Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Palladium-catalyzed [4+4] cycloaddition of 2-pyrones with 2-alkylidenetrimethylene carbonates: access to bridged eight-membered oxygen heterocycles

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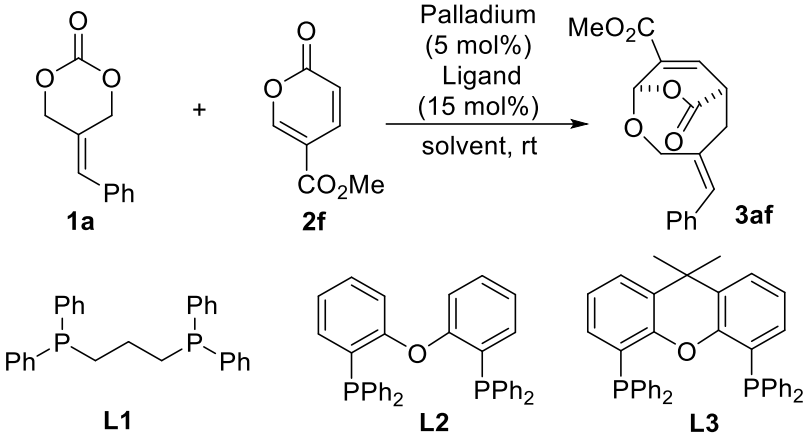
Contents

General Information

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 400 MHz NMR instrument (referenced internally to Me_4Si). Proton chemical shifts are reported in parts per million (δ scale). Organic solutions were concentrated under reduced pressure on a rotary evaporator. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Accurate mass measurements were performed using Agilent 1260/1290infinty II-6546QTOF. Melting points were determined on a Stuard SMP_3 melting point apparatus. X-ray crystallographic data were collected using a Bruker APEX-II CCD. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All heating reactions are performed by using an oil bath.

Table S1. Optimization of the reaction conditions[a]



Entry	Palladium	Ligand	Solvent	Yield(%)[b]	dr[c]
1	$Pd(PPh_3)_4$		CH_3CN	69%	>20:1
2	$Pd_2(dba)_3$•$CHCl_3$	**L1**	CH_2Cl_2	NR	>20:1
3	$Pd_2(dba)_3$•$CHCl_3$	**L2**	CH_2Cl_2	43	>20:1
4	$Pd_2(dba)_3$•$CHCl_3$	**L3**	CH_2Cl_2	50	>20:1
5	$Pd_2(dba)_3$•$CHCl_3$	PPh_3	CH_2Cl_2	17	>20:1
6	$Pd_2(dba)_3$•$CHCl_3$	**L3**	THF	40	>20:1

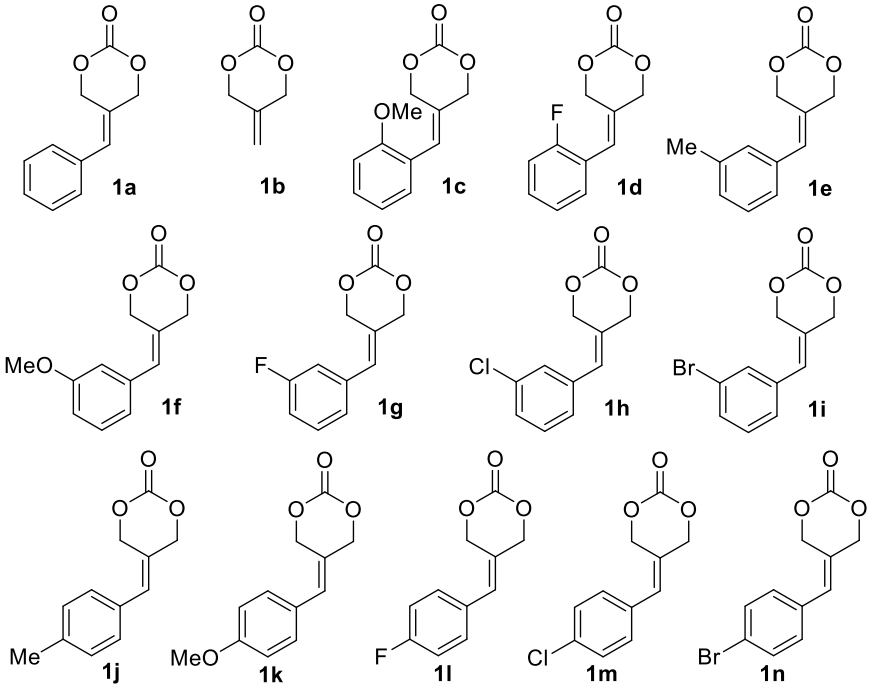
7	$Pd_2(dba)_3$•$CHCl_3$	**L3**	CH_3CN	NR	>20:1
8	$Pd_2(dba)_3$•$CHCl_3$	**L3**	DCE	90	>20:1
9	$Pd_2(dba)_3$•$CHCl_3$	**L3**	toluene	NR	>20:1

[a]Unless noted otherwise, reactions were performed with **1a** (0.18 mmol), **2f** (0.15 mmol), palladium (5 mol%), and ligand (15 mol%) in solvent at 25 °C. [b]Isolated yield. [c]Determined by ^1H NMR analysis, Z/E > 20:1.

General procedure for the Synthesis of matrerails

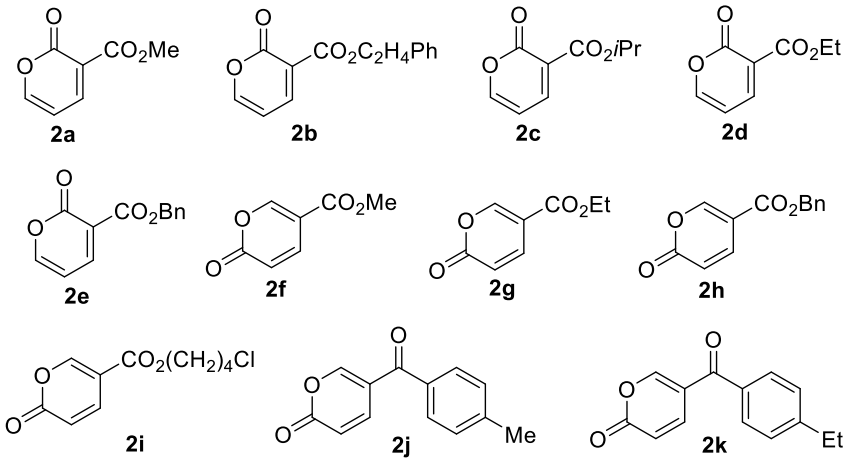
Preparation of 2-alkylidenetrimethylene carbonates 1a-1n. [1]

2-Alkylidenetrimethylene carbonates **1a-1n** was prepared by the reported procedure.



Preparation of 2-pyrones 2a-2k. [2],[3]

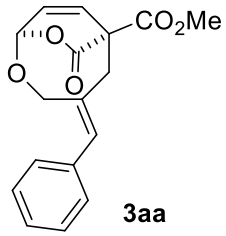
2-Pyrones **2a-2k** was prepared by the reported procedure.



General procedure for the reaction

Under a nitrogen atmosphere, an oven-dried 10 mL of Schlenk tube was charged with palladium catalyst (5 mol%, 0.0075 mmol), ligand (15 mol%, 0.0225 mmol) and 2-pyrones **2** (0.15 mmol) in 1 mL of solvent 25 ℃, then a solution of 2-alkylidenetrimethylene carbonates **1** (0.18 mmol, 1.2 equiv) in 1 mL of solvent was added after 30 min. The resulting mixture was stirred until the starting materials were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography to afford the corresponding products **3aa-3na**, **3ab-3ak**.

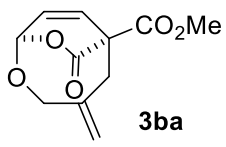
Characterization Data for 3, 4 and 5



3aa

Methyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3aa)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3aa** as a white solid (44.5 mg, 92% yield). m.p. 147-149 °C; **^{1}H NMR (400 MHz,$CDCl_3$)** δ 7.47 – 7.40 (m, 2H), 7.34 – 7.25 (m, 2H), 7.27 – 7.19 (m, 1H), 6.73 (s, 1H), 6.38 (d, *J* = 9.5 Hz, 1H), 6.11 – 6.05 (m, 1H), 6.06 – 5.98 (m, 1H), 4.26 (d, *J* = 12.4 Hz, 1H), 4.03 (d, *J* = 12.4 Hz, 1H), 3.78 (s, 3H), 3.35 (dd, *J* = 10.2, 0.03 Hz, 1H), 2.55 (dd, *J* = 11.3, 1.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.3, 167.9, 138.7, 134.6, 131.9, 130.0, 128.5, 127.2, 127.0, 120.0, 97.3, 61.7, 54.6, 52.5, 43.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{16}NaO_5^+$: 323.0890; Found: 323.0898.

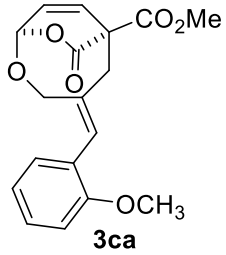


3ba

Methyl 4-methylene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ba)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ba** as a white solid (30.7 mg, 83% yield). m.p. 102-104 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.37 – 6.30 (m, 1H), 6.00 – 5.92 (m, 2H), 5.35 (s, 1H), 5.32 – 5.27 (m, 1H), 4.13 – 4.05 (m, 1H), 4.05 – 3.97 (m, 1H), 3.76 (s, 3H), 3.26 (dd, *J* =

13.9, 1.0 Hz, 1H), 2.40 (dd, *J* = 13.9, 1.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.2, 167.8, 138.6, 131.6, 125.7, 119.8, 97.0, 66.0, 54.3, 52.4, 41.5. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{12}NaO_5^+$: 247.0577; Found: 247.0585.

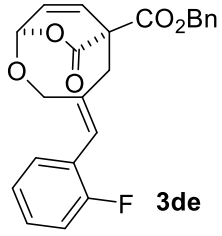


3ca

Methyl

(Z)-4-(2-methoxybenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ca)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ca** as a white solid (38.6 mg, 73% yield). m.p. 147-149 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 – 7.65 (m, 1H), 7.25 – 7.20 (m, 1H), 6.95 – 6.87 (m, 2H), 6.81 – 6.75 (m, 1H), 6.40 – 6.33 (m, 1H), 6.09 – 6.04 (m, 1H), 6.04 – 5.96 (m, 1H), 4.22 (d, *J* = 12.4 Hz, 1H), 4.02 (d, *J* = 12.4 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.41 (dd, *J* = 10.2, 1.1 Hz, 1H), 2.57 (dd, *J* = 13.7, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.4, 167.9, 156.2, 134.5, 132.0, 130.8, 129.5, 128.6, 123.6, 120.0, 119.3, 109.0, 97.3, 61.9, 54.6, 54.4, 52.4, 43.7. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_6^+$: 353.0996; Found: 353.1003.

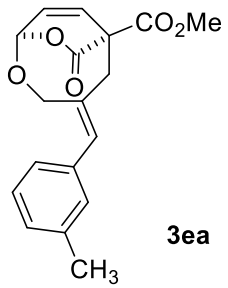


3de

Benzyl

(Z)-4-(2-fluorobenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3de)

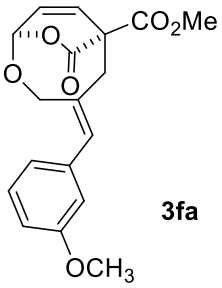
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3de** as a white solid (45.0 mg, 76% yield). m.p. 79-81 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.32 – 7.19 (m, 6H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.99 – 6.92 (m, 1H), 6.83 (s, 1H), 6.36 (d, *J* = 9.5 Hz, 1H), 6.13 – 5.84 (m, 2H), 5.21 (q, *J* = 12.3 Hz, 2H), 4.19 (d, *J* = 12.5 Hz, 1H), 4.03 (d, *J* = 12.5 Hz, 1H), 3.41 (d, *J* = 13.4 Hz, 1H), 2.58 (dd, *J* = 13.8, 1.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.6, 167.5, 159.3 (d, *J* = 248.7 Hz), 134.0, 132.0, 131.9, 131.2 (d, *J* = 4.6 Hz), 131.0 (d, *J* = 2.4 Hz), 129.0 (d, *J* = 8.2 Hz), 127.6, 127.5, 127.2, 122.9 (d, *J* = 3.7 Hz), 122.4 (d, *J* = 13.2 Hz), 120.0, 114.0 (d, *J* = 21.6 Hz), 97.2, 67.1, 61.3, 54.5, 43.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{19}FNaO_5^+$: 417.1109; Found: 417.1118.



3ea

Methyl (Z)-4-(3-methylbenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ea)

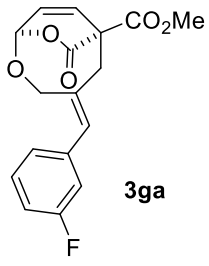
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ea** as a white solid (40.9 mg, 81% yield). m.p. 93-95 °C ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 – 7.21 (m, 2H), 7.20 – 7.18 (m, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 6.36 (d, *J* = 9.5 Hz, 1H), 6.07 (d, *J* = 4.2 Hz, 1H), 6.05 – 5.97 (m, 1H), 4.26 (d, *J* = 12.4 Hz, 1H), 4.01 (d, *J* = 12.4 Hz, 1H), 3.77 (s, 3H), 3.33 (dd, *J* = 13.7, 1.4 Hz, 1H), 2.54 (dd, *J* = 13.6, 1.6 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.4, 167.9, 138.8, 136.8, 134.6, 131.9, 129.9, 129.1, 127.8, 127.1, 125.6, 120.1, 97.3, 61.4, 54.6, 52.4, 43.5, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_5^+$: 337.1046; Found: 337.1043.



3fa

Methyl (Z)-4-(3-methoxybenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3fa)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3fa** as a white solid (42.3 mg, 80% yield). m.p. 156-158 °C ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.22 – 7.19 (m, 1H), 7.04 (dt, *J* = 2.1, 1.0 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.82 – 6.75 (m, 1H), 6.70 (s, 1H), 6.41 – 6.34 (m, 1H), 6.10 – 6.04 (m, 1H), 6.05 – 5.97 (m, 1H), 4.29 (d, *J* = 12.4 Hz, 1H), 4.02 (d, *J* = 12.4 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.33(dd, *J* = 10.3, 0.6 Hz, 1H), 2.54 (dd, *J* = 13.6, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.3, 167.9, 158.4, 138.5, 136.0, 131.9, 130.4, 128.2, 121.0, 120.1, 113.8, 112.9, 97.3, 61.4, 54.6, 54.2, 52.5, 43.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_6^+$: 353.0996; Found: 353.1005.

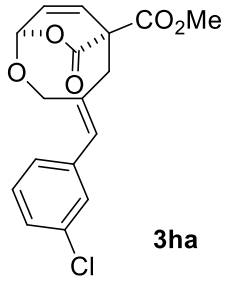


3ga

Methyl (Z)-4-(3-fluorobenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ga)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ga** as a white solid (43.4 mg, 85% yield). m.p. 156-158 °C ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.16

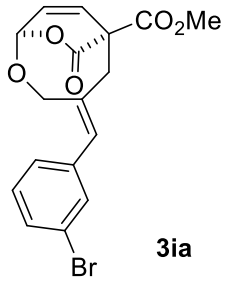
(m, 3H), 6.97 – 6.89 (m, 1H), 6.68 (s, 1H), 6.38 (d, *J* = 9.4 Hz, 1H), 6.08 (d, *J* = 4.2 Hz, 1H), 6.06 – 5.98 (m, 1H), 4.23 (d, *J* = 12.5 Hz, 1H), 4.03 (d, *J* = 12.5 Hz, 1H), 3.78 (s, 3H), 3.33 (dd, *J* = 10.3, 0.7 Hz, 1H), 2.54 (dd, *J* = 13.6, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.2, 167.8, 161.6 (d, *J* = 245.5 Hz), 137.3 (d, *J* = 2.2 Hz), 136.7 (d, *J* = 7.9 Hz), 131.9, 131.5, 128.7 (d, *J* = 8.6 Hz), 124.3 (d, *J* = 2.9 Hz), 120.0, 115.4, 115.2, 114.0, 113.8, 97.3, 61.1, 54.5, 52.5, 43.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}FNaO_5^+$: 341.0796; Found: 341.0803.



3ha

Methyl (Z)-4-(3-chlorobenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ha)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ha** as a white solid (43.9 mg, 82% yield). m.p. 149-151 °C ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.43 (m, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.20 (m, 2H), 6.66 (s, 1H), 6.42 – 6.35 (m, 1H), 6.11 – 6.06 (m, 1H), 6.06 – 5.98 (m, 1H), 4.21 (d, *J* = 12.5 Hz, 1H), 4.02 (d, *J* = 12.5 Hz, 1H), 3.78 (s, 3H), 3.33 (dd, *J* = 10.2, 0.7 Hz, 1H), 2.54 (dd, *J* = 13.6, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.2, 167.7, 137.1, 136.3, 133.2, 131.9, 131.7, 128.5, 128.4, 127.1, 126.7, 120.0, 97.2, 61.07, 54.5, 52.5, 43.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}ClNaO_5^+$: 357.0500; Found: 357.0505.

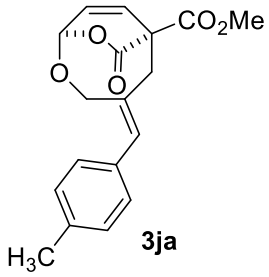


3ia

Methyl (Z)-4-(3-bromobenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ia)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ia** as a white solid (52.2 mg, 87% yield). m.p. 161-163 °C ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (s, 1H), 7.38 – 7.33 (m, 2H), 7.21 – 7.13 (m, 1H), 6.65 (s, 1H), 6.38 (d, *J* = 9.5 Hz, 1H), 6.11 – 6.06 (m, 1H), 6.06 – 5.98 (m, 1H), 4.20 (d, *J* = 12.5 Hz, 1H), 4.02 (d, *J* = 12.5 Hz, 1H), 3.78 (s, 3H), 3.32 (dd, *J* = 9.7, 0.2 Hz, 1H), 2.54 (dd, *J* = 13.6, 1.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.2, 167.7, 137.0, 136.6, 131.9, 131.8, 131.2, 130.0, 128.8, 127.2, 121.3, 120.0, 97.2, 61.1, 54.5, 52.5, 43.2. **HRMS** (ESI) m/z: $[M+Na]^+$

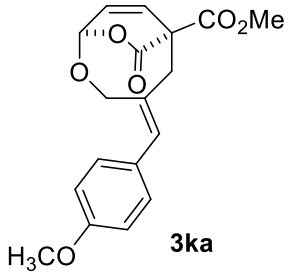
calcd for $C_{17}H_{15}BrNaO_5^+$: 400.9995; Found: 401.0000.



3ja

Methyl (Z)-4-(4-methylbenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ja)

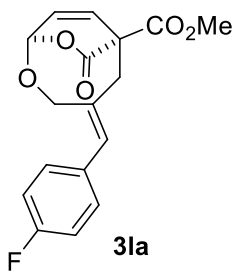
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ja** as a white solid (39.9 mg, 79% yield). m.p. 178-180 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.29 (m, 2H), 7.12 – 7.07 (m, 2H), 6.69 (s, 1H), 6.40 – 6.33 (m, 1H), 6.09 – 6.04 (m, 1H), 6.05 – 5.97 (m, 1H), 4.26 (d, *J* = 12.4 Hz, 1H), 4.02 (d, *J* = 12.4 Hz, 1H), 3.77 (s, 3H), 3.33 (dd, *J* = 10.2, 0.5 Hz, 1H), 2.53 (dd, *J* = 13.6, 1.6 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.4, 167.9, 138.6, 136.9, 131.9, 131.9, 129.2, 128.5, 128.0, 120.0, 97.3, 61.5, 54.7, 52.4, 43.5, 20.2. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_5^+$: 337.1046; Found: 337.1054.



3ka

Methyl (Z)-4-(4-methoxybenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ka)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ka** as a white solid (41.8 mg, 79% yield). m.p. 164-166 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.34 (m, 2H), 6.86 – 6.79 (m, 2H), 6.66 (s, 1H), 6.39 – 6.34 (m, 1H), 6.09 – 6.03 (m, 1H), 6.05 – 5.97 (m, 1H), 4.27 (d, *J* = 12.4 Hz, 1H), 4.03 (d, *J* = 12.4 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.32 (dd, *J* = 10.2, 0.6 Hz, 1H), 2.52 (dd, *J* = 13.6, 1.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.4, 168.0, 158.5, 138.2, 131.9, 130.0, 128.2, 127.4, 120.0, 112.7, 97.3, 61.6, 54.8, 54.3, 52.4, 43.6. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_6^+$: 353.0996; Found: 353.1005.

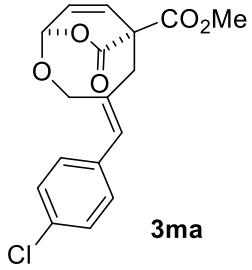


3la

Methyl (Z)-4-(4-fluorobenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3la)

The product mixture was purified by silica gel column

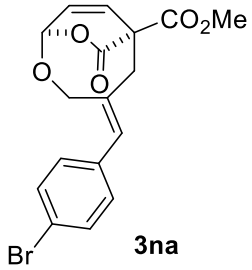
chromatography (PE/EtOAc = 7:1) to afford **3la** as a white solid (41.4 mg, 81% yield). m.p. 176-178 °C ;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.37 (m, 2H), 7.01 – 6.94 (m, 2H), 6.68 (s, 1H), 6.38 (d, *J* = 9.4 Hz, 1H), 6.09 – 6.04 (m, 1H), 6.06 – 5.98 (m, 1H), 4.21 (d, *J* = 12.4 Hz, 1H), 4.02 (d, *J* = 12.5 Hz, 1H), 3.78 (s, 3H), 3.33 (dd, *J* = 10.2, 0.5 Hz, 1H), 2.53 (dd, *J* = 13.6, 1.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.3, 167.8, 161.5 (d, *J* = 247.8 Hz), 137.5, 131.9, 130.7 (d, *J* = 3.5 Hz), 130.4 (d, *J* = 8.1 Hz), 130.1 (d, *J* = 1.0 Hz), 120.0, 114.2 (d, *J* = 21.7 Hz), 97.3, 61.3, 54.6, 52.5, 43.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}FNaO_5^+$: 341.0796; Found: 341.0805.



3ma

Methyl (Z)-4-(4-chlorobenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ma)

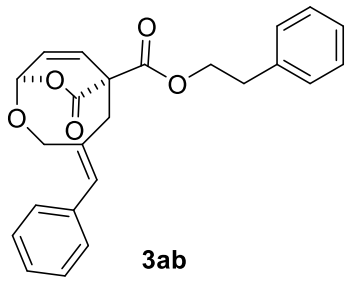
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ma** as a white solid (43.4 mg, 81% yield). m.p. 150-152 °C ; **^{1}H NMR (400 MHz, $CDCl_3$)**δ 7.40 – 7.33 (m, 2H), 7.28 – 7.23 (m, 2H), 6.67 (s, 1H), 6.38 (d, *J* = 9.4 Hz, 1H), 6.10 – 6.04 (m, 1H), 6.06 – 5.98 (m, 1H), 4.19 (d, *J* = 12.5 Hz, 1H), 4.02 (d, *J* = 12.5 Hz, 1H), 3.78 (s, 3H), 3.33 (dd, *J* = 13.7, 1.3 Hz, 1H), 2.54 (dd, *J* = 13.6, 1.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.2, 167.8, 137.3, 133.0, 133.0, 131.9, 130.9, 129.9, 127.5, 120.0, 97.2, 61.2, 54.6, 52.5, 43.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}ClNaO_5^+$: 357.0500; Found: 357.0508.



