

## REFERENCES

1. Aitken, R. A. and Kilenyi, S. N. *Asymmetric Synthesis*; Glasgow: Blackie Academic & Professional, 1992.
2. Calani, L.; Sherrington, D. C. "Utilisation of Homogeneous and Supported Chiral Metal(Salen) Complexes in Asymmetric Catalyst" *Chem. Soc. Rev.* **1999**, 28, 85.
3. Katsuki, T.; Sharpless, K. B. "The First Practical Method for Asymmetric Epoxidation" *J. Am. Chem. Soc.* **1980**, 102, 5974.
4. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. "Enantioselective Epoxidation of Unfunctionalized Olefins Catalyzed by (Salen)Manganese Complexes" *J. Am. Chem. Soc.* **1990**, 112, 2801.
5. Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. "Highly Enantioselective Epoxidation Catalysts Derived from 1,2-Diaminocyclohexane" *J. Am. Chem. Soc.* **1991**, 113, 7063.
6. Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. "Catalytic Asymmetric Epoxidation of Unfunctional Olefins Using Chiral(salen) Manganese (III) complex" *Tetrahedron: Asymmetry* **1991**, 2, 481.
7. Linker, T. "The Jacobsen-Katsuki Epoxidation and Its Controversial Mechanism" *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2060.
8. Palucki, M.; Pospisil, P. J.; Zhang, W.; Jacobsen, E. N. "Highly Enantioselective, Low-Temperature Epoxidation of Styrene" *J. Org. Chem.* **1994**, 116, 9333.
9. Katsuki, T. "Mn-salen Catalyst, Competitor of Enzyme, for Asymmetric Epoxidation" *J. Mol. Catal. A.: Chemical* **1996**, 133, 87.
10. Mukaiyama, T.; Yamada, T. "Recent Advance in Aerobic Oxygenation" *Bull. Chem. Soc. Jpn.* **1995**, 68, 17.
11. Tu, Y.; Wang, Z.-X.; Shi, Y. "An Efficient Asymmetric Epoxidation Method for trans-Olefins Mediated by a Fructose-Derived Ketone" *J. Am. Chem. Soc.* **1996**, 118, 9806.

12. a) Brandes, B. D.; Jacobsen, E. N. "Synthesis of Enantiopure 3-chlorostyrene Oxide via an Asymmetric Epoxidation-Hydrolytic Kinetic Resolution Sequence" *Tetrahedron: Asymmetry* **1997**, *8*, 3927.
- b) Tokunaka, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. "Asymmetric Catalysis with Water: Efficient Kinetic Resolution of Terminal Epoxide by Means of Catalytic Hydrolysis" *Science* **1997**, *277*, 936.
13. Jacobsen, E. N.; Kakiuchi, F.; Konsler, R. G.; Larrow, J. F.; Tokunaga, M. "Enantioselective Catalytic Ring Opening of Epoxides with Carboxylic Acid" *Tetrahedron Lett.* **1997**, *38*, 733.
14. Wu, M. H.; Jacobsen, E. N. "Asymmetric Ring Opening of Meso Epoxide with Thiols: Enantiomeric Enrichment Using a Bifunctional Nucleophile" *J. Org. Chem.* **1998**, *63*, 5252.
15. a) Martinez, L. E.; Leighton, J. I.; Carsten, D. H.; Jacobsen, E. N. "Highly Enantioselective Ring Opening of Epoxides Catalyzed by (Salen)Cr(III) Complexes" *J. Am. Chem. Soc.* **1995**, *117*, 5897.
- b) Wu, M. H.; Jacobsen, E. N. "An Efficient Formal Synthesis of Balanol via the Asymmetric Epoxide Ring Opening Reaction" *Tetrahedron Lett.* **1997**, *38*, 1693.
- c) Schaus, S. E.; Larrow, J. F.; Jacobsen, E. N. "Practical Synthesis of Enantiopure Cyclic 1,2-Amino Alcohol via Catalytic Asymmetric Ring Opening of Meso Epoxide" *J. Org. Chem.* **1997**, *62*, 4197.
16. Schaus, S. E.; Branalt, J.; Jacobsen, E. N. "Asymmetric Hetero-Diels-Alder Reactions Catalyzed by Chiral (Salen)Chromium(III) Complexes" *J. Org. Chem.* **1998**, *63*, 403.
17. Sigman, M. S.; Jacobsen, E. N. "Enantioselective Addition of Hydrogen Cyanide to Imine Catalyzed by a Chiral (Salen)Al(III) Complex" *J. Am. Chem. Soc.* **1998**, *120*, 5315.
18. Tararov, V. I.; Hibbs, D. E.; Hursthouse, M. B.; Ikonnikov, N. S.; Malik, K. M. A.; North, M.; Orizu, C.; Belokon, Y. N. "First Structurally Defined Catalyst for the Asymmetric Addition of Trimethylsilyl Cyanide to Benzaldehyde" *Chem. Commun.* **1998**, 387.
19. De, B. B.; Lohray, B. B.; Sivaram, S.; Dhal, P. K. "Enantioselective Epoxidation of Olefin Catalyzed by Polymer-Bound Optically Active Mn(III)-Salen Complex" *Tetrahedron: Asymmetry* **1995**, *6*, 2105.

20. Minutolo, F.; Pini, D.; Salvadori, P. "Heterogeneous Asymmetric Epoxidation of Unfunctionalized Olefins Catalyzed by Polymer-Bound (Salen)Manganese Complexes" *Tetrahedron: Asymmetry* **1996**, *7*, 2293.
21. Annis, D. A.; Jacobsen E. N. "Polymer-Supported Chiral Co(Salen) Complexes: Synthetic Applications and Mechanistic Investigations in the Hydrolytic Kinetic Resolution of Terminal Epoxides" *J. Am. Chem. Soc.* **1999**, *121*, 4147.
22. Reger, T. S.; Janda, K. D. "Polymer-Supported (Salen)Mn Catalysts for Asymmetric Epoxidation: A Comparison between Soluble and Insoluble Matrices" *J. Am. Chem. Soc.* **2000**, *122*, 6929.
23. Trost, B. M.; Radinov, R. "On the Effect of a Cation Binding Site in an Asymmetric Ligand for a Catalyzed Nucleophilic Substitution Reaction" *J. Am. Chem. Soc.* **1997**, *119*, 5962.
24. Bergbreiter, D. E.; Osburn, P. L.; Lui, Y.-S. "Tridentate SCS Palladium(II) Complexes: New, Highly Stable, Recyclable Catalysts for the Heck Reaction" *J. Am. Chem. Soc.* **1999**, *121*, 953.
25. Cervinka, O. *Enantioselective Reactions in Organic Chemistry*, 1<sup>st</sup> ed., Prague: Publishing House of the Academy of Sciences of the Czech Republic, 1995.
26. Mitsunobu, O. "The Use of Diethylazodicarboxylate and Triphenylphosphine in Synthesis and Transformation of Natural Products" *Synthesis* **1981**, 1-5-28.
27. Duff, J. C.; Bills, E. J. "Reactions between Hexamethylenetetramine and Phenolic Compound. Part II. Formation of Phenolic Aldehydes. Distinctive Behavior of *p*-Nitrophenol." *J. Chem. Soc.* **1934**, 1305.
28. Casiraghi, G; Casnati, G.; Puglia, G.; Sartori, G; Terenghi, G. "Selective Reactions between Phenols and Formaldehyde. A Novel Route to Salicylaldehydes" *J. Chem. Soc., Perkin Trans. 1* **1980**, 1862.
29. Hofsløkken, N. U.; Skattebøl, L. "Convenient Method for the Ortho-Formylation of Phenols" *Acta Chem. Scand.* **1999**, *53*, 258.
30. Finney, N. S.; Pospisil, P. J.; Chang, S.; Palucki, M.; Konsler, R. G.; Hansen, K. B.; Jacobsen, E. N. "On the Viability of Oxamethacyclic Intermediates in the (salen)Mn-Catalyzed Asymmetric Epoxidation" *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1.



**APPENDIXES**

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

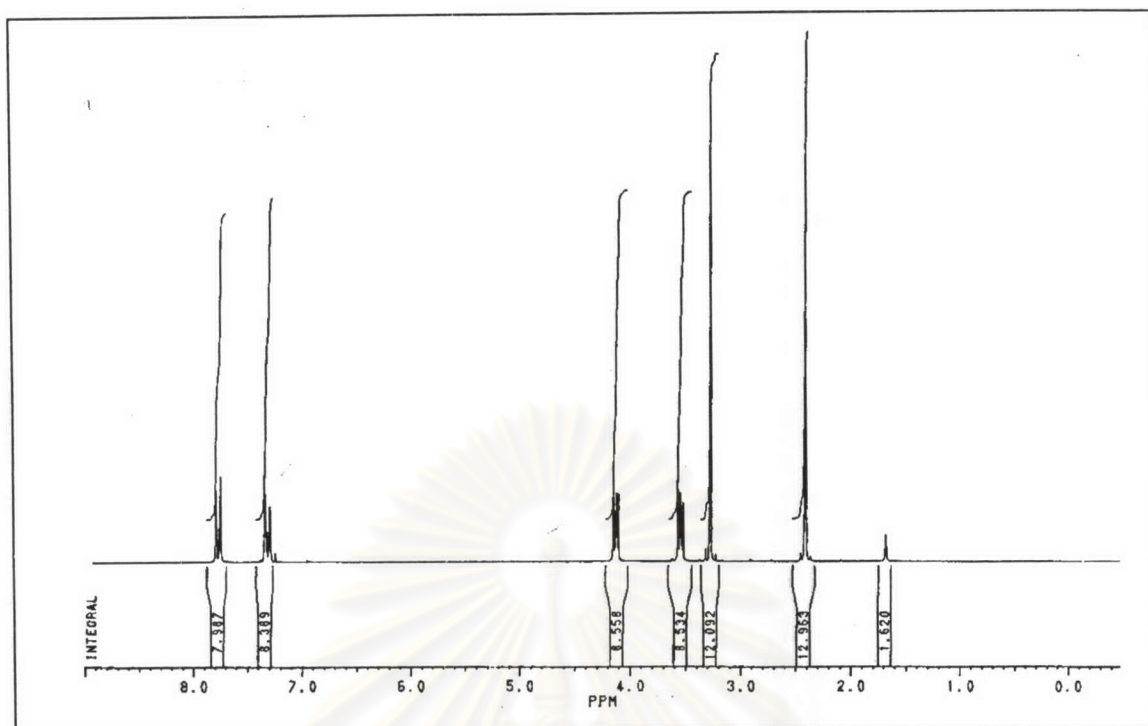


Figure A.1 The  $^1\text{H-NMR}$  spectrum of ethylene glycol monomethyl tosylate, 1.

