Supporting Information

Base-promoted [4+2] Annulation of Pyrrole-2-carbaldehyde Derivatives with β,γ-Unsaturated α-Ketoesters: Syntheses of 5,6-Dihydroindolizines

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1. General Information

Reagents, solvents and analytical methods:

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ^{1}NMR spectra were recorded on a Bruker Avance operating at for ^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz and ^{19}F NMR at 471 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ (^{1}H NMR δ 7.27, ^{13}C NMR δ 77.0) as solvent. High-resolution mass spectra (HRMS) is produced by Thermo Fisher Scientific. Its main body is composed of two parts: Thermo Scientific's UltiMate 3000 Series liquid system and Thermo Scientific Q-Exactive combined quadrupole Orbitrap mass spectrometer. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad.

2 Preparation of the Compounds 1a-1n

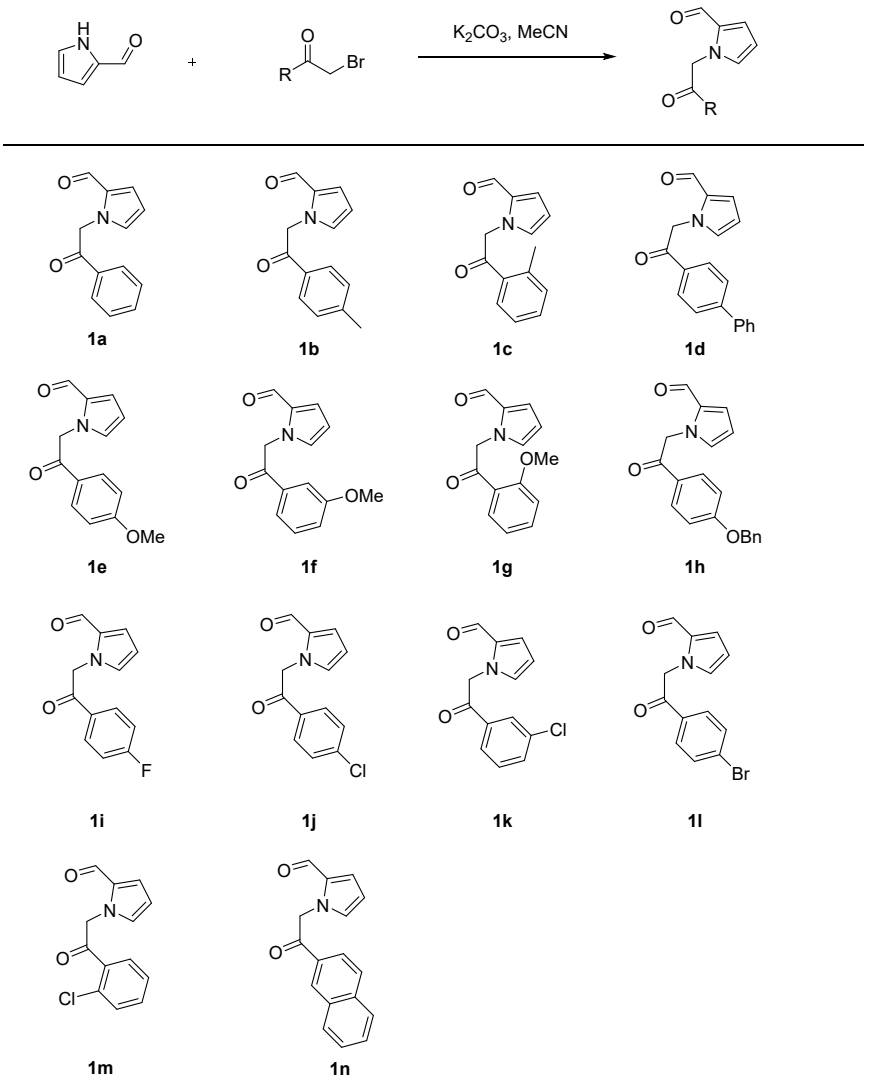


Figure S1 Substrates of H-pyrrole-2-carbaldehyde

Compounds **1a, 1e, 1f, 1h, 1i, 1k, 1l** were prepared according to the previous literature.[S1]

Compounds **1b-1d, 1g** were prepared according to the previous literature.[S2]

Compounds **1m** were prepared according to the previous literature.[S3]

Compounds **1n** were prepared according to the previous literature.[S4]

3 Preparation of the Compounds 2a-2u

3.1 Preparation of the Compounds 2a-2m,2o-2u

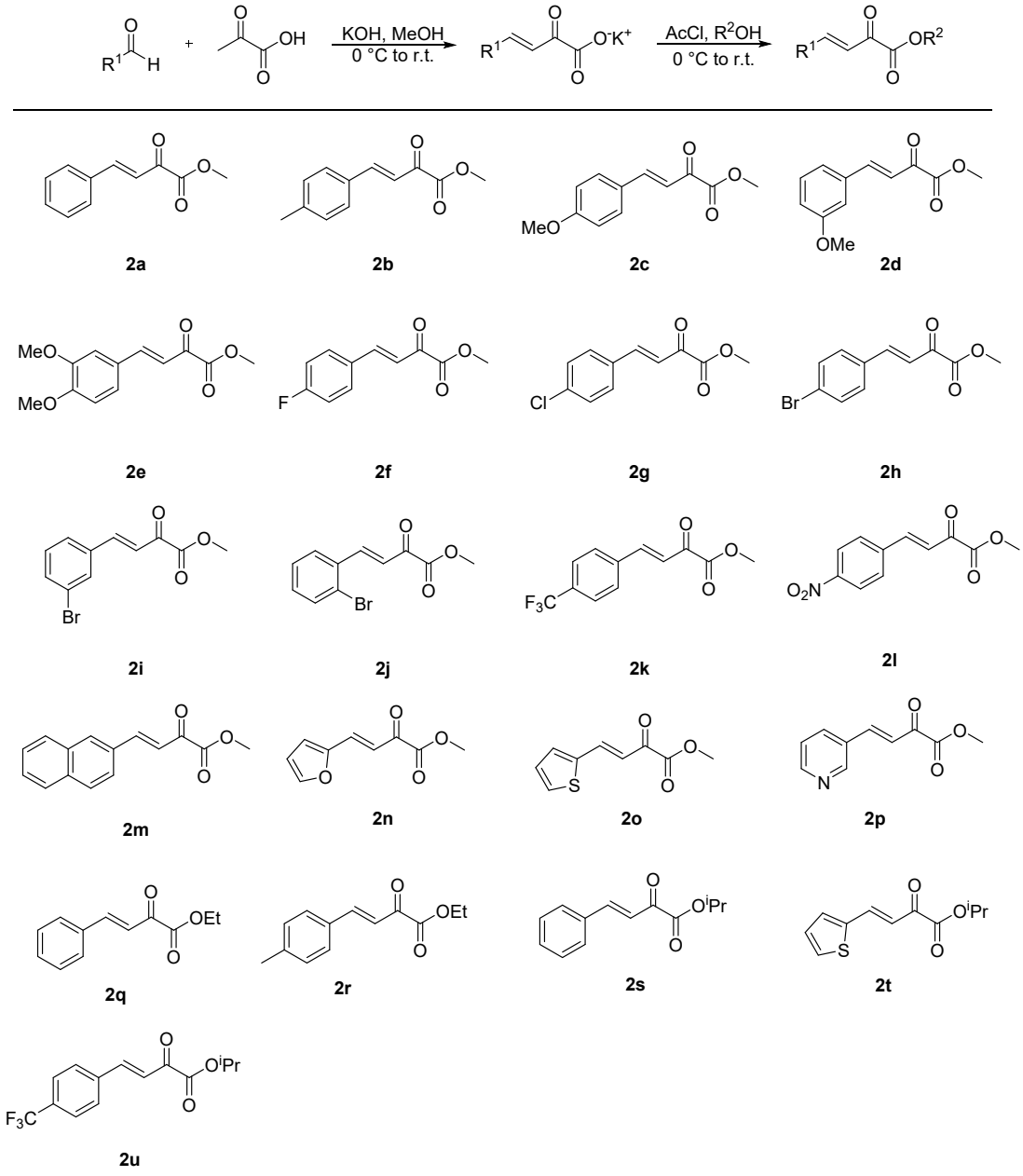


Figure S2 Substrates of β,γ-unsaturated α-ketoesters

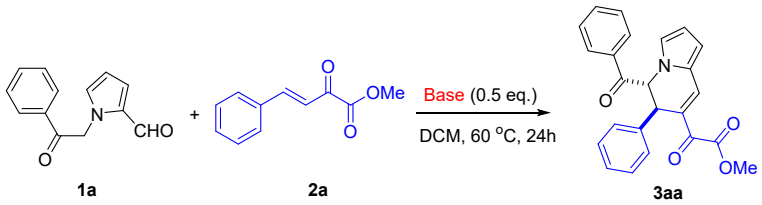
Compounds **2a-2k, 2m, 2o** were prepared according to the previous literature.[S5]

Compounds **2n, 2p, 2q, 2s** were prepared according to the previous literature.[S6]

Compounds **2l, 2r, 2t, 2u** were prepared according to the previous literature.[S7]

4 Optimization of Reaction Conditions

Table S1. Optimization of the Base.[a]

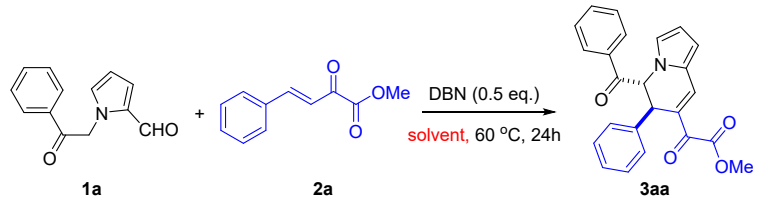


1a 2a 3aa

Entry	Base	Yield (%)[b]
1	DBU	20
2	Cinchonine	NR
3	Quinidine	NR
4	K_2CO_3	15
5	*t*-BuOK	trace
6	Cs_2CO_3	20
7	DIPEA	NR
8	2,4,6-Collidine	NR
9	TEA	33
10	DBN	60
11	TMG	47
12[c]	Cs_2CO_3	30
13[d]	Cs_2CO_3	ND

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Base (50 mol%), DCM (1.5 mL), N_2 atmosphere, 60 °C for 24 h. [b] Isolated yield. [c] the reaction was performed in MeCN. [d] the reaction was performed in DMF.

Table S2. Optimization of Solvent.[a]



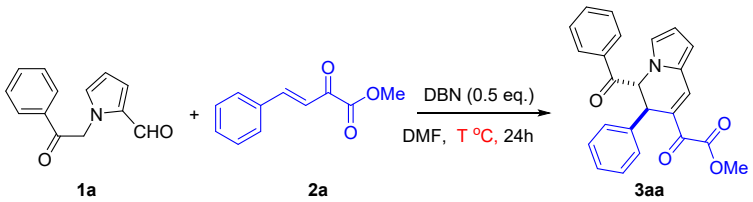
1a 2a 3aa

Entry	Solvent	Yield (%)[b]
1	THF	57
2	DCE	54
3	DMF	85
4	DMSO	70
5	MeOH	38
6	1,4-Dioxane	41
7	MeCN	53

8	Toluene	31
9	DCM	60
10	EA	36
11	H_2O	NR
12	DMA	63

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), DBN (50 mol%), solvent (1.5 mL), N_2 atmosphere, 60 °C for 24 h. [b] Isolated yield.

Table S3. Optimization of Temperature.[a]

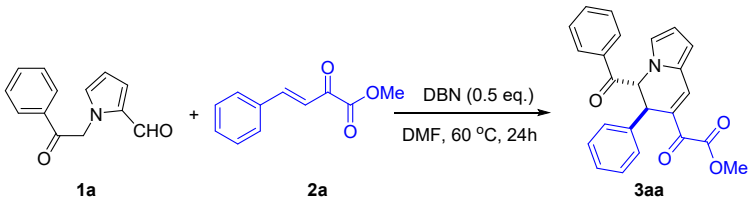


1a **2a** **3aa**

Entry	Temp. (°C)	Yield (%)[b]
1	30	57
2	60	85
3	80	50
4	100	37

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), DBN (50 mol%), DMF (1.5 mL), N_2 atmosphere, T °C for 24 h. [b] Isolated yield.

Table S4. Optimization of ratio of starting materials.[a]

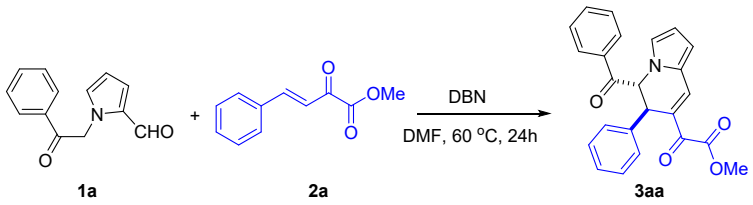


1a **2a** **3aa**

Entry	**1a:2a**	Yield (%)[b]
1	1.5:1	85
2	1:1	62
3	1:1.5	70
4	1:1.2	64
5	1.2:1	63
6	2:1	75

[a] Reaction conditions: **1a** (x mmol), **2a** (0.2 mmol), DBN (50 mol%), DMF (1.5 mL), N_2 atmosphere, 60 °C for 24 h. [b] Isolated yield.

Table S5. Optimization of the proportion of Base.[a]



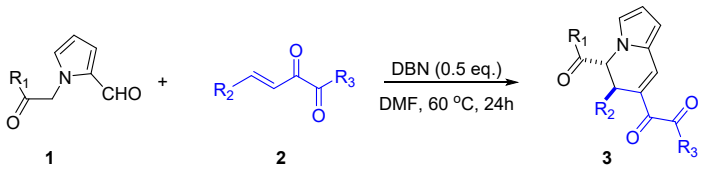
1a 2a 3aa

Entry	Base	Yield (%)[b]
1	0.2 equiv	45
2	0.5 equiv	85
3	0.8 equiv	52
4	1 equiv	48

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), DBN (x equiv.), DMF (1.5 mL), N_2 atmosphere, 60 °C for 24 h. [b] Isolated yield.

5 General Procedure and Substrate Scope

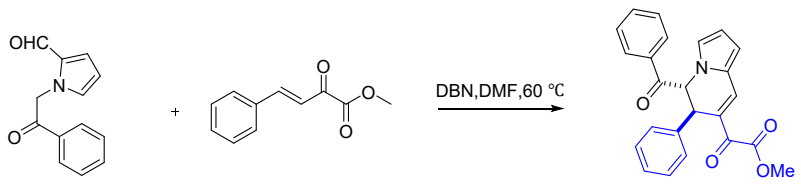
5.1. General Procedure



1 2 3

1 (0.3 mmol, 1.5 equiv), **2** (0.2 mmol,1 equiv) were transferred into a 15 mL tube. Then the tube was sealed with a septum. The tube was connected to an nitrogen-vacuum line, evacuated and backfilled with N_2 (x3). DBN (50 mol%) and DMF (1.5 mL) were added to the reaction tube.The reaction mixture was stirred at 60 °C for 24 hours. Then the mixture was extracted with EA (3 x 6 mL) and washed with a saturated solution of NaCl (5 mL x 2), and the combined extracts were dried over anhydrous Na_2SO_4.The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc (v/v = 30:1 to 5:1) to afford the products **3**.

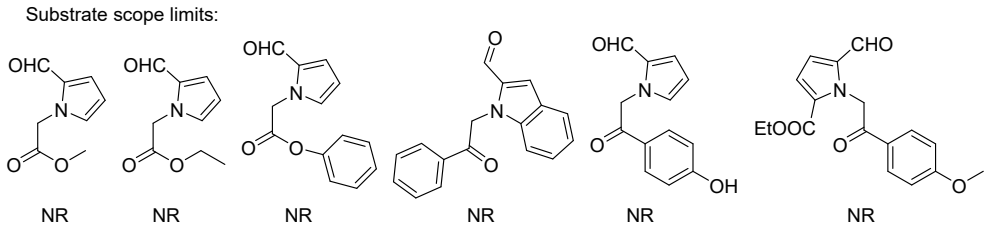
5.2. Gram Scale Synthesis



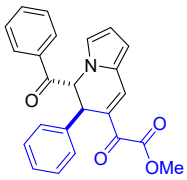
1 (4.5 mmol, 1.5 equiv), **2** (3 mmol,1 equiv) were transferred into a 100 mL bottle. Then the bottle was sealed with a septum. The bottle was connected to an nitrogen-vacuum line, evacuated and backfilled with N_2 (x3). DBN (0.185 mL) and DMF (30 mL) were added to the reaction bottle.The reaction mixture was stirred at 60 °C for 36 hours. Then the mixture was extracted with EA and washed with a saturated solution of NaCl, and the combined extracts were dried over anhydrous Na_2SO_4.The mixture was concentrated under reduced pressure and the residue was

purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc (v/v = 30:1 to 5:1) to afford the products **3** (924 mg, 80%).

5.3. Substrate scope limits



6 Experimental Characterization Data for the Products



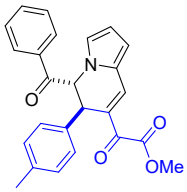
Methyl 2-(*trans*-5-benzoyl-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3aa)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol), following the general procedure , the title compound (65.5 mg, 85%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.96 – 7.89 (m, 2H), 7.85 (s, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 6.9 Hz, 2H), 7.10 (dd, *J* = 7.4, 1.8 Hz, 2H), 6.80 – 6.72 (m, 1H), 6.69 (s, 1H), 6.39 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.73 (s, 1H), 4.58 (s, 1H), 3.77 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.7, 183.2, 163.7, 141.0, 134.8, 134.4, 133.1, 129.4, 129.3, 129.1, 128.8, 128.0, 127.7, 127.4, 124.3, 117.6, 113.1, 65.9, 52.7, 41.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}NO_4H^+$ 386.1387; Found 386.1380.

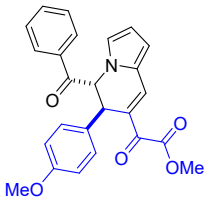


Methyl 2-(*trans*-5-benzoyl-6-(*p*-tolyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ab)

From methyl (*E*)-2-oxo-4-(*p*-tolyl)but-3-enoate (40.8 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol), following the general procedure, the title compound (75.5 mg, 95%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 8.01 – 7.95 (m, 2H), 7.89 (s, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.07 (q, *J* = 8.2 Hz, 4H), 6.80 (dd, *J* = 3.9, 1.1 Hz, 1H), 6.74 (s, 1H), 6.44 (dd, *J* = 3.8, 2.6 Hz, 1H), 5.78 (s, 1H), 4.62 (s, 1H), 3.82 (s, 3H), 2.30 (s, 3H).

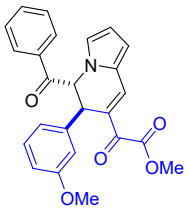
^{13}C NMR (126 MHz, CDCl3) δ 193.7, 183.3, 163.7, 138.0, 137.6, 134.6, 134.3, 133.1, 129.9, 129.3, 129.0, 128.7, 127.6, 127.2, 124.5, 117.4, 113.0, 66.0, 52.6, 40.6, 21.2.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}NO_4H^+$ 400.1543; Found 400.1537.



Methyl 2-(*trans*-5-benzoyl-6-(4-methoxyphenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ac)

From methyl (*E*)-4-(4-methoxyphenyl)-2-oxobut-3-enoate (44 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol), following the general procedure , the title compound (68.9 mg, 83%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

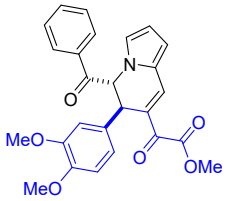
^{1}H NMR (500 MHz, CDCl3) δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.88 (s, 1H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 3H), 6.75 (s, 1H), 6.50 – 6.39 (m, 1H), 5.78 (s, 1H), 4.61 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H).
^{13}C NMR (126 MHz, CDCl3) δ 193.7, 183.3, 163.7, 159.2, 134.4, 134.3, 133.1, 133.1, 129.3, 129.0, 128.7, 128.4, 127.6, 124.6, 117.4, 114.6, 113.0, 66.1, 55.3, 52.6, 40.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}NO_5H^+$ 416.1492; Found 416.1485.



Methyl 2-(*trans*-5-benzoyl-6-(3-methoxyphenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ad)

From methyl (*E*)-4-(3-methoxyphenyl)-2-oxobut-3-enoate (44 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol), following the general procedure, the title compound (58.9 mg, 71%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 8.00 – 7.95 (m, 2H), 7.91 (s, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.84 – 6.72 (m, 4H), 6.71 – 6.65 (m, 1H), 6.44 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.80 (s, 1H), 4.62 (s, 1H), 3.83 (s, 3H), 3.71 (s, 3H).
^{13}C NMR (126 MHz, CDCl3) δ 193.6, 183.2, 163.6, 160.0, 142.4, 134.7, 134.3, 133.0, 130.2, 129.3, 128.9, 128.7, 127.7, 124.2, 119.6, 117.6, 113.2, 113.0, 113.0, 65.7, 55.2, 52.6, 40.9.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{21}NO_5Na^+$ 438.1317; Found 438.1312.



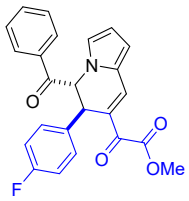
Methyl 2-(*trans*-5-benzoyl-6-(3,4-dimethoxyphenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ae)

From methyl (*E*)-4-(3,4-dimethoxyphenyl)-2-oxobut-3-enoate (51 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol), following the general procedure, the title compound (83.5 mg, 93%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.2 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 8.04 – 7.95 (m, 2H), 7.88 (s, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 6.90 – 6.71 (m, 4H), 6.60 (s, 1H), 6.45 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.80 (s, 1H), 4.59 (s, 1H), 3.83 (d, *J* = 5.1 Hz, 6H), 3.71 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.6, 183.3, 163.6, 149.2, 148.6, 134.3, 134.3, 133.5, 133.1, 129.3, 128.7, 128.7, 127.5, 124.6, 119.4, 117.3, 112.9, 111.5, 110.2, 65.8, 55.9, 55.7, 52.6, 40.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}NO_6H^+$ 446.1598 Found 446.1593.



Methyl 2-(*trans*-5-benzoyl-6-(4-fluorophenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3af)

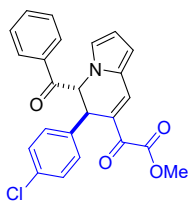
From methyl (*E*)-4-(4-fluorophenyl)-2-oxobut-3-enoate (42 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (50.0 mg, 62%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.98 (d, *J* = 7.4 Hz, 3H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.15 (dd, *J* = 8.6, 5.3 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.79 (s, 1H), 6.49 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.78 (s, 1H), 4.65 (s, 1H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.5, 183.2, 163.6, 163.4, 161.4, 135.7 (d, *J* = 268.4 Hz),134.5, 133.0, 129.4, 129.0, 128.9 (d, *J* = 6.3 Hz), 128.7, 127.8, 124.3, 117.8, 116.1 (d, *J* = 21.4 Hz), 113.2, 65.8, 52.7, 40.3.

^{19}F NMR (471 MHz, CDCl3) δ -114.27 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}FNO_4H^+$ 404.1293; Found 404.1287.



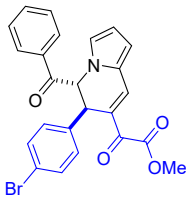
Methyl 2-(*trans*-5-benzoyl-6-(4-chlorophenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ag)

From methyl (*E*)-4-(4-chlorophenyl)-2-oxobut-3-enoate (45 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (54.5 mg, 65%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 8.01 – 7.90 (m, 3H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (dd, *J* = 3.8, 0.8 Hz, 1H), 6.76 (s, 1H), 6.46 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.75 (s, 1H), 4.62 (s, 1H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.4, 183.1, 163.5, 139.5, 134.8, 134.5, 133.8, 133.0, 129.4, 129.4, 128.9, 128.7, 128.7, 127.8, 123.9, 117.9, 113.3, 65.6, 52.7, 40.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}ClNO_4H^+$ 420.0997; Found 420.0992.



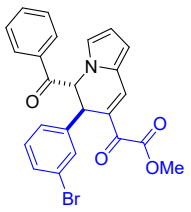
Methyl 2-(*trans*-5-benzoyl-6-(4-bromophenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ah)

From methyl (*E*)-4-(4-bromophenyl)-2-oxobut-3-enoate (54 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (56.6 mg, 61%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.97 – 7.91 (m, 3H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 3.8 Hz, 1H), 6.76 (s, 1H), 6.48 – 6.42 (m, 1H), 5.75 (s, 1H), 4.60 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.4, 183.1, 163.5, 140.0, 134.8, 134.5, 133.0, 132.4, 129.4, 129.1, 128.9, 128.7, 127.8, 123.9, 121.9, 118.0, 113.3, 65.5, 52.7, 40.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}BrNO_4H^+$ 464.0492; Found 464.0485.



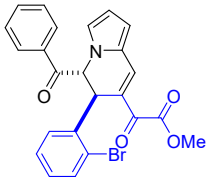
Methyl 2-(*trans*-5-benzoyl-6-(3-bromophenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ai)

From methyl (*E*)-4-(3-bromophenyl)-2-oxobut-3-enoate (54 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (60.3 mg, 65%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.87 (d, *J* = 6.0 Hz, 3H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.24 (s, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 3.7 Hz, 1H), 6.70 (s, 1H), 6.41 – 6.37 (m, 1H), 5.69 (s, 1H), 4.53 (s, 1H), 3.77 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.4, 183.0, 163.5, 143.1, 135.0, 134.5, 133.0, 131.1, 130.8, 130.4, 129.4, 128.8, 128.7, 128.0, 125.9, 123.6, 123.1, 118.1, 113.3, 65.4, 52.7, 40.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}BrNO_4H^+$ 464.0484; Found 464.0492.



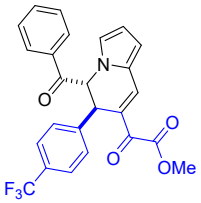
Methyl 2-(*trans*-5-benzoyl-6-(2-bromophenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3aj)

From methyl (*E*)-4-(2-bromophenyl)-2-oxobut-3-enoate (54 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (67.8 mg, 73%) was obtained as a yellow oil. $\mathbf{R_f}$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.94 (dd, *J* = 16.8, 9.5 Hz, 3H), 7.57 – 7.50 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.03 – 6.97 (m, 2H), 6.76 – 6.70 (m, 2H), 6.63 (s, 1H), 6.30 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.62 (s, 1H), 5.04 (s, 1H), 3.76 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 194.1, 182.9, 163.6, 139.3, 135.5, 134.2, 133.7, 133.6, 129.4, 129.3, 129.0, 1290, 128.7, 128.2, 127.7, 125.0, 123.9, 117.6, 113.0, 63.8, 52.7, 39.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}BrNO_4H^+$ 464.0492; Found 464.0487.



Methyl 2-(*trans*-5-benzoyl-6-(4-(trifluoromethyl)phenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ak)

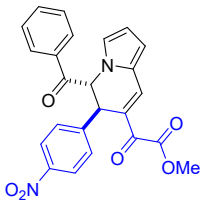
From methyl (*E*)-2-oxo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (52 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (47.2 mg, 52%) was obtained as a yellow solid. $\mathbf{R_f}$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.98 – 7.93 (m, 3H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.56 (dd, *J* = 15.6, 8.0 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 3.8 Hz, 1H), 6.78 (s, 1H), 6.47 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.77 (s, 1H), 4.69 (s, 1H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.2, 183.0, 163.4, 135.0 134.5, 132.9, 130.3 130.0, 129.5, 128.8, 128.7, 128.0, 127.8, 126.3 (q, *J* = 3.4 Hz), 125.1, 123.6, 118.2, 113.4, 65.3, 52.8, 40.8.

^{19}F NMR (471 MHz, CDCl$_3$) δ -62.61.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{18}F_3NO_4H^+$ 454.1261; Found 454.1254.



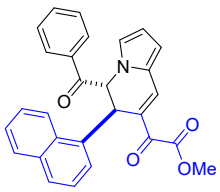
Methyl 2-(*trans*-5-benzoyl-6-(4-nitrophenyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3al)

From methyl (*E*)-4-(4-nitrophenyl)-2-oxobut-3-enoate (47 mg, 0.2 mmol) and 1-(2-oxo-2-

phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (68.8 mg, 80%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 2H), 8.02 (s, 1H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 3.9 Hz, 1H), 6.83 (s, 1H), 6.52 (dd, *J* = 3.7, 2.8 Hz, 1H), 5.78 (s, 1H), 4.75 (s, 1H), 3.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 182.9, 163.3, 148.1, 147.6, 135.3, 134.7, 132.9, 129.6, 128.8, 128.7, 128.4, 128.2, 124.6, 123.2, 118.7, 113.7, 65.0, 52.9, 40.8.



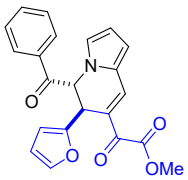
Methyl 2-(*trans*-5-benzoyl-6-(naphthalen-2-yl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3am)

From methyl (*E*)-4-(naphthalen-2-yl)-2-oxobut-3-enoate (48 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (47 mg, 54%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.91 (dd, *J* = 7.8, 7.2 Hz, 3H), 7.75 – 7.64 (m, 3H), 7.62 – 7.52 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.25 (m, 2H), 7.16 (dd, *J* = 4.7, 3.7 Hz, 1H), 6.77 (d, *J* = 3.8 Hz, 1H), 6.66 (s, 1H), 6.45 – 6.23 (m, 1H), 5.79 (s, 1H), 4.74 (s, 1H), 3.73 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.7, 183.3, 163.7, 138.2, 134.8, 134.4, 133.6, 133.1, 133.0, 129.4, 129.3, 129.0, 128.8, 128.1, 127.7, 127.7, 126.4, 126.4, 126.2, 125.1, 124.2, 117.7, 113.2, 65.8, 52.7, 41.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{21}NO_4H^+$ 436.1543; Found 436.1540.

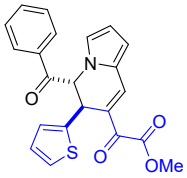


methyl 2-((*trans*-5-benzoyl-6-(furan-2-yl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3an)

From methyl (*E*)-4-(furan-2-yl)-2-oxobut-3-enoate (36 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (69 mg, 92%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.91 (s, 1H), 7.66 (m, 1H), 7.58 – 7.54 (m, 2H), 7.40 (d, *J* = 1.4 Hz, 1H), 6.80 – 6.76 (m, 2H), 6.40 (dd, *J* = 3.9, 2.6 Hz, 1H), 6.23 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.16 (d, *J* = 0.8 Hz, 1H), 5.96 (m, 1H), 4.93 (s, 1H), 3.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 183.1, 163.8, 151.9, 142.5, 135.9, 134.5, 132.8, 129.4, 128.9, 128.5, 128.1, 120.8, 118.1, 113.0, 110.8, 107.3, 63.5, 52.8, 35.4.



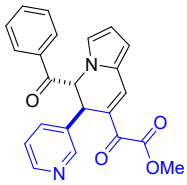
Methyl 2-(*trans*-5-benzoyl-6-(thiophen-2-yl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ao)

From methyl (*E*)-2-oxo-4-(thiophen-2-yl)but-3-enoate (40 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (50.8 mg, 65%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.99 – 7.95 (m, 2H), 7.86 (s, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.84 – 6.81 (m, 2H), 6.48 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.89 (s, 1H), 5.06 (s, 1H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.1, 182.7, 163.5, 142.7, 134.5, 134.3, 133.0, 129.4, 128.7, 128.6, 128.0, 126.9, 125.6, 124.2, 124.1, 118.1, 113.4, 66.2, 52.7, 36.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}NO_4SH^+$ 392.0951; Found 392.0945.

