

REFERENCES

- [1] Wulff, G. and Sarhan, A. The use of polymers with enzyme-analogous structures for the resolution of racemates. Angewandte Chemie International Edition in English 11 (1972): 341.
- [2] Arshady, R. and Mosbach, K. Synthesis of substrate-selective polymers by host-guest polymerization. Die Makromolekulare Chemie 182 (2) (1981): 687-692.
- [3] Whitcombe, M.J., Rodriguez, M.E., Villar, P., and Vulfson, E.N. A New Method for the Introduction of Recognition Site Functionality into Polymers Prepared by Molecular Imprinting: Synthesis and Characterization of Polymeric Receptors for Cholesterol. Journal of the American Chemical Society 117 (27) (1995): 7105-7111.
- [4] Mayes, A.G. and Whitcombe, M.J. Synthetic strategies for the generation of molecularly imprinted organic polymers. Advanced Drug Delivery Reviews 57 (12) (2005): 1742-1778.
- [5] Piletsky, S.A., Turner, N.W., and Laitenberger, P. Molecularly imprinted polymers in clinical diagnostics—Future potential and existing problems. Medical Engineering & Physics 28 (10) (2006): 971-977.
- [6] Spivak, D.A. Optimization, evaluation, and characterization of molecularly imprinted polymers. Advanced Drug Delivery Reviews 57 (12) (2005): 1779-1794.
- [7] Maeda, M. and Bartsch, R.A. Molecular and ionic recognition with imprinted polymers: a brief overview. in ACS symposium series, pp. 1-9: ACS Publications, 1998.
- [8] Yan, M. Molecularly imprinted materials: science and technology. CRC press, 2004.
- [9] Kugimiya, A., et al. Recognition of sialic acid using molecularly imprinted polymer. Polymer—Plastics Technology and Engineering 28 (13) (1995): 2317-2323.
- [10] Kugimiya, A., Matsui, J., Abe, H., Aburatani, M., and Takeuchi, T. Synthesis of castasterone selective polymers prepared by molecular imprinting. Analytica Chimica Acta 365 (1-3) (1998): 75-79.
- [11] Sallacan, N., Zayats, M., Bourenko, T., Kharitonov, A.B., and Willner, I. Imprinting of nucleotide and monosaccharide recognition sites in acrylamidephenylboronic acid-acrylamide copolymer membranes associated with electronic transducers. Analytical chemistry 74 (3) (2002): 702-712.
- [12] Gao, S., Wang, W., and Wang, B. Building Fluorescent Sensors for Carbohydrates Using Template-Directed Polymerizations. Bioorganic Chemistry 29 (5) (2001): 308-320.



- [13] Bossi, A., Piletsky, S.A., Piletska, E.V., Righetti, P.G., and Turner, A.P. Surface-grafted molecularly imprinted polymers for protein recognition. Analytical Chemistry 73 (21) (2001): 5281-5286.
- [14] Shea, K. and Dougherty, T. Molecular recognition on synthetic amorphous surfaces. The influence of functional group positioning on the effectiveness of molecular recognition. Journal of the American Chemical Society 108 (5) (1986): 1091-1093.
- [15] Wulff, G., Best, W., and Akelah, A. Enzyme-analogue built polymers, 17 Investigations on the racemic resolution of amino acids. Reactive Polymers. Ion Exchangers. Sorbents 2 (3) (1984): 167-174.
- [16] Wulff, G. and Vietmeier, J. Enzyme-analogue built polymers, 26. Enantioselective synthesis of amino acids using polymers possessing chiral cavities obtained by an imprinting procedure with template molecules. Die Makromolekulare Chemie 190 (7) (1989): 1727-1735.
- [17] Israelachvili, J.N. Intermolecular and surface forces: revised third edition. Academic press, 2011.
- [18] Pichon, V. Selective sample treatment using molecularly imprinted polymers. Journal of Chromatography A 1152 (1-2) (2007): 41-53.
- [19] Komiyama, M., Takeuchi, T., Mukawa, T., and Asanuma, H. Molecular imprinting: from fundamentals to applications. Molecular Imprinting: From Fundamentals to Applications, by Makoto Komiyama, Toshifumi Takeuchi, Takashi Mukawa, Hiroyuki Asanuma, pp. 148. ISBN 3-527-30569-6. Wiley-VCH, March 2003. 1 (2003).
- [20] Vlatakis, G., Andersson, L.I., Müller, R., and Mosbach, K. Drug assay using antibody mimics made by molecular imprinting. Nature 361 (1993): 645-647.
- [21] Pomerantz, M., et al. Processable polymers and copolymers of 3-alkylthiophenes and their blends. Synthetic Metals 41 (3) (1991): 825-830.
- [22] Negishi, E., Takahashi, T., Baba, S., Van Horn, D.E., and Okukado, N. Nickel- or palladium-catalyzed cross coupling. 31. Palladium- or nickel-catalyzed reactions of alkenylmetals with unsaturated organic halides as a selective route to arylated alkenes and conjugated dienes: scope, limitations, and mechanism. Journal of the American Chemical Society 109 (8) (1987): 2393-2401.
- [23] Tamao, K., Kiso, Y., Sumitani, K., and Kumada, M. Alkyl group isomerization in the cross-coupling reaction of secondary alkyl Grignard reagents with organic halides in the presence of nickel-phosphine complexes as catalysts. Journal of the American Chemical Society 94 (26) (1972): 9268-9269.



