Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoredox-catalyzed, oxygen-directed unactivated *δ*-C(sp^3)–H functionalization toward oxepanes

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1. General information

^{1}H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR, and 564 or 377 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 Waters GCT Primier (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

Blue LED strips produced by Xuzhou Ai Jia electronic technology Co. LTD (22W, 454 nm, distance app. 3.0 cm from the strips) were coiled around the inside of an 8 cm diameter glassware. There is a fan next to the reaction. In this case, the reaction temperature is approximately room temperature (Figure S1). Optimum yields were then observed.

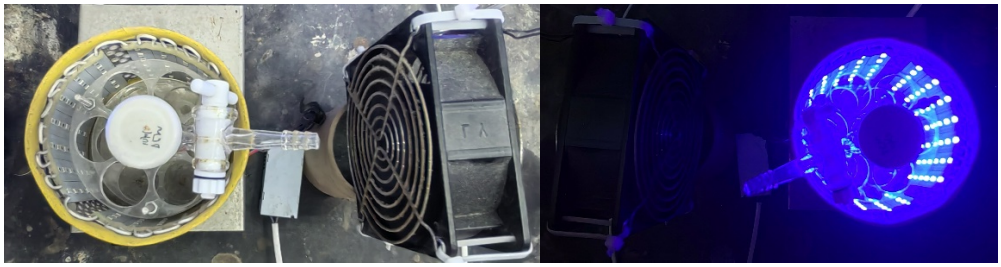
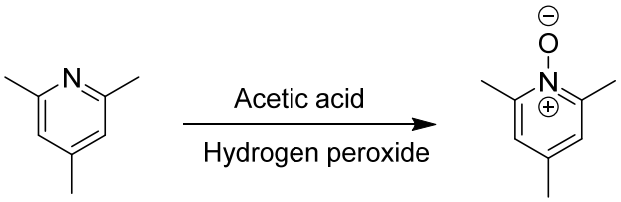


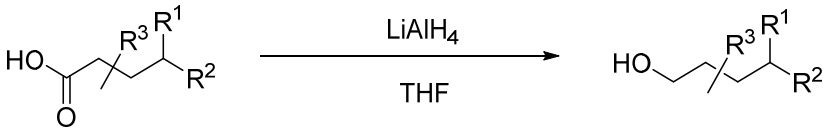
Figure S1 Reaction setup.

3. Preparation and characterization data of substrates

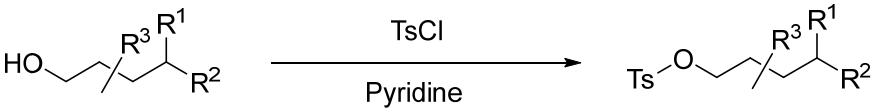
3.1 Preparation of *N*-alkoxypyridinium salts



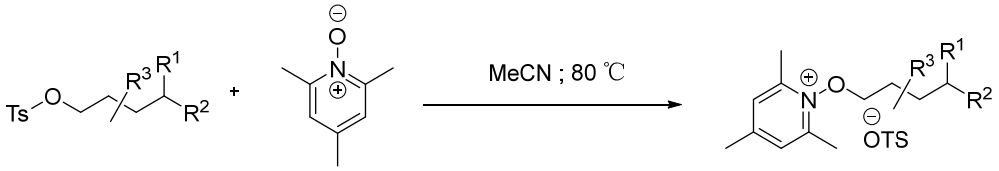
To a stirred solution of commercially available 2,4,6-collidine (10.2 mL, 77 mmol), AcOH (85 mL) and 30% aq. H_2O_2 solution (33 mL) were added. The mixture was heated at 80 ℃ for 6 h. The reaction progress was followed by TLC. After cooling, the mixture was poured into H_2O (50 mL) and neutralized by the addition of a saturated Na_2CO_3 solution. The aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL) and the combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure.[1]



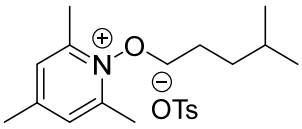
The alkyl acid (1.0 equiv) dissolved in anhydrous THF (1.7 mol/L) was added dropwise to a cooled (0 °C, ice bath) stirred $LiAlH_4$ powder (1.2 equiv.) under an argon atmosphere. Upon completion of the addition the mixture was allowed to warm to rt and stirred for further 2 h. The reaction mixture was carefully poured onto a cooled, stirred saturated solution of NaCl. The resultant mixture was filtered through a pad of celite to remove inorganic material, which was subsequently washed with diethyl ether. The combined organics were extracted into diethyl ether, washed with water, dried ($MgSO_4$) and concentrated *in vacuo* to afford the title compound as an oil.[2]



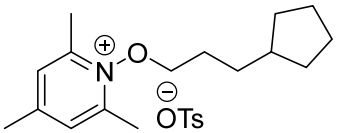
A solution of alcohols (1.0 equiv.) and *p*-toluenesulfonyl chloride (1.2 equiv) in dry pyridine was stirred under N_2 at 0 °C for 7 h. The solution was poured ice and extracted with Et_2O. The combined organic layers were washed successively with 1:1 concentrated HCl-H_2O, and saturated NaCl. The solution was dried ($MgSO_4$) and solvent evaporated to give a clear liquid.[3,4]



To a solution of *p*-toluenesulfonate (1.2 equiv.) in CH_3CN was added pyridine 2,4,6-trimethylpyridine N-oxide (1.0 equiv.) at room temperature. The reaction mixture was stirred at 80 ℃ for 12 h, then the solvent was removed under reduced pressure. The reaction solvent was evaporated under reduced pressure. The product was recrystallized twice from diethyl ether and CH_2Cl_2 solution at -20 ℃. A white solid product was obtained.[5]



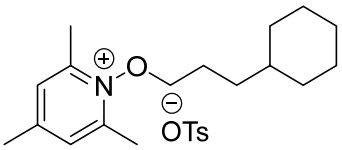
2,4,6-Trimethyl-1-((4-methylpentyl)oxy)pyridin-1-ium 4-methylbenzenesulfonate (1a): White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.53 (m, 2H), 7.50 (s, 2H), 7.03 – 6.96 (m, 2H), 4.33 (t, *J* = 6.4 Hz, 2H), 2.70 (s, 6H), 2.38 (s, 3H), 2.24 (s, 3H), 1.81 – 1.69 (m, 2H), 1.52 (dp, *J* = 13.3, 6.6 Hz, 1H), 1.32 – 1.22 (m, 2H), 0.84 (d, *J* = 6.6 Hz, 6H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 157.5, 151.7, 144.5, 138.6, 129.0, 128.3, 125.9, 80.4, 34.4, 27.8, 25.7, 22.3, 21.6, 21.2, 17.5.



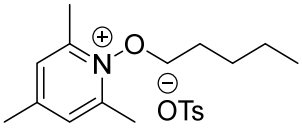
1-(3-Cyclopentylpropoxy)-2,4,6-trimethylpyridin-1-ium 4-methylbenzenesulfonate (1b): White solid; m.p. 101 – 106 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.57 (m, 2H), 7.52 (s, 2H), 7.07 – 7.00 (m, 2H), 4.40 (t, *J* = 6.4 Hz, 2H), 2.74 (s, 6H), 2.43 (s, 3H), 2.27 (s, 3H), 1.84 – 1.68 (m, 5H), 1.65 – 1.54 (m, 2H), 1.54 – 1.47 (m, 2H), 1.47 – 1.38 (m, 2H), 1.11 – 0.98 (m, 2H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 157.5, 151.7, 144.3, 138.7, 129.0, 128.3, 125.9, 80.4, 39.8, 32.5, 31.9, 27.1, 25.1, 21.7, 21.2, 17.6.

IR (KBr): *v* (cm^{-1}) 2937, 1478, 1373, 1188, 815.

HRMS (ESI) calcd for $C_{16}H_{26}NO$ $[M\text{-}OTs]^+$: 248.2009, found: 248.2010.



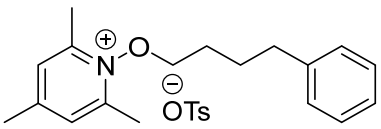
1-(3-Cyclohexylpropoxy)-2,4,6-trimethylpyridin-1-ium 4-methylbenzenesulfonate (1c): White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.51 (s, 2H), 7.07 – 7.01 (m, 2H), 4.38 (t, *J* = 6.4 Hz, 2H), 2.74 (s, 6H), 2.43 (s, 3H), 2.27 (s, 3H), 1.84 – 1.72 (m, 2H), 1.71 – 1.58 (m, 5H), 1.34 – 1.26 (m, 2H), 1.25 – 1.21 (m, 1H), 1.19 – 1.08 (m, 3H), 0.93 – 0.79 (m, 2H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 156.5, 150.7, 143.2, 137.7, 128.0, 127.4, 124.9, 79.5, 36.5, 32.1, 32.1, 25.5, 25.2, 24.3, 20.7, 20.2, 16.6.



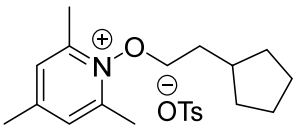
2,4,6-Trimethyl-1-(pentyloxy)pyridin-1-ium 4-methylbenzenesulfonate (1d): White solid; m.p. 93 – 98 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.67 – 7.55 (m, 2H), 7.51 (s, 2H), 7.11 – 6.98 (m, 2H), 4.39 (t, *J* = 6.4 Hz, 2H), 2.73 (s, 6H), 2.43 (s, 3H), 2.27 (s, 3H), 1.84 – 1.73 (m, 2H), 1.45 – 1.38 (m, 2H), 1.38 – 1.30 (m, 2H), 0.89 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 157.5, 151.7, 144.2, 138.7, 129.0, 128.3, 125.9, 80.2, 27.6, 27.5, 22.4, 21.7, 21.2, 17.5, 13.8.

IR (KBr): *v* (cm^{-1}) 2957, 1481, 1382, 1194, 824.

HRMS (ESI) calcd for $C_{13}H_{22}NO$ $[M\text{-}OTs]^+$: 208.1696, found: 208.1695.



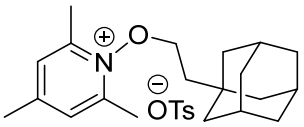
2,4,6-Trimethyl-1-(4-phenylbutoxy)pyridin-1-ium 4-methylbenzenesulfonate (1e): White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.64 – 7.57 (m, 2H), 7.49 (s, 2H), 7.31 – 7.22 (m, 2H), 7.22 – 7.11 (m, 3H), 7.03 (d, *J* = 7.9 Hz, 2H), 4.49 – 4.41 (m, 2H), 2.72 (s, 6H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.27 (s, 3H), 1.88 – 1.71 (m, 4H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 156.5, 150.7, 143.2, 140.3, 137.7, 128.0, 127.5, 127.4, 127.3, 125.1, 124.9, 79.0, 34.5, 26.3, 26.3, 20.7, 20.2, 16.6.



1-(2-Cyclopentylethoxy)-2,4,6-trimethylpyridin-1-ium 4-methylbenzenesulfonate (1f): White solid; m.p. 85 – 90 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.61 – 7.54 (m, 2H), 7.51 (s, 2H), 7.04 – 6.97 (m, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 2.71 (s, 6H), 2.40 (s, 3H), 2.24 (s, 3H), 1.94 – 1.82 (m, 1H), 1.81 – 1.71 (m, 4H), 1.63 – 1.53 (m, 2H), 1.52 – 1.43 (m, 2H), 1.14 – 1.02 (m, 2H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 157.5, 151.6, 144.4, 138.6, 129.0, 128.3, 125.9, 79.7, 36.2, 33.8, 32.7, 25.0, 21.6, 21.2, 17.5.

IR (KBr): *v* (cm^{-1}) 2946, 1481, 1382, 1186, 818.

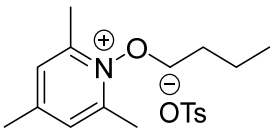
HRMS (ESI) calcd for $C_{15}H_{24}NO$ [M-OTs]$^+$: 234.1852, found: 234.1853.



1-(2-((*3r,5r,7r*)-Adamantan-1-yl)ethoxy)-2,4,6-trimethylpyridin-1-ium 4-methylbenzenesulfonate (1g): White solid; m.p. 100 – 105 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.63 – 7.59 (m, 2H), 7.56 (s, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.44 (t, *J* = 7.4 Hz, 2H), 2.74 (s, 6H), 2.44 (s, 3H), 2.26 (s, 3H), 1.95 – 1.89 (m, 3H), 1.70 – 1.66 (m, 1H), 1.66 – 1.62 (m, 2H), 1.62 – 1.55 (m, 5H), 1.49 (d, *J* = 2.9 Hz, 6H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 156.6, 150.6, 143.5, 137.5, 128.1, 127.3, 125.0, 76.2, 41.5, 40.4, 35.7, 35.7, 30.9, 27.5, 27.4, 20.7, 20.2, 16.7.

IR (KBr): *v* (cm^{-1}) 2896, 1480, 1388, 1119, 815.

HRMS (ESI) calcd for $C_{20}H_{30}NO$ [M-OTs]$^+$: 300.2322, found: 300.2322.



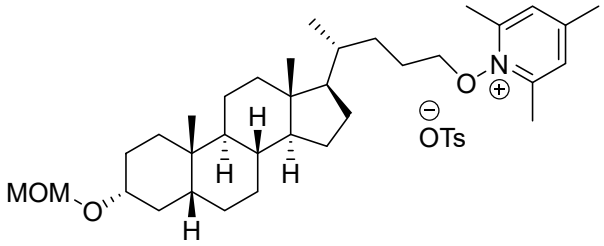
1-Butoxy-2,4,6-trimethylpyridin-1-ium 4-methylbenzenesulfonate (1h):

White solid; m.p. 85 – 90 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.63 – 7.50 (m, 2H), 7.47 (s, 2H), 7.09 – 6.94 (m, 2H), 4.35 (t, *J* = 6.4 Hz, 2H), 2.69 (s, 6H), 2.39 (s, 3H), 2.24 (s, 3H), 1.73 (ddt, *J* = 9.3, 8.0, 6.4 Hz, 2H), 1.43 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.91

(t, *J* = 7.4 Hz, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 157.5, 151.7, 144.2, 138.8, 129.0, 128.3, 125.9, 79.9, 29.8, 21.6, 21.2, 18.9, 17.5, 13.8.

IR (KBr): *v* (cm^{-1}) 2957, 1481, 1380, 1194, 821.

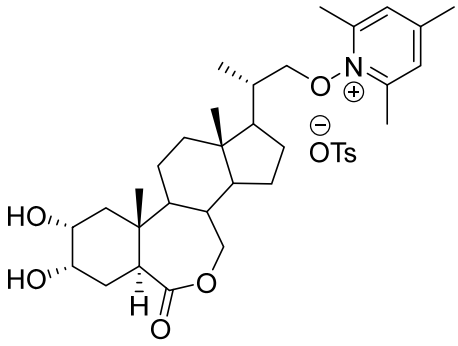
HRMS (ESI) calcd for $C_{12}H_{20}NO$ [M-OTs]$^+$: 194.1539, found: 194.1538.



1-(((*R*)-4-*((3R,5R,8R,9S,10S,13R,14S,17R*)-3-(Methoxymethoxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentyl)oxy)-2,4,6-trimethylpyridin-1-ium 4-methylbenzenesulfonate (1i): White solid; m.p. 100 – 105 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.65 – 7.58 (m, 2H), 7.54 (s, 2H), 7.08 – 7.02 (m, 2H), 4.66 (s, 2H), 4.44 (t, *J* = 6.3 Hz, 2H), 3.56 – 3.44 (m, 1H), 3.34 (s, 3H), 2.77 (s, 6H), 2.47 (s, 3H), 2.28 (s, 3H), 1.98 – 1.63 (m, 9H), 1.59 – 1.49 (m, 3H), 1.44 – 1.30 (m, 7H), 1.22 – 1.13 (m, 3H), 1.13 – 1.00 (m, 5H), 0.95 – 0.88 (m, 7H), 0.62 (s, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 156.5, 150.7, 143.3, 137.6, 128.0, 127.3, 124.9, 93.6, 79.7, 75.9, 55.5, 54.9, 54.1, 41.7, 41.1, 39.3, 39.2, 34.8, 34.6, 34.3, 33.7, 32.6, 30.7, 27.3, 26.7, 26.2, 25.4, 23.6, 23.2, 22.4, 20.7, 20.3, 19.8, 17.4, 16.7, 11.0.

IR (KBr): *v* (cm^{-1}) 2930, 1449, 1378, 1105, 817.

HRMS (ESI) calcd for $C_{34}H_{56}NO_3$ [M-OTs]$^+$: 526.4255, found: 526.4258.



1-((*2S*)-2-*((3aS,5S,6R,7aR,9aR*)-5,6-Dihydroxy-7a,9a-dimethyl-3-oxohexadecahydro-1H-benzo[c]indeno[5,4-e]oxepin-10-yl)propoxy)-2,4,6-trimethylpyridin-1-ium 4-methylbenzenesulfonate (1j): White solid; m.p. > 300 ℃, decomposed; **^{1}H NMR (400 MHz, D$_2$O)** δ 7.52 – 7.46 (m, 2H), 7.40 (s, 2H), 7.20 – 7.15 (m, 2H), 4.14 – 3.92

(m, 4H), 3.88 – 3.83 (m, 1H), 3.57 (ddd, J = 12.5, 4.7, 2.7 Hz, 1H), 3.04 (dd, J = 12.4, 4.6 Hz, 1H), 2.59 (s, 6H), 2.34 (s, 3H), 2.22 (s, 3H), 1.97 – 1.80 (m, 3H), 1.75 – 1.46 (m, 7H), 1.42 – 1.00 (m, 12H), 0.72 (s, 3H), 0.61 (s, 3H); **^{13}C NMR (151 MHz, D_2O)** δ 180.4, 157.7, 151.9, 142.2, 139.6, 129.3, 128.2, 125.3, 83.6, 71.3, 67.6, 67.4, 57.2, 51.3, 50.1, 42.6, 40.9, 40.1, 38.8, 38.4, 37.8, 36.0, 30.6, 27.3, 24.4, 21.7, 20.6, 20.5, 16.8, 16.1, 14.7, 10.9.

IR (KBr): v (cm^{-1}) 2918, 1471, 1318, 1127, 818.

HRMS (ESI) calcd for $C_{30}H_{46}NO_5$ $[M\text{-}OTs]^+$: 500.3371, found: 500.3369.

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.[6]

4. Stern-Volmer fluorescence quenching experiments

Emission intensities were recorded using F-320 Luminescence Spectrometer for all experiments. CH_2Cl_2 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 425-650 nm. In a typical experiment, the CH_2Cl_2 solution of *fac*-Ir(ppy)$_3$ (0.05 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.

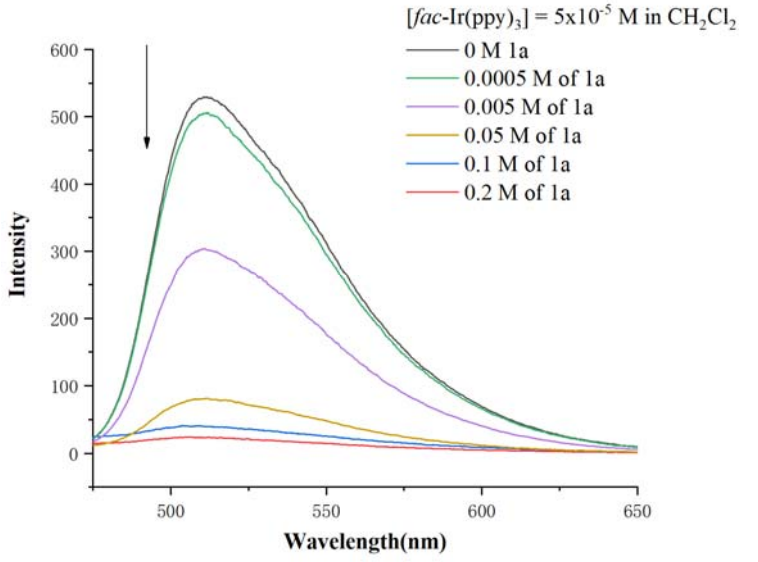


Figure S2. Fluorescence quenching by 1a.

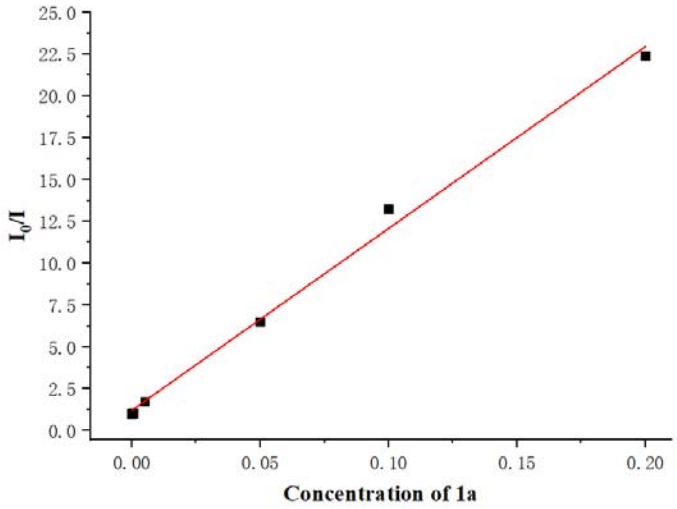
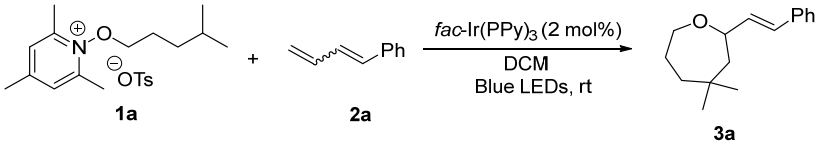
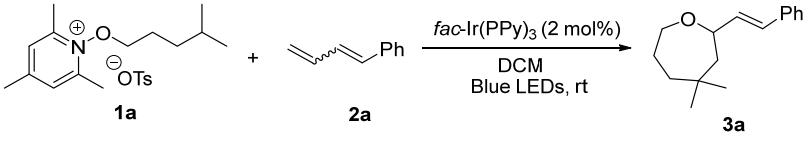


Figure S3. Stern−Volmer fluorescence quenching

5. Typical procedures of synthesis of products

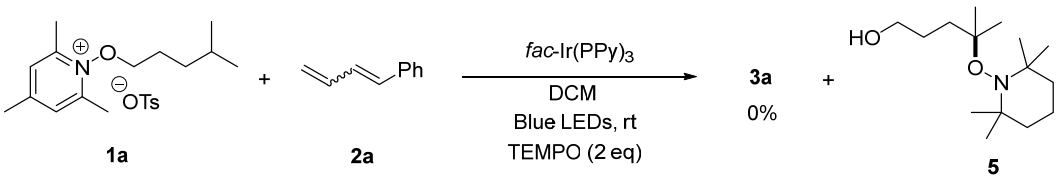


Typical procedure: In a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with **1a** (78.0 mg, 0.20 mmol), **2a** (39.0 mg, 0.30 mmol), and *fac*-Ir(PPy)$_3$ (2.6 mg, 0.004 mmol, 2 mol%), followed by the addition of CH_2Cl_2 (2.0 mL). The mixture was degassed and refilled with N_2 gas, and then irradiated with blue LEDs (22 W) at room temperature for 2.5 h. The solvent was removed under vaccum and the residue was purified by column chromatography on silica gel using PE/EA (30:1) as eluent to afford **3a** in 78% yield.



Gram-scale transformation: In a flame-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with **1a** (1.01 g, 2.5 mmol), **2a** (488 mg, 3.75 mmol), and *fac*-Ir(PPy)$_3$ (32.7 mg, 0.05 mmol, 2 mol%), followed by the

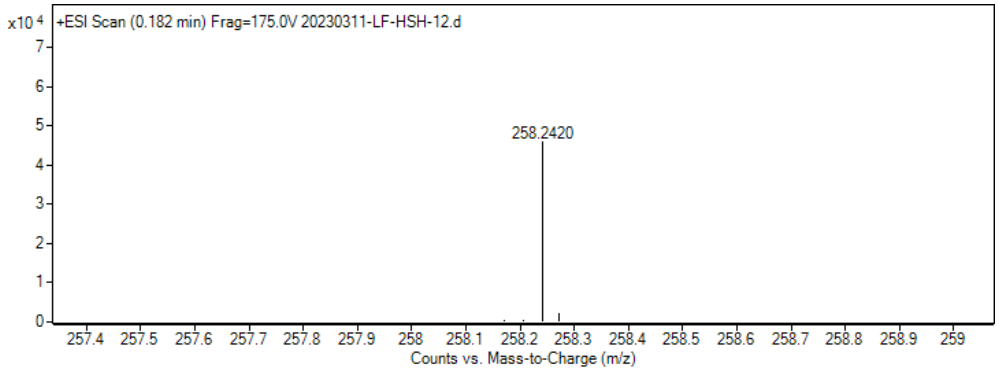
addition of CH_2Cl_2 (25 mL). The mixture was degassed and refilled with N_2 gas, and then irradiated with blue LEDs (22 W) at room temperature for 6 h. The solvent was removed under vaccum and the residue was purified by column chromatography on silica gel using PE/EA (30:1) as eluent to afford **3a** (386 mg) in 67% yield.



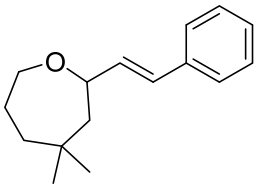
1a 2a 5

Control experiment: In a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with **1a** (78.0 mg, 0.20 mmol), **2a** (39.0 mg, 0.30 mmol), *fac*-Ir(PPy)$_3$ (2.6 mg, 0.004 mmol, 2 mol%), and TEMPO (62.4 mg, 0.40 mmol), followed by the addition of CH_2Cl_2 (2.0 mL). The mixture was degassed and refilled with N_2 gas, and then irradiated with blue LEDs (22 W) at room temperature for 2.5 h. TEMPO-trapped product **5** was determined by HRMS.

HRMS (ESI) of 5: calcd for $C_{15}H_{31}NO_2$ $[M + H]^+$: 258.2428, found: 258.2420.



6. Characterization of the products



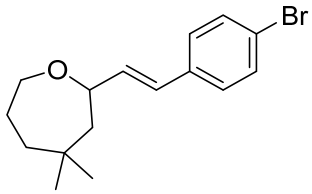
(*E*)-4,4-Dimethyl-2-styryloxepane (3a):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (36 mg, 78% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 6.54 (dd, *J* = 15.9, 1.5 Hz, 1H),

6.20 (dd, *J* = 15.9, 5.5 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.87 (ddd, *J* = 12.2, 8.3, 4.1 Hz, 1H), 3.73 (ddd, *J* = 12.1, 5.7, 4.3 Hz, 1H), 1.85 – 1.66 (m, 3H), 1.62 – 1.50 (m, 3H), 1.08 (s, 3H), 1.00 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 137.2, 132.0, 128.49, 128.47, 127.3, 126.4, 75.4, 68.1, 48.9, 40.8, 33.1, 32.9, 26.6, 26.6.

IR (KBr): *v* (cm^{-1}) 2951, 1371, 1242, 747, 693.

HRMS (ESI) calcd for $C_{16}H_{23}O$ $[M + H]^+$: 231.1743, found: 231.1734.

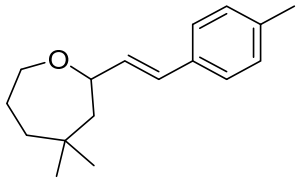


(*E*)-2-(4-Bromostyryl)-4,4-dimethyloxepane (3b):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a yellow solid (42 mg, 68% yield); m.p. 115 – 120 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.38 (m, 2H), 7.25 – 7.19 (m, 2H), 6.47 (dd, *J* = 15.9, 1.6 Hz, 1H), 6.18 (dd, *J* = 15.9, 5.4 Hz, 1H), 4.26 – 4.17 (m, 1H), 3.86 (ddd, *J* = 12.3, 8.2, 4.2 Hz, 1H), 3.71 (ddd, *J* = 12.1, 5.7, 4.2 Hz, 1H), 1.85 – 1.62 (m, 3H), 1.61 – 1.48 (m, 3H), 1.06 (s, 3H), 0.99 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 136.2, 132.9, 131.6, 127.9, 127.3, 121.0, 75.2, 68.2, 48.8, 40.7, 33.1, 32.9, 26.6, 26.5.

IR (KBr): *v* (cm^{-1}) 2953, 1463, 1184, 845, 800.

HRMS (ESI) calcd for $C_{16}H_{21}{}^{79}BrONa$ $[M + Na]^+$: 331.0668, found: 331.0659.



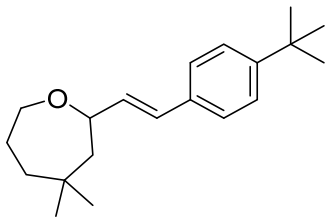
(*E*)-4,4-Dimethyl-2-(4-methylstyryl)oxepane (3c):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (36 mg, 74% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.22 (m, 2H), 7.13 – 7.06 (m, 2H), 6.49 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.14 (dd, *J* = 15.9, 5.6 Hz, 1H), 4.26 – 4.17 (m, 1H), 3.86 (ddd, *J* = 12.3, 8.3, 4.1 Hz, 1H), 3.71 (ddd, *J* = 12.1, 5.7, 4.3 Hz, 1H), 2.32 (s, 3H), 1.84 – 1.62 (m, 3H), 1.60 – 1.46 (m, 3H), 1.06 (s,

3H), 0.99 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 137.0, 134.4, 131.0, 129.2, 128.4, 126.3, 75.5, 68.1, 49.0, 40.8, 33.1, 32.9, 26.6, 26.6, 21.2.

IR (KBr): *v* (cm^{-1}) 2953, 1470, 1180, 738, 699.

HRMS (ESI) calcd for $C_{17}H_{24}ONa$ $[M + Na]^+$: 267.1719, found: 267.1718.

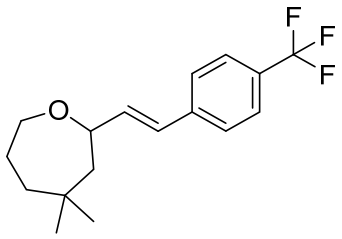


(*E*)-2-(4-(*tert*-Butyl)styryl)-4,4-dimethyloxepane (3d):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (42 mg, 73% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.27 (m, 4H), 6.51 (dd, *J* = 15.9, 1.5 Hz, 1H), 6.16 (dd, *J* = 15.9, 5.5 Hz, 1H), 4.28 – 4.19 (m, 1H), 3.86 (ddd, *J* = 12.3, 8.3, 4.1 Hz, 1H), 3.72 (ddd, *J* = 12.1, 5.7, 4.2 Hz, 1H), 1.85 – 1.65 (m, 3H), 1.63 – 1.50 (m, 3H), 1.32 (s, 9H), 1.07 (s, 3H), 1.00 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 150.3, 134.4, 131.3, 128.2, 126.1, 125.4, 75.5, 68.0, 48.9, 40.8, 34.5, 33.1, 32.9, 31.3, 26.64, 26.60.

IR (KBr): *v* (cm^{-1}) 2953, 1464, 1108, 738, 703.

HRMS (ESI) calcd for $C_{20}H_{31}O$ $[M + H]^+$: 287.2369, found: 287.2360.



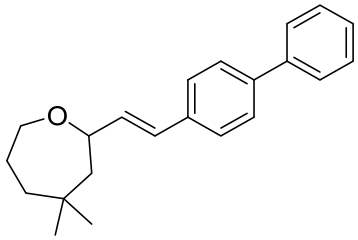
(*E*)-4,4-Dimethyl-2-(4-(trifluoromethyl)styryl)oxepane (3e):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (38 mg, 63% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 16.0, 5.2 Hz, 1H), 4.30 – 4.21 (m, 1H), 3.88 (ddd, *J* = 12.3, 8.2, 4.2 Hz, 1H), 3.73 (ddd, *J* = 12.2, 4.9, 4.9 Hz, 1H), 1.85 – 1.64 (m, 3H), 1.64 – 1.50 (m, 3H), 1.07 (s, 3H), 1.00 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 140.8, 134.8, 129.0 (q, *J* = 32.2 Hz), 127.1,

126.5, 125.4 (q, J = 3.9 Hz), 124.3 (q, J = 272.0 Hz), 75.1, 68.2, 48.8, 40.7, 33.1, 32.8, 26.6, 26.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.44 (s, 3F).

IR (KBr): v (cm^{-1}) 2949, 1460, 1178, 745, 724.

HRMS (ESI) calcd for $C_{17}H_{21}F_3ONa$ $[M + Na]^+$: 321.1437, found: 321.1430.

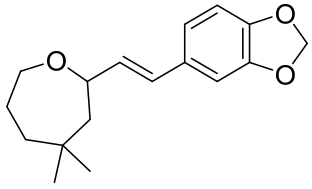


(*E*)-2-(2-([1,1'-Biphenyl]-4-yl)vinyl)-4,4-dimethyloxepane (3f):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a yellow solid (35 mg, 57% yield); m.p. 120 – 125 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, J = 7.7 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 15.8 Hz, 1H), 6.25 (dd, J = 15.9, 5.5 Hz, 1H), 4.31 – 4.22 (m, 1H), 3.89 (ddd, J = 12.4, 8.1, 4.1 Hz, 1H), 3.74 (dt, J = 11.2, 5.0 Hz, 1H), 1.85 – 1.66 (m, 3H), 1.64 – 1.51 (m, 3H), 1.09 (s, 3H), 1.01 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 140.8, 140.0, 136.3, 132.2, 128.8, 128.0, 127.23, 127.19, 126.9, 126.8, 75.4, 68.1, 48.9, 40.8, 33.2, 32.9, 26.64, 26.62.

IR (KBr): v (cm^{-1}) 2953, 1488, 1116, 723, 692.

HRMS (ESI) calcd for $C_{22}H_{27}O$ $[M + H]^+$: 307.2056, found: 307.2047.



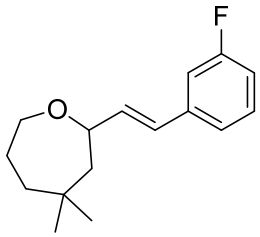
(*E*)-5-(2-(4,4-Dimethyloxepan-2-yl)vinyl)benzo[d][1,3]dioxole (3g):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (43 mg, 78% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.90 (d, J = 1.7 Hz, 1H), 6.79 (dd, J = 8.0, 1.7 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.44 (dd, J = 15.9, 1.5 Hz, 1H), 6.02 (dd, J = 15.9, 5.6 Hz, 1H), 5.93 (s, 2H), 4.24 – 4.15 (m, 1H), 3.85 (ddd, J = 12.2, 8.2, 4.2 Hz, 1H), 3.70 (ddd, J = 12.1, 5.7, 4.3 Hz, 1H), 1.83 – 1.61 (m, 3H), 1.59 – 1.48 (m, 3H), 1.06 (s, 3H), 0.99 (s, 3H); **^{13}C{1H} NMR (101**

MHz, $CDCl_3$) δ 147.9, 146.9, 131.7, 130.3, 128.2, 120.9, 108.2, 105.7, 101.0, 75.4, 68.1, 49.0, 40.7, 33.1, 32.9, 26.7, 26.6.

IR (KBr): *v* (cm^{-1}) 2949, 1492, 1191, 795, 738.

HRMS (ESI) calcd for $C_{17}H_{22}O_3Na$ $[M + Na]^+$: 275.1642, found: 275.1644.

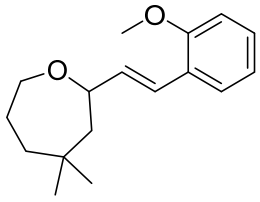


(*E*)-2-(3-Fluorostyryl)-4,4-dimethyloxepane (3h):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (34 mg, 69% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.19 (m, 1H), 7.10 (d, *J* = 7.8, 1H), 7.05 (dt, *J* = 10.3, 2.1 Hz, 1H), 6.89 (td, *J* = 8.3, 2.3 Hz, 1H), 6.50 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.18 (dd, *J* = 15.9, 5.3 Hz, 1H), 4.27 – 4.17 (m, 1H), 3.85 (ddd, *J* = 12.2, 8.2, 4.1 Hz, 1H), 3.71 (ddd, *J* = 12.1, 5.7, 4.3 Hz, 1H), 1.85 – 1.62 (m, 3H), 1.60 – 1.48 (m, 3H), 1.06 (s, 3H), 0.99 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 163.1 (d, *J* = 244.9 Hz), 139.7 (d, *J* = 7.6 Hz), 133.5, 129.9 (d, *J* = 8.4 Hz), 127.4 (d, *J* = 2.6 Hz), 122.3 (d, *J* = 2.7 Hz), 114.0 (d, *J* = 21.4 Hz), 112.8 (d, *J* = 21.6 Hz), 75.1, 68.1, 48.8, 40.7, 33.1, 32.9, 26.6, 26.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.81 (s, 1F).

