Supporting Information

Nitrogen-directed unactivated γ-C(sp^3)–H functionalization of amides toward 7-membered lactones via photoredox catalysis

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1. General Information

^{1}H NMR spectra were recorded on 400 or 600 MHz (101 or 150 MHz for ^{13}C NMR, and 377 or 564 MHz for ^{19}F NMR) agilent NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.16 ppm (for ^{13}C NMR); ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.00 ppm. HRMS was recorded on an Agilent 6540 Q-TOF (ESI) or GCT-TOF (EI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1}. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified.

2. Photochemical Reaction Setup

Household blue LED strips (22 W) were coiled around the inside of a glassware with 15 cm diameter (**Figure S1**). The LED strips were wrapped in aluminum foil to maintain a specific reaction temperature. In this case, the reaction temperature is approximately 35 °C. Optimum yields were then observed.

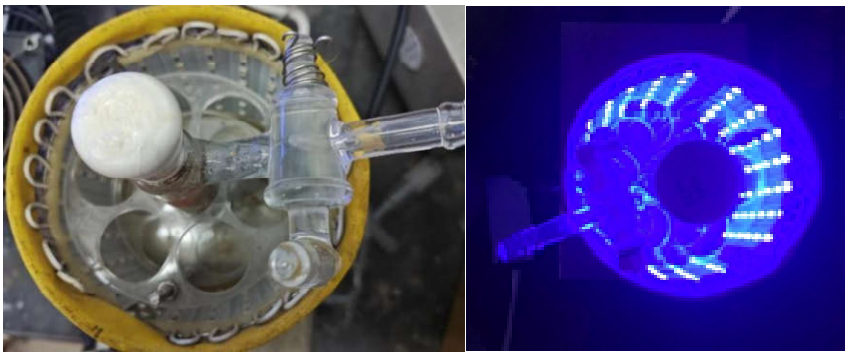
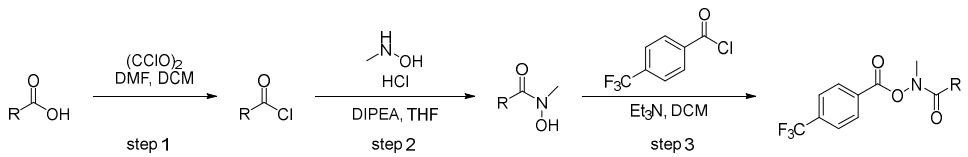


Figure S1 Reaction setup

3. Procedures and Characterization Data of Substrates

3.1 General Procedure for the Synthesis of Amide Substrates[1-3]

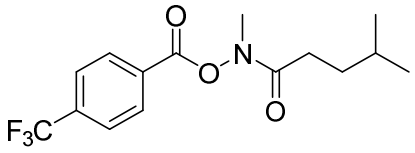


Step 1: To a solution of carboxylic acid (1.0 equiv) and 3-5 drops of anhydrous *N,N*-dimethylformamide (DMF) in anhydrous dichloromethane (CH_2Cl_2, 0.5 M) at 0 ºC was added dropwise oxalyl chloride (1.5 equiv). The reaction was stirred vigorously for 2 hours at room temperature. The solvent was removed under vacuum. The resulting acyl chloride was then redissolved in anhydrous acetonitrile and used directly for the next step without further purification.

Step 2: To a solution of the *N*-methylhydroxylamine hydrochloride (1.2 equiv) in

anhydrous tetrahydrofuran (THF, 0.4 M), DIPEA (2.0 equiv) was added at 0 ºC and the reaction was stirred for 15 minutes. Acyl chloride (1.0 equiv) in anhydrous acetonitrile was added dropwise over 15 minutes and the mixture was allowed to warm to room temperature overnight. The mixture was diluted with saturated $NaHCO_{3\ aq}$ and ethyl acetate (EtOAc) and the layers were separated. The aqueous layer was extracted with ethyl acetate (50 mL × 2) and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine, successively, and then evaporated. Purification by column chromatography on silica gel eluting with petroleum ether: EtOAc gave the hydroxylamine intermediate.

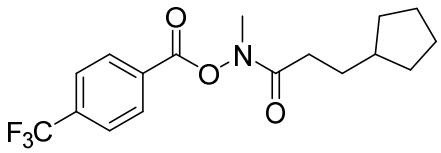
Step 3: To a solution of hydroxylamine intermediate (1.05 equiv) in anhydrous dichloromethane (0.35 M) at 0 ºC, Et_3N (1.5 equiv) was added dropwise. 4-Trifluoromethyl-benzoyl chloride (1.0 equiv) was then added dropwise over 5 minutes. The reaction was stirred vigorously for 2 h at room temperature. The reaction was quenched with aqueous 1M HCl and transferred to a separatory funnel. The crude mixture was diluted with CH_2Cl_2 and water. The organic layer was removed, and the aqueous layer was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were washed with saturated aqueous $NaHCO_3$ and then brine, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Purification by column chromatography on silica gel eluting with Petroleum ether: ethyl acetate gave amide substrates.



***N*,4-Dimethyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)pentanamide (1a)**

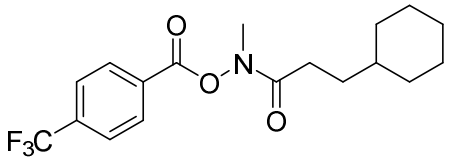
1a was prepared from 4-methyl pentanoic acid according to the reference.[1] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.21 (d, J = 8.1 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 3.42 (s, 3H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.62-147 (m, 3H), 0.85 (d, *J* = 5.4 Hz, 6H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ

163.2, 135.8 (q, J = 33.5 Hz), 130.4, 130.2, 125.9, 128.3, 123.3 (q, J = 273.1Hz), 33.2, 30.3, 27.6, 22.2, 22.0. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -63.42. **IR (KBr):** v (cm^{-1}) 2953, 2929, 2866, 1758, 1729, 1448, 1241, 1025, 729, 692. **HRMS (ESI)** calcd for $C_{15}H_{18}F_3NO_3Na$ $[M + Na]^+$: 340.1131, found: 340.1138.



3-Cyclopentyl-*N*-methyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)propenamide (1b)

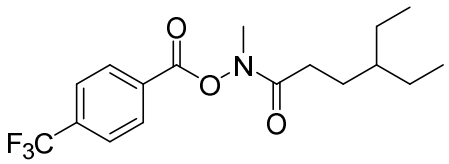
1b was prepared from 3-cyclopentylpropionic acid according to the reference.[1] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.20 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 3.41 (s, 3H), 2.31 (t, J = 7.6 Hz, 2H), 1.82-1.57 (m, 5H), 1.56-1.52 (m, 2H), 1.48-1.44 (m, 2H), 1.010-1.00 (m, 2H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 163.2, 135.8 (q, J = 33.2 Hz), 130.4, 130.2, 125.9, 123.3 (q, J = 272.8Hz), 39.5, 32.4, 31.5, 30.5, 25.0. **^{19}F NMR (376 MHz, CDCl$_3$)**δ -63.41. **IR (KBr):** v (cm^{-1}) 2930, 2867, 1758, 1732, 1448, 1241, 1026, 729, 693. **HRMS (ESI)** calcd for $C_{17}H_{20}F_3NO_3Na$ $[M + Na]^+$: 366.1287, found: 366.1294.



3-Cyclohexyl-*N*-methyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)propenamide (1c)

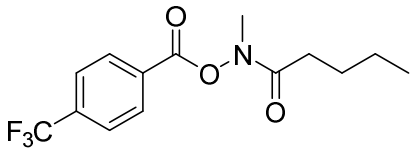
1c was prepared from 3-Cyclohexylpropionic acid according to the reference.[1] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.20 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 3.40 (s, 3H), 2.31 (t, J = 7.6 Hz, 2H), 1.69-1.57 (m, 5H), 1.52 (q, J = 7.4 Hz, 2H), 1.24-1.03 (m, 4H), 0.83 (q, J = 11.2 Hz, 2H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)**δ 163.2, 135.7 (q, J = 32.0 Hz), 130.4, 130.2, 125.9, 123.3 (q, J = 272.9 Hz), 37.1, 33.0, 31.7, 29.7, 26.4, 26.1. **^{19}F NMR (376 MHz,**

$CDCl_3$) δ -63.40. **IR (KBr):** *v* (cm^{-1}) 2924, 2853, 1768, 1730, 1448, 1242, 1065, 698. **HRMS (ESI)** calcd for $C_{18}H_{22}F_3NO_3Na$ $[M + Na]^+$: 380.1444, found: 380.1452.



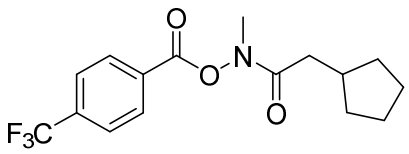
4-Ethyl-*N*-methyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)hexanamide (1d)

1d was prepared from 4-ethyl-hexansaeure according to the reference.[3] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.20 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 3.41 (s, 3H), 2.28 (s, 2H), 1.59 (q, *J* = 7.5 Hz, 2H), 1.32-1.16 (m, 5H), 0.78 (t, *J* = 7.4 Hz, 6H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 163.2, 135.8 (q, *J* = 33.1 Hz), 130.4, 130.2, 125.9 , 123.3(q, *J* = 273.1 Hz), 39.9, 29.8, 27.3, 25.1, 10.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.42. **IR (KBr):** *v* (cm^{-1}) 2962, 2874, 1769, 1731, 1460, 1251, 1065, 700. **HRMS (ESI)** calcd for $C_{17}H_{22}F_3NO_3Na$ $[M + H]^+$: 368.1444, found: 368.1445.



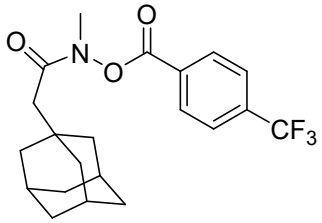
***N*-Methyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)pentanamide (1e)**

1e was prepared from Valeryl chloride according to the reference.[3] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 3.41 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.64-1.59 (m, 2H), 1.31 (q, *J* = 7.5 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 163.2, 135.7 (q, *J* = 32.9 Hz), 130.4, 130.2, 125.9, 123.3 (q, *J* = 273.1 Hz), 31.9, 26.4, 22.3, 13.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.42. **IR (KBr):** *v* (cm^{-1}) 2960, 2921, 2874, 1768, 1681, 1411, 1322, 1065, 768, 700. **HRMS (ESI)** calcd for $C_{14}H_{16}F_3NO_3Na$ $[M + Na]^+$: 326.0974, found: 326.0980.



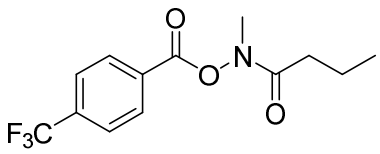
2-Cyclopentyl-*N*-methyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)acetamide (1f)

1f was prepared from 2-cyclopentylacetic acid according to the reference.[1] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.20 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 3.41 (s, 3H), 2.49-2.14 (m, 3H), 1.85-1.82 (m, 2H), 1.67-1.41 (m, 4H), 1.12-1.09 (m, 2H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 163.2, 135.7 (q, *J* = 33.3 Hz), 130.4, 130.2, 125.9,123.3 (q, *J* = 273.1 Hz), 38.3, 35.9, 32.6, 24.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.40. **IR (KBr):** *v* (cm^{-1}) 2951, 2869, 1760, 1680, 1411, 1322, 1065, 768, 699. **HRMS (ESI)** calcd for $C_{16}H_{18}F_3NO_3Na$ $[M + Na]^+$: 352.1131, found: 352.1138.



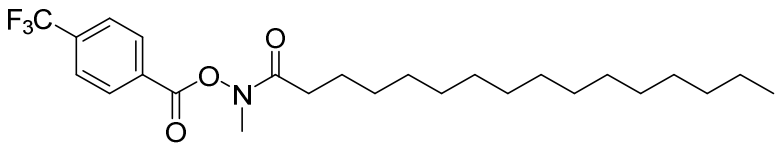
2-((*3r,5r,7r*)-Adamantan-1-yl)-*N*-methyl-*N*-((4-(trifluoromethyl)benzoyl)oxy) acetamide (1g)

1g was prepared from 1-Adamantaneacetic acid according to the reference.[1] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v). white solid, m.p. 122-126 ℃. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 3.42 (s, 3H), 2.11 (d, *J* = 11.7 Hz, 2H), 1.95 (s, 3H), 1.69-1.61 (m, 12H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)**δ 163.1, 135.4 (q, *J* = 33.3Hz), 130.4, 125.9, 123.3 (q, *J* = 273.1Hz), 45.7, 42.6, 36.7, 33.5, 29.7, 28.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.36. **IR (KBr):** *v* (cm^{-1}) 2910, 2848, 1769, 1654, 1409, 1326, 1066, 692. **HRMS (ESI)** calcd for $C_{21}H_{24}F_3NO_3Na$ $[M + Na]^+$: 418.1600, found:418.1608.



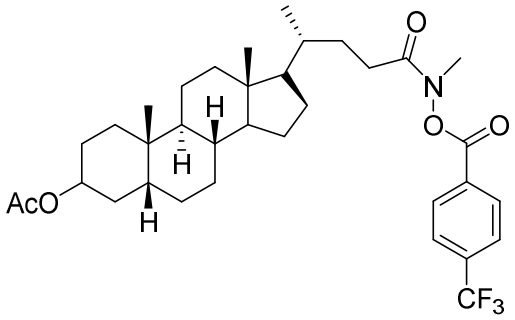
***N*-Methyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)butyramide (1h)**

1h was prepared from Butyryl chloride according to the reference.[3] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.19 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 3.39 (s, 3H), 2.27 (t, *J* = 7.3 Hz, 2H), 1.64 (q, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 163.2, 135.7 (q, *J* = 32.8 Hz), 130.4, 130.2, 125.9, 123.3(q, *J* = 273.1 Hz), 34.1, 17.7, 13.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.40. **IR (KBr):** *v* (cm^{-1}) 2935, 2872, 1768, 1731, 1683, 1413, 1242, 1065, 700. **HRMS (ESI)** calcd for$C_{13}H_{14}F_3NO_3Na$ $[M + Na]^+$: 312.0818, found: 312.0821.



***N*-Methyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)palmitamide (1i)**

1i was prepared from Palmitic acid according to the reference. [1] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 3.42 (s,3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.63 (q, *J* = 7.3 Hz, 2H), 1.34 -1.16 (m, 24H), 0.87 (t, *J* = 6.9 Hz,3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 163.2, 135.7 (q, *J* = 32.8 Hz), 130.4, 130.2, 125.9, 123.3(q, *J* = 273.1Hz) , 32.3, 31.9, 29.7,29.6, 29.6, 29.4, 29.3, 29.2, 24.3, 22.7, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.36. **IR (KBr):** *v* (cm^{-1}) 2926, 2855, 1769, 1732, 1683, 1425, 1323, 1241, 1065, 700. **HRMS (ESI)** calcd for $C_{25}H_{38}F_3NO_3Na$ $[M + Na]^+$: 480.2696, found: 480.2702.



(*5R,8R,9S,10S,13R,17S*)-10,13-Dimethyl-17-((*R*)-5-(methyl((4-(trifluoromethyl)benzoyl)oxy)amino)-5-oxopentan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (1j)

1j was prepared from lithocholic acid according to the reference.[2] Purification by column chromatography on silica gel with petroleum ether/ ethyl acetate (~ 15:1, v: v): white solid, m.p. 288-293 ℃. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 4.72-4.66(m, 1H), 3.41 (s, 3H), 2.34-2.28 (m, 1H), 2.24-2.17(m,1H), 2.01 (s, 3H), 1.92 -1.88 (m, 1H), 1.84 -1.76 (m, 6H), 1.67-1.63 (m, 1H), 1.53-1.49 (m, 2H), 1.46-1.30 (m, 8H), 1.27-1.16 (m, 3H), 1.10-0.98 (m, 5H), 0.89 (s, 3H), 0.83 (d, *J* = 6.0 Hz, 3H), 0.59 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 170.7, 163.2, 135.8 (q, *J* = 33.4 Hz), 130.4, 130.2, 125.9, 123.3 (q, *J* = 273.1 Hz), 74.4, 56.5, 56.1, 42.7, 41.9, 40.4, 40.1, 35.7, 35.4, 35.0, 34.5, 32.2, 30.5, 29.4, 28.2, 27.0, 26.6, 26.3, 24.1, 23.3, 21.4, 20.8, 18.4, 12.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.35. **IR (KBr):** *v* (cm^{-1}) 2929, 2866, 1770, 1732, 1680, 1448, 1323, 1241, 1066, 700. **HRMS (ESI)** calcd for$C_{35}H_{48}F_3NO_5Na$ $[M + Na]^+$: 642.3377, found: 642.3375.

3.2 Preparation of 1,3-Dienes and 1,3-Enynes

1,3-Dienes were synthesized by Wittig reaction and 1,3-enynes were prepared by Sonogashira coupling as our previous publication.[4]

4. Stern-Volmer Fluorescence Quenching Experiments

Emission intensities were recorded using F-320 Luminescence Spectrometer for all experiments. DCE was degassed with argon for at least 30 minutes by ultrasonic

treatment. All *fac*-Ir(ppy)$_3$ solutions were excited at 395 nm and the emission intensity was collected at 450-650 nm. In a typical experiment, the DCE solution of *fac*-Ir(ppy)$_3$ (0.1 mM) was added the appropriate amount of substrate **1a** in a screw-top 1.0 cm quartz cuvette. After degassing with argon for 10 min, the emission spectra of the samples were collected.

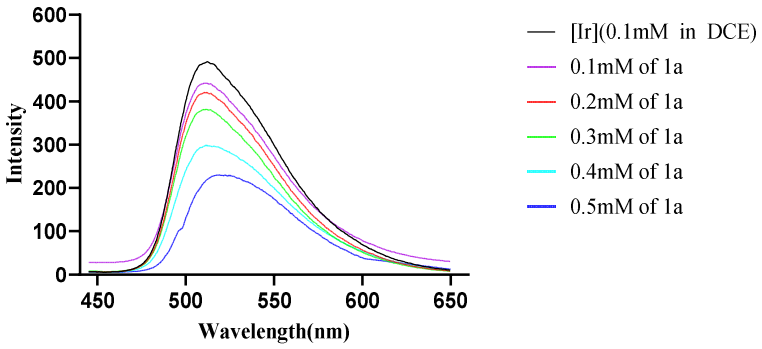


Figure S2. Fluorescence quenching by 1a

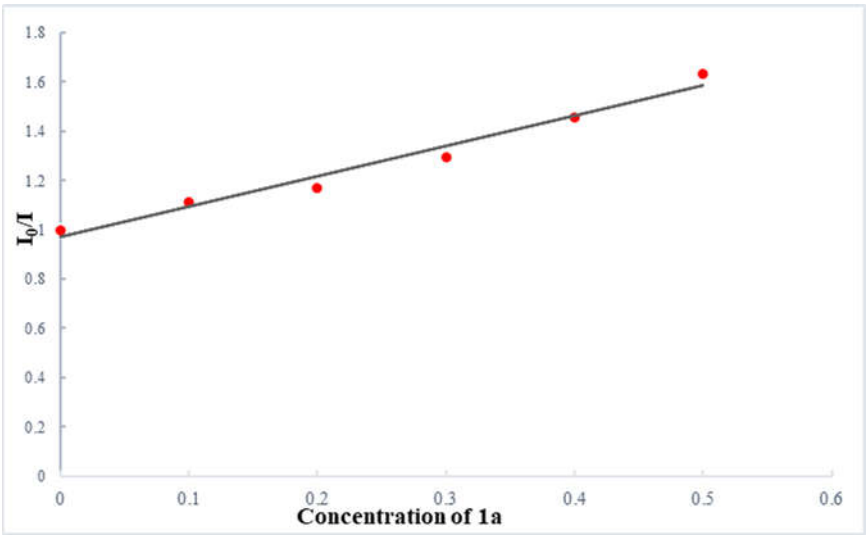
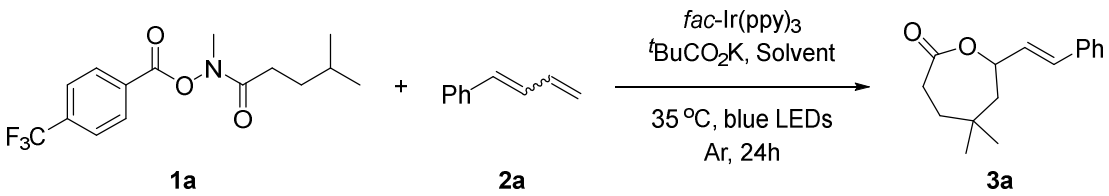


Figure S3. Stern−Volmer fluorescence quenching

5 The Optimization of the Reaction

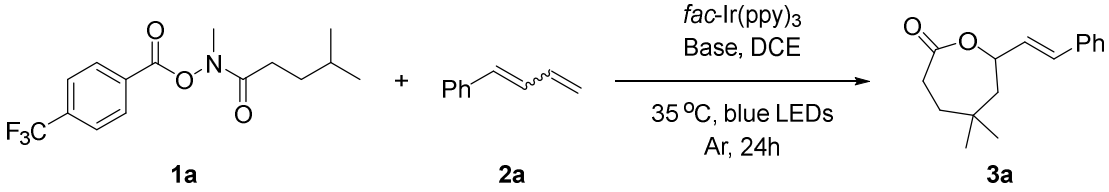
Table S1. The optimization of solvents



Entry	Solvent	Yield (%)[a]
1	CH_3CN	51
2	NMP	< 5
3	**DCE**	**63**
4	DMF	35
5	DME	30
6	THF	30
7	1,4-Dioxane	20
8	DMSO	< 5
9	Toluene	0
10	MeOH	0

Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), ^{t}BuCO$_2$K (0.4mmol), *fac*-Ir(ppy)$_3$ (3 mol%), and Solvent (2 mL, 0.1 M) for 24 h at 35 °C under Ar, blue LEDs (22 W). [a]Isolated yield.

Table S2. The optimization of bases

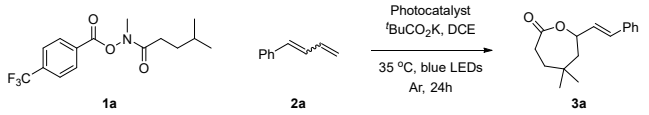


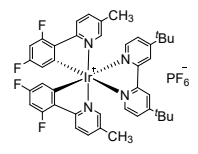
Entry	Base	Yield (%)[a]
1	–	0
2	K_3PO_4	44
3	K_2CO_3	< 5
4	Cs_2CO_3	35
5	NaOH	< 5
6	Na_3PO_4	15

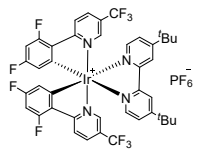
7	Na_2CO_3	25
8	**^{t}BuCO$_2$K**	**63**
9	DBU	35
10	Et_3N	< 5
11	CH_3OK	0

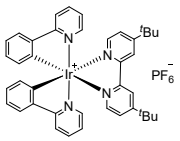
Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), Base (0.4mmol), *fac*-Ir(ppy)$_3$ (3 mol%), and DCE (2 mL, 0.1 M) for 24 h at 35 ℃ under Ar, blue LEDs (22 W). [a]Isolated yield.

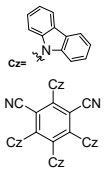
Table S3. The optimization of Photocatalysts

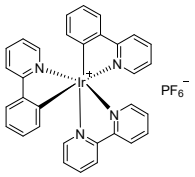


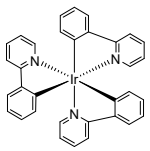

[Ir(dF(CH$_3$)ppy)$_2$(dtbbpy)]PF$_6$

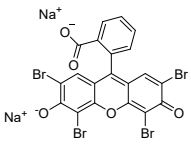

[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$


[Ir(ppy)$_2$(dtbbpy)]PF$_6$


4CzIPN


[Ir(ppy)$_2$(bpy)]PF$_6$


fac-Ir(ppy)$_3$

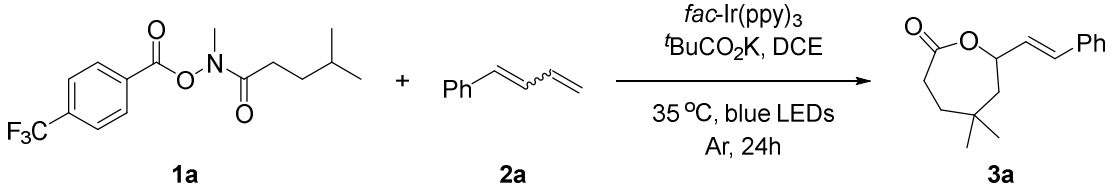

EosinY

Entry	Photocatalyst	Yield (%)[a]
1	–	0
2	4CzIPN	0
3	Eosin Y	0
4	[Ir(dF(CH$_3$)ppy)$_2$(dtbbpy)]PF$_6$	30
5	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	25
6	[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$	20
7	[Ir(ppy$_)2$(bpy)]PF$_6$	45

8	***fac*-Ir(ppy)$_3$**	**63**
9[b]	*fac*-Ir(ppy)$_3$	0

Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), ^{t}BuCO$_2$K (0.4mmol), Photocatalyst (3 mol%), and DCE (2 mL, 0.1 M) for 24 h at 35 °C under Ar, blue LEDs (22 W). [a]Isolated yield. [b]In the dark.

Table S4. The optimization of the equivalent of base

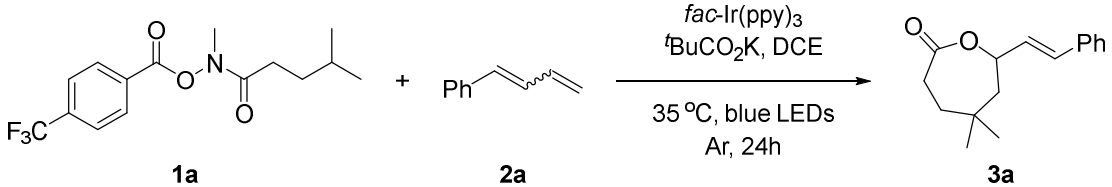


1a **2a** **3a**

Entry	Base	Yield (%)[a]
1	–	0
2	^{t}BuCO$_2$K (1.0 eq)	42
3	^{t}BuCO$_2$K (2.0 eq)	63
4	^{t}BuCO$_2$K (3.0 eq)	68
5	^{t}BuCO$_2$K (4.0 eq)	70
6	**^{t}BuCO$_2$K (5.0 eq)**	**75**
7	^{t}BuCO$_2$K (6.0 eq)	70
8[b]	^{t}BuCO$_2$K (5.0 eq)	25

Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), ^{t}BuCO$_2$K, *fac*-Ir(ppy)$_3$ (3 mol%), and DCE (2 mL, 0.1 M) for 24 h at 35 °C under Ar, blue LEDs (22 W). [a]Isolated yield. [b]Reaction was performed in air.

6. Typical procedures



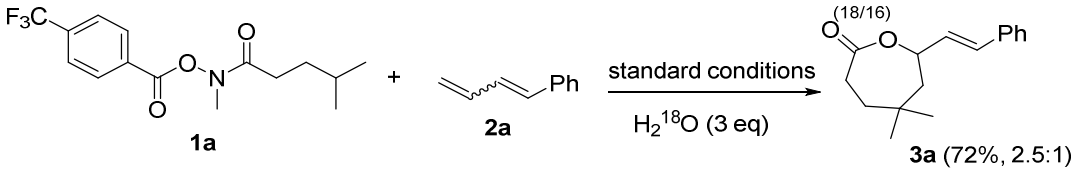
1a **2a** **3a**

Typical procedure: In a flame-dried 10 mL Schlenk tube equipped with a magnetic

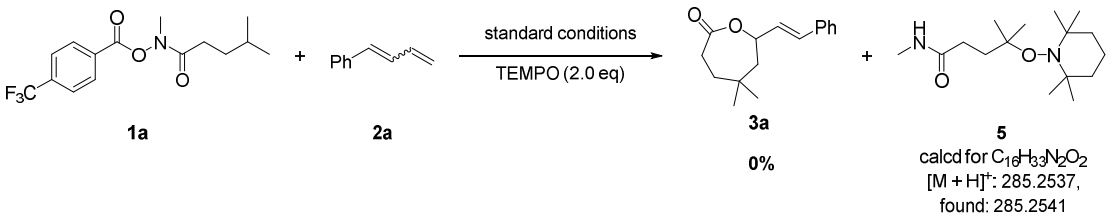
stir bar was charged sequentially with **1a** (65.5 mg, 0.20 mmol), **2a** (52.1 mg, 0.40 mmol), *fac*-Ir(PPy)$_3$ (3.9 mg, 0.006 mmol) and ^{t}BuCO$_2$K (142.2 mg, 1.0 mmol), followed by the addition of DCE (2.0 mL). The mixture was degassed and refilled with Ar, and then irradiated with blue LEDs (22 W) for 24 h at 35 ℃. The solvent was removed under vaccum and the residue was purified by column chromatography on silica gel using PE/EA (12:1) as eluent to afford **3a** in 75% yield.

Scale-up experiment: In a flame-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with **1a** (1.11 g, 3.5 mmol), **2a** (920 mg, 7.0 mmol), *fac*-Ir(PPy)$_3$ (68.7 mg, 0.10 mmol) and ^{t}BuCO$_2$K (2.50 g, 17.5 mmol), followed by the addition of DCE (25 mL). The mixture was degassed and refilled with N_2 gas, and then irradiated with blue LEDs (22 W) for 24 h at 35 ℃. The solvent was removed under vaccum and the residue was purified by column chromatography on silica gel using PE/EA (12:1) as eluent to afford **3a** (564.4 mg) in 66% yield.

7. Control Experiment

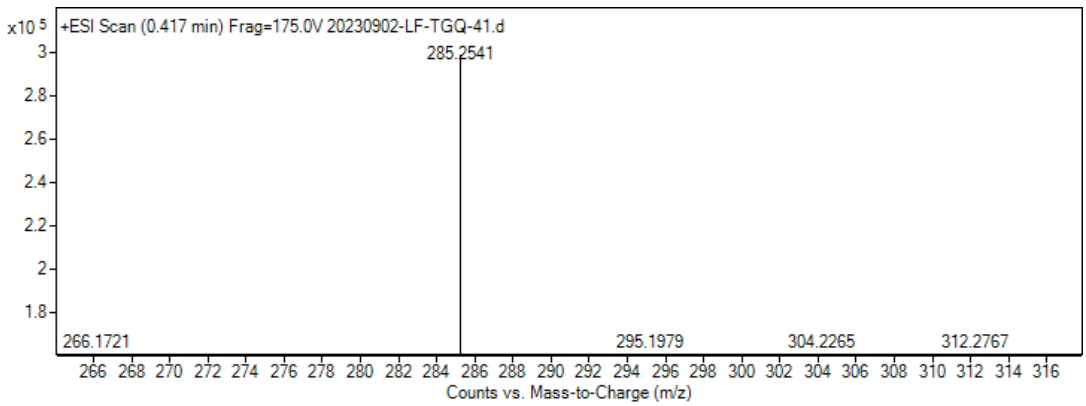


In a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with **1a** (65.5 mg, 0.20 mmol), **2a** (52.1 mg, 0.40 mmol), *fac*-Ir(PPy)$_3$ (3.9 mg, 0.006 mmol), ^{t}BuCO$_2$K (142.2 mg, 1.0 mmol), and $H_2{}^{18}O$ (12.1 mg, 0.60 mmol), followed by the addition of DCE (2.0 mL). The mixture was degassed and refilled with Ar gas, and then irradiated with blue LEDs (22 W) at 35 ℃ for 24 h. The solvent was removed under vaccum and the residue was purified by column chromatography on silica gel using PE/EA (12:1) as eluent to afford **3a** in 72% yield. The isotopic ratio of the product was determined by ESI-MS: $C_{16}H_{21}O_2$ $[M + H]^+$ (245 for **3a**-^{16}O and 247 for **3a**-^{18}O).

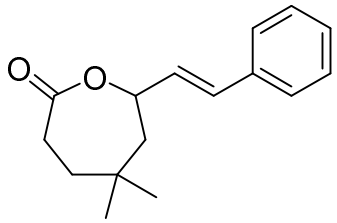


In a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with **1a** (65.5 mg, 0.20 mmol), **2a** (52.1 mg, 0.40 mmol), *fac*-Ir(PPy)$_3$ (3.9 mg, 0.006 mmol), ^{t}BuCO$_2$K (142.2 mg, 1.0 mmol), and TEMPO (64.4 mg, 0.4 mmol), followed by the addition of DCE (2.0 mL). The mixture was degassed and refilled with Ar gas, and then irradiated with blue LEDs (22 W) at 35 ℃ for 24 h. TEMPO-trapped product **5** was determined by HRMS.

HRMS (ESI) of 5: calcd for $C_{16}H_{33}N_2O_2[M + H]^+$: 285.2537, found:285.2541

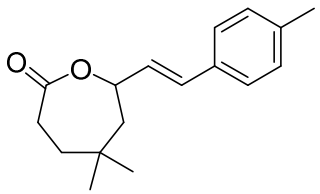


8. Characterization of the Products



(*E*)-5,5-Dimethyl-7-styryloxepan-2-one (3a)

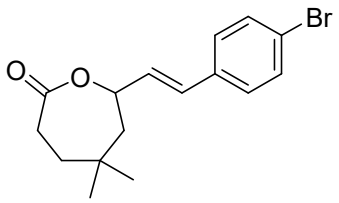
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a white solid (37 mg, 75% yield); m.p.134-138 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39-7.35 (m, 2H), 7.35-7.29 (m, 2H), 7.28-7.23 (m, 1H), 6.68 (dd, *J* = 16.0, 1.3 Hz, 1H), 6.19 (dd, *J* = 15.9, 6.2 Hz, 1H), 5.02 (dd, *J* = 9.6, 6.2 Hz, 1H), 2.81-2.74 (m, 1H), 2.60 -2.54 (m, 1H), 1.80 (dd, *J* = 15.3, 9.6 Hz, 1H), 1.72 -1.61 (m, 3H), 1.13 (s, 3H), 1.02 (s, 3H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 175.0, 136.2, 131.0, 128.6, 128.0, 126.6, 75.9, 48.4, 35.7, 32.6, 32.2, 30.6, 25.0. **IR (KBr):** *v* (cm^{-1}) 2956, 2920, 1714, 1445, 1260, 691. **HRMS (ESI)** calcd for $C_{16}H_{20}O_2Na$ [M + Na]$^+$: 267.1356, found: 267.1364.



(*E*)-5,5-Dimethyl-7-(4-methylstyryl)oxepan-2-one (3b)

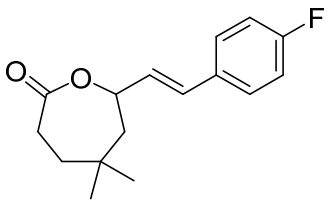
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a white solid (34 mg, 65% yield), m.p. 136-139 ℃; **^{1}H NMR (400 MHz, CDCl3)** δ 7.26 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.00 (dd, *J* = 9.8, 6.3 Hz, 1H), 2.79-2.74 (m, 1H), 2.58-2.54 (m, 1H), 2.33 (s, 3H), 1.79 (dd, *J* = 15.3, 9.8 Hz, 1H), 1.68-1.61 (m, 3H), 1.12 (s, 3H), 1.01 (s, 3H). **^{13}C{1H} NMR (101 MHz, CDCl3)** δ 175.1, 137.9, 133.4, 130.9, 129.3, 126.9, 126.5, 76.0, 48.4, 35.6, 32.6, 32.1, 30.6, 24.9, 21.2. **IR (KBr):** *v*

(cm^{-1}) 2957, 2920, 1715, 1646, 1259, 798. **HRMS (ESI)** calcd for $C_{17}H_{23}O_2$ $[M + H]^+$: 259.1693, found:259.1698.



(*E*)-7-(4-Bromostyryl)-5,5-dimethyloxepan-2-one (3c)

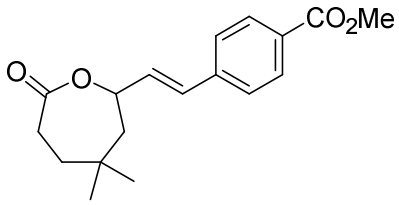
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (43 mg, 66% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45-7.42 (m, 2H), 7.24-7.21 (m, 2H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 6.1 Hz, 1H), 5.00 (dd, *J* = 9.7, 6.1 Hz, 1H), 2.78-2.73 (m, 1H), 2.58-2.55 (m, 1H), 1.77 (dd, *J* = 15.3, 9.8 Hz, 1H), 1.70-1.61 (m, 3H), 1.12 (s, 3H), 1.02 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.9, 135.1, 131.8, 129.7, 128.7, 128.1, 121.8, 75.5, 48.2, 35.6, 32.6, 32.1, 30.6, 24.9. **IR (KBr):** *v* (cm^{-1}) 2956, 2921, 1720, 1468, 1258, 803. **HRMS (ESI)** calcd for $C_{16}H_{19}BrO_2Na$ $[M + Na]^+$: 345.0461, found: 345.0468



(*E*)-7-(4-Fluorostyryl)-5,5-dimethyloxepan-2-one (3d)

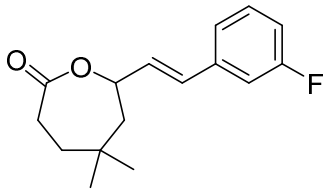
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a yellow oil (39 mg, 74% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35-7.30 (m, 2H), 7.03-6.97 (m, 2H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 15.9, 6.2 Hz, 1H), 5.00 (dd, *J* = 9.9, 6.2 Hz, 1H), 2.79-2.74 (m, 1H), 2.58-2.54 (m, 1H), 1.78 (dd, *J* = 15.3, 9.8 Hz, 1H), 1.71-1.62 (m, 3H), 1.12 (s, 3H), 1.01 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.9, 162.5 (d, *J* = 247.6 Hz), 132.3 (d, *J* = 3.3 Hz), 129.8, 128.1 (d, *J* = 8.0 Hz), 127.7, 115.6, 115.5, 75.7, 48.3, 35.6, 32.6, 32.1, 30.6, 24.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.83. (s, 1F). **IR (KBr):** *v* (cm^{-1}) 2955, 2923, 1712, 1508, 1259, 806. **HRMS (ESI)** calcd for $C_{16}H_{19}FO_2Na$ $[M + Na]^+$: 285.1261, found:

285.1270.



