Supplementary Information

For

Visible-Light-Mediated Synthesis of Polysubstituted Pyrroles via C_{Ar}-I Reduction Triggered 1,5-Hydrogen Atom Transfer Process

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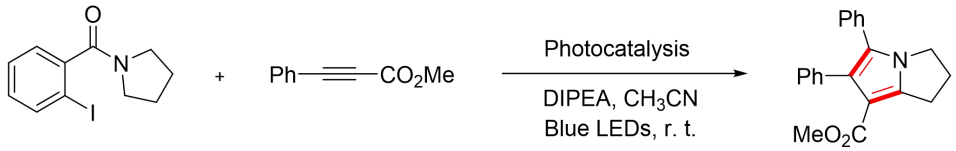
Contents

1. General Information

All of reactions were performed under an ambient temperature, magnetically stirred, and monitored by thin-layer chromatography (TLC) using Qingdao Puke Separation Materials Co., Ltd TLC plates pre-coated with 250 um thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. All of the manipulations were carried out using oven-dried glassware, including standard Schlenk techniques. All of the reagents were purchased from Alfa, Energy-Chemical or Sigma-Aldrich and used without further purification. Solvents were purified according to the method of Grubbs.[1] ^{1}H NMR, ^{13}C NMR were recorded on a Bruker AV-400 (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, ^{19}F NMR at 376 MHz) spectrometers using tetramethylsilane (TMS) as internal standard. ^{1}H and ^{19}F multiplicities are indicated as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), quartet (q), multiplet (m), and broad resonance (br). Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). High resolution massspectra (HRMS) were collected on Bruker Esquire LC mass spectrometer using electrospray ionization. Flash column chromatography was carried out on silica gel (particle size 300-400 mesh) and eluted with petroleum/ethyl acetate.

2. Optimization Studies

Table S1. Photocatalyst Screening.[a,b]

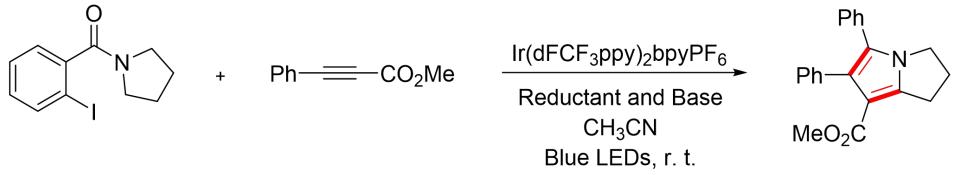


1a **2a** **3a**

Entry	Photocatalyst	Reductant	Solvent	Conversion(%)	Y(%)[b]
1	$Ru(bpy)_3Cl_2$	DIPEA	CH_3CN	75	28
2	Eosin Y	DIPEA	CH_3CN	7	trace
3	4-CzIPN	DIPEA	CH_3CN	8	trace
4	*fac*-Ir(dFppy)$_3$	DIPEA	CH_3CN	14	trace
5	Ir(dFCF$_3$ppy)$_2$dCF$_3$bpyPF$_6$	DIPEA	CH_3CN	58	24
6	Ir(dFppy)$_2$bpyPF$_6$	DIPEA	CH_3CN	8	trace
7	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	DIPEA	CH_3CN	82	22
8	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	DIPEA	CH_3CN	62	48
9	DPA	DIPEA	CH_3CN	0	0
11	Thioxanthen-9-one	DIPEA	CH_3CN	9	trace
12	Benzophenone	DIPEA	CH_3CN	0	0

[a] Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv.), Reductant (4 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 2*12 W blue LEDs. [b] isolated yields.

Table S2. Reductant and Base Screening.[a,b]



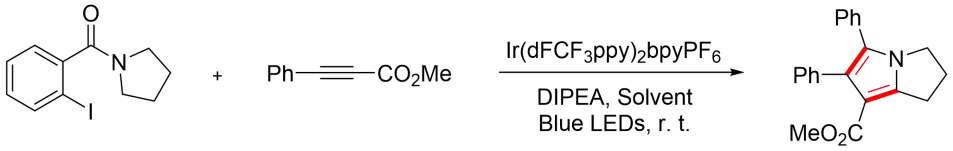
1a **2a** **3a**

Entry	Photocatalyst	Reductant	Solvent	Conversion(%)	Y(%)[b]
1	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	DIPEA	CH_3CN	62	48
2	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	Et_3N	CH_3CN	95	0
3	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	TMEDA	CH_3CN	8	trace
4	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	quinuclidine	CH_3CN	0	0
5	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	Hantzsch Esters	CH_3CN	0	0
6	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	DIPEA, K_2CO_3	CH_3CN	75	23
7	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	DIPEA,Na_2HPO_4	CH_3CN	84	33
8	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	DIPEA, Na_2CO_3	CH_3CN	65	18
9	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	DIPEA, NaOAc	CH_3CN	85	36
10	Ir(dFCF$_3$ppy)$_2$bpyPF$_6$	DIPEA, NaF	CH_3CN	72	31

[a] Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv.), reductant (4 equiv.), base (2 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 2*12 W blue

LEDs. [b] isolated yields.

Table S3. Solvent Screening.[a]

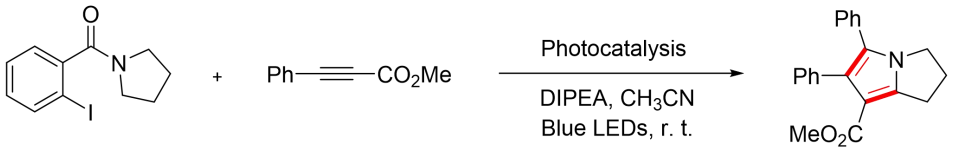


1a **2a** **3a**

Entry	Photocatalyst	Reductant	Solvent	Conversion(%)	Y(%)[b]
1	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	DCM	80	14
2	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	DCE	64	21
3	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	DMF	63	28
4	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	DMSO	55	19
5	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	DMA	42	24
6	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	NMP	66	23
7	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	THF	12	trace
8	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	EtOAc	55	20
9	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	CH_3OH	6	trace
10	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	1,4-dioxane	8	trace
11	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	Benzotrifluoride	13	trace
12	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	TFE	7	trace
13	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	HFIP	none	none

[a] Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv.), reductant (4 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 2*12 W blue LEDs. [b] isolated yields.

Table S4. Additive Screening.[a]

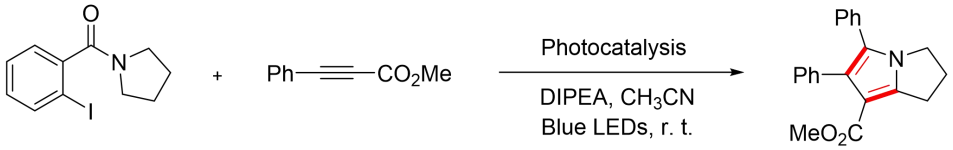


1a **2a** **3a**

Entry	Photocatalyst	Reductant	Additive	Solvent	Conversion(%)	Y(%)[b]
1	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	-	CH_3CN	62	48
2	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	Bu_4NCl	CH_3CN	89	43
3	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	Bu_4NBr	CH_3CN	69	27
4	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	Bu_4NI	CH_3CN	78	37
5	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	LiCl	CH_3CN	89	41
6	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	LiBr	CH_3CN	66	25

[a] Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv), Reductant (4 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 2*12 W blue LEDs. [b] isolated yields.

Table S5. Light and amount of reductant screening.

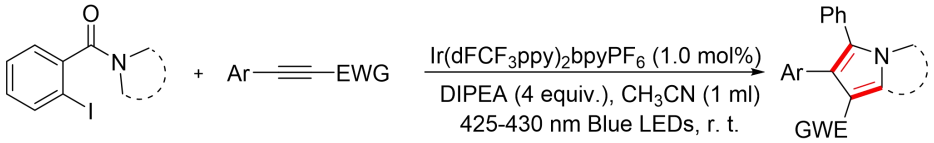


1a **2a** **3a**

Entry[a]	Photocatalyst	Reductant	Light source	Solvent	Conversion(%)	Y(%)[b]
1	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	450 nm	CH_3CN	100	56
2	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	390-395 nm	CH_3CN	100	trace
3	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	400-405 nm	CH_3CN	100	trace
4	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	425-430 nm	CH_3CN	100	60
5[c]	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	430 nm	CH_3CN	100	40
6[d]	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	430 nm	CH_3CN	100	46

[a] Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2 equiv.), Reductant (4 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere. [b] isolated yields. [c] the reaction was conducted with 3 equiv DIPEA. [d] the reaction was conducted with 5 equiv DIPEA.

3. General Procedure for the synthesis of polysubstituted pyrroles.

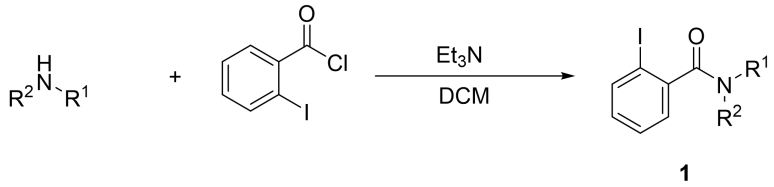


1 **2** **3, 4, 5**

In a dried sealed tube**, 1** (0.1 mmol), **2** (0.2 mmol), $Ir(dFCF_3ppy)_2bpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 ºC. Subsequently, the reaction mixture was exposed to 2 *12 W blue LEDs at room temperature until the starting materials was completely consumed (monitored by TLC). After the reaction finished, the reaction solvent was distill under vacuum, the residue was purified by flash column chromatography on silica gel with ethyl acetate (EA) and petroleum ether (PE) to afford the corresponding products.

4. General procedure for the synthesis of corresponding substrates.

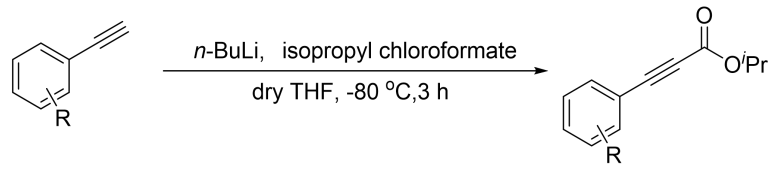
General procedure for the synthesis of amides[1-3].



1

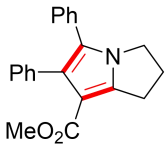
Amine (1.0 equiv.), Et_3N (2 equiv.) were dissolved in DCM (0.2 M). And 2-iodo-benzoylchlorid (1.0 equiv.) was added in dropwise at 0 °C. After addition, the reaction mixture was stirred at room temperature for 12 hours. After the material was completed consumed, 10 mL 1M HCl was added in the reaction mixture, and extracted with EA (20 mL*3), the combine solvents was washed with brine (30 mL), dried over Na_2SO_4. The solvent was concentrated and purification by chromatography on silica gel to afford the desired substrates.

General procedure for the synthesis of esters[4].



Ethynylbenzene (2 mmol, 1.0 equiv) was dissolved in dry THF (20 mL). And *n*-BuLi (1 mL, 2.5 M in hexanes, 0.3 mmol, 1.25 equiv) was added at -80 °C , the reaction mixture was stirred for 30 min at -80 °C. Isopropyl chloroformate(1.2 equiv., 2.4mmol) was added with dropwise, and the reaction mixture was stirred for additional 2.5 h. When the substrate was completely consumed, the reaction was quenched with ice water (20 mL) and extracted with EA (20 mL*3). The organic layers were then combined and washed with brine (30 mL), dried over $MgSO_4$. The solvent was concentrated and purification by chromatography on silica gel to afford the desired substrates.

5. Product Characterization



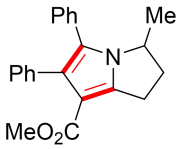
3a

The phtotoredox reaction was performed according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 36 h, the corresponding product **3a** was purified by flash column chromatography with PE/EA (30:1) to provide **3a** (19.0 mg, 60% yield) as a colorless oil..

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.19-7.07 (m, 8H), 7.06-6.98 (m, 2H), 3.95 (t, J = 7.1 Hz, 1H), 3.60 (s, 3H), 3.14 (t, J = 7.4 Hz, 2H), 2.45 (p, J = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.5, 144.8, 135.4, 132.0, 131.1, 129.3, 128.3, 127.5, 127.2, 127.1, 126.9, 126.3, 105.95, 50.7, 47.2, 26.8, 26.5.

HRMS (ESI): calcd for $C_{21}H_{20}NO_2^+$, $(M+H)^+$: 318.1489, found: 318.1492.



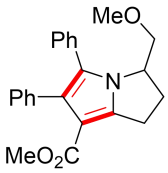
3b

The phtotoredox reaction was performed according to the general procedure using **1b** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **3b** was purified by flash column chromatography with PE/EA (30:1) to provide **3b** (12.6 mg, 38% yield) as a colorless oil, (14.3 mg, 43% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26-7.16 (m, 8H), 7.16-7.12 (m, 2H), 4.67 (dqd, J = 12.9, 6.4, 3.5 Hz, 1H), 3.68 (s, 3H), 3.29-3.10 (m, 2H), 2.77 (dq, J = 12.9, 8.2 Hz, 1H), 2.16 (qdd, J = 7.8, 6.2, 4.0 Hz, 1H), 1.00 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.6, 144.1, 135.3, 132.1, 131.1, 129.7, 128.3, 127.7, 127.3, 127.1, 126.8, 126.1, 105.5, 55.1, 50.6, 34.5, 25.4, 21.0.

HRMS (ESI): calcd for $C_{22}H_{22}NO_2^+$, $(M+H)^+$: 332.1645, found: 332.1649.



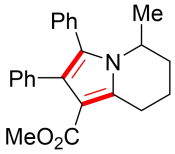
3c

The phtotoredox reaction was performed according to the general procedure using **1c** with CH_3CN as the solvent.. The reaction was run for 48 h, the corresponding product **3c** was purified by flash column chromatography with PE/EA (30:1) to provide **3c** (13.0 mg, 36% yield) as a colorless oil, (15.9 mg, 44% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.16 (m, 8H), 7.13 (dd, J = 7.8, 1.7 Hz, 2H), 4.66 (ddt, J = 8.8, 6.0, 2.9 Hz, 1H), 3.67 (s, 3H), 3.17 (ddd, J = 14.1, 9.4, 4.7 Hz, 3H), 3.07 (s, 3H), 3.03 (dd, J = 9.9, 6.3 Hz, 1H), 2.69 (dq, J = 13.1, 8.8 Hz, 1H), 2.50 (dtd, J = 8.6, 6.0, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.6, 145.3, 135.2, 132.1, 131.2, 129.7, 128.4, 127.9, 127.4 127.2, 126.9, 126.2, 105.8, 73.2, 59.2, 58.5, 50.7, 29.96, 25.8.

HRMS (ESI): calcd for $C_{23}H_{23}NO_3^+$, $(M+H)^+$: 362.1751, found: 362.1754.



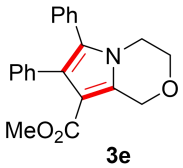
3d

The phtotoredox reaction was performed according to the general procedure using **1d** with CH_3CN as the solvent.. The reaction was run for 48 h, the corresponding product **3d** was purified by flash column chromatography with PE/EA (30:1) to afford **3d** (13.8 mg, 40% yield) as a colorless oil, (17.6 mg, 51% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27-7.23 (m, 3H), 7.19-7.05 (m, 7H), 4.44 (dt, J = 12.0, 3.3 Hz, 1H), 3.60 (s, 3H), 3.45 (ddd, J = 12.9, 8.7, 4.4 Hz, 1H), 2.94 (ddd, J = 18.0, 10.7, 7.3 Hz, 1H), 2.18-2.03 (m, 1H), 1.99-1.85 (m, 2H), 1.79 (dd, J = 12.9, 2.8 Hz, 1H), 1.00 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.3, 136.4, 135.8, 132.3, 131.5, 130.98, 130.7, 128.3, 127.6, 127.0, 125.7, 124.8, 109.3, 50.4, 48.2, 29.6, 24.1, 21.4, 15.8.

HRMS (ESI): calcd for $C_{23}H_{24}NO_2^+$, $(M+H)^+$: 346.1802, found: 346.1800.



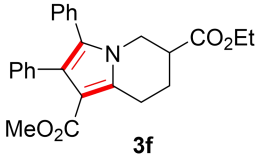
3e

The phtotoredox reaction was performed according to the general procedure using **1e** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **3e** was purified by flash column chromatography with PE/EA (10:1) to afford **3e** (16.0 mg, 48% yield) as a colorless oil, (22.3 mg, 67% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29-7.26 (m, 1H), 7.25 (dd, J = 5.0, 1.6 Hz, 1H), 7.21-7.11 (m, 2H), 5.18 (s, 2H), 4.06 - 3.97 (t, 2H), 3.87-3.81 (t, 2H), 3.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.4, 134.8, 133.6, 131.5, 131.0, 130.99, 130.7, 128.4, 127.8, 127.4, 126.3, 124.2, 108.3, 65.8, 64.0, 50.8, 43.8.

HRMS (ESI): calcd for $C_{21}H_{20}NO_3^+$, $(M+H)^+$: 334.1438, found: 334.1429.



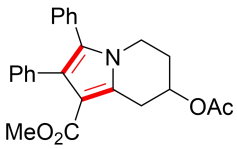
3f

The phtotoredox reaction was performed according to the general procedure using **1f** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **3f** was purified by flash column chromatography with PE/EA (30:1) to afford **3f** (11.7 mg, 29% yield) as a colorless oil, (13.7 mg, 34% brsm)..

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26 (dd, J = 8.6, 3.5 Hz, 2H), 7.21-7.07 (m, 7H), 4.21-4.11 (m, 2H), 4.01-3.87 (m, 2H), 3.61 (s, 3H), 3.48-3.36 (m, 1H), 3.21-3.08 (m, 1H), 2.94-2.82 (m, 1H), 2.32 (dd, J = 8.5, 4.8 Hz, 1H), 2.11-1.97 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.7, 166.0, 135.6, 135.5, 131.3, 131.2, 130.9, 128.3, 127.7, 127.2, 125.98, 124.5, 109.6, 53.6, 50.55, 45.6, 39.9, 23.7, 23.4, 14.3.

HRMS (ESI): calcd for $C_{25}H_{26}NO_4^+$, $(M+H)^+$:404.1856, found: 404.1862.



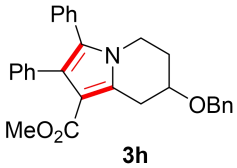
3g

The phtotoredox reaction was performed according to the general procedure using **1g** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **3g** was purified by flash column chromatography with PE/EA (20:1) to afford **3g** (13.2 mg, 34% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.20-7.14 (m, 3H), 7.12-7.01 (m, 7H), 5.34-5.22 (m, 1H), 3.84 (ddd, J = 13.2, 8.1, 5.2 Hz, 1H), 3.79-3.70 (m, 1H), 3.55 (s, 3H), 3.43 (dd, J = 18.5, 5.3 Hz, 1H), 3.28 (dd, J = 18.5, 5.1 Hz, 1H), 2.07 (dd, J = 11.1, 5.5 Hz, 2H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.6, 165.7, 135.3, 133.5, 131.3, 131.2, 131.1, 130.9, 128.3, 127.7, 127.3, 126.0, 124.6, 110.2, 66.2, 50.6, 40.8, 30.4, 27.6, 21.4.

HRMS (ESI): calcd for $C_{24}H_{24}NO_4^+$, $(M+H)^+$: 390.1700, found: 390.1701.



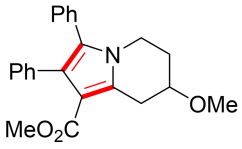
3h

The phtotoredox reaction was performed according to the general procedure using **1h** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **3h** was purified by flash column chromatography with PE/EA (20:1) to afford **3h** (24.9 mg, 57% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41-7.34 (m, 4H), 7.33-7.28 (m, 1H), 7.23 (dd, J = 5.6, 4.3 Hz, 3H), 7.13 (dt, J = 5.3, 3.7 Hz, 7H), 4.67 (q, J = 12.0 Hz, 2H), 4.08-3.93 (m, 2H), 3.82-3.70 (m, 1H), 3.62 (s, 3H), 3.43 (qd, J = 18.1, 5.2 Hz, 2H), 2.23-2.02 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.0, 138.4, 135.6, 134.7, 131.6, 131.3, 130.96, 130.9, 128.6, 128.2, 127.9, 127.8, 127.6, 127.2, 125.9, 124.4, 110.0, 70.5, 70.2, 50.5, 41.3, 30.5, 28.2.

HRMS (ESI): calcd for $C_{29}H_{28}NO_3^+$, $(M+H)^+$: 438.2064, found: 438.2072.



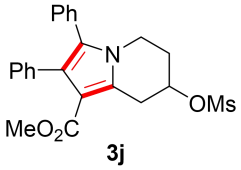
3i

The phtotoredox reaction was performed according to the general procedure using **1i** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **3i** was purified by flash column chromatography with PE/EA (20:1) to provide **3i** (15.3 mg, 40% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.24 (t, J = 5.1 Hz, 3H), 7.20-7.05 (m, 7H), 3.93 (ddd, J = 13.1, 8.1, 5.1 Hz, 1H), 3.84 (q, J = 7.7 Hz, 1H), 3.78-3.70 (m, 1H), 3.62 (s, 3H), 3.45 (s, 3H), 3.42-3.30 (m, 2H), 2.20-2.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.0, 135.6, 134.5, 131.6, 131.3, 130.9, 128.2, 127.6, 127.2, 125.9, 124.4, 110.1, 72.3, 56.4, 50.5, 41.0, 30.0, 27.7.

HRMS (ESI): calcd for $C_{23}H_{23}NNaO_3^+$, $(M+Na)^+$:384.1570, found: 384.1561.



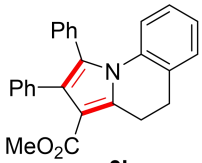
3j

The phtotoredox reaction was performed according to the general procedure using **1j** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3j** was purified by flash column chromatography with PE/EA (10:1) to afford **3j** (27.2 mg, 64% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.18 (dd, J = 4.5, 2.5 Hz, 3H), 7.14- 6.97 (m, 7H), 5.30-5.17 (m, 1H), 3.94 (ddd, J = 13.8, 9.6, 4.6 Hz, 1H), 3.84-3.72 (m, 1H), 3.55 (s, 3H), 3.53-3.41 (m, 2H), 3.03 (s, 3H), 2.35 (dq, J = 14.8, 5.0 Hz, 1H), 2.24-2.09 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.7, 135.2, 131.9, 131.4, 131.2, 131.0, 130.9, 128.4, 127.9, 127.3, 126.1, 124.6, 110.6, 73.8, 50.7, 40.1, 39.1, 31.1, 28.9.

HRMS (ESI): calcd for $C_{23}H_{24}NSO_5^+$, $(M+H)^+$: 426.1370, found: 426.1373.



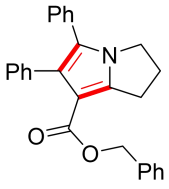
3k

The reaction was conducted according to the general procedure using **1k** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3k** was purified by flash column chromatography with PE/EA (10:1) to afford **3k** as a colorless oil, 58% isolated yield (75% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.58-7.50 (m, 1H), 7.44 (dd, J = 10.7, 4.1 Hz, 1H), 7.39-7.34 (m, 2H), 7.34-7.27 (m, 5H), 7.23-7.16 (m, 3H), 6.91 (d, J = 7.7 Hz, 1H), 6.85 (s, 1H), 3.50 (s, 3H), 2.98-2.82 (m, 2H), 2.75 (ddd, J = 13.1, 9.1, 7.0 Hz, 1H), 2.40-2.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 168.9, 136.1, 135.5, 134.1, 134.1, 132.97, 130.3, 128.6, 128.4, 128.3, 128.3, 128.2, 128.2, 127.96, 126.6, 126.6, 126.3, 125.2, 57.2, 51.9, 25.99.

HRMS (ESI): calcd for $C_{26}H_{22}NO_2^+$, $(M+H)^+$: 380.1645, found: 380.1644.



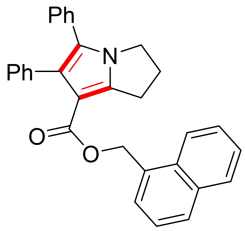
4a

The phtotoredox reaction was performed according to the general procedure using **2b** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4a** was purified by flash column chromatography with PE/EA (30:1) to afford 4**a** (19.2 mg, 49% yield) as a colorless oil (55% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.31-7.16 (m, 13H), 7.13-7.07 (m, 2H), 5.16 (s, 2H), 4.02 (t, J = 7.1 Hz, 2H), 3.21 (dd, J = 9.4, 5.5 Hz, 2H), 2.59-2.44 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.8, 145.1, 137.0, 135.5, 131.99, 131.2, 129.3, 128.4, 128.3, 127.9, 127.7, 127.6, 127.3, 127.2, 126.9, 126.3, 105.96, 65.1, 47.2, 26.9, 26.5.

HRMS (ESI): calcd for $C_{27}H_{24}NO_2^+$, $(M+H)^+$: 394.1802, found: 394.1809.



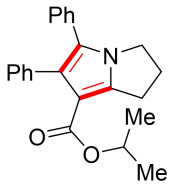
4b

The phtotoredox reaction was performed according to the general procedure using **2c** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4b** was purified by flash column chromatography with PE/EA (60:1) to give **4b** (28.9 mg, 62% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (dd, J = 5.4, 4.3 Hz, 1H), 7.86 (dd, J = 6.2, 3.3 Hz, 1H), 7.80 (dd, J = 6.3, 3.1 Hz, 1H), 7.51-7.46 (m, 2H), 7.37 (dd, J = 6.7, 3.5 Hz, 2H), 7.25-7.13 (m, 8H), 7.10 (dd, J = 8.0, 1.5 Hz, 2H), 5.62 (s, 2H), 3.99 (t, J = 7.1 Hz, 2H), 3.09 (t, J = 7.5 Hz, 2H), 2.49-2.34 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.8, 145.2, 135.4, 133.7, 132.5, 131.98, 131.8, 131.1, 129.3, 128.8, 128.6, 128.3, 127.5, 127.3, 127.2, 127.1, 126.9, 126.4, 126.3, 125.8, 125.4, 124.0, 105.9, 63.5, 47.2, 26.8, 26.5.

HRMS (ESI): calcd for $C_{31}H_{25}NNaO_2^+$, $(M+Na)^+$: 466.1778, found: 466.1774.



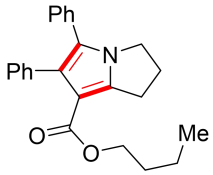
4c

The phtotoredox reaction was performed according to the general procedure using **2d** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4c** was purified by flash column chromatography with PE/EA (30:1) to give **4c** (22.4 mg, 61% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.15 (m, 8H), 7.14-7.08 (m, 2H), 5.06 (dt, J = 12.5, 6.2 Hz, 1H), 4.03 (t, J = 7.1 Hz, 2H), 3.23 (t, J = 7.4 Hz, 2H), 2.54 (p, J = 7.3 Hz, 2H), 1.16 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.6, 144.6, 135.6, 132.1, 131.2, 129.3, 128.3, 127.4, 127.1, 126.96, 126.8, 126.2, 106.8, 66.3, 47.1, 26.8, 26.5, 22.2.

HRMS (ESI): calcd for $C_{23}H_{23}NNaO_2^+$, $(M+Na)^+$:368.1621, found: 368.1620.



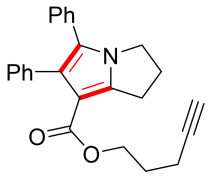
4d

The phtotoredox reaction was performed according to the general procedure using **2e** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4d** was purified by flash column chromatography with PE/EA (40:1) to afford **4d** (23.0 mg, 64% yield) as a colorless oil, (27.3 mg, 76% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.14 (m, 8H), 7.14-7.07 (m, 2H), 4.09 (t, J = 6.4 Hz, 2H), 4.03 (t, J = 7.1 Hz, 2H), 3.22 (t, J = 7.5 Hz, 2H), 2.60-2.45 (m, 2H), 1.51 (dt, J = 14.5, 6.5 Hz, 2H), 1.25 (dd, J = 15.1, 7.4 Hz, 2H), 0.86 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.3, 144.8, 135.6, 132.1, 131.2, 129.3, 128.3, 127.5, 127.2, 127.0, 126.8, 126.2, 106.4, 63.2, 47.2, 30.95, 26.8, 26.5, 19.4, 13.9.

HRMS (ESI): calcd for $C_{24}H_{26}NO_2^+$, $(M+H)^+$: 360.1958, found: 360.1964.



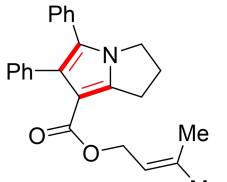
4e

The phtotoredox reaction was performed according to the general procedure using **2f** with CH_3CN as the solvent. The reaction was run for 72 h, the corresponding product **4e** was purified by flash column chromatography with PE/EA (60:1) to afford **4e** (15.1 mg, 41% yield) as a colorless oil, (16.6 mg, 45% brsm)..

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.15 (m, 8H), 7.14-7.08 (m, 2H), 4.17 (t, J = 6.0 Hz, 2H), 4.04 (t, J = 7.1 Hz, 2H), 3.23 (t, J = 7.4 Hz, 2H), 2.55 (p, J = 7.3 Hz, 2H), 2.03 (td, J = 7.2, 2.6 Hz, 2H), 1.92 (t, J = 2.6 Hz, 1H), 1.79-1.64 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.1, 144.9, 135.7, 132.0, 131.1, 129.3, 128.3, 127.5, 127.1, 127.1, 126.9, 126.4, 106.2, 83.7, 68.8, 61.8, 47.2, 27.9, 26.7, 26.6, 15.4.

HRMS (ESI): calcd for $C_{25}H_{24}NO_2^+$, $(M+H)^+$: 370.1802, found: 370.1800.



