Supplementary Information

For

Selective *N*-*α*-C-H Alkylation of Cyclic Tertiary Amides via Visible-Light-Mediated 1,5-Hydrogen Atom Transfer

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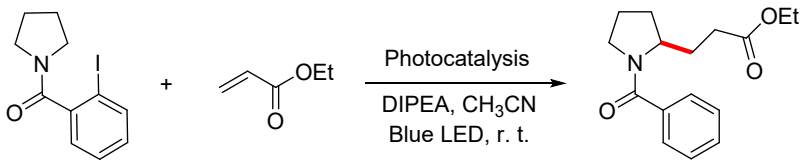
1. General Information

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]

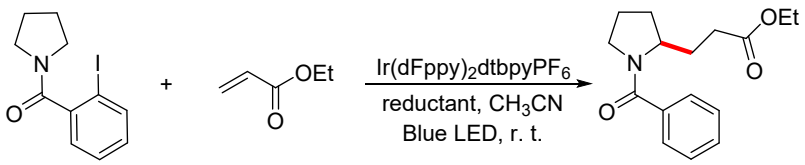


1a **2a** **3a**

Entry	Photocatalyst	Reductant	Solvent	Conversion(%)	Y(%)[b]
1	$Ru(bpy)_3Cl_2$	DIPEA	CH_3CN	10	5
2	Eosin Y	DIPEA	CH_3CN	0	0
3	4-CzIPN	DIPEA	CH_3CN	42	57
4	*fac*-$Ir(dFppy)_3$	DIPEA	CH_3CN	6	3
5	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	CH_3CN	65	61
6	$Ir(dFppy)_2bpyPF_6$	DIPEA	CH_3CN	57	54
7	$Ir(dFCF_3ppy)_2dtbpyPF_6$	DIPEA	CH_3CN	38	61
8	$Ir(dFCF_3ppy)_2bpyPF_6$	DIPEA	CH_3CN	6	2

[a]Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv.), Reductant (2 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs, 72 h. [b]The isolated yields are shown.

Table S2. Reductant Screening.[a,b]

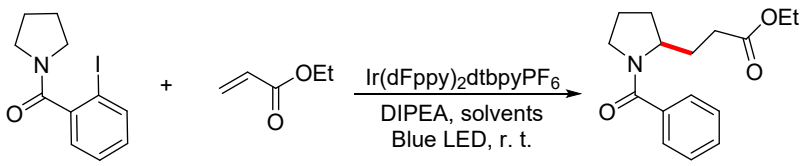


1a **2a** **3a**

Entry	Photocatalyst	Reductant	Solvent	Conversion(%)	Y(%)[b]
1	$Ir(dFppy)_2dtbpyPF_6$	Et_3N	CH_3CN	25	40
2	$Ir(dFppy)_2dtbpyPF_6$	TMEDA	CH_3CN	10	30
3	$Ir(dFppy)_2dtbpyPF_6$	quinuclidine	CH_3CN	0	0
4	$Ir(dFppy)_2dtbpyPF_6$	Hantzsch Esters	CH_3CN	47	38
5	$Ir(dFppy)_2dtbpyPF_6$	Et_3SiH	CH_3CN	0	0

[a]Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv.), Reductant (2 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs, 72 h. [b]The isolated yields are shown.

Table S3. Solvent Screening.[a,b]

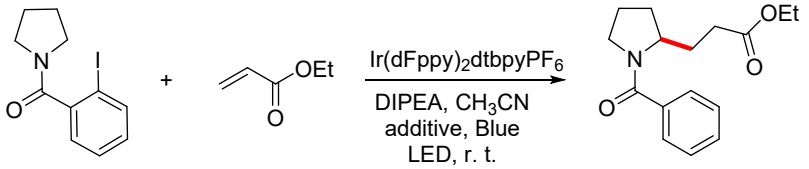


1a **2a** **3a**

Entry	Photocatalyst	Reductant	Solvent	Conversion(%)	Y(%)[b]
1	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	DCM	36	37
2	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	DCE	42	29
3	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	DMF	0	0
4	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	DMSO	55	38
5	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	DMA	30	39
6	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	$PhCF_3$	3	trace
7	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	THF	6	trace
8	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	HFIP	0	0
9	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	CF_3CH_2OH	0	0
10	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	1,4-dioxane	0	0

[a]Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2 equiv.), Reductant (2 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs, 72 h. [b]The isolated yields are shown.

Table S4. Additive Screening.[a,b]

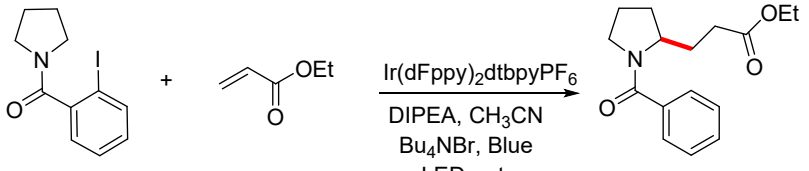


1a **2a** **3a**

Entry	Photocatalyst	Reductant	Additive	Solvent	Conversion(%)	Y(%)[b]
1	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	NH_4Cl	CH_3CN	68	59
2	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NCl	CH_3CN	77	74
3	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NBr	CH_3CN	87	78
4	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NI	CH_3CN	46	41

[a]Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2 equiv.), Reductant (2 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs, 72 h. [b]The isolated yields are shown.

Table S5. Reductant Amount Screening.[a,b]

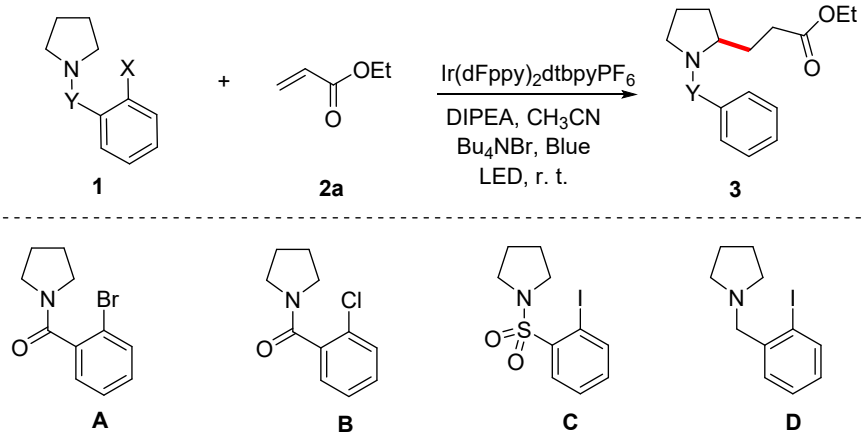


1a **2a** **3a**

Entry	Photocatalyst	Reductant	Additive	Solvent	Conversion(%)	Y(%)[b]
1[c]	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NBr	CH_3CN	100	81
2[d]	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NBr	CH_3CN	100	80

[a]Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2 equiv.), Reductant (2 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs, 72 h. [b]The isolated yields are shown. [c]the reaction was conducted with DIPEA (4 equiv.). [d]the reaction was conducted with DIPEA (6 equiv.).

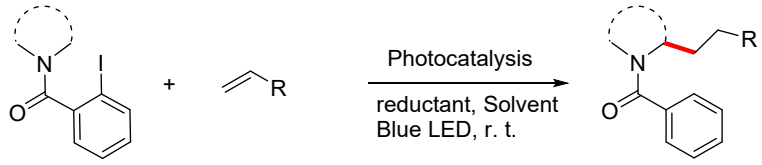
Table S6. Directing Group Screening.[a,b]



Entry	Photocatalyst	Reductant	Additive	Solvent	Substrate	Y(%)[b]
1	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NBr	CH_3CN	A	5
2	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NBr	CH_3CN	B	0
3	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NBr	CH_3CN	C	50
4	$Ir(dFppy)_2dtbpyPF_6$	DIPEA	Bu_4NBr	CH_3CN	D	0

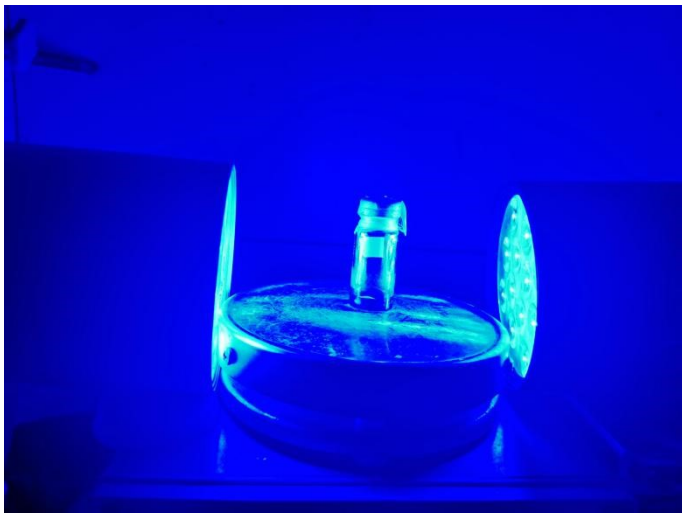
[a]Reaction conditions: photocatalyst (1 mol%), **1** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2 equiv.), Reductant (2 equiv.), CH_3CN (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs, 72 h. [b]The isolated yields are shown.

3. General Procedure for Alkylation Reactions

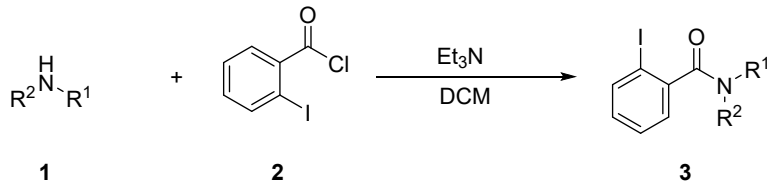


1 **2** **3-5**

In a dried sealed tube**, 1** (0.1 mmol), **2** (0.2 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 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. And then, the reaction flask was exposed to 12 W*2 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 a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the desired products. The reaction set-up with blue LEDs (2*12 W, Manufacturer: ouying, Model: 5317 (blue), WLP: 459.1 nm, Φ: 436.9 lm, Tc: 25000 K) as the light source. The irradiation vessel was in the middle of the two spotlights, approximate 7 cm to the light source.



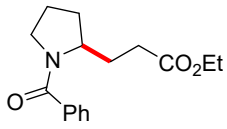
4. General procedure for the synthesis of substrates.



1 **2** **3**

Amine **1** (1.0 equiv.), Et_3N (2 equiv.) were dissolved in DCM (0.2 M). And 2-iodo-benzoylchloride **2** (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 1N 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.[2-5]

5. Product Characterization



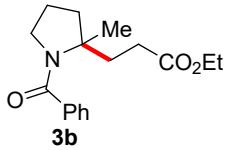
3a

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3a** was purified by flash column chromatography with PE/EA (10:1) to afford **3a** (19.8 mg, 81% yield) as a colorless oil, 81% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.50 (d, J = 5.9 Hz, 2H), 7.38 (d, J = 5.8 Hz, 3H), 4.42-4.28 (m, 1H), 4.19-4.07 (m, 2H), 3.51-3.33 (m, 2H), 2.49-2.34 (m, 2H), 2.25 (dd, J = 13.2, 6.1 Hz, 1H), 2.11-2.04 (m, 1H), 1.94-1.84 (m, 2H), 1.78-1.70 (m, 1H), 1.70 - 1.61 (m, 1H), 1.24 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.6, 170.4, 137.3, 130.1, 128.3, 127.5, 60.6, 56.7, 50.2, 31.4, 30.3, 29.4, 25.1, 14.3.

HRMS (ESI): calcd for $C_{16}H_{22}NO_3^+$, $(M+H)^+$: 276.1594, found: 276.1600.



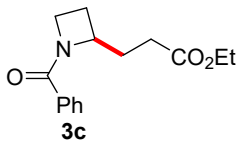
3b

The reaction was conducted according to the general procedure using **1b** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3b** was purified by flash column chromatography with PE/EA (10:1) to afford **3b** (23.1 mg, 80% yield) as a colorless oil, 80% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (ddd, J = 9.7, 6.8, 3.4 Hz, 5H), 4.13 (q, J = 7.1 Hz, 2H), 3.39 (t, J = 6.5 Hz, 2H), 2.59-2.47 (m, 1H), 2.44 - 2.26 (m, 3H), 1.97 (dt, J = 11.1, 6.9 Hz, 1H), 1.83 - 1.70 (m, 3H), 1.57 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.8, 169.6, 138.9, 129.4, 128.4, 126.4, 64.6, 60.6, 52.2, 38.5, 32.8, 30.3, 24.5, 23.3, 14.4.

HRMS (ESI): calcd for $C_{17}H_{24}NO_3^+$, $(M+H)^+$: 290.1751, found: 290.1750.



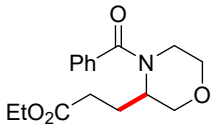
3c

The reaction was conducted according to the general procedure using **1c** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3c** was purified by flash column chromatography with PE/EA (10:1) to afford **3c** (19.6 mg, 75% yield) as a colorless oil, 75% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 (d, J = 7.1 Hz, 2H), 7.48 - 7.34 (m, 3H), 4.70 - 4.56 (m, 1H), 4.30 (s, 1H), 4.12 (d, J = 6.7 Hz, 2H), 4.02 (s, 1H), 2.50 (s, 2H), 2.29 (s, 1H), 2.16 (s, 1H), 1.98 (s, 1H), 1.25 (dd, J = 14.7, 7.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.6, 171.6, 136.2, 131.1, 128.5, 128.0, 61.2, 60.6, 51.0, 30.9, 30.8, 22.4, 14.3.

HRMS (ESI): calcd for $C_{15}H_{20}NO_3^+$, $(M+H)^+$, 262.1438, found: 262.1445.



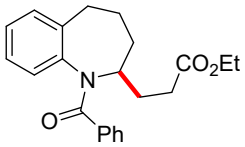
3d

The reaction was conducted according to the general procedure using **1d** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3d** was purified by flash column chromatography with PE/EA (10:1) to afford **3d** (20.7 mg, 71% yield) as a colorless oil, 71% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (dd, J = 7.1, 2.9 Hz, 3H), 7.36 (dd, J = 6.7, 3.2 Hz, 2H), 4.83 - 4.27 (m, 1H), 4.12 (s, 2H), 3.80 (s, 2H), 3.69-3.61 (m, 1H), 3.43 (s, 3H), 2.35 (s, 3H), 2.00 (s, 1H), 1.24 (d, J = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.1, 170.9, 135.7, 129.9, 128.7, 126.99, 69.7, 67.3, 60.7, 48.8, 43.7, 31.0, 24.3, 14.3.

HRMS (ESI): calcd for $C_{16}H_{22}NO_4^+$, $(M+H)^+$: 292.1543, found: 292.1540.



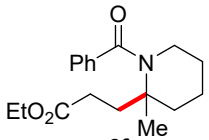
3e

The reaction was conducted according to the general procedure using **1e** with CH_3CN as the solvent. The reaction was run for 96 h, the desired product **3e** was purified by flash column chromatography with PE/EA (10:1) to afford **3e** (12.3 mg, 35% yield) as a colorless oil, 35% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.18 (t, J = 7.3 Hz, 2H), 7.12 (q, J = 7.6 Hz, 4H), 7.06 (t, J = 7.4 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 5.27 - 5.09 (m, 1H), 4.17 - 4.00 (m, 2H), 3.08 - 2.94 (m, 1H), 2.90 - 2.78 (m, 1H), 2.39-2.24 (m, 2H), 2.04 (ddd, J = 15.3, 7.6, 3.7 Hz, 1H), 1.94-1.84 (m, 1H), 1.74 (ddd, J = 28.4, 12.9, 2.7 Hz, 1H), 1.58 (dd, J = 12.5, 7.5 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.2, 170.1, 139.6, 139.5, 136.9, 130.6, 130.0, 129.5, 127.9, 127.8, 127.6, 126.8, 60.6, 51.8, 34.9, 32.9, 31.6, 26.3, 21.0, 14.3.

HRMS (ESI): calcd for $C_{22}H_{25}NNaO_3^+$, $(M+Na)^+$: 374.1727, found: 327.1722.



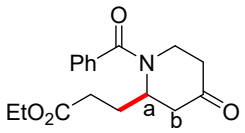
3f

The reaction was conducted according to the general procedure using **1f** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3f** was purified by flash column chromatography with PE/EA (10:1) to afford **3f** (25.7 mg, 85% yield) as a colorless oil, 85% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44-7.34 (m, 3H), 7.34-7.28 (m, 2H), 4.81 (s, 1H), 4.11 (d, J = 5.4 Hz, 3H), 2.45 (s, 1H), 1.96 (s, 3H), 1.82 (td, J = 12.9, 6.4 Hz, 1H), 1.66 (s, 3H), 1.56-1.43 (m, 2H), 1.35-1.15 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.5, 171.9, 137.7, 128.99, 128.6, 125.9, 60.5, 49.6, 47.7, 32.2, 30.6, 30.1, 28.3, 21.1, 14.6, 14.3.

HRMS (ESI): calcd for $C_{18}H_{26}NO_3^+$, $(M+H)^+$, 304.1907, found, 304.1915.



3g

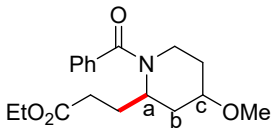
The reaction was conducted according to the general procedure using **1g** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3g** was purified by flash column chromatography with PE/EA (10:1) to afford **3g** (13.6 mg, 45% yield) as a colorless oil, a:b = 1.6:1 (determined by NMR), 45% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.67-7.31 (m, 5H), 5.27 (s, 0.62H), 4.96 (s, 0.38H), 4.22-3.98 (m, 3H), 3.58-3.13 (m, 1H), 2.75 (s, 1H), 2.33 (s, 4H), 1.93 (dd, J = 17.8, 10.4 Hz, 2H), 1.33-1.15 (m, 4H).

Major: **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 206.5, 172.50, 171.3, 135.5, 130.2, 128.8, 126.7, 60.8, 60.6, 45.7, 40.97, 31.7, 27.8, 14.23, 14.18.

Minor: **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 206.6, 172.6, 171.5, 135.5, 130.2, 128.7, 126.6, 60.98, 60.5, 41.9, 33.8, 31.6, 27.1, 14.20, 14.11.

HRMS (ESI): calcd for $C_{17}H_{22}NO_4^+$, $(M+H)^+$: 304.1543, found: 304.1537.



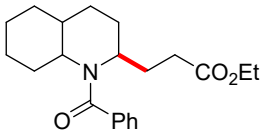
3h

The reaction was conducted according to the general procedure using **1h** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3h** was purified by flash column chromatography with PE/EA (10:1) to afford **3h** (10.8 mg, 34% yield) as a colorless oil, a:c = 1.5:1 (determined by NMR), 34% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 (dd, J = 6.6, 2.7 Hz, 3H), 7.34 (dd, J = 6.6, 3.0 Hz, 2H), 4.87 (d, J = 137.3 Hz, 1H), 4.12 (s, 2H), 3.73-3.44 (m, 2H), 3.39-3.28 (m, 3H), 3.03 (t, J = 68.9 Hz, 1H), 2.39 (s, 2H), 1.85 (ddd, J = 39.9, 34.8, 29.7 Hz, 5H), 1.55 (s, 1H), 1.24 (t, J = 9.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.4, 170.98, 136.4, 129.6, 128.7, 126.6, 73.5, 60.7, 55.8, 48.6, 41.6, 34.7, 32.2, 31.5, 26.2, 14.3.

HRMS (ESI): calcd for $C_{18}H_{25}NNaO_4^+$, $(M+Na)^+$: 342.1676, found: 342.1683.



3i

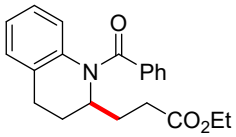
The reaction was conducted according to the general procedure using **1i** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **3i** was purified by flash column chromatography with PE/EA (10:1) to afford **3i** (10.6 mg, 31% yield) as a colorless oil, 31% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 -7.39 (m, 2H), 7.39 - 7.33 (m, 3H), 4.16 - 4.05 (m, 2H), 3.91 - 3.80 (m, 1H), 2.94 (td, J = 11.3, 3.7 Hz, 1H), 2.38 (ddd, J = 19.1, 14.6, 5.1 Hz, 1H), 2.27 (dt, J = 9.7, 5.3

Hz, 2H), 2.23 - 2.13 (m, 1H), 2.12 - 2.00 (m, 1H), 1.87 - 1.82 (m, 1H), 1.81-1.78 (m, 1H), 1.78 - 1.69 (m, 3H), 1.63 (dd, J = 13.1, 2.6 Hz, 2H), 1.46 (ddd, J = 10.9, 3.9, 2.0 Hz, 1H), 1.37 (dd, J = 11.1, 4.0 Hz, 1H), 1.33 - 1.27 (m, 1H), 1.24 (dd, J = 9.3, 4.9 Hz, 3H), 1.19 (dt, J = 13.0, 3.1 Hz, 1H), 1.02 (ddd, J = 15.5, 12.0, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.5, 173.2, 139.0, 129.6, 128.6, 127.0, 60.7, 58.97, 56.8, 39.3, 33.99, 31.5, 30.2, 29.2, 27.97, 26.96, 25.7, 25.3, 14.3.

HRMS (ESI): calcd for $C_{21}H_{30}NO_3^+$, $(M+H)^+$: 344.2220, found: 344.2223.



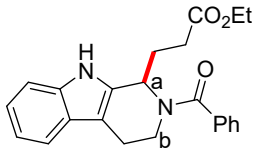
3j

The reaction was conducted 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** (10.6 mg, 38% yield) as a colorless oil, 38% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29 (ddd, J = 8.6, 3.6, 1.7 Hz, 1H), 7.25-7.17 (m, 3H), 7.15 (d, J = 7.1 Hz, 1H), 7.00 (td, J = 7.5, 0.9 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.51 (d, J = 7.2 Hz, 1H), 4.97- 4.81 (m, 1H), 4.17-4.04 (m, 2H), 2.80 (t, J = 6.8 Hz, 2H), 2.53 - 2.29 (m, 3H), 1.95-1.75 (m, 2H), 1.69 (tt, J = 12.9, 6.3 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.4, 170.1, 138.0, 136.4, 132.6, 130.0, 128.7, 128.0, 126.9, 126.1, 125.3, 60.6, 51.9, 31.2, 29.9, 28.8, 25.2, 14.4.

HRMS (ESI): calcd for $C_{21}H_{24}NO_3^+$, $(M+H)^+$: 338.1751, found: 338.1743.



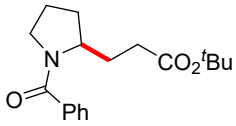
3k

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** (17.3 mg, 46% yield) as a colorless oil, a:b = 3:1 (determined by NMR), 46% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.33 (s, 0.76H), 7.81 (s, 0.24H), 7.45 (s, 6H), 7.33 (d, J = 7.9 Hz, 0.79H), 7.25-7.22 (m, 0.18H), 7.21-7.07 (m, 2H), 5.56 (d, J = 17.1 Hz, 0.76H), 5.37 (s, 0.24H), 4.55 (dd, J = 64.8, 17.4 Hz, 0.49H), 4.36-4.19 (m, 1.55H), 4.12 (dd, J = 14.2, 7.1 Hz, 1H), 4.00 (dd, J = 6.9, 2.6 Hz, 1H), 3.15 (d, J = 15.5 Hz, 1H), 2.73 (t, J = 20.2 Hz, 1H), 2.56-2.14 (m, 2H), 2.11-2.00 (m, 1H), 1.80-1.69 (m, 1H), 1.28-1.15 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.6, 172.1, 136.6, 136.4, 130.1, 128.9, 128.7, 127.4, 126.8, 122.0, 119.7, 117.9, 111.2, 106.0, 60.8, 53.8, 37.3, 31.1, 27.1, 26.4, 14.3.

HRMS (ESI): calcd for $C_{23}H_{25}N_2O_3^+$, $(M+H)^+$: 377.1860, found: 377.1859.



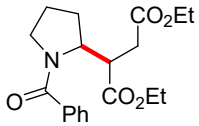
4a

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4a** was purified by flash column chromatography with PE/EA (20:1) to afford **4a** (23.9 mg, 79% yield) as a colorless oil, 79% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.56-7.47 (m, 2H), 7.43 - 7.36 (m, 3H), 4.40 - 4.22 (m, 1H), 3.52 - 3.33 (m, 2H), 2.35 (dd, J = 15.7, 6.4 Hz, 2H), 2.27 - 2.17 (m, 1H), 2.12 - 2.03 (m, 1H), 1.96 - 1.86 (m, 1H), 1.79 (dd, J = 20.4, 6.0 Hz, 2H), 1.69 (dd, J = 11.5, 5.7 Hz, 1H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.9, 170.3, 137.4, 129.95, 128.3, 127.4, 80.3, 56.7, 50.1, 32.5, 30.3, 29.4, 28.2, 25.1.

HRMS (ESI): calcd for $C_{18}H_{26}NO_3^+$, $(M+H)^+$: 304.1907, found: 304.1900.



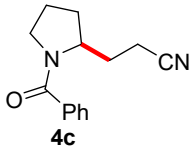
4b

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4b** was purified by flash column chromatography with PE/EA (20:1) to afford **4b** (14.6 mg, 42% yield) as a colorless oil, 42% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.54 - 7.46 (m, 2H), 7.45 -7.33 (m, 3H), 4.52 (dd, J = 12.8, 7.2 Hz, 1H), 4.26 - 3.99 (m, 4H), 3.64 (dt, J = 10.1, 4.8 Hz, 1H), 3.41 (dd, J = 9.0, 6.1 Hz, 2H), 2.83 (dd, J = 16.7, 10.4 Hz, 1H), 2.53 (dd, J = 16.7, 4.5 Hz, 1H), 2.12-2.03 (m, 1H), 2.00 -1.81 (m, 2H), 1.77-1.70 (m, 1H), 1.33-1.19 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.2, 171.8, 170.5, 137.0, 130.3, 128.4, 127.6, 61.0, 60.9, 58.3, 50.8, 43.1, 34.0, 27.4, 25.1, 14.4, 14.3.

HRMS (ESI): calcd for $C_{19}H_{26}NO_5^+$, $(M+H)^+$: 348.1805, found: 348.1798.



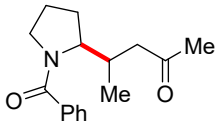
4c

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4c** was purified by flash column chromatography with PE/EA (20:1) to afford **4c** (8.4 mg, 37% yield) as a colorless oil, 37% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_C 7.53 (d, J = 6.9 Hz, 2H), 7.41 (q, J = 6.1 Hz, 3H), 4.49 - 4.29 (m, 1H), 3.58-3.36 (m, 1H), 2.58-2.41 (m, 2H), 2.20 (ddd, J = 19.3, 13.0, 6.9 Hz, 2H), 2.01 - 1.90 (m, 2H), 1.75 (dq, J = 14.5, 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) :δ_C 171.1, 136.9, 130.4, 128.4, 127.5, 119.98, 56.5, 50.4, 30.7, 30.2, 25.2, 14.5.

HRMS (ESI): calcd for $C_{14}H_{17}N_2O^+$, $(M+H)^+$: 229.1335, found: 229.1341.



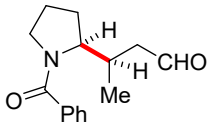
4d

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4d** was purified by flash column chromatography with PE/EA (20:1) to afford **4d** (16.0 mg, 62% yield) as a colorless oil, dr = 1.9:1 (determined by NMR), 62% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57-7.44 (m, 2H), 7.44-7.32 (m, 3H), 4.31 (ddd, J = 19.3, 12.2, 7.4 Hz, 1H), 3.4813.26 (m, 2H), 2.97-2.50 (m, 2H), 2.28 (dd, J = 16.2, 6.5 Hz, 1H), 2.13 (d, J = 4.6 Hz, 3H), 2.04-1.82 (m, 2H), 1.73 (ddd, J = 14.6, 11.8, 9.7 Hz, 2H), 0.97 (dd, J = 11.1, 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 209.2, 209.1, 171.3, 170.9, 137.1, 130.4, 130.2, 128.4, 128.3, 127.7, 127.6, 61.1, 51.8, 50.4, 48.6, 47.5, 32.4, 32.1, 30.4, 29.6, 27.1, 26.6, 25.4, 24.99, 16.9, 16.4.

HRMS (ESI): calcd for $C_{16}H_{22}NO_2^+$, $(M+H)^+$, 260.1645, found, 260.1646.



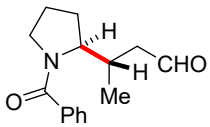
4e

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4e** was purified by flash column chromatography with PE/EA (20:1) to afford **4e** (11.3 mg, 45% yield) as a colorless oil, 45% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.74 (s, 1H), 7.49-7.39 (m, 2H), 7.37-7.28 (m, 3H), 4.26 (dd, J = 13.4, 6.9 Hz, 1H), 3.42 – 3.27 (m, 2H), 2.73 (dt, J = 13.7, 6.8 Hz, 1H), 2.63 (dd, J = 16.5, 5.5 Hz, 1H), 2.23 (ddd, J = 16.4, 7.3, 1.7 Hz, 1H), 1.95-1.81 (m, 2H), 1.74-1.62 (m, 2H), 0.94 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 202.6, 171.0, 137.1, 130.3, 128.4, 127.6, 61.1, 50.8, 48.5, 30.8, 26.8, 25.2, 15.8.

HRMS (ESI): calcd for $C_{15}H_{20}NO_2^+$, $(M+H)^+$: 246.1489, found: 246.1494.



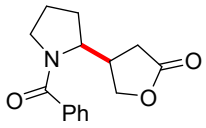
4e′

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4e´** was purified by flash column chromatography with PE/EA (20:1) to afford **4e´** (7.8 mg, 32% yield) as a colorless oil, 32% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.65 (d, J = 3.6 Hz, 1H), 7.57-7.47 (m, 2H), 7.44-7.35 (m, 3H), 4.32 (dd, J = 7.8, 4.2 Hz, 1H), 3.48-3.39 (m, 1H), 3.30-3.12 (m, 2H), 2.52-2.40 (m, 1H), 2.32-2.22 (m, 1H), 2.08-1.96 (m, 1H), 1.84 (d, J = 5.7 Hz, 1H), 1.84 (d, J = 5.7 Hz, 1H), 1.75-1.60 (m, 3H), 1.05 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 202.3, 171.4, 136.8, 130.6, 128.4, 127.7, 61.5, 51.7, 46.8, 30.3, 25.6, 25.4, 17.5.

HRMS (ESI): calcd for $C_{15}H_{20}NO_2^+$, $(M+H)^+$: 246.1489, found: 246.1491.



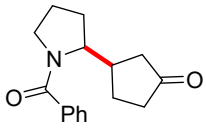
4f

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4f** was purified by flash column chromatography with PE/EA (20:1) to afford **4f** (9.6 mg, 37% yield) as a colorless oil, dr = 1:1 (determined by NMR), 37% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.50 (d, J = 7.2 Hz, 2H), 7.47- 7.36 (m, 3H), 4.39 (ddd, J = 51.7, 38.0, 6.3 Hz, 3H), 3.48 (dd, J = 17.2, 8.4 Hz, 2H), 3.30 - 2.99 (m, 1H), 2.55 (tdd, J = 64.1, 17.6, 8.9 Hz, 2H), 2.22-2.04 (m, 1H), 2.01-1.87 (m, 1H), 1.78 (s, 1H), 1.73 - 1.61 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 176.9, 176.5, 171.7, 171.5, 136.4, 136.4, 130.6, 130.6, 128.4, 127.5, 127.5, 71.8, 69.9, 58.5, 58.3, 51.7, 51.2, 40.2, 38.6, 31.8, 31.4, 28.6, 27.7, 25.1.

HRMS (ESI): calcd for $C_{15}H_{17}NNaO_3^+$, $(M+Na)^+$: 282.1101, found: 282.1100.



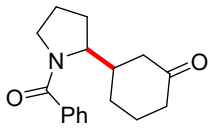
4g

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4g** was purified by flash column chromatography with PE/EA (20:1) to afford **4g** (20.6 mg, 80% yield) as a colorless oil, dr = 1.4:1, 80% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.50 (d, J = 5.6 Hz, 2H), 7.45-7.37 (m, 3H), 4.69 - 4.44 (m, 1H), 3.47 (t, J = 6.6 Hz, 2H), 2.84 -2.59 (m, 1H), 2.45-2.29 (m, 2H), 2.24 - 2.02 (m, 4H), 1.91 (dd, J = 23.0, 9.3 Hz, 2H), 1.84-1.66 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 218.8, 218.7, 171.2, 137.1, 130.3, 128.4, 127.5, 59.4, 59.3, 50.8, 50.6, 42.6, 41.4, 41.2, 40.9, 38.7, 38.5, 28.0, 27.9, 26.7, 25.6, 25.2, 25.1.

HRMS (ESI): calcd for $C_{16}H_{20}NO_2^+$, $(M+H)^+$: 258.1489, found: 258.1483.



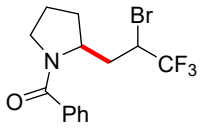
4h

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 48 h, the desired product **4h** was purified by flash column chromatography with PE/EA (20:1) to afford **4h** (21.9 mg, 81% yield) as a colorless oil, dr = 2:1 (determined by NMR), 81% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.55-7.46 (m, 2H), 7.42-7.33 (m, 3H), 4.52-4.30 (m, 1H), 3.55-3.26 (m, 2H), 2.44 (d, J = 9.9 Hz, 1H), 2.37 (dd, J = 14.1, 1.7 Hz, 1H), 2.31-2.22 (m, 2H), 2.10 (ddd, J = 19.7, 9.8, 6.6 Hz, 1H), 2.04-1.95 (m, 1H), 1.94-1.82 (m, 3H), 1.80-1.67 (m, 2H), 1.66-1.46 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 211.4, 211.3, 171.1, 170.96, 137.0, 130.3, 130.3, 128.3, 127.6, 127.6, 60.3, 51.0, 50.8, 45.1, 43.1, 42.2, 41.5, 41.3, 28.3, 27.3, 27.0, 26.5, 25.4, 25.3, 25.2.

HRMS (ESI): calcd for $C_{17}H_{22}NO_2^+$, $(M+H)^+$, 272.1645, found, 272.1653.



4i

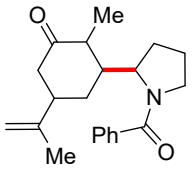
The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4i** was purified by flash column chromatography with PE/EA (20:1) to afford **4i** (16.1 mg, 46% yield) as a colorless oil, dr = 1:1 (determined by NMR), 46% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.53 (d, J = 6.3 Hz, 2H), 7.41 (t, J = 6.3 Hz, 3H), 4.53 (s, 1H), 3.60 - 3.36 (m, 2H), 3.06 (dd, J = 14.6, 3.3 Hz, 1H), 2.77 - 2.62 (m, 1H), 2.14 (d, J = 6.7 Hz, 1H), 1.97 - 1.85 (m, 1H), 1.74 (dt, J = 15.8, 8.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.3, 137.1, 130.2, 128.7, 128.4, 127.71 (dd, J = 312.6 Hz), 127.5, 126.6, 126.6, 56.1, 50.6, 34.1, 29.9, 29.8 (q, J = 30.4 Hz), 29.6, 25.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -82.49 (d, J = 40.8 Hz), -89.00 (d, J = 40.8 Hz).

HRMS (ESI): calcd for $C_{14}H_{16}BrF_3NO^+$, $(M+H)^+$, 350.0362, found, 350.0370.



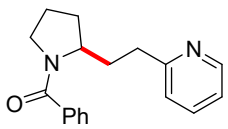
4j

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4j** was purified by flash column chromatography with PE/EA (20:1) to afford **4j** (26.3 mg, 81% yield) as a colorless oil, dr = 1:1 (determined by NMR), 81% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57-7.46 (m, 2H), 7.44 -7.33 (m, 3H), 4.89 - 4.79 (m, 1H), 4.69 (s, 1H), 4.52 (td, J = 8.1, 5.0 Hz, 1H), 3.64-3.49 (m, 1H), 3.43 (td, J = 10.7, 5.4 Hz, 1H), 2.83 (s, 1H), 2.75 -2.60 (m, 2H), 2.49 (dd, J = 14.9, 6.1 Hz, 1H), 2.15 (dq, J = 12.9, 6.5 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.95-1.84 (m, 2H), 1.82- 1.69 (m, 3H), 1.28-1.23 (m, 1H), 1.19 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 211.9, 170.2, 145.8, 137.3, 130.3, 128.5, 127.5, 113.1, 58.6, 52.1, 47.4, 44.5, 40.1, 39.0, 26.9, 25.7, 25.1, 21.8, 11.8.

HRMS (ESI): calcd for $C_{21}H_{28}NO_2^+$, $(M+H)^+$, 326.2115, found, 326.2110.



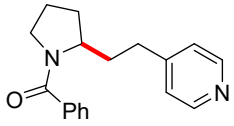
4k

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 68 h, the desired product **4k** was purified by flash column chromatography with PE/EA (20:1) to afford **4k** (21.3 mg, 76% yield) as a colorless oil, 76% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_C 8.52 (d, J = 4.3 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.48 (d, J = 7.4 Hz, 2H), 7.38 (d, J = 6.7 Hz, 3H), 7.29 (d, J = 7.9 Hz, 1H), 7.16 - 7.07 (m, 1H), 4.44 - 4.33 (m, 1H), 3.54 - 3.35 (m, 2H), 2.92 (t, J = 8.1 Hz, 2H), 2.49 - 2.40 (m, 1H), 2.19-2.09 (m, 1H), 1.94 (dt, J = 11.9, 7.4 Hz, 2H), 1.76 (ddd, J = 22.0, 12.9, 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.3, 161.7, 149.0, 137.5, 136.8, 130.0, 128.3, 127.5, 123.1, 121.3, 57.2, 50.3, 34.9, 33.8, 30.5, 25.3.

