# Electronic Supplementary Information (ESI) for

# Highly Selective and Efficient Olefin Epoxidation with Pure Inorganic-ligand Supported Iron Catalysts

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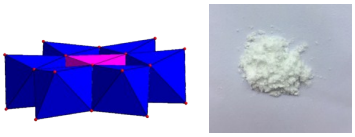
Contents

## 1. General Experimental Conditions

Anderson POMs were prepared according to literature methods[1]. All reagents obtained from Admas-beta were used without further purification. $^1$H Nuclear Magnetic Resonance ($^1$H NMR) spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for proton) spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ or DMSO-$d_6$ as solvent in all cases, and chemical shifts were reported in parts per million (ppm, δ). FT-IR spectra were recorded on Thermo fisher Nicolet 6700. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detectorequipped with an Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or a Stabilwaxcapillary column (internal diameter = 0.25 mm, length = 30 m). GC mass spectra were recorded on Shimadzu GCMS-QP2010 with a capillary column (0.25 mm× 30 m). Column chromatography was performed using 200-300 mesh base-washed silica gel.

## 2. Synthesis and Characterizations of Catalyst.



$(NH_4)_3[FeMo_6O_{18}(OH)_6]$ ( $Fe^{III}Mo_6$)

$(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$ was synthesized according to a published procedure[1] with suitable modification:$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (15.9 g) was dissolved in water (250 mL) and then heated to 100 $^oC$.$Fe_2(SO_4)_3$ (3.8 g) was dissolved in water (60mL), which was slowly added in the solution with stirring. The pH value of mixed solution was kept to about 2.5~3.0. The mixture was still being stirred for 1h after complete adding, and then the crude ammonium salt filtrate obtained from the hot solution. The brown block crystals were filtered off after the filtrate stewed for 12h at room temperature. The colorless aim product (11.8 g) was collected after recrystallized in hot water (80 $^oC$) for two times. IR: 3165 ($\nu_{as}$NH, m), 1640.57 (δOH m), 1400.95 (δNH, s), 946.05(ν Mo=O, vs), 845.10(ν Mo=O, vs), 649.37 (νMo-O-Mo, vs), 574.83 (νM-O-Mo, w) $cm^{-1}$.

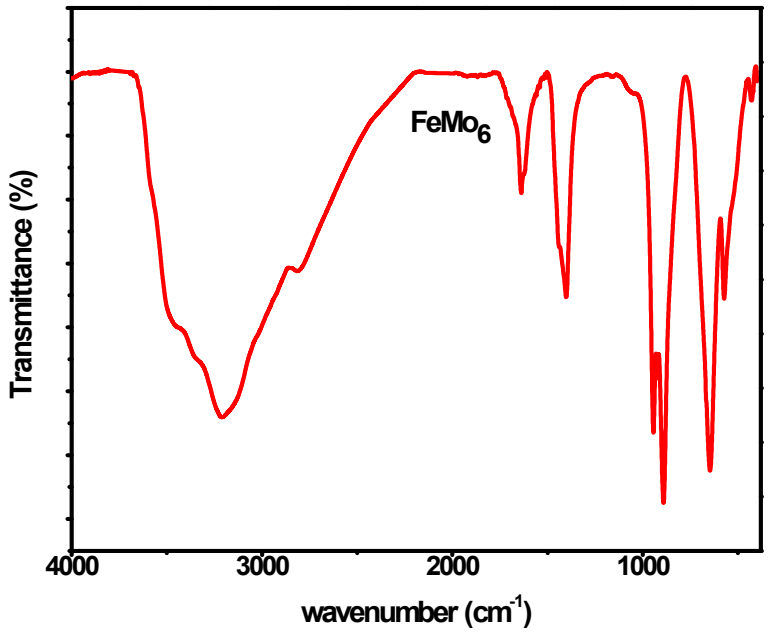



**Figure S1.** FT-IR spectra of prepared $(NH_4)_3[FeMo_6O_{18}(OH)_6]$

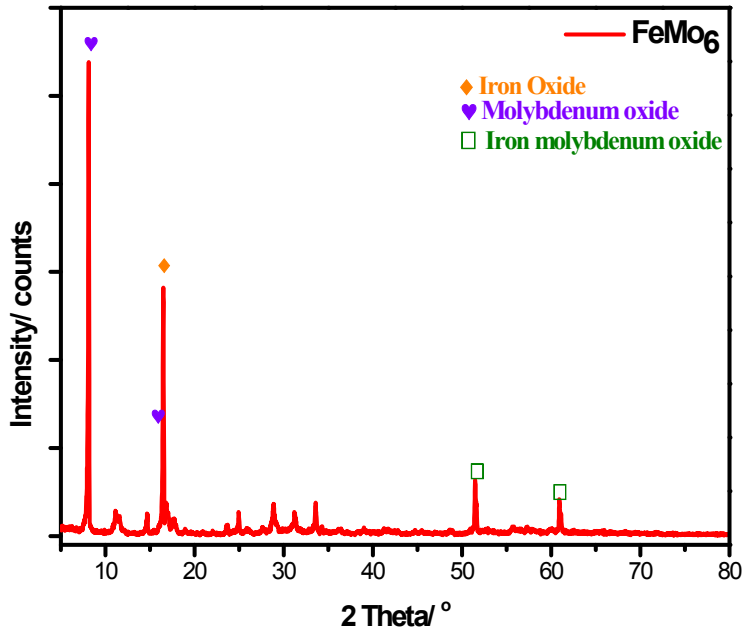



**Figure S2.** XRD analysis of prepared $(NH_4)_3[FeMo_6O_{18}(OH)_6]$

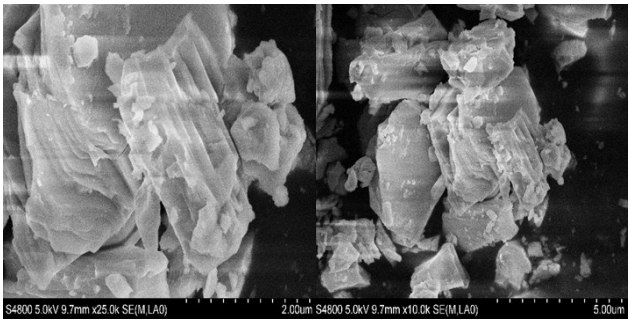



**Figure S3.** SEM analysis of prepared $(NH_4)_3[FeMo_6O_{18}(OH)_6]$

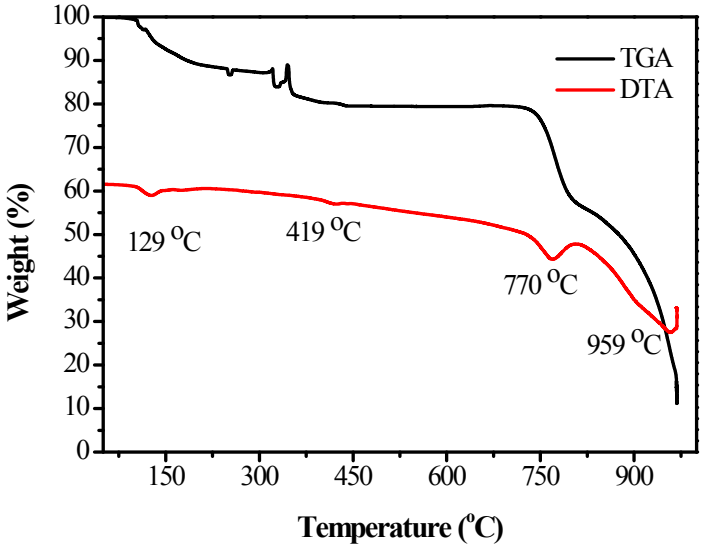



**Figure S4.** TGA analysis of prepared $(NH_4)_3[FeMo_6O_{18}(OH)_6]$

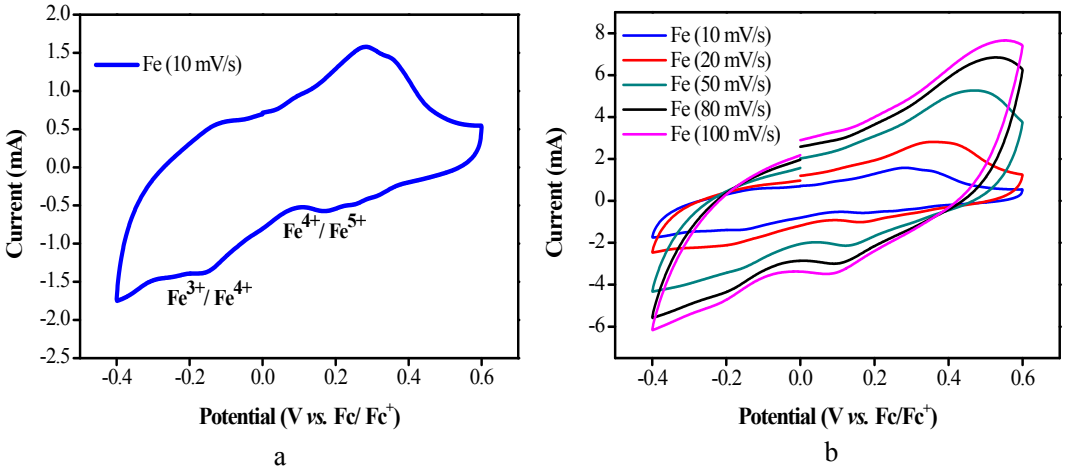


**Figure S5.** Cyclic voltammetry curve of catalyst **1**

## 3. General Procedure for Catalytic Epoxidation of Olefins

Olefin (1.00 mmol), anhydrous NaHCO3 (8.4 mg, 0.1 mmol), catalyst **1** (0.1 mol%) and acetonitrile (2.0 mL) were added in tube. Then the mixture was stirred at 50 °C, and the reaction progress was monitored by TLC and GC-MS. Yields are determined by GC-MS analysis. After completion of the reaction, 3×2 mL of ether was added, the solid catalyst was isolated by filtration and used for the next runs, and the organic phase was extracted with ethyl acetate (3×5 mL), dried over Na2SO4, then the crude product was obtained by evaporating the solvent and purified through flash column chromatography on a silica gel using (Petroleum ether/ Ethyl acetate=10:1 v/v) to afford the desired product.

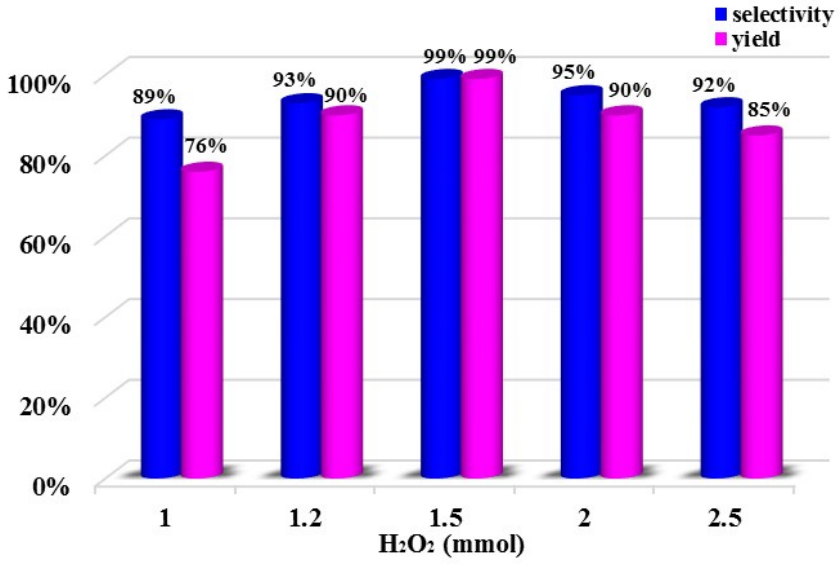



**Figure S6.** Effect of varying $H_2O_2$ amount on the oxidation of cyclohexene catalyzed by catalyst **1**. Reaction conditions: Cat.**1** (0.1 mol%), cyclohexene (1 mmol), $H_2O_2$ (x equiv.), $NaHCO_3$ (0.1 equiv.), $CH_3CN$ (2 mL), selectivity and yield were determined by GC-MS analysis of the crude reaction mixture.

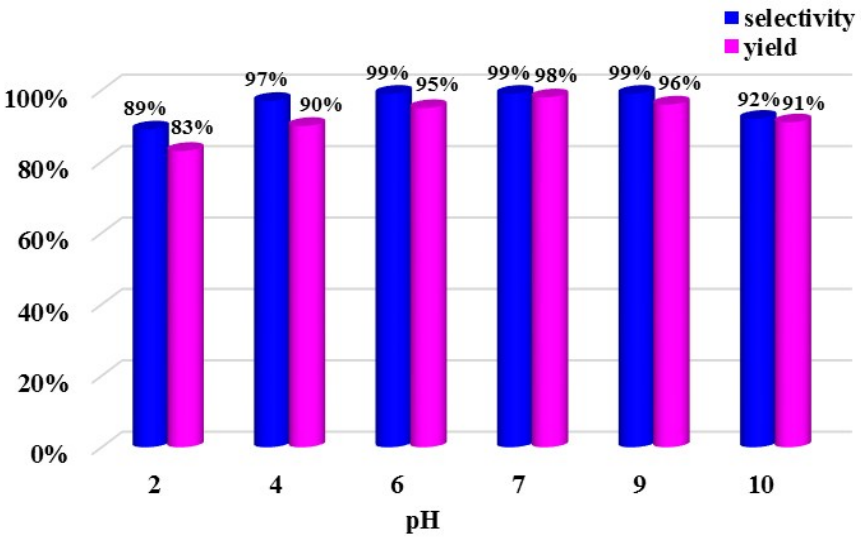



**Figure S7.** Screening of pH in the aqueous oxidation of cyclohexene using 1.5 equiv. $H_2O_2$ catalyzed by 0.1 mol % catalyst **1** at 50 °C. Reaction conditions: Cat.**1** (0.1 mol%), cyclohexene (1 mmol), $H_2O_2$ (1.5 equiv.), $NaHCO_3$ (0.1 equiv.), $CH_3CN$ (2 mL).Selectivity and yield were determined by GC-MS analysis of the crude reaction mixture.

