Supporting Information

Alkoxycarbonylation-triggered nitrile insertion/remote C(sp^2)-H and C(sp^3)-H functionalization to access esterified quinazolinones and amidines

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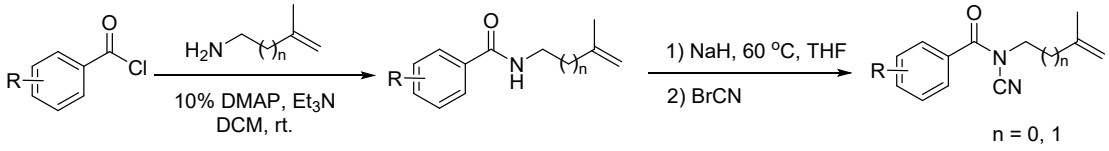
1. General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 600 MHz spectrometer in $CDCl_3$, fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a 565 MHz spectrometer in $CDCl_3$, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 150 MHz spectrometer in $CDCl_3$ unless otherwise noted. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet, dt = doublet triplet, dq =double quartet, br = broad), integration, coupling constant (Hz), and assignment. UV detection was monitored at 254 nm. Blue LEDs (40 W, λ_{max} = 455 nm) were used for blue light irradiation. Electrospray ionization high-resolution mass spectrometry (ESI-HRMS) was recorded on AB SCIEX Triple-TOF 5600. High-resolution mass spectra were obtained with a Bruker Impact II UHR-QTOF by ESI on a TOF mass analyzer. Melting points were measured on a melting point apparatus and are uncorrected. All absorbance measurement was surveyed on SHIMADZU UV-2600. Column chromatography was performed on silica gel (300-400 mesh) eluting with ethyl acetate (EtOAc), petroleum ether (PE). TLC was performed on glass-backed silica plates. UV light and I_2 were used to visualize products or starting materials, all reagents were obtained from commercial suppliers and used without further purification. All experiments were performed under an atmosphere of argon atmosphere, using anhydrous solvents.

2. Preparation of Starting Materials

General procedure for the synthesis of N-cyanobenzamide derivatives S1. General Procedure 1 (1a-1o, 1s, 1t).[1]

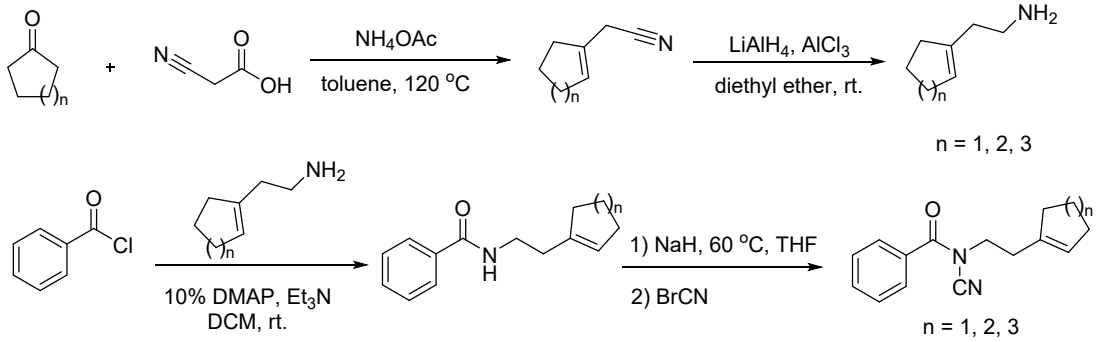


To a CH_2Cl_2 solution containing amine (10 mmol, 1.0 equiv.) and DMAP (122 mg, 1 mmol, 0.1 equiv.), triethylamine (2.8 mL, 20 mmol, 2.0 equiv.) was added. After the mixture was stirred for 10 min, benzoyl chloride (1.25 mL, 10.5 mmol, 1.05 equiv.) was added dropwise at 0 ℃ over 30 min under Ar atmosphere. The reaction mixture was allowed to warm to ambient temperature and stirred for 5 h. When the reaction was finished, the mixture was then quenched with saturated NH_4Cl solution. The mixture was extracted with DCM (3 x 15 mL) and the organic phases were combined, dried over Na_2SO_4, concentrated and purified by column chromatography to afford the desired product.

A round-bottom flask was charged with NaH (640 mg, 60% wt, 16 mmol, 4.0 equiv.), which was then evacuated and backfilled with argon for three times. THF was added and the solution was cooled to 0 ℃. Then benzamide (4 mmol, 1.0 equiv.) in

THF was added dropwise and the reaction was kept at 60 ℃ for 2 h. Next, cyanogenbromide (1.7 g, 16 mmol, 4.0 equiv.) was added into the reaction solution at 0 ℃. The reaction mixture was stirred at room temperature for 12 h. Afterwards, the solution was filtered and the filtrate was concentrated, the residue was purified via column chromatography to give the product.

General Procedure 2 (1p-1r).[2]



Cyanoacetic acid (2.8 g, 33 mmol, 1.1 equiv.) and ammonium acetate (4.62 g, 60 mmol, 2.0 equiv.) was added to a toluene solution of ketone (30 mmol, 1.0 equiv.), heating the mixture to reflux for 3 h at 120 ℃ in an oil bath. When the reaction was finished, removed the solvent and extracted with EA (3 x 15 mL) and the organic phases were combined, dried over Na_2SO_4, concentrated and purified by column chromatography to afford the desired product.

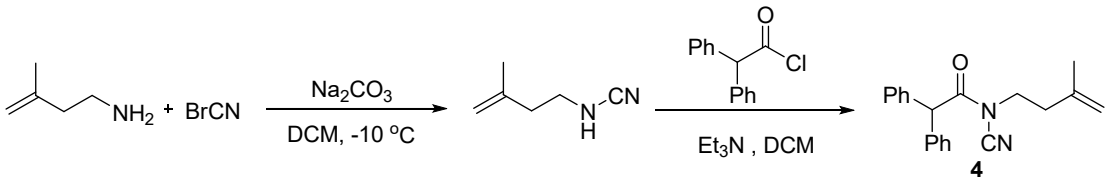
To a solution of $LiAlH_4$ (0.63 g, 16.5 mmol, 1.1 equiv.) in diethyl ether was added aluminum chloride (2.2 g, 16.5 mmol, 1.1 equiv.) in one portion under argon at 0 °C. The mixture was stirred for 15 min. The nitrile derivative (15 mmol, 1.0 equiv.) in diethyl ether was added dropwise to the mixed solution and stirred for 12 h at room temperature. After the reaction was completed, the reaction was re-cooled to 0 °C, diluted with diethyl ether and quenched with NaOH aq, then stirred at 0 °C for 15 min. The mixture was extracted with EA (3 x 15 mL) and the organic phases were combined, dried over Na_2SO_4 and concentrated to obtain crude amines which were used in the next step without further purification.

To a CH_2Cl_2 solution containing amine (10 mmol, 1.0 equiv.) and DMAP (122 mg, 1 mmol, 0.1 equiv.), triethylamine (2.8 mL, 20 mmol, 2.0 equiv.) was added and the mixture was stirred for 10 min, and benzoyl chloride (1.25 mL, 10.5 mmol, 1.05 equiv.) was added dropwise at 0 ℃ over 30 min under Ar atmosphere. The reaction mixture was allowed to warm to ambient temperature and stirred for 5 h. When the reaction was finished, the reaction was quenched with saturated NH_4Cl solution. The mixture was extracted with DCM (3 x 15 mL) and the organic phases were combined, dried over Na_2SO_4, concentrated and purified by column chromatography to afford the desired product.

A round-bottom flask was charged with NaH (640 mg, 60% wt, 16 mmol, 4.0 equiv.), which was then evacuated and backfilled with argon for three times. THF was added and the solution was cooled to 0 ℃. Then benzamide (4 mmol, 1.0 equiv.) in

THF was added dropwise and the reaction was kept at 60 °C for 2 h. Next, cyanogenbromide (1.7 g, 16 mmol, 4.0 equiv.) was added into the reaction solution at 0 °C. The reaction mixture was stirred at room temperature for 12 h. Afterwards, the solution was filtered and the filtrate was concentrated, the residue was purified via column chromatography to give the product.

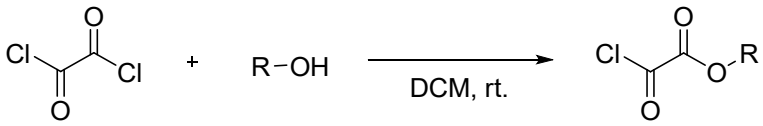
General Procedure 3 (4).[3]



To a stirring solution of BrCN (1.27 g, 12 mmol, 1.2 equiv.) and Na_2CO_3 (1.27 g, 12 mmol, 1.2 equiv.) in DCM at -10 °C, amine (0.85 g, 10 mmol, 1.0 equiv.) was added. The reaction mixture was stirred for two hours at -10 °C. Then the reaction was warmed to room temperature and stirred for 2 h. After completion, the reaction mixture was used to the next step without further purification.

To a suspension of N-(3-methylbut-3-en-1-yl) cyanamide (1.1 g, 10 mmol, 1.0 equiv.) in DCM was added Et_3N (1.7 mL, 12 mmol, 1.2 equiv.) The reaction flask was cooled to 0 °C and a solution of 2,2-diphenylacetyl chloride (2.8 g, 12 mmol, 1.2 equiv.) in DCM was added dropwise. The resulting mixture was allowed to warm up to room temperature and stirred for overnight. Upon completion, the reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired compound (62% yield, 1.9 g).

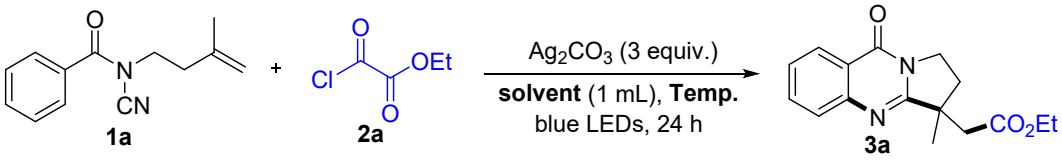
General procedure for the synthesis of chloro-oxoacetates S2.[4]



To a solution of oxalyl chloride (1.71 mL, 20 mmol, 2.0 equiv.) in DCM was added dropwise a solution of alcohol (10 mmol, 1.0 equiv.) in DCM at 0 °C. Then the reaction was warmed to room temperature and stirred for 3 h. Upon completion, solvent and excess oxalyl chloride was evaporated in vacuo. The product obtained was used in the next step without further purification.

3. Optimization of Reaction Conditions

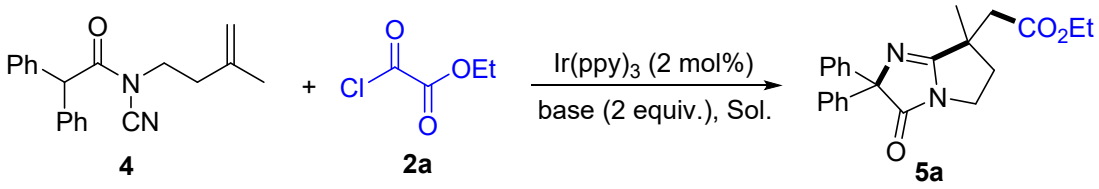
Table S1. Optimization the Reaction Conditions for Constructing Esterified Quinazolinones[a]



Entry	Cat.	Solvent	Temp. (°C)	Yield[b]
1	---	DMSO	35	0%
2	---	THF	35	63%
3	---	Et_2O	35	54%
4	---	Toluene	35	39%
5	---	1,4-Dioxane	45	46%
6	---	1,4-Dioxane	60	23%
7[c]	$Ir(ppy)_3$	1,4-Dioxane	35	56%

[a]Unless noted otherwise, reactions were performed with **1a** (0.2 mmol), **2a** (0.6 mmol), Ag_2CO_3 (3 equiv.) in solvent (1 mL), blue LEDs, Ar, 24 h. [b]Isolated yield. [c]$Ir(ppy)_3$ (2 mol%), 2,6-lutidine (0.4 mmol), Ag_2CO_3 (0.6 mmol) was used.

Table S2. Optimization the Reaction Conditions for Constructing Esterified Amidines[a]



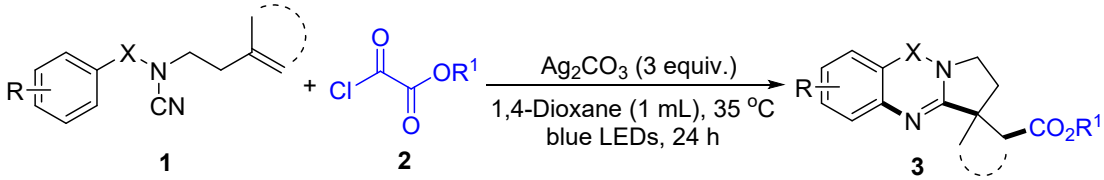
Entry	Cat.	Base	Sol.	Yield[b]
1	---	Ag_2CO_3 (3 eq.)	1,4-dioxane	0
2	$Ir(ppy)_3$	2,6-lutidine	MeCN	55%
3	$Ir(ppy)_3$	2,6-lutidine, Ag_2CO_3(3 eq.)	MeCN	trace
4	$Ir(ppy)_3$	2,6-lutidine	1,4-dioxane	24%
5	$Ir(ppy)_3$	2,6-lutidine (3 eq.)	MeCN	74%
6	$Ir(ppy)_3$	2,4,6-Collidine	MeCN	40%
7	$Ir(ppy)_3$	DABCO	MeCN	61%
8	$Ir(ppy)_3$	$^iPr_2NEt$	MeCN	trace
9	$Ir(ppy)_3$	K_2CO_3	MeCN	0

[a]Unless noted otherwise, reaction conditions were as follows: **4** (0.2 mmol), **2a** (0.6 mmol), $Ir(ppy)_3$ (2 mol%), MeCN (2 mL), blue LEDs, Ar, 24 h. [b]Isolated yields.

4. Procedures for the Catalytic Reactions and Characterization Data

4.1 Procedures for the catalytic reactions

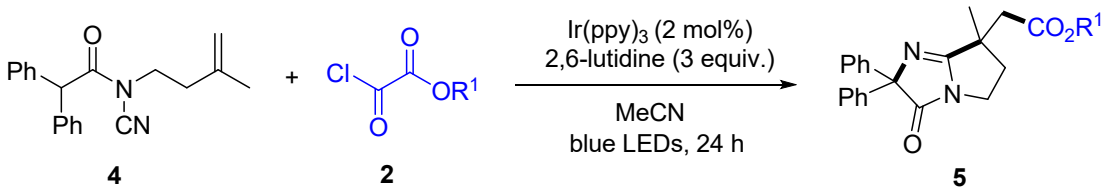
Typical procedure for synthesis of 3:



A dried 10 mL Schlenk tube containing N-cyano-N-(3-methylbut-3-en-1-yl) benzamide **1a** (0.2 mmol, 1.0 equiv.), Ag_2CO_3 (165.5 mg, 0.6 mmol, 3.0 equiv.) was

evacuated and purged with argon three times. Afterwards, chloro oxoacetates **2** (64 uL, 0.6 mmol, 3.0 equiv.) and anhydrous 1,4-dioxane (1 mL, 0.2 M) were added under an argon atmosphere. The reaction mixture was then stirred and irradiated with 40 W blue LEDs with fans placed beside for cooling and the solution was kept at 35 ℃ for 24 h. After completion, the reaction mixture was purified by flash chromatography to give the desired compounds.

Typical procedure for synthesis of 5:



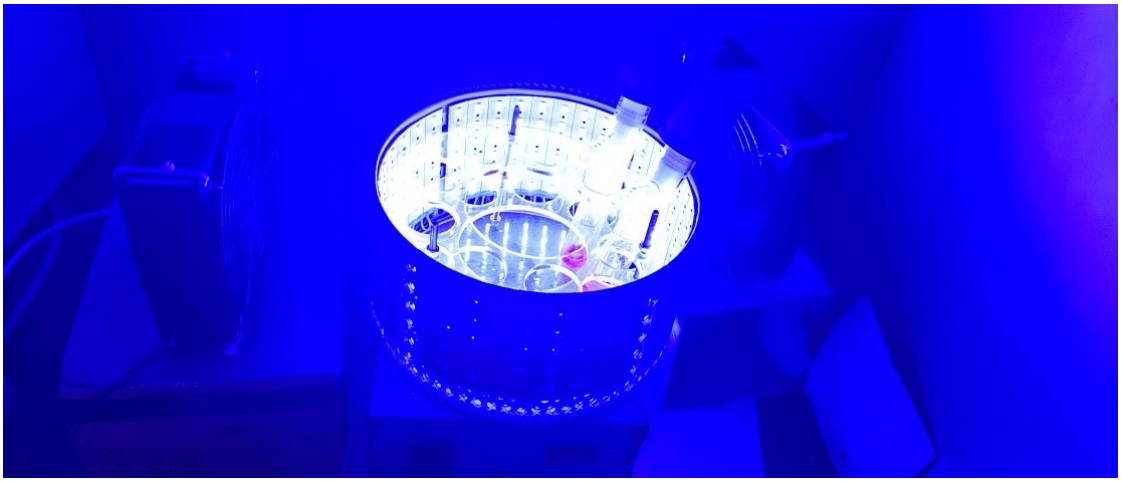
4 **2** **5**

A dried 10 mL Schlenk tube containing **4** (60.8 mg, 0.2 mmol, 1.0 equiv.), $Ir(ppy)_3$ (2.6 mg, 0.004 mmol, 0.02 equiv.) was evacuated and purged with argon three times. Afterwards, chloro oxoacetates **2** (64 uL, 0.6 mmol, 3.0 equiv.), 2,6-lutidine (70 uL, 0.6 mmol, 3.0 equiv.) and anhydrous MeCN (2 mL, 0.1 M) were added under an argon atmosphere. The reaction mixture was then stirred and irradiated with 40 W blue LEDs with fans placed beside for cooling and the solution was kept at 35 ℃ for 24 h. After completion, the reaction mixture was purified by flash chromatography to give the desired compounds.

4.2 Standard reaction setup

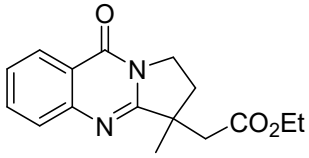
All reactions were run using the blue LEDs (40 W, λ_{max} = 455 nm) below (2.5 cm from reaction vial), with fans for cooling.
Manufacturer: Xuzhou Aijia Electronic Technology Co., Ltd
Wavelength of peak intensity: 450-460 nm
Material of the irradiation vessel (10 mL Schlenk tubes): borosilicate glass.
Distance of the irradiation vessel from the light source: approximately 2.5 cm.
No use any filters.

Reaction Setup:



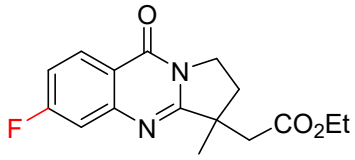
4.3 Characterization data for products

Ethyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3a).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 87% yield (49.8 mg); mp 87-89 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.41 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.09 – 4.03 (m, 3H), 2.85 (dd, *J* = 37.1, 16.0 Hz, 2H), 2.47 (ddd, *J* = 13.0, 9.1, 8.0 Hz, 1H), 2.18 – 2.12 (m, 1H), 1.44 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7, 163.4, 161.0, 149.5, 133.9, 127.0, 126.3, 126.0, 120.8, 60.5, 45.0, 43.4, 42.7, 32.2, 25.1, 14.1; HRMS (ESI) for $C_{16}H_{18}N_2O_3Na$ $[M+Na]^+$ calcd. 309.1215, found 309.1219.

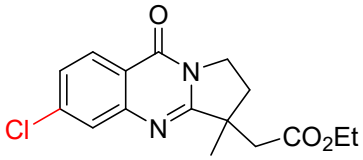
Ethyl 2-(6-fluoro-3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3b).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 81% yield (49.2 mg); mp 70-71 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.8, 6.2 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.13 (td, *J* = 8.5, 2.5 Hz, 1H), 4.23 (ddd, *J* = 12.9, 9.3, 3.9 Hz, 1H), 4.11 – 4.00 (m, 3H), 2.90 (d, *J* = 16.2 Hz, 1H), 2.80 (d, *J* = 16.2 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.19 – 2.11 (m, 1H), 1.44 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7, 166.3 (d, *J* = 253.3 Hz), 164.8, 160.3, 151.8 (d, *J* = 13.1 Hz), 128.9 (d, *J* = 10.7 Hz), 117.5 (d, *J* = 1.7 Hz), 114.8 (d, *J* = 23.6 Hz), 112.4 (d, *J* = 21.9 Hz), 60.6, 45.1, 43.5, 42.6, 32.1, 25.3, 14.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -104.27 to -104.36 (m, 1F); HRMS (ESI) for $C_{16}H_{17}FN_2O_3Na$ $[M+Na]^+$ calcd. 327.1121,

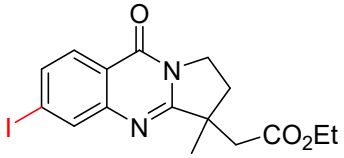
found 327.1121.

Ethyl 2-(6-chloro-3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3c).



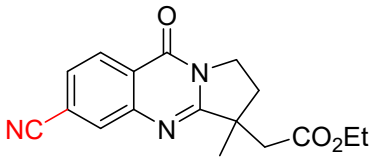
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 90% yield (57.3 mg); mp 94-96 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.37 (dd, *J* = 8.5, 1.9 Hz, 1H), 4.24 (ddd, *J* = 12.8, 9.3, 3.8 Hz, 1H), 4.10 – 4.02 (m, 3H), 2.91 (d, *J* = 16.3 Hz, 1H), 2.80 (d, *J* = 16.3 Hz, 1H), 2.48 (dt, *J* = 12.9, 8.8 Hz, 1H), 2.18 – 2.12 (m, 1H), 1.44 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 164.9, 160.4, 150.8, 140.2, 127.8, 126.9, 126.7, 119.5, 60.6, 45.3, 43.6, 43.0, 32.4, 25.3, 14.1; HRMS (ESI) for $C_{16}H_{17}ClN_2O_3Na$ $[M+Na]^+$ calcd. 343.0826, found 343.0827.

Ethyl 2-(6-iodo-3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl) acetate (3d).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 84% yield (69.0 mg); mp 140-141 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.5 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.72 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.23 (ddd, *J* = 13.1, 9.3, 3.9 Hz, 1H), 4.05 (ddd, *J* = 12.4, 11.2, 5.7 Hz, 3H), 2.90 (d, *J* = 16.3 Hz, 1H), 2.79 (d, *J* = 16.3 Hz, 1H), 2.47 (dt, *J* = 13.0, 8.7 Hz, 1H), 2.17 – 2.12 (m, 1H), 1.43 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7, 164.6, 160.7, 150.3, 136.2, 135.0, 127.6, 120.1, 101.3, 60.6, 45.1, 43.6, 42.6, 32.0, 25.4, 14.1; HRMS (ESI) for $C_{16}H_{17}IN_2O_3Na$ $[M+Na]^+$ calcd. 435.0182, found 435.0183.

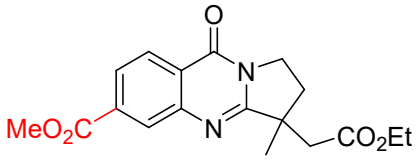
Ethyl 2-(6-cyano-3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3e).



Column chromatography on silica gel (PE/EtOAc = 2.5:1). White solid; 79% yield (49.2 mg); mp 135-137 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 1.0 Hz, 1H), 7.61 (dd, *J* = 8.2, 1.4 Hz, 1H), 4.27 (ddd, *J* = 12.9, 9.4, 3.8 Hz, 1H), 4.07 (qd, *J* = 8.4, 3.6 Hz, 3H), 2.96 (d, *J* = 16.5 Hz, 1H), 2.81 (d, *J* = 16.5 Hz, 1H), 2.50 (dt, *J* = 13.0, 9.1 Hz, 1H), 2.19 – 2.13 (m, 1H), 1.45 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 165.6, 159.8, 149.4, 131.9, 127.8, 127.6,

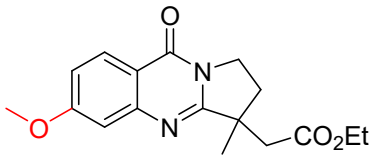
123.7, 117.8, 117.2, 60.6, 45.1, 43.8, 42.5, 31.8, 25.5, 14.0; HRMS (ESI) for $C_{17}H_{17}N_3O_3Na$ $[M+Na]^+$ calcd. 334.1168, found 334.1172.

Methyl 3-(2-ethoxy-2-oxoethyl)-3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b] quinazoline-6-carboxylate (3f).



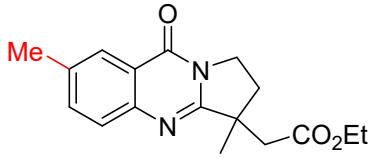
Column chromatography on silica gel (PE/EtOAc = 1.5:1). White solid; 80% yield (55.0 mg); mp 136-138 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 10.5, 4.7 Hz, 2H), 8.02 (dd, *J* = 8.3, 1.5 Hz, 1H), 4.26 (ddd, *J* = 12.9, 9.3, 3.9 Hz, 1H), 4.07 (dt, *J* = 6.9, 4.5 Hz, 3H), 3.96 (s, 3H), 2.93 (d, *J* = 16.3 Hz, 1H), 2.82 (d, *J* = 16.3 Hz, 1H), 2.50 (dt, *J* = 12.9, 8.9 Hz, 1H), 2.20 – 2.13 (m, 1H), 1.45 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7, 166.2, 164.4, 160.5, 149.4, 135.0, 129.0, 126.7, 126.1, 123.8, 60.6, 52.5, 45.0, 43.6, 42.7, 32.0, 25.4, 14.1; HRMS (ESI) for $C_{18}H_{20}N_2O_5Na$ $[M+Na]^+$ calcd. 367.1270, found 367.1273.

Ethyl 2-(6-methoxy-3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3 -yl)acetate (3g).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 81% yield (51.0 mg); mp 60-62 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.21 (ddd, *J* = 13.1, 9.2, 4.0 Hz, 1H), 4.05 (ddd, *J* = 20.3, 13.2, 5.7 Hz, 3H), 3.89 (s, 3H), 2.84 (dd, *J* = 37.5, 16.0 Hz, 2H), 2.46 (ddd, *J* = 13.0, 9.0, 8.0 Hz, 1H), 2.17 – 2.11 (m, 1H), 1.44 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7, 164.3, 164.1, 160.6, 151.8, 127.8, 116.2, 114.3, 107.7, 60.5, 55.6, 45.1, 43.3, 42.7, 32.2, 25.1, 14.1; HRMS (ESI) for $C_{17}H_{20}N_2O_4Na$ $[M+Na]^+$ calcd. 339.1321, found 339.1321.

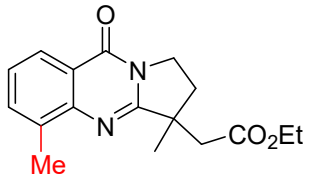
Ethyl 2-(3,7-dimethyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)ace-tate (3h).



Column chromatography on silica gel (PE/EtOAc = 3:1). White solid; 32% yield (17.6 mg); mp 62-63 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.53 (dt, *J* = 8.3, 5.1 Hz, 2H), 4.24 – 4.19 (m, 1H), 4.09 – 4.04 (m, 3H), 2.84 (q, *J* = 16.0 Hz, 2H), 2.48 (dd, *J* = 7.0, 6.0 Hz, 1H), 2.46 (s, 3H), 2.17 – 2.12 (m, 1H), 1.44 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 162.6, 161.1, 147.5, 136.2, 135.4,

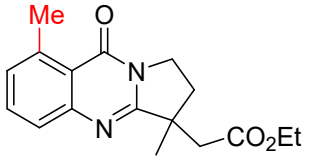
126.9, 125.8, 120.5, 60.5, 44.9, 43.4, 42.8, 32.3, 25.1, 21.2, 14.1; HRMS (ESI) for $C_{17}H_{20}N_2O_3Na$ $[M+Na]^+$ calcd. 323.1372, found 323.1371.

Ethyl 2-(3,5-dimethyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3h′).



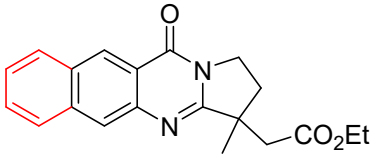
Column chromatography on silica gel (PE/EtOAc = 3:1). White solid; 60% yield (32.9 mg); mp 57-59 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 – 8.11 (m, 1H), 7.55 – 7.52 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 4.25 – 4.21 (m, 1H), 4.09 (qd, *J* = 7.1, 0.8 Hz, 2H), 4.05 – 4.01 (m, 1H), 2.88 – 2.81 (m, 2H), 2.57 (s, 3H), 2.47 (dt, *J* = 13.0, 8.7 Hz, 1H), 2.17 (ddd, *J* = 12.8, 8.1, 3.8 Hz, 1H), 1.44 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.9, 161.9, 161.5, 148.1, 135.7, 134.5, 125.6, 124.0, 120.7, 60.5, 45.0, 43.3, 42.8, 32.4, 25.1, 17.4, 14.2; HRMS (ESI) for $C_{17}H_{20}N_2O_3Na$ $[M+Na]^+$ calcd. 323.1372, found 323.1377.

Ethyl 2-(3,8-dimethyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3i).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 87% yield (52.3 mg); mp 63-65 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.1 Hz, 1H), 4.19 (ddd, *J* = 13.0, 9.2, 4.0 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 4.05 – 3.98 (m, 1H), 2.88 (s, 3H), 2.82 (t, *J* = 15.3 Hz, 2H), 2.45 (ddd, *J* = 13.0, 9.0, 8.0 Hz, 1H), 2.16 – 2.11 (m, 1H), 1.43 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 162.9, 161.8, 151.2, 140.9, 133.0, 128.7, 125.3, 119.3, 60.5, 44.9, 43.4, 42.6, 32.2, 25.0, 23.0, 14.1; HRMS (ESI) for $C_{17}H_{20}N_2O_3Na$ $[M+Na]^+$ calcd. 323.1372, found 323.1370.

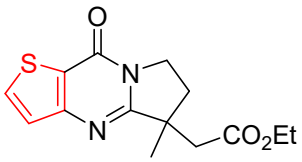
Ethyl 2-(3-methyl-11-oxo-1,2,3,11-tetrahydrobenzo[g]pyrrolo[2,1-b]quinazolin-3-yl)acetate (3j).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 87% yield (58.4 mg); mp 105-107 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.05 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 1H), 7.91 – 7.88 (m, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.66 (dtd, *J* = 16.4, 6.9, 1.4 Hz, 2H), 4.33 (ddd, *J* = 12.9, 9.2, 3.9 Hz, 1H), 4.15 (dt, *J* = 12.3, 8.0 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.99 – 2.93 (m, 2H), 2.55 (ddd, *J* = 12.9, 9.0, 8.1 Hz,

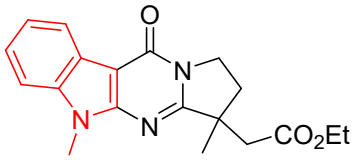
1H), 2.27 – 2.22 (m, 1H), 1.53 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 163.5, 161.1, 148.4, 136.1, 130.0, 128.9, 127.7, 126.5, 126.3, 125.2, 121.7, 117.0, 60.6, 45.4, 43.8, 42.9, 32.4, 25.2, 14.1; HRMS (ESI) for $C_{20}H_{21}N_2O_3$ $[M+H]^+$ calcd. 337.1554, found 337.1555.

Ethyl 2-(5-methyl-9-oxo-5,6,7,9-tetrahydropyrrolo[1,2-a]thieno[3,2-d]pyrimidin-5-yl)acetate (3k).



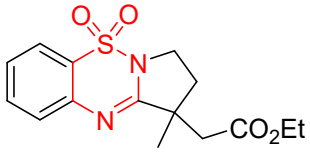
Column chromatography on silica gel (PE/EtOAc = 3:1). White solid; 71% yield (41.4 mg); mp 94-96 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, J = 5.3 Hz, 1H), 7.28 (d, J = 5.2 Hz, 1H), 4.29 – 4.24 (m, 1H), 4.08 (dt, J = 10.4, 4.8 Hz, 3H), 2.88 (d, J = 16.1 Hz, 1H), 2.80 (d, J = 16.1 Hz, 1H), 2.52 (ddd, J = 13.0, 9.1, 8.0 Hz, 1H), 2.21 – 2.16 (m, 1H), 1.44 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 165.4, 158.6, 157.2, 133.8, 124.8, 121.5, 60.6, 44.8, 43.4, 42.8, 32.5, 25.4, 14.1; HRMS (ESI) for $C_{14}H_{16}N_2O_3SNa$ $[M+Na]^+$ calcd. 315.0780, found 315.0784.

Ethyl 2-(3,5-dimethyl-10-oxo-2,3,5,10-tetrahydro-1H-pyrrolo[1',2':1,2]pyrimido[4,5-b]indol-3-yl)acetate (3l).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 89% yield (60.3 mg); mp 161-163 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.24 (d, J = 7.7 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 1H), 4.31 (ddd, J = 12.9, 9.2, 4.0 Hz, 1H), 4.16 – 4.08 (m, 3H), 3.83 (s, 3H), 2.86 (s, 2H), 2.52 (dt, J = 12.9, 8.9 Hz, 1H), 2.24 – 2.18 (m, 1H), 1.46 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 165.8, 157.8, 154.7, 137.3, 123.9, 121.9, 121.6, 121.6, 109.0, 98.5, 60.5, 45.4, 43.4, 42.8, 32.6, 27.9, 25.0, 14.1; HRMS (ESI) for $C_{19}H_{21}N_3O_3Na$ $[M+Na]^+$ calcd. 362.1481, found 362.1483.

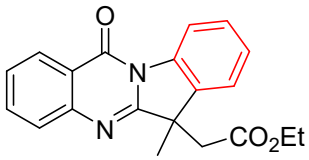
Ethyl 2-(1-methyl-5,5-dioxido-2,3-dihydro-1H-benzo[e]pyrrolo[1,2-b][1,2,4]thiadiazin-1-yl)acetate (3m).



Column chromatography on silica gel (PE/EtOAc = 3:1). White solid; 16% yield (10.4 mg); mp 93-94 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.9, 1.1 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.40 (dd, J = 11.2, 4.0 Hz, 1H), 4.14 – 4.08 (m, 3H), 4.06 (dd, J = 16.2, 8.5 Hz, 1H), 2.81 – 2.74 (m, 2H), 2.41 (dt, J = 12.8,

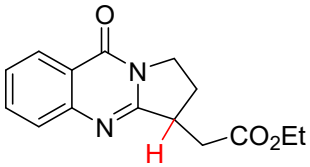
8.6 Hz, 1H), 2.14 (ddd, *J* = 12.7, 7.3, 3.7 Hz, 1H), 1.39 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 163.2, 144.0, 133.7, 127.7, 126.4, 124.9, 122.0, 60.6, 45.2, 41.8, 41.7, 31.3, 23.6, 14.1; HRMS (ESI) for $C_{15}H_{18}N_2O_4SNa$ $[M+Na]^+$ calcd. 345.0885, found 345.0890.

Ethyl 2-(6-methyl-12-oxo-6,12-dihydroindolo[2,1-b]quinazolin-6-yl)acetate (3n).



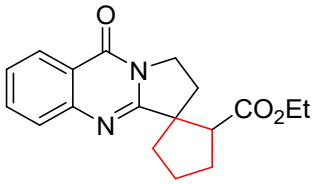
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 89% yield (59.4 mg); mp 102-104 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.46 – 8.41 (m, 1H), 7.79 – 7.74 (m, 2H), 7.51 (ddd, *J* = 8.1, 6.0, 2.3 Hz, 1H), 7.45 (td, *J* = 8.0, 1.2 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.33 (dt, *J* = 7.5, 3.7 Hz, 1H), 3.79 – 3.69 (m, 2H), 3.39 (d, *J* = 16.3 Hz, 1H), 3.09 (d, *J* = 16.3 Hz, 1H), 1.63 (s, 3H), 0.83 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.3, 163.3, 160.1, 147.6, 139.5, 135.0, 134.2, 128.8, 127.3, 126.9, 126.6, 126.4, 122.2, 121.5, 117.2, 60.5, 46.5, 43.9, 26.7, 13.6 ; HRMS (ESI) for $C_{20}H_{18}N_2O_3Na$ $[M+Na]^+$ calcd. 357.1215, found 357.1214.

Ethyl 2-(9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3o).



Column chromatography on silica gel (PE/EtOAc = 1:1). White solid; 80% yield (43.6 mg); mp 84-87 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 11.1, 3.9 Hz, 1H), 4.31 (ddd, *J* = 12.0, 9.1, 2.8 Hz, 1H), 4.17 (dddd, *J* = 17.9, 10.8, 7.2, 3.6 Hz, 2H), 3.98 (ddd, *J* = 12.2, 9.0, 7.8 Hz, 1H), 3.66 (qd, *J* = 9.2, 4.0 Hz, 1H), 3.18 (dd, *J* = 16.8, 4.0 Hz, 1H), 2.66 (dd, *J* = 16.8, 9.2 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.01 – 1.94 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.3, 160.9, 160.0, 149.1, 134.0, 127.0, 126.33, 126.26, 120.7, 60.8, 44.7, 40.2, 36.4, 26.6, 14.2; HRMS (ESI) for $C_{15}H_{16}N_2O_3Na$ $[M+Na]^+$ calcd. 295.1059, found 295.1064.

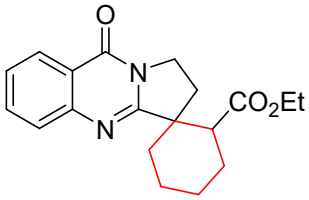
Ethyl 9'-oxo-1',2'-dihydro-9'H-spiro[cyclopentane-1,3'-pyrrolo[2,1-b]quinazoline]-2-carboxylate (3p).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 70% yield (44.0 mg); 7.3:1 dr; mp 55-57 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 1.06H),

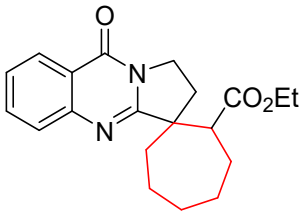
7.73 – 7.60 (m, 2.25H), 7.41 (ddd, *J* = 15.0, 7.9, 1.0 Hz, 1.15H), 4.20 – 4.09 (m, 0.4H), 4.09 – 4.05 (m, 1.98H), 4.04 – 3.97 (m, 2H), 3.88 – 3.83 (m, 0.16H), 3.77 – 3.70 (m, 0.15H), 3.44 (t, *J* = 9.4 Hz, 1H), 2.93 (t, *J* = 8.2 Hz, 0.14H), 2.53 – 2.44 (m, 0.3H), 2.36 (dt, *J* = 12.9, 8.0 Hz, 0.19H), 2.32 – 2.18 (m, 3.27H), 2.16 – 2.07 (m, 1.25H), 2.06 – 1.84 (m, 5.09H), 1.80 – 1.70 (m, 0.2H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.1 Hz, 0.41H); The carbon spectrum data of major isomer was shown: **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.9, 162.8, 161.0, 149.6, 133.9, 127.1, 126.3, 126.0, 120.7, 60.5, 56.4, 52.7, 44.0, 39.8, 29.4, 27.0, 22.6, 14.0; HRMS (ESI) for $C_{18}H_{20}N_2O_3Na$ $[M+Na]^+$ calcd. 335.1372, found 335.1371.

Ethyl 9'-oxo-1',2'-dihydro-9'H-spiro[cyclohexane-1,3'-pyrrolo[2,1-b]quinazoline]-2-carboxylate (3q).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 74% yield (48.2 mg); 8.8:1 dr; mp 110-112 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 7.9, 1.0 Hz, 1.05H), 7.69 (ddd, *J* = 20.8, 11.1, 4.3 Hz, 2.20H), 7.43 – 7.38 (m, 1.13H), 4.11 (dddd, *J* = 18.7, 12.4, 9.6, 5.8 Hz, 2.38H), 4.00 – 3.84 (m, 2.35H), 3.06 (dd, *J* = 12.6, 3.5 Hz, 0.98H), 2.63 – 2.56 (m, 0.24H), 2.46 – 2.36 (m, 1.2H), 2.22 – 2.08 (m, 2.4H), 2.07 – 1.84 (m, 3.14H), 1.81 – 1.70 (m, 2.17H), 1.59 – 1.39 (m, 3.77H), 0.98 (t, *J* = 7.1 Hz, 0.34H), 0.91 (t, *J* = 7.1 Hz, 3H); The carbon spectrum data of major isomer was shown: **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.2, 164.2, 161.1, 149.7, 133.8, 127.0, 126.3, 125.8, 120.8, 60.4, 49.7, 48.6, 44.0, 36.7, 26.0, 25.4, 24.8, 21.8, 13.8; HRMS (ESI) for $C_{19}H_{22}N_2O_3Na$ $[M+Na]^+$ calcd. 349.1528, found 349.1532.

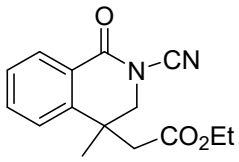
Ethyl 9'-oxo-1',2'-dihydro-9'H-spiro[cycloheptane-1,3'-pyrrolo[2,1-b]quinazoline]-2-carboxylate (3r).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 63% yield (43.0 mg); 4.7:1 dr; mp 101-102 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 (ddd, *J* = 6.2, 5.1, 1.2 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.65 – 7.61 (m, 1H), 7.43 – 7.36 (m, 1H), 4.22 (ddd, *J* = 12.5, 9.9, 3.5 Hz, 1H), 4.00 (ddd, *J* = 11.8, 10.4, 5.9 Hz, 1H), 3.94 – 3.82 (m, 2H), 3.30 – 3.22 (m, 1H), 2.66 (ddd, *J* = 18.0, 12.1, 9.4 Hz, 1H), 2.52 – 2.21 (m, 1H), 2.12 (ddt, *J* = 18.9, 15.6, 7.6 Hz, 2H), 1.96 – 1.87 (m, 2H), 1.83 – 1.66 (m, 5H), 1.60 (ddt, *J* = 14.2, 8.6, 3.0 Hz, 1H), 0.93 (t, *J* = 7.1 Hz, 2.5H), 0.90 (t, *J* = 7.1 Hz, 0.5H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.9, 173.8, 165.2, 164.2, 161.2, 161.1, 149.73,

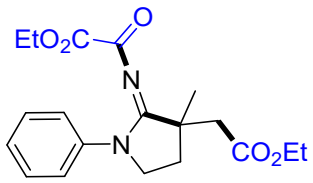
149.69, 133.8, 133.7, 127.4, 127.0, 126.3, 126.2, 125.8, 125.7, 120.8, 120.6, 60.6, 60.3, 54.6, 52.3, 51.6, 50.6, 43.8, 43.3, 39.8, 38.5, 33.6, 30.5, 30.2, 27.2, 27.01, 26.97, 26.8, 26.7, 23.9, 23.5, 14.0, 13.9; HRMS (ESI) for $C_{20}H_{24}N_2O_3Na$ $[M+Na]^+$ calcd. 363.1685, found 363.1687.

Ethyl 2-(2-cyano-4-methyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate (3s).



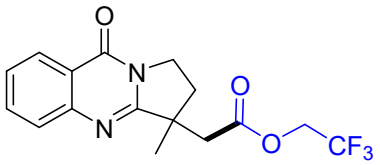
Column chromatography on silica gel (PE/EtOAc = 3:1). Colorless oil; 20% yield (11.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.63 (td, *J* = 7.7, 1.5 Hz, 1H), 7.44 (td, *J* = 7.7, 1.1 Hz, 1H), 7.37 (dd, *J* = 7.9, 0.6 Hz, 1H), 4.19 (d, *J* = 12.3 Hz, 1H), 4.10 (dtd, *J* = 14.3, 7.1, 3.6 Hz, 2H), 3.85 (d, *J* = 12.3 Hz, 1H), 2.74 (d, *J* = 14.9 Hz, 1H), 2.60 (d, *J* = 14.9 Hz, 1H), 1.54 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 163.0, 145.3, 134.8, 130.0, 128.2, 124.7, 124.6, 109.1, 61.0, 56.2, 43.0, 36.5, 23.0, 14.1; HRMS (ESI) for $C_{15}H_{16}N_2O_3Na$ $[M+Na]^+$ calcd. 295.1059, found 295.1063.

Ethyl 2-((3-(2-ethoxy-2-oxoethyl)-3-methyl-1-phenylpyrrolidin-2-ylidene)amino)-2-oxoacetate (3t).



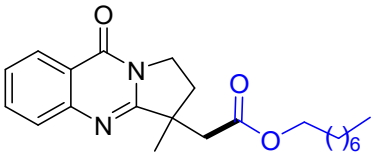
Column chromatography on silica gel (PE/EtOAc = 1:1). White solid; 54% yield (39.0 mg); mp 77-80 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 4H), 7.24 – 7.21 (m, 1H), 4.16 – 4.10 (m, 4H), 3.97 (dt, *J* = 10.3, 7.7 Hz, 1H), 3.90 (ddd, *J* = 10.3, 8.7, 4.5 Hz, 1H), 2.88 (d, *J* = 16.2 Hz, 1H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.48 (ddd, *J* = 12.8, 8.6, 7.3 Hz, 1H), 2.10 (ddd, *J* = 12.6, 7.9, 4.5 Hz, 1H), 1.49 (s, 3H), 1.26 – 1.23 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.9, 169.2, 164.0, 161.5, 139.1, 129.3, 127.0, 123.8, 61.9, 60.6, 51.2, 46.7, 42.1, 32.5, 23.9, 14.2, 14.0; HRMS (ESI) for $C_{19}H_{24}N_2O_5Na$ $[M+Na]^+$ calcd. 383.1583, found 383.1586.

2,2,2-trifluoroethyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3u).



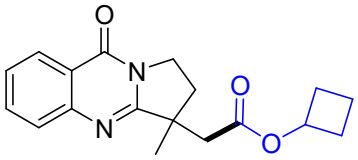
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 81% yield (55.0 mg); mp 88-90 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.42 (m, 1H), 4.47 – 4.40 (m, 2H), 4.28 (ddd, *J* = 12.5, 9.3, 3.3 Hz, 1H), 4.05 (dt, *J* = 12.4, 8.2 Hz, 1H), 3.03 – 2.97 (m, 2H), 2.44 (dt, *J* = 13.0, 8.9 Hz, 1H), 2.19 (ddd, *J* = 12.9, 8.0, 3.3 Hz, 1H), 1.46 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.2, 162.8, 161.0, 149.4, 134.1, 127.1, 126.4, 126.3, 122.8 (q, *J* = 277.2 Hz), 120.8, 60.3 (q, *J* = 36.7 Hz), 44.9, 43.3, 41.9, 32.2, 24.9; HRMS (ESI) for $C_{16}H_{15}F_3N_2O_3Na$ $[M+Na]^+$ calcd. 363.0932, found 363.0927.

Propyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3v).