HRMS (ESI): calcd for $C_{21}H_{28}N_2O^+$, $(M+H)^+$: 281.1648, found: 281.1644.



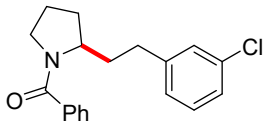
4l

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 60 h, the desired product **4l** was purified by flash column chromatography with PE/EA (20:1) to afford **4l** (23.4 mg, 83% yield) as a colorless oil, 83% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.42 (d, J = 5.1 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 7.36 -7.27 (m, 3H), 7.13 (d, J = 5.0 Hz, 2H), 4.25 (d, J = 14.7 Hz, 1H), 3.39 (t, J = 6.5 Hz, 2H), 2.66 (t, J = 8.0 Hz, 2H), 2.38 - 2.27 (m, 1H), 2.091 2.03 (m, 1H), 1.85 (d, J = 10.3 Hz, 2H), 1.78 - 1.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.4, 151.0, 149.8, 137.3, 130.2, 128.4, 127.4, 123.99, 57.1, 50.4, 34.3, 31.8, 30.6, 25.3.

HRMS (ESI): calcd for $C_{21}H_{28}N_2O^+$, $(M+H)^+$: 281.1648, found: 281.1639.



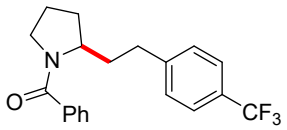
4m

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4m** was purified by flash column chromatography with PE/EA (20:1) to afford **4m** (21.6 mg, 69% yield) as a colorless oil, 69% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (d, J = 7.3 Hz, 2H), 7.44 -7.34 (m, 3H), 7.23 (s, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.16 (s, 2H), 4.34 (s, 1H), 3.52-3.36 (m, 2H), 2.70 (t, J = 6.8 Hz, 2H), 2.37 (dd, J = 10.1, 5.9 Hz, 1H), 2.18-2.07 (m, 1H), 1.92 (dd, J = 11.2, 5.3 Hz, 1H), 1.82-1.69 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.2, 144.1, 137.5, 134.2, 130.1, 129.8, 128.6, 128.4, 127.5, 126.7, 126.2, 57.2, 50.3, 35.4, 32.2, 30.6, 25.3.

HRMS (ESI): calcd for $C_{19}H_{21}ClNO^+$, $(M+H)^+$: 314.1306, found: 314.1311.



4n

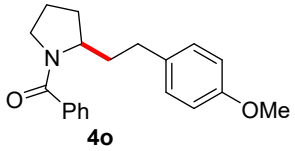
The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4n** was purified by flash column chromatography with PE/EA (20:1) to afford **4n** (26.7 mg, 77% yield) as a colorless oil, 77% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.53 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.39 (dd, J = 12.6, 6.8 Hz, 5H), 4.34 (s, 1H), 3.45 (t, J = 6.6 Hz, 2H), 2.79 (t, J = 8.0 Hz, 2H), 2.45 - 2.33 (m, 1H), 2.15 (dd, J = 15.2, 8.5 Hz, 1H), 1.92 (dd, J = 10.9, 5.1 Hz, 1H), 1.77 (ddd, J = 18.9, 12.1, 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.2, 146.0, 137.3, 129.97, 128.7, 128.7, 128.3 (m).128.2, 127.3, 125.3 (dd, J = 7.6, 3.9 Hz), 57.0, 50.2, 35.0, 32.2, 30.5 , 25.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -62.30.

HRMS (ESI): calcd for $C_{20}H_{21}F_3NO^+$, $(M+H)^+$: 348.1570, found: 348.1568.



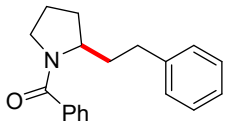
4o

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4r** was purified by flash column chromatography with PE/EA (20:1) to afford **4r** (7.1 mg, 23% yield) as a colorless oil, 23% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 (d, J = 6.8 Hz, 1H), 7.39 (t, J = 6.1 Hz, 3H), 7.17 (d, J = 8.1 Hz, 2H), 6.89-6.78 (m, 2H), 6.70 (s, 1H), 4.33 (s, 1H), 3.54-3.24 (m, 2H), 2.66 (t, J = 7.4 Hz, 1H), 2.43- 2.30 (m, 1H), 2.12 (m, 1H), 1.90 (m, 1H), 1.74 (d, J = 5.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.1, 157.9, 137.6, 134.1, 129.99, 129.4, 128.3, 127.5, 113.9, 57.3, 55.4, 50.3, 35.7, 31.5, 30.5, 25.3.

HRMS (ESI): calcd for $C_{20}H_{24}NO_2^+$, $(M+H)^+$, 310.1802, found, 310.1809.



4r

The reaction was conducted according to the general procedure using **1a** with CH_3CN as the solvent. The reaction was run for 72 h, the desired product **4r** was purified by flash column chromatography with PE/EA (20:1) to afford **4r** (8.6 mg, 31% yield) as a colorless oil, 31% isolated yield.

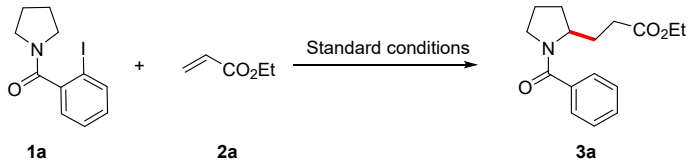
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (d, J = 7.1 Hz, 2H), 7.39 (t, J = 5.9 Hz, 4H), 7.29 (d, J = 7.5 Hz, 1H), 7.25 - 7.22 (m, 1H), 7.21-7.09 (m, 2H), 4.35 (s, 1H), 3.44 (dd, J = 13.0, 6.4 Hz, 2H), 2.73 (t, J = 8.1 Hz, 2H), 2.45 - 2.34 (m, 1H), 2.20- 2.10 (m, 1H), 1.91 (dd, J = 15.8, 10.6 Hz, 1H), 1.83-1.69 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.1, 142.1, 137.6, 130.0, 129.97, 128.5, 128.3, 127.5, 125.9, 57.3, 50.3, 35.6, 32.5, 30.5, 25.3.

HRMS (ESI): calcd for $C_{19}H_{22}NO^+$, $(M+H)^+$, 280.1696, found, 280.1690.

6. Synthetic applications

a) Gram Scale-up Reaction



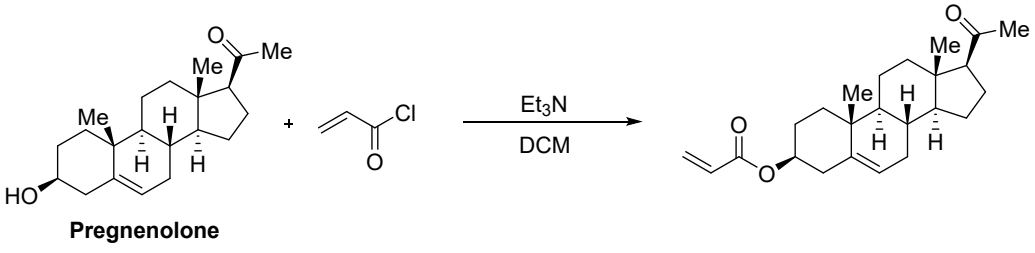
1a **2a** **3a**

In a dried sealed tube**, 1a** (3.3 mmol), **2a** (6.6 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (13.2 mmol), Bu_4NBr (6.6 mmol) were dissolved in CH_3CN (33.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 blue LEDs at room temperature until the starting materials was completely consumed (monitored by TLC). After the reaction finished (96 h), the reaction solvent was distill under vacuum, 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 desired products **3a** in 79% yield.

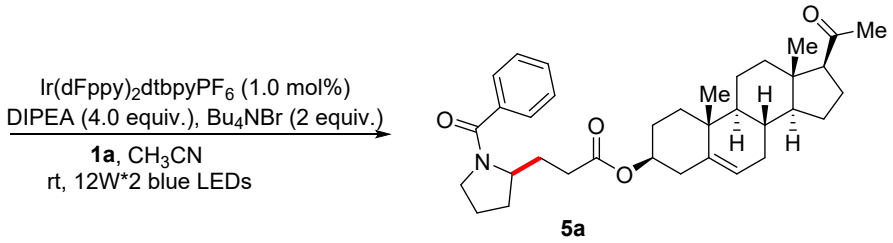
b) Late-stage alkylation of complex molecules

Synthesis of 5a:

Synthesis of substrate Pregnenolone derivative: Pregnenolone (632 mg, 2.0 mmol), Et_3N (404 mg, 4 mmol) were added in DCM (20 mL) at 0-5 °C, acryloyl chloride (216 mg, 2.4 mmol) was added with dropwise. After that, the reaction was removed to room temperature, and stirring overnight at room temperature. When the starting material was completely consumed, 20 ml saturated NH_4Cl was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over Na_2SO_4, concentrated and purified by chromatography on silica gel to afford the desired substrate.



Pregnenolone



5a

Characterization data of substrate:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.38 (dd, J = 17.3, 1.4 Hz, 1H), 6.10 (dd, J = 17.3, 10.4 Hz, 1H), 5.80 (dd, J = 10.4, 1.4 Hz, 1H), 5.38 (d, J = 4.9 Hz, 1H), 4.69 (tdd, J = 11.1, 6.7, 4.4 Hz, 1H), 2.53 (t, J = 8.9 Hz, 1H), 2.36 (d, J = 7.1 Hz, 2H), 2.18 (dt, J = 20.2, 10.0 Hz, 1H), 2.12 (s, 3H), 2.01 (ddd, J = 17.4, 9.7, 5.9 Hz, 2H), 1.94-1.85 (m, 2H), 1.73-1.52 (m, 6H), 1.48 (dd, J = 16.4, 6.9 Hz, 2H), 1.28 – 1.11 (m, 3H), 1.03 (s, 4H), 0.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 209.7, 165.8, 139.8, 130.5, 129.1, 122.6, 74.1, 63.8, 56.98, 50.0, 44.1, 38.9, 38.2, 37.1, 36.8, 31.96, 31.9, 31.7, 27.9, 24.6, 22.98, 21.2, 19.5, 13.4.

Photoredox reaction: In a dried sealed tube**, 1a** (0.2 mmol), **Pregnenolone derivative** (0.1 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 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 a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the desired products.

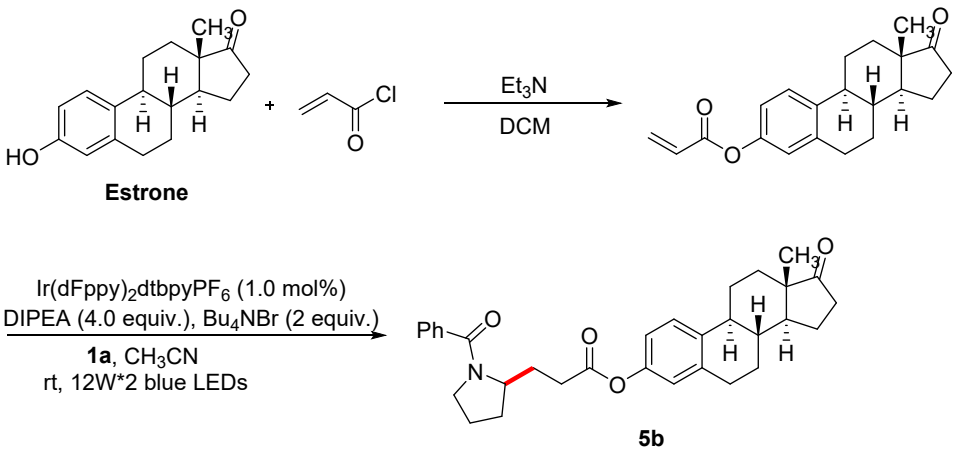
Characterization data of 5a:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.50 (d, J = 6.8 Hz, 2H), 7.41-7.33 (m, 3H), 5.47-5.13 (m, 1H), 4.72 – 4.44 (m, 1H), 4.34 (s, 1H), 3.60-3.33 (m, 2H), 2.52 (t, J = 8.9 Hz, 1H), 2.40 (dd, J = 15.5, 8.0 Hz, 1H), 2.34-2.25 (m, 2H), 2.25-2.14 (m, 2H), 2.11 (s, 3H), 2.06-1.99 (m, 2H), 1.96 (s, 1H), 1.92-1.76 (m, 5H), 1.75-1.63 (m, 4H), 1.62-1.48 (m, 4H), 1.45 (t, J = 9.2 Hz, 2H), 1.28- 1.20 (m, 1H), 1.20-1.10 (m, 2H), 1.04-0.94 (m, 4H), 0.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 209.7, 173.0, 170.4, 139.8, 137.3, 130.1, 128.3, 127.5, 122.4, 73.96, 63.8, 56.95, 56.7, 50.2, 49.98, 44.1, 38.9, 38.1, 37.1, 36.7, 31.9, 31.9, 31.7, 30.3, 29.4, 27.8, 27.8, 25.1, 24.6, 22.9, 21.1, 19.4, 13.3.

HRMS (ESI): calcd for $C_{35}H_{48}NO_4^+$, $(M+H)^+$: 546.3578, found: 546.3582.

Synthesis of 5b:



Synthesis of substrate Estrone derivative: Estrone (540 mg, 2.0 mmol), Et_3N (404 mg, 4 mmol) were added in DCM (20 mL) at 0-5 °C, acryloyl chloride (216 mg, 2.4 mmol) was added with dropwise. After that, the reaction was removed to room temperature, and stirring overnight at room temperature. When the starting material was completely consumed, 20 ml saturated was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over Na_2SO_4, concentrated and purified by chromatography on silica gel to afford the desired product.

Characterization data of substrate:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H7.30 (d, J = 8.4 Hz, 1H), 6.90 (dd, J = 8.4, 2.5 Hz, 1H), 6.86 (d, J

= 2.4 Hz, 1H), 6.59 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.00 (dd, *J* = 10.4, 1.3 Hz, 1H), 2.96 – 2.88 (m, 2H), 2.51 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.45 - 2.38 (m, 1H), 2.35 - 2.25 (m, 1H), 2.05 (dddd, *J* = 12.8, 12.0, 9.5, 6.5 Hz, 3H), 1.73-1.38 (m, 7H), 0.91 (s, 3H),

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 220.9, 165.0, 148.6, 138.2, 137.6, 132.6, 128.2, 126.6, 121.7, 118.8, 50.6, 48.1, 44.3, 38.1, 36.0, 31.7, 29.5, 26.5, 25.9, 21.7, 13.97.

Photoredox reaction: In a dried sealed tube**, 1a** (0.2 mmol), **Estrone derivative** (0.1 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 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 a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the desired product **5b**.

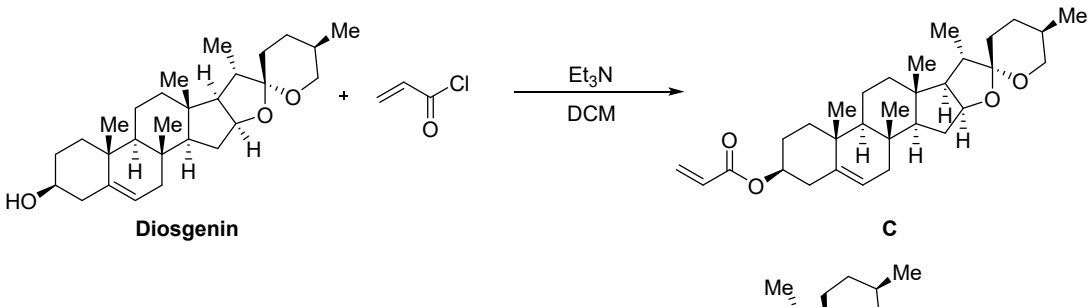
Characterization data of 5b:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52 (d, *J* = 7.3 Hz, 2H), 7.43 - 7.34 (m, 3H), 7.25 (d, *J* = 6.6 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 1H), 4.46 (dd, *J* = 12.6, 6.4 Hz, 1H), 3.46 (ddd, *J* = 22.5, 14.0, 7.2 Hz, 2H), 2.93-2.82 (m, 2H), 2.69 (tt, *J* = 16.2, 8.0 Hz, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.42 -2.36 (m, 1H), 2.35-2.22 (m, 2H), 2.20-2.09 (m, 2H), 2.08-2.03 (m, 1H), 2.02-1.92 (m, 4H), 1.82-1.69 (m, 2H), 1.63-1.59 (m, 1H), 1.59-1.47 (m, 4H), 1.45-1.39 (m, 1H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 220.98, 172.5, 170.6, 148.7, 138.1, 137.4, 137.3, 130.1, 128.3, 127.5, 126.5, 121.8, 118.9, 56.7, 50.6, 50.2, 48.1, 44.3, 38.1, 35.99, 31.7, 31.5, 30.5, 29.5, 26.5, 25.9, 25.1, 21.7, 13.96.

HRMS (ESI): calcd for $C_{32}H_{38}NO_4^+$, $(M+H)^+$: 500.2795, found: 500.2800.

Synthesis of 5c:



Synthesis of substrate Diosgenin derivative: Diosgenin (856 mg, 2.0 mmol), Et_3N (404 mg, 4 mmol) were added in DCM (20 mL) at 0-5 °C, acryloyl chloride (216 mg, 2.4 mmol) was added with dropwise. After that, the reaction was removed to room temperature, and stirring overnight at room temperature. When the starting material was completely consumed, 20 ml saturated was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over Na_2SO_4, concentrated and purified by

chromatography on silica gel to afford the desired substrate.

Characterization data of substrate:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.38 (dd, J = 17.3, 1.3 Hz, 1H), 6.10 (dd, J = 17.3, 10.4 Hz, 1H), 5.80 (dd, J = 10.4, 1.2 Hz, 1H), 5.39 (d, J = 4.7 Hz, 1H), 4.75-4.60 (m, 1H), 4.41 (dd, J = 14.9, 7.5 Hz, 1H), 3.47 (dd, J = 10.1, 3.2 Hz, 1H), 3.37 (t, J = 10.9 Hz, 1H), 2.37 (d, J = 6.2 Hz, 2H), 1.99 (dt, J = 12.3, 5.4 Hz, 2H), 1.94-1.82 (m, 3H), 1.81-1.72 (m, 2H), 1.70-1.55 (m, 7H), 1.54-1.40 (m, 3H), 1.35-1.24 (m, 2H), 1.23-1.06 (m, 4H), 1.04 (d, J = 10.0 Hz, 3H), 0.99 (dd, J = 11.2, 7.0 Hz, 3H), 0.79 (d, J = 4.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.7, 139.8, 130.4, 129.1, 122.6, 109.4, 80.9, 74.1, 66.9, 62.2, 56.6, 50.1, 41.7, 40.4, 39.8, 38.2, 37.1, 36.9, 32.2, 31.95, 31.5, 30.4, 28.9, 27.9, 20.9, 19.5, 17.3, 16.4, 14.6.

Photoredox reaction: In a dried sealed tube**, 1a** (0.2 mmol), **Diosgenin derivative** (0.1 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 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 a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the desired product **5c**.

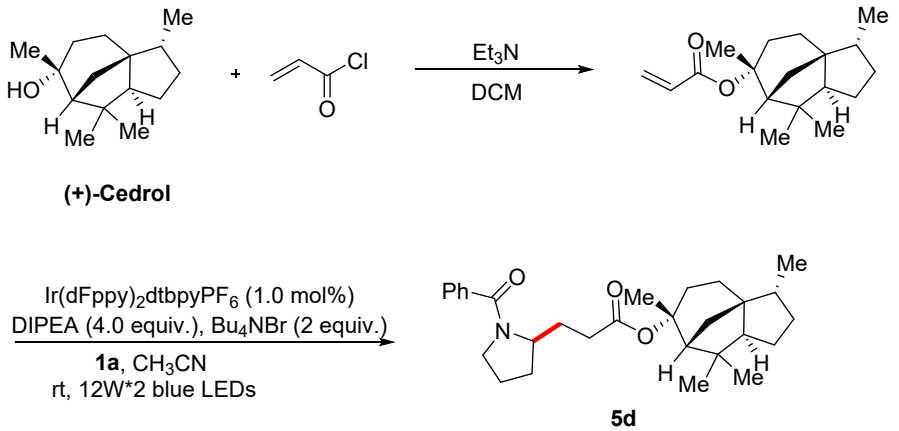
Characterization data of 5c:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.50 (d, J = 6.4 Hz, 2H), 7.42-7.33 (m, 3H), 5.42-5.22 (m, 1H), 4.70 - 4.51 (m, 1H), 4.38 (dt, J = 17.9, 6.6 Hz, 2H), 3.57-3.32 (m, 4H), 2.40 (dd, J = 15.7, 8.5 Hz, 2H), 2.33 - 2.19 (m, 3H), 2.13-2.05 (m, 1H), 2.02-1.92 (m, 3H), 1.85 (td, J = 12.5, 7.0 Hz, 4H), 1.71 (ddd, J = 16.4, 12.5, 6.4 Hz, 6H), 1.60 (dd, J = 14.2, 9.7 Hz, 5H), 1.54-1.37 (m, 4H), 1.27 (dt, J = 14.2, 6.8 Hz, 2H), 1.18 (dd, J = 12.6, 4.7 Hz, 1H), 1.14-1.05 (m, 2H), 1.01 (s, 3H), 0.95 (dd, J = 12.4, 6.1 Hz, 4H), 0.78 (d, J = 4.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.0, 170.4, 139.9, 137.3, 130.1, 128.3, 127.5, 122.4, 109.4, 80.9, 74.0, 66.95, 62.2, 56.7, 56.6, 50.2, 50.1, 41.7, 40.4, 39.8, 38.2, 38.2, 37.1, 36.8, 32.2, 31.95, 31.7, 31.5, 30.4, 30.3, 29.4, 28.9, 27.8, 25.1, 20.9, 19.5, 17.3, 16.4, 14.6.

HRMS (ESI): calcd for $C_{42}H_{60}NO_5^+$, $(M+H)^+$: 658.4466, found: 658.4474.

Synthesis of 5d:



Synthesis of substrate (+)-Cedrol derivative: (+)-Cedrol (444 mg, 2.0 mmol), Et_3N (404 mg, 4 mmol) were added in DCM (20 mL) at 0-5 °C, acryloyl chloride (216 mg, 2.4 mmol) was added with dropwise.

After that, the reaction was removed to room temperature, and stirring overnight at room temperature. When the starting material was completely consumed, 20 ml saturated was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over Na_2SO_4, concentrated and purified by chromatography on silica gel to afford the desired substrate.

Characterization data of substrate:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.27 (dd, J = 17.3, 1.6 Hz, 1H), 6.01 (dd, J = 17.3, 10.3 Hz, 1H), 5.70 (dd, J = 10.3, 1.6 Hz, 1H), 2.44 (d, J = 5.2 Hz, 1H), 2.07 (ddt, J = 13.5, 5.6, 1.6 Hz, 1H), 2.03 – 1.92 (m, 1H), 1.85 (ddd, J = 22.6, 14.1, 7.0 Hz, 2H), 1.70-1.61 (m, 2H), 1.57 (s, 3H), 1.51 (ddd, J = 14.6, 7.3, 4.9 Hz, 1H), 1.47-.42 (m, 1H), 1.42-1.31 (m, 3H), 1.30-1.20 (m, 1H), 1.13 (s, 3H), 0.96 (s, 3H), 0.83 (d, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.5, 130.8, 129.3, 86.7, 56.97, 56.9, 54.1, 43.6, 41.4, 41.1, 37.1, 33.3, 31.4, 28.6, 27.2, 26.0, 25.4, 15.6.

Photoredox reaction: In a dried sealed tube**, 1a** (0.2 mmol), **(+)-Cedrol derivative** (0.1 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 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 a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the desired product **5d**.

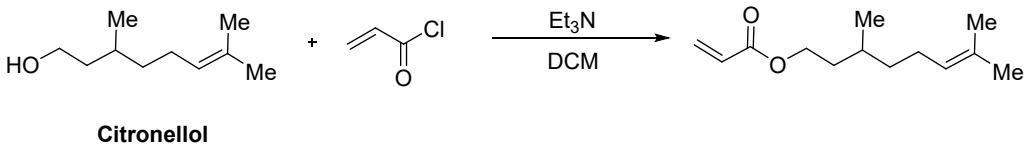
Characterization data of 5d:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 (d, J = 6.4 Hz, 2H), 7.41-7.32 (m, 3H), 4.31 (s, 1H), 3.55-3.29 (m, 2H), 2.38 (d, J = 4.4 Hz, 1H), 2.34-2.15 (m, 3H), 2.05 (dd, J = 12.8, 6.9 Hz, 2H), 1.97-1.87 (m, 3H), 1.87-1.80 (m, 2H), 1.79-1.72 (m, 2H), 1.67-1.58 (m, 3H), 1.56-1.45 (m, 4H), 1.44-1.28 (m, 5H), 1.28-1.23 (m, 1H), 1.15 (s, 2H), 0.95 (s, 3H), 0.81 (d, J = 7.1 Hz, 3H).

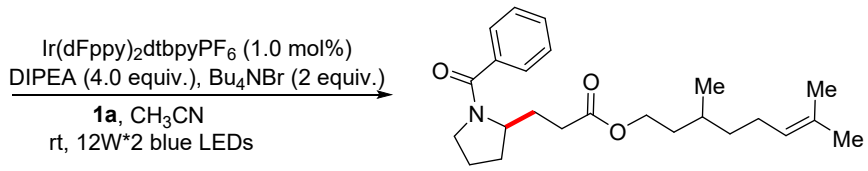
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.6, 170.3, 137.4, 129.95, 128.3, 127.4, 86.5, 57.0, 56.7, 54.0, 50.1, 43.5, 41.4, 41.1, 37.0, 33.2, 32.7, 31.3, 30.3, 29.3, 28.6, 27.2, 25.9, 25.4, 25.1, 15.6.

HRMS (ESI): calcd for $C_{29}H_{42}NO_3^+$, $(M+H)^+$: 452.3159, found: 452.3161.

Synthesis of 5e:



Citronellol



5e

Synthesis of substrate Citronellol derivative: Citronellol (312 mg, 2.0 mmol), Et_3N (404 mg, 4 mmol) were added in DCM (20 mL) at 0-5 °C, acryloyl chloride (216 mg, 2.4 mmol) was added with dropwise. After that, the reaction was removed to room temperature, and stirring overnight at room temperature.

When the starting material was completely consumed, 20 ml saturated was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over Na_2SO_4, concentrated and purified by chromatography on silica gel to afford the desired substrate.

Characterization data of substrate:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.39 (dd, J = 17.3, 1.5 Hz, 1H), 6.12 (dd, J = 17.3, 10.4 Hz, 1H), 5.81 (dd, J = 10.4, 1.5 Hz, 1H), 5.15-5.02 (m, 1H), 4.26-4.09 (m, 2H), 2.08-1.88 (m, 2H), 1.78-1.69 (m, 1H), 1.68 (s, 3H), 1.59-1.50 (m, 2H), 1.50-1.40 (m, 1H), 1.36 (ddd, J = 8.7, 6.4, 3.2 Hz, 1H), 1.28- 1.16 (m, 2H), 0.94 (t, J = 6.8 Hz, 3H), 0.90-0.82 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.5, 131.5, 130.5, 128.8, 124.7, 63.3, 37.1, 35.6, 29.7, 25.9, 25.5, 19.6, 17.8.

Photoredox reaction: In a dried sealed tube**, 1a** (0.2 mmol), **Citronellol derivative** (0.1 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 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 a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the desired product **5e**.

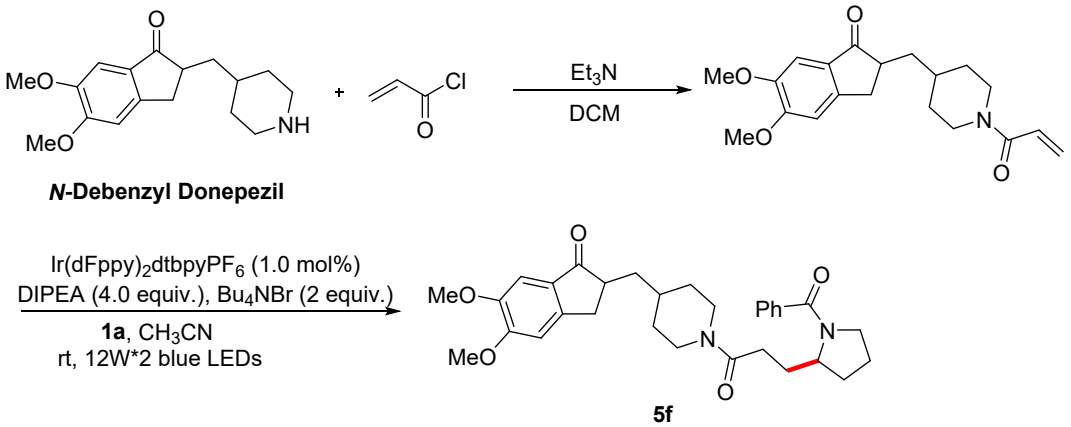
Characterization data of 5e:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (d, J = 7.1 Hz, 2H), 7.41-7.34 (m, 3H), 5.07 (t, J = 7.1 Hz, 1H), 4.41-4.23 (m, 1H), 4.11 (dd, J = 14.1, 7.0 Hz, 2H), 3.61-3.33 (m, 2H), 2.42 (dd, J = 16.0, 9.3 Hz, 2H), 2.28-2.15 (m, 1H), 2.08 (dd, J = 12.3, 6.0 Hz, 1H), 2.01-1.85 (m, 4H), 1.74 (dd, J = 13.9, 6.3 Hz, 2H), 1.67 (s, 4H), 1.59 (s, 3H), 1.52 (dd, J = 12.6, 5.9 Hz, 1H), 1.41 (dd, J = 7.7, 4.5 Hz, 1H), 1.32 (ddd, J = 9.1, 6.7, 3.6 Hz, 1H), 1.20-1.12 (m, 1H), 0.89 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 173.7, 170.4, 137.3, 131.4, 130.1, 128.3, 127.5, 124.7, 63.2, 56.7, 50.2, 37.1, 35.5, 31.4, 30.3, 29.6, 29.4, 25.8, 25.5, 25.1, 19.5, 17.8.

HRMS (ESI): calcd for $C_{24}H_{36}NO_3^+$, $(M+H)^+$, 386.2690, found, 386.2697.

Synthesis of 5f:



Synthesis of substrate *N*-Debenzyl Donepezil derivatve: *N*-Debenzyl Donepezil (578 mg, 2.0 mmol), Et_3N (404 mg, 4 mmol) were added in DCM (20 mL) at 0-5 °C, acryloyl chloride (216 mg, 2.4 mmol) was added with dropwise. After that, the reaction was removed to room temperature, and stirring

overnight at room temperature. When the starting material was completely consumed, 20 ml saturated was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over Na_2SO_4, concentrated and purified by chromatography on silica gel to afford the desired product.

Characterization data of substrate:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.11 (s, 1H), 6.82 (s, 1H), 6.54 (dd, *J* = 16.8, 10.6 Hz, 1H), 6.20 (dd, *J* = 16.8, 2.0 Hz, 1H), 5.61 (dd, *J* = 10.6, 2.0 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 3.96 (s, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.22 (dd, *J* = 17.4, 8.0 Hz, 1H), 3.02 (t, *J* = 12.6 Hz, 1H), 2.73-2.53 (m, 3H), 1.85 (dd, *J* = 9.0, 4.3 Hz, 1H), 1.76 (d, *J* = 8.8 Hz, 3H), 1.33 (dd, *J* = 16.5, 10.0 Hz, 1H), 1.23-1.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 207.3, 165.4, 155.6, 149.5, 148.6, 129.2, 128.0, 127.2, 107.4, 104.4 , 56.3, 56.1, 46.1, 45.0(d, *J* = 22.3 Hz), 42.3, 38.5 (d, *J* = 24.0 Hz), 34.6 (d, *J* = 29.6 Hz), 33.8-32.9 (m), 32.5 (d, *J* = 18.0 Hz), 31.43.

Photoredox reaction: In a dried sealed tube**, 1a** (0.2 mmol), ***N*-Debenzyl Donepezil derivatve** (0.1 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 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 a eluent of petroleum ether (PE) and ethyl acetate (EA) to give the desired products.

Characterization data of 5f:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 (s, 2H), 7.41-7.31 (m, 3H), 7.16 (s, 1H), 6.85 (s, 1H), 4.62 (d, *J* = 9.4 Hz, 1H), 4.45-4.34 (m, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 3.54-3.44 (m, 1H), 3.41-3.31 (m, 1H), 3.23 (dd, *J* = 14.9, 5.5 Hz, 1H), 2.99 (t, *J* = 11.7 Hz, 1H), 2.73-2.62 (m, 2H), 2.57-2.51 (m, 1H), 2.48- 2.38 (m, 1H), 2.18 (d, *J* = 3.9 Hz, 1H), 2.11-2.03 (m, 1H), 1.95 (dd, *J* = 12.0, 5.9 Hz, 1H), 1.84 (dd, *J* = 17.7, 4.6 Hz, 2H), 1.79-1.68 (m, 7H), 1.35-1.26 (m, 1H), 1.24-1.07 (m, 2H).

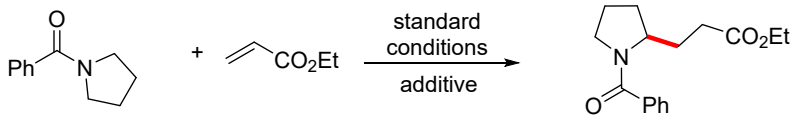
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 207.5, 171.1, 170.4, 155.6, 149.5, 148.7, 137.3, 129.9, 129.2, 128.3 , 127.3, 107.4, 104.4, 56.85 (d, *J* = 5.6 Hz), 56.3, 56.1, 49.9, 45.9 (d, *J* = 8.6 Hz), 45.3-44.96, 41.9 (d, *J* = 6.8 Hz), 38.7-38.4 (m), 34.8-34.6 (m), 33.5-33.2 (m), 32.6-32.2 (m), 31.5, 30.7, 30.5, 30.1, 24.9.

HRMS (ESI): calcd for $C_{31}H_{39}N_2O_5^+$, $(M+H)^+$, 519.2853, found, 519.2849.

7. Mechanistic Studies

a) Control experiment

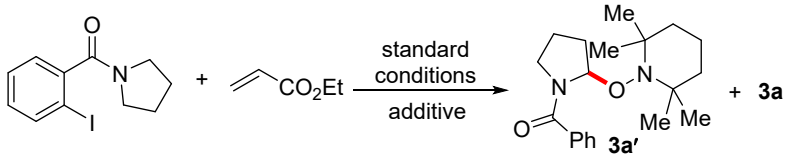
To illustrate the mechanism, the control experiment were conducted: In a dried sealed tube, **8** (0.1 mmol), **2a** (0.2 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 12 W*2 blue leds until full completely consumed (monitored by TLC) 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 **3a** in 0% yield, which demonstrate the activation of C-I bond are crucial to the successful transformation of the procedure.



6 **3a**, 0%

b) Radical inhibition experiments

In a dried sealed tube, **1a** (0.1 mmol), **2a** (0.2 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol), TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 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 and filtered with an inch of silica gel. Subsequently, the reaction mixture was detected only trace of desired product **3a** on GC-MS, with 5% isolated yield. When the inhibitor BHT (2,6-di-tert-butyl-4-methylphenol) (0.2 mmol) was used, the alkylation process was completely inhibited, which indicate the novel transformation was radical intermediate involved through a single-electron transfer.



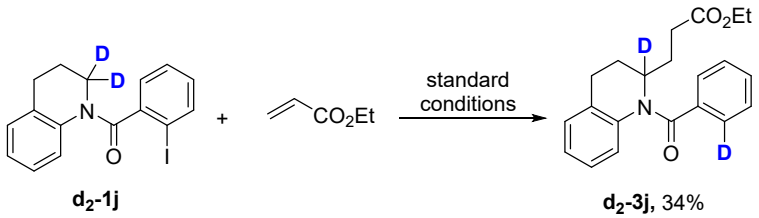
1a **2a** **3a′**

additive (2 equiv.)	yield of **3a′**	yield of **3a**
--	--	81%
Tempo	0%	5%
BHT	--	0%

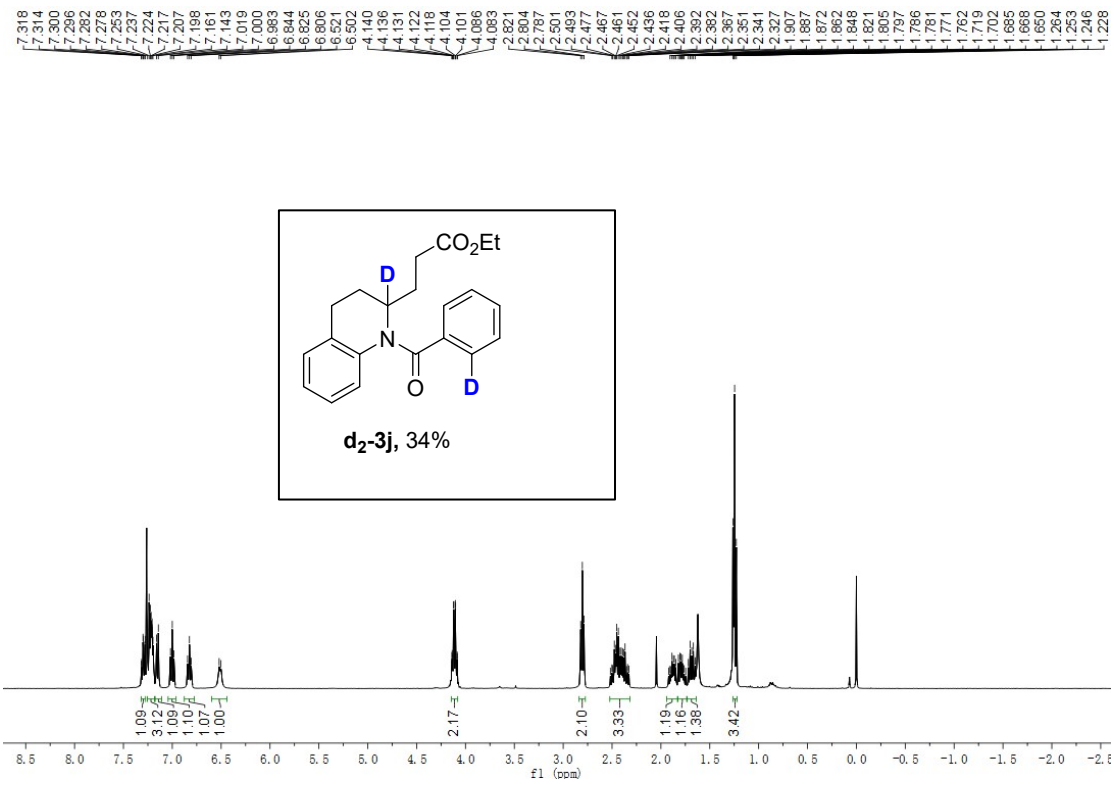
c) Deuterium labeling experiment

To illustrate the mechanism, the deuterium labeling experiments were conducted: In a dried sealed tube, **d_2-1j** (0.1 mmol), **2a** (0.2 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (0.2 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 12 W*2 blue leds until full completely consumed (monitored by TLC) 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_2-3j** in 34% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.32-7.27 (m, 3H), 7.22 (dt, J = 7.5, 4.9 Hz, 1H), 7.15 (d, J = 7.4 Hz, 1H), 7.00 (t, J = 7.2 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H),

6.51 (d, *J* = 7.4 Hz, 1H), 4.17-4.05 (m, 2H), 2.80 (t, *J* = 6.8 Hz, 2H), 2.52 – 2.32 (m, 3H), 1.88 (ddd, *J* = 15.5, 9.8, 5.8 Hz, 1H), 1.78 (ddd, *J* = 13.8, 9.8, 6.3 Hz, 1H), 1.73-1.64 (m, 1H), 1.25 (dd, *J* = 8.6, 5.7 Hz, 3H).