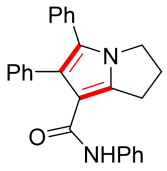
4f

The phtotoredox reaction was performed according to the general procedure using **2g** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4f** was purified by flash column chromatography with PE/EA (10:1) to provide **4f** (12.2 mg, 33% yield) as a colorless oil, (16.3 mg, 44% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.15 (m, 8H), 7.14-7.08 (m, 2H), 5.29 (ddd, J = 7.0, 5.7, 1.3 Hz, 1H), 4.60 (d, J = 7.0 Hz, 2H), 4.03 (t, J = 7.1 Hz, 2H), 3.22 (t, J = 7.4 Hz, 2H), 2.53 (p, J = 7.3 Hz, 2H), 1.70 (d, J = 12.4 Hz, 3H), 1.63 (d, J = 11.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.1, 144.8, 137.7, 135.5, 132.2, 131.2, 129.4, 128.3, 127.5, 127.3, 127.1, 126.9, 126.2, 119.7, 106.3, 60.3, 47.2, 26.8, 26.5, 25.8, 18.2.

HRMS (ESI): calcd for $C_{25}H_{26}NO_2^+$, $(M+H)^+$: 372.1958, found: 372.1966.



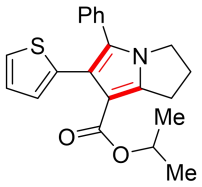
4g

The phtotoredox reaction was performed according to the general procedure using **2h** with CH_3CN as the solvent. The reaction was run for 72 h, the corresponding product **4g** was purified by flash column chromatography with PE/EA (10:1) to provide **4g** (15.9 mg, 42% yield) as a colorless oil, (20.4 mg, 54% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (t, J = 3.5 Hz, 5H), 7.25 - 7.19 (m, 3H), 7.18-7.08 (m, 7H), 6.96 (t, J = 7.2 Hz, 1H), 4.06 (t, J = 7.1 Hz, 2H), 3.36 (t, J = 7.4 Hz, 2H), 2.62-2.50 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.4, 144.7, 138.8, 135.4, 131.9, 131.7, 129.2, 129.0, 128.9, 128.4, 127.9, 126.9, 126.5, 123.5, 123.2, 119.1, 110.2, 46.96, 26.8, 26.5.

HRMS (ESI): calcd for $C_{26}H_{23}N_2O^+$, $(M+H)^+$: 379.1805, found: 379.1810.



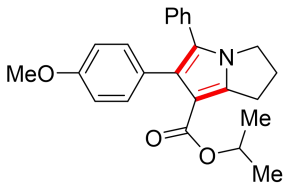
4h

The phtotoredox reaction was performed according to the general procedure using **2i** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4h** was purified by flash column chromatography with PE/EA (20:1) to afford **4h** (15.1 mg, 43% yield) as a colorless oil, (18.9 mg, 54% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 -7.10 (m, 6H), 6.99-6.85 (m, 2H), 5.09 (dt, J = 12.5, 6.2 Hz, 1H), 4.00 (t, J = 7.1 Hz, 2H), 3.21 (t, J = 7.5 Hz, 2H), 2.62 - 2.41 (m, 2H), 1.20 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.3, 144.6, 136.7, 131.8, 129.3, 128.6, 128.4, 128.2, 127.3, 126.3, 125.0, 118.6, 107.7, 66.4, 47.2, 26.7, 26.5, 22.2.

HRMS (ESI): calcd for $C_{21}H_{22}NSO_2^+$, $(M+H)^+$: 352.1366, found: 352.1368.



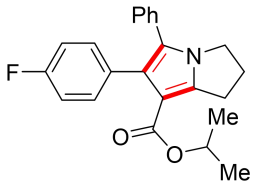
4i

The phtotoredox reaction was performed according to the general procedure using **2j** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4i** was purified by flash column chromatography with PE/EA (10:1) to give **4i** (12.7 mg, 34% yield) as a colorless oil, (16.1 mg, 43% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.09 (m, 7H), 6.80-6.72 (m, 2H), 5.07 (dt, J = 12.5, 6.2 Hz, 1H), 4.03 (t, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.21 (t, J = 7.5 Hz, 2H), 2.52 (p, J = 7.3 Hz, 2H), 1.18 (d, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.6, 158.2, 144.5, 132.3, 132.2, 129.3, 128.3, 127.9, 126.9, 126.8, 126.8, 113.0, 106.7, 66.2, 55.3, 47.2, 29.8, 26.9, 26.5, 22.3.

HRMS (ESI): calcd for $C_{24}H_{26}NO_3^+$, $(M+H)^+$: 376.1907, found: 376.1913.



4j

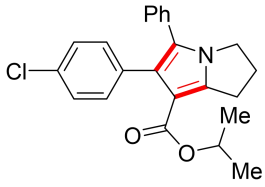
The phtotoredox reaction was performed according to the general procedure using **2k** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4j** was purified by flash column chromatography with PE/EA (15:1) to give **4j** (26.1 mg, 72% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.15 (m, 5H), 7.13-7.05 (m, 2H), 6.97-6.86 (m, 2H), 5.07 (dt, J = 12.5, 6.2 Hz, 1H), 4.03 (t, J = 7.1 Hz, 2H), 3.22 (t, J = 7.5 Hz, 2H), 2.54 (p, J = 7.3 Hz, 2H), 1.18 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.5,161.73 (d, J = 244.3 Hz), 144.7, 132.69 (d, J = 8.0 Hz), 131.9, 131.53 (d, J = 3.4 Hz), 131.5, 129.3, 128.4, 127.1, 126.98, 126.0, 114.34 (d, J = 21.2 Hz), 106.7, 66.4, 47.1, 29.8, 26.8, 26.5, 22.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -117.1.

HRMS (ESI): calcd for $C_{23}H_{23}FNO_2^+$, $(M+H)^+$: 364.1707, found: 364.1710.



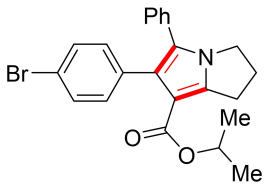
4k

The phtotoredox reaction was performed according to the general procedure using **2l** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4k** was purified by flash column chromatography with PE/EA (10:1) to afford **4k** (14.4 mg, 38% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.14 (m, 7H), 7.12-7.07 (m, 2H), 5.06 (dt, J = 12.4, 6.2 Hz, 1H), 4.02 (t, J = 7.1 Hz, 2H), 3.22 (t, J = 7.4 Hz, 2H), 2.53 (p, J = 7.3 Hz, 2H), 1.18 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.5, 144.8, 134.1, 132.5, 132.1, 131.8, 129.3, 128.5, 127.7, 127.2, 127.1, 125.8, 106.6, 66.5, 47.1, 29.8, 26.8, 26.5, 22.2.

HRMS (ESI): calcd for $C_{23}H_{23}ClNO_2^+$, $(M+H)^+$: 380.1412, found: 380.1407.



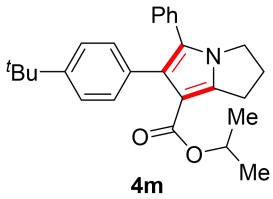
4l

The phtotoredox reaction was performed according to the general procedure using **2m** with CH_3CN as the solvent. The reaction was run for 72 h, the corresponding product **4l** was purified by flash column chromatography with PE/EA (10:1) to afford **4l** (12.3 mg, 29% yield) as a colorless oil, (16.5 mg, 39% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.24-7.17 (m, 7H), 7.12 (d, J = 6.9 Hz, 2H), 5.06 (dt, J = 12.4, 6.2 Hz, 1H), 4.03 (t, J = 7.1 Hz, 2H), 3.23 (t, J = 7.4 Hz, 2H), 2.54 (p, J = 7.3 Hz, 2H), 1.15 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.6, 144.6, 135.6, 132.2, 131.2, 129.3, 128.3, 127.4, 127.2, 126.97, 126.8, 126.2, 106.8, 66.3, 47.1, 26.8, 26.5, 22.2.

HRMS (ESI): calcd for $C_{23}H_{23}BrNO_2^+$, $(M+H)^+$: 424.0907, found: 424.0915.



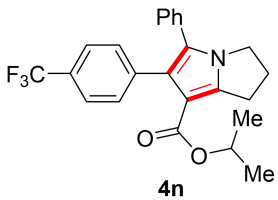
4m

The phtotoredox reaction was performed according to the general procedure using **2n** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4m** was purified by flash column chromatography with PE/EA (10:1) to provide **4m** (19.2 mg, 48% yield) as a colorless oil, (23.2 mg, 58% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.19-7.11 (m, 5H), 7.11-7.02 (m, 5H), 4.98 (dt, J = 12.4, 6.2 Hz, 1H), 3.94 (t, J = 7.1 Hz, 2H), 3.14 (t, J = 7.4 Hz, 2H), 2.43 (dd, J = 14.6, 7.2 Hz, 2H), 1.22 (s, 9H), 1.07 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.6, 148.8, 144.5, 132.4, 132.3, 130.7, 129.4, 128.2, 127.2, 126.9, 126.7, 124.3, 106.9, 66.1, 47.1, 34.5, 31.6, 26.8, 26.5, 22.2.

HRMS (ESI): calcd for $C_{27}H_{32}NO_2^+$, $(M+H)^+$: 402.2428, found: 402.2431.



4n

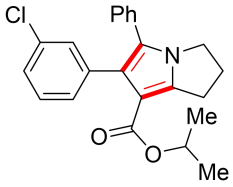
The phtotoredox reaction was performed according to the general procedure using **2o** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4n** was purified by flash column chromatography with PE/EA (10:1) to give **4n** (23.1 mg, 56% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.20-7.13 (m, 3H), 7.01 (dd, J = 7.8, 1.6 Hz, 2H), 4.98 (dt, J = 12.5, 6.2 Hz, 1H), 3.95 (t, J = 7.1 Hz, 2H), 3.15 (t, J = 7.5 Hz, 2H), 2.47 (p, J = 7.3 Hz, 2H), 1.10 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.4, 144.96, 139.5, 131.6, 131.5, 129.4, 128.5, 127.3, 126.0, 128.4-125.9 (m), 125.6, 124.4 (q, J = 3.8 Hz), 123.3, 106.6, 66.5, 47.1, 26.8, 26.5, 22.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -62.25 (s).

HRMS (ESI): calcd for $C_{24}H_{23}F_3NO_2^+$, $(M+H)^+$: 414.1675, found: 414.1667.



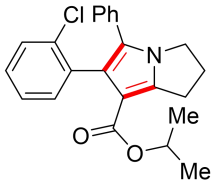
4o

The phtotoredox reaction was performed according to the general procedure using **2p** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4o** was purified by flash column chromatography with PE/EA (10:1) to give **4o** (16.7 mg, 44% yield) as a colorless oil, (20.8 mg, 55% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.12 (m, 4H), 7.11-7.01 (m, 4H), 7.01-6.96 (m, 1H), 4.98 (dt, J = 12.5, 6.2 Hz, 1H), 3.95 (t, J = 7.1 Hz, 2H), 3.15 (t, J = 7.4 Hz, 2H), 2.46 (p, J = 7.3 Hz, 2H), 1.08 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.5, 144.9, 137.7, 133.0, 131.7, 131.5, 129.4, 129.3, 128.6, 128.5, 127.2, 127.2, 126.3, 125.4, 106.8, 66.5, 47.1, 26.7, 26.6, 22.2.

HRMS (ESI): calcd for $C_{23}H_{23}ClNO_2^+$, $(M+H)^+$:380.1412, found: 380.1409.



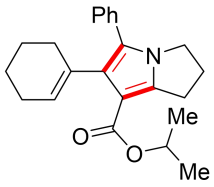
4p

The phtotoredox reaction was performed according to the general procedure using **2q** with CH_3CN as the solvent. The reaction was run for 72 h, the corresponding product **4p** was purified by flash column chromatography with PE/EA (10:1) to give **4p** (20.1 mg, 53% yield) as a colorless oil, (26.1 mg, 69% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37 (dd, J = 7.9, 0.6 Hz, 1H), 7.22 (dd, J = 7.9, 6.3 Hz, 2H), 7.19-7.06 (m, 6H), 5.00 (dt, J = 12.4, 6.2 Hz, 1H), 4.14 (dt, J = 10.7, 7.3 Hz, 1H), 4.01 (dt, J = 10.7, 6.9 Hz, 1H), 3.32-3.12 (m, 2H), 2.56 (p, J = 7.3 Hz, 2H), 1.10 (d, J = 6.2 Hz, 3H), 1.04 (d, J = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.4, 144.5, 135.8, 135.6, 132.7, 131.9, 128.8, 128.6, 128.4, 128.0, 127.1, 126.9, 126.1, 123.9, 107.6, 66.2, 47.2, 26.7, 26.4, 22.1, 21.9.

HRMS (ESI): calcd for $C_{23}H_{23}ClNO_2^+$, $(M+H)^+$:380.1412, found: 380.1417.



4q

The phtotoredox reaction was performed according to the general procedure using **2q** with CH_3CN as the solvent. The reaction was run for 48 h, the corresponding product **4q** was purified by flash column chromatography with PE/EA (10:1) to give **4q** (11.5 mg, 33% yield) as a colorless oil, (15.0 mg, 43% brsm).

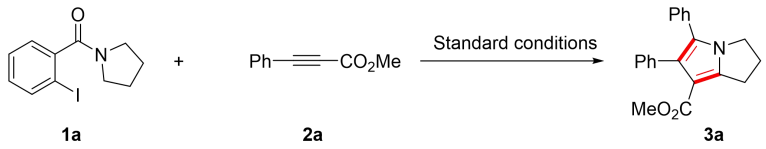
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.33 (t, J = 6.5 Hz, 4H), 7.23 (dd, J = 8.7, 4.4 Hz, 1H), 5.44 (s, 1H), 5.17 (dt, J = 12.5, 6.2 Hz, 1H), 3.97 (t, J = 7.1 Hz, 2H), 3.15 (t, J = 7.4 Hz, 2H), 2.47 (p, J = 7.3 Hz, 2H), 2.26 (d, J = 1.8 Hz, 2H), 2.05-1.95 (m, 2H), 1.74-1.66 (m, 2H), 1.60 (dd, J = 7.4, 3.8 Hz, 2H), 1.29 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.7, 144.4, 132.8, 132.6, 130.0, 128.7, 128.2, 127.2, 126.6, 125.97, 106.6, 66.1, 47.1, 30.7, 29.8, 26.7, 26.5, 25.8, 23.4, 22.5, 22.3.

HRMS (ESI): calcd for $C_{23}H_{28}NO_2^+$, $(M+H)^+$: 350.2115, found: 350.2124.

6. Synthetic applications

a) Gram Scale-up Reaction

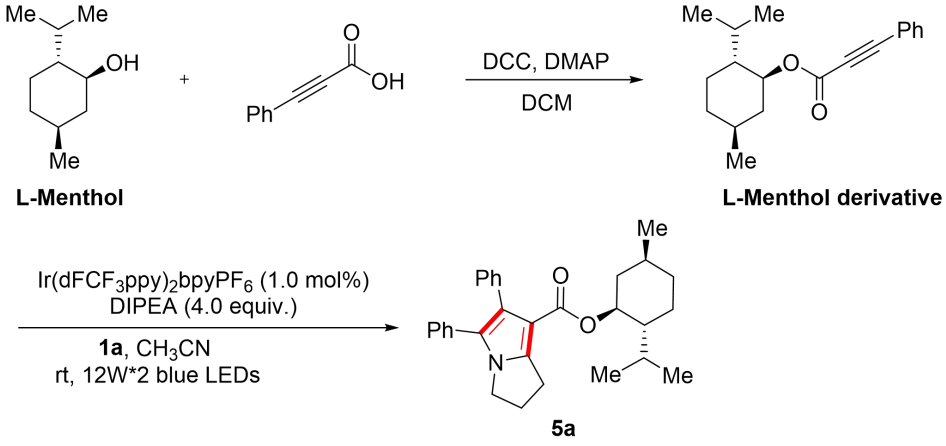


In a sealed tube**,** **1** (2.0 mmol), **2** (4.0 mmol), Ir(dFCF$_3$ppy)$_2$bpyPF$_6$ (1.0 mol %), DIPEA (4.0 mmol) were dissolved in CH_3CN (10.0 mL). The reaction mixture was degassed oxygen with N_2 for three times at -78 °C. Subsequently, the reaction was exposed to 430 nm blue LEDs at room temperature until **1a** was completely consumed. When the reaction finished, the solvent was removed under vacuum, the residue was purified by flash column chromatography on silica gel with a eluent of ethyl acetate (EA) and petroleum ether (PE) to provide the corresponding product **3a** in 53% yield.

b) Late-stage modification of complex molecules

Synthesis of 5a:

Synthesis of substrate L-Menthol derivative: L-Menthol (312 mg, 2.0 mmol), DMAP (244 mg, 2 mmol) were added in DCM (20 mL) at room temperature and then stirring overnight at the same temperature. 20 ml saturated NH_4Cl was added to the reaction system when the starting material was completely consumed, extracted with EA (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to provide the L-Menthol derivative.



Characterization data of L-Menthol derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.64-7.55 (m, 2H), 7.50-7.41 (m, 1H), 7.36 (dd, J = 11.5, 4.4 Hz, 2H), 4.85 (td, J = 10.9, 4.4 Hz, 1H), 2.14-2.03 (m, 1H), 1.97 (dtd, J = 13.9, 7.0, 2.6 Hz, 1H), 1.75-1.65 (m, 2H), 1.56-1.42 (m, 2H), 1.16-1.01 (m, 2H), 0.89 (ddd, J = 15.7, 9.3, 2.0 Hz, 7H), 0.80 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 153.9, 133.1, 130.6, 128.7, 119.9, 85.98, 81.1, 76.5, 47.0, 40.8, 34.3, 31.6, 26.3, 23.5, 22.1, 20.9, 16.4.

Photoredox reaction: In a dried sealed tube**,** **1a** (0.2 mmol), L-Menthol derivative (0.1 mmol),

$Ir(dFCF_3ppy)_2bpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 ºC. Subsequently, the reaction mixture was exposed to blue LEDs (425-430 nm, 10 W) at room temperature. The reaction finished when the starting materials was completely consumed (monitored by TLC). The residue was purified by flash column chromatography on silica gel with a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the corresponding product **5a**.

Characterization data of 5a:

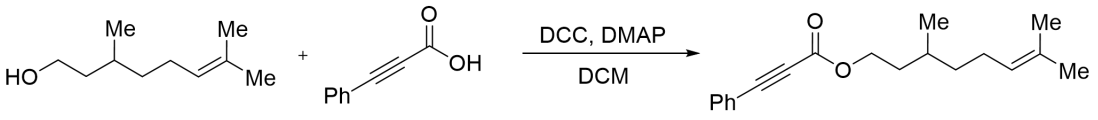
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25 - 7.14 (m, 8H), 7.14-7.05 (m, 2H), 4.69 (td, J = 10.7, 4.3 Hz, 1H), 4.03 (tdd, J = 14.4, 9.0, 5.4 Hz, 2H), 3.33-3.14 (m, 2H), 2.54 (p, J = 7.3 Hz, 2H), 2.08 (d, J = 11.6 Hz, 1H), 1.97-1.86 (m, 1H), 1.80-1.73 (m, 1H), 1.67 (d, J = 11.4 Hz, 1H), 1.59 (d, J = 3.1 Hz, 1H), 1.43 (dd, J = 7.7, 4.4 Hz, 1H), 1.25 (d, J = 5.4 Hz, 1H), 1.12 (dd, J = 8.2, 5.2 Hz, 1H), 1.03-0.95 (m, 1H), 0.87 (d, J = 6.5 Hz, 3H), 0.79 (d, J = 7.0 Hz, 3H), 0.68 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.6, 144.7, 135.7, 132.1, 131.3, 129.3, 128.3, 127.4, 127.2, 127.0, 126.8, 126.2, 106.8, 72.8, 47.3, 47.1, 41.5, 34.5, 31.5, 26.8, 26.5, 25.99, 23.3, 22.2, 21.1, 16.3.

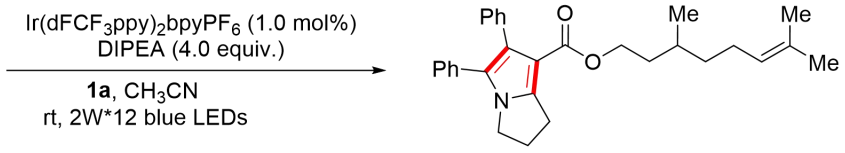
HRMS (ESI): calcd for $C_{30}H_{36}NO_2^+$, $(M+H)^+$: 442.2741, found: 442.2750.

Synthesis of 5b:

Synthesis of substrate Citronellol derivative: Citronellol (312 mg, 2.0 mmol), DMAP (244 mg, 2 mmol) were added in DCM (20 mL) at room temperature and then stirring overnight at the same temperature. 20 ml saturated NH_4Cl was added to the reaction system when the starting material was completely consumed, extracted with EA (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel with a eluent of ethyl acetate (EA) and petroleum ether (PE) to provide the corresponding substrate.



Citronellol Citronellol derivative



5b

Characterization data of Citronellol derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.58 (dd, J = 5.2, 3.2 Hz, 2H), 7.45 (ddd, J = 6.6, 3.8, 1.3 Hz, 1H), 7.40 - 7.32 (m, 2H), 5.10 (ddd, J = 7.1, 5.8, 1.3 Hz, 1H), 4.38-4.16 (m, 2H), 2.14 - 1.88 (m, 2H), 1.81-1.72 (m, 1H), 1.69 (s, 3H), 1.65-1.58 (m, 4H), 1.56-1.45 (m, 1H), 1.43-1.31 (m, 1H), 1.27-1.17 (m, 1H), 0.94 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 154.4, 133.1, 131.6, 130.7, 128.7, 124.6, 119.9, 86.2, 80.9, 64.8, 37.1, 35.4, 29.5, 25.9, 25.5, 19.5, 17.8.

Photoredox reaction: In a dried sealed tube**,** **1a** (0.2 mmol), L-Menthol derivative (0.1 mmol),

$Ir(dFCF_3ppy)_2bpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 ºC. Subsequently, the reaction mixture was exposed to blue LEDs (425-430 nm, 10 W) at room temperature. The reaction finished when the starting materials was completely consumed (monitored by TLC). The residue was purified by flash column chromatography on silica gel with a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the corresponding products.

Characterization data of 5b:

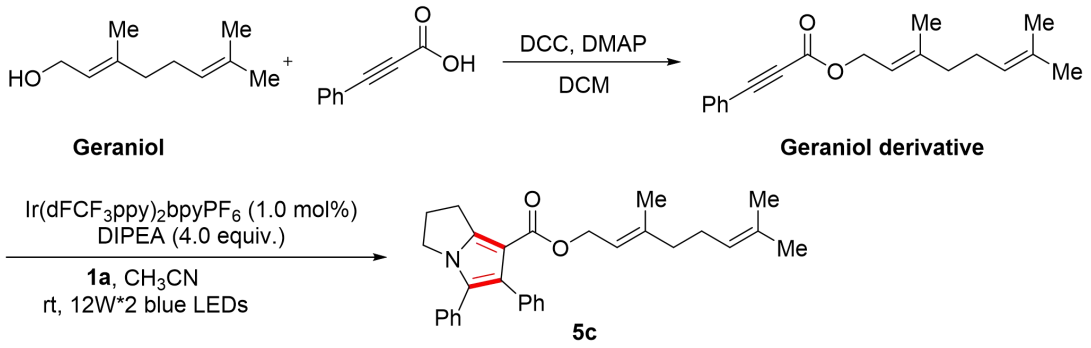
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.17-7.07 (m, 8H), 7.06-6.99 (m, 2H), 5.00 (t, J = 7.1 Hz, 1H), 4.14 – 4.00 (m, 2H), 3.97 (t, J = 7.1 Hz, 2H), 3.15 (t, J = 7.4 Hz, 2H), 2.47 (p, J = 7.3 Hz, 2H), 1.95-1.74 (m, 2H), 1.60 (s, 3H), 1.52 (s, 3H), 1.53-1.45 (m, 1H), 1.35 (dd, J = 12.6, 6.1 Hz, 1H), 1.25 (d, J = 6.7 Hz, 1H), 1.21-1.17 (m, 1H), 1.09-0.98 (m, 1H), 0.76 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.2, 144.7, 135.6, 132.1, 131.3, 131.2, 129.3, 128.3, 127.5, 127.2, 127.1, 126.9, 126.3, 124.93, 106.4, 61.7, 47.2, 37.2, 35.8, 29.4, 26.8, 26.6, 25.9, 25.5, 19.3, 17.8.

HRMS (ESI): calcd for $C_{30}H_{36}NO_2^+$, $(M+H)^+$: 442..2741, found: 442.2739.

Synthesis of 5c:

Synthesis of substrate Geraniol derivative: Geraniol (308 mg, 2.0 mmol), DMAP (244 mg, 2 mmol) were added in DCM (20 mL) at room temperature and then stirring overnight at the same temperature. 20 ml saturated NH_4Cl was added to the reaction system when the starting material was completely consumed, extracted with EA (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to provide the Geraniol derivative.



Characterization data of Geraniol derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62-7.50 (m, 2H), 7.41 (ddd, J = 6.5, 3.8, 1.3 Hz, 1H), 7.37-7.29 (m, 2H), 5.41 (td, J = 7.2, 1.1 Hz, 1H), 5.14-5.02 (m, 1H), 4.74 (d, J = 7.3 Hz, 2H), 2.22-1.99 (m, 4H), 1.73 (s, 3H), 1.67 (s, 3H), 1.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 154.0, 143.5, 132.9, 131.9, 130.6, 128.6, 123.7, 119.7, 117.5, 86.1, 80.8, 62.8, 39.5, 26.3, 25.7, 17.7, 16.5.

Photoredox reaction: In a dried sealed tube**, 1a** (0.2 mmol), Geraniol derivative (0.1 mmol), $Ir(dFCF_3ppy)_2bpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 ºC. Subsequently, the reaction mixture was exposed to blue LEDs (425-430 nm, 10 W) at room temperature. The reaction finished when the starting materials was completely consumed (monitored by TLC). The residue was purified

by flash column chromatography on silica gel with a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the corresponding product **5c**.

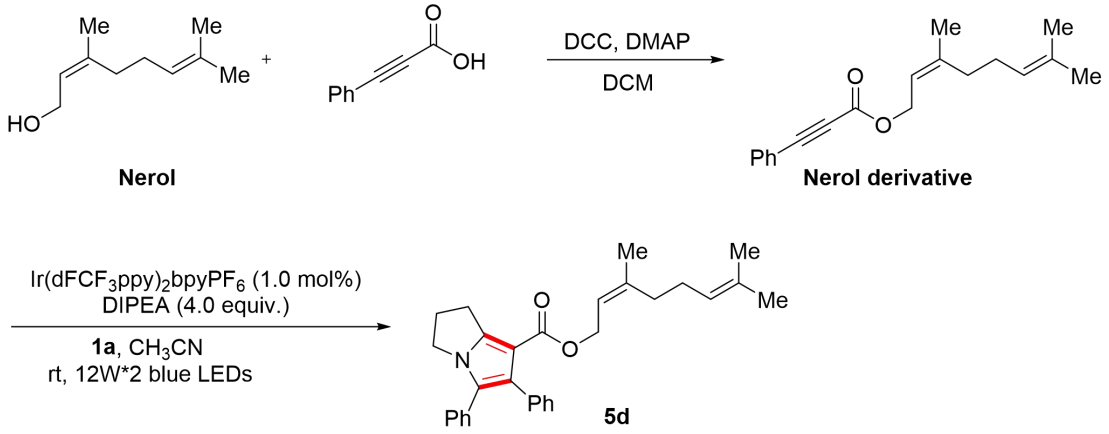
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.17-7.07 (m, 8H), 7.06-7.00 (m, 2H), 5.31-5.15 (m, 1H), 5.02 (dd, *J* = 9.5, 4.0 Hz, 1H), 4.54 (d, *J* = 6.8 Hz, 2H), 3.96 (t, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 7.4 Hz, 2H), 2.46 (p, *J* = 7.3 Hz, 2H), 2.01 (dd, *J* = 15.1, 6.7 Hz, 2H), 1.92 (dd, *J* = 12.7, 7.5 Hz, 2H), 1.61 (s, 3H), 1.57 (s, 3H), 1.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.1, 144.8, 140.98, 135.5, 132.2, 131.8, 131.2, 129.4, 128.3, 127.5, 127.3, 127.1, 126.9, 126.2, 124.1, 119.4, 106.4, 60.3, 47.2, 39.6, 26.8, 26.6, 26.5, 25.8, 17.8, 16.6.

HRMS (ESI): calcd for $C_{30}H_{33}NNaO_2^+$, $(M+Na)^+$: 462.2404, found: 462.2411.

Synthesis of 5d:

Synthesis of substrate Nerol derivative: Nerol (308 mg, 2.0 mmol), DMAP (244 mg, 2 mmol) were added in DCM (20 mL) at room temperature and then stirring overnight at the same temperature. 20 ml saturated NH_4Cl was added to the reaction system when the starting material was completely consumed, extracted with EA (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to provide the Nerol derivative.



Characterization data of Nerol derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61-7.51 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 5.43 (t, *J* = 7.3 Hz, 1H), 5.11 (t, *J* = 6.3 Hz, 1H), 4.72 (d, *J* = 7.4 Hz, 2H), 2.21-2.04 (m, 4H), 1.79 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 154.2, 144.0, 133.1, 132.5, 130.7, 128.7, 123.6, 119.9, 118.4, 86.2, 80.8, 62.7, 32.3, 26.7, 25.8, 23.7, 17.8.

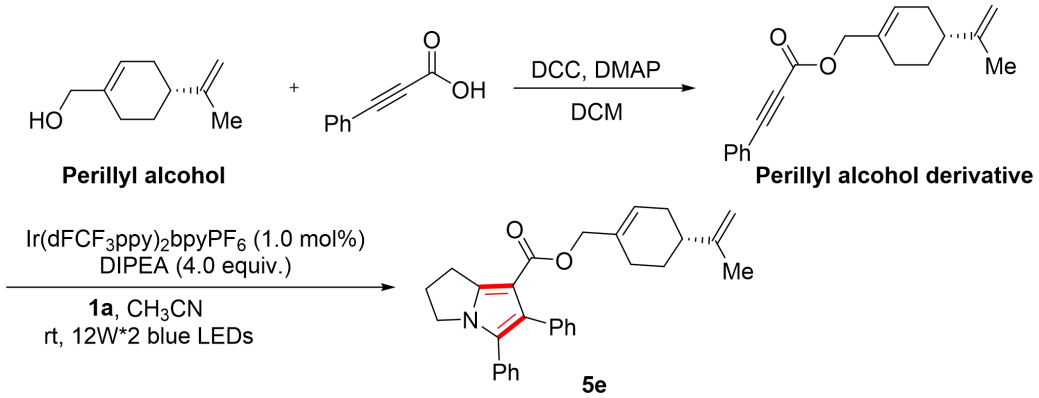
Photoredox reaction: In a dried sealed tube**,** **1a** (0.2 mmol), Nerol derivative (0.1 mmol), $Ir(dFCF_3ppy)_2bpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. Subsequently, the reaction mixture was exposed to blue LEDs (425-430 nm, 10 W) at room temperature. The reaction finished when the starting materials was completely consumed (monitored by TLC). The residue was purified by flash column chromatography on silica gel with a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the corresponding product **5d**.