3na

Methyl (Z)-4-(4-bromobenzylidene)-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3na)

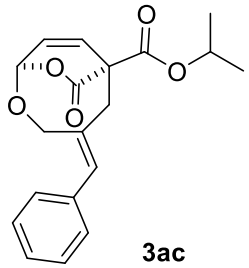
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3na** as a white solid (49.8 mg, 83% yield). m.p. 150-152 °C ;**^{1}H NMR (400 MHz, $CDCl_3$)**δ 7.43 – 7.39 (m, 2H), 7.32 – 7.28 (m, 2H), 6.64 (s, 1H), 6.38 (d, *J* = 9.4 Hz, 1H), 6.09 – 6.04 (m, 1H), 6.05 – 5.97 (m, 1H), 4.18 (d, *J* = 12.5 Hz, 1H), 4.01 (d, *J* = 12.5 Hz, 1H), 3.77 (s, 3H), 3.32 (dd, *J* = 13.7, 1.3 Hz, 1H), 2.52 (dd, *J* = 13.7, 1.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.2, 167.8, 137.3, 133.5, 131.9, 131.0, 130.4, 130.1, 121.3, 119.9, 97.2, 61.1, 54.5, 52.5, 43.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}BrNaO_5^+$: 400.9995; Found: 401.0003.



3ab

Phenethyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ab)

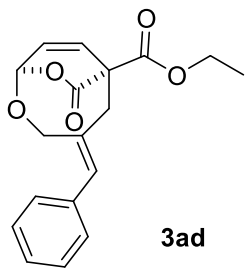
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ab** as a yellow solid (50.1 mg, 81% yield). m.p. 97-99 ^{o}C ; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.46 – 7.39 (m, 2H), 7.33 – 7.24 (m, 2H), 7.27 – 7.18 (m, 3H), 7.19 – 7.13 (m, 3H), 6.71 (s, 1H), 6.24 – 6.17 (m, 1H), 6.09 – 6.03 (m, 1H), 6.01 – 5.93 (m, 1H), 4.43 – 4.34 (m, 2H), 4.25 (d, *J* = 12.4 Hz, 1H), 4.00 (d, *J* = 12.4 Hz, 1H), 3.31 (dd, *J* = 13.8, 1.4 Hz, 1H), 2.99 – 2.87 (m, 2H), 2.48 (dd, *J* = 13.6, 1.6 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.9, 167.7, 138.6, 136.3, 134.7, 131.9, 130.1, 128.5, 128.0, 127.5, 127.2, 127.0, 125.7, 119.9, 97.2, 65.8, 61.4, 54.7, 43.4, 33.8. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{22}NaO_5^+$: 413.1359; Found: 413.1368.



3ac

Isopropyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ac)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ac** as a yellow solid (34.5 mg, 73% yield). m.p. 115-117 ^{o}C ; **^{1}H NMR (400 MHz, CDCl$_3$)**δ 7.46 – 7.41 (m,2 H), 7.33 – 7.26 (m, 2H), 7.26 – 7.21 (m, 1H), 6.72 (s, 1H), 6.37 – 6.30 (m, 1H), 6.09 – 6.03 (m, 1H), 6.04 – 5.96 (m, 1H), 5.12 – 5.03 (m, 1H), 4.25 (d, *J* = 12.3 Hz, 1H), 4.03 (d, *J* = 12.4 Hz, 1H), 3.33 (dd, *J* = 13.8, 1.4 Hz, 1H), 2.52 (dd, *J* = 13.7, 1.6 Hz, 1H), 1.26 – 1.19 (m, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.9, 167.3, 138.5, 134.7, 132.2, 130.3, 128.5, 127.2, 126.9, 119.9, 97.2, 69.3, 61.4, 54.6, 43.4, 20.6, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{20}NaO_5^+$: 351.1203; Found: 351.1205.

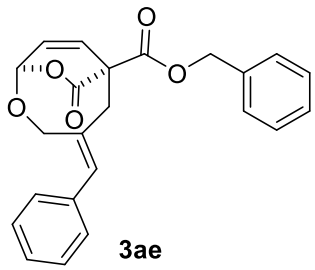


3ad

Ethyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ad)

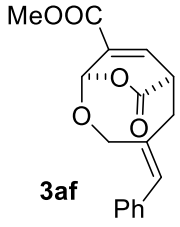
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ad** as a yellow solid (36.3 mg, 72% yield). m.p. 120-122 ^{o}C ; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.46 –

7.40 (m, 2H), 7.33 – 7.25 (m, 2H), 7.25 – 7.20 (m, 1H), 6.72 (s, 1H), 6.40 – 6.33 (m, 1H), 6.09 – 6.04 (m, 1H), 6.04 – 5.97 (m, 1H), 4.32 – 4.17 (m, 3H), 4.03 (d, *J* = 12.4 Hz, 1H), 3.34 (dd, *J* = 13.7, 1.4 Hz, 1H), 2.53 (dd, *J* = 10.2, 0.9 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.9, 167.8, 138.6, 134.7, 132.1, 130.2, 128.5, 127.2, 127.0, 120.0, 97.2, 61.6, 61.4, 54.6, 43.4, 13.0. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_5^+$: 337.1046; Found: 337.1054.



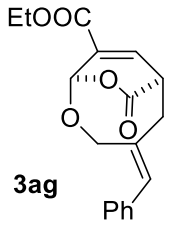
Benzyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-6-carboxylate (3ae)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ae** as a yellow solid (38.6 mg, 76% yield). m.p. 117-119 ºC; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.39 (m, 2H), 7.31 – 7.26 (m, 7H), 7.24 – 7.19 (m, 1H), 6.72 (s, 1H), 6.37 – 6.30 (m, 1H), 6.07 – 6.02 (m, 1H), 6.02 – 5.94 (m, 1H), 5.27 – 5.19 (m, 1H), 5.20 – 5.13 (m, 1H), 4.25 (d, *J* = 12.4 Hz, 1H), 4.01 (d, *J* = 12.4 Hz, 1H), 3.35 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.54 (dd, *J* = 13.6, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.8, 167.7, 138.7, 134.7, 134.1, 131.8, 130.1, 128.5, 127.6, 127.5, 127.2, 127.2, 127.0, 120.1, 97.3, 67.1, 61.4, 54.7, 43.5. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{20}NaO_5^+$: 399.1203; Found: 399.1210.



Methyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-9-carboxylate (3af)

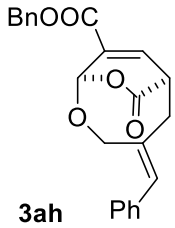
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3af** as a yellow solid (43.6 mg, 90% yield). m.p. 170-172 ºC; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.37 (m, 3H), 7.32 – 7.24 (m, 2H), 7.26 – 7.18 (m, 1H), 6.65 (s, 1H), 6.46 (s, 1H), 4.27 (d, *J* = 12.8 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.77 (s, 3H), 3.74 – 3.66 (m, 1H), 2.96 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.56 (dd, *J* = 10.4, 1.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.7, 161.9, 141.3, 137.9, 134.5, 130.3, 128.5, 127.3, 127.0, 124.9, 95.9, 61.4, 51.6, 40.7, 39.9. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{16}NaO_5^+$: 323.0890; Found:.323.0899.



3ag

Ethyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-9-carboxylate (3ag)

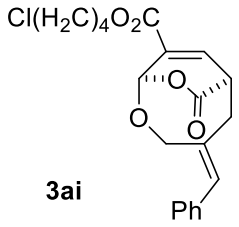
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ag** as a yellow solid (39.3 mg, 79% yield). m.p. 150-152 ^{o}C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.45 – 7.38 (m, 3H), 7.32 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 6.64 (s, 1H), 6.46 (s, 1H), 4.30 – 4.18 (m, 3H), 3.91 – 3.85 (m, 1H), 3.73 – 3.65 (m, 1H), 2.96 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.56 (dd, *J* = 13.6, 1.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.9, 161.5, 141.0, 137.8, 134.5, 130.4, 128.5, 127.3, 127.0, 125.2, 95.9, 61.3, 60.7, 40.7, 39.9, 13.2. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_5^+$: 337.1046; Found: 337.1055.



3ah

Benzyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-9-carboxylate (3ah)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ah** as a yellow solid (39.7 mg, 78% yield). m.p. 121-123 ^{o}C ; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.44 – 7.38 (m, 3H), 7.31 – 7.25 (m, 7H), 7.24 – 7.21 (m, 1H), 6.63 (s, 1H), 6.52 – 6.45 (m, 1H), 5.22 – 5.17 (m, 2H), 4.31 – 4.19 (m, 1H), 3.87 (d, *J* = 12.8 Hz, 1H), 3.72 – 3.63 (m, 1H), 2.95 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.55 (dd, *J* = 13.5, 1.9 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.8, 161.3, 141.5, 137.9, 134.5, 134.1, 130.3, 128.5, 127.7, 127.6, 127.3, 127.3, 127.0, 125.1, 95.8, 66.3, 61.3, 40.7, 40.0. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{20}NaO_5^+$: 399.1203; Found: 399.1209.

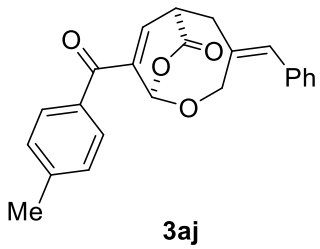


3ai

4-chlorobutyl (Z)-4-benzylidene-7-oxo-2,8-dioxabicyclo[4.2.2]dec-9-ene-9-carboxylate (3ai)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ai** as a yellow solid (39.7 mg, 78% yield). m.p. 116-118 ^{o}C ; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.44 – 7.38 (m, 3H), 7.31 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 6.64 (s, 1H), 6.45 (s, 1H), 4.26 (d, *J* = 12.8 Hz,

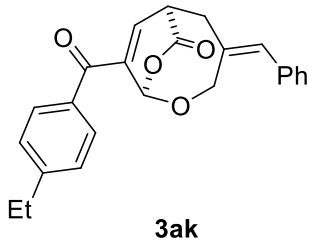
1H), 4.23 – 4.18 (m, 2H), 3.88 (d, *J* = 12.8 Hz, 1H), 3.74 – 3.66 (m, 1H), 3.53 – 3.44 (m, 2H), 2.97 (dd, *J* = 13.6, 6.7 Hz, 1H), 2.57 (dd, *J* = 13.7, 1.8 Hz, 1H), 1.85 – 1.76 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 161.4, 141.2, 137.9, 134.5, 130.3, 128.5, 127.3, 127.0, 125.2, 95.8, 63.8, 61.4, 43.3, 40.7, 40.1, 28.0, 24.9. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{21}ClNaO_5^+$: 399.0970; Found: 399.0978.



3aj

(Z)-4-benzylidene-9-(4-methylbenzoyl)-2,8-dioxabicyclo [4.2.2]dec-9-en-7-one (3aj)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3aj** as a yellow solid (51.1 mg, 89% yield). m.p. 116-118 ^oC ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.33 – 7.24 (m, 3H), 7.27 – 7.19 (m, 2H), 7.02 – 6.95 (m, 1H), 6.68 (s, 1H), 6.56 (s, 1H), 4.36 – 4.26 (m, 1H), 4.03 – 3.95 (m, 1H), 3.78 – 3.69 (m, 1H), 3.02 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.63 (dd, *J* = 13.7, 1.9 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.4, 170.2, 143.1, 141.2, 137.8, 134.4, 132.6, 132.0, 130.5, 128.5, 128.4, 127.3, 127.1, 96.3, 61.4, 40.8, 40.5, 20.6. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{20}NaO_4^+$: 383.1254; Found: 383.1263.



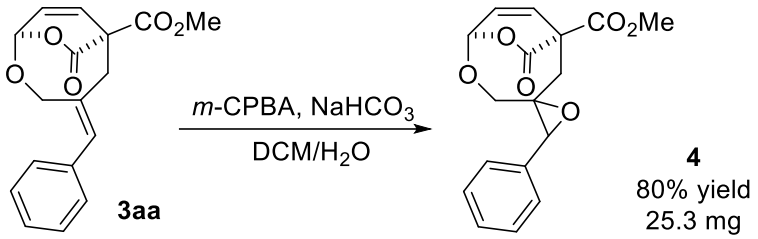
3ak

(Z)-4-benzylidene-9-(4-ethylbenzoyl)-2,8-dioxabicyclo[4. 2.2]dec-9-en-7-one (3ak)

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **3ak** as a yellow solid (47.6 mg, 80% yield). m.p. 95-97 ^oC ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.52 (m, 2H), 7.48 – 7.40 (m, 2H), 7.33 – 7.25 (m, 2H), 7.26 – 7.18 (m, 3H), 7.03 – 6.94 (m, 1H), 6.69 (s, 1H), 6.57 (s, 1H), 4.36 – 4.27 (m, 1H), 4.04 – 3.91 (m, 1H), 3.78 – 3.70 (m, 1H), 3.03 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.71 – 2.60 (m, 3H), 1.19 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.4, 170.2, 149.2, 141.2, 137.8, 134.5, 132.8, 132.0, 130.6, 128.6, 128.5, 127.3, 127.2, 127.1, 96.3, 61.4, 40.8, 40.5, 27.9, 14.2. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{22}NaO_4^+$: 397.1410; Found: 397.1419.

Transformations of products 3aa and 3na

1. Oxidation of 3aa with *m*-chloroperoxybenzoic acid (*m*-CPBA)



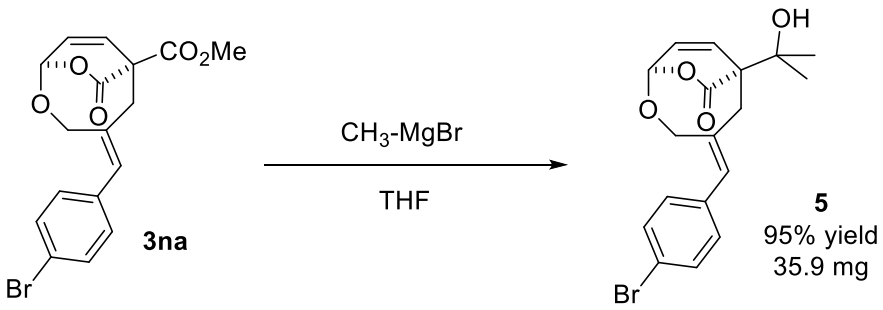
To a solution of **3aa** (0.1 mmol, 1.0 equiv) in 1mL CH_2Cl_2 was added *m*-CPBA (2.0 equiv), $NaHCO_3$ (4.0 equiv) and 0.5mL H_2O. The resulting reaction mixture was stirred at room temperature. and the reaction process was monitored by TLC. Upon full conversion, the crude product was purified by FC in silica (PE/EtOAc 4:1) to yield the product **4** (27.1 mg, 80% yield).

Methyl

8-oxo-3'-phenyl-5,7-dioxaspiro[bicyclo[4.2.2]decane-3,2'-oxiran]-9-ene-1-carboxylate (4)

The product mixture was purified by silica gel column chromatography (PE/EtOAc 4:1) to afford **4** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.34 (m, 2H), 7.33 – 7.24 (m, 3H), 6.44 – 6.37 (m, 1H), 5.99 – 5.91 (m, 1H), 5.81 – 5.76 (m, 1H), 4.05 (d, *J* = 13.3 Hz, 1H), 3.91 (s, 1H), 3.78 (s, 3H), 3.53 (d, *J* = 13.3 Hz, 1H), 2.41 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.7, 167.5, 133.1, 131.9, 127.0, 126.9, 125.5, 120.2, 96.7, 65.2, 63.5, 59.3, 52.7, 51.1, 41.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{16}NaO_6^+$: 339.0839; Found: 339.0844.

2. Nucleophilic addition of 3na



To a solution of **3na** (0.1 mmol) in 1mL THF was added dropwisely a solution of methylmagnesium bromide (0.5 M in THF, 5.0 equiv) at 0 °C. The resulting reaction

mixture was stirred at room temperature for 4h and the reaction process was monitored by TLC. Upon full conversion, the crude product was purified by FC in silica (PE/EtOAc 7:1) to yield the product **5** (38.1 mg, 95% yield).

(Z)-4-(4-bromobenzylidene)-6-(2-hydroxypropan-2-yl)-2,8-dioxabicyclo[4.2.2]dec-9-en-7-one (5)

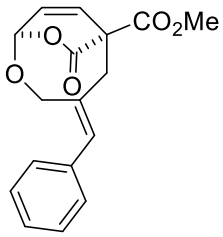
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 7:1) to afford **5** as a white solid. m.p. 161-163 ^{o}C ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.38 (m, 2H), 7.34 – 7.27 (m, 2H), 6.61 (s, 1H), 6.31 (d, *J* = 9.7 Hz, 1H), 6.05 – 6.00 (m, 1H), 6.01 – 5.93 (m, 1H), 4.92 (s, 1H), 4.19 (d, *J* = 12.3 Hz, 1H), 4.00 (d, *J* = 12.3 Hz, 1H), 3.26 (dd, *J* = 12.9, 1.5 Hz, 1H), 2.30 (dd, *J* = 12.8, 1.4 Hz, 1H), 1.23 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.9, 136.4, 133.8, 133.7, 132.6, 130.4, 130.2, 121.1, 120.2, 96.8, 72.2, 61.5, 53.4, 41.8, 26.6, 21.7. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}BrNaO_4^+$: 401.0359; Found: 401.0358.

References:

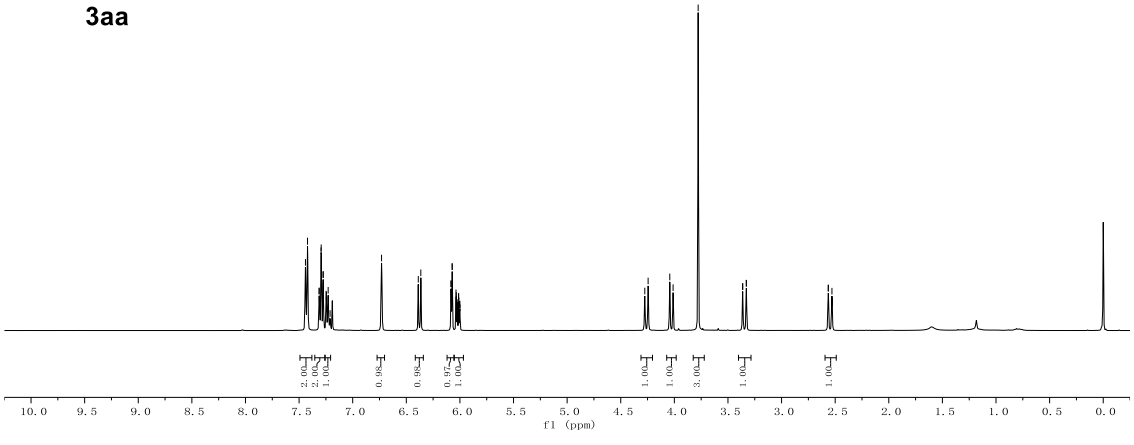
[1] R. Shintani, K. Moriya and T. Hayashi, Guiding the nitrogen nucleophile to the middle: palladium-catalyzed decarboxylative cyclopropanation of 2-alkylidenetrimethylene carbonates with isocyanates, *Chem. Commun.*, **2011**, 47, 3057-3059.

[2] X. G. Si, Z. M. Zhang, C. G. Zheng, Z. T. Li and Q. Cai, Enantioselective Synthesis of cis-Decalin Derivatives by the Inverse-Electron-Demand Diels–Alder Reaction of 2-Pyrones, *Angew. Chem., Int. Ed.*, **2020**, 59, 18412-18417.

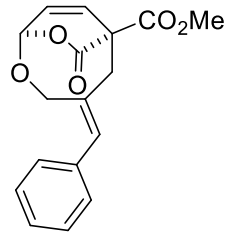
[3] X. Gao, M. Xia, C. Yuan, L. Zhou, W. Sun, C. Li, B. Wu, D. Zhu, C. Zhang, B. Zheng, D. Wang and H. Guo, Enantioselective Synthesis of Chiral Medium-Sized Cyclic Compounds via Tandem Cycloaddition/Cope Rearrangement Strategy, *ACS Catal.*, **2019**, 9, 1645-1654.