- [24] Groenendaal, L., Jonas, F., Freitag, D., Pielartzik, H., and Reynolds, J.R. Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future. Advanced Materials 12 (7) (2000): 481-494.
- [25] Meng, H., et al. Solid-state synthesis of a conducting polythiophene via an unprecedented heterocyclic coupling reaction. Journal of the American Chemical Society 125 (49) (2003): 15151-15162.
- [26] Meng, H., Perepichka, D.F., and Wudl, F. Facile Solid-State Synthesis of Highly Conducting Poly(ethylenedioxythiophene). Angewandte Chemie International Edition 42 (6) (2003): 658-661.
- [27] Yin, Y., Li, Z., Jin, J., Tusy, C., and Xia, J. Facile synthesis of poly (3, 4-ethylenedioxythiophene) by acid-assisted polycondensation of 5-bromo-2, 3-dihydro-thieno [3, 4-b][1, 4] dioxine. Synthetic Metals 175 (2013): 97-102.
- [28] Kubo, H., Yoshioka, N., and Takeuchi, T. Fluorescent imprinted polymers prepared with 2-acrylamidoquinoline as a signaling monomer. Organic Letters 7 (3) (2005): 359-362.
- [29] Pardieu, E., et al. Molecularly imprinted conducting polymer based electrochemical sensor for detection of atrazine. Analytica Chimica Acta 649 (2) (2009): 236-245.
- [30] Ho, K.-C., Yeh, W.-M., Tung, T.-S., and Liao, J.-Y. Amperometric detection of morphine based on poly(3,4-ethylenedioxythiophene) immobilized molecularly imprinted polymer particles prepared by precipitation polymerization. Analytica Chimica Acta 542 (1) (2005): 90-96.
- [31] Bunte, G., Hürttlen, J., Pontius, H., Hartlieb, K., and Krause, H. Gas phase detection of explosives such as 2,4,6-trinitrotoluene by molecularly imprinted polymers. Analytica Chimica Acta 591 (1) (2007): 49-56.
- [32] Alizadeh, T., Zare, M., Ganjali, M.R., Norouzi, P., and Tavana, B. A new molecularly imprinted polymer (MIP)-based electrochemical sensor for monitoring 2,4,6-trinitrotoluene (TNT) in natural waters and soil samples. Biosensors and Bioelectronics 25 (5) (2010): 1166-1172.
- [33] Xu, S., et al. Dummy Molecularly Imprinted Polymers-Capped CdTe Quantum Dots for the Fluorescent Sensing of 2,4,6-Trinitrotoluene. ACS Applied Materials & Interfaces 5 (16) (2013): 8146-8154.
- [34] Overberger, C.G., Mallon, H.J., and Fine, R. Cyclic Sulfones. II. The Polymerization of Styrene in the Presence of 3,4-Diphenylthiophene-1-dioxide and 3,4-Di-(p-chlorophenyl)-thiophene-1-dioxide. Journal of American Chemical Society 72 (1950): 4958-4961.