Characterization data of 5d:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.15 (m, 8H), 7.14-7.08 (m, 2H), 5.30 (dd, J = 7.0, 5.9 Hz, 1H), 5.14-5.01 (m, 1H), 4.60 (d, J = 7.0 Hz, 2H), 4.03 (t, J = 7.1 Hz, 2H), 3.22 (t, J = 7.4 Hz, 2H), 2.58-2.47 (m, 2H), 2.10-2.01 (m, 4H), 1.73 (d, J = 1.0 Hz, 3H), 1.66 (s, 3H), 1.58 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.0, 144.8, 141.0, 135.5, 132.1, 132.1, 131.2, 129.3, 128.3, 127.5, 127.3, 127.0, 126.8, 126.2, 123.9, 120.3, 106.3, 60.1, 47.2, 32.31, 26.8, 26.8, 26.5, 25.8, 23.6, 17.8.
HRMS (ESI): calcd for $C_{30}H_{33}NNaO_2^+$, $(M+Na)^+$: 462.2404, found: 462.2401.

Synthesis of 5e:

Synthesis of substrate Perillyl alcohol derivative: Perillyl alcohol (312 mg, 2.0 mmol), DMAP (244 mg, 2 mmol) were added in DCM (20 mL) at room temperature and then stirring overnight at the same temperature. 20 ml saturated NH_4Cl was added to the reaction system when the starting material was completely consumed, extracted with EA (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to provide the corresponding substrate.



Characterization data of Perillyl alcohol derivative:
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 (dd, J = 5.2, 3.3 Hz, 2H), 7.39-7.31 (m, 1H), 7.30-7.22 (m, 2H), 5.75 (s, 1H), 4.70-4.60 (m, 2H), 4.53 (s, 2H), 2.16- 2.01 (m, 4H), 1.96-1.84 (m, 1H), 1.82- 1.72 (m, 1H), 1.65 (s, 3H), 1.42 (tt, J = 12.6, 8.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 154.0, 149.4, 133.0, 131.9, 130.7, 128.6, 127.2, 119.7, 108.9, 86.3, 80.7, 70.0, 40.7, 30.5, 27.3, 26.5, 20.8.

Photoredox reaction: In a dried sealed tube**, 1a** (0.2 mmol), Perillyl alcohol derivative (0.1 mmol), $Ir(dFCF_3ppy)_2bpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. Subsequently, the reaction mixture was exposed to blue LEDs (425-430 nm, 10 W) at room temperature. The reaction finished when the starting materials was completely consumed (monitored by TLC). The residue was purified by flash column chromatography on silica gel with a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the corresponding product **5e**.

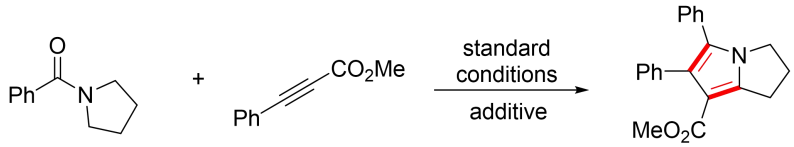
Characterization data of 5e:
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.14 (m, 8H), 7.13-7.07 (m, 2H), 5.59 (d, J = 3.1 Hz, 1H), 4.73 -4.63 (m, 2H), 4.55-4.43 (m, 2H), 4.04 (t, J = 7.1 Hz, 2H), 3.24 (t, J = 7.5 Hz, 2H), 2.61-2.45 (m, 2H), 2.09 (dt, J = 12.5, 7.3 Hz, 2H), 1.97-1.85 (m, 3H), 1.80-1.71 (m, 4H), 1.40 (ddd, J = 20.2, 12.4, 8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.0, 150.0, 144.9, 135.7, 133.3, 132.1, 131.2, 129.3, 128.3, 127.5, 127.3, 127.1, 126.9, 126.3, 124.6, 108.7, 106.3, 67.5, 47.2, 41.1, 30.6, 27.6, 26.8, 26.6, 26.5, 20.9.
HRMS (ESI): calcd for $C_{30}H_{32}NO_2^+$, $(M+H)^+$: 438.2428, found: 438.2427.

7. Mechanistic Studies

a) Control experiment

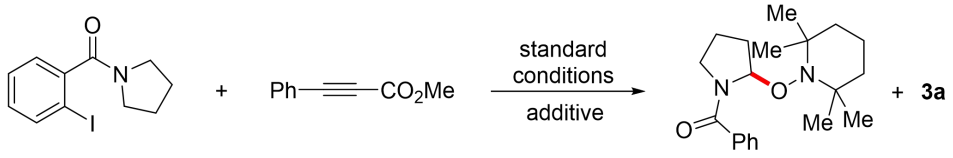
To illustrate the mechanism, control experiment was performed: In a dried sealed tube, **6** (0.1 mmol), **ethyl acrylate** (0.2 mmol), Ir(dFCF$_3$ppy)$_2$bpyPF$_6$ (1.0 mol %), DIPEA (0.4 mmol) were dissolved in CH$_3$CN (1.0 mL). The reaction was caped and degassed oxygen with N$_2$ for three times at -78 °C. Subsequently, the reaction flask was exposed to 425-430 nm blue leds. After 24 hours, the mixture was extracted with DCM (5 mL*3). The combined solvent were dried over Na$_2$SO$_4$, filtered,and detected with GC, there was no desired product **3a** detected, which demonstrate the activation of C-I bond are crucial to the successful transformation of the procedure.



6 **2a** **3a**

b) Radical inhibition experiments

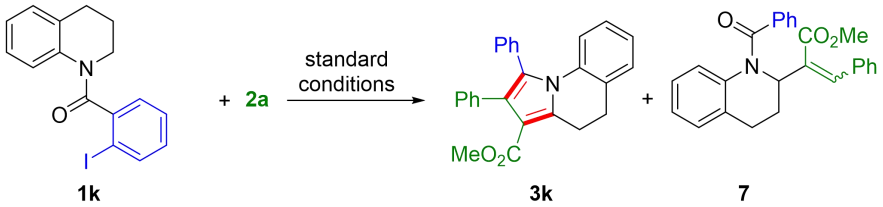
In a dried sealed tube, **1a** (0.1 mmol), **2a** (0.2 mmol), Ir(dFCF$_3$ppy)$_2$bpyPF$_6$ (1.0 mol %), DIPEA (0.4 mmol), TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (0.2 mmol) were dissolved in CH$_3$CN (1.0 mL). The reaction was degassed with N$_2$ for three times at -78 °C. Subsequently, the reaction flask was exposed to 425-430 nm blue LEDs at room temperature. 36 hours later, the reaction was stopped, **3a** was isolated in 8% yield and there was no other radical product isolated from the reaction mixture. The yield was obviously decreased to 8%, which indicate this transformation was radical involved through a single-electron transfer process.

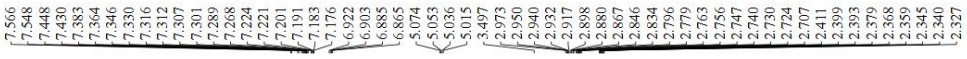


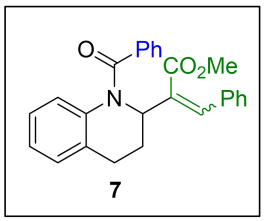
1a **2a** **3a′**

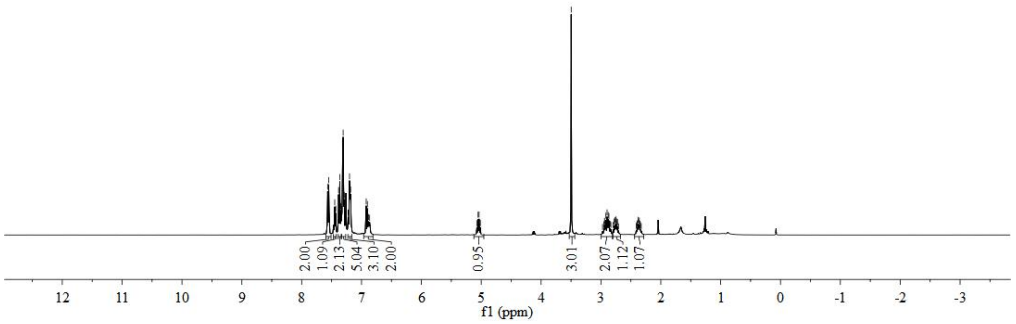
c) Radical addition procedure

To illustrate the mechanism, the radical addition experiment was conducted: In a dried sealed tube, **1k** (0.1 mmol), **2a** (0.2 mmol), Ir(dFCF$_3$ppy)$_2$bpyPF$_6$ (1.0 mol %), DIPEA (0.4 mmol) were dissolved in CH$_3$CN (1.0 mL). The flask was caped and degassed oxygen with N$_2$ for three times at -78 °C. Subsequently, the reaction flask was exposed to 425-430 nm blue leds until the starting material completely consumed and quenched with 4 mL saturated NH$_4$Cl. The mixture was extracted with DCM (5 mL*3). The combined solvent were dried over Na$_2$SO$_4$ and filtered. The filtrate was concentrated and purification by chromatography on silica gel with a eluent of petroleum ether (PE) and ethyl acetate (EA) to afford the alkylation product **3k** in 58% yield, and the radical addition product **7** was also isolated in 17% yield. **^{1}H NMR (400 MHz, CDCl$_3$) of** 7: δ_H 7.56 (d, J = 7.3 Hz, 2H), 7.44 (d, J = 7.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.33-7.27 (m, 5H), 7.23-7.17 (m, 3H), 6.89 (dd, J = 15.0, 7.9 Hz, 2H), 5.04 (dd, J = 15.1, 8.4 Hz, 1H), 3.50 (s, 3H), 3.01-2.82 (m, 2H), 2.74 (ddd, J = 13.5, 9.1, 6.6 Hz, 1H), 2.46-2.30 (m, 1H).



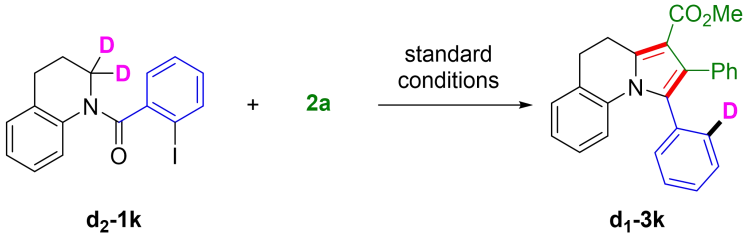


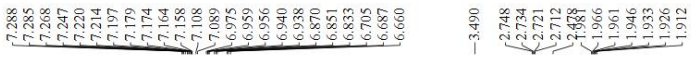




d) Deuterium labeling experiment to rule out 1,5-HAT of intermolecular

To illustrate the mechanism, the radical addition experiment was conducted: In a dried sealed tube, **d_2-1k** (0.1 mmol), **2a** (0.2 mmol), $Ir(dFCF_3ppy)_2bpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 ^oC. Subsequently, the reaction flask was exposed to 425-430 nm blue leds until the starting material completely consumed and quenched with 4 mL saturated NH_4Cl. The mixture was extracted with DCM (5 mL*3). The combined solvent were dried over Na_2SO_4 and filtered. The filtrate was concentrated and purification by chromatography on silica gel with a eluent of petroleum ether (PE) and ethyl acetate (EA) to afford the alkylation product **d_1-3k** in 49% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 11.8, 4.7 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.24 (dd, J = 6.1, 2.3 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.81 – 6.70 (m, 1H), 3.56 (s, 1H), 2.80 (dd, J = 10.1, 4.7 Hz, 1H), 2.64 – 2.49 (m, 1H), 2.06 – 1.94 (m, 1H)

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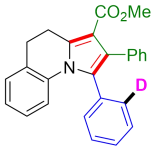
1.912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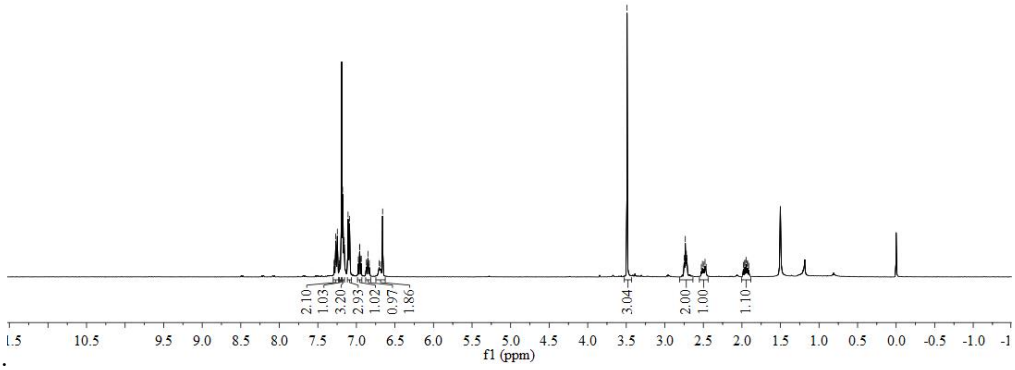
Ph
D
N

d_1-3k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3.20
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1.02
0.97
1.86
3.04
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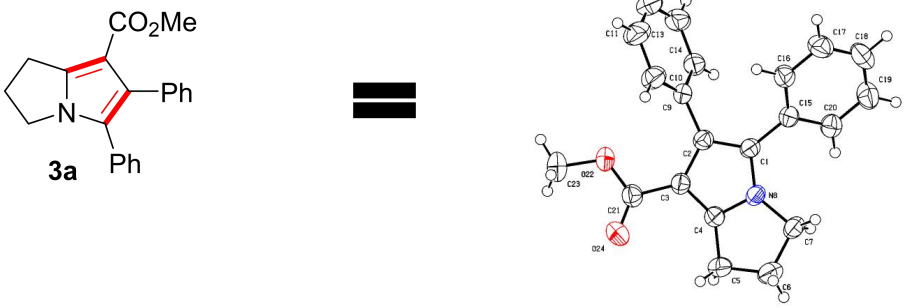
1.00
1.10
f1 (ppm)

8. Reference

1. S. Sarkar, W. Sidhant, X. Jia, V. Gevorgyan, *Chem* **2022**, *8*, 3096-3108.
2. R. Guo, H. Xiao, S. Li, Y. Luo, J. Bai, M. Zhang, Y. Guo, X. Qi, G. Zhang, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202208232.
3. J. B. McManus, N. P. R. Onuska, D. A. Nicewicz, *J. Am. Chem. Soc.*, **2018**, *140*, 9056-9060.
4. Z. Han, G. Liu, X. Zhang, A. Li, X. Dong, X. Zhang. *Org. Lett.* **2019**, *21*, 3923-3926.

9. The crystallographic data



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	Calculated		Reported
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Space group	C c		C c
Hall group	C -2yc		C -2yc
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Sum formula	C21 H19 N O2		C21 H19 N O2
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Dx,g cm-3	1.266		1.266
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F000'	673.94		673.94
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Tmin'			
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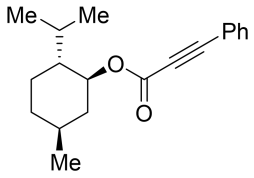
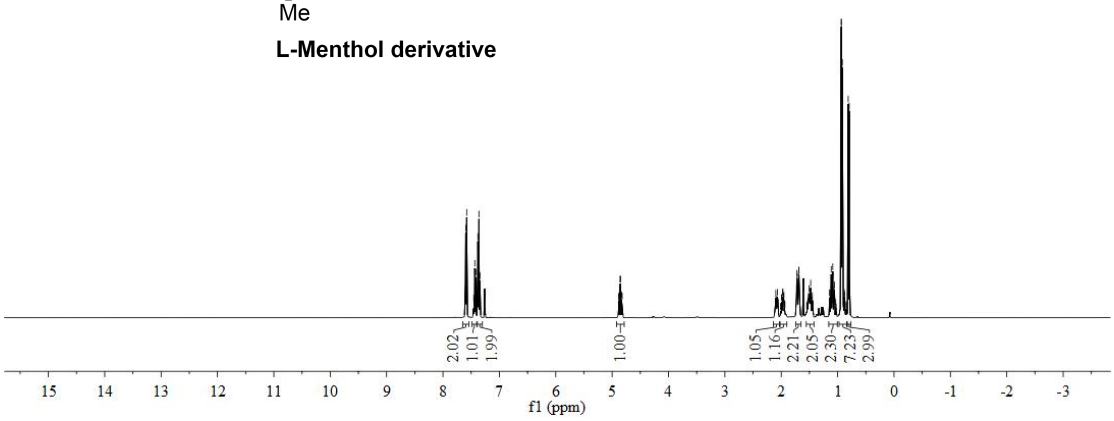
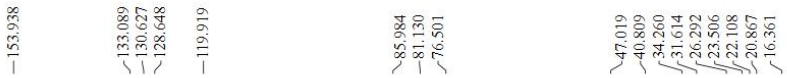
10. Spectra for Substrates and Products Product Characterization

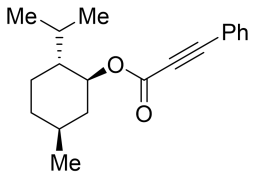
L-Menthol derivative, $^{1}H+^{13}C$ NMR



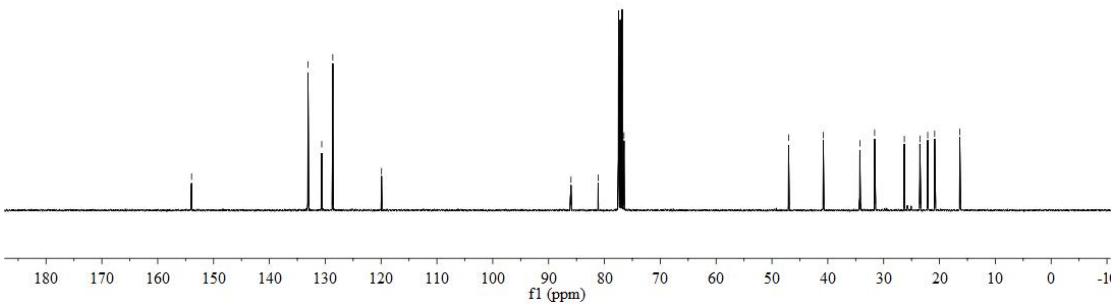
L-Menthol derivative



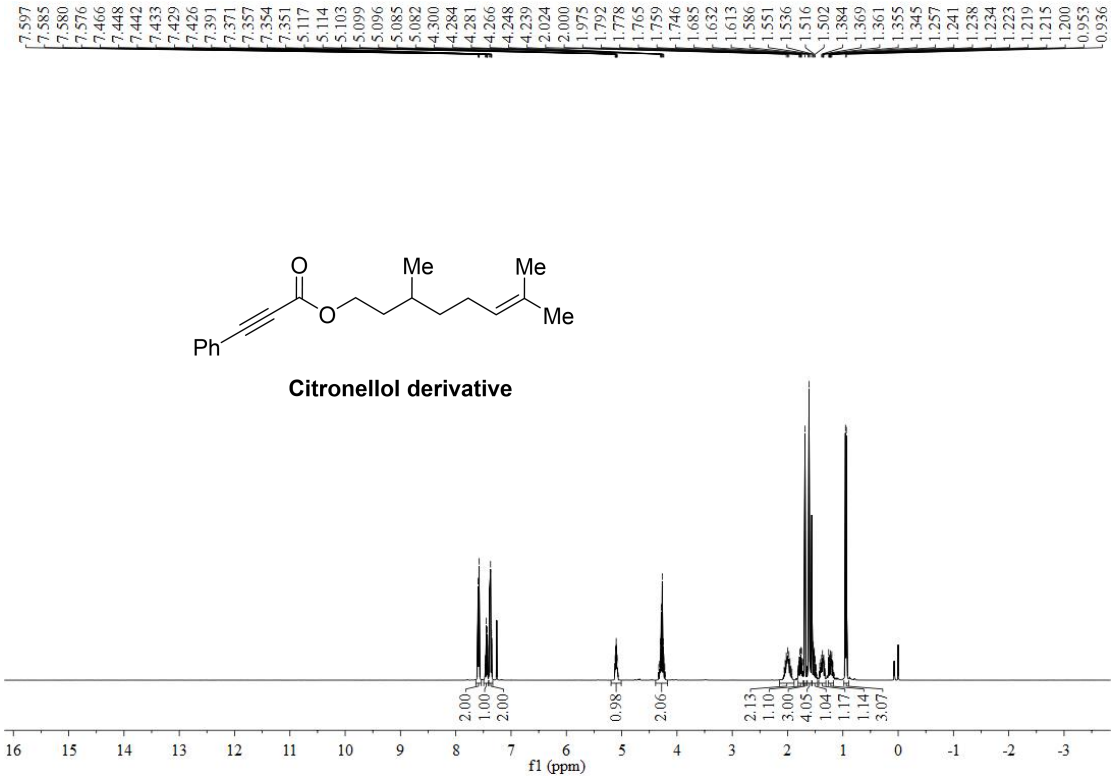


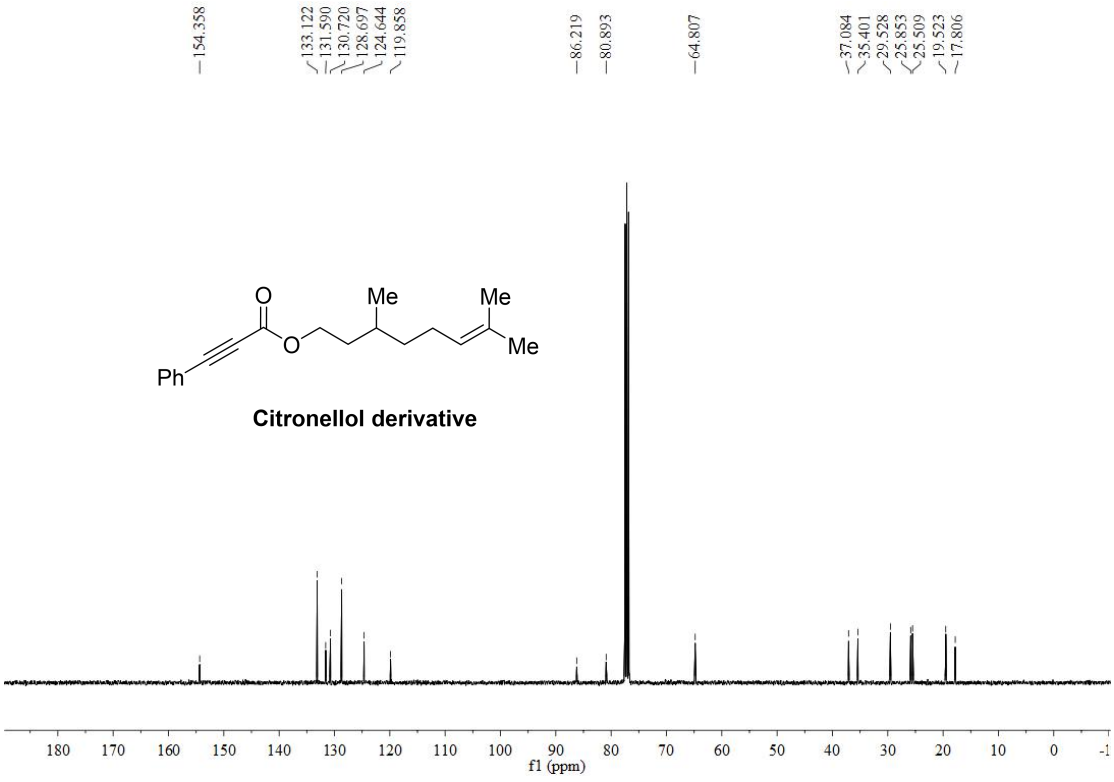


L-Menthol derivative

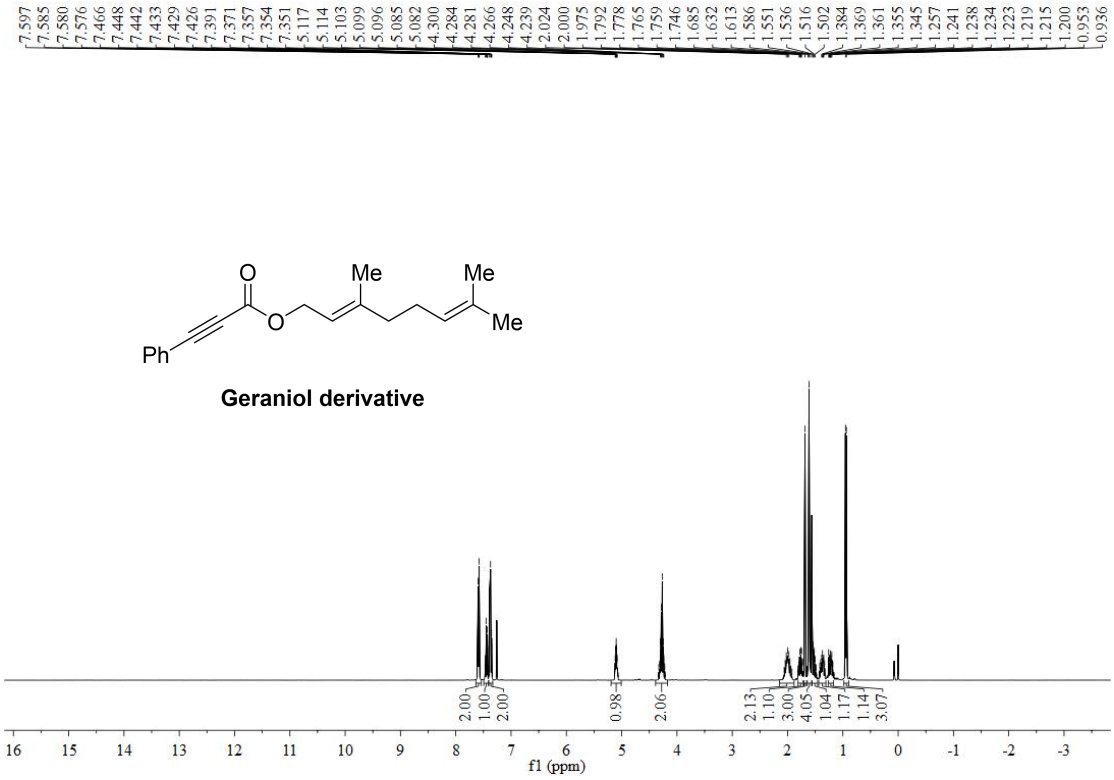


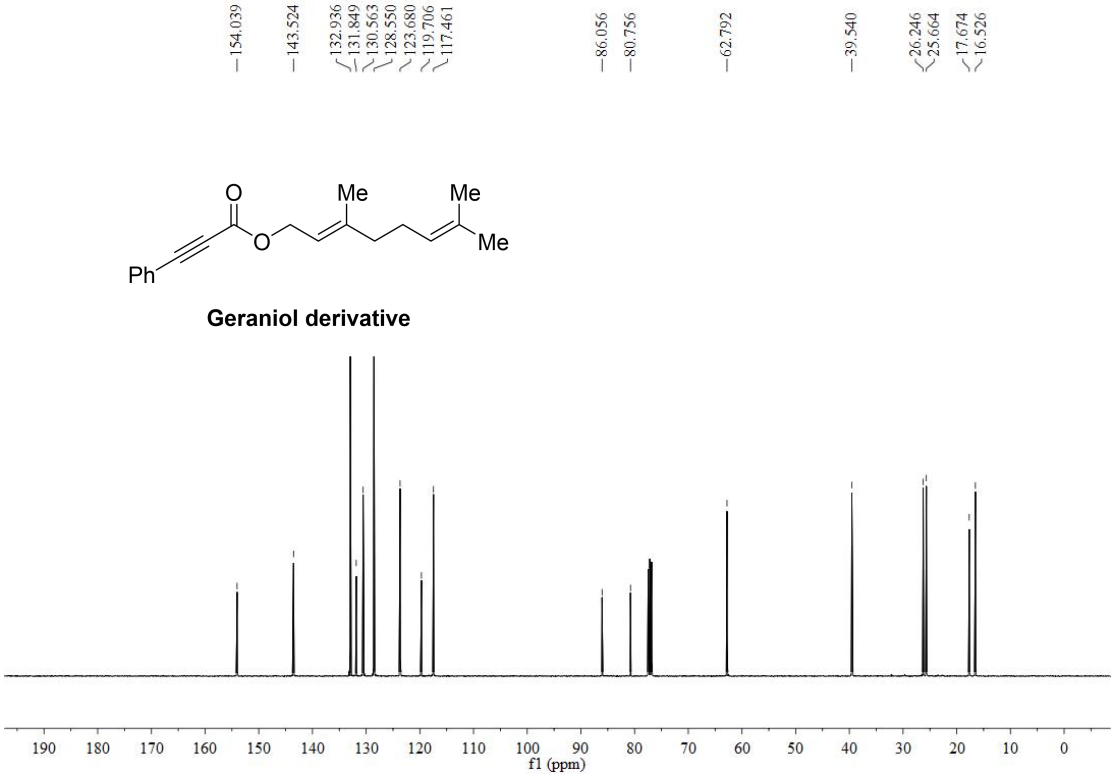
Citronellol derivative, $^{1}H+^{13}C$ NMR