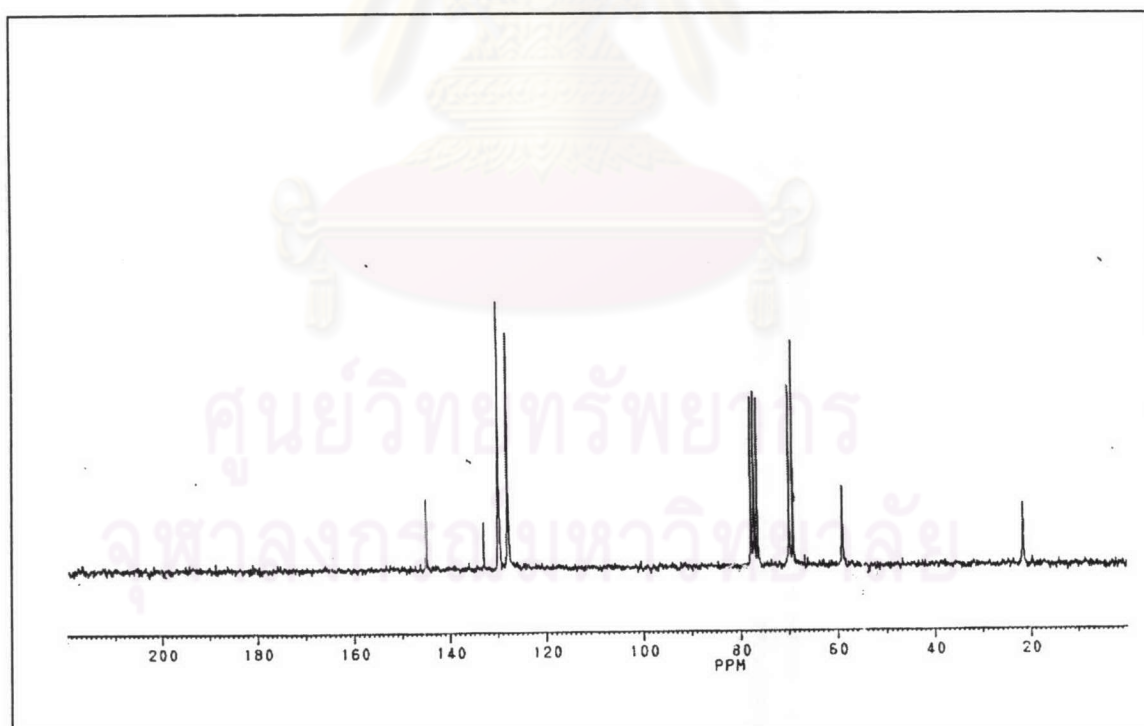


Figure A.2 The  $^{13}\text{C-NMR}$  spectrum of ethylene glycol monomethyl tosylate, 1.

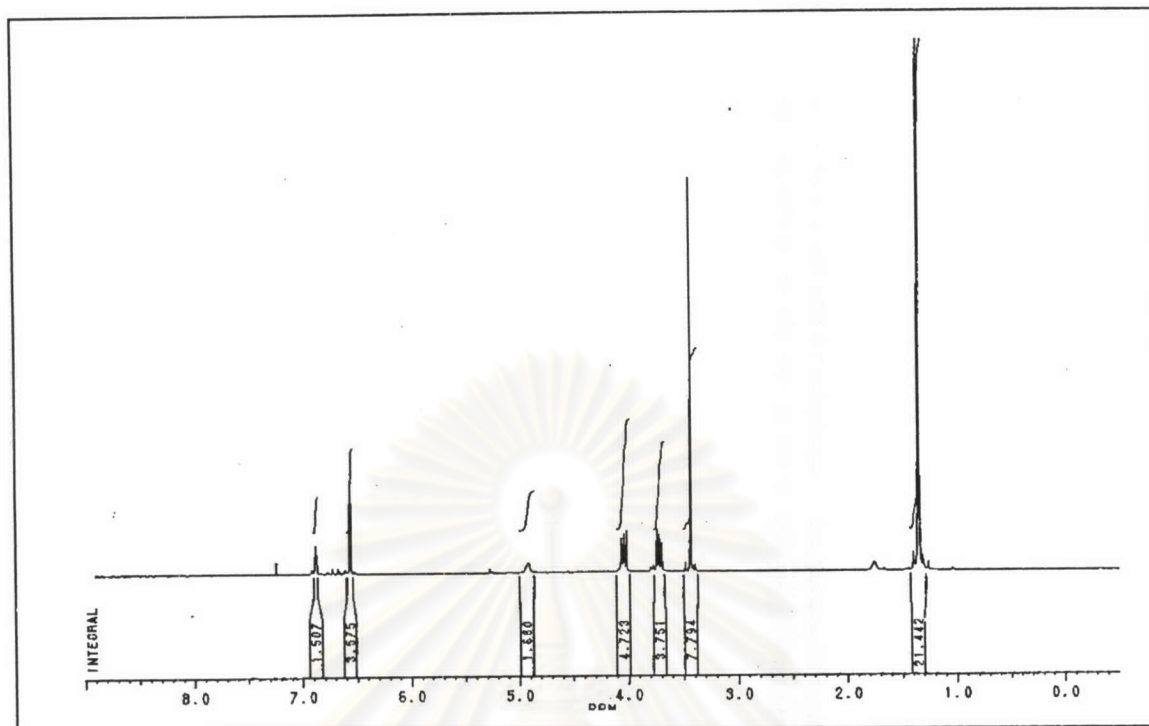


Figure A.3 The <sup>1</sup>H-NMR spectrum of 2-*t*-butyl-4-(2-methoxyethoxy)phenol, **2**.

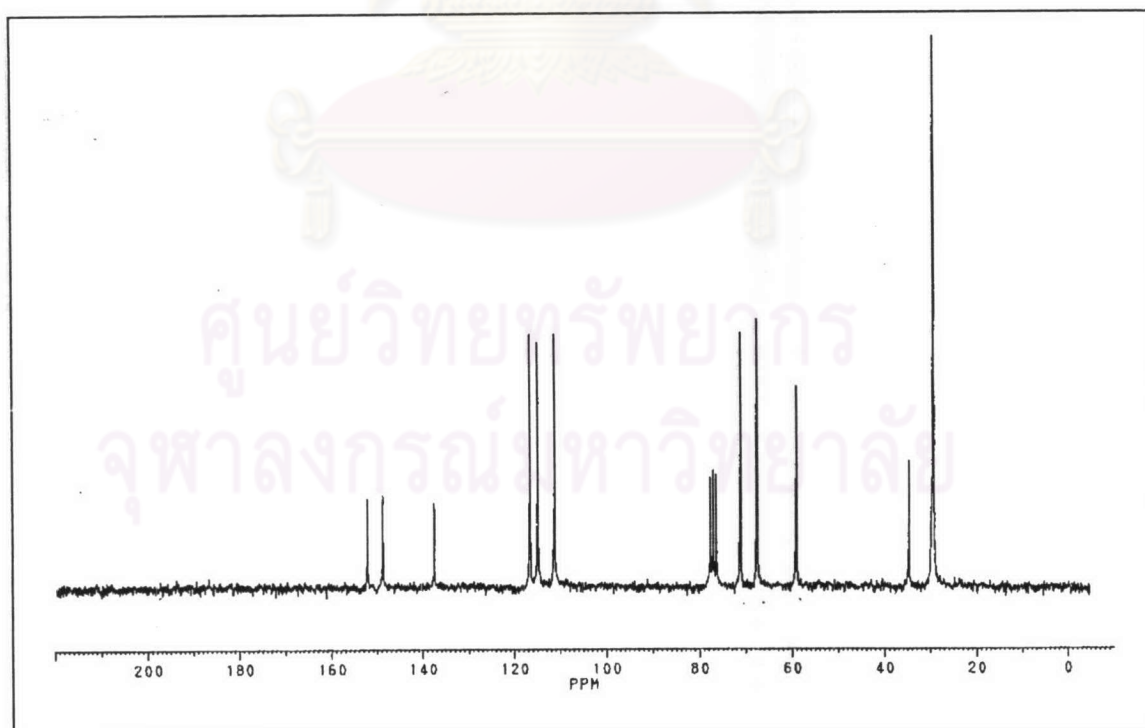
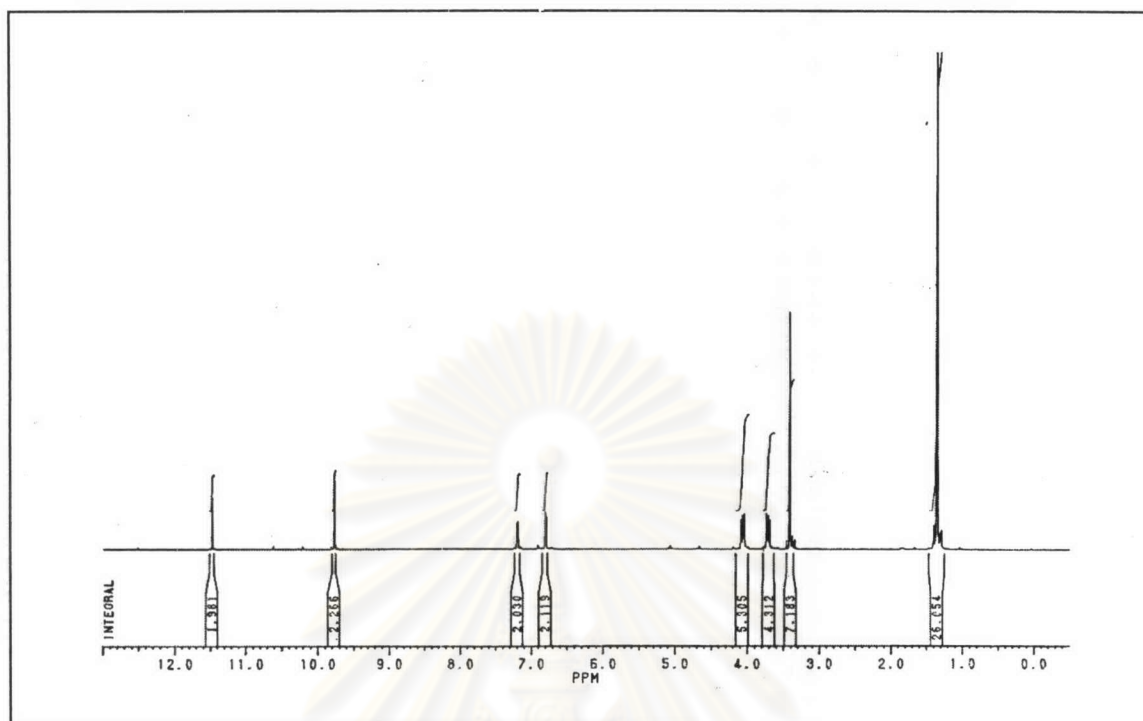
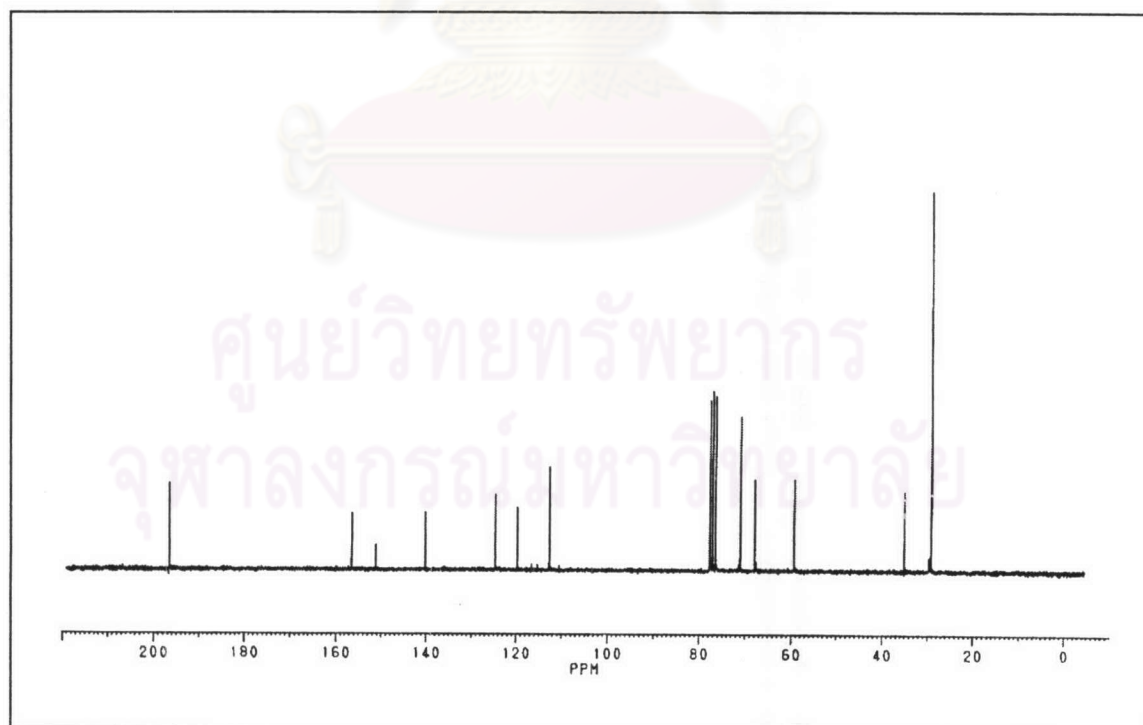


