

Supporting Information

An Ionic Liquid immobilized Copper complex for catalytic epoxidation

Including:

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1. Experimental procedure for the preparation of catalysts

To a solution of $[\text{CuCl}_2(\text{PPh}_3)_2]$ (0.2 mmol) in alcohol (20 mL) the corresponding Schiff base ligand (0.2 mmol) was added. The mixture was refluxed for 3 h. The solvent was evaporated to 1/3rd and n-hexane was added to separate the solid complex. The complex was filtered, washed with ethanol and then with hexane and dried in *vacuo*. The formation of complex was checked by TLC (*Inorganic Chemistry Communications*, 14 (2011) 690–693).

2. Characterization data for the catalysts

Table 1 Infrared spectral data (cm^{-1}) for Cu(II) complexes

Compound	$\nu_{(\text{C}=\text{N})}$	$\nu_{(\text{C}-\text{O})}$	$\nu_{(\text{Ni}-\text{O})}$	$\nu_{(\text{Ni}-\text{N})}$	Bands due to PPh_3
1	1589	1370	528	457	1433, 1095, 691
2	1594	1384	532	455	1435, 1096, 693
3	1588	1356	527	455	1434, 1093, 695
4	1579	1364	529	459	1437, 1098, 694
5	1575	1371	529	456	1435, 1097, 695

Table 2 Analytical and Electronic spectral data of the copper complexes

Complex	Melting point (°C)	% Found (calculated)			UV-Vis Spectral Data (λ_{\max} (nm))	
		C	H	N	d-d bands	Intraligand and C.T.
1	289	62.77(62.83)	4.32(4.39)	7.18(7.33)	12478,16949, 22727	30303,41666, 46511
2	287	59.08(59.27)	3.86(3.98)	6.75(6.91)	12405,16915, 22752	30298,41605, 46498
3	286	55.15(55.23)	3.65(3.71)	6.32(6.44)	12450,16901, 22767	30259,41701, 46551
4	288	58.16(58.26)	3.82(3.91)	9.01(9.06)	12510,16925, 22776	30321,41640, 46598
5	291	61.59(61.69)	4.45(4.51)	6.66(6.96)	12498,17001, 22699	30309,41629, 46548

Table 3 ESR spectral data of the Cu^{II} complexes

Complex	g_{\parallel}	g_{\perp}	A_{\parallel} x 10 ⁻⁴ cm ⁻¹	A_{\perp} x 10 ⁻⁴ cm ⁻¹	α^2	β^2
1	2.269	2.064	158.00	16.8	0.75	0.69
2	2.164	2.048	134.00	18.2	0.87	0.86
3	2.202	2.044	146.00	20.4	0.66	0.71
4	2.215	2.066	152.20	22.8	0.73	0.64
5	2.226	2.046	144.00	23.6	0.79	0.61

3. Catalytic procedure

In a typical reaction, the catalyst (8 mmol) was dissolved in 2 mL of 1:1 mixture of Ethyl-Methyl-Imidazolium (EMIM) ionic liquid and dichloromethane. Substrate (1 mmol) was added and followed by addition of phosphoric acid (4 mmol). The pH was adjusted to near