Methyl (*E*)-4-(2-(4,4-dimethyl-7-oxooxepan-2-yl)vinyl)benzoate (3e)

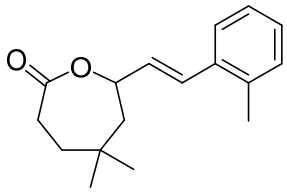
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give a white solid (37 mg, 61% yield); m.p. 138-142 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03-8.00 (m, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 11.6 Hz, 1H), 5.87 (dd, *J* = 11.6, 8.9 Hz, 1H), 5.19 (t, *J* = 9.5 Hz, 1H), 3.91 (s, 3H), 2.60-2.55 (m, 1H), 2.49-2.45 (m, 1H), 1.84 (dd, *J* = 15.5, 10.0 Hz, 1H), 1.65-1.53 (m, 3H), 0.98 (s, 3H), 0.97 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.9, 166.7, 140.8, 132.2, 129.9, 129.7, 129.2, 128.5, 72.0, 52.2, 47.9, 35.6, 32.6, 32.4, 30.6, 24.9. **IR (KBr):** *v* (cm^{-1}) 2955, 2920, 1711, 1434, 1277, 701. **HRMS (ESI)** calcd for $C_{18}H_{22}O_4Na$ $[M + Na]^+$: 325.1410, found: 325.1419.



(*E*)-7-(3-Fluorostyryl)-5,5-dimethyloxepan-2-one (3f)

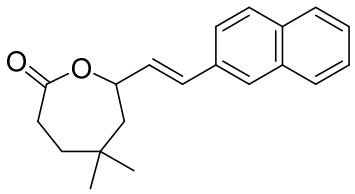
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a white solid (37 mg, 61% yield); m.p. 124-128 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31-7.24 (m, 1H), 7.16-7.04 (m, 2H), 6.97-6.92(m, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 6.0 Hz, 1H), 5.02 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.81-2.73 (m, 1H), 2.60 -2.54 (m, 1H), 1.78 (dd, *J* = 15.3, 9.6 Hz, 1H), 1.71-1.60 (m, 3H), 1.13 (s, 3H), 1.03 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.9, 163.1 (d, *J* = 245.6 Hz), 138.6 (d, *J* = 7.9 Hz), 130.1 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 2.8 Hz), 129.4, 122.5 (d, *J* = 2.9 Hz), 114.8 (d, *J* = 21.2 Hz), 113.0 (d, *J* = 21.8 Hz), 75.4, 48.3, 35.6, 32.6, 32.2, 30.6, 24.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.31 (s, 1F). **IR (KBr):** *v* (cm^{-1}) 2952,

2923, 1716, 1580, 1297, 786, 681. **HRMS (ESI)** calcd for $C_{16}H_{19}FO_2Na$ $[M + Na]^+$: 285.1261, found:285.1268.



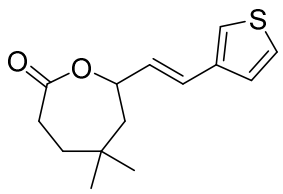
(*E*)-5,5-Dimethyl-7-(2-methylstyryl)oxepan-2-one (3g)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (31 mg, 60% yield). **^{1}H NMR (400 MHz, CDCl3)** δ 7.44-7.37 (m, 1H), 7.22-7.11 (m, 3H), 6.86 (dd, *J* = 15.8, 1.3 Hz, 1H), 6.07 (dd, *J* = 15.7, 6.4 Hz, 1H), 5.03 (dd, *J* = 9.7, 6.4 Hz, 1H), 2.82-2.75 (m, 1H), 2.60-2.54 (m, 1H), 2.35 (s, 3H), 1.81 (dd, *J* = 15.3, 9.6 Hz, 1H), 1.70-1.62 (m, 3H), 1.14 (s, 3H), 1.02 (s, 3H). **^{13}C{1H} NMR (101 MHz, CDCl3)** δ 175.1, 135.7, 135.3, 130.3, 129.4, 128.9, 127.9, 126.1, 125.8, 76.1, 48.4, 35.7, 32.7, 32.2, 30.6, 25.0, 19.8. **IR (KBr):** *v* (cm^{-1}) 2950, 2913, 1722, 1455, 1295, 1026, 742. **HRMS (ESI)** calcd for $C_{17}H_{22}O_2Na$ $[M + Na]^+$: 281.1512, found: 281.1520.



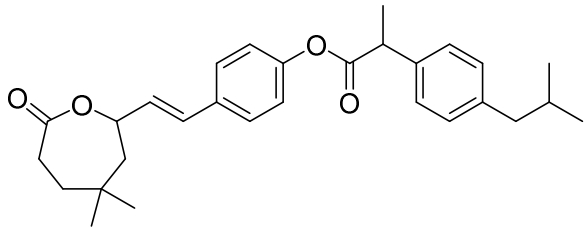
(*E*)-5,5-Dimethyl-7-(2-(naphthalen-2-yl)vinyl)oxepan-2-one (3h)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a white solid (40 mg, 68% yield); m.p. 135-140 ℃; **^{1}H NMR (400 MHz, CDCl3)** δ 7.81-7.77 (m, 3H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.57 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.49-7.43 (m, 2H), 6.83 (d, *J* = 15.9 Hz, 1H), 6.32 (dd, *J* = 15.9, 6.2 Hz, 1H), 5.07 (dd, *J* = 9.8, 6.2 Hz, 1H), 2.82-2.77 (m, 1H), 2.61-2.57 (m, 1H), 1.83 (dd, *J* = 15.4, 9.7 Hz, 1H), 1.74 -1.64 (m, 3H), 1.15 (s, 3H), 1.04 (s,3H). **^{13}C{1H} NMR (101 MHz, CDCl3)** δ 175.0, 133.6, 133.5, 133.1, 131.1, 128.3, 128.0, 127.7, 126.8, 126.3, 126.1, 123.4, 75.9, 48.4, 35.6, 32.7, 32.2, 30.6, 25.0. **IR (KBr):** *v* (cm^{-1}) 2950, 2921, 1709, 1444, 1258, 807. **HRMS (ESI)** calcd for $C_{20}H_{22}O_2Na$ $[M + Na]^+$: 317.1512, found:317.1518.



(*E*)-5,5-Dimethyl-7-(2-(thiophen-3-yl)vinyl)oxepan-2-one (3i)

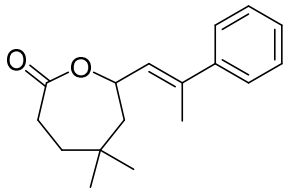
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (30 mg, 60% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.28-7.25 (m, 1H), 7.19-7.16 (m, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.04 (dd, *J* = 15.9, 6.2 Hz, 1H), 4.97 (dd, *J* = 9.8,6.2 Hz, 1H), 2.78-2.73 (m, 1H), 2.57-2.53 (m, 1H),1.76 (dd, *J* = 15.3, 9.7 Hz, 1H), 1.69-1.59 (m, 3H), 1.11 (s, 3H), 1.00 (s, 3H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 175.0, 138.8, 127.8, 126.2, 125.1, 124.8, 122.9, 75.7, 48.3, 35.6, 32.6, 32.1, 30.6, 24.9. **IR (KBr):** *v* (cm^{-1}) 2950, 2921, 1712, 1443, 1293, 965, 773. **HRMS (ESI)** calcd for $C_{14}H_{19}O_2S$ $[M + H]^+$: 251.1100, found: 251.1107.



(*E*)-4-(2-(4,4-Dimethyl-7-oxooxepan-2-yl)vinyl)phenyl 2-(4-isobutylphenyl) propanoate (3j)

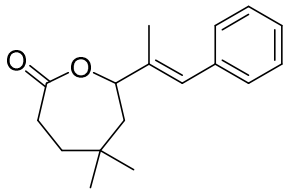
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a white solid (62 mg, 69% yield); m.p. 199-204 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.36-7.27 (m, 4H), 7.17-7.12 (m, 2H), 6.99-6.94 (m, 2H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.9, 6.1 Hz, 1H), 5.00 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 1H), 2.79-2.72 (m, 1H), 2.58-2.46 (m, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.92-1.82 (m,1H), 1.77 (dd, *J* =15.3, 9.6 Hz, 1H), 1.69-1.58 (m, 6H), 1.11 (s, 3H), 1.01 (s, 3H), 0.91(d, *J* = 6.6 Hz, 6H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 175.0, 173.2, 150.6, 140.9, 137.2, 133.9, 130.0, 129.6, 128.2, 127.5, 127.2, 121.7, 75.7, 48.3, 45.3, 45.1, 35.7, 32.6, 32.2, 30.6, 30.2, 24.9, 22.4, 18.5. **IR (KBr):** *v* (cm^{-1}) 2954, 2920, 1733,

1731, 1506, 1453, 1162, 1121, 1062, 735. **HRMS (ESI)** calcd for $C_{29}H_{36}O_4Na$ [M + Na]$^+$: 471.2506, found: 471.2512.



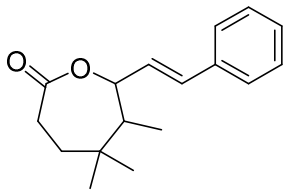
(*E*)-5,5-Dimethyl-7-(2-phenylprop-1-en-1-yl)oxepan-2-one (3k)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a white solid (31 mg, 60% yield); m.p. 125-128 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.29-7.25 (m, 1H), 5.90 (dd, *J* = 7.8, 1.5 Hz,1H), 5.27 (dd, *J* = 9.9, 7.9 Hz, 1H), 2.84-2.79 (m, 1H), 2.59-2.55 (m, 1H), 2.08 (d, *J* = 1.2 Hz, 3H), 1.86 (dd, *J* = 15.5, 10.0 Hz, 1H), 1.69-1.61 (m, 3H), 1.17 (s, 3H), 1.01 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 175.4, 142.3, 136.9, 128.3, 127.5, 126.9, 125.9, 73.3, 48.5, 35.6, 32.6, 32.2, 30.7, 24.9, 16.5. **IR (KBr):** *v* (cm^{-1}) 2949, 1704, 1341, 1260, 1158, 1062, 760, 691. **HRMS (ESI)** calcd for $C_{17}H_{22}O_2Na$ [M + Na]$^+$: 281.1512, found: 281.1520.



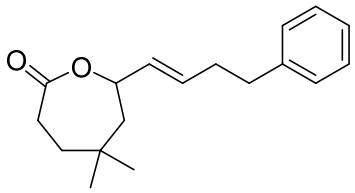
(*E*)-5,5-Dimethyl-7-(1-phenylprop-1-en-2-yl)oxepan-2-one (3l)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a white solid (27 mg, 52% yield); m.p. 120-124 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36-7.30 (m, 2H), 7.28-7.19 (m, 3H), 6.57 (s, 1H), 4.85 (d, *J* = 9.6 Hz, 1H), 2.84-2.76 (m, 1H), 2.58-2.53 (m, 1H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.86 (dd, *J* = 15.2, 9.7 Hz, 1H), 1.69-1.59 (m, 3H), 1.14 (s, 3H), 1.03 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 175.2, 136.9, 136.7, 129.0, 128.2, 127.0, 126.8, 81.0, 47.1, 35.8, 32.8, 32.1, 30.7, 24.7, 13.8. **IR (KBr):** *v* (cm^{-1}) 2955, 2920, 1728, 1446, 1254, 1161, 1064, 698. **HRMS (ESI)** calcd for $C_{17}H_{22}O_2Na$ [M + Na]$^+$: 281.1512, found: 281.1518.



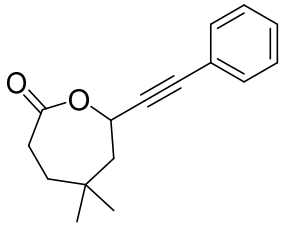
(*E*)-5,5,6-Trimethyl-7-styryloxepan-2-one (3m)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (35 mg, 68% yield). dr = 2:1. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41-7.36 (m, 2H), 7.33-7.31 (m, 2H), 7.28-7.23 (m, 1H), 6.73 (dd, *J* = 16.0, 1.6 Hz, 0.32H)/6.54 (d, *J* = 15.8 Hz, 0.64H), 6.22-6.13 (m, 1H), 5.26 (dd, *J* =5.1, 1.7 Hz, 0.32H)/4.79 (t, *J* = 8.3 Hz, 0.67H), 2.83-2.78 (m, 0.66H) /2.75-2.70 (m, 0.33H), 2.54-2.48 (m, 1H), 1.82-1.58 (m, 3H), 1.18 (s, 1H)/1.03 (s, 2H), 0.99 (s, 2H)/0.96 (s, 1H), 0.91 (d, *J* = 7.1 Hz, 1H)/0.83 (d, *J* = 7.3 Hz, 2H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 175.2, 174.8, 136.4, 136.1, 132.2, 131.1, 128.6, 128.0, 127.8, 127.5, 127.2, 126.6, 126.5, 81.6, 46.9, 46.3, 38.2, 35.2, 34.8, 30.9, 30.7, 30.6, 30.2, 29.8, 26.7, 19.7, 13.4, 8.1. IR (KBr): ν (cm^{-1}) 2958, 2920, 1725, 1448, 1284, 1160, 791, 693. HRMS (ESI) calcd for $C_{17}H_{22}O_2Na$ [M + Na]$^+$: 281.1512, found: 281.1518.



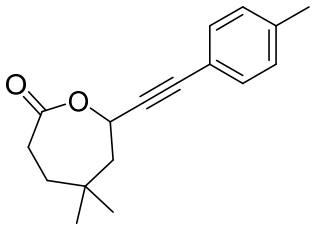
(*E*)-5,5-Dimethyl-7-(3-phenylprop-1-en-1-yl)oxepan-2-one (3n)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (24 mg, 44% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.31-7.25 (m, 2H), 7.21-7.14 (m, 3H), 5.81-5.76 (m, 1H), 5.59-5.48 (m, 1H), 4.78 (dd, *J* = 9.9, 6.7 Hz, 1H), 2.74-2.65 (m, 3H), 2.52-2.48 (m, 1H), 2.40-2.31 (m, 2H), 1.66 (dd, *J* = 15.3, 9.9 Hz, 1H), 1.59-1.51 (m, 3H), 1.06 (s, 3H), 0.97 (s, 3H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 175.2, 141.5, 131.8, 129.5, 128.4, 128.3, 125.9, 76.0, 48.3, 35.6, 35.3, 33.9, 32.6, 32.0, 30.6, 24.9. **IR (KBr):** *ν* (cm^{-1}) 2950, 2922, 1730, 1452, 1257, 1161, 1026, 698. **HRMS (ESI)** calcd for $C_{18}H_{24}O_2Na$ [M + Na]$^+$: 295.1669, found: 295.1673.



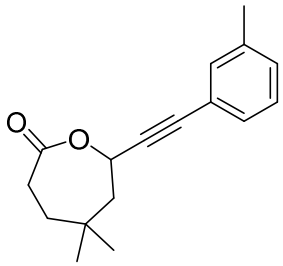
5,5-Dimethyl-7-(phenylethynyl)oxepan-2-one (3o)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (25 mg, 52% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45-7.42 (m, 2H), 7.34-7.29 (m, 3H), 5.32 (d, *J* = 9.5 Hz, 1H), 2.72-2.67 (m, 1H), 2.64-2.60 (m, 1H), 2.07 (dd, *J* = 15.5, 9.6 Hz, 1H), 2.00-1.96 (m, 1H). 1.65-1.60 (m, 2H), 1.12 (s, 3H), 1.06 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.1, 131.7, 128.8, 128.3, 122.0, 86.1, 85.8, 66.6, 48.9, 35.4, 32.2, 32.0, 30.3, 25.3. **IR (KBr):** *v* (cm^{-1}) 2955, 2921, 1737, 1443, 1251, 1160, 755, 690. **HRMS (ESI)** calcd for $C_{16}H_{18}O_2Na$ $[M + Na]^+$: 265.1199, found: 265.1204.



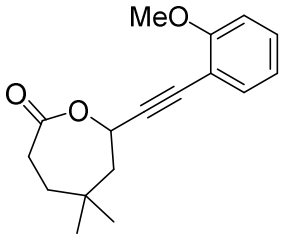
5,5-Dimethyl-7-(p-tolylethynyl)oxepan-2-one (3p)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a pale yellow oil (28 mg, 54% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.31 (d, *J* = 9.4 Hz, 1H), 2.71-2.67 (m, 1H), 2.63-2.59 (m, 1H), 2.34 (s, 3H), 2.06 (dd, *J* = 15.6, 9.5 Hz, 1H), 2.0-1.96 (m, 1H), 1.66-1.59 (m, 2H), 1.11 (s, 3H), 1.05 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.1, 139.0, 131.6, 129.1, 118.9, 86.3, 85.2, 66.7, 48.9, 35.5, 32.2, 32.0, 30.3, 25.3, 21.5. **IR (KBr):** *v* (cm^{-1}) 2955, 2923, 1742, 1509, 1250, 1160, 815. **HRMS (ESI)** calcd for $C_{17}H_{20}O_2Na$ $[M + Na]^+$: 279.1356, found: 279.1363.



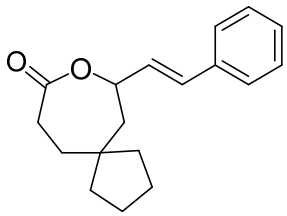
5,5-Dimethyl-7-(m-tolylethynyl)oxepan-2-one (3q)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a pale yellow oil (27 mg, 52% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27-7.17 (m, 3H), 7.18-7.13 (m, 1H), 5.32-5.28 (m, 1H), 2.72-2.67 (m, 1H), 2.64-2.60 (m, 1H), 2.32 (s, 3H), 2.06 (dd, *J* = 15.5, 9.5 Hz, 1H), 2.00-1.95 (m, 1H), 1.67-1.58 (m, 2H), 1.12 (s, 3H), 1.06 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.1, 138.0, 132.3, 129.7, 128.8, 128.2, 121.7, 86.3, 85.5, 66.6, 48.9, 35.5, 32.2, 30.3, 25.3, 21.2. **IR (KBr):** *v* (cm^{-1}) 2955, 2922, 1738, 1449, 1251, 1161, 1120, 783, 690. **HRMS (ESI)** calcd for $C_{17}H_{20}O_2Na$ $[M + Na]^+$: 279.1356, found: 279.1361.



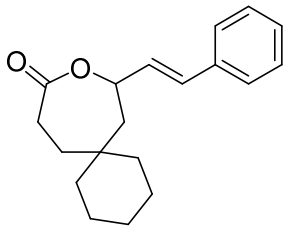
7-((2-Methoxyphenyl)ethynyl)-5,5-dimethyloxepan-2-one (3r)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give a pale yellow oil (27 mg, 50% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.32-7.28 (m, 1H), 6.93-6.83 (m, 2H), 5.37 (dd, *J* = 9.0, 1.5 Hz, 1H), 3.86 (s, 3H), 2.75-2.57 (m, 2H), 2.08 (dd, *J* = 15.6, 9.0 Hz, 1H), 2.03-1.98 (m,1H), 1.66-1.54 (m, 2H), 1.10 (s, 3H), 1.06 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.3, 160.2, 133.9, 130.3, 120.5, 111.2, 110.7, 89.8, 82.7, 66.9, 55.8, 48.8, 35.6, 32.3, 31.8, 30.4, 25.7. **IR (KBr):** *v* (cm^{-1}) 2953, 2920, 1733, 1493, 1259, 1101, 752. **HRMS (ESI)** calcd for $C_{17}H_{20}O_3Na$ $[M + Na]^+$: 295.1305, found: 295.1313.



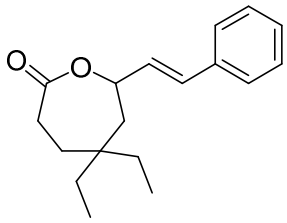
(*E*)-7-Styryl-8-oxaspiro[4.6]undecan-9-one (4a)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (36 mg, 67% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38-7.36 (m, 2H), 7.33-7.30 (m, 2H), 7.28-7.22 (m, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.22 (dd, *J* = 16.0, 6.3 Hz, 1H), 4.98 (dd, *J* = 9.4, 6.4 Hz, 1H), 2.78-2.70 (m, 1H), 2.64-2.57 (m, 1H), 1.87 (dd, *J* = 15.8, 9.4 Hz,1H), 1.80 (d, *J* = 15.3 Hz,1H), 1.74-1.68 (m, 4H), 1.67-1.59 (m, 4H), 1.48-1.39 (m, 2H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 175.1, 136.2, 130.9, 128.6, 128.1, 128.0 126.6, 47.4, 44.5, 42.1, 35.2, 34.5, 31.7, 24.7, 24.2. **IR (KBr):** *v* (cm^{-1}) 2939, 2859, 1728, 1277, 1159, 692. **HRMS (ESI)** calcd for $C_{18}H_{22}O_2Na$ $[M + Na]^+$: 293.1512, found: 293.1521.



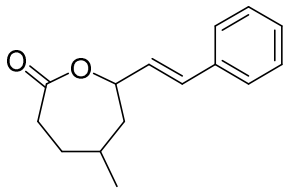
(*E*)-8-Styryl-9-oxaspiro[5.6]dodecan-10-one (4b)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (35 mg, 61% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40-7.36 (m, 2H), 7.34-7.29 (m, 2H), 7.27-7.22 (m, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.02 (dd, *J* = 9.7, 6.4 Hz, 1H), 2.80-2.71 (m, 1H), 2.55-2.49 (m,1H), 1.97 (dd, *J* = 15.5, 2.3 Hz, 1H), 1.91-1.84 (m, 1H), 1.68-1.54 (m, 3H), 1.52-1.40 (m, 7H), 1.32-1.24 (m, 2H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 175.2, 136.2, 130.8, 128.7, 128.4, 128.0, 126.6, 75.0, 45.8, 41.0, 34.0, 33.2, 32.3, 29.6, 26.4, 21.3 , 21.2. **IR (KBr):** *v* (cm^{-1}) 2923, 2852, 1729, 1447, 1279, 746, 691. **HRMS (ESI)** calcd for $C_{19}H_{25}O_2$ $[M + H]^+$: 285.1849, found: 285.1849.



(*E*)-5,5-Diethyl-7-styryloxepan-2-one (4c)

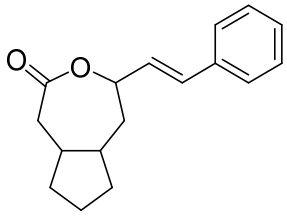
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a pale yellow oil (38 mg, 70% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40-7.36 (m, 2H), 7.33-7.30 (m, 2H), 7.28-7.22 (m, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.02 (dd, *J* = 9.7, 6.4 Hz, 1H), 2.81-2.71 (m, 1H), 2.55-2.51 (m, 1H), 1.77 (dd, *J* = 15.5, 2.2 Hz, 1H), 1.72-1.63 (m, 2H), 1.58-1.46 (m, 3H), 1.33-1.23 (m, 2H), 0.83 (t, *J* = 7.5 Hz, 3H), 0.80 (t, *J* = 7.6 Hz, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 175.2, 136.2, 130.8, 128.6, 128.2, 128.0, 126.6, 75.3, 44.1, 36.5, 32.6, 31.2, 29.8, 24.9, 7.4 , 7.3. **IR (KBr):** *v* (cm^{-1}) 2964, 2936, 1729, 1448, 1277, 1168, 744, 692. **HRMS (ESI)** calcd for $C_{18}H_{24}O_2Na$ $[M + Na]^+$: 295.1669, found: 295.1674.



(*E*)-5-Methyl-7-styryloxepan-2-one (4d)

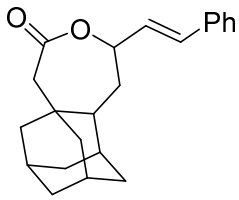
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (24 mg, 52% yield). dr = 2.4:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 7.0 Hz, 2H), 7.33-7.30 (m, 2H), 7.27-7.22 (m, 1H), 6.67 (m, 1H), 6.25-6.20 (m, 1H), 5.09 (t, *J* =7.1 Hz, 0.30H)/4.94 (dd, *J* = 9.6, 6.4 Hz, 0.71H), 2.87-2.85 (m, 0.3H), 2.73-2.65 (m, 1.4H), 2.63-2.58 (m, 0.3H), 2.15-1.97 (m, 1H), 1.95-1.84 (m, 2H), 1.64-1.51 (m, 1H), 1.39-1.32 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 0.9H)/1.00 (d, *J* = 6.4 Hz, 2.1H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 174.9, 174.7, 136.2, 136.1, 131.4, 131.0, 128.7, 128.6, 128.1, 128.0, 127.9, 127.5, 126.6, 126.5, 79.7, 75.9, 43.7, 41.5, 35.4, 34.1, 31.3, 30.9, 28.7, 28.6, 22.6, 19.9. **IR (KBr):** *v* (cm^{-1})

2968, 2921, 1725, 1448, 1284, 1160, 791, 693. **HRMS (ESI)** calcd for $C_{15}H_{18}O_2Na$ [M + Na]$^+$: 253.1199, found: 253.1204



(*E*)-4-Styryloctahydro-2H-cyclopenta[d]oxepin-2-one (4e)

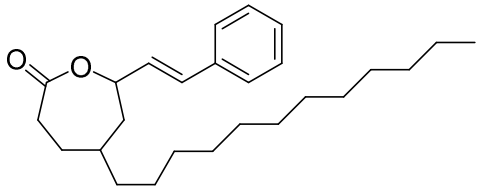
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (34 mg, 66% yield). dr = 20:1:1. For the major isomer: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.38-7.35 (m, 2H), 7.32-7.30 (m, 2H), 7.27-7.23 (m, 1H), 6.68 (dd, *J* = 16.0, 1.3 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.3 Hz, 1H), 4.93 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.80 (d, *J* = 14.0 Hz, 1H), 2.55 (dd, *J* = 14.0, 11.4 Hz, 1H), 2.22-2.15 (m, 1H), 1.96-1.84 (m, 2H), 1.74-1.64 (m, 2H), 1.63-1.50 (m, 3H), 1.34-1.23 (m, 2H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 174.0, 136.2, 131.0, 128.6, 128.0, 127.9, 126.6, 80.6, 49.2, 41.3, 39.7, 39.0, 32.5, 31.9, 21.4. **IR (KBr):** *v* (cm^{-1}) 2922, 2862, 1724, 1449, 1246, 966, 750, 694. **HRMS (ESI)** calcd for $C_{17}H_{20}O_2Na$ [M + Na]$^+$: 279.1356, found: 279.1362.



(*5aS,7R,9S,11R,11aS*)-2-((*E*)-Styryl)octahydro-2H-5a,9:7,11-dimethanocycloocta [d]oxepin-4(5H)-one (4f)

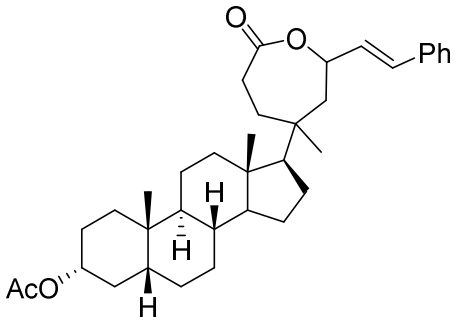
Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a white solid (44 mg, 68% yield); m.p.145-150 ℃; dr = 4.5:1. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.27-7.22 (m, 1H), 6.69 (d, *J* = 15.9 Hz, 0.81H)/6.64 (d, *J* = 16.1 Hz, 0.19H), 6.27 (dd, *J* = 16.1,5.4 Hz, 0.18H)/6.23 (dd, *J* =15.9, 6.2 Hz, 0.82H), 5.06 (m, 0.17H)/4.95 (dd, *J* = 9.6, 6.2 Hz, 0.83H), 2.72

(d, *J* =13.3Hz, 0.84H)/2.50 (d, *J* = 13.4 Hz, 0.16H), 2.38-2.29 (m, 0.39H)/2.25-2.19 (m, 1.61H), 2.03-1.92 (m, 2H), 1.88-1.76 (m, 4H), 1.75-1.66 (m, 4H), 1.66-1.58 (m, 2H), 1.57-1.47 (m, 3H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 173.1, 172.8, 136.2, 136.1, 131.7, 130.9, 128.7, 128.6, 128.1, 128.0, 127.9, 127.3, 126.6, 79.9, 77.2, 50.1, 48.4, 46.7, 46.0, 43.3, 38.6, 38.3, 38.1, 37.1, 37.0, 36.8, 35.8, 35.3, 34.4, 33.3, 33.1, 32.9, 31.1, 31.0, 28.8, 28.7, 28.5, 28.3, 27.1. **IR (KBr):** *v* (cm^{-1}) 2904, 2849, 1711, 1450, 1264, 971, 744, 693. **HRMS (ESI)** calcd for $C_{22}H_{26}O_2Na$ [M + Na]$^+$: 345.1825, found: 345.1829.



(*E*)-5-Dodecyl-7-styryloxepan-2-one (4h)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (52.3 mg, 68% yield). dr = 4:1. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.39 -7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.28-7.23 (m, 1H), 6.71-6.64 (m, 1H), 6.23 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.09-5.06 (m, 0.20H)/4.93 (dd, *J* = 9.6, 6.4 Hz, 0.80H), 2.86-2.82 (m, 0.20 H), 2.75-2.64 (m, 1.60 H), 2.63-2.60 (m, 0.20 H), 2.09-2.04 (m, 1H), 2.00-1.95 (m, 1H), 1.90-1.84 (m, 0.40H)/1.74-1.63 (m, 1.60H), 1.57-1.51 (m, 1H), 1.38-1.26 (m, 22H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 175.0, 174.7, 136.2, 136.1, 131.3, 131.0, 128.6, 128.1, 128.0, 128.0, 127.6, 126.6, 79.8, 76.2, 41.9, 40.3, 39.8, 36.9, 34.1, 33.9, 33.9, 31.9, 31.5, 29.7, 29.6, 29.6, 29.4, 29.1, 27.2, 26.7, 26.6, 22.7, 14.1. **IR (KBr):** *v* (cm^{-1}) 2929, 2866, 1729, 1448, 1241, 1025, 729, 692. **HRMS (ESI)** calcd for $C_{26}H_{40}O_2Na$ [M+Na]$^+$: 407.2921, found: 407.2918.



(*5R,8R,9S,10S,13S,17R*)-10,13-Dimethyl-17-(4-methyl-7-oxo-2-((*E*)-styryl)oxepan-4-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (4i)

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 12:1) to give a colorless oil (55 mg, 50% yield). dr = 2.9:1.7:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 -7.35 (m, 2H), 7.34-7.29 (m, 2H), 7.27-7.22 (m, 1H), 6.72 (d, *J* = 15.9 Hz, 0.18H)/6.69-6.63 (m, 0.82H), 6.21-6.11 (m, 1H), 5.16 (dd, *J* = 9.6, 6.0 Hz, 0.18H)/5.08 (dd, *J* = 9.4, 6.3 Hz, 0.30H)/5.03 (dd, *J* = 9.9, 6.2 Hz, 0.52H), 4.76-4.64 (m, 1H), 2.94 (t, *J* = 13.7 Hz, 0.35 H) / 2.84-2.76 (m, 0.74 H)/2.55-2.46 (m, 1H), 2.22 -2.09 (m, 1H), 2.04-2.01 (m, 3H), 2.01-1.91 (m, 2H), 1.90-1.75 (m, 4H), 1.73-1.07 (m, 23H), 0.95-0.89 (m, 3H), 0.81-0.74 (m, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 175.3, 175.1, 170.6, 136.3, 136.2, 131.3, 130.9, 130.8, 130.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.3, 126.6, 75.4, 75.1, 74.3, 74.2, 62.9, 62.8, 57.1, 56.5, 50.7, 49.0, 47.2, 47.1, 44.1, 44.1, 43.8, 41.8, 41.4, 41.4, 40.6, 40.4, 40.4, 40.3, 38.9, 38.8, 37.6, 35.3, 35.2, 35.0, 34.5, 34.5, 34.1, 33.9, 32.2, 30.3, 30.2, 29.9, 27.0, 26.9, 26.6, 26.2, 26.1, 26.1, 23.4, 23.3, 23.1, 22.8, 22.7, 21.5, 20.9, 20.7, 15.4, 15.2, 14.9, 14.8. **IR (KBr):** *v* (cm^{-1}) 2929, 2866, 1723, 1448, 1241, 1024, 729, 692. **HRMS (ESI)** calcd for $C_{36}H_{50}O_4Na$ $[M + Na]^+$: 569.3601, found: 569.3603.

9. References

1. Chen, H., Guo, L., Yu, S. Primary, Secondary, and Tertiary γ-C(sp^3)−H Vinylation of Amidesvia Organic Photoredox-Catalyzed Hydrogen Atom Transfer. *Org. Lett*. **2018**, *20*, 6255.

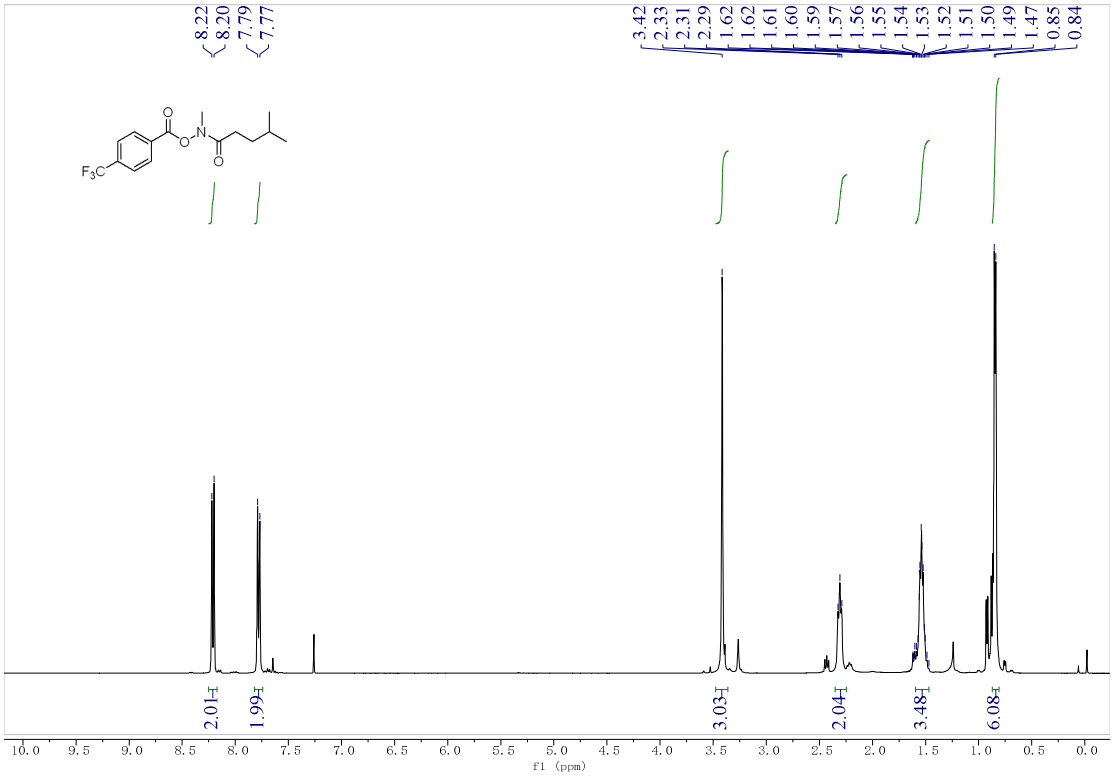
2. Chen, H., Fan W., Yuan, X. A., Yu, S. Site-Selective Remote C(sp^3)–H Heteroarylation of Amides via Organic Photoredox Catalysis. *Nat. Commun*. **2019**, *10*, 4743.

3. Chen, H., Jin, W., Yu, S. Enantioselective Remote C(sp^3)−H Cyanation via Dual Photoredox and Copper Catalysis. *Org. Lett*. **2020**, *22*, 5910.