IR (KBr): *v* (cm^{-1}) 2953, 1463, 1103, 751, 701.

HRMS (ESI) calcd for $C_{16}H_{21}FONa$ $[M + Na]^+$: 271.1469, found: 271.1473.



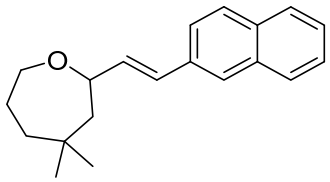
(*E*)-2-(2-Methoxystyryl)-4,4-dimethyloxepane (3i):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (39 mg, 75% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.20 (td, *J* = 7.8, 1.7 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.87 – 6.80 (m, 2H), 6.23 (dd, *J* = 16.0, 5.9 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.88 (td, *J* = 8.1, 4.0 Hz,

1H), 3.84 (s, 3H), 3.72 (dt, *J* = 12.1, 4.9 Hz, 1H), 1.86 – 1.64 (m, 3H), 1.64 – 1.56 (m, 2H), 1.55 – 1.45 (m, 2H), 1.07 (s, 3H), 1.00 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 156.7, 132.6, 128.3, 126.8, 126.2, 123.4, 120.6, 110.8, 76.0, 68.0, 55.4, 49.0, 40.7, 33.1, 33.0, 26.7, 26.6.

IR (KBr): *v* (cm^{-1}) 2953, 1449, 1145, 783, 680.

HRMS (ESI) calcd for $C_{17}H_{24}O_2Na$ $[M + Na]^+$: 283.1669, found: 283.1671.

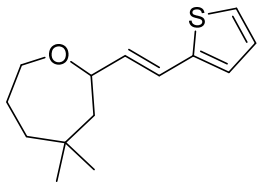


(*E*)-4,4-Dimethyl-2-(2-(naphthalen-2-yl)vinyl)oxepane (3j):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (32 mg, 57% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 – 8.14 (m, 1H), 7.87-7.83 (m, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.44 (t, 1H), 7.31 (dd, *J* = 15.6, 1.9 Hz, 1H), 6.23 (dd, *J* = 15.6, 5.3 Hz, 1H), 4.42 – 4.34 (m, 1H), 3.94 (ddd, *J* = 12.3, 8.4, 3.9 Hz, 1H), 3.80 (ddd, *J* = 12.1, 5.6, 4.2 Hz, 1H), 1.92 – 1.63 (m, 4H), 1.59 – 1.53 (m, 2H), 1.13 (s, 3H), 1.04 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 135.3, 135.1, 133.6, 131.3, 128.5, 127.6, 125.9, 125.7, 125.6, 125.6, 124.0, 123.7, 75.5, 68.0, 48.9, 40.9, 33.2, 33.0, 26.7, 26.6.

IR (KBr): *v* (cm^{-1}) 2951, 1464, 1119, 734, 703.

HRMS (ESI) calcd for $C_{20}H_{25}O$ $[M + H]^+$: 281.1900, found: 281.1891.



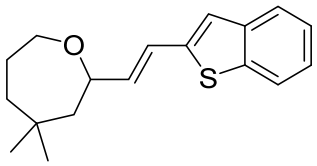
(*E*)-4,4-Dimethyl-2-(2-(thiophen-2-yl)vinyl)oxepane (3k):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (34 mg, 72% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.11 (d, *J* = 5.6 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.67 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.03 (dd, *J* = 15.7, 5.3 Hz, 1H), 4.24 – 4.16 (m, 1H), 3.85 (ddd, *J* = 12.3, 8.3, 4.1 Hz, 1H), 3.70 (ddd, *J* = 12.1, 5.6, 4.2 Hz, 1H), 1.83 – 1.61 (m, 3H), 1.60 – 1.47 (m, 3H), 1.06 (s, 3H), 0.99 (s,

3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 142.5, 131.8, 127.3, 125.3, 123.8, 121.8, 74.9, 68.0, 48.7, 40.8, 33.1, 32.9, 26.6, 26.5.

IR (KBr): *v* (cm^{-1}) 2948, 1467, 1180, 739, 693.

HRMS (ESI) calcd for $C_{14}H_{20}OSNa$ $[M + Na]^+$: 259.1127, found: 259.1119.

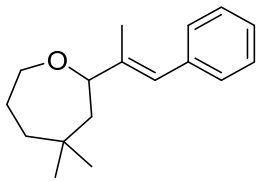


(*E*)-2-(2-(Benzo[b]thiophen-2-yl)vinyl)-4,4-dimethyloxepane (3l):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (37 mg, 65% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 – 7.72 (m, 1H), 7.68 – 7.64 (m, 1H), 7.32 – 7.24 (m, 2H), 7.11 (s, 1H), 6.78 (ddd, *J* = 15.7, 1.7, 0.7 Hz, 1H), 6.12 (dd, *J* = 15.6, 5.0 Hz, 1H), 4.30 – 4.21 (m, 1H), 3.88 (ddd, *J* = 12.3, 8.3, 4.1 Hz, 1H), 3.73 (ddd, *J* = 12.1, 5.6, 4.3 Hz, 1H), 1.85 – 1.65 (m, 3H), 1.63 – 1.50 (m, 3H), 1.07 (s, 3H), 1.01 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 142.6, 140.2, 138.8, 134.6, 124.4, 124.3, 123.3, 122.4, 122.3, 122.2, 74.8, 68.1, 48.6, 40.7, 33.1, 32.9, 26.6, 26.5.

IR (KBr): *v* (cm^{-1}) 2949, 1487, 1119, 1006, 759, 692.

HRMS (ESI) calcd for $C_{18}H_{23}OS$ $[M + H]^+$: 287.1464, found: 287.1459.

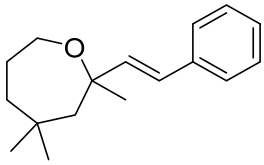


(*E*)-4,4-Dimethyl-2-(1-phenylprop-1-en-2-yl)oxepane (3m):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (33 mg, 67% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.25 (m, 4H), 7.23 – 7.12 (m, 1H), 6.48 (s, 1H), 4.00 (d, *J* = 10.0 Hz, 1H), 3.93 (ddd, *J* = 12.0, 7.4, 4.7 Hz, 1H), 3.72 (ddd, *J* = 12.0, 6.0, 4.3 Hz, 1H), 1.85 (s, 3H), 1.80 – 1.68 (m, 3H), 1.61 – 1.52 (m, 3H), 1.06 (s, 3H), 1.01 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 140.3, 138.0, 129.0, 128.0, 126.1, 123.8, 80.2, 69.5, 48.1, 40.4, 32.9, 32.7, 27.3, 26.3, 14.7.

IR (KBr): *v* (cm^{-1}) 2951, 1446, 1186, 751, 696.

HRMS (ESI) calcd for $C_{17}H_{25}O$ $[M + H]^+$: 245.1900, found: 245.1900.

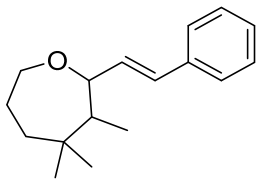


(*E*)-2,4,4-Trimethyl-2-styryloxepane (3n):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (29 mg, 60% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 16.2 Hz, 1H), 6.23 (d, *J* = 16.2 Hz, 1H), 3.77 – 3.69 (m, 1H), 3.68 – 3.60 (m, 1H), 1.85 (d, *J* = 15.0 Hz, 1H), 1.81 – 1.65 (m, 3H), 1.42 – 1.36 (m, 2H), 1.33 (s, 3H), 1.09 (s, 3H), 1.01 (s, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 138.8, 137.6, 128.5, 127.0, 126.3, 126.0, 77.6, 64.3, 51.0, 44.0, 34.9, 30.5, 29.6, 29.5, 28.3.

IR (KBr): *v* (cm^{-1}) 2946, 1447, 1096, 745, 690.

HRMS (ESI) calcd for $C_{17}H_{24}ONa$ $[M + Na]^+$: 267.1719, found: 267.1710.

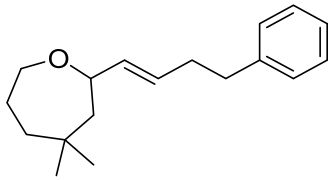


(*E*)-3,4,4-Trimethyl-2-styryloxepane (3o):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (6 mg, 13% yield, only one isomer). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.23 (dd, *J* = 15.8, 7.3 Hz, 1H), 3.82 – 3.73 (m, 2H), 3.67 (dt, *J* = 12.0, 5.0 Hz, 1H), 1.88 – 1.75 (m, 1H), 1.74 – 1.64 (m, 1H), 1.63 – 1.52 (m, 3H), 1.00 (s, 3H), 0.94 (s, 3H), 0.80 (d, *J* = 7.0 Hz, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 137.2, 131.0, 130.5, 128.5, 127.4, 126.4, 82.6, 67.1, 47.2, 41.1, 35.9, 31.5, 26.1, 21.2, 14.0.

IR (KBr): *v* (cm^{-1}) 2954, 1450, 1156, 748, 690.

HRMS (ESI) calcd for $C_{17}H_{24}ONa$ $[M + Na]^+$: 267.1719, found: 267.1710.

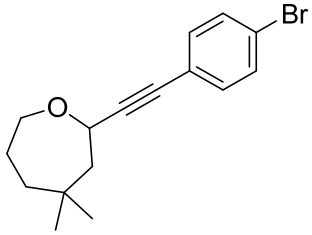


(*E*)-4,4-Dimethyl-2-(4-phenylbut-1-en-1-yl)oxepane (3p):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (9 mg, 18% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.31 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 5.64 (dtd, *J* = 15.4, 6.5, 1.2 Hz, 1H), 5.49 (ddt, *J* = 15.4, 5.9, 1.4 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.80 (ddd, *J* = 12.2, 8.1, 4.2 Hz, 1H), 3.64 (ddd, *J* = 12.1, 5.8, 4.2 Hz, 1H), 2.73 – 2.64 (m, 2H), 2.37 – 2.28 (m, 2H), 1.78 – 1.58 (m, 3H), 1.51 – 1.40 (m, 3H), 1.01 (s, 3H), 0.96 (s, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 142.0, 132.8, 129.0, 128.5, 128.3, 125.8, 75.5, 68.0, 49.0, 40.8, 35.7, 34.2, 33.0, 32.9, 26.7, 26.6.

IR (KBr): *v* (cm^{-1}) 2951, 1457, 1180, 742, 698.

HRMS (ESI) calcd for $C_{18}H_{26}ONa$ [M + Na]$^+$: 259.2056, found: 259.2047.



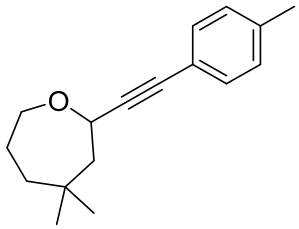
2-((4-Bromophenyl)ethynyl)-4,4-dimethyloxepane (3q):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a yellow solid (32 mg, 53% yield) m.p. 95 – 100 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.44 – 7.39 (m, 2H), 7.30 – 7.26 (m, 2H), 4.56 (dd, *J* = 10.5, 3.8 Hz, 1H), 3.87 (ddd, *J* = 12.5, 8.9, 3.7 Hz, 1H), 3.73 (ddd, *J* = 12.3, 5.3, 4.2 Hz, 1H), 1.97 (dd, *J* = 14.9, 10.4 Hz, 1H), 1.85 – 1.62 (m, 3H), 1.50 (dd, *J* = 7.5, 4.8 Hz, 2H), 1.05 (s, 3H), 1.01 (s, 3H);

^{13}C{1H} NMR (101 MHz, CDCl$_3$) δ 133.2, 131.5, 122.4, 122.0, 91.1, 83.1, 67.4, 66.2, 49.0, 41.0, 33.6, 32.7, 26.7, 25.9.

IR (KBr): *v* (cm^{-1}) 2956, 1484, 1384, 1070, 823.

HRMS (ESI) calcd for $C_{16}H_{20}{}^{79}BrO$ [M + H]$^+$: 307.0692, found: 307.0695.

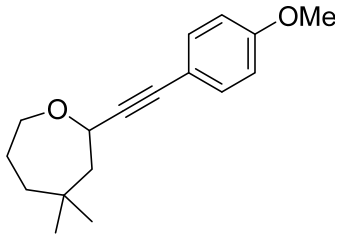


4,4-Dimethyl-2-(p-tolylethynyl)oxepane (3r):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (24 mg, 50% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.35 – 7.29 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.58 (dd, *J* = 10.4, 3.9 Hz, 1H), 3.89 (ddd, *J* = 12.4, 8.9, 3.7 Hz, 1H), 3.73 (ddd, *J* = 12.4, 5.3, 4.1 Hz, 1H), 2.33 (s, 3H), 1.99 (dd, *J* = 14.9, 10.4 Hz, 1H), 1.86 – 1.59 (m, 3H), 1.53 – 1.46 (m, 2H), 1.06 (s, 3H), 1.02 (s, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 138.2, 131.6, 129.0, 119.9, 89.2, 84.3, 67.3, 66.2, 49.2, 41.0, 33.6, 32.7, 26.7, 26.0, 21.5.

IR (KBr): *v* (cm^{-1}) 2960, 1473, 1368, 1118, 818.

HRMS (ESI) calcd for $C_{17}H_{23}O$ $[M + H]^+$: 243.1743, found: 243.1734.

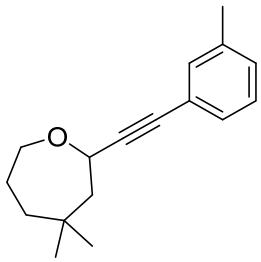


2-((4-Methoxyphenyl)ethynyl)-4,4-dimethyloxepane (3s):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (36 mg, 69% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 – 7.33 (m, 2H), 6.83 – 6.78 (m, 2H), 4.57 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.88 (ddd, *J* = 12.4, 8.8, 3.7 Hz, 1H), 3.79 (s, 3H), 3.72 (dt, *J* = 12.3, 4.6 Hz, 1H), 1.98 (dd, *J* = 14.9, 10.4 Hz, 1H), 1.86 – 1.61 (m, 3H), 1.52 – 1.46 (m, 2H), 1.05 (s, 3H), 1.01 (s, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 159.5, 133.1, 115.1, 113.8, 88.5, 84.0, 67.3, 66.3, 55.3, 49.2, 41.0, 33.5, 32.7, 26.7, 26.0.

IR (KBr): *v* (cm^{-1}) 2951, 1464, 1364, 1101, 830.

HRMS (ESI) calcd for $C_{17}H_{22}O_2Na$ $[M + Na]^+$: 281.1512, found: 281.1516.

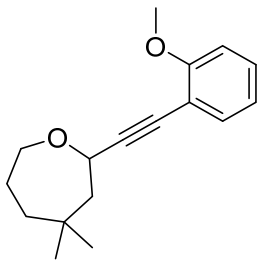


4,4-Dimethyl-2-(m-tolylethynyl)oxepane (3t):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (23 mg, 47% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.26 – 7.21 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 4.58 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.89 (ddd, *J* = 12.5, 8.9, 3.6 Hz, 1H), 3.73 (ddd, *J* = 12.4, 5.2, 4.1 Hz, 1H), 2.31 (s, 3H), 1.99 (dd, *J* = 14.9, 10.4 Hz, 1H), 1.86 – 1.63 (m, 3H), 1.53 – 1.47 (m, 2H), 1.06 (s, 3H), 1.02 (s, 3H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 137.8, 132.3, 129.0, 128.7, 128.1, 122.8, 89.6, 84.3, 67.2, 66.2, 49.1, 41.0, 33.6, 32.7, 26.8, 25.9, 21.2.

IR (KBr): *v* (cm^{-1}) 2921, 1454, 1104, 783, 690.

HRMS (EI) calcd for $C_{17}H_{22}O$ $[M]^+$: 242.1671, found: 242.1674.

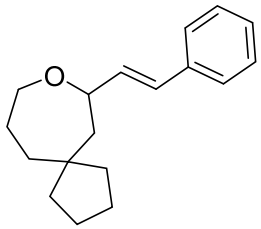


2-((2-Methoxyphenyl)ethynyl)-4,4-dimethyloxepane (3u):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20:1) to give a colorless oil (32 mg, 62% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.90 – 6.83 (m, 2H), 4.64 (dd, *J* = 10.3, 3.9 Hz, 1H), 3.94 – 3.87 (m, 1H), 3.86 (s, 3H), 3.74 (dt, *J* = 12.5, 4.7 Hz, 1H), 2.01 (dd, *J* = 14.9, 10.3 Hz, 1H), 1.88 – 1.65 (m, 3H), 1.54 – 1.47 (m, 2H), 1.06 (s, 3H), 1.02 (s, 3H). **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 160.0, 133.8, 129.6, 120.3, 112.2, 110.6, 94.0, 80.5, 67.2, 66.4, 55.8, 49.1, 40.9, 33.6, 32.7, 26.7, 26.0.

IR (KBr): *v* (cm^{-1}) 2921, 1455, 1102, 783, 690.

HRMS (EI) calcd for $C_{17}H_{22}O_2$ $[M]^+$: 258.1620, found: 258.1617.

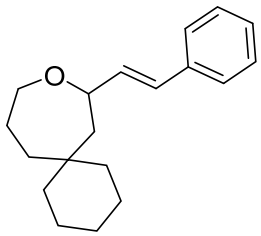


(*E*)-7-Styryl-8-oxaspiro[4.6]undecane (4a):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (33 mg, 63% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 6.54 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.21 (dd, *J* = 15.9, 5.5 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.87 (ddd, *J* = 12.1, 8.2, 4.7 Hz, 1H), 3.75 (dt, *J* = 12.1, 5.0 Hz, 1H), 1.85 – 1.54 (m, 12H), 1.52 – 1.43 (m, 2H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 137.2, 132.0, 128.52, 128.48, 127.3, 126.4, 76.0, 67.8, 47.6, 45.2, 42.4, 38.7, 35.9, 27.1, 24.4, 23.8.

IR (KBr): *v* (cm^{-1}) 2922, 1447, 1130, 739, 693.

HRMS (ESI) calcd for $C_{18}H_{25}O$ $[M + H]^+$: 257.1900, found: 257.1905.

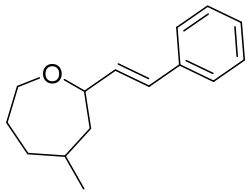


(*E*)-8-Styryl-9-oxaspiro[5.6]dodecane (4b):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (36 mg, 66% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 6.53 (dd, *J* = 16.0, 1.4 Hz, 1H), 6.22 (dd, *J* = 15.9, 5.5 Hz, 1H), 4.29 – 4.22 (m, 1H), 3.87 (ddd, *J* = 11.8, 7.8, 3.8 Hz, 1H), 3.68 (ddd, *J* = 12.2, 6.2, 3.9 Hz, 1H), 1.86 – 1.57 (m, 5H), 1.56 – 1.27 (m, 11H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 137.2, 132.2, 128.5, 128.4, 127.2, 126.4, 75.2, 68.0, 40.3, 35.3, 34.9, 26.5, 26.1, 22.1, 22.0.

IR (KBr): *v* (cm^{-1}) 2925, 1449, 1178, 736, 689.

HRMS (ESI) calcd for $C_{19}H_{26}ONa$ $[M + Na]^+$: 293.1876, found: 293.1878.

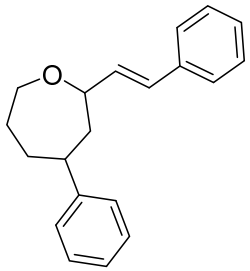


(*E*)-4-Methyl-2-styryloxepane (4c):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (25 mg, 57% yield); dr = 1:1.2; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.43 –7.36 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.60 (dd, *J* = 6.4, 1.5 Hz, 0.43H)/6.56 (dd, *J* = 6.5, 1.5 Hz, 0.55H), 6.26 (t, *J* = 5.8 Hz, 0.56H)/6.22 (t, *J* = 5.8 Hz, 0.45H), 4.34 (qd, *J* = 5.9, 1.5 Hz, 0.43H)/4.26 – 4.17 (m, 0.58H), 4.05 – 3.97 (m, 0.45H), 3.91 – 3.76 (m, 1.19H), 3.64 – 3.53 (m, 0.44H), 2.07 – 1.26 (m, 7H), 1.02 (d, *J* = 1.8 Hz, 1.49H)/1.01 (d, *J* = 2.1 Hz, 1.43H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 137.24, 137.21, 131.93, 131.74, 128.9, 128.7, 128.5, 127.31, 127.30, 126.43, 126.41, 78.0, 77.6, 69.4, 67.2, 45.2, 42.9, 36.2, 35.0, 33.6, 30.7, 29.8, 29.1, 24.0, 23.2.

IR (KBr): *v* (cm^{-1}) 2923, 1448, 1108, 741, 692.

HRMS (ESI) calcd for $C_{15}H_{20}ONa$ $[M + Na]^+$: 239.1406, found: 239.1399.

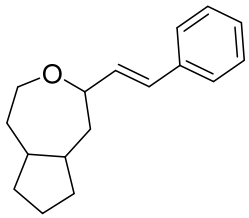


(*E*)-4-Phenyl-2-styryloxepane (4d):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (14 mg, 25% yield); dr = 1:1.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.15 (m, 4H), 6.66 – 6.55 (m, 1H), 6.30 – 6.21 (m, 1H), 4.54 – 4.44 (m, 0.39H)/4.39 – 4.29 (m, 0.65H), 4.13 (ddt, *J* = 12.7, 4.2, 2.1 Hz, 0.40H), 3.99 – 3.87 (m, 1.38H), 3.72 – 3.63 (m, 0.39H), 3.12 – 3.03 (m, 0.38H)/2.96 – 2.84 (m, 0.65H), 2.33 – 1.76 (m, 6H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 148.8, 148.3, 137.11, 137.06, 131.4, 131.2, 129.4, 129.1, 128.52, 128.51, 128.49, 127.38, 127.36, 126.64, 126.62, 126.44, 126.40, 126.0, 125.9, 78.0, 77.8, 69.8, 66.9, 45.4, 44.6, 43.0, 41.0, 36.1, 34.6, 31.7, 29.5.

IR (KBr): *v* (cm^{-1}) 2924, 1447, 1130, 745, 694.

HRMS (ESI) calcd for $C_{20}H_{23}O$ $[M + H]^+$: 279.1743, found: 279.1734.

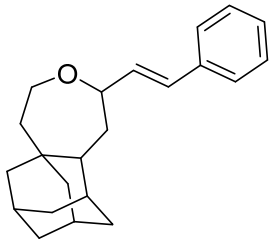


(*E*)-2-styryloctahydro-2H-cyclopenta[d]oxepine (4e):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (30 mg, 62% yield); dr = 1:6:10; **^{1}H NMR (400 MHz, $CDCl_3$)** 7.42 – 7.35 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 6.60 – 6.52 (m, 1H), 6.29 – 6.21 (m, 1H), 4.30 (qd, *J* = 6.5, 1.5 Hz, 0.34H)/4.22 – 4.15 (m, 0.61H), 4.13 (ddd, *J* = 12.4, 4.3, 2.1 Hz, 0.37H)/3.92 (ddd, *J* = 12.3, 8.1, 5.6 Hz, 0.64H), 3.82 – 3.74 (m, 0.63H)/3.50 (td, *J* = 12.3, 2.1 Hz, 0.37H), 2.09 – 1.22 (m, 12H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 137.2, 132.0, 131.57, 128.82, 128.71, 128.49, 128.47, 127.30, 127.28, 126.40, 126.39, 80.0, 79.7, 70.9, 66.9, 46.6, 45.4, 45.3, 42.3, 41.3, 39.6, 37.7, 34.7, 34.4, 34.0, 33.9, 33.8, 23.8, 23.4.

IR (KBr): *v* (cm^{-1}) 2946, 1452, 1118, 748, 692.

HRMS (ESI) calcd for $C_{17}H_{22}ONa$ $[M + Na]^+$: 265.1563, found: 265.1554.



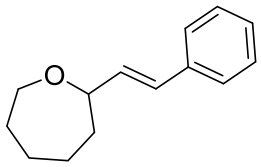
(*5aS,7R,9S,11R,11aS)*-2-((*E*)-styryl)decahydro-2H-5a,9:7,11-dimethanocycloocta[d]oxepine (4f):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (37 mg, 60% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 5.5 Hz, 1H), 4.37 – 4.27 (m, 1H), 3.84 – 3.74 (m, 1H), 3.71 – 3.62 (m, 1H), 2.20 – 1.99 (m, 2H), 1.95 – 1.67 (m, 8H), 1.64 – 1.41 (m, 6H), 1.35 – 1.17 (m, 2H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 137.2, 131.9, 128.7, 128.5, 127.3,

126.4, 78.3, 61.7, 47.2, 47.0, 45.8, 39.2, 38.8, 37.8, 37.6, 36.2, 33.8, 31.4, 28.8, 28.6.

IR (KBr): *v* (cm^{-1}) 2901, 1454, 1159, 748, 695.

HRMS (ESI) calcd for $C_{22}H_{28}ONa$ $[M + Na]^+$: 331.2032, found: 331.2024.

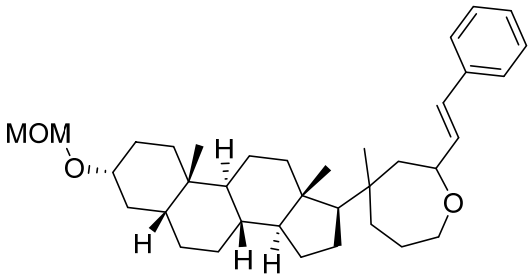


(*E*)-2-styryloxepane (4g):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30:1) to give a colorless oil (9 mg, 23% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** 1H NMR (400 MHz, CDCl3) δ 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 6.56 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.24 (dd, *J* = 16.0, 5.5 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.95 – 3.86 (m, 1H), 3.68 (ddd, *J* = 12.2, 7.3, 3.8 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.86 – 1.75 (m, 2H), 1.75 – 1.65 (m, 3H), 1.65 – 1.57 (m, 2H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 137.2, 131.8, 128.9, 128.5, 127.3, 126.4, 79.4, 67.9, 36.0, 31.2, 27.2, 25.4.

IR (KBr): *v* (cm^{-1}) 2925, 1447, 1131, 731, 693.

HRMS (ESI) calcd for $C_{14}H_{19}O^+$ $[M + H]^+$: 203.1430, found: 203.1421.



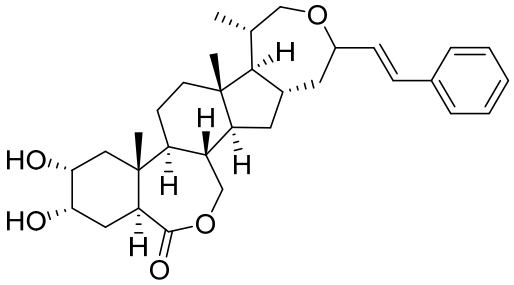
(*4R*)-4-((*3R,5R,8R,9S,10S,13S,14S,17R*)-3-(methoxymethoxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-4-methyl-2-((*E*)-styryl)oxepane (4h):

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) to give a colorless oil (34 mg, 32% yield); m.p. 90 – 95 ℃; dr = 1:1.4; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40 – 7.34 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.17 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.25 – 6.12 (m, 1H), 4.71 – 4.66 (m, 2H), 4.26 – 4.16 (m, 1H), 3.95 (dt, *J* = 12.0, 4.6 Hz, 0.43H), 3.88 – 3.79 (m, 0.62H), 3.74 – 3.65 (m, 0.64H), 3.62 – 3.47 (m, 1.59H), 3.37 (s, 3H), 2.10 – 1.99 (m, 1H), 1.98 – 1.57 (m,

13H), 1.44 – 1.20 (m, 12H), 1.15 – 1.00 (m, 4H), 0.98 – 0.74 (m, 8H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 137.2, 132.39, 132.36, 132.2, 128.5, 128.32, 128.27, 127.24, 126.39, 126.37, 94.6, 76.93, 76.90, 76.2, 74.8, 74.3, 69.8, 68.3, 68.2, 62.3, 62.0, 57.1, 56.7, 56.6, 55.2, 48.5, 47.9, 47.1, 44.2, 44.1, 44.0, 42.1, 41.5, 41.1, 40.44, 40.40, 40.4, 40.3, 39.72, 39.69, 39.65, 38.8, 38.4, 35.42, 35.38, 35.35, 35.3, 34.73, 34.71, 33.62, 33.59, 27.8, 27.3, 27.1, 26.6, 26.3, 26.2, 26.1, 26.0, 23.8, 23.71, 23.65, 23.44, 23.42, 23.2, 23.1, 23.0, 22.8, 20.79, 20.76, 14.94, 14.87, 14.6.

IR (KBr): *v* (cm^{-1}) 2922, 1447, 1146, 736, 693.

HRMS (ESI) calcd for $C_{36}H_{55}O_3$ $[M + H]^+$: 535.4146, found: 535.4137.



4i derived from Brassinosteroid:

Purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5:1) to give a colorless oil (34 mg, 48% yield); dr = 1:1.5; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.17 (m, 1H), 6.62 – 6.47 (m, 1H), 6.27 – 6.15 (m, 1H), 4.43 – 4.31 (m, 2H), 4.20 – 3.95 (m, 3.6H), 3.85 – 3.68 (m, 1H), 3.34 – 3.24 (m, 1H), 3.15 – 3.03 (m, 0.4H), 2.38 – 2.19 (m, 2H), 2.08 – 1.96 (m, 1H), 1.83 – 1.54 (m, 9H), 1.33 – 1.18 (m, 7H), 1.16 – 1.05 (m, 3H), 0.91 – 0.77 (m, 7H); **^{13}C{1H} NMR (151 MHz, $CDCl_3$)** δ 176.57, 176.53, 137.0, 131.5, 131.0, 129.5, 128.7, 128.49, 128.46, 127.4, 126.4, 107.60, 107.56, 82.7, 80.2, 79.8, 77.5, 73.08, 73.06, 72.5, 71.2, 71.1, 63.4, 61.5, 54.8, 54.7, 50.1, 49.9, 45.8, 45.6, 44.9, 43.0, 40.4, 40.3, 40.2, 39.7, 39.43, 39.37, 39.1, 37.7, 37.5, 37.0, 35.99, 35.97, 34.0, 33.6, 33.49, 33.46, 27.7, 26.63, 26.60, 23.6, 22.8, 21.0, 19.7, 15.6, 14.4, 12.7.

IR (KBr): *v* (cm^{-1}) 2933, 1448, 1175, 730, 694.

HRMS (ESI) calcd for $C_{32}H_{45}O_5$ $[M + H]^+$: 509.3262, found: 509.3266.

7. References

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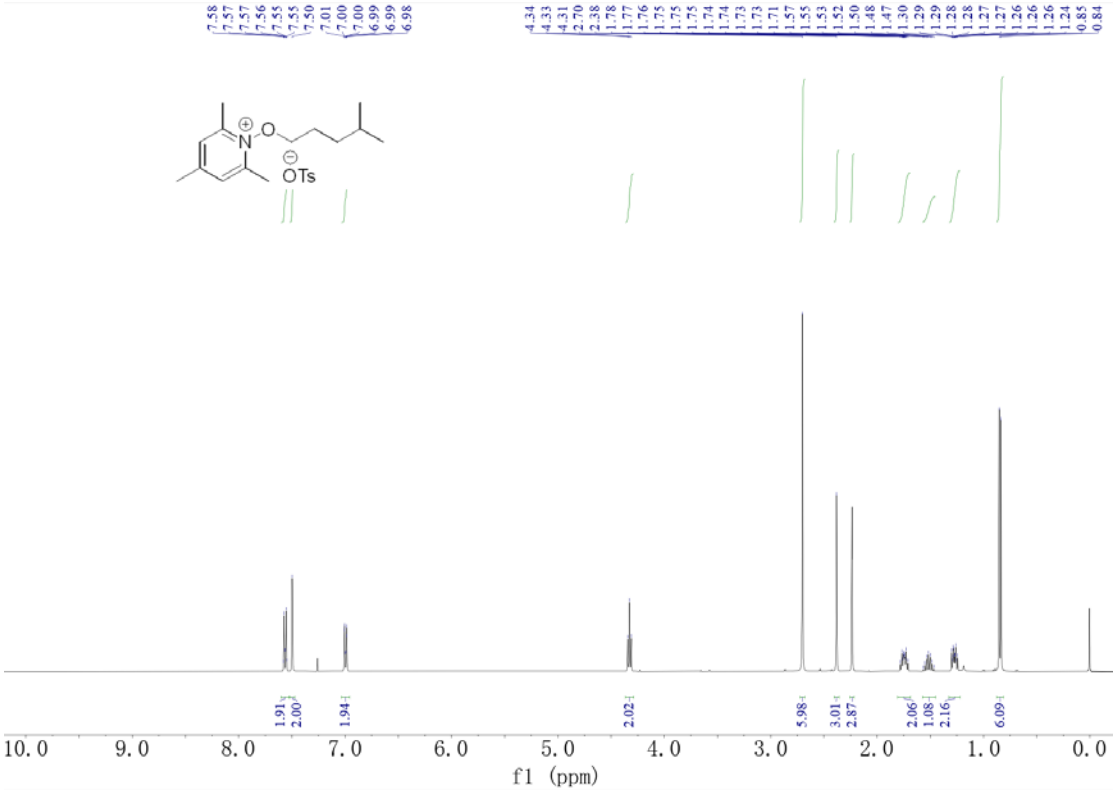
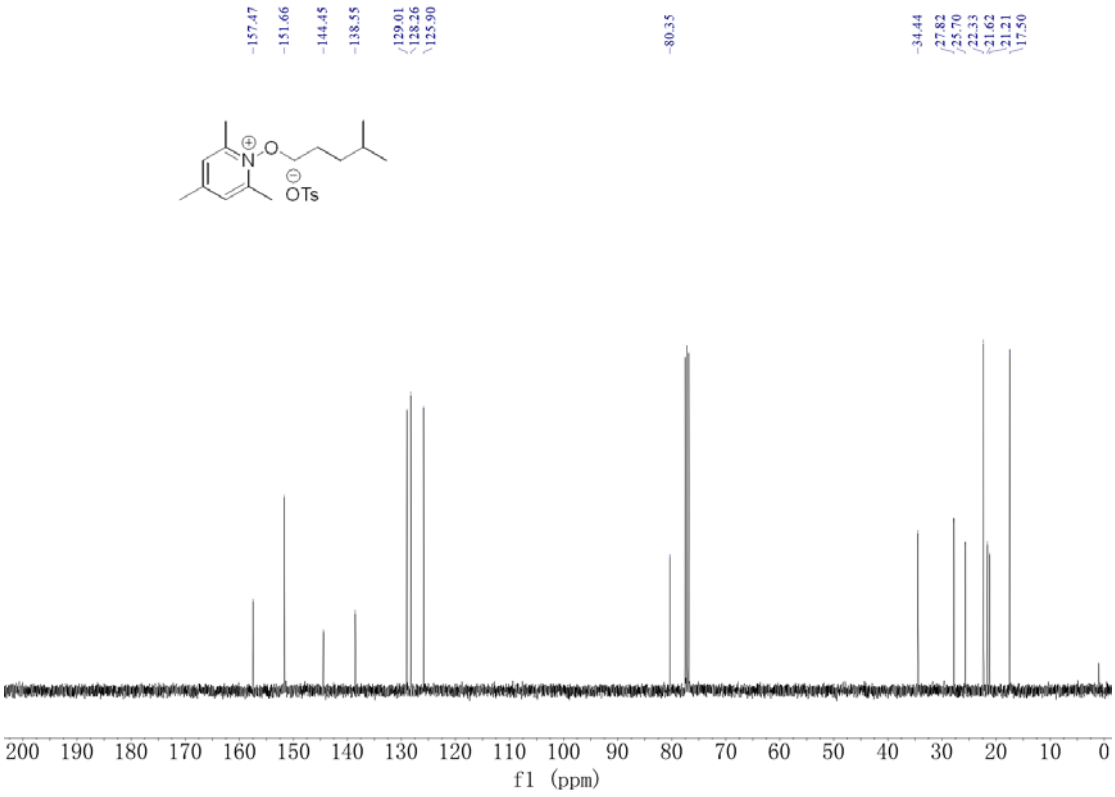
8. NMR spectra of the substrates and products