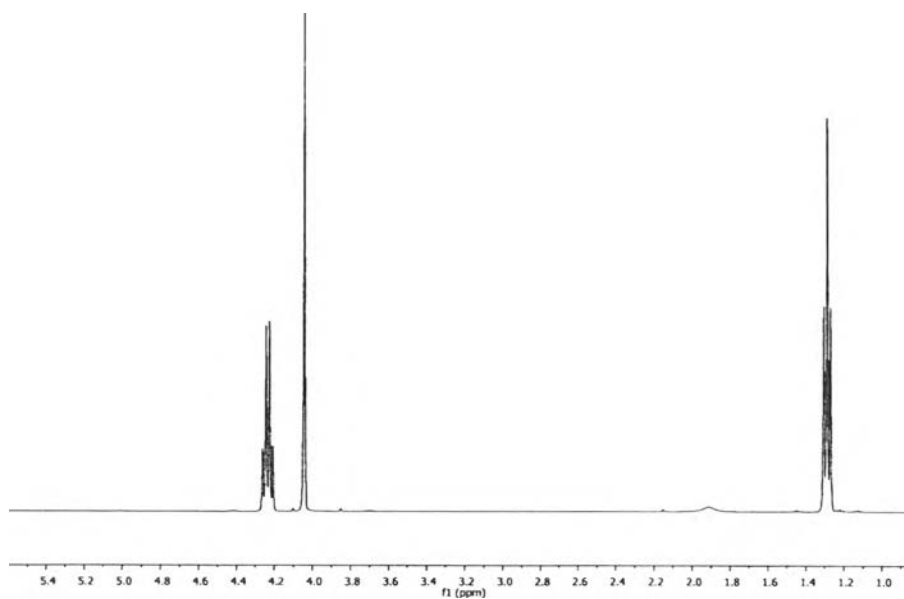
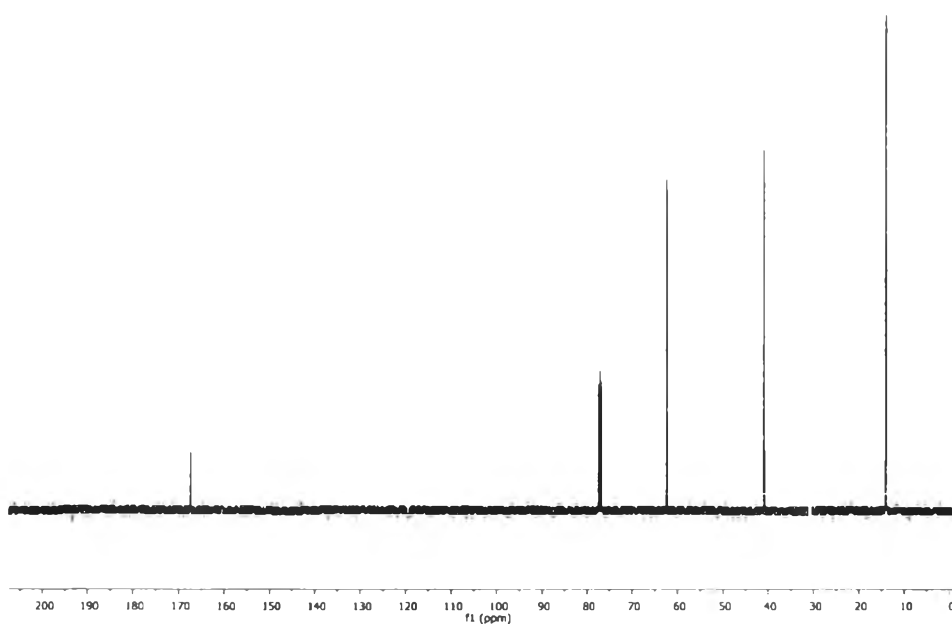
- [35] Wynberg, H. and Kooreman, H. The Mechanism of the Hinsberg Thiophene Ring Synthesis 1, 2. Journal of the American Chemical Society 87 (8) (1965): 1739-1742.
- [36] Fager, E.W. Some derivatives of 3, 4-dioxythiophene. Journal of the American Chemical Society 67 (12) (1945): 2217-2218.
- [37] Caras-Quintero, D. and Bäuerle, P. Efficient synthesis of 3, 4-ethylenedioxythiophenes (EDOT) by Mitsunobu reaction. Chemical Communications (22) (2002): 2690-2691.
- [38] Lima, A., Schottland, P., Sadki, S., and Chevrot, C. Electropolymerization of 3, 4-ethylenedioxythiophene and 3, 4-ethylenedioxythiophene methanol in the presence of dodecylbenzenesulfonate. Synthetic Metals 93 (1) (1998): 33-41.
- [39] Bayer, A.G. European Patent (1988): 339-340.
- [40] Kellogg, R.M., Schaap, A.P., Harper, E.T., and Wynbert, H. Acid-catalyzed brominations, deuterations, rearrangements, and debrominations of thiophenes under mild conditions. The Journal of Organic Chemistry 33 (7) (1968): 2902-2909.
- [41] Sotzing, G.A., Reynolds, J.R., and Steel, P.J. Poly(3,4-ethylenedioxythiophene) (PEDOT) prepared via electrochemical polymerization of EDOT, 2,2'-Bis(3,4-ethylenedioxythiophene) (BiEDOT), and their TMS derivatives. Advanced Materials 9 (10) (1997): 795-798.
- [42] Srinivasan, P., Gunasekaran, M., Kanagasekaran, T., Gopalakrishnan, R., and Ramasamy, P. 2,4,6-trinitrophenol (TNP): An organic material for nonlinear optical (NLO) applications. Journal of Crystal Growth 289 (2) (2006): 639-646.
- [43] Russell, R.A., Switzer, R.W., and Longmore, R.W. The stepwise nitration of toluene: A multistep microscale synthesis based on an industrial process. Journal of Chemical Education 67 (1) (1990): 68.
- [44] He, J.-f., Zhu, Q.-h., and Deng, Q.-y. Investigation of imprinting parameters and their recognition nature for quinine-molecularly imprinted polymers. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 67 (5) (2007): 1297-1305.
- [45] Yoon, S.-D. and Byun, H.-S. Molecularly imprinted polymers for selective separation of acetaminophen and aspirin by using supercritical fluid technology. Chemical Engineering Journal 226 (2013): 171-180.
- [46] Ni Mhuircheartaigh, É.M., Blau, W.J., Prato, M., and Giordani, S. Spectroscopic changes induced by sonication of porphyrin-carbon nanotube composites in chlorinated solvents. Carbon 45 (13) (2007): 2665-2671.



APPENDICES



APPENDIX A

Figure A.1 ^1H NMR (CDCl_3) spectrum of compound 1Figure A.2 ^{13}C NMR (CDCl_3) spectrum of compound 1