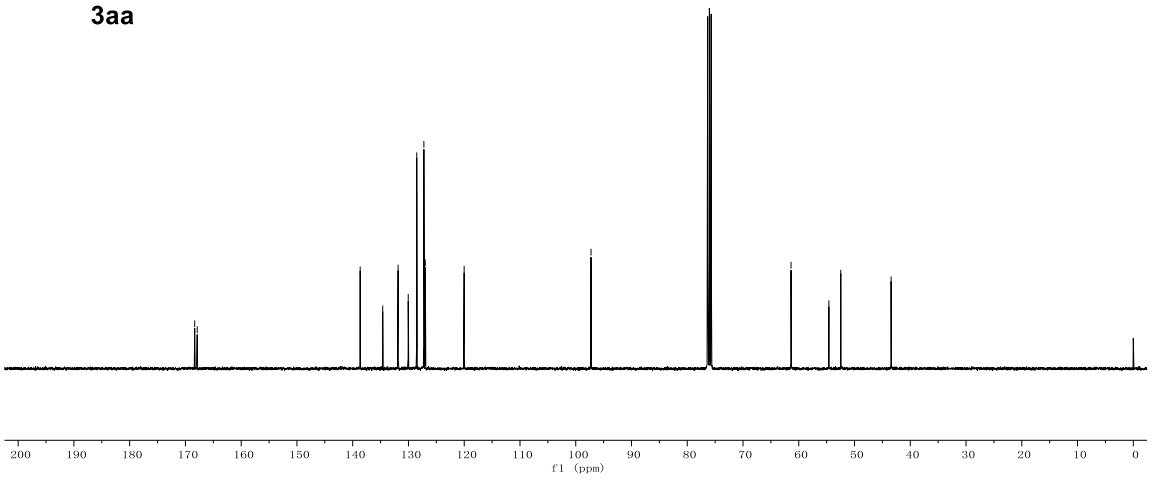
3aa



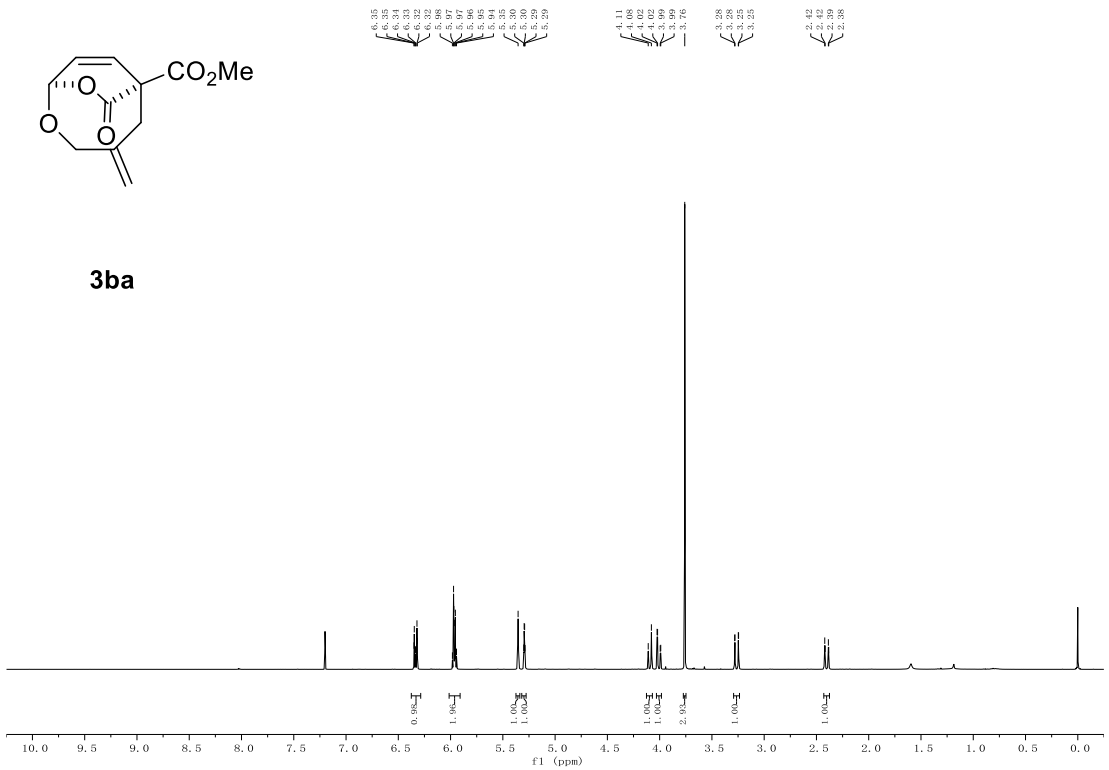
^{1}H NMR of 3aa (400 MHz, $CDCl_3$)



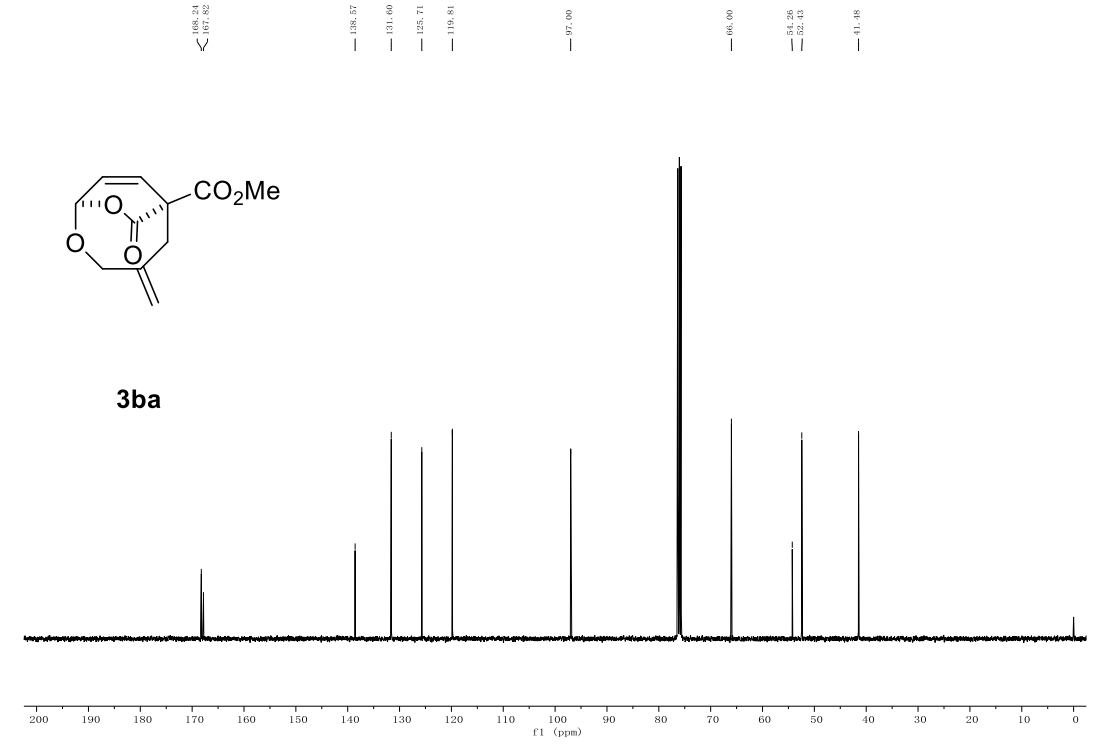
3aa



^{13}C NMR of 3aa (101 MHz, $CDCl_3$)



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



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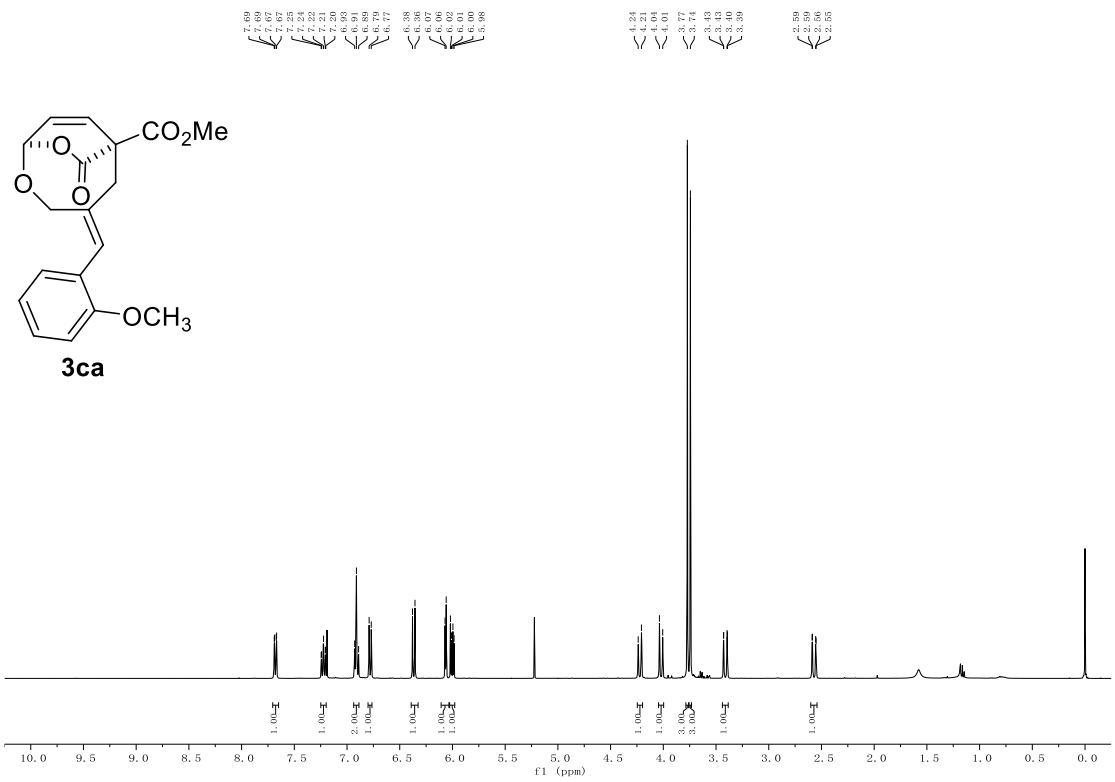
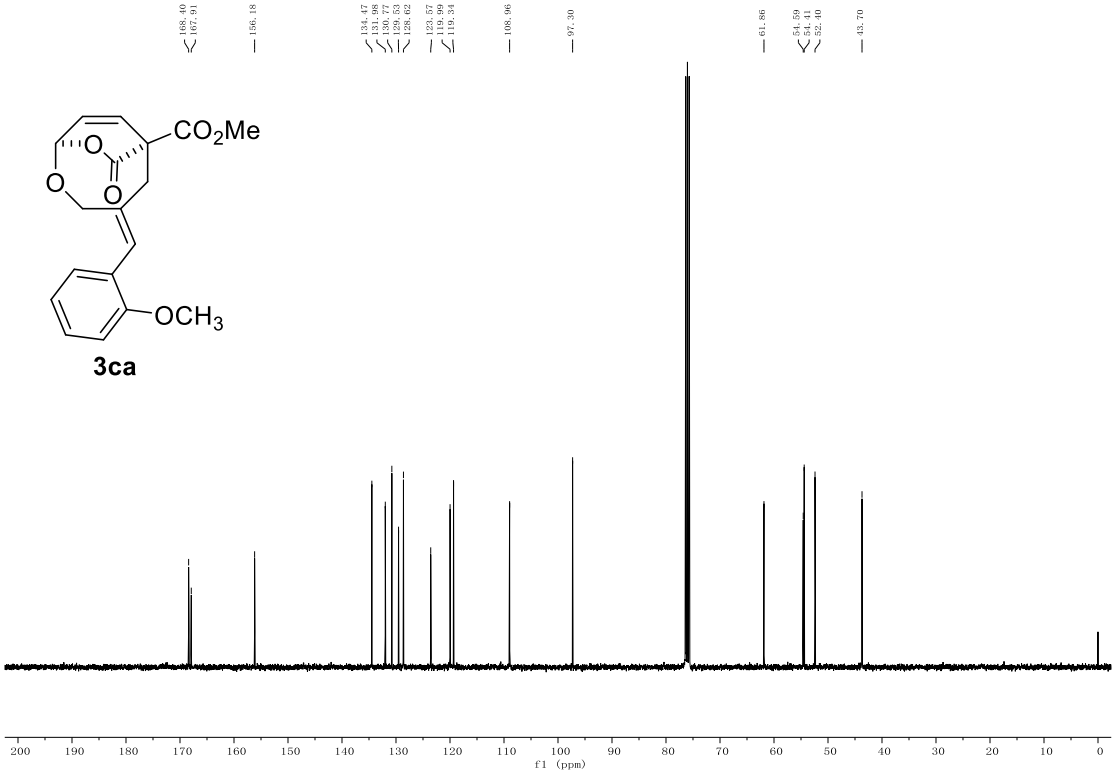
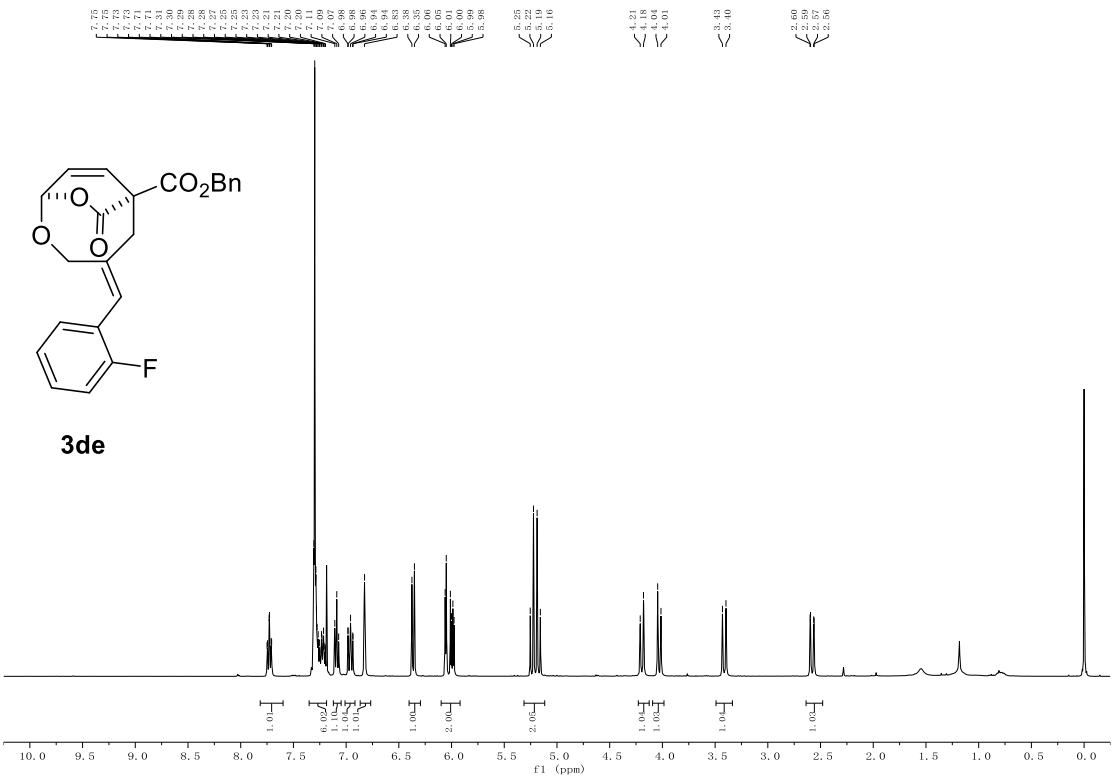


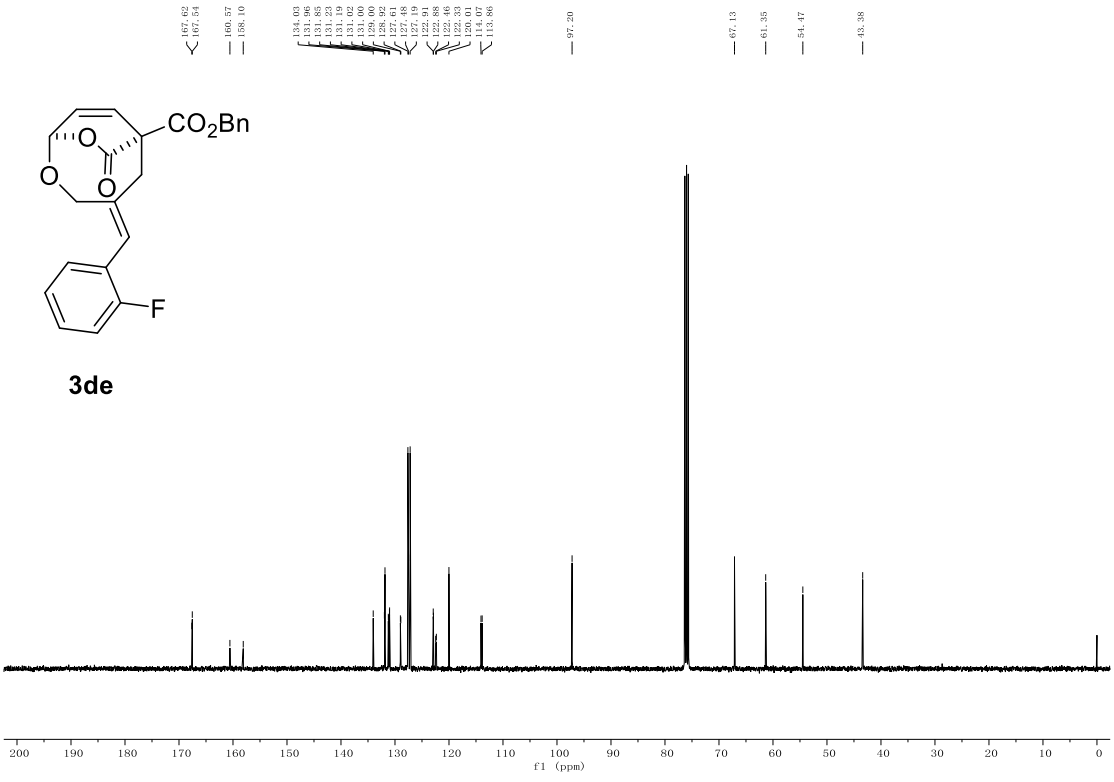
^{1}H NMR of 3ca (400 MHz, $CDCl_3$)



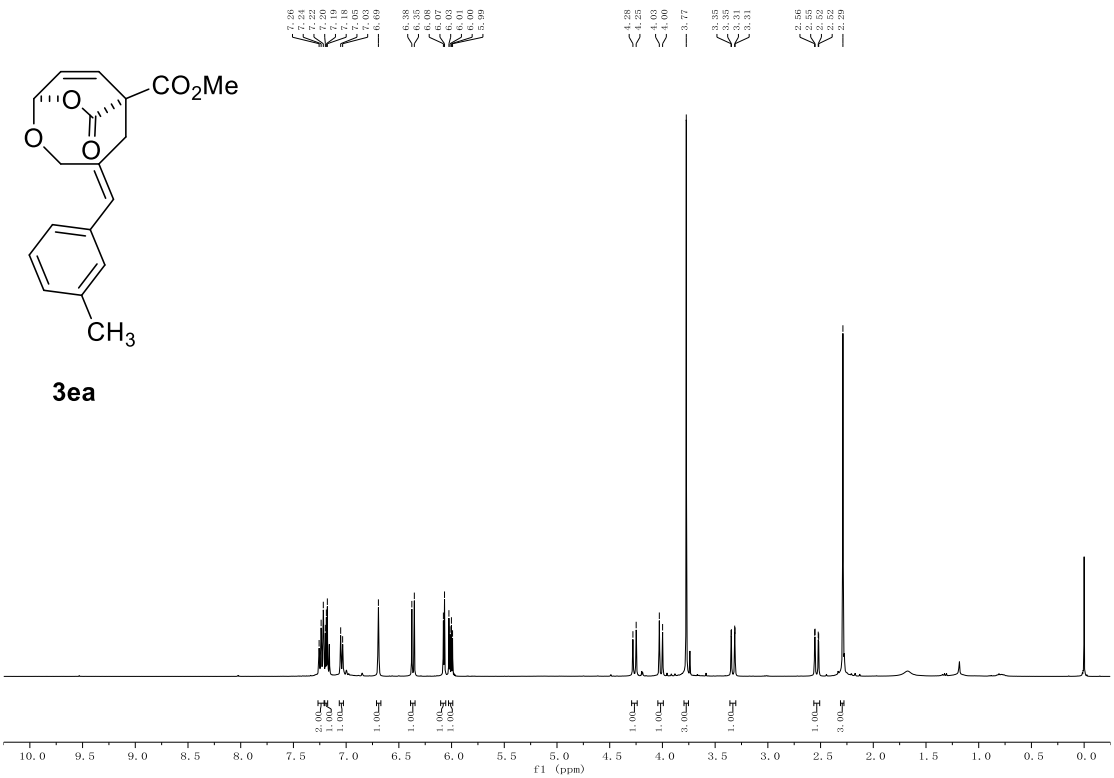
^{13}C NMR of 3ca (101 MHz, $CDCl_3$)



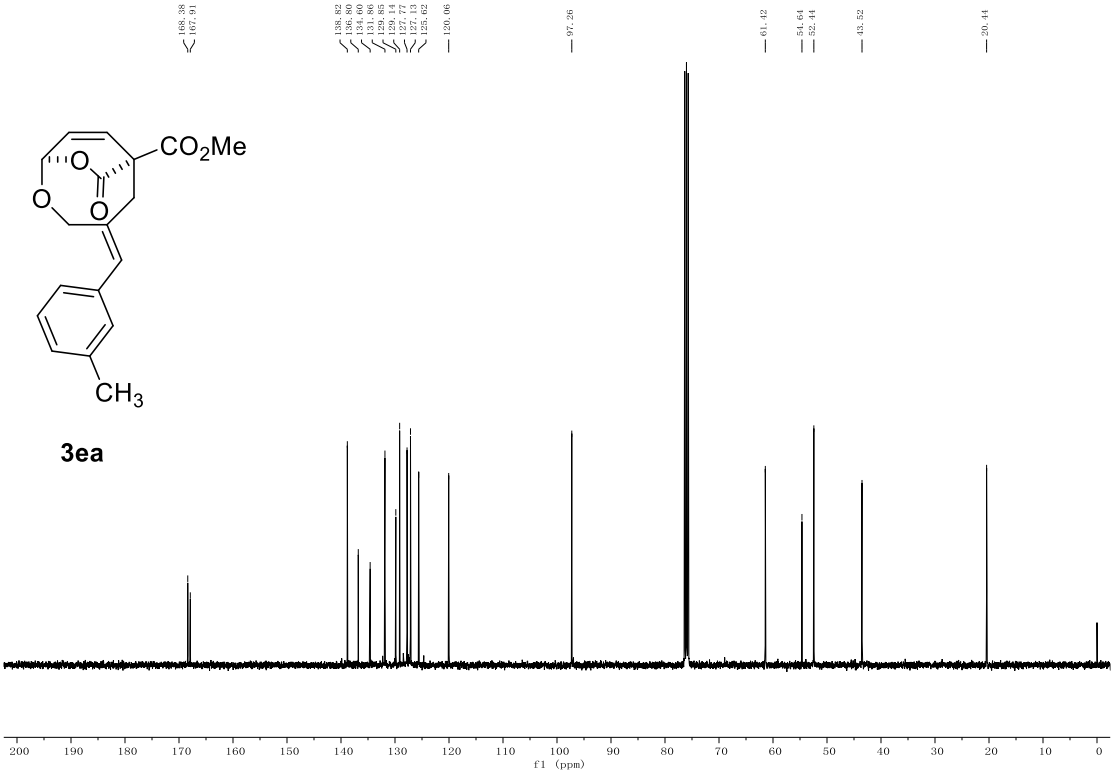
^{1}H NMR of 3de (400 MHz, $CDCl_3$)



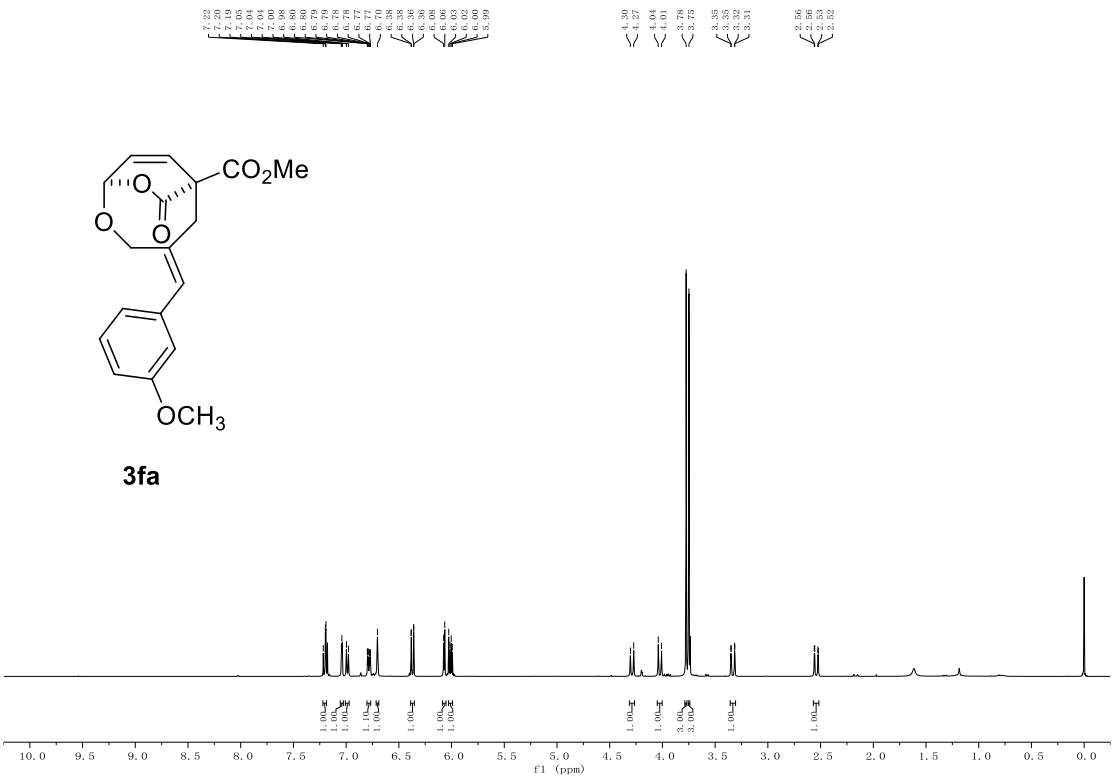
^{13}C NMR of 3de (101 MHz, $CDCl_3$)