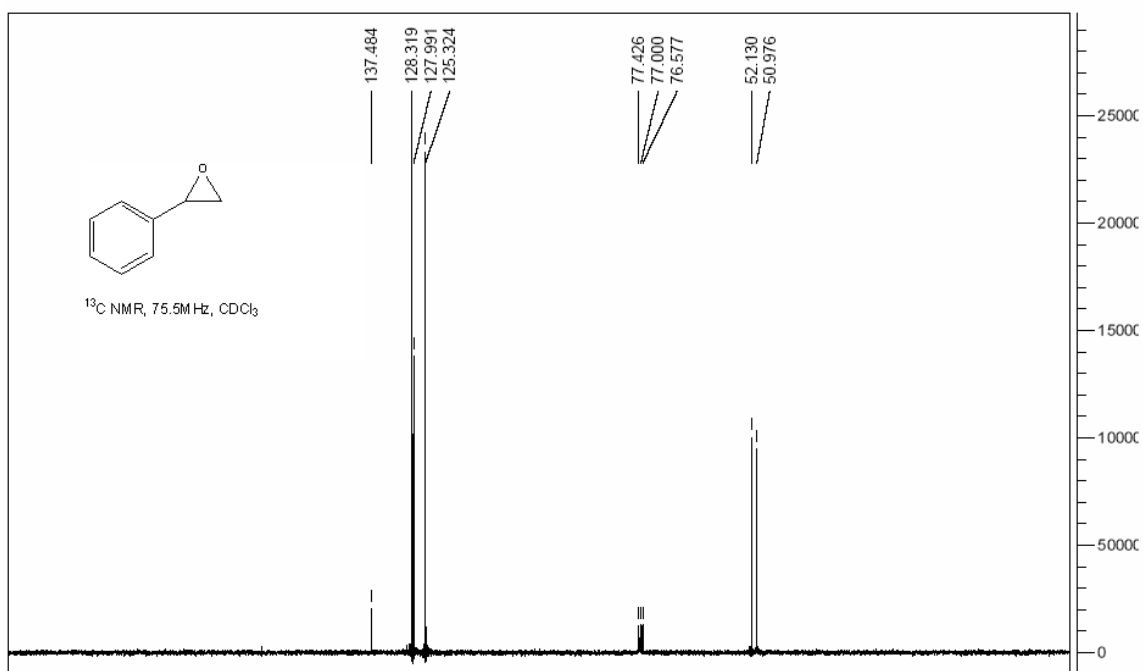
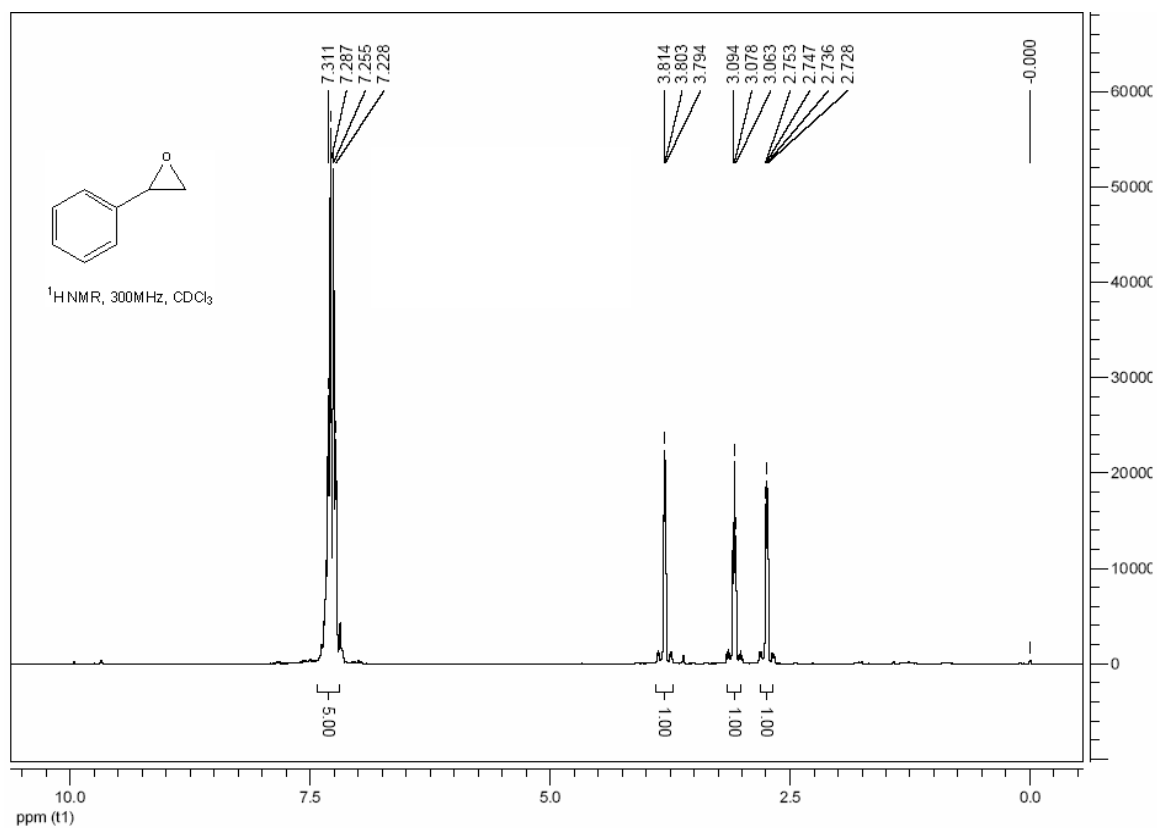
neutral condition using aqueous solution of sodium hydroxide and the solution was stirred for about 2-3 minutes. This was followed by the addition of hydrogen peroxide (30% in water) (2.6 equiv). The reaction mixture was stirred at room temperature for about 3 hours (25°C and 12 hours for terpenes). The completion of the reaction was monitored by GC.

