− Supporting Information –

Cp*Rh(III)-Catalyzed Regioselective Cyclization of Aromatic Amides with Allenes

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1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame-dried glassware. If reaction was not carried out at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: THF (Na-benzophenone), CH_2Cl_2 (CaH_2). Anhydrous triethylamine, DMF, dioxane, EtOH and MeOH were purchased from Acros Organics and stored over molecular sieves under argon.

Proton NMR (^1H) were recorded at 300/400/500 MHz, and Carbon NMR (^{13}C) at 101/126 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

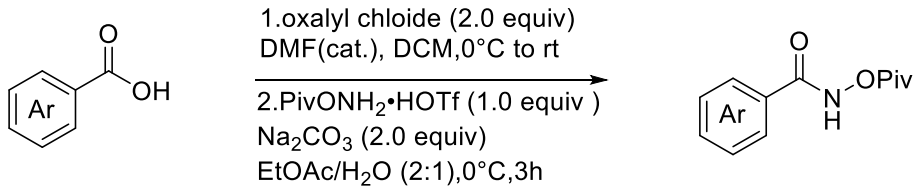
Analytical thin layer chromatography was performed on Polygram SILG/UV254 plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh or 600-800 mesh) with solvents distilled prior to use.

^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicate. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm; d_6-DMSO: δH = 2.50 ppm, δC = 39.52 ppm; d_4-CD_3OD: δH = 3.31 ppm, δC = 49.00 ppm). ESI mass spectra were recorded on a Bruker Daltonics MicroTof. No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of Starting Materials

2.1 Synthesis of *N*-(pivaloyloxy)benzamide

General Procedure 1a

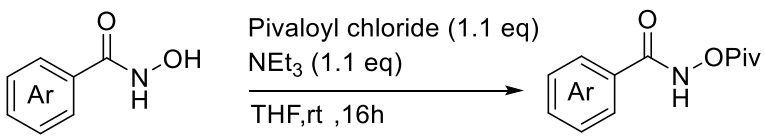


N-(pivaloyloxy)benzamide were prepared according to the literature reported procedures:

1)To a solution of the carboxylic acid (3.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) at 0 ℃ was added dropwise oxalyl chloride (1.0 mL, 6 mmol, 2.0 equiv) followed by a catalytic amount of dry DMF (2 drops). The reaction was allowed to stir at room temperature until completion (typically 2h). The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride.

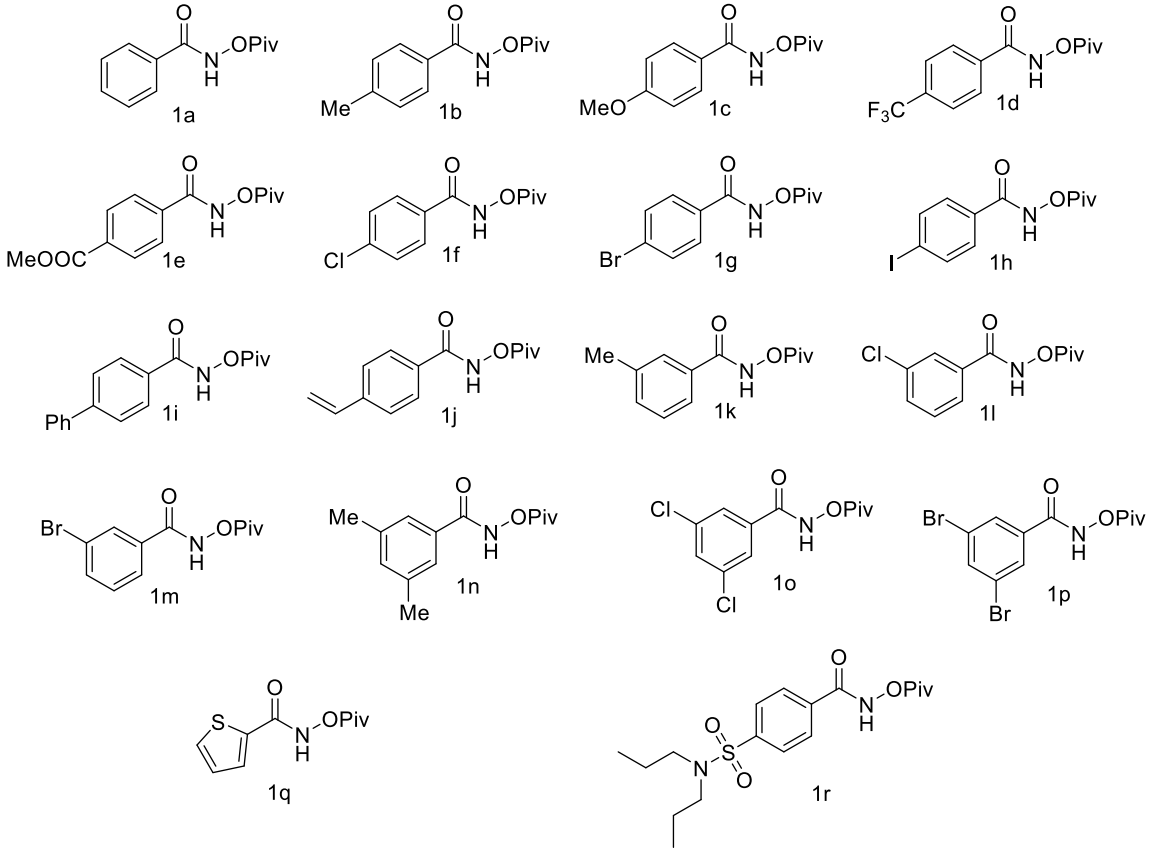
2) *O*-pivaloylhydroxamine triflic acid (801 mg, 3.0 mmol, 1.2 equiv) was added to a biphasic mixture of Na_2CO_3 (635 mg, 6.0 mmol, 2.0 equiv) in a 2:1 mixture of EtOAc (20 mL) and H_2O (10 mL). The resulting solution was cooled to 0℃ followed by dropwise addition of the unpurified acid chloride dissolved in a minimum amount of EtOAc. The flask containing the acid chloride was then rinsed with additional EtOAc. The reaction was allowed to stir for 3h. Afterwards, the phases were separated and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The pure products were obtained without any further purification or purified by column chromatography.

General Procedure 1b



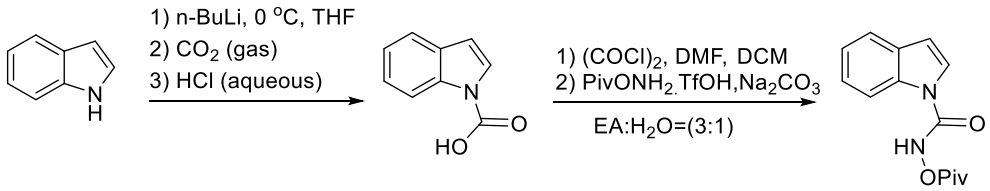
Benzhydroxamic acid (1.37 g, 10.0 mmol, 1.0 equiv), triethylamine (1.5 mL, 11 mmol, 1.1 equiv) and pivaloyl chloride (1.4 mL, 11 mmol, 1.1 equiv) in dry THF (30 mL) was stirred for overnight at rt. EtOAc (20 mL) was added and the reaction was washed with 1 M HCl (20 mL), water (2 x 20 mL) and then brine (20 mL). After drying theorganic layer over Na_2SO_4, evaporation of the solvent gave a white solid. Recrystallization from pentane/EtOAc gave the pure product as a white solid (1.5 g, 6.8 mmol, 68%).

Others have previously reported the synthesis of *N*-(pivaloyloxy)benzamides shown below. Substrates of **1a-1r**[1-3] were synthesized according to the above general procedure, and all the spectroscopic data matched those reported.



2.2 Synthesis of O-pivaloyl 1-indolehydroxamic acid

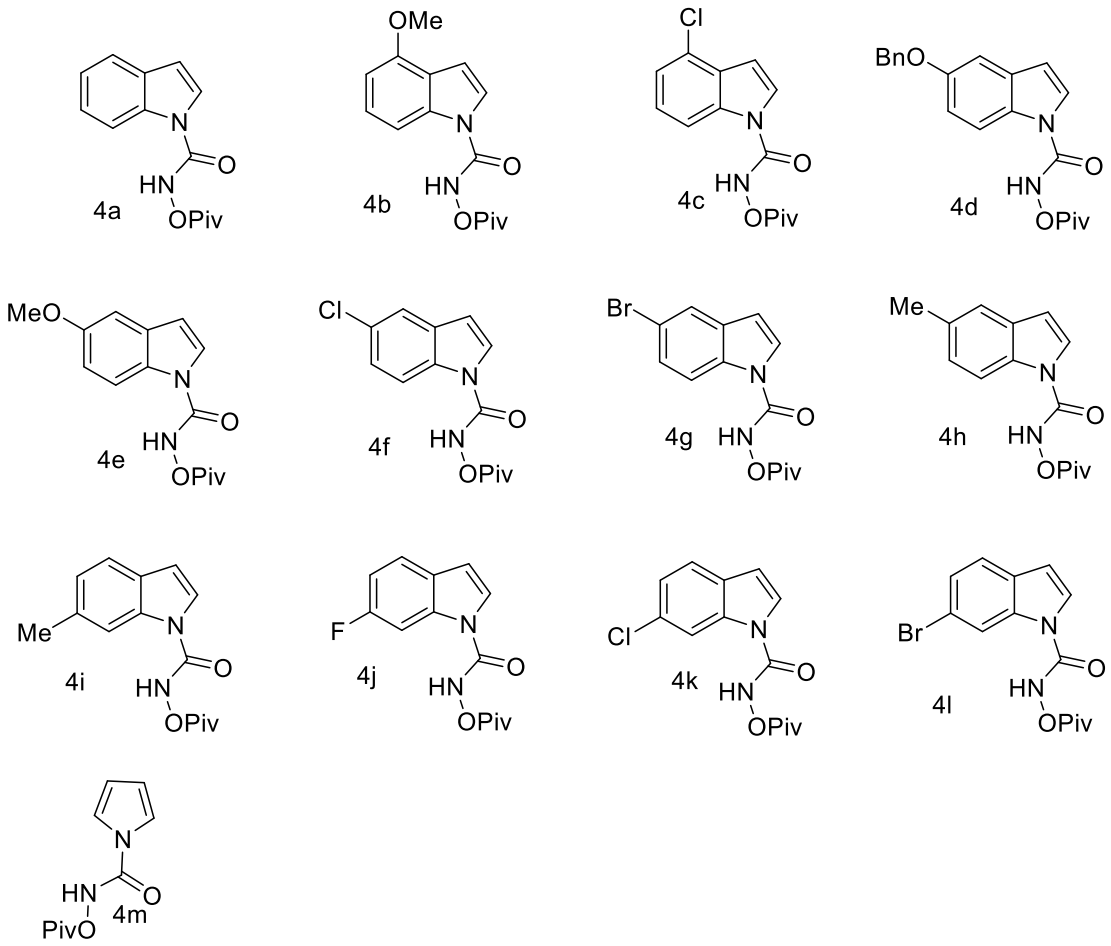
General Procedure 2



The synthesis of 1H-indole-1-carboxylic acid: To a cold (0 ℃) solution of indole (2 g, 17 mmol) in THF (30 mL) was added dropwise a solution of n-BuLi (13 mL, 1.6 M in hexane) under a nitrogen atmosphere. After stirring at 0 ^{o}C for 2 h, the flask is freed of nitrogen by alternately evacuating and repressuring with CO_2 gas to 1 atmosphere. The mixture was stirred for 3 hours, then, quenched carefully with water (5.0 mL). The solution was then concentrated to 10 mL, followed by adding HCl solution (3 M aq.) to adjust the pH to 2. The organic phase was extracted by ethyl acetate and dried over anhydrous Mg_2SO_4. The pure product could be obtained by recrystallization by using hexane as a white solid (2.45 g, 89% yield), which could be used directly in next step without further purification.

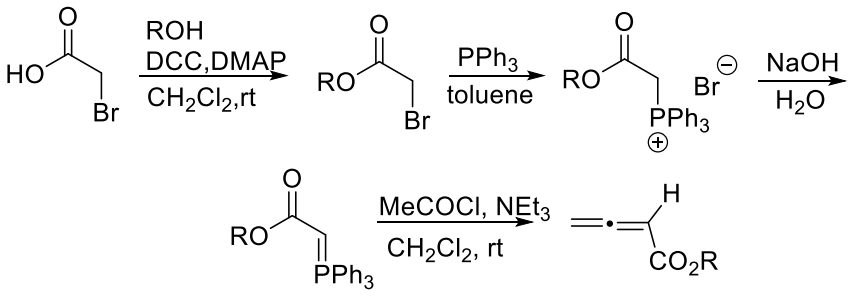
The synthesis of O-pivaloyl 1-indolehydroxamic acid: In a nitrogen-filled flask, the mixture of 1H-indole-1-carboxylic acid (1.61 g, 10 mmol, 1.0 equiv), oxalyl chloride (2.2 mL, 25 mmol, 2.5 equiv) and few drops of DMF (ca. 0.1 equiv) in dichloromethane (15 mL) was stirred 3 h at room temperature. After evaporated under vacuum, the obtained residue was reacted with $PivONH_4$•TfOH (2.67 g, 10 mmol, 1.0 equiv) and Na_2CO_3 (2.14 g, 20 mmol, 2.0 equiv) for 3 h at 0 ^{o}C by using EtOAc/water (20 mL, 3:1) as a solvent. After reaction, the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$. The solvent was removed in vacuo and 3a was obtained by silica gel column chromatography (PE/EtOAc) in 54% yield (white solid, 1.4 g)

Others have previously reported the synthesis of O-pivaloyl 1-indolehydroxamic acid shown below. 4a-4m[4-6]were synthesized according to the above general procedure, and all the spectroscopic data matched those reported.



2.3 Synthesis of allenes 3

General Procedure 3a for Synthesizing Allenoate



Step 1: To a solution of ROH (3 mmol, 1.0 equiv.) and 2-Bromoacetic acid (3.6 mmol, 1.2 equiv.) in CH_2Cl_2 (30 mL) were added DCC (3.6 mmol, 1.2 equiv.) and DMAP (0.3 mmol, 0.1 equiv.) at room temperature. The reaction was stirred overnight. After the alcohol was consumed completely as determined by TLC analysis, the solvent was

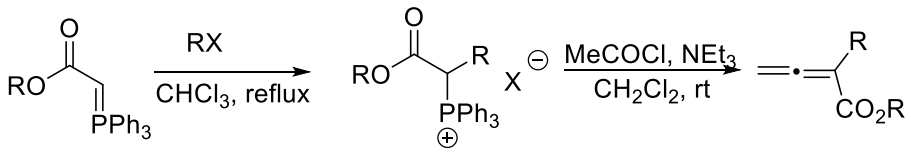
evaporated. The residue was purified by column chromatography on silica gel (5% EtOAc/petroleum ether) to afford bromoacetic esters.

Step 2: To a solution of PPh_3 (1.5 mmol, 1.0 equiv.) in toluene 20 mL) was added bromoacetic esters (1.5 mmol, 1.0 equiv.) at room temperature. The reaction was stirred overnight. The formed precipitate was filtered, washed with toluene and dried t to afford the phosphonium salts.

Step 3: To a solution of the phosphonium salt (1.5 mmol) in a mixed solvent of CH_2Cl_2(20 mL) and H_2O (10 mL) was added 1 drop solution of phenolphthalein in alcohol. sat. aq. NaOH was added dropwise until a permanent pink color was obtained. The mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure to give phosphorus ylide.

Step 4: To a solution of phosphorus ylide (1.0 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) was added Et_3N (1.2 mmol, 1.2 equiv.). The reaction mixture was stirred for 0.5 h at room temperature before adding a solution of acetyl chloride (1.0 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) at room temperature. The reaction was stirred overnight at room temperature. After the phosphorus ylide was consumed completely as determined by TLC analysis, the solvent was evaporated under reduced pressure. The residue was treated with petroleum ether (30 mL) and EtOAc (15 mL) with stirring for 0.5 h. The mixture was filtered and the filtrate was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (5% EtOAc/ petroleum ether) to afford allenoates .

General Procedure 3b

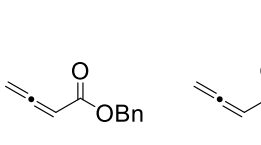


Step 1: To a solution of 2-(triphenylphosphanylidene)acetate in 25 mL $CHCl_3$ was added the RX (1.1 equiv, 1.0 mmol) at room temperature. The reaction mixture was

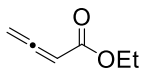
heated under reflux until 2-(triphenylphosphanylidene)acetate disappeared as monitored by TLC. The solvent was evaporated under reduced pressure to afford the phosphonium salts.

Step 2: The mixture of the above phosphonium salt and triethylamine (2.2 equiv, 2.2 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 1 h before addition of a solution of acyl chloride (1.0 equiv, 1.0 mmol) in CH_2Cl_2 (20 mL) slowly over 30 min using a syringe pump. The mixture was stirred overnight before passing through a Buchner funnel packed with silica gel and washing several times with CH_2Cl_2. The combined filtrates were carefully concentrated under reduced pressure. The residue was purified by a flash column chromatography (eluent: 10–15% EtOAc in hexanes) to afford allenoates 2.

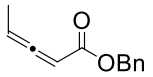
Others have previously reported the synthesis of allenes shown below. **2a-2i**[7-9] were synthesized according to the above general procedure, and all the spectroscopic data matched those reported.



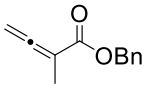
2a



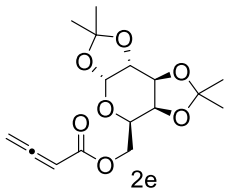
2b



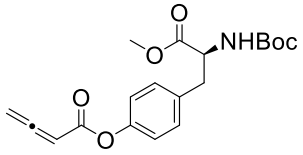
2c



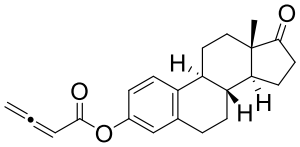
2d



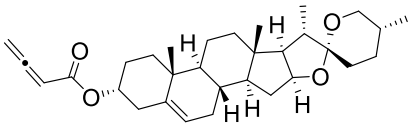
2e



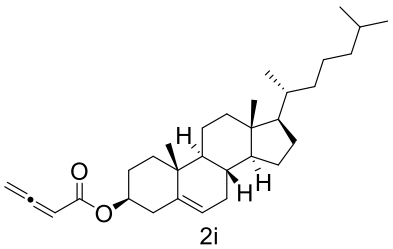
2f



2g

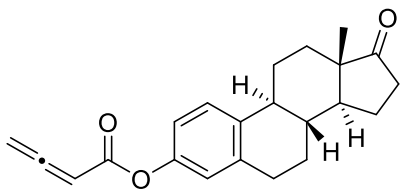


2h



2i

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl buta-2,3-dienoate (2g)

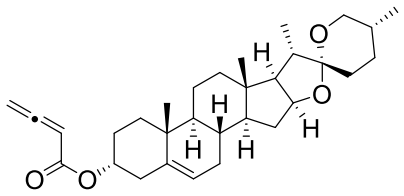


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (s, 1H), 6.86 (d, *J* = 7.1 Hz, 2H), 5.80 (t, *J* = 6.5 Hz, 1H), 5.44 (s, 1H), 5.31 (d, *J* = 6.5 Hz, 1H), 3.58 (s, 1H), 2.90 (dd, *J* = 9.4, 4.3 Hz, 2H), 2.53 (d, *J* = 9.0 Hz, 1H), 2.47 (d, *J* = 7.7 Hz, 1H), 2.42 (s, 1H), 2.27 (s, 1H), 2.16 (t, *J* = 8.7 Hz, 1H), 2.00 (d, *J* = 16.3 Hz, 3H), 1.58 (s, 1H), 1.56 – 1.46 (m, 3H), 1.26 (d, *J* = 6.8 Hz, 1H), 0.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 216.7, 169.9, 164.6, 148.8, 138.1, 137.6, 126.5, 121.6, 118.8, 87.8, 79.8, 50.6, 48.1, 44.3, 38.1, 36.0, 31.7, 29.5, 26.5, 25.9, 21.7, 14.0.

HRMS (ESI): m/z calculated for $C_{31}H_{45}O_4^+$ $[M+H]^+$, 337.1798; found, 337.1805

(4R,5'R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl buta-2,3-dienoate（2h）



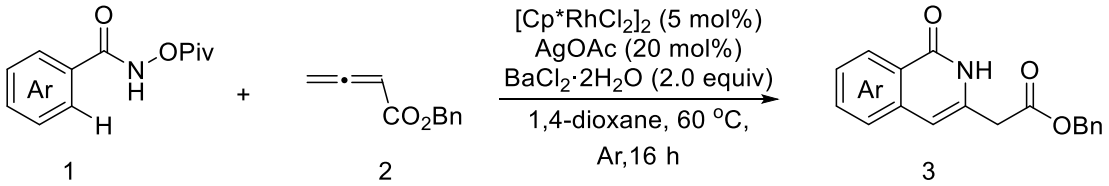
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.60 (t, *J* = 6.5 Hz, 1H), 5.37 (d, *J* = 5.1 Hz, 1H), 5.19 (d, *J* = 6.5 Hz, 2H), 4.65 (dp, *J* = 11.0, 5.3 Hz, 1H), 4.40 (q, *J* = 7.4 Hz, 1H), 3.50 – 3.31 (m, 2H), 2.36 (s, 2H), 1.98 (dd, *J* = 11.6, 6.6 Hz, 2H), 1.89 – 1.82 (m, 3H), 1.79 (s, 1H), 1.78 – 1.69 (m, 3H), 1.66 (d, *J* = 4.3 Hz, 1H), 1.63 – 1.57 (m, 5H), 1.31 (s, 1H), 1.29 – 1.22 (m, 2H), 1.19 – 1.09 (m, 3H), 1.03 (s, 3H), 0.96 (d, *J* = 6.9 Hz, 4H), 0.77 (d, *J* = 4.7 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 215.78, 165.28, 139.78, 122.55, 109.38, 88.50, 80.92, 79.35, 74.66, 66.95, 62.22, 56.56, 50.06, 41.74, 40.38, 39.84, 38.17, 37.07, 36.85, 32.17, 31.96, 31.53, 30.41, 29.81, 28.93, 27.82, 20.94, 19.46, 17.25, 16.39, 14.64.

HRMS (ESI): m/z calculated for $C_{31}H_{45}O_4^+$ $[M+H]^+$,481.3313; found,481.3323.

3. General Procedure for the synthesis of products

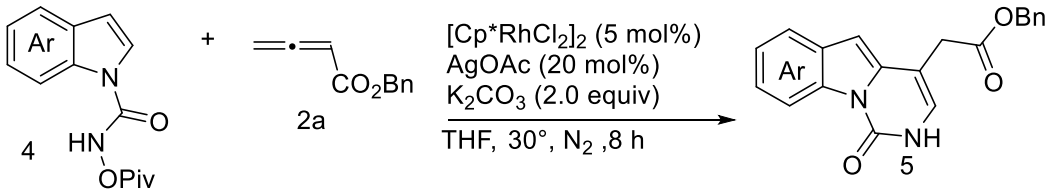
3.1 General procedure 4 for the synthesis of isoquinolin-1(2*H*)-ones 3



1 2 3

To a 10 mL reaction tube equipped with a stirring bar, corresponding N–OPiv benzamide (1, 0.2 mmol, 1.0 equiv), allenes 2 (1.2 equiv, 41.8 mg), $[Cp^*RhCl_2]_2$ (5 mol%, 6.1 mg), AgOAc (20 mol%, 6.7 mg), $BaCl_2 \cdot 2H_2O$ (2.0 equiv，98 mg) and 1,4-dioxane (2 ml) were added under Ar atmosphere. Then the reaction tube was capped and placed in a pre-heated oil bath at 60 °C for the given time. After completion of the reaction as monitored by TLC, Then saturated aqueous NH_4Cl was added to quench the reaction. The aqueous layer was then extracted with EtOAc, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified using column chromatography on silica gel (300-400 mesh), and Petroleum/EA mixture as eluent to yield the corresponding isoquinolin-1(2*H*)-ones 3.

3.2 General procedure 5 for the synthesis of pyrimido[1,6-a]indol-1(2*H*)-ones (5)



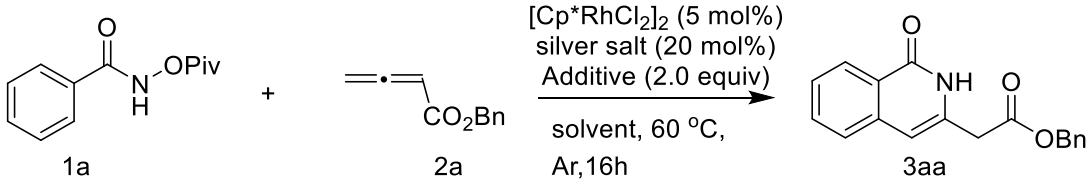
4 2a 5

To a 10 mL reaction tube equipped with a stirring bar, corresponding N-(pivaloyloxy)indol (0.2 mmol, 1.0 equiv), allenes 2 (1.5 equiv, 52.6 mg), $[Cp^*RhCl_2]_2$

(5 mol%, 6.1 mg), AgOAc (20 mol%, 6.7 mg), K_2CO_3 (2.0 equiv，55 mg) and THF (2 ml) were added under N_2 atmosphere. Then the reaction tube was capped and placed in a pre-heated oil bath at 30 ^oC for the given time. After completion of the reaction as monitored by TLC, Transfer to 25 ml flask and concentrate. The residue was purified using column chromatography on silica gel (300-400 mesh), and The residue was purified by flash column chromatography on silica gel using Petroleum ether /EtOAc as eluant.

3.3 Optimization conditions

3.3.1 Optimization of the Rh(III)-caltlyzed regioselective annulation of benzamide with allene

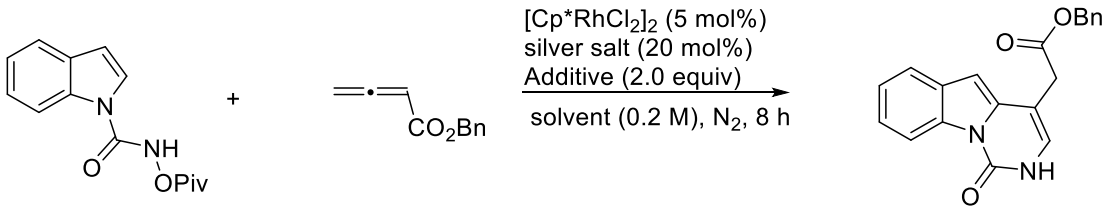


1a 2a 3aa

Entry	1a:2a	Catalyst	Silver salt (x 20 mol%)	Additive（2.0 equiv）	Solvent (0.2 M)	Yield (%)
1	1:1	$[Cp^*RhCl_2]_2$	$AgSbF_6$	NaOAc	CH_3CN	44%
2	1:1	$[Cp^*RhCl_2]_2$	$AgBF_6$	NaOAc	CH_3CN	40%
3	1:1	$[Cp^*RhCl_2]_2$	AgOAc	NaOAc	CH_3CN	49%
4	1:1	$[Cp^*RhCl_2]_2$	AgOAc	PivOH	CH_3CN	39%
5	1:1	$[Cp^*RhCl_2]_2$	AgOAc	$Zn(OAc)_2$	CH_3CN	45%
6	1:1	$[Cp^*RhCl_2]_2$	AgOAc	$BaCl_2·2H_2O$	CH_3CN	56%
7	1:1	$[Cp^*RhCl_2]_2$	AgOAc	$BaCl_2·2H_2O$	THF	66%
8	1:1	$[Cp^*RhCl_2]_2$	AgOAc	$BaCl_2·2H_2O$	DCM	35%
9	1:1	$[Cp^*RhCl_2]_2$	AgOAc	$BaCl_2·2H_2O$	1,4-dioxane	71%
10	1:1.2	$[Cp^*RhCl_2]_2$	AgOAc	$BaCl_2·2H_2O$	1,4-dioxane	83%
11	1:1.2	$[Cp^*RhCl_2]_2$	AgOAc	K_2CO_3	THF	26%
12	1:1.2	$[Cp^*IrCl_2]_2$	AgOAc	$BaCl_2·2H_2O$	1,4-dioxane	-
13	1:1.2	$Pd(OAc)_2$	AgOAc	$BaCl_2·2H_2O$	1,4-dioxane	-
14	1:1.2	$[Cp^*Co(CO)I_2]_2$	AgOAc	$BaCl_2·2H_2O$	1,4-dioxane	-

Conditions: 1a (0.2 mmol), isolated yields

3.3.2 Optimization of the Rh(III)-caltlyzed regioselective annulation of indole-1-carboxamide with allene



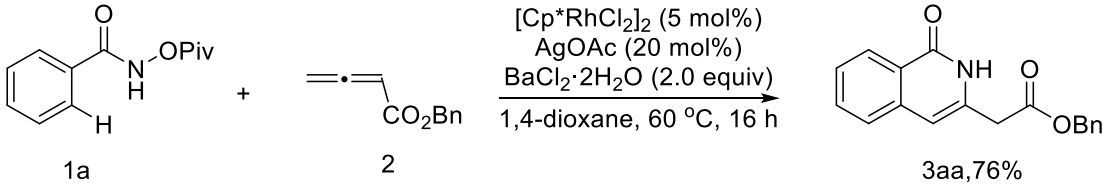
4a (0.2 mol, 1.0 equiv) **2a** (0.3 mol, 1.5 equiv) 5aa

Entry	Catalyst	Silver salt (20 mol%)	Additive（2.0 equiv）	Solvent	Yield (%)
1	$[Cp^*RhCl_2]_2$	AgOAc	AcOH	CH_3CN	15%
2	$[Cp^*RhCl_2]_2$	AgOAc	NaOAc	CH_3CN	-
3	$[Cp^*RhCl_2]_2$	AgOAc	K_3PO_4	CH_3CN	45%
4	$[Cp^*RhCl_2]_2$	AgOAc	$Zn(OAc)_2$	CH_3CN	12%
5	$[Cp^*RhCl_2]_2$	AgOAc	NaH_2PO_4	CH_3CN	20%
6	$[Cp^*RhCl_2]_2$	AgOAc	$BaCl_2 \cdot 2H_2O$	THF	-
7	$[Cp^*RhCl_2]_2$	AgOAc	K_3PO_4	MeOH	-
8	$[Cp^*RhCl_2]_2$	AgOAc	K_3PO_4	DCE	-
9	$[Cp^*RhCl_2]_2$	AgOAc	K_3PO_4	1,4-dioxane	42%
10	$[Cp^*RhCl_2]_2$	AgOAc	K_3PO_4	DCM	43%
11	$[Cp^*RhCl_2]_2$	AgOAc	K_3PO_4	THF	71%
12	$[Cp^*RhCl_2]_2$	$AgSbF_6$	K_3PO_4	THF	30%
13	$[Cp^*RhCl_2]_2$	Ag_2CO_3	K_3PO_4	THF	60%
14	$[Cp^*RhCl_2]_2$	$AgNO_3$	K_3PO_4	THF	44%
15	$[Cp^*RhCl_2]_2$	AgOAc	K_2HPO_4	THF	27%
16	$[Cp^*RhCl_2]_2$	AgOAc	KO^tBu	THF	68%
17	$[Cp^*RhCl_2]_2$	AgOAc	K_2CO_3	THF	87%
18	$[Cp^*RhCl_2]_2$	AgOAc	$BaCl_2 \cdot 2H_2O$	1,4-dioxane	-
19	$[Cp^*IrCl_2]_2$	AgOAc	K_2CO_3	THF	-
20	$Pd(OAc)_2$	AgOAc	K_2CO_3	THF	-
21	$[Cp^*Co(CO)I_2]_2$	AgOAc	K_2CO_3	THF	-

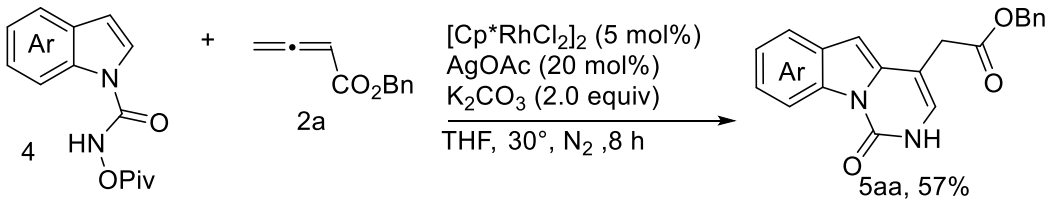
Conditions: 4a (0.2 mmol), isolated yields

4.Application and Preliminary mechanistic investigation

4.1 Large-scale synthesis



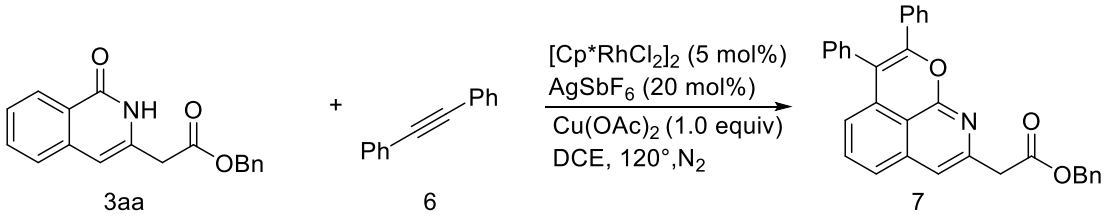
To a 100 mL reaction tube equipped with a stirring bar, corresponding N–OPiv benzamide 1 (1 mmol, 1.0 equiv), allenyl 2a (1.2 equiv, 209 mg), $[Cp^*RhCl_2]_2$ (5 mol%, 30 mg), AgOAc (20 mol%, 34 mg), $BaCl_2 \cdot 2H_2O$ (2.0 equiv，490 mg) and 1,4-dioxane(10 ml) were added under Ar atmosphere. Then the reaction tube was capped and placed in a pre-heated oil bath at 60 ℃ for the given time. After completion of the reaction as monitored by TLC, Then saturated aqueous NH_4Cl was added to quench the reaction. The aqueous layer was then extracted with EtOAc, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using Petroleum ether/EtOAc as eluant afforded as oil 3aa (223 mg, 76%)



To a 35 mL reaction tube equipped with a stirring bar, corresponding N–OPiv benzamide 1 (1 mmol, 1.0 equiv), allenyl 2a (1.5 equiv, 261 mg), $[Cp^*RhCl_2]_2$ (5 mol%, 30 mg), AgOAc (20 mol%, 34 mg), K_2CO_3 (2.0 equiv，276 mg) and THF (10 ml) were added under N_2 atmosphere. Then the reaction tube was capped and placed in a pre-heated oil bath at 30 °C for the given time. After completion of the reaction as monitored by TLC, Transfer to 25 ml flask and concentrate. The residue was purified using column chromatography on silica gel (300-400 mesh), and The residue was

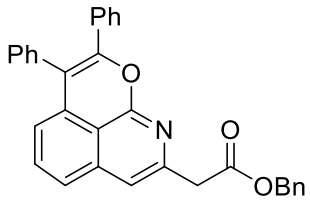
purified by flash column chromatography on silica gel using Petroleum ether /EtOAc as eluant afforded as oil 5aa (188 mg, 57%)

4.2 Late-state functionalization of product



To an oven dried screw cap reaction tube, isoquinolin-1(2*H*)-one derivative 3aa (0.1 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol%, 3.1 mg) , $Cu(OAc)_2 \cdot H_2O$ (1.2 equiv, 0.1 mmol, 18.0 mg) ,diphenylacetylene (1.0 equiv, 0.1 mmol, 17.8 mg) and DCE (1.0 ml) were added under N_2 atmosphere. After that, the reaction mixture was stirred at 110 ^oC for 12 hours. The crude mixture was diluted with ethyl acetate, concentrated and purified by column chromatography on silica gel (300-400 mesh) and ethyl acetate /hexane as eluent (35/65) to yield corresponding annulation product in 68% yield (32.0 mg).

benzyl 2-(2,3-diphenylpyrano[4,3,2-ij]isoquinolin-8-yl)ethaneperoxoate(7)

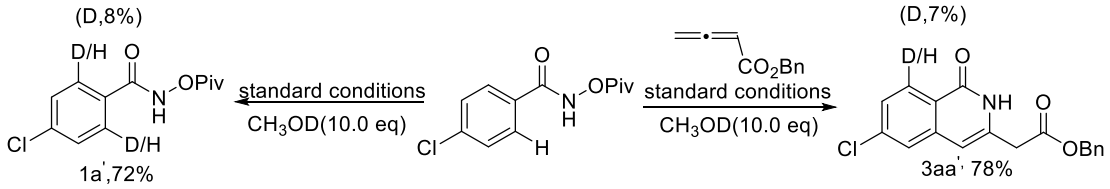


^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 10H), 7.14 (s, 3H), 7.10 (d, *J* = 6.3 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 2H), 7.02 (s, 1H), 6.61 (d, *J* = 7.4 Hz, 1H), 5.09 (s, 2H), 3.78 (s, 2H).

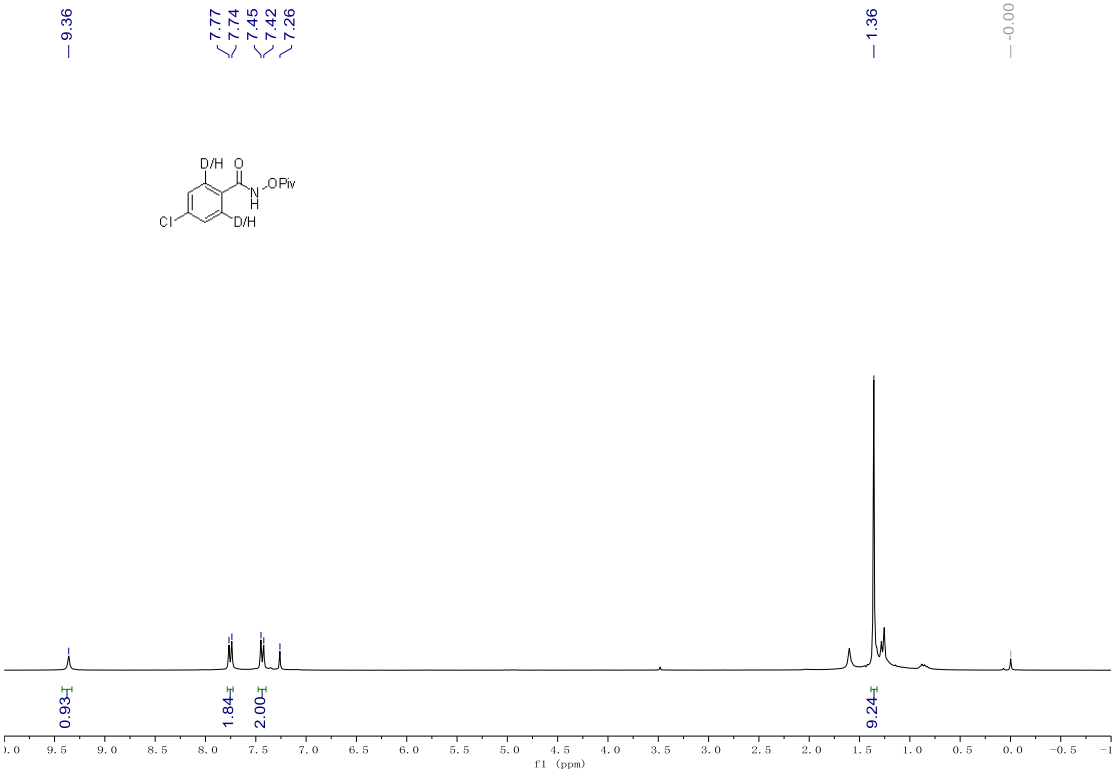
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 159.6, 150.9, 147.6, 139.5, 136.0, 134.9, 134.4, 133.3, 132.6, 130.9, 129.5, 129.3, 128.9, 128.7, 128.4, 128.3, 128.1, 127.8, 121.0, 117.9, 117.9, 116.1, 114.6, 66.9, 43.6.

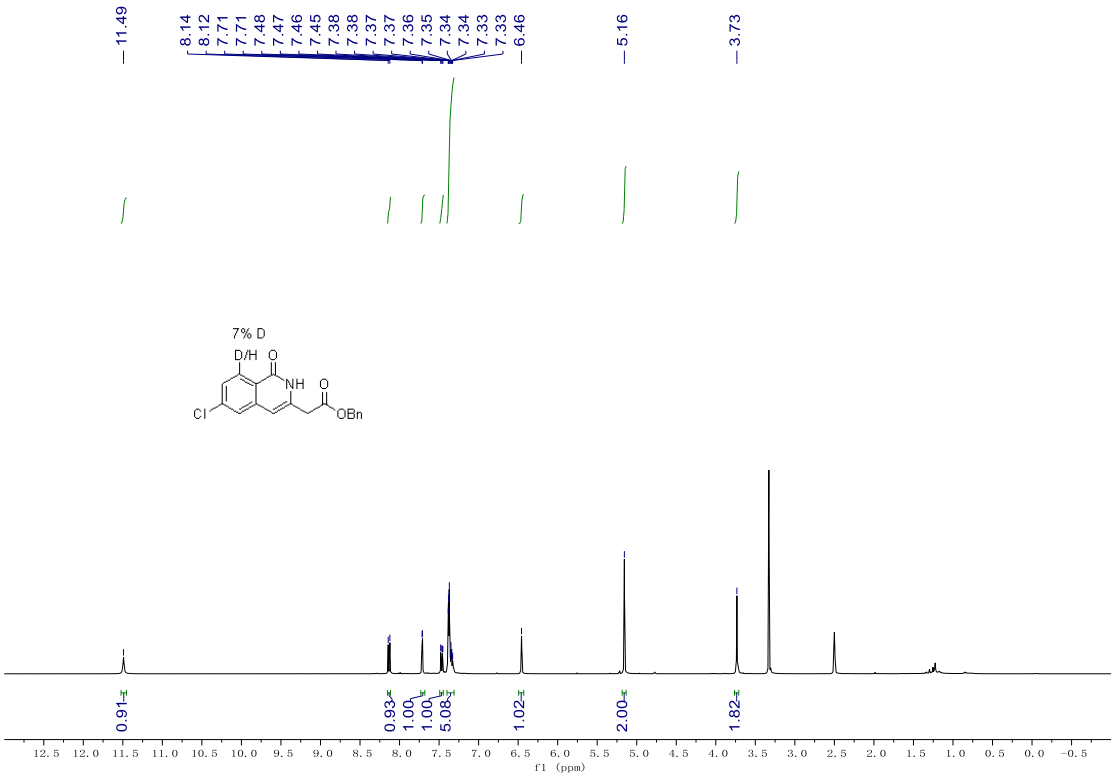
HRMS (ESI): m/z calculated for $C_{32}H_{24}NO_4^+$ $[M+H]^+$,486.1700; found,486.1705

4.3 Deuterium exchange experiment



N–OPiv benzamide 1a (0.1 mmol, 1.0 equiv) was reacted with allenyl 2a in presence of CH_3COD (10.0 equiv) under standard conditions. The reaction was monitored by TLC and stopped after 6 h., followed by column chromatography of the crude mixture gave the isoquinolin-1-(2*H*)-one product 3aa' in 78% yield with 7% deuterium incorporation in the ortho proton. When the reaction was carried out in absence of allene coupling partner, the starting amide 1a' was isolated in 72% yield with 8% deuterium incorporation.




11.49
8.14
8.12
7.71
7.71
7.48
7.47
7.46
7.45
7.38
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
6.46
5.16
3.73
7% D
D/H
O
NH
O
Cl
OBn
0.91
0.93
1.00
1.00
5.08
1.02
2.00
1.82
f1 (ppm)

5. X-Ray crystal data for compound 3oa and 5ja.

Crystal structure of 3oa

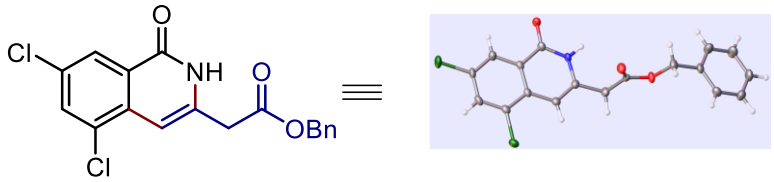


Figure S1: The crystal structure of 3oa by X-ray analysis.

X-ray-quality crystal was obtained by slow diffusion of Petroleum ether into a methyl alcohol solution of 5ja at room temperature under air. Thermal ellipsoids drawn at the 50% probability level. A suitable crystal was selected and on a **SuperNova, Dual, Cu at zero, AtlasS2** diffractometer. The crystal was kept at 150.00(16) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Crystal structure determination of 3oa

Crystal Data for $C_{18}H_{13}Cl_2NO_3$ (M =362.19 g/mol): monoclinic, space group C2/c (no. 15), a = 30.7988(15) Å, b = 4.6614(3) Å, c = 22.7529(15) Å, β = 94.524(5) °, V = 3256.4(3) Å^3, Z = 8, T = 150.00(16) K, μ(Mo Kα) = 0.415 mm^{-1}, $Dcalc$ = 1.478 g/cm^3, 6399 reflections measured (4.294° ≤ 2Θ ≤ 49.996°), 2875 unique (R_{int} = 0.0380, R_{sigma} = 0.0519) which were used in all calculations. The final R_1 was 0.0392 (I > 2σ(I)) and wR_2 was 0.0970 (all data).

Table 1 Crystal data and structure refinement for 3oa.

