.5, 120.6, 116.4, 101.2, 49.7, 42.2, 25.9, 21.2 (one signal was overlapped by other ones);

HRMS (ESI) calcd for calcd for $C_{24}H_{23}N_2O$ $[M + H]^+$ 355.1805, found 355.1800.

4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-(4-methoxyphenyl)butan-2-one (3c)



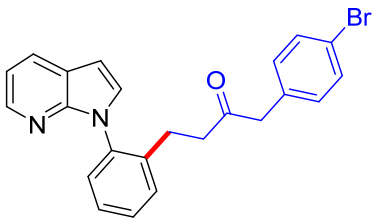
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/10) as a colorless oil in 72% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (dd, J = 4.6, 1.3 Hz, 1H), 7.97 (dd, J = 7.8, 1.3 Hz, 1H), 7.39-7.30 (m, 3H), 7.29-7.25 (m, 1H), 7.20 (d, J = 3.5 Hz, 1H), 7.10 (dd, J = 7.8, 4.7 Hz, 1H), 6.89 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 6.60 (d, J = 3.5 Hz, 1H), 3.77 (s, 3H), 3.35 (s, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.6, 158.7, 148.6, 143.8, 139.1, 137.0, 130.39, 130.37, 129.5, 129.2, 129.0, 127.4, 126.2, 120.6, 116.4, 114.2, 101.2, 55.4, 49.2, 42.1, 25.9 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{24}H_{23}N_2O_2$ $[M + H]^+$ 371.1754, found 371.1751.

4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-(4-bromophenyl)butan-2-one (3d)



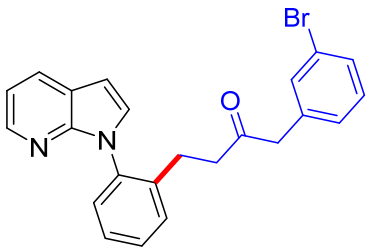
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 80% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28-8.23 (m, 1H), 7.98 (dd, J = 7.8, 1.2 Hz, 1H), 7.40-7.32 (m, 5H), 7.30-7.26 (m, 1H), 7.20 (d, J = 3.5 Hz, 1H), 7.11 (dd, J = 7.8, 4.7 Hz, 1H), 6.82 (d, J = 8.2 Hz, 2H), 6.61 (d, J = 3.5 Hz, 1H), 3.36 (s, 2H), 2.68 (t, J = 7.6 Hz, 2H), 2.47 (t, J = 7.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.8, 148.7, 143.9, 143.8, 139.6, 137.1, 134.2, 134.1, 130.5, 129.6, 129.2, 129.1, 128.19, 128.18, 127.5, 120.6, 116.4, 101.3, 39.4, 26.7, 21.7;

HRMS (ESI) calcd for $C_{23}H_{20}BrN_2O$ $[M + H]^+$ 419.0754, found 419.0752.

4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-(3-bromophenyl)butan-2-one (3e)



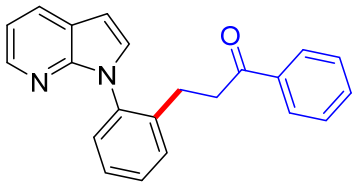
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 83% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (dd, J = 4.7, 1.5 Hz, 1H), 7.97 (dd, J = 7.8, 1.6 Hz, 1H), 7.40-7.32 (m, 4H), 7.28 (dd, J = 6.7, 2.6 Hz, 1H), 7.21 (d, J = 3.5 Hz, 1H), 7.15-7.13 (m, 1H), 7.12-7.07 (m, 2H), 6.89 (d, J = 7.7 Hz, 1H), 6.62 (d, J = 3.5 Hz, 1H), 3.36 (s, 2H), 2.69 (t, J = 7.6 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.3, 148.5, 143.8, 138.8, 137.0, 136.1, 132.4, 130.4, 130.18, 130.17, 129.4, 129.3, 129.02, 129.00, 128.0, 127.6, 122.7, 120.5, 116.5, 101.3, 49.3, 42.4, 25.9;

HRMS (ESI) calcd for $C_{23}H_{20}BrN_2O$ $[M + H]^+$ 419.0754, found 419.0750.

3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylpropan-1-one (3f)



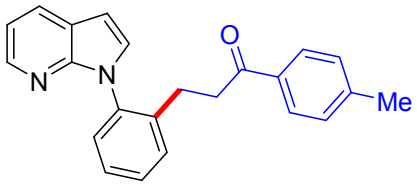
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 64% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (dd, J = 4.7, 1.5 Hz, 1H), 7.98 (dd, J = 7.8, 1.6 Hz, 1H), 7.65-7.61 (m, 2H), 7.48-7.45 (m, 2H), 7.44-7.40 (m, 1H), 7.39-7.36 (m, 1H), 7.34-7.30 (m, 4H), 7.10 (dd, J = 7.8, 4.7 Hz, 1H), 6.64 (d, J = 3.5 Hz, 1H), 3.02 (t, J = 7.8 Hz, 2H), 2.87 (t, J = 7.8 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.2, 148.7, 143.9, 139.5, 137.1, 136.6, 133.0, 130.5, 129.6, 129.3, 129.2, 129.1, 128.6, 128.1, 127.5, 120.7, 116.5, 101.3, 39.5, 26.7;

HRMS (ESI) calcd for $C_{22}H_{19}N_2O$ $[M + H]^+$ 327.1492, found 327.1486.

3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-(*p*-tolyl)propan-1-one (3g)



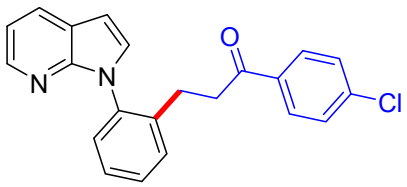
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 60% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (dd, J = 4.7, 1.4 Hz, 1H), 7.98 (dd, J = 7.8, 1.5 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.47 (dd, J = 7.6, 1.1 Hz, 1H), 7.44-7.40 (m, 1H), 7.38-7.35 (m, 1H), 7.32 (dd, J = 10.2, 2.4 Hz, 2H), 7.14-7.07 (m, 3H), 6.64 (d, J = 3.5 Hz, 1H), 3.02-2.97 (m, 2H), 2.89-2.82 (m, 2H), 2.35 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.8, 148.7, 143.9, 143.8, 139.6, 137.1, 134.2, 130.6, 129.7, 129.29, 129.26, 129.2, 129.1, 128.2, 127.5, 120.7, 116.5, 101.3, 39.4, 26.7, 21.7;

HRMS (ESI) calcd for $C_{23}H_{21}N_2O$ $[M + H]^+$ 341.1648, found 341.1645.

3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-(4-chlorophenyl)propan-1-one (3h)



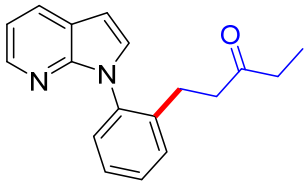
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 55% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (dd, J = 4.7, 1.3 Hz, 1H), 7.99 (dd, J = 7.8, 1.3 Hz, 1H), 7.53 (d, J = 8.5 Hz, 2H), 7.47-7.41 (m, 2H), 7.40-7.35 (m, 1H), 7.34-7.31 (m, 1H), 7.31-7.30 (m, 1H), 7.29-7.26 (m, 2H), 7.11 (dd, J = 7.8, 4.7 Hz, 1H), 6.65 (d, J = 3.5 Hz, 1H), 2.98 (t, J = 7.7 Hz, 2H), 2.86 (t, J = 7.7 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.0, 148.7, 143.9, 139.5, 139.2, 137.1, 134.9, 130.6, 129.6, 129.5, 129.3, 129.20, 129.20, 128.9, 127.7, 120.6, 116.5, 101.3, 39.5, 26.8;

HRMS (ESI) calcd for $C_{22}H_{18}ClN_2O$ $[M + H]^+$ 361.1102, found 361.1101.

1-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (3i)



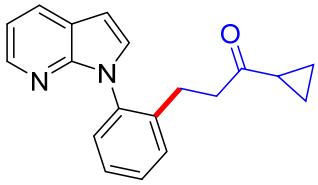
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 63% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (dd, J = 4.7, 1.5 Hz, 1H), 7.91 (dd, J = 7.8, 1.6 Hz, 1H), 7.35-7.30 (m, 2H), 7.29-7.26 (m, 1H), 7.22 (dd, J = 9.8, 5.4 Hz, 2H), 7.03 (dd, J = 7.8, 4.7 Hz, 1H), 6.56 (d, J = 3.5 Hz, 1H), 2.62 (t, J = 7.7 Hz, 2H), 2.39 (t, J = 7.7 Hz, 2H), 2.07 (q, J = 7.3 Hz, 2H), 0.80 (t, J = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 210.5, 148.6, 143.8, 139.3, 137.0, 130.3, 129.6, 129.3, 129.0, 129.0, 127.4, 120.6, 116.4, 101.2, 42.6, 35.8, 25.9, 7.8;

HRMS (ESI) calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$ 279.1492, found: 279.1487.

3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-cyclopropylpropan-1-one (3j)



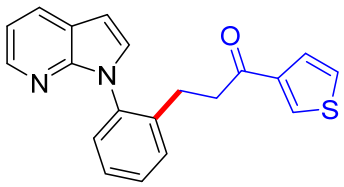
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 67% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (dd, J = 4.7, 1.5 Hz, 1H), 7.98 (dd, J = 7.8, 1.5 Hz, 1H), 7.40 (d, J = 3.8 Hz, 2H), 7.38-7.33 (m, 1H), 7.32-7.28 (m, 2H), 7.10 (dd, J = 7.8, 4.7 Hz, 1H), 6.64 (d, J = 3.5 Hz, 1H), 2.72 (t, J = 7.6 Hz, 2H), 2.61 (t, J = 7.6 Hz, 2H), 1.62 (tt, J = 7.9, 4.6 Hz, 1H), 0.86-0.82 (m, 2H), 0.73-0.69 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 209.8, 148.6, 143.8, 139.3, 137.0, 130.3, 129.6, 129.2, 129.03, 129.00, 127.4, 120.6, 116.4, 101.2, 43.5, 25.9, 20.4, 10.6;

HRMS (ESI) calcd for $C_{19}H_{19}N_2O$ $[M + H]^+$ 291.1492, found 291.1489.

3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-(thiophen-3-yl)propan-1-one (3k)



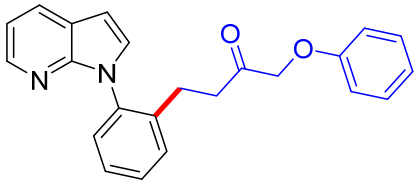
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 62% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (dd, J = 4.7, 1.4 Hz, 1H), 7.99 (dd, J = 7.8, 1.4 Hz, 1H), 7.57 (dd, J = 2.8, 1.0 Hz, 1H), 7.46 (dd, J = 7.6, 1.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.39-7.35 (m, 1H), 7.34-7.29 (m, 3H), 7.18 (dd, J = 5.0, 2.9 Hz, 1H), 7.11 (dd, J = 7.8, 4.7 Hz, 1H), 6.65 (d, J = 3.5 Hz, 1H), 2.92-2.83 (m, 4H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 193.6, 148.7, 143.9, 142.0, 139.4, 137.1, 132.0, 130.6, 129.6, 129.3, 129.17, 129.15, 127.6, 126.9, 126.2, 120.7, 116.5, 101.3, 40.6, 26.8;

HRMS (ESI) calcd for $C_{20}H_{17}N_2OS$ $[M + H]^+$ 333.1056, found 333.1049.

4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenoxybutan-2-one (3l)



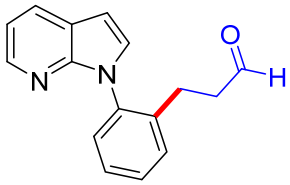
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 65% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (dd, J = 4.7, 1.5 Hz, 1H), 7.89 (dd, J = 7.8, 1.6 Hz, 1H), 7.34-7.31 (m, 2H), 7.30-7.26 (m, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.18-7.15 (m, 3H), 7.01 (dd, J = 7.8, 4.7 Hz, 1H), 6.91-6.86 (m, 1H), 6.65-6.61 (m, 2H), 6.54 (d, J = 3.5 Hz, 1H), 4.22 (s, 2H), 2.68 (t, J = 7.7 Hz, 2H), 2.60 (t, J = 7.7 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.6, 157.7, 148.5, 143.8, 138.8, 137.0, 130.4, 129.7, 129.5, 129.3, 129.09, 129.06, 127.6, 121.7, 120.6, 116.5, 114.5, 101.3, 72.6, 39.4, 25.2;

HRMS (ESI) calcd for $C_{23}H_{21}N_2O_2$ $[M + H]^+$ 357.1598, found 357.1594.

3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)propanal (3m)



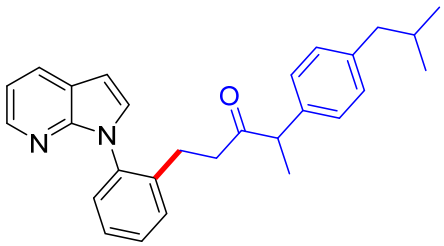
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 80% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.55 (s, 1H), 8.35-8.28 (m, 1H), 7.99 (dd, J = 7.8, 1.3 Hz, 1H), 7.43-7.36 (m, 3H), 7.31 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 3.5 Hz, 1H), 7.12 (dd, J = 7.8, 4.7 Hz, 1H), 6.65 (d, J = 3.5 Hz, 1H), 2.78 (t, J = 7.6 Hz, 2H), 2.55-2.52 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 201.3, 148.5, 143.9, 138.5, 137.1, 130.2, 129.14, 129.07, 129.1, 129.1, 127.7, 120.6, 116.5, 101.4, 44.2, 24.1 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{16}H_{15}N_2O$ $[M + H]^+$ 251.1179, found 251.1176.

1-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-4-(4-isobutylphenyl)pentan-3-one (3n)



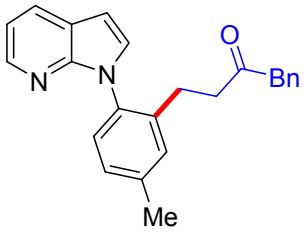
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 58% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (dd, J = 4.7, 1.3 Hz, 1H), 7.96 (dd, J = 7.8, 1.5 Hz, 1H), 7.35-7.29 (m, 2H), 7.26-7.21 (m, 2H), 7.08 (dd, J = 7.8, 4.7 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 3.5 Hz, 1H), 3.45 (q, J = 6.9 Hz, 1H), 2.68-2.57 (m, 2H), 2.47-2.34 (m, 4H), 1.83 (dp, J = 13.6, 6.8 Hz, 1H), 1.21 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 209.9, 148.5, 143.8, 140.5, 139.2, 137.6, 136.9, 130.4, 129.7, 129.5, 129.1, 128.9, 127.5, 127.3, 120.5, 116.3, 101.1, 52.5, 45.1, 41.1, 30.3, 26.0, 22.53, 22.52, 17.3;

HRMS (ESI) calcd for $C_{28}H_{31}N_2O$ $[M + H]^+$ 411.2431, found 411.2427.

4-(5-Methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3o)



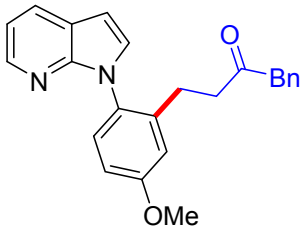
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 90% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (dd, J = 4.7, 1.5 Hz, 1H), 7.94 (dd, J = 7.8, 1.6 Hz, 1H), 7.24-7.19 (m, 3H), 7.17-7.12 (m, 3H), 7.11 (s, 1H), 7.07 (dd, J = 7.8, 4.7 Hz, 1H), 6.99-6.95 (m, 2H), 6.57 (d, J = 3.5 Hz, 1H), 3.40 (s, 2H), 2.62 (t, J = 7.6 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H), 2.35 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.2, 148.6, 143.75, 138.83, 138.6, 134.3, 134.0, 130.9, 129.5, 129.3, 129.1, 128.7, 128.1, 126.9, 120.4, 116.3, 100.9, 50.0, 42.3, 25.7, 21.2 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{24}H_{23}N_2O$ $[M + H]^+$ 355.1805, found 355.1802.

4-(5-Methoxy-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3p)



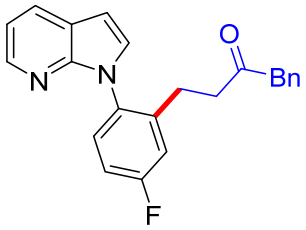
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/10) as a colorless oil in 81% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (dd, J = 4.7, 1.5 Hz, 1H), 7.96 (dd, J = 7.8, 1.5 Hz, 1H), 7.26-7.18 (m, 4H), 7.16 (d, J = 3.5 Hz, 1H), 7.09 (dd, J = 7.8, 4.7 Hz, 1H), 7.01-6.95 (m, 2H), 6.87-6.83 (m, 2H), 6.58 (d, J = 3.5 Hz, 1H), 3.82 (s, 3H), 3.42 (s, 2H), 2.60 (t, J = 7.5 Hz, 2H), 2.49 (t, J = 7.5 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.1, 159.7, 148.7, 143.8, 140.4, 134.0, 129.9, 129.73, 129.68, 129.3, 129.1, 128.7, 127.0, 120.4, 116.2, 115.5, 112.5, 100.8, 55.5, 50.0, 42.2, 26.0;

HRMS (ESI) calcd for $C_{24}H_{23}N_2O_2$ $[M + H]^+$ 371.1754, found 371.1751.

4-(5-Fluoro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3q)



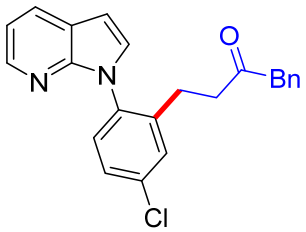
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 75% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (dd, J = 4.7, 1.5 Hz, 1H), 7.96 (dd, J = 7.8, 1.6 Hz, 1H), 7.26-7.20 (m, 4H), 7.14 (d, J = 3.5 Hz, 1H), 7.10 (dd, J = 7.8, 4.7 Hz, 1H), 7.03-6.98 (m, 4H), 6.59 (d, J = 3.5 Hz, 1H), 3.44 (s, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.51 (t, J = 7.4 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.7, 162.5 (d, $J_{C\text{-}F}$ = 248.1 Hz), 148.6, 143.9, 141.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 133.9, 132.9 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.6, 130.5, 129.4 (d, $J_{C\text{-}F}$ = 16.4 Hz), 129.3, 128.8, 127.1, 120.5, 116.9 (d, $J_{C\text{-}F}$ = 22.7 Hz), 116.5, 114.3 (d, $J_{C\text{-}F}$ = 22.6 Hz), 101.38, 50.1, 41.7, 25.7;

HRMS (ESI) calcd for $C_{23}H_{20}FN_2O$ $[M + H]^+$ 359.1554, found 359.1547.

4-(5-Chloro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3r)



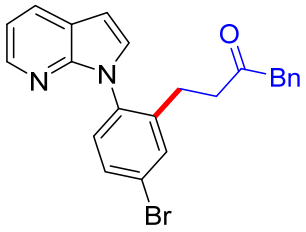
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 83% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (dd, J = 4.7, 1.5 Hz, 1H), 7.89 (dd, J = 7.8, 1.5 Hz, 1H), 7.24-7.20 (m, 2H), 7.18-7.11 (m, 4H), 7.07 (d, J = 3.5 Hz, 1H), 7.02 (dd, J = 7.8, 4.7 Hz, 1H), 6.95-6.89 (m, 2H), 6.53 (d, J = 3.5 Hz, 1H), 3.37 (s, 2H), 2.55 (t, J = 7.5 Hz, 2H), 2.43 (t, J = 7.5 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.6, 148.5, 143.9, 141.0, 135.5, 134.6, 133.9, 130.3, 130.2, 129.4, 129.3, 129.2, 128.8, 127.6, 127.1, 120.6, 116.6, 101.6, 50.1, 41.7, 25.6;

HRMS (ESI) calcd for $C_{23}H_{20}ClN_2O$ $[M + H]^+$ 375.1259, found 375.1254.

4-(5-Bromo-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3s)



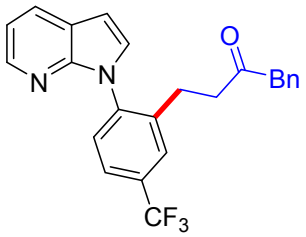
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 80% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (dd, J = 4.7, 1.5 Hz, 1H), 7.96 (dd, J = 7.8, 1.6 Hz, 1H), 7.72-7.60 (m, 2H), 7.27-7.21 (m, 3H), 7.14 (d, J = 3.5 Hz, 1H), 7.10 (dd, J = 7.8, 4.7 Hz, 1H), 6.99 (d, J = 8.0 Hz, 3H), 6.60 (d, J = 3.5 Hz, 1H), 3.44 (s, 2H), 2.62 (t, J = 7.6 Hz, 2H), 2.49 (t, J = 7.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.7, 148.4, 144.0, 141.4, 139.3, 136.8, 136.6, 133.9, 130.7, 129.3, 129.1, 128.8, 127.1, 120.6, 116.7, 101.7, 94.6, 50.1, 41.8, 25.4 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{23}H_{20}BrN_2O$ $[M + H]^+$ 419.0754, found 419.0744.

4-(2-(1*H*-Pyrrolo[2,3-*b*]pyridin-1-yl)-5-(trifluoromethyl)phenyl)-1-phenylbutan-2-one (3t)



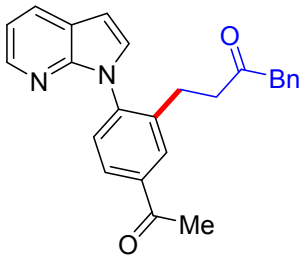
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 72% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (dd, J = 4.7, 1.5 Hz, 1H), 7.98 (dd, J = 7.9, 1.6 Hz, 1H), 7.59 (d, J = 6.9 Hz, 2H), 7.39 (d, J = 8.6 Hz, 1H), 7.27-7.20 (m, 3H), 7.17 (d, J = 3.6 Hz, 1H), 7.12 (dd, J = 7.8, 4.7 Hz, 1H), 6.99 (dd, J = 7.6, 1.5 Hz, 2H), 6.64 (d, J = 3.6 Hz, 1H), 3.46 (s, 2H), 2.75 (t, J = 7.5 Hz, 2H), 2.53 (t, J = 7.5 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.5, 148.4, 144.1, 140.2, 140.0, 133.9, 130.9 (q, $J_{C\text{-}F}$ = 32.6 Hz), 129.5, 129.3, 128.9, 128.8, 127.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 127.1, 124.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 273.4 Hz), 120.7, 116.8, 102.1, 50.1, 41.6, 25.7 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{24}H_{20}F_3N_2O$ $[M + H]^+$ 409.1522, found 409.1518.

4-(5-Acetyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3u)



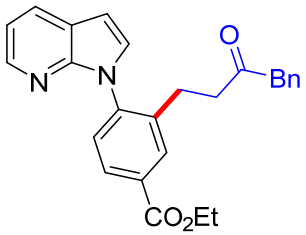
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 64% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (dd, J = 4.7, 1.5 Hz, 1H), 7.98 (dd, J = 7.8, 1.5 Hz, 1H), 7.95-7.90 (m, 2H), 7.38 (d, J = 8.1 Hz, 1H), 7.27-7.18 (m, 4H), 7.12 (dd, J = 7.8, 4.7 Hz, 1H), 7.02-6.95 (m, 2H), 6.64 (d, J = 3.5 Hz, 1H), 3.46 (s, 2H), 2.77 (t, J = 7.6 Hz, 2H), 2.61 (s, 3H), 2.55 (t, J = 7.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.8, 197.4, 148.4, 144.0, 141.2, 139.3, 137.2, 134.0, 130.4, 129.45, 129.35, 129.2, 128.9, 128.8, 127.4, 127.1, 120.7, 116.8, 102.1, 50.1, 41.8, 26.8, 25.9;

HRMS (ESI) calcd for $C_{25}H_{23}N_2O_2$ $[M + H]^+$ 383.1754, found 383.1751.

Ethyl 3-(3-oxo-4-phenylbutyl)-4-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)benzoate (3v)



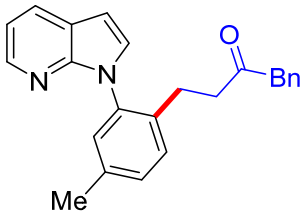
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 78% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (dd, J = 4.7, 1.5 Hz, 1H), 8.04 (d, J = 1.8 Hz, 1H), 8.00 (dd, J = 8.1, 2.0 Hz, 1H), 7.96 (dd, J = 7.8, 1.6 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.26-7.17 (m, 4H), 7.10 (dd, J = 7.8, 4.7 Hz, 1H), 7.03-6.93 (m, 2H), 6.62 (d, J = 3.6 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 3.45 (s, 2H), 2.75 (t, J = 7.7 Hz, 2H), 2.56 (t, J = 7.7 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.7, 165.9, 148.4, 143.9, 140.9, 139.0, 133.9, 131.5, 130.7, 129.3, 128.9, 128.9, 128.7, 128.6, 127.0, 120.6, 116.7, 101.9, 61.3, 50.0, 41.8, 25.8, 14.4 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{26}H_{25}N_2O_3$ $[M + H]^+$ 413.1860, found 413.1855.

4-(4-Methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3w)



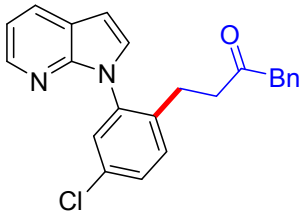
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 73% yield;

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.30 (dd, J = 4.7, 1.5 Hz, 1H), 8.00 (dd, J = 7.8, 1.6 Hz, 1H), 7.28-7.23 (m, 4H), 7.21 (dd, J = 4.4, 2.4 Hz, 2H), 7.13 (dd, J = 7.8, 4.7 Hz, 2H), 7.05-6.97 (m, 2H), 6.62 (d, J = 3.5 Hz, 1H), 3.45 (s, 2H), 2.65 (t, J = 7.6 Hz, 2H), 2.51 (t, J = 7.6 Hz, 2H), 2.38 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.4, 148.5, 143.8, 137.3, 136.7, 135.9, 134.1, 130.2, 129.9, 129.54, 129.52, 129.4, 129.2, 128.8, 127.0, 120.5, 116.3, 101.1, 50.1, 42.5, 25.5, 20.9;

HRMS (ESI) calcd for $C_{24}H_{23}N_2O$ $[M + H]^+$ 355.1805, found 355.1802.

4-(4-Chloro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3x)



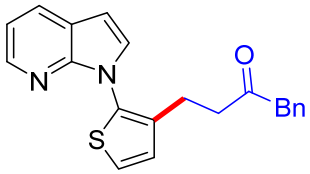
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 81% yield;

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.30 (dd, J = 4.7, 1.4 Hz, 1H), 8.00 (dd, J = 7.8, 1.4 Hz, 1H), 7.36 (dd, J = 8.3, 2.2 Hz, 1H), 7.31-7.25 (m, 5H), 7.18-7.13 (m, 2H), 7.06-6.97 (m, 2H), 6.64 (d, J = 3.5 Hz, 1H), 3.47 (s, 2H), 2.67 (t, J = 7.5 Hz, 2H), 2.51 (t, J = 7.5 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 206.9, 148.3, 143.9, 137.9, 137.7, 133.9, 132.6, 131.5, 129.5, 129.4, 129.2, 129.12, 129.09, 128.8, 127.1, 120.6, 116.7, 101.8, 50.2, 41.9, 25.3;

HRMS (ESI) calcd for $C_{23}H_{20}ClN_2O$ $[M + H]^+$ 375.1259, found 375.1256.

4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)thiophen-3-yl)-1-phenylbutan-2-one (3ab)



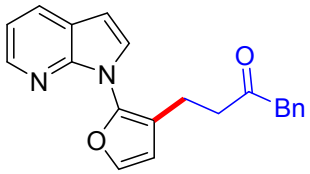
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 76% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (dd, J = 4.7, 1.5 Hz, 1H), 7.93 (dd, J = 7.8, 1.5 Hz, 1H), 7.28-7.19 (m, 5H), 7.11 (dd, J = 7.8, 4.7 Hz, 1H), 7.08-7.03 (m, 2H), 6.88 (d, J = 5.7 Hz, 1H), 6.59 (d, J = 3.6 Hz, 1H), 3.54 (s, 2H), 2.67-2.62 (m, 4H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.2, 149.2, 144.1, 137.5, 134.1, 133.4, 130.4, 129.4, 129.3, 128.8, 127.5, 127.1, 123.6, 120.8, 116.9, 102.1, 50.2, 41.9, 21.9;

HRMS (ESI) calcd for $C_{21}H_{19}N_2OS$ $[M + H]^+$ 347.1213, found 347.1208.