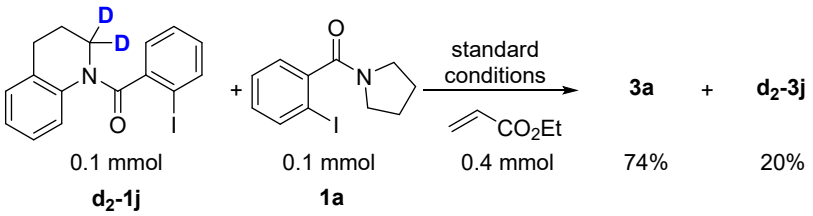


d_2-1j **d_2-3j**, 34%



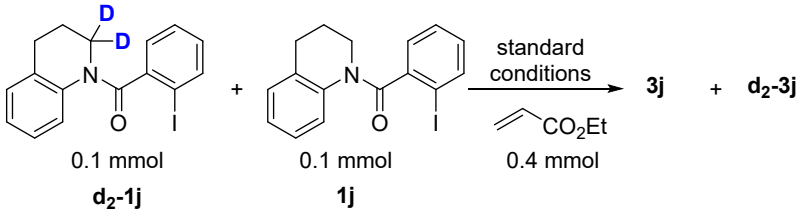
d) Deuterium labeling experiment to rule out 1,5-HAT of intermolecular

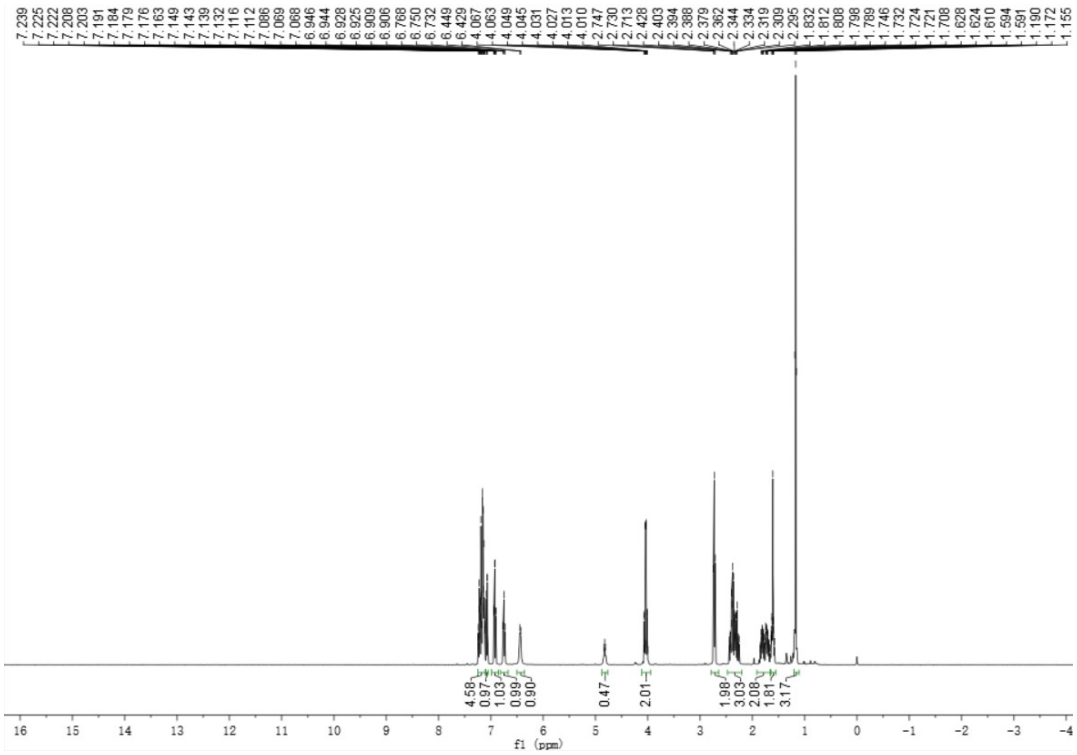
In a dried sealed tube, **1a** (0.1 mmol), **d_2-1j** (0.1 mmol), **2a** (0.4 mmol), $Ir(dFppy)_2dtbpyPF_6$ (2.0 mol %), DIPEA (0.8 mmol), Bu_4NBr (0.4 mmol) were dissolved in CH_3CN (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 12 W*2 blue leds until full completely consumed (monitored by TLC) 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 **3a** and **d_2-3j** in 74% and 20% yields respectively, without finding the intermolecular 1,5-HAT product.



e) Deuterium labeling experiment to evaluate the KIE value

To illustrate the mechanism, the deuterium labeling experiments were conducted: In a dried sealed tube, **d_2-1j** (0.1 mmol), **1j** (0.1 mmol), **2a** (0.4 mmol), $Ir(dFppy)_2dtbpyPF_6$ (1.0 mol %), DIPEA (0.4 mmol), Bu_4NBr (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 °C. Then, the reaction flask was exposed to 12 W*2 blue leds until full completely consumed (monitored by TLC) 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_2-3j** and **3j** in 25% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.25-7.10 (m, 4H), 7.09-7.04 (m, 1H), 6.93 (td, J = 7.5, 1.1 Hz, 1H), 6.75 (t, J = 7.2 Hz, 1H), 6.44 (d, J = 7.7 Hz, 1H), 4.90-4.75 (m, 0.47H), 4.14-3.97 (m, 2H), 2.73 (t, J = 6.8 Hz, 1H), 2.48- 2.20 (m, 3H), 1.91-1.66 (m, 2H), 1.66-1.55 (m, 1H), 1.17 (t, J = 7.1 Hz, 3H).





8. Reference

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2. S. Sarkar, W. Sidhant, X. Jia, V. Gevorgyan, *Chem* **2022**, *8*, 3096-3108.
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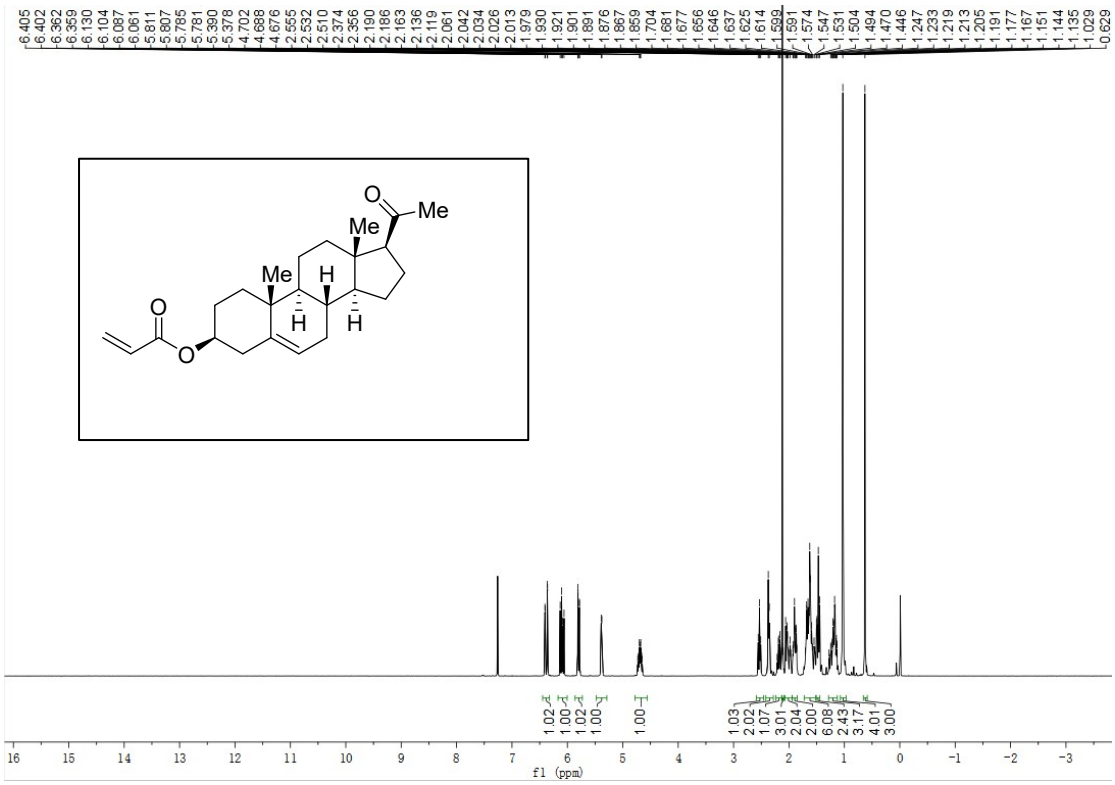
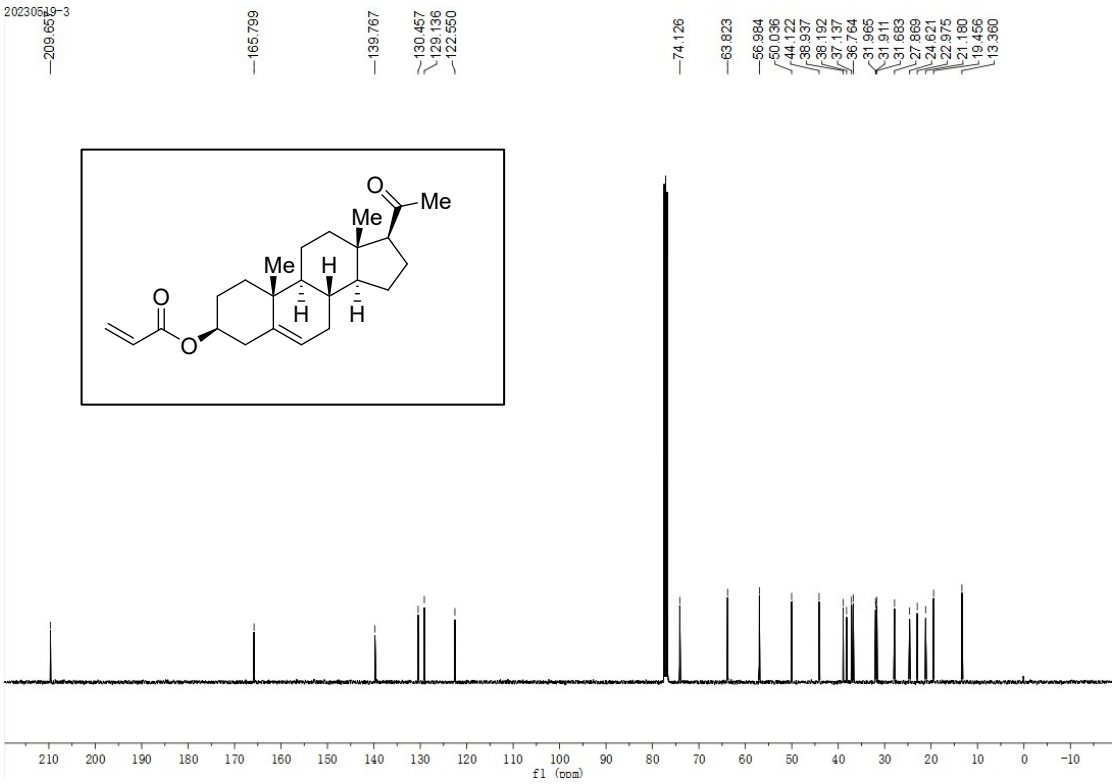
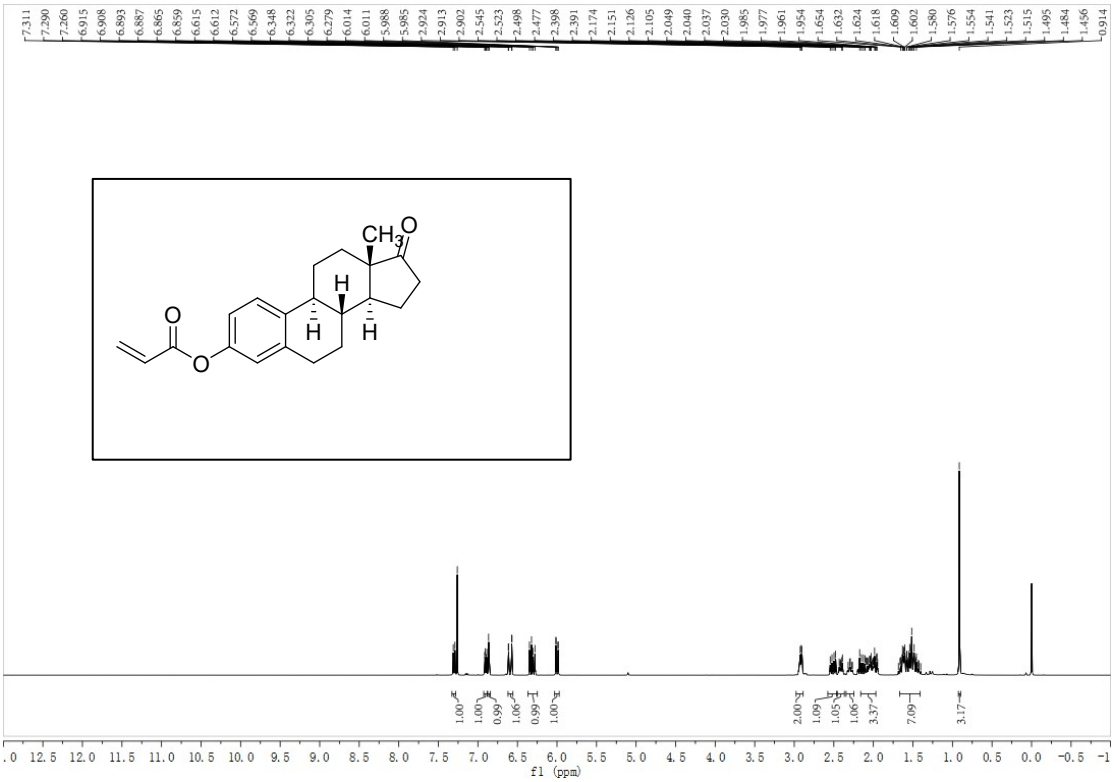
9. Spectra for Substrates and Products Product Characterization