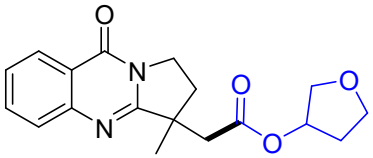
Column chromatography on silica gel (PE/EtOAc = 2:1). Colorless oil; 53% yield (39.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.70 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.43 (dd, *J* = 10.9, 4.0 Hz, 1H), 4.24 (ddd, *J* = 9.9, 9.2, 3.9 Hz, 1H), 4.09 – 4.04 (m, 1H), 4.01 (dt, *J* = 10.1, 5.1 Hz, 2H), 2.87 (dd, *J* = 45.0, 16.0 Hz, 2H), 2.48 (dt, *J* = 12.9, 8.6 Hz, 1H), 2.16 (ddd, *J* = 12.7, 8.2, 3.9 Hz, 1H), 1.53 – 1.48 (m, 2H), 1.45 (s, 3H), 1.28 – 1.19 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.9, 163.4, 161.1, 149.5, 134.0, 127.1, 126.4, 126.1, 120.8, 64.8, 45.0, 43.4, 42.8, 32.2, 31.8, 29.1, 29.1, 28.5, 25.9, 25.2, 22.6, 14.1; HRMS (ESI) for $C_{22}H_{30}N_2O_3Na$ $[M+Na]^+$ calcd. 393.2154, found 393.2147.

Cyclobutyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3w).



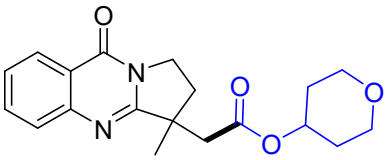
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 73% yield (45.5 mg); mp 90-93 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.68 – 7.65 (m, 1H), 7.45 – 7.41 (m, 1H), 4.92 (p, *J* = 7.2 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.06 (dt, *J* = 12.3, 8.0 Hz, 1H), 2.84 (dd, *J* = 36.6, 16.0 Hz, 2H), 2.53 – 2.44 (m, 1H), 2.30 – 2.24 (m, 2H), 2.18 – 2.13 (m, 1H), 1.99 – 1.90 (m, 2H), 1.73 (dt, *J* = 10.1, 2.6 Hz, 1H), 1.59 – 1.52 (m, 1H), 1.45 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 163.4, 161.0, 149.5, 134.0, 127.1, 126.4, 126.1, 120.8, 69.0, 45.0, 43.4, 42.7, 32.3, 30.2, 30.1, 25.2, 13.5; HRMS (ESI) for $C_{18}H_{20}N_2O_3Na$ $[M+Na]^+$ calcd. 335.1372, found 335.1378.

Tetrahydrofuran-3-yl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3x).



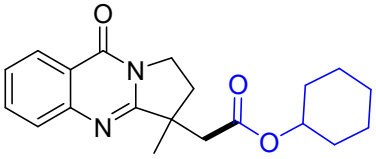
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 79% yield (52.0 mg); 1.5:1 dr; mp 80-82 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.40 (m, 1H), 5.24 (td, *J* = 4.4, 2.2 Hz, 1H), 4.27 (ddt, *J* = 12.7, 9.2, 3.6 Hz, 1H), 4.07 (t, *J* = 6.2 Hz, 0.61H), 4.05 (t, *J* = 6.2 Hz, 0.42H),, 3.86 – 3.78 (m, 3H), 3.73 (t, *J* = 9.0 Hz, 1H), 2.94 – 2.83 (m, 2H), 2.51 – 2.45 (m, 1H), 2.19 – 2.14 (m, 1H), 2.12 – 2.05 (m, 1H), 1.88 (ddd, *J* = 11.4, 7.2, 3.4 Hz, 1H), 1.45 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.60, 170.55, 163.2, 161.0, 149.44, 149.43, 134.03, 134.02, 127.05, 127.03, 126.4, 126.2, 120.8, 75.12, 75.10, 73.0, 66.9, 45.05, 45.02, 43.38, 43.36, 42.64, 42.62, 32.62, 32.61, 32.34, 32.28, 25.2, 25.1; HRMS (ESI) for $C_{18}H_{20}N_2O_4Na$ $[M+Na]^+$ calcd. 351.1321, found 351.1316.

Tetrahydro-2H-pyran-4-yl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b] quinazolin-3-yl)acetate (3y).



Column chromatography on silica gel (PE/EtOAc = 1:1). White solid; 74% yield (50.4 mg); mp 140-141 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.45 – 7.40 (m, 1H), 4.89 (tt, *J* = 8.5, 4.1 Hz, 1H), 4.24 (ddd, *J* = 12.9, 9.2, 3.8 Hz, 1H), 4.05 (dt, *J* = 12.3, 8.1 Hz, 1H), 3.81 (dq, *J* = 8.6, 4.5 Hz, 2H), 3.45 (ddd, *J* = 11.6, 9.5, 5.1 Hz, 2H), 2.92 (d, *J* = 16.0 Hz, 1H), 2.83 (d, *J* = 16.0 Hz, 1H), 2.51 – 2.46 (m, 1H), 2.18 – 2.13 (m, 1H), 1.85 – 1.78 (m, 2H), 1.60 – 1.52 (m, 2H), 1.45 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 163.2, 161.0, 149.4, 134.0, 127.0, 126.4, 126.1, 120.7, 69.4, 65.2 (2C), 45.0, 43.4, 42.9, 32.2, 31.62, 31.55, 25.2; HRMS (ESI) for $C_{19}H_{22}N_2O_4Na$ $[M+Na]^+$ calcd. 365.1477, found 365.1472.

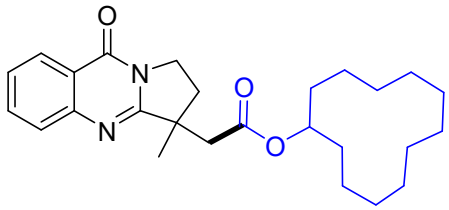
Cyclohexyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl) acetate (3z).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 62% yield (42.3 mg); mp 91-92 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.66 – 7.64 (m, 1H), 7.45 – 7.40 (m, 1H), 4.71 (dt, *J* = 8.7, 4.5 Hz, 1H), 4.24 (ddd, *J* = 12.9, 9.2, 3.9 Hz, 1H), 4.08 – 4.03 (m, 1H), 2.89 (d, *J* = 15.8 Hz, 1H), 2.81 (d, *J* = 15.9 Hz, 1H), 2.50 (dd, *J* = 8.2, 4.0 Hz, 1H), 2.17 – 2.13 (m, 1H), 1.75

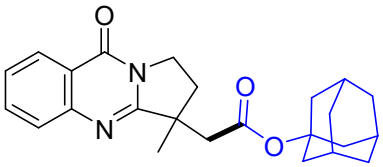
(d, J = 26.2 Hz, 3H), 1.62 (dd, J = 8.9, 3.8 Hz, 2H), 1.45 (s, 3H), 1.33 – 1.26 (m, 4H), 1.19 (dd, J = 11.1, 8.3 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.2, 163.4, 161.0, 149.5, 133.9, 127.0, 126.3, 126.1, 120.8, 73.0, 45.1, 43.4, 43.1, 32.2, 31.50, 31.47, 25.2, 23.6; HRMS (ESI) for $C_{20}H_{24}N_2O_3Na$ $[M+Na]^+$ calcd. 363.1685, found 363.1682.

Cyclododecyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3aa).



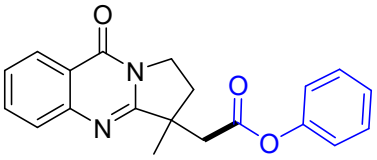
Column chromatography on silica gel (PE/EtOAc = 2:1). Colorless oil; 35% yield (30.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.27 (dd, J = 8.0, 1.3 Hz, 1H), 7.69 (ddd, J = 8.4, 7.1, 1.5 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.43 – 7.39 (m, 1H), 4.93 (tt, J = 7.2, 4.7 Hz, 1H), 4.24 (ddd, J = 12.7, 9.3, 3.8 Hz, 1H), 4.04 (dt, J = 12.3, 8.1 Hz, 1H), 2.88 (d, J = 15.9 Hz, 1H), 2.79 (d, J = 15.9 Hz, 1H), 2.50 (dt, J = 12.9, 9.0 Hz, 1H), 2.16 – 2.10 (m, 1H), 1.56 (dt, J = 14.1, 7.1 Hz, 2H), 1.44 (s, 3H), 1.32 – 1.20 (m, 20H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 163.4, 161.0, 149.5, 133.9, 127.0, 126.3, 126.0, 120.7, 72.8, 45.0, 43.4, 43.1, 32.2, 28.9, 28.8, 25.2, 24.03 (2C), 23.8, 23.18, 23.15, 23.01, 22.99, 20.68, 20.67; HRMS (ESI) for $C_{26}H_{36}N_2O_3Na$ $[M+Na]^+$ calcd. 447.2624, found 447.2621.

(3s,5s,7s)-adamantan-1-yl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3ac).



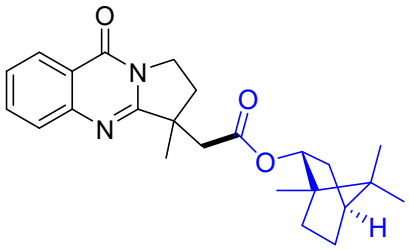
Column chromatography on silica gel (PE/EtOAc = 1.5:1). Colorless oil; 42% yield (33.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (dd, J = 8.0, 1.1 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.67 – 7.64 (m, 1H), 7.43 – 7.40 (m, 1H), 4.22 (ddd, J = 13.1, 9.2, 4.1 Hz, 1H), 4.05 (dt, J = 12.3, 8.1 Hz, 1H), 2.82 (d, J = 15.6 Hz, 1H), 2.71 (d, J = 15.6 Hz, 1H), 2.52 – 2.46 (m, 1H), 2.12 (ddd, J = 12.7, 8.3, 4.1 Hz, 1H), 2.08 (s, 3H), 1.96 (d, J = 2.7 Hz, 6H), 1.59-1.57 (m, 6H), 1.43 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 163.6, 161.0, 149.5, 133.9, 127.0, 126.3, 126.0, 120.7, 81.1, 45.2, 44.2, 43.4, 41.2, 36.0, 32.2, 30.7, 25.2; HRMS (ESI) for $C_{24}H_{28}N_2O_3Na$ $[M+Na]^+$ calcd. 415.1998, found 415.2003.

Phenyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3ad).



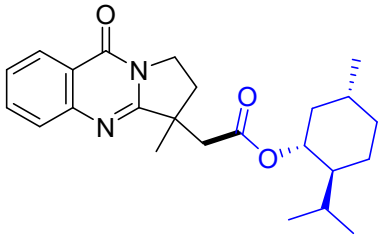
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 52% yield (35.0 mg); mp 104-106 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.44 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.22 – 7.18 (m, 1H), 7.05 – 7.00 (m, 2H), 4.29 (ddd, *J* = 12.6, 9.3, 3.6 Hz, 1H), 4.08 (dt, *J* = 12.3, 8.2 Hz, 1H), 3.15 (dd, *J* = 36.8, 16.4 Hz, 2H), 2.57 (dt, *J* = 13.0, 8.9 Hz, 1H), 2.24 (ddd, *J* = 12.9, 8.1, 3.6 Hz, 1H), 1.54 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.5, 163.1, 161.0, 150.3, 149.5, 134.0, 129.5, 127.1, 126.4, 126.2, 126.0, 121.4, 120.9, 45.1, 43.4, 42.5, 32.4, 25.2; HRMS (ESI) for $C_{20}H_{19}N_2O_3$ $[M+H]^+$ calcd. 335.1397, found 335.1399.

(1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3ae).



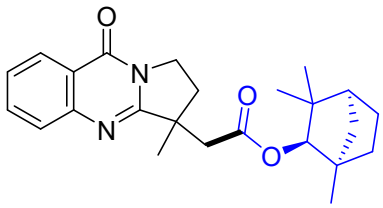
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 63% yield (50.0 mg); 1.6:1 dr; mp 61-63 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.9 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.67 (d, *J* = 4.9 Hz, 1H), 7.43 (dd, *J* = 7.9, 7.0 Hz, 1H), 4.88 – 4.80 (m, 1H), 4.33 – 4.23 (m, 1H), 4.06 (ddt, *J* = 13.8, 12.5, 6.9 Hz, 1H), 2.96 (dd, *J* = 15.8, 2.9 Hz, 1H), 2.85 (d, *J* = 15.9 Hz, 0.63H), 2.83 (d, *J* = 15.9 Hz, 0.39H), 2.56 – 2.48 (m, 1H), 2.29 (tdd, *J* = 16.8, 8.0, 5.0 Hz, 1H), 2.20 – 2.13 (m, 1H), 1.74 – 1.69 (m, 1H), 1.65 – 1.60 (m, 2H), 1.46 (d, *J* = 2.9 Hz, 3H), 1.23 – 1.16 (m, 1H), 1.05 – 1.00 (m, 1H), 0.86 – 0.81 (m, 7H), 0.73 (d, *J* = 2.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.1, 163.4, 161.0, 149.5, 134.0, 127.1, 126.4, 126.1, 120.8, 80.52, 80.47, 48.65, 48.62, 47.8, 47.7, 45.2, 45.1, 44.8, 43.4, 43.4, 43.0, 42.8, 36.73, 36.67, 32.25, 32.19, 27.91, 27.88, 27.00, 25.3, 25.2, 19.6, 18.7, 13.41, 13.39; HRMS (ESI) for $C_{24}H_{30}N_2O_3Na$ $[M+Na]^+$ calcd. 417.2154, found 417.2157.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3af).



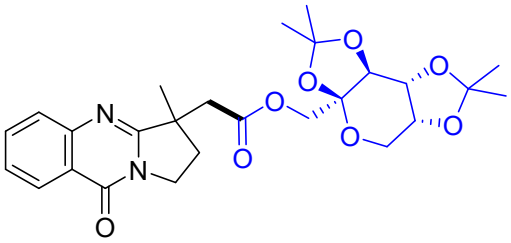
Column chromatography on silica gel (PE/EtOAc = 1.5:1). Colorless oil; 51% yield (40.0 mg); 1:1 dr. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (ddd, *J* = 7.9, 3.3, 1.3 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.65 – 7.62 (m, 1H), 7.44 – 7.39 (m, 1H), 4.60 (ddd, *J* = 22.8, 11.1, 4.4 Hz, 1H), 4.26 (dtd, *J* = 13.3, 9.6, 3.7 Hz, 1H), 4.05 (dt, *J* = 12.3, 8.2 Hz, 1H), 2.95 (d, *J* = 16.1 Hz, 0.51H), 2.91 (d, *J* = 16.0 Hz, 0.51H), 2.79 (dd, *J* = 16.1, 2.6 Hz, 1H), 2.58 (dt, *J* = 12.9, 9.1 Hz, 0.55H), 2.52 – 2.45 (m, 0.54H), 2.14 (dddd, *J* = 17.4, 12.9, 8.3, 3.6 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.75 – 1.71 (m, 1H), 1.60 (dddd, *J* = 17.0, 13.5, 7.0, 3.2 Hz, 2H), 1.44 (d, *J* = 3.6 Hz, 3H), 1.42 – 1.35 (m, 1H), 1.28 – 1.12 (m, 1H), 0.94 (ddd, *J* = 16.4, 12.9, 6.6 Hz, 1H), 0.88 – 0.74 (m, 7H), 0.69 – 0.62 (m, 3H), 0.56 (d, *J* = 6.9 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.4, 170.3, 163.5, 163.4, 161.02, 161.00, 149.52, 149.50, 133.94, 133.86, 127.0, 126.34, 126.31, 126.03, 126.02, 120.8, 120.7, 74.6, 74.5, 46.9, 46.8, 45.04, 45.03, 43.43, 43.40, 43.2, 42.8, 40.83, 40.77, 34.1, 34.0, 32.11, 32.08, 31.3, 26.1, 26.0, 25.6, 25.5, 23.2, 23.0, 21.89, 21.88, 20.7, 20.5, 16.0, 15.9; HRMS (ESI) for $C_{24}H_{32}N_2O_3Na$ $[M+Na]^+$ calcd. 419.2311, found 419.2314.

(1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3ag).



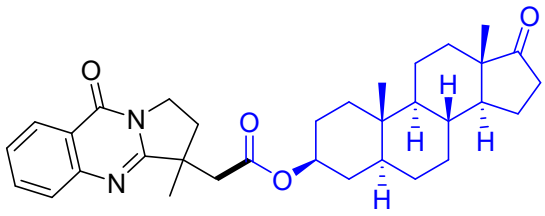
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 72% yield (57.0 mg); 1:1 dr; mp 59-61 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.68 (ddd, *J* = 30.5, 10.8, 4.4 Hz, 2H), 7.43 (dd, *J* = 7.9, 7.1 Hz, 1H), 4.35 – 4.22 (m, 2H), 4.11 – 4.00 (m, 1H), 2.94 (ddd, *J* = 27.5, 25.5, 13.8 Hz, 2H), 2.53 (ddt, *J* = 34.3, 12.8, 8.9 Hz, 1H), 2.18 (tdd, *J* = 13.0, 8.0, 3.2 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.56 – 1.50 (m, 2H), 1.46 (s, 3H), 1.25 (s, 2H), 1.15 (dd, *J* = 15.1, 5.7 Hz, 1H), 1.06 (s, 1.5H), 1.01 (s, 1.5H), 0.97 (d, *J* = 11.1 Hz, 3H), 0.71 (d, *J* = 19.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.3, 171.2, 163.5, 161.1, 149.50, 149.47, 134.0, 127.03, 127.01, 126.4, 126.1, 120.8, 87.0, 86.9, 48.24, 48.22, 48.12, 48.09, 44.94, 44.92, 43.4, 42.6, 42.4, 41.3, 39.4, 39.3, 32.2, 32.1, 29.7, 29.62, 29.58, 26.53, 26.46, 25.7, 25.6, 25.2, 25.1, 20.3, 20.2, 19.3; HRMS (ESI) for $C_{24}H_{30}N_2O_3Na$ $[M+Na]^+$ calcd. 417.2154, found 417.2158.

((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazolin-3-yl)acetate (3ah).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 85% yield (85.0 mg); 1:1 dr; mp 47-50 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.70 (tdd, *J* = 7.0, 3.8, 1.5 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.44 – 7.39 (m, 1H), 4.57 (dd, *J* = 7.9, 2.6 Hz, 0.46H), 4.40 – 4.35 (m, 1H), 4.33 (d, *J* = 11.6 Hz, 0.6H), 4.29 – 4.20 (m, 2H), 4.15 (dd, *J* = 7.9, 1.1 Hz, 0.55H), 4.09 – 4.01 (m, 1.65H), 3.96 (t, *J* = 12.0 Hz, 1H), 3.83 (ddd, *J* = 18.3, 13.0, 1.8 Hz, 1H), 3.70 (dd, *J* = 31.1, 13.0 Hz, 1H), 3.02 (d, *J* = 16.2 Hz, 0.57H), 2.97 (d, *J* = 16.6 Hz, 0.53H), 2.90 (d, *J* = 16.6 Hz, 0.53H), 2.84 (d, *J* = 16.2 Hz, 0.57H), 2.53 – 2.44 (m, 1H), 2.20 – 2.13 (m, 1H), 1.51 (s, 1.53H), 1.48 (s, 1.57H), 1.47 – 1.44 (m, 4H), 1.39 (d, *J* = 6.6 Hz, 3H), 1.33 (d, *J* = 2.6 Hz, 3H), 1.28 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.02, 169.97, 163.3, 163.2, 161.03, 161.00, 149.5, 133.9, 133.8, 127.1, 126.4, 126.3, 126.04, 126.01, 120.9, 120.7, 109.1, 109.0, 108.8, 108.7, 101.3, 101.2, 70.7, 70.61, 70.60, 70.3, 70.0, 69.8, 65.6, 65.4, 61.2, 45.1, 44.9, 43.4, 42.5, 42.3, 32.1, 31.9, 26.41, 26.35, 25.9, 25.8, 25.7, 25.3, 25.20, 25.18, 24.1, 23.9; HRMS (ESI) for $C_{26}H_{32}N_2O_8Na$ $[M+Na]^+$ calcd. 523.2056, found 523.2052.

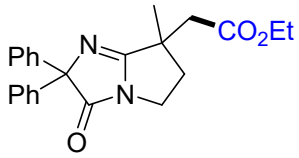
(3S,5S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(3-methyl-9-oxo-1,2,3,9-tetrahydropyrrolo[2,1-b]quinazo-lin-3-yl)acetate (3ai).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 83% yield (87.9 mg); 1.2:1 dr; mp 149-150 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.65 – 4.58 (m, 1H), 4.25 – 4.20 (m, 1H), 4.07 (d, *J* = 8.0 Hz, 0.56H), 4.04 (d, *J* = 8.1 Hz, 0.47H), 2.86 (d, *J* = 15.7 Hz, 1H), 2.78 (d, *J* = 15.8 Hz, 1H), 2.52 – 2.37 (m, 2H), 2.14 (ddd, *J* = 12.6, 8.3, 4.0 Hz, 1H), 2.07 – 2.00 (m, 1H), 1.92 – 1.87 (m, 1H), 1.77 – 1.64 (m, 4H), 1.62 – 1.57 (m, 1H), 1.48 (dd, *J* = 12.5, 9.2 Hz, 3H), 1.44 (s, 3H), 1.39 – 1.31 (m, 1H), 1.28 – 1.16 (m, 6H), 1.09 (dd, *J* = 17.0, 7.4 Hz, 1H), 0.93 (ddd, *J* = 12.2, 10.9, 7.3 Hz, 2H), 0.82 (s, 3H), 0.74 (d, *J* = 5.8 Hz, 3H), 0.65 (td, *J* = 11.4, 3.8 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 221.17, 221.15, 170.23, 170.18, 163.42, 163.41, 161.0, 149.5, 133.9, 127.0, 126.3, 126.1, 120.76, 120.75, 73.80, 73.79, 54.2, 51.3, 47.7, 45.13, 45.08, 44.5, 43.42, 43.40, 43.23, 43.21, 36.54, 36.53, 35.8, 35.5, 34.9, 33.82, 33.77, 32.29, 32.27, 31.4, 30.7, 28.1, 27.3, 27.2, 25.3, 25.2, 21.7, 20.4, 13.8, 12.1, 12.0; HRMS

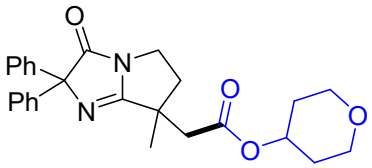
(ESI) for $C_{33}H_{42}N_2O_4Na$ $[M+Na]^+$ calcd. 553.3042, found 553.3041.

Ethyl 2-(7-methyl-3-oxo-2,2-diphenyl-2,5,6,7-tetrahydro-3H-pyrrolo[1,2-a] imidazol-7-yl)acetate (5a).



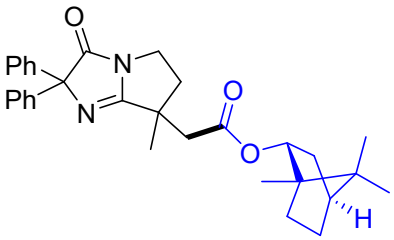
Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 74% yield (56.0 mg); mp 114-117 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.50 – 7.47 (m, 2H), 7.35 – 7.30 (m, 4H), 7.28 (dd, *J* = 8.7, 5.4 Hz, 2H), 4.06 (qd, *J* = 10.8, 7.1 Hz, 2H), 3.70 (ddd, *J* = 11.2, 9.1, 4.2 Hz, 1H), 3.57 (ddd, *J* = 11.2, 8.1, 7.2 Hz, 1H), 2.90 (d, *J* = 16.2 Hz, 1H), 2.79 (d, *J* = 16.2 Hz, 1H), 2.71 (ddd, *J* = 13.3, 9.0, 7.1 Hz, 1H), 2.33 – 2.28 (m, 1H), 1.49 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.3, 173.8, 170.4, 140.3 (2C), 128.3, 128.2, 127.6, 127.5, 127.2, 127.0, 86.5, 60.7, 41.8, 38.2 (2C), 38.1, 24.7, 14.0; HRMS (ESI) for $C_{23}H_{24}N_2O_3Na$ $[M+Na]^+$ calcd. 399.1685, found 399.1688.

Tetrahydro-2H-pyran-4-yl 2-(7-methyl-3-oxo-2,2-diphenyl-2,5,6,7-tetrahydro-3 H-pyrrolo[1,2-a]imidazol-7-yl)acetate (5b).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 61% yield (52.8 mg); mp 154-156 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 13.3, 7.5 Hz, 4H), 7.35 – 7.25 (m, 6H), 4.87 – 4.82 (m, 1H), 3.89 – 3.81 (m, 2H), 3.72 (td, *J* = 11.3, 3.9 Hz, 1H), 3.57 (dt, *J* = 11.0, 7.8 Hz, 1H), 3.46 (dtd, *J* = 14.8, 12.0, 2.7 Hz, 2H), 2.92 (d, *J* = 16.3 Hz, 1H), 2.81 (d, *J* = 16.4 Hz, 1H), 2.74 (dt, *J* = 13.3, 8.8 Hz, 1H), 2.34 – 2.27 (m, 1H), 1.84 – 1.68 (m, 3H), 1.60 – 1.54 (m, 1H), 1.50 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.2, 173.8, 169.9, 140.4, 140.3, 128.4, 128.2, 127.7, 127.5, 127.3, 127.0, 86.5, 69.8, 65.3, 42.0, 38.3, 38.2, 38.1, 31.6, 31.5, 24.9; HRMS (ESI) for $C_{26}H_{28}N_2O_4Na$ $[M+Na]^+$ calcd. 455.1947, found 455.1949.

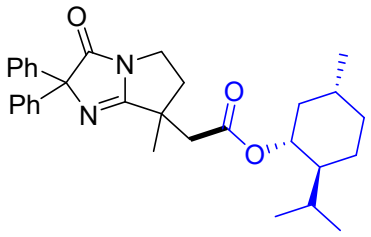
(1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(7-methyl-3-oxo-2,2-diph-e nyl-2,5,6,7-tetrahydro-3H-pyrrolo[1,2-a]imidazol-7-yl)acetate (5c).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 74% yield

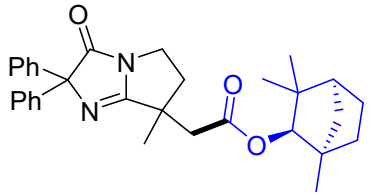
(71.7 mg); 1.5:1 dr; mp 112-114 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.45 (dd, *J* = 12.1, 4.3 Hz, 2H), 7.34 – 7.22 (m, 6H), 4.90 – 4.86 (m, 0.6H), 4.85 – 4.78 (m, 0.4H), 3.76 – 3.49 (m, 2H), 2.86 (s, 2H), 2.72 (dddd, *J* = 16.4, 13.3, 9.0, 7.4 Hz, 1H), 2.36 – 2.20 (m, 2H), 1.90 – 1.83 (m, 1H), 1.76 – 1.69 (m, 1H), 1.66 (dt, *J* = 9.1, 4.5 Hz, 1H), 1.47 (d, *J* = 4.4 Hz, 3H), 1.32 – 1.24 (m, 1H), 1.16 (tdd, *J* = 13.7, 9.6, 4.4 Hz, 1H), 0.93 (dd, *J* = 13.7, 3.4 Hz, 1H), 0.89 (d, *J* = 3.3 Hz, 3H), 0.86 (m, 3H), 0.78 (d, *J* = 23.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.2, 174.1, 174.0, 171.0, 170.8, 140.3, 128.4, 128.3, 127.6, 127.5, 127.3, 127.2, 127.1, 127.0, 80.7, 80.5, 48.8, 48.6, 47.8, 47.7, 44.78, 44.77, 41.8, 38.4, 38.31, 38.28, 38.22, 38.16, 38.14, 38.07, 28.00, 27.9, 27.1, 24.5, 24.4, 19.7, 18.78, 18.76, 13.5; HRMS (ESI) for $C_{31}H_{36}N_2O_3Na$ $[M+Na]^+$ calcd. 507.2624, found 507.2624.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(7-methyl-3-oxo-2,2-diphenyl-2,5,6,7-tetrahydro-3H-pyrrolo[1,2-a]imidazol-7-yl)acetate (5d).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 52% yield (50.5 mg); 1.1:1 dr; mp 121-123 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 (ddd, *J* = 9.9, 8.5, 7.5 Hz, 4H), 7.33 – 7.23 (m, 6H), 4.65 (tdd, *J* = 10.8, 4.2, 1.9 Hz, 1H), 3.68 (dddd, *J* = 9.8, 9.3, 5.8, 4.2 Hz, 1H), 3.57 – 3.51 (m, 1H), 2.87 (dd, *J* = 19.3, 16.3 Hz, 1H), 2.79 (dd, *J* = 16.3, 5.2 Hz, 1H), 2.65 (dddd, *J* = 40.2, 13.3, 9.0, 7.2 Hz, 1H), 2.29 (dtd, *J* = 12.4, 8.3, 4.0 Hz, 1H), 1.93 (d, *J* = 11.8 Hz, 1H), 1.84 – 1.76 (m, 1H), 1.64 (ddd, *J* = 10.2, 7.7, 4.3 Hz, 2H), 1.48 – 1.39 (m, 4H), 1.29 (ddd, *J* = 15.1, 8.5, 5.5 Hz, 1H), 1.06 – 0.97 (m, 1H), 0.88 (dd, *J* = 11.4, 5.4 Hz, 5H), 0.85 – 0.80 (m, 3H), 0.74 (d, *J* = 7.0 Hz, 1.42H), 0.67 (d, *J* = 7.0 Hz, 1.58H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.24, 179.21, 174.0, 173.9, 170.14, 170.06, 140.5, 140.4 140.3, 140.2, 128.3, 128.23, 128.22, 127.59, 127.57, 127.53, 127.52, 127.24, 127.23, 127.01, 126.99, 86.4, 74.85, 74.77, 46.67, 46.66, 42.0, 41.9, 40.8, 40.6, 38.3, 38.20, 38.17, 38.16, 38.07, 34.06, 34.0, 31.33, 31.32, 26.3, 26.1, 24.62, 24.57, 23.3, 23.2, 22.0, 21.9, 21.7, 21.6, 16.3, 16.0; HRMS (ESI) for $C_{31}H_{38}N_2O_3Na$ $[M+Na]^+$ calcd. 509.2780, found 509.2779.

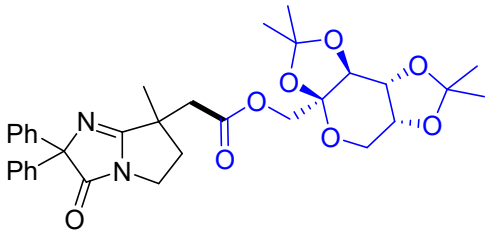
(1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2-(7-methyl-3-oxo-2,2-diphenyl-2,5,6,7-tetrahydro-3H-pyrrolo[1,2-a]imidazol-7-yl)acetate (5e).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 72% yield (69.7 mg); 1.1:1 dr; mp 128-129 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 – 7.42 (m,

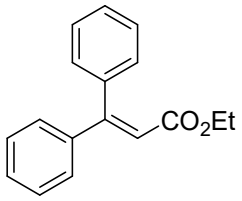
4H), 7.33 – 7.23 (m, 6H), 4.35 (d, *J* = 1.8 Hz, 0.45H), 4.32 (d, *J* = 1.8 Hz, 0.5H), 3.77 – 3.65 (m, 1H), 3.54 (ddd, *J* = 11.3, 9.0, 4.3 Hz, 1H), 2.95 – 2.82 (m, 2H), 2.67 (tdd, *J* = 9.4, 8.4, 2.4 Hz, 1H), 2.39 – 2.26 (m, 1H), 1.73 – 1.62 (m, 3H), 1.57 (dd, *J* = 13.3, 4.9 Hz, 1H), 1.48 (d, *J* = 1.6 Hz, 3H), 1.46 – 1.40 (m, 1H), 1.21 – 1.16 (m, 1H), 1.10 (s, 1.6H), 1.08 – 1.04 (m, 1H), 1.02 (d, *J* = 1.9 Hz, 3H), 0.98 (s, 1.48H), 0.77 (s, 1.48H), 0.63 (s, 1.6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.24, 179.21, 174.1, 174.0, 171.0, 170.9, 140.4, 128.4, 128.32, 128.29, 128.26, 127.61, 127.60, 127.54, 127.49, 127.4, 127.2, 127.0, 87.0, 86.9, 48.3, 48.23, 48.19, 48.1, 41.5, 41.4, 41.3, 39.4, 38.4, 38.3, 38.16, 38.15, 38.1, 38.0, 29.7, 29.6, 26.6, 26.5, 25.7, 24.5, 24.1, 20.4, 20.0, 19.38, 19.37; HRMS (ESI) for $C_{31}H_{36}N_2O_3Na$ $[M+Na]^+$ calcd. 507.2624, found 507.2625.

((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 2-(7-methyl-3-oxo-2,2-diphenyl-2,5,6,7-tetrahydro-3H-pyrrolo[1,2-a]imidazol-7-yl)acetate (5f).



Column chromatography on silica gel (PE/EtOAc = 2:1). White solid; 80% yield (94.4 mg); 1.8:1 dr; mp 68-69 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.34 – 7.20 (m, 6H), 4.59 (ddd, *J* = 7.5, 4.8, 2.6 Hz, 1H), 4.43 (dd, *J* = 13.5, 11.6 Hz, 1H), 4.24 (ddd, *J* = 7.6, 5.2, 2.8 Hz, 2H), 3.99 (d, *J* = 11.6 Hz, 0.65H), 3.95 (d, *J* = 11.6 Hz, 0.36H), 3.90 – 3.88 (m, 1H) , 3.79 – 3.67 (m, 2H), 3.53 (dt, *J* = 11.2, 7.8 Hz, 1H), 2.90 (qd, *J* = 16.9, 3.8 Hz, 2H), 2.73 – 2.63 (m, 1H), 2.31 (ddd, *J* = 17.2, 8.2, 4.1 Hz, 1H), 1.53 (d, *J* = 11.5 Hz, 3H), 1.47 (dd, *J* = 7.9, 4.3 Hz, 6H), 1.38 (s, 1H), 1.34 (m, 5H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.30, 179.26, 173.8, 173.7, 169.8, 169.7, 140.34, 140.27, 128.3, 128.24, 128.22, 127.64, 127.60, 127.57, 127.55, 127.24, 127.19, 127.1, 109.11, 109.08, 108.8, 108.7, 101.30, 101.28, 86.5, 70.71, 70.68, 70.60, 70.57, 69.99, 69.96, 65.7, 65.4, 61.3, 61.2, 41.4, 41.3, 38.1, 38.0, 26.42, 26.38, 25.89, 25.88, 25.4, 25.2, 24.54, 24.50, 24.06, 24.04; HRMS (ESI) for $C_{33}H_{38}N_2O_8Na$ $[M+Na]^+$ calcd. 613.2526, found 613.2531.

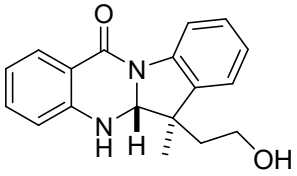
Ethyl 3,3-diphenylacrylate (3aj).



Column chromatography on silica gel (PE/EtOAc = 10:1). Colorless oil; 42% yield (21.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 4.1, 2.4 Hz, 3H), 7.38 – 7.32 (m, 5H), 7.26 – 7.23 (m, 2H), 6.40 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz,

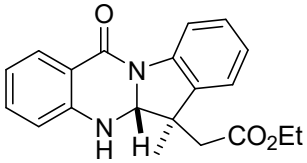
3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.1, 156.4, 140.8, 139.0, 129.3, 129.1, 128.3, 128.2, 128.1, 127.8, 117.4, 60.0, 14.0 ; HRMS (ESI) for $C_{17}H_{16}O_2Na$ $[M+Na]^+$ calcd. 275.1048, found 275.1052.

6-(2-hydroxyethyl)-6-methyl-5a,6-dihydroindolo[2,1-b]quinazolin-12(5H)-one (6).



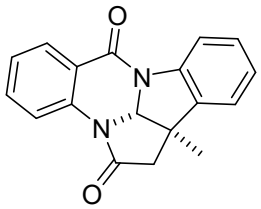
Column chromatography on silica gel (PE/EtOAc = 1:1). White solid; 75% yield (44.0 mg); mp 55-57 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.13 (d, *J* = 6.8 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 1H), 5.24 (s, 1H), 4.02 (ddd, *J* = 13.9, 7.9, 3.0 Hz, 2H), 2.19 – 2.16 (m, 1H), 2.08 – 2.02 (m, 1H), 1.28 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.6, 147.9, 139.5, 138.6, 133.5, 128.4 (2C), 124.2, 122.1, 119.4, 116.6, 116.4, 115.3, 79.8, 59.5, 46.9, 39.5, 20.0; HRMS (ESI) for $C_{18}H_{18}N_2O_2Na$ $[M+Na]^+$ calcd. 317.1266, found 317.1270.

Ethyl 2-((5aR,6R)-6-methyl-12-oxo-5,5a,6,12-tetrahydroindolo[2,1-b]quinazolin-6-yl)acetate (7).



Column chromatography on silica gel (PE/EtOAc = 4:1). White solid; 68% yield (92.0 mg); mp 45-47 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.14 (d, *J* = 6.9 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 1H), 5.34 (s, 1H), 4.23 (tdd, *J* = 10.7, 7.2, 3.6 Hz, 2H), 3.13 (d, *J* = 17.2 Hz, 1H), 2.75 (d, *J* = 17.2 Hz, 1H), 1.38 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.8, 161.4, 147.8, 139.3, 136.7, 133.6, 128.8, 128.4, 124.2, 122.1, 119.5, 116.6, 116.4, 115.3, 79.4, 61.3, 45.8, 43.3, 21.01, 14.2; HRMS (ESI) for $C_{20}H_{20}N_2O_2Na$ $[M+Na]^+$ calcd. 359.1372, found 359.1375.

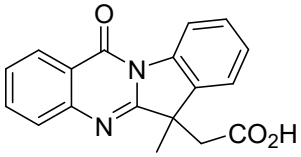
(2a^1,11b)-11b-methyl-2a^1,11b-dihydro-7H-2a,7a-diazabenzo[b]cyclopenta[lm]fluorene-2,7(1H)-dione (8).



Column chromatography on silica gel (DCM/MeOH = 20:1). White solid; 91%

yield (53.0 mg); mp 156-158 °C. **^{1}H NMR** (600 MHz, CD_3OD) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.09 (td, *J* = 7.5, 0.6 Hz, 1H), 6.86 – 6.81 (m, 2H), 5.31 (s, 1H), 3.11 (d, *J* = 17.0 Hz, 1H), 2.79 (d, *J* = 17.0 Hz, 1H), 1.34 (s, 3H). **^{13}C NMR** (151 MHz, CD_3OD) δ 175.6, 163.3, 149.8, 140.2, 139.0, 135.0, 129.3, 128.9, 125.8, 123.9, 120.2, 117.3, 117.0, 116.4, 79.9, 46.8, 43.3, 21.9; HRMS (ESI) for $C_{18}H_{15}N_2O_2$ $[M+H]^+$ calcd. 291.1135, found 291.1132.

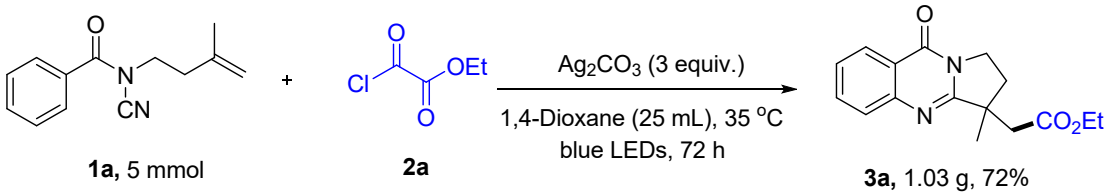
2-(6-methyl-12-oxo-6,12-dihydroindolo[2,1-b]quinazolin-6-yl)acetic acid (9).



Column chromatography on silica gel (DCM/MeOH = 20:1). White solid; 90% yield (55.1 mg); mp 72-74 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.0 Hz, 1H), 8.41 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.47 – 7.42 (m, 1H), 7.39 – 7.32 (m, 2H), 3.32 (d, *J* = 16.8 Hz, 1H), 3.03 (d, *J* = 16.8 Hz, 1H), 1.62 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.4, 163.8, 159.8, 146.4, 138.9, 134.7, 134.5, 129.0, 127.1, 127.0, 126.8, 126.7, 122.2, 121.3, 117.3, 46.0, 43.2, 26.2 ; HRMS (ESI) for $C_{18}H_{14}N_2O_3Na$ $[M+Na]^+$ calcd. 329.0902, found 329.0907.

5. Scale-up Reaction and Application

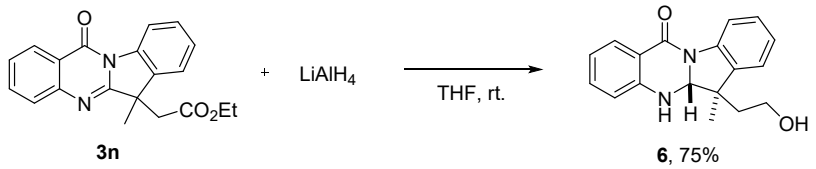
5.1 Scale-up Reaction:



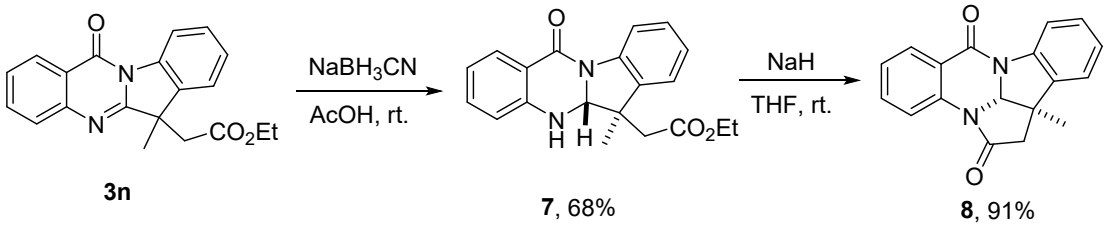
1a, 5 mmol **2a** **3a,** 1.03 g, 72%

A dry round-bottom flask with N-cyano-N-(3-methylbut-3-en-1-yl) benzamide **1a** (1.07 g, 5 mmol, 1.0 equiv.), Ag_2CO_3 (4.14 g, 15 mmol, 3.0 equiv.) was evacuated and purged with argon three times. Afterwards, ethyl oxalyl monochloride **2a** (1.6 mL, 15 mmol, 3.0 equiv.) and anhydrous 1,4-dioxane (25 mL, 0.2 M) were added under an argon atmosphere. The reaction mixture was then stirred and irradiated with 40 W blue LEDs with fans placed beside for cooling and the solution was kept at 35 °C for 72 h. After completion, the reaction mixture was purified by flash chromatography to give the desired compounds.

5.2 Application:

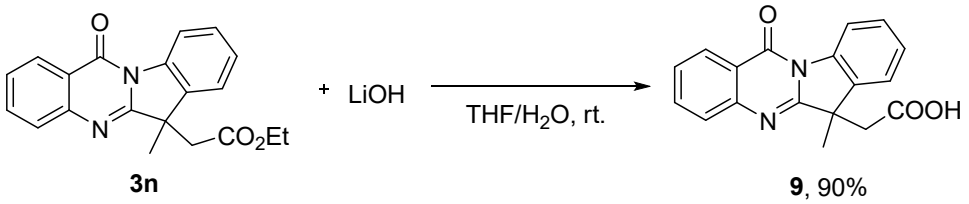


$LiAlH_4$ (15.2 mg, 0.4 mmol, 2.0 equiv.) was added in one portion to the solution of ethyl 2-(6-methyl-12-oxo-6,12-dihydroindolo[2,1-b]quinazolin-6-yl)acetate **3n** (66.8 mg, 0.2 mmol, 1.0 equiv.) in THF at 0 °C and the reaction mixture was stirred at room temperature for 12 h. When the reaction was finished, the reaction was quenched with saturated NH_4Cl solution. The mixture was extracted with EA (3 x 15 mL) and the organic phases were combined, dried over Na_2SO_4, concentrated and purified by column chromatography to afford the desired product **6** (44.0 mg).



$NaBH_3CN$ (52 mg, 0.8 mmol, 2.0 equiv.) was added slowly to the solution of ethyl 2-(6-methyl-12-oxo-6,12-dihydroindolo[2,1-b]quinazolin-6-yl)acetate **3n** (133.6 mg, 0.4 mmol, 1.0 equiv.) in AcOH at 0 °C and the reaction mixture was stirred at room temperature for 24 h. After the reaction was completed, the reaction was quenched with 50% NaOH saturated solution and diluted with ethyl acetate. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the product **7** (92.0 mg).

To a THF solution containing **7** (64.4 mg, 0.2 mmol, 1.0 equiv.), NaH (8.8 mg, 60% wt, 0.22 mmol, 1.1 equiv.) was added at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. When the reaction was finished, the reaction was quenched with saturated NH_4Cl solution. The mixture was extracted with EA (3 x 15 mL) and the organic phases were combined, dried over Na_2SO_4, concentrated and purified by column chromatography to afford the desired product **8** (53.0 mg).

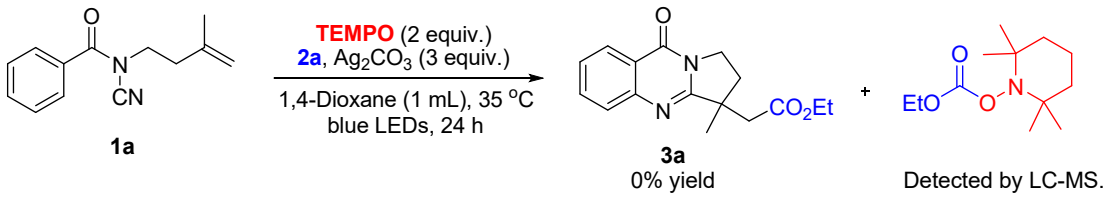


To the solution of **3n** (66.8 mg, 0.2 mmol, 1.0 equiv.) in THF/H_2O (4 mL/1 mL), LiOH (12 mg, 0.5 mmol, 2.5 equiv.) was added and the reaction mixture was stirred at room temperature for 24 h. After the reaction was completed, the reaction was quenched

with with 1 M HCl aqueous solution and diluted with ethyl acetate. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the product **9** (55.1 mg).