Identification code	3oa

Empirical formula	$C_{18}H_{13}Cl_2NO_3$
Formula weight	362.19
Temperature/K	150.00(16)
Crystal system	monoclinic
Space group	C2/c
a/Å	30.7988(15)
b/Å	4.6614(3)
c/Å	22.7529(15)
α/°	90
β/°	94.524(5)
γ/°	90
Volume/Å^3	3256.4(3)
Z	8
ρ_{calc}g/cm^3	1.478
μ/mm^{-1}	0.415
F(000)	1488.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.294 to 49.996
Index ranges	$-22 \leq h \leq 36$, $-4 \leq k \leq 5$, $-27 \leq l \leq 26$
Reflections collected	6399
Independent reflections	2875 [R_{int} = 0.0380, R_{sigma} = 0.0519]
Data/restraints/parameters	2875/0/217
Goodness-of-fit on F^2	1.061

Final R indexes [I>=2σ (I)] $R_1 = 0.0392$, $wR_2 = 0.0900$

Final R indexes [all data] $R_1 = 0.0481$, $wR_2 = 0.0970$

Largest diff. peak/hole / e $Å^{-3}$ 0.22/-0.23

Refinement model description

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for hn-cl. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	4698.0(2)	6703.0(13)	6068.7(3)	38.01(19)
Cl2	4313.1(2)	-442.8(10)	4256.4(2)	29.52(17)
O1	3010.1(4)	8081(3)	5401.2(6)	27.3(4)
O2	2621.1(5)	5733(3)	3200.0(7)	29.5(4)
O3	2014.4(4)	3085(3)	3196.3(6)	27.1(4)
N1	2856.9(5)	4963(3)	4647.6(7)	21.9(4)
C1	3137.7(6)	6213(4)	5065.6(9)	22.1(5)
C2	3586.2(6)	5156(4)	5092.3(9)	20.6(4)
C3	3888.0(6)	6267(4)	5524.6(9)	24.4(5)
C4	4308.6(7)	5290(4)	5553.6(9)	25.8(5)
C5	4441.3(7)	3204(4)	5165.1(9)	25.6(5)
C6	4143.0(7)	2128(4)	4743.4(9)	23.5(5)
C7	3704.3(6)	3052(4)	4688.4(9)	20.5(5)
C8	3381.8(7)	1939(4)	4262.3(9)	23.3(5)
C9	2966.2(7)	2877(4)	4254.4(9)	22.1(5)
C10	2595.4(7)	1713(4)	3858.2(10)	26.0(5)
C11	2420.5(6)	3776(4)	3388.6(9)	20.9(5)
C12	1815.2(7)	4891(5)	2725.3(10)	31.1(5)
C13	1376.3(7)	3646(4)	2548.9(9)	26.0(5)
C14	1326.1(7)	1616(4)	2105.6(10)	29.8(5)
C15	920.6(7)	424(5)	1950.4(10)	34.9(6)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for hn-cl. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C16	564.9(7)	1273(5)	2239.0(10)	35.5(6)
C17	612.1(8)	3286(5)	2679.3(11)	40.8(6)
C18	1014.2(8)	4476(5)	2830.8(11)	37.6(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for hn-cl. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	22.1(3)	55.3(4)	34.9(4)	-4.6(3)	-9.0(2)	-2.3(3)
Cl2	25.2(3)	26.3(3)	37.4(3)	0.5(2)	4.9(2)	5.6(2)
O1	18.5(8)	36.3(8)	27.0(8)	-5.7(7)	2.3(6)	1.8(6)
O2	23.6(8)	28.6(8)	35.8(9)	4.9(7)	-0.5(7)	-7.8(7)
O3	17.5(8)	33.0(8)	29.7(9)	6.4(7)	-5.0(6)	-5.4(6)
N1	13.3(9)	27.2(9)	24.9(10)	1.0(8)	-0.6(7)	0.0(7)
C1	17.0(11)	26.1(11)	23.7(11)	3.5(9)	3.6(9)	-2.3(9)
C2	16.1(10)	23.6(10)	22.2(11)	7.6(9)	1.8(8)	-0.7(8)
C3	20.3(12)	30.4(11)	22.3(11)	1.4(9)	1.3(9)	-1.6(9)
C4	17.4(11)	32.6(11)	26.3(12)	6.6(10)	-5.7(9)	-3.7(9)
C5	16.6(11)	28.6(11)	31.5(13)	10.1(10)	1.3(9)	1.9(9)
C6	20.0(11)	22.7(10)	28.0(12)	7.0(9)	3.7(9)	0.6(9)
C7	18.3(11)	20.8(10)	22.2(11)	7.5(8)	0.7(9)	-1.4(8)
C8	23.1(12)	20.4(10)	26.2(12)	3.4(9)	2.1(9)	-0.4(9)
C9	23.1(11)	21.6(10)	21.4(11)	3.6(9)	0.2(9)	-2.9(9)
C10	23.0(12)	22.8(10)	31.5(13)	1.7(9)	-1.3(9)	-4.7(9)
C11	16.6(11)	22.1(10)	23.8(11)	-6.4(9)	1.1(9)	-1.2(9)
C12	26.7(13)	35.0(12)	30.5(13)	6.6(10)	-6.0(10)	-1.6(10)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for hn-cl. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C13	21.1(11)	28.9(11)	26.7(12)	5.5(10)	-5.5(9)	0.2(9)
C14	22.8(12)	35.5(12)	31.3(13)	0.5(10)	3.8(10)	3.9(10)
C15	33.7(14)	39.4(13)	30.6(13)	-8.1(11)	-2.7(10)	-2.9(11)
C16	20.3(12)	47.0(14)	38.2(14)	-1.4(12)	-4.3(10)	-5.3(10)
C17	22.7(13)	57.2(16)	43.1(16)	-12.5(13)	6.6(11)	0.4(11)
C18	31.1(14)	46.8(14)	34.9(14)	-15.0(11)	2.3(11)	-0.6(11)

Table 4 Bond Lengths for 3oa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C4	1.739(2)	C5	C6	1.370(3)
Cl2	C6	1.741(2)	C6	C7	1.414(3)
O1	C1	1.242(2)	C7	C8	1.430(3)
O2	C11	1.200(2)	C8	C9	1.351(3)
O3	C11	1.332(2)	C9	C10	1.499(3)
O3	C12	1.459(2)	C10	C11	1.505(3)
N1	C1	1.365(3)	C12	C13	1.496(3)
N1	C9	1.381(3)	C13	C14	1.383(3)
C1	C2	1.463(3)	C13	C18	1.385(3)
C2	C3	1.398(3)	C14	C15	1.387(3)
C2	C7	1.411(3)	C15	C16	1.379(3)
C3	C4	1.370(3)	C16	C17	1.372(3)
C4	C5	1.396(3)	C17	C18	1.376(3)

Table 5 Bond Angles for 3oa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O3	C12	115.55(15)	C6	C7	C8	123.88(19)

Table 5 Bond Angles for 3oa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C9	125.35(17)	C9	C8	C7	119.89(19)
O1	C1	N1	120.91(18)	N1	C9	C10	115.55(17)
O1	C1	C2	123.64(18)	C8	C9	N1	119.89(18)
N1	C1	C2	115.44(17)	C8	C9	C10	124.51(19)
C3	C2	C1	118.51(18)	C9	C10	C11	114.12(16)
C3	C2	C7	121.61(18)	O2	C11	O3	124.27(18)
C7	C2	C1	119.87(18)	O2	C11	C10	125.02(18)
C4	C3	C2	119.0(2)	O3	C11	C10	110.68(16)
C3	C4	Cl1	120.38(17)	O3	C12	C13	106.96(16)
C3	C4	C5	121.59(19)	C14	C13	C12	120.5(2)
C5	C4	Cl1	118.01(16)	C14	C13	C18	118.8(2)
C6	C5	C4	118.98(19)	C18	C13	C12	120.7(2)
C5	C6	Cl2	118.62(16)	C13	C14	C15	120.5(2)
C5	C6	C7	122.25(19)	C16	C15	C14	119.8(2)
C7	C6	Cl2	119.13(15)	C17	C16	C15	120.1(2)
C2	C7	C6	116.60(18)	C16	C17	C18	120.0(2)
C2	C7	C8	119.51(18)	C17	C18	C13	120.9(2)

Table 6 Torsion Angles for 3oa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C4	C5	C6	-177.94(15)	C5	C6	C7	C2	0.0(3)
Cl2	C6	C7	C2	-179.49(14)	C5	C6	C7	C8	-178.68(18)
Cl2	C6	C7	C8	1.9(3)	C6	C7	C8	C9	177.72(18)
O1	C1	C2	C3	1.1(3)	C7	C2	C3	C4	0.3(3)
O1	C1	C2	C7	-179.20(18)	C7	C8	C9	N1	1.7(3)
O3	C12	C13	C14	-90.6(2)	C7	C8	C9	C10	-175.35(17)
O3	C12	C13	C18	88.6(2)	C8	C9	C10	C11	-111.1(2)
N1	C1	C2	C3	-177.71(17)	C9	N1	C1	O1	179.92(18)
N1	C1	C2	C7	2.0(3)	C9	N1	C1	C2	-1.2(3)
N1	C9	C10	C11	71.7(2)	C9	C10	C11	O2	23.8(3)

Table 6 Torsion Angles for 3oa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	N1	C9	C8	-0.6(3)	C9	C10	C11	O3	-157.99(17)
C1	N1	C9	C10	176.71(17)	C11	O3	C12	C13	176.35(17)
C1	C2	C3	C4	179.95(18)	C12	O3	C11	O2	0.0(3)
C1	C2	C7	C6	-179.71(17)	C12	O3	C11	C10	-178.17(17)
C1	C2	C7	C8	-1.0(3)	C12	C13	C14	C15	178.75(19)
C2	C3	C4	Cl1	177.85(15)	C12	C13	C18	C17	-178.4(2)
C2	C3	C4	C5	-0.4(3)	C13	C14	C15	C16	0.2(3)
C2	C7	C8	C9	-0.9(3)	C14	C13	C18	C17	0.8(3)
C3	C2	C7	C6	0.0(3)	C14	C15	C16	C17	-0.1(4)
C3	C2	C7	C8	178.69(18)	C15	C16	C17	C18	0.4(4)
C3	C4	C5	C6	0.4(3)	C16	C17	C18	C13	-0.8(4)
C4	C5	C6	Cl2	179.32(15)	C18	C13	C14	C15	-0.5(3)
C4	C5	C6	C7	-0.1(3)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3oa.

Atom	*x*	*y*	*z*	U(eq)
H1	2583.7	5533.48	4626.94	26
H3	3802.6	7677.16	5794.09	29
H5	4733.92	2542.07	5192.83	31
H8	3459.46	541.95	3985.25	28
H10A	2356.12	1168.91	4102.1	31
H10B	2693.89	-49.66	3665.65	31
H12A	1996.89	4906.67	2385.28	37
H12B	1785.81	6885.41	2866.47	37
H14	1570.92	1034.8	1906	36
H15	888.09	-973.13	1646.11	42
H16	286.69	461.9	2132.92	43
H17	367.09	3858.75	2879.55	49
H18	1043.79	5886.53	3132.7	45

Crystal structure of 5ja

Figure S2: The crystal structure of 5ja by X-ray analysis.

X-ray-quality crystal was obtained by slow diffusion of Petroleum ether into a methyl alcohol solution of 5ja at room temperature under air. Thermal ellipsoids drawn at the 50% probability level. A suitable crystal was selected on a **SuperNova, Dual, Cu at zero, AtlasS2** diffractometer. The crystal was kept at 150.00(16) K during data collection. Using Olex2 , the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Crystal structure determination of 5ja

Crystal Data for $C_{20}H_{15}BrN_2O_3$ (M =411.25 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 5.3629(4) Å, b = 17.7232(15) Å, c = 18.1847(18) Å, β = 94.638(8) °, V = 1722.7(3) Å^3, Z = 4, T = 150.00(18) K, μ(Cu Kα) = 3.452 mm^{-1}, *Dcalc* = 1.586 g/cm^3, 6971 reflections measured (6.976° ≤ 2Θ ≤ 147.824 °), 3388 unique (R_{int} = 0.1122, R_{sigma} = 0.1316) which were used in all calculations. The final R_1 was 0.0913 (I > 2σ(I)) and wR_2 was 0.2834 (all data).

Table 8 Crystal data and structure refinement for 5ja

Identification code	5ja
Empirical formula	$C_{20}H_{15}BrN_2O_3$

Formula weight	411.25
Temperature/K	150.00(18)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.3629(4)
b/Å	17.7232(15)
c/Å	18.1847(18)
α/°	90
β/°	94.638(8)
γ/°	90
Volume/$Å^3$	1722.7(3)
Z	4
$\rho_{calc}g/cm^3$	1.586
μ/mm^{-1}	3.452
F(000)	832.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.976 to 147.824
Index ranges	$-6 \leq h \leq 5$, $-21 \leq k \leq 19$, $-20 \leq l \leq 22$
Reflections collected	6971
Independent reflections	3388 [R_{int} = 0.1122, R_{sigma} = 0.1316]
Data/restraints/parameters	3388/363/235
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0913, wR_2 = 0.2469

Final R indexes [all data]	R_1 = 0.1268, wR_2 = 0.2834
Largest diff. peak/hole / e Å^{-3}	1.68/-2.24

Table 9 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for br0525. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	10417.8(14)	3123.5(4)	6826.8(4)	38.2(3)
O1	2847(7)	4660(2)	5463(2)	20.3(8)
O2	7279(7)	7896(2)	5679(2)	26.7(9)
O3	5256(7)	8882(2)	6126(2)	20.8(8)
N1	4971(8)	5588(3)	6123(2)	15.7(8)
N2	1402(9)	5872(3)	5378(2)	19.5(8)
C1	8436(10)	5682(3)	6908(3)	18.7(9)
C2	10580(11)	5408(3)	7313(3)	21.6(10)
C3	11122(10)	4644(3)	7278(3)	21.5(10)
C4	9520(11)	4156(3)	6862(3)	23.1(10)
C5	7407(10)	4401(3)	6449(3)	18.9(9)
C6	6900(10)	5171(3)	6475(3)	17.7(9)
C7	7358(10)	6420(3)	6809(3)	20.5(9)
C8	5284(10)	6357(3)	6340(3)	18.2(9)
C9	3426(11)	6877(3)	6053(3)	19.8(9)
C10	1533(10)	6619(3)	5591(3)	20.2(9)
C11	3048(9)	5325(3)	5648(3)	15.1(8)
C12	3475(10)	7689(3)	6306(3)	20.4(9)
C13	5562(10)	8148(3)	6000(3)	19.1(9)
C14	7074(10)	9371(3)	5826(3)	20.6(10)
C15	6347(10)	10178(3)	5912(3)	19.2(9)
C16	4326(10)	10414(3)	6281(3)	21.8(10)
C17	3830(11)	11184(3)	6347(3)	23.8(10)
C18	5303(12)	11719(4)	6049(3)	26.2(11)
C19	7325(11)	11482(4)	5687(3)	27.5(11)
C20	7872(11)	10719(3)	5612(3)	23.6(10)

Table 10 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for br0525. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	36.8(5)	24.4(5)	50.3(5)	0.7(3)	-15.6(3)	11.9(3)
O1	15.0(16)	16.6(13)	27.5(17)	-2.7(12)	-9.9(13)	-0.9(12)
O2	18.6(16)	23.4(18)	38.0(19)	2.5(16)	1.3(14)	3.2(14)
O3	19.7(14)	18.9(12)	23.7(14)	-1.4(11)	0.1(11)	-1.2(11)
N1	14.1(13)	16.8(13)	15.3(14)	-0.5(11)	-5.0(10)	0.4(11)
N2	16.4(14)	18.8(13)	22.0(15)	-0.6(12)	-7.4(12)	0.7(11)
C1	17.7(14)	18.3(14)	19.3(16)	0.2(12)	-3.5(12)	-1.0(12)
C2	18.8(15)	22.4(15)	22.1(17)	-0.3(13)	-7.4(13)	-1.3(13)
C3	18.0(16)	23.8(14)	21.8(17)	0.6(13)	-3.2(13)	1.9(12)
C4	22.6(15)	22.2(16)	23.3(17)	-0.4(13)	-4.8(13)	3.5(13)
C5	19.4(15)	17.2(14)	19.5(16)	-1.4(13)	-2.8(12)	0.4(13)
C6	16.1(14)	17.1(13)	18.8(16)	1.6(12)	-5.0(11)	0.2(11)
C7	19.2(15)	17.8(15)	23.0(16)	-0.6(13)	-6.9(12)	-2.1(12)
C8	16.9(14)	16.6(14)	20.1(15)	-0.4(12)	-4.8(12)	-1.0(11)
C9	18.8(15)	18.2(14)	21.6(16)	0.6(12)	-3.0(12)	1.4(11)
C10	18.3(15)	19.9(15)	21.9(16)	-1.4(13)	-2.0(12)	1.8(12)
C11	12.5(14)	16.6(13)	15.8(15)	-0.8(11)	-2.1(11)	-1.3(11)
C12	18.2(16)	19.7(14)	22.8(17)	-0.8(13)	-2.1(13)	0.7(13)
C13	15.7(15)	17.9(13)	22.6(16)	0.3(12)	-5.6(12)	1.0(11)
C14	18.3(16)	20.2(14)	22.7(17)	0.3(13)	-2.1(14)	-1.0(12)
C15	16.5(15)	20.3(14)	19.9(16)	0.2(13)	-4.7(12)	0.0(12)
C16	17.1(16)	22.8(15)	24.5(17)	0.8(13)	-3.8(13)	-0.3(13)
C17	23.2(17)	24.3(14)	23.2(17)	-0.4(13)	-1.3(14)	2.0(13)
C18	26.2(17)	23.8(16)	28.0(18)	0.1(14)	-2.0(14)	0.7(13)
C19	26.5(17)	25.2(15)	30.4(18)	0.8(14)	-1.2(14)	-1.2(14)
C20	20.6(16)	23.1(14)	26.1(18)	0.7(13)	-3.2(14)	-2.9(13)

Table 11 Bond Lengths for 5ja.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C4	1.895(6)	C4	C5	1.378(8)

O1	C11	1.228(6)	C5	C6	1.394(8)
O2	C13	1.214(7)	C7	C8	1.350(7)
O3	C13	1.333(7)	C8	C9	1.425(7)
O3	C14	1.444(6)	C9	C10	1.344(8)
N1	C6	1.386(7)	C9	C12	1.512(7)
N1	C8	1.425(7)	C12	C13	1.525(7)
N1	C11	1.372(6)	C14	C15	1.495(8)
N2	C10	1.380(7)	C15	C16	1.384(7)
N2	C11	1.374(7)	C15	C20	1.399(8)
C1	C2	1.401(7)	C16	C17	1.396(8)
C1	C6	1.419(7)	C17	C18	1.374(8)
C1	C7	1.435(8)	C18	C19	1.379(8)
C2	C3	1.387(8)	C19	C20	1.393(8)
C3	C4	1.398(8)			

Table 12 Bond Angles for 5ja.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	O3	C14	115.1(4)	C8	C9	C12	120.6(5)
C6	N1	C8	108.4(4)	C10	C9	C8	118.7(5)
C11	N1	C6	127.2(5)	C10	C9	C12	120.5(5)
C11	N1	C8	124.4(5)	C9	C10	N2	121.4(5)
C11	N2	C10	124.0(5)	O1	C11	N1	122.9(5)
C2	C1	C6	119.0(5)	O1	C11	N2	122.6(5)
C2	C1	C7	133.4(5)	N1	C11	N2	114.5(5)
C6	C1	C7	107.6(5)	C9	C12	C13	113.1(4)
C3	C2	C1	118.8(5)	O2	C13	O3	123.4(5)
C2	C3	C4	120.4(5)	O2	C13	C12	125.9(5)
C3	C4	Br1	117.9(4)	O3	C13	C12	110.7(5)
C5	C4	Br1	119.0(4)	O3	C14	C15	110.2(4)
C5	C4	C3	123.0(5)	C16	C15	C14	124.2(5)
C4	C5	C6	116.3(5)	C16	C15	C20	119.1(5)
N1	C6	C1	107.1(5)	C20	C15	C14	116.7(5)

Table 12 Bond Angles for 5ja.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C6	C5	130.3(5)	C15	C16	C17	120.0(5)
C5	C6	C1	122.6(5)	C18	C17	C16	121.4(5)
C8	C7	C1	107.9(5)	C17	C18	C19	118.5(6)
C7	C8	N1	109.0(5)	C18	C19	C20	121.5(6)
C7	C8	C9	134.0(5)	C19	C20	C15	119.5(5)
C9	C8	N1	116.9(5)				

Table 13 Torsion Angles for 5ja.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C4	C5	C6	-177.6(4)	C8	N1	C6	C5	179.4(5)
O3	C14	C15	C16	4.7(8)	C8	N1	C11	O1	179.0(5)
O3	C14	C15	C20	-176.9(5)	C8	N1	C11	N2	0.9(7)
N1	C8	C9	C10	-1.0(7)	C8	C9	C10	N2	-1.9(8)
N1	C8	C9	C12	174.5(4)	C8	C9	C12	C13	72.8(6)
C1	C2	C3	C4	-1.7(8)	C9	C12	C13	O2	-10.8(8)
C1	C7	C8	N1	-0.2(6)	C9	C12	C13	O3	168.7(4)
C1	C7	C8	C9	178.0(6)	C10	N2	C11	O1	178.0(5)
C2	C1	C6	N1	-178.6(5)	C10	N2	C11	N1	-4.0(7)
C2	C1	C6	C5	1.4(8)	C10	C9	C12	C13	-111.8(6)
C2	C1	C7	C8	178.7(6)	C11	N1	C6	C1	179.9(4)
C2	C3	C4	Br1	178.9(4)	C11	N1	C6	C5	-0.1(9)
C2	C3	C4	C5	2.4(9)	C11	N1	C8	C7	-179.9(5)
C3	C4	C5	C6	-1.2(8)	C11	N1	C8	C9	1.5(7)
C4	C5	C6	N1	179.2(5)	C11	N2	C10	C9	4.6(8)
C4	C5	C6	C1	-0.7(8)	C12	C9	C10	N2	-177.4(5)
C6	N1	C8	C7	0.6(6)	C13	O3	C14	C15	172.4(4)
C6	N1	C8	C9	-178.0(5)	C14	O3	C13	O2	2.4(8)
C6	N1	C11	O1	-1.6(8)	C14	O3	C13	C12	-177.2(4)
C6	N1	C11	N2	-179.7(5)	C14	C15	C16	C17	178.5(5)
C6	C1	C2	C3	-0.1(8)	C14	C15	C20	C19	-178.7(5)
C6	C1	C7	C8	-0.2(6)	C15	C16	C17	C18	0.4(9)

Table 13 Torsion Angles for 5ja.

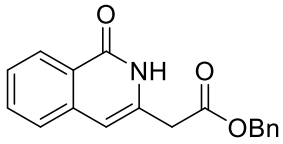
A	B	C	D	Angle/°	A	B	C	D	Angle/°
C7	C1	C2	C3	-178.9(6)	C16	C15	C20	C19	-0.2(8)
C7	C1	C6	N1	0.5(6)	C16	C17	C18	C19	-0.8(9)
C7	C1	C6	C5	-179.6(5)	C17	C18	C19	C20	0.8(10)
C7	C8	C9	C10	-179.1(6)	C18	C19	C20	C15	-0.2(10)
C7	C8	C9	C12	-3.6(9)	C20	C15	C16	C17	0.2(8)
C8	N1	C6	C1	-0.6(5)					

Table 14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5ja.

Atom	*x*	*y*	*z*	U(eq)
H2	219.59	5740.14	5055.49	23
H2A	11619.31	5731.39	7599.38	26
H3	12561.4	4455.22	7533.2	26
H5	6376	4069.71	6167.44	23
H7	7978.56	6862.38	7029.21	25
H10	285.13	6950.65	5412.14	24
H12A	3684.54	7702.09	6840.66	25
H12B	1880.17	7922.26	6153.17	25
H14A	7175.09	9257.56	5307.04	25
H14B	8708.44	9283.24	6080.16	25
H16	3299.47	10061	6483.67	26
H17	2472.8	11336.55	6597.76	29
H18	4944.19	12230.17	6090.92	31
H19	8347.48	11840.24	5488.71	33
H20	9241.14	10570.03	5364.66	28

6. Characterization Data

benzyl 2-(1-oxo-1,2-dihydroisoquinolin-3-yl)acetate（3aa）



Prepared from 1a (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3aa** (49 mg, 83% yield) as solid.

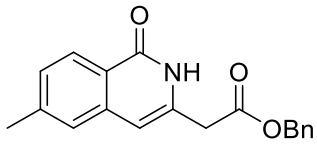
Rf = 0.36 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.05 (s, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 14.2, 7.3 Hz, 2H), 7.37-7.29 (m, 5H), 6.41 (s, 1H), 5.18 (s, 2H), 3.72 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 164.2, 138.1, 135.4, 133.4, 132.8, 128.7, 128.6, 128.5, 127.6, 126.7, 126.1, 125.1, 106.5, 67.5, 38.8.

HRMS (ESI): m/z calculated for $C_{18}H_{16}NO_3^+$ $[M+H]^+$, 294.1125; found, 294.1136.

benzyl 2-(6-methyl-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ba)



Prepared from 1b (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ba** (31 mg, 50% yield) as solid.

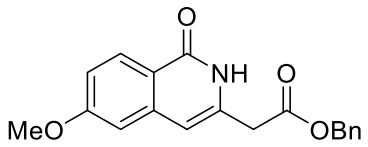
Rf = 0.34 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.27 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.40-7.27 (m, 7H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.38 (s, 1H), 5.15 (s, 2H), 3.71 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.3, 162.2, 142.6, 137.9, 135.9, 135.1, 128.5, 128.1, 128.0, 127.7, 126.6, 125.6, 122.7, 104.9, 66.1, 37.7, 21.3.

HRMS (ESI): m/z calculated for $C_{19}H_{18}NO_3^+$ $[M+H]^+$, 308.1281; found, 308.1292.

benzyl 2-(6-methoxy-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ca)



Prepared from 1c (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ca** (26 mg, 40% yield) as solid.

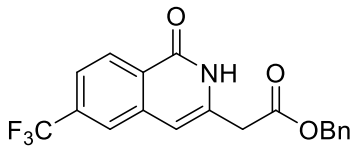
Rf = 0.22 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.17 (s, 1H), 8.05 (d, J = 9.5 Hz, 1H), 7.42-7.32 (m, 5H), 7.05-7.00 (m, 2H), 6.38 (s, 1H), 5.15 (s, 2H), 3.85 (s, 3H), 3.70 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.2, 162.4, 161.9, 139.9, 135.9, 135.6, 128.6, 128.4, 128.0, 127.9, 118.5, 115.4, 107.0, 104.8, 66.0, 55.4, 37.7.

HRMS (ESI): m/z calculated for $C_{19}H_{18}NO_4^+$ $[M+H]^+$, 324.1230; found, 324.1242.

benzyl 2-(1-oxo-6-(trifluoromethyl)-1,2-dihydroisoquinolin-3-yl)acetate（3da）



Prepared from 1d (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3da** (56 mg, 78% yield) as solid.

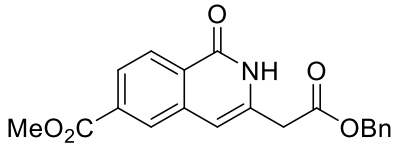
Rf = 0.31 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.51 (s, 1H), 8.42 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.37 – 7.29 (m, 5H), 6.47 (s, 1H), 5.19 (s, 2H), 3.76 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.81, 163.58, 138.03, 135.30, 135.24, 134.45 (q, J_{C-F} = 32.8 Hz), 128.76, 128.67, 128.62, 128.50, 126.0 (q, J_{C-F} = 280.99) 123.47 (q, J_{C-F} = 3.78 Hz), 123.41, 122.7 (q, J_{C-F}= 3.78), 106.28, 67.60, 38.66.

HRMS (ESI): m/z calculated for $C_{19}H_{14}F_3NaNO_3^+$ $[M+Na]^+$, 384.0818; found, 384.0824.

methyl 3-(2-(benzyloxy)-2-oxoethyl)-1-oxo-1,2-dihydroisoquinoline-6-carboxylate (3ea)



Prepared from 1e (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ea** (65 mg, 93% yield) as solid.

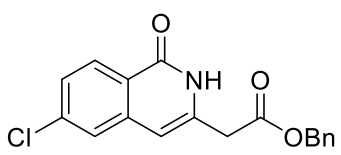
Rf = 0.28 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.60 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.19 (s, 1H), 7.94 (d, J = 6.8 Hz, 1H), 7.44-7.30 (m, 5H), 6.63 (s, 1H), 5.16 (s, 2H), 3.91 (s, 3H), 3.75 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.1, 165.8, 161.7, 137.7, 136.3, 135.9, 132.9, 128.4, 128.1, 128.0, 127.6, 127.5, 127.4, 125.6, 105.1, 66.2, 52.6, 37.8.

HRMS (ESI): m/z calculated for $C_{20}H_{18}NO_5^+$ $[M+H]^+$, 352.1179; found, 352.1176.

benzyl 2-(6-chloro-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate（3fa）



Prepared from 3f (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3fa** (59 mg, 90% yield) as solid.

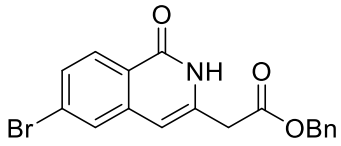
Rf = 0.35 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.51 (s, 1H), 8.13 (d, J = 8.6 Hz, 1H), 7.71 (s, 1H), 7.49 – 7.42 (m, 1H), 7.42 – 7.30 (m, 5H), 6.46 (s, 1H), 5.15 (s, 2H), 3.73 (s, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.1, 161.7, 139.3, 137.5, 136.8, 135.9, 128.9, 128.5, 128.1, 128.0, 126.4, 125.1, 123.3, 104.1, 66.1, 37.8.

HRMS (ESI): m/z calculated for $C_{18}H_{15}ClNO_3^+$ $[M+H]^+$, 328.0735; found, 328.0744.

benzyl 2-(6-bromo-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate（3ga）



Prepared from 1g (0.2 mmol, 1.0 equiv) and 2a (0.24mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ga** (68 mg, 91% yield) as solid.

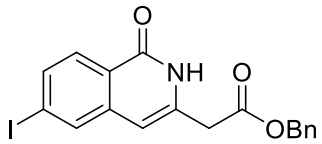
Rf = 0.38 (EtOAc/Petroleum Ether = 1/2)

H NMR (500 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.87 (s, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.42-7.34 (m, 5H), 6.45 (s, 1H), 5.15 (s, 2H), 3.73 (s, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.1, 161.8, 139.5, 136.8, 135.9, 129.1, 128.9, 128.5, 128.2, 128.1, 128.0, 126.6, 123.6, 104.0, 66.2, 37.8.

HRMS (ESI): m/z calculated for $C_{18}H_{15}BrNO_3^+$ $[M+H]^+$, 372.0230; found, 372.0238.

benzyl 2-(6-iodo-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ha)



Prepared from 1h (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ha** (65 mg, 78% yield) as solid.

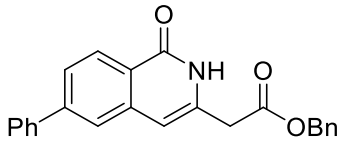
Rf = 0.34 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.47 (s, 1H), 8.05 (s, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.43-7.31 (m, 5H), 6.41 (s, 1H), 5.15 (s, 2H), 3.72 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 163.9, 139.5, 135.8, 135.2, 134.9, 134.7, 129.0, 128.8, 128.7, 128.5, 124.1, 105.3, 100.9, 67.6, 38.7.

HRMS (ESI): m/z calculated for $C_{18}H_{14}INaNO_3^+$ $[M+Na]^+$, 441.9911; found, 441.9911.

benzyl 2-(1-oxo-6-phenyl-1,2-dihydroisoquinolin-3-yl)acetate (3ia)



Prepared from 1i (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ia** (40 mg, 54% yield) as solid.

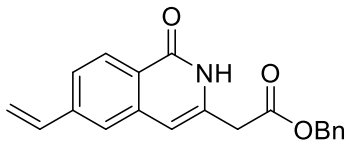
Rf = 0.32 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.42 (d, J = 8.3 Hz, 1H), 7.70-7.65 (m, 4H), 7.51-7.41 (m, 4H), 7.37-7.31 (m, 4H), 6.49 (s, 1H), 5.20 (s, 2H), 3.73 (s, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 170.4, 147.3, 138.0, 136.0, 131.1, 130.9, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 126.4, 121.9, 119.0, 116.7, 103.8, 95.7, 66.0, 33.5.

HRMS (ESI): m/z calculated for $C_{24}H_{20}NO_3^+$ $[M+H]^+$, 370.1438; found, 370.1447.

benzyl 2-(1-oxo-6-vinyl-1,2-dihydroisoquinolin-3-yl)acetate (3ja)



Prepared from 1j (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3)

afforded **3ja** (36 mg, 57% yield) as solid.

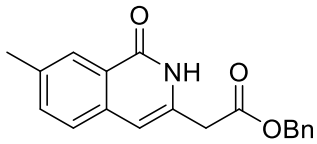
Rf = 0.37 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.36 (s, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 8.9 Hz, 2H), 7.40-7.34 (m, 5H), 6.85 (dd, J = 17.6, 10.8 Hz, 1H), 6.45 (s, 1H), 6.03 (d, J = 17.6 Hz, 1H), 5.44 (d, J = 11.0 Hz, 1H), 5.16 (s, 2H), 3.73 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.3, 162.0, 140.9, 138.2, 136.1, 135.9, 135.5, 128.5, 128.1, 128.0, 127.0, 124.1, 123.9, 123.5, 117.2, 105.0, 66.1, 37.7.

HRMS (ESI): m/z calculated for $C_{20}H_{18}NO_3^+$ $[M+H]^+$,320.1281; found,320.1287.

benzyl 2-(7-methyl-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ka)



Prepared from 1k (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ka** (37mg, 60% yield) as solid.

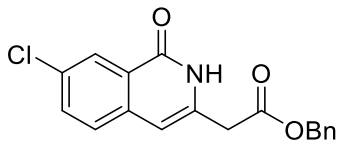
Rf = 0.39 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.16 (s, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.40-7.36 (m, 1H), 7.35-7.29 (m, 5H), 6.38 (s, 1H), 5.18 (s, 2H), 3.69 (s, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.4, 162.2, 135.9, 135.6, 135.5, 134.0, 133.8, 128.4, 128.1, 129.0, 126.1, 126.0, 124.8, 104.9, 66.1, 37.7, 21.0.

HRMS (ESI): m/z calculated for $C_{19}H_{18}NO_3^+$ $[M+H]^+$, 308.1281; found, 308.1285.

benzyl 2-(7-chloro-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3la)



Prepared from 1l (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3la** (42 mg, 63% yield) as solid.

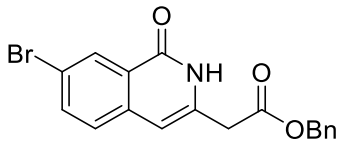
Rf = 0.39 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.03 (s, 1H), 8.29 – 8.24 (m, 1H), 7.69 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.38 – 7.30 (m, 6H), 6.79 (s, 1H), 5.20 (s, 2H), 3.75 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.2, 161.6, 137.1, 135.9, 135.3, 132.8, 129.1, 128.5, 128.1, 128.0, 126.7, 126.4, 126.0, 100.7, 66.2, 37.9.

HRMS (ESI): m/z calculated for $C_{18}H_{14}ClNaNO_3^+$ $[M+Na]^+$, 350.0554; found, 350.0564.

benzyl 2-(7-bromo-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ma)



Prepared from 1m (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ma** (51 mg, 69% yield) as solid.

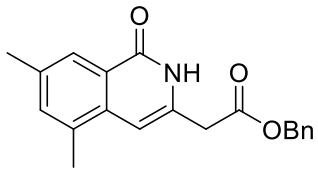
Rf = 0.39 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.67 (s, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.44 - 7.30 (m, 6H), 6.67 (s, 1H), 5.16 (s, 2H), 3.83 (s, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.1, 161.6, 137.2, 136.7, 136.3, 135.9, 128.4, 128.1, 128.0, 127.1, 126.7, 126.5, 119.8, 103.2, 66.1, 37.9.

HRMS (ESI): m/z calculated for $C_{18}H_{14}BrNaNO_3^+$ $[M+Na]^+$,394.0049; found, 394.0047.

benzyl 2-(5,7-dimethyl-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3na)



Prepared from 1n (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3)

afforded **3na** (32 mg, 50% yield) as solid.

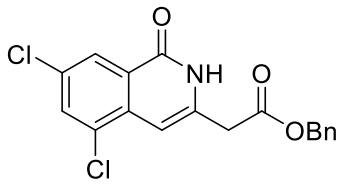
Rf = 0.34 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 8.04 (s, 1H), 7.36 - 7.30 (m, 6H), 6.46 (s, 1H), 5.19 (s, 2H), 3.69 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.4, 162.4, 136.0, 135.0, 134.5, 134.3, 133.7, 132.9, 128.4, 128.1, 128.0, 125.0, 124.1, 101.8, 66.0, 37.9, 21.0, 18.6.

HRMS (ESI): m/z calculated for $C_{20}H_{20}NO_3^+$ $[M+H]^+$, 322.1438; found, 322.1445

benzyl 2-(5,7-dichloro-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3oa)



Prepared from 1o (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3oa** (60 mg, 83% yield) as solid.

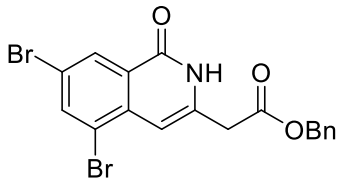
Rf = 0.34 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.85 (s, 1H), 8.07 (s, 1H), 7.99 (s, 1H), 7.42 -7.31 (m, 5H), 6.69 (s, 1H), 5.16 (s, 2H), 3.83 (s, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.0, 160.6, 137.7, 135.9, 134.2, 132.4, 130.5, 130.4, 128.4, 128.1, 128.0, 127.0, 125.2, 100.4, 66.2, 37.9.

HRMS (ESI): m/z calculated for $C_{18}H_{14}Cl_2NO_3^+$ $[M+H]^+$, 362.0345; found, 362.0347.

benzyl 2-(5,7-dibromo-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3pa)



Prepared from 1p (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3pa** (60 mg, 67% yield) as solid.

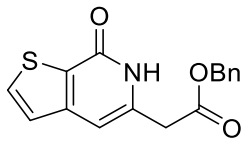
Rf = 0.39 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.85 (s, 1H), 8.25 (s, 1H), 8.22 (s, 1H), 7.45 – 7.30 (s, 5H), 6.65 (s, 1H), 5.16 (s, 2H), 3.83 (s, 2H)

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.0, 160.5, 138.0, 137.9, 135.9, 129.5, 128.9, 128.5, 128.1, 128.0, 127.3, 121.0, 118.6, 103.0, 66.2, 37.9.

HRMS (ESI): m/z calculated for $C_{18}H_{13}Br_2NaNO_3^+$ $[M+Na]^+$, 471.9154; found, 471.9153.

benzyl 2-(7-oxo-6,7-dihydrothieno[2,3-c]pyridin-5-yl)acetate (3qa)



Prepared from 1q (0.2 mmol, 1.0 equiv) and 2a (0.24mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3)

afforded **3qa** (35mg, 58% yield) as solid.

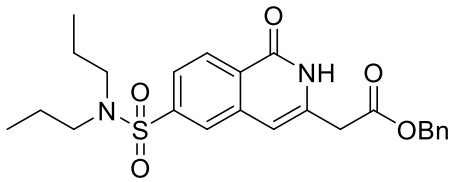
Rf = 0.43(EtOAc/Petroleum Ether = 1/1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.74 (s, 1H), 7.72 (d, *J* = 5.3 Hz, 1H), 7.37 – 7.23 (m, 7H), 5.13 (s, 2H), 3.70 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 160.9, 146.9, 135.5, 133.9, 129.6, 129.1, 128.7, 128.5, 128.4, 123.2, 109.7, 67.1, 36.2

HRMS (ESI): m/z calculated for $C_{16}H_{14}NO_3S^+$ $[M+H]^+$, 300.0689; found, 300.0691

benzyl 2-(6-(N,N-dipropylsulfamoyl)-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ra)



Prepared from 1r (0.2 mmol, 1.0 equiv) and 2a (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3)

afforded **3ra** (36 mg, 40% yield) as oil.

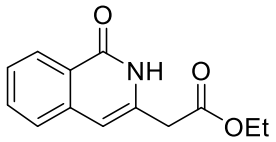
Rf = 0.33 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.68 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.07 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.34 (m, 5H), 6.67 (s, 1H), 5.16 (s, 2H), 3.76 (s, 2H), 3.07 (t, *J* = 7.6 Hz, 4H), 1.47 (q, *J* = 7.5 Hz, 4H), 0.80 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.1, 161.5, 143.0, 138.1, 137.0, 135.9, 128.5, 128.3, 128.2, 128.1, 126.9, 124.8, 123.3, 105.0, 66.2, 49.7, 37.8, 21.7, 11.0.

HRMS (ESI): m/z calculated for $C_{24}H_{29}N_2O_5S^+$ $[M+H]^+$, 457.1792; found, 457.1794

ethyl 2-(1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ab)



Prepared from 1(0.2 mmol, 1.0 equiv) and 2b (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ab** (33 mg, 72% yield) as solid.

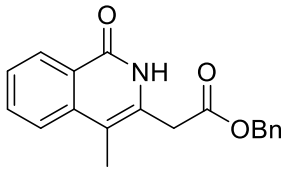
Rf = 0.4 (EtOAc/Petroleum Ether = 1/2).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.30 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 6.45 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.64 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.3, 162.2, 137.8, 135.2, 132.5, 126.6, 126.1, 126.0, 124.8, 104.9, 60.6, 37.8, 14.1.

HRMS (ESI): m/z calculated for $C_{13}H_{14}NO_3^+$ $[M+H]^+$, 232.0968; found, 232.0978

benzyl 2-(4-methyl-1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ac)



Prepared from 1(0.2 mmol, 1.0 equiv) and 2c (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ac** (47 mg, 76% yield) as solid.

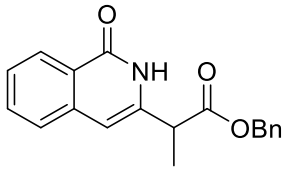
Rf = 0.4 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.70 (q, J = 9.1, 8.6 Hz, 2H), 7.50 (d, J = 6.5 Hz, 1H), 7.34 – 7.28 (m, 5H), 5.16 (s, 2H), 3.78 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.2, 161.5, 138.2, 136.0, 132.5, 131.1, 128.4, 128.1, 127.9, 126.8, 126.0, 125.2, 123.4, 108.8, 66.1, 35.9, 12.2.

HRMS (ESI): m/z calculated for $C_{19}H_{18}NO_3^+$ $[M+H]^+$, 308.1281; found, 308.1284

benzyl 2-(1-oxo-1,2-dihydroisoquinolin-3-yl)propanoate (3ad)



Prepared from 1(0.2 mmol, 1.0 equiv) and 2d (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3)

afforded **3ad** (48 mg, 79% yield) as solid.

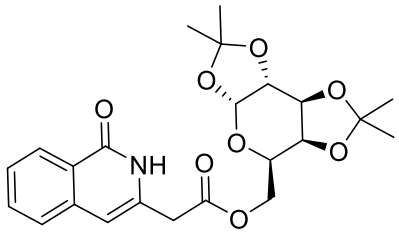
Rf = 0.38 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.50 – 7.41 (d, 2H), 7.32 - 7.24 (m, 5H), 6.38 (s, 1H), 5.23 – 5.10 (m, 2H), 3.77 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 164.0, 138.9, 138.1, 135.4, 132.8, 128.7, 128.5, 128.3, 127.6, 126.7, 126.3, 125.3, 104.5, 67.4, 43.5, 17.0.

HRMS (ESI): m/z calculated for $C_{19}H_{17}NaNO_3^+$ $[M+Na]^+$, 330.1101; found, 330.1103

(2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 2-(1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ae)



Prepared from 1(0.2 mmol, 1.0 equiv) and 2i (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ae** (46 mg, 52% yield) as oil.

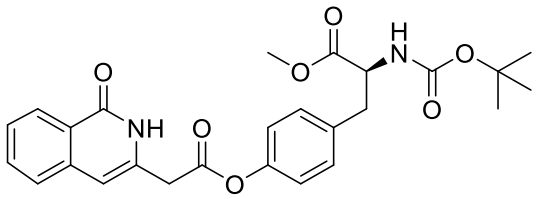
Rf = 0.38 (EtOAc/Petroleum Ether = 1/1)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.31 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 6.45 (s, 1H), 5.46 (d, *J* = 5.0 Hz, 1H), 4.61 (d, *J* = 7.9 Hz, 1H), 4.37 (s, 1H), 4.26 (d, *J* = 8.9 Hz, 1H), 4.14 (d, *J* = 6.1 Hz, 2H), 3.95 (d, *J* = 6.3 Hz, 1H), 3.68 (s, 2H), 1.35 (s, 6H), 1.27 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.4, 162.3, 137.8, 135.0, 132.4, 126.6, 126.1, 126.0, 124.8, 108.7, 108.0, 104.9, 95.6, 70.2, 70.0, 69.7, 65.3, 63.7, 37.7, 25.9, 25.7, 24.9, 24.3.

HRMS (ESI): m/z calculated for $C_{23}H_{28}NO_8^+$ $[M+H]^+$, 446.1809; found, 446.1815

methyl 2-((tert-butoxycarbonyl)amino)-3-(4-(2-(1-oxo-1,2-dihydroisoquinolin-3-yl)acetoxy)phenyl)propanoate (3af)



Prepared from 1(0.2 mmol, 1.0 equiv) and 2f (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3af** (53 mg, 55% yield) as oil.

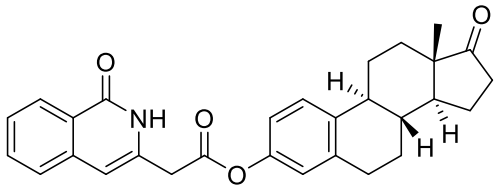
Rf = 0.38 (EtOAc/Petroleum Ether = 1/1)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.46 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.55 (s, 1H), 3.94 (s, 2H), 3.60 (s, 3H), 3.00 (dd, *J* = 14.5, 5.0 Hz, 1H), 2.83 (d, *J* = 12.2 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 172.6, 168.3, 162.3, 155.4, 149.1, 137.7, 135.3, 134.7, 132.5, 130.2, 128.2, 127.5, 126.6, 126.3, 126.1, 124.9, 121.4, 105.3, 78.3, 55.1, 51.8, 37.8, 35.8, 28.1.

HRMS (ESI): m/z calculated for $C_{26}H_{28}NaN_2O_7^+$ $[M+Na]^+$, 503.1789; found, 503.1794

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-(1-oxo-1,2-dihydroisoquinolin-3-yl)acetate (3ag)



Prepared from 1 (0.2 mmol, 1.0 equiv) and 2g (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ag** (29 mg, 32% yield) as solid.

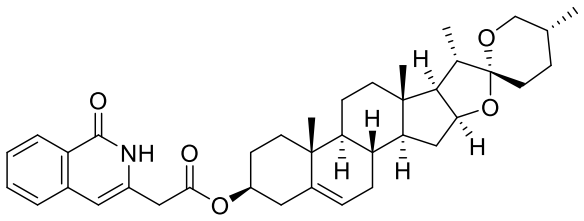
Rf = 0.38 (EtOAc/Petroleum Ether = 1/3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.06 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.48 (m, 2H), 7.30 (s, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.87 (s, 1H), 6.56 (s, 1H), 3.93 (s, 2H), 2.85 (q, *J* = 4.8, 3.8 Hz, 2H), 2.60 – 2.48 (m, 1H), 2.45 - 2.36 (m, 1H), 2.32 - 2.25 (m, 1H), 2.22 – 2.14 (m, 1H), 2.06 – 1.98 (m, 2H), 1.66 – 1.46 (m, 6H), 1.39 – 1.33 (m, 1H), 0.93 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 164.2, 148.5, 138.3, 138.1, 138.0, 133.0, 127.7, 127.0, 126.6, 126.2, 125.23, 124.3, 121.5, 118.6, 106.9, 50.6, 48.1, 44.3, 39.0, 38.1, 36.0, 31.7, 29.8, 29.5, 26.4, 25.9, 21.7, 14.0.

HRMS (ESI): m/z calculated for $C_{29}H_{30}NO_4^+$ $[M+H]^+$, 456.2169; found, 456.2168

(4S,5'R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl 2-(1-oxo-1,2-dihydroisoquinolin-3-yl)acetate(3ah)



Prepared from 1(0.2 mmol, 1.0 equiv) and 2h (0.24 mmol, 1.2 equiv) according to the general procedure 4, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **3ah** (47 mg, 39% yield) as solid.

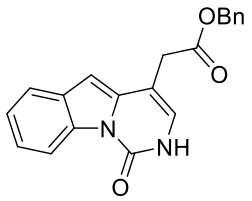
Rf = 0.38 (EtOAc/Petroleum Ether = 1/3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 2H), 6.43 (s, 1H), 5.39 (d, *J* = 5.0 Hz, 1H), 4.72 (d, *J* = 10.2 Hz, 1H), 4.45 (q, *J* = 7.4 Hz, 1H), 3.63 (s, 2H), 3.54 – 3.38 (m, 2H), 2.38 (d, *J* = 8.3 Hz, 2H), 2.07 – 2.03 (m, 1H), 2.03 – 1.99 (m, 1H), 1.93 -1.88 (m, 2H), 1.86 – 1.83 (m, 1H), 1.82 – 1.77 (s, 2H), 1.75 – 1.68 (m, 5H), 1.55 – 1.50 (m, 2H), 1.49 – 1.45 (m, 1H), 1.44 – 1.40 (m, 1H), 1.39 – 1.34 (m, 1H), 1.33 – 1.28 (m, 3H), 1.22 – 1.18 (m, 1H), 1.17 – 1.12 (m, 2H), 1.06 (s, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.84 (3, 3H), 0.82 (3, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 163.5, 139.4, 138.0, 133.2, 132.9, 127.7, 126.8, 126.1, 125.3, 122.9, 109.4, 106.3, 80.9, 75.7, 67.0, 62.2, 56.6, 50.0, 41.8, 40.4, 39.8, 39.2, 38.1, 37.0, 36.8, 32.2, 32.0, 31.5, 31.5, 30.4, 29.0, 27.8, 21.0, 19.5, 17.3, 16.4, 14.7.