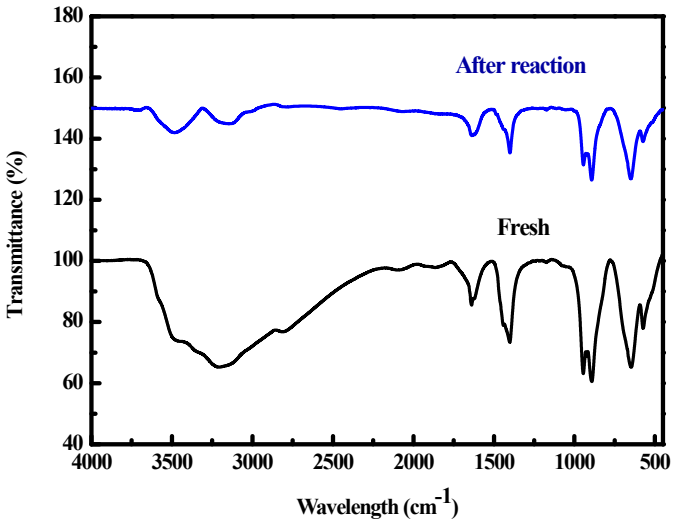



**Figure S8.** The FT-IR spectra of the catalyst before and after reaction.

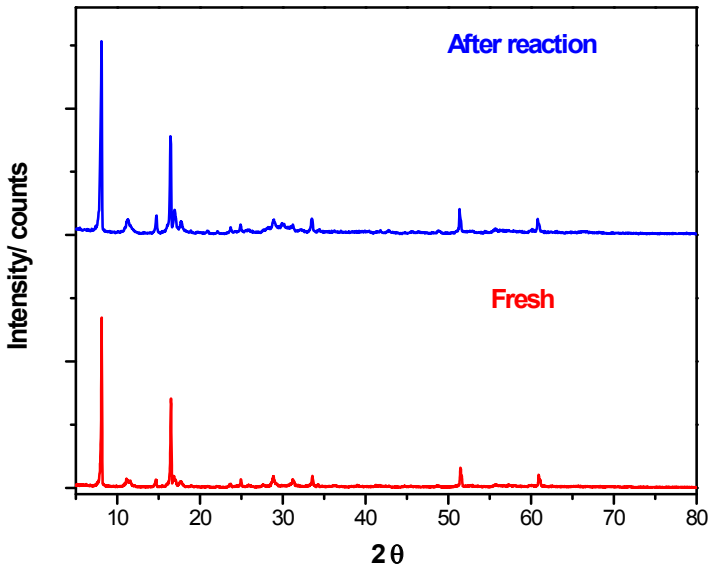
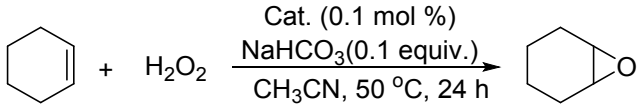


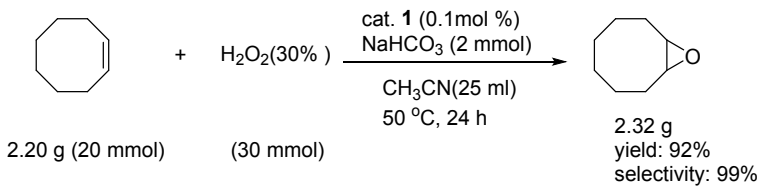

**Figure S9.** The XRD spectrum of the catalyst before and after reaction.

**Table S1** Influence of catalysts [a]




| Entry | Cat.(mol%) | Sel.(%)[b] | Yield(%)[c] |
|---|---|---|---|
| 1 | $Fe_2(SO_4)_3$ | - | - |
| 2 | $Fe(NO_3)_3$ | - | - |
| 3 | $Na_2MoO_4$ | - | - |
| 4 | $(NH_4)_6[\mathbf{MoMo_6}O_{18}(O)_6]$ | - | - |
| 5 | $(NH_4)_4[\mathbf{Cu}Mo_6O_{18}(OH)_6]$ | 62 | 52 |
| 6 | $(NH_4)_3[\mathbf{CoMo_6}O_{18}(OH)_6]$ | 79 | 57 |
| 7 | $(NH_4)_4[\mathbf{NiMo_6}O_{18}(OH)_6]$ | 51 | 36 |

[a]Reaction conditions: Cat. (0.1 mol %), cyclohexene (1 mmol), $H_2O_2$ (1.5 equiv.), $NaHCO_3$(0.1 equiv.), $CH_3CN$ (2 mL). [b,c]Selectivity and yield were determined by GC-MS analysis of the crude reaction mixture.




**Scheme S1. Gram-scale reaction.** Reaction conditions: Cat. **1** (0.1 mol%), olefins (1.0 mmol), $H_2O_2$ (1.5 equiv.), $NaHCO_3$ (0.1 equiv.), $CH_3CN$ (2 mL).

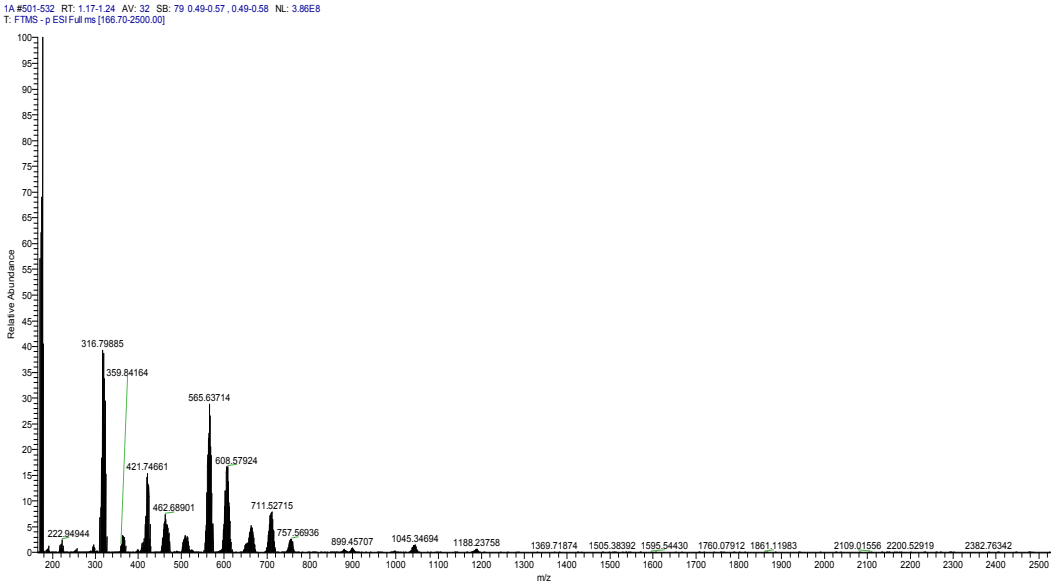



**Figure S10.** ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$

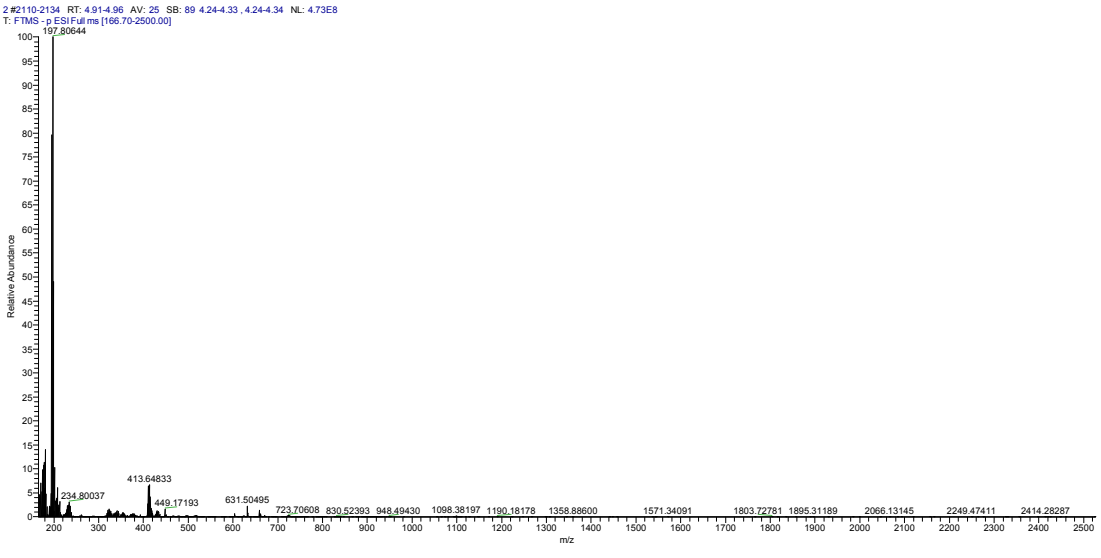



**Figure S11.** ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$+$H_2O_2$

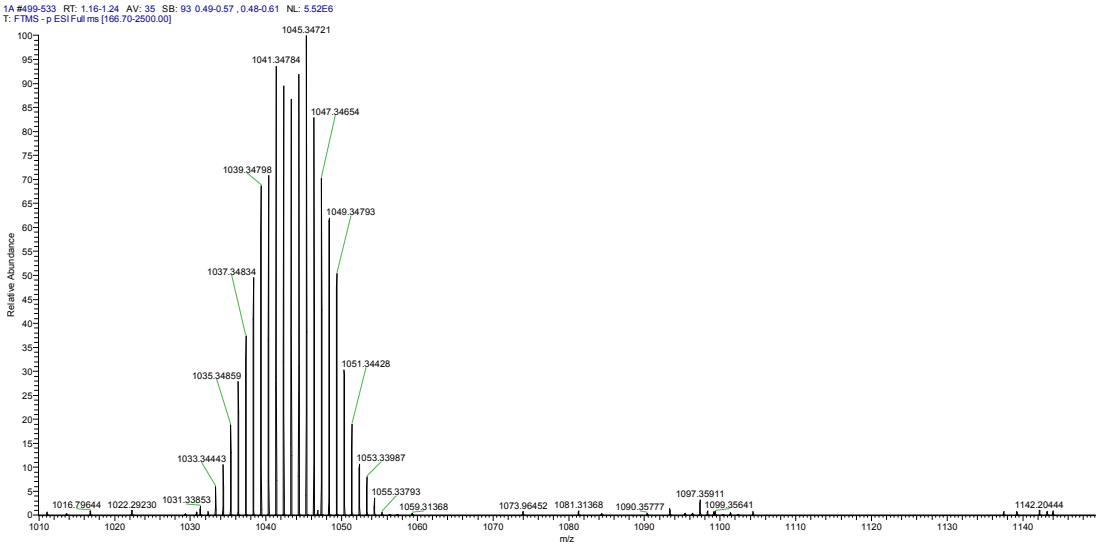



**Figure S12.** Zoom the area of ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$, (m/z = 1010-1500, $\{NH_4H[FeMo_6O_{24}H_6]\}^{1-}$=1043.34 g/mol)

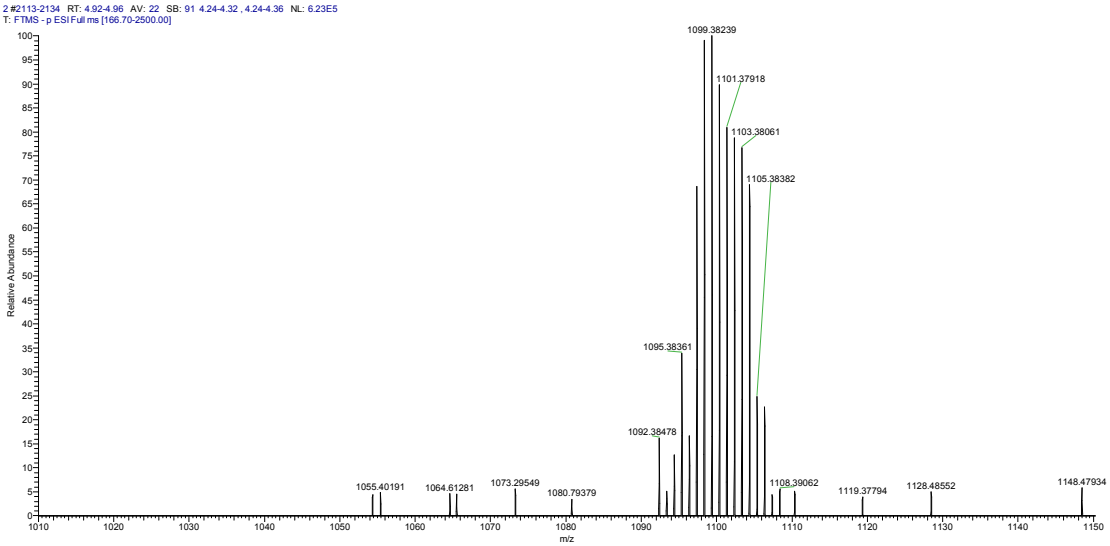



**Figure S13.** Zoom the area of ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ + $H_2O_2$, (m/z = 1010-1500, $\{Na_2[FeMo_6O_{24}H_6] + O\}^{1-}\cdot H_2O$ = 1100.61 g/mol)

## 4. NMR Data of Isolated Compounds.

**2-phenyloxirane (2):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.45-7.28 (m, 5H), 3.95-3.84 (m, 1H), 3.22-3.12 (m, 1H), 2.84 (dd, *J* = 5.4, 2.5 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 137.71, 128.54, 128.21, 125.56, 52.36, 51.16.

**2-(4-fluorophenyl)oxirane (3):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 3.85 (s, 1H), 3.13 (d, *J* = 5.2 Hz, 1H), 2.76 (dd, *J* = 5.3, 2.5 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.68, 161.73, 133.39, 127.17, 115.37, 51.80, 51.07.

**2-(4-chlorophenyl)oxirane (4):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.86 (s, 1H), 3.22-3.08 (m, 1H), 2.78 (dd, *J* = 5.2, 2.2 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 136.21, 133.97, 128.73, 125.85, 51.79, 51.20.

**2-(3-chlorophenyl)oxirane (5):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 4.8 Hz, 3H), 7.16 (d, *J* = 5.0 Hz, 1H), 3.81 (s, 1H), 3.19-3.06 (m, 1H), 2.76-2.67 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 139.92, 134.60, 129.80, 128.31, 125.54, 123.77, 51.68, 51.16.

**2-(2-chlorophenyl)oxirane (6):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.1 Hz, 1H), 7.29-7.15 (m, 3H), 4.22 (s, 1H), 3.24-3.10 (m, 1H), 2.69-2.55 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 135.66, 129.13, 128.91, 127.06, 125.70, 50.63, 49.99.

**2-(4-bromophenyl)oxirane (7):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.48 (t, *J* = 9.9 Hz, 2H), 7.22-7.11 (m, 2H), 3.84 (s, 1H), 3.25-3.08 (m, 1H), 2.76 (dt, *J* = 25.1, 12.6 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 136.78, 131.67, 127.19, 122.05, 51.83, 51.16.

**2-(4-methoxyphenyl)oxirane (8):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz,

2H), 6.91 (t, *J* = 10.8 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.68 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 10.9 Hz, 1H), 3.84 (d, *J* = 12.0 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.02, 132.21, 125.67, 113.88, 55.30, 29.69, 25.00.