6. Mechanistic Investigations

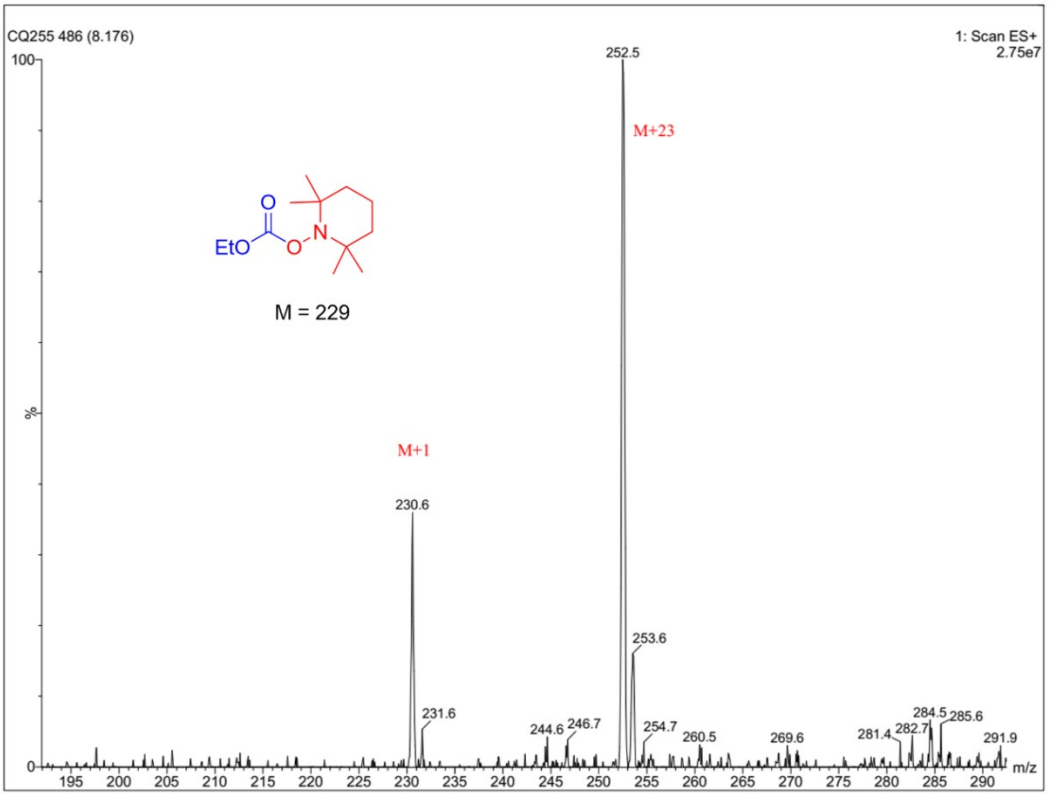
6.1 The TEMPO trapping experiments.



A dried 10 mL Schlenk tube containing N-cyano-N-(3-methylbut-3-en-1-yl) benzamide **1a** (42.8 mg, 0.2 mmol, 1.0 equiv.), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv.), Ag_2CO_3 (165.5 mg, 0.6 mmol, 3.0 equiv.) was evacuated and purged with argon three times. Afterwards, ethyl oxalyl monochloride **2a** (64 uL, 0.6 mmol, 3.0 equiv.) and anhydrous 1,4-dioxane (1 mL, 0.2 M) were added under an argon atmosphere. The reaction mixture was then stirred and irradiated with 40 W blue LEDs with fans placed beside for cooling and the solution was kept at 35 ℃ for 24 h. After completion, the reaction mixture was detected by LC-MS.

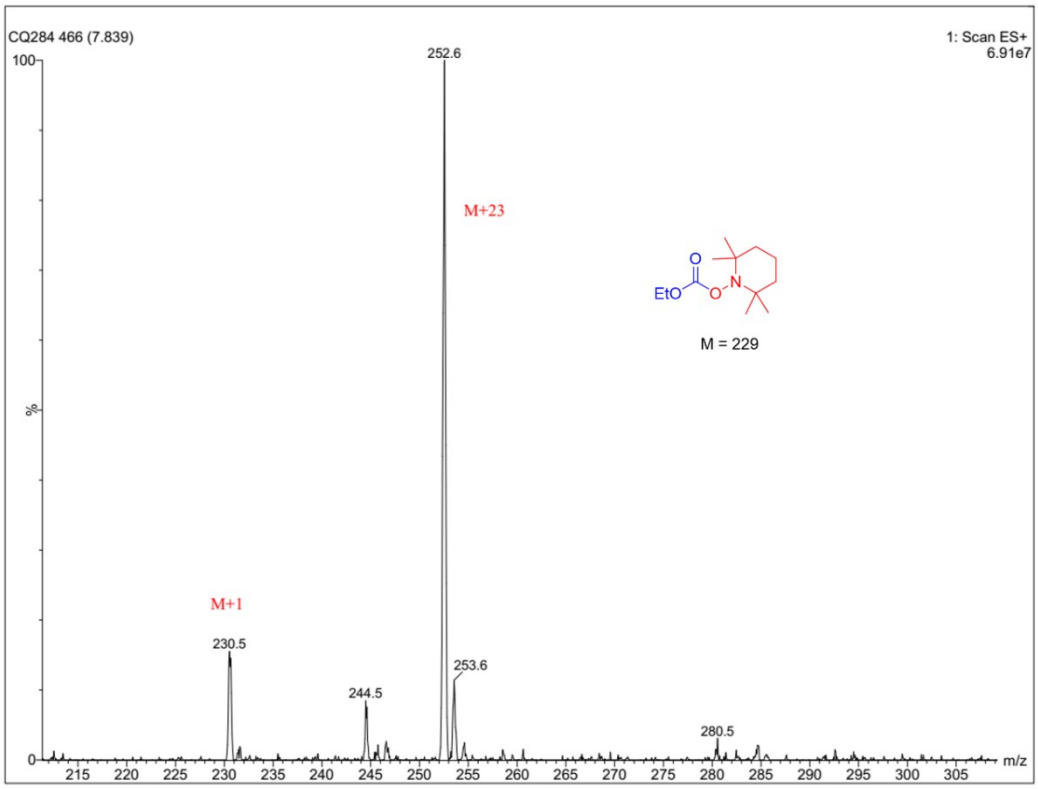
Mass spectrometry study on the reaction mixture:

ESI-MS data were obtained using a Waters SQ Detector mass spectrometer equipped with an ESI source and controlled by Mass Lynx software. The spray voltage was set to 3500 V for positive mode. The heated capillary temperature was at 350 ℃. The Mass range was adjusted between 100 to 1000 Da. The analysis was introduced as a solution in methanol/water 1:1 (v/v) dilution and injected in the infusion mode with a flow rate of 5 μL/min at an electrospray voltage of 3500 V.

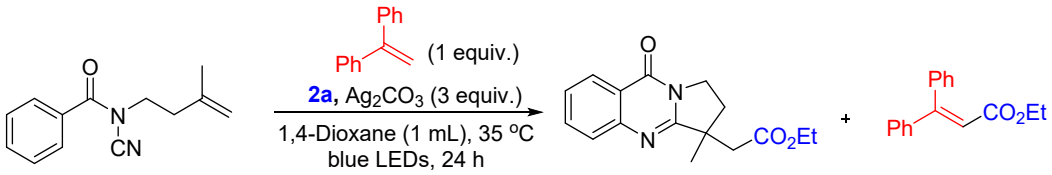


2a (0.6 mmol) (0.4 mmol) Detected by LC-MS.

A dried 10 mL Schlenk tube containing TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv.), Ag_2CO_3 (165.5 mg, 0.6 mmol, 3.0 equiv.) was evacuated and purged with argon three times. Afterwards, ethyl oxalyl monochloride **2a** (64 uL, 0.6 mmol, 3.0 equiv.) and anhydrous 1,4-dioxane (1 mL, 0.2 M) were added under an argon atmosphere. The reaction mixture was then stirred and irradiated with 40 W blue LEDs with fans placed beside for cooling and the solution was kept at 35 ℃ for 24 h. After completion, the reaction mixture was detected by LC-MS.



6.2 The radical trapping experiment with 1,1-diphenylethylene.



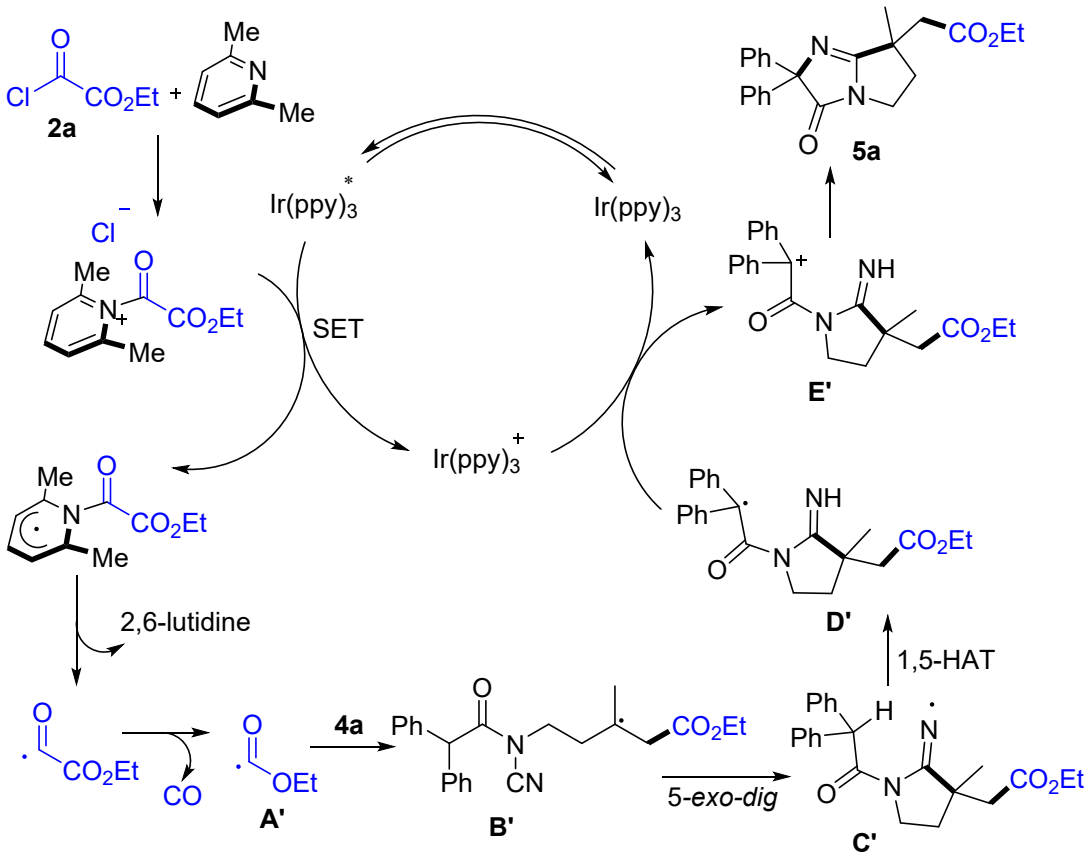
1a **3a,** 21% yield **3aj**, 42% yield

A dried 10 mL Schlenk tube containing N-cyano-N-(3-methylbut-3-en-1-yl) benzamide **1a** (42.8 mg, 0.2 mmol, 1.0 equiv.), Ag_2CO_3 (165.5 mg, 0.6 mmol, 3.0 equiv.) was evacuated and purged with argon three times. Afterwards, ethene-1,1-diyldibenzene (36 uL, 0.2 mmol, 1.0 equiv.), ethyl oxalyl monochloride **2a** (64 uL, 0.6 mmol, 3.0 equiv.) and anhydrous 1,4-dioxane (1 mL, 0.2 M) were added under an argon atmosphere. The reaction mixture was then stirred and irradiated with 40 W blue LEDs with fans placed beside for cooling and the solution was kept at 35 °C for 24 h. After completion, the reaction mixture was purified by flash chromatography to give the desired compounds **3a** (12.1 mg) and **3aj** (21.0 mg).

6.3 The plausible mechanism for synthesizing ester-substituted bicyclic amidines.

Initially, ethyl chlorooxoacetate (**2a**) reacted with 2,6-lutidine, giving rise to the corresponding acylpyridinium salt, which could be readily reduced by excited state photocatalyst $Ir(ppy)_3$* results in dihydropyridine radical. Then the C–N bond homolysis of the dihydropyridine radical and subsequent decarbonylation would generate the ethoxycarbonyl radical **A'**. The ethoxycarbonyl radical would then react with N-cyano-N-(3-methylbut-3-en-1-yl)-2,2-diphenylacetamide (**4a**) to afford the

corresponding alkyl radical **B'**. Subsequently, *5-exo-dig* cyclization of intermediate **B'** gives iminyl radical **C'**, which would undergo 1,5-HAT process to provide the radical species **D'**. A single electron transfer (SET) between alkyl radical **D'** and the $Ir(ppy)_3^+$ catalyst would give the corresponding carbocation intermediate **E'**. Finally, an imine cyclization process would occur to generate **5a**.



7. References

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(3) Z. Pan, S. Wang, J. T. Brethorst and C. J. Douglas, Palladium and Lewis-Acid-Catalyzed Intramolecular Aminocyanation of Alkenes: Scope, Mechanism, and Stereoselective Alkene Difunctionalizations, *J. Am. Chem. Soc.*, 2018, **140**, 3331-3338.
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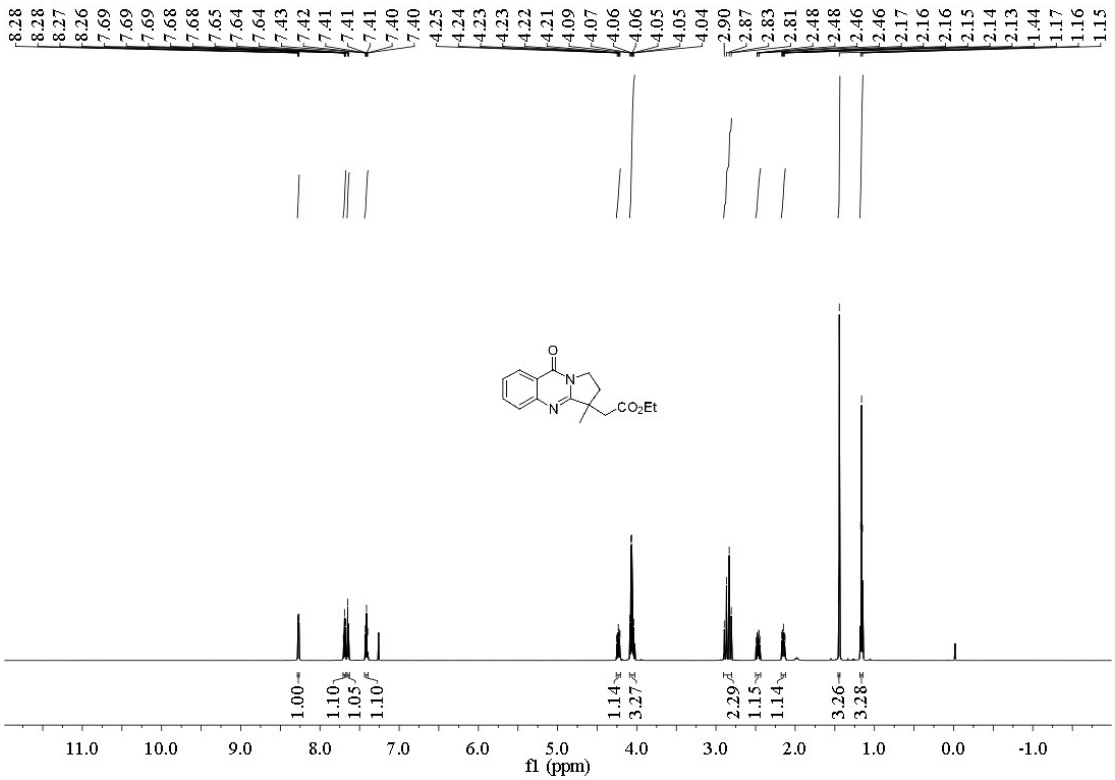
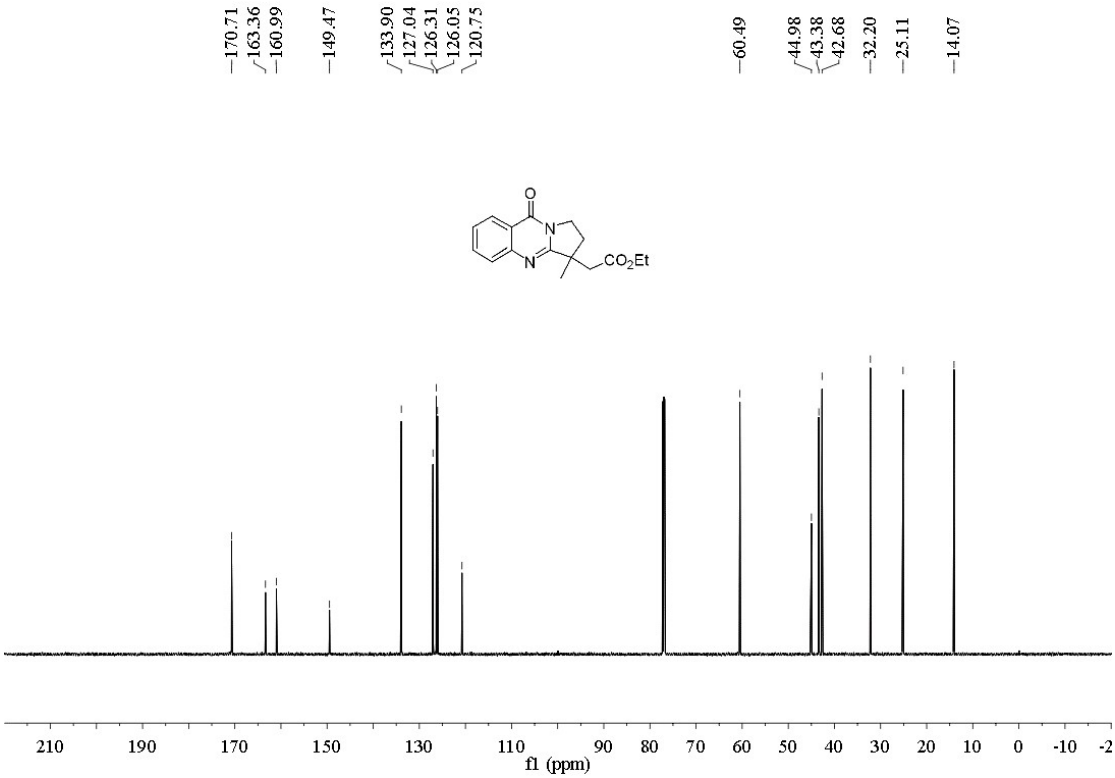
8. NMR Spectra of Compounds

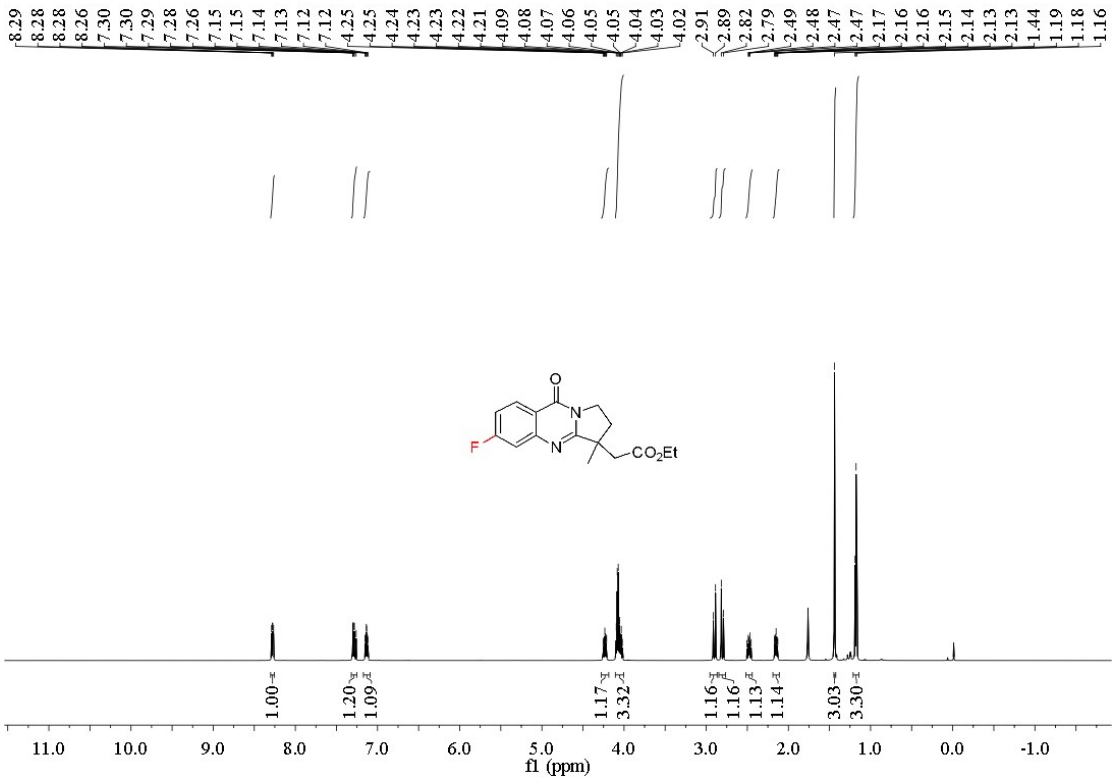
^{1}H NMR of **3a** (600 MHz, $CDCl_3$)



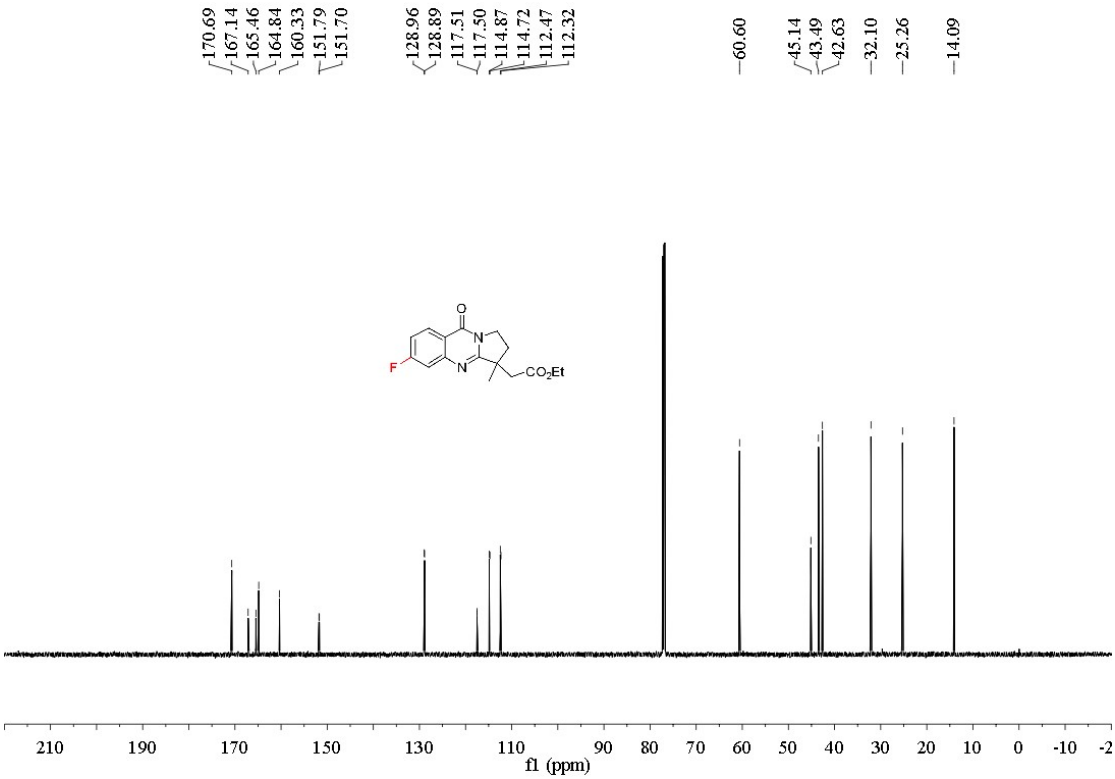
^{13}C NMR of **3a** (151 MHz, $CDCl_3$)



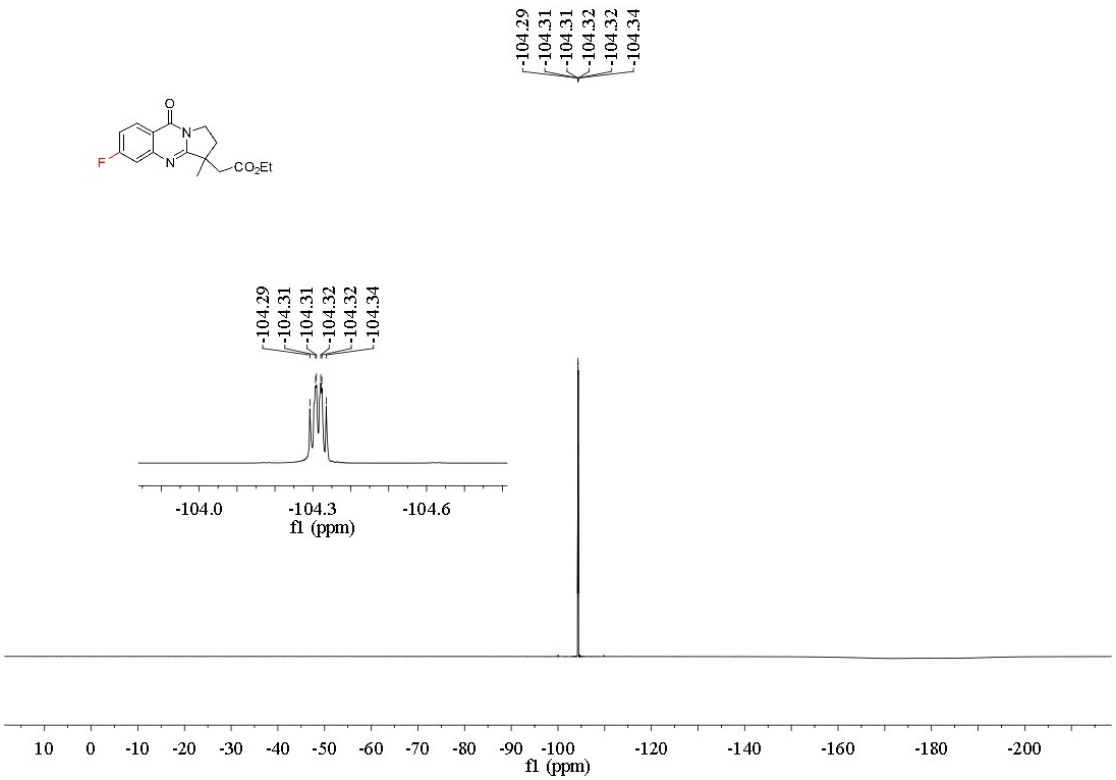
^{1}H NMR of **3b** (600 MHz, $CDCl_3$)



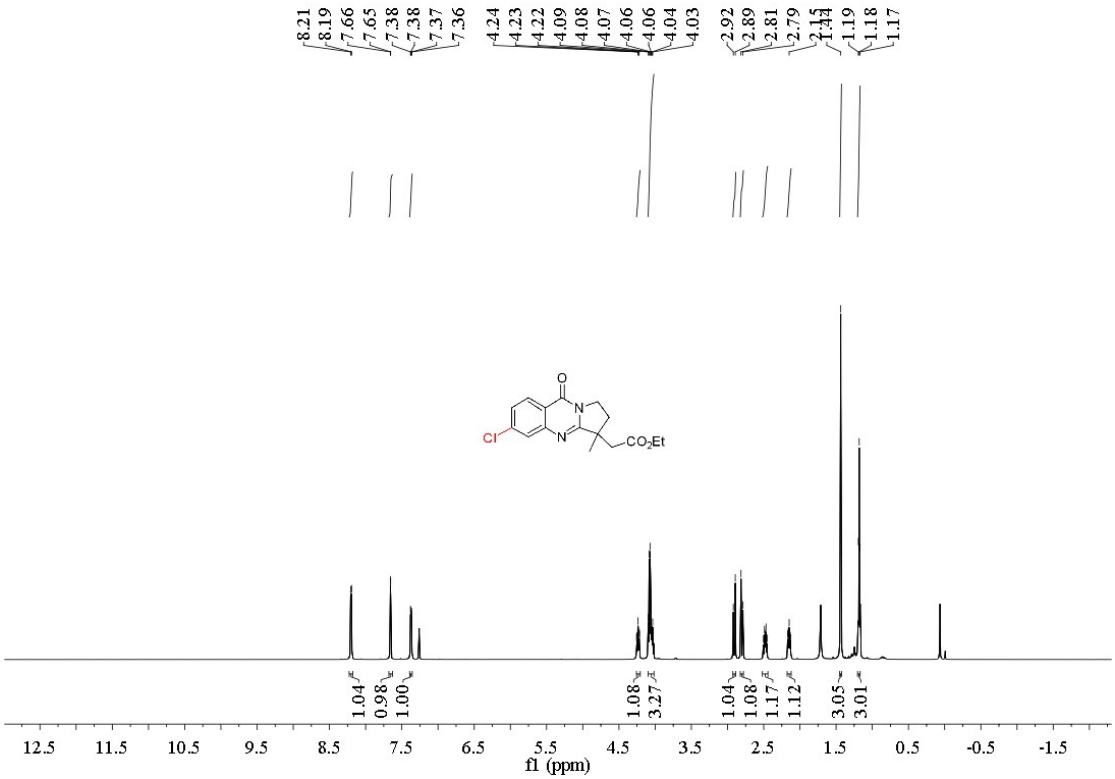
^{13}C NMR of **3b** (151 MHz, $CDCl_3$)



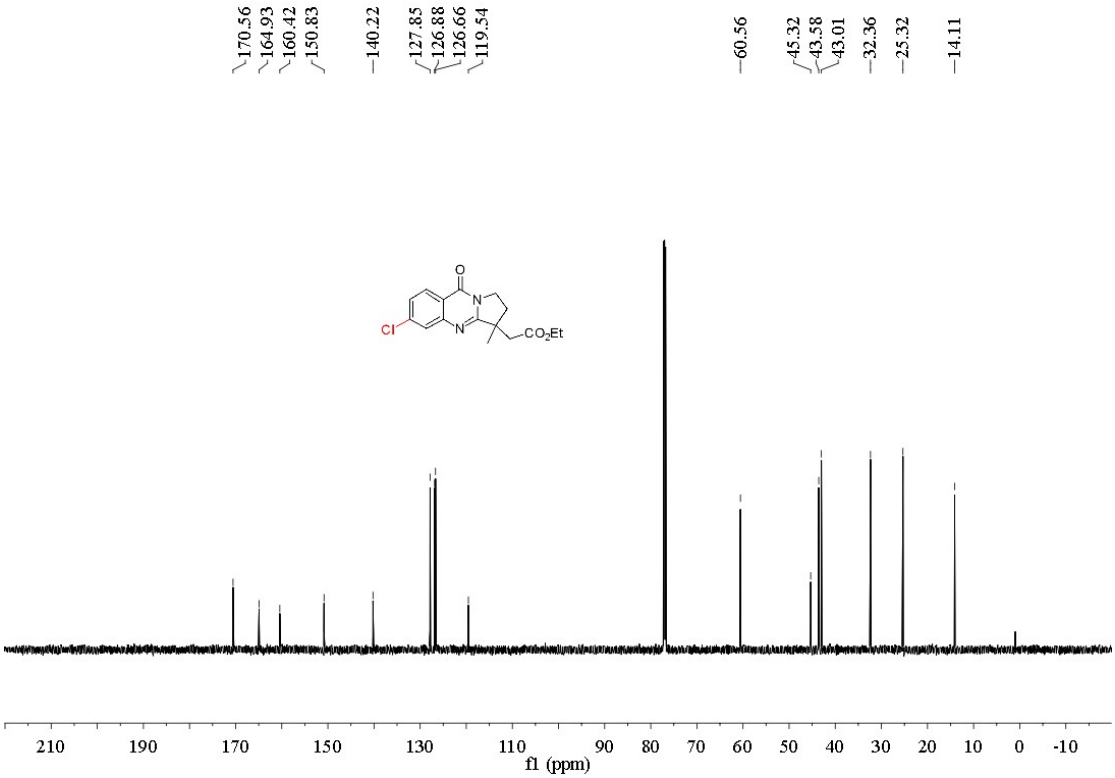
^{19}F NMR of **3b** (565 MHz, $CDCl_3$)



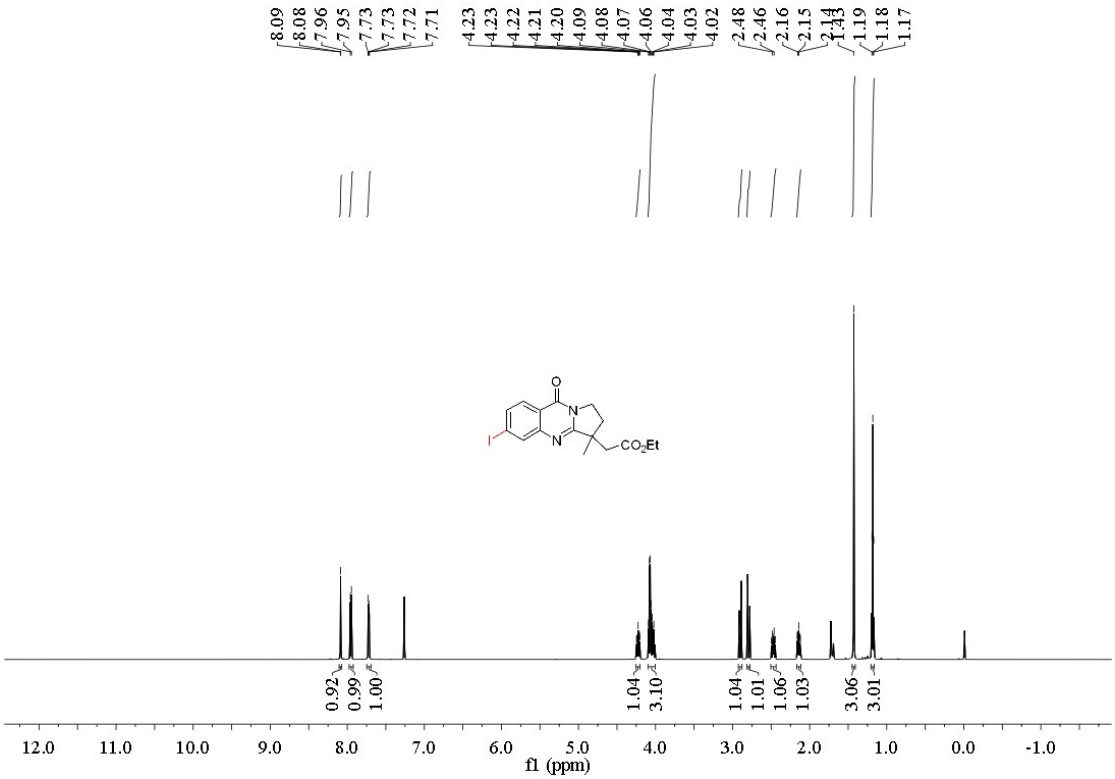
^{1}H NMR of **3c** (600 MHz, $CDCl_3$)



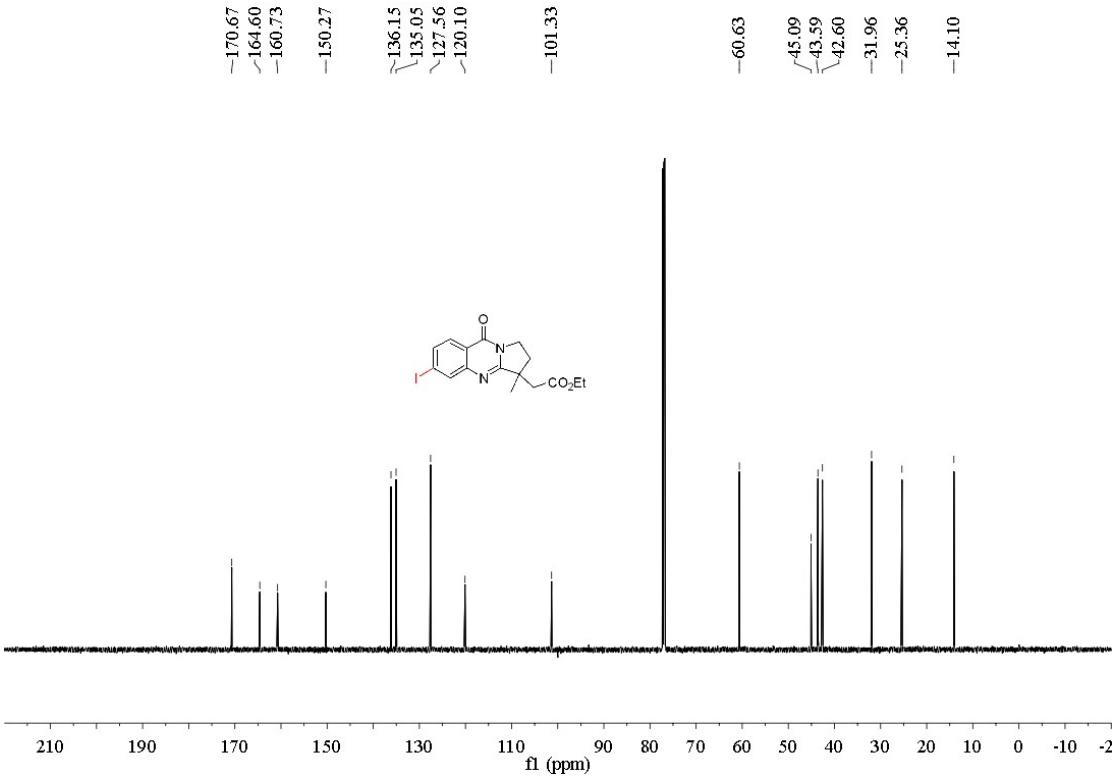
^{13}C NMR of **3c** (151 MHz, $CDCl_3$)



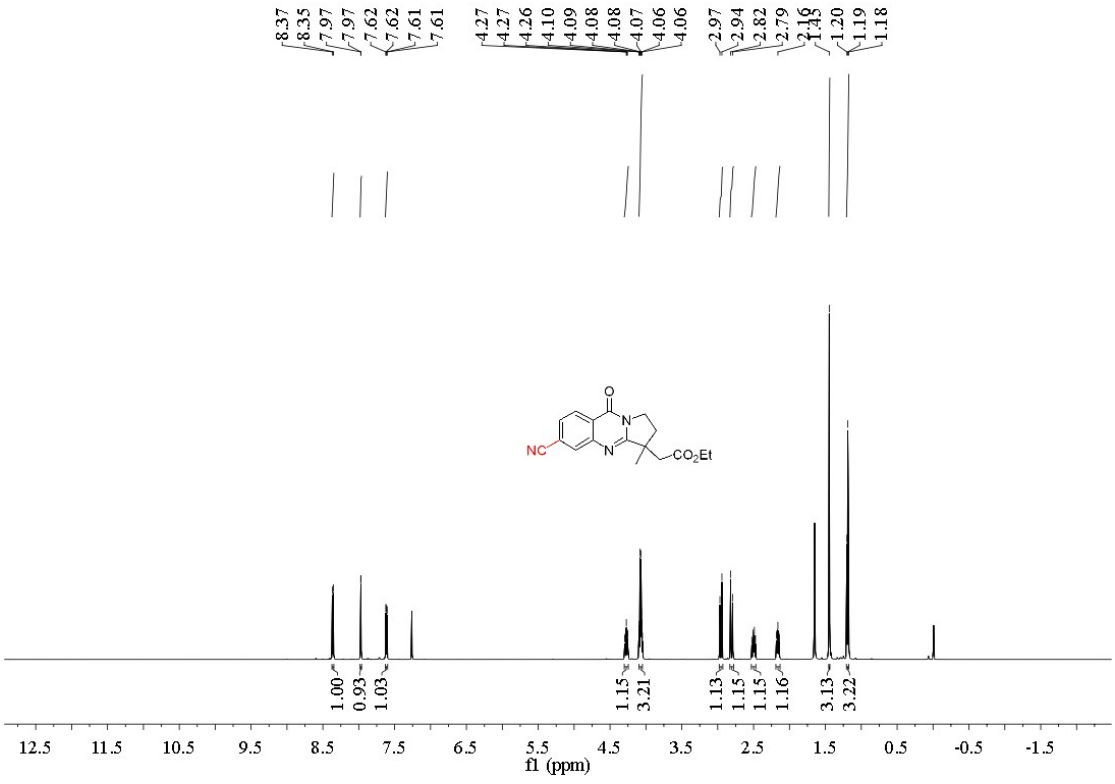
^{1}H NMR of **3d** (600 MHz, $CDCl_3$)



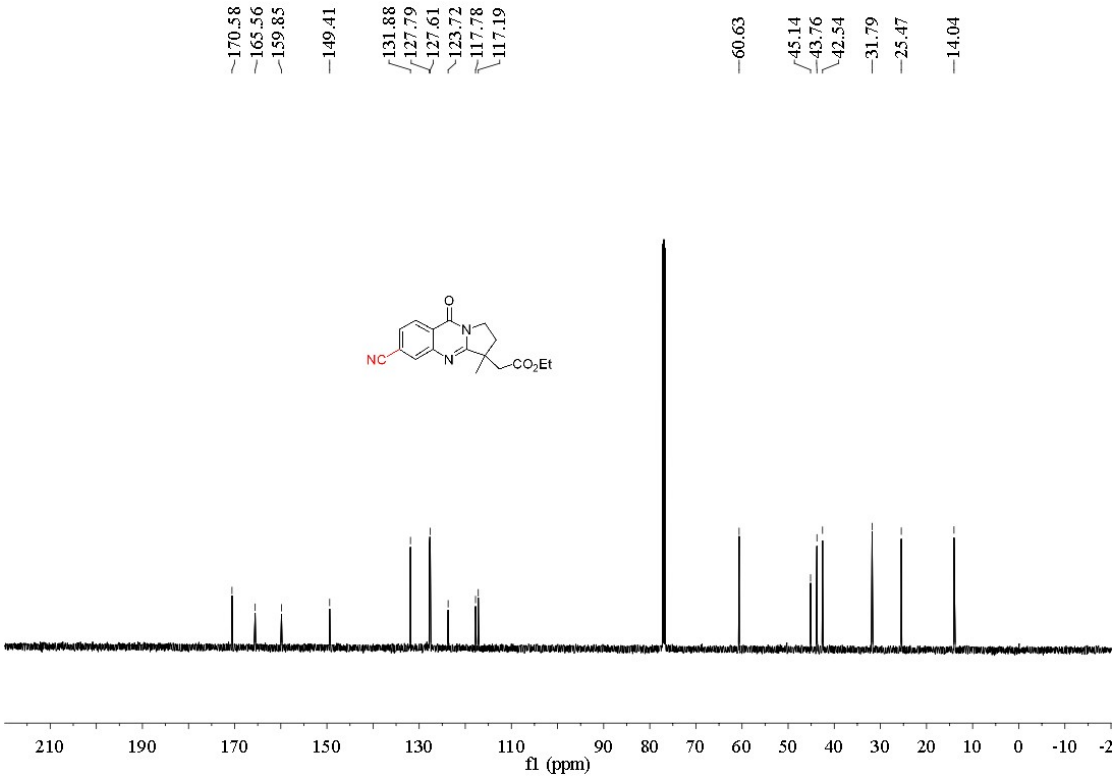
^{13}C NMR of **3d** (151 MHz, $CDCl_3$)



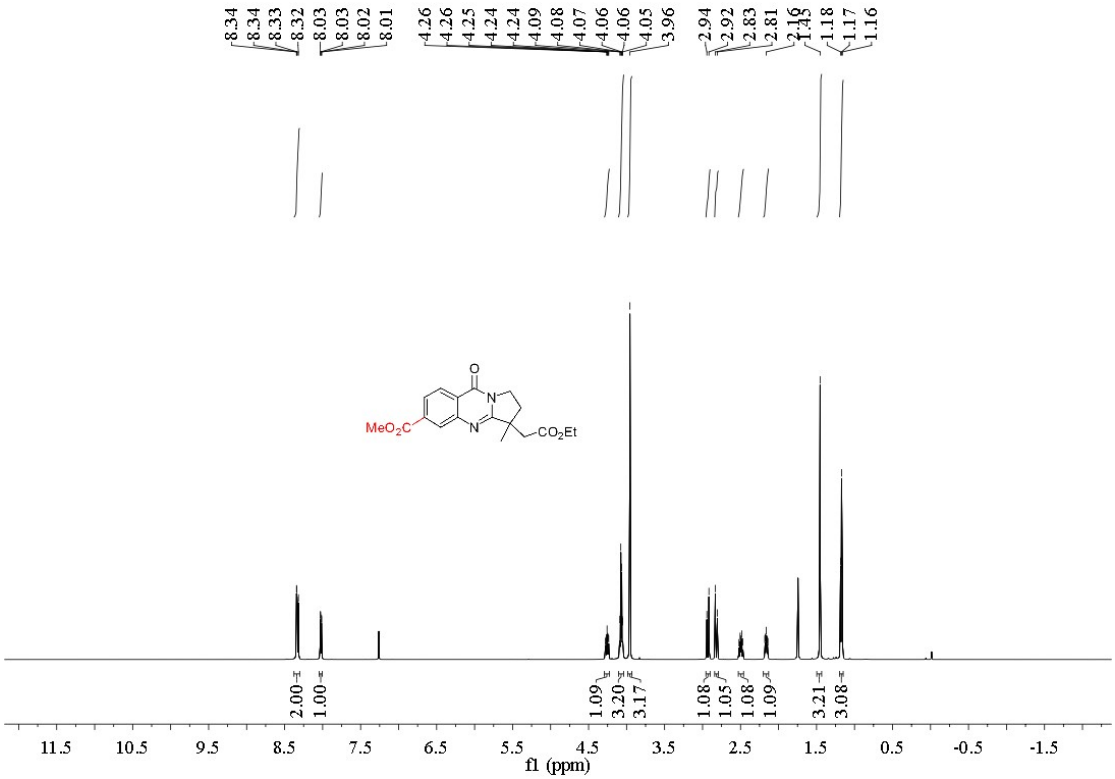
^{1}H NMR of **3e** (600 MHz, $CDCl_3$)