HRMS (ESI): m/z calculated for $C_{38}H_{54}NO_3^+$ $[M+H]^+$, 572.4098; found, 572.4107

benzyl 2-(1-oxo-1,2-dihydropyrimido[1,6-a]indol-3-yl)acetate (5aa)



Prepared from 4a (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5aa** (58mg, 87% yield) as solid.

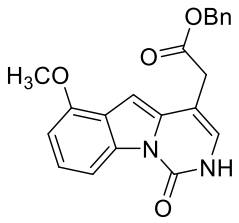
Rf = 0.38 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.69 – 8.61 (m, 1H), 7.67 – 7.61 (m, 1H), 7.40 – 7.32 (m, 6H), 7.26 (s, 1H), 6.75 (d, *J* = 5.3 Hz, 1H), 6.53 (s, 1H), 5.18 (s, 2H), 3.59 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 147.6, 136.5, 136.0, 132.4, 129.7, 128.4, 128.1, 128.0, 125.5, 123.5, 122.0, 119.7, 115.3, 103.9, 96.2, 66.0, 33.6.

HRMS (ESI): m/z calculated for $C_{20}H_{17}N_2O_3^+$ $[M+H]^+$, 333.1234; found, 333.1237.

benzyl 2-(6-methoxy-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5ba)



Prepared from 4b (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ba** (43 mg, 59% yield) as solid.

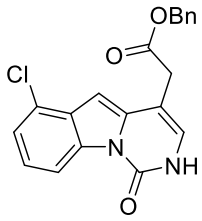
Rf = 0.37 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.84 (d, *J* = 4.0 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.31 (m, 5H), 7.23 (t, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 4.0 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.55 (s, 1H), 5.14 (s, 2H), 3.92 (s, 3H), 3.72 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.4, 151.8, 147.6, 136.0, 135.2, 133.4, 128.3, 128.0, 127.8, 124.9, 123.1, 120.2, 108.4, 104.1, 103.7, 93.4, 65.9, 55.2, 33.6.

HRMS (ESI): m/z calculated for $C_{21}H_{18}NaN_2O_4^+$ $[M+Na]^+$, 385.1159; found, 385.1162

benzyl 2-(6-chloro-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5ca)



Prepared from 4c (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ca** (45mg, 61% yield) as solid.

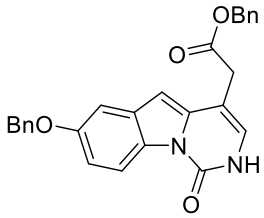
Rf = 0.33 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.13 (s, 1H), 8.50 (d, J = 8.2 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.40 – 7.27 (m, 6H), 7.07 (s, 1H), 6.60 (s, 1H), 5.16 (s, 2H), 3.80 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.4, 147.3, 137.6, 136.0, 133.1, 128.4, 128.0, 127.9, 126.6, 123.5, 123.1, 122.9, 114.3, 103.9, 94.0, 66.0, 33.5.

HRMS (ESI): m/z calculated for $C_{20}H_{16}ClN_2O_3^+$ $[M+H]^+$,367.0844; found, 367.0847.

benzyl 2-(7-(benzyloxy)-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5da)



Prepared from 4d (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5da** (55 mg, 63% yield) as solid.

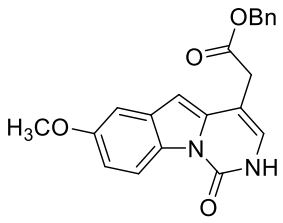
Rf = 0.38 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.85 (d, J = 5.2 Hz, 1H), 8.40 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 6.8 Hz, 2H), 7.40 (t, J = 7.1 Hz, 2H), 7.36 – 7.30 (m, 6H), 7.22 (d, J = 2.5 Hz, 1H), 7.03 – 6.92 (m, 2H), 6.42 (s, 1H), 5.15 (d, J = 7.0 Hz, 4H), 3.71 (s, 2H).

^{13}C NMR (75 MHz, DMSO) δ 170.4, 155.2, 147.3, 137.3, 137.1, 136.0, 130.7, 128.4, 128.0, 127.9, 127.7, 127.6, 127.3, 125.4, 116.0, 112.0, 103.7, 103.0, 96.0, 69.5, 65.9, 33.6.

HRMS (ESI): m/z calculated for $C_{27}H_{23}N_2O_4^+$ $[M+H]^+$,439.1652; found, 439.1650

benzyl 2-(7-methoxy-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5ea)



Prepared from 4e (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ea** (57 mg, 79% yield) as solid.

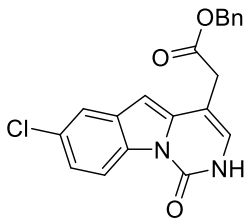
Rf = 0.28 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.87 (d, J = 5.3 Hz, 1H), 8.39 (d, J = 9.0 Hz, 1H), 7.40 – 7.31 (m, 5H), 7.13 (d, J = 2.5 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.43 (s, 1H), 5.14 (s, 2H), 3.81 (s, 3H), 3.71 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.5, 156.2, 147.4, 137.1, 136.1, 130.8, 128.4, 128.1, 128.0, 127.2, 125.4, 116.1, 111.4, 103.8, 101.6, 96.1, 66.0, 55.3, 33.7.

HRMS (ESI): m/z calculated for $C_{21}H_{19}N_2O_4^+$ $[M+H]^+$, 363.1339; found, 363.1321

benzyl 2-(7-chloro-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5fa)



Prepared from 4f (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5fa** (42 mg, 58% yield) as solid.

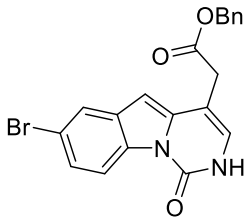
Rf = 0.27 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.03 (d, *J* = 4.3 Hz, 1H), 8.50 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.30 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.02 (d, *J* = 4.3 Hz, 1H), 6.52 (s, 1H), 5.14 (s, 2H), 3.74 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.4, 147.3, 138.0, 136.0, 131.2, 130.9, 128.4, 128.1, 128.1, 128.0, 126.4, 121.9, 119.0, 116.7, 103.8, 95.7, 66.0, 33.5.

HRMS (ESI): m/z calculated for $C_{20}H_{15}ClNaN_2O_3^+$ $[M+Na]^+$,389.0663,found, 389.0665

benzyl 2-(7-bromo-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5ga)



Prepared from 4g (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ga** (42 mg, 51% yield) as solid.

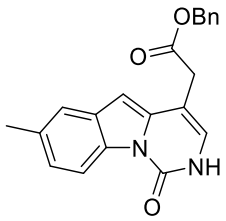
Rf = 0.30 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.05 (s, 1H), 8.45 (d, *J* = 8.8 Hz, 1H), 7.86 (s, 1H), 7.41 (d, *J* = 10.8 Hz, 1H), 7.38 – 7.31 (m, 5H), 7.02 (s, 1H), 6.51 (s, 1H), 5.14 (s, 2H), 3.73 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.4, 147.4, 137.9, 136.0, 131.7, 131.2, 128.4, 128.1, 128.0, 126.4, 124.5, 122.0, 117.1, 116.3, 103.8, 95.6, 66.0, 33.5.

HRMS (ESI): m/z calculated for $C_{20}H_{16}BrN_2O_3^+$ $[M+H]^+$, 411.0339; found, 411.0345

benzyl 2-(7-methyl-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5ha)



Prepared from 4h (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ha** (24 mg, 35% yield) as solid.

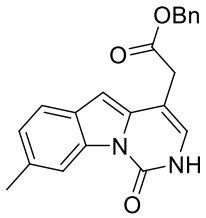
Rf = 0.31 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.84 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 7.43 (s, 1H), 7.39-7.31 (m, 5H), 7.11 (d, J = 8.5 Hz, 1H), 6.93 (d, J = 5.1 Hz, 1H), 6.43 (s, 1H), 5.14 (s, 2H), 3.71 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.5, 147.5, 136.6, 136.1, 132.5, 130.7, 130.0, 128.4, 128.1, 128.0, 125.3, 123.5, 119.4, 115.0, 103.9, 95.8, 66.0, 33.6, 21.3.

HRMS (ESI): m/z calculated for $C_{21}H_{19}N_2O_3^+$ $[M+H]^+$, 347.1390; found, 347.1395.

benzyl 2-(8-methyl-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5ia)



Prepared from 4i (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ia** (40 mg, 58% yield) as solid.

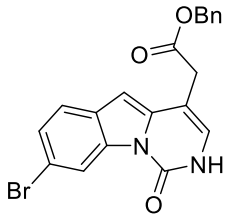
Rf = 0.33 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.80 (d, J = 5.0 Hz, 1H), 8.36 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.36 – 7.32 (m, 5H), 7.17 (d, J = 6.5 Hz, 1H), 6.90 (d, J = 4.8 Hz, 1H), 6.45 (s, 1H), 5.14 (s, 2H), 3.70 (s, 2H), 2.47 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6)) δ 170.5, 147.7, 136.1, 136.0, 132.8, 131.4, 128.4, 128.1, 128.0, 127.5, 125.1, 124.9, 119.4, 115.3, 104.0, 96.1, 66.0, 33.7, 21.6.

HRMS (ESI): m/z calculated for $C_{21}H_{19}N_2O_3^+$ $[M+H]^+$, 347.1390; found, 347.1395

benzyl 2-(8-bromo-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5ja)



Prepared from 4j (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ja** (49 mg, 60% yield) as solid.

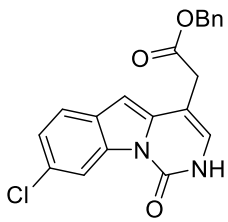
Rf = 0.31 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.76 (s, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.36 – 7.29 (m, 6H), 7.03 (s, 1H), 6.36 (s, 1H), 5.13 (s, 2H), 3.67 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.3, 147.4, 137.3, 136.0, 132.9, 128.8, 128.4, 128.0, 127.9, 126.4, 126.0, 121.5, 117.7, 114.2, 104.0, 96.1, 66.0, 33.5.

HRMS (ESI): m/z calculated for $C_{20}H_{16}BrN_2O_3^+$ $[M+H]^+$, 411.0339; found, 411.0341

benzyl 2-(8-chloro-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5ka)



Prepared from 4k (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ka** (42 mg, 57% yield) as solid.

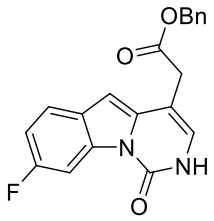
Rf = 0.34 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.02 (s, 1H), 8.52 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.36 – 7.31 (m, 5H), 6.99 (s, 1H), 6.54 (s, 1H), 5.14 (s, 2H), 3.73 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.4, 147.4, 137.4, 136.0, 132.6, 128.5, 128.4, 128.1, 128.0, 126.2, 125.9, 123.8, 121.1, 114.9, 104.0, 96.1, 66.0, 33.5.

HRMS (ESI): m/z calculated for $C_{20}H_{15}ClNaN_2O_3^+$ $[M+Na]^+$, 389.0663; found, 389.0673

benzyl 2-(8-fluoro-1-oxo-1,2-dihydropyrimido[1,6-a]indol-4-yl)acetate (5la)



Prepared from 4l(0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5la** (42 mg, 62% yield) as solid.

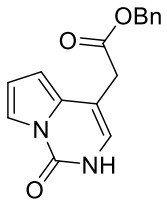
Rf = 0.32 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (dd, *J* = 10.4, 2.5 Hz, 1H), 7.63 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.37 – 7.30 (m, 6H), 7.19 (td, *J* = 9.1, 2.6 Hz, 1H), 6.97 (s, 1H), 6.44 (s, 1H), 5.14 (s, 2H), 3.69 (s, 2H).

^{13}C NMR (101 MHz, DMSO) δ 170.5, 158.3(d, *J* = 237.4 Hz),147.5, 137.2(d, *J* = 3.0 Hz), 136.0, 132.1(d, *J* = 13.1 Hz), 128.4, 128.1, 128.0, 126.4, 125.3, 120.9(d. *J* = 10.1 Hz), 112.0(d, *J* = 24.2 Hz), 104.1, 101.9(d, *J* = 28.3 Hz), 96.1, 66.0, 33.6.

HRMS (ESI): m/z calculated for $C_{20}H_{15}FNaN_2O_3^+$ $[M+Na]^+$, 373.0959; found, 373.0963

benzyl 2-(1-oxo-1,2-dihydropyrrolo[1,2-c]pyrimidin-4-yl)acetate(5ma)



Prepared from 4m (0.2 mmol, 1.0 equiv) and 2a (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ma** (46 mg, 82% yield) as solid.

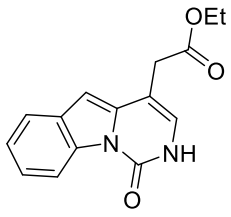
Rf = 0.3 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.88 (s, 1H), 7.49 (dd, J = 3.1, 1.4 Hz, 1H), 7.36 – 7.36 – 7.30 (m, 5H), 6.74 (s, 1H), 6.61 (t, J = 3.3 Hz, 1H), 6.25 (dd, J = 3.6, 1.5 Hz, 1H), 5.12 (s, 2H), 3.64 (s, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 170.5, 146.0, 136.0, 132.0, 128.4, 128.1, 127.9, 121.2, 114.0, 113.8, 104.9, 102.7, 65.9, 33.7.

HRMS (ESI): m/z calculated for $C_{16}H_{15}N_2O_3^+$ $[M+H]^+$, 283.1077; found, 283.1075

ethyl 2-(1-oxo-1,2-dihydropyrimido[1,6-a]indol-3-yl)acetate (5ab)



Prepared from 4(0.2 mmol, 1.0 equiv) and 2b (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ab** (19 mg, 69% yield) as oil.

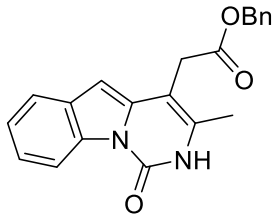
Rf = 0.43 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.67 – 8.63 (m, 1H), 7.69 – 7.65 (m, 1H), 7.40 – 7.35 (t, 2H), 6.77 (d, *J* = 5.2 Hz, 1H), 6.59 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 2H), 1.31 – 1.25 (t, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 149.0, 135.9, 133.4, 130.2, 124.1, 123.3, 123.1, 120.1, 116.2, 105.5, 98.0, 61.5, 35.0, 14.3.

HRMS (ESI): m/z calculated for $C_{15}H_{15}N_2O_3^+$ $[M+H]^+$, 271.1077; found, 271.1077

benzyl 2-(4-methyl-1-oxo-1,2-dihydropyrimido[1,6-a]indol-3-yl)acetate (5ac)



Prepared from 4 (0.2 mmol, 1.0 equiv) and 2c (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ca** (23mg, 33% yield) as solid.

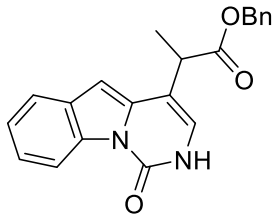
Rf = 0.37 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.78 (s, 1H), 8.50 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.32 (m, 5H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.62 (s, 1H), 5.17 (s, 2H), 3.74 (s, 2H), 2.10 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 168.9, 147.6, 137.9, 135.9, 132.5, 130.1, 128.4, 128.1, 127.9, 127.7, 123.5, 121.8, 119.7, 115.3, 104.3, 96.1, 66.2, 34.5, 11.7.

HRMS (ESI): m/z calculated for $C_{21}H_{19}N_2O_3^+$ $[M+H]^+$, 347.1390; found, 347.1392

benzyl 2-(1-oxo-1,2-dihydropyrimido[1,6-a]indol-3-yl)propanoate (5ad)



Prepared from 4 (0.2 mmol, 1.0 equiv) and 2d (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ad** (37 mg, 54% yield) as solid.

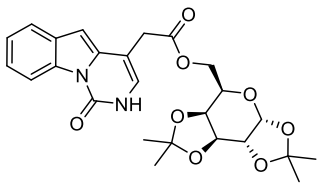
Rf = 0.40 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.21 – 7.16 (m, 4H), 7.15 (d, *J* = 2.7 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.09 (d, *J* = 6.7 Hz, 1H), 6.39 (s, 1H), 6.26 (d, *J* = 1.7 Hz, 1H), 5.00 (s, 2H), 3.62 (q, *J* = 7.2 Hz, 1H), 1.33 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 171.5, 148.0, 137.8, 135.9, 135.7, 132.0, 130.3, 128.4, 128.1, 127.8, 123.5, 121.7, 119.6, 115.2, 96.8, 95.8, 66.2, 41.7, 15.7.

HRMS (ESI): m/z calculated for $C_{21}H_{19}N_2O_3^+$ $[M+H]^+$, 347.1390; found, 347.1393

(2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 2-(1-oxo-1,2-dihydropyrimido[1,6-a]indol-3-yl)acetate (5ae)



Prepared from 4 (0.2 mmol, 1.0 equiv) and 2e (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/3) afforded **5ae** (60 mg, 62% yield) as oil.

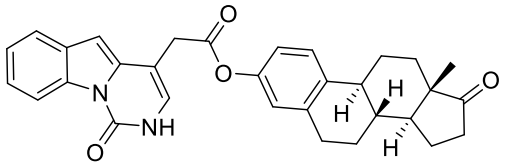
Rf = 0.35 (EtOAc/Petroleum Ether = 1/2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.29 (d, *J* = 5.3 Hz, 1H), 8.67 – 8.62 (t, 1H), 7.69 – 7.62 (t, 1H), 7.39 – 7.33 (t, 2H), 6.83 (d, *J* = 5.2 Hz, 1H), 6.59 (s, 1H), 5.54 (d, *J* = 5.0 Hz, 1H), 4.58 (d, *J* = 10.4 Hz, 1H), 4.34 (d, *J* = 4.1 Hz, 1H), 4.32 (m, *J* = 3.2 Hz, 2H), 4.19 (d, *J* = 7.8 Hz, 1H), 4.06 – 4.02 (m, 1H), 3.58 (d, *J* = 5.0 Hz, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 149.1, 135.8, 133.4, 130.3, 124.0, 123.5, 123.0, 120.2, 116.2, 109.9, 109.0, 105.2, 97.9, 96.4, 71.1, 70.8, 70.5, 66.1, 64.4, 34.7, 26.1, 25.9, 25.0, 24.6.

HRMS (ESI): m/z calculated for $C_{25}H_{29}N_2O_8^+$ $[M+H]^+$,485.1918; found, 485.1920

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-(1-oxo-1,2-dihydropyrimido[1,6-a]indol-3-yl)acetate (5ag)



Prepared from 4 (0.2 mmol, 1.0 equiv) and 2g (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/4) afforded **5ag** (28 mg, 28% yield) as solid.

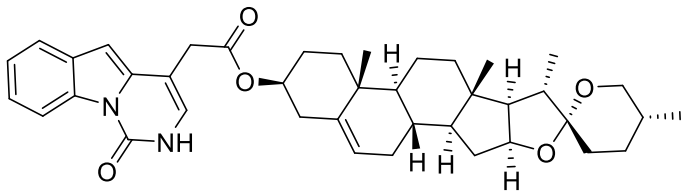
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.25 (d, *J* = 5.3 Hz, 1H), 8.69 (d, *J* = 5.3 Hz, 1H), 7.70 (dd, *J* = 6.3, 2.9 Hz, 1H), 7.41 (dt, *J* = 6.3, 3.8 Hz, 2H), 7.30 – 7.26 (m, 1H), 6.89 – 6.82 (m, 2H), 6.80 (d, *J* = 2.5 Hz, 1H), 6.71 (s, 1H), 3.79 (s, 2H), 2.89 (dd, *J* = 9.0, 4.3 Hz, 2H), 2.52 (dd, *J* = 18.6, 8.5 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.31 – 2.21 (m, 1H), 2.17 (d, *J* = 9.2 Hz, 1H), 2.07 – 2.01 (m, 2H), 1.98 (d, *J* = 2.9 Hz, 1H), 1.64 – 1.57 (m, 2H), 1.41 (d, *J* = 10.2 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.30 – 1.26 (m, 2H), 0.91 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 149.0, 148.6, 138.3, 137.8, 135.7, 133.5, 130.2, 126.6, 124.2,123.7, 123.2, 121.5, 120.2, 118.6,116.2,105.0, 98.1, 50.6, 48.1, 44.3, 38.1, 36.0, 35.1, 31.7, 29.8, 29.5, 26.4,25.9, 21.7,13.9.

HRMS (ESI): m/z calculated for $C_{31}H_{31}N_2O_4^+$ $[M+H]^+$, 495.2278; found, 495.2284

(4S,5'R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12bicosahydrospiro[naphtho[2',1'

:4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl 2-(1-oxo-1,2-dihydropyrimido[1,6-a]indol-3-yl)acetate (5ah)



Prepared from 4 (0.2 mmol, 1.0 equiv) and 2h (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/4) afforded **5ah** (42 mg, 33% yield) as oil.

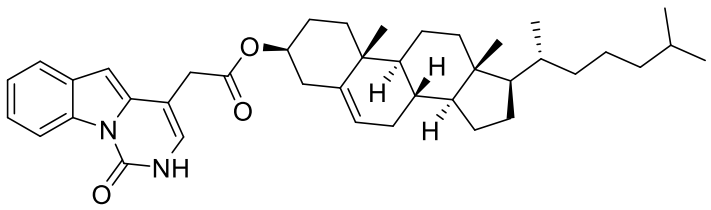
Rf = 0.35 (EtOAc/Petroleum Ether = 1/3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 8.1, 5.3 Hz, 2H), 7.67 (t, *J* = 3.5 Hz, 1H), 7.38 (q, *J* = 3.6, 2.9 Hz, 2H), 6.75 (d, *J* = 5.3 Hz, 1H), 6.59 (s, 1H), 5.36 (d, *J* = 5.1 Hz, 1H), 4.71 – 4.62 (m, 1H), 4.46 – 4.38 (m, 1H), 3.52 (s, 2H), 3.46 – 3.31 (m, 2H), 2.33 (d, *J* = 8.2 Hz, 2H), 2.00 (d, *J* = 5.6 Hz, 1H), 1.96 (d, *J* = 5.6 Hz, 1H), 1.88 – 1.81 (m, 3H), 1.75 (d, *J* = 6.5 Hz, 1H), 1.48 (q, *J* = 5.8, 4.6 Hz, 4H), 1.42 (d, *J* = 4.1 Hz, 1H), 1.26 (s, 7H), 1.17 (d, *J* = 5.7 Hz, 1H), 1.11 (d, *J* = 4.3 Hz, 2H), 1.03 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 7.5 Hz, 2H), 0.78 (s, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 139.4, 135.7, 133.3, 130.1, 124.0, 123.1, 123.0, 122.6, 1200, 116.1, 109.3, 105.5, 97.9, 80.8, 75.0, 66.9, 62.1, 56.4, 49.9,41.6, 40.3, 39.7, 38.0, 36.9, 36.7, 35.1, 32.0, 31.8, 31.4, 30.3, 29.7, 28.8, 27.7, 20.8, 19.3, 17.1, 16.3, 14.5, 14.1.

HRMS (ESI): m/z calculated for $C_{40}H_{51}N_2O_5^+$ $[M+H]^+$, 639.3793; found, 639.3796

(3S,8S,9S,10R,13R,14S,17R)-17-((R)-heptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(1-oxo-1,2-dihydropyrimido[1,6-a]indol-3-yl)acetate (5ai)



Prepared from 4 (0.2 mmol, 1.0 equiv) and 2i (0.3 mmol, 1.5 equiv) according to the general procedure 5, Purification by flash column (EtOAc/Petroleum Ether = 1/4) afforded **5ai** (82 mg, 69% yield) as solid.

Rf = 0.35 (EtOAc/Petroleum Ether = 1/3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.0 Hz, 1H), 8.35 (s, 1H), 7.65 (s, 1H), 7.38 (s, 2H), 6.75 (s, 1H), 6.59 (s, 1H), 5.37 (s, 1H), 4.67 (d, *J* = 10.2 Hz, 1H), 3.52 (s, 2H), 2.33 (d, *J* = 8.3 Hz, 2H), 1.96 (d, *J* = 15.4 Hz, 3H), 1.85 (d, *J* = 11.9 Hz, 3H), 1.48 (s, 4H), 1.33 (s, 4H), 1.26 (s, 4H), 1.15 – 1.09 (m, 5H), 1.04 – 0.96 (m, 6H), 0.91 (d, *J* = 6.2 Hz, 4H), 0.86 (d, *J* = 6.7 Hz, 7H), 0.67 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 149.9, 139.6, 134.0, 131.1, 124.1, 123.1, 123.1, 120.1, 116.2, 105.7, 98.1, 75.3, 56.9, 56.3, 50.2, 42.5, 39.9, 39.7, 38.2, 37.1, 36.8, 36.4, 35.9, 35.3, 32.0, 28.4, 28.2, 27.9, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0.

HRMS (ESI): m/z calculated for $C_{40}H_{55}N_2O_3^+$ $[M+H]^+$,611.4207; found,611.4211

7. References

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[5] Zhang, J.; Wang, M.; Wang, H..; Xu, H.; Chen, J.; Guo, Z.; Ma, B.; Ban S.-R.; Dai H.-X. *Chem. Commun*., **2021**, *57*, 8656-8659.

[6] Zhang, Y.; Wang, D.; Cui, S. *Org. Lett*. **2015**, *17*, 2494-2497.

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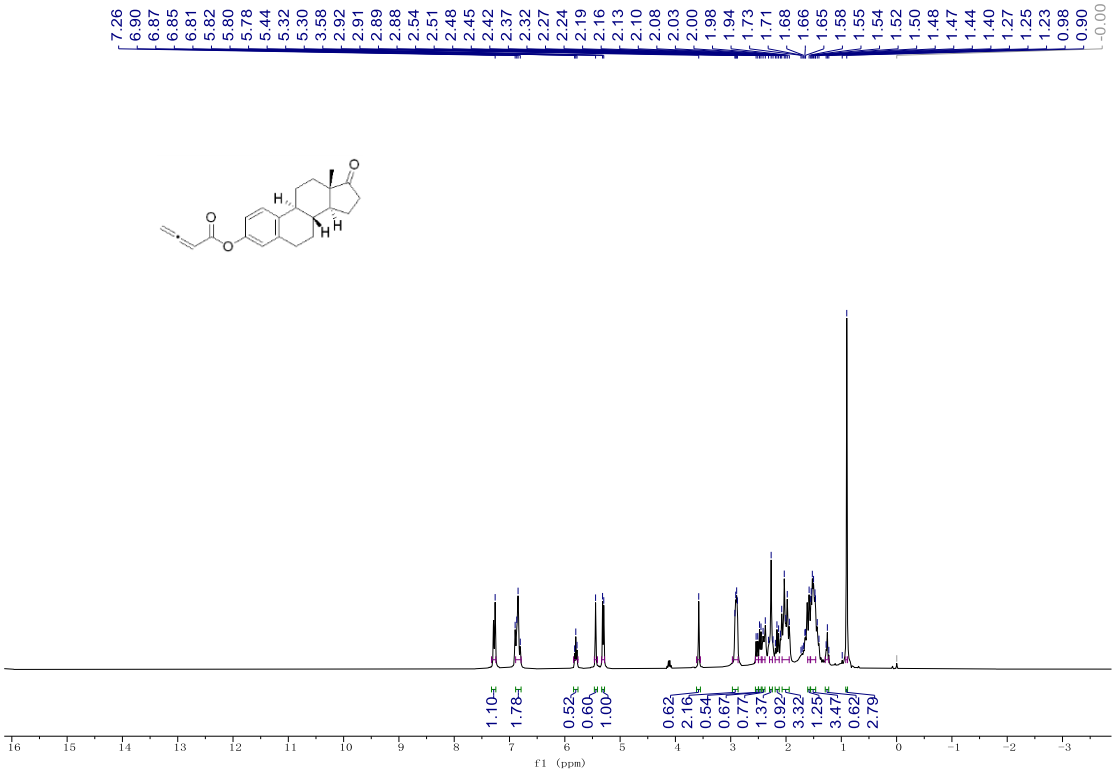
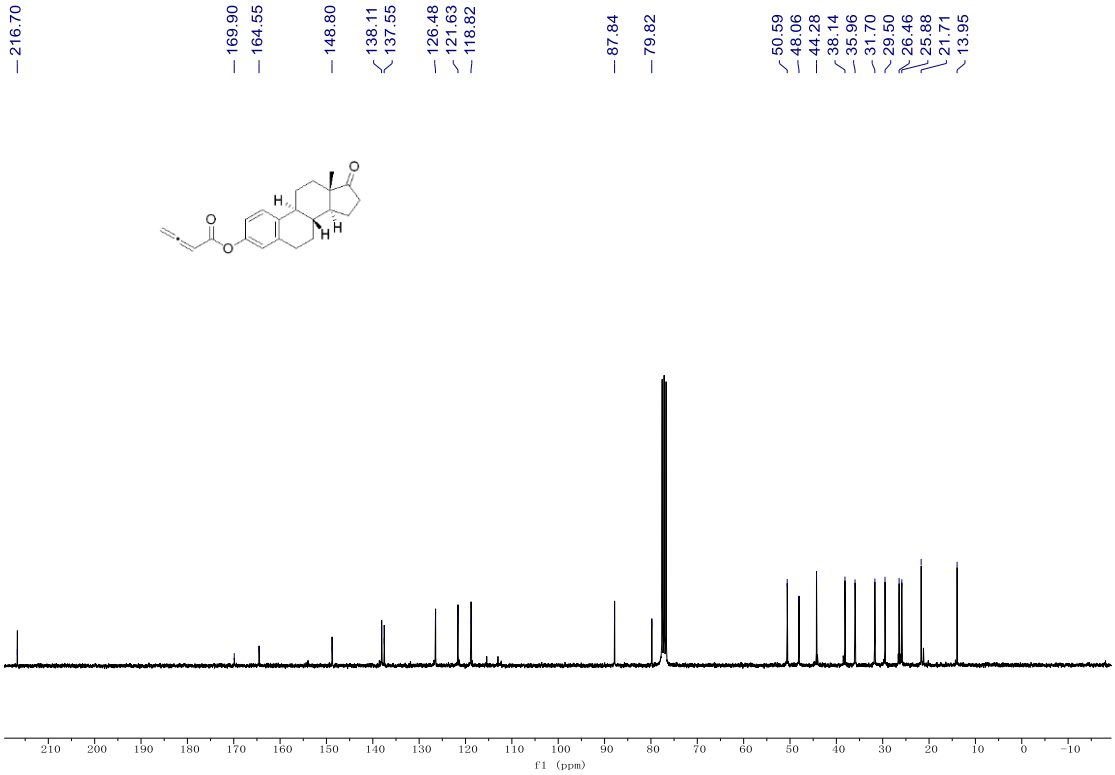
[9] Tang, X.; Zhang, Y.; Tang, Y.; Li, Y.; Zhou, J.; Wang, D.; Gao, L.; Su, Z.; Song, Z. *ACS Catal*. **2022**, *12*, 5185-5196.

8. Characterization of NMR spectra

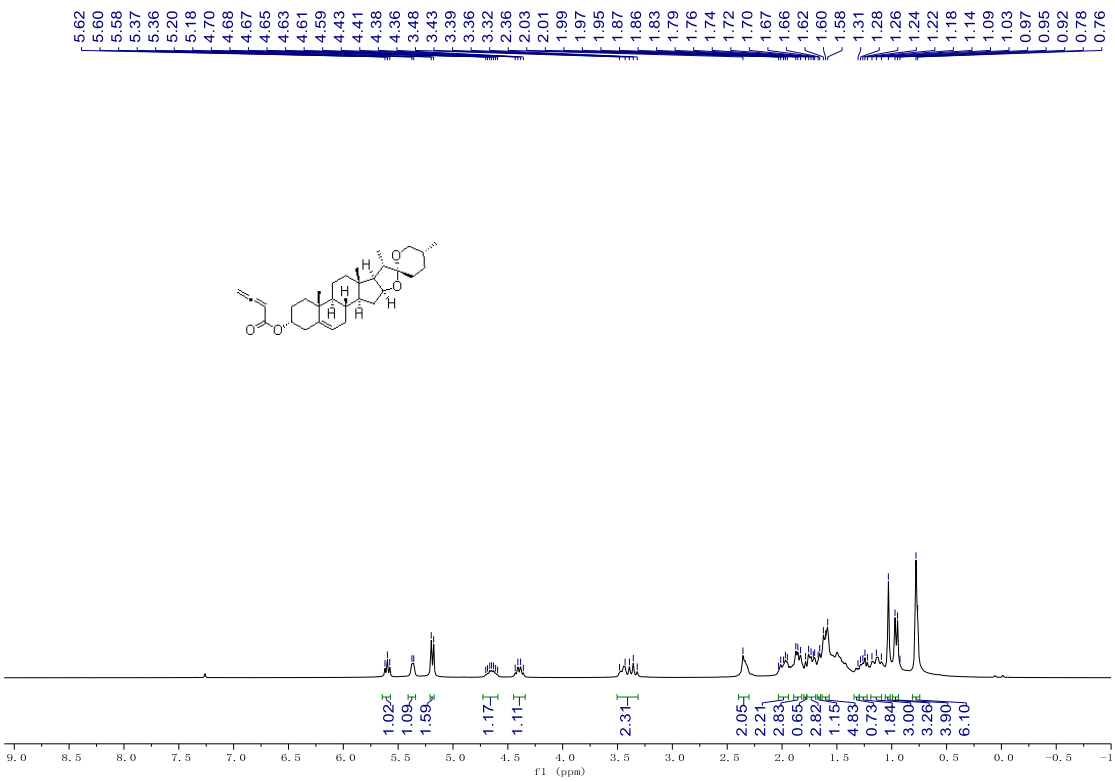
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 2g



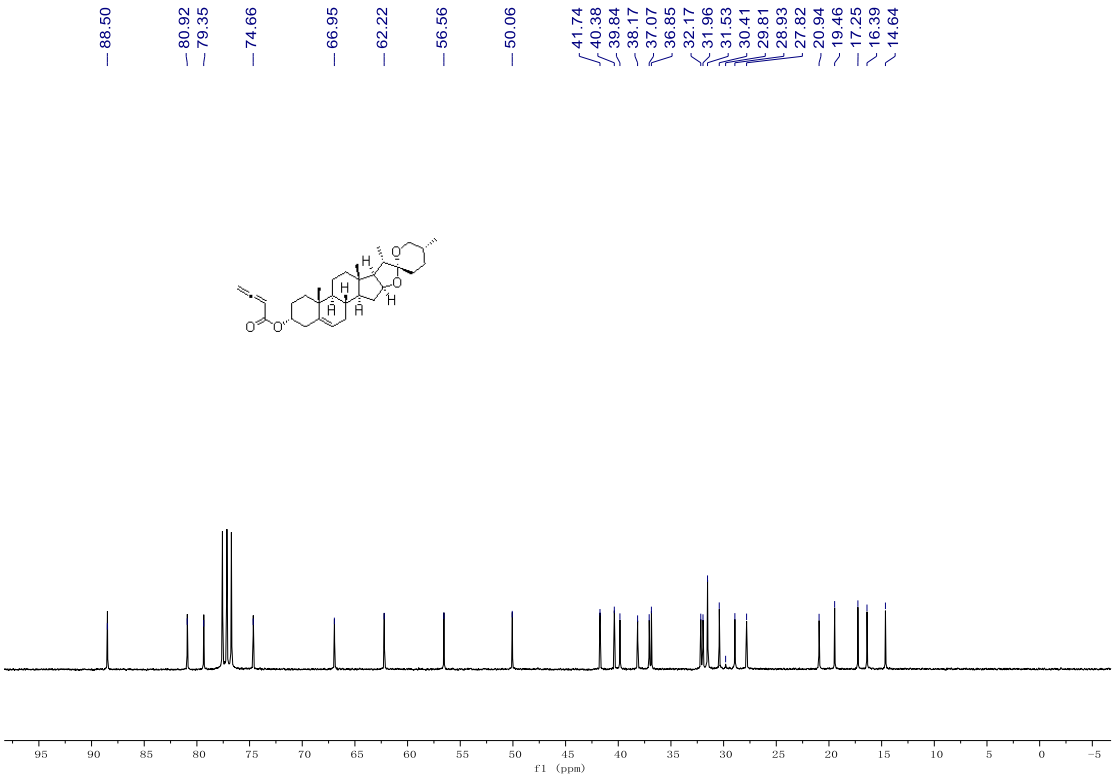
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 2g



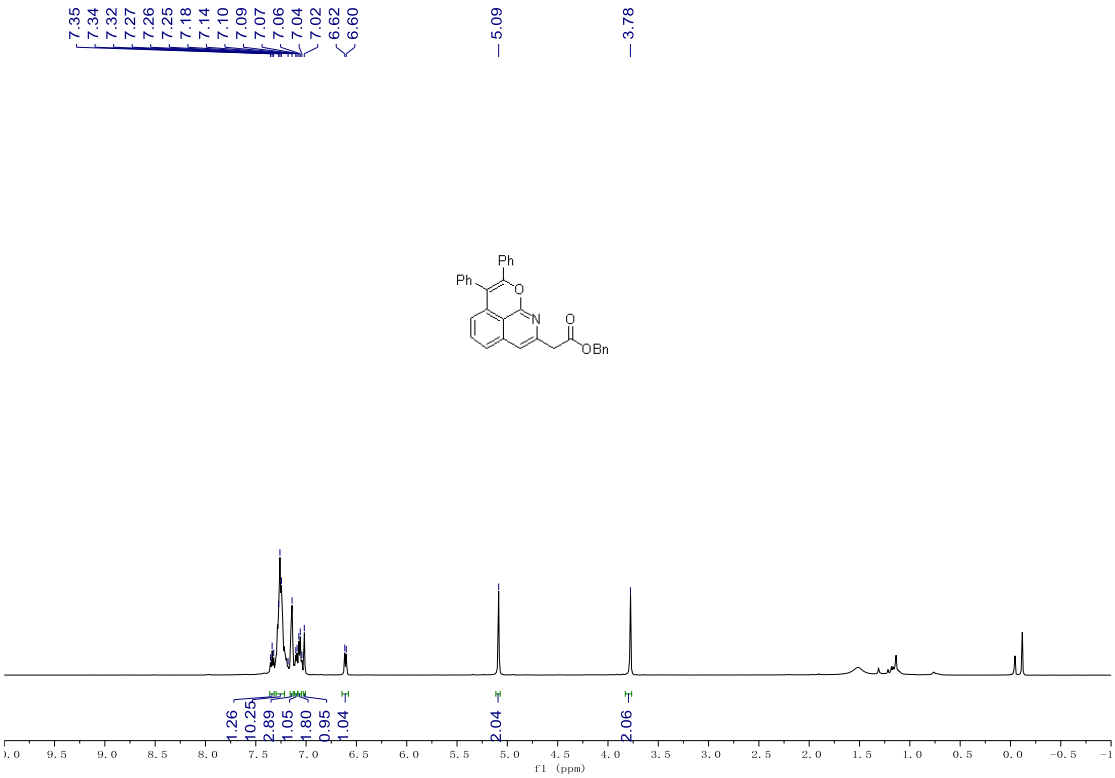
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 2h



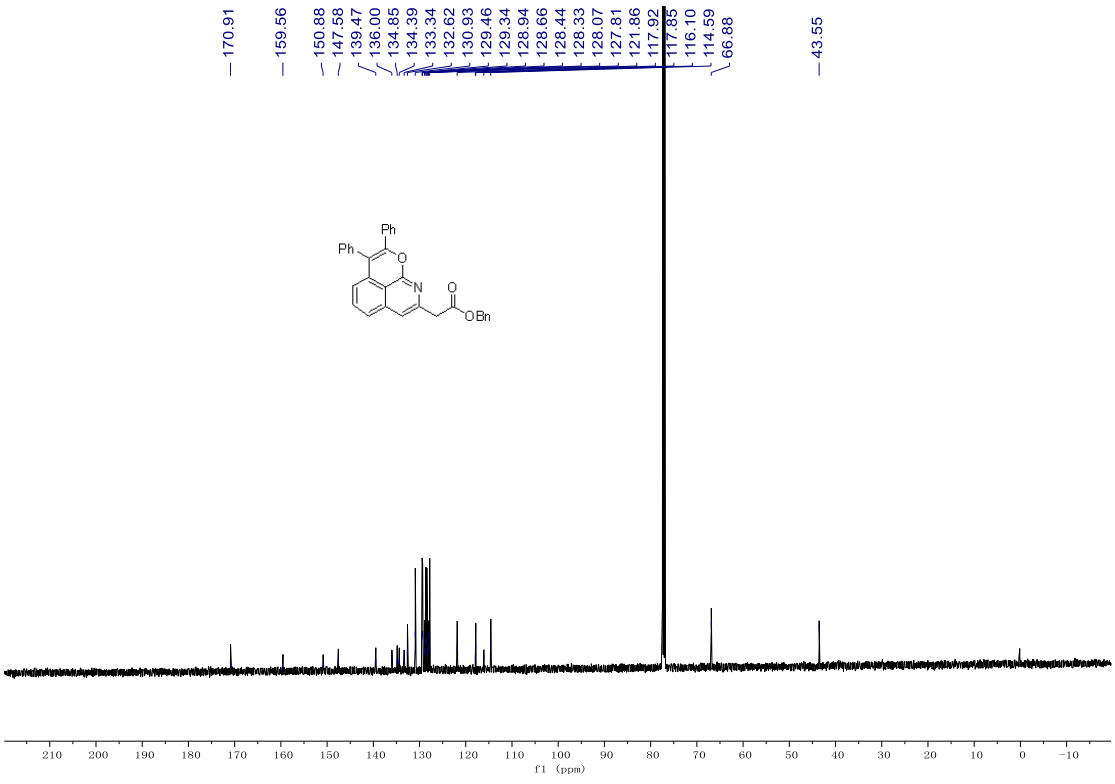
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 2h



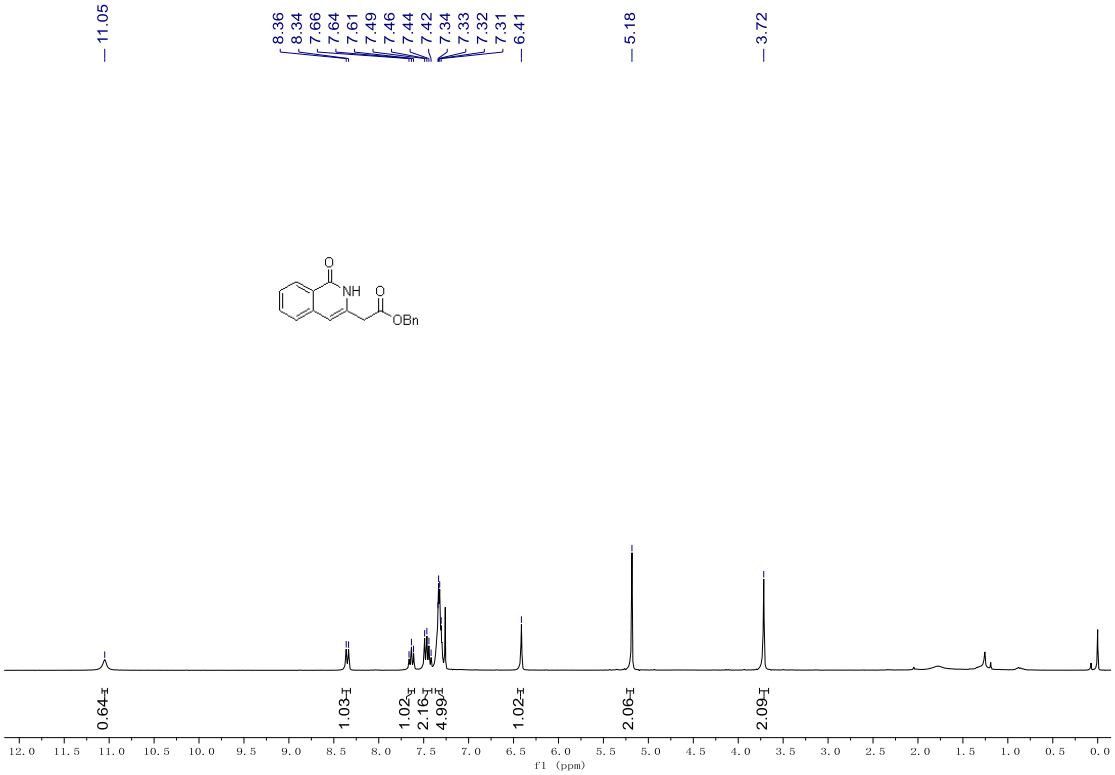
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 7



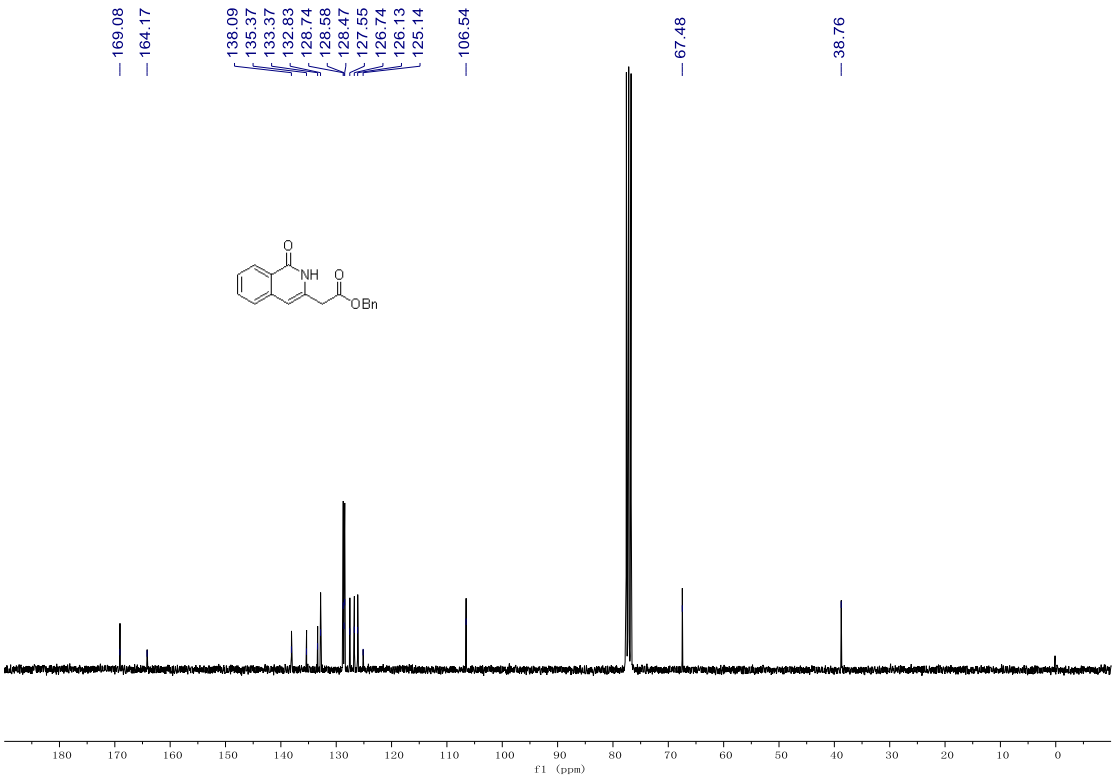
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 7