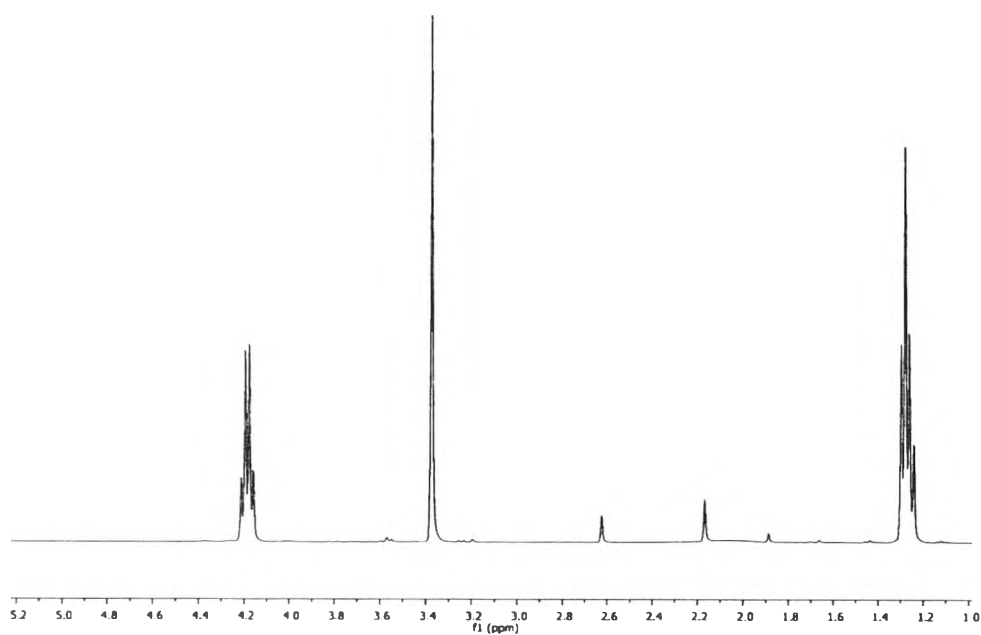


Figure A.3 ^1H NMR (CDCl_3) spectrum of compound 2

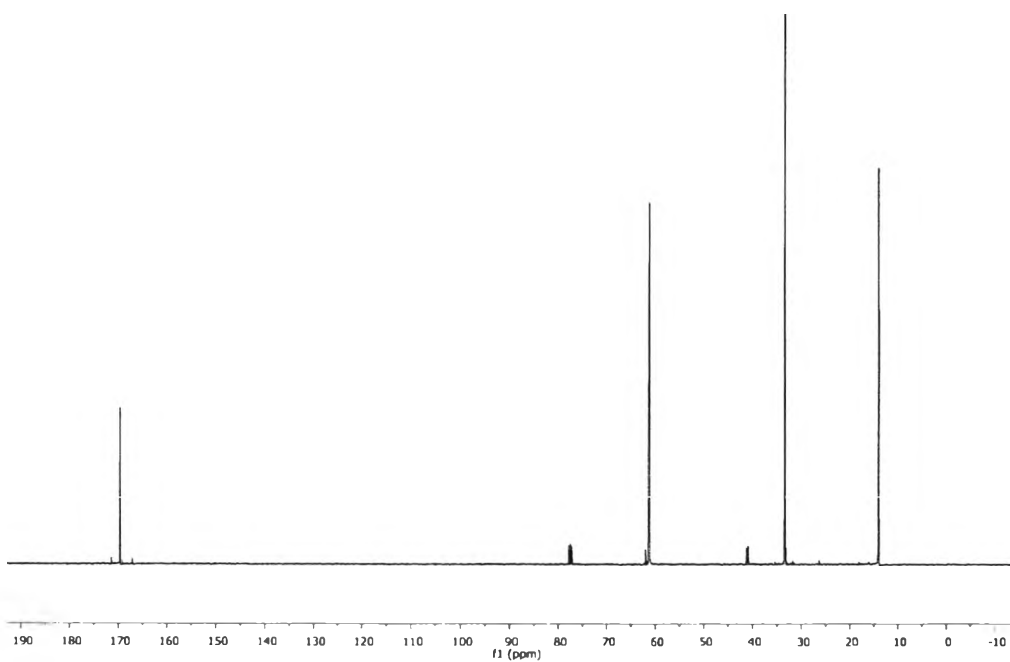


Figure A.4 ^{13}C NMR (CDCl_3) spectrum of compound 2

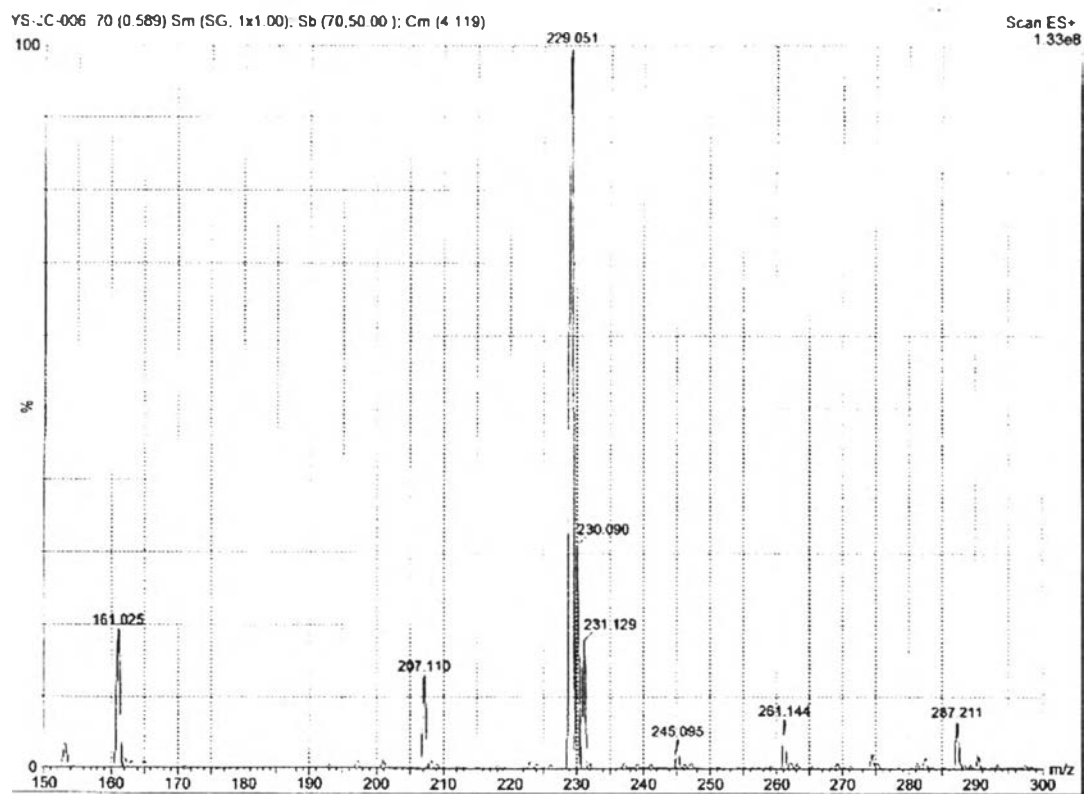


