Supporting Information

for

Catalyst-Free Synthesis of α-Carboline Derivatives via Chromone Skeleton Remodeling

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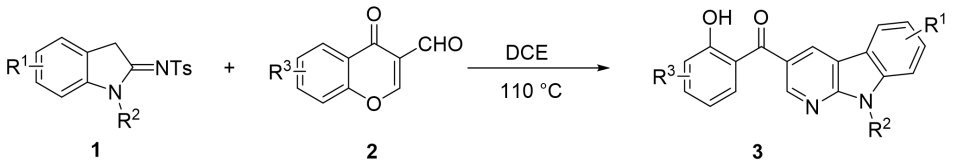
1. General Information

All isolated compounds were characterized on Bruker 500 MHz and JEOL 400 MHz spectrometer in $CDCl_3$. Chemical shifts were reported as δ values relative to internal $CHCl_3$ (δ 7.26 for ^1H NMR and δ 77.2 for ^{13}C NMR). ^{19}F NMR spectra were recorded on a JEOL 400 MHz spectrometer. High-resolution mass spectra (HRMS) were recorded on a ZenoTOF 7600 system (SCIEX, Concord, ON, Canada) with information dependent acquisition (IDA) mode. All melting points were measured with the samples after column chromatography and uncorrected. Column chromatography was performed on silica gel. All solvents and reagents were used as obtained from commercial sources without further purification. The reactants indolin-2-imines and 3-formylchromones were prepared according to the literature procedures[1].

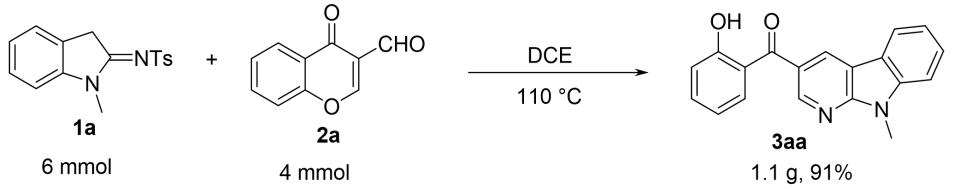
2. Experimental Procedures

2.1 General Procedure for the Synthesis of 3



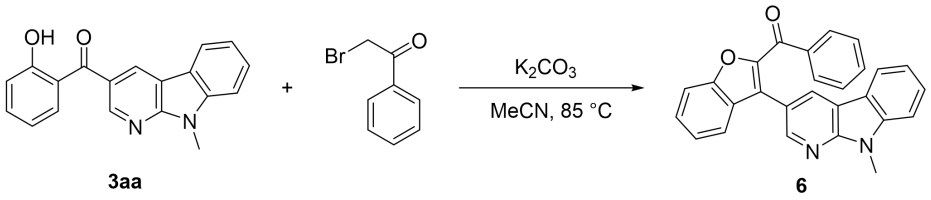
To a 25-mL glass vial equipped with a magnetic stir bar were successively added indolin-2-imines **1** (0.3 mmol, 1.5 equiv), 3-formylchromones **2** (0.2 mmol), and DCE (1 mL). The mixture was stirred at 110 °C for 2–23 h. After TLC indicated the complete consumption of 3-formylchromones **2**, the resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 40:1 to 30:1) to afford the target product **3**.

2.2 Scale-Up Experiment for the Synthesis of 3aa.



A mixture of **1a** (1.8 g, 6.0 mmol, 1.5 equiv), **2a** (697 mg, 4.00 mmol, 1.0 equiv) in DCE (20 mL) was stirred at 110 °C for 20 h. After TLC indicated the complete consumption of **2a**, the resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 30:1) to afford the target product **3aa** (1.1 g, 91%).

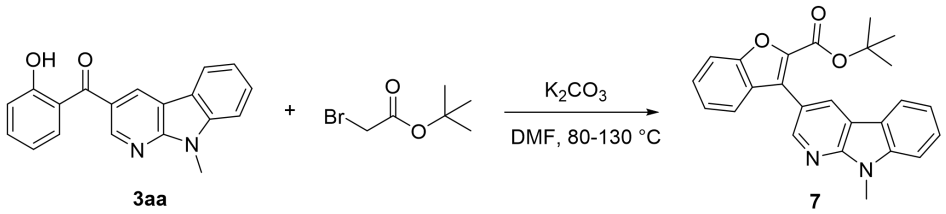
2.3 Procedure for the Synthesis of 6[2]



3aa **6**

To a 25-mL glass vial equipped with a magnetic stir bar were successively added **3aa** (91 mg, 0.3 mmol), 2-bromoacetophenone (60 mg, 0.3 mmol, 1.0 equiv), K_2CO_3 (41 mg, 1.0 equiv), and MeCN (3 mL). After the mixture was stirred at 85 °C for 6 h, it was concentrated in vacuo and the residue was dissolved in EtOAc and washed with water. The EtOAc layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and the resulting residue was purified by column chromatography (PE/EtOAc = 15:1) to afford the target product **6** (114 mg, 94%).

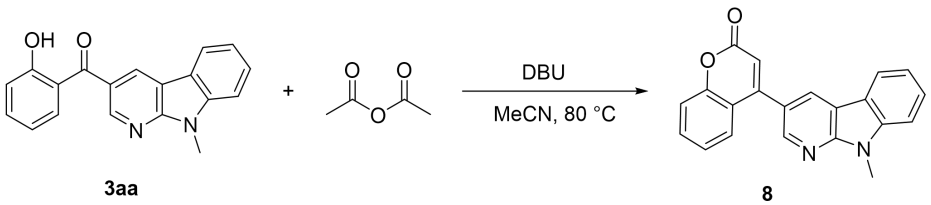
2.4 Procedure for the Synthesis of 7[3]



3aa **7**

To a 25-mL glass vial equipped with a magnetic stir bar were successively added **3aa** (30 mg, 0.1 mmol), *tert*-butyl 2-bromoacetate (19 μL, 0.13 mmol, 1.3 equiv), K_2CO_3 (28 mg, 2.0 equiv), and DMF (1 mL). After the mixture was stirred at 80 °C for 0.5 h and then heated up to 130 °C for 2 h, it was quenched with water and extracted with EtOAc. The combined EtOAc layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 12:1) to afford the target product **7** (33 mg, 83%).

2.4 Procedure for the Synthesis of 8[4]

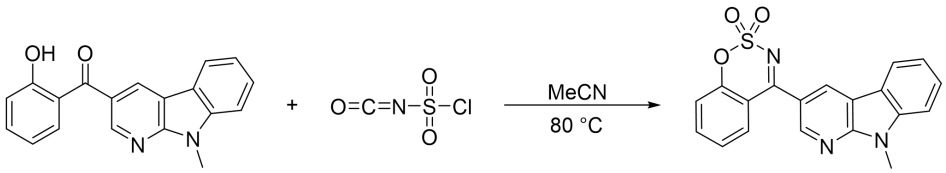


3aa **8**

To a 25-mL glass vial equipped with a magnetic stir bar were successively added **3aa** (30 mg, 0.1 mmol), acetic anhydride (18 μL, 0.2 mmol, 2.0 equiv), DBU (45 μL, 3.0 equiv), and MeCN (2 mL). After the mixture was stirred at 80 °C for 0.5 h, it was concentrated in vacuo. The residue was purified

by column chromatography (PE/EtOAc = 5:1) to afford the target product **8** (24 mg, 73%).

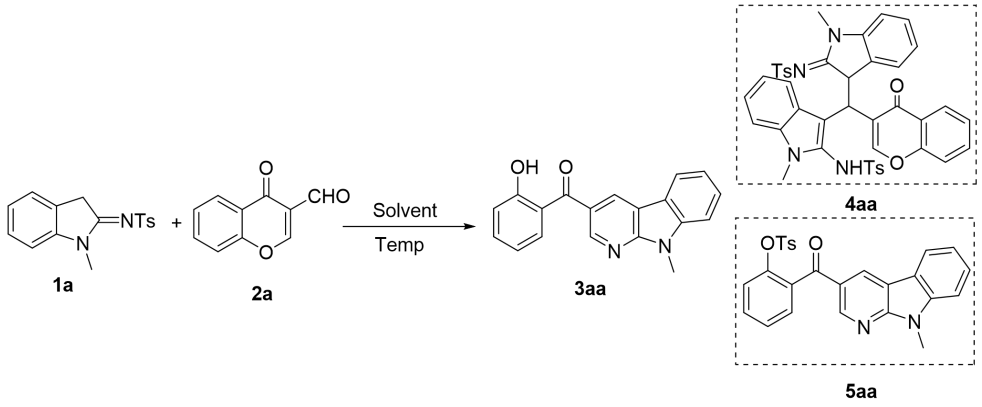
2.6 Procedure for the Synthesis of 9[5]



3aa **9**

To a 25-mL glass vial equipped with a magnetic stir bar were successively added **3aa** (30 mg, 0.1 mmol), chlorosulfonyl isocyanate (35 μL, 0.4 mmol, 4.0 equiv), and anhydrous MeCN (1 mL). After the mixture was stirred at 80 °C for 0.5 h under nitrogen atmosphere, it was quenched with water and extracted with EtOAc. The combined EtOAc layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 4:1) to afford the target product **9** (22 mg, 61%).

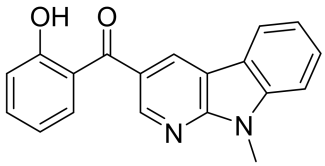
3. Table S1 Optimization of the Reaction Conditions [a]



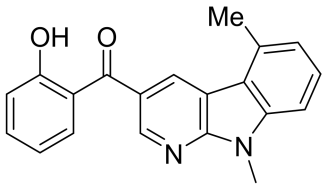
Entry	Base	Additive	Temp (°C)	Solvent	Time (h)	Yield (%)[b]		
						3aa	**4aa**	**5aa**
1[d]	$NaHCO_3$	$ZnCl_2$	60	DCM	19	10[c]	10[c]	ND
2[e]	-	$ZnCl_2$	25 to 60	DCM	35	34[c]	2[c]	30[c]
3[f]	Py	-	85 to 110	DCE	9	67[c]	ND	ND
4	-	-	110	DCE	17	93[c]	ND	ND
5	-	-	110	MeCN	2	87	ND	ND
6	-	-	110	Acetone	2	80	ND	ND
7	-	-	110	THF	10	88	ND	ND
8	-	-	110	$CHCl_3$	23	89	ND	ND
9	-	-	110	EtOAc	10	68	ND	ND
10	-	-	110	Dioxane	23	69	ND	ND
11	-	-	110	EtOH	2	92[c]	ND	ND
12	-	-	110	DMF	1	94[c]	ND	ND
13[g]	-	-	110	DCE	48	90	ND	ND
14[h]	-	-	110	DCE	48	83	ND	ND
15	-	-	85	DCE	48	28	ND	ND
16[i]	-	-	110	DCE	29	95[c]	ND	ND
17[j]	-	-	**110**	**DCE**	**13**	**97**[c]	ND	ND

[a]Unless otherwise noted, the reaction was conducted with **1a** (0.3 mmol, 1.5 equiv), **2a** (0.2 mmol), solvent (2 mL) in air. [b]Yield was determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as the internal standard. [c]Isolated yield.[d]$NaHCO_3$ (1.0 equiv), $ZnCl_2$ (0.1 equiv). [e]$ZnCl_2$ (0.5 equiv). [f]Py (2.0 equiv). [g]**1a** (0.26 mmol, 1.3 equiv), **2a** (0.2 mmol) was applied instead. [h]**1a** (0.24 mmol, 1.2 equiv), **2a** (0.2 mmol) was applied instead. [i]Solvent (3 mL) was applied instead. [j]Solvent (1 mL) was applied instead.

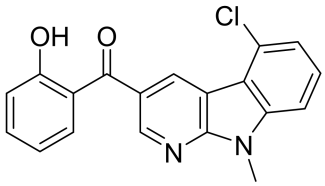
4. Characterization Data



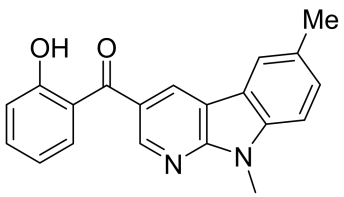
(2-Hydroxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3aa** (13 h, 58 mg, Yield = 97%, R_f = 0.56 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.98 (s, 1H), 8.86 (d, *J* = 2.0 Hz, 1H), 8.64 (d, *J* = 2.1 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.55–7.49 (m, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 9.4 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 163.0, 153.1, 148.3, 141.0, 136.2, 133.4, 129.6, 127.8, 125.3, 121.5, 121.1, 120.4, 119.7, 118.9, 118.5, 115.5, 109.7, 28.0; ESI-HRMS *m/z* calcd for $C_{19}H_{15}N_2O_2$ $[M + H]^+$ 303.1128 found 303.1128.



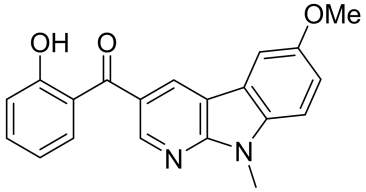
(5,9-Dimethyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3ab** (18 h, 44 mg, Yield = 70%, R_f = 0.49 (PE/EA = 3:1)) was isolated as a yellow solid; mp 188–189 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.00 (s, 1H), 8.87 (d, *J* = 2.0 Hz, 1H), 8.75 (d, *J* = 2.1 Hz, 1H), 7.72 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57–7.48 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.96–6.91 (m, 1H), 4.01 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 163.1, 153.1, 147.8, 141.1, 136.2, 134.7, 133.5, 131.4, 127.7, 125.4, 122.7, 119.8, 119.2, 118.9, 118.6, 116.3, 107.3, 28.1, 20.6; ESI-HRMS *m/z* calcd for $C_{20}H_{17}N_2O_2$ $[M + H]^+$ 317.1285, found 317.1285.



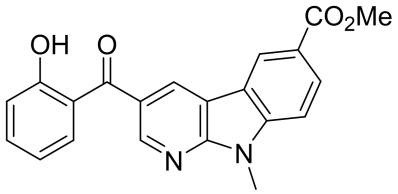
(5-Chloro-9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3ac** (23 h, 50 mg, Yield = 75%, R_f = 0.38 (PE/EA = 3:1)) was isolated as a yellow solid; mp 181–182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.00 (s, 1H), 9.10 (d, *J* = 2.1 Hz, 1H), 8.91 (d, *J* = 2.2 Hz, 1H), 7.70 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57–7.52 (m, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 9.5 Hz, 1H), 6.93 (t, *J* = 7.0 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 163.2, 152.9, 148.6, 142.0, 136.4, 133.4, 132.2, 129.9, 128.1, 125.9, 121.7, 119.7, 119.0, 118.7, 118.2, 114.6, 108.2, 28.3; ESI-HRMS *m/z* calcd for $C_{19}H_{14}ClN_2O_2$ $[M + H]^+$ 337.0738, found 337.0738.



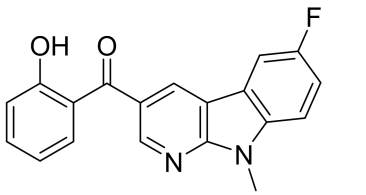
(6,9-Dimethyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3ad** (13 h, 59 mg, Yield = 94%, R_f = 0.47 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.99 (s, 1H), 8.86 (d, J = 2.0 Hz, 1H), 8.66 (d, J = 2.0 Hz, 1H), 7.90 (s, 1H), 7.71 (dd, J = 8.0, 1.7 Hz, 1H), 7.56–7.51 (m, 1H), 7.44–7.38 (m, 2H), 7.12 (d, J = 9.5 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 3.99 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 163.1, 153.3, 148.2, 139.3, 136.2, 133.5, 130.7, 129.6, 129.2, 125.2, 121.5, 120.6, 119.8, 118.9, 118.6, 115.5, 109.5, 28.1, 21.6; ESI-HRMS *m/z* calcd for $C_{20}H_{17}N_2O_2$ $[M + H]^+$ 317.1285, found 317.1284.



(2-Hydroxyphenyl)(6-methoxy-9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ae** (12.5 h, 55 mg, Yield = 83%, R_f = 0.31 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.97 (s, 1H), 8.87 (d, J = 2.1 Hz, 1H), 8.67 (d, J = 2.0 Hz, 1H), 7.71 (dd, J = 8.0, 1.7 Hz, 1H), 7.58 (d, J = 2.5 Hz, 1H), 7.56–7.51 (m, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.23 (dd, J = 8.8, 2.5 Hz, 1H), 7.12 (dd, J = 8.4, 1.2 Hz, 1H), 6.96–6.92 (m, 1H), 3.99 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 163.0, 155.1, 153.4, 148.4, 136.2, 135.8, 133.5, 129.8, 125.0, 120.9, 119.8, 118.9, 118.6, 116.9, 115.5, 110.6, 104.4, 56.2, 28.2; ESI-HRMS *m/z* calcd for $C_{20}H_{17}N_2O_3$ $[M + H]^+$ 333.1234, found 333.1235.

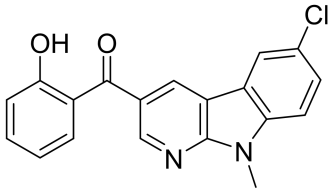


Methyl 3-(2-hydroxybenzoyl)-9-methyl-9*H*-pyrido[2,3-*b*]indole-6-carboxylate. Compound **3af** (5 h, 67 mg, Yield = 93%, R_f = 0.58 (PE/EA = 1:1)) was isolated as a yellow solid; mp 178–179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.92 (s, 1H), 8.90 (d, J = 2.1 Hz, 1H), 8.78 (d, J = 1.7 Hz, 1H), 8.69 (d, J = 2.1 Hz, 1H), 8.27 (dd, J = 8.7, 1.7 Hz, 1H), 7.66 (dd, J = 8.0, 1.7 Hz, 1H), 7.56–7.52 (m, 1H), 7.50 (d, J = 8.6 Hz, 1H), 7.11 (dd, J = 8.4, 1.1 Hz, 1H), 6.96–6.90 (m, 1H), 4.01 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 167.3, 163.1, 153.8, 148.8, 143.7, 136.4, 133.3, 130.1, 129.2, 126.3, 123.8, 123.0, 120.2, 119.6, 119.0, 118.7, 115.5, 109.4, 52.3, 28.3; ESI-HRMS *m/z* calcd for $C_{21}H_{17}N_2O_4$ $[M + H]^+$ 361.1183, found 361.1182.

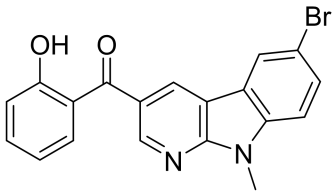


(6-Fluoro-9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3ag** (9 h, 61 mg, Yield = 95%, R_f = 0.44 (PE/EA = 3:1)) was isolated as a yellow solid; mp 170–171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.94 (s, 1H), 8.90 (d, J = 2.1 Hz, 1H), 8.66 (d, J = 2.1 Hz, 1H), 7.77 (dd, J = 8.4, 2.5 Hz, 1H), 7.68 (d, J = 6.3 Hz, 1H), 7.54 (t, J = 6.8 Hz, 1H), 7.45 (dd, J = 8.9, 4.1 Hz, 1H), 7.34 (td, J = 9.0, 2.5 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 163.1, 158.4 (d, J = 237.3 Hz), 153.6, 148.9, 137.4, 136.4, 133.4, 130.2, 125.4, 121.0

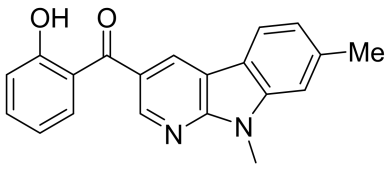
(d, J = 9.5 Hz), 119.7, 119.0, 118.7, 115.7 (d, J = 25.1 Hz), 115.2 (d, J = 4.1 Hz), 110.6 (d, J = 9.0 Hz), 107.6 (d, J = 24.1 Hz), 28.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −121.4 (m, 1F); ESI-HRMS *m/z* calcd for $C_{19}H_{14}FN_2O_2$ $[M + H]^+$ 321.1034, found 321.1036.



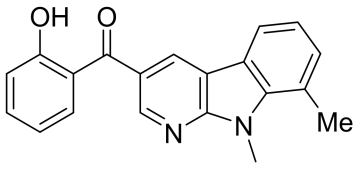
(6-Chloro-9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3ah** (11 h, 56 mg, Yield = 84%, R_f = 0.49 (PE/EA = 3:1)) was isolated as a yellow solid; mp 140–142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.93 (s, 1H), 8.90 (d, J = 2.1 Hz, 1H), 8.65 (d, J = 2.1 Hz, 1H), 8.06 (d, J = 2.0 Hz, 1H), 7.67 (dd, J = 8.0, 1.7 Hz, 1H), 7.57–7.52 (m, 2H), 7.44 (d, J = 8.7 Hz, 1H), 7.12 (dd, J = 8.4, 1.2 Hz, 1H), 6.96–6.91 (m, 1H), 4.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 163.1, 153.4, 148.9, 139.4, 136.4, 133.3, 130.2, 128.0, 126.8, 125.8, 121.5, 121.4, 119.6, 119.0, 118.7, 114.7, 110.8, 28.2; ESI-HRMS *m/z* calcd for $C_{19}H_{14}ClN_2O_2$ $[M + H]^+$ 337.0738, found 337.0738.



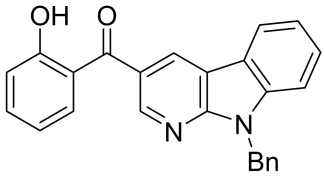
(6-Bromo-9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3ai** (8.5 h, 66 mg, Yield = 87%, R_f = 0.38 (PE/EA = 3:1)) was isolated as a yellow solid; mp 176–177 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.96 (s, 1H), 8.93 (d, J = 2.0 Hz, 1H), 8.66 (d, J = 2.1 Hz, 1H), 8.24 (d, J = 1.9 Hz, 1H), 7.73–7.67 (m, 2H), 7.61–7.54 (m, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 8.5 Hz, 1H), 6.96 (t, J = 7.0 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 163.1, 153.2, 149.0, 139.7, 136.4, 133.3, 130.6, 130.1, 125.9, 124.4, 122.1, 119.6, 119.0, 118.7, 114.5, 114.0, 111.3, 28.2; ESI-HRMS *m/z* calcd for $C_{19}H_{14}BrN_2O_2$ $[M + H]^+$ 381.0233, found 381.0230.



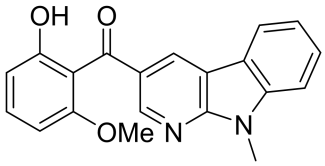
(7,9-Dimethyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3aj** (10 h, 54 mg, Yield = 86%, R_f = 0.53 (PE/EA = 3:1)) was isolated as a yellow solid; mp 159–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.98 (s, 1H), 8.85 (d, J = 2.1 Hz, 1H), 8.66 (d, J = 2.1 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.72 (dd, J = 8.0, 1.7 Hz, 1H), 7.57–7.51 (m, 1H), 7.32 (s, 1H), 7.19 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.96–6.91 (m, 1H), 4.00 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 163.1, 153.4, 147.8, 141.6, 138.5, 136.2, 133.5, 129.2, 125.4, 122.7, 121.3, 119.8, 118.9, 118.6, 118.2, 115.8, 110.0, 28.0, 22.5; ESI-HRMS *m/z* calcd for $C_{20}H_{17}N_2O_2$ $[M + H]^+$ 317.1285, found 317.1286.



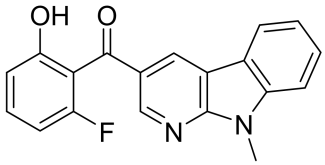
(8,9-Dimethyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3ak** (7 h, 51 mg, Yield = 81%, R_f = 0.57 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.98 (s, 1H), 8.88 (d, J = 2.1 Hz, 1H), 8.66 (d, J = 2.1 Hz, 1H), 7.95 (d, J = 6.8 Hz, 1H), 7.71 (dd, J = 7.9, 1.7 Hz, 1H), 7.57–7.51 (m, 1H), 7.30 (d, J = 7.3 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.12 (dd, J = 8.4, 1.1 Hz, 1H), 6.96–6.91 (m, 1H), 4.30 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 163.1, 153.6, 148.2, 139.7, 136.2, 133.5, 130.8, 129.4, 125.4, 121.8, 121.2, 119.8, 119.4, 118.9, 118.6, 115.6, 31.2, 20.0, (1C is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{20}H_{17}N_2O_2$ $[M + H]^+$ 317.1285, found 317.1286.



(9-Benzyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(2-hydroxyphenyl)methanone. Compound **3al** (13.5 h, 73 mg, Yield = 96%, R_f = 0.76 (PE/EA = 3:1)) was isolated as a yellow solid; mp 143–144 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.00 (s, 1H), 8.92 (d, J = 2.1 Hz, 1H), 8.74 (d, J = 2.1 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 7.75 (dd, J = 8.0, 1.7 Hz, 1H), 7.58–7.49 (m, 2H), 7.44 (d, J = 8.2 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.32–7.23 (m, 5H), 7.13 (d, J = 7.3 Hz, 1H), 6.97–6.93 (m, 1H), 5.76 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 163.1, 153.2, 148.5, 140.4, 136.7, 136.3, 133.5, 129.9, 128.9, 127.9, 127.8, 127.2, 125.9, 121.7, 121.3, 120.8, 119.7, 119.0, 118.6, 115.6, 110.6, 45.5; ESI-HRMS *m/z* calcd for $C_{25}H_{19}N_2O_2$ $[M + H]^+$ 379.1441, found 379.1438.

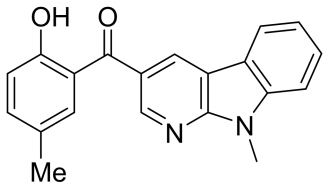


(2-Hydroxy-6-methoxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ba** (6 h, 24mg, Yield = 36%, R_f = 0.39 (PE/EA = 2:1)) was isolated as a white solid; mp 252–253 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.80 (d, J = 2.0 Hz, 1H), 8.69 (d, J = 2.1 Hz, 1H), 8.10 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.42 (t, J = 8.3 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 8.3 Hz, 1H), 6.49 (d, J = 8.3 Hz, 1H), 4.01 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 161.7, 159.8, 153.3, 149.0, 141.0, 135.5, 129.2, 128.0, 127.5, 121.4, 121.1, 120.9, 115.3, 112.2, 110.7, 109.7, 102.5, 55.6, 28.1; ESI-HRMS *m/z* calcd for $C_{20}H_{17}N_2O_3$ $[M + H]^+$ 333.1234, found 333.1239.

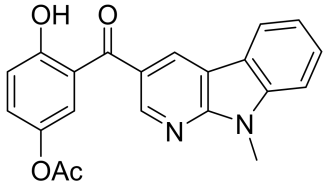


(2-Fluoro-6-hydroxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ca** (9 h, 30 mg, Yield = 45%, R_f = 0.28 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.88 (s, 1H), 8.88 (dd, J = 4.1, 2.1 Hz, 1H), 8.70 (t, J = 2.4 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.61–7.56 (m, 1H), 7.51–7.44 (m, 2H), 7.38–7.33 (m, 1H), 6.93 (d, J = 8.5 Hz, 1H), 6.71–6.65 (m, 1H), 4.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.7, 162.1 (d, J = 3.8 Hz), 161.4 (d, J = 252.9 Hz),

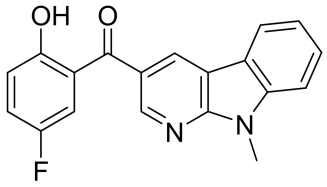
153.6, 148.7 (d, J = 5.0 Hz), 141.1, 135.8 (d, J = 11.8 Hz), 129.3 (d, J = 2.8 Hz), 127.8, 127.0 (d, J = 3.1 Hz), 121.6, 121.3, 120.7, 115.6, 114.2 (d, J = 3.0 Hz), 111.1 (d, J = 15.1 Hz), 109.8, 107.0 (d, J = 23.1 Hz), 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −101.3 (m, 1F); ESI-HRMS *m/z* calcd for $C_{19}H_{14}FN_2O_2$ $[M + H]^+$ 321.1034, found 321.1040.



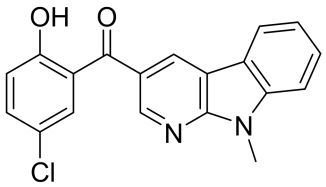
(2-Hydroxy-5-methylphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3da** (12 h, 55 mg, Yield = 87%, R_f = 0.55 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.78 (s, 1H), 8.88 (d, J = 2.1 Hz, 1H), 8.72 (d, J = 2.1 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.64–7.59 (m, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 2.3 Hz, 1H), 7.40–7.34 (m, 2H), 7.03 (d, J = 8.5 Hz, 1H), 4.03 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 161.0, 153.2, 148.3, 141.1, 137.3, 133.1, 129.7, 128.1, 127.9, 125.7, 121.6, 121.2, 120.6, 119.5, 118.4, 115.8, 109.8, 28.1, 20.7; ESI-HRMS *m/z* calcd for $C_{20}H_{17}N_2O_2$ $[M + H]^+$ 317.1285, found 317.1287.



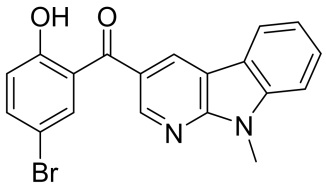
4-Hydroxy-3-(9-methyl-9*H*-pyrido[2,3-*b*]indole-3-carbonyl)phenyl acetate. Compound **3ea** (9 h, 43 mg, Yield = 60%, R_f = 0.43 (PE/EA = 2:1)) was isolated as a yellow solid; mp 140–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.25 (s, 1H), 8.88 (d, J = 2.0 Hz, 1H), 8.69 (d, J = 2.0 Hz, 1H), 8.13 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.64–7.59 (m, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.38 (t, J = 6.7 Hz, 1H), 6.88 (d, J = 2.3 Hz, 1H), 6.71 (dd, J = 8.8, 2.3 Hz, 1H), 4.03 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 168.7, 164.7, 156.6, 153.3, 148.2, 141.1, 134.7, 129.6, 127.9, 125.4, 121.7, 121.2, 120.5, 117.7, 115.7, 112.9, 111.5, 109.8, 28.1, 21.4; ESI-HRMS *m/z* calcd for $C_{21}H_{17}N_2O_4$ $[M + H]^+$ 361.1183, found 361.1181.



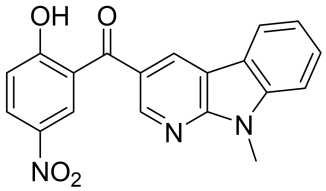
(5-Fluoro-2-hydroxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3fa** (14 h, 62 mg, Yield = 97%, R_f = 0.58 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.66 (s, 1H), 8.87 (d, J = 2.1 Hz, 1H), 8.67 (d, J = 2.0 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.63–7.58 (m, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.41–7.34 (m, 2H), 7.30–7.24 (m, 1H), 7.08 (dd, J = 9.1, 4.5 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5 (d, J = 2.4 Hz), 159.1 (d, J = 1.5 Hz), 154.8 (d, J = 237.4 Hz), 153.3, 148.2, 141.1, 129.5, 128.0, 124.9, 123.8, 123.6, 121.7 (d, J = 23.4 Hz), 120.4, 119.9 (d, J = 7.2 Hz), 119.3 (d, J = 6.1 Hz), 118.2 (d, J = 23.6 Hz), 115.7, 109.8, 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −123.6 (m, 1F); ESI-HRMS *m/z* calcd for $C_{19}H_{14}FN_2O_2$ $[M + H]^+$ 321.1034, found 321.1036.



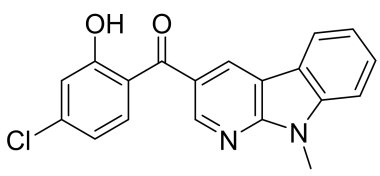
(5-Chloro-2-hydroxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ga** (7 h, 57 mg, Yield = 85%, R_f = 0.47 (PE/EA = 3:1)) was isolated as a yellow solid; mp 183–184 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.83 (s, 1H), 8.86 (d, J = 2.1 Hz, 1H), 8.68 (d, J = 2.1 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 2.7 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.47 (dd, J = 8.9, 2.6 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.9 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 161.5, 153.4, 148.3, 141.2, 136.0, 132.2, 129.6, 128.0, 124.8, 123.7, 121.7, 121.3, 120.4, 120.2, 115.9, 109.8, 28.1, (1C is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{19}H_{14}ClN_2O_2$ $[M + H]^+$ 337.0738, found 337.0743.



(5-Bromo-2-hydroxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ha** (9 h, 72 mg, Yield = 95%, R_f = 0.58 (PE/EA = 3:1)) was isolated as a yellow solid; mp 182–183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.86 (d, J = 2.1 Hz, 1H), 8.69 (d, J = 2.1 Hz, 1H), 8.13 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 2.5 Hz, 1H), 7.64–7.58 (m, 2H), 7.52 (d, J = 8.2 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 8.9 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 161.9, 153.4, 148.3, 141.2, 138.8, 135.2, 129.6, 128.0, 124.8, 121.7, 121.3, 121.1, 120.6, 120.4, 115.9, 110.6, 109.8, 28.1; ESI-HRMS *m/z* calcd for $C_{19}H_{14}BrN_2O_2$ $[M + H]^+$ 381.0233, found 381.0235.

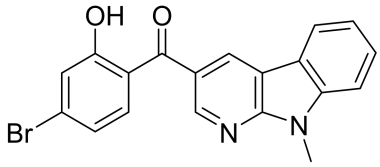


(2-Hydroxy-5-nitrophenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ia** (2 h, 48 mg, Yield = 70%, R_f = 0.21 (PE/EA = 3:1)) was isolated as a yellow solid; mp 212–213 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.65 (s, 1H), 8.90 (d, J = 2.1 Hz, 1H), 8.73 (d, J = 2.1 Hz, 1H), 8.71 (d, J = 2.7 Hz, 1H), 8.42 (dd, J = 9.3, 2.7 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.66–7.62 (m, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.42–7.38 (m, 1H), 7.22 (d, J = 9.2 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 167.9, 153.7, 148.4, 141.3, 139.7, 130.8, 129.6, 129.4, 128.3, 124.1, 121.8, 121.6, 120.4, 119.7, 118.7, 116.1, 110.0, 28.2; ESI-HRMS *m/z* calcd for $C_{19}H_{14}N_3O_4$ $[M + H]^+$ 348.0979, found 348.0982.

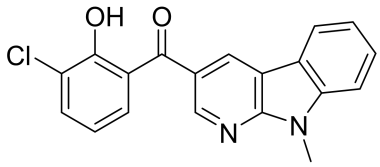


(4-Chloro-2-hydroxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ja** (2 h, 61 mg, Yield = 91%, R_f = 0.50 (PE/EA = 3:1)) was isolated as a yellow solid; mp 185–186 °C. ^{1}H NMR

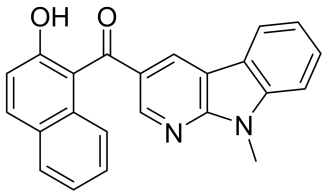
(500 MHz, $CDCl_3$) δ 12.15 (s, 1H), 8.85 (d, J = 2.1 Hz, 1H), 8.67 (d, J = 2.1 Hz, 1H), 8.11 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.62–7.59 (m, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 2.1 Hz, 1H), 6.91 (dd, J = 8.5, 2.0 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 163.8, 153.3, 148.2, 142.1, 141.1, 134.3, 129.6, 128.0, 125.1, 121.6, 121.3, 120.4, 119.6, 118.7, 118.3, 115.7, 109.8, 28.1; ESI-HRMS *m/z* calcd for $C_{19}H_{14}ClN_2O_2$ $[M + H]^+$ 337.0738, found 337.0738.



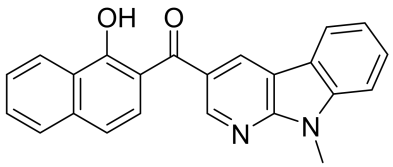
(4-Bromo-2-hydroxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ka** (4 h, 70 mg, Yield = 92%, R_f = 0.53 (PE/EA = 3:1)) was isolated as a yellow solid; mp 193–194 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.10 (s, 1H), 8.87 (d, J = 2.0 Hz, 1H), 8.70 (d, J = 2.1 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.65–7.61 (m, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.41–7.37 (m, 1H), 7.32 (d, J = 1.9 Hz, 1H), 7.08 (dd, J = 8.5, 1.9 Hz, 1H), 4.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 163.6, 153.4, 148.2, 141.2, 134.3, 130.8, 129.7, 128.1, 125.2, 122.5, 121.9, 121.7, 121.4, 120.5, 118.7, 115.8, 109.9, 28.2; ESI-HRMS *m/z* calcd for $C_{19}H_{14}BrN_2O_2$ $[M + H]^+$ 381.0233, found 381.0234.



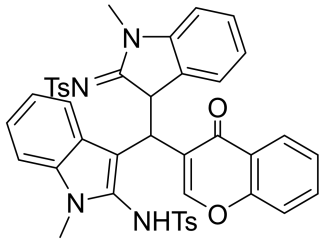
(3-Chloro-2-hydroxyphenyl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3la** (2 h, 60 mg, Yield = 90%, R_f = 0.53 (PE/EA = 3:1)) was isolated as a yellow solid; mp 147–148 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.47 (s, 1H), 8.87 (d, J = 2.0 Hz, 1H), 8.70 (d, J = 2.0 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.66–7.60 (m, 3H), 7.53 (d, J = 8.2 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 7.9 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 158.6, 153.4, 148.5, 141.2, 136.1, 131.9, 129.8, 128.0, 125.0, 123.2, 121.7, 121.4, 120.8, 120.5, 119.0, 115.8, 109.9, 28.1; ESI-HRMS *m/z* calcd for $C_{19}H_{14}ClN_2O_2$ $[M + H]^+$ 337.0738, found 337.0736.



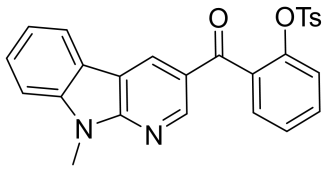
(2-Hydroxynaphthalen-1-yl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3ma** (12 h, 39 mg, Yield = 56%, R_f = 0.25 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.78 (s, 1H), 8.70 (d, J = 2.0 Hz, 1H), 8.68 (d, J = 2.0 Hz, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.57 (t, J = 7.7 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.30–7.25 (m, 2H), 7.18–7.12 (m, 1H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 160.0, 153.4, 149.4, 141.0, 135.7, 132.6, 129.6, 128.7, 128.6, 127.8, 127.5, 127.1, 126.1, 123.9, 121.6, 121.2, 120.7, 119.1, 115.8, 115.4, 109.7, 28.1; ESI-HRMS *m/z* calcd for $C_{23}H_{17}N_2O_2$ $[M + H]^+$ 353.1285, found 353.1285.



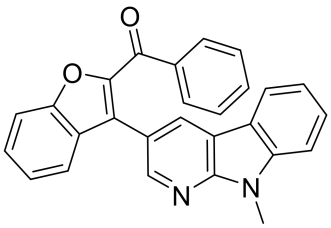
(3-Hydroxynaphthalen-2-yl)(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)methanone. Compound **3na** (9 h, 66 mg, Yield = 94%, R_f = 0.56 (PE/EA = 3:1)) was isolated as a yellow solid; mp 187–188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.94 (s, 1H), 8.93 (d, J = 2.1 Hz, 1H), 8.74 (d, J = 2.0 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 7.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.70–7.64 (m, 2H), 7.63–7.55 (m, 2H), 7.51 (d, J = 8.2 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 163.8, 153.1, 148.2, 141.1, 137.3, 130.4, 129.7, 127.8, 127.6, 127.4, 126.1, 125.7, 125.4, 124.6, 121.6, 121.1, 120.5, 118.2, 115.6, 113.1, 109.7, 28.1; ESI-HRMS *m/z* calcd for $C_{23}H_{17}N_2O_2$ $[M + H]^+$ 353.1285, found 353.1285.