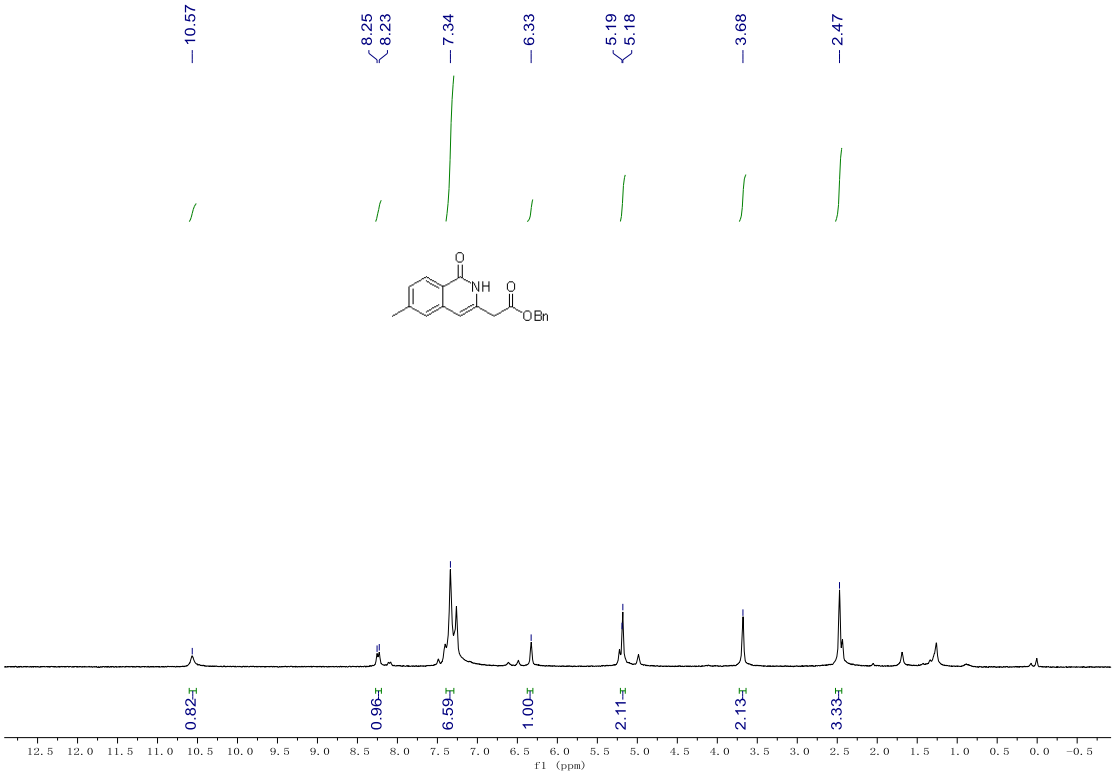
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound **3aa**



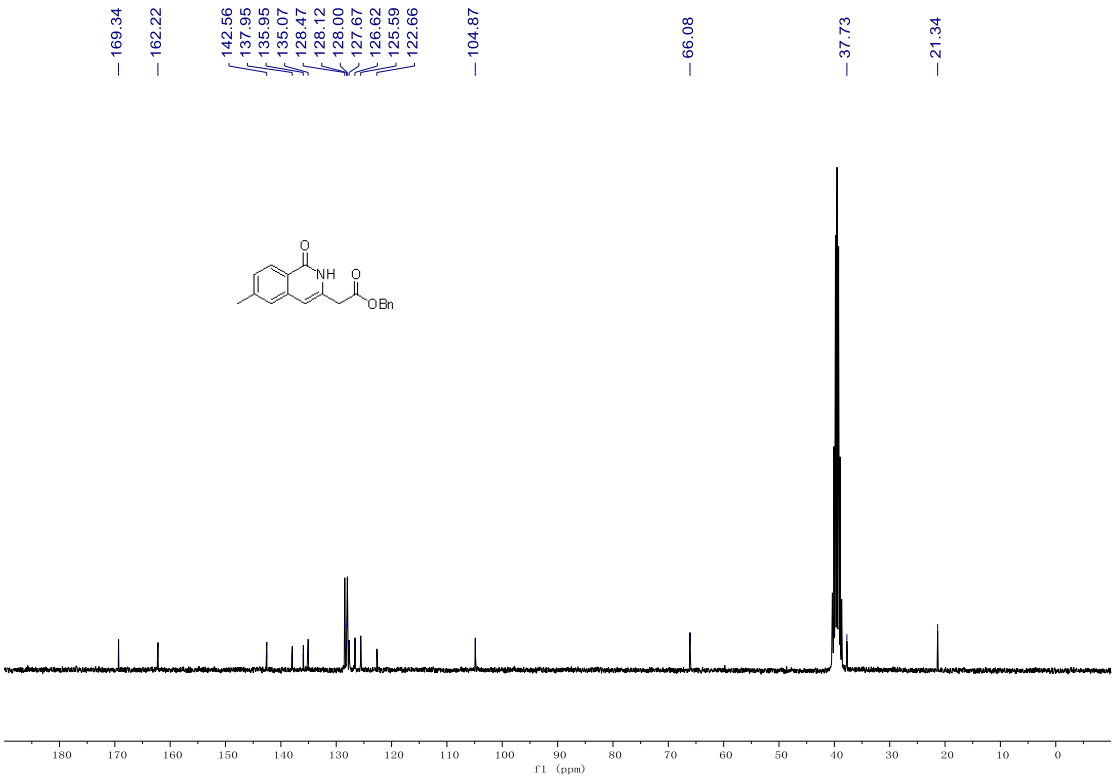
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound **3aa**



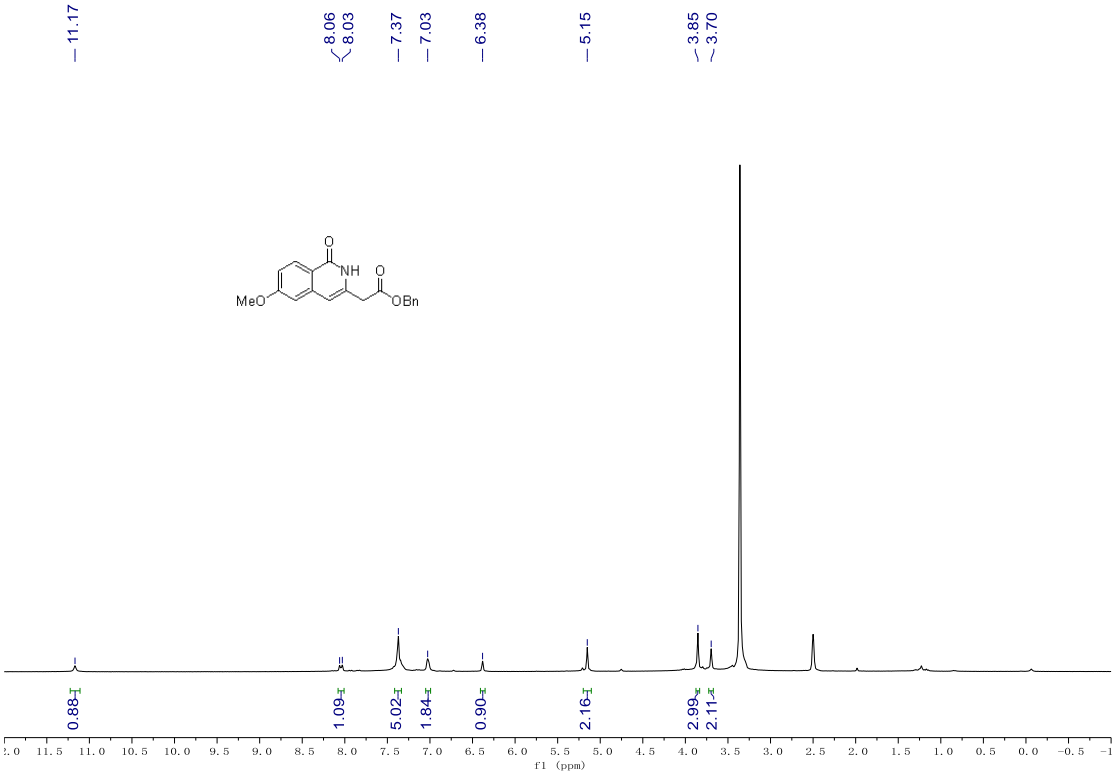
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound **3ba**



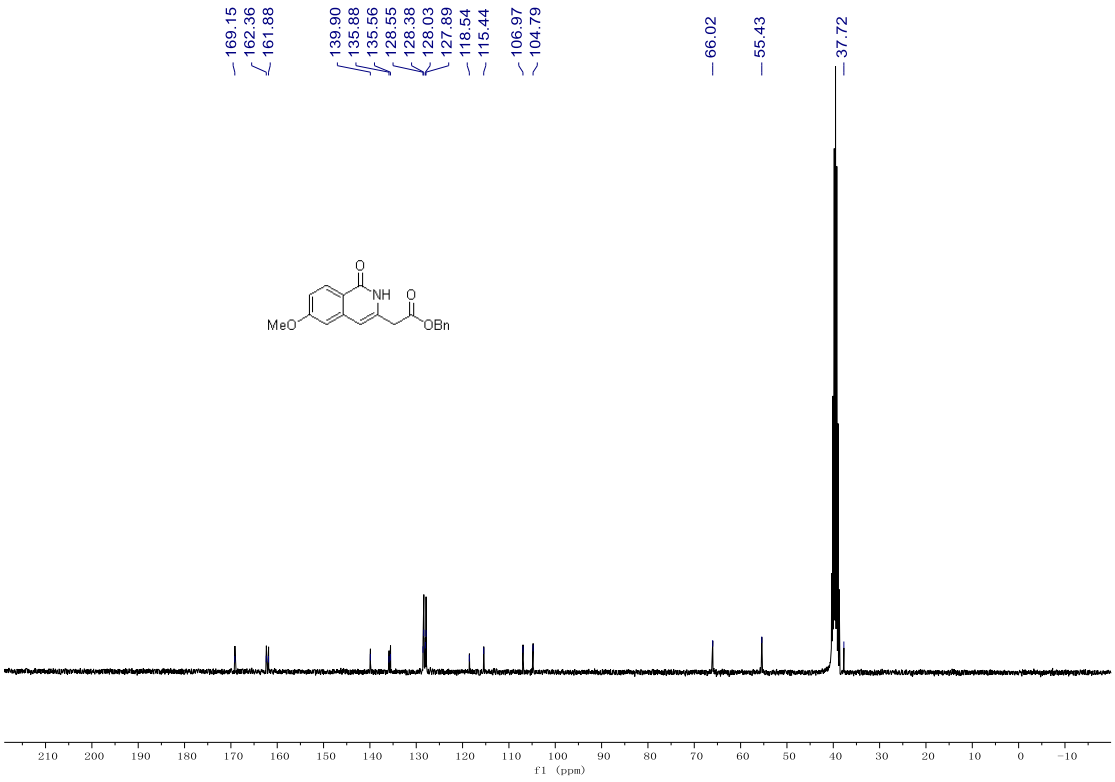
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound **3ba**



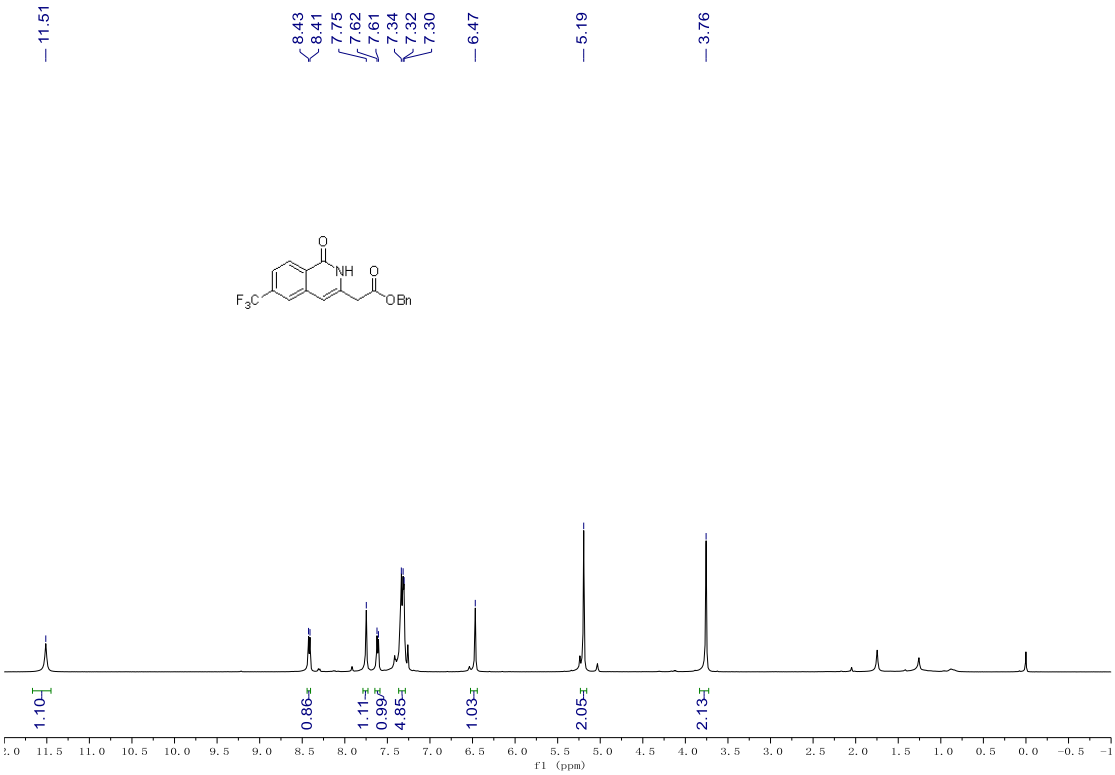
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 3ca



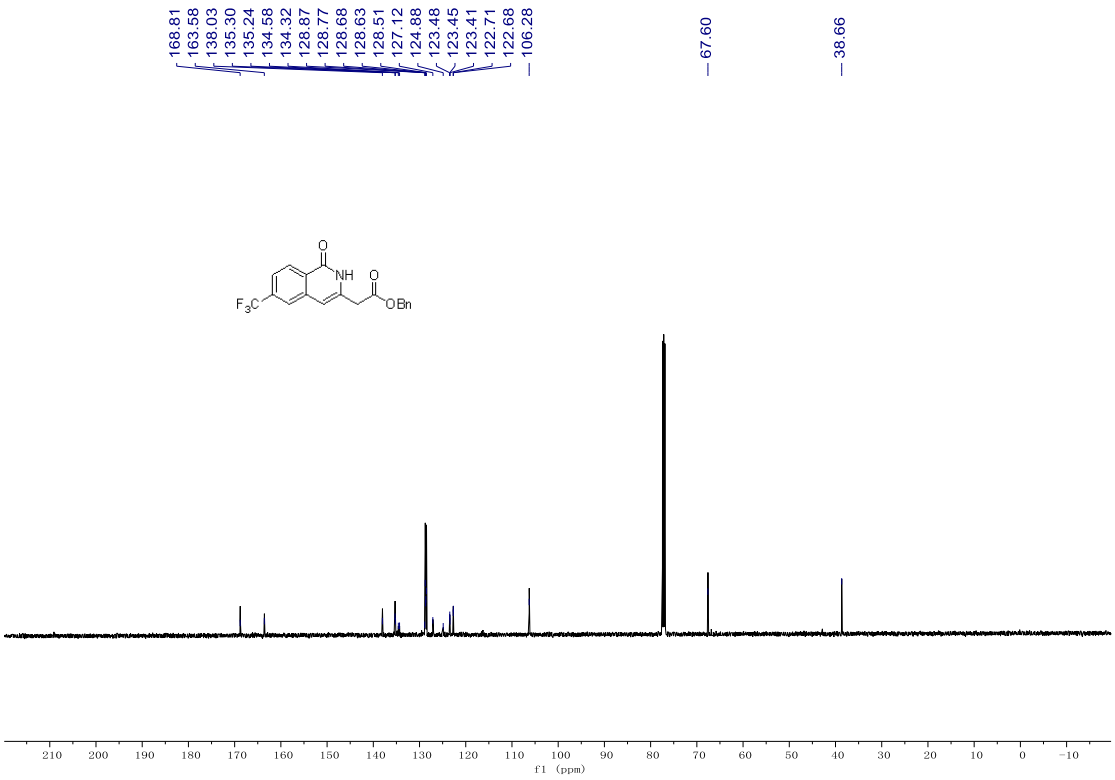
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 3ca



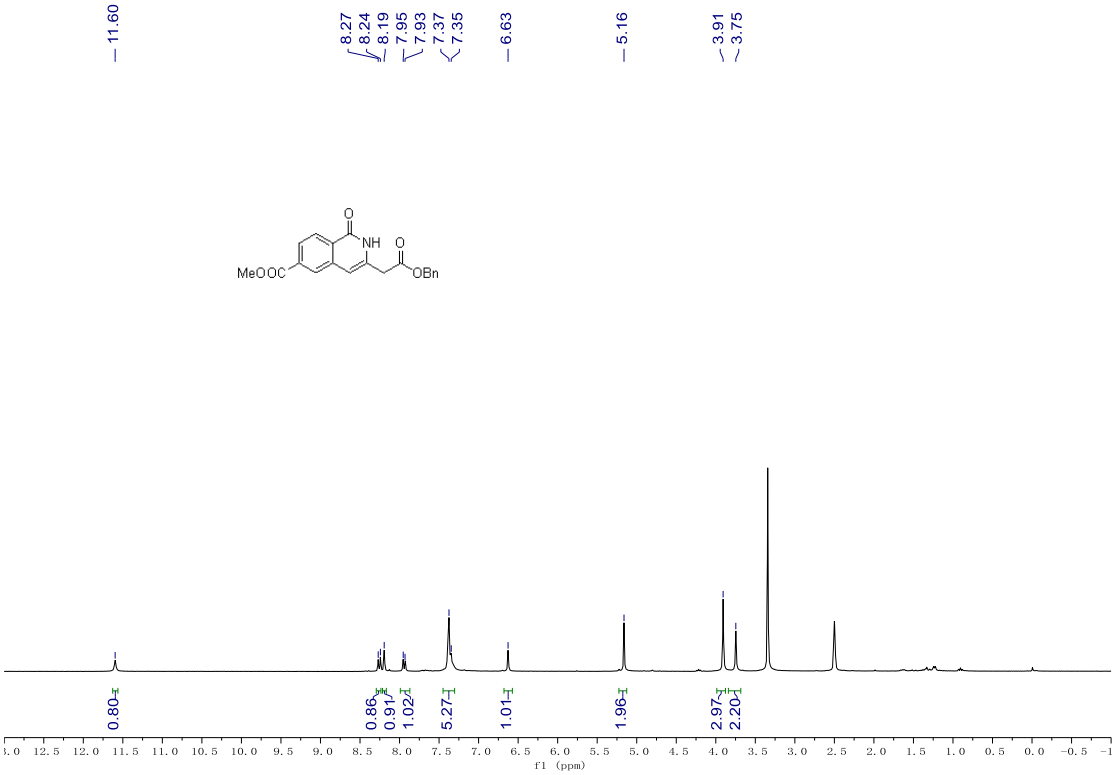
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound **3da**



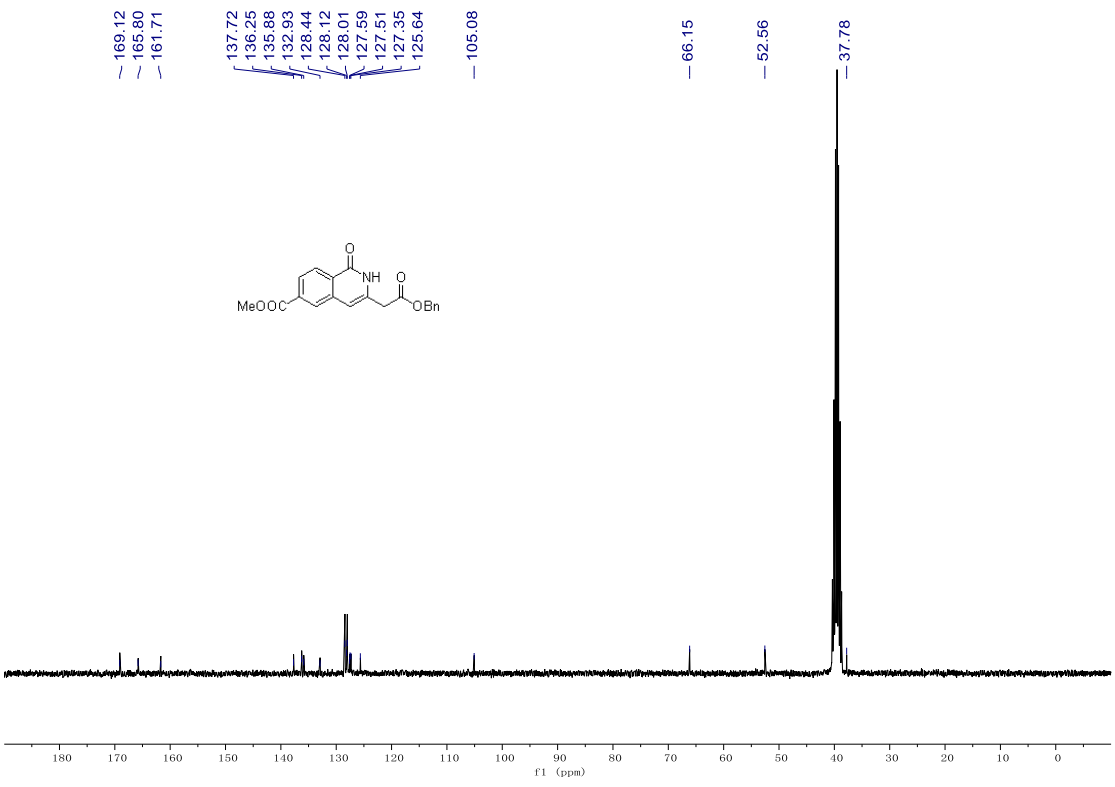
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound **3da**



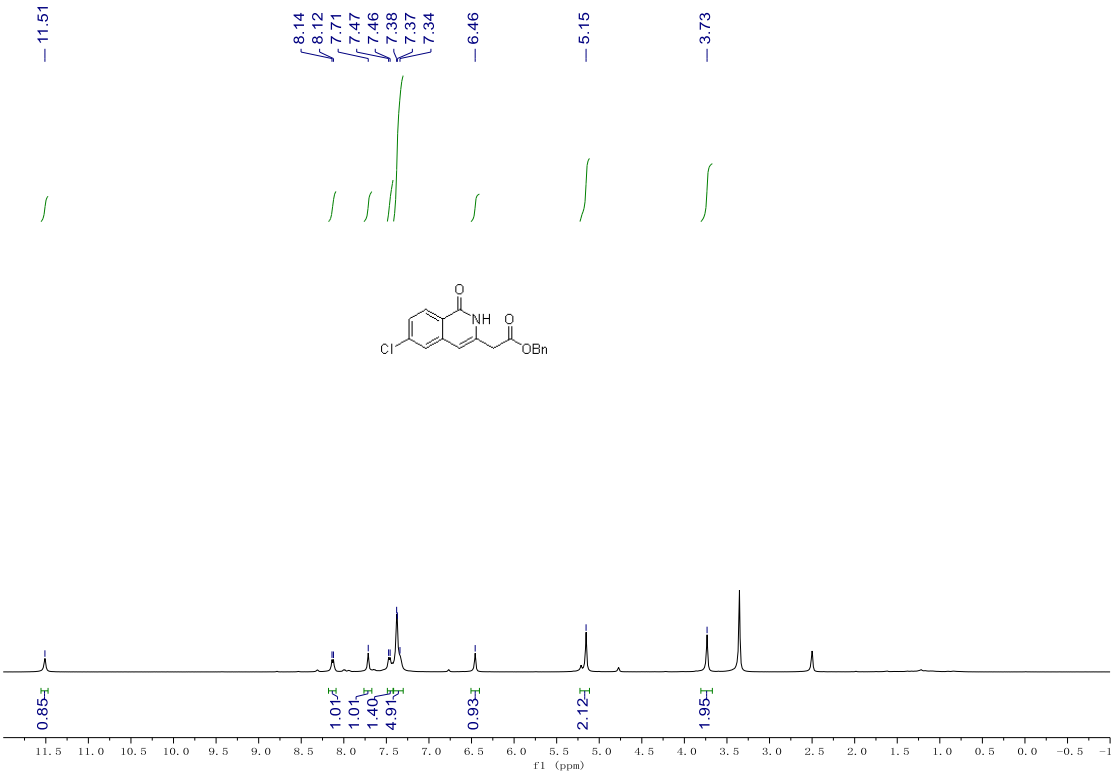
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 3ea



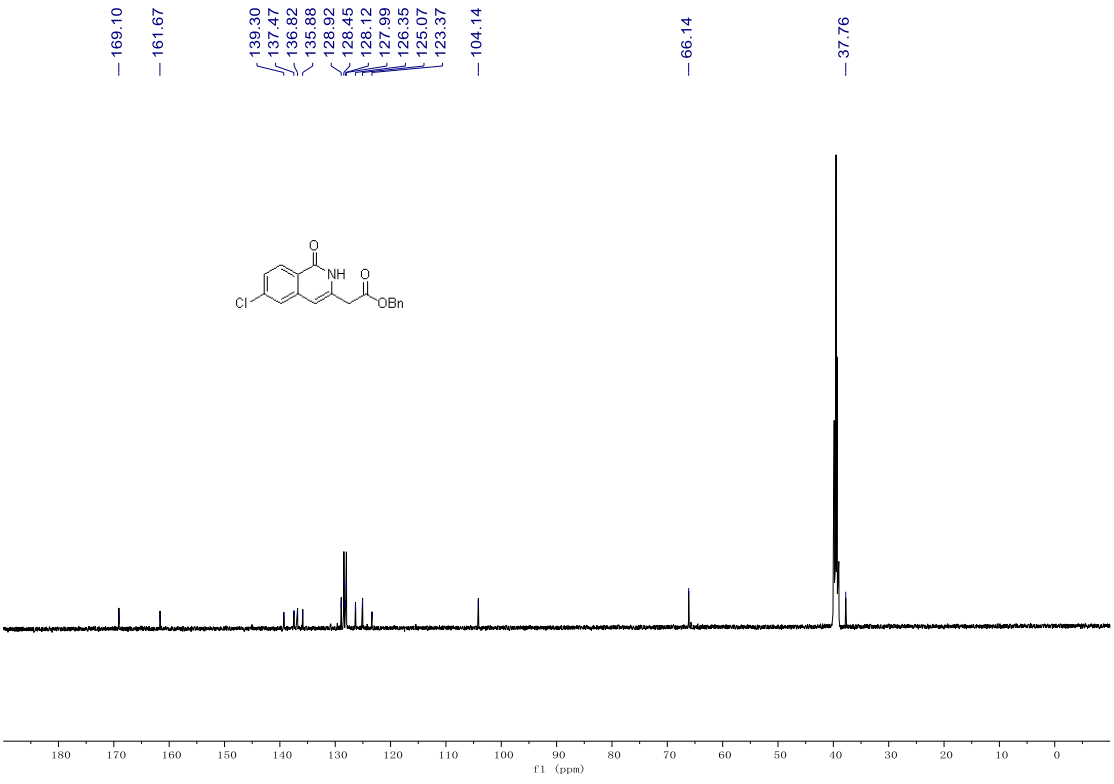
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 3ea



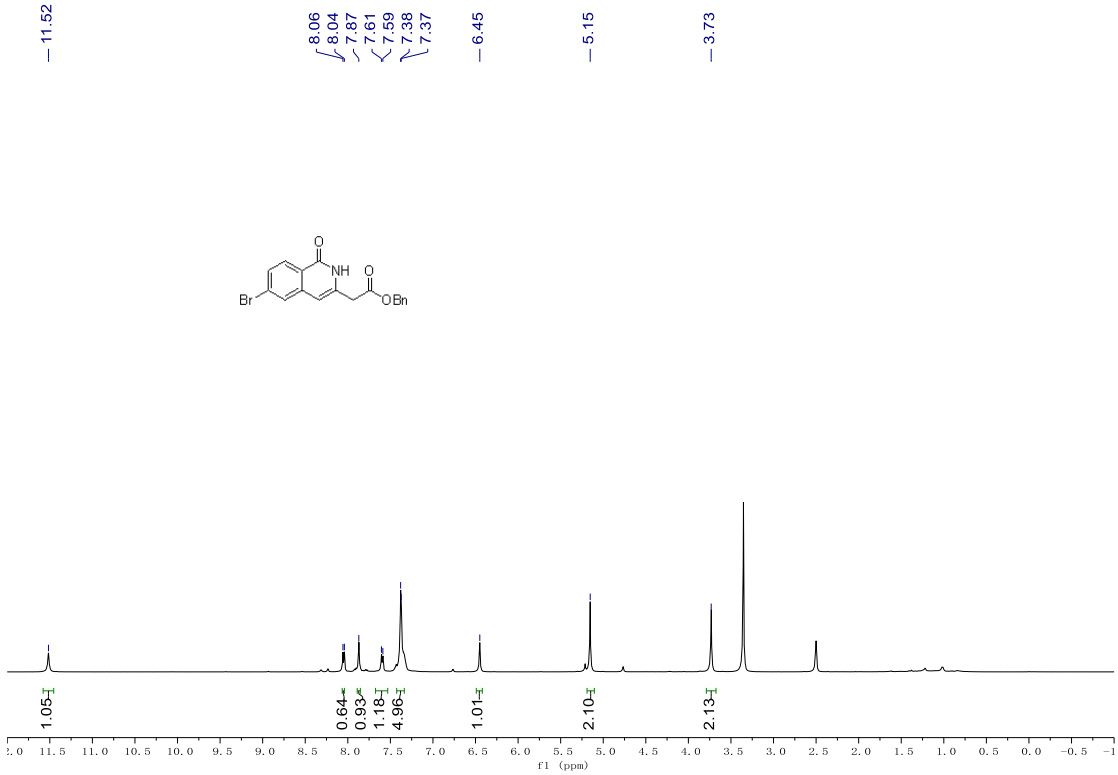
^{1}H NMR (500 MHz, DMSO-d_6) Spectra of compound 3fa



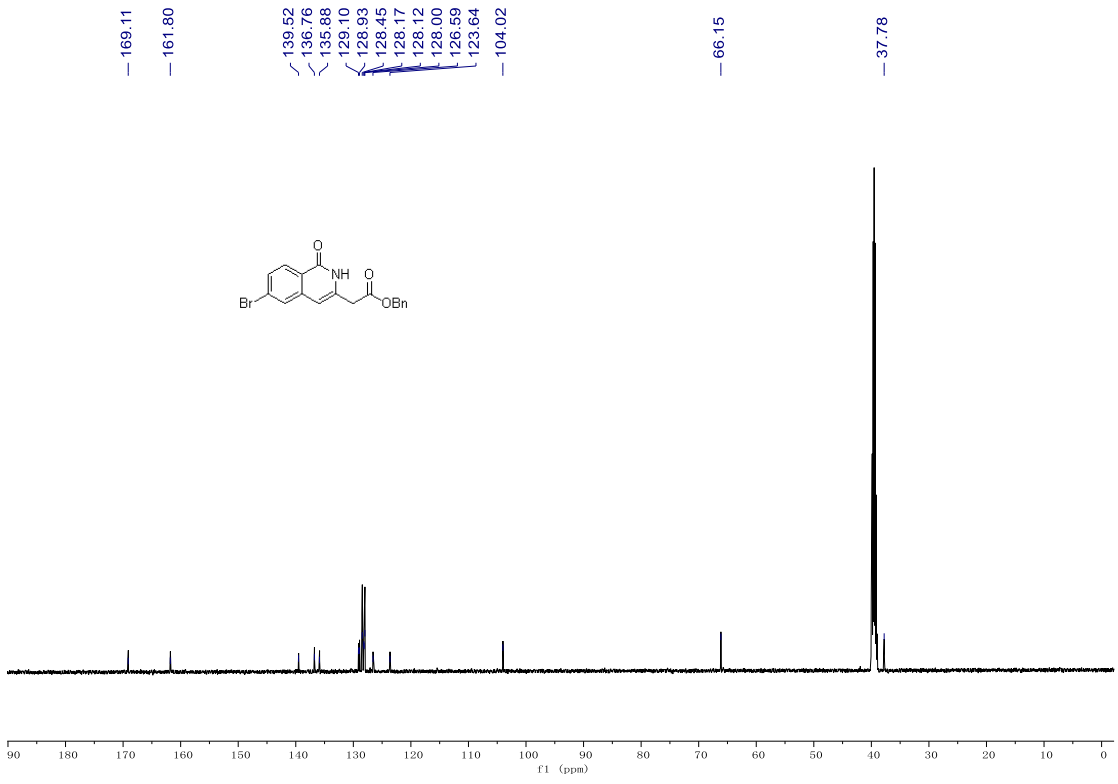
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound 3fa



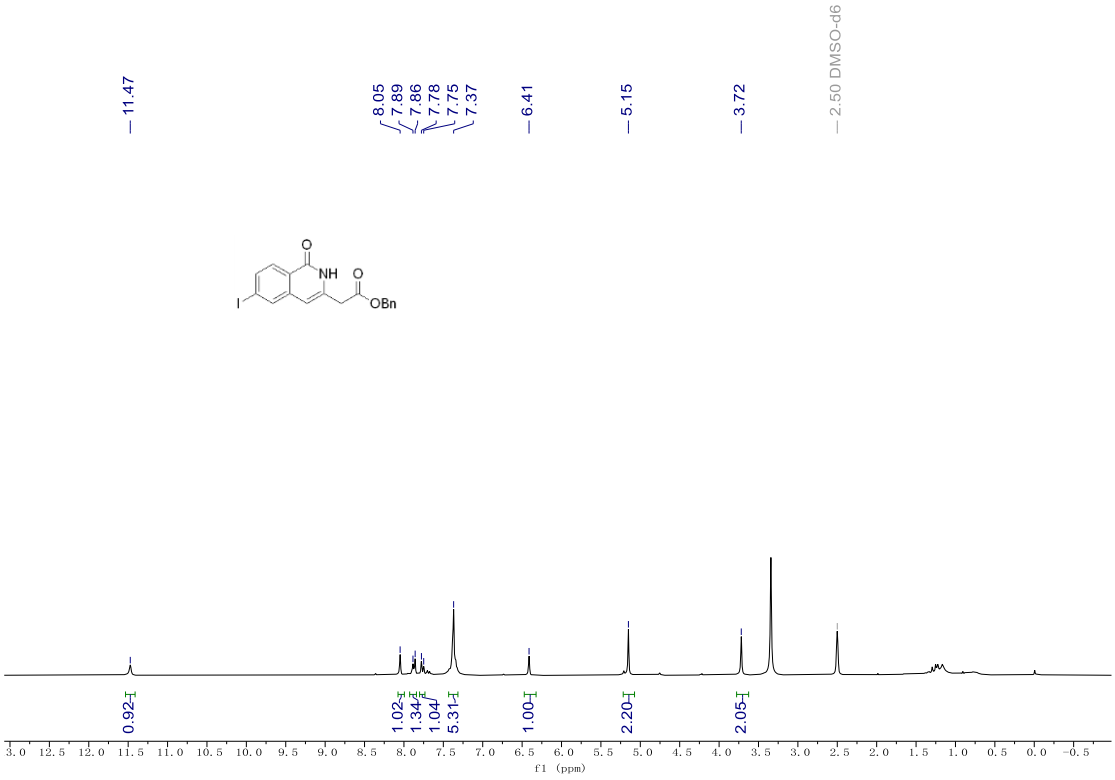
^{1}H NMR (500 MHz, DMSO-d_6) Spectra of compound 3ga



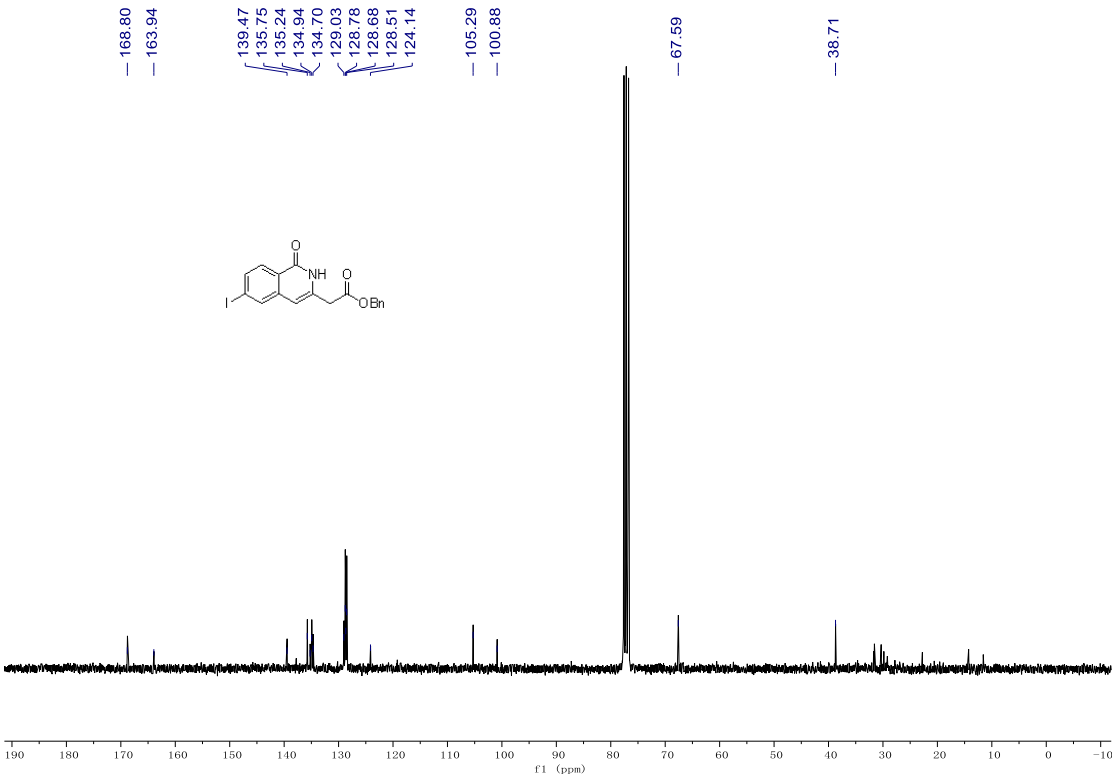
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound 3ga



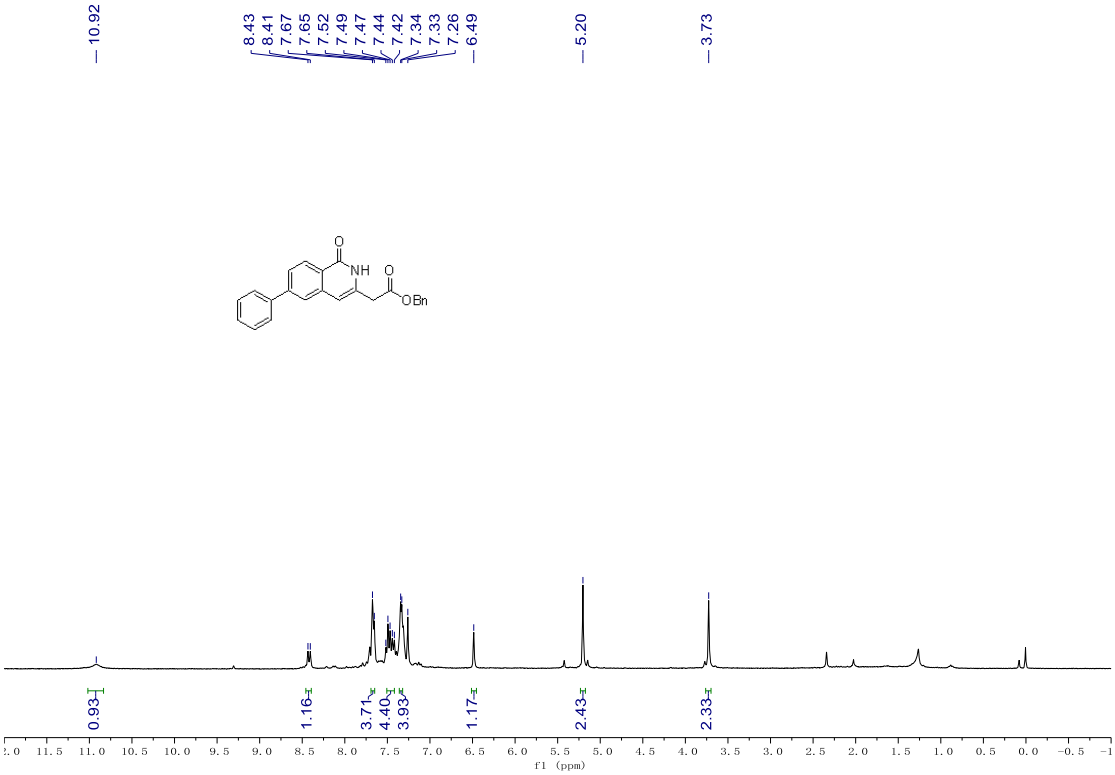
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound **3ha**



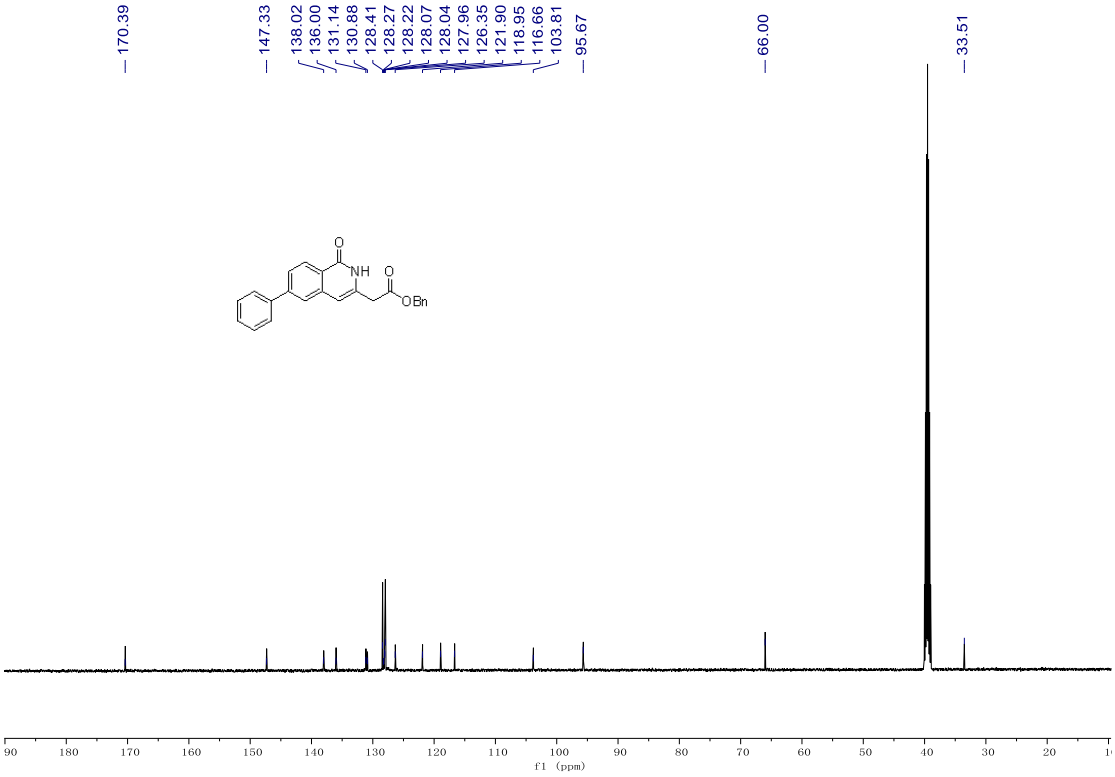
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound **3ha**



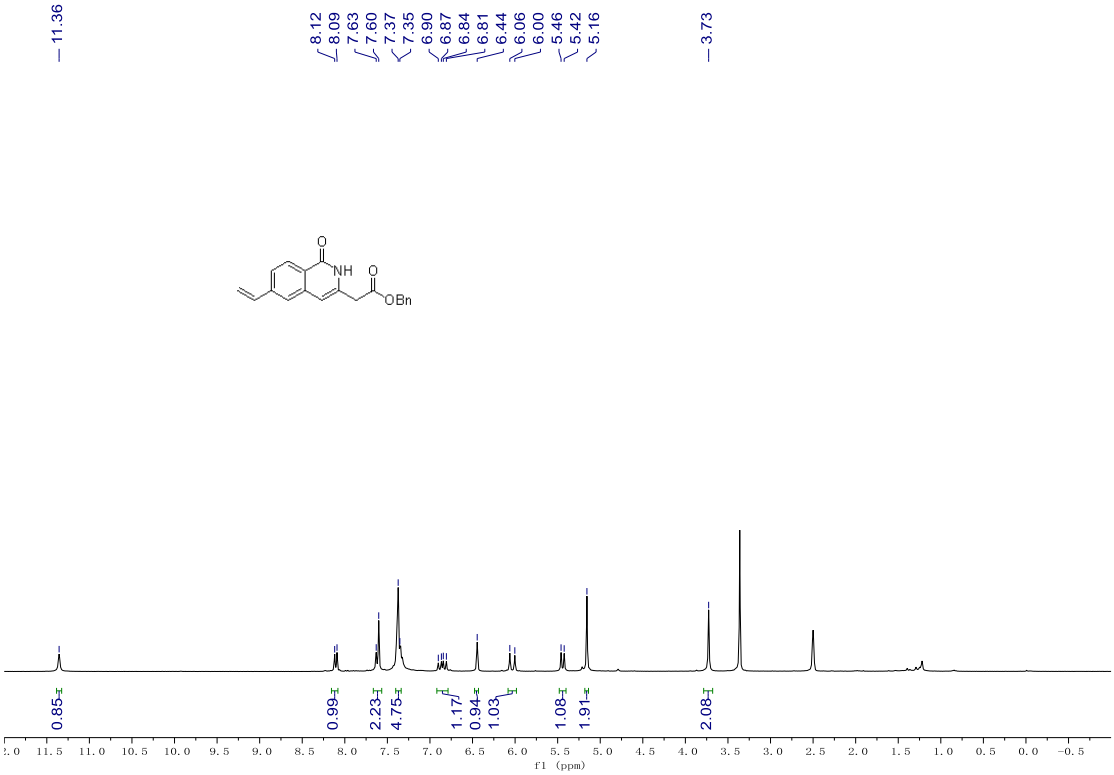
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound **3ia**



