Supporting Information

Photoredox-catalyzed sequential Dowd–Beckwith ring expansion and C–H functionalization of THIQs

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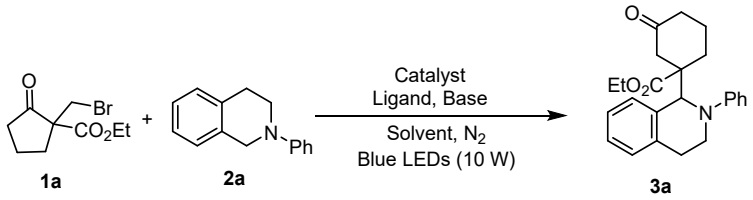
1 General information

The reactions were conducted in oven-dried reaction tube. And the photoinduced reactions were carried out in oven-dried Schlenk-tube with Wattecs blue LEDs Irradiation Parallel Reactor. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz (100 MHz for ^{13}C NMR) spectrometer at ambient temperature. Chemical shift are reported in ppm from TMS with the solvent resonance as internal standard ($CDCl_3$: ^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.0$). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). Active hydrogen of products didn't show due to hydrogen deuterium exchange in $CDCl_3$. FT-IR spectra were recorded on a Bruker V 70 spectrometer and only major peaks are reported in cm^{-1}. HRMS were obtained on a WATERS I-Class VION IMS Q-Tof. Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60F-254. Compounds were visualized by exposure to UV-light or by dipping the plates in 2,4-dinitrophenylhydrazine stain followed by heating.

2 Starting materials

The Dowd-Beckwith halides **1** and tetrahydroisoquinoline derivatives **2** were prepared according to the literature.[1, 2] The NMR spectra of the known compounds were in full accordance with the data in the literatures.

3 Detailed optimization of reaction conditions

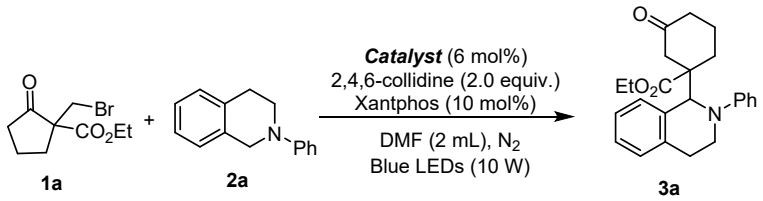


1a **2a** **3a**

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with *N*-phenyltetrahydroisoquinoline **2a** (0.20 mmol, 1.0 equiv.), catalyst, ligand and base under N_2 atmosphere (glovebox) (See Table S1). Subsequently, a solution of ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv.) in solvent (2.0 mL) was added by a syringe. The tube was capped with a pressure screw cap. The reaction mixture was stirred under the irradiation of a 10 W blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for a specified time. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/EtOAc: 8:1 to 5:1) furnishes the desired product **3a** as a light-yellow oil.

Table S1. Optimization of the reaction of ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate and *N*-phenyltetrahydroisoquinoline [a]

Catalysts

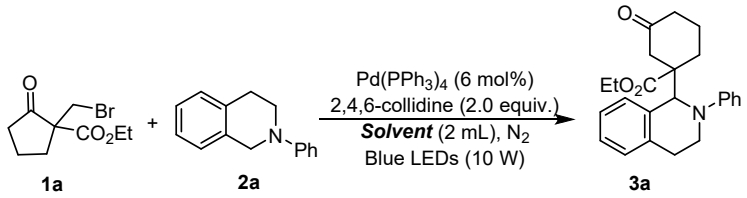


1a **2a** **3a**

Entry	Catalyst (6 mol%)	Yields (%)[b]
1	$Pd(PPh_3)_4$	44
2	$Pd_2(dba)_3$	30
3	$Pd(PPh_3)_2Cl_2$	17
4	$Pd(CH_3CN)_2Cl_2$	9
5	$Pd(PhCN)_2Cl_2$	24
6	$Pd(acac)_2$	15
7	$Pd(PPh_3)(OAc)_2$	16
8	$PdCl_2$	10
9	$Pd(OAc)_2$	21
10	$Pd(TFA)_2$	16
11[d]	$Pd(PPh_3)_4$	42
12	$Cu(MeCN)_4PF_6$	n.r.
13	$NiBr_2$	trace
14	$Fe(NO_3)_2 \cdot 9H_2O$	trace

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 6 mol% of catalyst, 10 mol% of Xantphos, 2,4,6-collidine (0.4 mmol, 2.0 equiv.), DMF (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2. [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard, d.r. =1:1. [c]n.r. = no reaction. [d]Without Xantphos.

Solvent

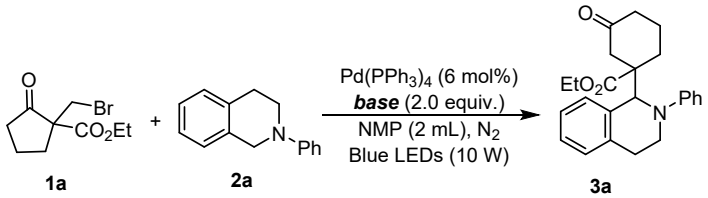


1a **2a** **3a**

Entry	Solvent	Yields (%)[b]
1	CH_3CN	36
2	DMSO	26
3	DMA	33
4	DMF	42
5	1,4-dioxane	18
6	THF	24
7	MTBE	15
8	acetone	26
9	toluene	17
10	$PhCF_3$	21
11	EA	15
12	NMP	56 (53)[c]
13	*n*-hexane	21
14	HMPA	48
15	MeOH	trace
16	CH_3NO_2	trace
17	DCM	trace

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 6 mol% of $Pd(PPh_3)_4$, 2,4,6-collidine (0.4 mmol, 2.0 equiv.), Solvent (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2. [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard, d.r. =1:1. [c]Yields of isolated product.

Base

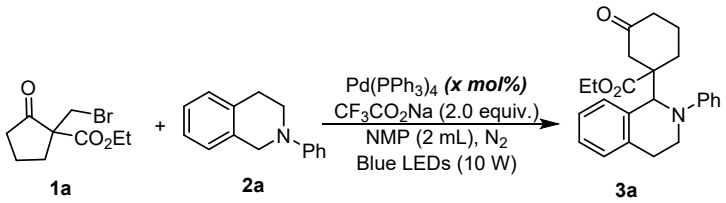


1a **2a** **3a**

Entry	Base (2.0 equiv.)	Yields (%)[b]
1	Et_3N	14
2	DIPEA	16
3	Pyridine	14
4	2,6-Lutidine	45
5	DABCO	20
6	DBU	trace
7	TMG	< 10
8	DMAP	36
9	2,4-Lutidine	42
10	4-pyrrolidinopyridine	23
11	4-cyanopyridine	trace
12	4-picoline	54 (45)[c]
13[d]	2- picoline	30
14	K^{t}BuO	trace
15	4-methoxypyridine	38
16	K_2CO_3	< 10
17	K_3PO_4	< 10
18	Cs_2CO_3	trace
19	Li_2CO_3	35
20	$NaHCO_3$	45
21	2,4,6-collidine	56 (53)[c]
22	CF_3CO_2Na	58 (55)[c]
23	$NaHPO_4$	48
24	$NaSO_2CF_3$	trace
25	NaOAc	trace
26	KOAc	< 10

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 6 mol% of $Pd(PPh_3)_4$, base (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2. [b]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard, d.r. =1:1. [c]Yields of isolated product.

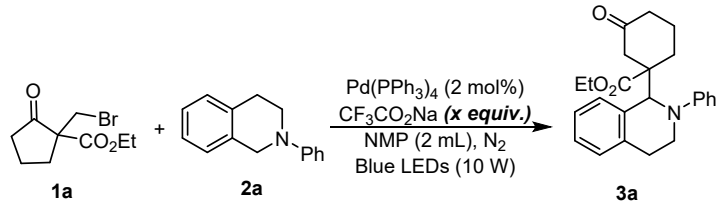
Ratio of catalyst



Entry	$Pd(PPh_3)_4$ (x mol%)	Yields (%)[b]
1	1	36
2	2	66 (64)[c]
3	4	60
4	6	58
5	8	54

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), x mol% of $Pd(PPh_3)_4$, CF_3CO_2Na (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2. [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard, d.r. =1:1. [c]Yield of isolated product.

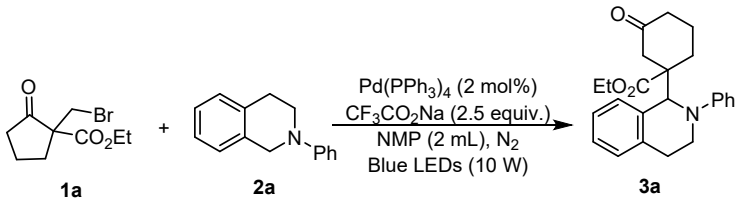
Ratio of base



Entry	CF_3CO_2Na (x equiv.)	Yields (%)[b]
1	3.5	48
2	3	67
3	2.5	72 (69)[c]
4	2	66 (64)[c]
5	1.5	57
6	1	36
7	0.5	18
8	0.2	24

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 2 mol% of $Pd(PPh_3)_4$, CF_3CO_2Na (x equiv.), NMP (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2. [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard, d.r. =1:1. [c]Yield of isolated product.

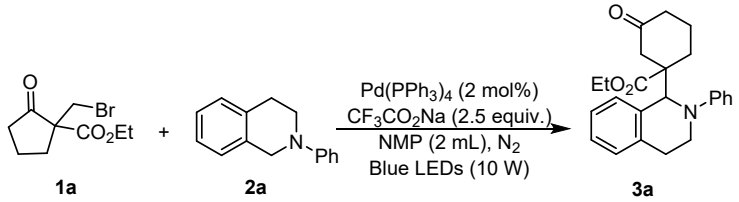
Ratio of 1a:2a



Entry	**1a**:**2a**	Yields (%)[b]
1	1:1	48
2	1.5:1	72 (69)[c]
3	2:1	48
4	1:2	48

[a]Reaction conditions: **1a** : **2a** = x, 2 mol% of $Pd(PPh_3)_4$, CF_3CO_2Na (2.5 equiv.), NMP (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2. [b]Yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard, d.r. =1:1. [c]Yield of isolated product.

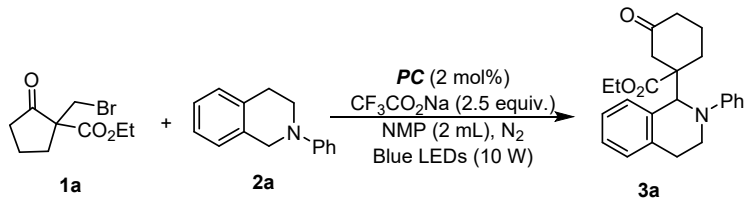
Controlled experiments



Entry	Conditions	Yields (%)[b]
1	-	72
2	Without $Pd(PPh_3)_4$	n.r.
3	Without CF_3CO_2Na	trace
4	In the dark	n.r.
5	O_2	0
6	PPh_3 (5 mol%)	62
7	Xantphos (5 mol%)	60

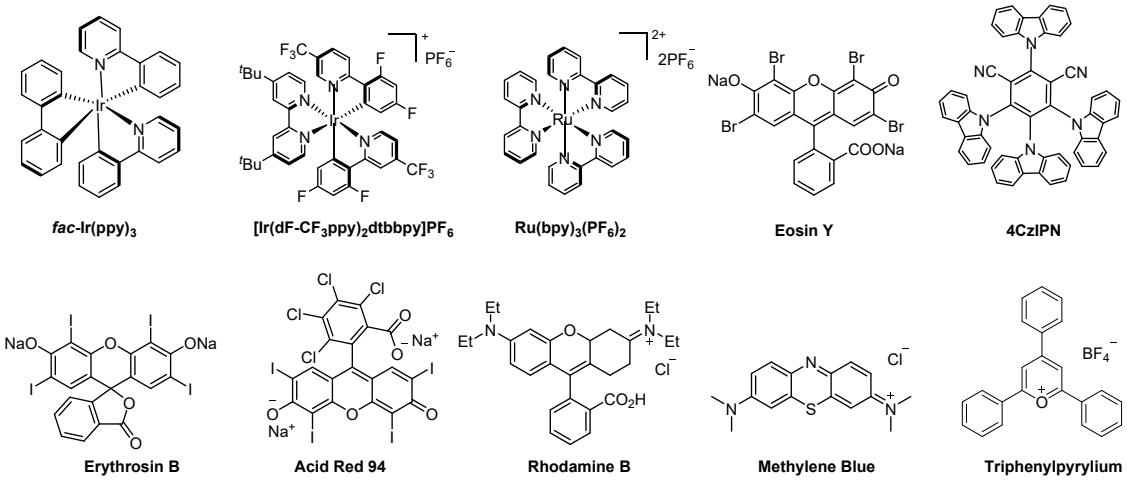
[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 2 mol% of $Pd(PPh_3)_4$, CF_3CO_2Na (2.5 equiv.), NMP (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2. [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard, d.r. =1:1.

Photocatalyst (PC)

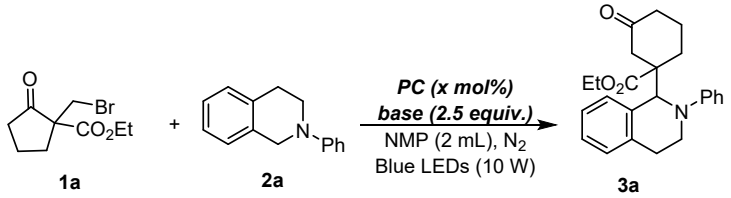


Entry	PC	Yields (%)[b]
1	*fac*-Ir(ppy)$_3$	60
2	Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$	48
3	Ru(bpy)$_3$Cl$_2$	trace
4	Eosin Y	54
5	4CzIPN	48
6	Erythrosin B	42
7	Acid Red 94	48
8	Rhodamine B	42
9	Methylene Blue	36
10	Triphenylpyrylium	48

[a] Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 2 mol% of PC, CF_3CO_2Na (2.5 equiv.), NMP (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2. [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard, d.r. =1:1.



Others

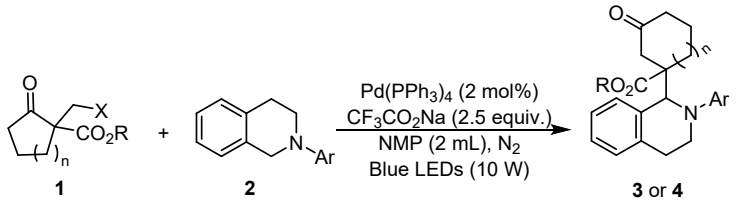


Entry	PC (x mol%)	Base	Yields (%) [b]
1	Eosin Y (1)	CF_3CO_2Na	18
2	*fac*-Ir(ppy)$_3$ (1)	CF_3CO_2Na	78
3	*fac*-Ir(ppy)$_3$ (0.5)	CF_3CO_2Na	68
4	*fac*-Ir(ppy)$_3$ (2)	CF_3CO_2Na	60
5	*fac*-Ir(ppy)$_3$ (1)	$NaHCO_3$	54
6	*fac*-Ir(ppy)$_3$ (1)	K_2CO_3	50
7	*fac*-Ir(ppy)$_3$ (1)	NaOAc	53
8	*fac*-Ir(ppy)$_3$ (1)	2,4,6-collidine	38
9	*fac*-Ir(ppy)$_3$ (1)	Et_3N	60
10	*fac*-Ir(ppy)$_3$ (1)	DABCO	trace
11	*fac*-Ir(ppy)$_3$ (1)	DIPEA	42
12	*fac*-Ir(ppy)$_3$ (1)	-	24

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), x mol% of PC, base (2.5 equiv.), NMP (2.0 mL), Blue LEDs (10 W), r.t., for 24 h, under N_2, d.r. =1:1. [b]Yield of isolated product.

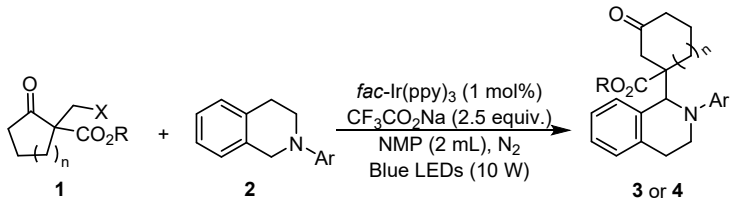
4 Representative procedure for the coupling of Dowd-Beckwith halides 1 with tetrahydroisoquinoline Derivatives 2

(1) Palladium-catalyzed procedure



A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with tetrahydroisoquinoline derivatives **2** (0.20 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (4.6 mg, 2 mol%), CF_3CO_2Na (0.50 mmol, 2.5 equiv.) under N_2 atmosphere (glovebox). Subsequently, a solution of Dowd-Beckwith halides **1** (0.30 mmol, 1.5 equiv.) in NMP (2.0 mL) was added by a syringe. The tube was capped with a pressure screw cap. The reaction mixture was stirred under the irradiation of a 10 W blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for a specified time. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/EtOAc: 8:1 to 5:1) furnishes the desired products **3** and **4** in yields listed in Scheme 3 and Scheme 4.

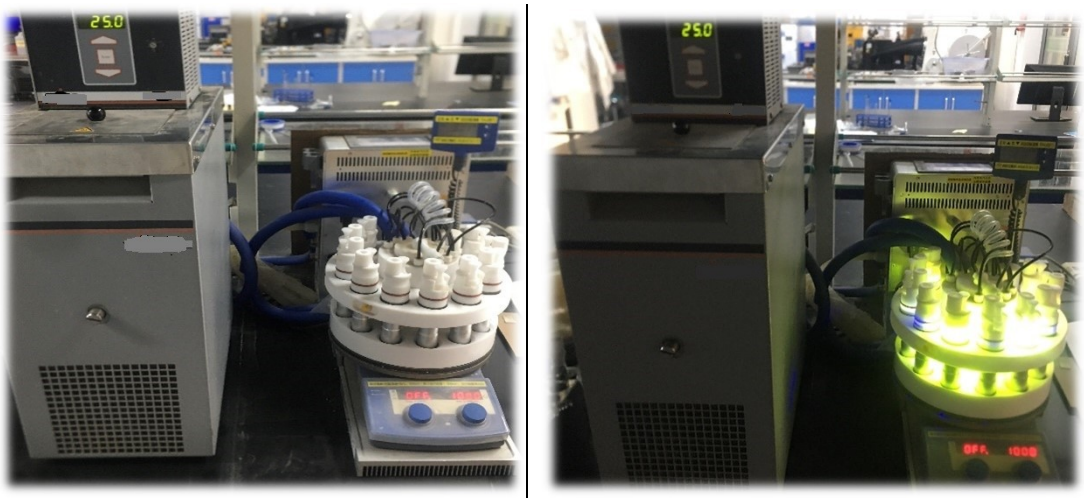
(2) Iridium-catalyzed procedure



A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with tetrahydroisoquinoline derivatives **2** (0.20 mmol, 1.0 equiv.), *fac*-$Ir(ppy)_3$ (1.3 mg, 1 mol%) and CF_3CO_2Na (0.50 mmol, 2.5 equiv.) under N_2 atmosphere (glovebox). Subsequently, a solution of Dowd-Beckwith halides **1** (0.30 mmol, 1.5 equiv.) in NMP (2.0 mL) was added by a syringe. The tube was capped with a pressure screw cap. The reaction mixture was stirred under the irradiation of a 10 W blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for a specified time.

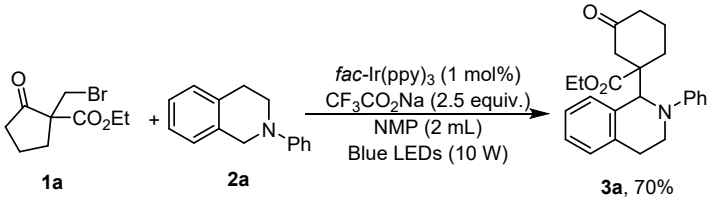
After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/EtOAc: 8:1 to 5:1) furnishes the desired products **3** and **4** in yields listed in Scheme 3 and Scheme 4.

The Visible-Light Photoredox Catalysis Experimental Setup (photographed by author Li-Na Guo)



Scale-up reaction

A 50 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with *N*-phenyltetrahydroisoquinoline **2a** (2 mmol, 1.0 equiv.), *fac*-Ir(ppy)$_3$ (13 mg, 1 mol%) and CF_3CO_2Na (5 mmol, 2.5 equiv.) under N_2 atmosphere (glovebox). Subsequently, a solution of Dowd-Beckwith bromide **1a** (3 mmol, 1.5 equiv.) in NMP (20 mL) was added by a syringe. The tube was capped with a pressure screw cap. The reaction mixture was stirred under the irradiation of a 10 W blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 60 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/EtOAc: 8:1 to 5:1) furnishes the desired product **3a** (70%, 527.8 mg).

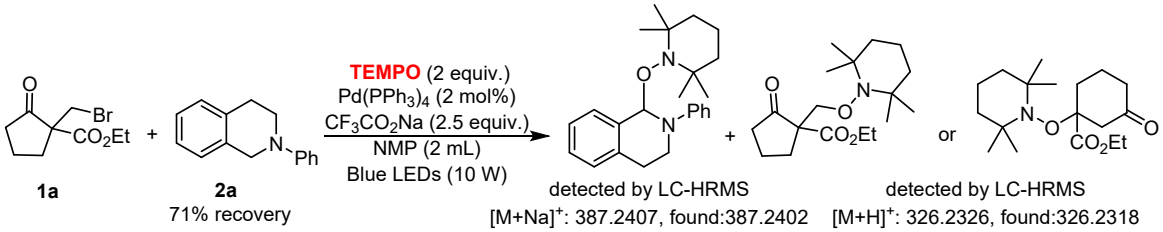


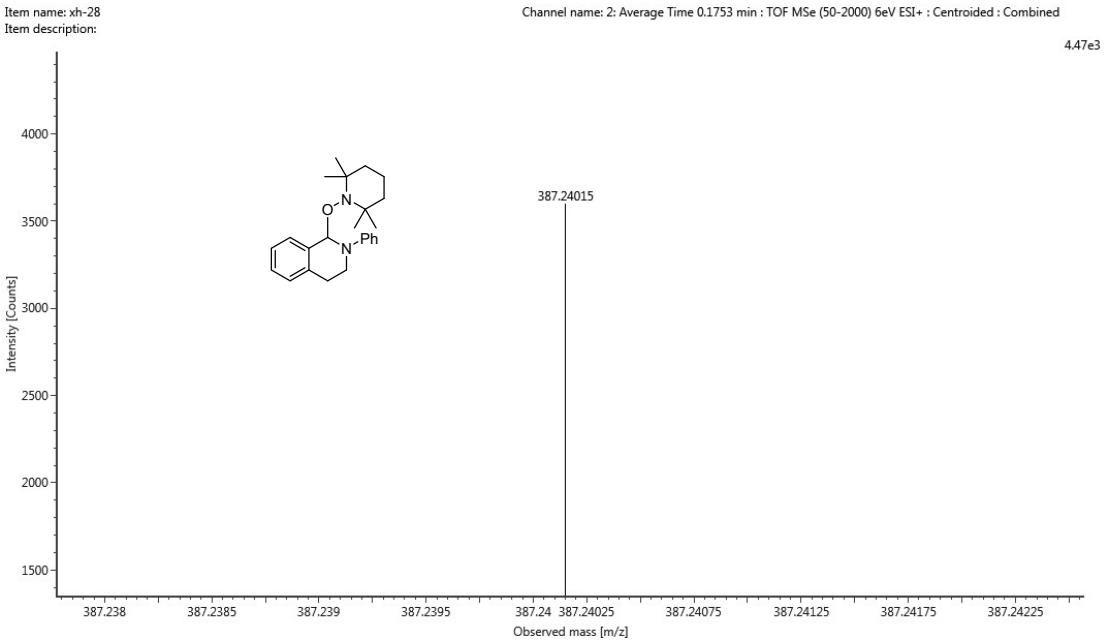
1a **2a** **3a**, 70%

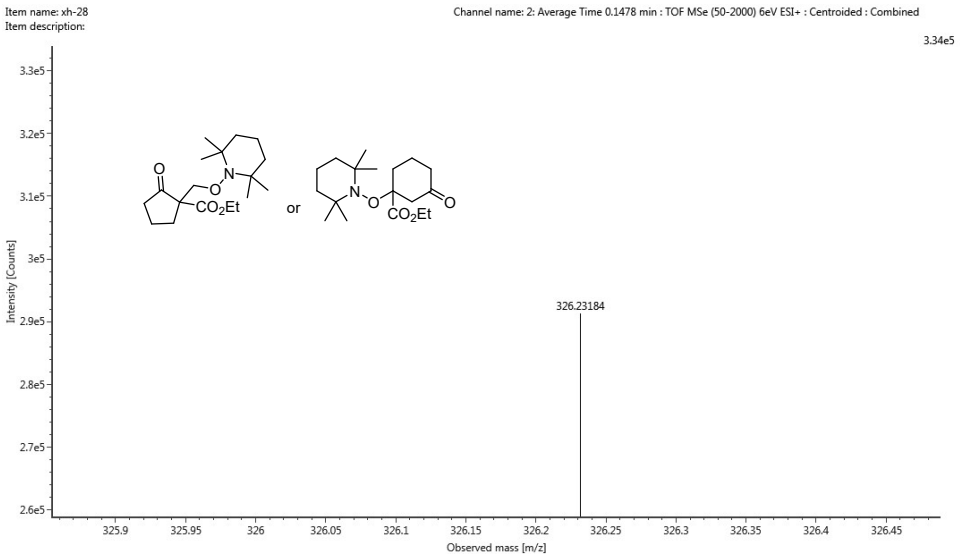
5 Mechanistic investigation

(1) Radical inhibiting experiment

a) Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv.), *N*-phenyltetrahydroisoquinoline **2a** (0.20 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (4.6 mg, 2 mol%), CF_3CO_2Na (0.50 mmol, 2.5 equiv.), TEMPO (0.4 mmol, 2.0 equiv.), NMP (2.0 mL) under N_2 for 24 h, with the irradiation of 10 W Blue LEDs.

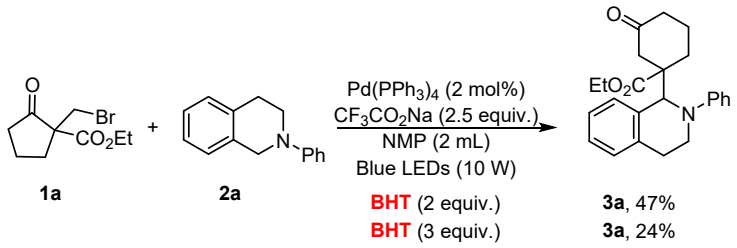






When 2.0 equiv. of TEMPO was subjected into the reaction of **1a** with **2a** under the standard conditions (Pd catalytic system), only a trace amount of **3a** was observed, along with the TEMPO adducts were detected by LC-HRMS (Calcd for $C_{24}H_{32}N_2NaO$ $[M+Na]^+$: 387.2407, found:387.2402, Calcd for $C_{18}H_{32}NO_4$ $[M+H]^+$: 326.2326, found: 326.2318). In this case, 71% of **2a** was recovered. This result indicates that a radical intermediate might be involved in this transformation.

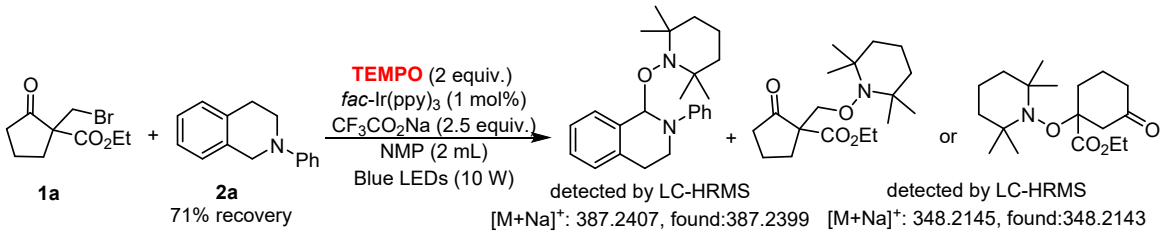
b) Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv.), *N*-phenyltetrahydroisoquinoline **2a** (0.20 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (4.6 mg, 2 mol%), CF_3CO_2Na (0.50 mmol, 2.5 equiv.), BHT (2.0 equiv., 3.0 equiv.), NMP (2.0 mL) under N_2 for 24 h, with the irradiation of 10 W Blue LEDs.