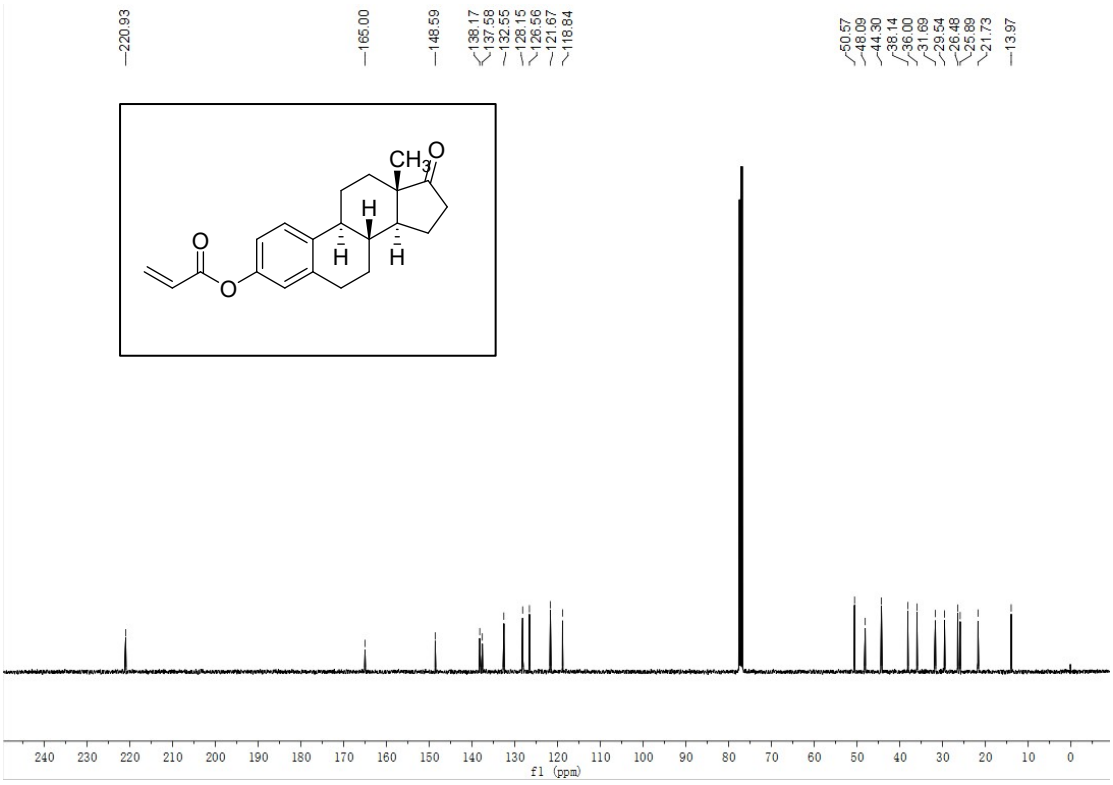
Pregnenolone derivative, $^{1}H+^{13}C$



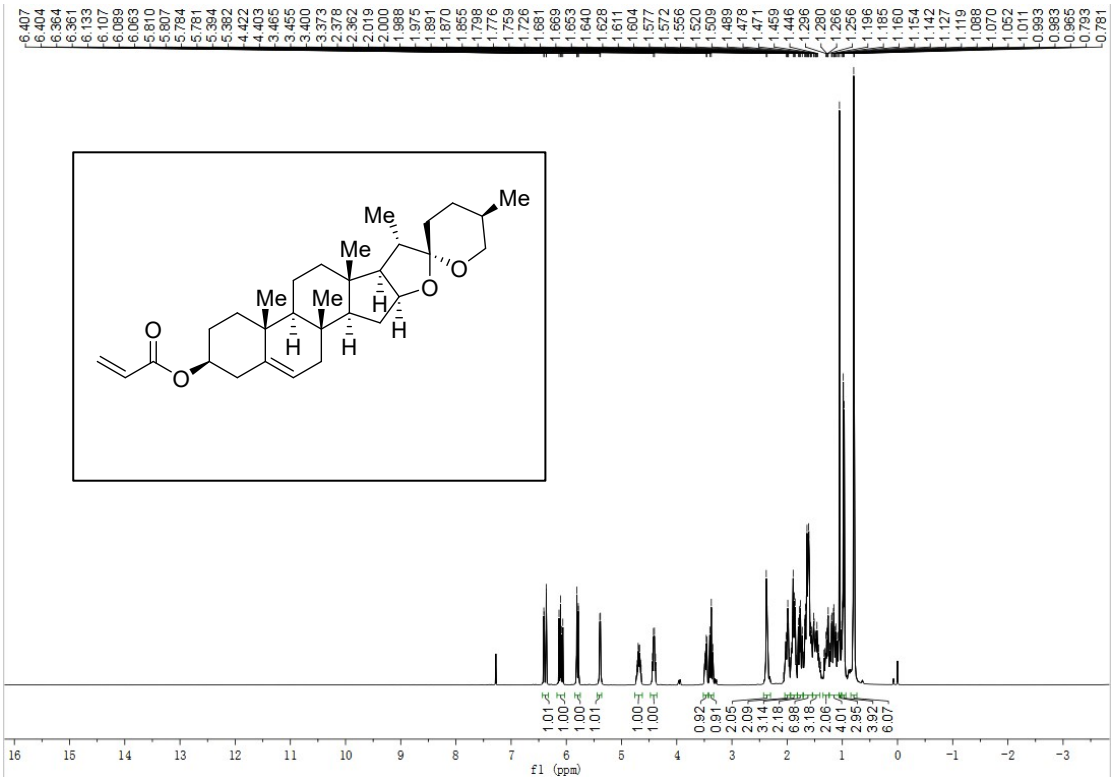


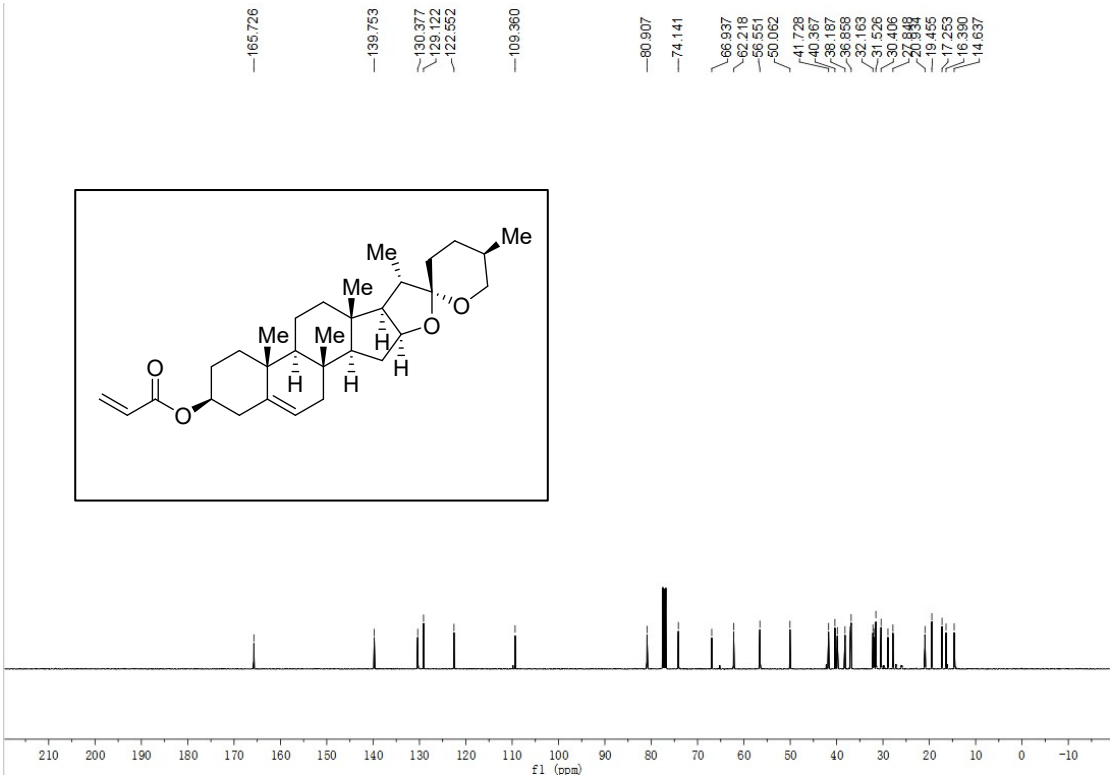
Estrone derivative, $^{1}H+^{13}C$



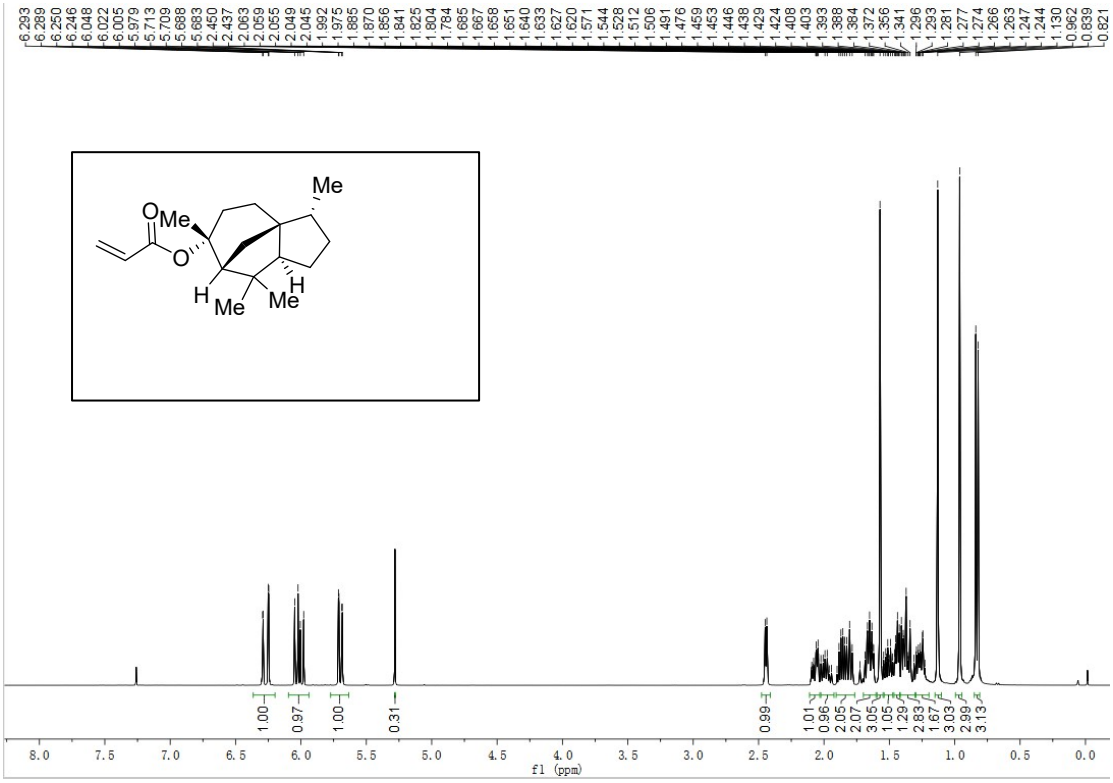


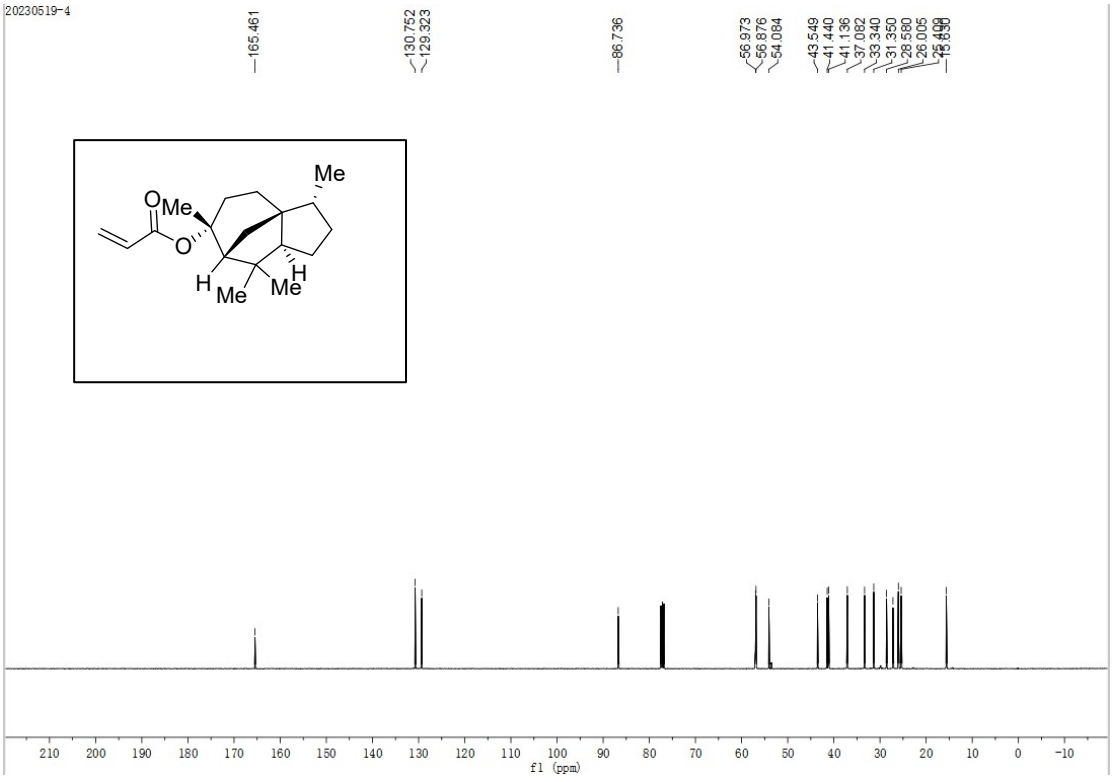
Diosgenin derivative, $^{1}H+^{13}C$



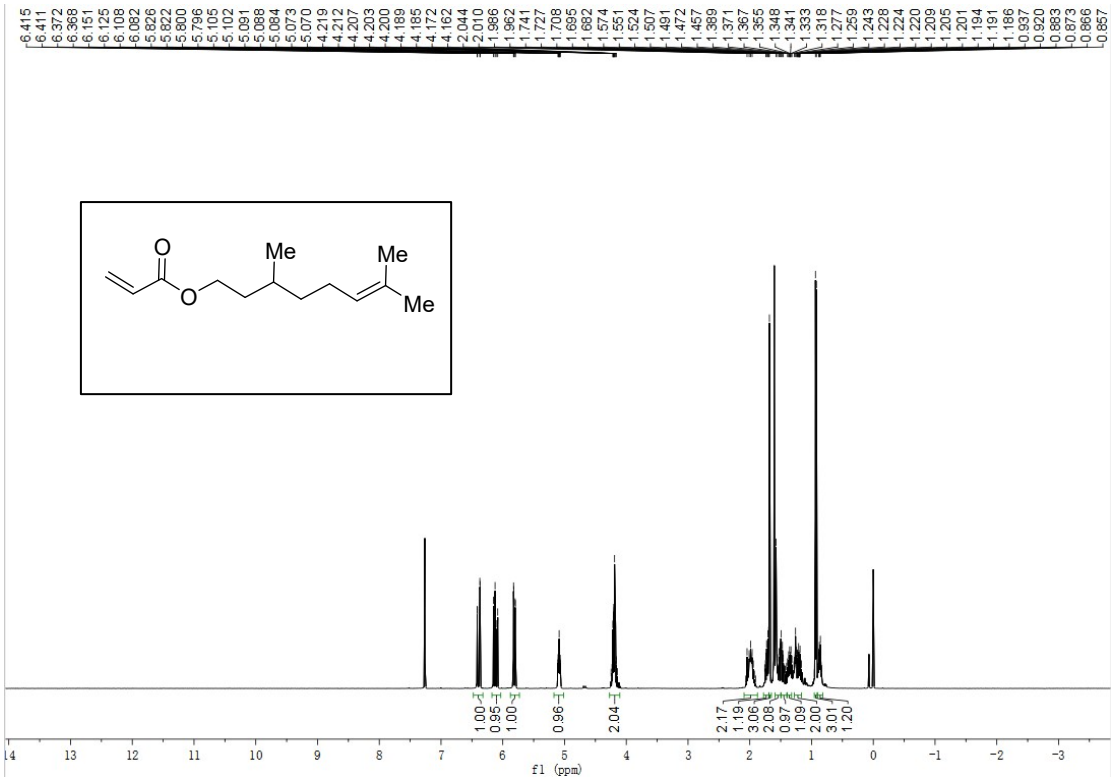


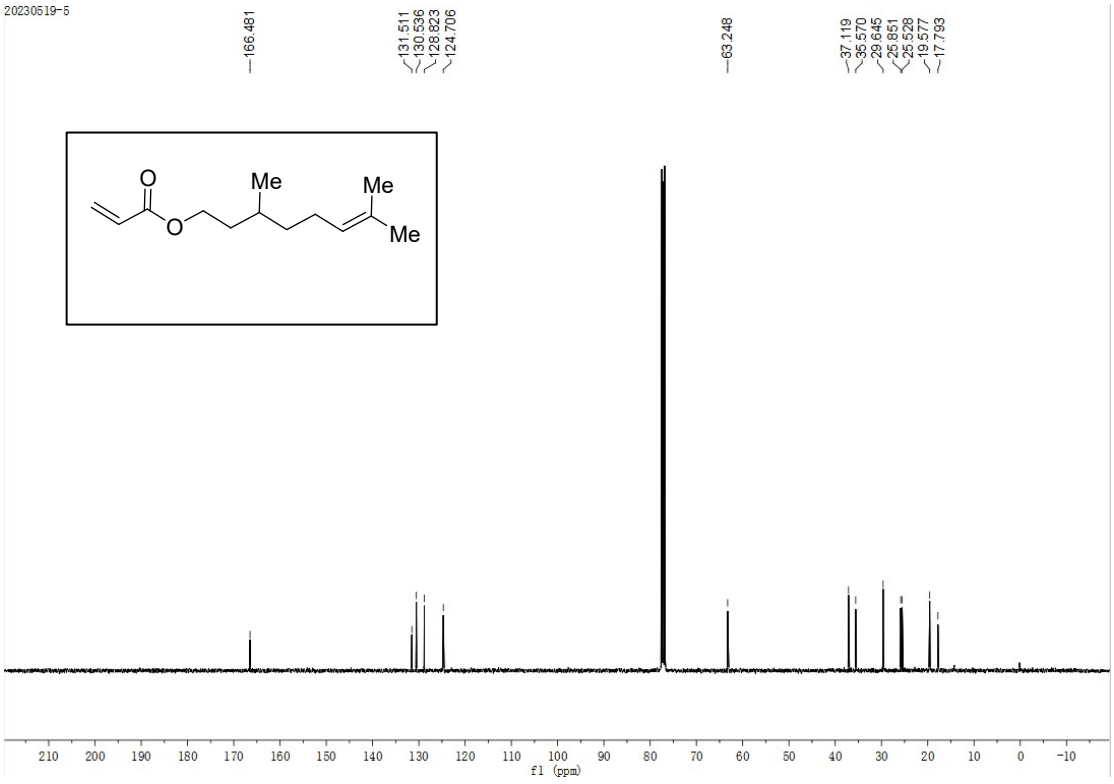
(+)-Cedrol derivative, $^{1}H+^{13}C$



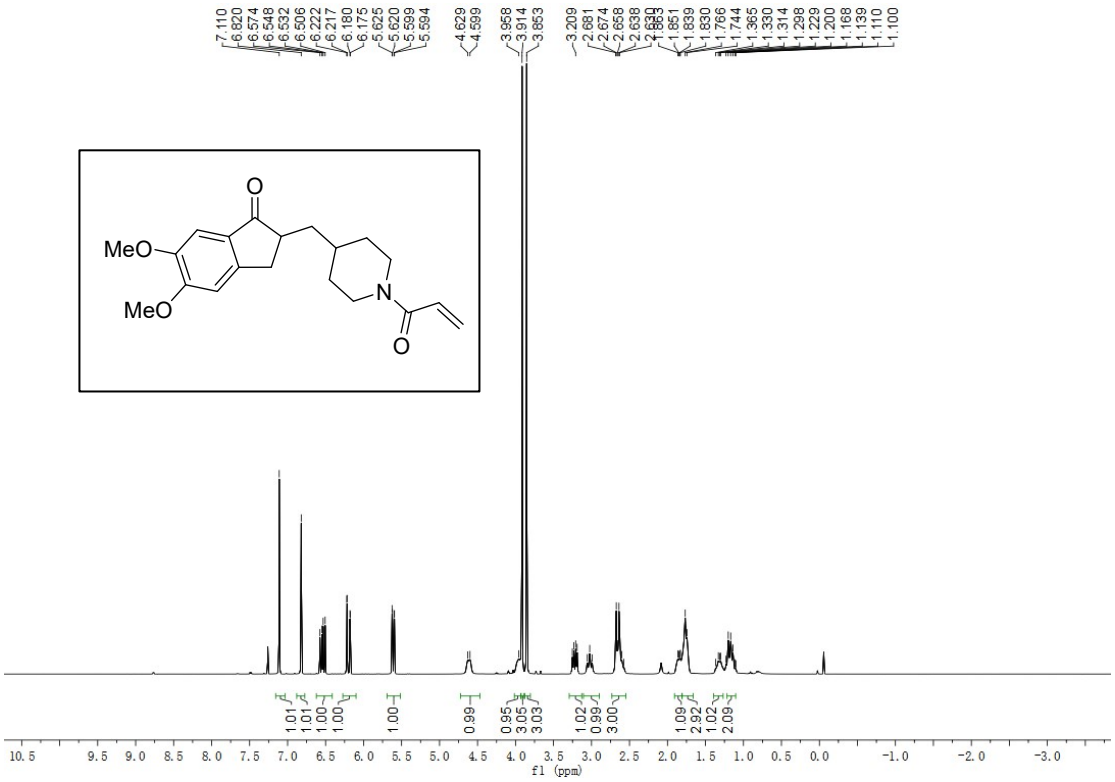


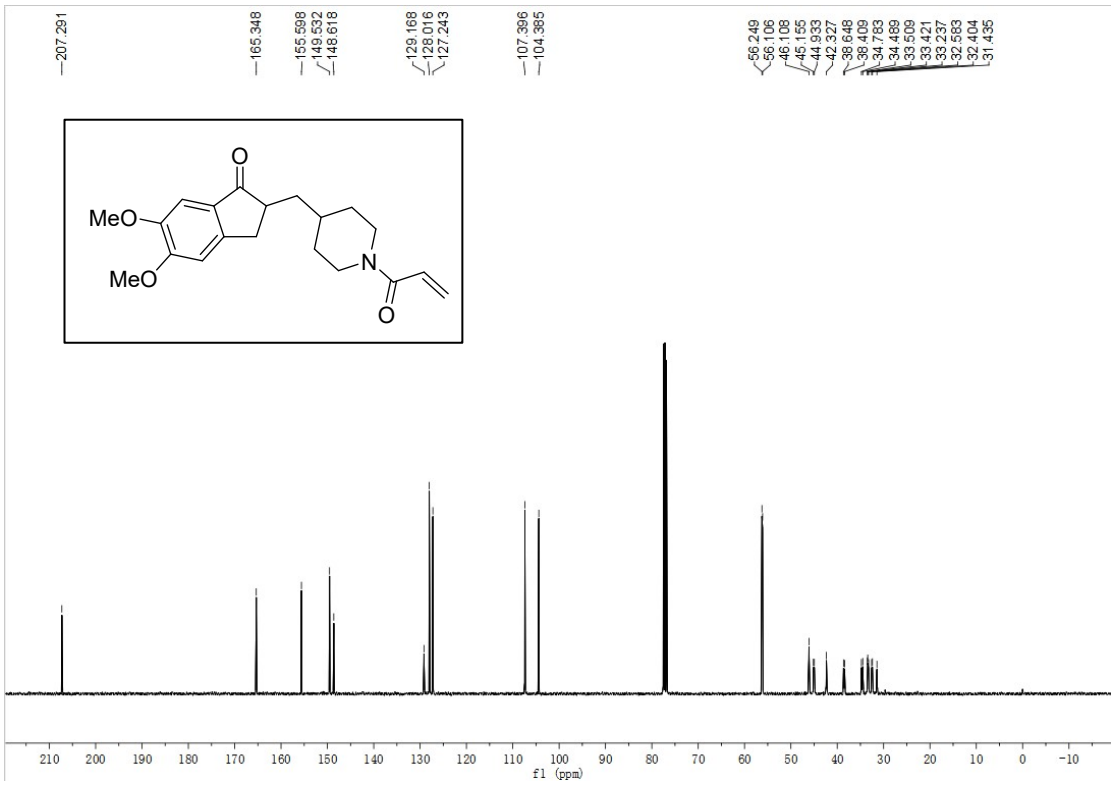
Citronellol derivative, $^{1}H+^{13}C$



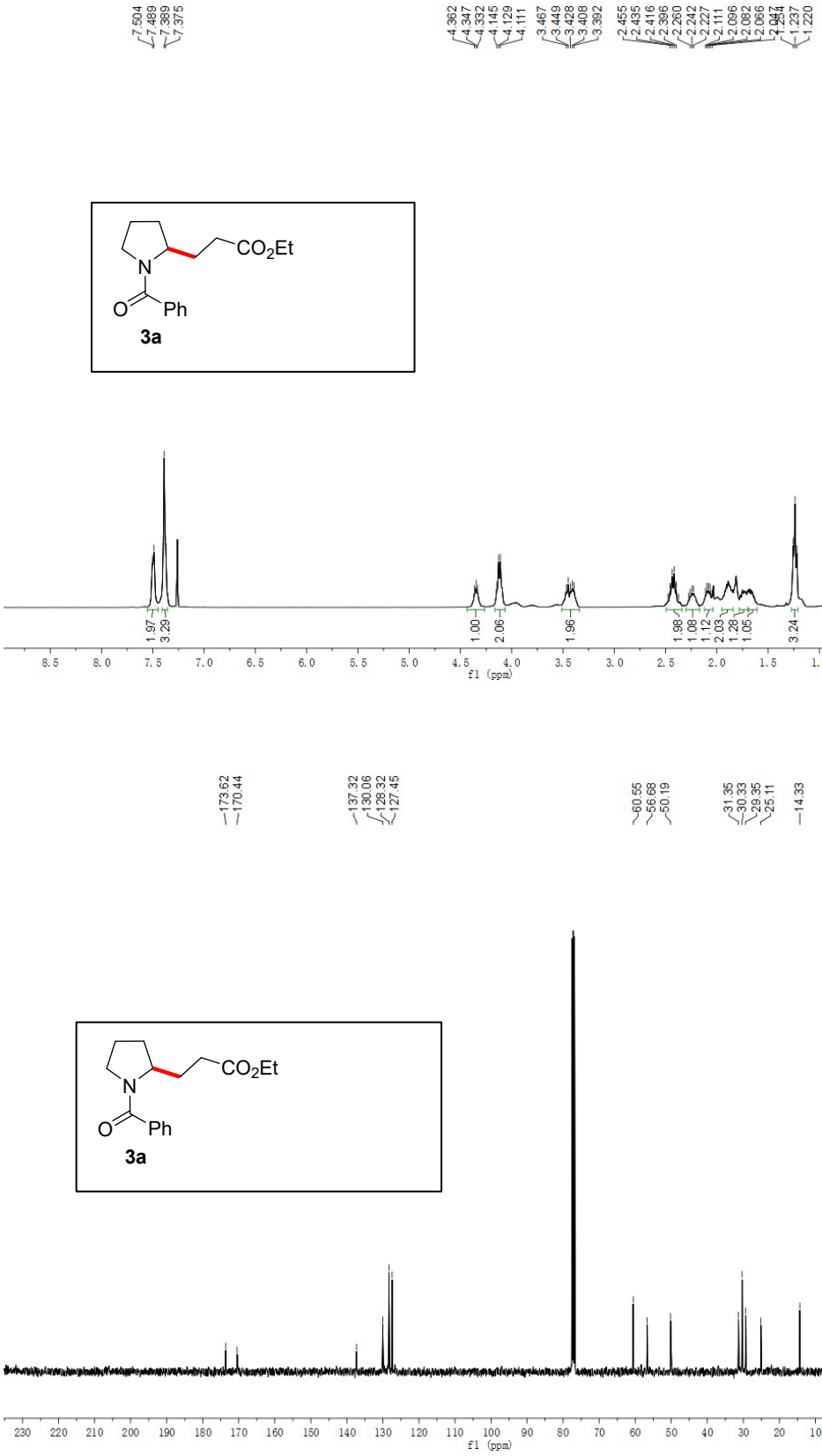


N-Debenzyl Donepezil derivatve, $^{1}H+^{13}C$

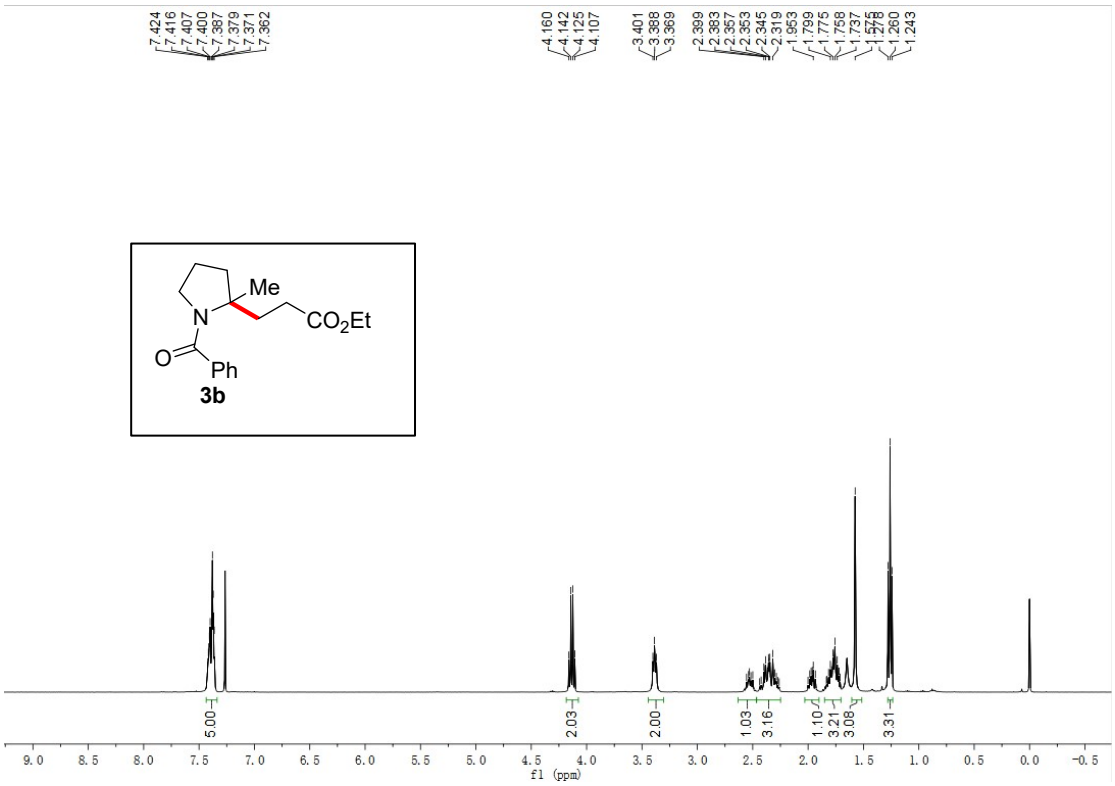


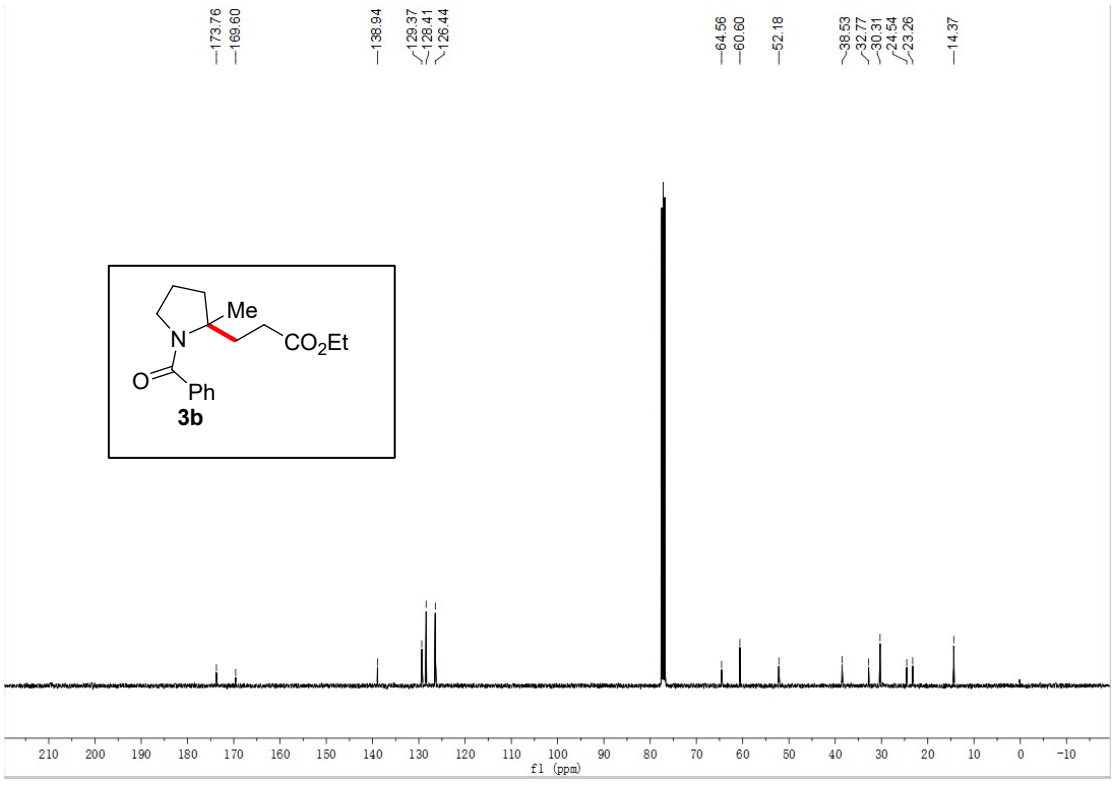


3a, $^{1}H+^{13}C$

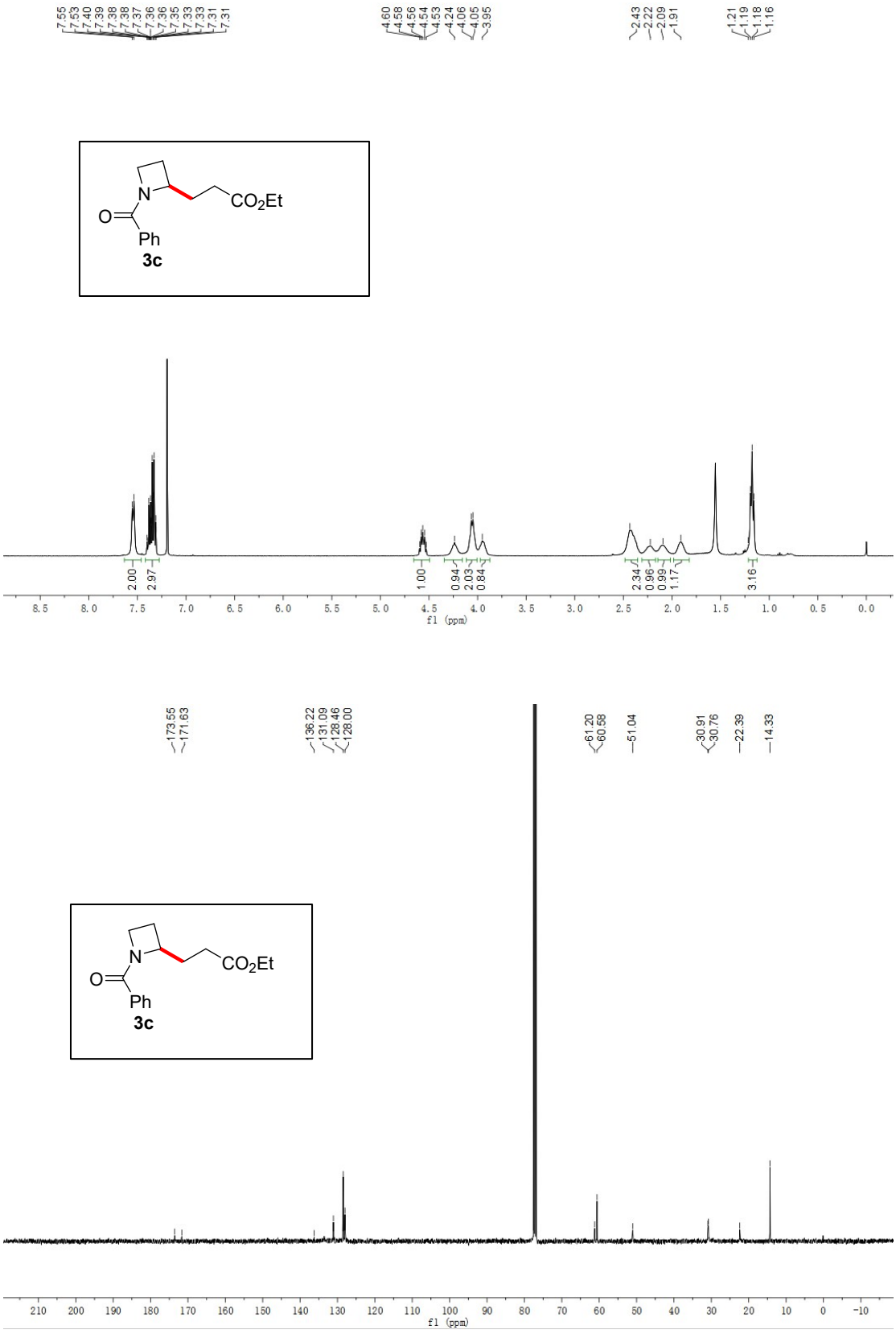

7.504
7.489
7.389
7.375
4.362
4.347
4.332
4.145
4.129
4.111
3.467
3.449
3.428
3.408
3.392
2.455
2.435
2.416
2.396
2.260
2.242
2.227
2.111
2.096
2.082
2.066
1.254
1.237
1.220
CO2Et
N
O
Ph
3a
1.97
3.29
1.00
2.06
1.96
1.98
1.08
1.12
2.03
1.28
1.05
3.24
f1 (ppm)
173.62
170.44
137.32
130.06
128.32
127.45
60.55
56.68
50.19
31.35
30.33
29.35
25.11
14.33
CO2Et
N
O
Ph
3a
f1 (ppm)

3b, $^{1}H+^{13}C$

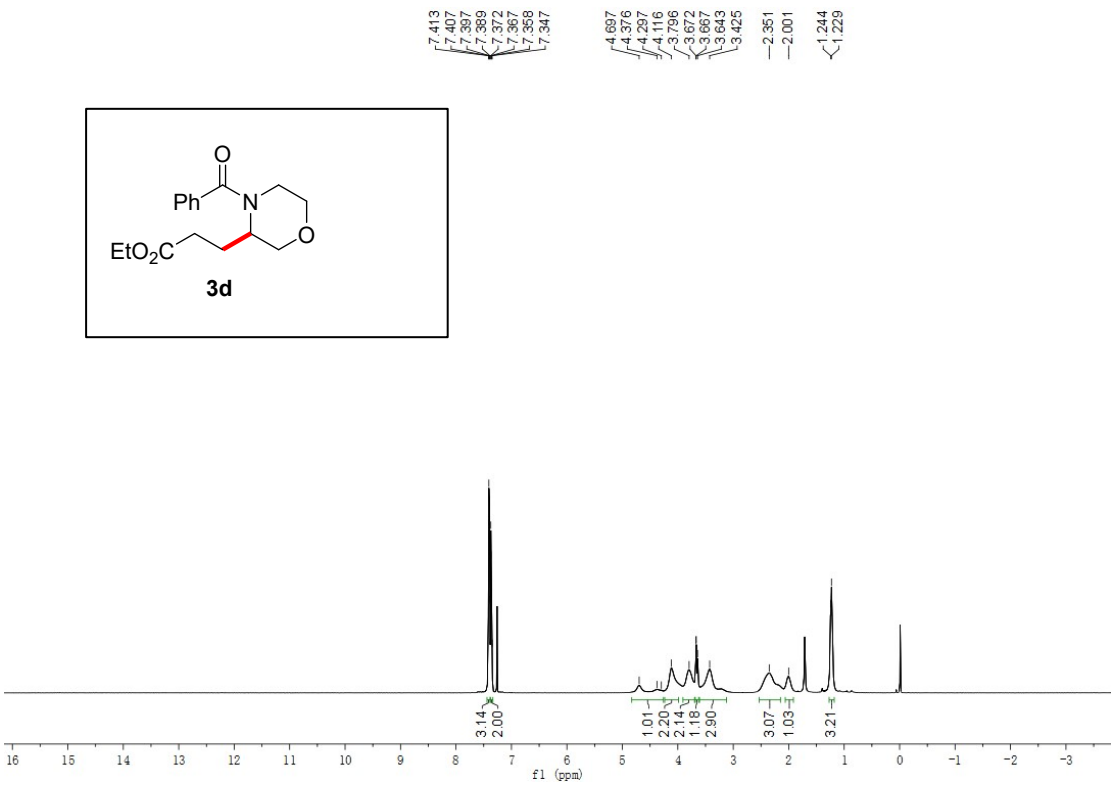

7.424
7.416
7.407
7.400
7.387
7.379
7.371
7.362
4.160
4.142
4.125
4.107
3.401
3.388
3.369
2.399
2.383
2.367
2.353
2.345
2.319
1.953
1.799
1.775
1.758
1.737
1.260
1.243
Me
N
O
Ph
CO2Et
3b
5.00
2.03
2.00
1.03
3.16
1.10
3.21
3.08
3.31
f1 (ppm)

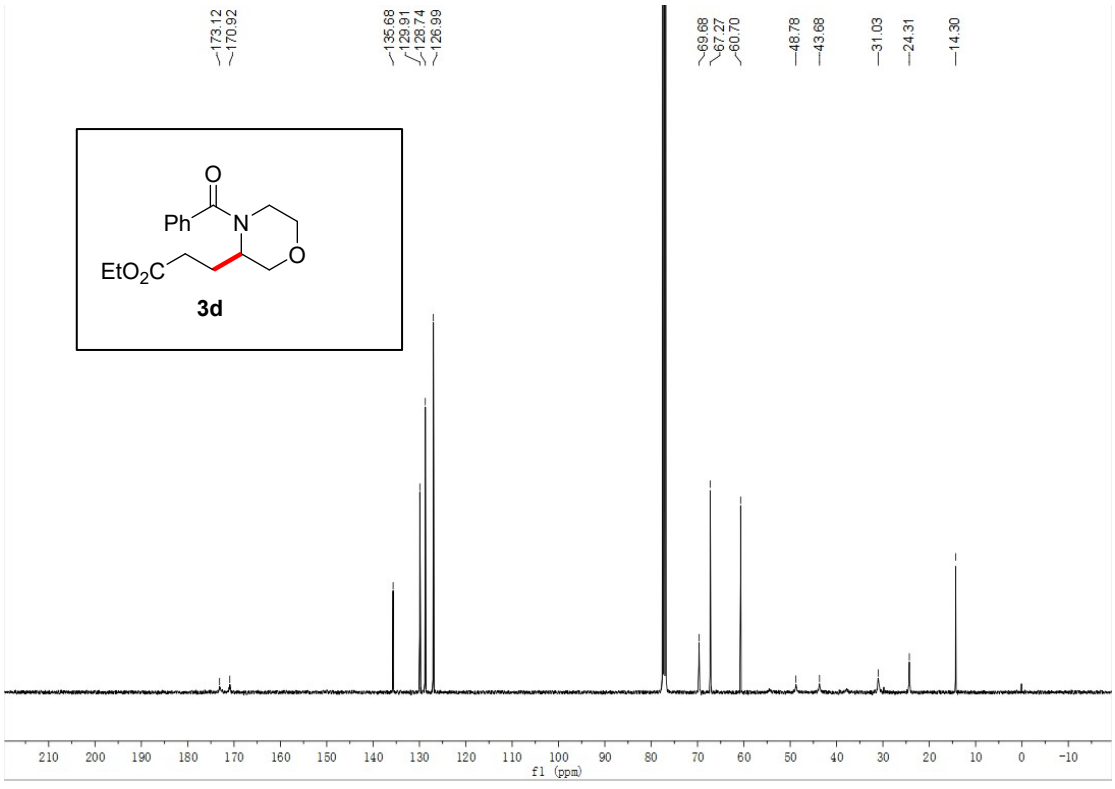

173.76
169.60
138.94
129.37
128.41
126.44
64.56
60.60
52.18
38.53
32.77
30.31
24.54
23.26
14.37
Me
N
O
Ph
CO2Et
3b
f1 (ppm)

3c, $^{1}H+^{13}C$

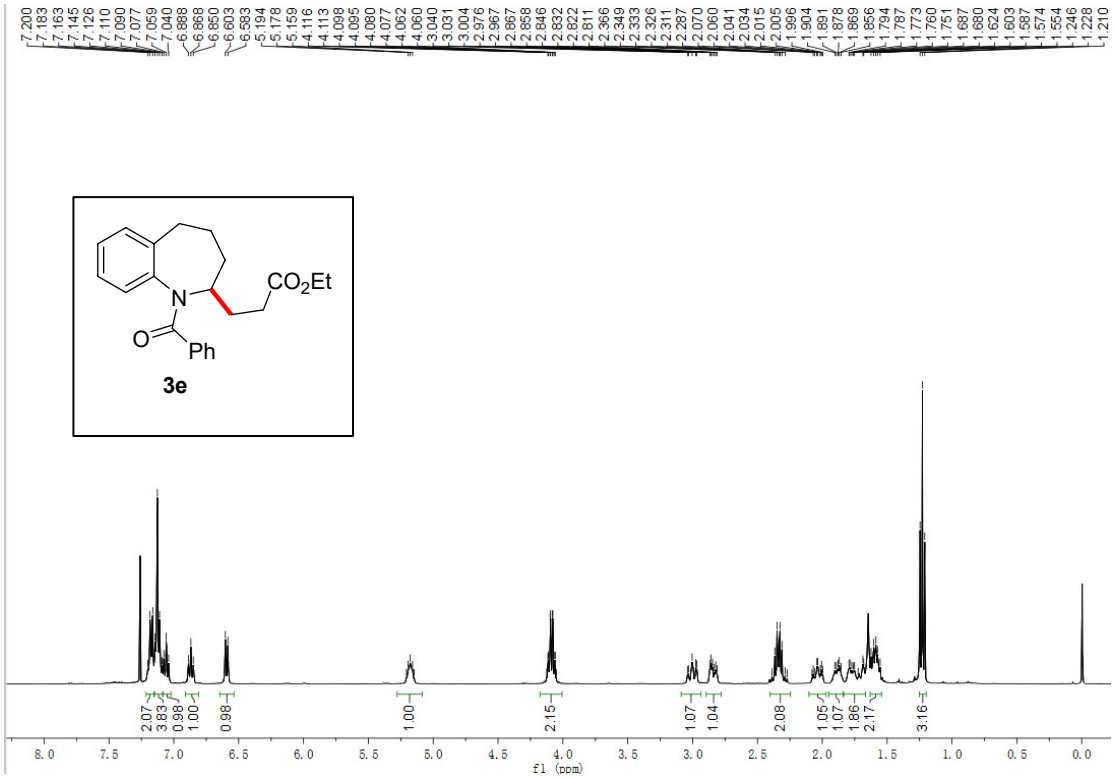

7.55
7.53
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.33
7.33
7.31
7.31
4.60
4.58
4.56
4.54
4.53
4.24
4.06
4.05
3.95
2.43
2.22
2.09
1.91
1.21
1.19
1.18
1.16
N
O
CO2Et
Ph
3c
2.00
2.97
1.00
0.94
2.03
0.84
2.34
0.96
0.99
1.17
3.16
f1 (ppm)
173.55
171.63
136.22
131.09
128.46
128.00
61.20
60.58
51.04
30.91
30.76
22.39
14.33
N
O
CO2Et
Ph
3c
f1 (ppm)

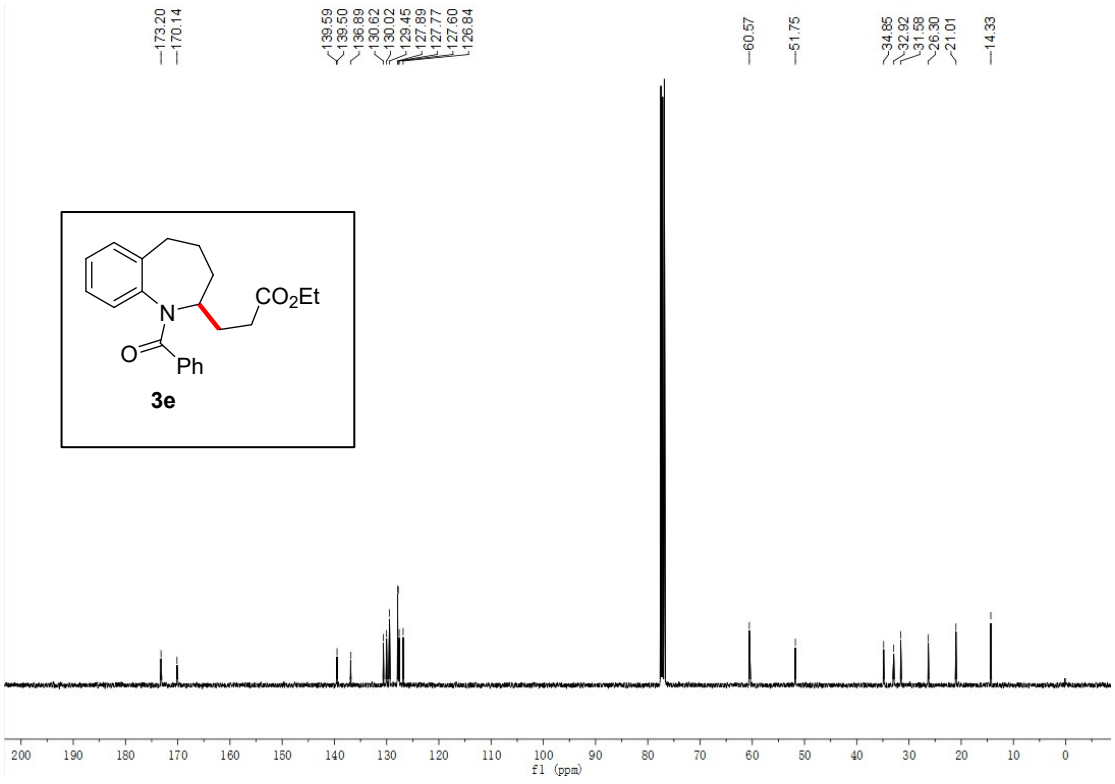
3d, $^{1}H+^{13}C$


7.413
7.407
7.397
7.389
7.372
7.367
7.358
7.347
4.697
4.376
4.297
4.116
3.796
3.672
3.667
3.643
3.425
2.351
2.001
1.244
1.229
Ph
N
O
EtO2C
3d
3.14
2.00
1.01
2.20
2.14
1.18
2.90
3.07
1.03
3.21
f1 (ppm)

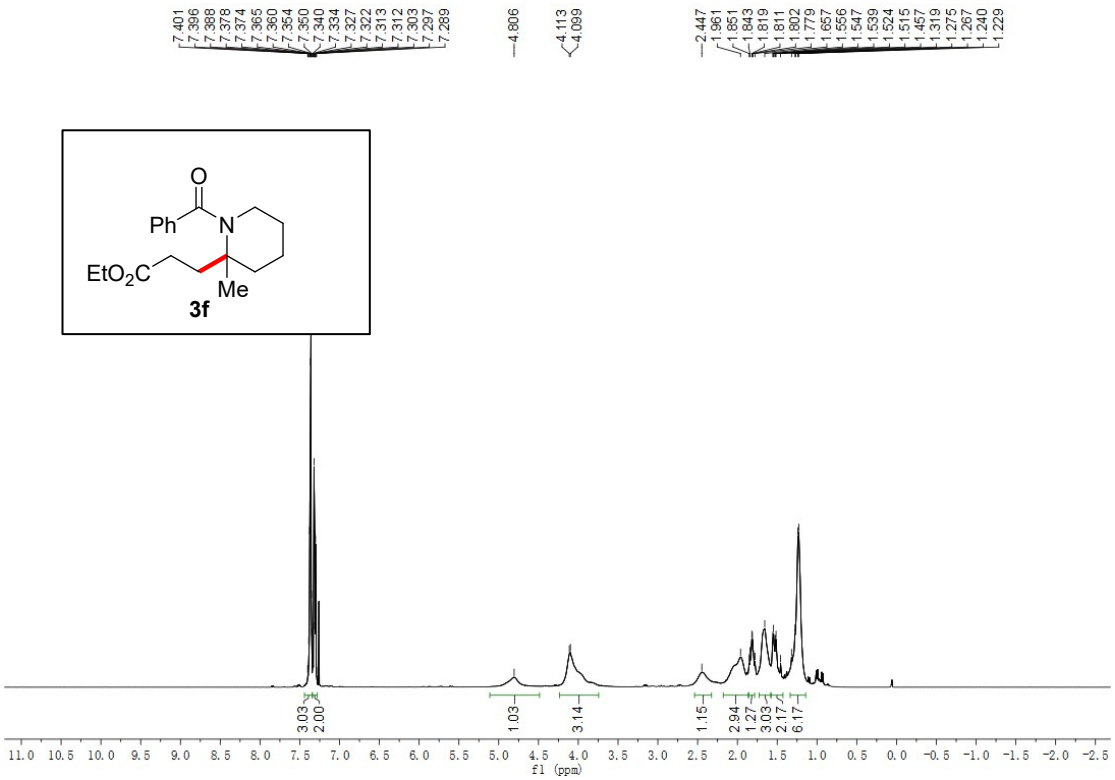

173.12
170.92
135.68
129.91
128.74
126.99
69.68
67.27
60.70
48.78
43.68
31.03
24.31
14.30
Ph
N
O
EtO2C
3d
f1 (ppm)

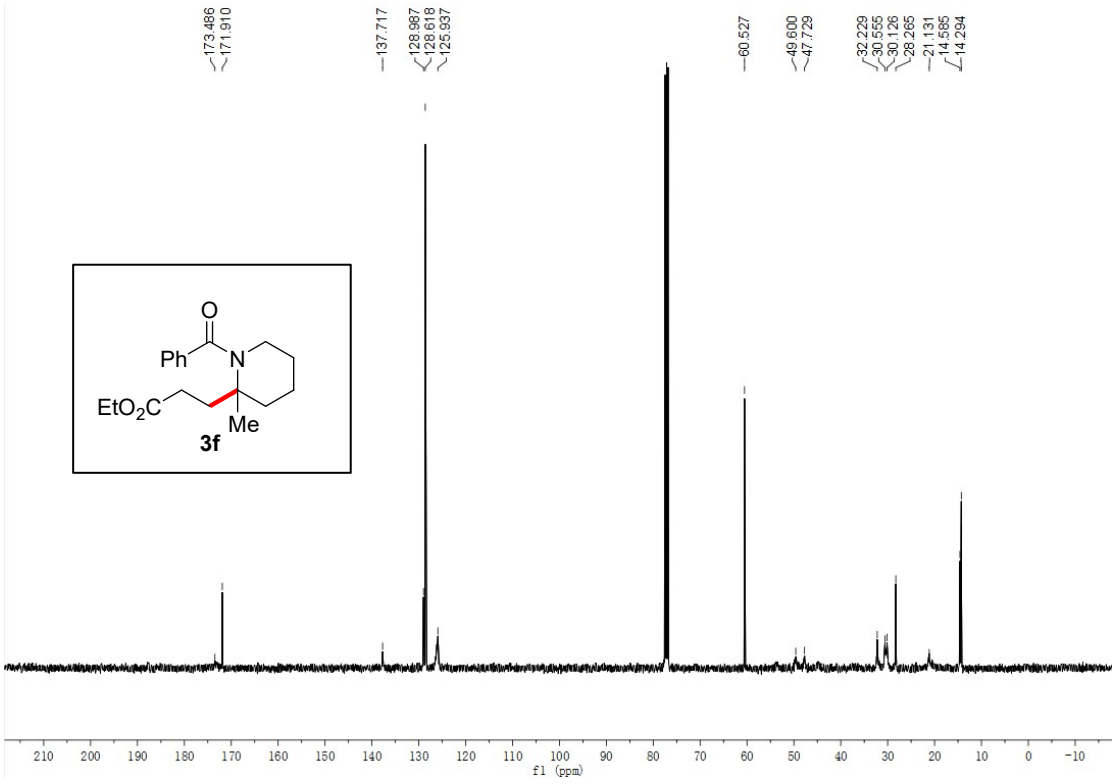
3e, $^{1}H+^{13}C$


7.200
7.183
7.163
7.145
7.126
7.110
7.090
7.077
7.059
7.040
6.888
6.868
6.850
6.603
6.583
5.194
5.178
5.159
4.116
4.113
4.098
4.095
4.080
4.077
4.062
4.060
4.040
3.031
3.004
2.976
2.967
2.867
2.858
2.846
2.832
2.822
2.811
2.366
2.349
2.333
2.326
2.311
2.287
2.070
2.060
2.041
2.034
2.015
2.005
1.996
1.904
1.891
1.878
1.869
1.856
1.794
1.787
1.773
1.760
1.751
1.687
1.680
1.624
1.603
1.587
1.574
1.554
1.246
1.228
1.210
CO2Et
N
O
Ph
3e
2.07
3.83
0.98
1.00
0.98
1.00
2.15
1.07
1.04
2.08
1.05
1.07
1.86
2.17
3.16
f1 (ppm)

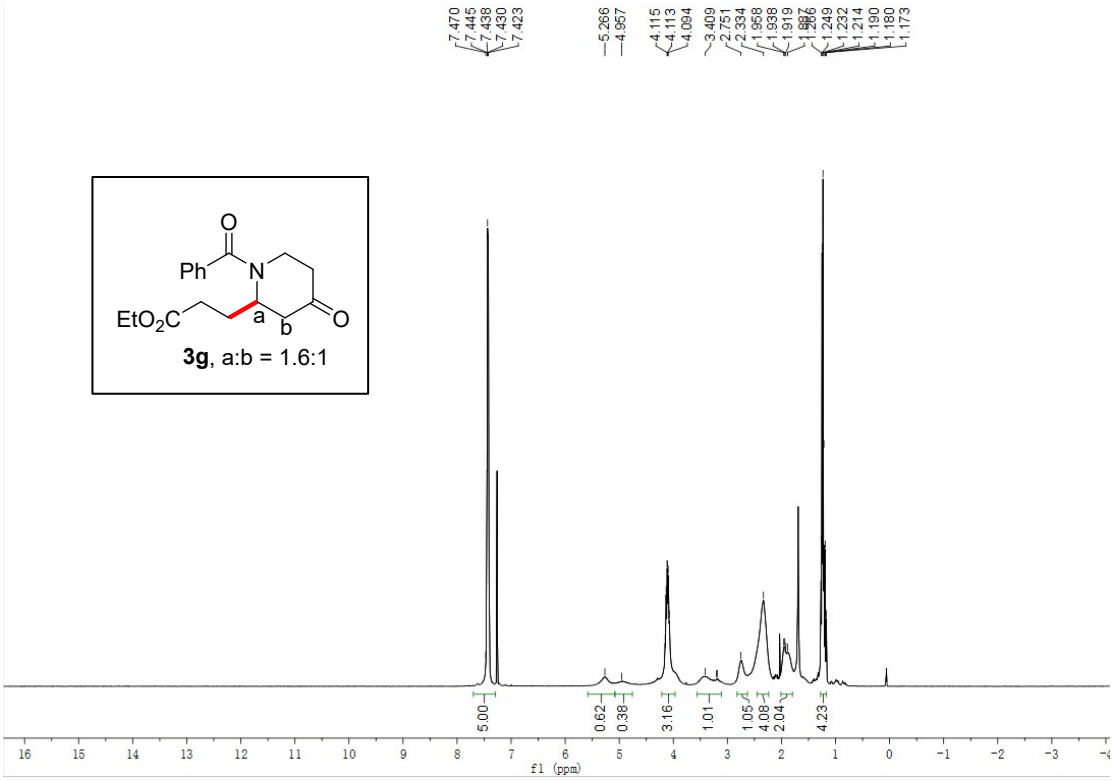

173.20
170.14
139.59
139.50
136.89
130.62
130.02
129.45
127.89
127.77
127.60
126.84
60.57
51.75
34.85
32.92
31.58
26.30
21.01
14.33
CO2Et
N
O
Ph
3e
f1 (ppm)