4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)furan-3-yl)-1-phenylbutan-2-one (3ac)



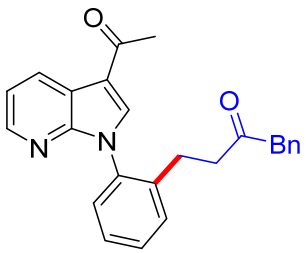
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 71% yield;

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (dd, J = 4.7, 1.4 Hz, 1H), 7.88 (dd, J = 7.8, 1.5 Hz, 1H), 7.24 (d, J = 2.1 Hz, 1H), 7.22-7.15 (m, 4H), 7.06 (dd, J = 7.8, 4.7 Hz, 1H), 7.05-6.99 (m, 2H), 6.53 (d, J = 3.6 Hz, 1H), 6.29 (d, J = 2.1 Hz, 1H), 3.51 (s, 2H), 2.61 (t, J = 7.4 Hz, 2H), 2.51 (t, J = 7.4 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.4, 148.9, 144.1, 140.3, 140.0, 134.2, 129.5, 129.5, 129.2, 128.8, 127.1, 120.9, 117.3, 117.2, 112.6, 102.7, 50.3, 41.6, 18.6;

HRMS (ESI) calcd for $C_{21}H_{19}N_2O_2$ $[M + H]^+$ 331.1441, found 331.1439.

4-(2-(3-Acetyl-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3ae)



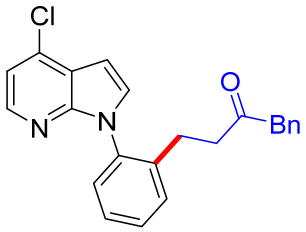
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 64% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.63 (dd, J = 7.9, 1.5 Hz, 1H), 8.22 (dd, J = 4.6, 1.4 Hz, 1H), 7.74 (s, 1H), 7.34 (dd, J = 11.0, 4.1 Hz, 1H), 7.28 (dd, J = 12.1, 7.5 Hz, 2H), 7.20-7.13 (m, 5H), 6.90 (dd, J = 7.0, 1.9 Hz, 2H), 3.39 (s, 2H), 2.57 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.45 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.8, 193.2, 149.1, 145.4, 138.8, 135.8, 135.5, 133.9, 131.5, 130.4, 129.8, 129.3, 128.8, 128.7, 127.6, 127.1, 119.0, 118.5, 116.7, 50.2, 41.9, 27.3, 25.4;

HRMS (ESI) calcd for $C_{25}H_{23}N_2O_2$ $[M + H]^+$ 383.1754, found 383.1752.

4-(2-(4-Chloro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylbutan-2-one (3af)



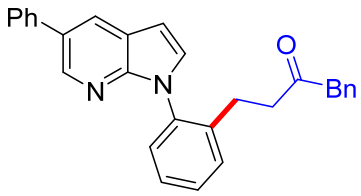
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 75% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 5.1 Hz, 1H), 7.32-7.28 (m, 1H), 7.25 (dd, J = 10.7, 3.9 Hz, 2H), 7.18-7.13 (m, 4H), 7.12 (d, J = 3.5 Hz, 1H), 7.04 (d, J = 5.1 Hz, 1H), 6.90 (dd, J = 7.6, 1.7 Hz, 2H), 6.62 (d, J = 3.5 Hz, 1H), 3.37 (s, 2H), 2.57 (t, J = 7.6 Hz, 2H), 2.42 (t, J = 7.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.0, 149.0, 144.1, 138.9, 136.5, 136.4, 134.0, 130.4, 130.0, 129.30, 129.29, 128.8, 128.8, 127.5, 127.1, 119.9, 116.6, 99.7, 50.1, 42.0, 25.7;

HRMS (ESI) calcd for $C_{23}H_{20}ClN_2O$ $[M + H]^+$ 375.1259, found 375.1254.

1-Phenyl-4-(2-(5-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)butan-2-one (3ag)



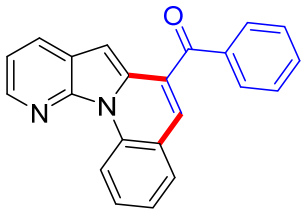
Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/15) as a colorless oil in 82% yield;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, J = 2.1 Hz, 1H), 8.06 (d, J = 2.1 Hz, 1H), 7.54 (dd, J = 8.2, 1.1 Hz, 2H), 7.40 (dd, J = 10.6, 4.8 Hz, 2H), 7.32-7.25 (m, 4H), 7.21 (dd, J = 6.6, 2.7 Hz, 1H), 7.16-7.08 (m, 4H), 6.94-6.85 (m, 2H), 6.57 (d, J = 3.5 Hz, 1H), 3.37 (s, 2H), 2.64 (t, J = 7.6 Hz, 2H), 2.46 (t, J = 7.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.2, 148.1, 143.3, 139.6, 139.0, 136.9, 134.1, 130.4, 130.3, 130.2, 129.4, 129.1, 129.0, 128.8, 127.64, 127.55, 127.49, 127.2, 127.0, 120.6, 101.5, 50.1, 42.3, 25.8 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{29}H_{25}N_2O$ $[M + H]^+$ 417.1961, found 417.1958.

Phenyl(pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl)methanone (4a)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/20) as an orange solid in 58% yield;

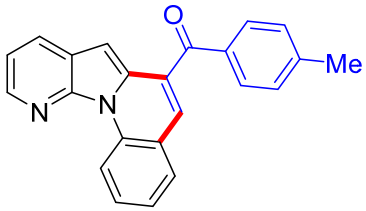
M.p. = 164-165 °C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (d, J = 8.6 Hz, 1H), 8.58 (dd, J = 4.6, 1.6 Hz, 1H), 8.12 (dd, J = 7.9, 1.6 Hz, 1H), 7.91 (dd, J = 8.3, 1.2 Hz, 2H), 7.76-7.71 (m, 1H), 7.65-7.59 (m, 2H), 7.54-7.49 (m, 3H), 7.35-7.30 (m, 2H), 7.25-7.22 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 194.6, 146.0, 142.5, 138.0, 137.1, 133.0, 132.9, 132.1, 131.9, 130.0, 129.9, 129.1, 128.7, 127.8, 123.0, 122.4, 121.8, 118.5, 118.2, 96.4;

HRMS (ESI) calcd for $C_{22}H_{15}N_2O$ $[M + H]^+$ 323.1179, found 323.1176.

Pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl(*p*-tolyl)methanone (4b)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/20) as an orange solid in 54% yield;

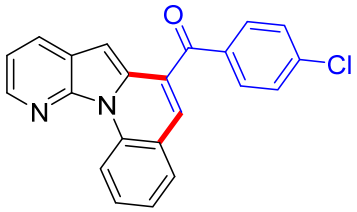
M.p. = 200-201 °C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.21 (d, J = 8.5 Hz, 1H), 8.60 (dd, J = 4.6, 1.6 Hz, 1H), 8.14 (dd, J = 7.9, 1.6 Hz, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.77-7.74 (m, 1H), 7.64 (dd, J = 7.7, 1.4 Hz, 1H), 7.51 (s, 1H), 7.38-7.30 (m, 4H), 7.17 (s, 1H), 2.47 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 194.3, 146.1, 144.0, 142.5, 137.1, 135.3, 133.1, 131.8, 131.3, 130.3, 129.9, 129.4, 129.1, 128.3, 123.8, 122.5, 122.0, 118.5, 118.2, 96.3, 21.9;

HRMS (ESI) calcd for $C_{23}H_{17}N_2O$ $[M + H]^+$ 337.1335, found 337.1331.

(4-Chlorophenyl)(pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl)methanone (4c)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/20) as an orange solid in 52% yield;

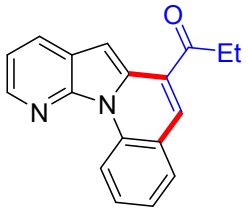
M.p. = 196-197 °C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.22 (d, J = 8.6 Hz, 1H), 8.61 (dd, J = 4.6, 1.6 Hz, 1H), 8.16 (dd, J = 7.9, 1.6 Hz, 1H), 7.91-7.83 (m, 2H), 7.81-7.76 (m, 1H), 7.66 (dd, J = 7.7, 1.3 Hz, 1H), 7.56-7.47 (m, 3H), 7.40-7.34 (m, 2H), 7.20 (s, 1H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 193.4, 146.1, 142.7, 139.5, 137.2, 136.3, 132.7, 132.2, 132.1, 131.4, 130.0, 129.2, 129.1, 127.6, 124.0, 122.4, 121.7, 118.6, 118.4, 96.5;

HRMS (ESI) calcd for $C_{22}H_{14}ClN_2O$ $[M + H]^+$ 357.0789, found 357.0781.

1-(Pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl)propan-1-one (4d)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/20) as an orange solid in 46% yield;

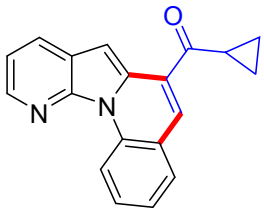
M.p. = 130-131 °C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (d, J = 8.5 Hz, 1H), 8.58 (dd, J = 4.6, 1.6 Hz, 1H), 8.17 (dd, J = 7.9, 1.6 Hz, 1H), 7.89 (s, 1H), 7.78-7.73 (m, 1H), 7.69 (dd, J = 7.7, 1.3 Hz, 1H), 7.65 (s, 1H), 7.38-7.32 (m, 2H), 3.11 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.6, 145.9, 142.4, 137.5, 132.2, 131.9, 131.1, 130.0, 129.2, 127.1, 123.8, 122.8, 121.7, 118.5, 118.2, 97.5, 32.4, 8.7;

HRMS (ESI) calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$ 275.1179, found 275.1175.

Cyclopropyl(pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl)methanone (4e)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/20) as an orange solid in 50% yield;

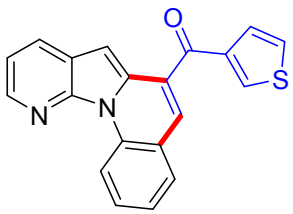
M.p. = 134-135 °C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.19 (d, J = 8.5 Hz, 1H), 8.58 (dd, J = 4.6, 1.6 Hz, 1H), 8.16 (dd, J = 7.9, 1.6 Hz, 1H), 8.00 (s, 1H), 7.79-7.71 (m, 2H), 7.50 (s, 1H), 7.41-7.30 (m, 2H), 2.79-2.71 (m, 1H), 1.36 (dq, J = 7.0, 3.7 Hz, 2H), 1.13 (dq, J = 7.2, 3.6 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.2, 146.0, 142.4, 137.4, 132.2, 132.0, 130.6, 130.0, 129.1, 128.8, 123.8, 122.7, 122.0, 118.5, 118.2, 96.9, 18.5, 12.02, 11.97;

HRMS (ESI) calcd for $C_{19}H_{15}N_2O$ $[M + H]^+$ 287.1179, found 287.1174.

Pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl(thiophen-3-yl)methanone (4f)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/20) as an orange solid in 63% yield;

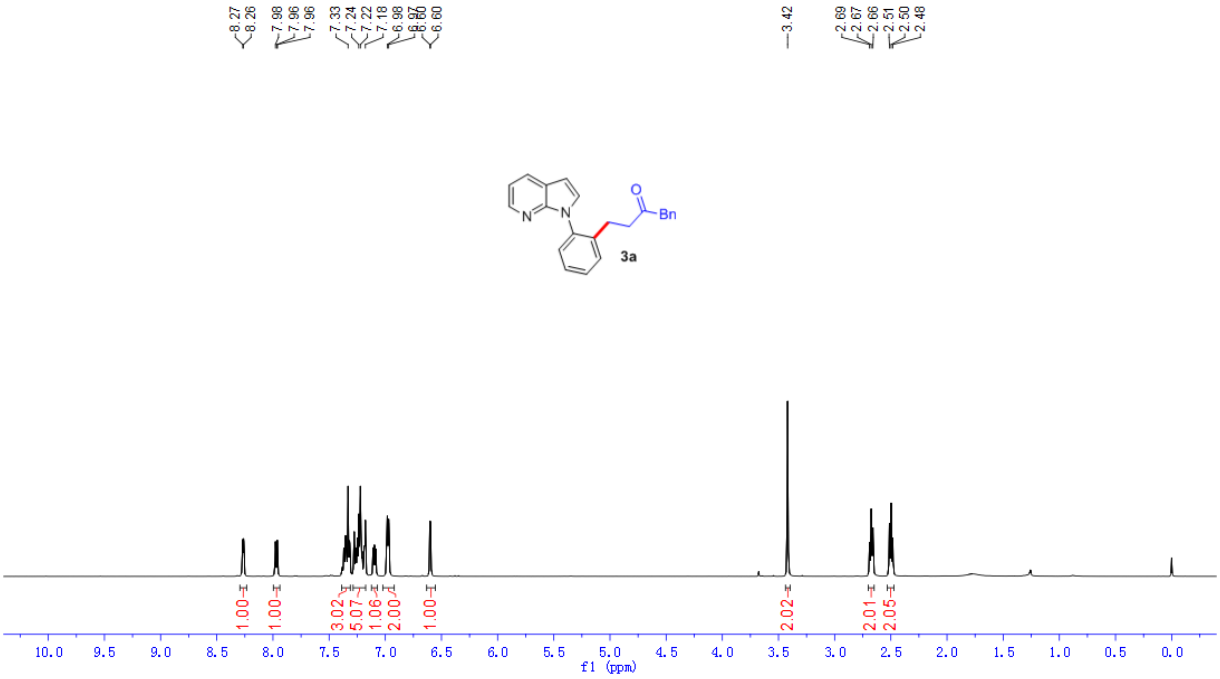
M.p. = 182-183 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.21 (d, J = 8.5 Hz, 1H), 8.60 (dd, J = 4.6, 1.4 Hz, 1H), 8.15 (dd, J = 7.9, 1.4 Hz, 1H), 8.10-8.02 (m, 1H), 7.80-7.74 (m, 1H), 7.71-7.64 (m, 3H), 7.44 (dd, J = 5.1, 2.9 Hz, 1H), 7.39-7.33 (m, 2H), 7.22 (s, 1H);

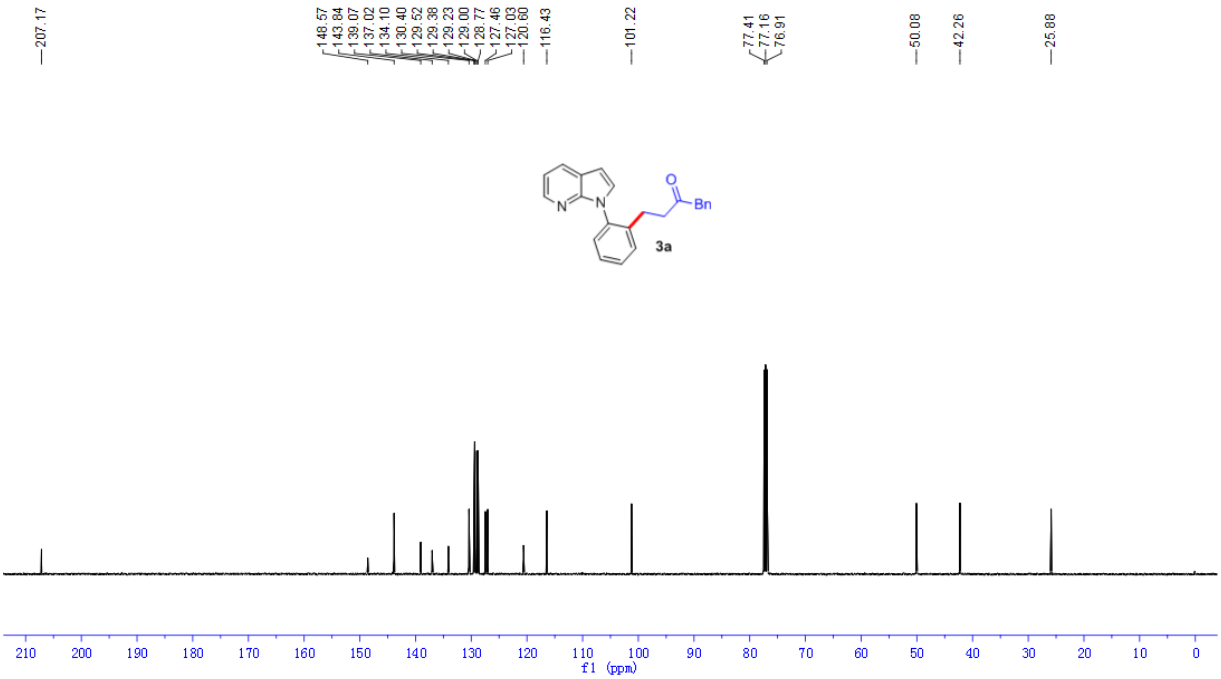
^{13}C NMR (126 MHz, $CDCl_3$): δ 187.8, 146.1, 142.6, 141.8, 137.1, 134.0, 132.8, 131.9, 130.6, 129.9, 129.2, 129.0, 128.5, 126.8, 123.9, 122.5, 121.9, 118.6, 118.3, 96.2;

HRMS (ESI) calcd for $C_{20}H_{13}N_2OS$ $[M + H]^+$ 329.0743, found 329.0741.

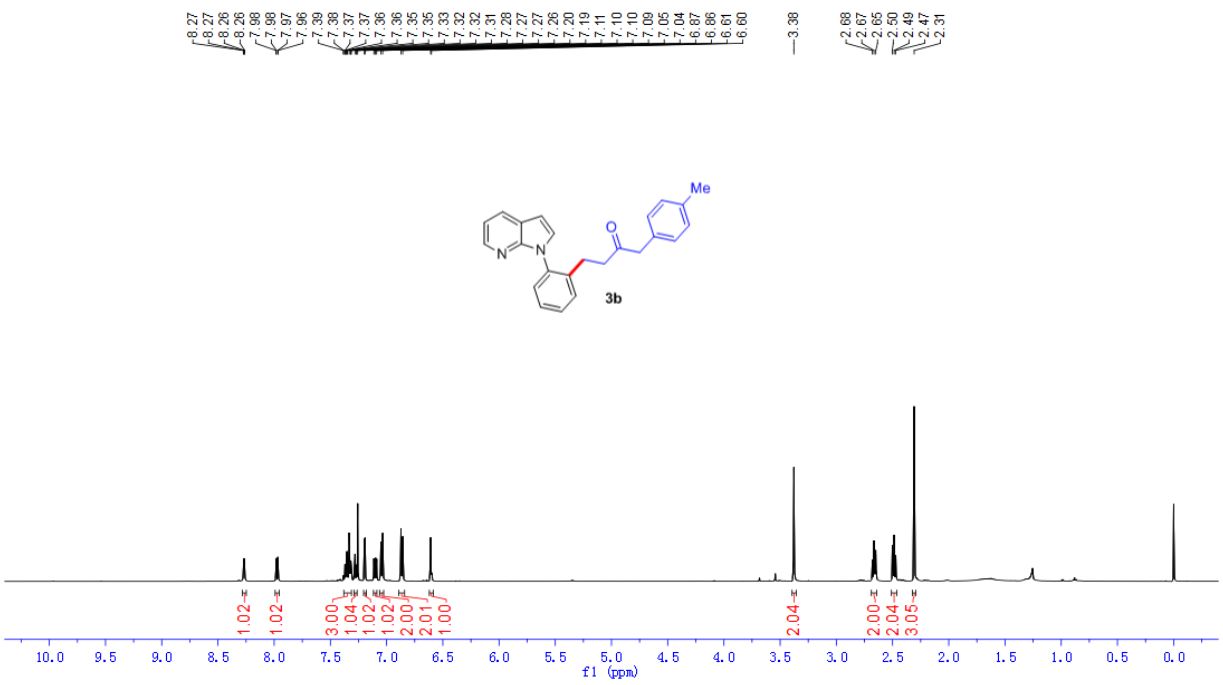
8. Copies of ^{1}H NMR and ^{13}C NMR spectra of 3 and 4