**2-(p-tolyl)oxirane (9):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 33.1, 7.6 Hz, 4H), 4.74 (s, 1H), 3.64 (d, *J* = 26.2 Hz, 2H), 2.35 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 134.57, 129.71, 125.00, 125.46, 125.33, 52.28, 51.00, 31.42.

**2-(4-(tert-butyl)phenyl)oxirane (10):** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.25 (t, *J* = 11.8 Hz, 2H), 3.88 (s, 1H), 3.17 (t, *J* = 4.7 Hz, 1H), 2.84 (dt, *J* = 27.2, 13.6 Hz, 1H), 1.36 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 151.34, 134.57, 129.71, 129.67, 125.46, 125.33, 52.28, 51.00, 34.61, 31.33.

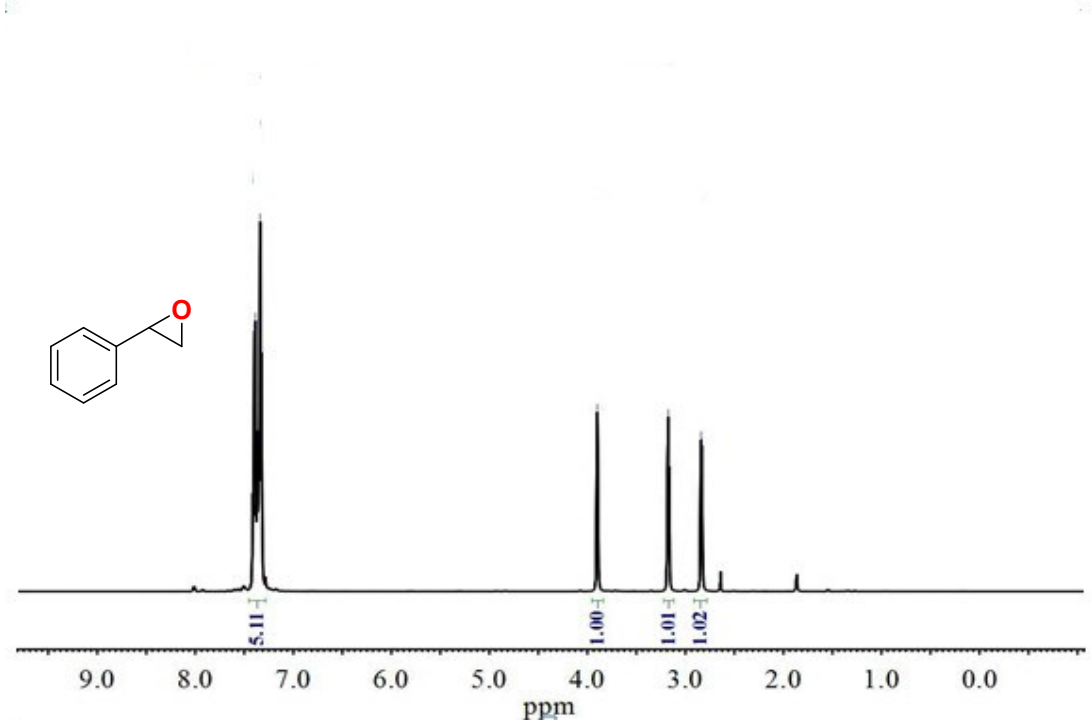
**(*R*)-methyl-6-isopropyl-2-oxo-4-((2R,3R)-3-phenyloxiran-2-yl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (44)**[2]**.** $^{1}$H NMR (500 MHz, $CDCl_3$) : δ7.55 (s, 1H), 7.45 (s, 1H), 7.37 (d, *J* = 5.9 Hz, 2H), 7.32 (t, *J* = 5.8 Hz, 2H), 7.28 (s, 1H), 5.03 (s, 1H), 4.14 – 4.09 (m, 1H), 3.93 (d, *J* = 12.6 Hz, 1H), 3.77 (s, 3H), 3.60 (dd, *J* = 12.6, 5.1 Hz, 1H), 1.18 (dd, *J* = 5.2, 2.8 Hz, 6H); ESI-MS m/z 317.13153 ($[M+H]^+$, $C_{17}H_{20}N_2O_4S$ found 316.12231), $^{13}$C NMR (500 MHz, $CDCl_3$) δ 176.36, 165.38, 151.59, 135.98, 131.16, 128.62, 128.15, 127.13, 126.76, 100.15, 63.67, 56.72, 53.73, 51.67, 27.31, 19.96, 19.62; ESI-MS m/z 317.13153 ($[M+H]^+$, $C_{17}H_{20}N_2O_4S$ found 316.1223).

**(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl-2-(3-phenyloxiran 2-yl) -acetate(45)**[3] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 0.61-1.59 (m, 6H), 1.73-2.15 (m, 27H), 2.32-2.64 (m, 8H), 4.23-4.50 (m, 2H), 7.27-7.51 (m, 5H); $^{13}$C NMR (500 MHz, $CDCl_3$) δ = 149.73, 146.45, 143.38, 145.65, 140.73, 139.32, 136.59, 128.68, 128.03, 85.79, 63.95, 54.69, 39.82, 37.81, 36.96, 32.65, 29.17, 33.85, 27.64, 27.96, 25.33, 24.68, 22.79, 21.03, 19.73, 18.62, 14.57, 14.92, 12.35; ESI-MS m/z 613.4223 ($[M+Na]^+$, $C_{39}H_{58}NaO_4$ found 613.4217).

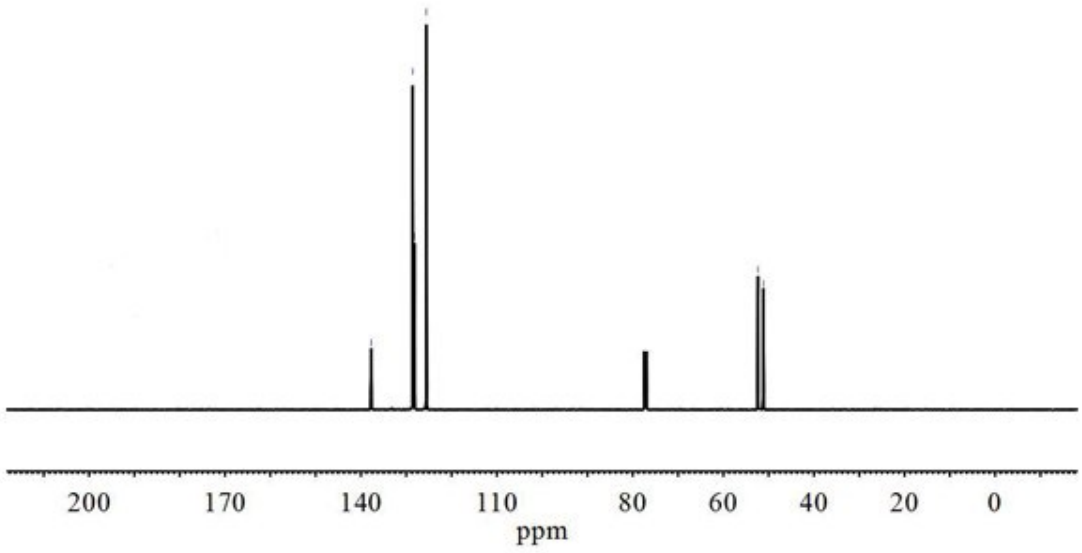
**3-Methyl-3-(4-methylpent-3-enyl)oxiran-2-yl)methyl acetate(46)**[3] $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 1.16-1.27 (m, 5H), 1.60-1.68 (m, 6H), 1.96-2.11 (m, 5H), 2.63 (t, *J* = 6.00 Hz, 1H), 4.46-4.60 (m, 2H), 5.31-5.36 (m,1H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ = 172.11, 142.23, 119.17, 65.72, 60.10, 59.02, 37.03, 28.09, 26.59, 25.17, 22.19, 18.69, 17.31; ESI-MS m/z 212.1417 ($[M+H]^+$, $C_{12}H_{20}O_3$ found 212.1411.).

**(3*S*,10*R*,13*S*,17*S*)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1Hcyclopenta[a]phenanthren-3-yl-2-(3-phenyloxiran-2-yl) acetate(47)**[3] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 0.47-0.68 (m, 4H), 0.93-1.25 (m, 10H), 1.51-1.78 (m, 6H), 1.81-2.12 (m, 6H), 2.23-2.61 (m, 4H), 3.96-4.06 (m, 2H), 4.53-5.01(m, 2H), 5.50-5.72 (m, 1H), 7.16-7.57 (m, 5H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ=210.89, 172.28, 137.85, 138.93, 131.18, 129.95, 129.06, 128.48, 127.86, 126.72, 74.47, 62.58, 60.70, 49.89, 49.87, 45.36, 44.59, 38.89, 37.70, 35.91, 31.63, 25.89, 24.97, 22.07, 21.89, 17. 84, 14.26, 13.20; ESI-MS m/z 499.2824 ($[M+Na]^+$, $C_{31}H_{40}NaO_4$ found 499.2831).