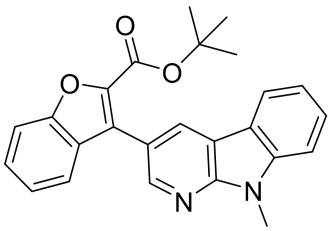
(Z)-4-methyl-N-(1-methyl-3-((1-methyl-2-((4-methylphenyl)sulfonamido)-1*H*-indol-3-yl)(4-oxo-4*H*-chromen-3-yl)methyl)indolin-2-ylidene)benzenesulfonamide. Compound **4aa** (19 h, 15 mg, Yield = 10%, R_f = 0.34 (PE/EA = 2:1)) was isolated as a white solid; mp 170–171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.41 (dd, J = 8.0, 1.7 Hz, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.76–7.69 (m, 3H), 7.51 (t, J = 7.6 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.25–7.19 (m, 2H), 7.01 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 1.6 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 7.9 Hz, 2H), 6.72 (d, J = 7.4 Hz, 1H), 6.50 (d, J = 6.0 Hz, 1H), 6.43 (d, J = 7.8 Hz, 1H), 6.38 (t, J = 7.6 Hz, 1H), 5.17 (d, J = 8.2 Hz, 1H), 5.09 (dd, J = 6.1, 1.6 Hz, 1H), 3.89 (s, 3H), 2.59 (s, 3H), 2.42 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 172.1, 155.8, 155.5, 144.8, 143.3, 142.8, 139.8, 137.1, 135.2, 133.9, 130.2, 130.0, 129.4, 129.3, 128.6, 127.9, 126.8, 126.6, 125.4, 125.2, 124.2, 124.0, 123.6, 121.9, 121.3, 121.0, 119.0, 118.1, 109.9, 109.6, 103.6, 48.7, 40.1, 30.6, 28.0, 21.7, 20.3; ESI-HRMS *m/z* calcd for $C_{42}H_{36}N_4O_6S_2Na$ $[M + Na]^+$ 779.1969, found 779.1971.



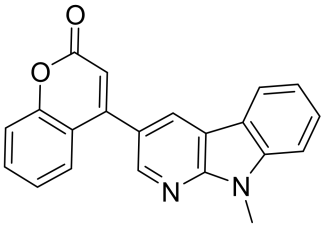
2-(9-Methyl-9*H*-pyrido[2,3-*b*]indole-3-carbonyl)phenyl 4-methylbenzenesulfonate. Compound **5aa** (35 h, 41 mg, Yield = 30%, R_f = 0.38 (PE/EA = 2:1)) was isolated as a brown solid; mp 142–143 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 2.0 Hz, 1H), 8.55 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.62–7.55 (m, 2H), 7.52–7.48 (m, 2H), 7.47–7.39 (m, 4H), 7.37 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.1 Hz, 2H), 3.99 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 153.3, 149.7, 146.7, 145.5, 141.1, 133.2, 132.3, 132.0, 130.5, 129.8, 129.6, 128.5, 127.9, 127.1, 124.8, 124.1, 121.6, 121.4, 120.7, 115.7, 109.8, 28.2, 21.5; ESI-HRMS *m/z* calcd for $C_{26}H_{21}N_2O_4S$ $[M + H]^+$ 457.1217, found 457.1217.



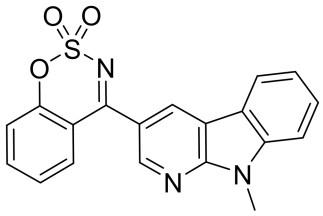
(3-(9-Methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)benzofuran-2-yl)(phenyl)methanone. Compound **6** (6 h, 114 mg, Yield = 94%, R_f = 0.46 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, J = 2.1 Hz, 1H), 8.53 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.98–7.94 (m, 2H), 7.78 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.59–7.54 (m, 2H), 7.48 (d, J = 8.2 Hz, 1H), 7.46–7.42 (m, 1H), 7.42–7.34 (m, 3H), 7.32–7.29 (m, 1H) 3.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.7, 154.8, 151.5, 147.6, 147.1, 140.8, 137.4, 132.8, 130.0, 129.7, 128.6, 128.5, 128.3, 127.7, 127.2, 124.3, 122.3, 121.4, 120.4, 120.3, 118.2, 115.7, 112.7, 109.3, 27.9; ESI-HRMS *m/z* calcd for $C_{27}H_{19}N_2O_2$ $[M + H]^+$ 403.1441, found 403.1441.



Tert-butyl 3-(9-methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)benzofuran-2-carboxylate. Compound **7** (2.5 h, 33 mg, Yield = 83%, R_f = 0.34 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 2.0 Hz, 1H), 8.52 (d, J = 2.1 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.60–7.56 (m, 1H), 7.53–7.48 (m, 2H), 7.35–7.30 (m, 2H), 4.04 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 154.6, 151.5, 147.3, 141.8, 140.8, 129.9, 128.8, 127.9, 127.1, 125.9, 123.9, 121.9, 121.2, 120.4, 120.3, 118.5, 115.4, 112.5, 109.4, 82.9, 28.3, 28.0; ESI-HRMS *m/z* calcd for $C_{25}H_{23}N_2O_2$ $[M + H]^+$ 399.1703, found 399.1703.

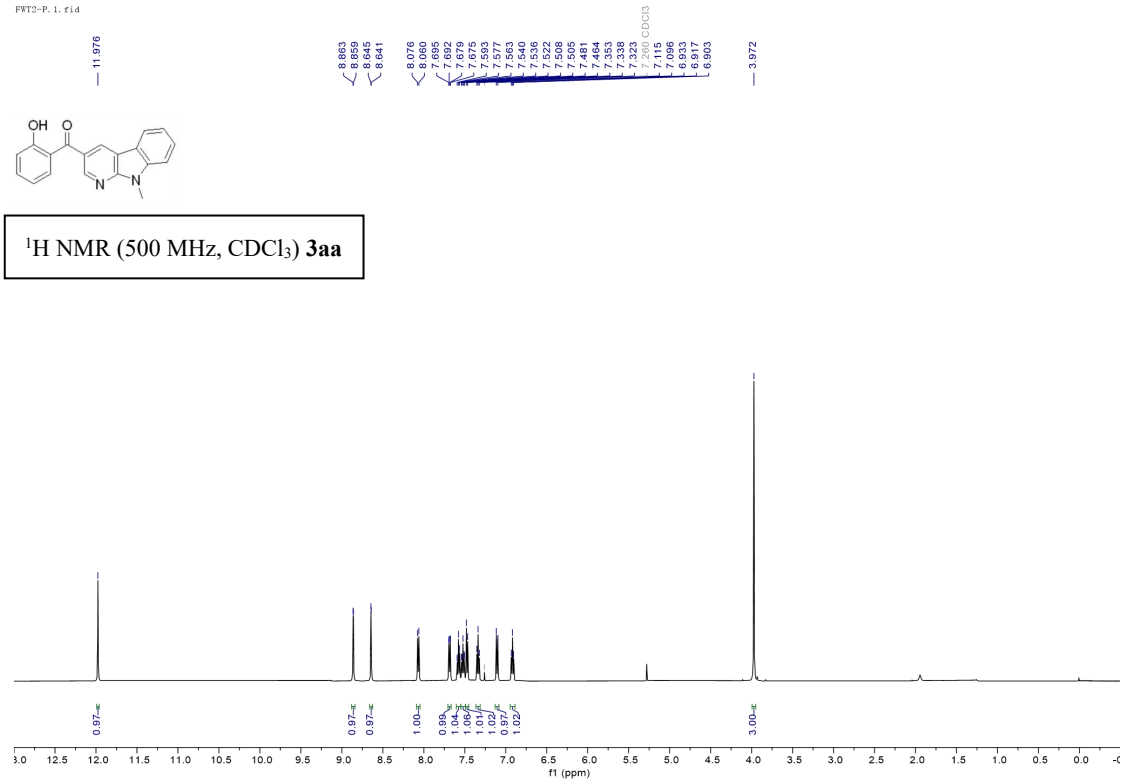


4-(9-Methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)-2H-chromen-2-one. Compound **8** (0.5 h, 24 mg, Yield = 73%, R_f = 0.18 (PE/EA = 5:1)) was isolated as a white oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 2.0 Hz, 1H), 8.43 (d, J = 2.1 Hz, 1H), 8.12 (d, J = 7.7 Hz, 1H), 7.64–7.57 (m, 3H), 7.54 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 6.50 (s, 1H), 4.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 154.4, 153.8, 152.3, 145.5, 141.1, 132.2, 128.2, 127.8, 127.0, 124.5, 122.5, 121.5, 120.8, 120.1, 119.4, 117.7, 115.9, 115.8, 109.7, 28.1; ESI-HRMS *m/z* calcd for $C_{21}H_{15}N_2O_2$ $[M + H]^+$ 327.1128, found 327.1127.

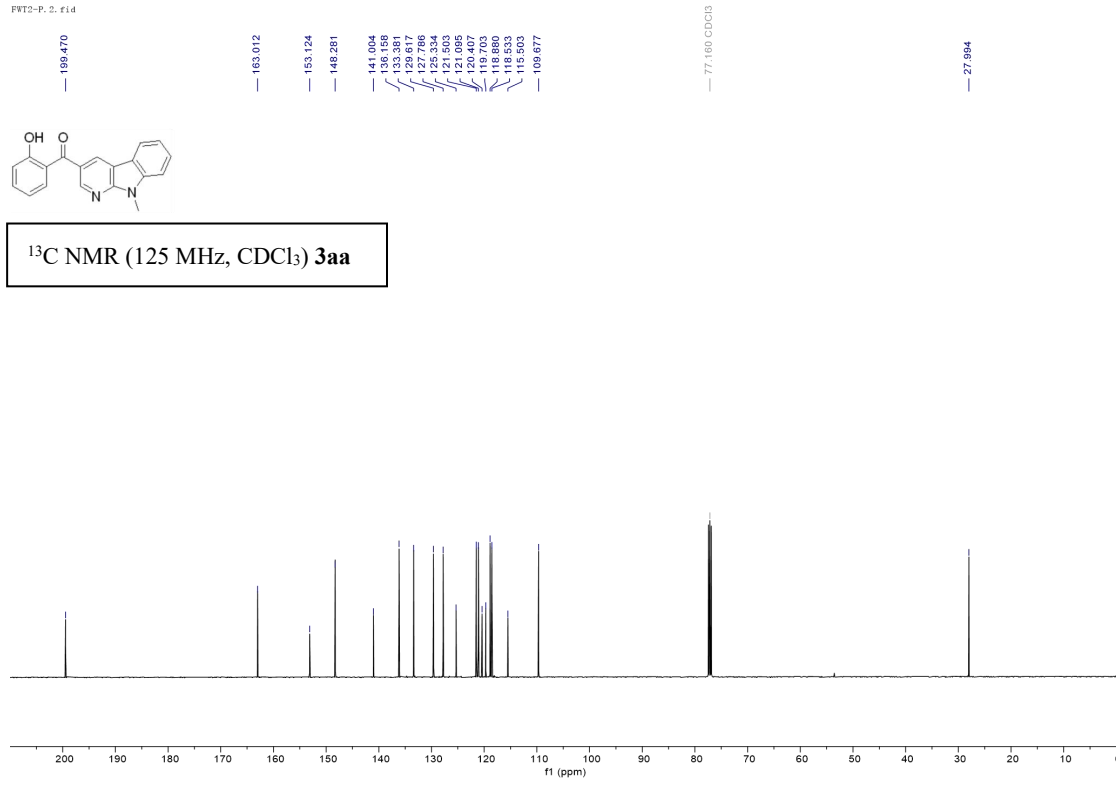


4-(9-Methyl-9*H*-pyrido[2,3-*b*]indol-3-yl)benzo[*e*][1,2,3]oxathiazine 2,2-dioxide. Compound **9** (0.5 h, 22 mg, Yield = 61%, R_f = 0.34 (PE/EA = 5:1)) was isolated as a yellow soild, mp 224–225 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (dd, J = 19.8, 2.1 Hz, 2H), 8.13 (d, J = 7.8 Hz, 1H), 7.83–7.75 (m, 2H), 7.63 (t, J = 7.7 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.49–7.36 (m, 3H), 4.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 154.8, 153.8, 149.1, 141.2, 136.9, 131.9, 130.5, 128.3, 125.9, 121.8, 121.7, 121.2, 120.3, 119.8, 117.0, 116.3, 110.0, 28.2; ESI-HRMS *m/z* calcd for $C_{19}H_{14}N_3O_3S$ $[M + H]^+$ 364.0750, found 364.0750.