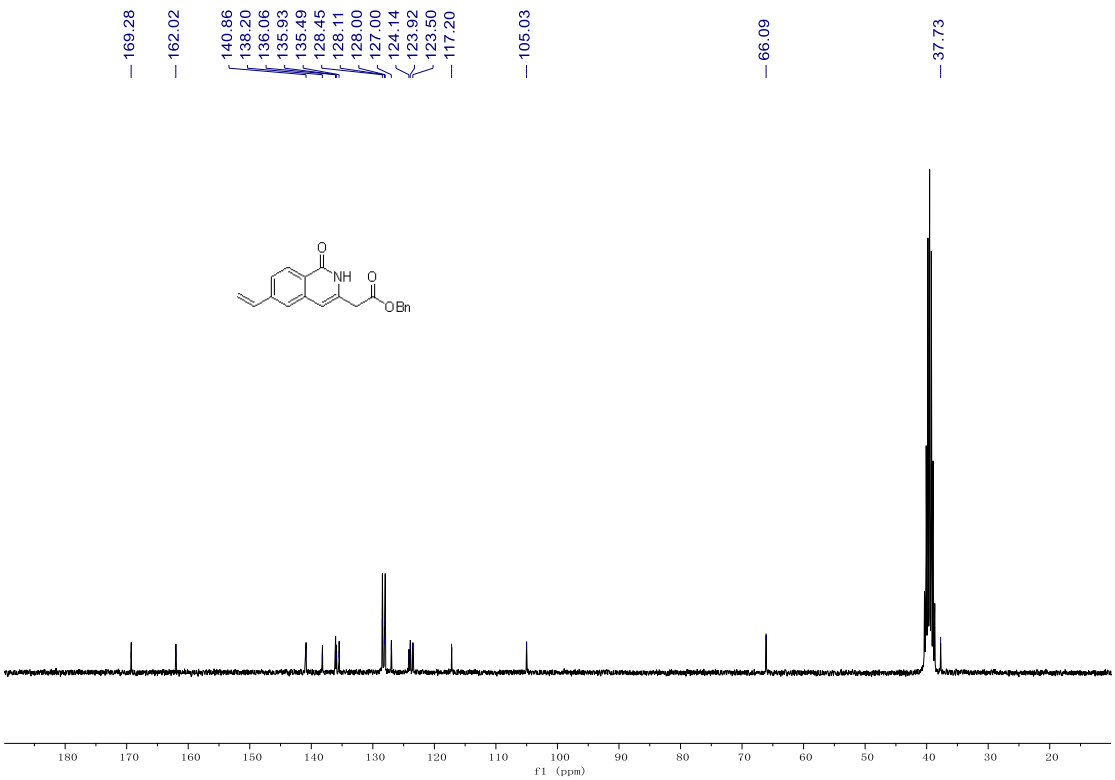
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound **3ia**



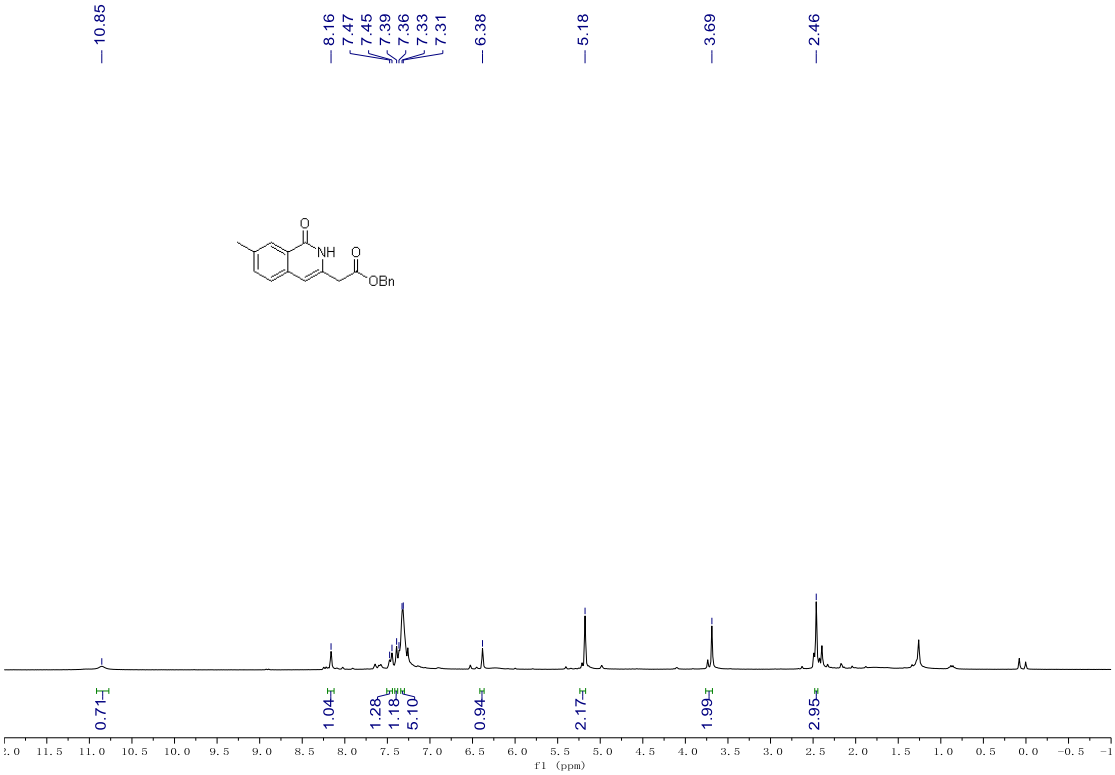
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 3ja



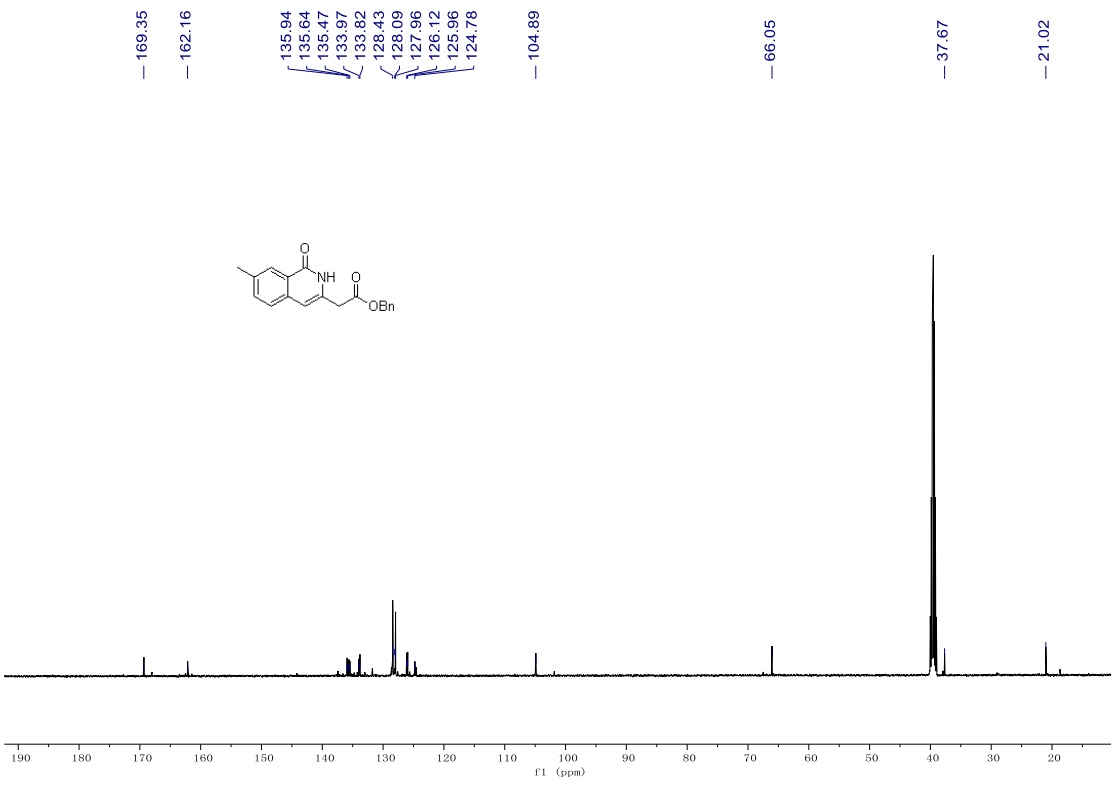
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 3ja



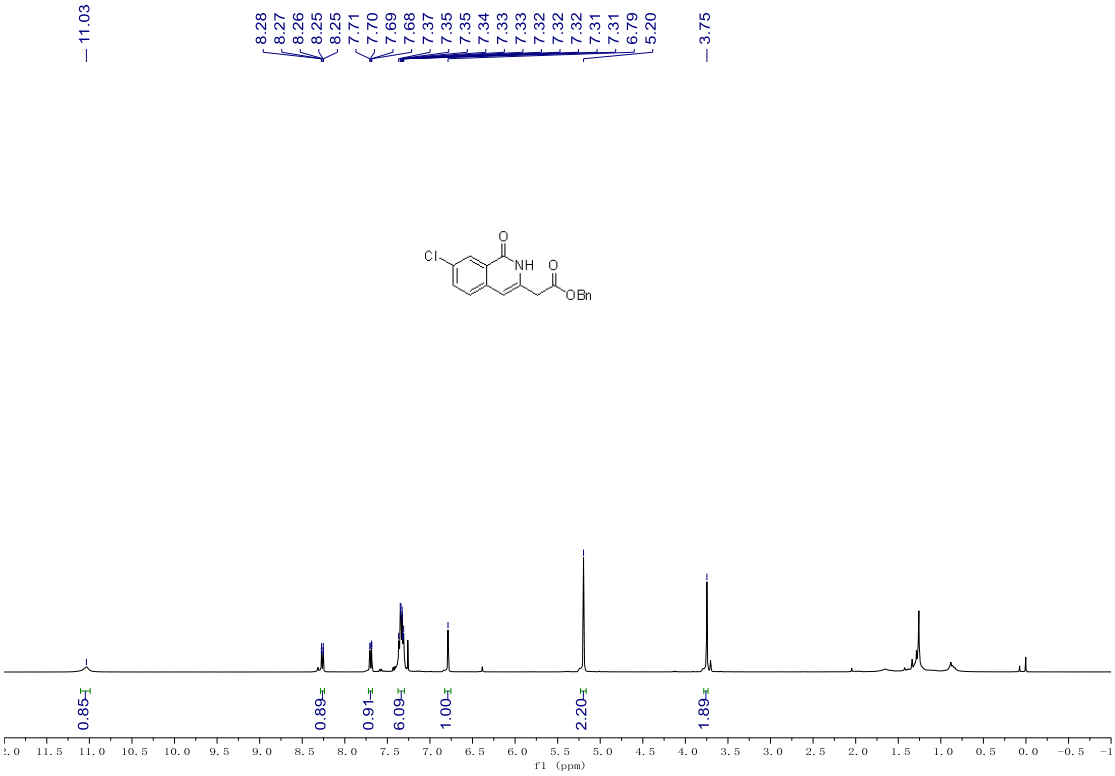
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound **3ka**



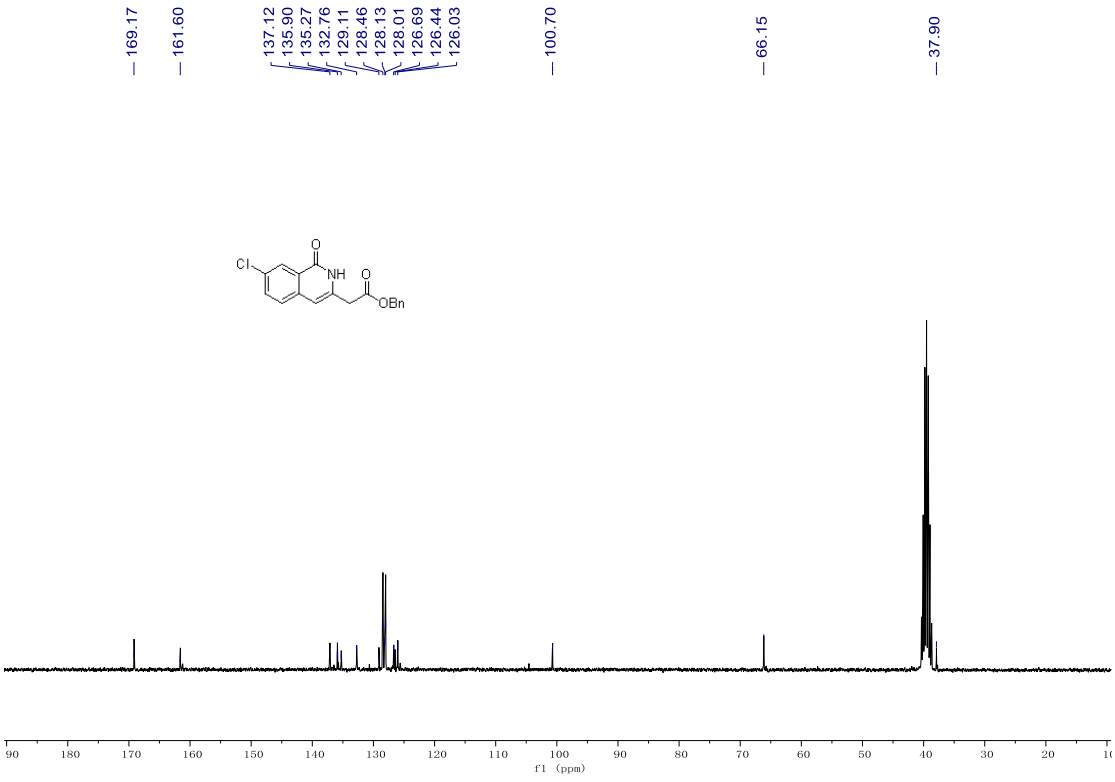
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound **3ka**



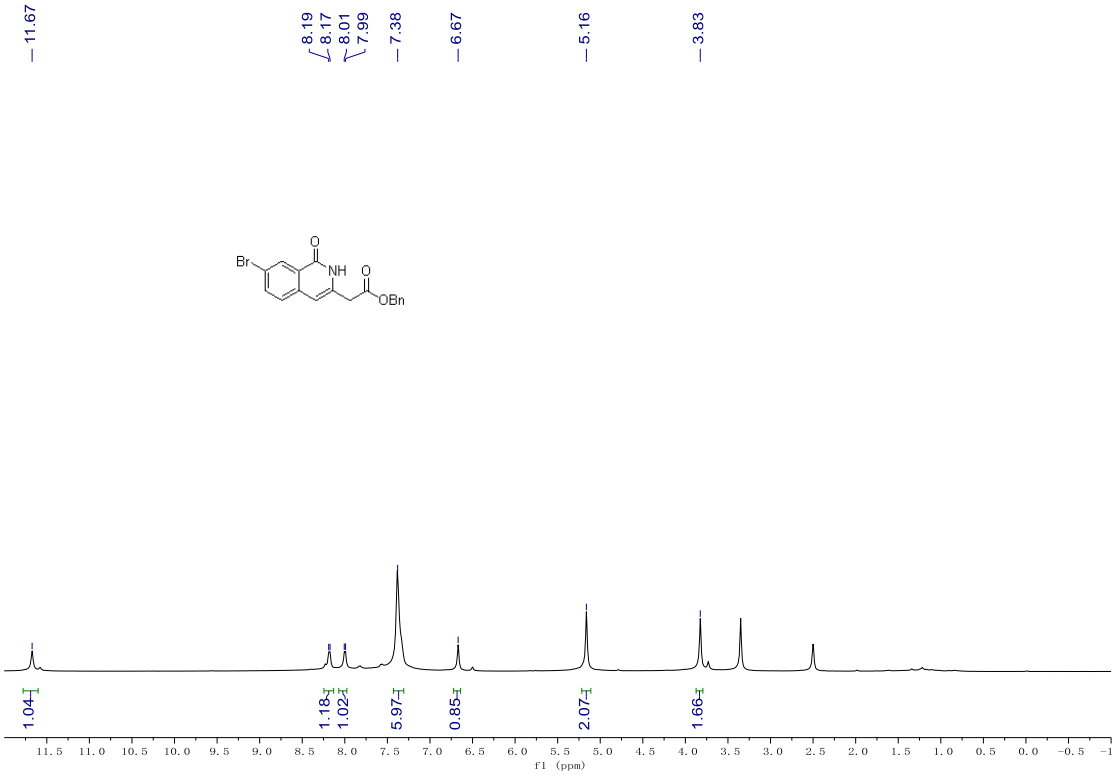
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound **3la**



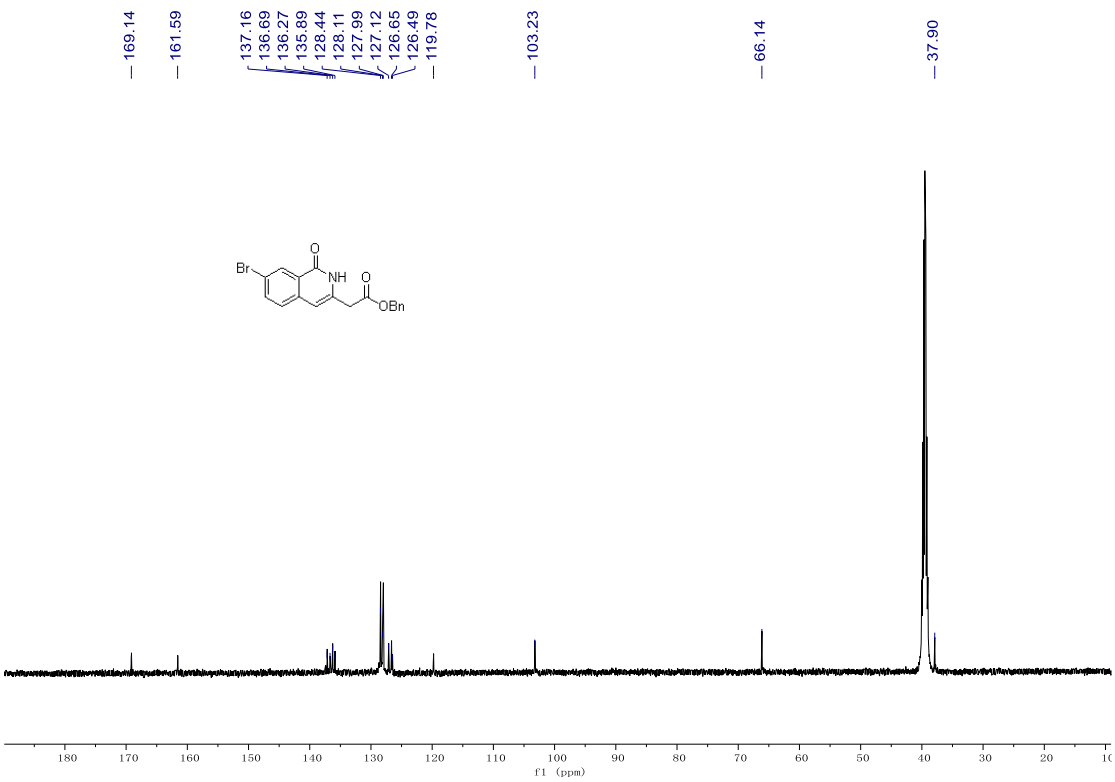
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound **3la**



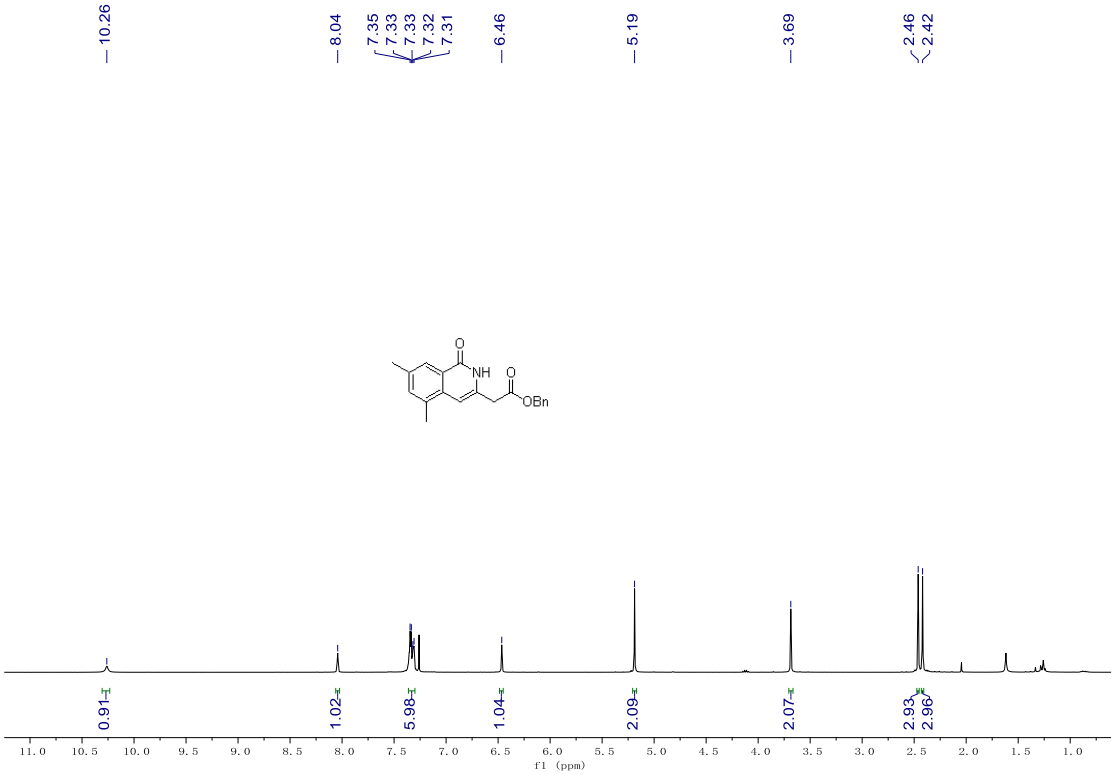
^{1}H NMR (500 MHz, DMSO-d_6) Spectra of compound **3ma**



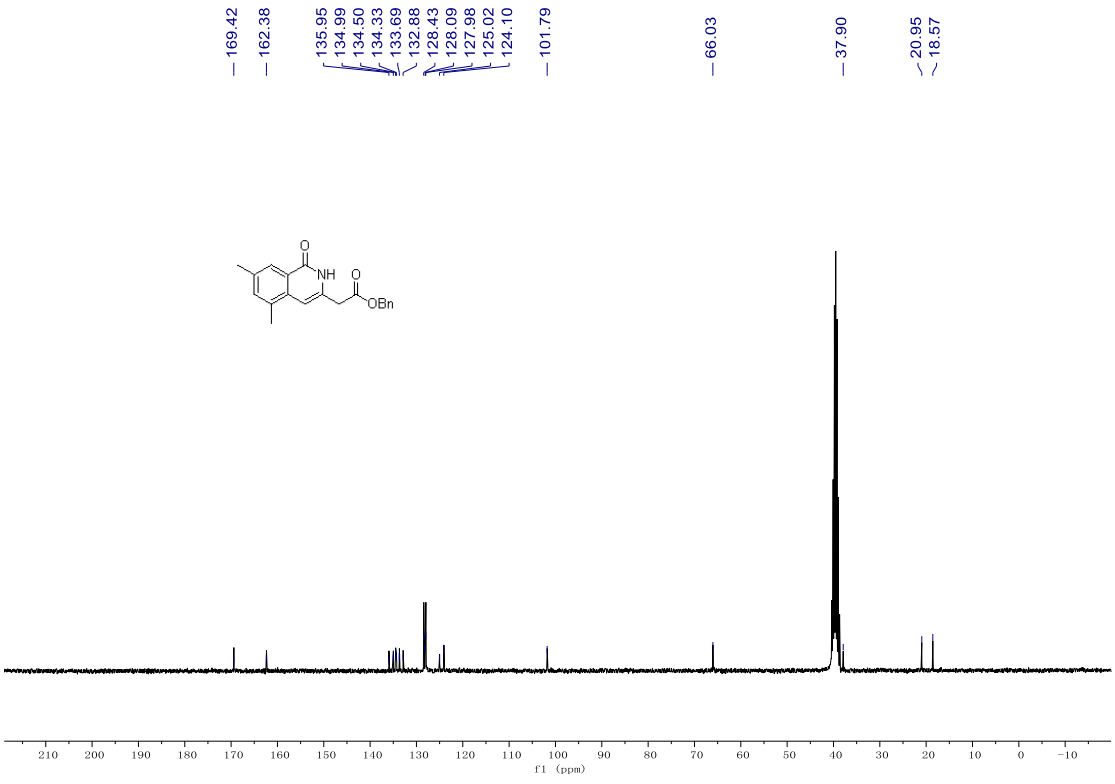
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound **3ma**



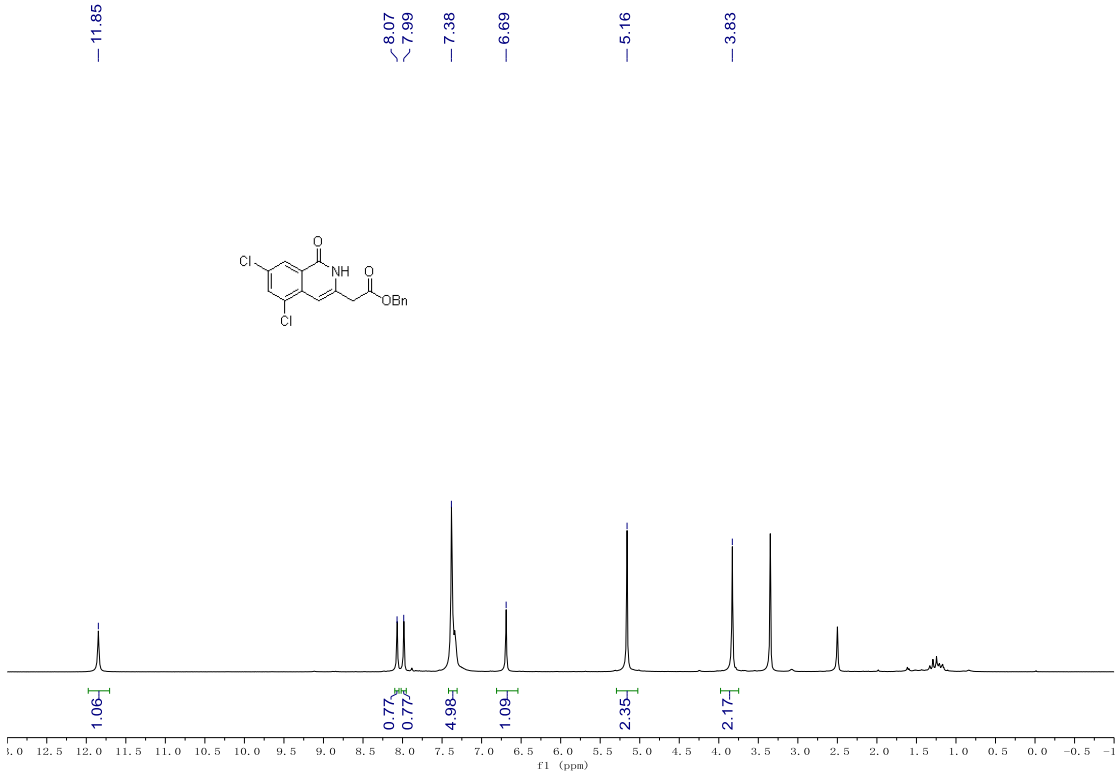
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound **3na**



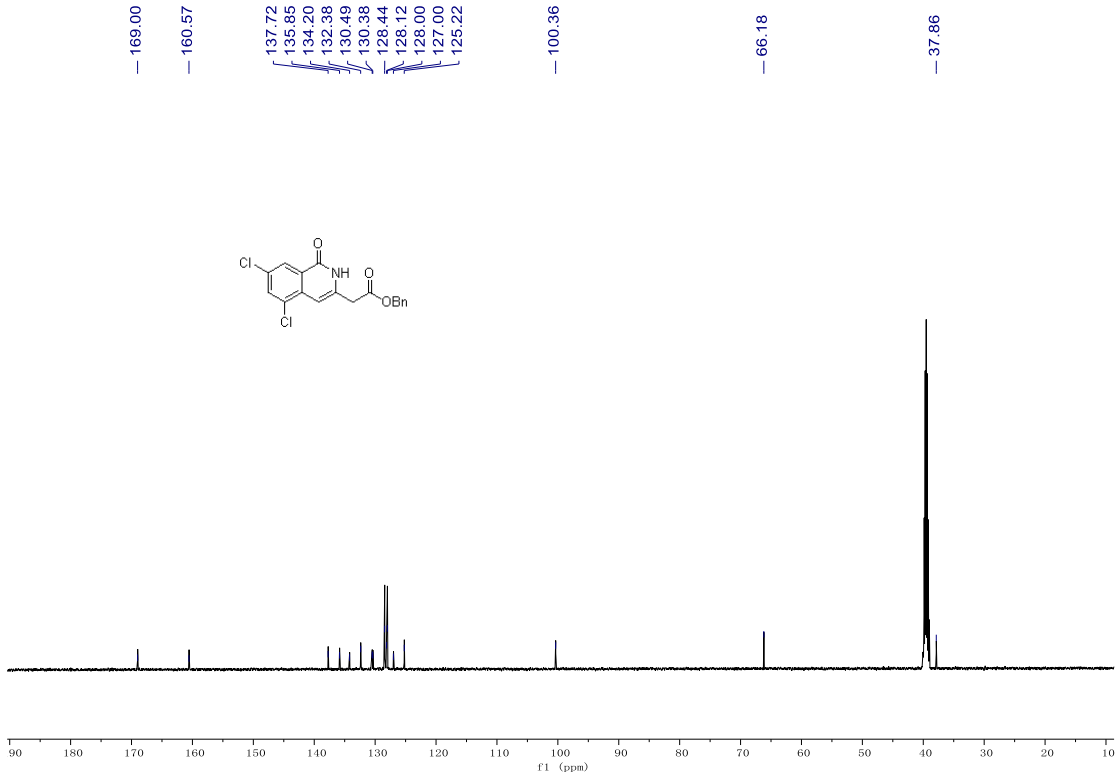
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound **3na**



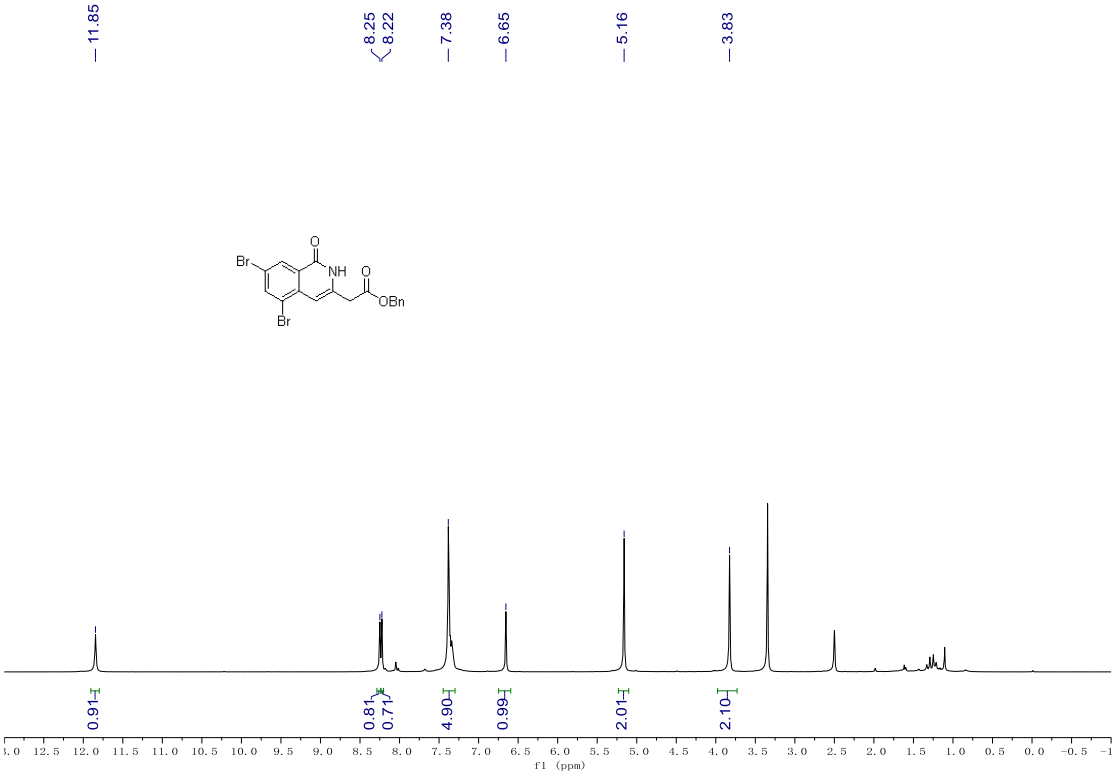
^{1}H NMR (500 MHz, DMSO-d_6) Spectra of compound **3oa**



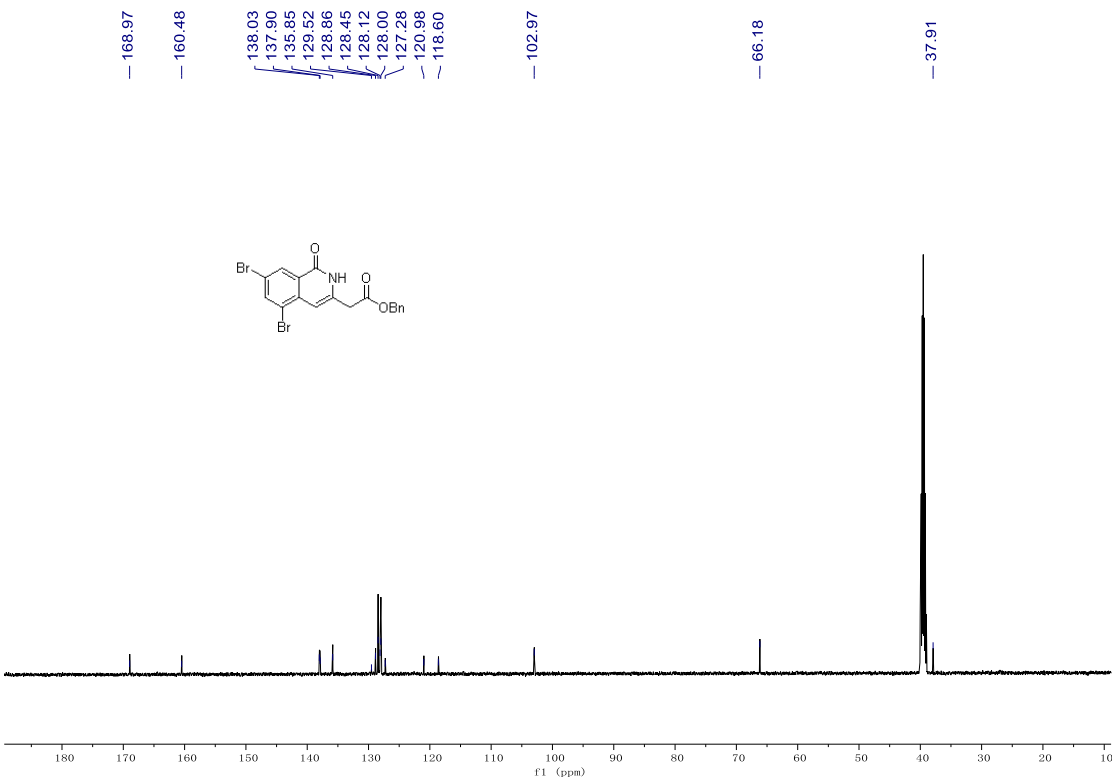
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound **3oa**



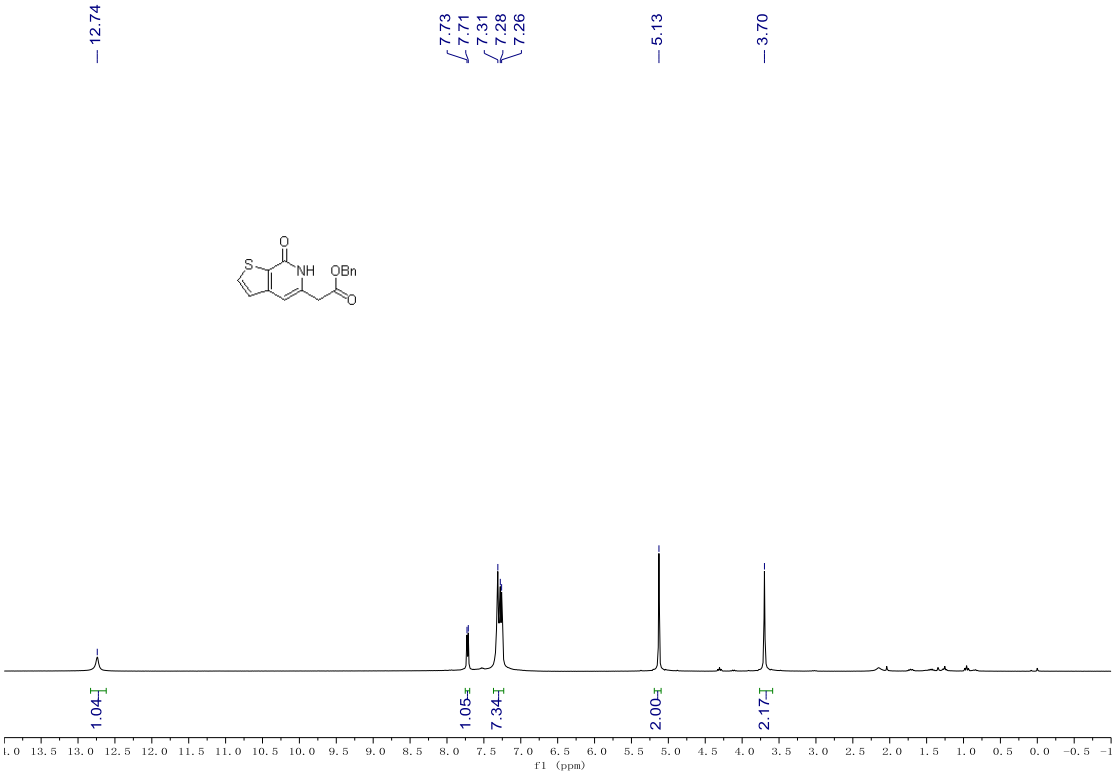
^{1}H NMR (500 MHz, DMSO-d_6) Spectra of compound 3pa



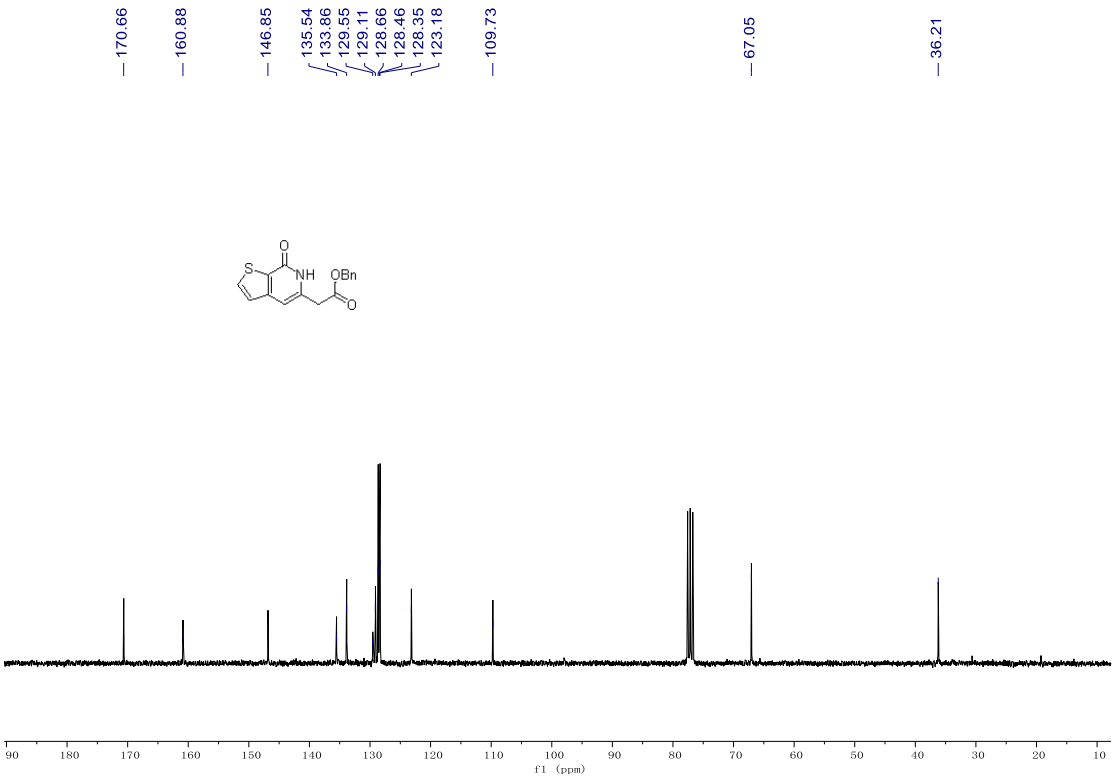
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound 3pa



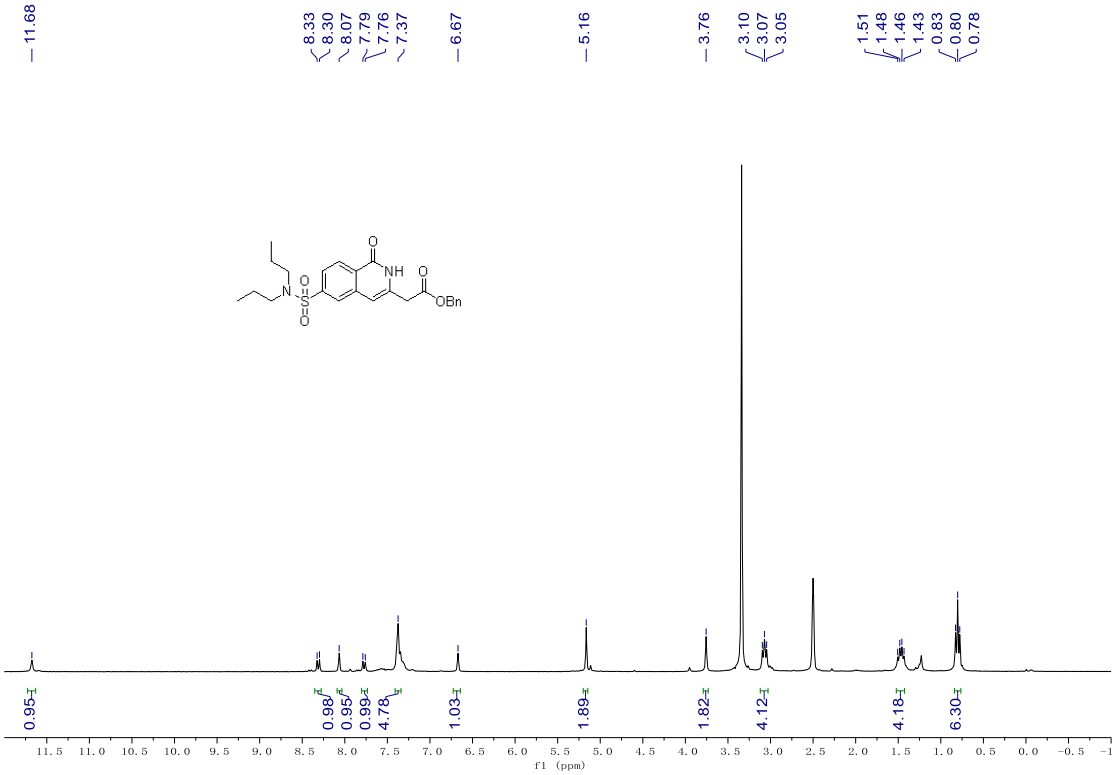
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 3qa



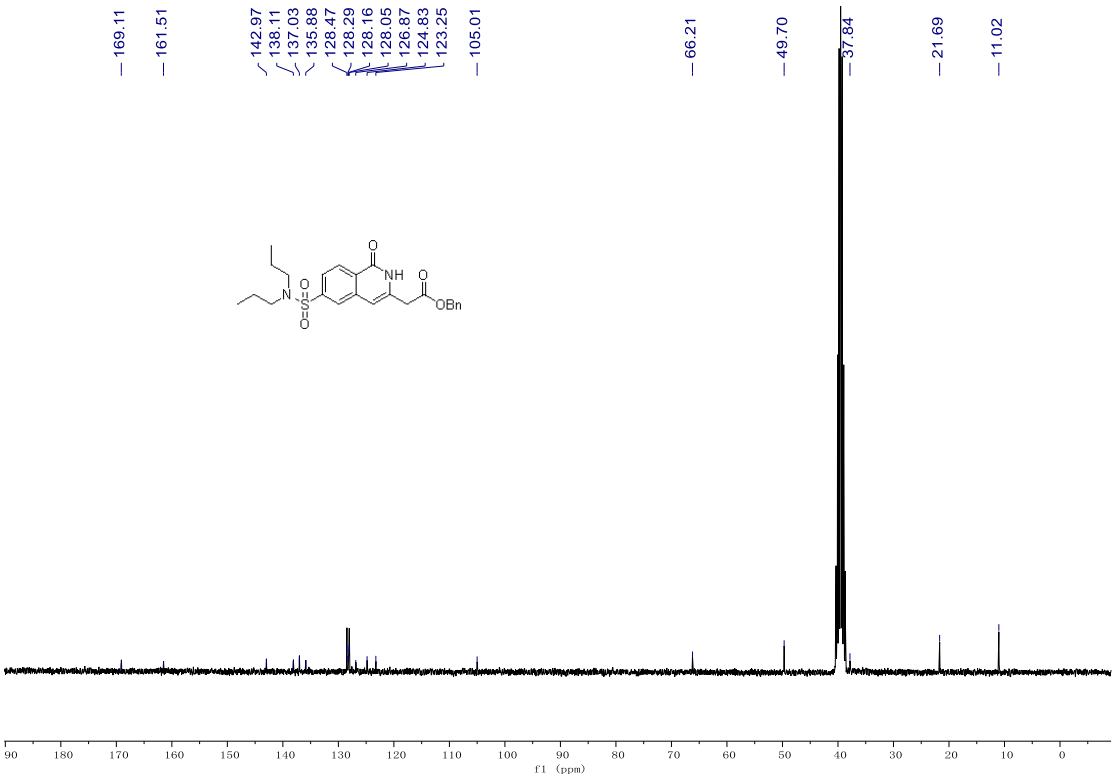
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 3qa



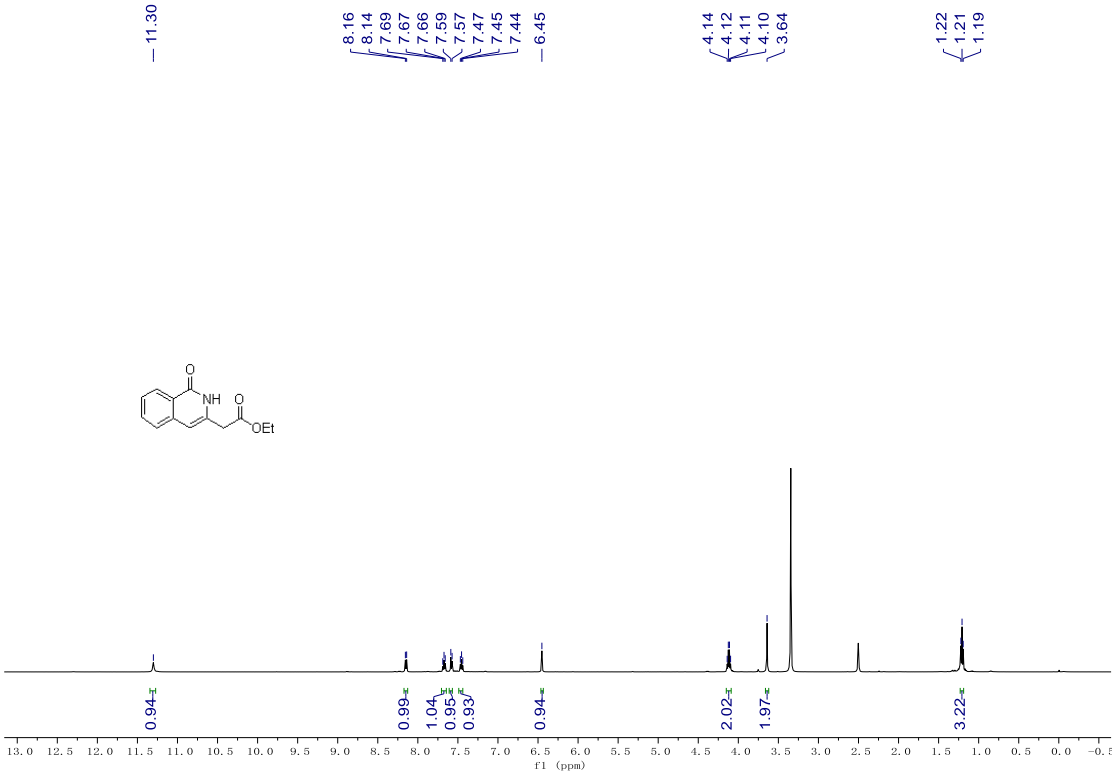
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound **3ra**