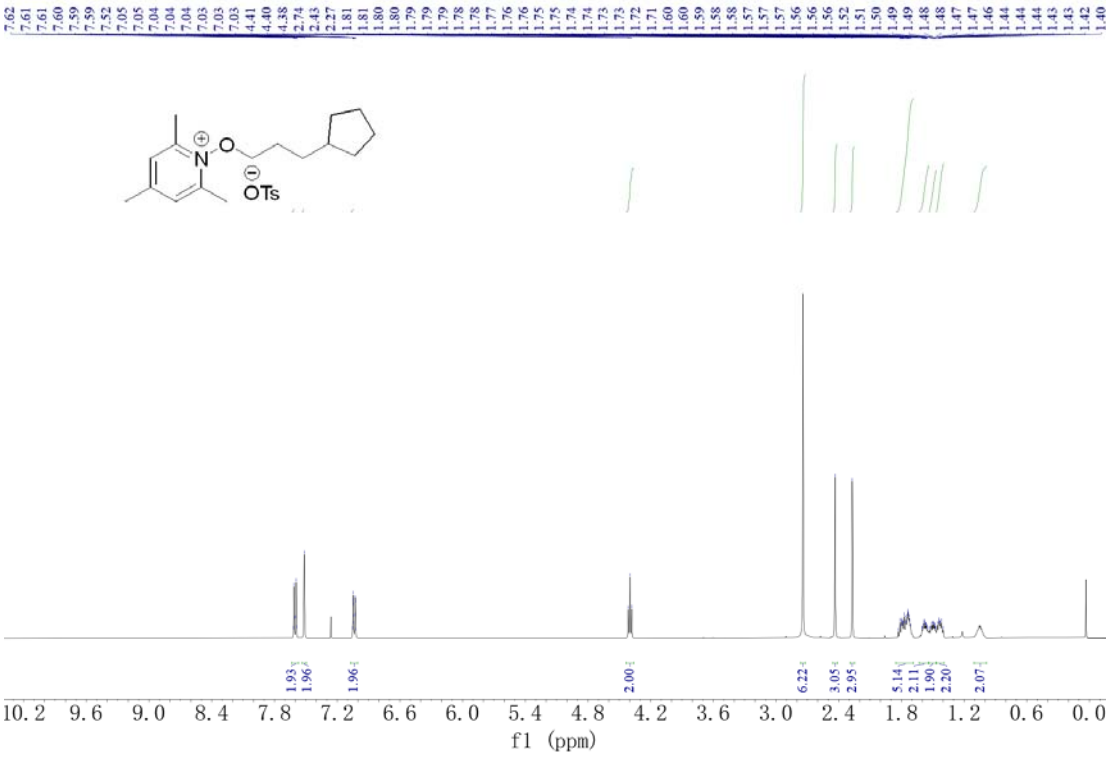
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



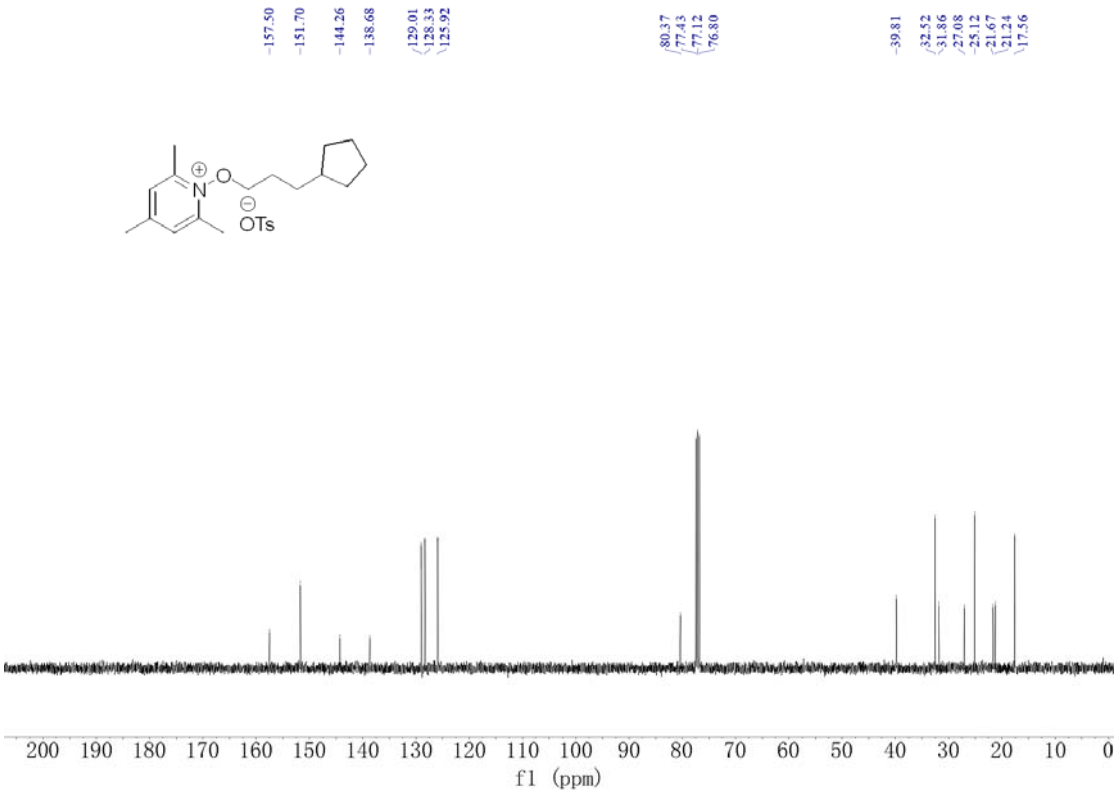
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1a**



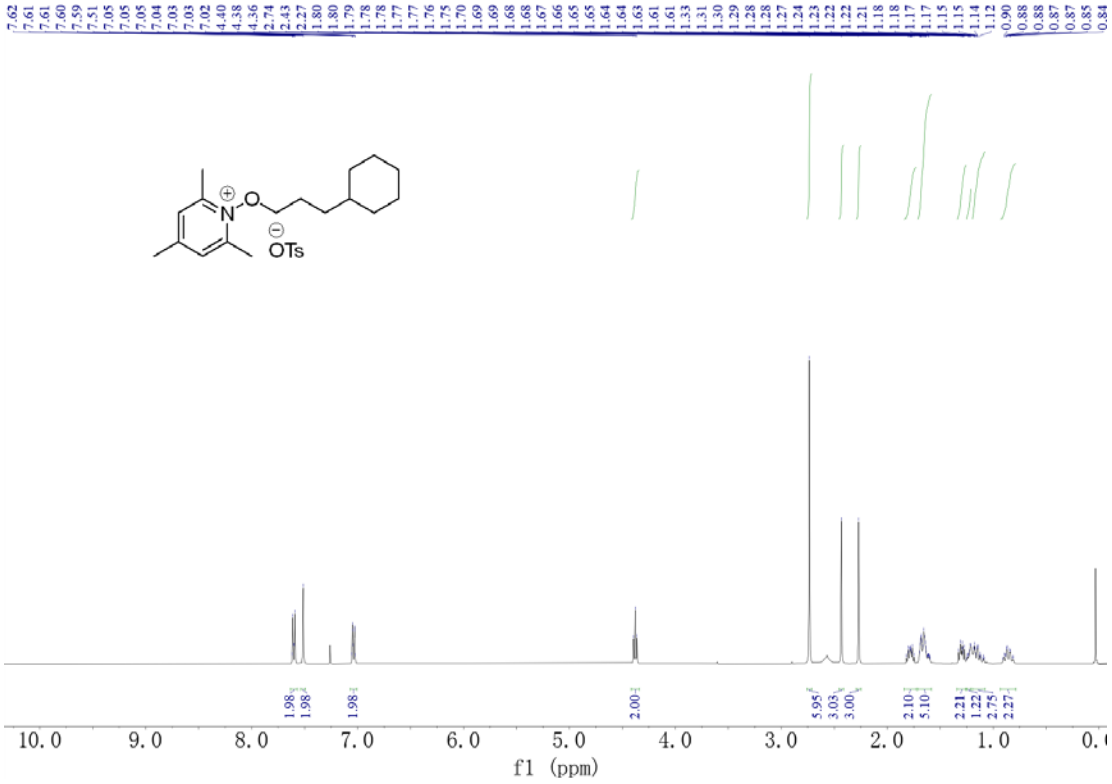
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



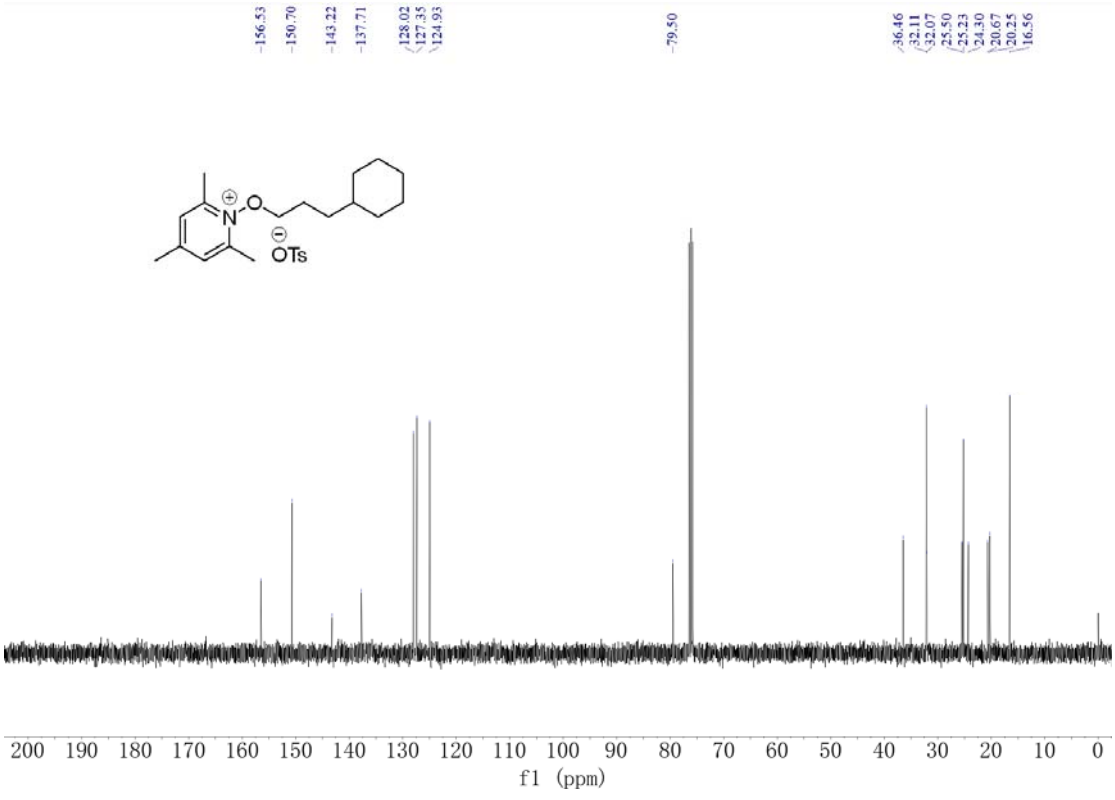
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1b**



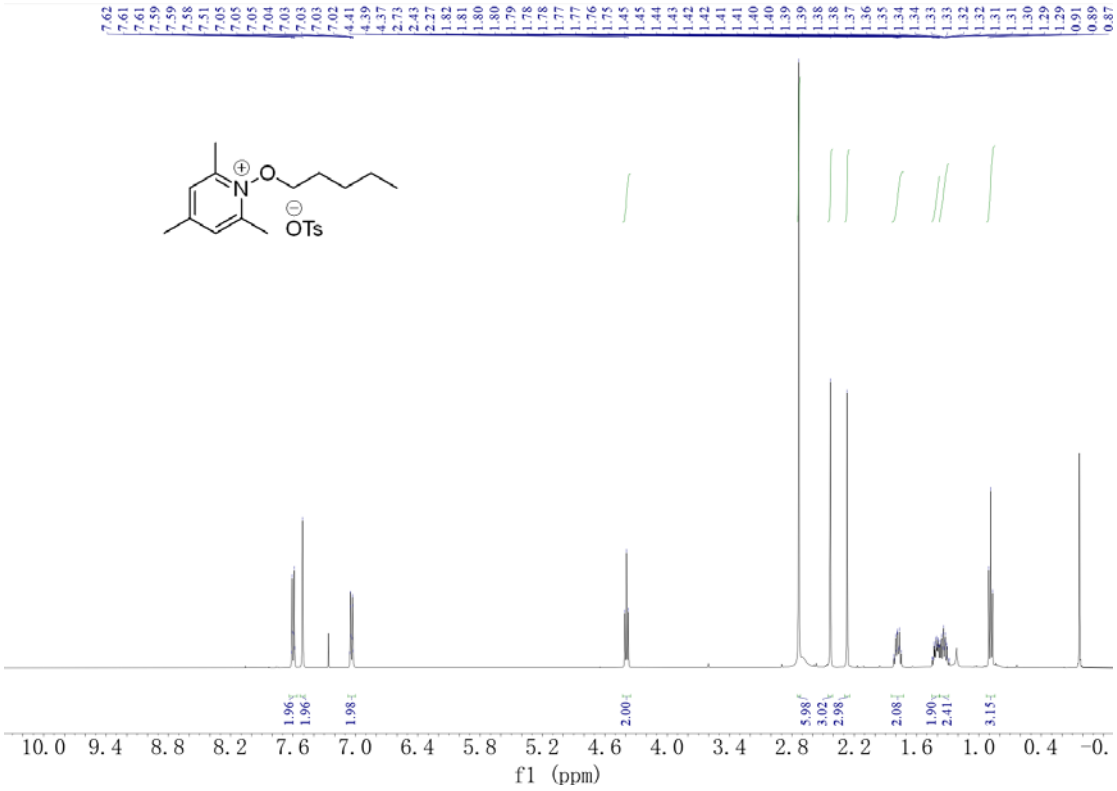
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



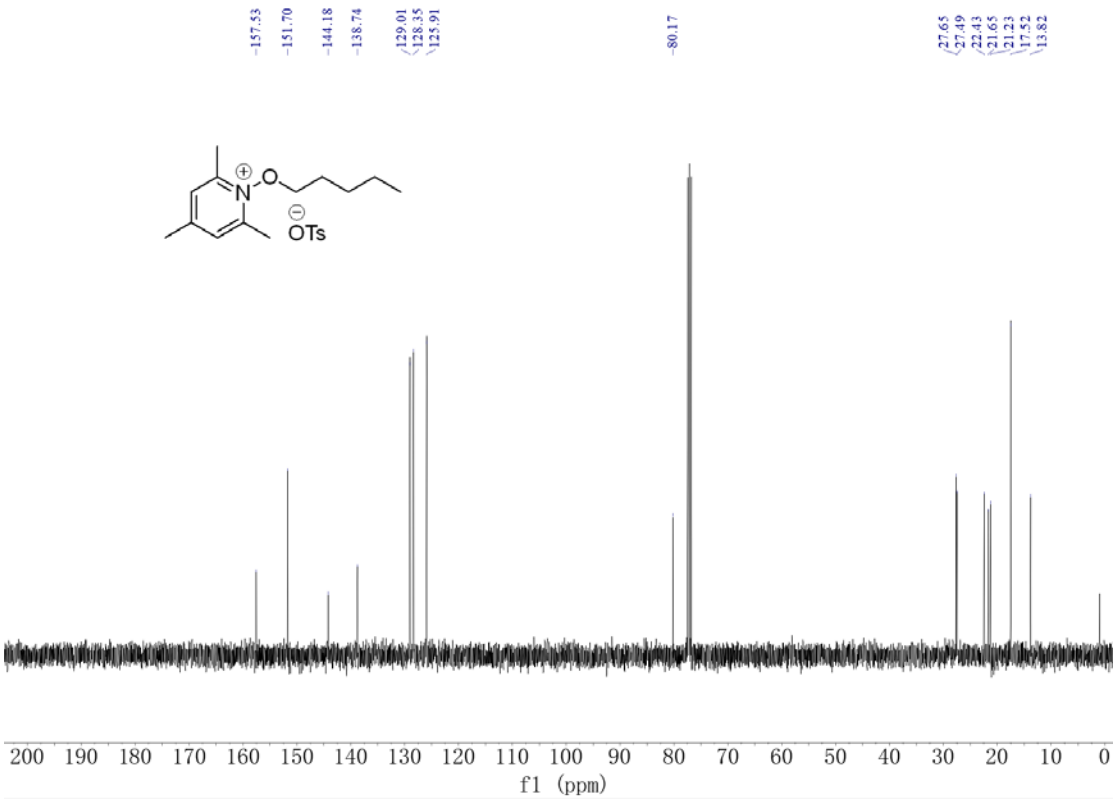
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1c**



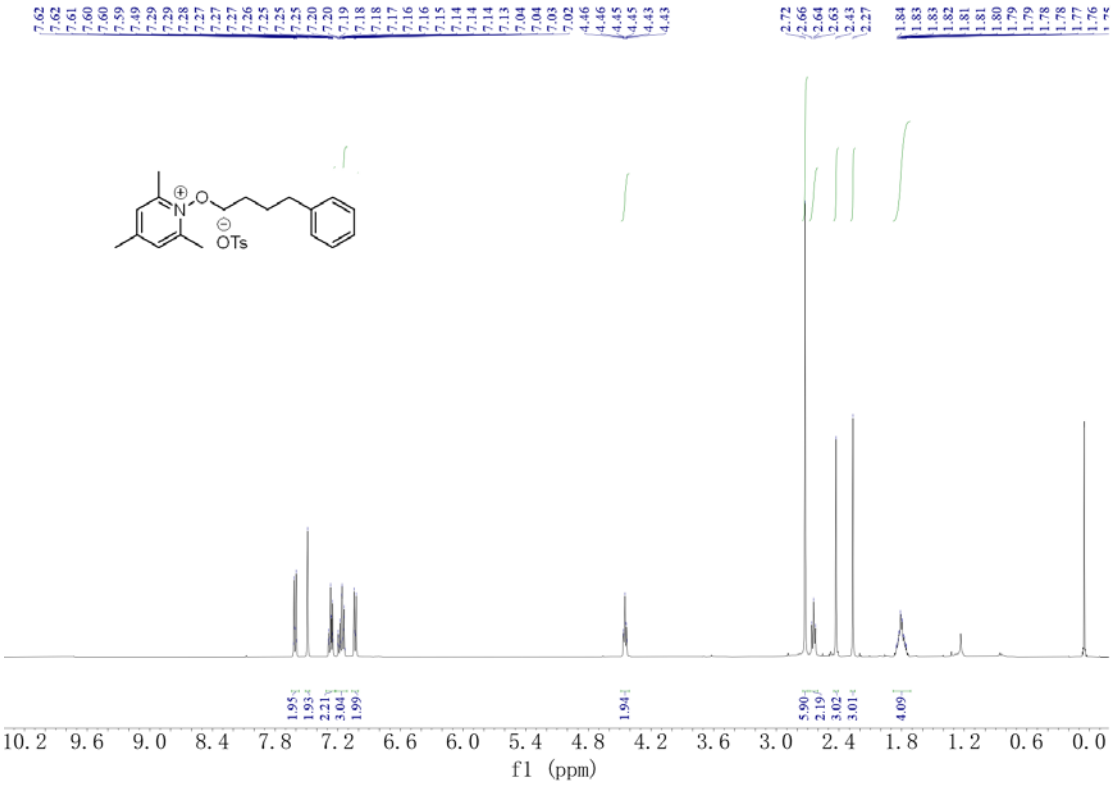
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



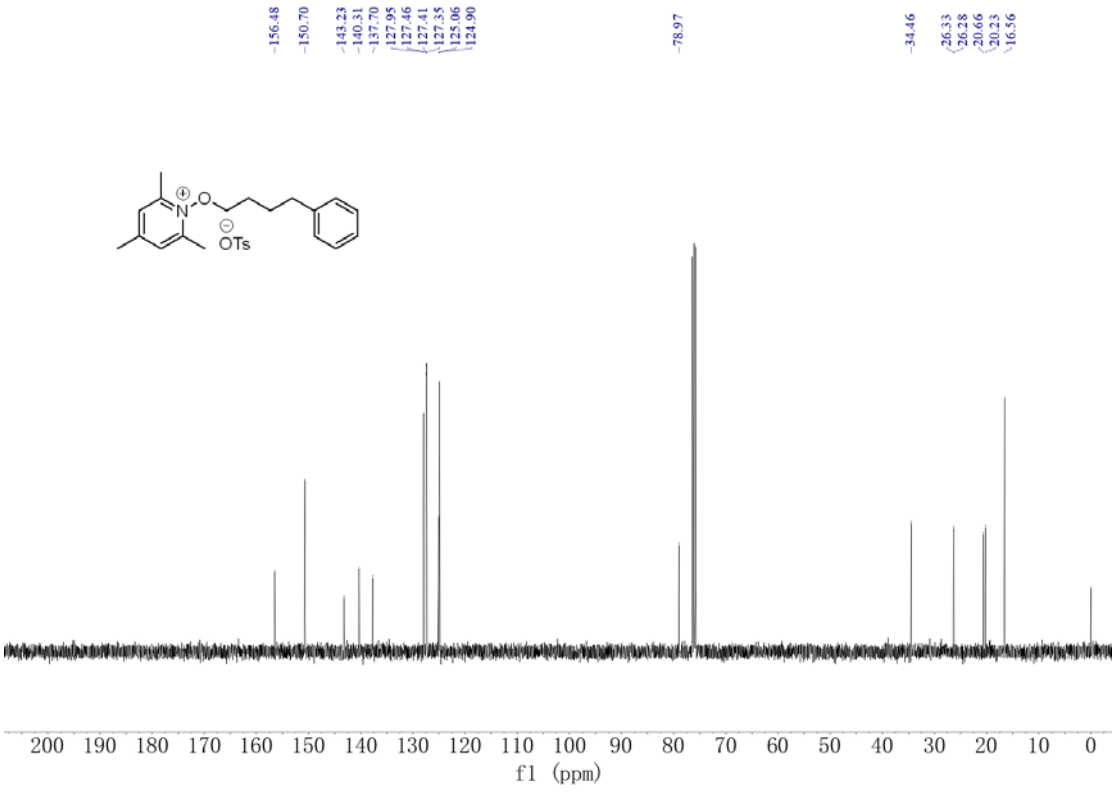
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1d**



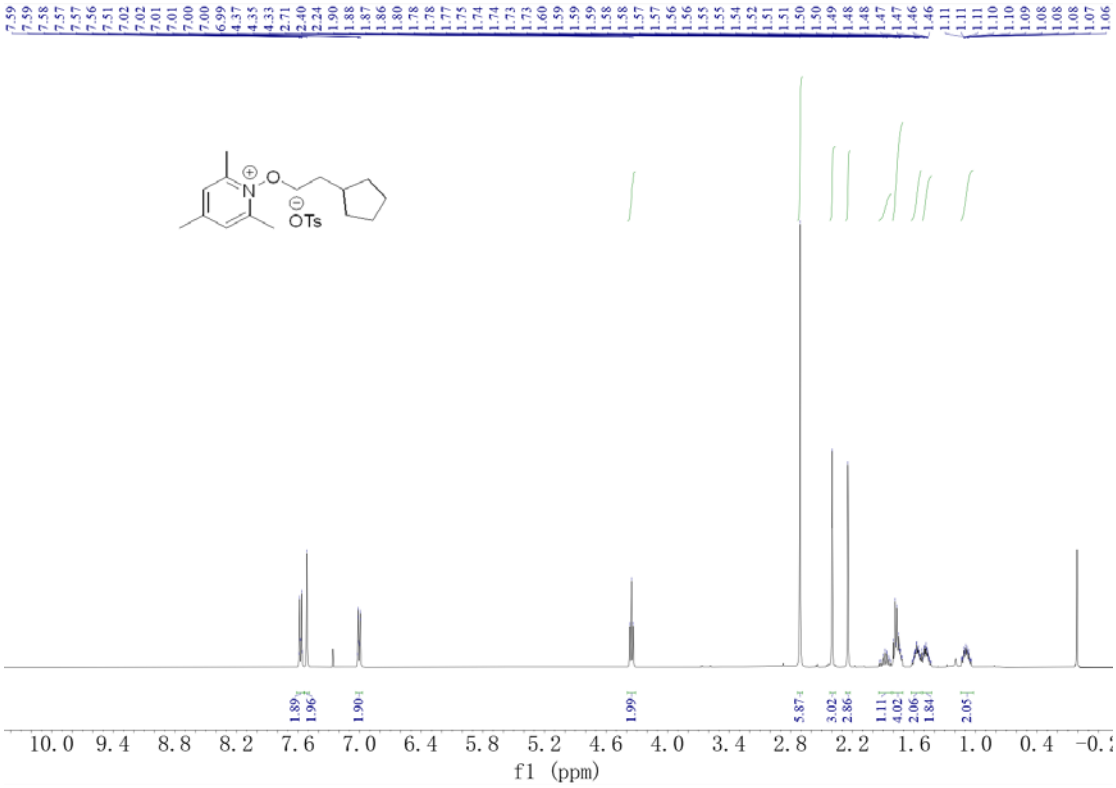
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



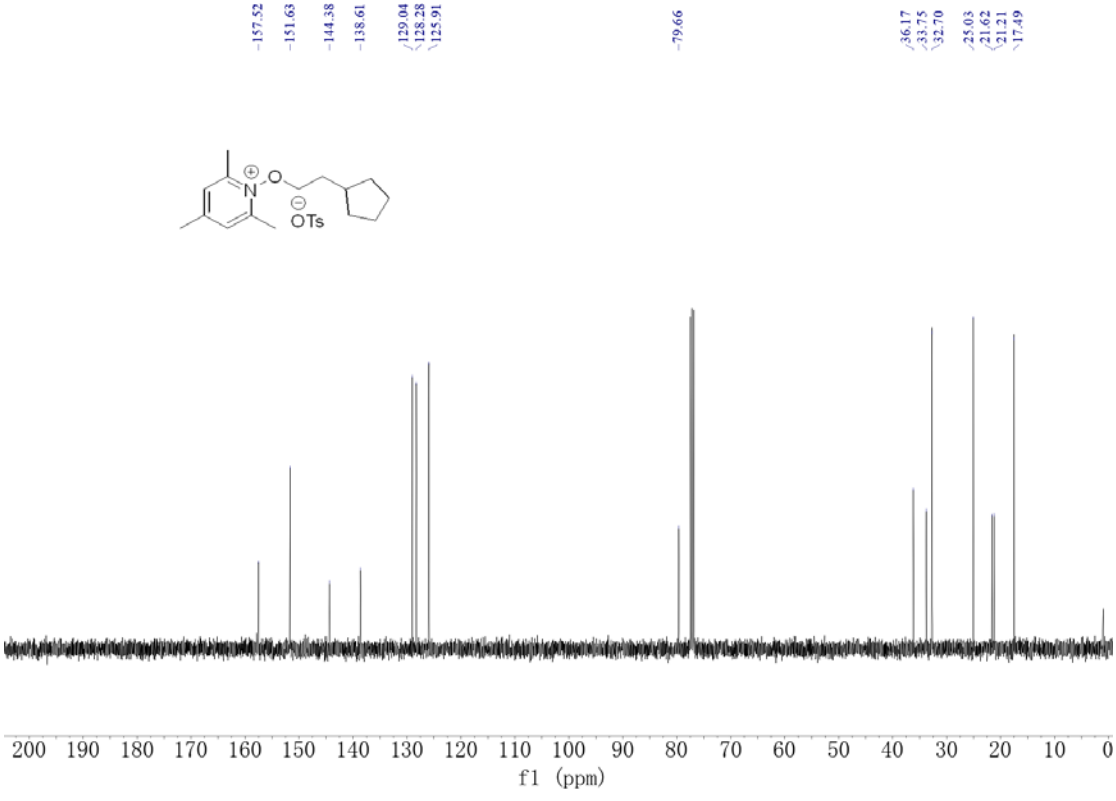
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1e**



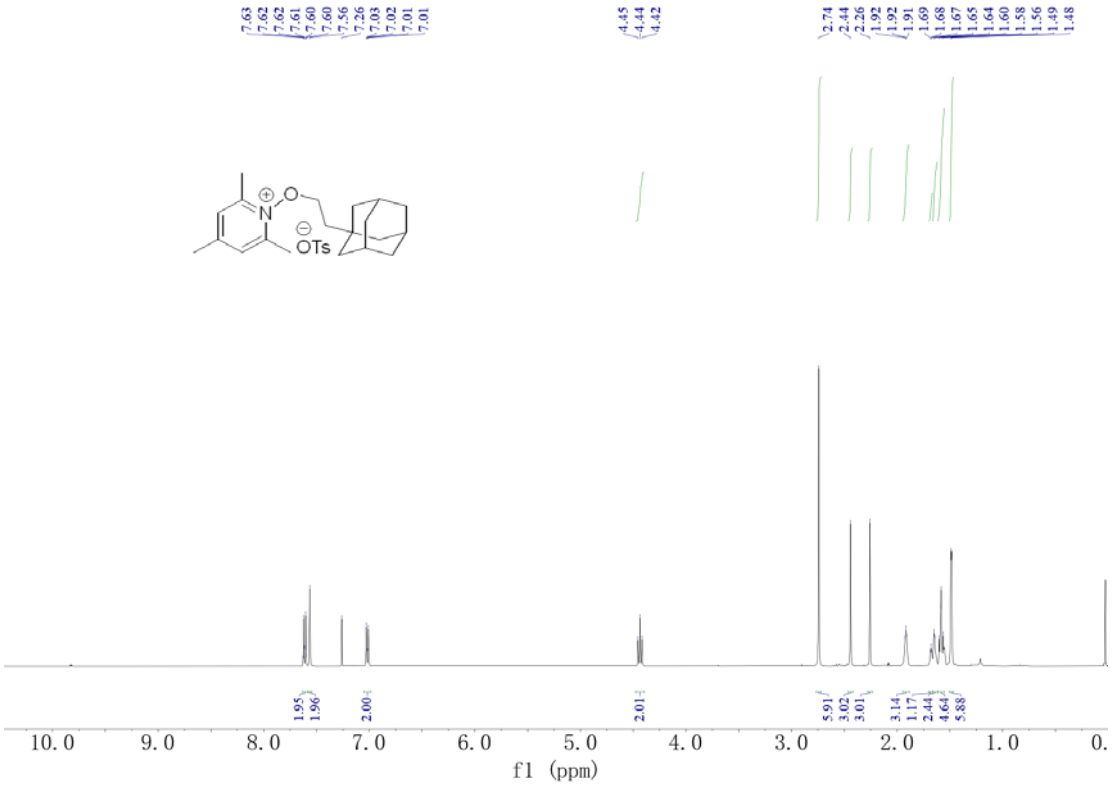
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



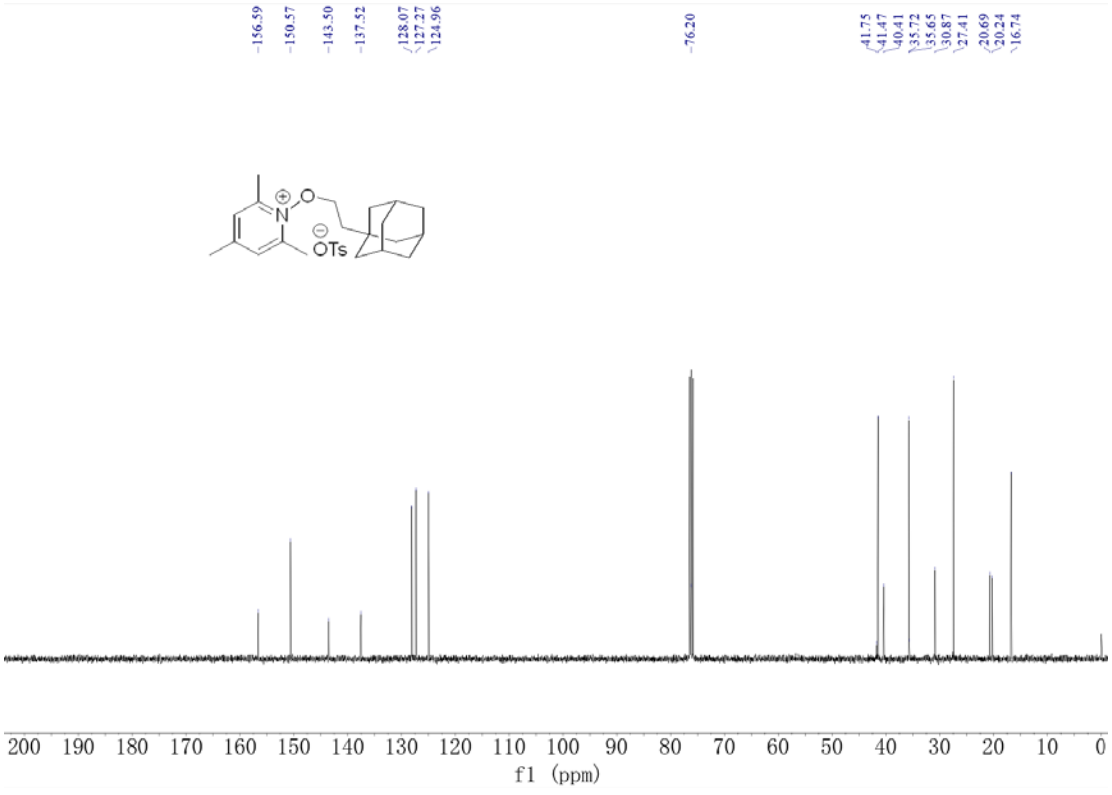
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1f**



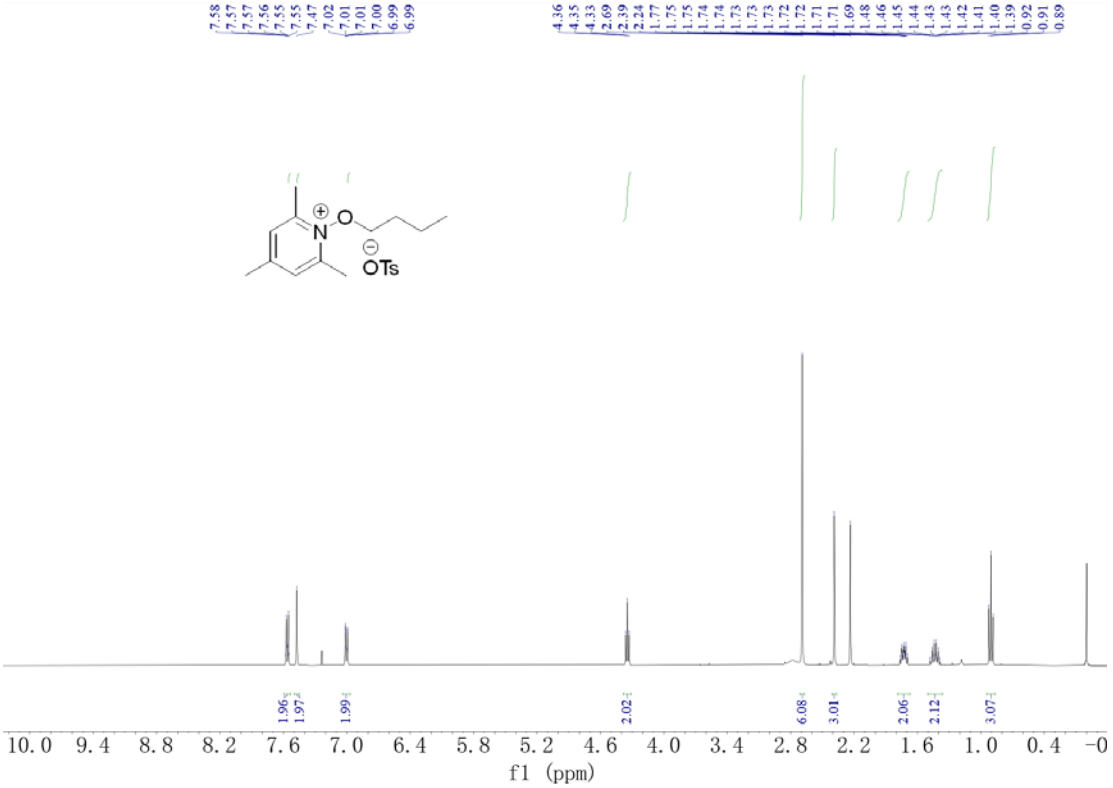
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