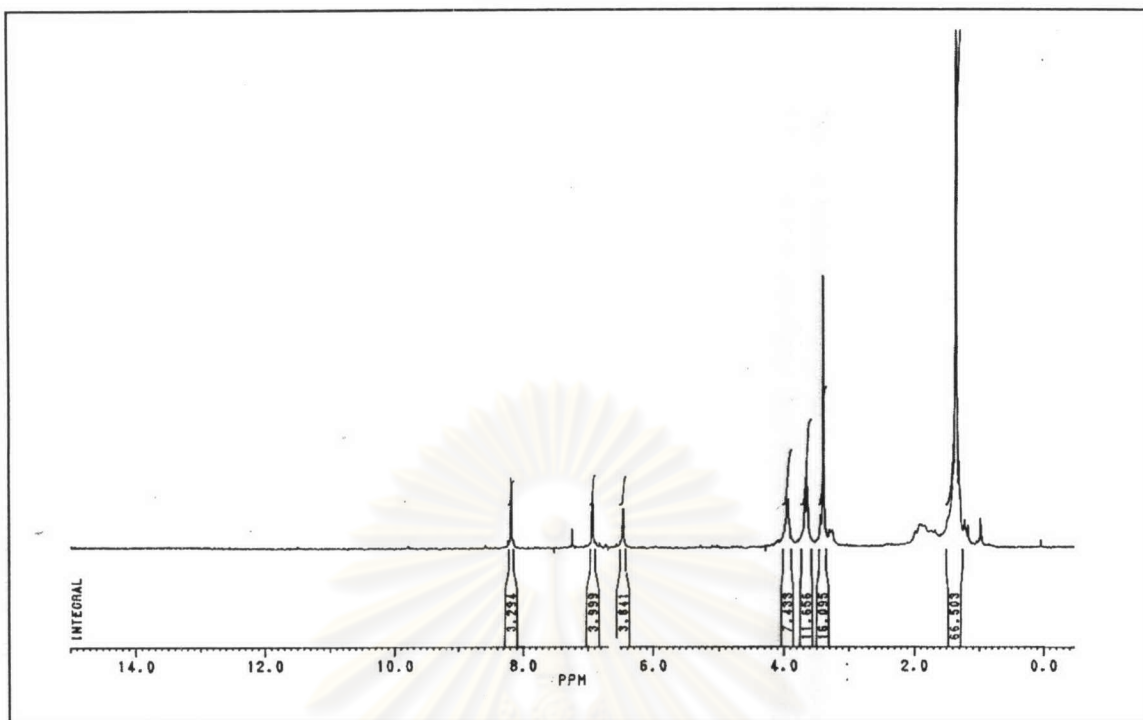
Figure A.4 The <sup>13</sup>C-NMR spectrum of 2-*t*-butyl-4-(2-methoxyethoxy)phenol, **2**.



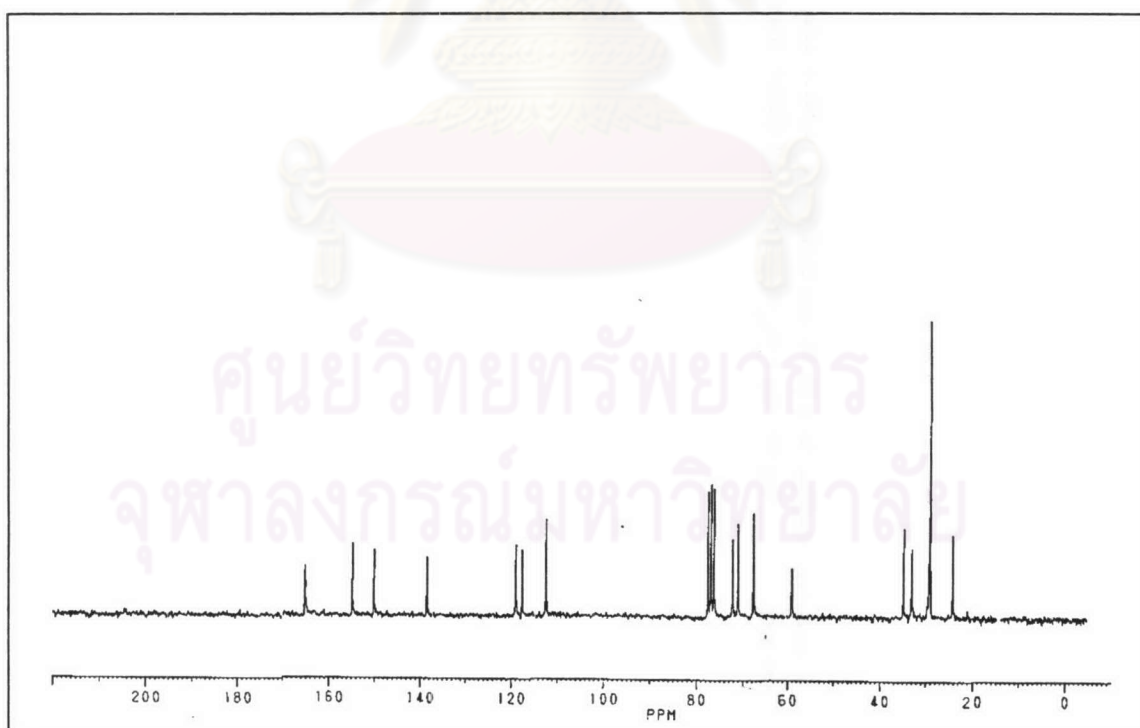
**Figure A.5** The <sup>1</sup>H-NMR spectrum of 3-*t*-butyl-5-(2-methoxyethoxy) salicylaldehyde, **3**.



**Figure A.6** The <sup>13</sup>C-NMR spectrum of 3-*t*-butyl-5-(2-methoxyethoxy) salicylaldehyde, **3**.

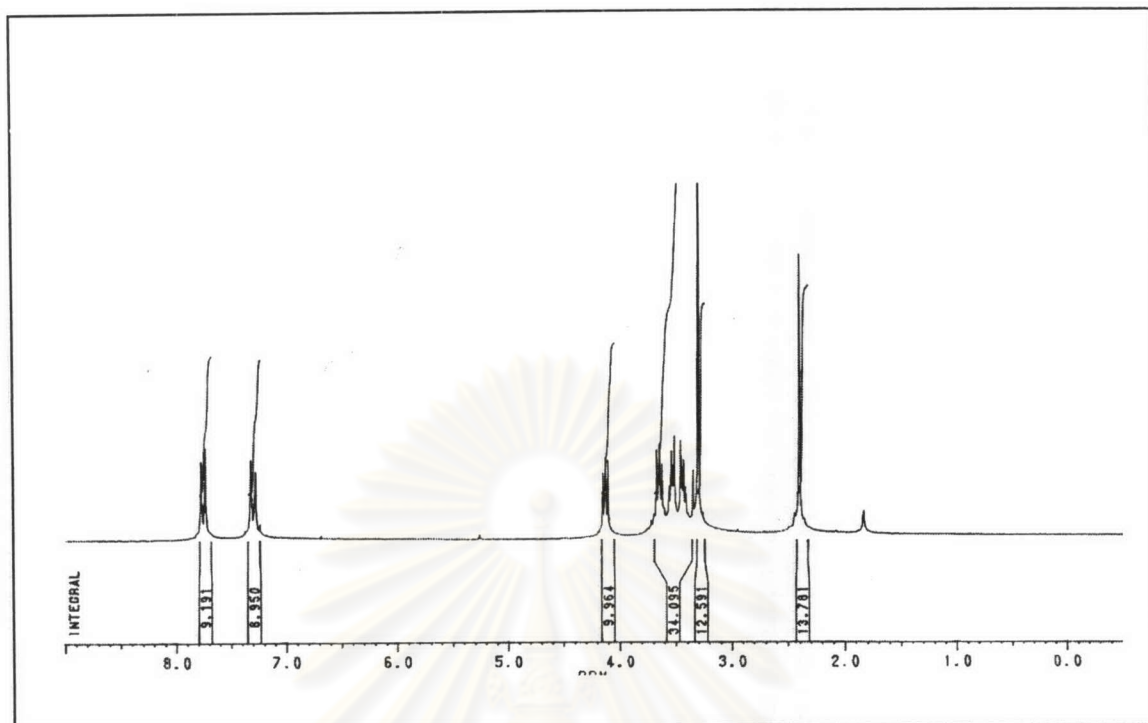


**Figure A.7** The <sup>1</sup>H-NMR spectrum of (*R,R*)-*N,N'*-bis(3-*t*-butyl-5-(2-methoxyethoxy)salicylidine)-1,2-cyclohexanediamine, **4**.