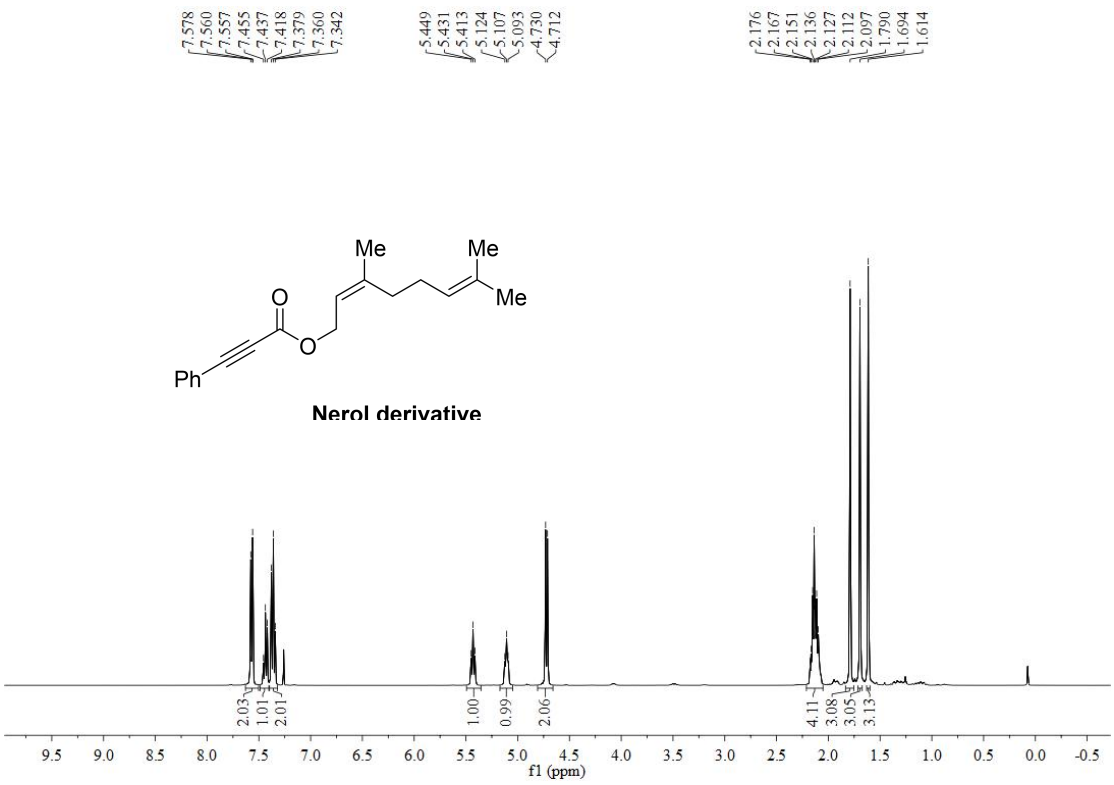


Geraniol derivative, $^{1}H+^{13}C$ NMR

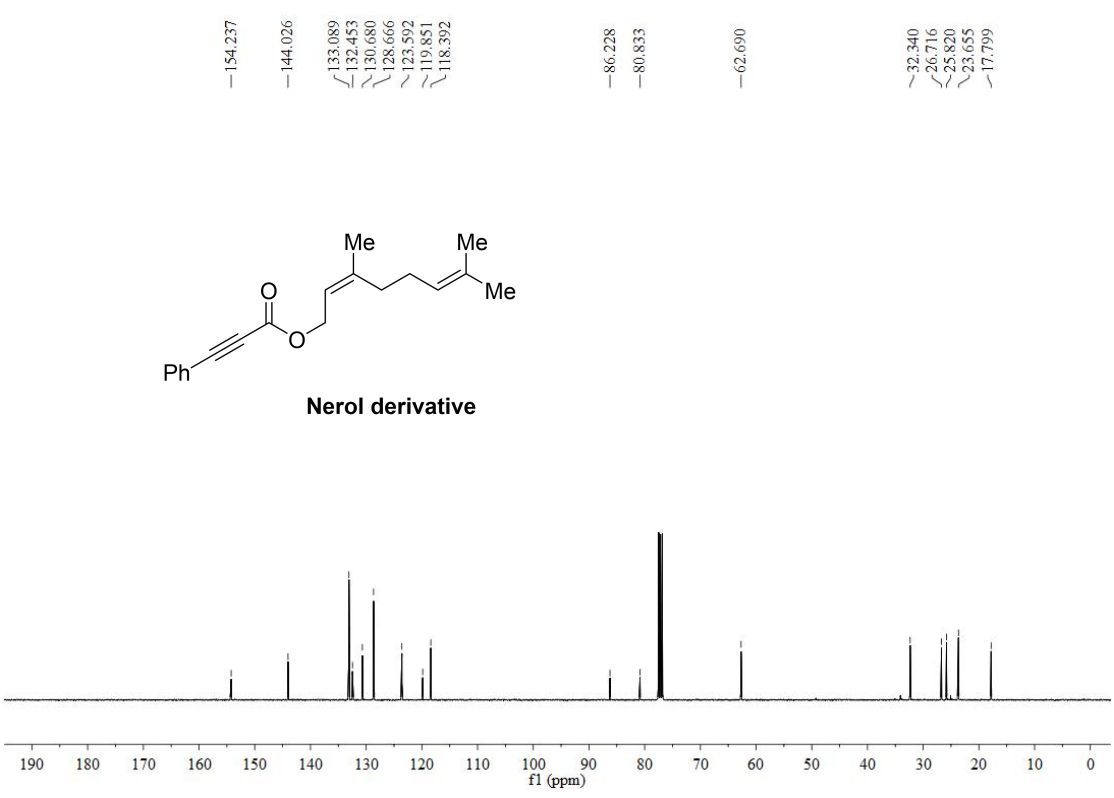




Nerol derivative, $^{1}H+^{13}C$ NMR

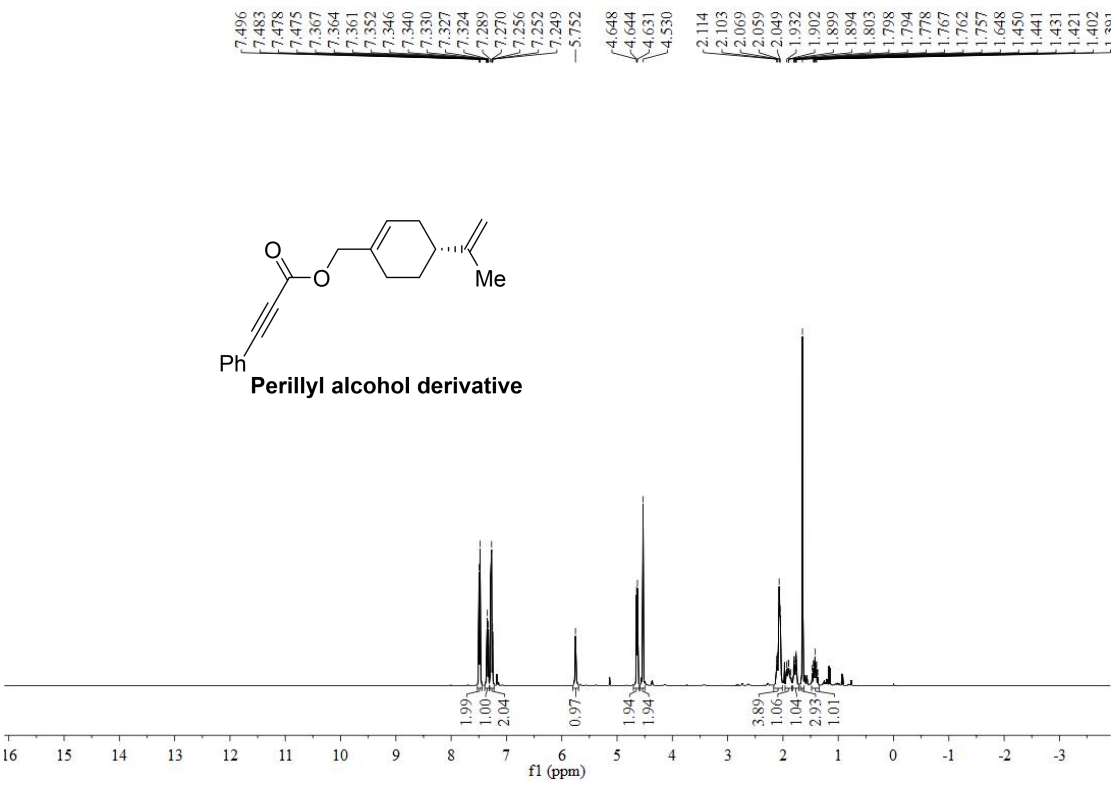


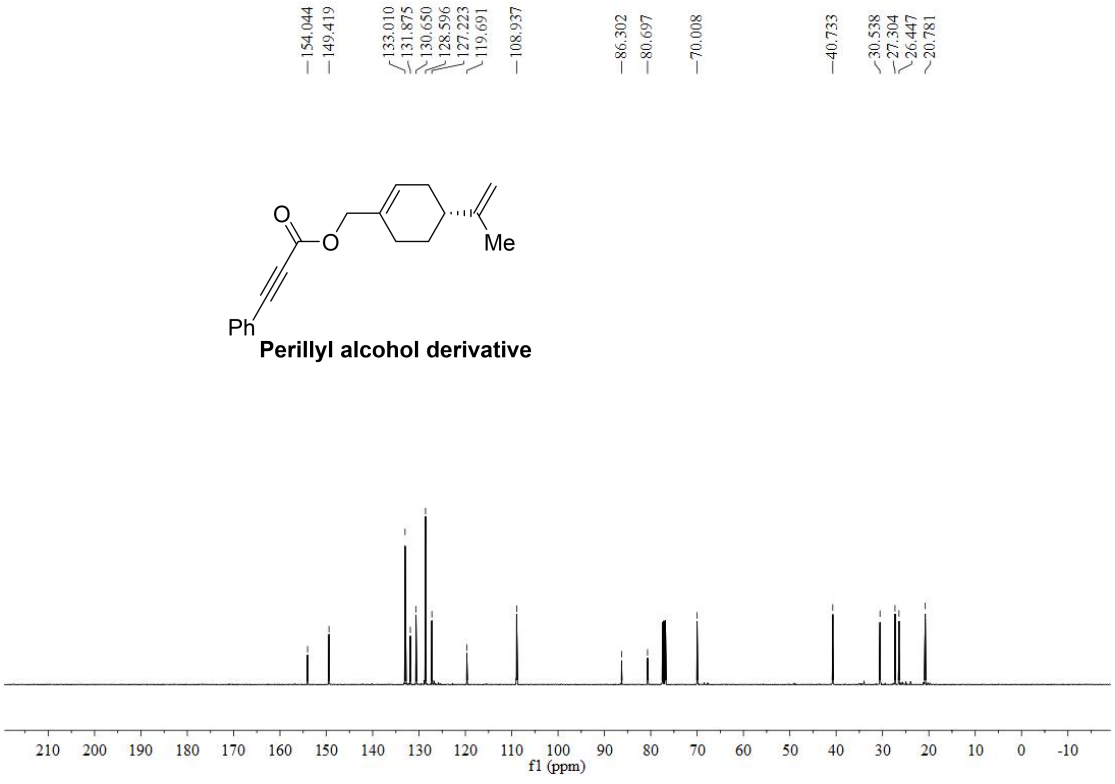
Nerol derivative



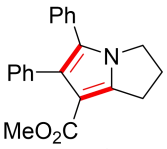
Nerol derivative

Perillyl alcohol derivative, $^{1}H+^{13}C$ NMR





3a, $^{1}H+^{13}C$ NMR



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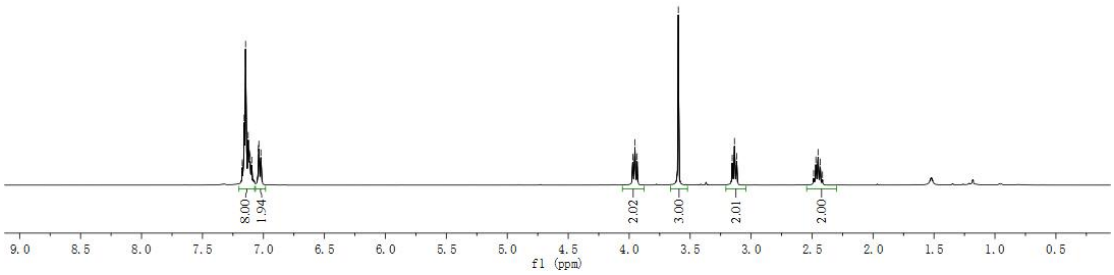

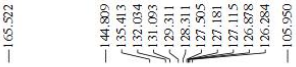

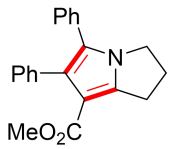

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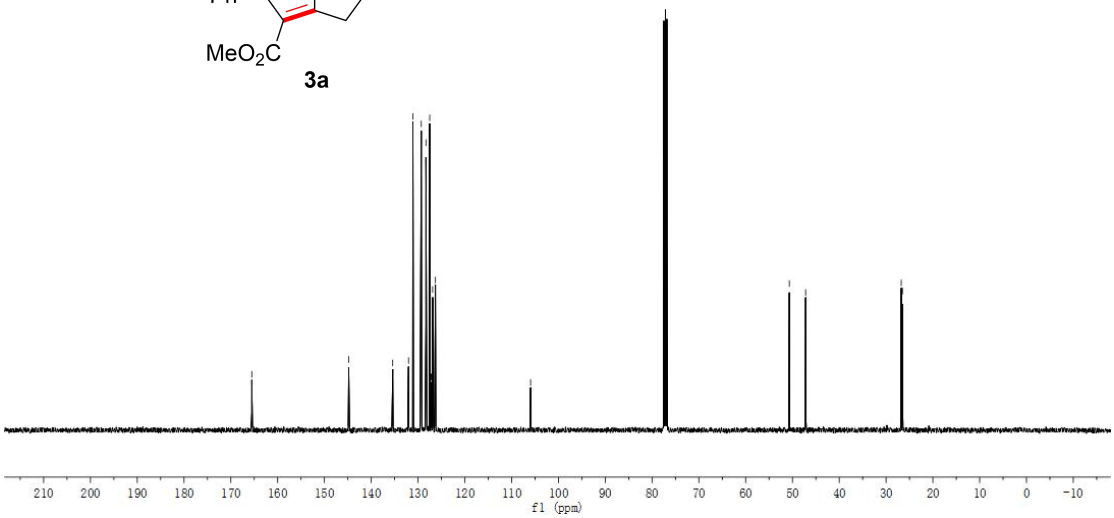
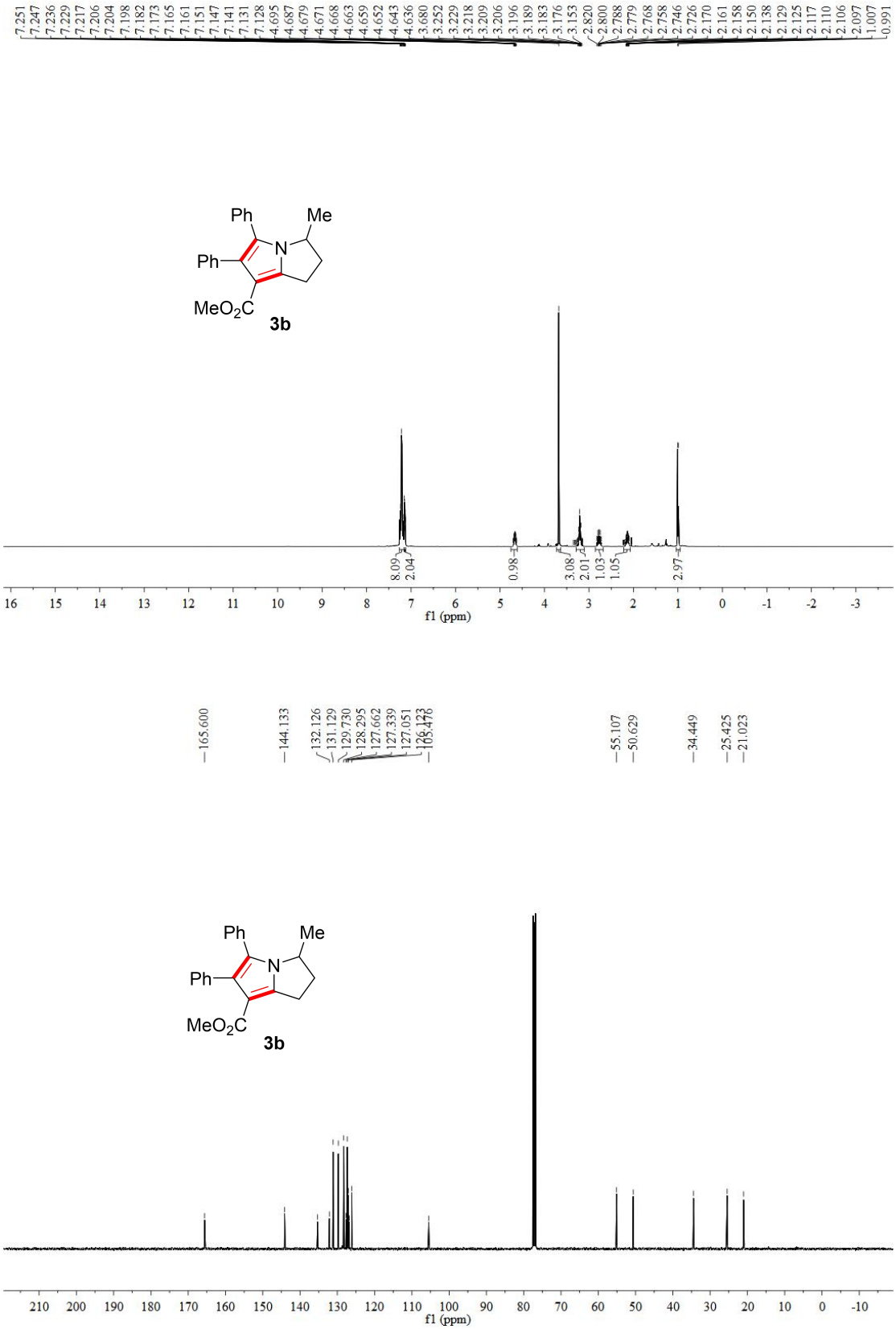


3b, $^{1}H+^{13}C$ NMR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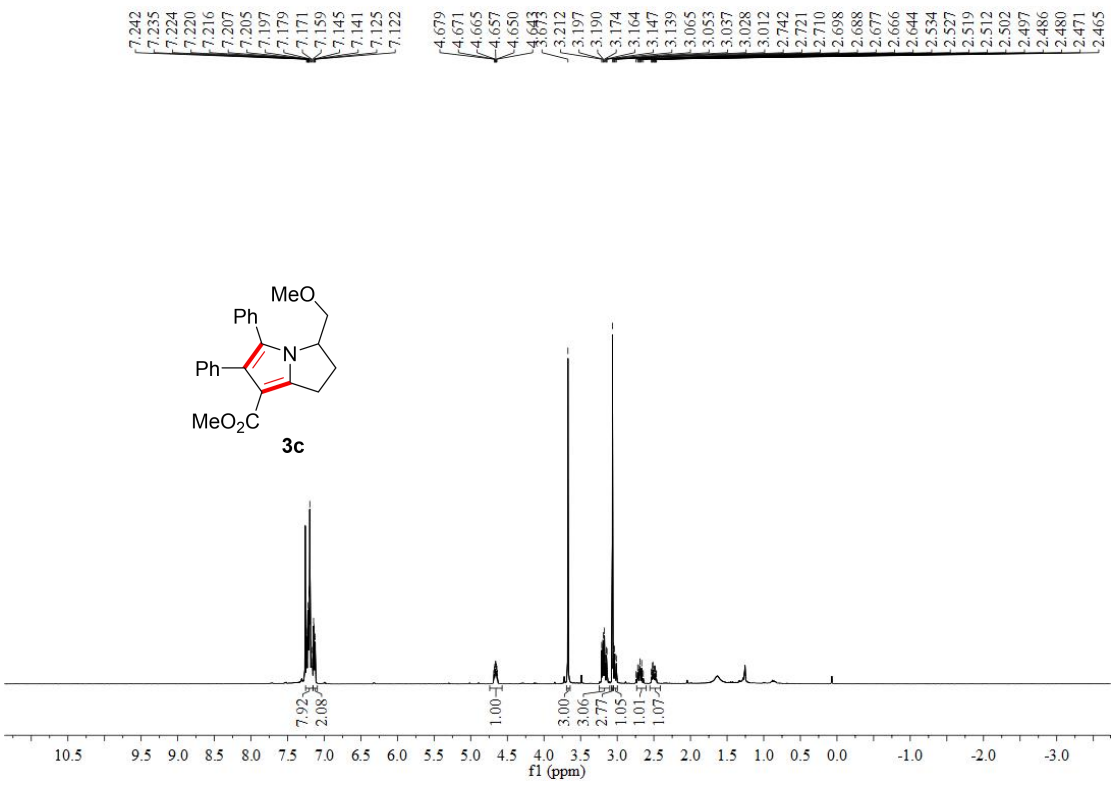
127.051
55.107
50.629
34.449
25.425
21.023
Ph
Me
N
Ph
MeO2C
3b
f1 (ppm)

3c, $^{1}H+^{13}C$ NMR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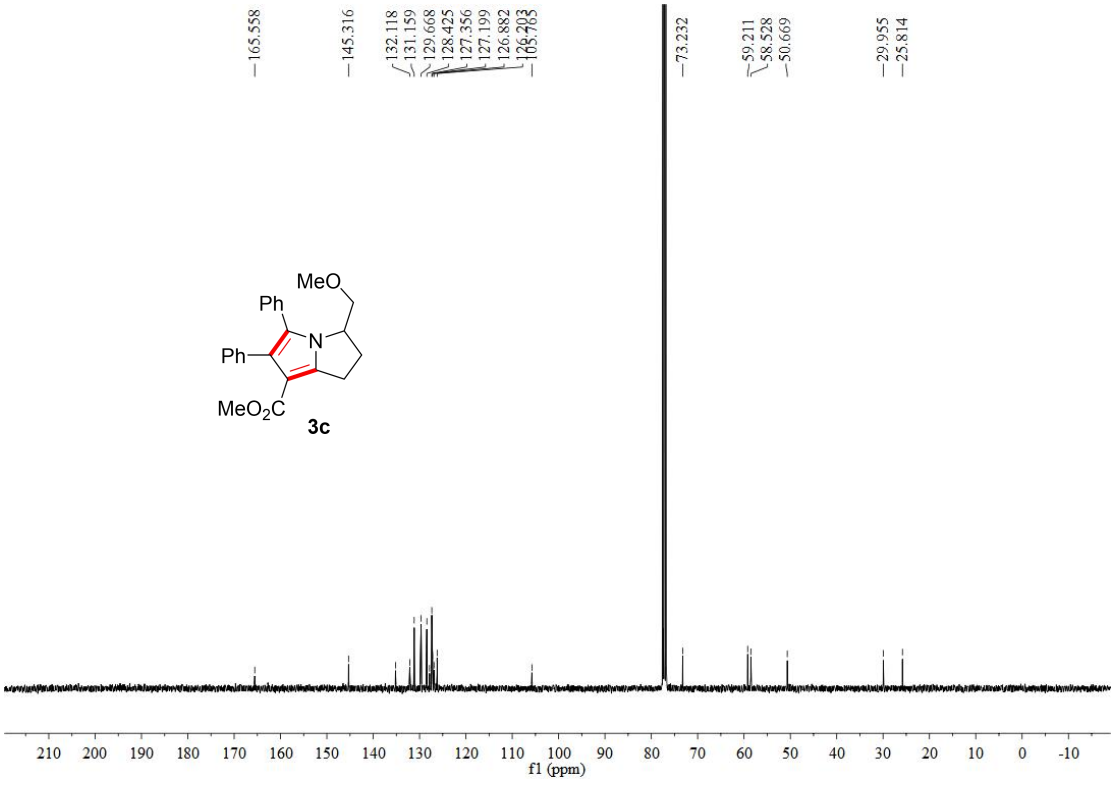
7.235
7.224
7.220
7.216
7.207
7.205
7.197
7.179
7.171
7.159
7.145
7.141
7.125
7.122
4.679
4.671
4.665
4.657
4.650
3.212
3.197
3.190
3.174
3.164
3.147
3.139
3.065
3.053
3.037
3.028
3.012
2.742
2.721
2.710
2.698
2.688
2.677
2.666
2.644
2.534
2.527
2.519
2.512
2.502
2.497
2.486
2.480
2.471
2.465
MeO
Ph
Ph
N
MeO2C
3c
7.92
2.08
1.00
3.00
3.06
2.77
1.05
1.01
1.07
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0 -3.0
f1 (ppm)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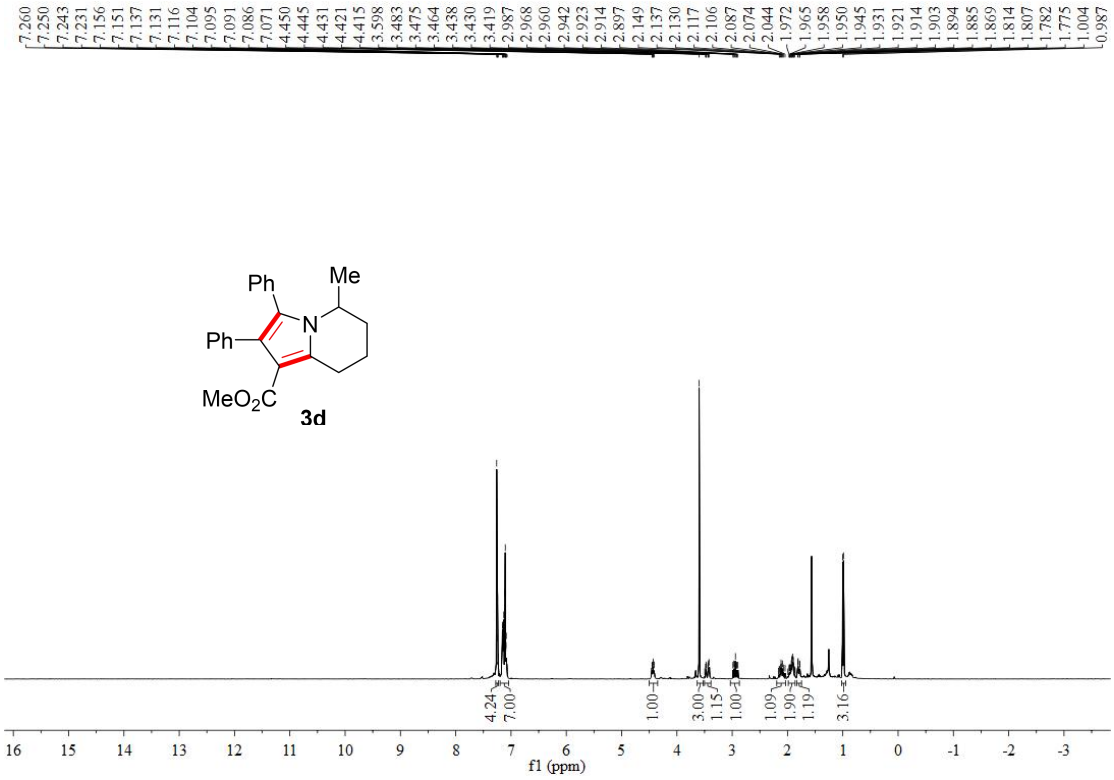
132.118
131.159
129.668
128.425
127.356
127.199
126.882
73.232
59.211
58.528
50.669
29.955
25.814
MeO
Ph
Ph
N
MeO2C
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3d, $^{1}H+^{13}C$ NMR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7.151
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7.131
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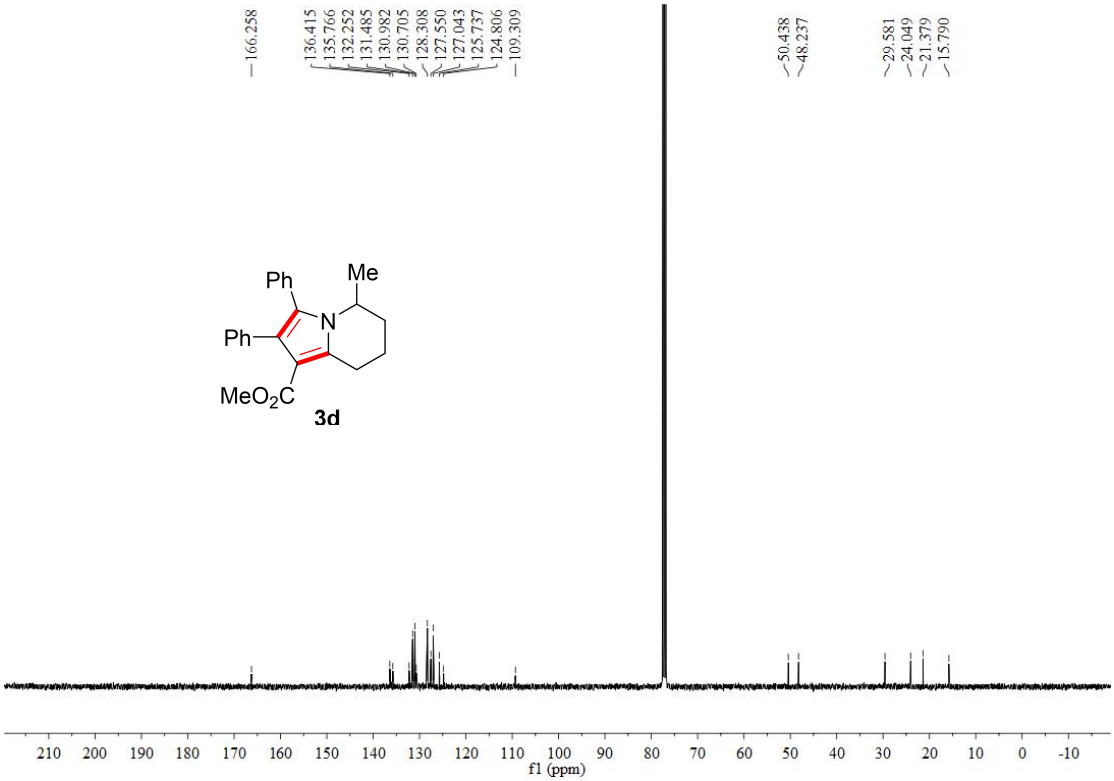
7.095
7.091
7.086
7.071
4.450
4.445
4.431
4.421
4.415
3.598
3.483
3.475
3.464
3.438
3.430
3.419
2.987
2.968
2.960
2.942
2.923
2.914
2.897
2.149
2.137
2.130
2.117
2.106
2.087
2.074
2.044
1.972
1.965
1.958
1.950
1.945
1.931
1.921
1.914
1.903
1.894
1.885
1.869
1.814
1.807
1.782
1.775
1.004
0.987
Ph
Me
Ph
N
MeO2C
3d
4.24
7.00
1.00
3.00
1.15
1.00
1.09
1.90
1.19
3.16
f1 (ppm)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135.766
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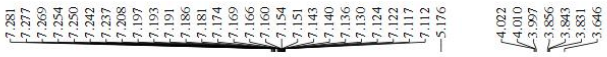
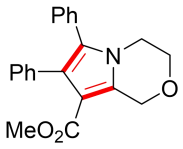
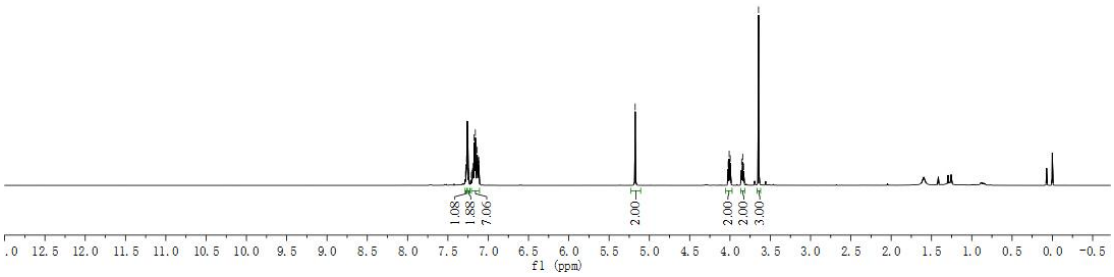
130.705
128.308
127.550
127.043
125.737
124.806
109.309
50.438
48.237
29.581
24.049
21.379
15.790
Ph
Me
Ph
N
MeO2C
3d
f1 (ppm)