Figure A.5 Mass spectrum of compound 2



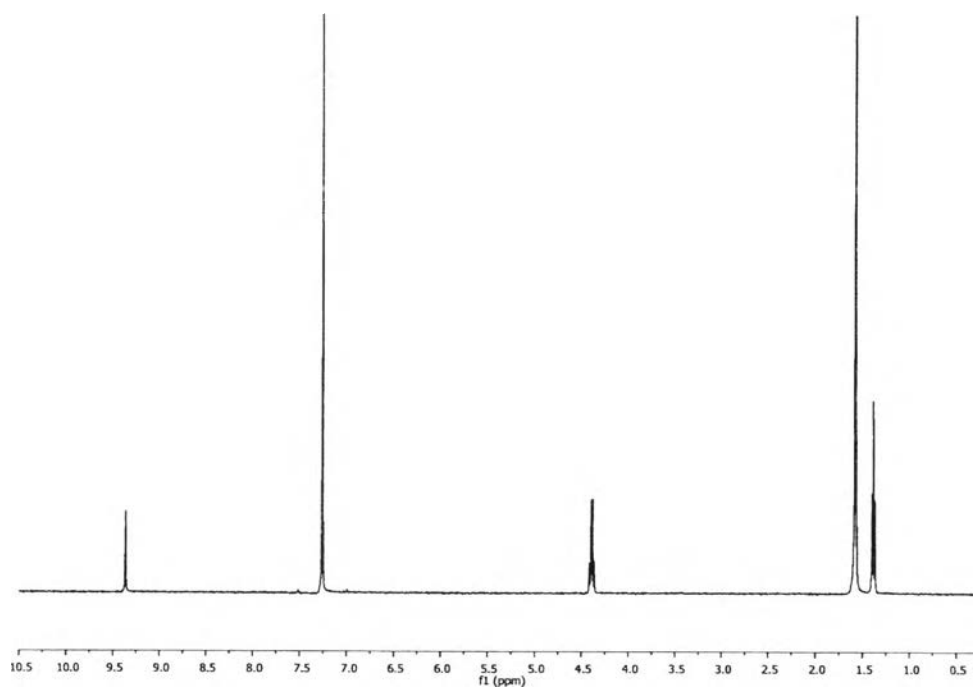


Figure A.6 ^1H NMR (CDCl_3) spectrum of compound DDTD

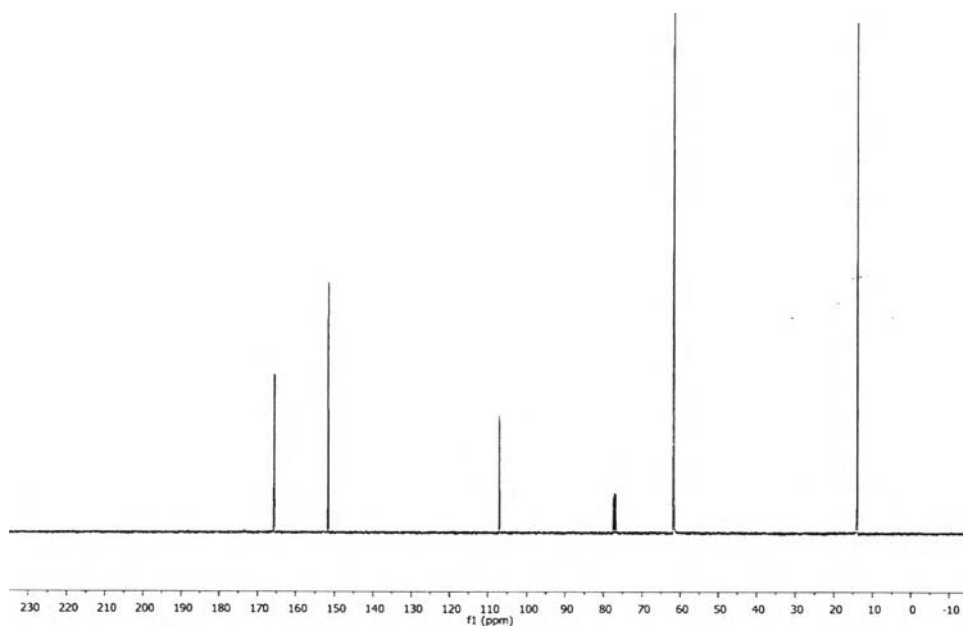


Figure A.7 ^{13}C NMR (CDCl_3) spectrum of compound DDTD