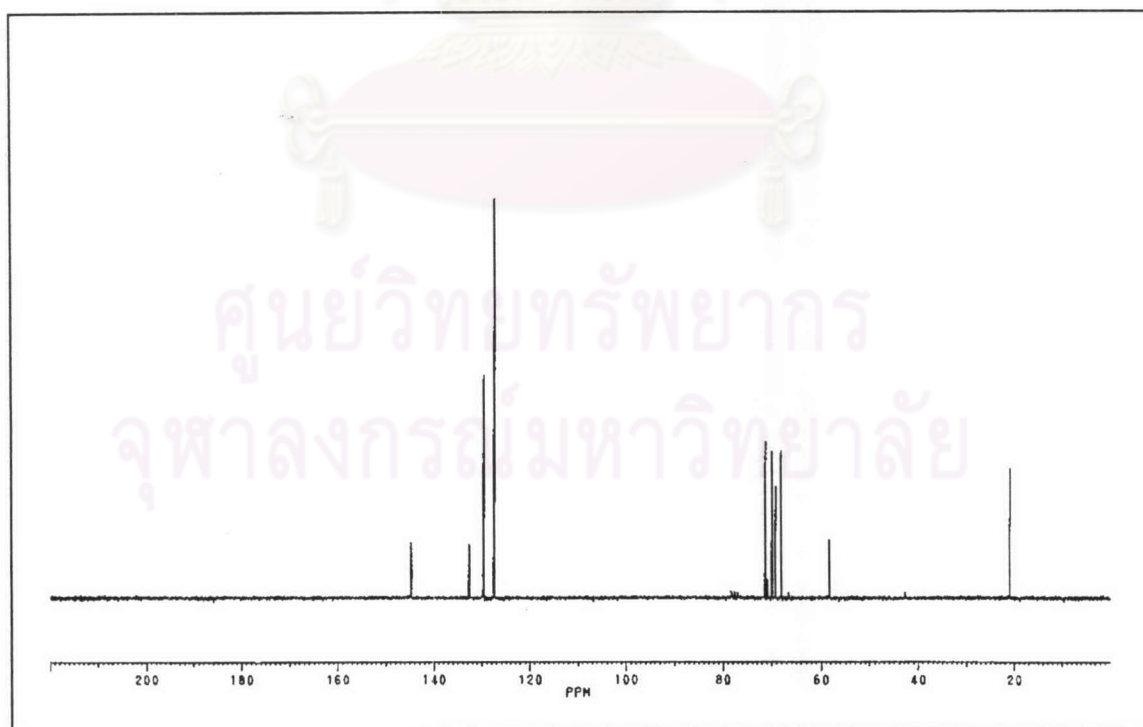


**Figure A.8** The <sup>13</sup>C-NMR spectrum of (*R,R*)-*N,N'*-bis(3-*t*-butyl-5-(2-methoxyethoxy)salicylidine)-1,2-cyclohexanediamine, **4**.

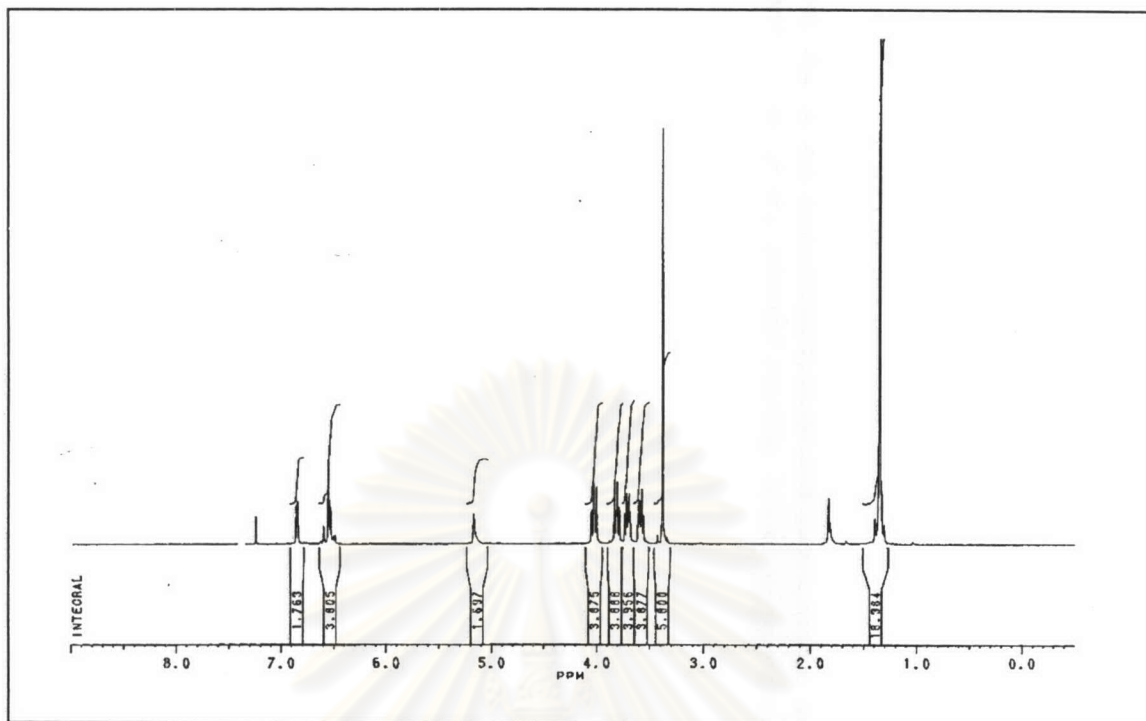




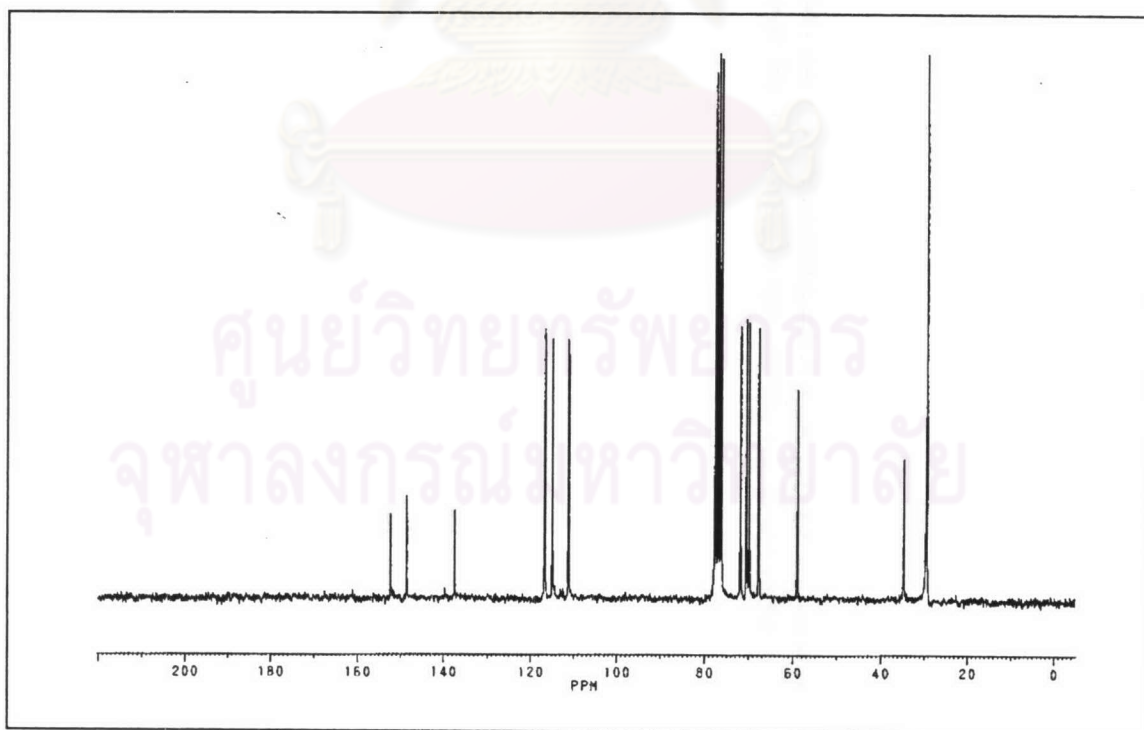
**Figure A.9** The  $^1\text{H-NMR}$  spectrum of diethylene glycol monomethyl tosylate, 5.