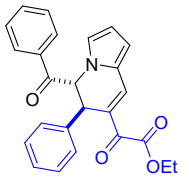


Methyl 2-(*trans*-5-benzoyl-6-(pyridin-3-yl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ap)

From methyl (*E)*-2-oxo-4-(pyridin-4-yl)but-3-enoate (38.2 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (60.2 mg, 78%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 27.3, 2.6 Hz, 2H), 7.97 (dd, *J* = 14.4, 7.2 Hz, 3H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.22 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.93 – 6.84 (m, 1H), 6.80 (s, 1H), 6.55 – 6.45 (m, 1H), 5.77 (s, 1H), 4.69 (s, 1H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 182.9, 163.4, 149.1, 148.8, 136.9, 135.1, 134.7, 132.9, 129.6, 128.7, 128.1, 124.3, 123.3, 118.4, 113.6, 65.4, 52.8, 38.9.



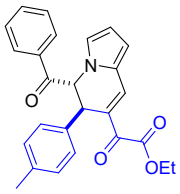
Ehyl 2-(*trans*-5-benzoyl-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate(3aq)

From ethyl (*E*)-2-oxo-4-phenylbut-3-enoate (44 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (55.8 mg, 70%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.91 (s, 1H), 7.66 (s, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 6.8 Hz, 3H), 7.17 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.84 – 6.77 (m, 1H), 6.74 (s, 1H), 6.45 (dd, *J* = 3.7, 2.7 Hz, 1H), 5.80 (s, 1H), 4.65 (s, 1H), 4.30 (qd, *J* = 7.1, 3.3 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.7, 183.6, 163.4, 141.0, 134.5, 134.3, 133.1, 129.3, 129.3, 129.0, 128.8, 127.9, 127.6, 127.3, 124.3, 117.4, 113.0, 65.9, 62.1, 41.0, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}NO_4H^+$ 400.1543; Found 400.1538.

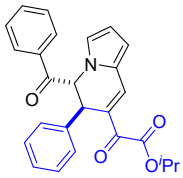


Ethyl 2-(*trans*-5-benzoyl-6-(p-tolyl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate(3ar)

From ethyl (E)-2-oxo-4-(p-tolyl)but-3-enoate (43.6 mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (68.6 mg, 83%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.88 (s, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.09 – 7.05 (m, 4H), 6.79 (d, *J* = 3.7 Hz, 1H), 6.73 (s, 1H), 6.44 – 6.41 (m, 1H), 5.78 (s, 1H), 4.62 (s, 1H), 4.28 (m, 2H), 2.29 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 183.7, 163.4, 138.1, 137.6, 134.3, 134.3, 133.1, 129.9, 129.3, 129.0, 128.7, 128.1, 127.5, 127.2, 124.5, 117.3, 112.9, 66.0, 62.1, 40.6, 21.1, 14.1.



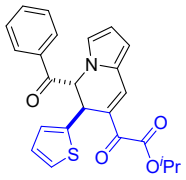
Isopropyl 2-(*trans*-5-benzoyl-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3as)

From isopropyl 4-(2,3-dimethyl-1H-indol-6-yl)-2-oxo-4-phenylbutanoate(43.6mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (56.2 mg, 68%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 8.02 – 7.95 (m, 2H), 7.89 (s, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 6.9 Hz, 3H), 7.17 (dd, *J* = 7.5, 1.8 Hz, 2H), 6.81 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.74 (s, 1H), 6.45 (dd, *J* = 3.8, 2.6 Hz, 1H), 5.79 (s, 1H), 5.21 – 5.11 (m, 1H), 4.65 (s, 1H), 1.34 – 1.30 (m, 6H).

^{13}C NMR (126 MHz, CDCl3) δ 193.7, 183.9, 163.0, 141.1, 134.4, 134.3, 133.1, 129.3, 129.3, 128.8, 127.9, 127.5, 127.3, 124.4, 117.3, 112.9, 70.3, 65.9, 41.1, 21.8, 21.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}NO_4H^+$ 414.1700; Found 414.1693.

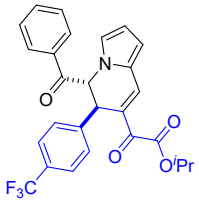


Isopropyl 2-(*trans*-5-benzoyl-6-(thiophen-2-yl)-5,6-dihydroindolizin-7-yl)-2-oxoacetate(3at)

From isopropyl (*E*)-2-oxo-4-(thiophen-2-yl)but-3-enoate (44.8mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (72.9 mg, 87%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.82 (s, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.12 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.92 – 6.87 (m, 2H), 6.84 – 6.79 (m, 2H), 6.47 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.89 (s, 1H), 5.17 (s, 1H), 5.06 (s, 1H), 1.32 (dd, *J* = 6.2, 4.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 183.4, 162.8, 142.8, 134.5, 133.9, 133.0, 129.4, 128.8, 128.6, 127.8, 126.9, 125.6, 124.7, 124.1, 117.8, 113.2, 70.4, 66.2, 36.6, 21.8, 21.7.



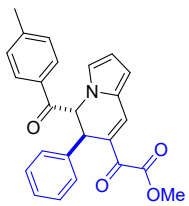
Isopropyl 2-(*trans*-5-benzoyl-6-(4-(trifluoromethyl)phenyl)-5,6-dihydroindolizin-7-yl)-2-oxo-acetate(3au)

From isopropyl (*E*)-2-oxo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (57.2mg, 0.2 mmol) and 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbaldehyde (63.9 mg, 0.3 mmol) , following the general procedure, the title compound (72.2 mg, 75%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 3H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.56 (m, 4H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.84 (dd, *J* = 3.9, 1.2 Hz, 1H), 6.78 – 6.75 (m, 1H), 6.47 (dd, *J* = 3.9, 2.6 Hz, 1H), 5.76 (s, 1H), 5.17 (m, 1H), 4.69 (s, 1H), 1.32 (dd, *J* = 7.3, 6.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 183.7, 162.8, 145.0, 134.6 (d, *J* = 7.1 Hz), 133.0, 129.5, 128.9, 128.7, 128.2, 127.8, 127., 126.3 (d, *J* = 3.7 Hz), 123.8, 118.0, 113.4, 70.6, 65.4, 40.9, 21.8 (d, *J* = 3.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.61 (s).



Methyl 2-(*trans*-5-(4-methylbenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ba)

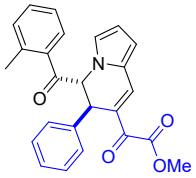
From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-oxo-2-(*p*-tolyl)ethyl)-1H-pyrrole-2-carbaldehyde (68.1 mg, 0.3 mmol) , following the general procedure, the title compound (74.2 mg, 93%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate

= 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.91 – 7.85 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 5.7 Hz, 3H), 7.16 (dd, *J* = 7.5, 1.9 Hz, 2H), 6.81 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.74 (s, 1H), 6.44 (dd, *J* = 3.8, 2.6 Hz, 1H), 5.77 (s, 1H), 4.64 (s, 1H), 3.82 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.3, 183.2, 163.7, 145.5, 141.1, 134.7, 130.5, 130.1, 129.3, 129.1, 128.9, 127.9, 127.7, 127.3, 124.4, 117.5, 113.0, 65.8, 52.7, 41.2, 21.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}NO_4H^+$ 400.1543; Found 400.1537.



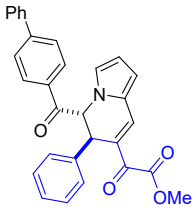
Methyl 2-(*trans*-5-(2-methylbenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ca)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-oxo-2-(*o*-tolyl)ethyl)-1H-pyrrole-2-carbaldehyde (68.1 mg, 0.3 mmol), following the general procedure, the title compound (63.8mg, 80%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.89 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.45 (m, 1H), 7.33 (m, 2H), 7.21 (dd, *J* = 5.1, 1.7 Hz, 3H), 7.04 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.84 – 6.74 (m, 2H), 6.43 (dd, *J* = 3.7, 2.7 Hz, 1H), 5.58 (s, 1H), 4.59 (s, 1H), 3.85 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 198.3, 183.4, 163.8, 140.5, 139.4, 135.0, 134.5, 132.7, 132.2, 129.2, 128.6, 128.2, 127.8, 127.2, 127.2, 126.0, 124.2, 117.7, 113.0, 68.5, 52.7, 40.2, 20.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}NO_4H^+$ 400.1543; Found 400.1539.



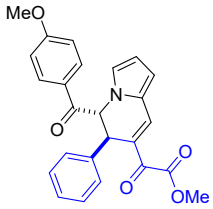
Methyl 2-(*trans*-5-([1,1'-biphenyl]-4-carbonyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3da)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (87 mg, 0.3 mmol), following the general procedure, the title compound (64.5 mg, 70%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.93 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.22 – 7.18 (m, 2H), 6.85 – 6.81 (m, 1H), 6.76 (s, 1H), 6.46 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.83 (s, 1H), 4.70 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.3, 183.3, 163.7, 147.1, 141.1, 139.6, 134.7, 131.6, 129.4, 129.3, 129.2, 129.1, 128.7, 128.0, 127.7, 127.5, 127.4, 124.4, 117.6, 113.1, 65.9, 52.7, 41.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{23}NO_4H^+$ 462.1700; Found 462.1692.



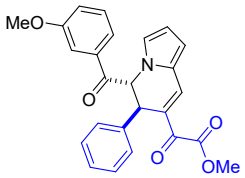
Methyl 2-(*trans*-5-(4-methoxybenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ea)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(4-methoxyphenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (72.9mg, 0.3 mmol), following the general procedure, the title compound (55.6 mg, 67%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.3 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.88 (d, *J* = 8.9 Hz, 2H), 7.83 (s, 1H), 7.19 (d, *J* = 7.2 Hz, 3H), 7.09 (dd, *J* = 7.5, 1.8 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.72 (dd, *J* = 3.8, 1.1 Hz, 1H), 6.66 (s, 1H), 6.36 (dd, *J* = 3.8, 2.6 Hz, 1H), 5.67 (s, 1H), 4.56 (s, 1H), 3.82 (s, 3H), 3.74 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 192.1, 183.3, 164.4, 163.7, 141.2, 134.7, 131.1, 129.2, 129.1, 127.9, 127.7, 127.3, 125.7, 124.4, 117.5, 114.6, 113.0, 65.5, 55.7, 52.6, 41.4

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}NO_5H^+$ 416.1492; Found 416.1486.



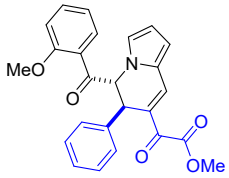
Methyl 2-(*trans*-5-(3-methoxybenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3fa)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(3-methoxyphenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (72.9 mg, 0.3 mmol), following the general procedure, the title compound (70.6 mg, 85%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.92 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.27 (d, *J* = 6.5 Hz, 4H), 7.22 – 7.14 (m, 2H), 6.89 – 6.70 (m, 2H), 6.45 (d, *J* = 2.4 Hz, 1H), 5.77 (s, 1H), 4.66 (s, 1H), 3.84 (d, *J* = 10.9 Hz, 6H).

^{13}C NMR (126 MHz, CDCl3) δ 193.6, 183.2, 163.7, 160.4, 141.0, 134.7, 134.4, 130.3, 129.3, 129.0, 128.0, 127.7, 127.3, 124.3, 121.0, 120.9, 117.6, 113.2, 113.1, 66.0, 55.6, 52.7, 41.1

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}NO_5H^+$ 416.1492; Found 416.1486.



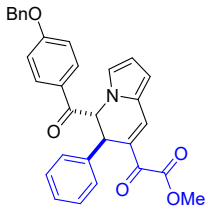
Methyl 2-(*trans*-5-(2-methoxybenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ga)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(2-methoxyphenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (72.9 mg, 0.3 mmol), following the general procedure, the title compound (55.6 mg, 67%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.83 (s, 1H), 7.70 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.24 – 7.19 (m, 3H), 7.10 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.03 (dd, *J* = 7.9, 5.5 Hz, 2H), 6.82 (s, 1H), 6.78 (d, *J* = 3.8 Hz, 1H), 6.43 (dd, *J* = 3.7, 2.7 Hz, 1H), 5.92 (s, 1H), 4.61 (s, 1H), 3.88 (s, 3H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6, 183.4, 163.9, 158.3, 141.5, 135.1, 134.9, 131.7, 128.8, 128.6, 128.2, 127.5, 127.5, 124.8, 124.1, 121.7, 117.3, 112.6, 111.5, 69.6, 55.7, 52.6, 40.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}NO_5H^+$ 416.1492; Found 416.1494.



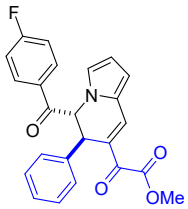
Methyl 2-(*trans*-5-(4-(benzyloxy)benzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ha)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(4-(benzyloxy)phenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (95.7 mg, 0.3 mmol), following the general procedure, the title compound (68.8 mg, 70%) was obtained as a green solid. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.98 – 7.89 (m, 3H), 7.43 (m, 4H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.26 (t, *J* = 6.9 Hz, 3H), 7.17 (dd, *J* = 7.4, 1.6 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.80 (dd, *J* = 3.8, 1.1 Hz, 1H), 6.73 (s, 1H), 6.43 (dd, *J* = 3.8, 2.6 Hz, 1H), 5.74 (s, 1H), 5.17 (s, 2H), 4.64 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 192.0, 183.3, 163.7, 163.6, 141.1, 136.0, 134.7, 131.1, 129.2, 129.1, 128.9, 128.5, 127.9, 127.6, 127.6, 127.3, 125.9, 124.4, 117.5, 115.4, 113.0, 70.4, 65.5, 52.6, 41.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{25}NO_5H^+$ 492.1805; Found 492.1797.



Methyl 2-(*trans*-5-(4-fluorobenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ia)

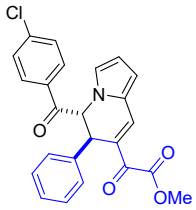
From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(4-fluorophenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (69.3 mg, 0.3 mmol), following the general procedure, the title compound (65.3 mg, 81%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 8.03 – 7.98 (m, 2H), 7.91 (s, 1H), 7.30 – 7.26 (m, 3H), 7.23 (t, *J* = 8.5 Hz, 2H), 7.18 – 7.13 (m, 2H), 6.82 (dd, *J* = 3.9, 1.1 Hz, 1H), 6.75 (s, 1H), 6.45 (dd, *J* = 3.8, 2.6 Hz, 1H), 5.75 (s, 1H), 4.62 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 192.2, 183.2, 166.4 (d, *J* = 257 Hz), 163.6, 140.9, 134.6, 131.5 (d, *J* = 9.4 Hz), 129.5 (d, *J* = 2.9 Hz), 129.3, 129.0, 128.0, 127.7, 127.3, 124.3, 117.7, 116.7 (d, *J* = 21 Hz), 113.2, 65.7, 52.7, 41.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.53 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}FNO_4H^+$ 404.1293; Found 404.1287.



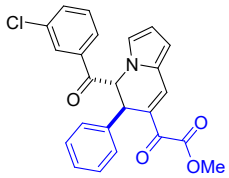
Methyl 2-(*trans*-5-(4-chlorobenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ja)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(4-chlorophenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (74.1 mg, 0.3 mmol), following the general procedure, the title compound (72.1 mg, 86%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.90 (d, *J* = 9.1 Hz, 3H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.27 (dd, *J* = 5.2, 1.7 Hz, 3H), 7.14 (dd, *J* = 7.1, 2.2 Hz, 2H), 6.81 (d, *J* = 3.2 Hz, 1H), 6.74 (s, 1H), 6.45 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.74 (s, 1H), 4.60 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 192.7, 183.2, 163.6, 141.0, 140.8, 134.6, 131.4, 130.1, 129.7, 129.3, 128.9, 128.1, 127.6, 127.3, 124.2, 117.7, 113.2, 65.8, 52.7, 41.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}ClNO_4H^+$ 420.0997; Found 420.0990.



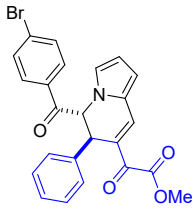
Methyl 2-(*trans*-5-(3-chlorobenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ka)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(3-chlorophenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (74.1 mg, 0.3 mmol), following the general procedure, the title compound (69.5 mg, 83%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.92 (d, *J* = 6.2 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 5.4 Hz, 3H), 7.15 (dd, *J* = 7.3, 1.8 Hz, 2H), 6.81 (d, *J* = 3.7 Hz, 1H), 6.74 (s, 1H), 6.44 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.73 (s, 1H), 4.61 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 192.6, 183.2, 163.6, 140.7, 135.8, 134.7, 134.6, 134.3, 130.7, 129.4, 128.9, 128.5, 128.1, 127.7, 127.3, 126.7, 124.2, 117.7, 113.2, 65.9, 52.7, 40.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}ClNO_4H^+$ 420.0997; Found 420.0988.



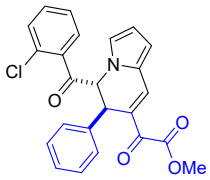
Methyl 2-(*trans*-5-(4-bromobenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3la)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(4-bromophenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (87.6 mg, 0.3 mmol), following the general procedure, the title compound (76.8 mg, 83%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, CDCl3) δ 7.91 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.27 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.14 (dd, *J* = 7.1, 2.3 Hz, 2H), 6.81 (d, *J* = 3.8 Hz, 1H), 6.74 (s, 1H), 6.45 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.73 (s, 1H), 4.59 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 192.9, 183.2, 163.6, 140.8, 134.6, 132.7, 131.8, 130.2, 129.8, 129.3, 128.9, 128.1, 127.6, 127.3, 124.2, 117.7, 113.2, 65.8, 52.7, 41.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}BrNO_4H^+$ 464.0492; Found 464.0486.

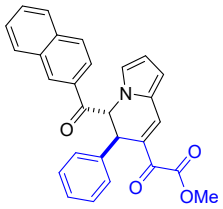


Methyl 2-(*trans*-5-(2-chlorobenzoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3ma)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(2-chlorophenyl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (74.1mg, 0.3 mmol), following the general procedure, the title compound (65.4 mg, 78%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.45 (dd, *J* = 5.4, 2.0 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.23 – 7.19 (m, 4H), 7.05 – 7.02 (m, 2H), 6.85 (s, 1H), 6.75 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.37 (dd, *J* = 3.8, 2.6 Hz, 1H), 5.65 (d, *J* = 0.8 Hz, 1H), 4.70 (s, 1H), 3.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 183.1, 163.7, 139.9, 136.6, 134.9, 132.5, 130.4, 130.2, 129.1, 128.8, 128.3, 128.1, 127.8, 127.6, 127.4, 124.4, 117.8, 112.9, 69.6, 52.8, 39.9.

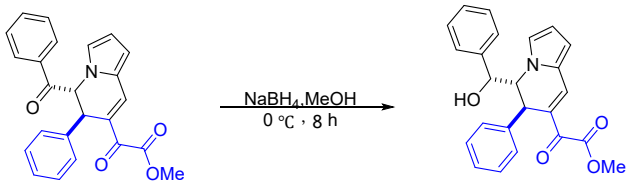


Methyl 2-(*trans*-5-(2-naphthoyl)-6-phenyl-5,6-dihydroindolizin-7-yl)-2-oxoacetate (3na)

From methyl (*E*)-2-oxo-4-phenylbut-3-enoate (38 mg, 0.2 mmol) and 1-(2-(naphthalen-2-yl)-2-oxoethyl)-1H-pyrrole-2-carbaldehyde (78.9 mg, 0.3 mmol), following the general procedure, the title compound (63.5 mg, 73%) was obtained as a yellow oil. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.98 (d, *J* = 5.7 Hz, 3H), 7.95 – 7.91 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.24 – 7.19 (m, 2H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.79 (s, 1H), 6.49 – 6.45 (m, 1H), 5.96 (s, 1H), 4.73 (s, 1H), 3.82 (s, 3H).

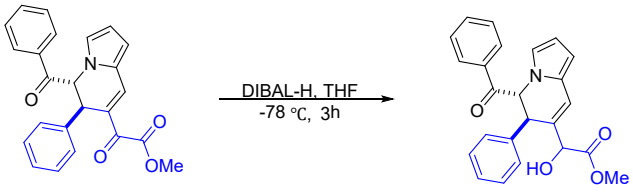
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 183.2, 163.7, 141.1, 136.1, 134.7, 132.6, 130.6, 130.3, 129.8, 129.4, 129.4, 129.3, 129.1, 128.1, 128.0, 127.7, 127.4, 127.4, 124.5, 124.1, 117.6, 113.1, 65.9, 52.7, 41.4.



The **3aa** (39 mg, 0.2 mmol, 1.0 eq.) was dissolved in super-dry MeOH (1 mL) under the protection of N_2 atmosphere. $NaBH_4$ (7.6 mg, 0.2 mmol, 1 eq.) was added portions at 0 °C. After a time period of 8.0 h, the mixture was extracted with EA (3 x 2 mL), and the combined extracts were dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash column chromatograph on silica gel using petroleum ether / ethyl acetate (8:1 - 4:1) as the eluent to yield the products **4** (56.5 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.42 (d, *J* = 6.8 Hz, 4H), 7.27 (d, *J* = 5.2 Hz, 2H), 7.17 – 7.13 (m, 3H), 7.03 (s, 1H), 6.82 (dd, *J* = 6.5, 2.8 Hz, 2H), 6.72 (d, *J* = 3.7 Hz, 1H), 6.39 – 6.34 (m, 1H), 4.68 (d, *J* = 8.3 Hz, 1H), 4.34 (d, *J* = 8.2 Hz, 1H), 4.18 (s, 1H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 183.5, 164.1, 141.1, 139.8, 134.5, 129.6, 129.1, 129.0, 128.8, 127.3, 127.2, 126.9, 126.8, 125.5, 117.1, 111.5, 76.2, 68.5, 52.7, 38.5.



The **3aa** (39 mg, 0.1 mmol, 1.0 eq.) was dissolved in super-dry THF (2 mL) under the protection of N_2 atmosphere. DIBAL-H (0.1 mL, 0.15 mmol, 1.5 eq.,1.5 M) was added portions at -78 °C. After a time period of 3.0 h, the saturated NH_4Cl was added carefully at -78 °C, then the mixture was extracted with EA (3 x 2 mL), and the combined extracts were dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash column chromatograph on silica gel using petroleum ether / ethyl acetate (4:1 - 1:1) as the eluent to yield the products **5** (32.1 mg, 83%, *d.r.* = 1:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (t, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.16 (d, *J* = 6.8 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.84 (s, 1H), 6.46 (s, 1H), 6.34 (s, 1H), 6.28 (d, *J* = 3.0 Hz, 1H), 5.57 (s, 1H),, 4.58 (s, 1H), 4.22 (s, 1H), 3.45 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 173.4, 141.5, 134.0, 133.9, 129.4, 129.3, 129.2, 129.2, 128.5, 127.8, 127.4, 122.6, 120.0, 110.2,109.0, 73.8, 66.5, 52.7, 44.5.

7 X-ray Crystal Structure Determination of the Products

To grow the crystals used to collect the X-ray data for **3am**, the following method was used: the sample was dissolved with 3 mL petroleum ether and 1 mL THF in a small vial, which was kept aside at room temperature to obtain crystals.

A suitable crystal was selectedon a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 150.00(10) K during data collection. Using Olex2, the structure was solved with

the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2159416).

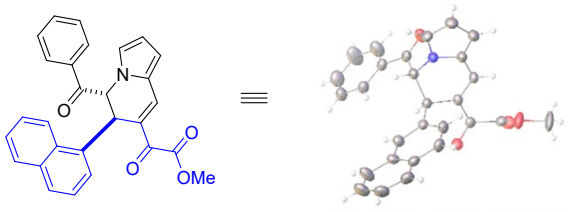


Figure S3. The X-ray Diffraction Configuration of **3am**.

Table S8. Crystallographic data for compounds **3am**.

Identification code	**3am**
Empirical formula	$C_{28}H_{21}NO_4$
Formula weight	435.46
Temperature/K	160.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.1241(6)
b/Å	12.2852(5)
c/Å	14.9183(7)
α/°	90
β/°	98.870(2)
γ/°	90
Volume/Å^3	2195.46(17)
Z	4
ρcalcg/cm^3	1.317
μ/mm^{-1}	0.088
F(000)	912.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.316 to 52.804
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 13, -18 ≤ l ≤ 17
Reflections collected	17130
Independent reflections	4472 [Rint = 0.0795, Rsigma = 0.0807]
Data/restraints/parameters	4472/0/299
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R1 = 0.0572, wR2 = 0.1096
Final R indexes [all data]	R1 = 0.1225, wR2 = 0.1397
Largest diff. peak/hole / e Å^{-3}	0.20/-0.22

8 References

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9 Copies of NMR Spectra for Compounds