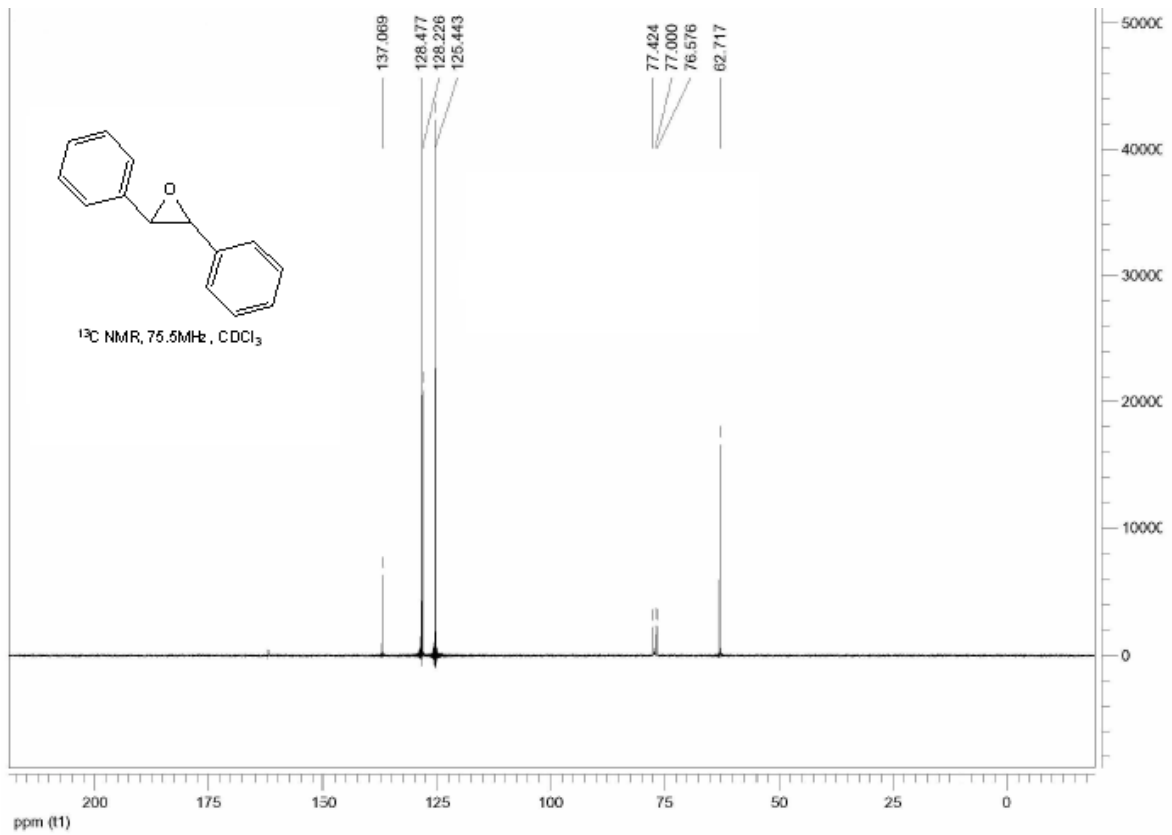
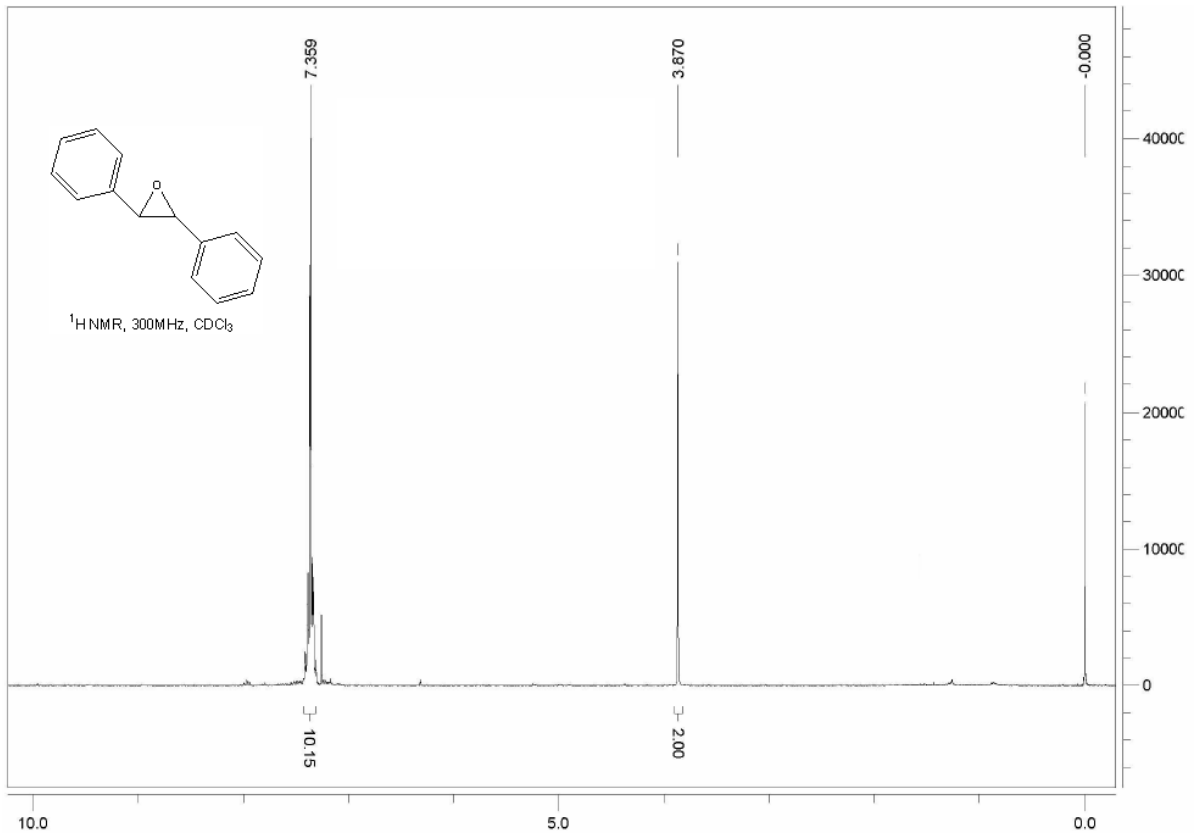
The reusability of the catalysts was also examined. After completion of the reaction, the reaction mixture was extracted with diethyl ether (3 X 3 cm³). The ether layer was collected and then a definite amount of toluene was added as an internal standard for GC analysis. The ionic liquid phase including the catalyst was washed with diethyl ether and then dried in vacuum at room temperature. Seven recycling experiments were performed.