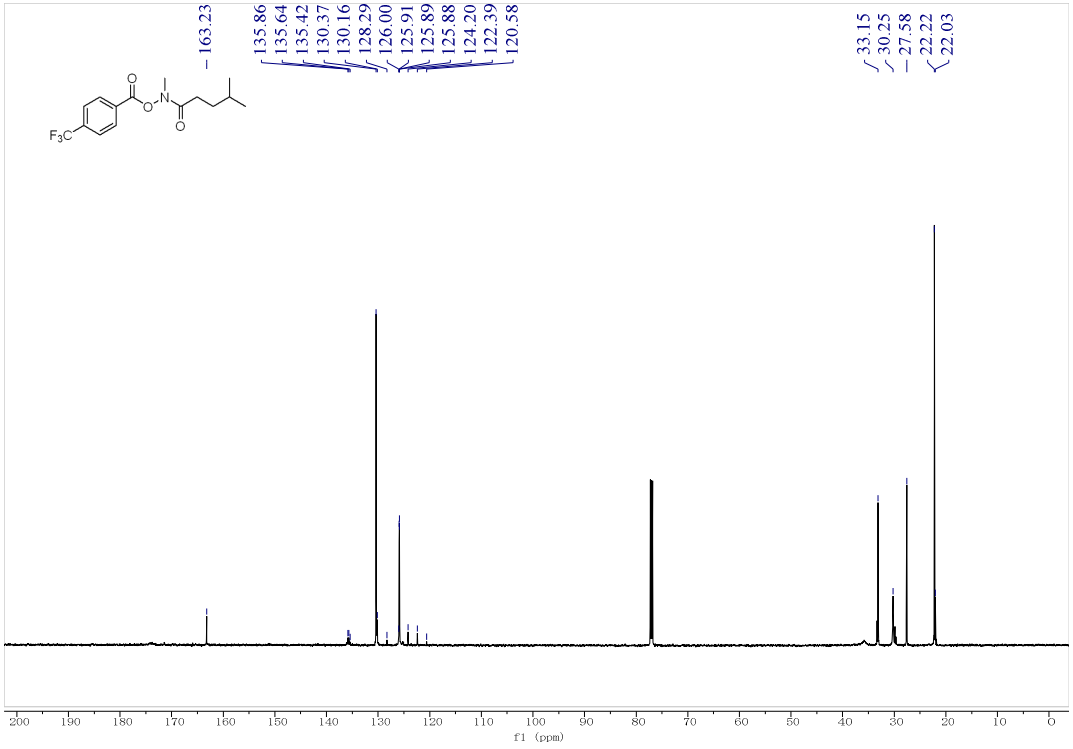
4. Yang, J. W., Tan, G. Q., Liang, K. C., Xu, K. D., Su, M., Liu, F. Copper-Catalyzed, N-Directed Distal C(sp^3)−H Functionalization toward Azepanes. *Org. Lett.* **2022**, *24*, 7796.

10. NMR Spectra of the Substrates and Products

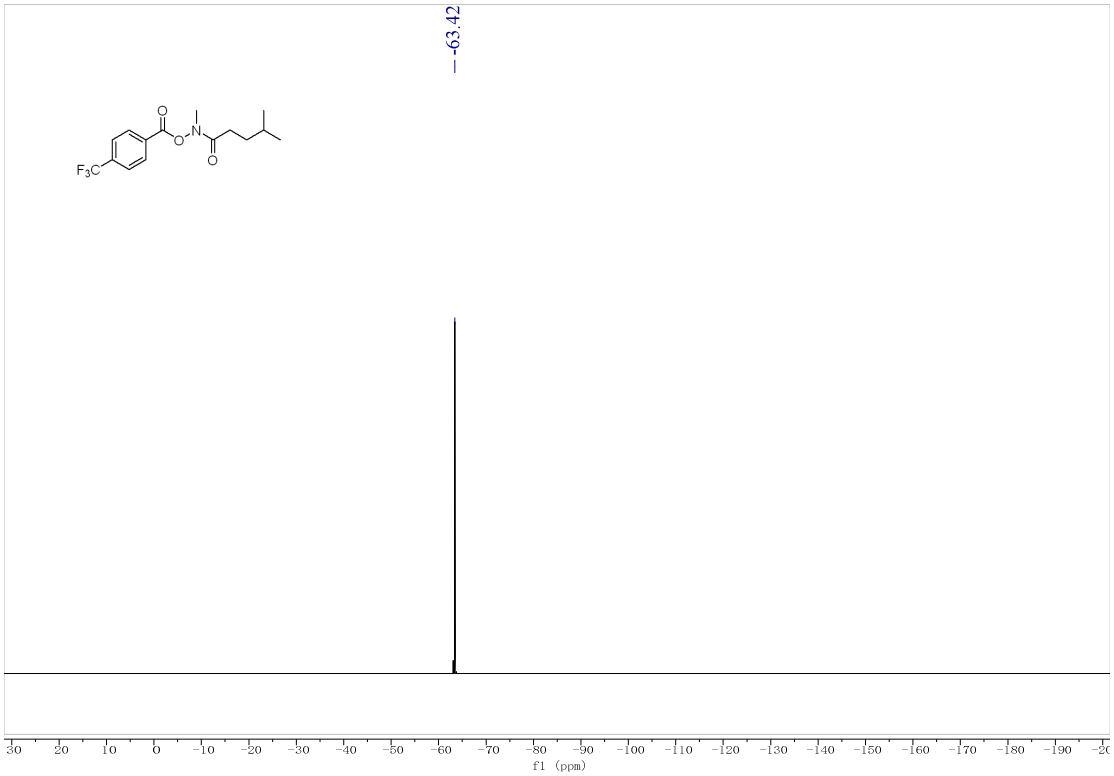
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



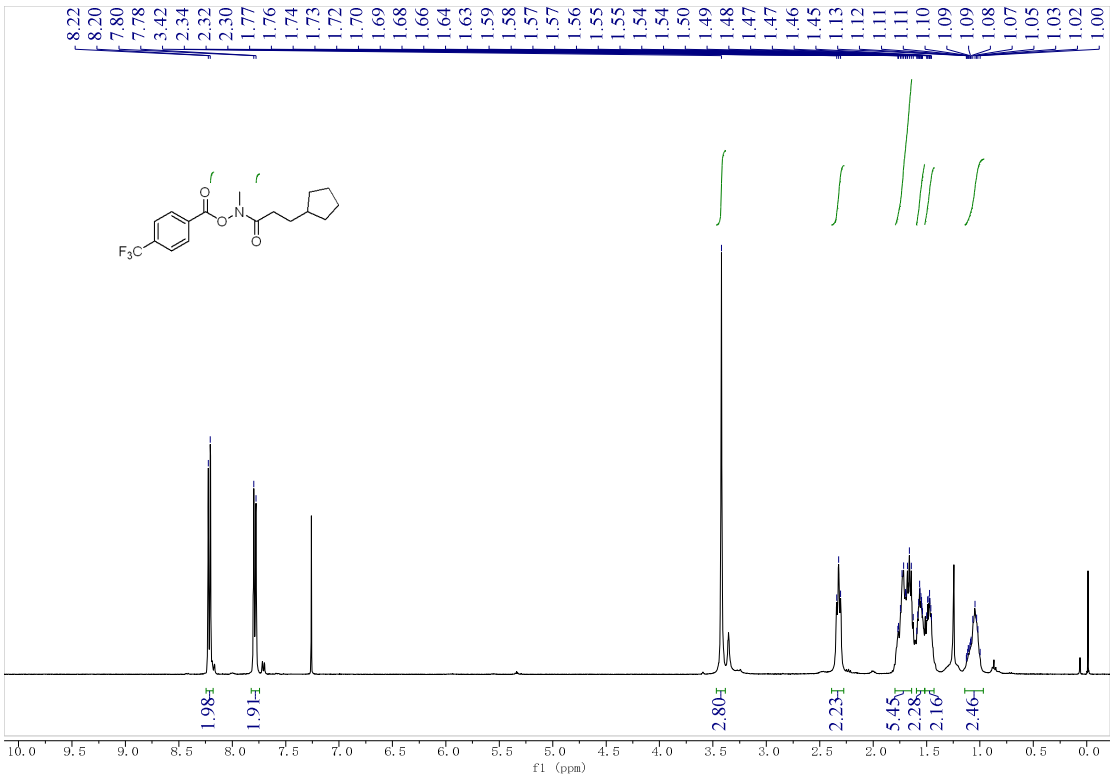
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1a**



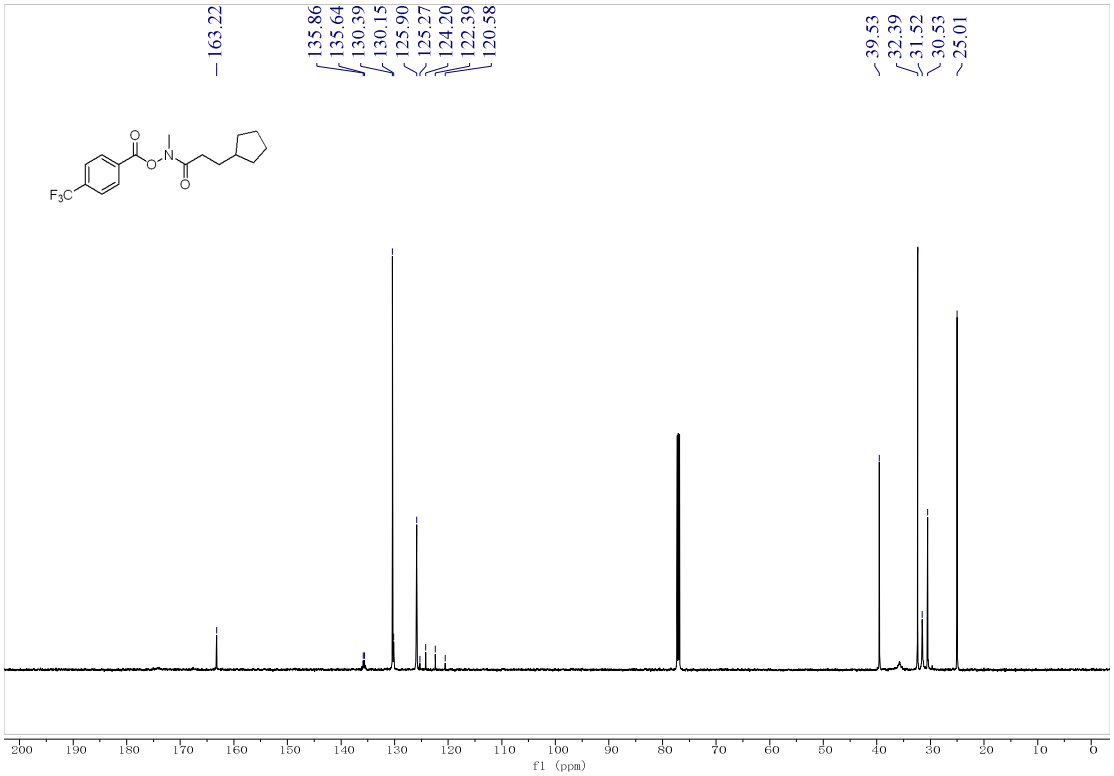
^{19}F NMR (376 MHz, $CDCl_3$) of **1a**



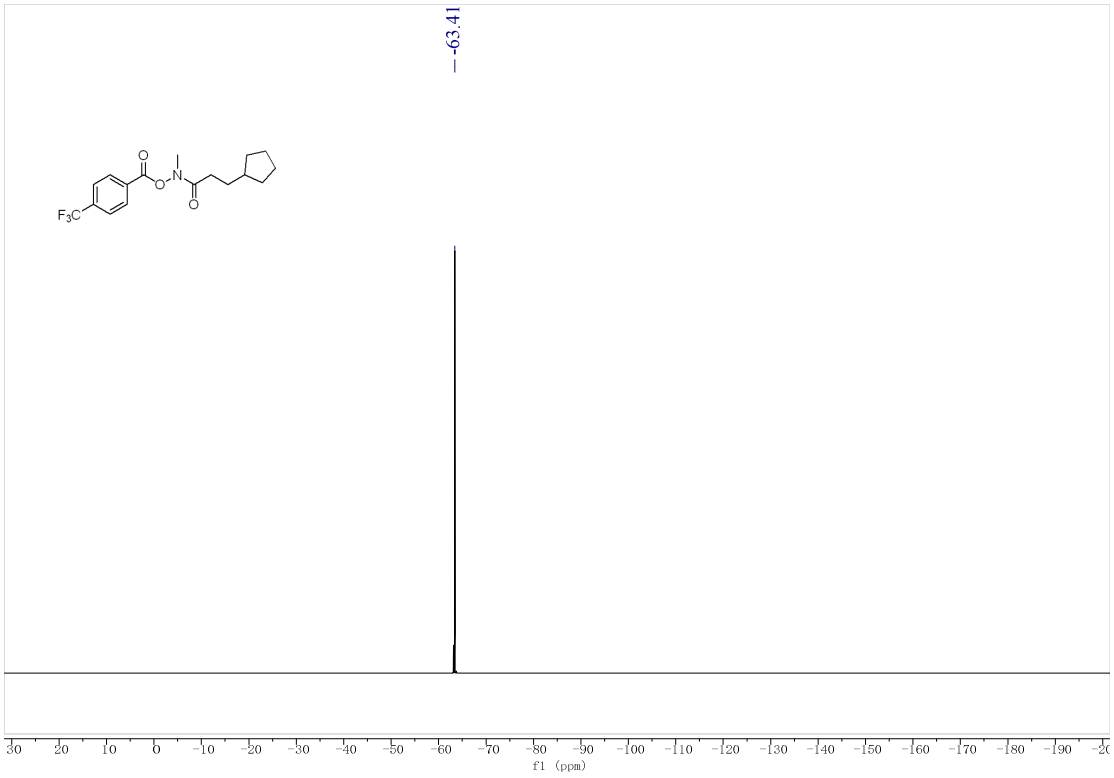
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



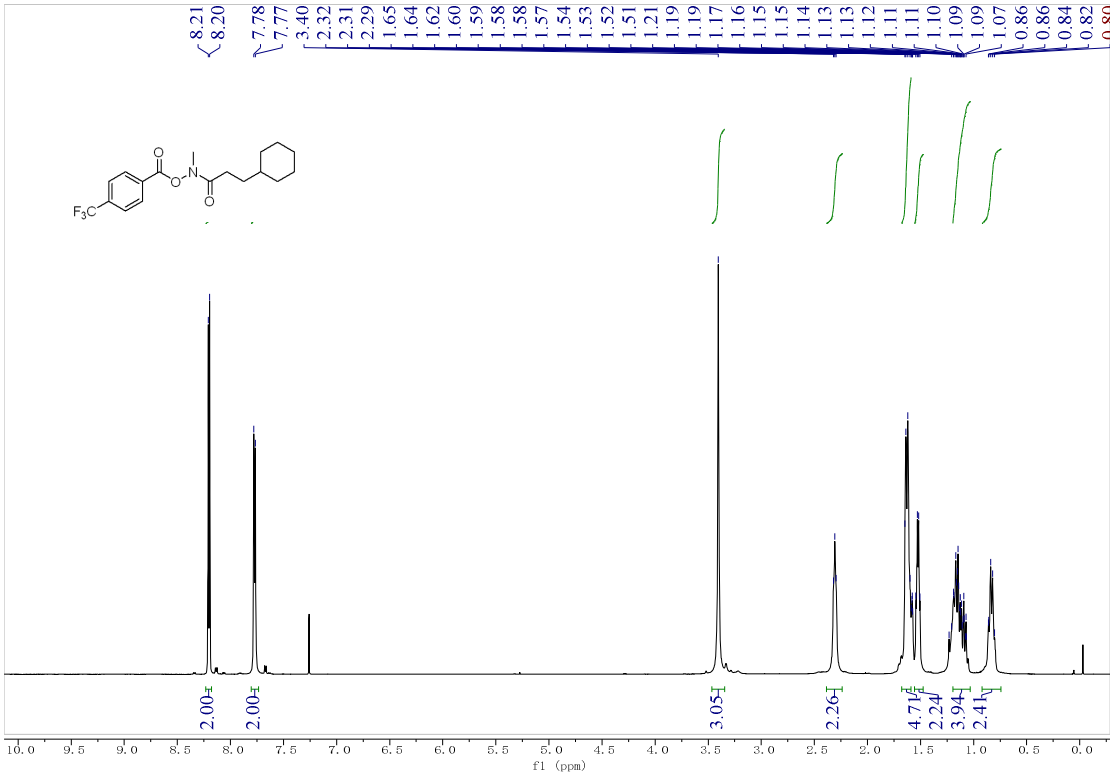
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **1b**



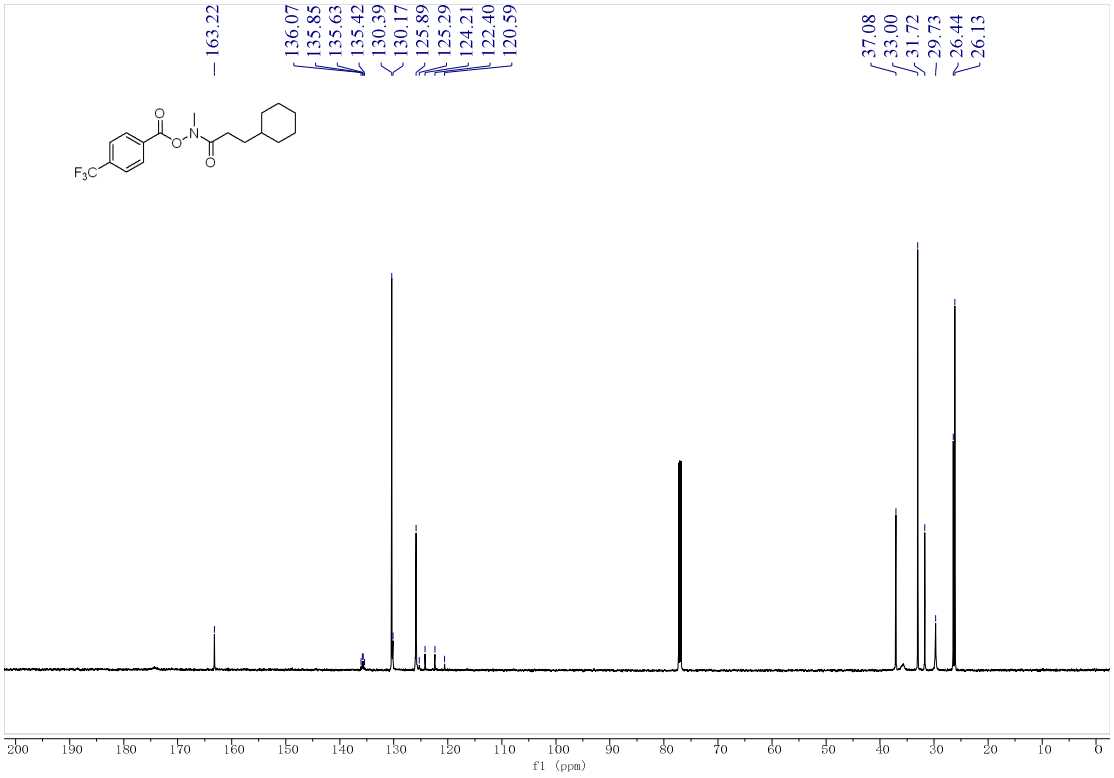
^{19}F NMR (376 MHz, $CDCl_3$) of **1b**



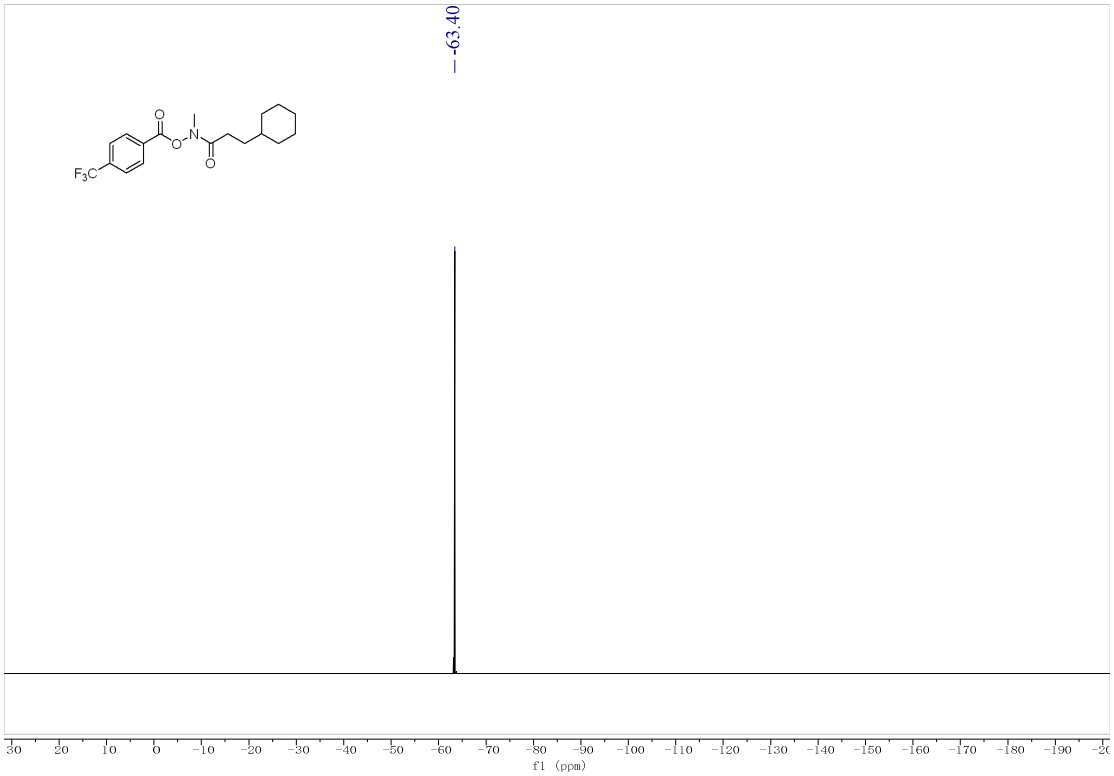
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



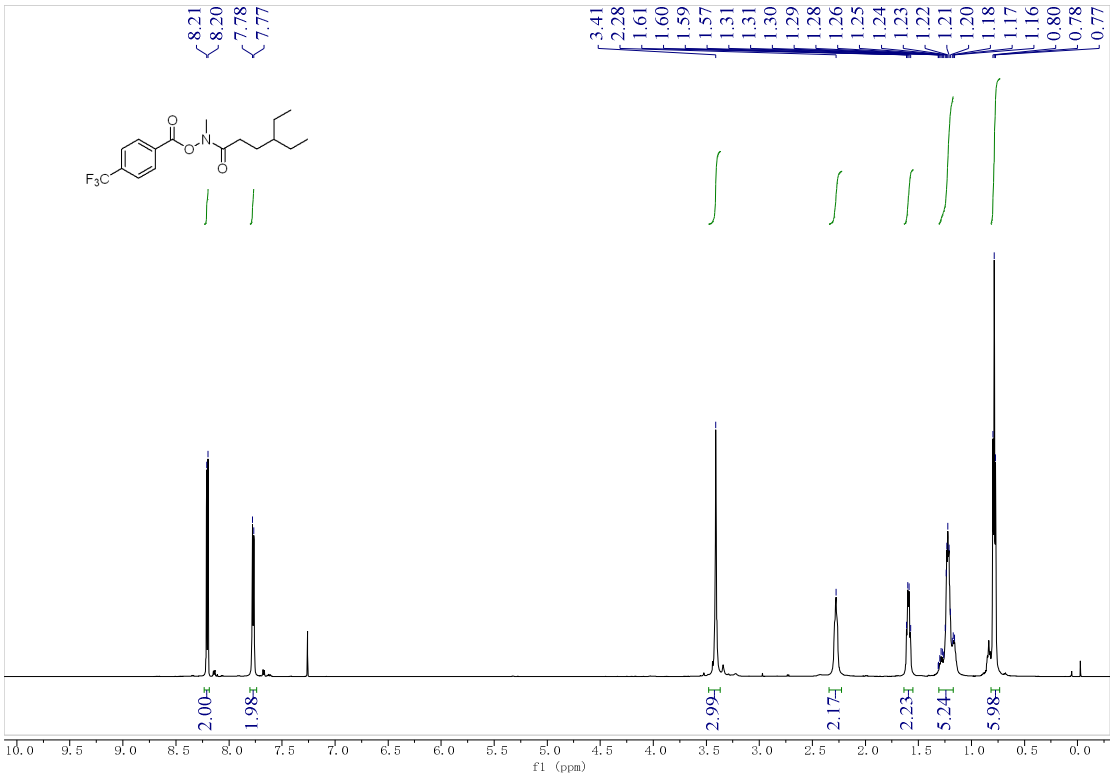
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1c**



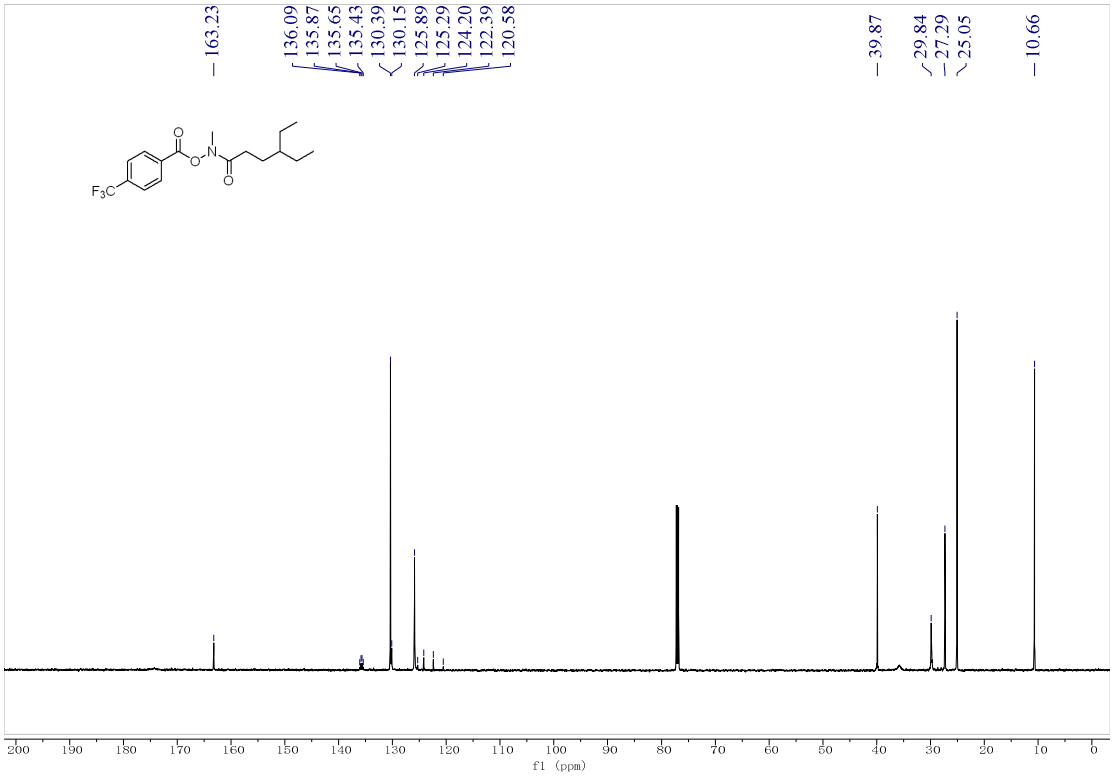
^{19}F NMR (376 MHz, $CDCl_3$) of **1c**



^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **1d**



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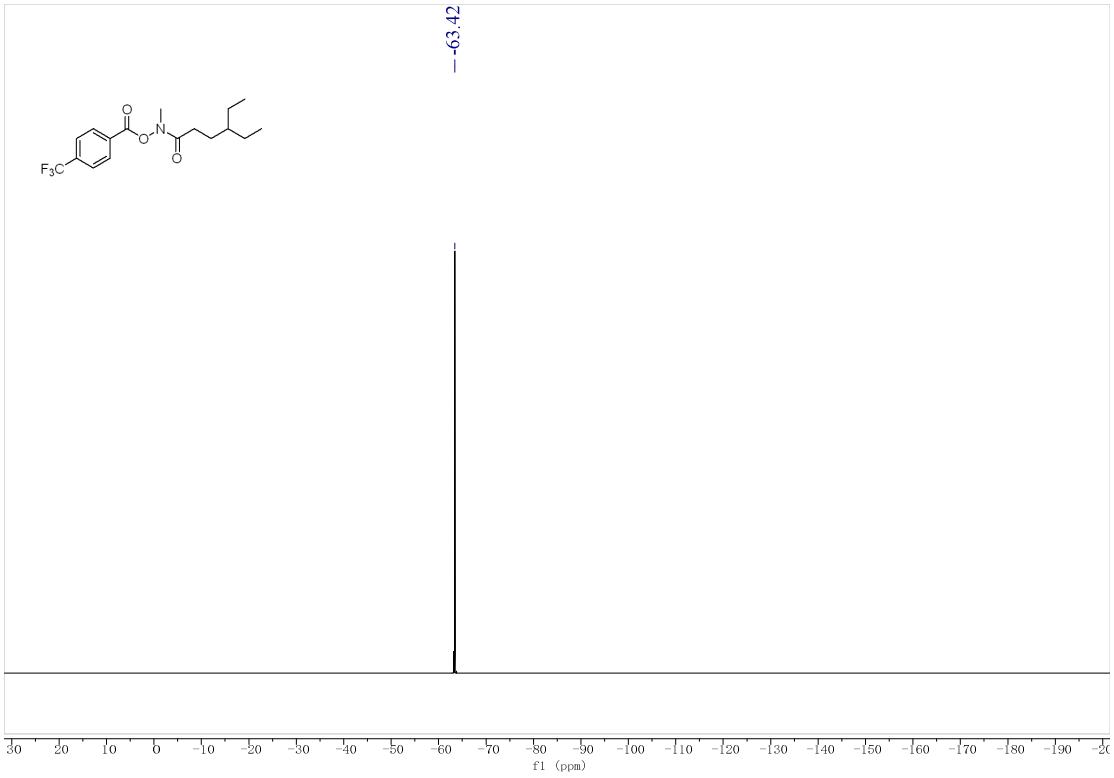
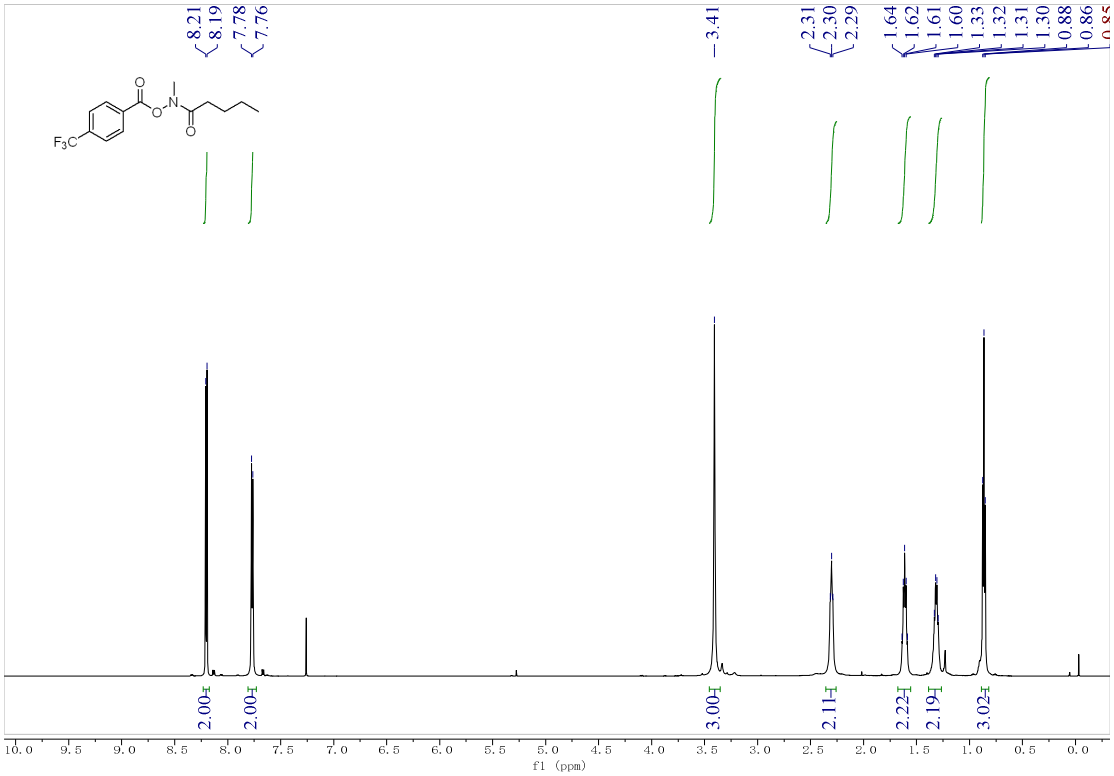
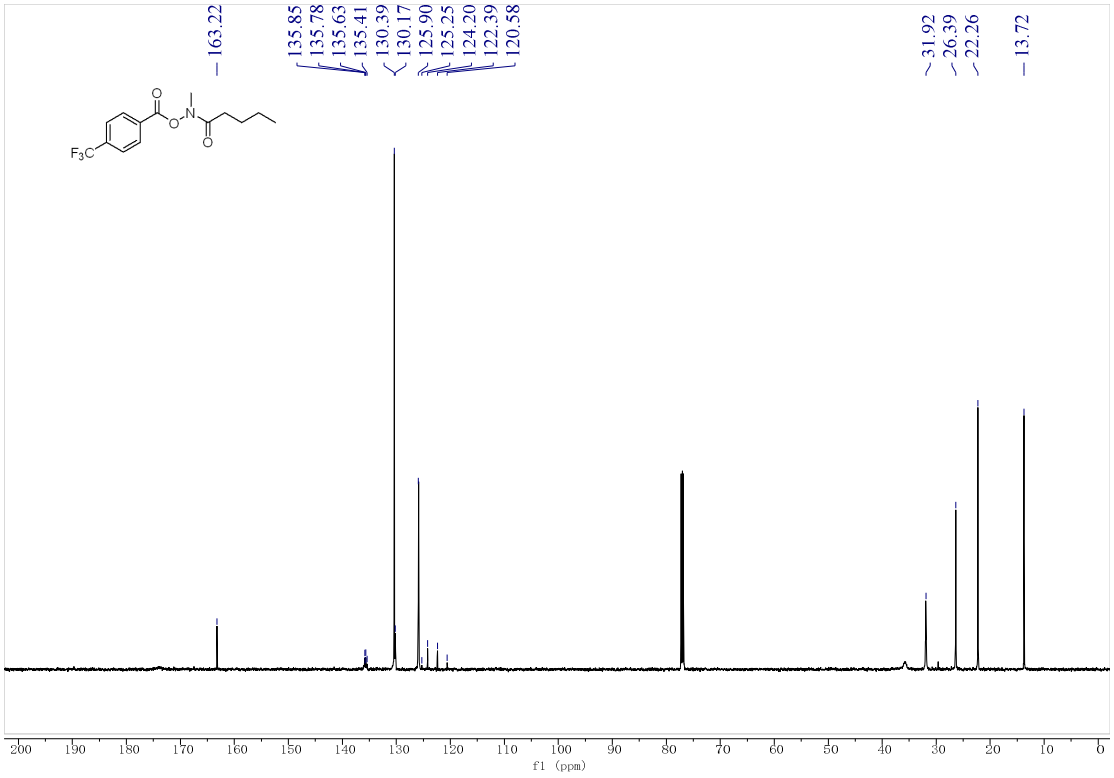


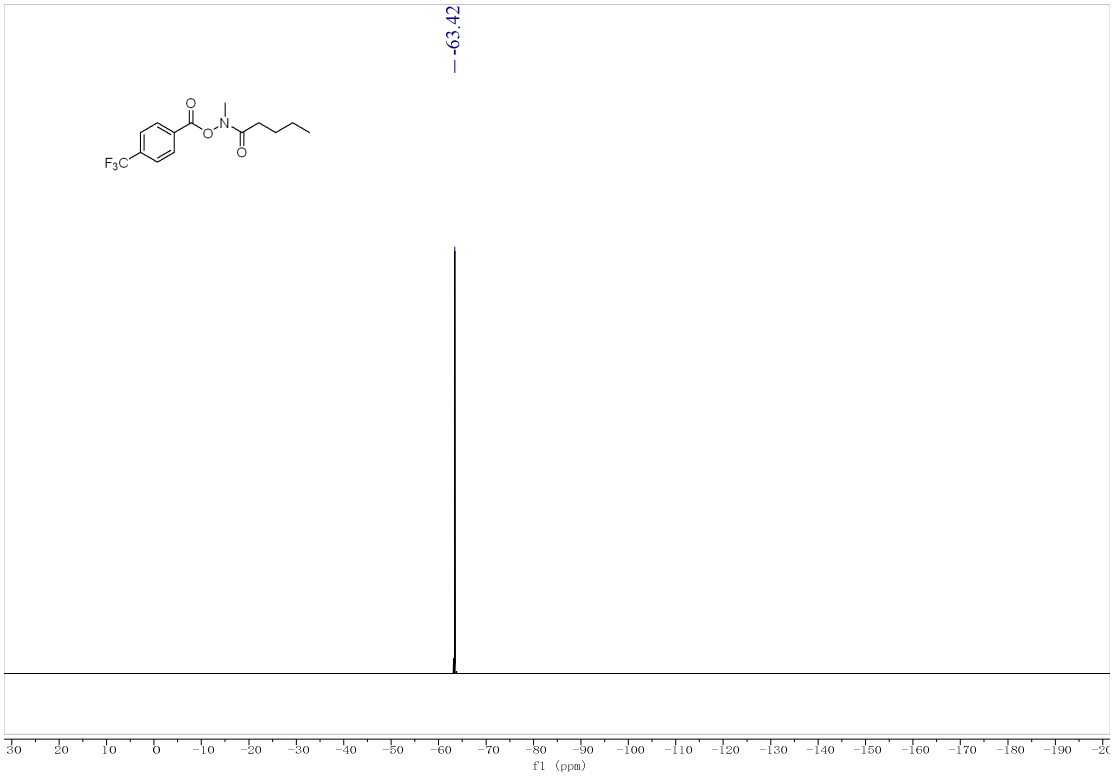
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1e**