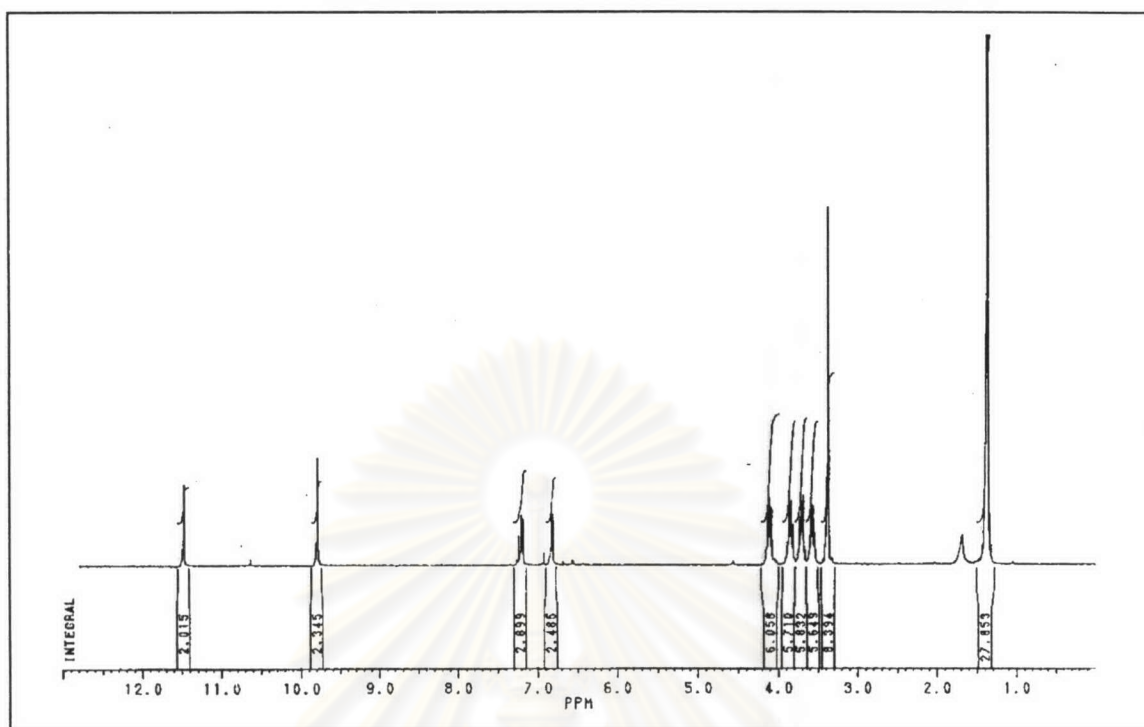
**Figure A.10** The  $^{13}\text{C-NMR}$  spectrum of diethylene glycol monomethyl tosylate, 5.



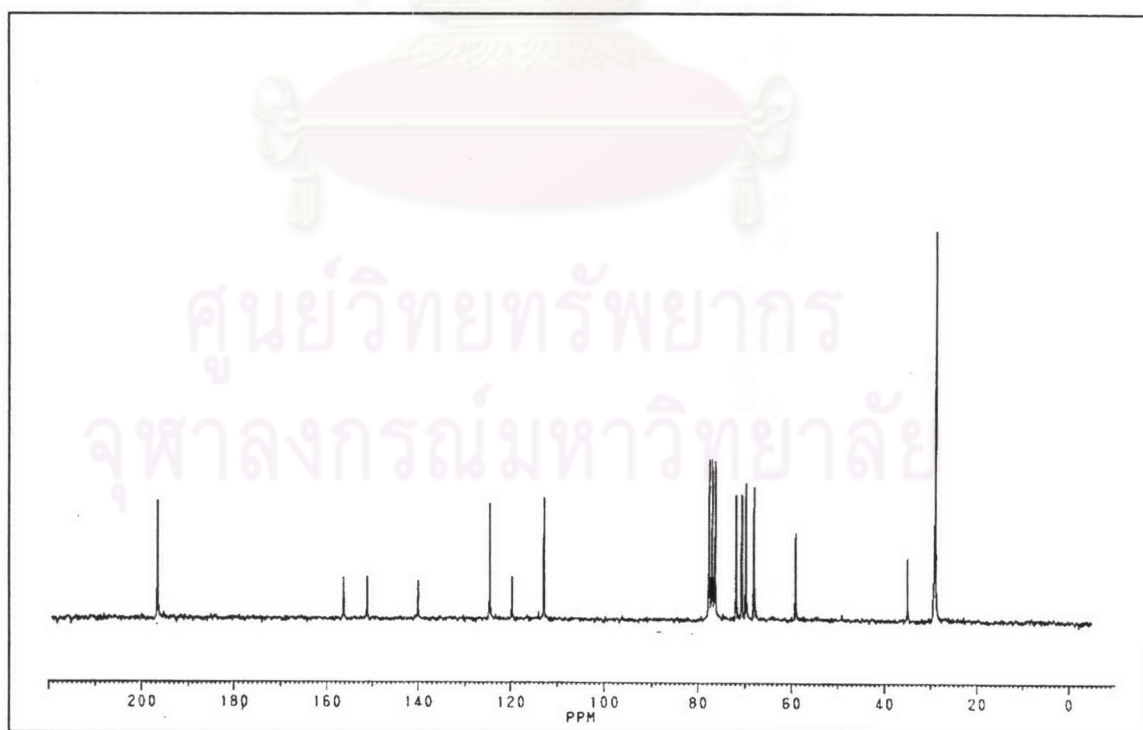
**Figure A.11** The  $^1\text{H-NMR}$  spectrum of 2-*t*-butyl-4-((2-(2-methoxy)ethoxy)ethoxy)phenol, 6.



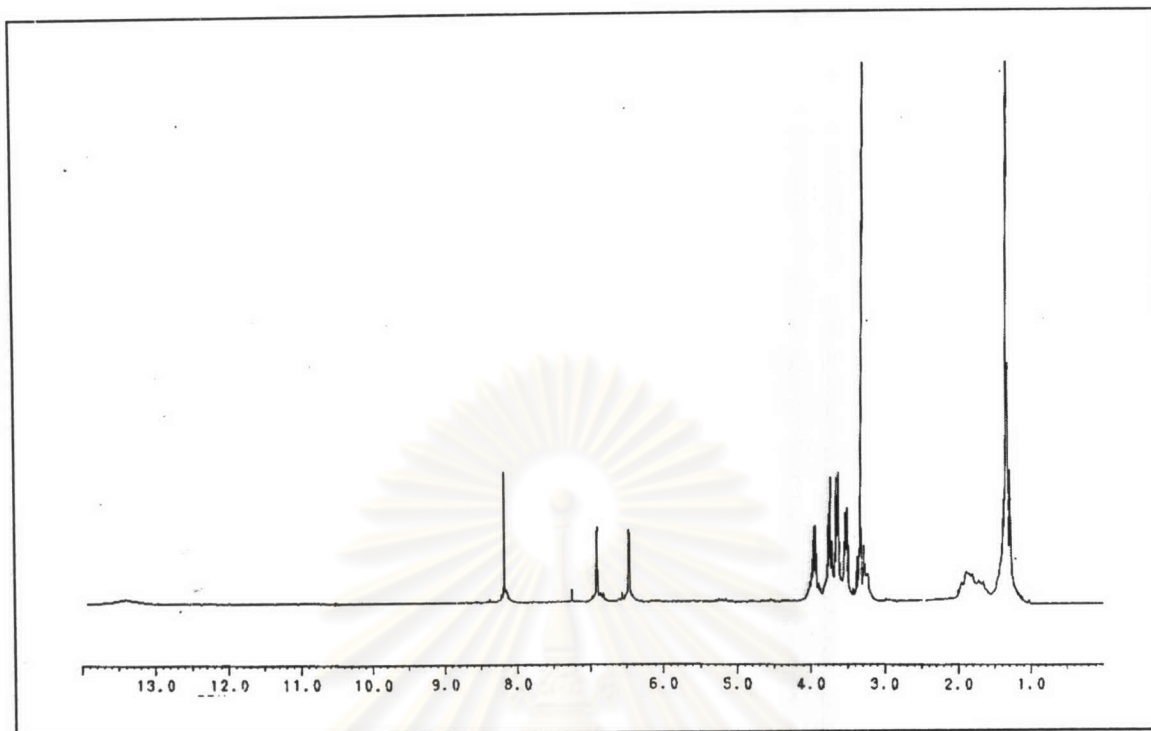
**Figure A.12** The  $^{13}\text{C-NMR}$  spectrum of 2-*t*-butyl-4-((2-(2-methoxy)ethoxy)ethoxy)phenol, 6.



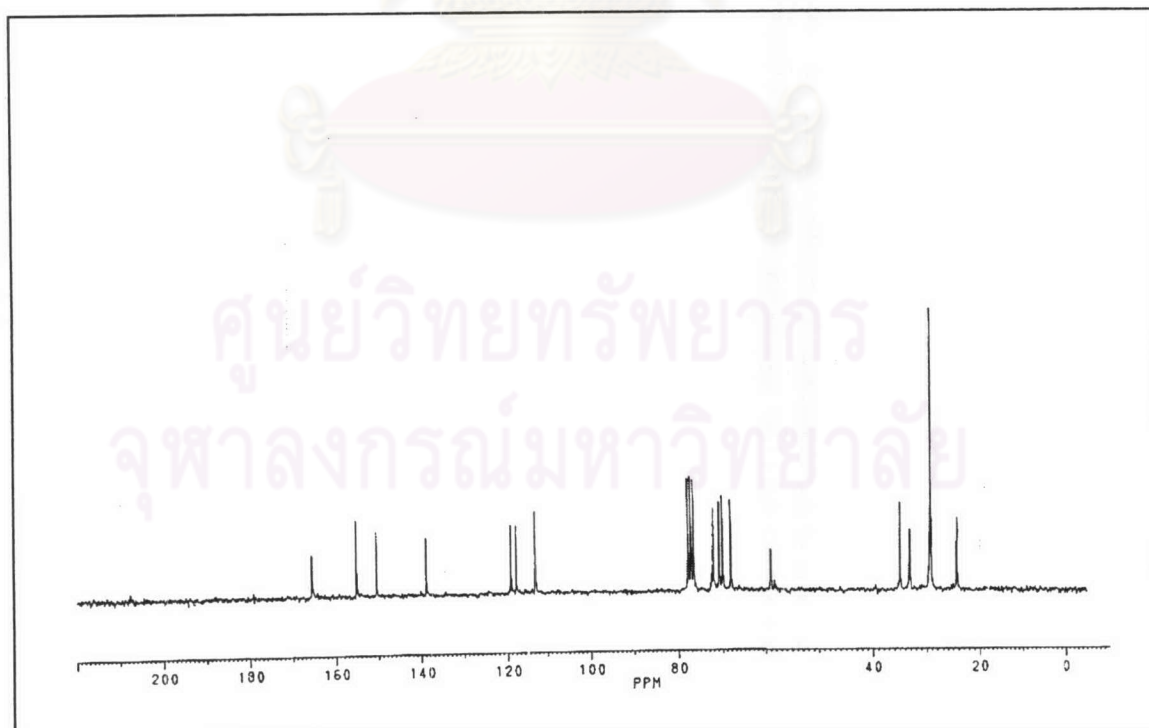
**Figure A.13** The  $^1\text{H}$ -NMR spectrum of 3-*t*-butyl-5-((2-(2-methoxy)ethoxy)ethoxy)salicylaldehyde, **7**.