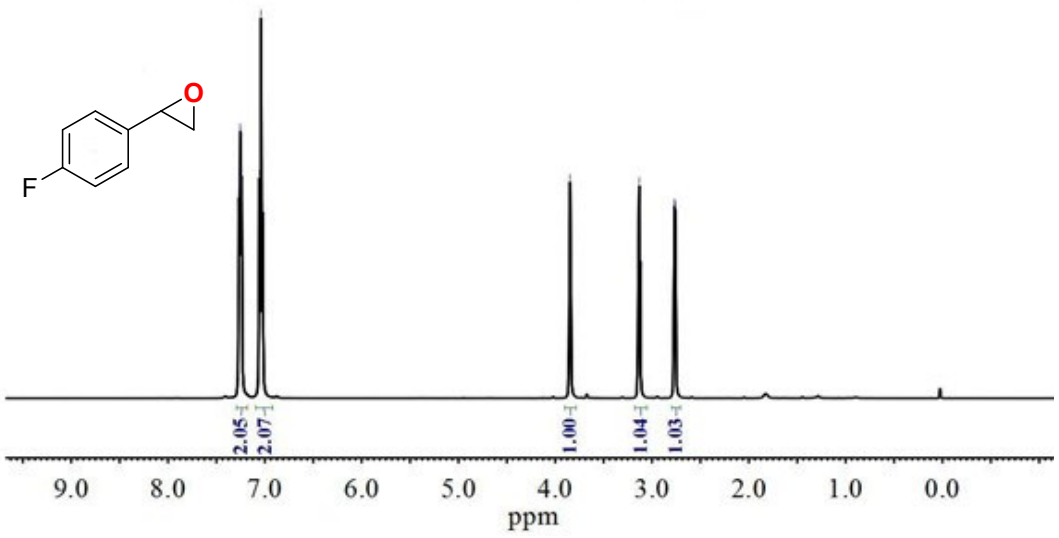
## 5. NMR spectra of isolated products



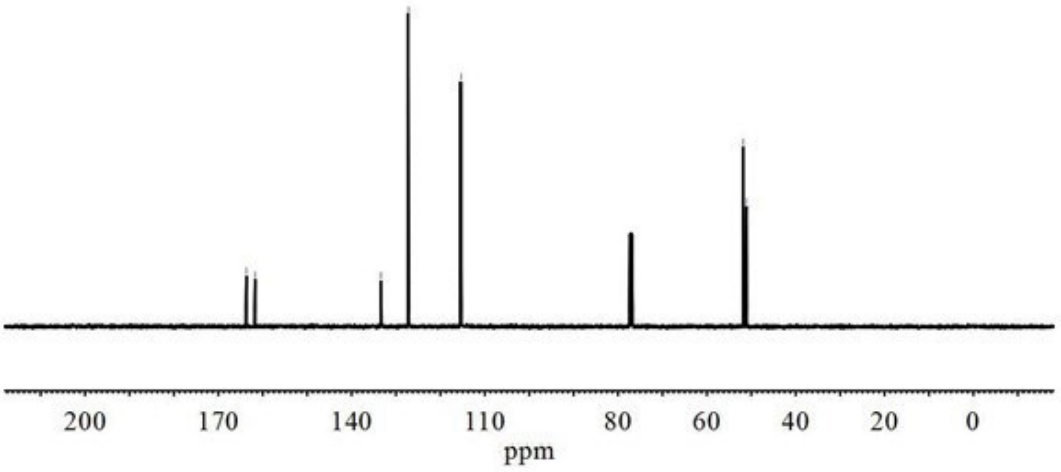

**$^{1}$H NMR spectra of 2**



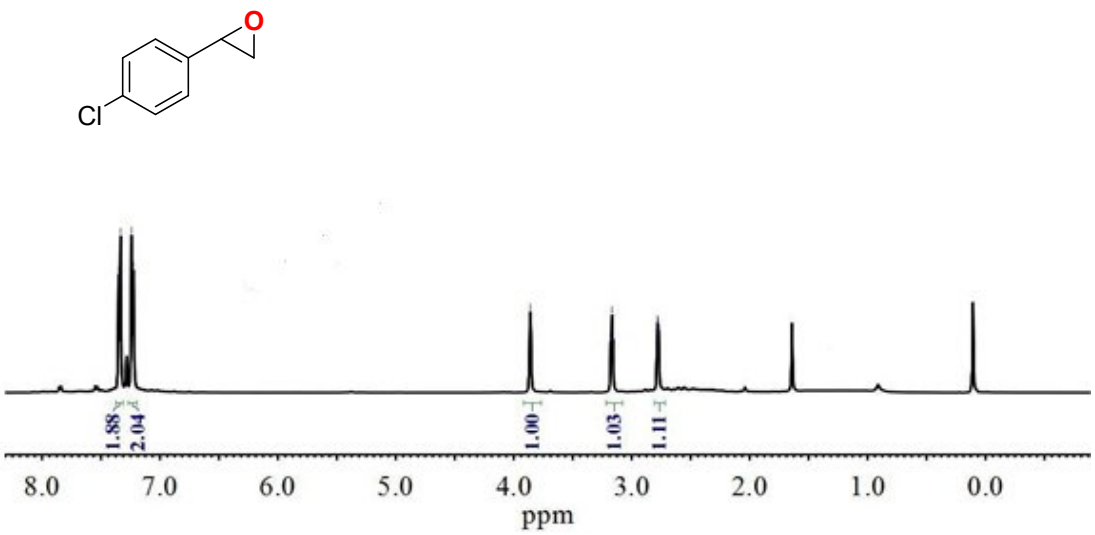

**$^{13}$C NMR spectra of 2**



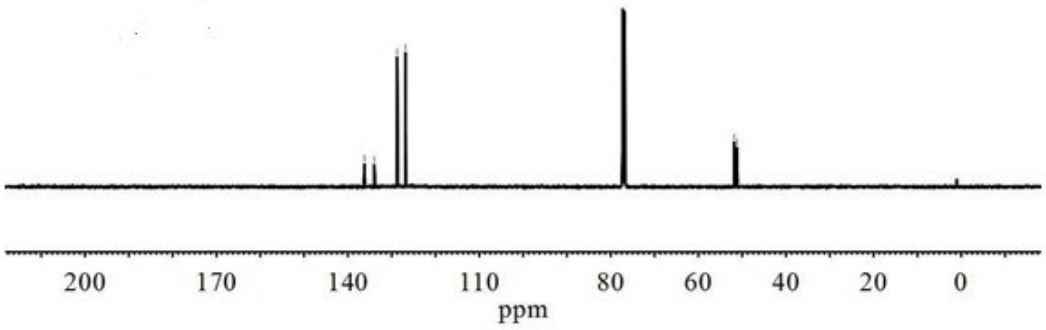

**$^{1}$H NMR spectra of 3**



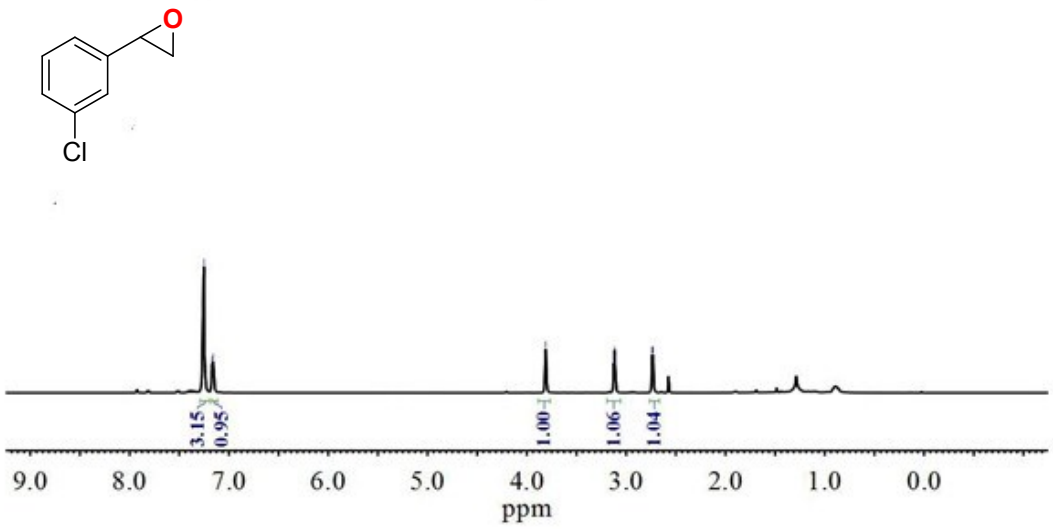

**$^{13}$C NMR spectra of 3**



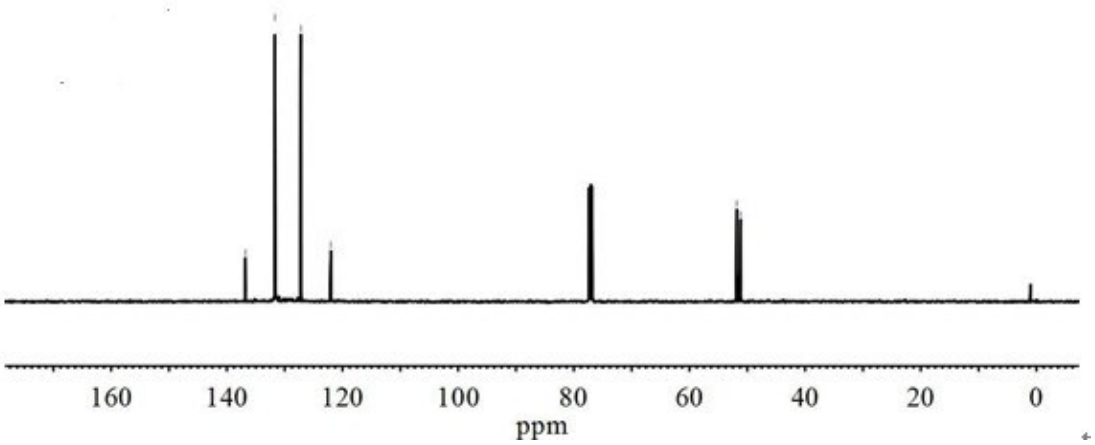

**$^{1}$H NMR spectra of 4**



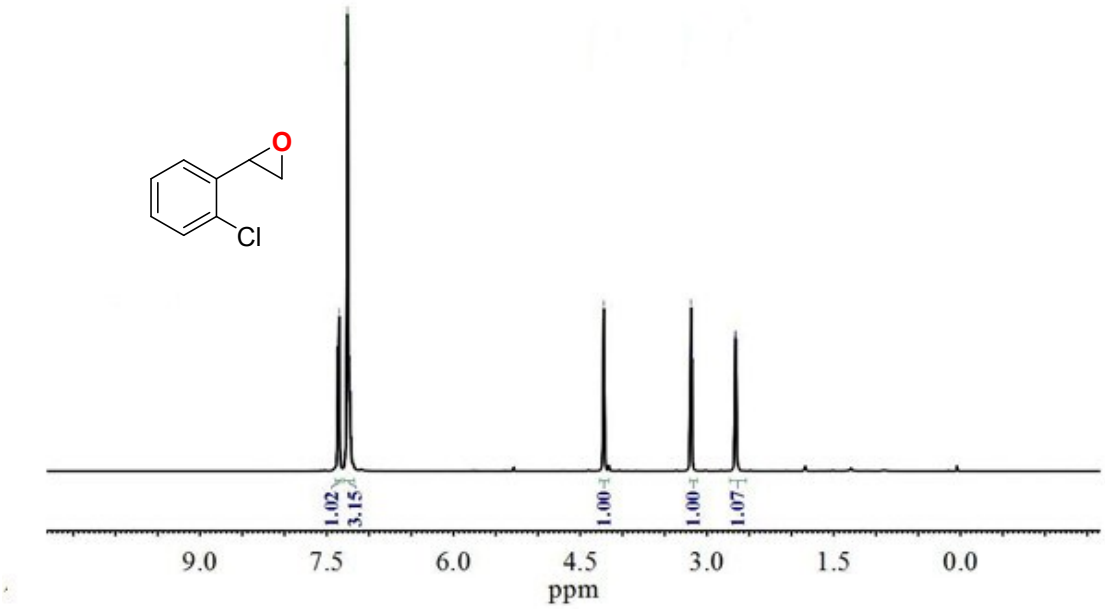

**$^{13}$C NMR spectra of 4**



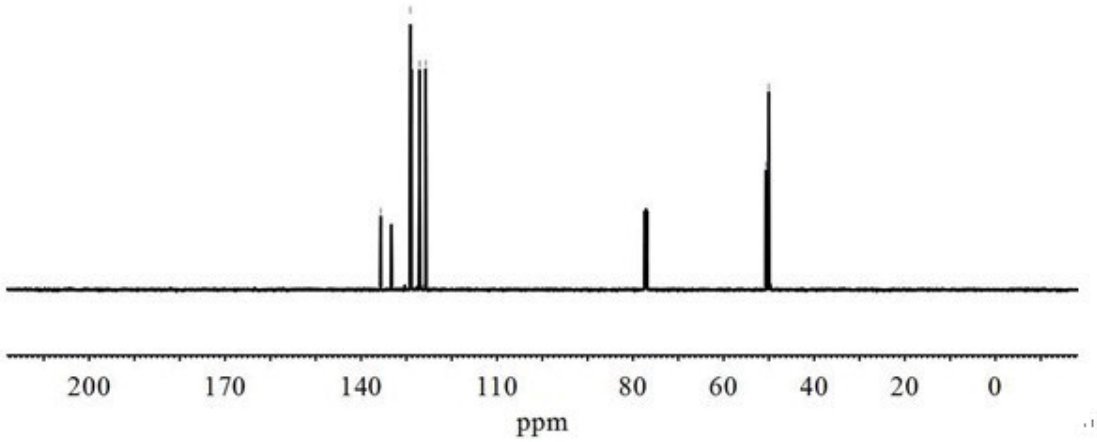

**$^{1}$H NMR spectra of 5**



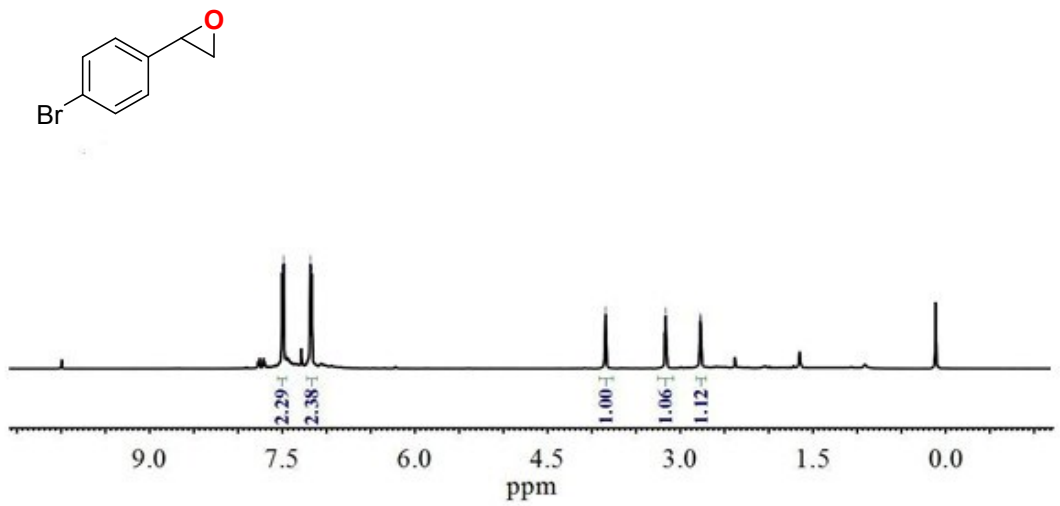