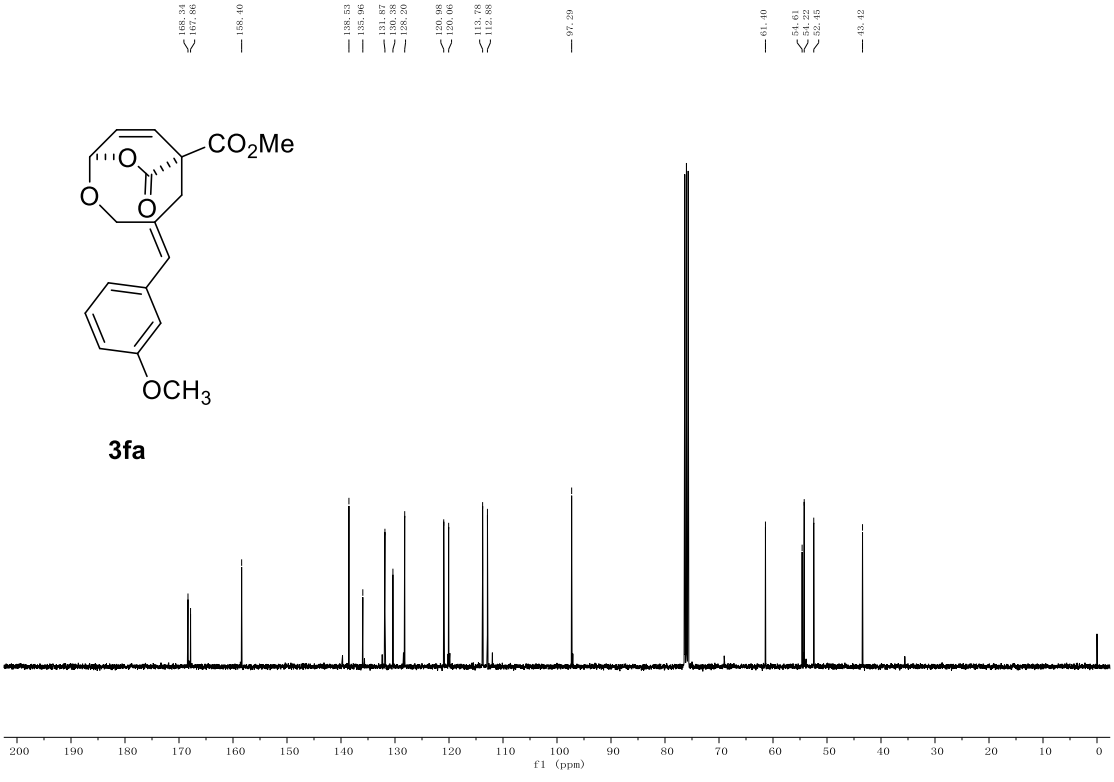
^{1}H NMR of 3ea (400 MHz, $CDCl_3$)



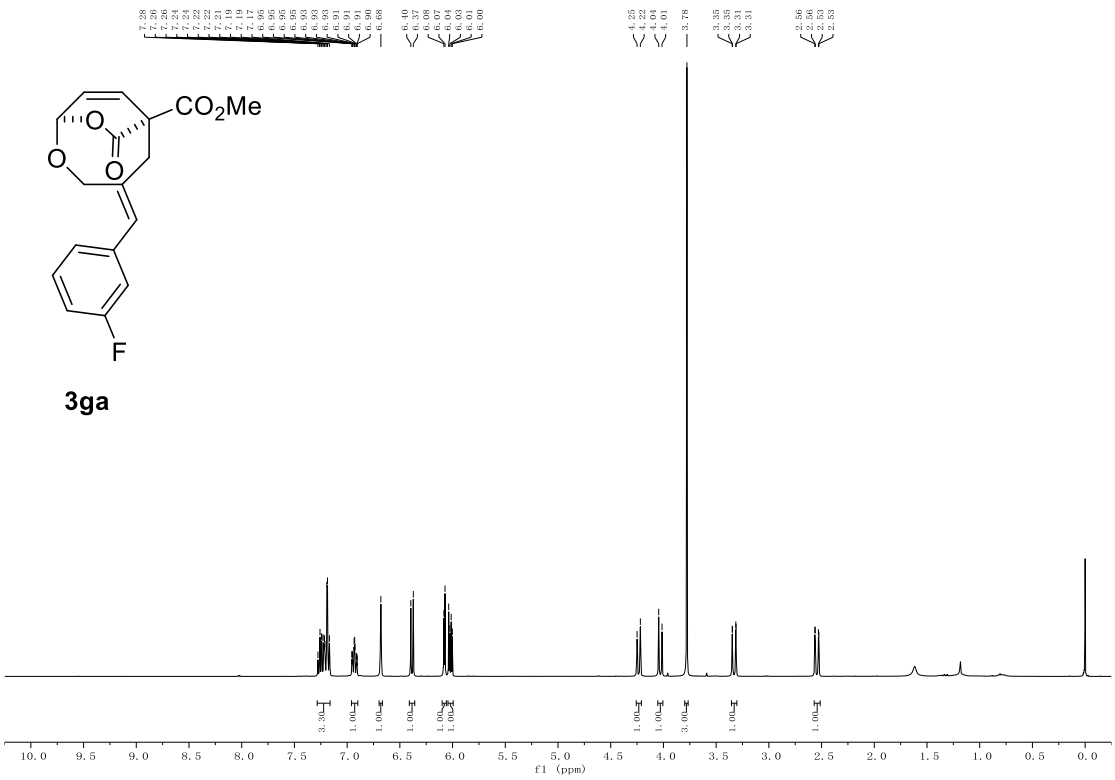
^{13}C NMR of 3ea (101 MHz, $CDCl_3$)



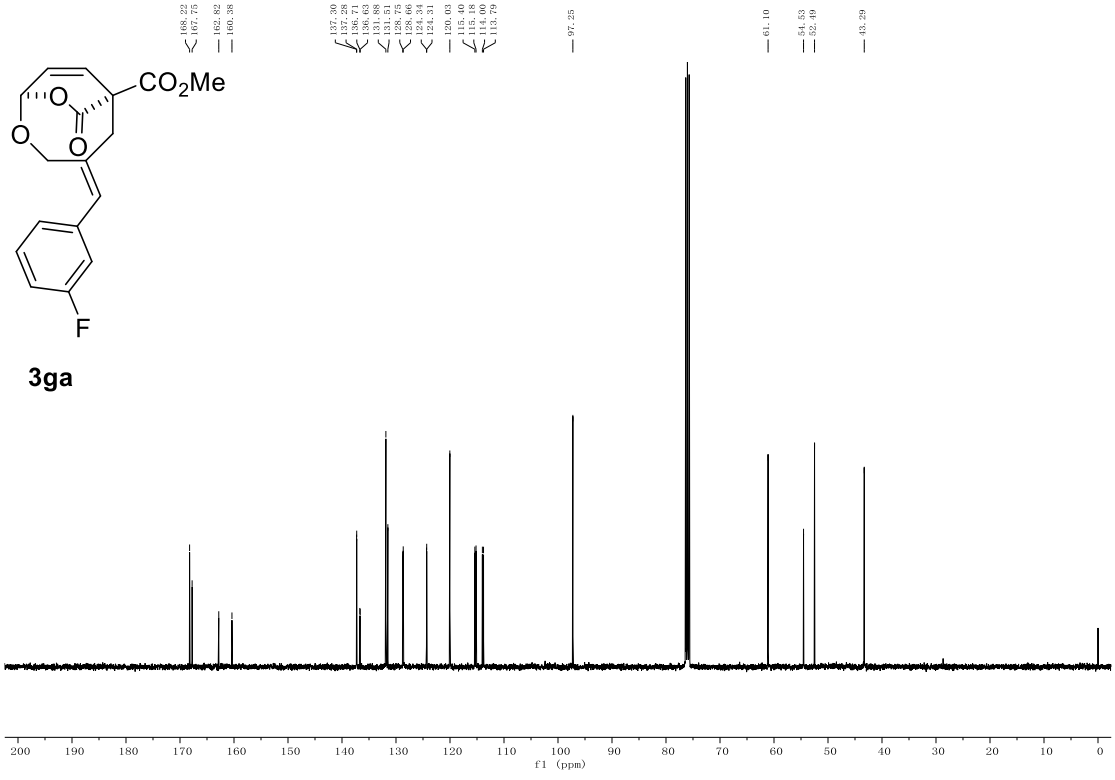
^{1}H NMR of 3fa (400 MHz, $CDCl_3$)



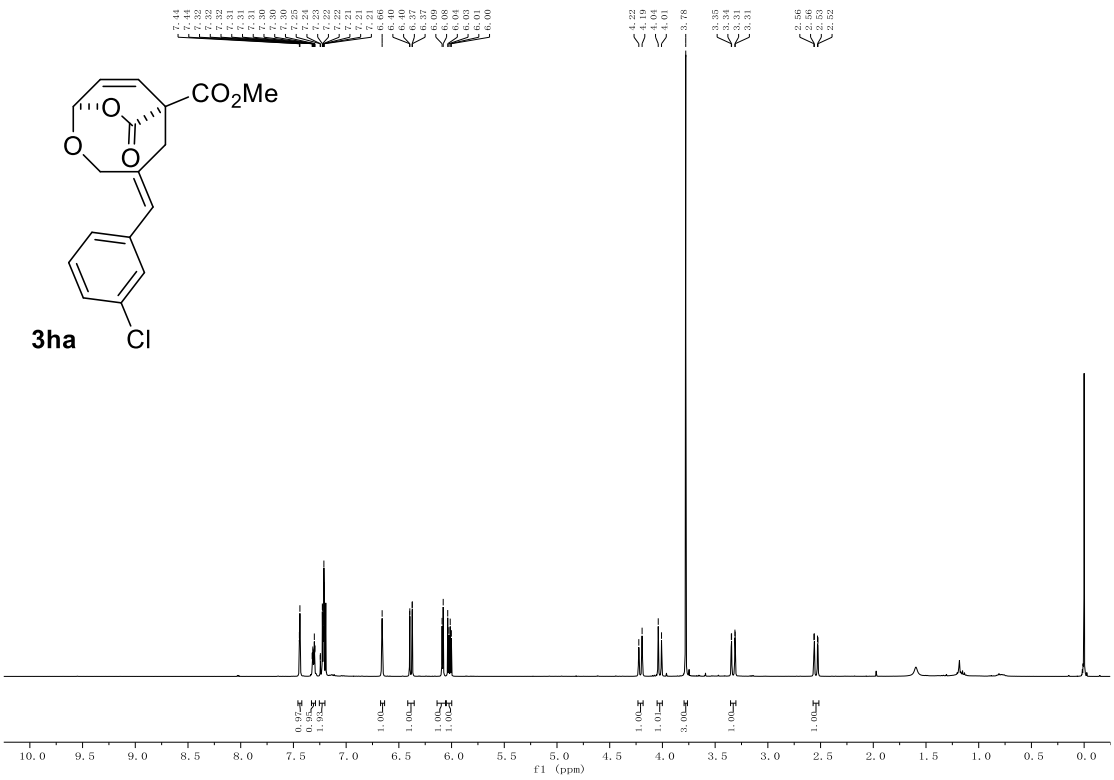
^{13}C NMR of 3fa (101 MHz, $CDCl_3$)



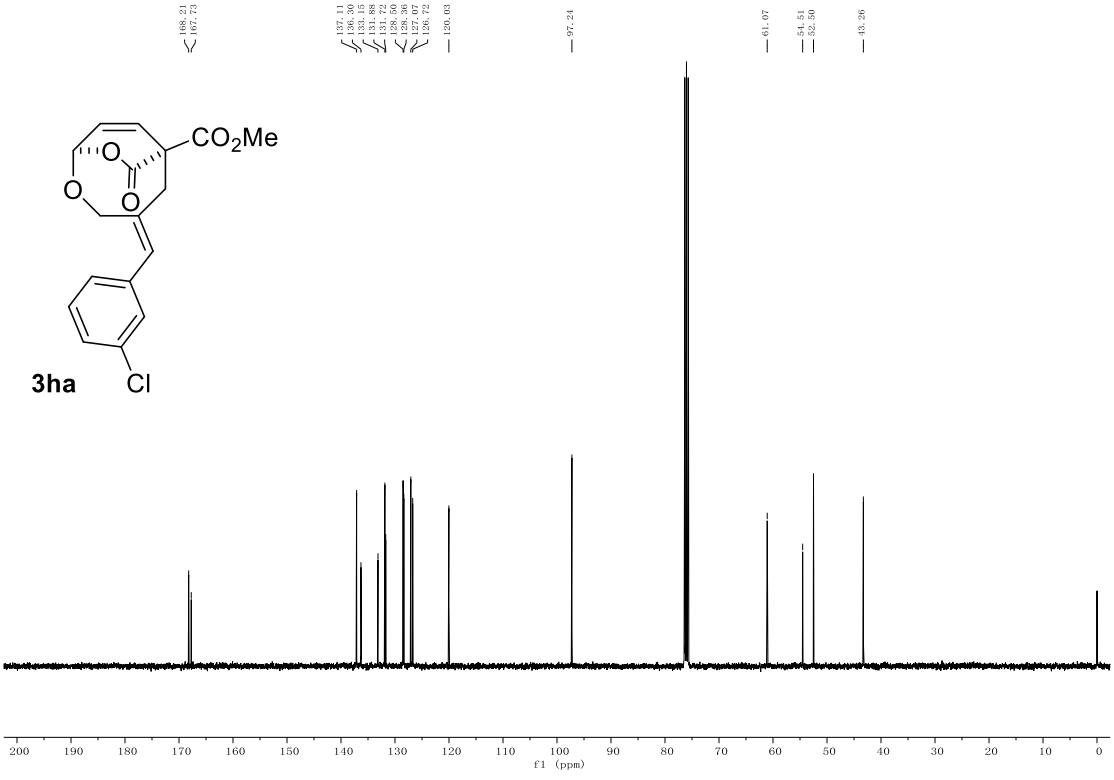
^{1}H NMR of 3ga (400 MHz, $CDCl_3$)



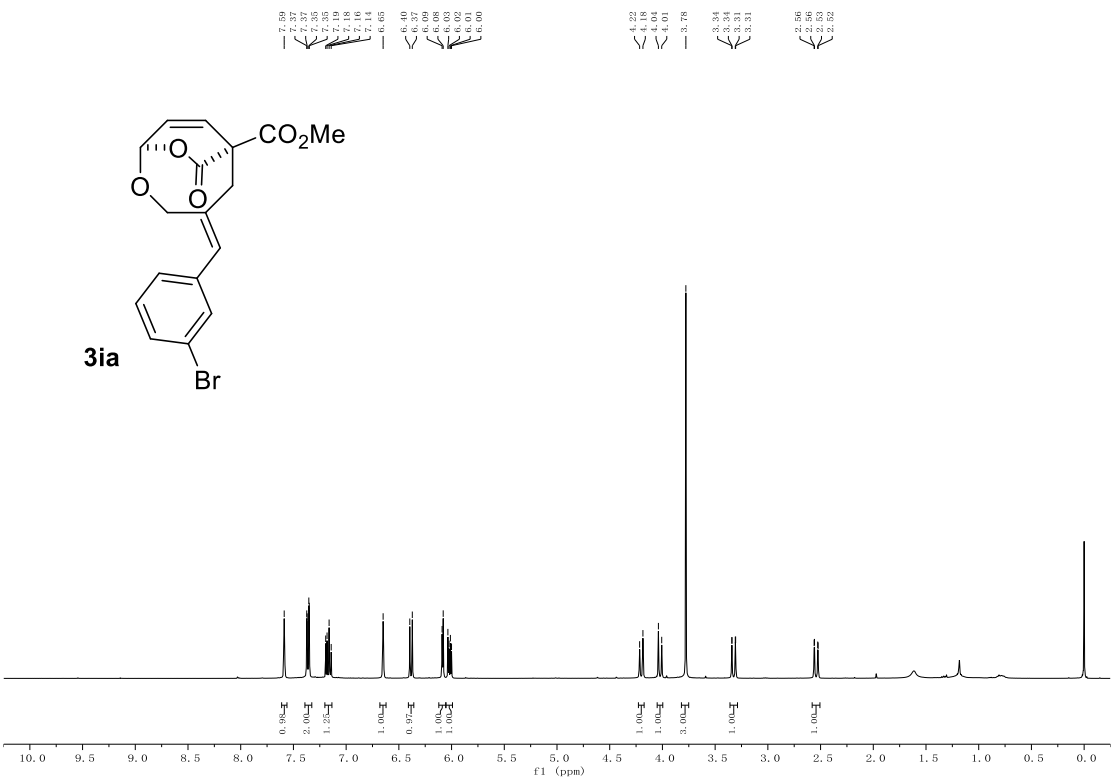
^{13}C NMR of 3ga (101 MHz, $CDCl_3$)



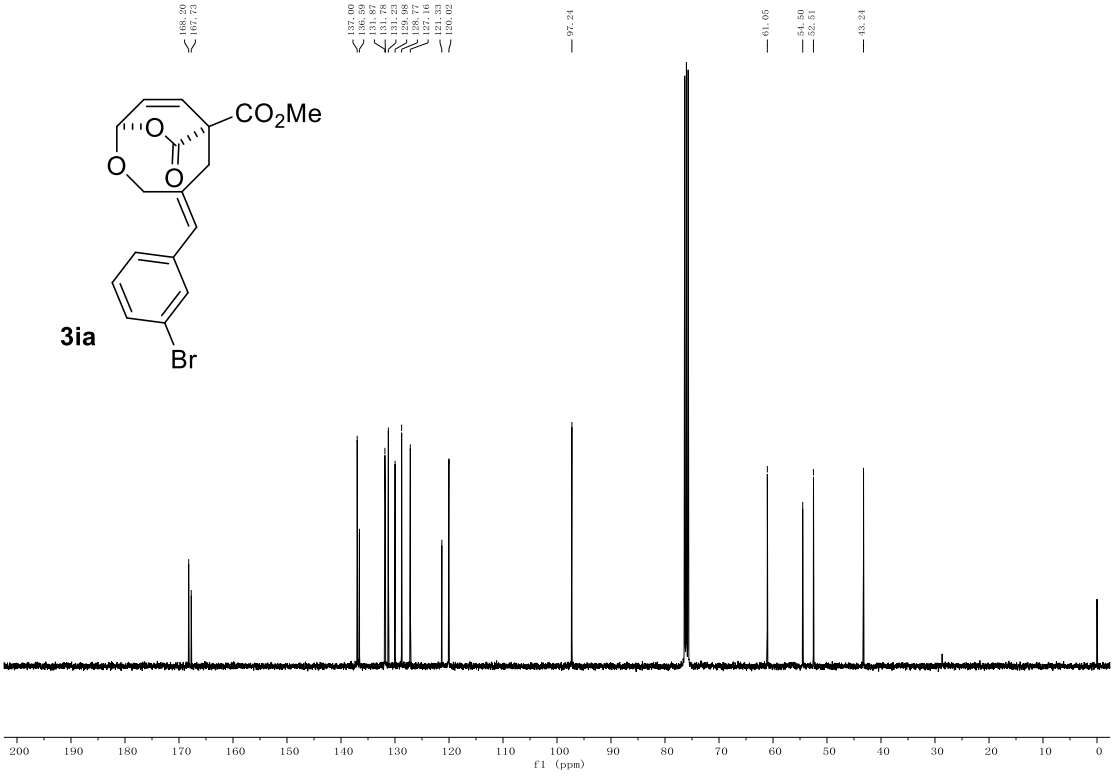
^{1}H NMR of 3ha (400 MHz, $CDCl_3$)



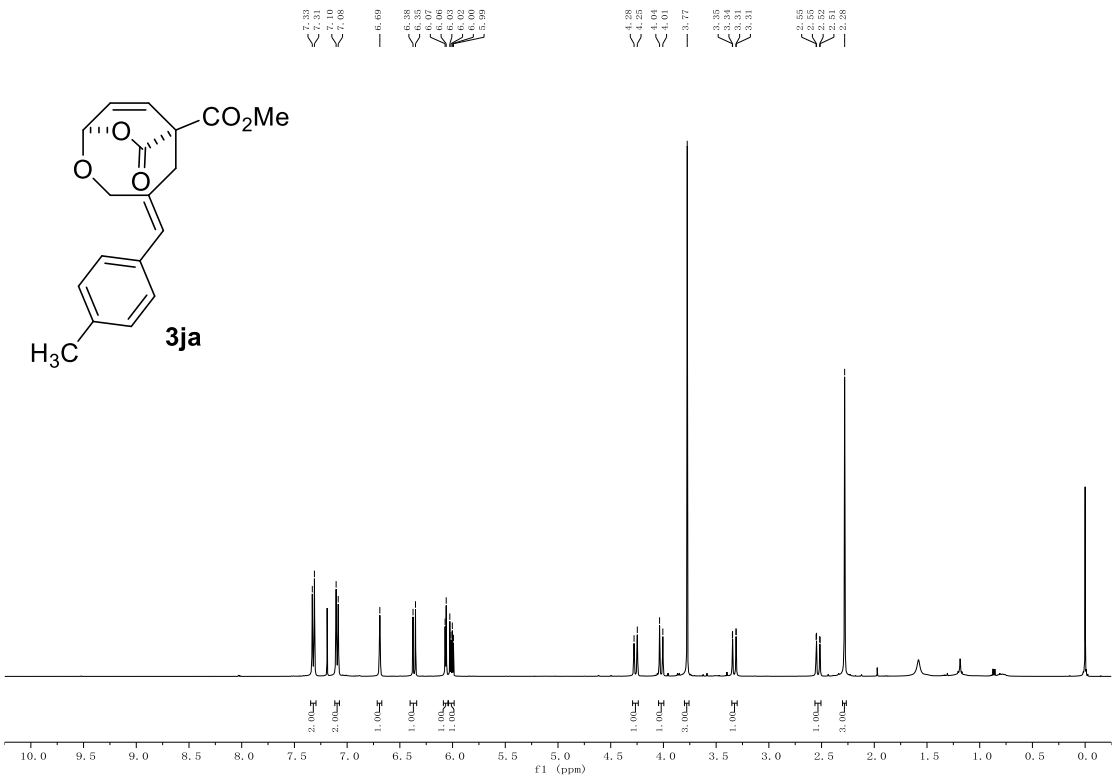
^{13}C NMR of 3ha (101 MHz, $CDCl_3$)