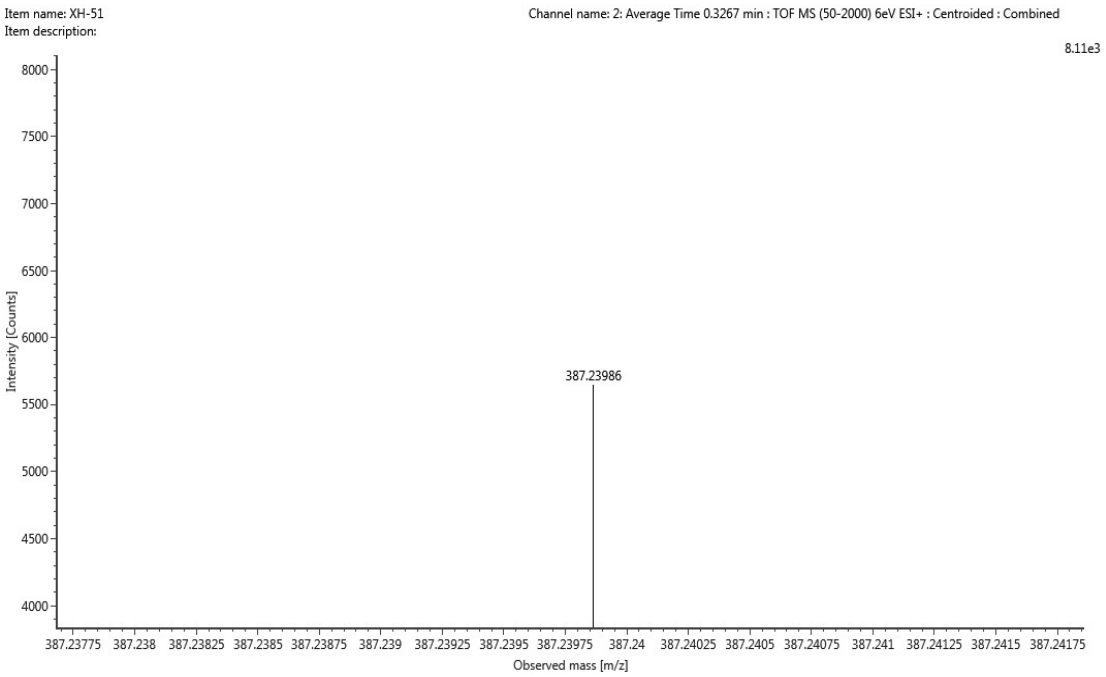


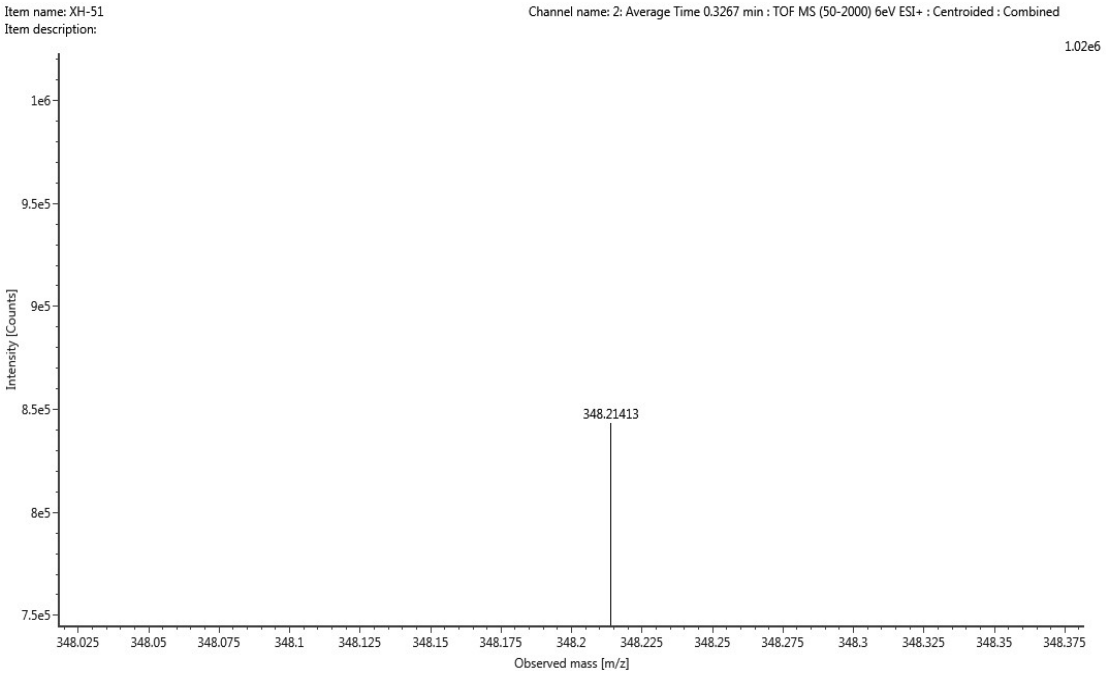
When 2.0 equiv and 3.0 equiv of BHT was added to the reaction of **1a** with **2a** under the standard conditions (Pd catalytic system), respectively, the yield of product **3a** was dramatically decreased (from 72% to 47% to and 24%). These results support a radical pathway for the reaction.

c) Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv.), *N*-phenyltetrahydroisoquinoline **2a** (0.20 mmol, 1.0 equiv.), *fac*-$Ir(ppy)_3$ (1.3 mg, 1 mol%),

CF_3CO_2Na (0.50 mmol, 2.5 equiv.), TEMPO (0.4 mmol, 2.0 equiv.), NMP (2.0 mL) under N_2 for 24 h, with the irradiation of 10 W Blue LEDs.

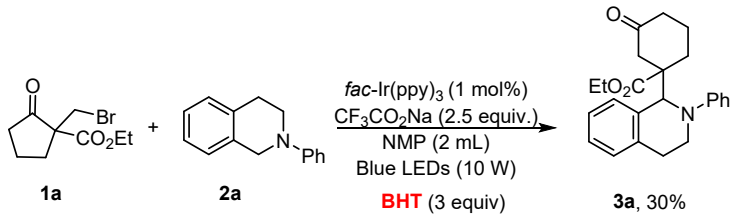






When 2.0 equiv of TEMPO was subjected into the reaction of **1a** with **2a** under the standard conditions (Ir catalytic system), the reaction is completely suppressed and the TEMPO adducts were detected by LC-HRMS (Calcd for $C_{24}H_{32}N_2NaO$ $[M+Na]^+$: 387.2407, found:387.2402, Calcd for $C_{18}H_{32}NO_4$ $[M+Na]^+$: 348.2145, found: 348.2143). This result indicates that a radical intermediate might be involved in this transformation.

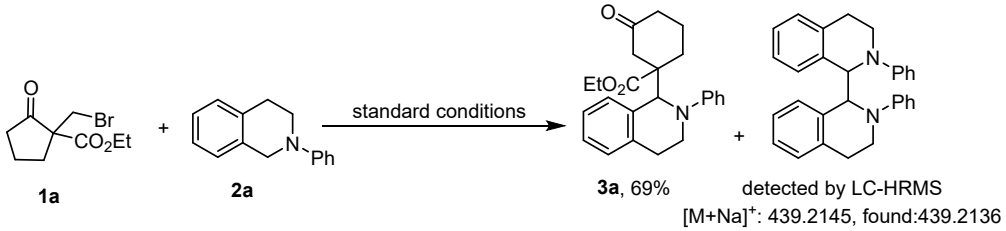
d) Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv), *N*-phenyltetrahydroisoquinoline **2a** (0.20 mmol, 1.0 equiv.), *fac*-Ir(ppy)$_3$ (1.3 mg, 1 mol%), CF_3CO_2Na (0.50 mmol, 2.5 equiv.), BHT (0.6 mmol, 3.0 equiv.), NMP (2.0 mL) under N_2 for 24 h, with the irradiation of 10 W Blue LEDs.

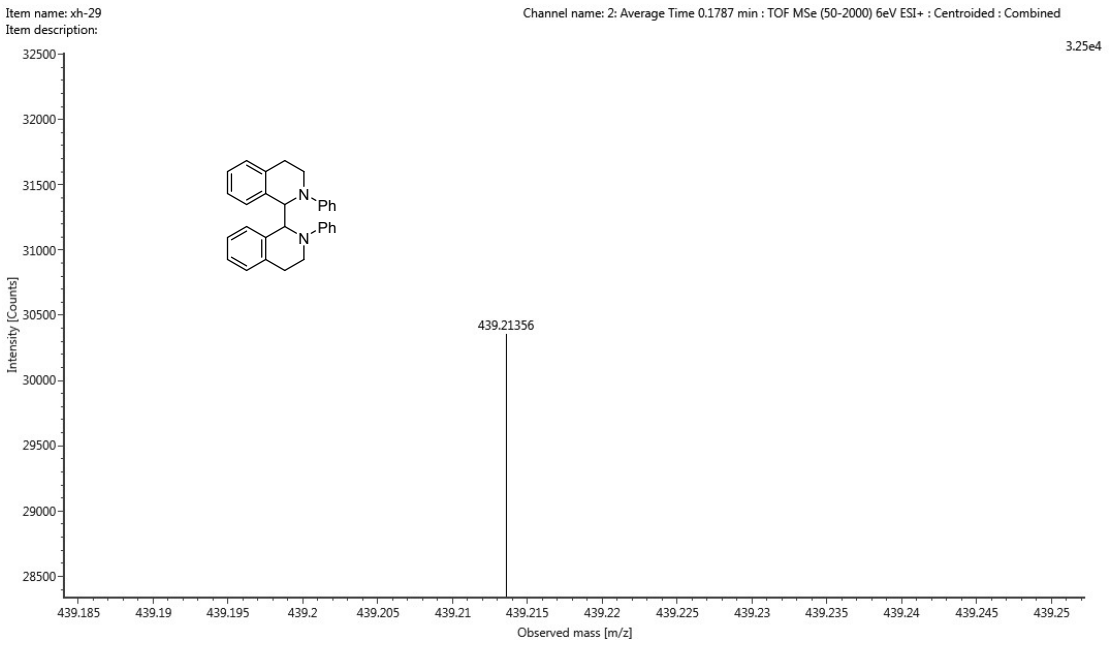


When 3.0 equiv of BHT was added to the reaction of **1a** with **2a** under the standard conditions (Ir catalytic system), the yield of product **3a** was dramatically decreased (from 78% to 30%). These results support a radical pathway for the reaction.

(2) Control experiments

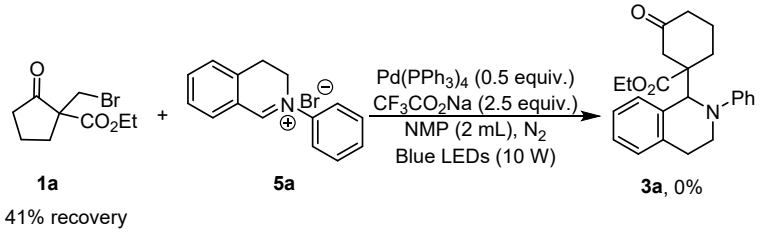
a) Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv.), *N*-phenyltetrahydroisoquinoline **2a** (0.20 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (4.6 mg, 2 mol%), CF_3CO_2Na (0.50 mmol, 2.5 equiv.), NMP (2.0 mL) under N_2 for 24 h, with the irradiation of 10 W Blue LEDs.



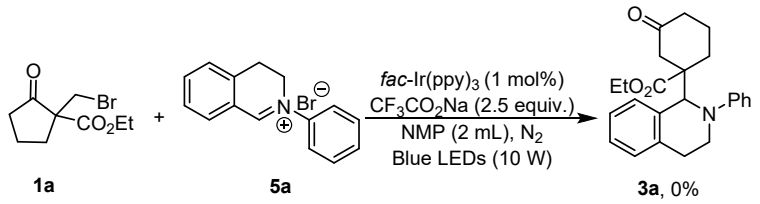


The product **3a** was isolated in 69% yield, along with the homo-coupling product was detected by LC-HRMS (Calcd for $C_{30}H_{28}N_2Na$ $[M+Na]^+$: 439.2145, found:439.2136) under standard condition . This result suggests that tetrahydroisoquinoline radical was generated in the reaction.

b) Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv.), the imide salt **5a** (0.20 mmol, 1.0 equiv.)[3], $Pd(PPh_3)_4$ (115.4 mg, 0.5 equiv.), CF_3CO_2Na (0.50 mmol, 2.5 equiv.), NMP (2.0 mL) under N_2 for 24 h, with the irradiation of 10 W Blue LEDs.



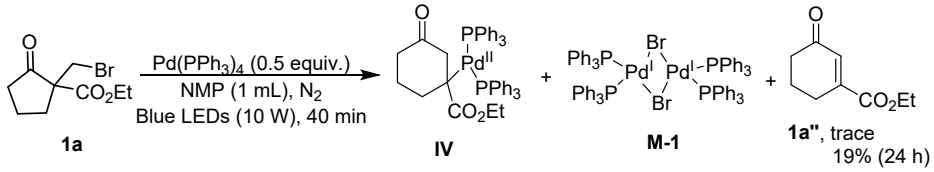
Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv.), the imide salt **5a** (0.20 mmol, 1.0 equiv.), *fac*-$Ir(ppy)_3$ (1.3 mg, 1 mol%), CF_3CO_2Na (0.50 mmol, 2.5 equiv.), NMP (2.0 mL) under N_2 for 24 h, with the irradiation of 10 W Blue LEDs.

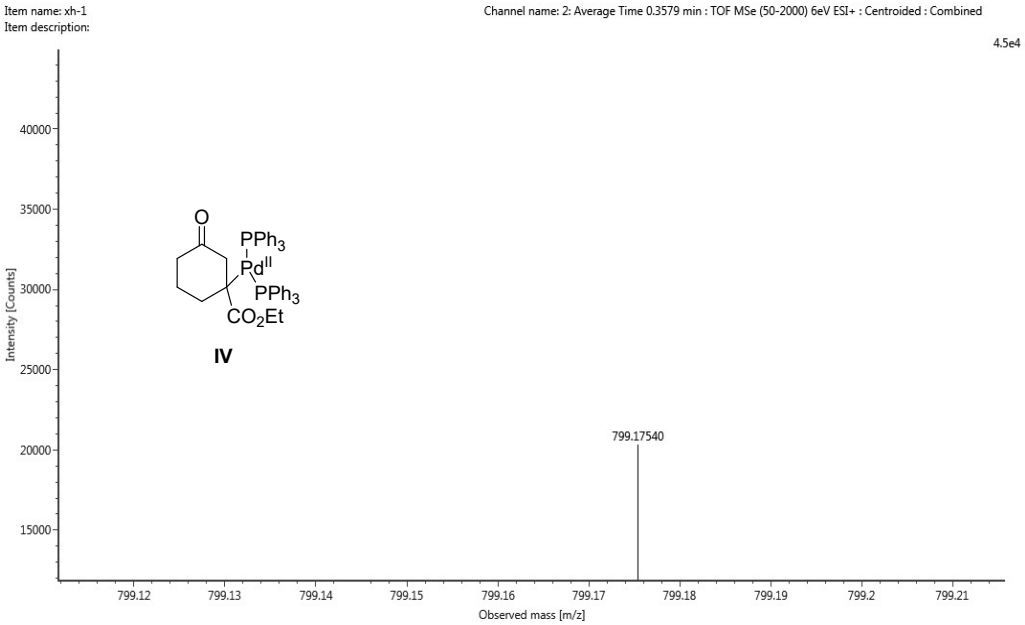


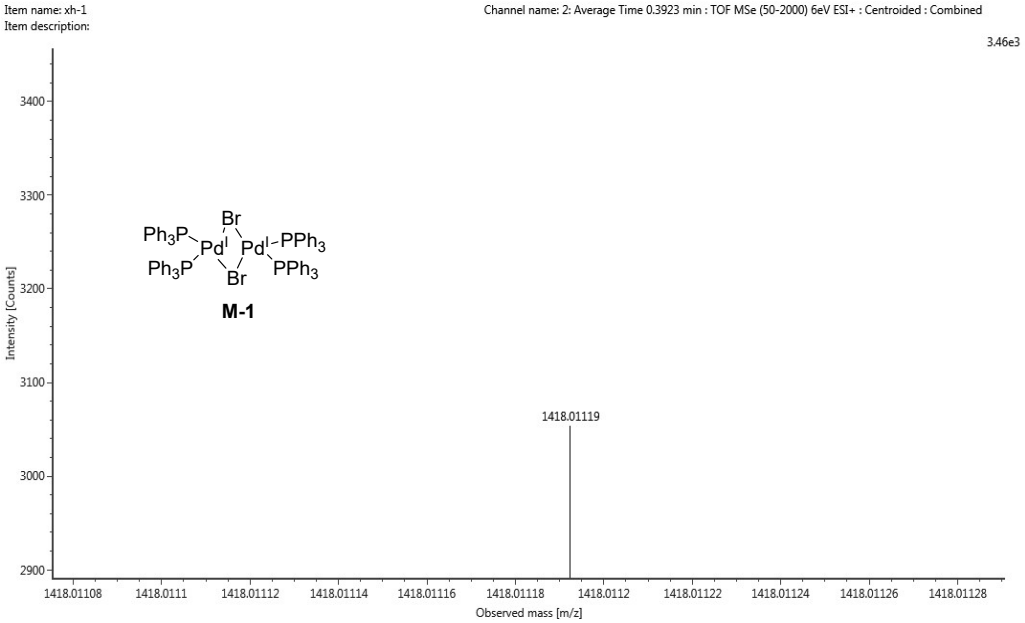
When the imide salt **5a** was used instead of **2a** under the standard conditions, no desired product **3a** was observed. This result indicates that the imide salt **5a** might not be the intermediate in this transformation.

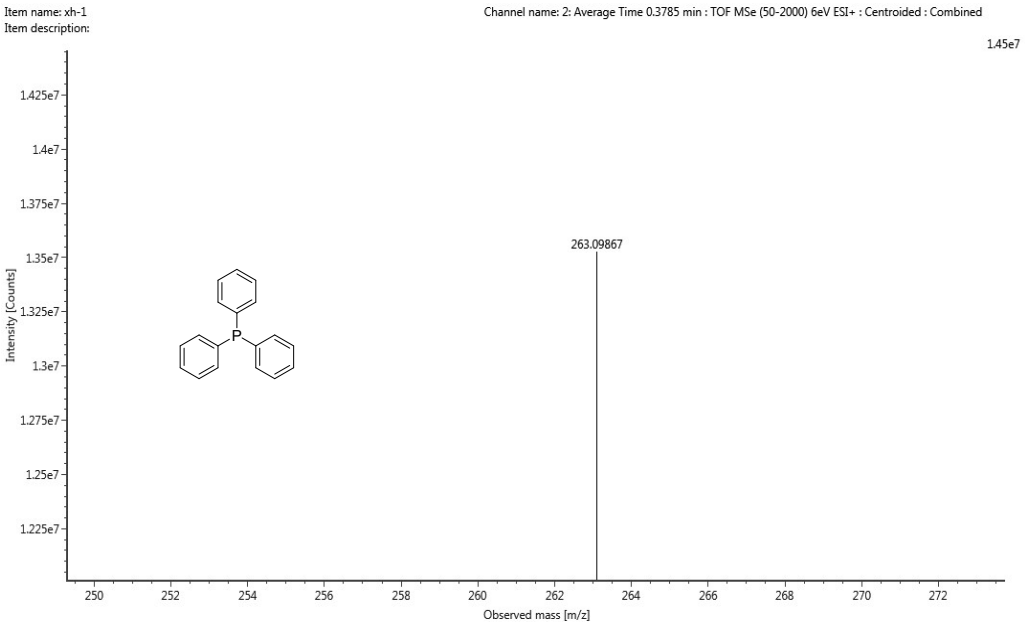
(3) Mass spectrometry experiments

Procedure 1: $Pd(PPh_3)_4$ (0.05 mmol) and Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.10 mmol) were dissolved in NMP (1 mL), and the mixture was stirred under the irradiation of a 10 W blue LED for 40 minutes. After 40 minutes, 5 μL reaction mixture was picked up and dissolvent into 1 mL MeCN. The mixture was injected into the LC-HRMS, and we collected MS data. In addition, the reaction time extended to 24 h, 19% yield of **1a''** was obtained.



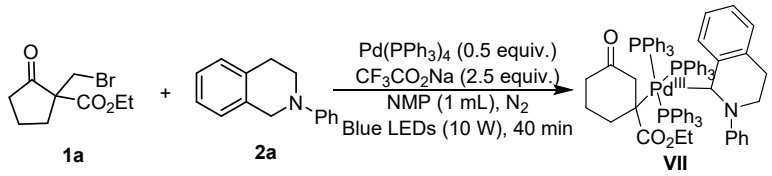


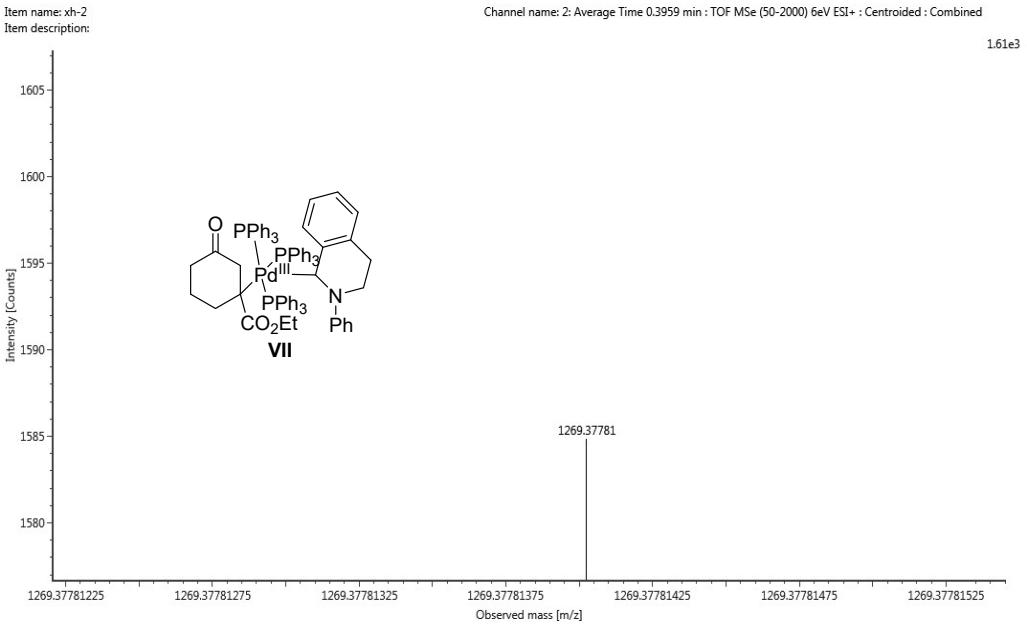




We successfully detected the intermediate **IV** singnal (Calcd for $C_{45}H_{43}O_3P_2Pd^{II}$ $[M]^+$:799.1722, found: 799.1754). In addition, the Pd(I) complex might undergo dimerization and release PPh_3 under visible-light irradiation, and the dimers **M-1** and PPh_3 was detected by LC-HRMS (**M-1**: Calcd for $C_{72}H_{60}Br_2P_4Pd_2^I$ $[M]^+$:1418.0082, found: 1418.0112; PPh_3: $C_{18}H_{16}P$ $[M+H]^+$: 263.0984, found: 263.0987).

Procedure 2: Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.15 mmol), *N*-phenyltetrahydroisoquinoline **2a** (0.10 mmol), $Pd(PPh_3)_4$ (0.05 mmol), CF_3CO_2Na (0.25 mmol), were dissolved in NMP (1 mL), and the mixture was stirred under the irradiation of a 10 W blue LED for 40 minutes. After 40 minutes, 5 μL reaction mixture was picked up and dissolvent into 1 mL MeCN. The mixture was injected into the LC-HRMS, and we collected MS data.





We successfully detected the intermediate **VII** singnal (Calcd for $C_{78}H_{72}NO_3P_3Pd^{III}$ $[M]^+$:1269.3760, found: 1269.3778). This result suggests that Pd(III) complex was generated in the reaction.

(4) ^{31}P NMR studies

$Pd(PPh_3)_4$ (0.05 mmol) and Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.10 mmol) were dissolved in DMF (1 mL), and the mixture was stirred under the irradiation of a 10 W blue LED for 4 h and 24 h .

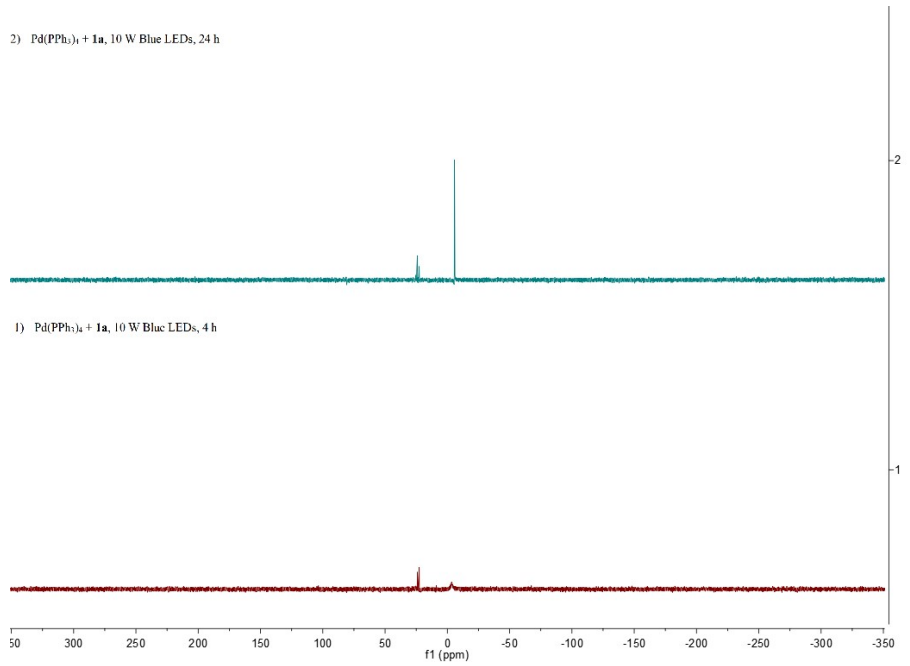


Figure S1 ^{31}P NMR Spectrum

The ^{31}P NMR spectrum of the solution of $Pd(PPh_3)_4$ in DMF exhibited a broad signal at 14.8 ppm[2]. When **1a** was added, new signals appeared at 22.6 ppm and 24.1 ppm after irradiation for 4 h and 24 h by 10 W Blue LEDs, this is attributable to the interaction between Pd species and **1a**, Pd(I) complex and Pd (II) complex would be generated. In addition, Pd(I) complex might undergo dimerization and release PPh_3 (-5.7 ppm) under visible-light irradiation after 24 h.

(5) Stern-volmer fluorescence quenching experiments

To a solution of $Pd(PPh_3)_4$ in anhydrous, N_2-saturated DMF (2×10^{-3} mol/L) in a quartz cuvette, different amounts of Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** and *N*-phenyltetrahydroisoquinoline **2a** were added, respectively, and the resulting changes in fluorescence intensity (concentration of **1a** and **2a**: 0.5×10^{-3} mol/L, 1.0×10^{-3} mol/L, 1.5×10^{-3} mol/L, 2.0×10^{-3} mol/L, 2.5×10^{-3} mol/L were collected. The emission intensity at 600 nm was collected with excited wavelength of 415 nm. The results are shown in Figure S2 and S3.

(a) (b)

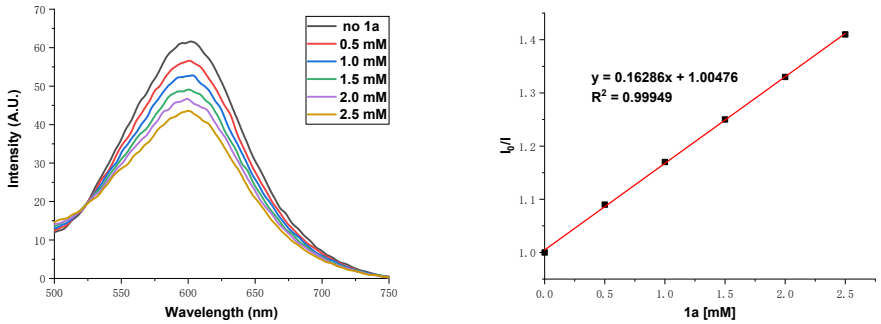


Figure S2 (a) The fluorescence emission spectra of $Pd(PPh_3)_4$ with different concentration of **1a** added. (b) The Stern–Volmer emission quenching studies of **1a**. I_0 is the inherent fluorescence intensity of $Pd(PPh_3)_4$. I is the fluorescence intensityof $Pd(PPh_3)_4$ in the presence of **1a**.

(c) (d)

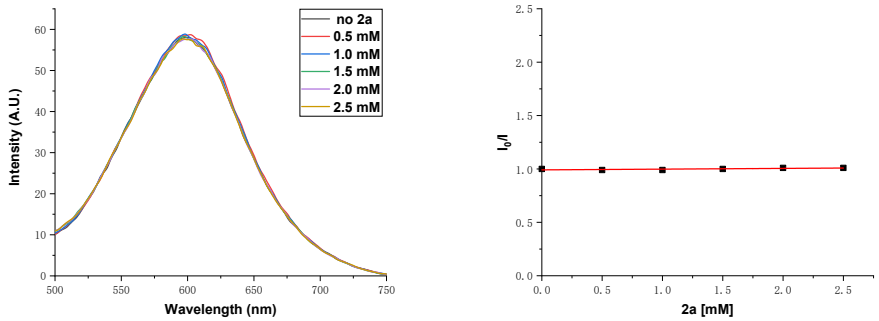
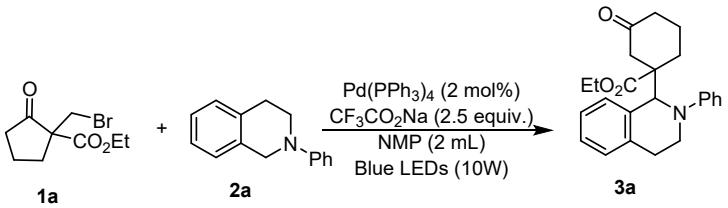


Figure S3 (c) The fluorescence emission spectra of $Pd(PPh_3)_4$ with different concentration of **2a** added. (d) The Stern–Volmer emission quenching studies of **2a**. I_0 is the inherent fluorescence intensity of $Pd(PPh_3)_4$. I is the fluorescence intensity of $Pd(PPh_3)_4$ in the presence of **2a**.

According to the results as well as the corresponding Stern-Volmer plots (Figure S2, Figure S3), the substrate **1a** showed an obvious quenching effect to the fluorescence intensity of $Pd(PPh_3)_4$, where it presumably engages in SET event with the photoexcited Pd(0) complex. While the substrate **2a** did not show an obvious quenching effect to the fluorescence intensity of $Pd(PPh_3)_4$.

(6) Light on-off experiments



1a 0.3 mmol

2a 0.2 mmol

3a

To further examine the impact of light, we conducted experiments under alternating periods of irradiation and darkness. The yield of **3a** was determined by crude ^1H NMR spectra using 1,3,5-

trimethoxybenzene as an internal standard.