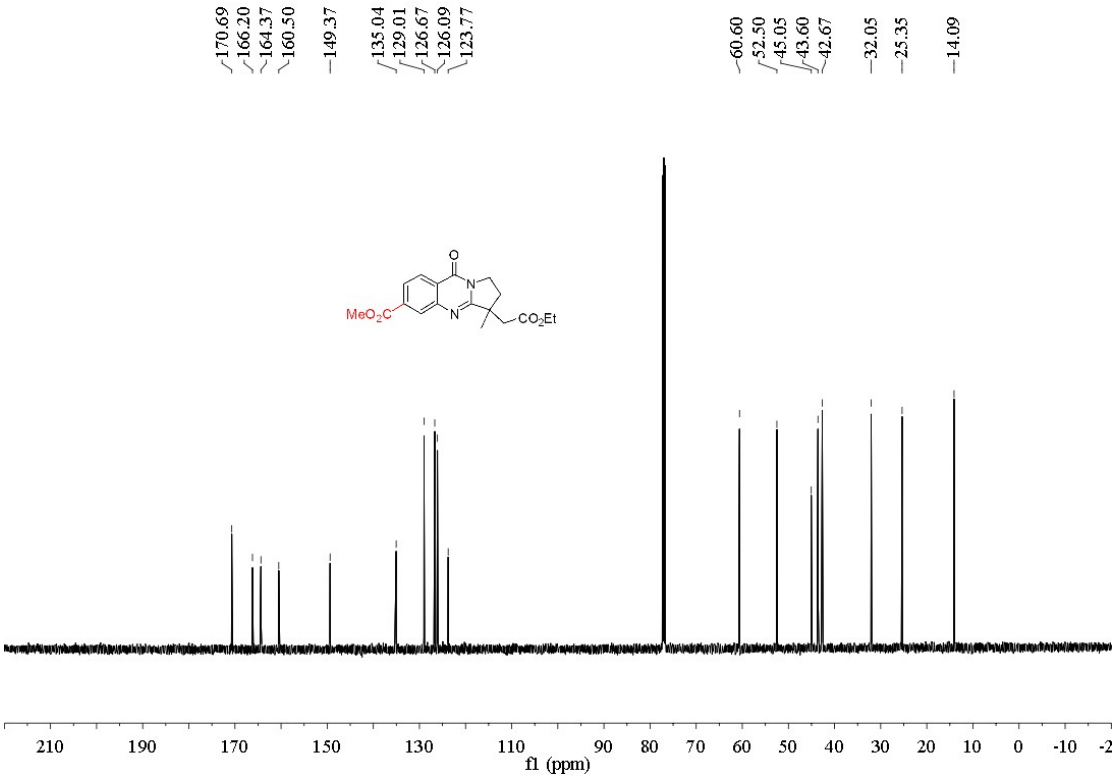
^{13}C NMR of **3e** (151 MHz, $CDCl_3$)



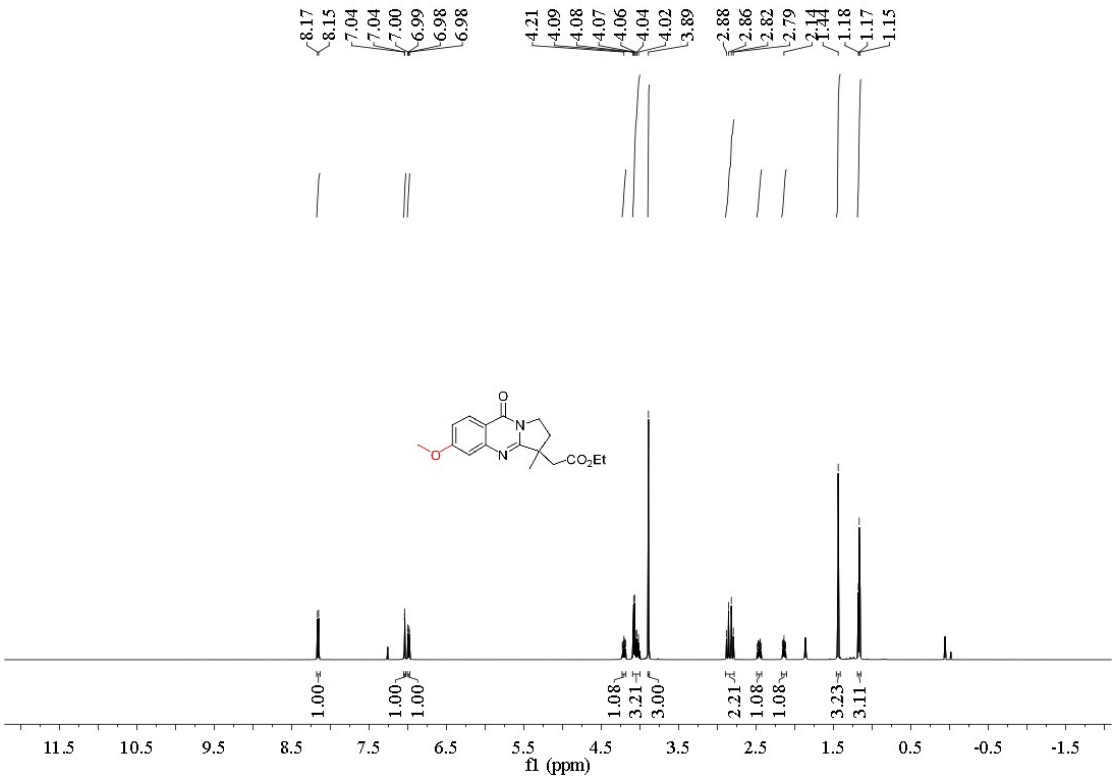
^{1}H NMR of **3f** (600 MHz, $CDCl_3$)



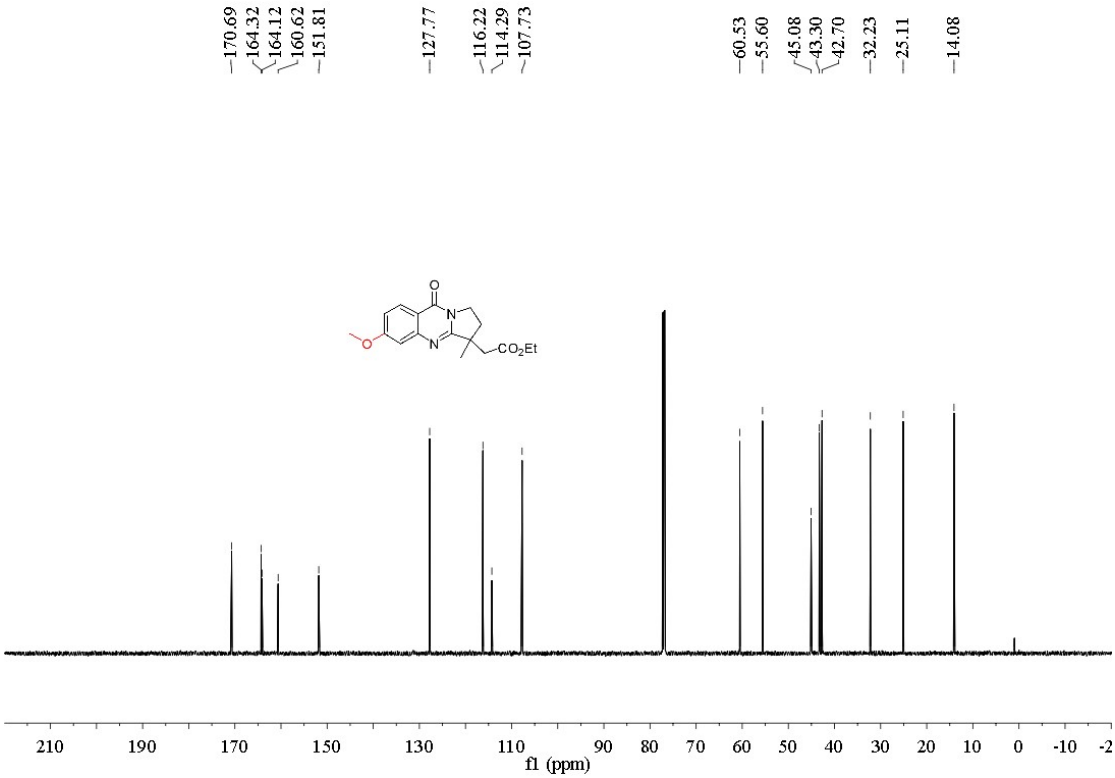
^{13}C NMR of **3f** (151 MHz, $CDCl_3$)



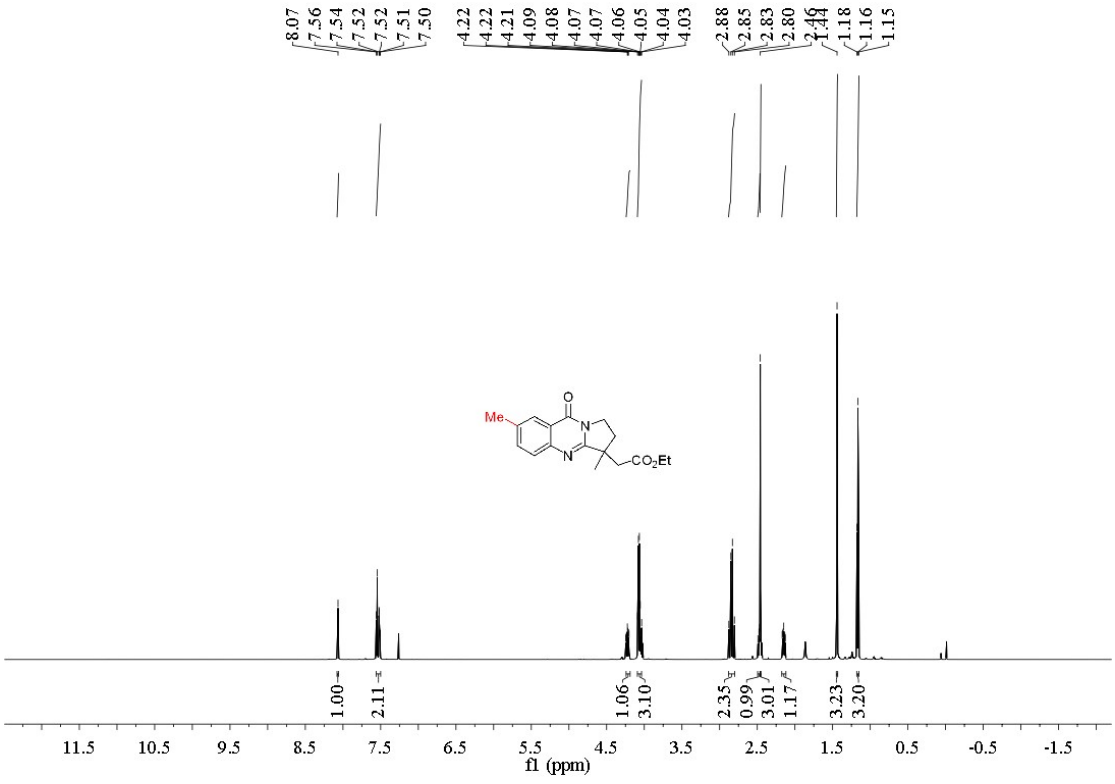
^{1}H NMR of **3g** (600 MHz, $CDCl_3$)



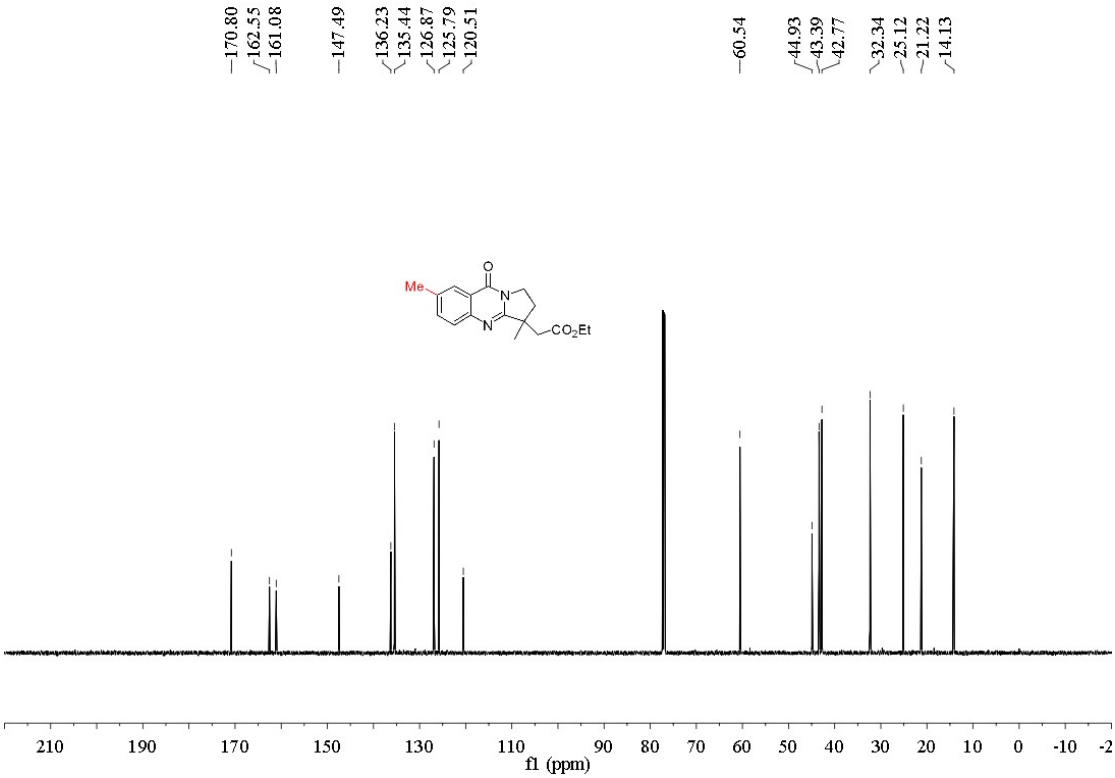
^{13}C NMR of **3g** (151 MHz, $CDCl_3$)



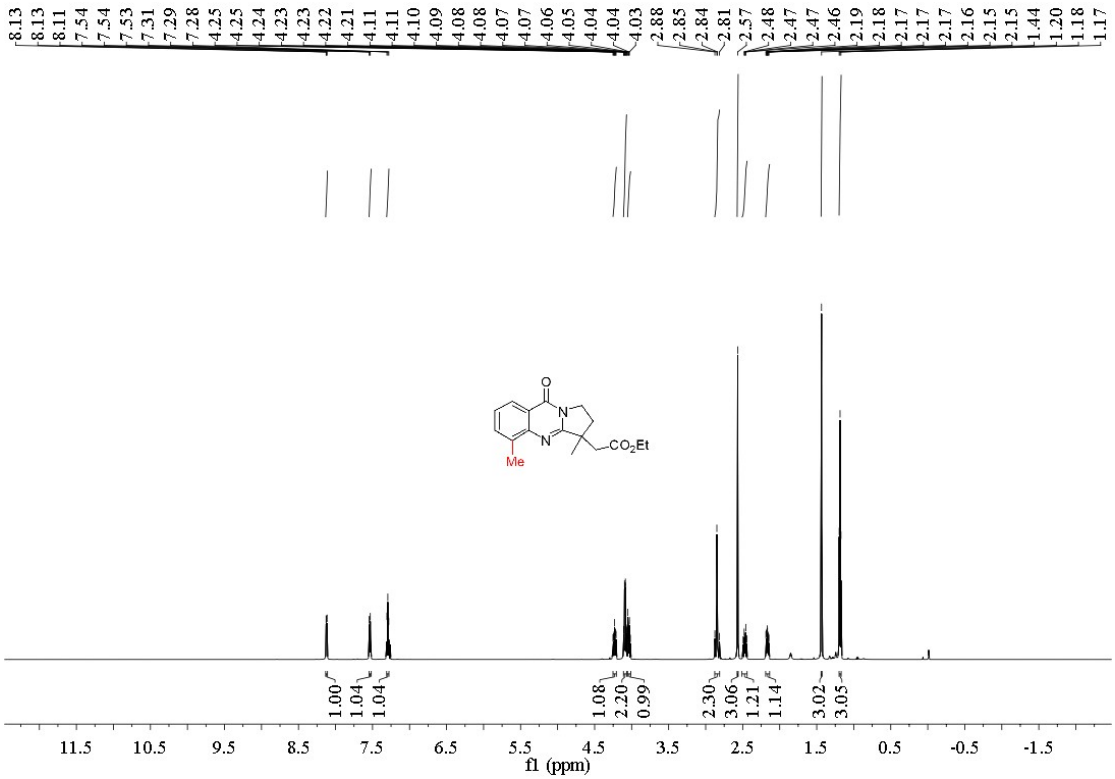
^{1}H NMR of **3h** (600 MHz, $CDCl_3$)



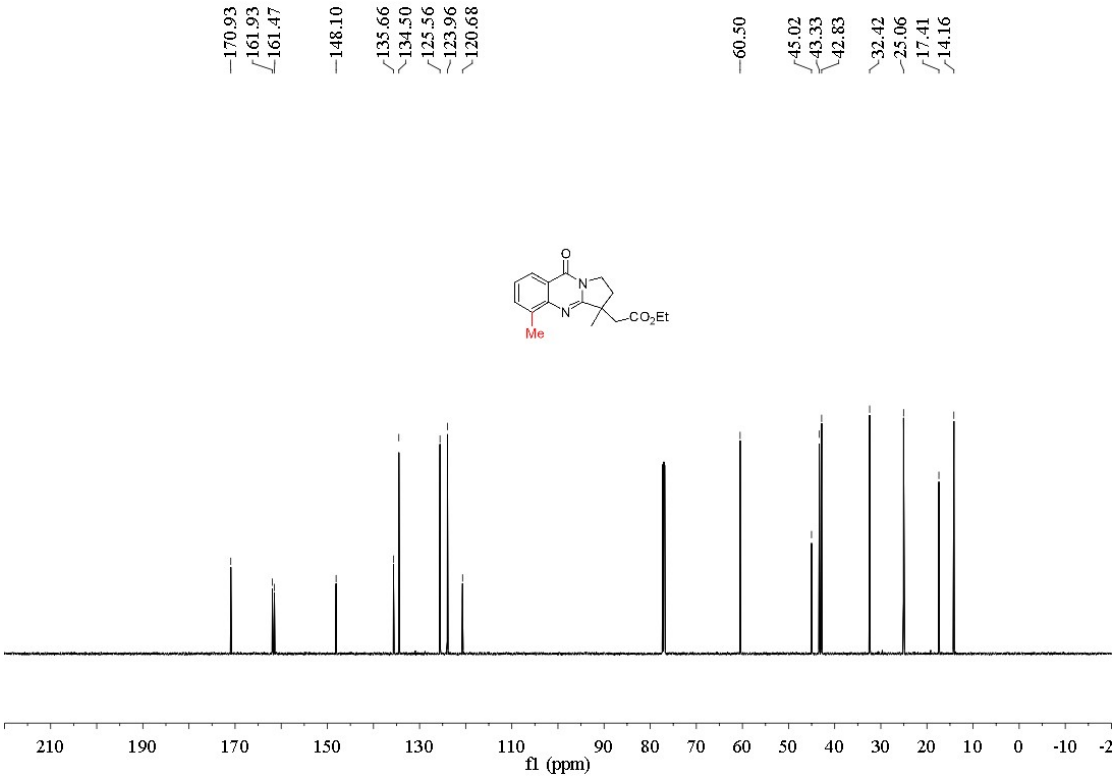
^{13}C NMR of **3h** (151 MHz, $CDCl_3$)



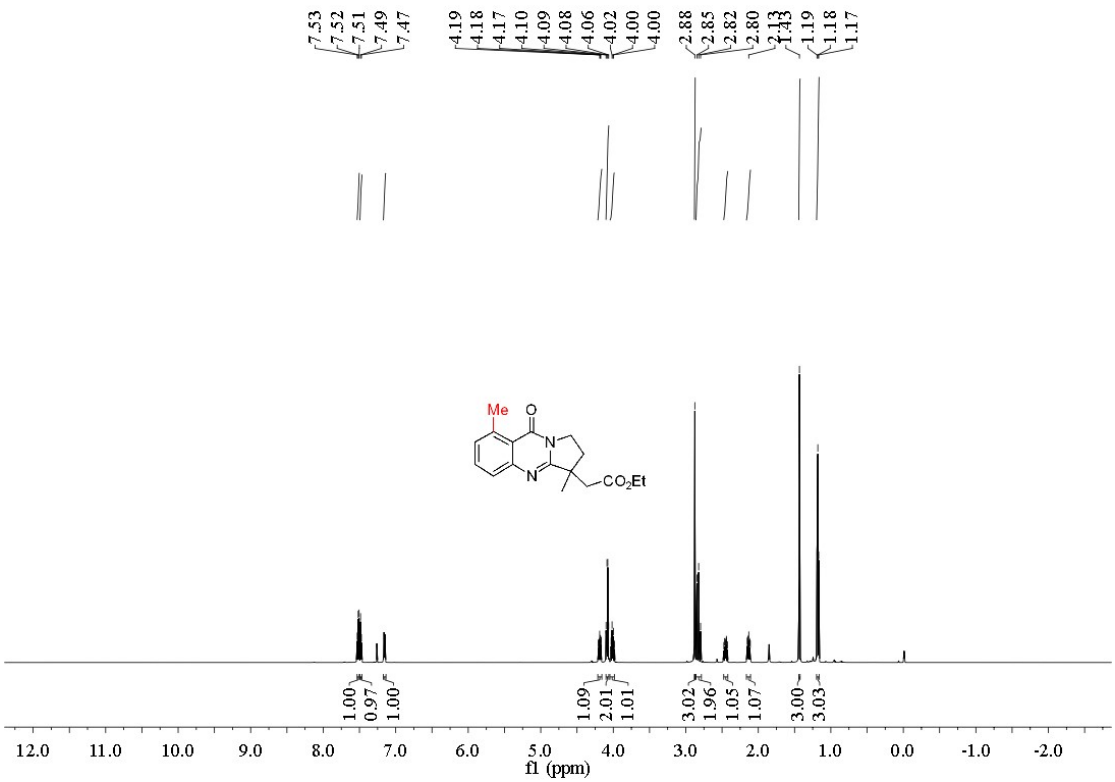
^{1}H NMR of **3h′** (600 MHz, $CDCl_3$)



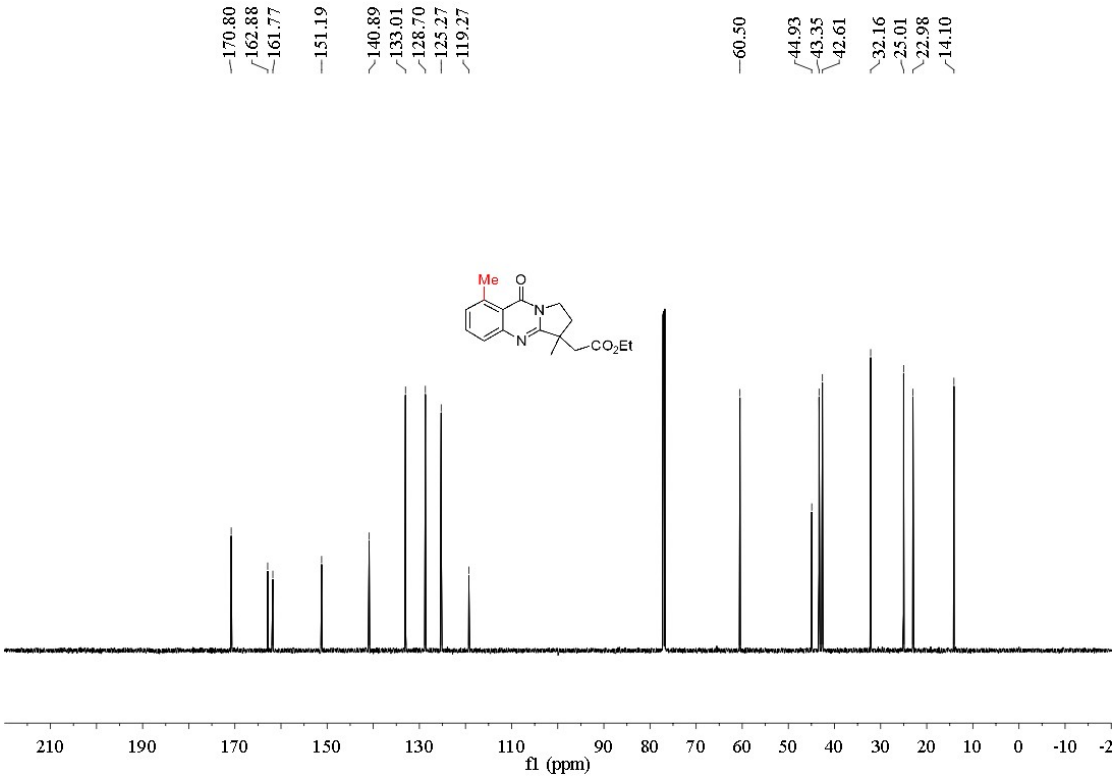
^{13}C NMR of **3h′** (151 MHz, $CDCl_3$)



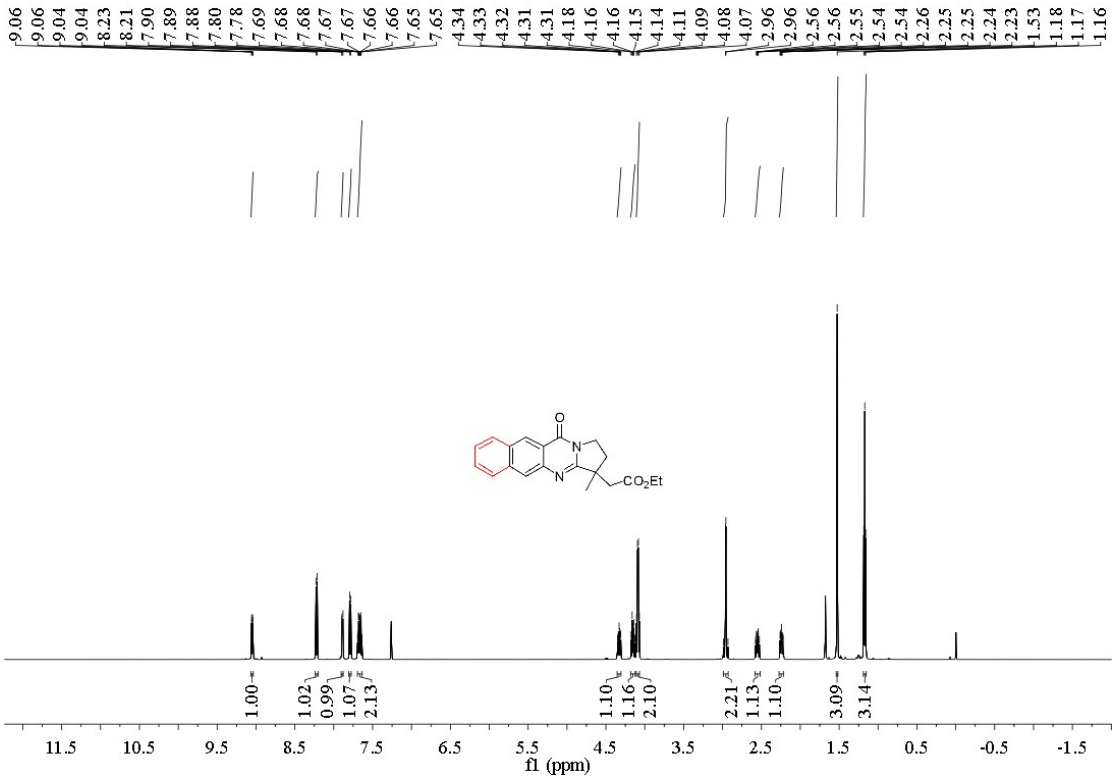
^{1}H NMR of **3i** (600 MHz, $CDCl_3$)



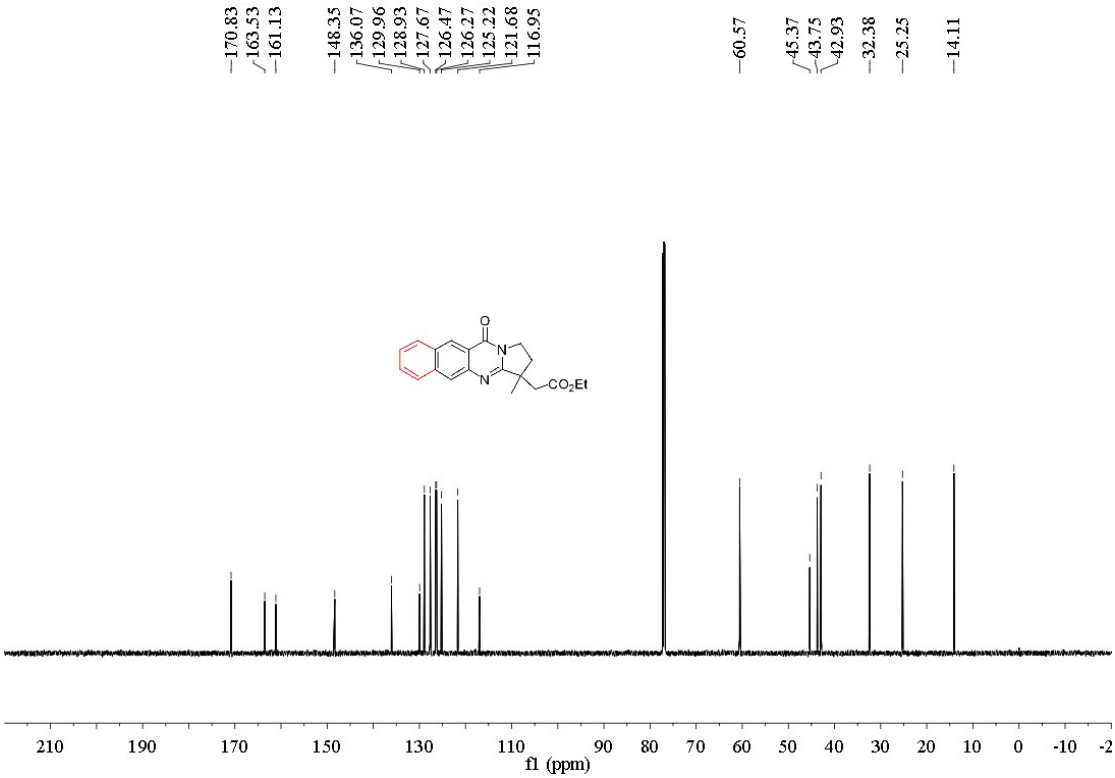
^{13}C NMR of **3i** (151 MHz, $CDCl_3$)



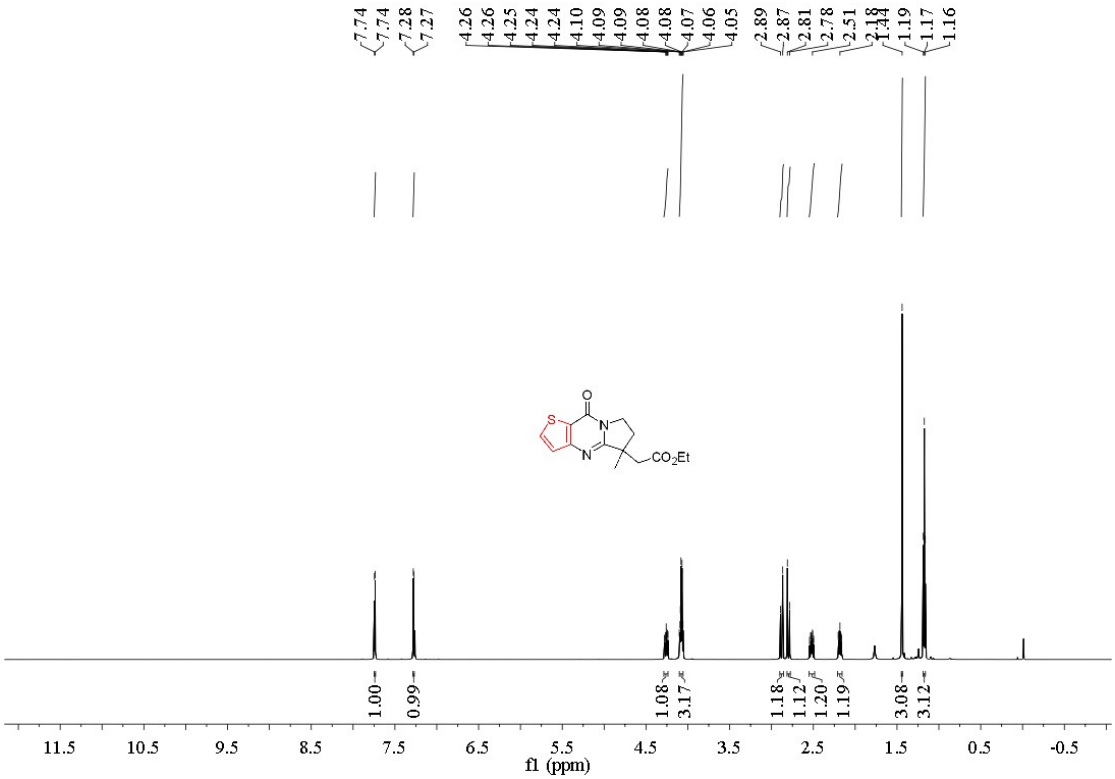
^{1}H NMR of **3j** (600 MHz, $CDCl_3$)



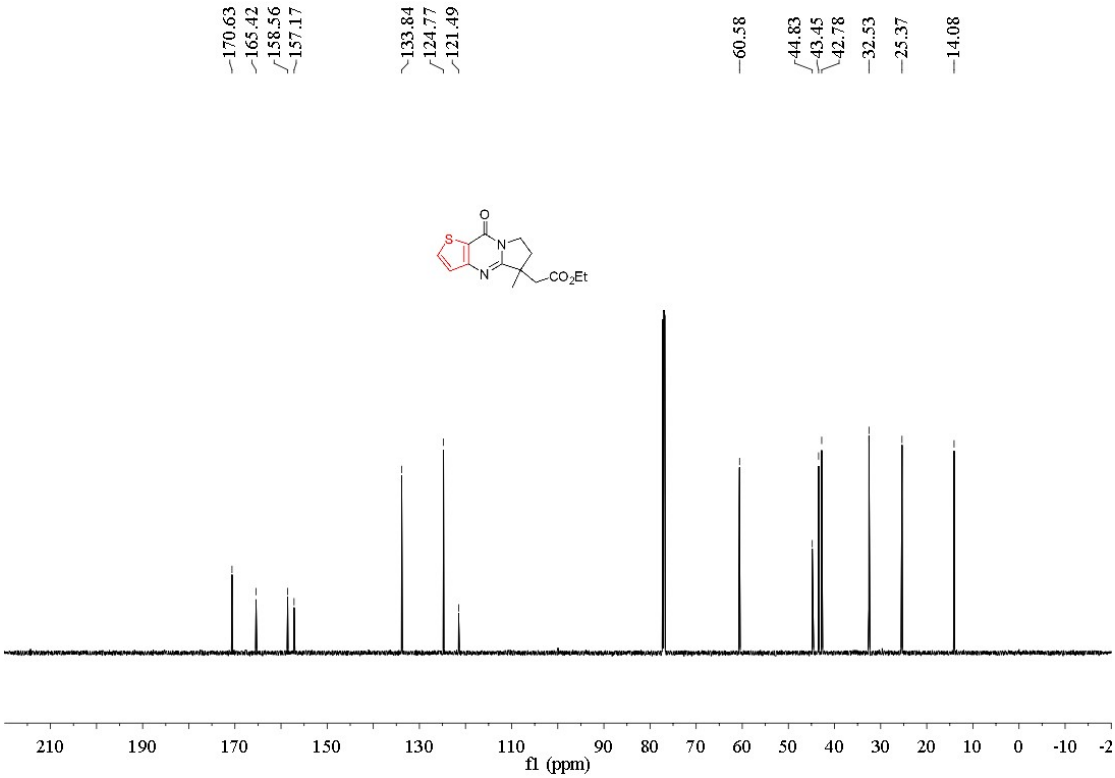
^{13}C NMR of **3j** (151 MHz, $CDCl_3$)



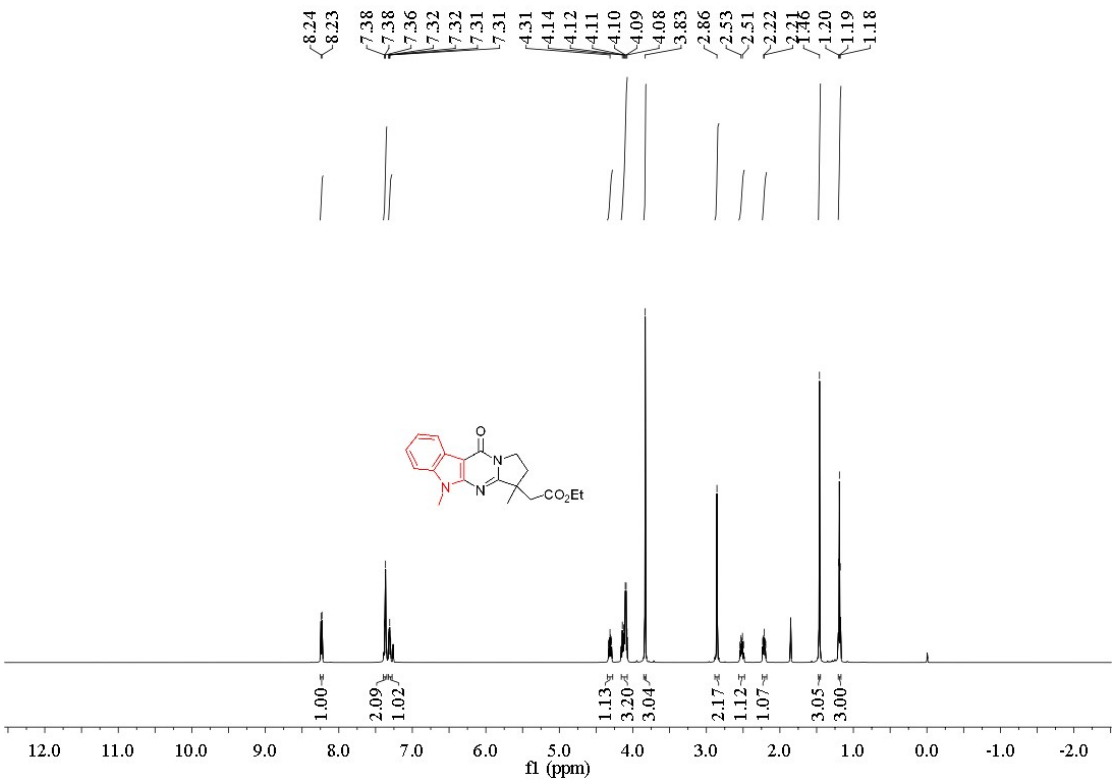
^{1}H NMR of **3k** (600 MHz, $CDCl_3$)



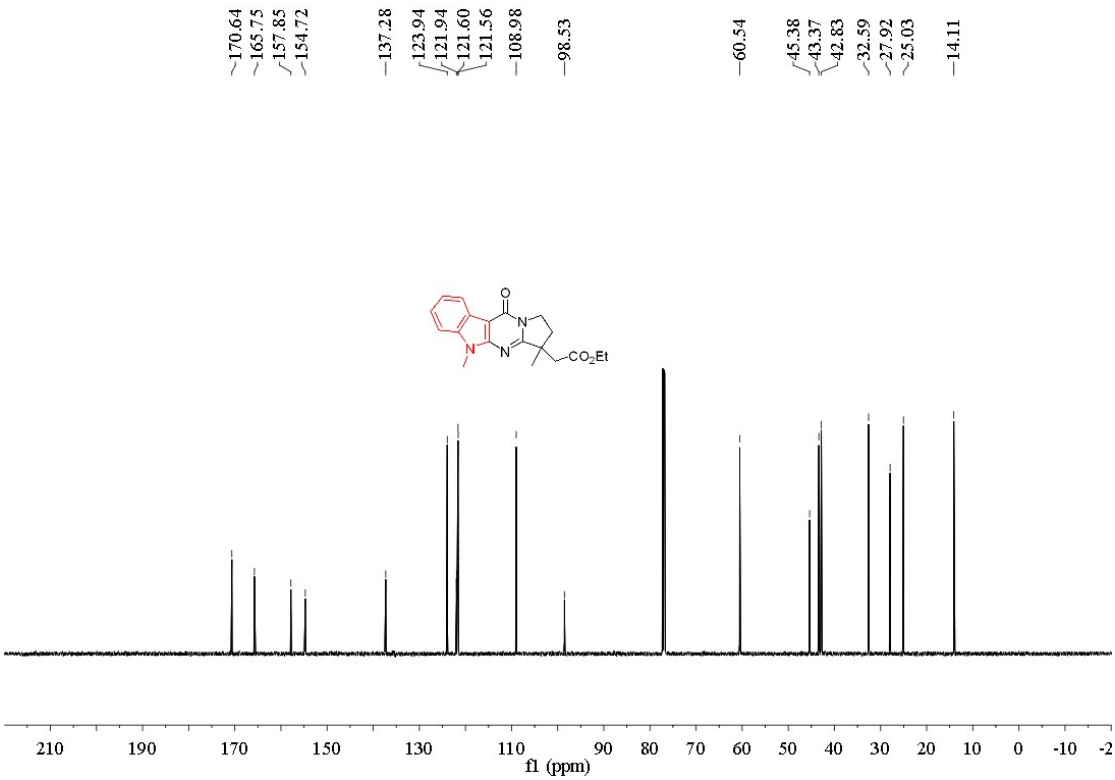
^{13}C NMR of **3k** (151 MHz, $CDCl_3$)



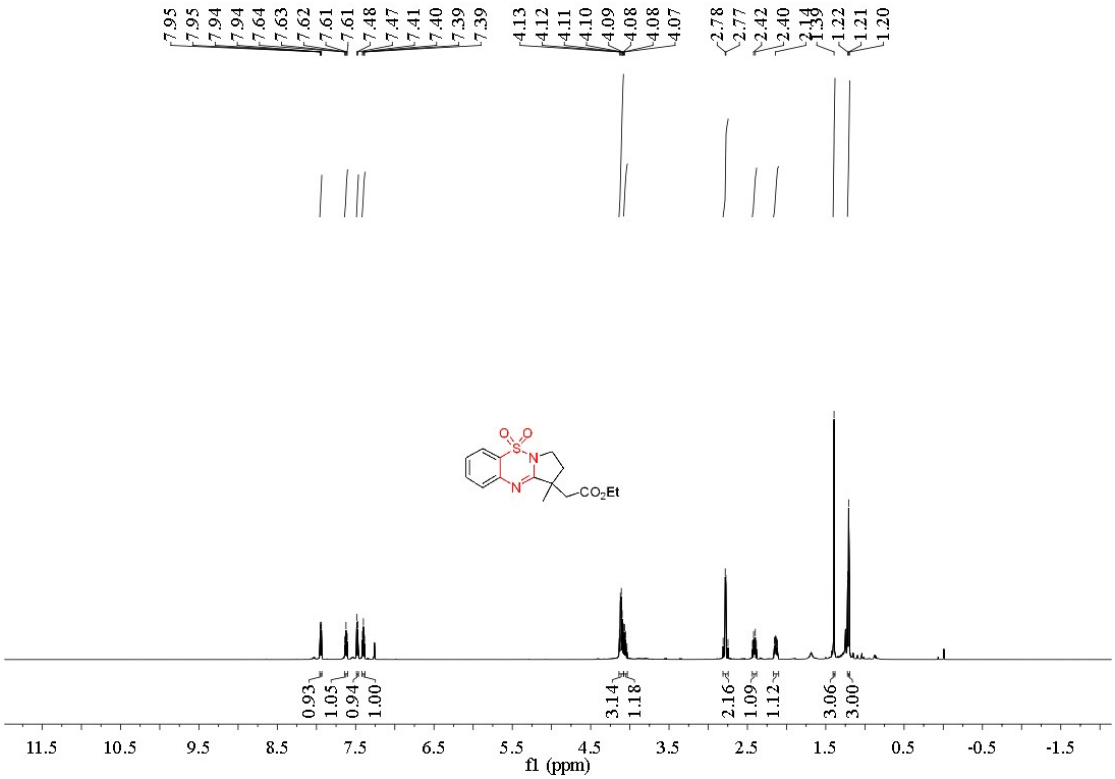
^{1}H NMR of **3l** (600 MHz, $CDCl_3$)



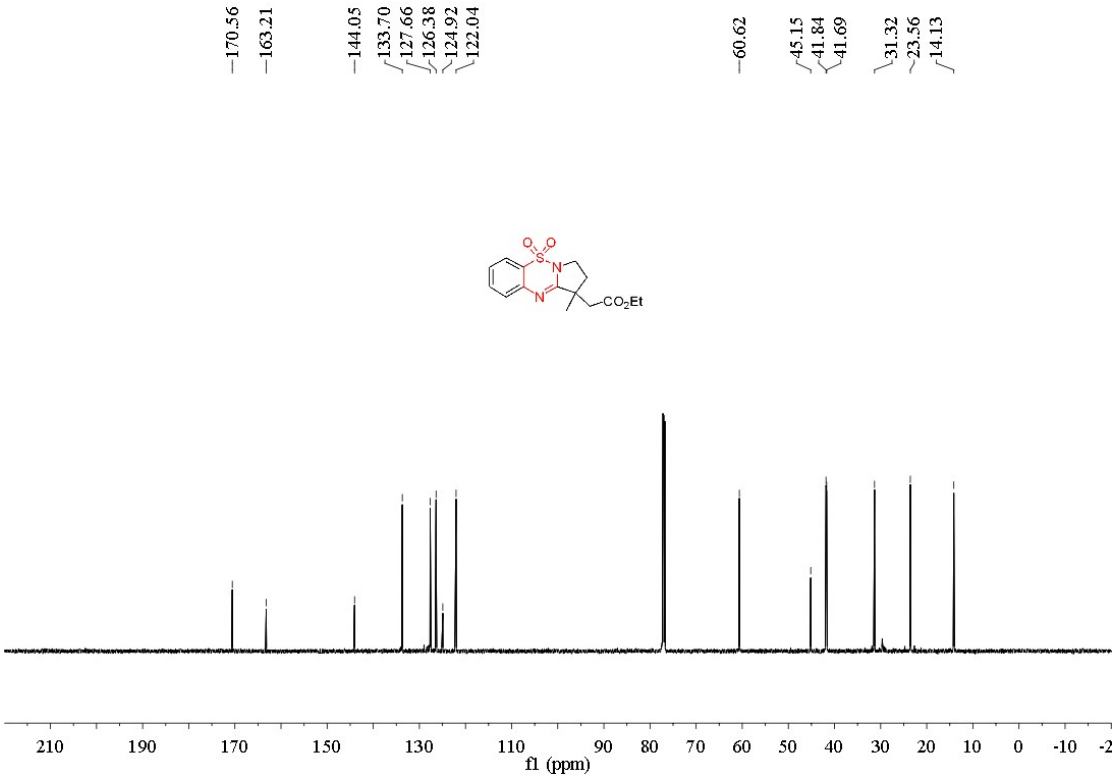
^{13}C NMR of **3l** (151 MHz, $CDCl_3$)