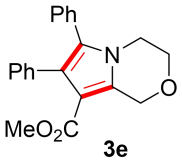
3e, $^{1}H+^{13}C$ NMR



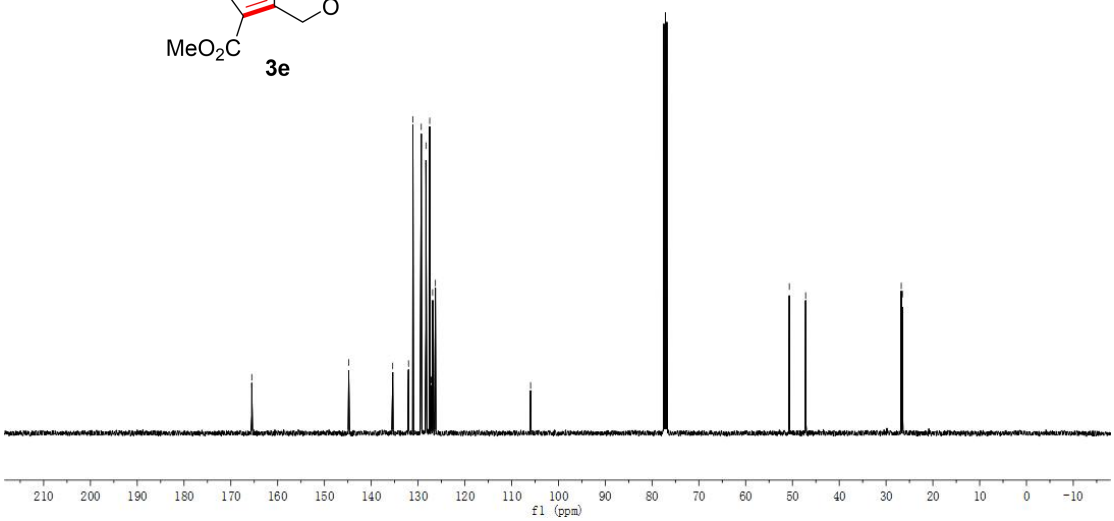


3e

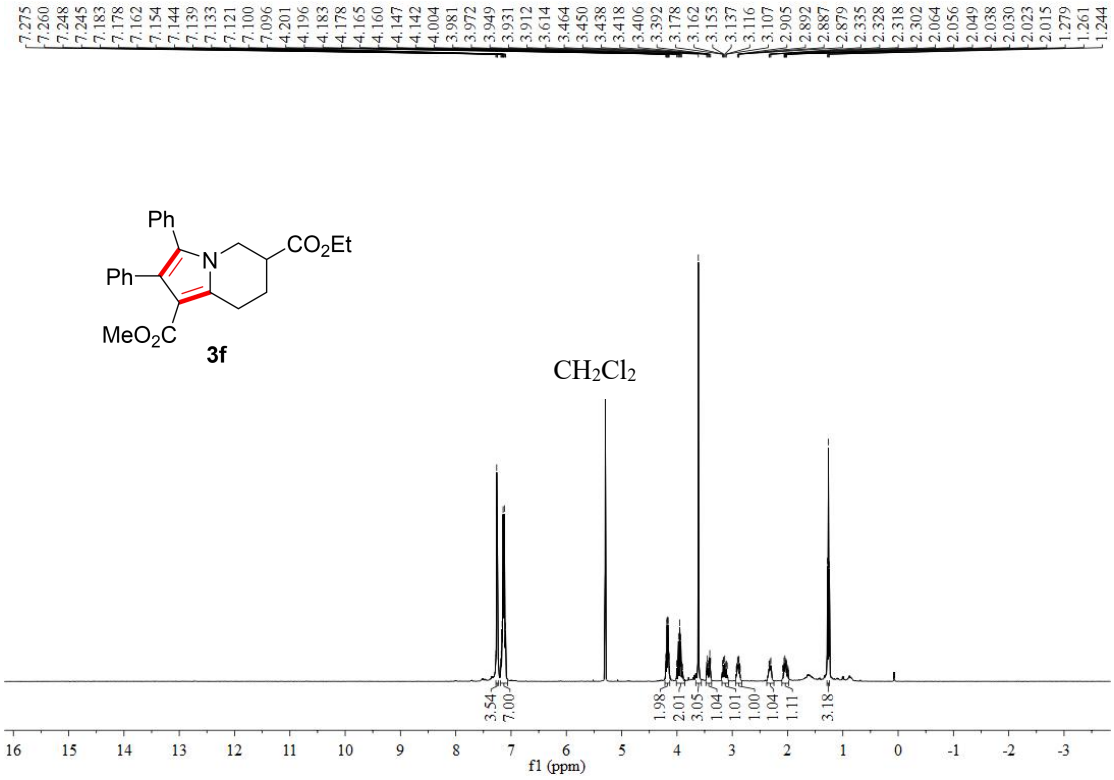




3e



3f, $^{1}H+^{13}C$ NMR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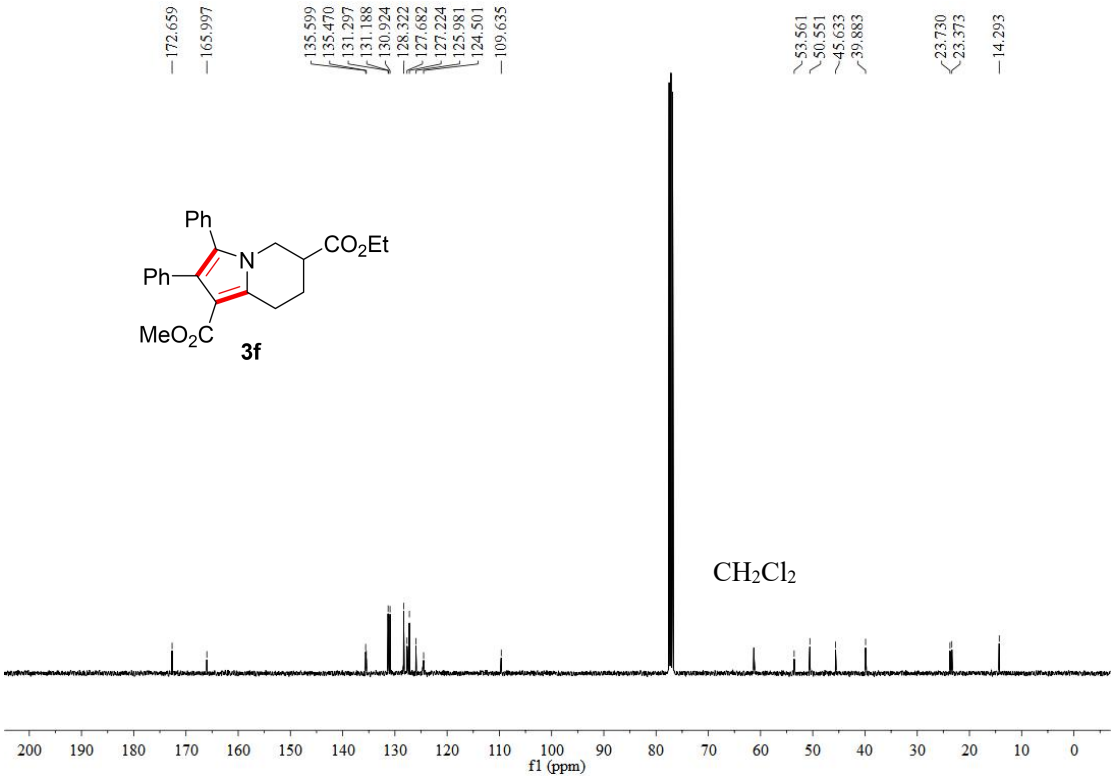
7.260
7.248
7.245
7.183
7.178
7.162
7.154
7.144
7.139
7.133
7.121
7.100
7.096
4.201
4.196
4.183
4.178
4.165
4.160
4.147
4.142
4.004
3.981
3.972
3.949
3.931
3.912
3.614
3.464
3.450
3.438
3.418
3.406
3.392
3.178
3.162
3.153
3.137
3.116
3.107
2.905
2.892
2.887
2.879
2.335
2.328
2.318
2.302
2.064
2.056
2.049
2.038
2.030
2.023
2.015
1.279
1.261
1.244
Ph
N
CO2Et
Ph
MeO2C
3f
CH2Cl2
3.54
7.00
1.98
2.01
3.05
1.04
1.01
1.00
1.04
1.11
3.18
f1 (ppm)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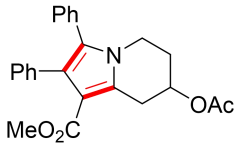
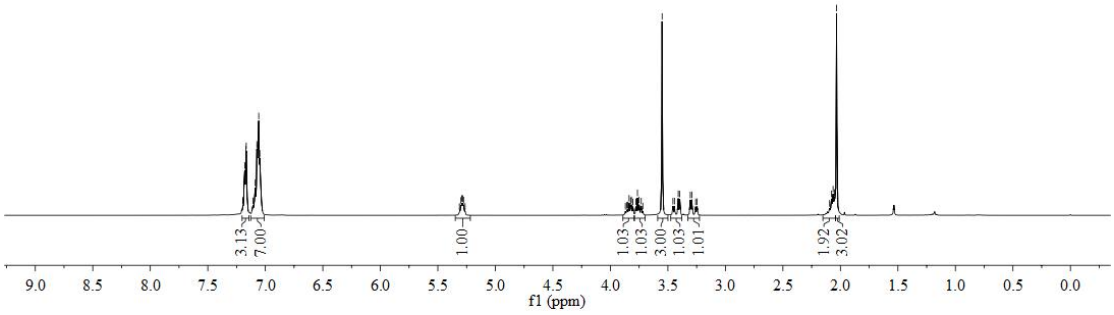
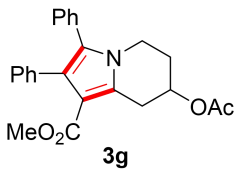
165.997
135.599
135.470
131.297
131.188
130.924
128.322
127.682
127.224
125.981
124.501
109.635
53.561
50.551
45.633
39.883
23.730
23.373
14.293
Ph
N
CO2Et
Ph
MeO2C
3f
CH2Cl2
f1 (ppm)

3g, $^{1}H+^{13}C$ NMR



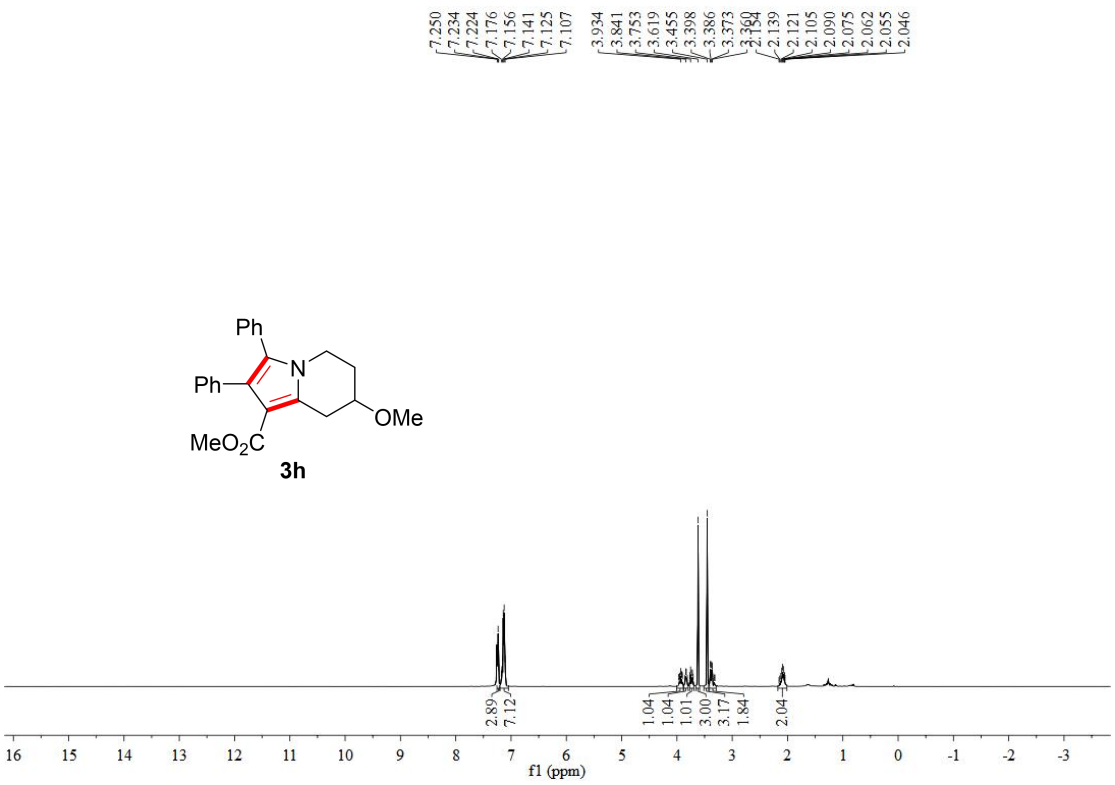
3g

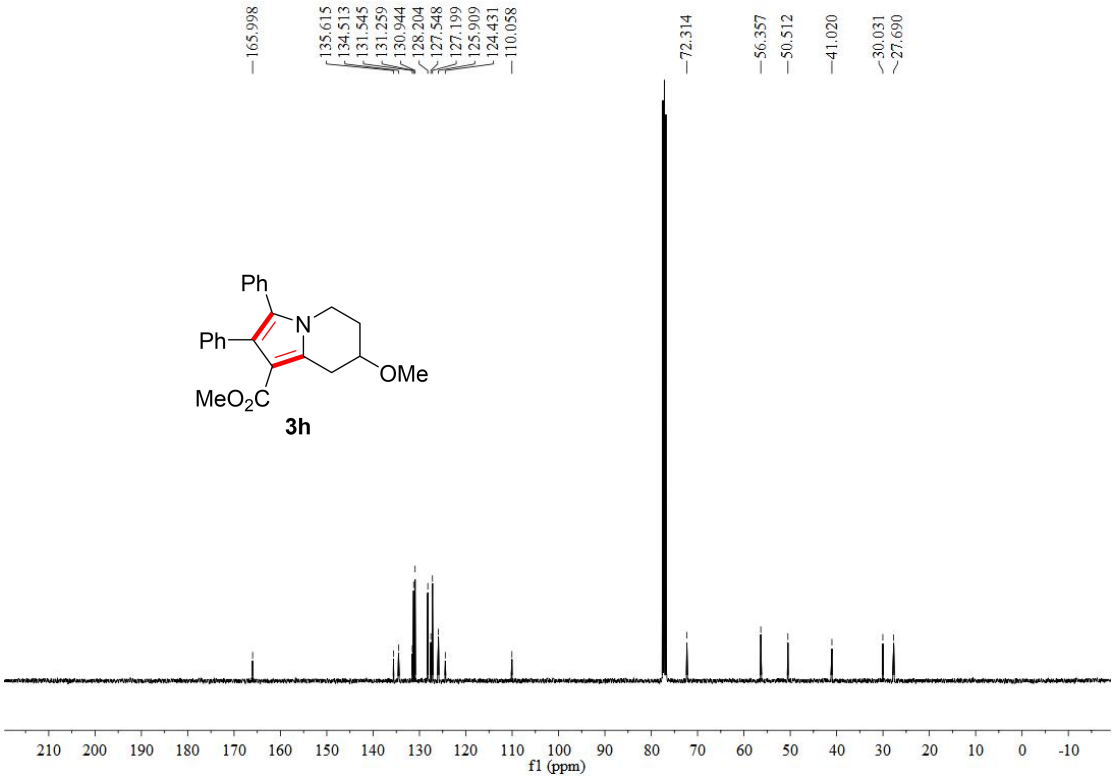




3g

3h, $^{1}H+^{13}C$ NMR


7.250
7.234
7.224
7.176
7.156
7.141
7.125
7.107
3.934
3.841
3.753
3.619
3.455
3.398
3.386
3.373
2.139
2.121
2.105
2.090
2.075
2.062
2.055
2.046
Ph
Ph
N
OMe
MeO2C
3h
2.89
7.12
1.04
1.04
1.01
3.00
3.17
1.84
2.04
f1 (ppm)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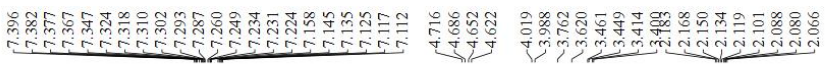
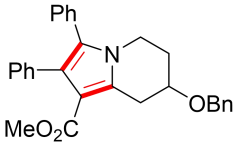
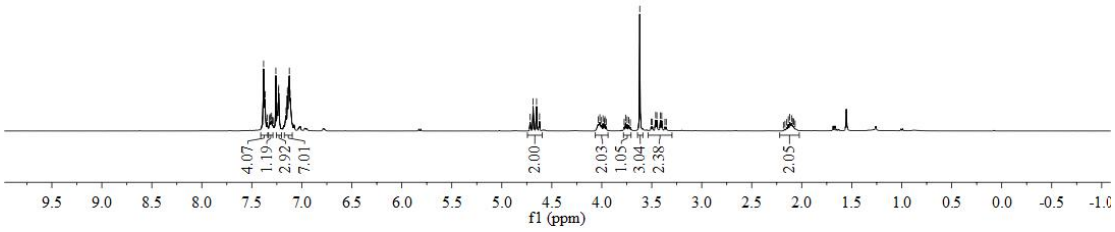
131.259
130.944
128.204
127.548
127.199
125.909
124.431
110.058
72.314
56.357
50.512
41.020
30.031
27.690
Ph
Ph
N
OMe
MeO2C
3h
f1 (ppm)

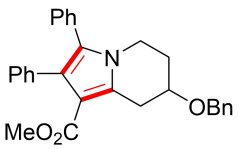
3i, $^{1}H+^{13}C$ NMR





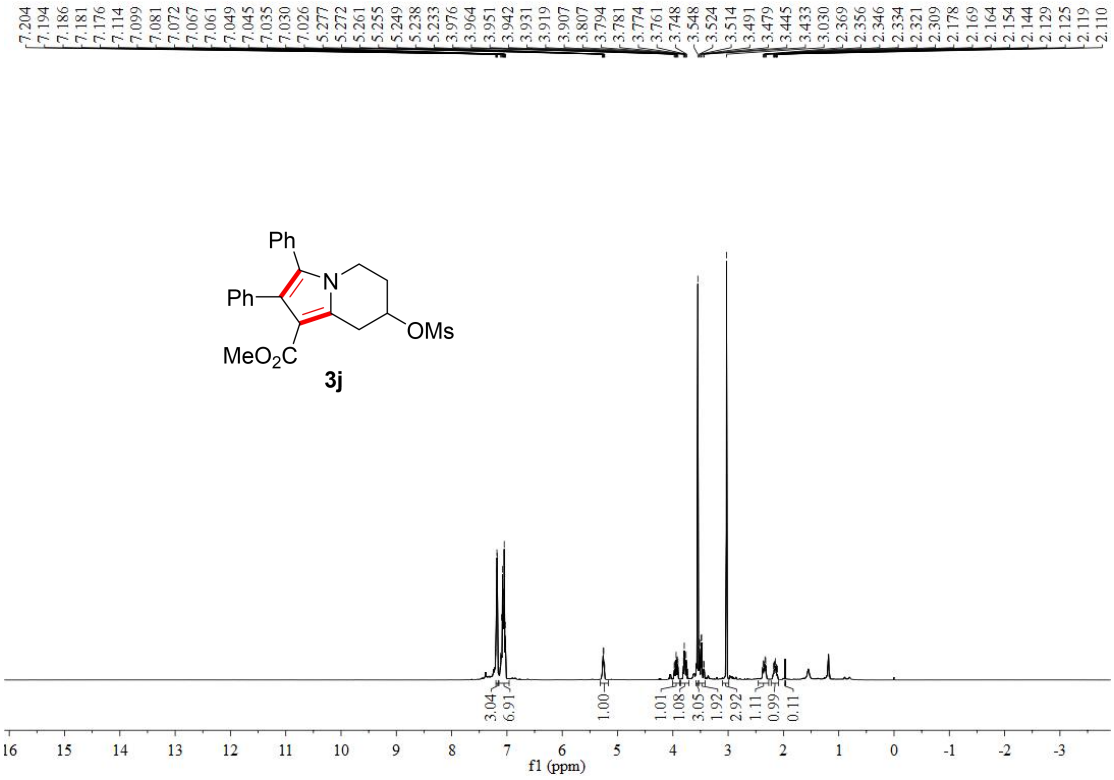
3i





3i

3j, $^{1}H+^{13}C$ NMR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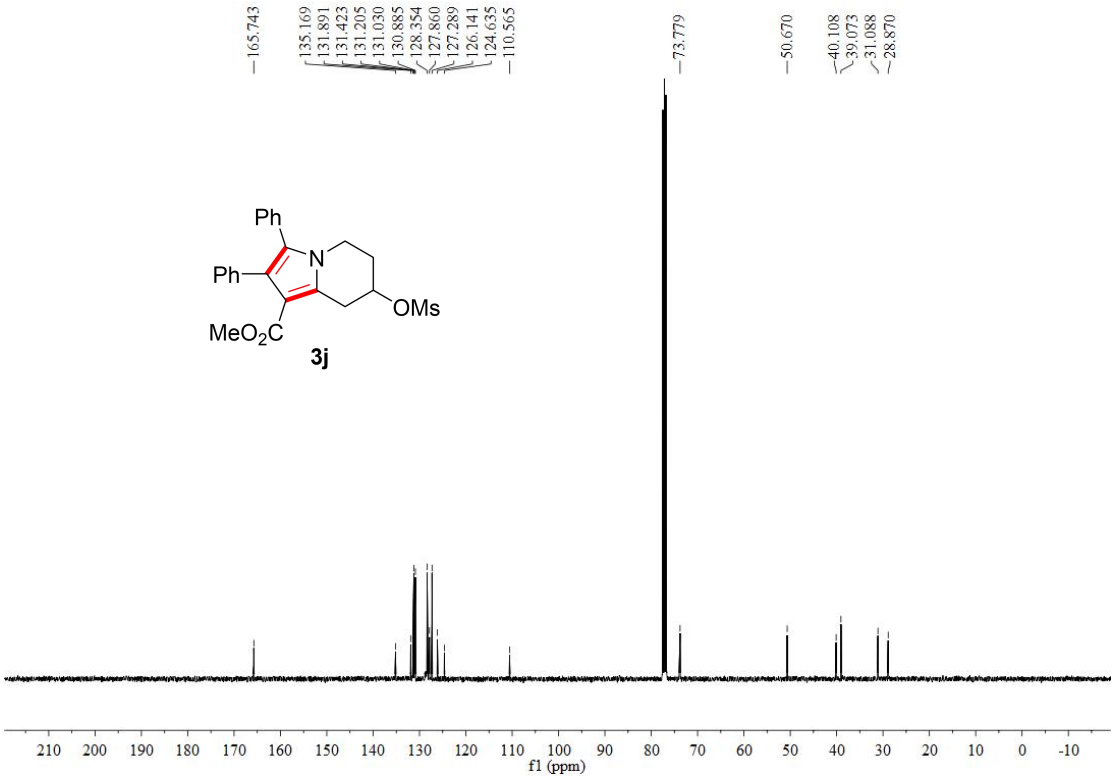
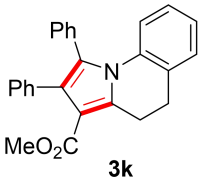
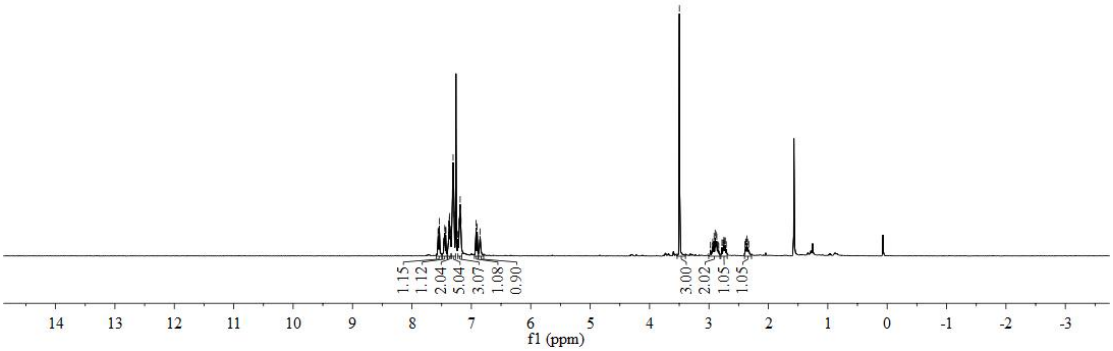
7.176
7.114
7.099
7.081
7.072
7.067
7.061
7.049
7.045
7.035
7.030
7.026
5.277
5.272
5.261
5.255
5.249
5.238
5.233
3.976
3.964
3.951
3.942
3.931
3.919
3.907
3.807
3.794
3.781
3.774
3.761
3.748
3.548
3.524
3.514
3.491
3.479
3.445
3.433
3.030
2.369
2.356
2.346
2.334
2.321
2.309
2.178
2.169
2.164
2.154
2.144
2.129
2.125
2.119
2.110
Ph
Ph
N
OMs
MeO2C
3j
3.04
6.91
1.00
1.01
1.08
3.05
1.92
2.92
1.11
0.99
0.11
f1 (ppm)

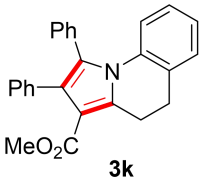

165.743
135.169
131.891
131.423
131.205
131.030
130.885
128.354
127.860
127.289
126.141
124.635
110.565
73.779
50.670
40.108
39.073
31.088
28.870
Ph
Ph
N
OMs
MeO2C
3j
f1 (ppm)

3k, $^{1}H+^{13}C$ NMR



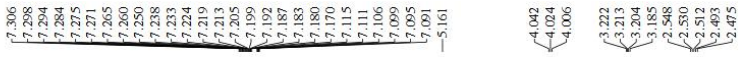
3k





3k

4a, $^{1}H+^{13}C$ NMR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7.275
7.271
7.265
7.260
7.250
7.238
7.233
7.224
7.219
7.213
7.205
7.199
7.192
7.187
7.183
7.180
7.170
7.115
7.111
7.106
7.099
7.095
7.091
5.161
4.042
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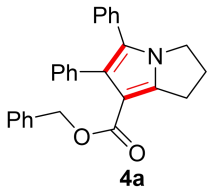
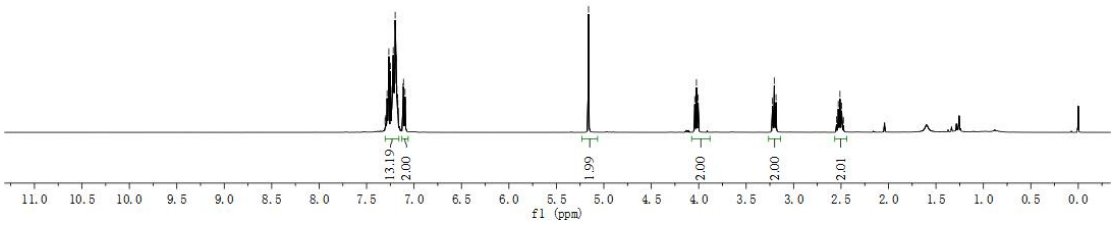
3.185
2.548
2.530
2.512
2.493
2.475


Ph
Ph
N
Ph
O
O
4a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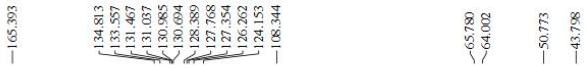
2.00
1.99
2.00
2.00
2.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


165.393
134.813
133.557
131.467
131.037
130.985
130.604
128.389
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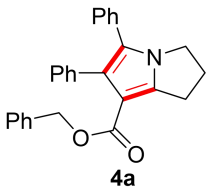
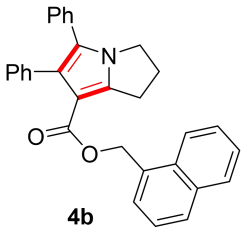
126.262
124.153
108.344
65.780
64.002
50.773
43.798