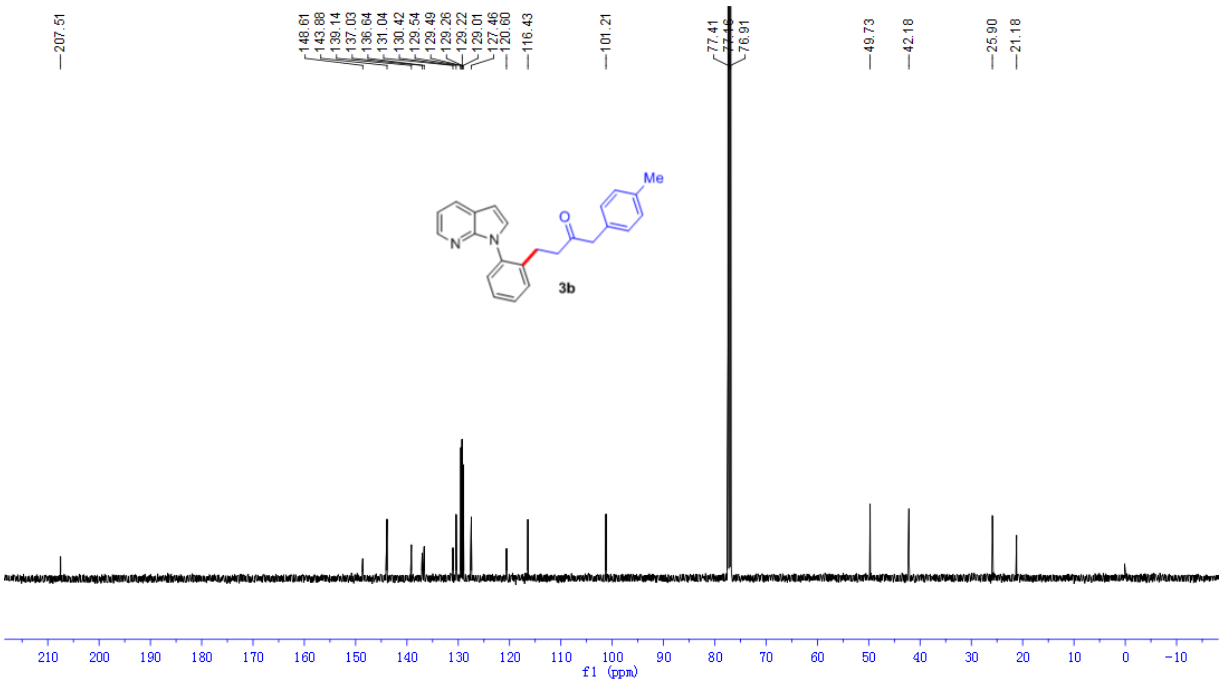
^{1}H NMR spectrum of **3a**



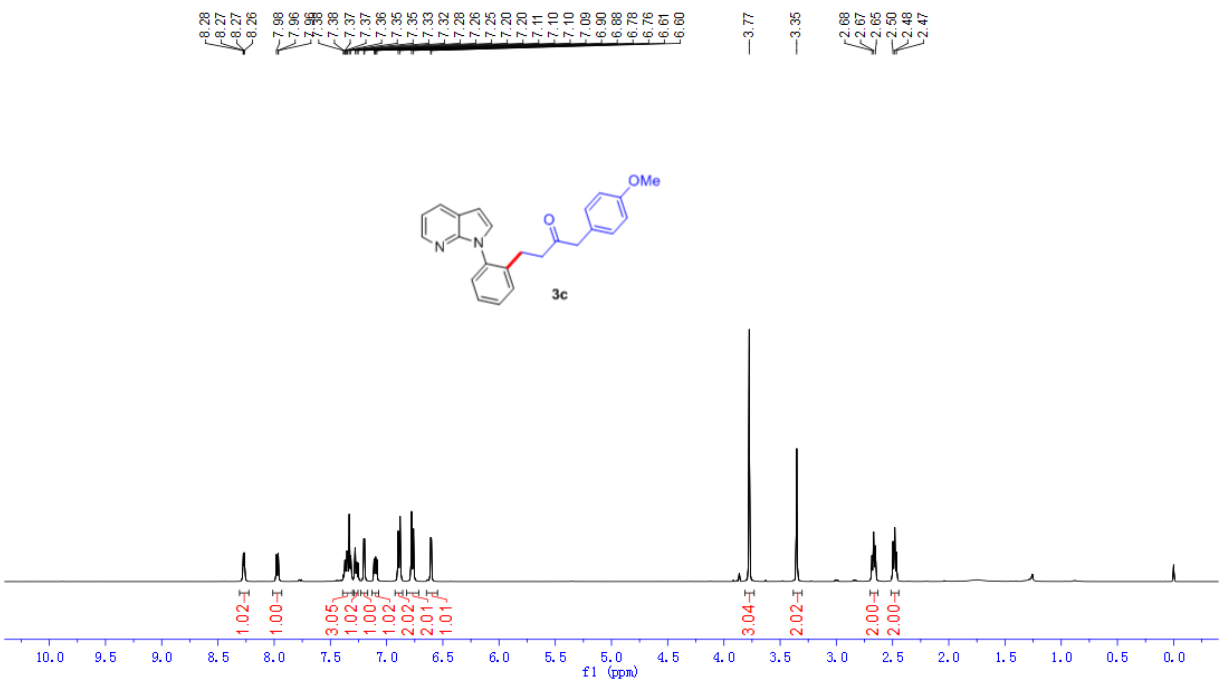
^{13}C NMR spectrum of **3a**



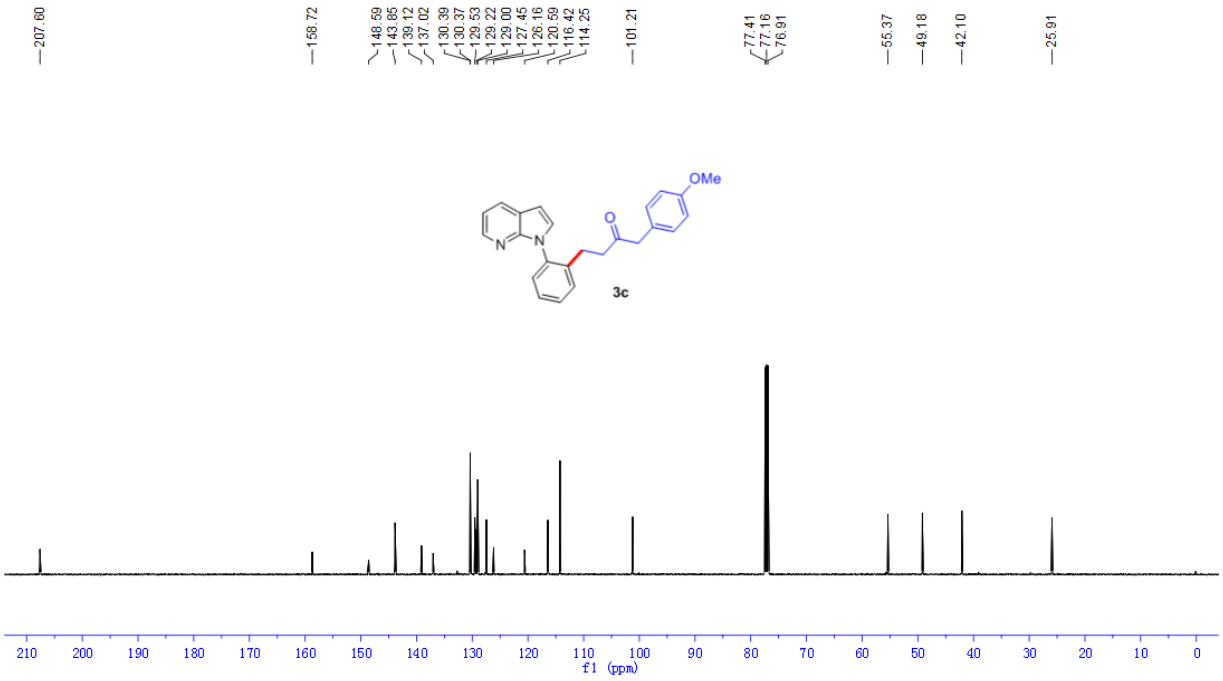
^{1}H NMR spectrum of **3b**



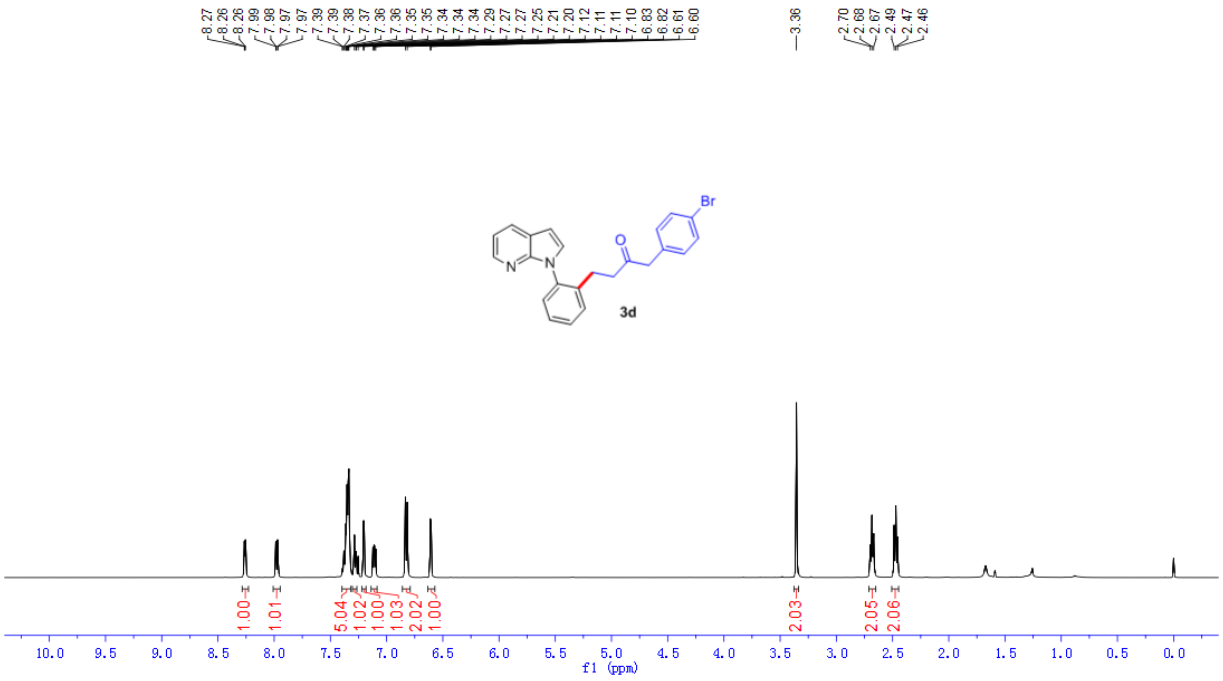
^{13}C NMR spectrum of **3b**



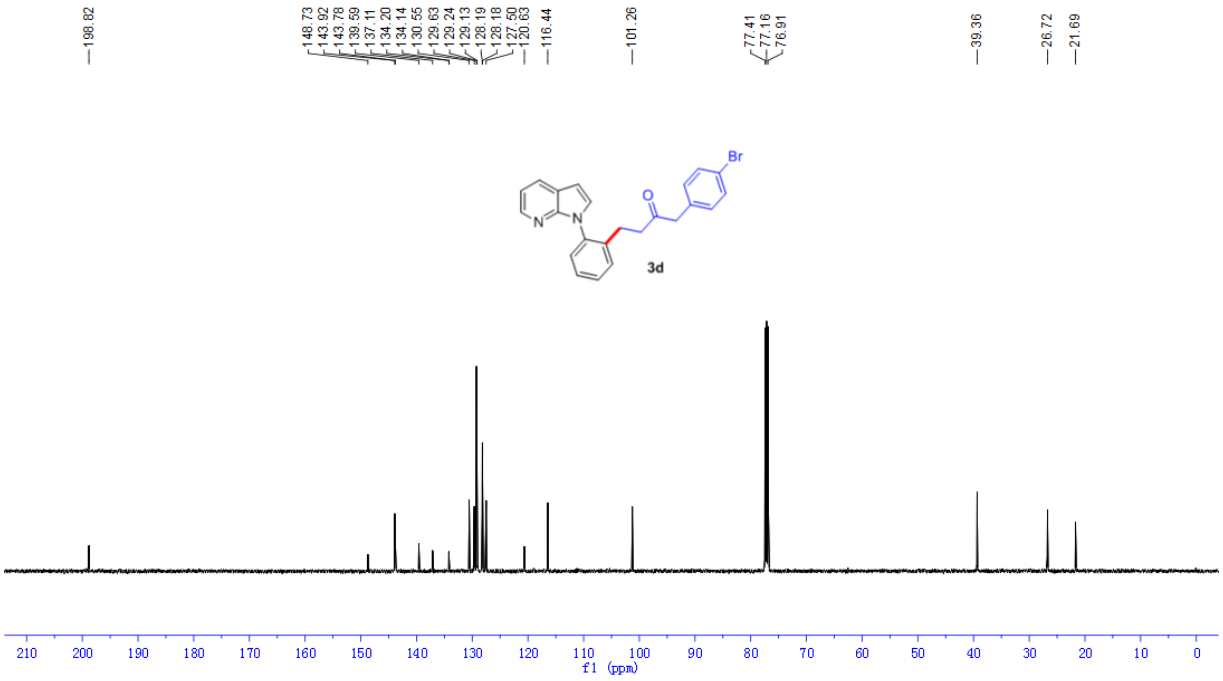
^{1}H NMR spectrum of **3c**



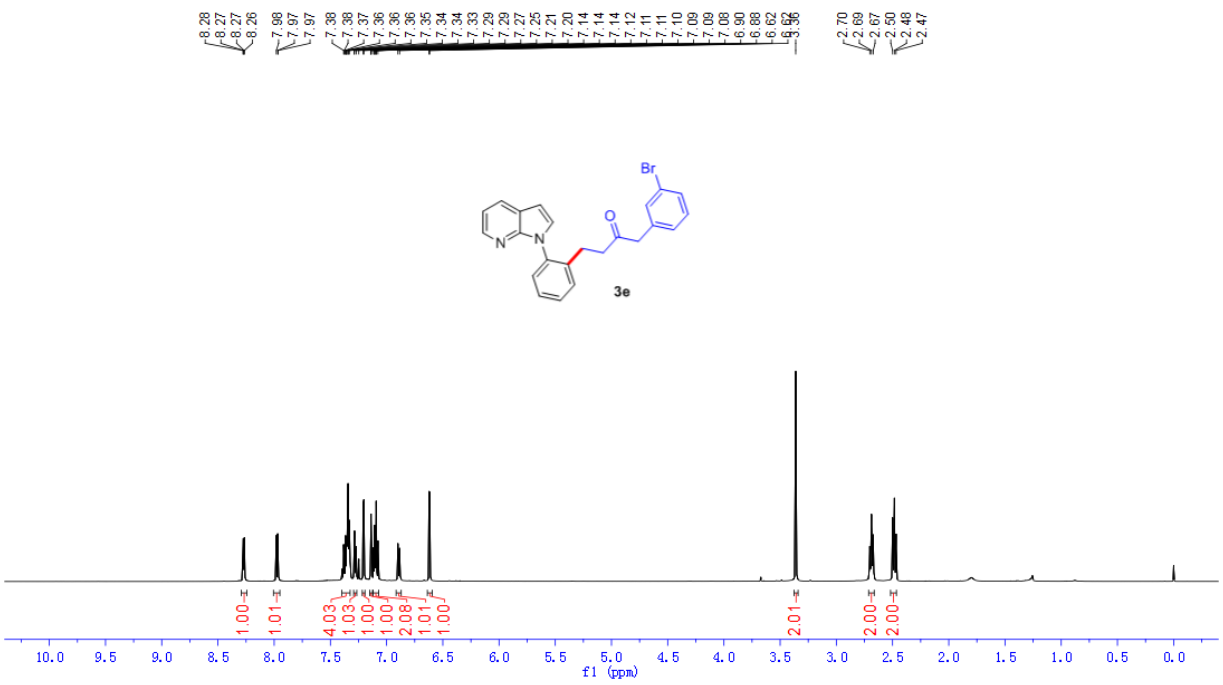
^{13}C NMR spectrum of **3c**



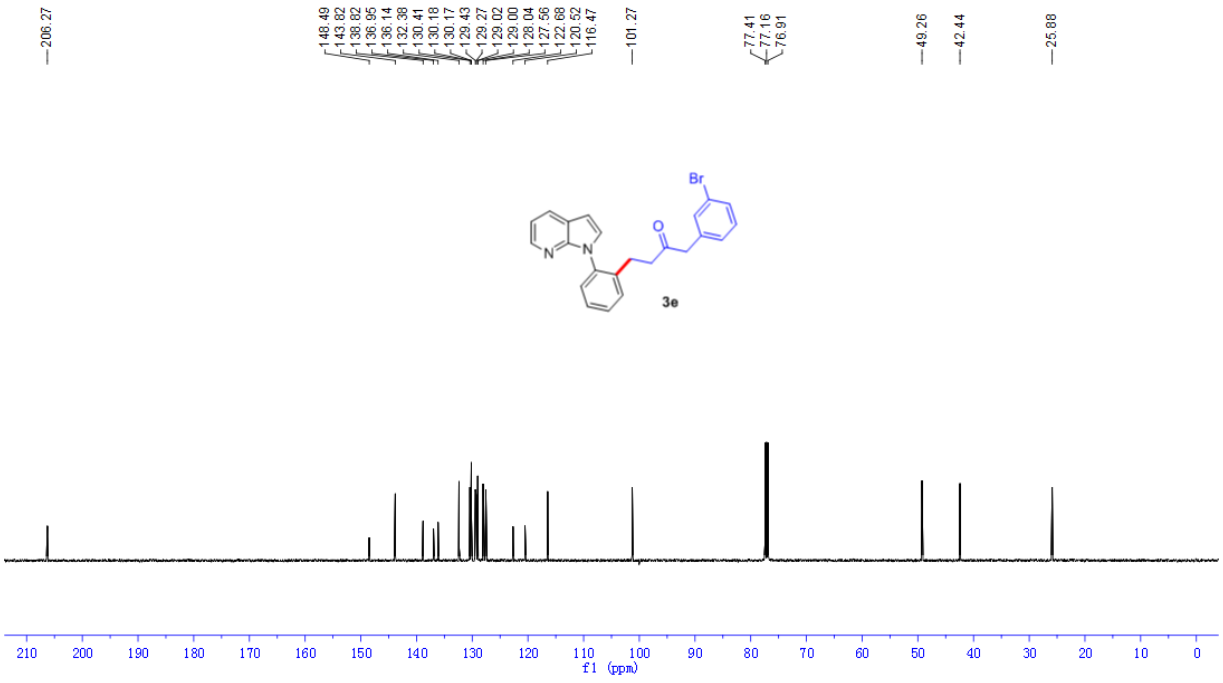
^{1}H NMR spectrum of **3d**



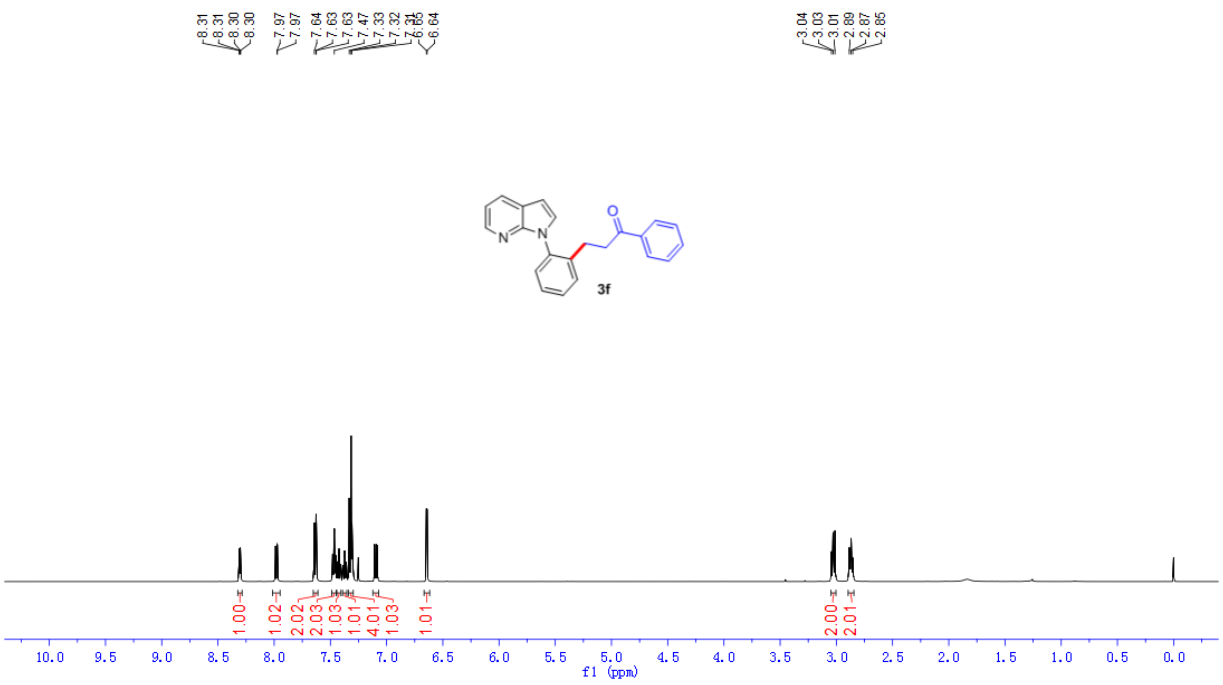
^{13}C NMR spectrum of **3d**



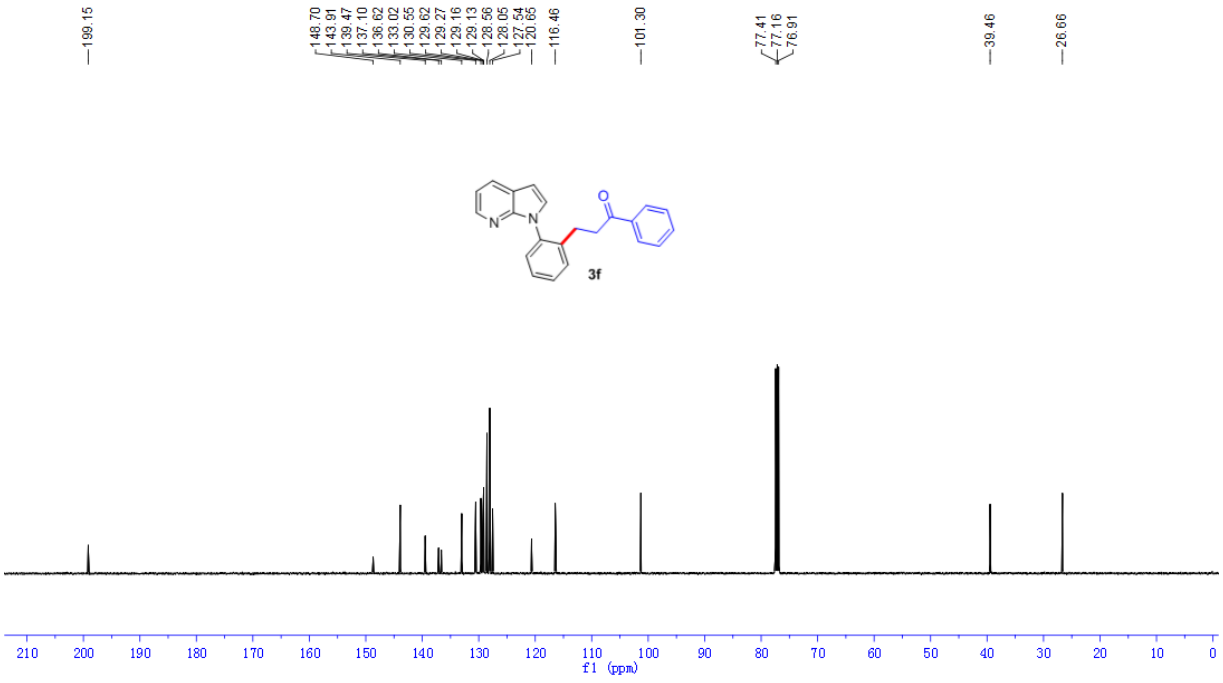
^{1}H NMR spectrum of **3e**



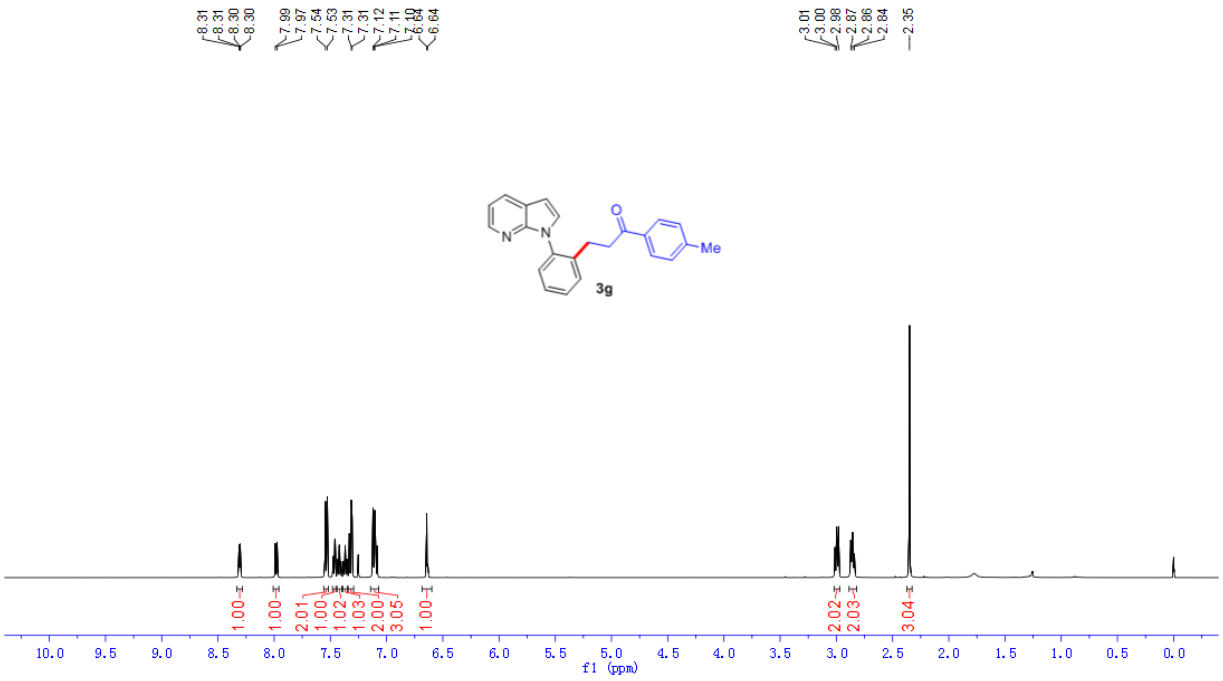
^{13}C NMR spectrum of **3e**



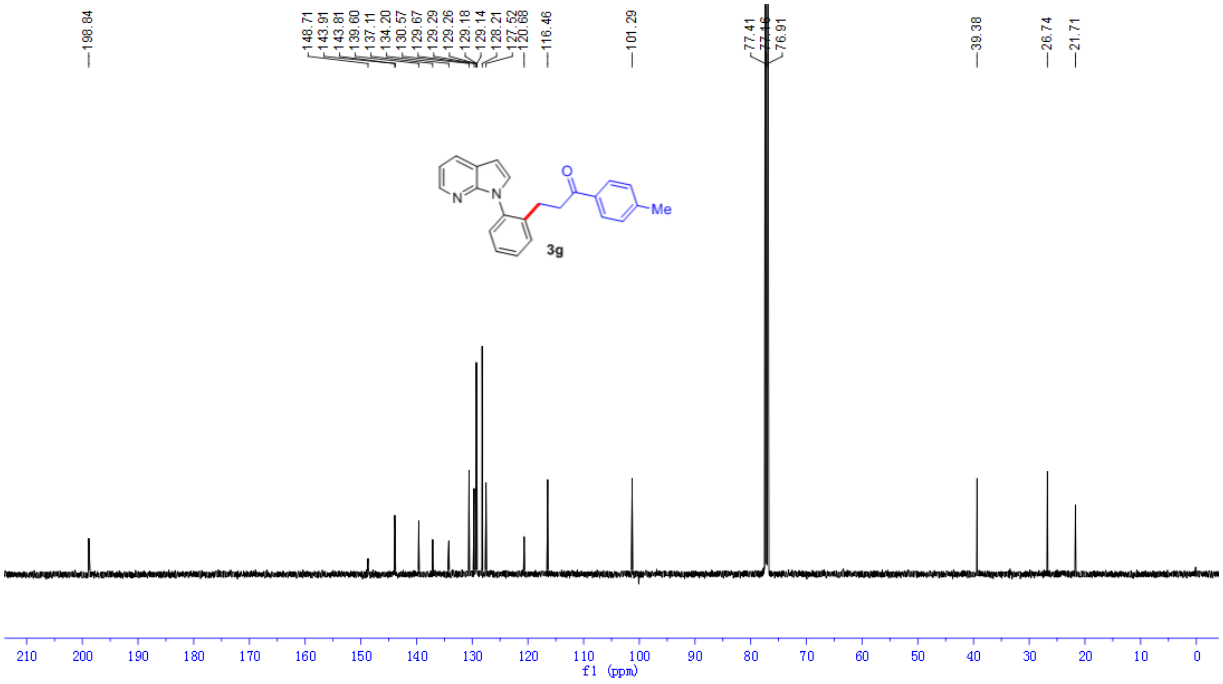
^{1}H NMR spectrum of **3f**



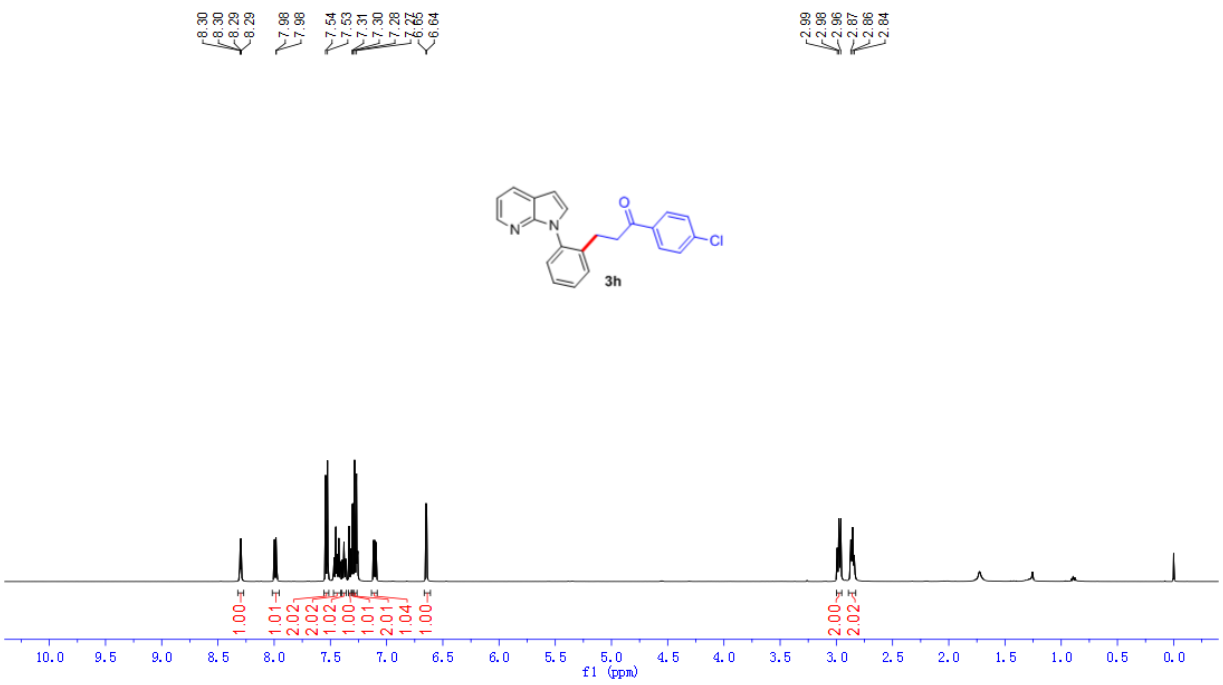