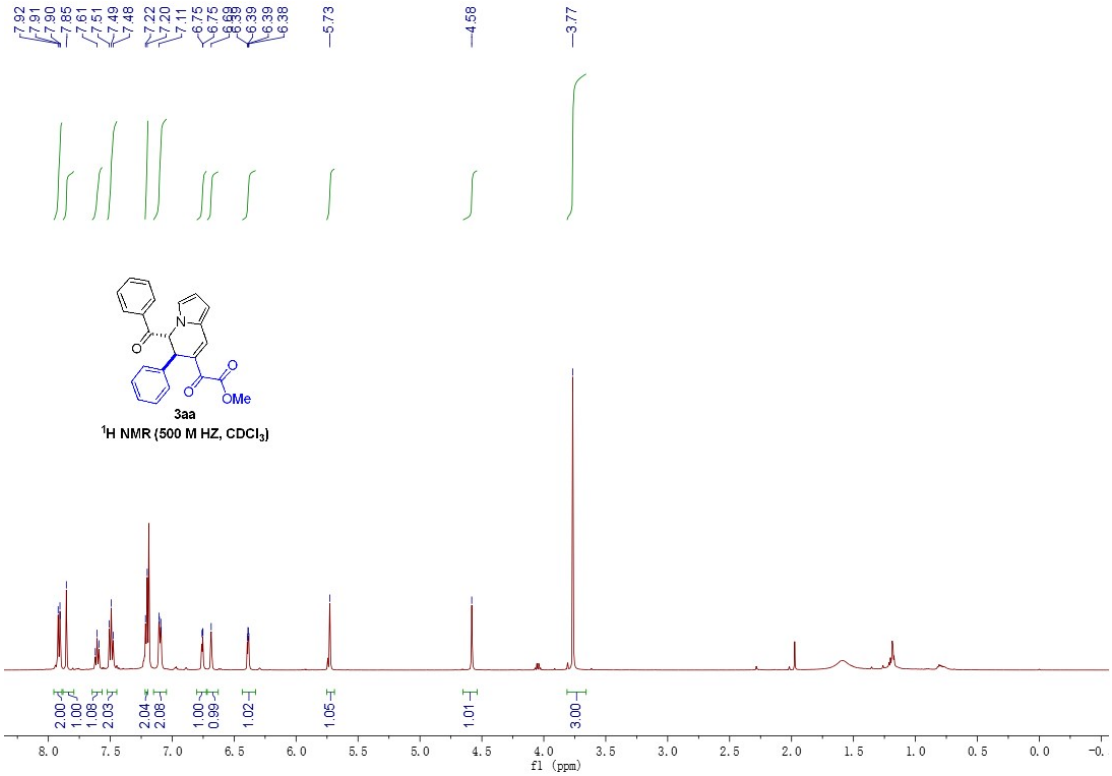

Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3aa

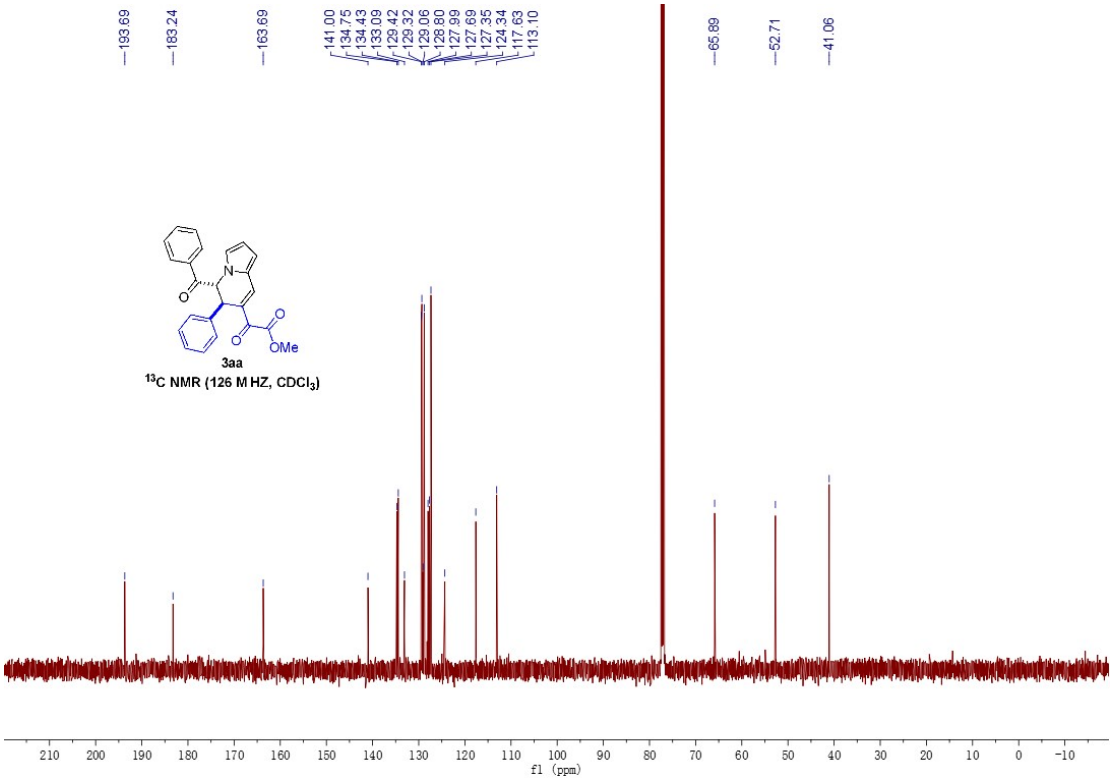

Figure S5. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3aa

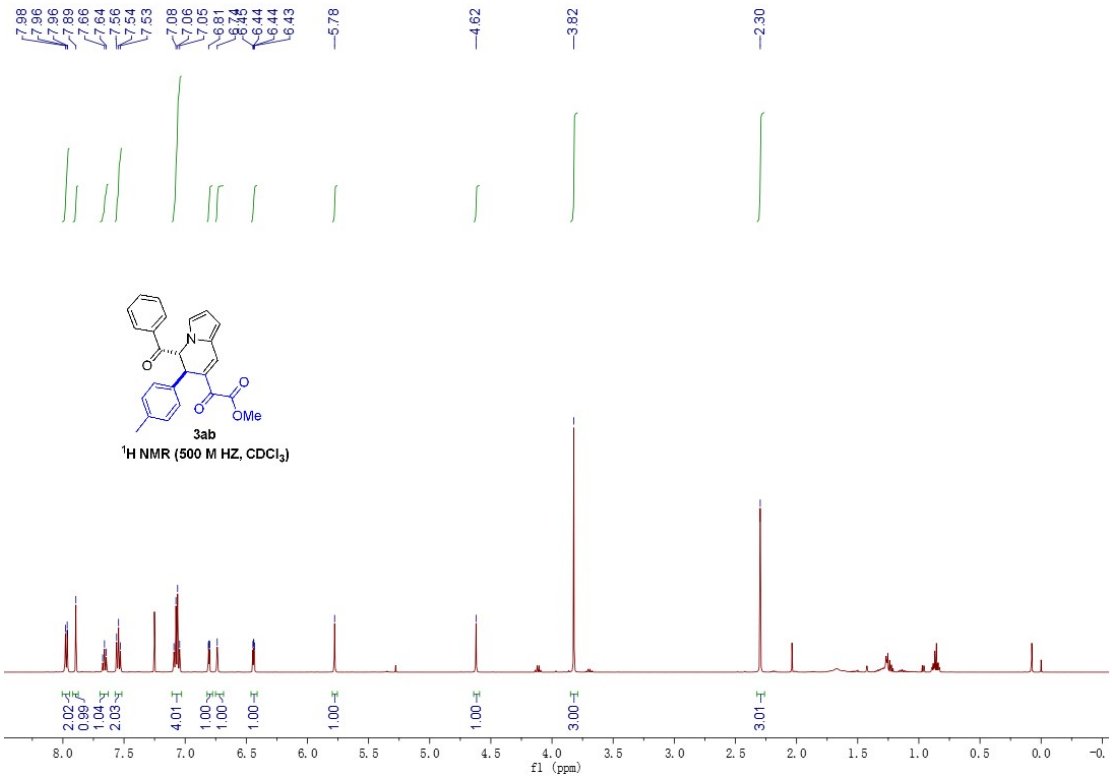

Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ab

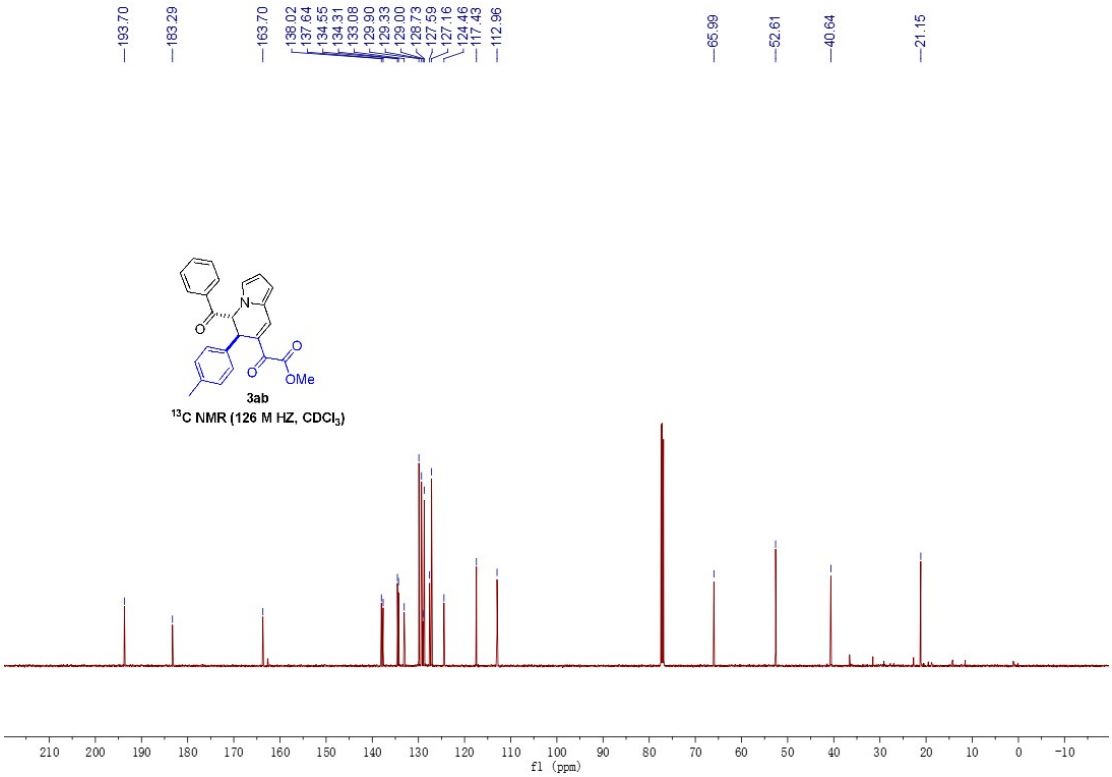

Figure S7. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ab

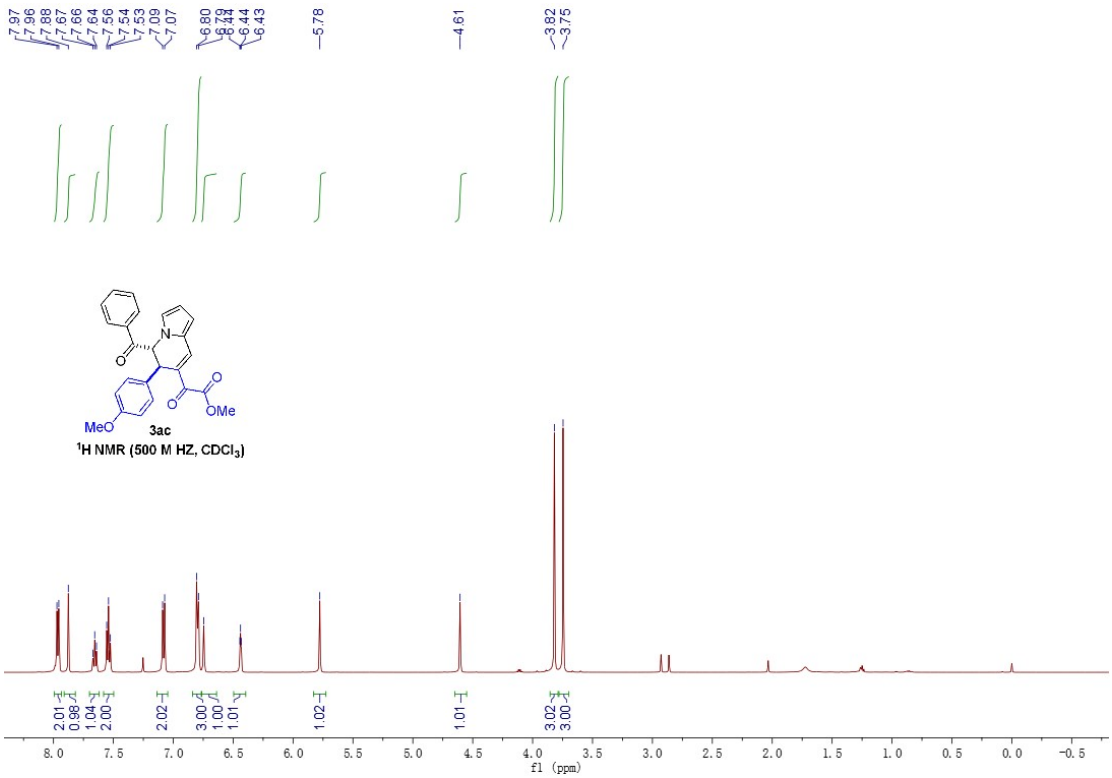

Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ac

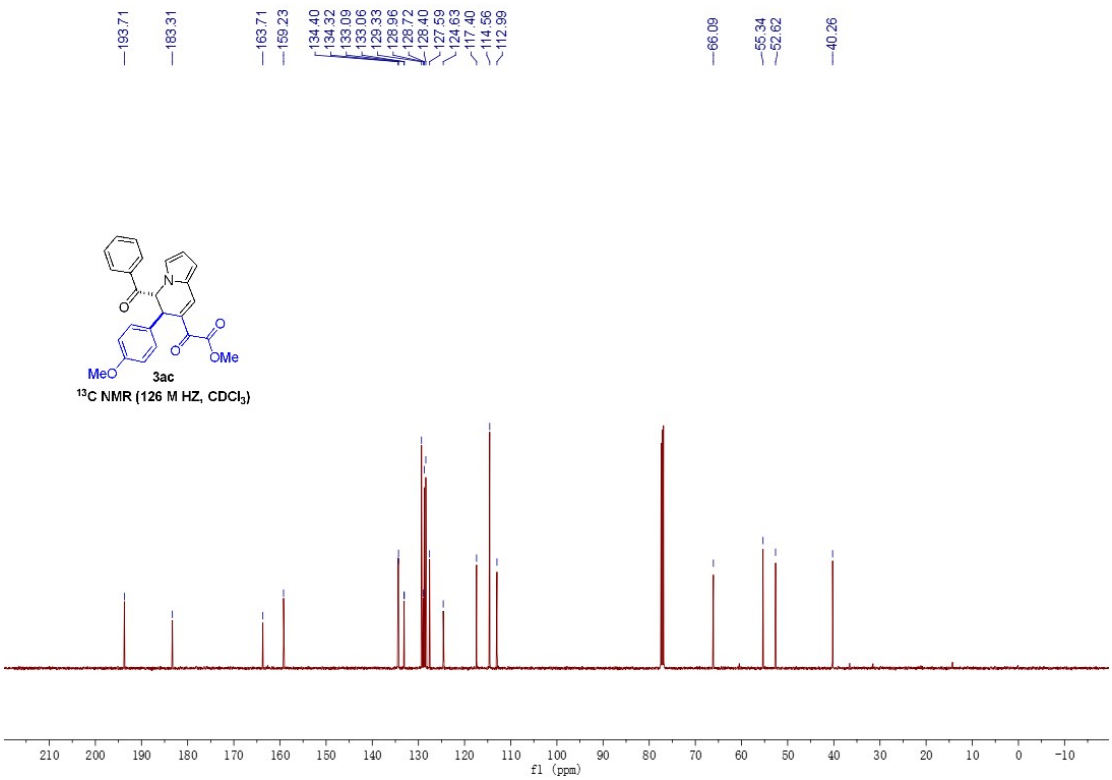

Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ac

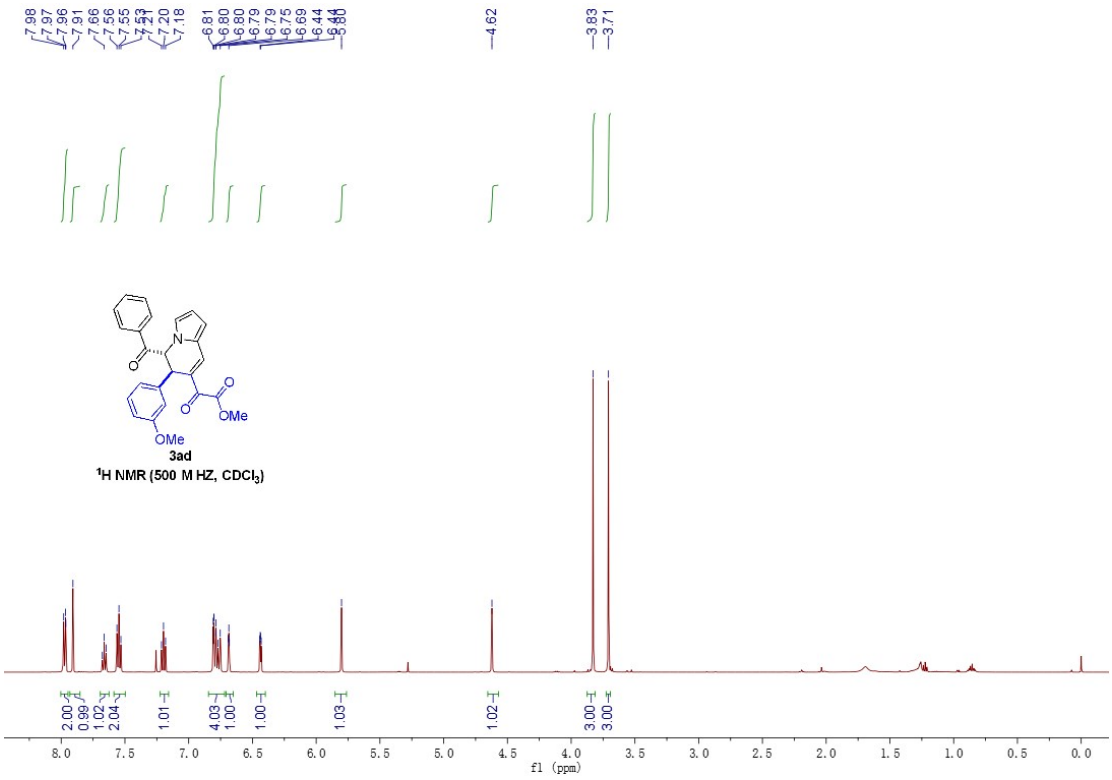

Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ad

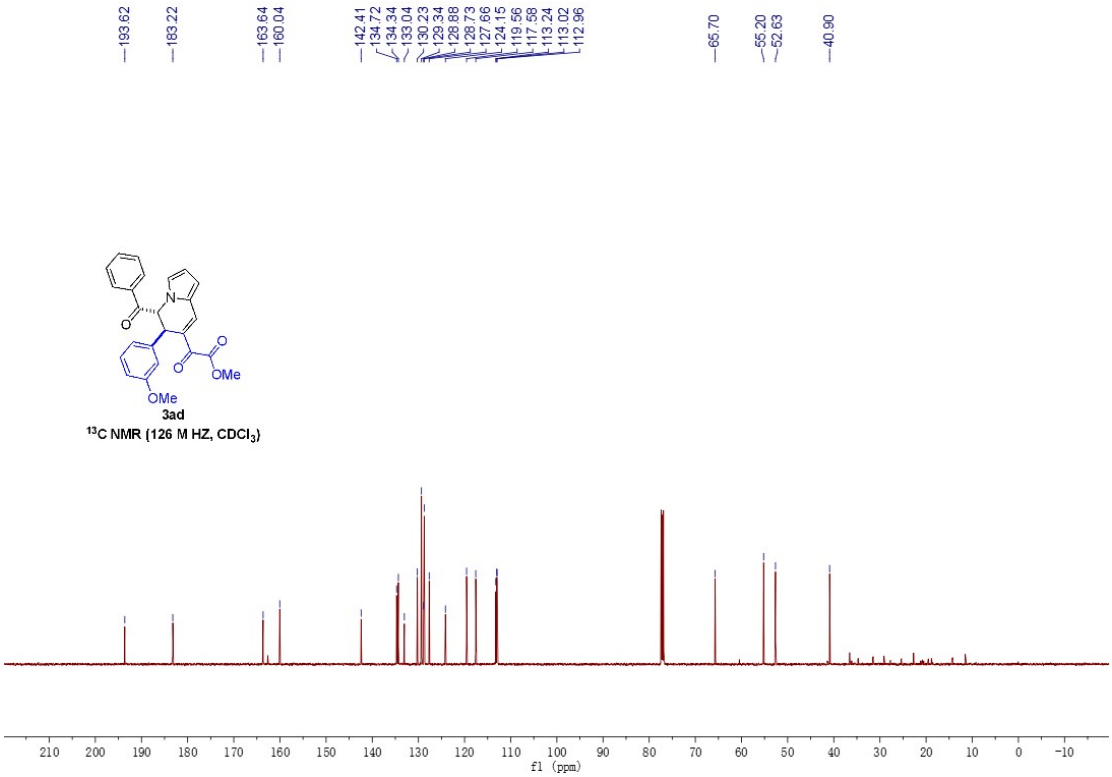

Figure S11. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ad

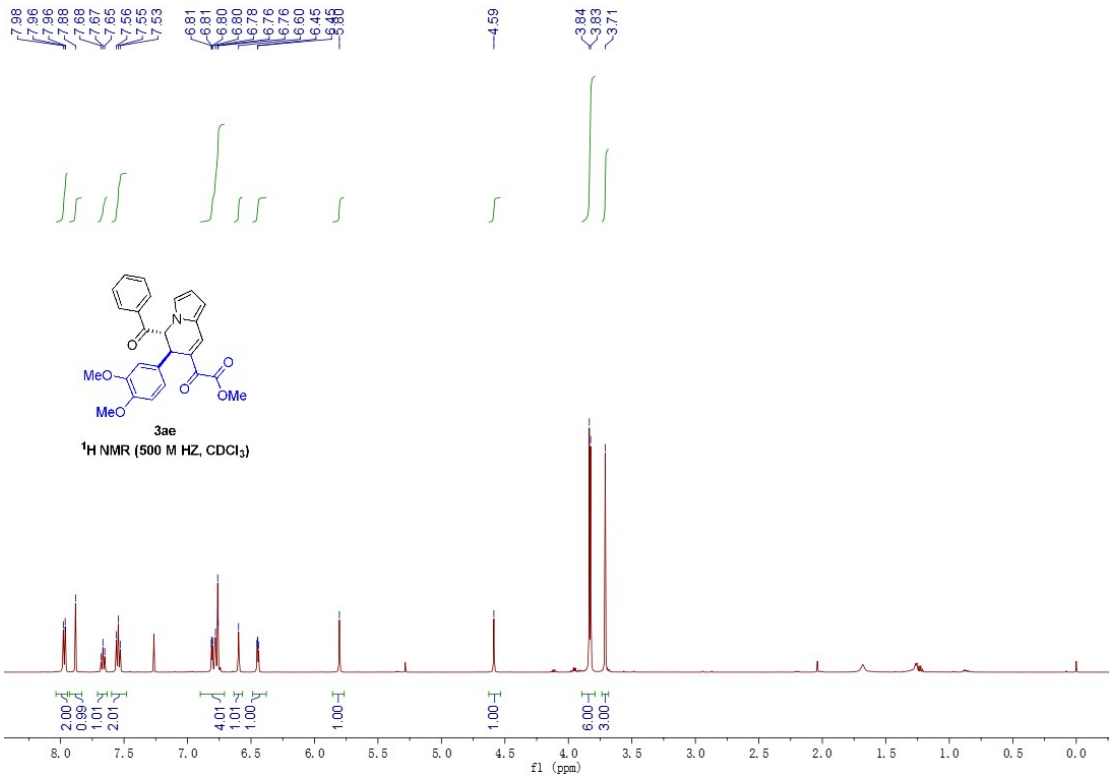

Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ae

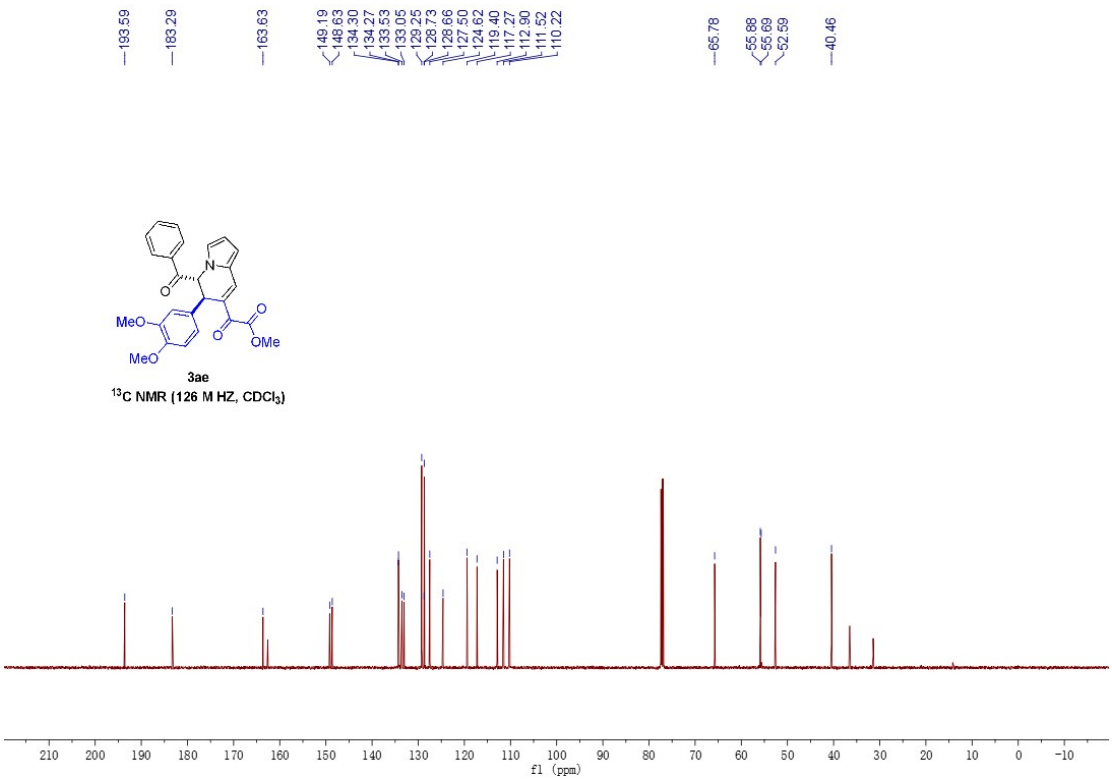

Figure S13. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ae

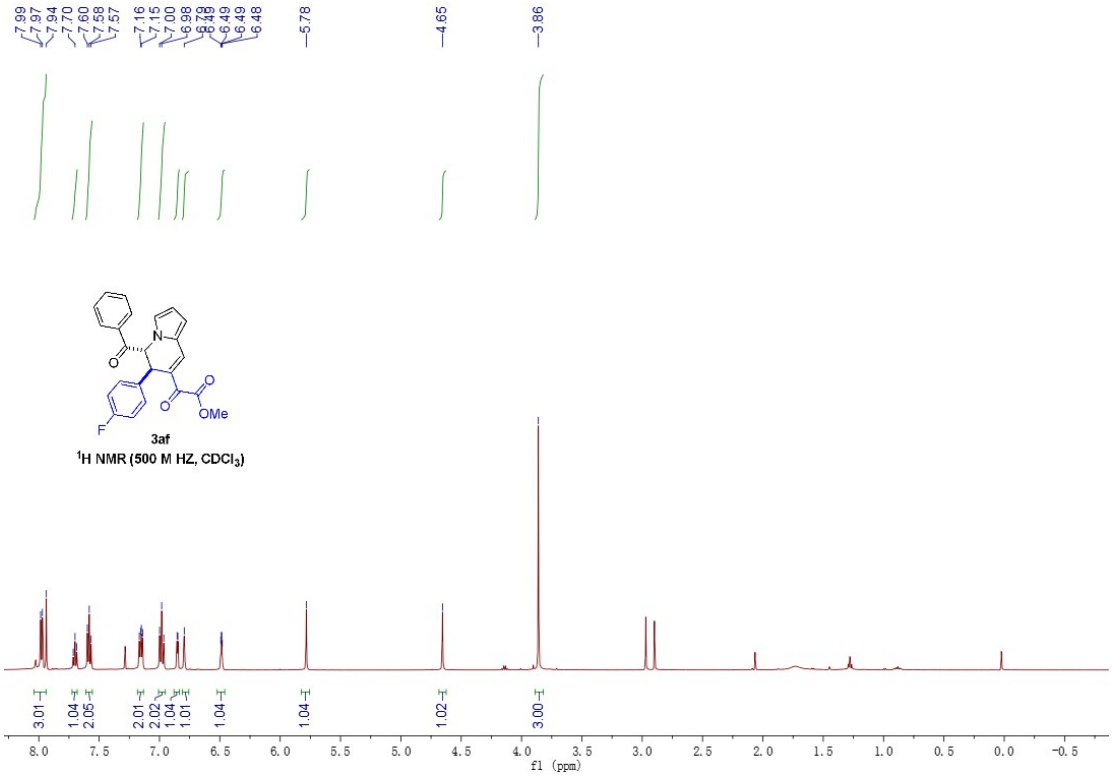

Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3af

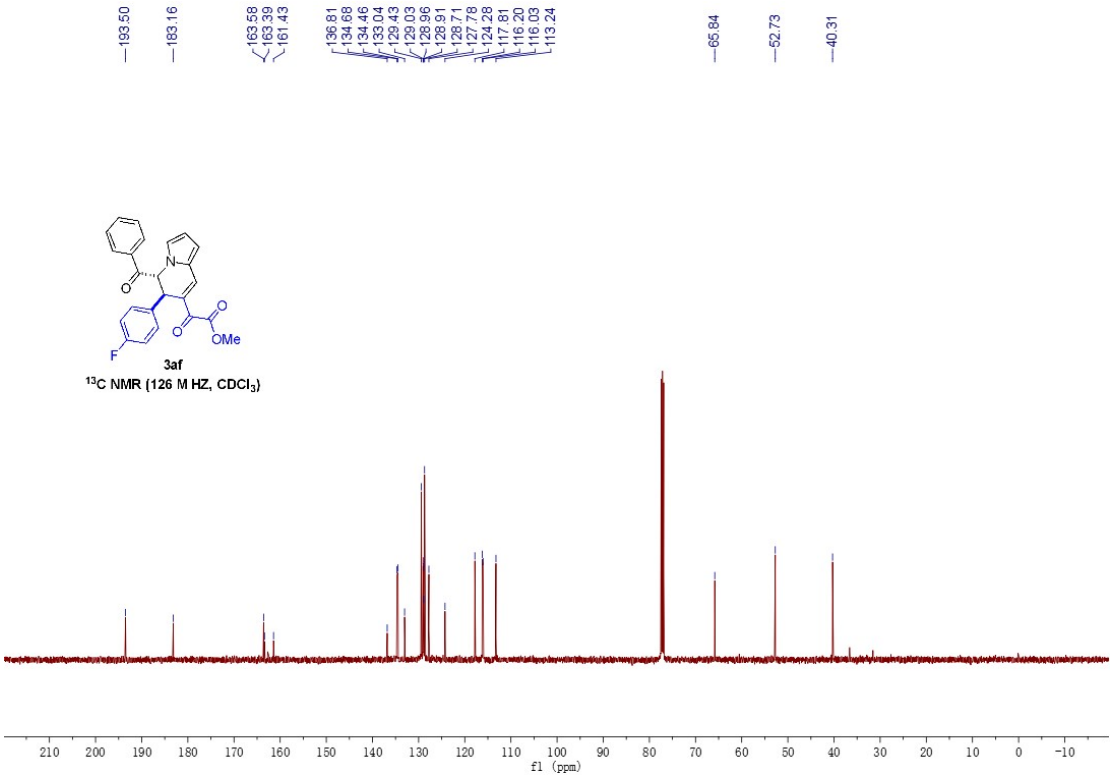

Figure S15. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3af

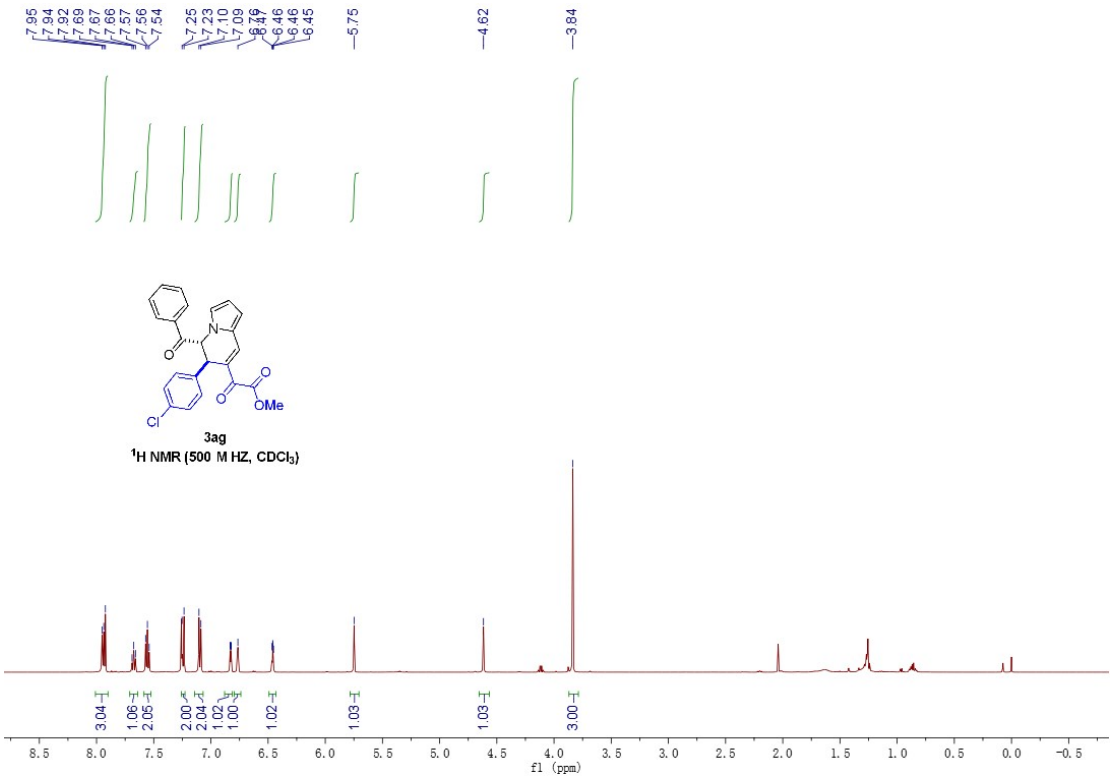

Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ag

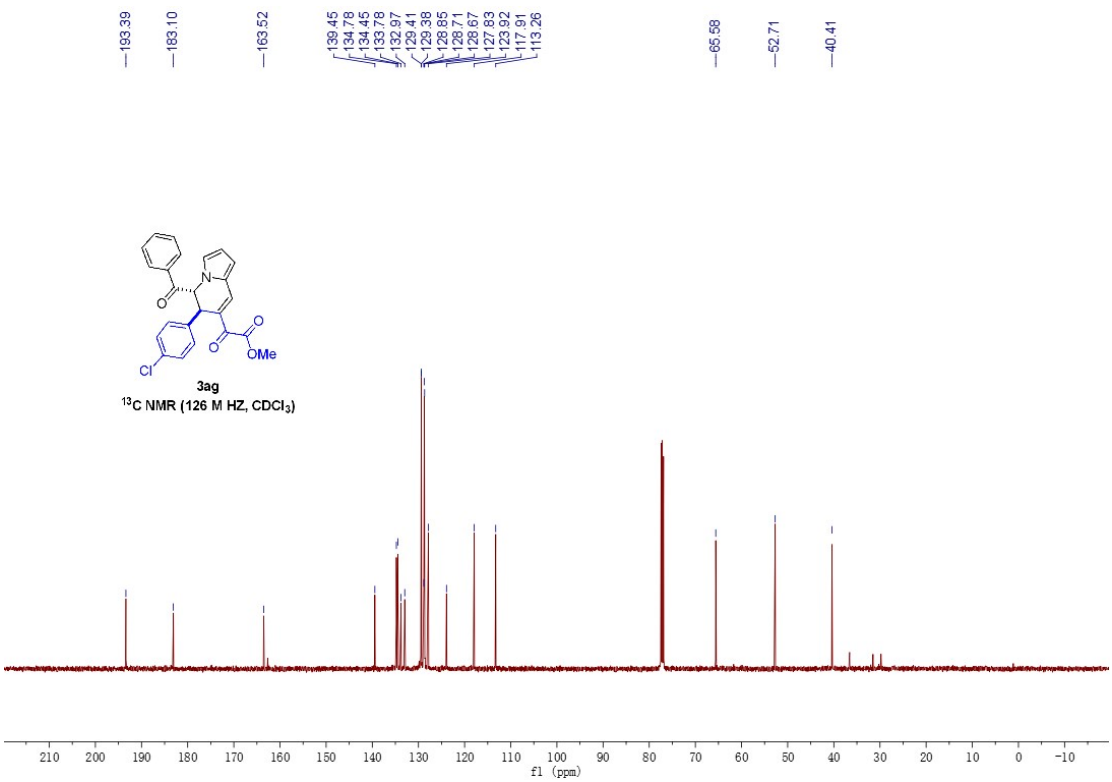

Figure S17. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ag

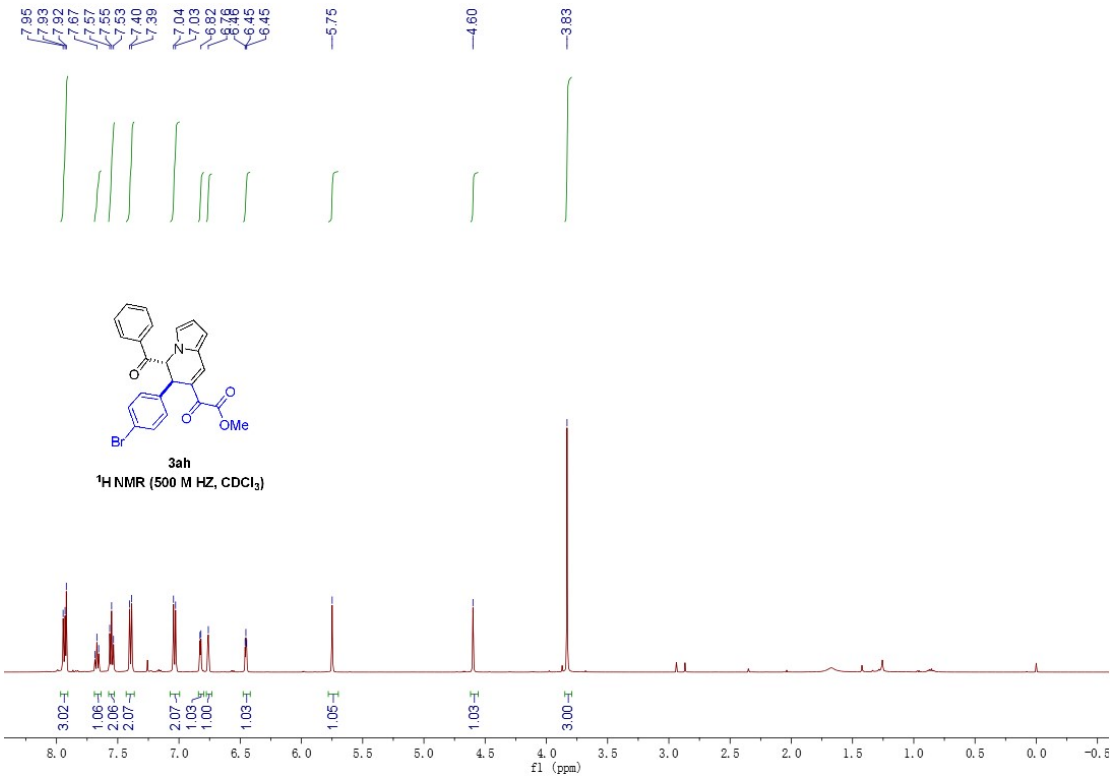

Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ah

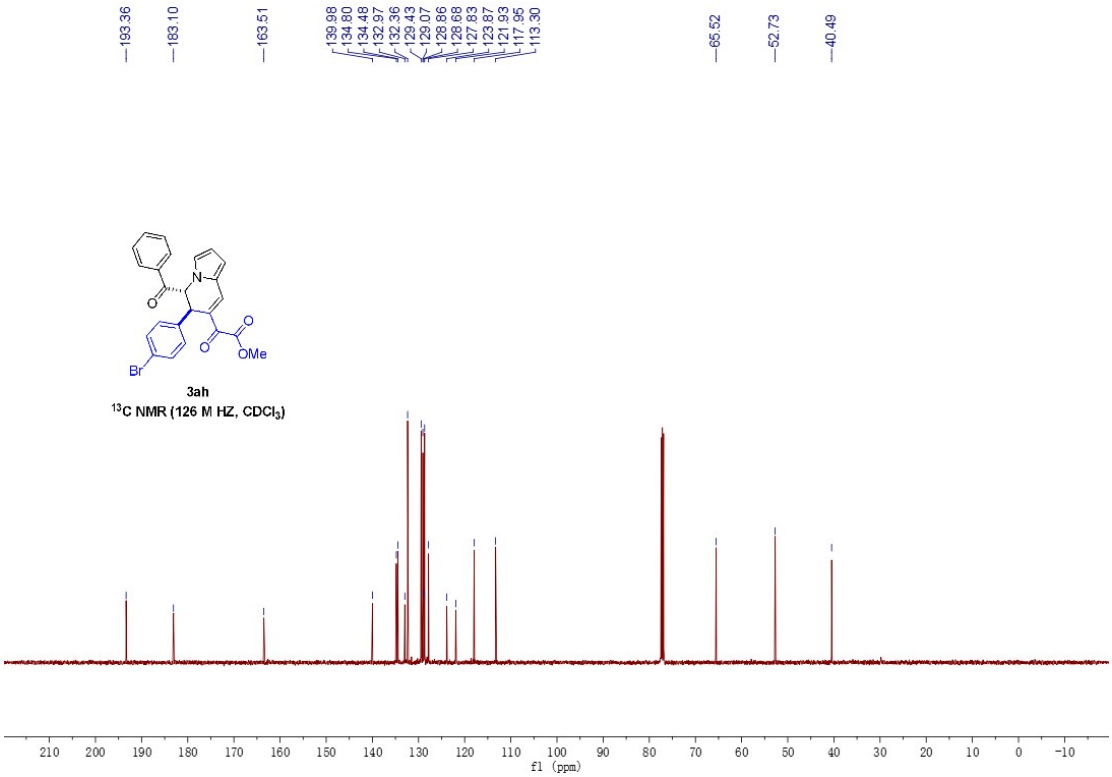

Figure S19. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ah

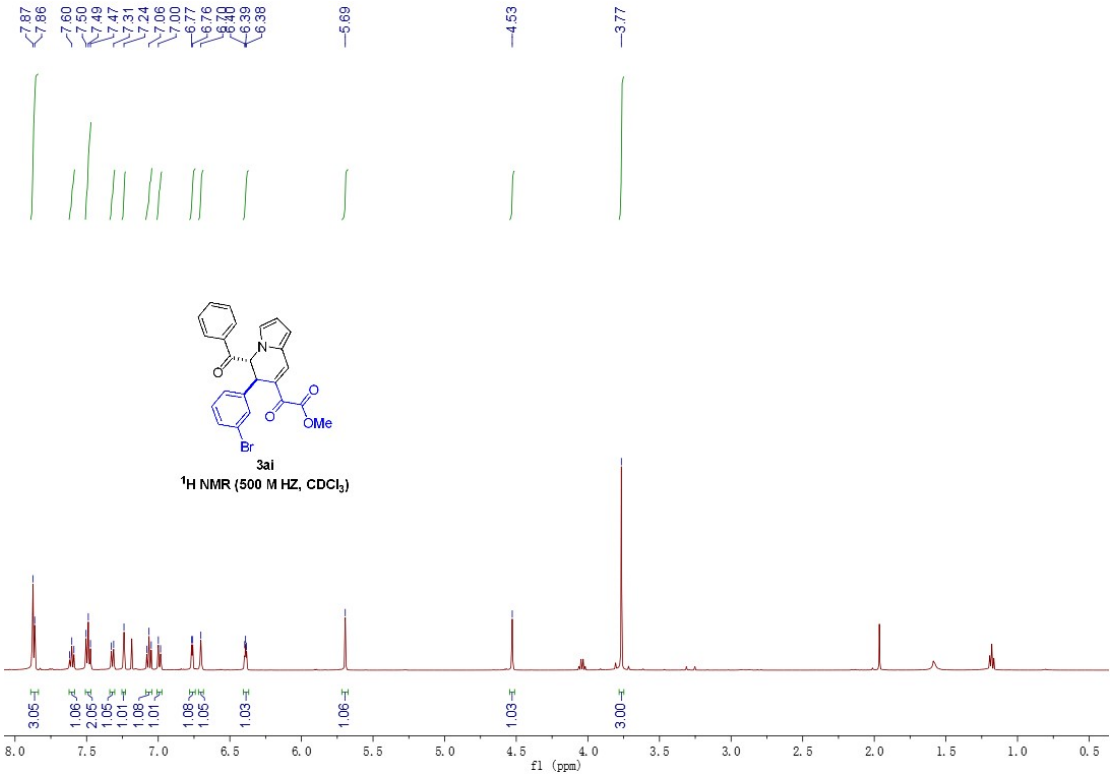

Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ai

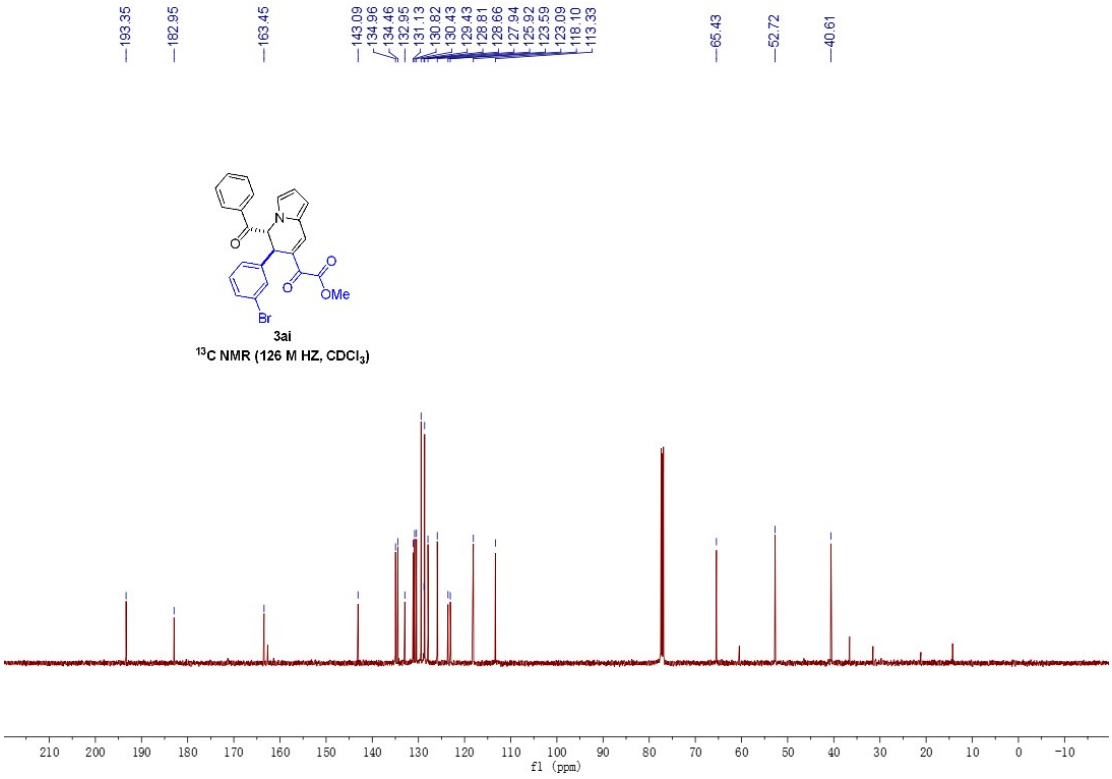

Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ai

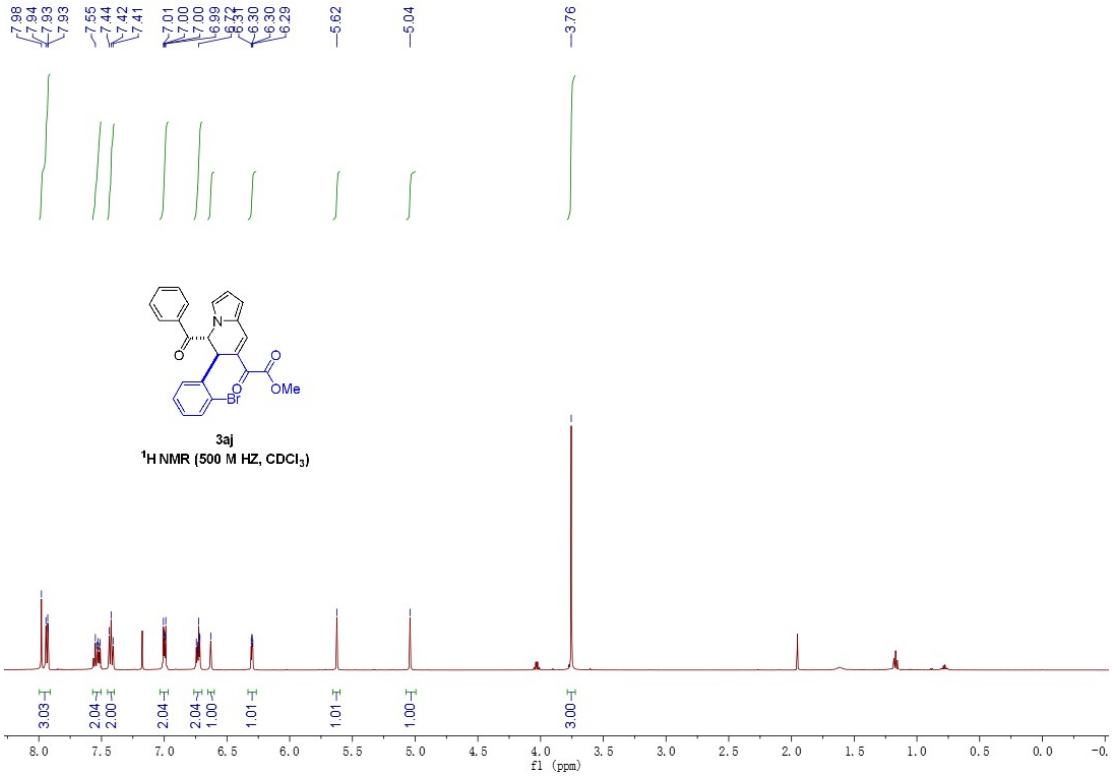

Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3aj

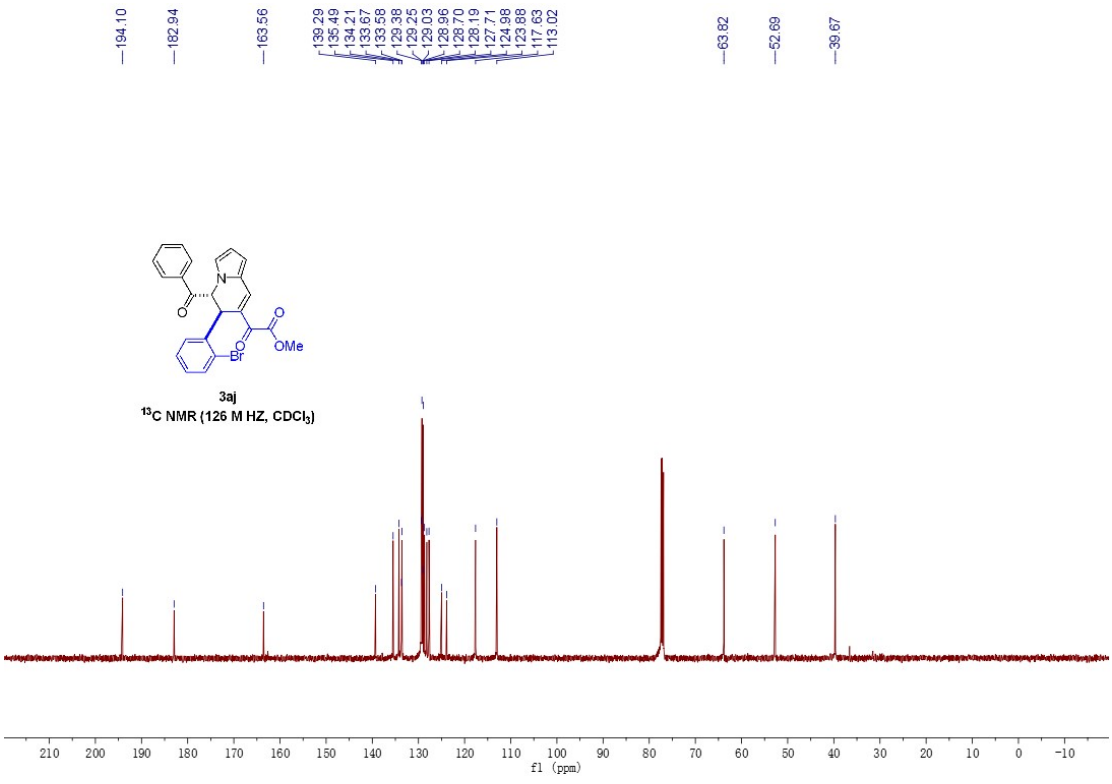

Figure S23. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3aj

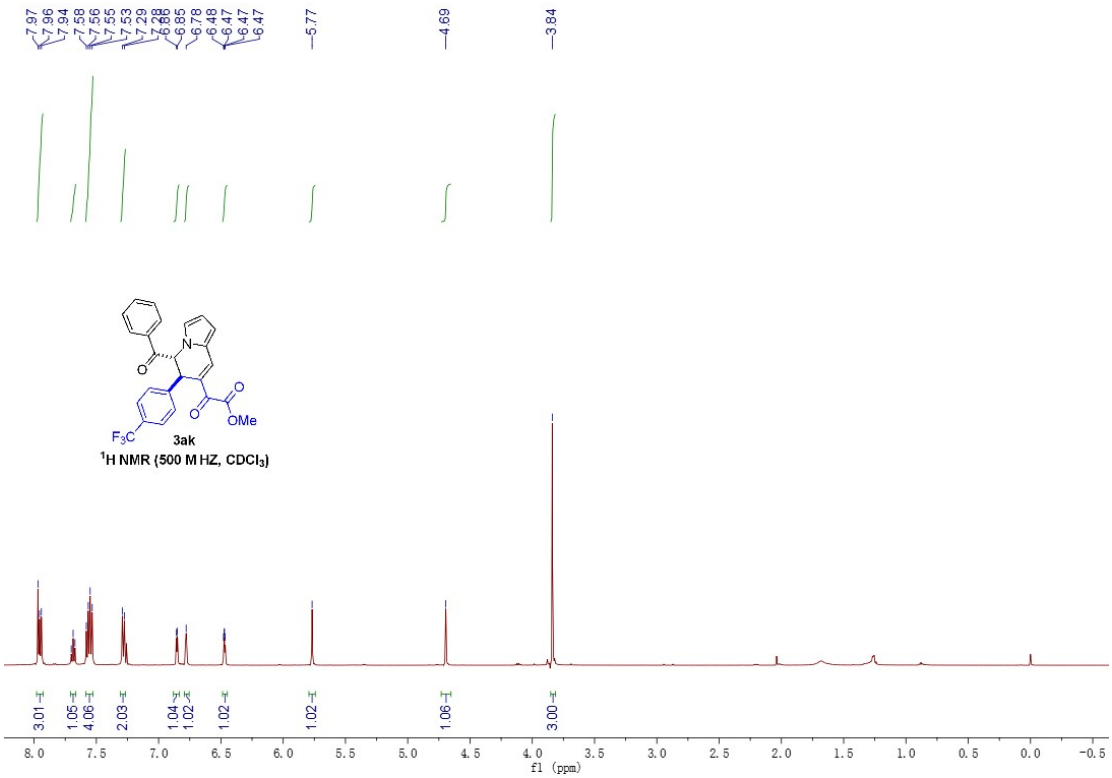

Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ak

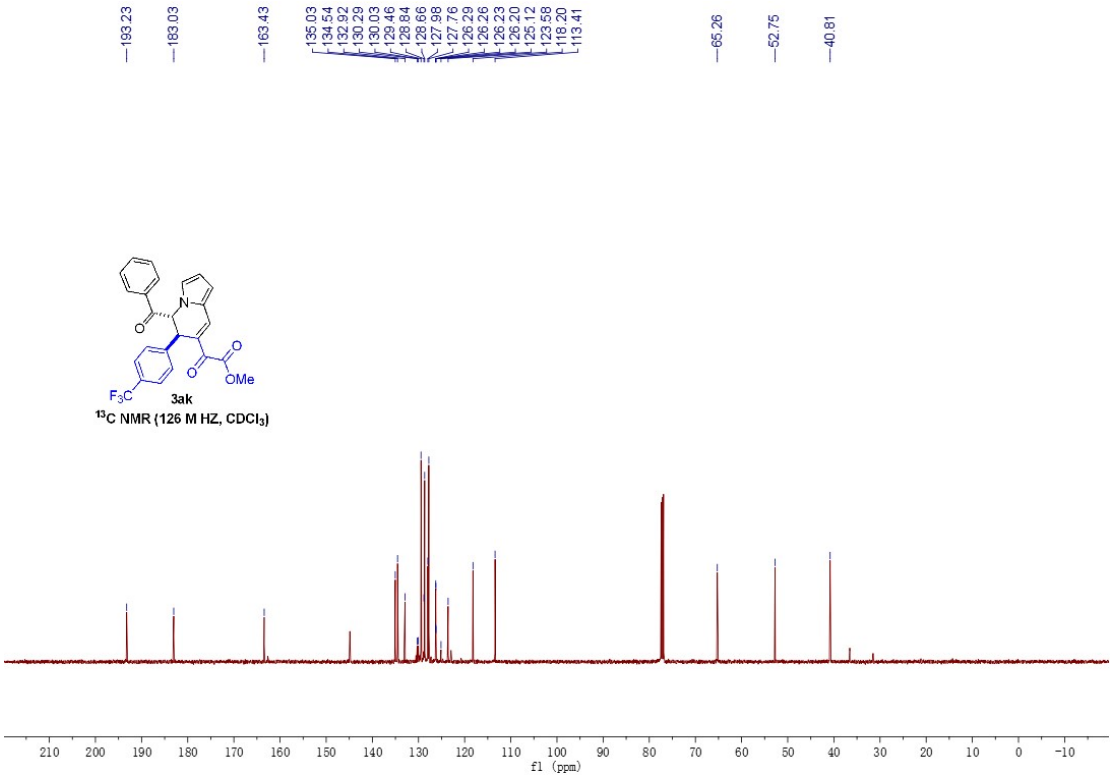

Figure S25. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ak

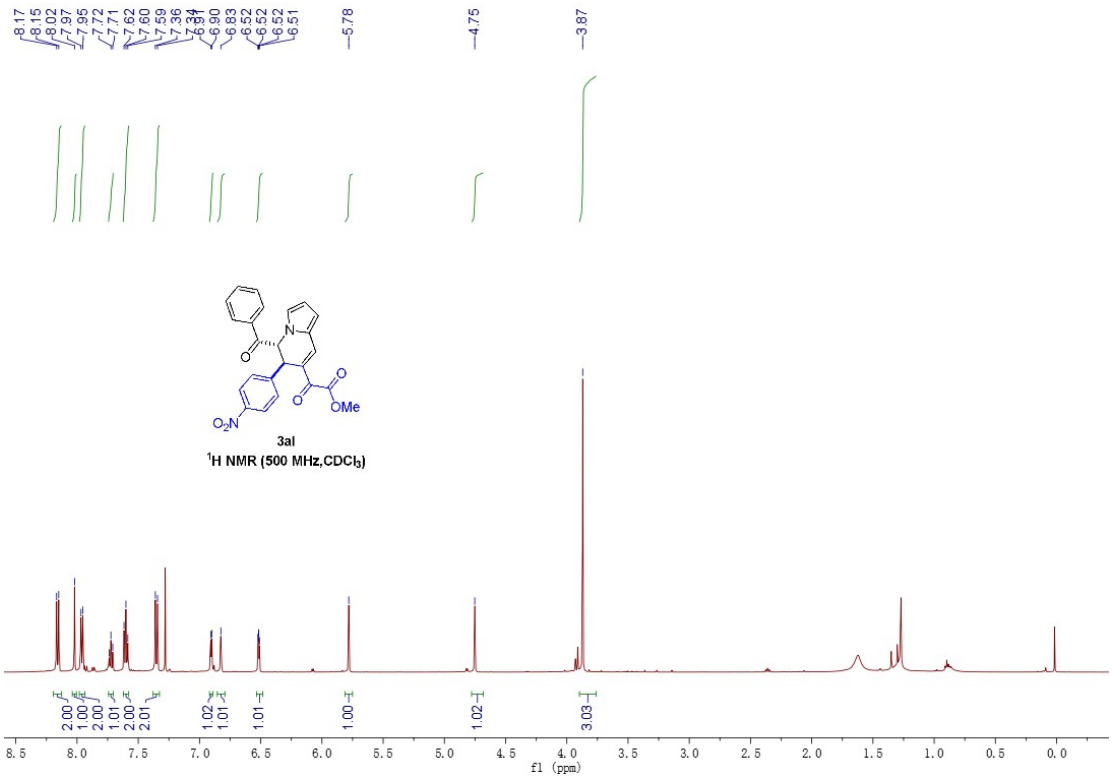

Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3al

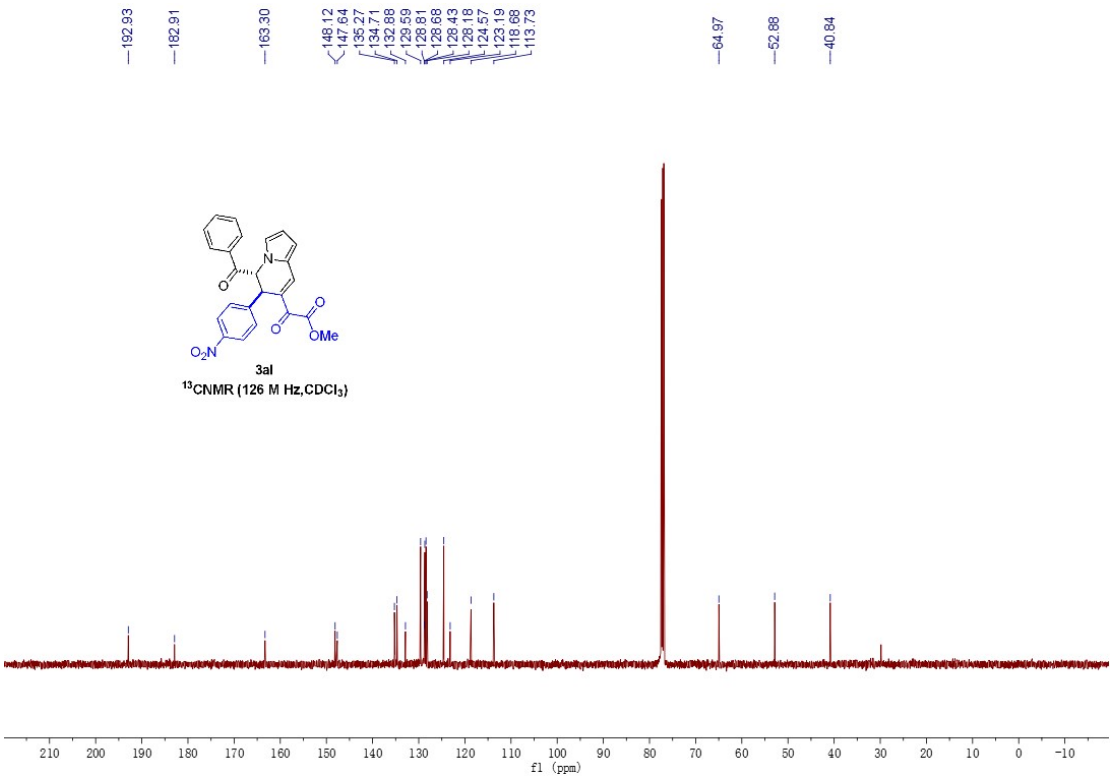

Figure S27. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3al

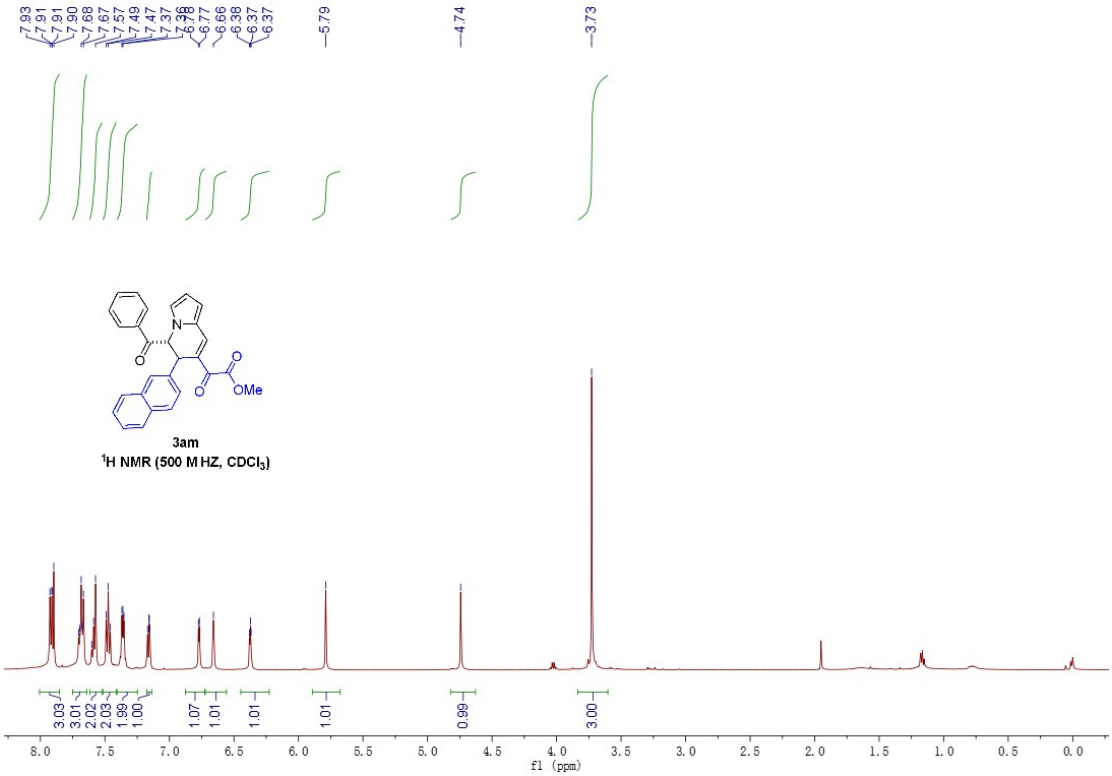

Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3am