**$^{13}$C NMR spectra of 5**



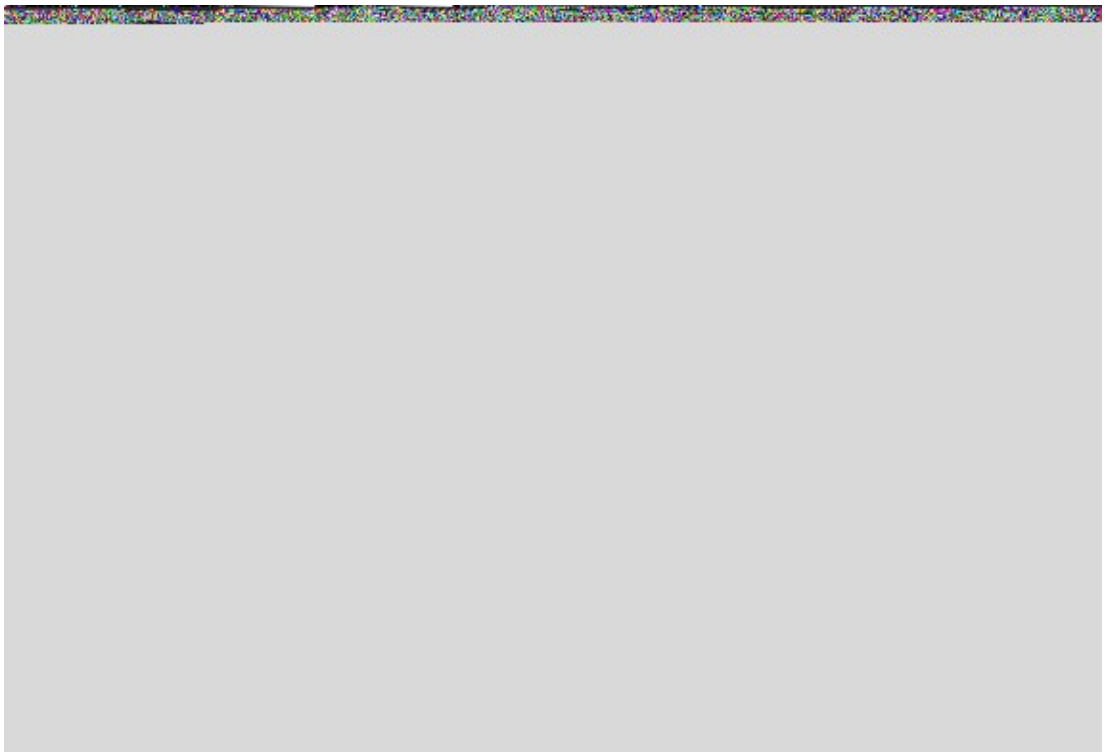

**$^{1}$H NMR spectra of 6**



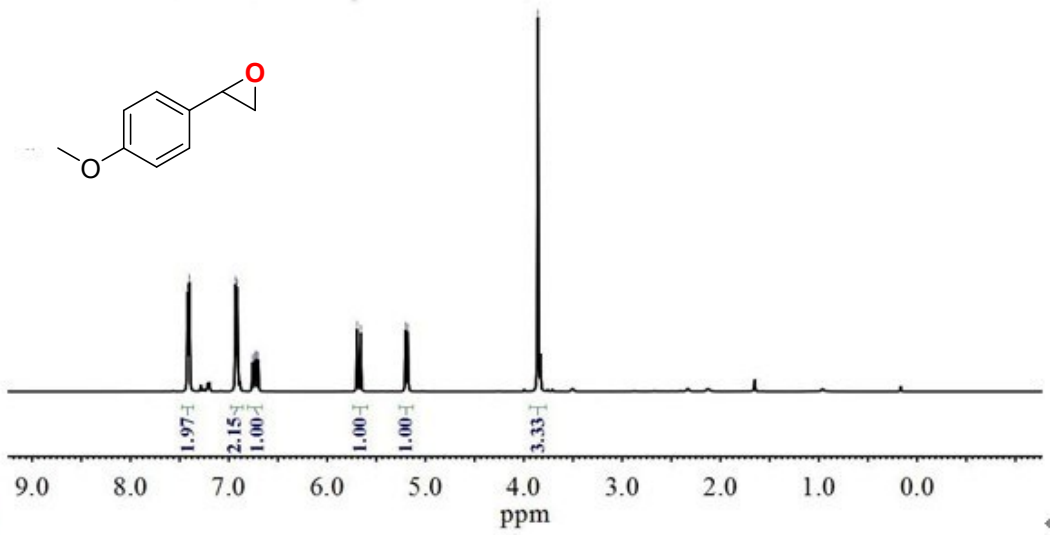

**$^{13}$C NMR spectra of 6**



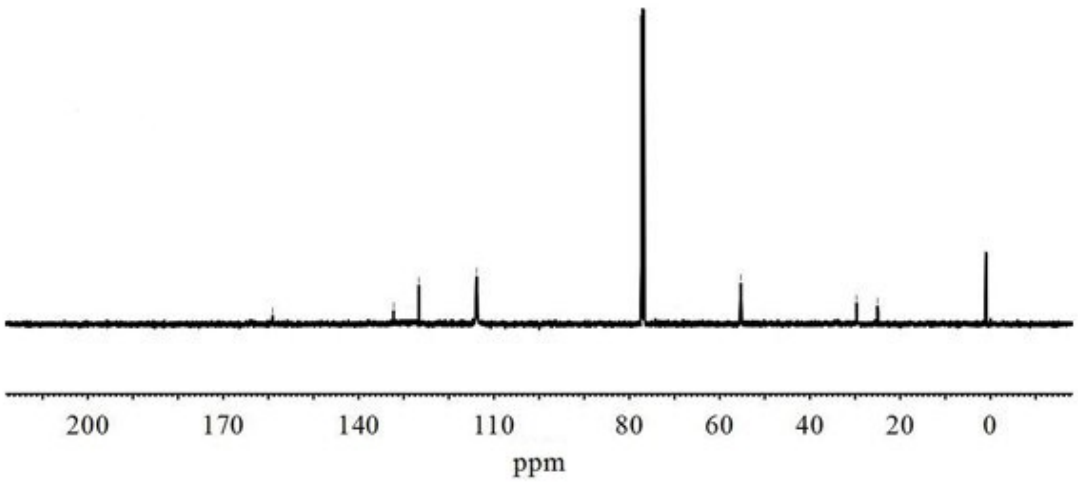

**$^{1}$H NMR spectra of 7**



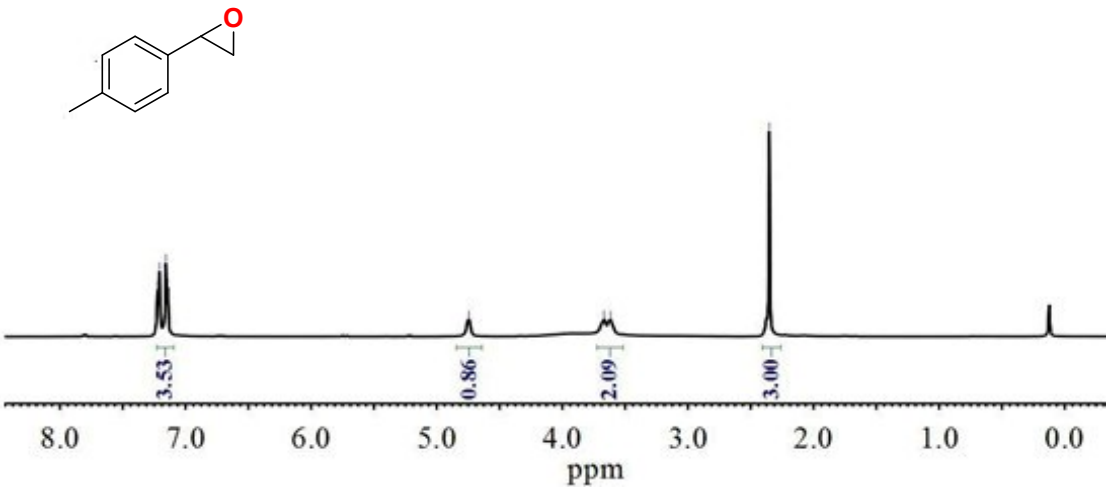
**$^{13}$C NMR spectra of 7**



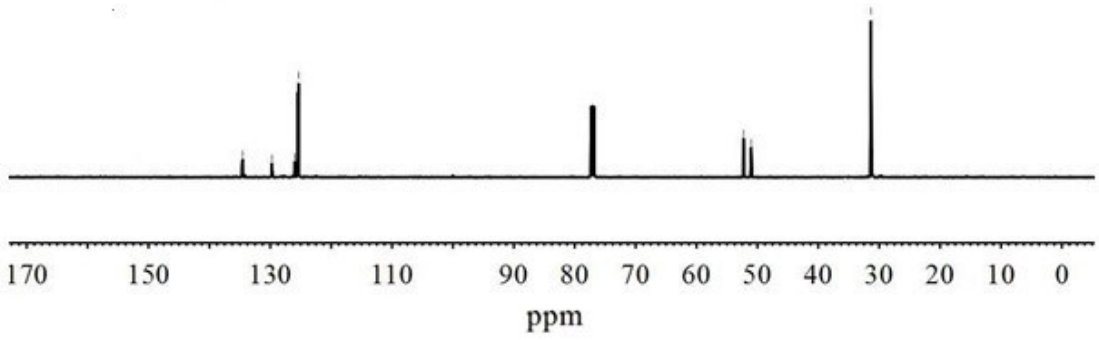

**$^{1}$H NMR spectra of 8**



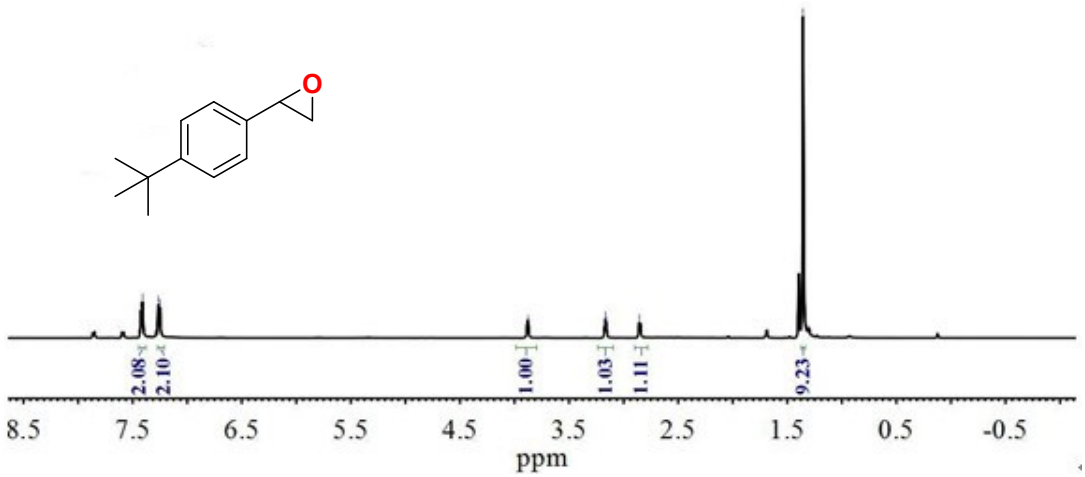

**$^{13}$C NMR spectra of 8**



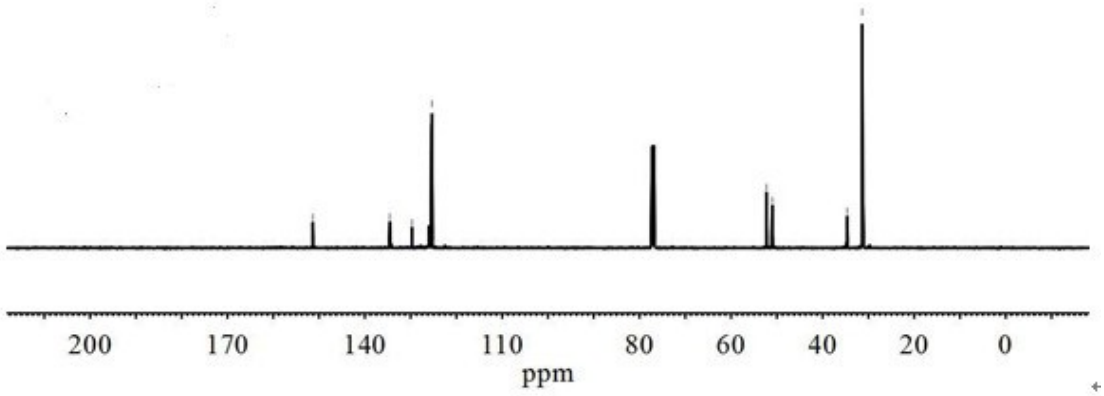

**$^{1}$H NMR spectra of 9**



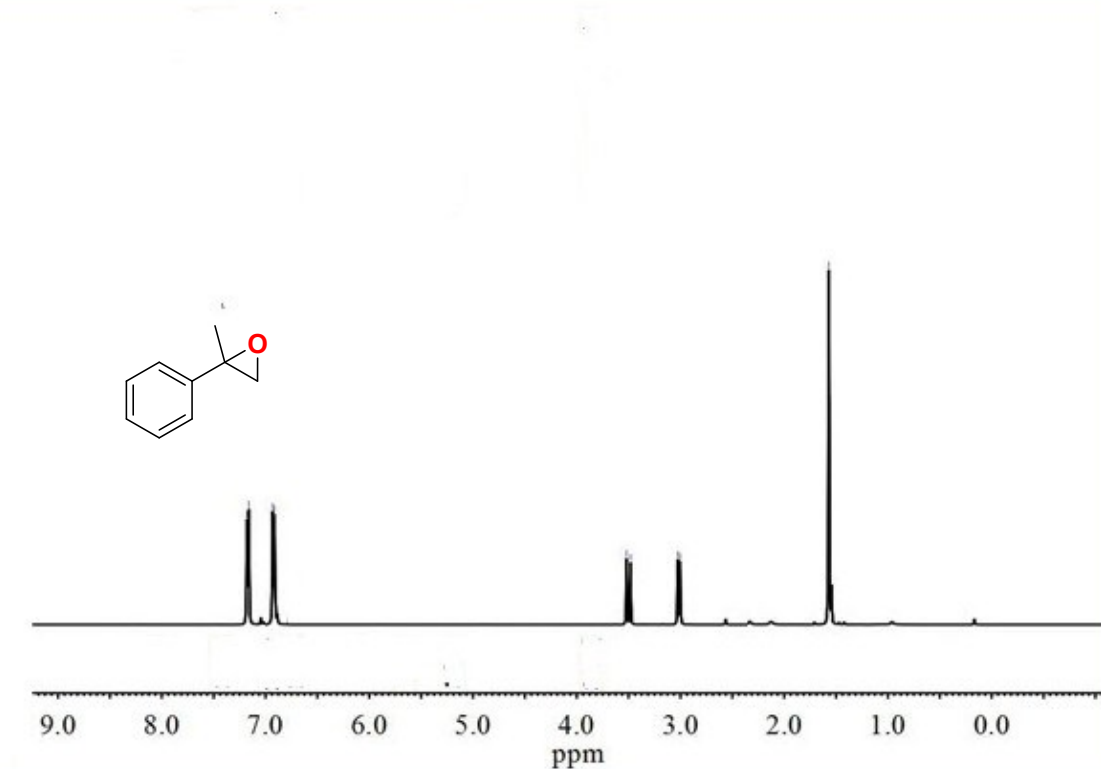