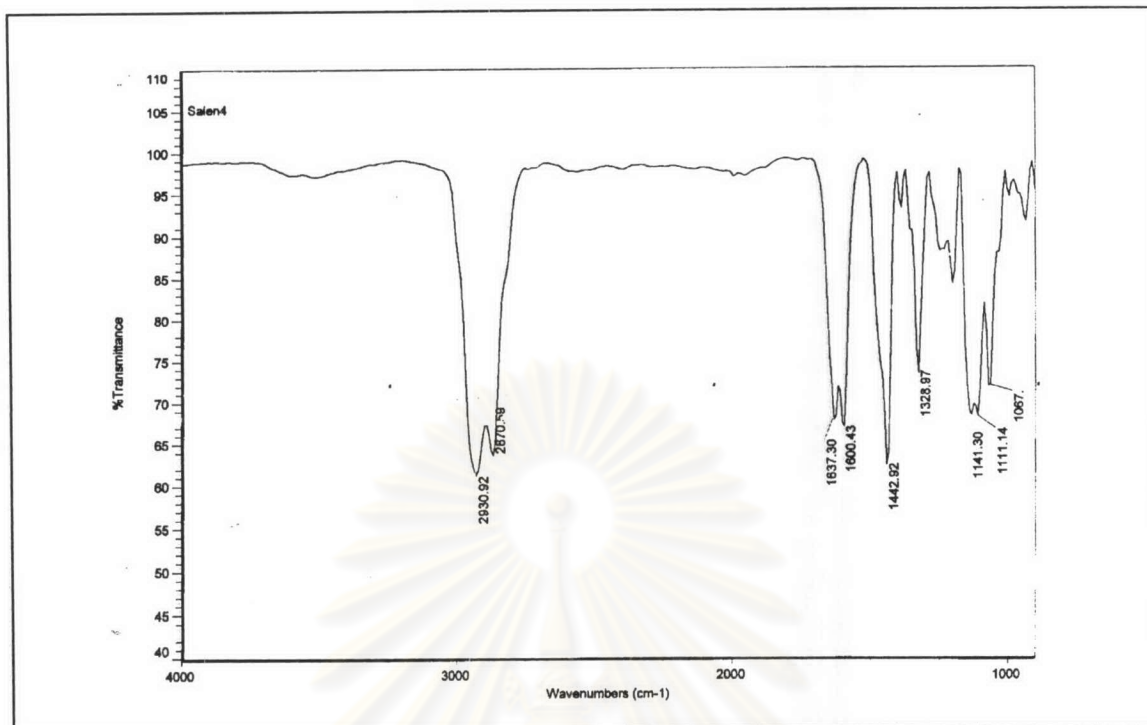
**Figure A.14** The  $^{13}\text{C}$ -NMR spectrum of 3-*t*-butyl-5-((2-(2-methoxy)ethoxy)ethoxy)salicylaldehyde, **7**.



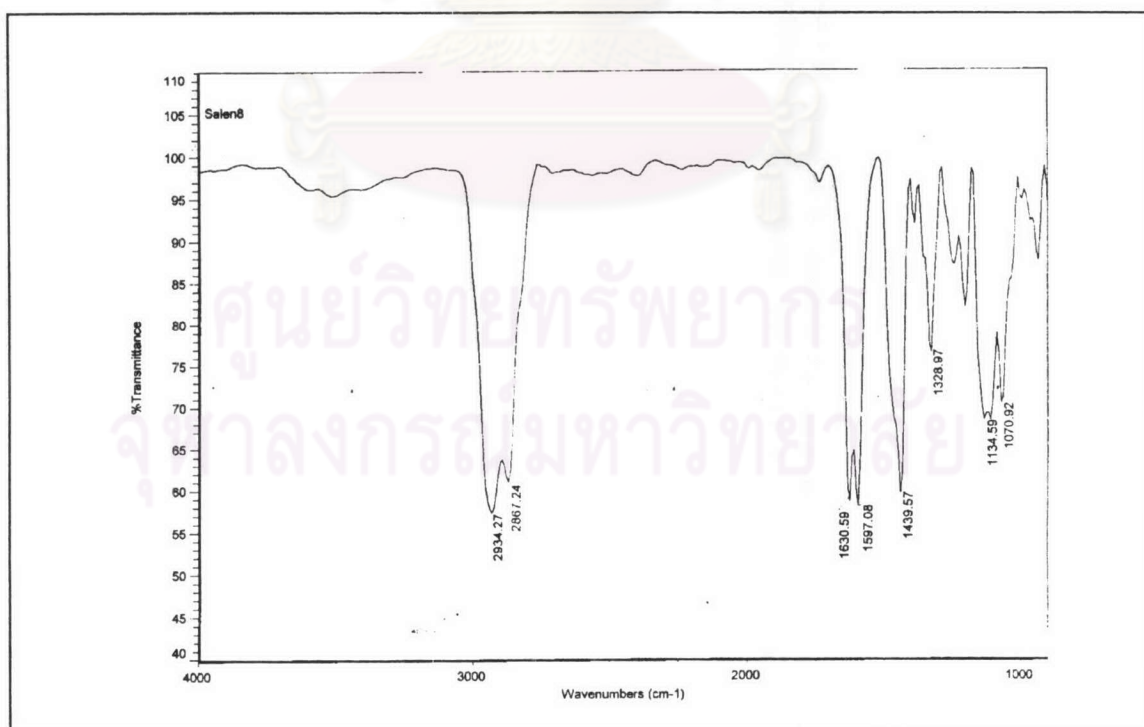
**Figure A.15** The <sup>1</sup>H-NMR spectrum of (*R,R*)-*N,N'*-bis(3-*t*-butyl-5-((2-(2-methoxy)ethoxy)ethoxy)salicylidine)-1,2-cyclohexanediamine, **8**.



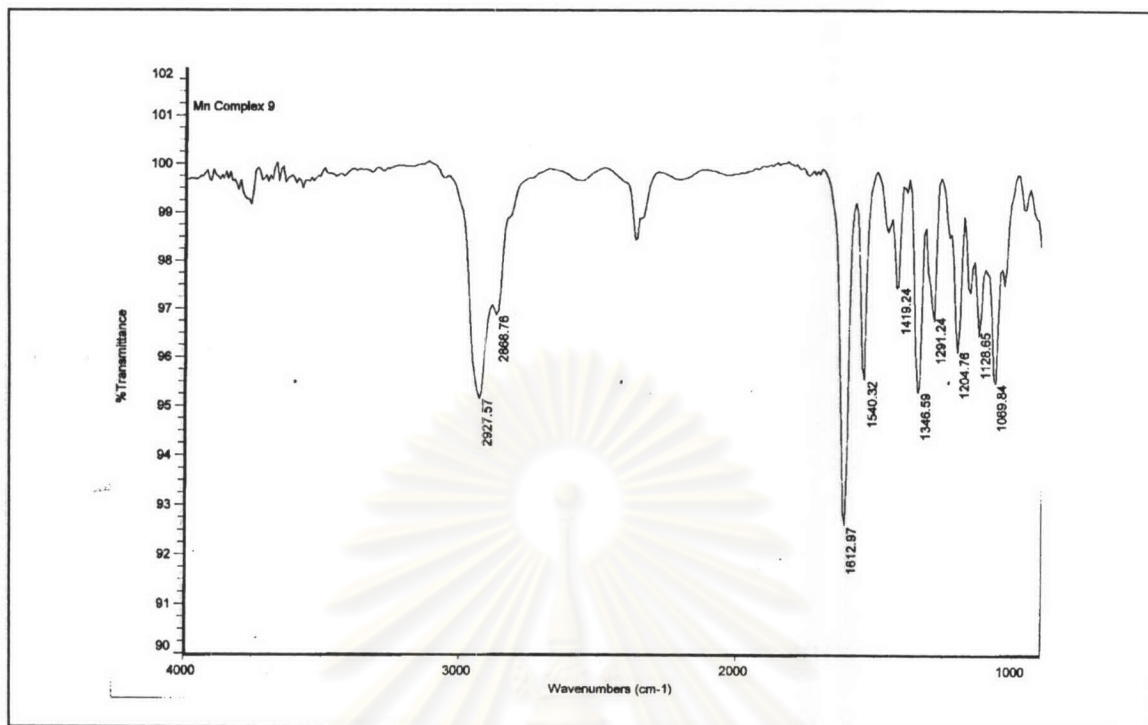
**Figure A.16** The <sup>13</sup>C-NMR spectrum of (*R,R*)-*N,N'*-bis(3-*t*-butyl-5-((2-(2-methoxy)ethoxy)ethoxy)salicylidine)-1,2-cyclohexanediamine, **8**.



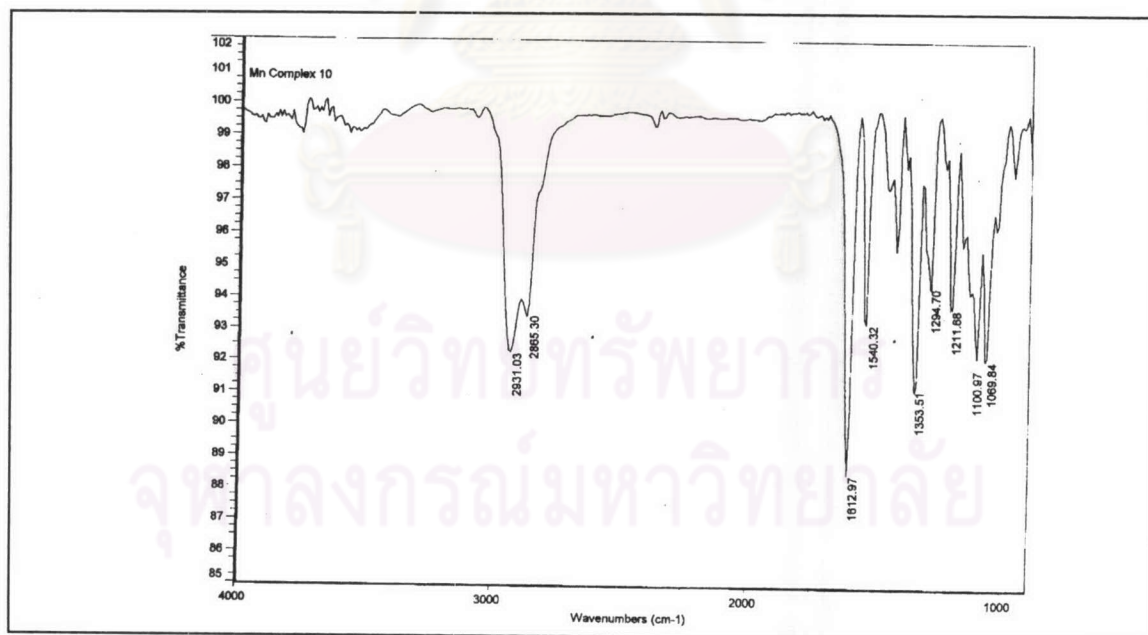
**Figure A.17** The IR spectrum of (R,R)-N,N'-bis(3-t-butyl-5-(2-methoxyethoxy)salicylidine)-1,2-cyclohexanediamine, **4**.