^{19}F NMR (376 MHz, $CDCl_3$) of **1e**



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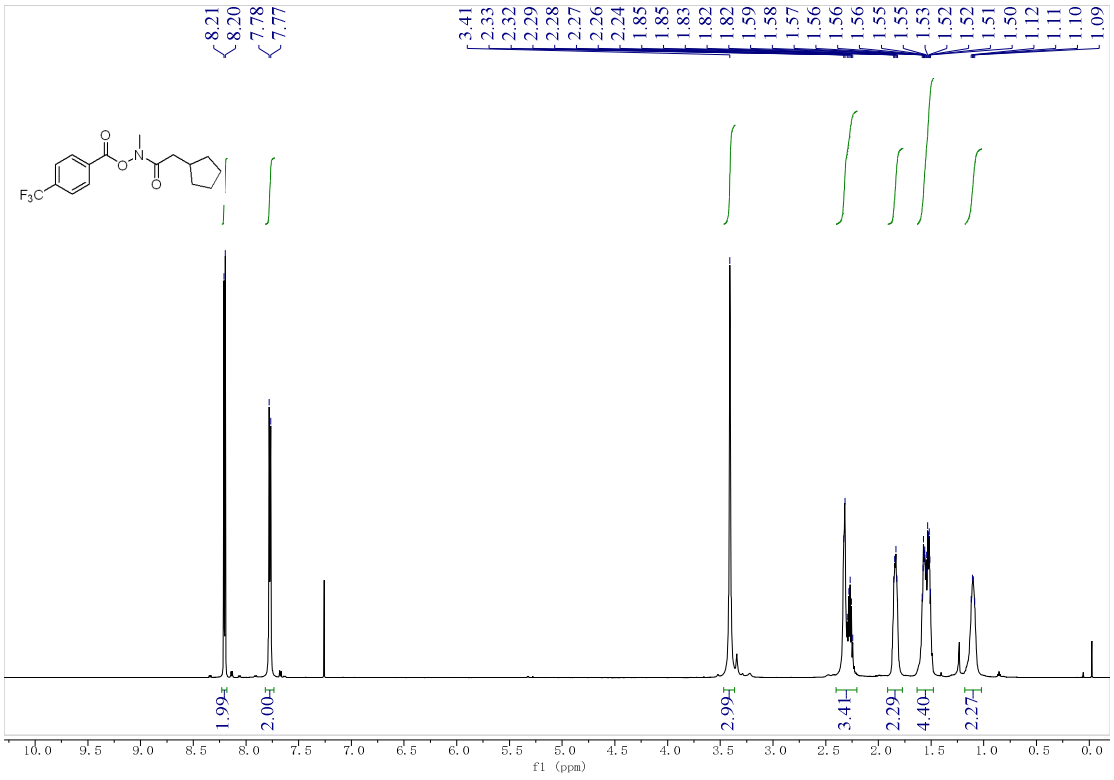
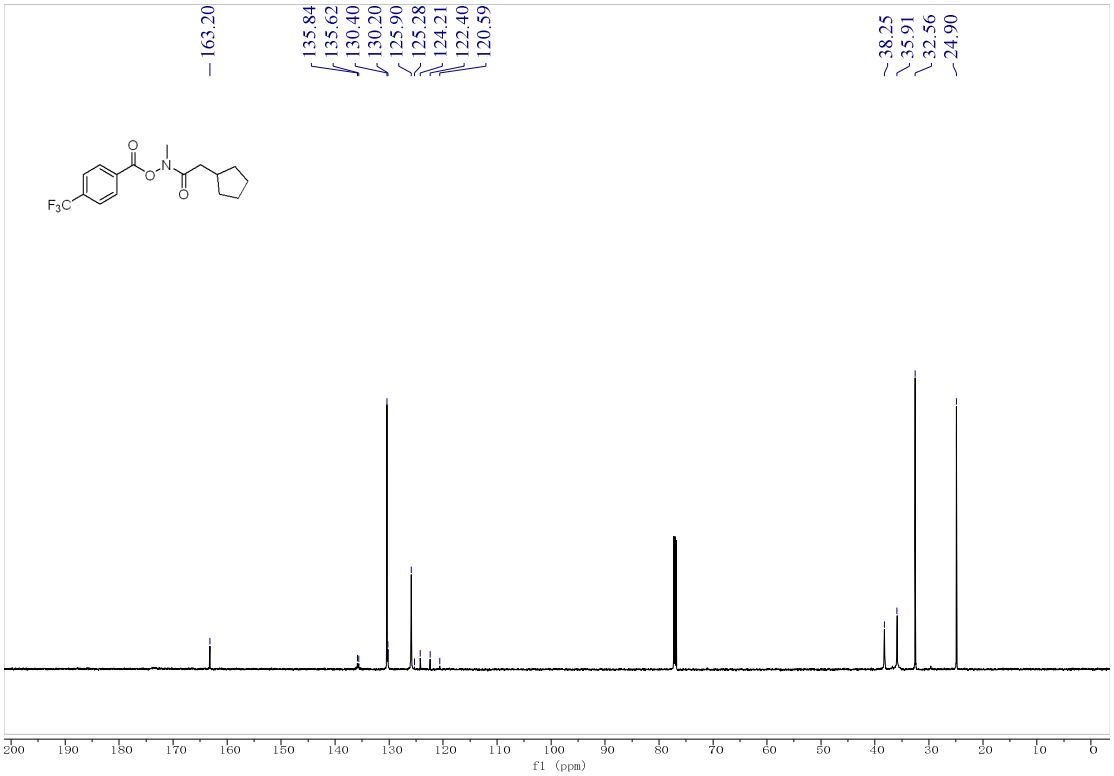
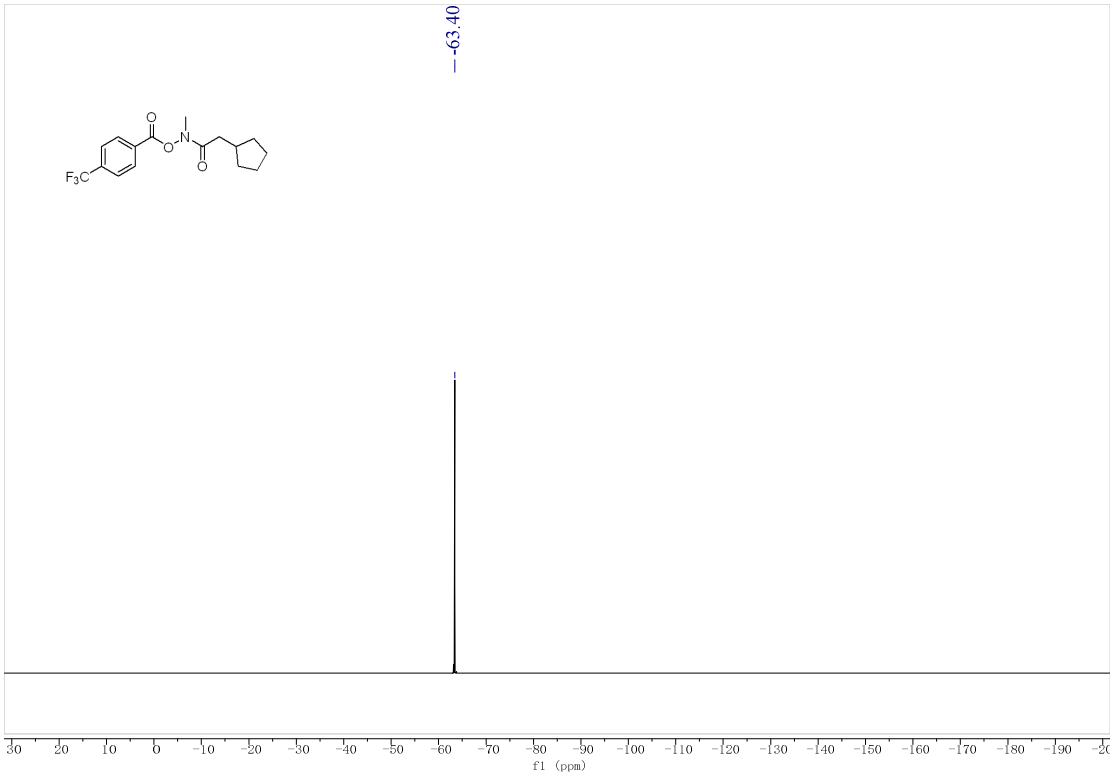


$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **1f**



^{19}F NMR (376 MHz, $CDCl_3$) of **1f**



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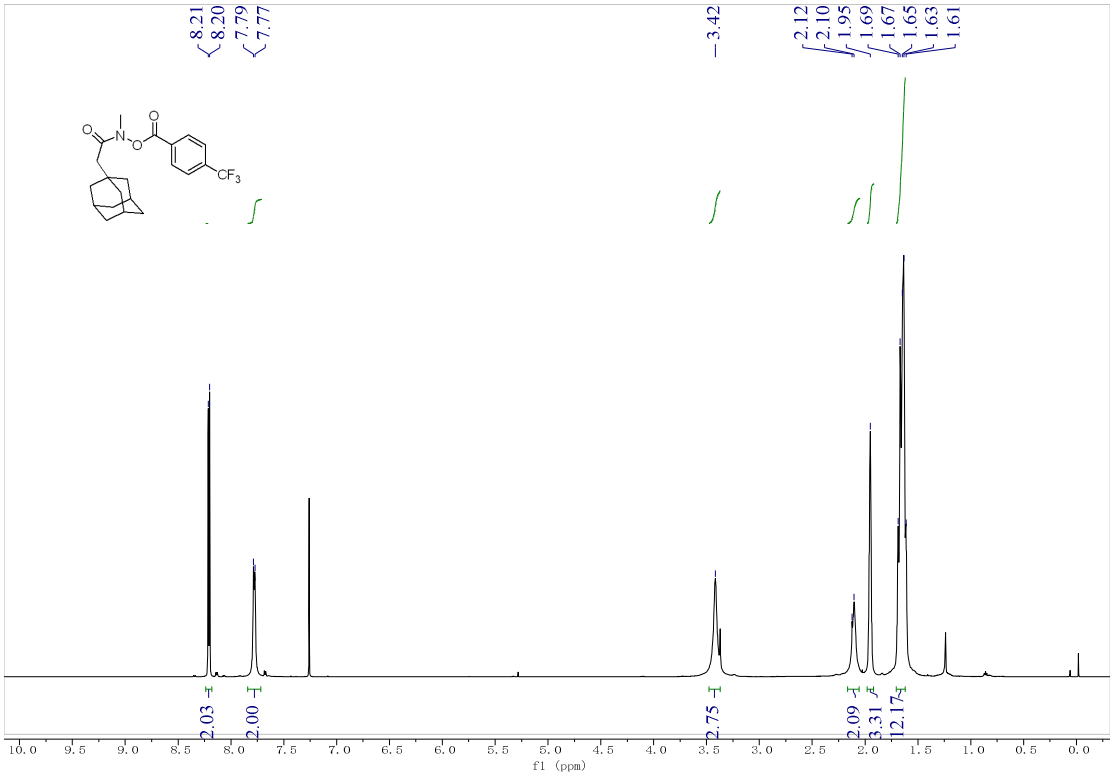
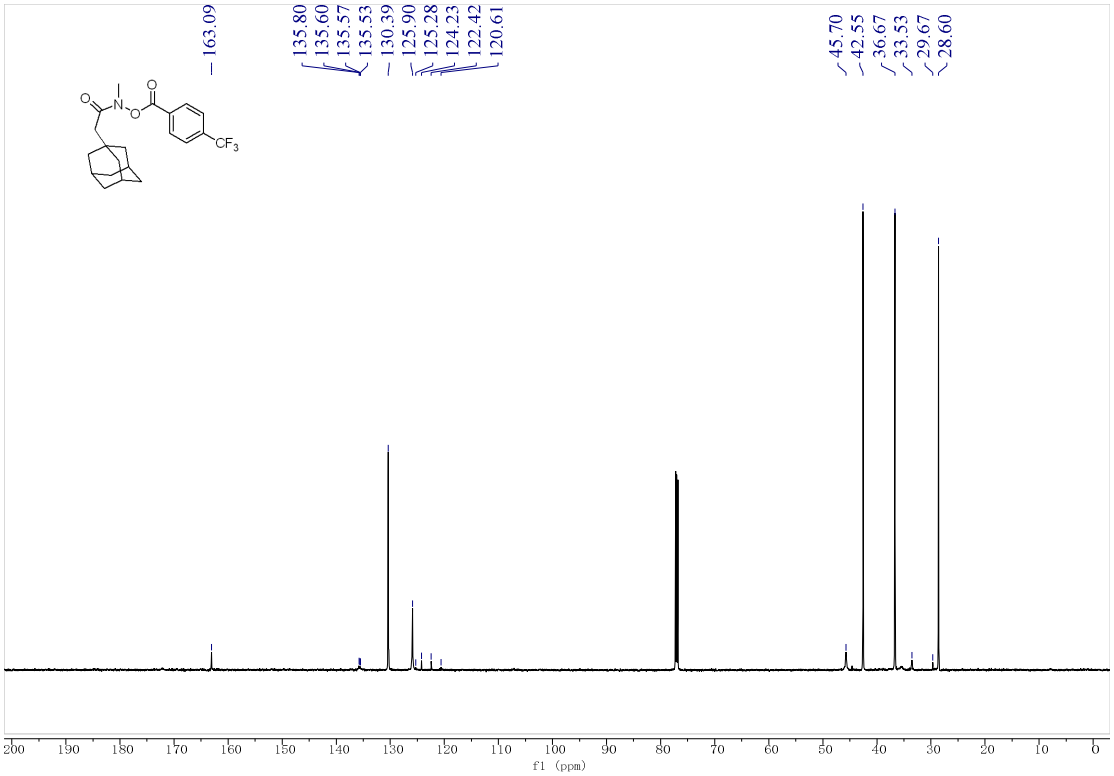
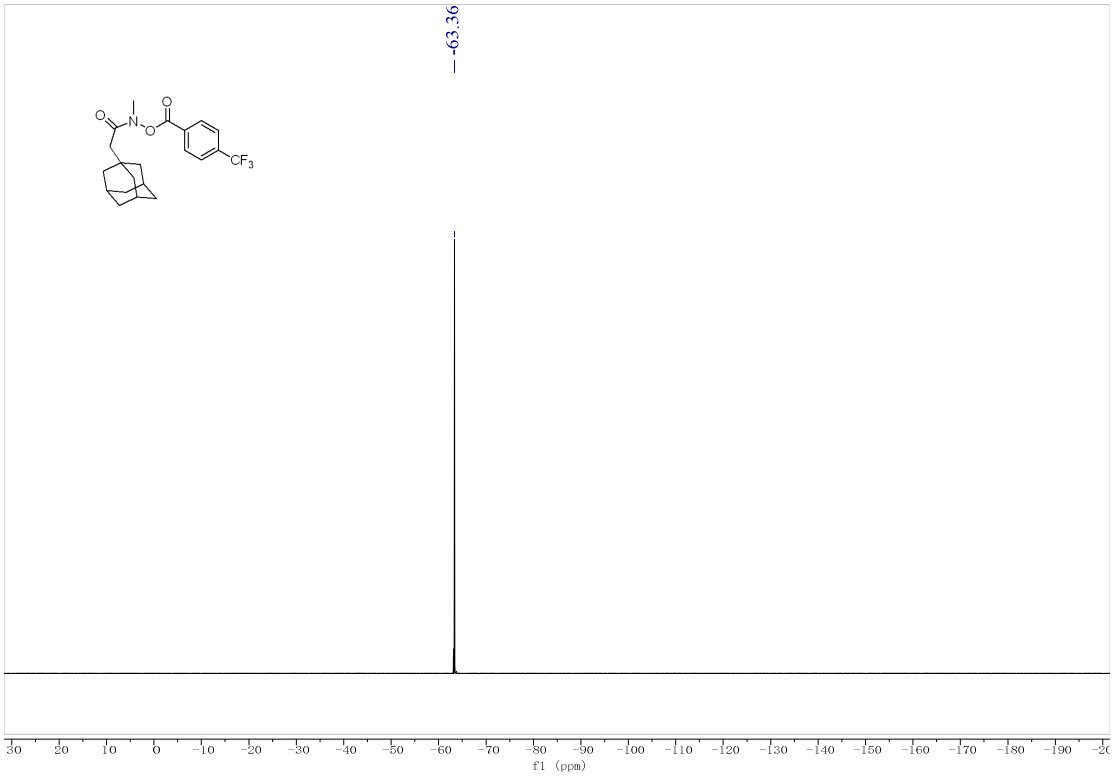


^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1g**



^{19}F NMR (376 MHz, $CDCl_3$) of **1g**



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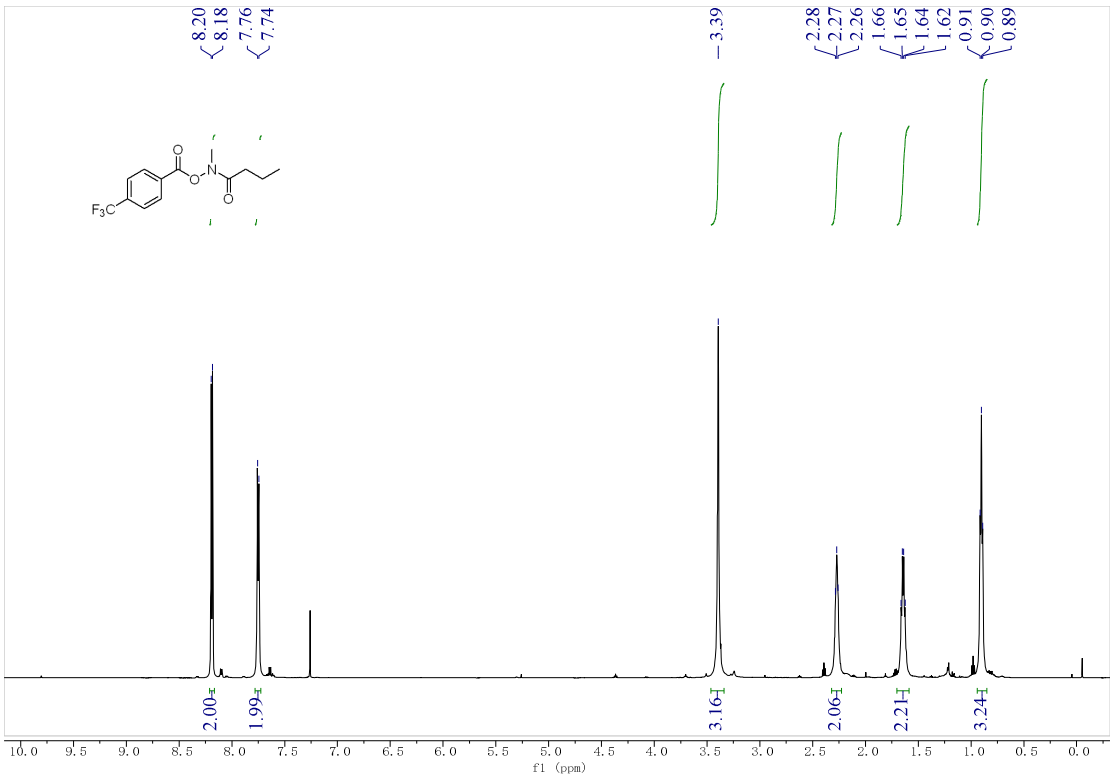
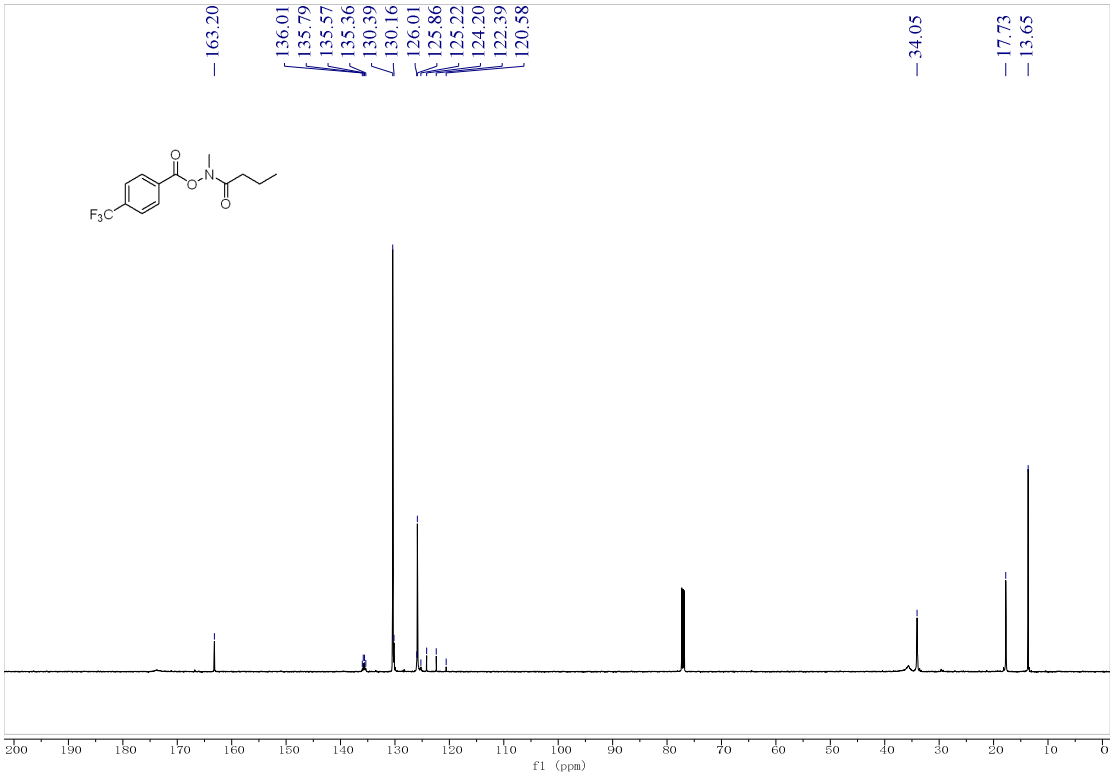
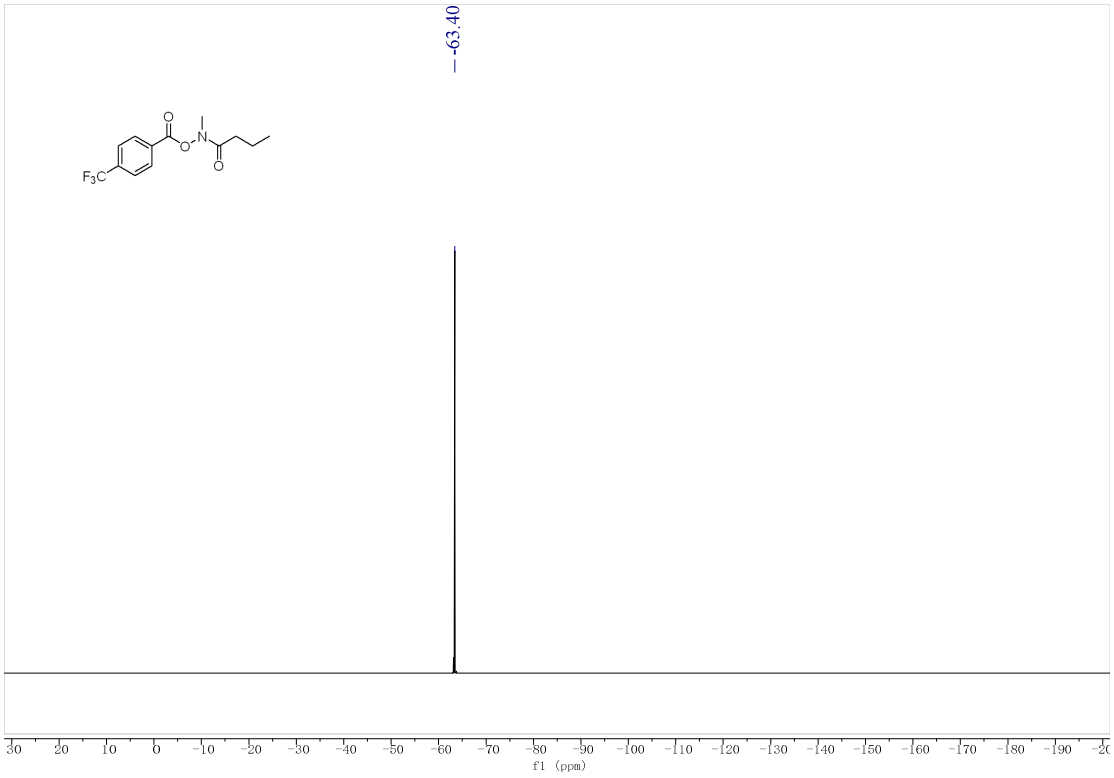


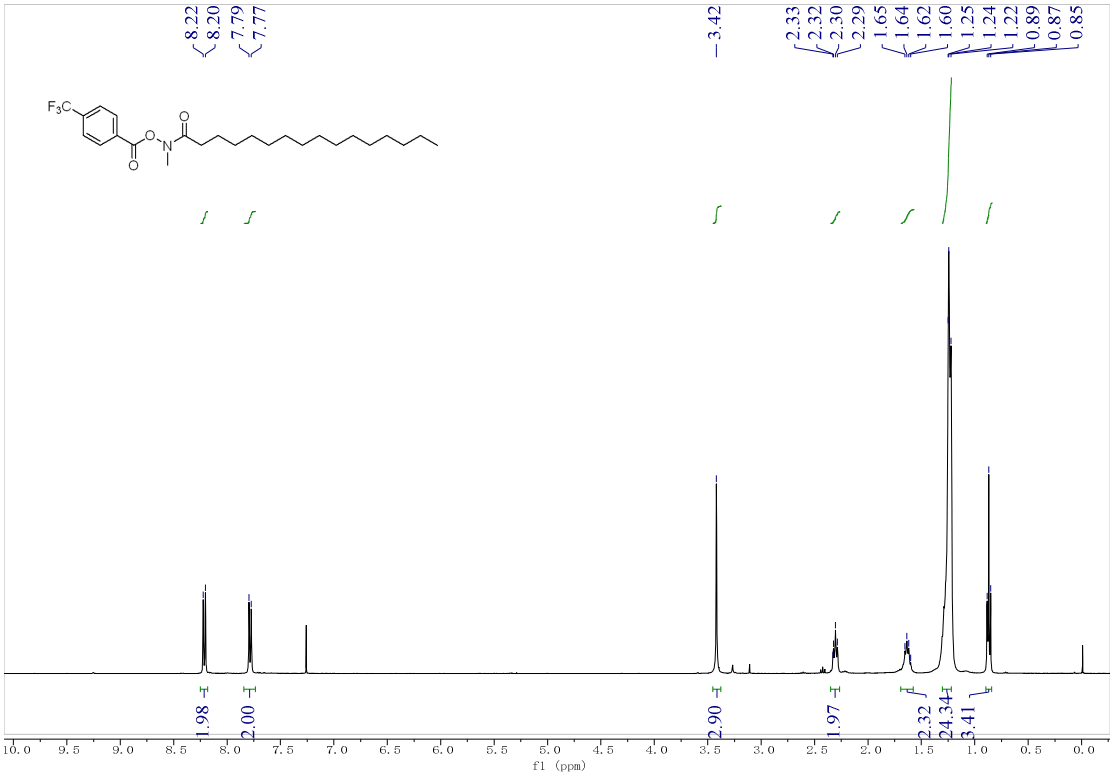
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) **1h**



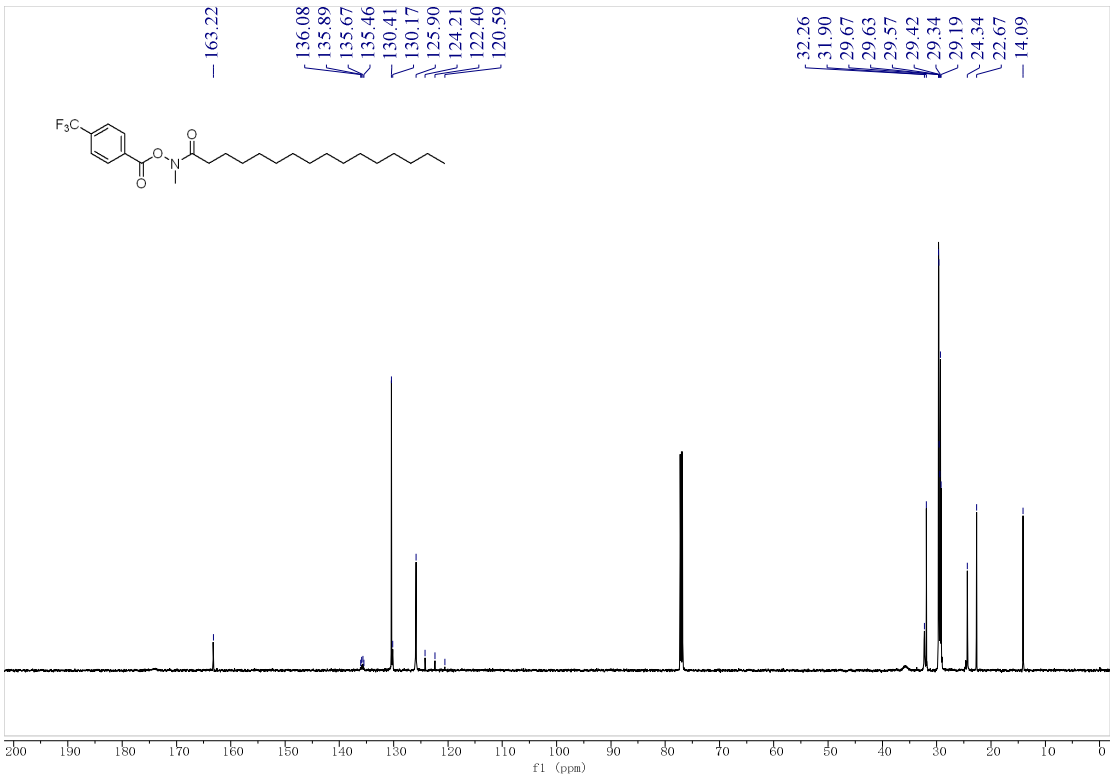
^{19}F NMR (376 MHz, $CDCl_3$) of **1h**



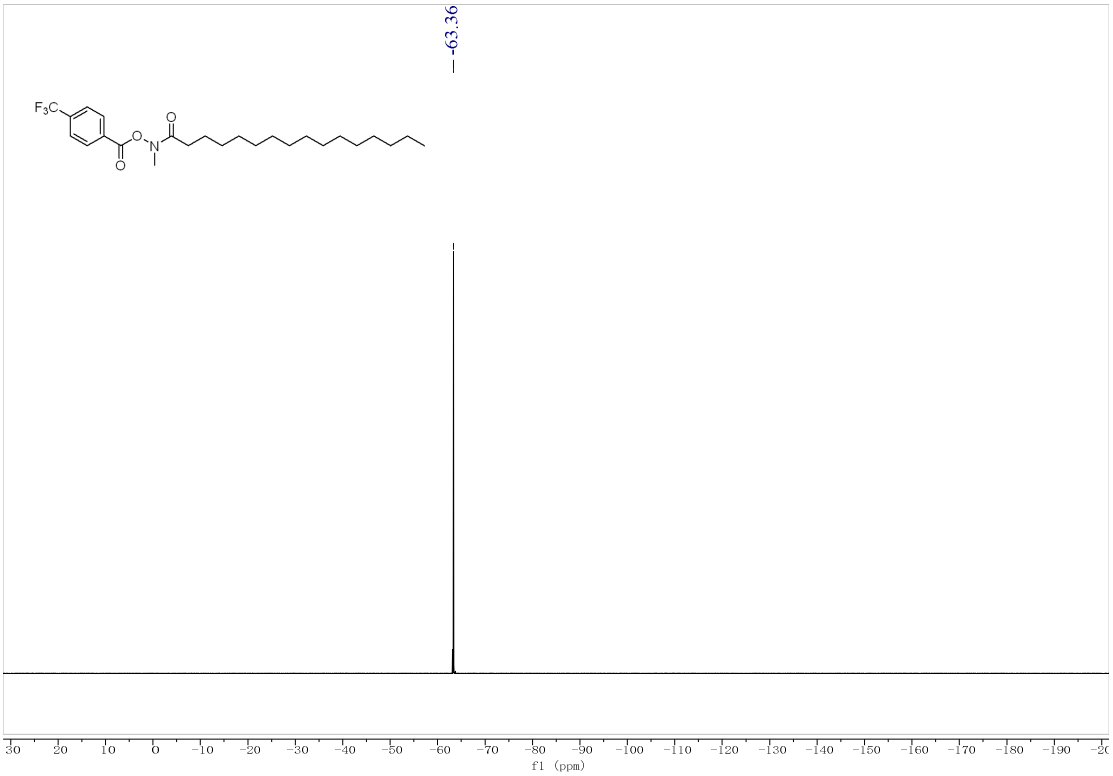
^{1}H NMR (400 MHz, $CDCl_3$) of **1i**



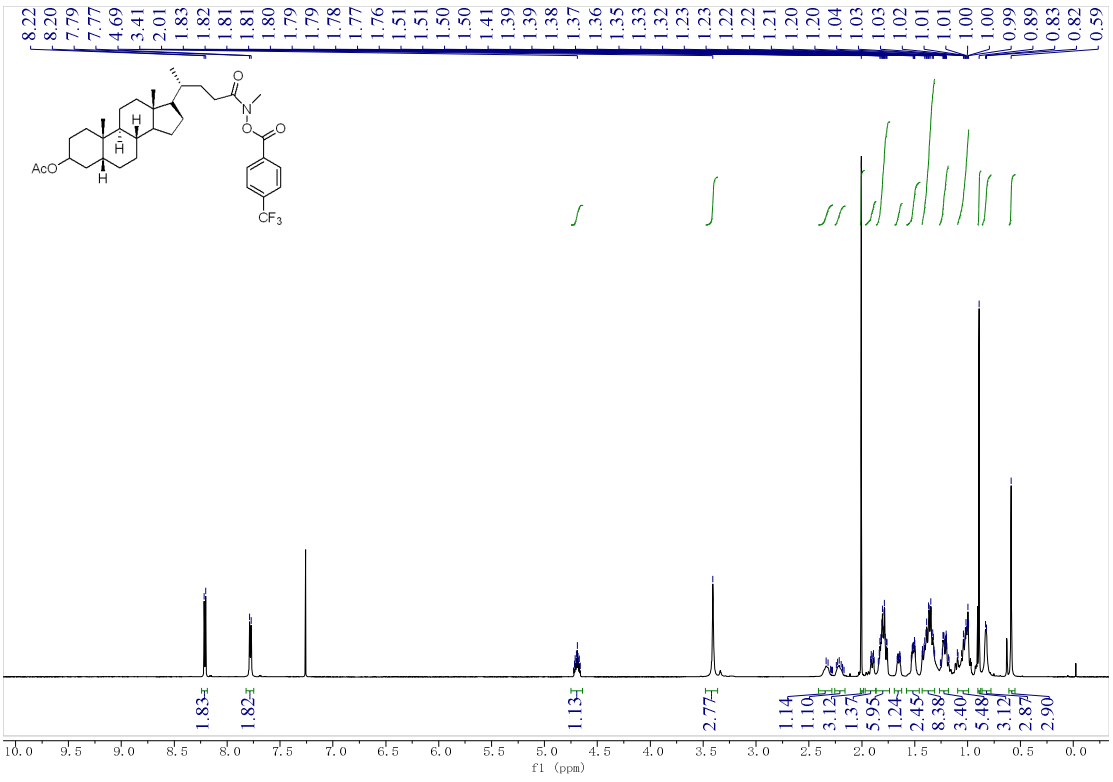
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1i**