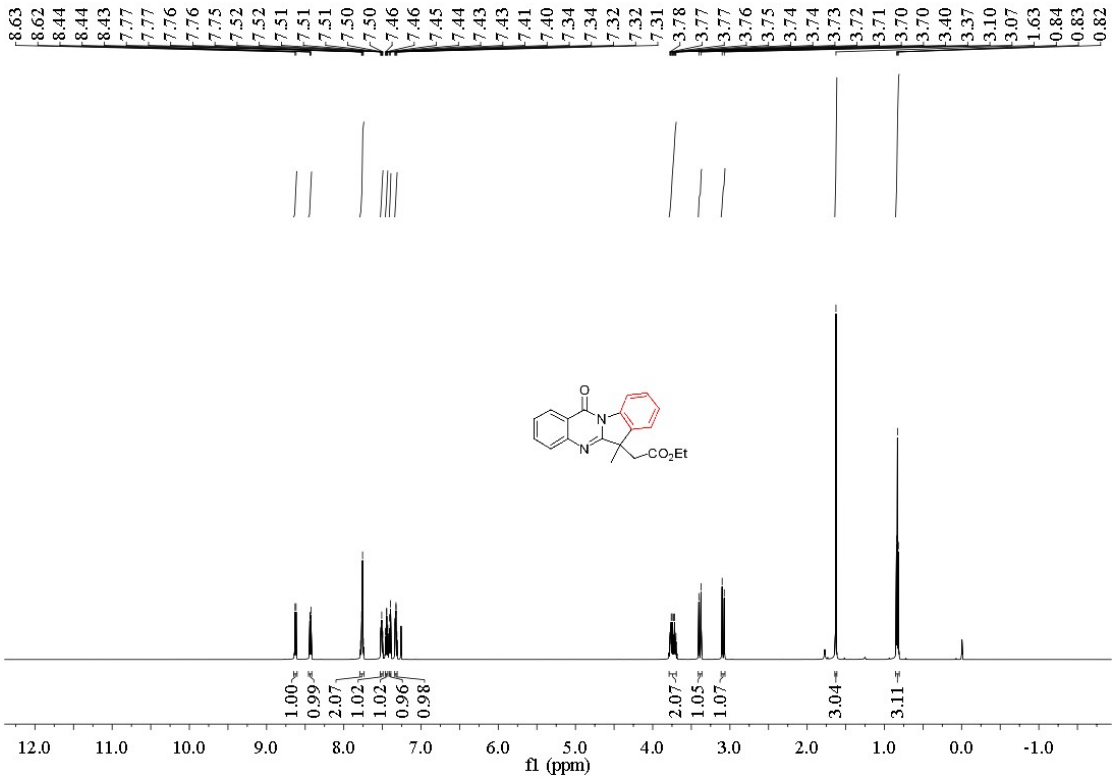
^{1}H NMR of **3m** (600 MHz, $CDCl_3$)



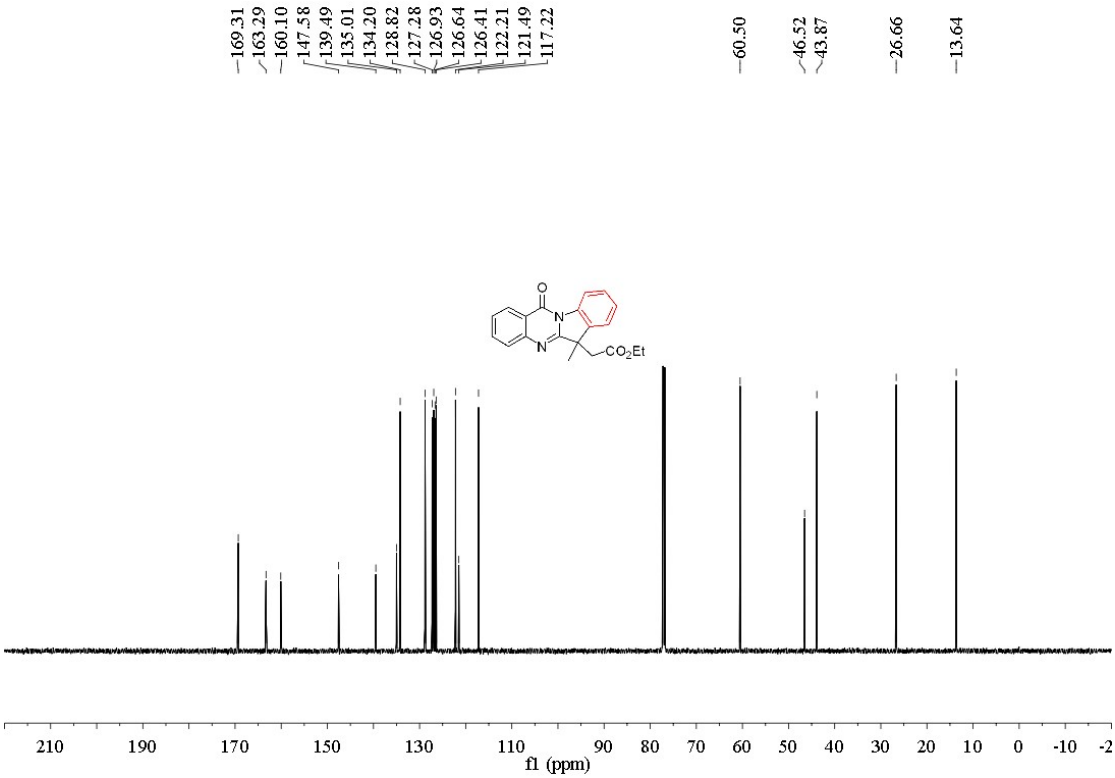
^{13}C NMR of **3m** (151 MHz, $CDCl_3$)



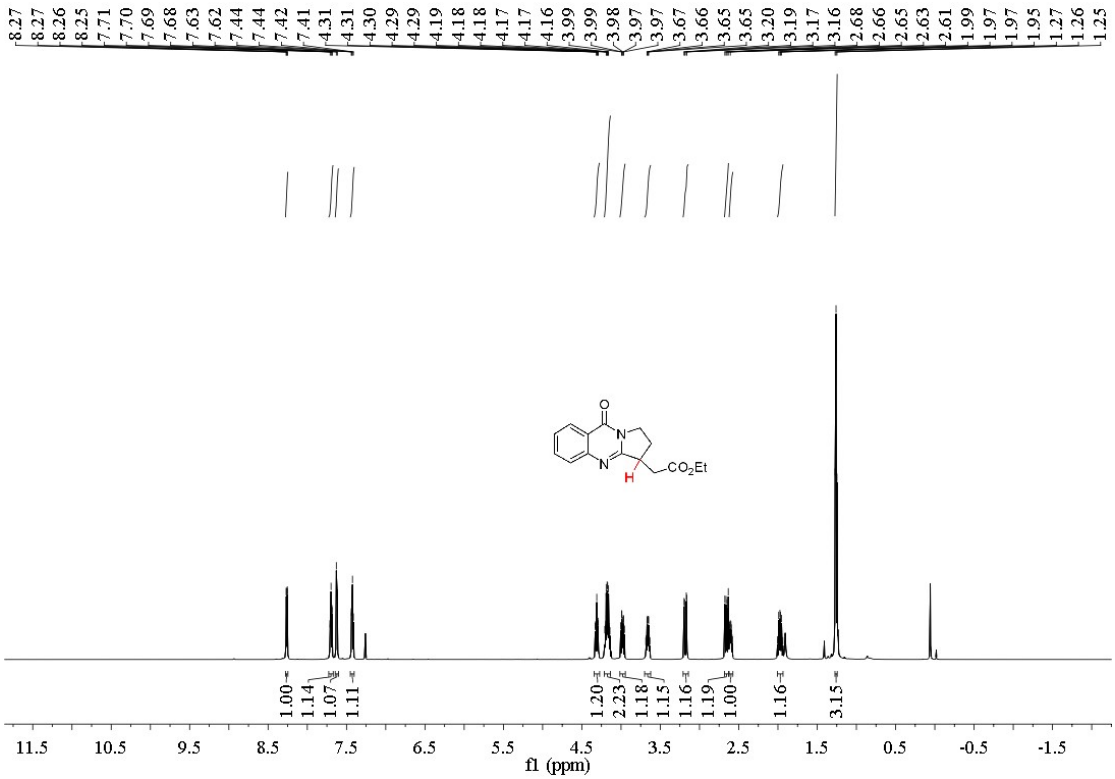
^{1}H NMR of **3n** (600 MHz, $CDCl_3$)



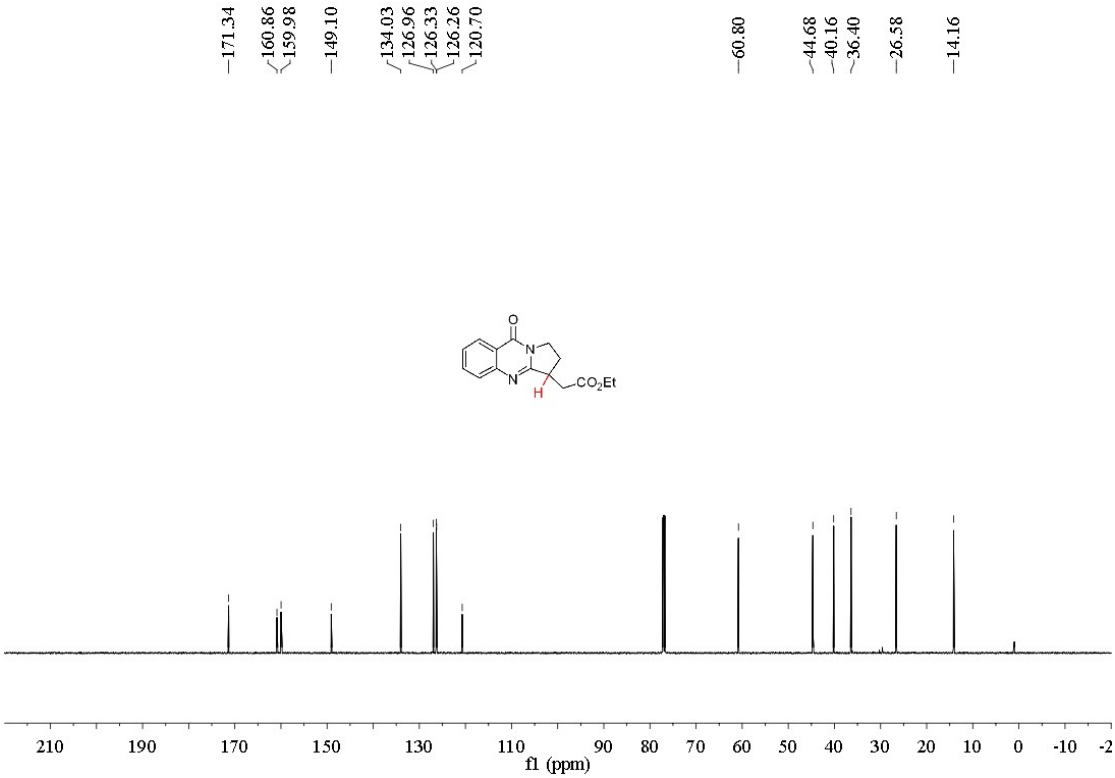
^{13}C NMR of **3n** (151 MHz, $CDCl_3$)



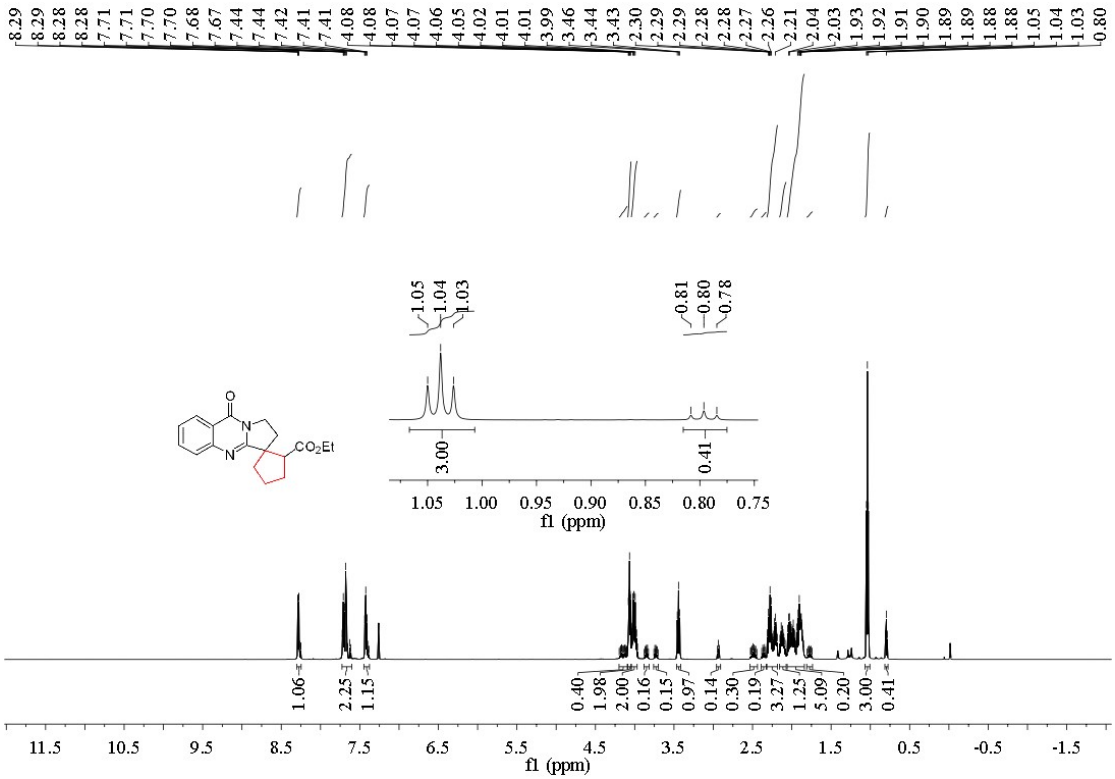
^{1}H NMR of **3o** (600 MHz, $CDCl_3$)



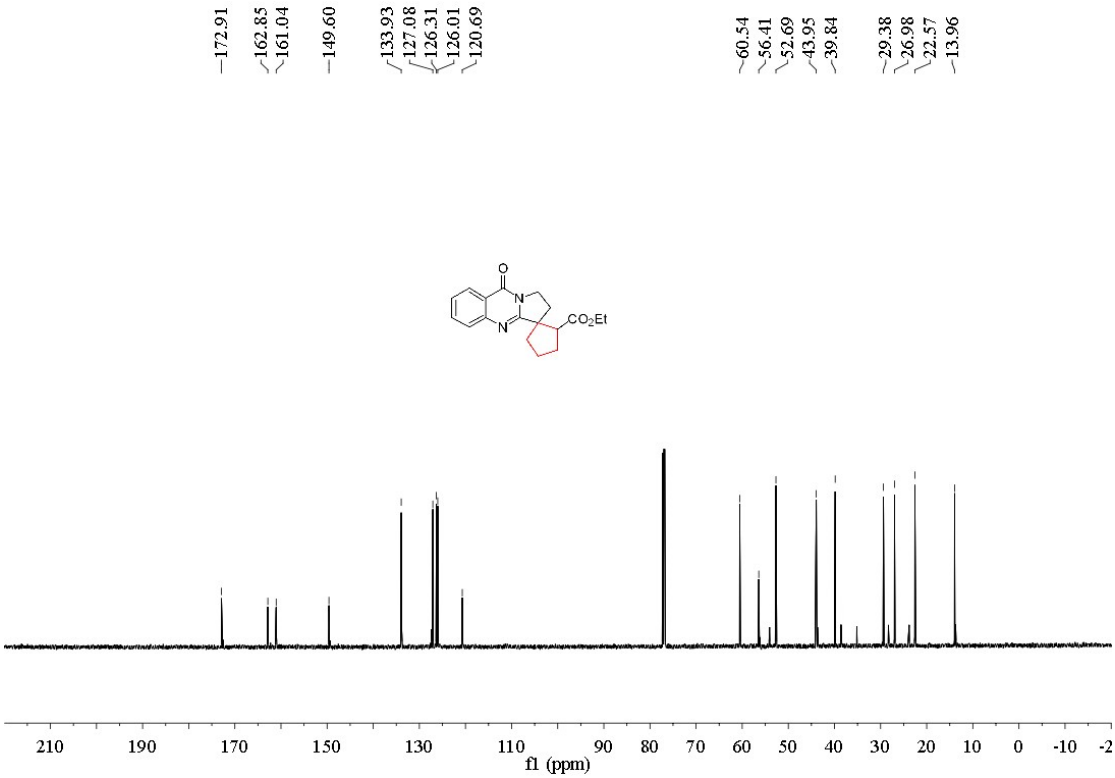
^{13}C NMR of **3o** (151 MHz, $CDCl_3$)



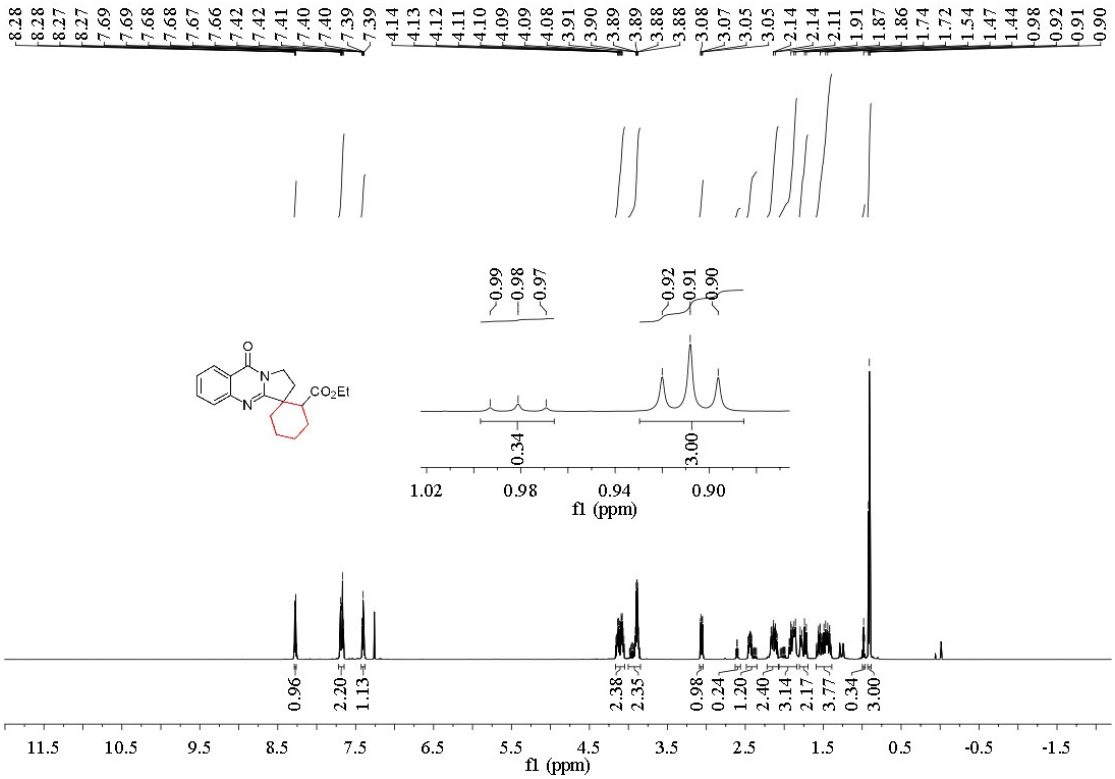
^{1}H NMR of **3p** (600 MHz, $CDCl_3$)



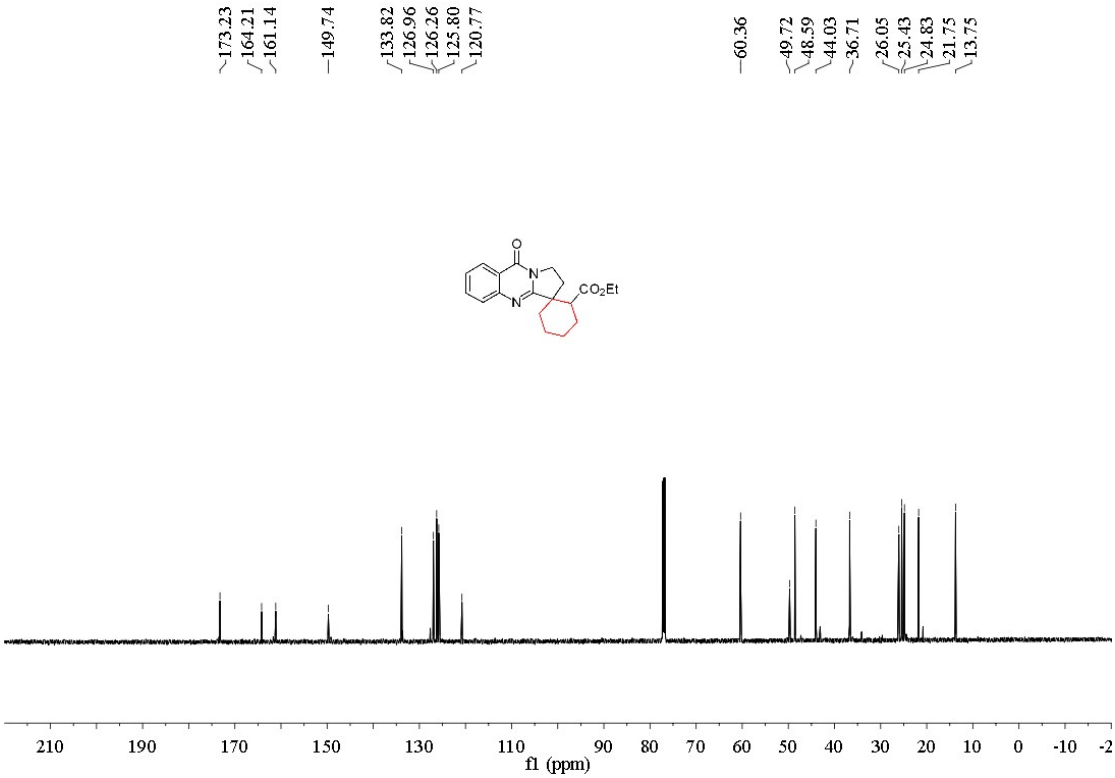
^{13}C NMR of **3p** (151 MHz, $CDCl_3$)



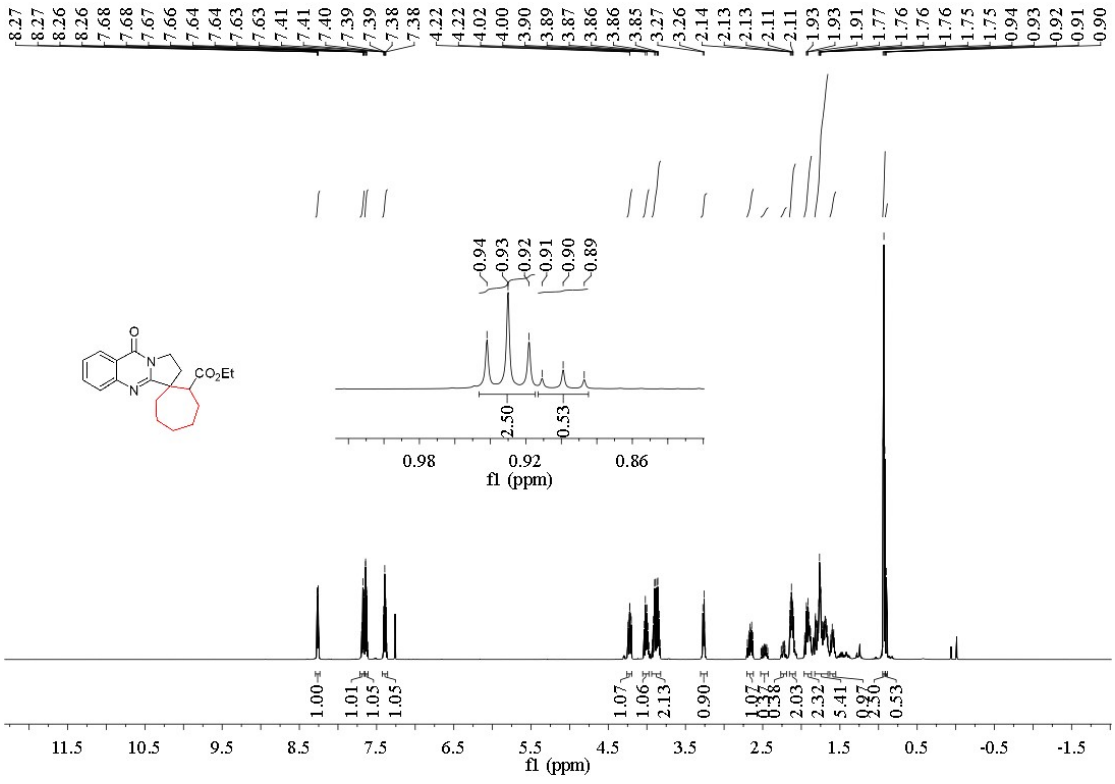
^{1}H NMR of **3q** (600 MHz, $CDCl_3$)



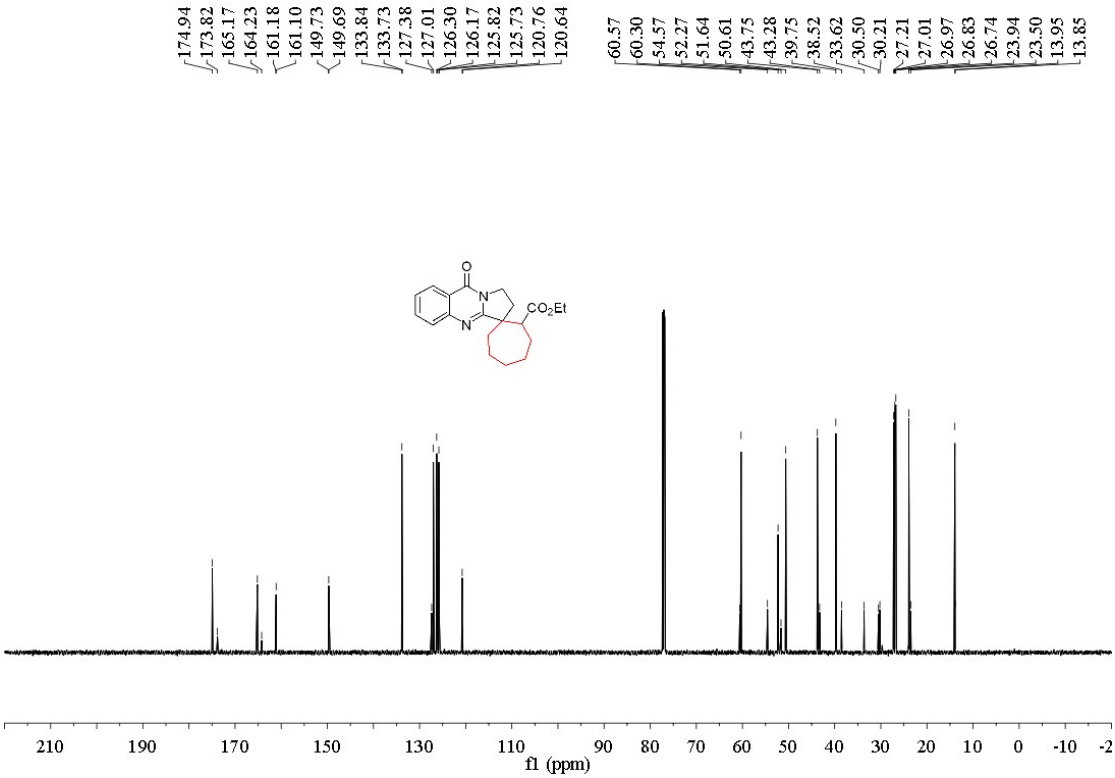
^{13}C NMR of **3q** (151 MHz, $CDCl_3$)



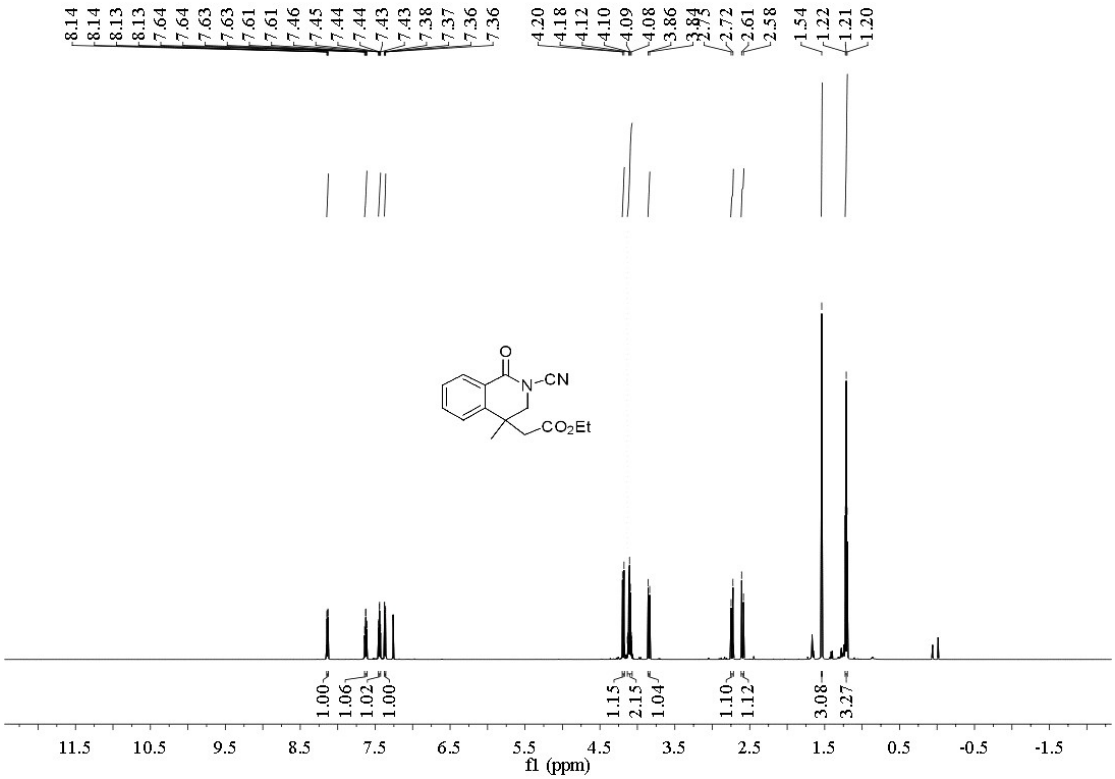
^{1}H NMR of **3r** (600 MHz, $CDCl_3$)



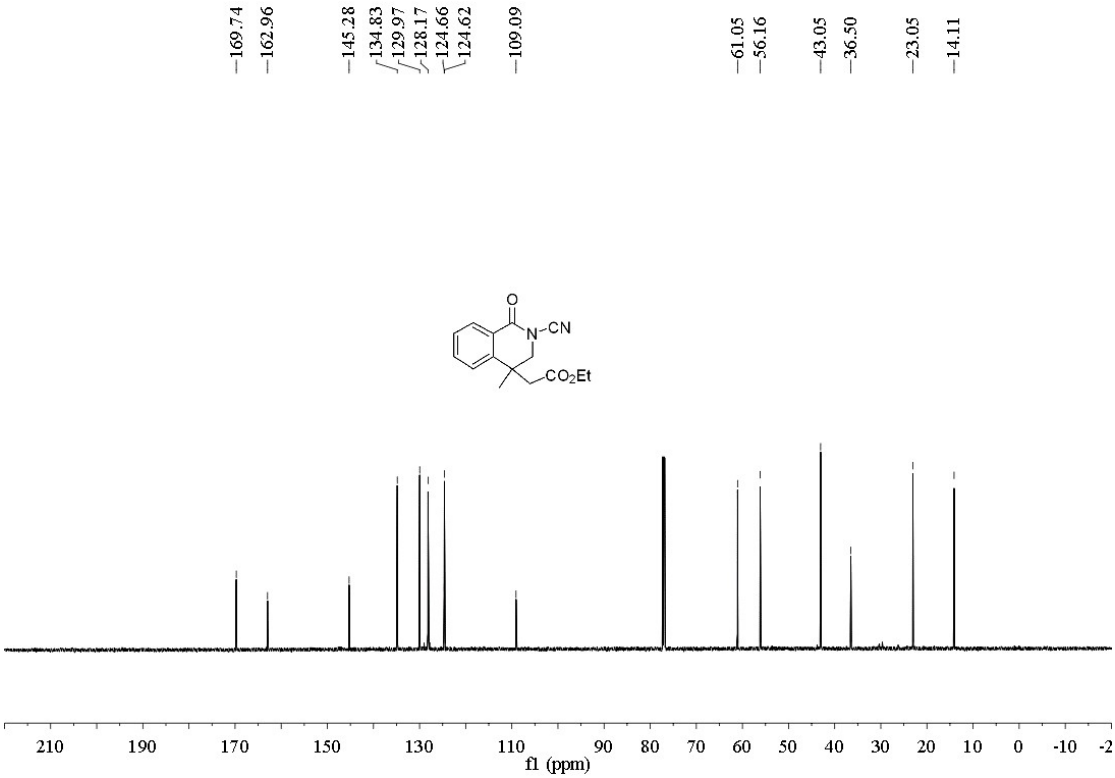
^{13}C NMR of **3r** (151 MHz, $CDCl_3$)



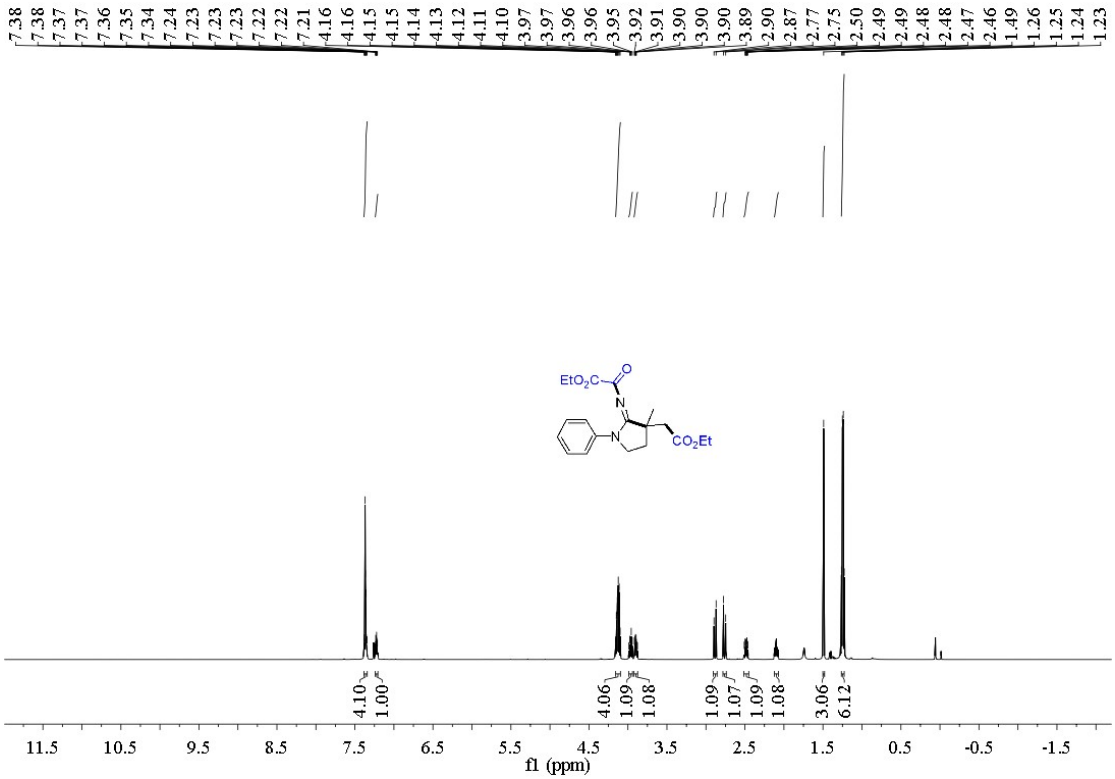
^{1}H NMR of **3s** (600 MHz, $CDCl_3$)



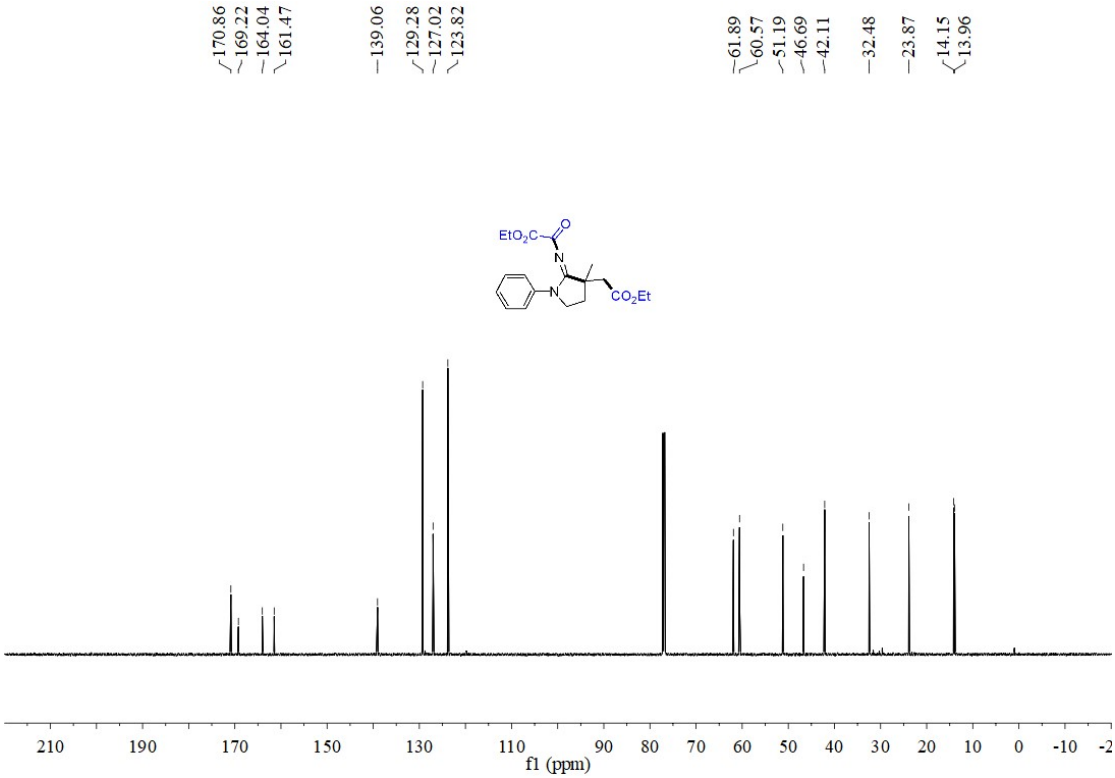
^{13}C NMR of **3s** (151 MHz, $CDCl_3$)



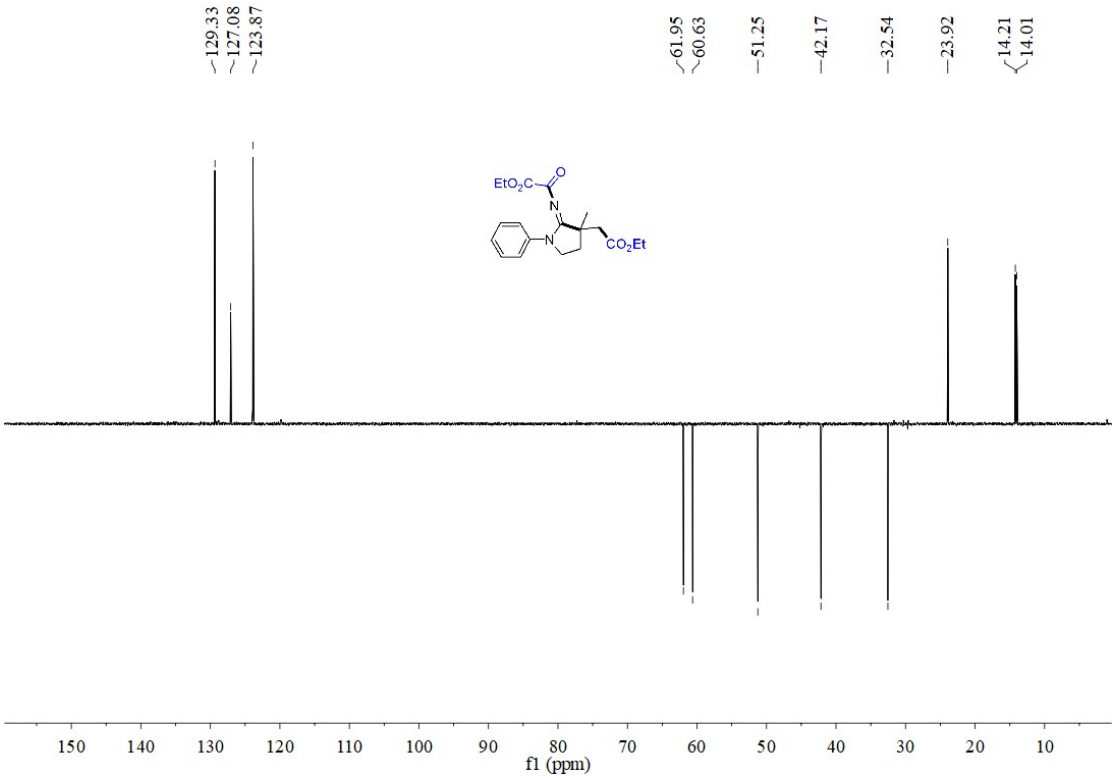
^{1}H NMR of **3t** (600 MHz, $CDCl_3$)



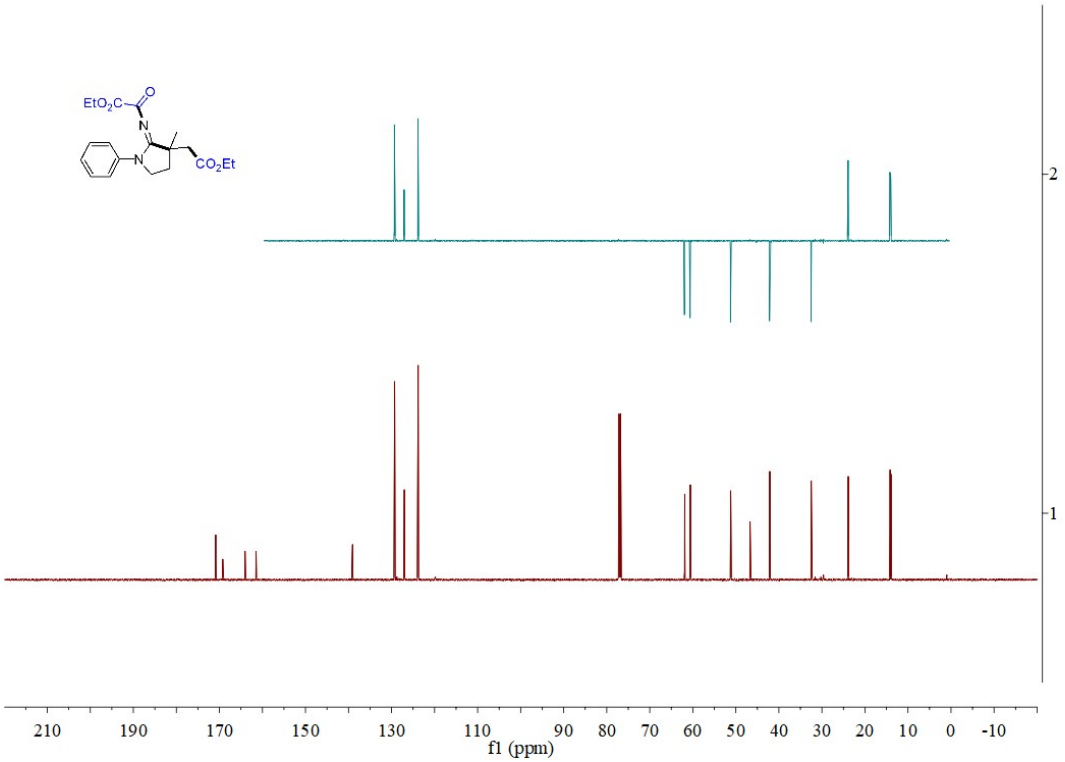
^{13}C NMR of **3t** (151 MHz, $CDCl_3$)