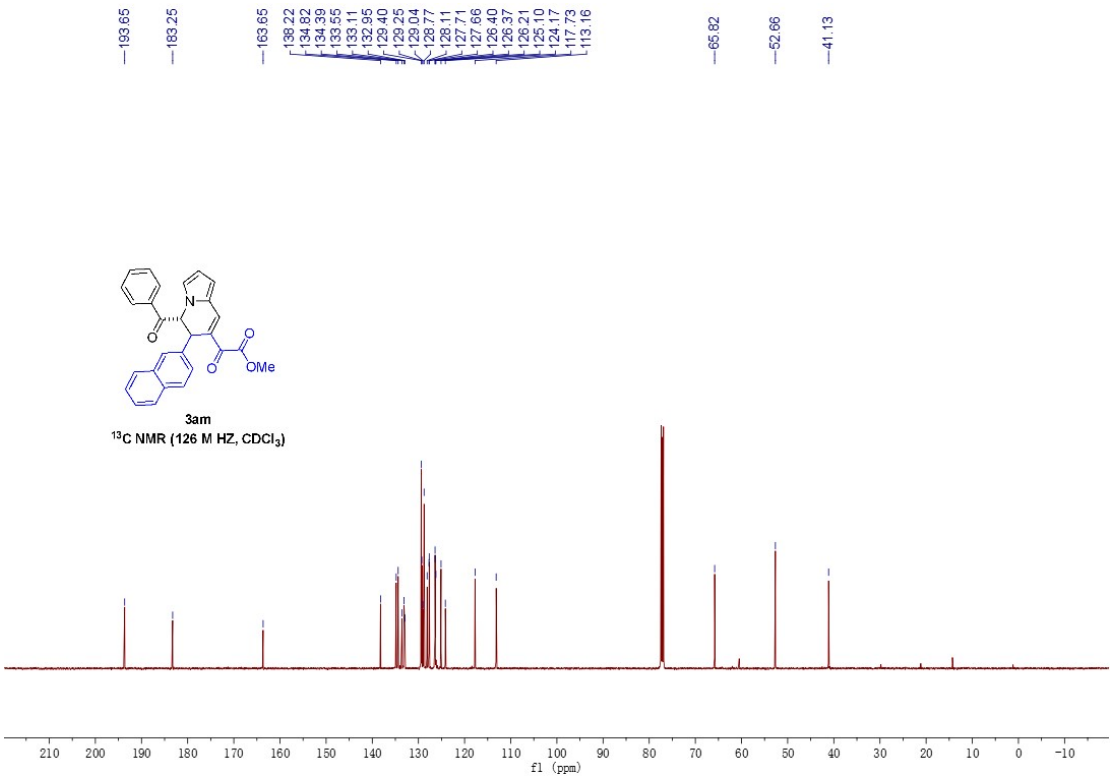

Figure S29. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3am

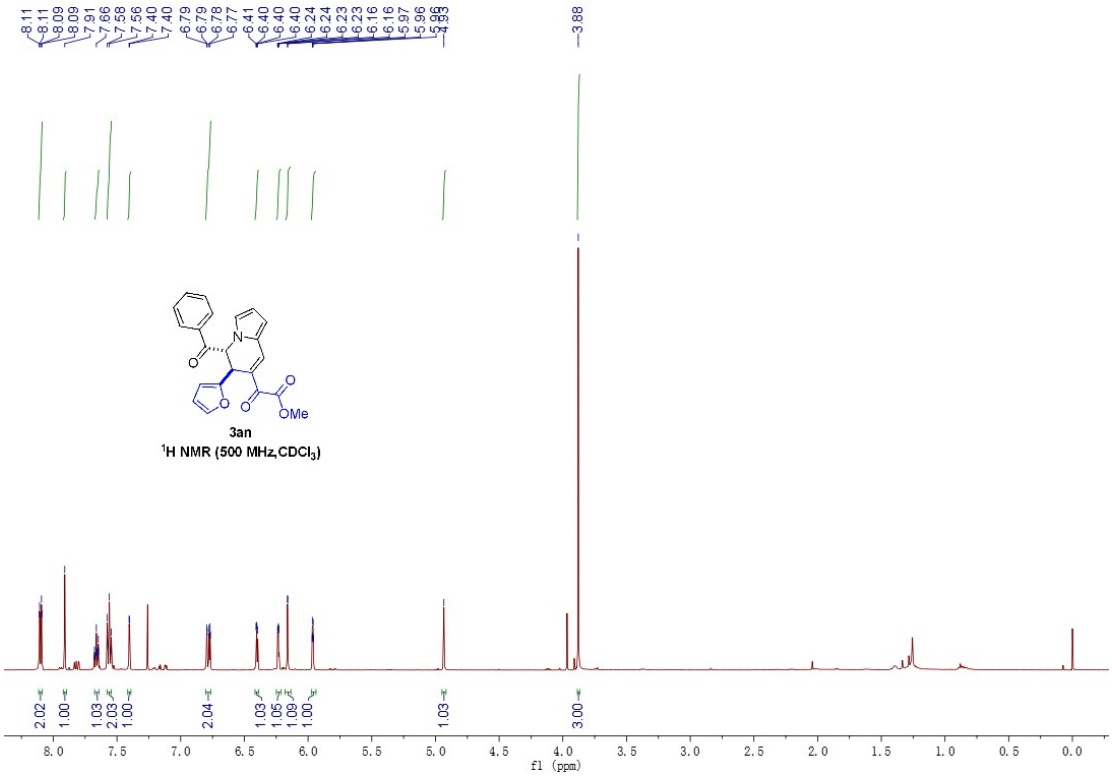

Figure S30. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3an

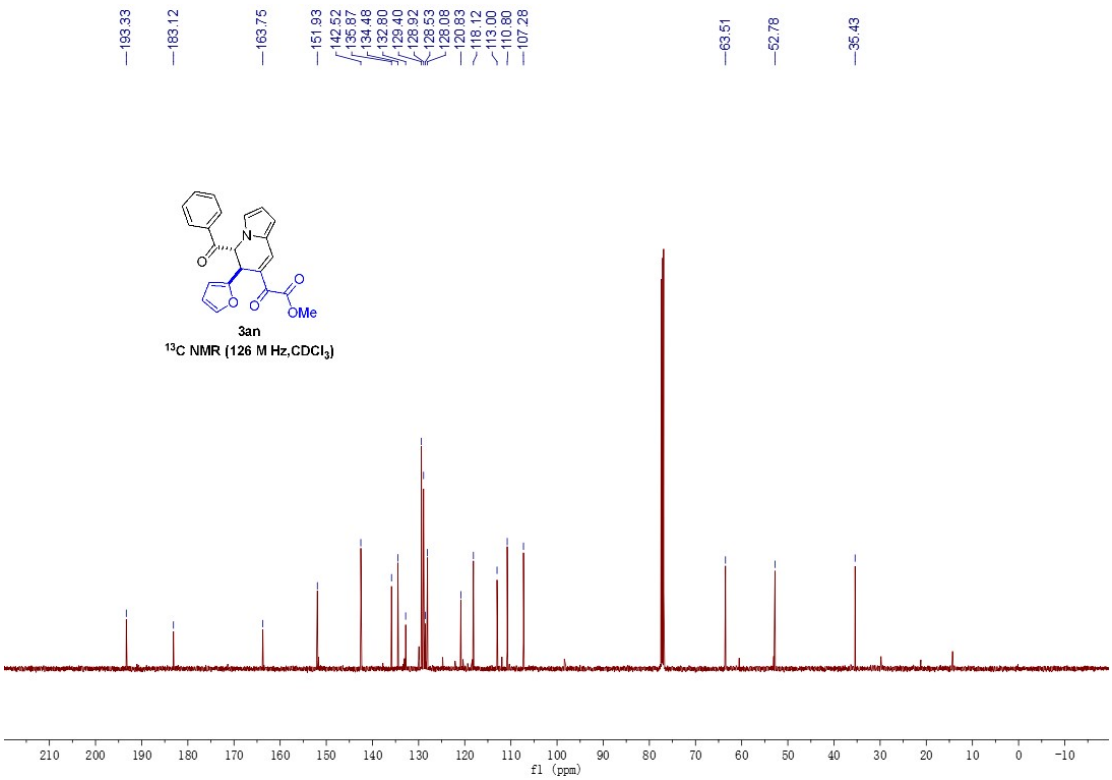

Figure S31. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3an

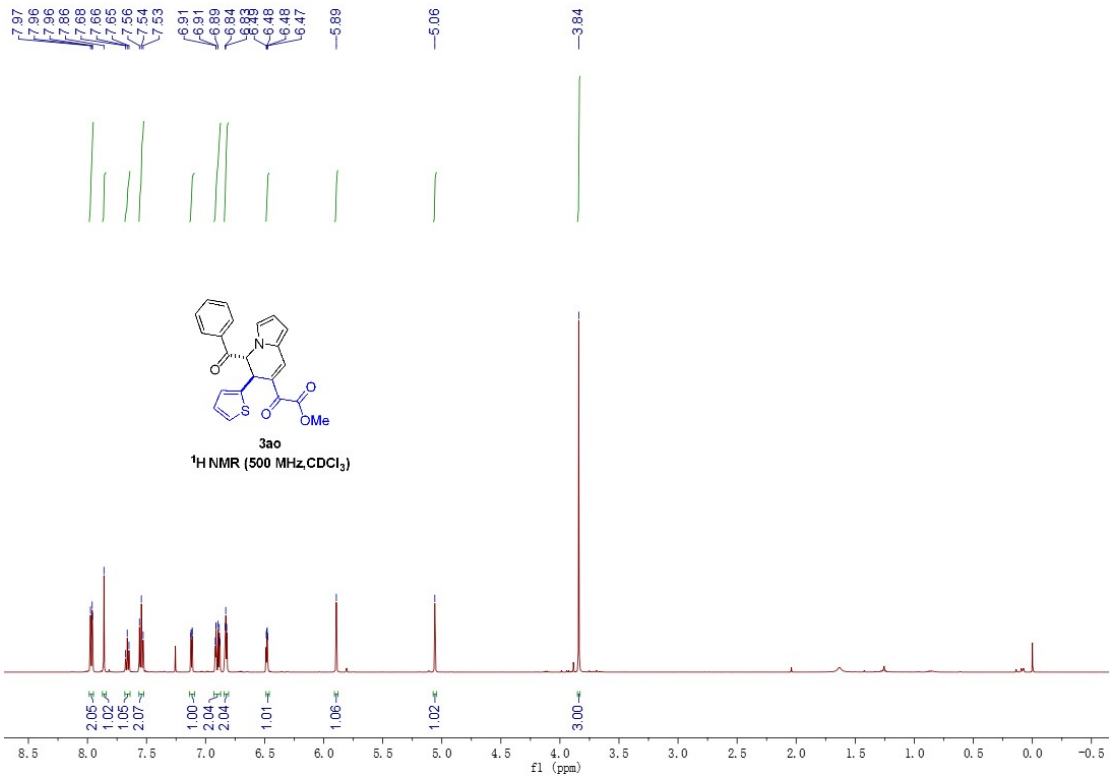

Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ao

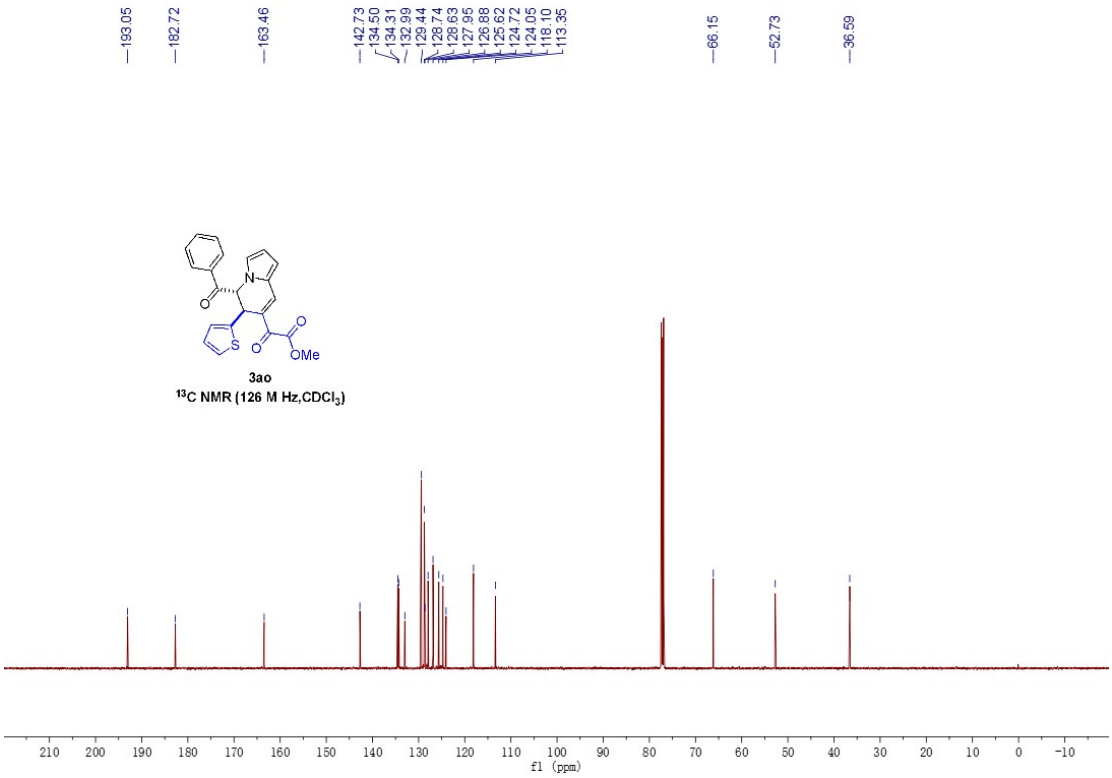

Figure S33. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ao

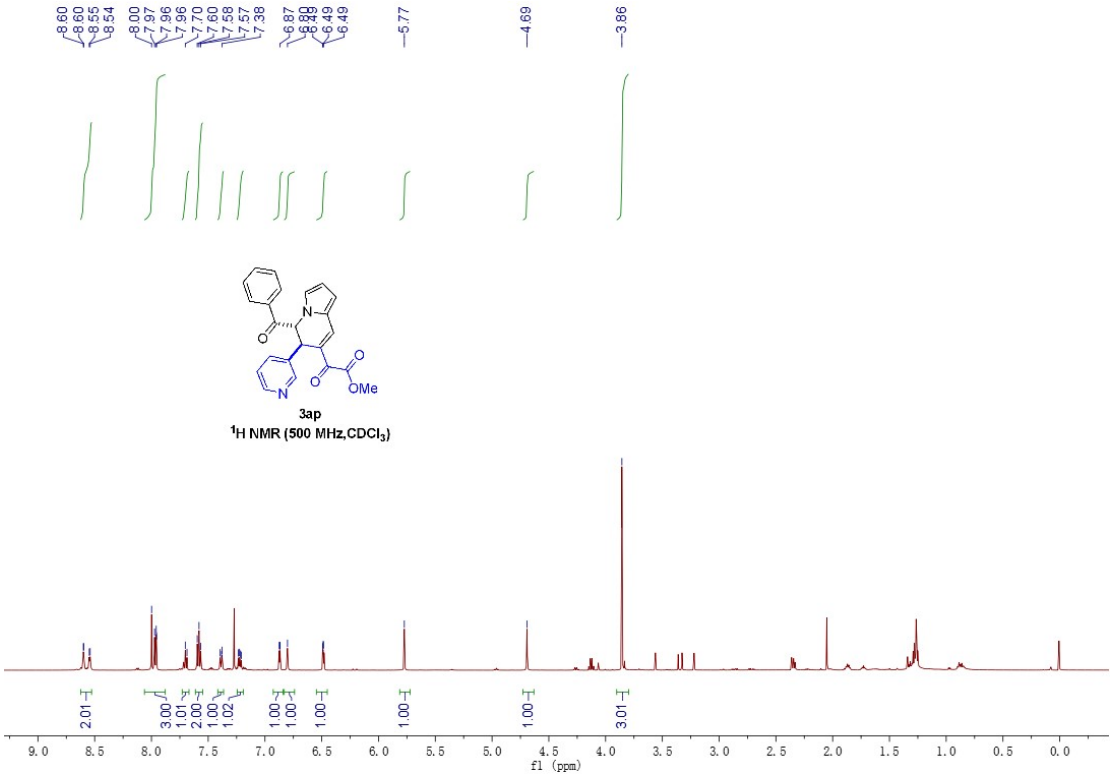

Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ap

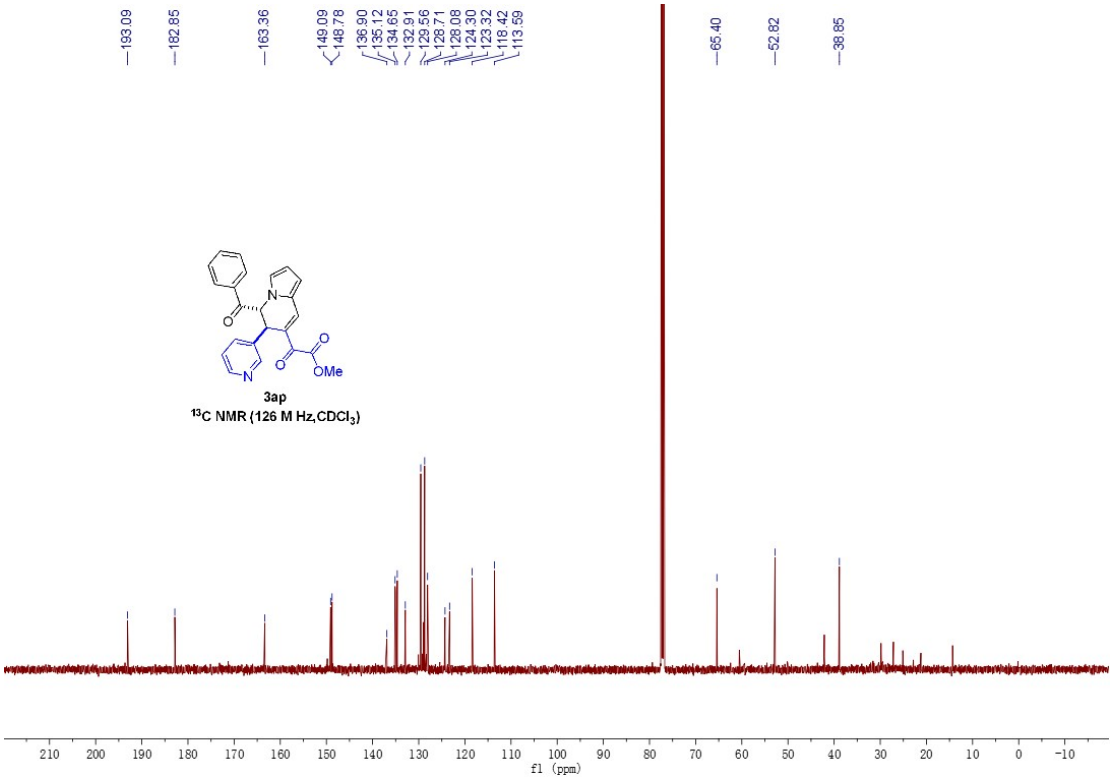

Figure S35. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ap

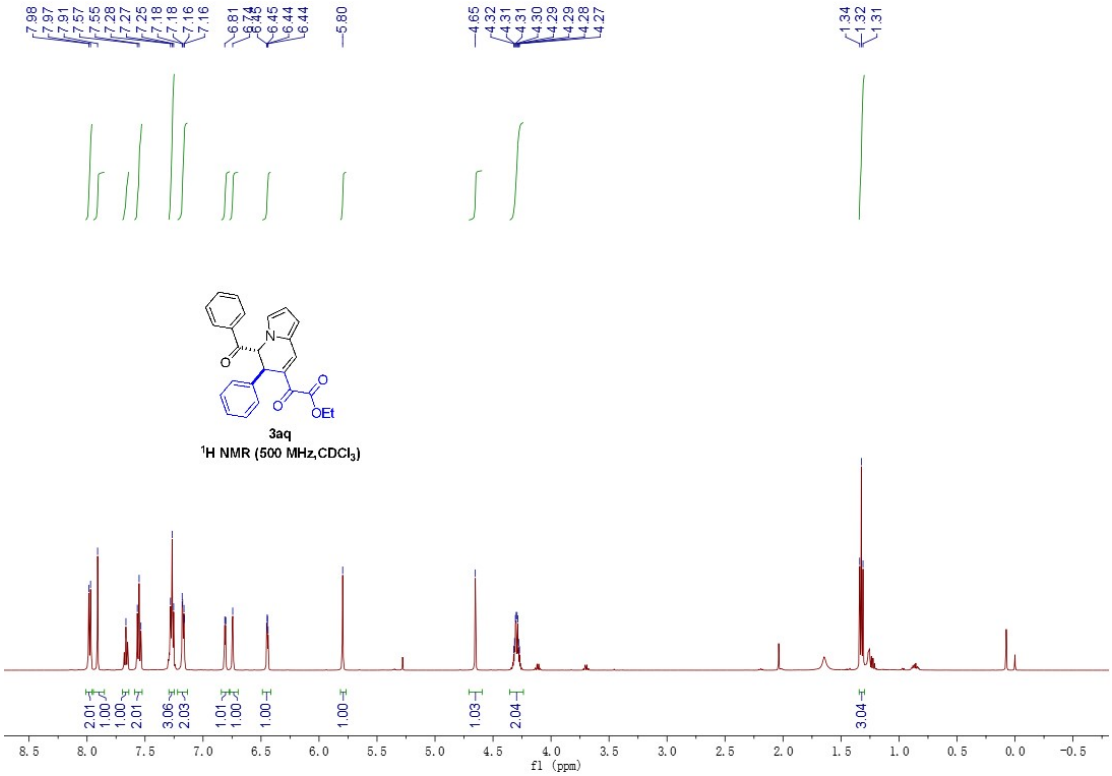

Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3aq

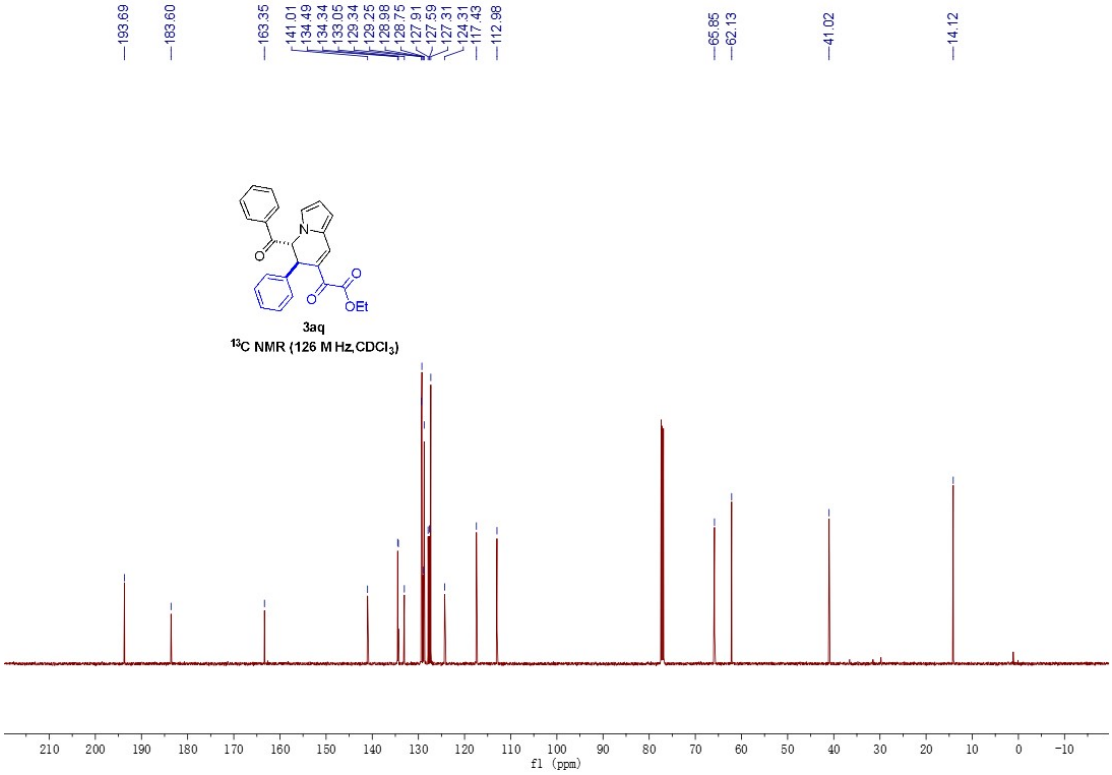

Figure S37. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3aq

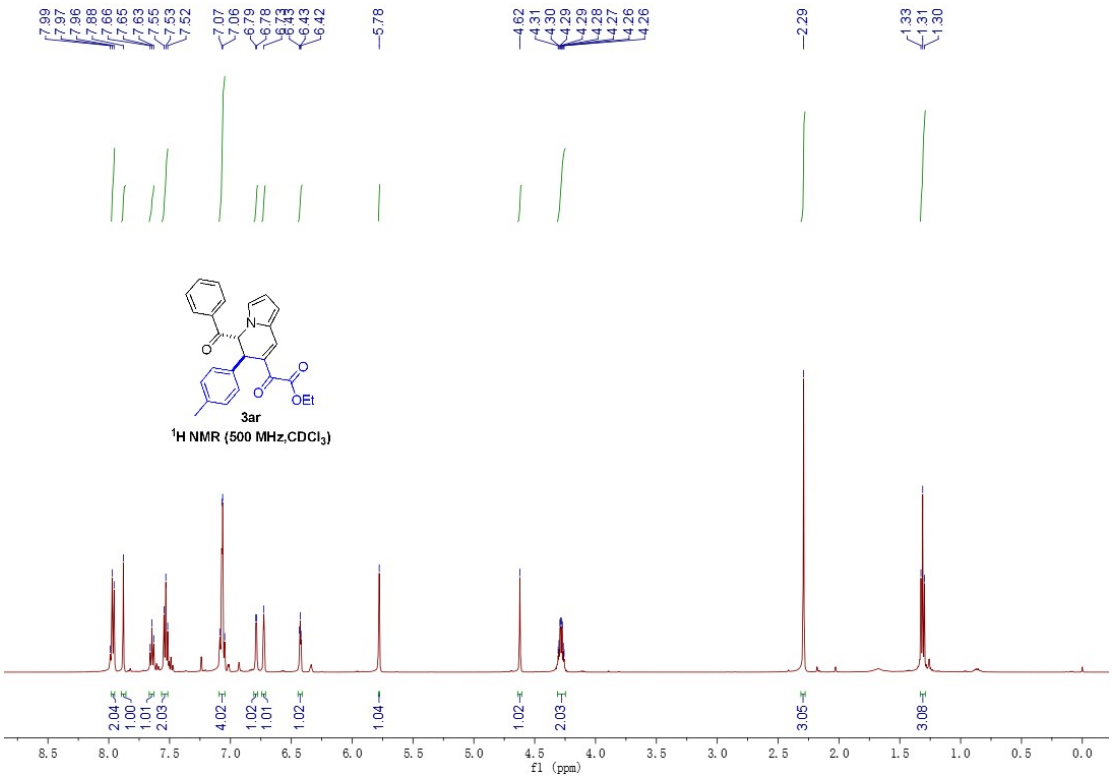

Figure S38. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ar

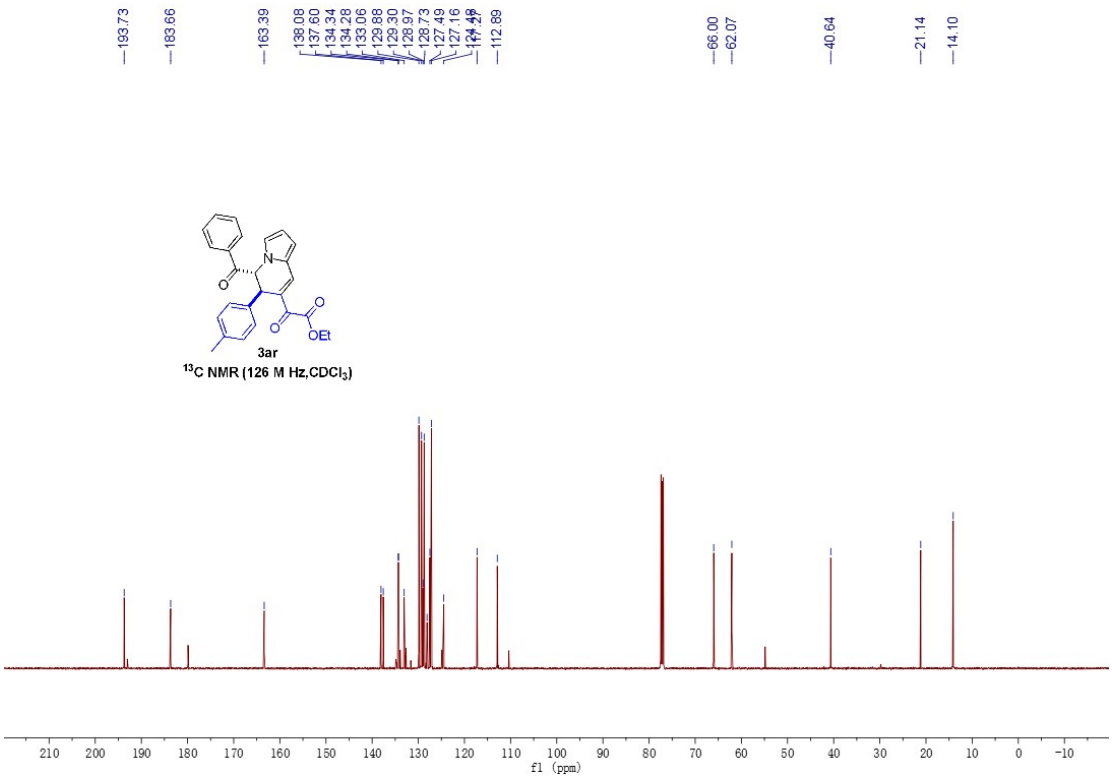

Figure S39. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ar

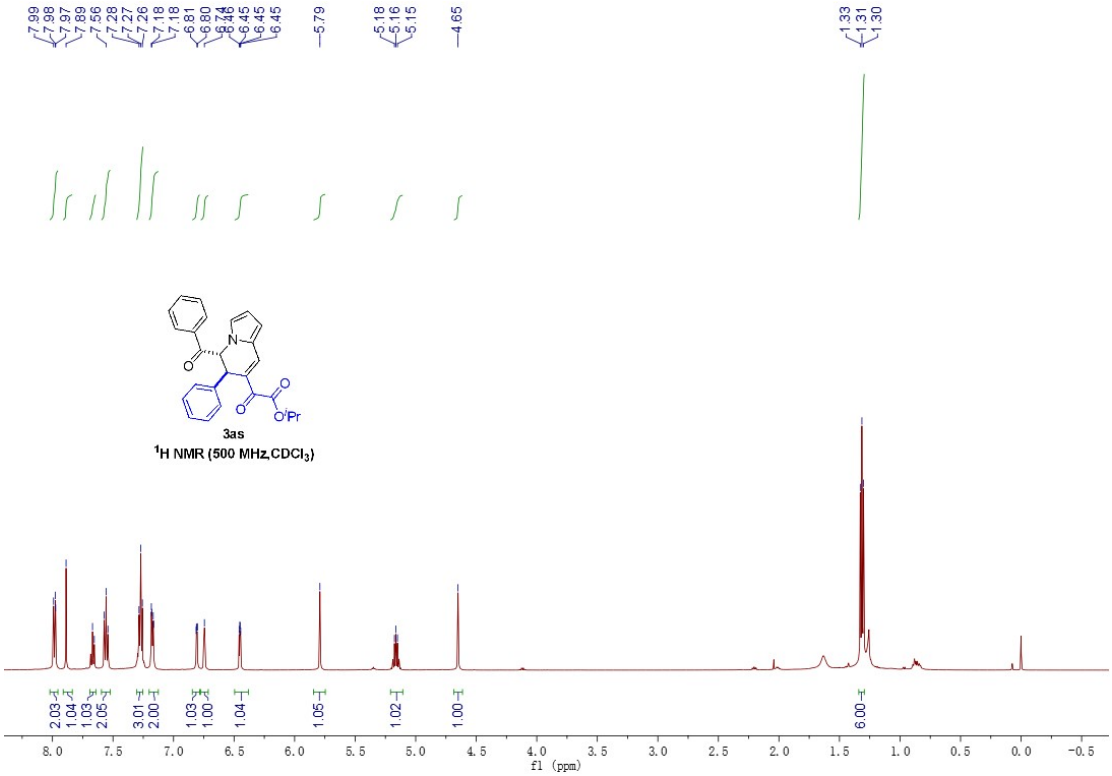

Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3as