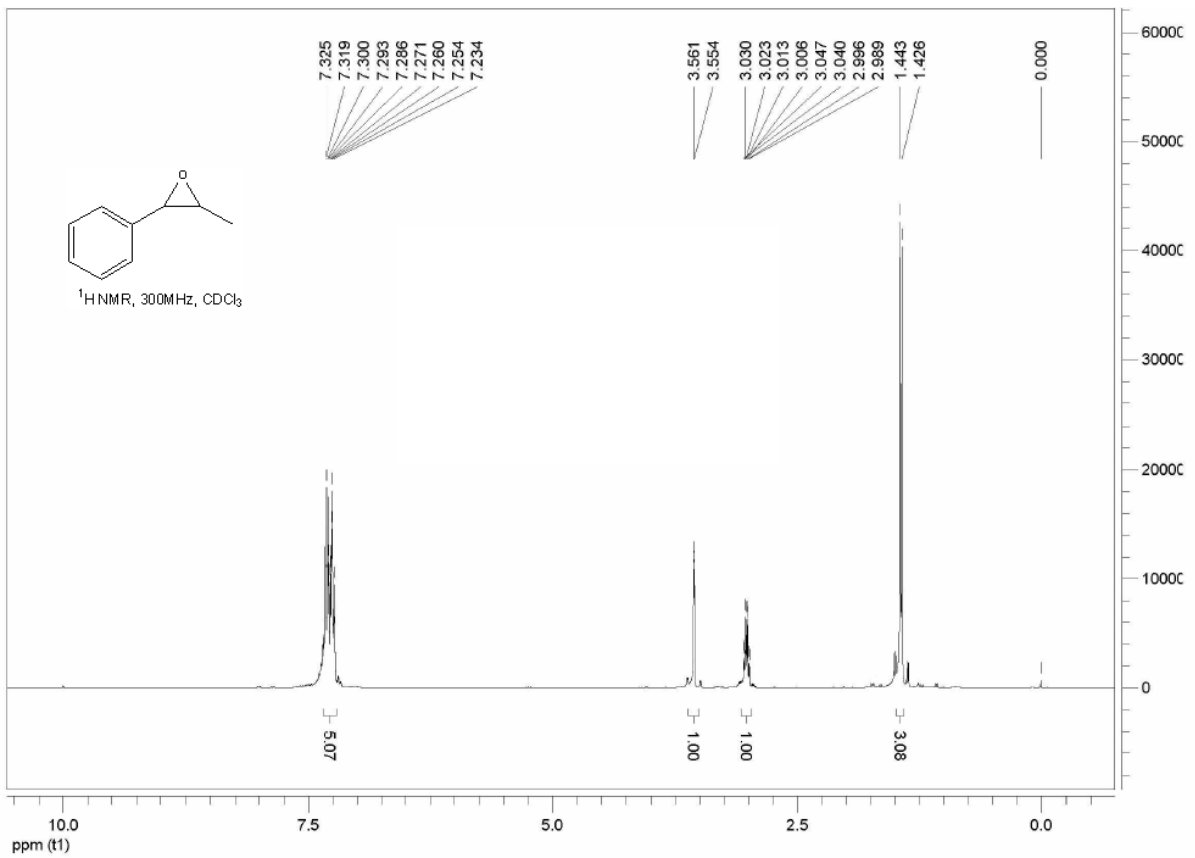
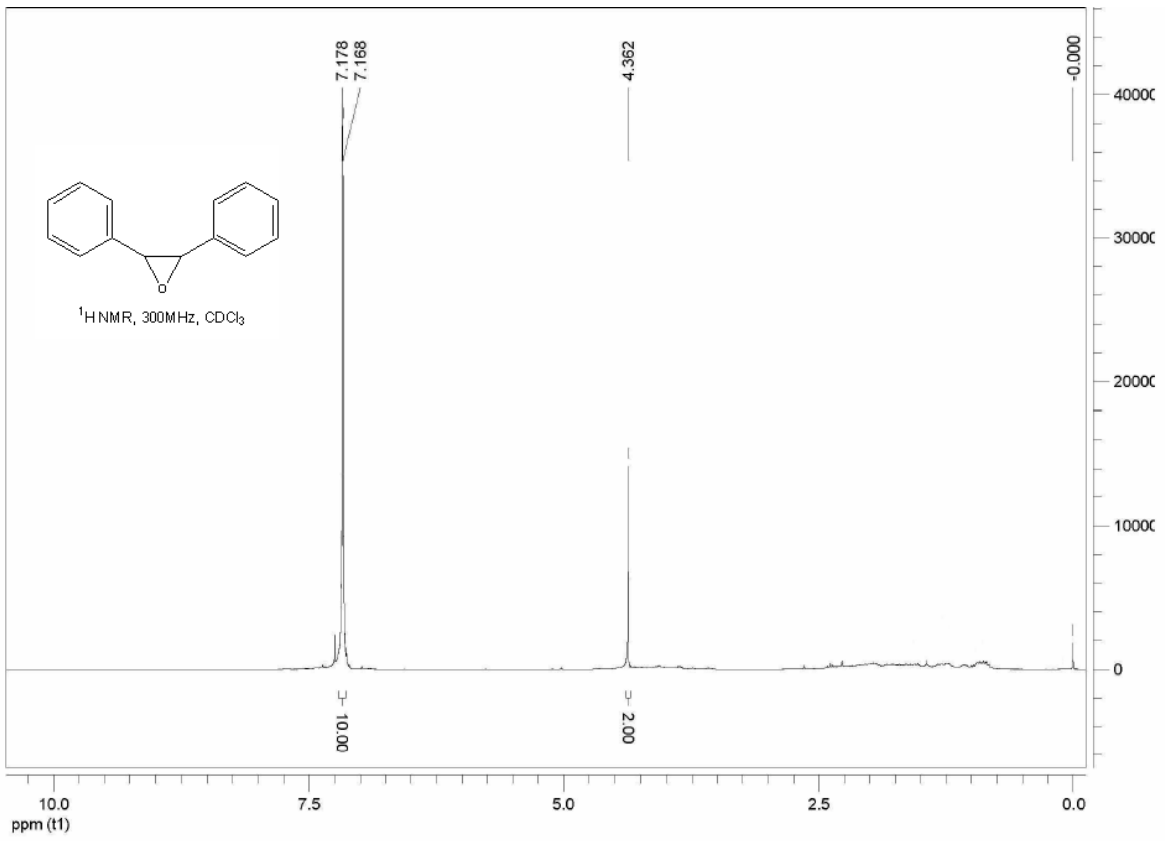
Product analysis