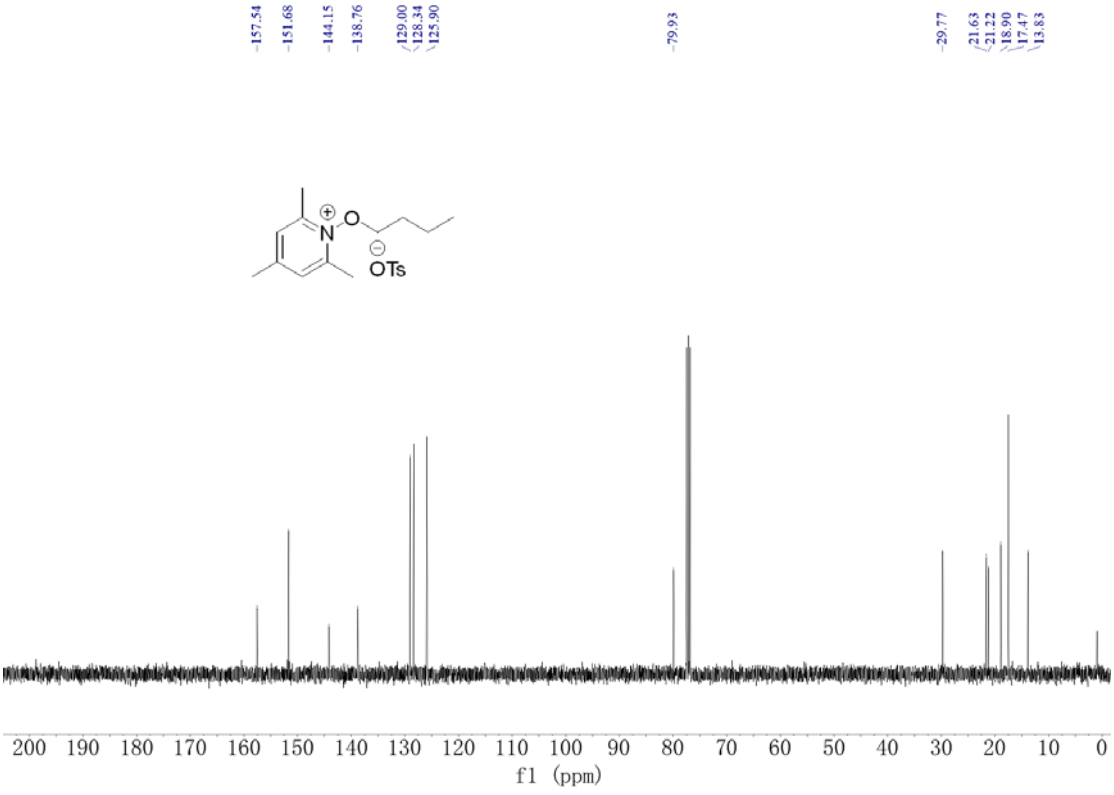
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1g**



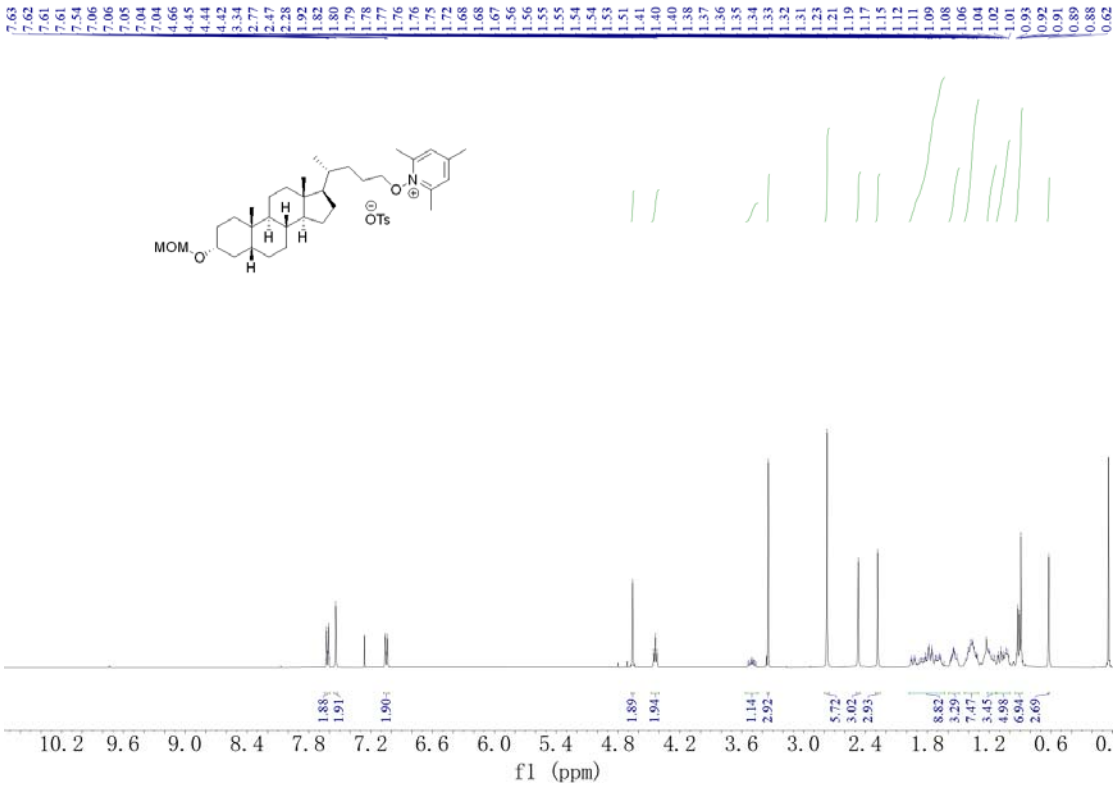
^{1}H NMR (400 MHz, $CDCl_3$) of **1h**



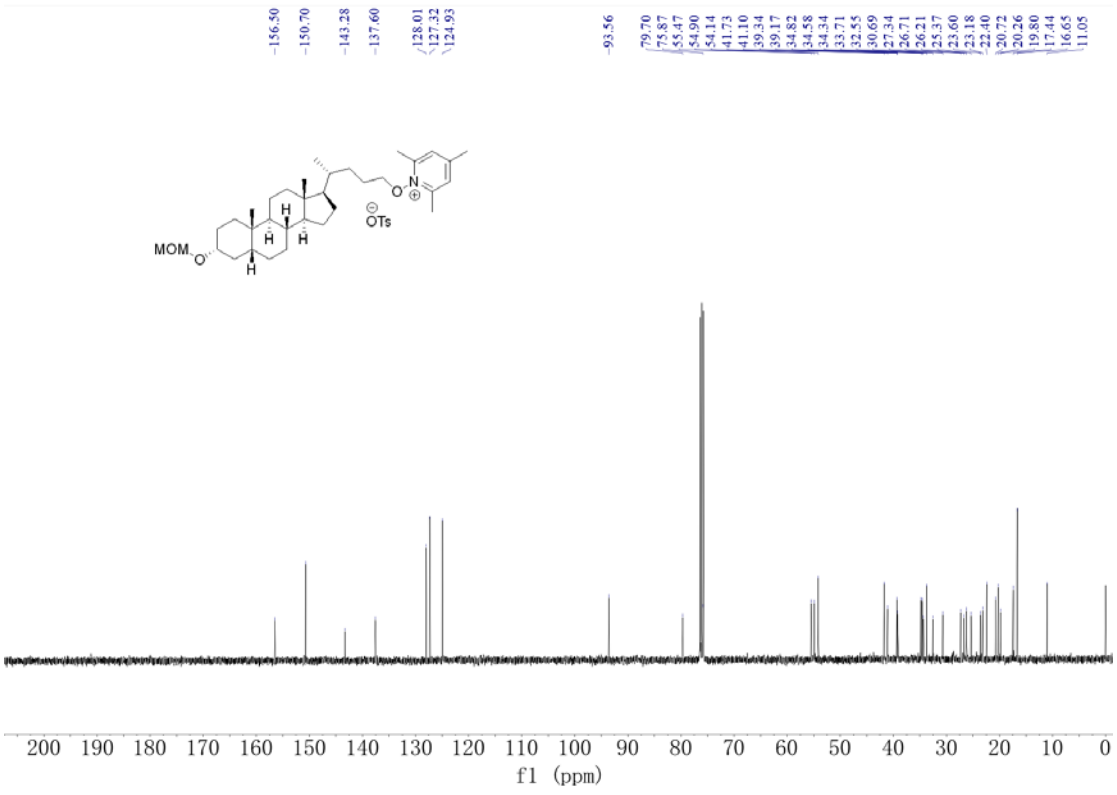
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1h**



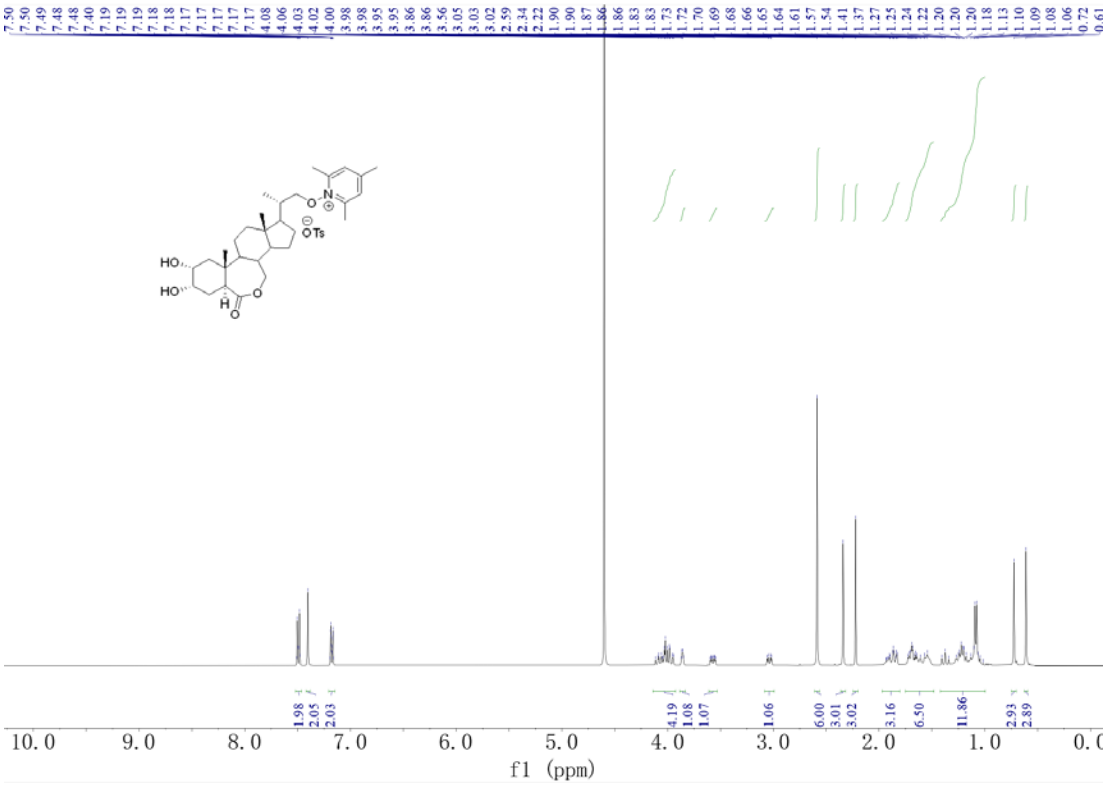
^{1}H NMR (400 MHz, $CDCl_3$) of **1i**



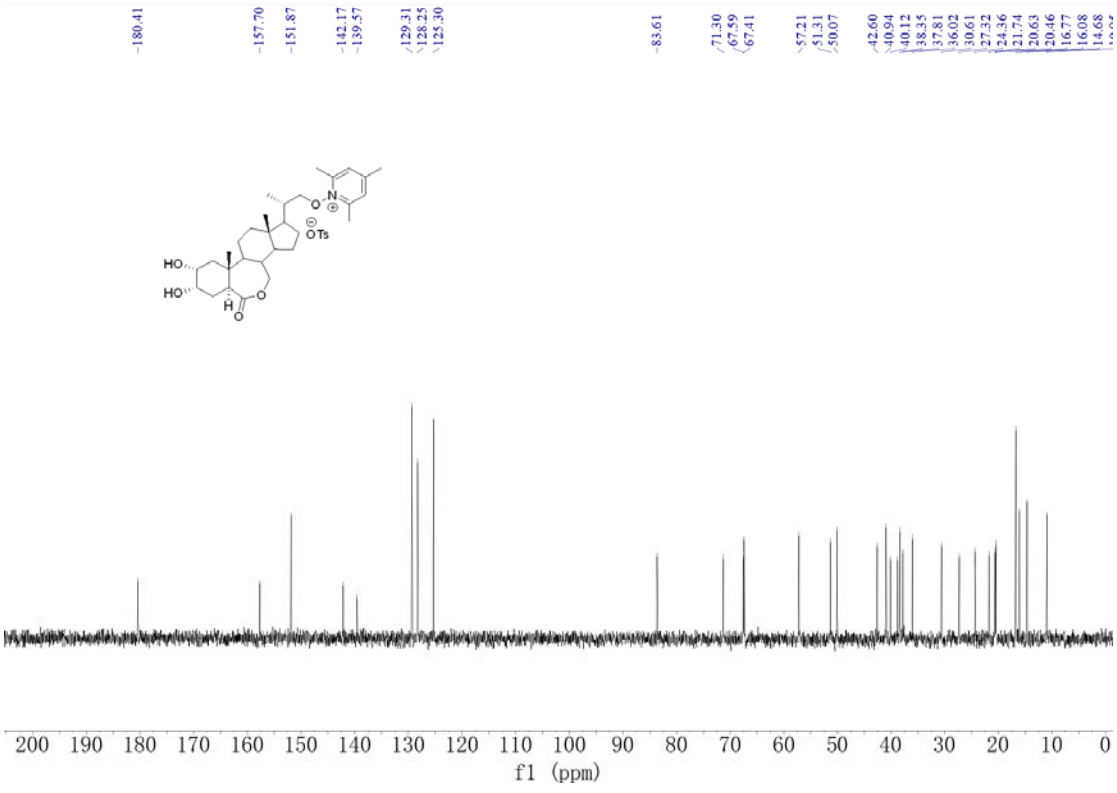
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **1i**



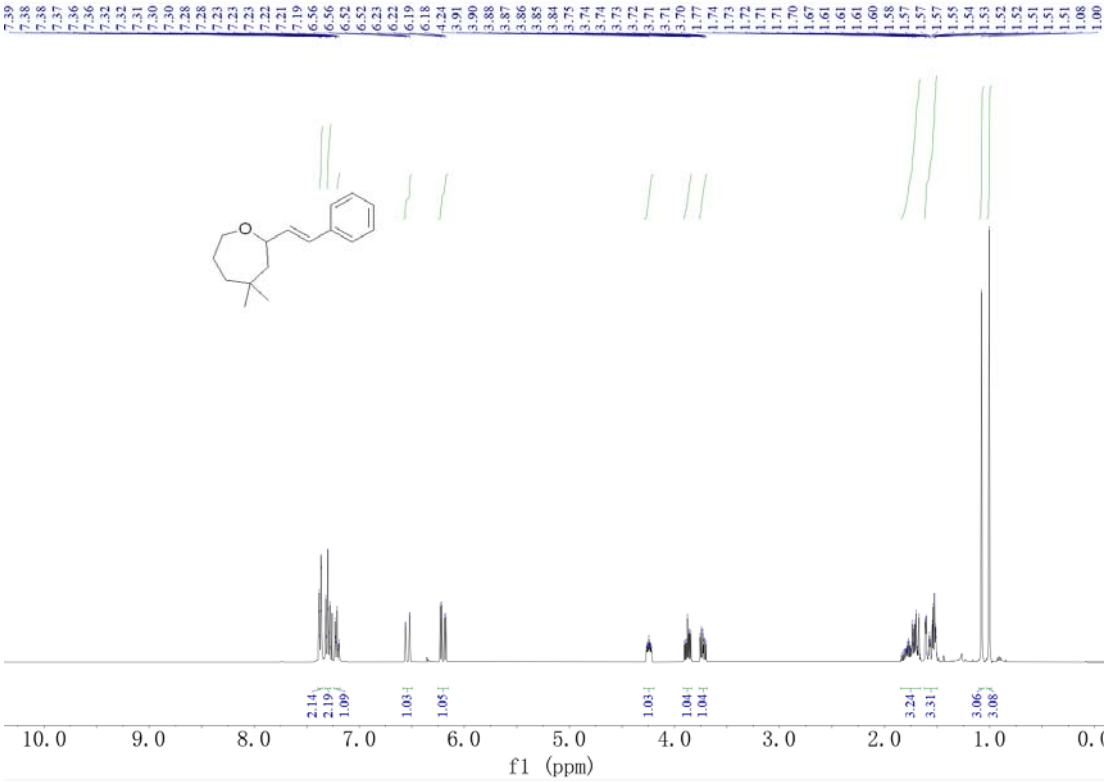
^{1}H NMR (400 MHz, D_2O) of **1j**



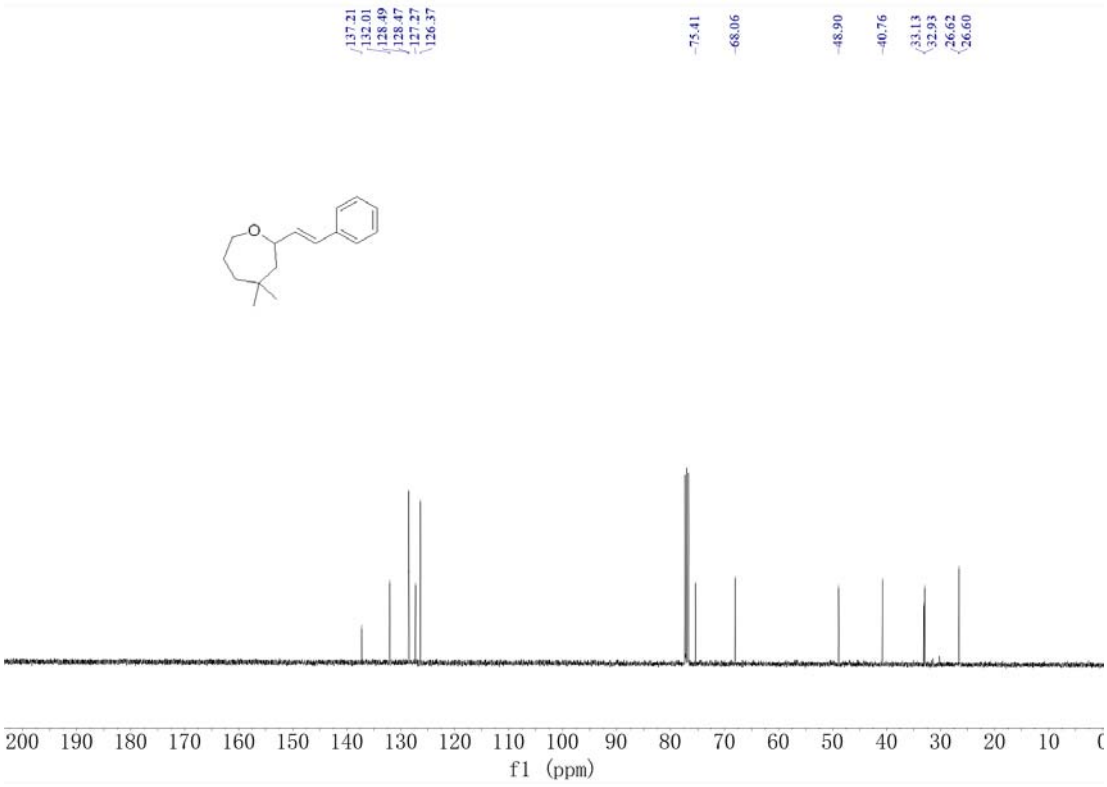
^{13}C NMR (151 MHz, D_2O) of **1j**



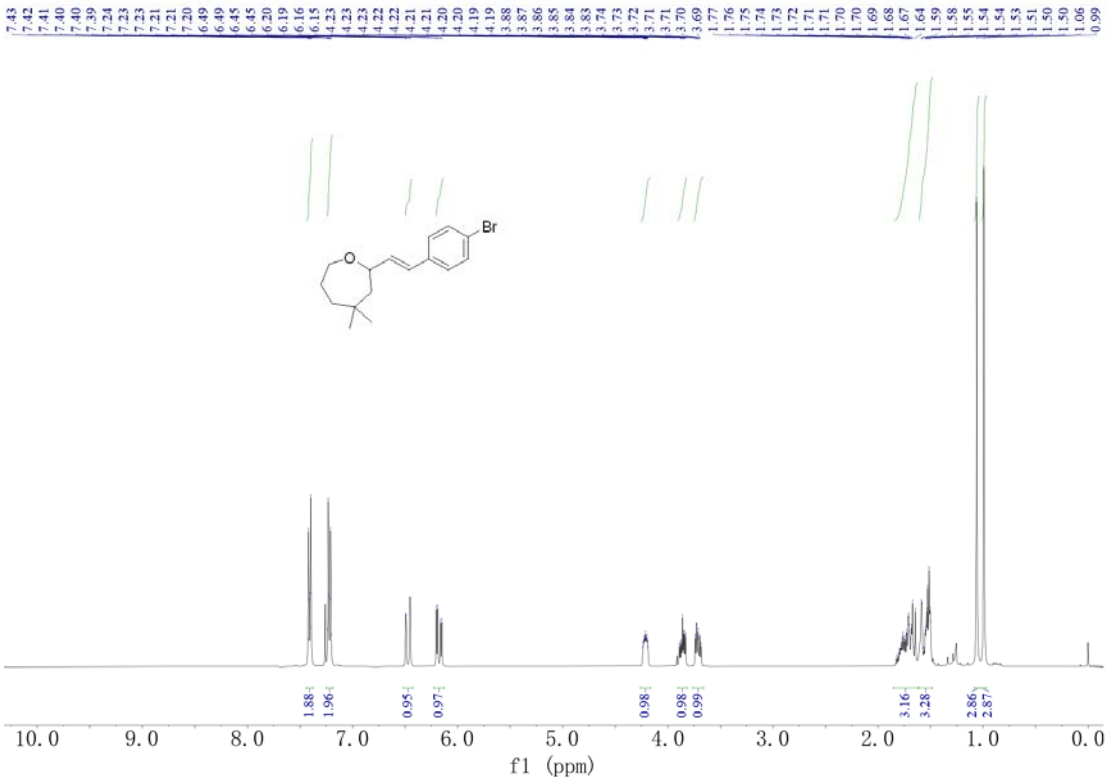
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



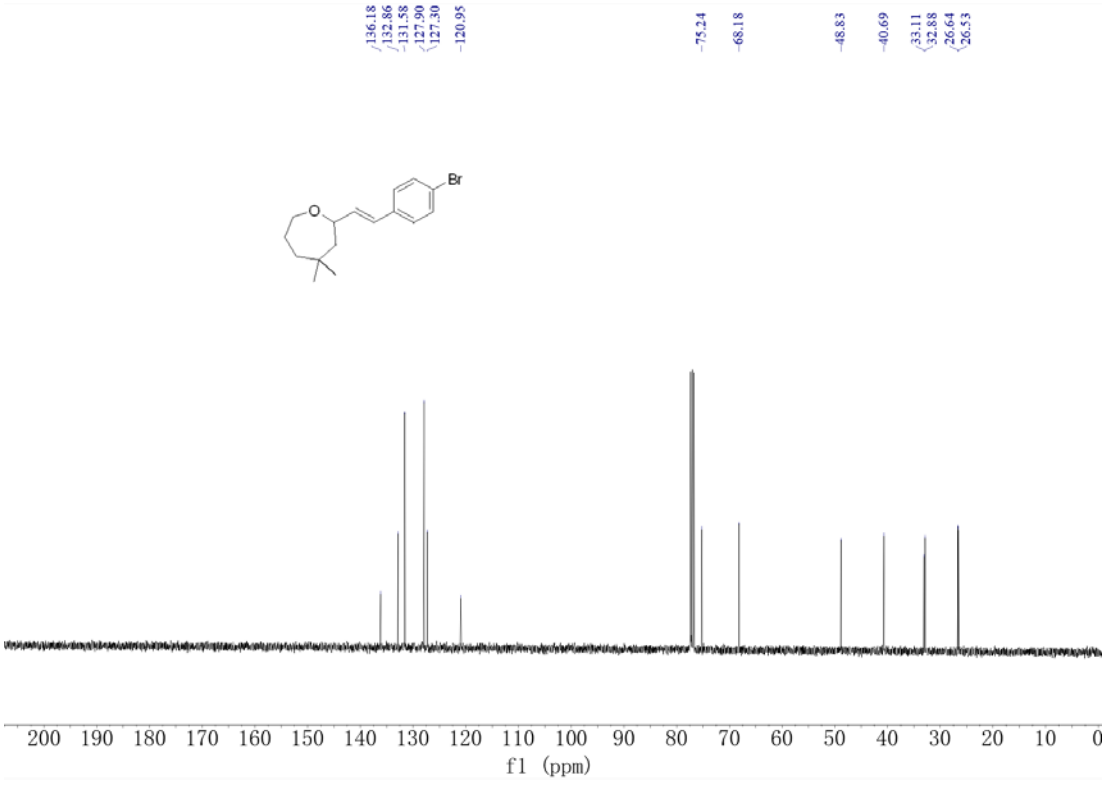
^{13}C{1H} NMR (101 MHz, $CDCl_3$) **3a**



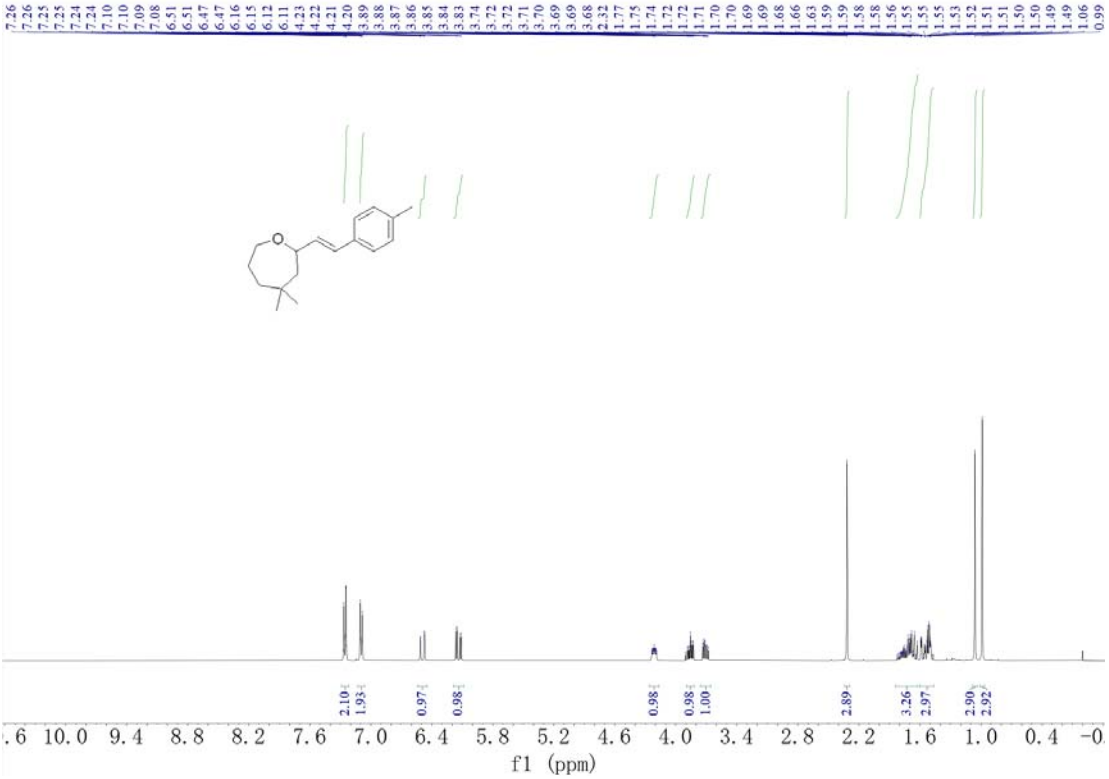
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



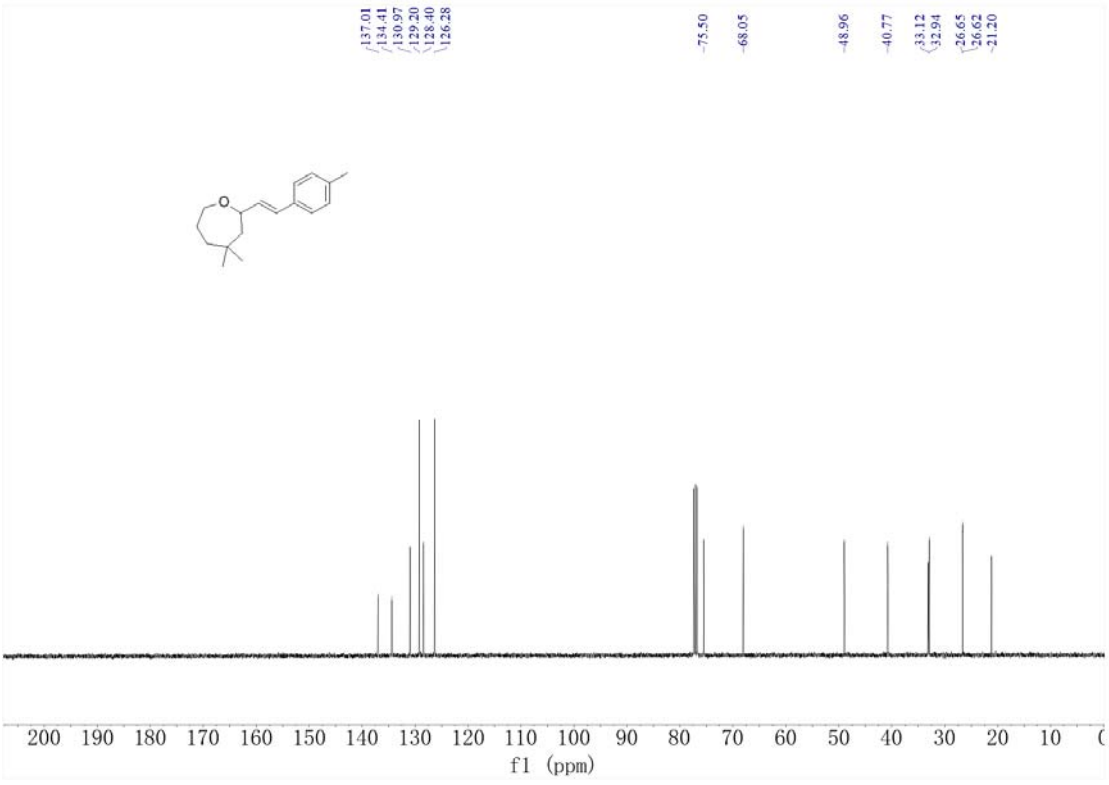
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3b**



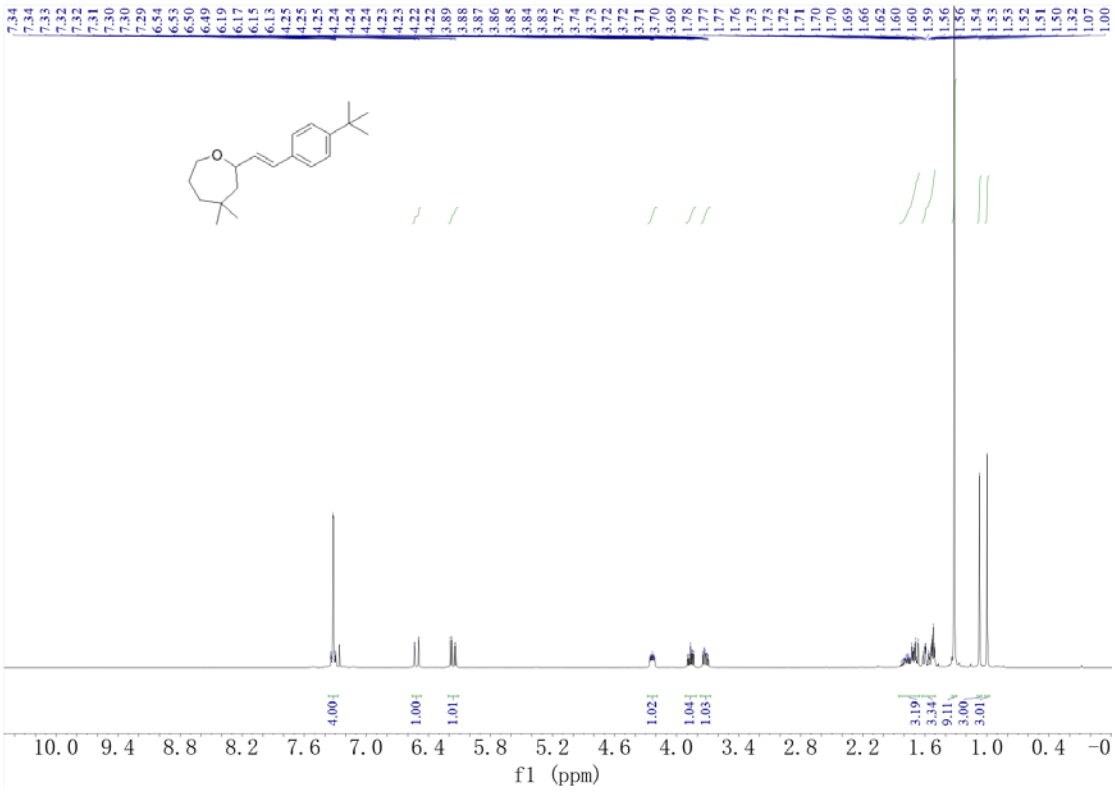
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



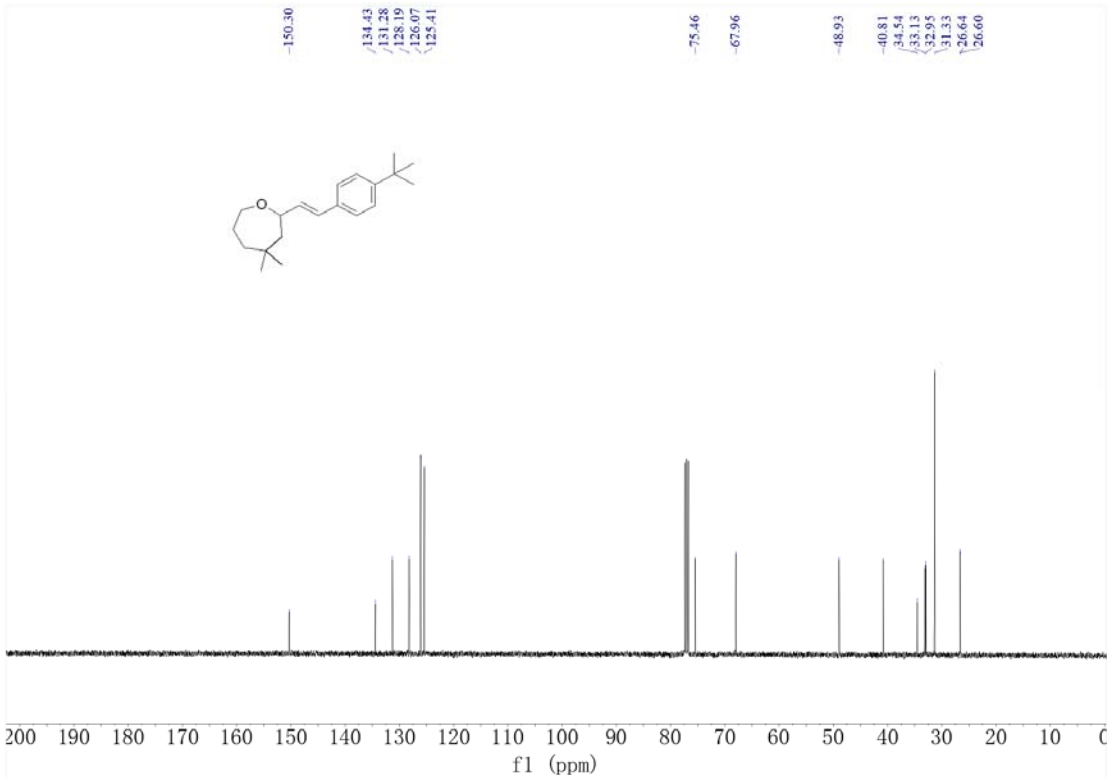
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3c**