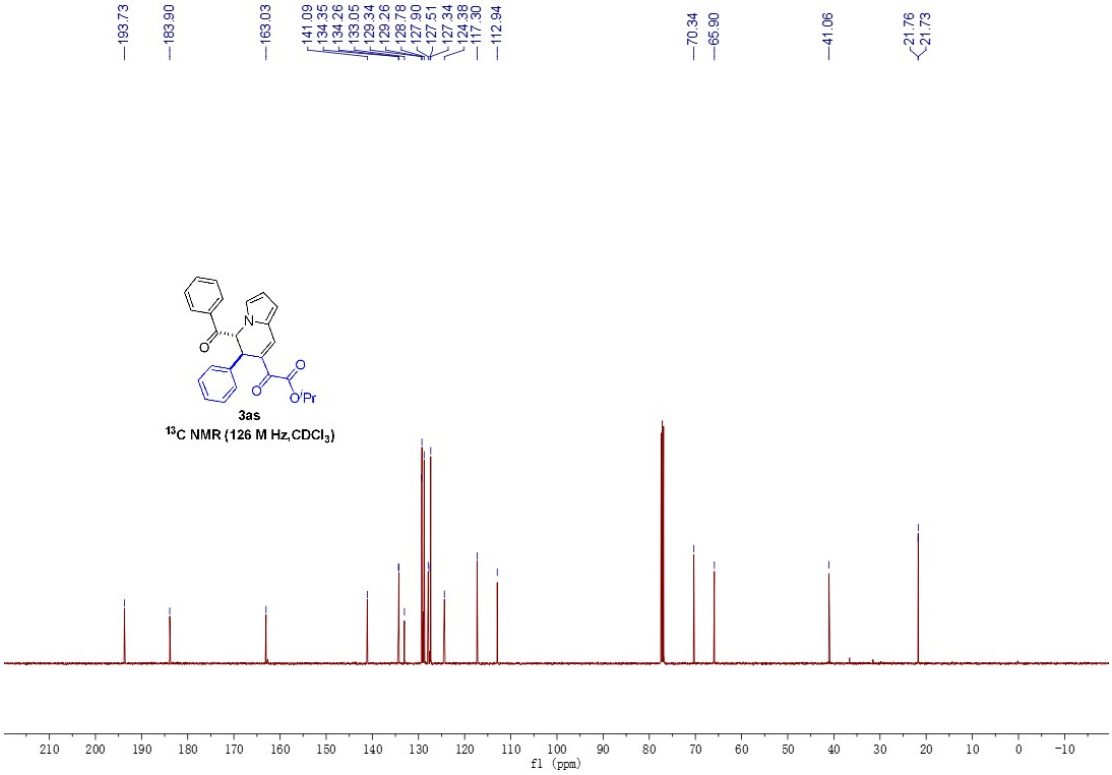

Figure S41. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3as

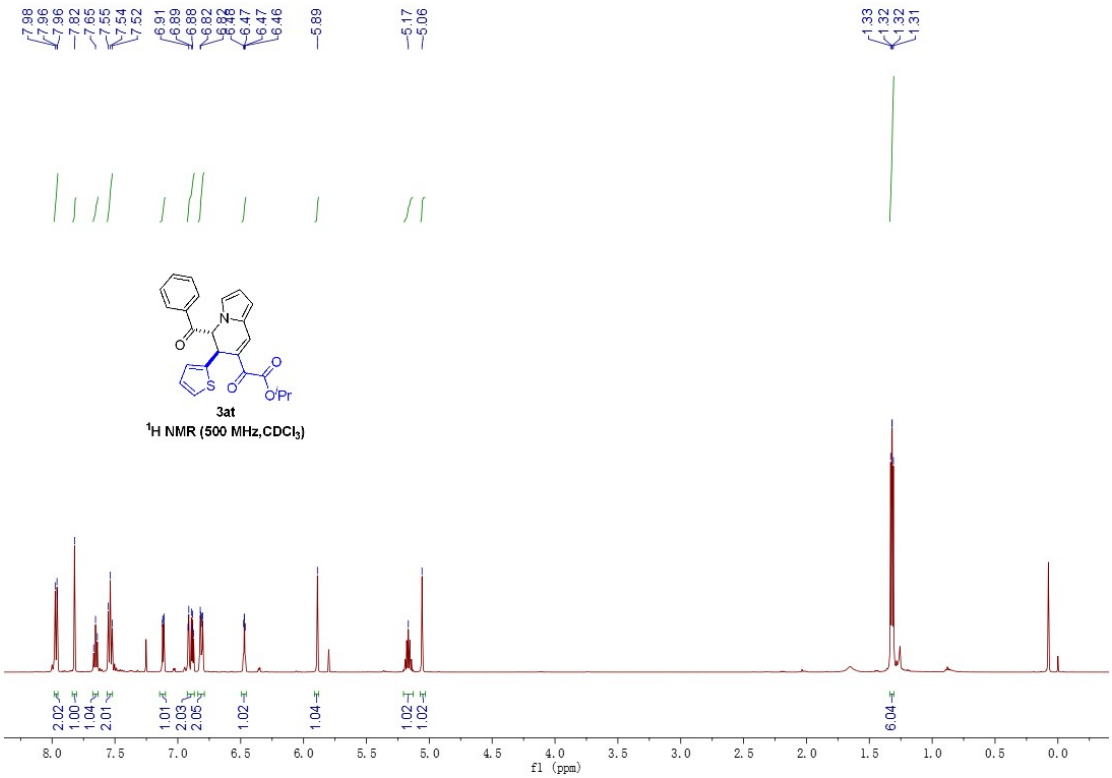

Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3at

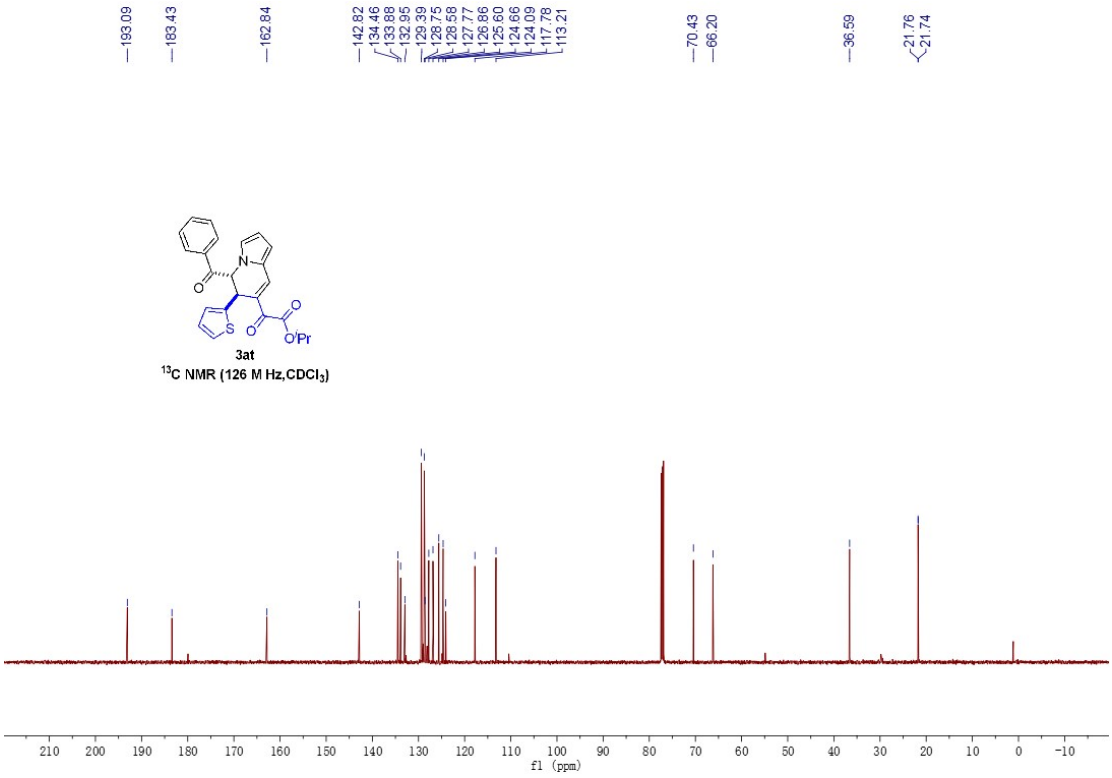

Figure S43. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3at

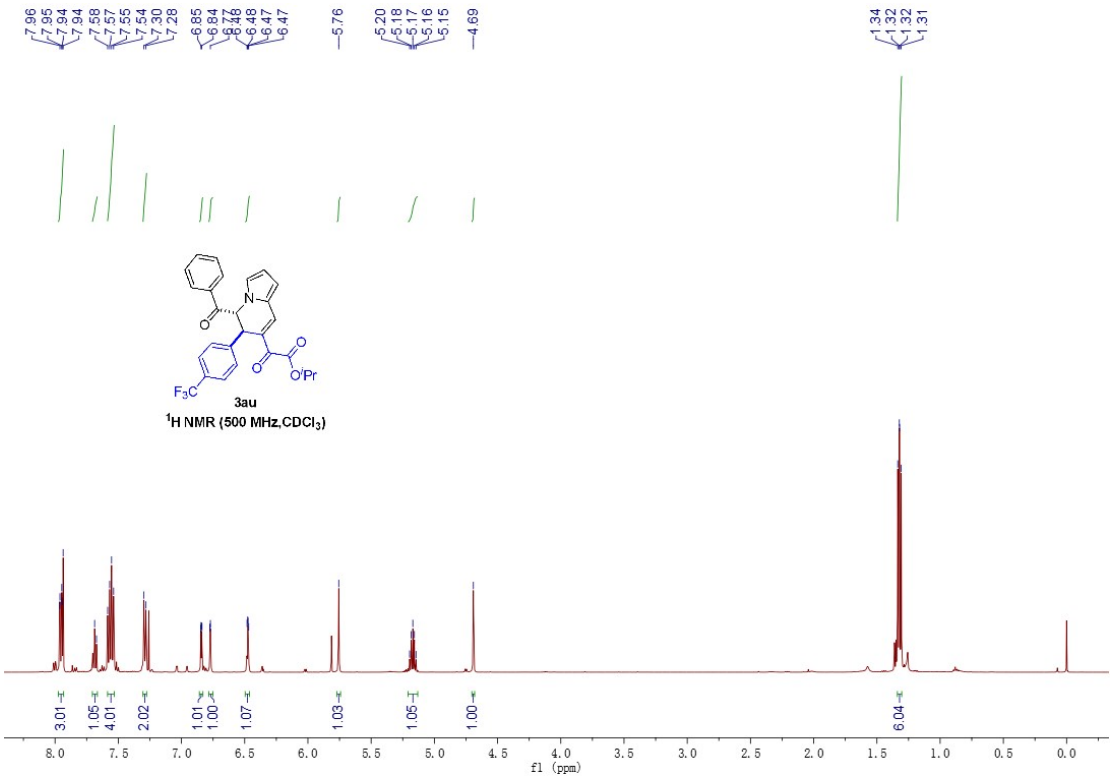

Figure S44. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3au

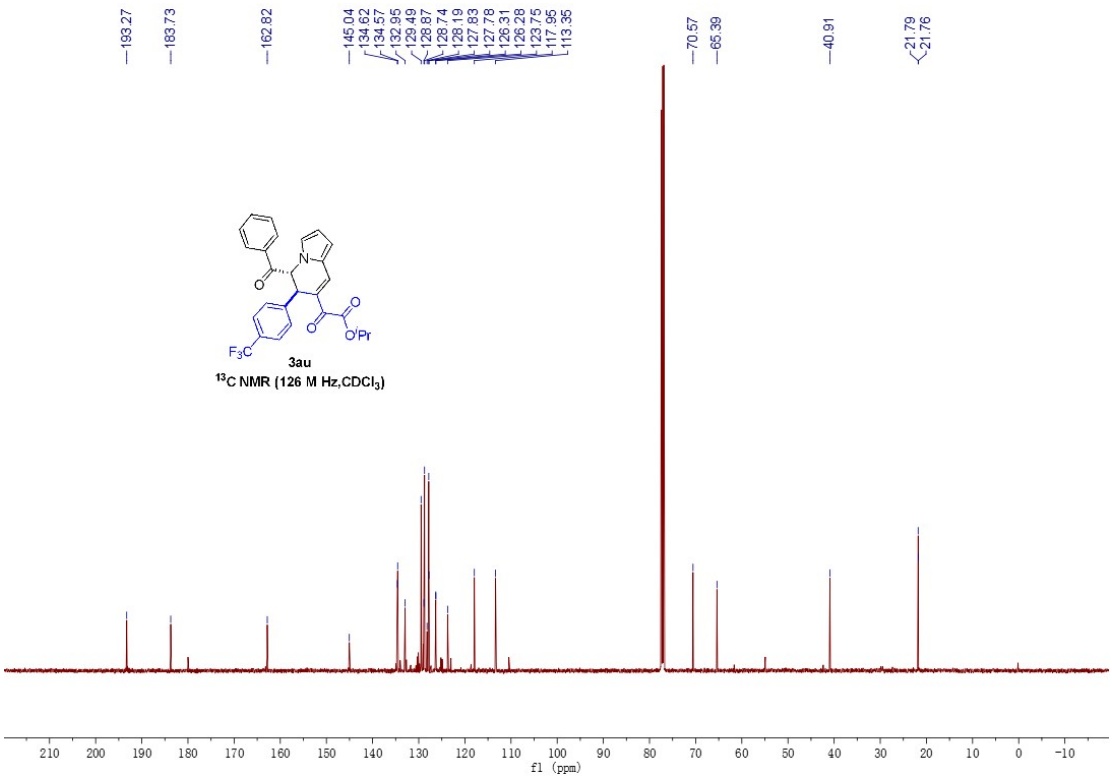

Figure S45. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3au

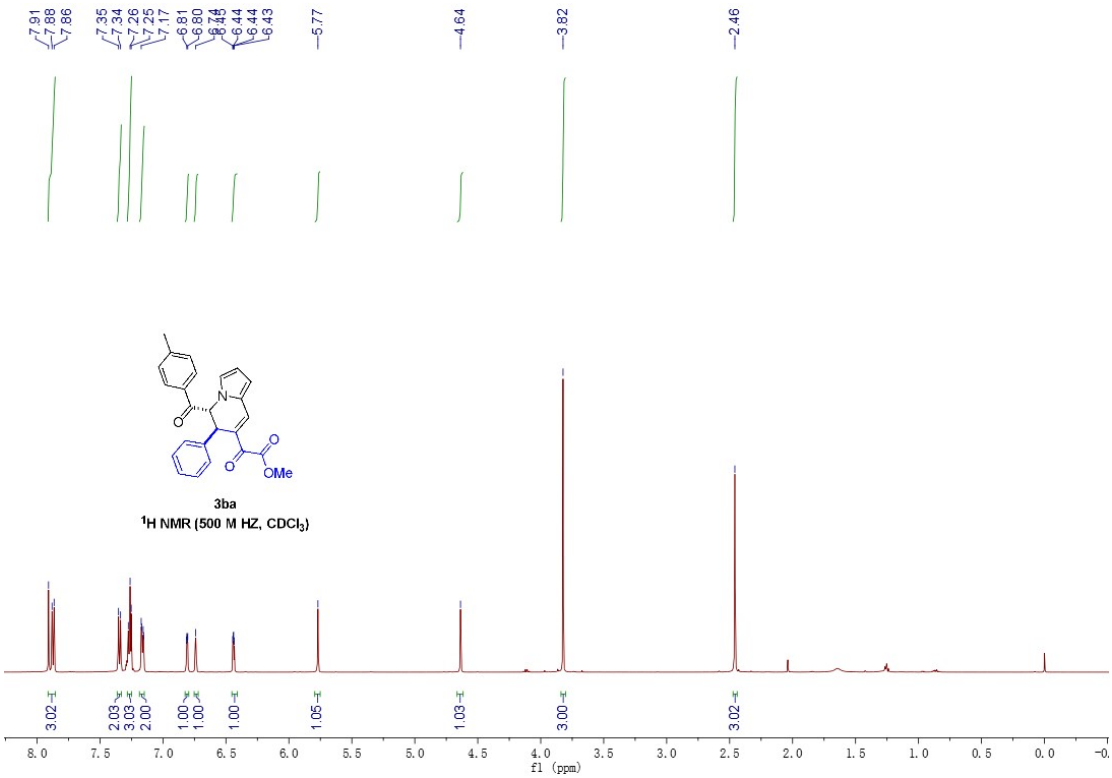

Figure S46. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ba

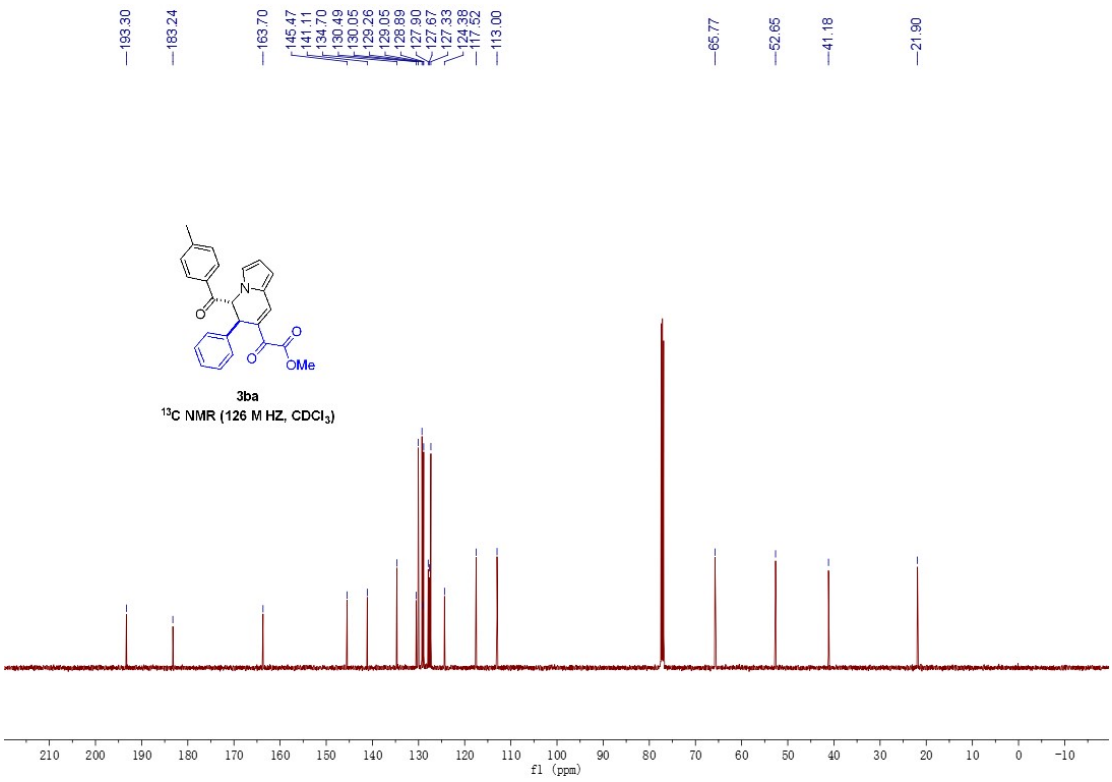

Figure S47. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ba

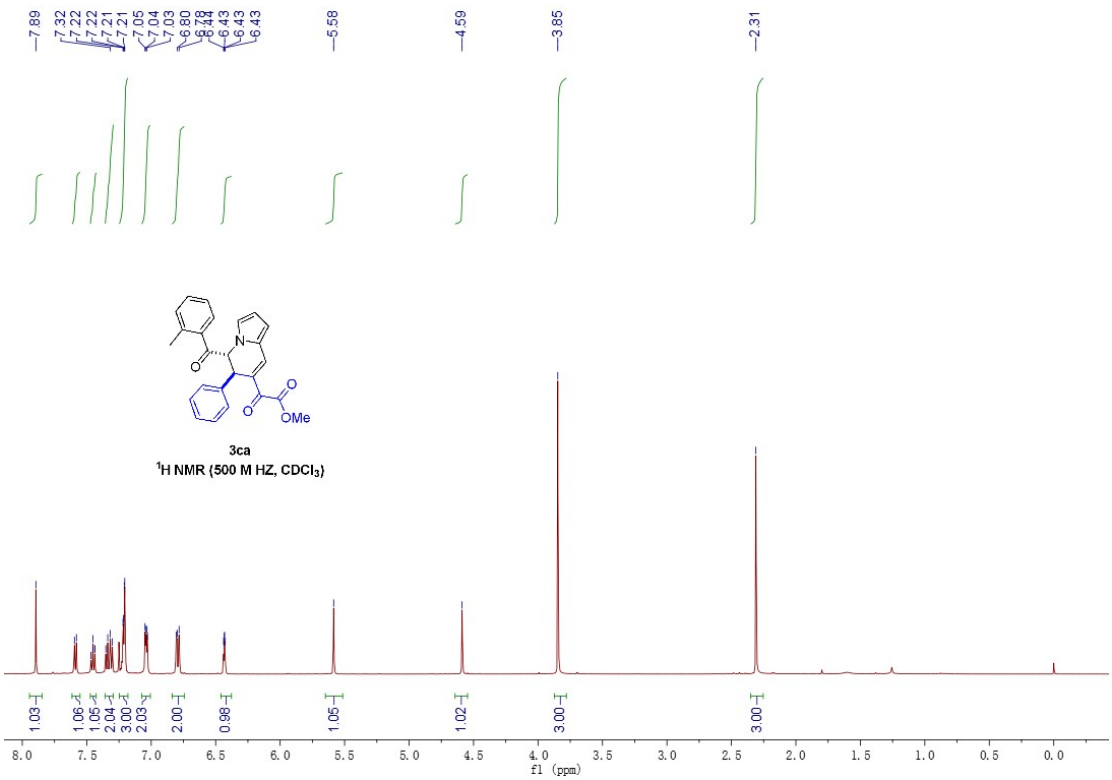

Figure S48 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ca

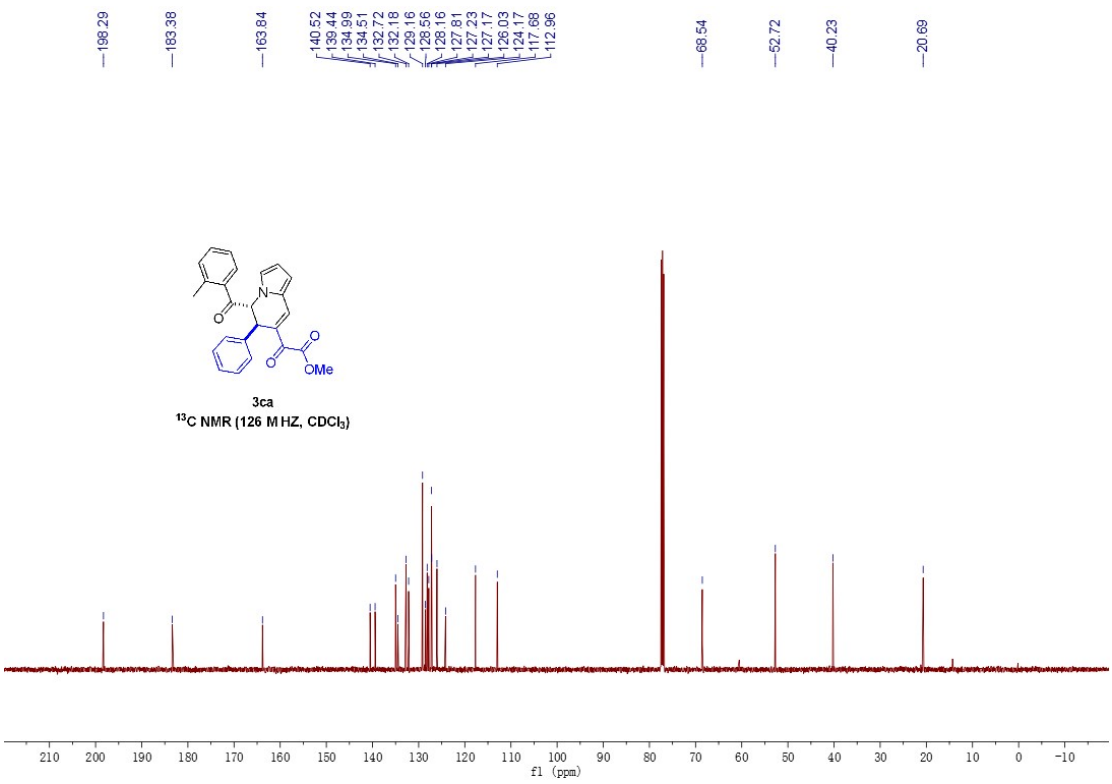

Figure S49. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ca

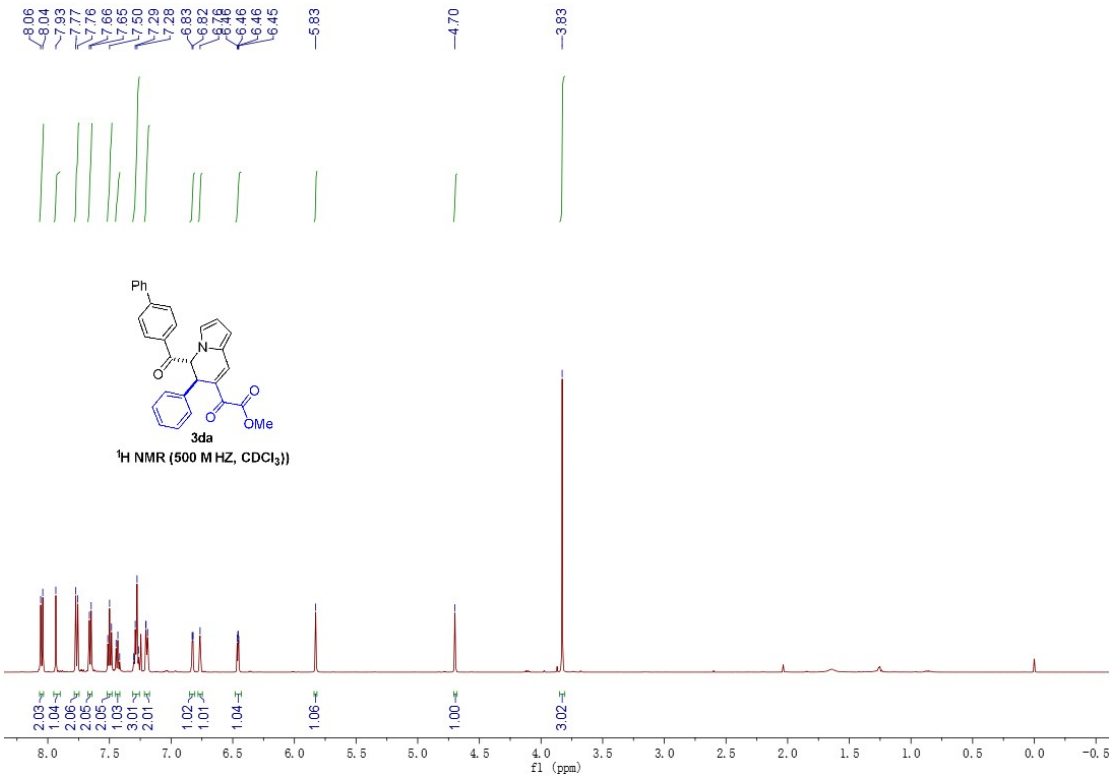

Figure S50. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3da

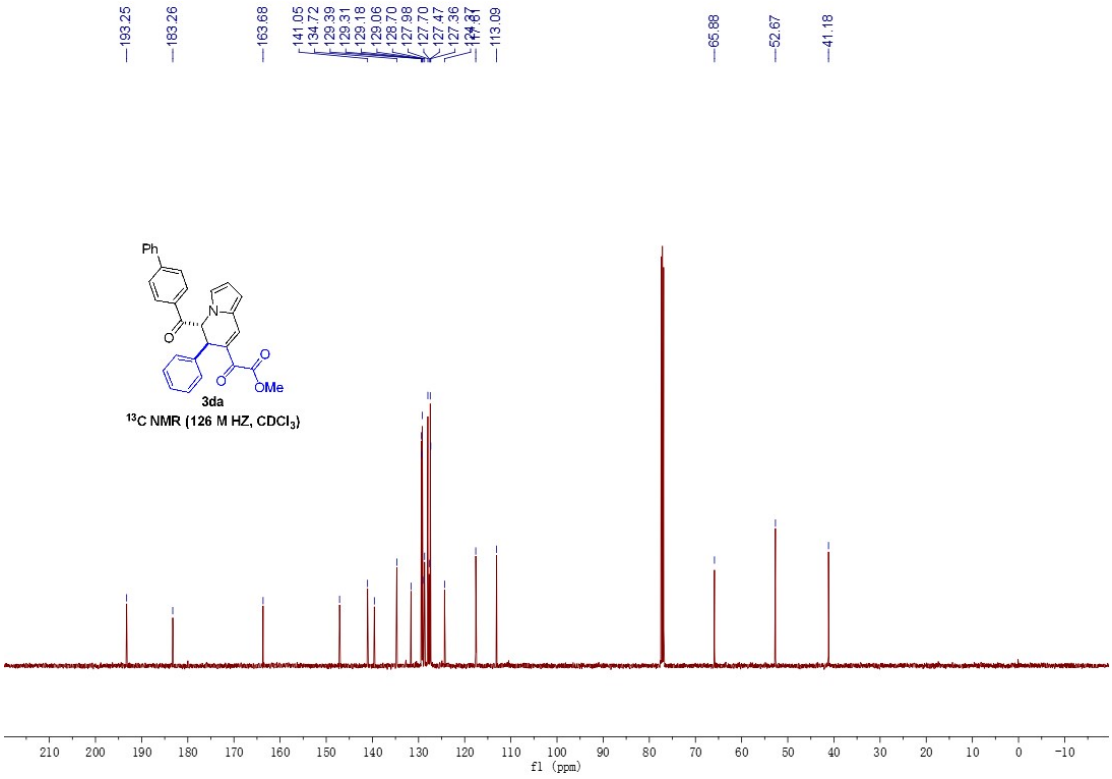

Figure S51. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3da

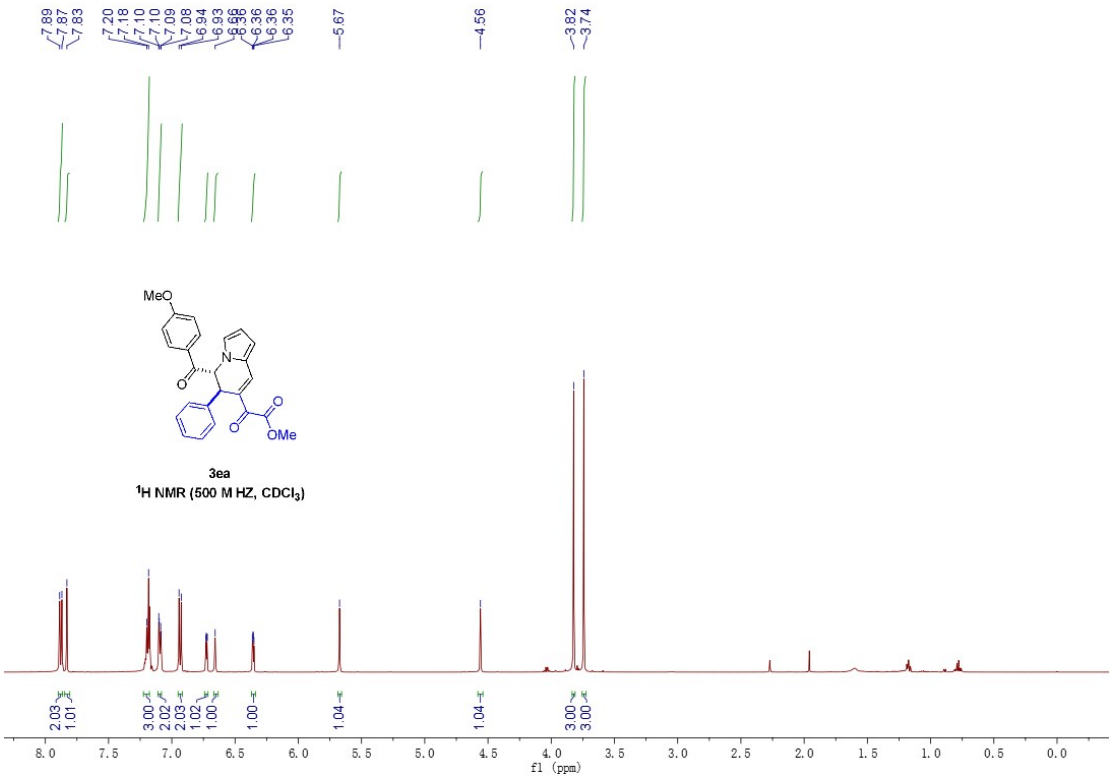