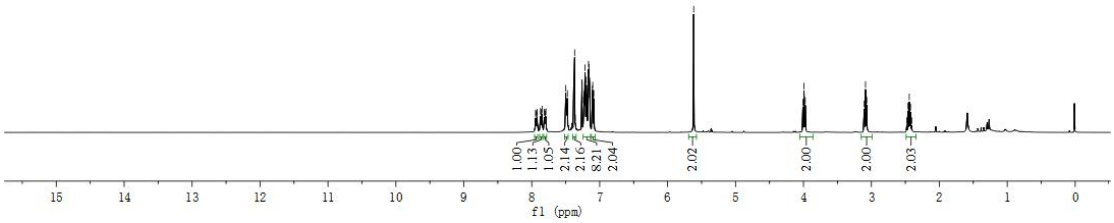

Ph
Ph
N
Ph
O
O
4a

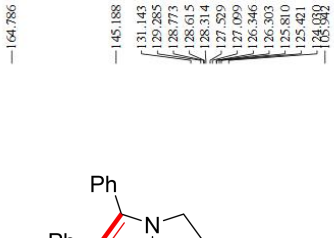
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4b, $^{1}H+^{13}C$ NMR



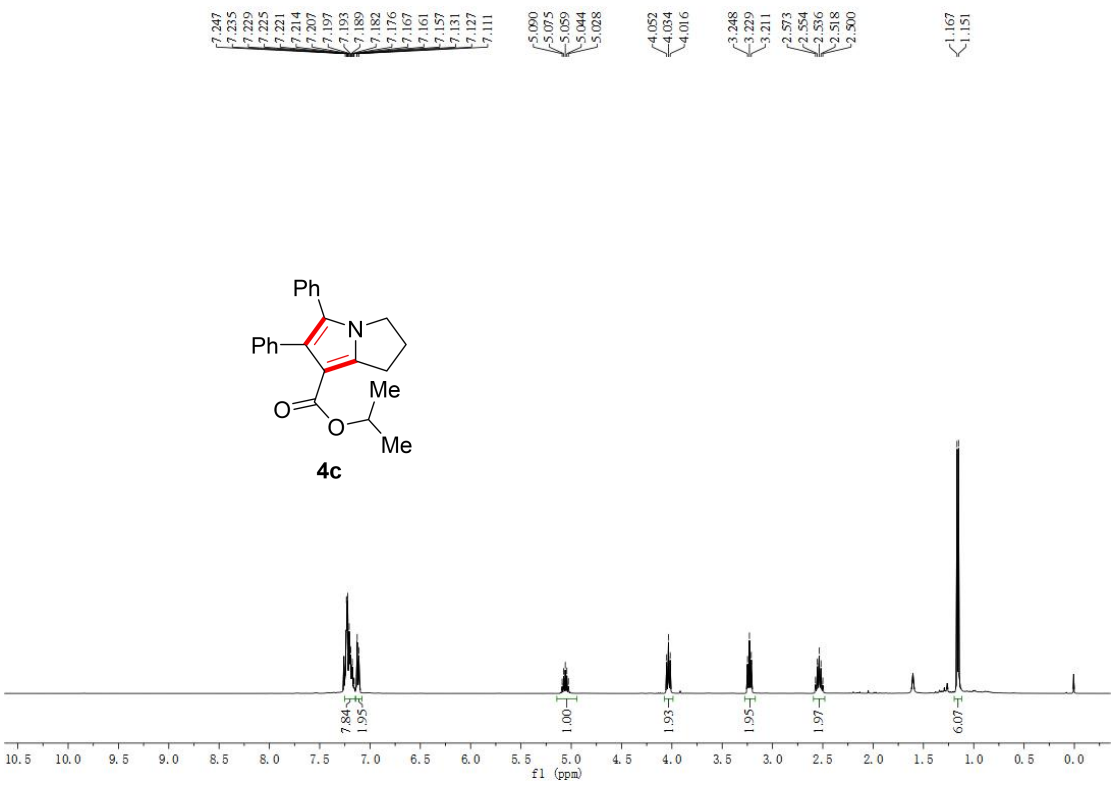
4b





4b

4c, $^{1}H+^{13}C$ NMR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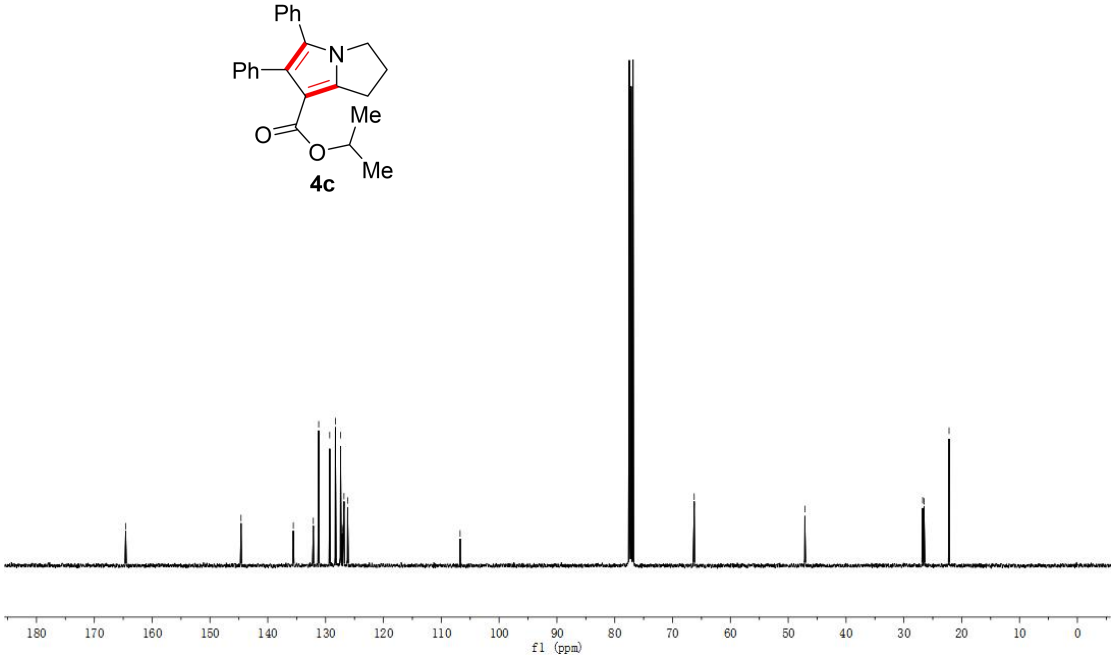
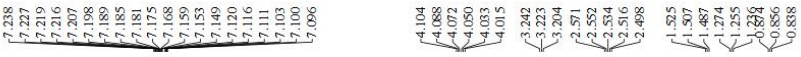
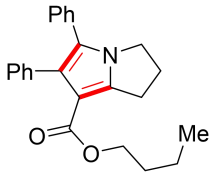
7.235
7.229
7.225
7.221
7.214
7.207
7.197
7.193
7.189
7.182
7.176
7.167
7.161
7.157
7.131
7.127
7.111
5.090
5.075
5.059
5.044
5.028
4.052
4.034
4.016
3.248
3.229
3.211
2.573
2.554
2.536
2.518
2.500
1.167
1.151
Ph
Ph
N
O
O
Me
Me
4c
7.84
1.95
1.00
1.93
1.95
1.97
6.07
f1 (ppm)

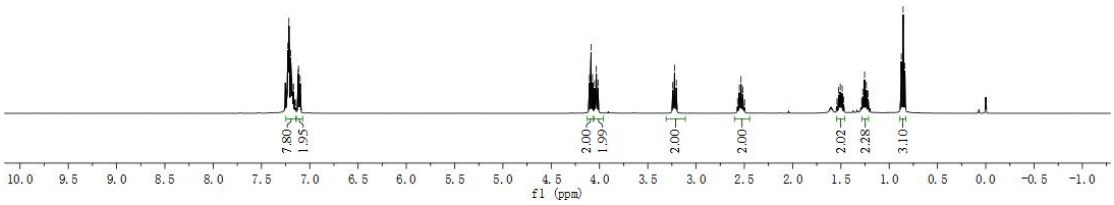

164.579
144.629
135.588
132.126
131.191
129.293
128.311
127.425
127.145
126.956
126.826
126.200
106.746
66.264
47.127
26.749
26.518
22.186
Ph
Ph
N
O
O
Me
Me
4c
f1 (ppm)

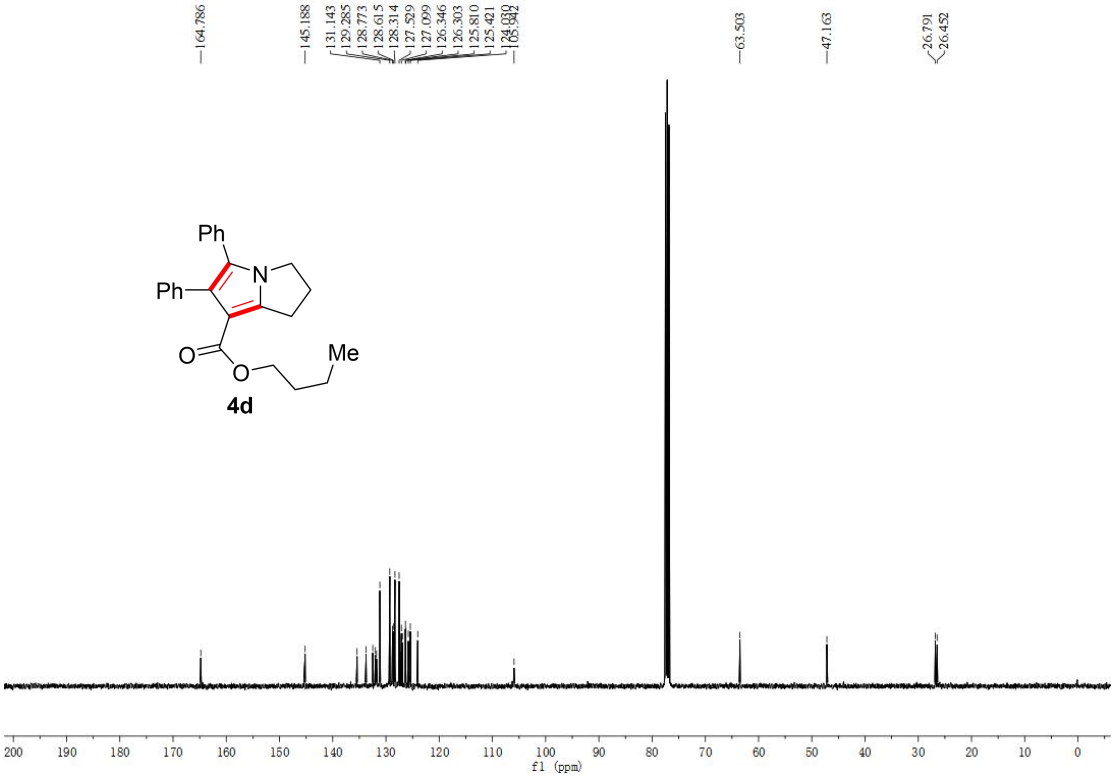
4d, $^{1}H+^{13}C$ NMR





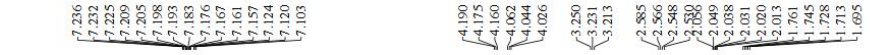
4d

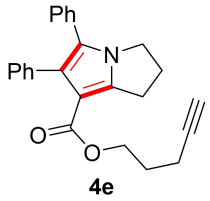




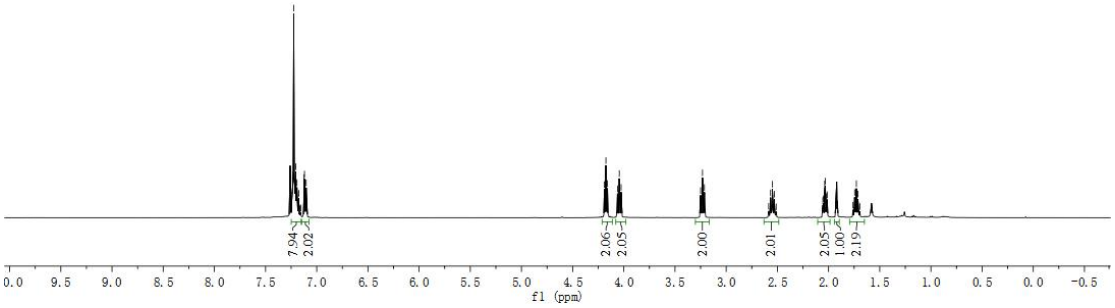
4d

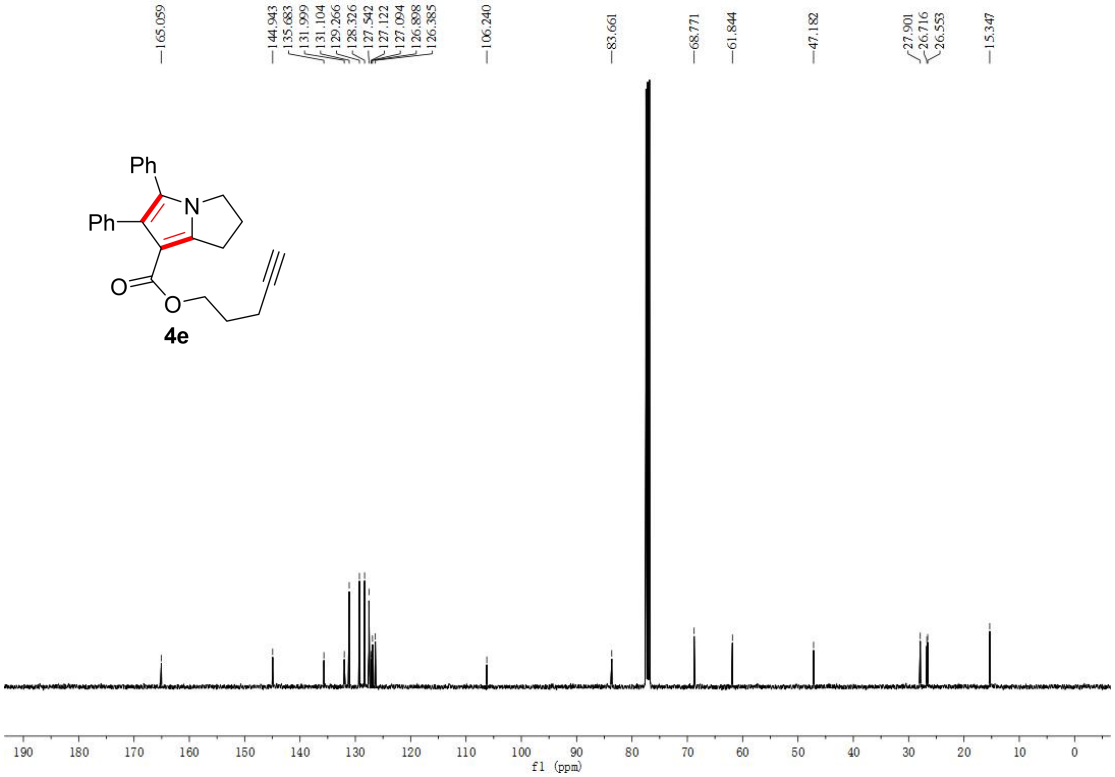
4e, $^{1}H+^{13}C$ NMR





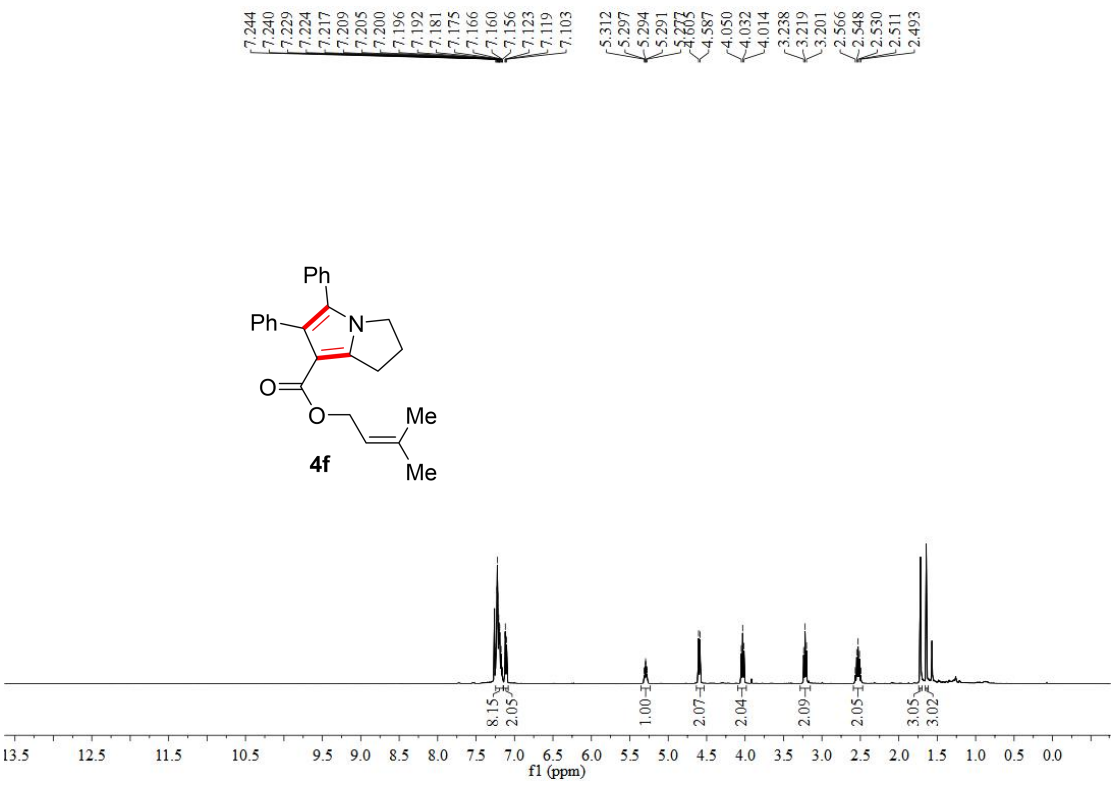
4e

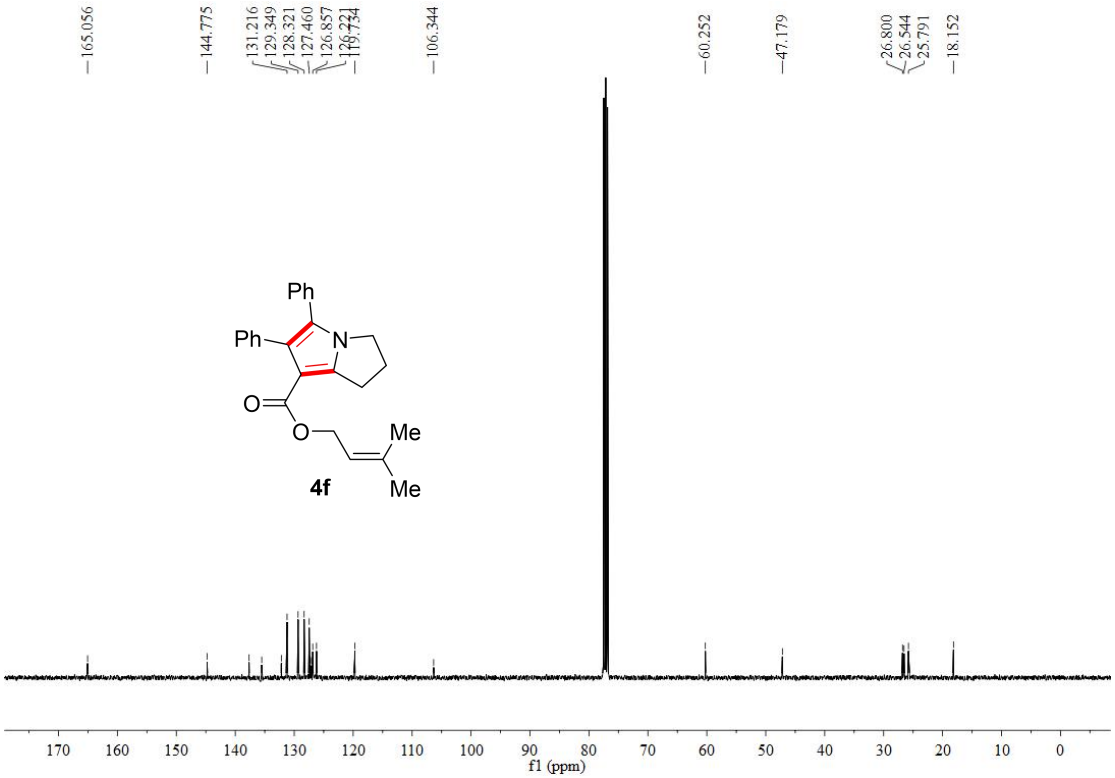




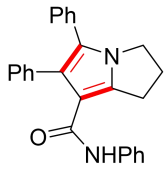
4e

4f, $^{1}H+^{13}C$ NMR

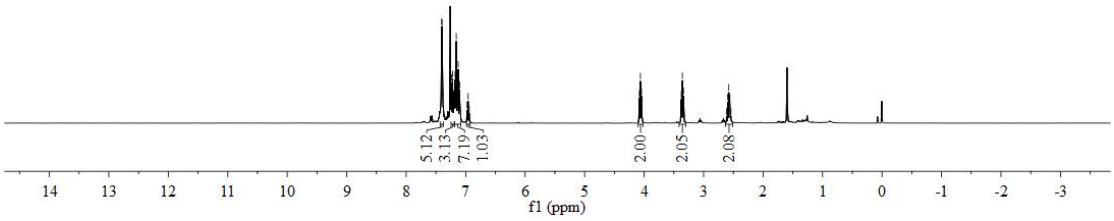

7.244
7.240
7.229
7.224
7.217
7.209
7.205
7.200
7.196
7.192
7.181
7.175
7.166
7.160
7.156
7.123
7.119
7.103
5.312
5.297
5.294
5.291
4.605
4.587
4.050
4.032
4.014
3.238
3.219
3.201
2.566
2.548
2.530
2.511
2.493
Ph
Ph
N
O
O
Me
Me
4f
8.15
2.05
1.00
2.07
2.04
2.09
2.05
3.05
3.02
f1 (ppm)

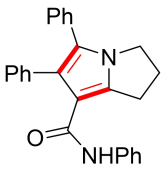

165.056
144.775
131.216
129.349
128.321
127.460
126.857
126.221
119.734
106.344
60.252
47.179
26.800
26.544
25.791
18.152
Ph
Ph
N
O
O
Me
Me
4f
f1 (ppm)

4g, $^{1}H+^{13}C$ NMR



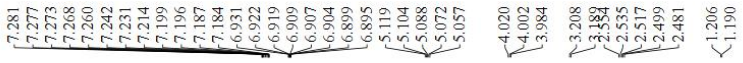
4g

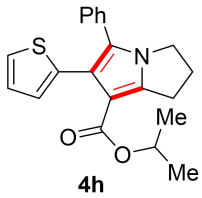




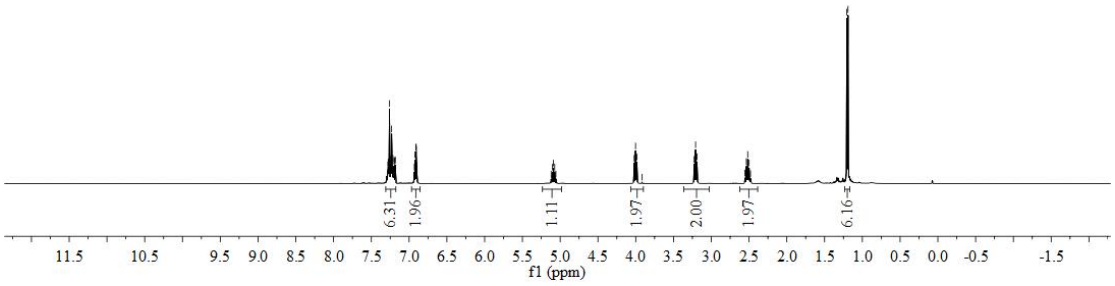
4g

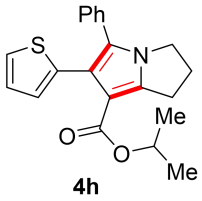
4h, $^{1}H+^{13}C$ NMR





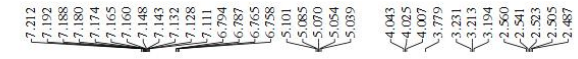
4h

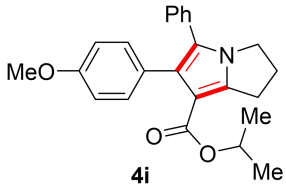


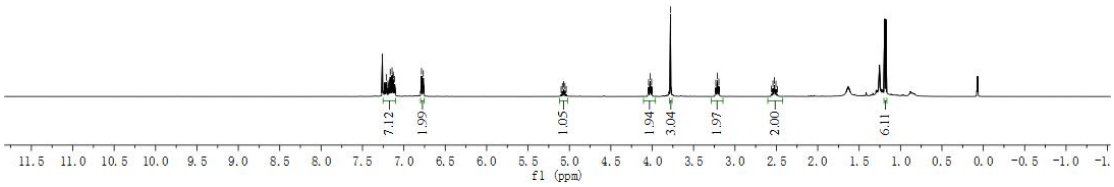


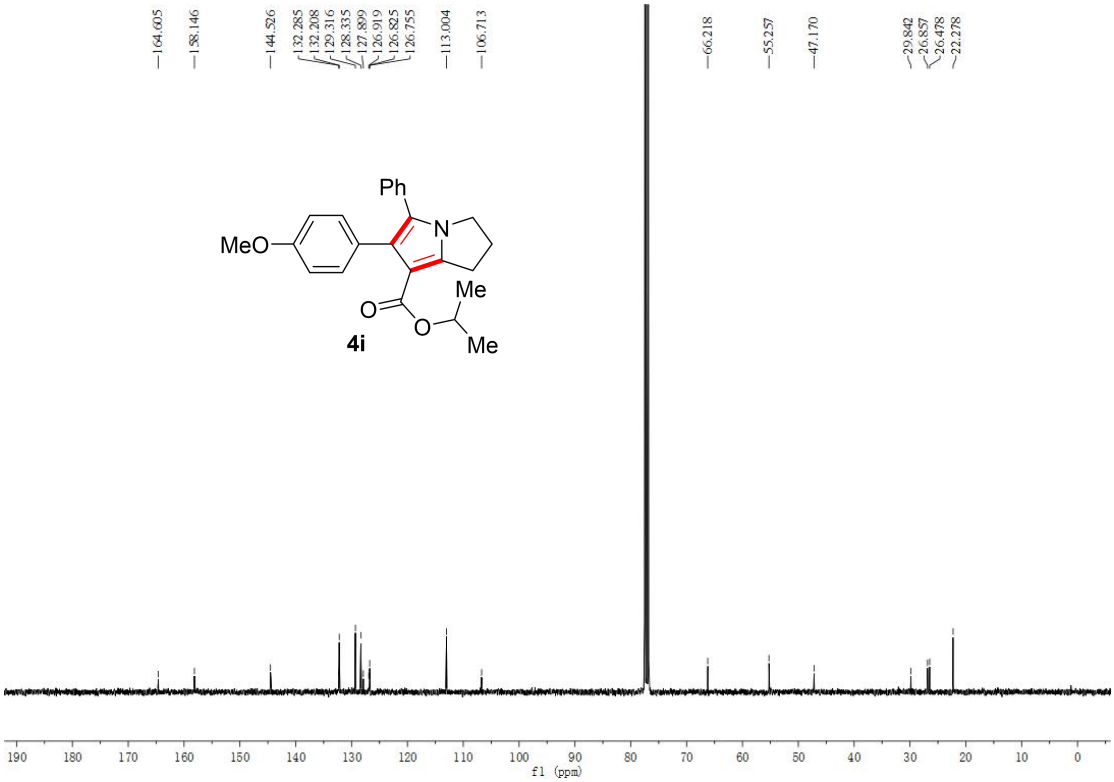
4h

4i, $^{1}H+^{13}C$ NMR

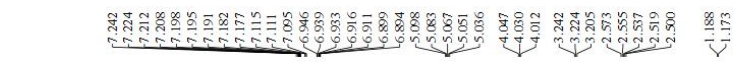

7.212
7.192
7.188
7.180
7.174
7.165
7.160
7.148
7.143
7.132
7.128
7.111
6.794
6.787
6.765
6.758
5.101
5.085
5.070
5.054
5.039
4.043
4.025
4.007
3.779
3.231
3.213
3.194
2.560
2.541
2.523
2.505
2.487

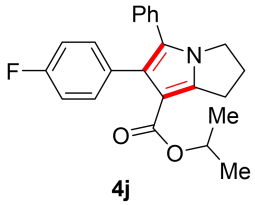

Ph
N
MeO
Me
O
O
Me
4i


7.12
1.99
1.05
1.94
3.04
1.97
2.00
6.11
f1 (ppm)

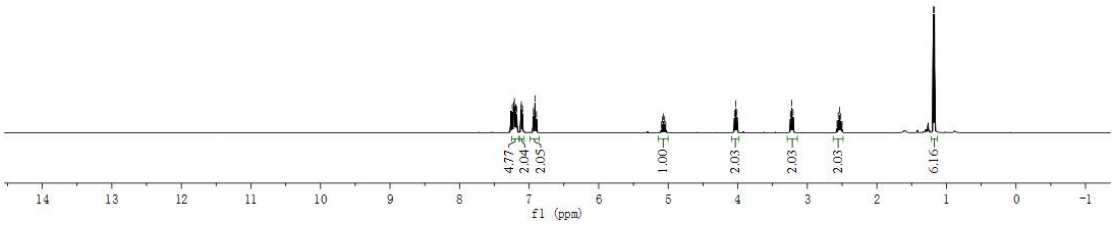

164.605
158.146
144.526
132.285
132.208
129.316
128.335
127.899
126.919
126.825
126.755
113.004
106.713
66.218
55.257
47.170
29.842
26.857
26.478
22.278
Ph
N
MeO
Me
O
O
Me
4i
f1 (ppm)