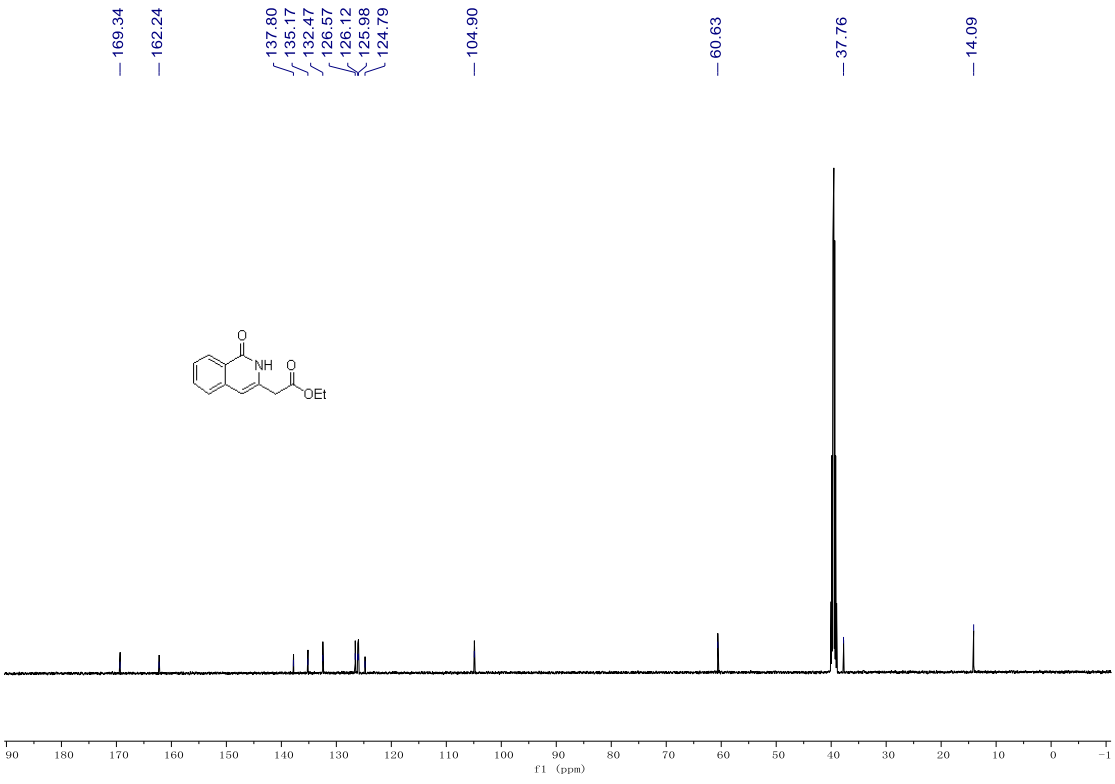
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound **3ra**



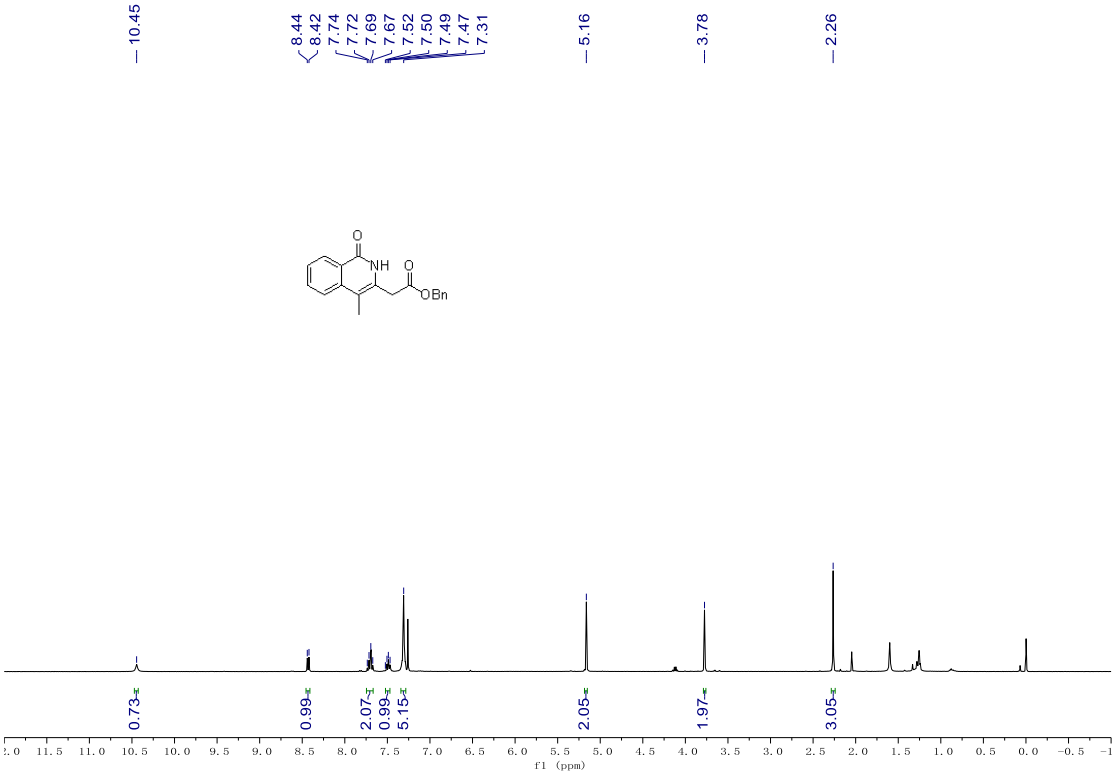
^{1}H NMR (500 MHz, DMSO-d_6) Spectra of compound 3ab



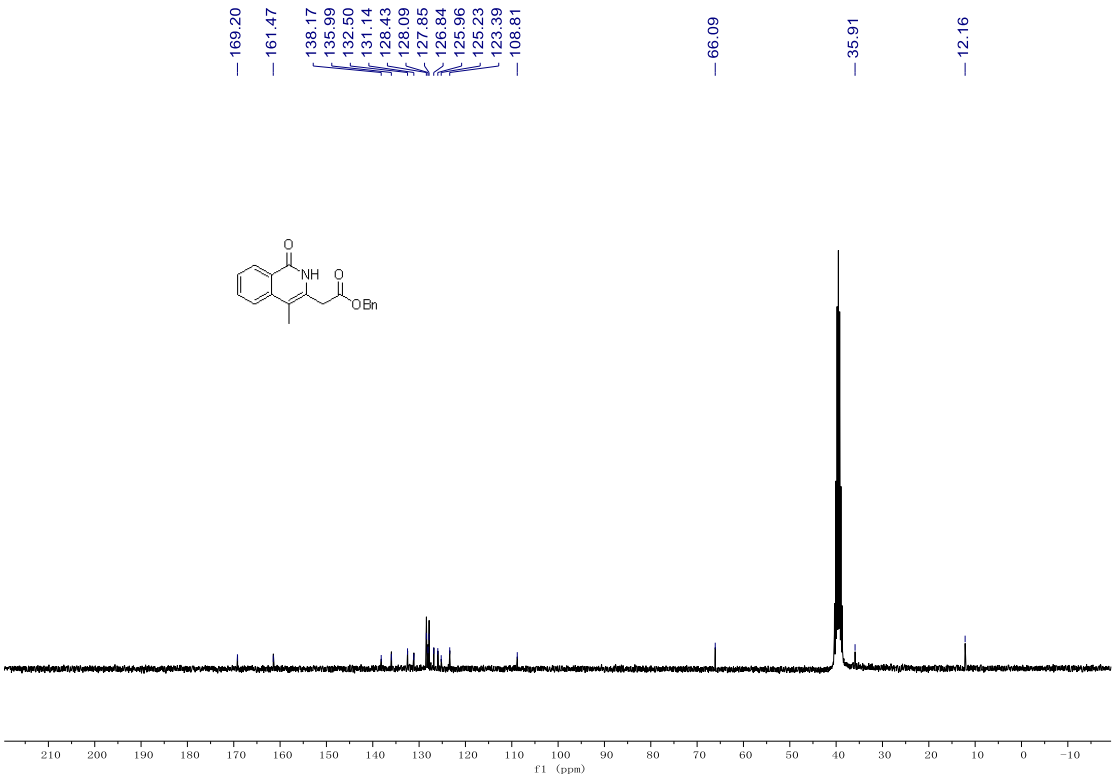
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound 3ab



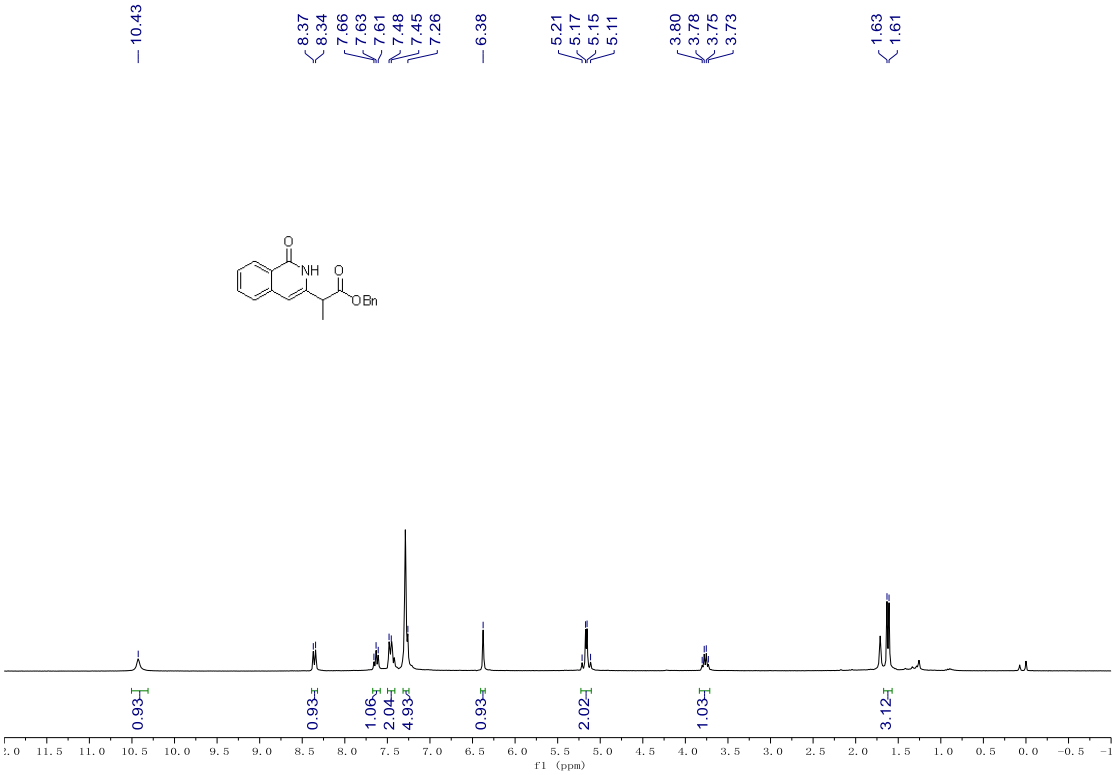
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 3ac



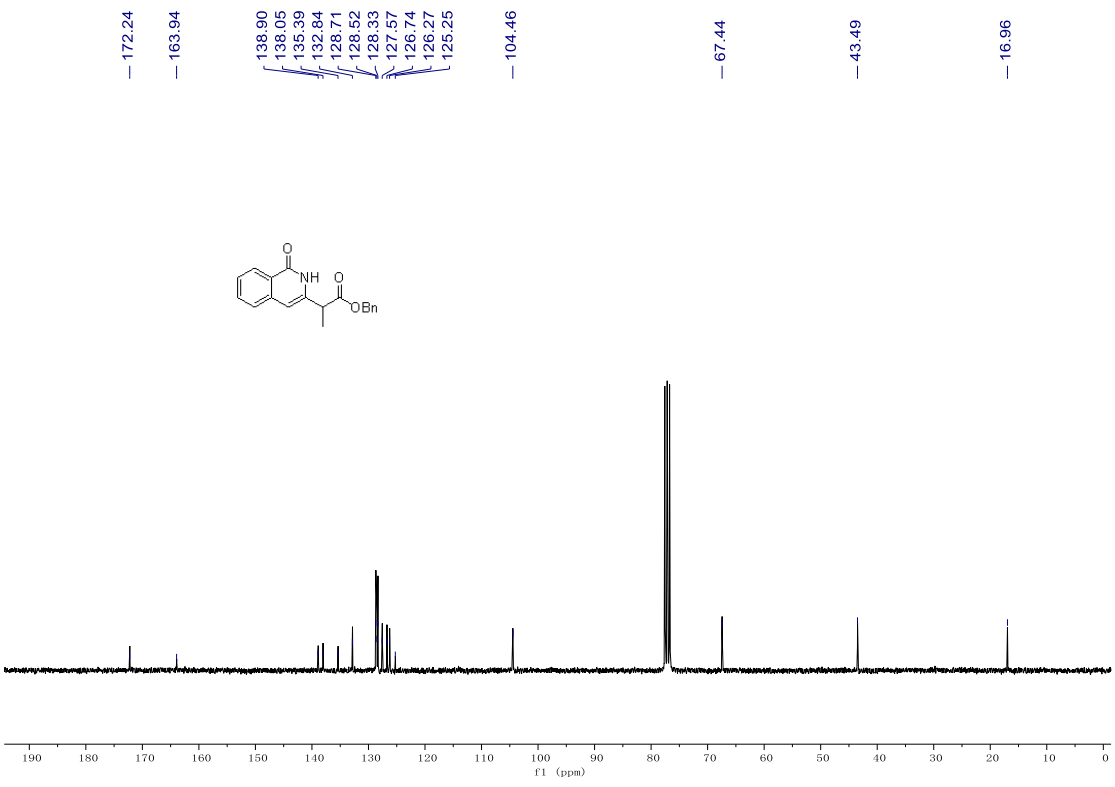
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 3ac



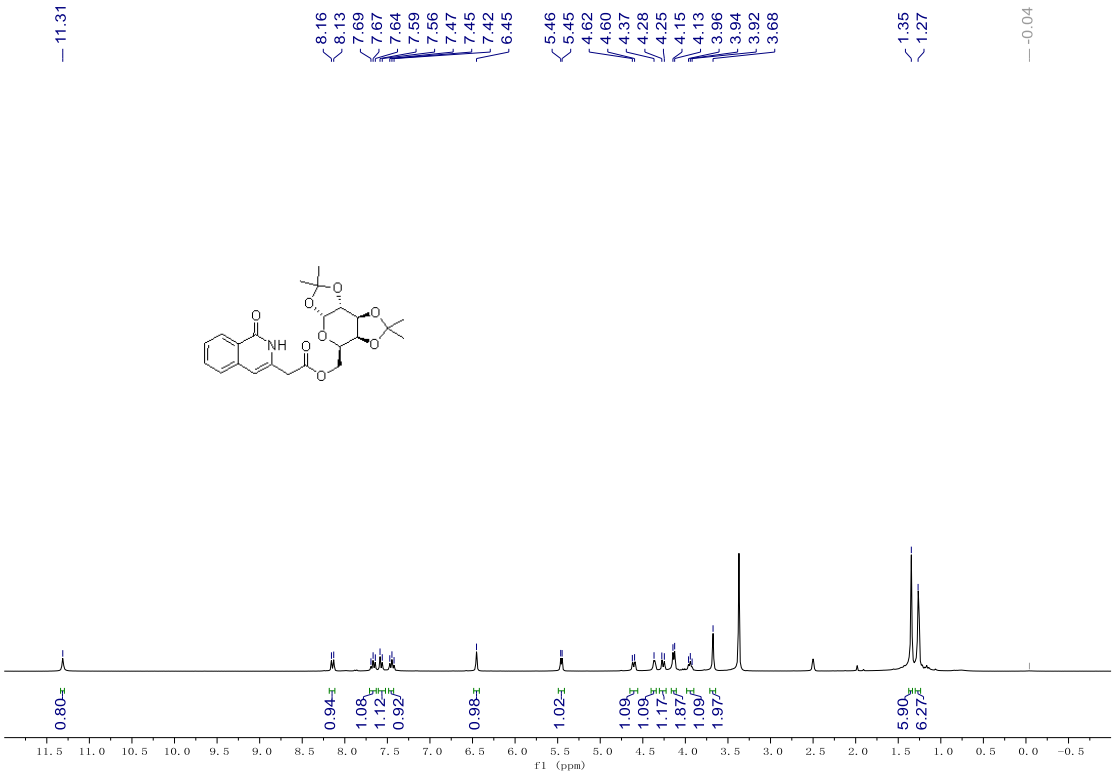
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound **3ad**



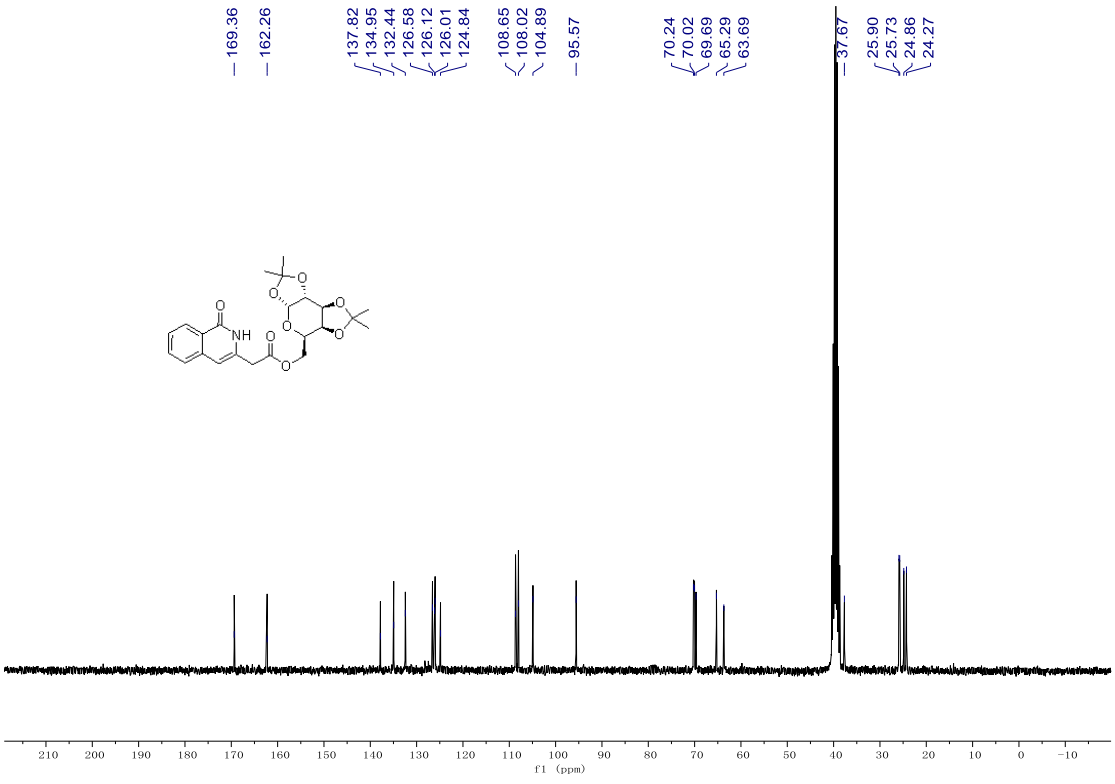
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound **3ad**



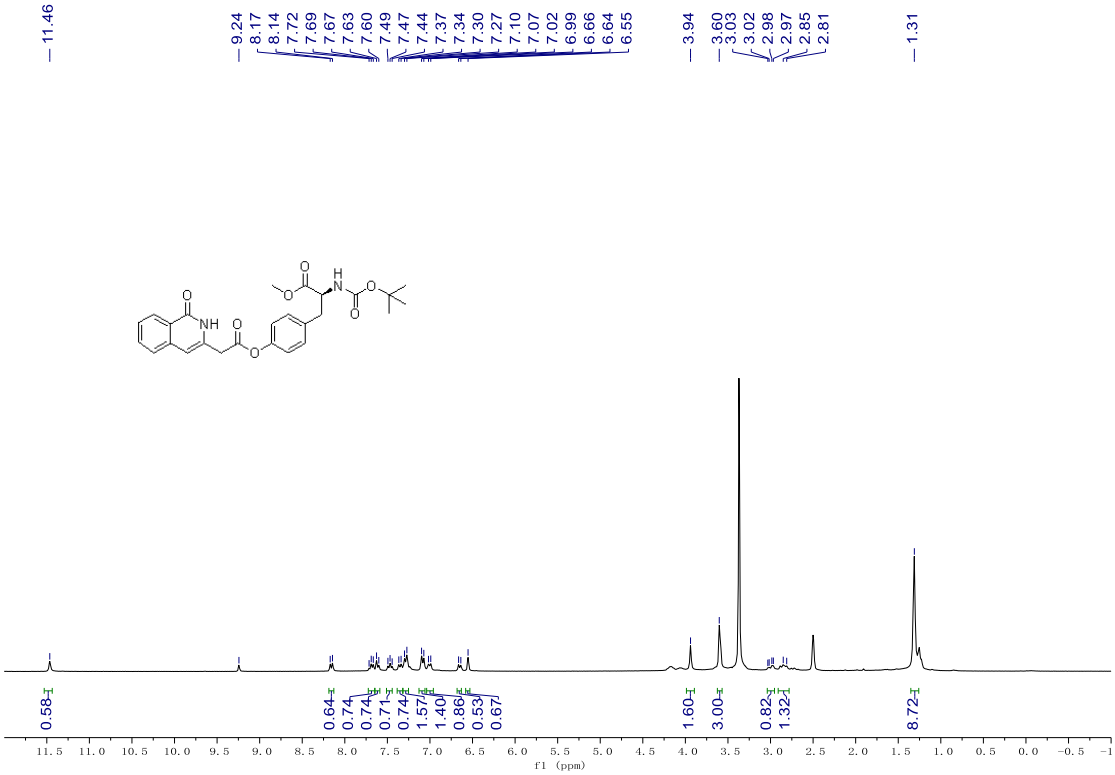
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 3ae



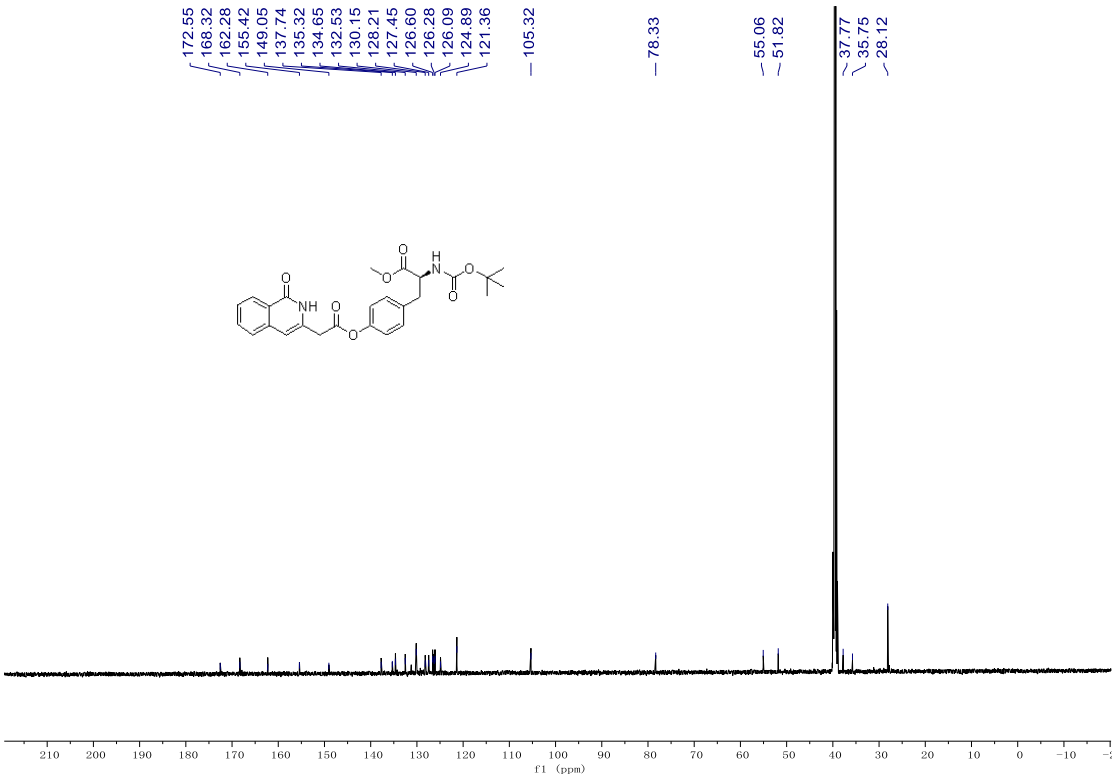
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 3ae



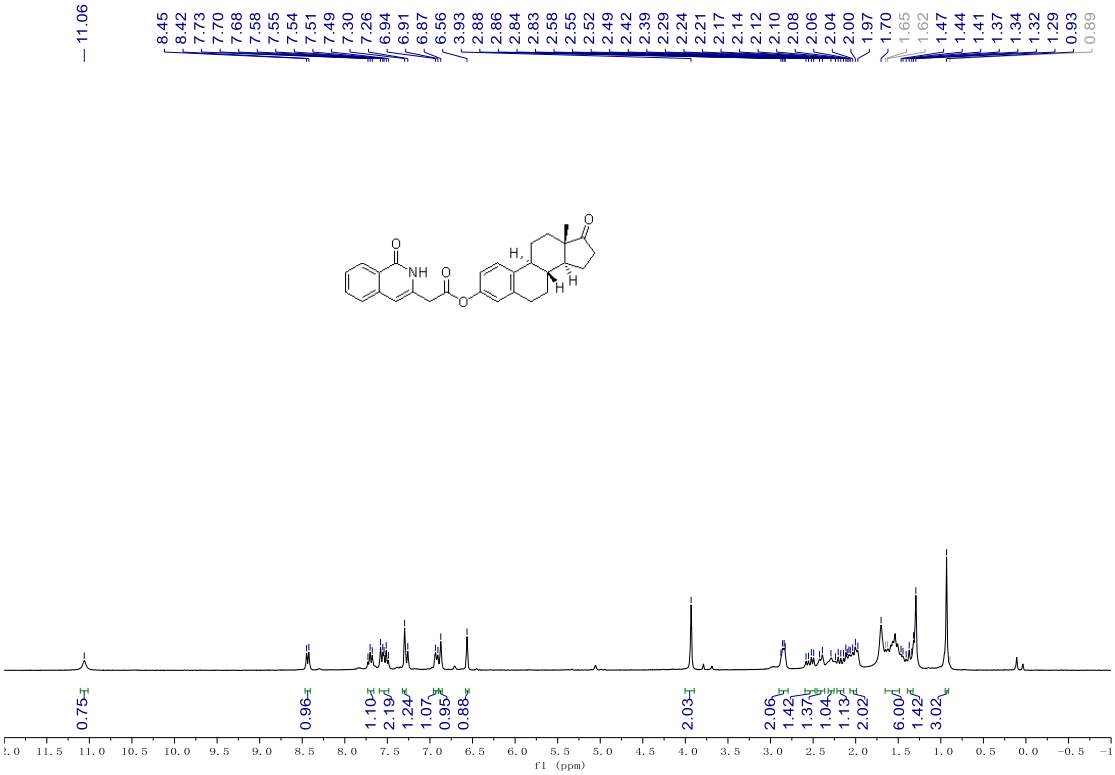
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound **3af**



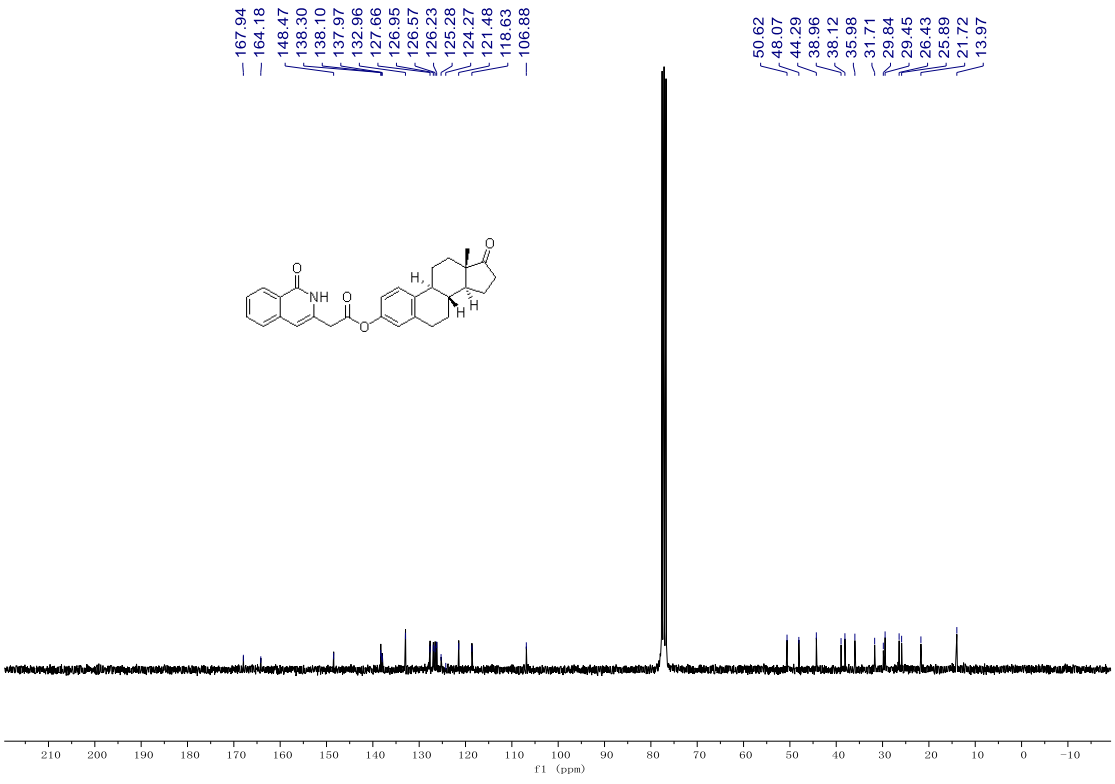
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound **3af**



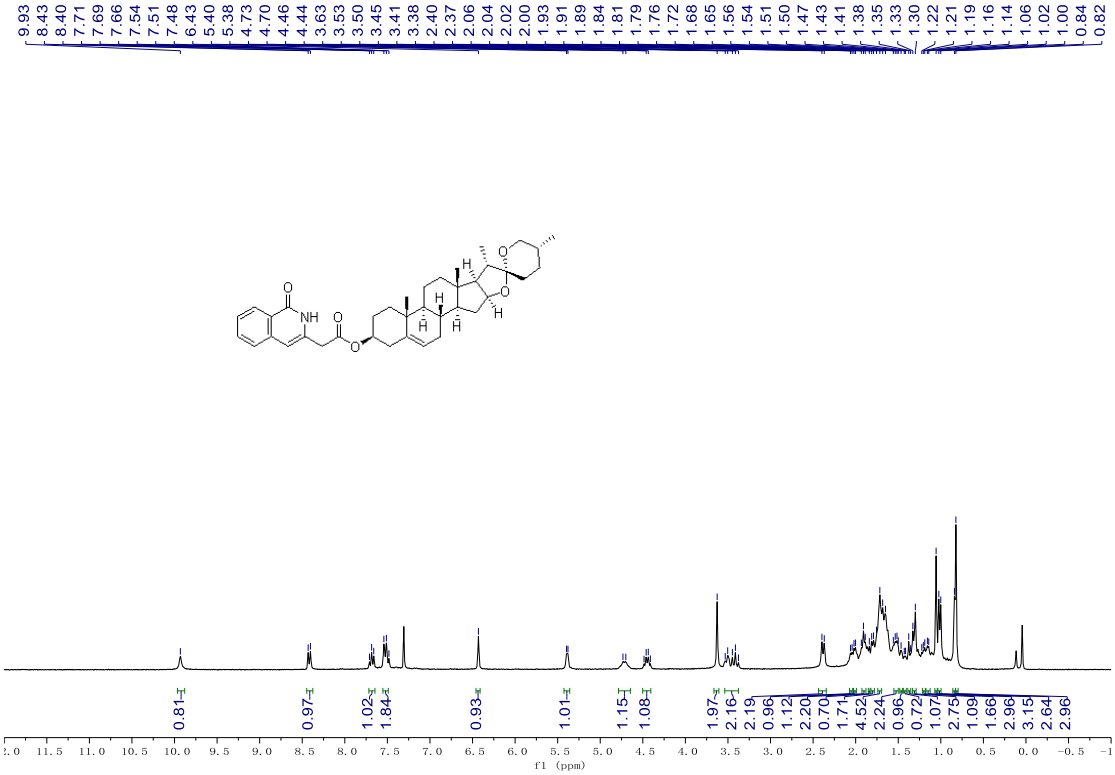
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 3ag.



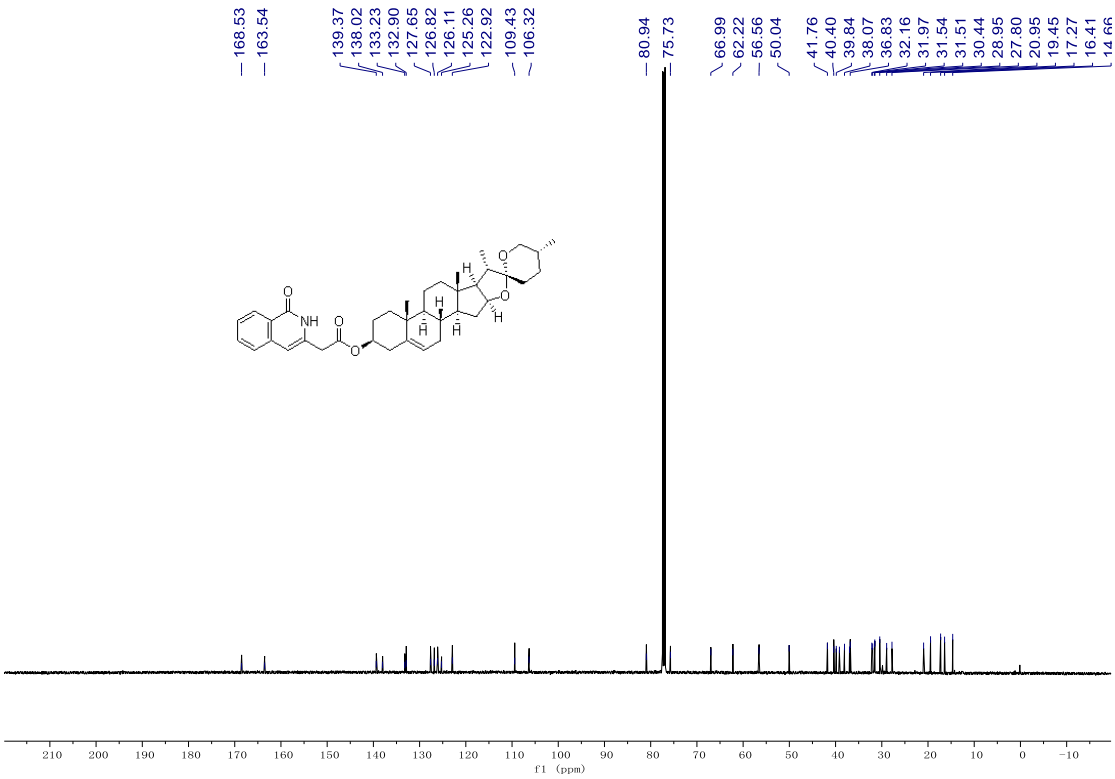
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 3ag



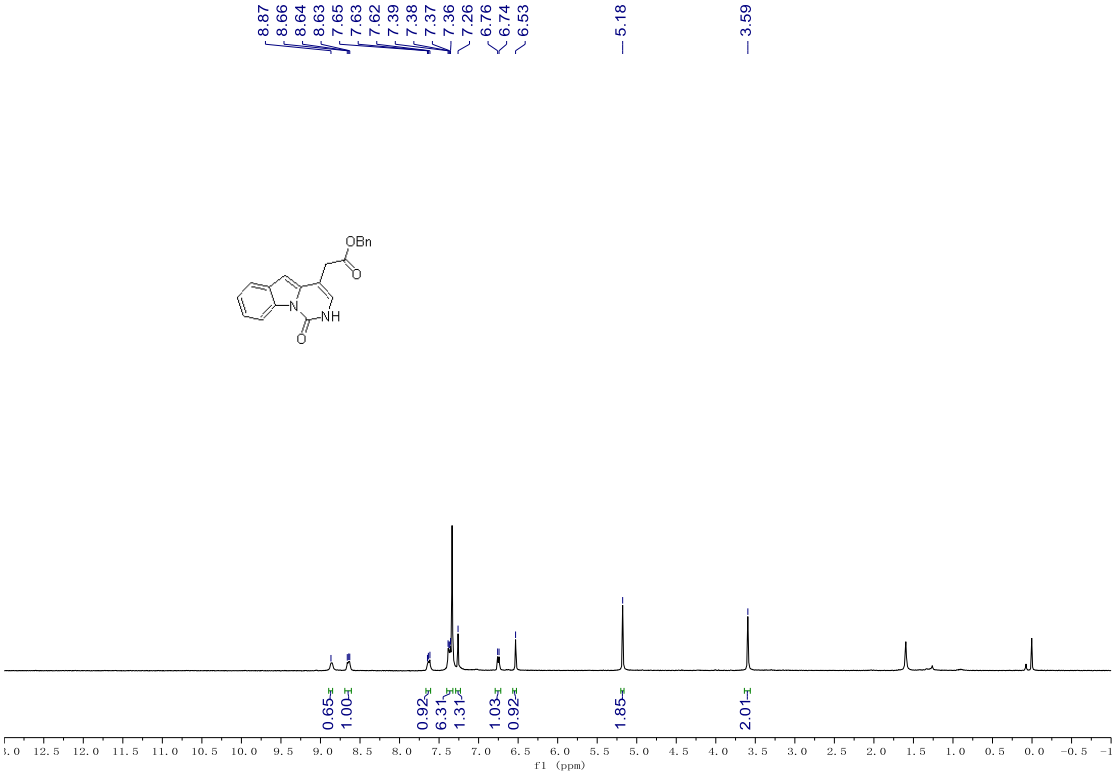
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound **3ah**



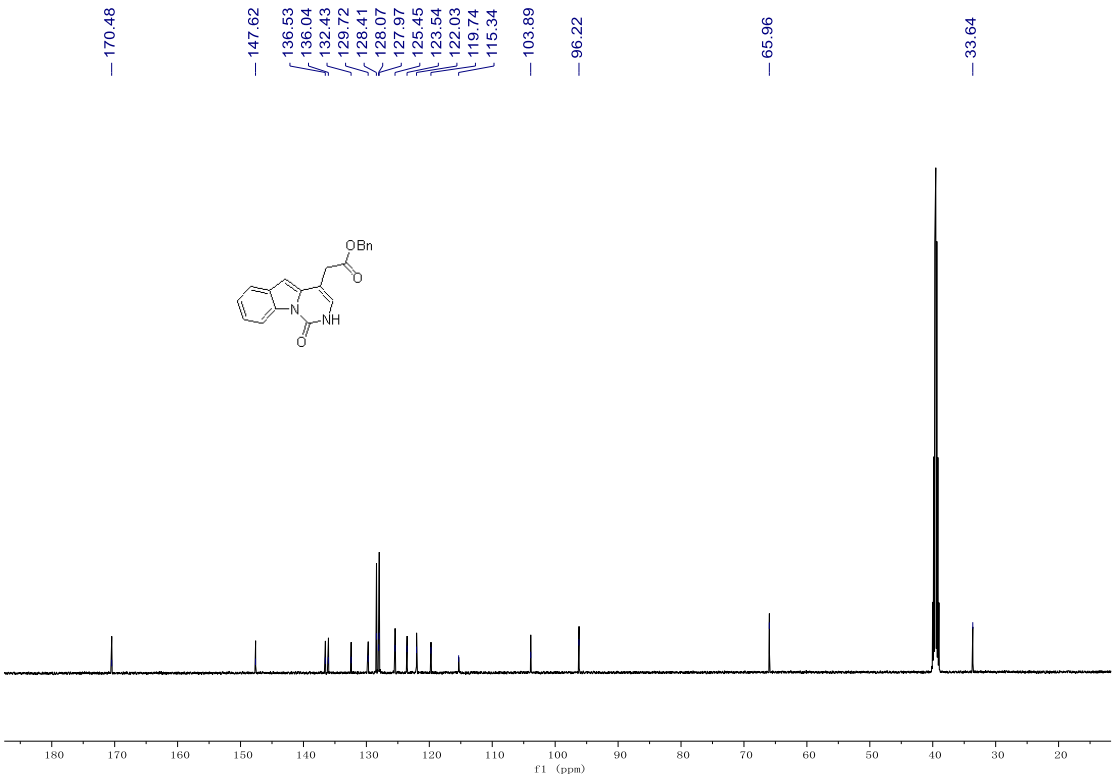
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound **3ah**



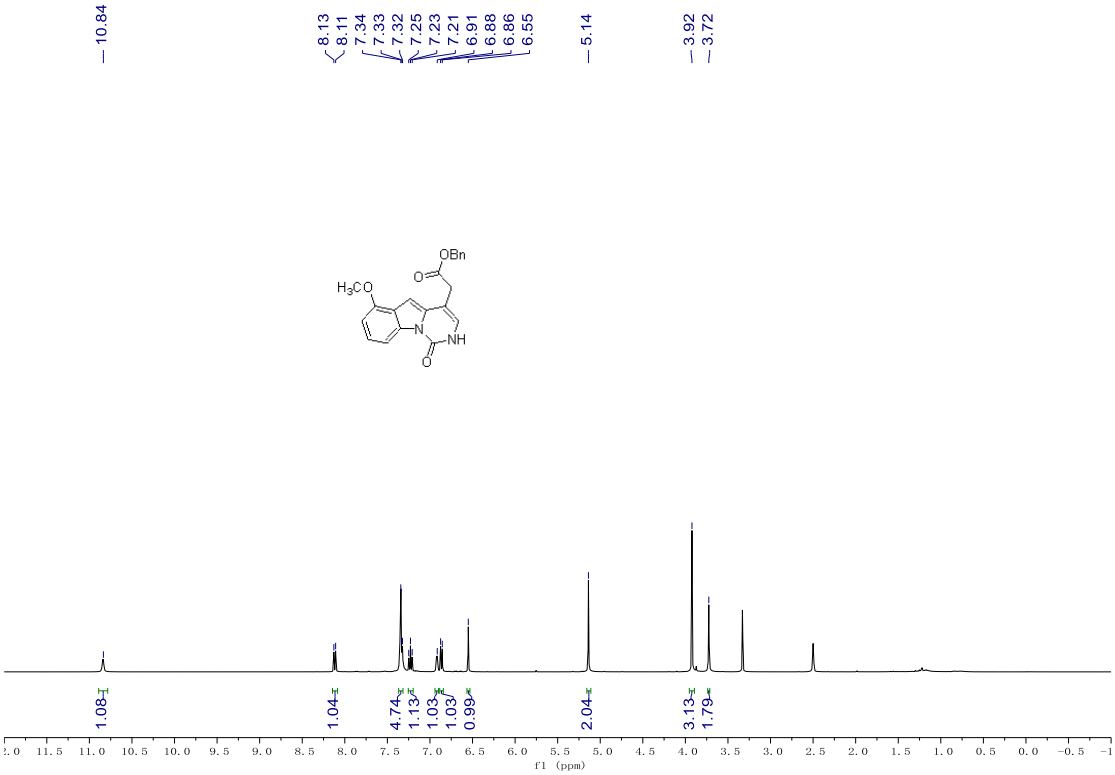
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 5aa



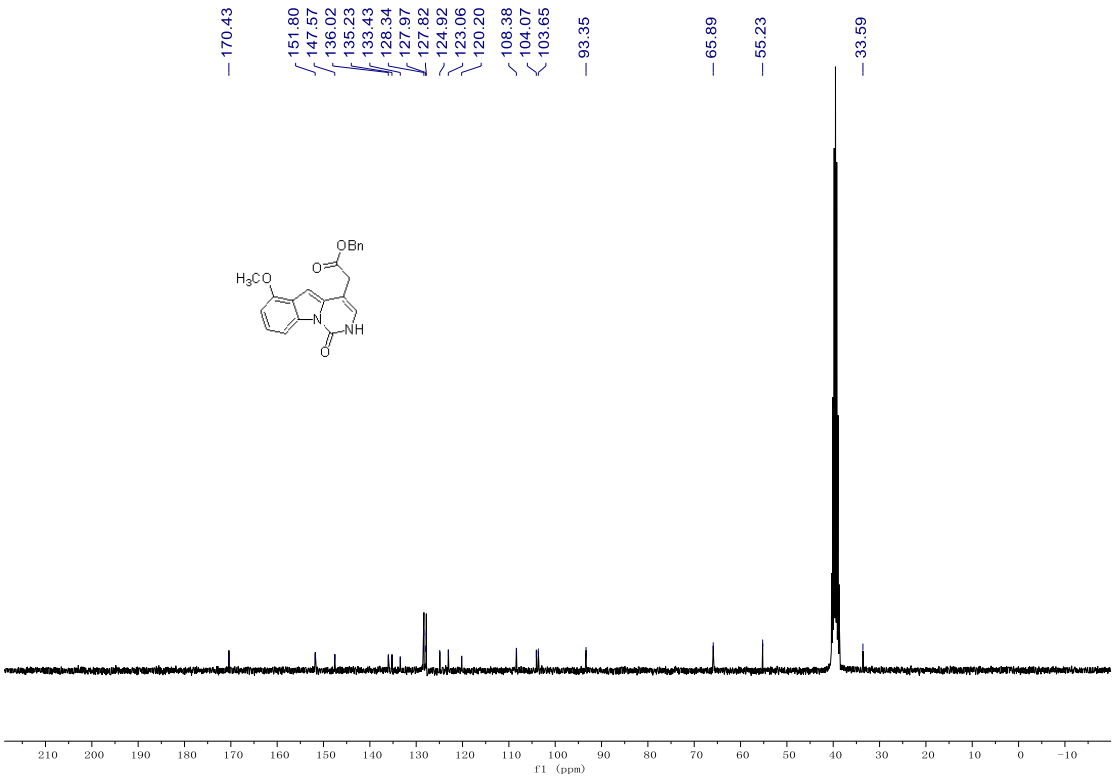
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 5aa