Figure S52. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ea

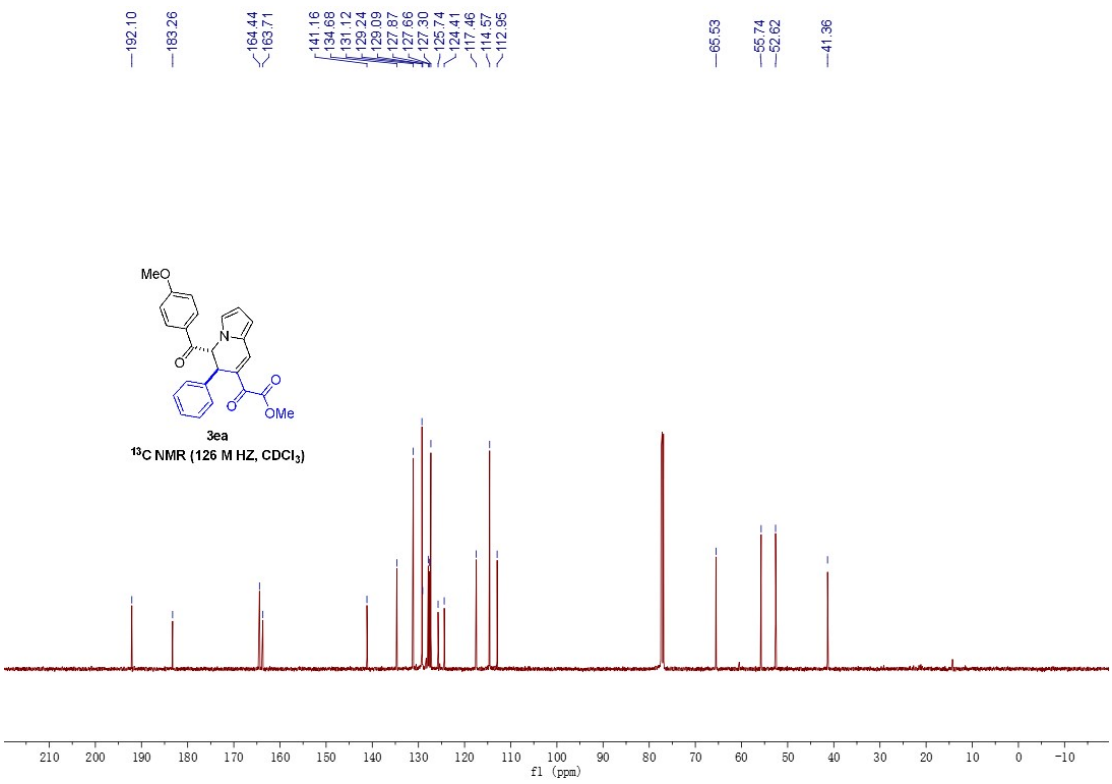

Figure S53. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ea

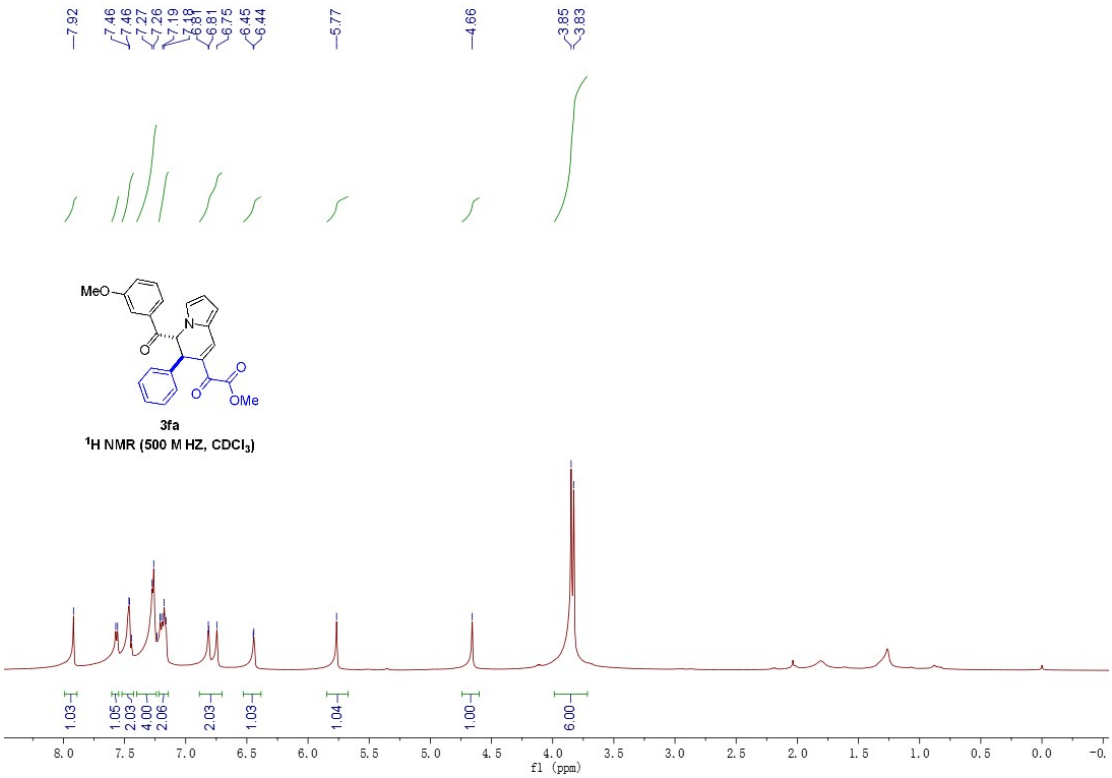

Figure S54. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3fa

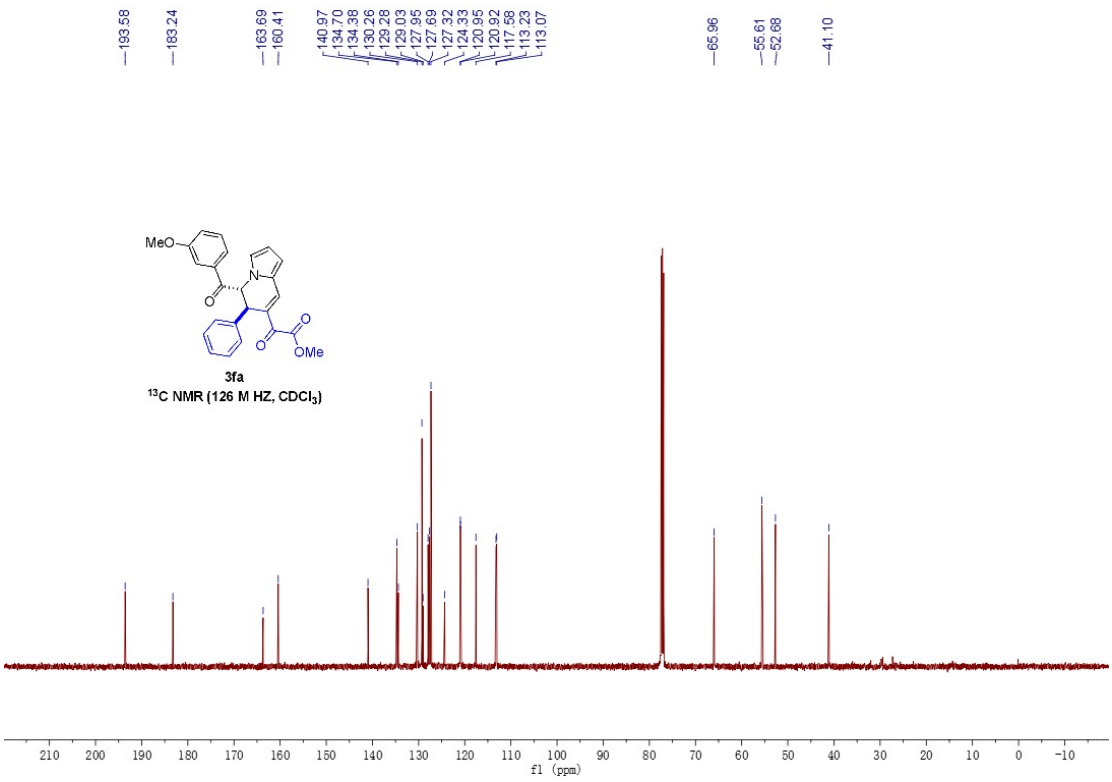

Figure S55. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3fa

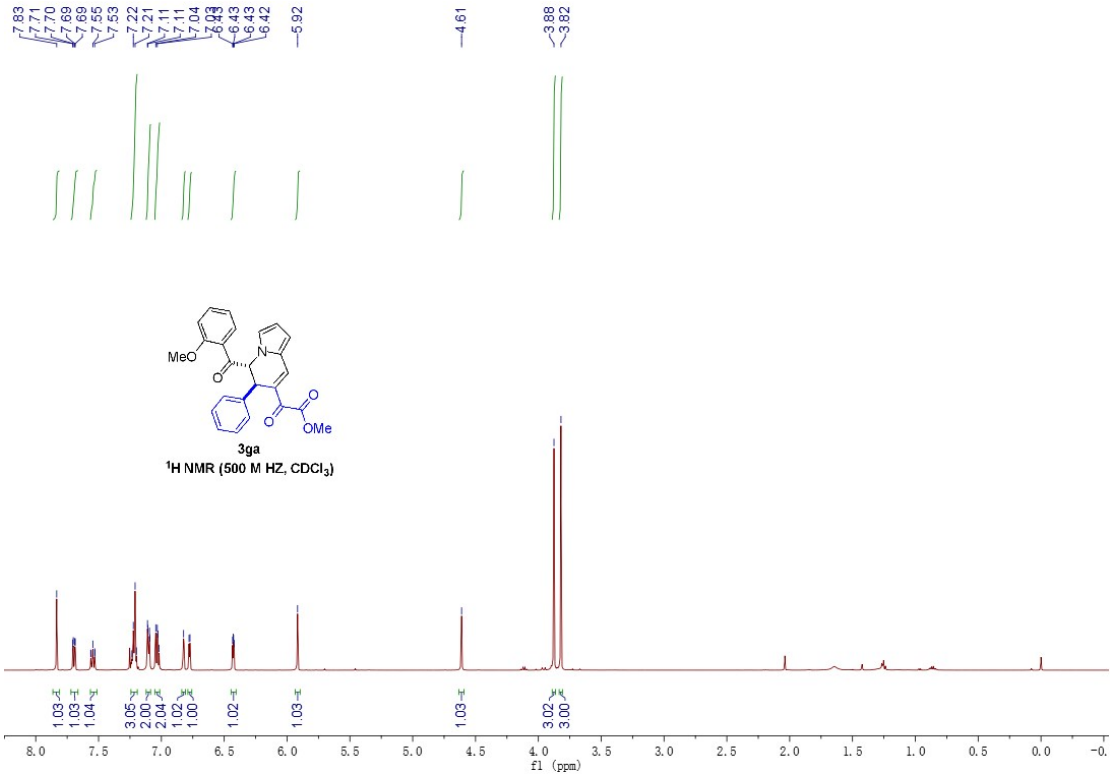

Figure S56. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ga

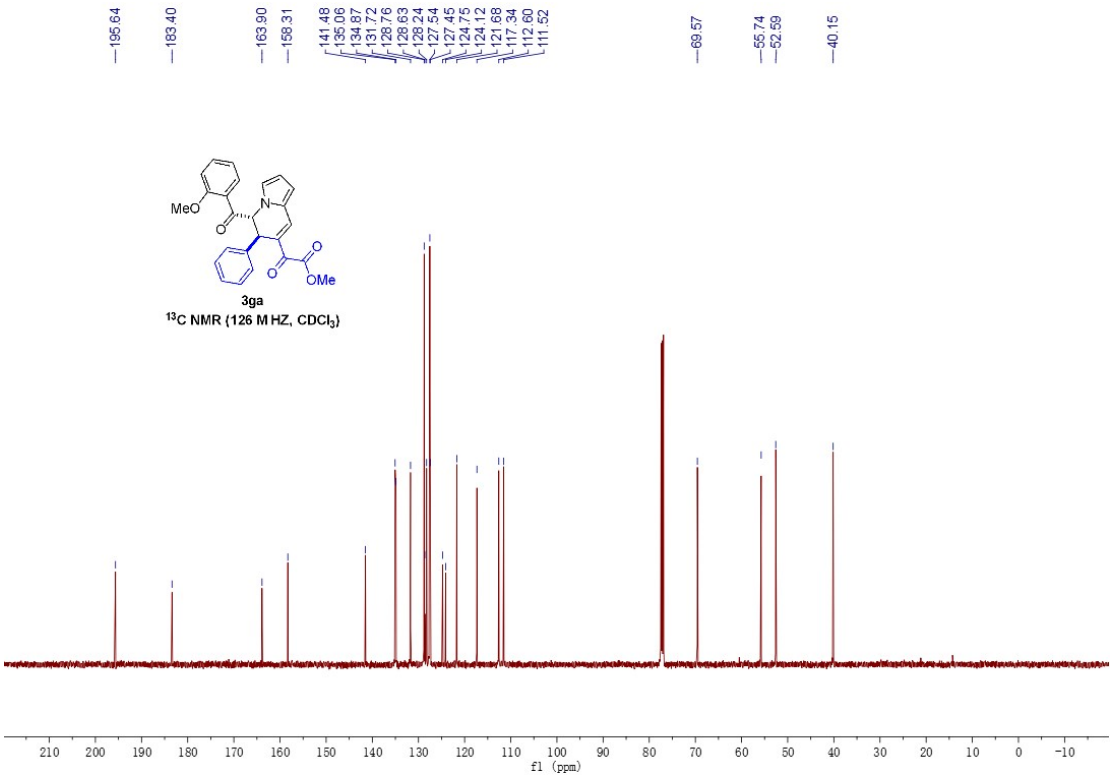

Figure S57. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ga

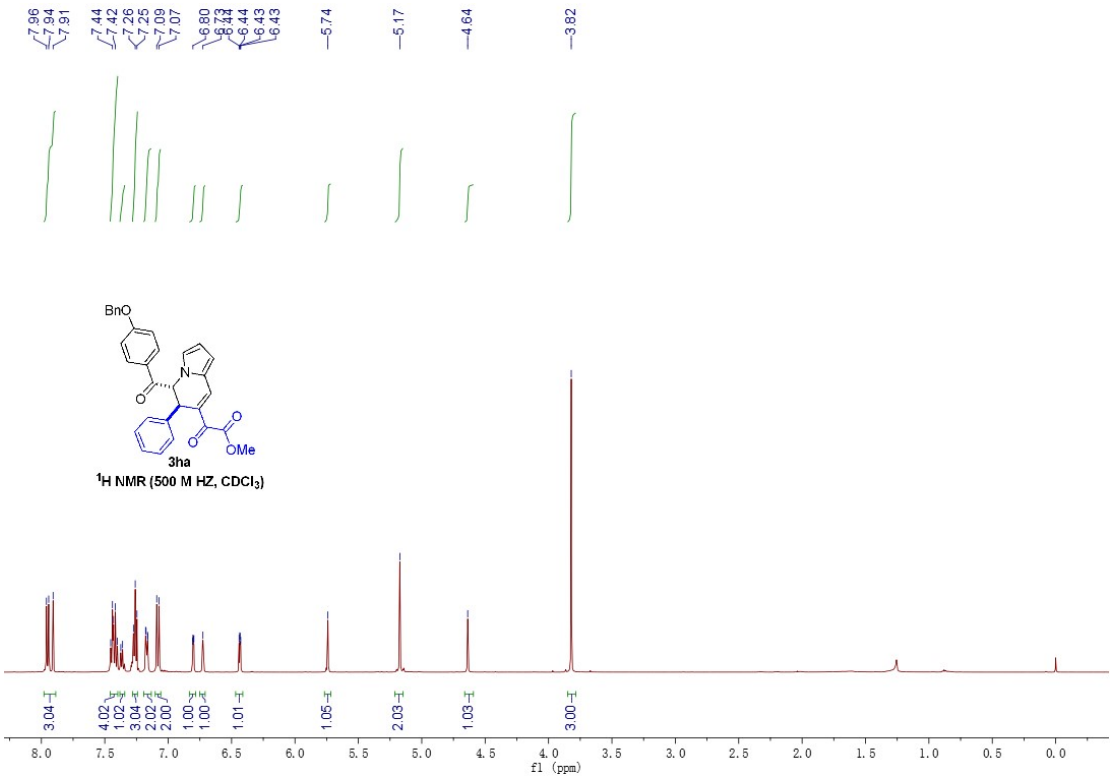

Figure S58. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ha

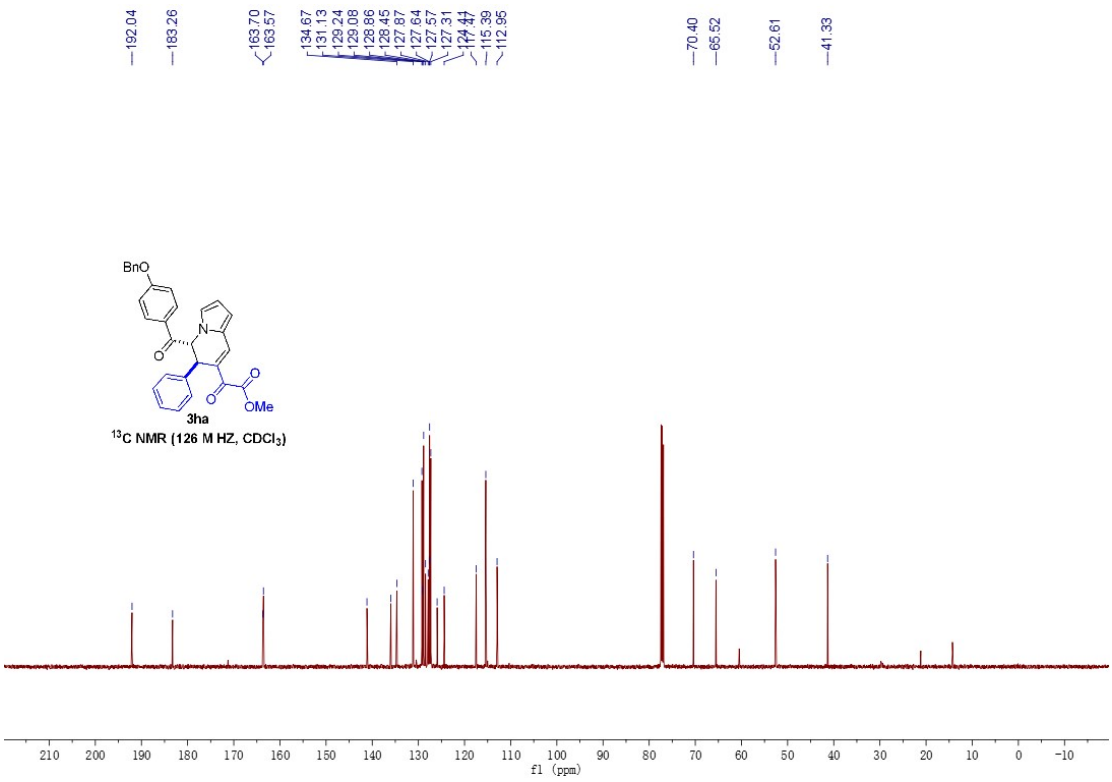

Figure S59. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ha

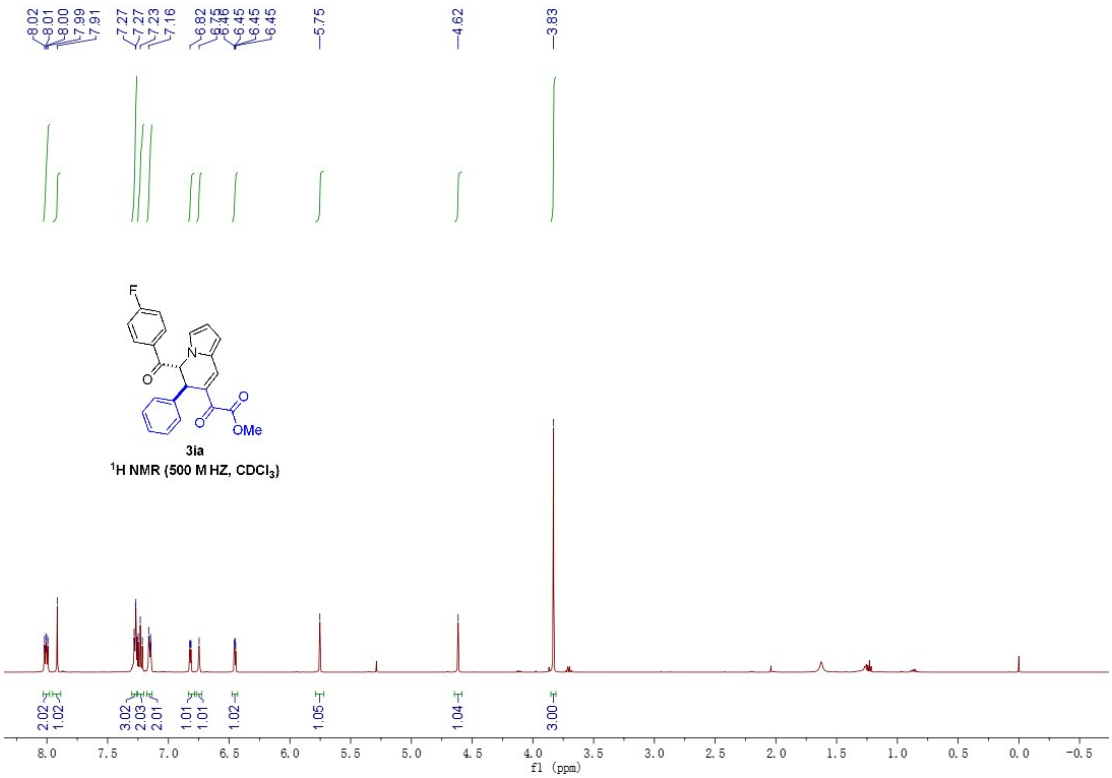

Figure S60. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ia

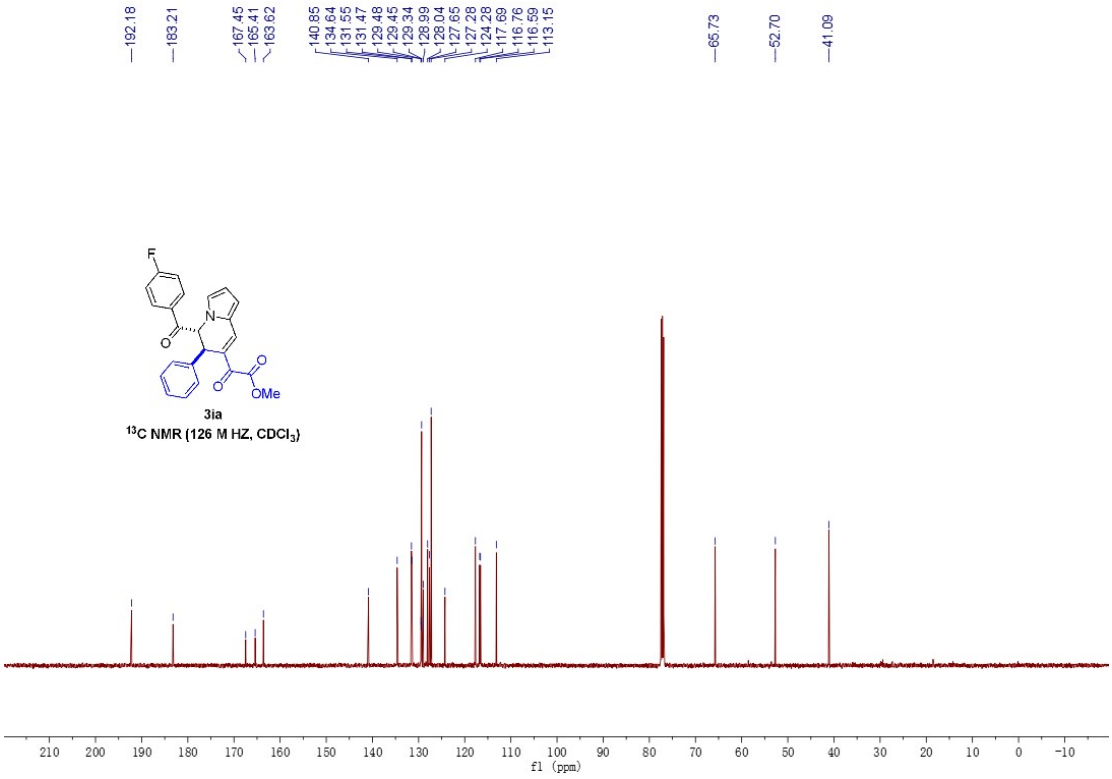

Figure S61. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ia

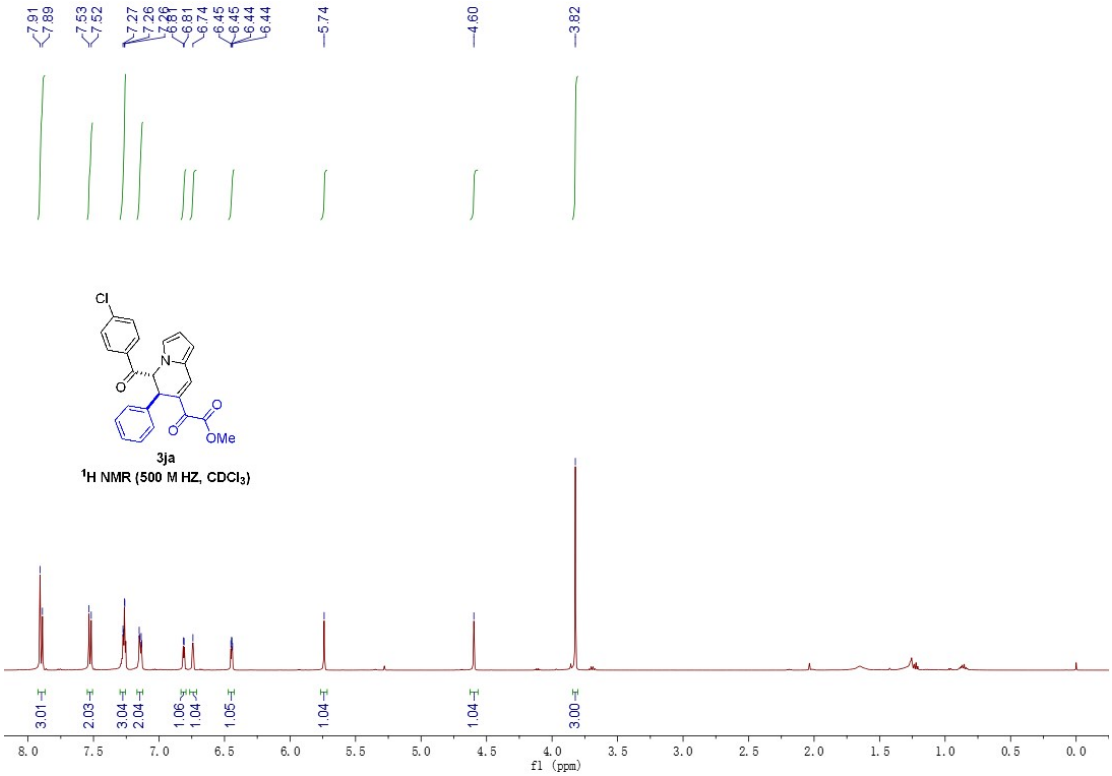

Figure S62. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ja

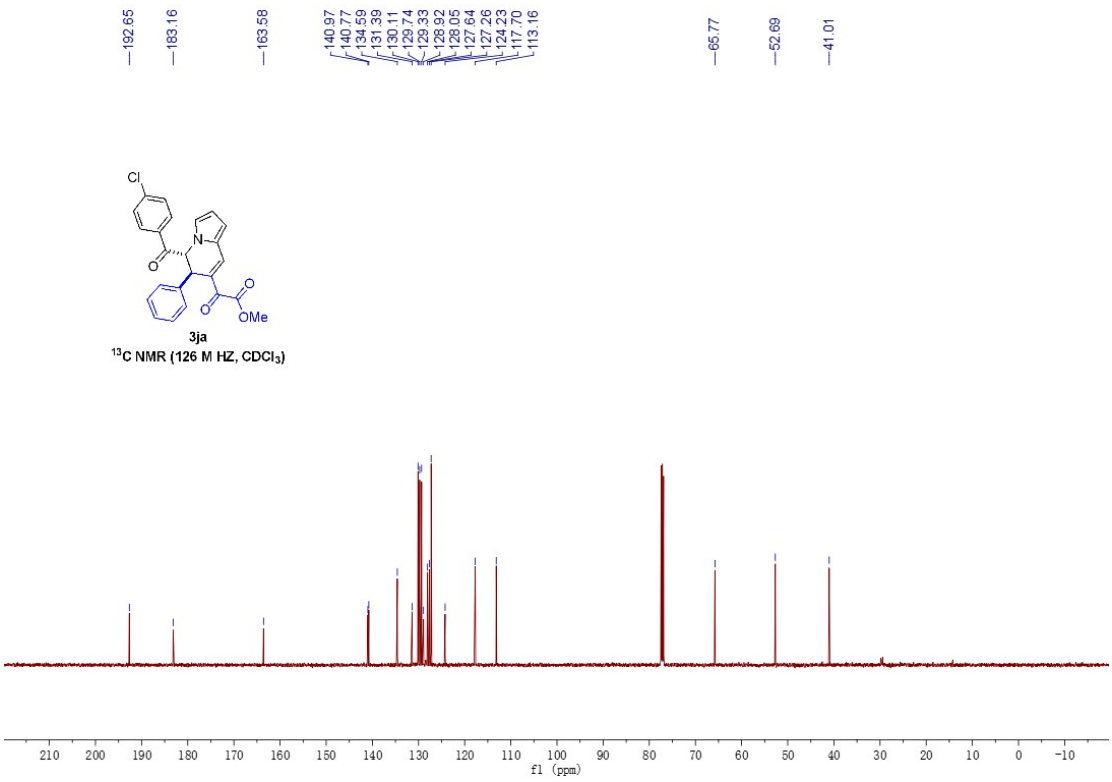

Figure S63. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ja

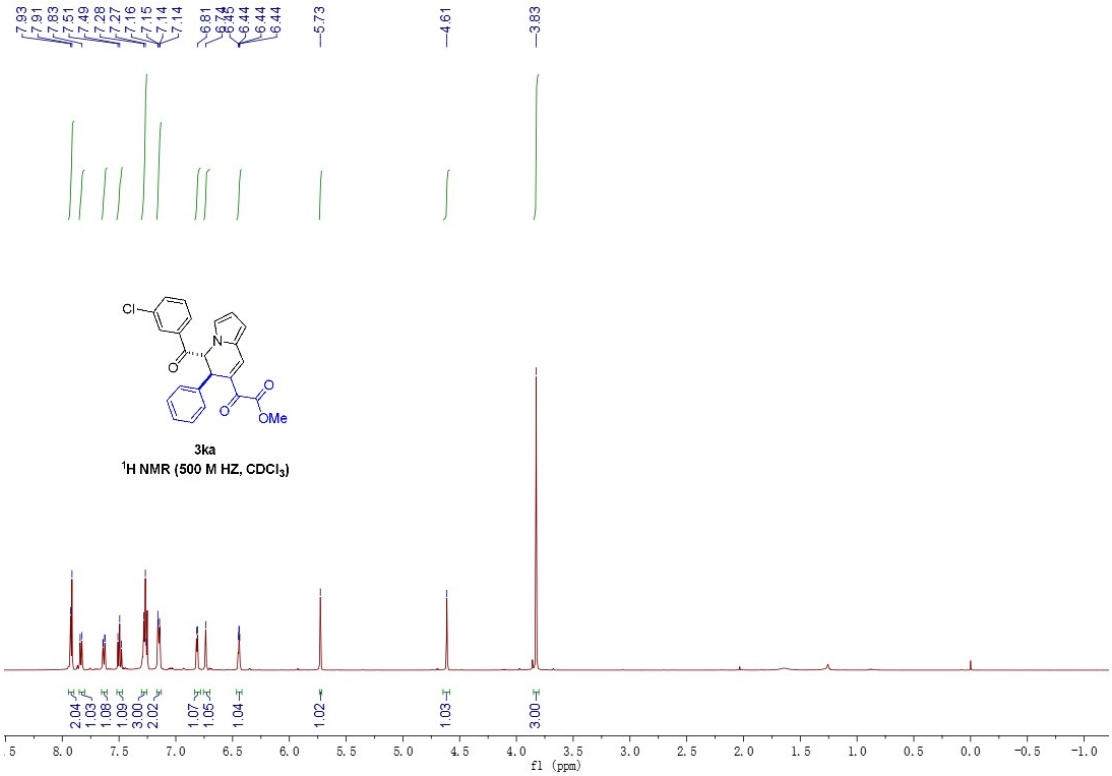