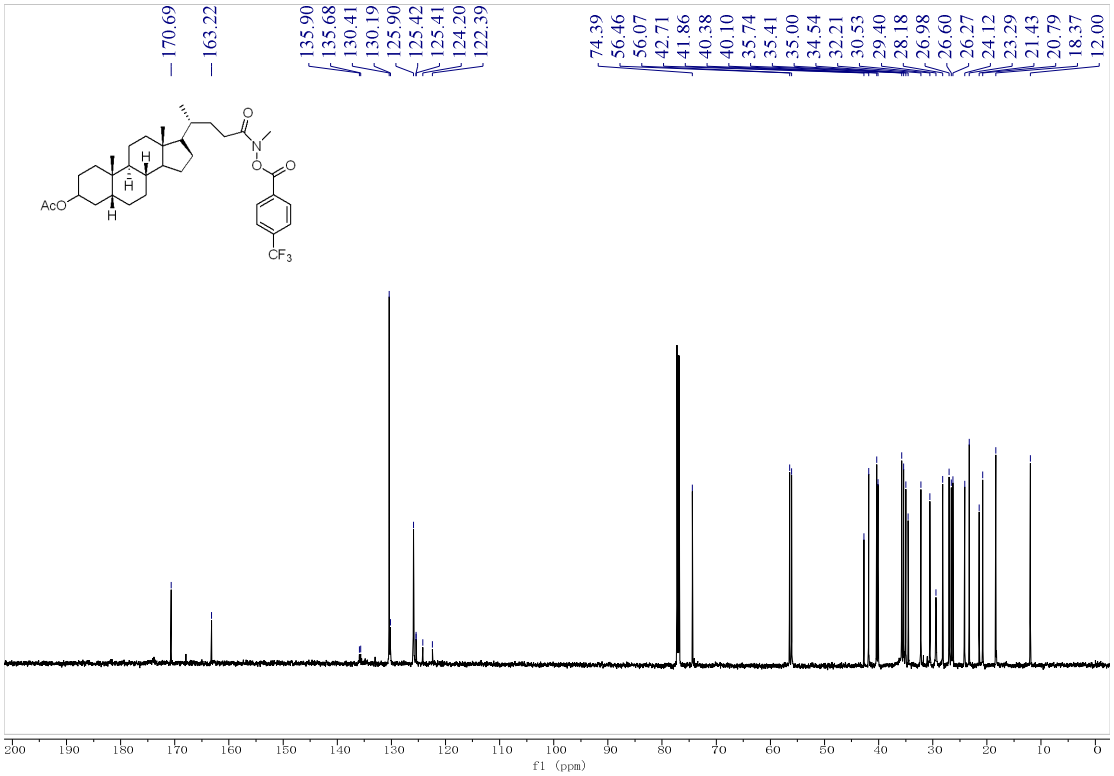
^{19}F NMR (376 MHz, $CDCl_3$) of **1i**



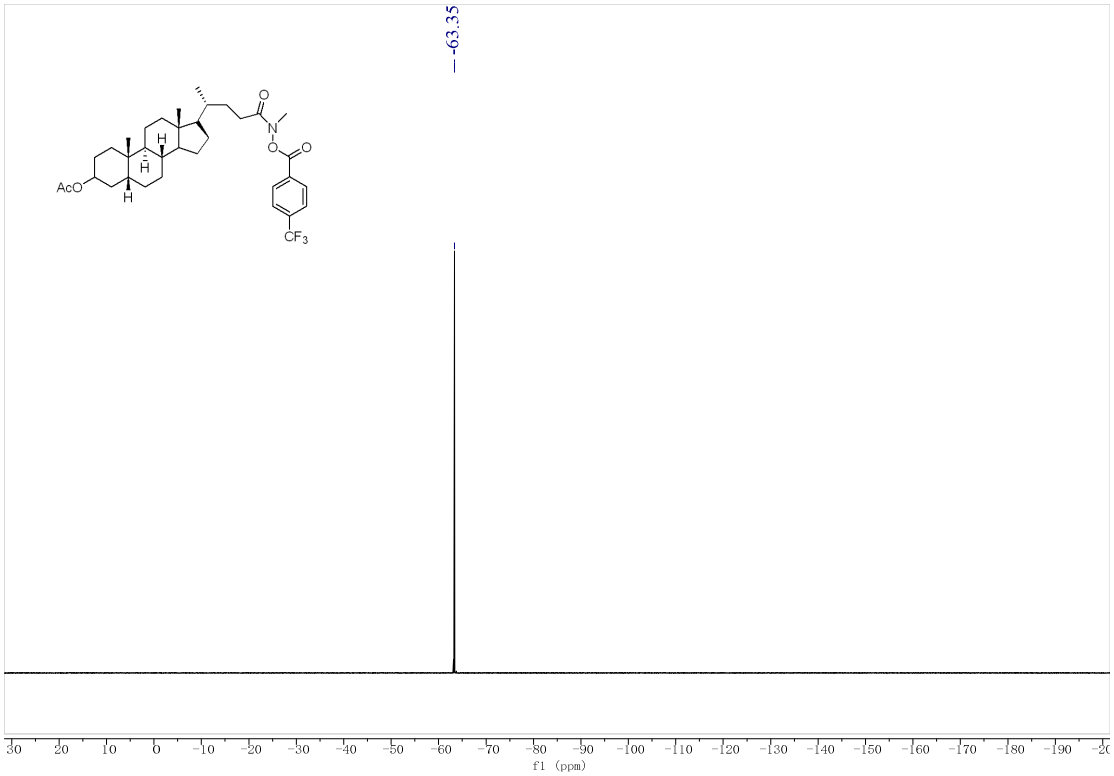
^{1}H NMR (400 MHz, $CDCl_3$) of **1j**



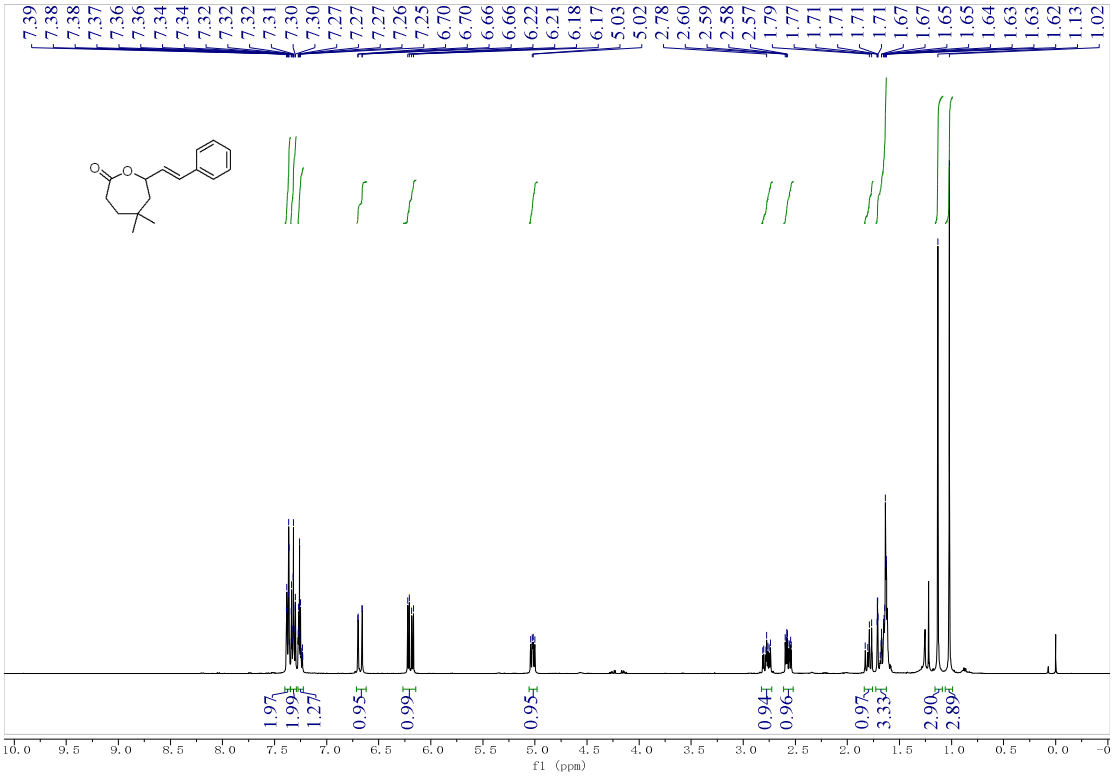
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **1j**



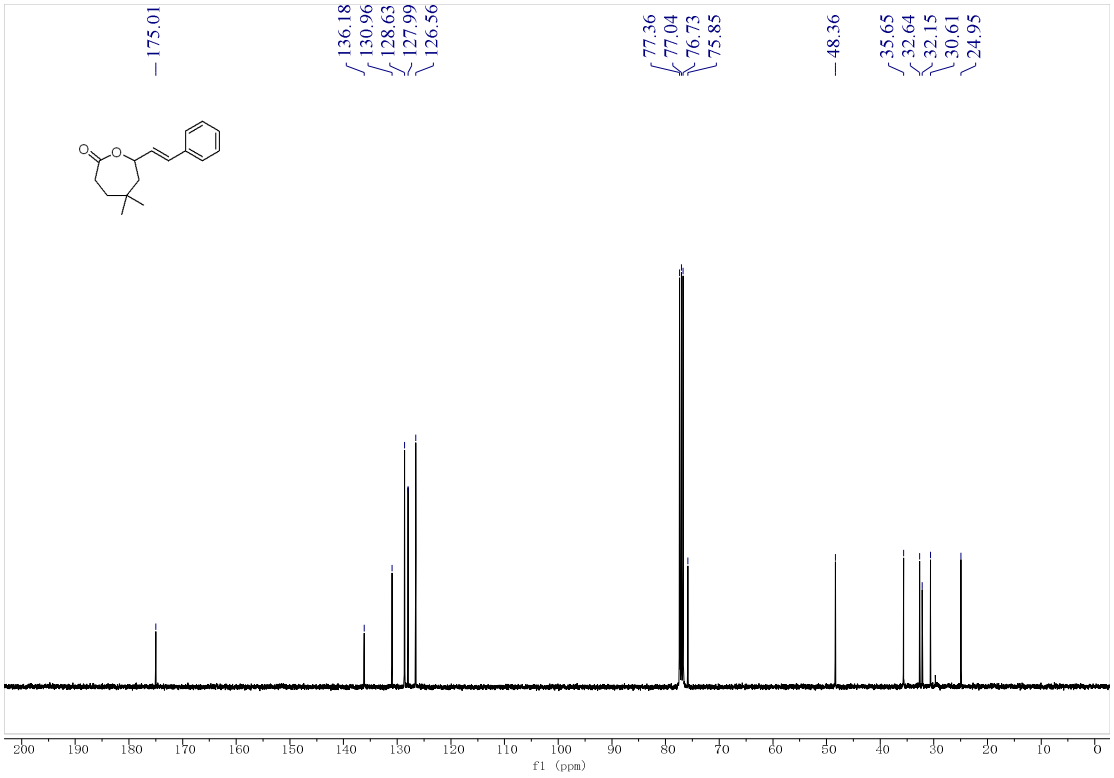
^{19}F NMR (376 MHz, $CDCl_3$) of **1j**



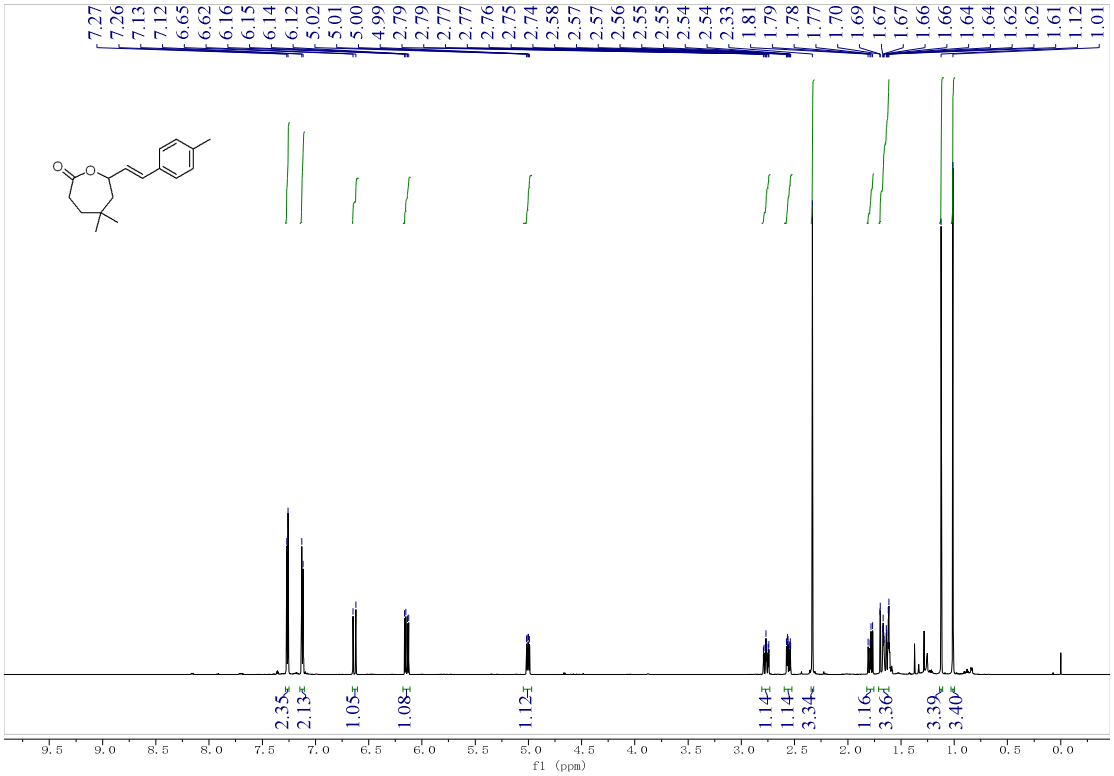
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



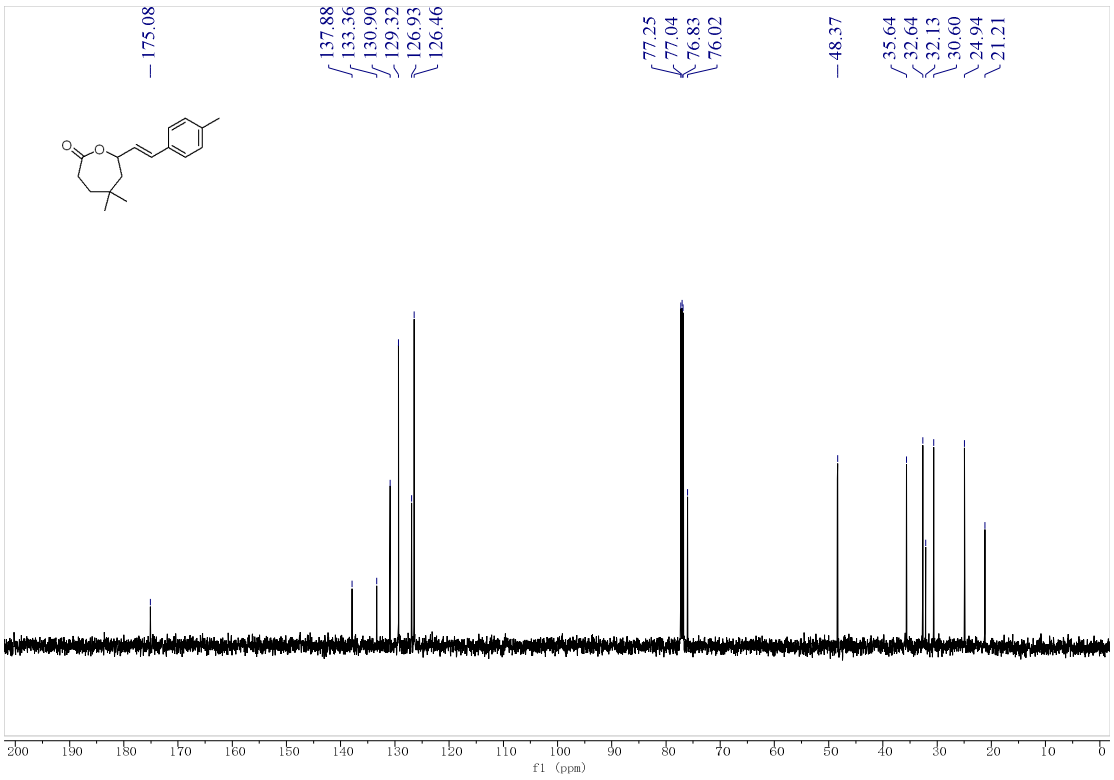
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3a**



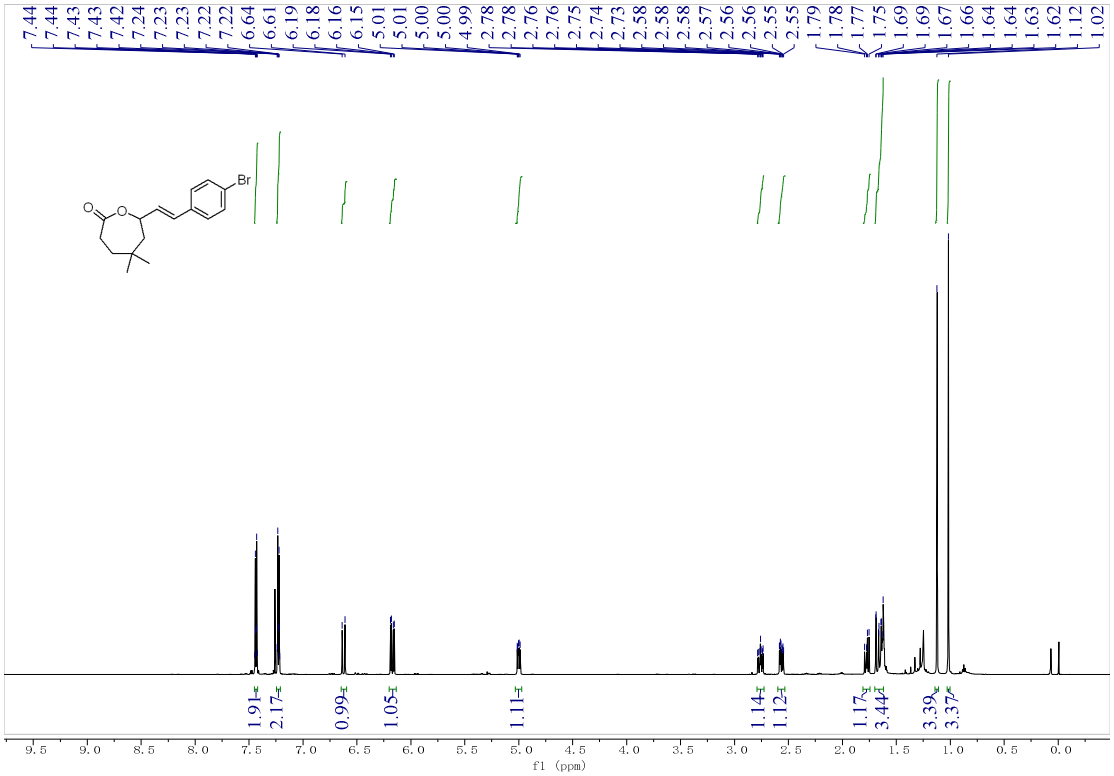
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



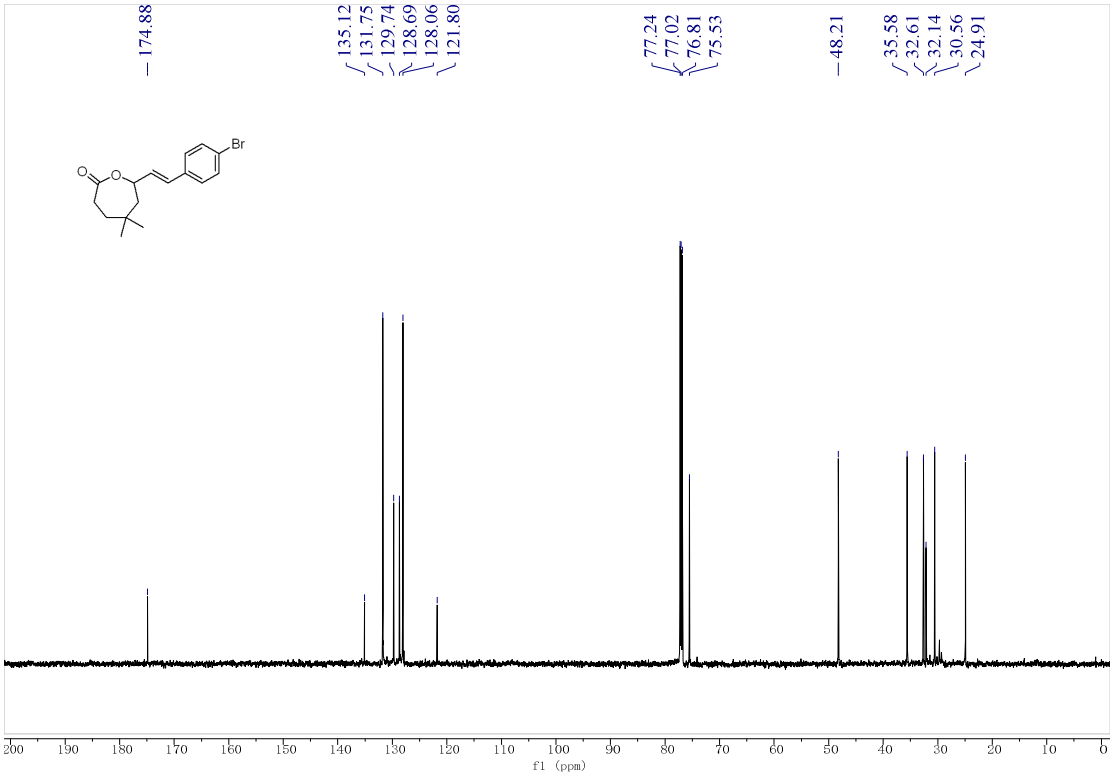
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3b**



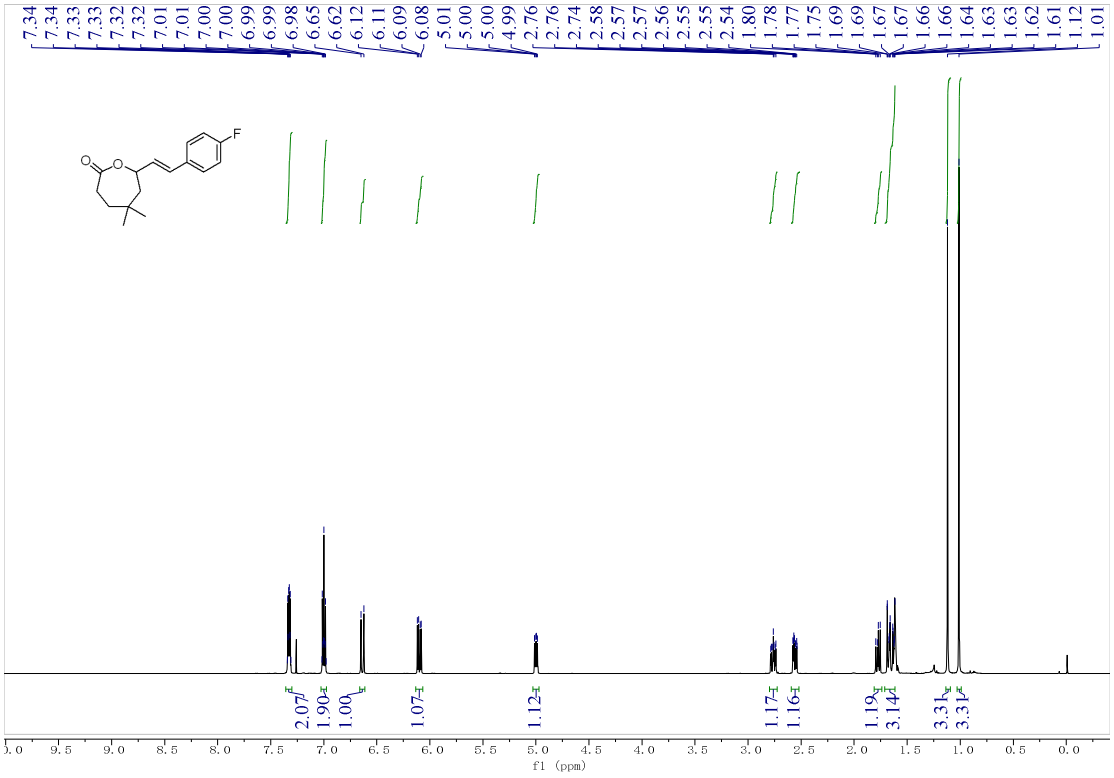
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



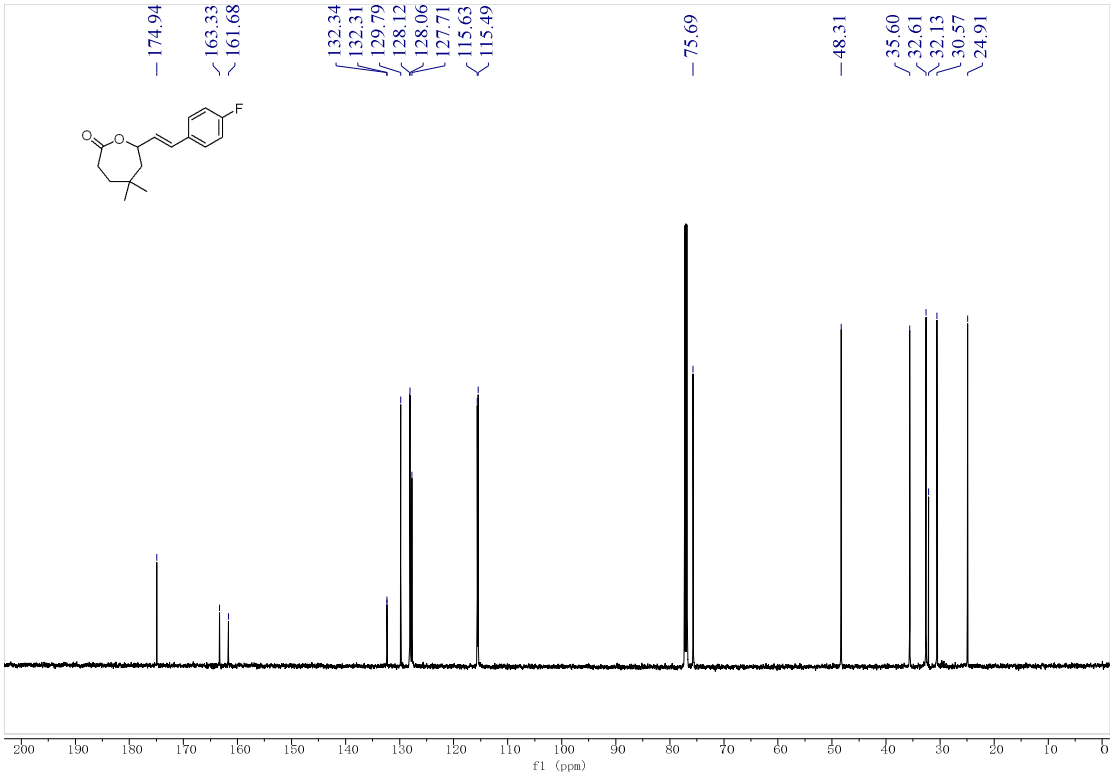
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3c**



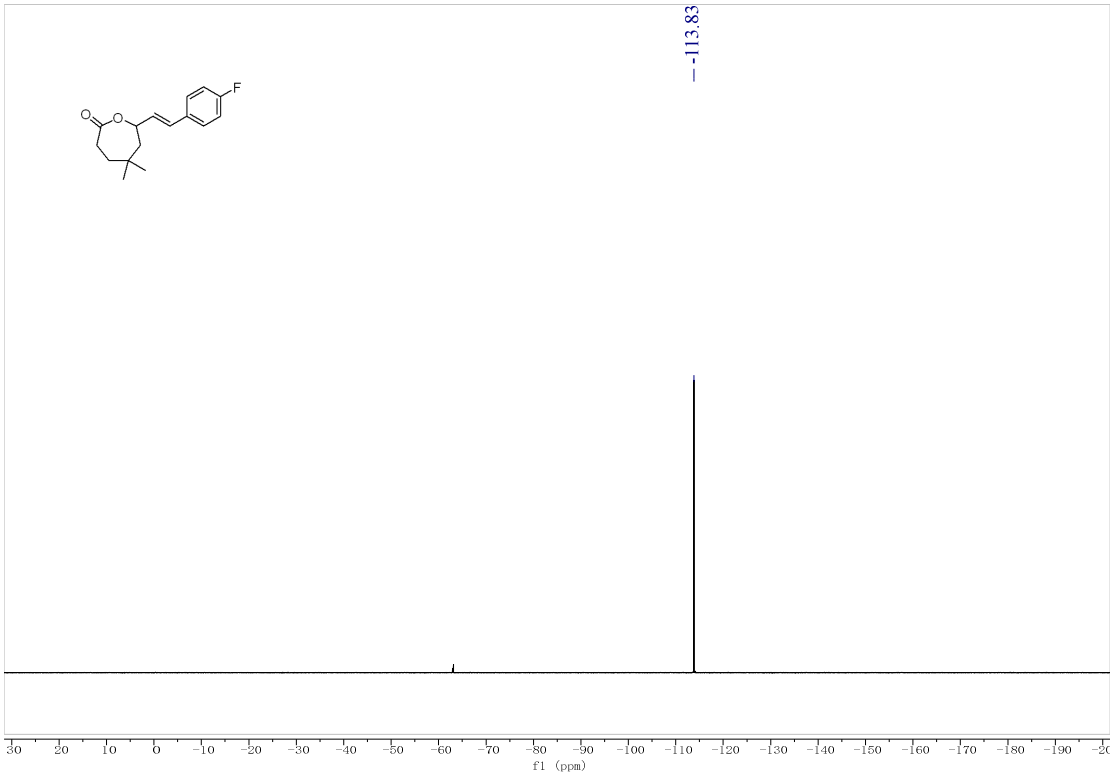
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



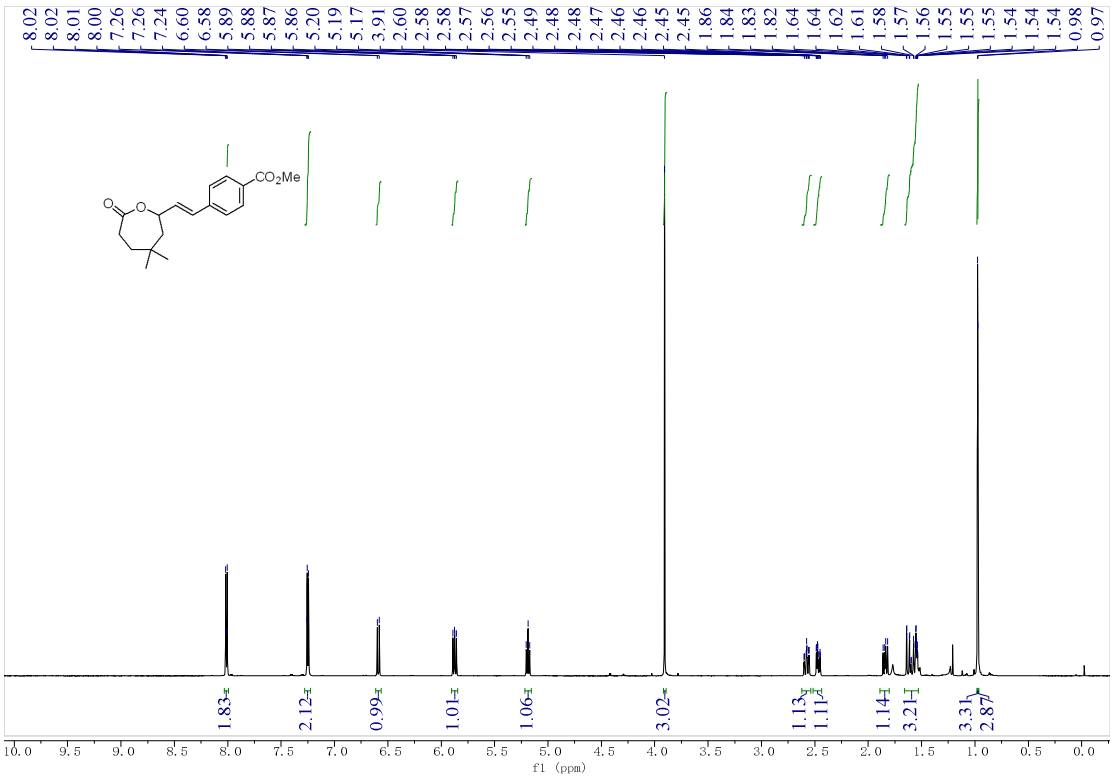
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3d**



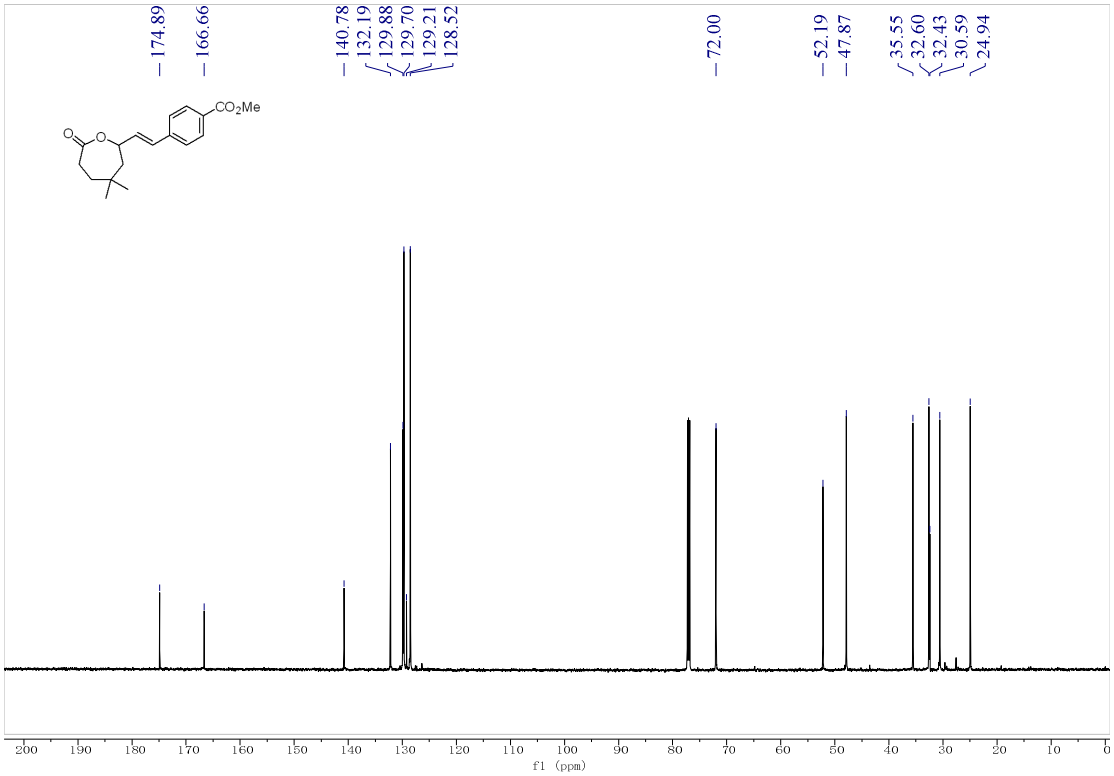
^{19}F NMR (376 MHz, $CDCl_3$) of **3d**



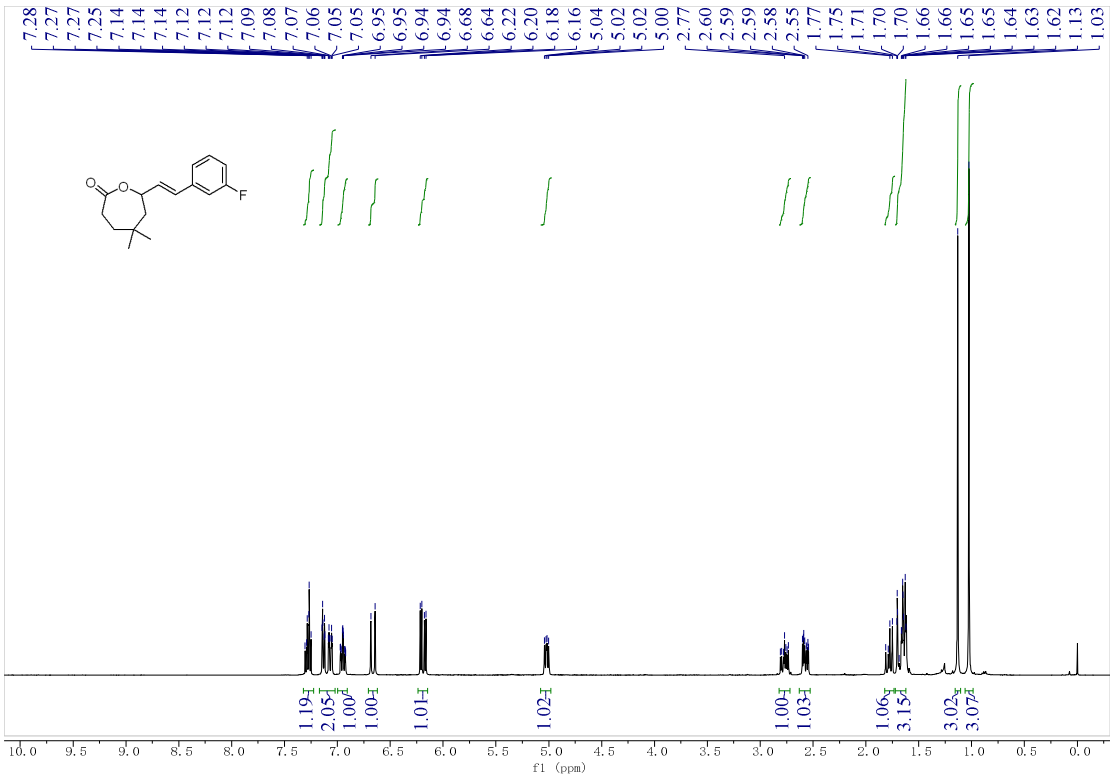
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