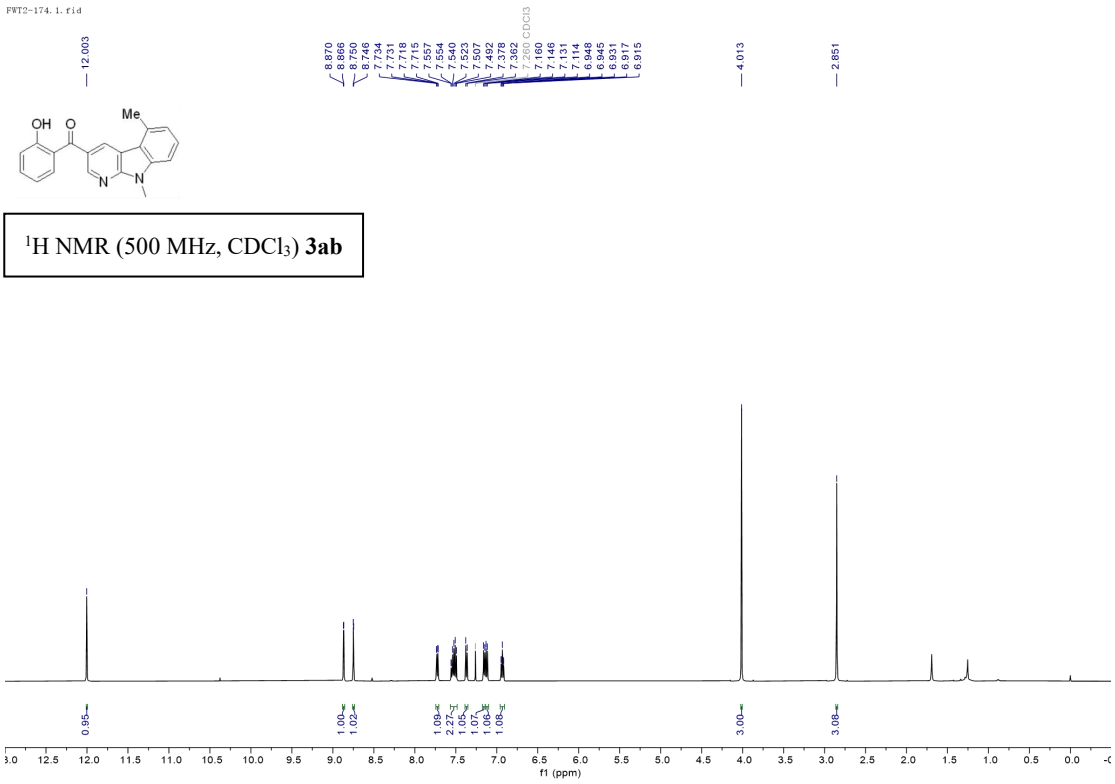
5. NMR Spectra



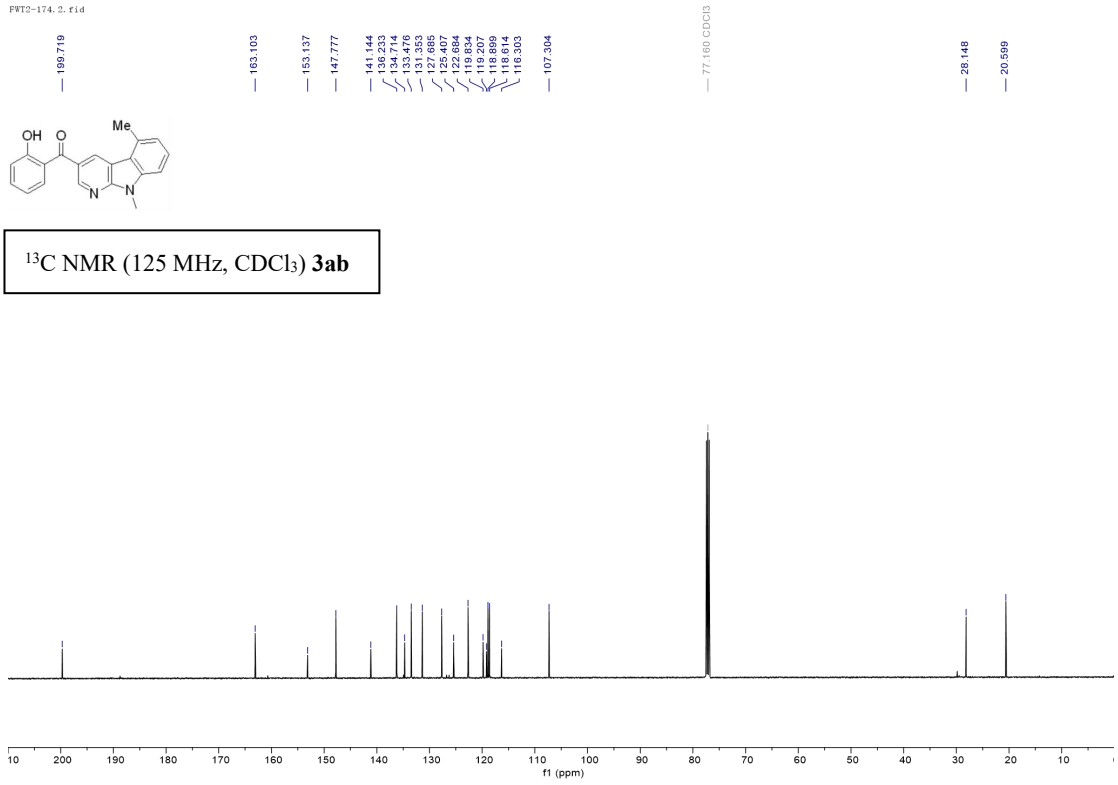
^{1}H NMR (500 MHz, $CDCl_3$) **3aa**



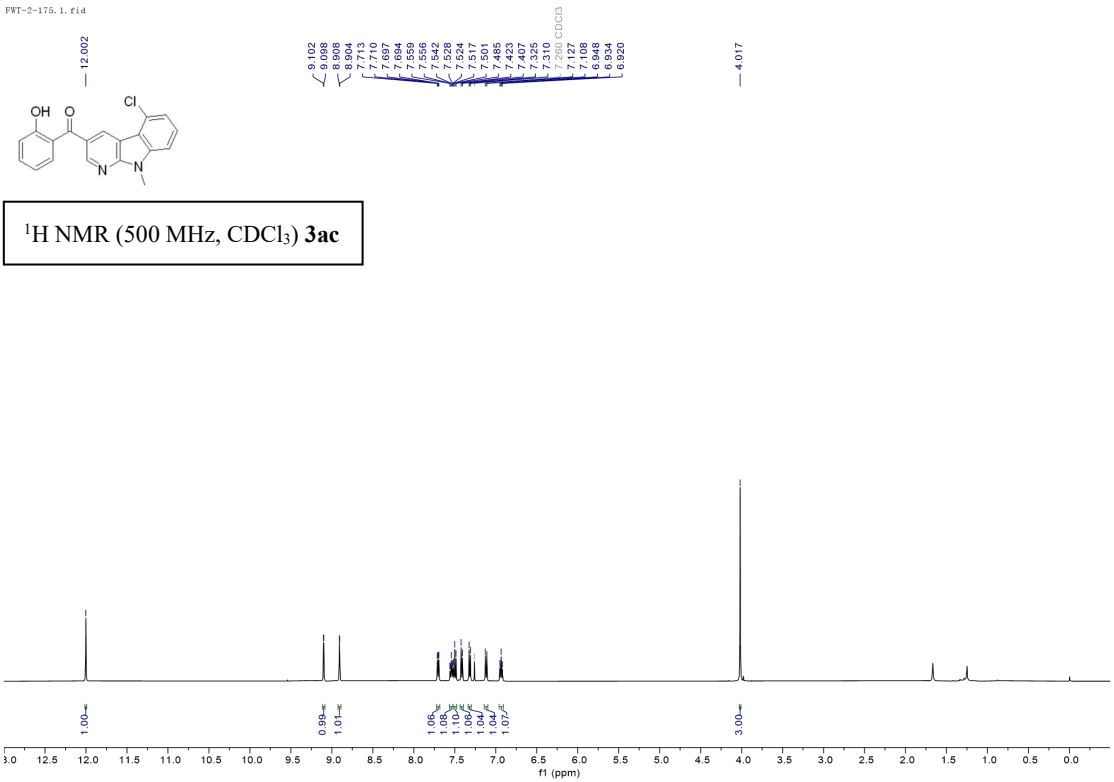
^{13}C NMR (125 MHz, $CDCl_3$) **3aa**



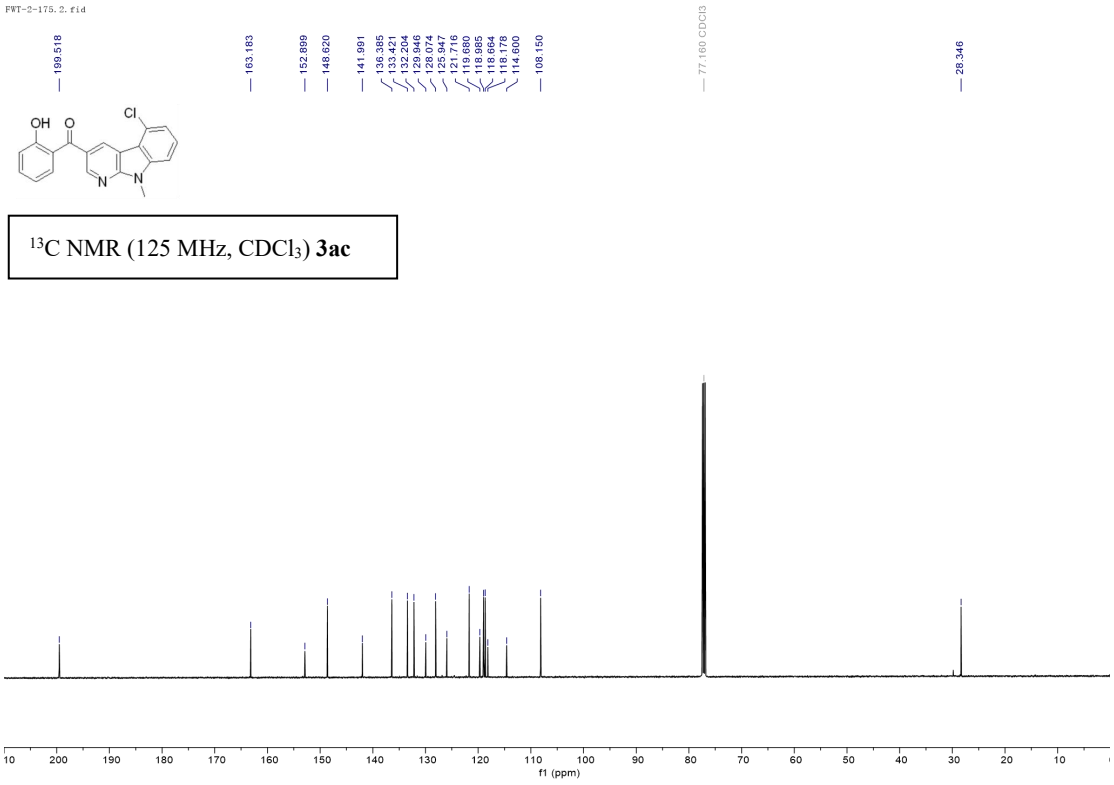
^{1}H NMR (500 MHz, $CDCl_3$) **3ab**



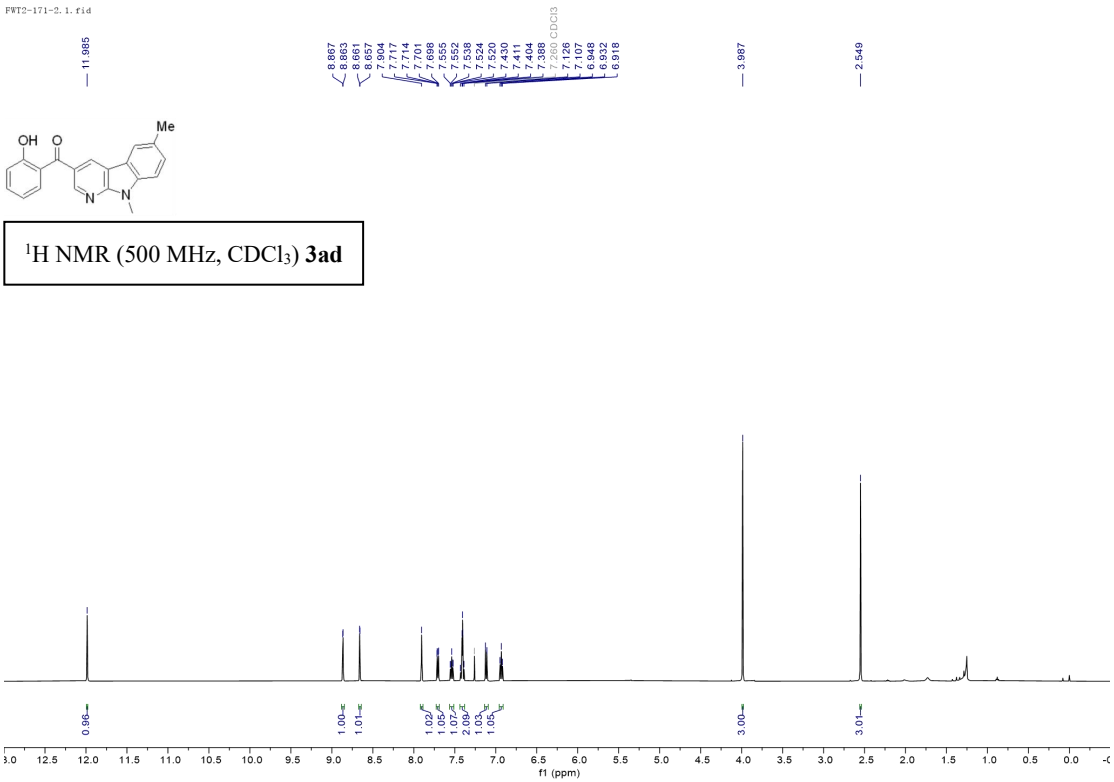
^{13}C NMR (125 MHz, $CDCl_3$) **3ab**



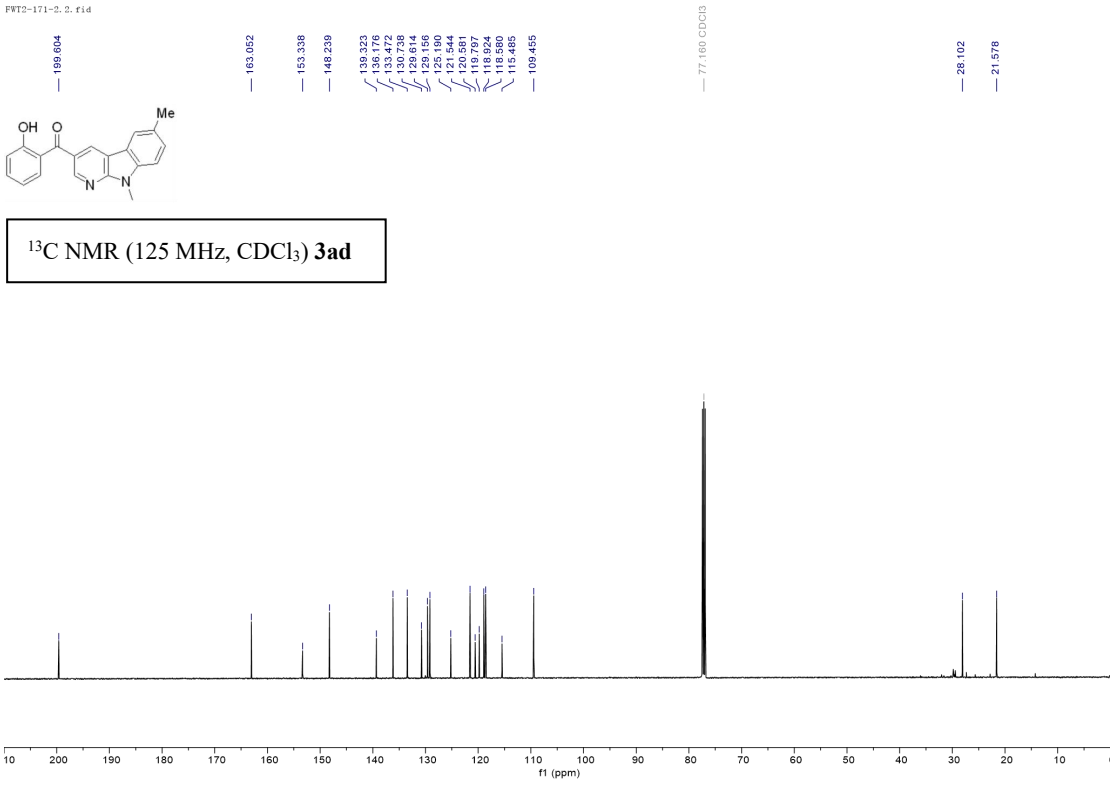
^{1}H NMR (500 MHz, $CDCl_3$) **3ac**



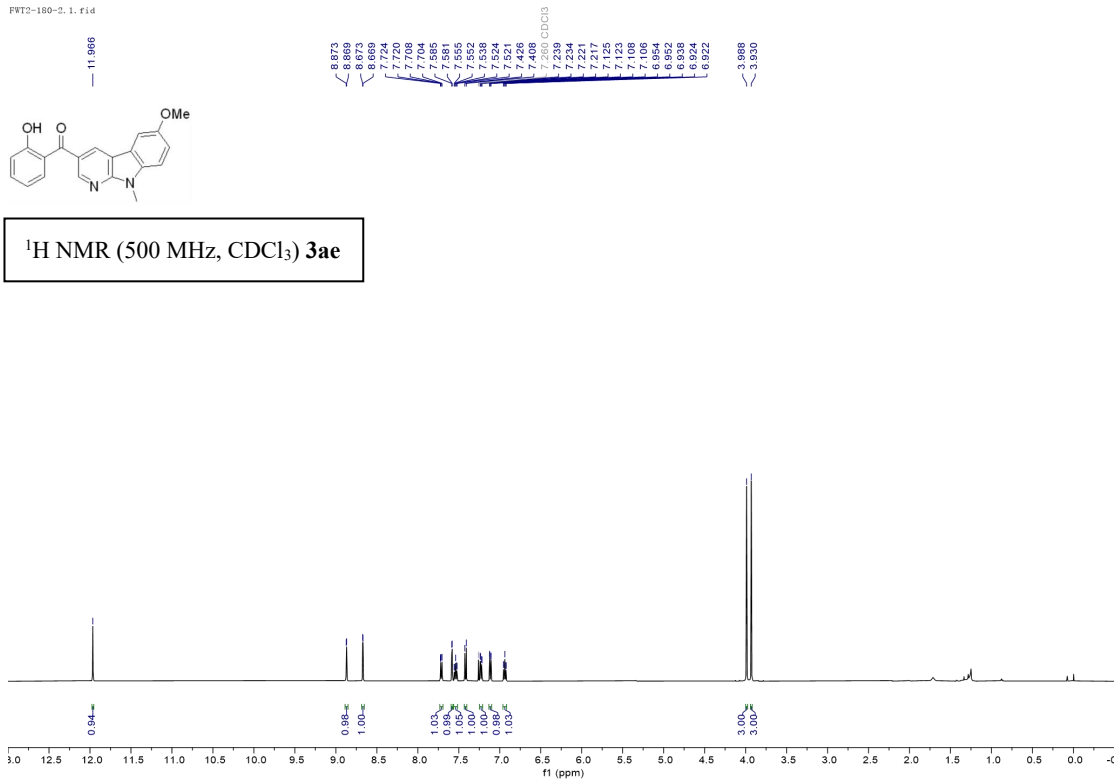
^{13}C NMR (125 MHz, $CDCl_3$) **3ac**



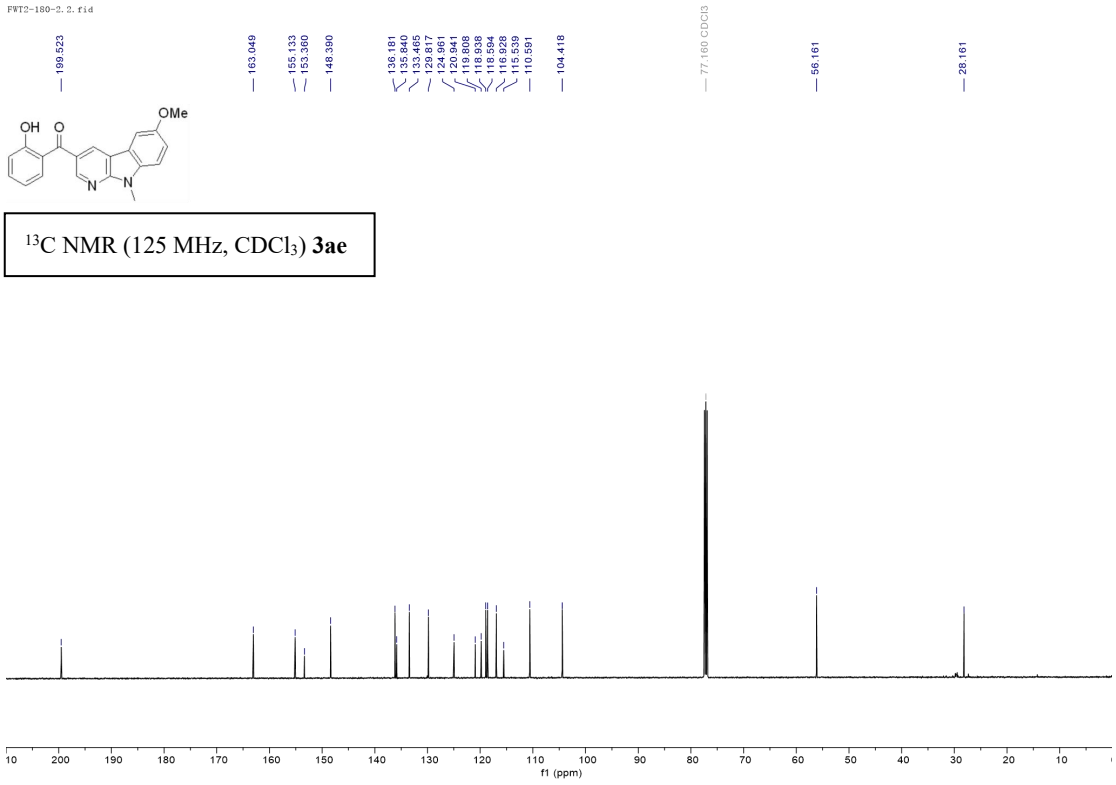
^{1}H NMR (500 MHz, $CDCl_3$) **3ad**



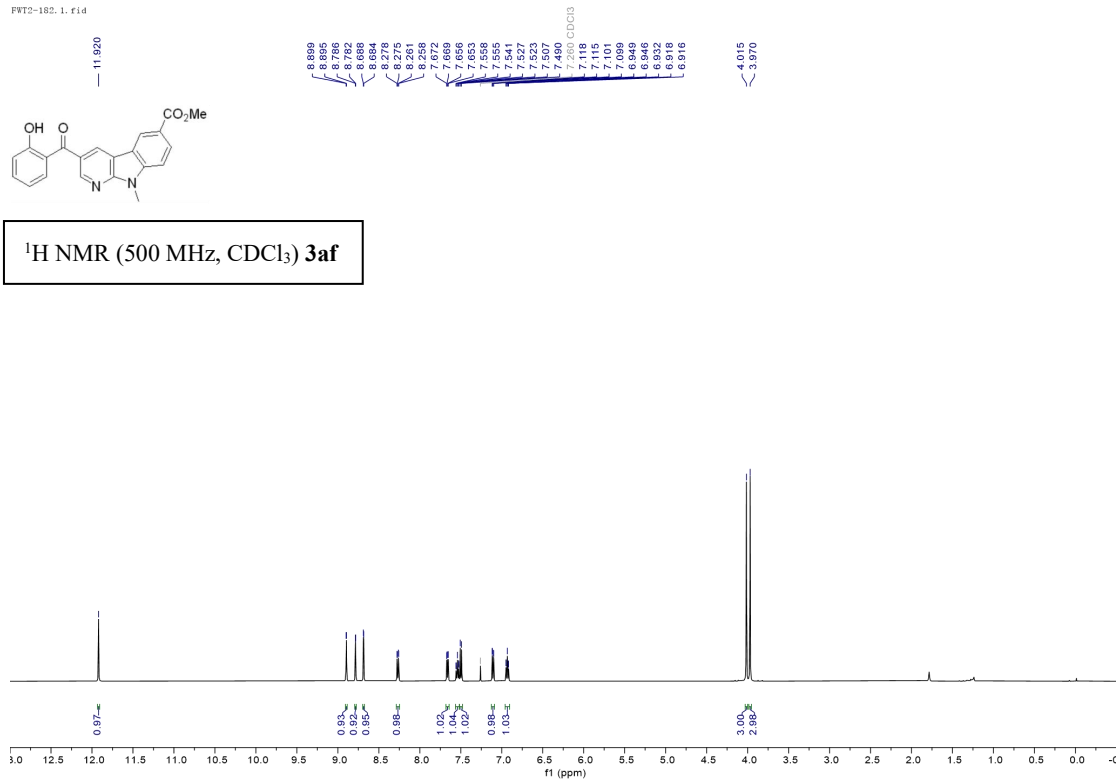
^{13}C NMR (125 MHz, $CDCl_3$) **3ad**



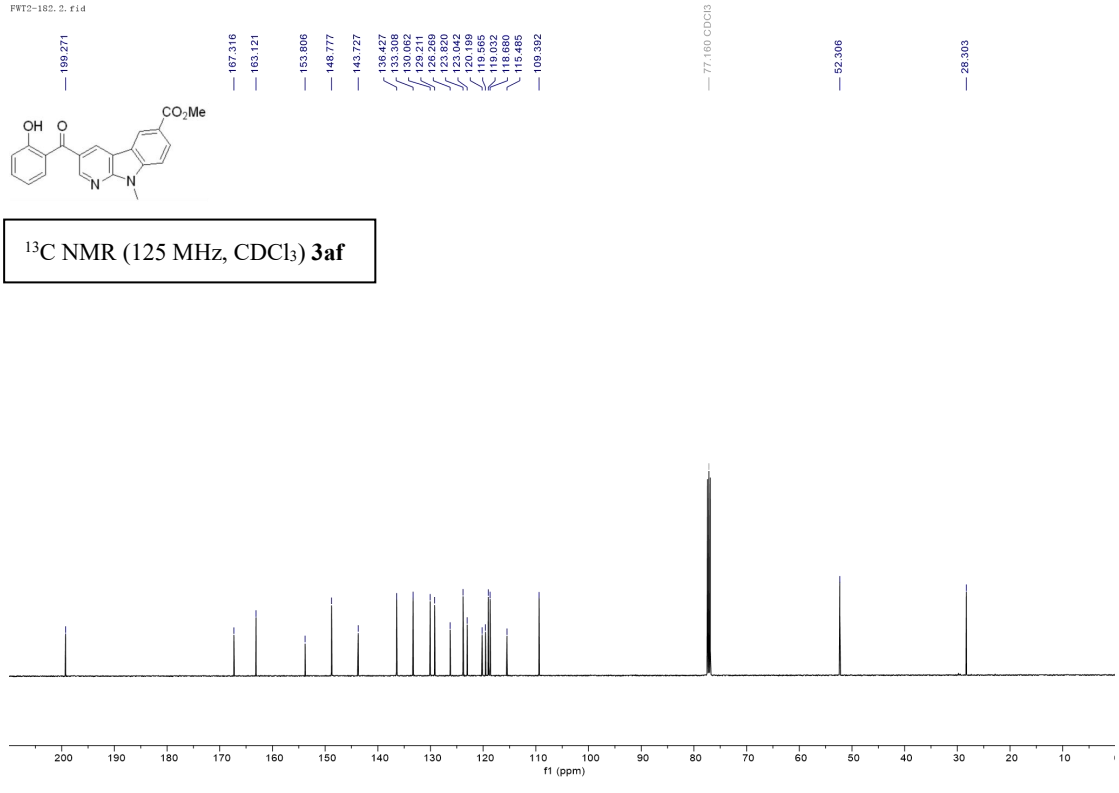
^{1}H NMR (500 MHz, $CDCl_3$) **3ae**



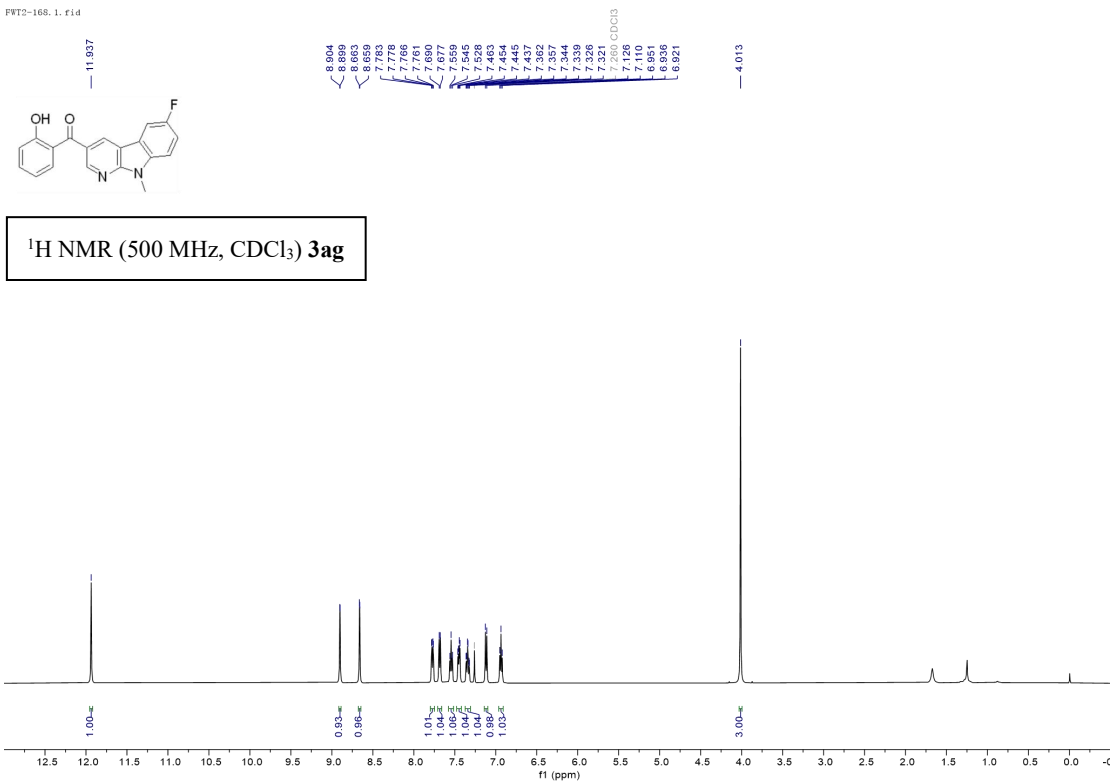
^{13}C NMR (125 MHz, $CDCl_3$) **3ae**



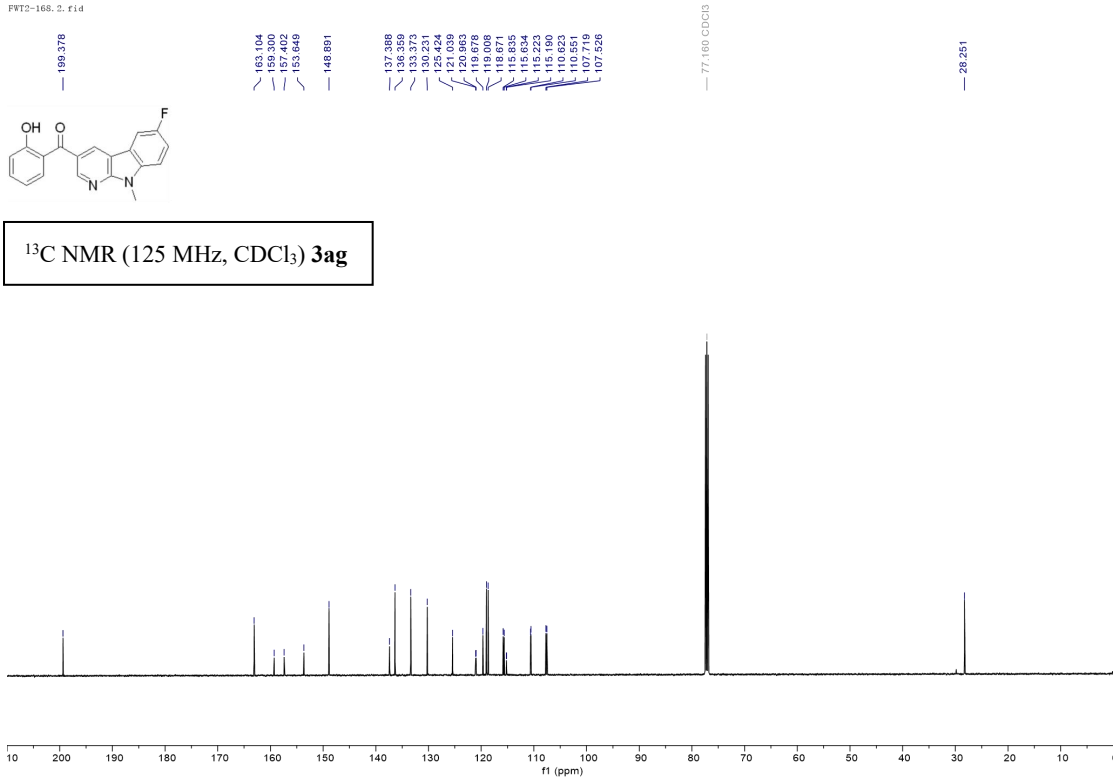
^{1}H NMR (500 MHz, $CDCl_3$) **3af**



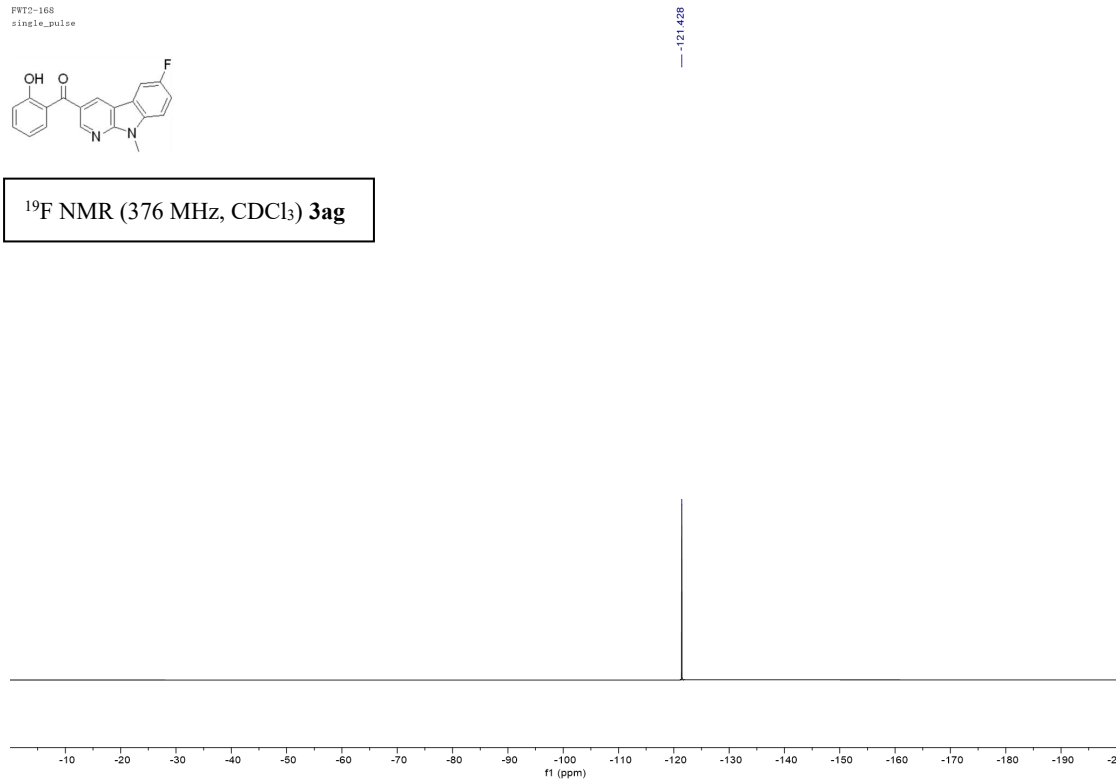
^{13}C NMR (125 MHz, $CDCl_3$) **3af**



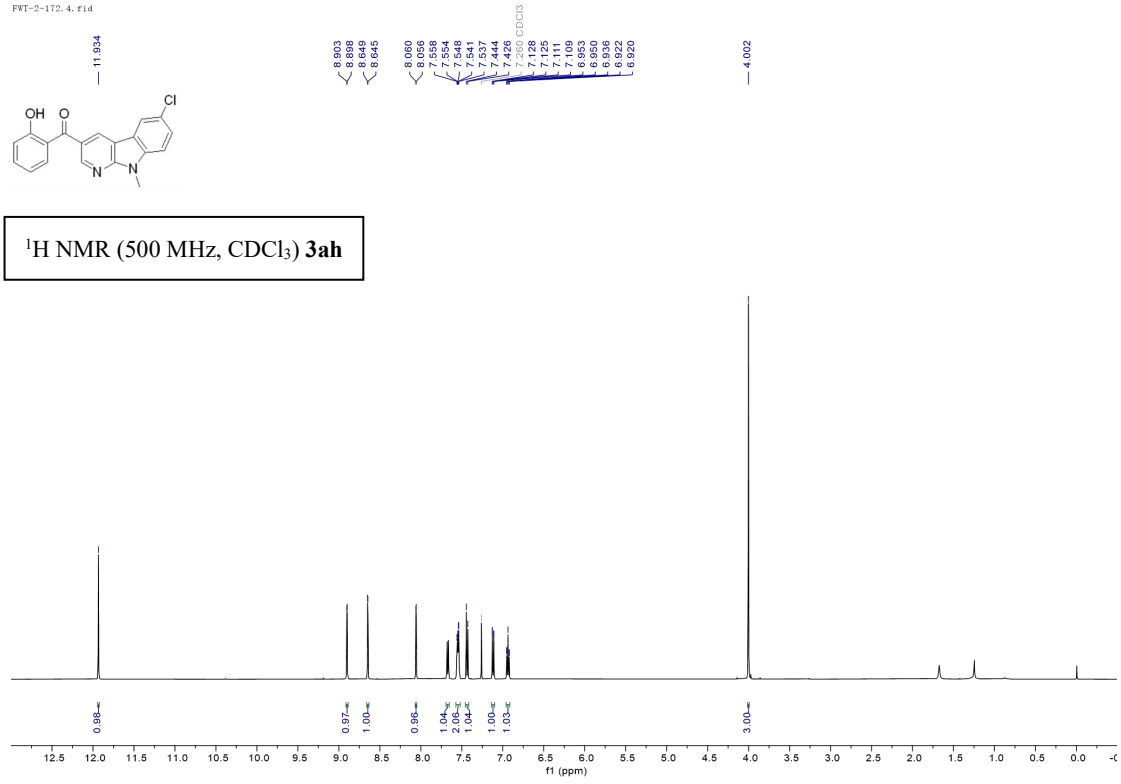
^{1}H NMR (500 MHz, $CDCl_3$) **3ag**



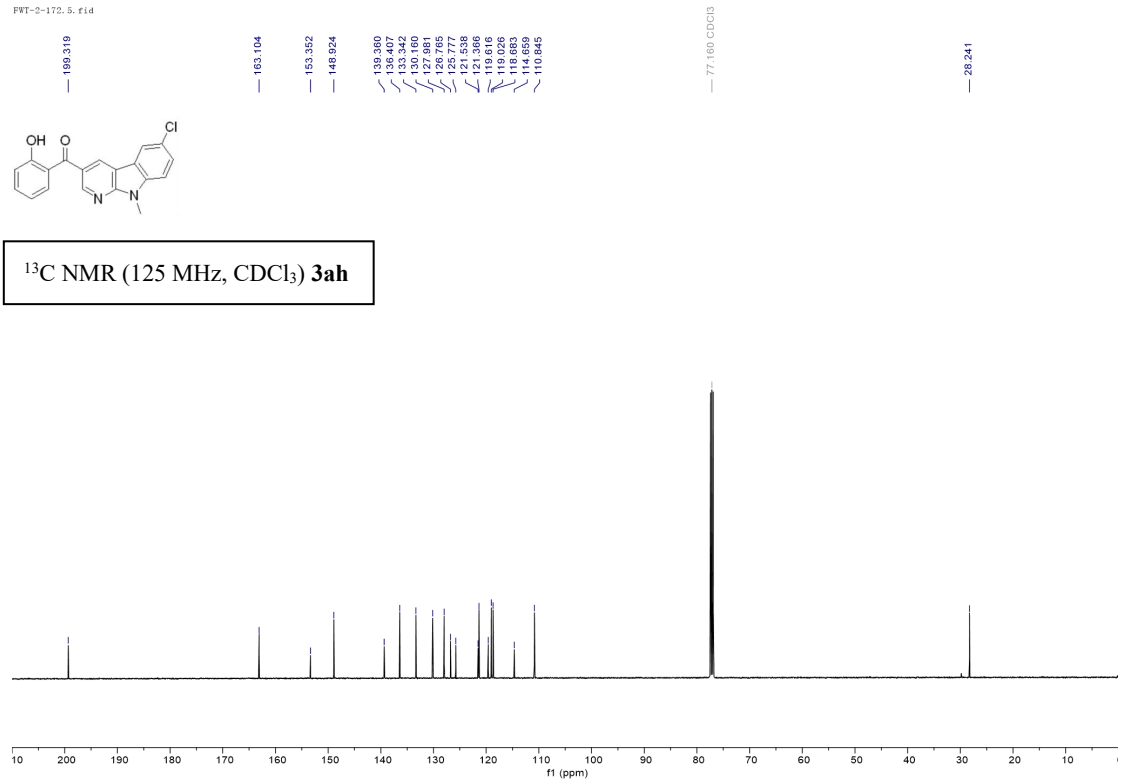
^{13}C NMR (125 MHz, $CDCl_3$) **3ag**



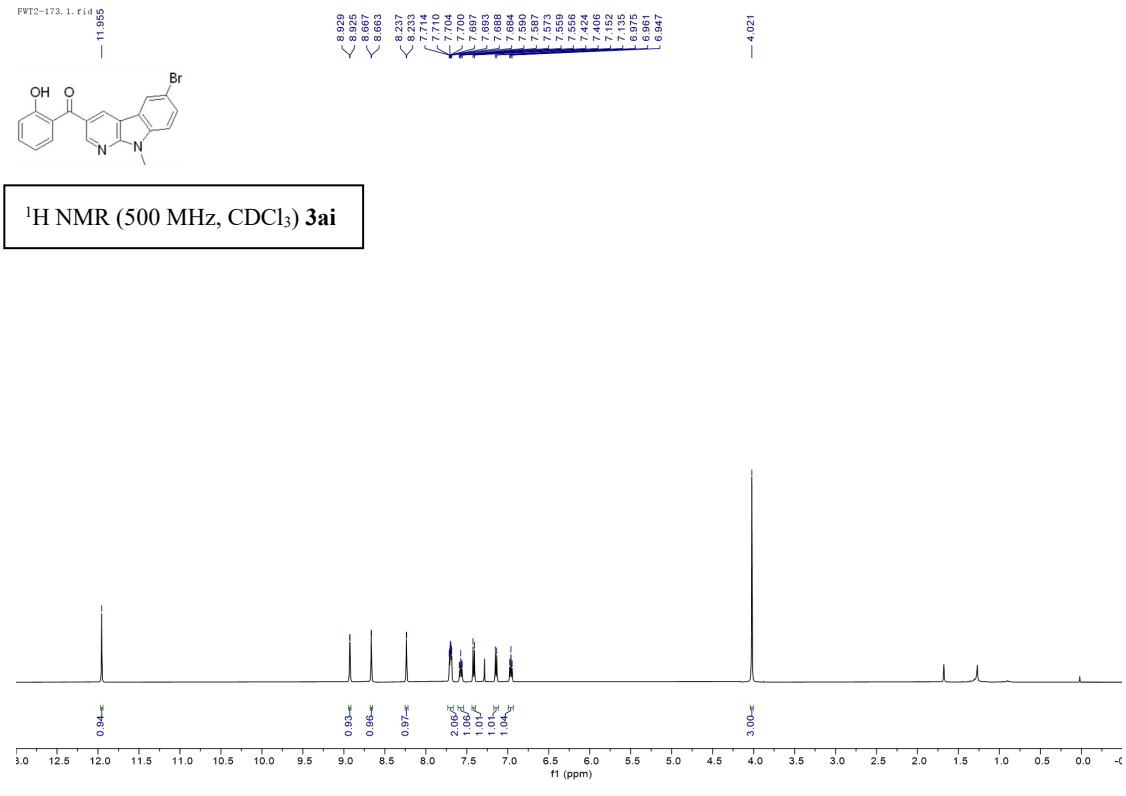
^{19}F NMR (376 MHz, $CDCl_3$) **3ag**



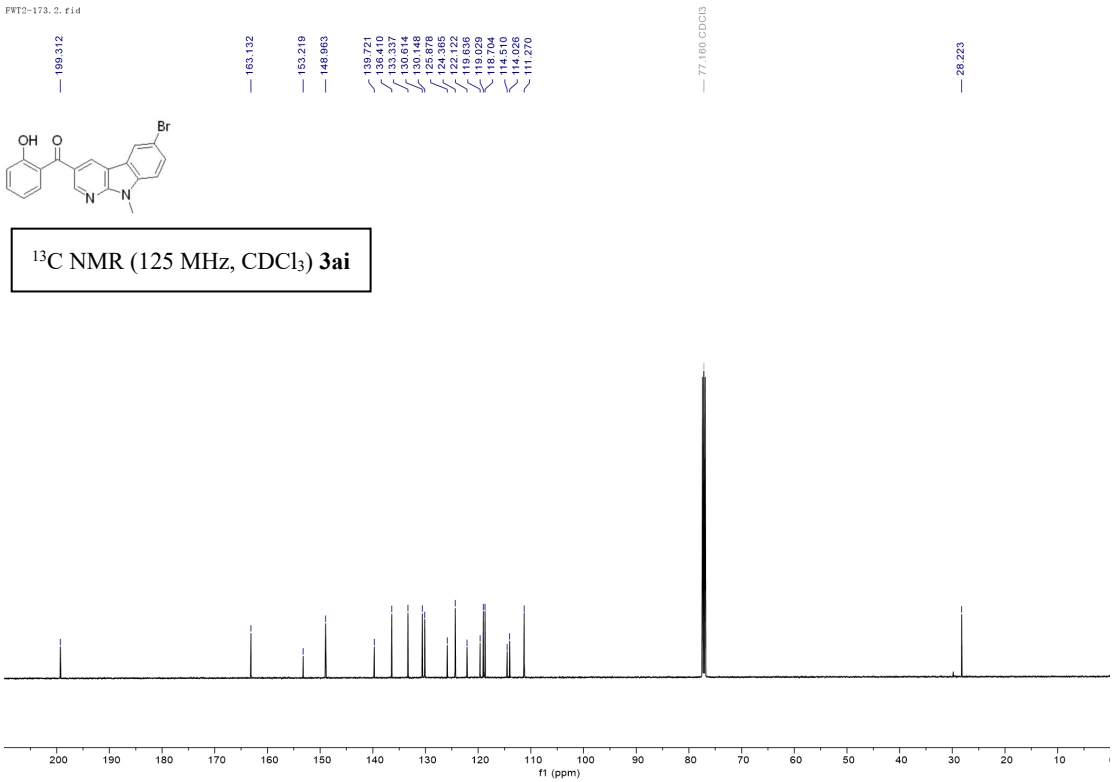
^{1}H NMR (500 MHz, $CDCl_3$) **3ah**



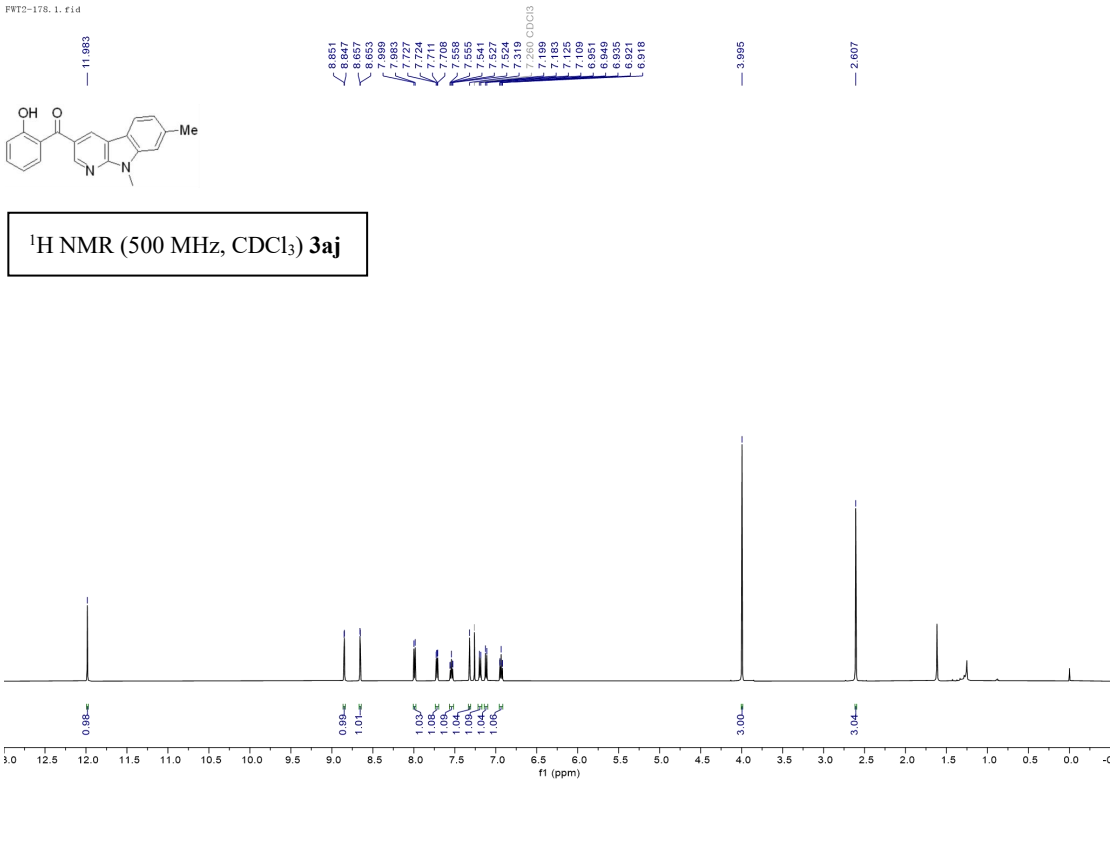
^{13}C NMR (125 MHz, $CDCl_3$) **3ah**



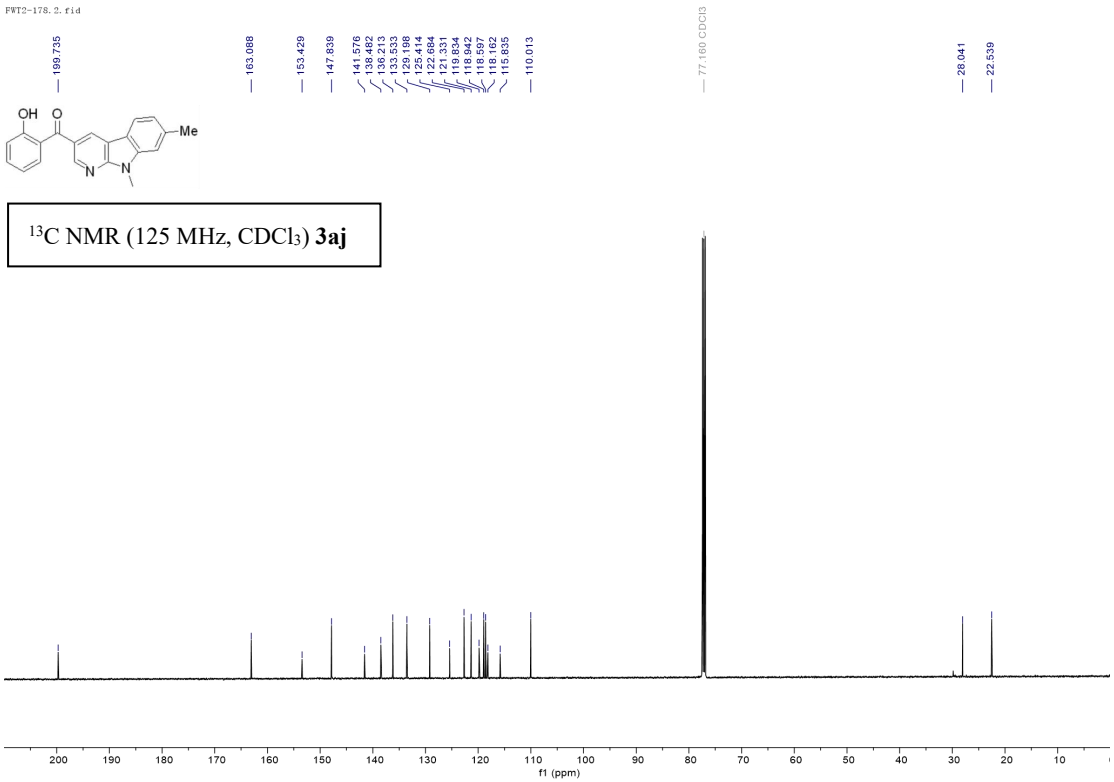
^{1}H NMR (500 MHz, $CDCl_3$) **3ai**



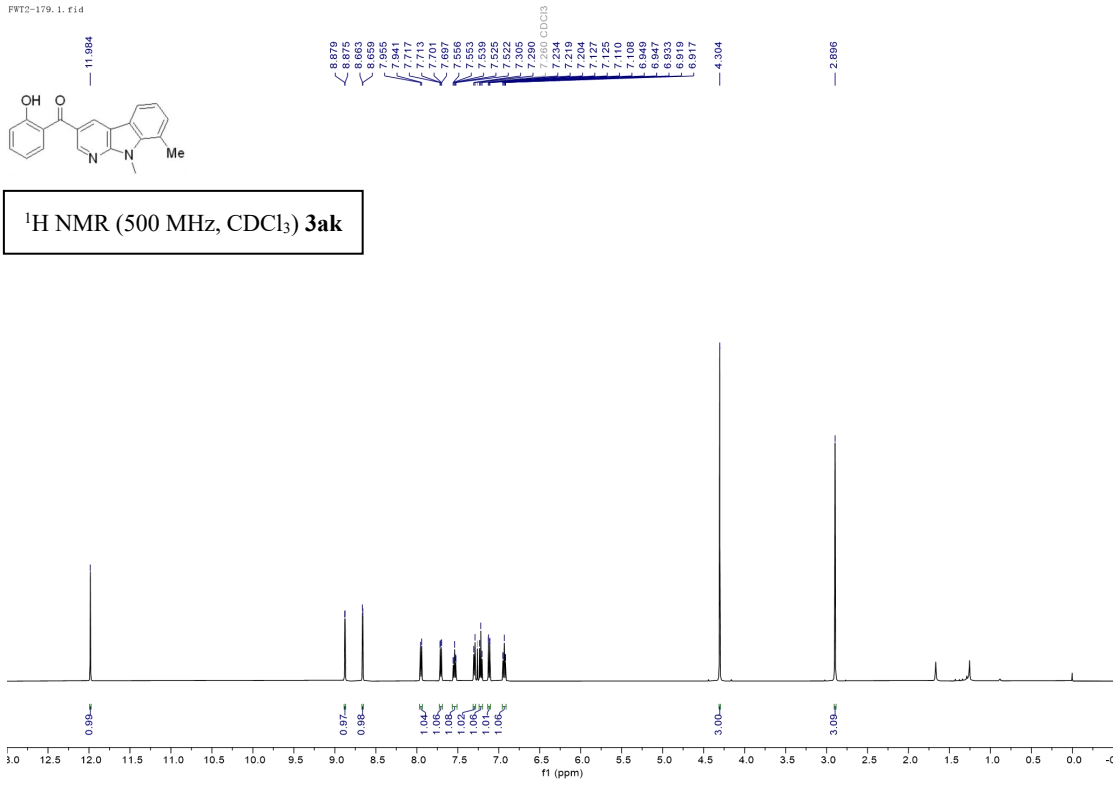
^{13}C NMR (125 MHz, $CDCl_3$) **3ai**



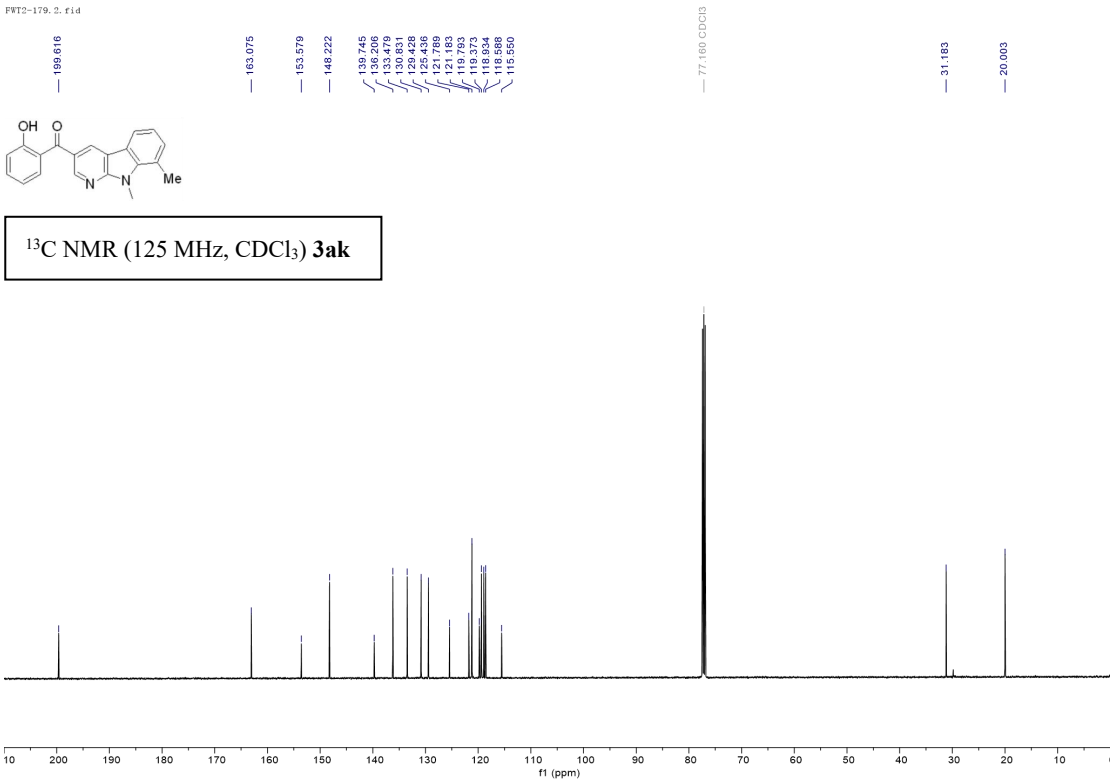
^{1}H NMR (500 MHz, $CDCl_3$) **3aj**



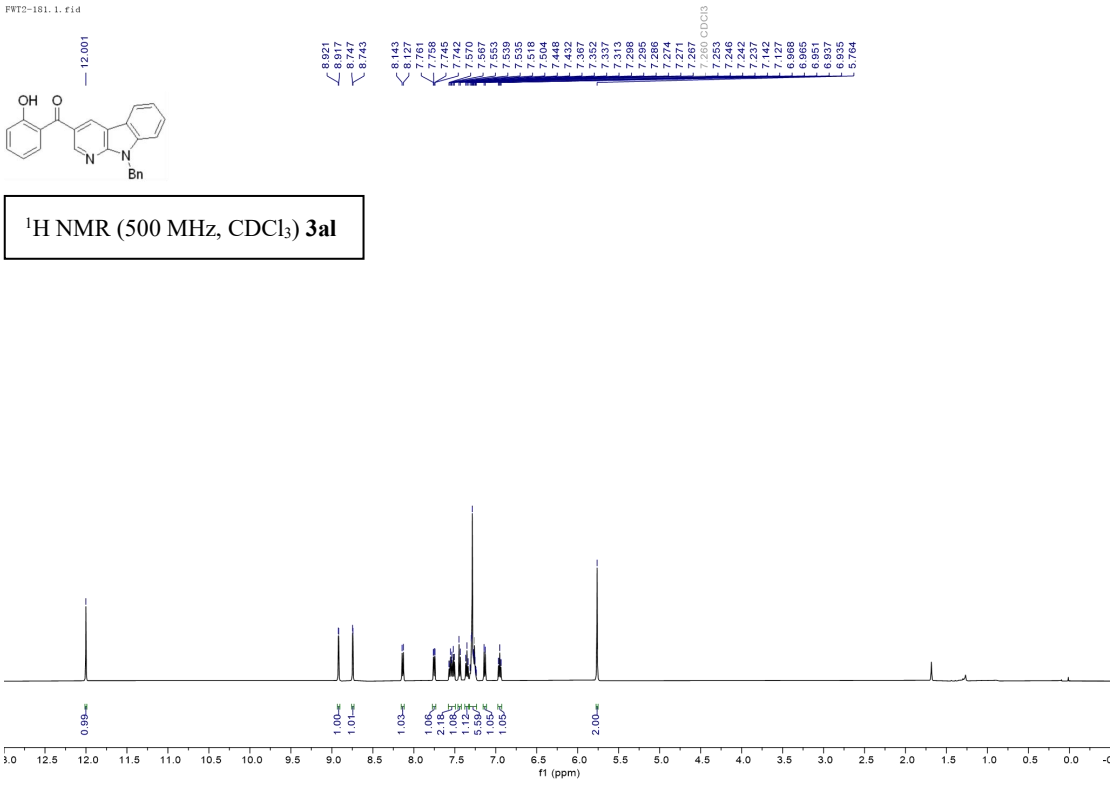
^{13}C NMR (125 MHz, $CDCl_3$) **3aj**



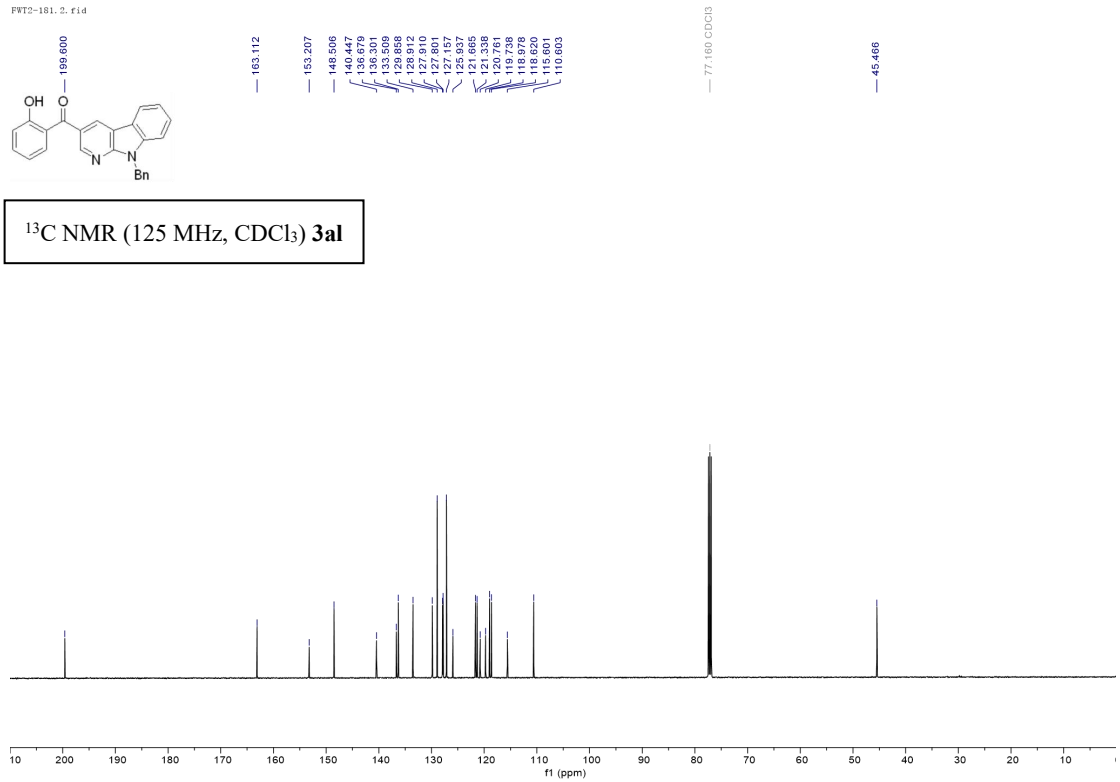
^{1}H NMR (500 MHz, $CDCl_3$) **3ak**



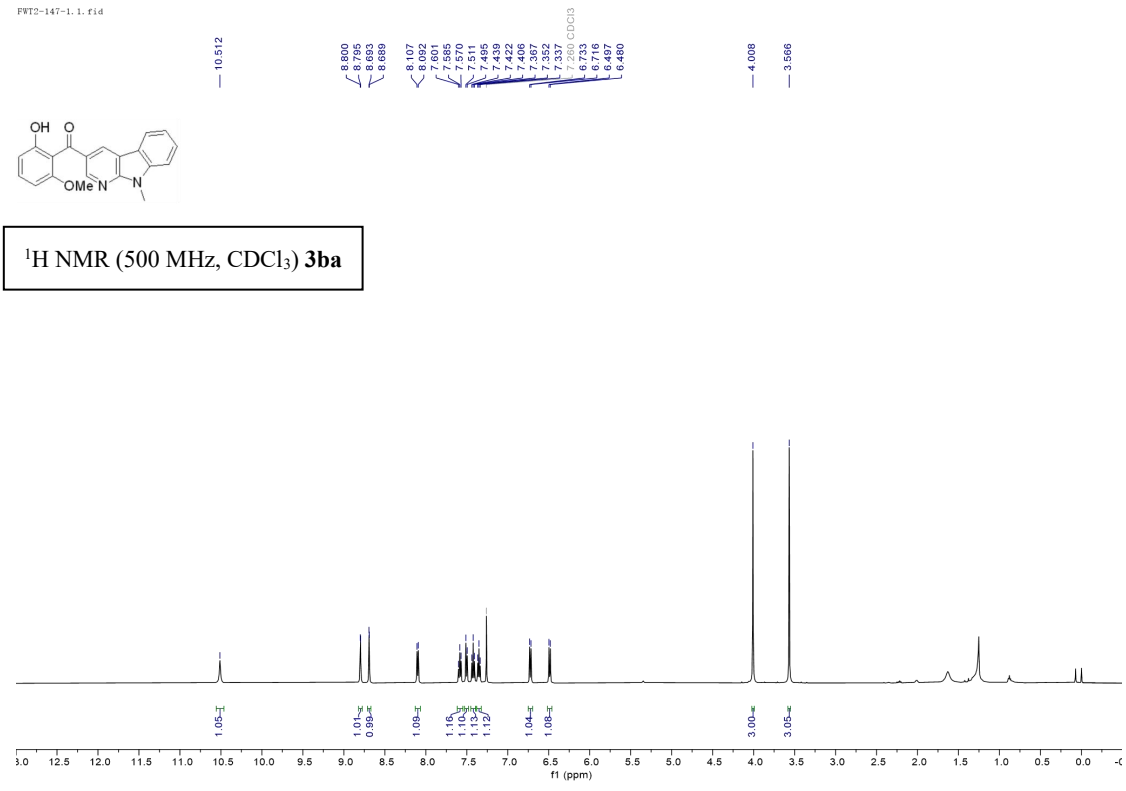
^{13}C NMR (125 MHz, $CDCl_3$) **3ak**



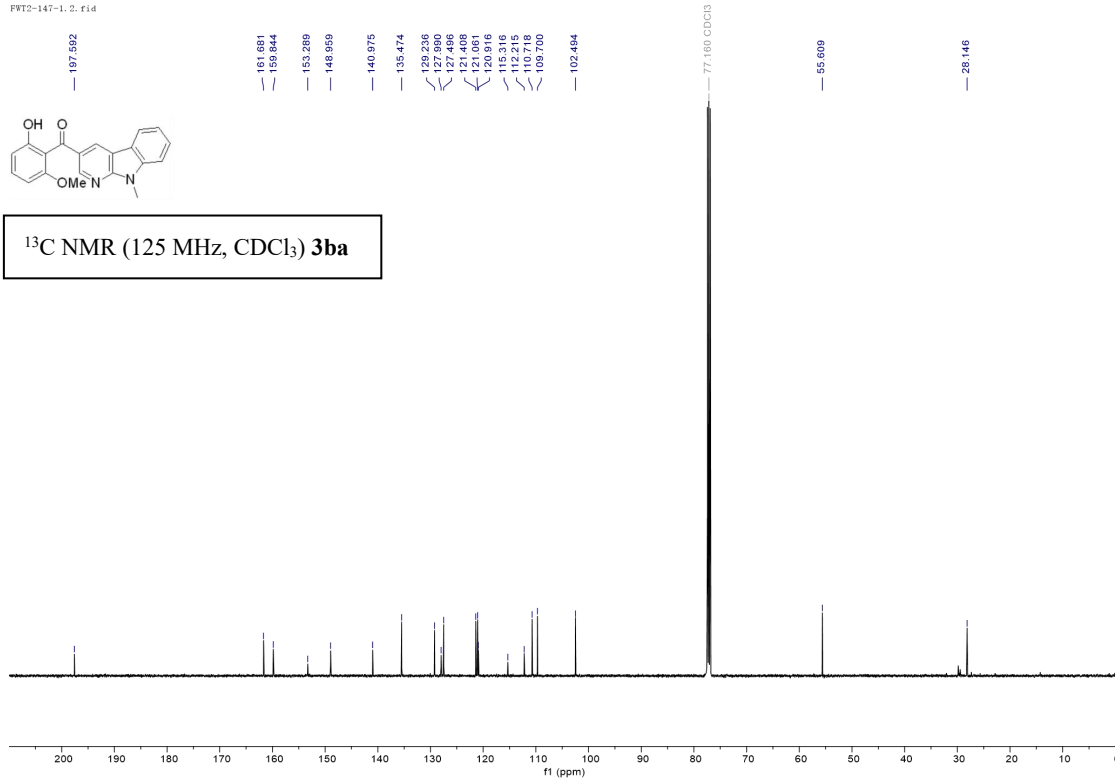
^{1}H NMR (500 MHz, $CDCl_3$) **3al**



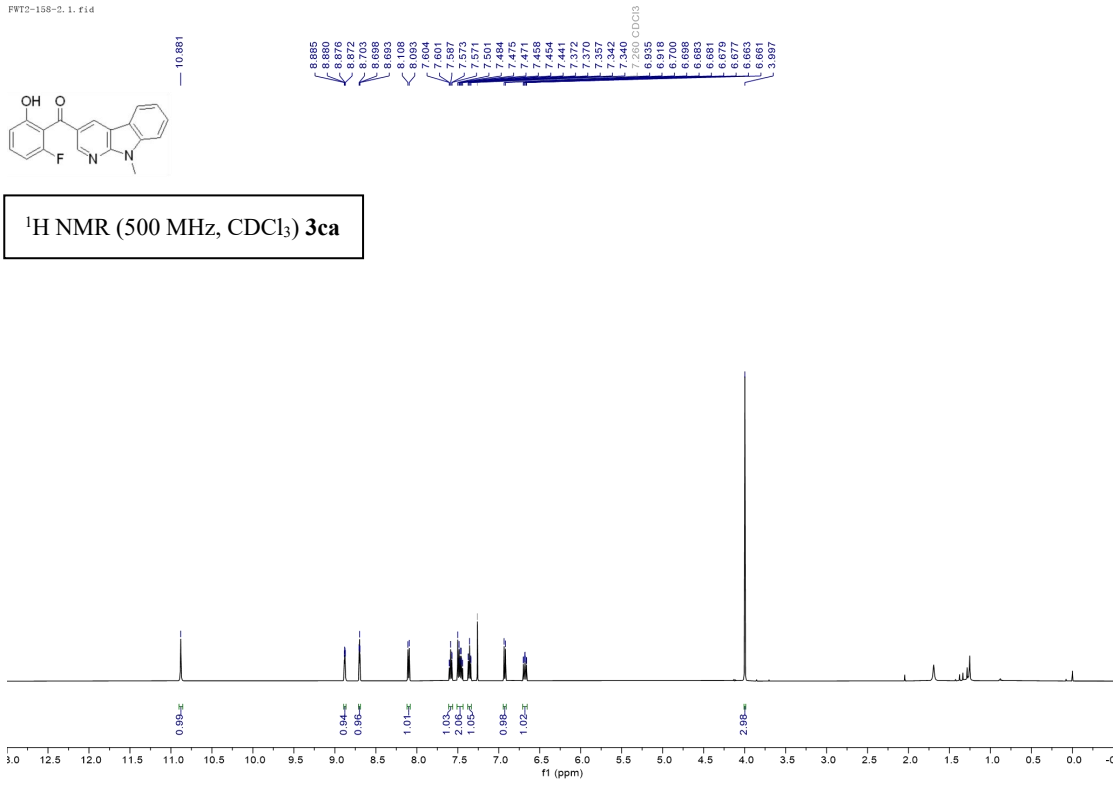
^{13}C NMR (125 MHz, $CDCl_3$) **3al**



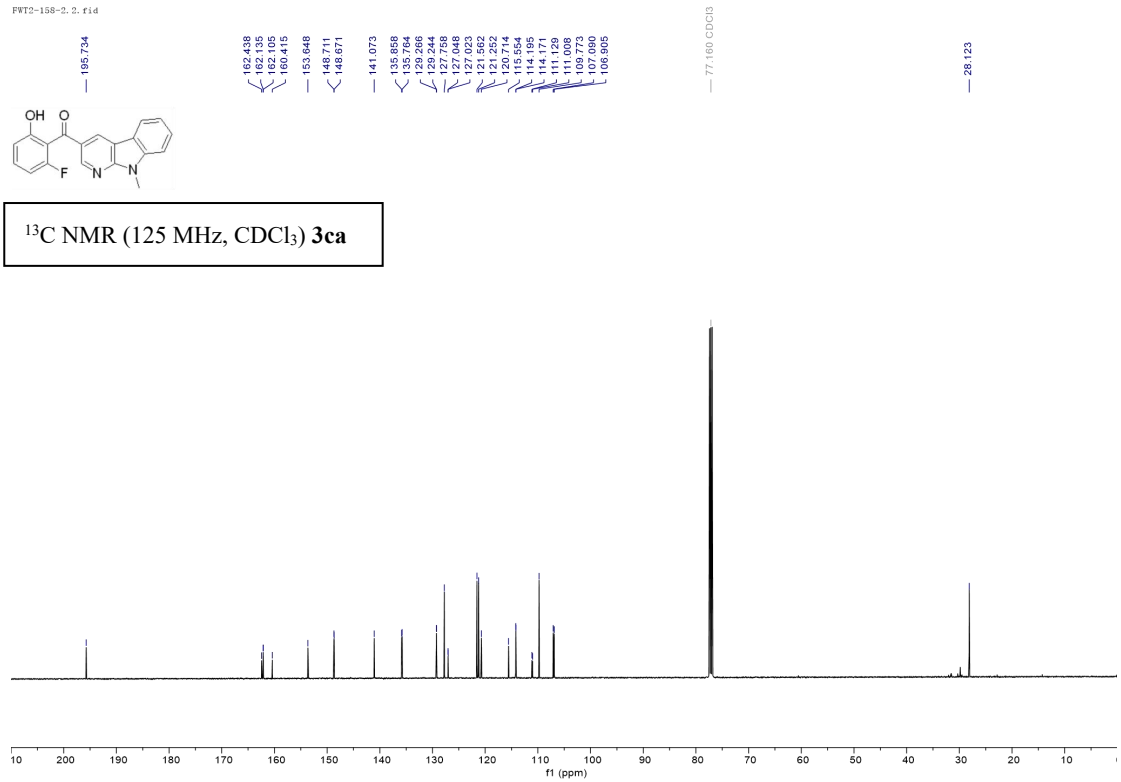
^{1}H NMR (500 MHz, $CDCl_3$) **3ba**



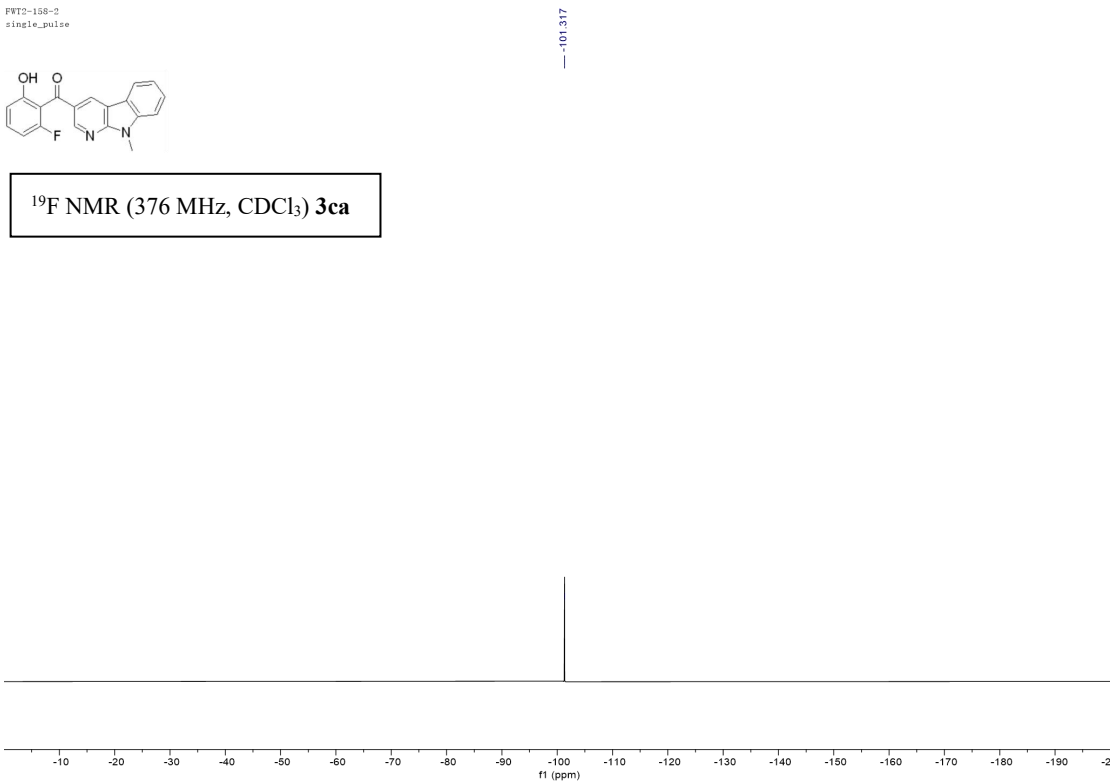
^{13}C NMR (125 MHz, $CDCl_3$) **3ba**



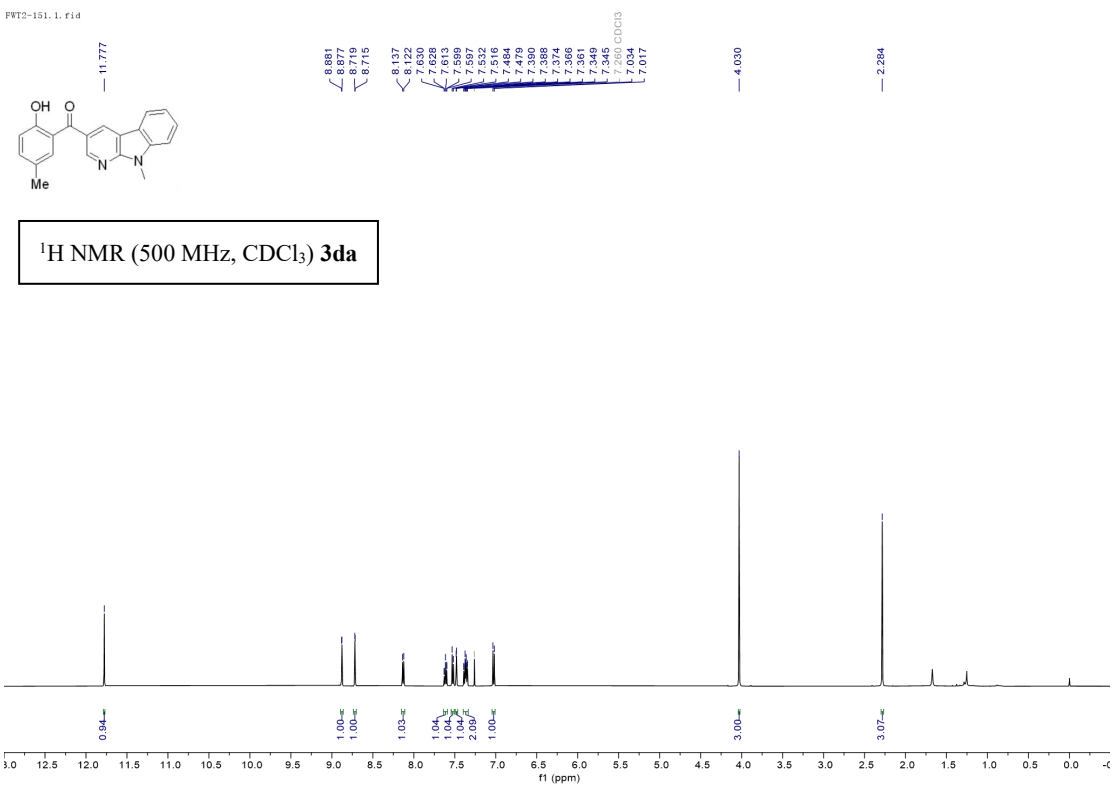
^{1}H NMR (500 MHz, $CDCl_3$) **3ca**



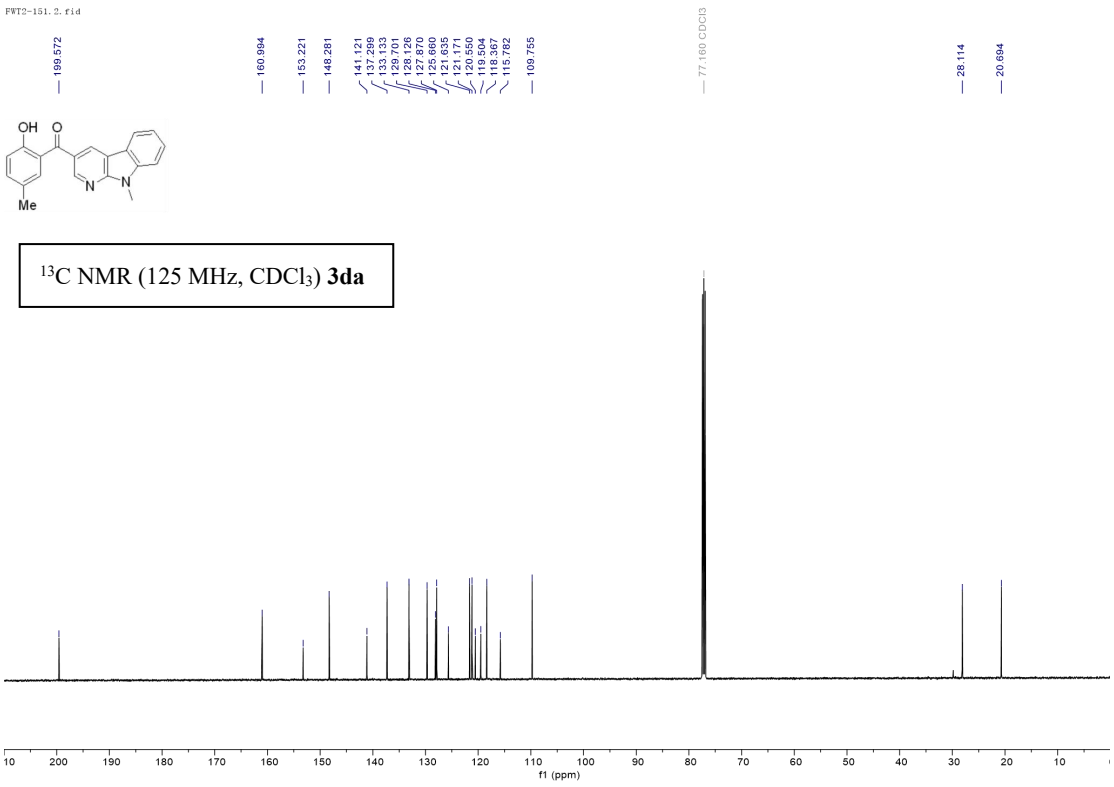
^{13}C NMR (125 MHz, $CDCl_3$) **3ca**



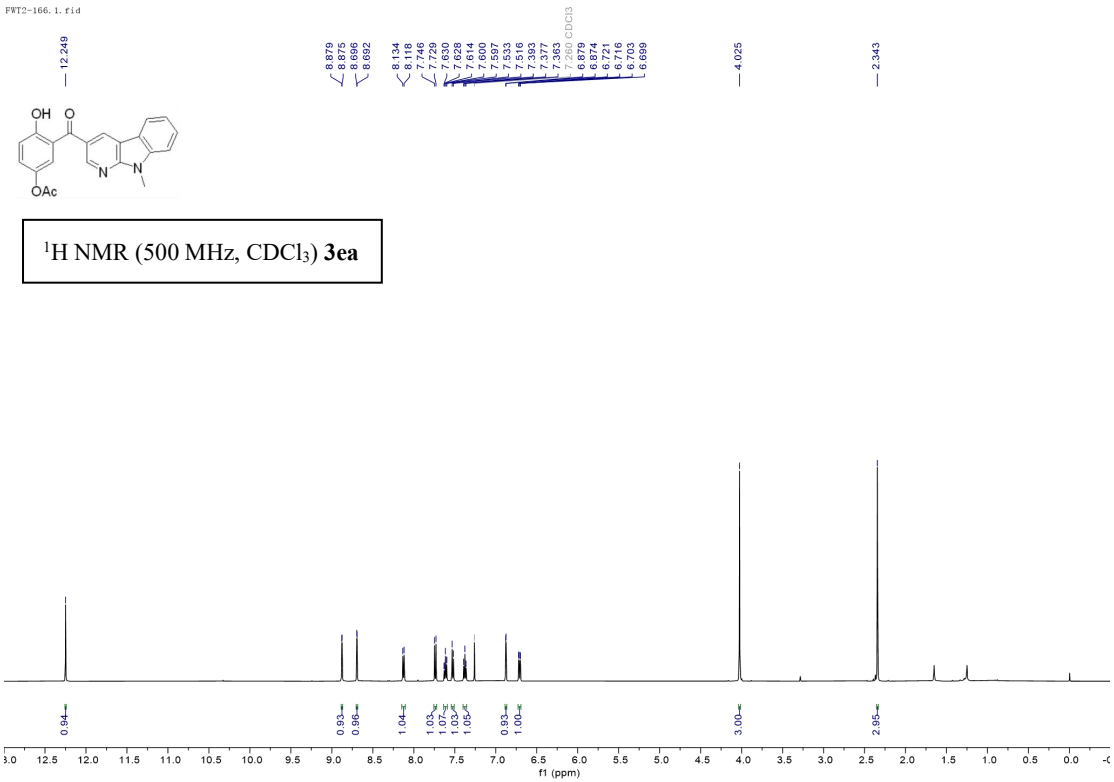
^{19}F NMR (376 MHz, $CDCl_3$) **3ca**



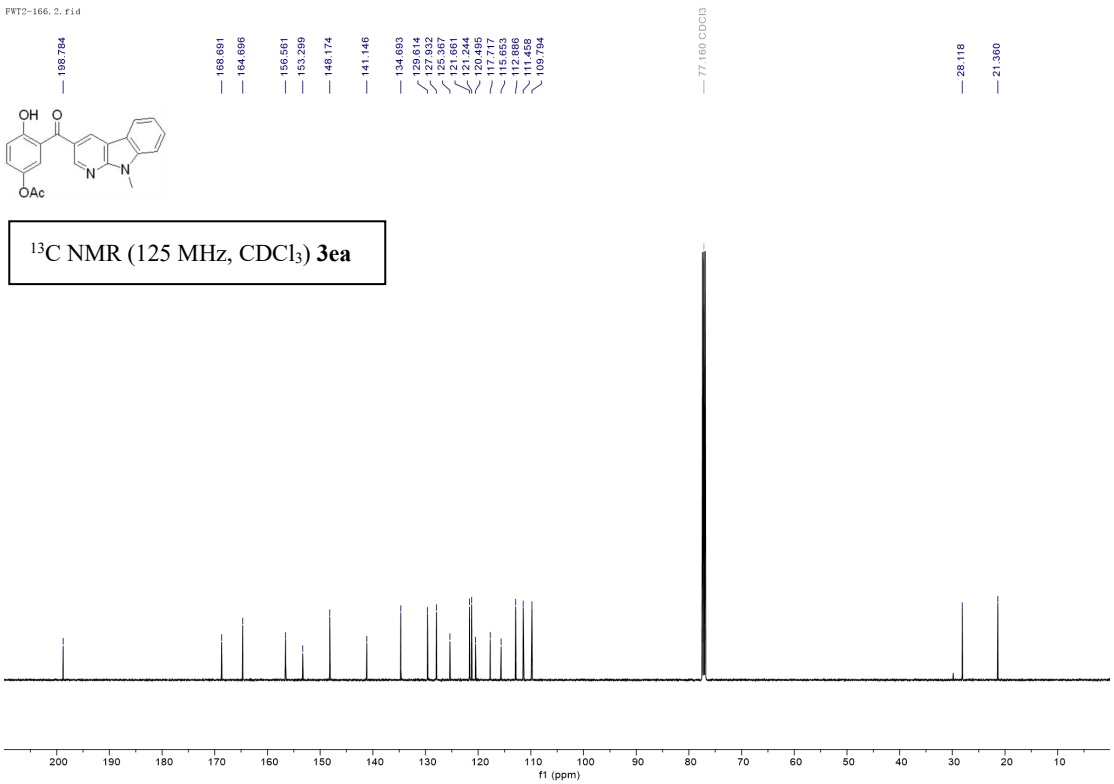
[1]H NMR (500 MHz, $CDCl_3$) **3da**



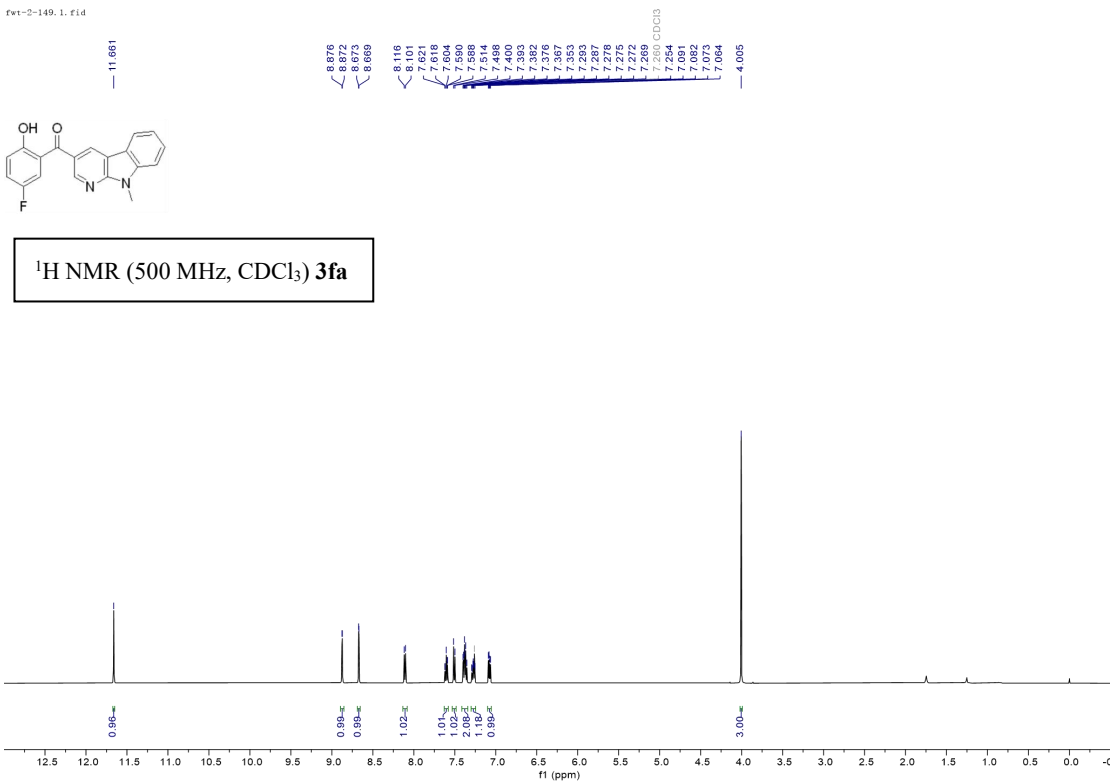
[13]C NMR (125 MHz, $CDCl_3$) **3da**



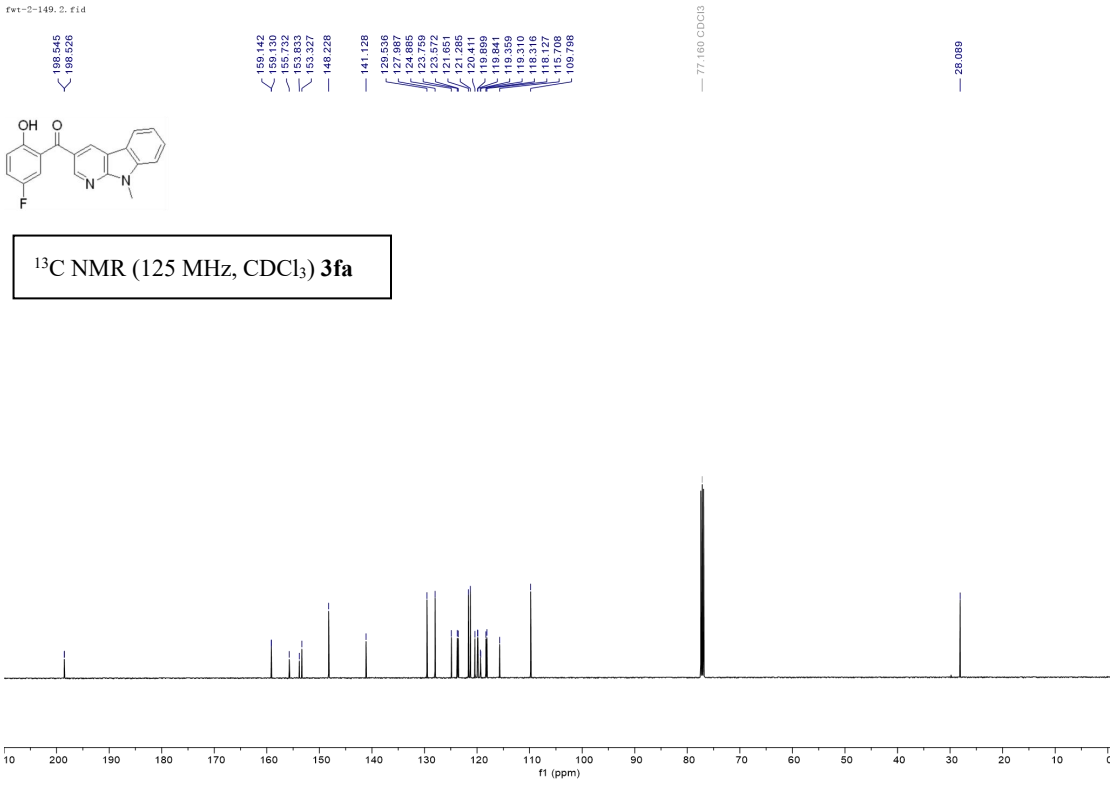
^{1}H NMR (500 MHz, $CDCl_3$) **3ea**



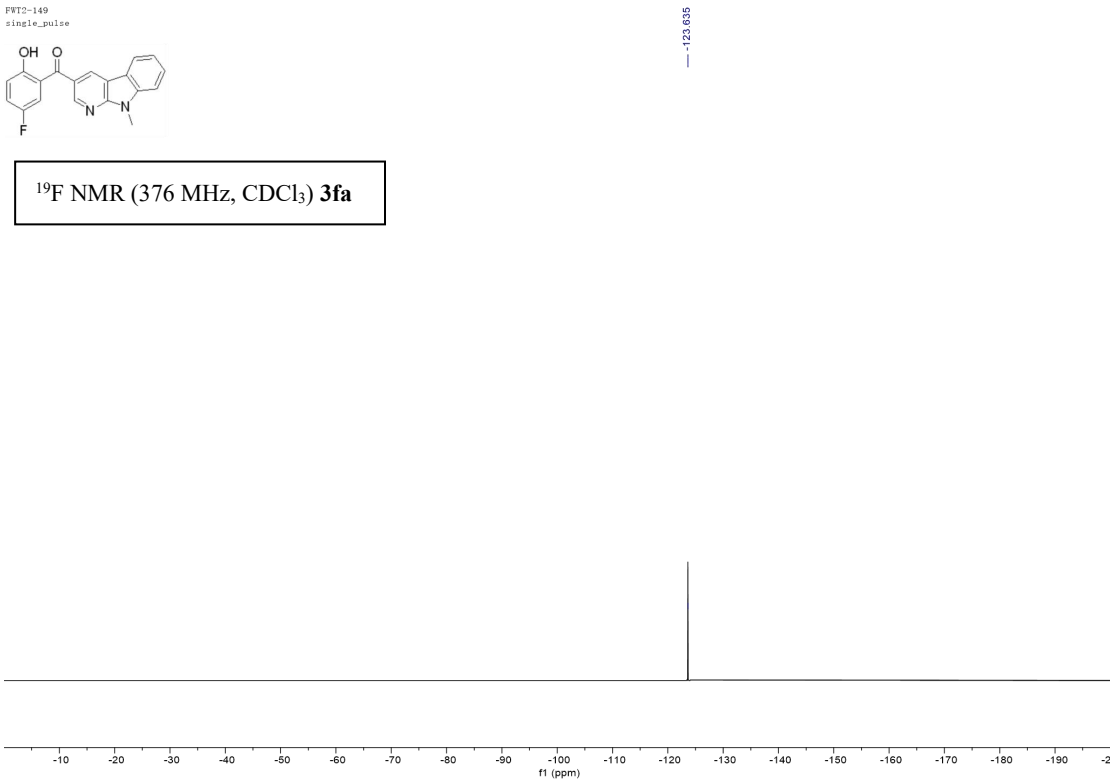
^{13}C NMR (125 MHz, $CDCl_3$) **3ea**



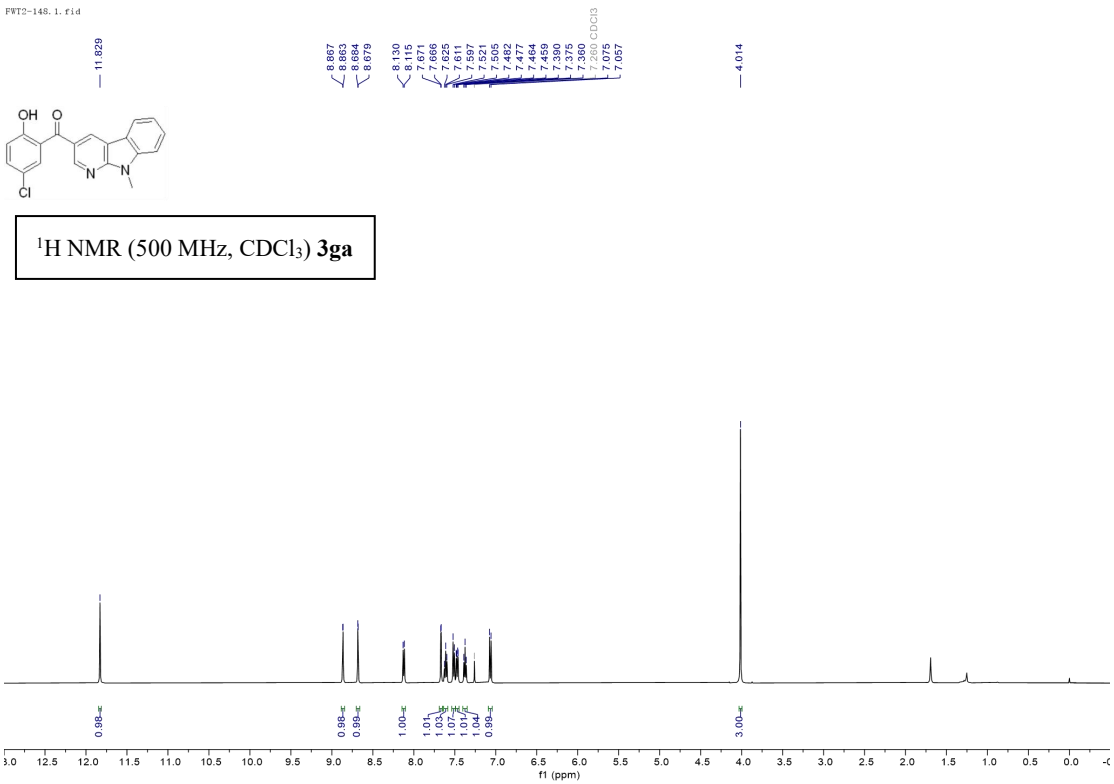
^{1}H NMR (500 MHz, $CDCl_3$) **3fa**



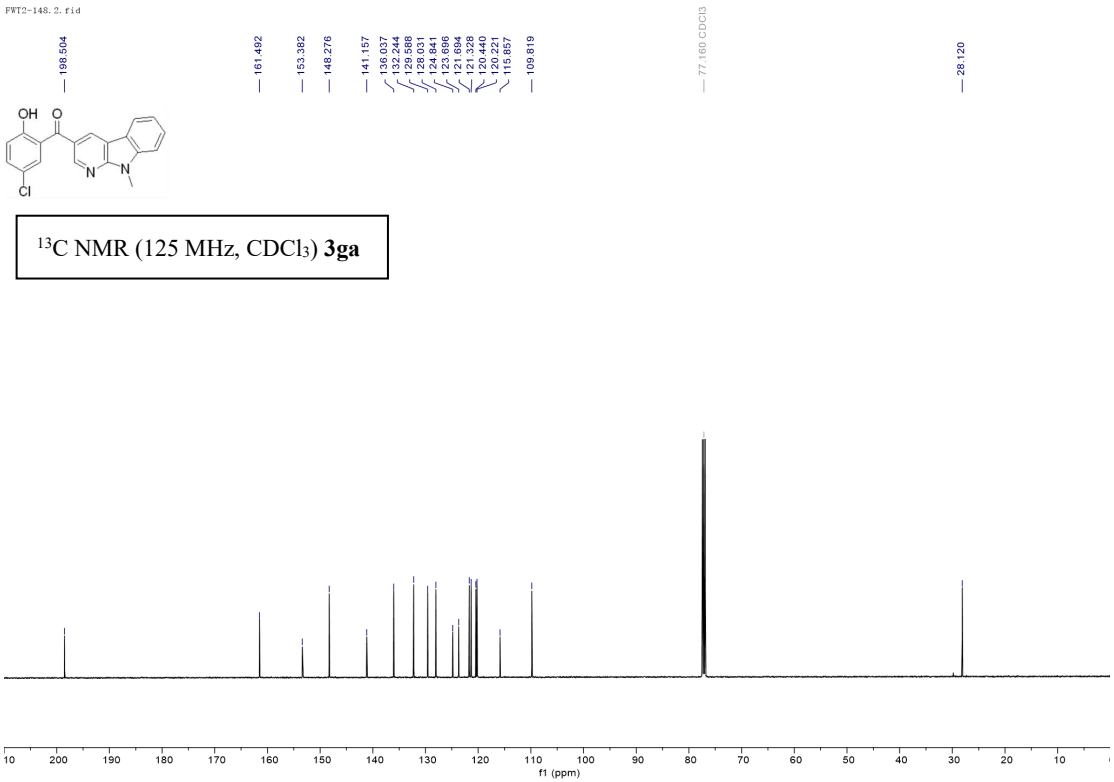
^{13}C NMR (125 MHz, $CDCl_3$) **3fa**



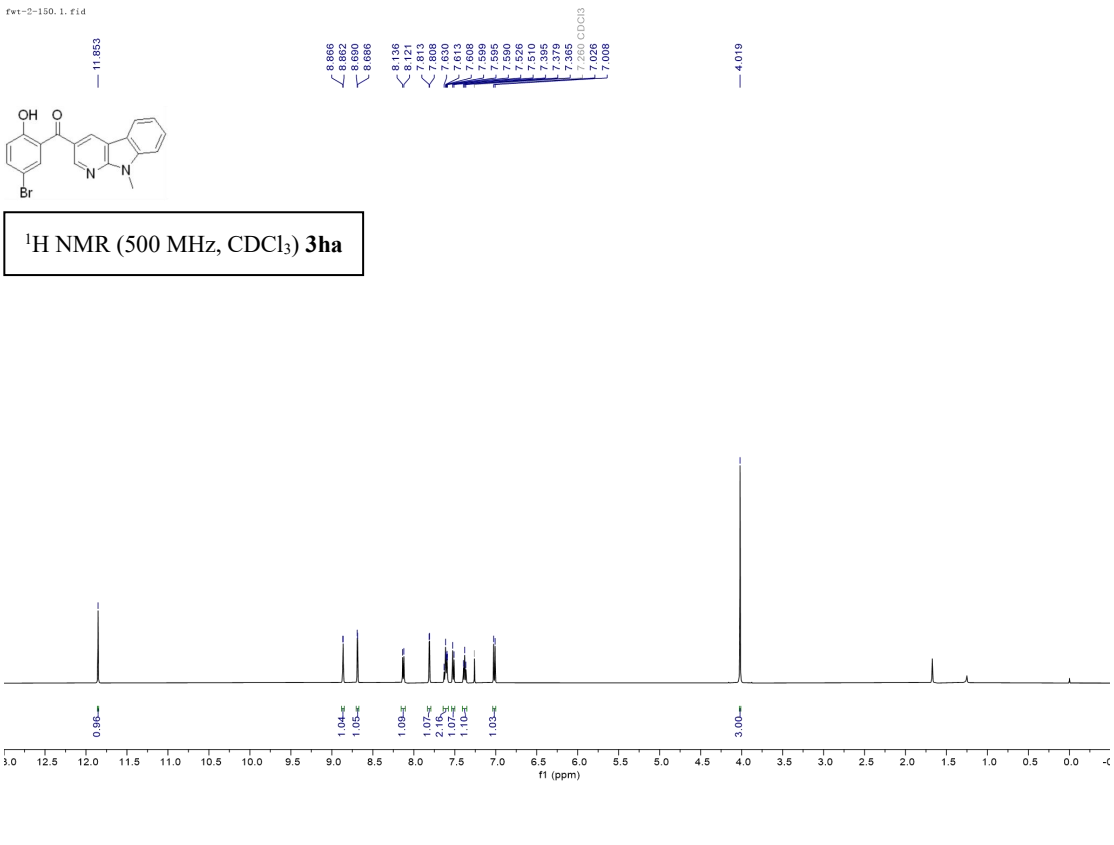
^{19}F NMR (376 MHz, $CDCl_3$) **3fa**



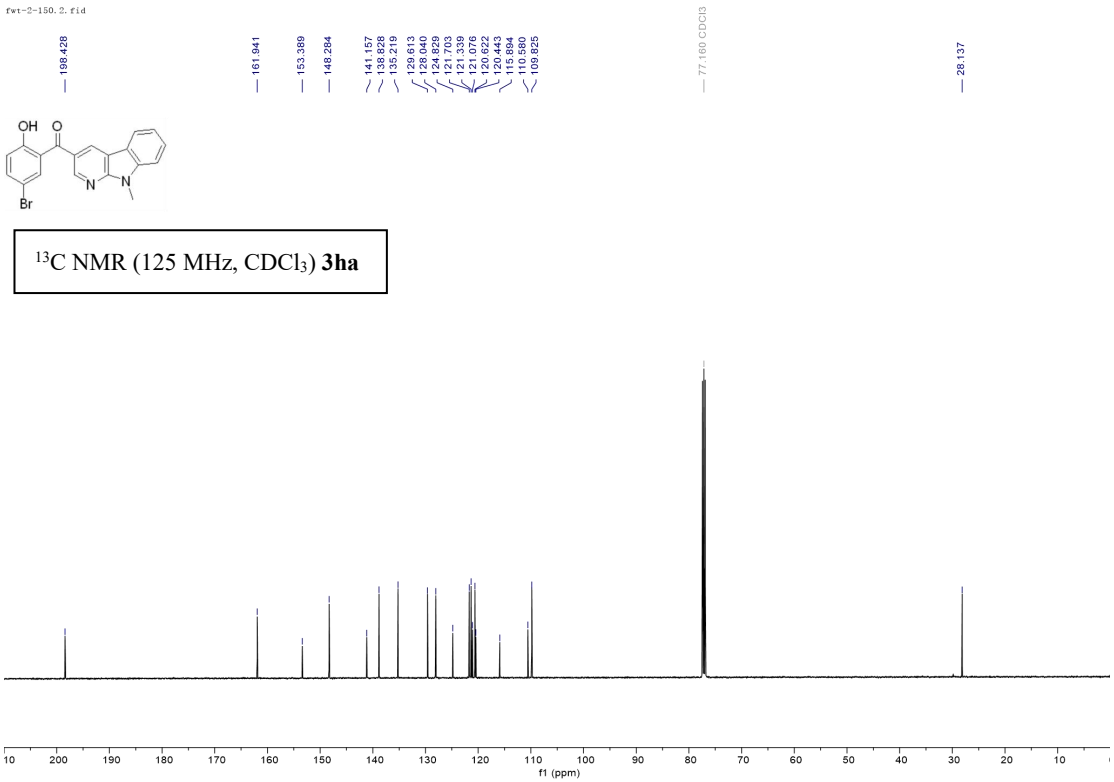