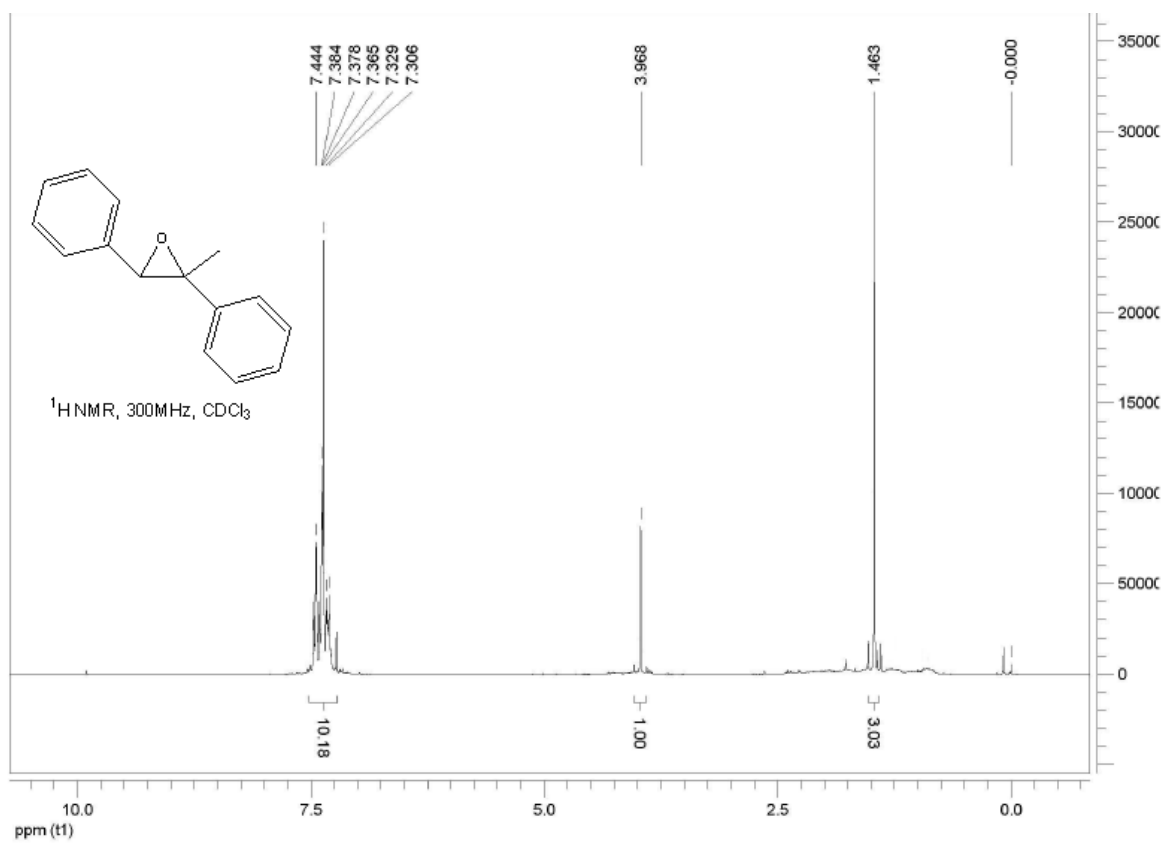
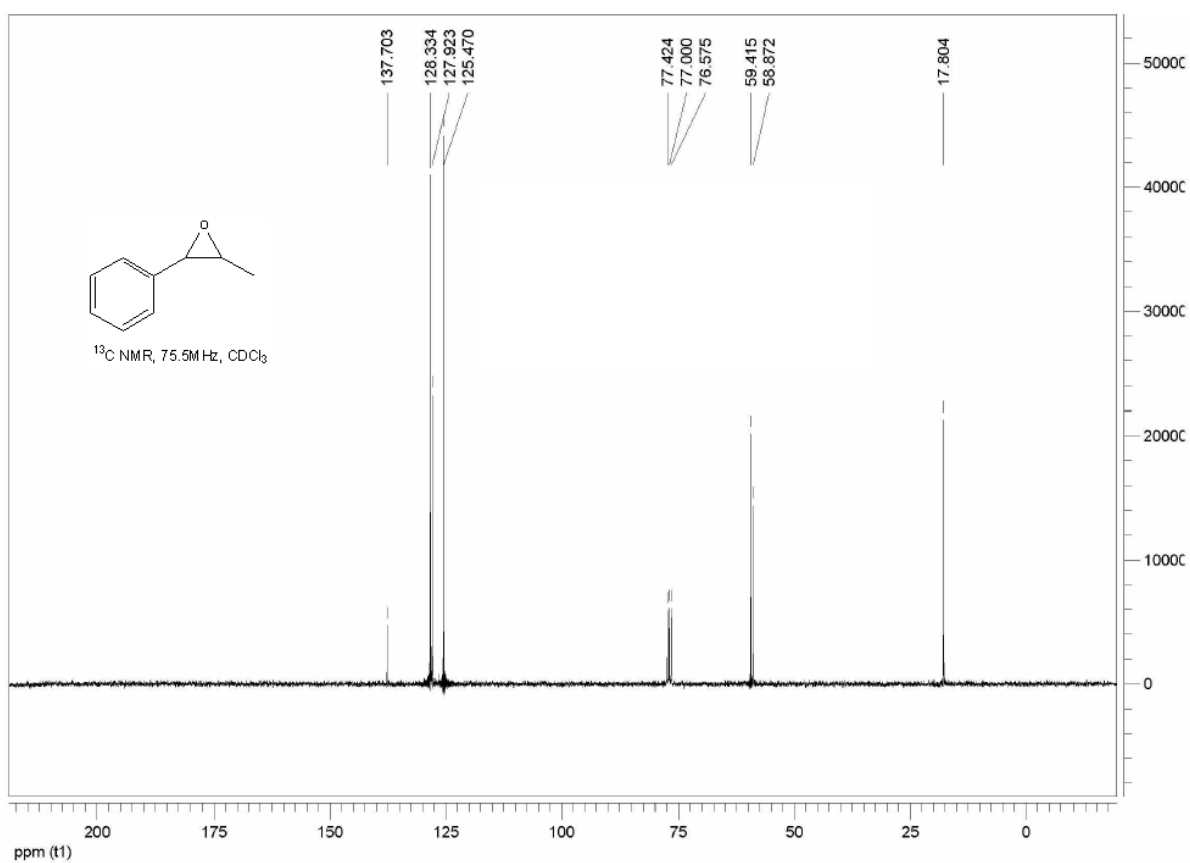
The reaction product analysis was carried out using GC (Shimadzu 2014) equipped with a 5% diphenyl and 95% dimethyl siloxane Restek capillary column (30 m length and 0.25 mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 60°C to 150°C at the rate of 10°C/min and then to 220°C at the rate of 40°/min. Nitrogen gas was used as a carrier gas. The temperatures of the injection port and FID were kept constant at 150°C and 250°C respectively during product analysis. Dodecane was used as an internal standard. The retention times for different compounds were determined by injecting pure compounds under identical conditions.