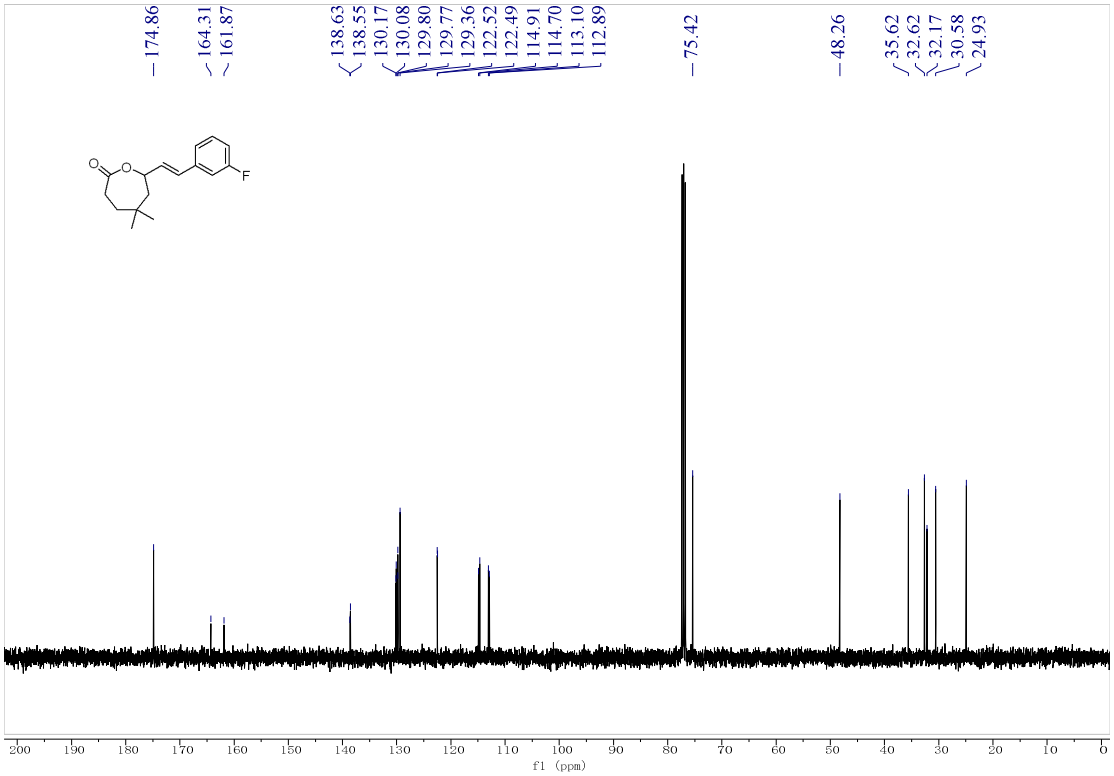
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **3e**



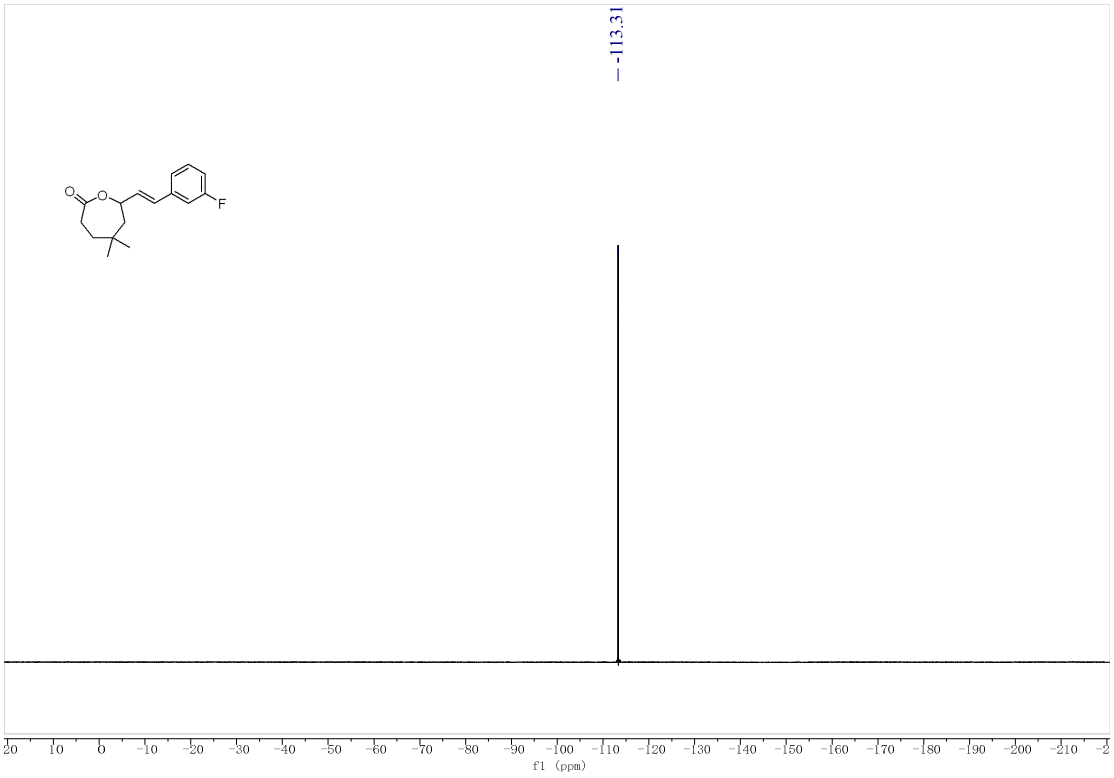
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



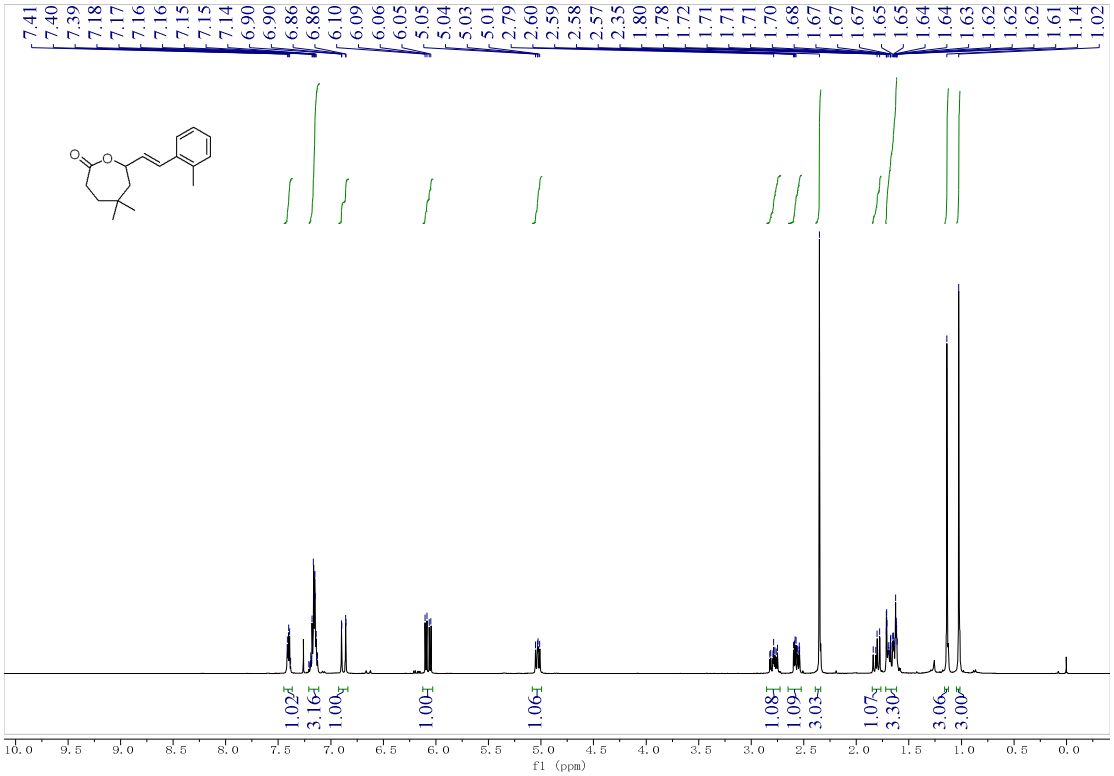
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) **3f**



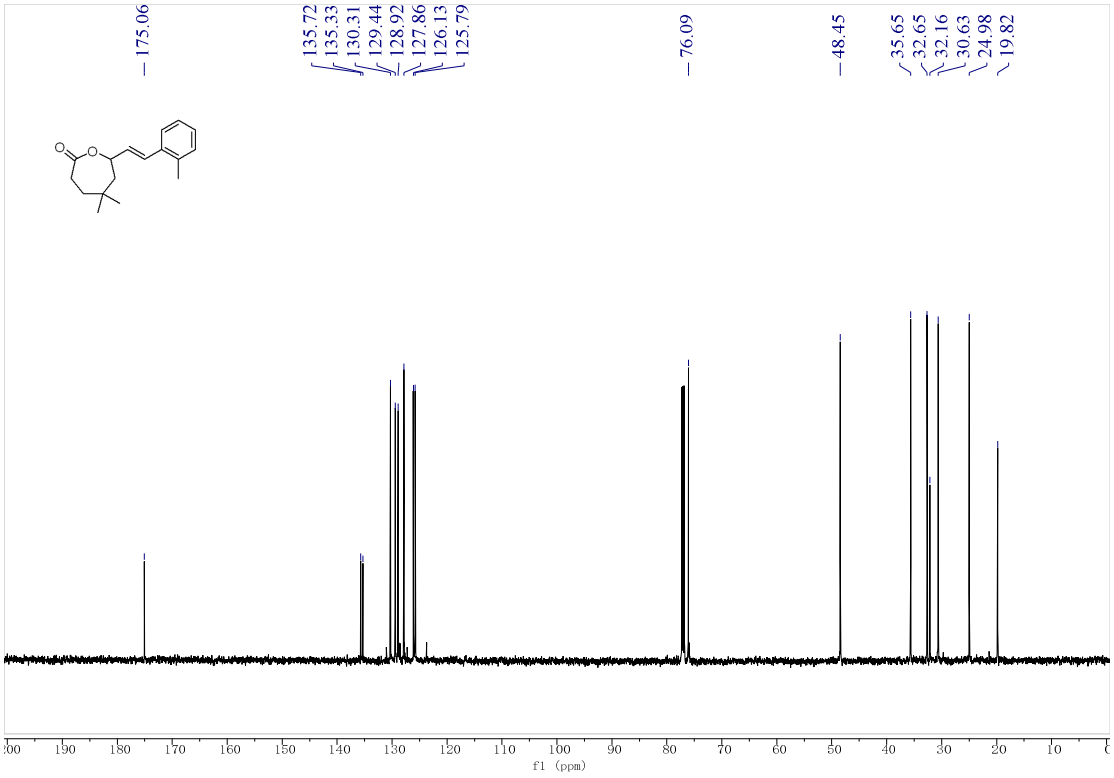
^{19}F NMR (376 MHz, $CDCl_3$) of **3f**



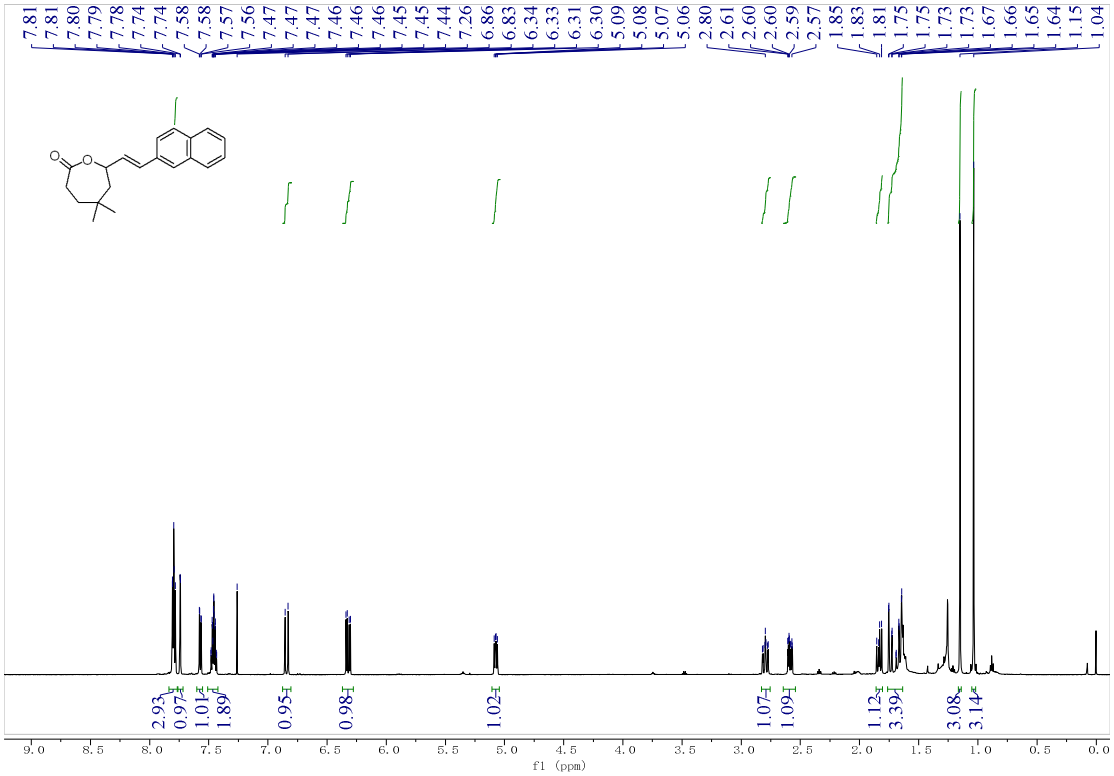
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



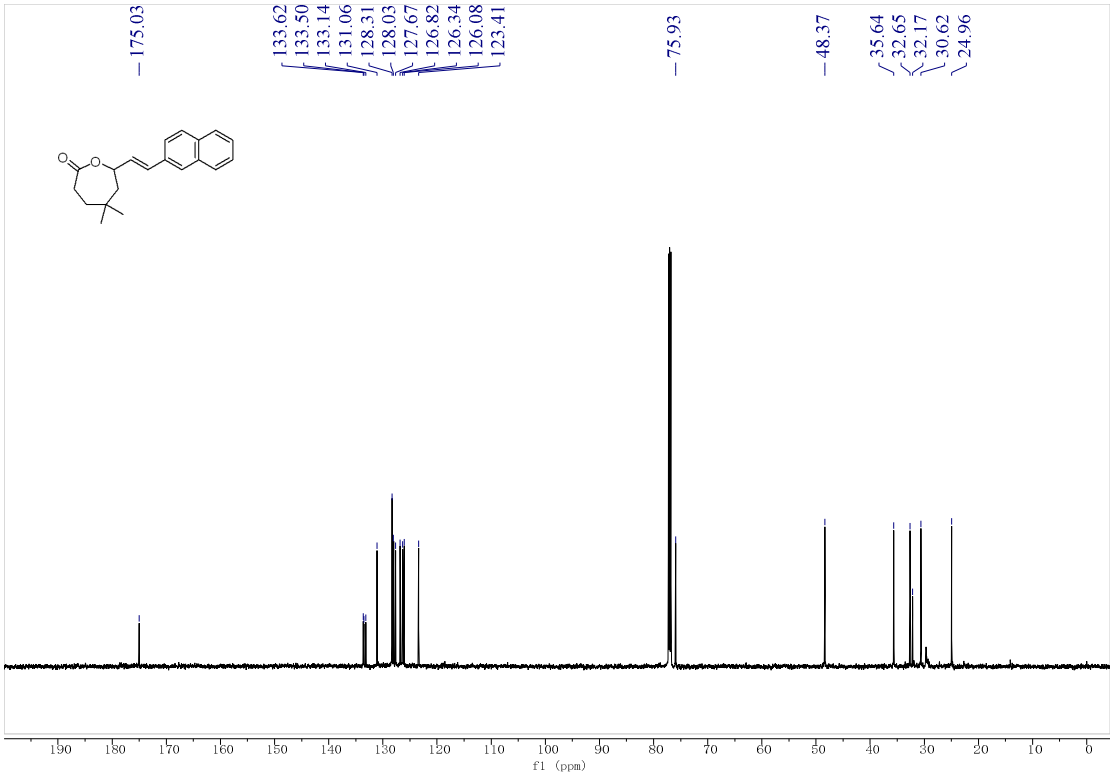
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3g**



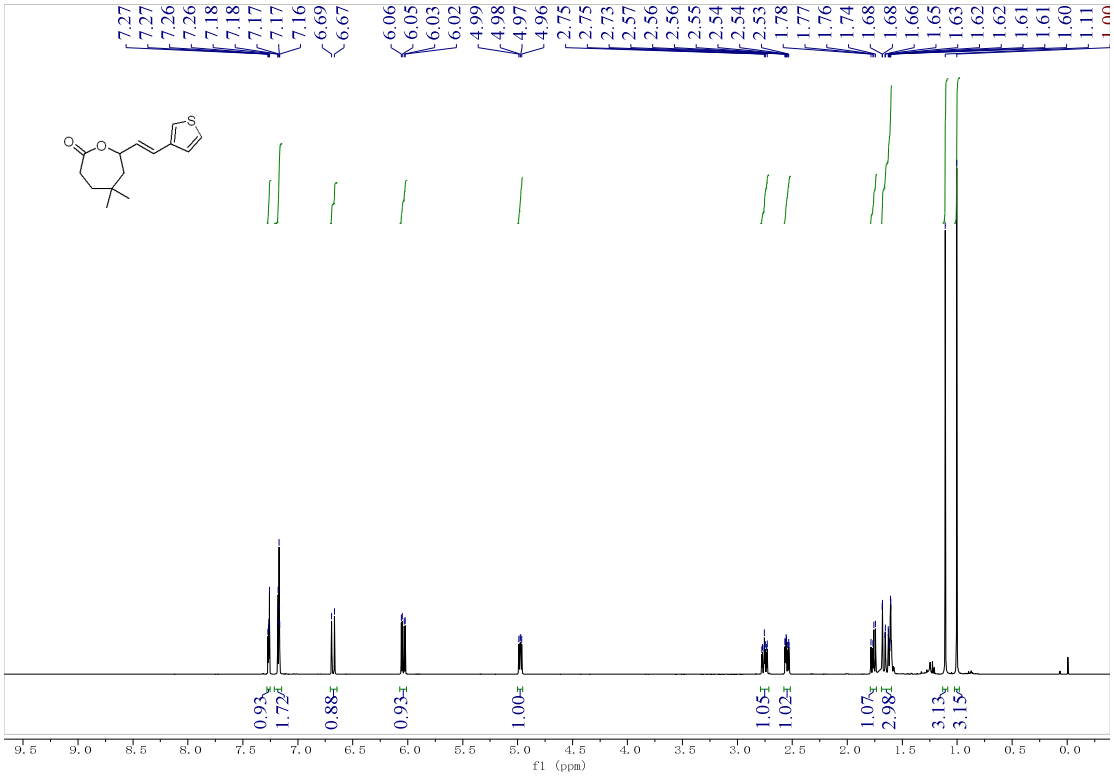
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



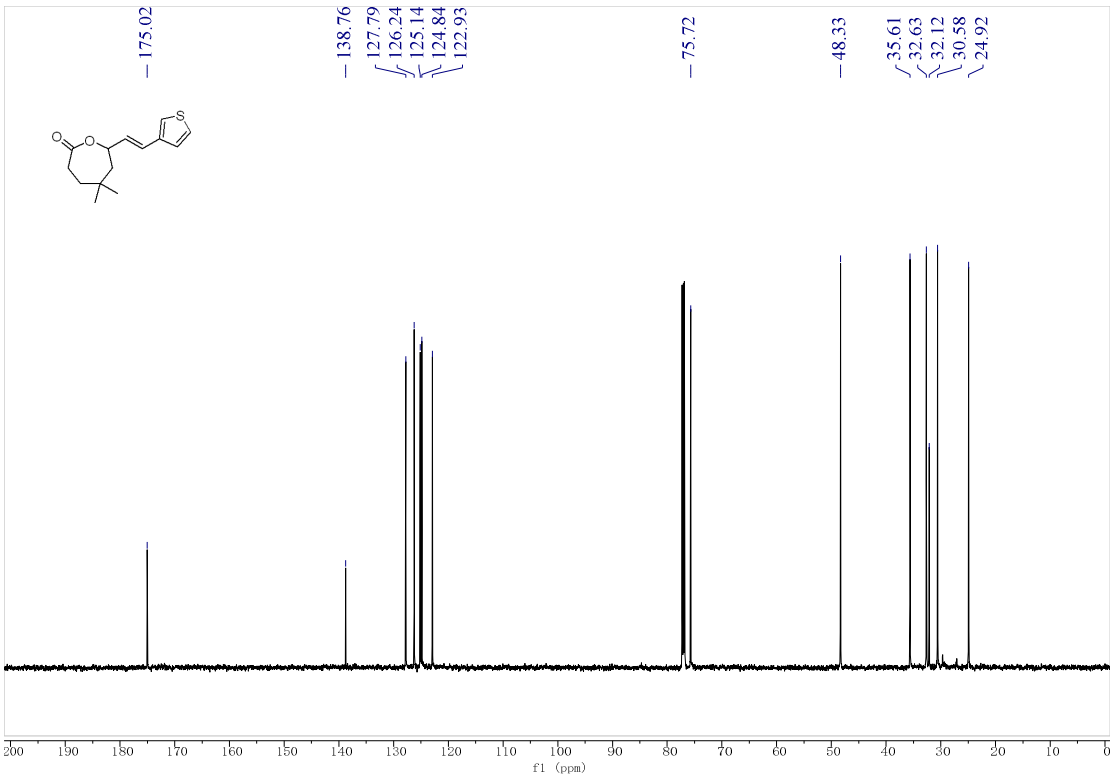
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3h**



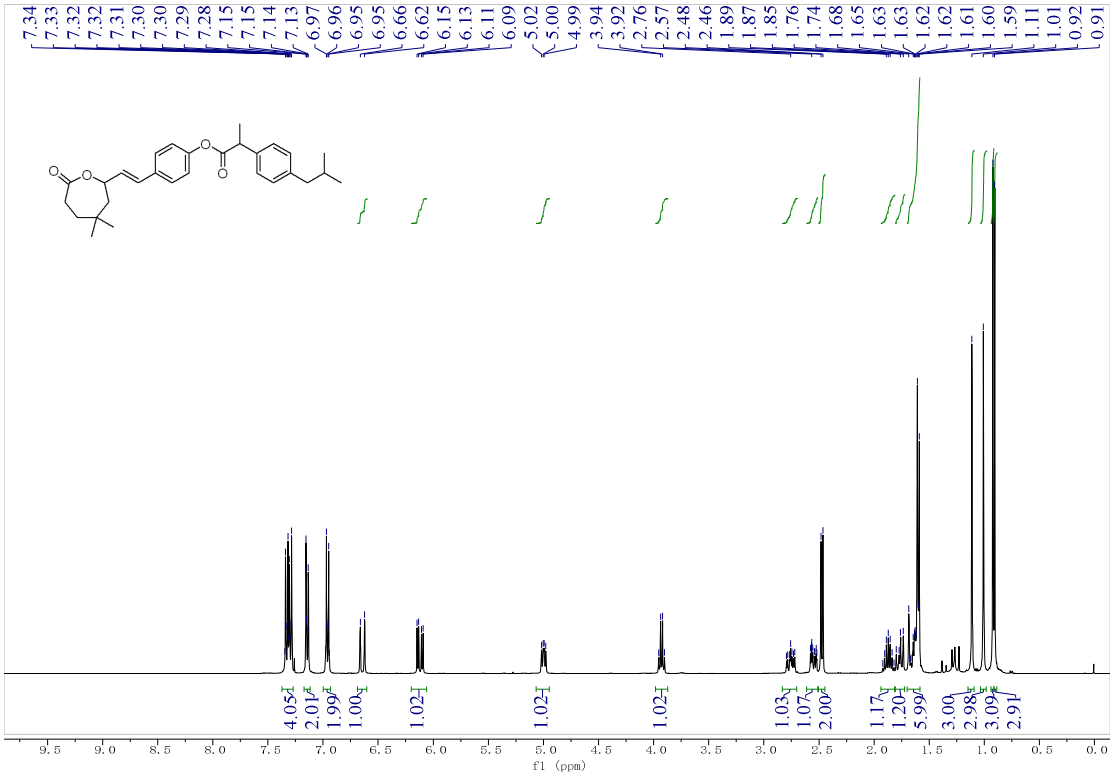
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



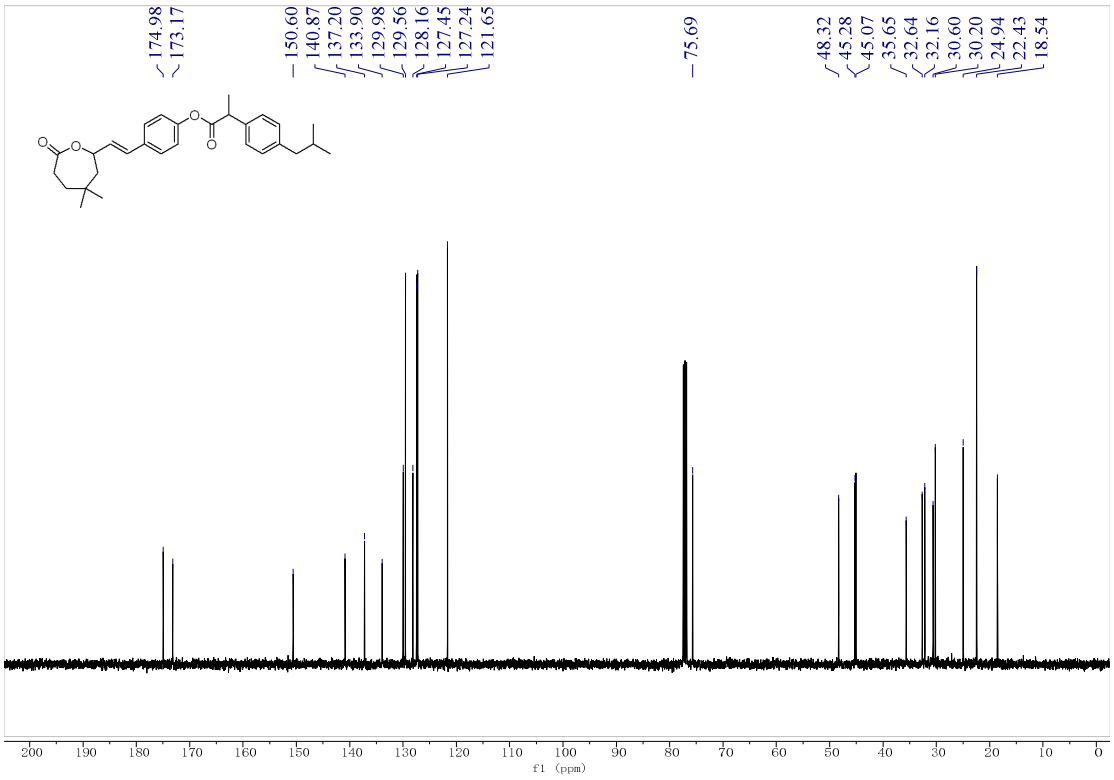
^{13}C{1H} NMR (101 MHz, $CDCl_3$)of **3i**



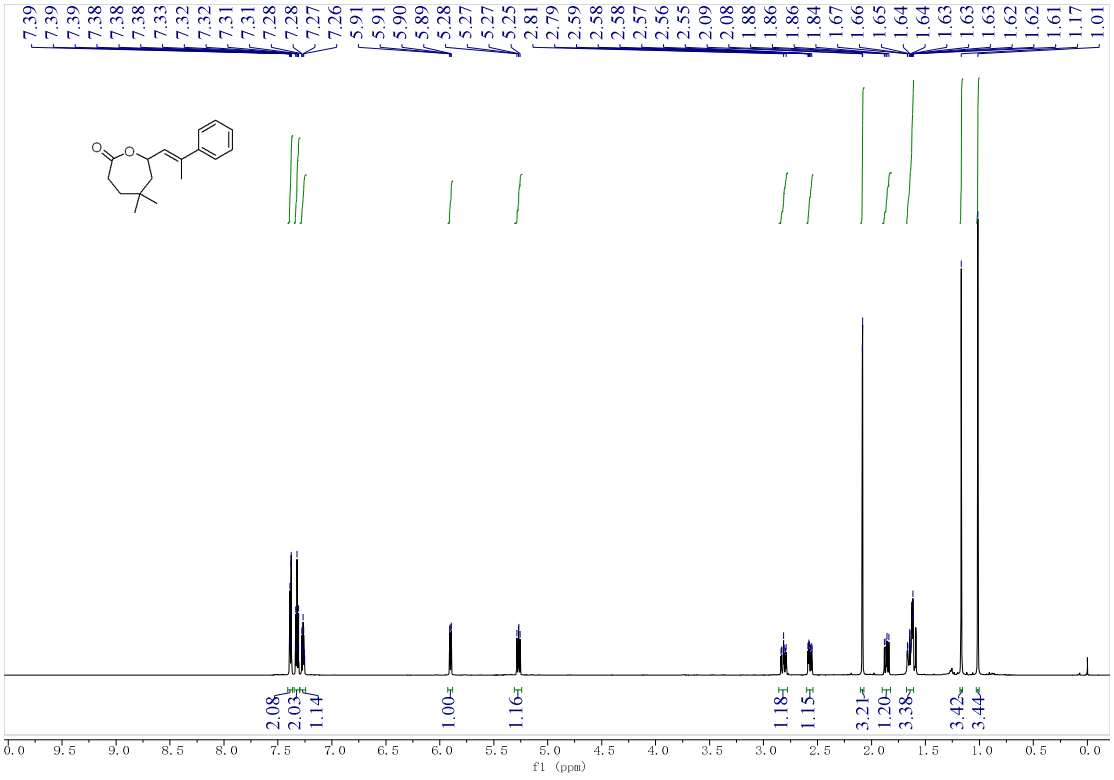
1H NMR (400 MHz, CDCl3) of **3j**



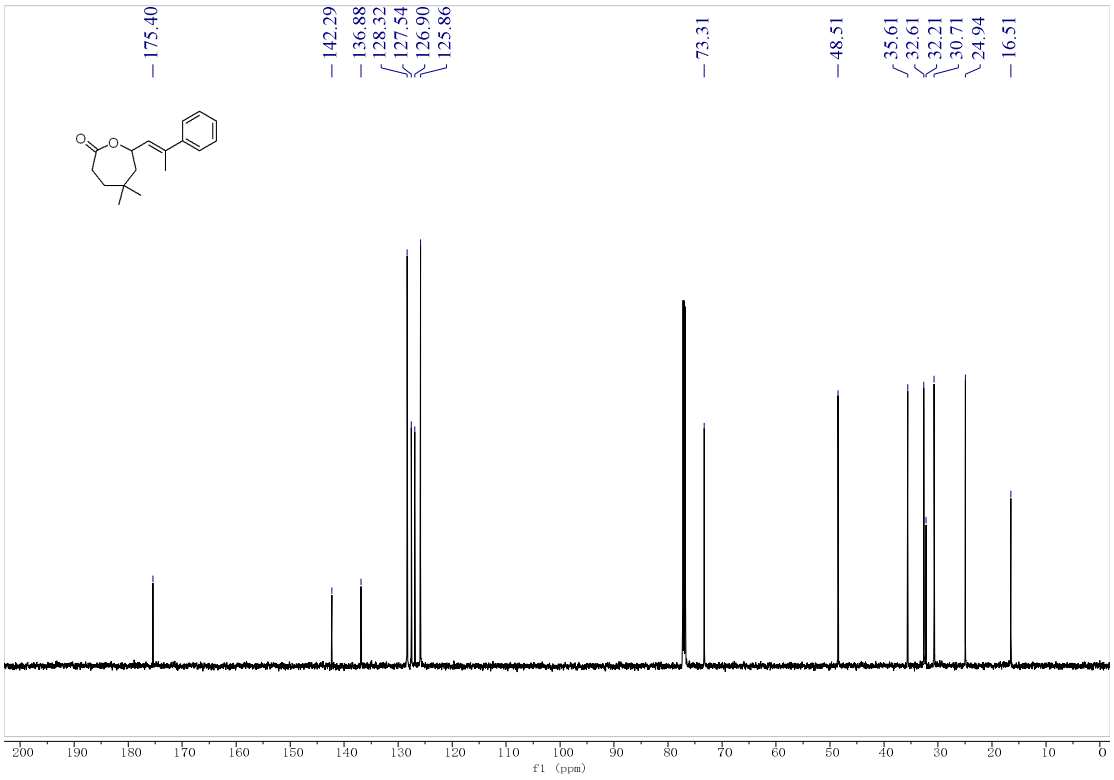
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **3j**



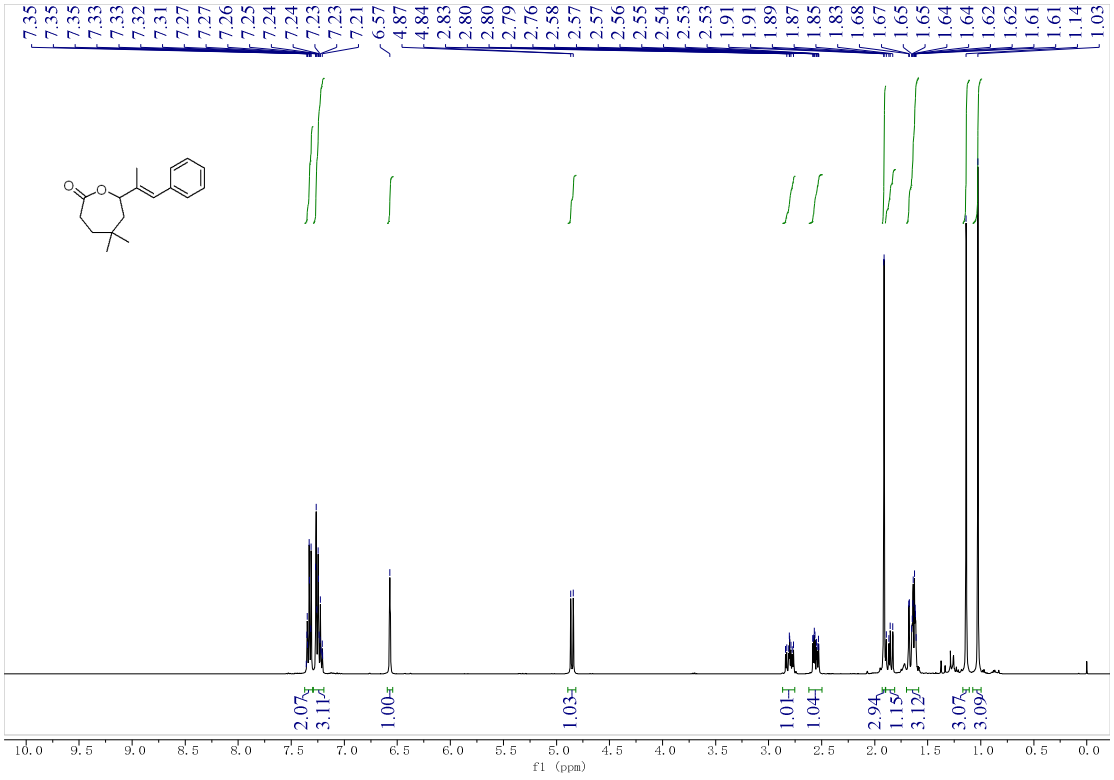
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



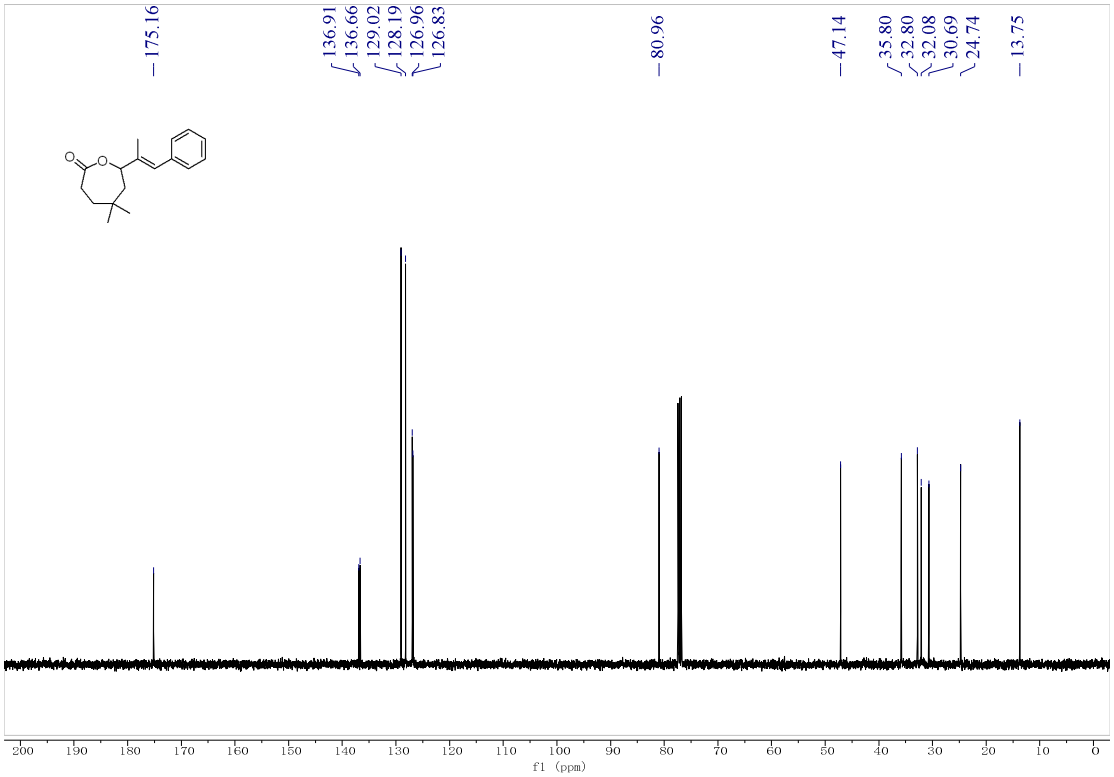
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3k**