^{1}H NMR (500 MHz, $CDCl_3$) **3ga**



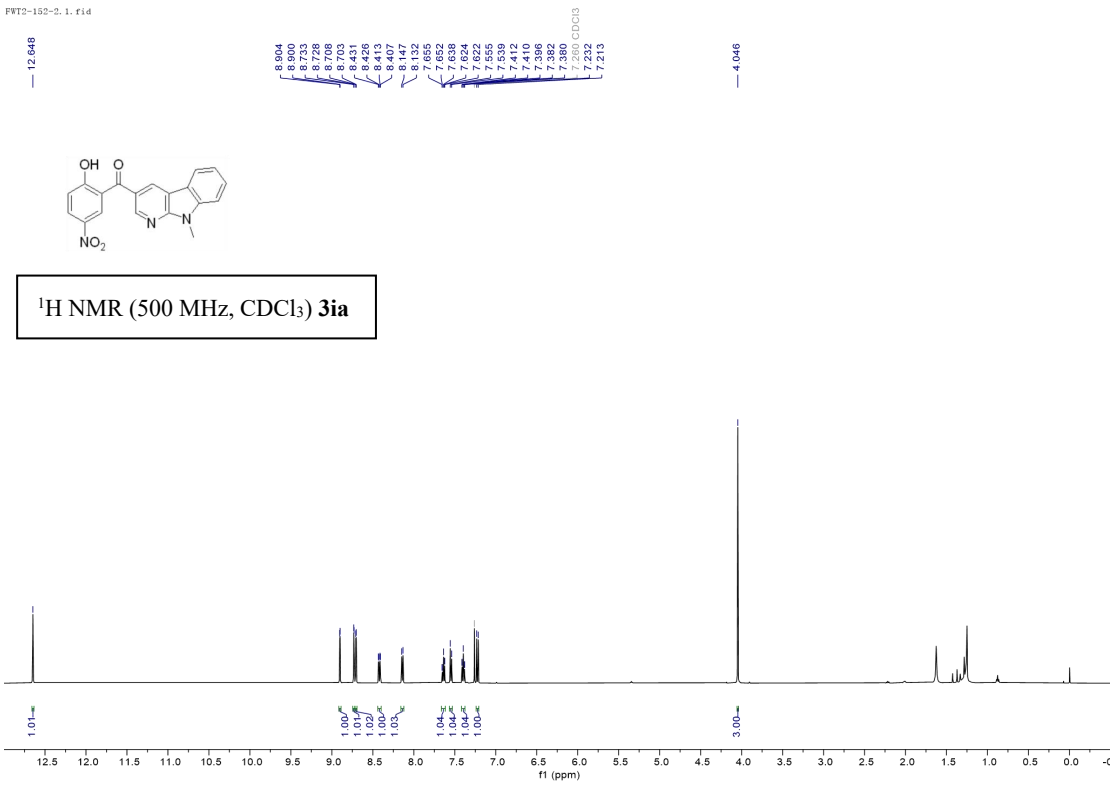
^{13}C NMR (125 MHz, $CDCl_3$) **3ga**



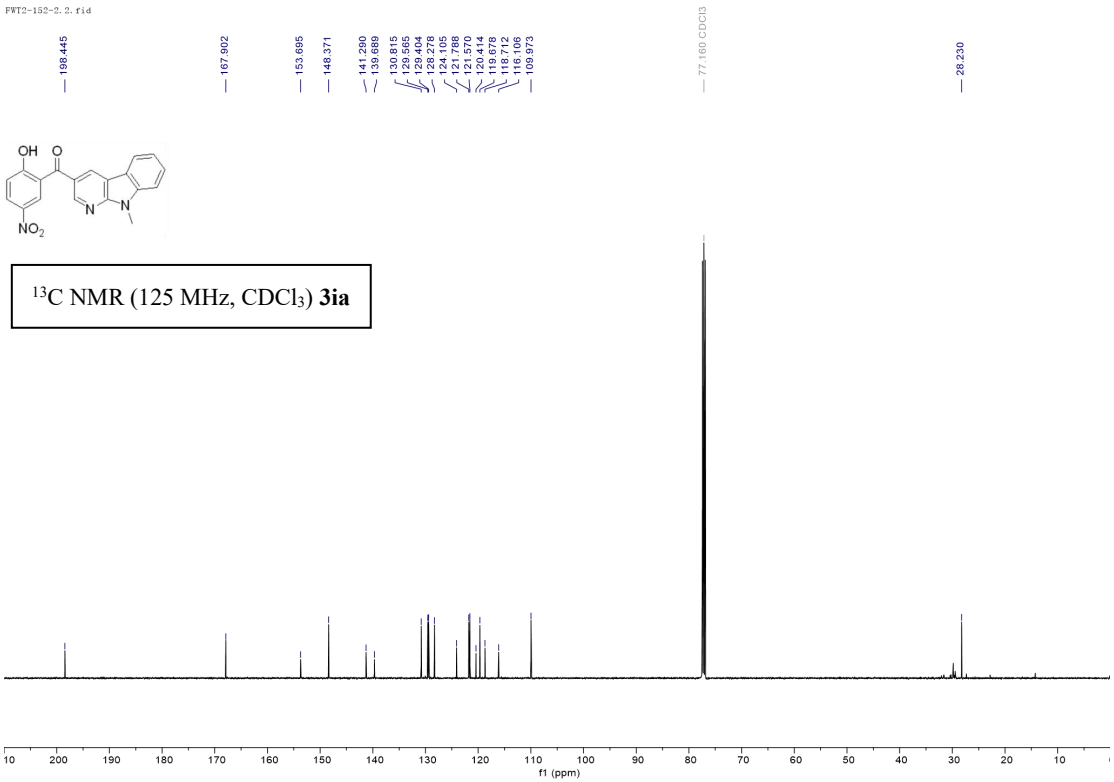
^{1}H NMR (500 MHz, $CDCl_3$) **3ha**



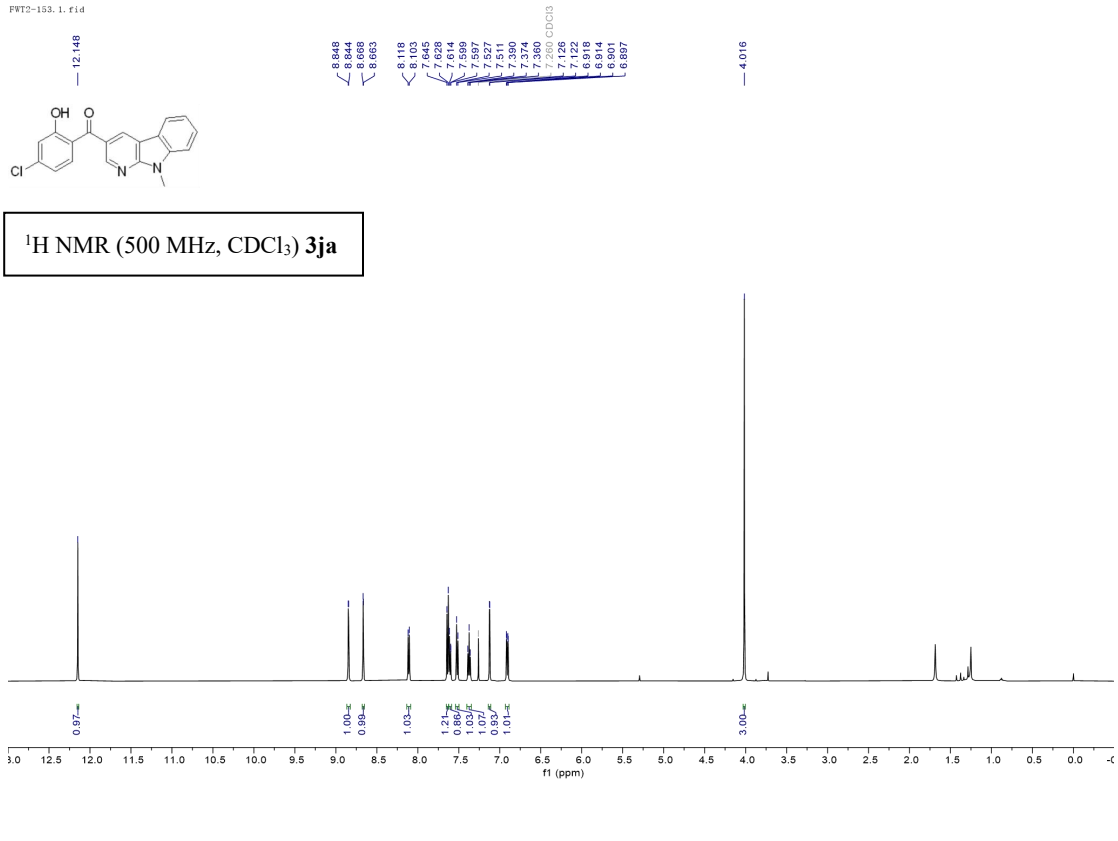
^{13}C NMR (125 MHz, $CDCl_3$) **3ha**



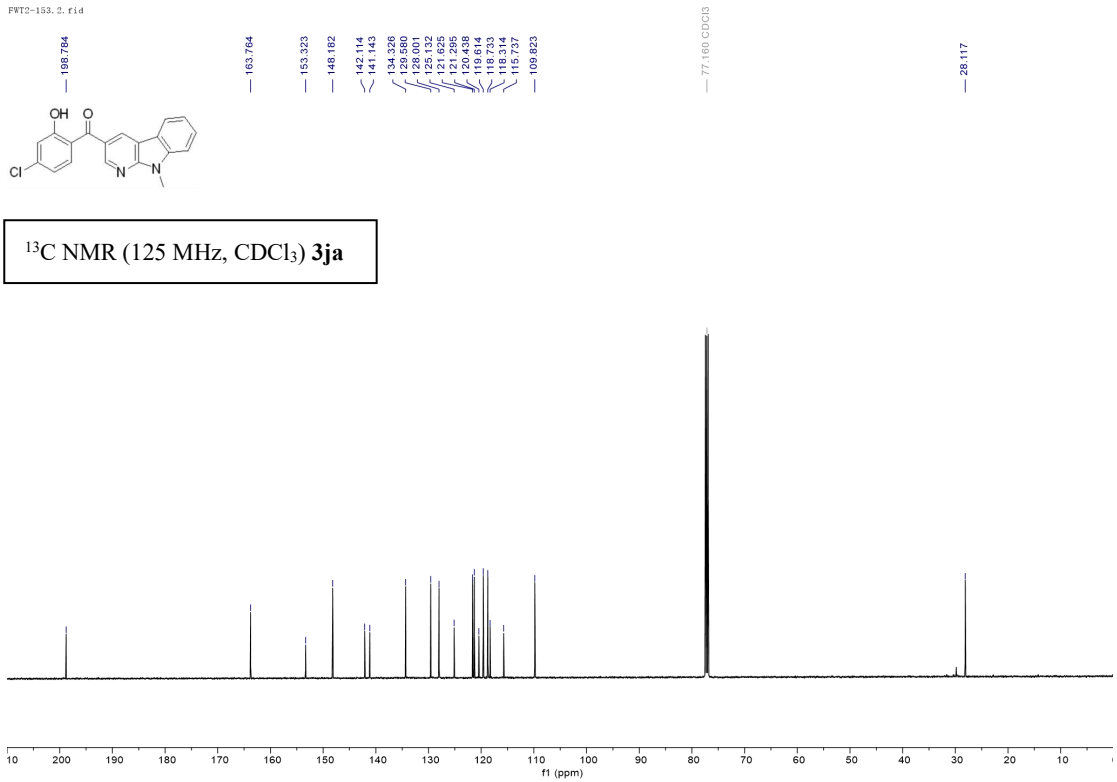
^{1}H NMR (500 MHz, $CDCl_3$) **3ia**



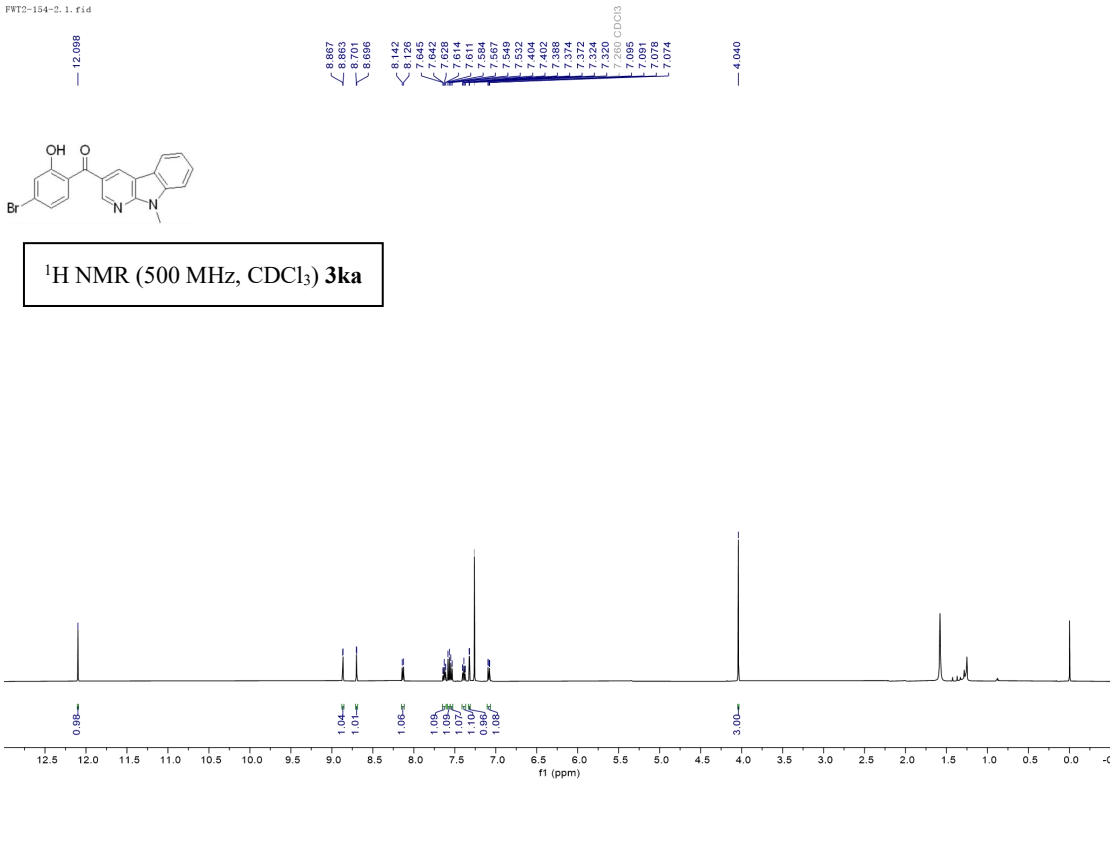
^{13}C NMR (125 MHz, $CDCl_3$) **3ia**



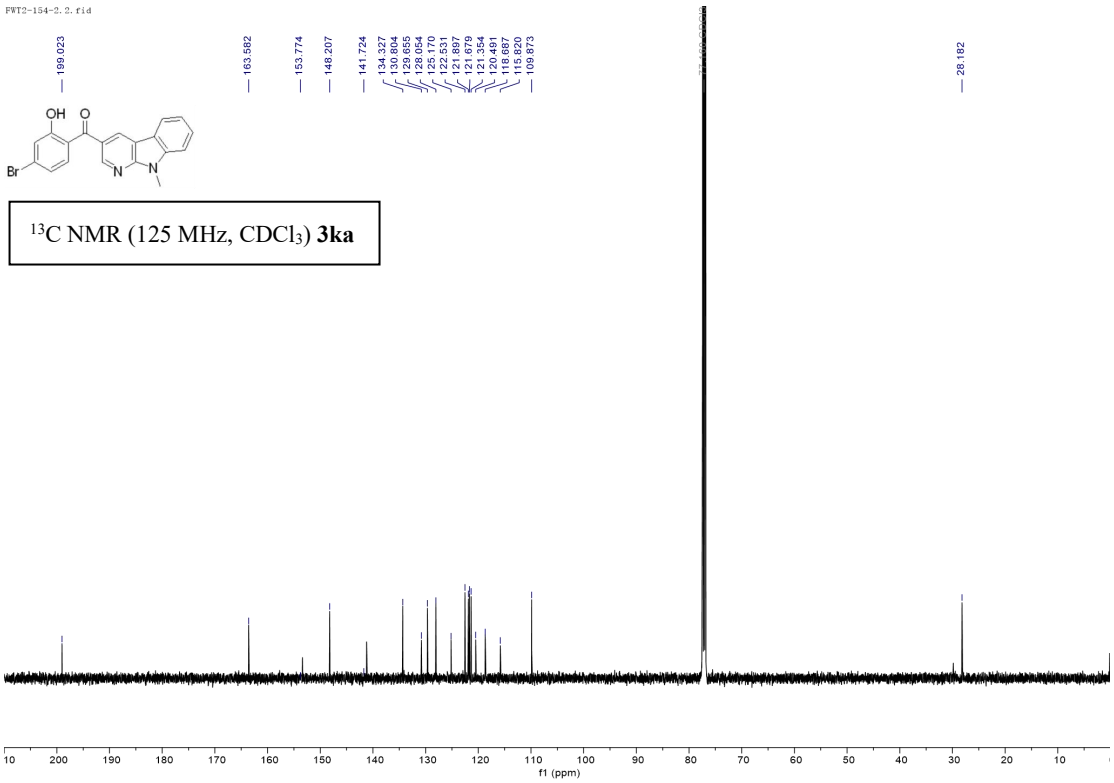
^{1}H NMR (500 MHz, $CDCl_3$) **3ja**



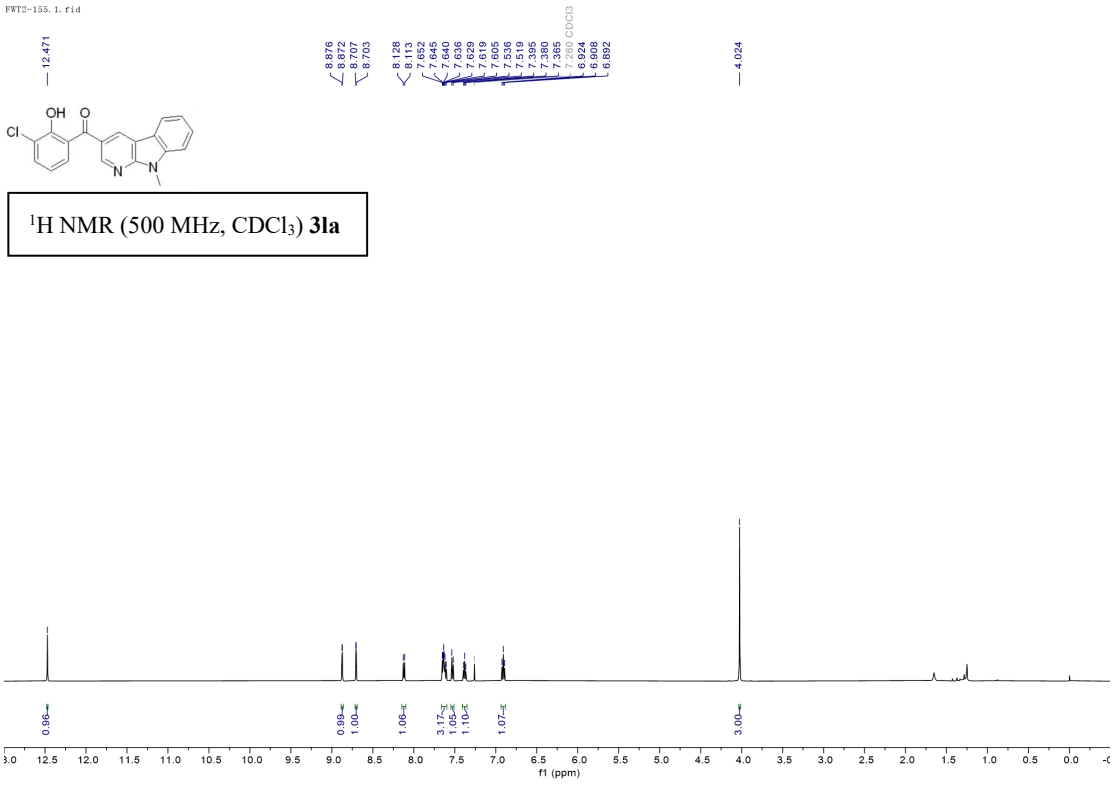
^{13}C NMR (125 MHz, $CDCl_3$) **3ja**



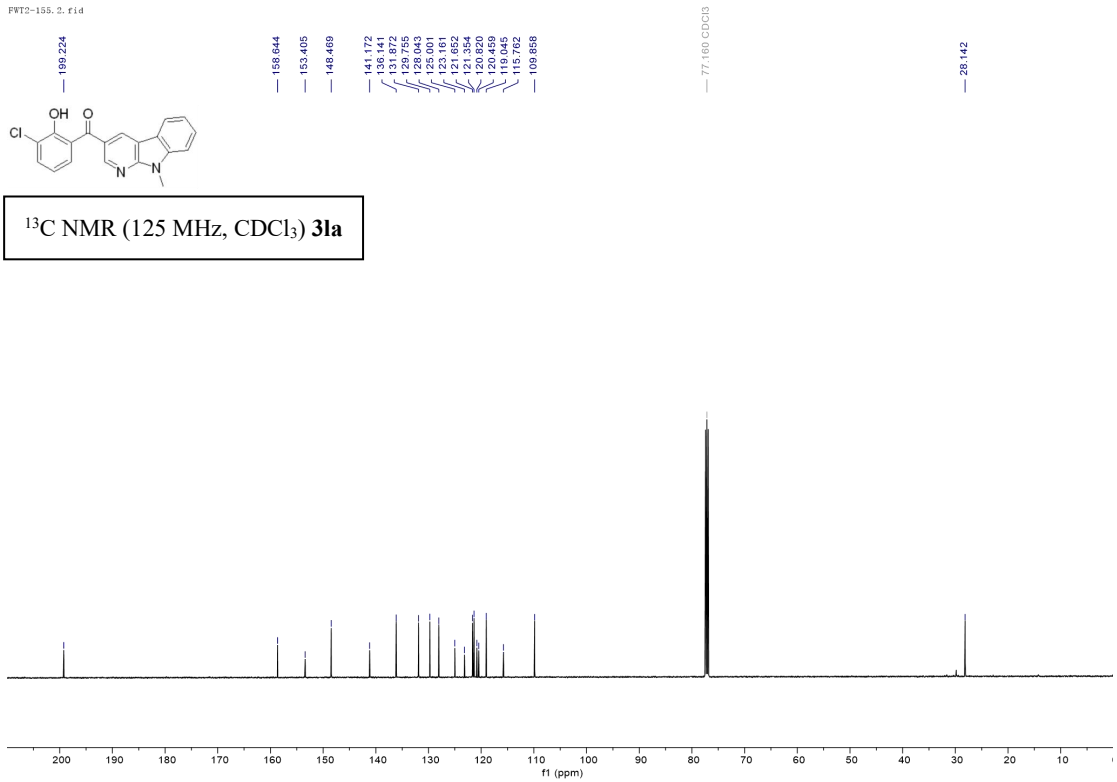
^{1}H NMR (500 MHz, $CDCl_3$) **3ka**



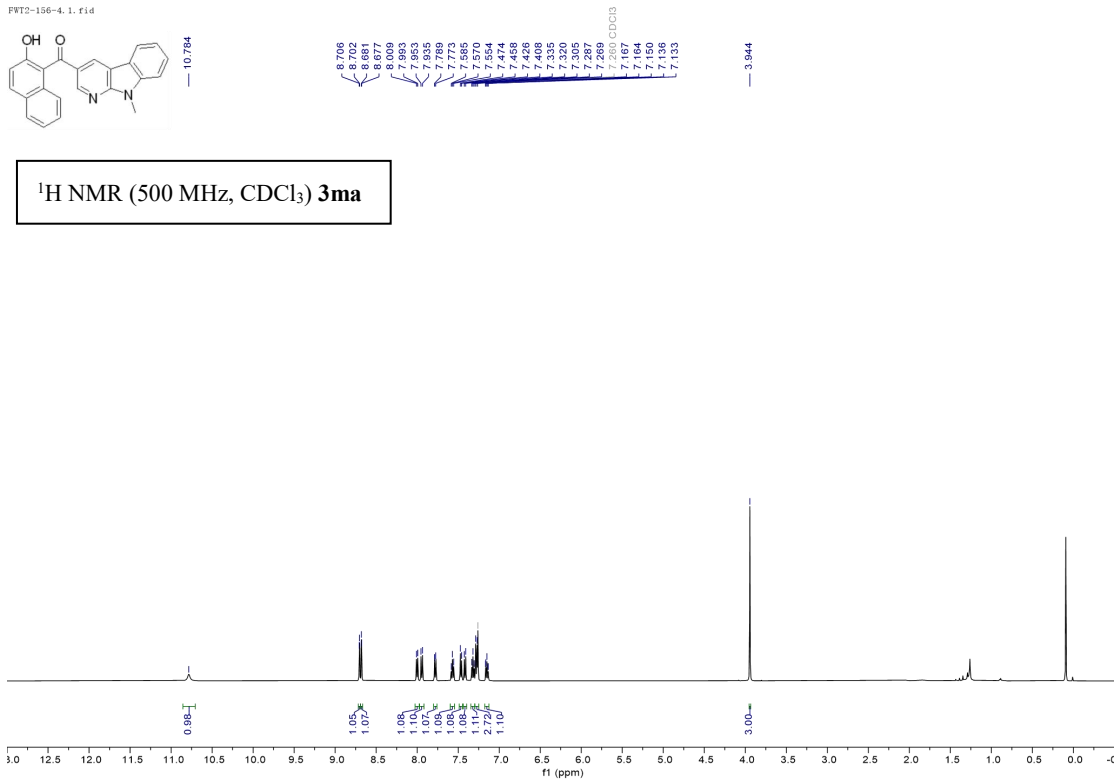
^{13}C NMR (125 MHz, $CDCl_3$) **3ka**



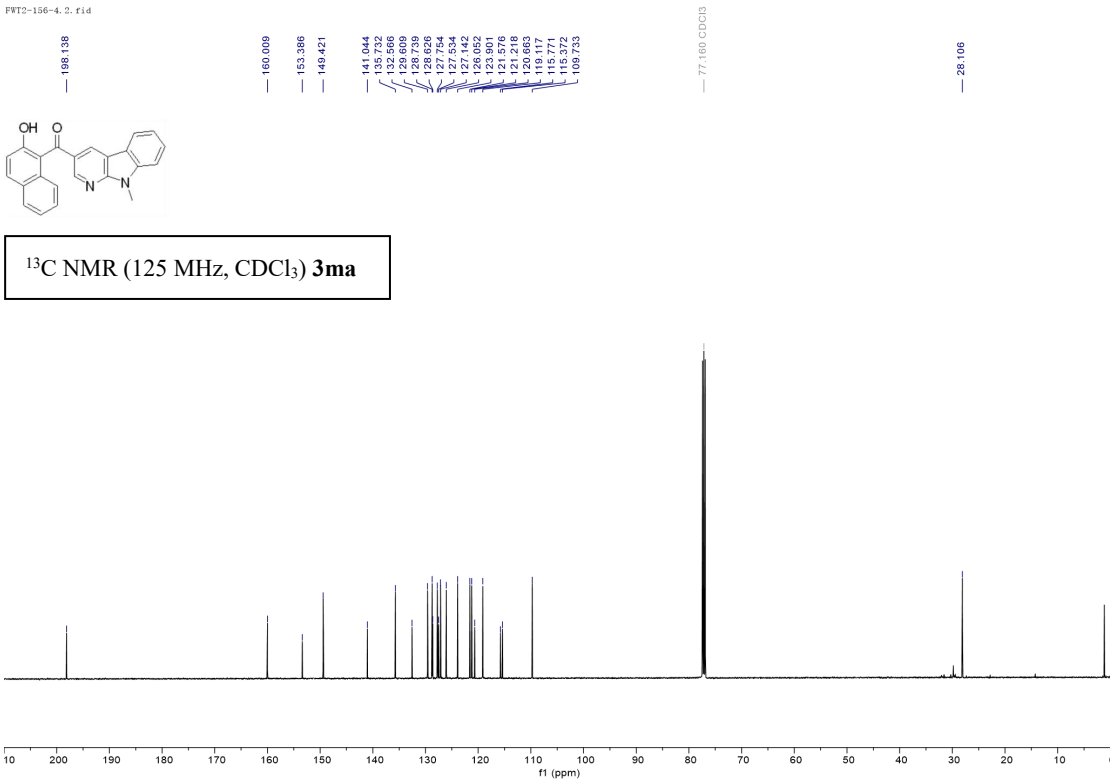
^{1}H NMR (500 MHz, $CDCl_3$) **3la**



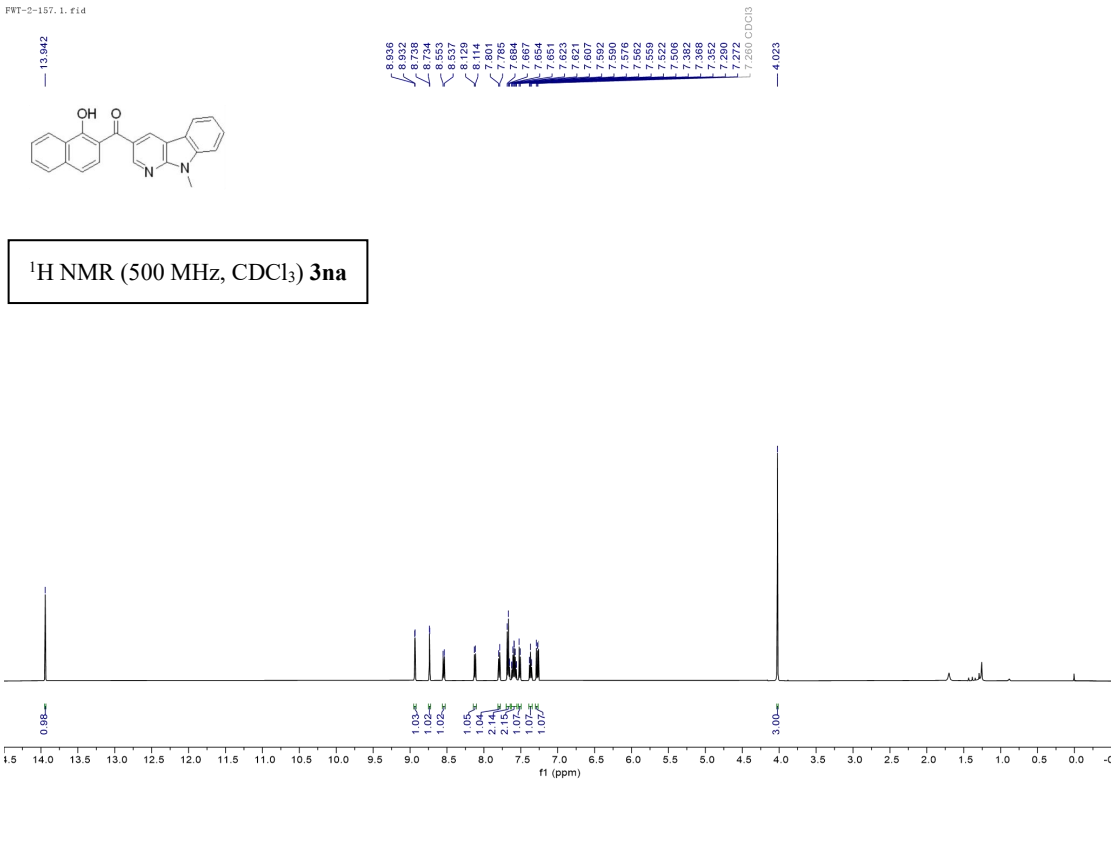
^{13}C NMR (125 MHz, $CDCl_3$) **3la**



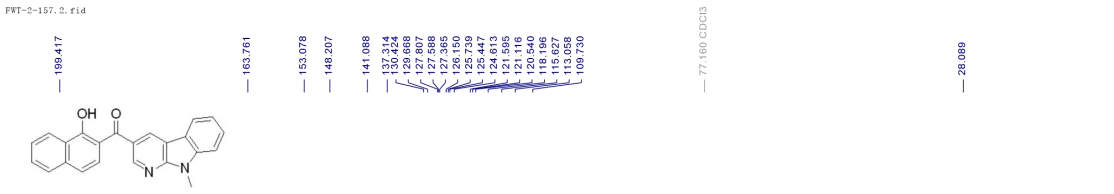
^{1}H NMR (500 MHz, $CDCl_3$) **3ma**



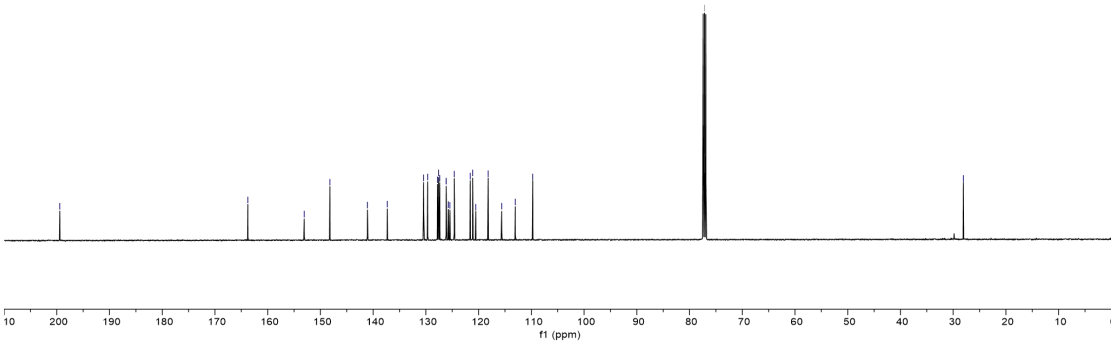
^{13}C NMR (125 MHz, $CDCl_3$) **3ma**

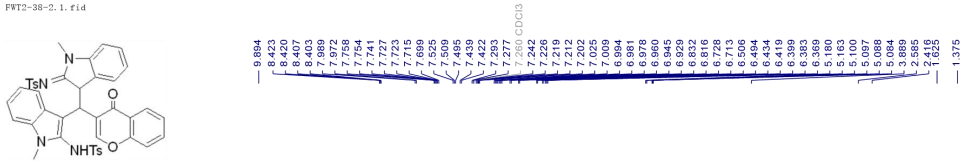


^{1}H NMR (500 MHz, $CDCl_3$) **3na**

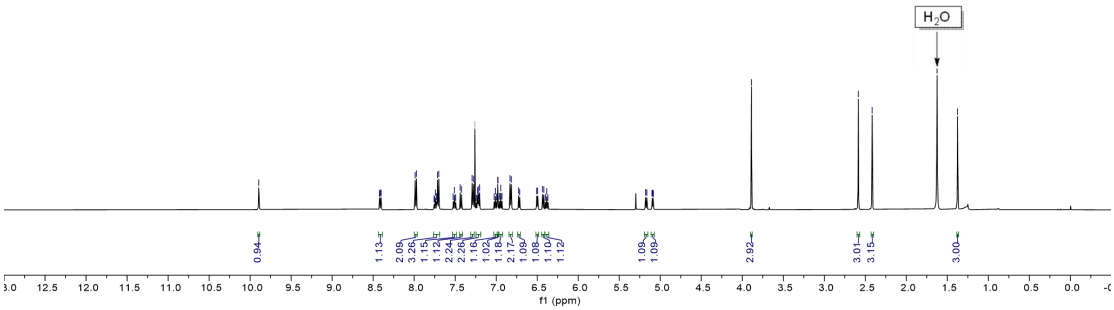


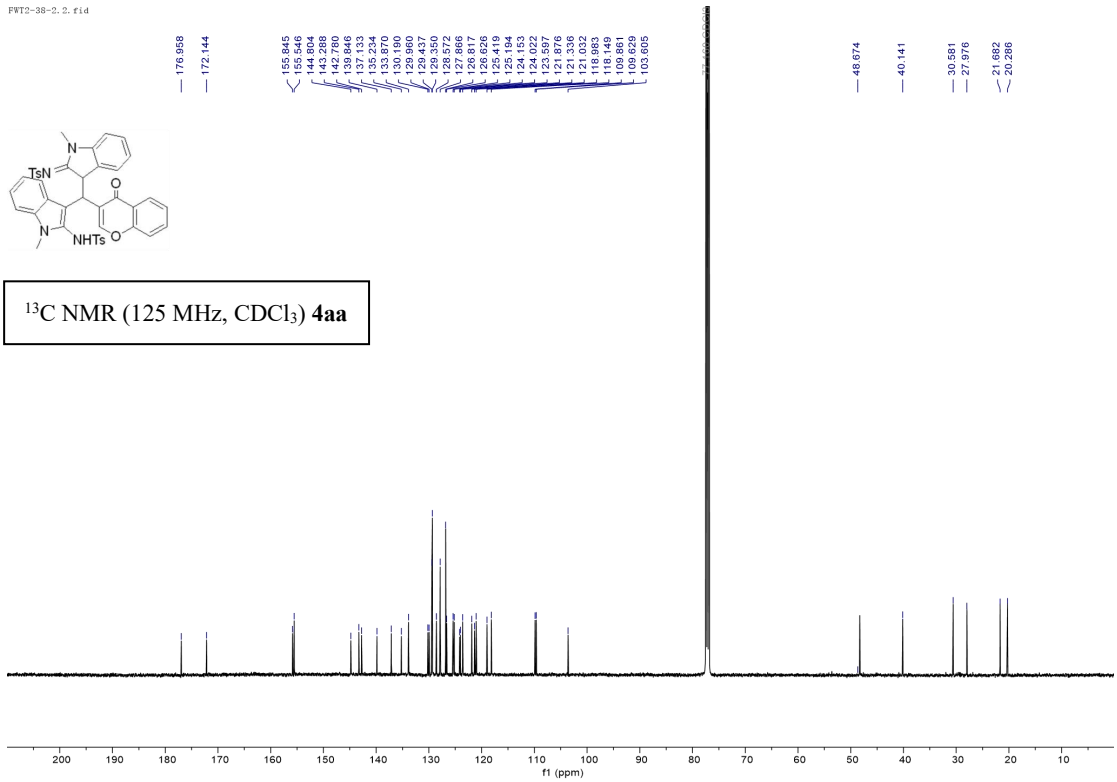
^{13}C NMR (125 MHz, $CDCl_3$) **3na**



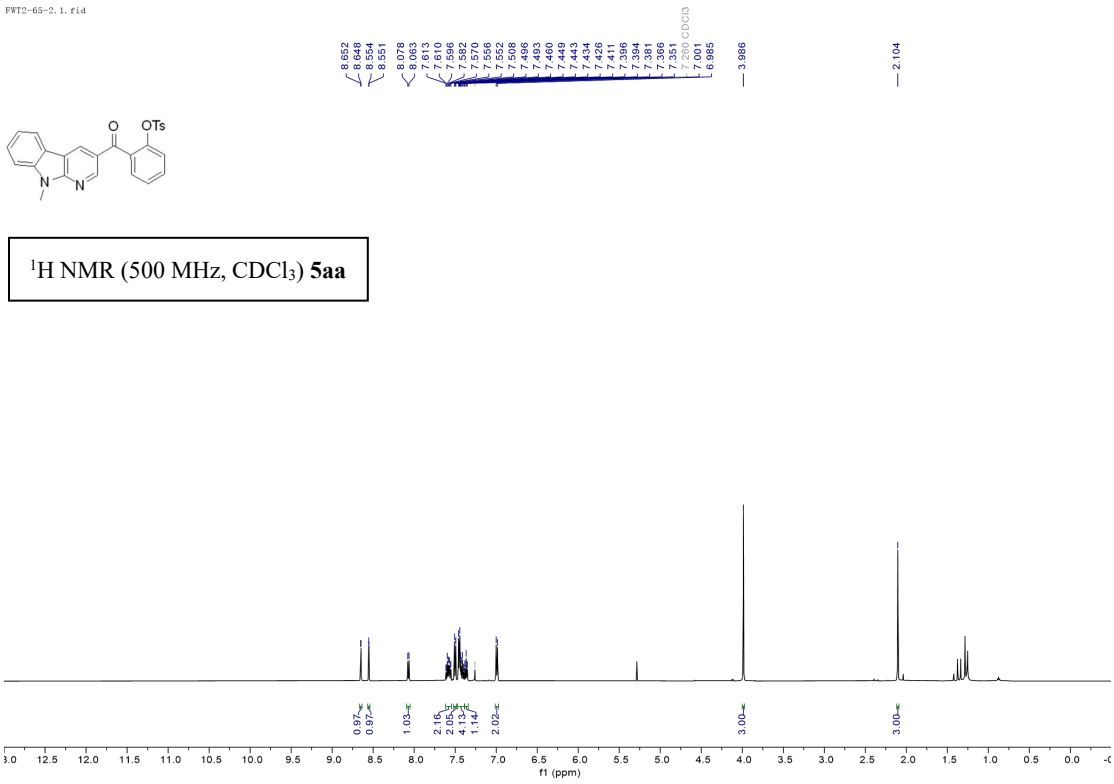


^{1}H NMR (500 MHz, $CDCl_3$) **4aa**

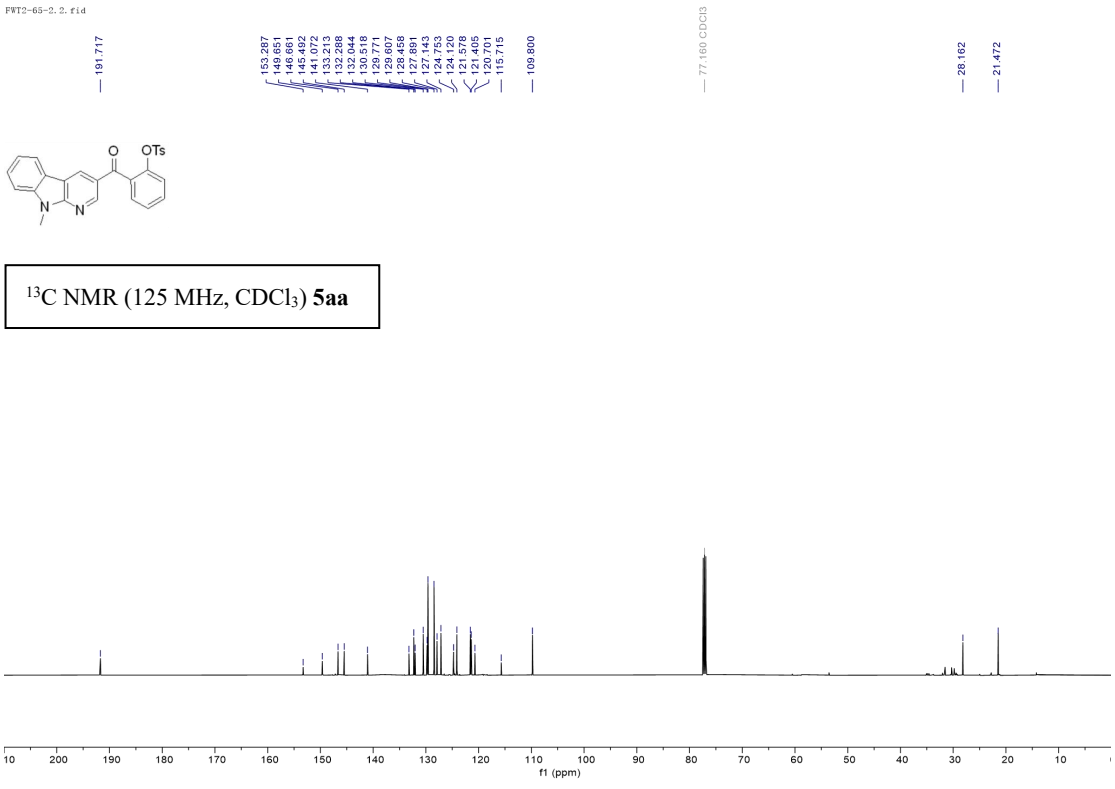




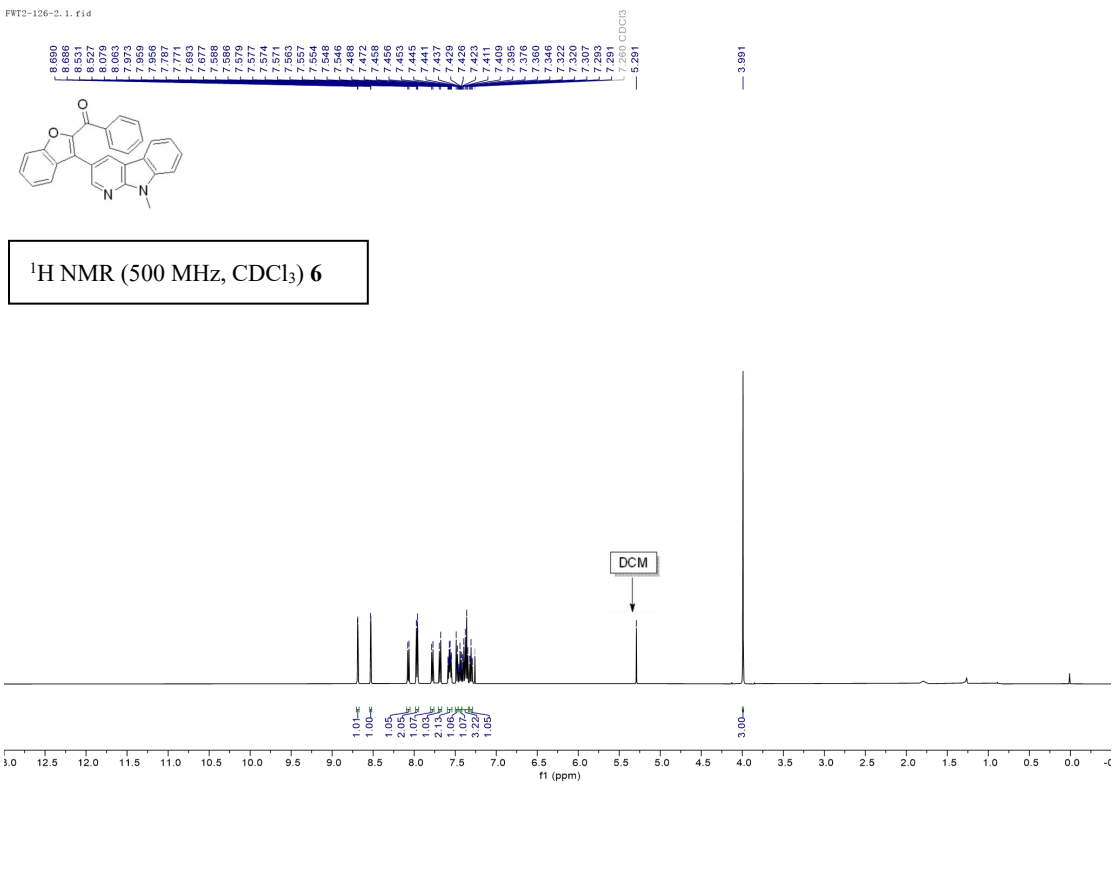
^{13}C NMR (125 MHz, $CDCl_3$) **4aa**



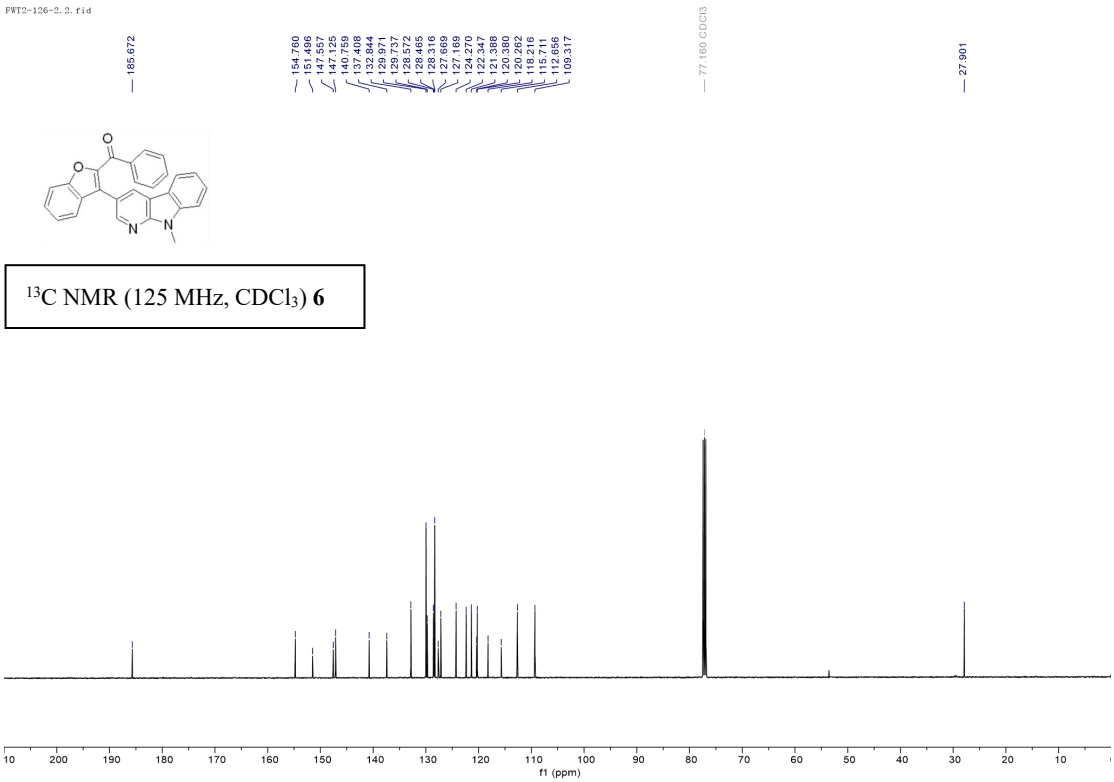
^{1}H NMR (500 MHz, $CDCl_3$) **5aa**



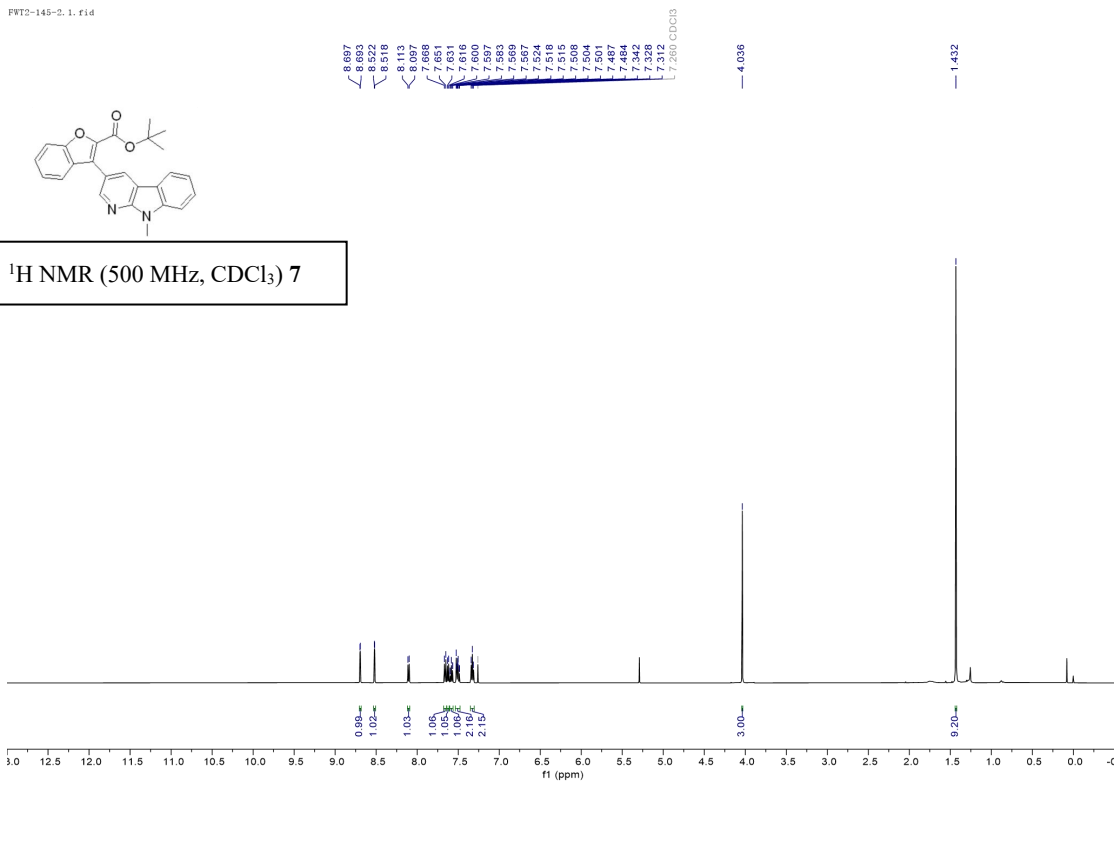
^{13}C NMR (125 MHz, $CDCl_3$) **5aa**



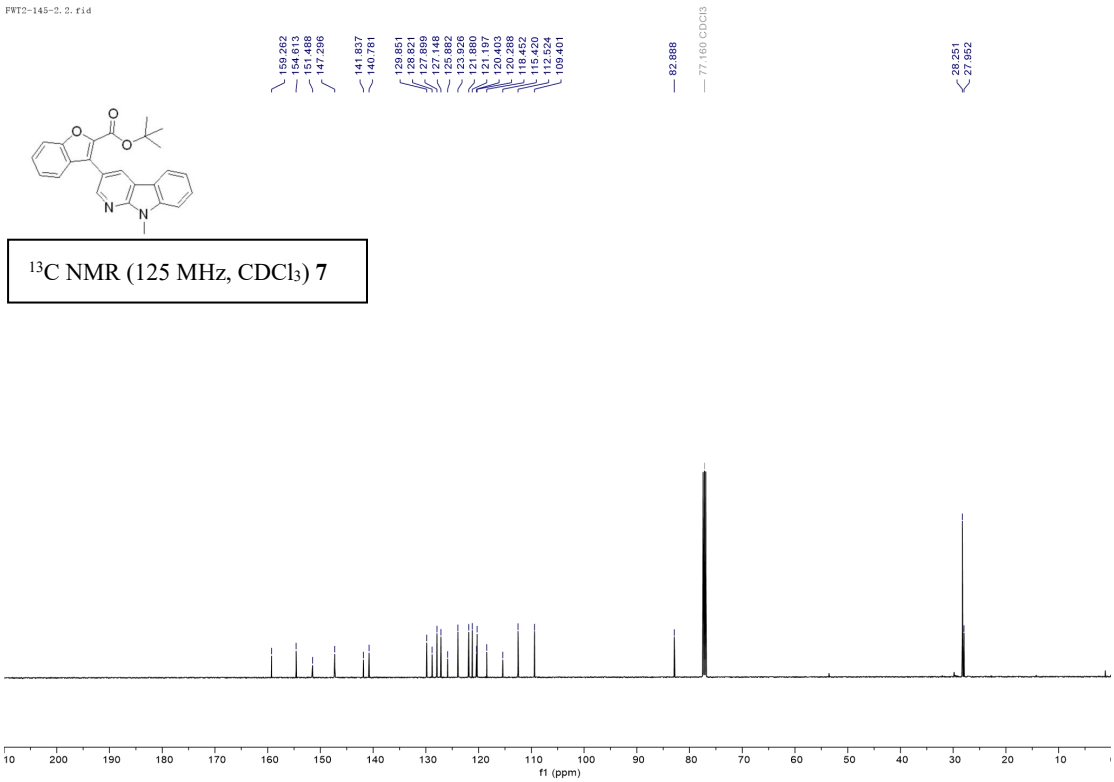
^{1}H NMR (500 MHz, $CDCl_3$) **6**



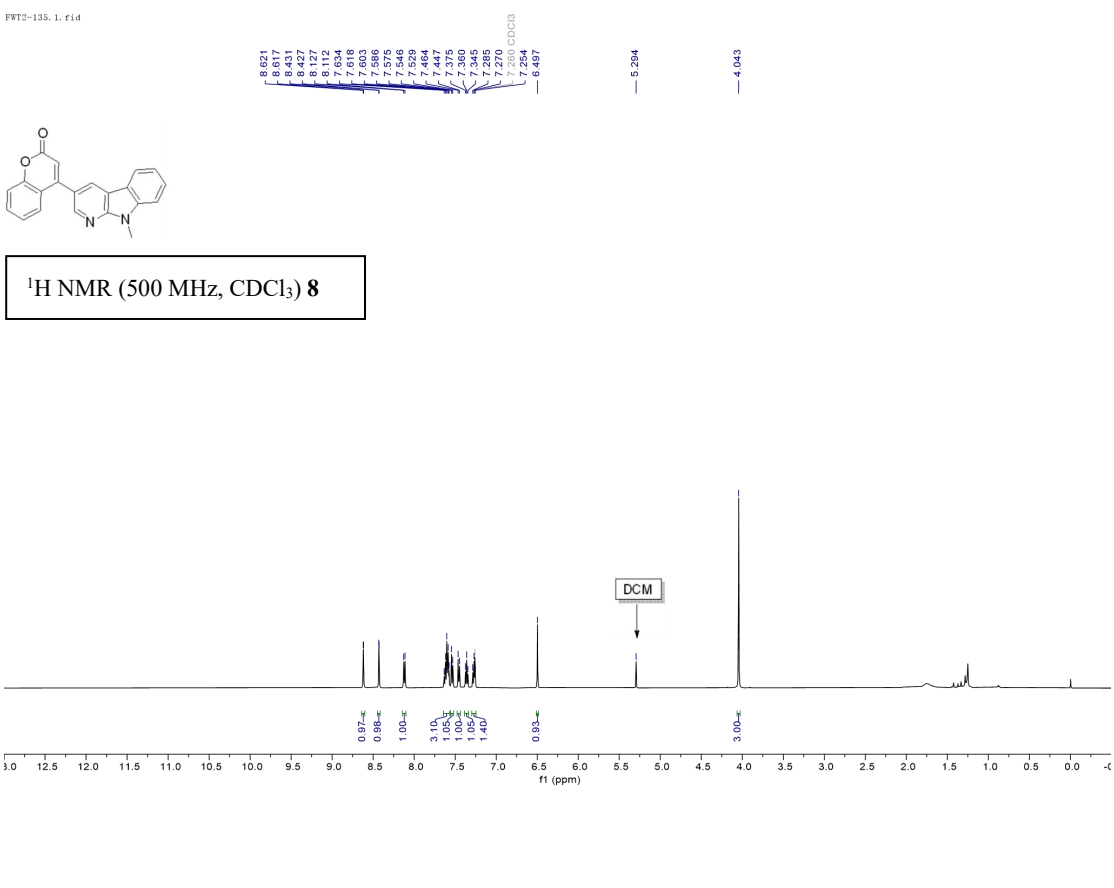
^{13}C NMR (125 MHz, $CDCl_3$) **6**



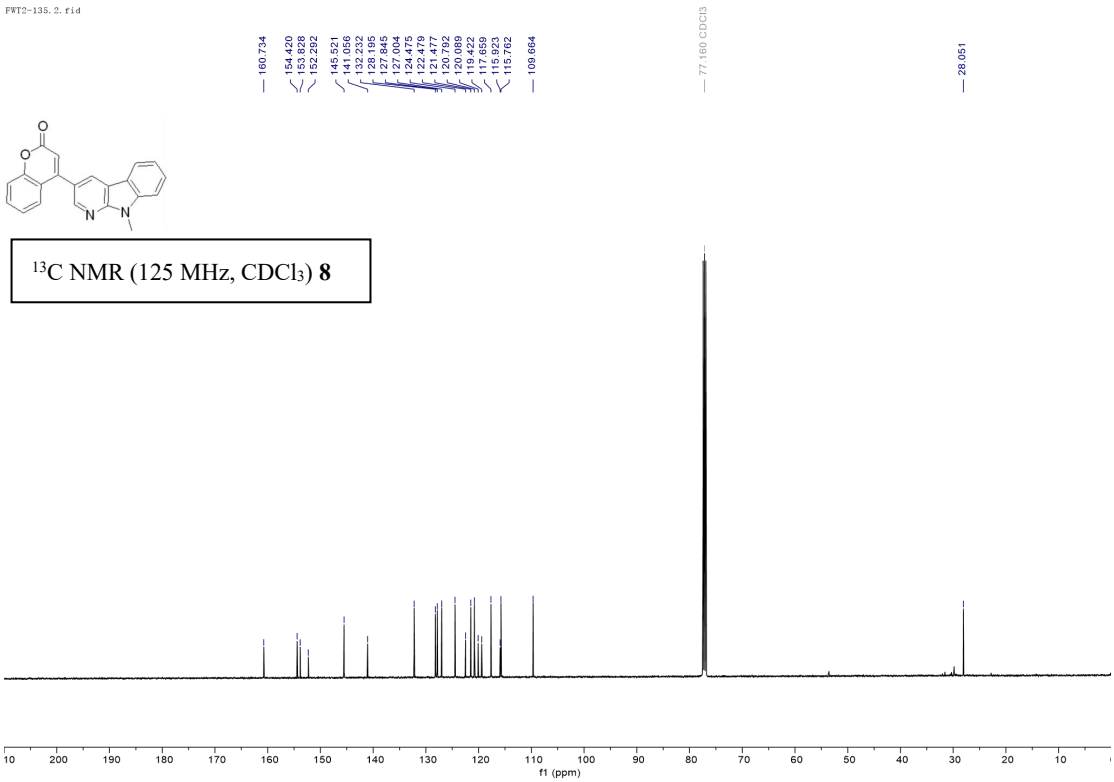
^{1}H NMR (500 MHz, $CDCl_3$) **7**



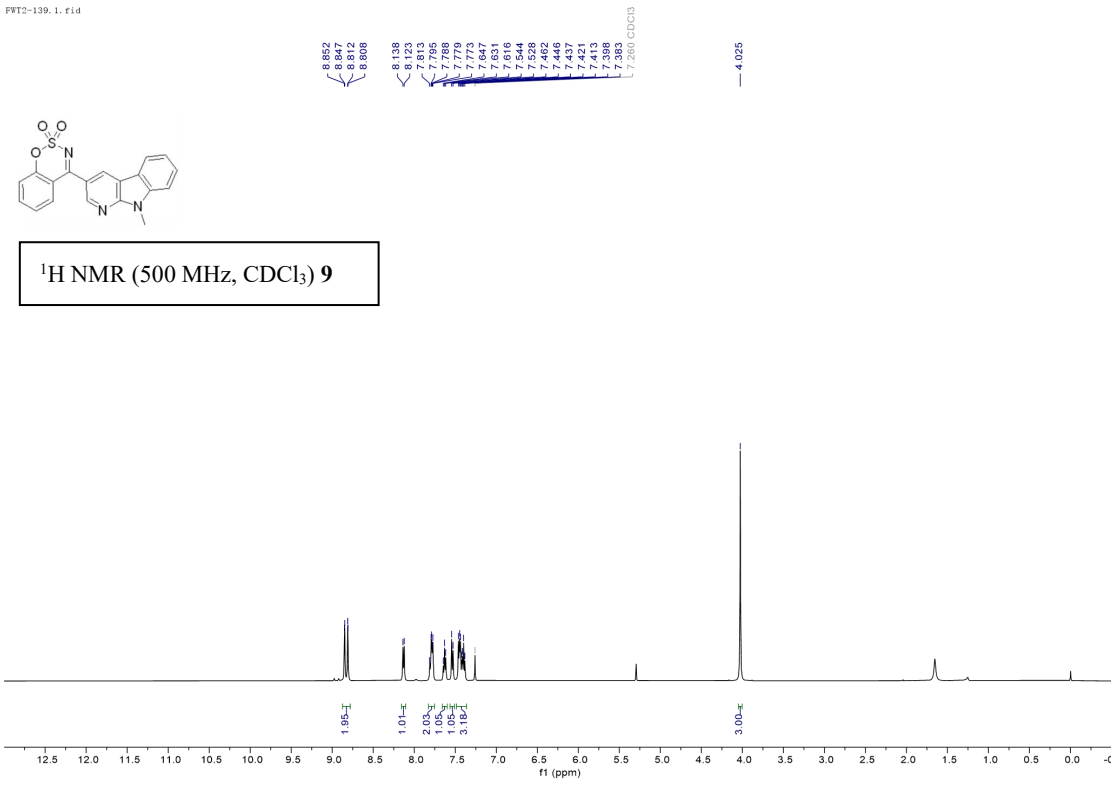
^{13}C NMR (125 MHz, $CDCl_3$) **7**



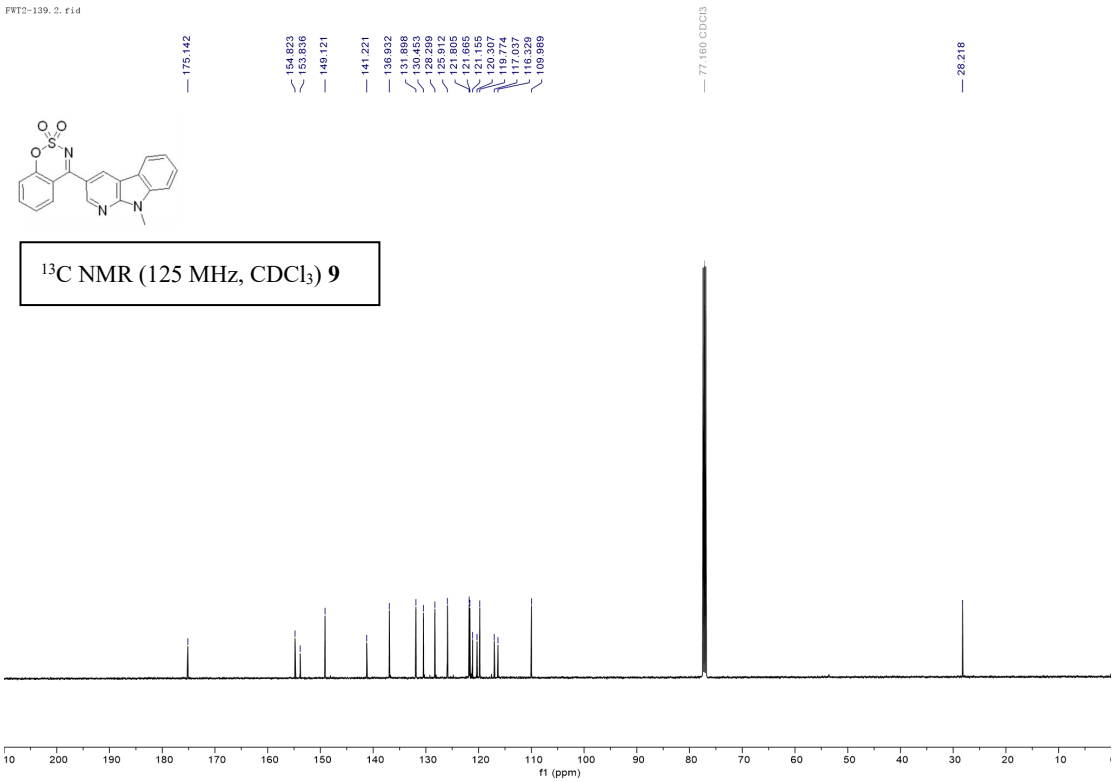
^{1}H NMR (500 MHz, $CDCl_3$) **8**



^{13}C NMR (125 MHz, $CDCl_3$) **8**

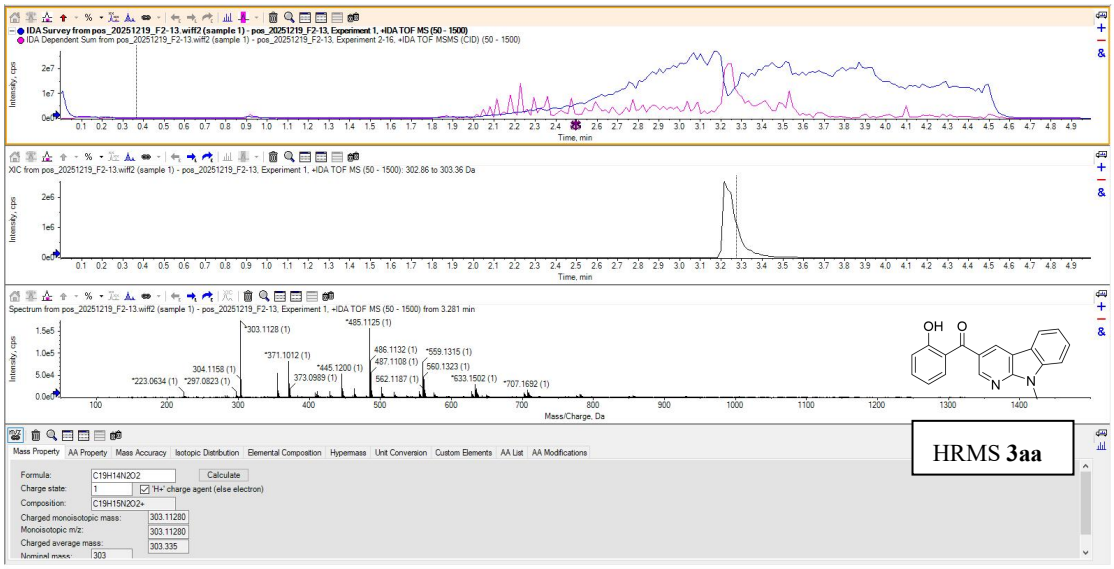


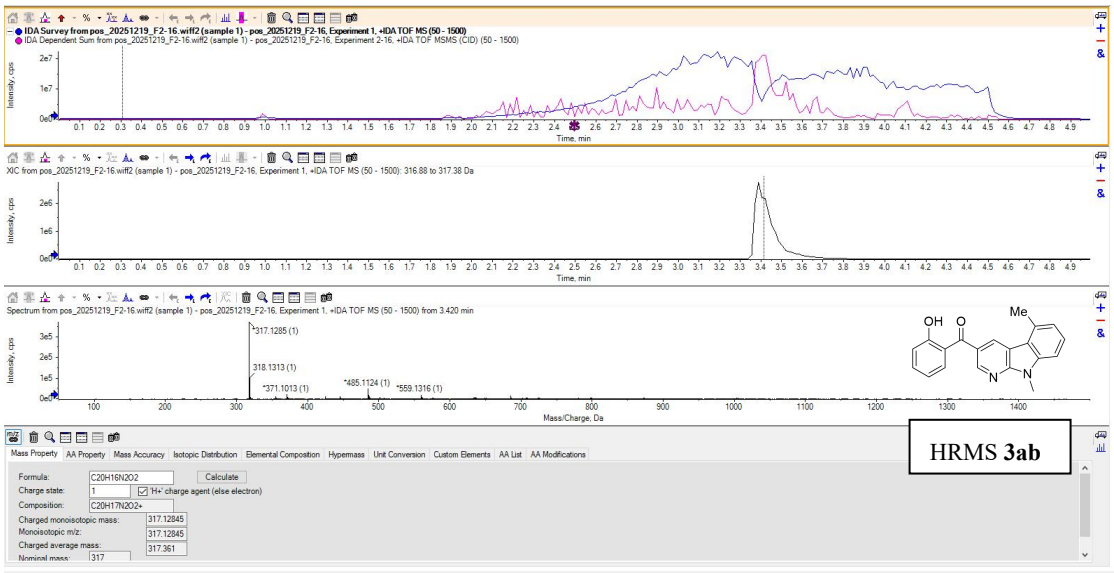
^{1}H NMR (500 MHz, $CDCl_3$) **9**

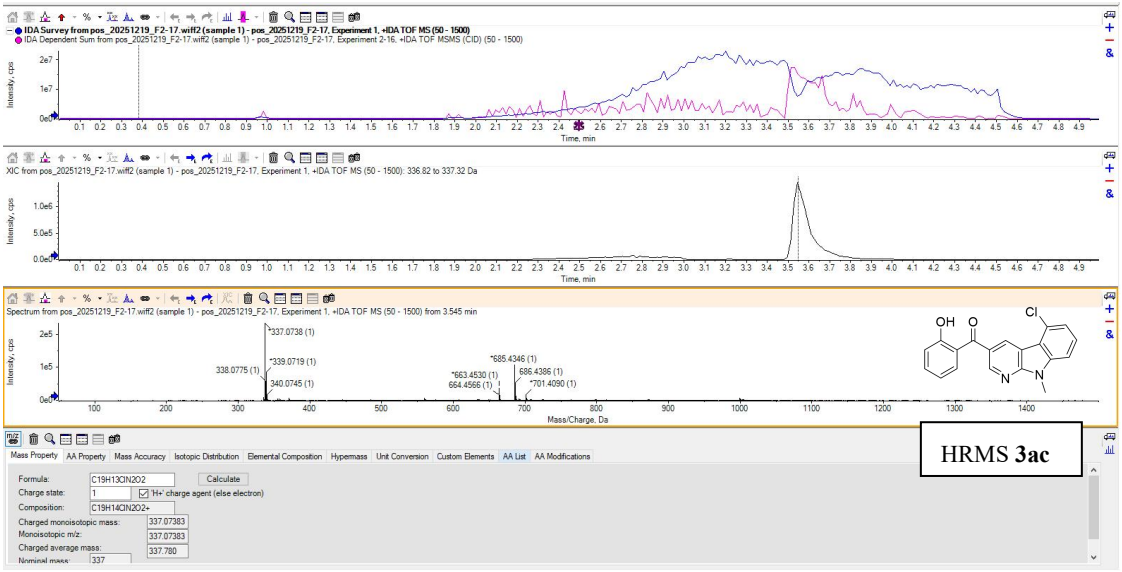


^{13}C NMR (125 MHz, $CDCl_3$) **9**

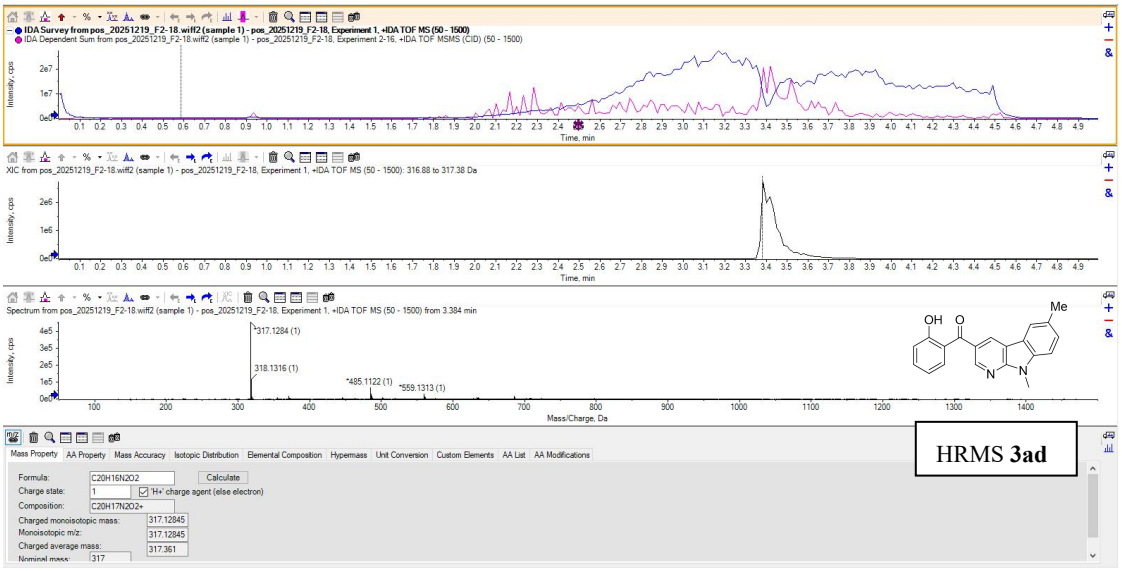
6. HRMS Spectra



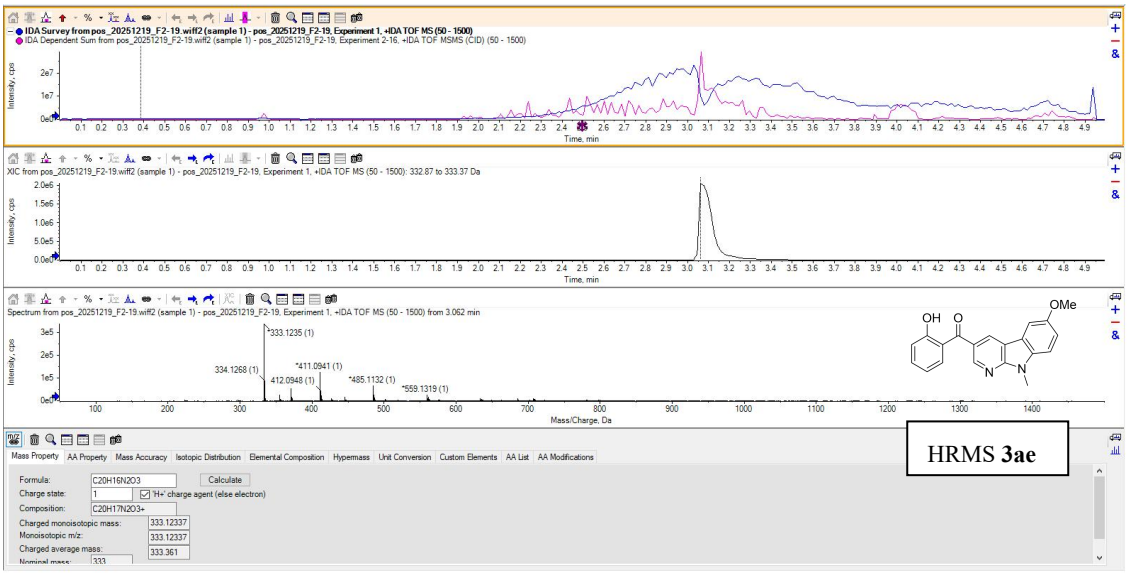




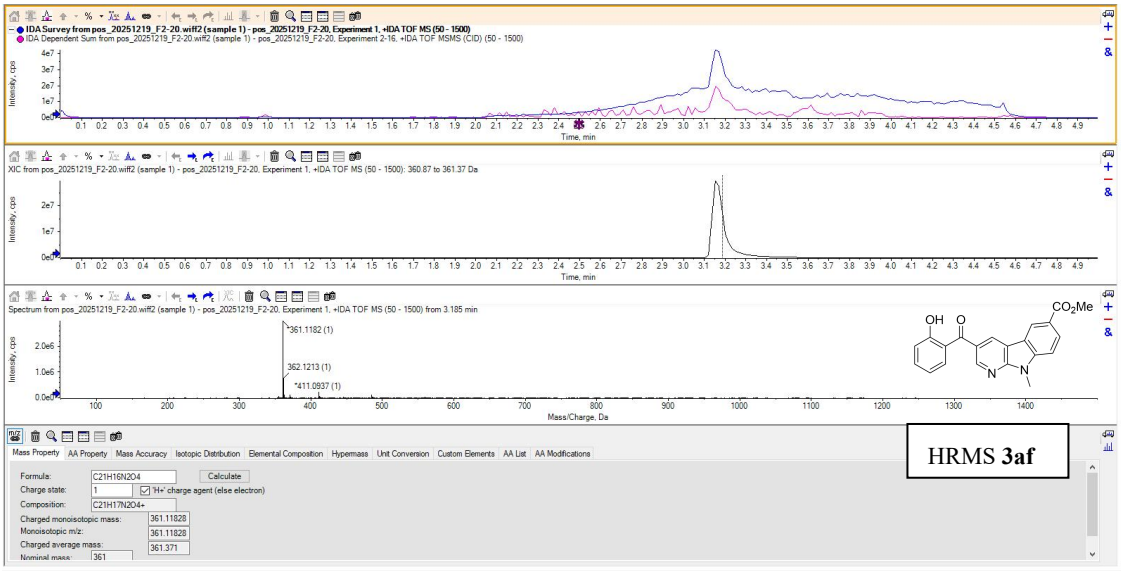
HRMS **3ac**



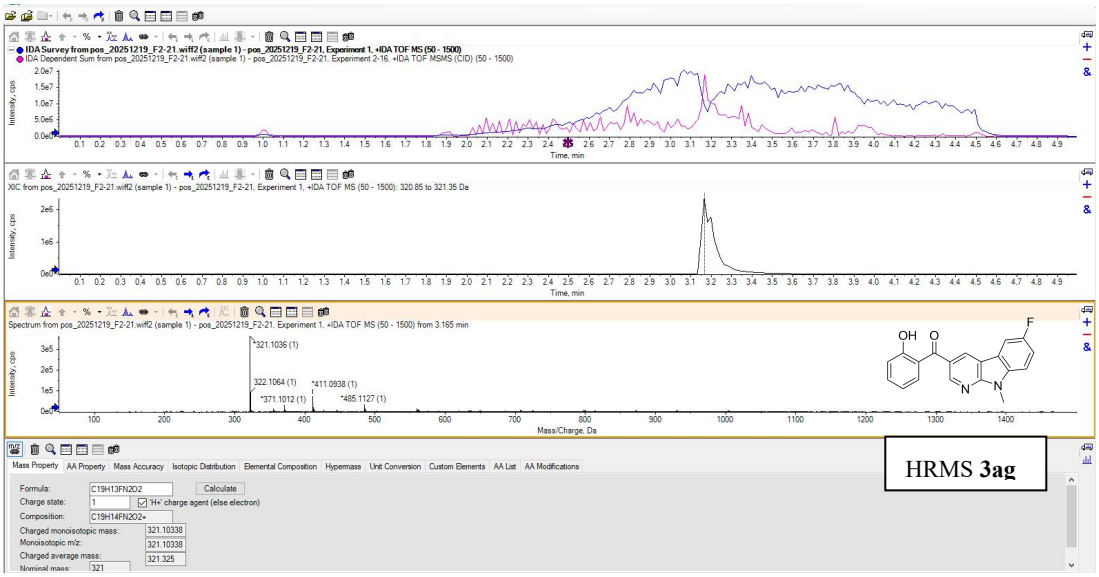
HRMS **3ad**



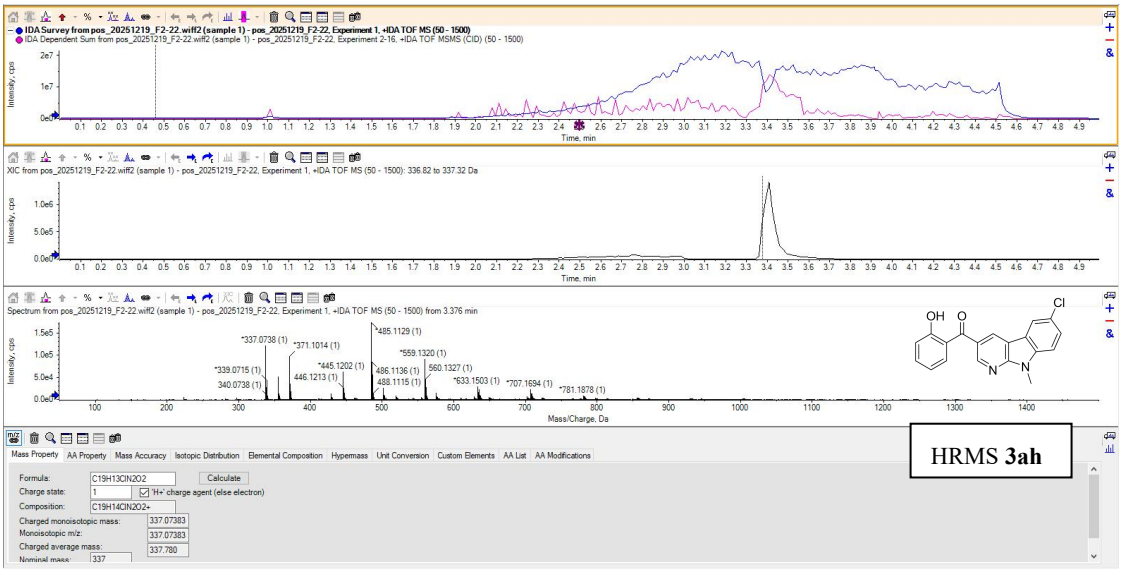
HRMS **3ae**



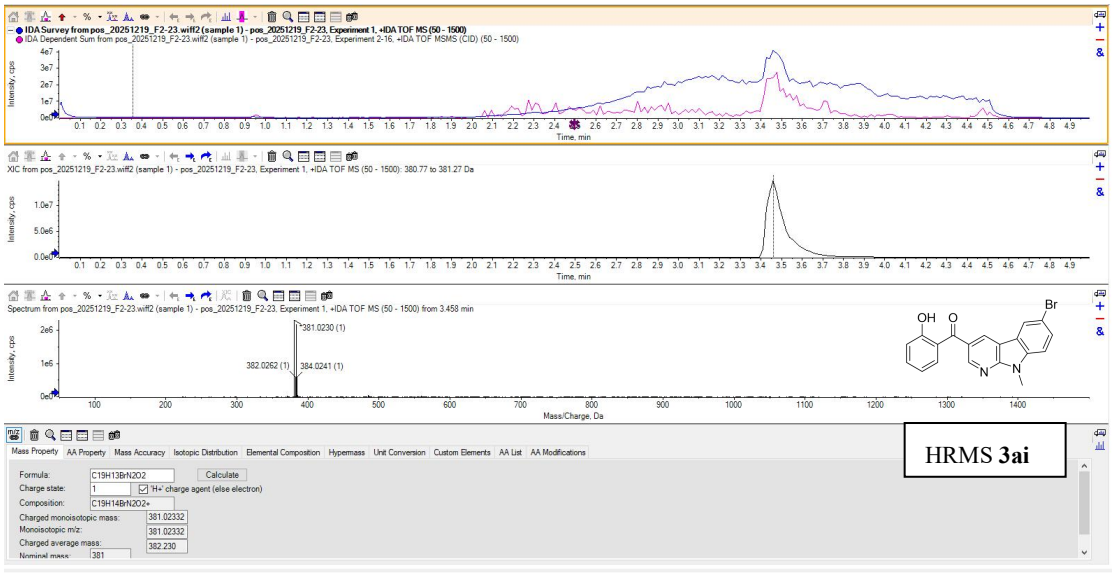
HRMS **3af**



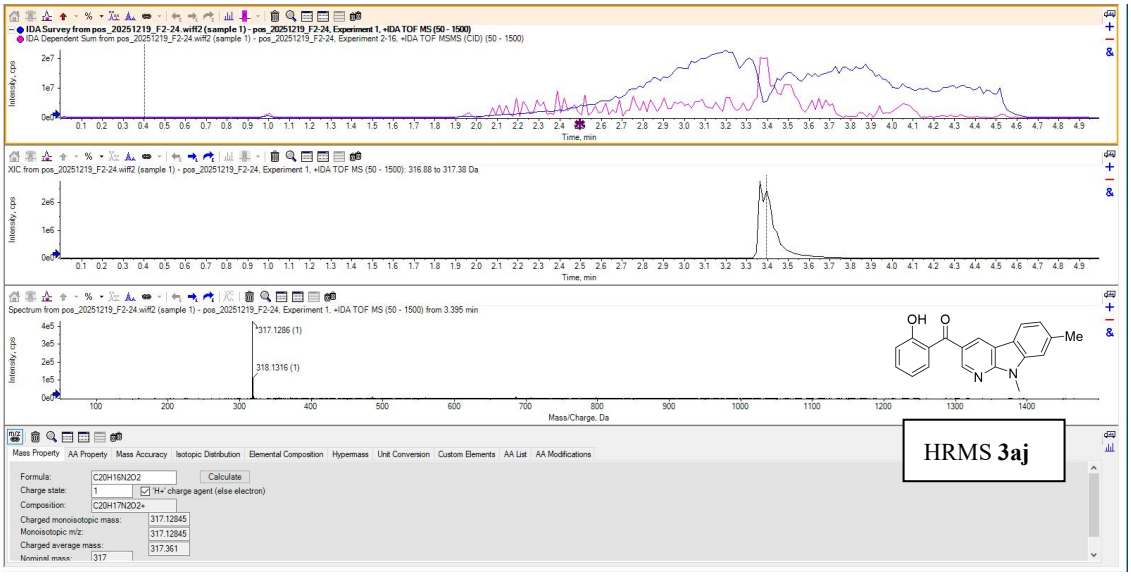
HRMS **3ag**



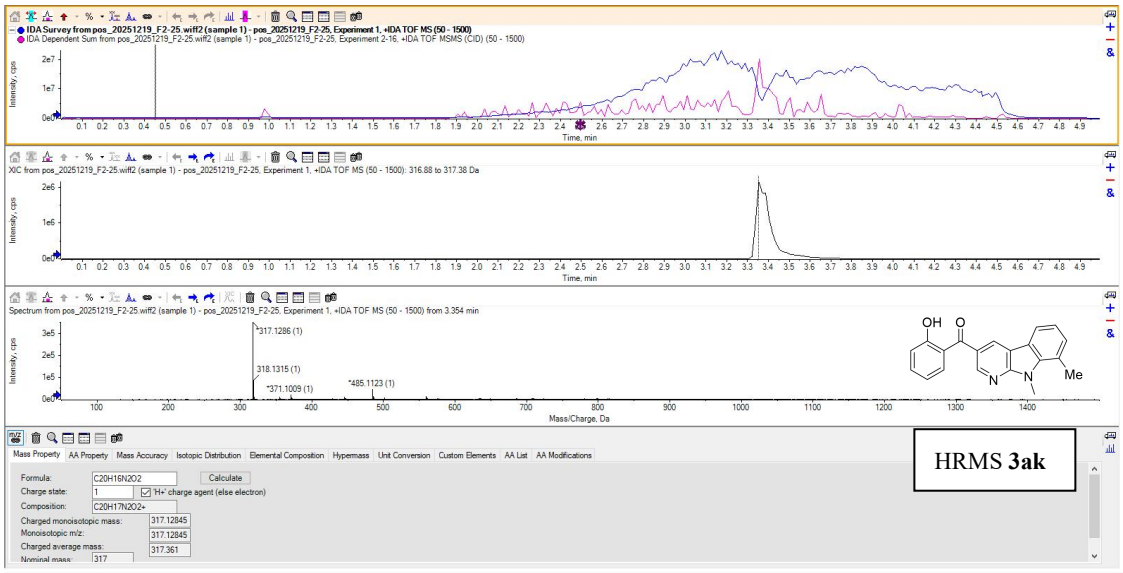
HRMS **3ah**



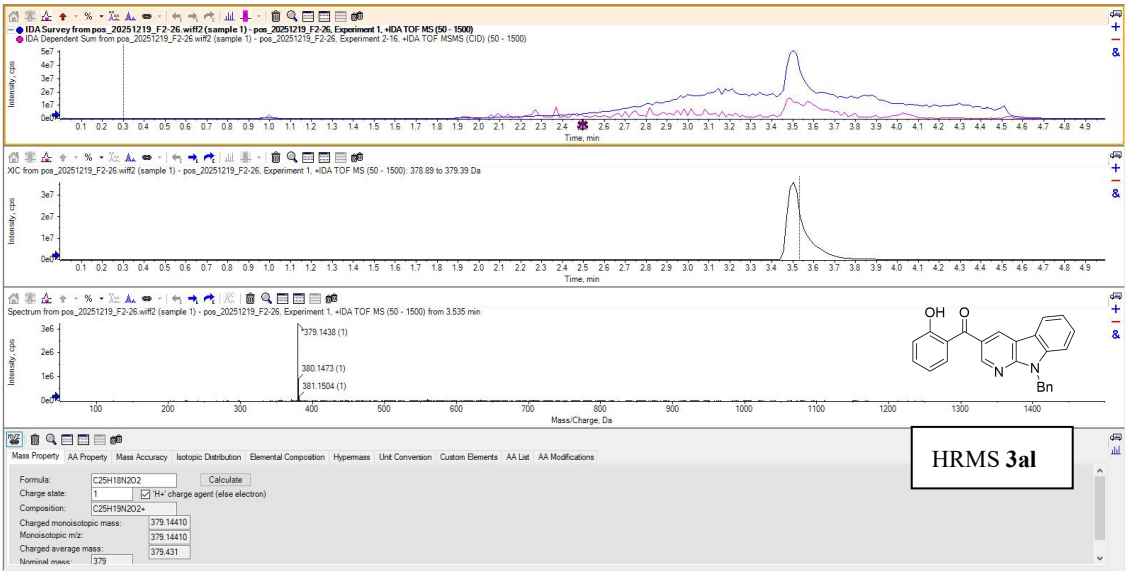
HRMS **3ai**



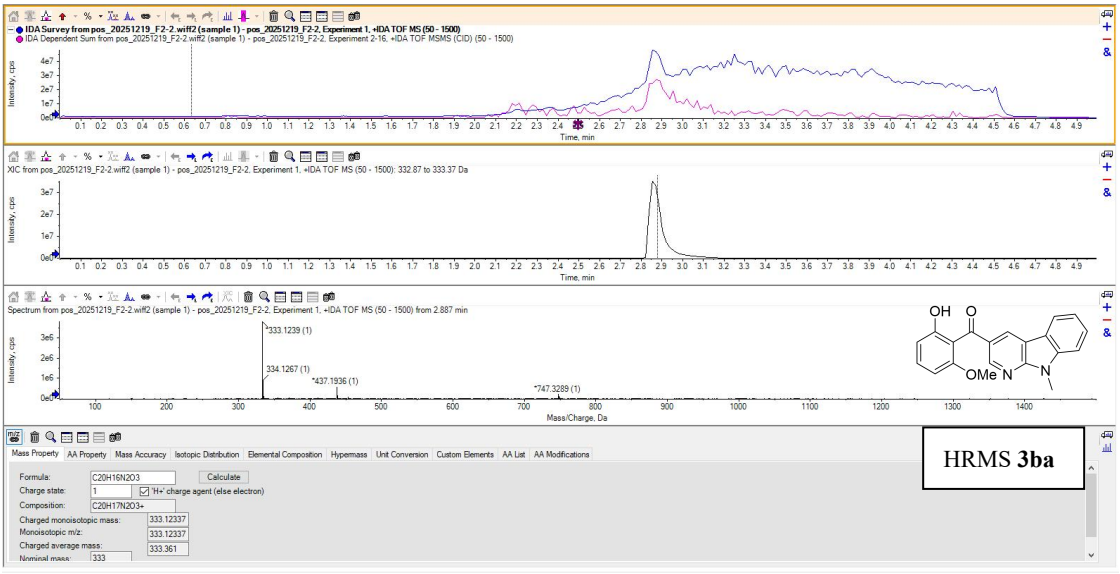
HRMS **3aj**



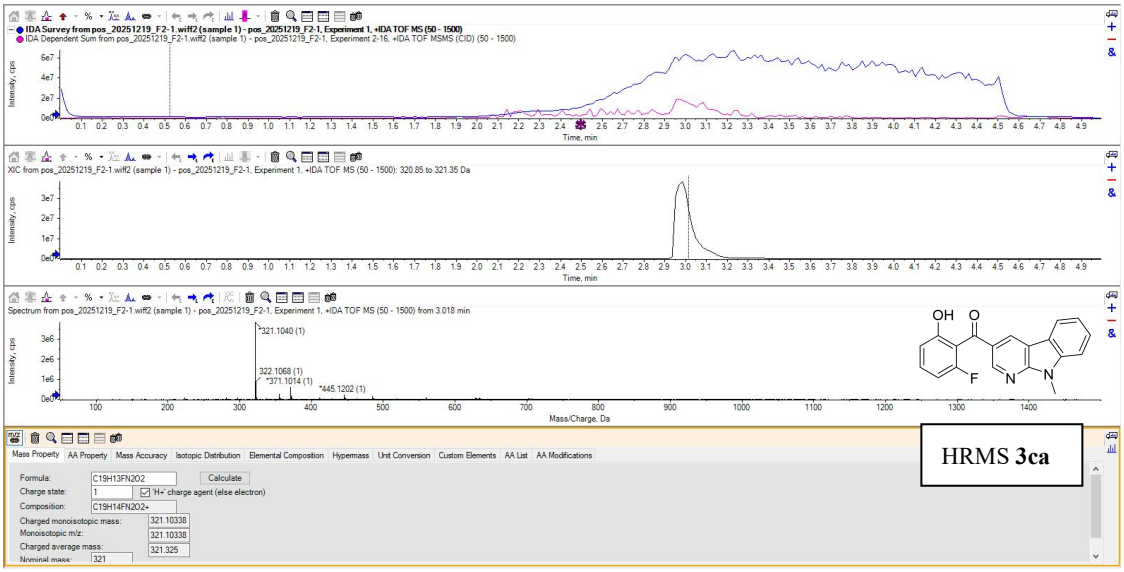
HRMS **3ak**



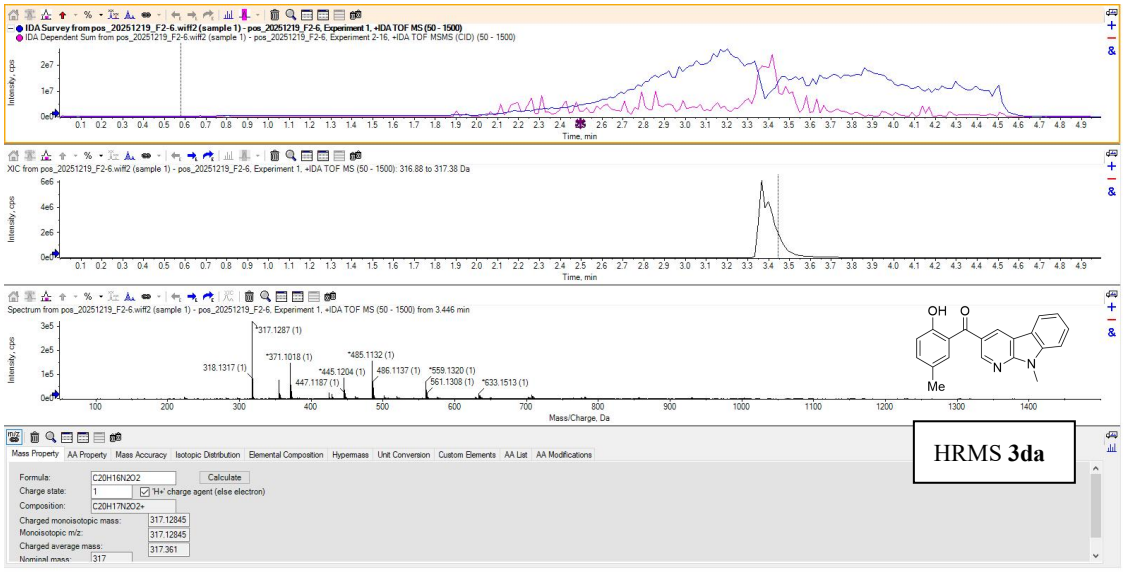
HRMS **3al**



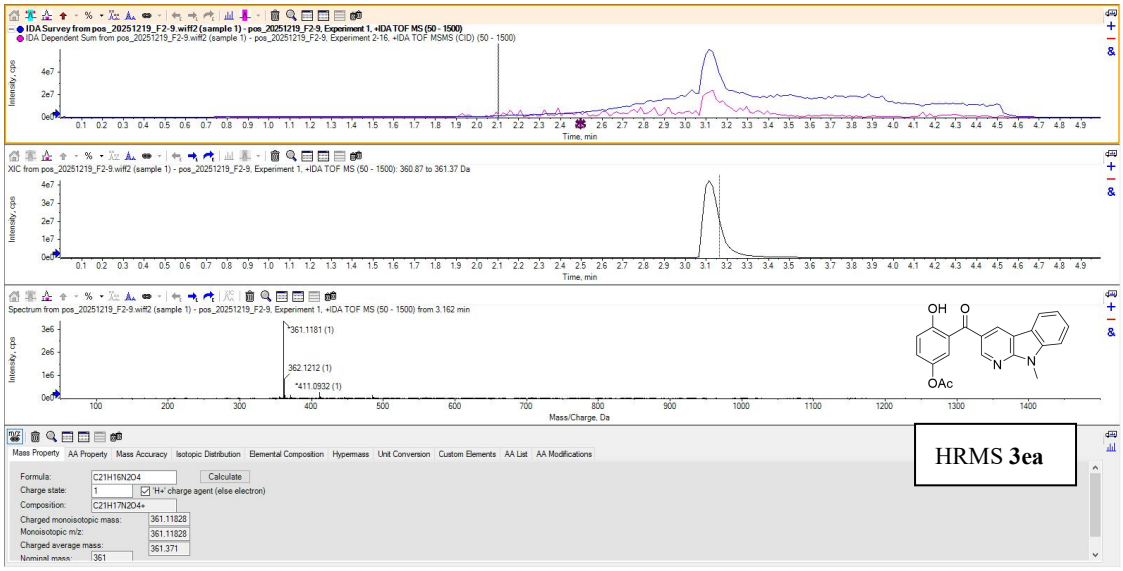
HRMS **3ba**



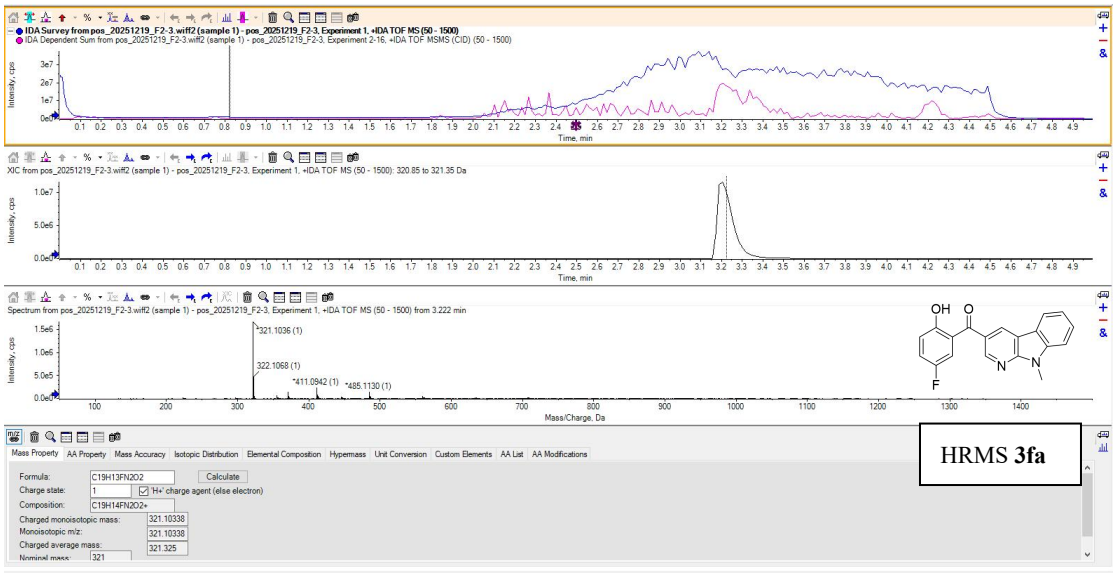
HRMS **3ca**