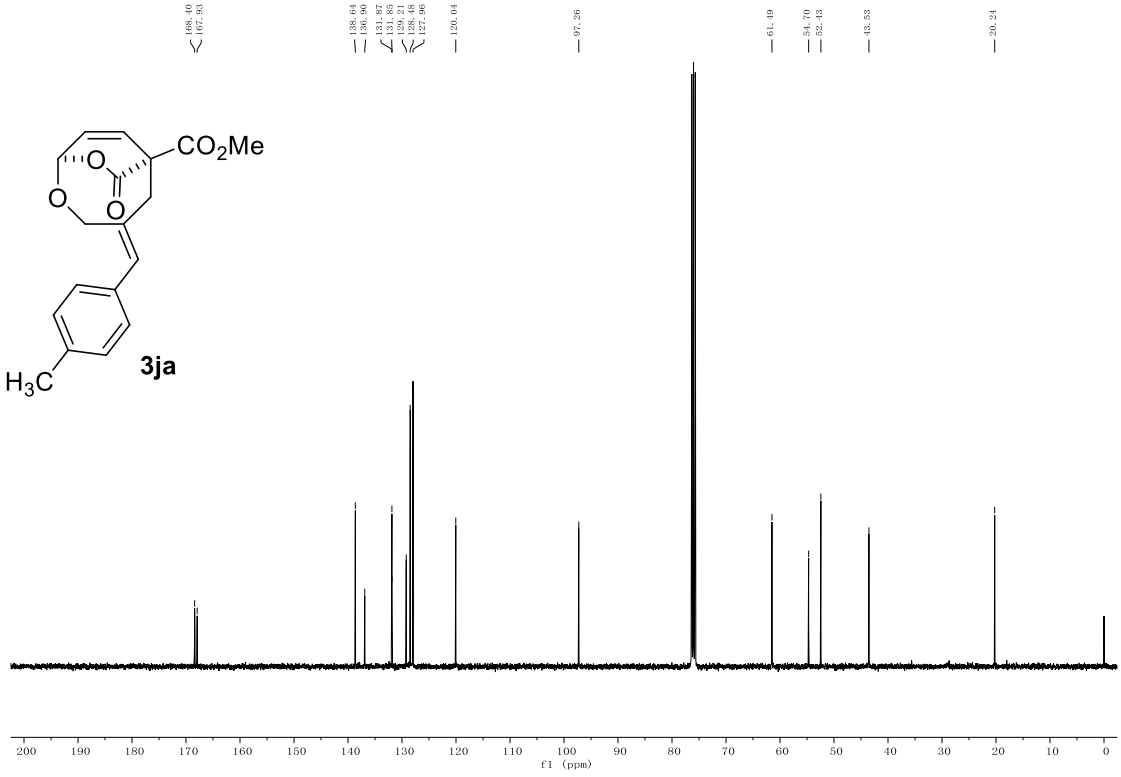
^{1}H NMR of 3ia (400 MHz, $CDCl_3$)



^{13}C NMR of 3ia (101 MHz, $CDCl_3$)



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



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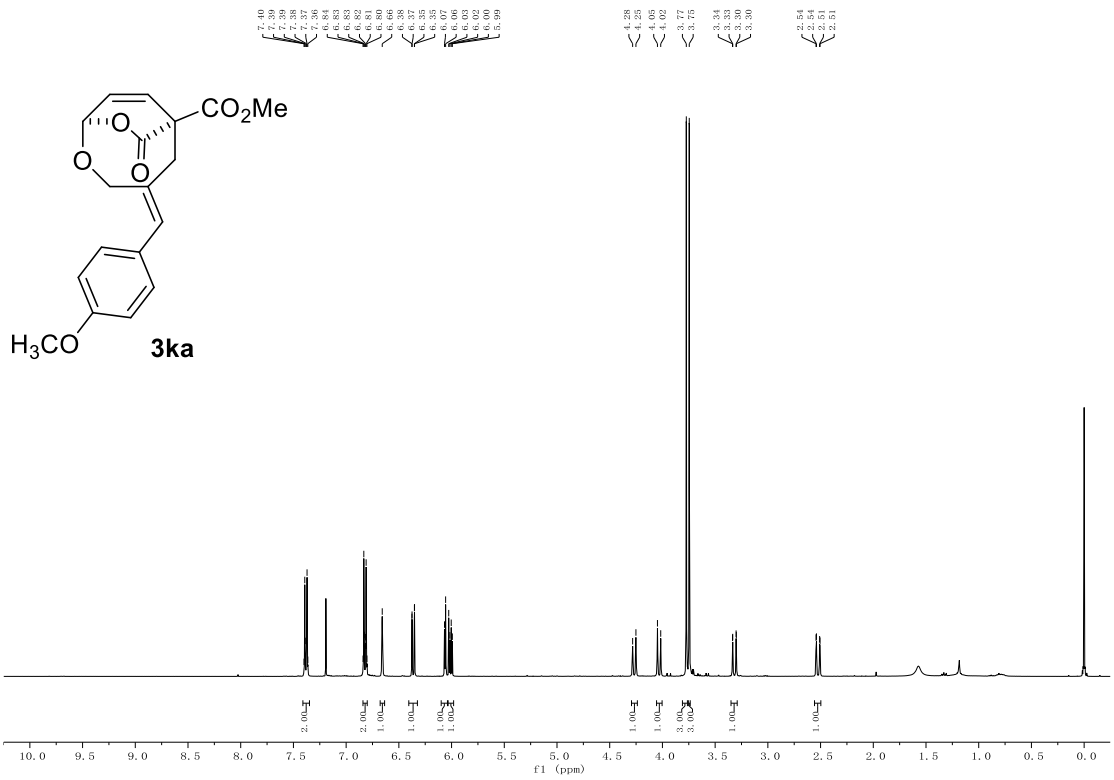
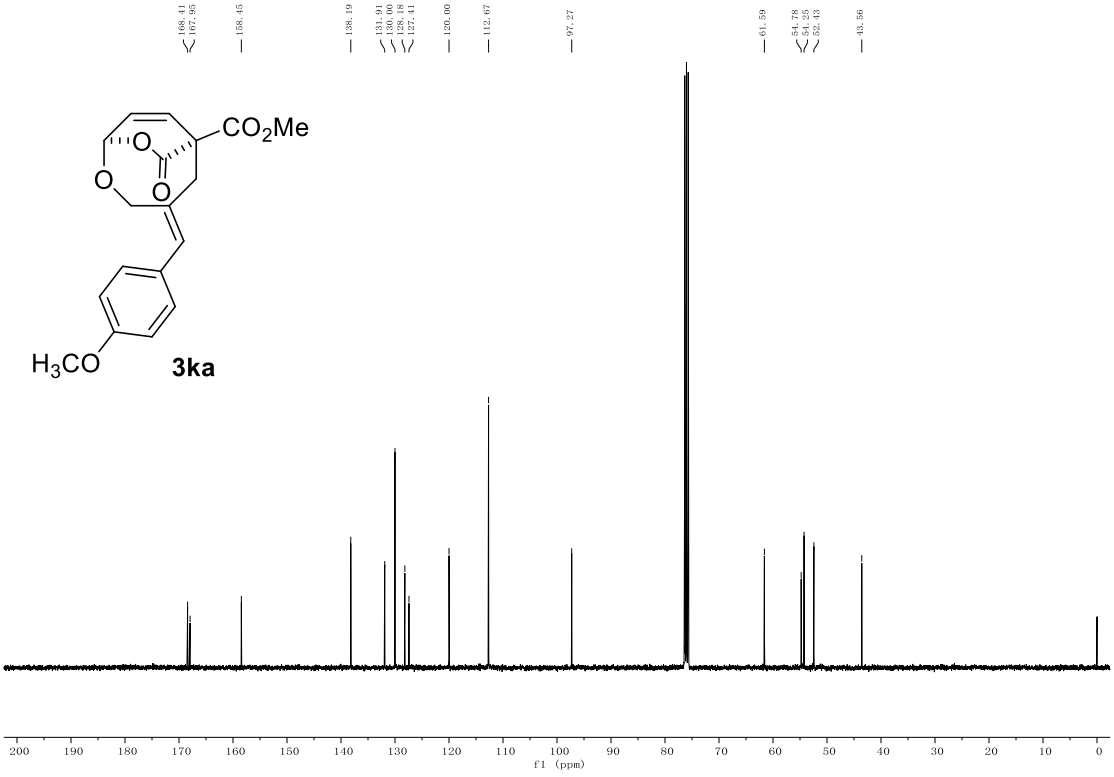


^{1}H NMR of 3ka (400 MHz, $CDCl_3$)



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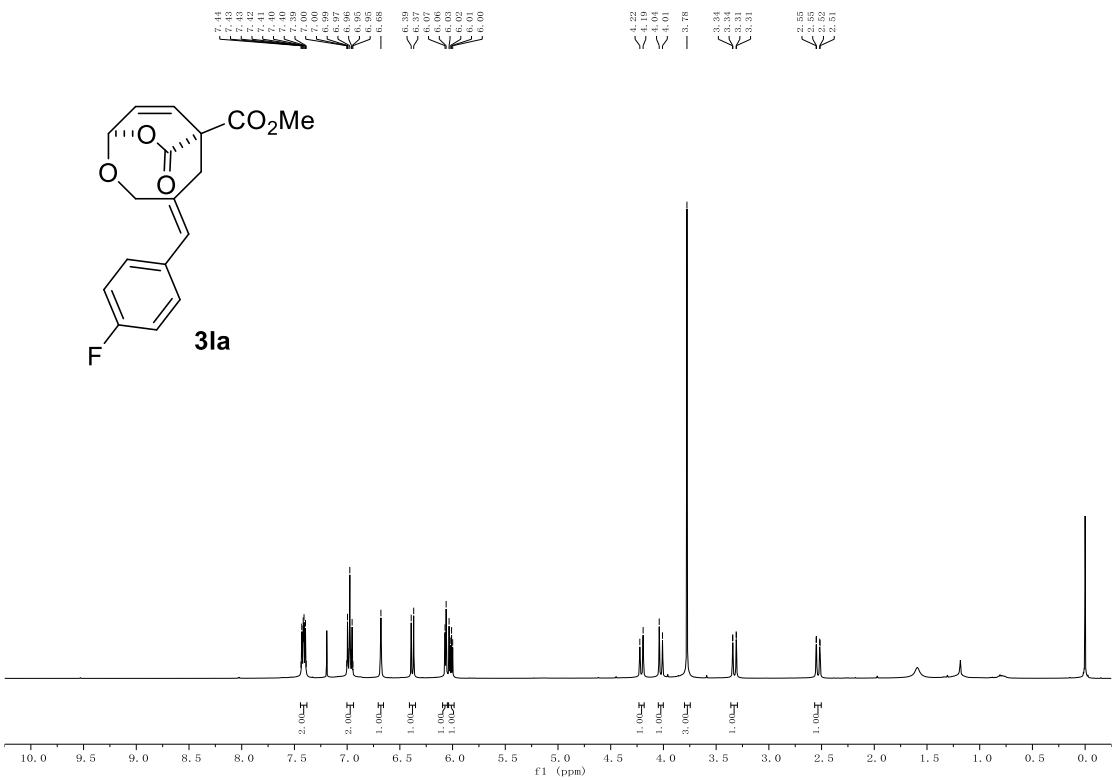

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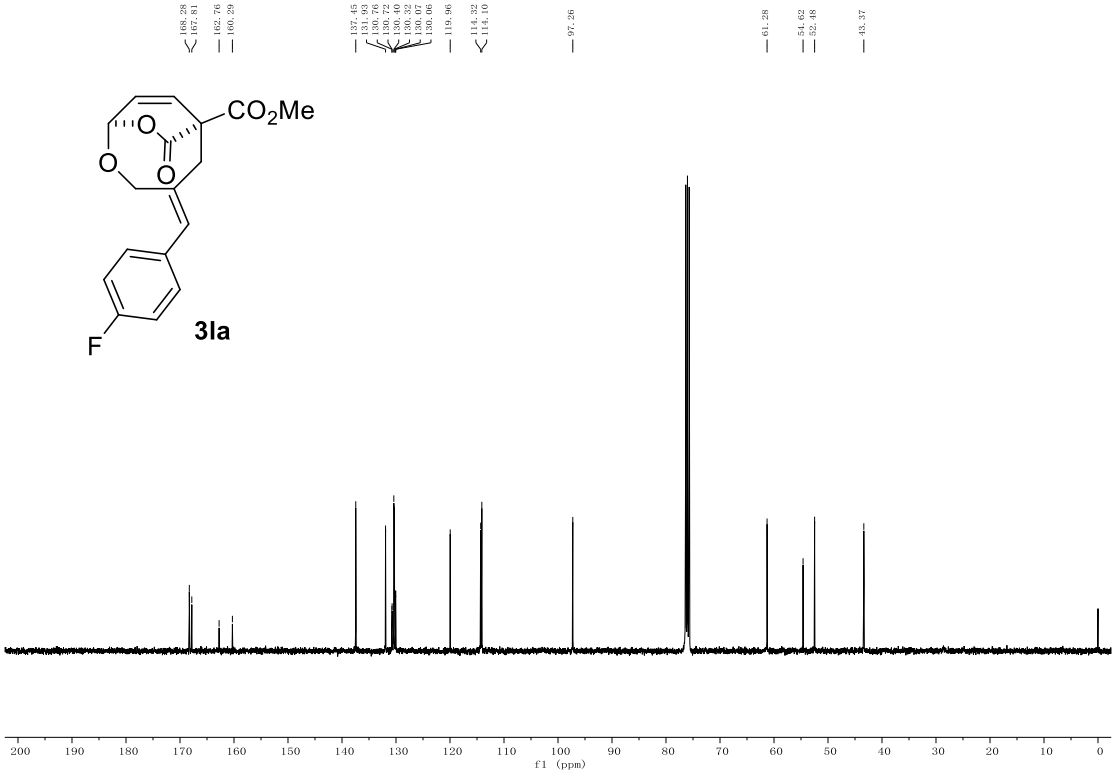
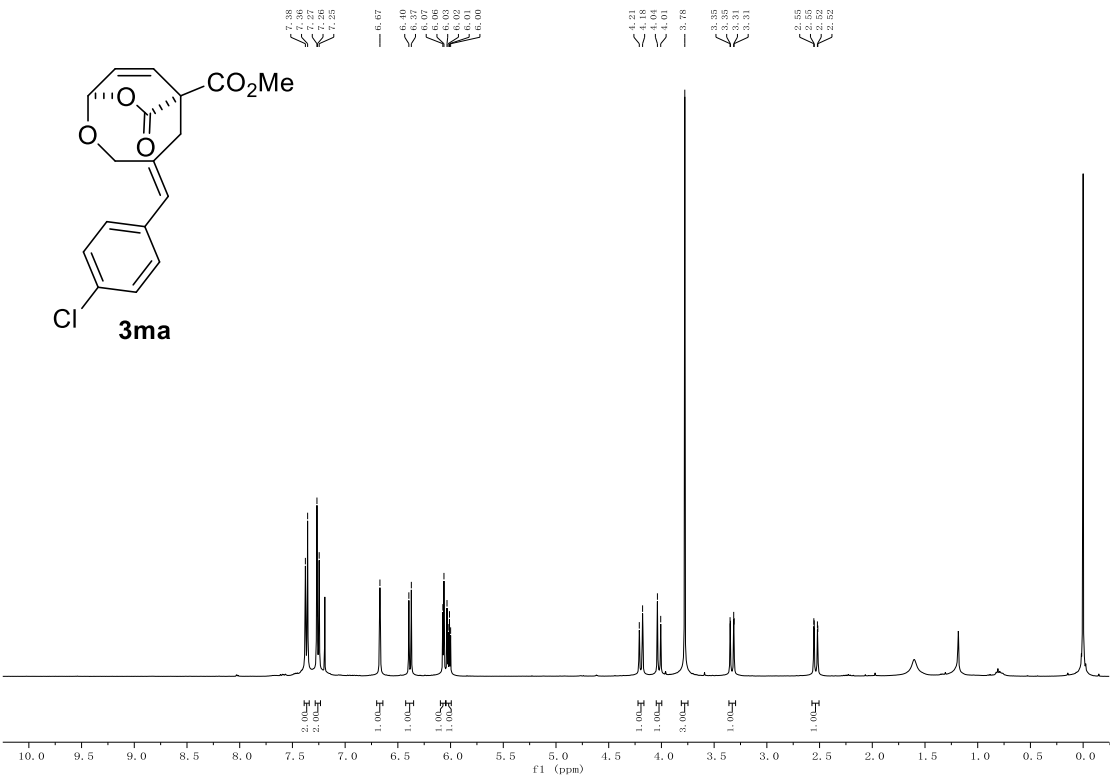
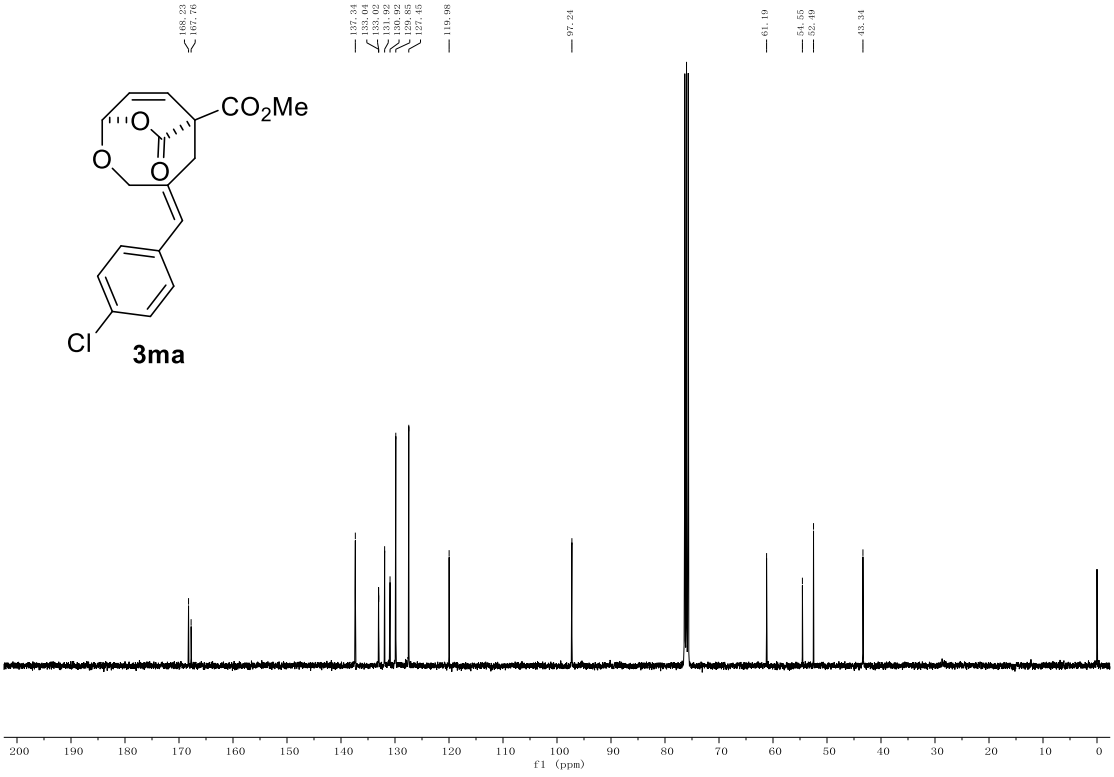


^{13}C NMR of 3la (101 MHz, $CDCl_3$)



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



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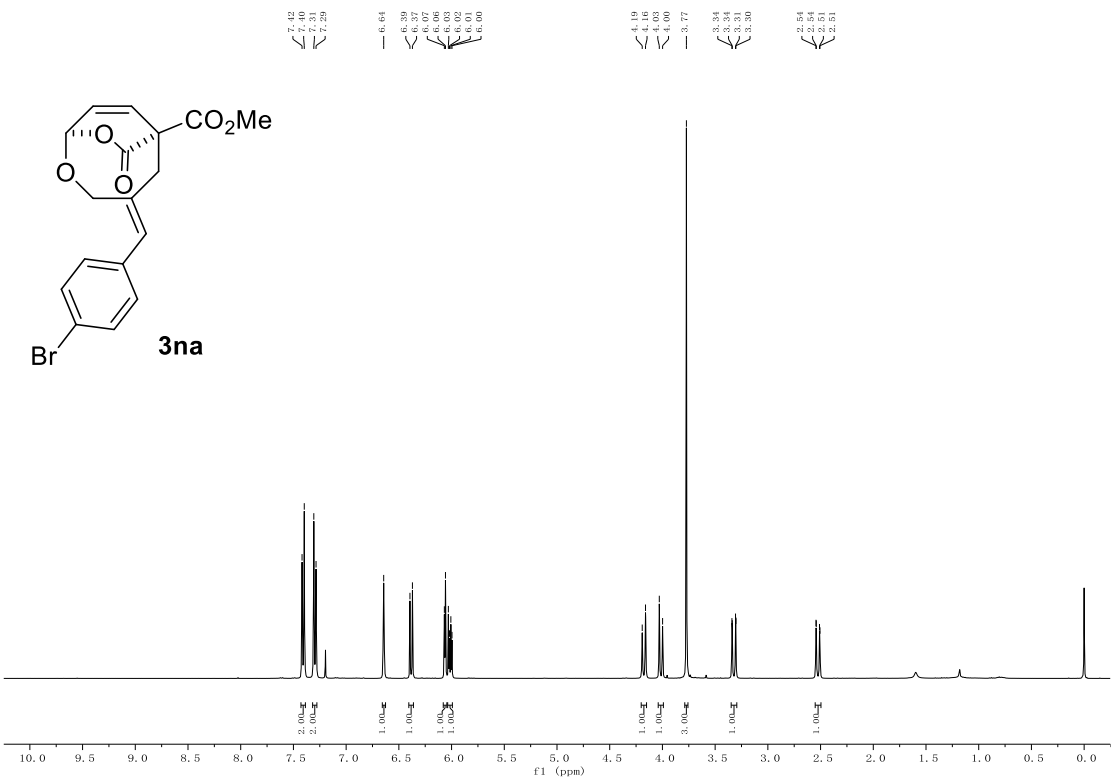
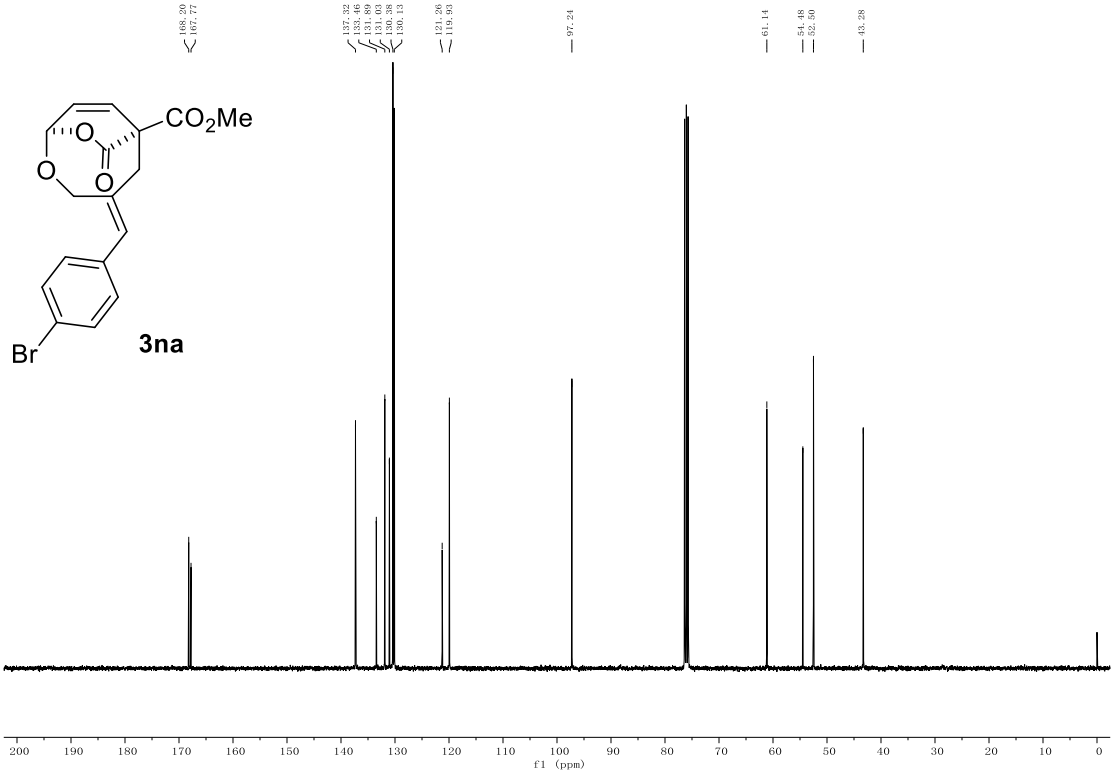
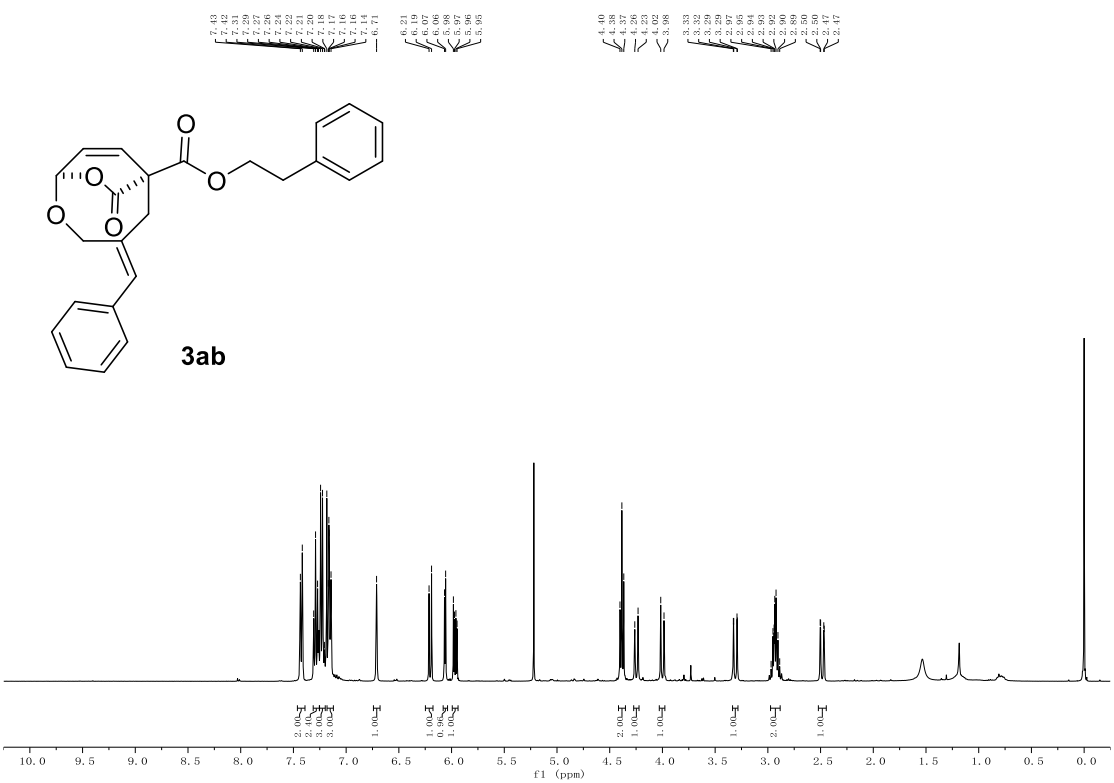