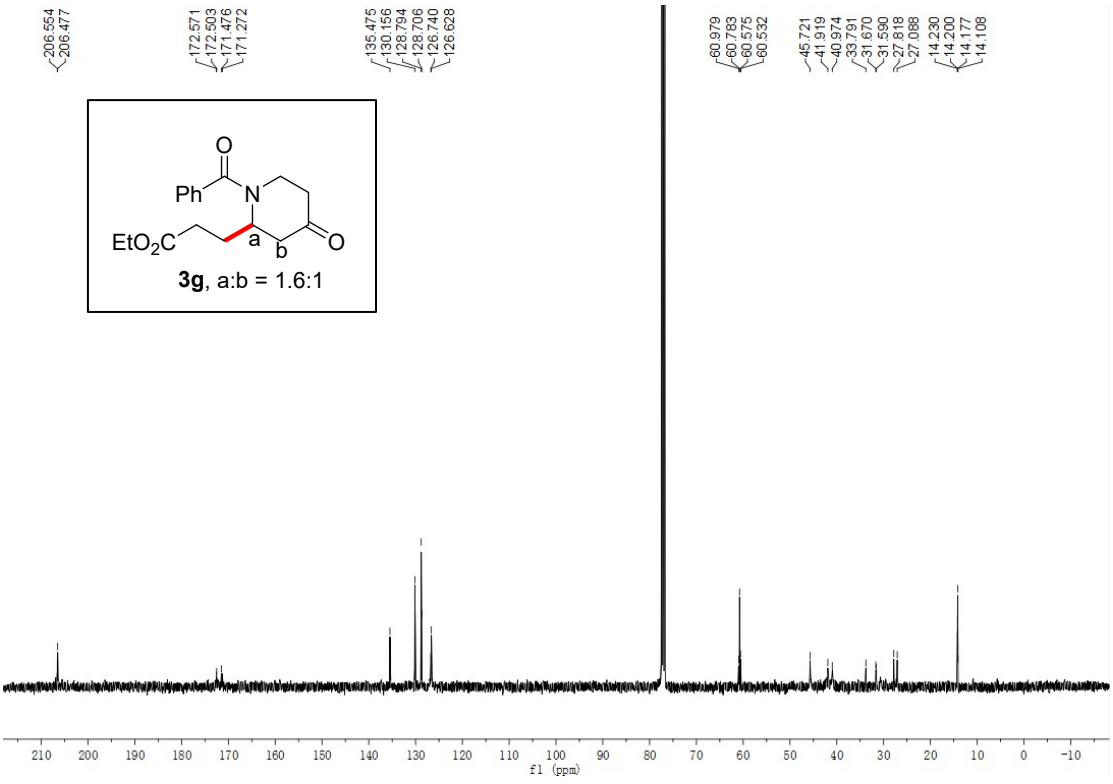
3f, $^{1}H+^{13}C$


7.401
7.396
7.388
7.378
7.374
7.365
7.360
7.354
7.350
7.340
7.334
7.327
7.322
7.313
7.312
7.303
7.297
7.289
4.806
4.113
4.099
2.447
1.961
1.851
1.843
1.819
1.811
1.802
1.779
1.657
1.556
1.547
1.539
1.524
1.515
1.457
1.319
1.275
1.267
1.240
1.229
O
Ph
N
EtO2C
Me
3f
3.03
2.00
1.03
3.14
1.15
2.94
1.27
3.03
2.17
6.17
f1 (ppm)

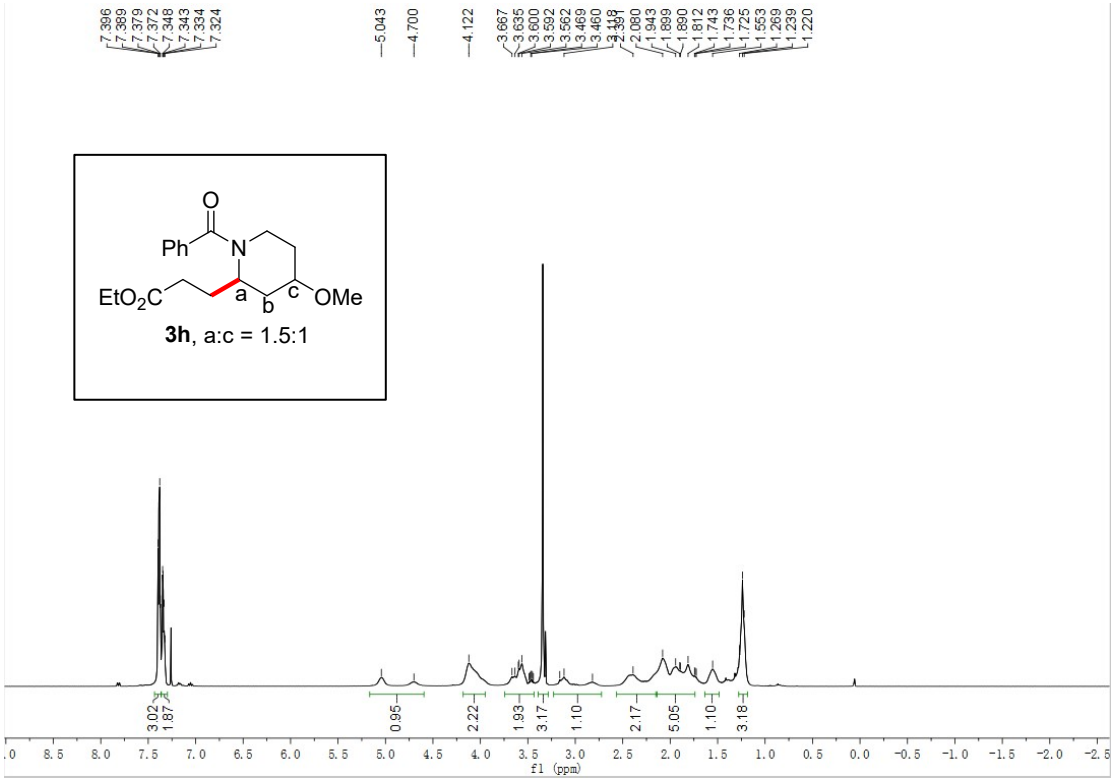

173.486
171.910
137.717
128.987
128.618
125.937
60.527
49.600
47.729
32.229
30.555
30.126
28.265
21.131
14.585
14.294
O
Ph
N
EtO2C
Me
3f
f1 (ppm)

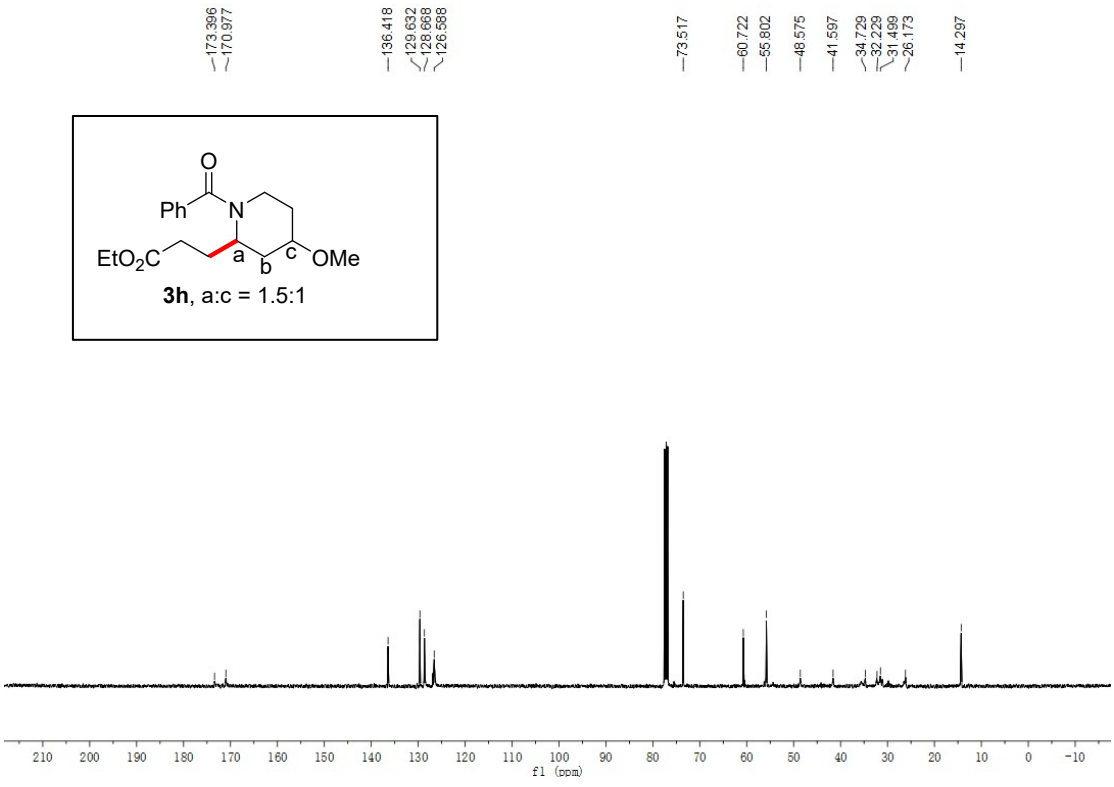
3g, $^{1}H+^{13}C$


7.470
7.445
7.438
7.430
7.423
5.266
4.957
4.115
4.113
4.094
3.409
2.751
2.334
1.958
1.938
1.919
1.249
1.232
1.214
1.190
1.180
1.173
Ph
N
O
EtO2C
a
b
O
3g, a:b = 1.6:1
5.00
0.62
0.38
3.16
1.01
1.05
4.08
2.04
4.23
f1 (ppm)

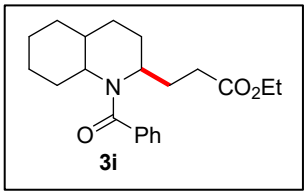

206.554
206.477
172.571
172.503
171.476
171.272
135.475
130.156
128.794
128.706
126.740
126.628
60.979
60.783
60.575
60.532
45.721
41.919
40.974
33.791
31.670
31.590
27.818
27.088
14.230
14.200
14.177
14.108
Ph
N
O
EtO2C
a
b
O
3g, a:b = 1.6:1
f1 (ppm)

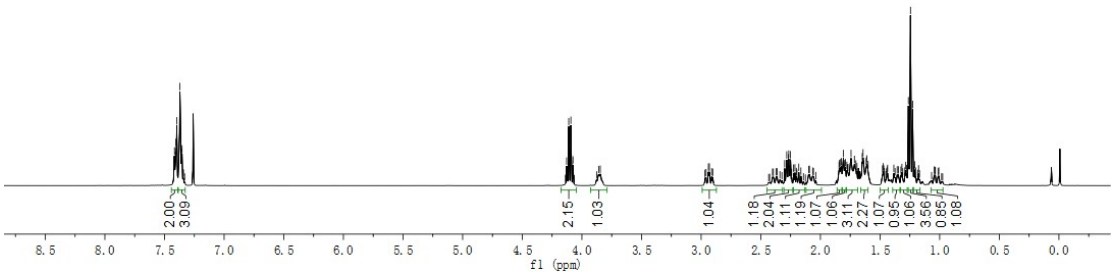
3h, $^{1}H+^{13}C$

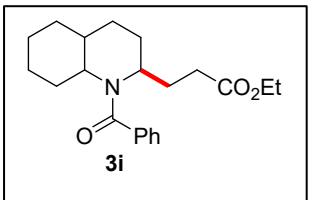

7.396
7.389
7.379
7.372
7.348
7.343
7.334
7.324
5.043
4.700
4.122
3.667
3.635
3.600
3.592
3.562
3.469
3.460
2.391
2.080
1.943
1.899
1.890
1.812
1.743
1.736
1.725
1.553
1.269
1.239
1.220
O
Ph
N
EtO2C
a
b
c
OMe
3h, a:c = 1.5:1
3.02
1.87
0.95
2.22
1.93
3.17
1.10
2.17
5.05
1.10
3.18
f1 (ppm)

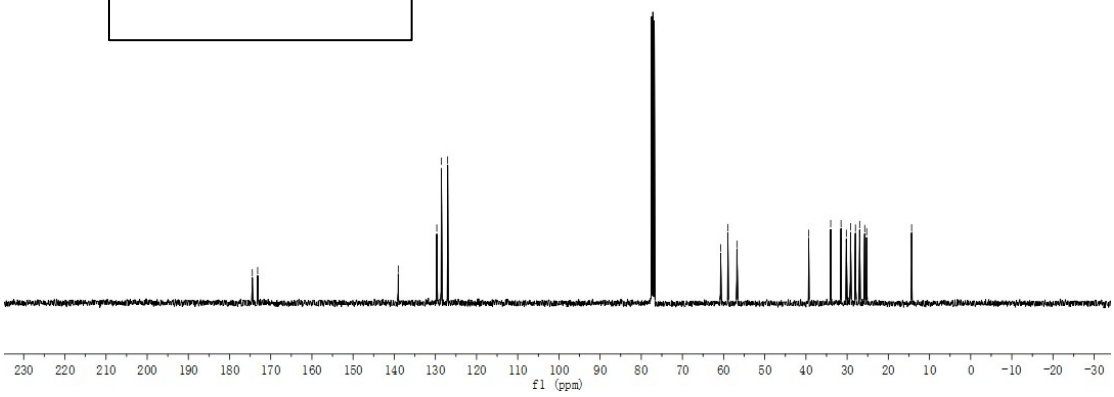

173.396
170.977
136.418
129.632
128.668
126.588
73.517
60.722
55.802
48.575
41.597
34.729
32.229
31.499
26.173
14.297
O
Ph
N
EtO2C
a
b
c
OMe
3h, a:c = 1.5:1
f1 (ppm)

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

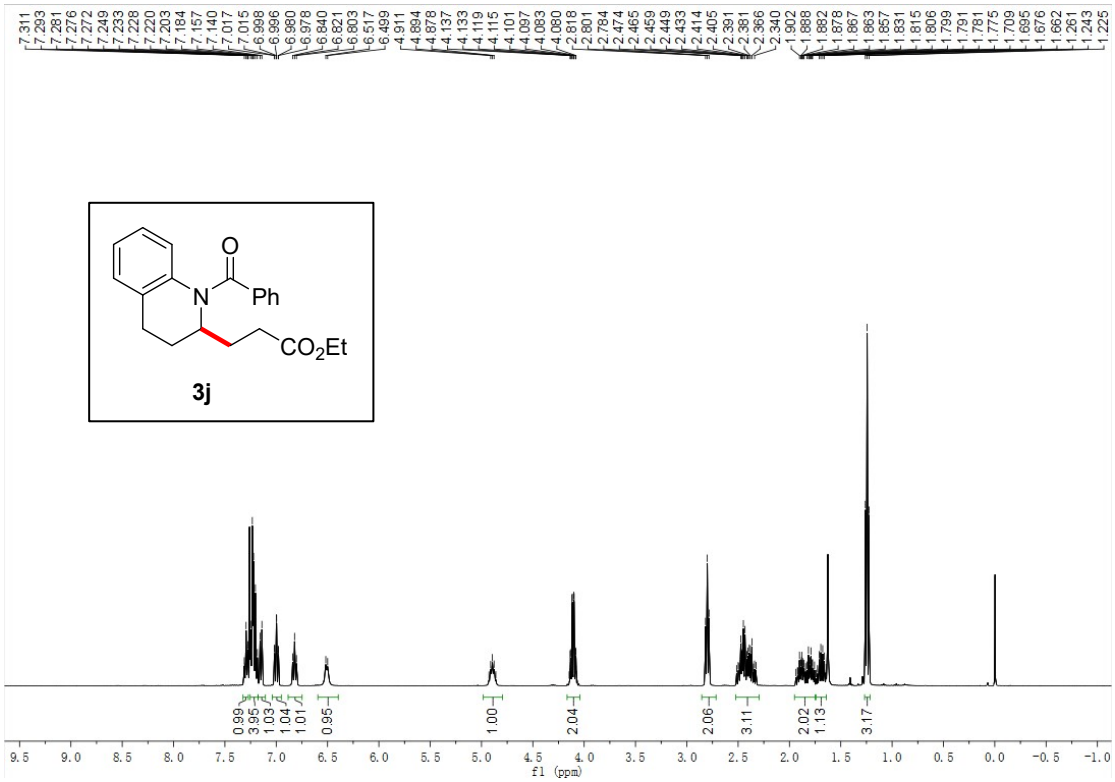

N
CO2Et
O
Ph
3i

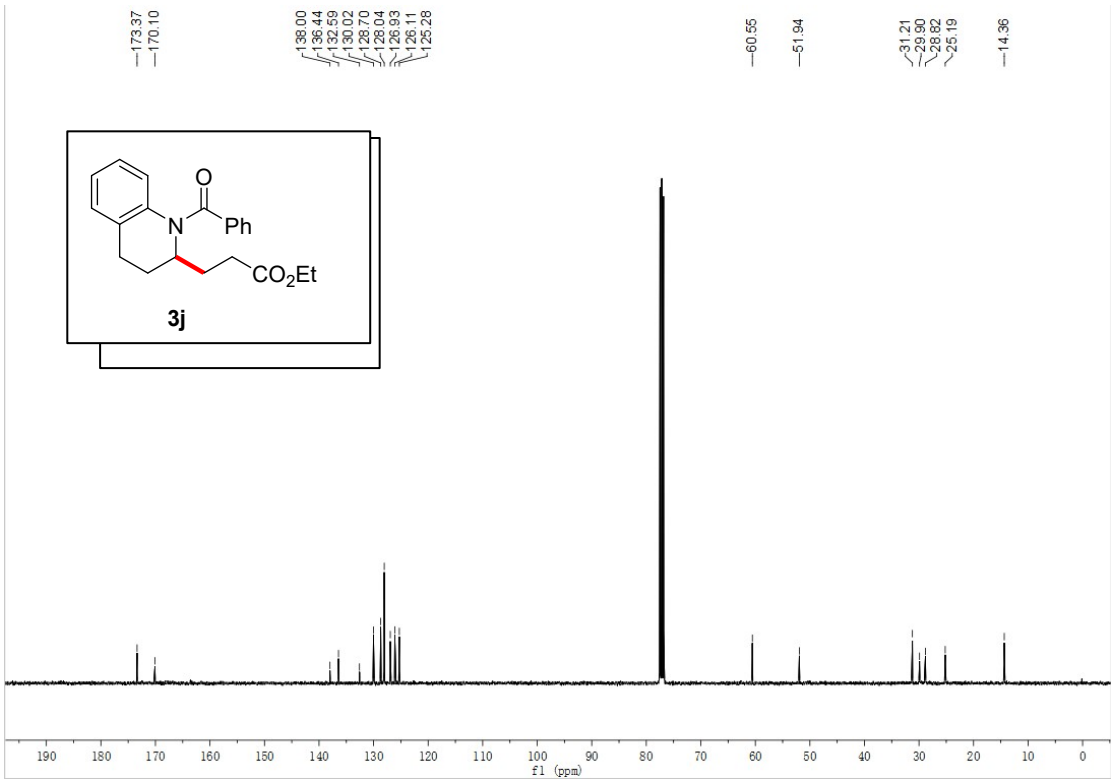

2.00
3.09
2.15
1.03
1.04
1.18
2.04
1.11
1.19
1.07
1.06
3.11
2.27
1.07
0.95
1.06
3.56
0.85
1.08
f1 (ppm)


N
CO2Et
O
Ph
3i

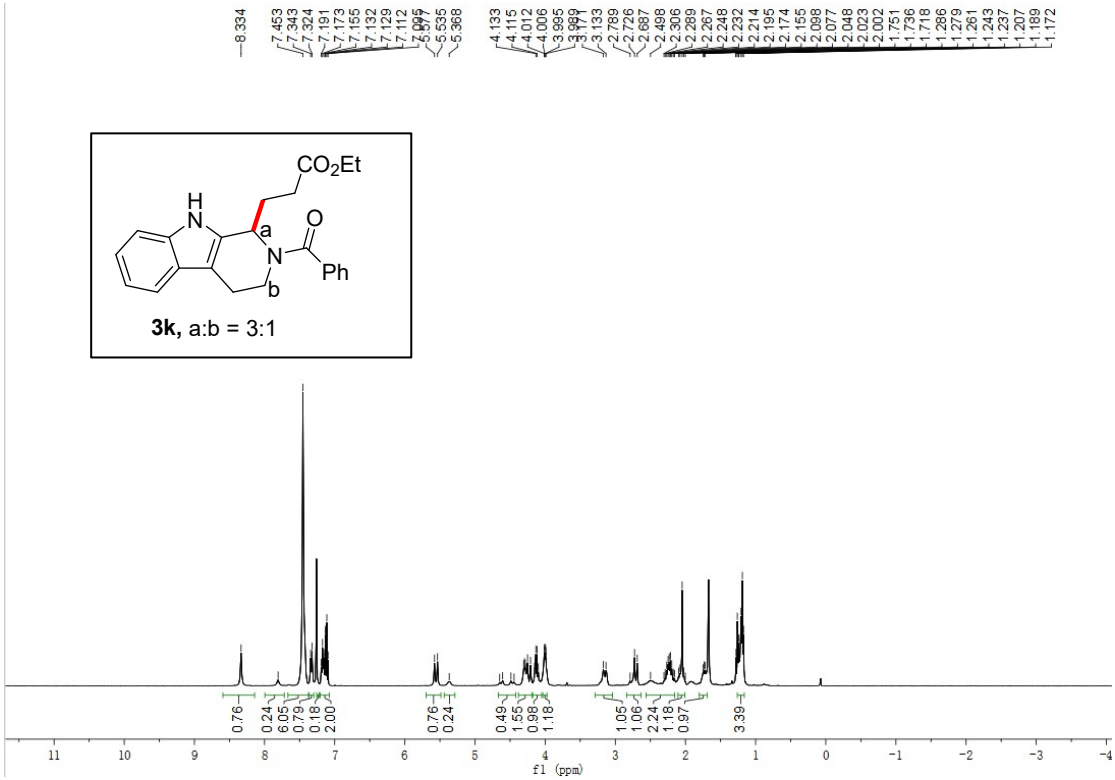

f1 (ppm)

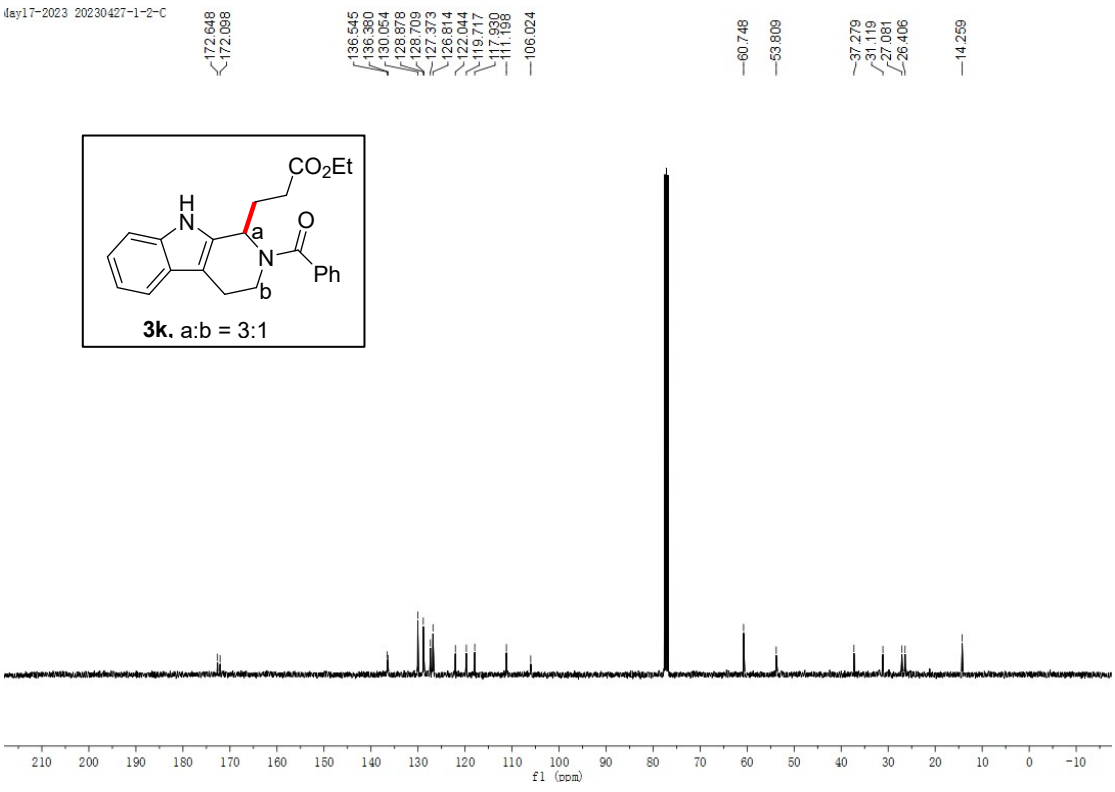
3j, $^{1}H+^{13}C$


7.311
7.293
7.281
7.276
7.272
7.249
7.233
7.228
7.220
7.203
7.184
7.157
7.140
7.017
7.015
6.998
6.996
6.980
6.978
6.840
6.821
6.803
6.517
6.499
4.911
4.894
4.878
4.137
4.133
4.119
4.115
4.101
4.097
4.083
4.080
2.818
2.801
2.784
2.474
2.465
2.459
2.449
2.433
2.414
2.405
2.391
2.381
2.366
2.340
1.902
1.888
1.882
1.878
1.867
1.863
1.857
1.831
1.815
1.806
1.799
1.791
1.781
1.775
1.709
1.695
1.676
1.662
1.261
1.243
1.225
O
N
Ph
CO2Et
3j
0.99
3.95
1.03
1.04
1.01
0.95
1.00
2.04
2.06
3.11
2.02
1.13
3.17
f1 (ppm)

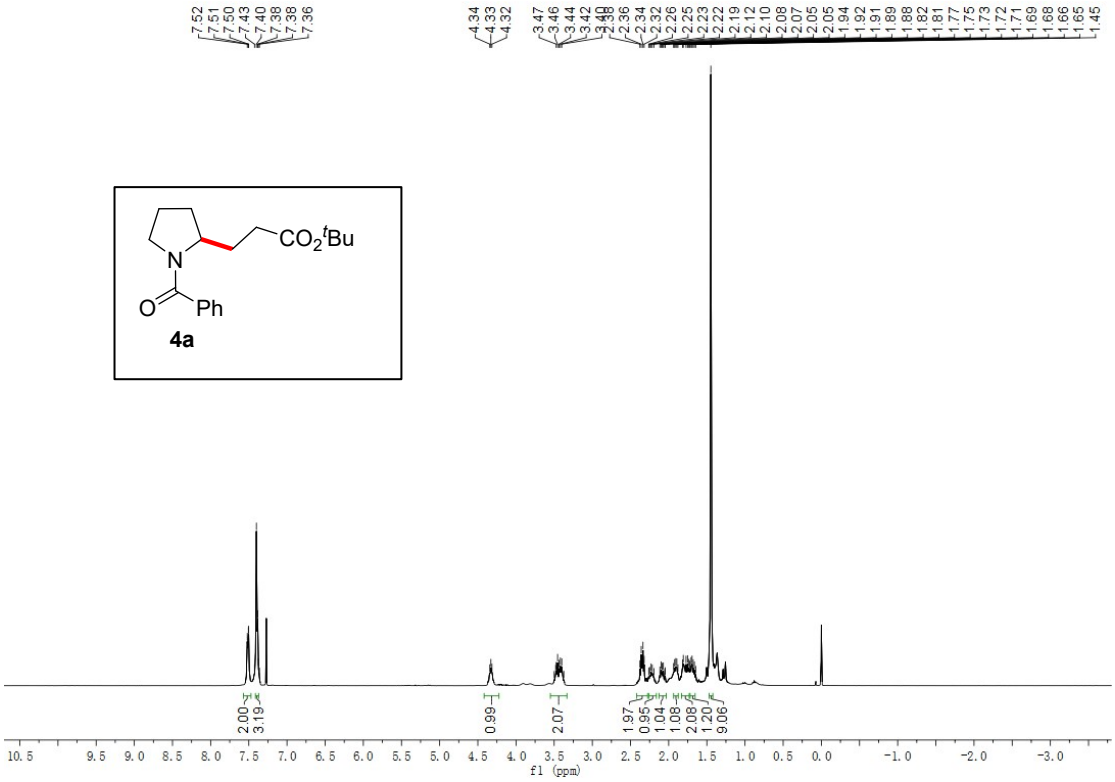

173.37
170.10
138.00
136.44
132.59
130.02
128.70
128.04
126.93
126.11
125.28
60.55
51.94
31.21
29.90
28.82
25.19
14.36
O
N
Ph
CO2Et
3j
f1 (ppm)

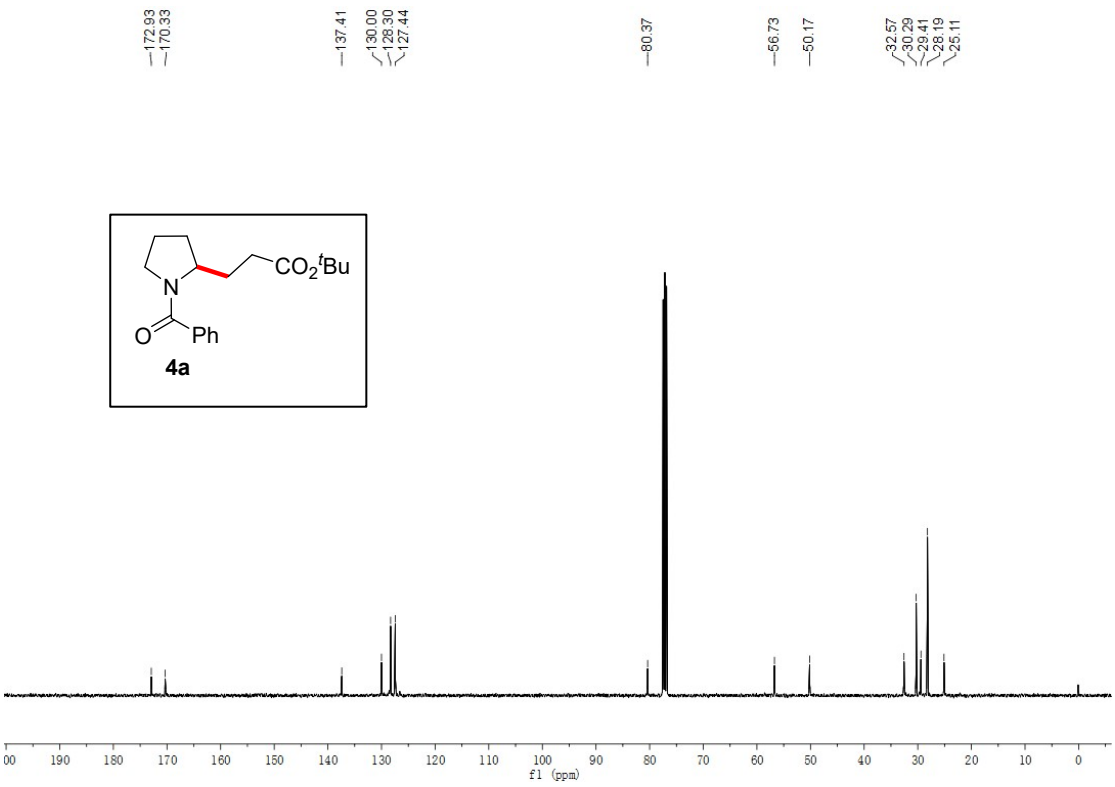
3k, $^{1}H+^{13}C$





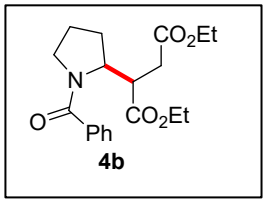
4a, $^{1}H+^{13}C$

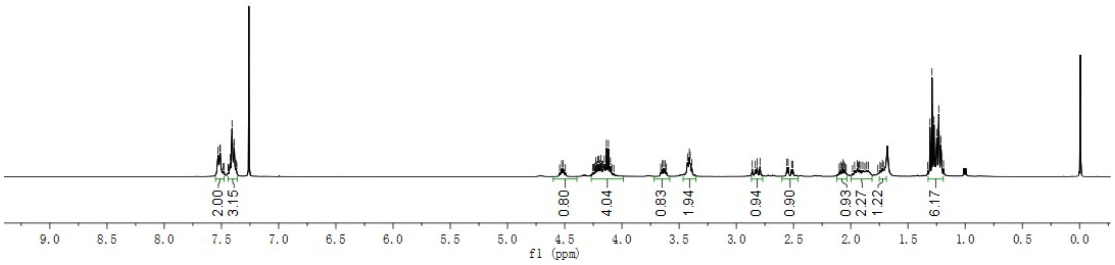

7.52
7.51
7.50
7.43
7.40
7.38
7.38
7.36
4.34
4.33
4.32
3.47
3.46
3.44
3.42
3.40
2.38
2.36
2.34
2.32
2.26
2.25
2.23
2.22
2.19
2.12
2.10
2.08
2.07
2.05
2.05
1.94
1.92
1.91
1.89
1.88
1.82
1.81
1.77
1.75
1.73
1.72
1.71
1.69
1.68
1.66
1.65
1.45
CO2tBu
N
O
Ph
4a
2.00
3.19
0.99
2.07
1.97
0.95
1.04
1.08
2.08
1.20
9.06
f1 (ppm)


172.93
170.33
137.41
130.00
128.30
127.44
80.37
56.73
50.17
32.57
30.29
29.41
28.19
25.11
CO2tBu
N
O
Ph
4a
f1 (ppm)

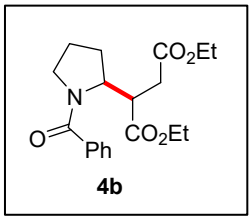
4b, $^{1}H+^{13}C$


7.529
7.514
7.510
7.484
7.479
7.423
7.413
7.407
7.388
7.373
7.366
4.527
4.513
4.238
4.229
4.220
4.211
4.202
4.193
4.184
4.175
4.166
4.154
4.136
4.118
4.100
3.649
3.636
3.623
3.426
3.411
3.403
3.389
2.861
2.835
2.819
2.793
2.558
2.547
2.516
2.505
2.088
2.077
2.069
2.057
2.049
1.966
1.944
1.935
1.926
1.913
1.894
1.877
1.861
1.847
1.744
1.734
1.723
1.714
1.327
1.308
1.290
1.278
1.272
1.262
1.249
1.231
1.213
1.206
1.189


CO2Et
N
O
Ph
CO2Et
4b

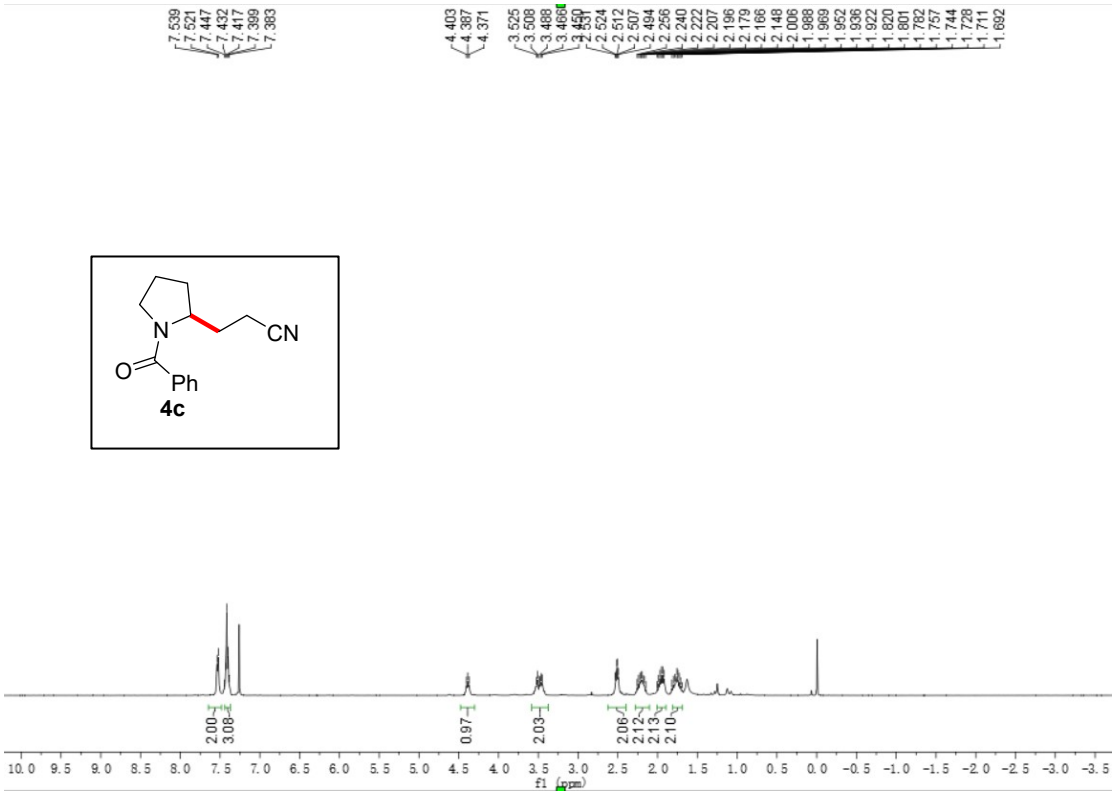

2.00
3.15
0.80
4.04
0.83
1.94
0.94
0.90
0.93
2.27
1.22
6.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