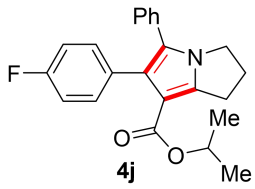
4j, $^{1}H+^{13}C$ NMR



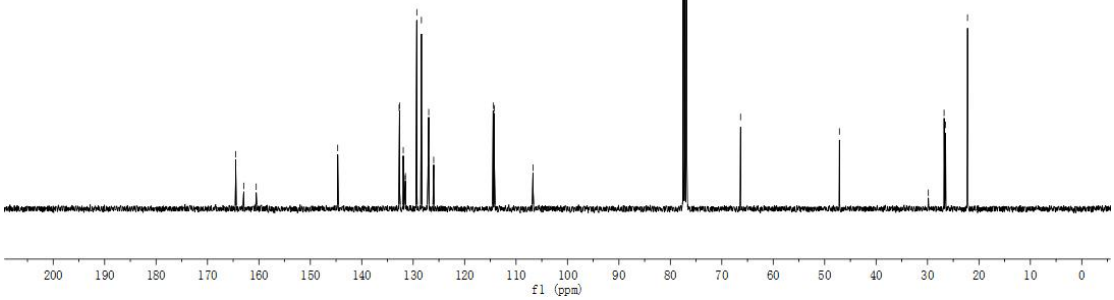


4j

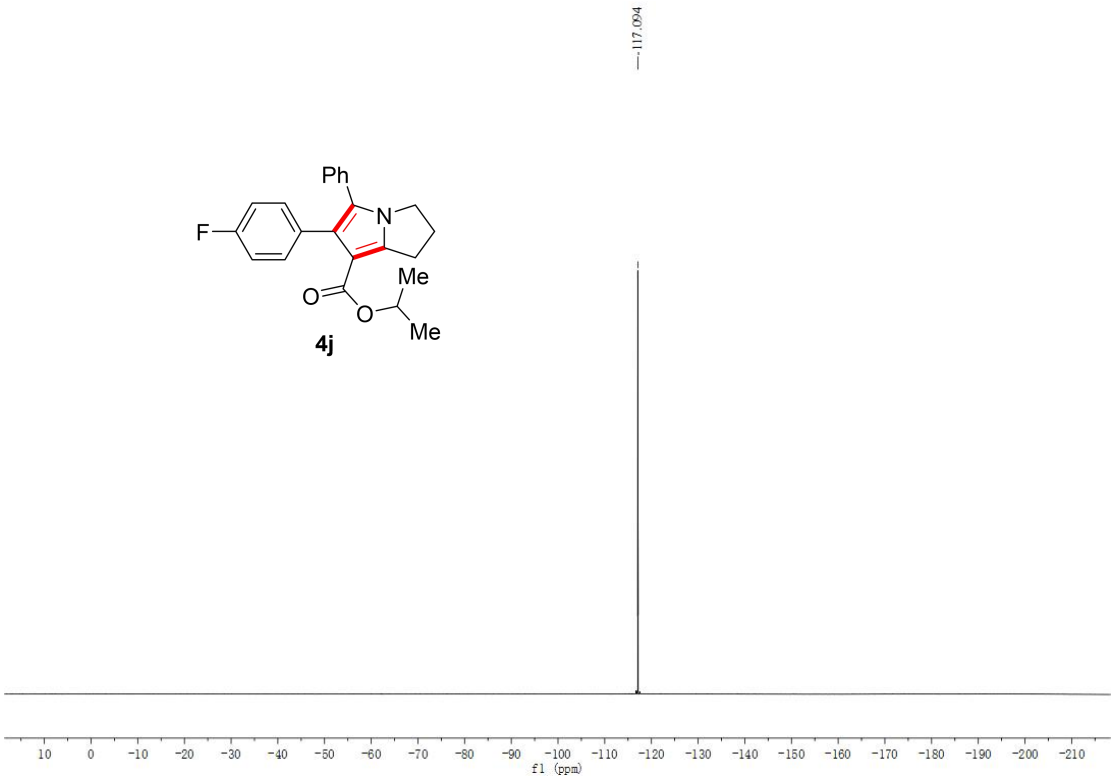




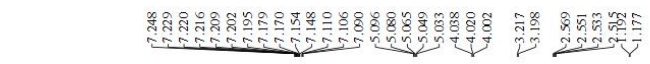
4j

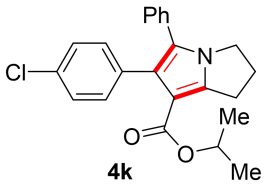


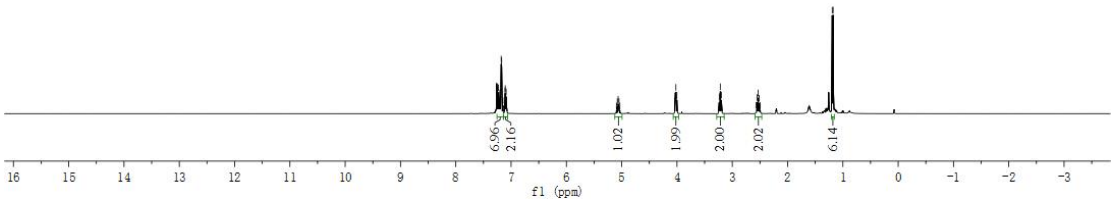
4j, ^{19}F NMR


-117.094
Ph
N
F
Me
O
O
Me
4j
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

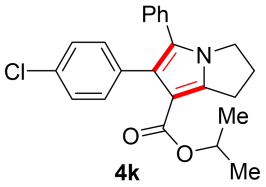
4k, $^{1}H+^{13}C$ NMR


7.248
7.229
7.220
7.216
7.209
7.202
7.195
7.179
7.170
7.154
7.148
7.110
7.106
7.090
5.096
5.080
5.065
5.049
5.033
4.038
4.020
4.002
3.217
3.198
2.569
2.551
2.533
1.192
1.177


Ph
N
Cl
Me
O
O
Me
4k

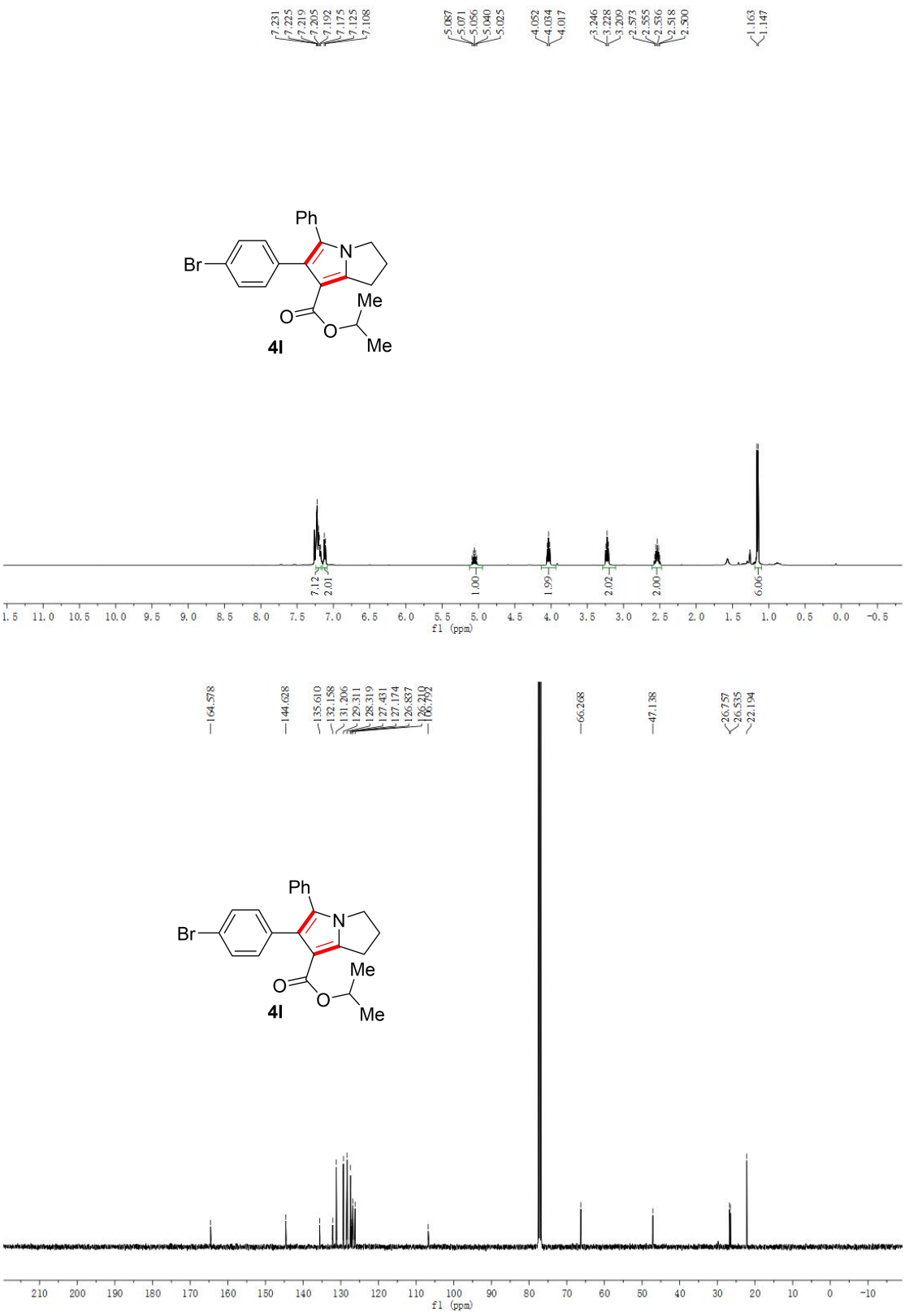

6.96
2.16
1.02
1.99
2.00
2.02
6.14
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


164.459
144.787
134.100
132.543
132.085
131.806
129.338
128.476
127.667
127.188
127.099
125.781
106.596
66.449
47.114
29.835
26.799
26.500
22.231

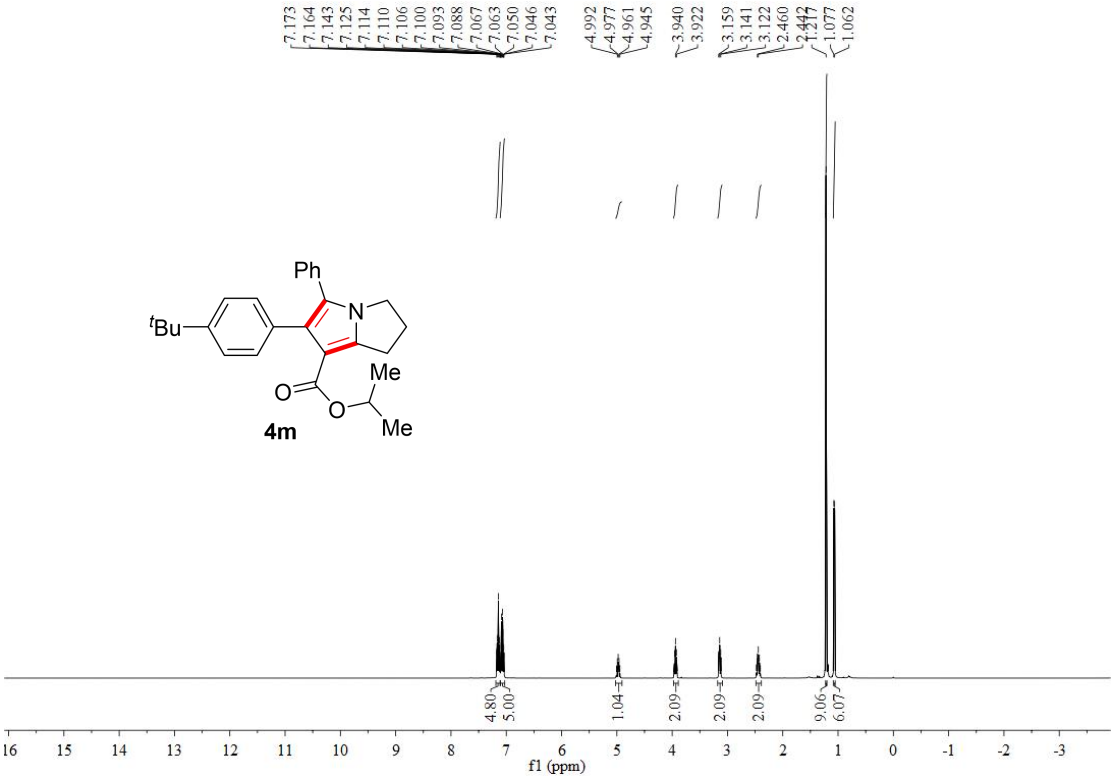

Ph
N
Cl
Me
O
O
Me
4k

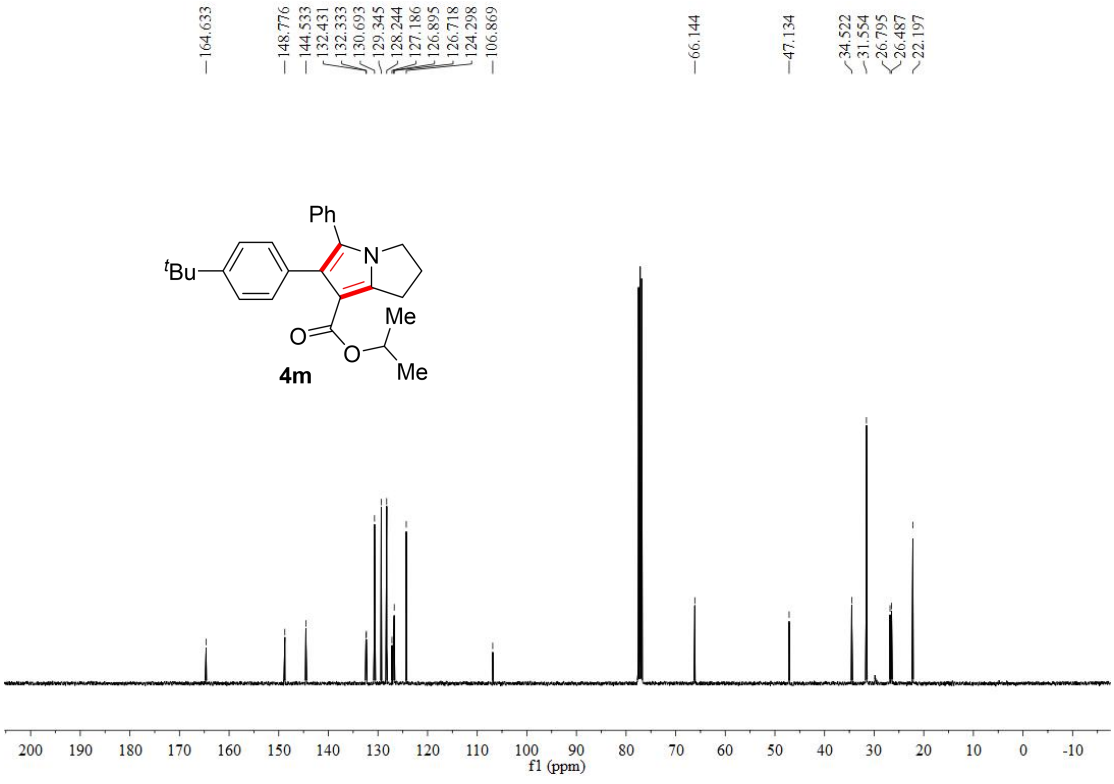
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4l, $^{1}H+^{13}C$ NMR

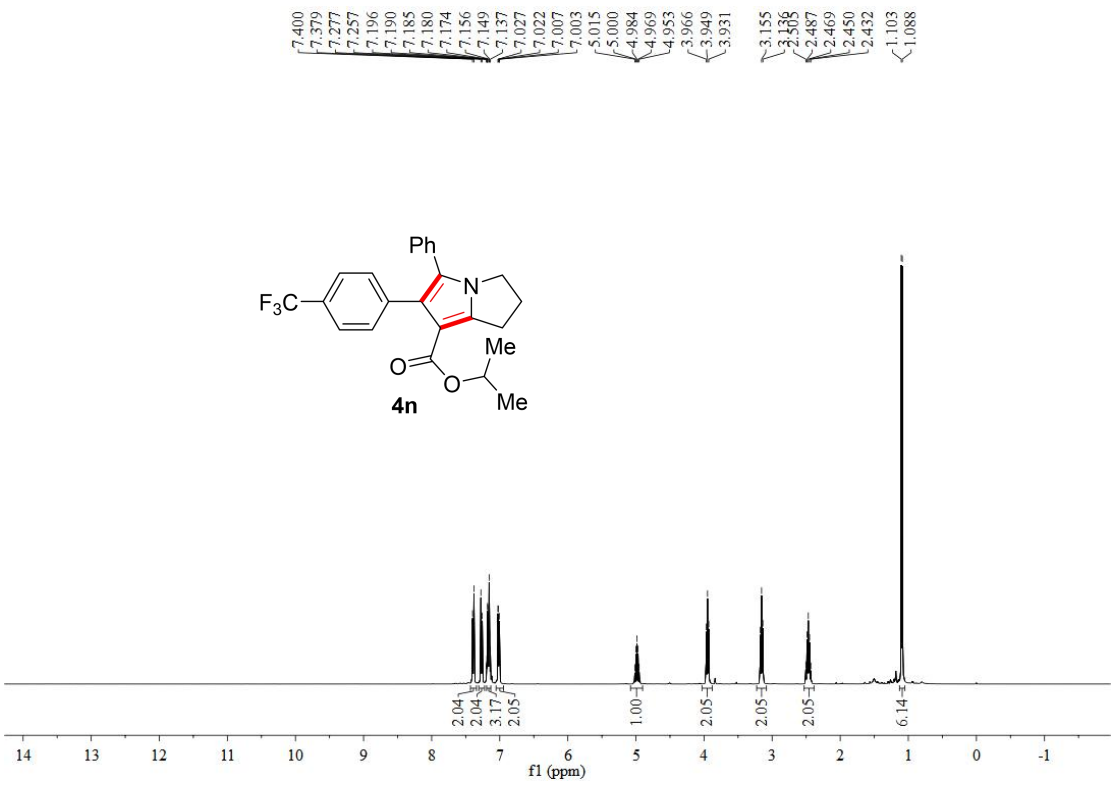

7.231
7.225
7.219
7.205
7.192
7.175
7.125
7.108
5.087
5.071
5.056
5.040
5.025
4.052
4.034
4.017
3.246
3.228
3.209
2.573
2.555
2.536
2.518
2.500
1.163
1.147
Ph
Br
N
Me
O
O
Me
4l
7.12
2.01
1.00
1.99
2.02
2.00
6.06
f1 (ppm)
164.578
144.628
135.610
132.158
131.206
129.311
128.319
127.431
127.174
126.837
126.210
66.268
47.138
26.757
26.535
22.194
Ph
Br
N
Me
O
O
Me
4l
f1 (ppm)

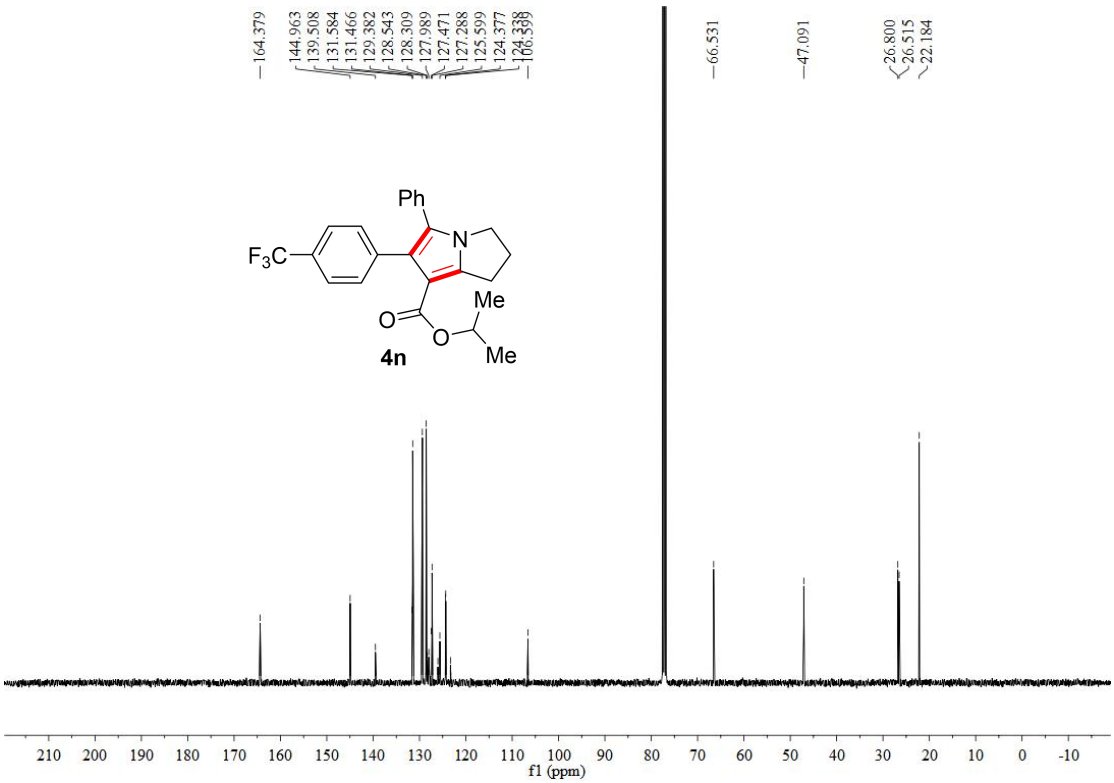
4m, $^{1}H+^{13}C$ NMR

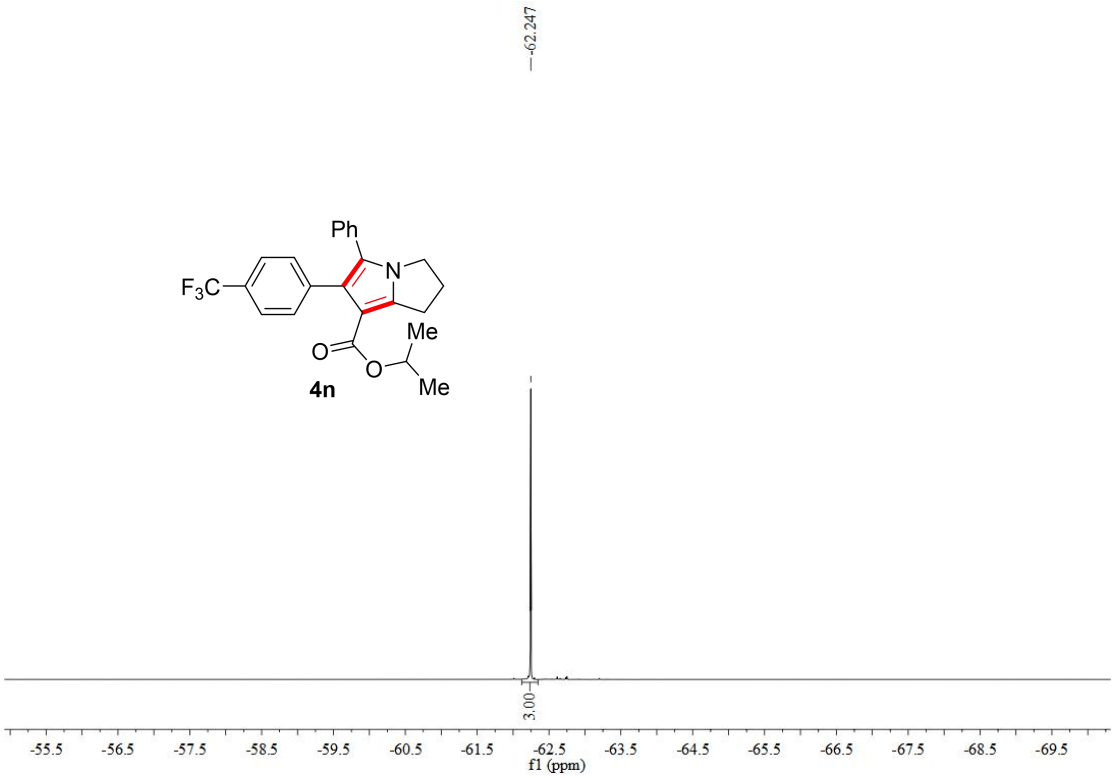

7.173
7.164
7.143
7.125
7.114
7.110
7.106
7.100
7.093
7.088
7.067
7.063
7.050
7.046
7.043
4.992
4.977
4.961
4.945
3.940
3.922
3.159
3.141
3.122
2.460
1.077
1.062
Ph
tBu
N
Me
O
O
Me
4m
4.80
5.00
1.04
2.09
2.09
2.09
9.06
6.07
f1 (ppm)


164.633
148.776
144.533
132.431
132.333
130.693
129.345
128.244
127.186
126.895
126.718
124.298
106.869
66.144
47.134
34.522
31.554
26.795
26.487
22.197
Ph
tBu
N
Me
O
O
Me
4m
f1 (ppm)

4n, $^{1}H+^{13}C+F^{19}$ NMR

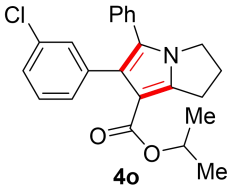


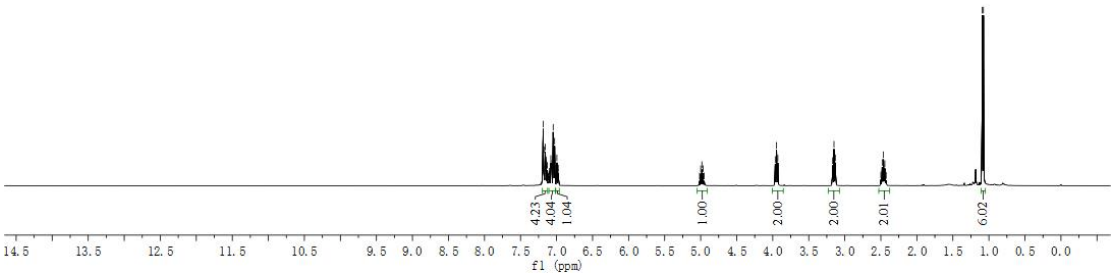



-62.247
Ph
N
F3C
Me
O
O
Me
4n
3.00
-55.5
-56.5
-57.5
-58.5
-59.5
-60.5
-61.5
-62.5
-63.5
-64.5
-65.5
-66.5
-67.5
-68.5
-69.5
f1 (ppm)

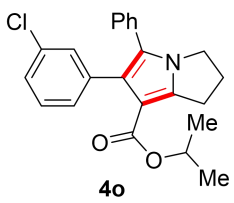
4o, $^{1}H+^{13}C$ NMR


7.189
7.185
7.175
7.157
7.151
7.147
7.143
7.137
7.130
7.120
7.115
7.111
7.103
7.099
7.094
7.083
7.079
7.075
7.065
7.047
7.027
6.999
6.996
6.992
6.981
6.977
5.015
4.999
4.984
4.968
4.953
3.965
3.947
3.929
3.169
3.150
3.131
2.499
2.481
2.463
2.445
2.426
1.092
1.076


Cl
Ph
N
O
O
Me
Me
4o

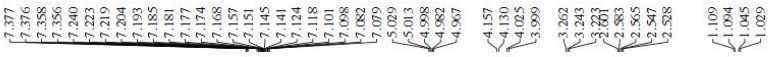

4.23
4.04
1.04
1.00
2.00
2.00
2.01
6.02
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

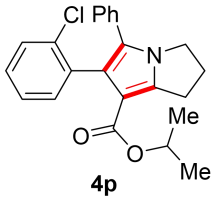

164.487
144.920
137.656
133.024
131.706
131.449
129.369
129.317
128.616
128.460
127.223
127.150
126.276
126.252
66.458
47.106
26.645
26.545
22.149


Cl
Ph
N
O
O
Me
Me
4o

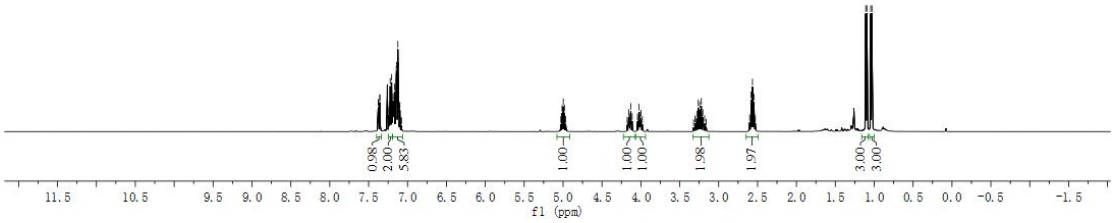
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