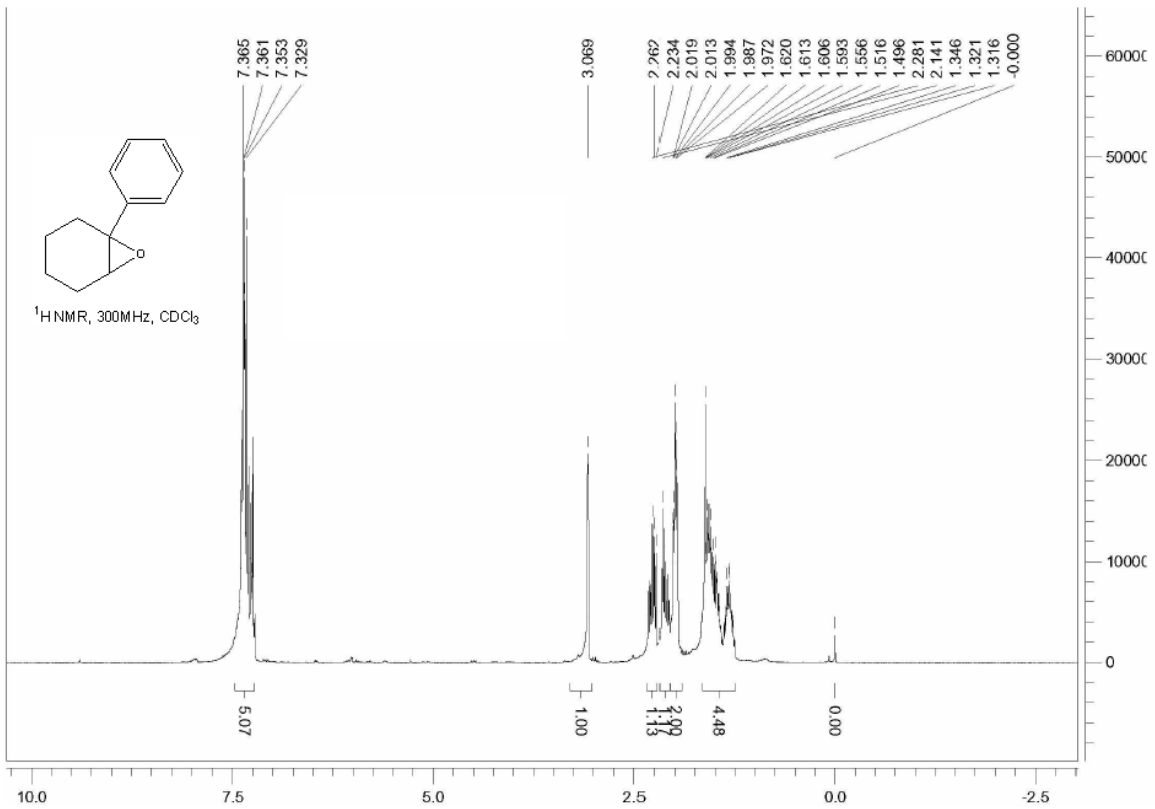
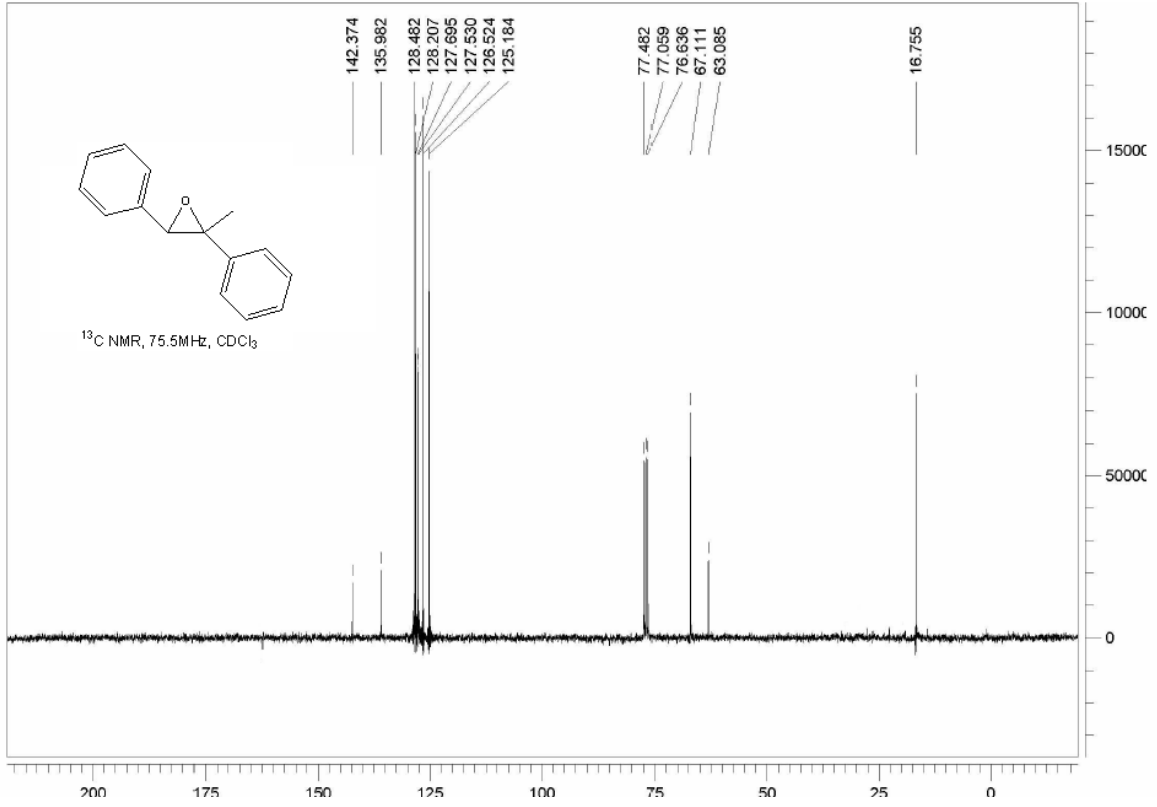
4. ^1H NMR and ^{13}C NMR Spectra of few epoxides