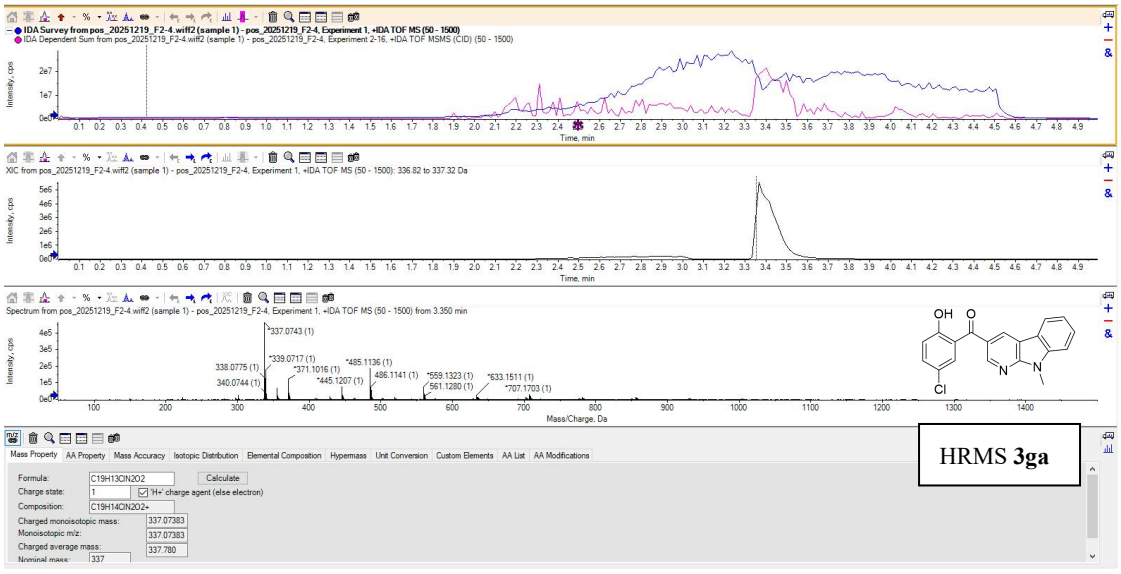
HRMS **3da**



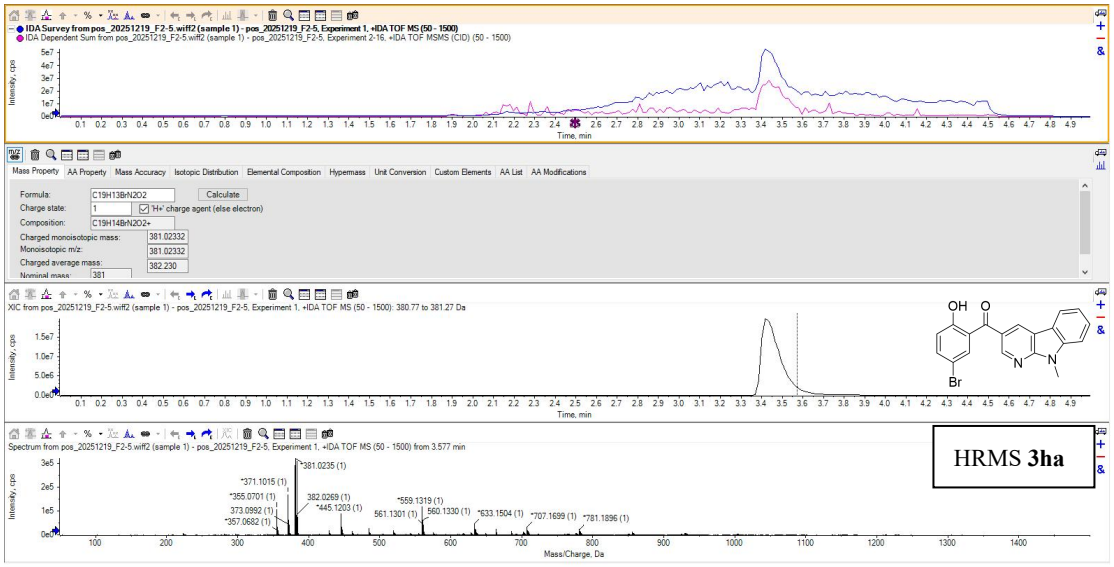
HRMS **3ea**



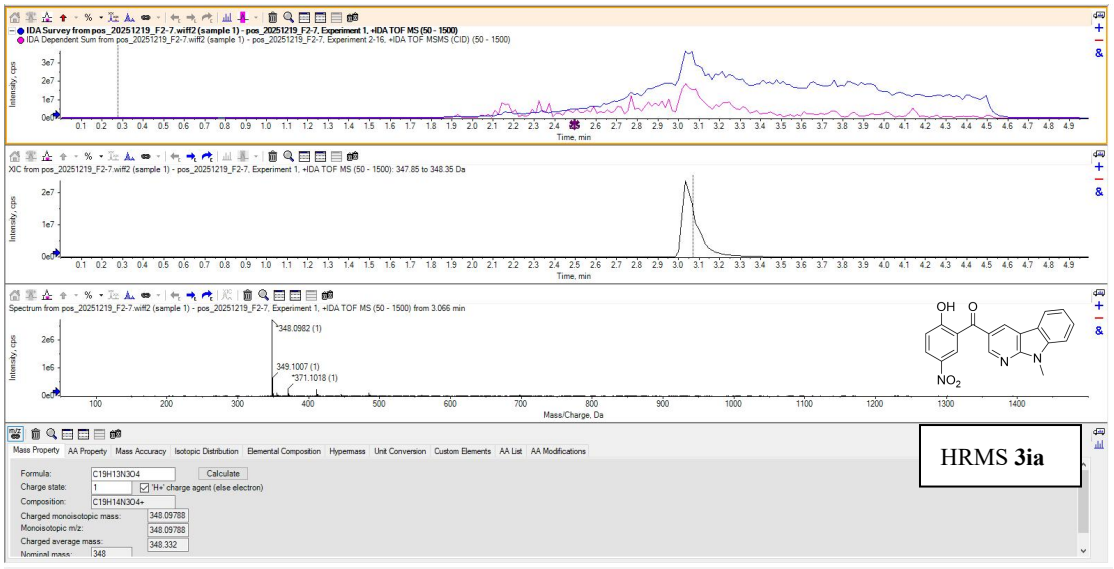
HRMS **3fa**



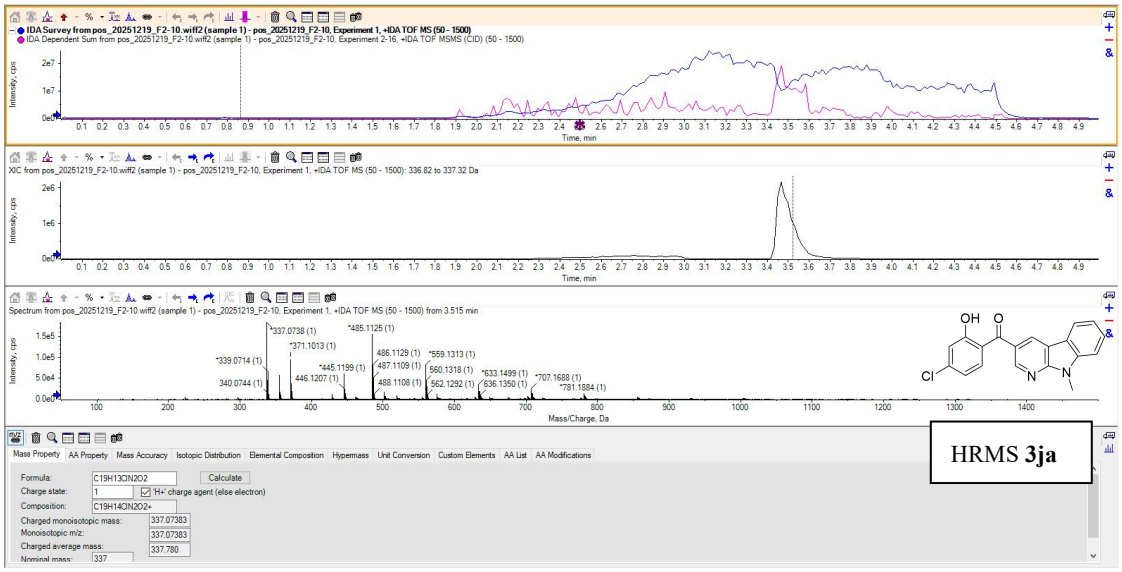
HRMS **3ga**



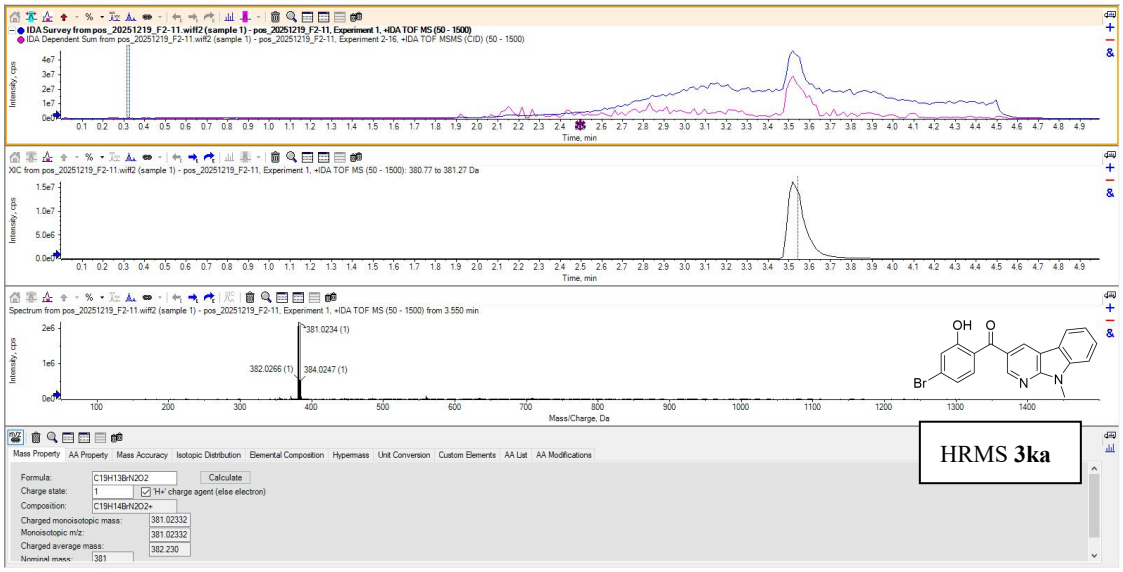
HRMS **3ha**



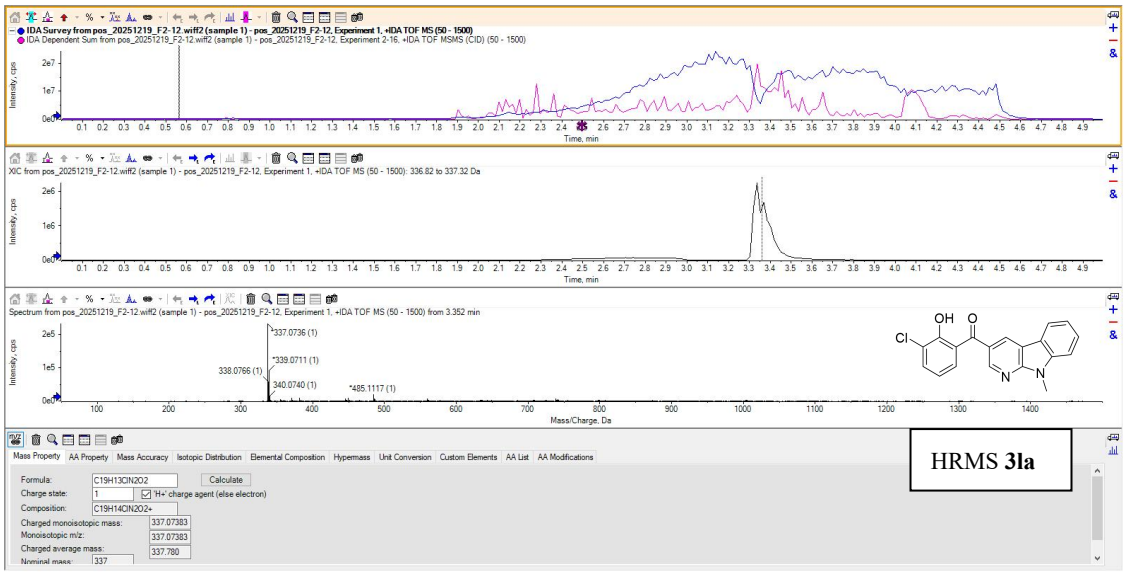
HRMS **3ia**



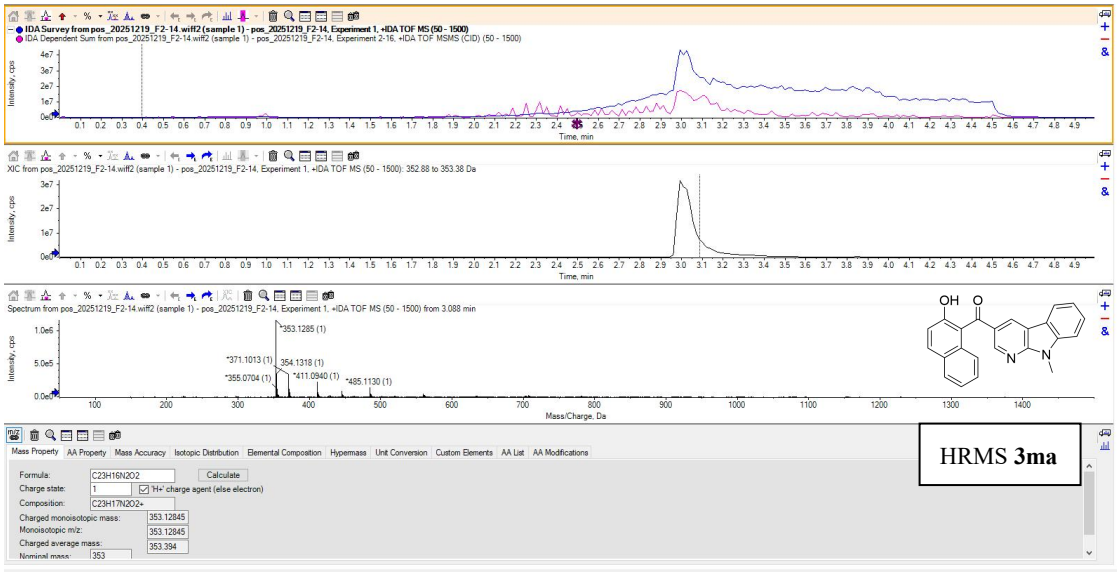
HRMS **3ja**



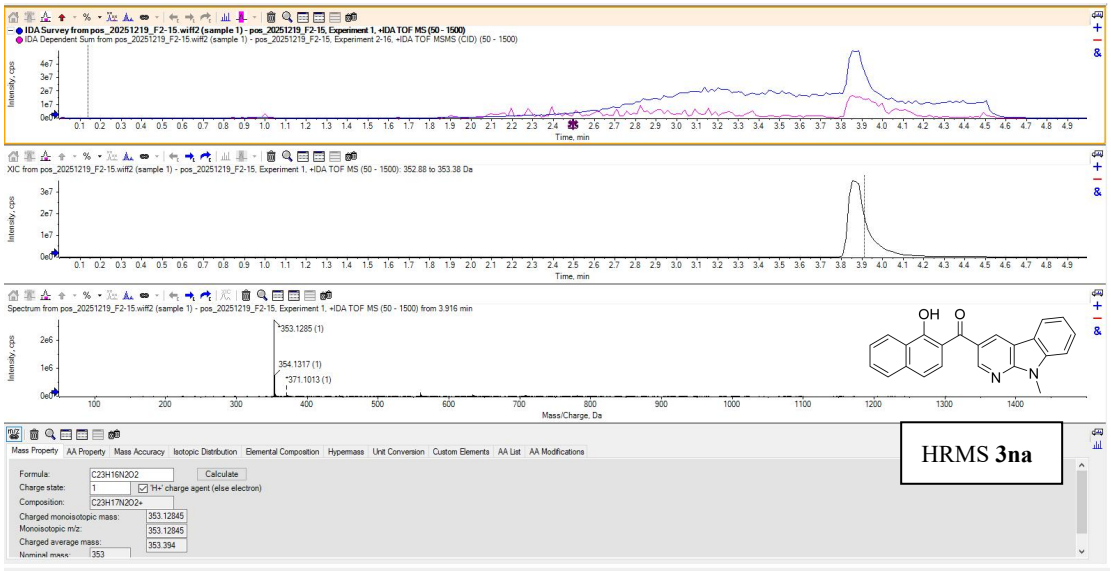
HRMS **3ka**



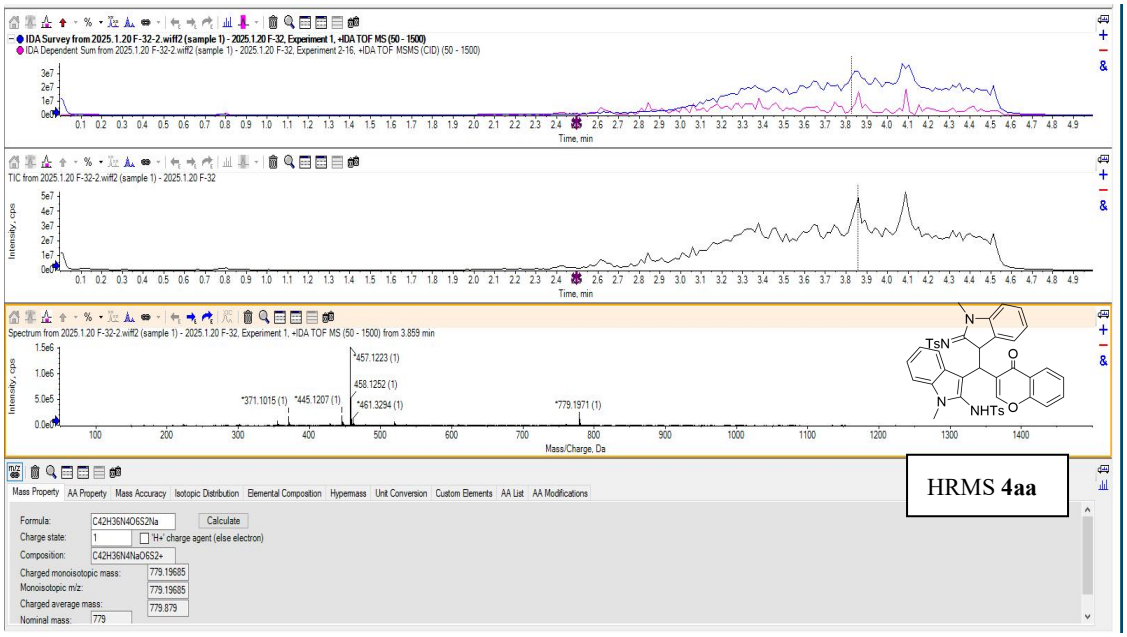
HRMS **3la**



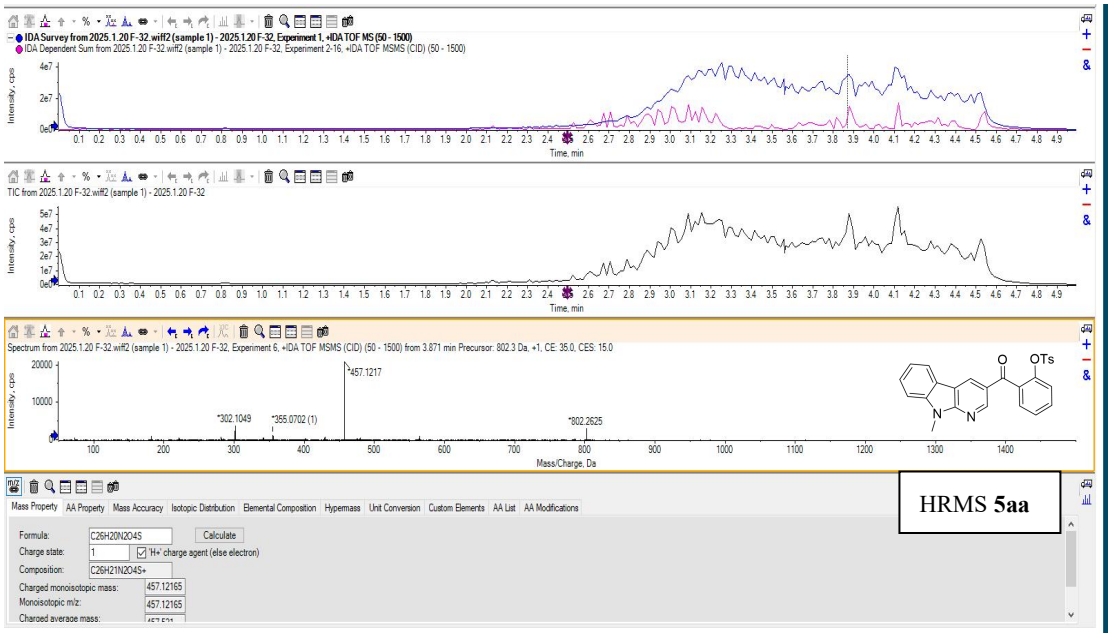
HRMS **3ma**



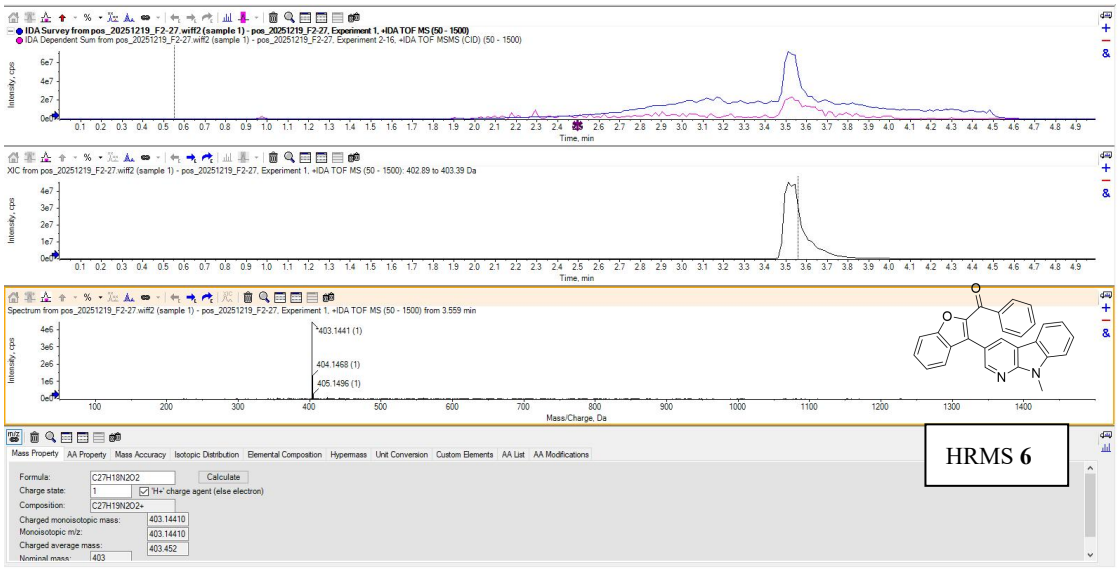
HRMS **3na**



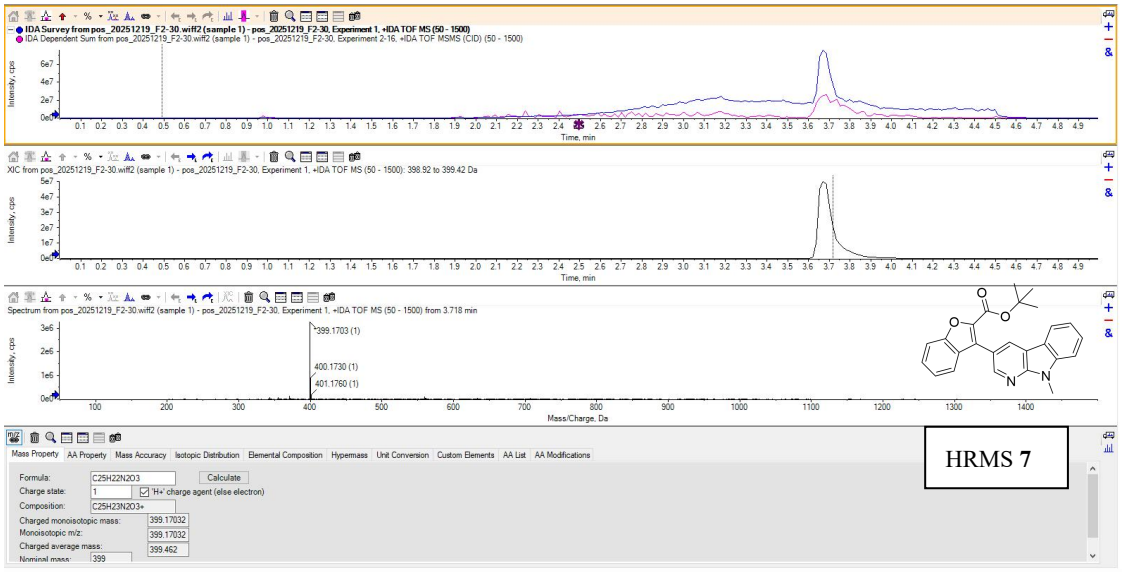
HRMS **4aa**



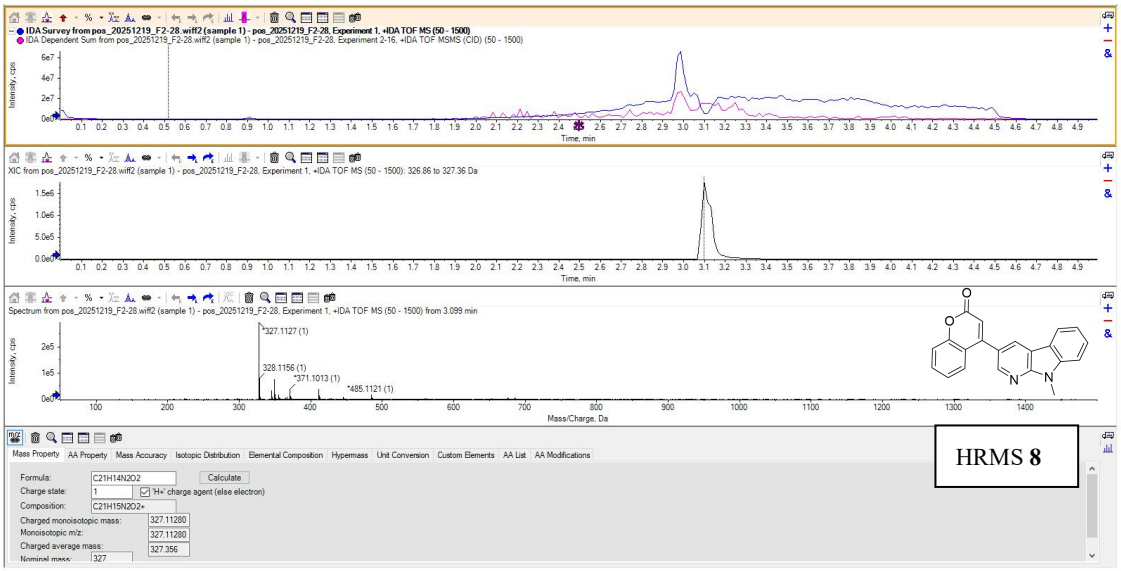
HRMS **5aa**



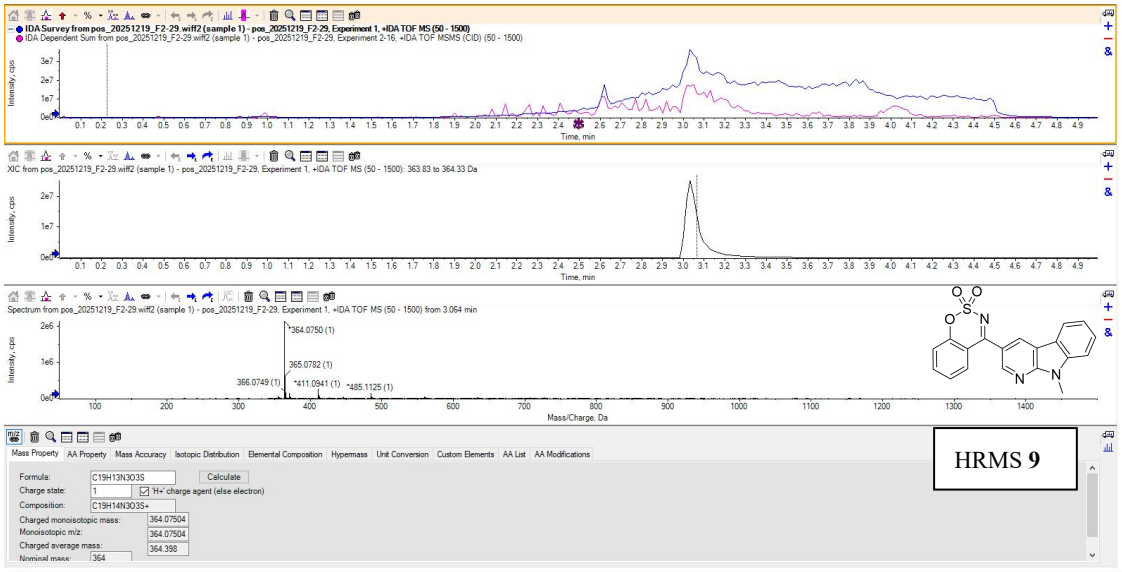
HRMS **6**


IDA Survey from pos_20251219_F2-30.wiff2 (sample 1) - pos_20251219_F2-30, Experiment 1, +IDA TOF MS (50 - 1500)
IDA Dependent Sum from pos_20251219_F2-30.wiff2 (sample 1) - pos_20251219_F2-30, Experiment 2-16, +IDA TOF MSMS (CID) (50 - 1500)
Intensity, cps
Time, min
XIC from pos_20251219_F2-30.wiff2 (sample 1) - pos_20251219_F2-30, Experiment 1, +IDA TOF MS (50 - 1500): 398.92 to 399.42 Da
Spectrum from pos_20251219_F2-30.wiff2 (sample 1) - pos_20251219_F2-30, Experiment 1, +IDA TOF MS (50 - 1500) from 3.718 min
399.1703 (1)
400.1730 (1)
401.1760 (1)
Mass/Charge, Da
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula: C25H22N2O3
Calculate
Charge state: 1
H+ charge agent (else electron)
Composition: C25H23N2O3+
Charged monoisotopic mass: 399.17032
Monoisotopic m/z: 399.17032
Charged average mass: 399.462
Nominal mass: 399

HRMS **7**


IDA Survey from pos_20251219_F2-28.wiff2 (sample 1) - pos_20251219_F2-28, Experiment 1, +IDA TOF MS (50 - 1500)
IDA Dependent Sum from pos_20251219_F2-28.wiff2 (sample 1) - pos_20251219_F2-28, Experiment 2-16, +IDA TOF MSMS (CID) (50 - 1500)
Intensity, cps
Time, min
XIC from pos_20251219_F2-28.wiff2 (sample 1) - pos_20251219_F2-28, Experiment 1, +IDA TOF MS (50 - 1500): 326.86 to 327.36 Da
Spectrum from pos_20251219_F2-28.wiff2 (sample 1) - pos_20251219_F2-28, Experiment 1, +IDA TOF MS (50 - 1500) from 3.099 min
327.1127 (1)
328.1156 (1)
371.1013 (1)
485.1121 (1)
Mass/Charge, Da
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula: C21H14N2O2
Calculate
Charge state: 1
H+ charge agent (else electron)
Composition: C21H15N2O2+
Charged monoisotopic mass: 327.11280
Monoisotopic m/z: 327.11280
Charged average mass: 327.356
Nominal mass: 327

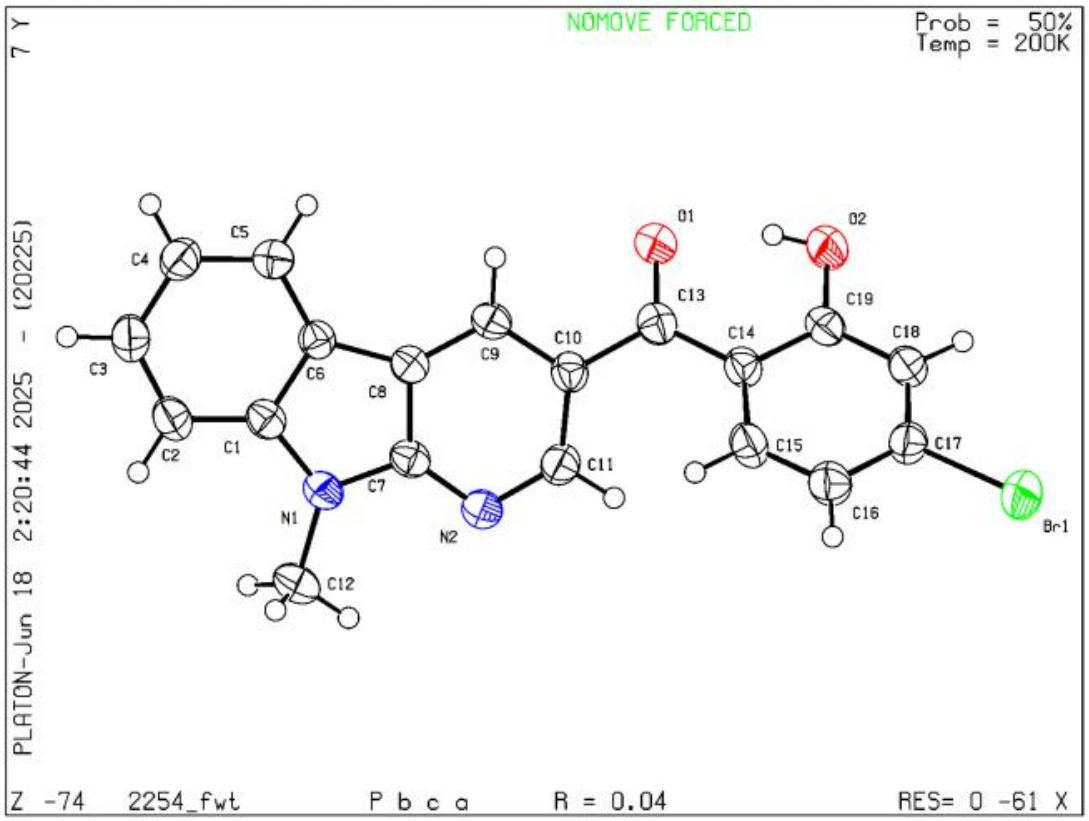
HRMS **8**


IDA Survey from pos_20251219_F2-29.wiff2 (sample 1) - pos_20251219_F2-29, Experiment 1, +IDA TOF MS (50 - 1500)
IDA Dependent Sum from pos_20251219_F2-29.wiff2 (sample 1) - pos_20251219_F2-29, Experiment 2-16, +IDA TOF MSMS (CID) (50 - 1500)
Intensity, cps
Time, min
XIC from pos_20251219_F2-29.wiff2 (sample 1) - pos_20251219_F2-29, Experiment 1, +IDA TOF MS (50 - 1500): 363.83 to 364.33 Da
Intensity, cps
Time, min
Spectrum from pos_20251219_F2-29.wiff2 (sample 1) - pos_20251219_F2-29, Experiment 1, +IDA TOF MS (50 - 1500) from 3.064 min
364.0750 (1)
365.0782 (1)
366.0749 (1)
411.0941 (1)
485.1125 (1)