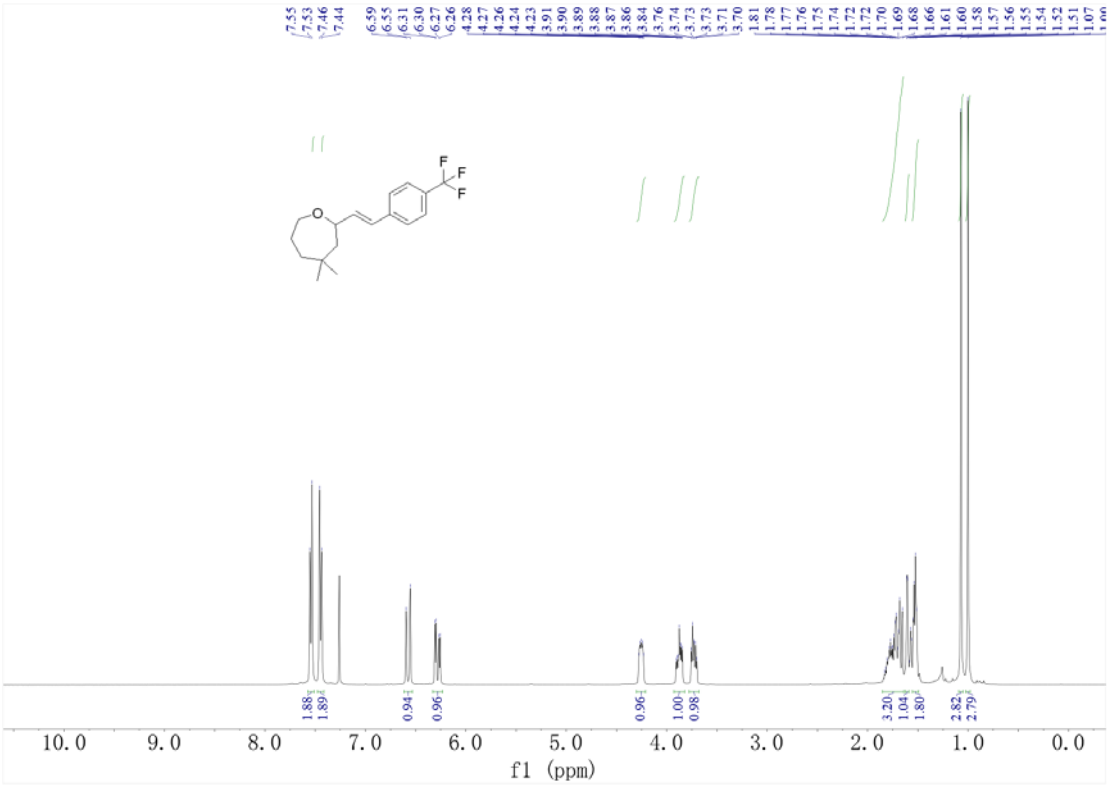
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



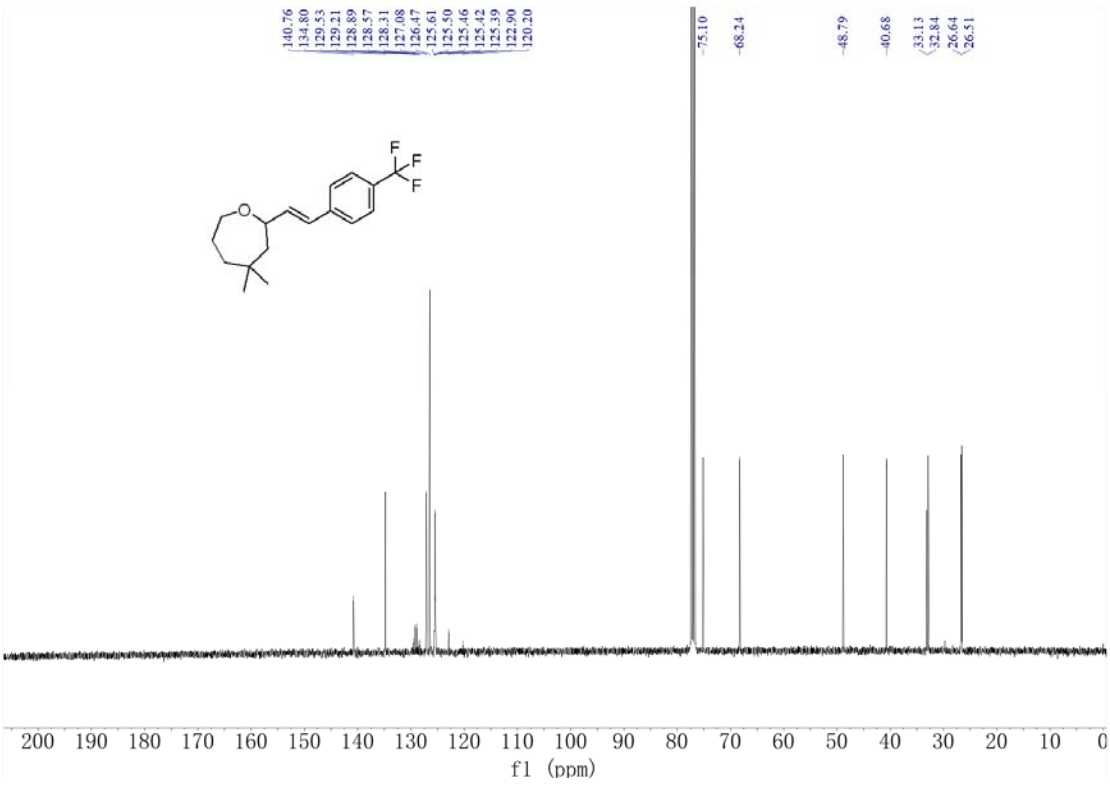
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3d**



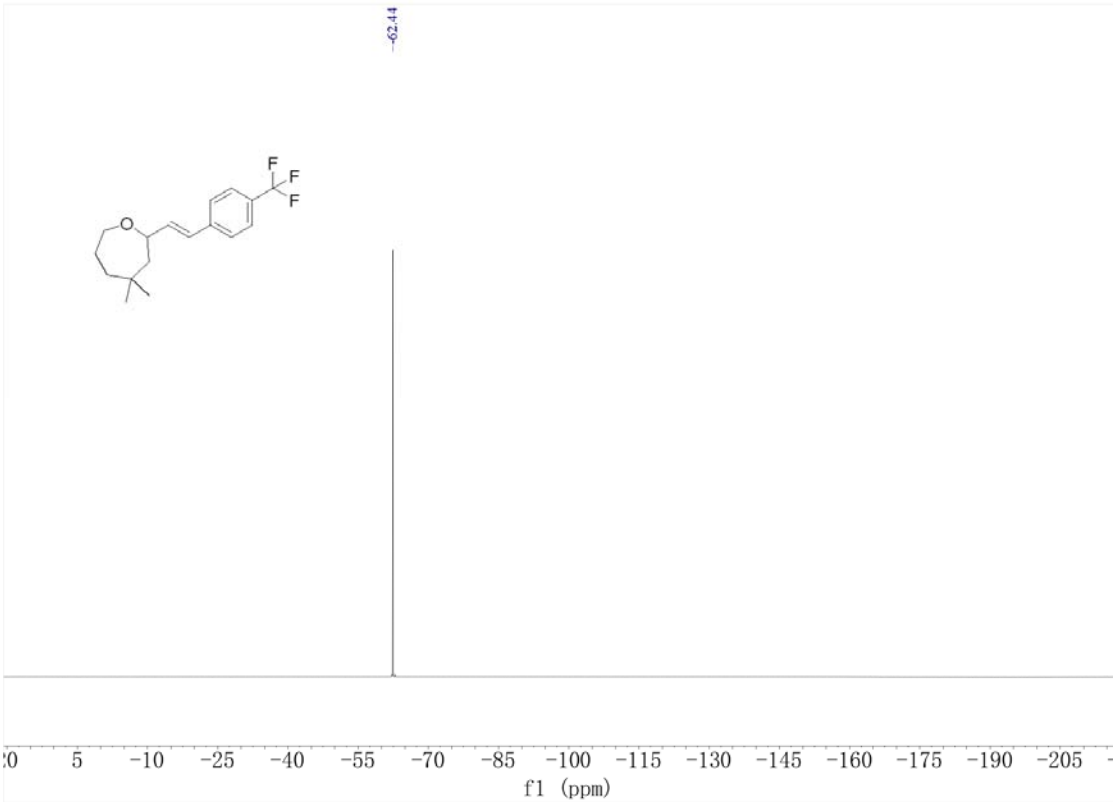
^{1}H NMR (400 MHz, $CDCl_3$) of 3e



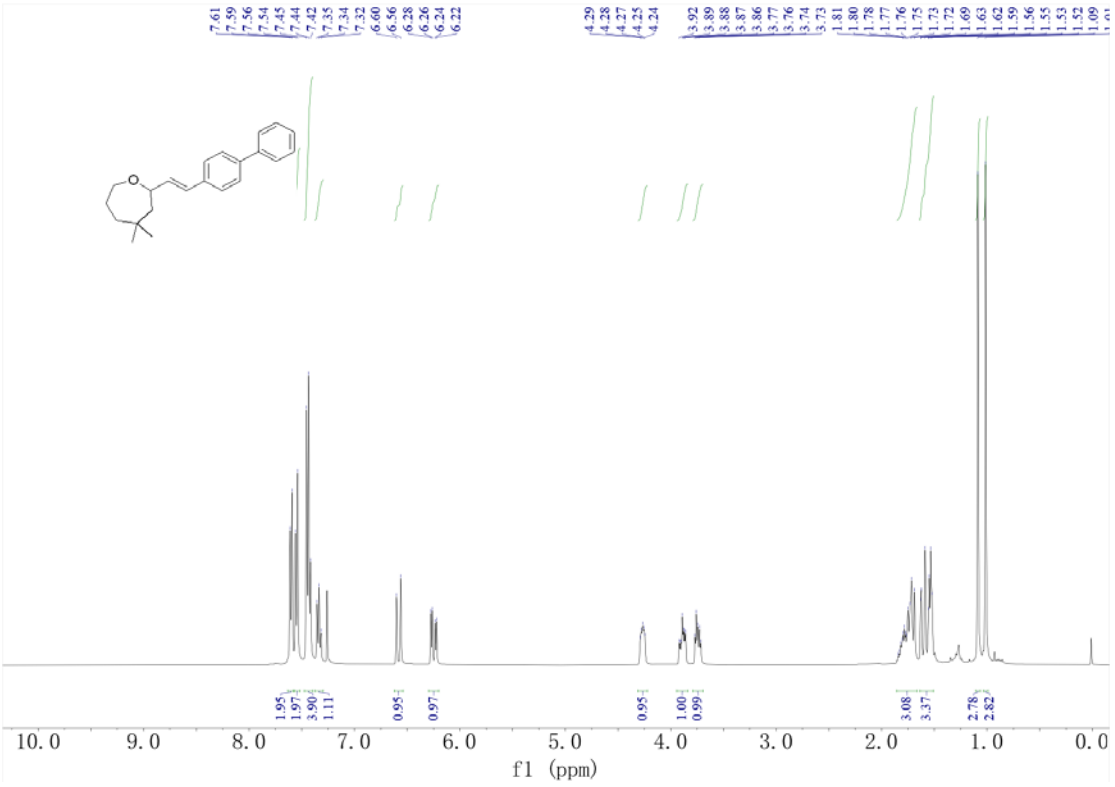
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3e**



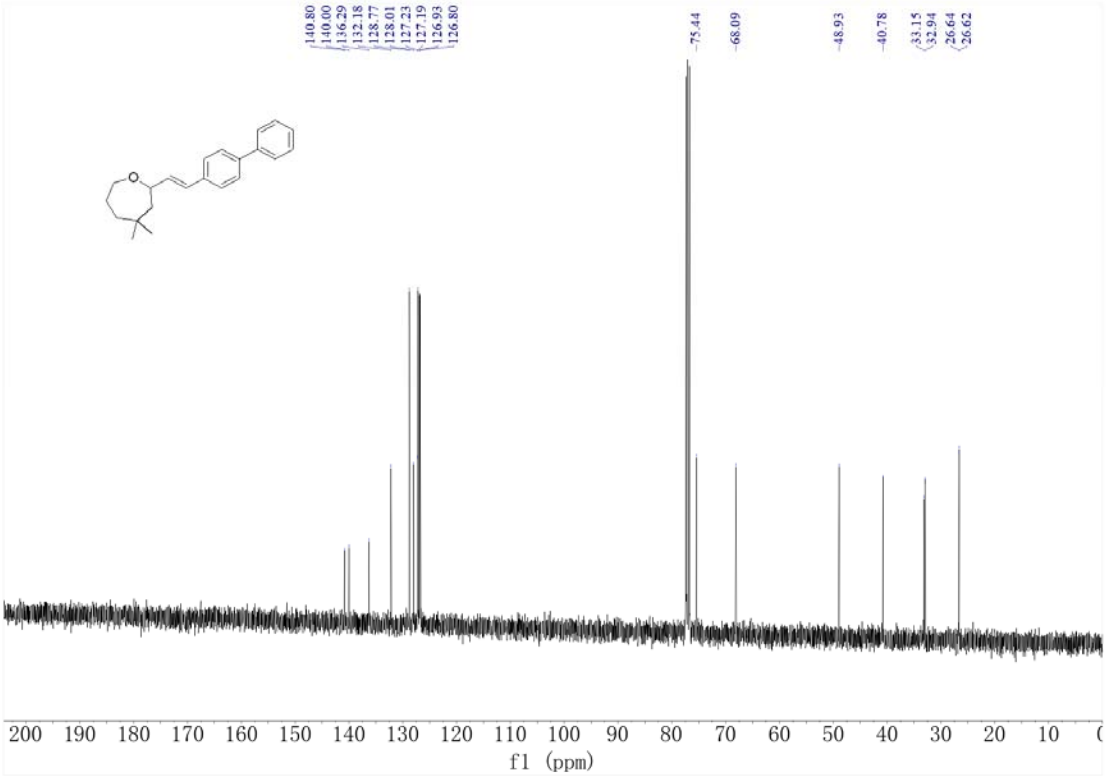
^{19}F NMR (376 MHz, $CDCl_3$) of **3e**



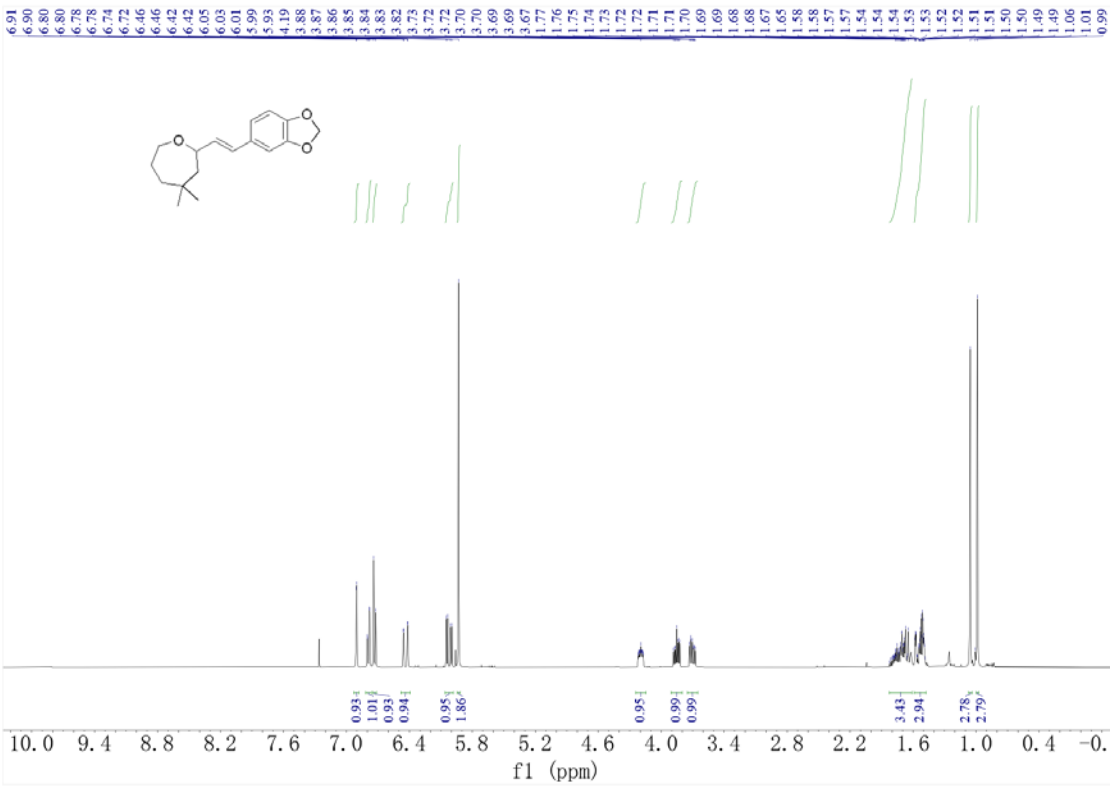
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



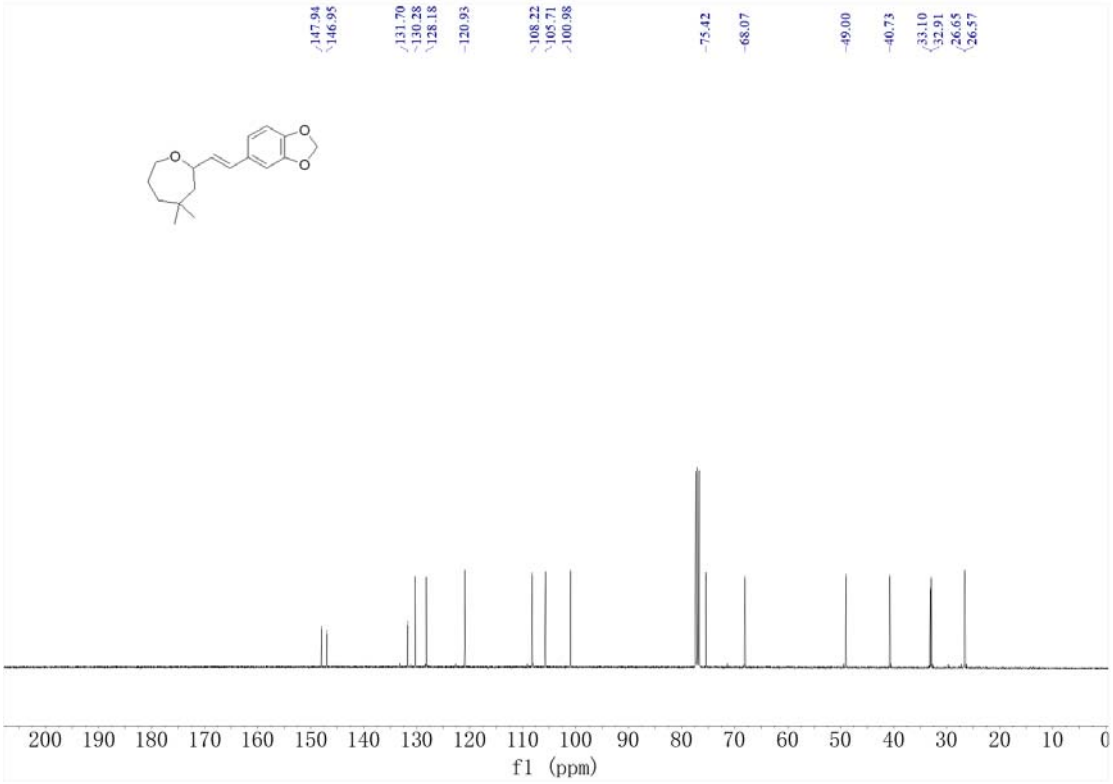
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **3f**



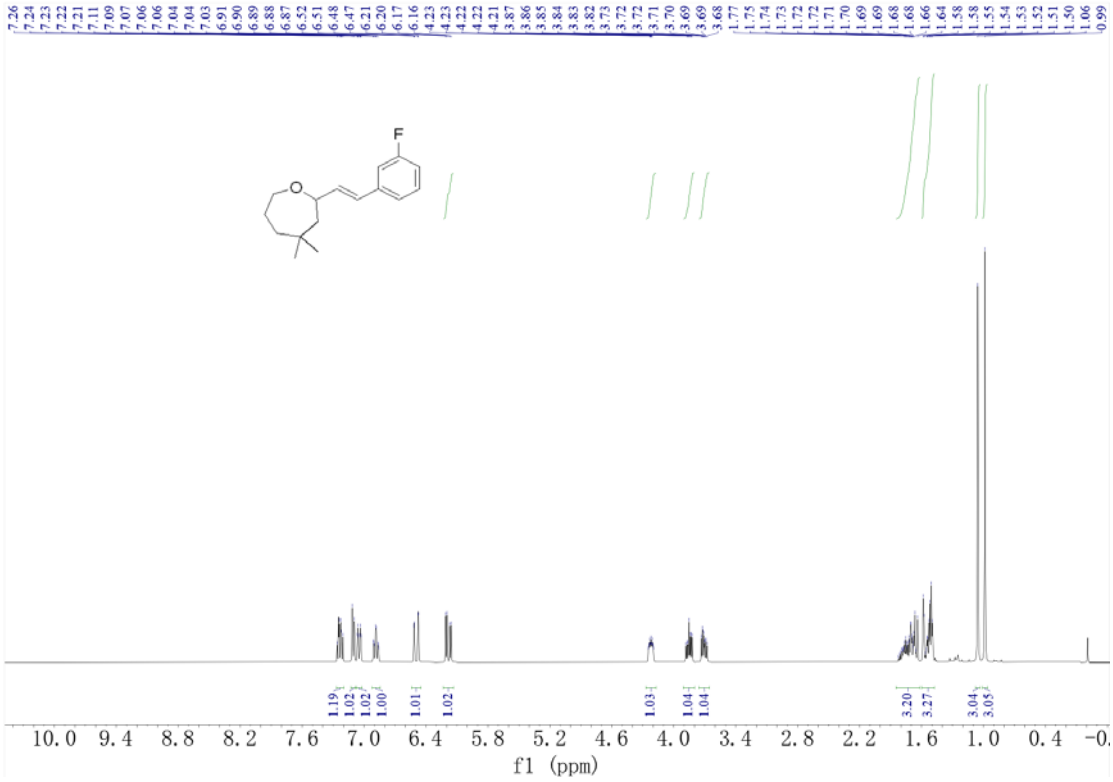
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



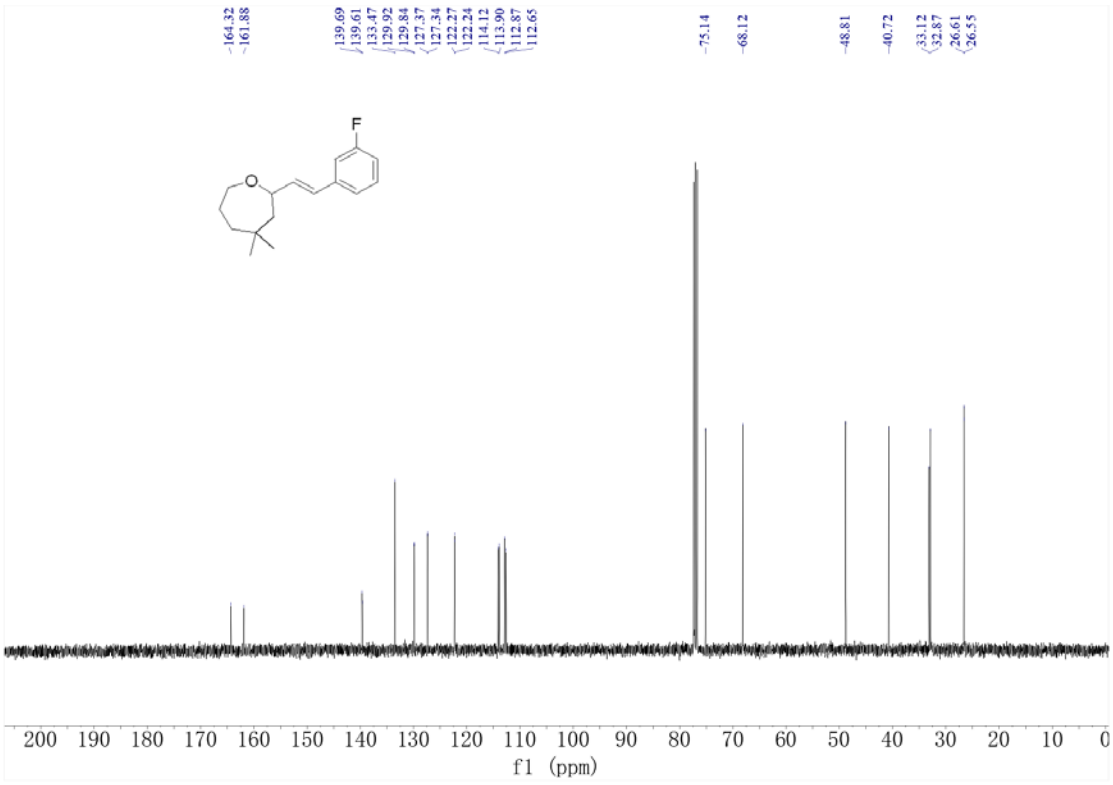
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **3g**



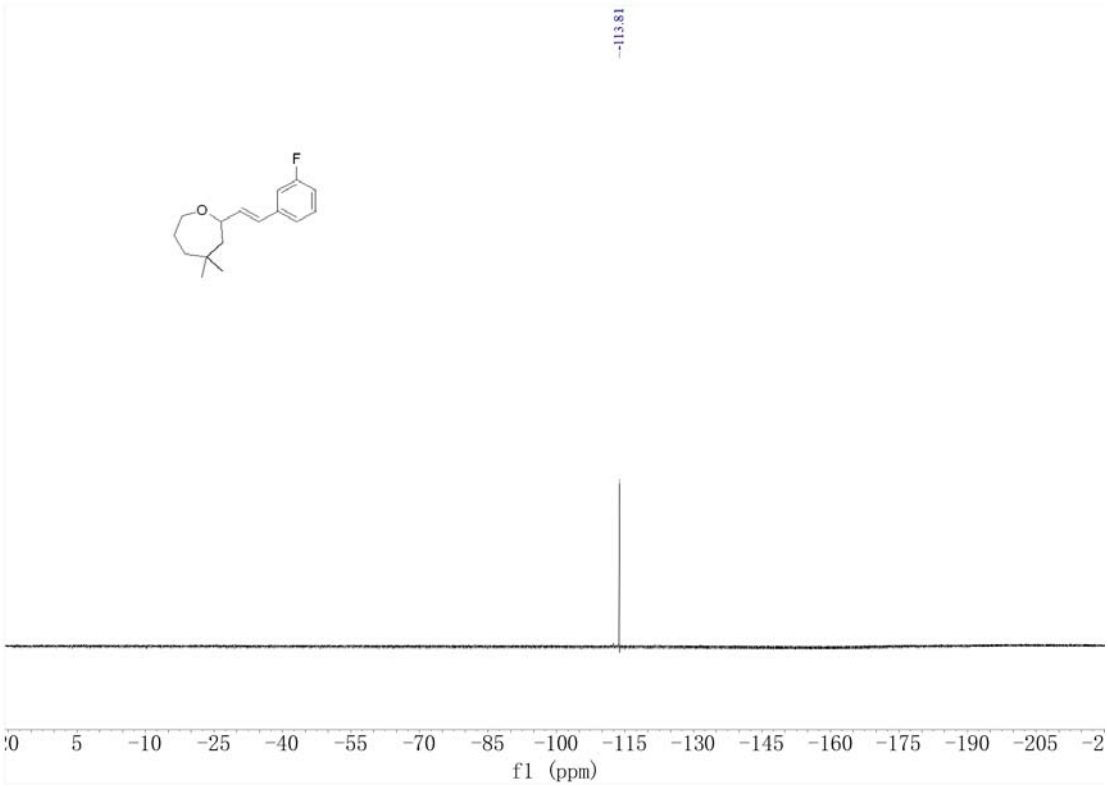
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



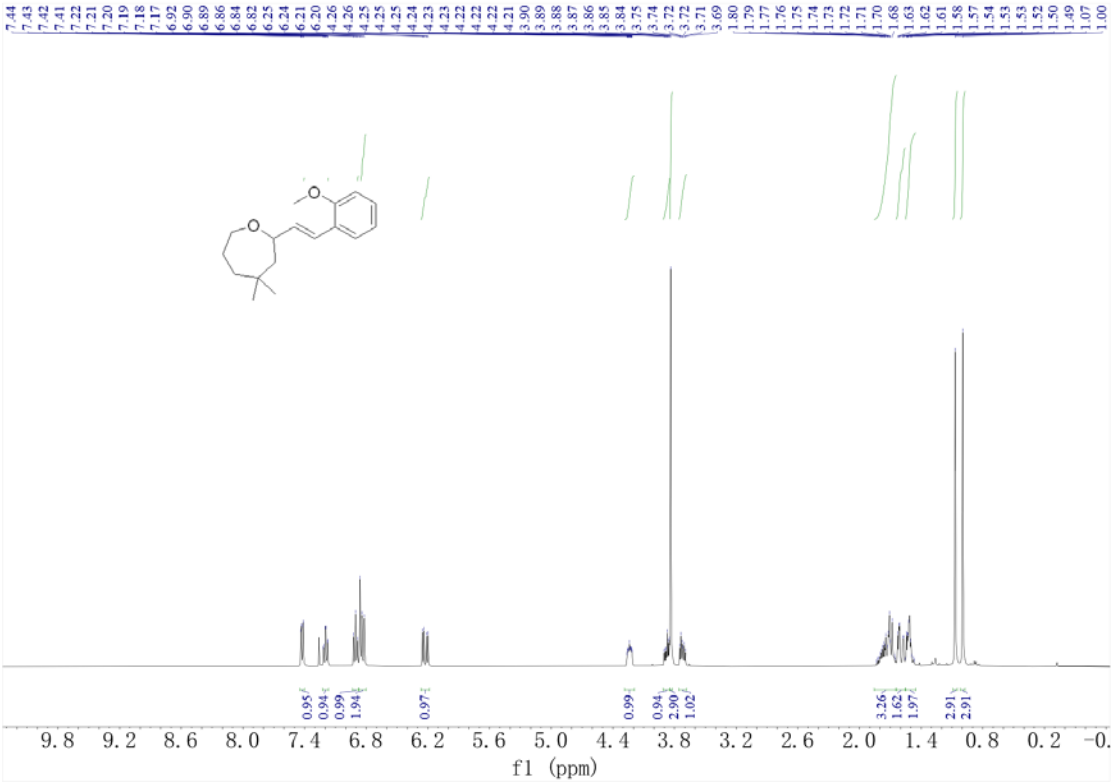
$^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) of **3h**



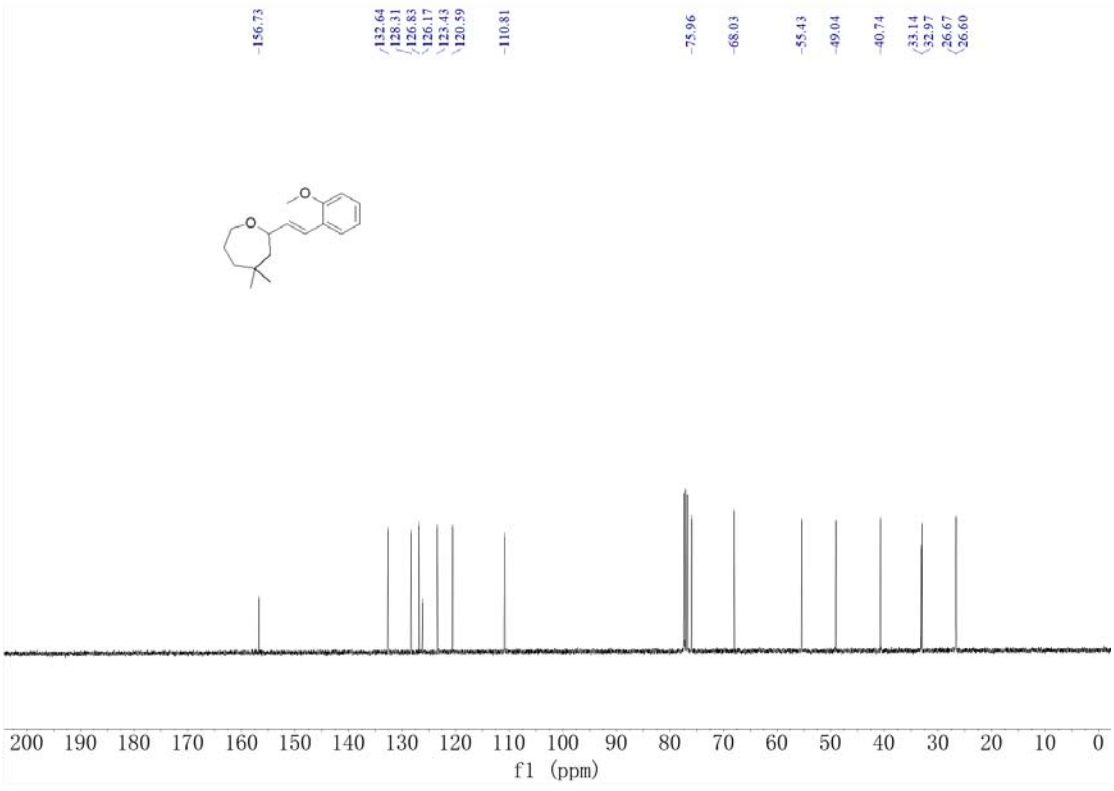
^{19}F NMR (376 MHz, $CDCl_3$) of **3h**



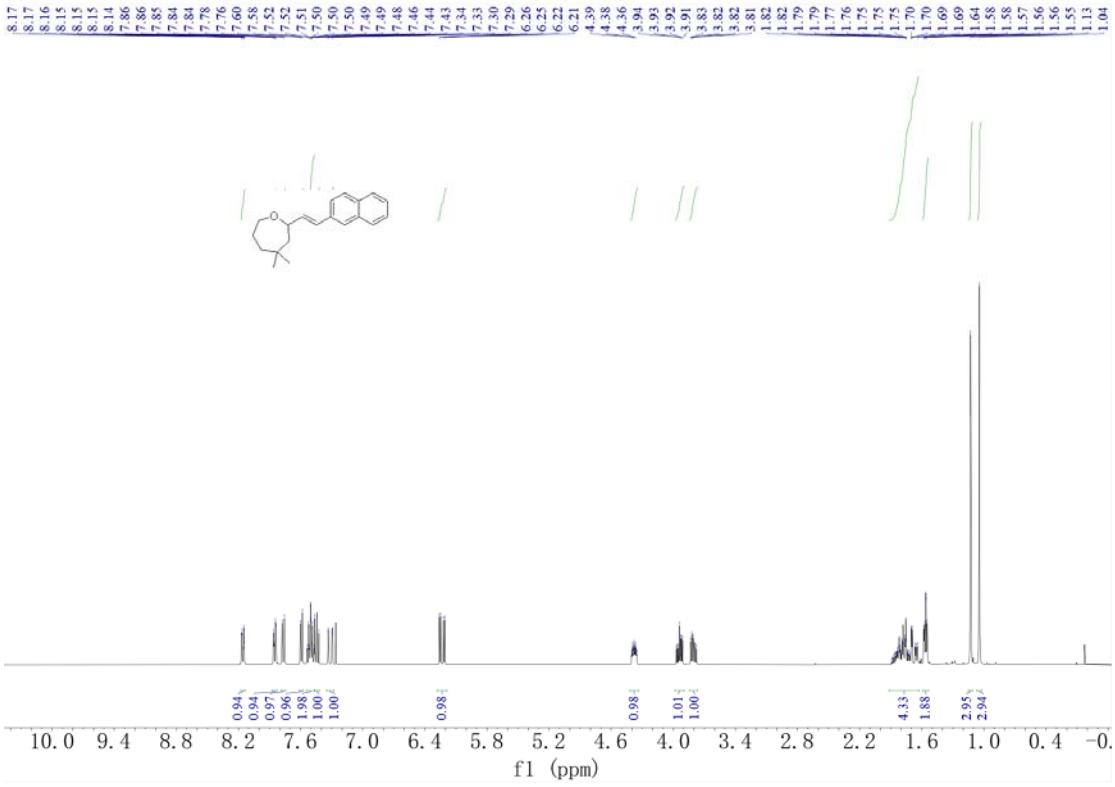
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