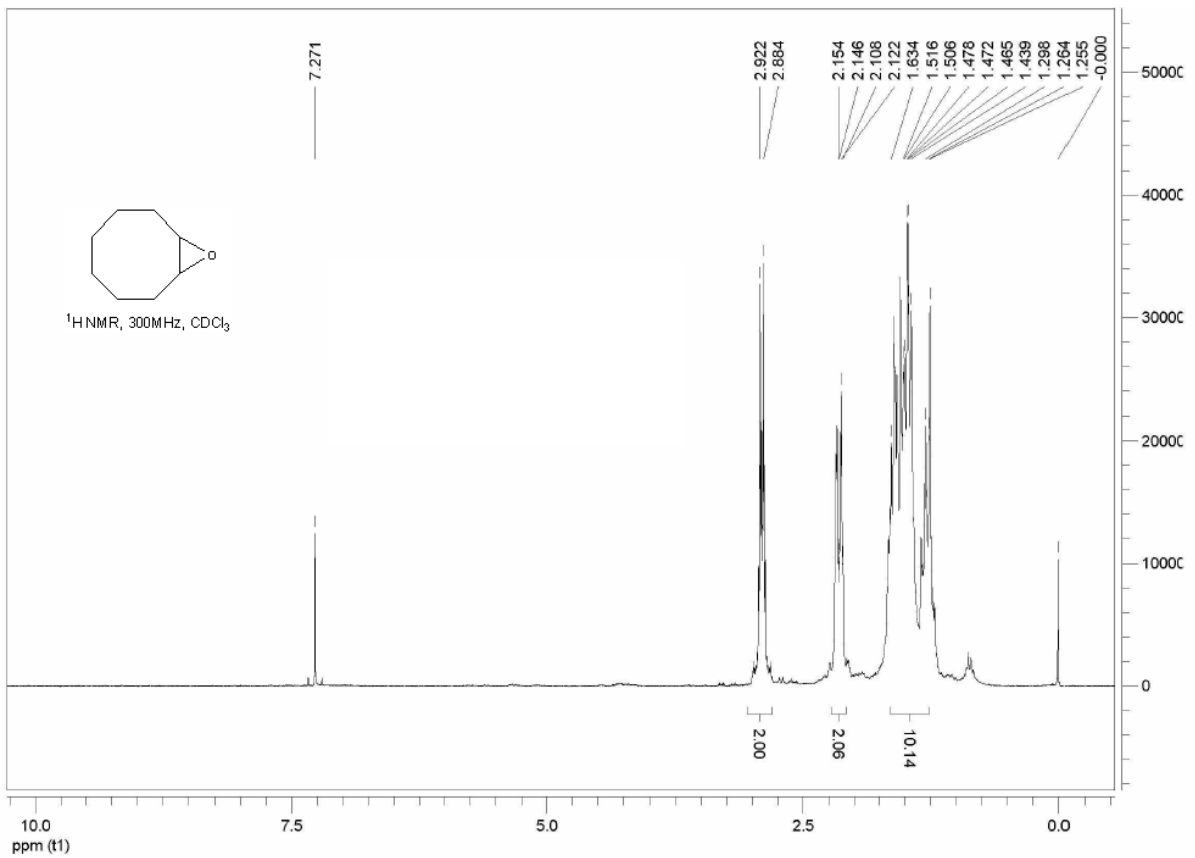
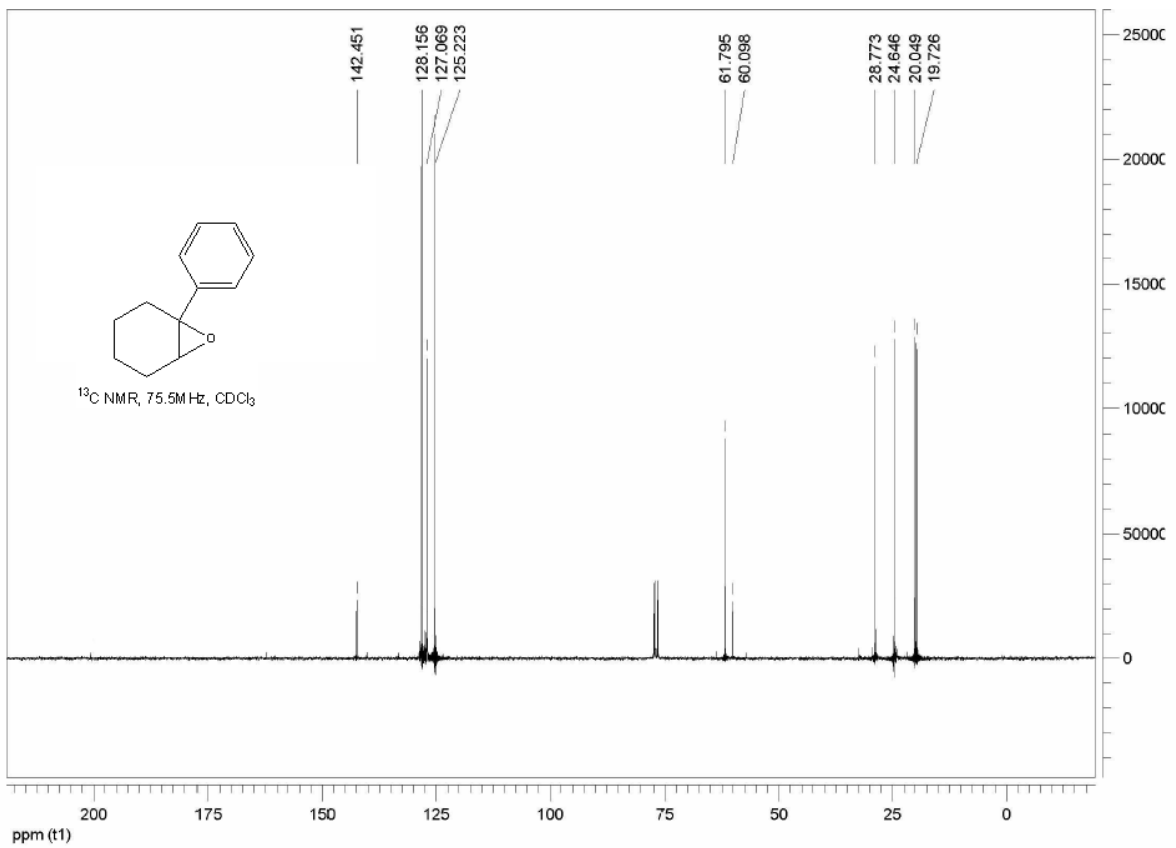