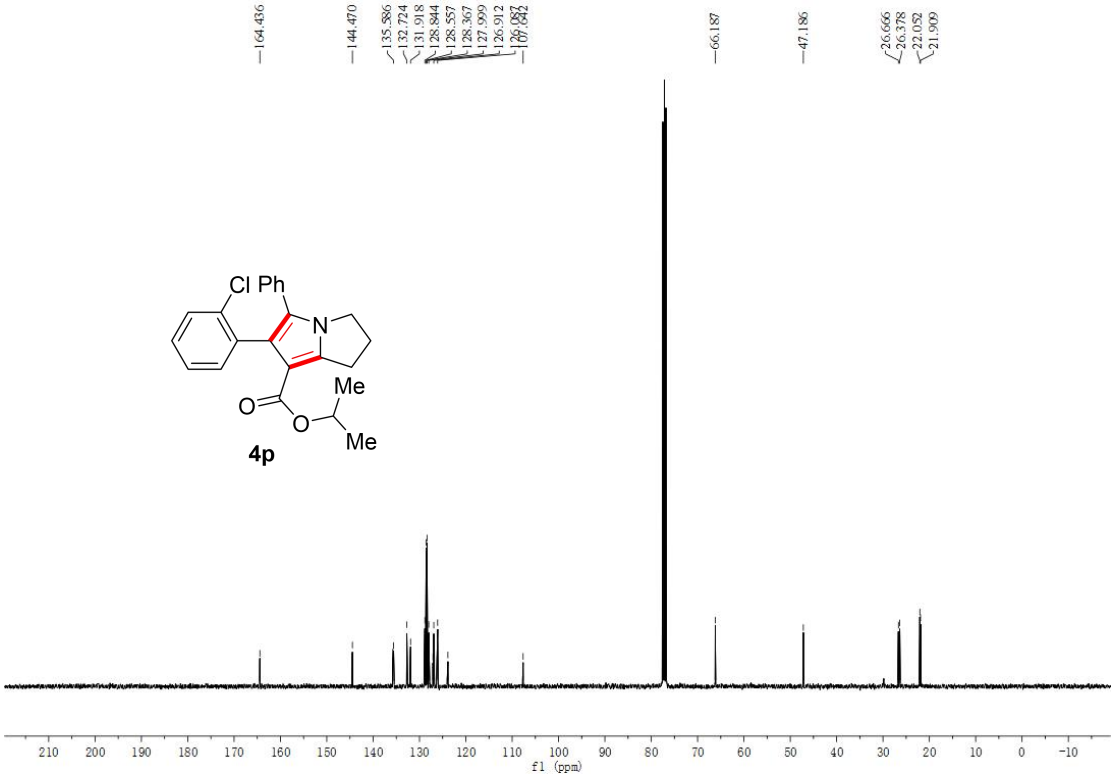
4p, $^{1}H+^{13}C$ NMR



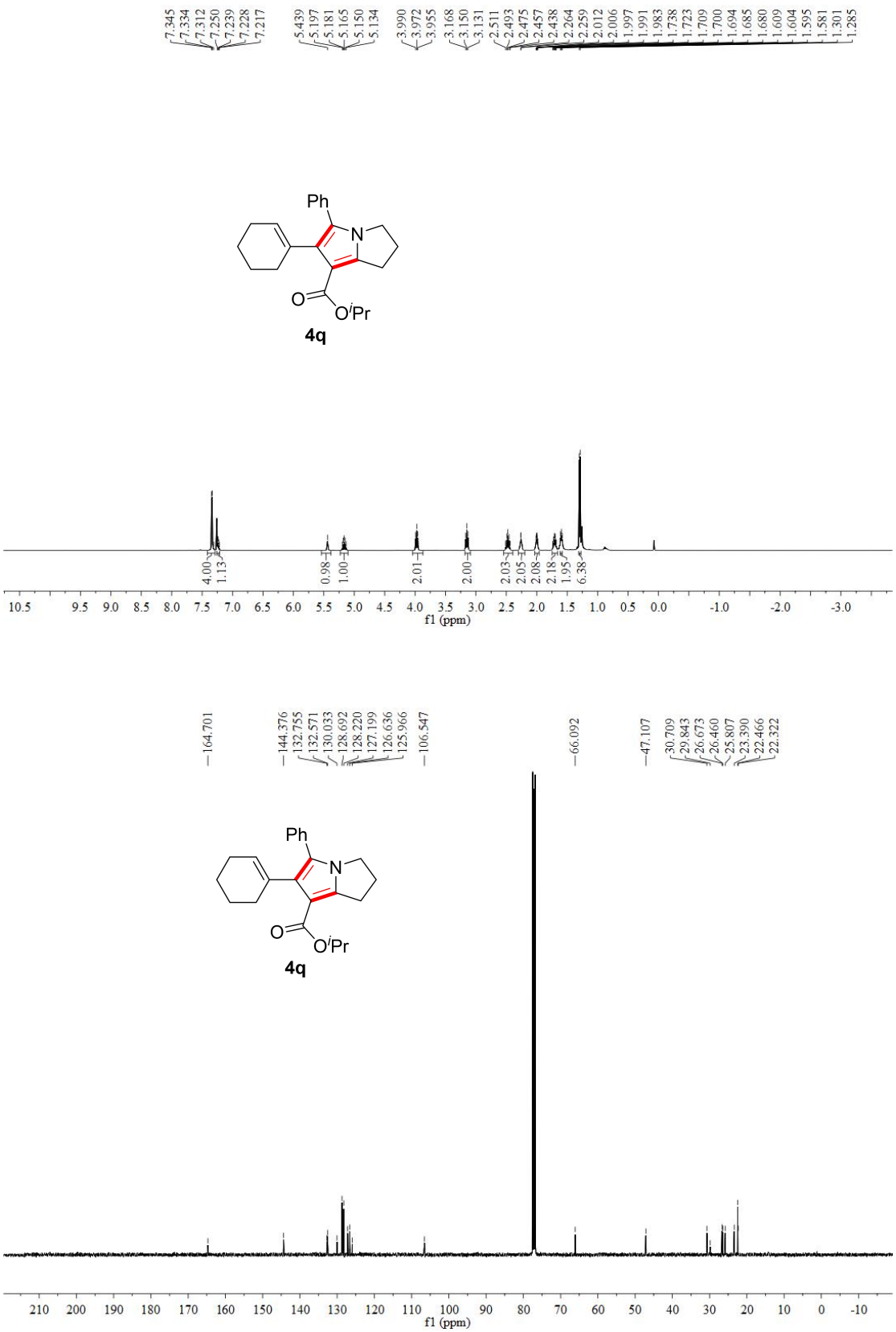


4p

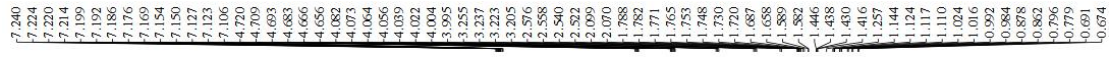


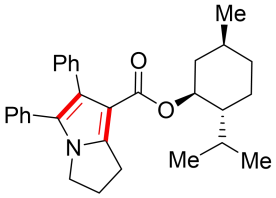


4q, $^{1}H+^{13}C$ NMR

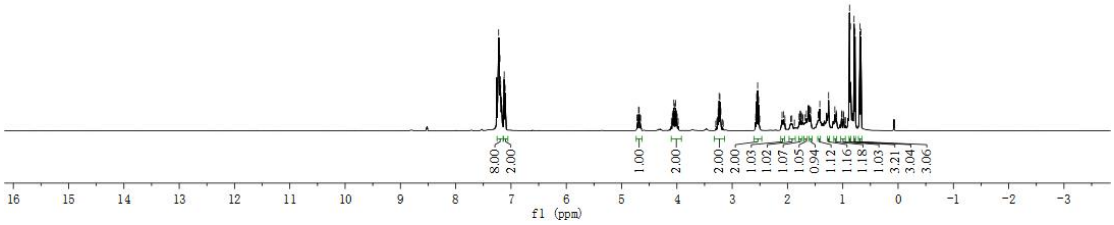

7.345
7.334
7.312
7.250
7.239
7.228
7.217
5.439
5.197
5.181
5.165
5.150
5.134
3.990
3.972
3.955
3.168
3.150
3.131
2.511
2.493
2.475
2.457
2.438
2.264
2.259
2.012
2.006
1.997
1.991
1.983
1.738
1.723
1.709
1.700
1.694
1.685
1.680
1.609
1.604
1.595
1.581
1.301
1.285
Ph
N
O
O^{i}Pr
4q
4.00
1.13
0.98
1.00
2.01
2.00
2.03
2.05
2.08
2.18
1.95
6.38
f1 (ppm)
164.701
144.376
132.755
132.571
130.033
128.692
128.220
127.199
126.636
125.966
106.547
66.092
47.107
30.709
29.843
26.673
26.460
25.807
23.390
22.466
22.322
f1 (ppm)

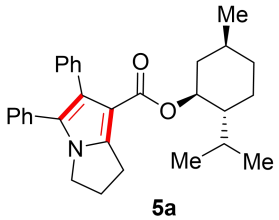
5a, $^{1}H+^{13}C$ NMR



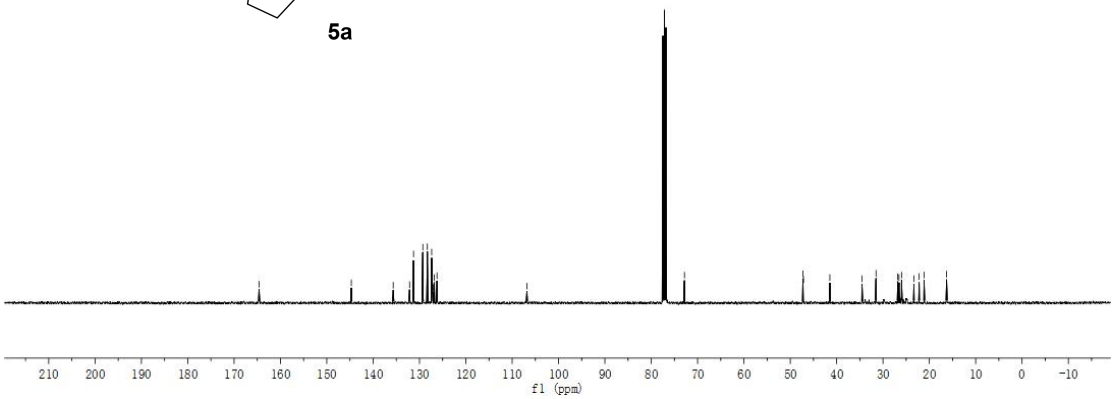


5a

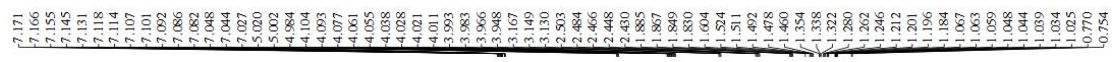


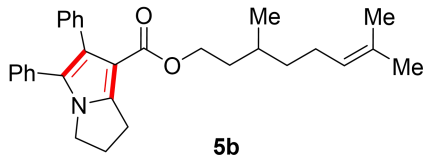


5a

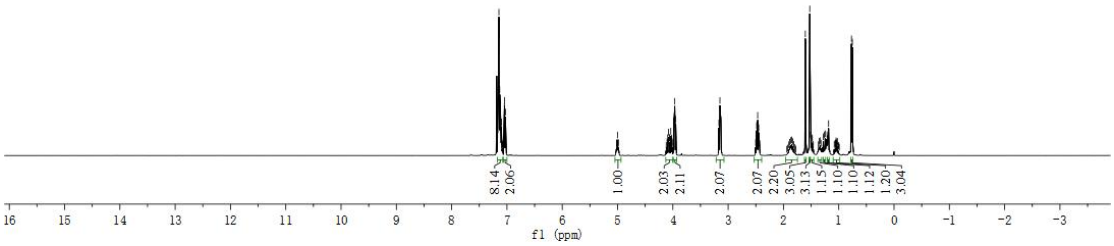


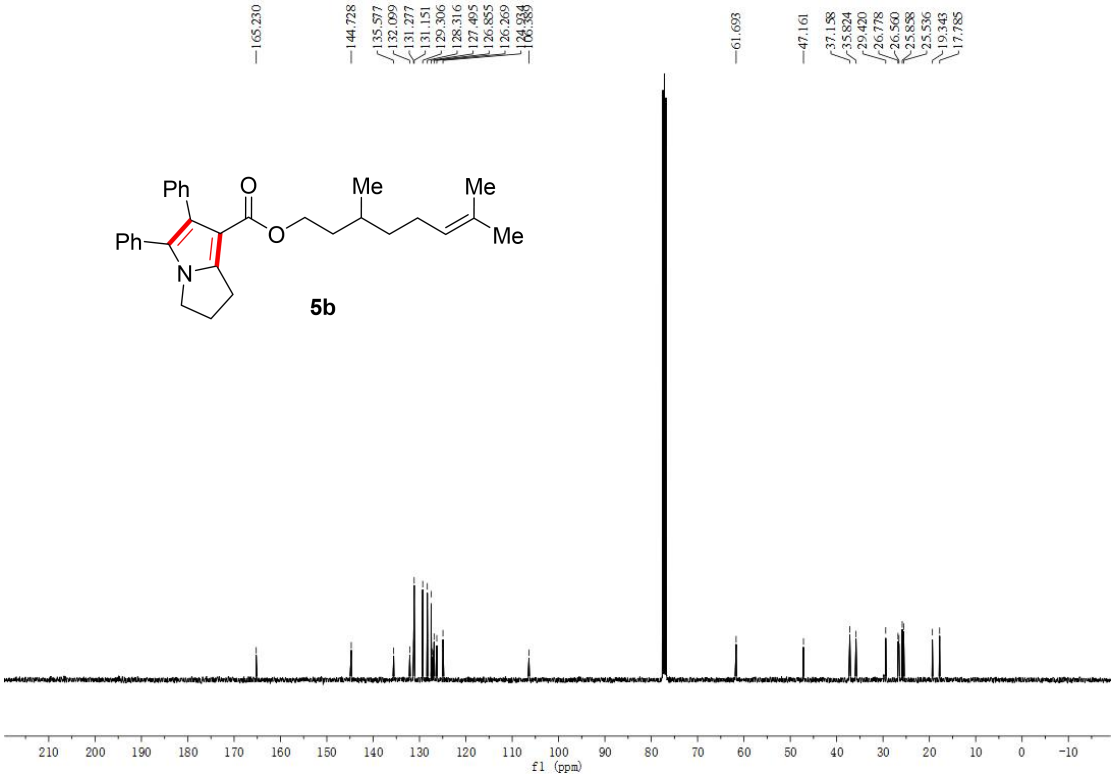
5b, $^{1}H+^{13}C$ NMR





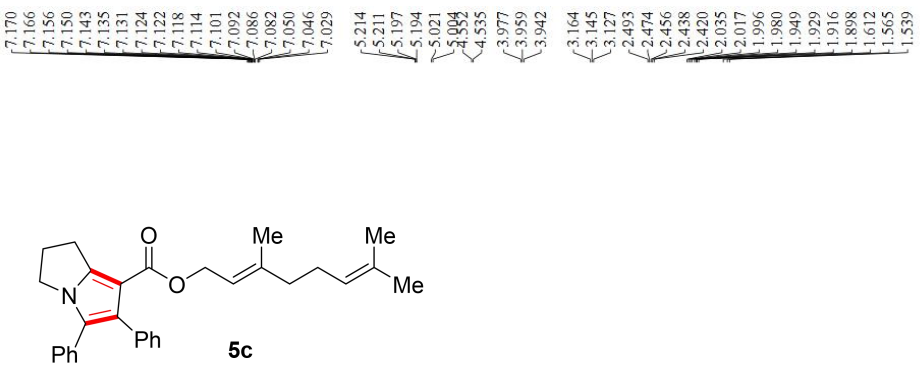
5b

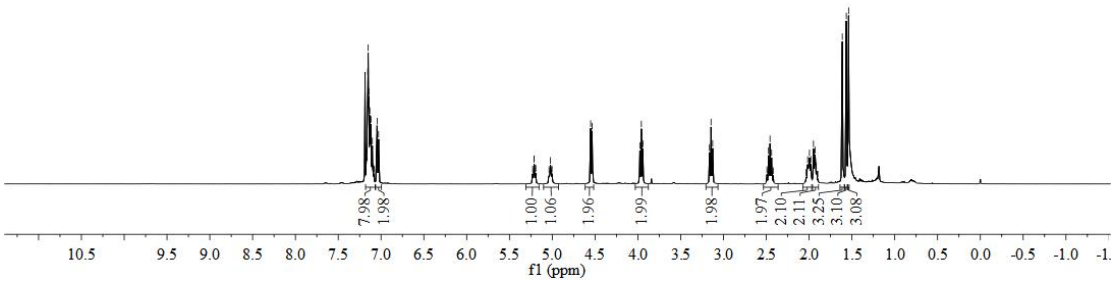


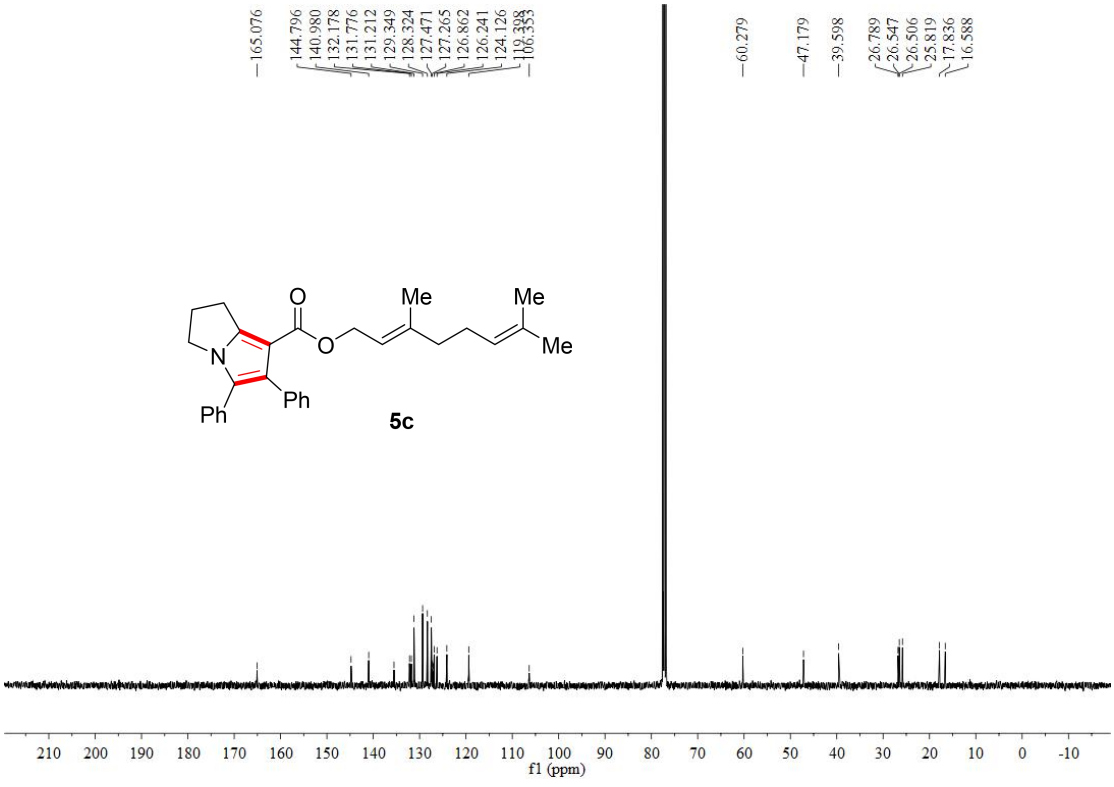


5b

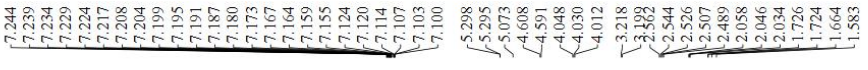
5c, $^{1}H+^{13}C$ NMR

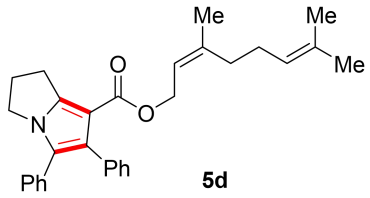

7.170
7.166
7.156
7.150
7.143
7.135
7.131
7.124
7.122
7.118
7.114
7.101
7.092
7.086
7.082
7.050
7.046
7.029
5.214
5.211
5.197
5.194
5.021
5.004
4.552
4.535
3.977
3.959
3.942
3.164
3.145
3.127
2.493
2.474
2.456
2.438
2.420
2.035
2.017
1.996
1.980
1.949
1.929
1.916
1.898
1.612
1.565
1.539
O
Me
Me
O
N
Me
Ph
Ph
5c


7.98
1.98
1.00
1.06
1.96
1.99
1.98
1.97
2.10
2.11
3.25
3.10
3.08
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

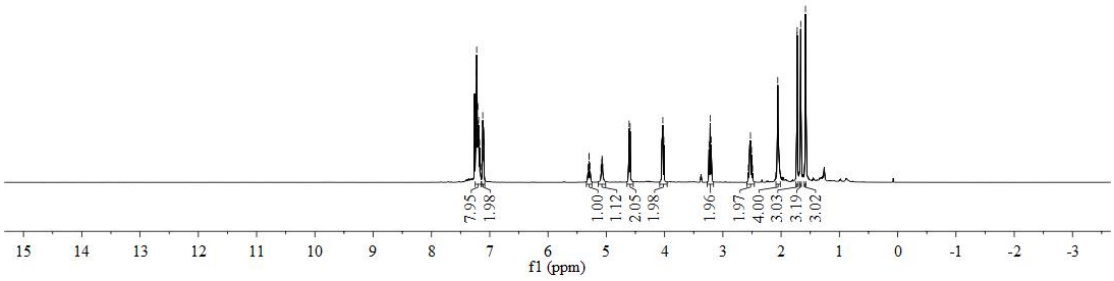

165.076
144.796
140.980
132.178
131.776
131.212
129.349
128.324
127.471
127.265
126.862
126.241
124.126
119.398
106.353
60.279
47.179
39.598
26.789
26.547
26.506
25.819
17.836
16.588
O
Me
Me
O
N
Me
Ph
Ph
5c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

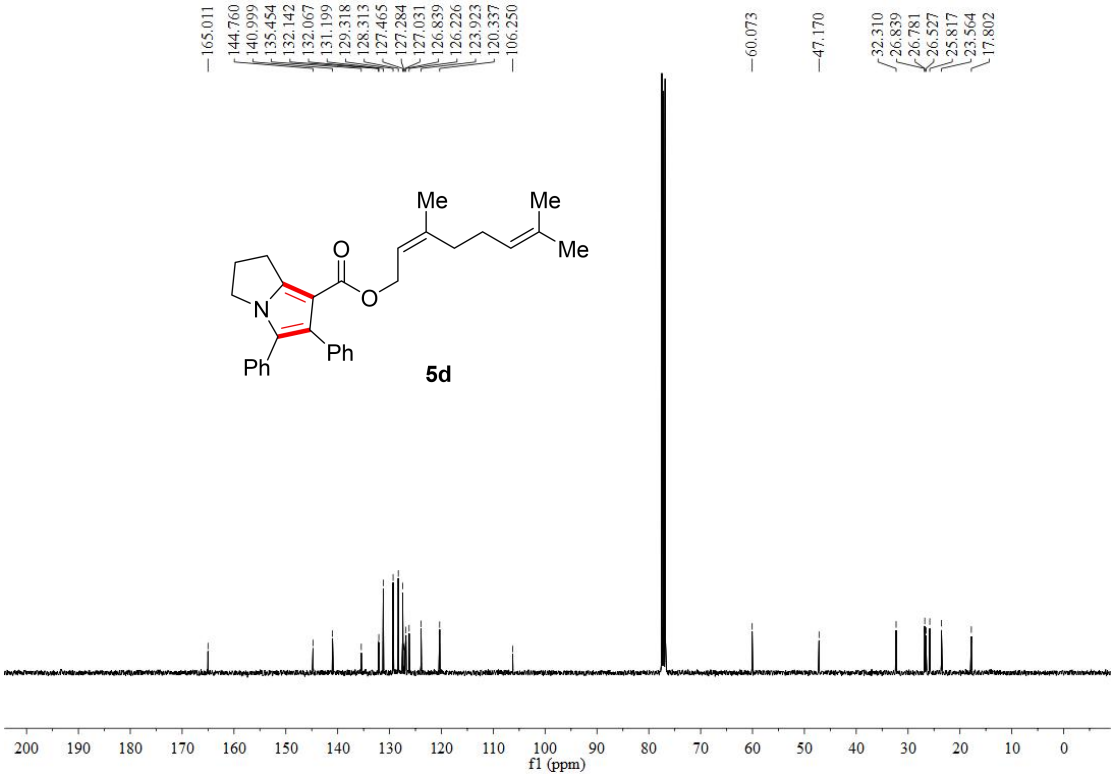
5d $^{1}H+^{13}C$ NMR





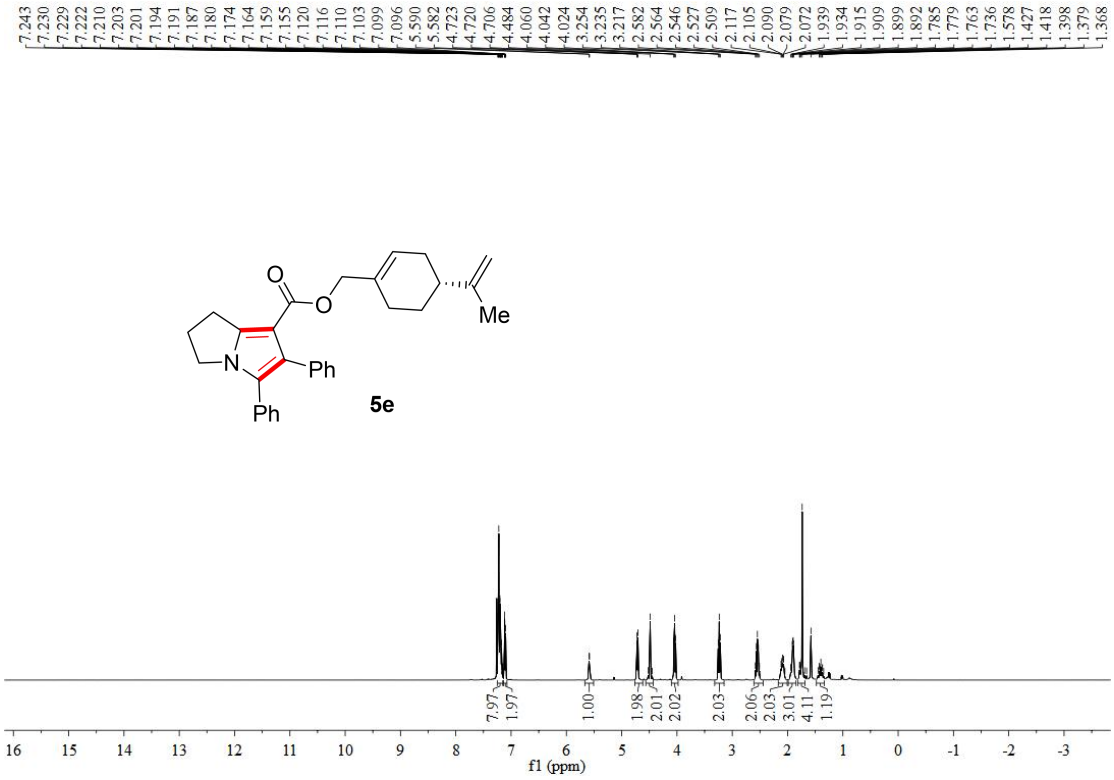
5d

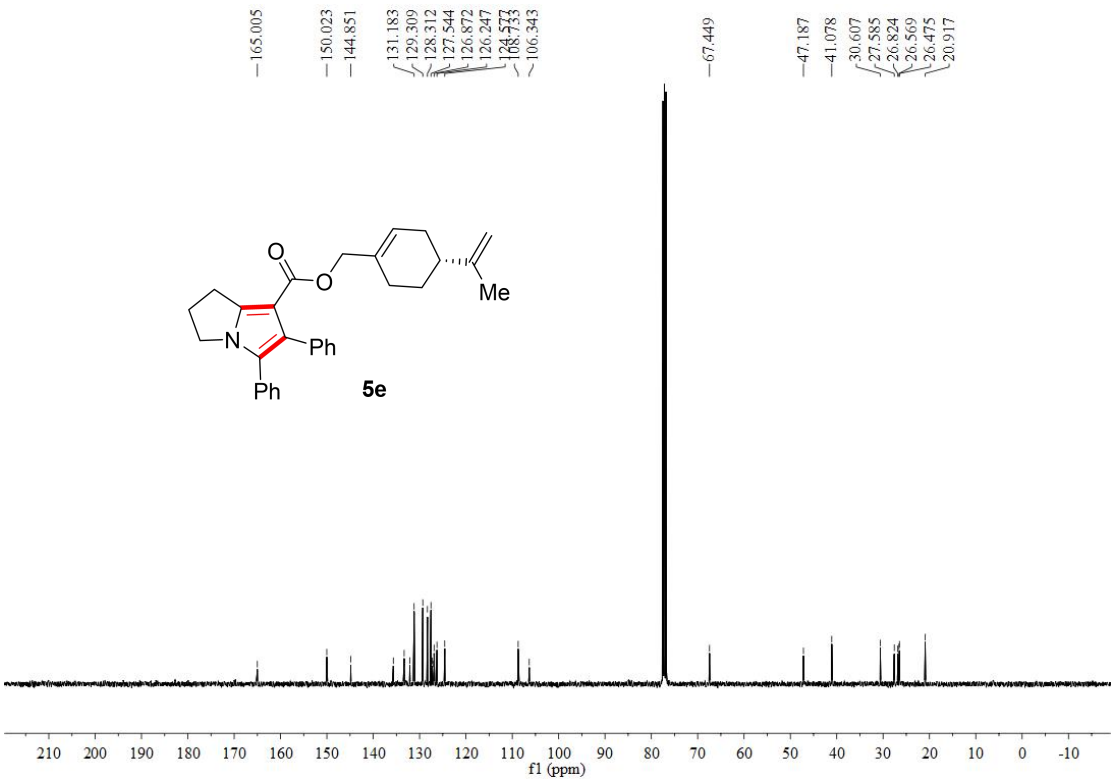




5d

5e, $^{1}H+^{13}C$ NMR


7.243
7.230
7.229
7.222
7.210
7.203
7.201
7.194
7.191
7.187
7.180
7.174
7.164
7.159
7.155
7.120
7.116
7.110
7.103
7.099
7.096
5.590
5.582
4.723
4.720
4.706
4.484
4.060
4.042
4.024
3.254
3.235
3.217
2.582
2.564
2.546
2.527
2.509
2.117
2.105
2.090
2.079
2.072
1.939
1.934
1.915
1.909
1.899
1.892
1.785
1.779
1.763
1.736
1.578
1.427
1.418
1.398
1.379
1.368
O
O
N
Ph
Ph
Me
5e
7.97
1.97
1.00
1.98
2.01
2.02
2.03
2.06
2.03
3.01
4.11
1.19
f1 (ppm)


165.005
150.023
144.851
131.183
129.309
128.312
127.544
126.872
126.247
124.573
108.733
106.343
67.449
47.187
41.078
30.607
27.585
26.824
26.569
26.475
20.917
O
O
N
Ph
Ph
Me
5e
f1 (ppm)