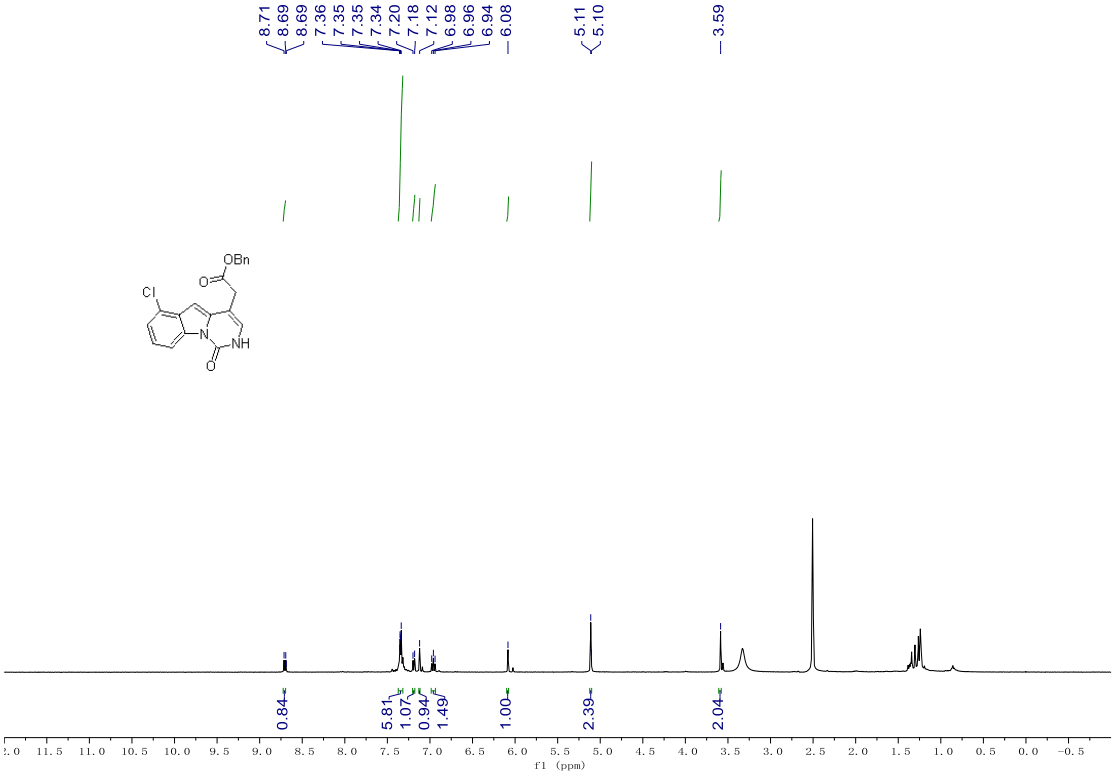
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound 5ba



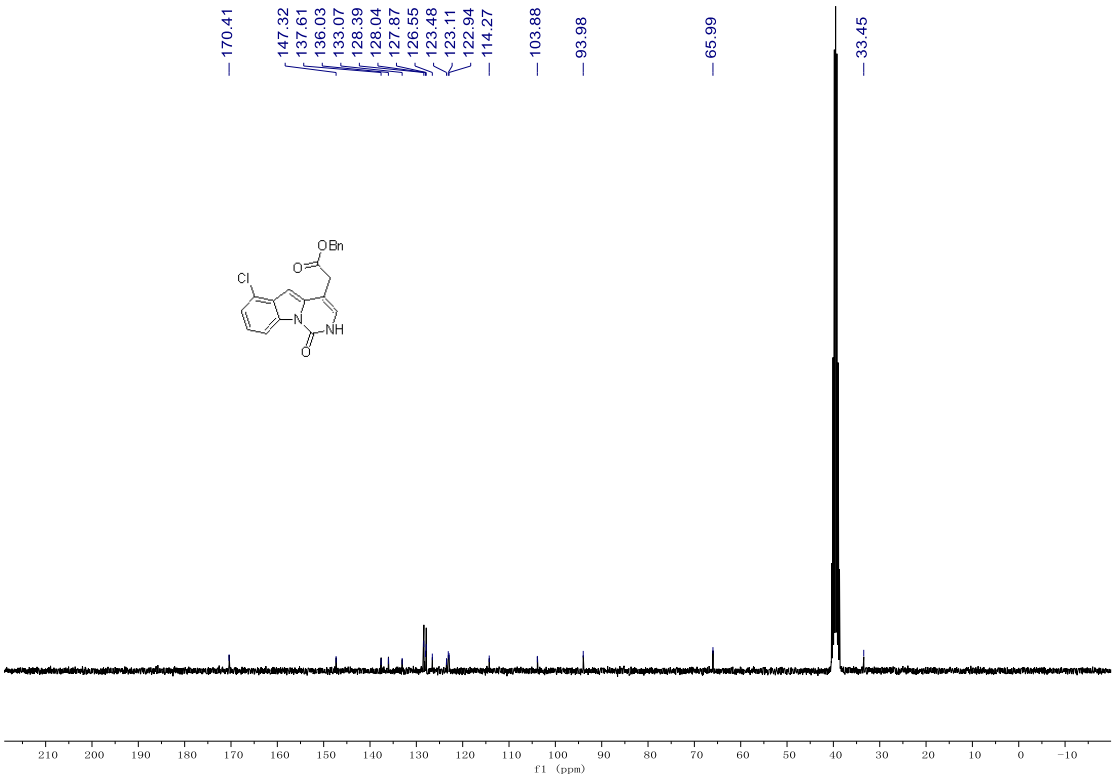
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5ba



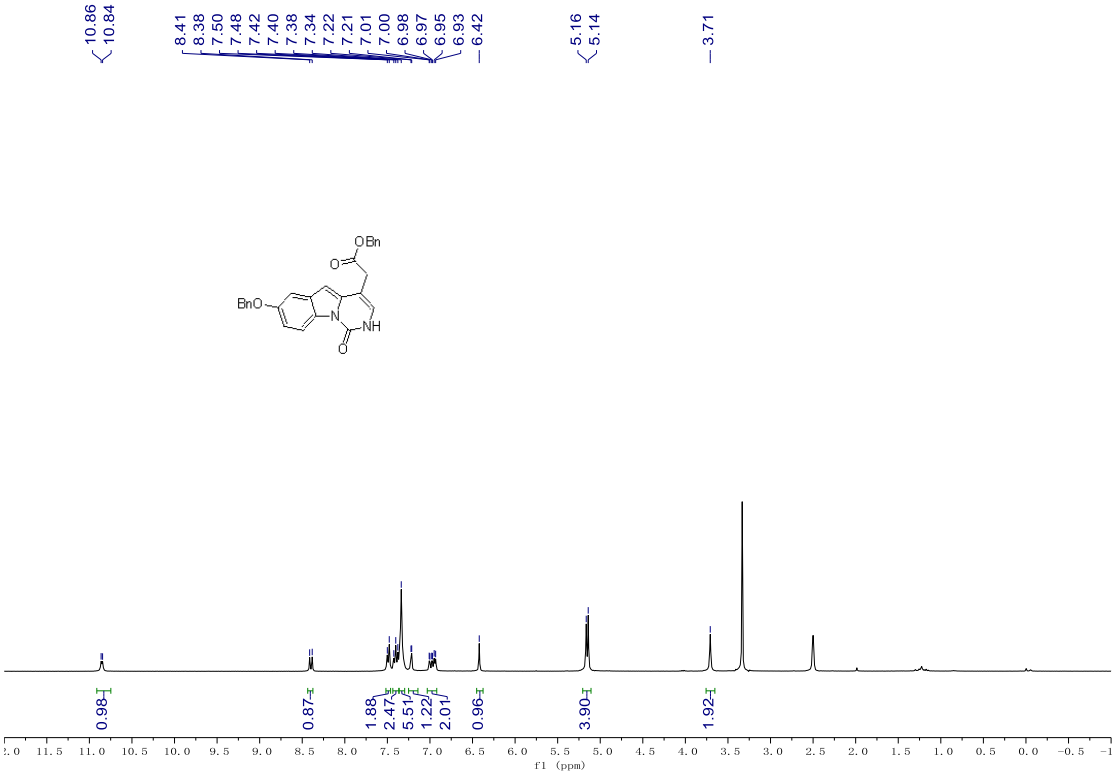
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound 5ca



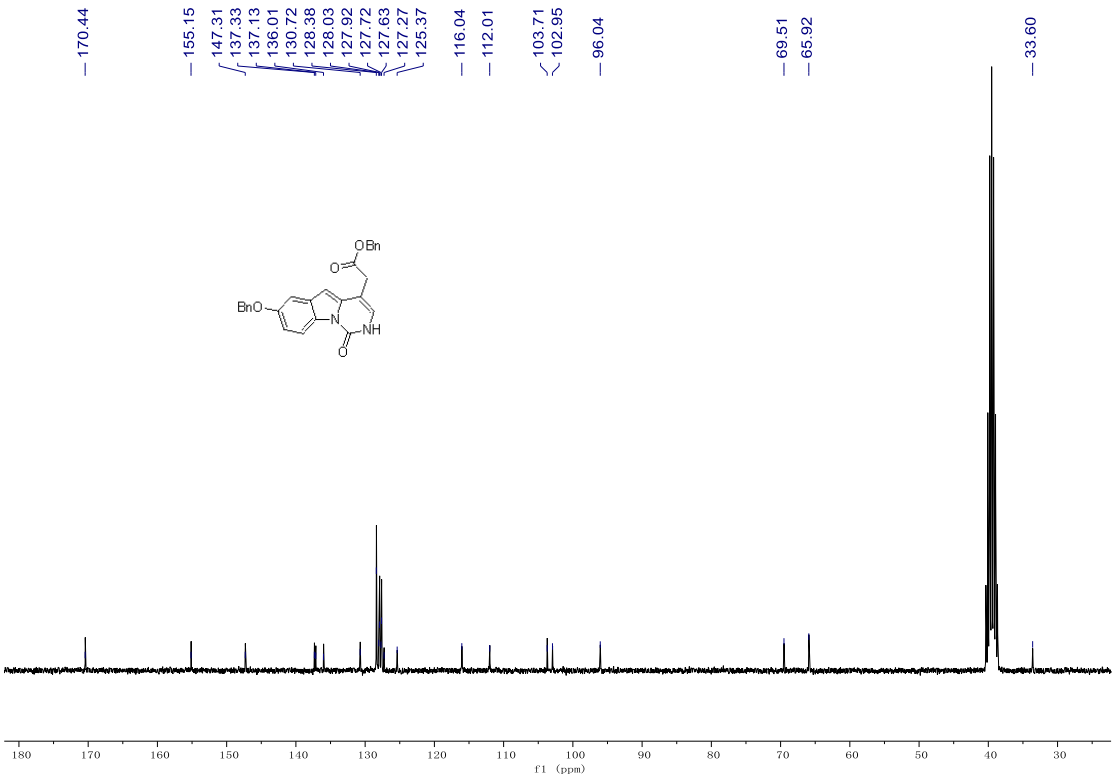
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5ca



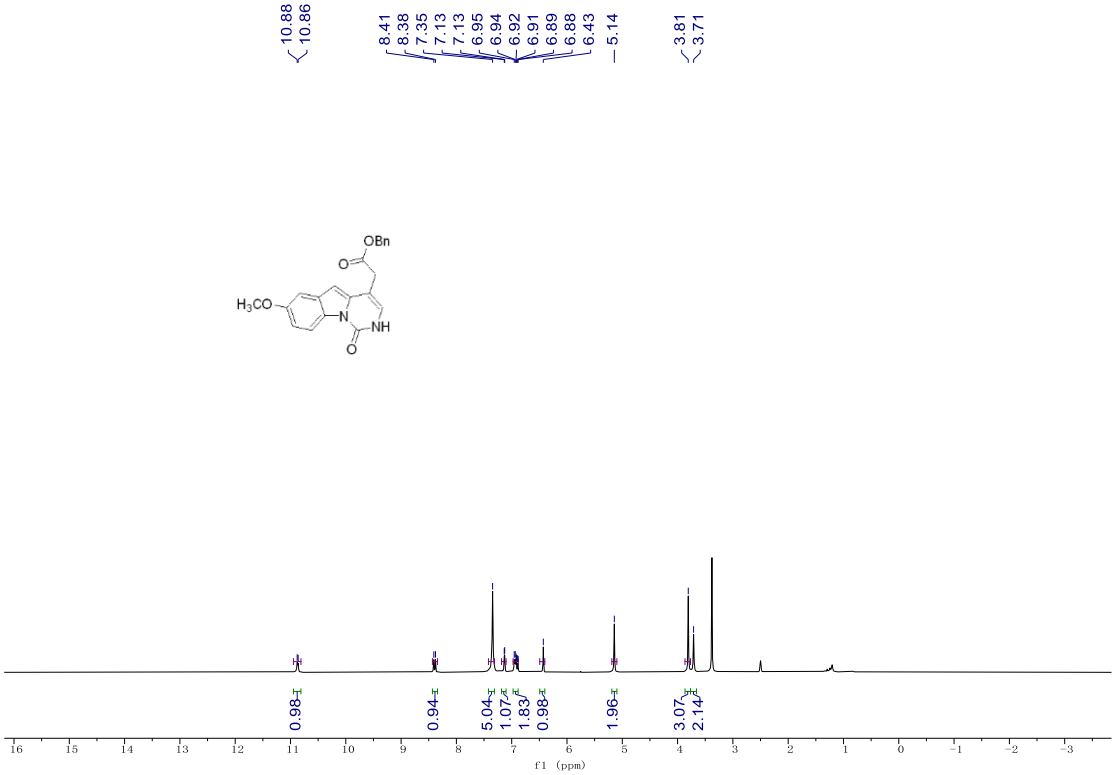
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 5da



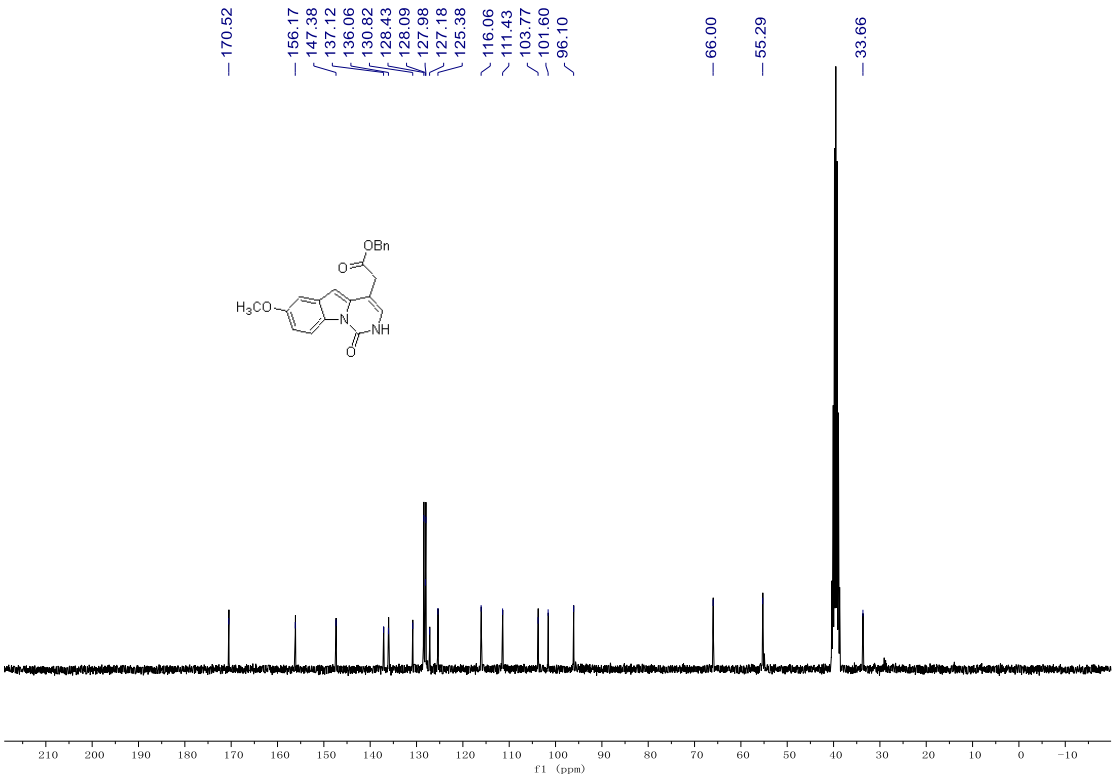
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5da



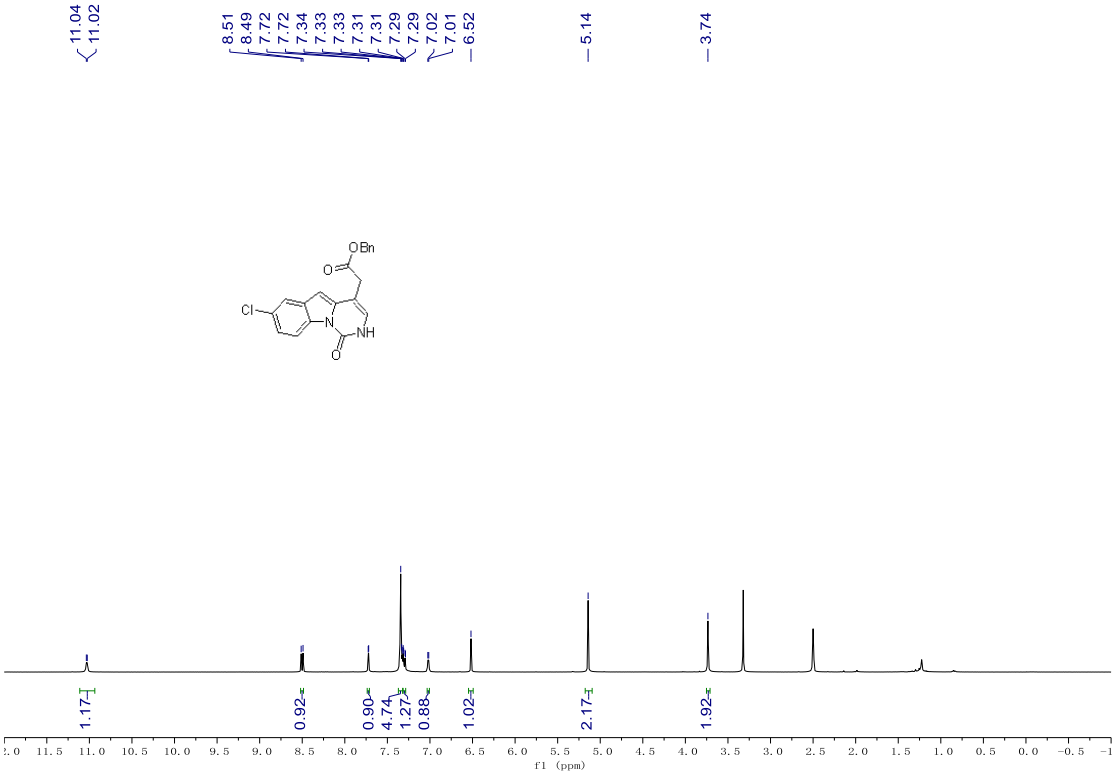
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 5ea



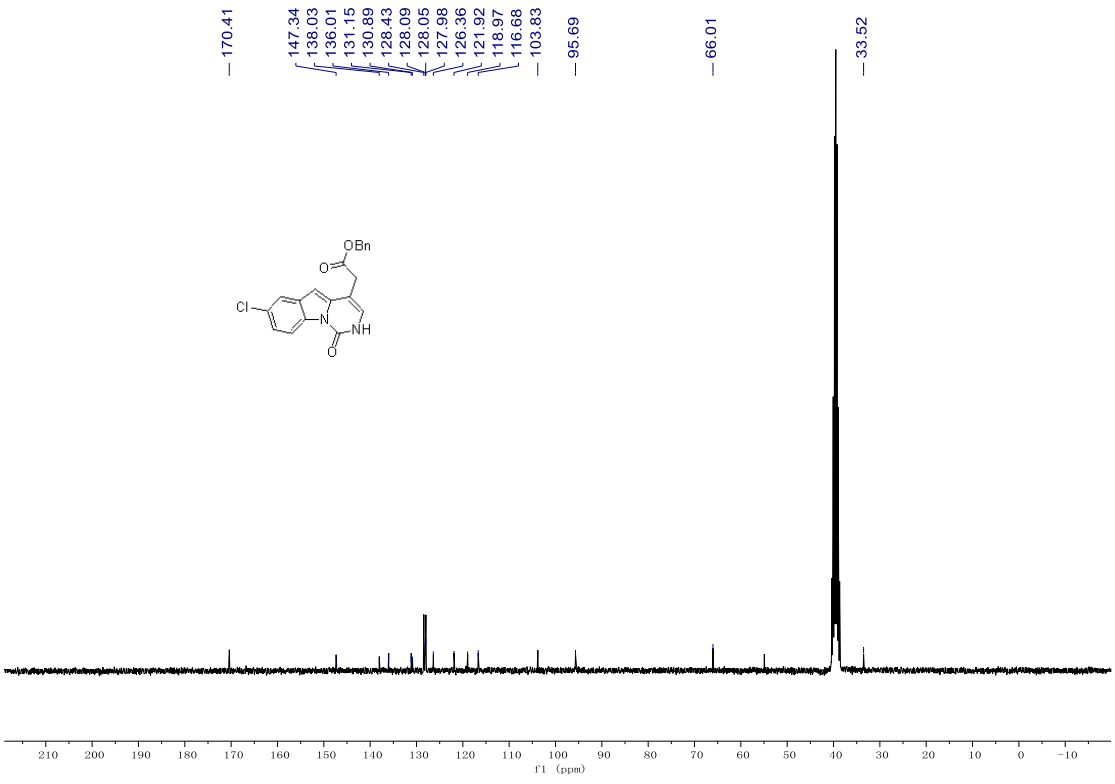
^{13}C NMR (300 MHz, DMSO-d_6) Spectra of compound 5ea



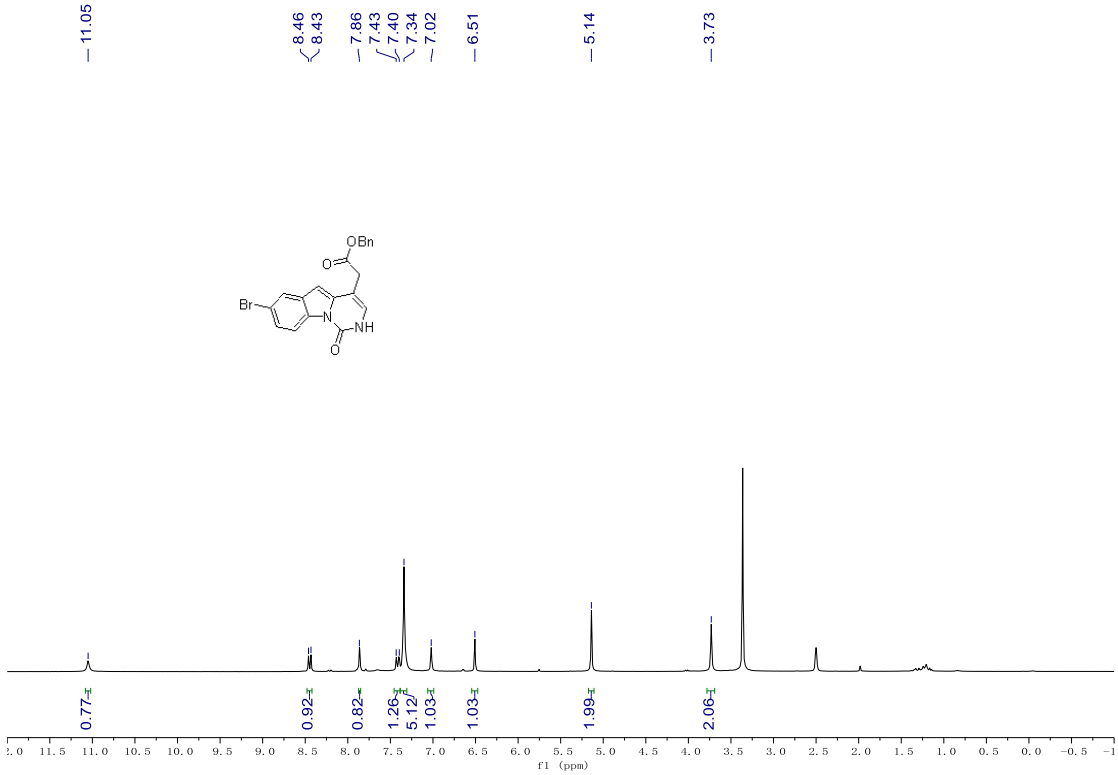
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound 5fa



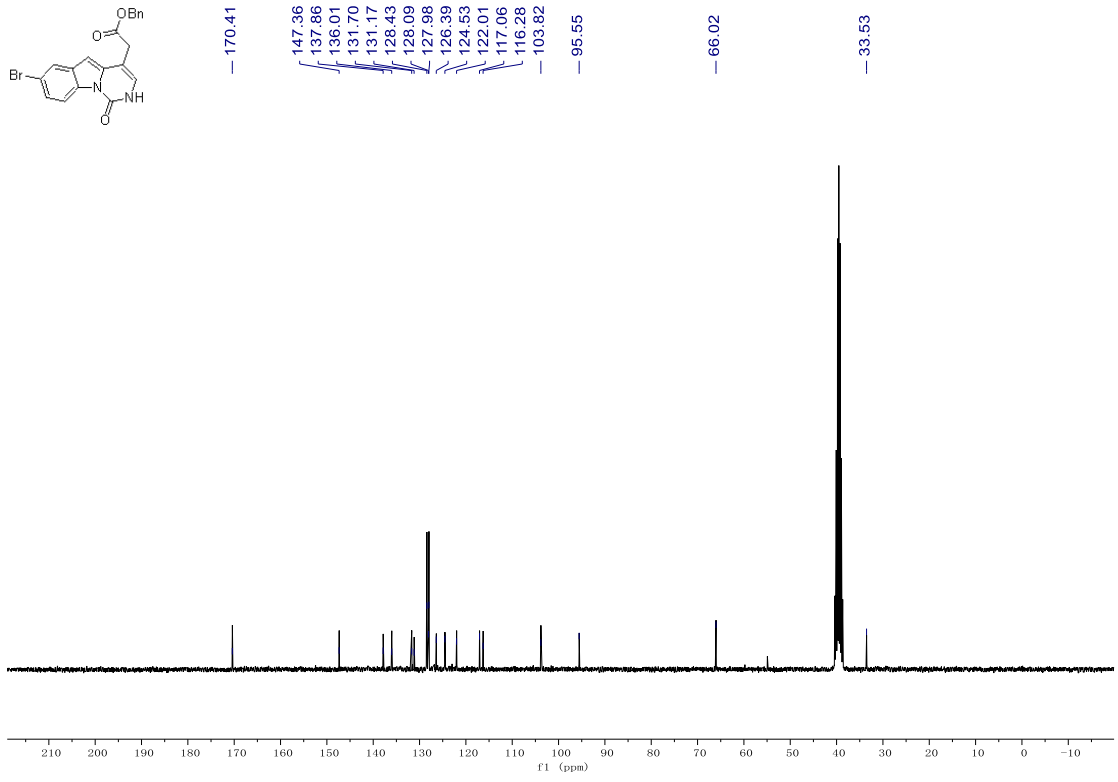
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5fa



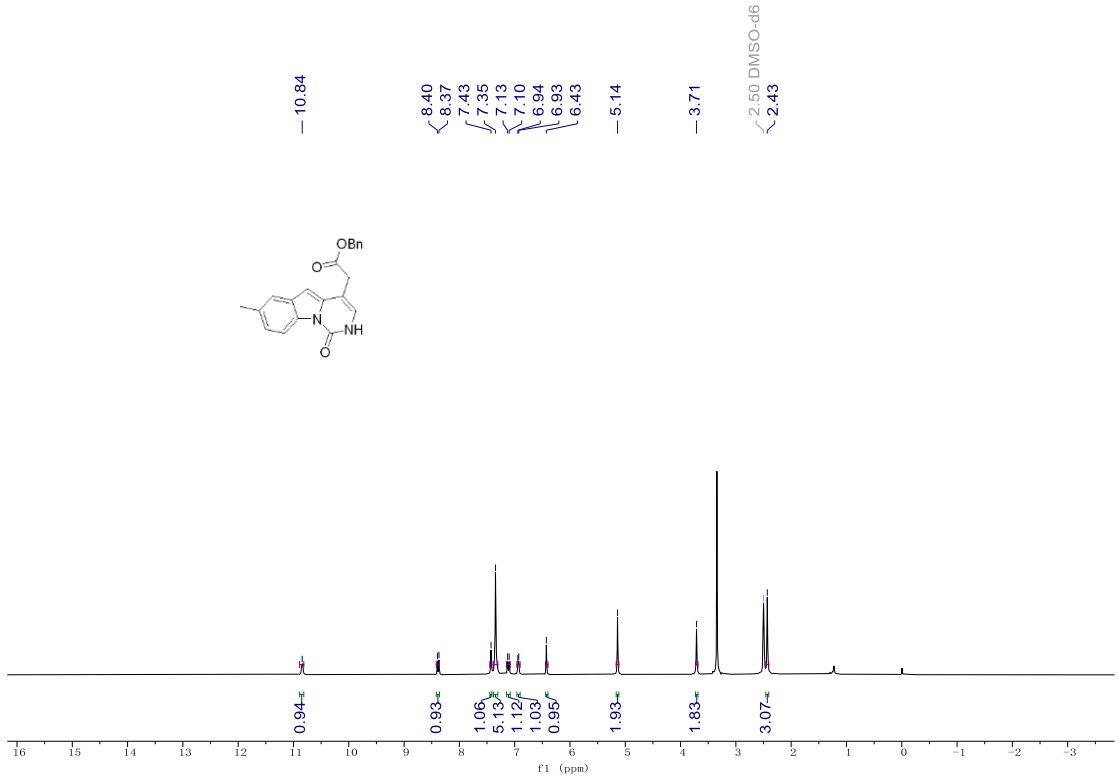
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 5ga



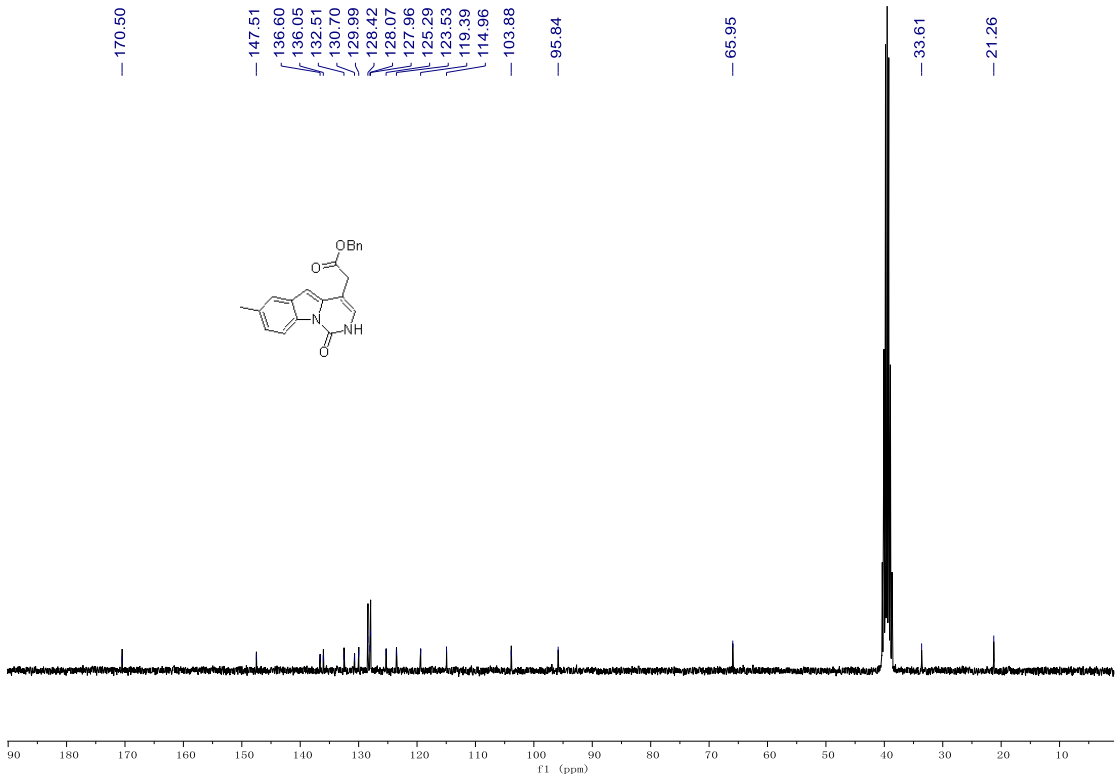
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5ga



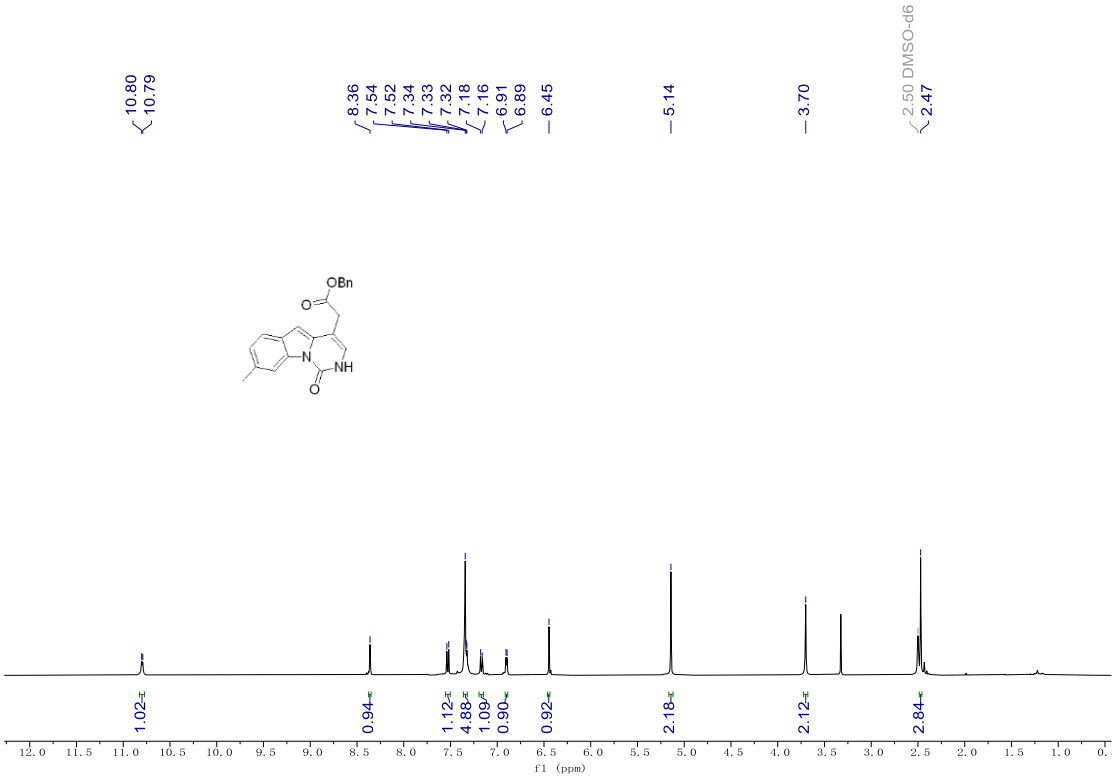
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound **5ha**



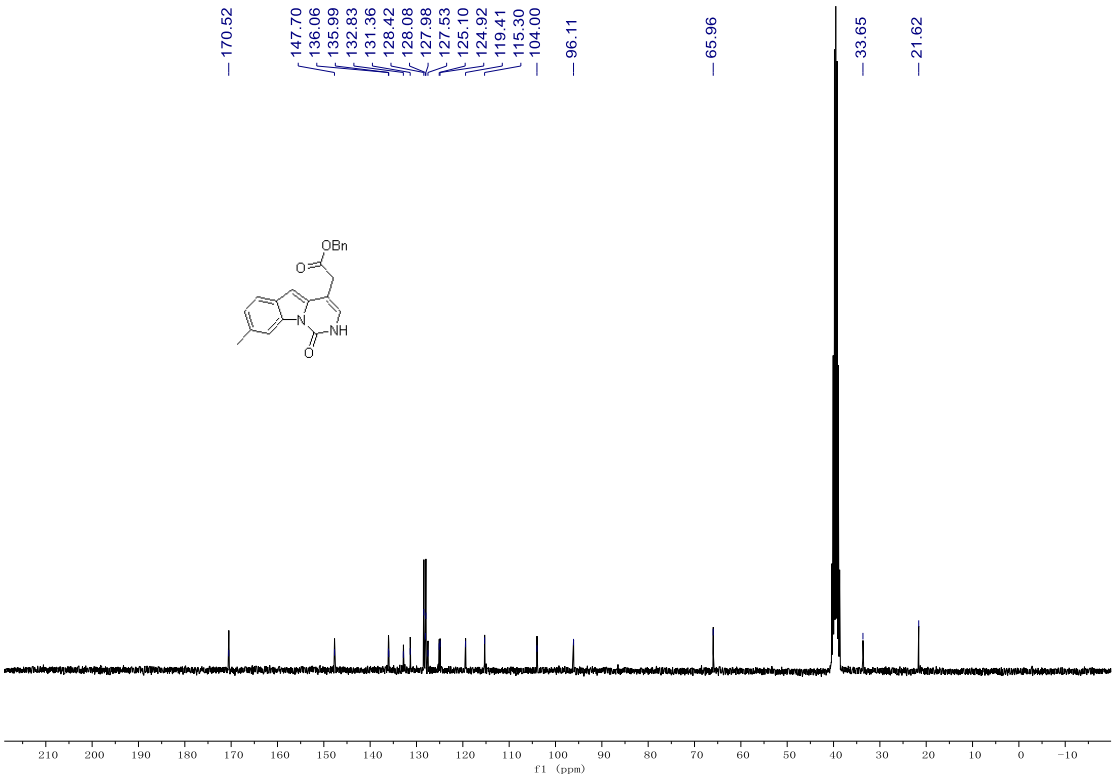
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound **5ha**



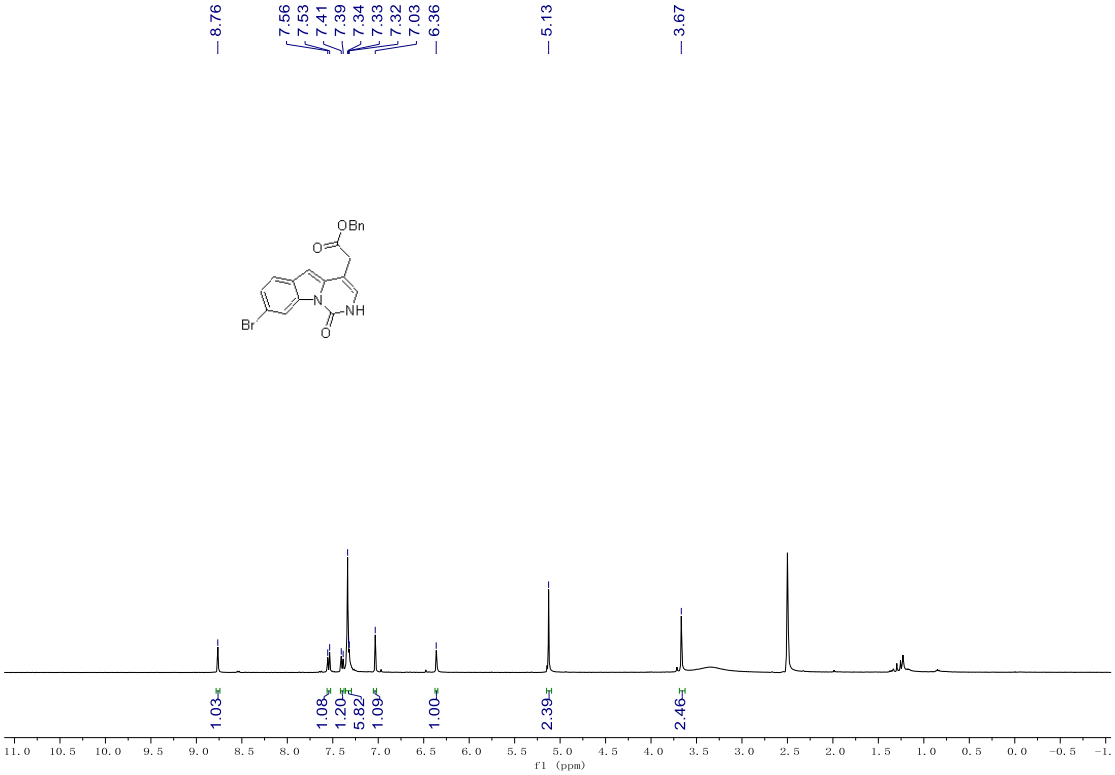
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound 5ia



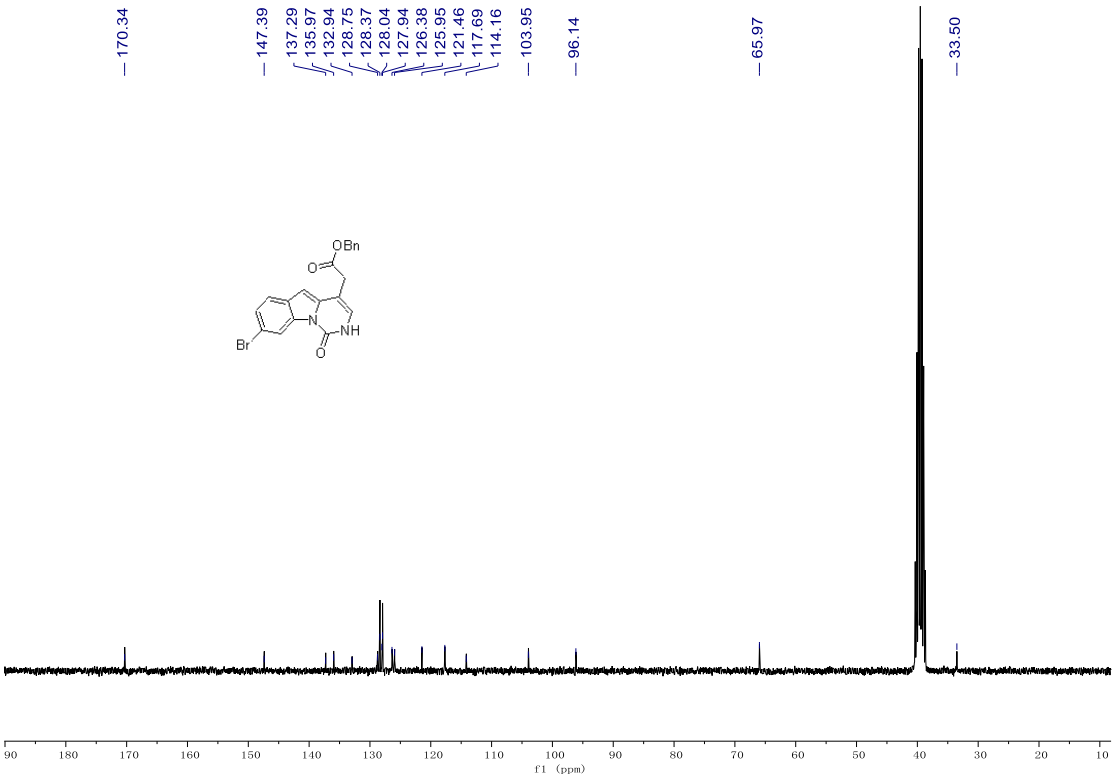
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5ia



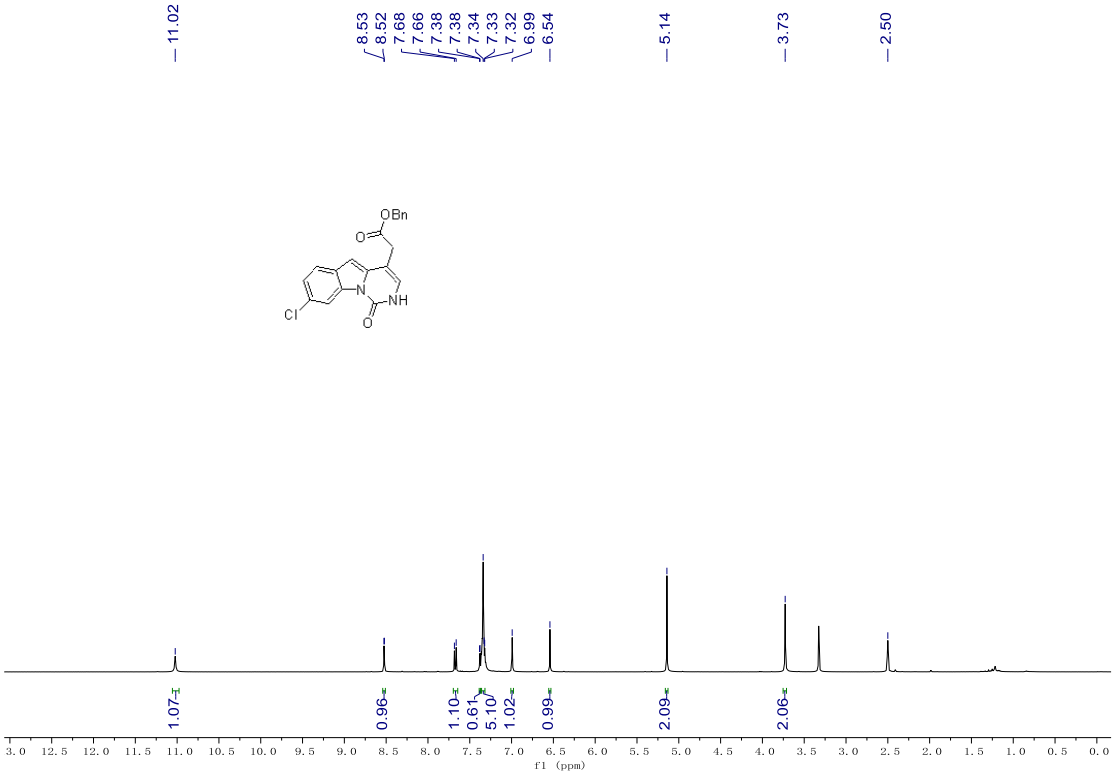
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound 5ja



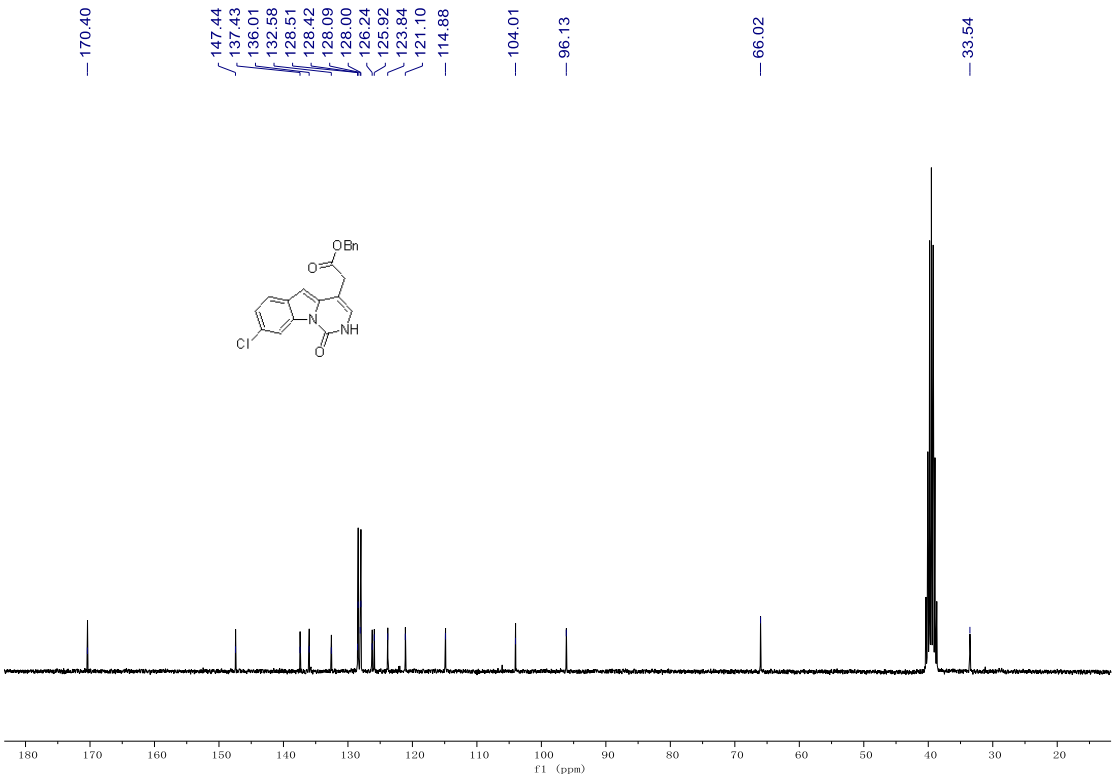
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5ja