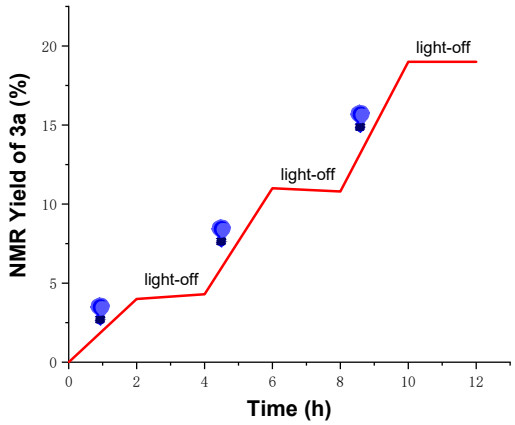
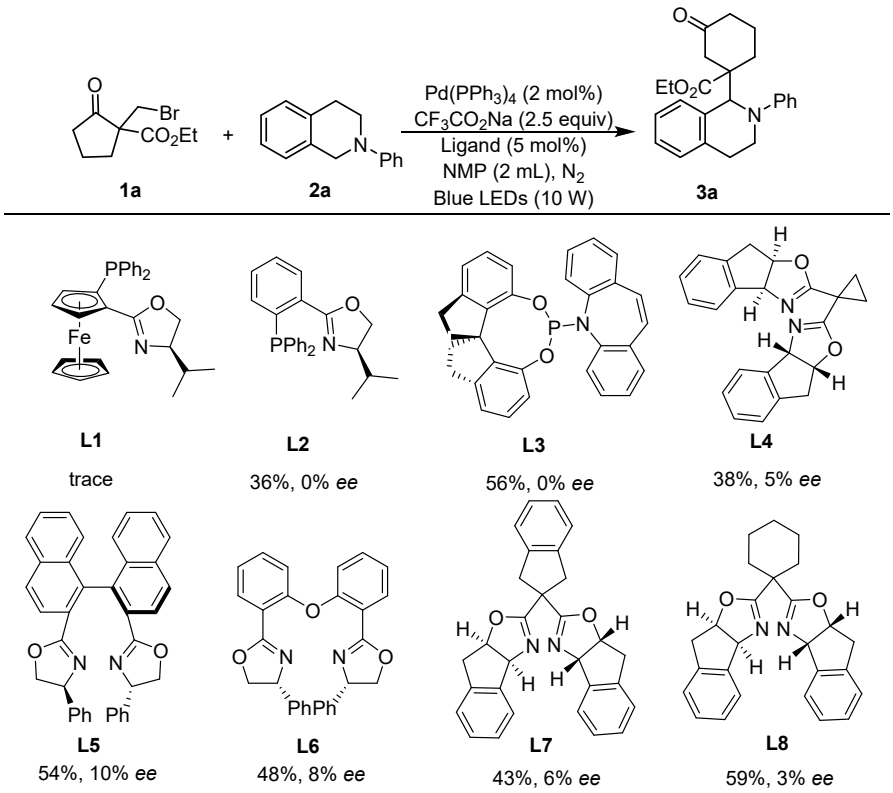


Figure S4 Yield of Light On-Off Experiments

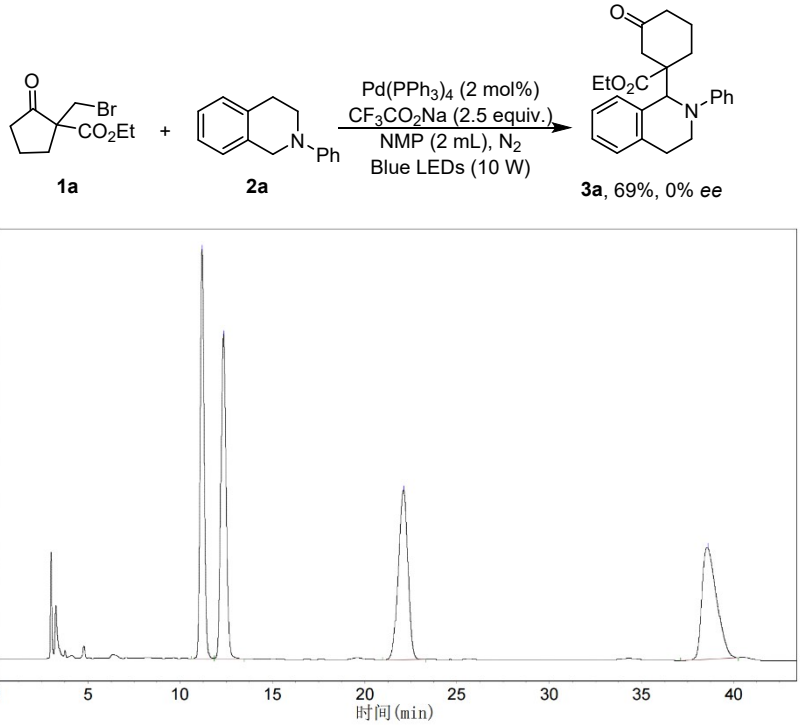
The results of light on-off experiments indicated that the reaction proceeded only under the irradiation of light, and the reaction maybe proceed by a catalytic process rather than by a radical chain process.

(7) Asymmetric experiments

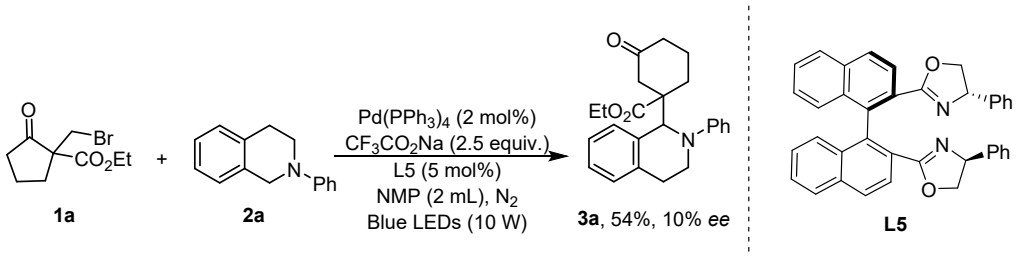
Ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate **1a** (0.30 mmol, 1.5 equiv.), *N*-phenyltetrahydroisoquinoline **2a** (0.20 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (4.6 mg, 2 mol%), CF_3CO_2Na (0.50 mmol, 2.5 equiv.), chiral ligands (5 mol%), NMP (2.0 mL) under N_2 for 24 h, with the irradiation of 10 W Blue LEDs.

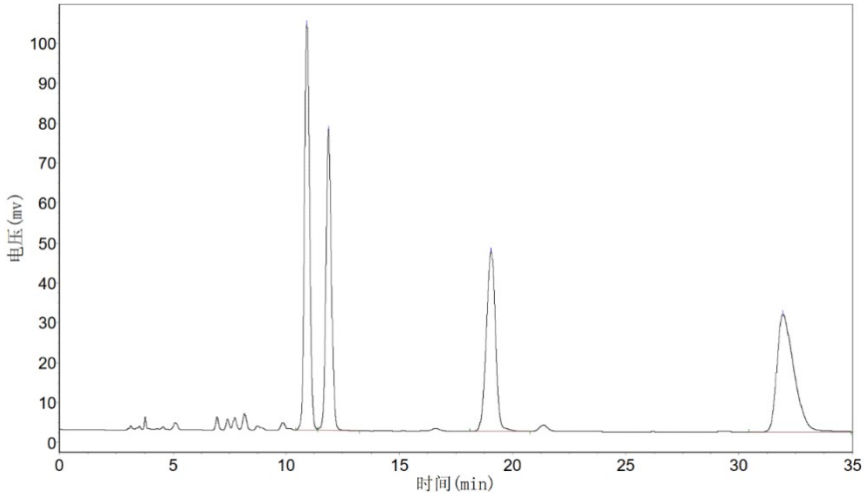


HPLC (CHIRALPAK AD-H, 4.6mm * 250mmL, 5 μm, hexane/isopropanol = 9/1, flow 1.0 mL/min)



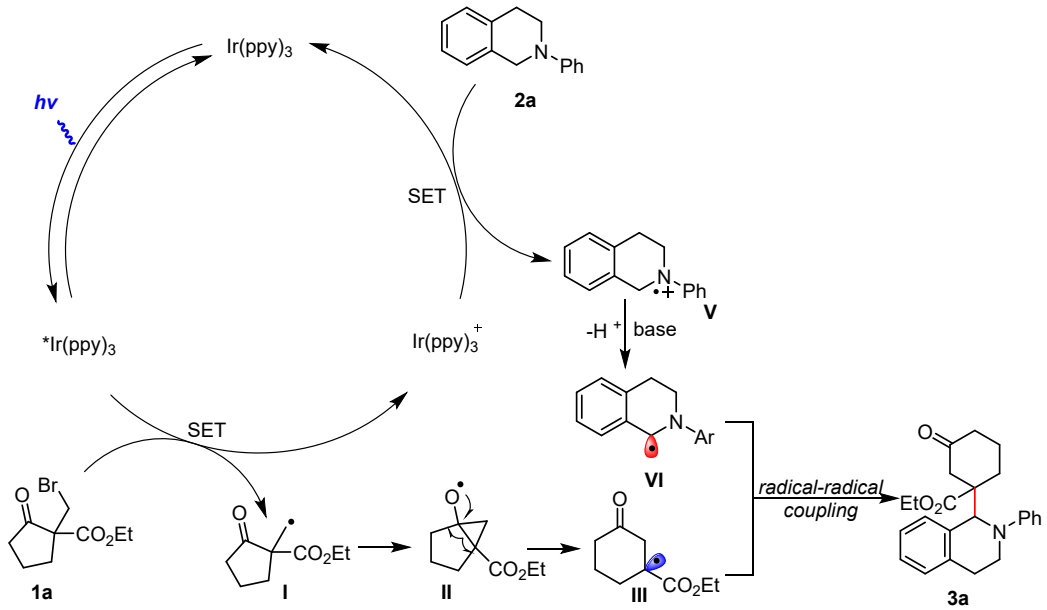
No.	Retention Time	Area	Height	% Area
1	11.190	1884636.250	119830.00	25.3350
2	12.357	1864140.000	95451.000	25.0595
3	22.123	1810259.375	49852.637	24.3352
4	38.590	1879822.000	33133.953	25.2703





No.	Retention Time	Area	Height	% Area
1	10.923	1548569.750	101432.953	27.5073
2	11.890	1279814.875	75485.898	22.7334
3	19.057	1266737.125	44853.840	22.5011
4	31.940	1534549.000	29339.334	27.2582

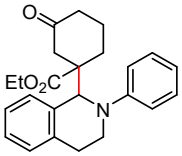
(8) Proposed reaction mechanism of Ir catalyst



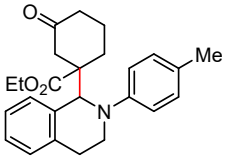
Based on the above results and the literature [2], a possible reaction pathway is proposed. Initially, the *fac*-Ir(ppy)$_3$ is activated to the excited state of *fac*-Ir(ppy)$_3$* under visible light irradiation.

Subsequently, bromide **1a** suffers from a single electron reduction with *fac*-Ir(ppy)$_3$* to produce the alkyl radical **I** and putative *fac*-Ir(ppy)$_3^+$. the generated C-centred radical of side chain attacks the intramolecular carbonyl group of cyclic ketones to form a high-energy oxygen centred radical **II**, which triggers a C–C bond cleavage to accomplish ring enlargement, forming the radical intermediate **III**. Meanwhile, *fac*-Ir(ppy)$_3^+$ undergoes a SET event with **2a** to produce the radical cation intermediate **V** and regenerate the *fac*-Ir(ppy)$_3$. Intermediate **V** is deprotonated by base to provide the radical intermediate **VI**. Finally, the radical-radical coupling between intermediates **III** and **VI** yields the desired product **3a**.

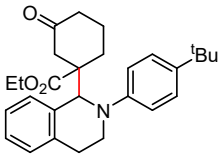
6 Characterization of products 3 and 4



Ethyl 3-oxo-1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexane-1-carboxylate (3a): Following the Ir-catalyzed procedure. Light yellow oil (78%, 58.8 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15-6.70 (m, 9H), 5.37 (s, 0.5H), 5.00 (s, 0.5H), 4.04-3.49 (m, 4H), 3.09-2.53 (m, 3H), 2.35-2.25 (m, 2H), 2.07-1.79 (m, 4H), 1.57-1.45 (m, 1H), 1.11 (t, *J* = 7.2 Hz, 1.5H), 0.95 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.1, 208.9, 175.2, 173.8, 151.1, 151.0, 135.9, 135.3, 134.2, 133.6, 129.2, 129.0, 128.8, 128.1, 127.6, 127.3, 126.0, 125.7, 119.5, 118.5, 117.7, 115.7, 65.1, 63.6, 61.0, 58.6, 58.5, 47.0, 46.1, 44.9, 44.6, 40.0, 39.8, 33.2, 32.6, 26.9, 25.9, 21.9, 21.7, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3061, 3022, 2940, 1715, 1596, 1497, 1451, 731 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{28}NO_3$ $[M+H]^+$ 378.2064, found 378.2067.

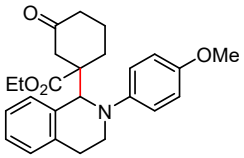


Ethyl 3-oxo-1-(2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexane-1-carboxylate (3b): Following the Pd-catalyzed procedure. Light yellow oil (72%, 56.3 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-6.86 (m, 8H), 5.35 (s, 0.5H), 5.00 (s, 0.5H), 4.13-3.45 (m, 4H), 3.16-2.58 (m, 3H), 2.42-2.23 (m, 6H), 2.12-1.85 (m, 3H), 1.57-1.51 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 1.5H), 1.03 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.2, 209.1, 175.2, 173.9, 149.3, 149.2, 137.2, 135.6, 134.3, 133.6, 131.1, 129.8, 128.2, 127.2, 126.0, 125.6, 118.6, 116.8, 65.6, 64.0, 60.9, 58.9, 58.6, 46.8, 45.9, 45.8, 40.0, 39.8, 33.1, 32.7, 27.1, 26.0, 21.9, 21.7, 20.3, 20.2, 13.8, 13.7 ppm; IR (neat): υ $_{max}$ 3057, 2959, 1717, 1614, 1569, 1451, 753 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{30}NO_3$ $[M+H]^+$ 392.2220, found 392.2223.

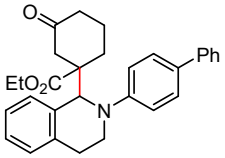


Ethyl 1-(2-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-

carboxylate (3c): Following the Ir-catalyzed procedure. Light yellow oil (72%, 62.4 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-6.89 (m, 8H), 5.39 (s, 0.5H), 5.04 (s, 0.5H), 4.17-3.48 (m, 4H), 3.17-2.59 (m, 3H), 2.39-2.31 (m, 2H), 2.04-1.86 (m, 4H), 1.58-1.49 (m, 1H), 1.28-1.25 (s, 9H), 1.18 (t, *J* = 7.2 Hz, 1.4H), 1.01 (t, *J* = 7.2 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 209.1, 175.3, 173.9, 148.9, 148.8, 142.5, 141.4, 136.2, 135.5, 134.4, 133.8, 129.2, 128.8, 128.2, 127.2, 126.0, 125.9, 125.7, 125.6, 117.8, 115.5, 65.5, 64.0, 61.4, 61.0, 58.6, 58.5, 46.9, 46.1, 45.4, 44.8, 40.0, 39.9, 33.9, 33.8, 33.0, 32.7, 31.4, 31.3, 27.0, 26.2, 22.0, 21.7, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3028, 2957, 1718, 1610, 1514, 1458, 738 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{36}NO_3$ $[M+H]^+$ 434.2690, found 434.2697.

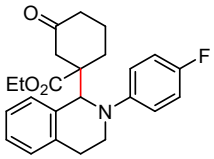


Ethyl 1-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3d): Following the Ir-catalyzed procedure. Light yellow oil (51%, 41.5 mg, 1:1 dr); R_f = 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-6.74 (m, 8H), 5.20 (s, 0.4H), 4.93 (s, 0.5H), 4.09-3.65 (m, 6H), 3.35-3.15 (m, 2H), 2.88-2.70 (m, 2H), 2.54-2.30 (m, 2H), 2.04-1.76 (m, 4H), 1.53-1.45 (m, 1H), 1.14 (t, *J* = 7.2 Hz, 1.4H), 1.02 (t, *J* = 7.2 Hz, 1.7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.5, 209.3, 175.1, 174.0, 154.3, 153.7, 146.5, 146.2, 136.8, 136.2, 134.4, 133.5, 129.2, 128.7, 128.5, 127.1, 126.0, 125.6, 122.1, 120.5, 114.6, 114.3, 66.4, 65.1, 61.1, 60.8, 59.4, 58.6, 55.5, 55.4, 48.2, 46.0, 45.5, 40.1, 39.9, 33.0, 32.7, 27.6, 26.6, 21.8, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3061, 2945, 1718, 1615, 1508, 1455, 754 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}NNaO_4$ $[M+Na]^+$ 430.1989, found 430.1998.

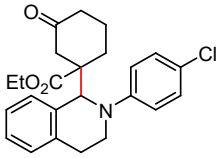


Ethyl 1-(2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3e): Following the Pd-catalyzed procedure. Light yellow oil (64%, 58.0 mg, 1:1.9 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-6.93 (m, 13H), 5.43 (s, 0.4H), 5.05 (s, 0.6H), 4.10-3.53 (m, 4H), 3.09-2.55 (m, 3H), 2.38-2.25 (m, 2H), 2.11-1.77 (m, 4H), 1.54-1.42 (m, 1H), 1.12 (t, *J* = 7.2 Hz, 1.2H), 0.97 (t, *J* = 7.2 Hz, 1.8H); ^{13}C NMR (100

MHz, $CDCl_3$): δ = 209.0, 208.8, 175.3, 173.8, 150.2, 140.8, 140.7, 135.8, 135.2, 133.6, 131.1, 128.6, 127.7, 127.3, 126.4, 126.3, 126.1, 125.8, 117.3, 115.5, 65.1, 63.6, 58.6, 58.5, 47.2, 46.2, 44.5, 44.3, 40.0, 39.8, 33.2, 32.7, 27.0, 26.0, 22.0, 21.7, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3057, 3028, 2963, 1721, 1607, 1522, 1452, 758 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{31}NNaO_3$ $[M+Na]^+$ 476.2196, found 476.2197.

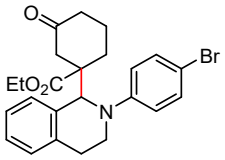


Ethyl 1-(2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3f): Following the Ir-catalyzed procedure. Light yellow oil (78%, 61.6 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-6.86 (m, 8H), 5.24 (s, 0.5H), 4.95 (s, 0.5H), 4.13-3.45 (m, 4H), 3.16-2.57 (m, 3H), 2.42-2.25 (m, 2H), 2.17-1.77 (m, 4H), 1.57-1.47 (m, 1H), 1.15 (t, *J* = 7.2 Hz, 1.5H), 1.02 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.1, 209.0, 175.0, 173.9, 157.4 (d, *J* = 238.3 Hz), 156.7 (d, *J* = 237.3 Hz), 136.3, 135.6, 134.0, 133.2, 129.3, 128.8, 128.4, 127.7, 127.4 (d, *J* = 4.5 Hz), 126.1, 125.8, 121.1 (d, *J* = 7.7 Hz), 118.9 (d, *J* = 7.5 Hz), 115.7 (d, *J* = 22.0 Hz), 115.4 (d, *J* = 22.0 Hz), 66.1, 64.7, 61.3, 60.9, 58.9, 58.6, 47.1, 46.7, 46.3, 45.9, 40.0, 39.8, 33.2, 32.6, 27.1, 26.2, 21.8, 21.7, 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -124.74, -126.32 (s, 1F); IR (neat): υ $_{max}$ 3061, 2948, 1719, 1611, 1507, 1455, 753 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}FNO_3$ $[M+H]^+$ 396.1969, found 396.1963.

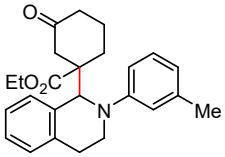


Ethyl 1-(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3g): Following the Ir-catalyzed procedure. Light yellow oil (75%, 61.7 mg, 1:1.2 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-6.86 (m, 8H), 5.35 (s, 0.5H), 4.99 (s, 0.4H), 4.16-3.47 (m, 4H), 3.12-2.59 (m, 3H), 2.42-2.32 (m, 2H), 2.17-1.77 (m, 4H), 1.58-1.49 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 1.6H), 1.04 (t, *J* = 7.2 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.9, 208.6, 175.1, 173.7, 149.6, 149.5, 135.7, 135.1, 133.9, 133.2, 129.4, 129.1, 128.9, 128.8, 128.1, 127.8, 127.5, 127.3, 126.2, 125.8, 124.4, 123.4, 118.9, 116.9, 65.3, 63.8, 61.5, 61.1, 58.6, 58.4, 46.9, 46.1, 45.0, 44.8, 40.0, 39.8, 33.3, 32.6, 26.9, 25.8, 21.9, 21.6, 13.9, 13.8 ppm;

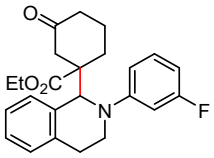
IR (neat): υ $_{max}$ 3060, 2938, 1718, 1593, 1495, 1452, 747 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}ClNO_3$ $[M+H]^+$ 412.1674, found 412.1681.



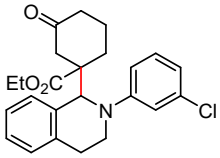
Ethyl 1-(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3h): Following the Ir-catalyzed procedure. Light yellow oil (55%, 50.1 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-6.81 (m, 8H), 5.37 (s, 0.4H), 4.99 (s, 0.5H), 4.14-3.49 (m, 4H), 3.11-2.57 (m, 3H), 2.43-2.33 (m, 2H), 2.18-1.80 (m, 4H), 1.61-1.48 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 1.3H), 1.05 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.9, 208.6, 175.0, 173.7, 149.9, 149.8, 135.6, 135.0, 133.7, 133.2, 132.0, 131.8, 129.4, 128.9, 128.1, 127.8, 127.5, 127.2, 126.2, 125.8, 119.1, 117.3, 111.5, 65.2, 61.6, 61.1, 58.5, 58.4, 47.0, 46.0, 44.7, 40.0, 39.8, 33.3, 32.5, 26.9, 25.7, 21.9, 21.6, 13.9 ppm; IR (neat): υ $_{max}$ 3058, 2931, 1721, 1601, 1495, 1451, 743 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}BrNO_3$ $[M+H]^+$ 456.1169, found 456.1171.



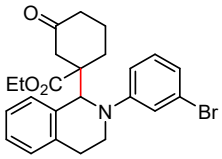
Ethyl 3-oxo-1-(2-(*m*-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexane-1-carboxylate (3i): Following the Ir-catalyzed procedure. Light yellow oil (72%, 56.3 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-6.61 (m, 8H), 5.43 (s, 0.5H), 5.07 (s, 0.5H), 4.16-3.52 (m, 4H), 3.16-2.60 (m, 3H), 2.38-2.28 (m, 6H), 2.18-1.74 (m, 3H), 1.62-1.48 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 1.5H), 1.04 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.1, 208.9, 175.3, 173.9, 151.2, 151.1, 139.0, 138.6, 136.0, 135.4, 134.3, 133.7, 128.9, 128.8,128.1, 127.5, 127.3, 127.2, 126.0, 125.6, 120.4, 119.5, 118.5, 116.6, 65.2, 63.7, 61.0, 58.6, 58.5, 47.1, 46.2, 44.9, 44.6, 40.0, 39.8, 33.1, 32.6, 27.0, 26.1, 22.0, 21.9, 21.7, 21.6, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3057, 2958, 1719, 1600, 1493, 1450, 759 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}NNaO_3$ $[M+Na]^+$ 414.2040, found 414.2038.



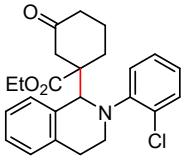
Ethyl 1-(2-(3-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3j): Following the Ir-catalyzed procedure. Light yellow oil (72%, 56.9 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13-6.43 (m, 8H), 5.41 (s, 0.5H), 5.04 (s, 0.5H), 4.17-3.56 (m, 4H), 3.11-2.61 (m, 3H), 2.45-2.29 (m, 2H), 2.17-1.79 (m, 4H), 1.63-1.48 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 1.5H), 1.06 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.8, 208.4, 175.0, 173.6, 163.9 (d, *J* = 241.3 Hz), 163.7 (d, *J* = 241.5 Hz), 152.3 (d, *J* = 6.0 Hz), 152.2(d, *J* = 5.9 Hz), 135.3, 134.8, 133.9, 133.3, 130.2 (d, *J* = 10.2 Hz), 130.0 (d, *J* = 10.0 Hz), 129.3, 129.0, 127.9,127.8, 127.5, 127.2, 126.1, 125.8, 111.8 (d, *J* = 2.2 Hz), 110.2 (d, *J* = 2.1 Hz), 105.4 (d, *J* = 21.3 Hz), 104.5 (d, *J* = 21.3 Hz), 103.4 (d, *J* = 25.0 Hz), 101.8 (d, *J* = 25.9 Hz), 65.0, 63.5, 61.5, 61.1, 58.3, 58.2, 47.2, 46.3, 43.9, 43.8, 39.9, 39.7, 33.2, 32.4, 26.8, 25.7, 21.9, 21.6, 13.8, 13.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -111.85, -112.38 (s, 1F); IR (neat): υ $_{max}$ 3063, 2980, 1720, 1614, 1578, 1451, 756 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}FNNaO_3$ $[M+Na]^+$ 418.1789, found 418.1794.



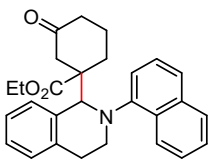
Ethyl 1-(2-(3-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3k): Following the Ir-catalyzed procedure. Light yellow oil (71%, 58.4 mg, 1:1.3 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-6.73 (m, 8H), 5.40 (s, 0.5H), 5.04 (s, 0.4H), 4.18-3.56 (m, 4H), 3.11-2.61 (m, 3H), 2.45-1.77 (m, 6H), 1.58-1.49 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 1.6H), 1.07 (t, *J* = 7.2 Hz, 1.3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.7, 208.4, 175.0, 173.7, 151.8, 135.4, 135.1, 134.9, 134.8, 133.8, 133.2, 130.2, 129.9, 129.4, 129.0, 127.9, 127.3, 126.2, 125.9, 119.0, 118.1, 116.8, 115.0, 114.8, 113.0, 65.0, 63.5, 61.2, 58.3, 58.2, 47.1, 46.3, 44.1, 44.0, 40.0, 39.8, 33.3, 32.5, 26.8, 25.8, 21.9, 21.6, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3052, 2983, 1722, 1592, 1485, 1451, 756 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}ClNO_3$ $[M+H]^+$ 412.1674, found 412.1681.



Ethyl 1-(2-(3-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3l): Following the Ir-catalyzed procedure. Light yellow oil (58%, 52.8 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-6.85 (m, 8H), 5.41 (s, 0.4H), 5.03 (s, 0.4H), 4.18-3.53 (m, 4H), 3.11-2.58 (m, 3H), 2.45-2.32 (m, 2H), 2.19-1.83 (m, 4H), 1.61-1.42 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 1.4H), 1.07 (t, *J* = 7.2 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.8, 208.5, 175.0, 173.6, 151.9, 151.7, 135.4, 134.8, 133.6, 133.2, 130.5, 130.2, 129.0, 128.1, 127.6, 127.2, 126.3, 125.9, 123.5, 123.0, 122.0, 119.7, 118.0, 115.3, 113.7, 65.0, 61.7, 61.2, 58.3, 47.1, 46.1, 44.2, 40.0, 39.8, 33.3, 32.4, 26.8, 25.8, 21.9, 21.6, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3060, 2987, 1718, 1597, 1485, 1451, 754 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}BrNO_3$ $[M+H]^+$ 456.1169, found 456.1165.

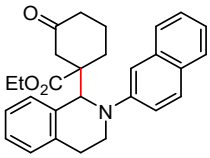


Ethyl 1-(2-(2-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3m): Following the Pd-catalyzed procedure. Light yellow oil (30%, 24.7 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-6.98 (m, 8H), 5.23 (s, 0.5H), 5.04 (s, 0.5H), 4.07-3.54 (m, 4H), 3.25-2.63 (m, 3H), 2.36-1.81 (m, 6H), 1.35-1.30 (m, 1H), 1.10 (t, *J* = 7.2 Hz, 1.5H), 0.97 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.2, 209.3, 174.8, 174.1, 151.3, 150.0 137.5, 137.3, 134.2, 133.5, 131.6, 131.3, 130.8, 130.5, 128.9, 128.5, 128.2, 127.5, 127.4, 127.1, 126.5, 126.2, 125.7, 125.4, 125.1, 66.9, 66.7, 61.2, 60.9, 58.9, 50.3, 48.7, 45.1, 43.5, 40.1, 39.8, 32.5, 32.4, 29.5, 28.1, 21.8, 21.4, 13.8, 13.6 ppm; IR (neat): υ $_{max}$ 3058, 2963, 1723, 1585, 1476, 755 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}ClNNaO_3$ $[M+Na]^+$ 434.1493, found 434.1497.

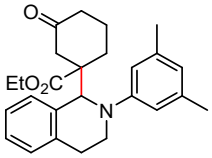


Ethyl 1-(2-(naphthalen-1-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3n): Following the Ir-catalyzed procedure. Light yellow oil (69%, 58.9 mg, 1:1 dr);

R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33-7.04 (m, 11H), 5.35 (s, 0.5H), 5.16 (s, 0.4H), 4.08-3.34 (m, 4H), 3.22-2.82 (m, 3H), 2.70-2.24 (m, 2H), 2.13-1.81 (m, 4H), 1.46-1.31 (m, 1H), 1.07 (t, *J* = 7.2 Hz, 1.6H), 0.61 (t, *J* = 7.2 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.0, 209.3, 174.8, 174.2, 151.0, 137.6, 137.3, 135.1, 134.6, 133.8, 129.8, 129.2, 128.7, 128.1, 127.5, 127.1, 126.2, 126.1, 126.0, 125.9, 125.8, 125.6, 124.5, 124.0, 123.4, 67.8, 67.4, 60.9, 60.7, 60.6, 59.4, 51.4, 50.2, 45.4, 44.5, 40.1, 39.8, 32.9, 32.5, 28.8, 21.7, 21.5, 13.8, 13.2 ppm; IR (neat): υ $_{max}$ 3054, 2943, 1720, 1580, 1455, 739 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{30}NO_3$ $[M+H]^+$ 428.2220, found 428.2231.

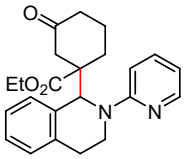


Ethyl 1-(2-(naphthalen-2-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3o): Following the Ir-catalyzed procedure. Light yellow oil (59%, 50.4 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73-7.08 (m, 11H), 5.59 (s, 0.3H), 5.21 (s, 0.7H), 4.15-3.70 (m, 4H), 3.20-2.65 (m, 3H), 2.49-2.33 (m, 2H), 2.12-1.87 (m, 4H), 1.64-1.49 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 1.6H), 0.97 (t, *J* = 7.2 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.0, 208.9, 175.2,173.8, 148.8, 148.7, 135.8, 135.3, 134.7, 134.4, 134.2, 133.5, 129.0, 128.3, 128.1, 127.8, 127.7, 127.4, 127.3, 126.5, 126.1, 125.8, 123.3, 123.1, 120.2, 118.7, 112.4, 110.6, 65.2, 63.7, 61.4, 61.1, 58.7, 58.6, 47.1, 46.2, 44.9, 44.8, 40.0, 39.8, 33.4, 32.7, 27.0, 25.8, 21.9, 21.7, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3052, 2984, 1722, 1627, 1596, 1508, 1469, 755 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}NNaO_3$ $[M+Na]^+$ 450.2040, found 450.2044.