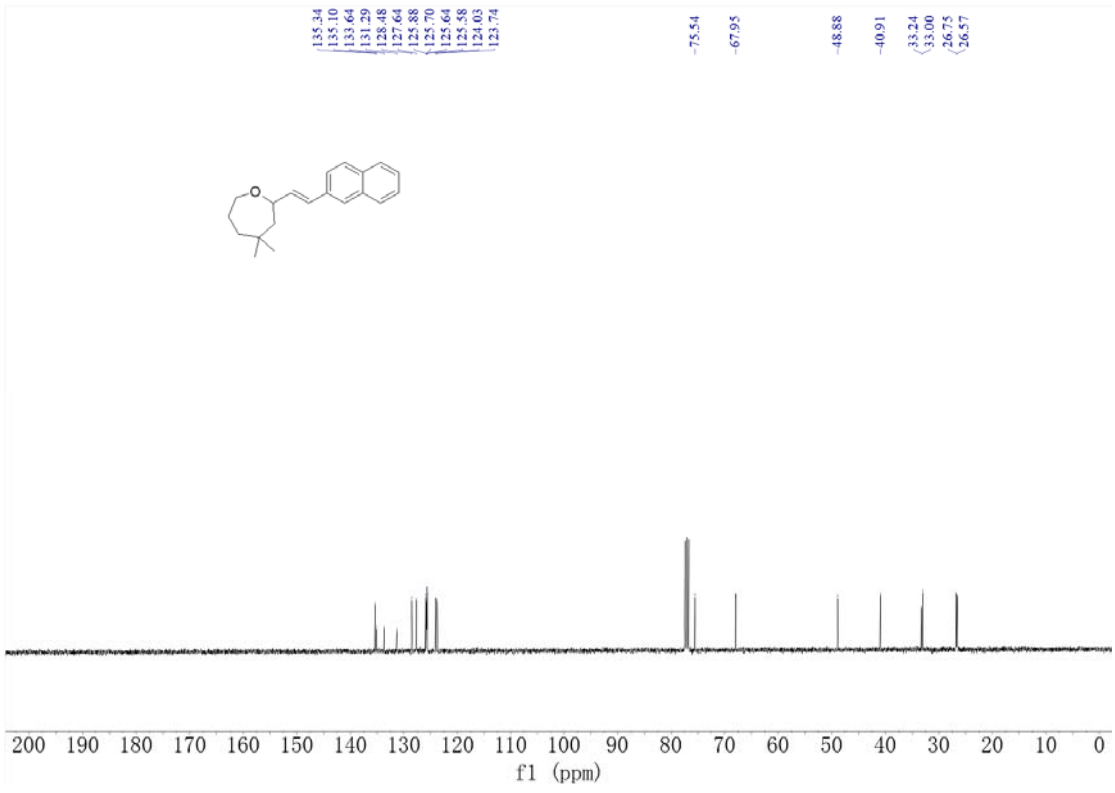
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3i**



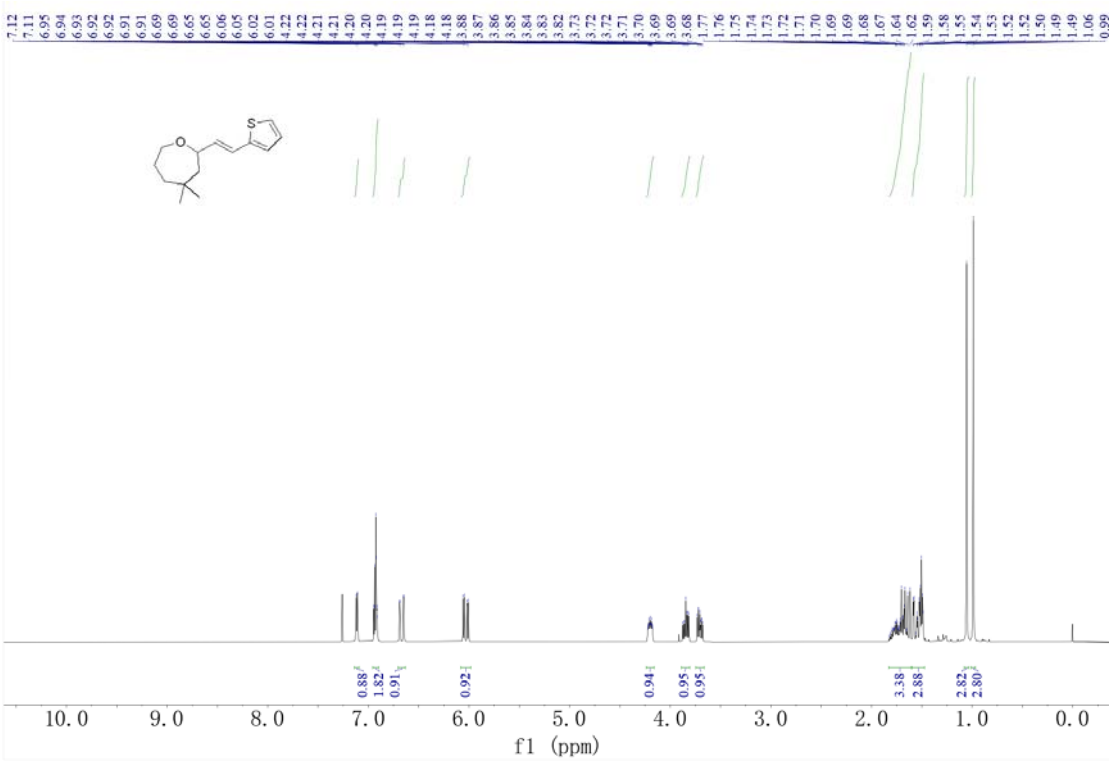
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



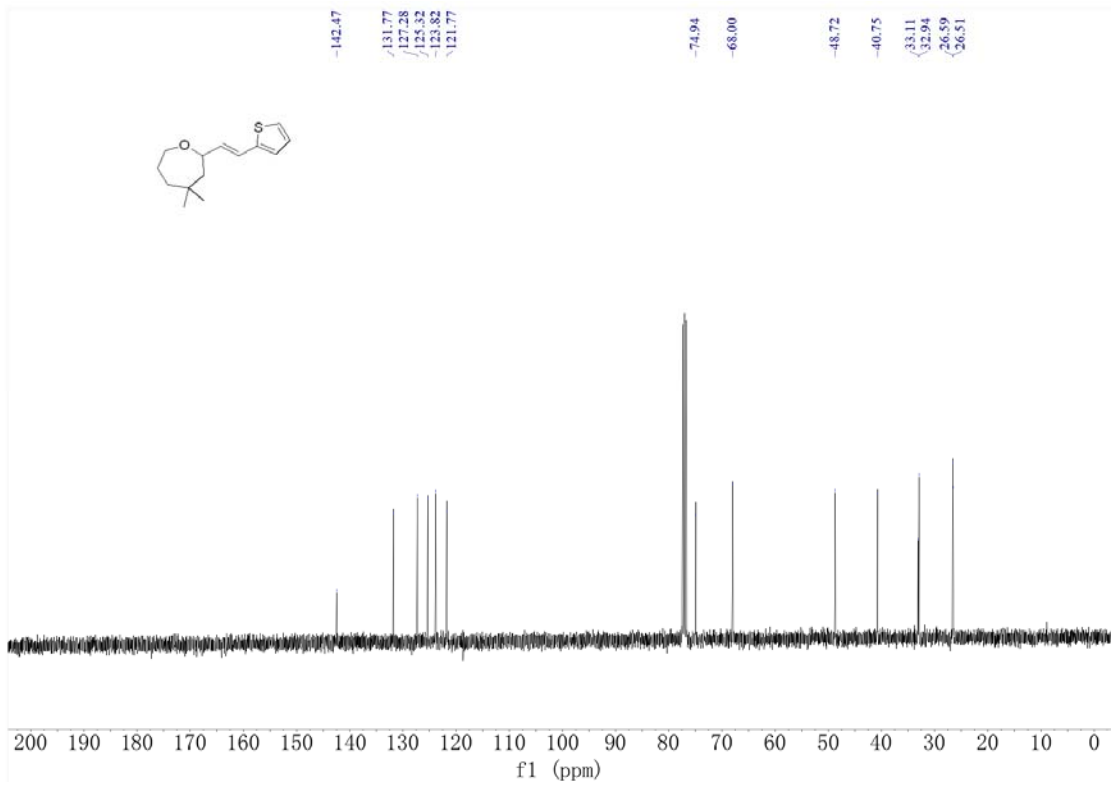
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3j**



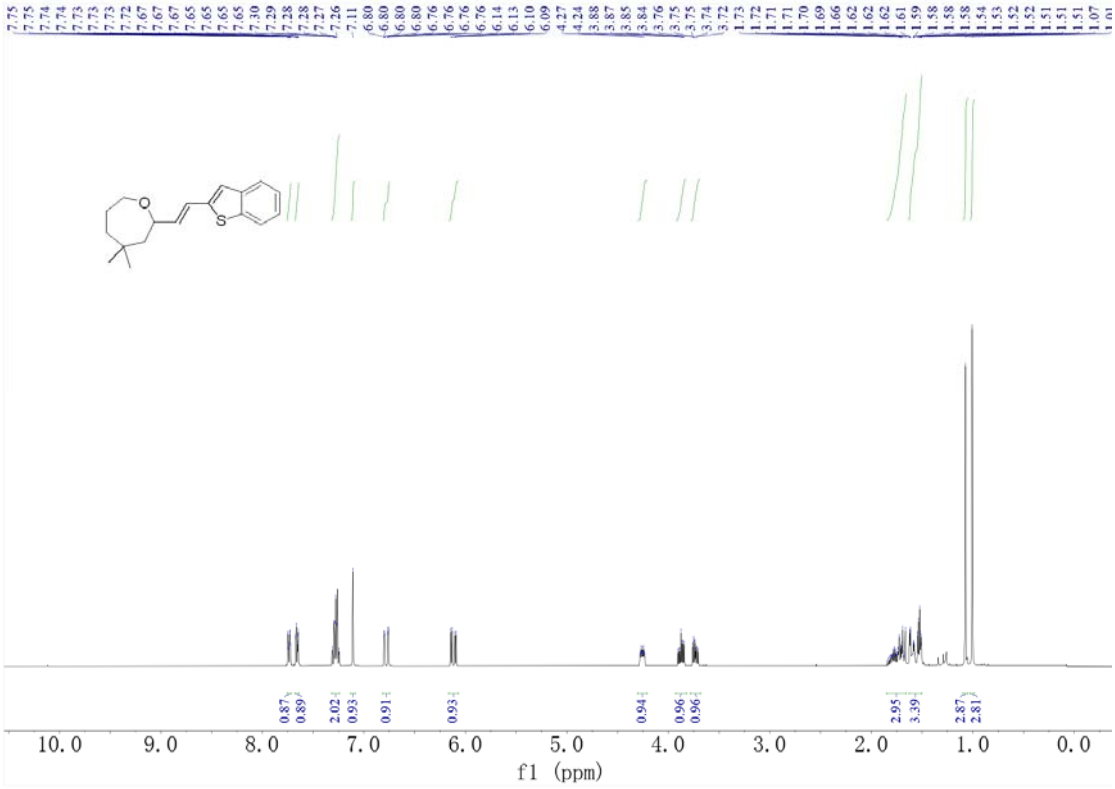
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



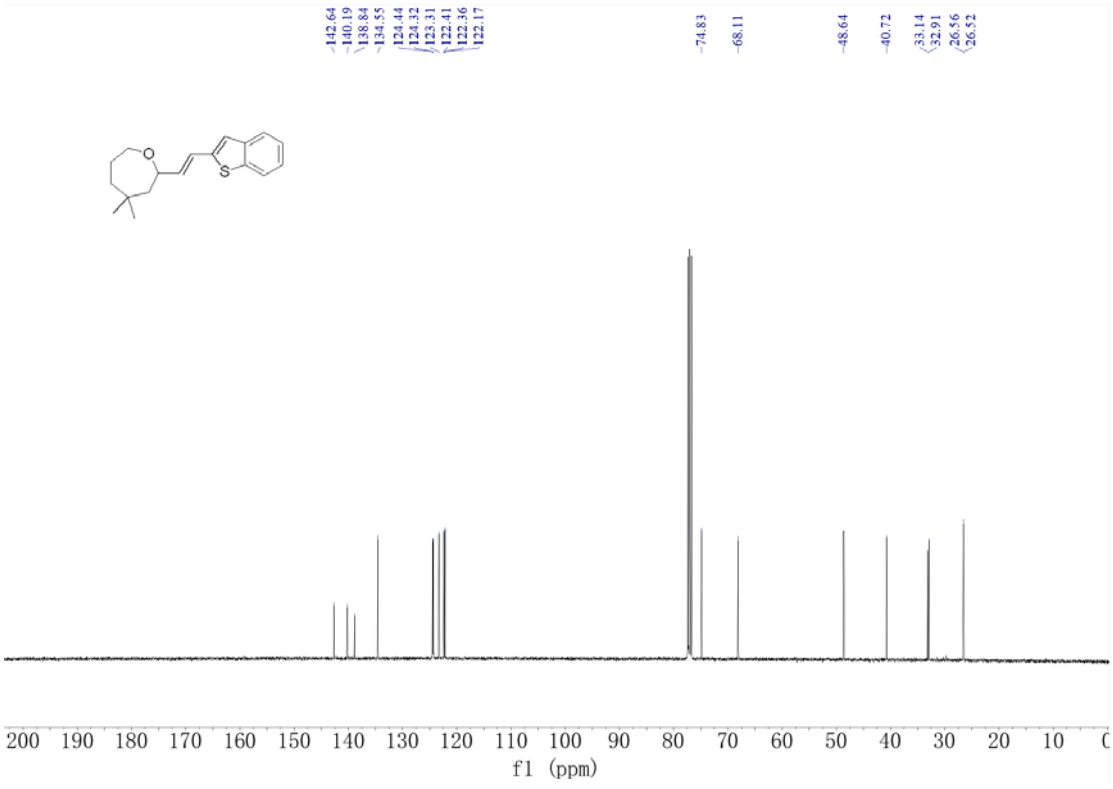
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3k**



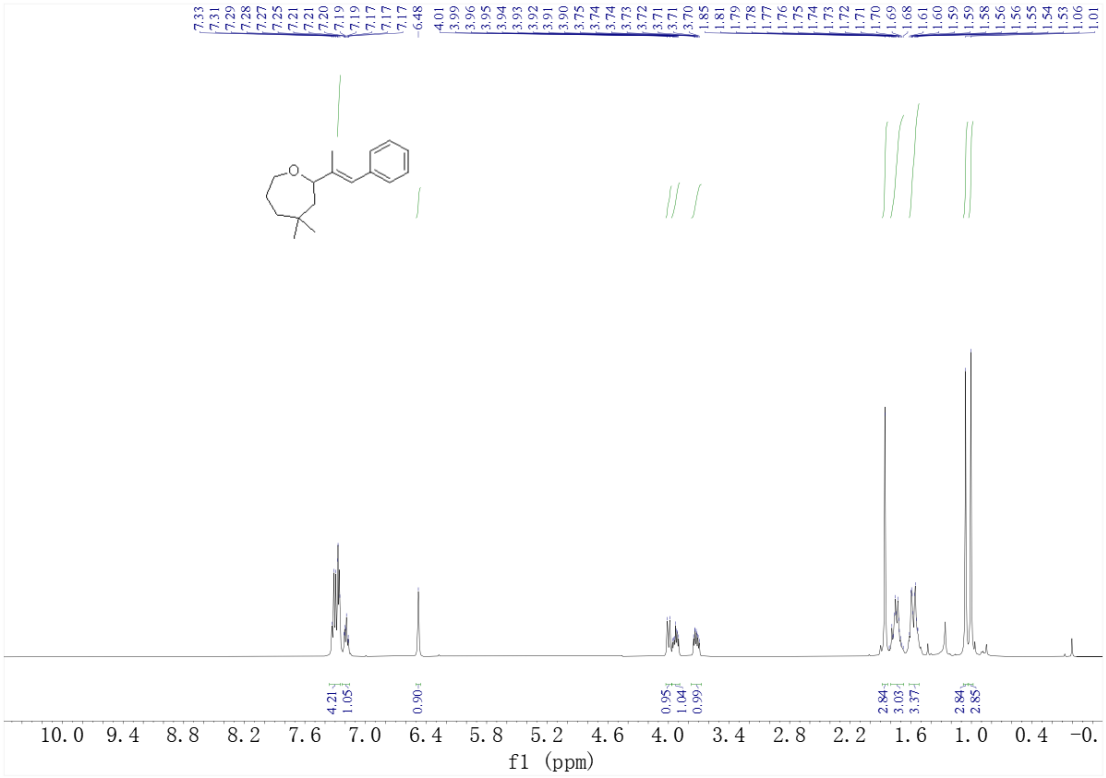
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



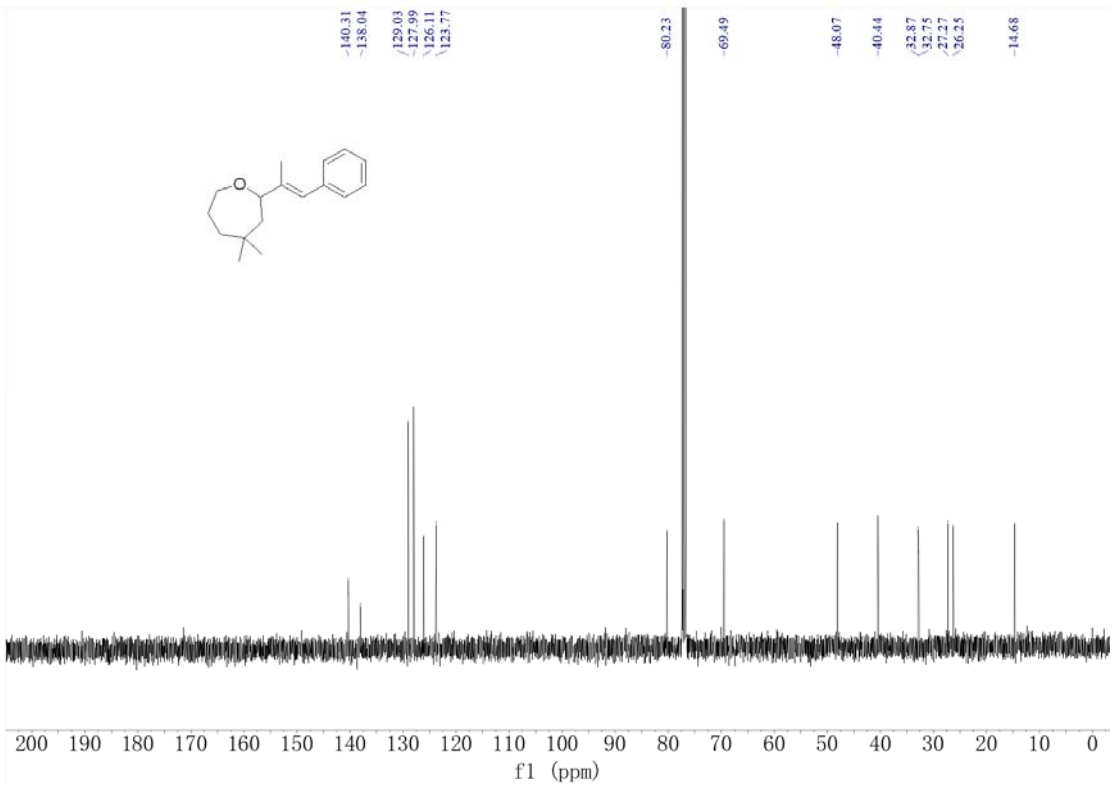
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3l**



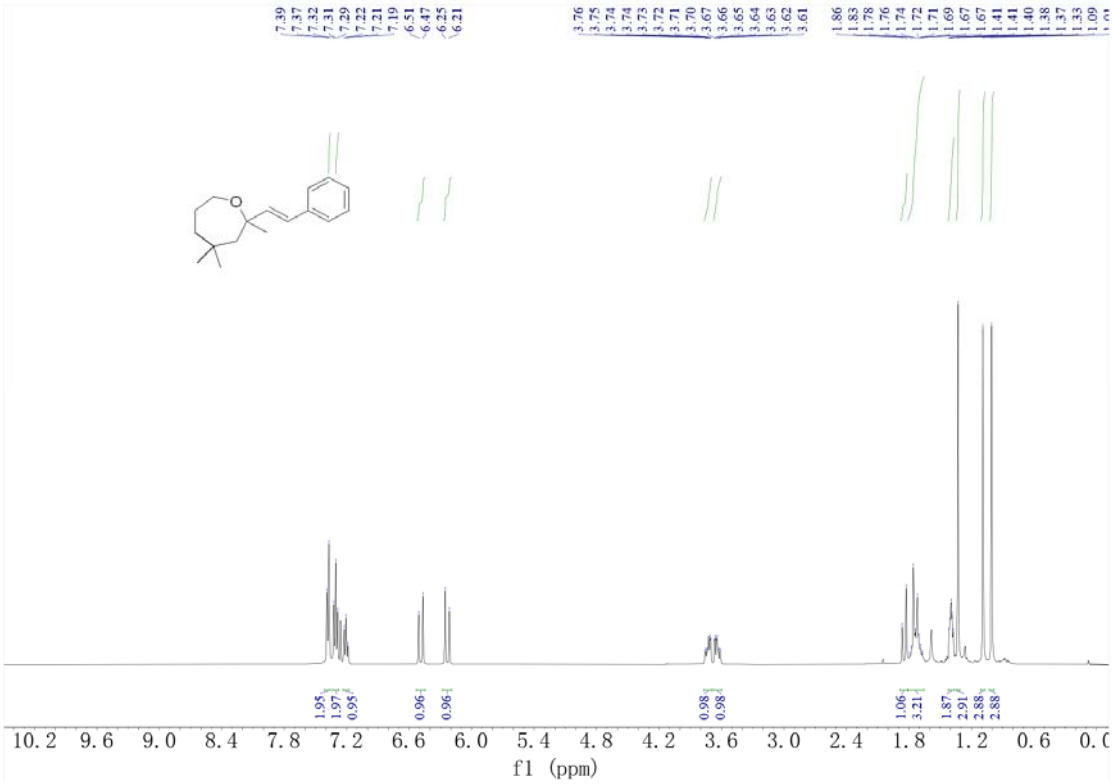
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



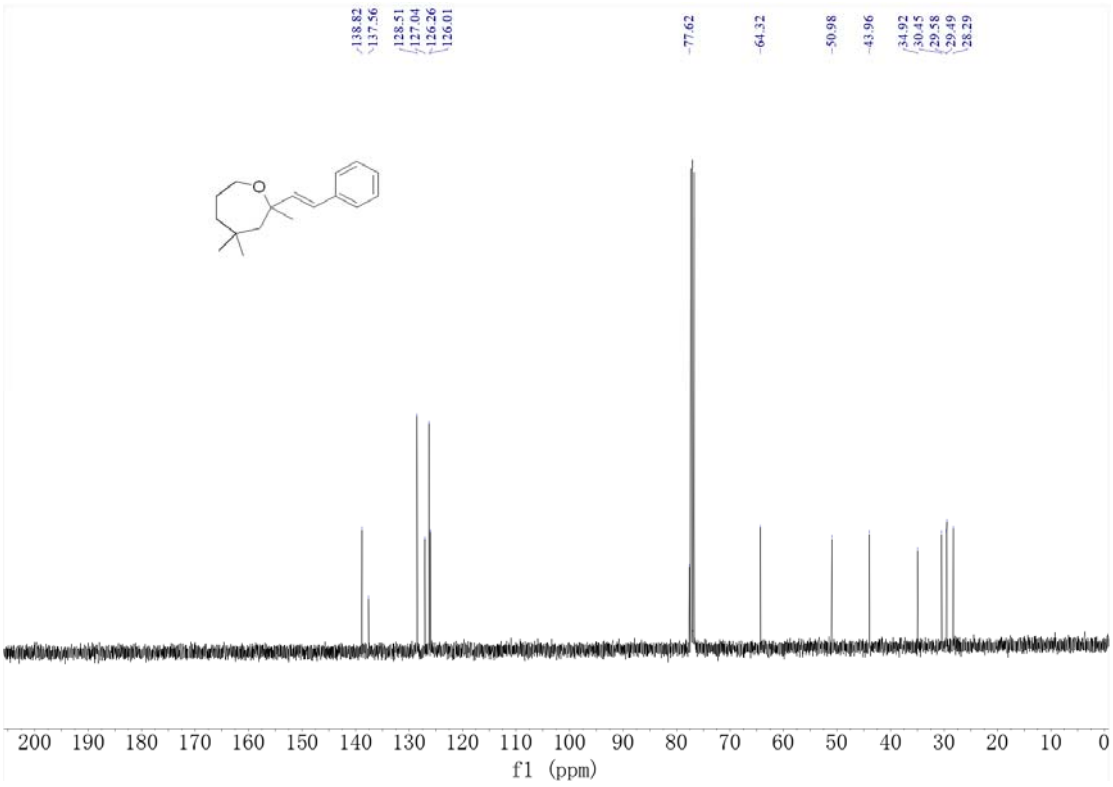
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3m**



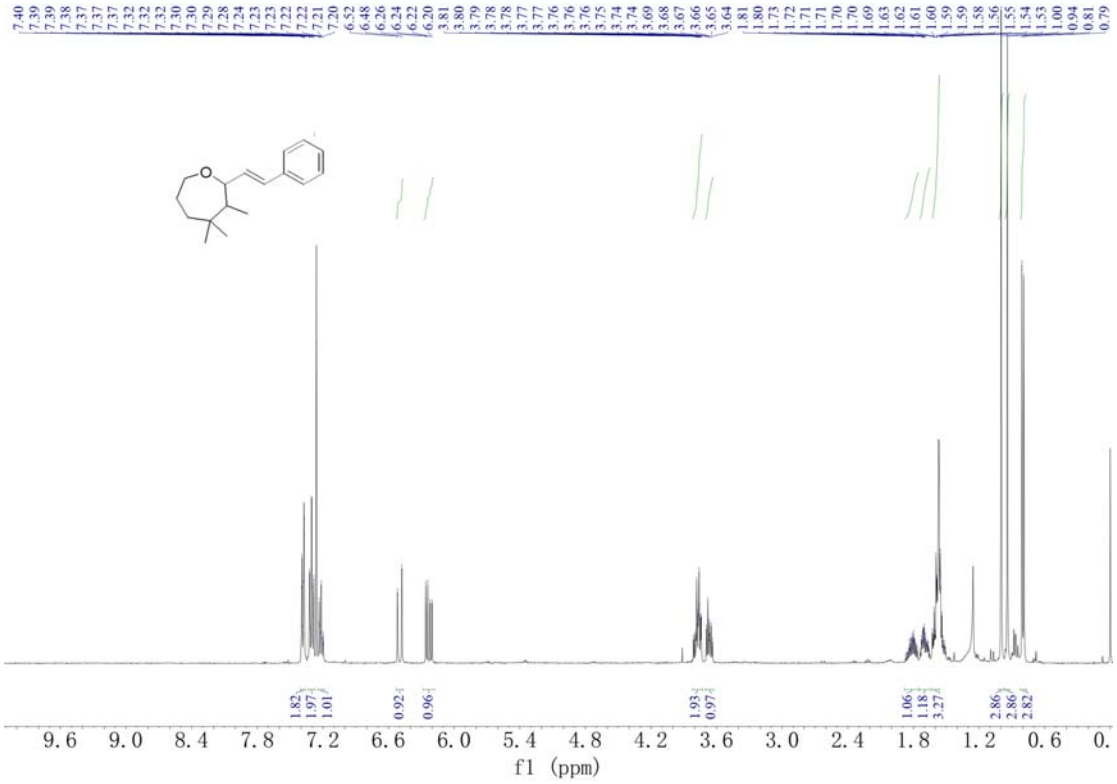
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



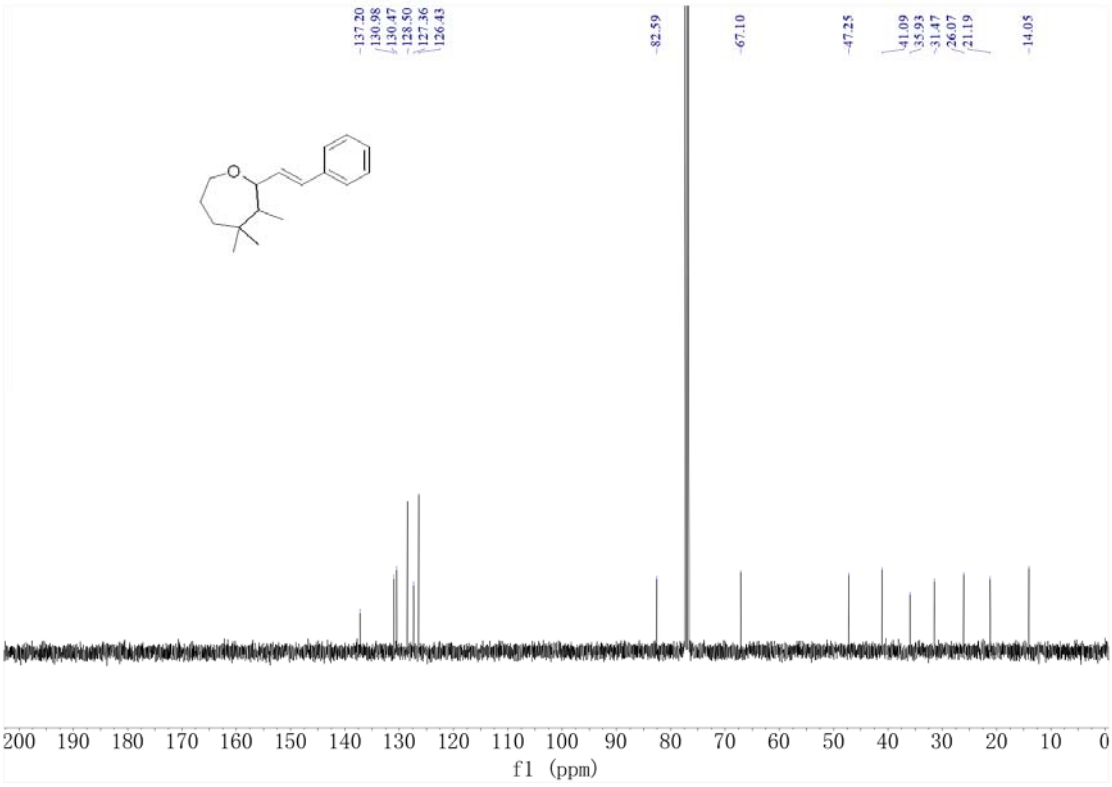
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3n**



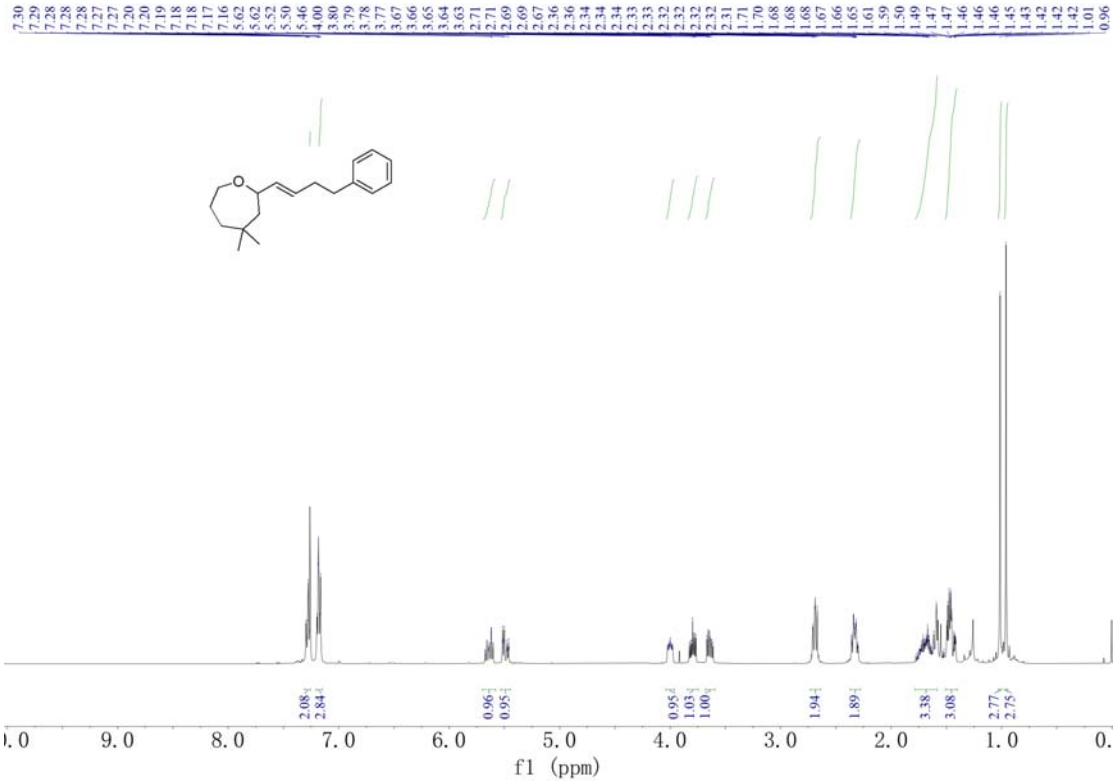
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



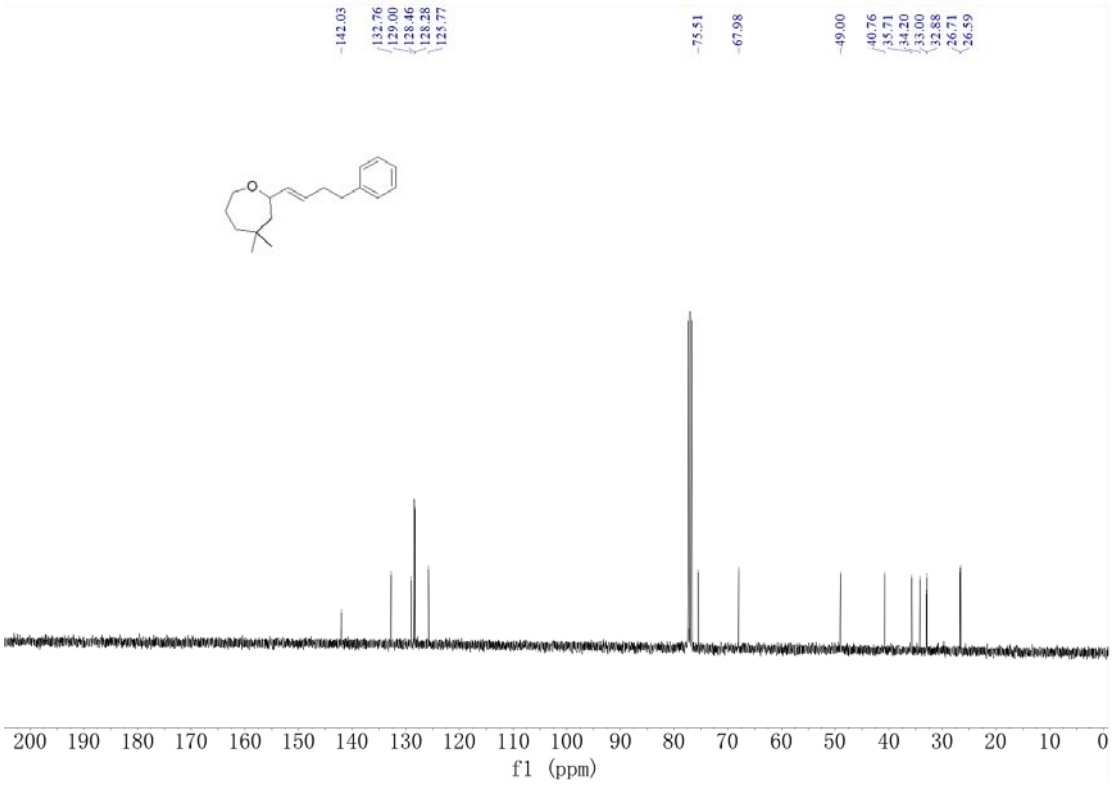
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3o**



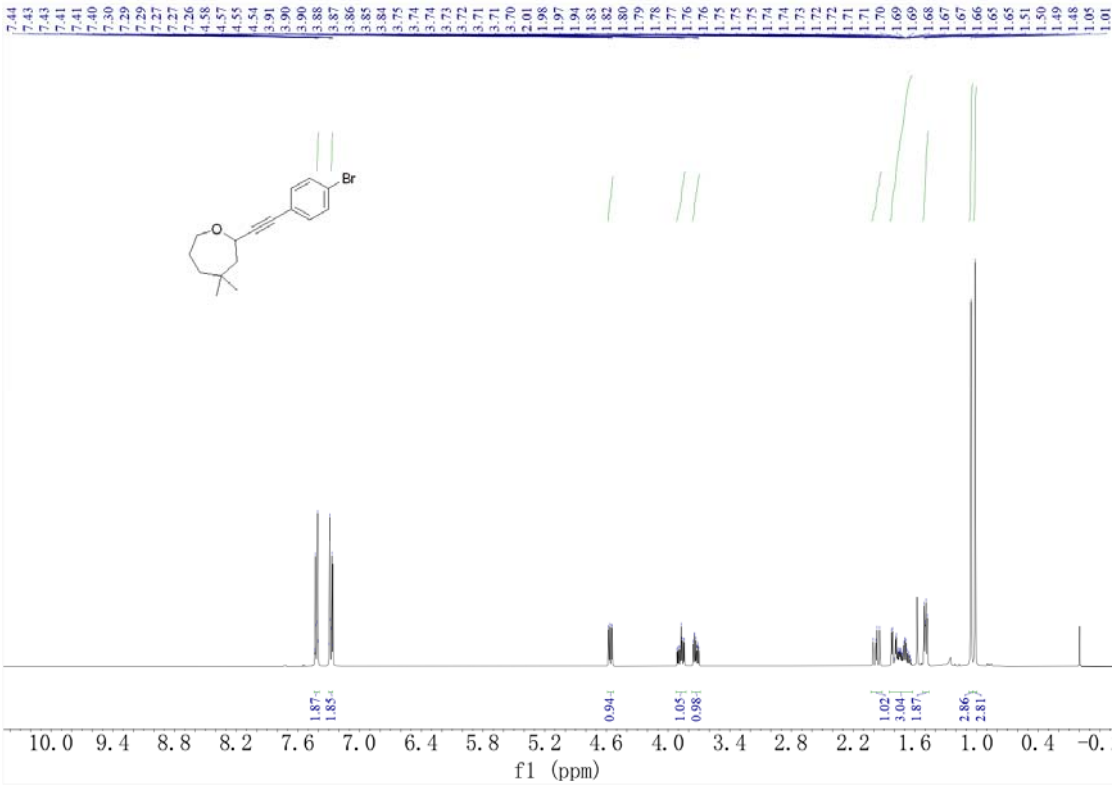
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