^{13}C NMR spectrum of **3f**



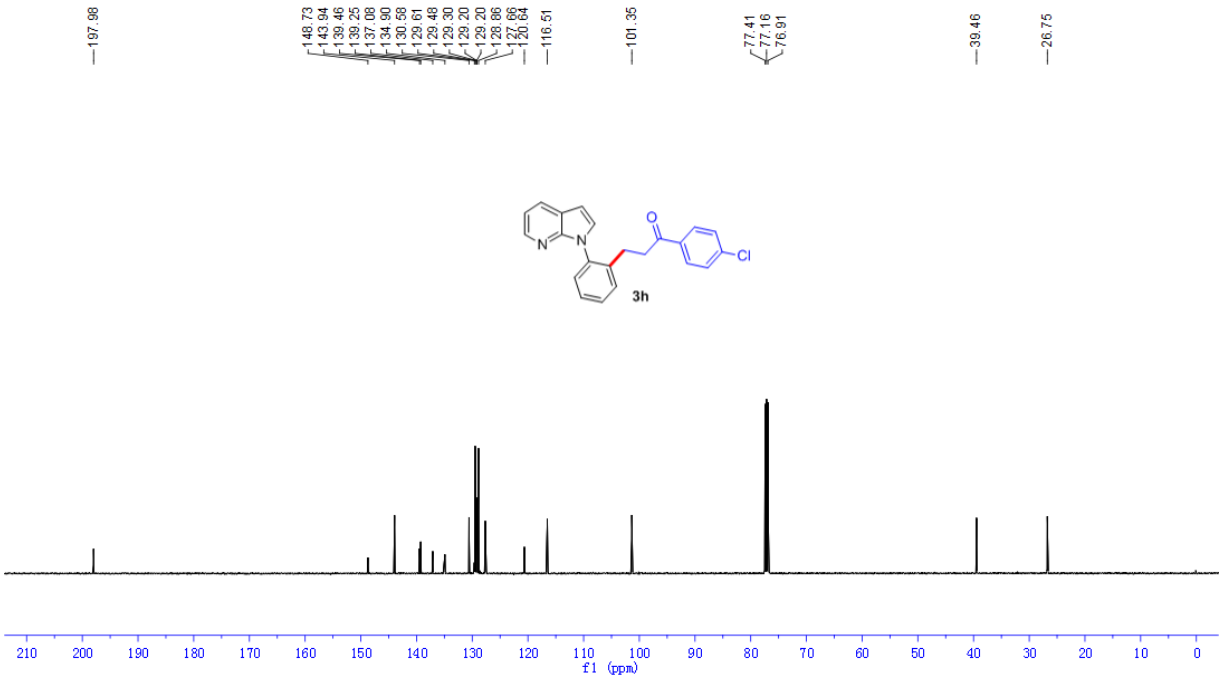
^{1}H NMR spectrum of **3g**



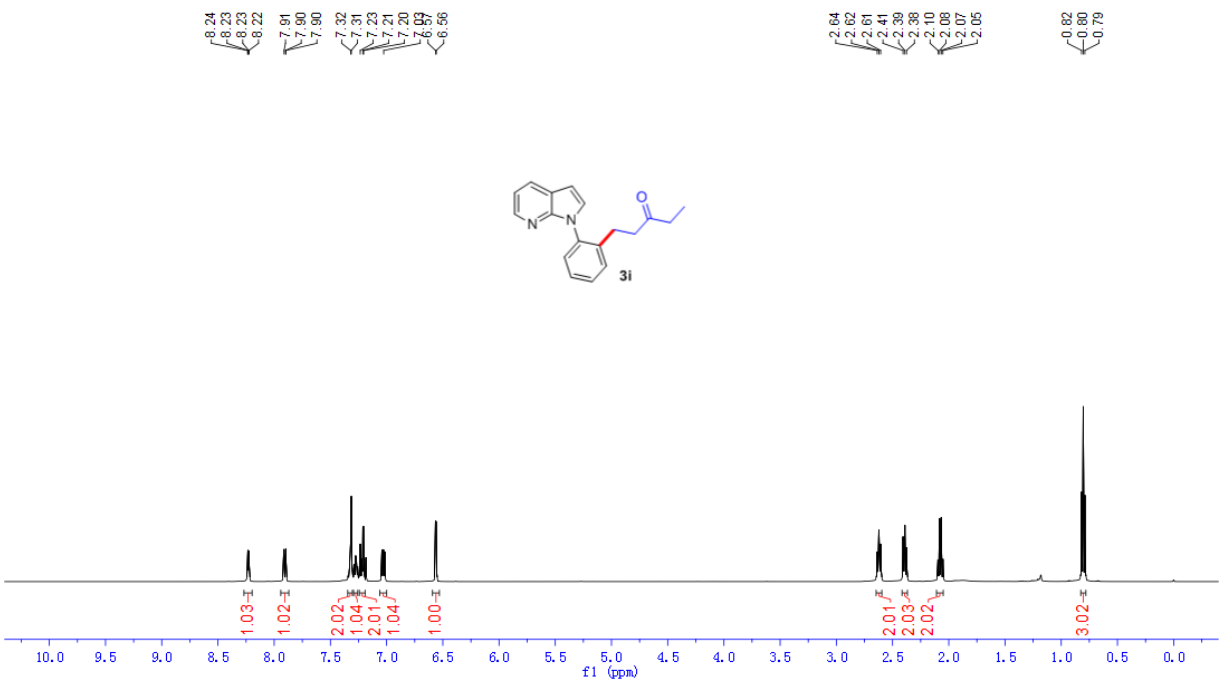
^{13}C NMR spectrum of **3g**



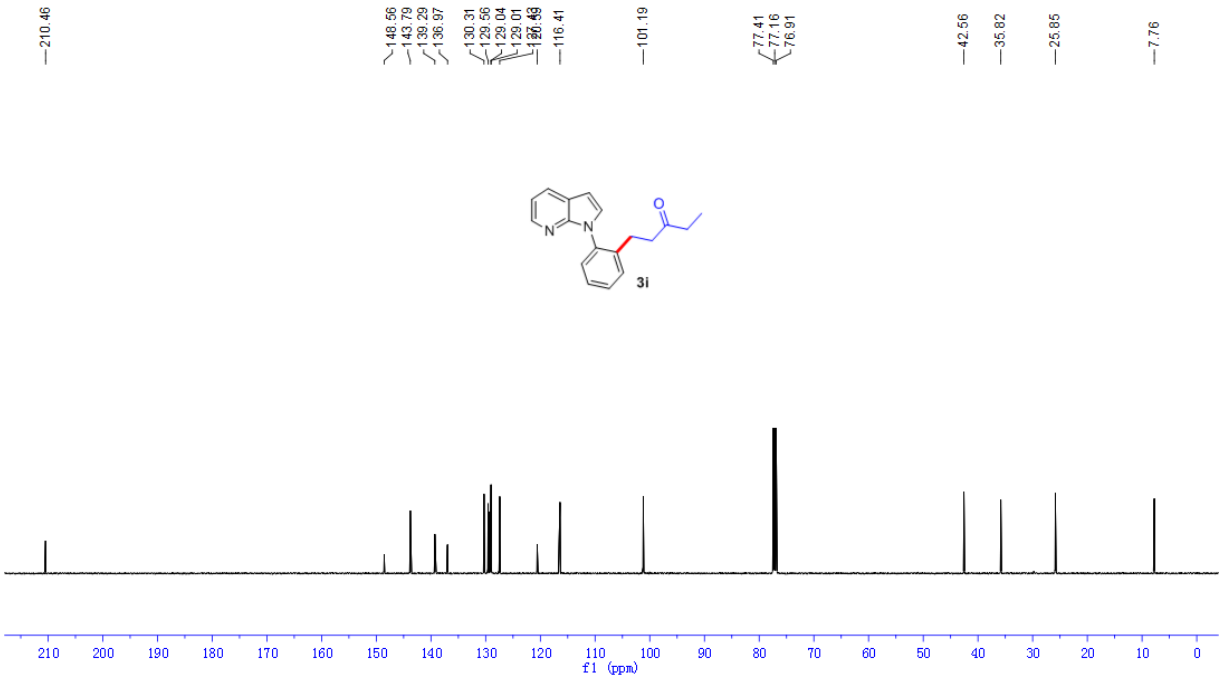
^{1}H NMR spectrum of **3h**



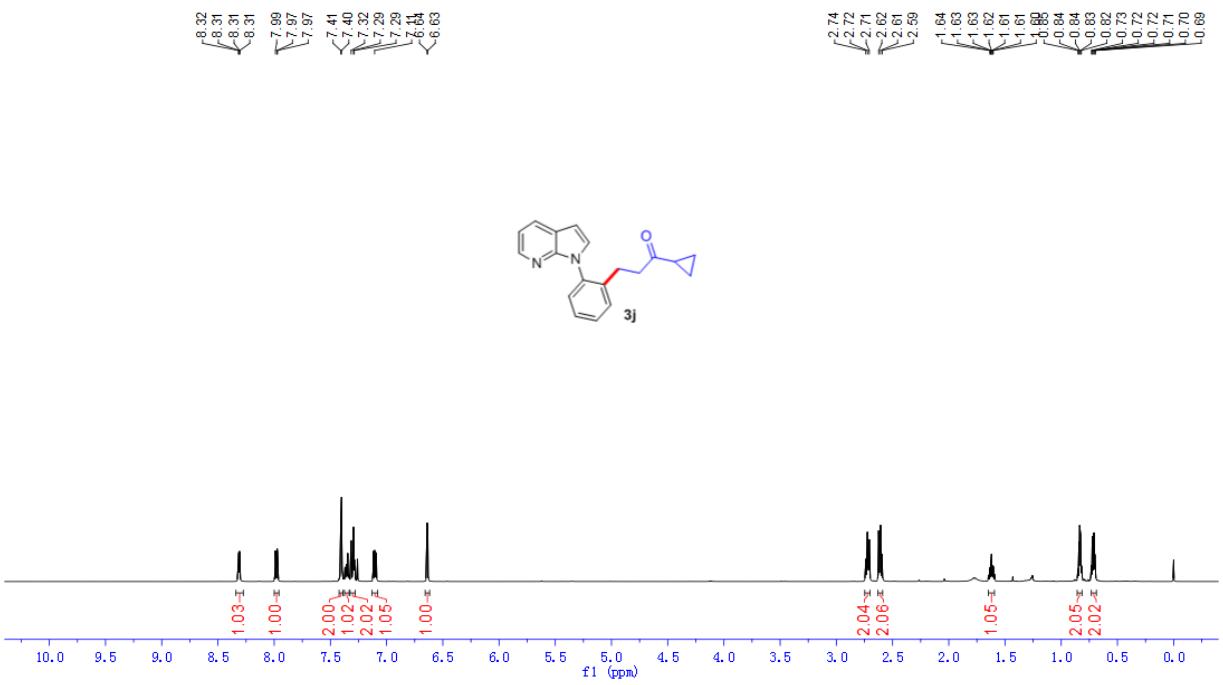
^{13}C NMR spectrum of **3h**



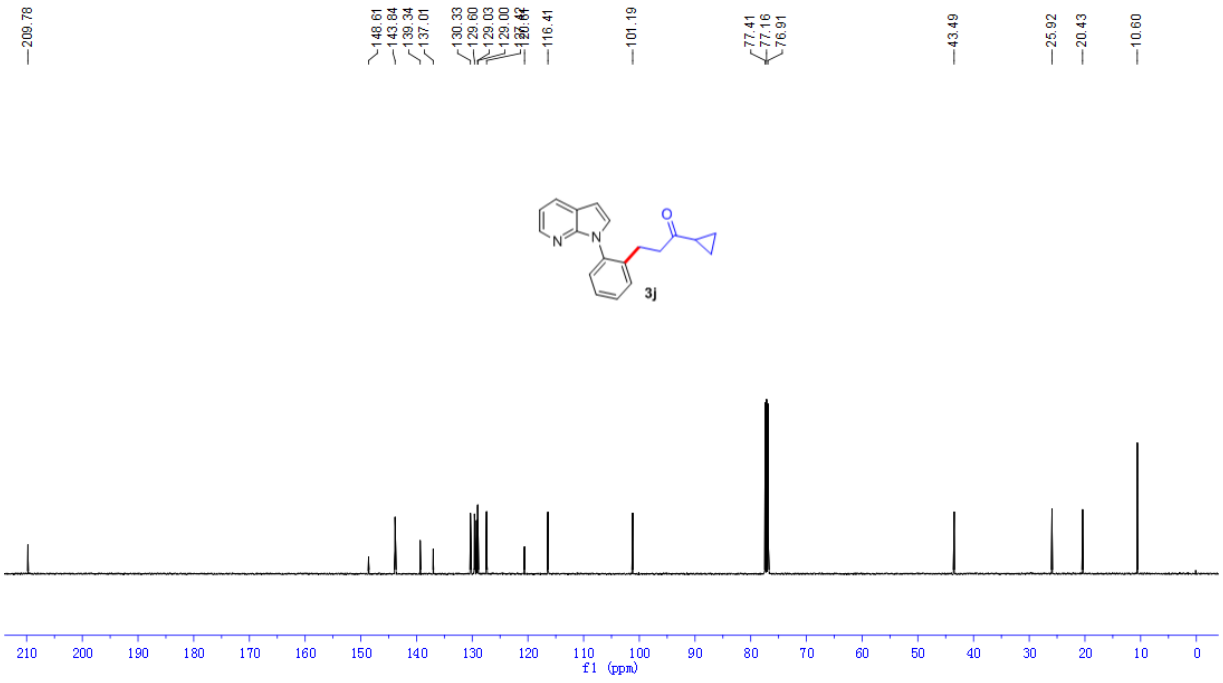
^{1}H NMR spectrum of **3i**



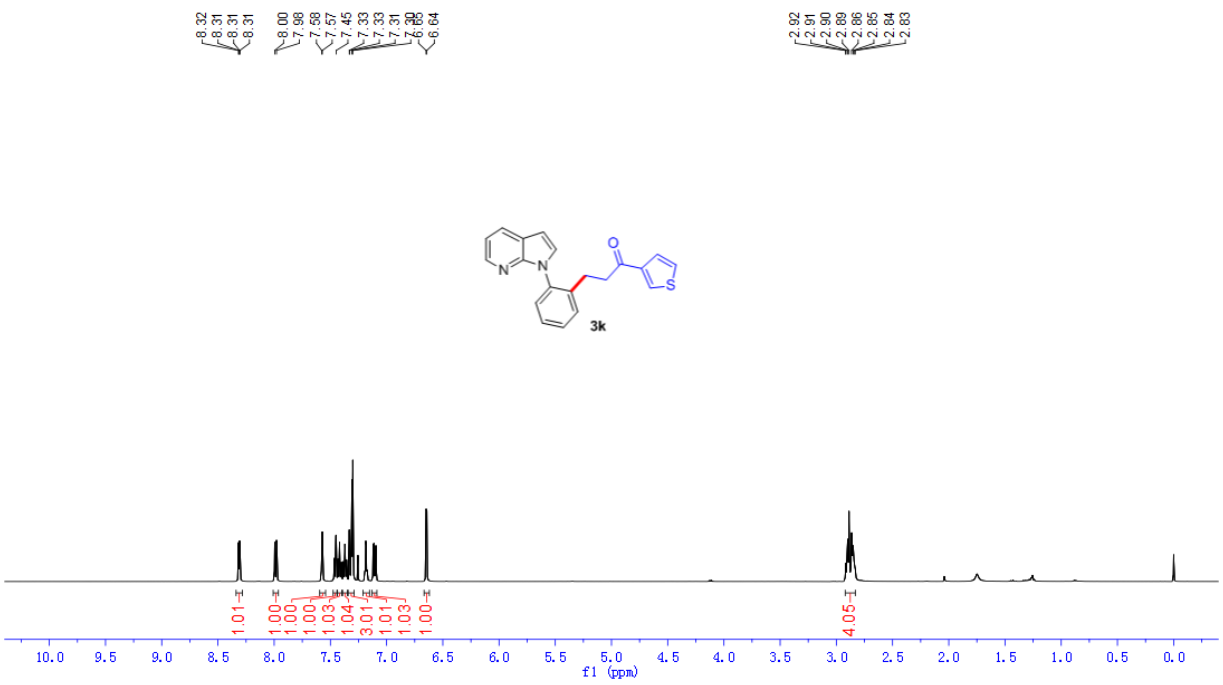
^{13}C NMR spectrum of **3i**



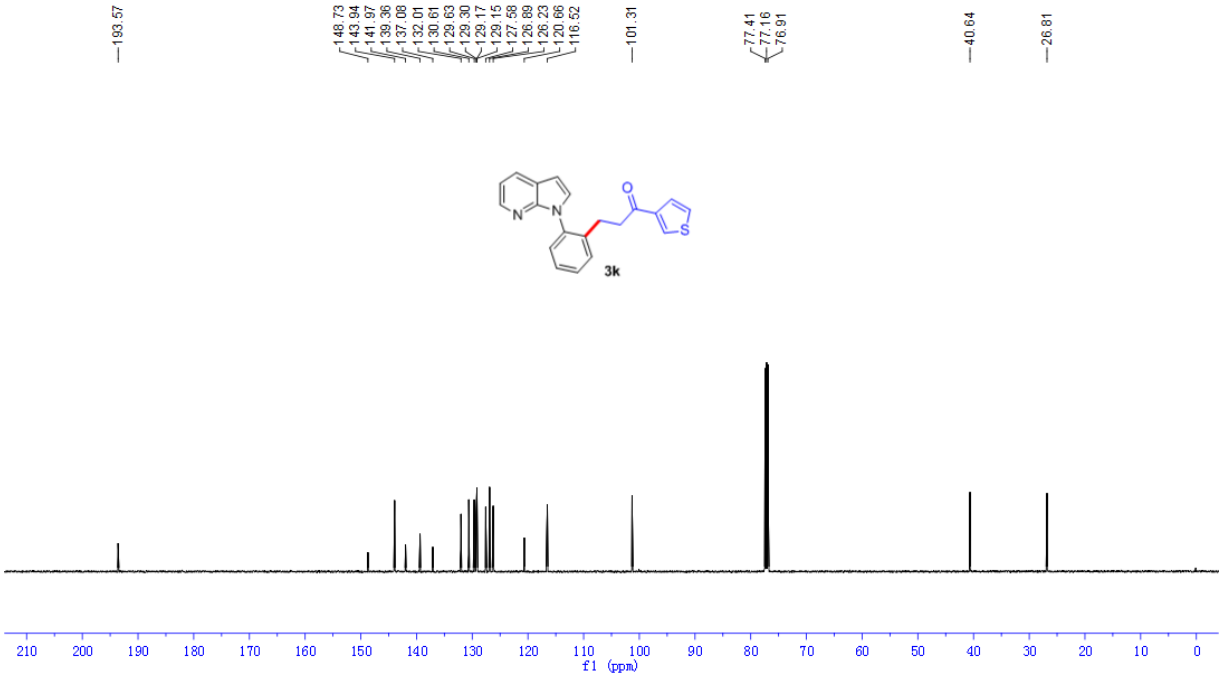
^{1}H NMR spectrum of **3j**



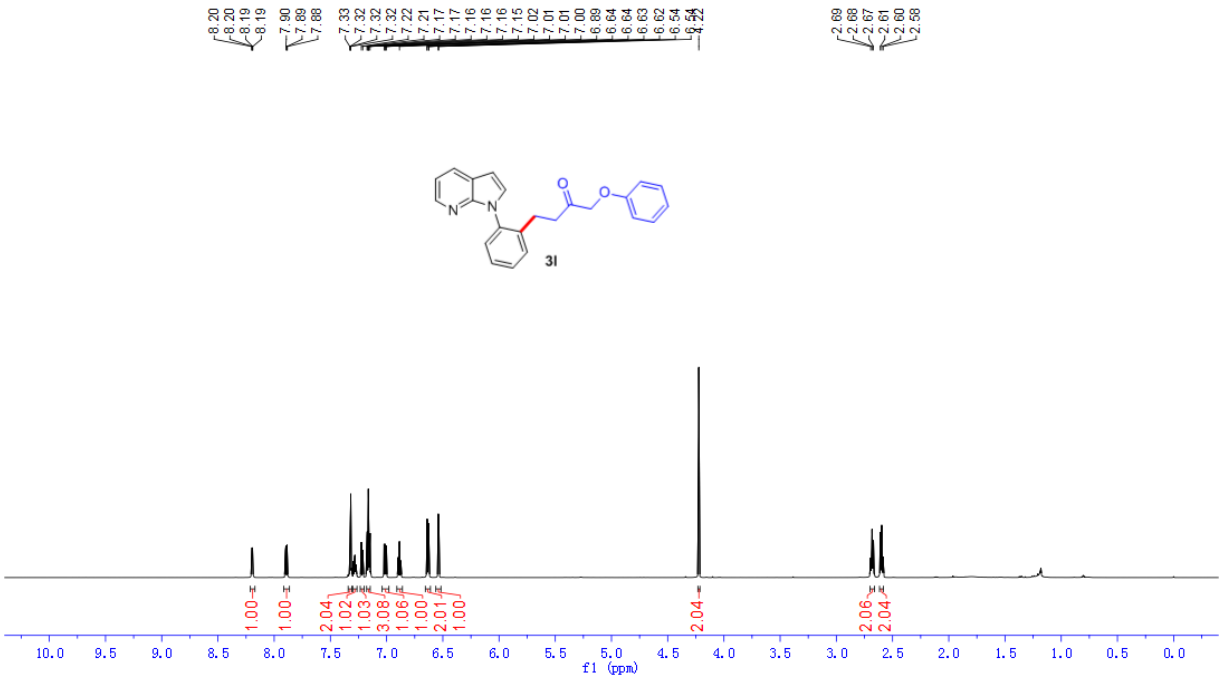
^{13}C NMR spectrum of **3j**



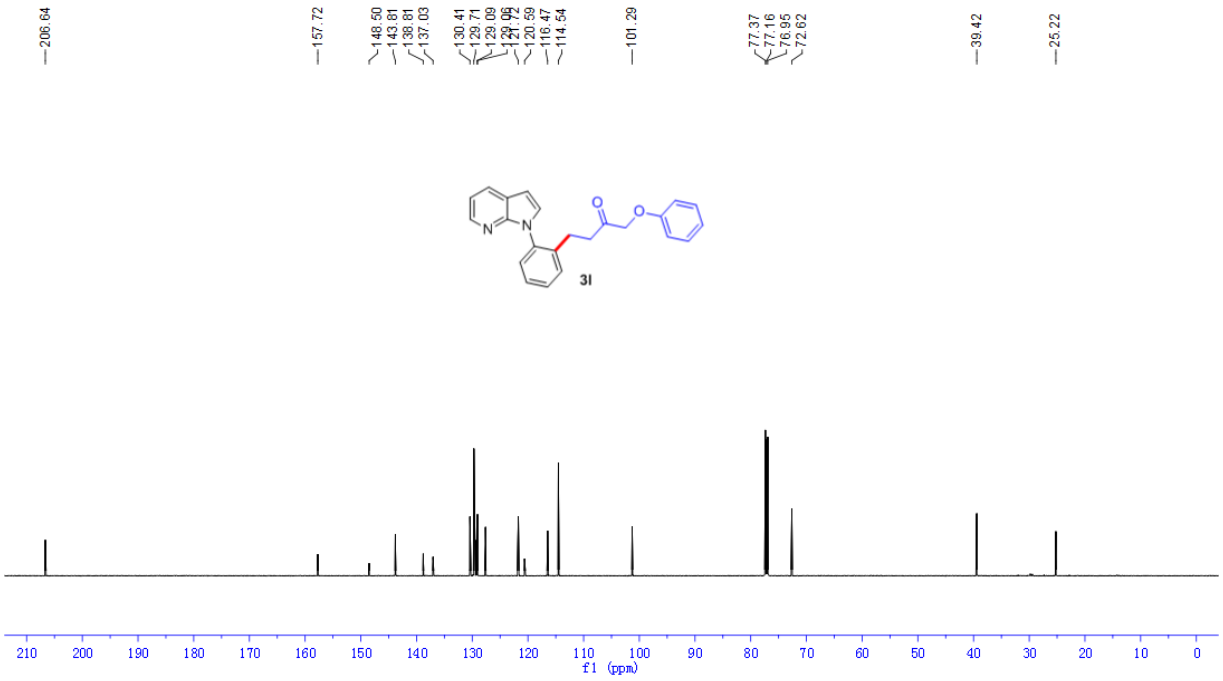
^{1}H NMR spectrum of **3k**



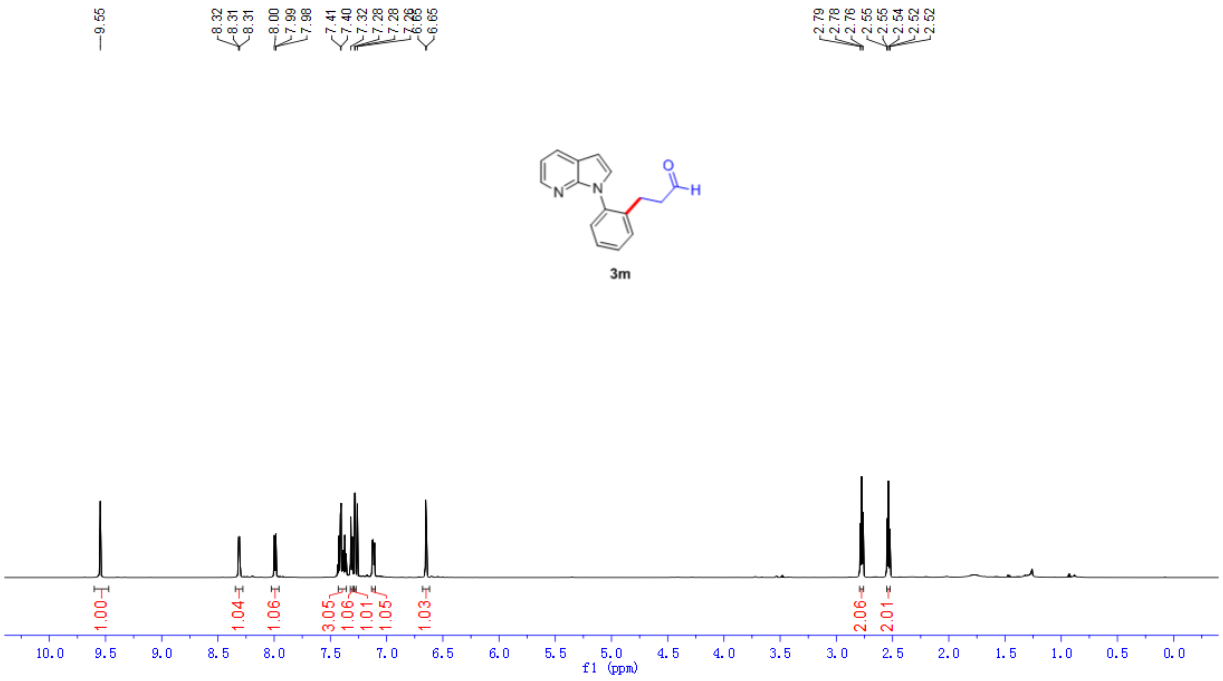
^{13}C NMR spectrum of **3k**



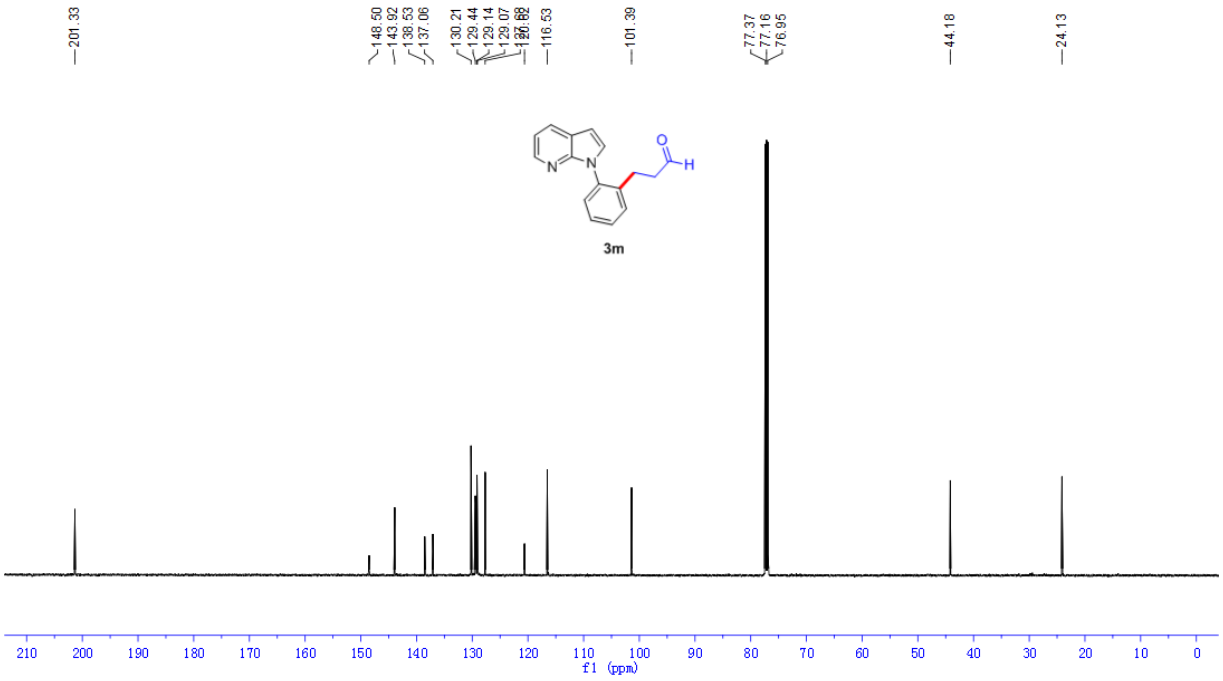
^{1}H NMR spectrum of **3l**