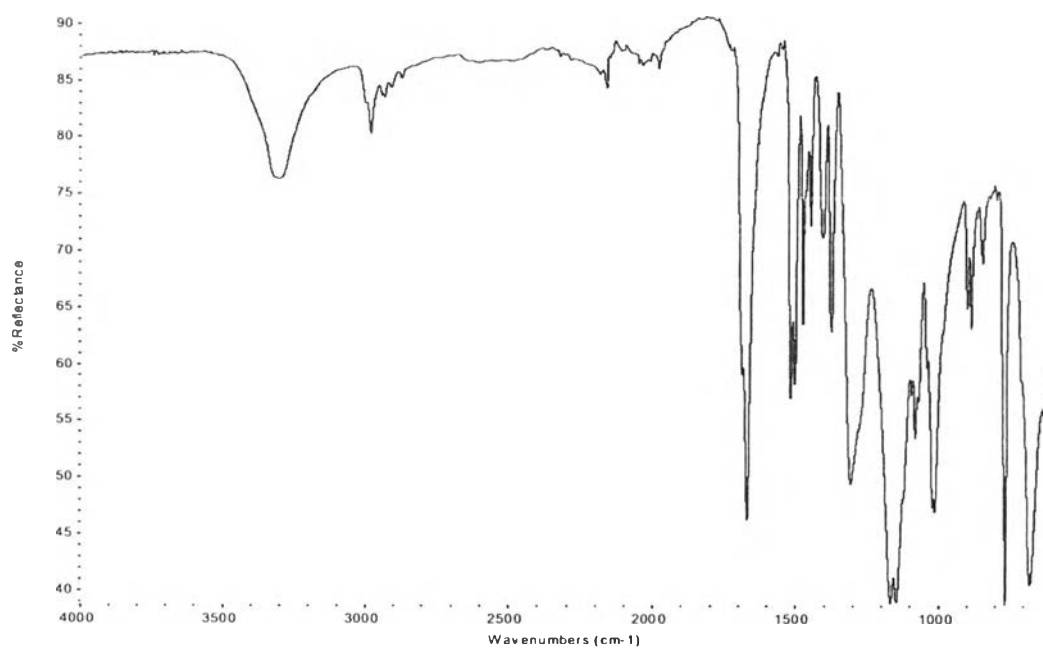


Figure A.8 IR spectrum of compound DDTD

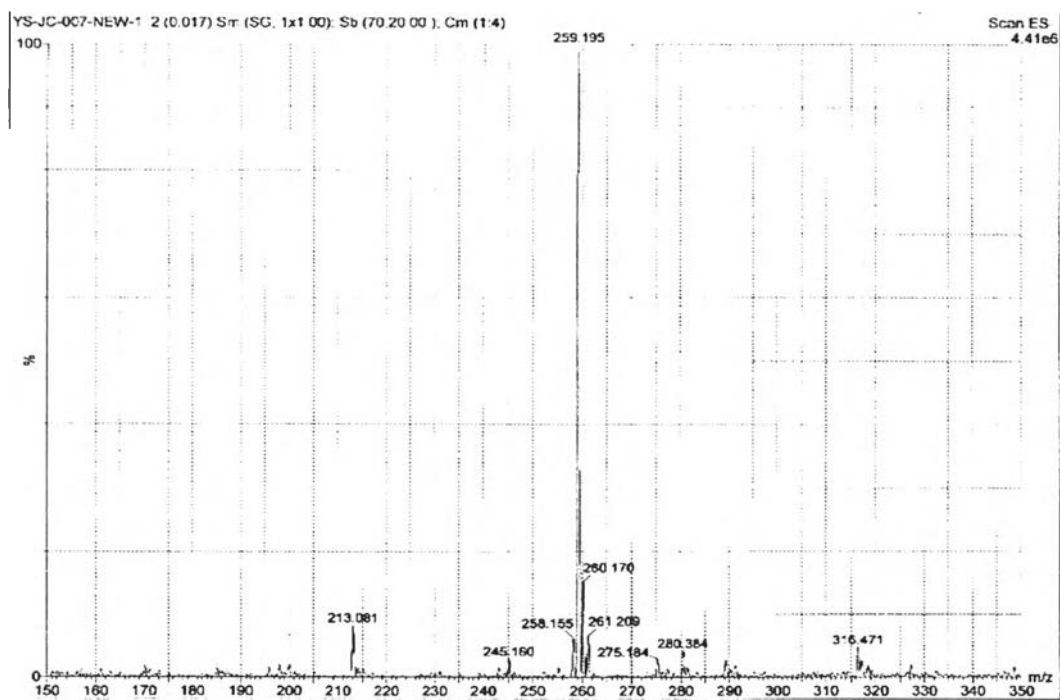
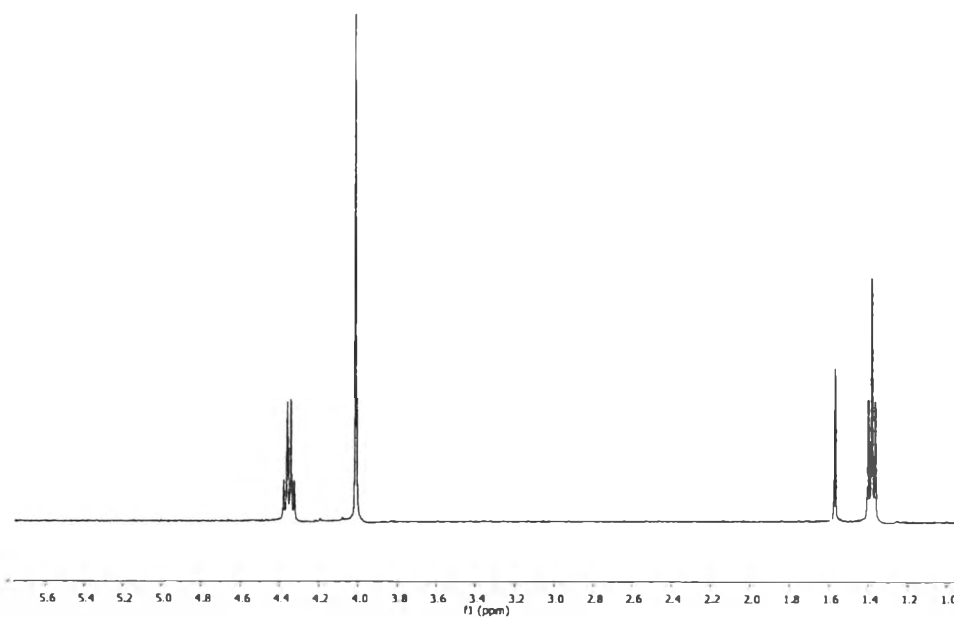
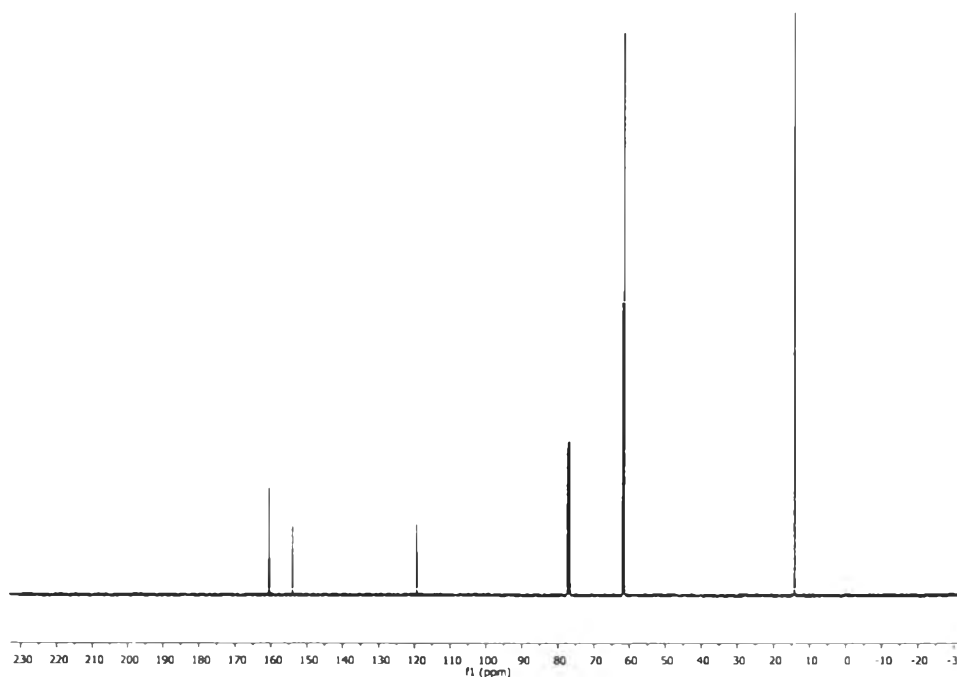