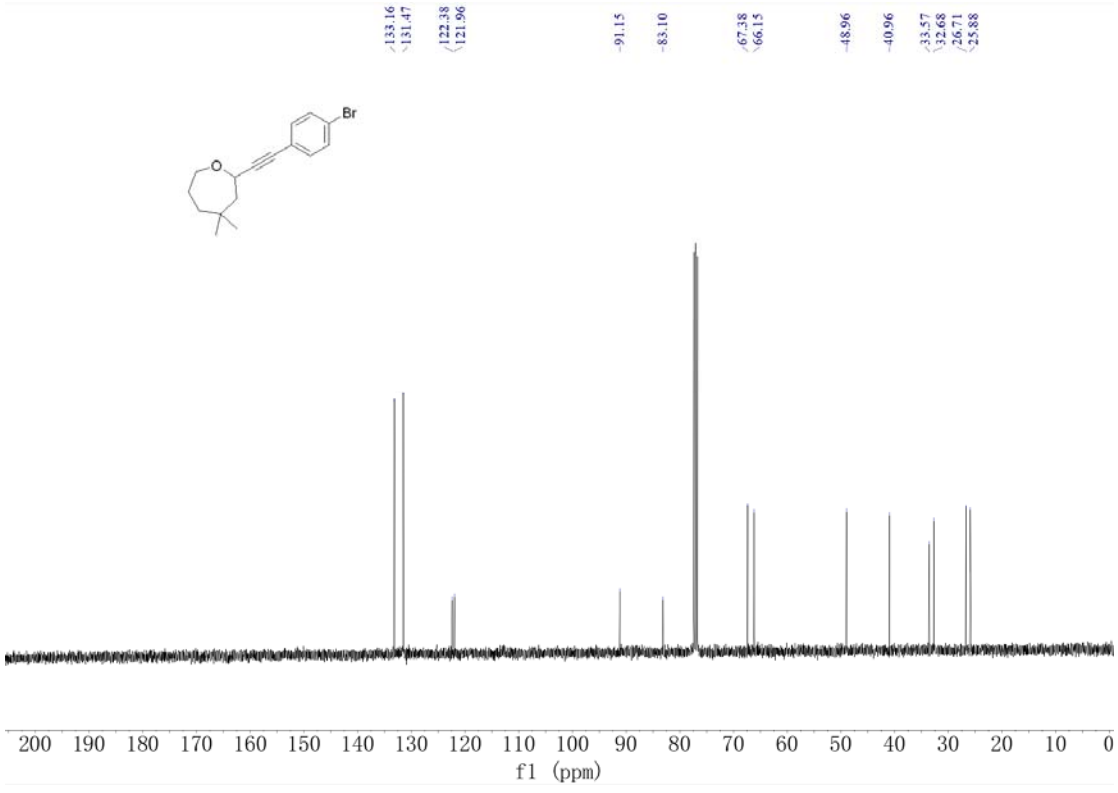
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3p**



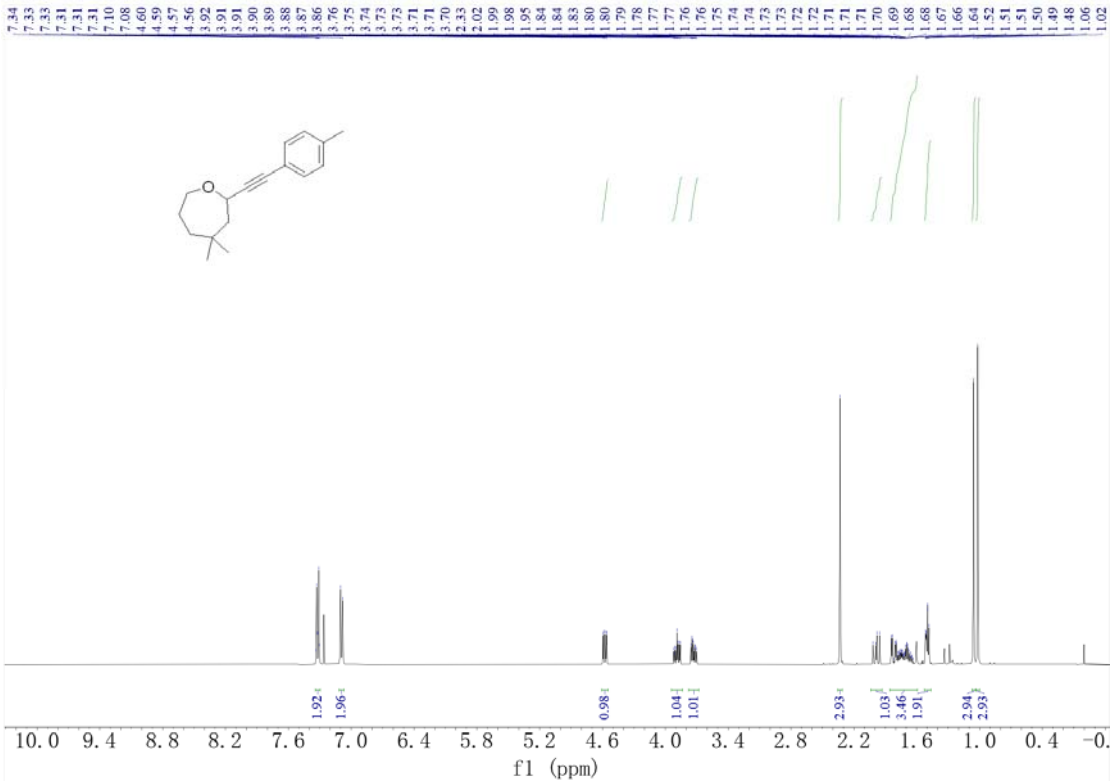
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



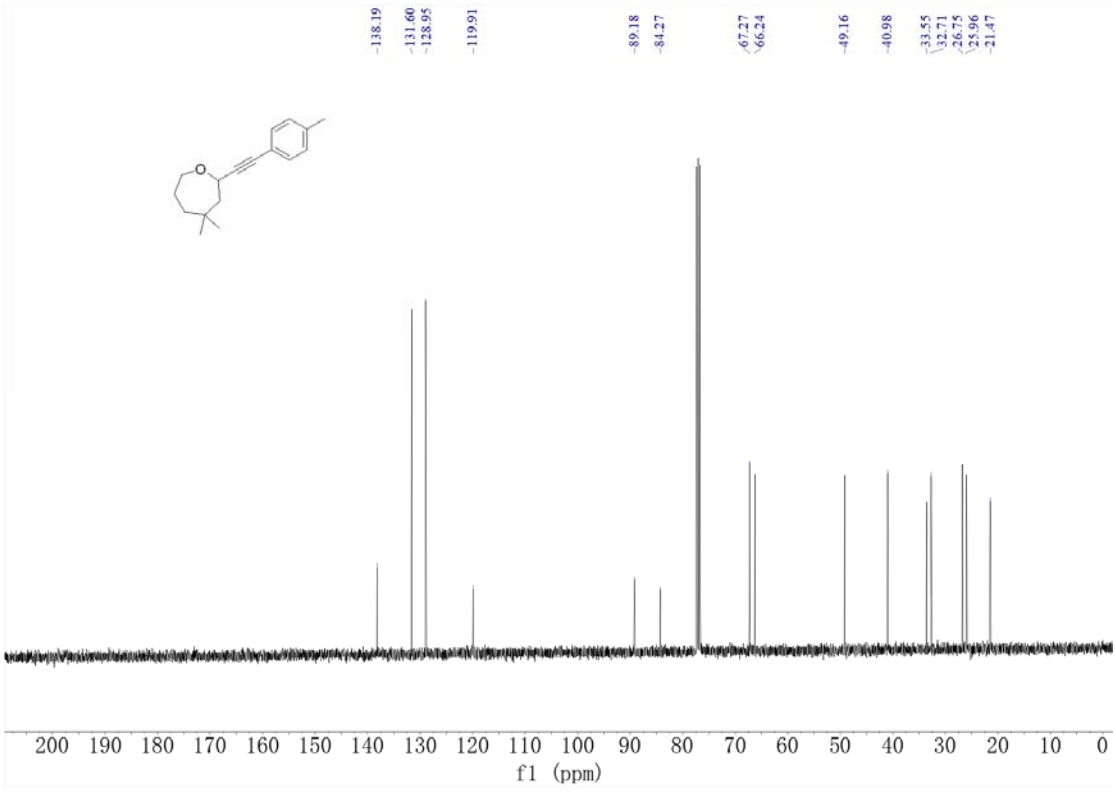
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3q**



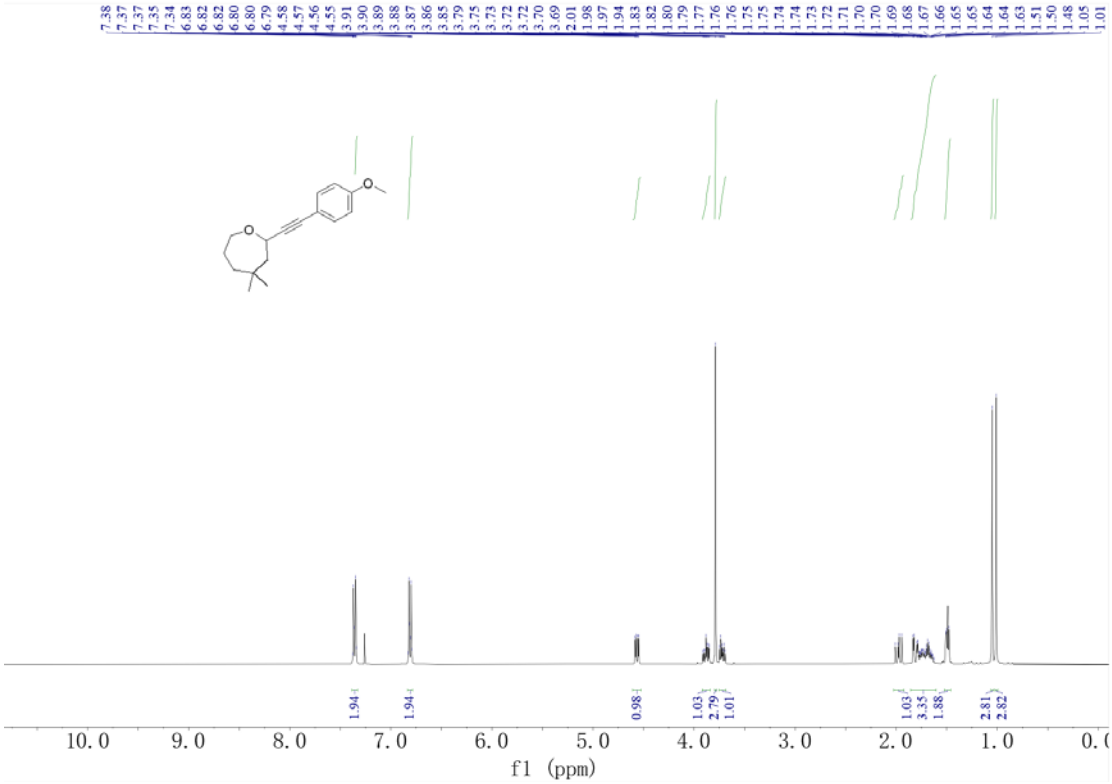
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



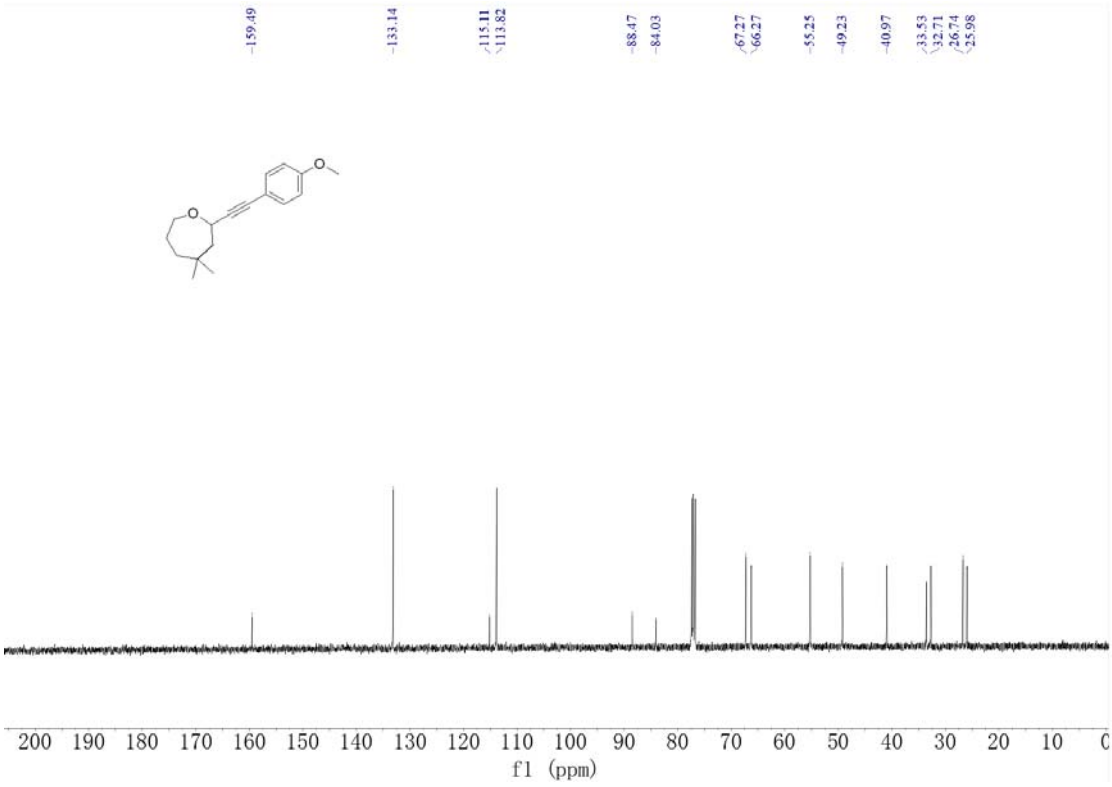
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3r**



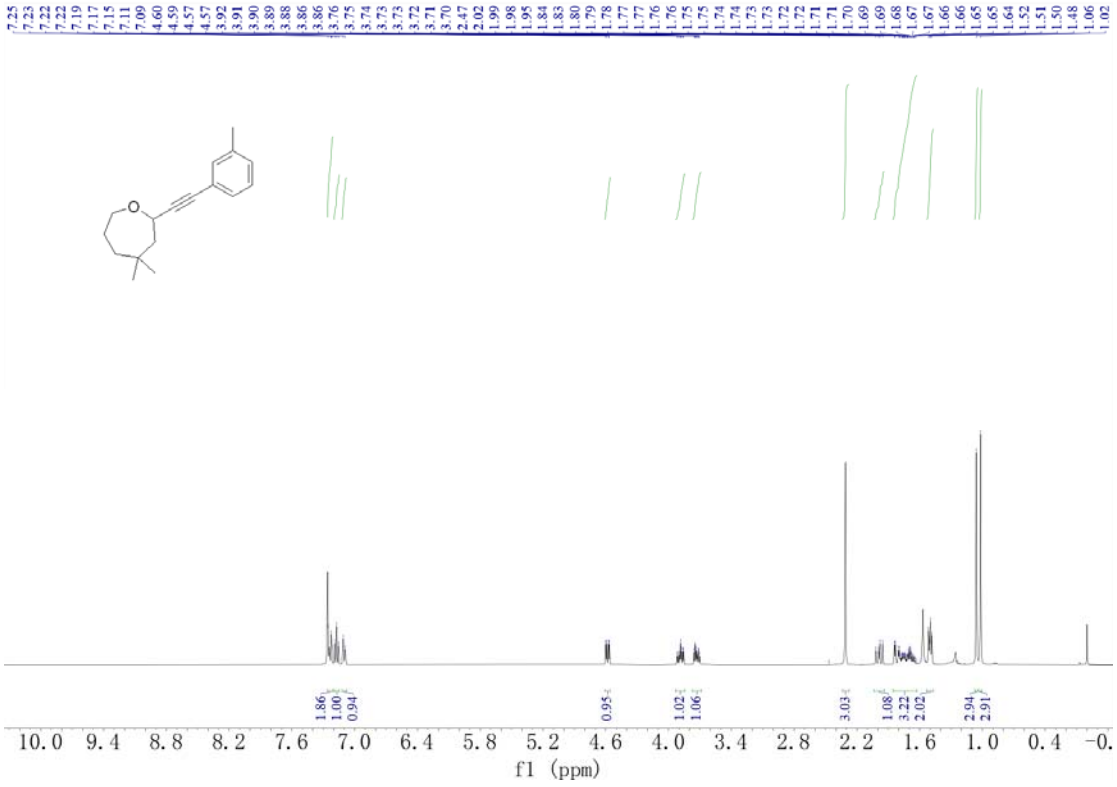
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



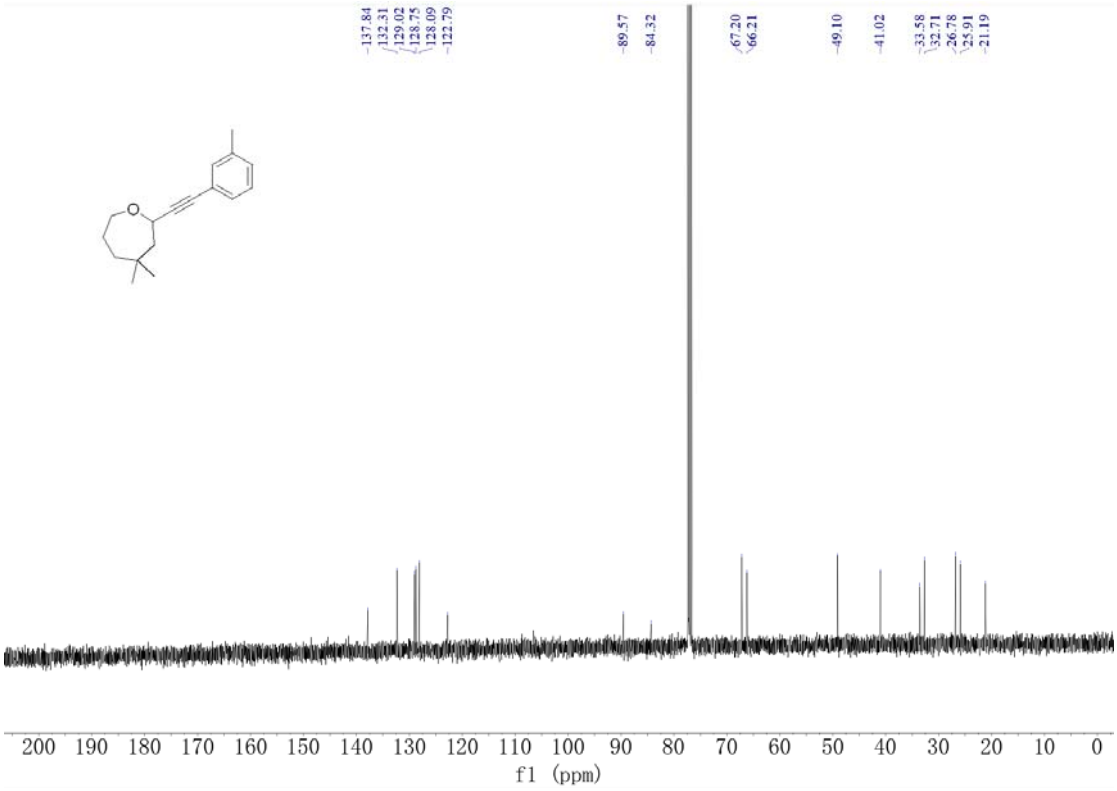
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3s**



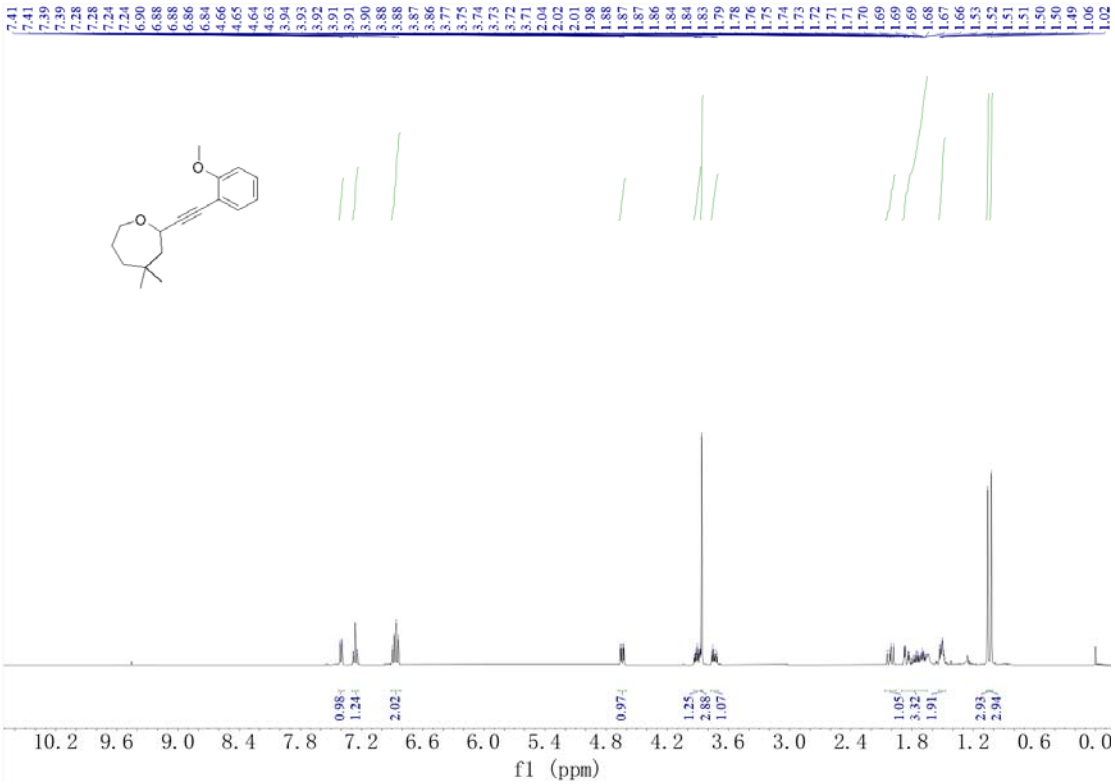
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



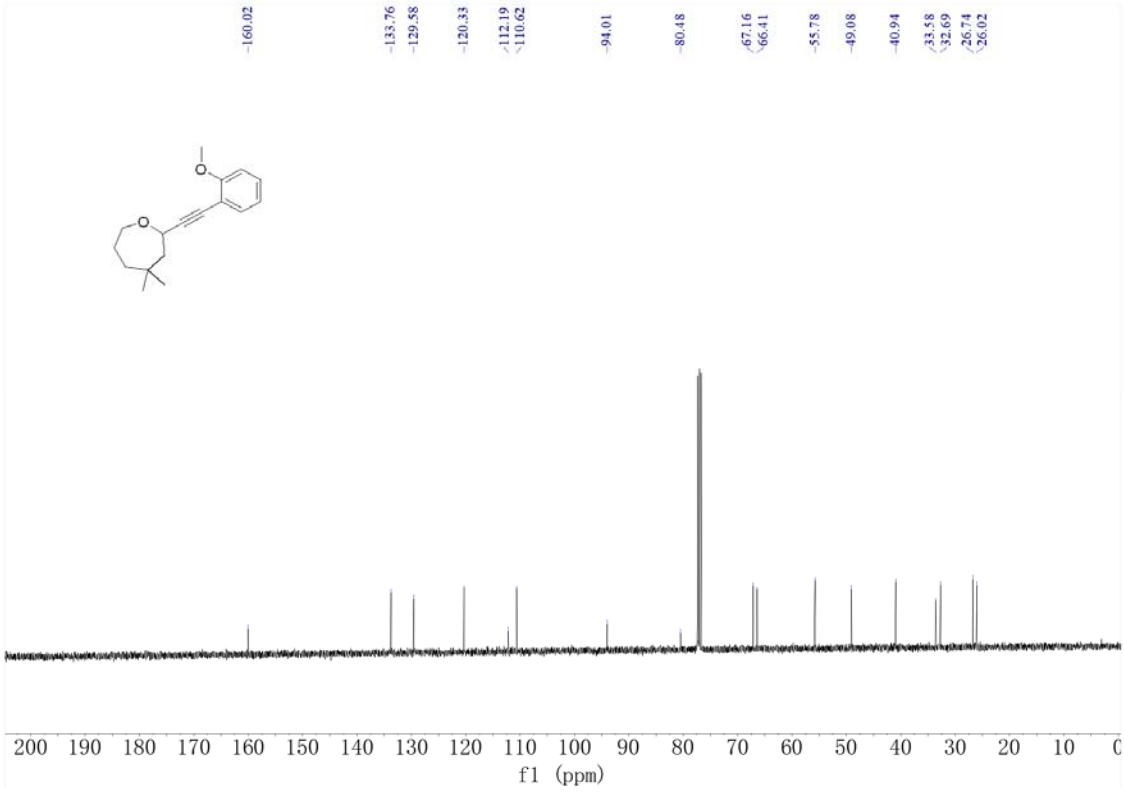
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3t**



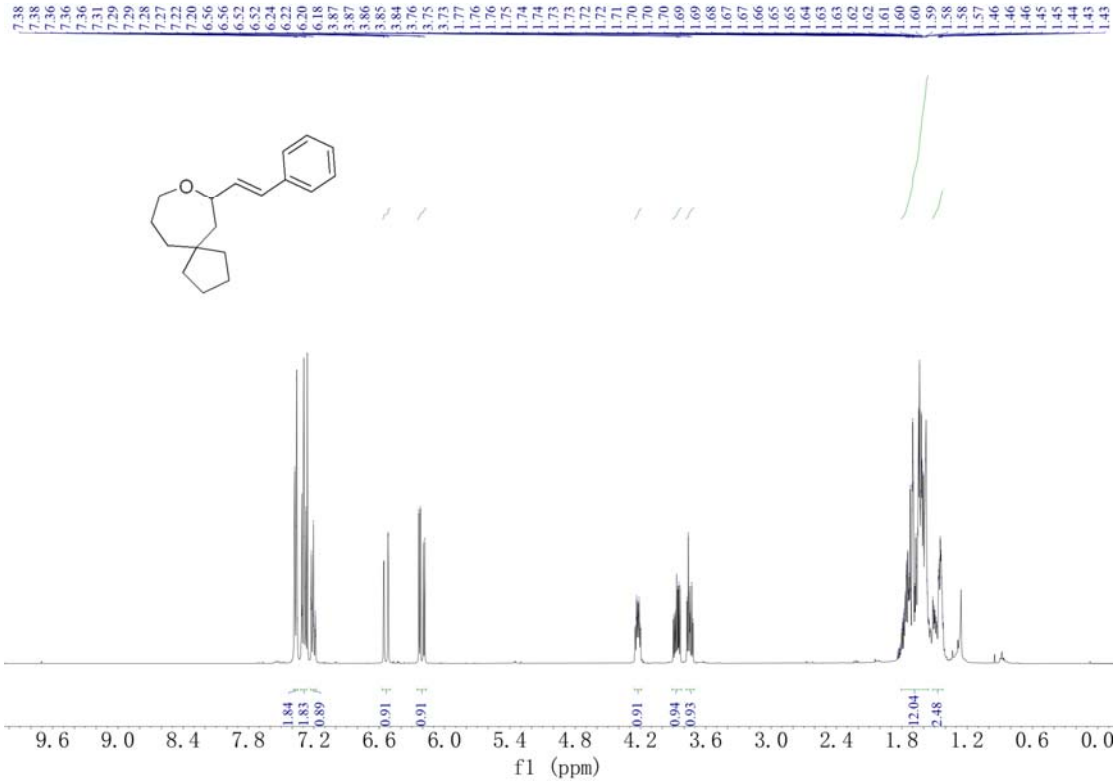
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



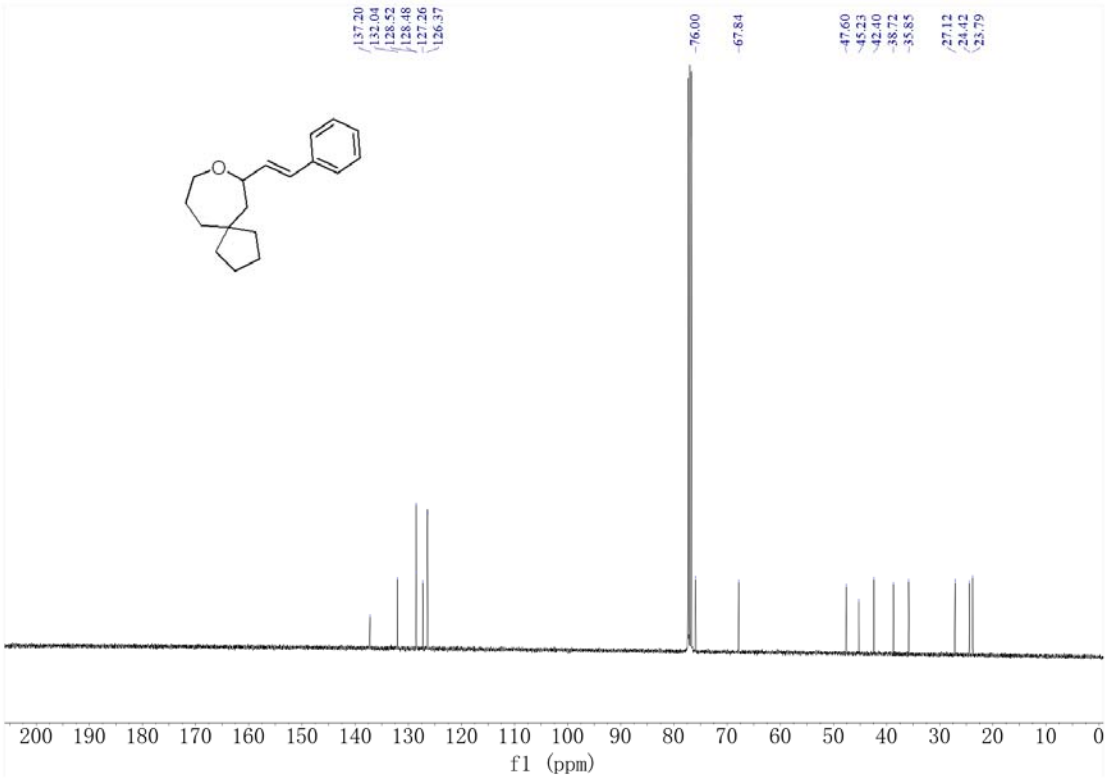
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **3u**



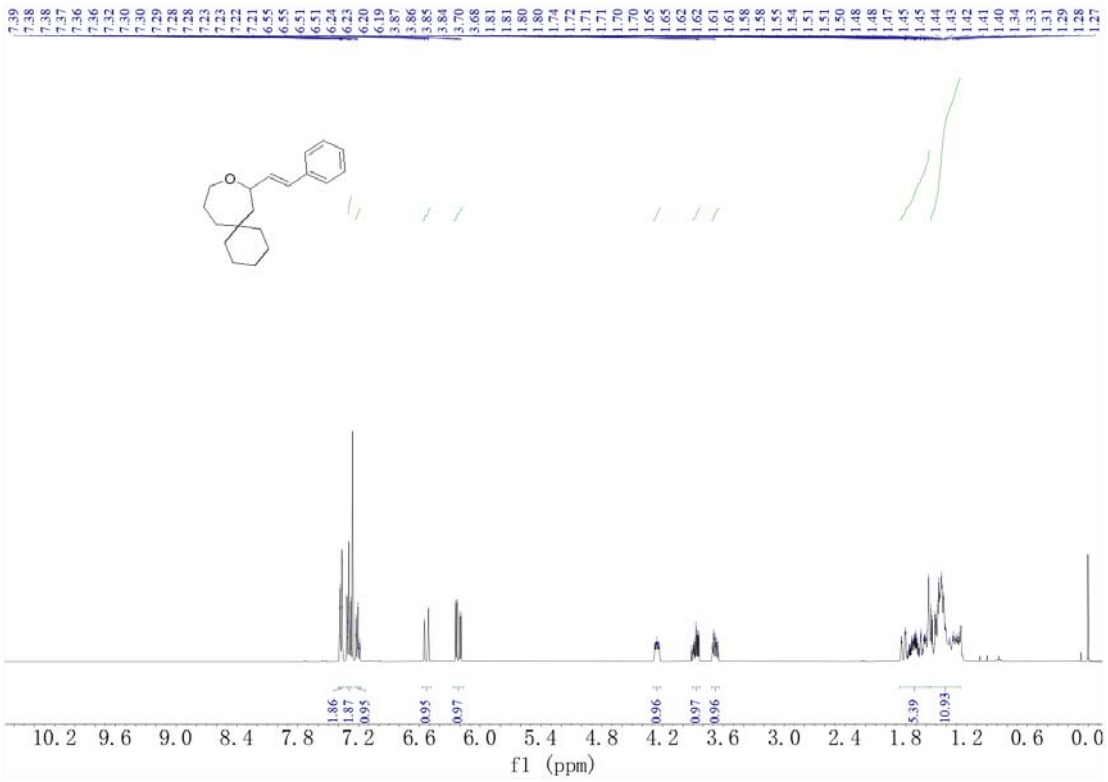
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



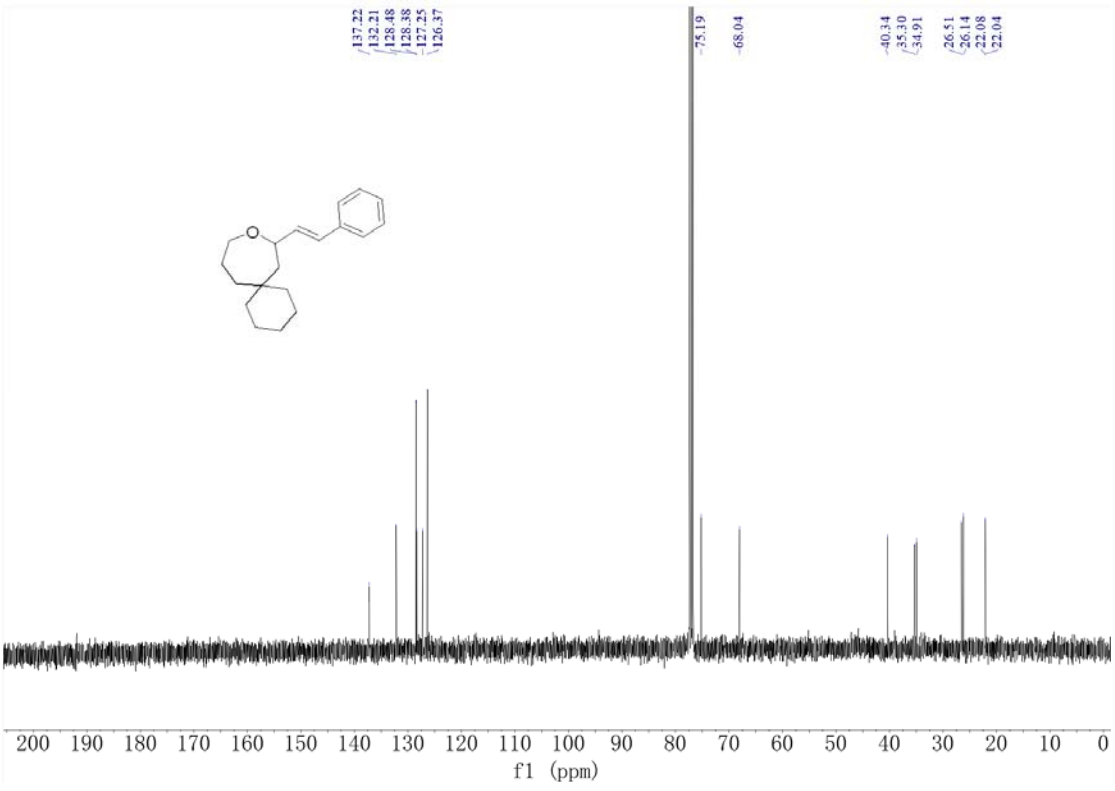
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4a**