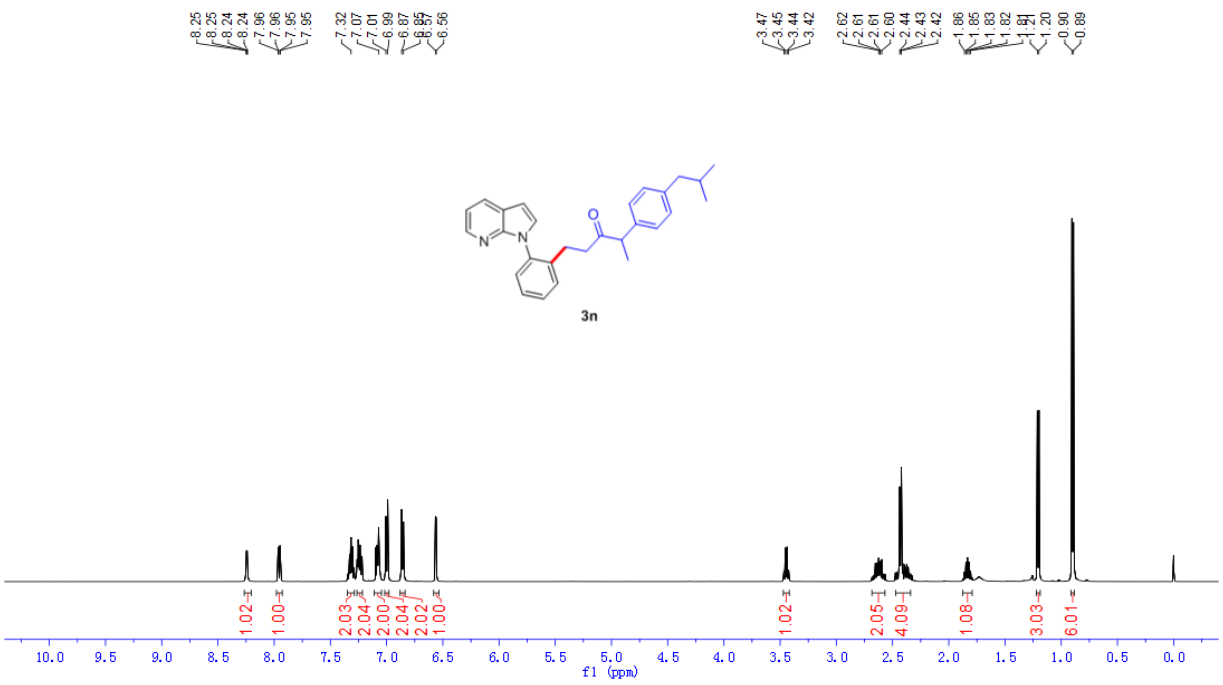
^{13}C NMR spectrum of **3l**



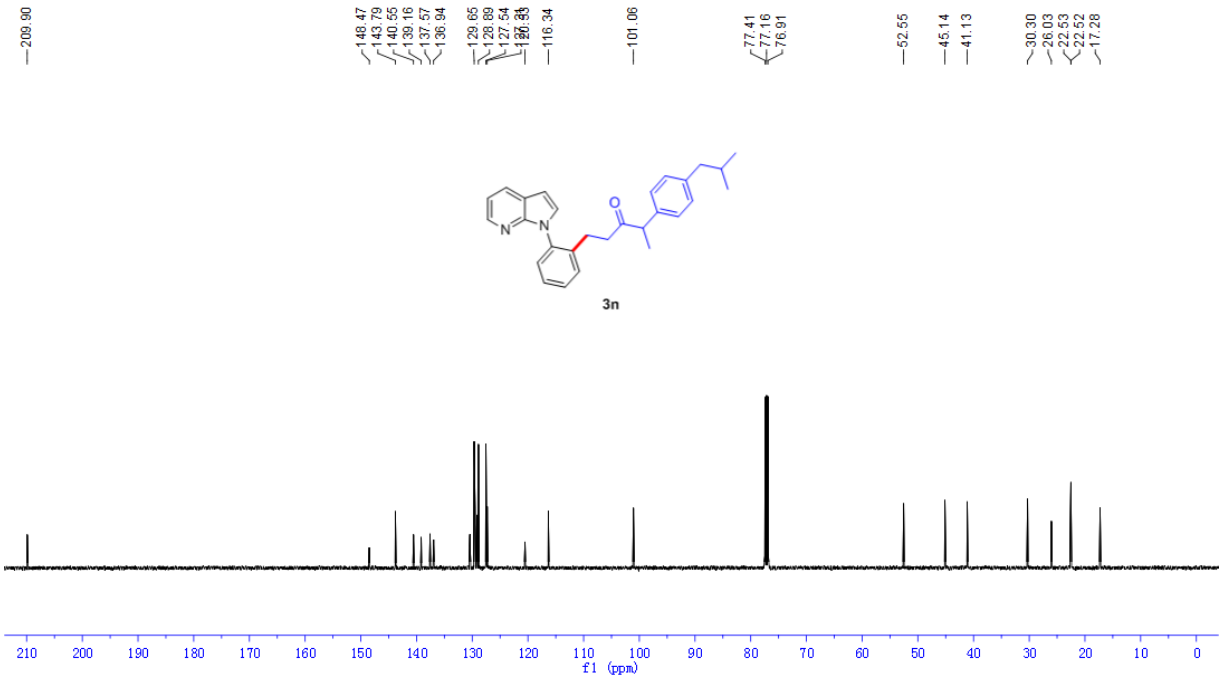
^{1}H NMR spectrum of **3m**



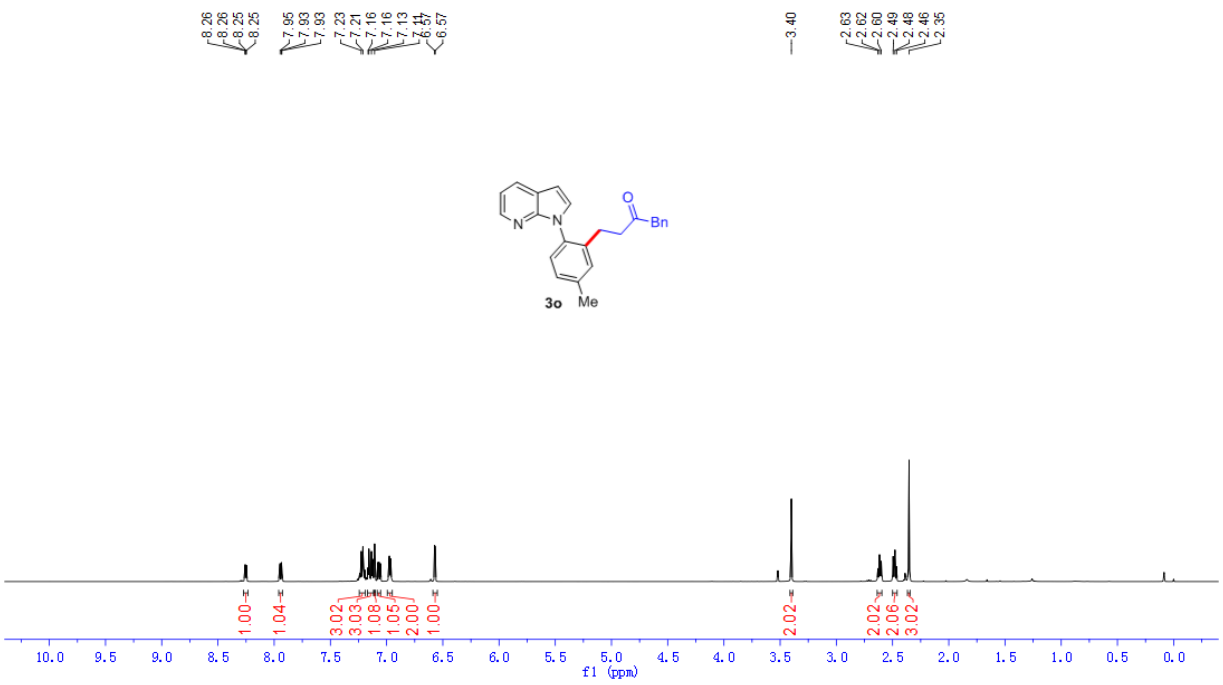
^{13}C NMR spectrum of **3m**



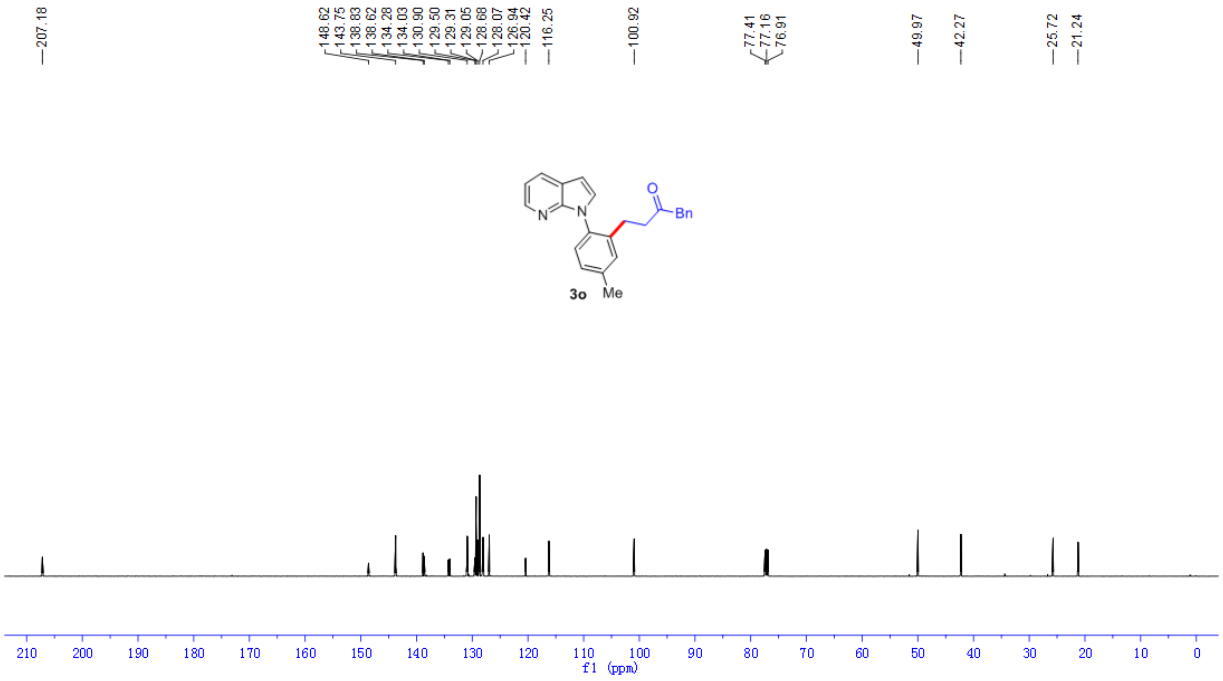
^{1}H NMR spectrum of **3n**



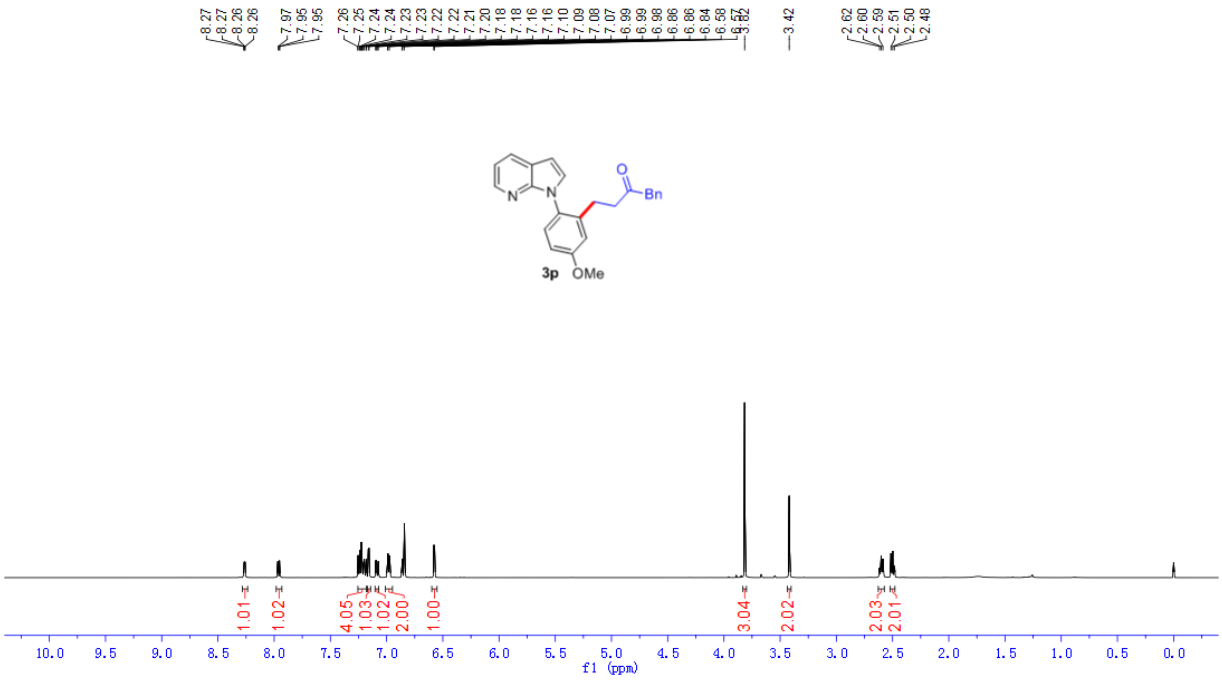
^{13}C NMR spectrum of **3n**



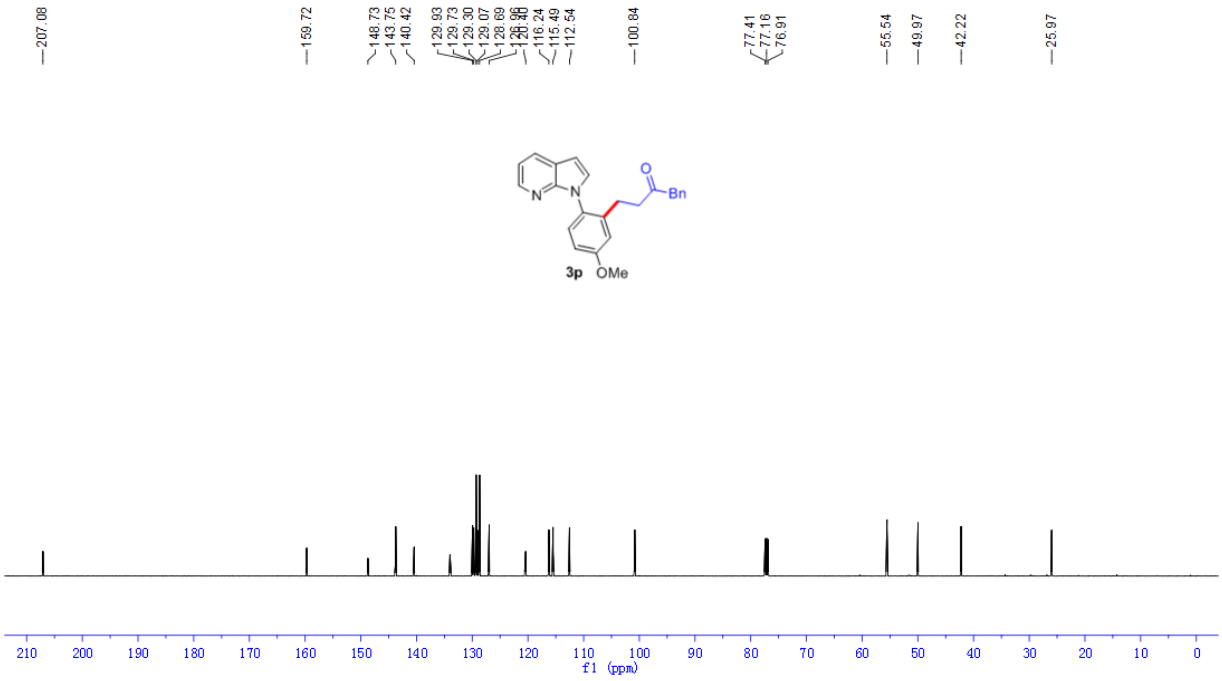
^{1}H NMR spectrum of **3o**



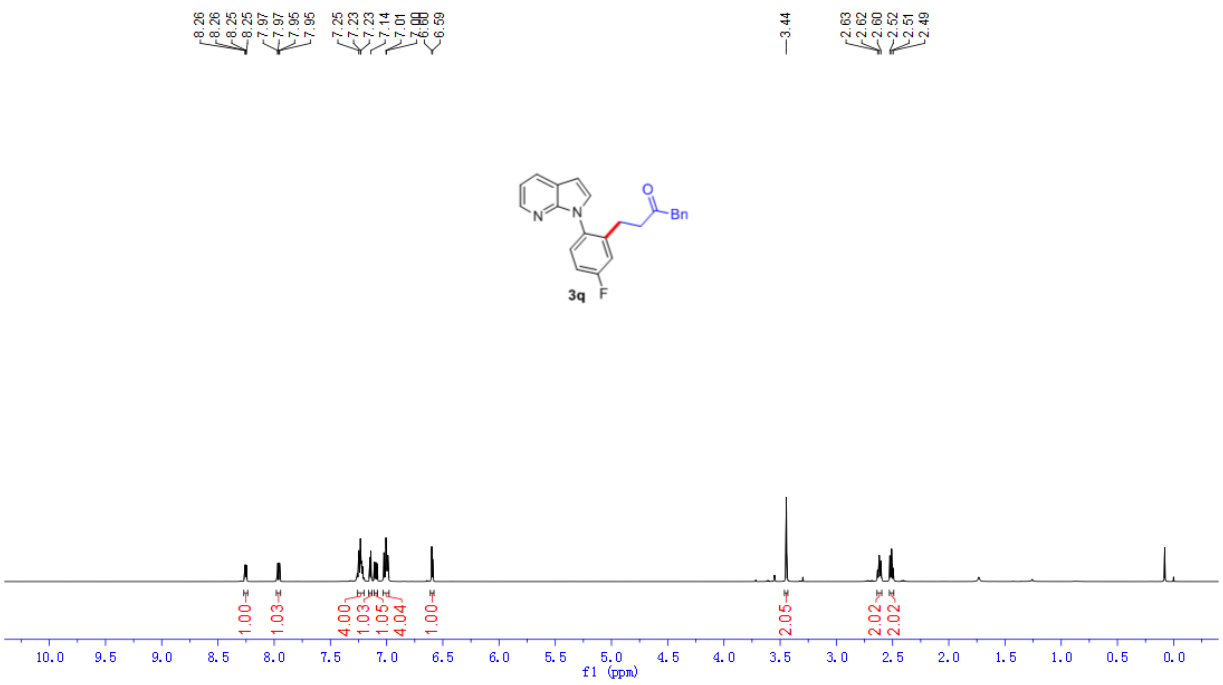
^{13}C NMR spectrum of **3o**



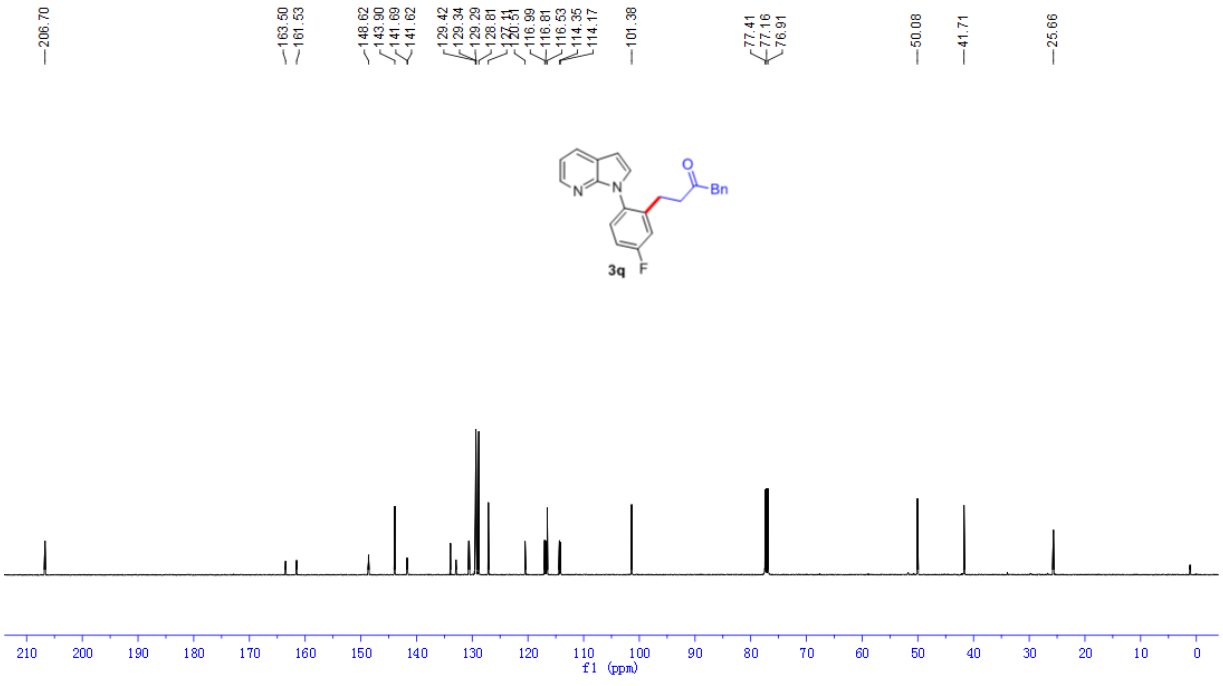
^{1}H NMR spectrum of **3p**



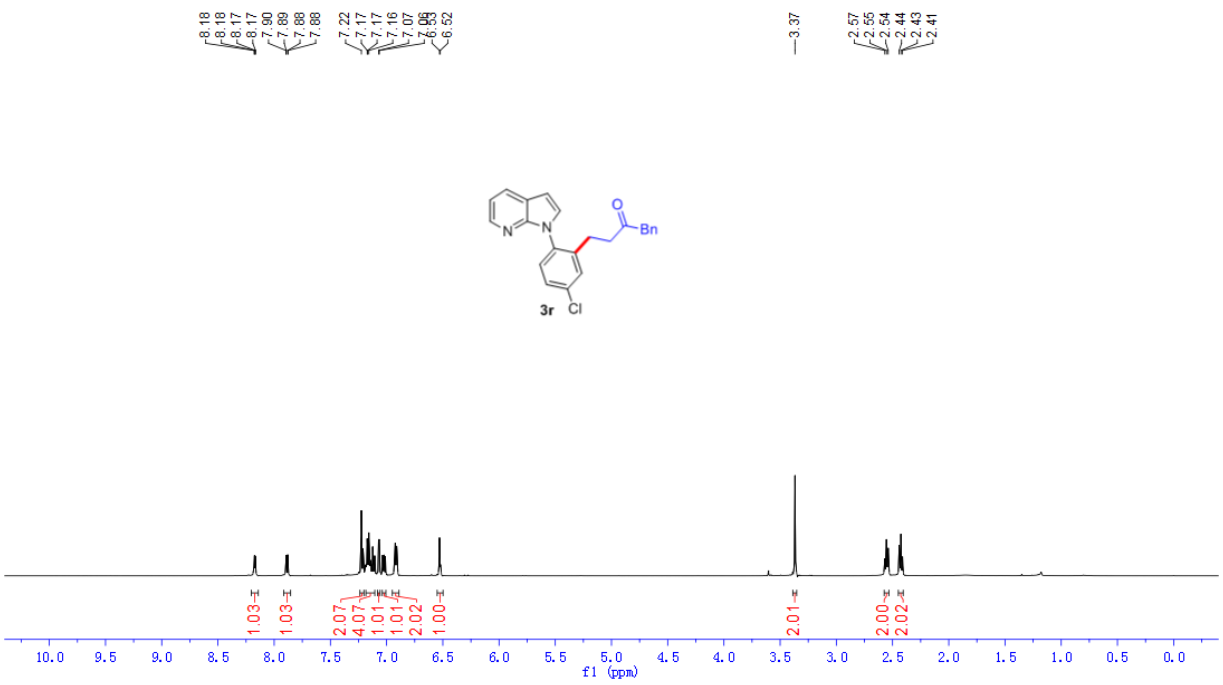
^{13}C NMR spectrum of **3p**



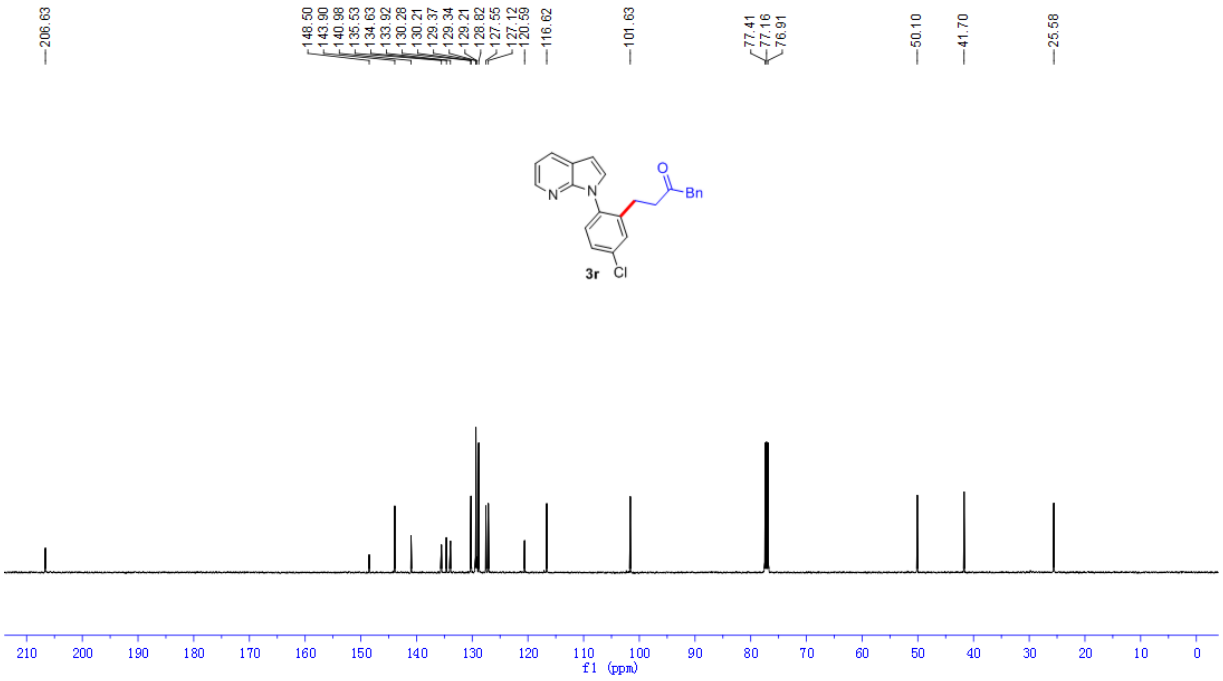
^{1}H NMR spectrum of **3q**



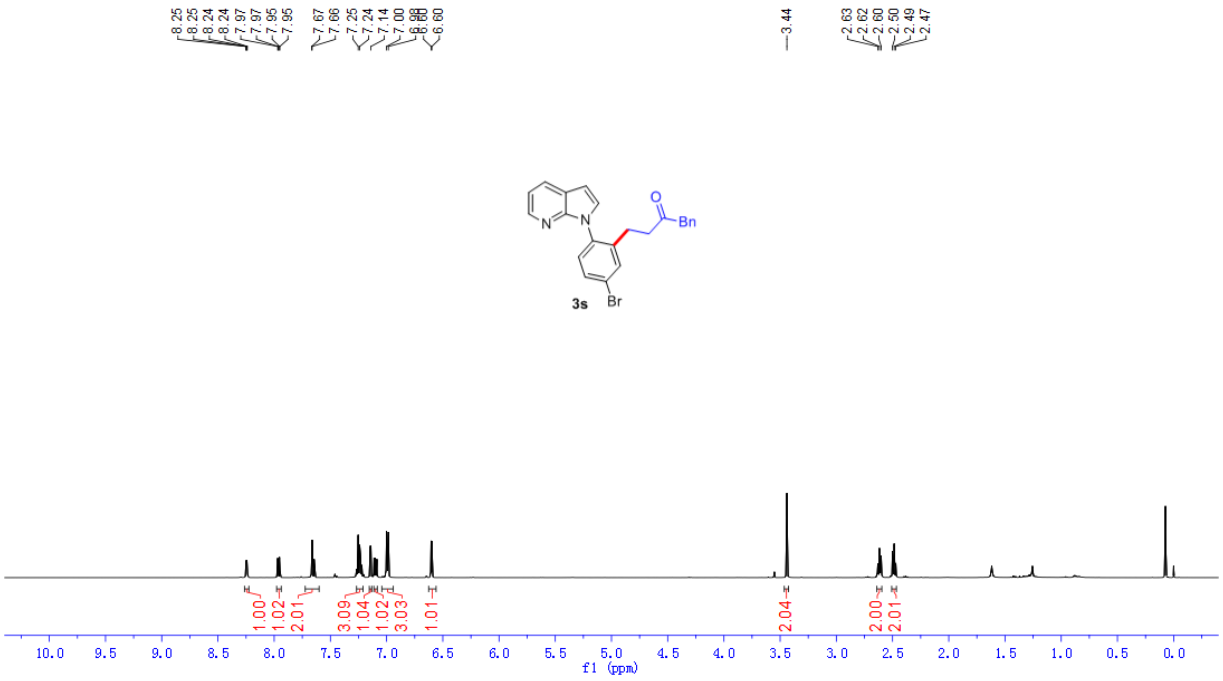
^{13}C NMR spectrum of **3q**