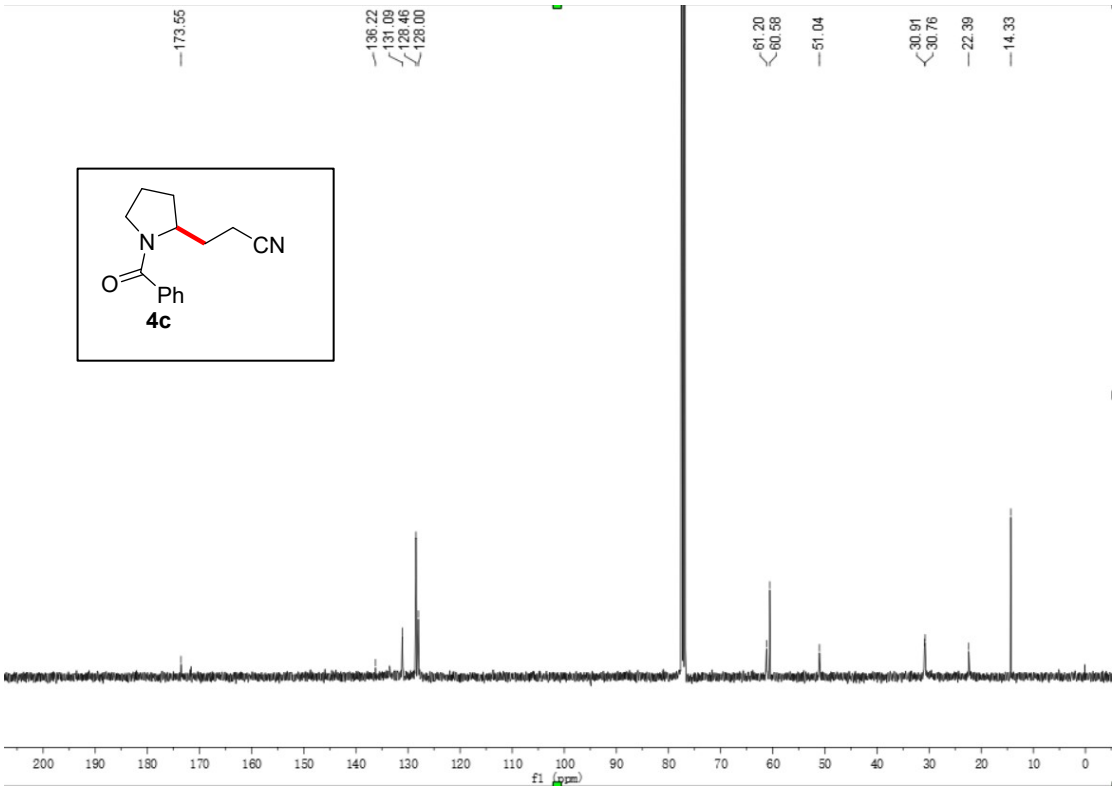

173.18
171.78
170.54
136.96
130.34
128.36
127.56
61.04
60.86
58.25
50.75
43.14
34.00
27.39
25.09
14.41
14.27


CO2Et
N
O
Ph
CO2Et
4b

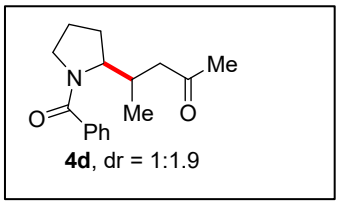
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4c, $^{1}H+^{13}C$

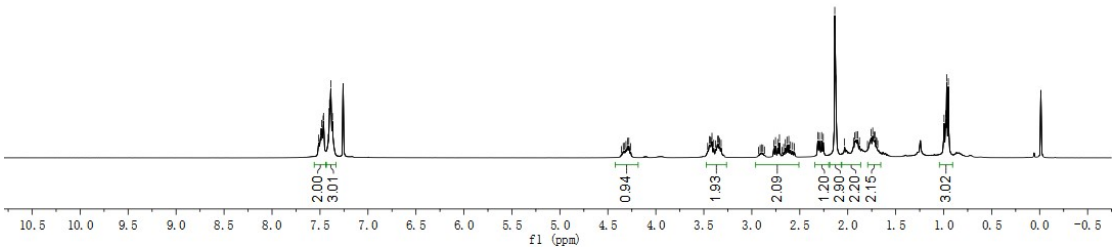

7.539
7.521
7.447
7.432
7.417
7.399
7.383
4.403
4.387
4.371
3.525
3.508
3.488
3.466
2.524
2.512
2.507
2.494
2.256
2.240
2.222
2.207
2.196
2.179
2.166
2.148
2.006
1.988
1.969
1.952
1.936
1.922
1.820
1.801
1.782
1.757
1.744
1.728
1.711
1.692
N
CN
O
Ph
4c
2.00
3.08
0.97
2.03
2.06
2.12
2.13
2.10
f1 (ppm)

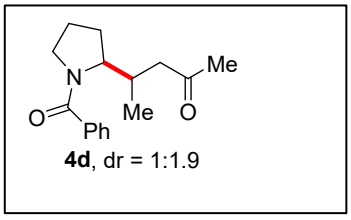

173.55
136.22
131.09
128.46
128.00
61.20
60.58
51.04
30.91
30.76
22.39
14.33
N
CN
O
Ph
4c
f1 (ppm)

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

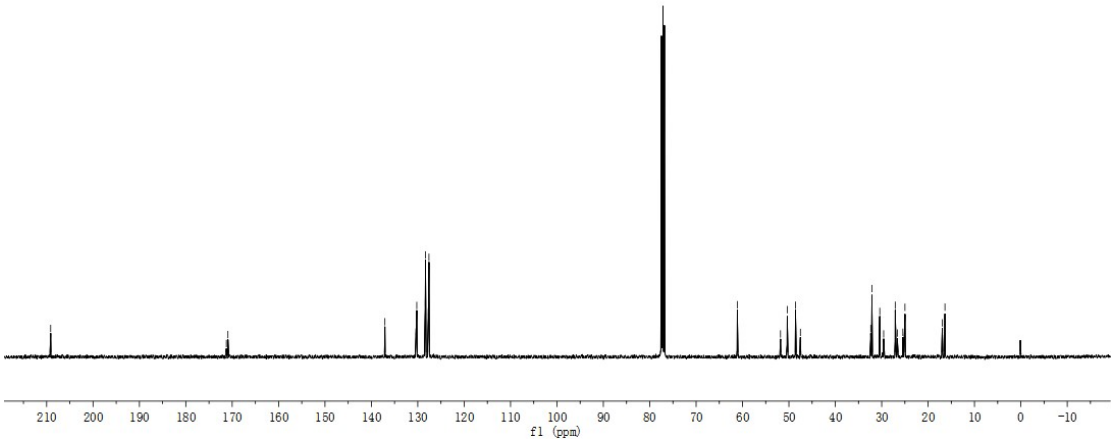


4d, dr = 1:1.9

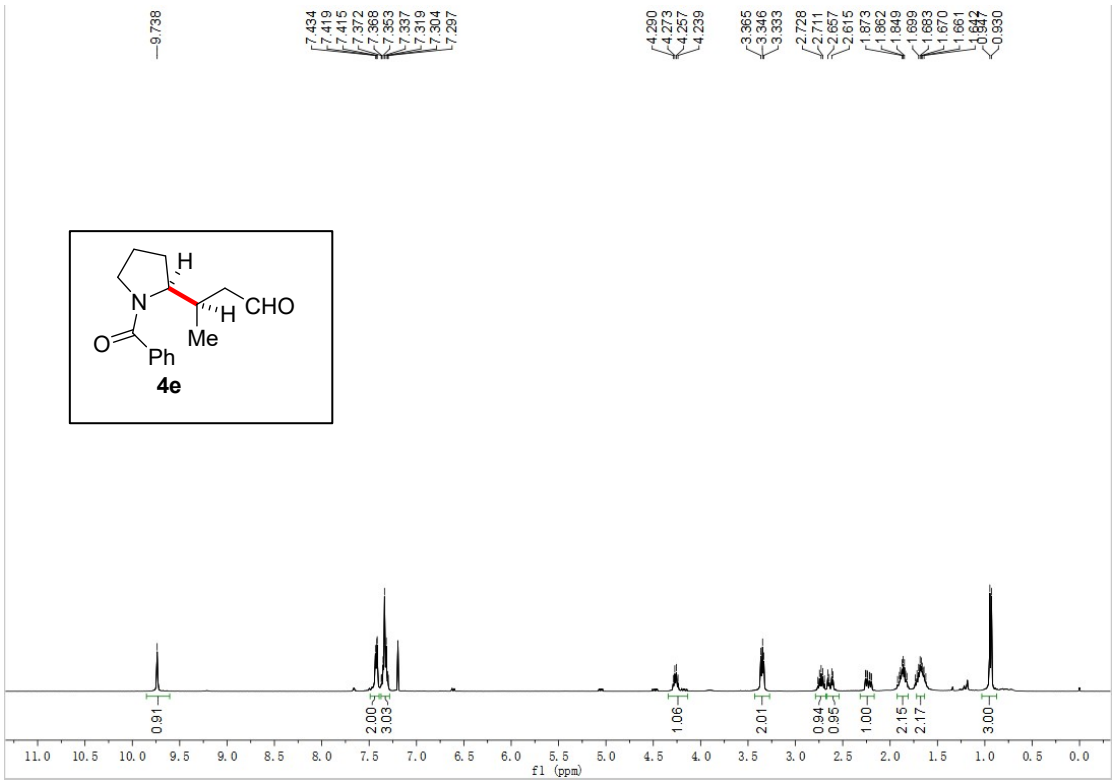


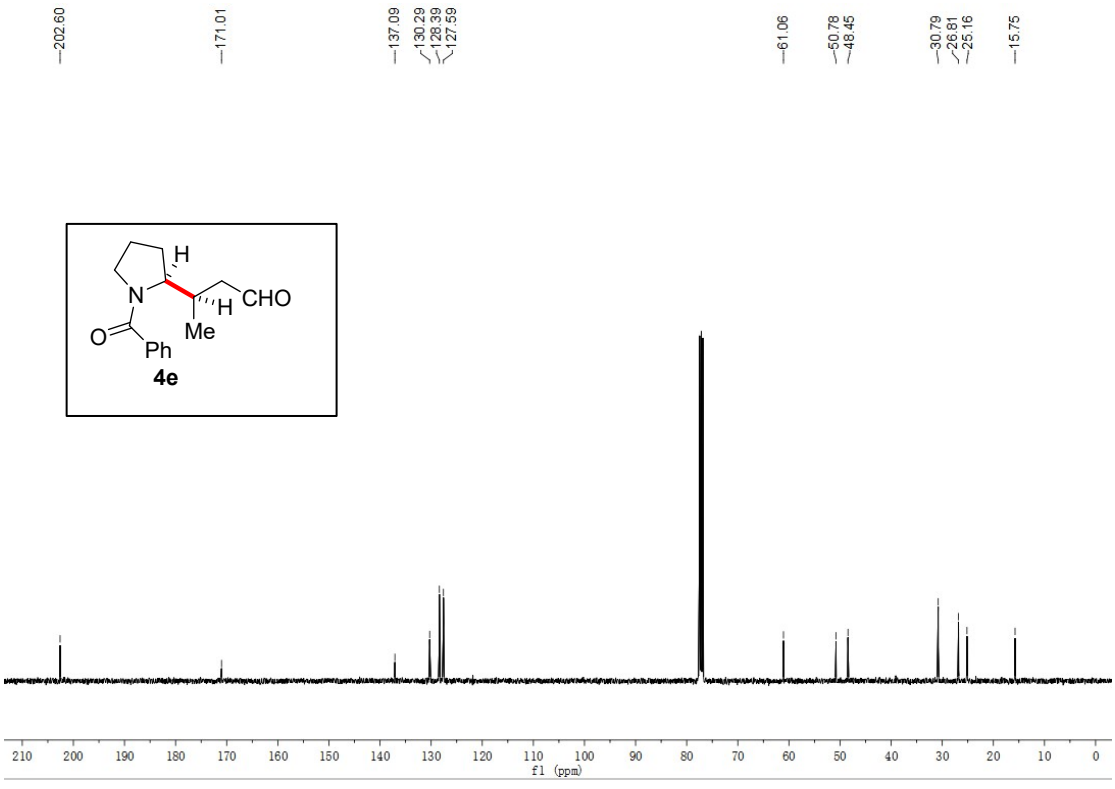


4d, dr = 1:1.9

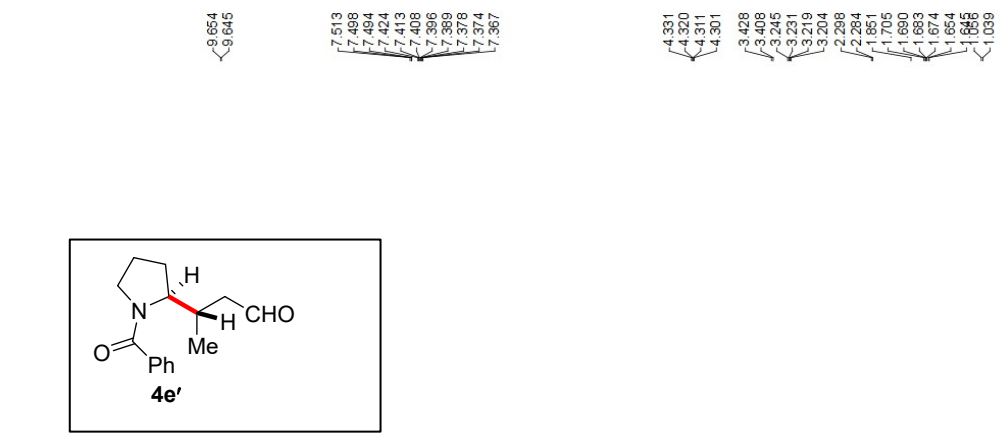


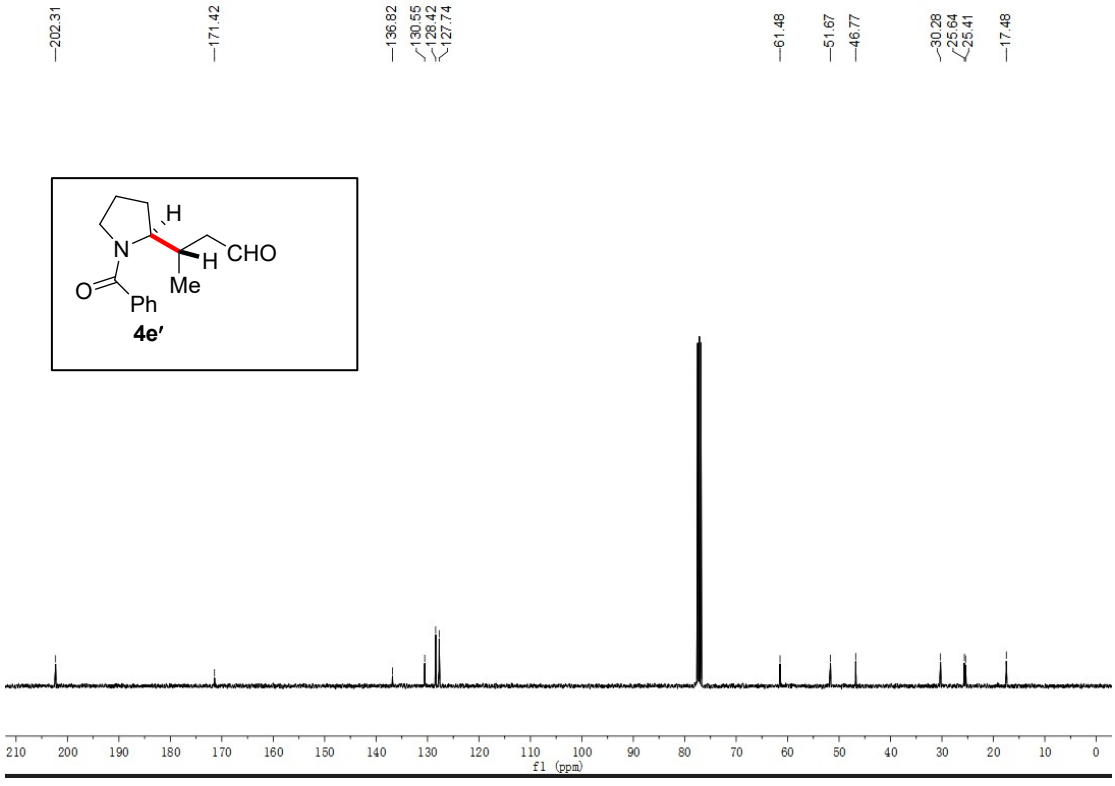
4e, $^{1}H+^{13}C$


9.738
7.434
7.419
7.415
7.372
7.368
7.353
7.337
7.319
7.304
7.297
4.290
4.273
4.257
4.239
3.365
3.346
3.333
2.728
2.711
2.657
2.615
1.873
1.862
1.849
1.699
1.683
1.670
1.661
1.642
0.947
0.930
H
N
O
Ph
Me
H
CHO
4e
0.91
2.00
3.03
1.06
2.01
0.94
0.95
1.00
2.15
2.17
3.00
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)

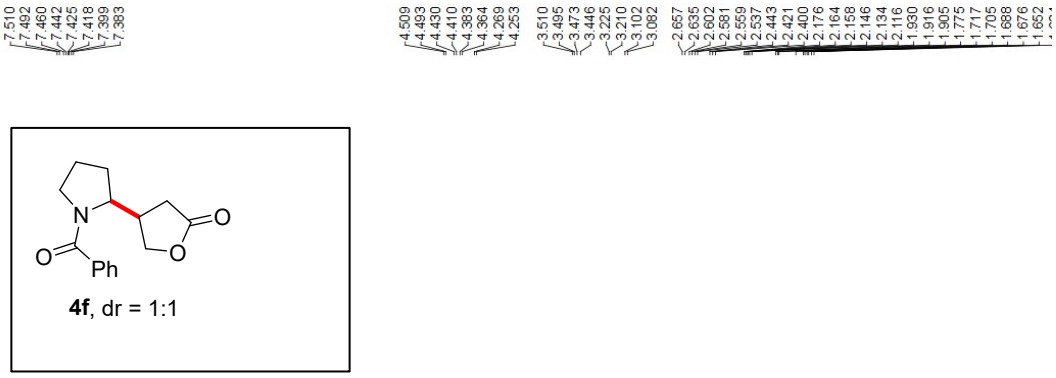

202.60
171.01
137.09
130.29
128.39
127.59
61.06
50.78
48.45
30.79
26.81
25.16
15.75
H
N
O
Ph
Me
H
CHO
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

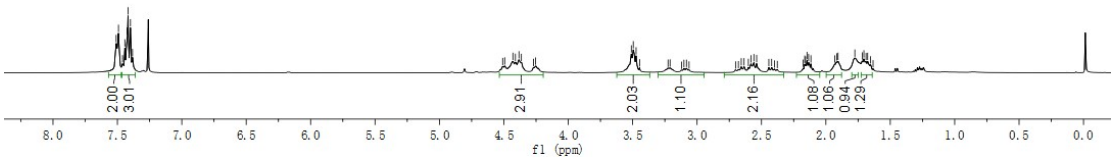
4e′, $^{1}H+^{13}C$

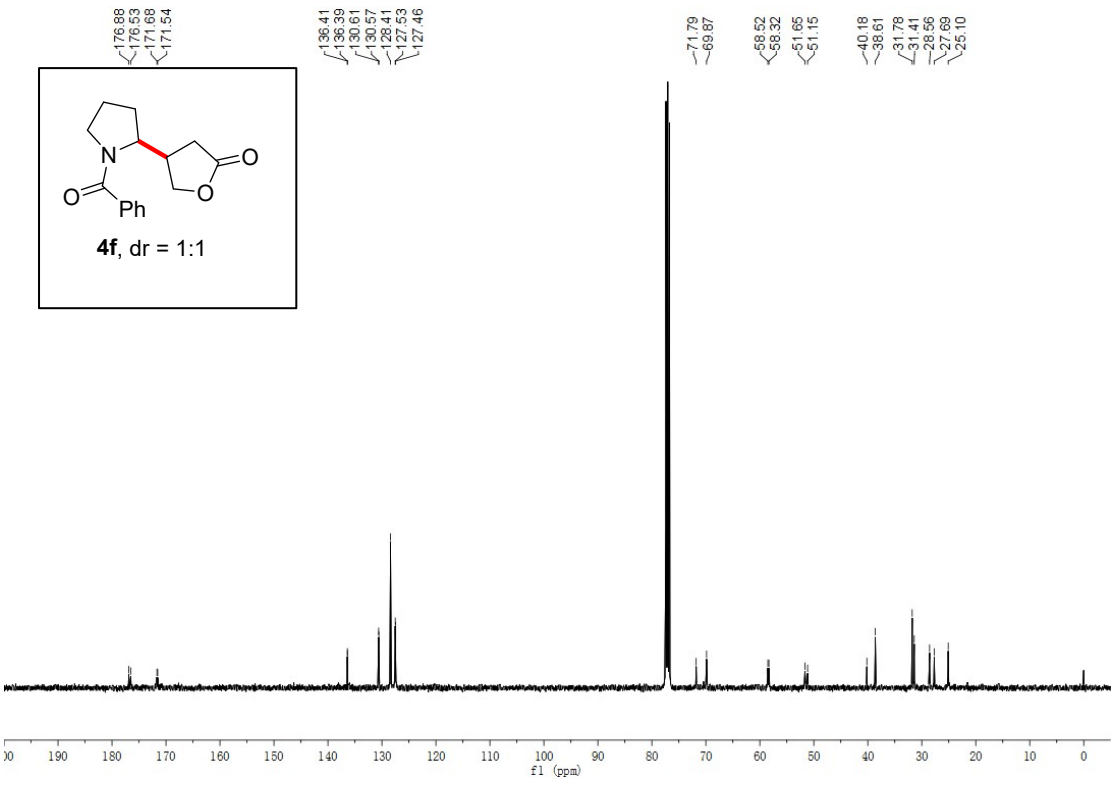

9.654
9.645
7.513
7.498
7.494
7.424
7.413
7.408
7.396
7.389
7.378
7.374
7.367
4.331
4.320
4.311
4.301
3.428
3.408
3.245
3.231
3.219
3.204
2.298
2.284
1.651
1.705
1.690
1.683
1.674
1.654
1.645
1.039
H
N
H
CHO
Me
O
Ph
4e′
1.00
2.00
3.04
1.06
1.05
1.81
1.00
1.07
1.10
1.13
3.23
0.38
2.83
f1 (ppm)


202.31
171.42
136.82
130.55
128.42
127.74
61.48
51.67
46.77
30.28
25.64
25.41
17.48
H
N
H
CHO
Me
O
Ph
4e′
f1 (ppm)

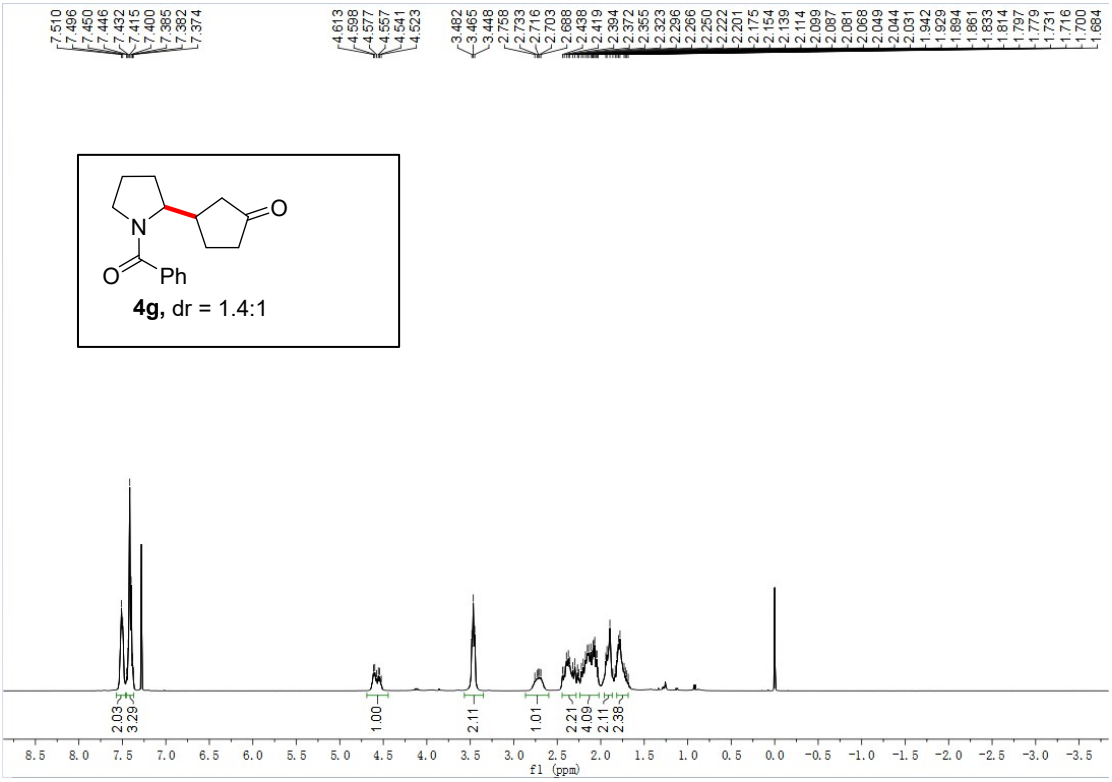
4f, $^{1}H+^{13}C$

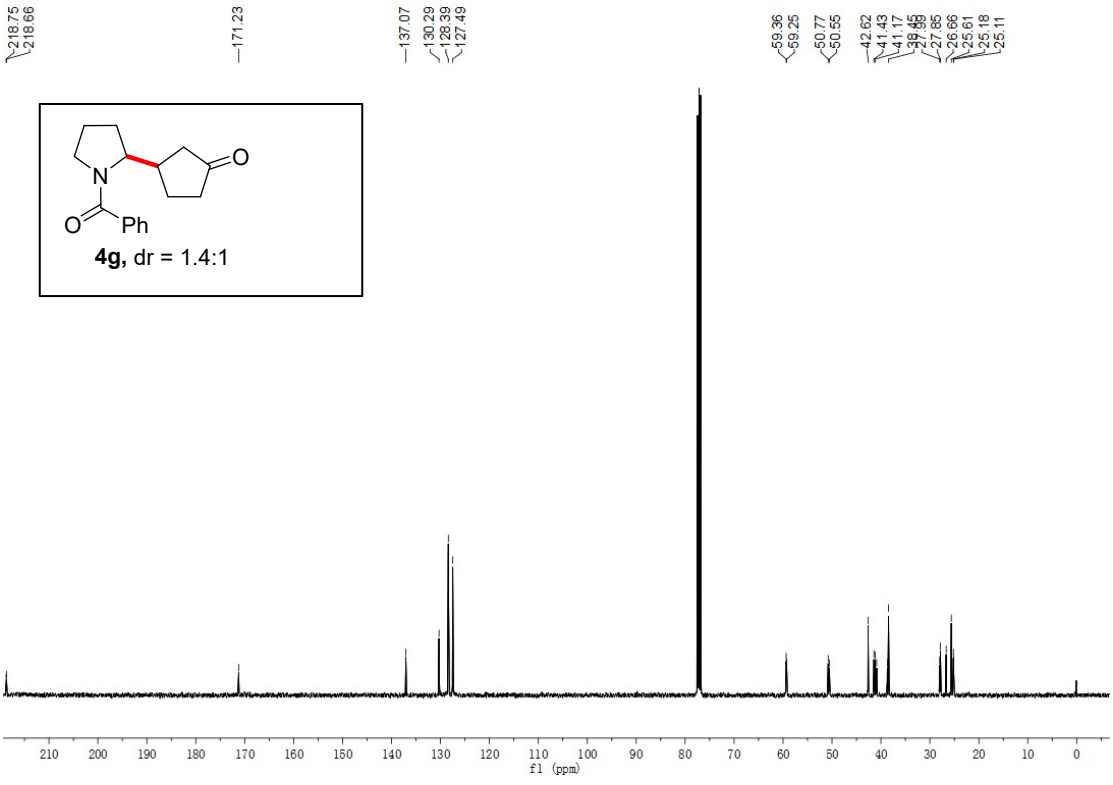

7.510
7.492
7.460
7.442
7.425
7.418
7.399
7.383
4.509
4.493
4.430
4.410
4.383
4.364
4.269
4.253
3.510
3.495
3.473
3.446
3.225
3.210
3.102
3.082
2.657
2.635
2.602
2.581
2.559
2.537
2.443
2.421
2.400
2.176
2.164
2.158
2.146
2.134
2.116
1.930
1.916
1.905
1.775
1.717
1.705
1.688
1.676
1.652
N
O
O
O
Ph
4f, dr = 1:1


2.00
3.01
2.91
2.03
1.10
2.16
1.08
1.06
0.94
1.29
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)

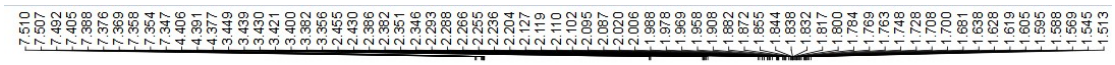

176.88
176.53
171.68
171.54
136.41
136.39
130.61
130.57
128.41
127.53
127.46
71.79
69.87
58.52
58.32
51.65
51.15
40.18
38.61
31.78
31.41
28.56
27.69
25.10
N
O
O
O
Ph
4f, dr = 1:1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

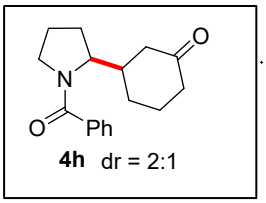
4g, $^{1}H+^{13}C$

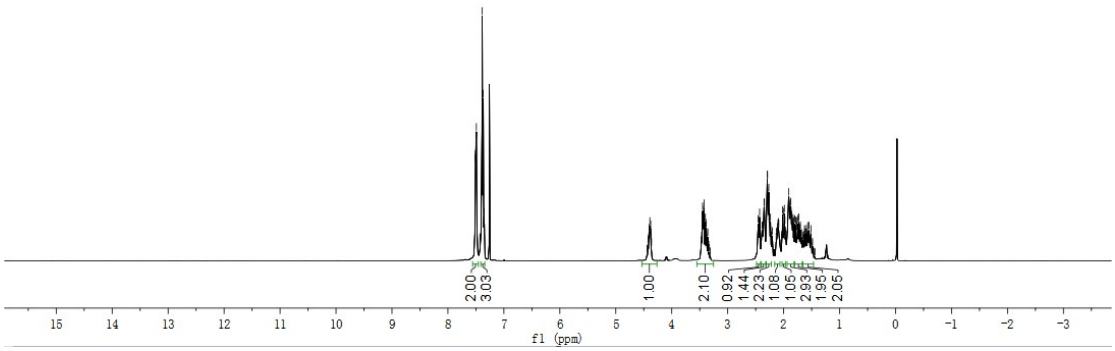

7.510
7.496
7.450
7.446
7.432
7.415
7.400
7.385
7.382
7.374
4.613
4.598
4.577
4.557
4.541
4.523
3.482
3.465
3.448
2.758
2.733
2.716
2.703
2.688
2.438
2.419
2.394
2.372
2.355
2.323
2.296
2.266
2.250
2.222
2.201
2.175
2.154
2.139
2.114
2.099
2.087
2.081
2.068
2.049
2.044
2.031
1.942
1.929
1.894
1.861
1.833
1.814
1.797
1.779
1.731
1.716
1.700
1.684
N
O
O
Ph
4g, dr = 1.4:1
2.03
3.29
1.00
2.11
1.01
2.21
4.09
2.11
2.38
f1 (ppm)

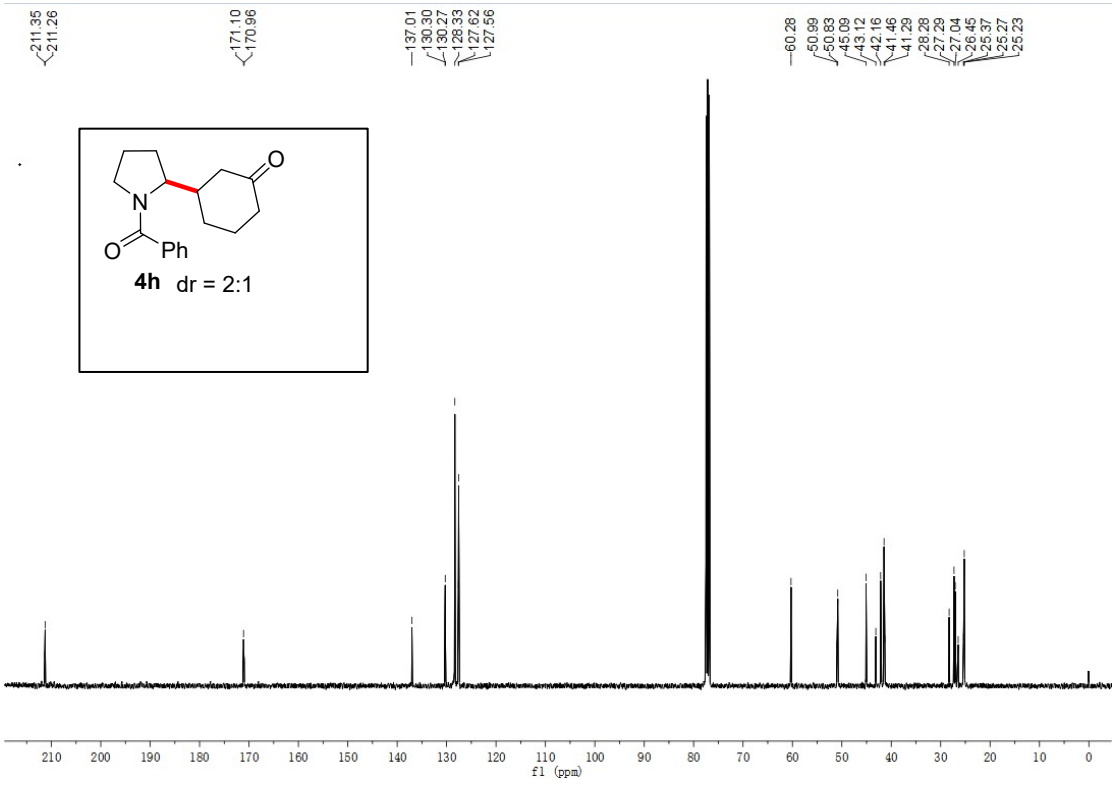

218.75
218.66
171.23
137.07
130.29
128.39
127.49
59.36
59.25
50.77
50.55
42.62
41.43
41.17
27.85
26.66
25.61
25.18
25.11
N
O
O
Ph
4g, dr = 1.4:1
f1 (ppm)