**$^{13}$C NMR spectra of 9**



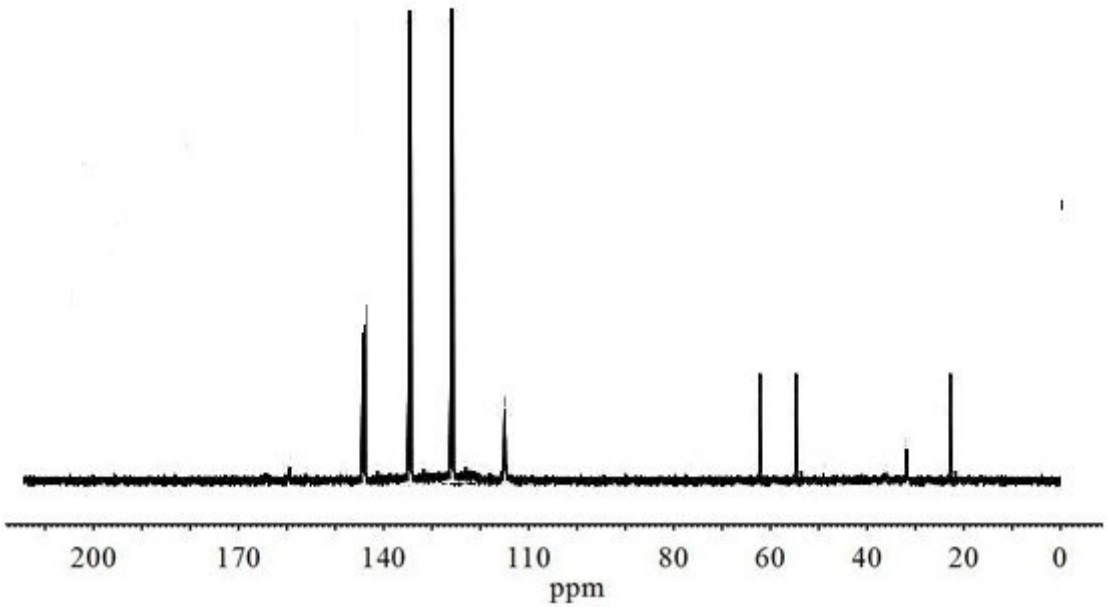

**$^{1}$H NMR spectra of 10**



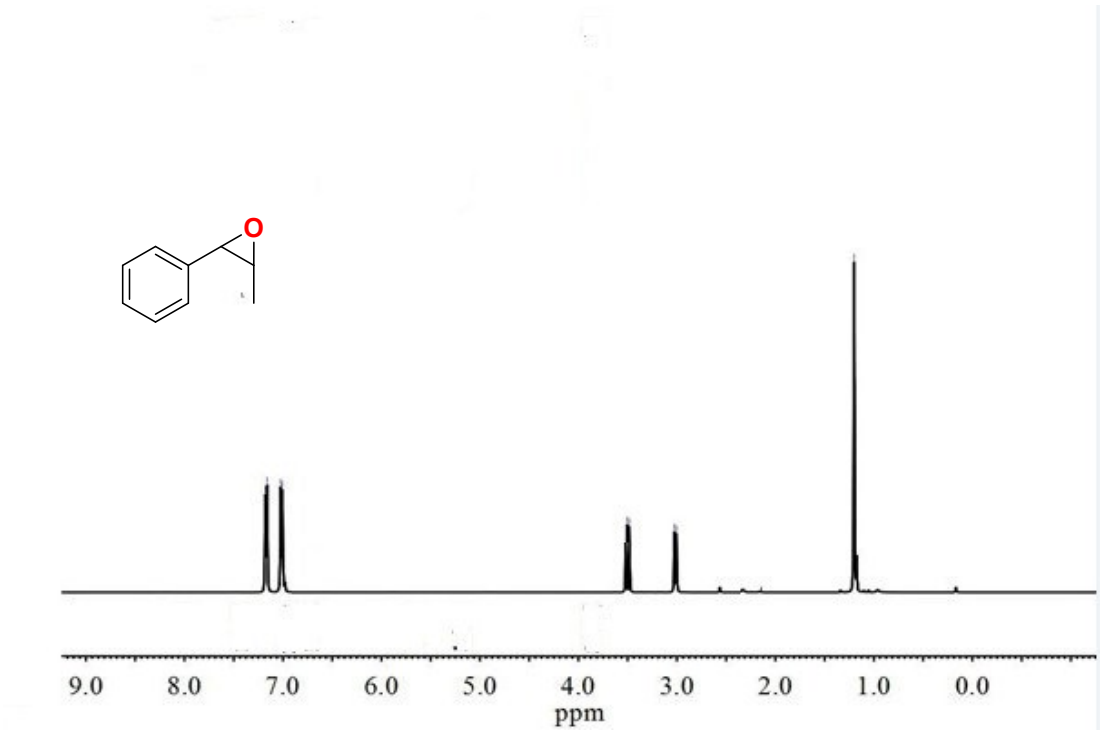

**$^{13}$C NMR spectra of 10**



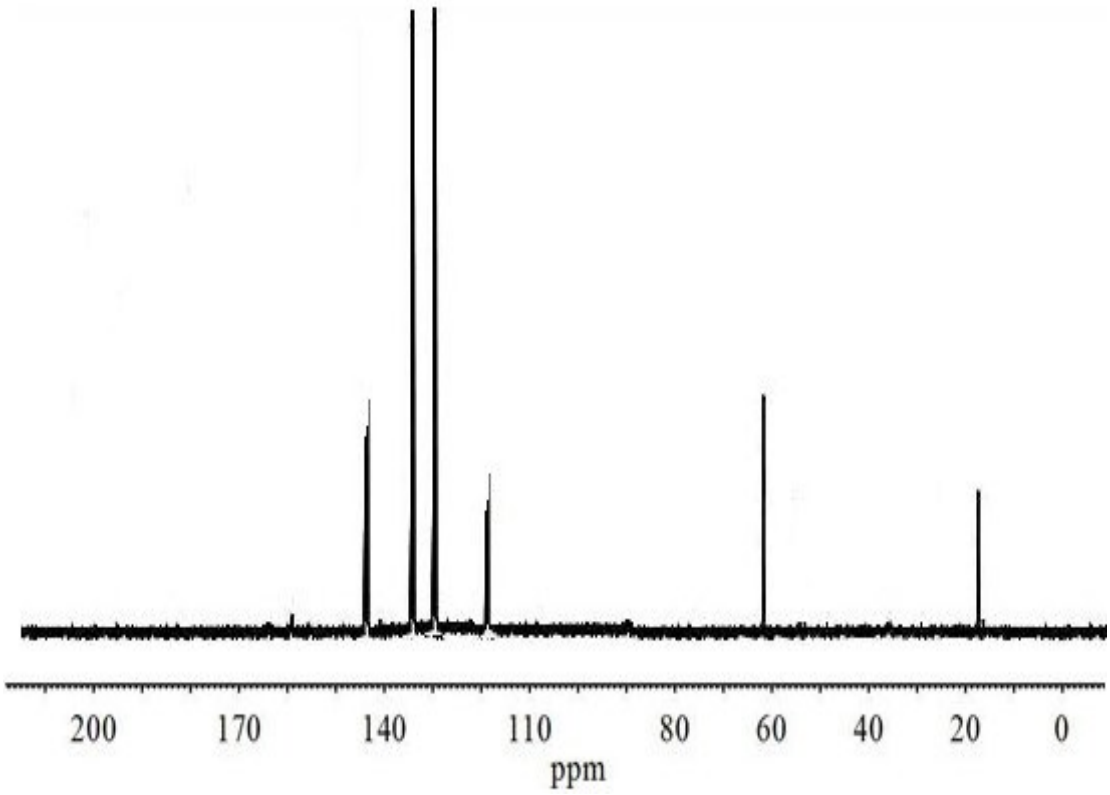

**$^{1}$H NMR spectra of 11**



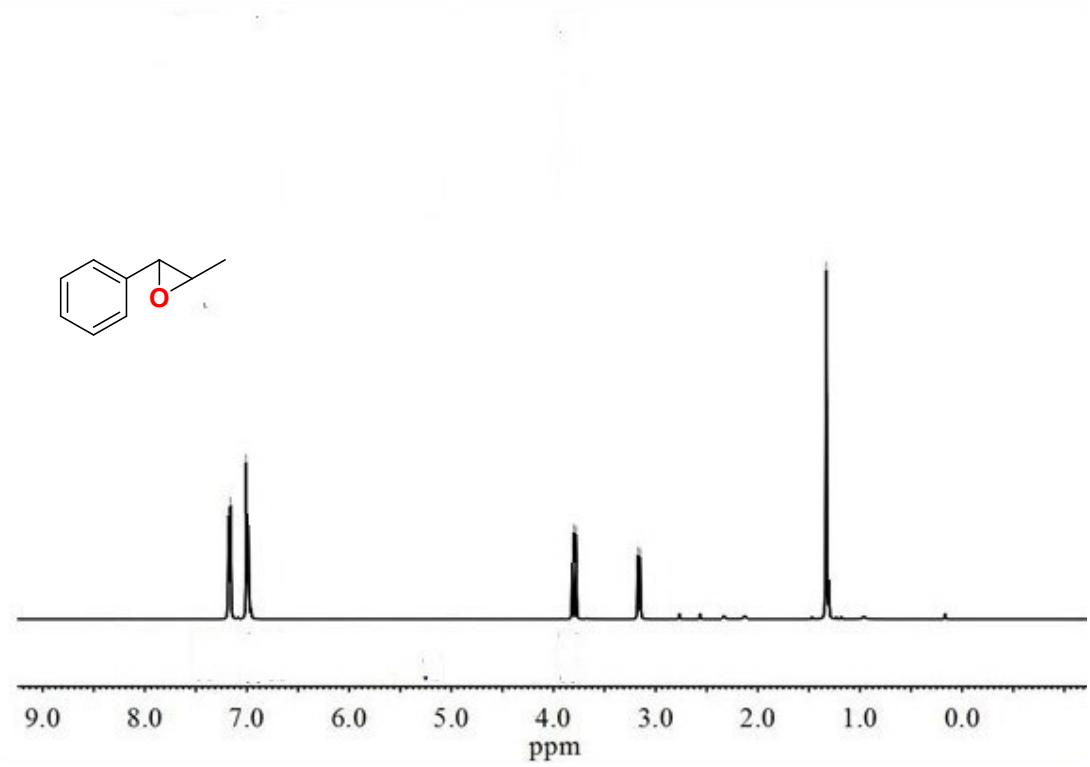

**$^{13}$C NMR spectra of 11**



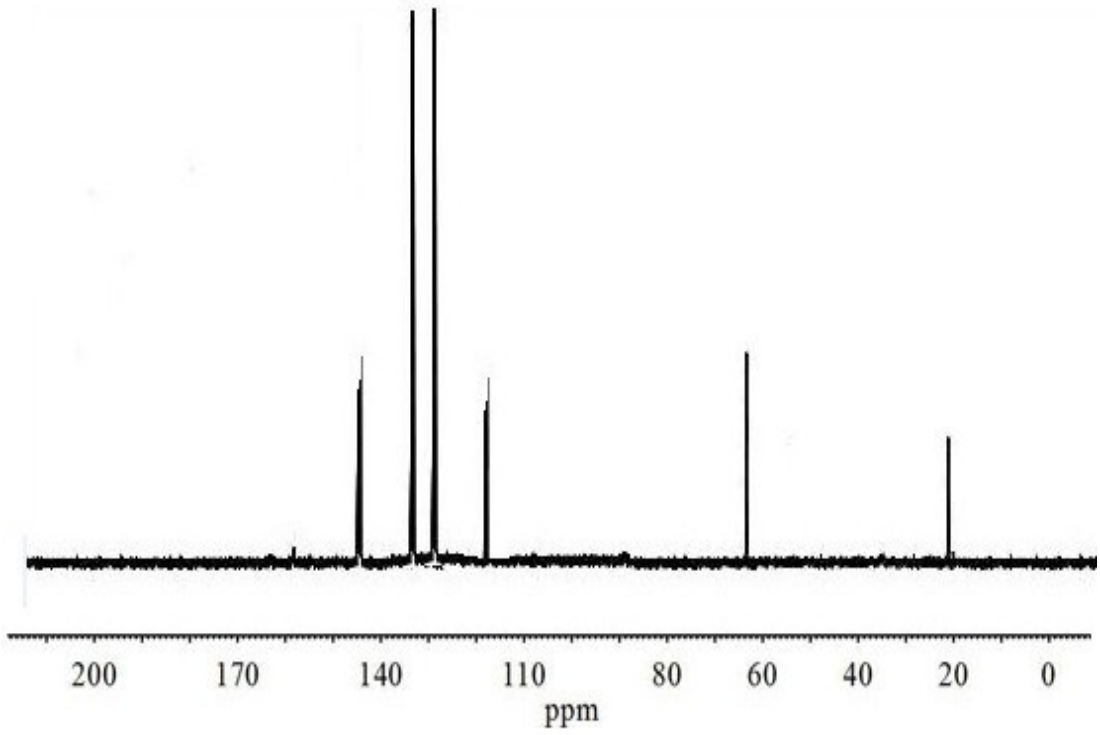

**$^{1}$H NMR spectra of 12**



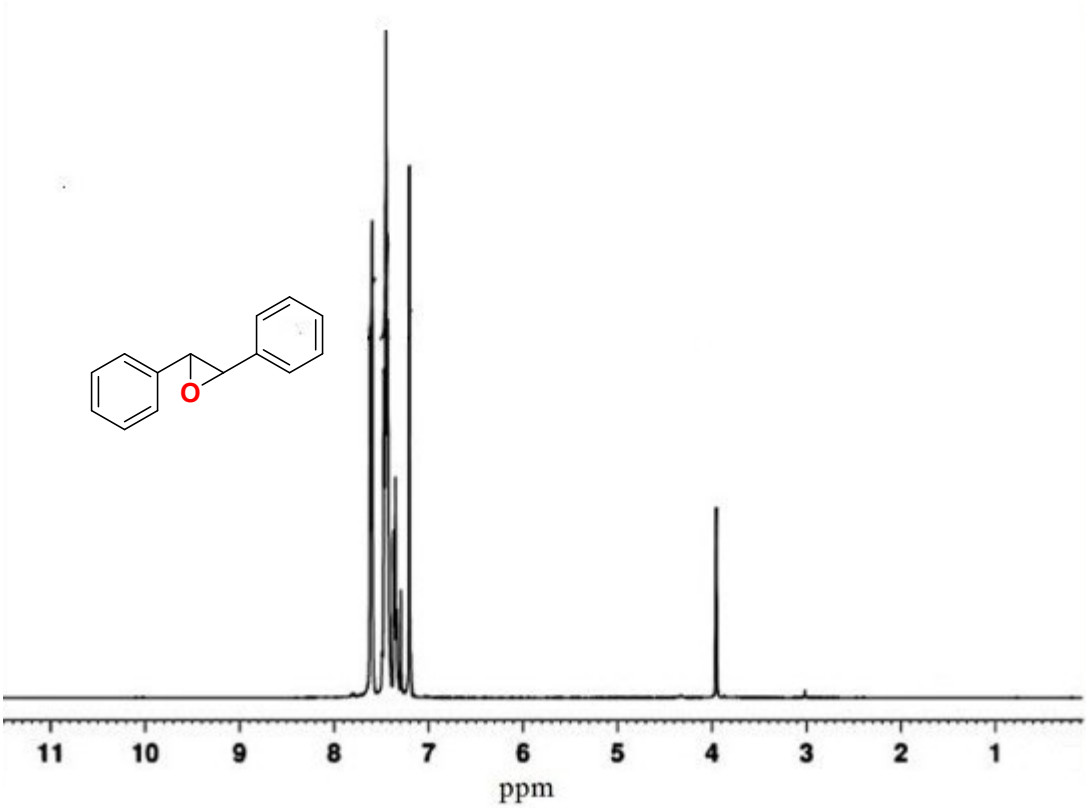

**$^{13}$C NMR spectra of 12**



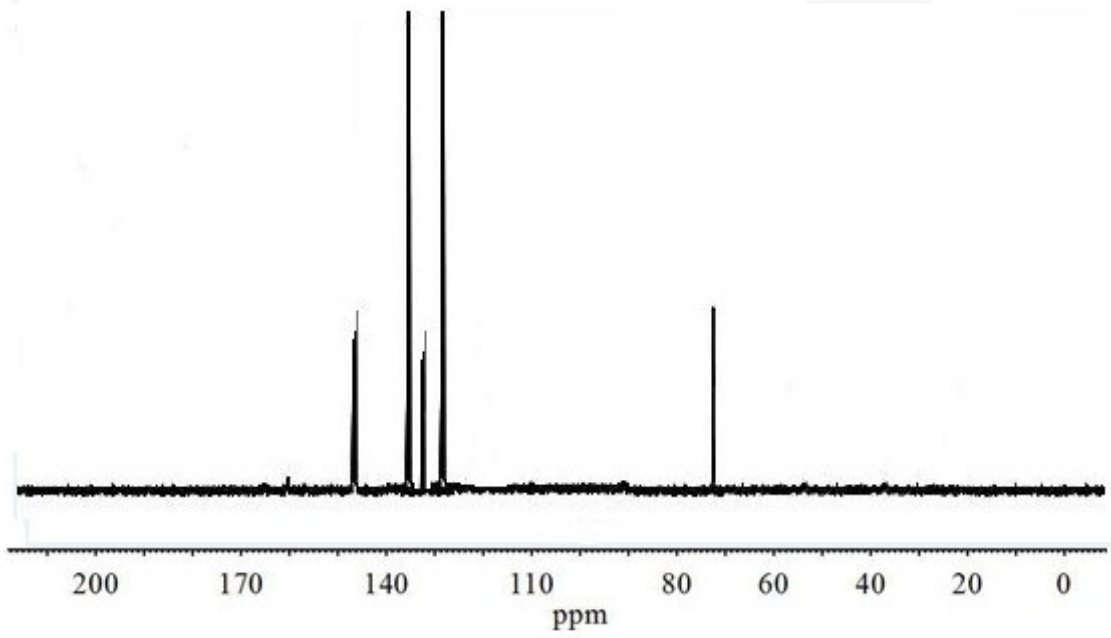

**$^{1}$H NMR spectra of 13**



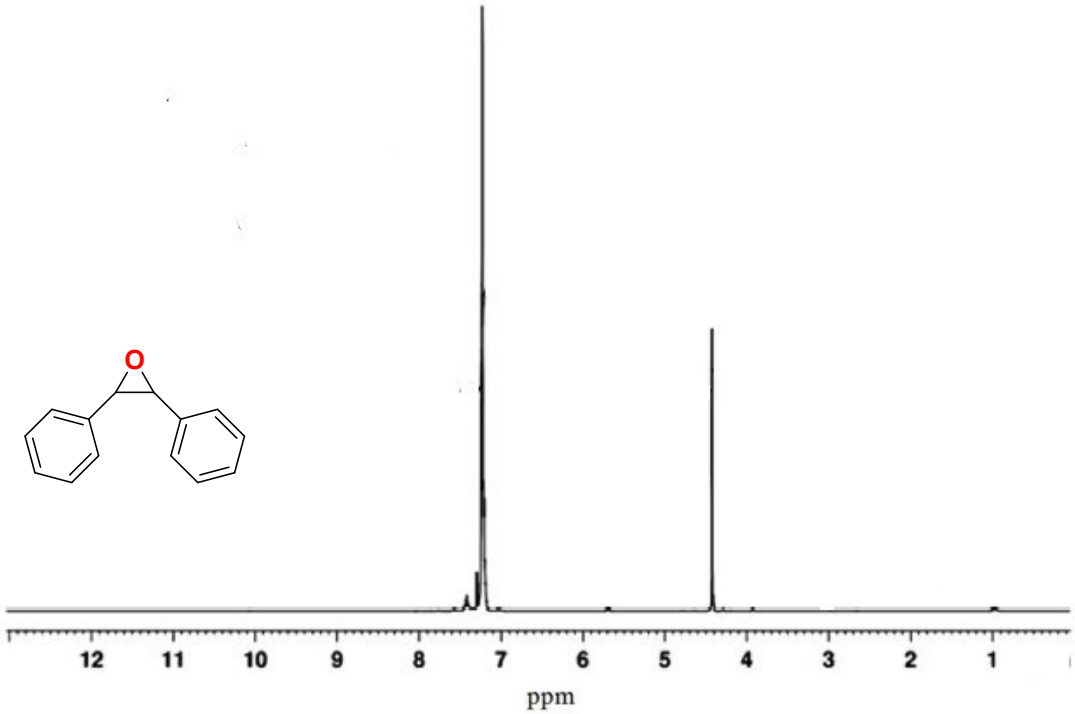