Intensity, cps
Mass/Charge, Da
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula: C19H13N3O3S
Calculate
Charge state: 1
'H+' charge agent (else electron)
Composition: C19H14N3O3S+
Charged monoisotopic mass: 364.07504
Monoisotopic m/z: 364.07504
Charged average mass: 364.398
Nominal mass: 364

HRMS **9**

7. X-ray Crystal Structure Information

7.1 X-ray Crystal Structure Information of Compound 3ka



3ka

Sample preparation: A small amount of sample **3ka** was dissolved in DCM in a vial, and then petroleum ether was dripped into the solution. Then the vial was sealed with a thin layer of parafilm and some holes were made on top of parafilm. The solvent volatilized slowly at room temperature to afford the single crystal of **3ka**.

Experimental Section

Single crystals of $C_{19}H_{13}BrN_2O_2$ [**3ka**] were []. A suitable crystal was selected and [] on a Bruker APEX-II CCD diffractometer. The crystal was kept at 200.0 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [**3ka**]

Crystal Data for $C_{19}H_{13}BrN_2O_2$ (M = 381.22 g/mol): orthorhombic, space group Pbca (no. 61), a = 12.3418(5) Å, b = 8.5375(4) Å, c = 29.6015(12) Å, V = 3119.1(2) Å^3, Z = 8, T = 200.0 K, μ(CuKα) = 3.712 mm^{-1}, *Dcalc* = 1.624 g/cm^3, 12229 reflections measured (5.972° ≤ 2Θ ≤ 136.506°), 2838 unique (R_{int} = 0.0563, R_{sigma} = 0.0443) which were used in all calculations. The final R_1 was 0.0400 (I > 2σ(I)) and wR_2 was 0.1123 (all data).

Refinement model description

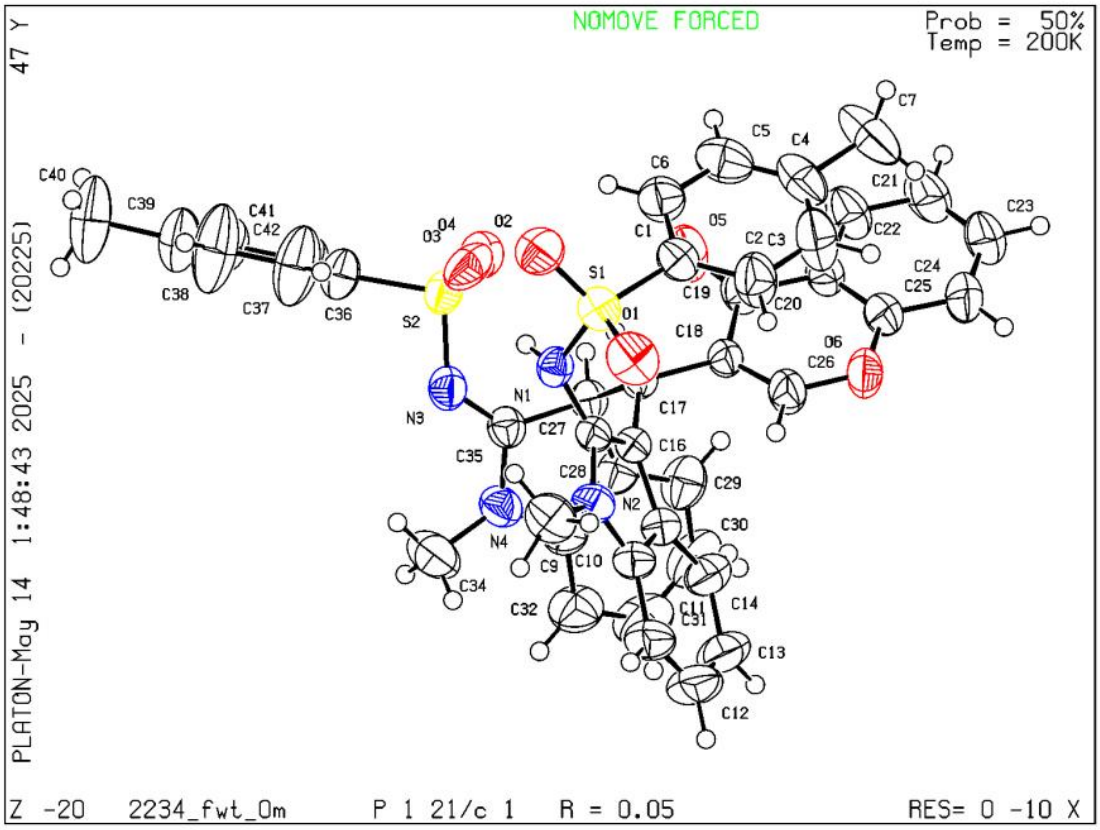
Number of restraints - 1, number of constraints - unknown.
Details:
1. Fixed Uiso
 At 1.2 times of:
 All C(H) groups, All O(H) groups
 At 1.5 times of:
 All C(H,H,H) groups
2. Restrained distances
 O2-H2
 0.84 with sigma of 0.02
3. a Aromatic/amide H refined with riding coordinates:
 C2(H2A), C3(H3), C4(H4), C5(H5), C9(H9), C11(H11), C15(H15), C16(H16), C18(H18)
3. b Idealised Me refined as rotating group:
 C12(H12A,H12B,H12C)
This report has been created with Olex2, compiled on 2020.02.04 svn.rd84adfe8 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Table S2 Crystal data and structure refinement for 3ka

Identification code	**3ka**
Empirical formula	$C_{19}H_{13}BrN_2O_2$
Formula weight	381.22
Temperature/K	200.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.3418(5)
b/Å	8.5375(4)
c/Å	29.6015(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3119.1(2)
Z	8
ρ_{calc}g/cm^3	1.624
μ/mm^{-1}	3.712
F(000)	1536.0
Crystal size/mm^3	0.48 × 0.15 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.972 to 136.506
Index ranges	-14 ≤ h ≤ 14, -7 ≤ k ≤ 10, -35 ≤ l ≤ 29
Reflections collected	12229
Independent reflections	2838 [R_{int} = 0.0563, R_{sigma} = 0.0443]
Data/restraints/parameters	2838/1/221

Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.1052
Final R indexes [all data]	R_1 = 0.0488, wR_2 = 0.1123
Largest diff. peak/hole / e $Å^{-3}$	0.50/-0.54

7.2 X-ray Crystal Structure Information of Compound 4aa



4aa