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



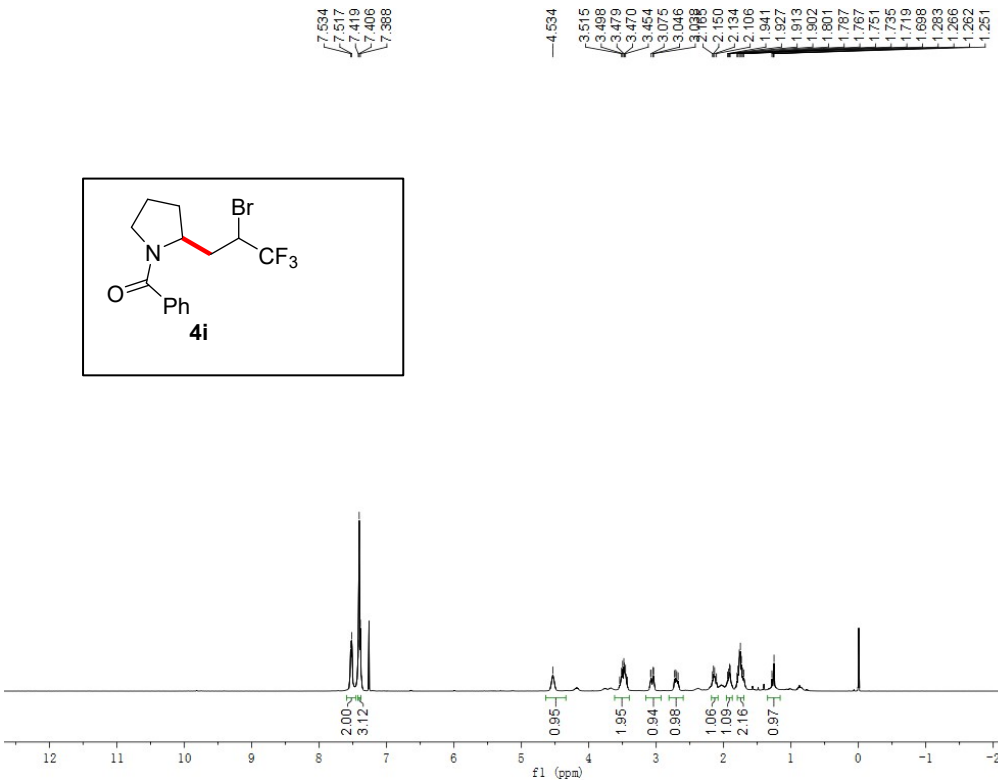

O
N
O
Ph
4h dr = 2:1

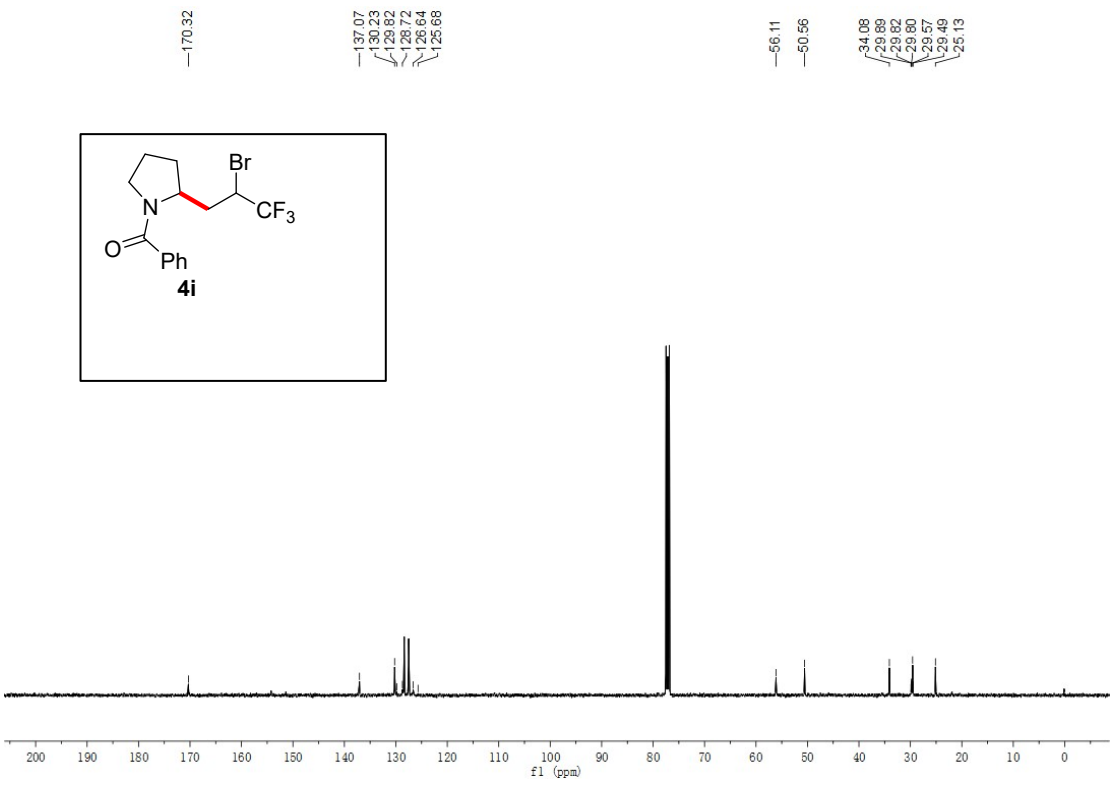

2.00
3.03
1.00
2.10
0.92
1.44
2.23
1.08
1.05
2.93
1.95
2.05
f1 (ppm)


211.35
211.26
171.10
170.96
137.01
130.30
130.27
128.33
127.62
127.56
60.28
50.99
50.83
45.09
43.12
42.16
41.46
41.29
28.28
27.29
27.04
26.45
25.37
25.27
25.23
f1 (ppm)

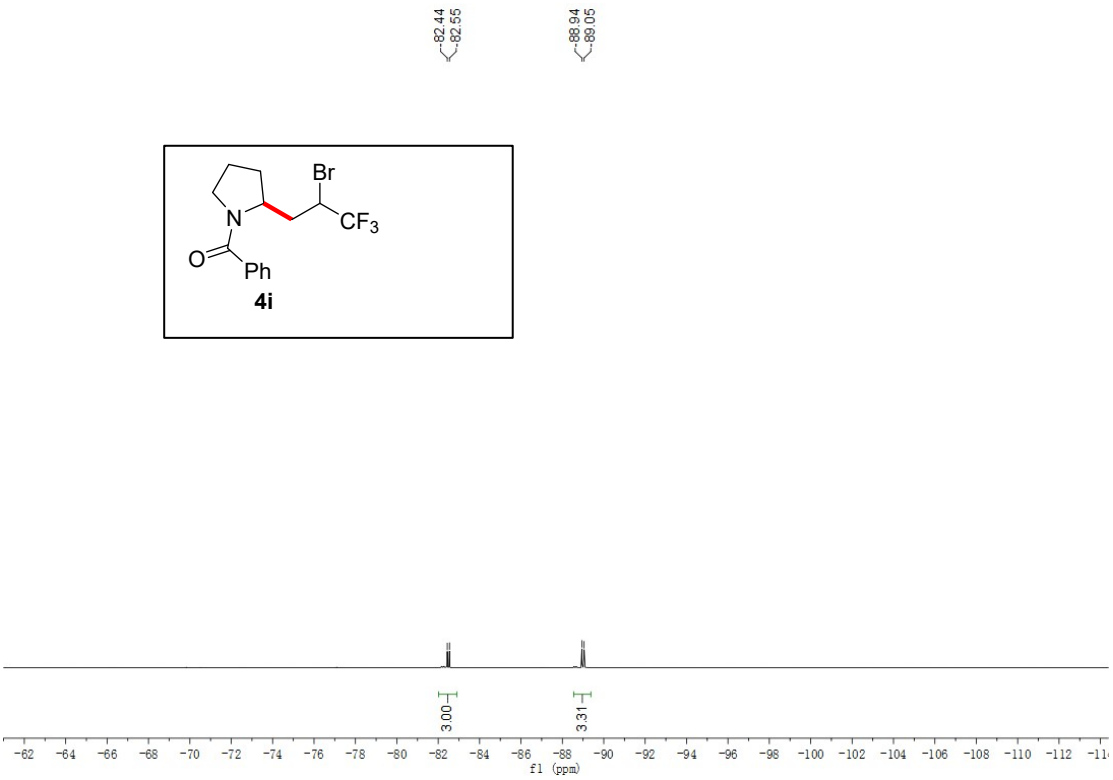
O
N
O
Ph
4h dr = 2:1

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

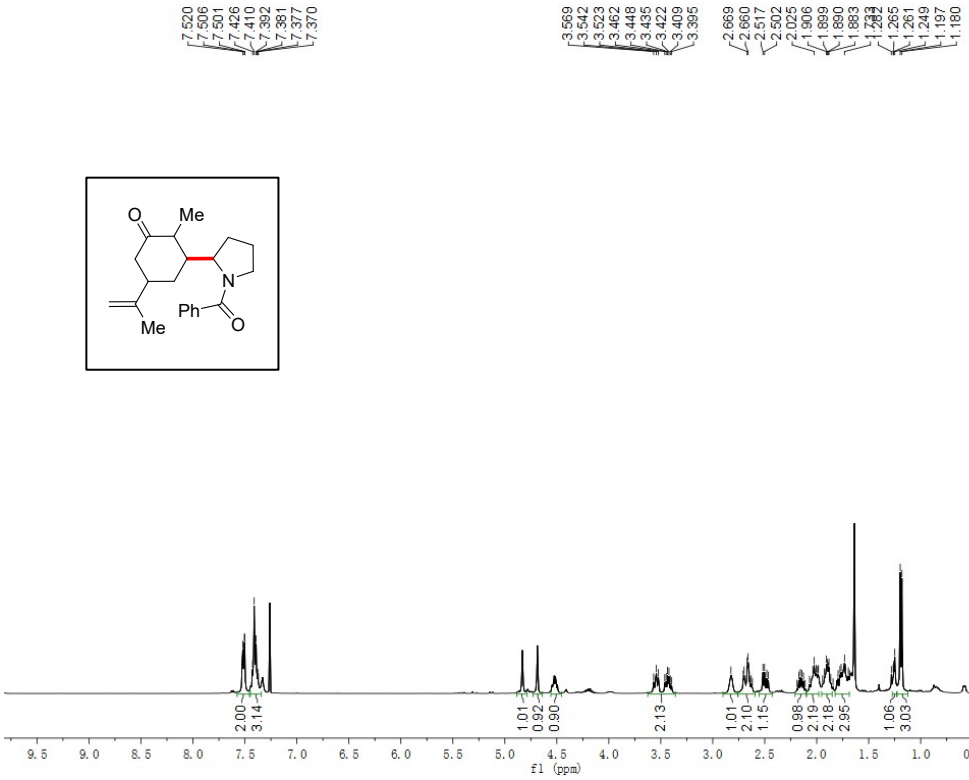

7.534
7.517
7.419
7.406
7.388
4.534
3.515
3.498
3.479
3.470
3.454
3.075
3.046
2.150
2.134
2.106
1.941
1.927
1.913
1.902
1.801
1.787
1.767
1.751
1.735
1.719
1.698
1.283
1.266
1.262
1.251
Br
N
CF3
O
Ph
4i
2.00
3.12
0.95
1.95
0.94
0.98
1.06
1.09
2.16
0.97
f1 (ppm)

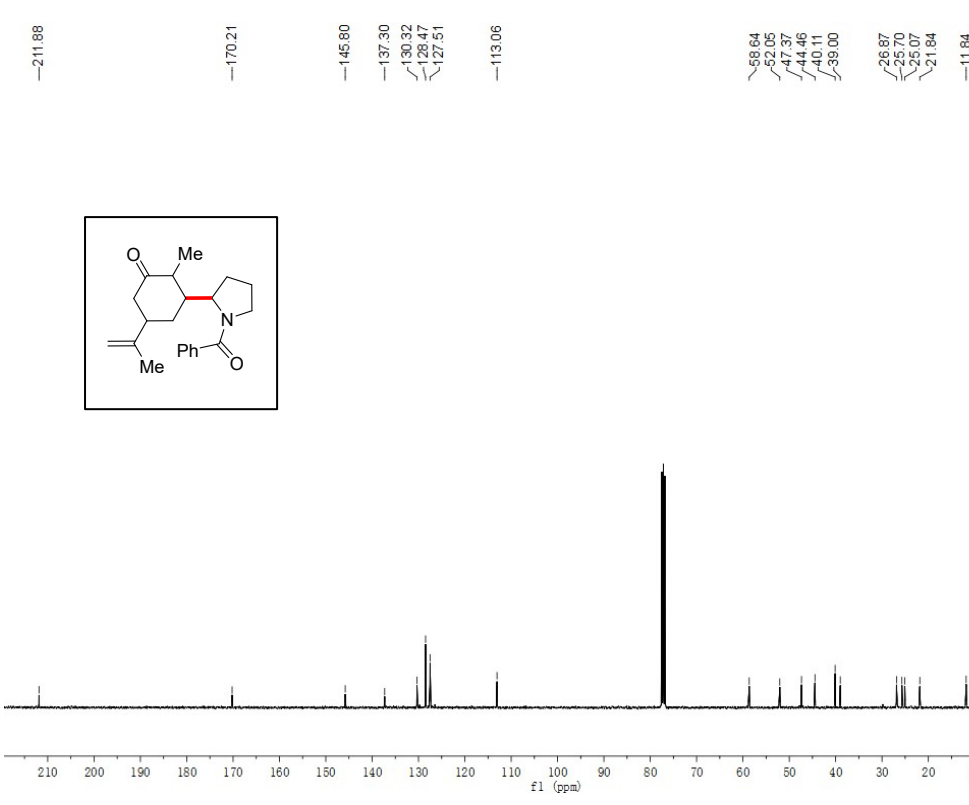

170.32
137.07
130.23
129.82
128.72
126.64
125.68
56.11
50.56
34.08
29.89
29.82
29.80
29.57
29.49
25.13
Br
N
CF3
O
Ph
4i
f1 (ppm)

4i, ^{19}F

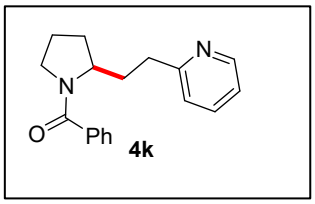

-82.44
-82.55
-88.94
-89.05
Br
N
CF3
O
Ph
4i
3.00
3.31
-62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112
f1 (ppm)

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

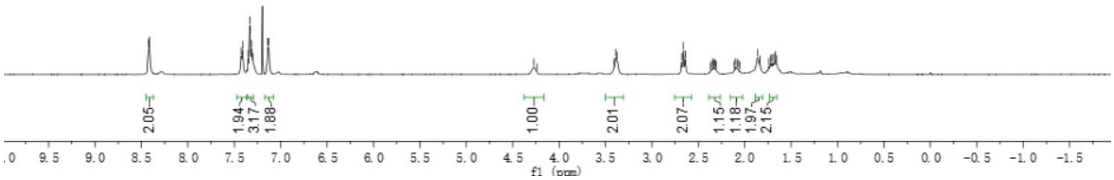

7.520
7.506
7.501
7.426
7.410
7.392
7.381
7.377
7.370
3.569
3.542
3.523
3.462
3.448
3.435
3.422
3.409
3.395
2.669
2.660
2.517
2.502
2.025
1.906
1.899
1.890
1.883
1.265
1.261
1.249
1.197
1.180
O
Me
N
Ph
O
Me
2.00
3.14
1.01
0.92
0.90
2.13
1.01
2.10
1.15
0.98
2.19
2.18
2.95
1.06
3.03
f1 (ppm)

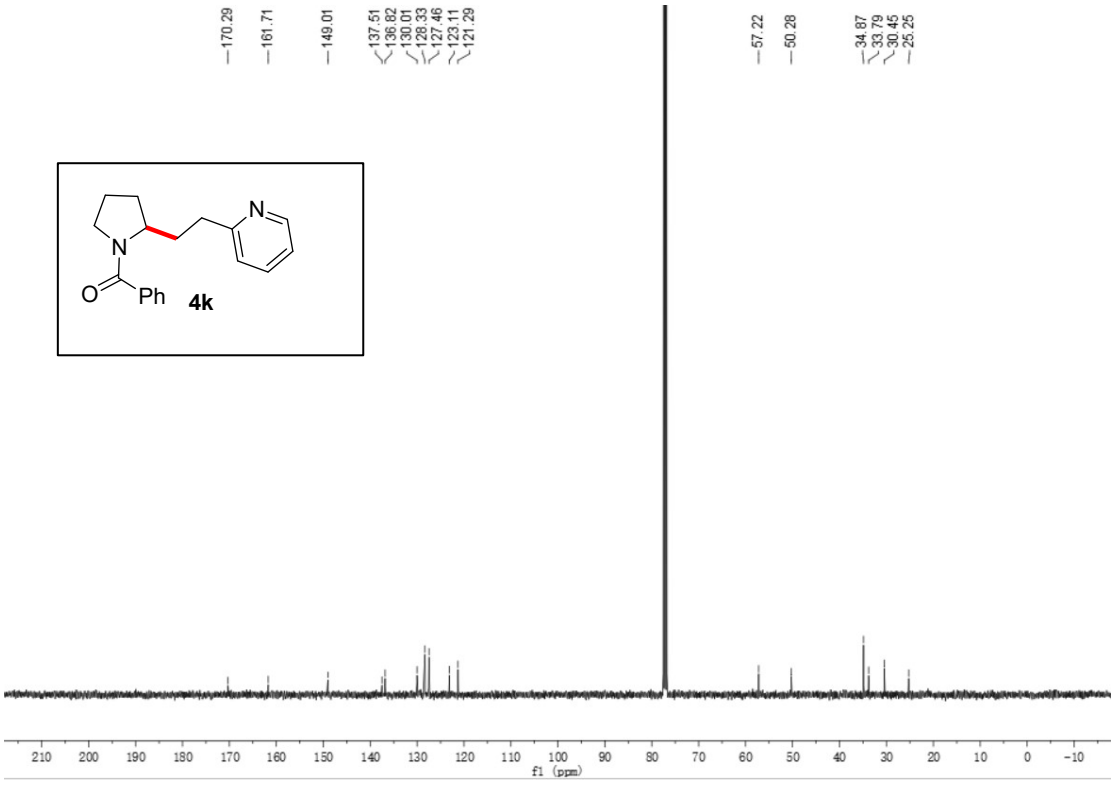

211.88
170.21
145.80
137.30
130.32
128.47
127.51
113.06
58.64
52.05
47.37
44.46
40.11
39.00
26.87
25.70
25.07
21.84
11.84
O
Me
N
Ph
O
Me
f1 (ppm)

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



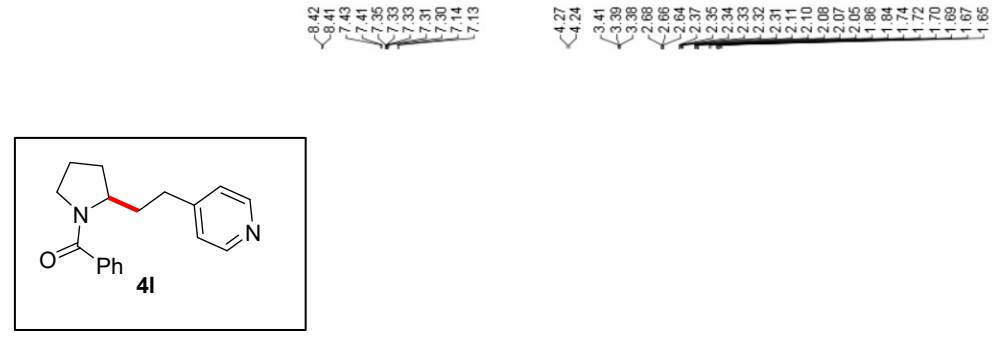
4k

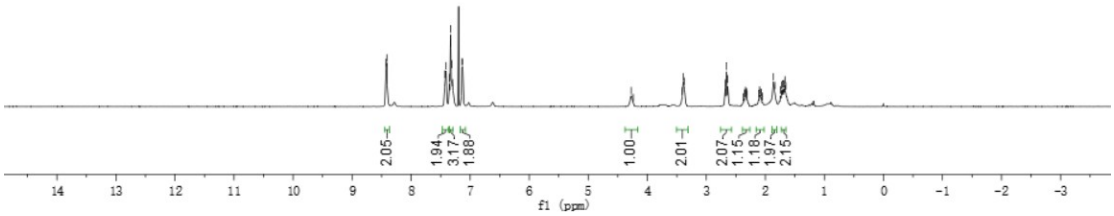


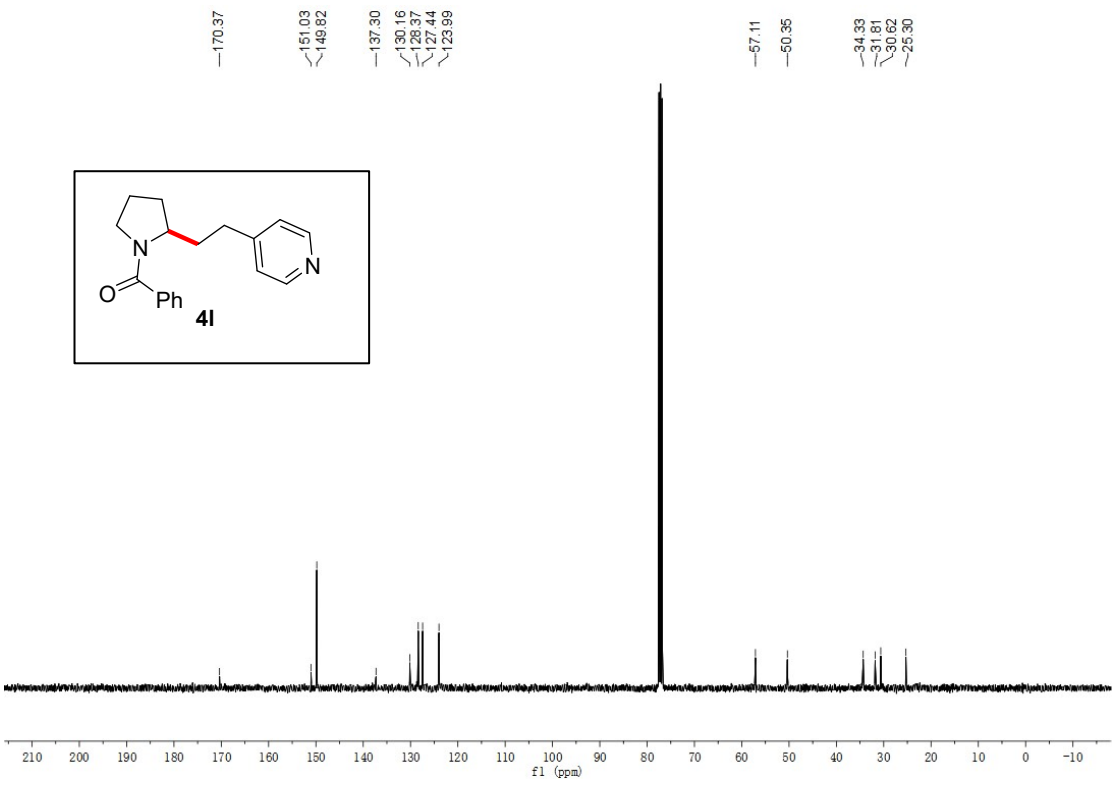


4k

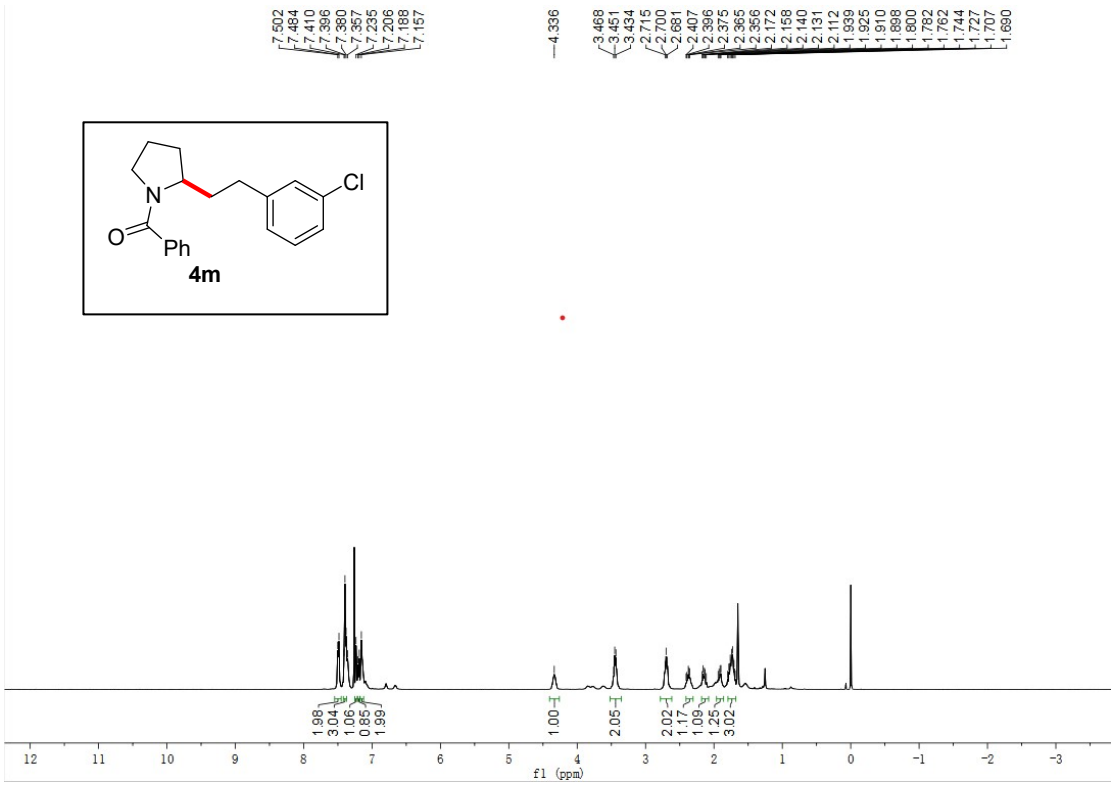
4l, $^{1}H+^{13}C$

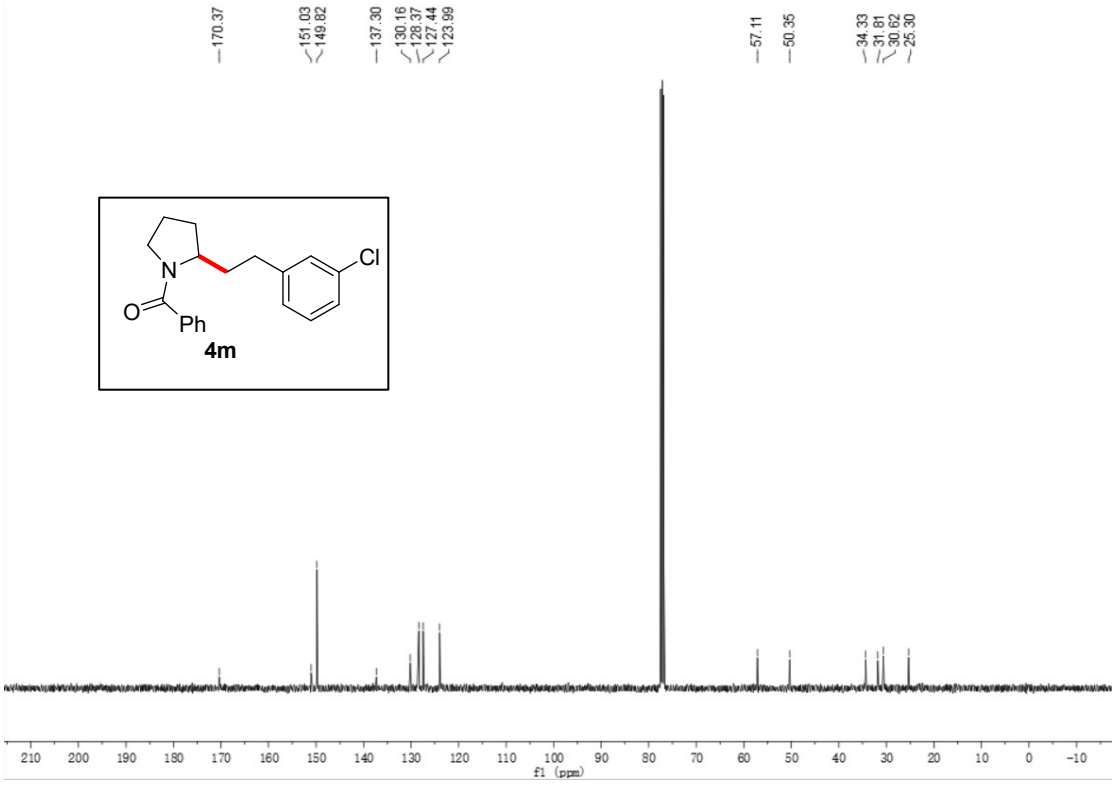

8.42
8.41
7.43
7.41
7.35
7.33
7.33
7.31
7.30
7.14
7.13
4.27
4.24
3.41
3.39
3.38
2.68
2.66
2.64
2.37
2.35
2.34
2.33
2.32
2.31
2.11
2.10
2.08
2.07
2.05
1.86
1.84
1.74
1.72
1.70
1.69
1.67
1.65
N
O
Ph
4l


2.05
1.94
3.17
1.88
1.00
2.01
2.07
1.15
1.18
1.97
2.15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

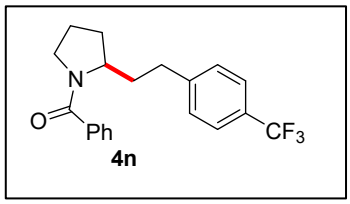

170.37
151.03
149.82
137.30
130.16
128.37
127.44
123.99
57.11
50.35
34.33
31.81
30.62
25.30
N
O
Ph
4l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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

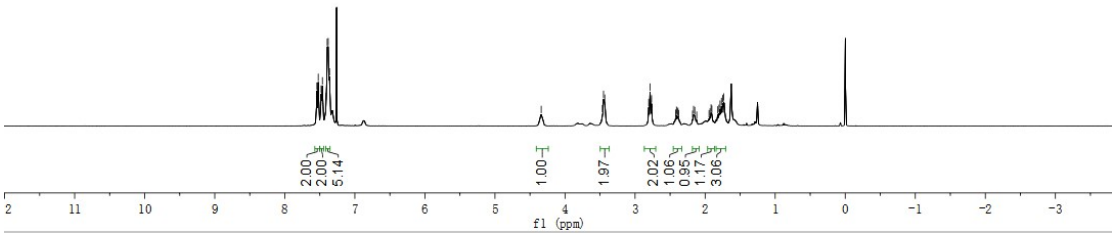

7.502
7.484
7.410
7.396
7.380
7.357
7.235
7.206
7.188
7.157
4.336
3.468
3.451
3.434
2.715
2.700
2.681
2.407
2.396
2.375
2.365
2.356
2.172
2.158
2.140
2.131
2.112
1.939
1.925
1.910
1.898
1.800
1.782
1.762
1.744
1.727
1.707
1.690
Cl
N
O
Ph
4m
1.98
3.04
1.06
0.85
1.99
1.00
2.05
2.02
1.17
1.09
1.25
3.02
f1 (ppm)

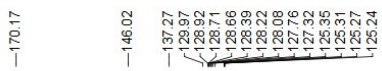

170.37
151.03
149.82
137.30
130.16
128.37
127.44
123.99
57.11
50.35
34.33
31.81
30.62
25.30
Cl
N
O
Ph
4m
f1 (ppm)

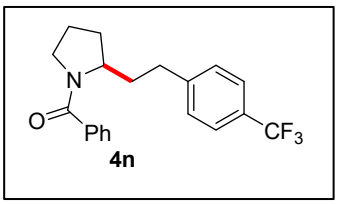
4n, $^{1}H+^{13}C$



4n

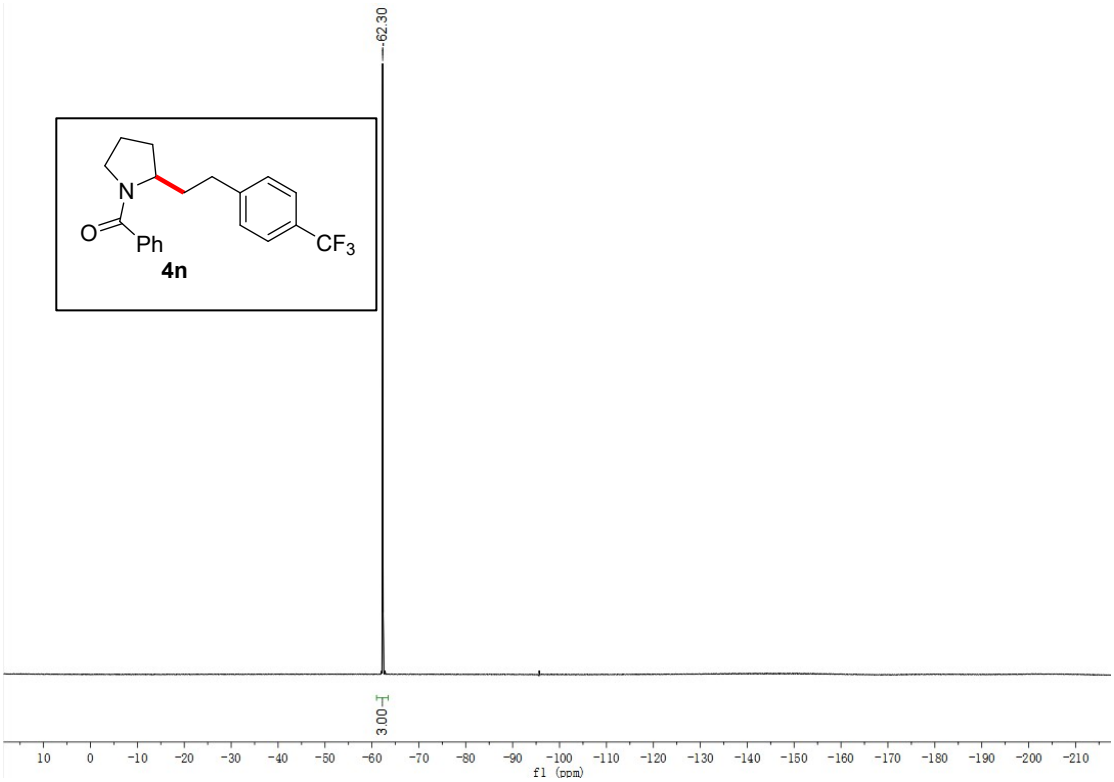




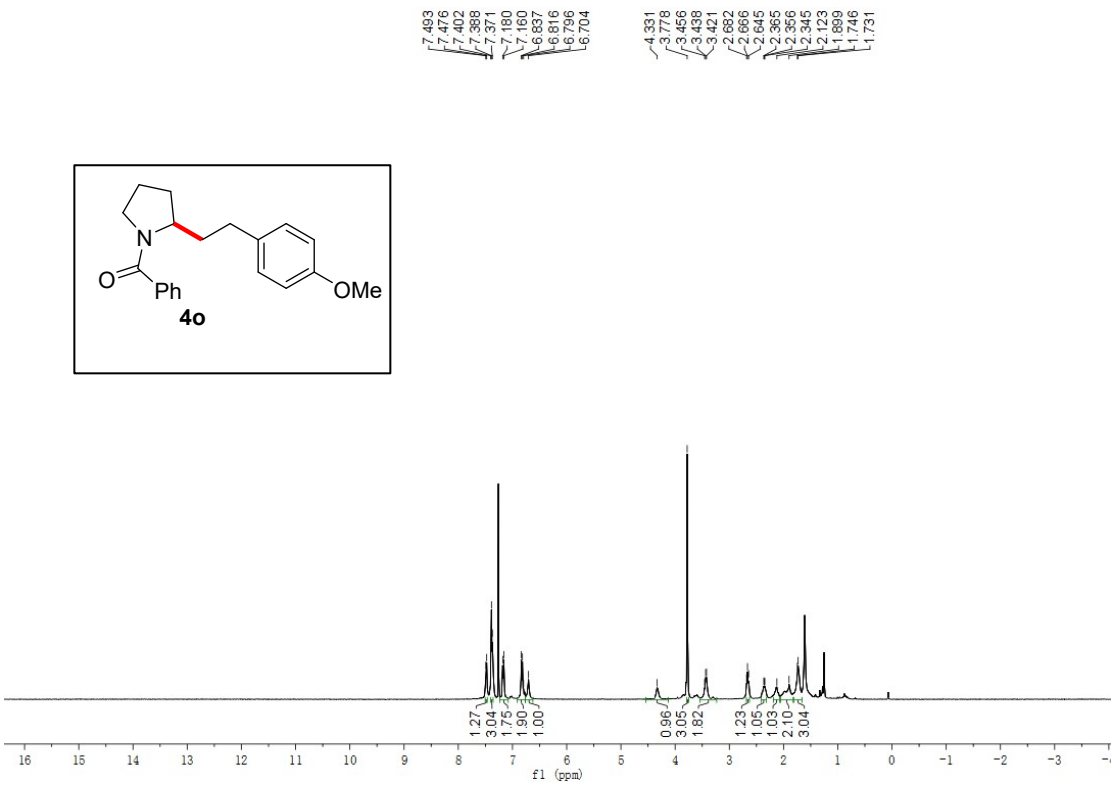


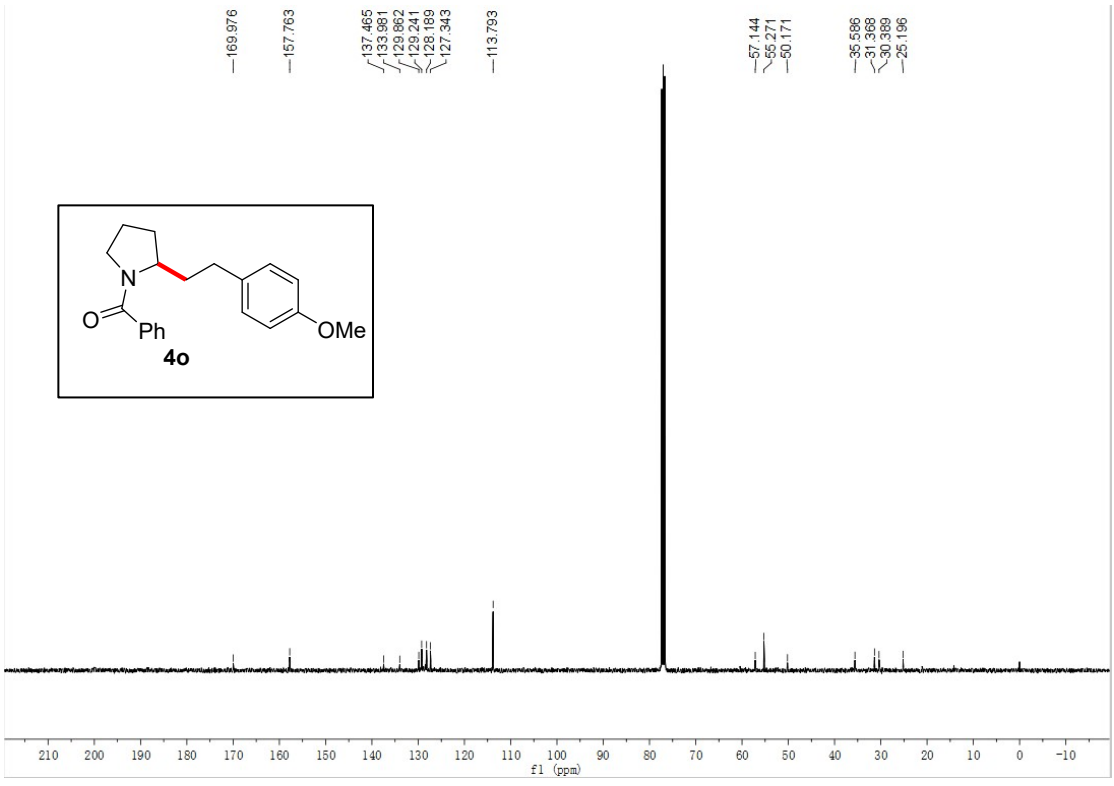
4n

4n, ^{19}F


-62.30
N
O
Ph
CF3
4n
3.00
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)