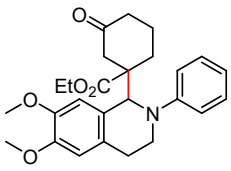


Ethyl 1-(2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3p): Following the Pd-catalyzed procedure. Light yellow oil (60%, 48.6 mg, 1:1.4 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-6.46 (m, 7H), 5.42 (s, 0.4H), 5.05 (s, 0.5H), 4.15-3.51 (m, 4H), 3.15-2.58 (m, 3H), 2.42-2.23 (m, 8H), 2.05-1.89 (m, 4H), 1.62-1.48 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 1.3H), 1.05 (t, *J* = 7.2 Hz, 1.7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 209.1, 175.4, 173.9, 151.3, 138.8, 138.4, 136.0, 135.4, 134.4, 133.8, 129.2,

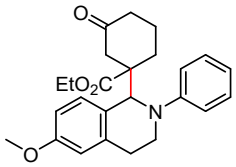
128.9, 128.1, 127.5, 127.3, 127.2, 126.0, 125.6, 121.5, 120.6, 115.6, 113.7, 65.3, 63.6, 61.4, 61.0, 58.5, 47.1, 46.2, 44.9, 44.6, 40.1, 39.9, 33.1, 32.7, 27.0, 26.1, 24.5, 22.0, 21.8, 21.7, 21.6, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3052, 2941, 1719, 1595, 1473, 1453, 752 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{32}NO_3$ $[M+H]^+$ 406.2377, found 406.2369.



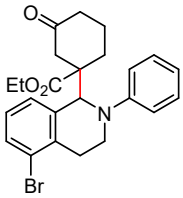
Ethyl 3-oxo-1-(2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexane-1-carboxylate (3q): Following the Ir-catalyzed procedure. Light yellow oil (67%, 50.7 mg, 1:1 dr); R_f = 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18-6.59 (m, 8H), 6.32 (s, 0.5H), 6.14 (s, 0.4H), 4.01-3.68 (m, 4H), 3.09-2.77 (m, 3H), 2.53-1.95 (m, 6H), 1.59-1.39 (m, 1H), 1.08 (t, *J* = 7.2 Hz, 1.8H), 1.01 (t, *J* = 7.2 Hz, 1.1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.6, 209.3, 174.8, 174.3, 147.3, 137.7, 135.1, 134.7, 128.4, 128.3, 128.0, 127.5, 127.4, 125.9, 125.8, 112.8, 106.6, 61.2, 61.0, 60.7, 60.3, 58.0, 57.9, 48.6, 46.7, 42.1, 42.0, 40.1, 40.0, 32.8, 32.4, 27.4, 27.3, 22.2, 21.9, 13.7 ppm; IR (neat): υ $_{max}$ 3057, 2979, 1718, 1593, 1471, 1436, 761 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3$ $[M+H]^+$ 379.2016, found 379.2022.



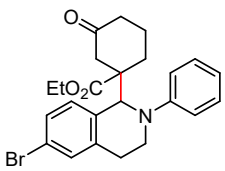
Ethyl 1-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3r): Following the Pd-catalyzed procedure. Light yellow oil (54%, 47.2 mg, 1:1 dr); R_f = 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-6.47 (m, 7H), 5.40 (s, 0.3H), 4.96 (s, 0.6H), 4.21-3.53 (m, 10H), 3.14-2.56 (m, 3H), 2.43-2.33 (m, 2H), 2.12-1.86 (m, 4H), 1.62-1.47 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 1.0H), 1.03 (t, *J* = 7.2 Hz, 1.7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.2, 209.0, 175.7, 173.9, 151.2, 148.4, 148.1, 147.1, 146.8, 129.2, 129.0, 128.3, 127.6, 125.9, 125.2, 119.6, 118.7, 117.9, 115.9, 111.8, 111.4, 111.3, 110.2, 65.0, 63.1, 61.0, 58.7, 58.5, 56.1, 55.8, 55.7, 47.0, 45.9, 44.8, 44.7, 40.0, 39.9, 33.3, 32.6, 26.5, 25.4, 22.0, 21.6, 14.0, 13.8 ppm; IR (neat): υ $_{max}$ 3056, 2939, 1721, 1599, 1512, 1461, 755 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{32}NO_5$ $[M+H]^+$ 438.2275, found 438.2271.



Ethyl 1-(6-methoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3s): Following the Pd-catalyzed procedure. Light yellow oil (57%, 46.4 mg, 1:1 dr); R_f = 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-6.65 (m, 8H), 5.37 (s, 0.5H), 5.01 (s, 0.5H), 4.16-3.52 (m, 7H), 3.14-2.60 (m, 3H), 2.41-1.83 (m, 6H), 1.54-1.48 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 1.5H), 1.02 (t, *J* = 7.2 Hz, 1.6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 209.1, 175.3, 173.9, 158.8, 158.7, 151.2, 137.4, 136.7, 129.2, 129.1, 129.0, 128.4, 126.4, 125.7, 119.6, 118.7, 117.9, 115.9, 113.8, 113.6, 112.0, 111.9, 64.8, 63.2, 61.4, 61.0, 58.8, 58.7, 55.2, 47.0, 46.2, 44.9, 44.7, 40.1, 39.9, 33.2, 32.6, 27.4, 26.3, 22.0, 21.8, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3055, 2928, 1710, 1610, 1515, 1454, 735 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{30}NO_4$ $[M+H]^+$ 408.2169, found 408.2169.

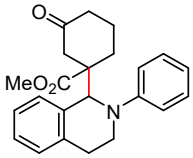


Ethyl 1-(5-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-carboxylate (3t): Following the Ir-catalyzed procedure. Light yellow oil (67%, 61.1 mg, 1:1 dr); R_f = 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-6.78 (m, 8H), 5.34 (s, 0.4H), 4.99 (s, 0.5H), 4.18-3.66 (m, 4H), 3.12-2.63 (m, 3H), 2.45-2.29 (m, 2H), 2.20-1.84 (m, 4H), 1.61-1.49 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 1.5H), 1.04 (t, *J* = 7.2 Hz, 1.6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.7, 208.4, 175.2, 173.5, 150.5, 136.8, 136.1, 135.4, 134.9, 131.8, 131.3, 129.3, 129.1, 127.1, 126.8, 126.1, 125.6, 119.7, 118.9, 117.3, 115.7, 65.4, 64.0, 61.6, 61.2, 58.2, 57.7, 47.5, 46.5, 43.7, 40.0, 39.8, 33.4, 32.7, 27.1, 26.4, 21.9, 21.5, 13.8 ppm; IR (neat): υ $_{max}$ 3060, 2923, 1715, 1610, 1505, 1451, 733 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}BrNO_3$ $[M+H]^+$ 456.1169, found 456.1182.

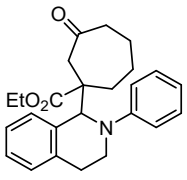


Ethyl 1-(6-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxocyclohexane-1-

carboxylate (3u): Following the Ir-catalyzed procedure. Light yellow oil (62%, 56.5 mg, 1:1 dr); R_f = 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-6.80 (m, 8H), 5.33 (s, 0.4H), 5.00 (s, 0.4H), 4.17-3.53 (m, 4H), 3.13-2.60 (m, 3H), 2.36-1.83 (m, 6H), 1.58-1.48 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 1.5H), 1.02 (t, *J* = 7.2 Hz, 1.6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.7, 208.5, 175.0, 173.6, 150.9, 150.8, 138.3, 137.7, 133.3, 132.7, 132.1, 131.7, 129.6, 129.3, 129.1, 128.8, 121.4, 121.0, 120.0, 119.1, 117.9, 116.1, 64.8, 63.5, 61.5, 61.1, 58.3, 47.0, 46.1, 44.6, 44.3, 40.0, 39.8, 33.1, 32.8, 26.6, 25.7, 21.9, 21.6, 13.9, 13.8 ppm; IR (neat): υ $_{max}$ 3064, 2918, 1718, 1610, 1512, 1450, 734 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}BrNO_3$ $[M+H]^+$ 456.1169, found 456.1168.

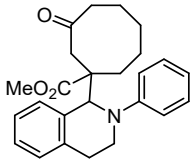


Methyl 3-oxo-1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexane-1-carboxylate (4a): Following the Pd-catalyzed procedure. Light yellow oil (71%, 51.5 mg, 1:1.2 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-6.79 (m, 9H), 5.43 (s, 0.3H), 5.08 (s, 0.6H), 3.85-3.75 (m, 1H), 3.63 (s, 1H), 3.60-3.49 (m, 1H), 3.42 (s, 2H), 3.16-2.59 (m, 3H), 2.43-2.25 (m, 2H), 2.17-1.83 (m, 4H), 1.59-1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.1, 209.0, 175.6, 174.3, 151.1, 136.0, 135.4, 133.5, 129.3, 129.0, 128.9, 128.2, 127.7, 127.4, 127.2, 126.1, 125.7, 119.8, 118.8, 118.1, 116.0, 65.3, 63.7, 59.2, 58.8, 52.2, 51.8, 46.9, 46.0, 45.3, 45.1, 40.1, 39.9, 33.0, 32.5, 27.1, 26.2, 22.0, 21.8 ppm; IR (neat): υ $_{max}$ 3058, 2950, 1726, 1597, 1498, 1451, 755 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{26}NO_3$ $[M+H]^+$ 364.1907, found 364.1913.

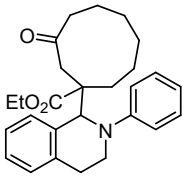


Ethyl 3-oxo-1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cycloheptane-1-carboxylate (4b): Following the Pd-catalyzed procedure. Light yellow oil (40%, 31.3 mg, 1:1.1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-6.76 (m, 9H), 5.29 (s, 0.5H), 5.05 (s, 0.5H), 4.16-3.54 (m, 4H), 3.24-2.68 (m, 3H), 2.61-2.15 (m, 4H), 2.04-1.70 (m, 4H), 1.59-1.39 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 1.5H), 1.03 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.9, 211.8, 175.1, 174.0, 151.1, 151.0, 135.7, 135.6, 134.4, 133.7, 129.4, 129.2, 129.1, 129.0,

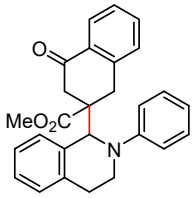
127.6, 127.5, 127.3, 127.2, 125.8, 125.6, 119.5, 118.8, 117.7, 116.2, 67.2, 66.0, 61.3, 60.9, 55.9, 55.7, 50.1, 50.0, 44.1, 43.9, 43.8, 40.4, 37.9, 27.5, 26.5, 26.2, 25.7, 23.6, 23.4, 13.8 ppm; IR (neat): υ_{max} 3060, 2979, 1721, 1698, 1596, 1497, 1451, 754 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{30}NO_3$ $[M+H]^+$ 392.2220, found 392.2227.



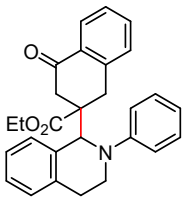
Methyl 3-oxo-1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclooctane-1-carboxylate (4c): Following the Pd-catalyzed procedure. Light yellow oil (57%, 44.6 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17-6.68 (m, 9H), 5.37 (s, 0.5H), 4.96 (s, 0.4H), 3.86-3.12 (m, 5H), 3.05-2.80 (m, 4H), 2.42-1.94 (m, 4H), 1.76-1.52 (m, 3H), 1.50-1.34 (m, 2H), 1.25-1.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.5, 214.2, 175.2, 174.0, 151.2, 150.9, 135.9, 135.2, 134.7, 134.4, 129.3, 129.1, 129.0, 128.7, 127.8, 127.3, 127.2, 125.8, 125.4, 119.2, 118.5, 117.2, 115.6, 66.1, 59.3, 59.1, 52.0, 51.4, 45.3, 44.7, 43.9, 43.7, 31.8, 30.6, 28.7, 28.4, 26.5, 26.4, 22.2 ppm; IR (neat): υ_{max} 3059, 2939, 1729, 1597, 1498, 1467, 755 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{30}NO_3$ $[M+H]^+$ 392.2220, found 392.2216.



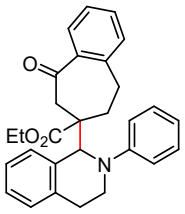
Ethyl 3-oxo-1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclononane-1-carboxylate (4d): Following the Pd-catalyzed procedure. Light yellow oil (41%, 34.4 mg, 1:1.2 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.14-6.65 (m, 9H), 5.40 (s, 0.5H), 5.09 (s, 0.5H), 4.01-3.51 (m, 4H), 3.13-2.61 (m, 5H), 2.38-2.29 (m, 2H), 1.91-1.62 (m, 4H), 1.45-1.27 (m, 5H), 1.01 (t, J = 7.2 Hz, 1.5H), 0.89 (t, J = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.3, 213.8, 175.4, 175.3, 151.0, 150.9, 135.4, 135.3, 135.1, 134.7, 129.2, 129.1, 129.0, 128.8, 128.4, 128.1, 127.0, 125.4, 125.0, 118.5, 118.1, 116.3, 115.5, 63.7, 63.4, 60.8, 60.7, 56.6, 56.4, 46.4, 44.3, 43.4, 42.7, 42.3, 29.5, 28.7, 27.2, 25.8, 25.4, 22.2, 22.1, 21.5, 19.7, 19.0, 13.7, 13.6 ppm; IR (neat): υ_{max} 3059, 2928, 1718, 1597, 1498, 1451, 754 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{34}NO_3$ $[M+H]^+$ 420.2533, found 420.2539.



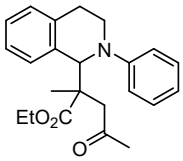
Methyl 4-oxo-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4e): Following the Ir-catalyzed procedure. Light yellow oil (41%, 33.7 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94-6.79 (m, 13H), 5.41 (s, 0.5H), 5.16 (s, 0.5H), 3.93-3.73 (m, 2H), 3.60-3.28 (m, 6H), 3.06-2.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 195.9, 175.0, 174.0, 150.9, 150.8, 141.1, 141.0, 135.8, 135.6, 133.9, 133.8, 133.5, 131.5, 131.4, 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.2, 127.7, 127.6, 127.5, 127.1, 127.0, 126.9, 126.7, 126.1, 125.8, 119.5, 119.1, 117.3, 116.3, 64.9, 63.8, 57.8, 57.1, 52.2, 52.0, 45.5, 45.3, 44.8, 44.5, 37.9, 37.8, 27.1, 26.2 ppm; ppm; IR (neat): υ $_{max}$ 3059, 2931, 1713, 1607, 1453, 748 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}NO_3$ $[M+H]^+$ 412.1907, found 412.1903.



Ethyl 4-oxo-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4f): Following the Ir-catalyzed procedure. Light yellow oil (45%, 38.3 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94-6.77 (m, 13H), 5.42 (s, 0.5H), 5.15 (s, 0.5H), 3.94-3.60 (m, 4H), 3.48-3.30(m, 3H), 3.04-3.00 (m, 1H), 2.82-2.40 (dd, *J* = 16.4, 16.8 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 1.5H), 0.82 (t, *J* = 7.2 Hz, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 196.0, 174.6, 173.5, 150.9, 150.7, 141.0, 135.7, 135.5, 133.9, 133.8, 133.6, 131.7, 131.5, 129.3, 129.1, 129.0, 128.9, 128.2, 127.5, 127.0, 126.6, 126.1, 125.8, 119.3, 118.9, 117.0, 116.0, 64.8, 63.6, 61.3, 61.0, 57.4, 56.9, 45.7, 44.9, 44.5, 44.4, 38.2, 38.1, 26.9, 26.1, 13.6, 13.5 ppm; IR (neat): υ $_{max}$ 3062, 2979, 1720, 1683, 1597, 1497, 1454, 756 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{28}NO_3$ $[M+H]^+$ 426.2064, found 426.2068.



Ethyl 5-oxo-7-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-7-carboxylate (4g): Following the Ir-catalyzed procedure. Light yellow oil (47%, 41.3 mg, 1:1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-6.72 (m, 13H), 5.13 (s, 0.4H), 5.11 (s, 0.4H), 3.81-3.62 (m, 3H), 3.52-3.44 (m, 1H), 3.32-3.17 (m, 1H), 3.07-2.98 (m, 2H), 2.91-2.72 (m, 3H), 2.14-1.91 (m, 2H), 0.91-0.84 (tt, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0, 201.7, 174.7, 173.7, 150.4, 142.1, 141.2, 138.1, 137.2, 135.7, 135.4, 134.6, 134.3, 132.8, 132.3, 129.2, 129.0, 128.6, 128.5, 128.2, 127.3, 126.6, 125.8, 125.6, 118.9, 118.4, 116.5, 115.4, 66.8, 64.2, 61.1, 60.9, 54.3, 54.1, 50.4, 48.0, 43.0, 42.8, 34.0, 31.9, 31.6, 31.4, 25.9, 25.6, 13.5 ppm; IR (neat): υ $_{max}$ 3062, 2979, 1720, 1683, 1597, 1497, 1454, 756 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{30}NO_3$ $[M+H]^+$ 440.2220, found 440.2214.



Ethyl 2-methyl-4-oxo-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)pentanoate (4h): Following the Pd-catalyzed procedure. Light yellow oil (46%, 33.6 mg, 1:1.1 dr); R_f = 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-6.72 (m, 9H), 5.24 (s, 0.5H), 5.00 (s, 0.5H), 4.15-3.56 (m, 4H), 3.26-2.67 (m, 4H), 2.10-2.03 (m, 3H), 1.33-1.28 (m, 3H), 1.20 (t, *J* = 7.2 Hz, 1.5H), 1.01 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.3, 205.8, 176.3, 174.8, 150.6, 150.5, 135.6, 135.3, 134.7, 134.5, 129.2, 129.1, 129.0, 128.8, 127.9, 127.8, 127.3, 127.1, 125.6, 125.4, 118.5, 118.4, 116.1, 115.6, 65.2, 63.9, 60.9, 60.6, 51.9, 51.8, 51.3, 50.9, 43.7, 43.4, 30.8, 26.1, 25.9, 20.9, 20.3, 13.9, 13.7 ppm; IR (neat): υ $_{max}$ 3060, 2983, 1717, 1597, 1498, 1453, 754 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{28}NO_3$ $[M+H]^+$ 366.2064, found 366.2057.

7 References

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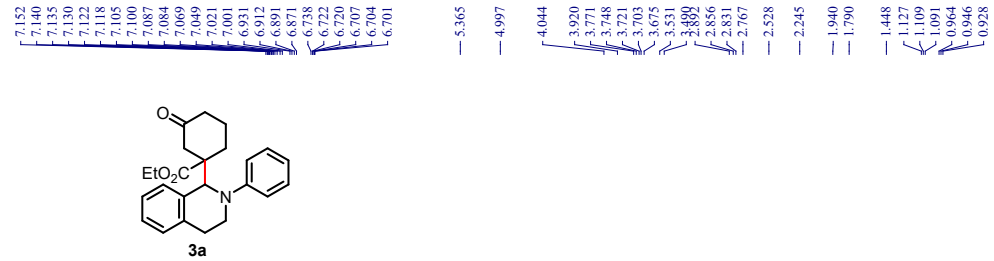
2 W.-J. Zhou , G.-M. Cao, G. Shen, X.-Y. Zhu, Y.-Y. Gui, J.-H. Ye, L. Sun, L.-L. Liao, J. Li and D.-G. Yu, Visible-Light-Driven Palladium-Catalyzed Radical Alkylation of C−H Bonds with Unactivated Alkyl Bromides, *Angew. Chem., Int. Ed*., 2017, **56**, 15683-15687.

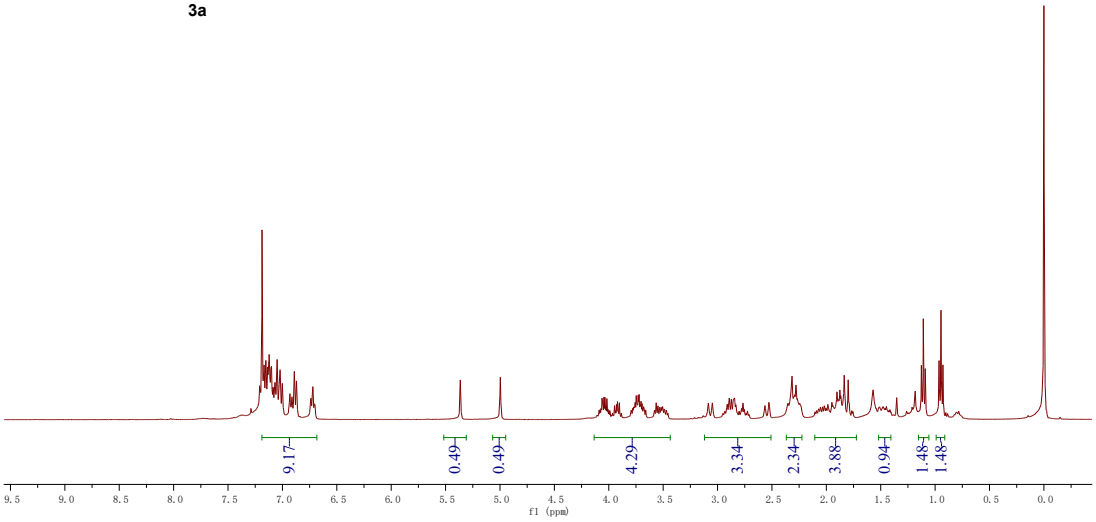
3 J. F. Franz, W. B. Kraus and K. Zeitler, No Photocatalyst Required–Versatile, Visible Light Mediated Transformations with Polyhalomethanes. *Chem. Commun*., 2015, **51**, 8280-8283.

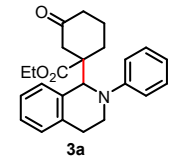
8 ^{1}H NMR and ^{13}C NMR spectra of products 3 and 4