**Figure A.18** The IR spectrum of (R,R)-N,N'-bis(3-t-butyl-5-((2-(2-methoxy)ethoxy)ethoxy)salicylidine)-1,2-cyclohexanediamine, **8**.



**Figure A.19** The IR spectrum of [(*R,R*)-*N,N'*-bis(3-*t*-butyl-5-(2-methoxyethoxy) salicylidine)-1,2-cyclohexanediaminato(2-)] manganese(III) chloride, **9**.



**Figure A.20** The IR spectrum of [(*R,R*)-*N,N'*-bis(3-*t*-butyl-5-5-((2-(2-methoxy)ethoxy)ethoxy)salicylidine)-1,2-cyclohexanediaminato(2-)] manganese(III) chloride, **10**.

## Display Report

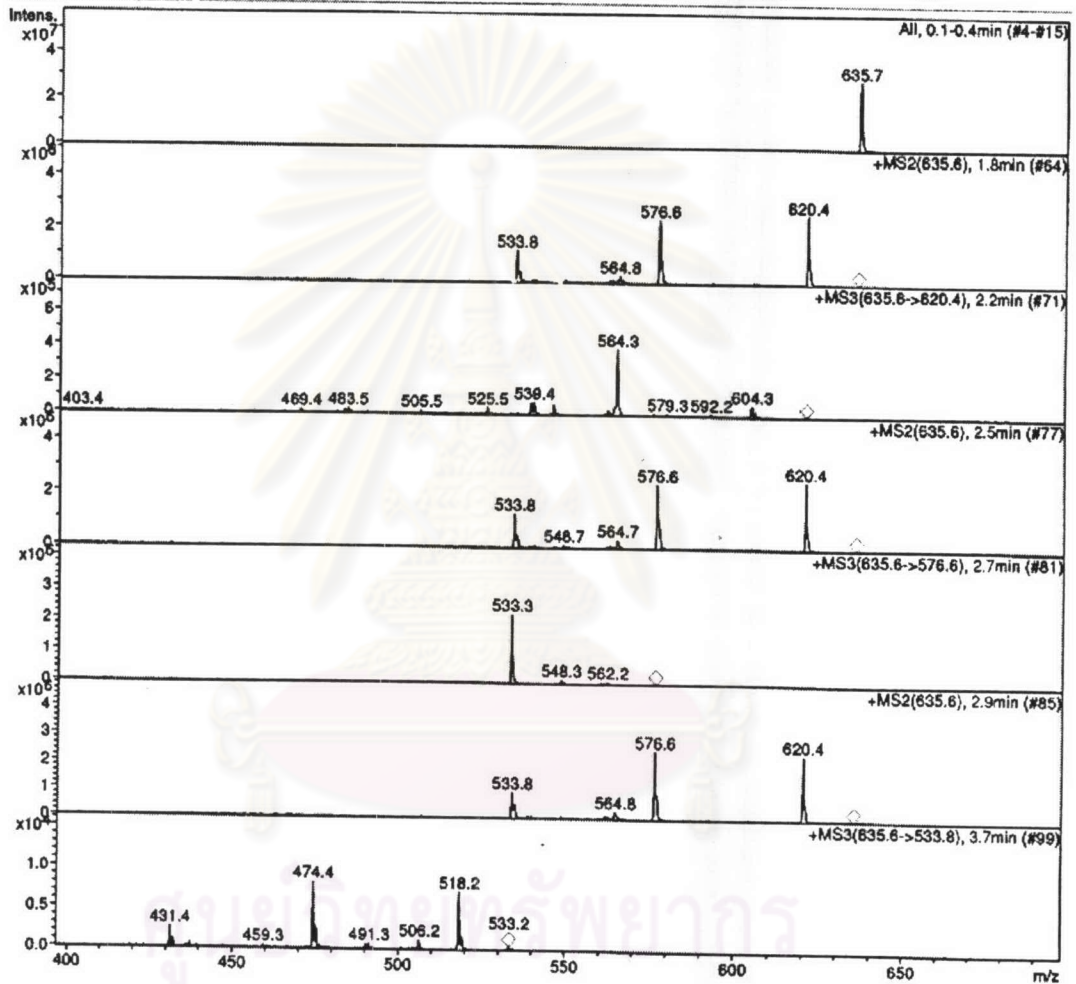
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 Comment in MeOH

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 Operator Administrator  
 Instrument esquire3000plus\_01012

**Acquisition Parameter**

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Accumulation Time	79 $\mu$ s	Averages	8 Spectra	Auto MS/MS	Off



**Figure A.21** The ESI mass spectrum of [(*R,R*)-*N,N'*-bis(3-*t*-butyl-5-(2-methoxyethoxy)salicylidine)-1,2-cyclohexanediaminato(2-)] manganese(III) chloride, 9.

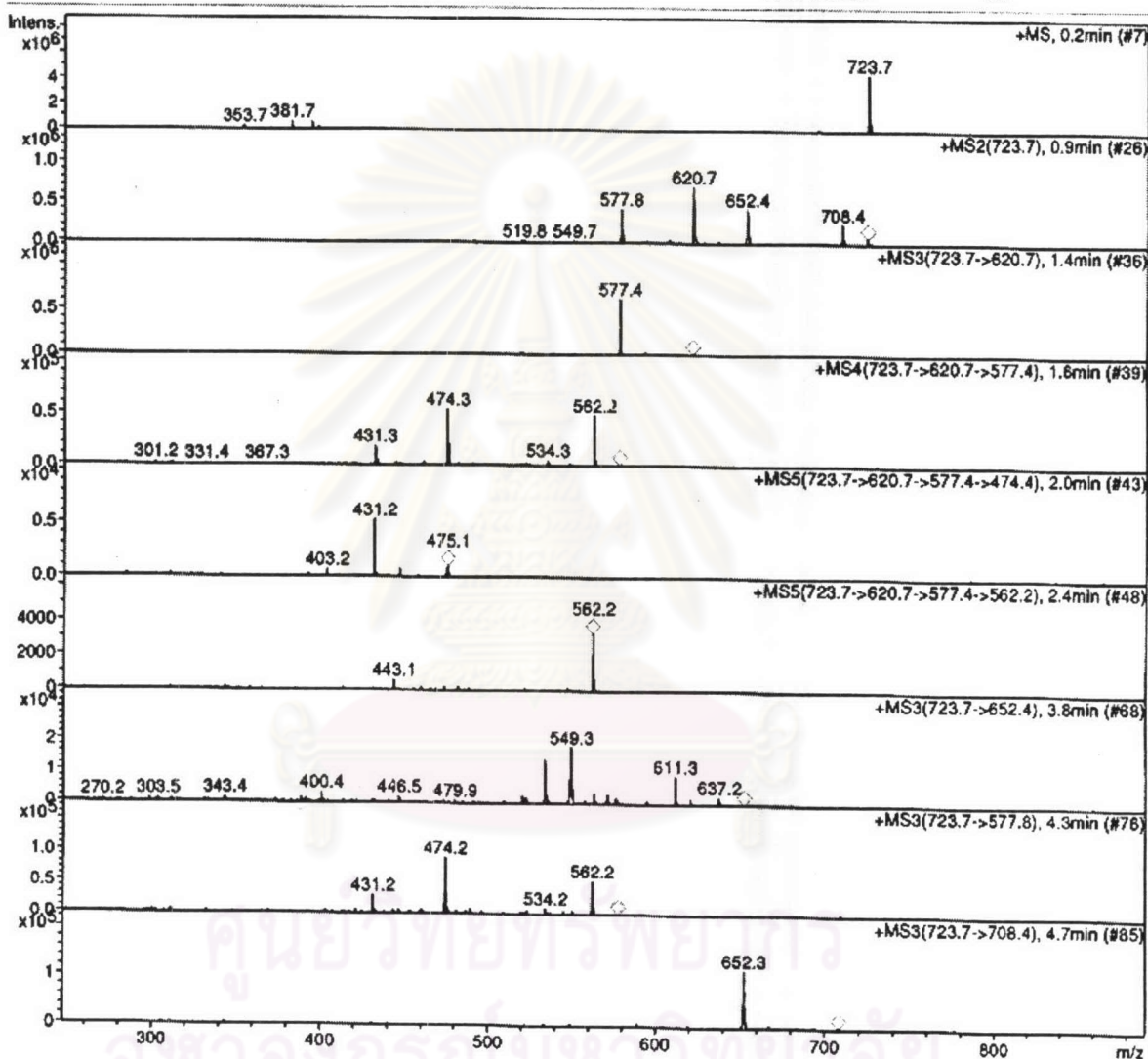
## Display Report

### Analysis Info

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Comment	in MeOH		

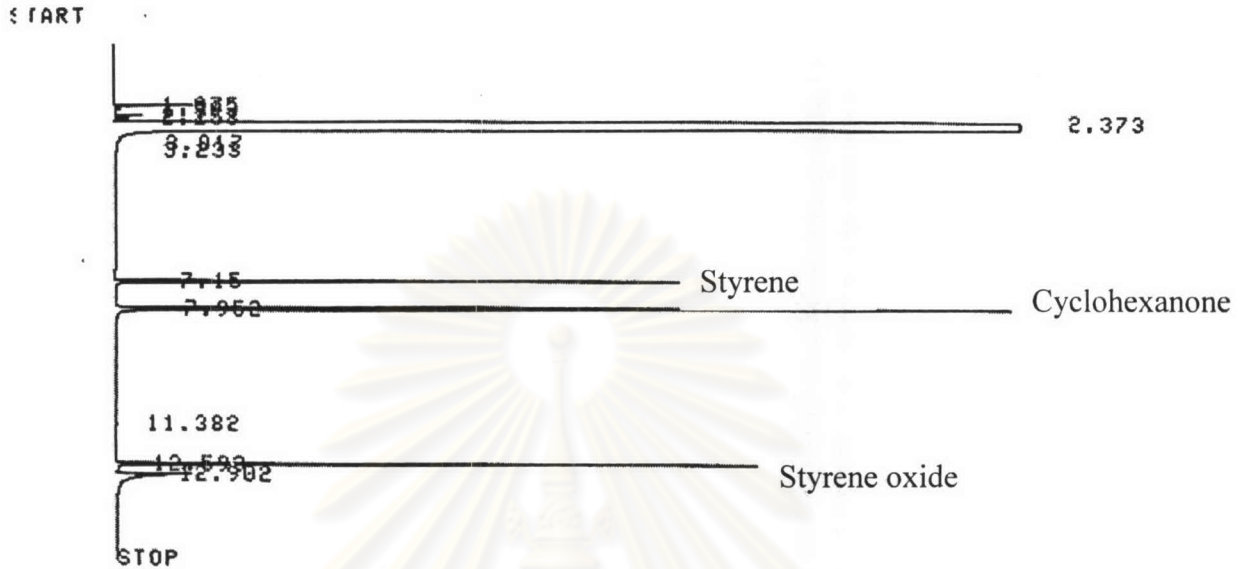
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**Figure A.22** The ESI mass spectrum of [(R,R)-N,N'-bis(3-*t*-butyl-5-5-((2-(2-methoxy)ethoxy)ethoxy)salicylidine)-1,2-cyclohexanediaminato(2-)] manganese(III) chloride, 10.