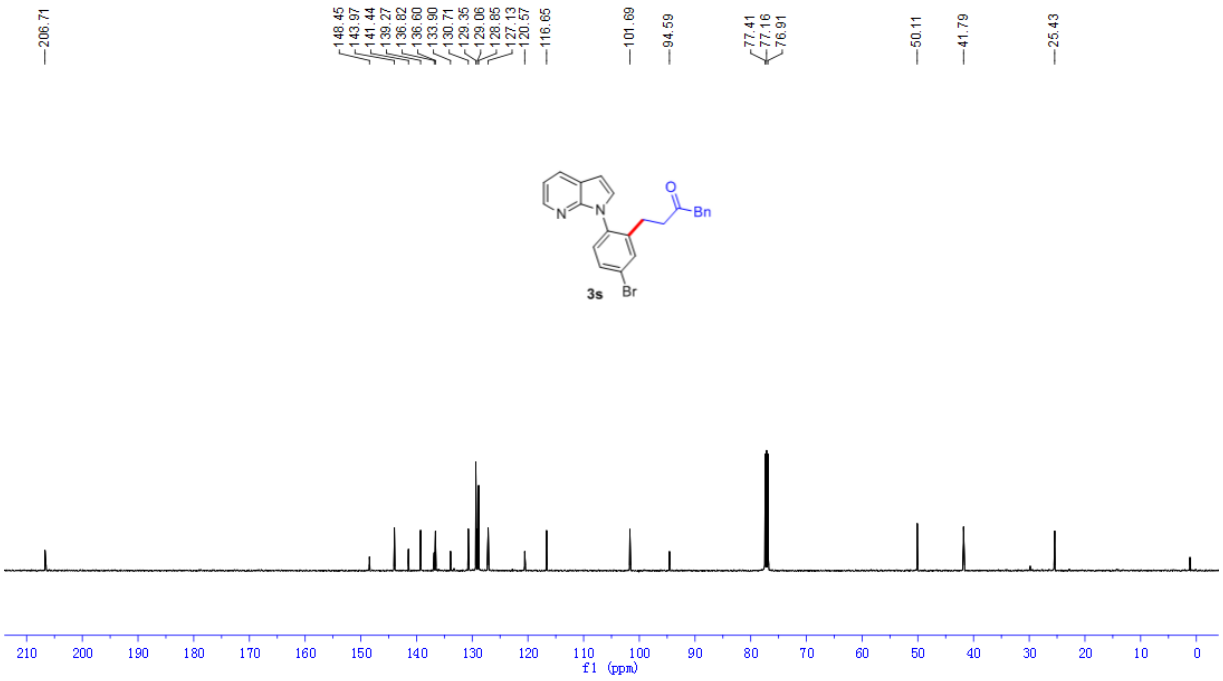
^{1}H NMR spectrum of **3r**



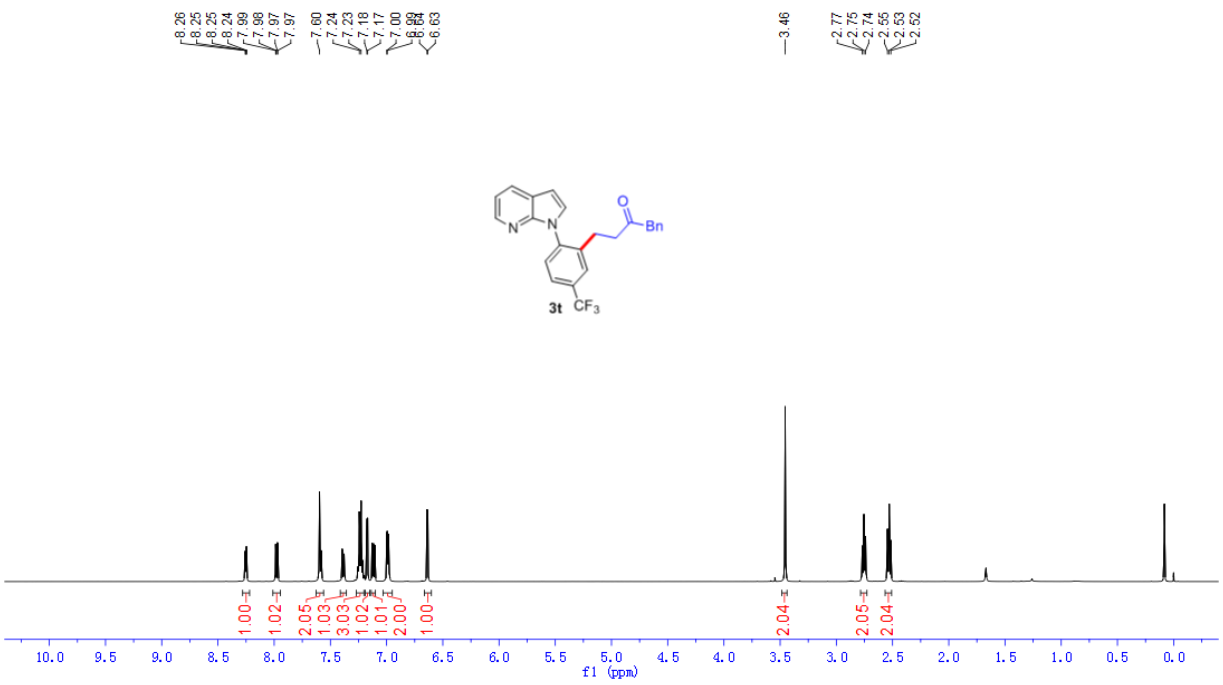
^{13}C NMR spectrum of **3r**



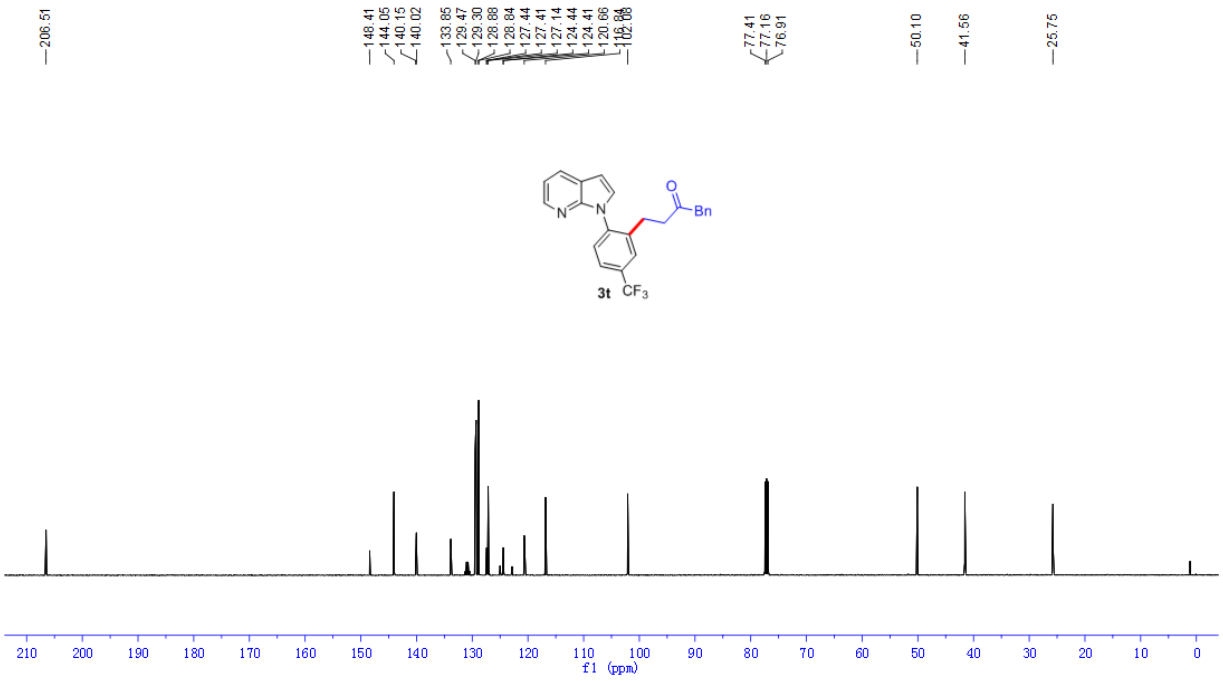
^{1}H NMR spectrum of **3s**



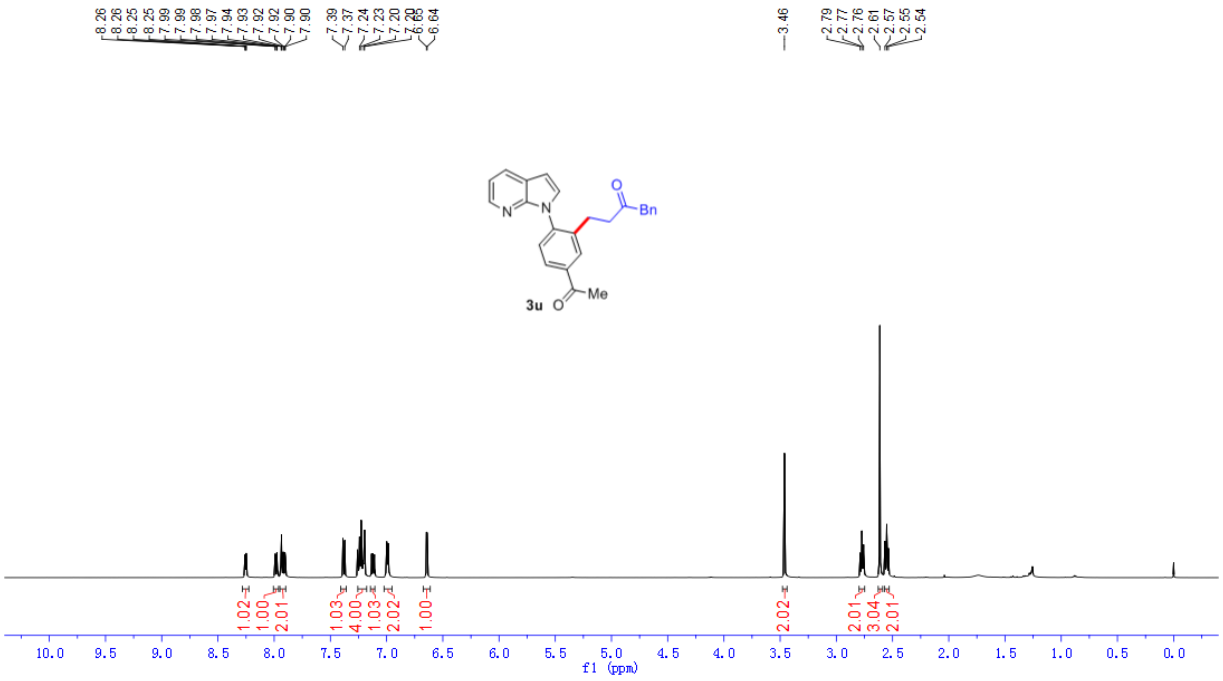
^{13}C NMR spectrum of **3s**



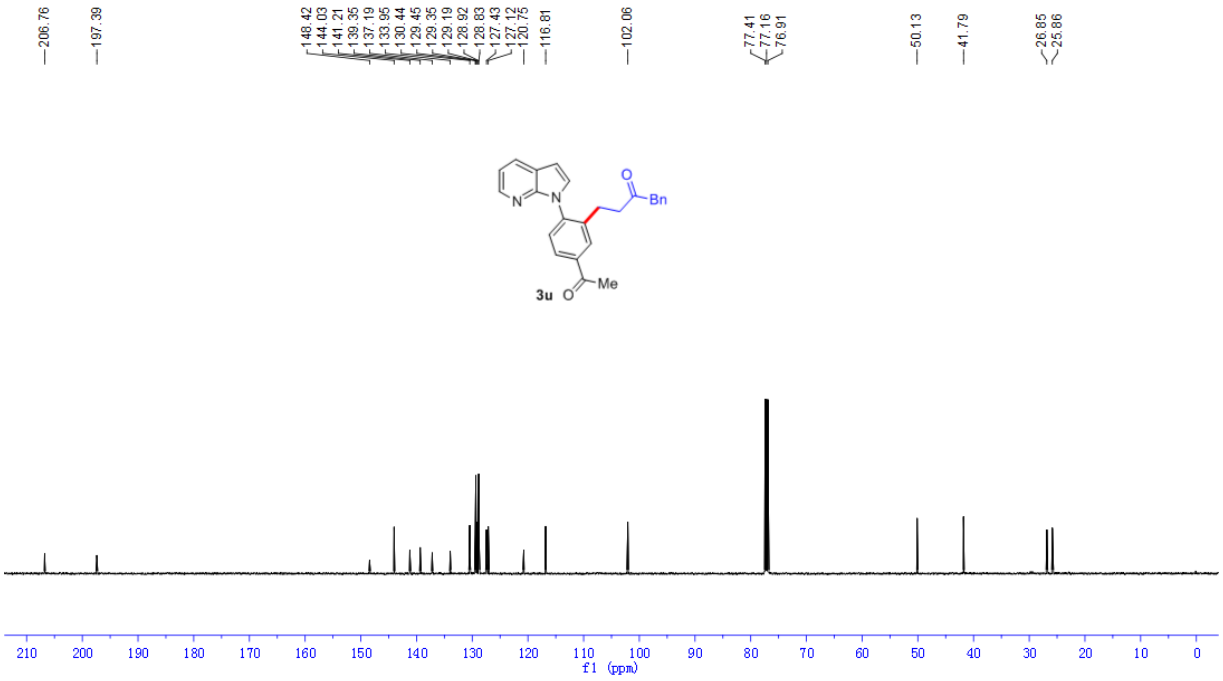
^{1}H NMR spectrum of **3t**



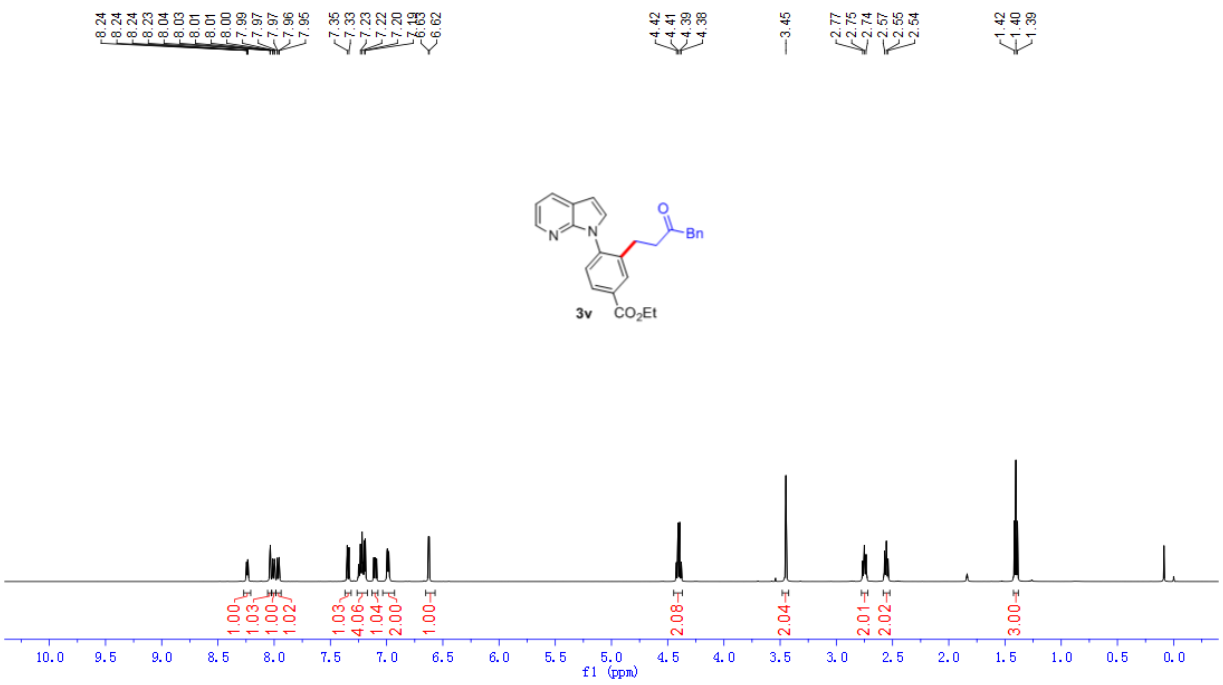
^{13}C NMR spectrum of **3t**



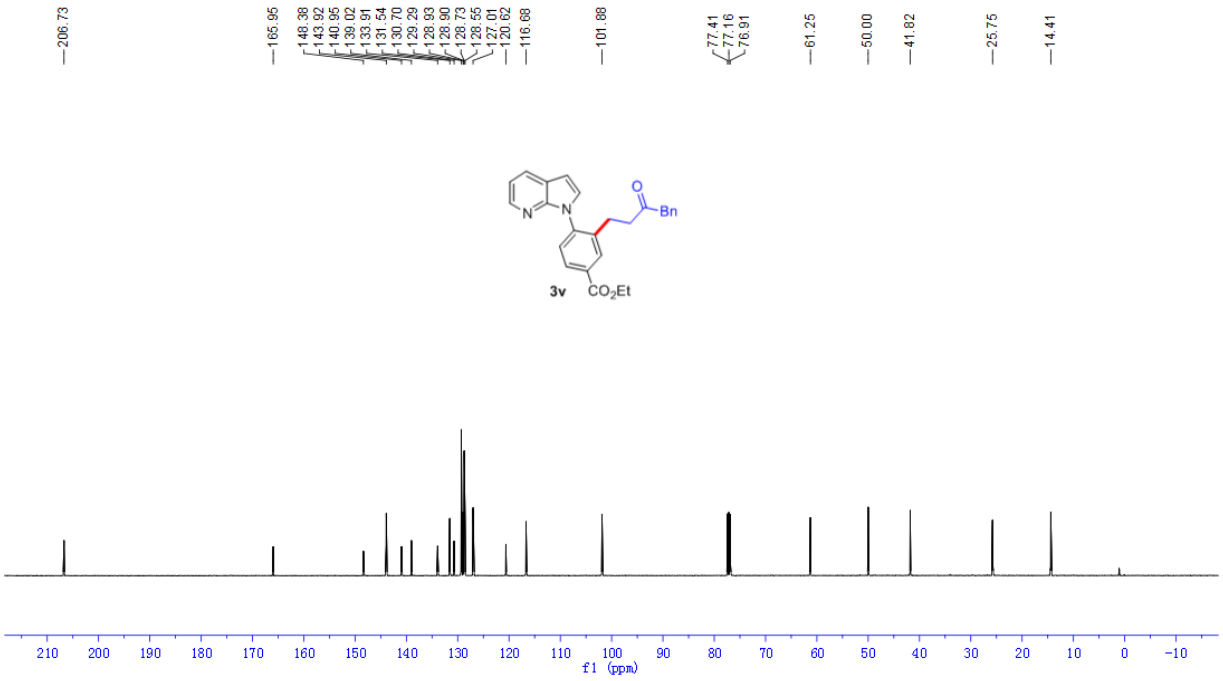
^{1}H NMR spectrum of **3u**



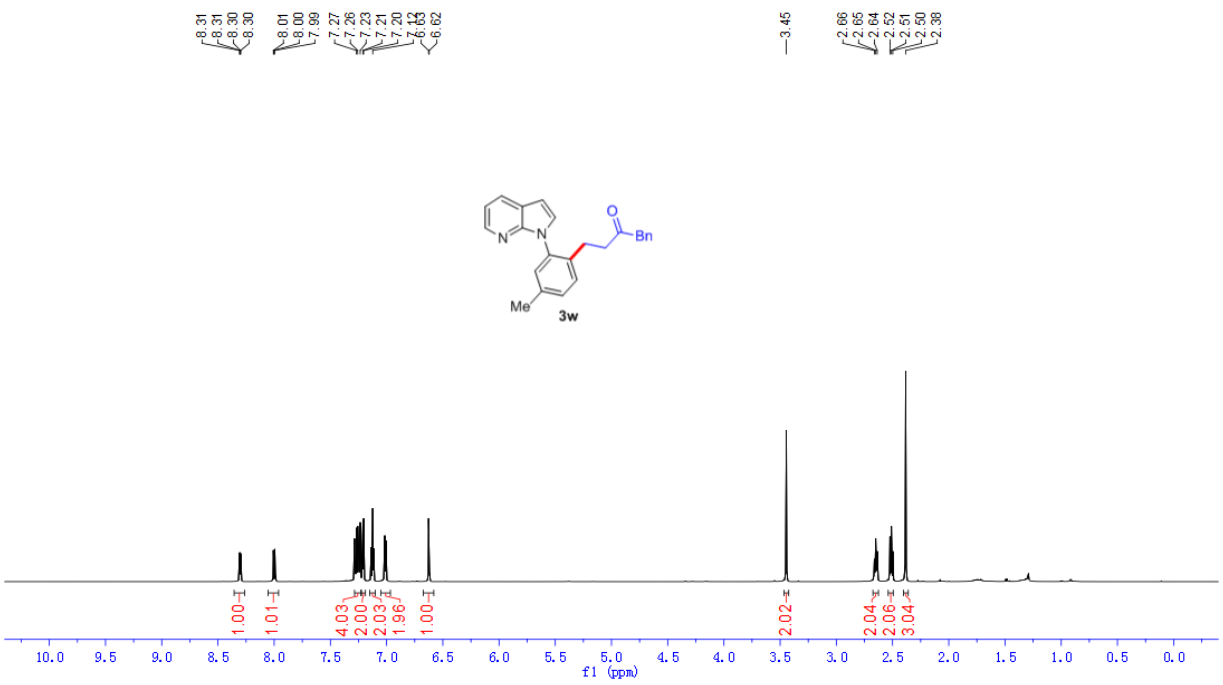
^{13}C NMR spectrum of **3u**



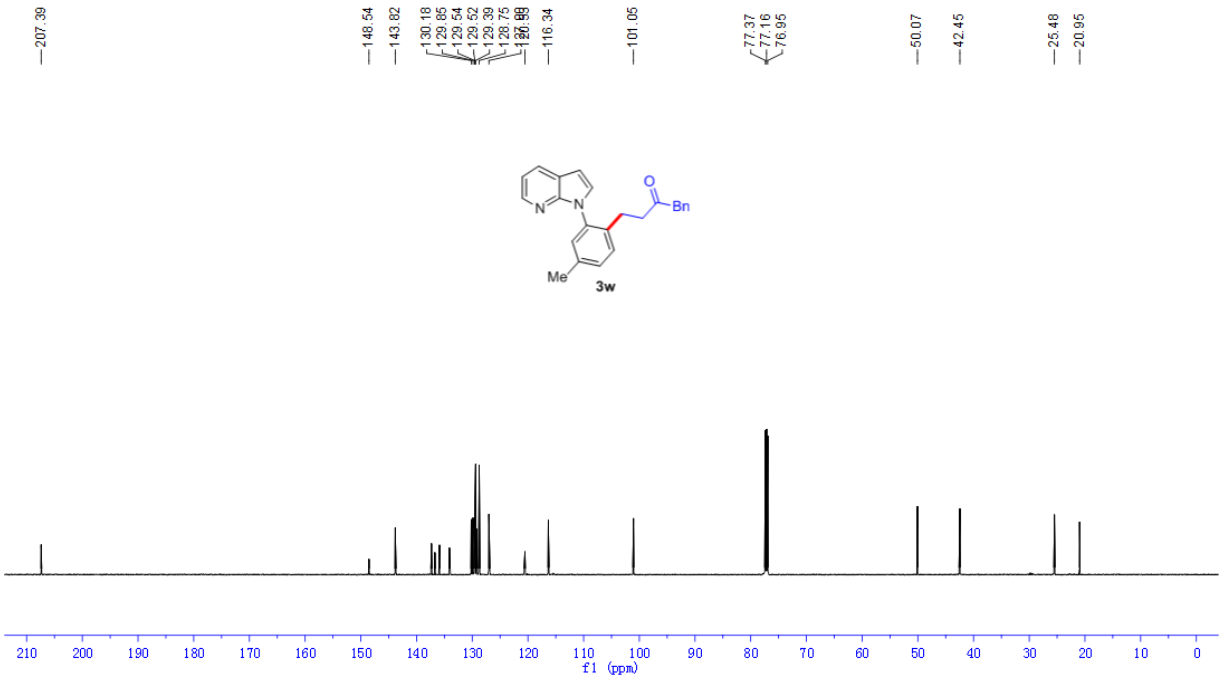
^{1}H NMR spectrum of **3v**



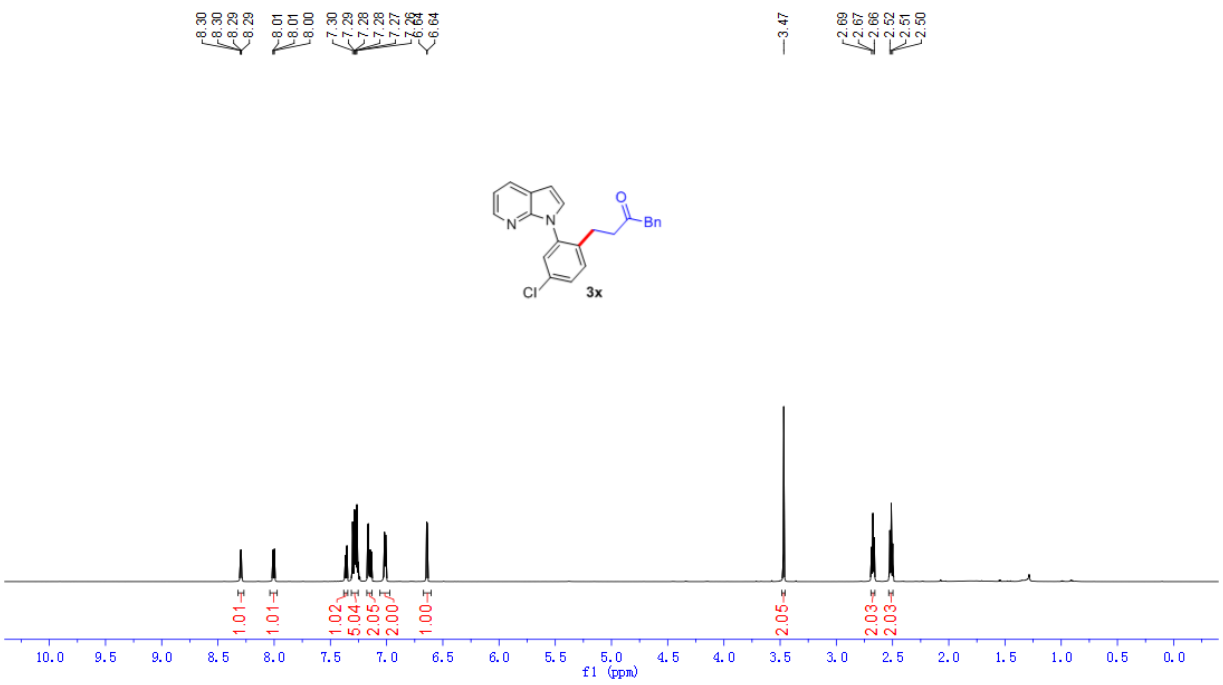
^{13}C NMR spectrum of **3v**



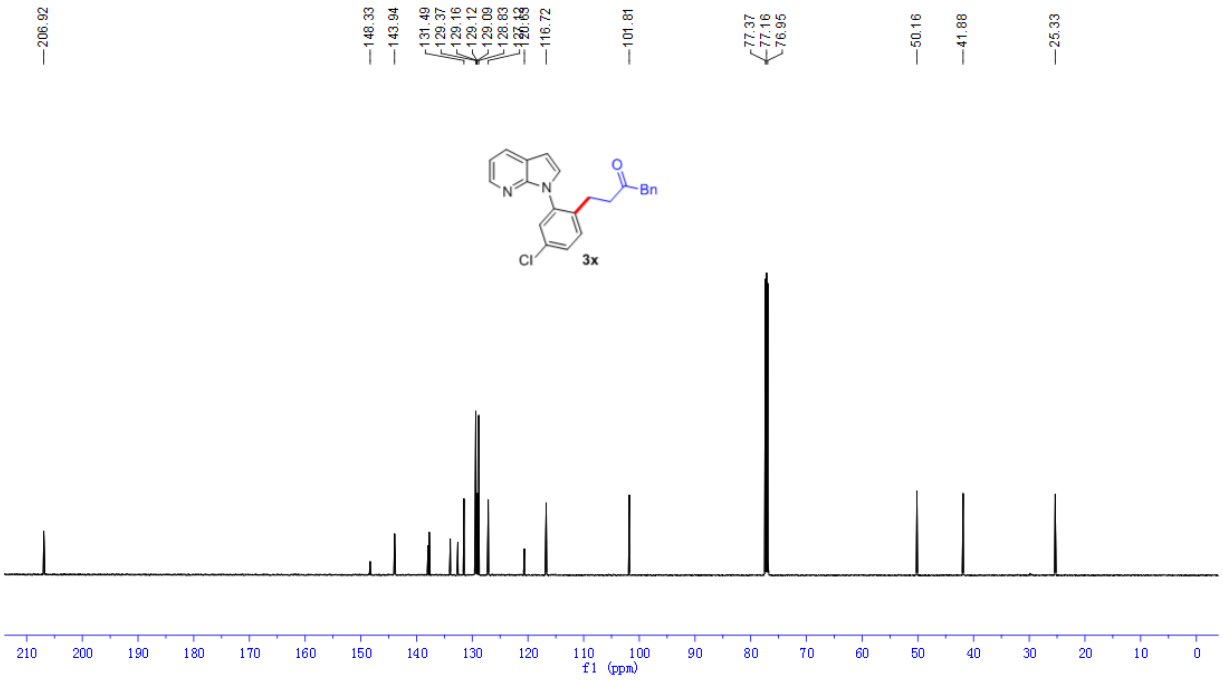
^{1}H NMR spectrum of **3w**



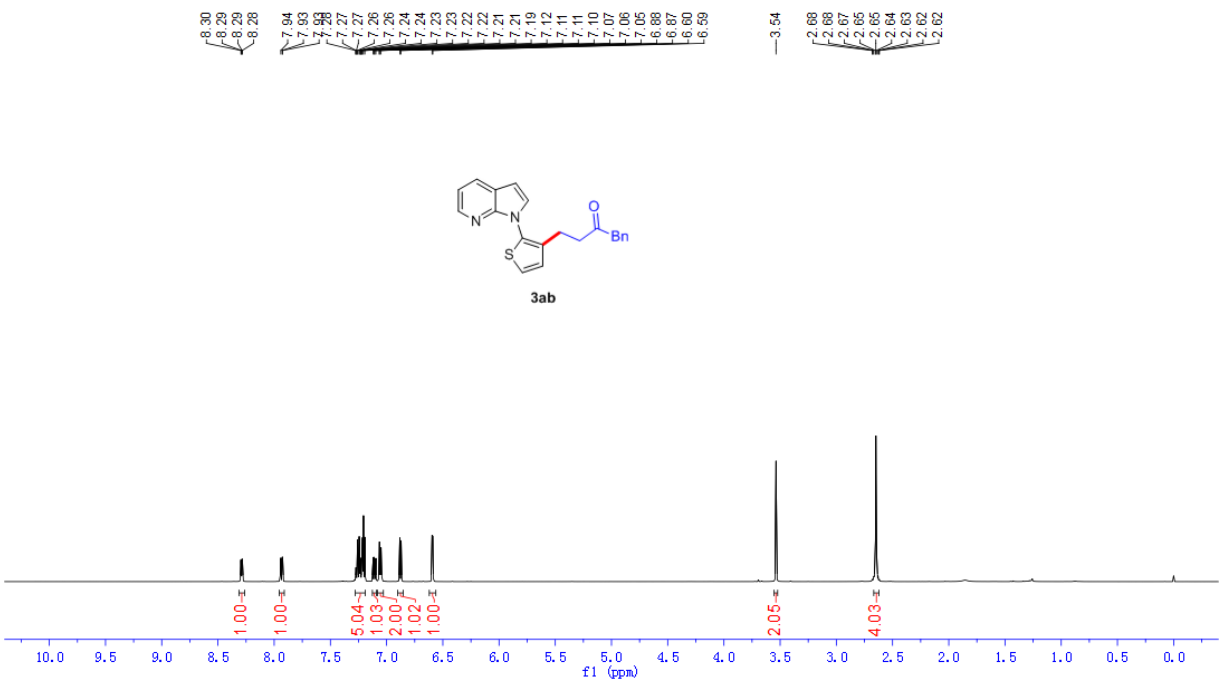