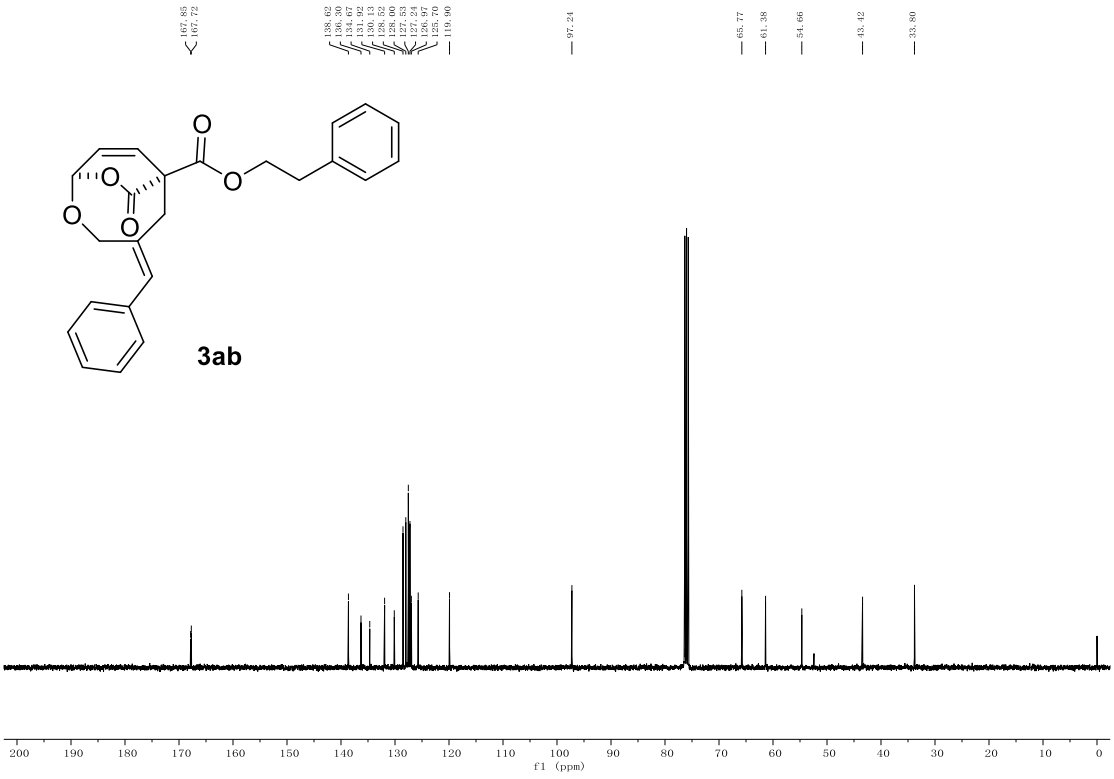
^{1}H NMR of 3na (400 MHz, $CDCl_3$)



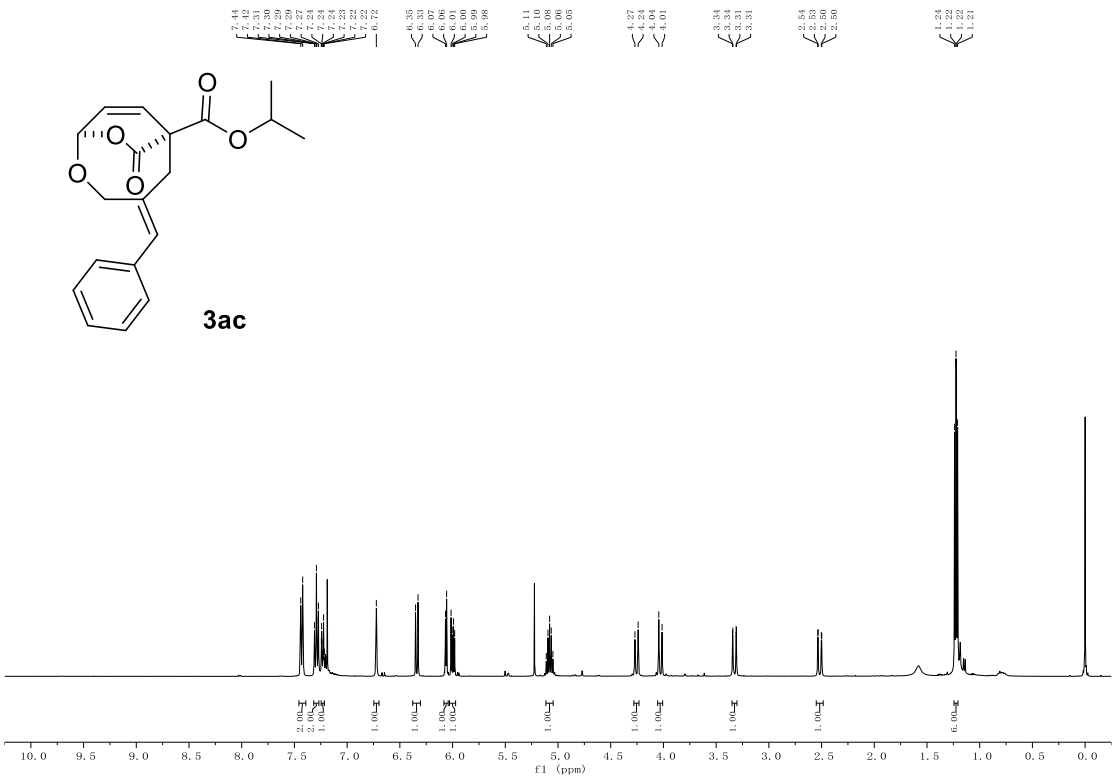
^{13}C NMR of 3na (101 MHz, $CDCl_3$)



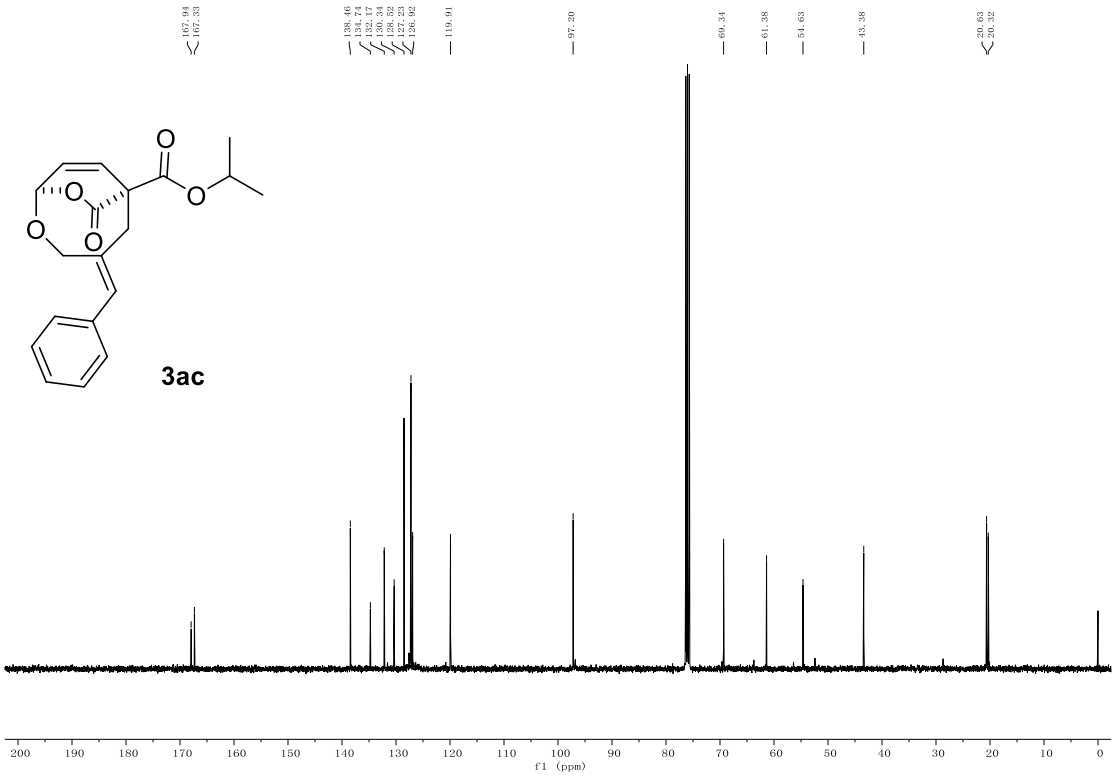
^{1}H NMR of 3ab (400 MHz, $CDCl_3$)



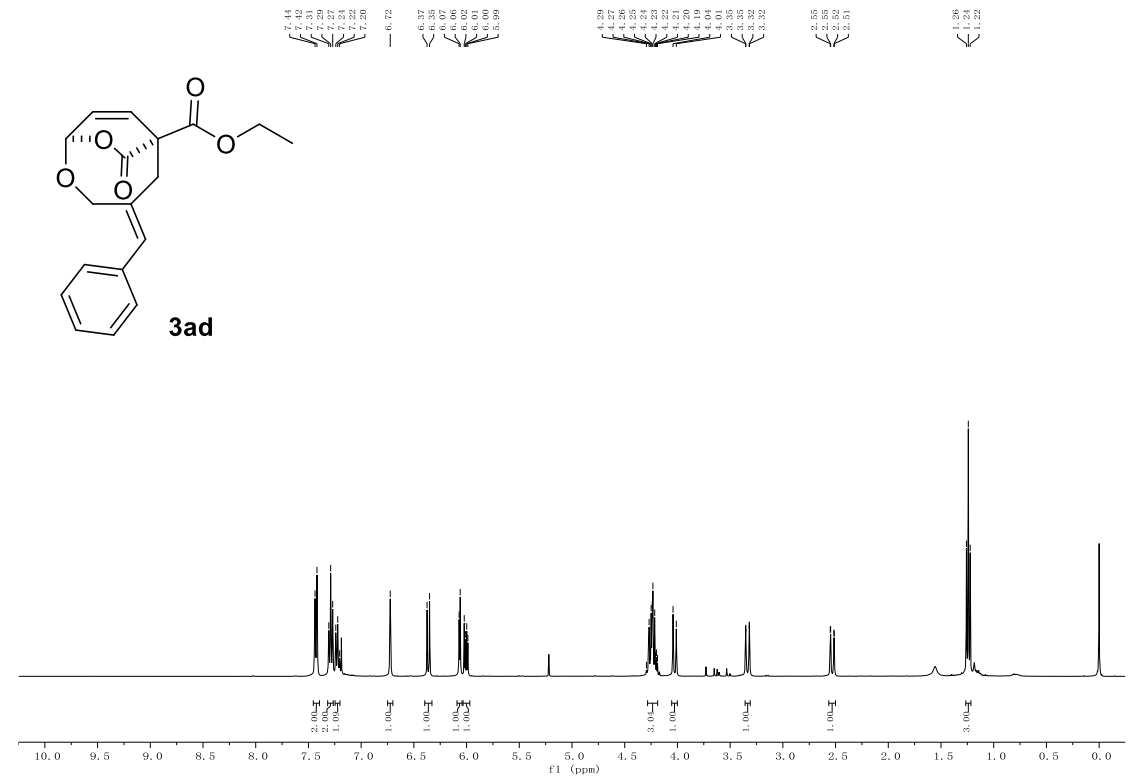
^{13}C NMR of 3ab (101 MHz, $CDCl_3$)



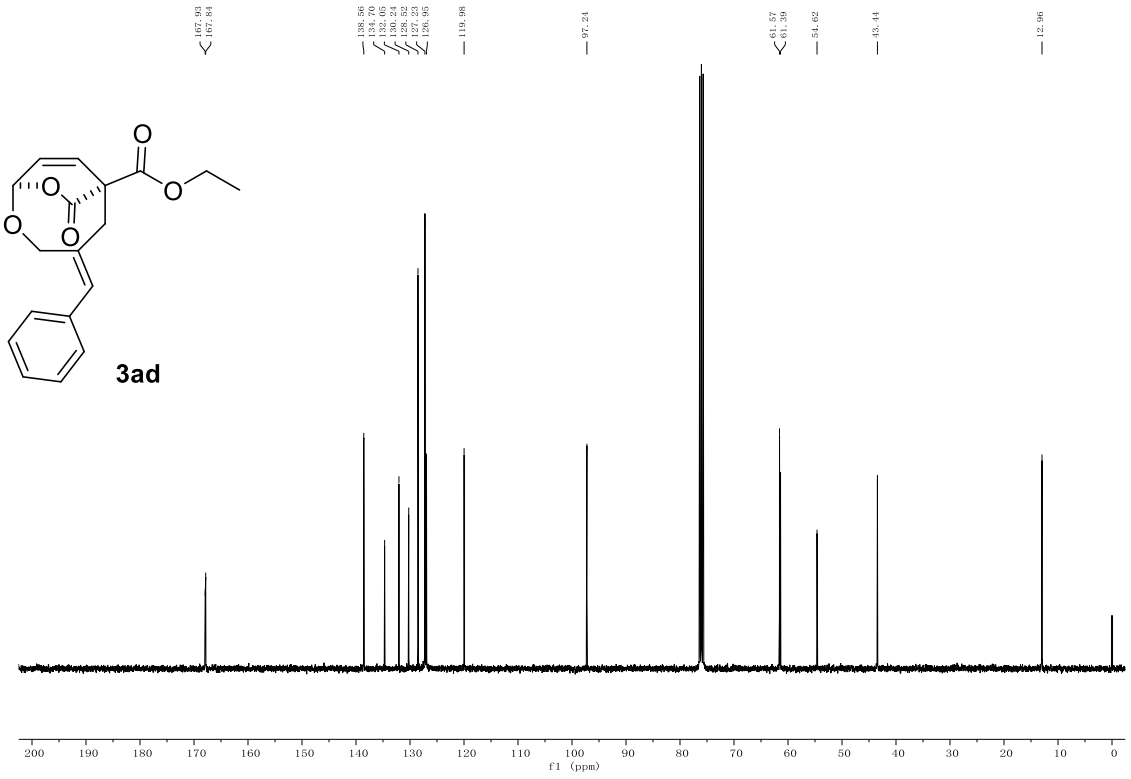
^{1}H NMR of 3ac (400 MHz, $CDCl_3$)



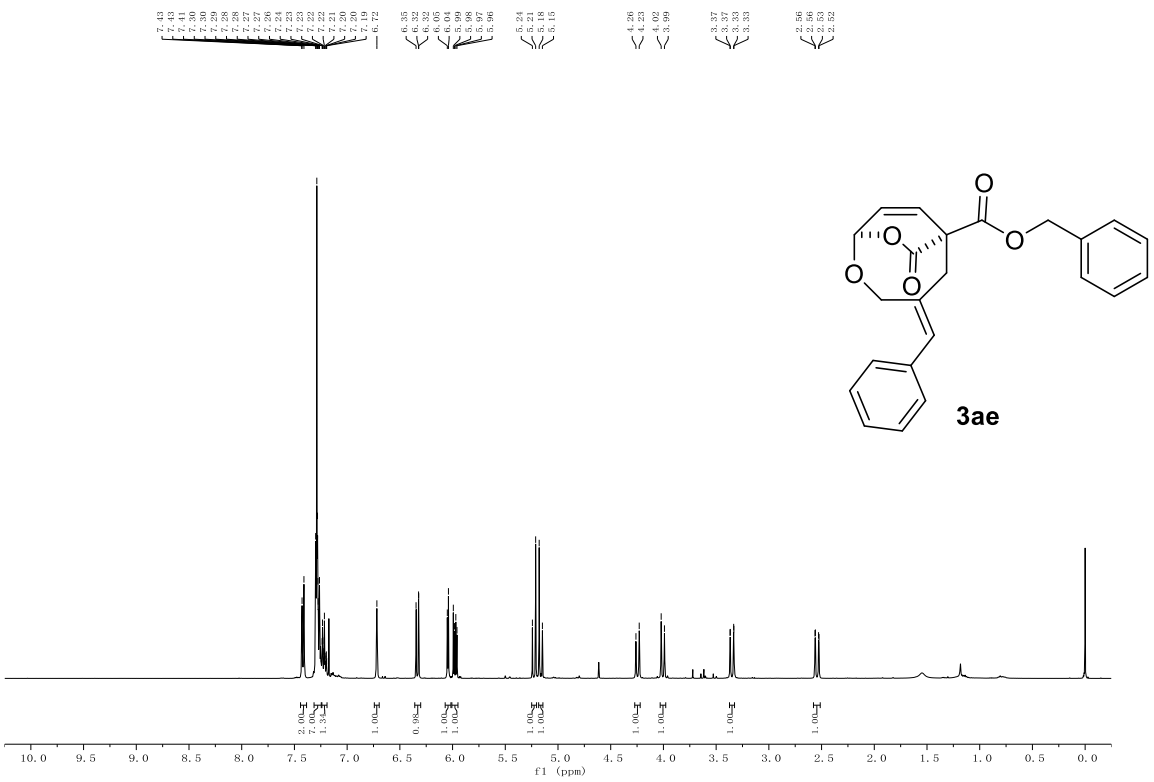
^{13}C NMR of 3ac (101 MHz, $CDCl_3$)



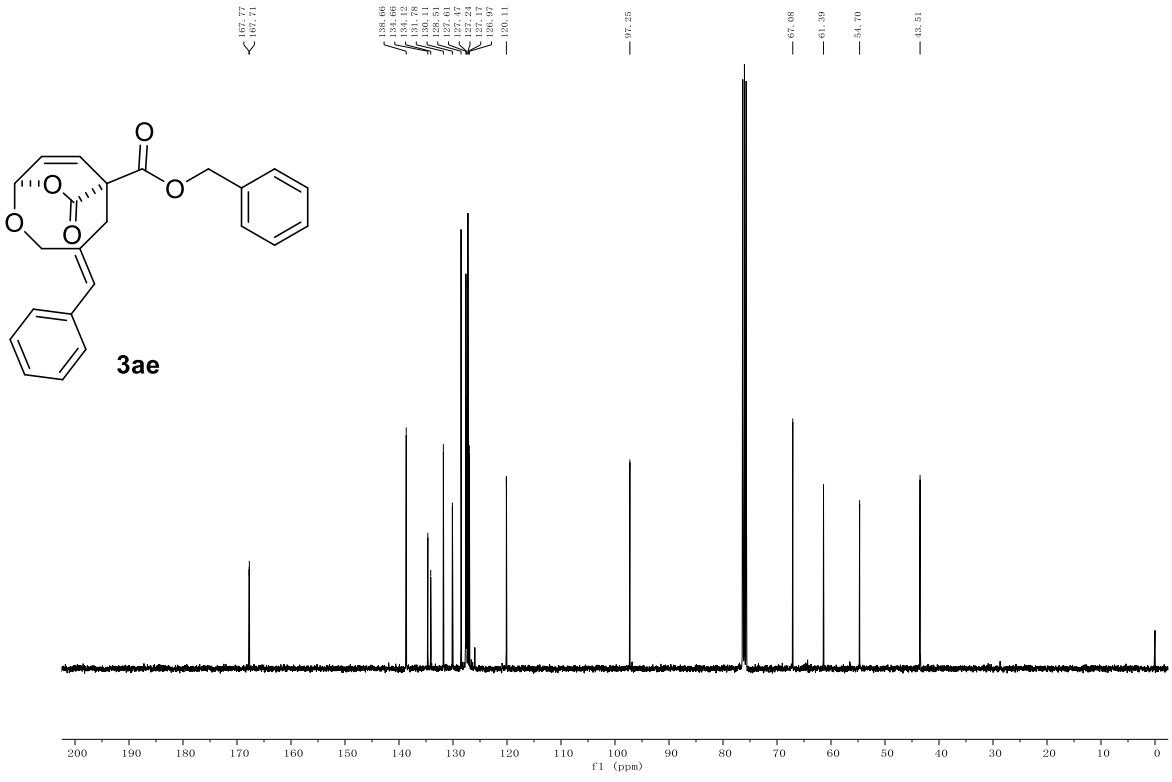
^{1}H NMR of 3ad (400 MHz, $CDCl_3$)