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3a**

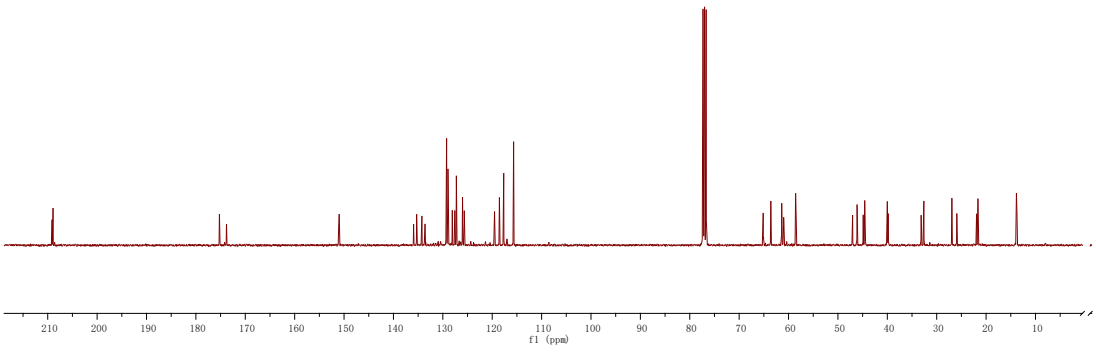


3a

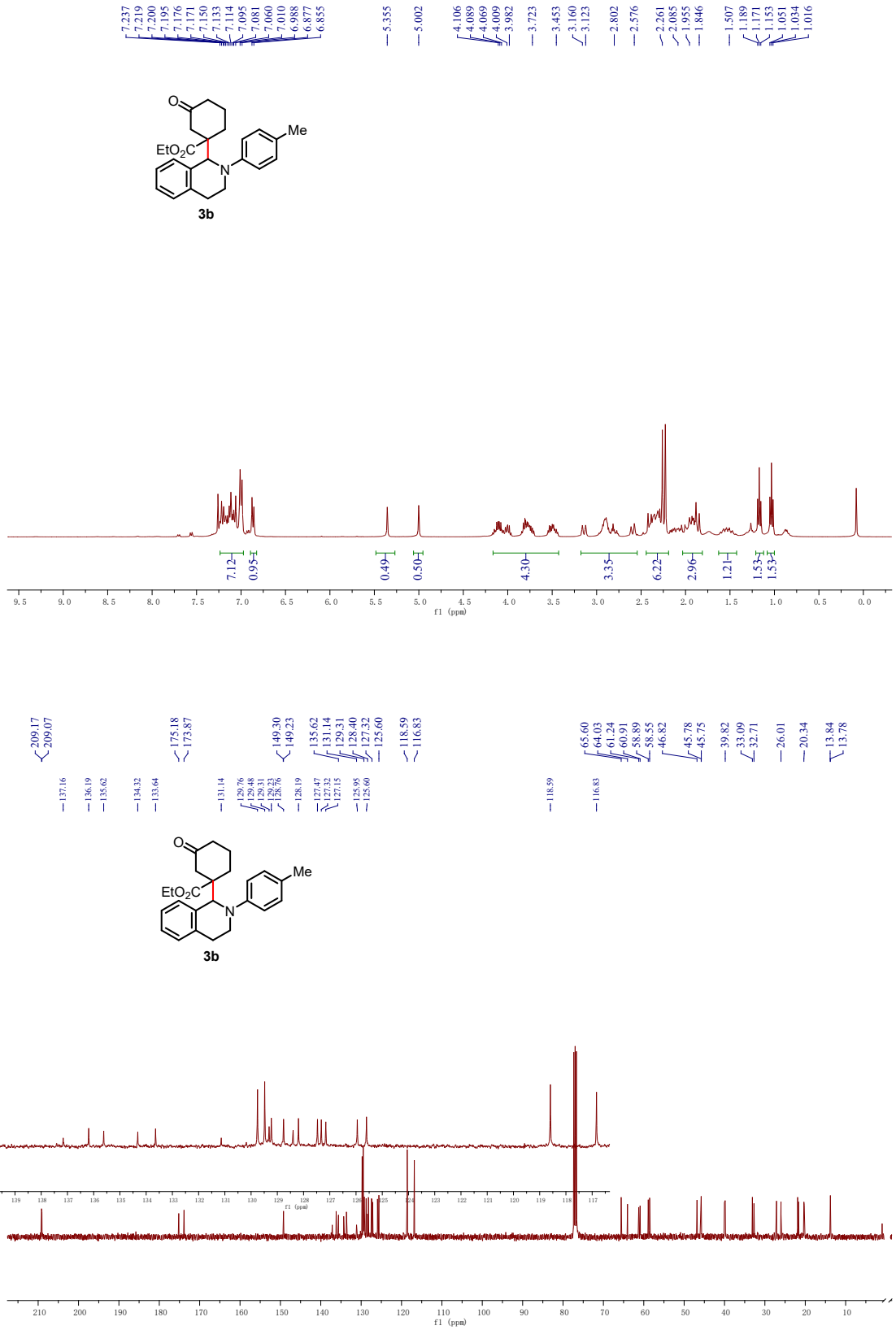




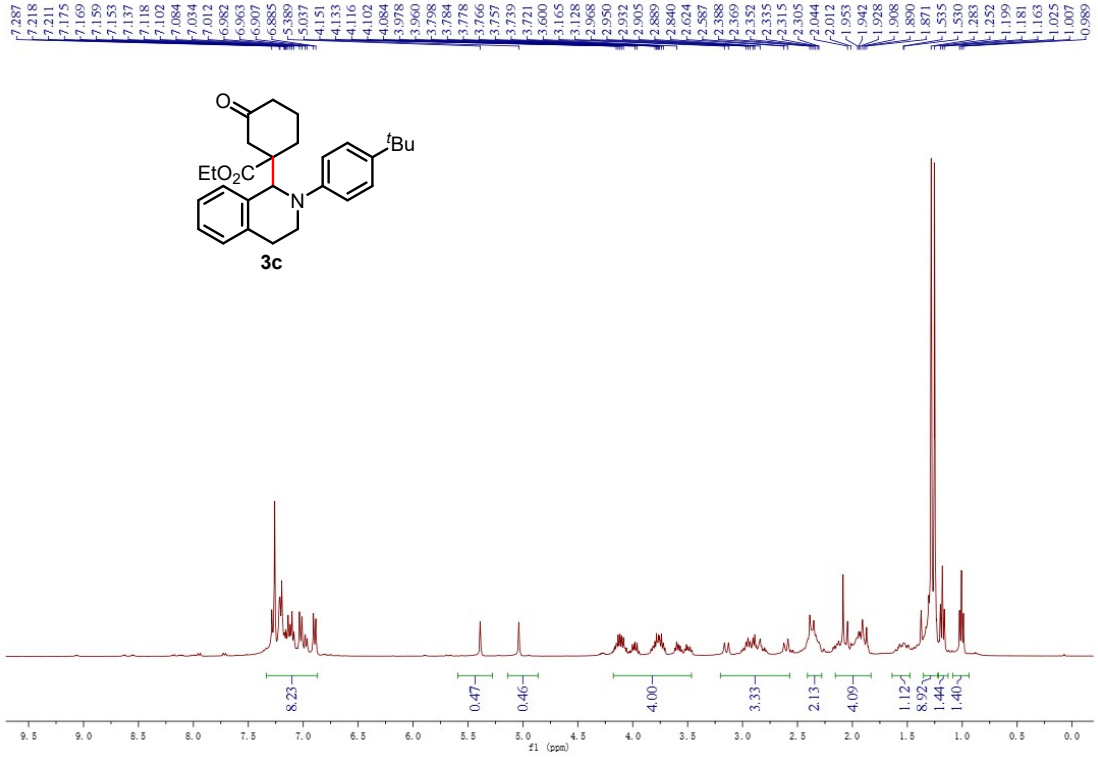
3a

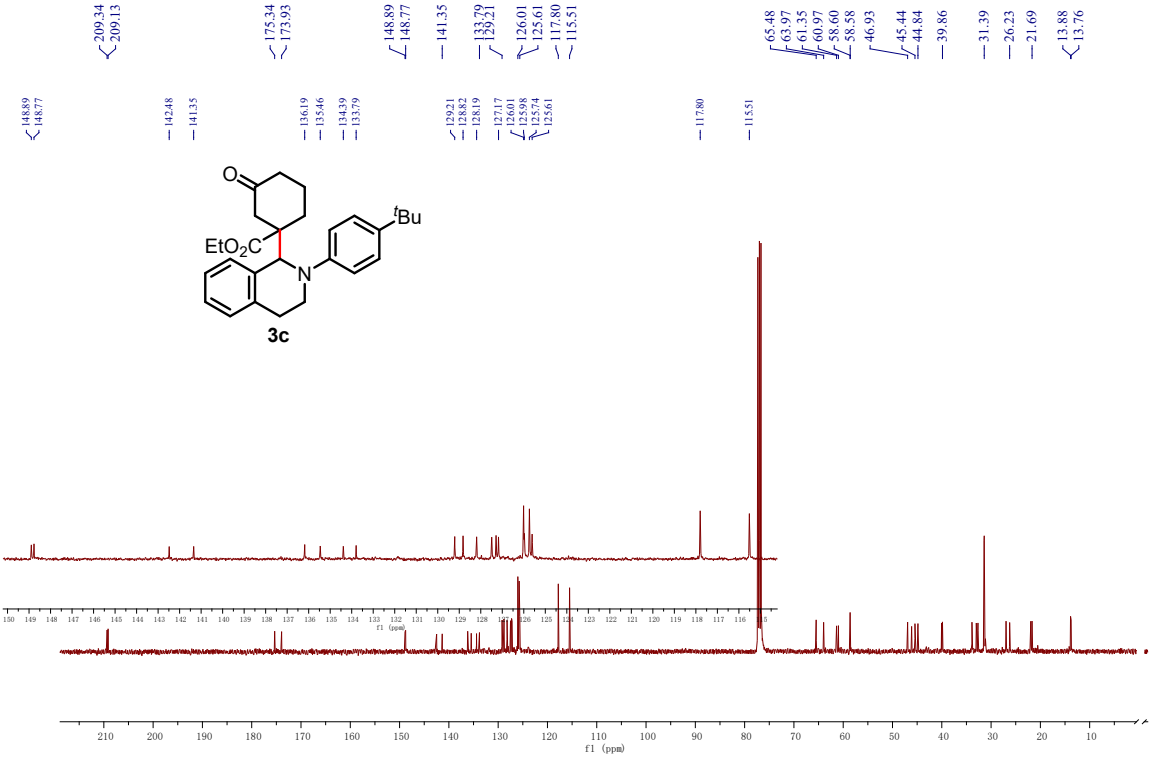


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3b**

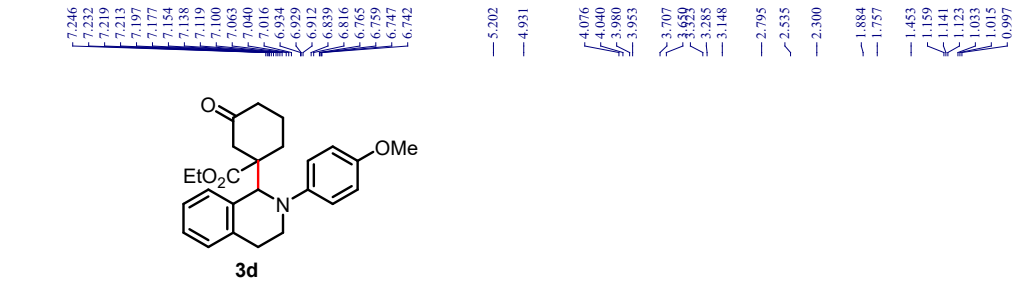


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3c**

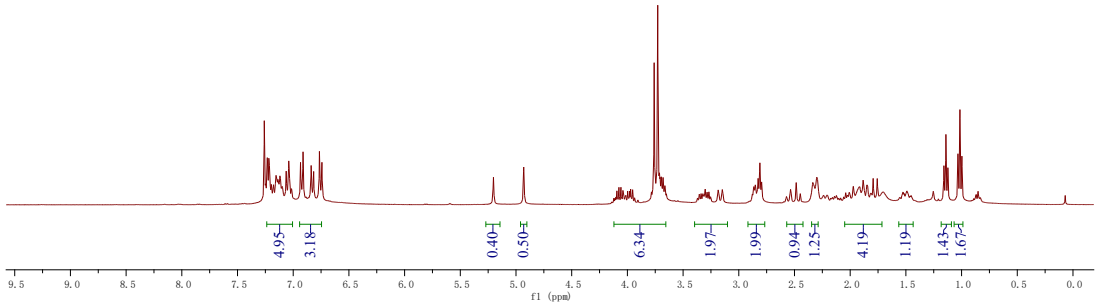


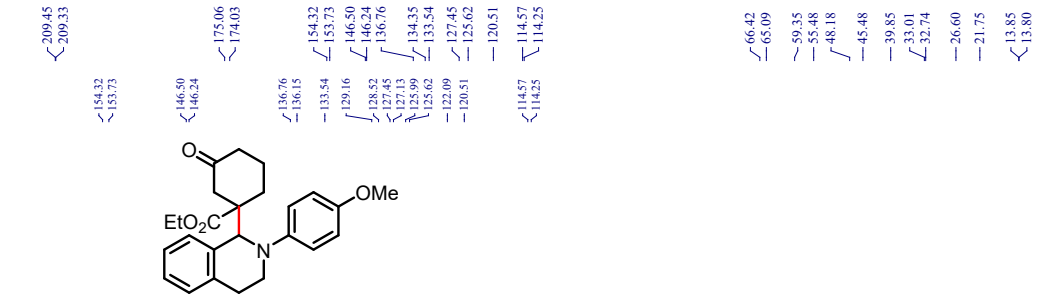


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3d**

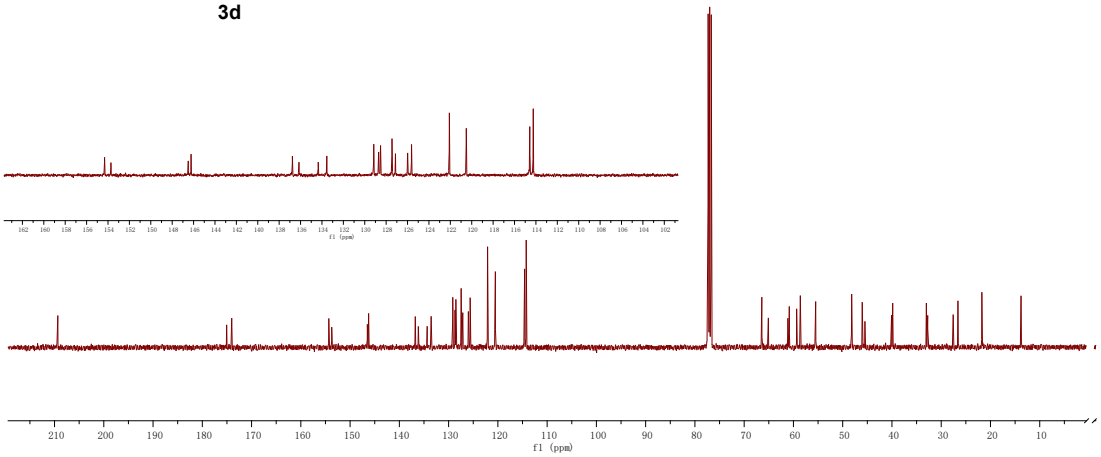


3d

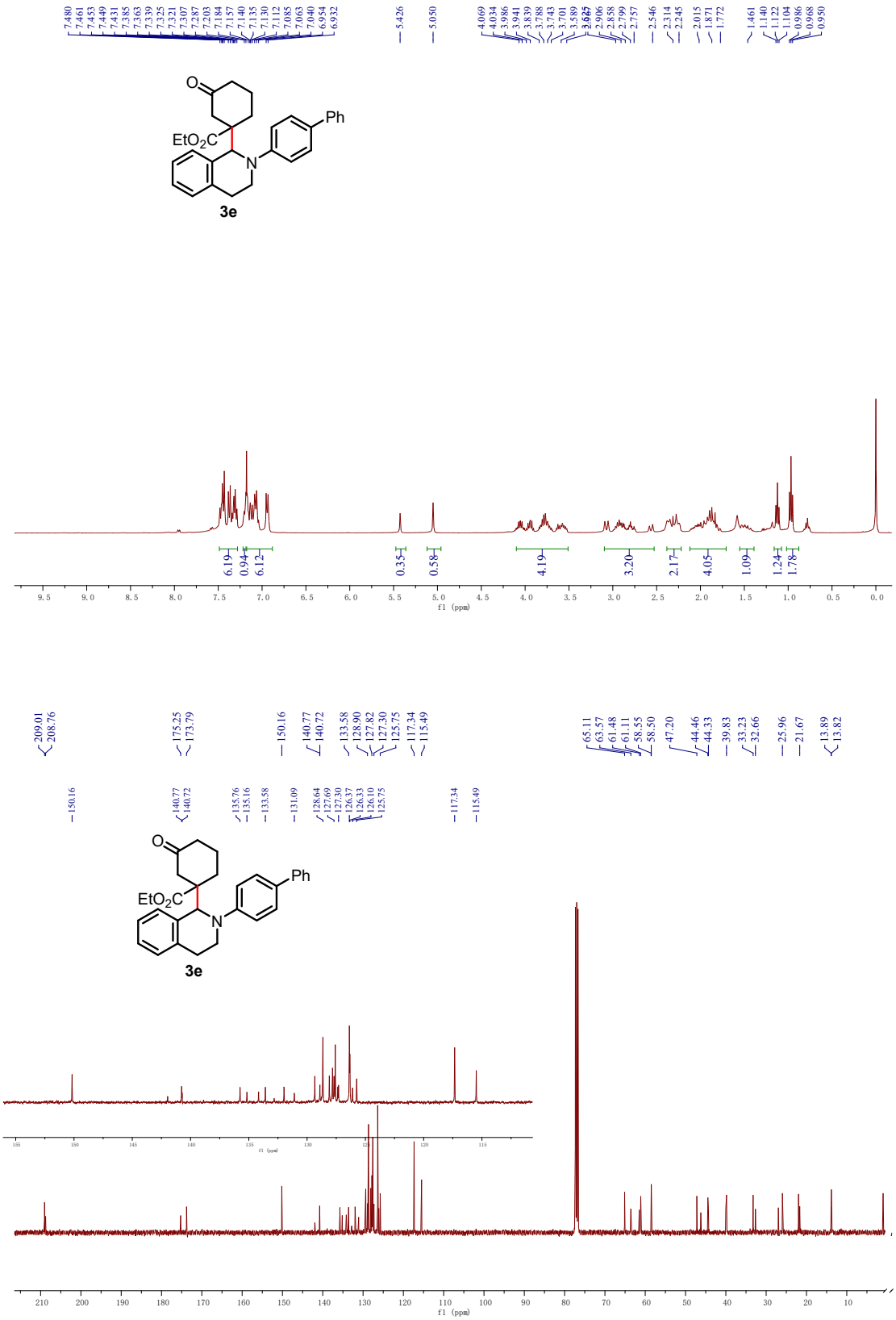




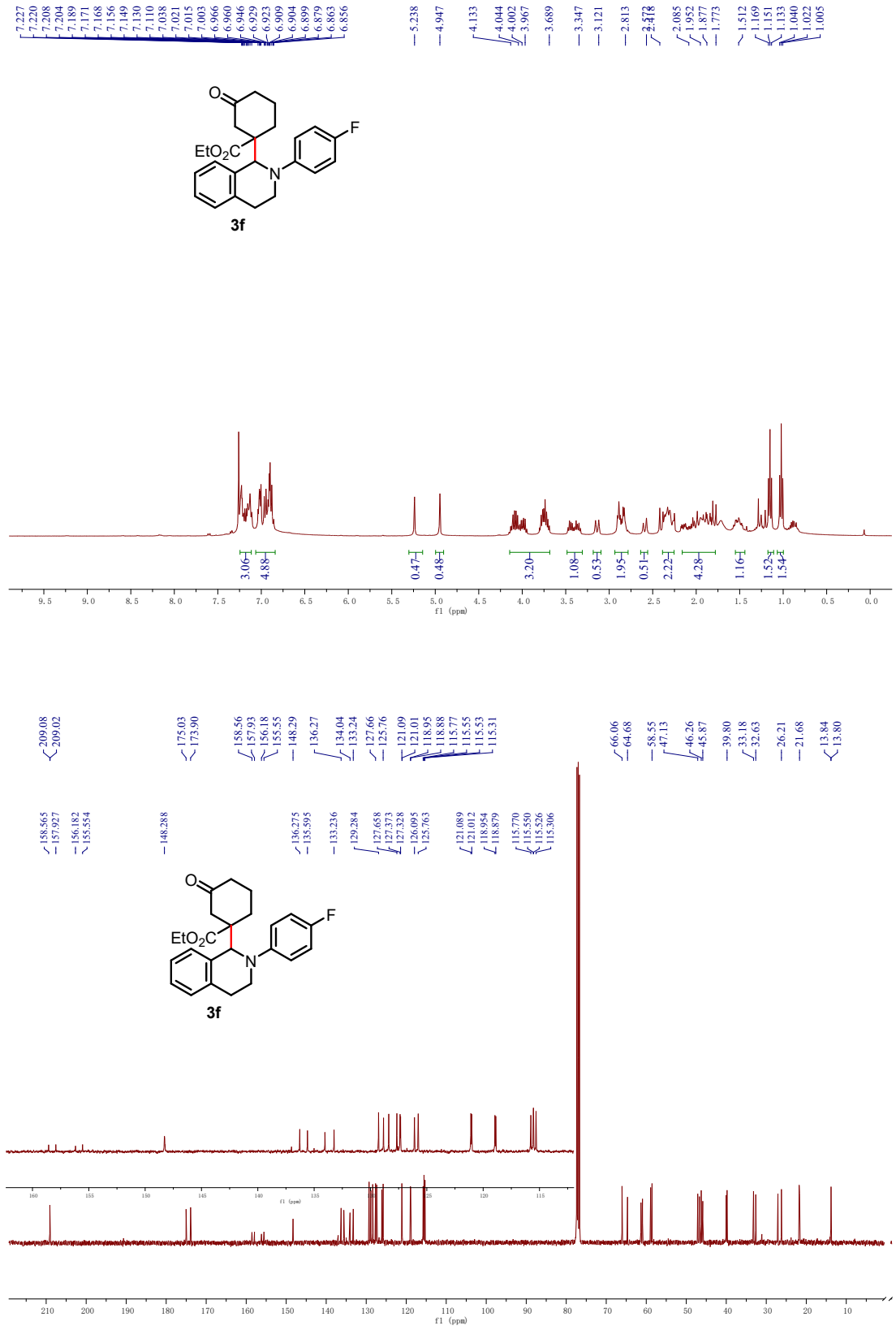
3d



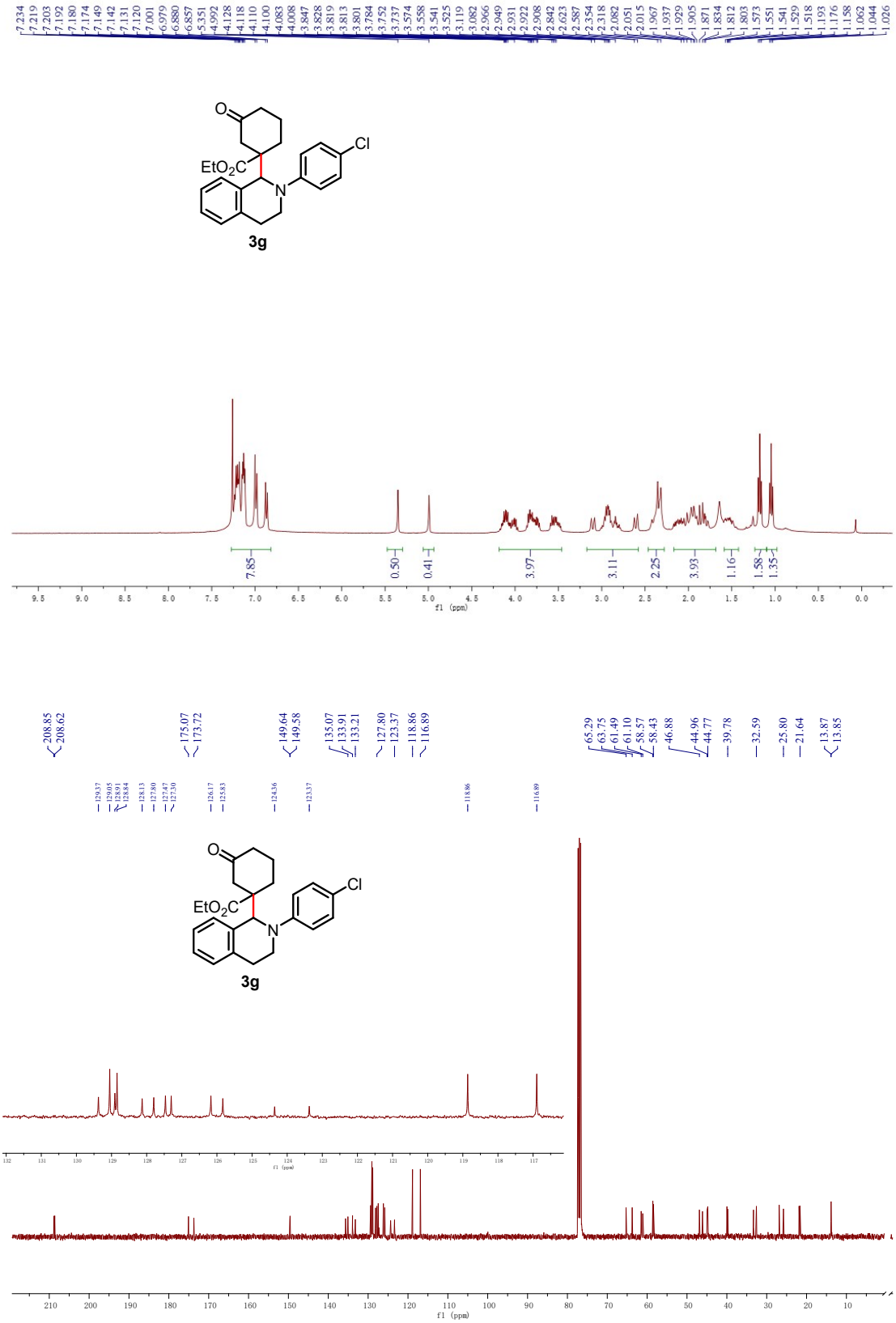
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3e**



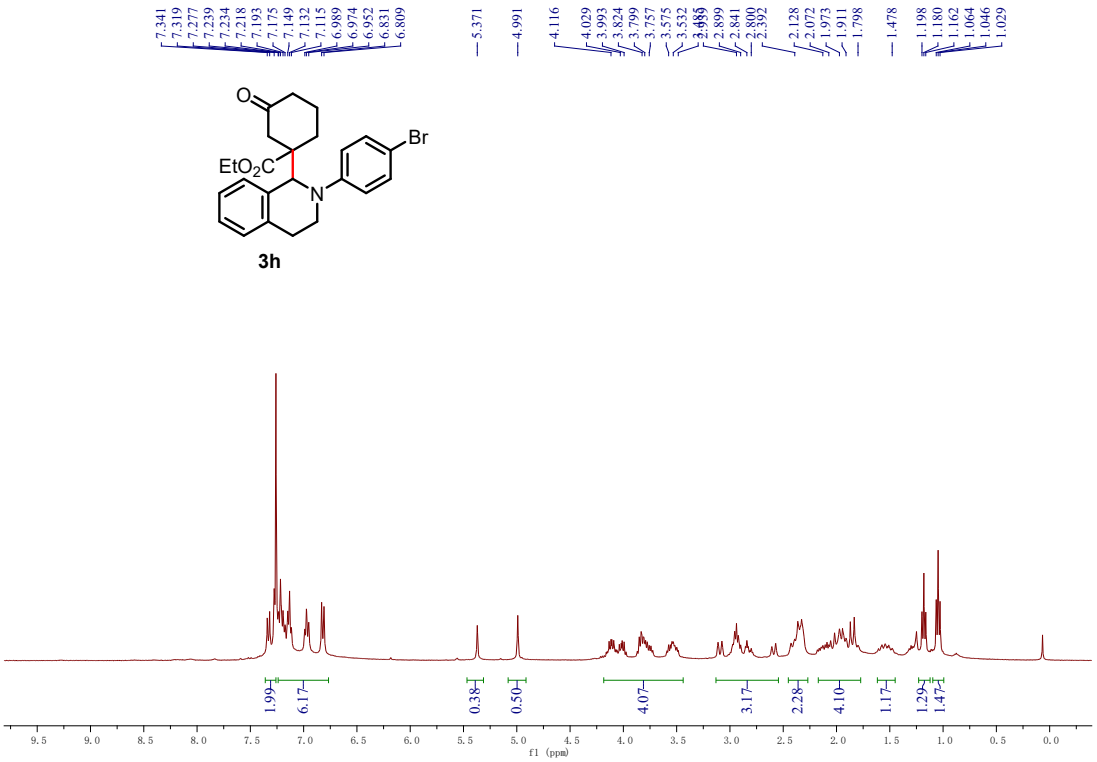
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3f**

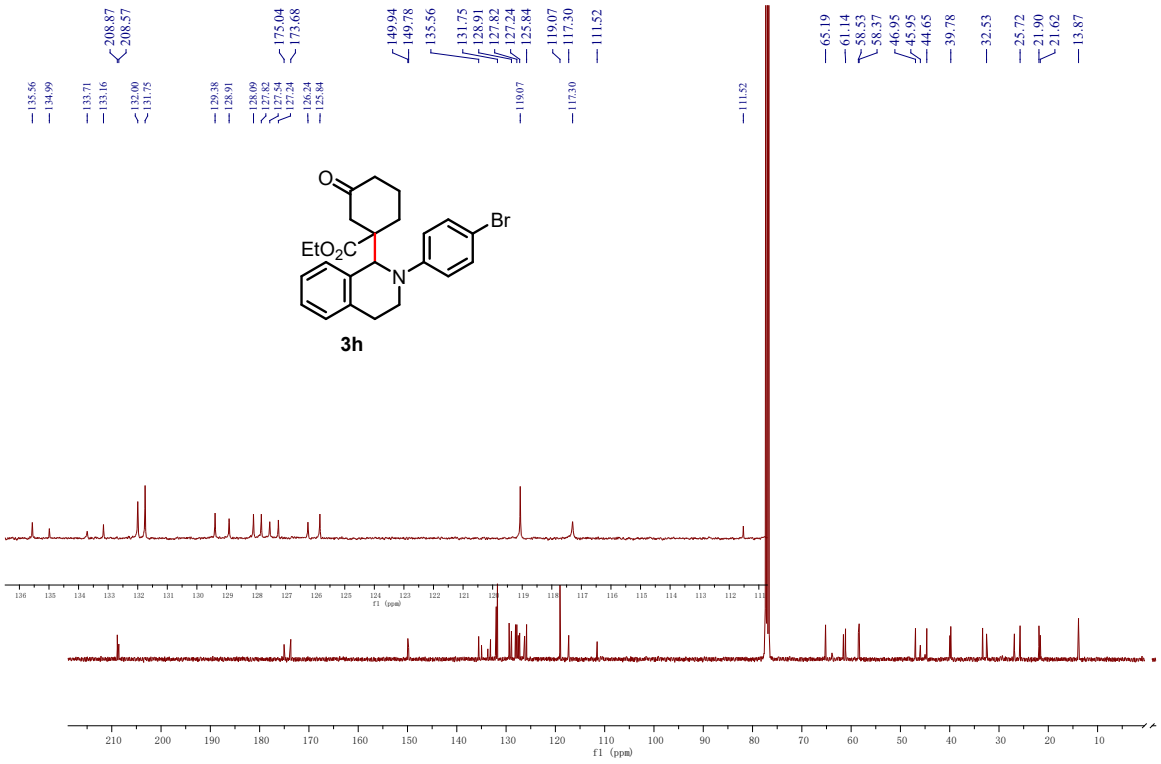


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3g**

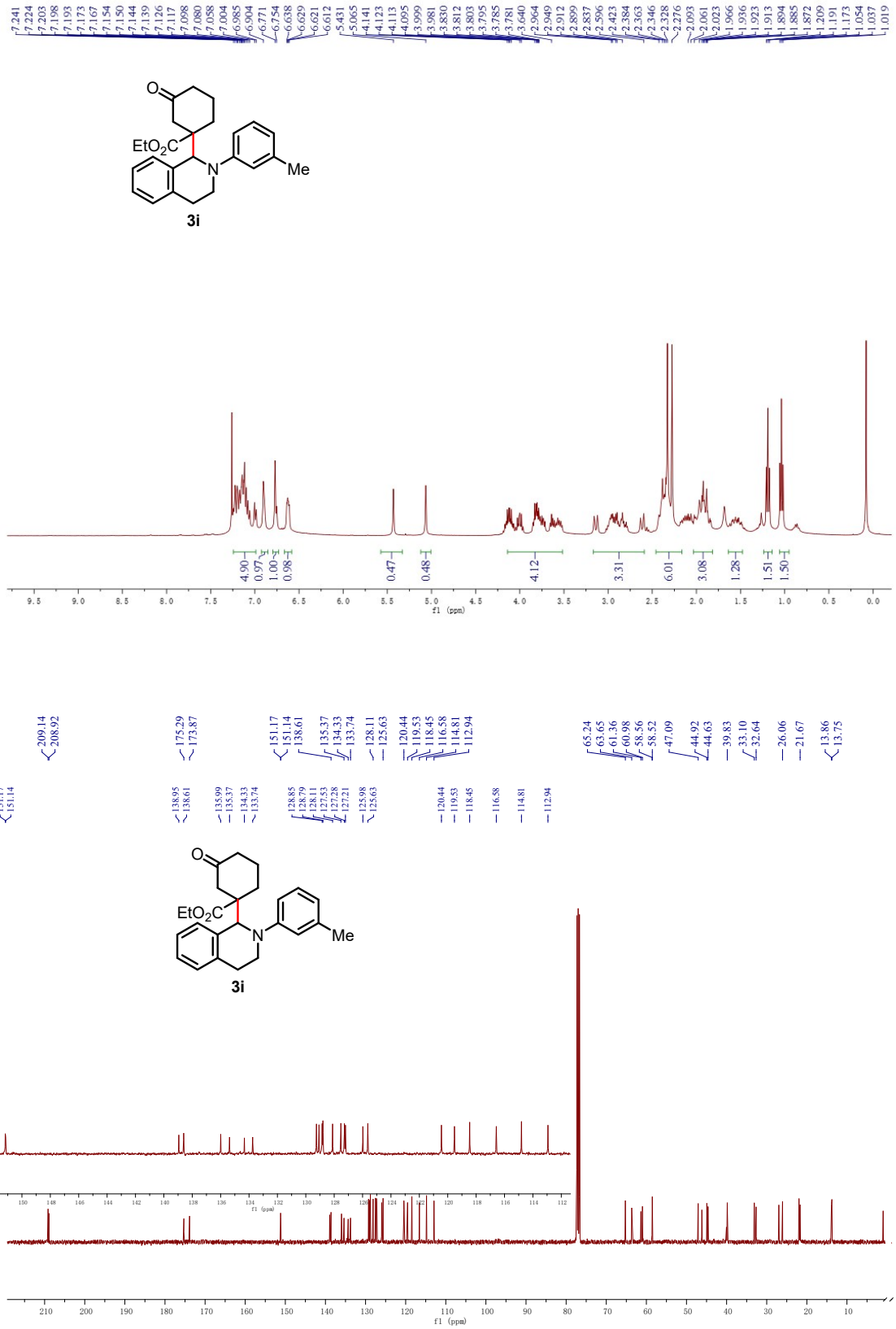


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3h**

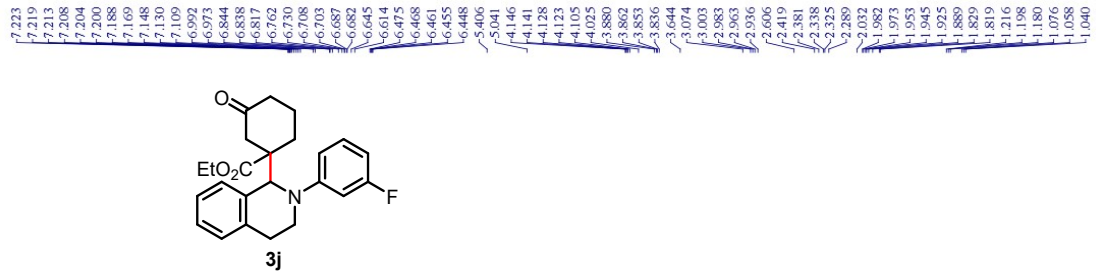


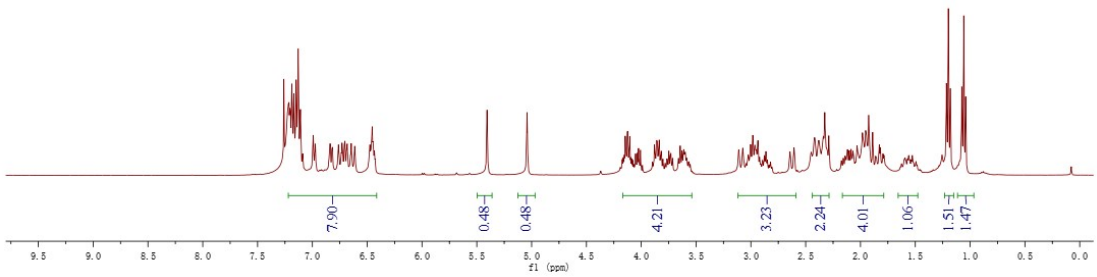


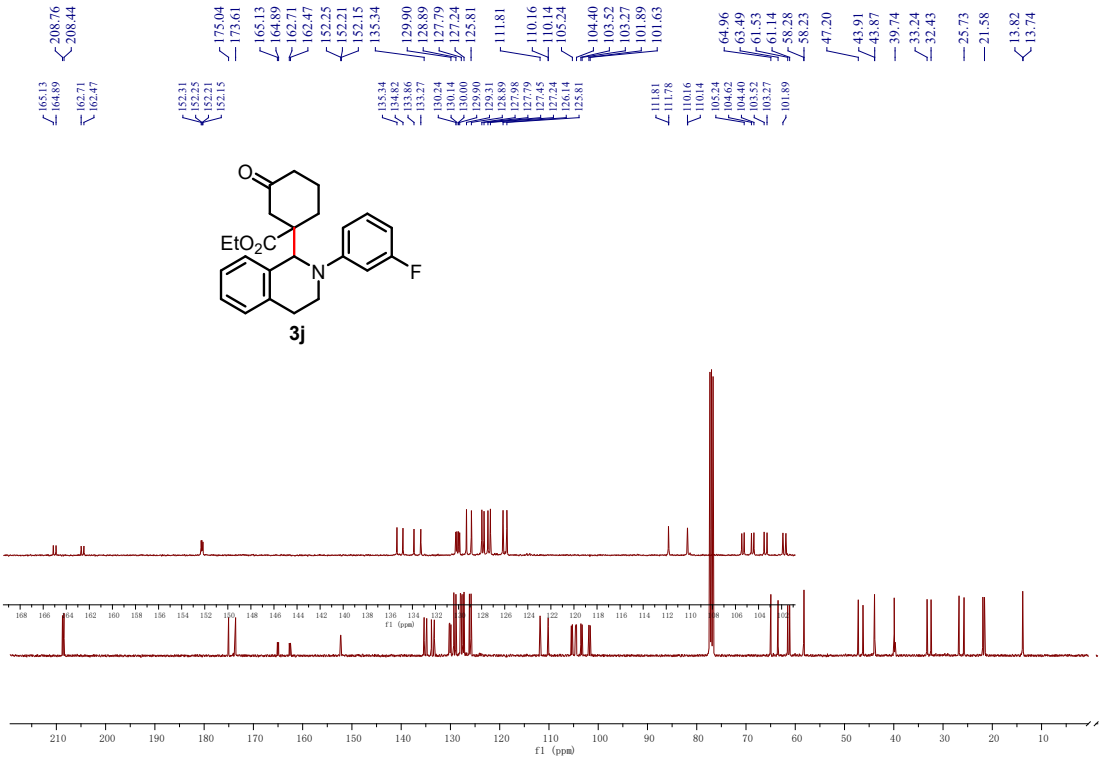
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3i**