^{13}C NMR spectrum of **3w**



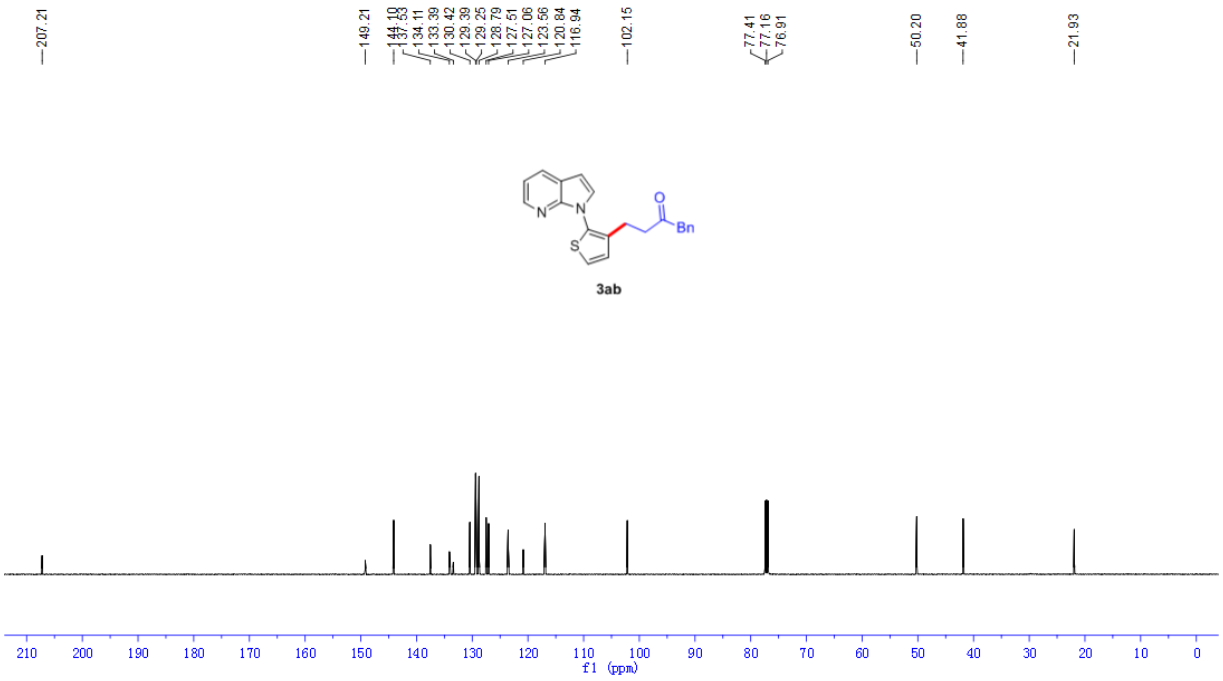
^{1}H NMR spectrum of **3x**



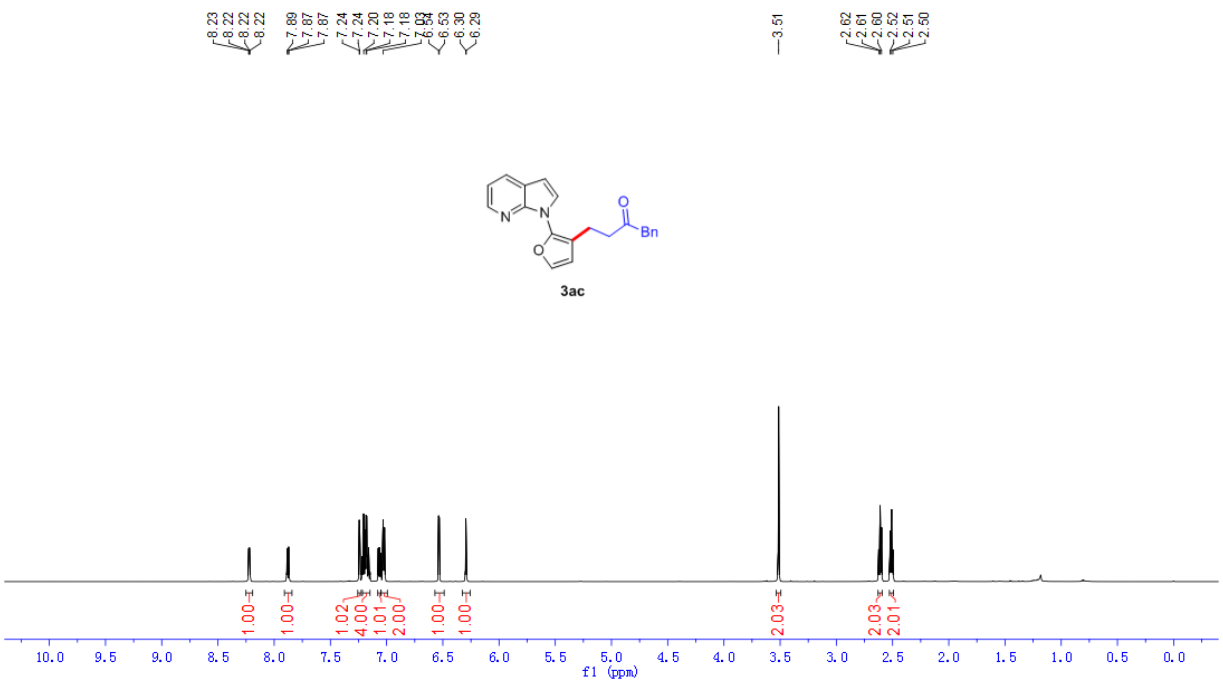
^{13}C NMR spectrum of **3x**



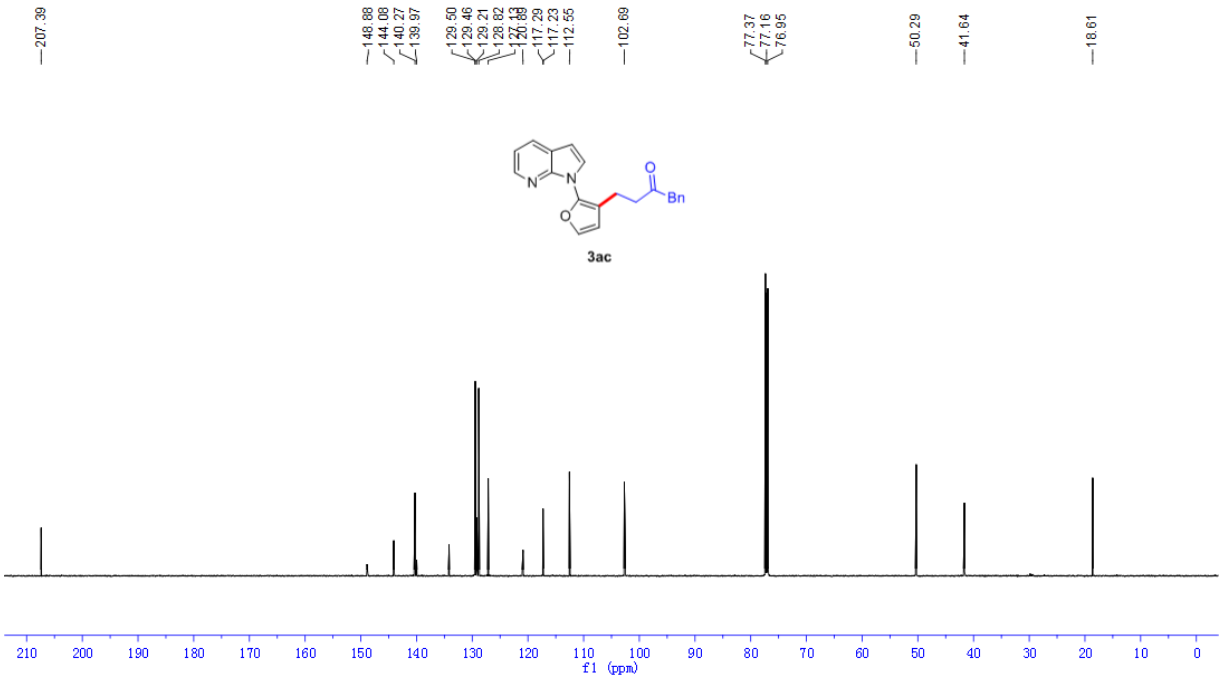
^{1}H NMR spectrum of **3ab**



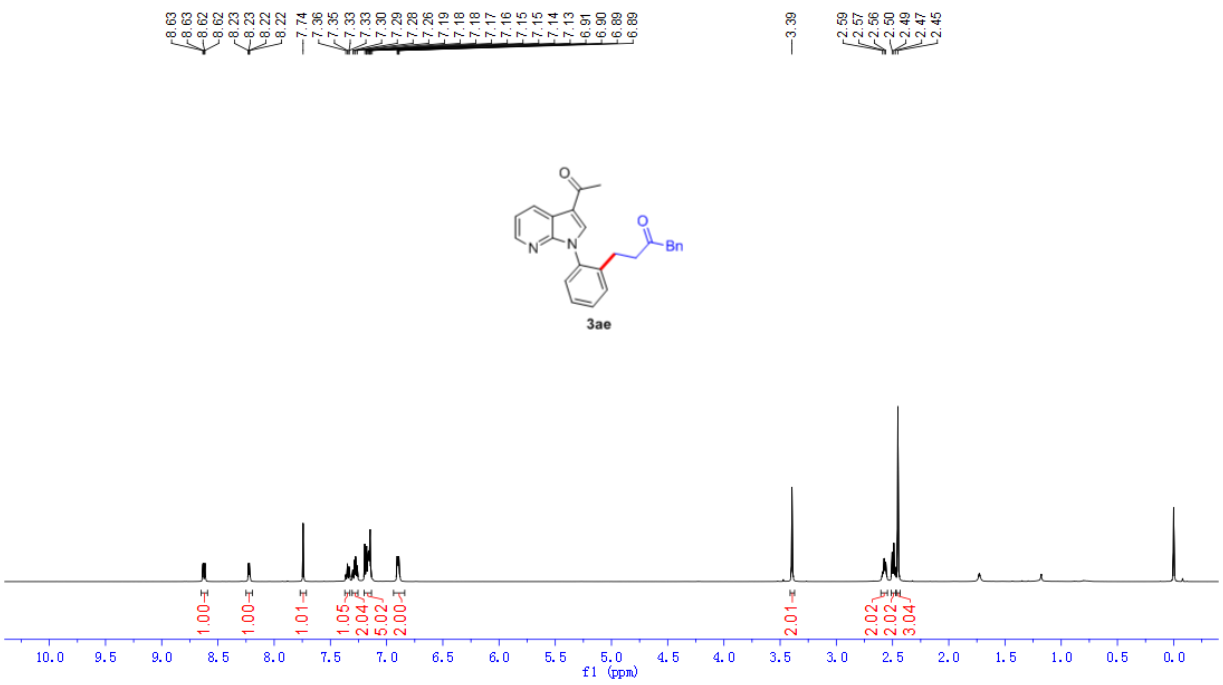
^{13}C NMR spectrum of **3ab**



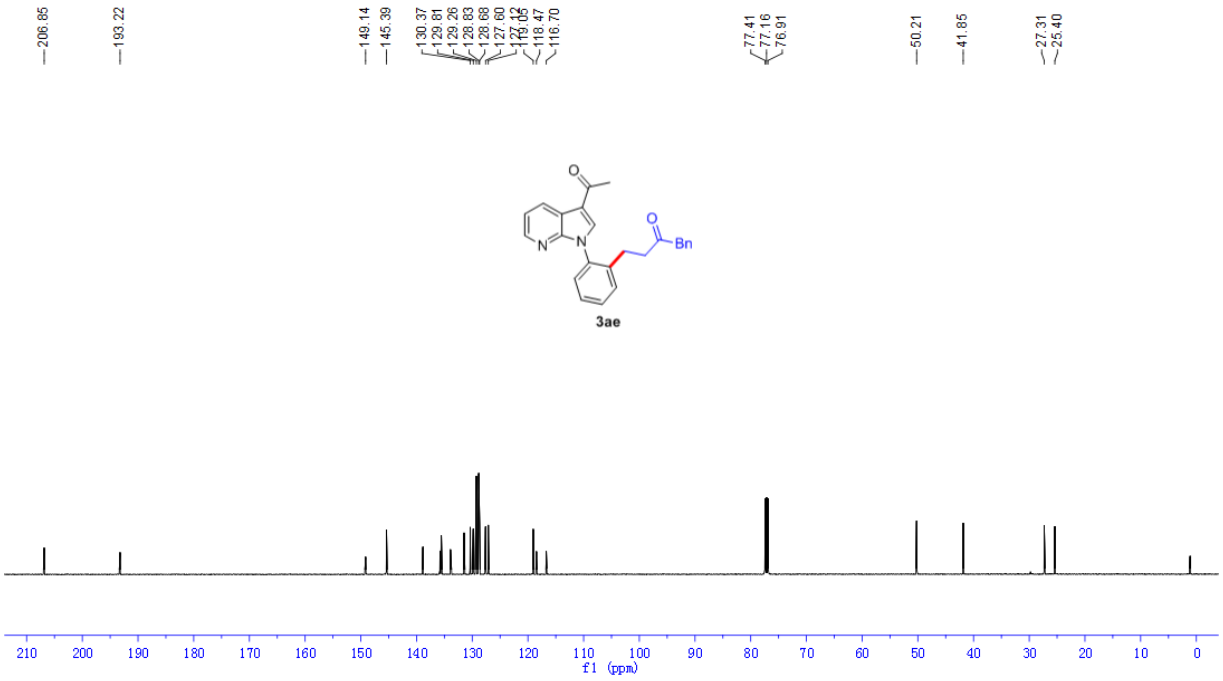
^{1}H NMR spectrum of **3ac**



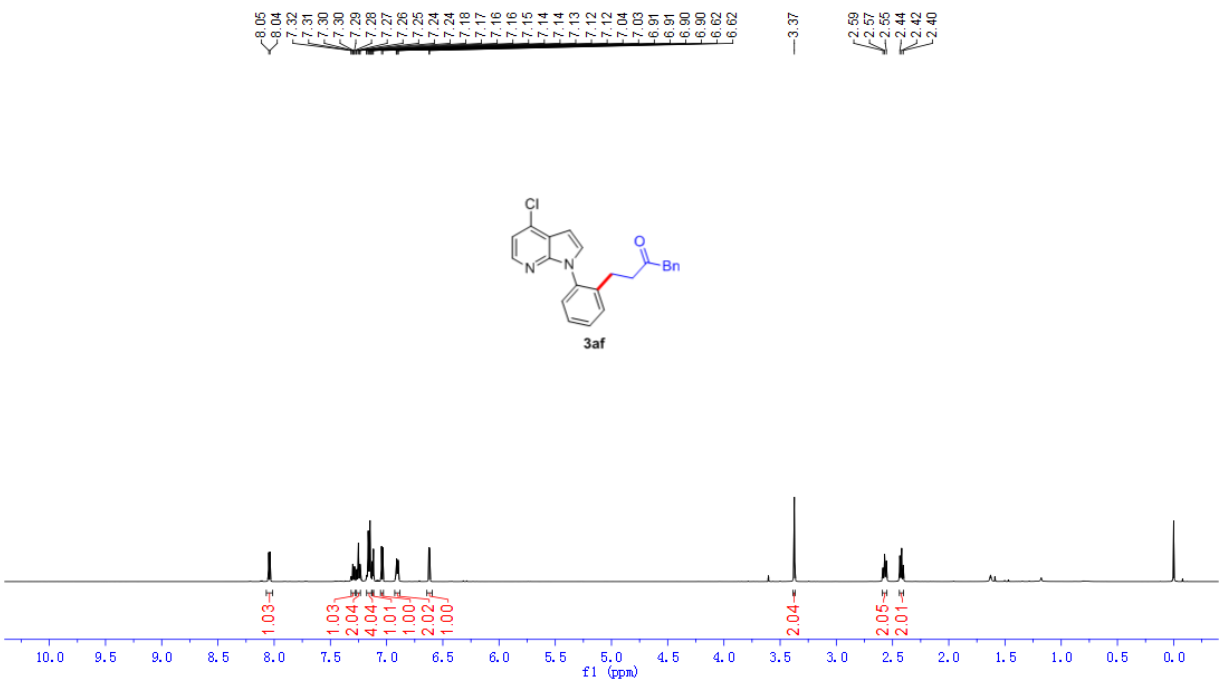
^{13}C NMR spectrum of **3ac**



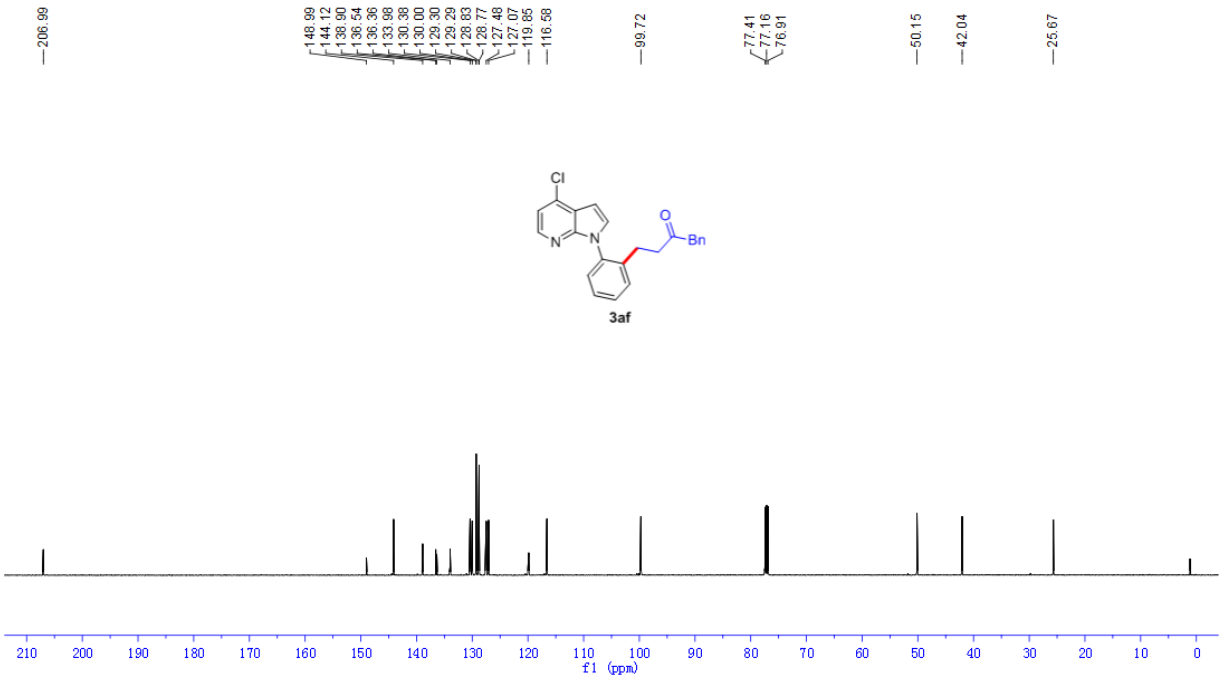
^{1}H NMR spectrum of **3ae**



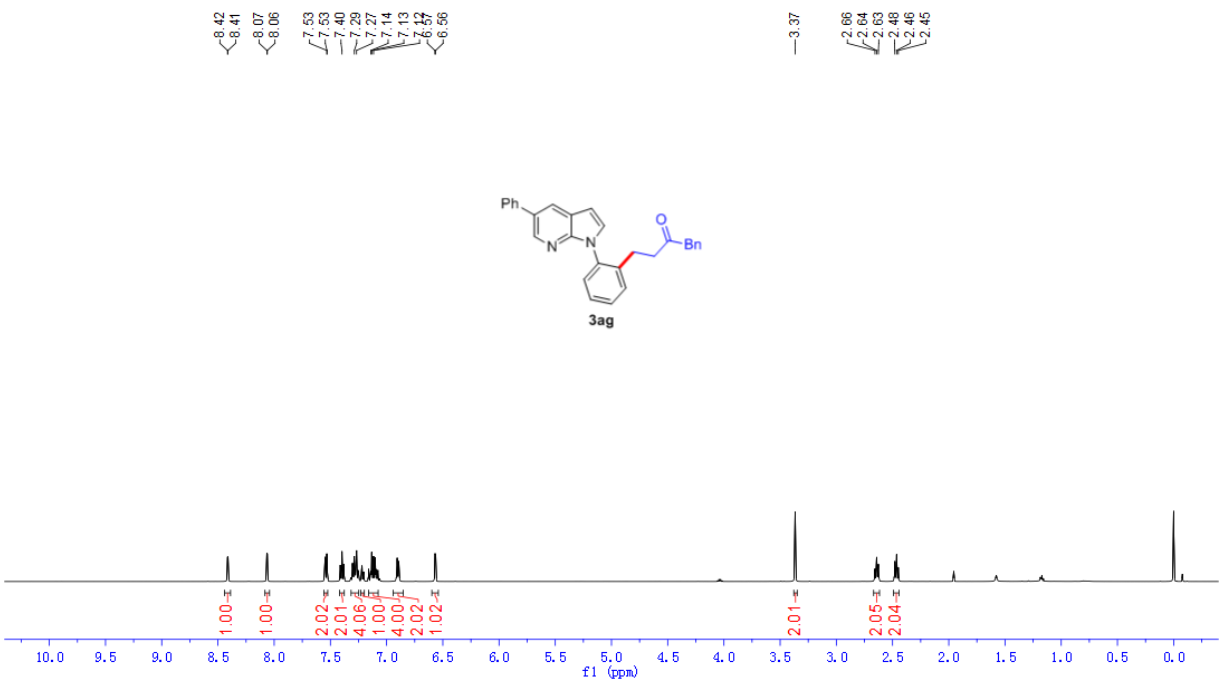
^{13}C NMR spectrum of **3ae**



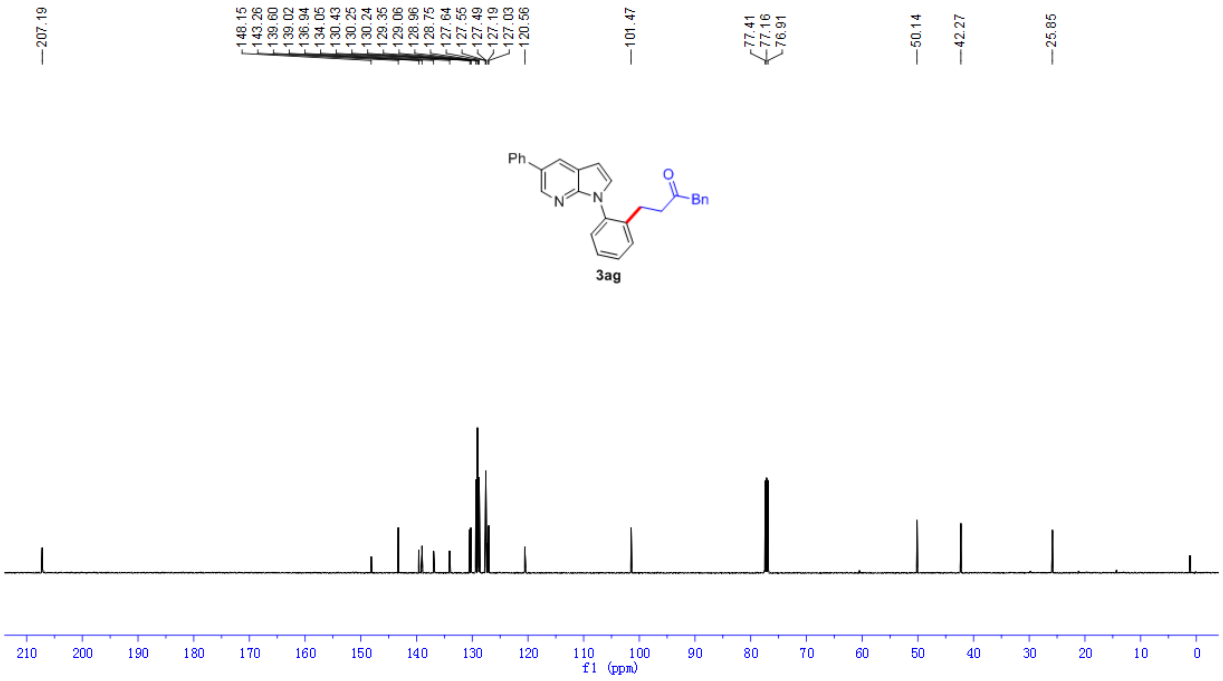
^{1}H NMR spectrum of **3af**



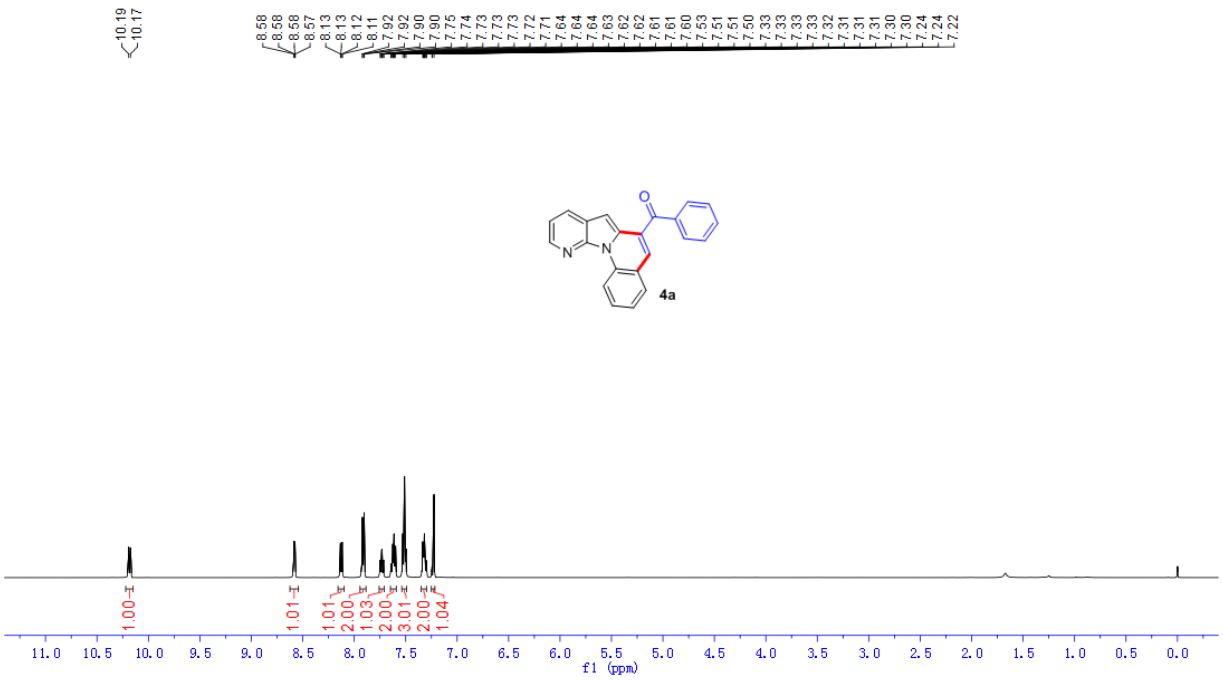
^{13}C NMR spectrum of **3af**



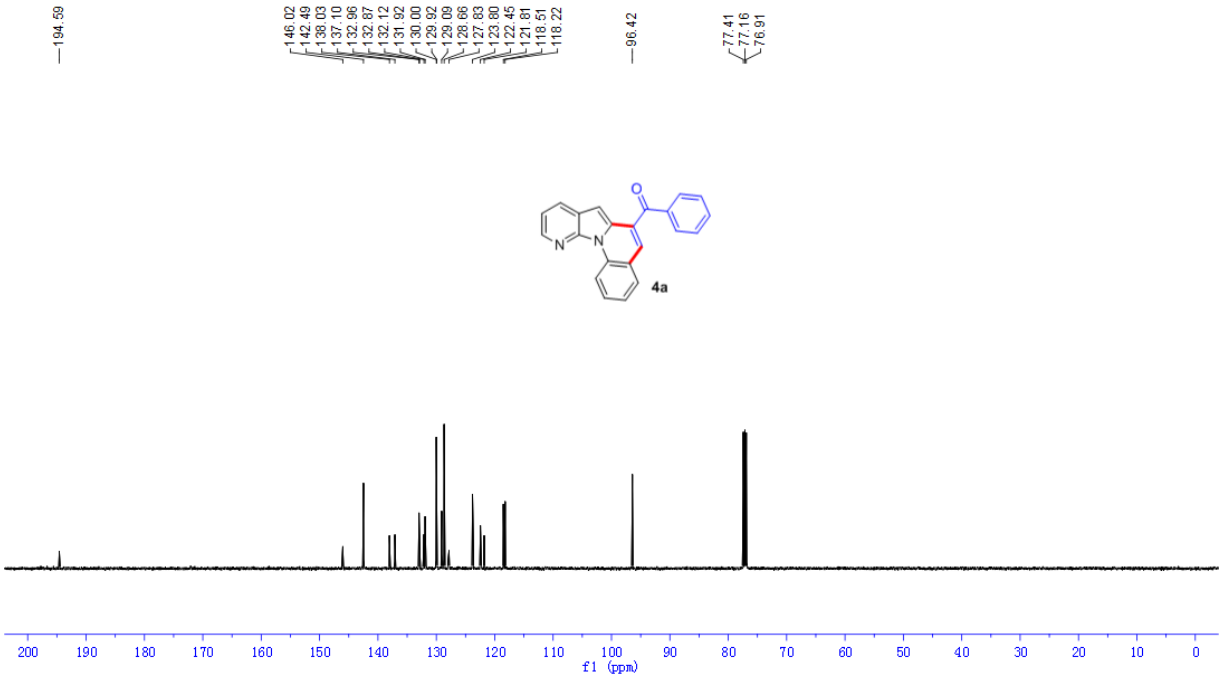
^{1}H NMR spectrum of **3ag**