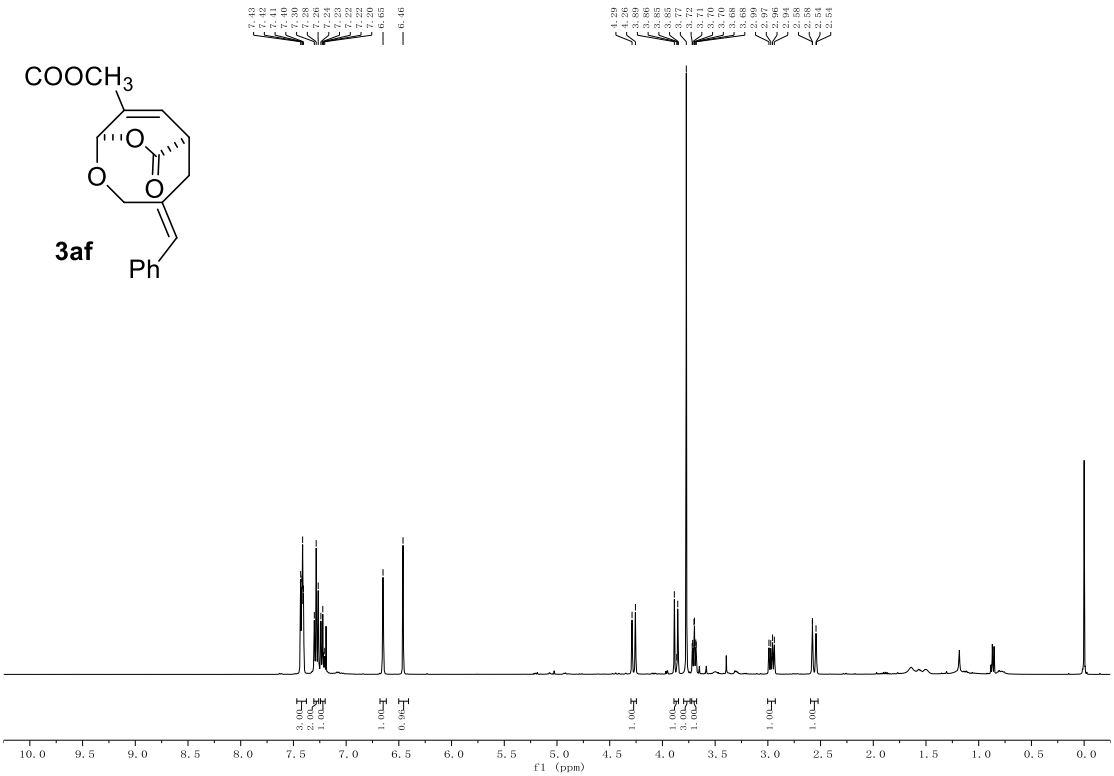
^{13}C NMR of 3ad (101 MHz, $CDCl_3$)



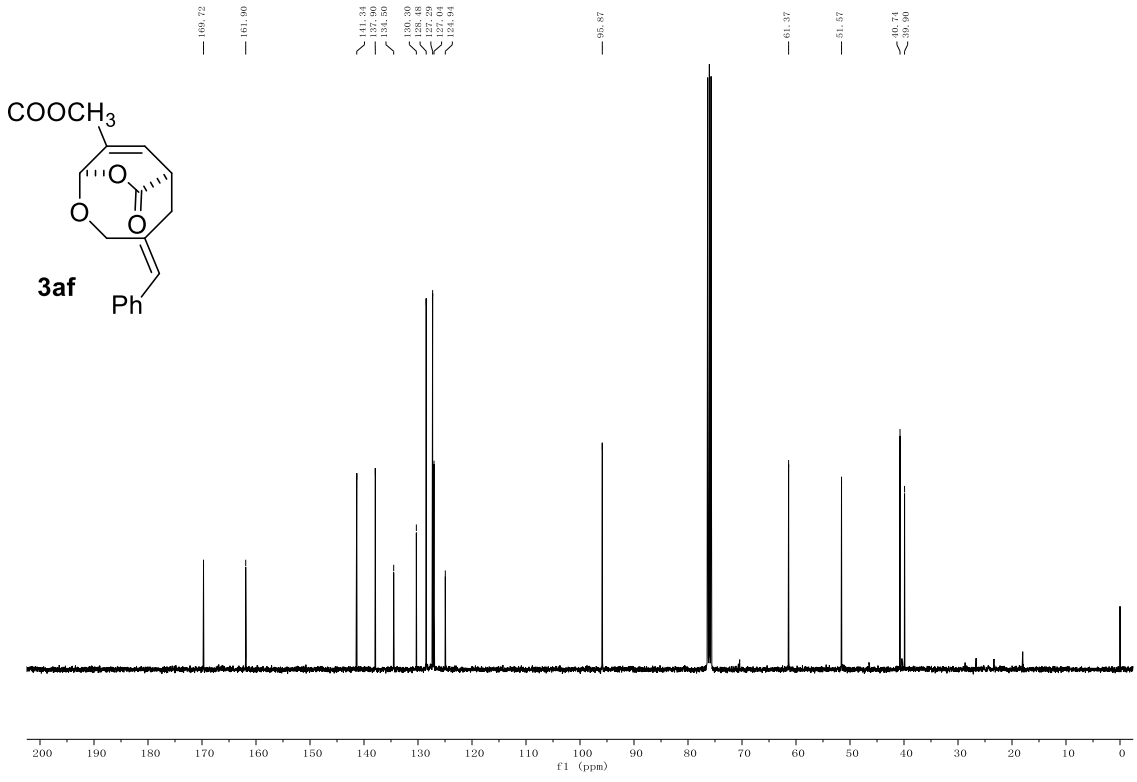
^{1}H NMR of 3ae (400 MHz, $CDCl_3$)



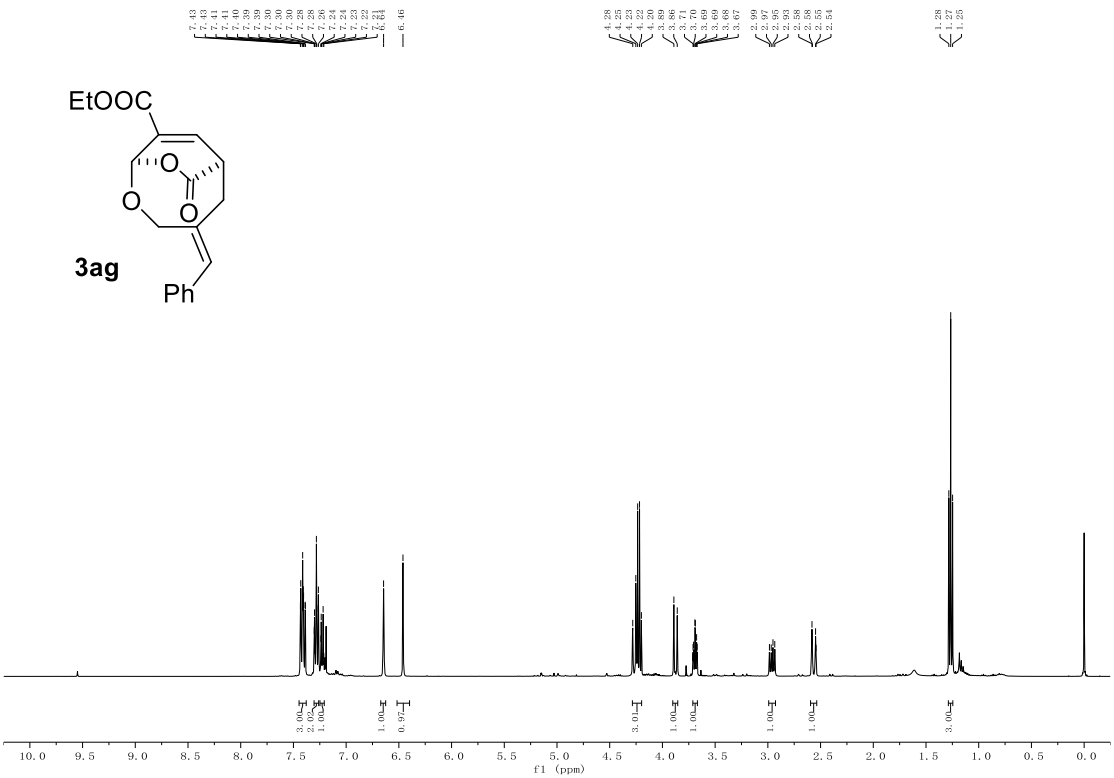
^{13}C NMR of 3ae (101 MHz, $CDCl_3$)



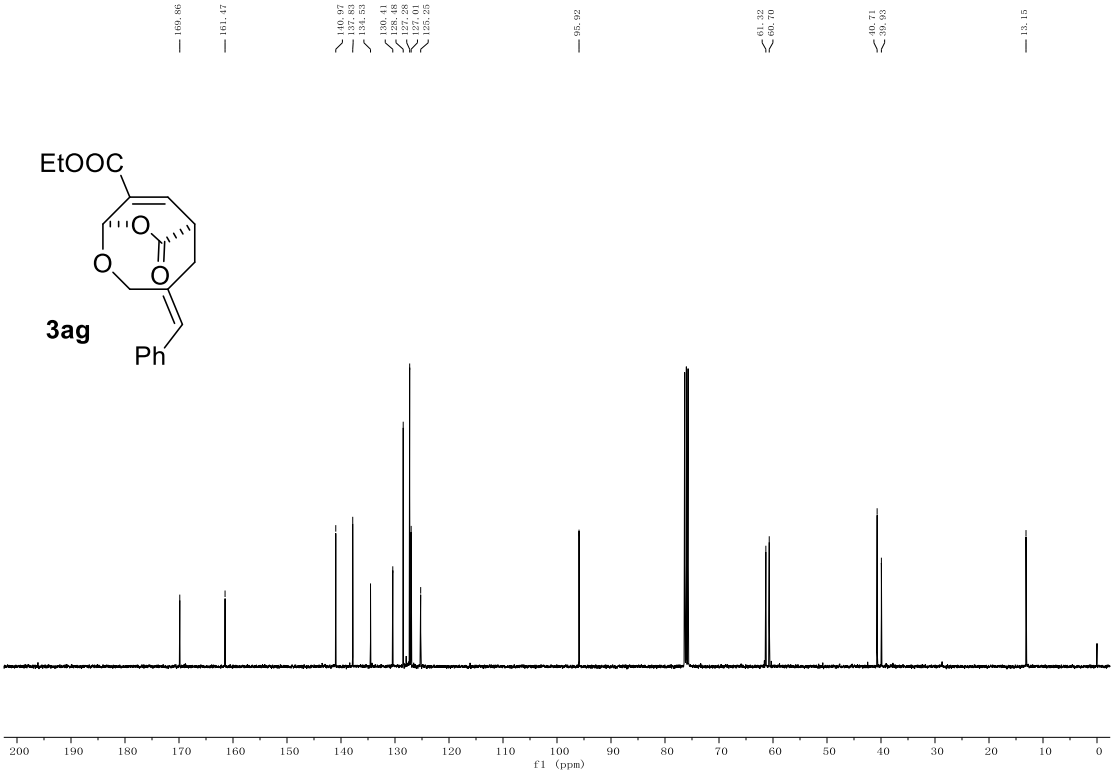
^{1}H NMR of 3af (400 MHz, $CDCl_3$)



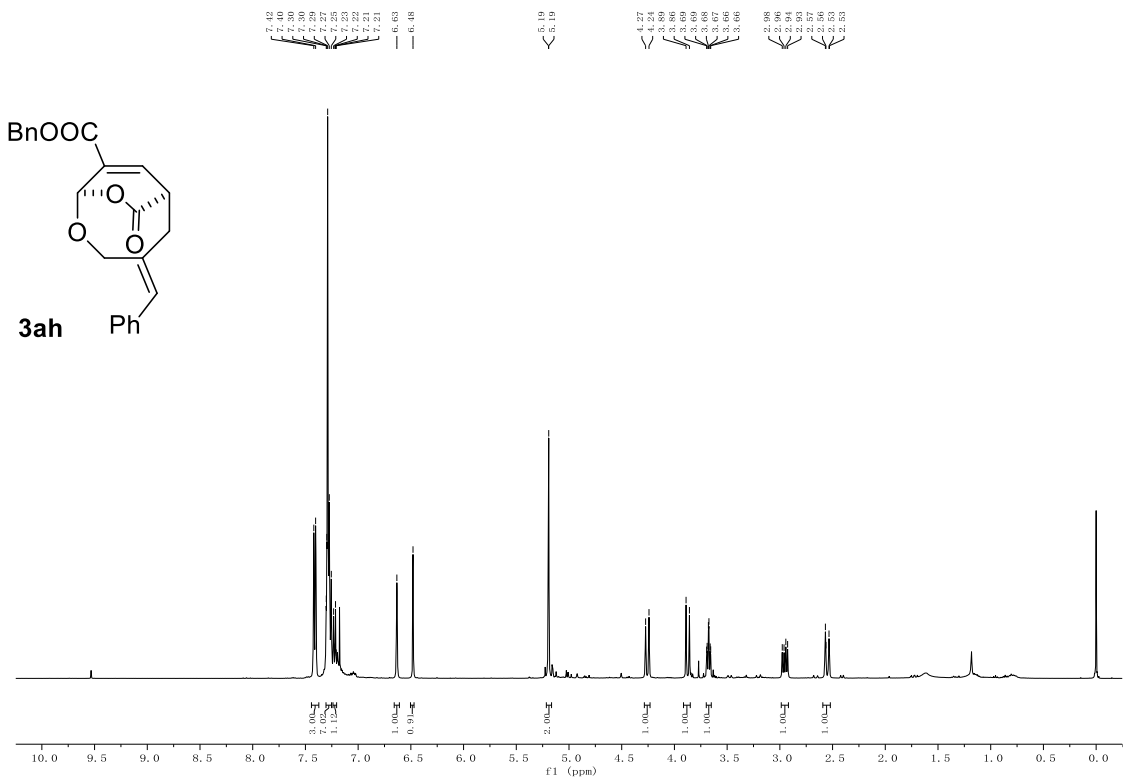
^{13}C NMR of 3af (101 MHz, $CDCl_3$)



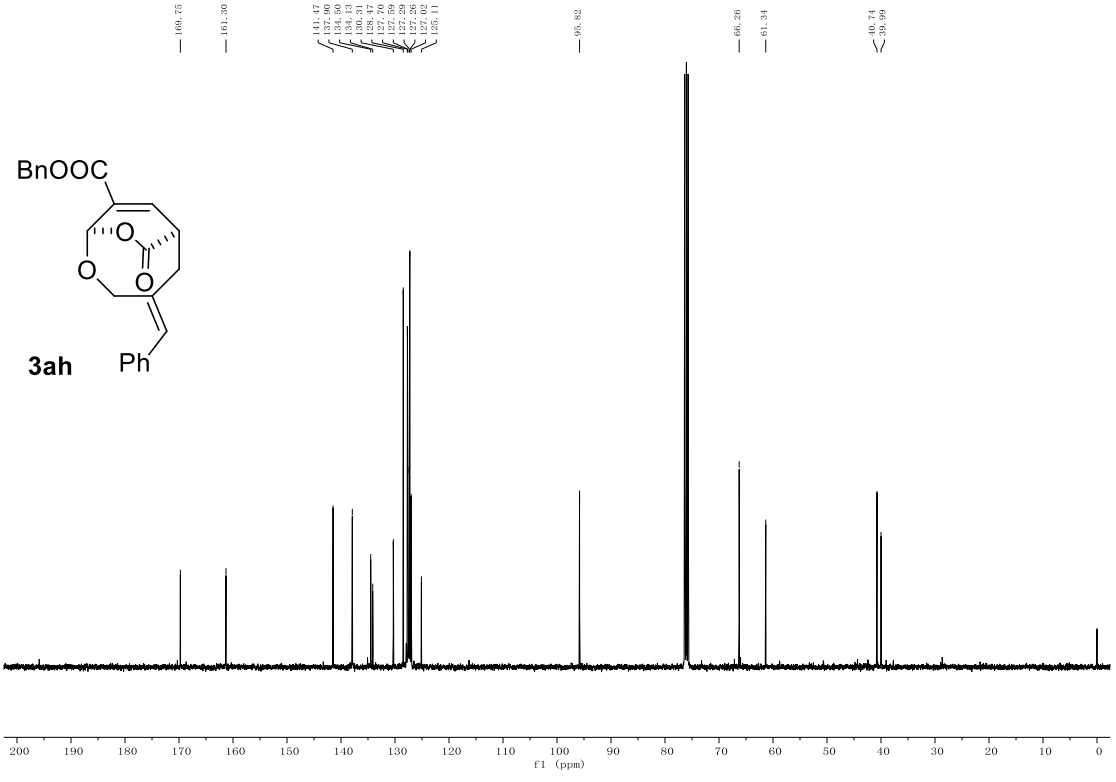
^{1}H NMR of 3ag (400 MHz, $CDCl_3$)



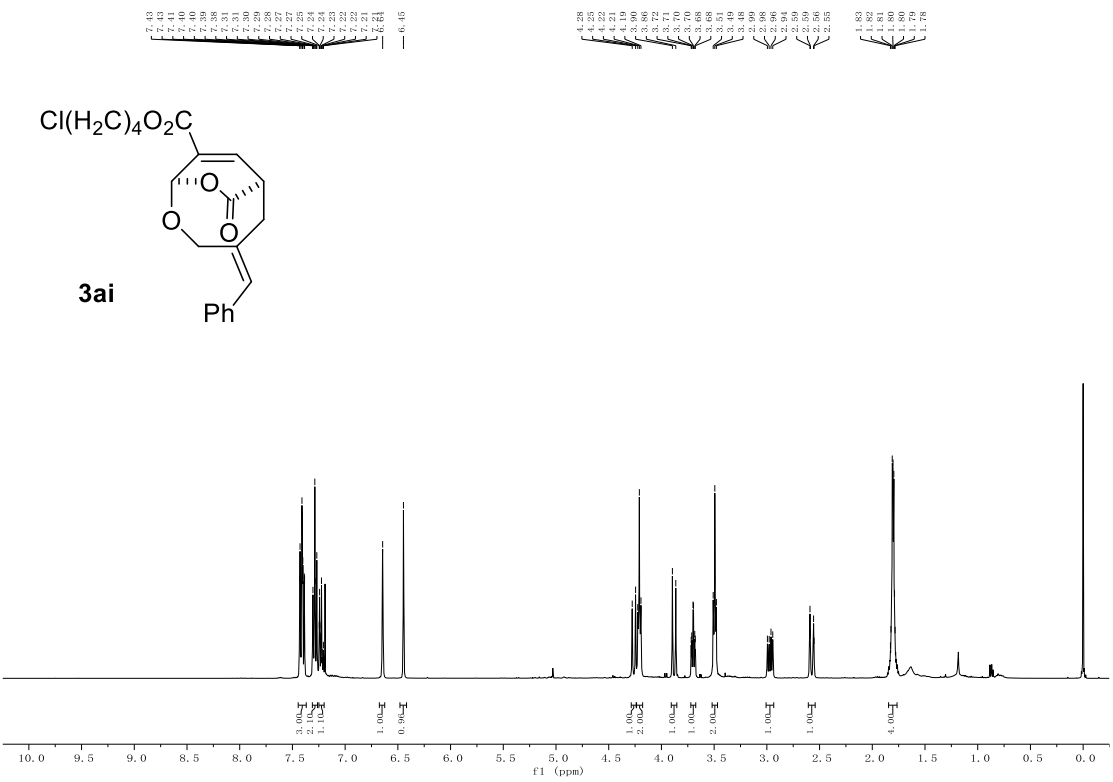
^{13}C NMR of 3ag (101 MHz, $CDCl_3$)



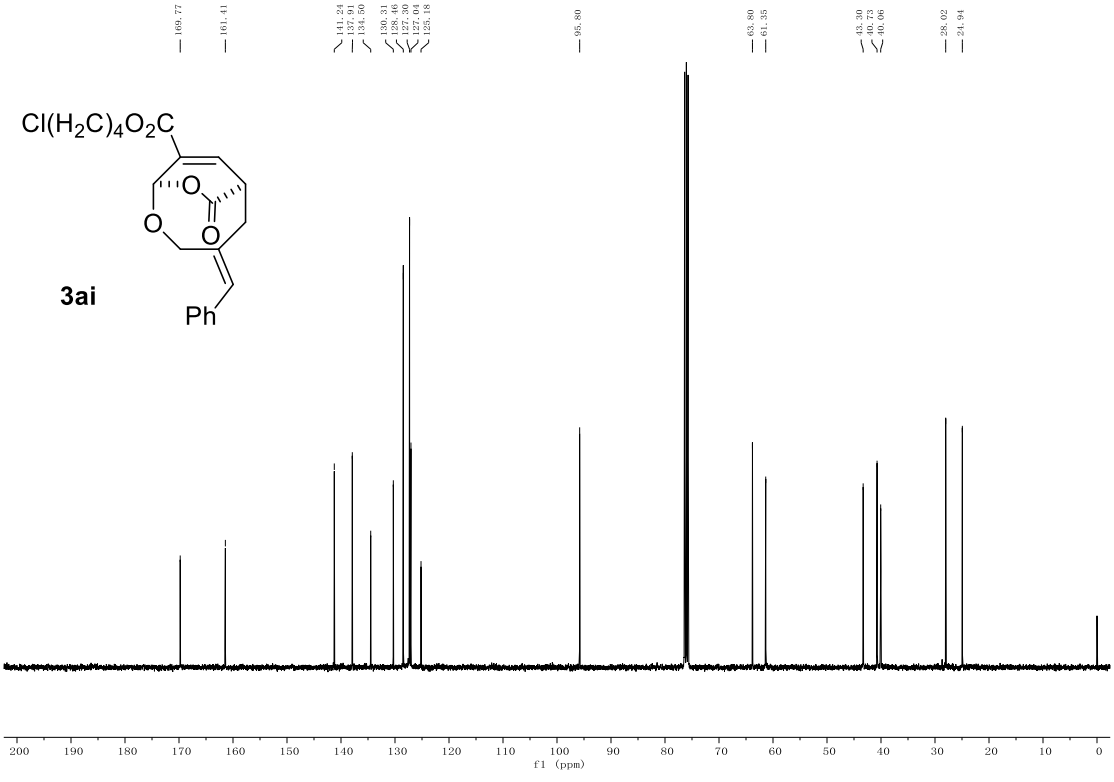
^{1}H NMR of 3ah (400 MHz, $CDCl_3$)



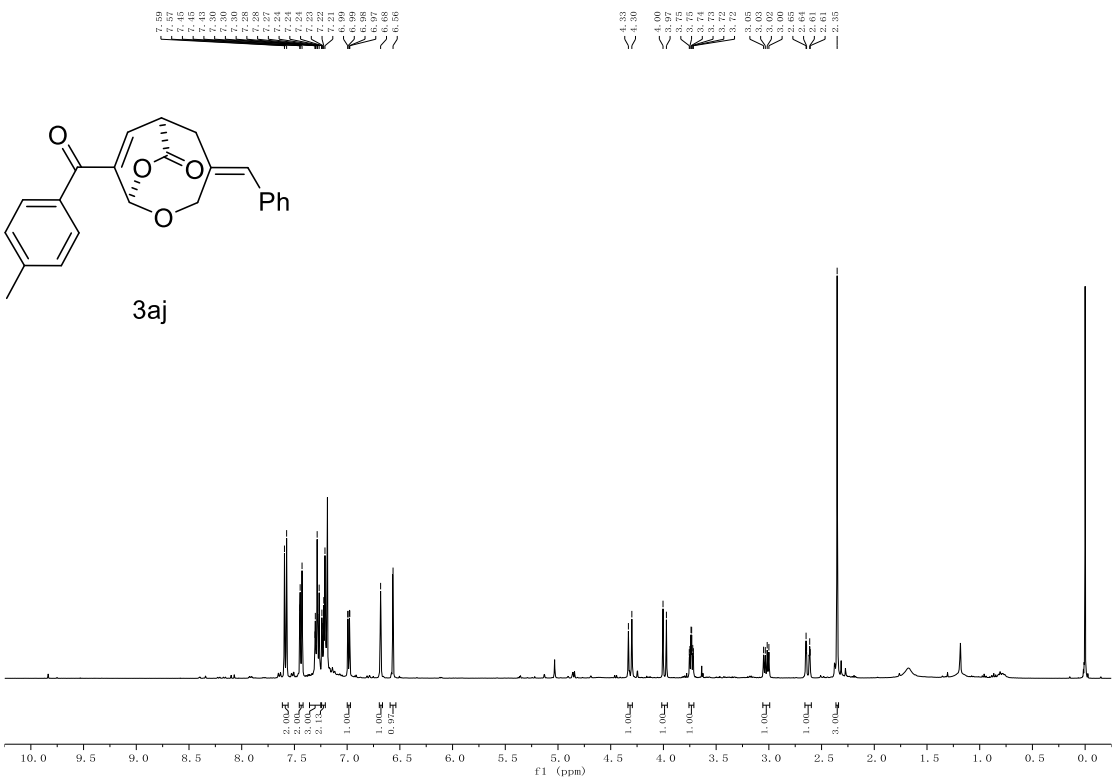
^{13}C NMR of 3ah (101 MHz, $CDCl_3$)