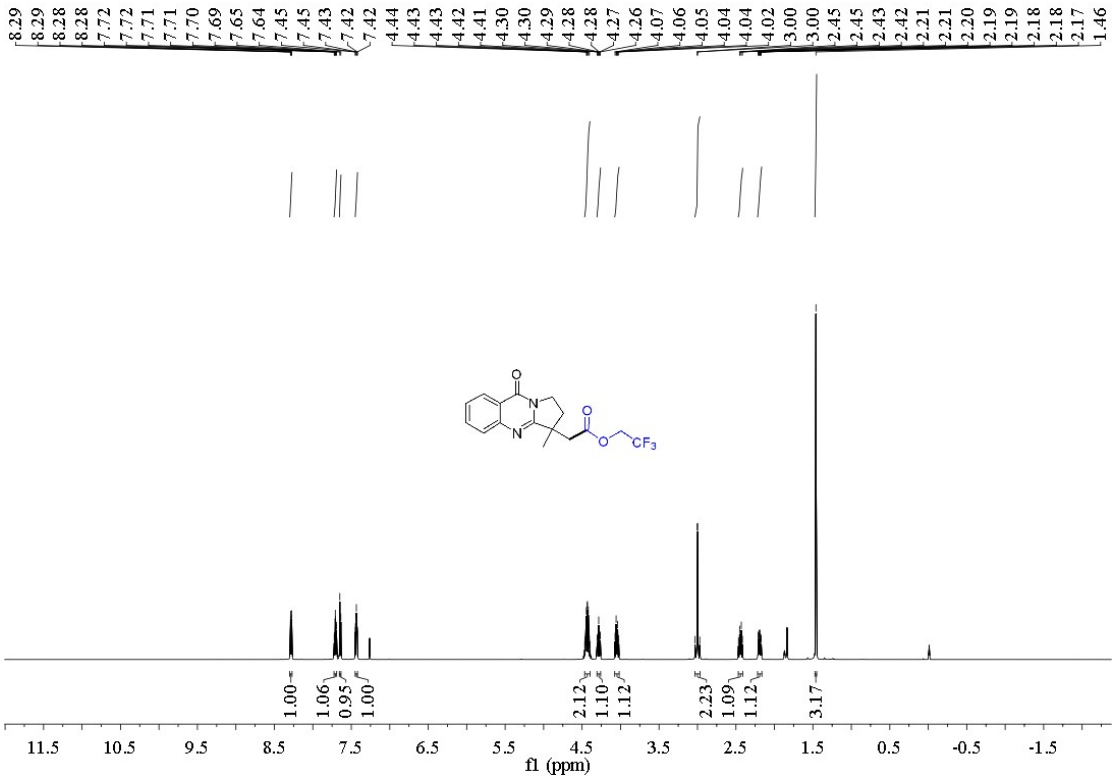
DEPT 135° spectrum of **3t**



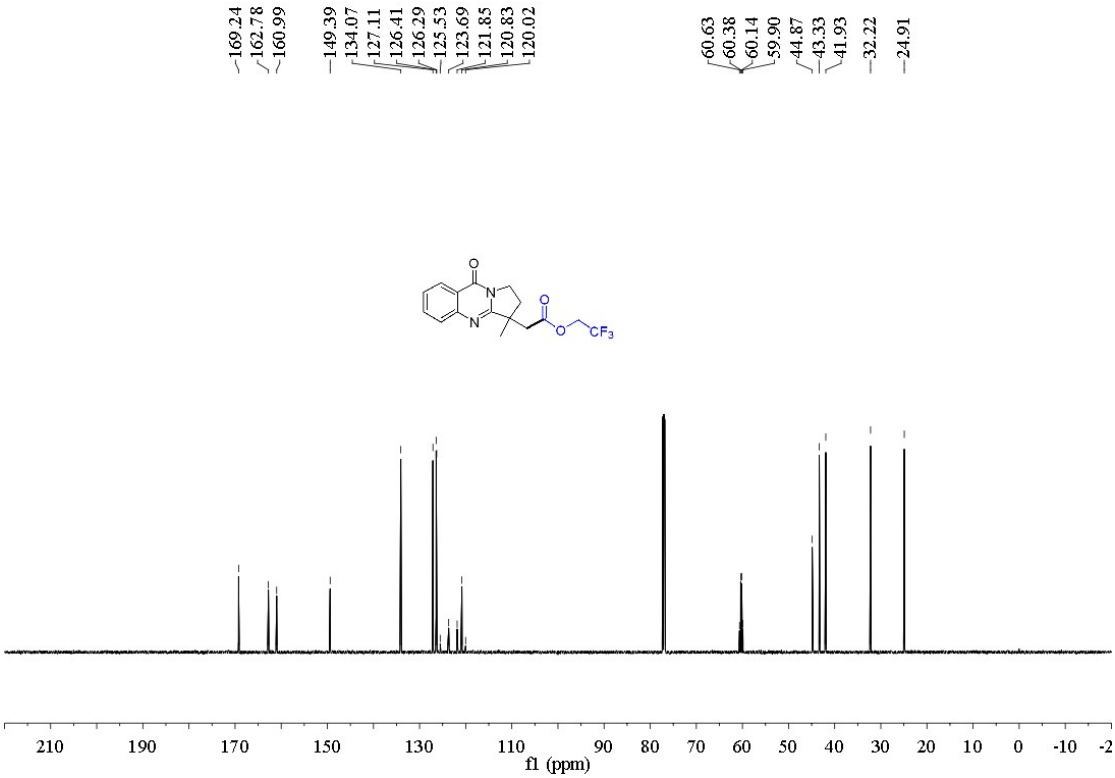
DEPT 135° spectrum of **3t**



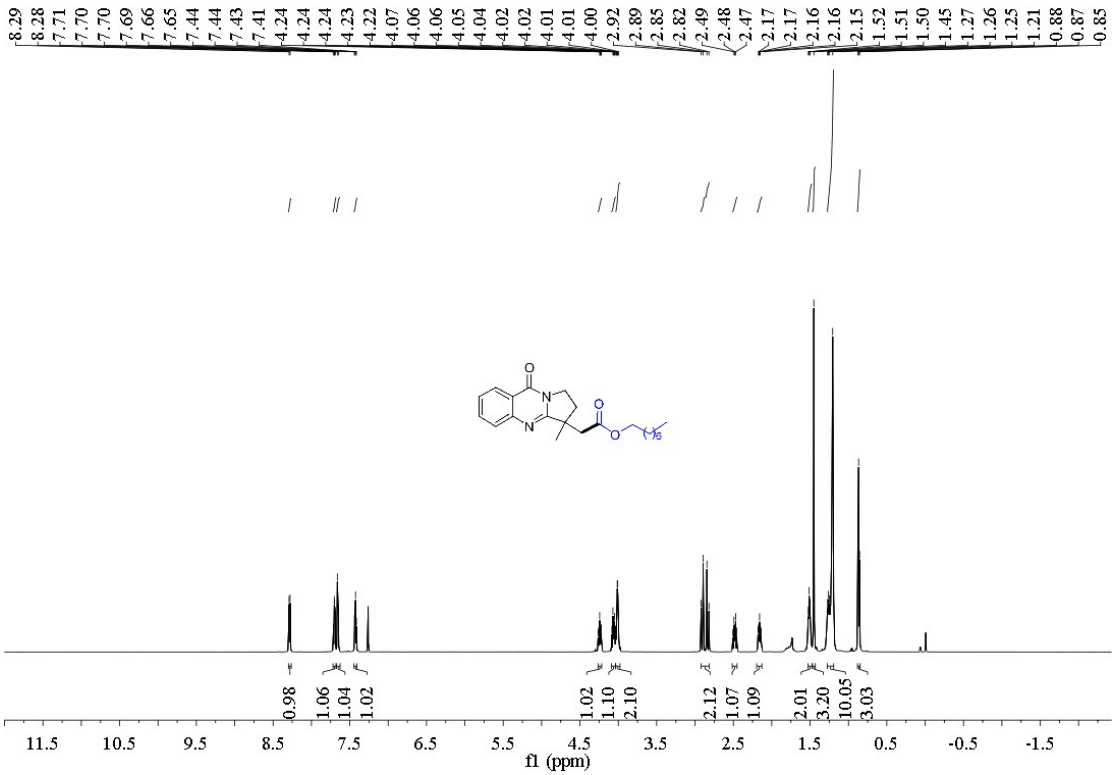
^{1}H NMR of **3u** (600 MHz, $CDCl_3$)



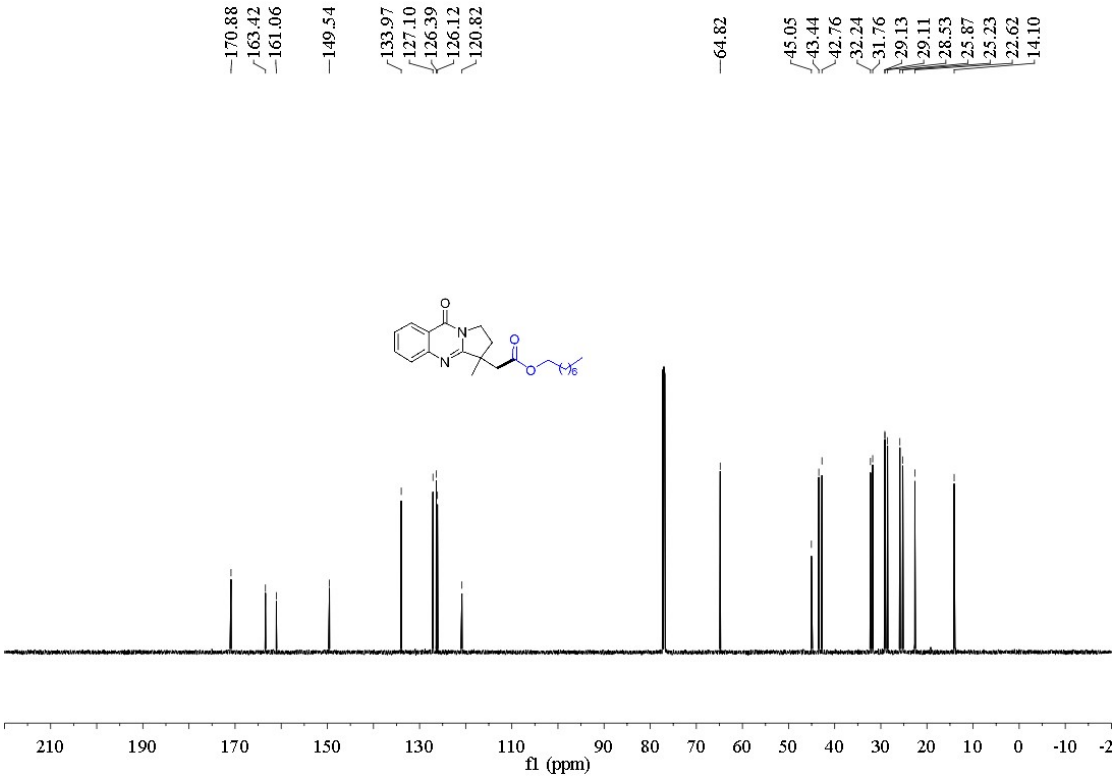
^{13}C NMR of **3u** (151 MHz, $CDCl_3$)



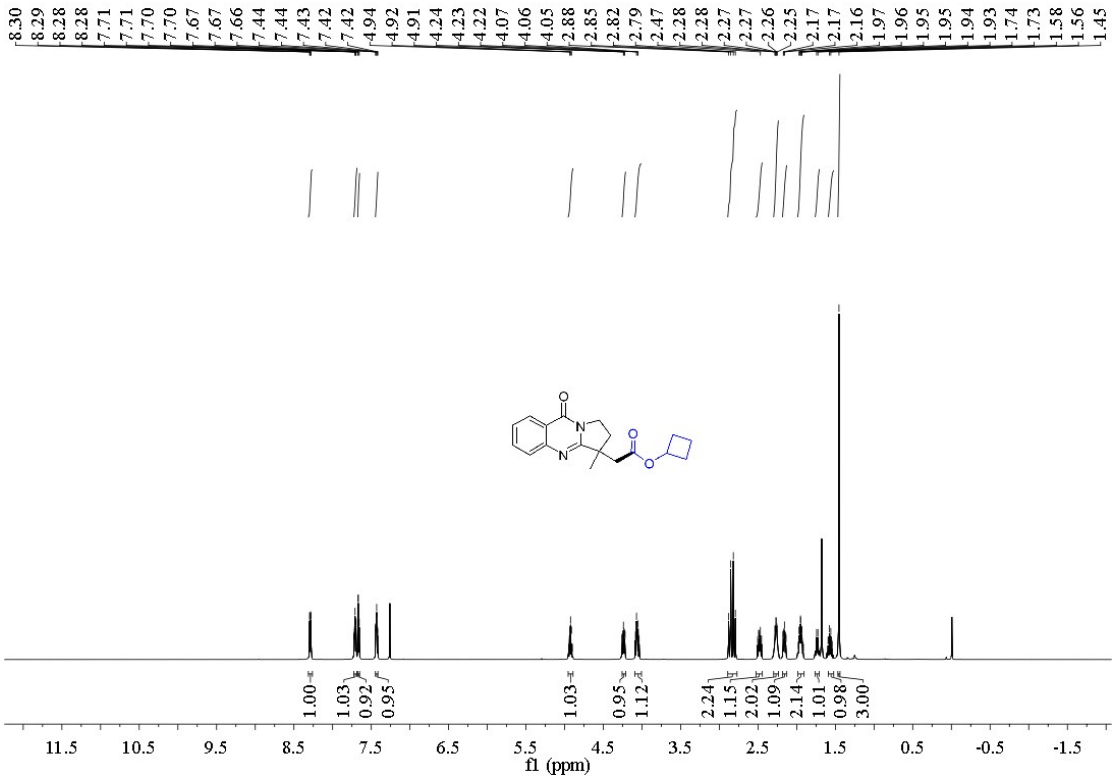
^{1}H NMR of **3v** (600 MHz, $CDCl_3$)



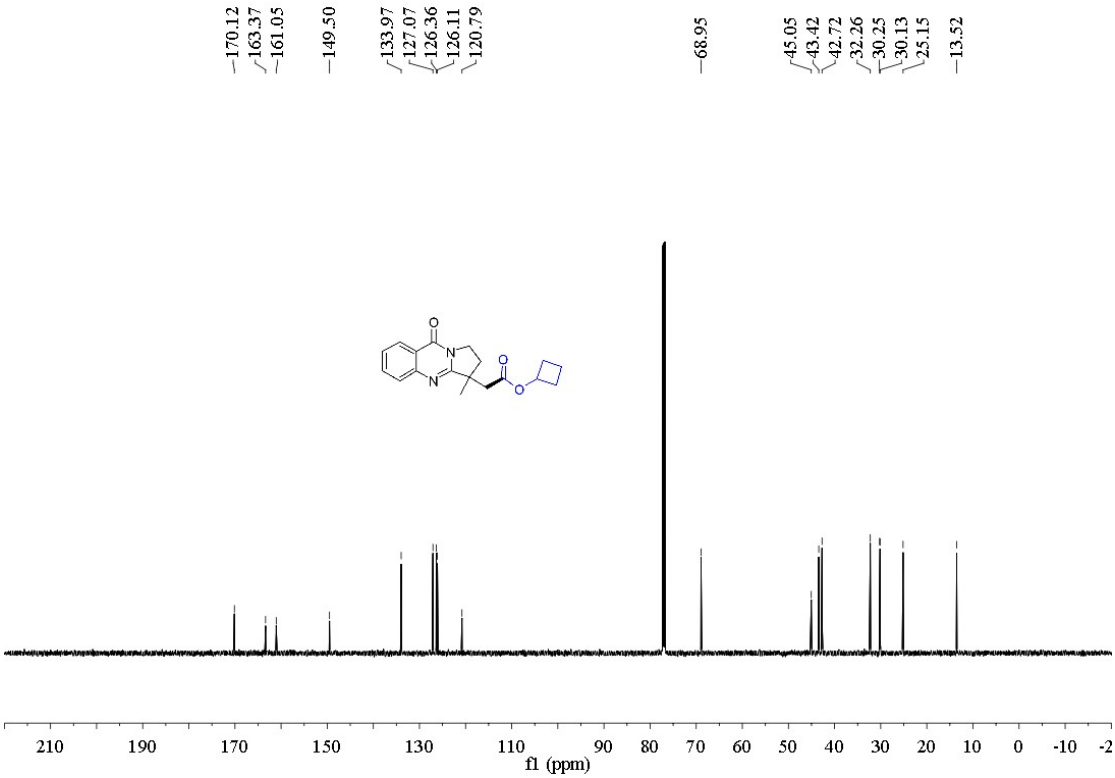
^{13}C NMR of **3v** (151 MHz, $CDCl_3$)



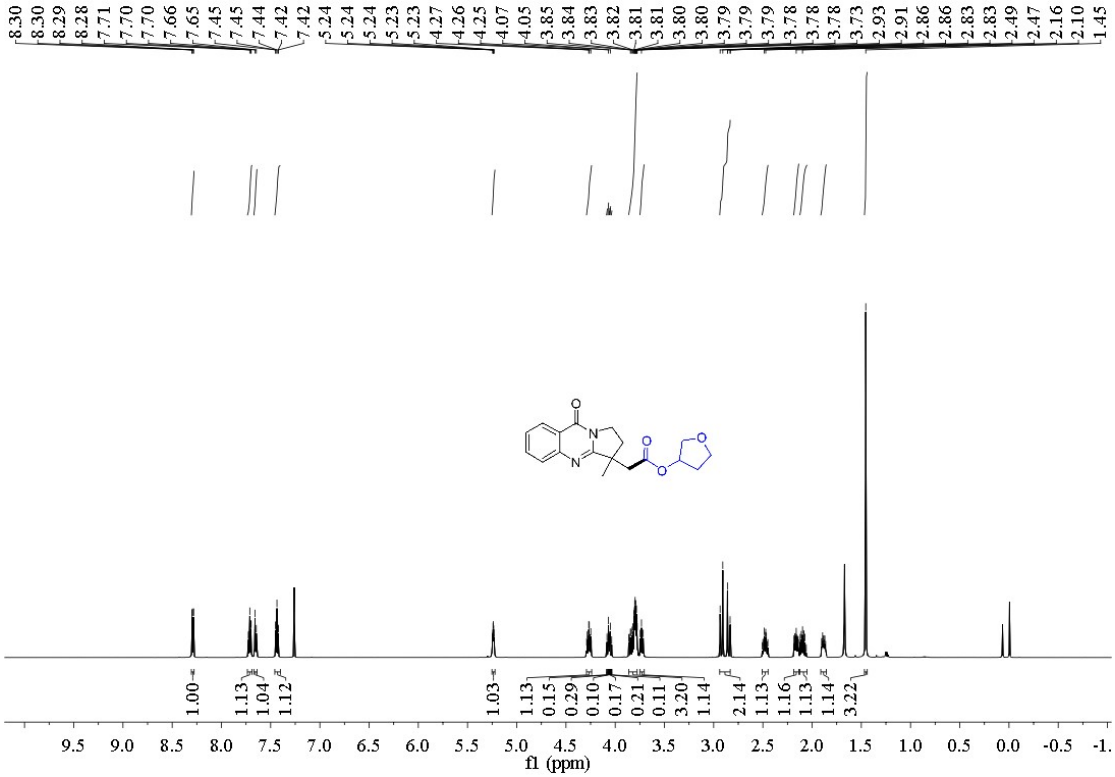
^{1}H NMR of **3w** (600 MHz, $CDCl_3$)



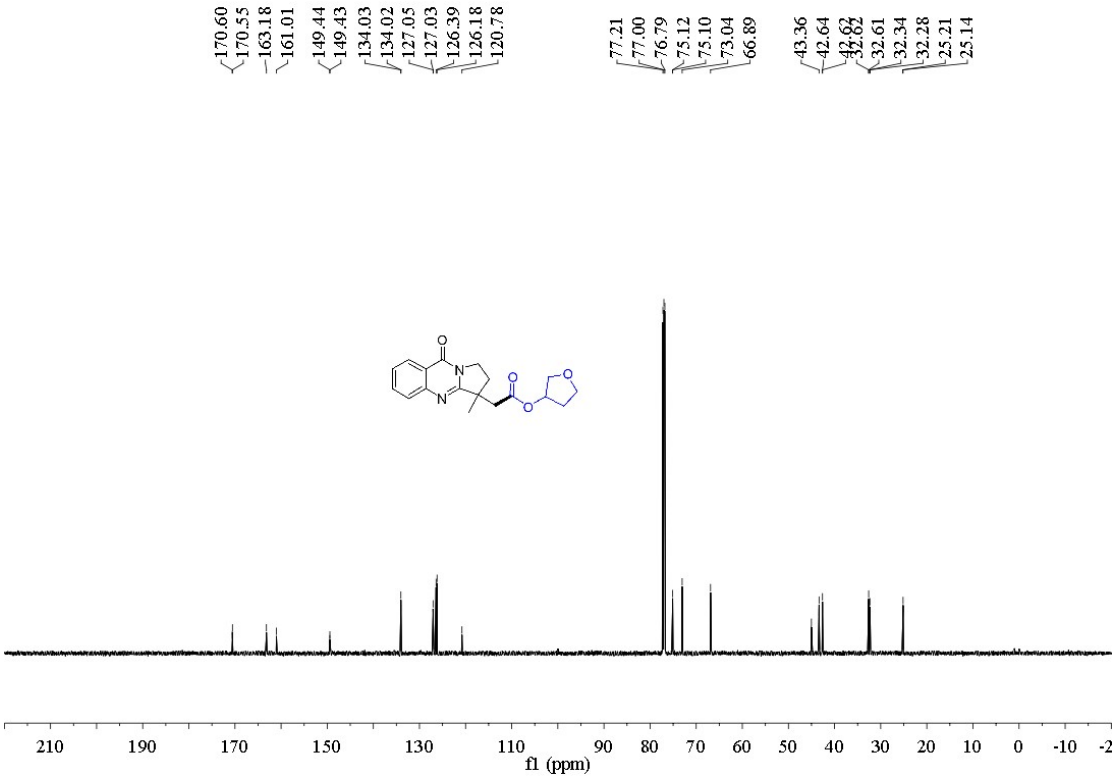
^{13}C NMR of **3w** (151 MHz, $CDCl_3$)



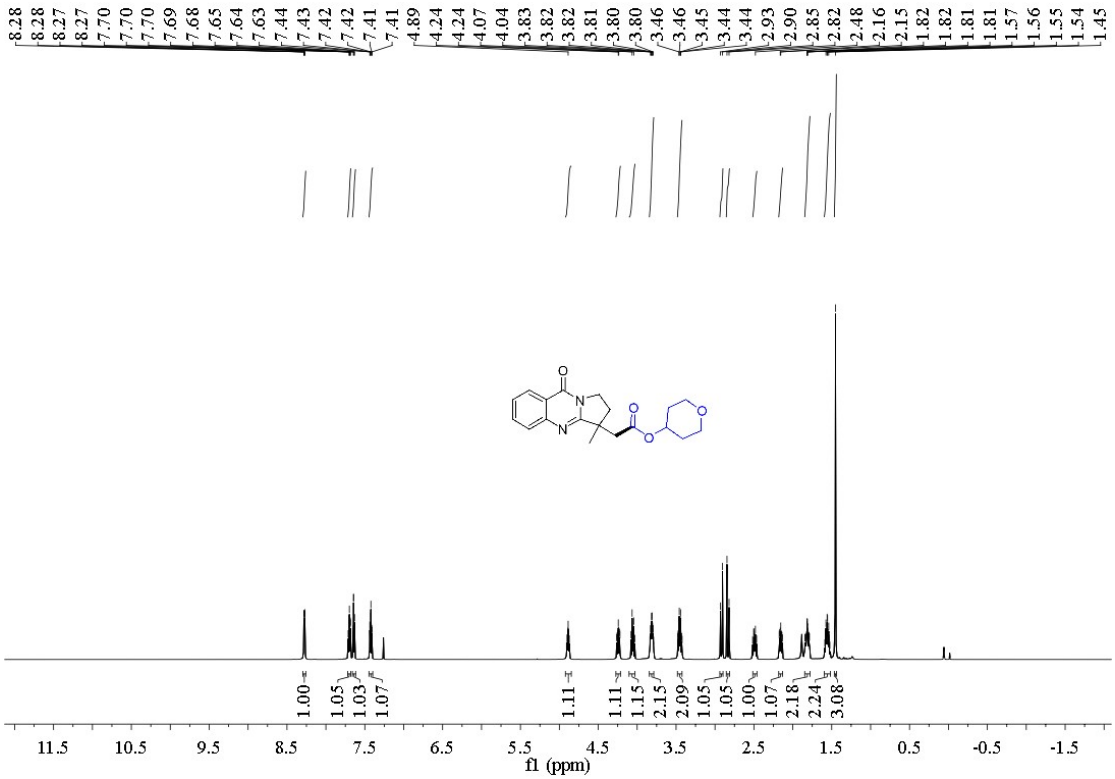
^{1}H NMR of **3x** (600 MHz, $CDCl_3$)



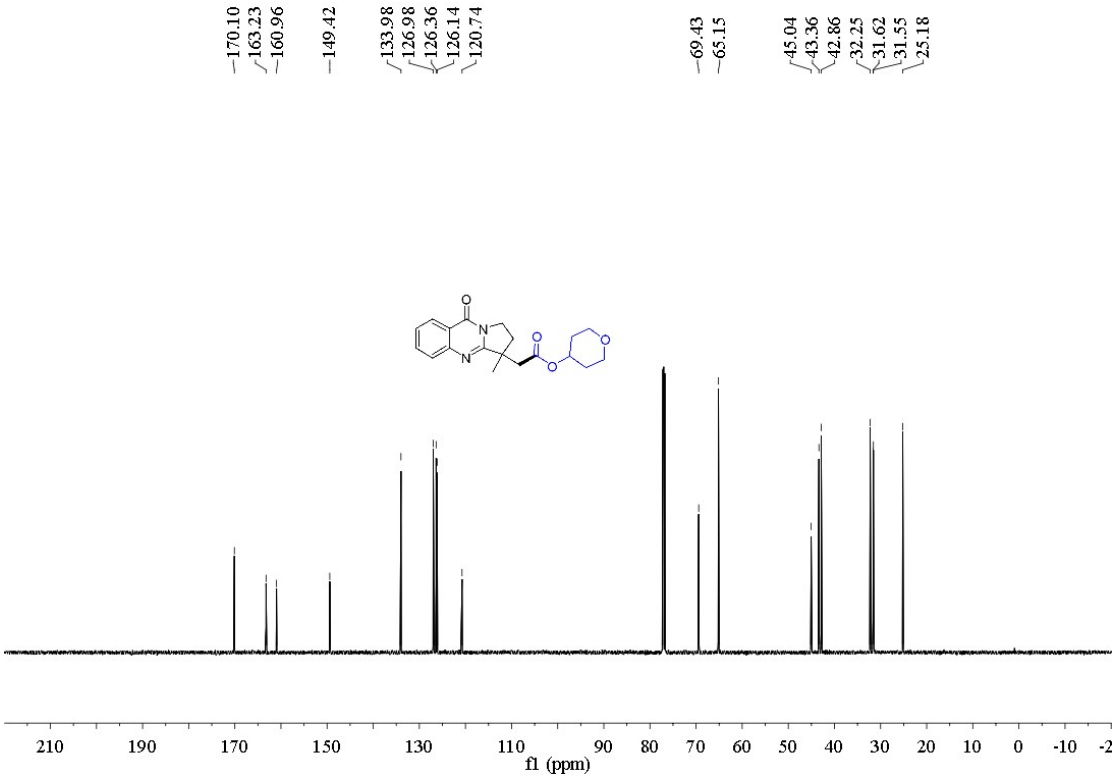
^{13}C NMR of **3x** (151 MHz, $CDCl_3$)



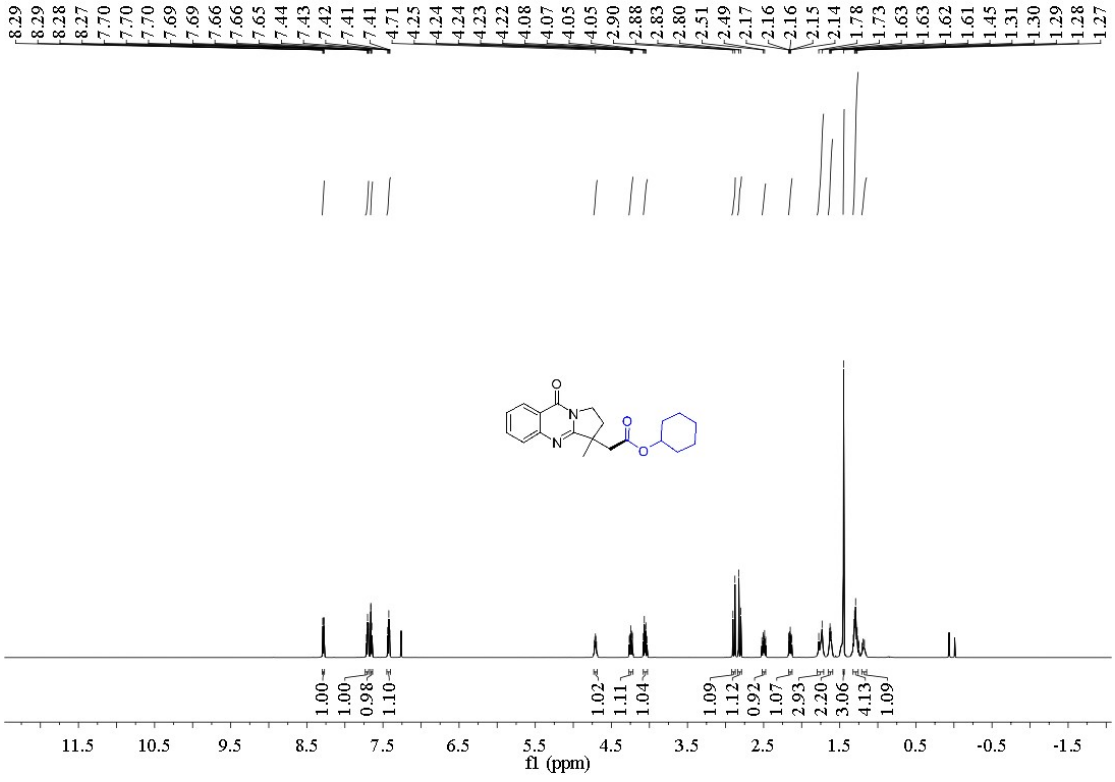
^{1}H NMR of **3y** (600 MHz, $CDCl_3$)



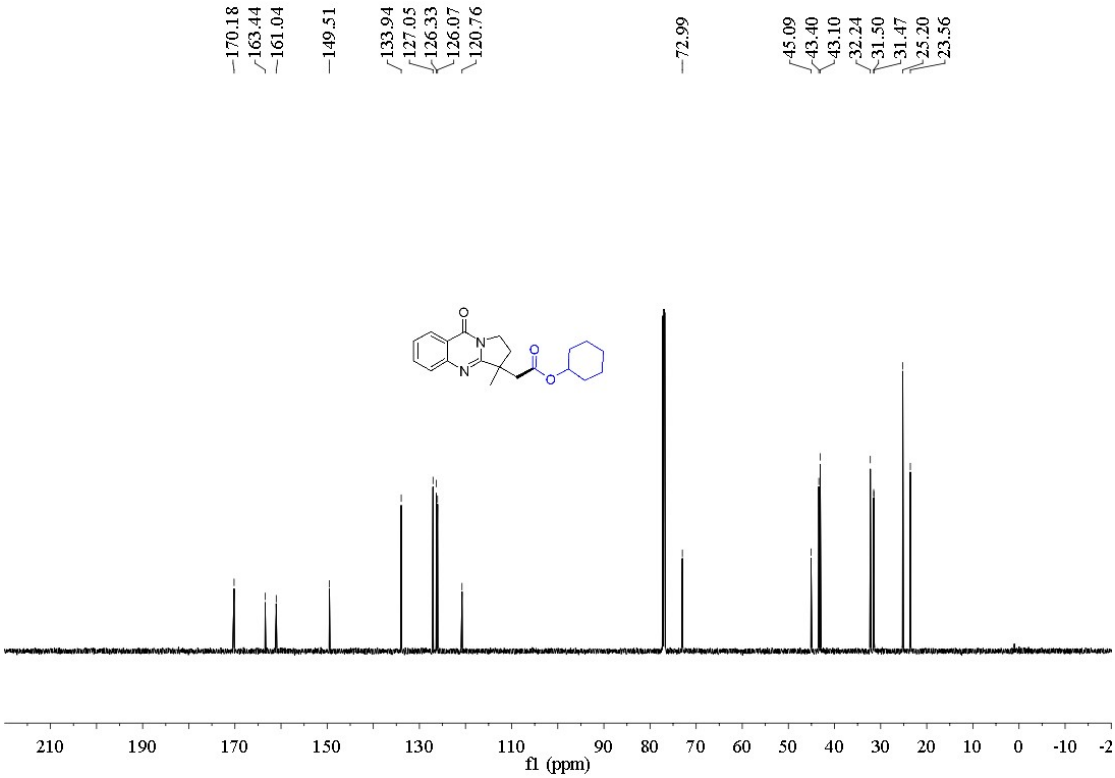
^{13}C NMR of **3y** (151 MHz, $CDCl_3$)



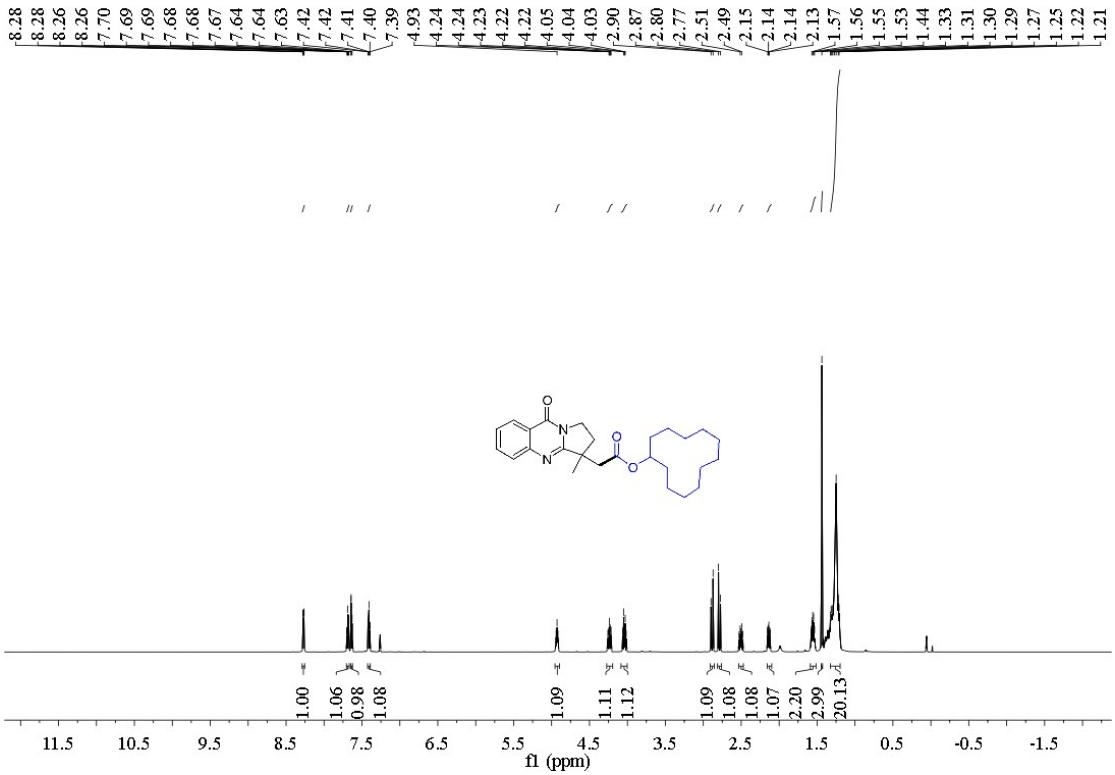
^{1}H NMR of **3z** (600 MHz, $CDCl_3$)



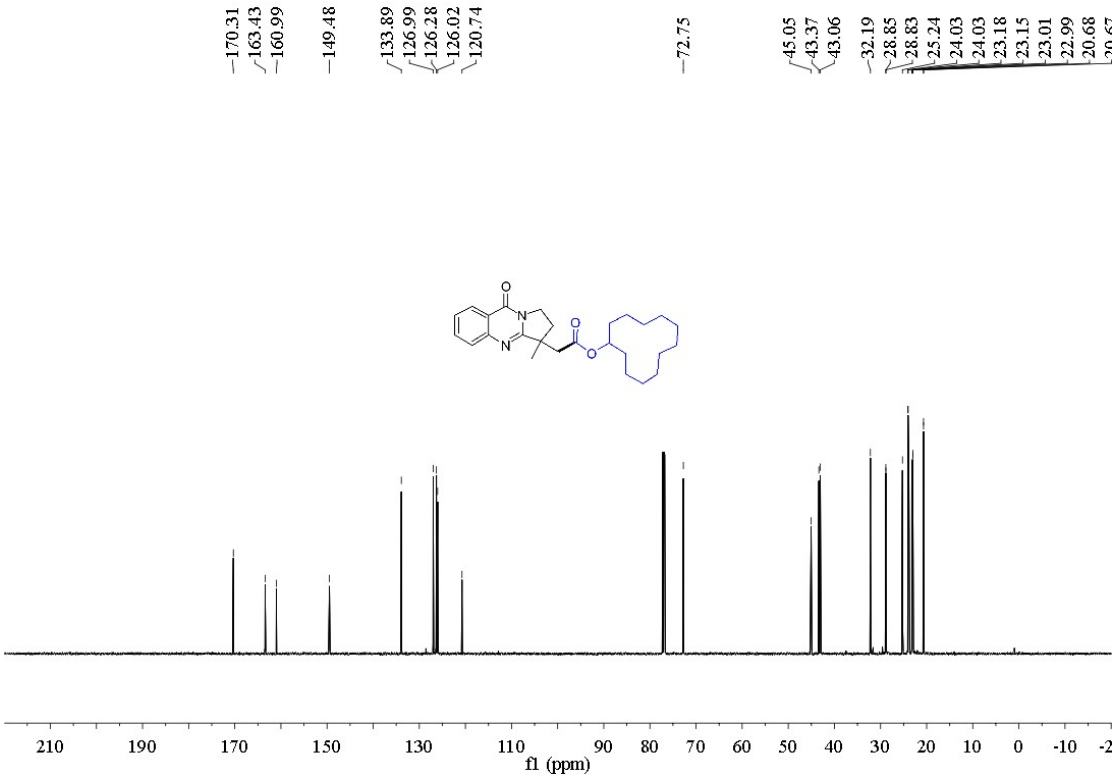
^{13}C NMR of **3z** (151 MHz, $CDCl_3$)



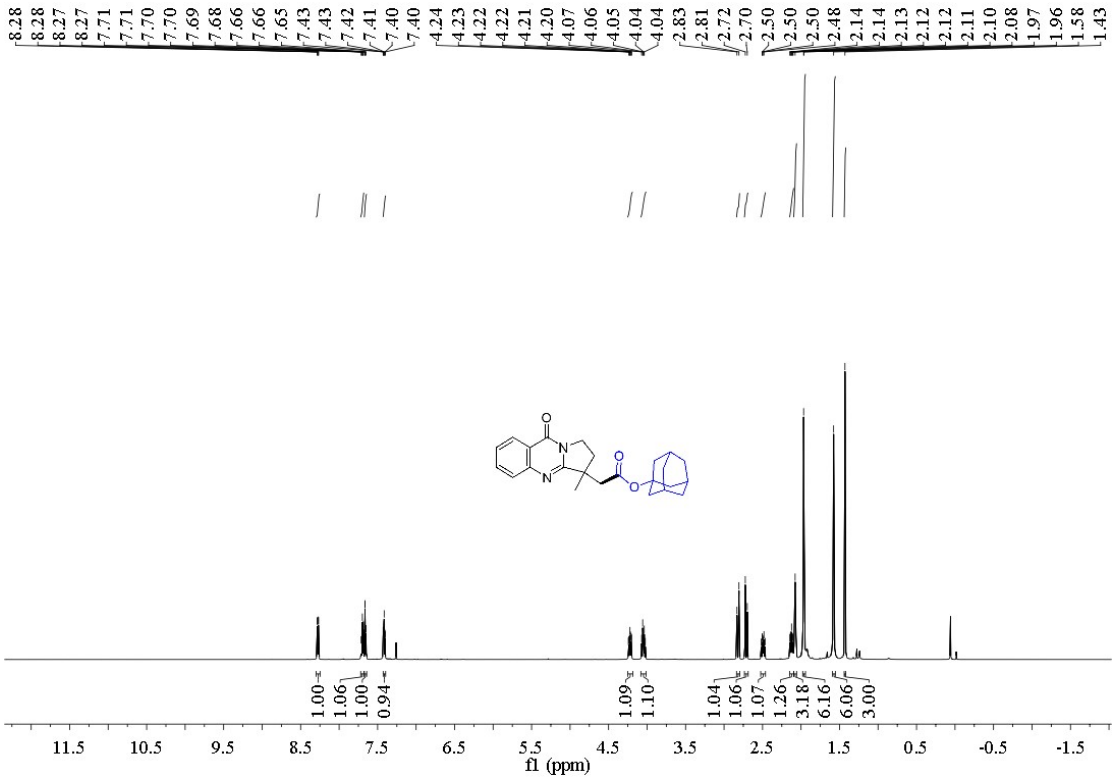
^{1}H NMR of **3aa** (600 MHz, $CDCl_3$)



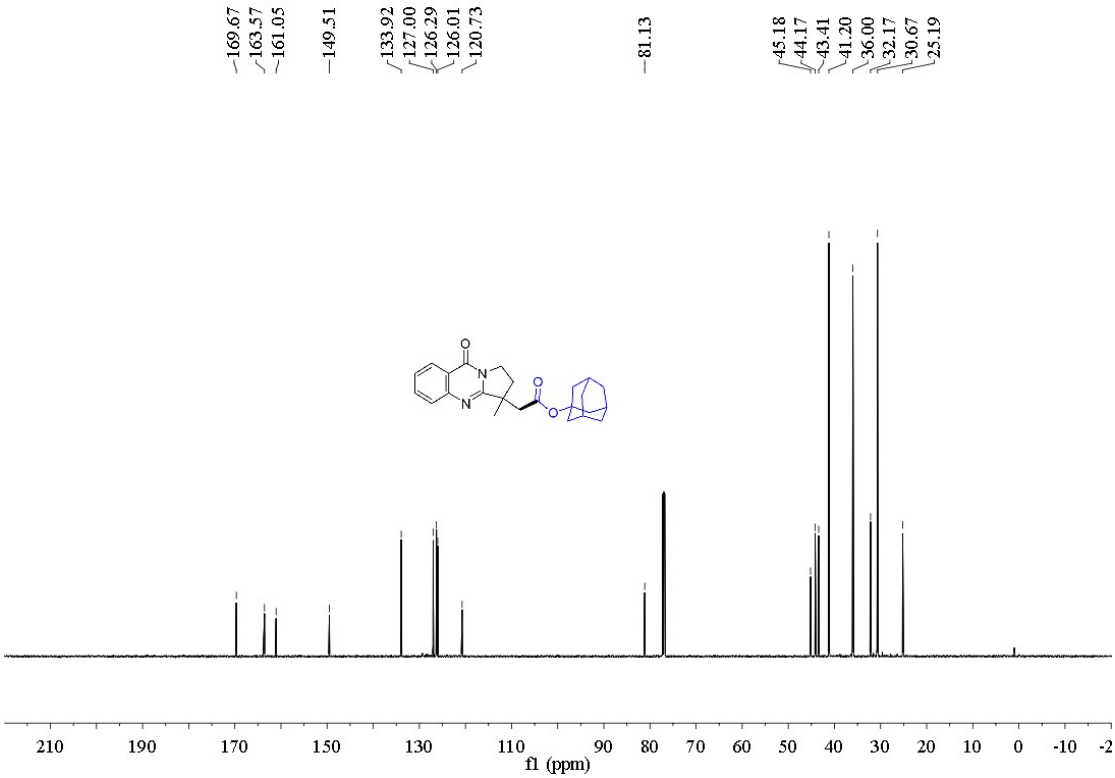
^{13}C NMR of **3aa** (151 MHz, $CDCl_3$)



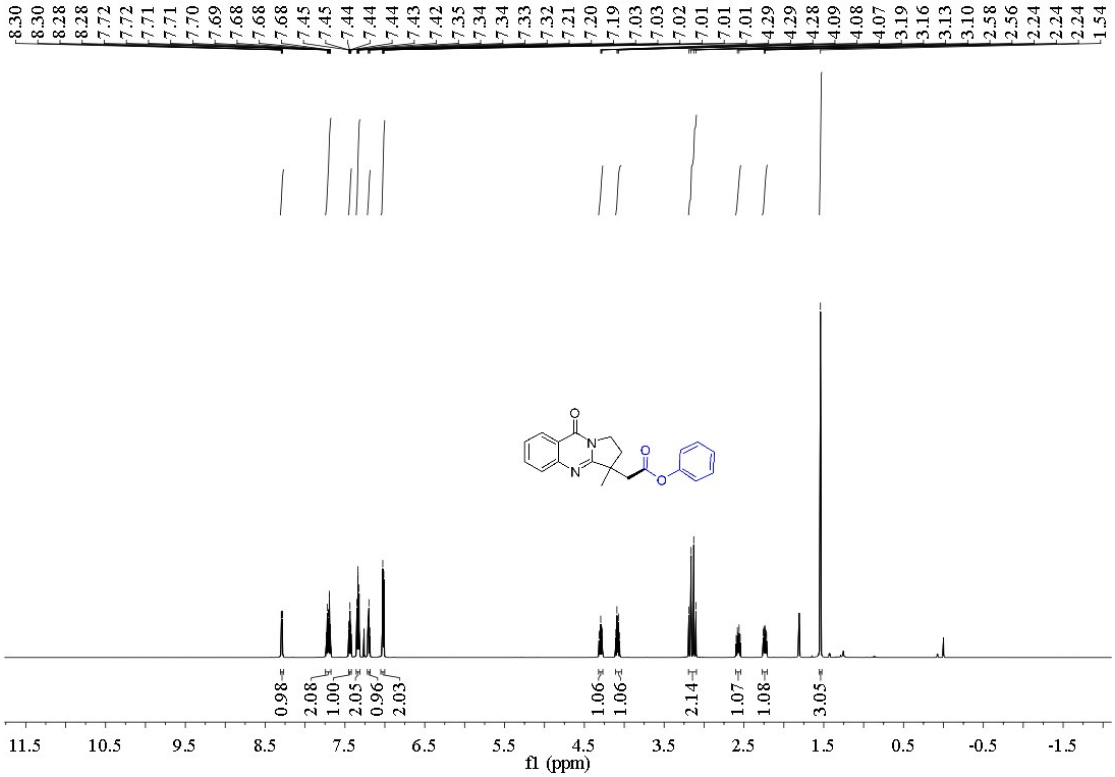
^{1}H NMR of **3ac** (600 MHz, $CDCl_3$)



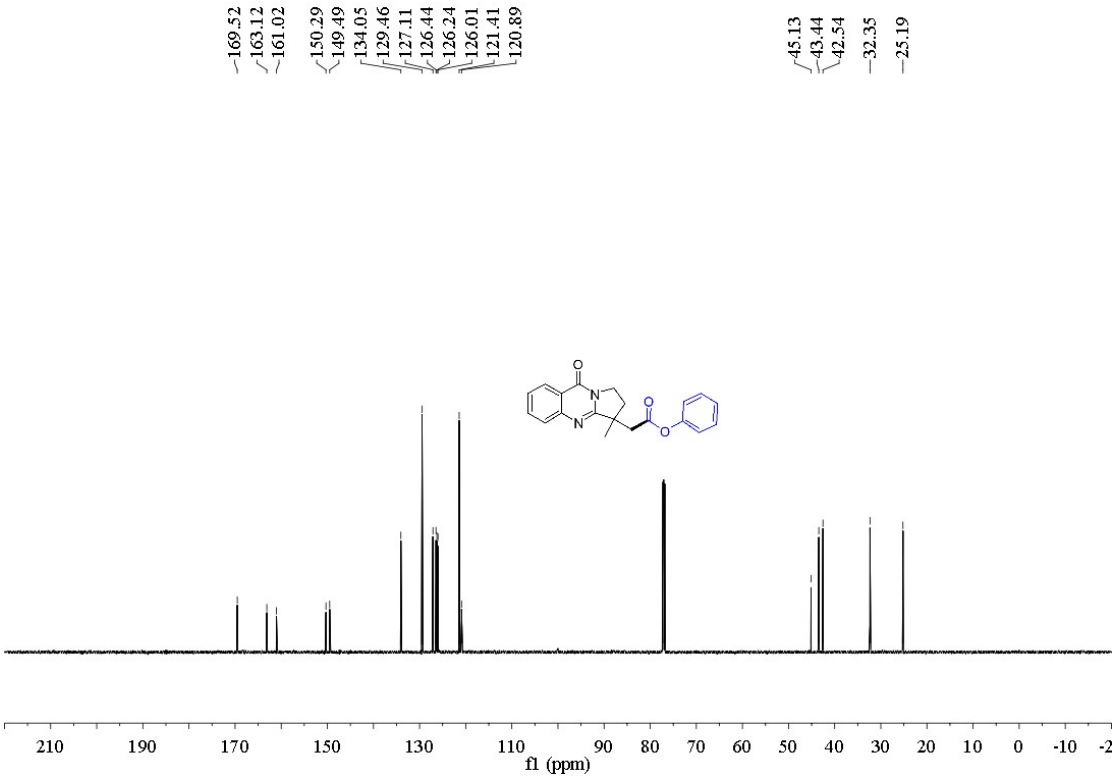
^{13}C NMR of **3ac** (151 MHz, $CDCl_3$)