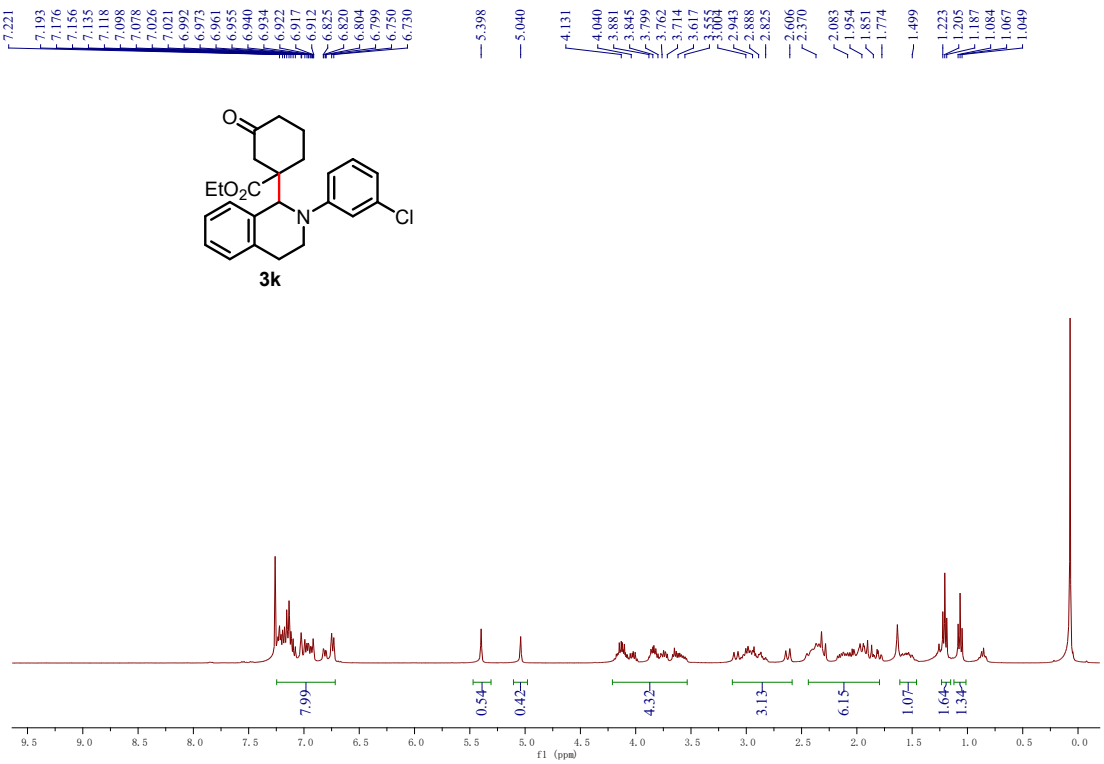
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3j**

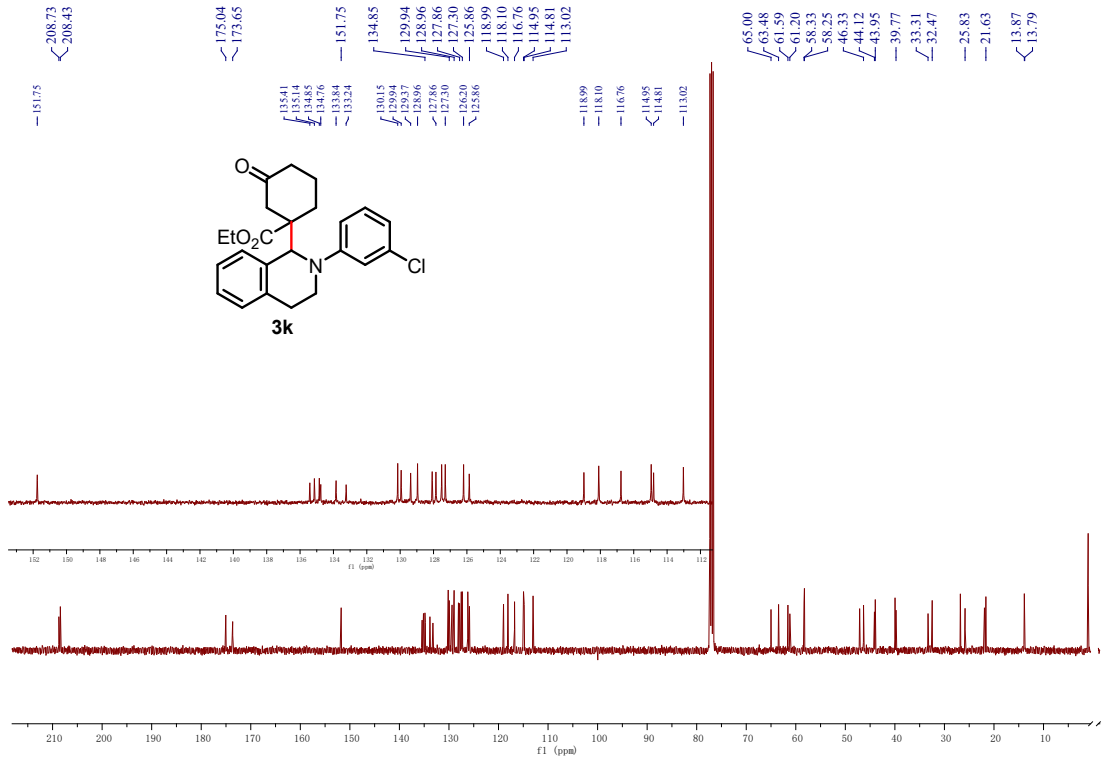




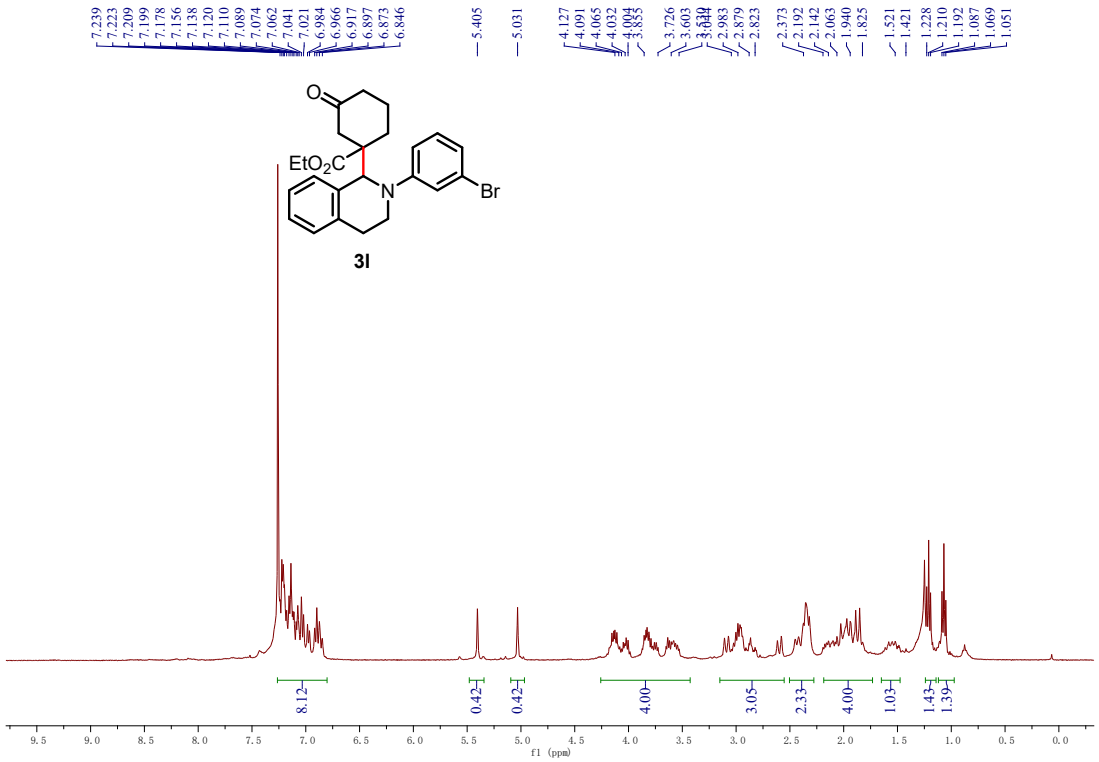


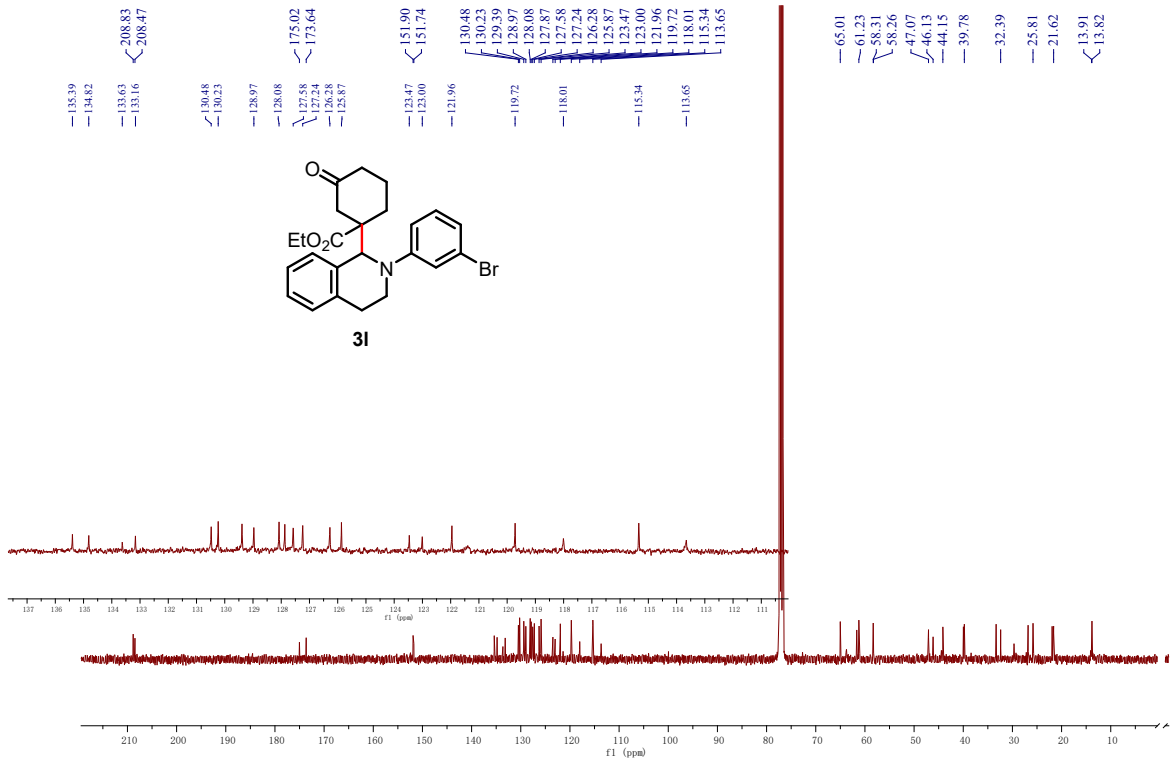
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3k**



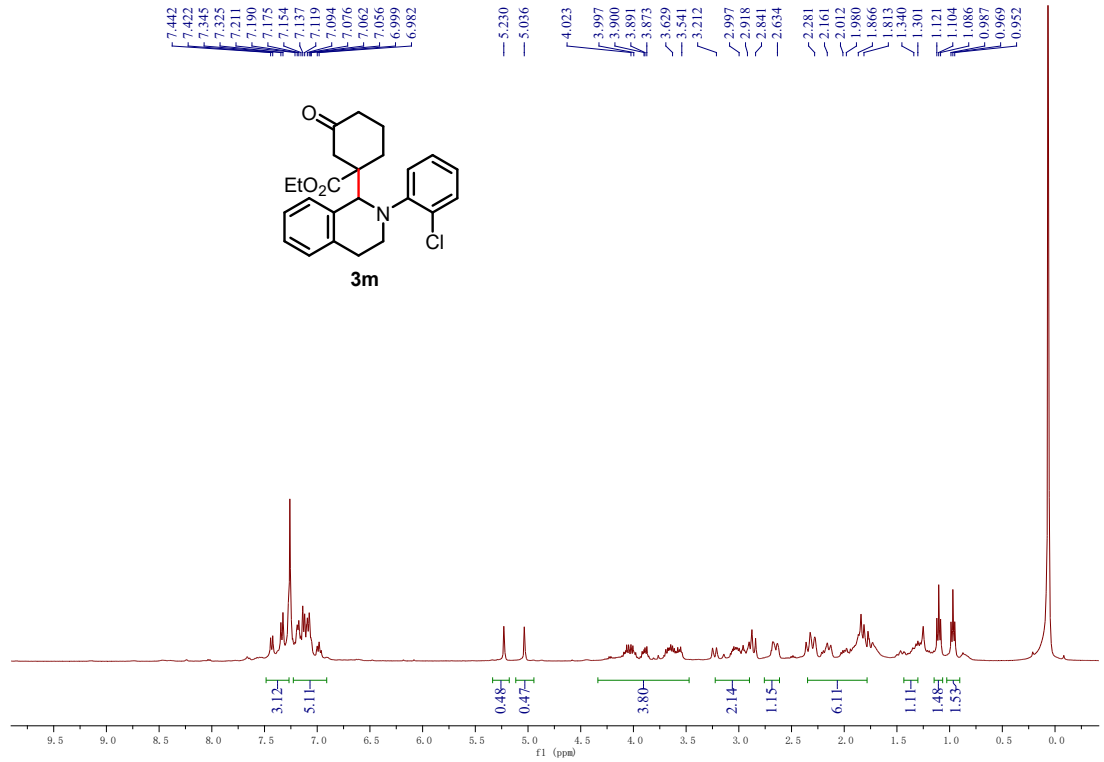


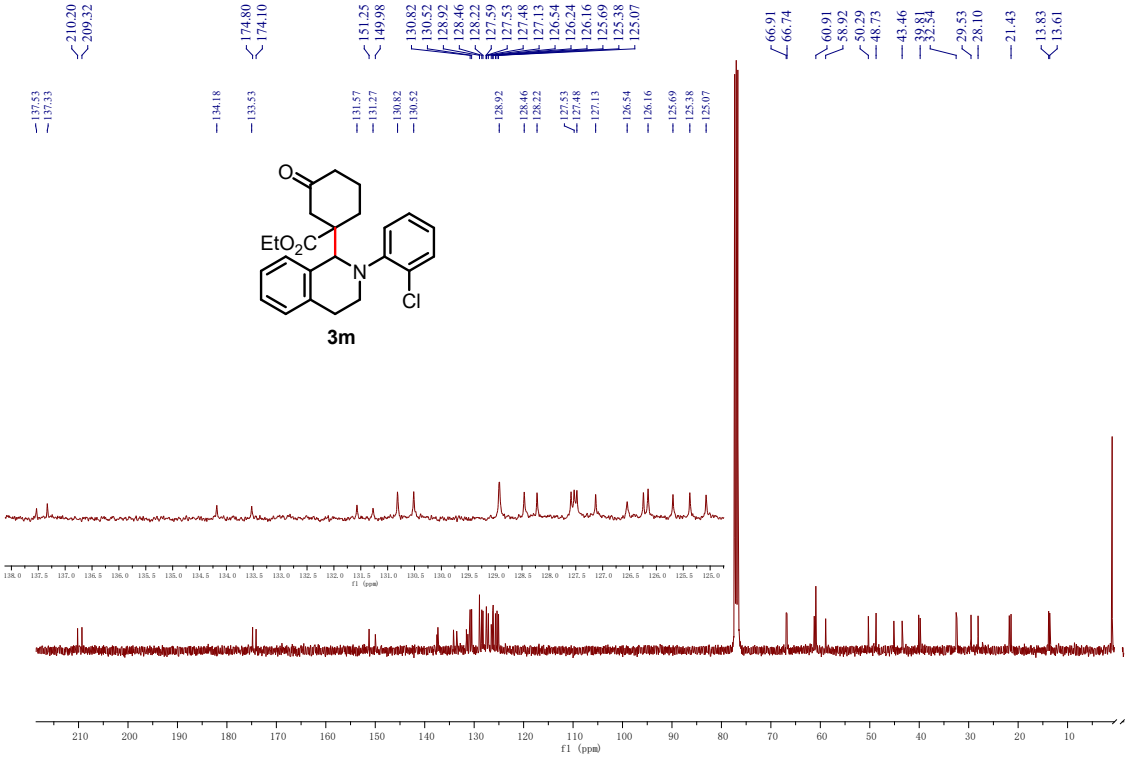
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3l**



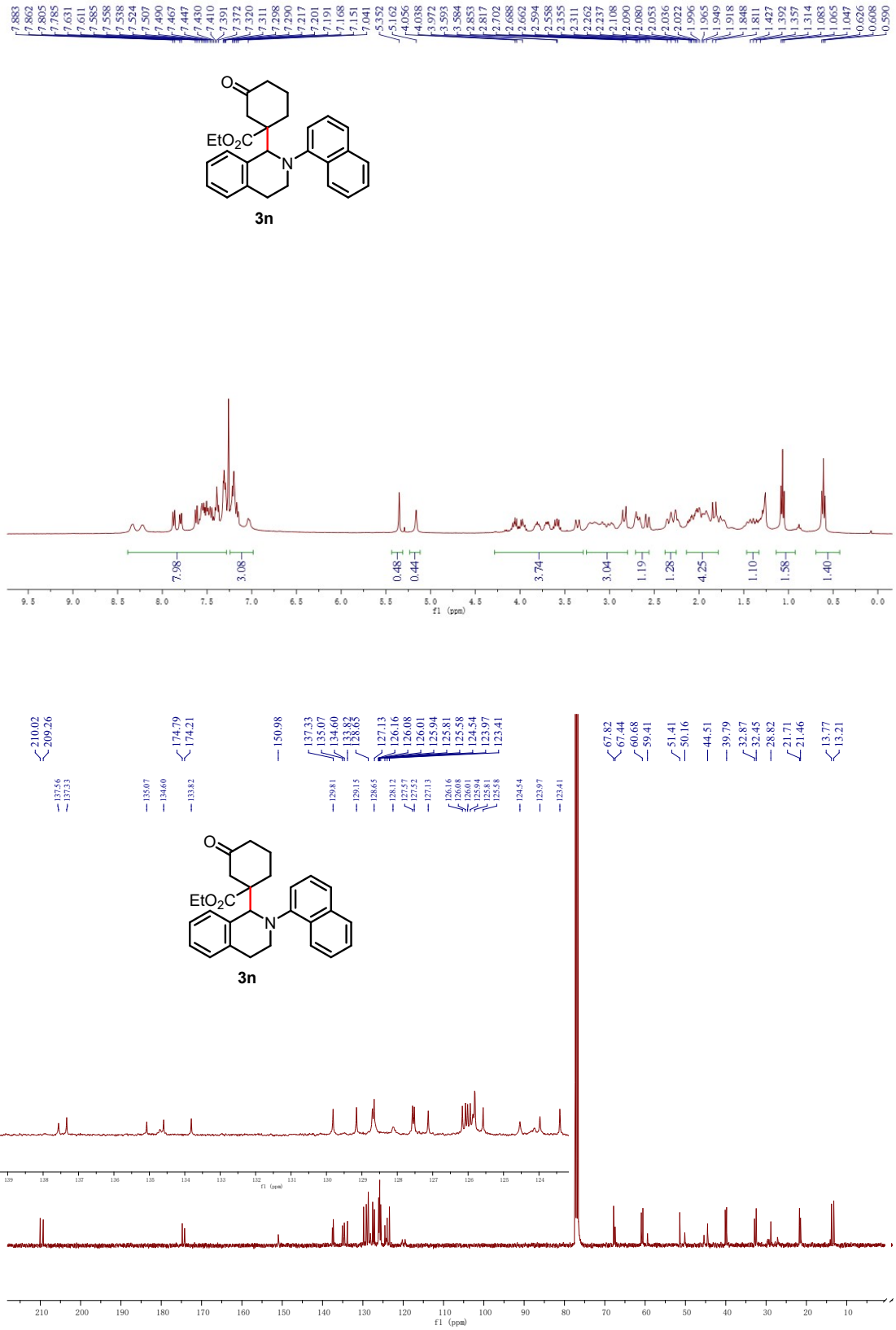


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3m**

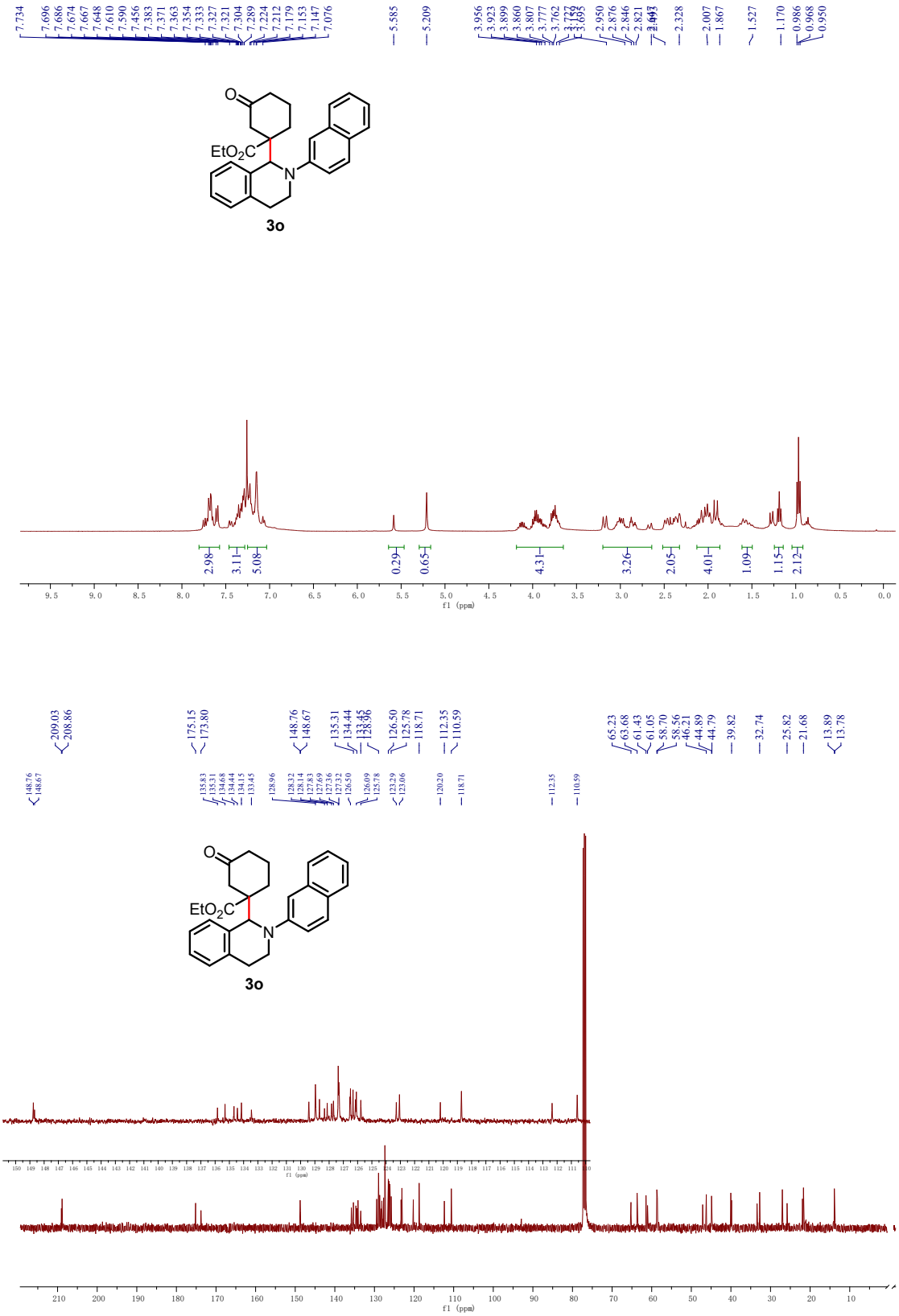




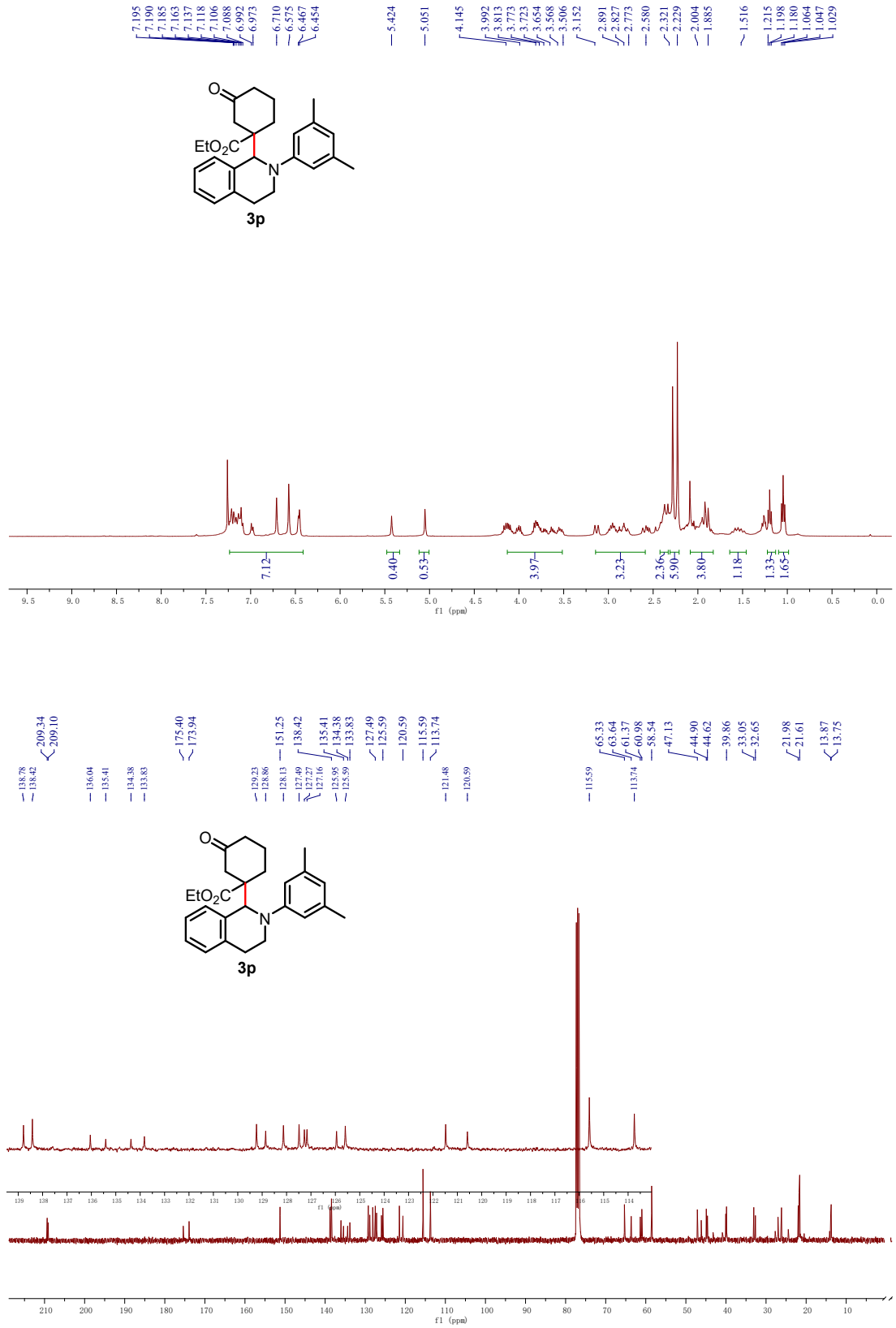
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3n**