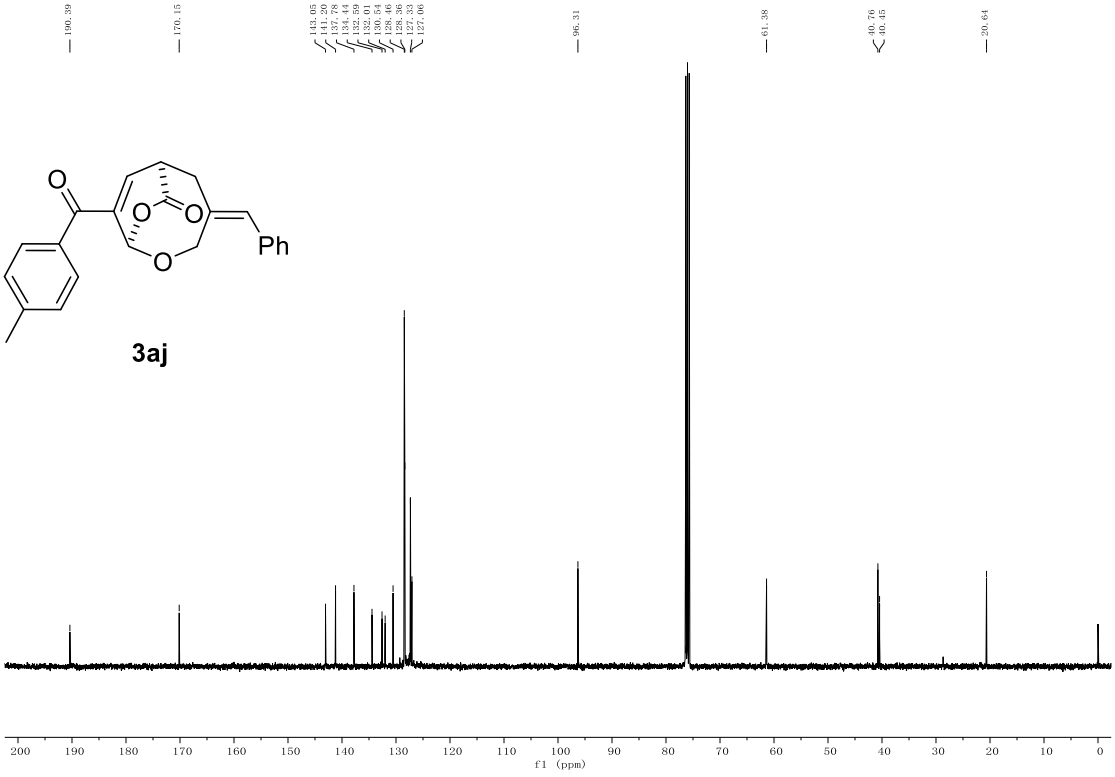
^{1}H NMR of 3ai (400 MHz, $CDCl_3$)



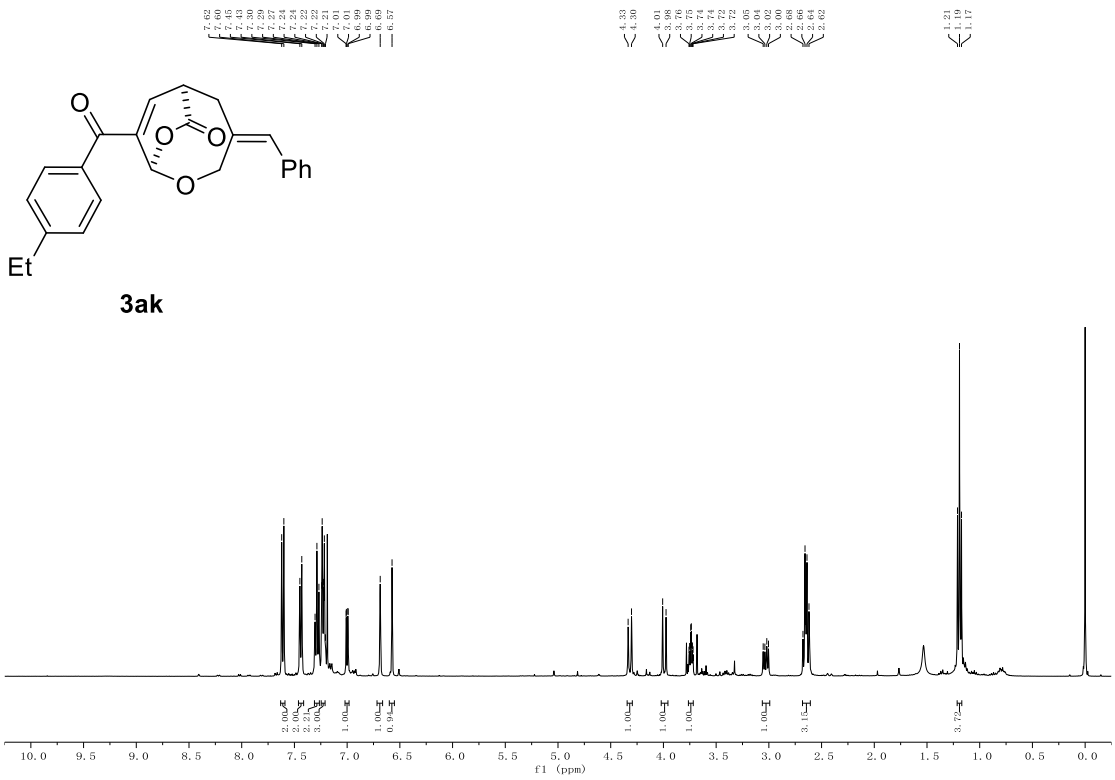
^{13}C NMR of 3ai (101 MHz, $CDCl_3$)



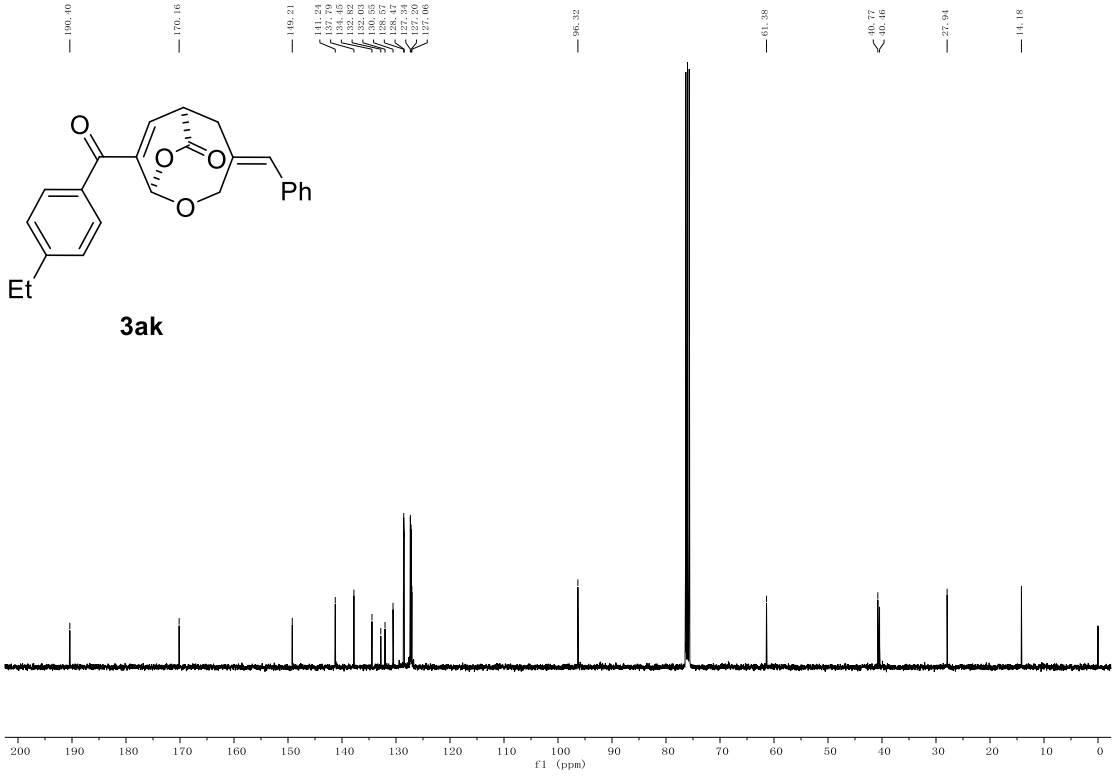
^{1}H NMR of 3aj (400 MHz, $CDCl_3$)



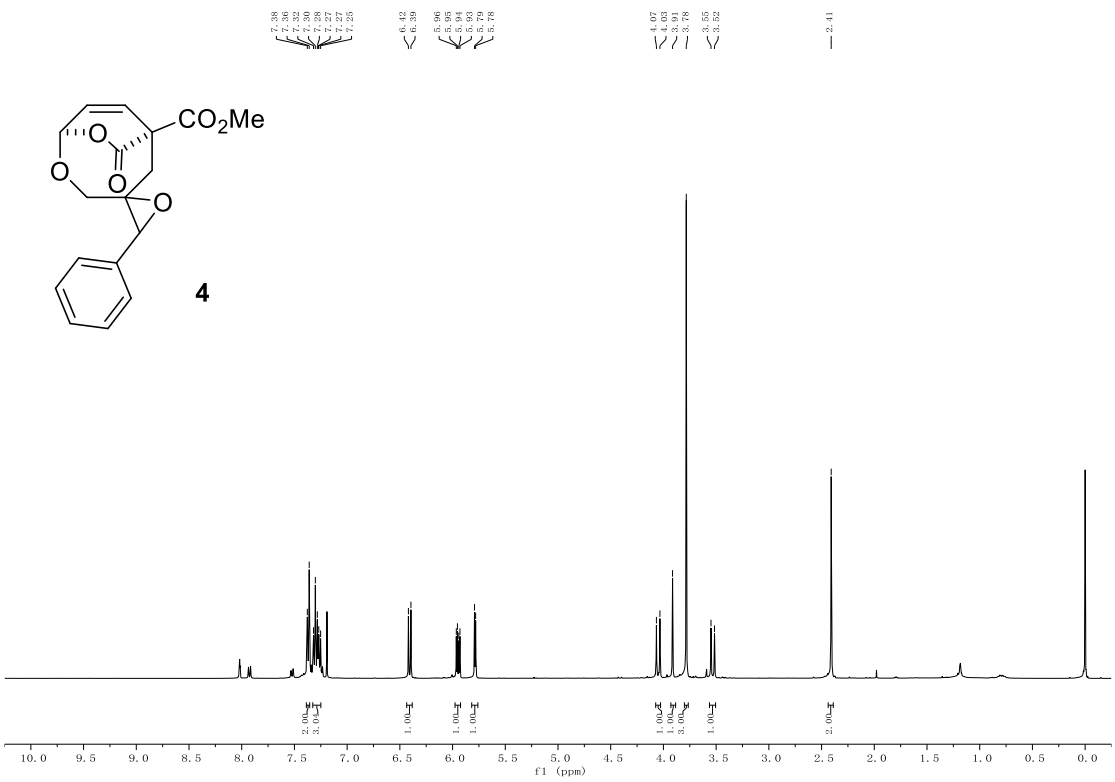
^{13}C NMR of 3aj (101 MHz, $CDCl_3$)



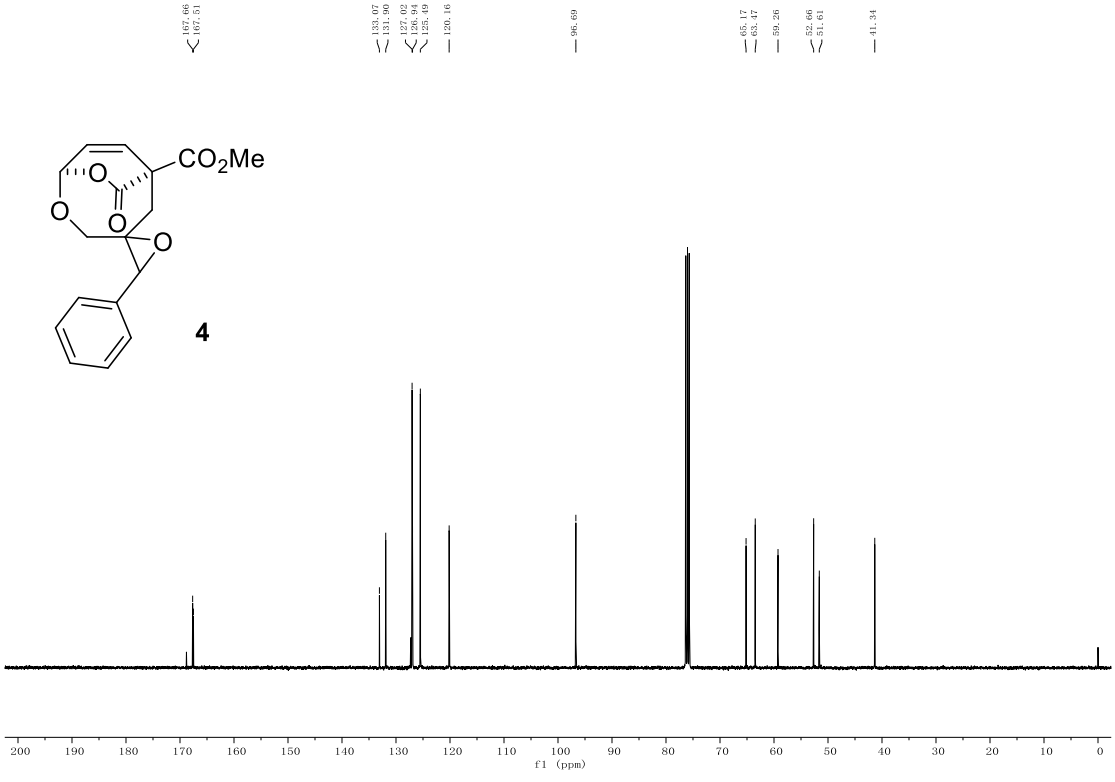
^{1}H NMR of 3ak (400 MHz, $CDCl_3$)



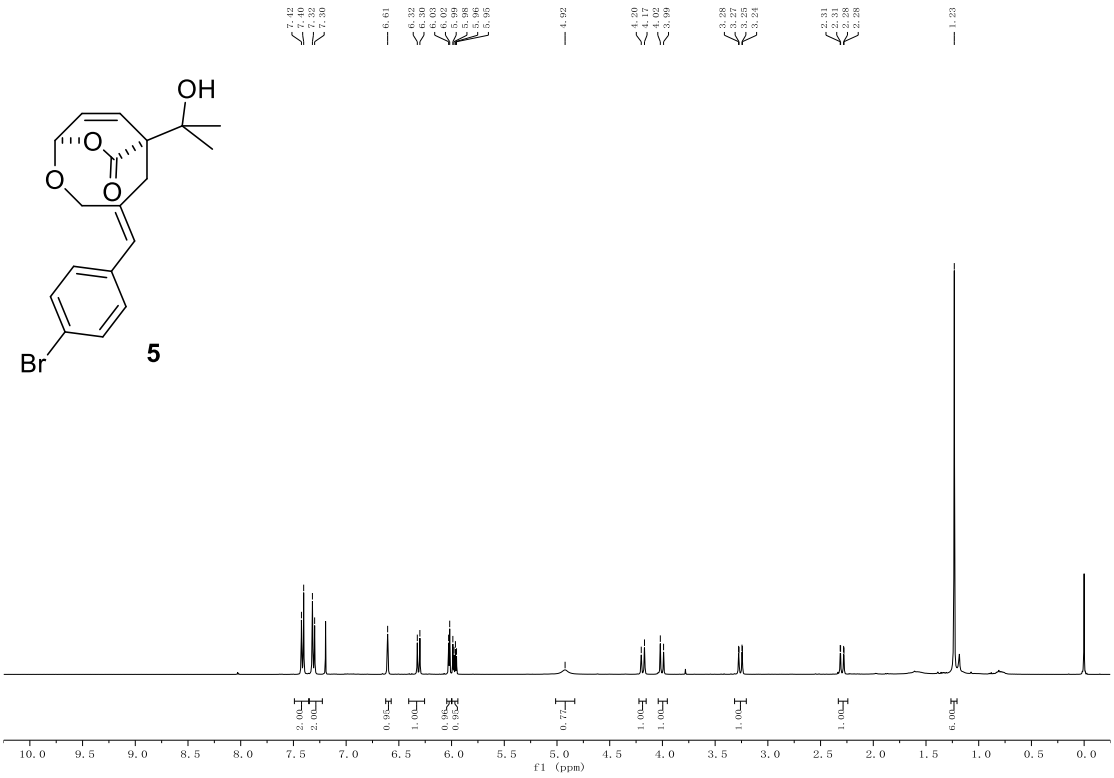
^{13}C NMR of 3ak (101 MHz, $CDCl_3$)



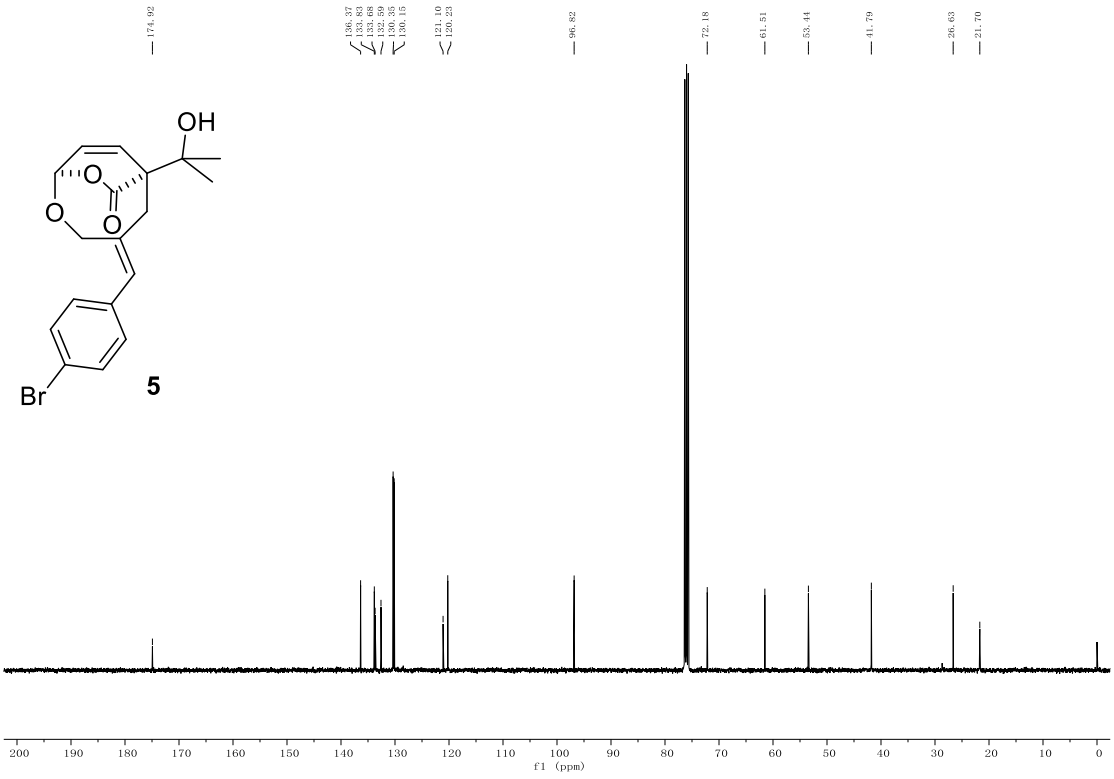
^{1}H NMR of 4 (400 MHz, $CDCl_3$)



^{13}C NMR of 4 (101 MHz, $CDCl_3$)



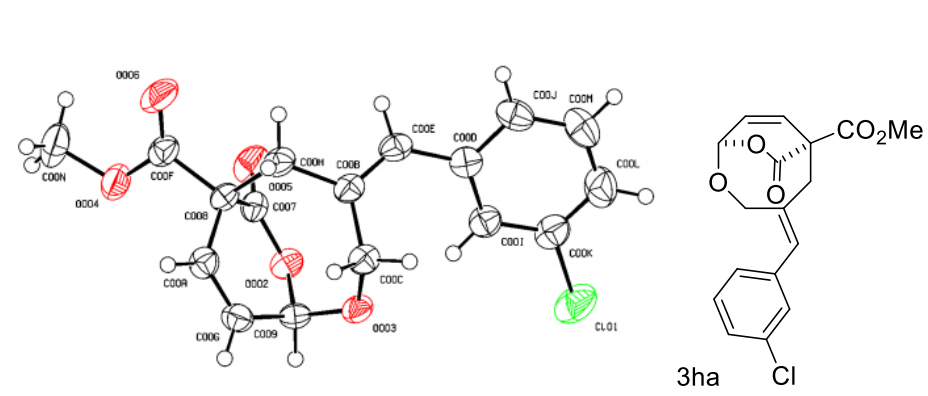
^{1}H NMR of 5 (400 MHz, $CDCl_3$)



^{13}C NMR of 5 (101 MHz, $CDCl_3$)

X-Ray single crystal data of product 3ha

The X-ray crystallographic structures for **3ha**. ORTEP view of the molecules of complex **3ha**, showing ellipsoids at 50% probability level. Crystal data have been deposited to CCDC, number **3ha** (2330507). A summary of the fundamental crystal and refinement data are given in the Table 1 of the Supporting Information. White crystals suitable for X-ray diffraction were grown by EtOH/CH_2Cl_2 solution of **3ha** in a 4 mL bottle.



Crystal structure of 3ha

Table 1 Crystal data and structure refinement for 3ha.

Identification code	3ha
Empirical formula	$C_{17}H_{15}ClO_5$
Formula weight	334.74
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.4419(16)
b/Å	7.0128(6)
c/Å	12.0067(11)
α/°	90
β/°	93.703(2)
γ/°	90
Volume/$Å^3$	1549.6(2)
Z	4
$\rho_{calc}g/cm^3$	1.435
μ/mm^{-1}	0.270
F(000)	696.0
Crystal size/mm^3	0.2 × 0.15 × 0.1

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.212 to 54.868
Index ranges	$-23 \leq h \leq 22$, $-8 \leq k \leq 9$, $-13 \leq l \leq 15$
Reflections collected	8964
Independent reflections	3460 [R_{int} = 0.0235, R_{sigma} = 0.0288]
Data/restraints/parameters	3460/0/209
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.0978
Final R indexes [all data]	R_1 = 0.0603, wR_2 = 0.1096
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.27