Sample preparation: A small amount of sample **4aa** was dissolved in DCM in a vial, and then petroleum ether was dripped into the solution. Then the vial was sealed with a thin layer of parafilm and some holes were made on top of parafilm. The solvent volatilized slowly at room temperature to afford the single crystal of **4aa**.

Experimental Section

Single crystals of $C_{42}H_{36}N_4O_6S_2$ [**4aa**] were []. A suitable crystal was selected and [] on a Bruker APEX-II CCD diffractometer. The crystal was kept at 200.0 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [**4aa**]

Crystal Data for $C_{42}H_{36}N_4O_6S_2$ (M = 756.87 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 17.0112(5) Å, b = 10.9345(3) Å, c = 23.5496(6) Å, V = 4244.8(2) $Å^3$, Z = 4, T = 200.0 K, μ(CuKα) =

1.532 mm^{-1}, *Dcalc* = 1.184 g/cm^3, 21774 reflections measured ($5.36° \leq 2\Theta \leq 136.932°$), 7736 unique ($R_{int}$ = 0.0602, R_{sigma} = 0.0628) which were used in all calculations. The final R_1 was 0.0527 ($I > 2\sigma(I)$) and wR_2 was 0.1570 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

 At 1.2 times of:

 All C(H) groups, All O(H) groups

 At 1.5 times of:

 All C(H,H,H) groups

2. Restrained distances

 N1-H1

 0.88 with sigma of 0.02

3. a A Ternary CH refined with riding coordinates

 C17(H17), C27(H27)

3. b Aromatic/amide H refined with riding coordinates:

 C2(H2), C3(H3), C5(H5), C6(H6), C11(H11), C12(H12), C13(H13), C14(H14),

 C21(H21), C22(H22), C23(H23), C24(H24), C26(H26), C29(H29), C30(H30), C31(H31),

 C32(H32), C37(H37), C38(H38), C41(H41), C42(H42)

3. c Idealised Me refined as rotating group:

 C7(H7A,H7B,H7C), C9(H9A,H9B,H9C), C34(H34A,H34B,H34C), C40(H40A,H40B,H40C)

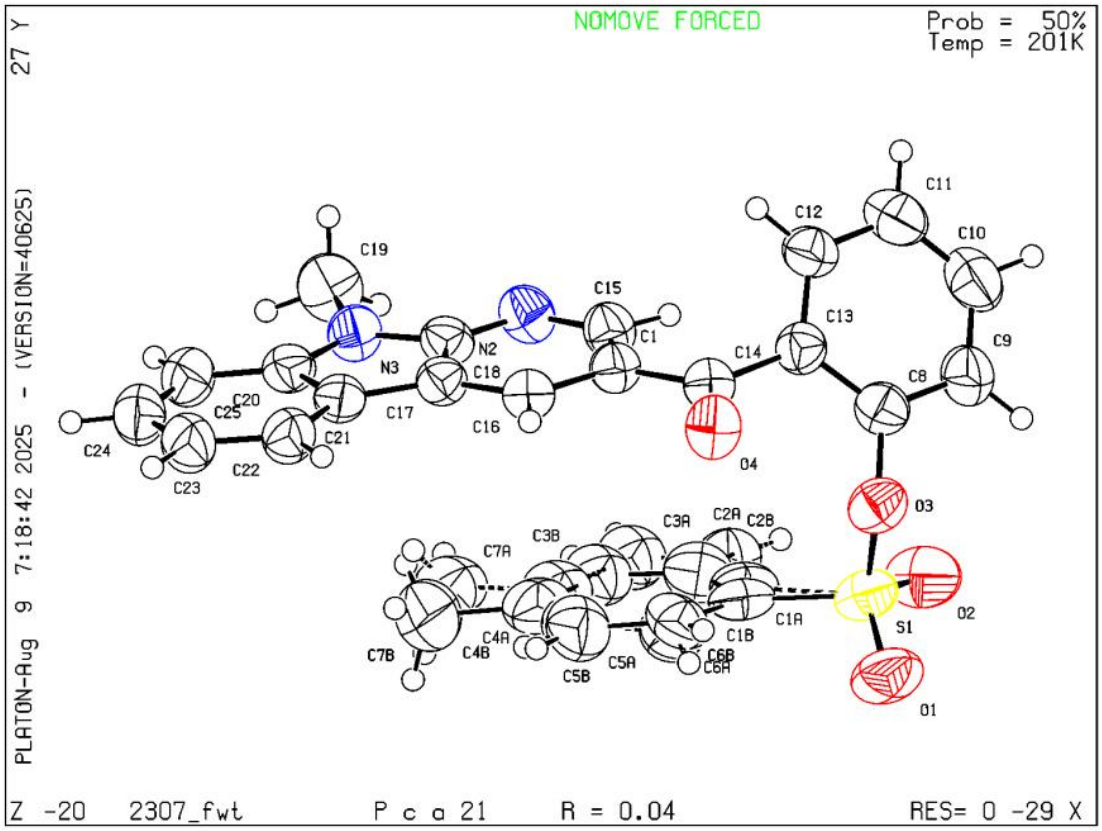
This report has been created with Olex2, compiled on 2020.11.12 svn.r5f609507 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Table S3 Crystal data and structure refinement for 4aa

Identification code	**4aa**
Empirical formula	$C_{42}H_{36}N_4O_6S_2$
Formula weight	756.87
Temperature/K	200.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.0112(5)
b/Å	10.9345(3)
c/Å	23.5496(6)
α/°	90
β/°	104.293(2)
γ/°	90
Volume/$Å^3$	4244.8(2)
Z	4
$\rho_{calc}g/cm^3$	1.184
μ/mm^{-1}	1.532
F(000)	1584.0

Crystal size/mm^3	0.41 × 0.18 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.36 to 136.932
Index ranges	-20 ≤ h ≤ 20, -10 ≤ k ≤ 13, -27 ≤ l ≤ 28
Reflections collected	21774
Independent reflections	7736 [R_{int} = 0.0602, R_{sigma} = 0.0628]
Data/restraints/parameters	7736/1/494
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0527, wR_2 = 0.1459
Final R indexes [all data]	R_1 = 0.0703, wR_2 = 0.1570
Largest diff. peak/hole / e Å^{-3}	0.34/-0.23

7.3 X-ray Crystal Structure Information of Compound 5aa



5aa

Sample preparation: A small amount of sample **5aa** was dissolved in DCM in a vial, and then petroleum ether was dripped into the solution. Then the vial was sealed with a thin layer of parafilm and some holes were made on top of parafilm. The solvent volatilized slowly at room temperature to afford the single crystal of **5aa**.

Experimental Section

Single crystals of $C_{26}H_{20}N_2O_4S$ [**5aa**] were []. A suitable crystal was selected and [] on a Bruker APEX-II CCD diffractometer. The crystal was kept at 201.0 K during data collection. Using Olex2 [1],