Figure A.9 Mass spectrum of compound DDTD

Figure A.10 ^1H NMR (CDCl_3) spectrum of compound 3aFigure A.11 ^{13}C NMR (CDCl_3) spectrum of compound 3a

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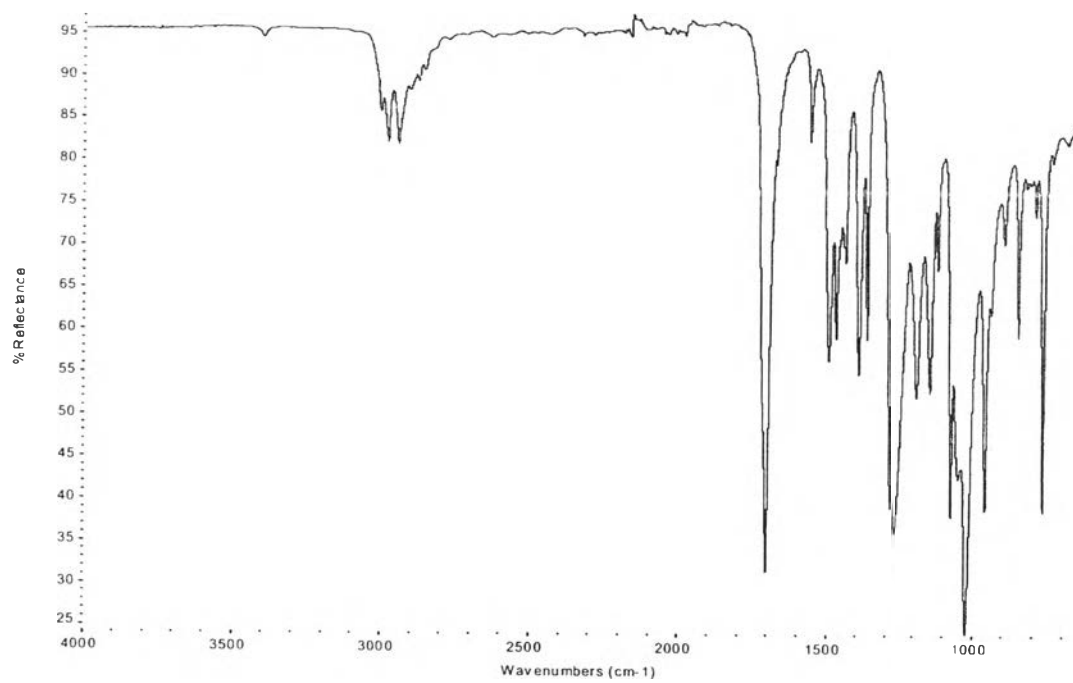