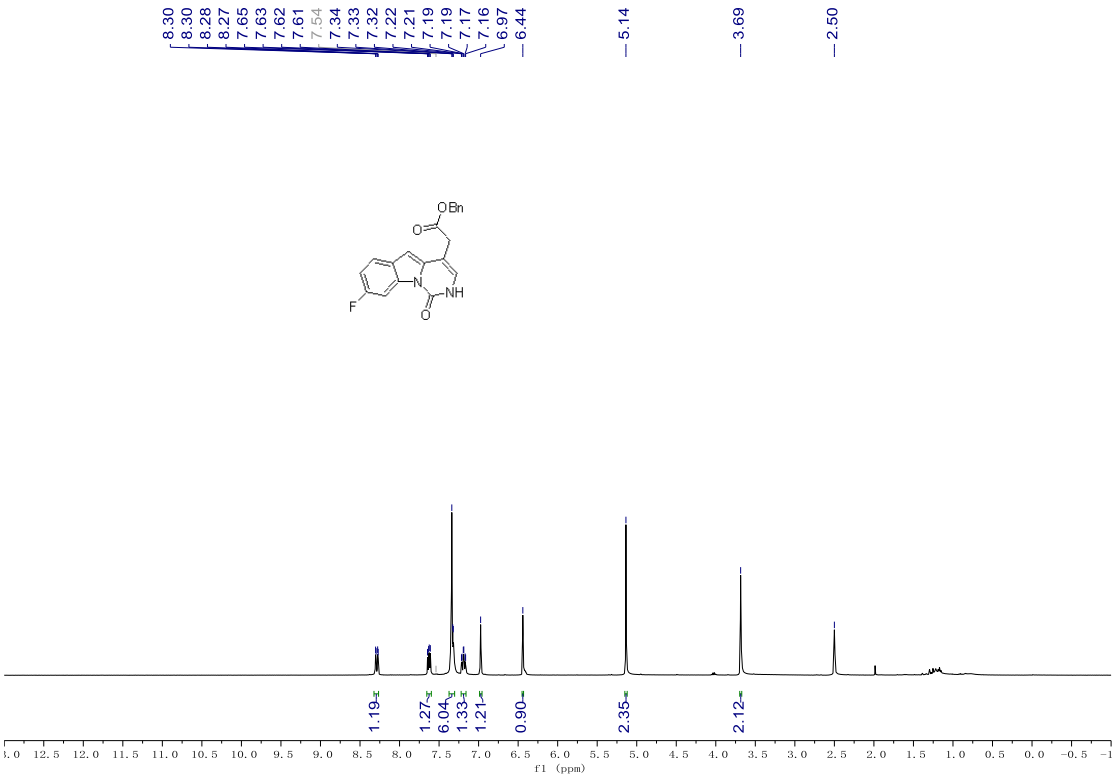
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound 5ka



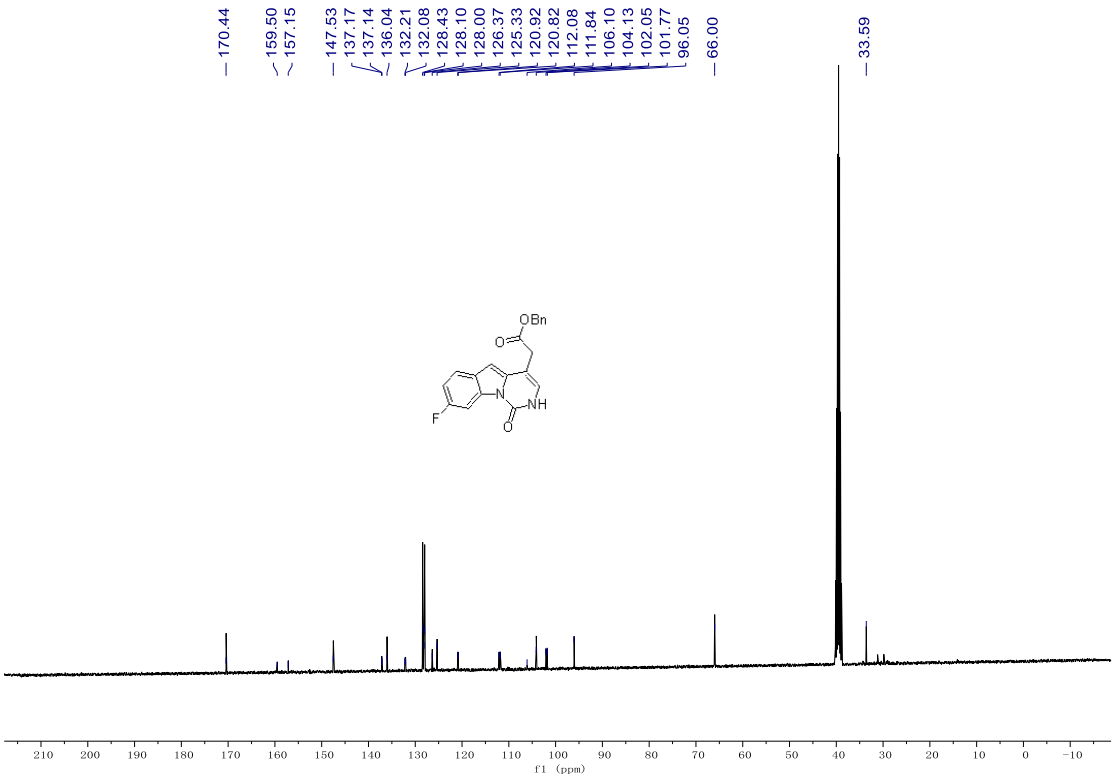
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5ka



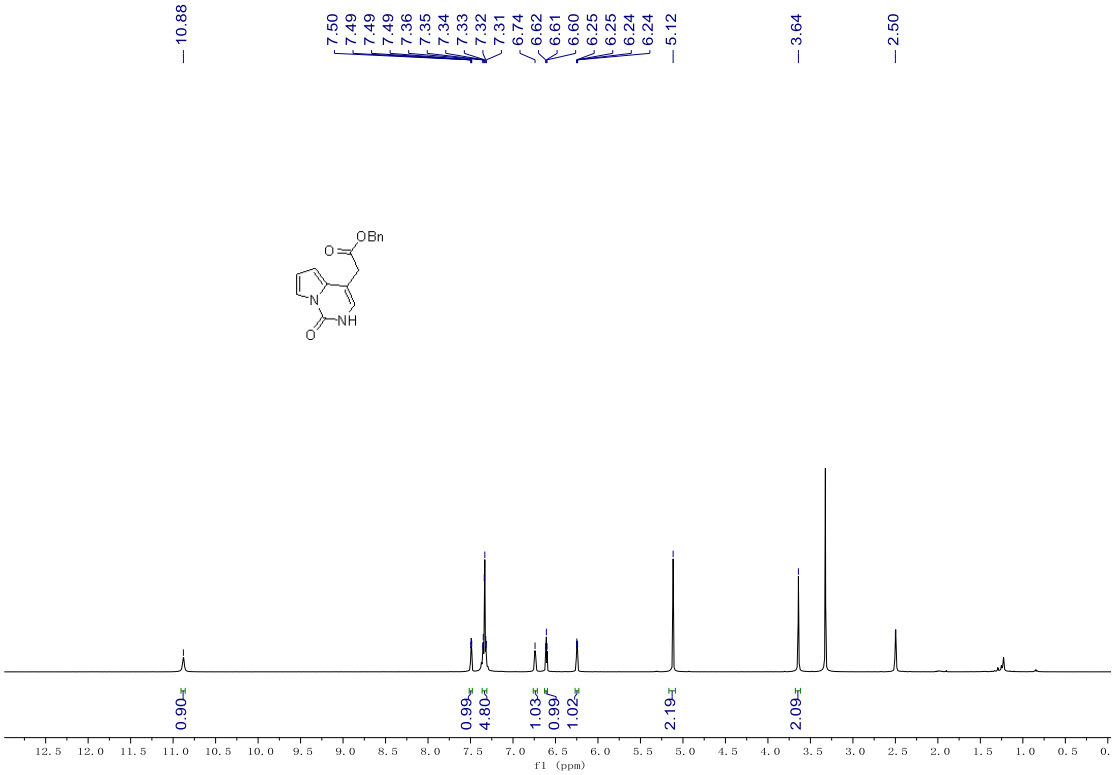
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound 5la



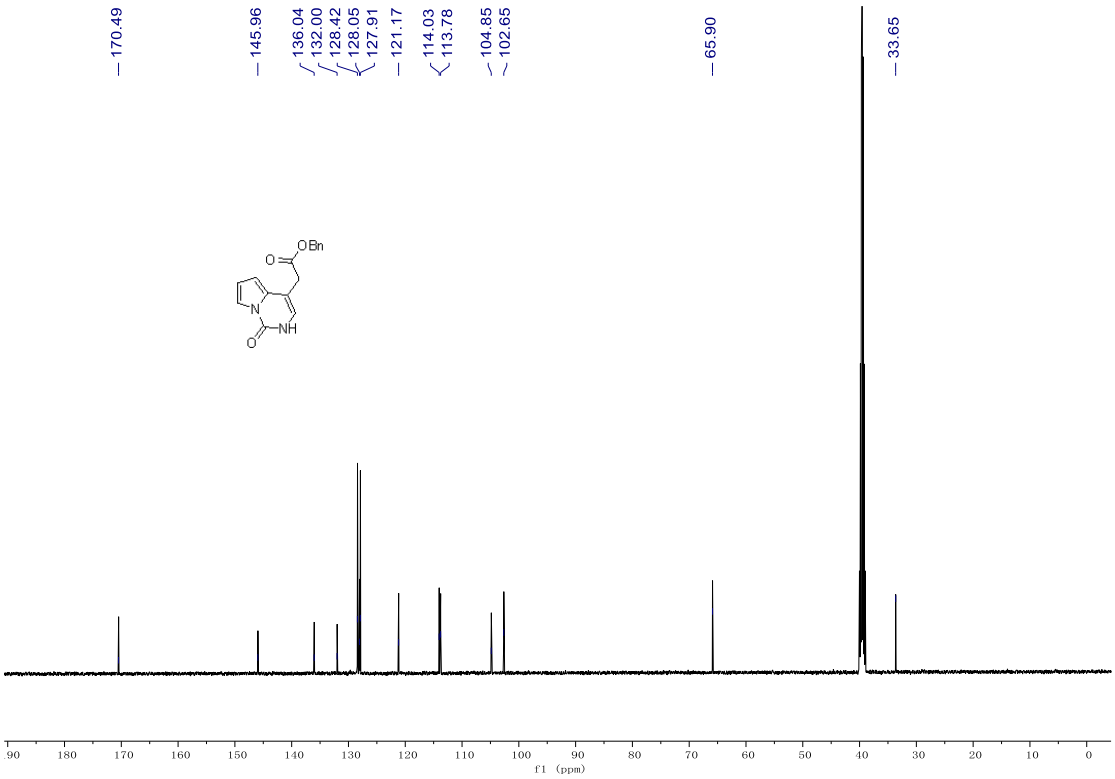
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound 5la



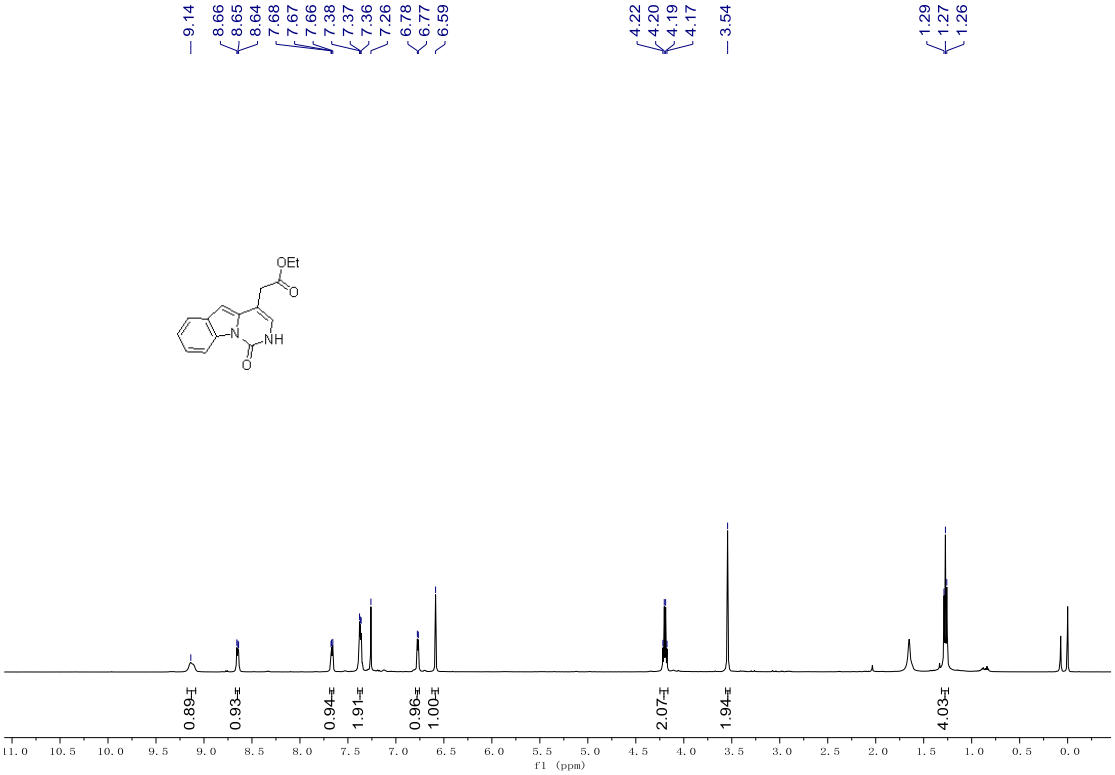
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **5ma**



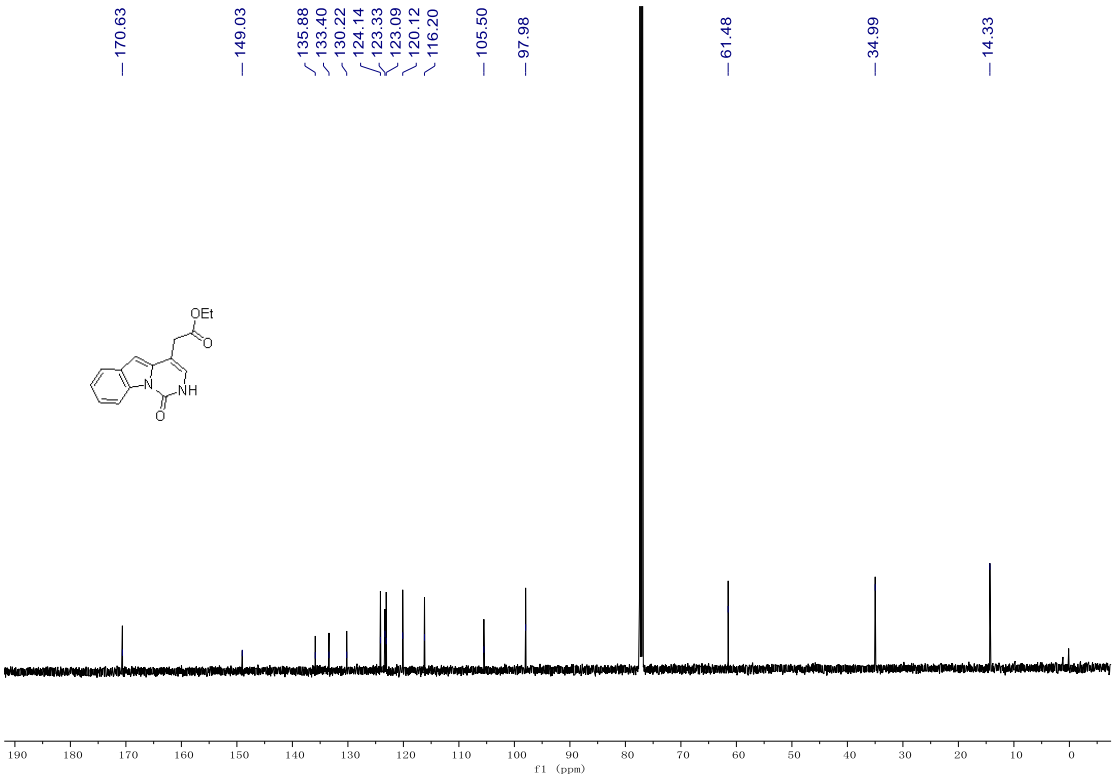
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound **5ma**



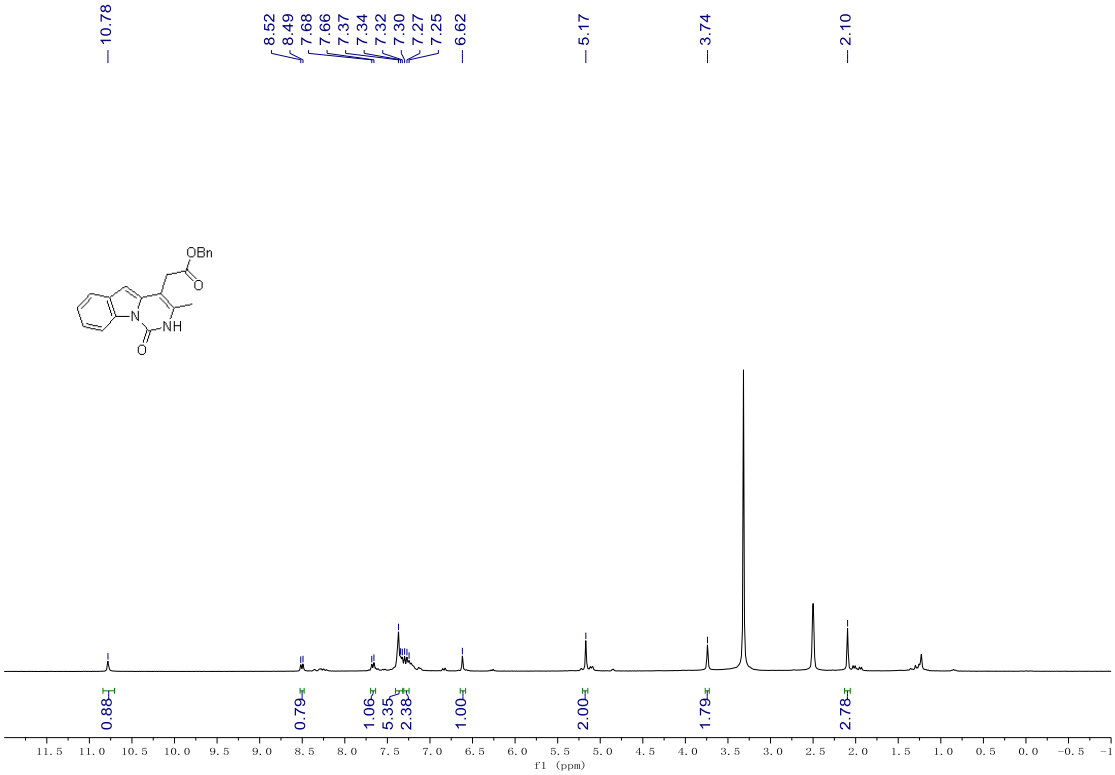
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound **5ab**



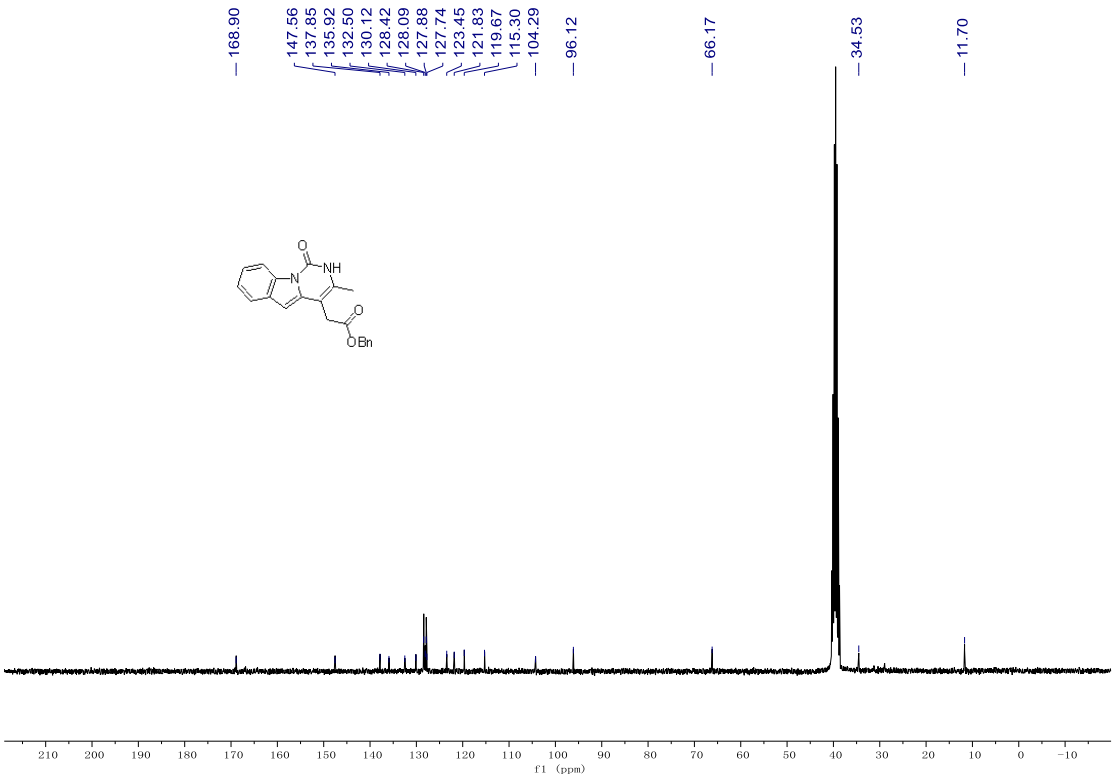
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound **5ab**



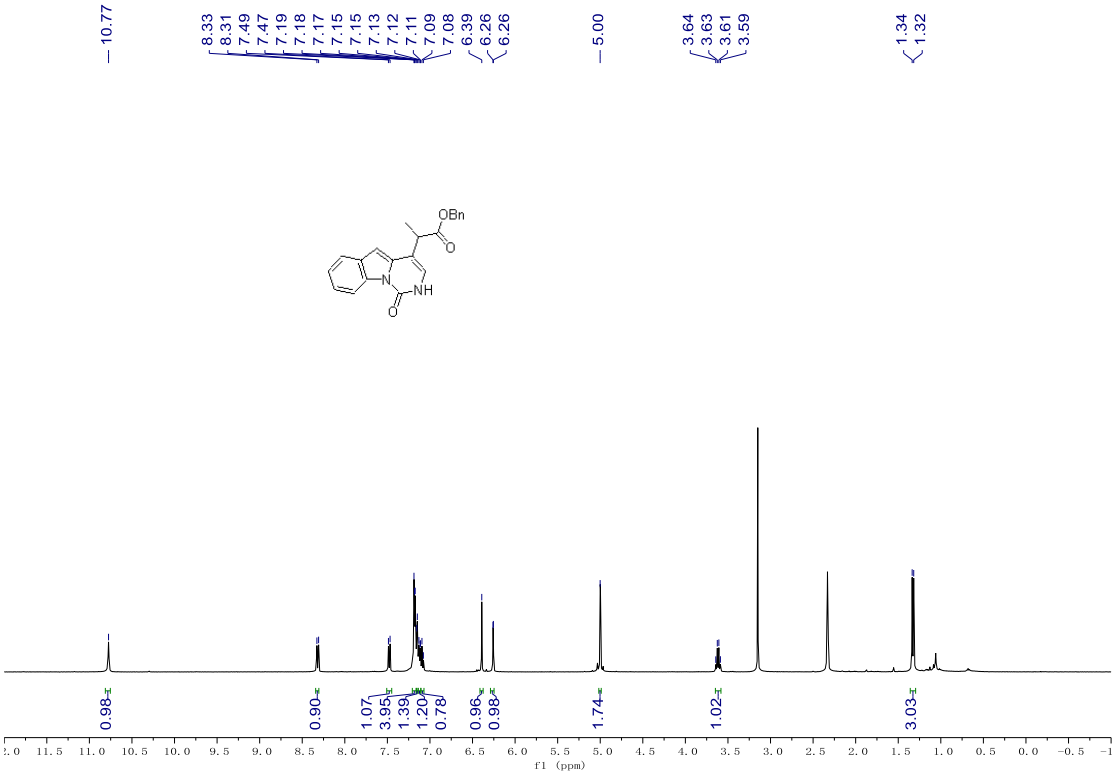
^{1}H NMR (300 MHz, DMSO-d_6) Spectra of compound 5ac



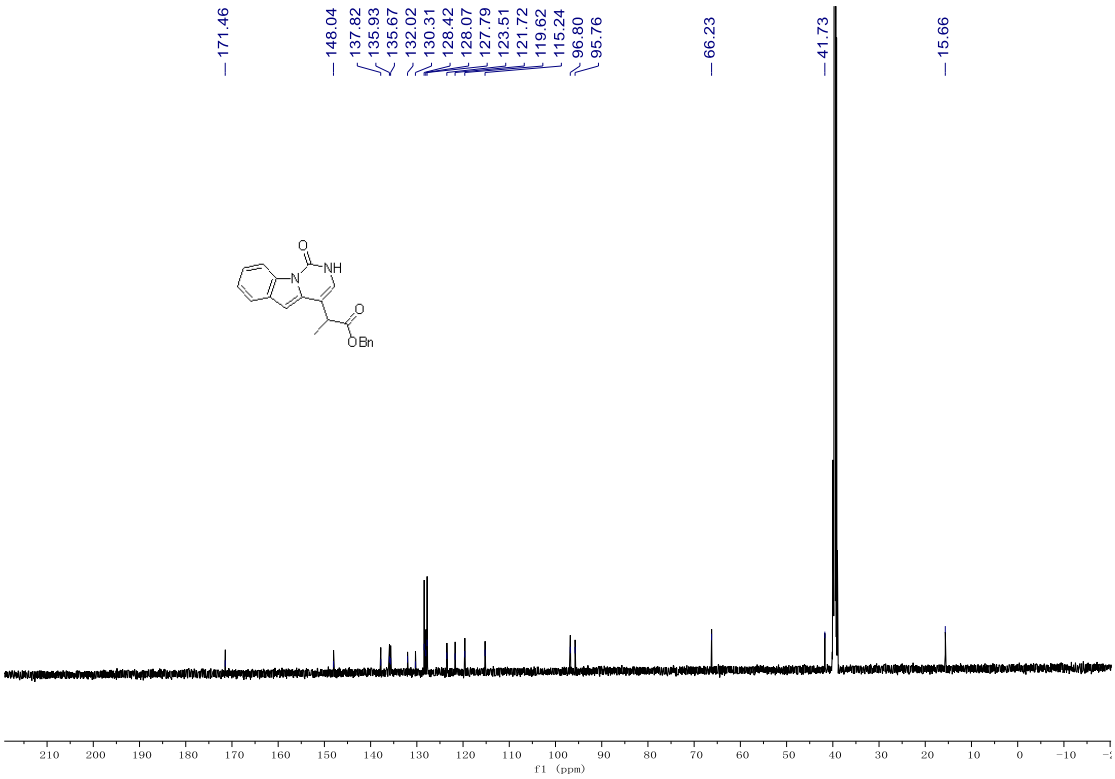
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of compound 5ac



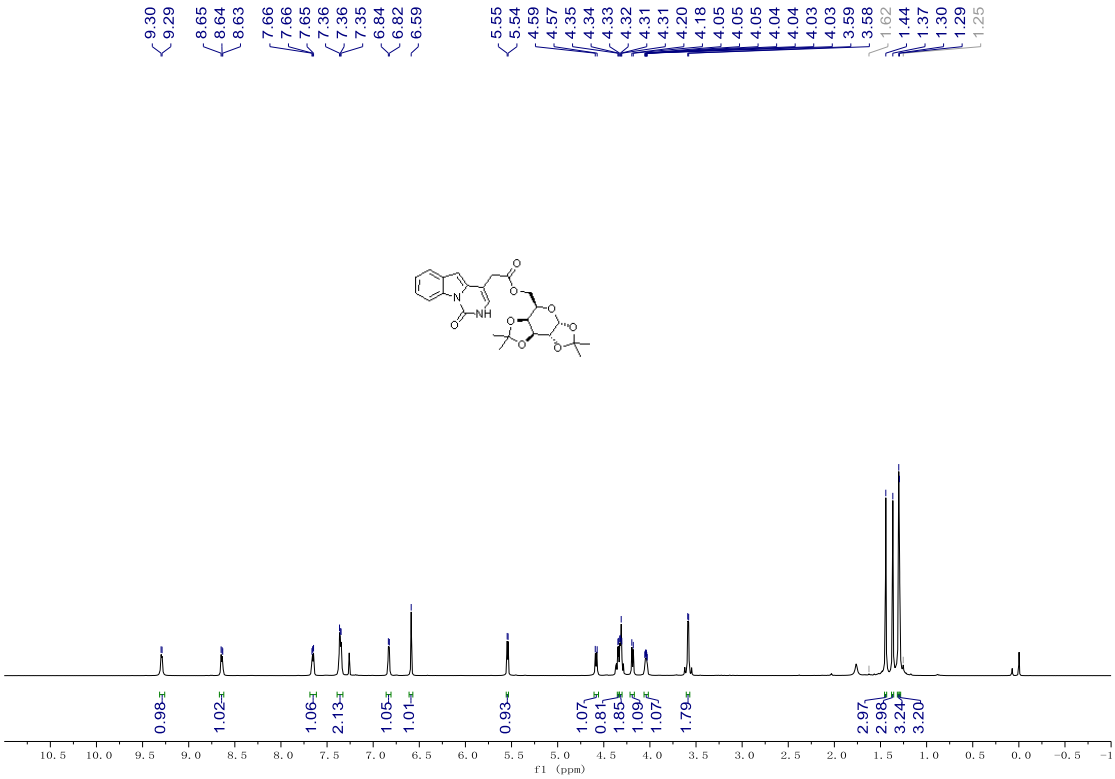
^{1}H NMR (500 MHz, DMSO-d_6) Spectra of compound **5ad**



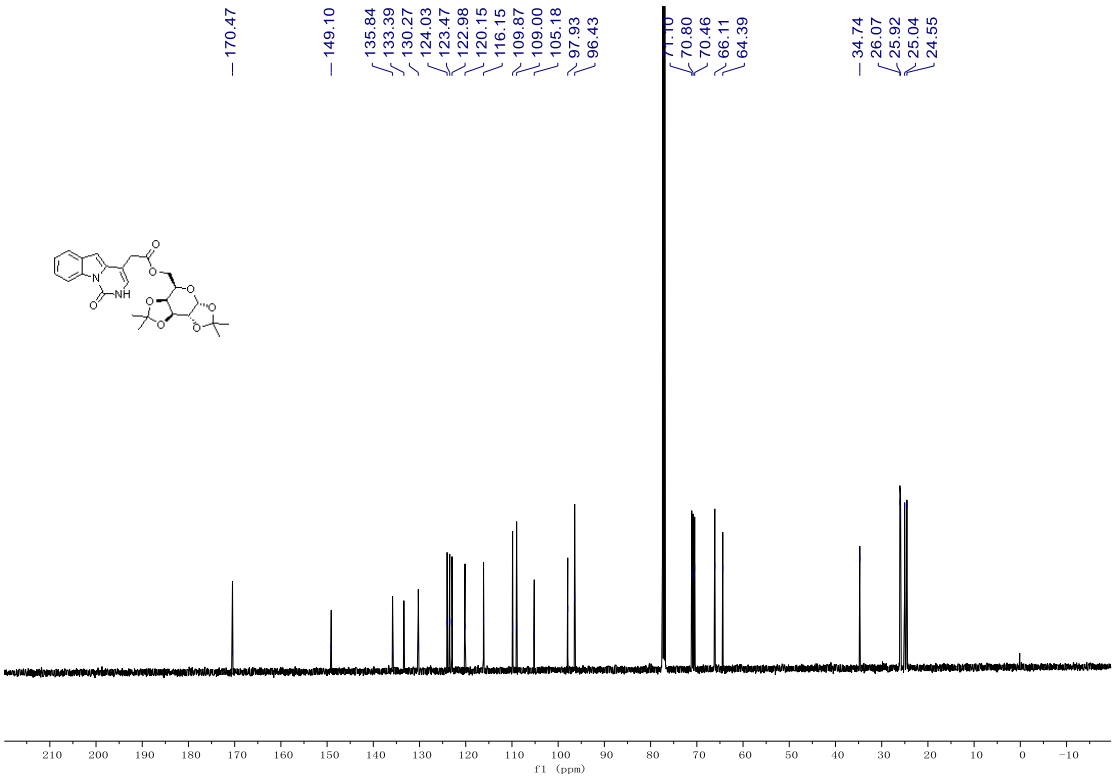
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound **5ad**



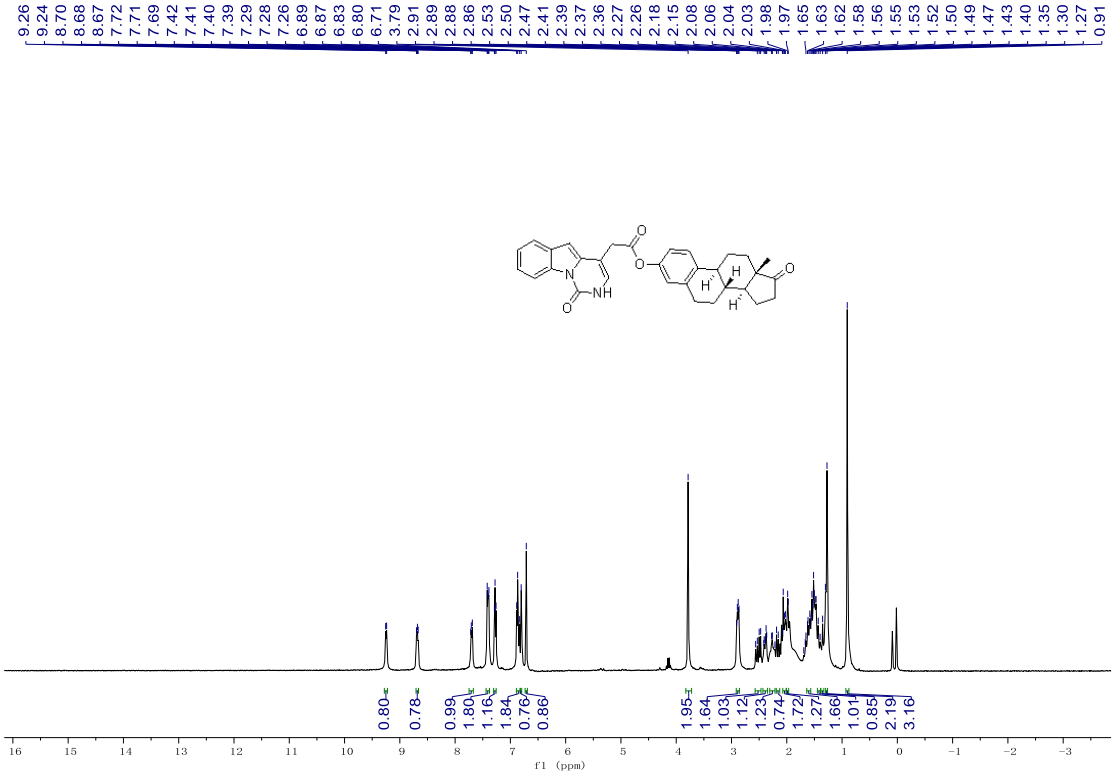
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 5ae



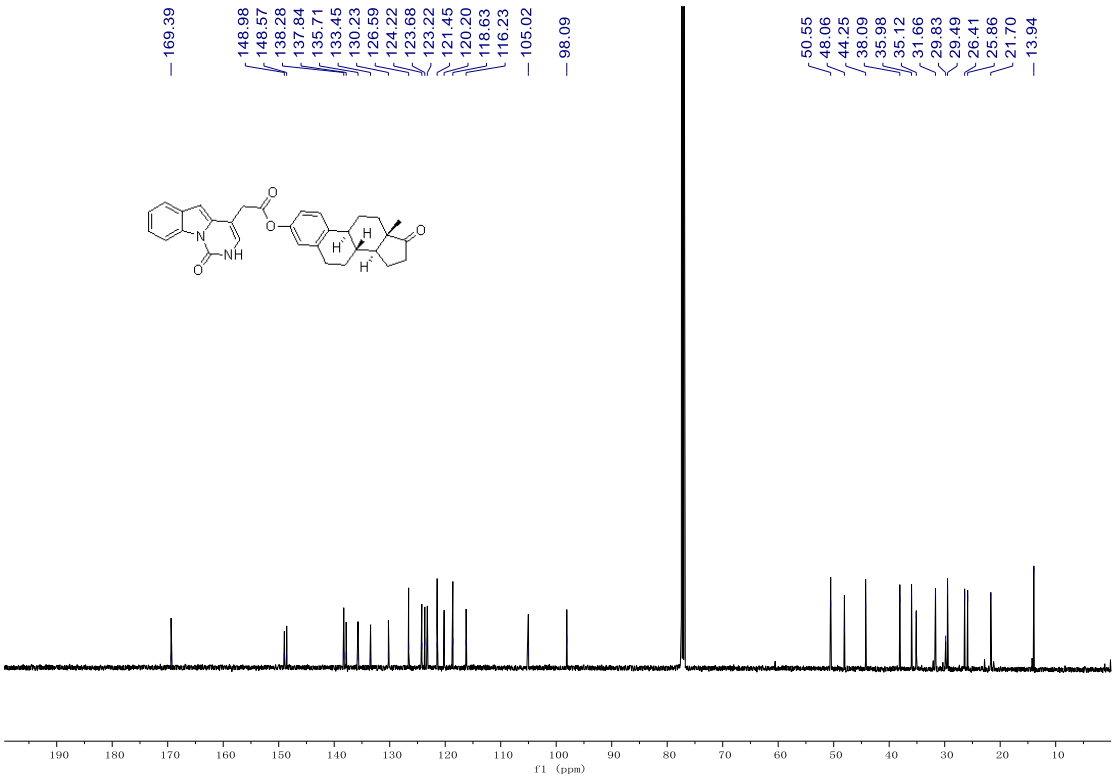
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 5ae



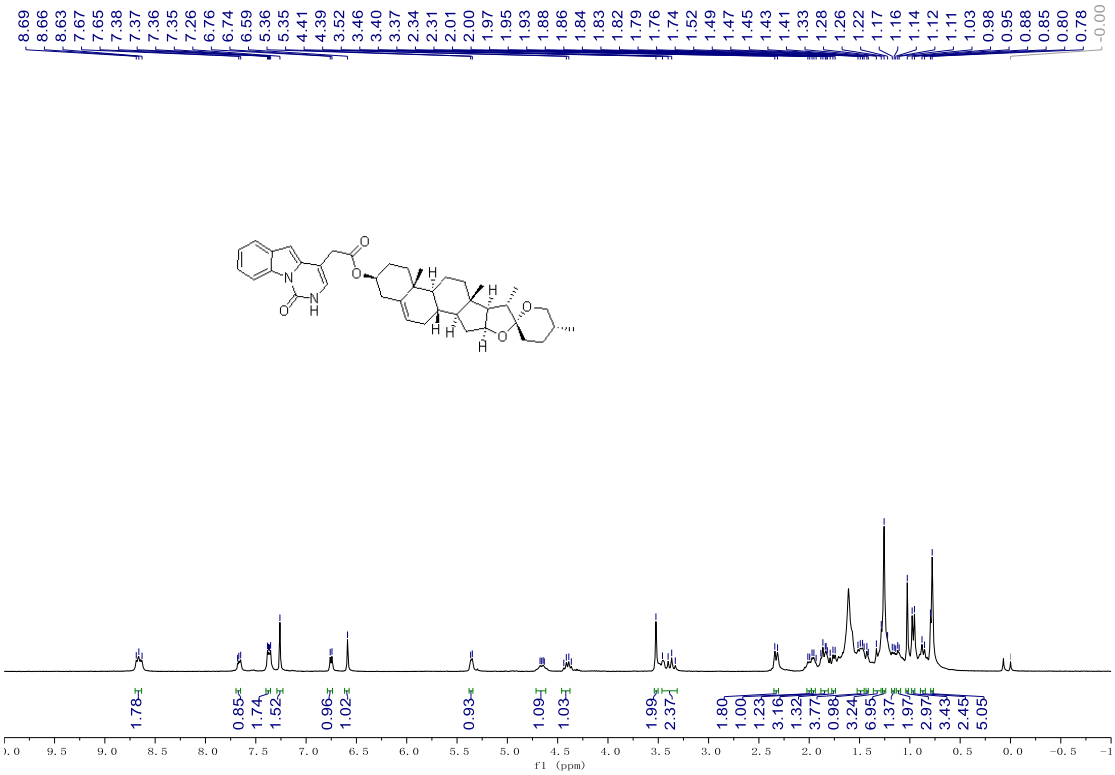
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 5ag



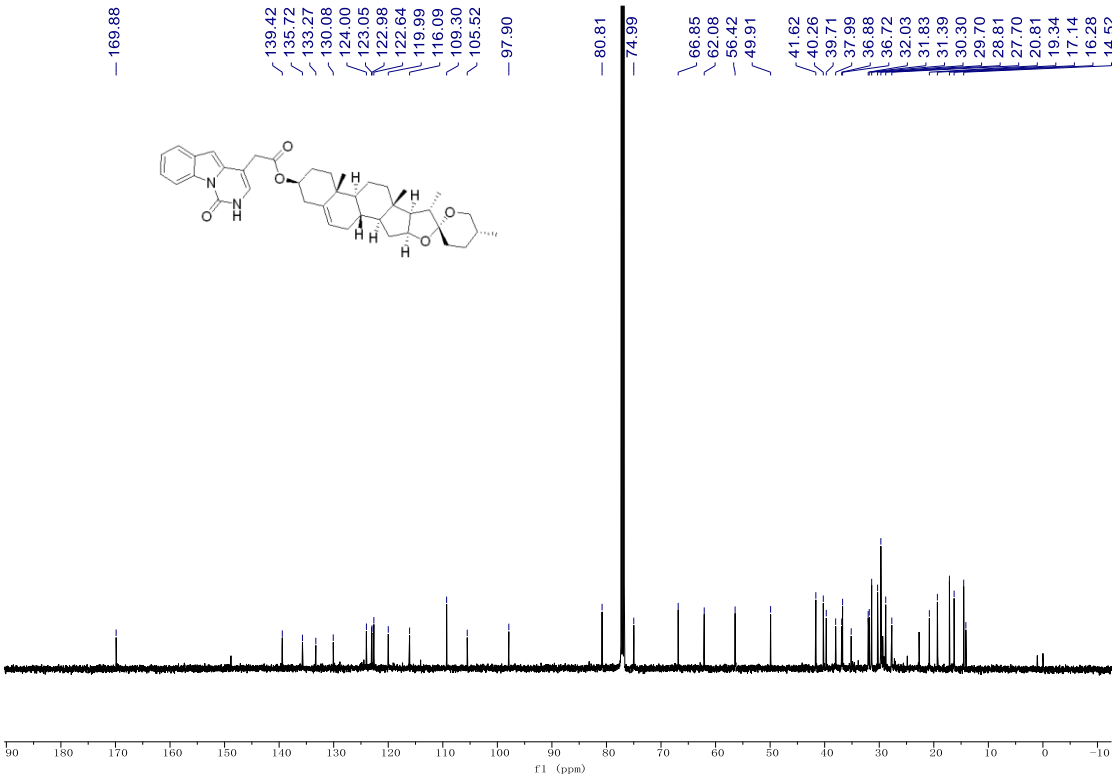
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 5ag



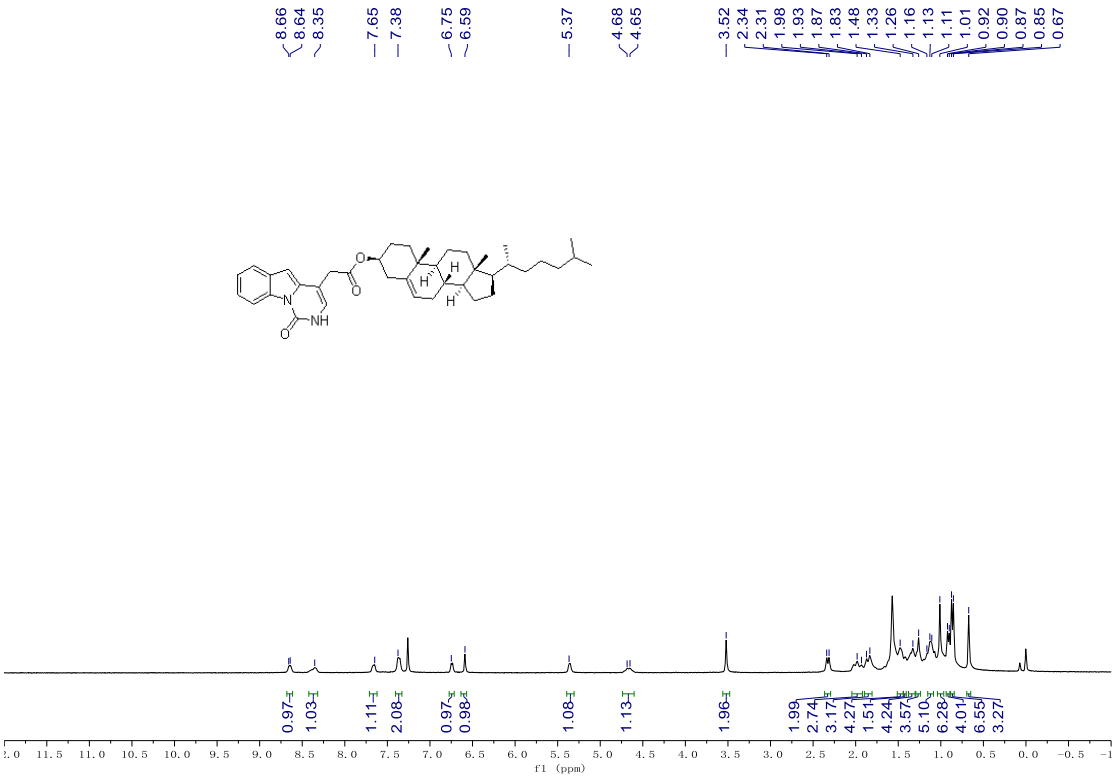
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound **5ah**



^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound **5ah**



^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 5ai



^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 5ai