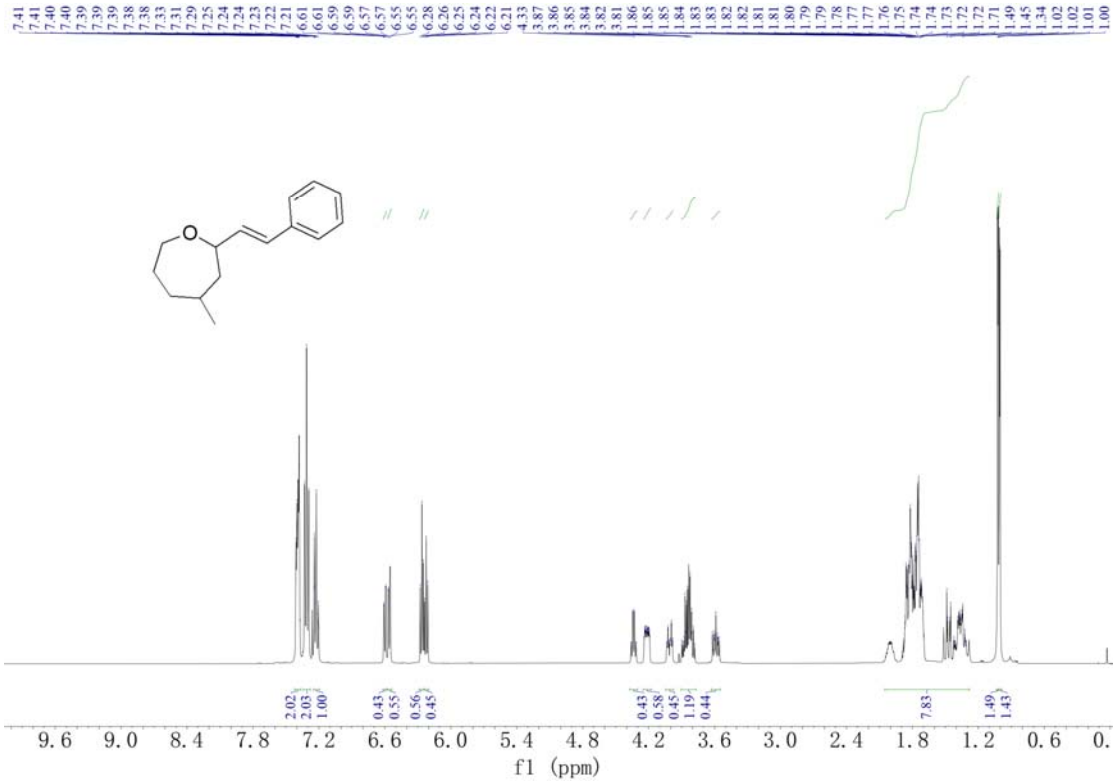
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



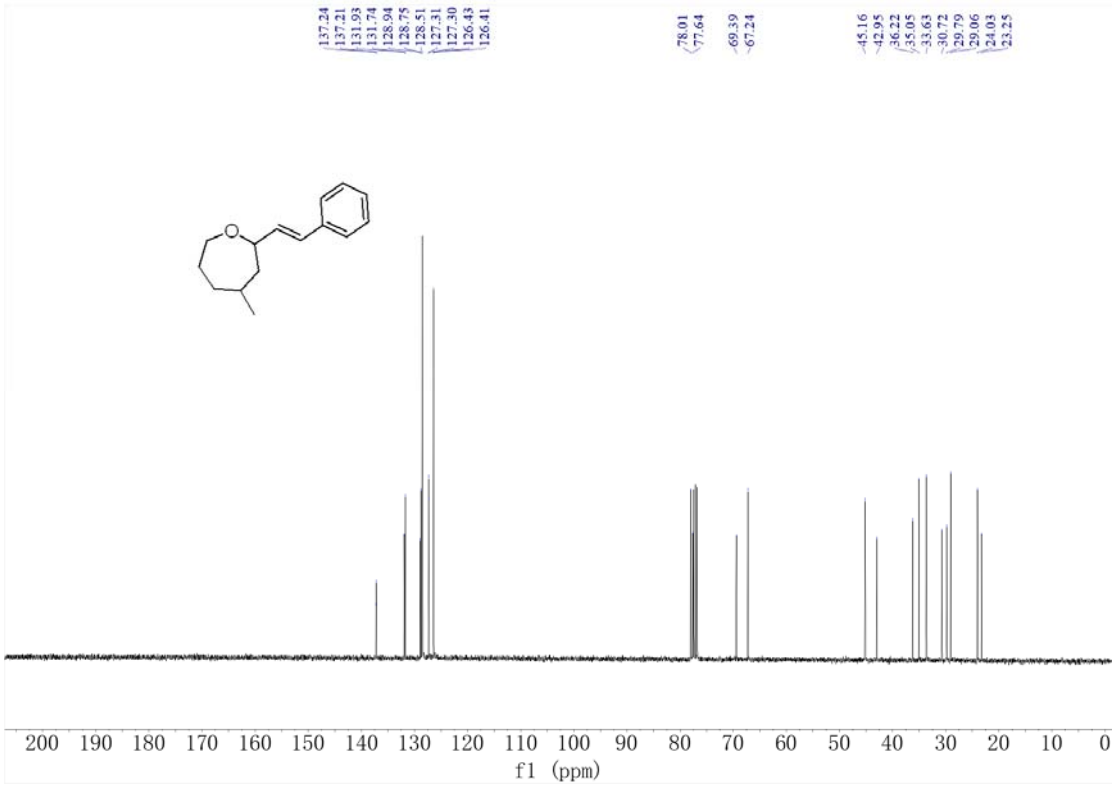
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4b**



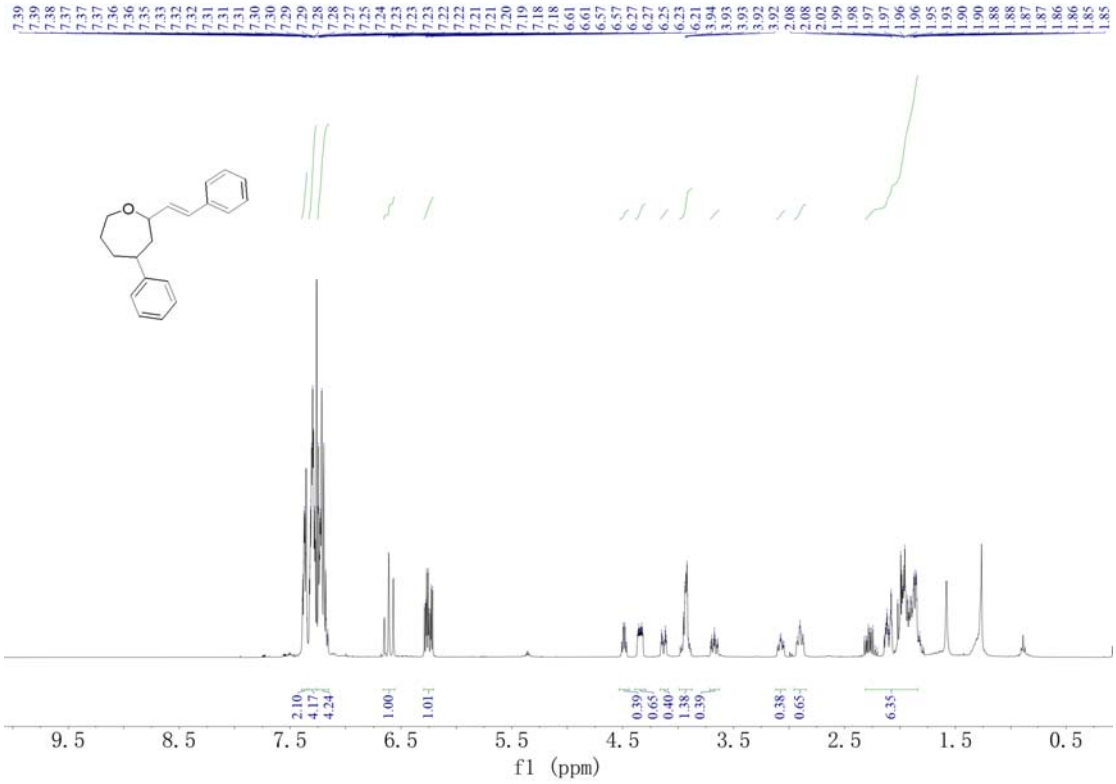
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



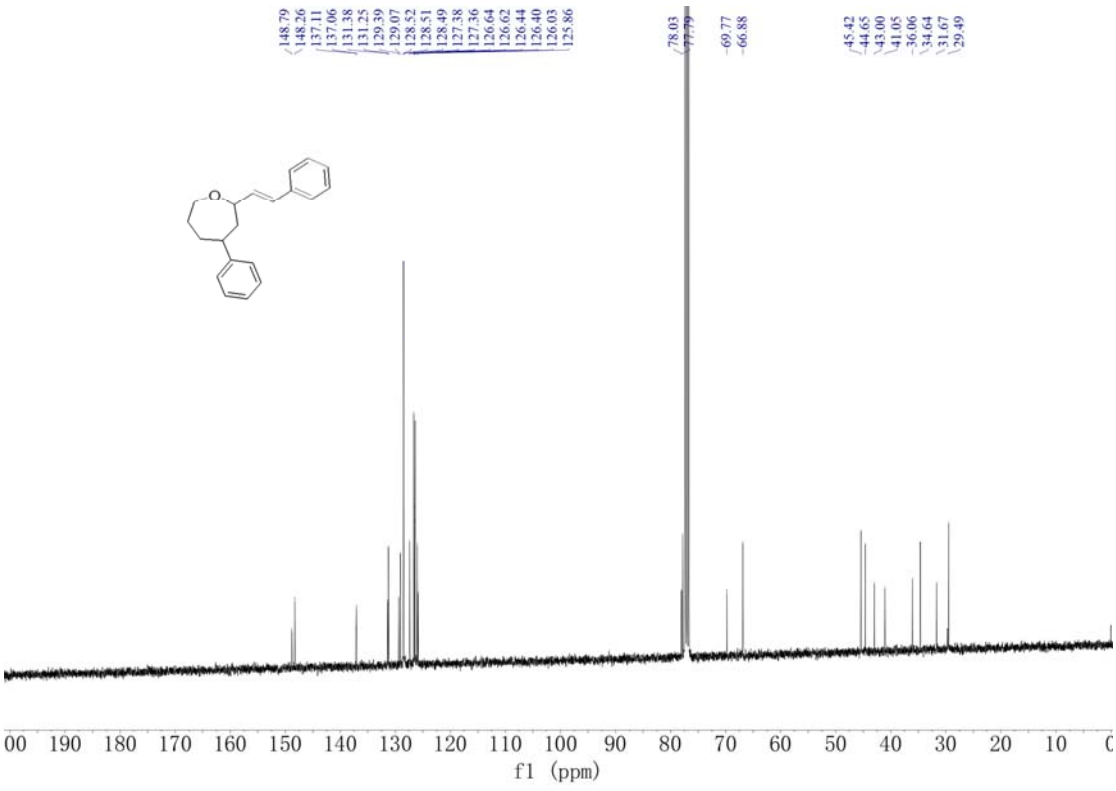
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4c**



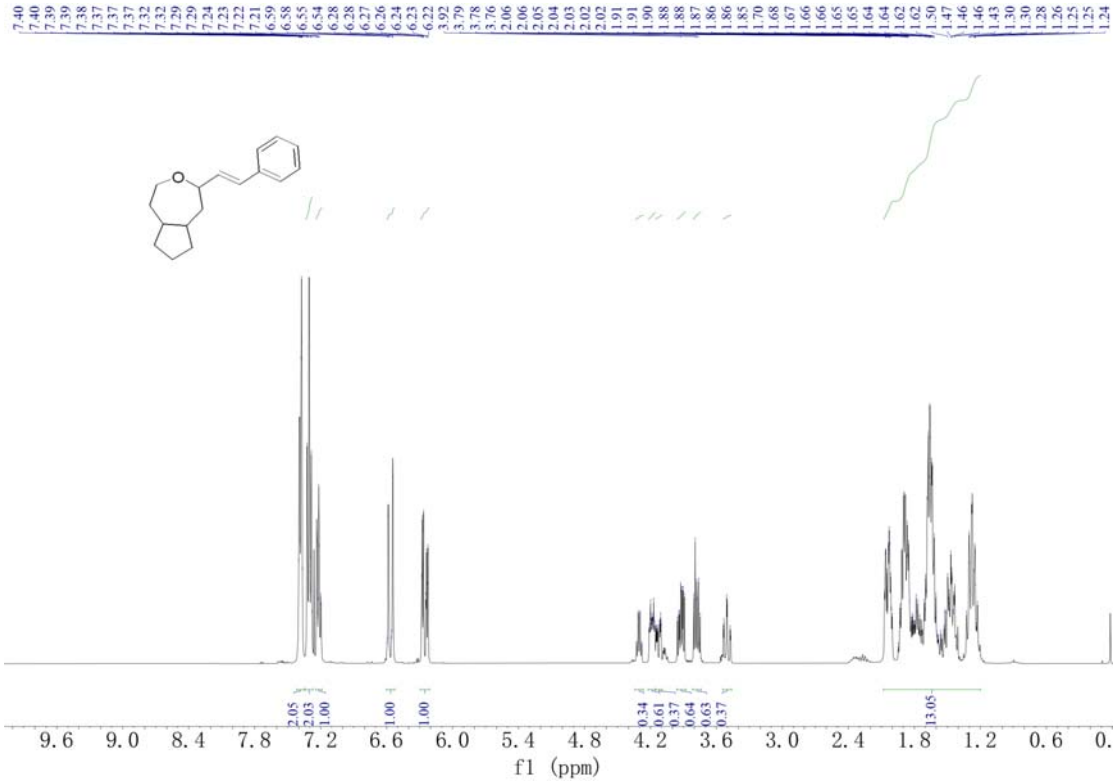
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



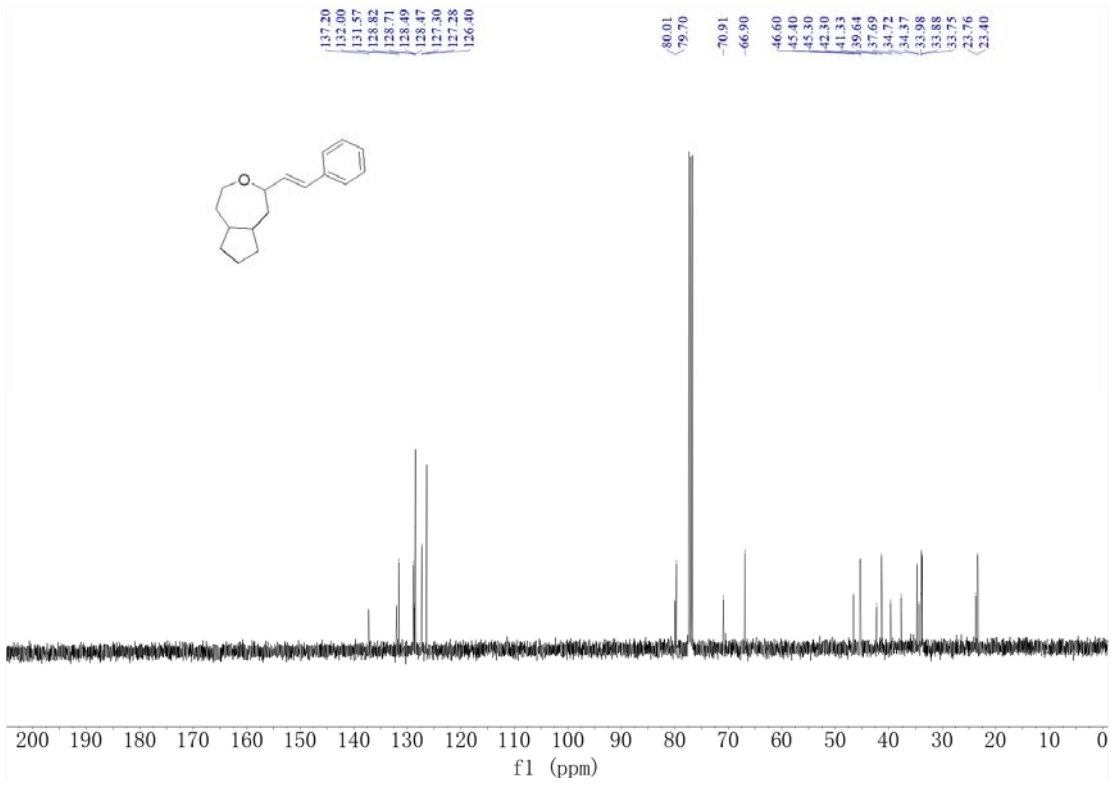
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4d**



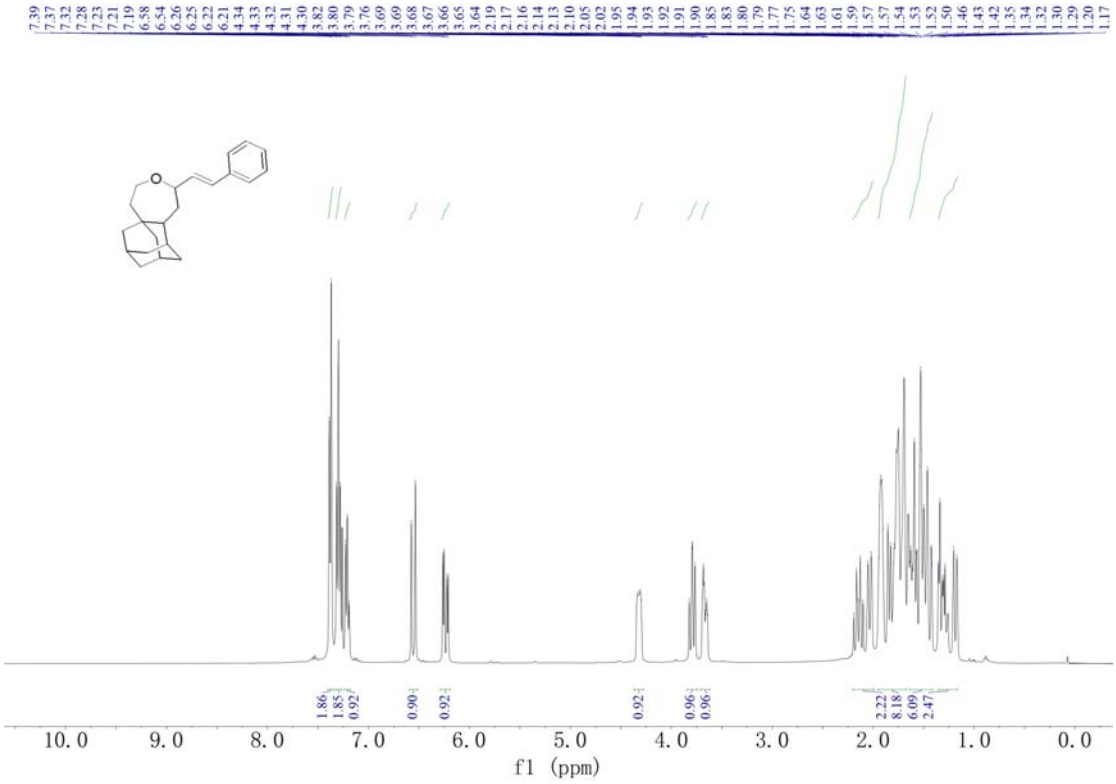
^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



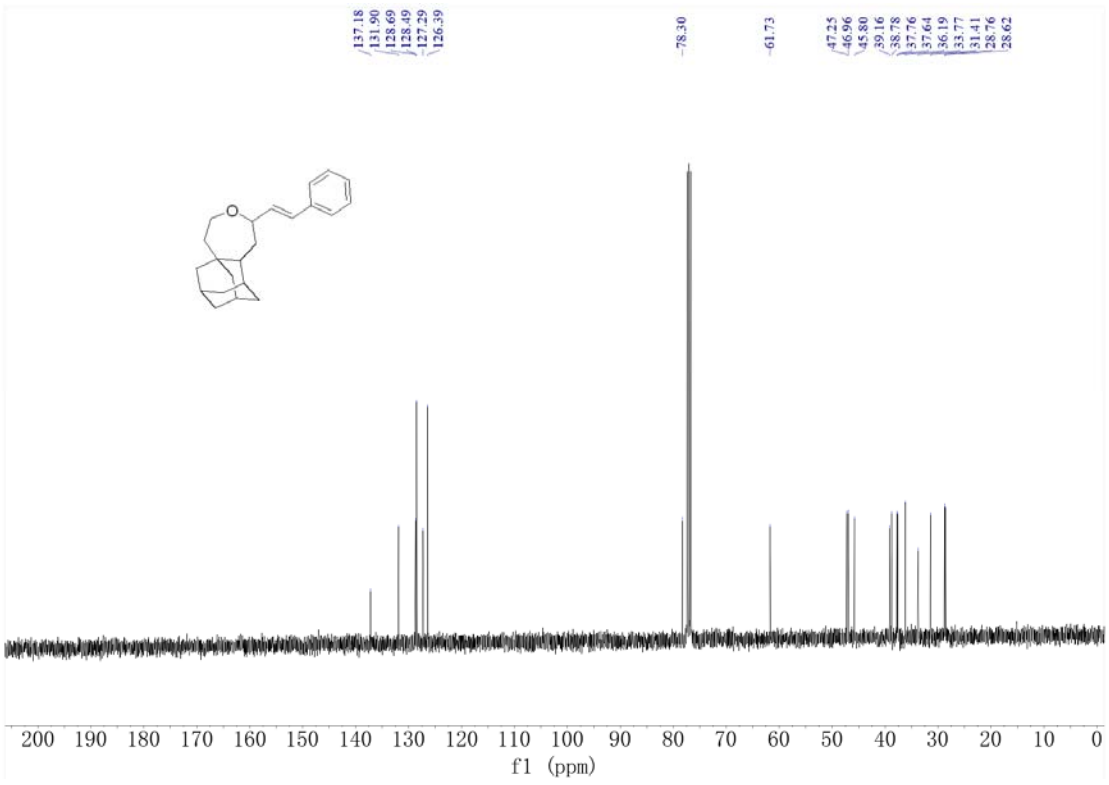
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4e**



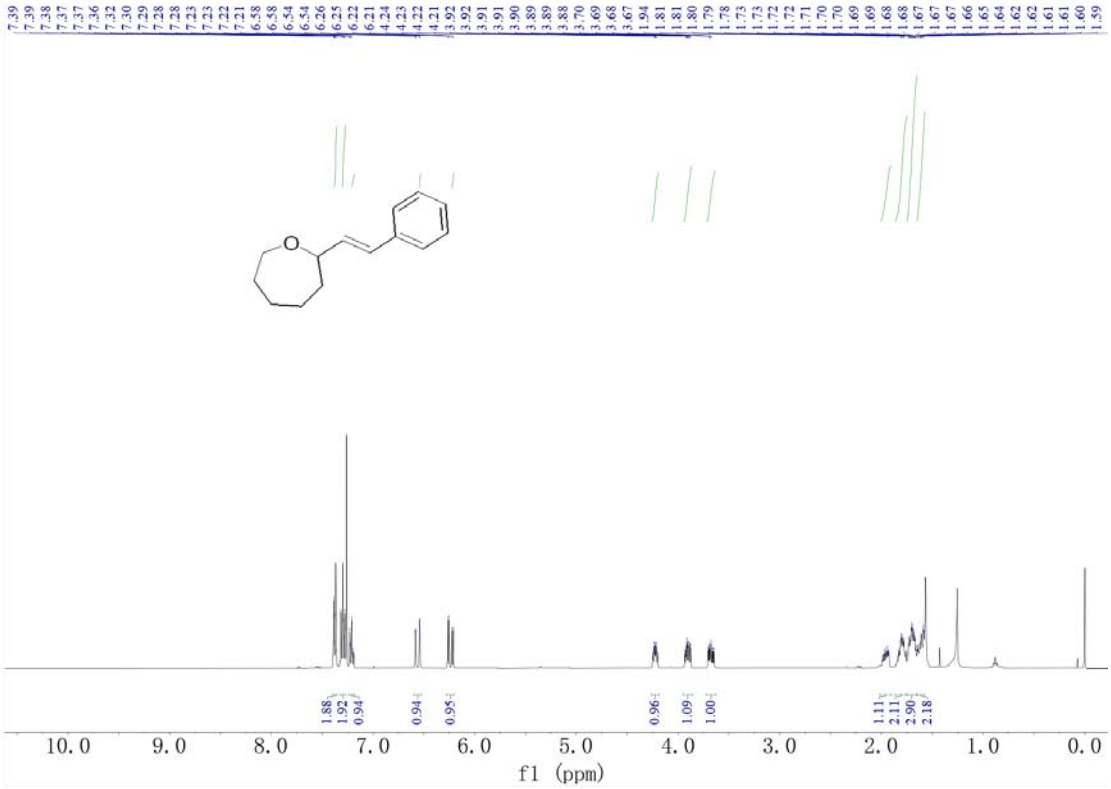
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



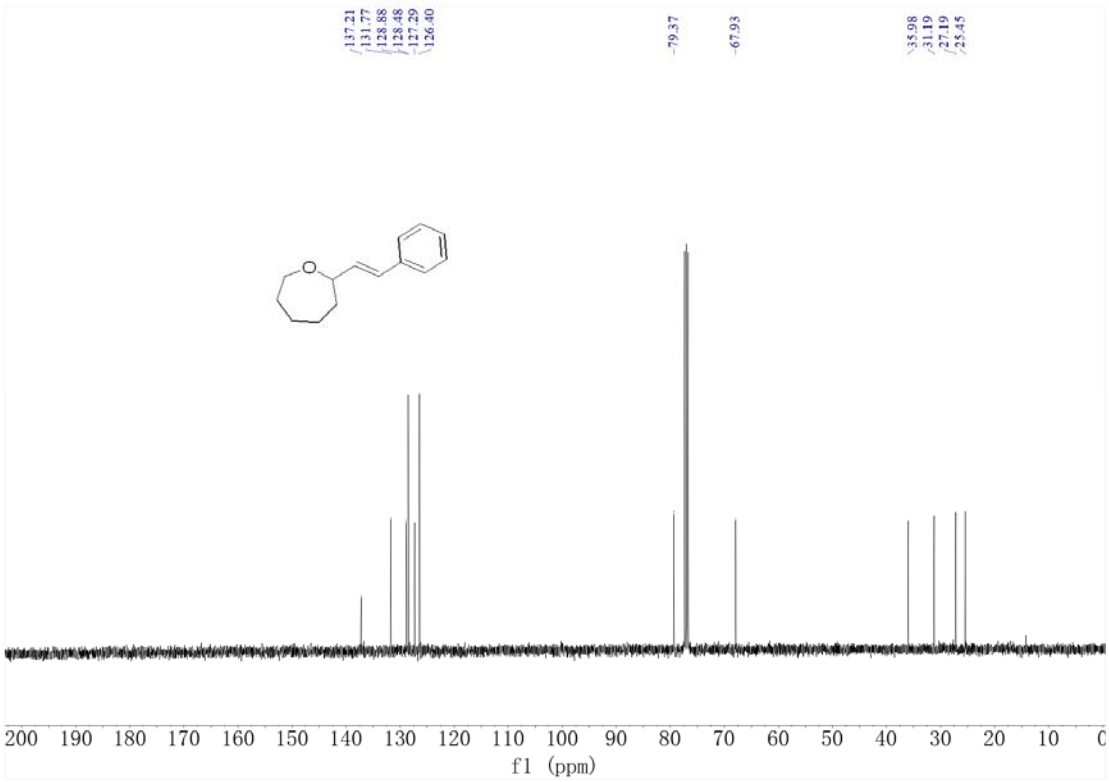
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4f**



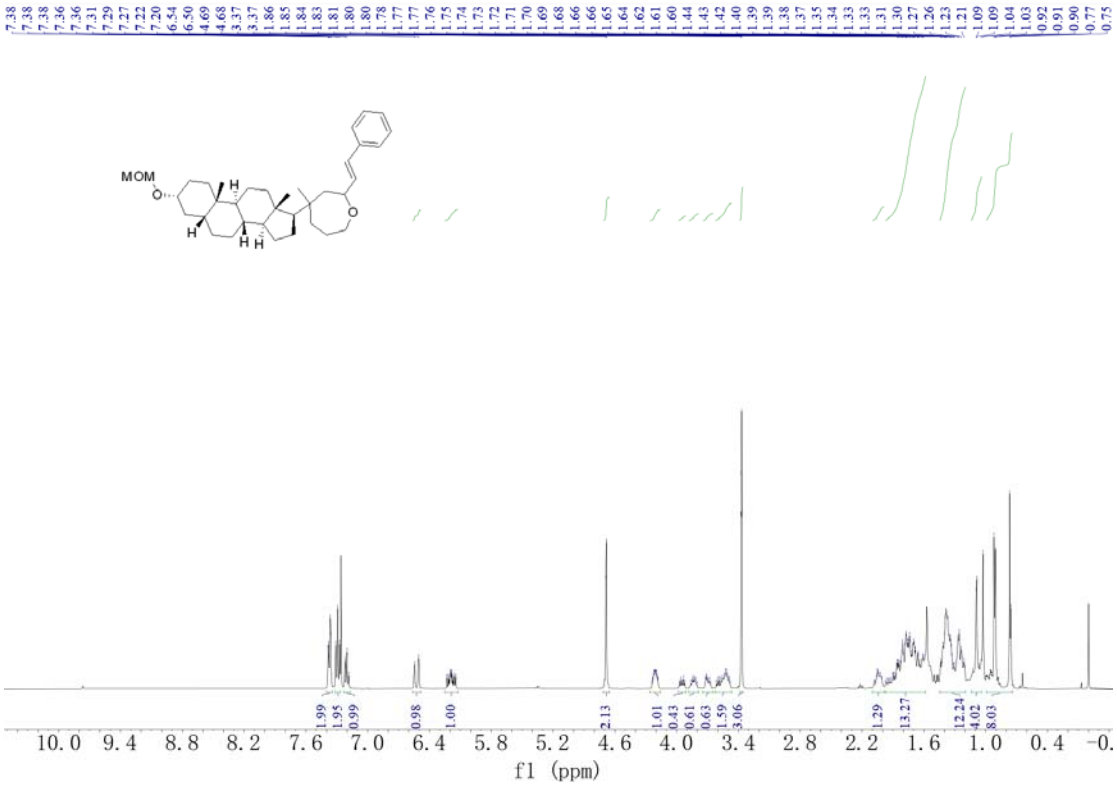
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



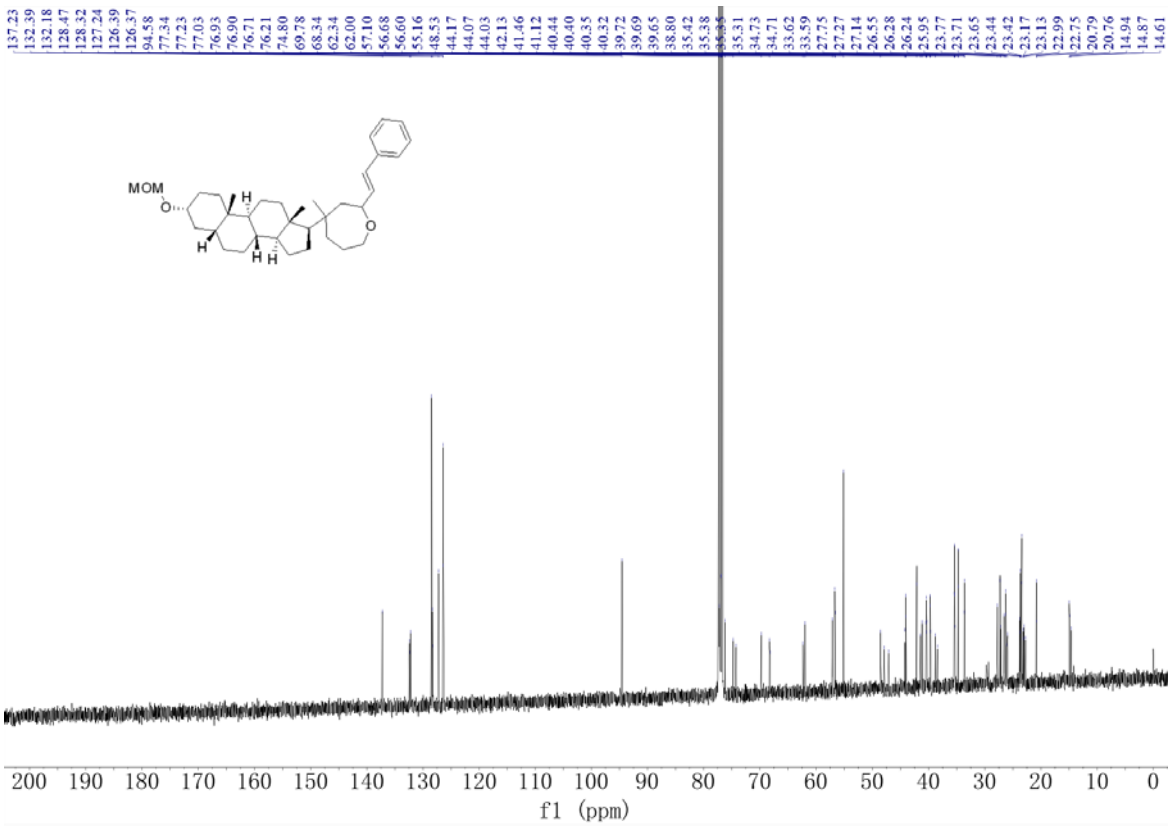
^{13}C{1H} NMR (101 MHz, $CDCl_3$) of **4g**



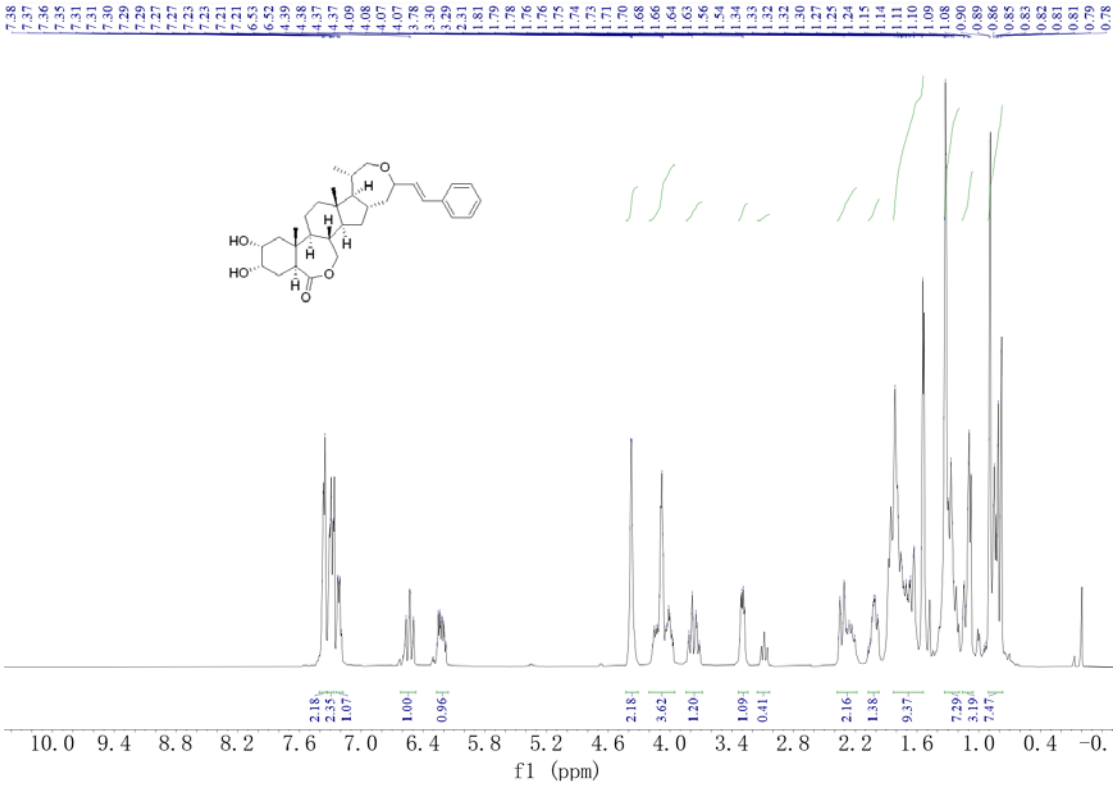
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



^{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**