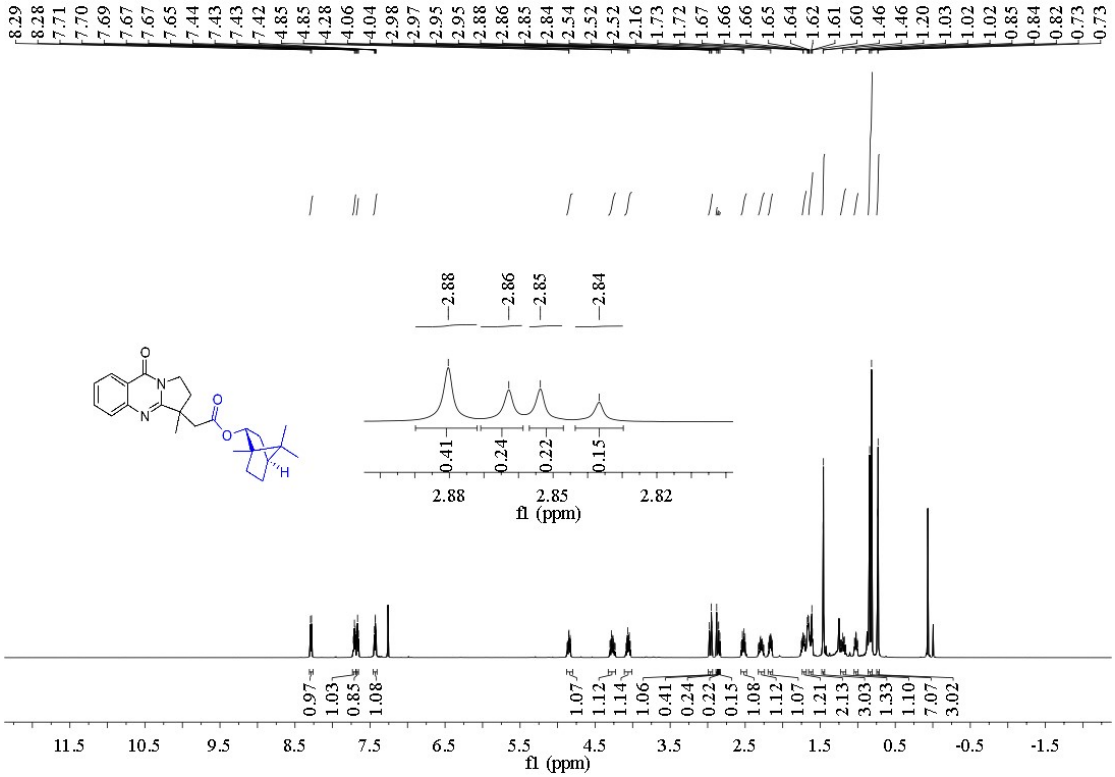
^{1}H NMR of **3ad** (600 MHz, $CDCl_3$)



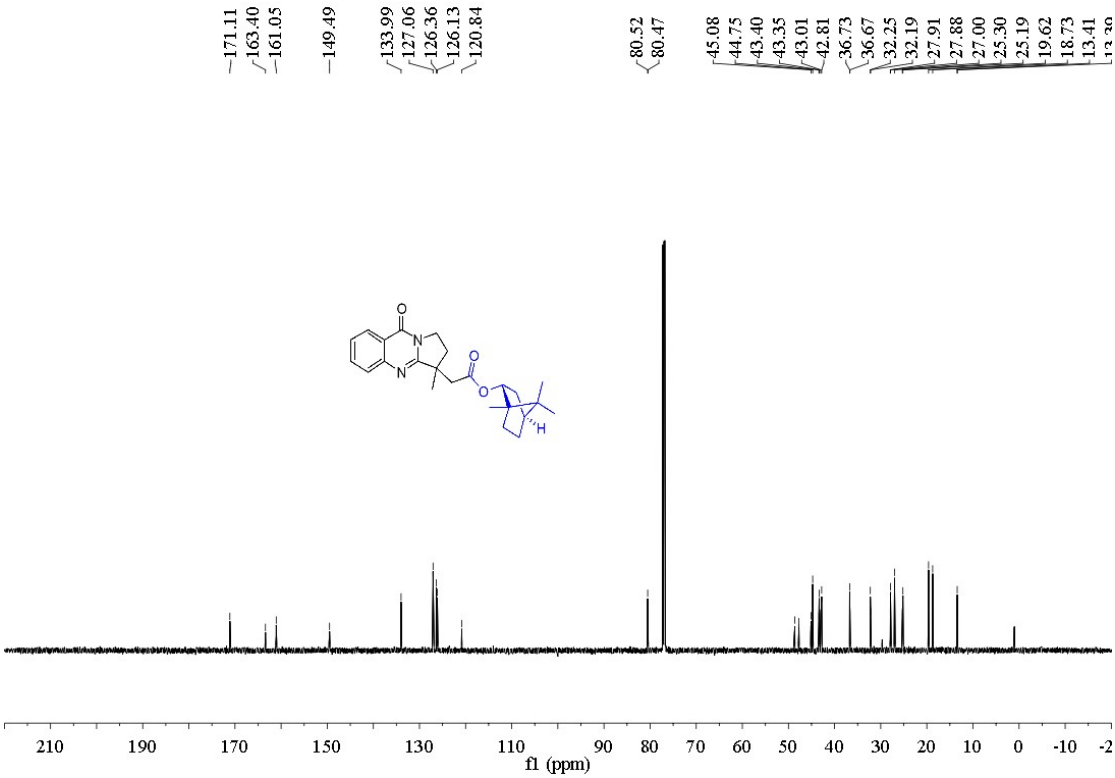
^{13}C NMR of **3ad** (151 MHz, $CDCl_3$)



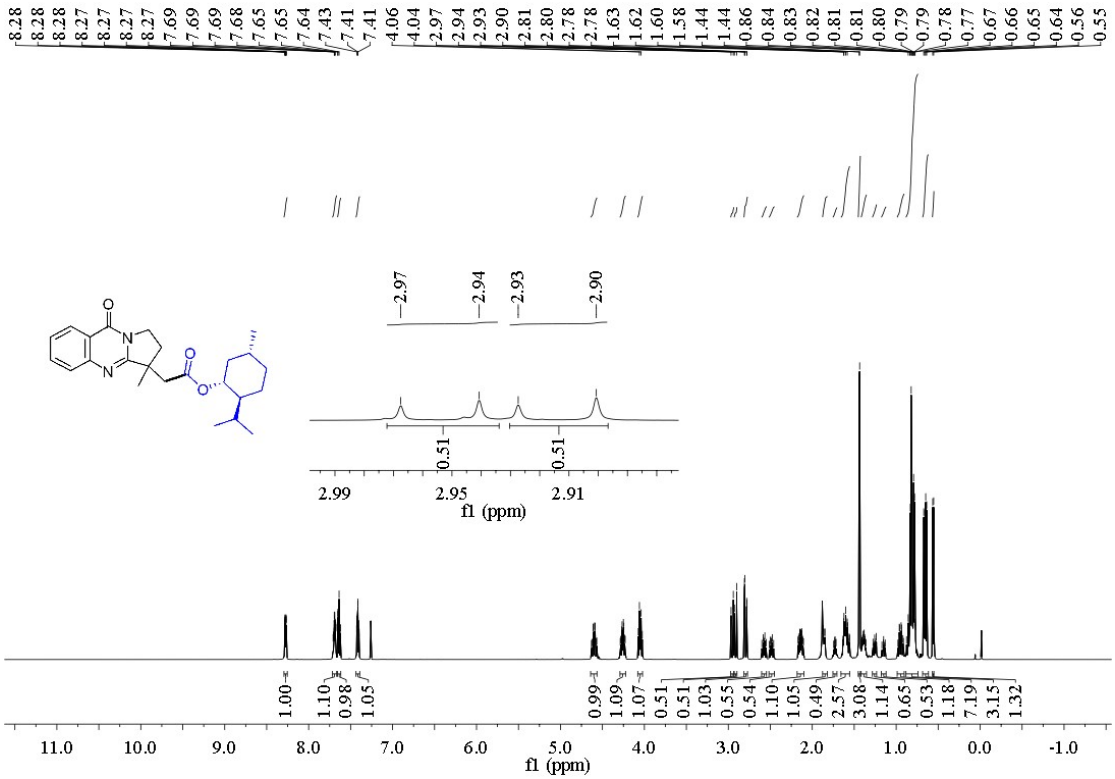
^{1}H NMR of **3ae** (600 MHz, $CDCl_3$)



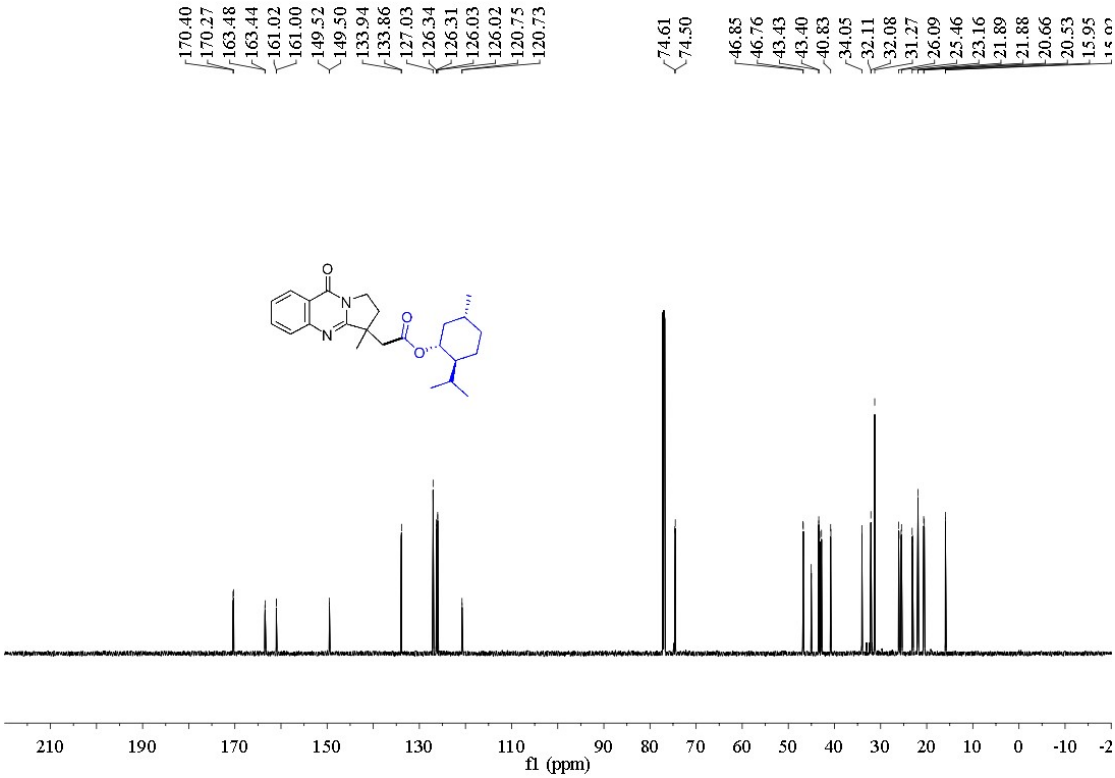
^{13}C NMR of **3ae** (151 MHz, $CDCl_3$)



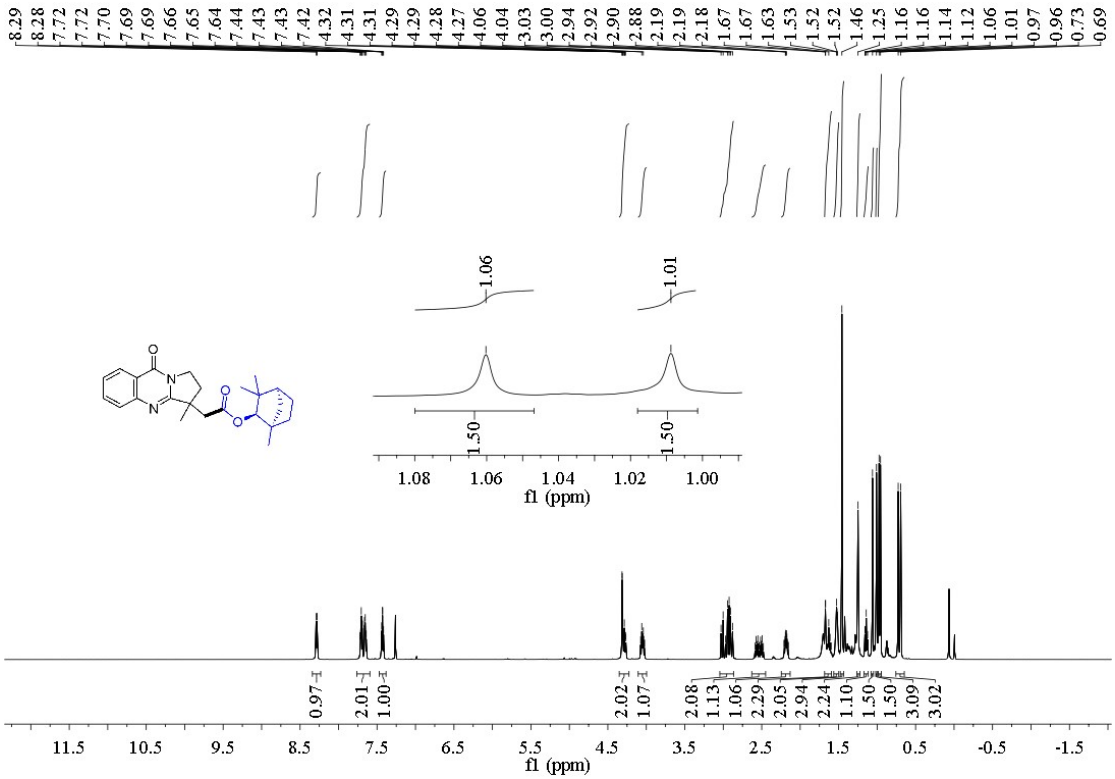
^{1}H NMR of **3af** (600 MHz, $CDCl_3$)



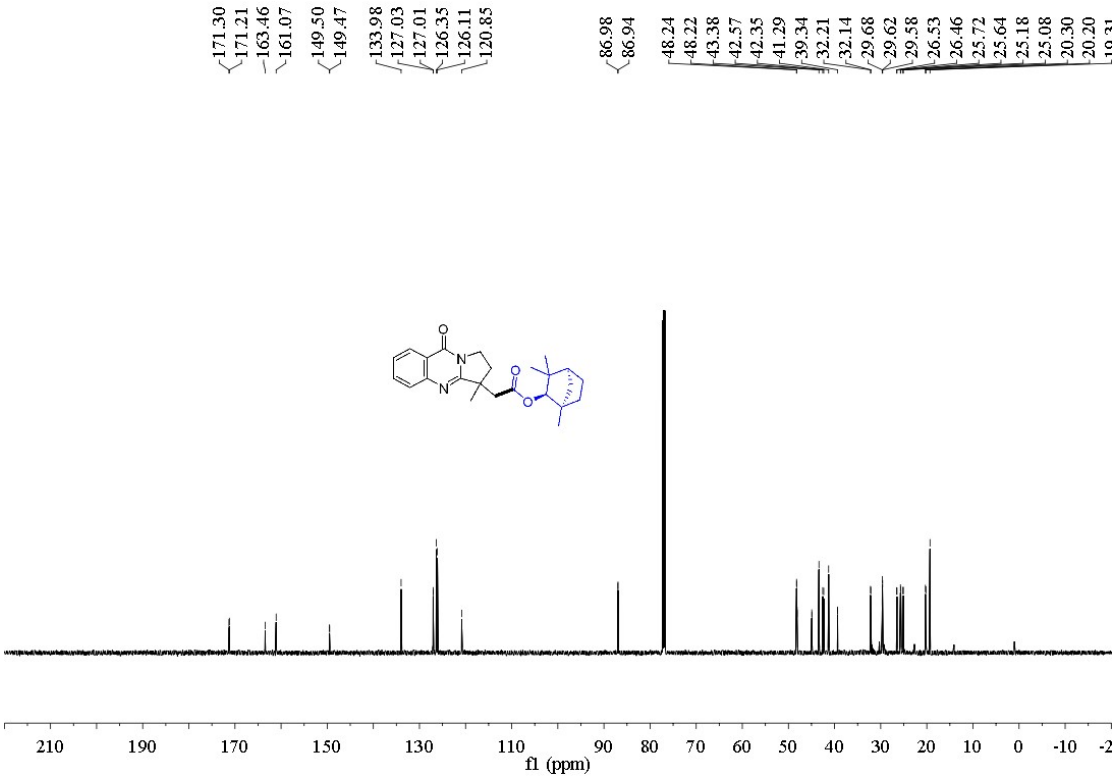
^{13}C NMR of **3af** (151 MHz, $CDCl_3$)



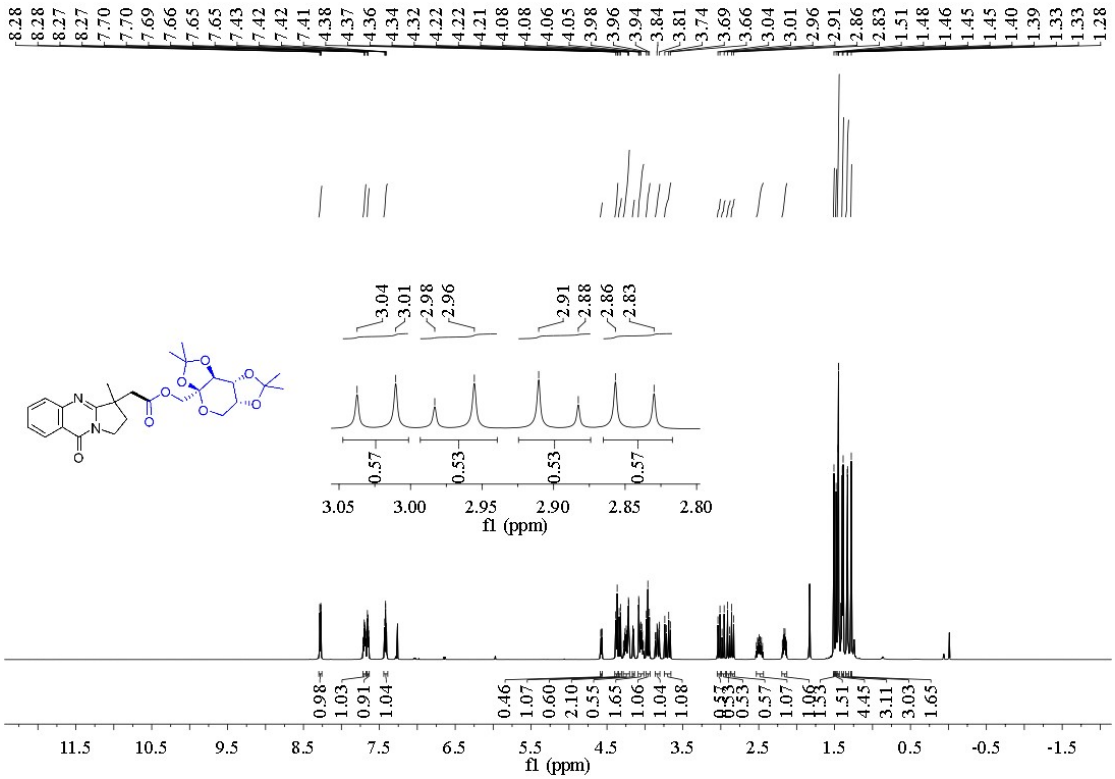
^{1}H NMR of **3ag** (600 MHz, $CDCl_3$)



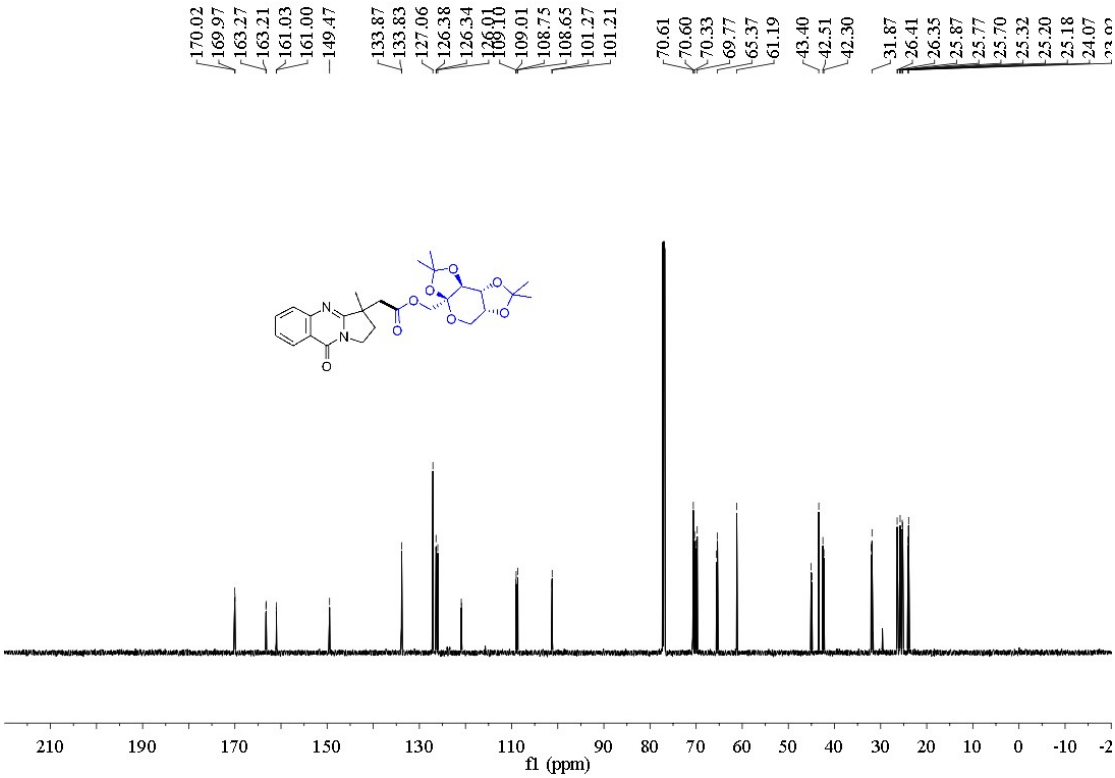
^{13}C NMR of **3ag** (151 MHz, $CDCl_3$)



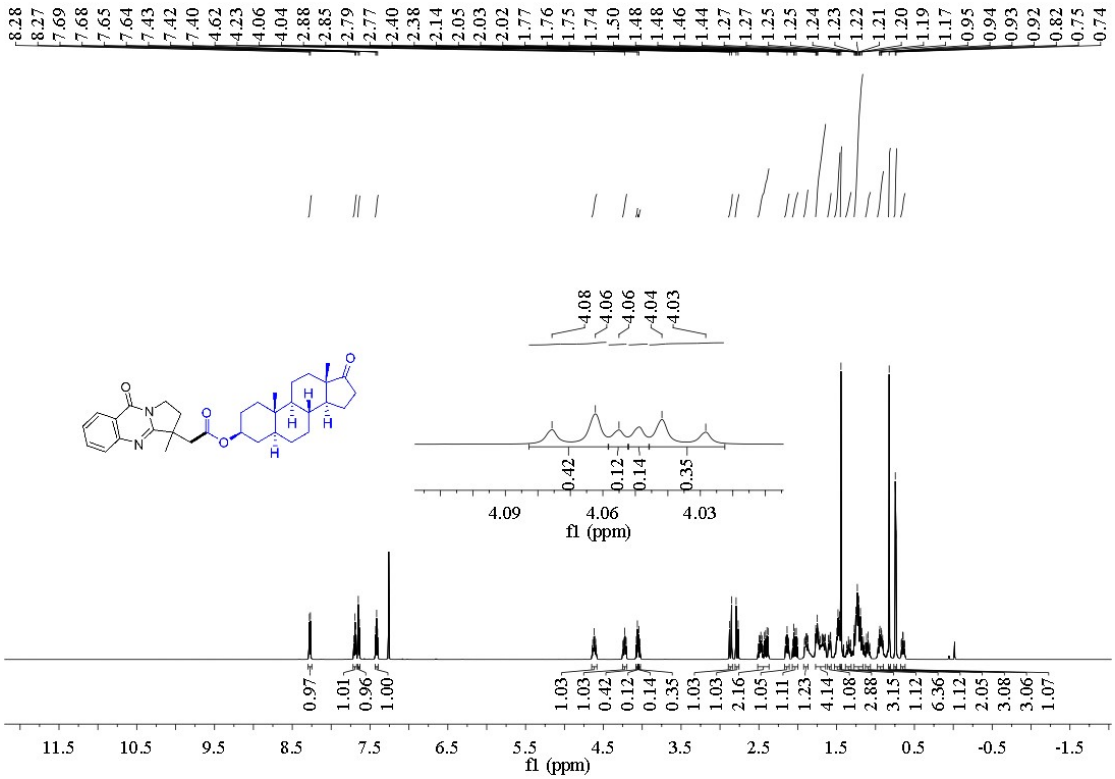
^{1}H NMR of **3ah** (600 MHz, $CDCl_3$)



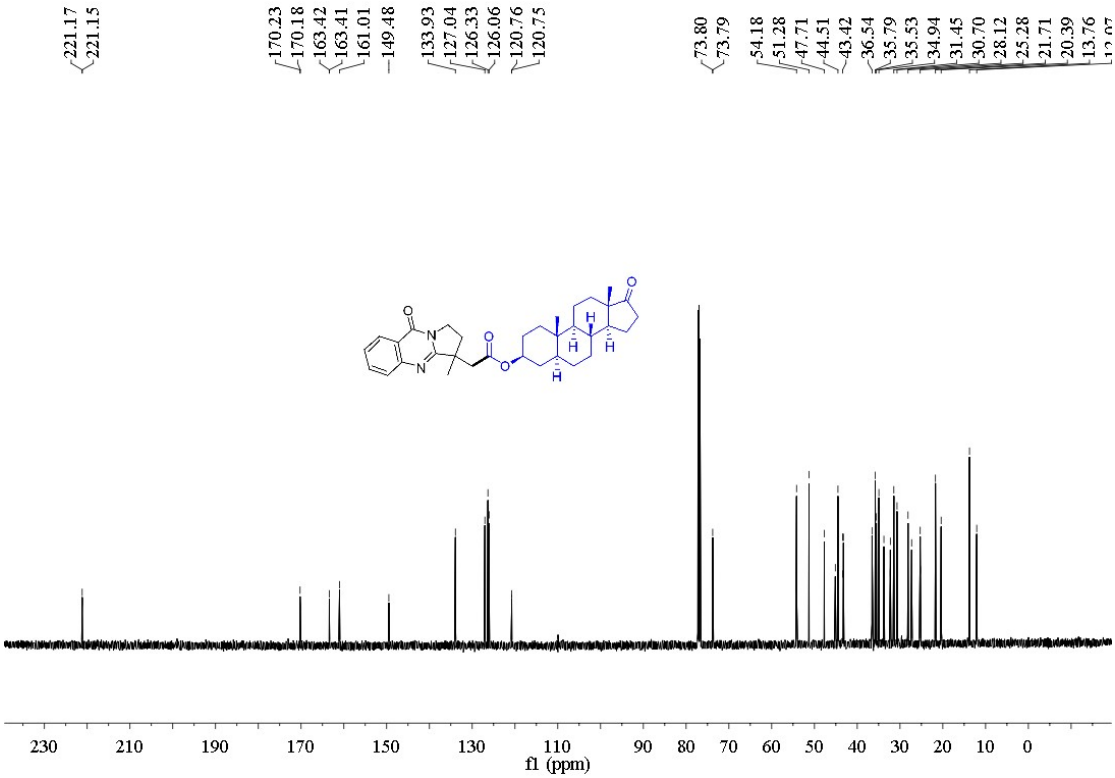
^{13}C NMR of **3ah** (151 MHz, $CDCl_3$)



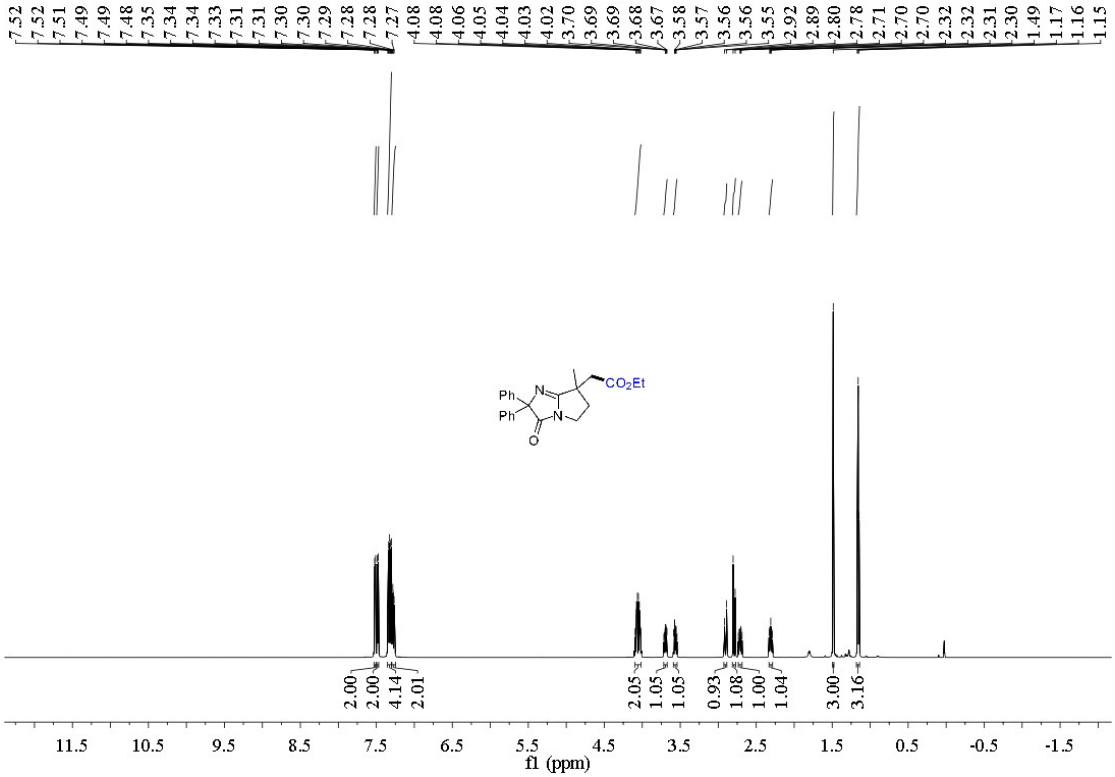
^{1}H NMR of **3ai** (600 MHz, $CDCl_3$)



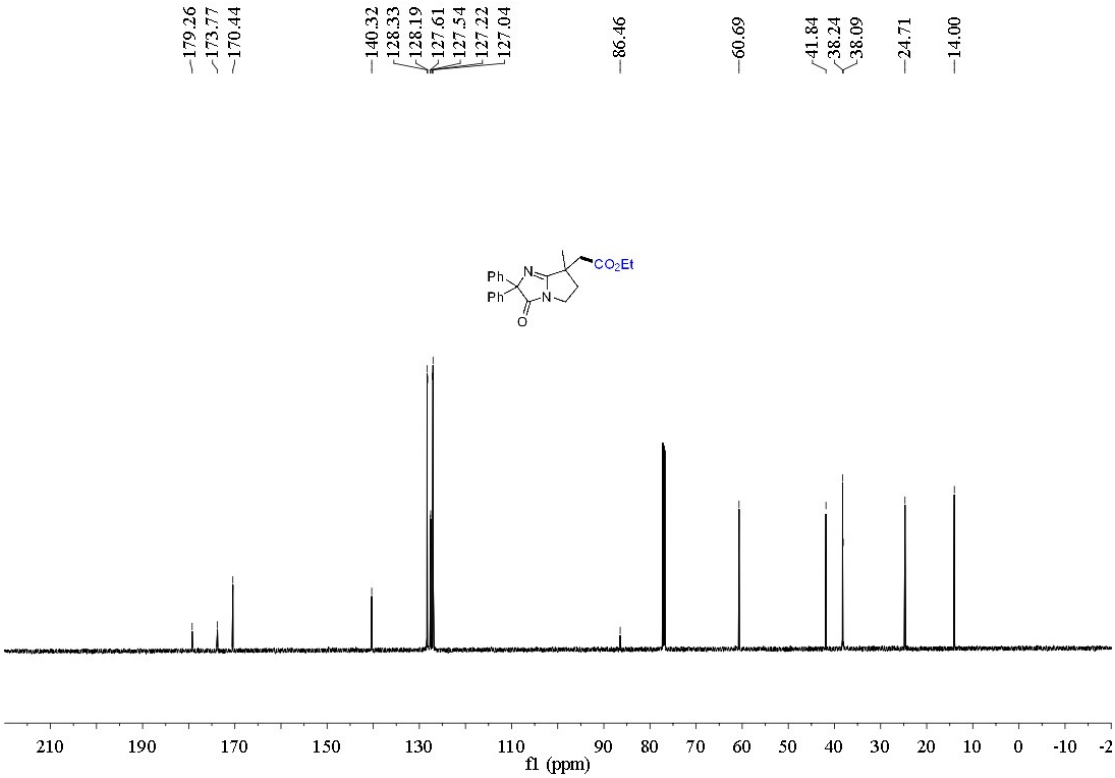
^{13}C NMR of **3ai** (151 MHz, $CDCl_3$)



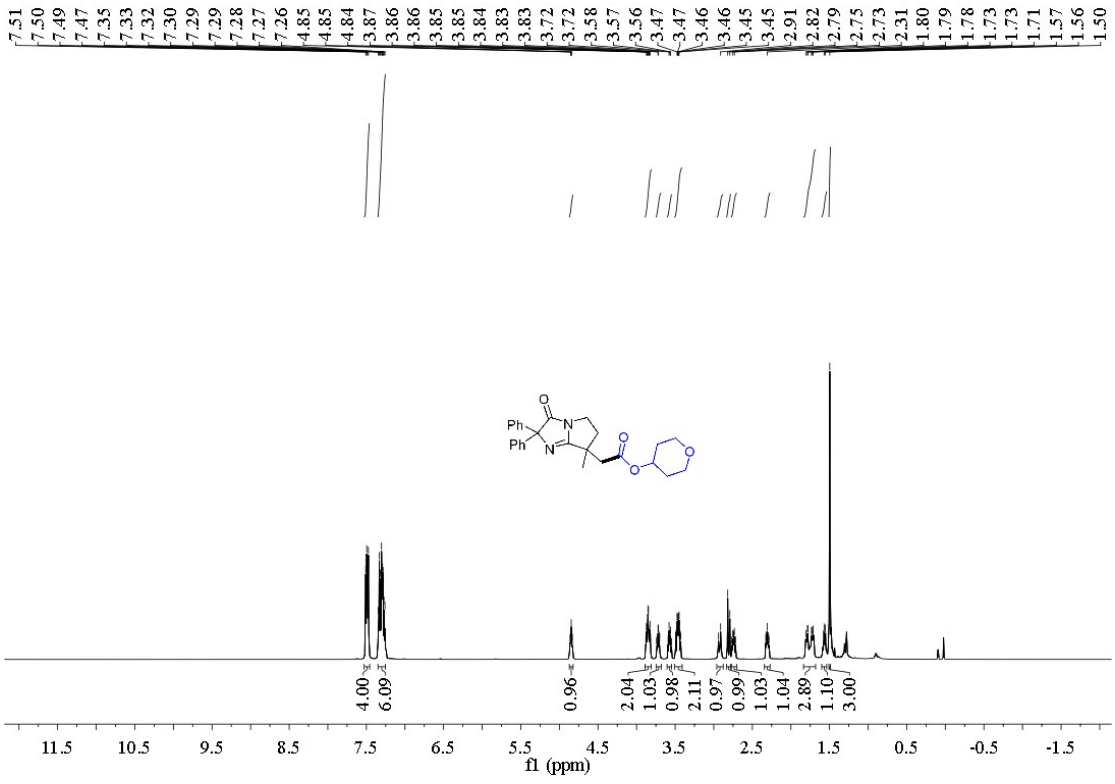
^{1}H NMR of **5a** (600 MHz, $CDCl_3$)



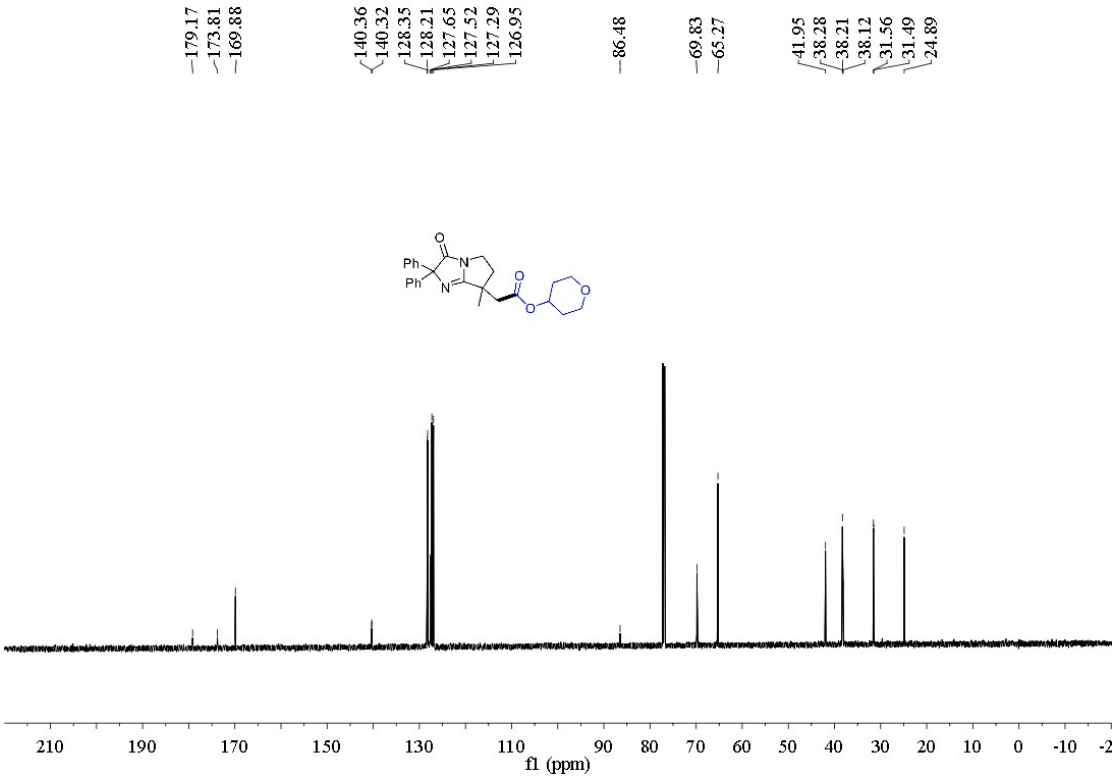
^{13}C NMR of **5a** (151 MHz, $CDCl_3$)



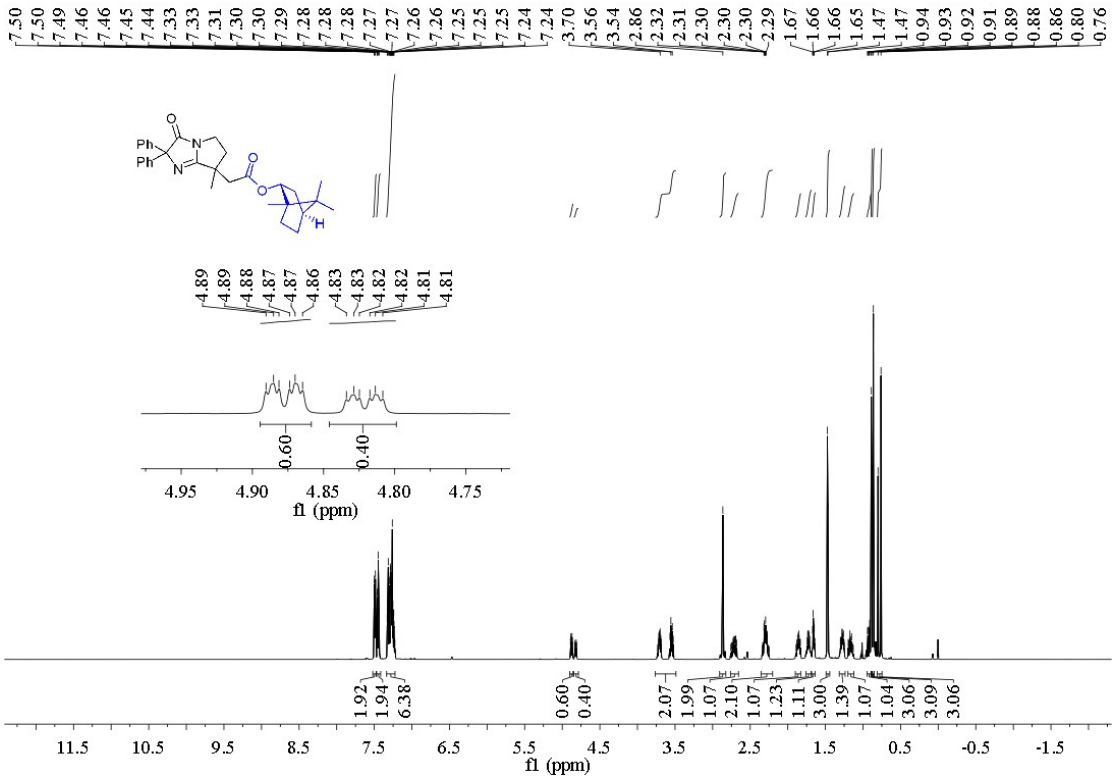
^{1}H NMR of **5b** (600 MHz, $CDCl_3$)



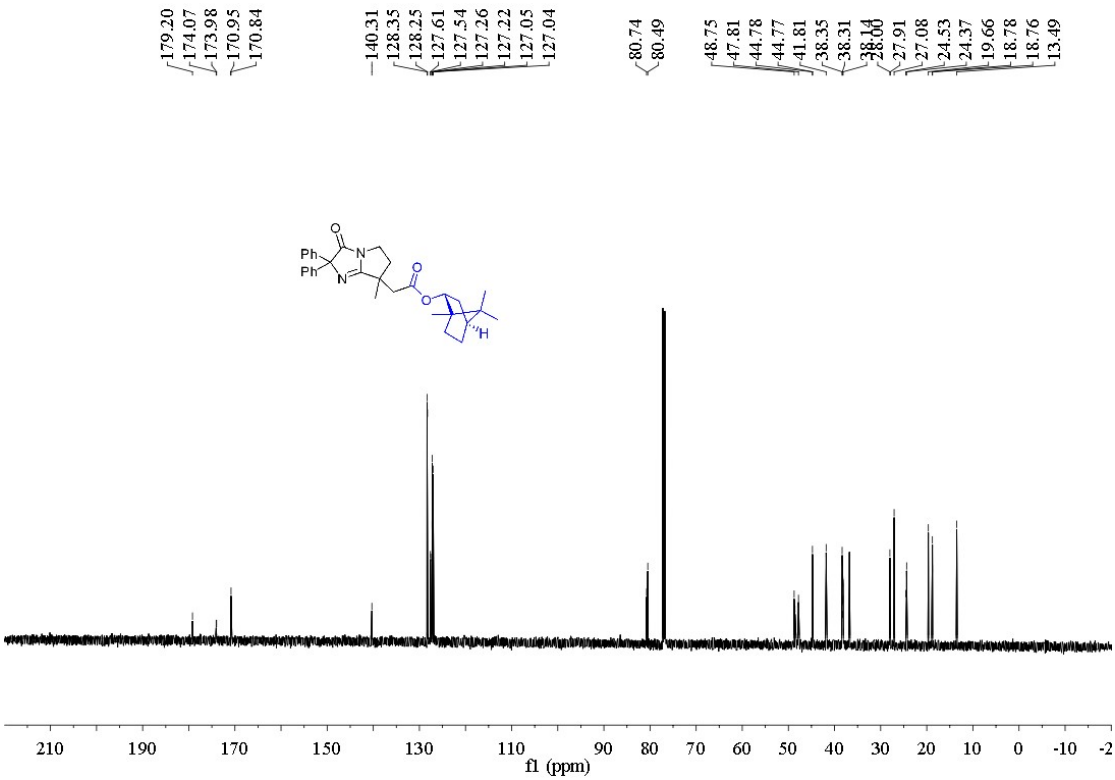
^{13}C NMR of **5b** (151 MHz, $CDCl_3$)



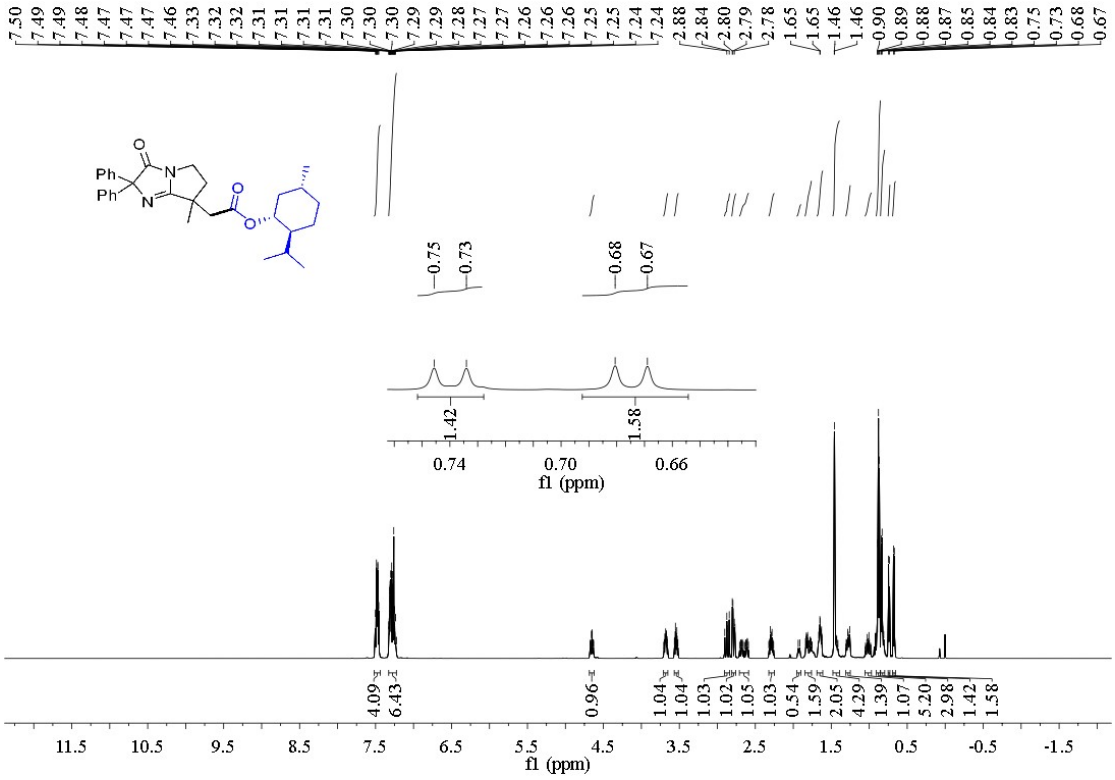
^{1}H NMR of **5c** (600 MHz, $CDCl_3$)