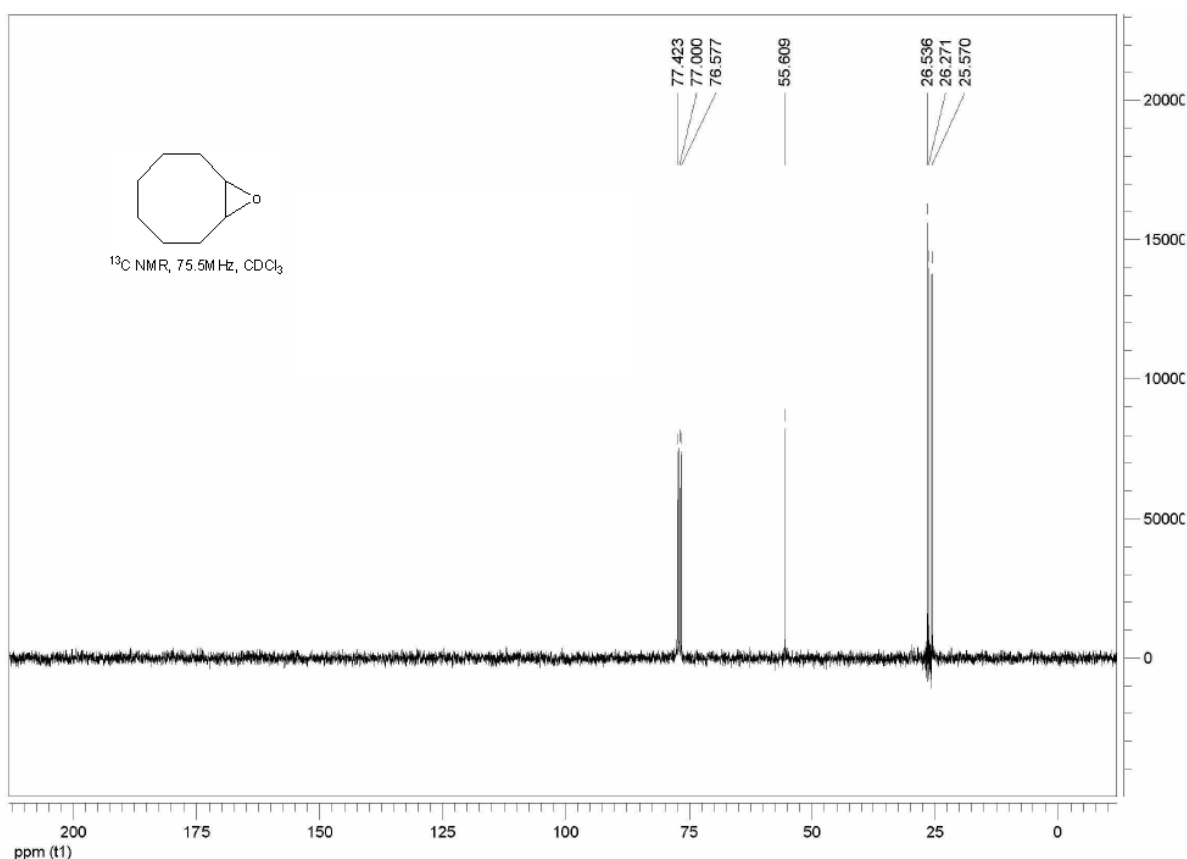












5. Characterization data for terpene epoxides

1-methyl-7-oxabicyclo[4.1.0]heptane: ^1H NMR δ 1.28 (s, 3H), .62 (d, $J = 9.6$ Hz, 1H), 1.43–1.60 (m, 4H), 1.66–1.70 (m, 4H), 2.86 (t, 1H); ^{13}C NMR δ 17.2, 23.6, 24.0, 26.7, 27.6, 65.3, 66.4.

3,8,8-trimethyl-4-oxatricyclo[5.1.0.0^{3,5}]octane: ^1H NMR δ 0.99 (s, 3H), 1.30 (s, 6H), 1.41 (m, 1H), 1.62–1.66 (m, 2H), 2.87 (d, $J = 3.2$ Hz, 1H); ^{13}C NMR δ 18.6, 20.1, 21.7, 23.2, 23.6, 30.7, 38.1, 60.1, 61.5.

2,7,7-trimethyl-3-oxatricyclo[4.1.1.0^{2,4}]octane: ^1H NMR δ 1.01 (s, 6H), 1.27 (s, 3H), 1.40 (dd, $J = 16.5, 2.3$ Hz, 1H), 1.47 (dd, 2H), 1.63 (dt, $J = 16.5, 2.3$ Hz, 2H), 1.73 (dd, $J = 16.5, 9.2$ Hz, 1H), 2.90 (t, 1H); ^{13}C NMR δ 22.0, 24.5, 25.6, 27.8, 39.9, 41.8, 45.4, 59.1, 63.6.

2-(6-methyl-7-oxabicyclo[4.1.0]heptan-3-yl)propan-2-ol: ^1H NMR δ 1.23 (s, 3H), 1.30 (s, 3H), 1.49 (m, 1H), 1.54 (t, 2H), 1.63–1.66 (m, 2H), 3.00 (d, $J = 5.5$ Hz, 1H); ^{13}C NMR δ 16.9, 22.8, 25.9, 27.8, 27.8, 29.5, 44.1, 58.5, 58.7, 72.2.

1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane: ^1H NMR δ 1.13–2.27 (m, 7H), 1.29 (s, 3H), 1.71 (s, 3H), 3.02 (t, 1H, $J = 5.5$ Hz), 4.75 (s, 2H); ^{13}C NMR δ 20.2, 22.1, 25.8, 28.5, 30.7, 40.7, 57.3, 59.2, 109.0, 148.8.

6. References

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