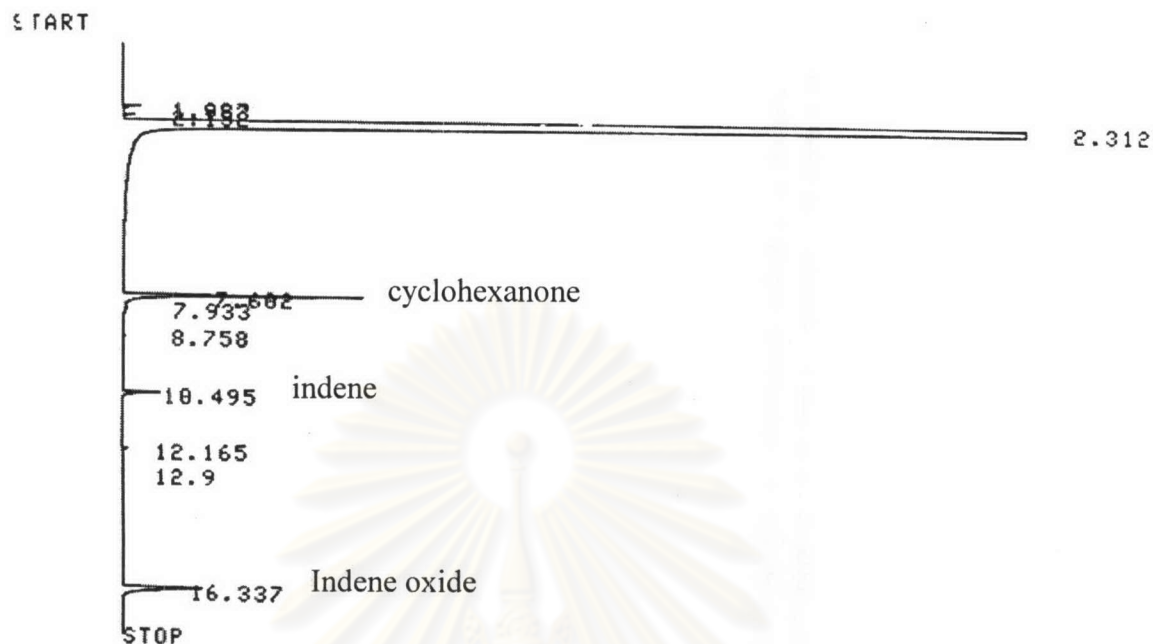




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 REPORT NO 1383

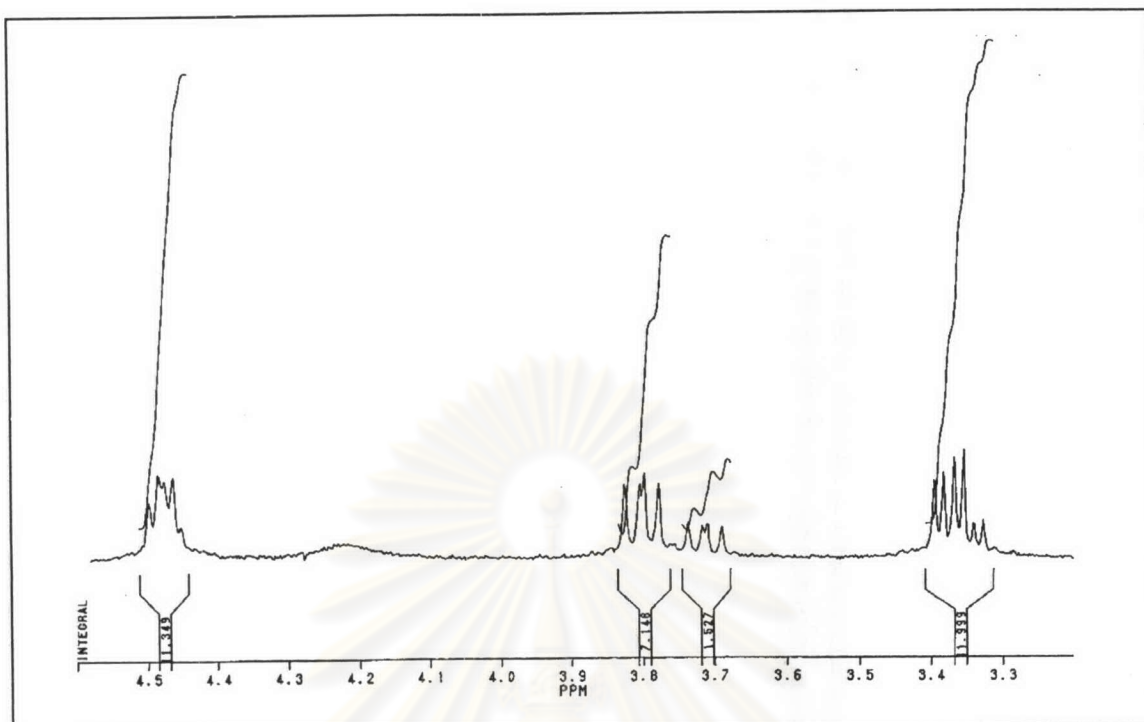
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3	2.373	1202776	S		97.9384	
4	7.15	5551			0.452	Styrene
5	7.952	11983			0.9757	Cyclohexanone
6	12.593	5241			0.4267	Styrene oxide
7	12.902	1993	V		0.1623	
TOTAL		1228095			100	

Figure A.23 The GC chromatogram of styrene, styrene oxide and cyclohexanone (internal standard).

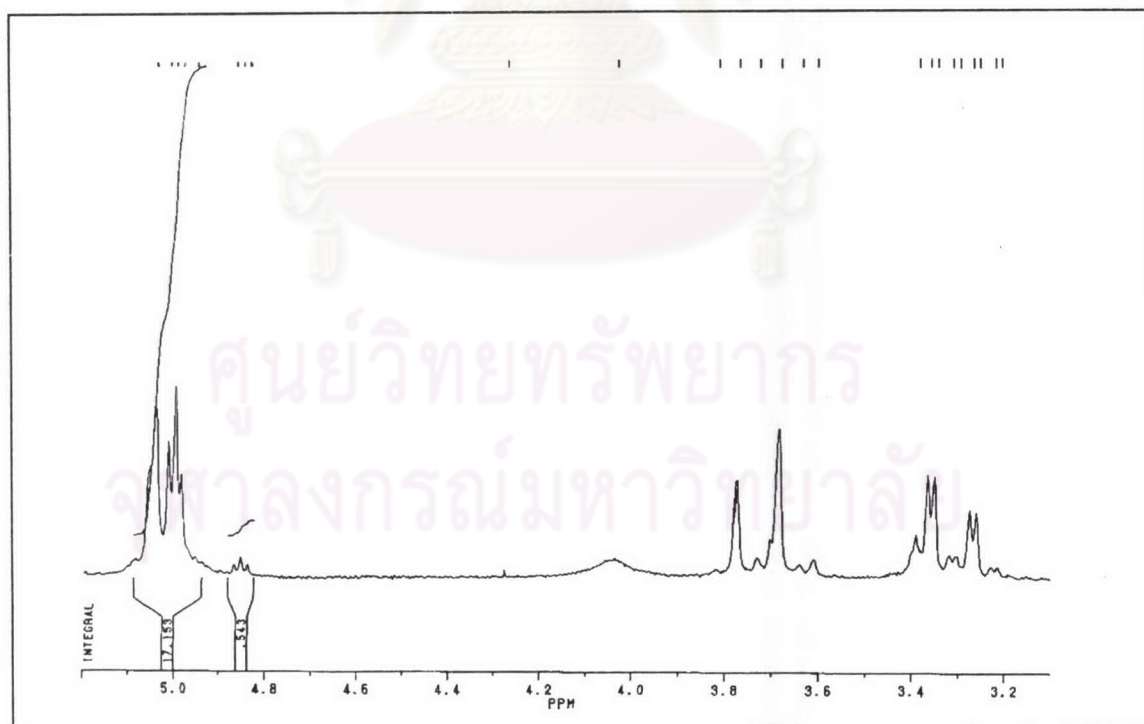


PKNO	TIME	AREA	MK	IDNO	CONC	NAME
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2	1.953	48	V		0.0071	
3	2.152	107			0.0159	
4	2.312	660848			98.9495	
5	7.602	3920	S		0.587	
6	7.933	66	T		0.0099	
7	8.758	65			0.0097	
8	10.495	575			0.0861	
9	12.165	96			0.0144	
10	16.337	2064			0.309	
TOTAL		667864			100	

**Figure A.24** The GC chromatogram of indene, indene oxide and cyclohexanone (internal standard).



**Figure A.25** The  $^1\text{H}$ -NMR spectrum of styrene oxide sample after adding  $\text{Eu}(\text{hfc})_3$ .



**Figure A.26** The  $^1\text{H}$ -NMR spectrum of indene oxide sample after adding  $\text{Eu}(\text{hfc})_3$ .

## VITAE

Mr. Panithan was born on February 16<sup>th</sup>, 1978 in Bangkok, Thailand. He received a Bachelor degree of Science, majoring in Chemistry from Chulalongkorn University in 1999. Since 1999, he has been a graduate student studying Organic Chemistry as his major course at Chulalongkorn University. During his study towards the Master's degree, he was awarded a teaching assistant scholarship by Faculty of Science during 1999-2001 and was supported by a research grant for his Master degree's research from the Graduate School, Chulalongkorn University.

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จุฬาลงกรณ์มหาวิทยาลัย