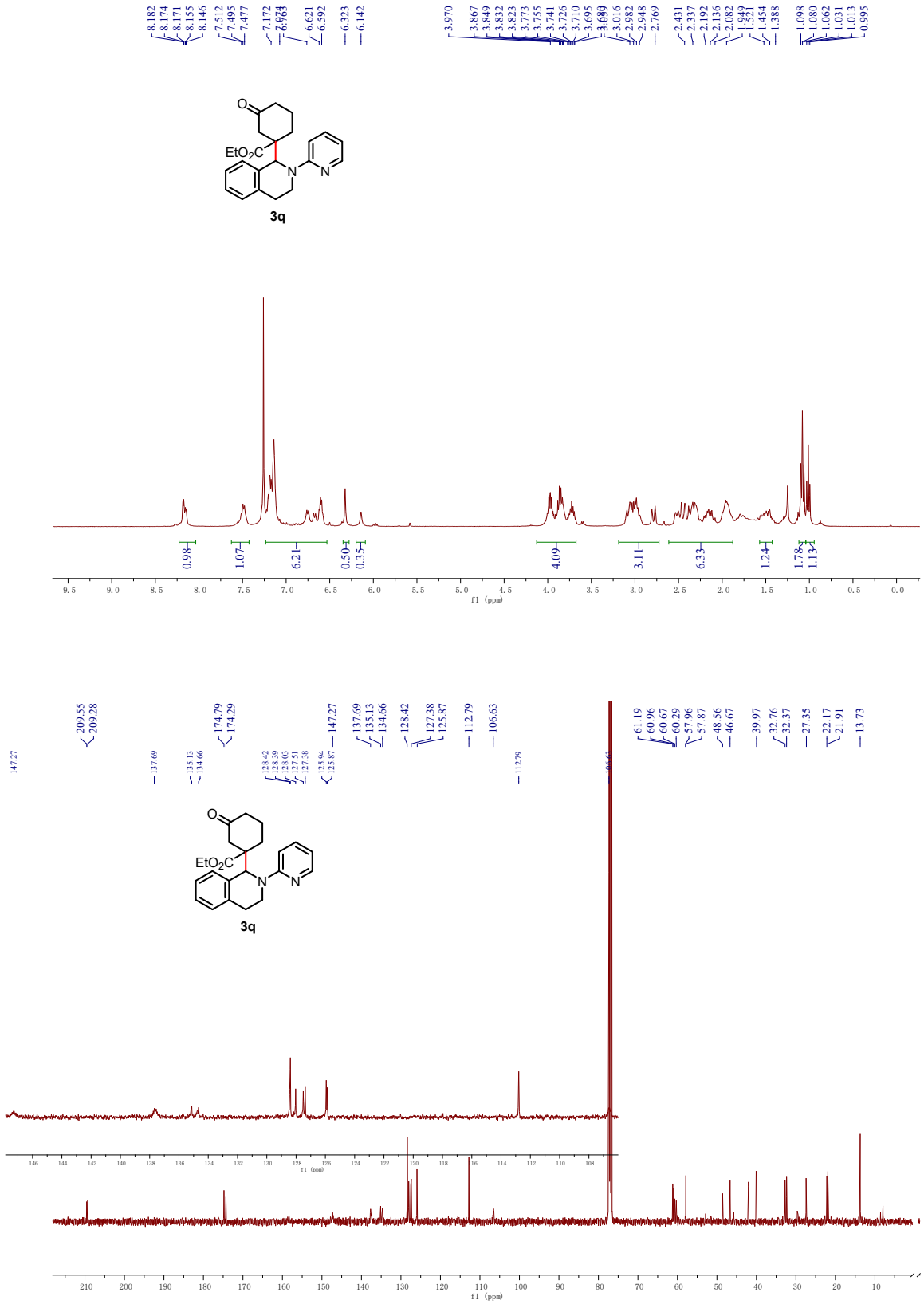
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3o**



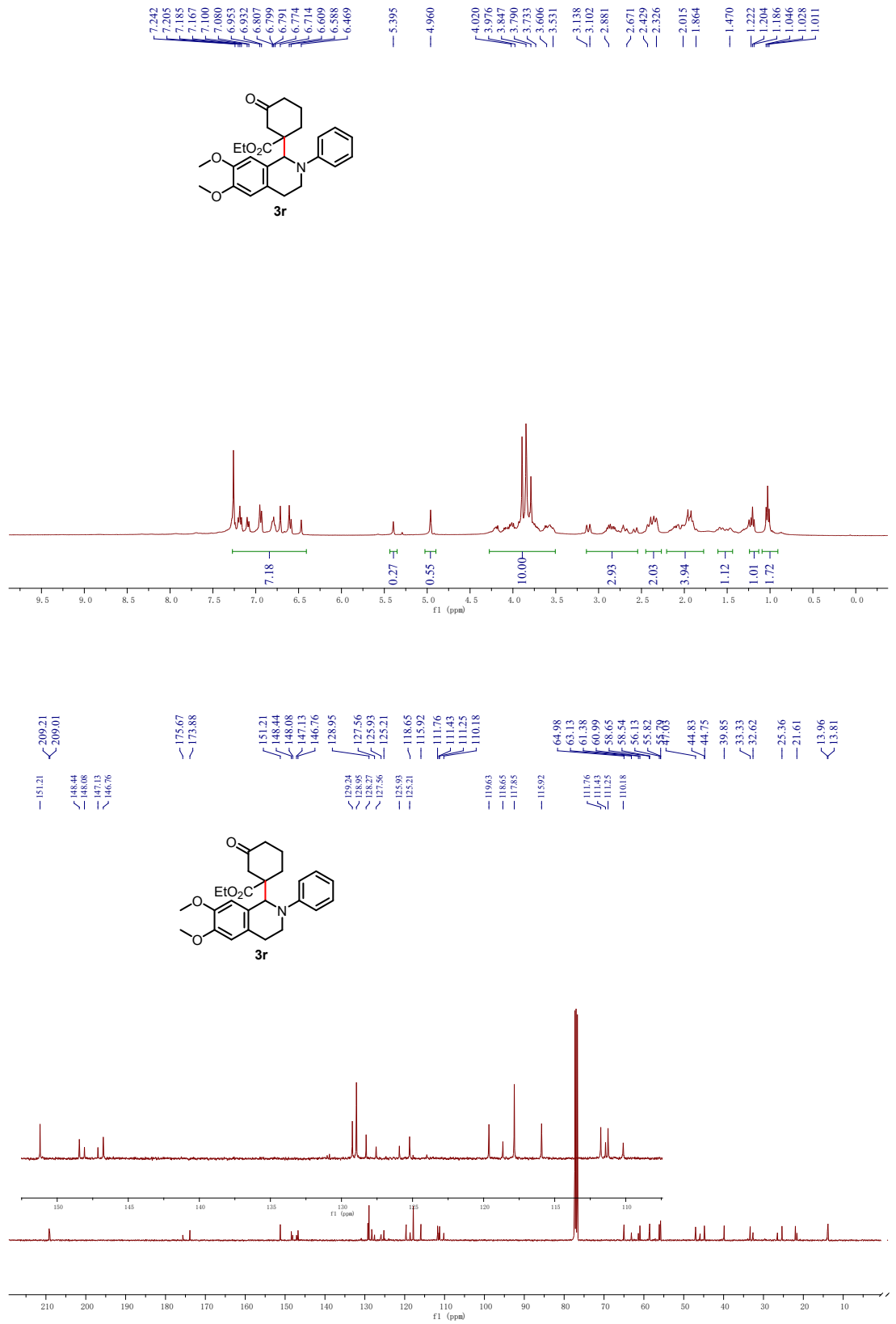
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3p**



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3q**



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3r**



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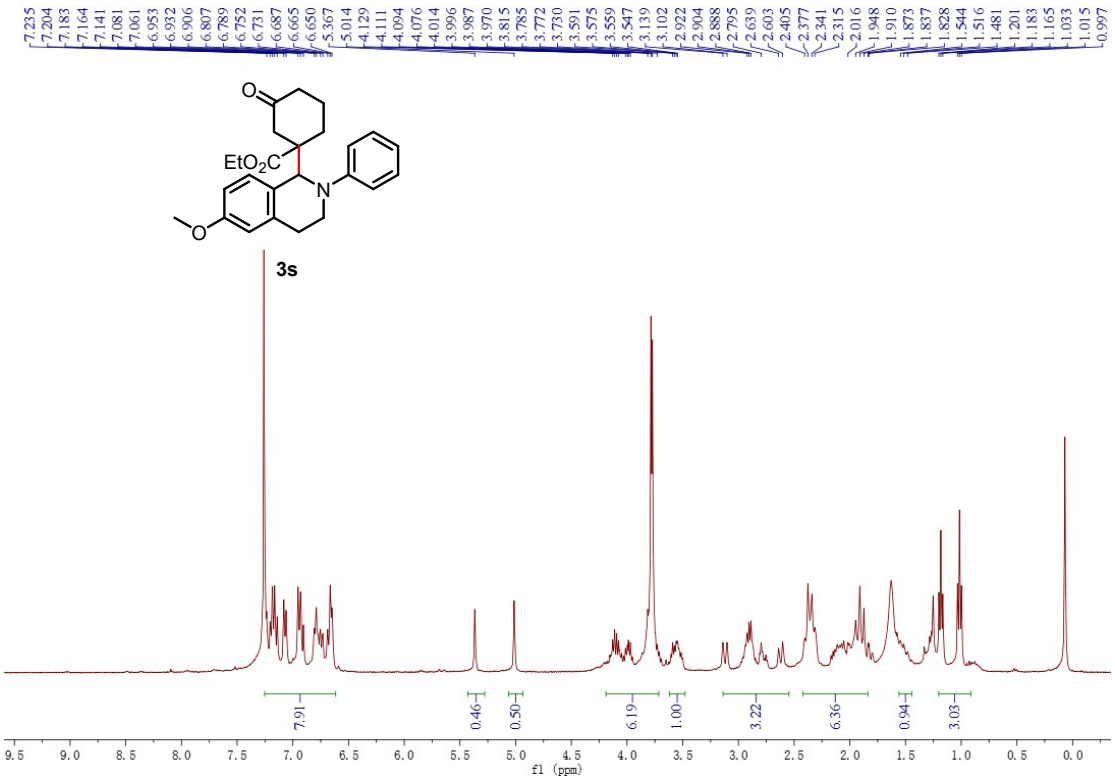
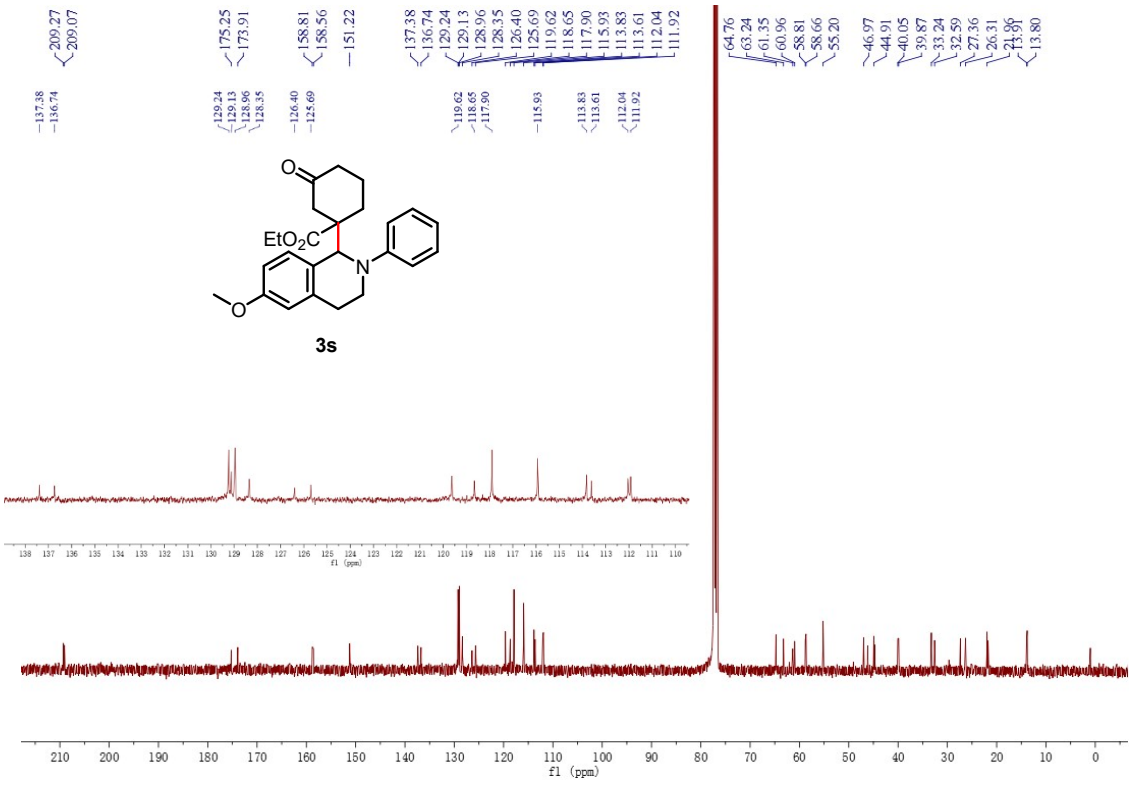
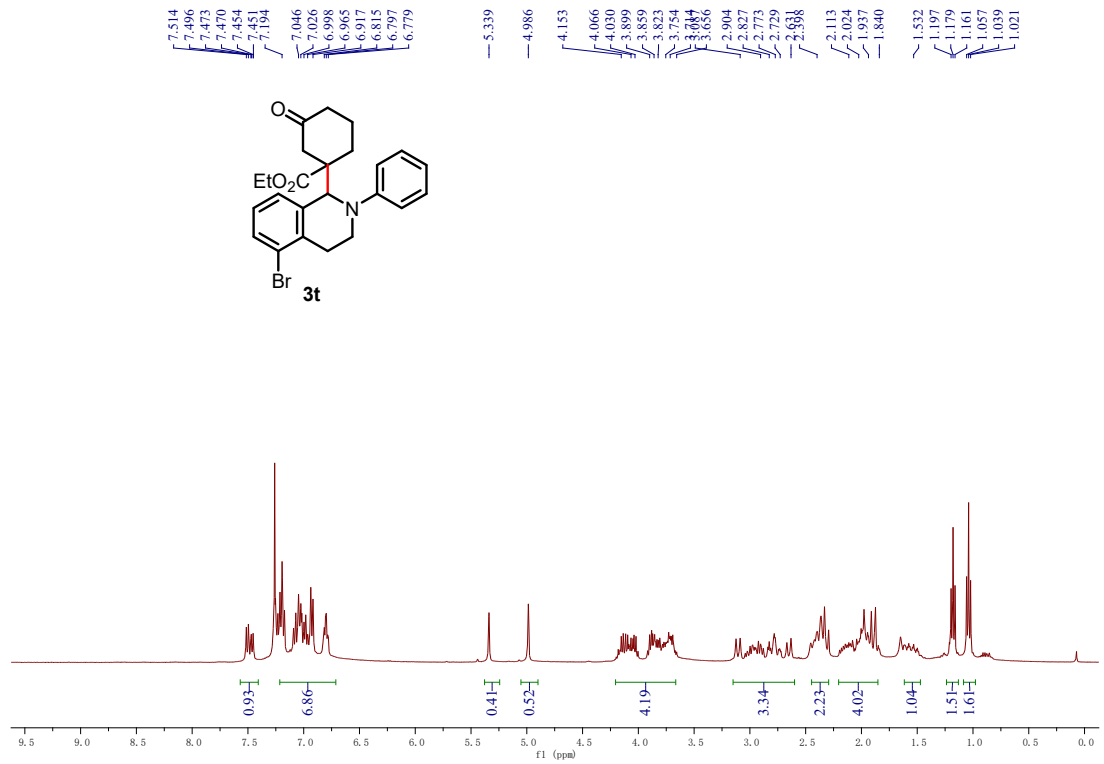
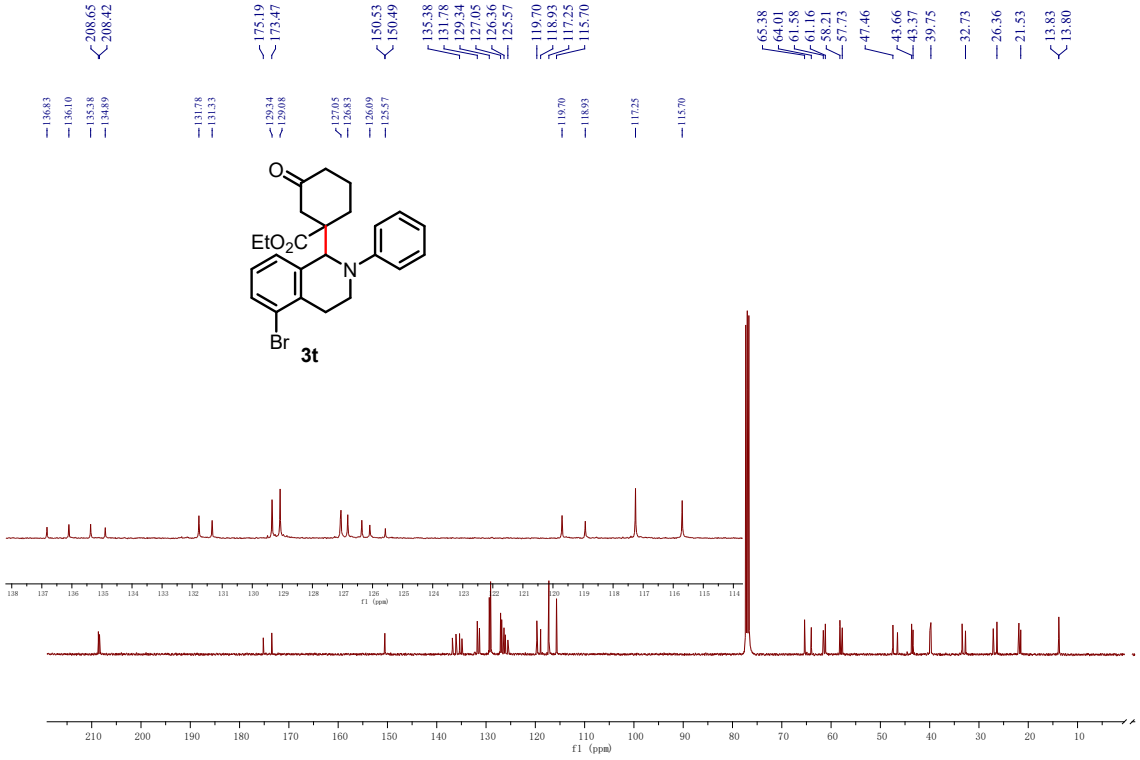


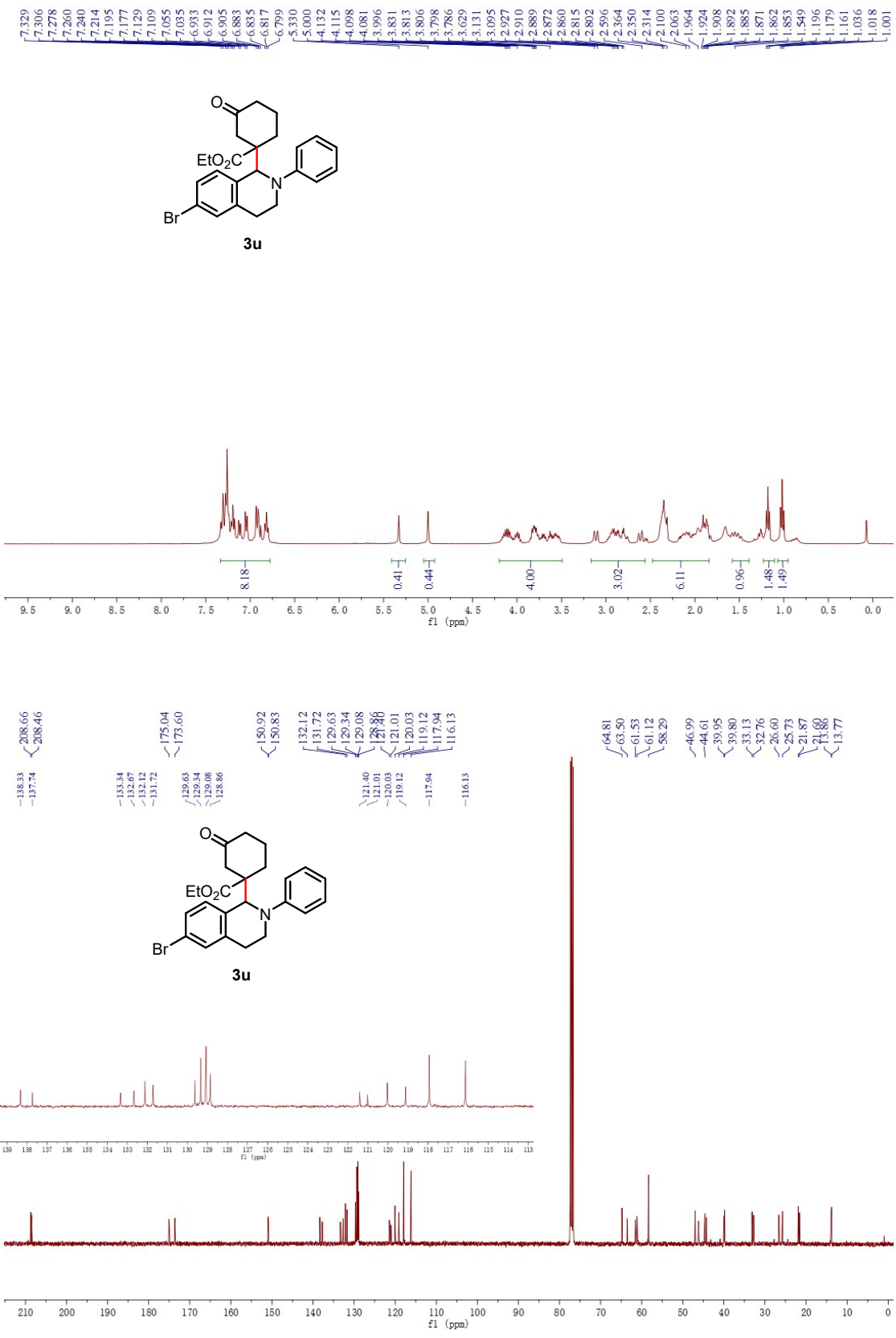


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3t**

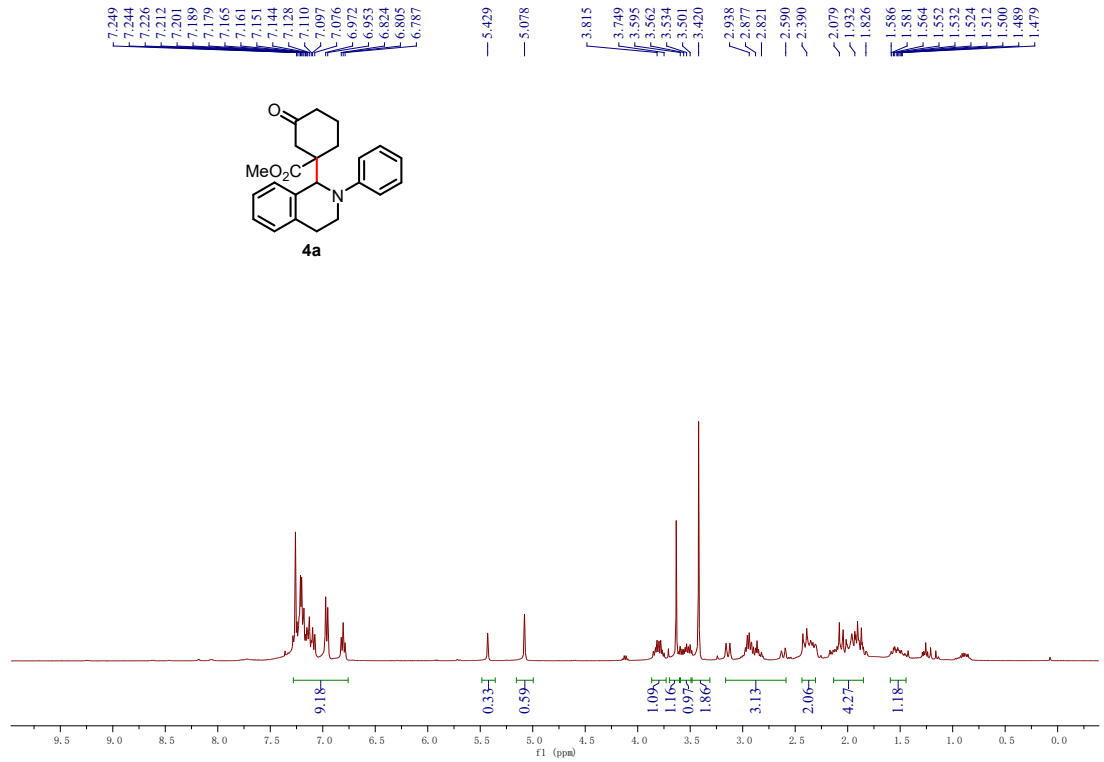


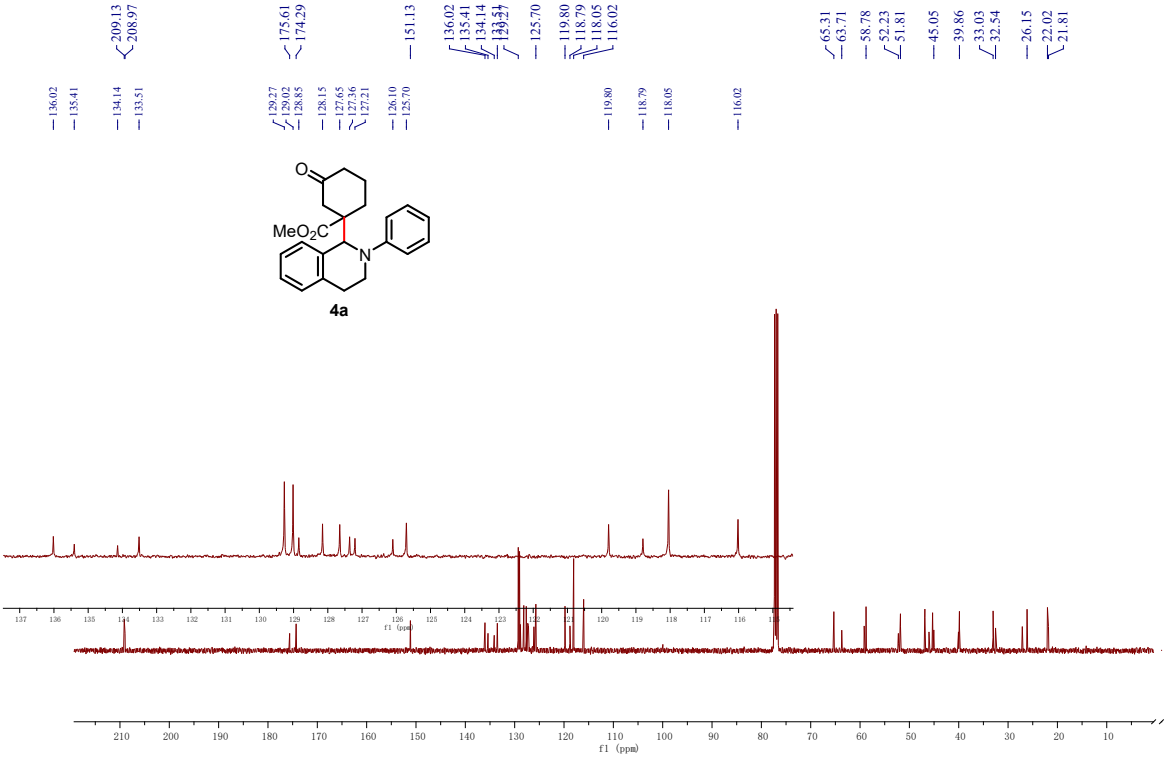


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3u**

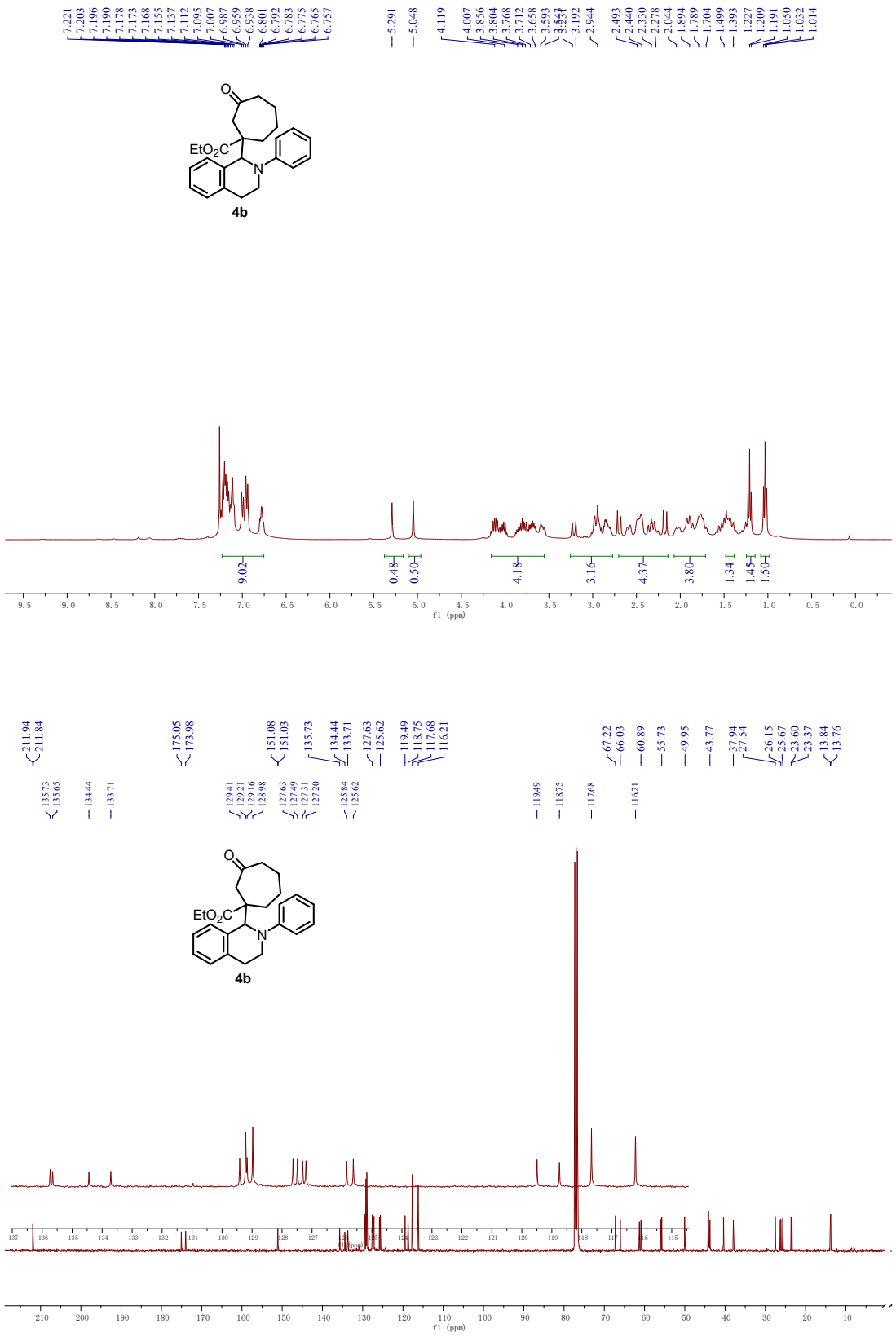


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4a**

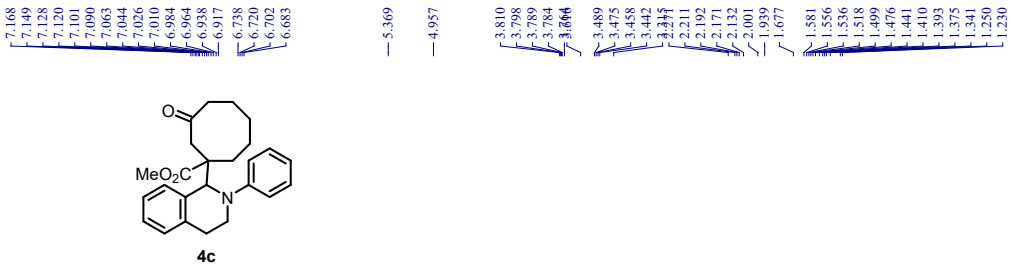




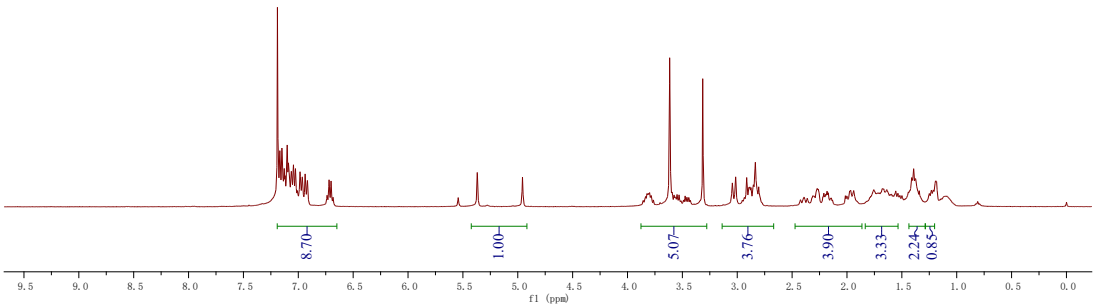
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4b**