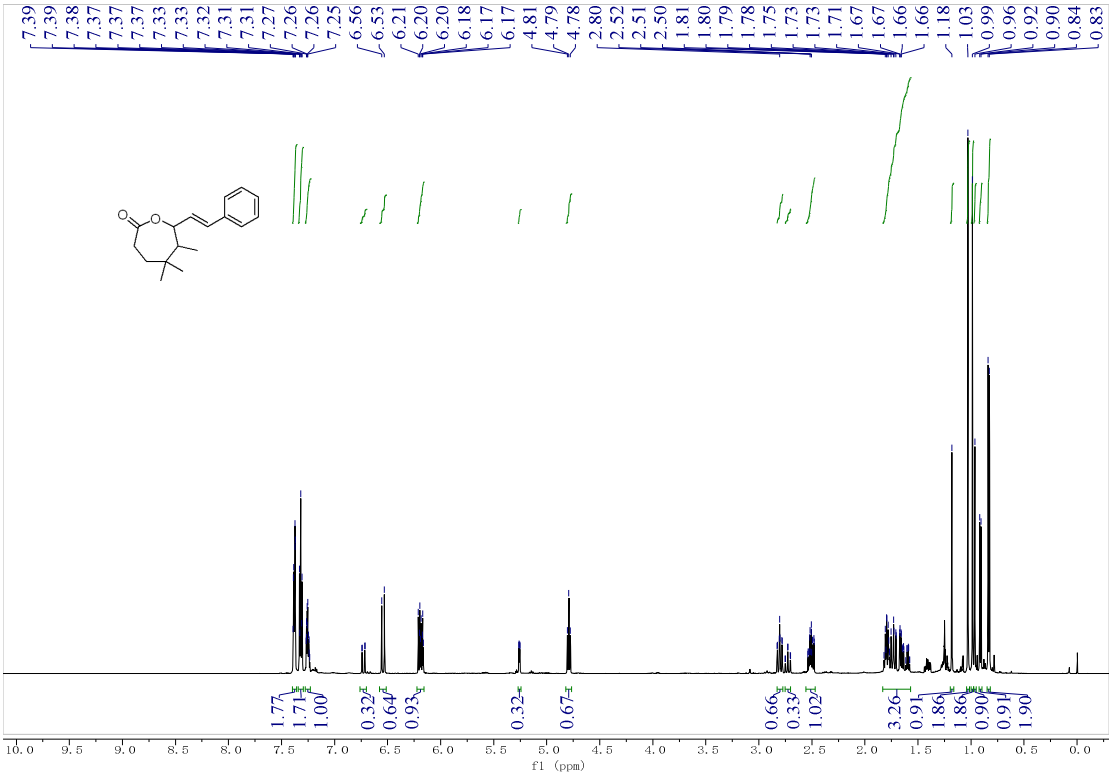
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



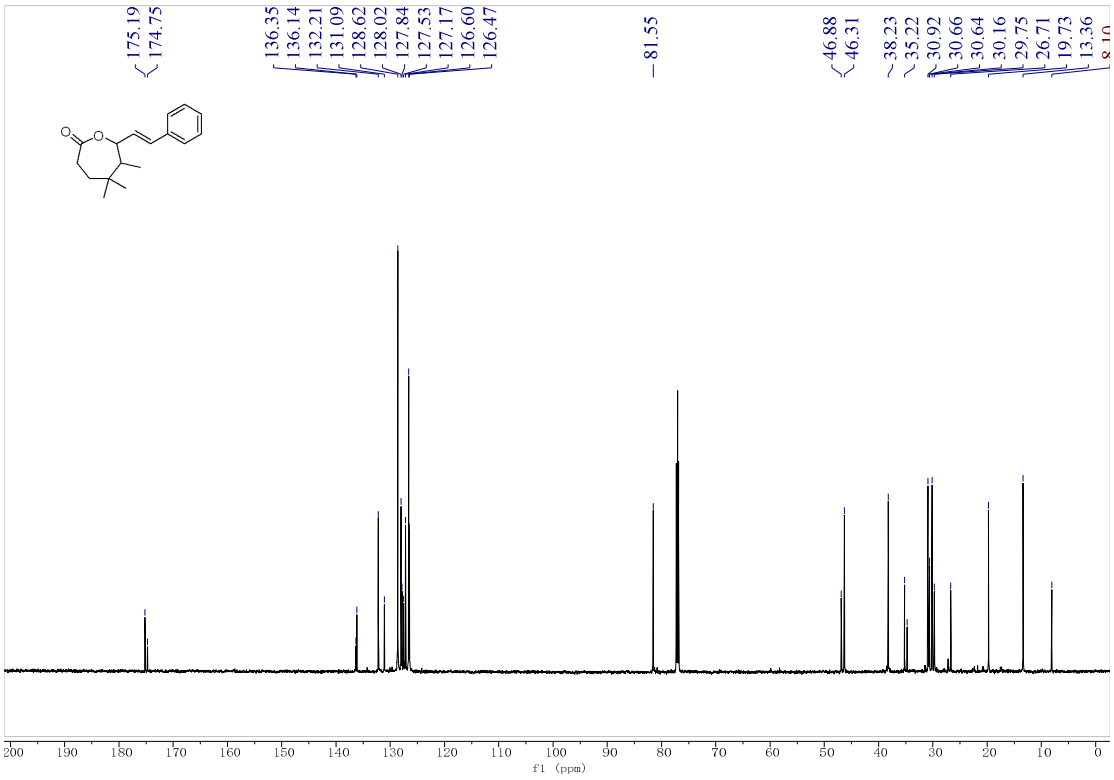
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3l**



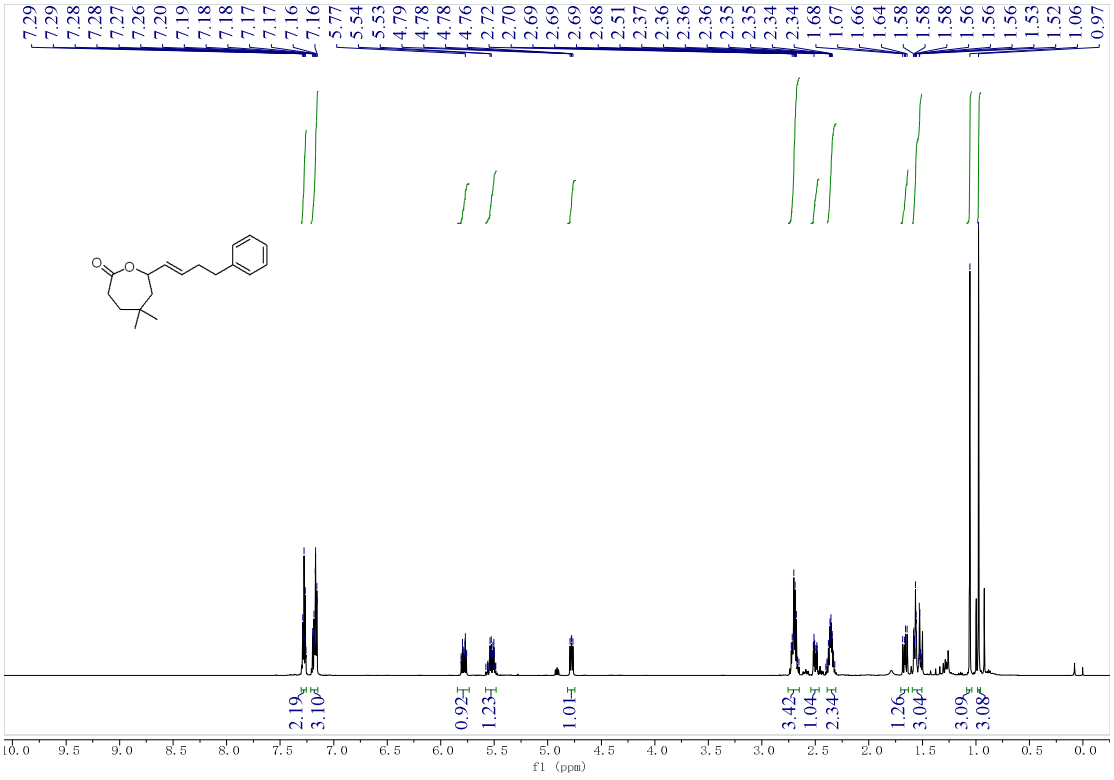
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



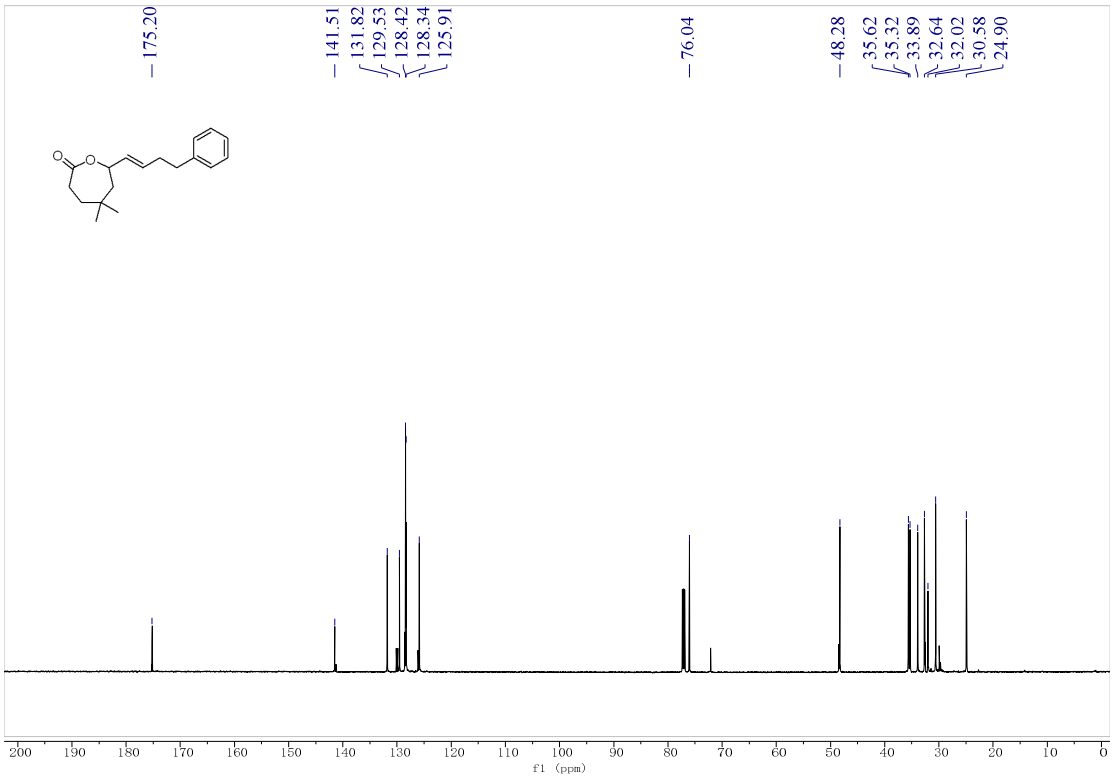
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3m**



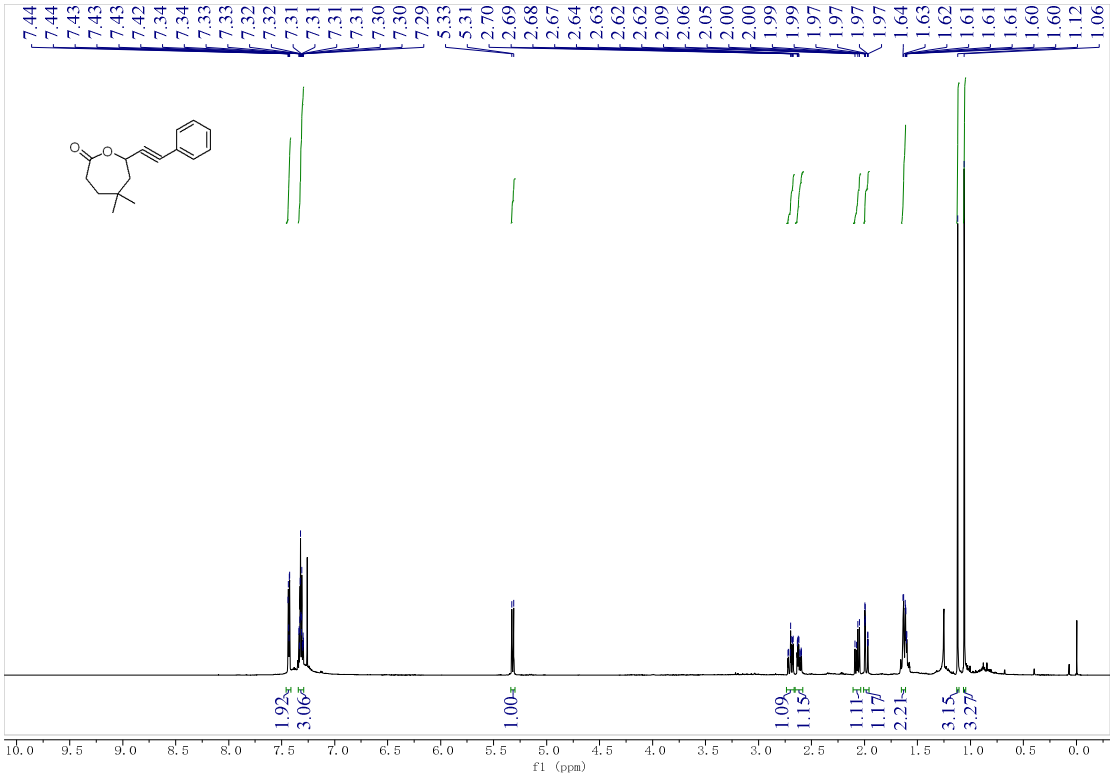
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



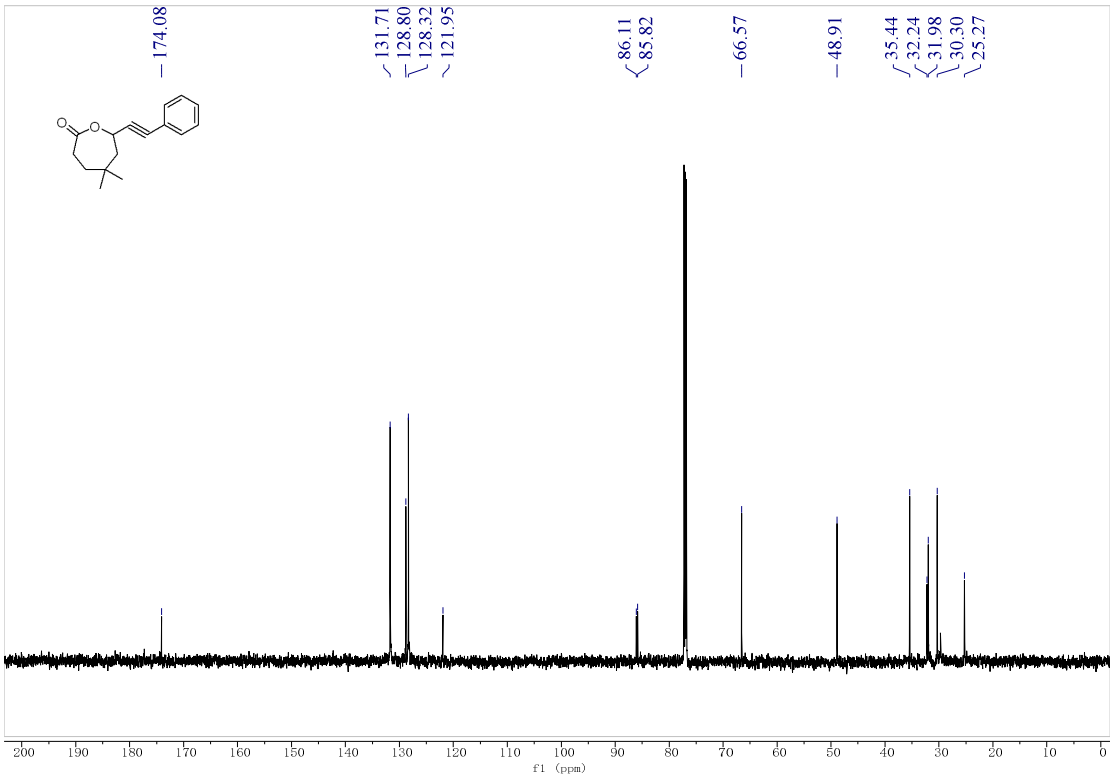
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3n**



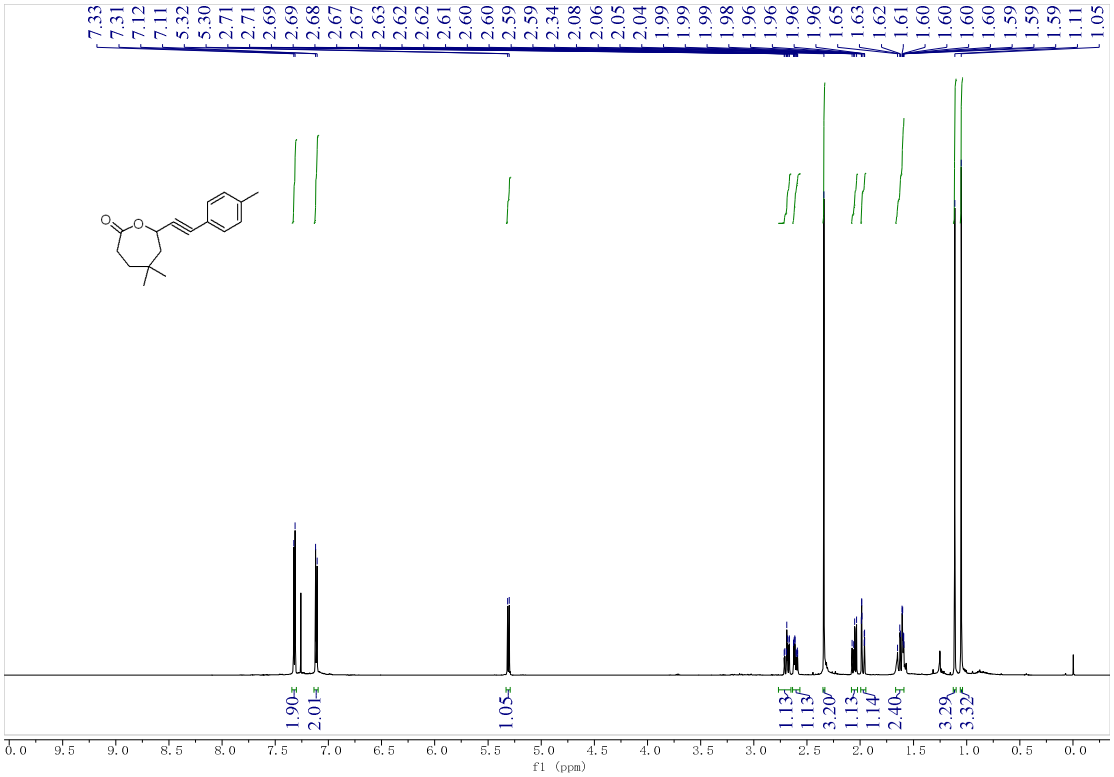
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



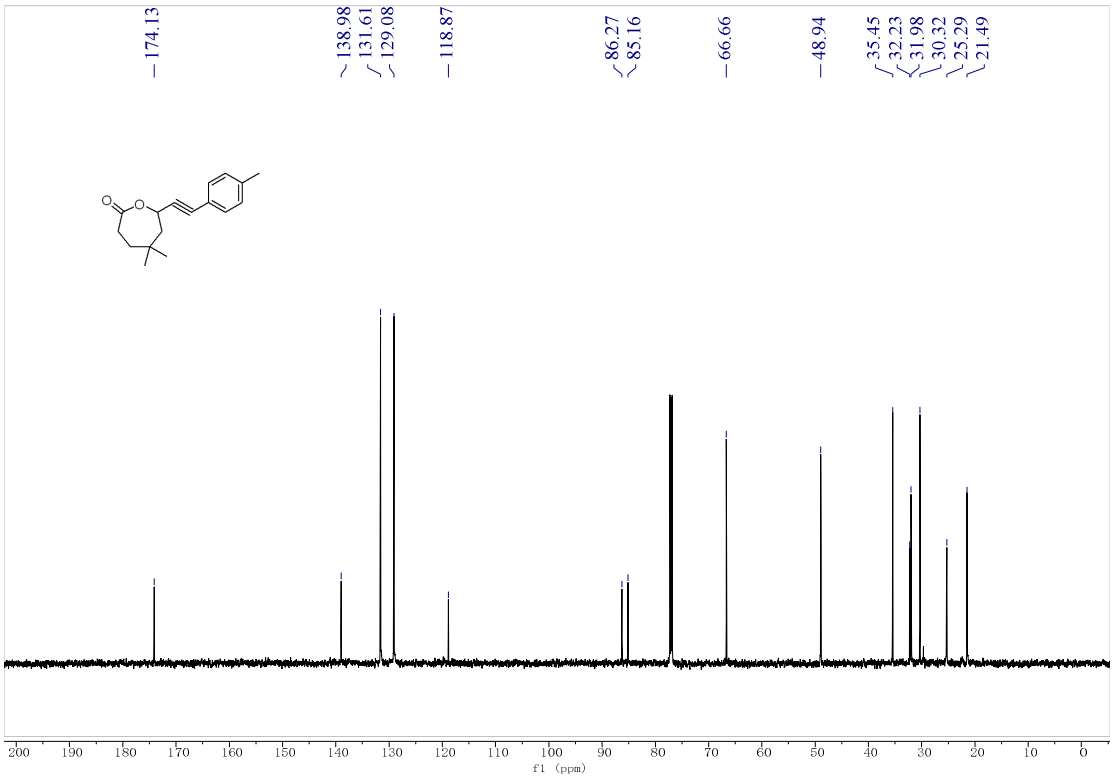
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3o**



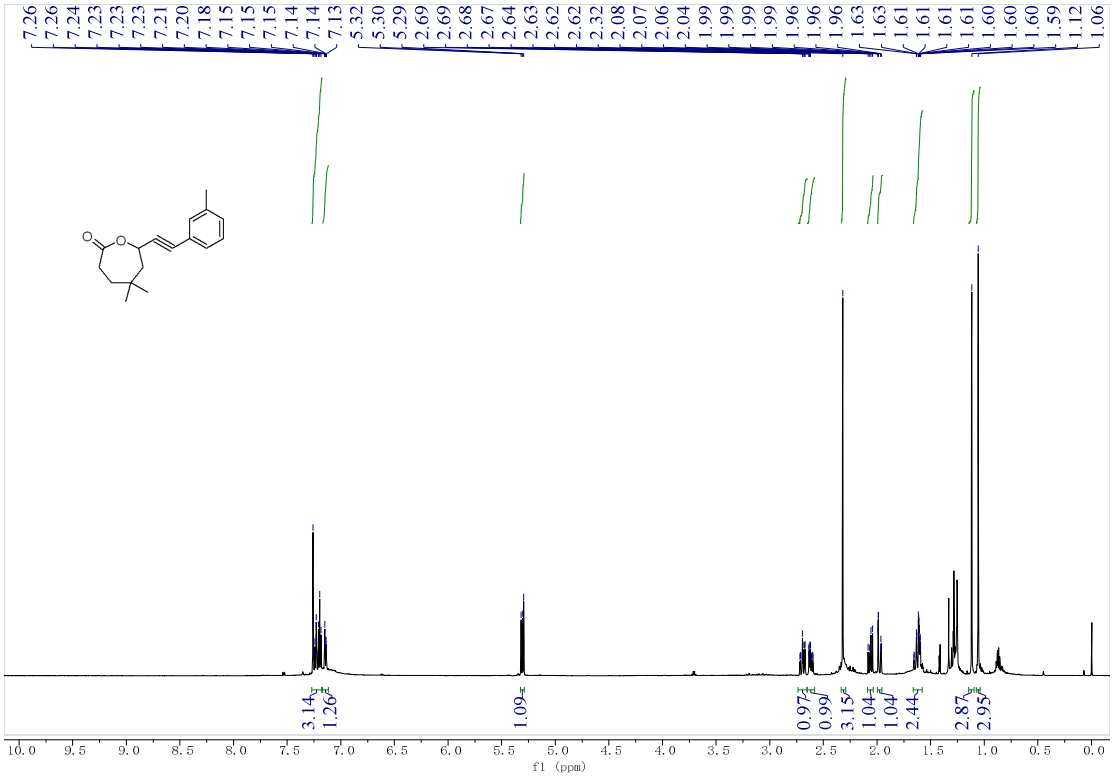
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



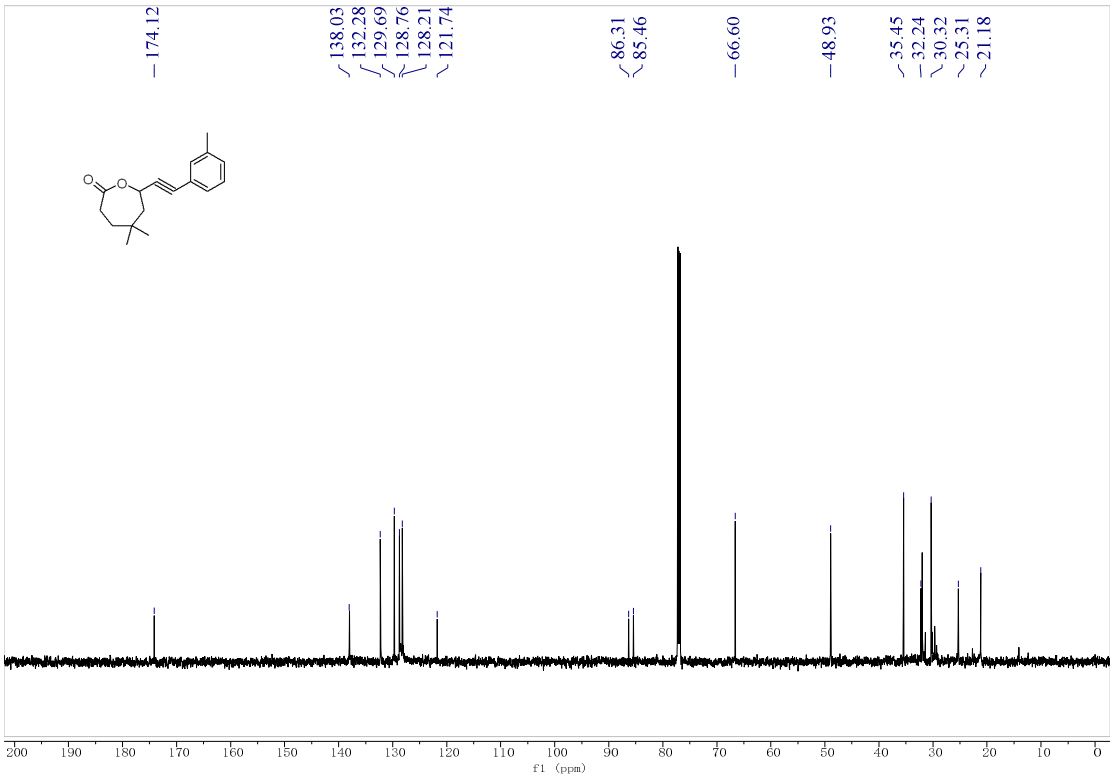
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3p**



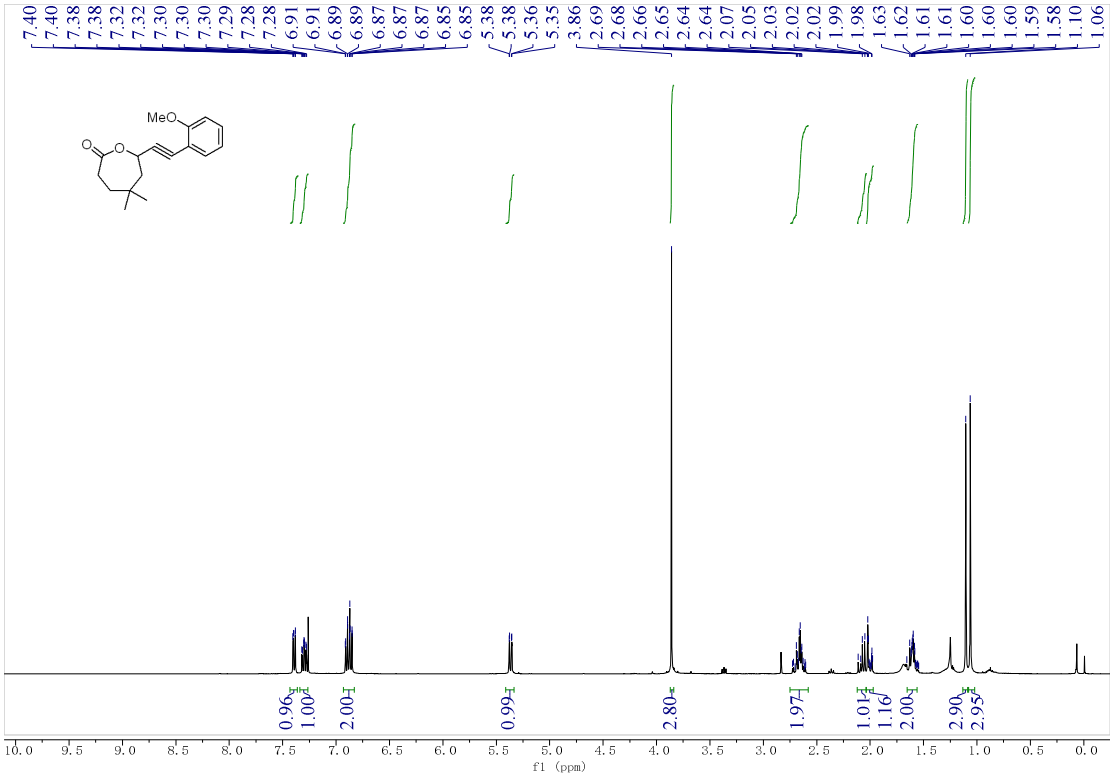
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



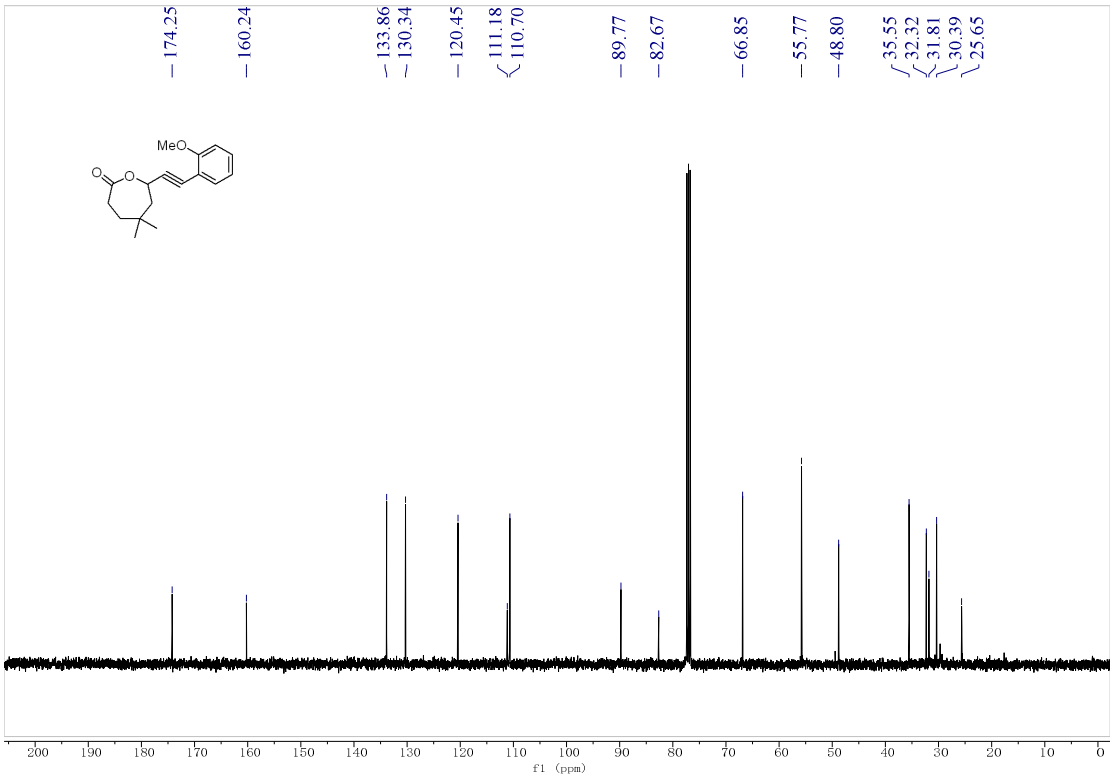
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3q**



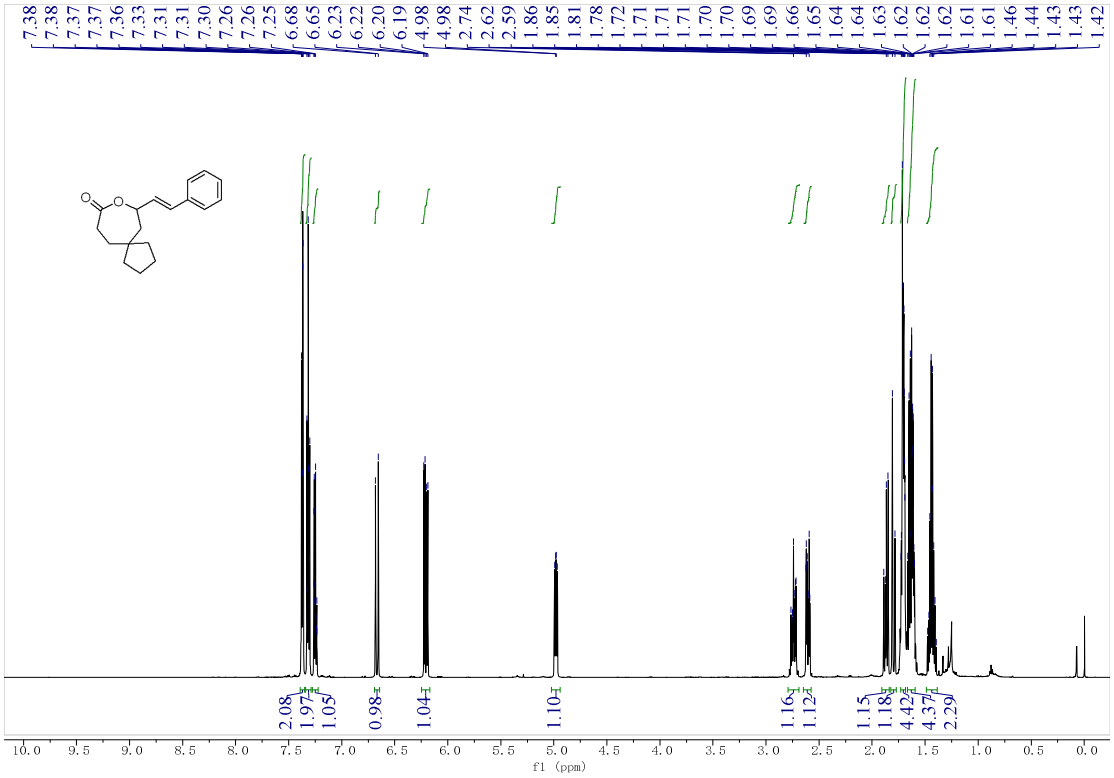
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



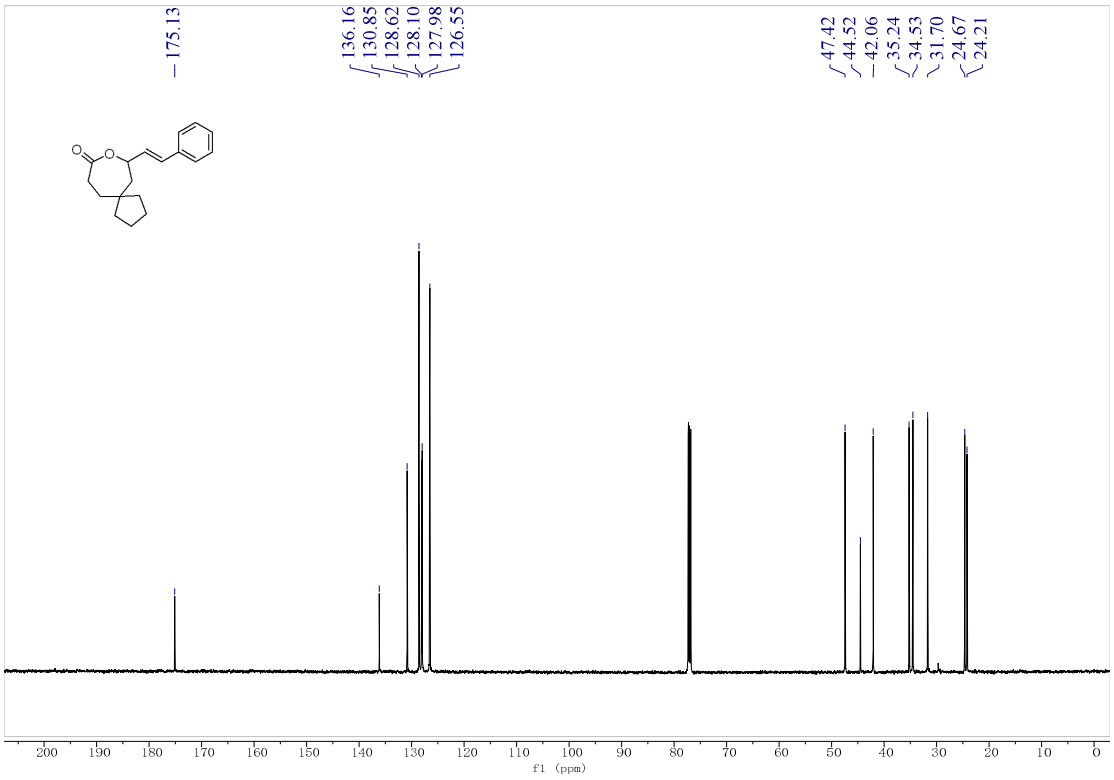
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3r**