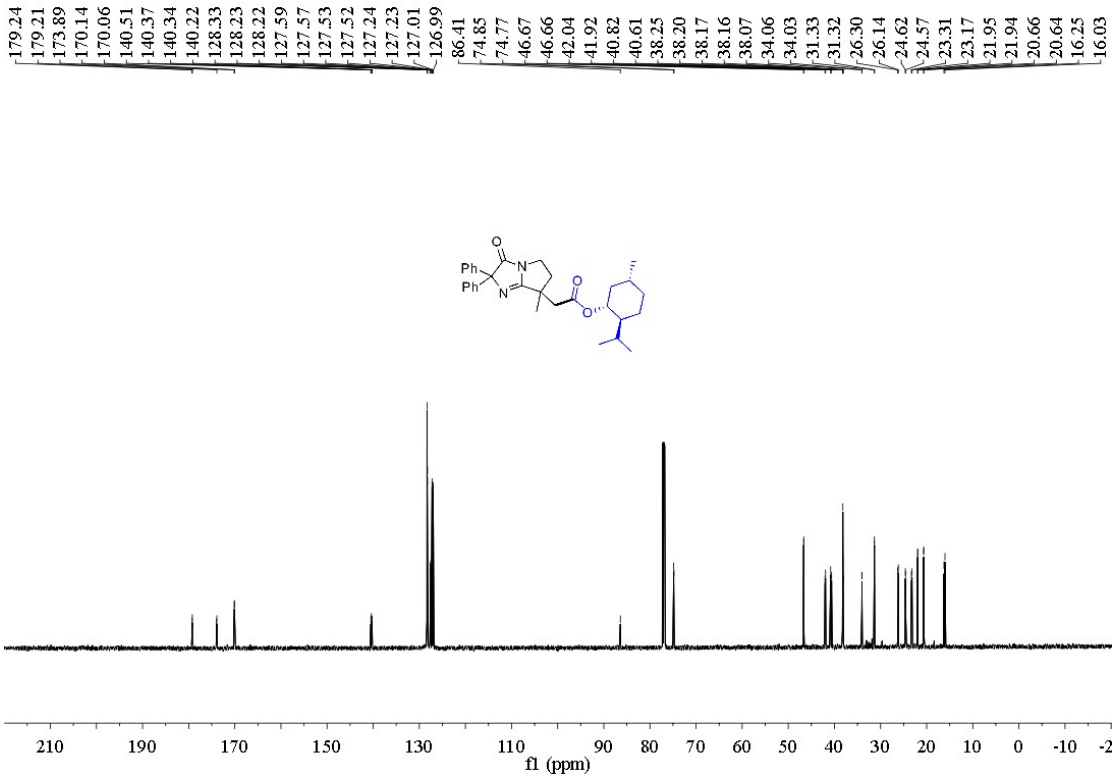
^{13}C NMR of **5c** (151 MHz, $CDCl_3$)



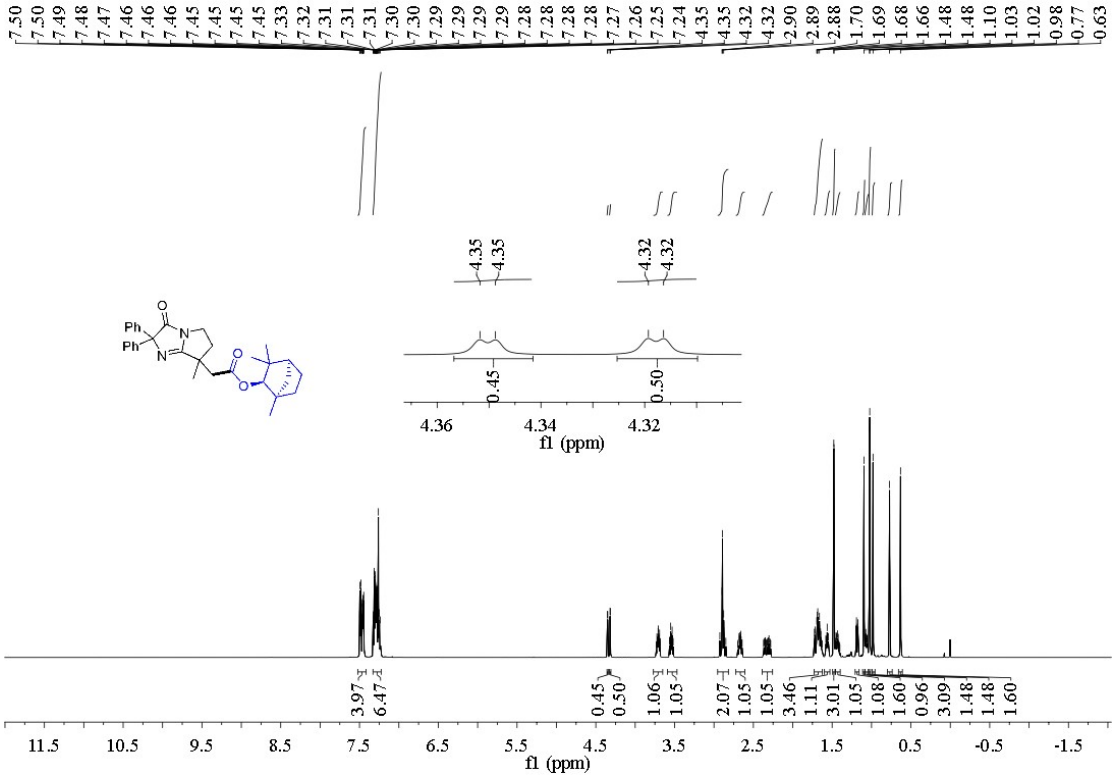
^{1}H NMR of **5d** (600 MHz, $CDCl_3$)



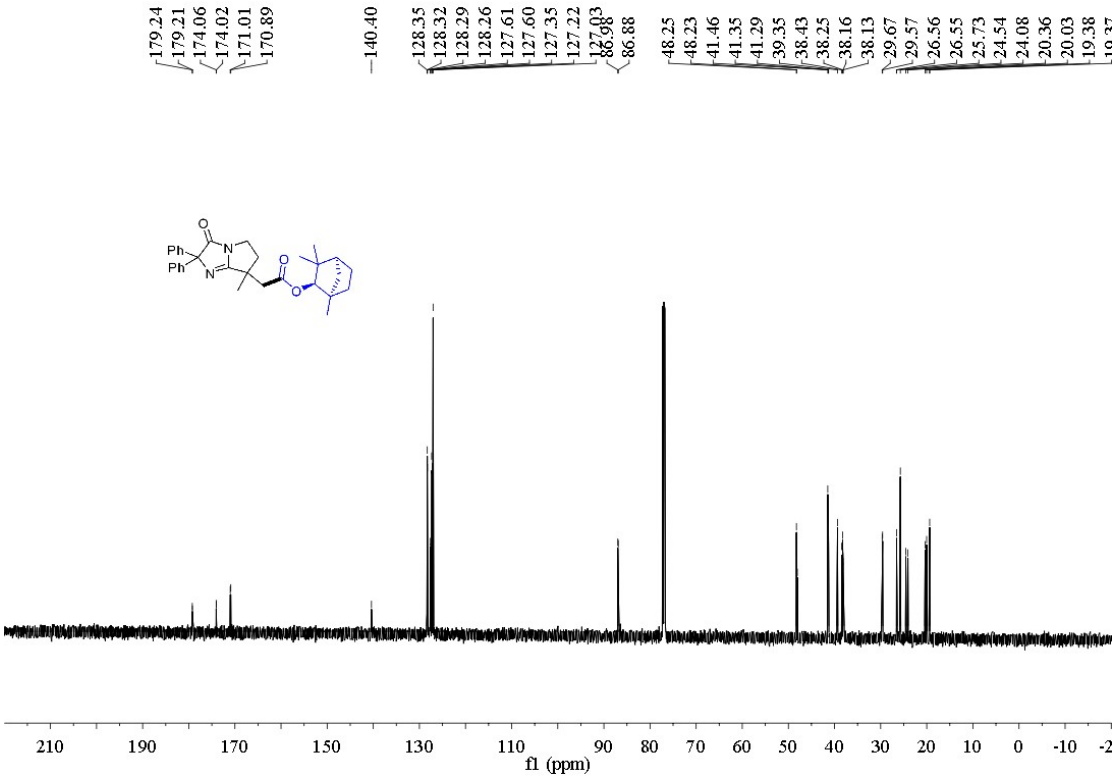
^{13}C NMR of **5d** (151 MHz, $CDCl_3$)



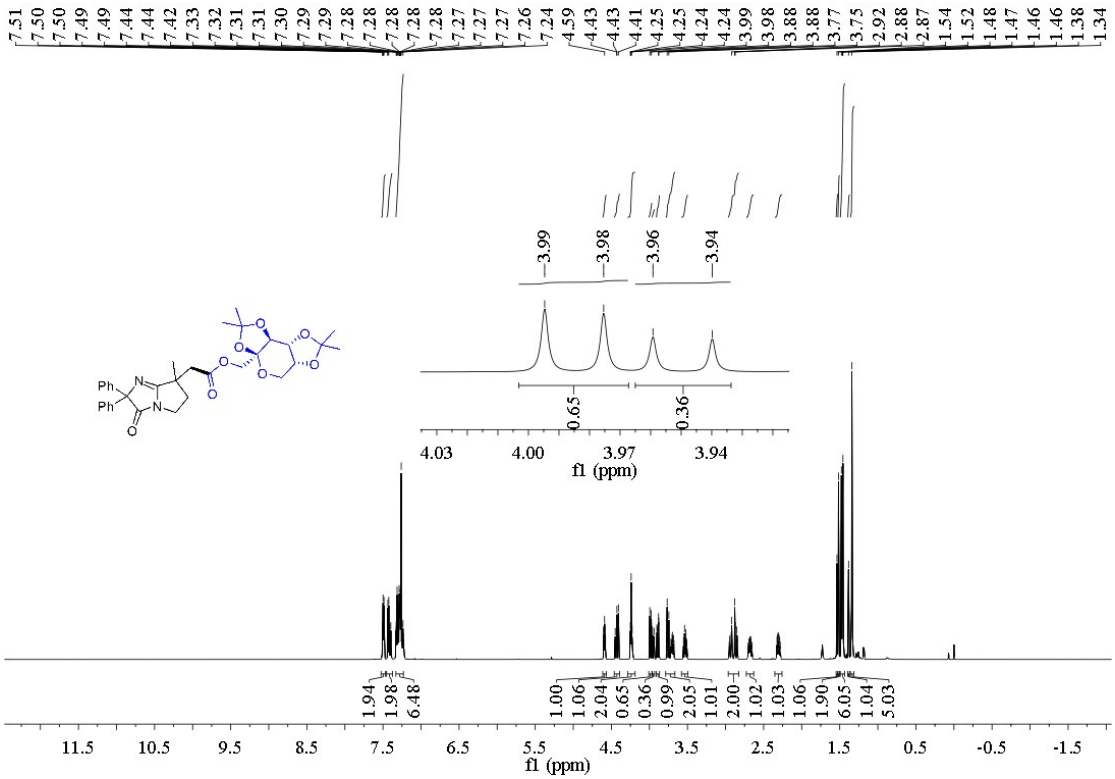
^{1}H NMR of **5e** (600 MHz, $CDCl_3$)



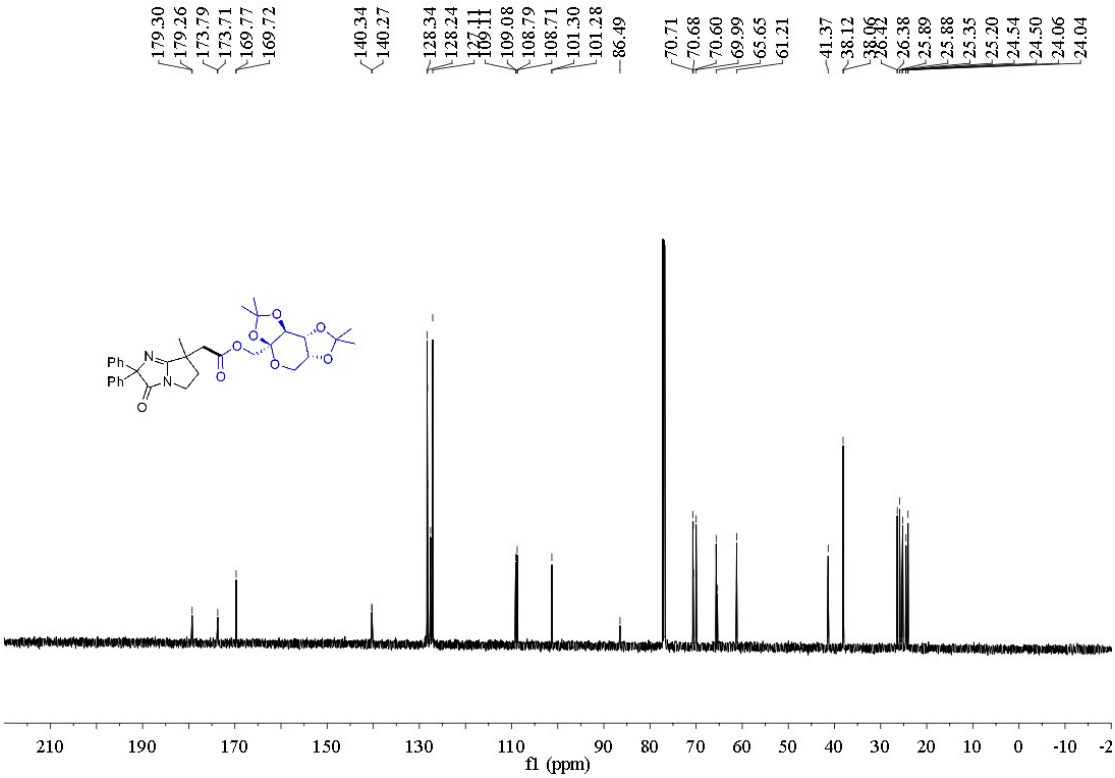
^{13}C NMR of **5e** (151 MHz, $CDCl_3$)



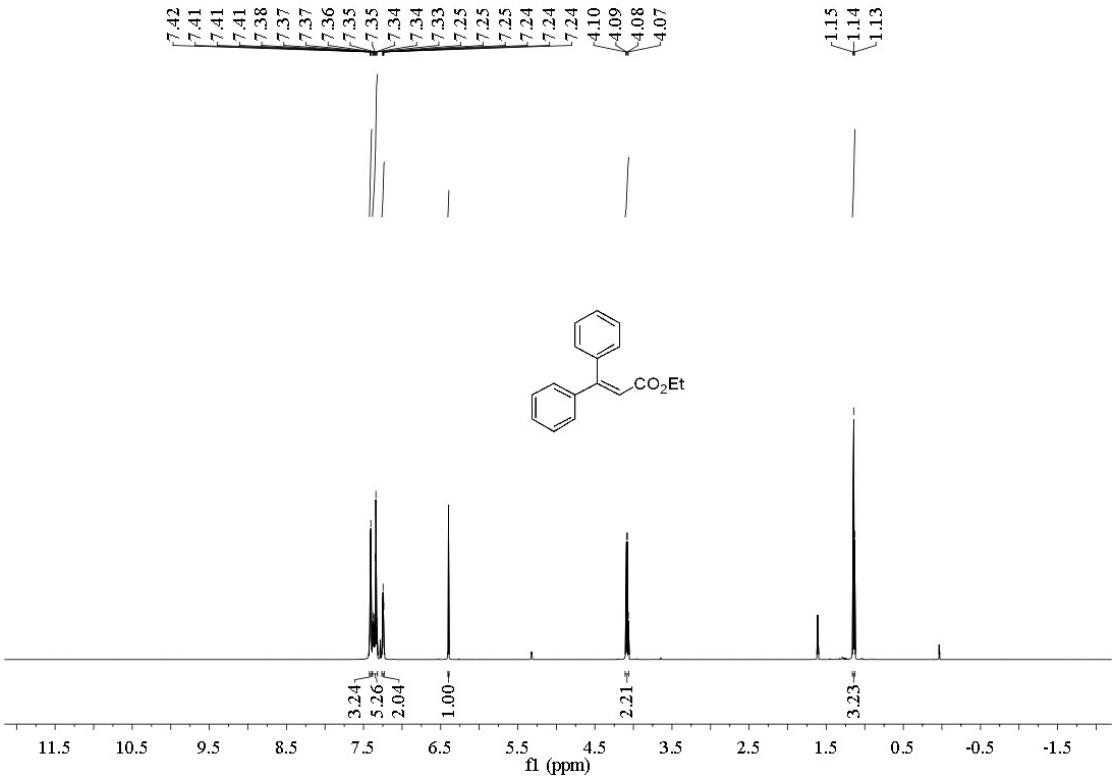
^{1}H NMR of **5f** (600 MHz, $CDCl_3$)



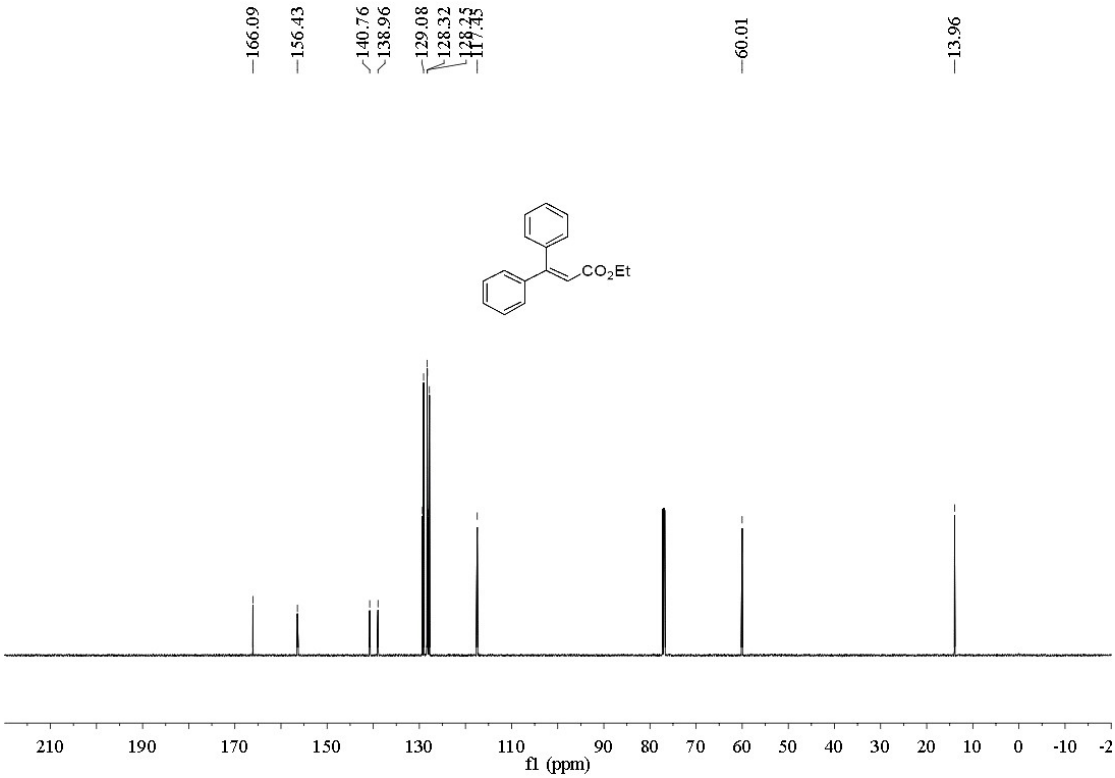
^{13}C NMR of **5f** (151 MHz, $CDCl_3$)



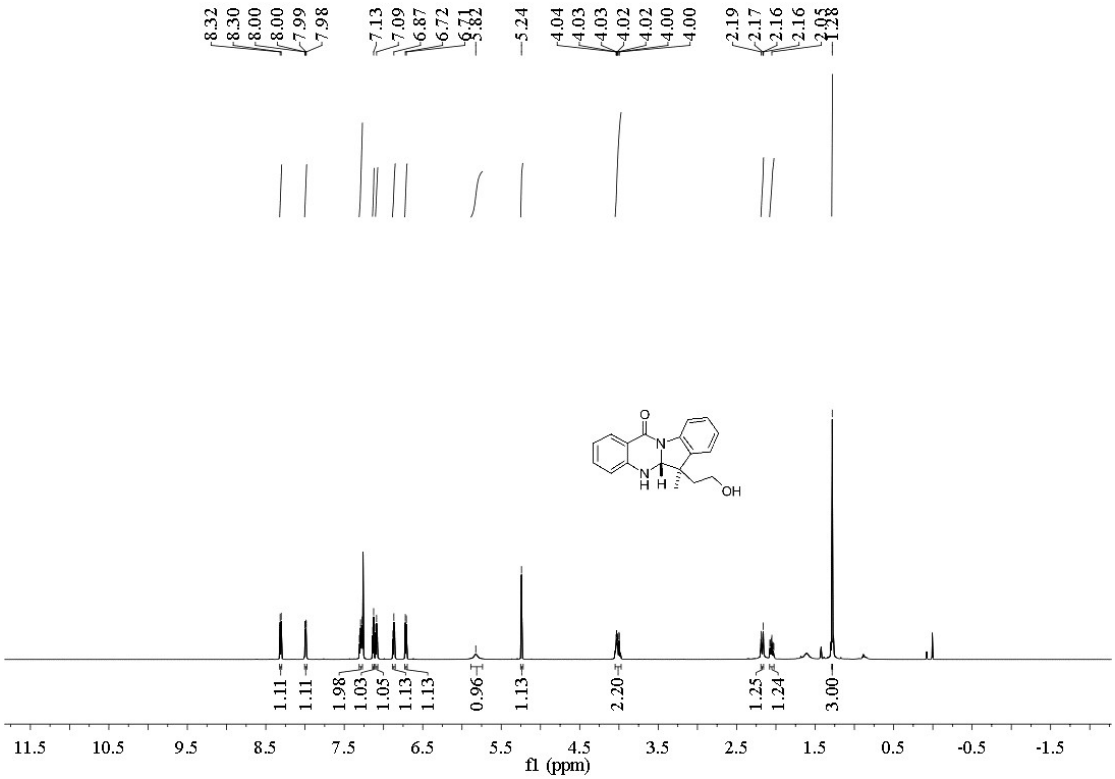
^{1}H NMR of **3aj** (600 MHz, $CDCl_3$)



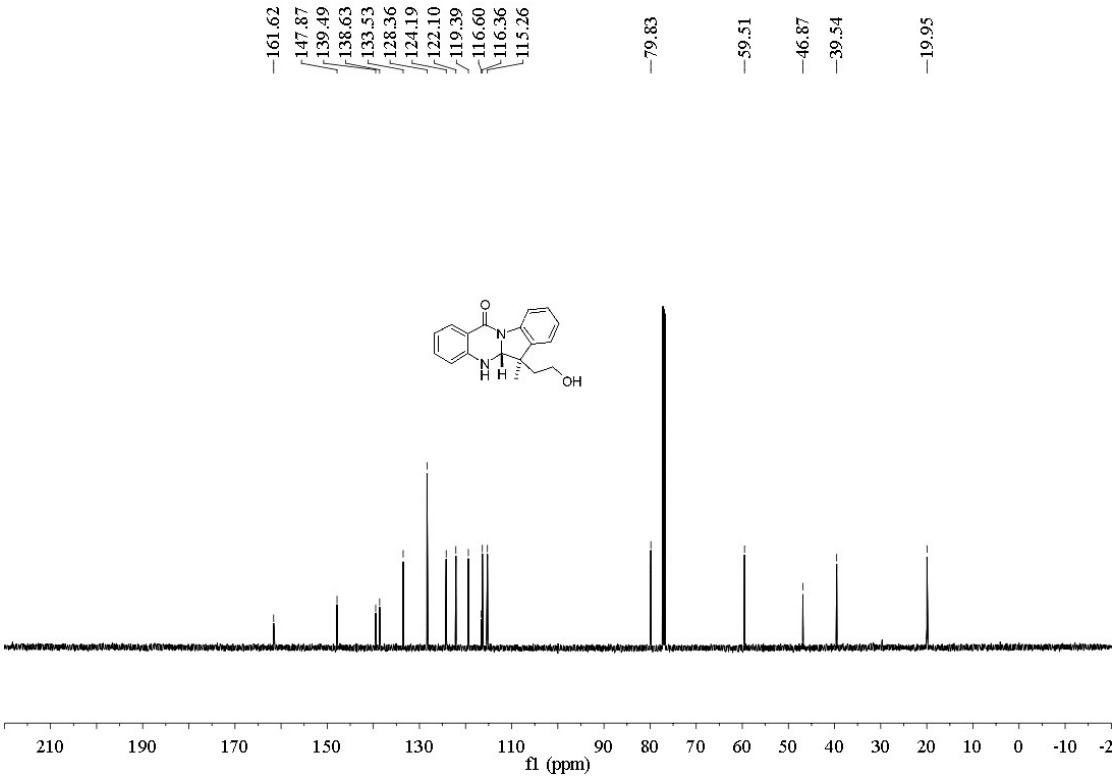
^{13}C NMR of **3aj** (151 MHz, $CDCl_3$)



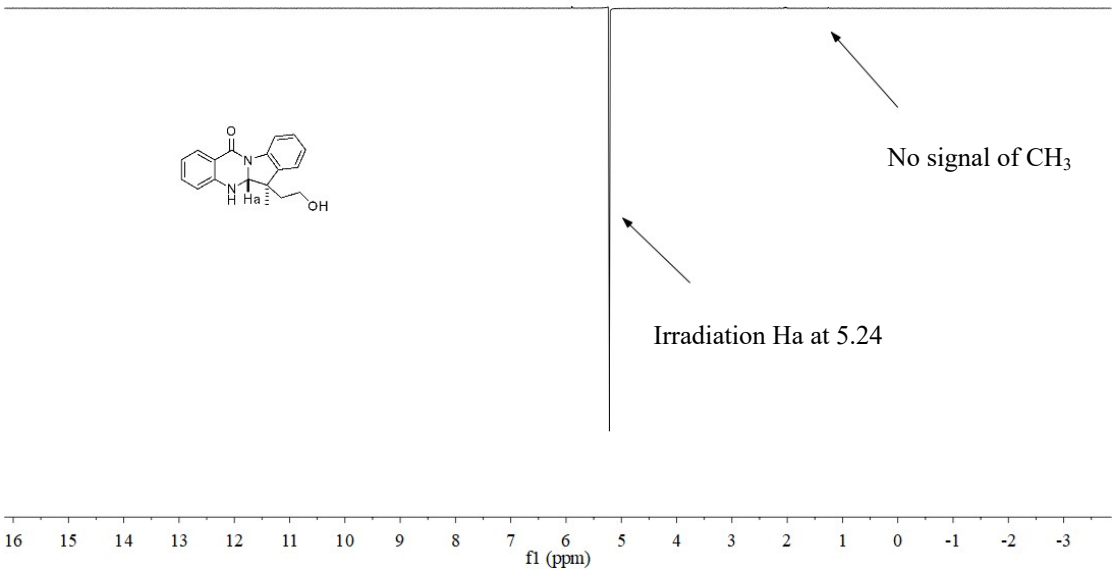
^{1}H NMR of **6** (600 MHz, $CDCl_3$)



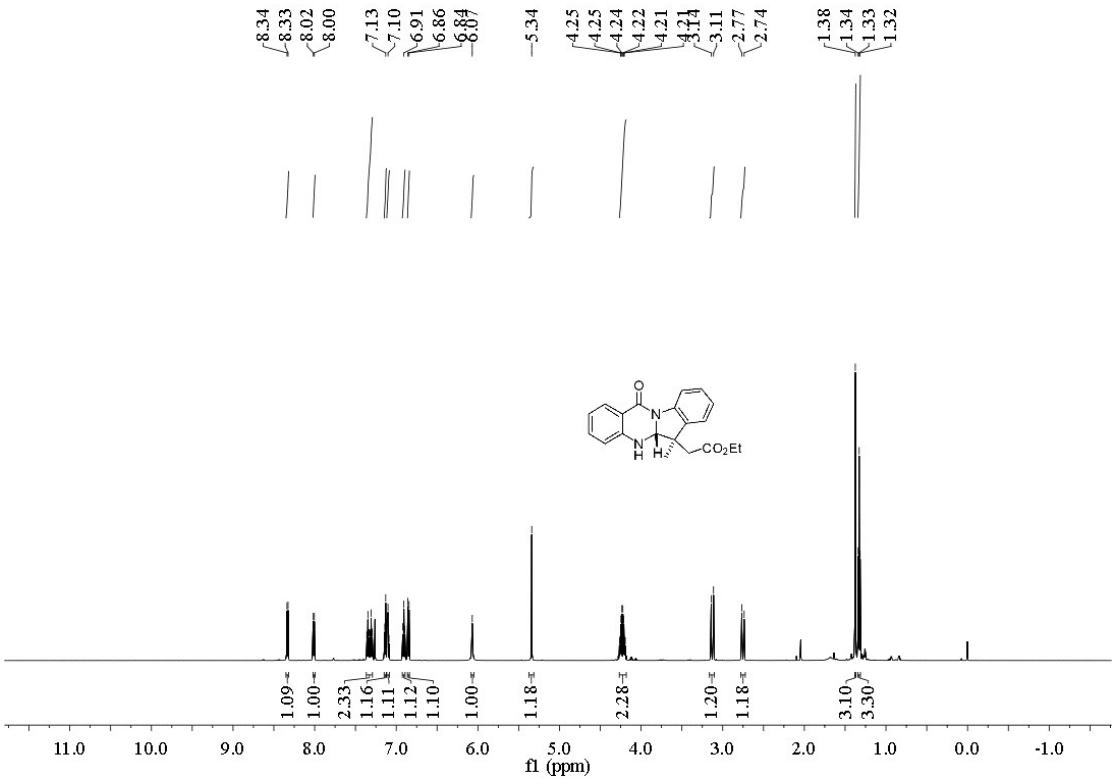
^{13}C NMR of **6** (151 MHz, $CDCl_3$)



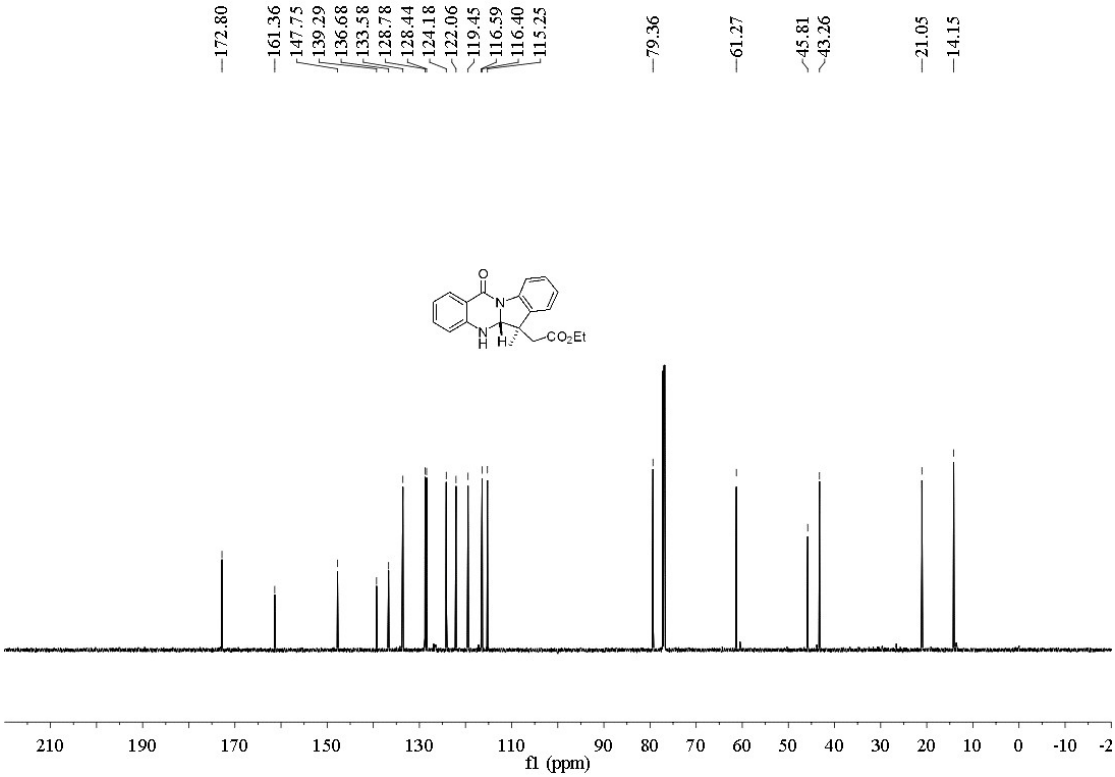
Noesy spectrum of **6** (600 MHz, $CDCl_3$)



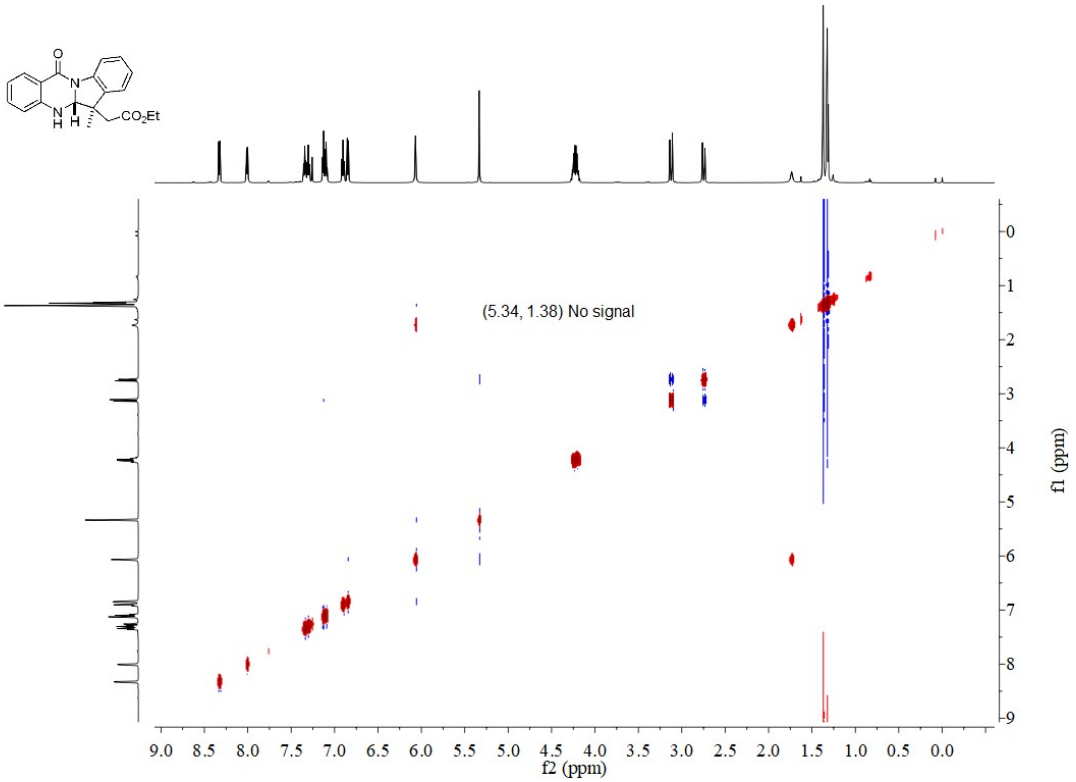
^{1}H NMR of **7** (600 MHz, $CDCl_3$)



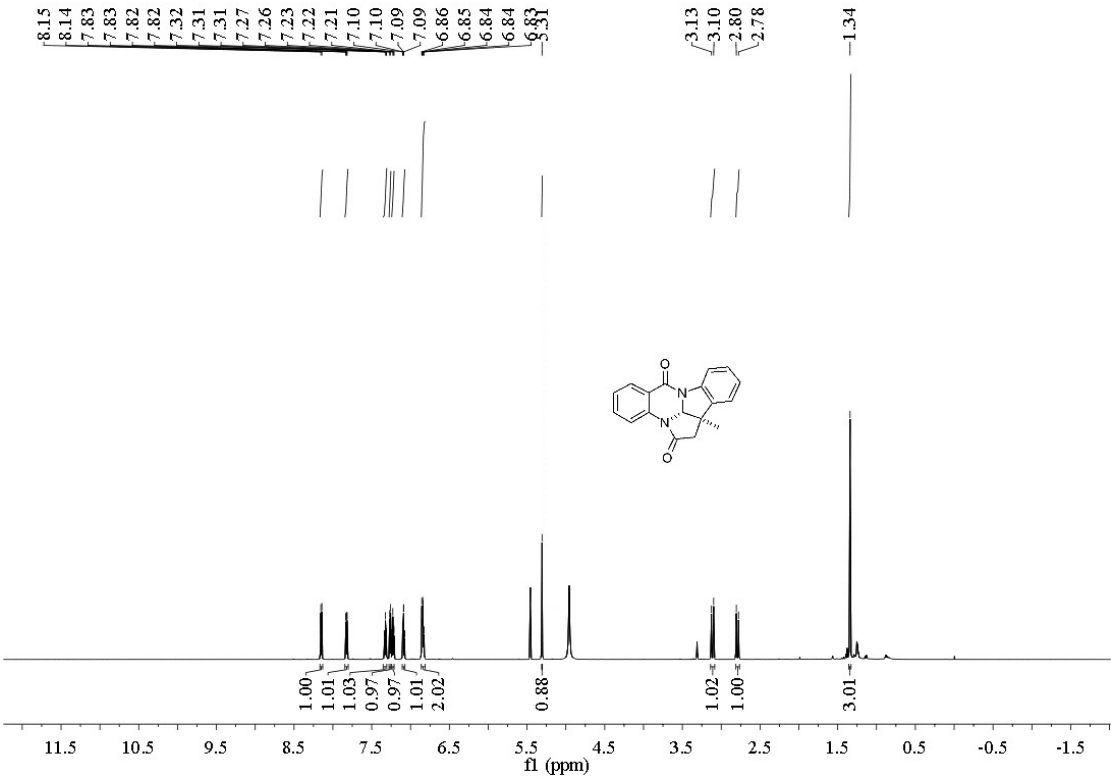
^{13}C NMR of **7** (151 MHz, $CDCl_3$)



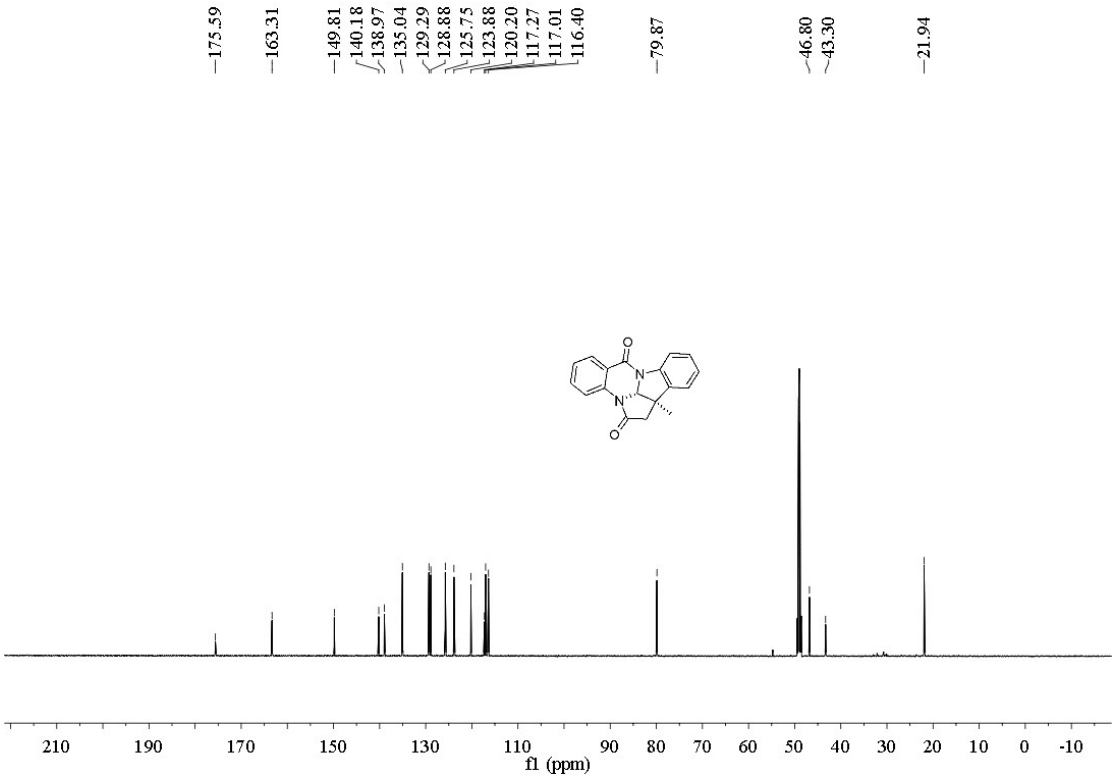
Noesy spectrum of **7** (600 MHz, $CDCl_3$)



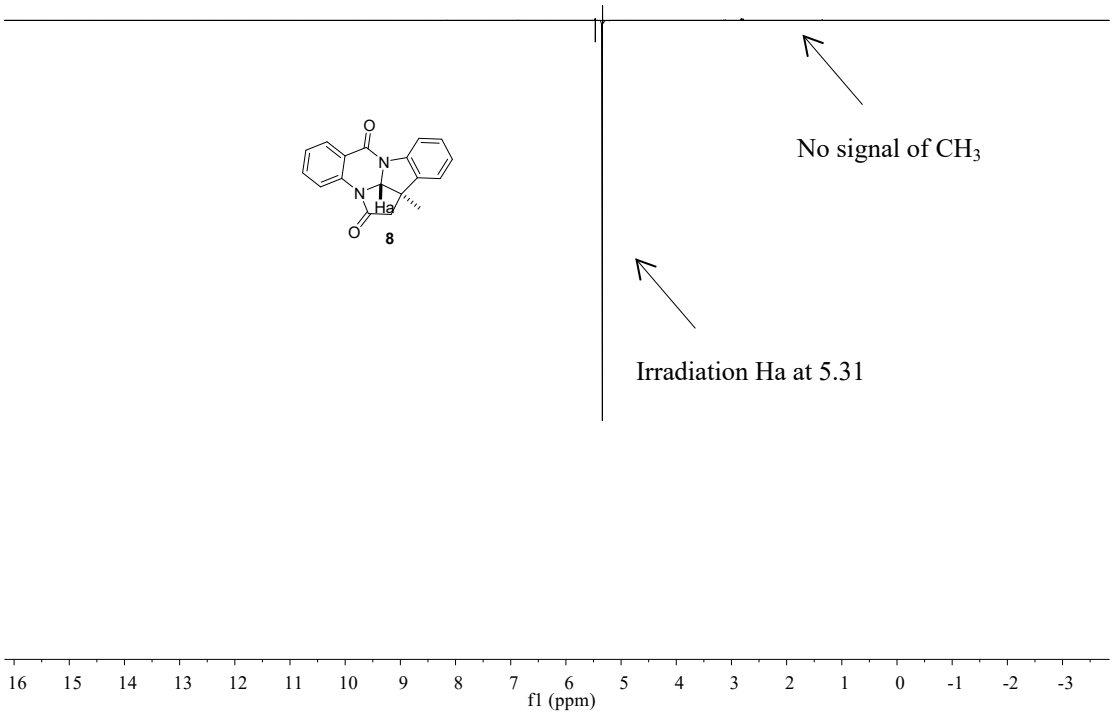
^{1}H NMR of **8** (600 MHz, CD_3OD)



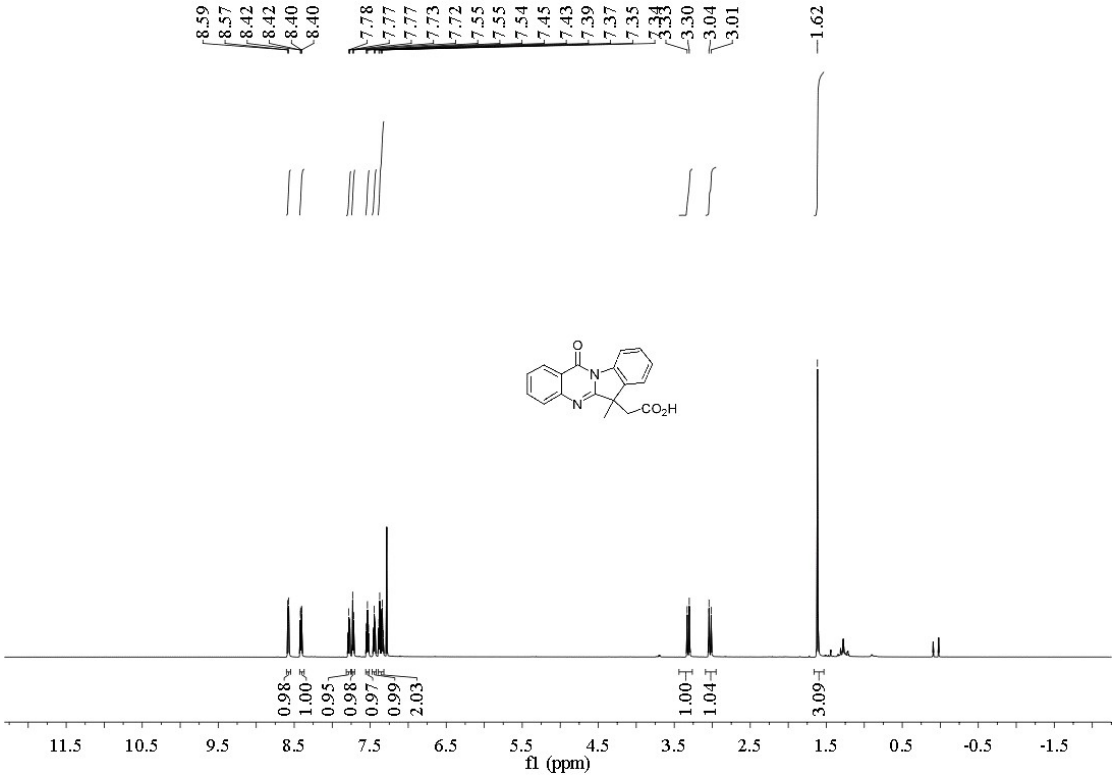
^{13}C NMR of **8** (151 MHz, CD_3OD)



Noesy spectrum of **8** (600 MHz, CD_3OD)



^{1}H NMR of **9** (600 MHz, $CDCl_3$)



^{13}C NMR of **9** (151 MHz, $CDCl_3$)