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

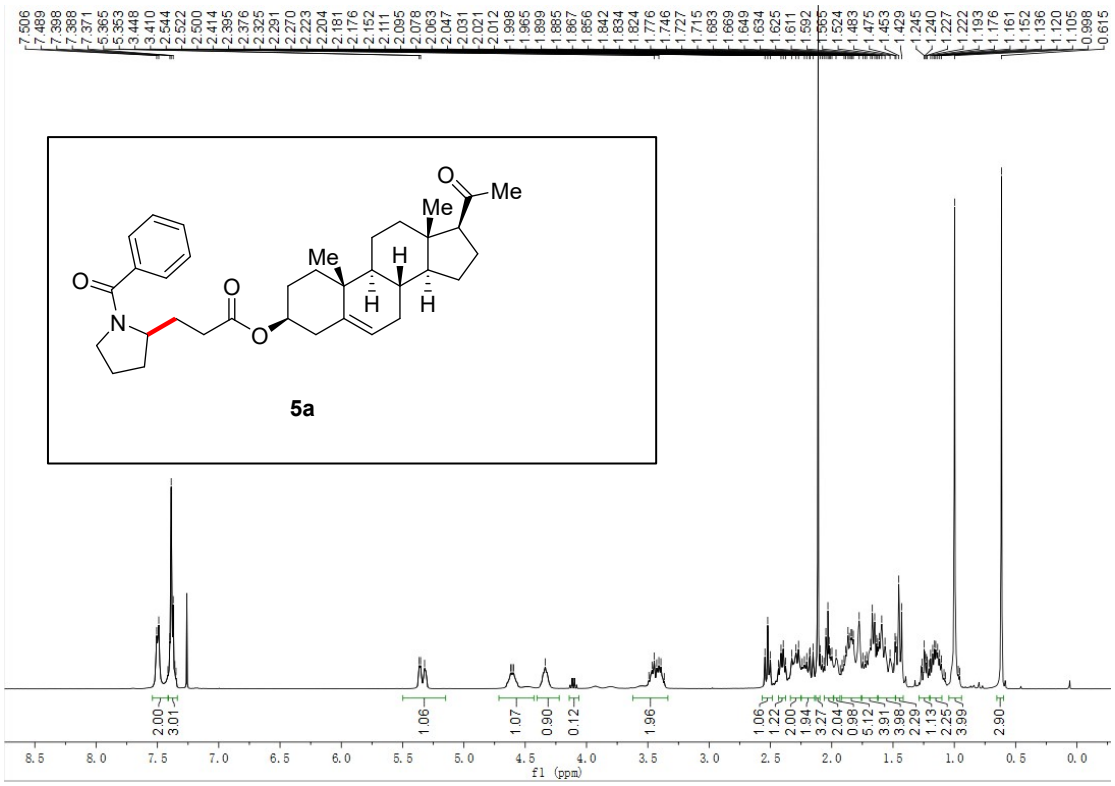

7.493
7.476
7.402
7.388
7.371
7.180
7.160
6.837
6.816
6.796
6.704
4.331
3.778
3.456
3.438
3.421
2.682
2.666
2.645
2.365
2.356
2.345
2.123
1.899
1.746
1.731
N
O
Ph
OMe
4o
1.27
3.04
1.75
1.90
1.00
0.96
3.05
1.82
1.23
1.05
1.03
2.10
3.04
f1 (ppm)

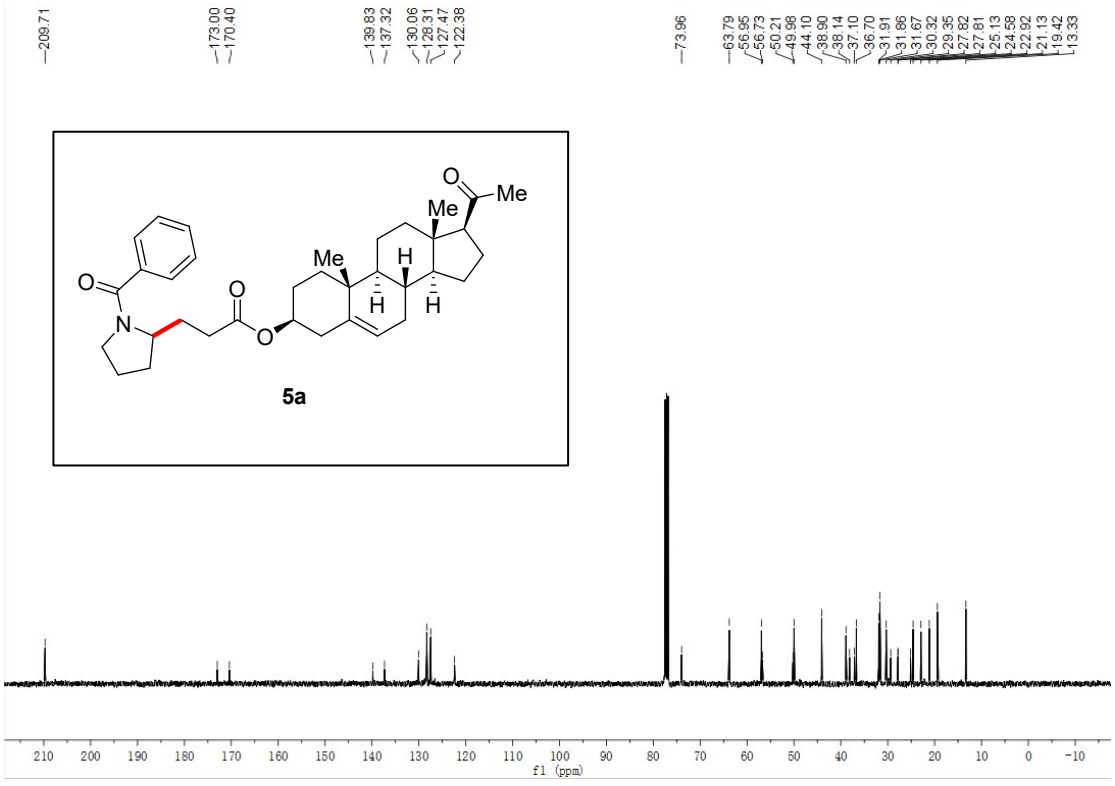

169.976
157.763
137.465
133.981
129.862
129.241
128.189
127.343
113.793
57.144
55.271
50.171
35.586
31.368
30.389
25.196
N
O
Ph
OMe
4o
f1 (ppm)

4r, $^{1}H+^{13}C$

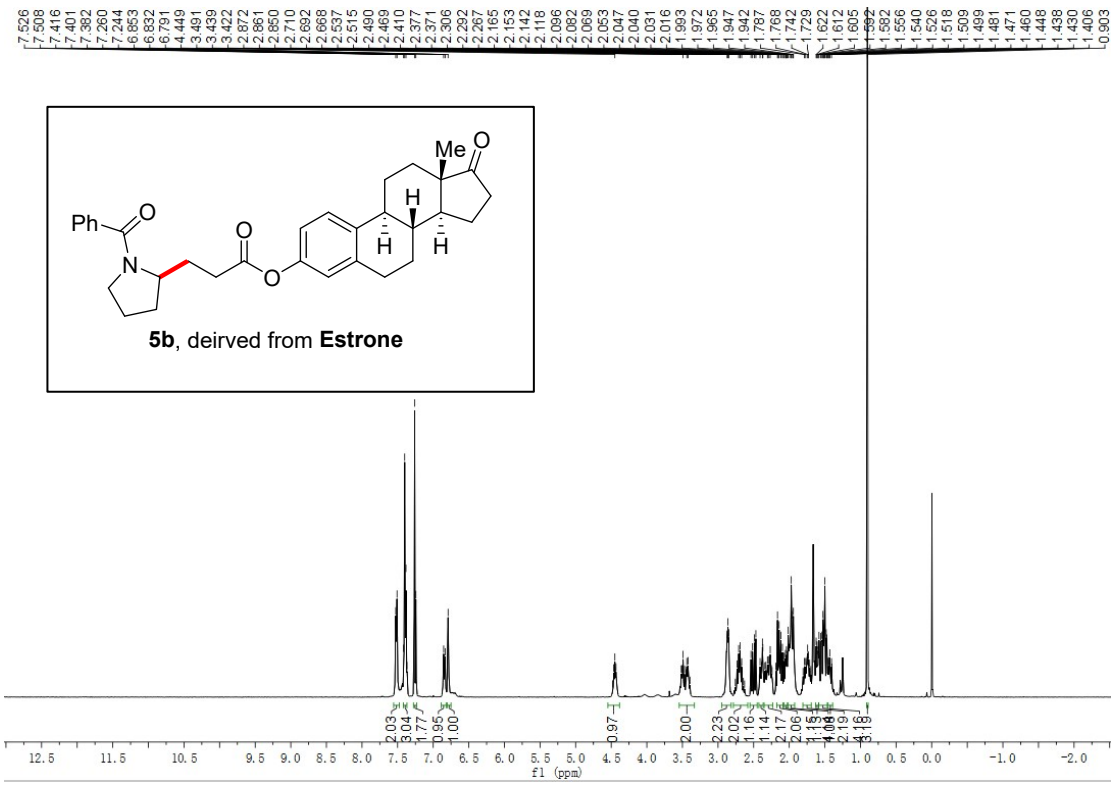

7.497
7.480
7.404
7.391
7.375
7.301
7.282
7.193
7.176
7.160
4.352
3.464
3.444
3.428
3.416
2.750
2.725
2.709
2.401
2.390
2.381
2.153
2.139
2.113
1.935
1.921
1.908
1.869
1.822
1.797
1.774
1.745
1.729
N
O
Ph
4r
1.98
4.11
0.99
1.00
1.89
1.00
2.03
2.01
1.11
1.09
1.18
3.11
f1 (ppm)
170.14
142.07
137.57
130.00
129.97
128.50
128.32
127.47
125.94
57.32
50.31
35.55
32.45
30.53
25.33
N
O
Ph
4r
f1 (ppm)

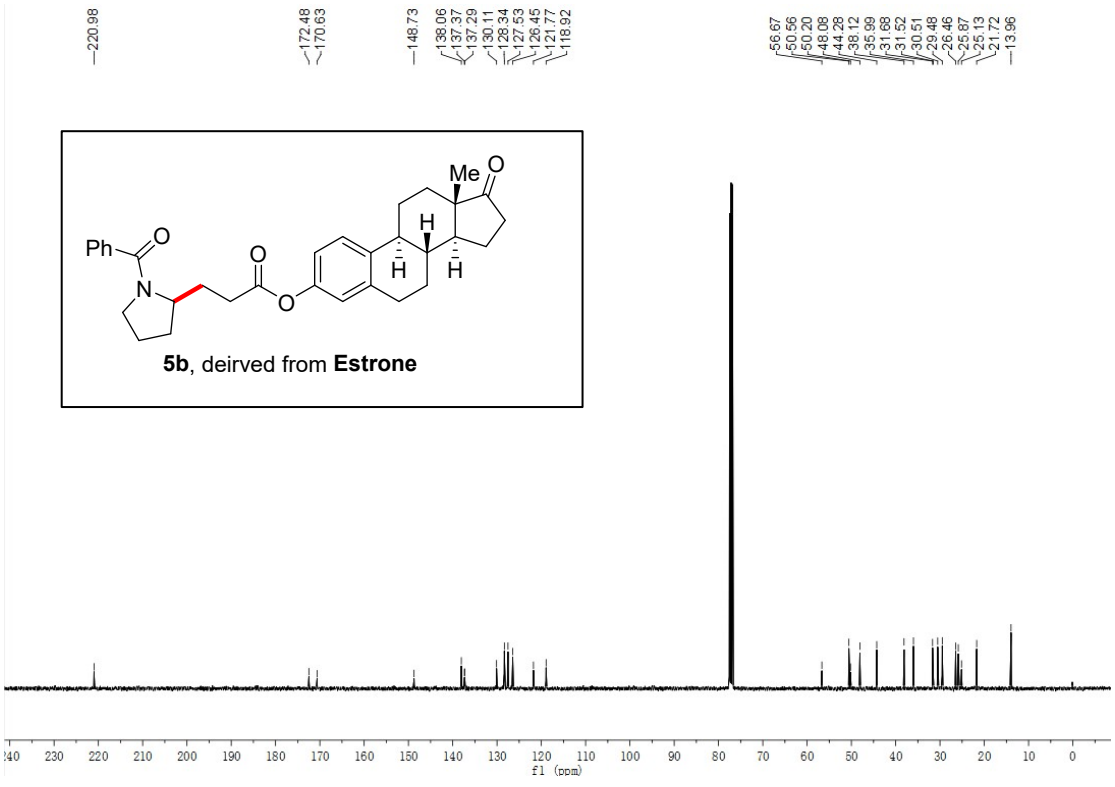
5a, $^{1}H+^{13}C$



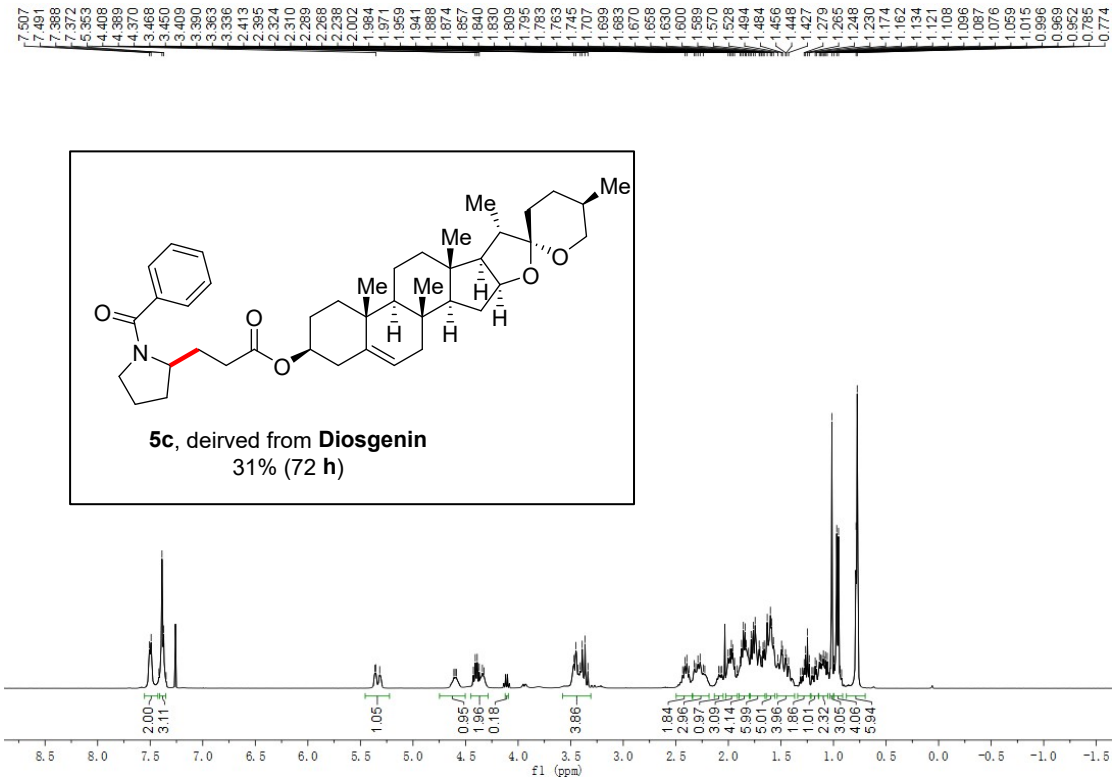


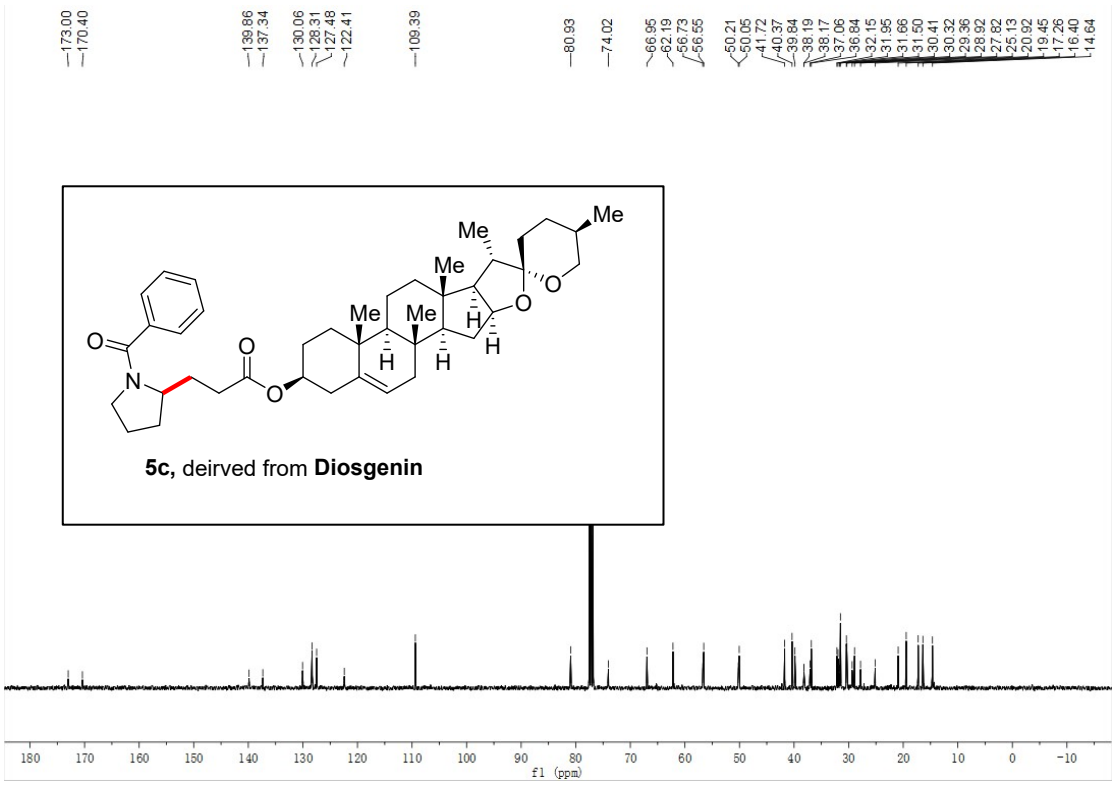
5b, $^{1}H+^{13}C$


7.526
7.508
7.416
7.401
7.382
7.260
7.244
6.853
6.832
6.791
4.449
3.491
3.439
3.422
2.872
2.861
2.850
2.710
2.692
2.668
2.537
2.515
2.490
2.469
2.410
2.377
2.371
2.306
2.292
2.267
2.165
2.153
2.142
2.118
2.096
2.082
2.069
2.053
2.047
2.040
2.031
2.016
1.993
1.972
1.965
1.947
1.942
1.787
1.768
1.742
1.729
1.622
1.612
1.605
1.582
1.556
1.540
1.526
1.518
1.509
1.499
1.481
1.471
1.460
1.448
1.438
1.430
1.406
0.903
Me
O
H
H
H
Ph
O
N
O
O
5b, deirved from Estrone
2.03
3.04
1.77
0.95
1.00
0.97
2.00
2.23
2.02
1.16
1.14
2.17
2.06
1.15
1.04
2.19
4.18
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
-1.0
-2.0
f1 (ppm)

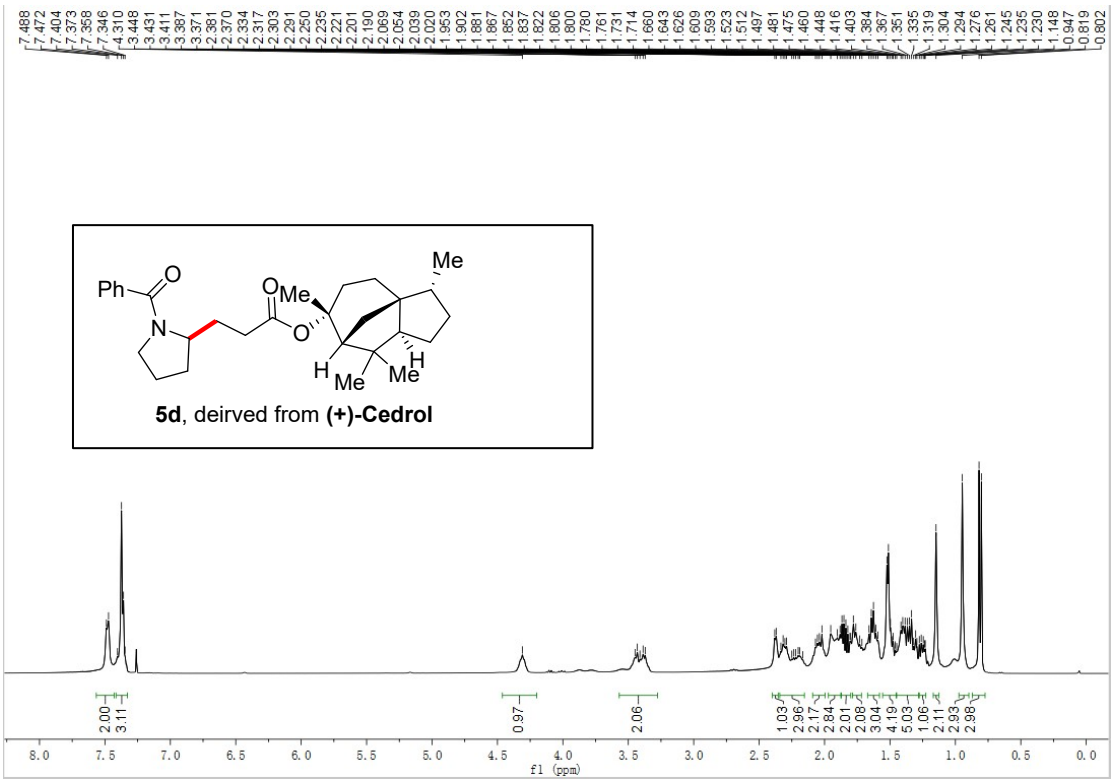

220.98
172.48
170.63
148.73
138.06
137.37
137.29
130.11
128.34
127.53
126.45
121.77
118.92
56.67
50.56
50.20
48.08
44.28
38.12
35.99
31.68
31.52
30.51
29.48
26.46
25.87
25.13
21.72
13.96
Me
O
H
H
H
Ph
O
N
O
O
5b, deirved from Estrone
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

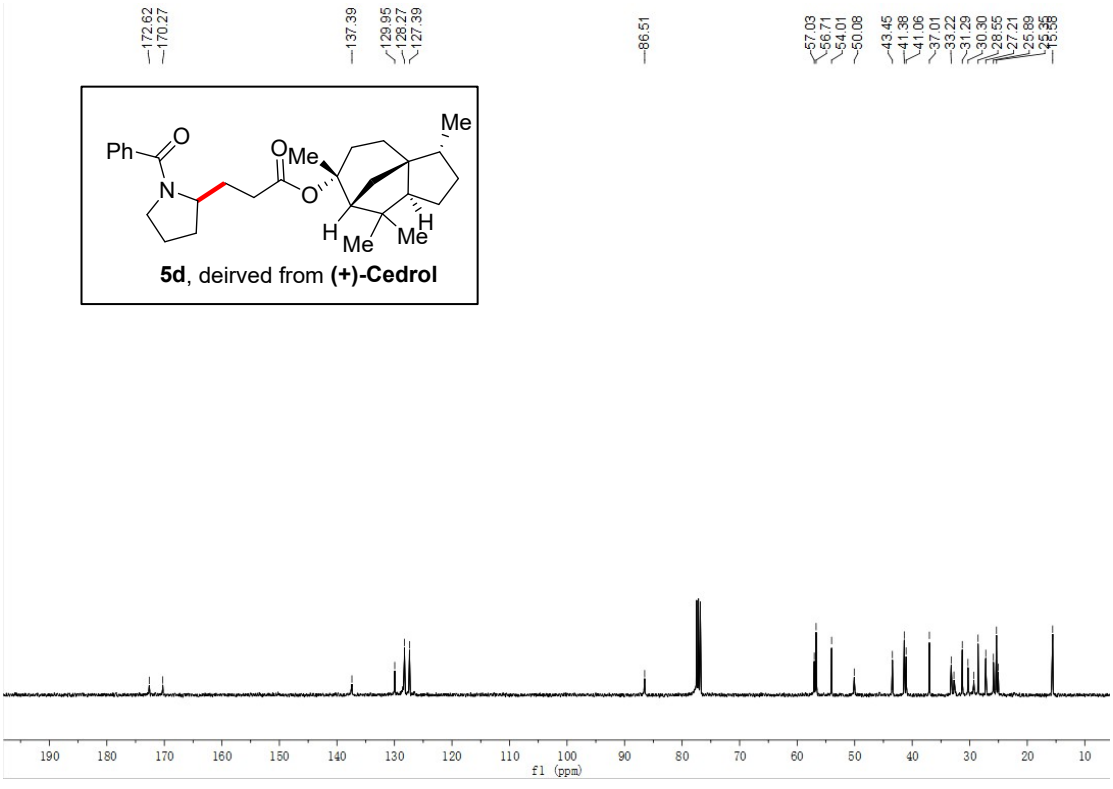
5c, $^{1}H+^{13}C$


7.507
7.491
7.388
7.372
5.353
4.408
4.389
4.370
3.468
3.450
3.409
3.390
3.363
3.336
2.413
2.395
2.324
2.310
2.289
2.268
2.238
2.002
1.984
1.971
1.959
1.941
1.888
1.874
1.857
1.840
1.830
1.809
1.795
1.783
1.763
1.745
1.707
1.699
1.683
1.670
1.658
1.630
1.600
1.589
1.570
1.528
1.494
1.484
1.456
1.448
1.427
1.279
1.265
1.248
1.230
1.174
1.162
1.134
1.121
1.108
1.096
1.087
1.076
1.059
1.015
0.996
0.969
0.952
0.785
0.774
Me
Me
Me
Me
Me
O
O
O
O
N
H
H
H
H
5c, deirved from Diosgenin
31% (72 h)
2.00
3.11
1.05
0.95
1.96
0.18
3.86
1.84
2.96
0.97
3.09
4.14
5.99
5.01
3.96
1.86
1.01
2.32
3.05
4.06
5.94
f1 (ppm)

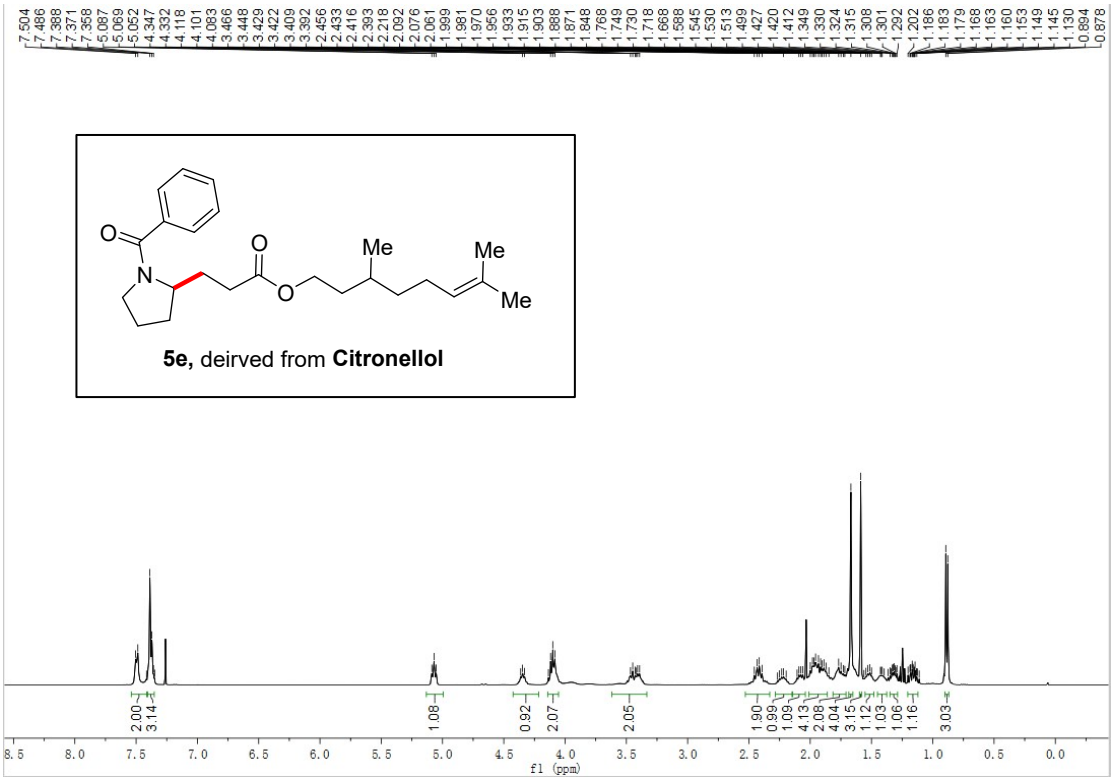

173.00
170.40
139.86
137.34
130.06
128.31
127.48
122.41
109.39
80.93
74.02
66.95
62.19
56.73
56.55
50.21
50.05
41.72
40.37
39.84
38.19
38.17
37.06
36.84
32.15
31.95
31.66
31.50
30.41
30.32
29.36
28.92
27.82
25.13
20.92
19.45
17.26
16.40
14.64
Me
Me
Me
Me
Me
O
O
O
O
N
H
H
H
H
5c, deirved from Diosgenin
f1 (ppm)

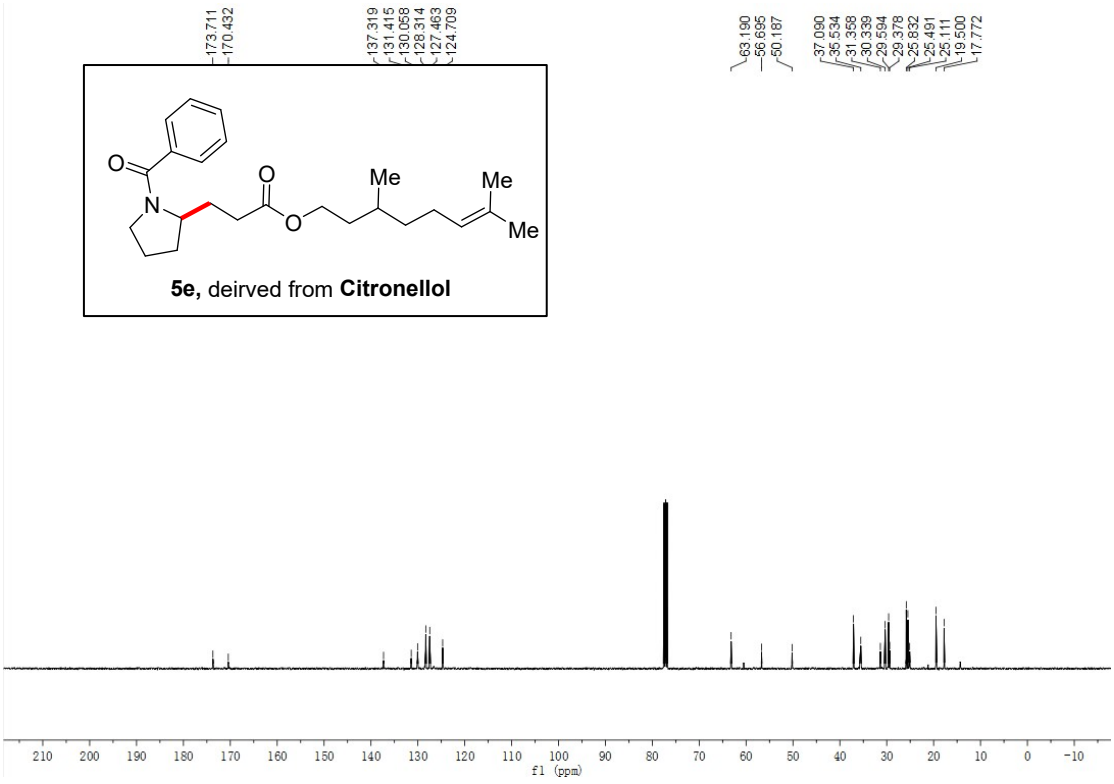
5d, $^{1}H+^{13}C$


Ph
O
N
O
Me
O
Me
H
Me
Me
H
5d, deirved from (+)-Cedrol
f1 (ppm)

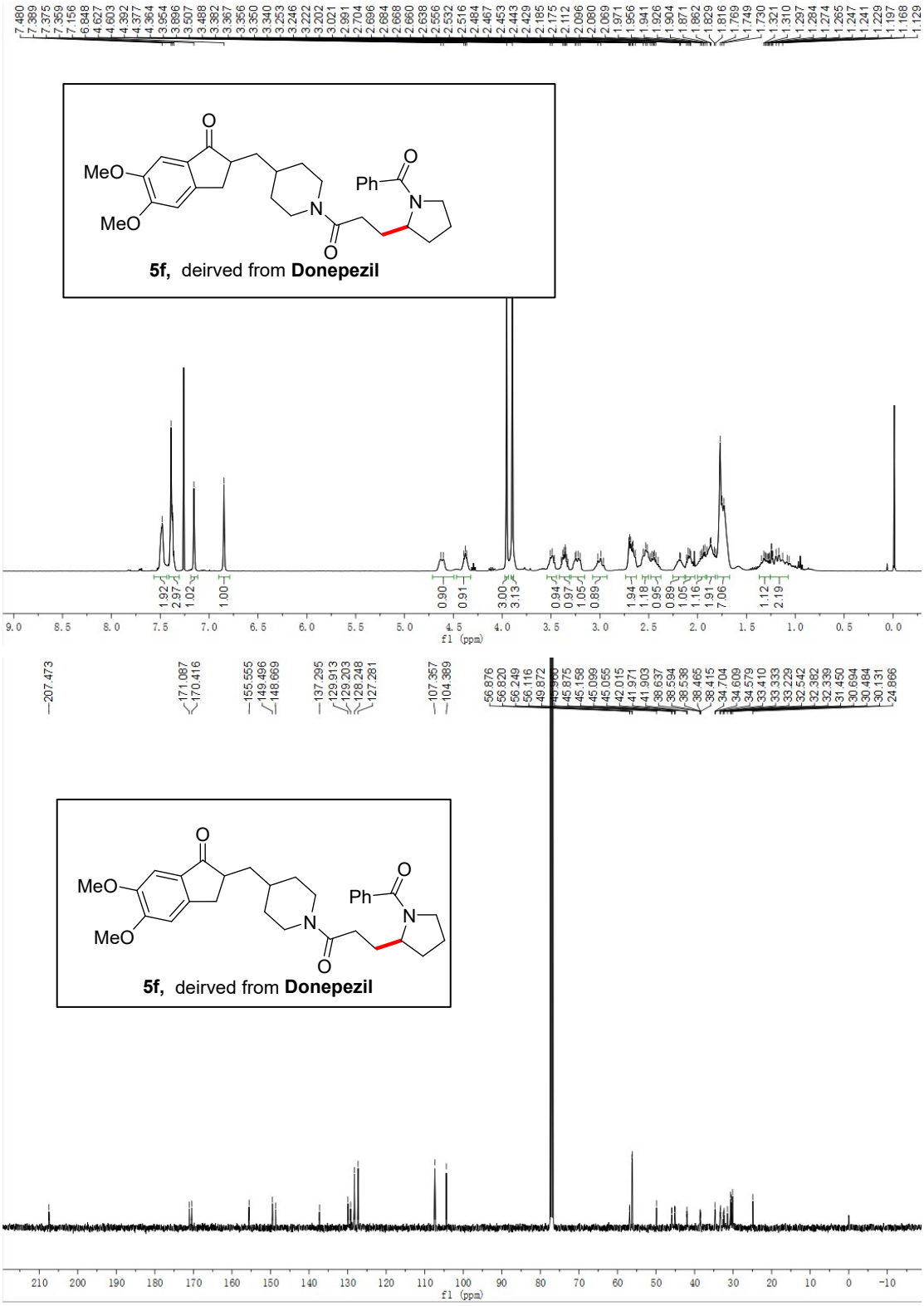

Ph
O
N
O
Me
O
Me
H
Me
Me
H
5d, deirved from (+)-Cedrol
f1 (ppm)

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


7.504
7.486
7.388
7.371
7.358
5.087
5.069
5.052
4.347
4.332
4.118
4.101
4.083
3.466
3.448
3.429
3.422
3.409
3.392
2.456
2.433
2.416
2.393
2.218
2.092
2.076
2.061
1.999
1.981
1.970
1.956
1.933
1.915
1.903
1.888
1.871
1.848
1.768
1.749
1.730
1.718
1.668
1.588
1.545
1.530
1.513
1.499
1.427
1.420
1.412
1.349
1.330
1.324
1.315
1.308
1.301
1.292
1.202
1.186
1.183
1.179
1.168
1.163
1.160
1.153
1.149
1.145
1.130
0.894
0.878
O
N
O
O
Me
Me
Me
5e, deirved from Citronellol
2.00
3.14
1.08
0.92
2.07
2.05
1.90
0.99
1.09
4.13
2.08
4.04
3.15
1.12
1.03
1.06
1.16
3.03
f1 (ppm)


173.711
170.432
137.319
131.415
130.058
128.314
127.463
124.709
63.190
56.695
50.187
37.090
35.534
31.358
30.339
29.594
29.378
25.832
25.491
25.111
19.500
17.772
O
N
O
O
Me
Me
Me
5e, deirved from Citronellol
f1 (ppm)

5f, $^{1}H+^{13}C$


MeO
MeO
O
N
Ph
O
O
5f, deirved from Donepezil
f1 (ppm)
MeO
MeO
O
N
Ph
O
O
5f, deirved from Donepezil
f1 (ppm)