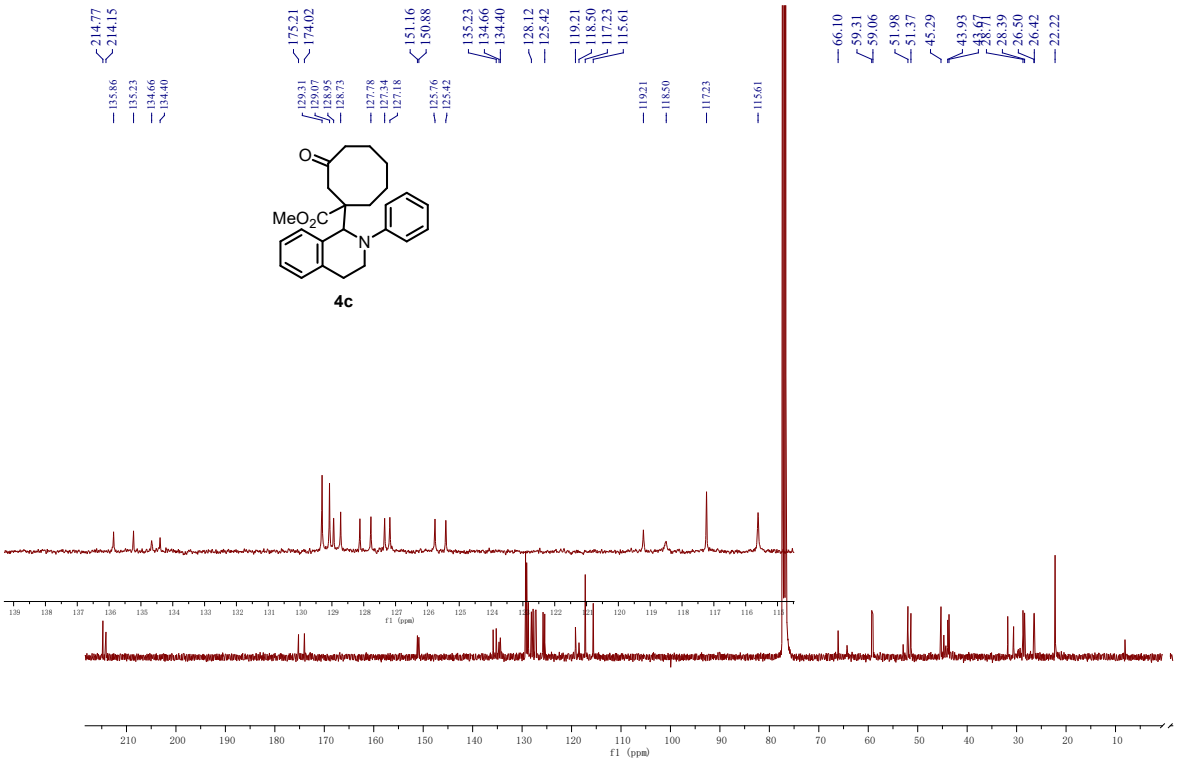


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4c**



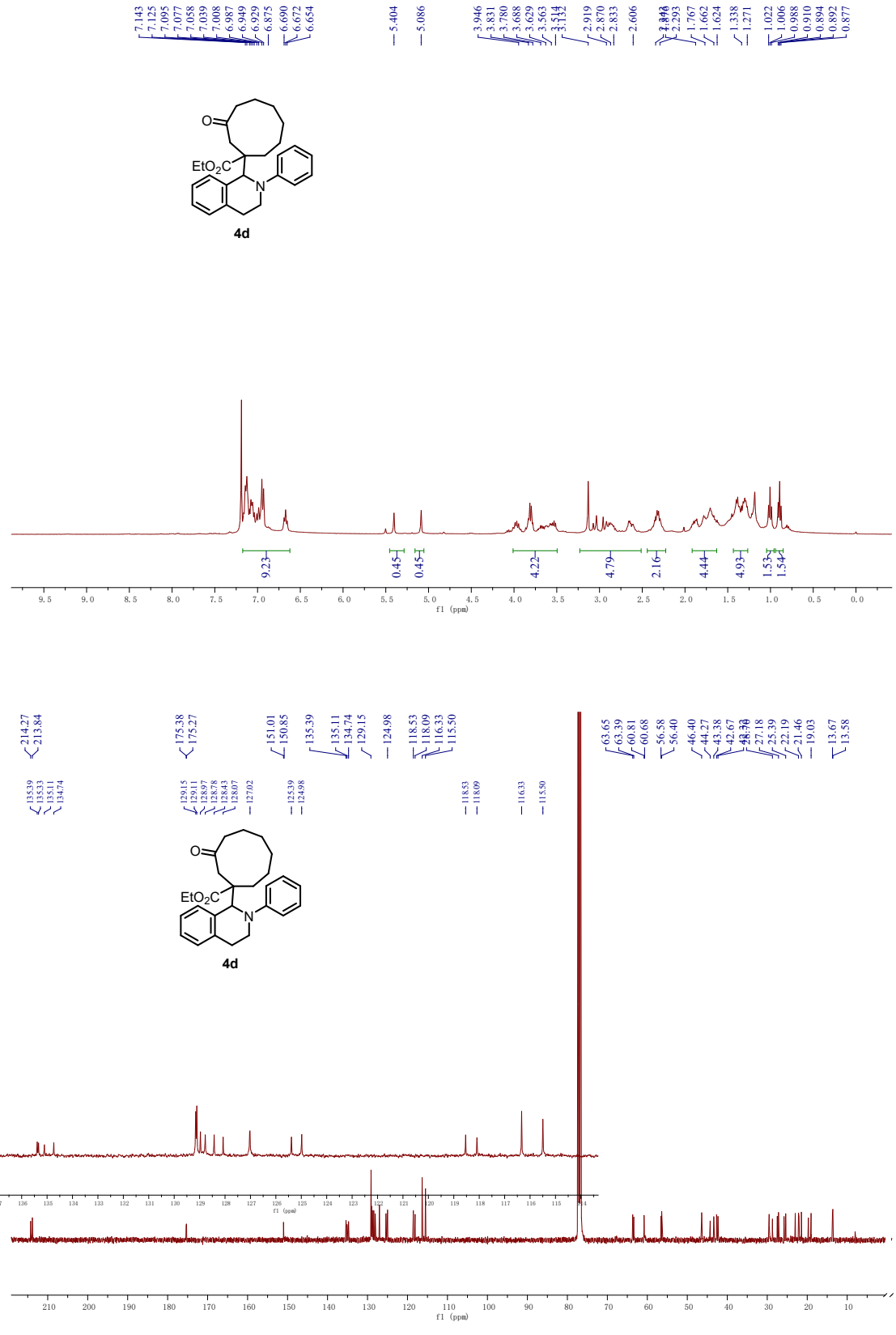
4c



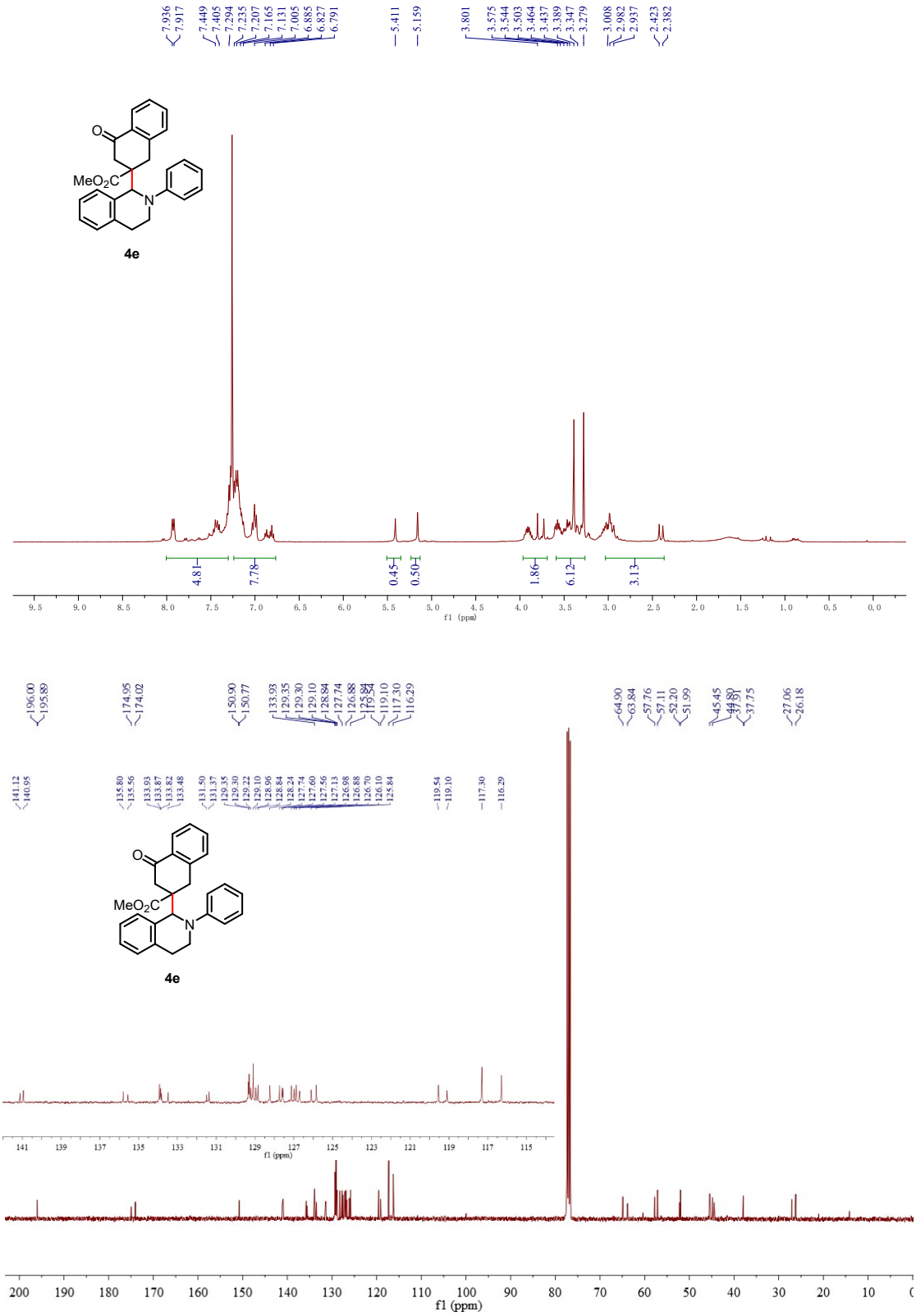


4c

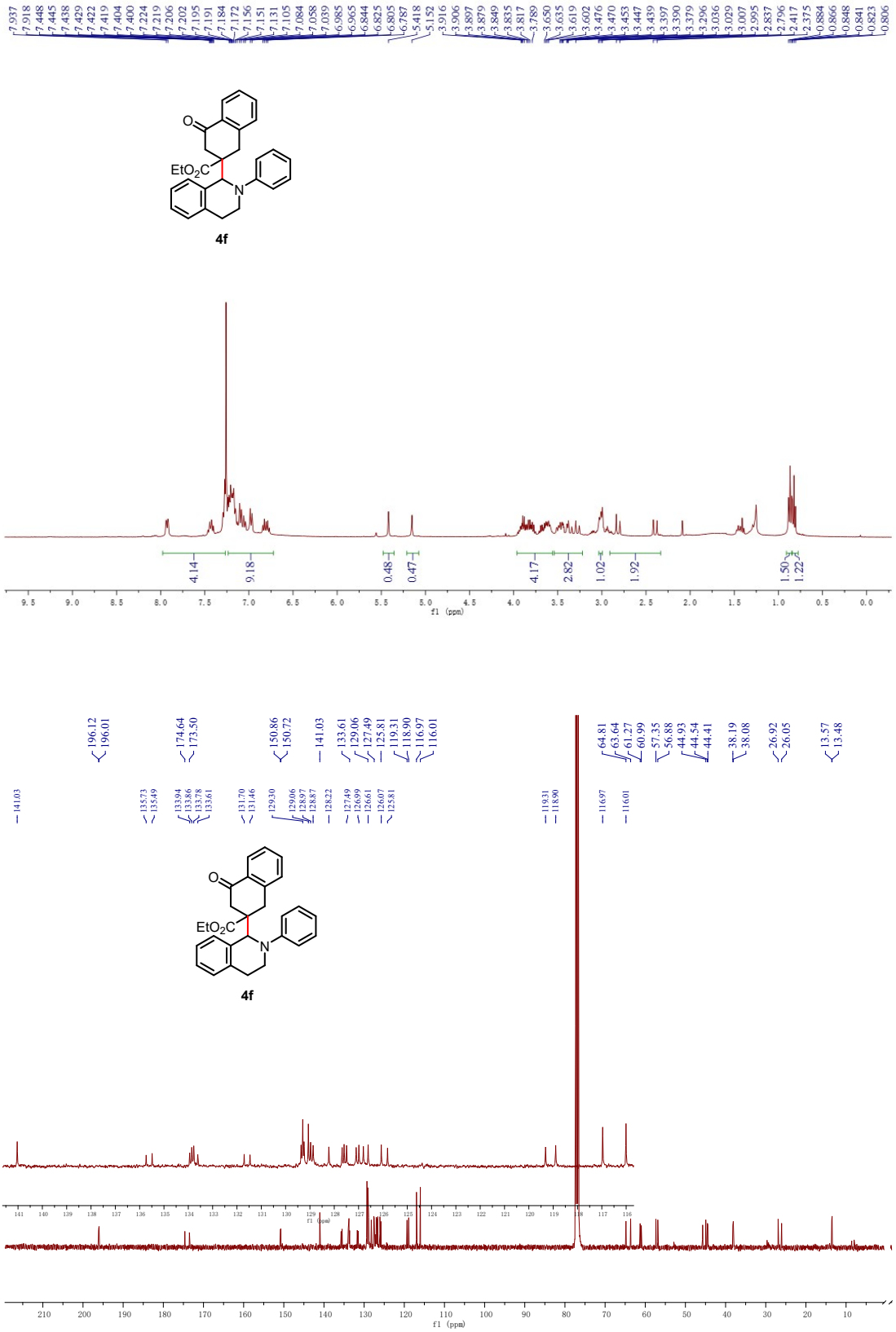
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4d**



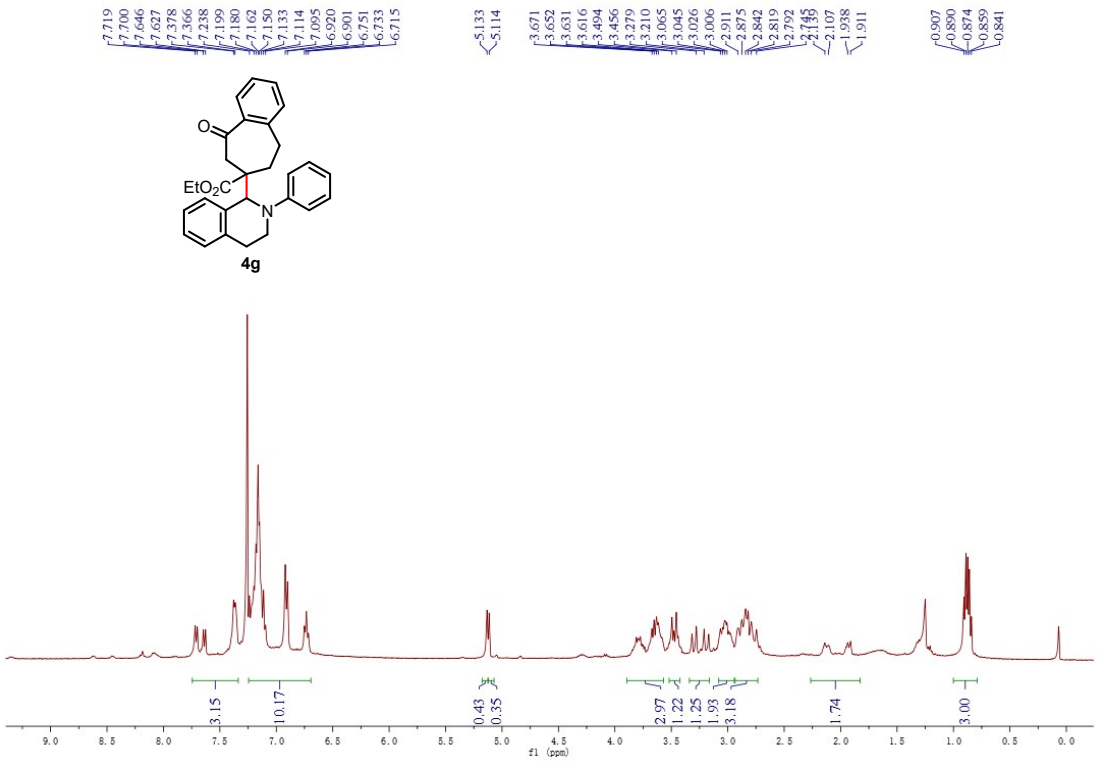
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4e**

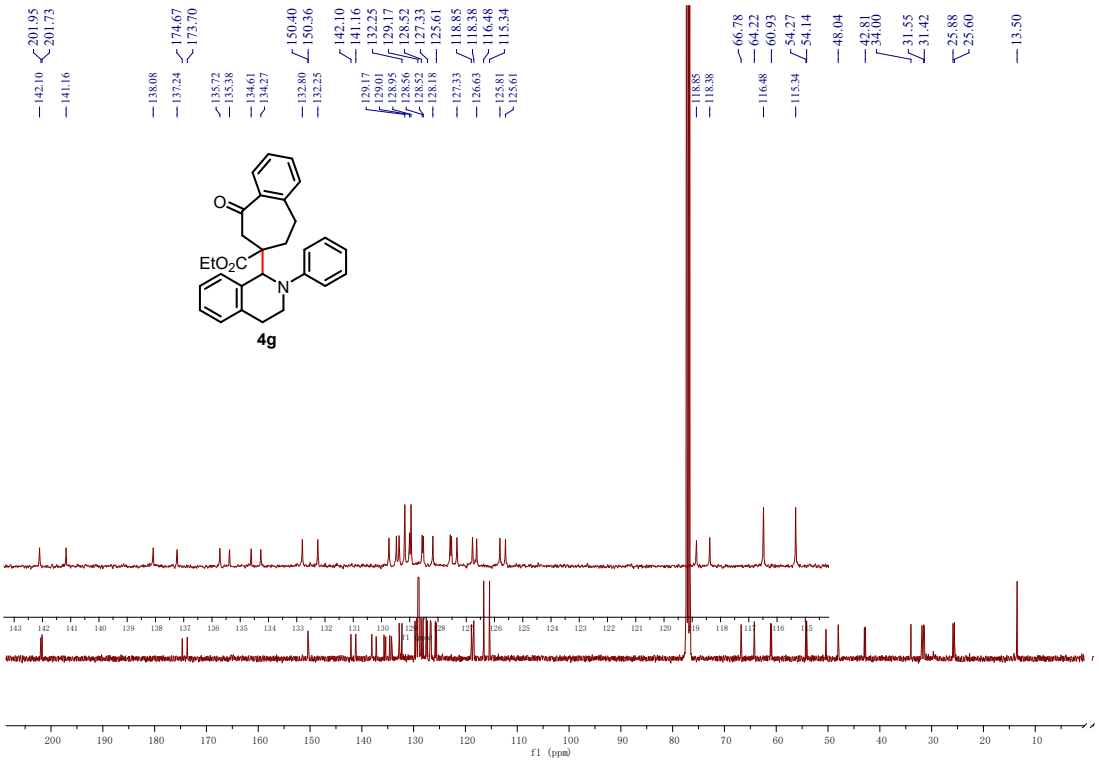


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4f**

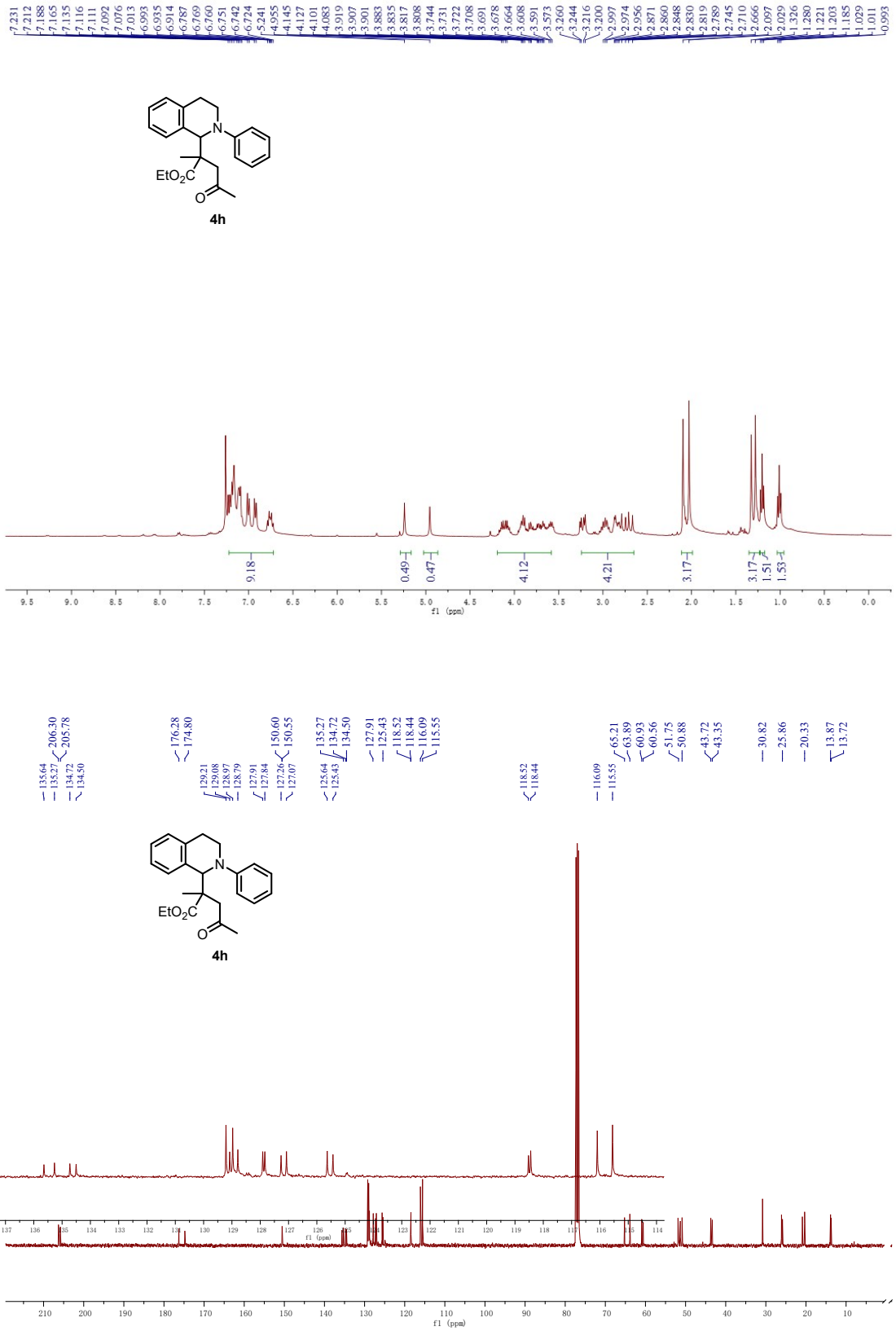


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4g**

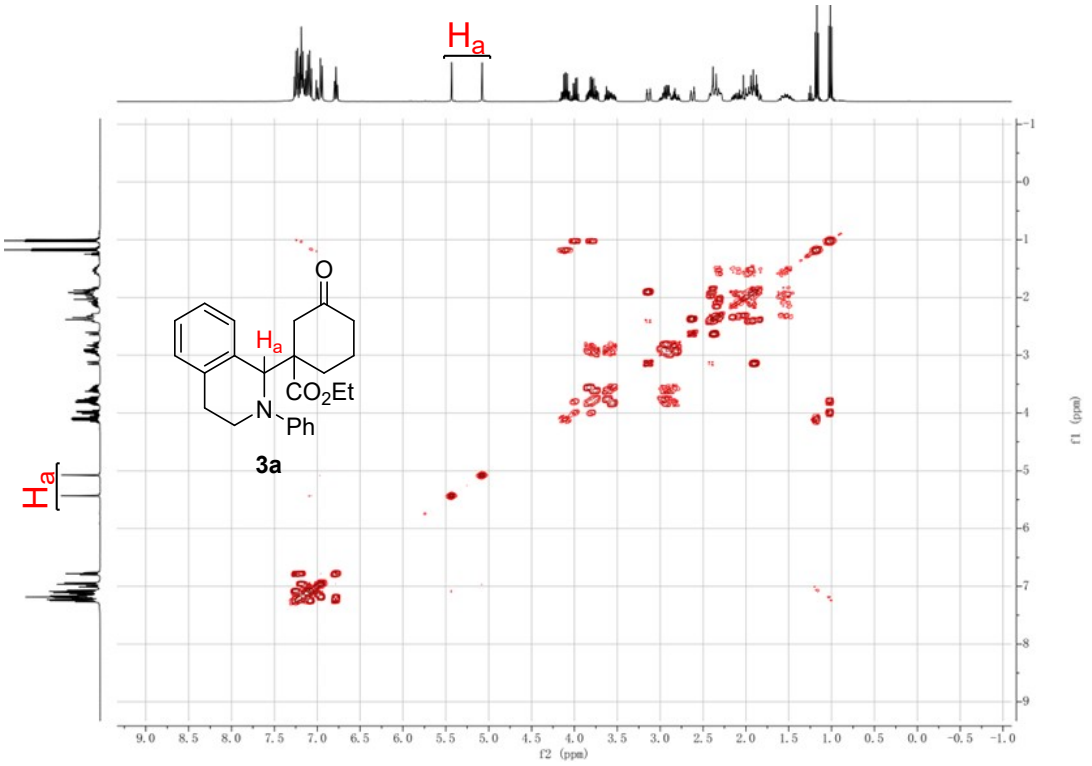




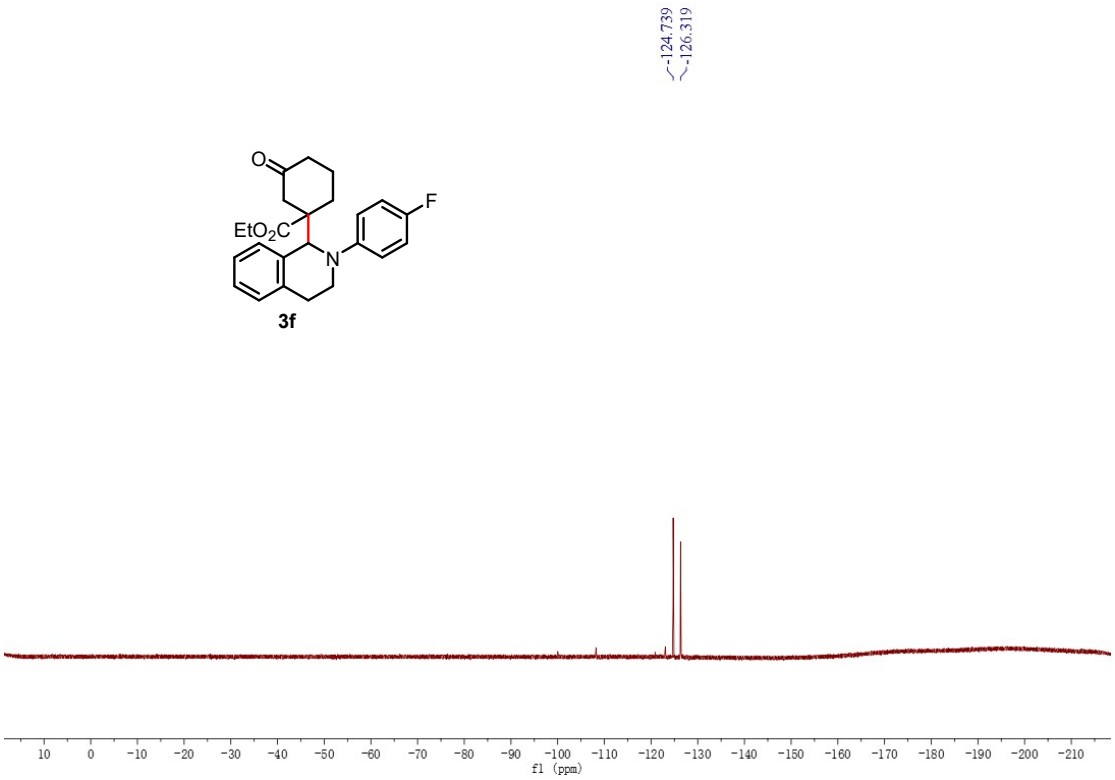
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4h**



2D-COSY experiment of **3a** (400 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3f**



^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3j**