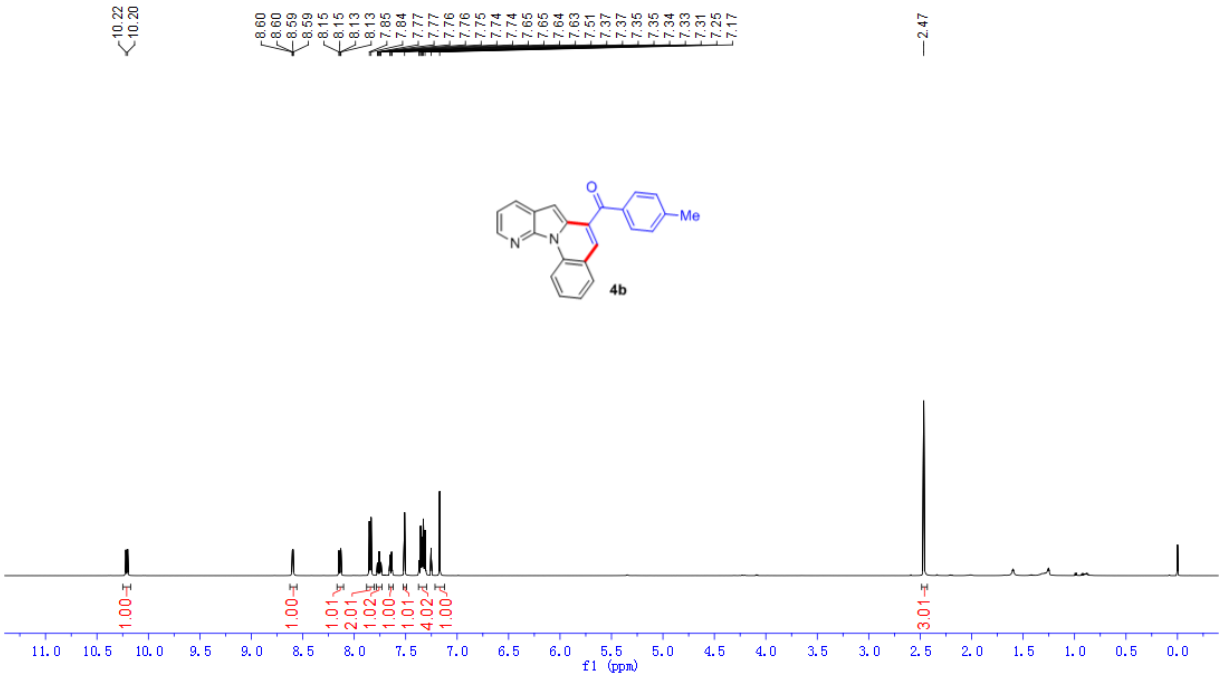
^{13}C NMR spectrum of **3ag**



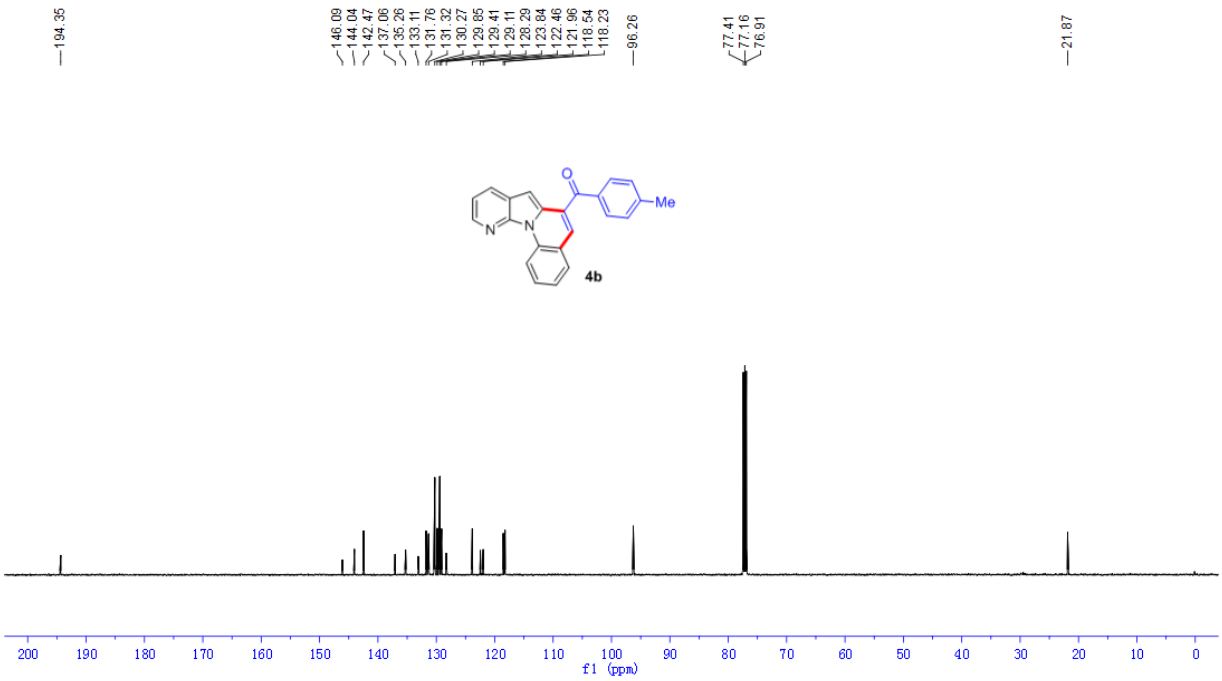
^{1}H NMR spectrum of **4a**



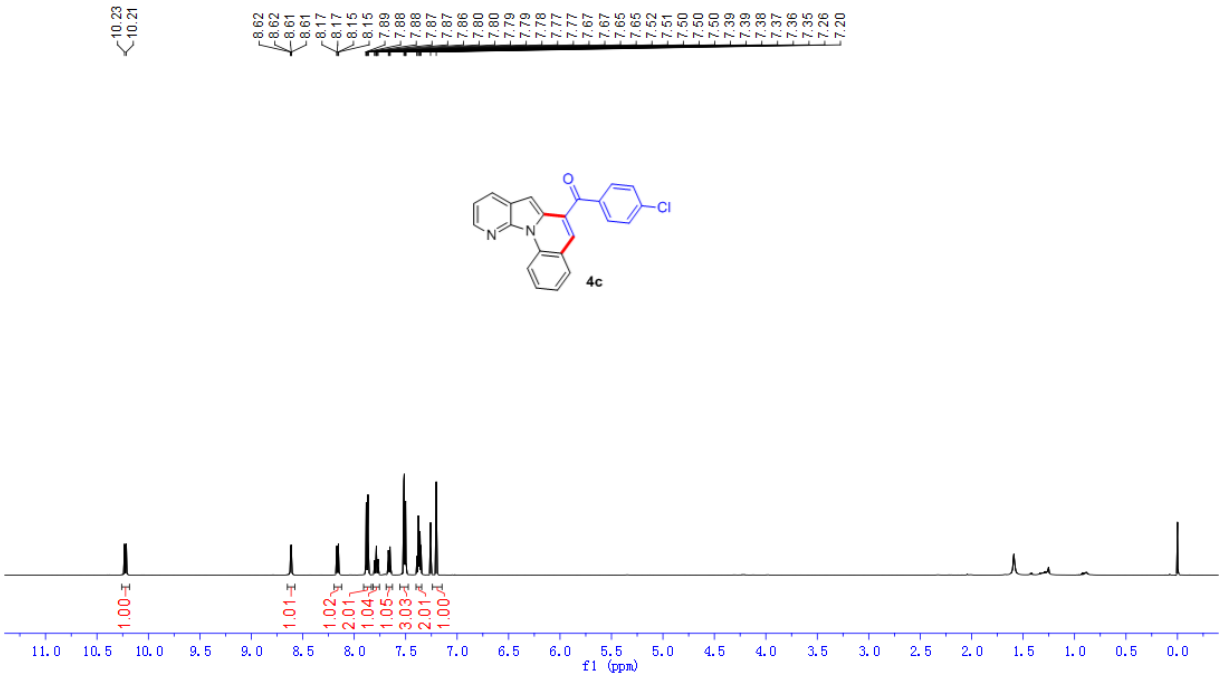
^{13}C NMR spectrum of **4a**



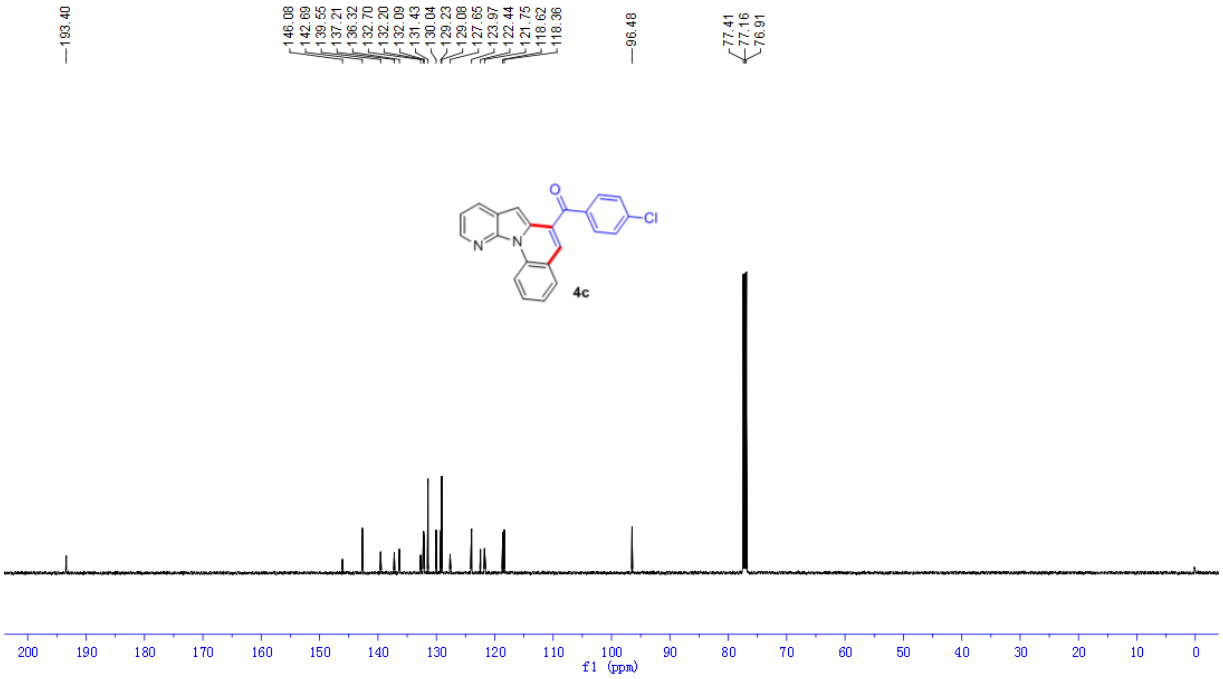
^{1}H NMR spectrum of **4b**



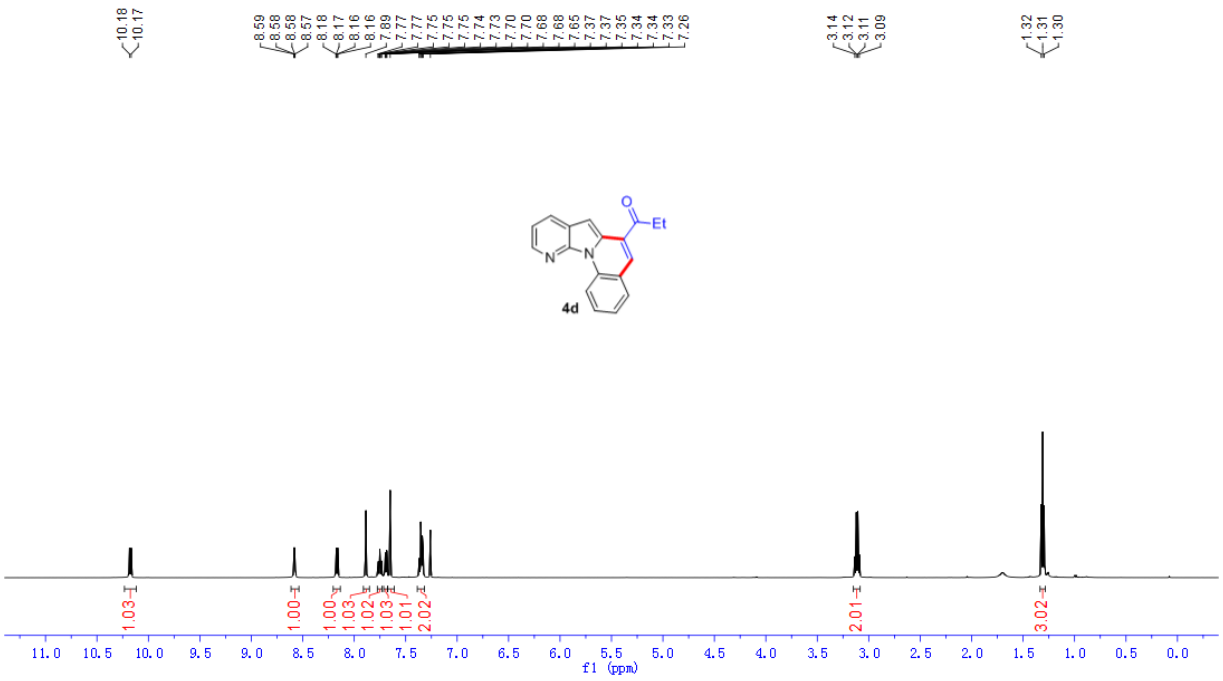
^{13}C NMR spectrum of **4b**



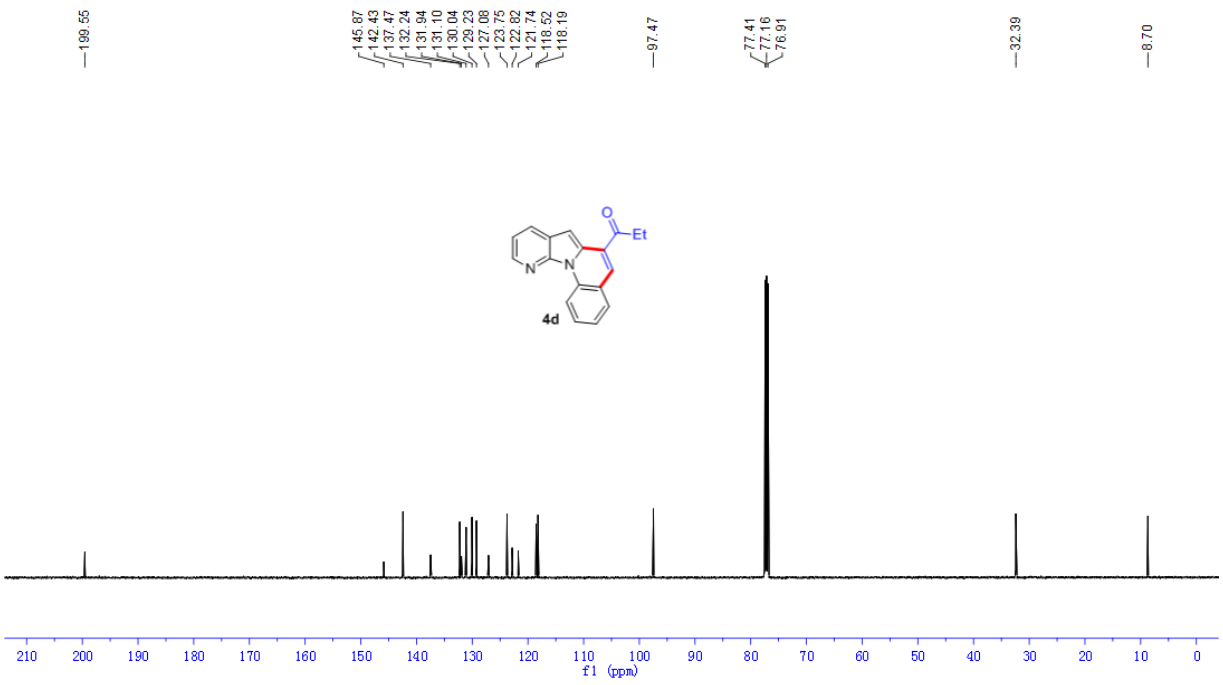
^{1}H NMR spectrum of **4c**



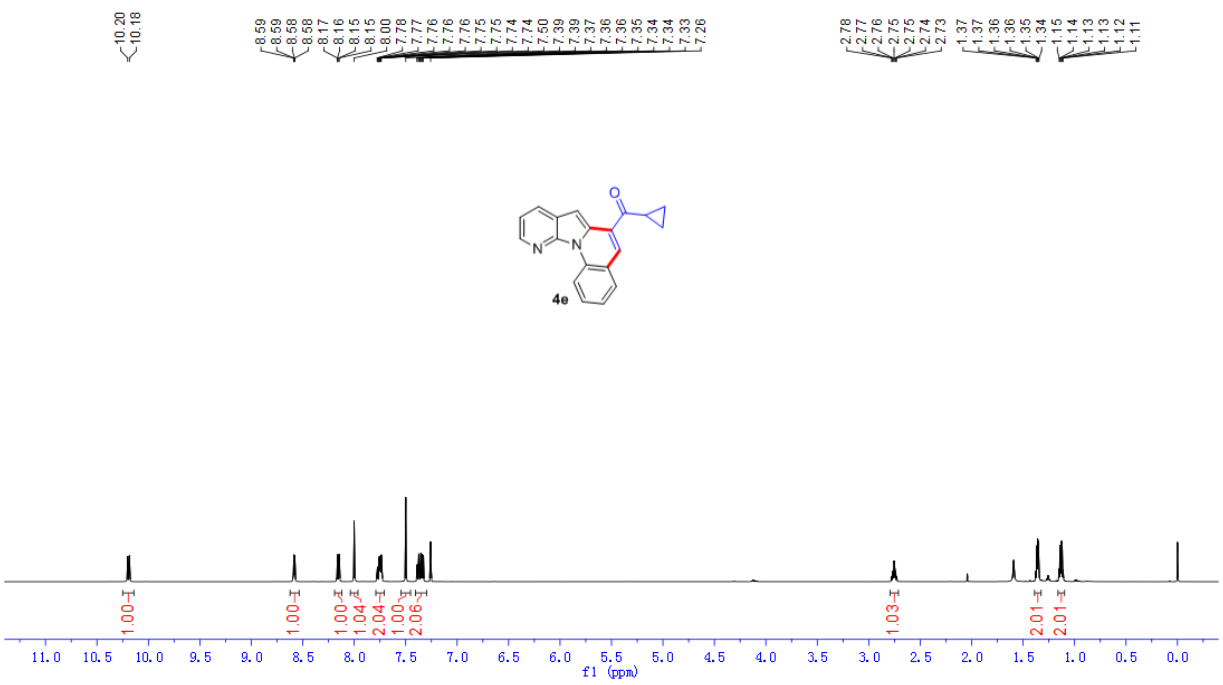
^{13}C NMR spectrum of **4c**



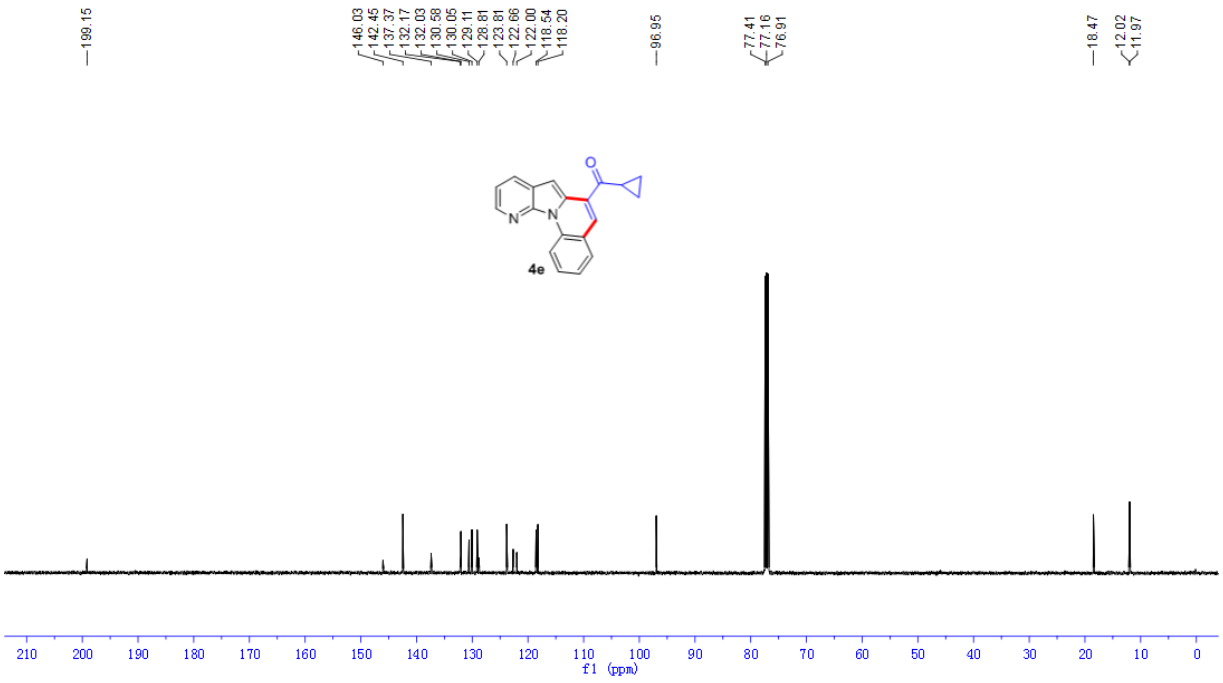
^{1}H NMR spectrum of **4d**



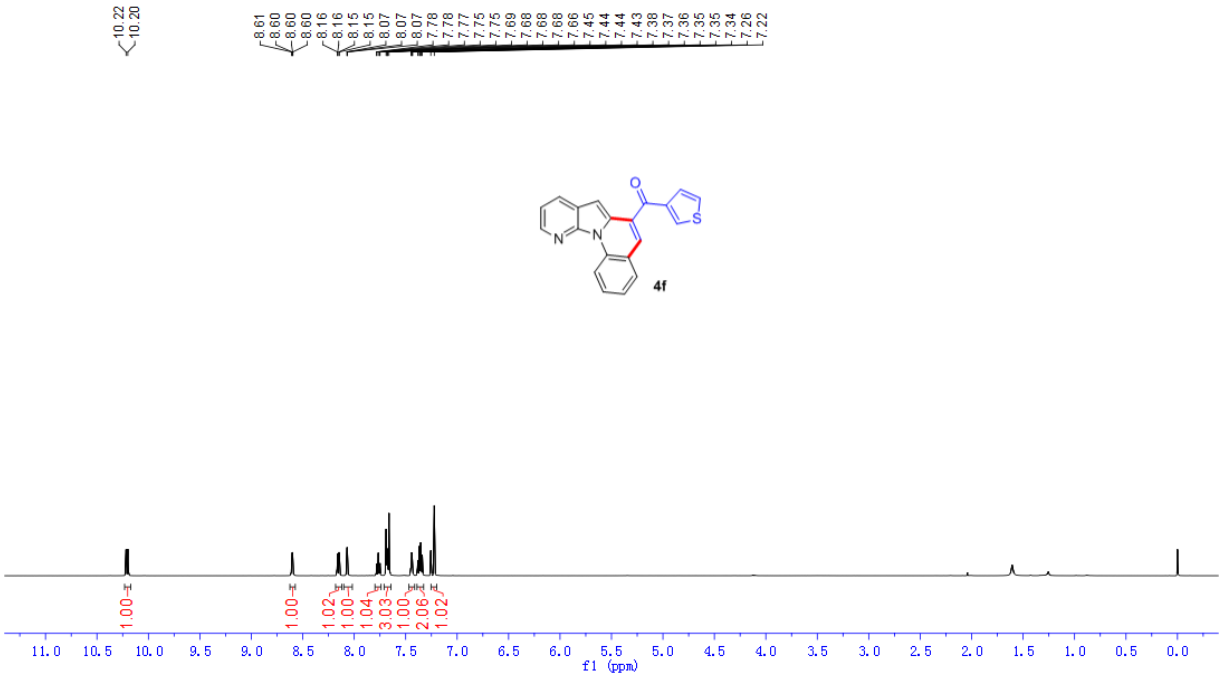
^{13}C NMR spectrum of **4d**



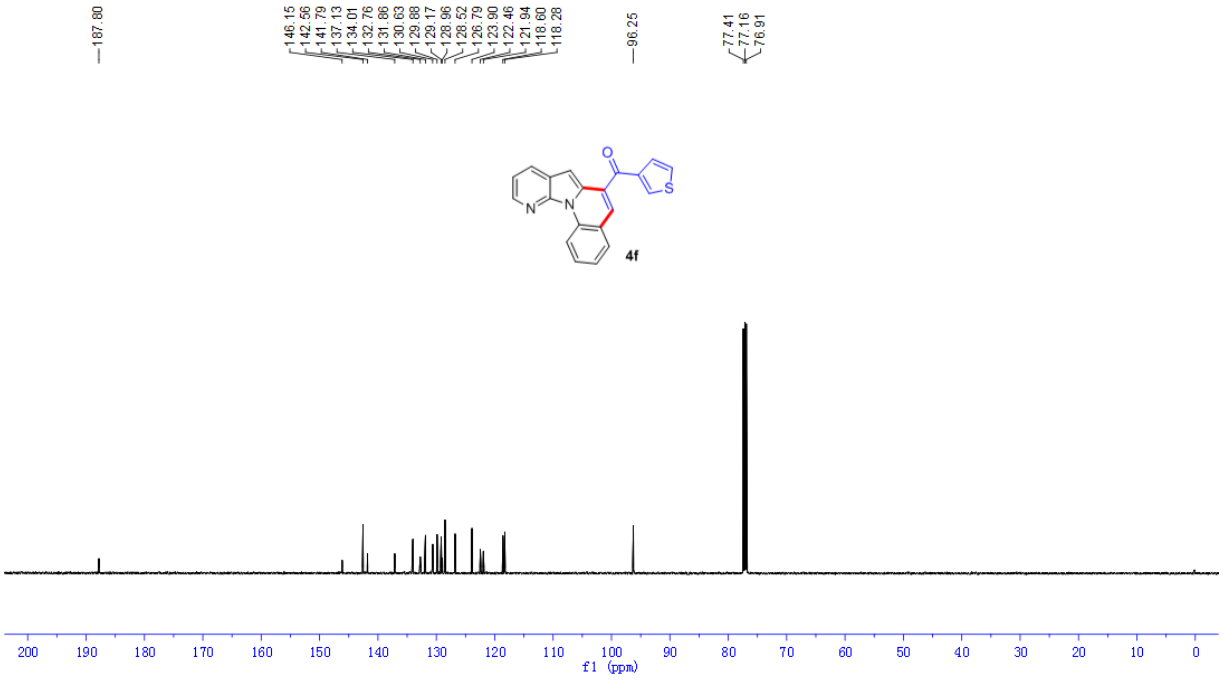
^{1}H NMR spectrum of **4e**



^{13}C NMR spectrum of **4e**



^{1}H NMR spectrum of **4f**



^{13}C NMR spectrum of **4f**