**$^{13}$C NMR spectra of 13**



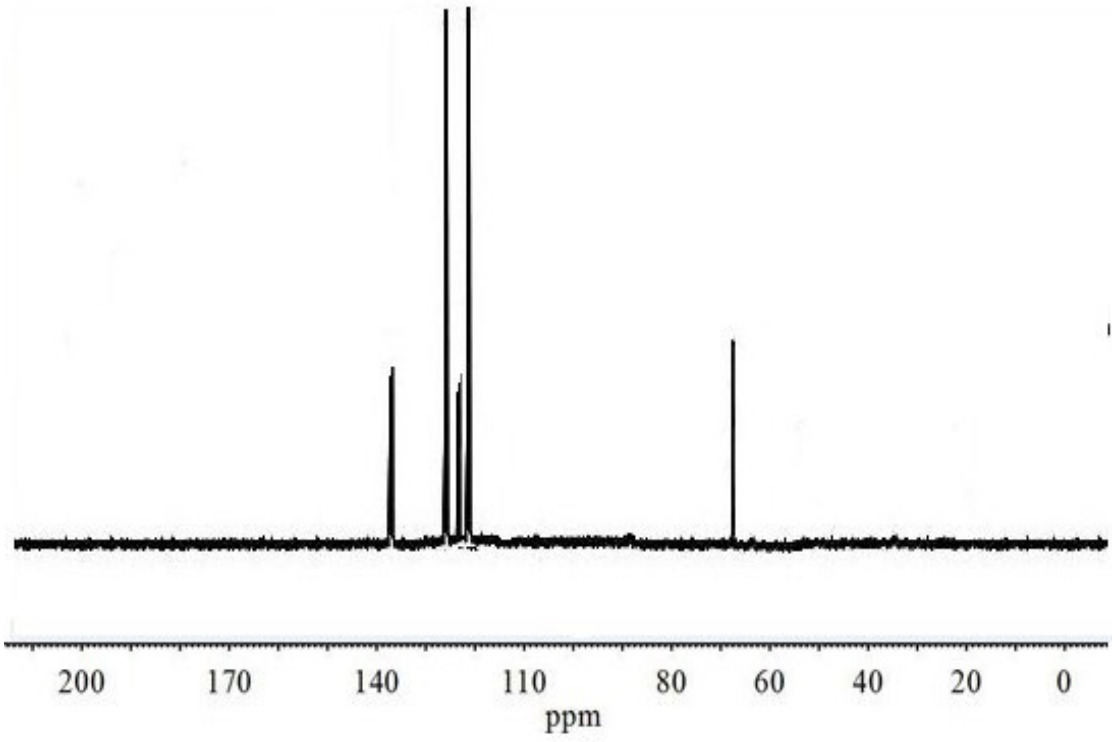

**$^{1}$H NMR spectra of 14**



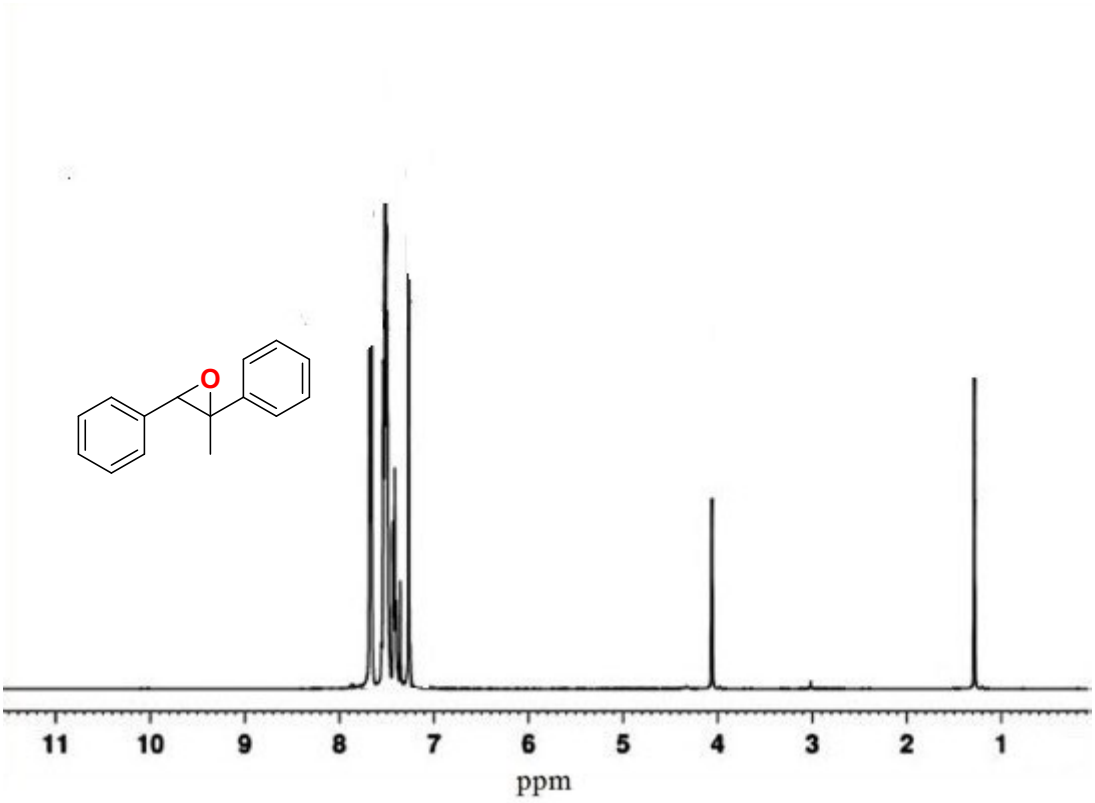

**$^{13}$C NMR spectra of 14**



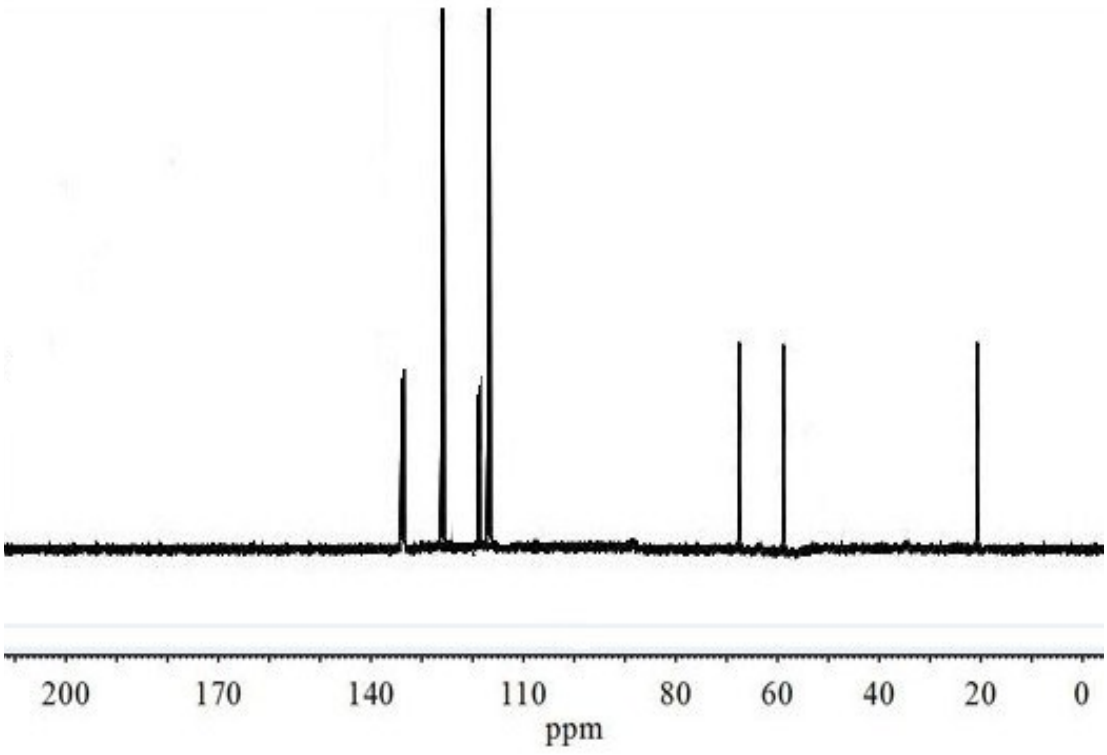

**$^{1}$H NMR spectra of 15**



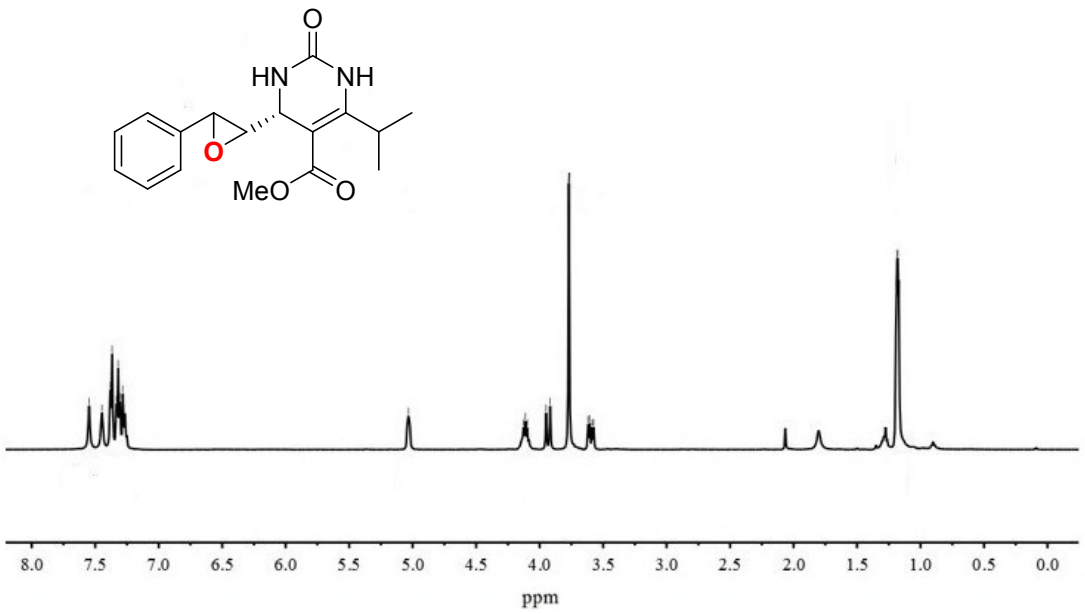

**$^{13}$C NMR spectra of 15**



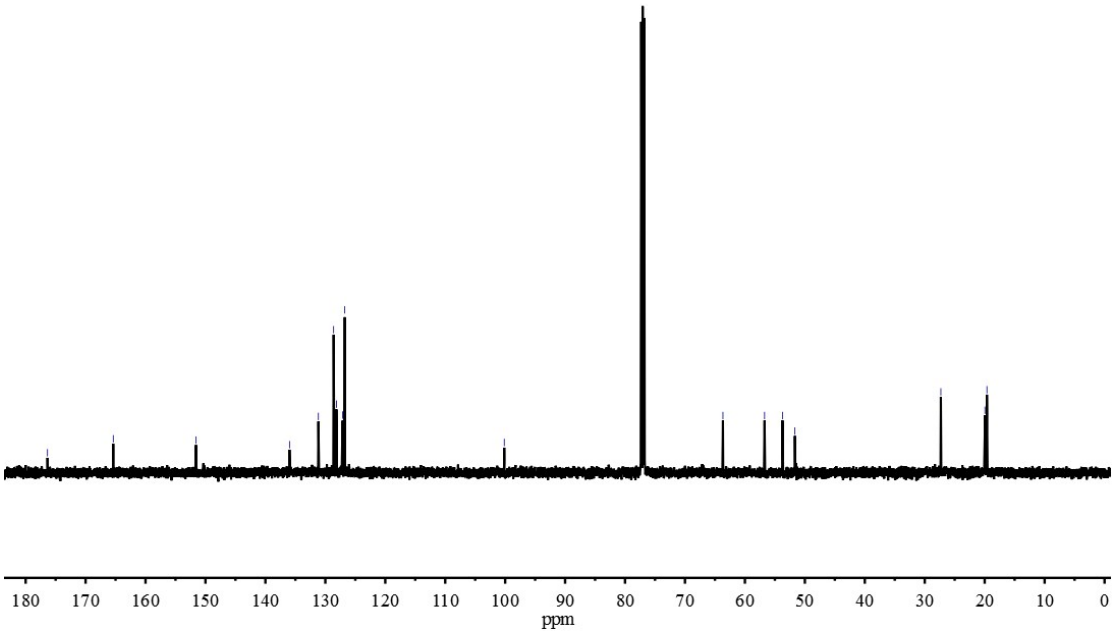

**$^{1}$H NMR spectra of 16**



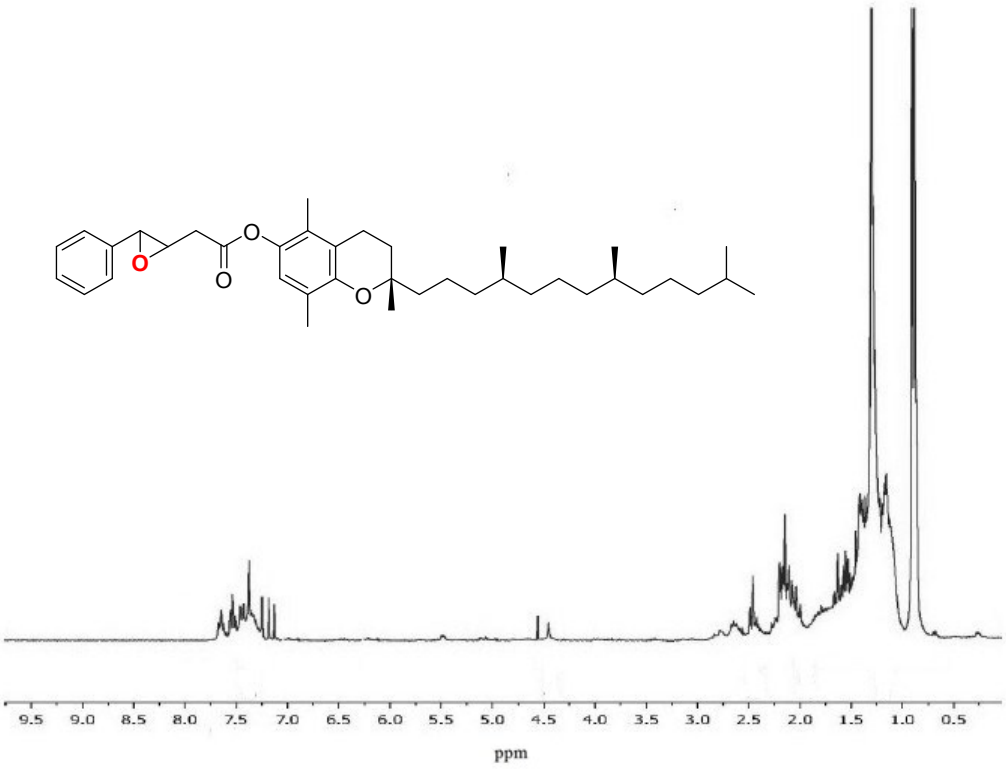

**$^{13}$C NMR spectra of 16**



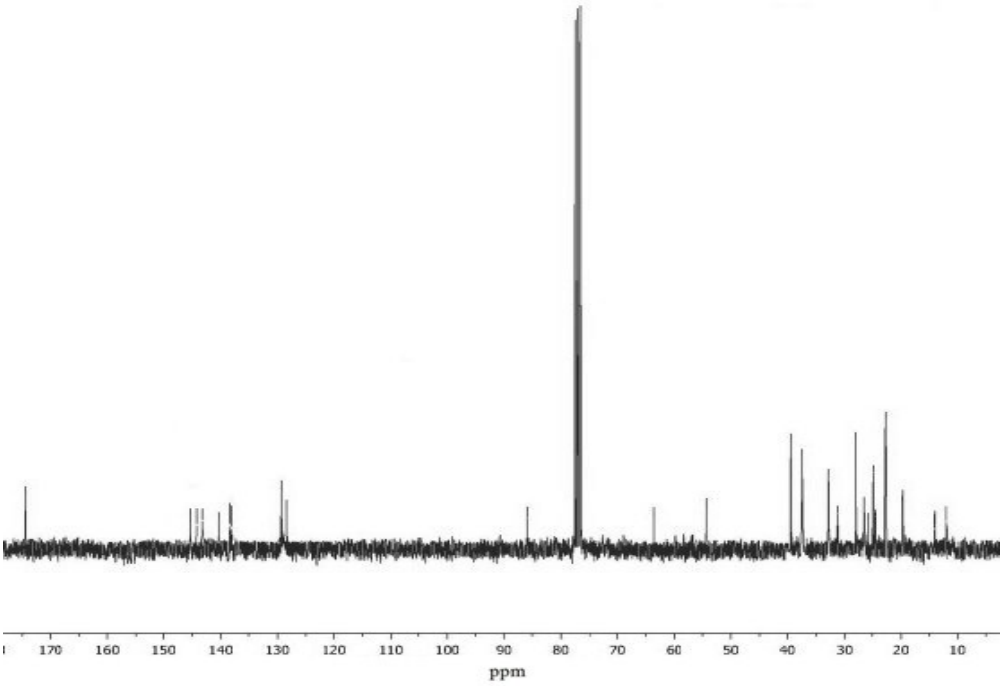

**$^{1}$H NMR spectra of 44**



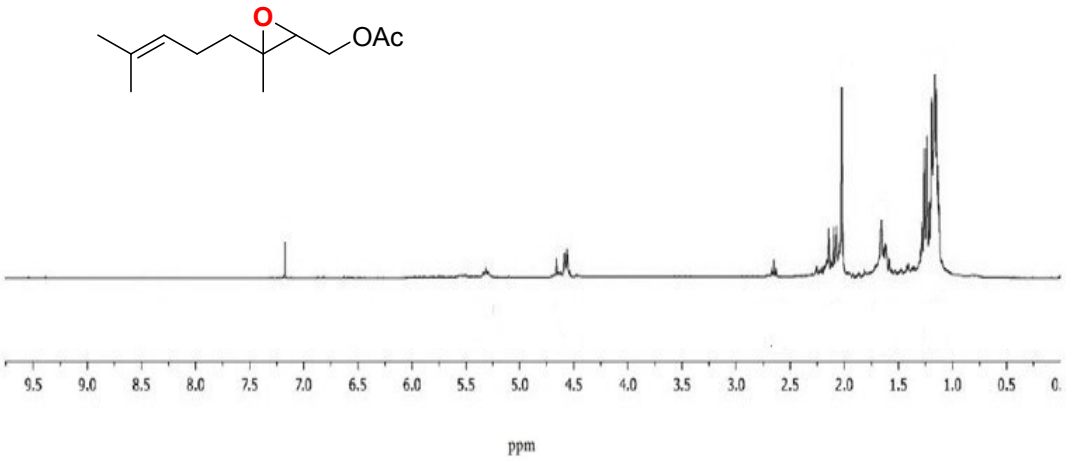

**$^{13}$C NMR spectra of 44**



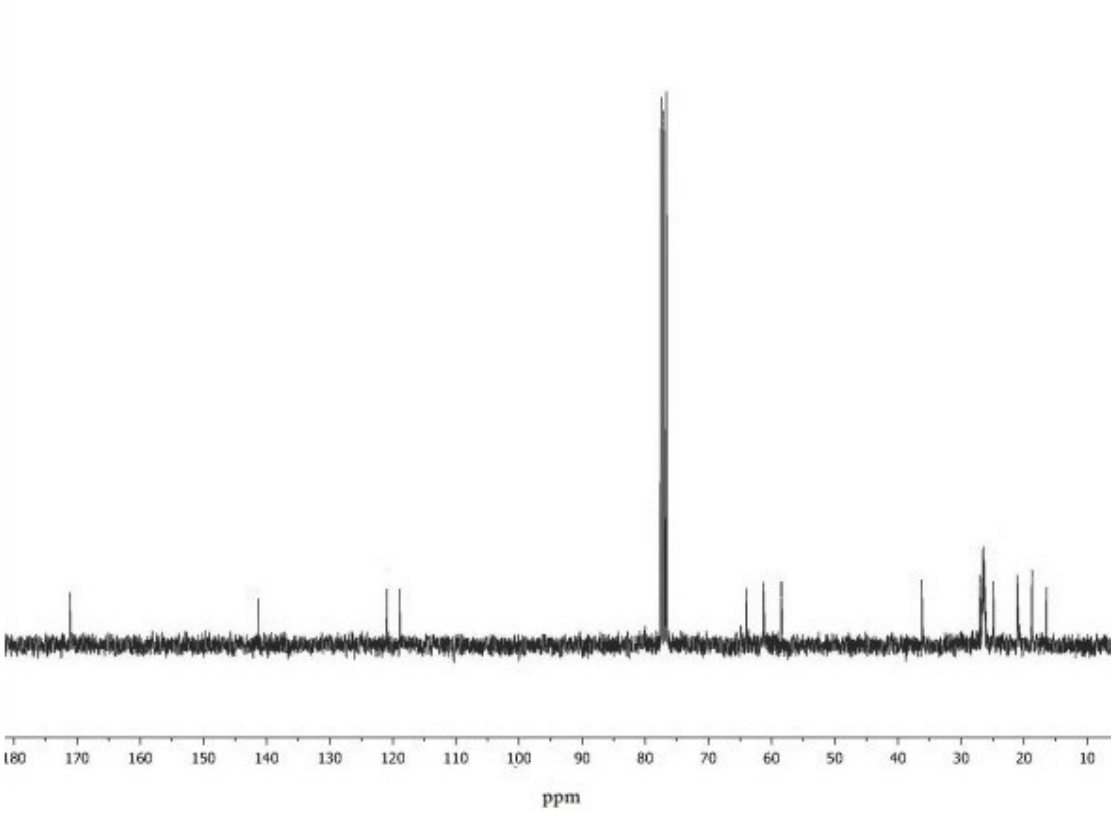