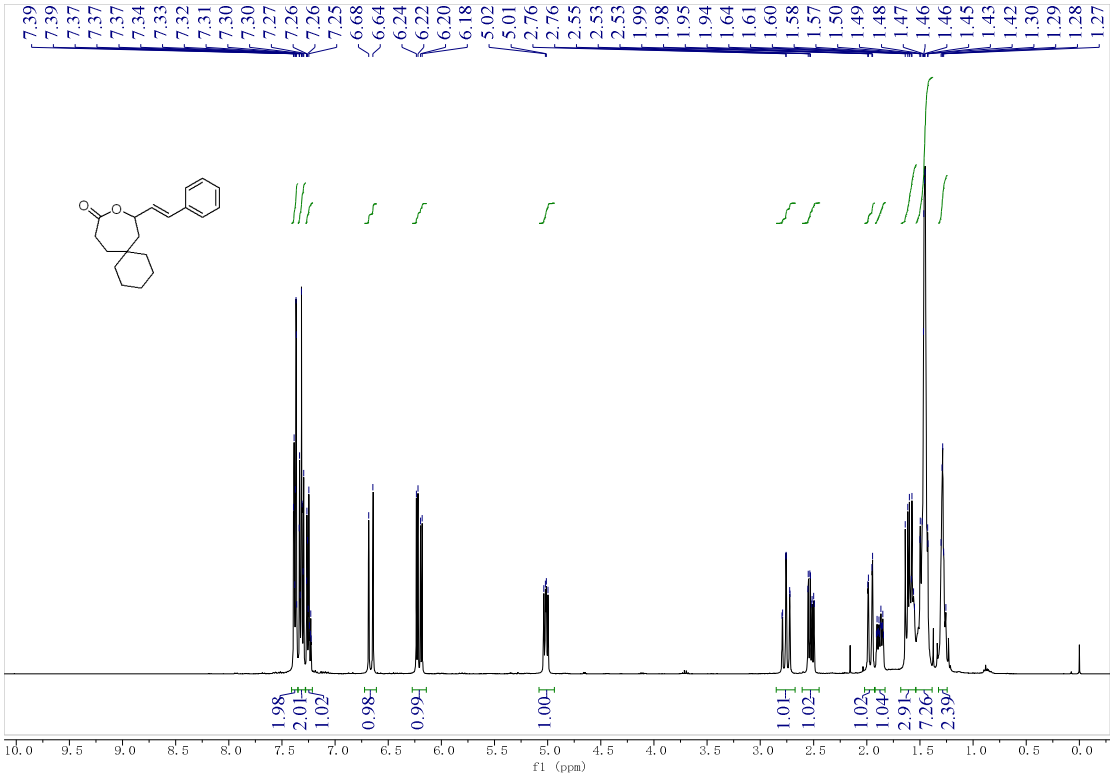
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



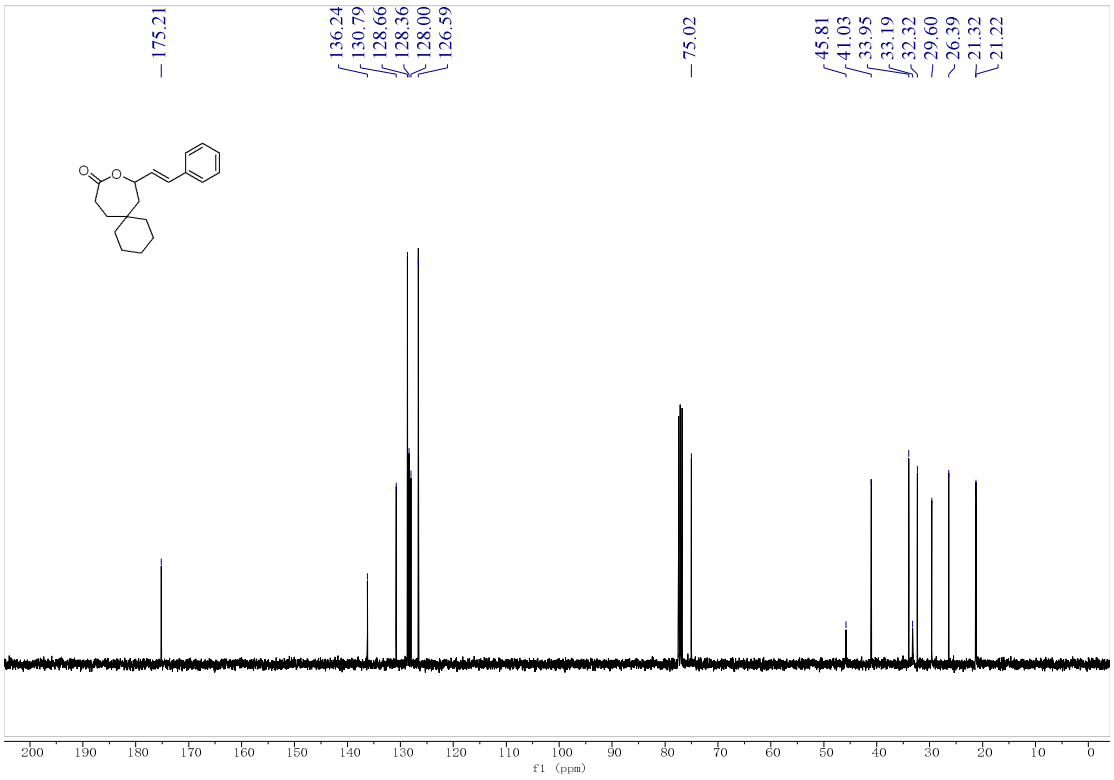
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4a**



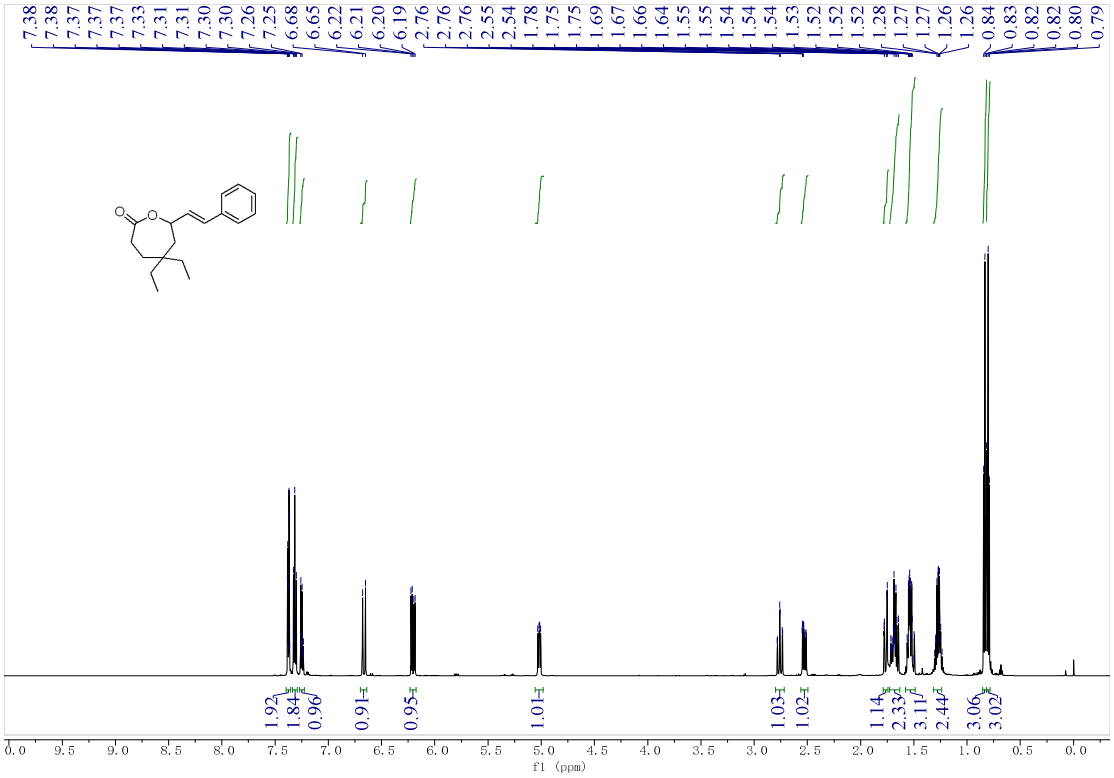
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



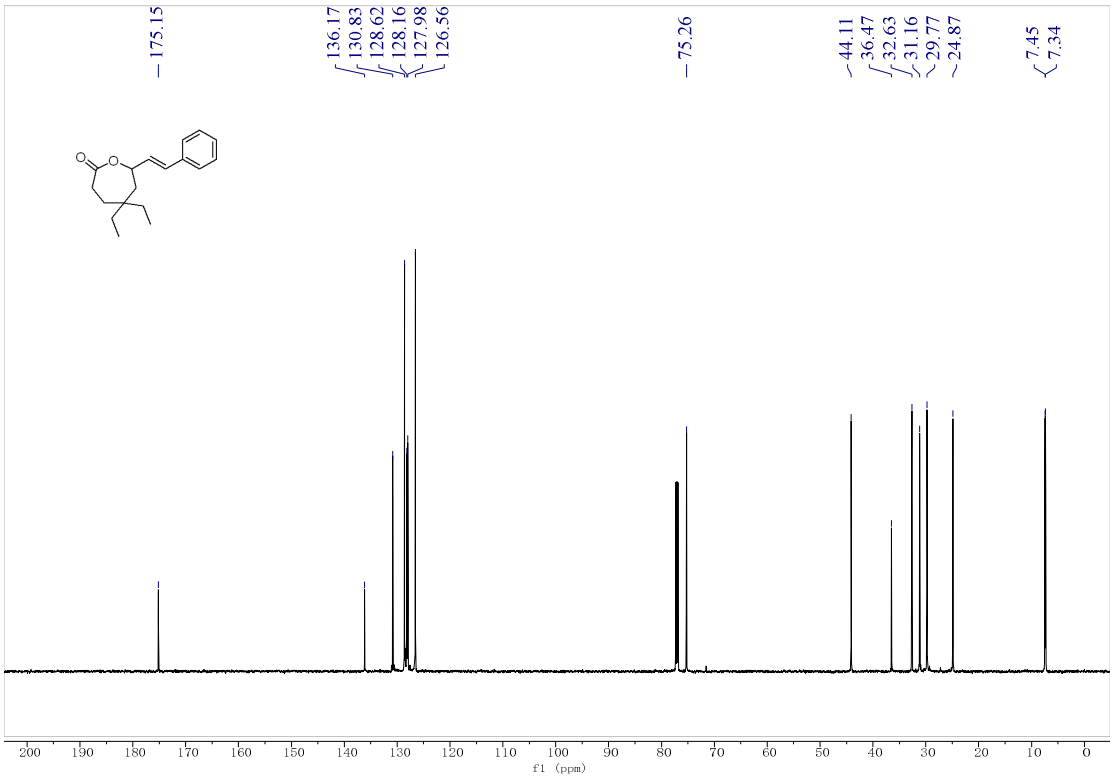
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4b**



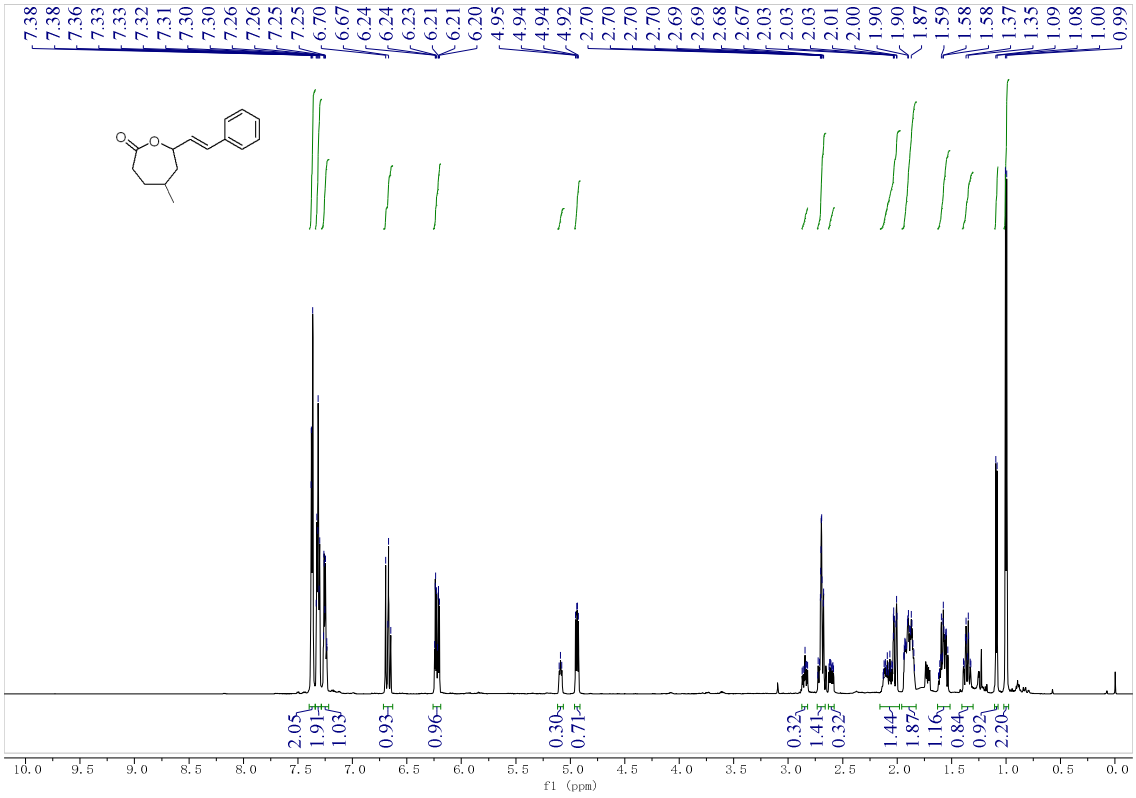
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



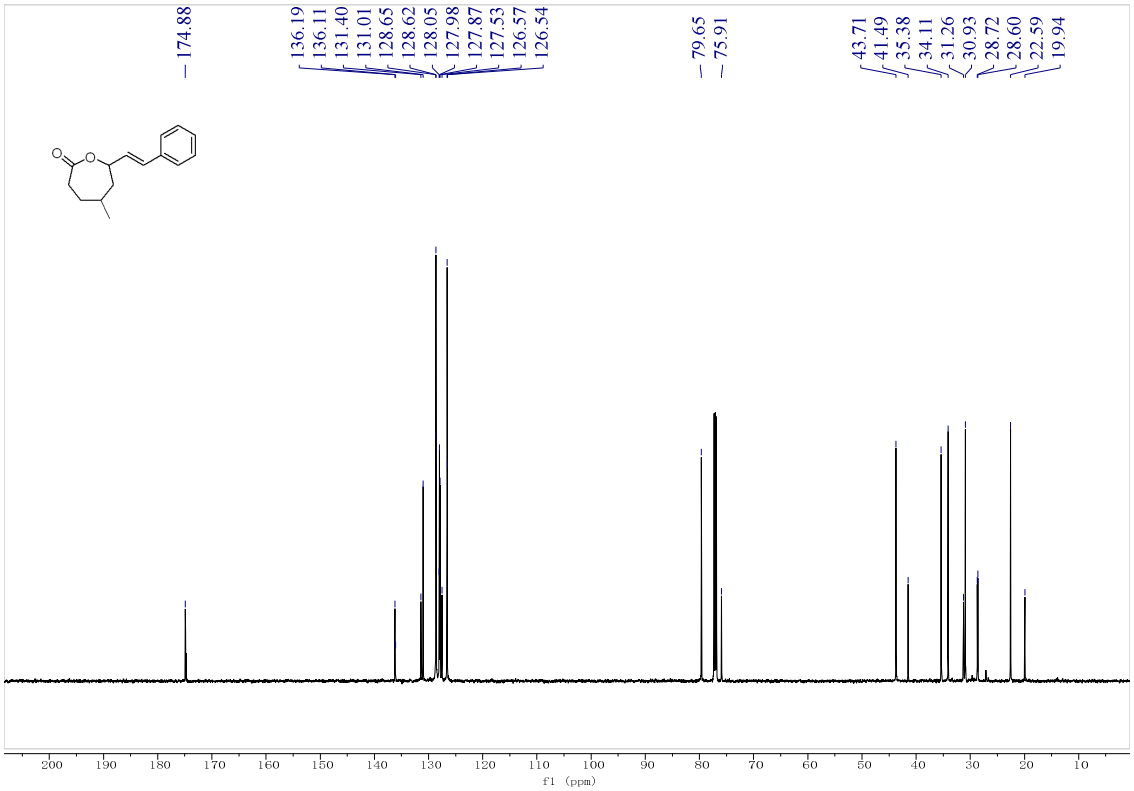
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4c**



^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4d**



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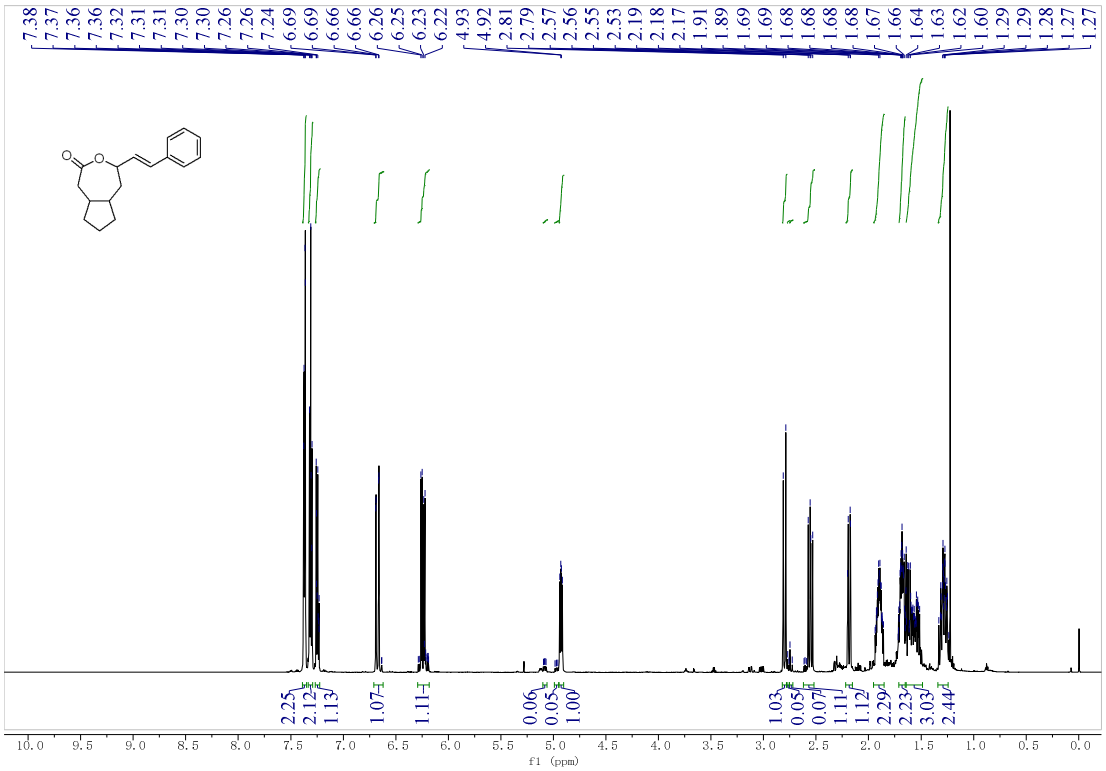
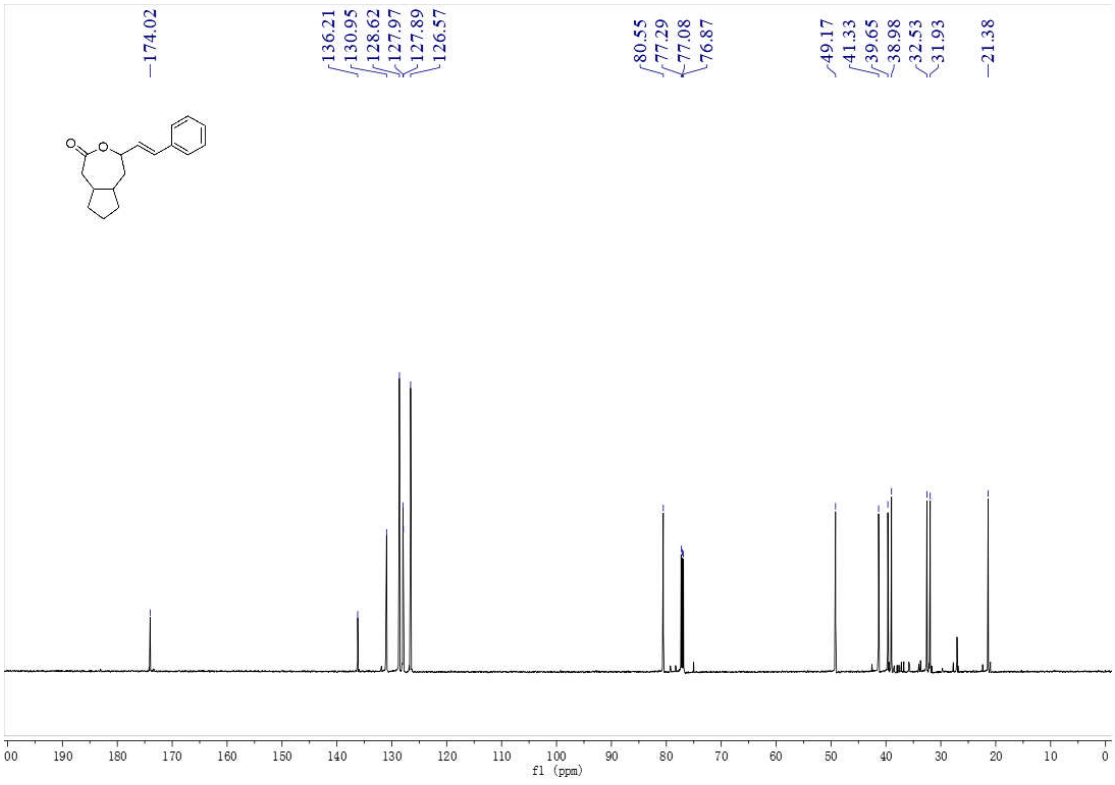
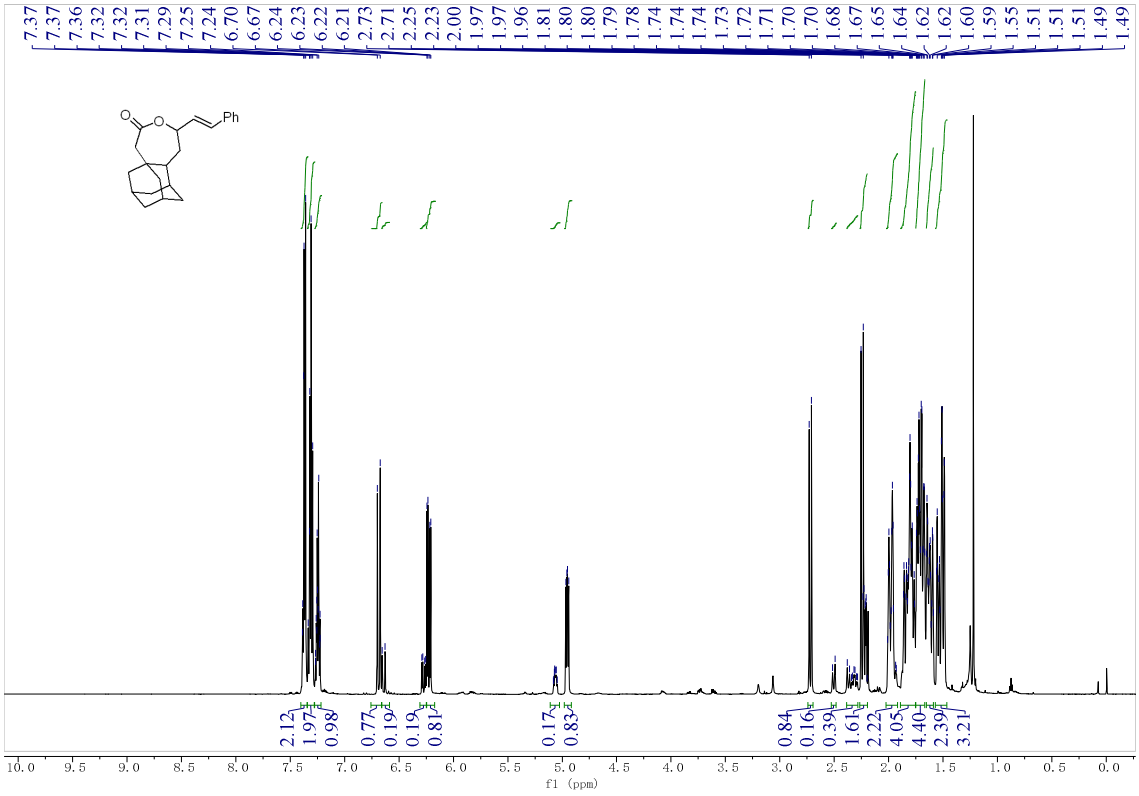


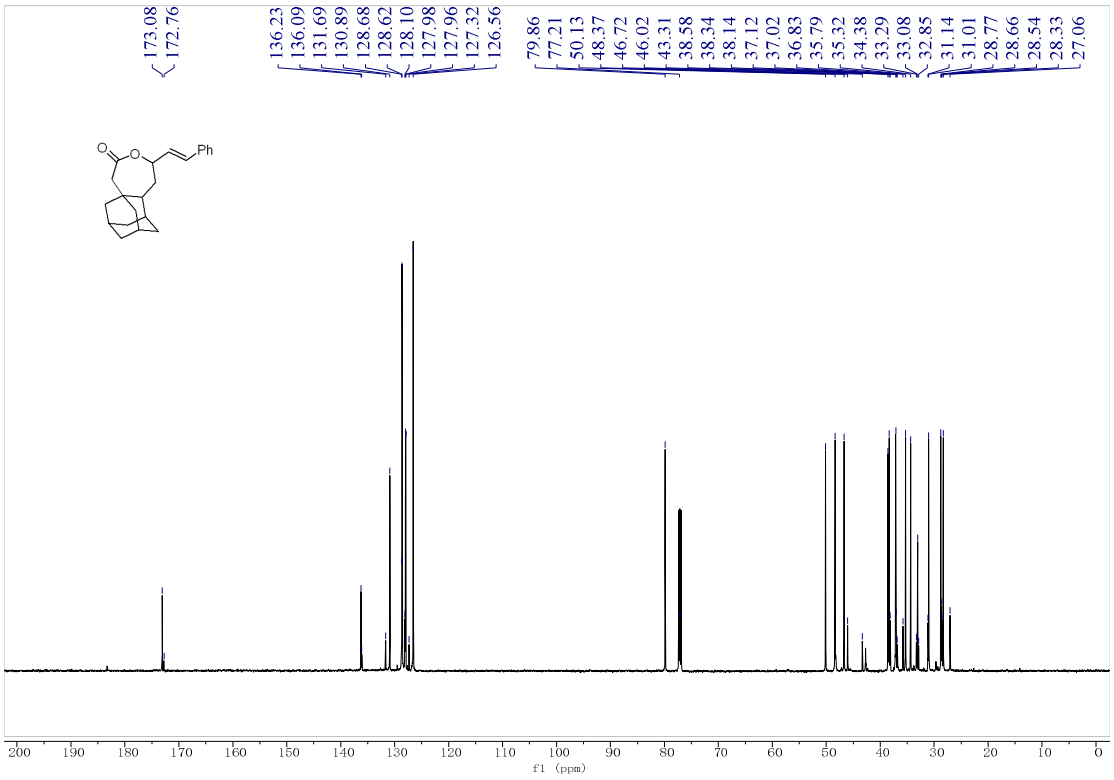
^{13}C{1H} NMR (101 MHz, $CDCl_3$) **4e**



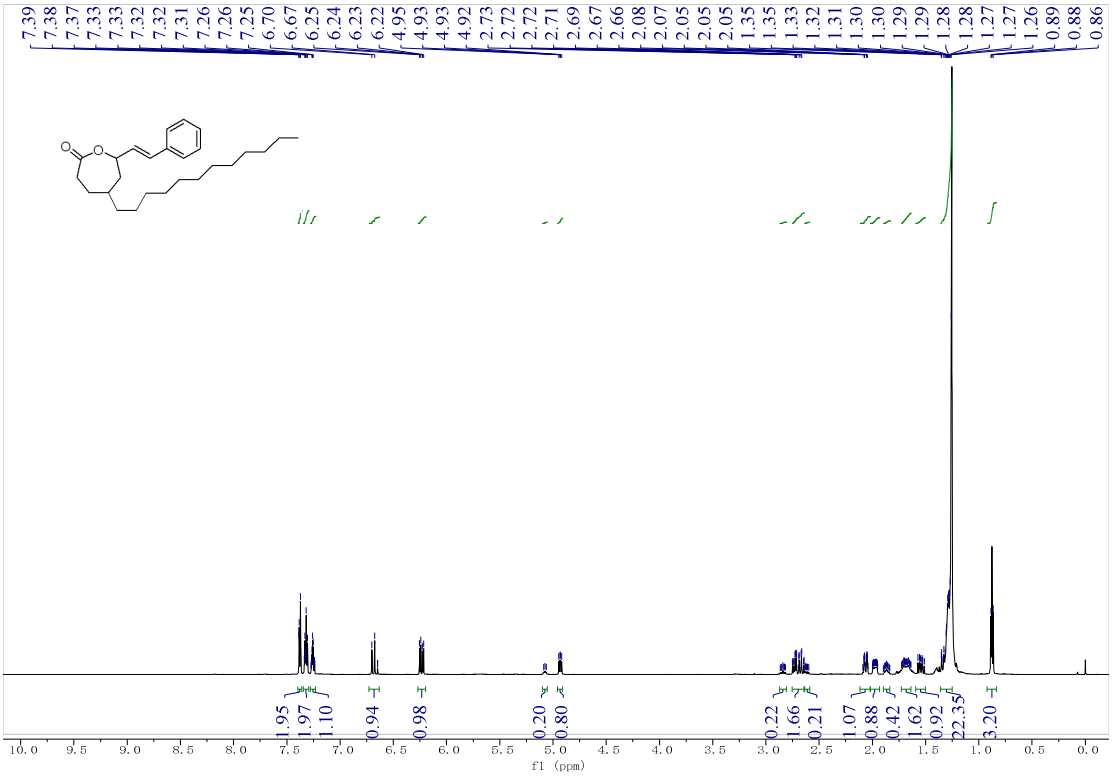
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



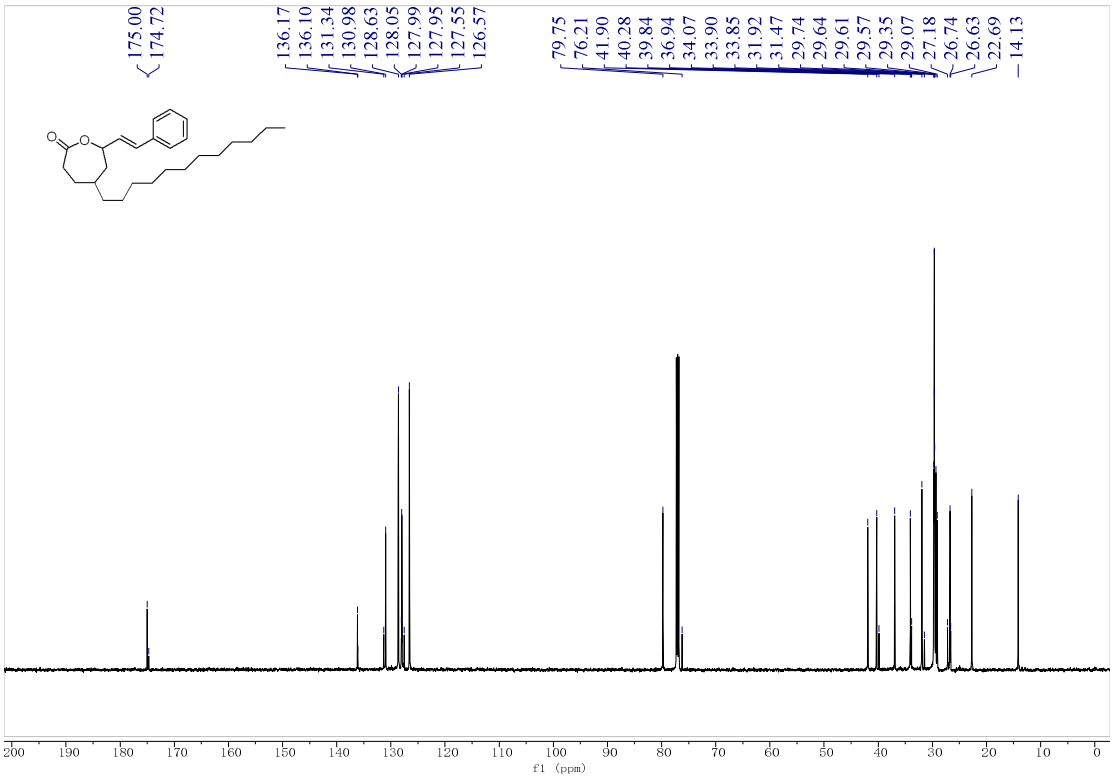
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4f**



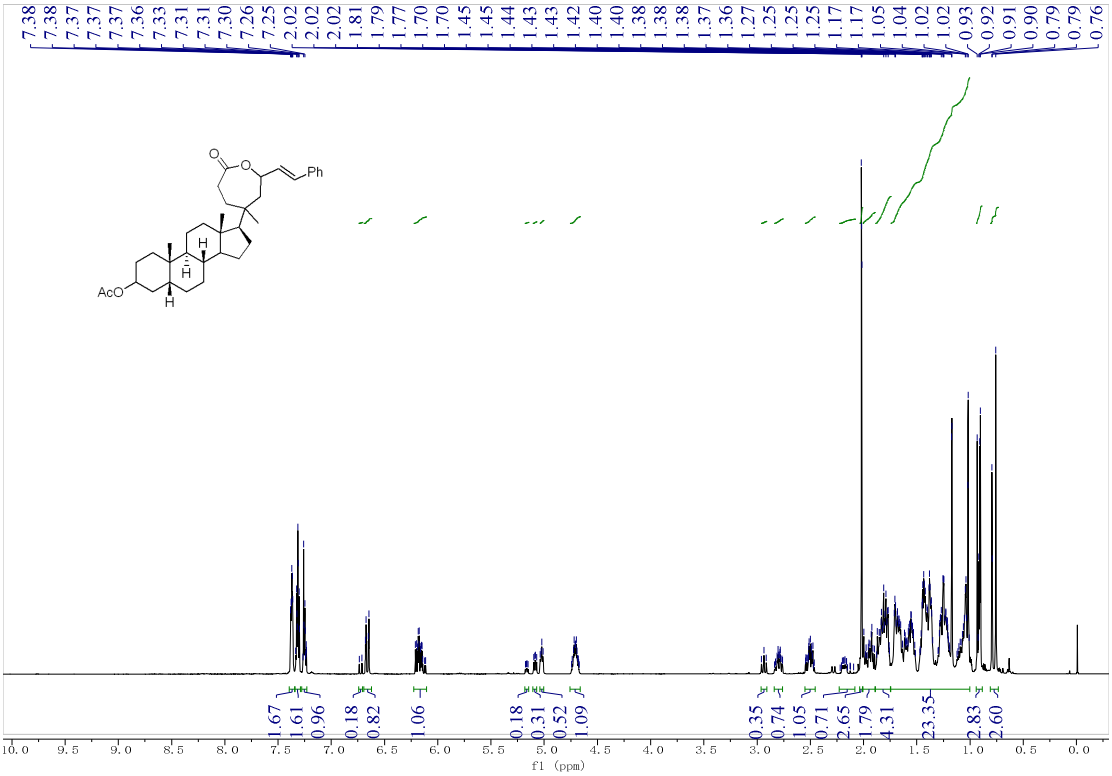
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4h**



^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4i**