Figure S64. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ka

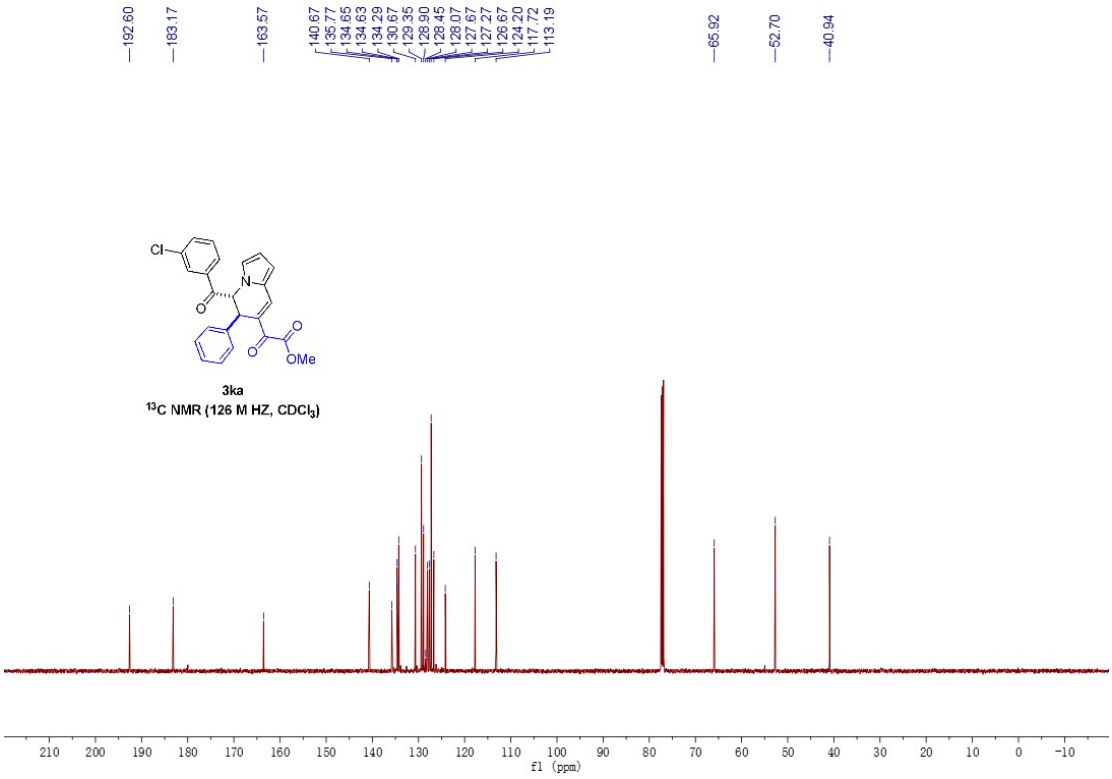

Figure S65. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ka

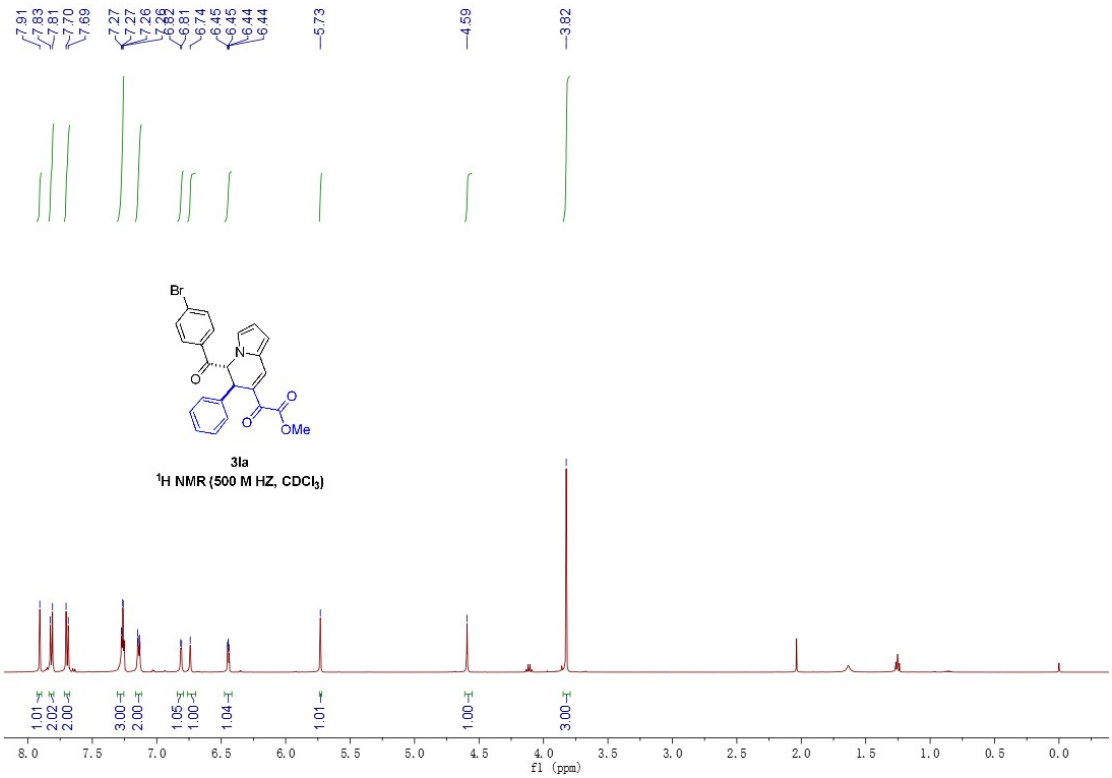

Figure S66. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3la

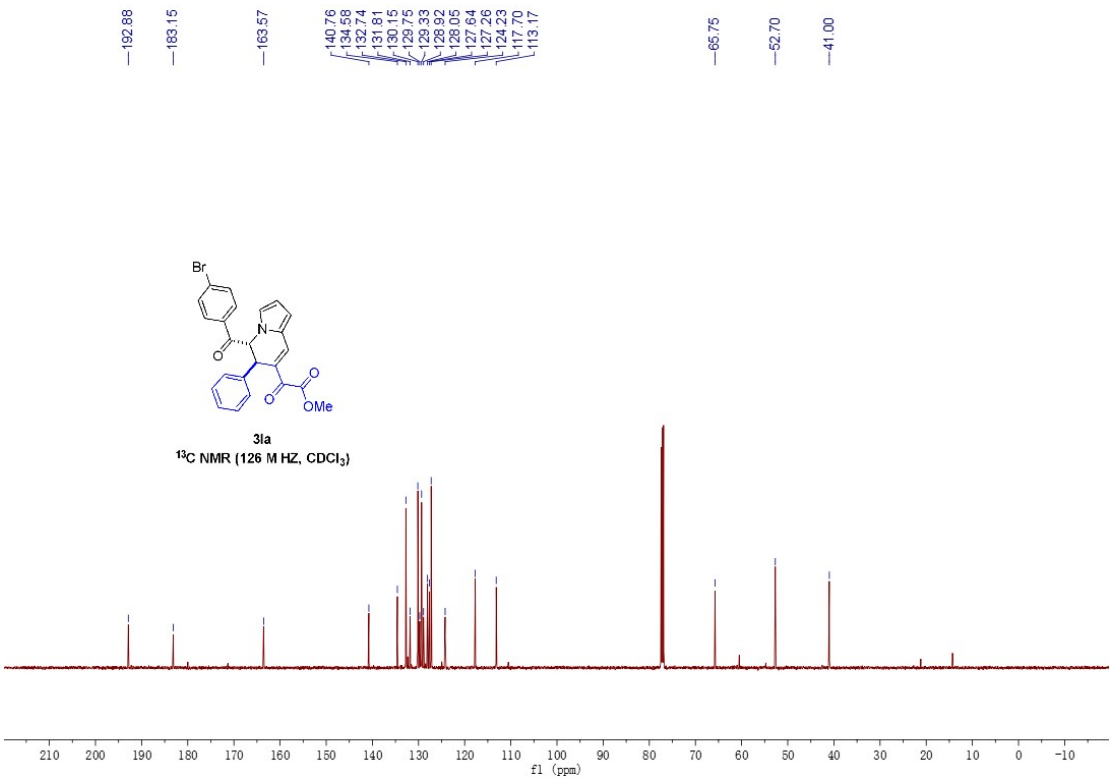

Figure S67. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3la

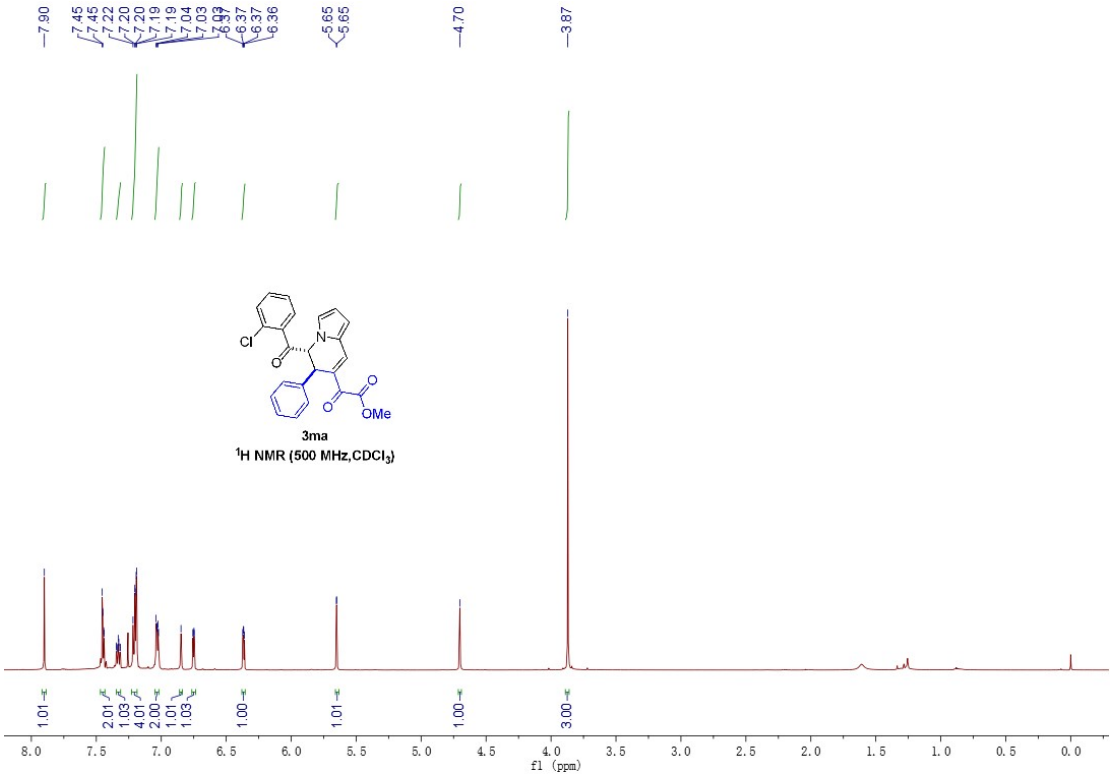

Figure S68. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ma

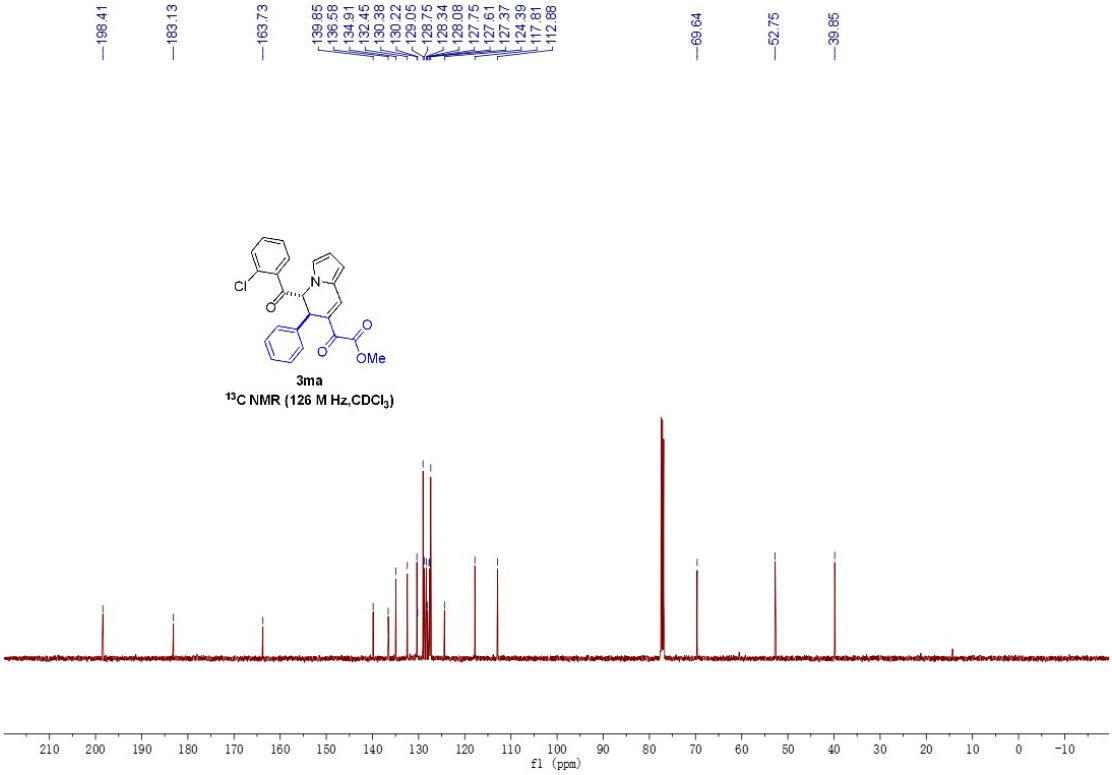

Figure S69. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ma

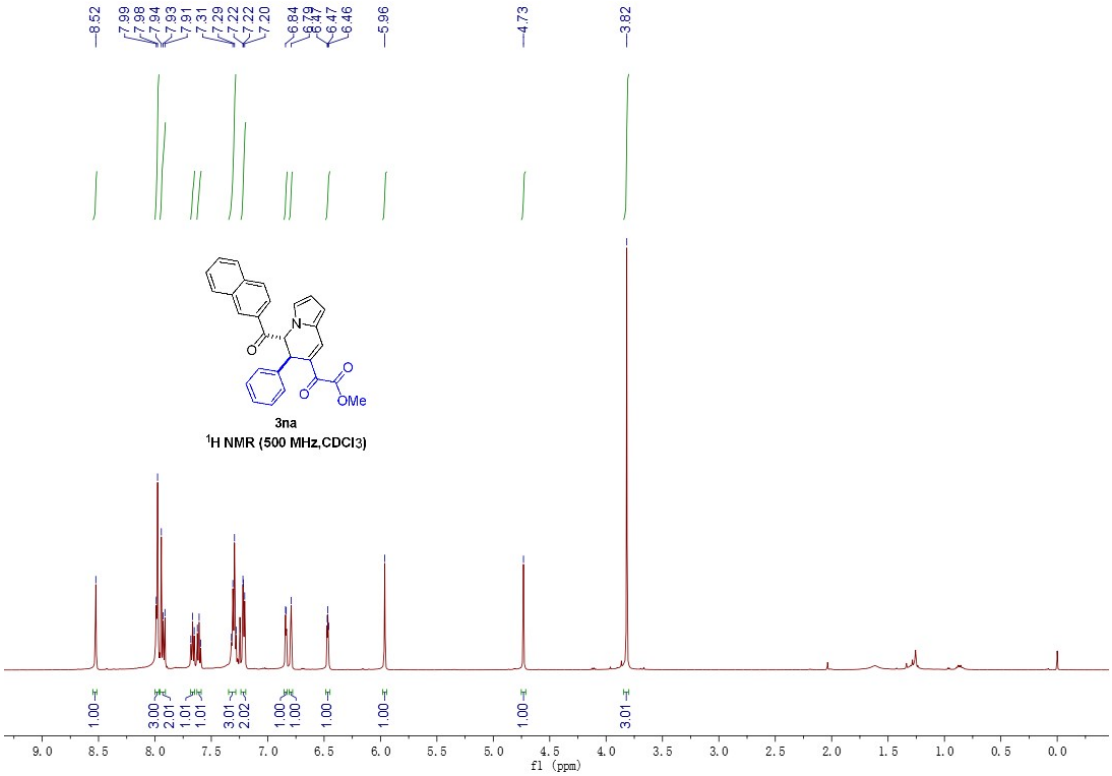

Figure S70. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3na

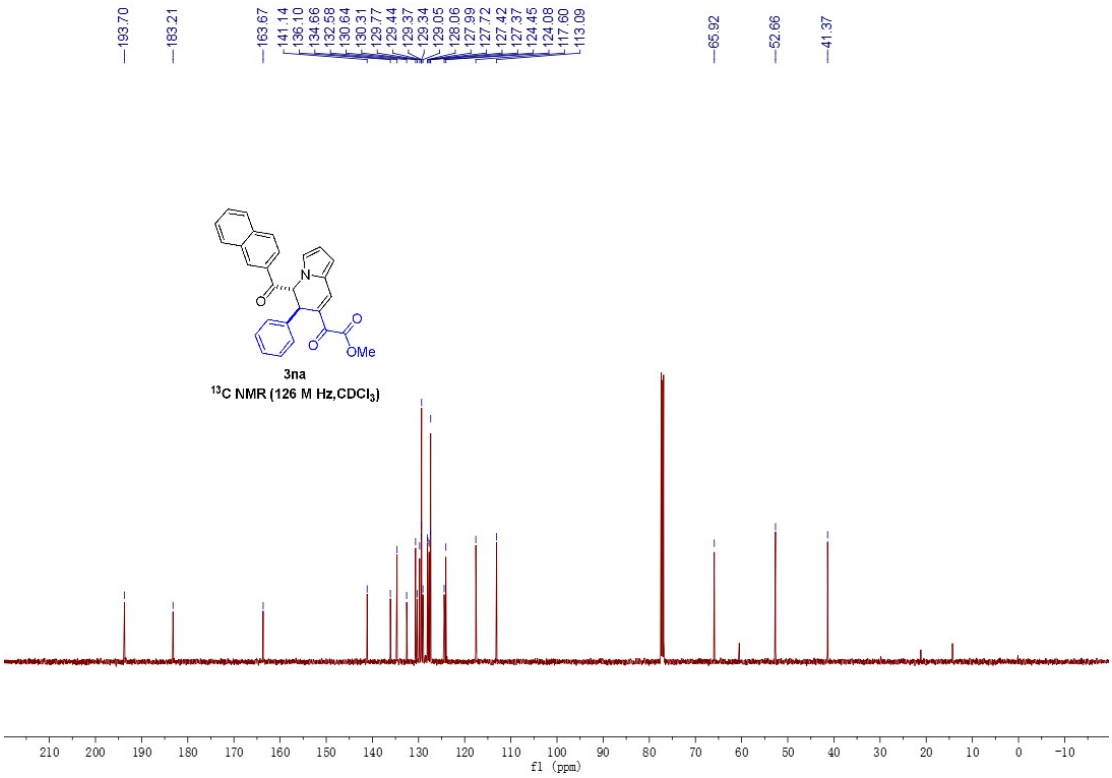

Figure S71. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3na

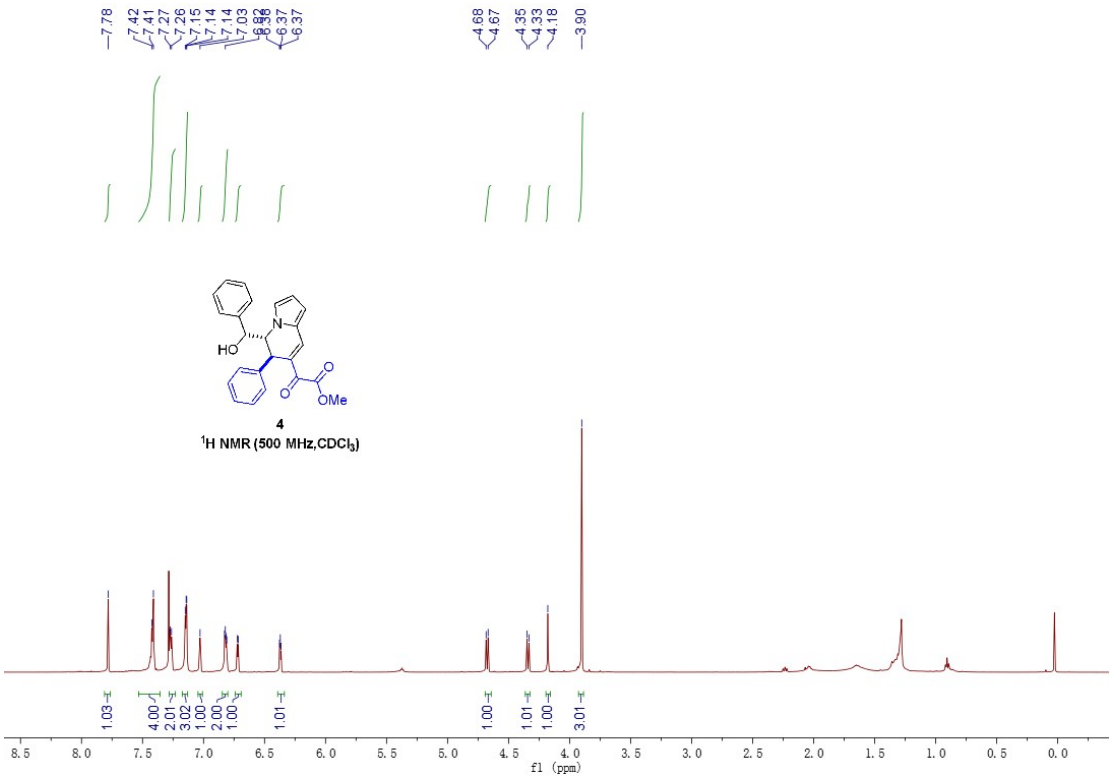

Figure S72. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4

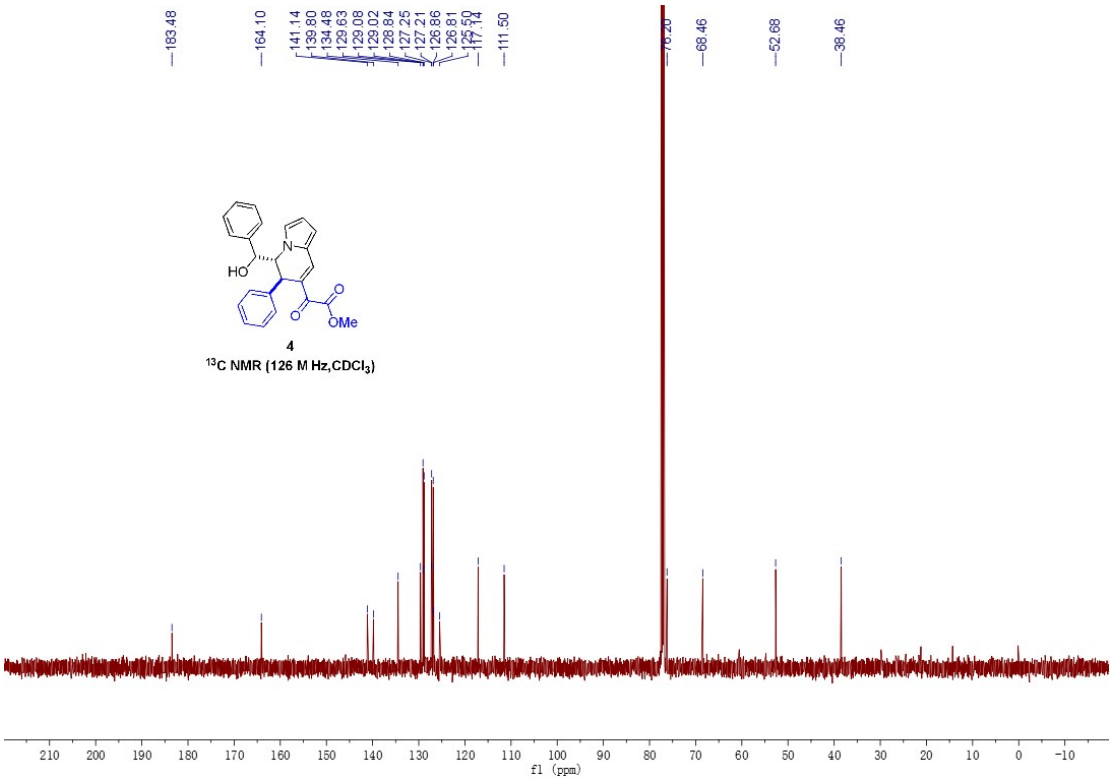

Figure S73. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4

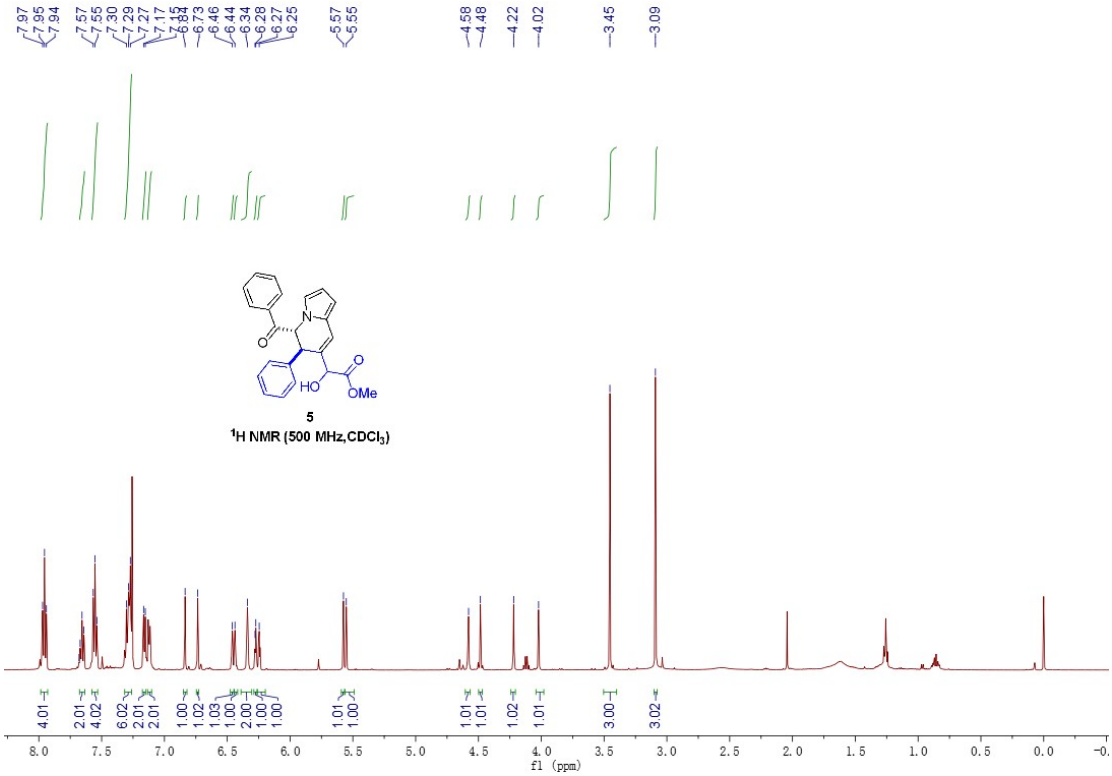

Figure S74. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 5

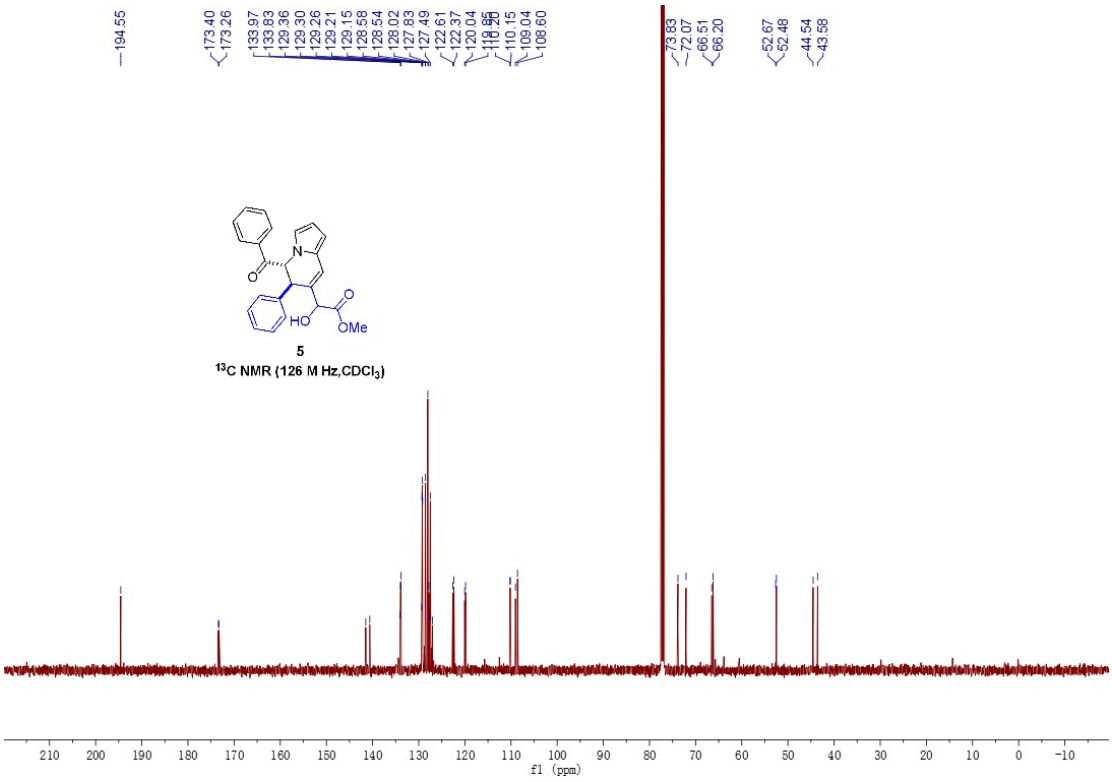

Figure S75. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 5