**$^{1}$H NMR spectra of 45**



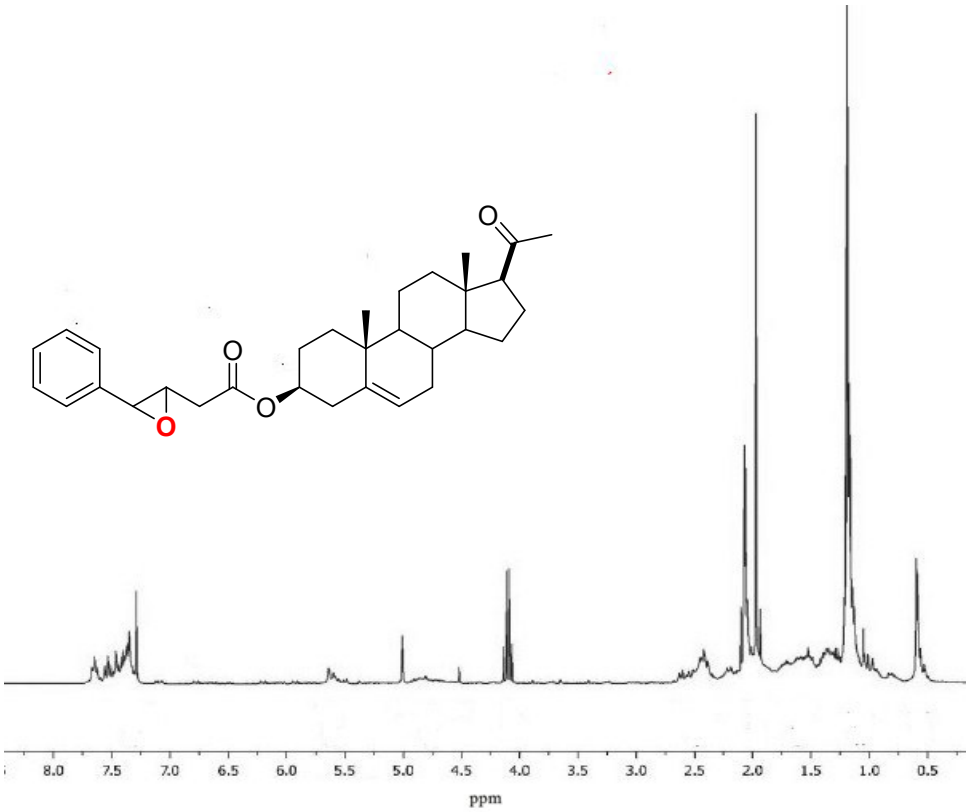

**$^{13}$C NMR spectra of 45**



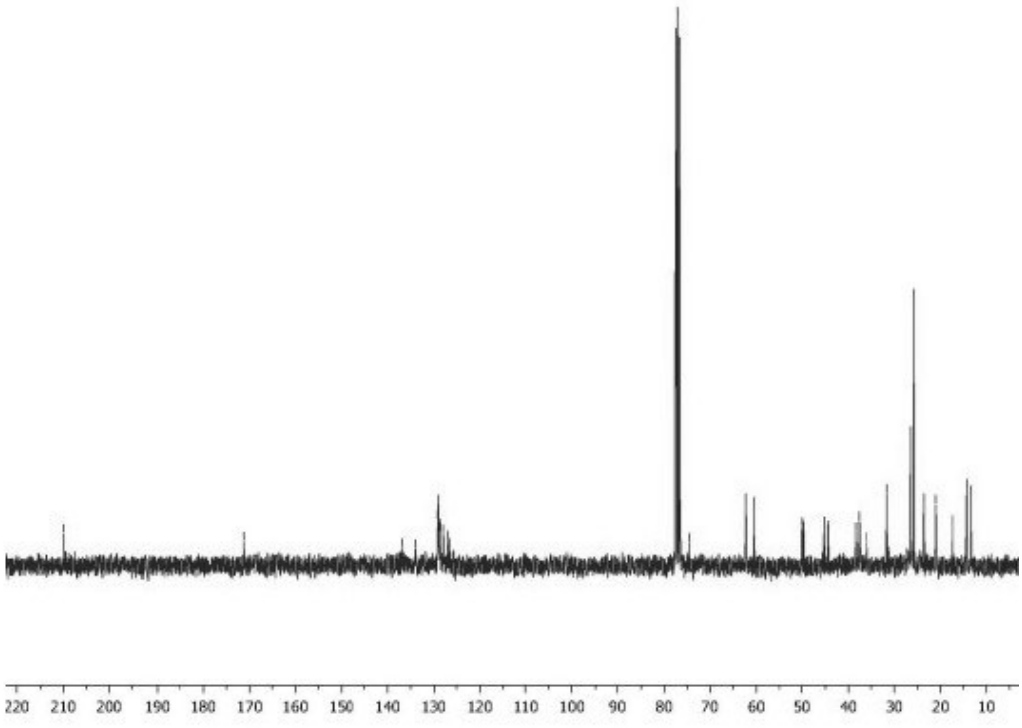

**$^{1}$H NMR spectra of 46**




**$^{13}$C NMR spectra of 46**




**$^{1}$H NMR spectra of 47**




**$^{13}$C NMR spectra of 47**

## 6. Reference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2. H. Yu, P. Xu, H. He, J. Zhu, H. Lin, S. Han, *Tetrahedron: Asymmetry*. **2017**, *28*, 257-265.
3. D. Banerjee, R. Jagadeesh, K. Junge, M. Pohl, J. Radnik, A. Brückner, M. Beller, *Angew. Chem. Int. Ed.* **2014**, *53*, 4359-4363.