the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [**5aa**]

Crystal Data for $C_{26}H_{20}N_2O_4S$ (M = 456.50 g/mol): orthorhombic, space group $Pca2_1$ (no. 29), a = 21.0365(12) Å, b = 7.9263(4) Å, c = 13.4019(7) Å, V = 2234.7(2) Å^3, Z = 4, T = 201.0 K, μ(CuKα) = 1.590 mm^{-1}, *Dcalc* = 1.357 g/cm^3, 11043 reflections measured (10.692° ≤ 2Θ ≤ 136.578°), 3900 unique (R_{int} = 0.0521, R_{sigma} = 0.0543) which were used in all calculations. The final R_1 was 0.0445 (I > 2σ(I)) and wR_2 was 0.1148 (all data).

Refinement model description

Number of restraints - 339, number of constraints - unknown.

Details:

1. Twinned data refinement
   Scales: 0.96(4)
0.04(4)
2. Fixed Uiso
   At 1.2 times of:
   All C(H) groups
   At 1.5 times of:
   All C(H,H,H) groups
3. Restrained distances
   C3A-C4A ≈ C3B-C4B ≈ C5A-C4A ≈ C5B-C4B ≈ C6B-C5B ≈ C6A-C5A
≈ C1B-C6B ≈ C1A-C6A
   ≈ C1B-C2B ≈ C1A-C2A ≈ C2B-C3B ≈ C2A-C3A
   with sigma of 0.02
   S1-C1A ≈ S1-C1B
   with sigma of 0.02
   C4A-C7A ≈ C4B-C7B
   with sigma of 0.02
4. Rigid bond restraints
S1, C1A, C1B, C2A, C2B, C3A, C3B, C4A, C4B, C5A, C5B, C6A, C6B, C7A, C7B
   with sigma for 1-2 distances of 0.04 and sigma for 1-3 distances of 0.08
5. Uiso/Uaniso restraints and constraints
S1 ≈ C1A ≈ C1B ≈ C2A ≈ C2B ≈ C3A ≈ C3B ≈ C4A ≈
C4B ≈ C5A ≈ C5B ≈ C6A ≈ C6B ≈ C7A ≈ C7B: within 2A with
sigma of 0.02 and sigma for terminal atoms of 0.04 within 2A
6. Others
Sof(C1B)=Sof(C2B)=Sof(H2B)=Sof(C3B)=Sof(H3B)=Sof(C4B)=Sof(C5B)=Sof(H5B)=
   Sof(C6B)=Sof(H6B)=Sof(C7B)=Sof(H7BC)=Sof(H7BA)=Sof(H7BB)=1-FVAR(1)
   Sof(C1A)=Sof(C2A)=Sof(H2A)=Sof(C3A)=Sof(H3A)=Sof(C4A)=Sof(C5A)=Sof(H5A)=
   Sof(C6A)=Sof(H6A)=Sof(C7A)=Sof(H7AC)=Sof(H7AA)=Sof(H7AB)=FVAR(1)
7. a Aromatic/amide H refined with riding coordinates:

C2A(H2A), C2B(H2B), C3A(H3A), C3B(H3B), C5A(H5A), C5B(H5B), C6A(H6A), C6B(H6B), C9(H9), C10(H10), C11(H11), C12(H12), C16(H15), C17(H16), C26(H22), C25(H23), C24(H24), C23(H25)

7. b Idealised Me refined as rotating group:
C7A(H7AC,H7AA,H7AB), C7B(H7BC,H7BA,H7BB), C22(H19A,H19B,H19C)

This report has been created with Olex2, compiled on 2020.11.12 svn.r5f609507 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Table S4 Crystal data and structure refinement for 5aa

Identification code	**5aa**
Empirical formula	$C_{26}H_{20}N_2O_4S$
Formula weight	456.50
Temperature/K	201.0
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	21.0365(12)
b/Å	7.9263(4)
c/Å	13.4019(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2234.7(2)
Z	4
ρ_{calc}g/cm^3	1.357
μ/mm^{-1}	1.590
F(000)	952.0
Crystal size/mm^3	0.46 × 0.06 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.692 to 136.578
Index ranges	-24 ≤ h ≤ 25, -9 ≤ k ≤ 8, -16 ≤ l ≤ 16
Reflections collected	11043
Independent reflections	3900 [R_{int} = 0.0521, R_{sigma} = 0.0543]
Data/restraints/parameters	3900/339/367
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1037
Final R indexes [all data]	R_1 = 0.0581, wR_2 = 0.1148
Largest diff. peak/hole / e Å^{-3}	0.20/-0.19
Flack parameter	0.04(4)

8. References

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