Figure A.12 IR spectrum of compound 3a



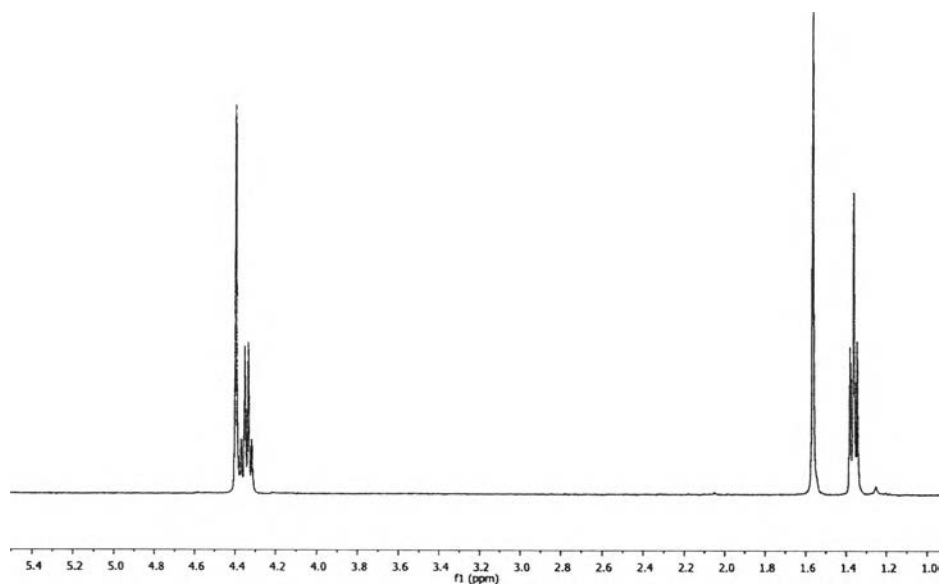


Figure A.13 ^1H NMR (CDCl_3) spectrum of compound 3b

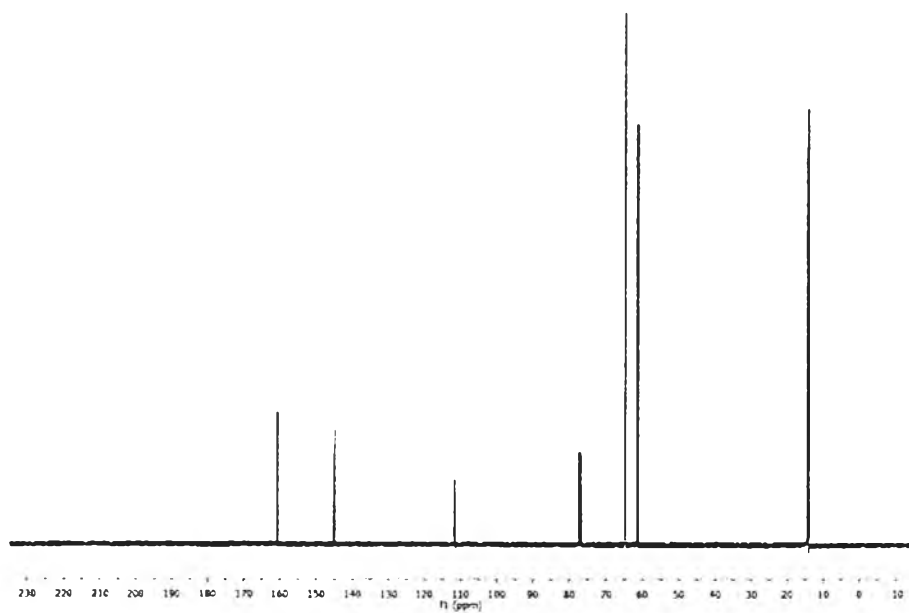


Figure A.14 ^{13}C NMR (CDCl_3) spectrum of compound 3b



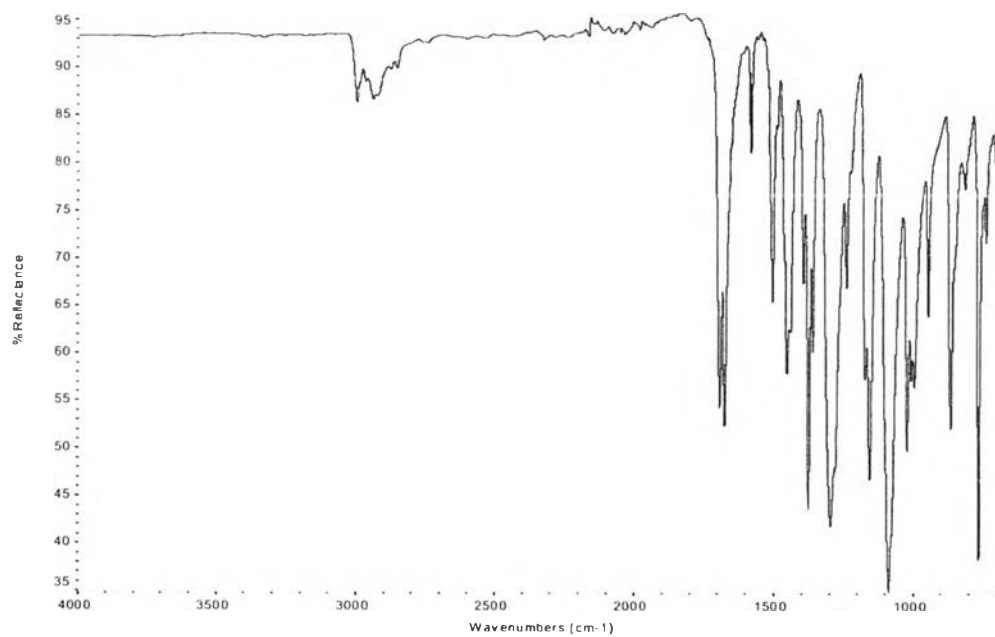


Figure A.15 IR spectrum of compound 3b

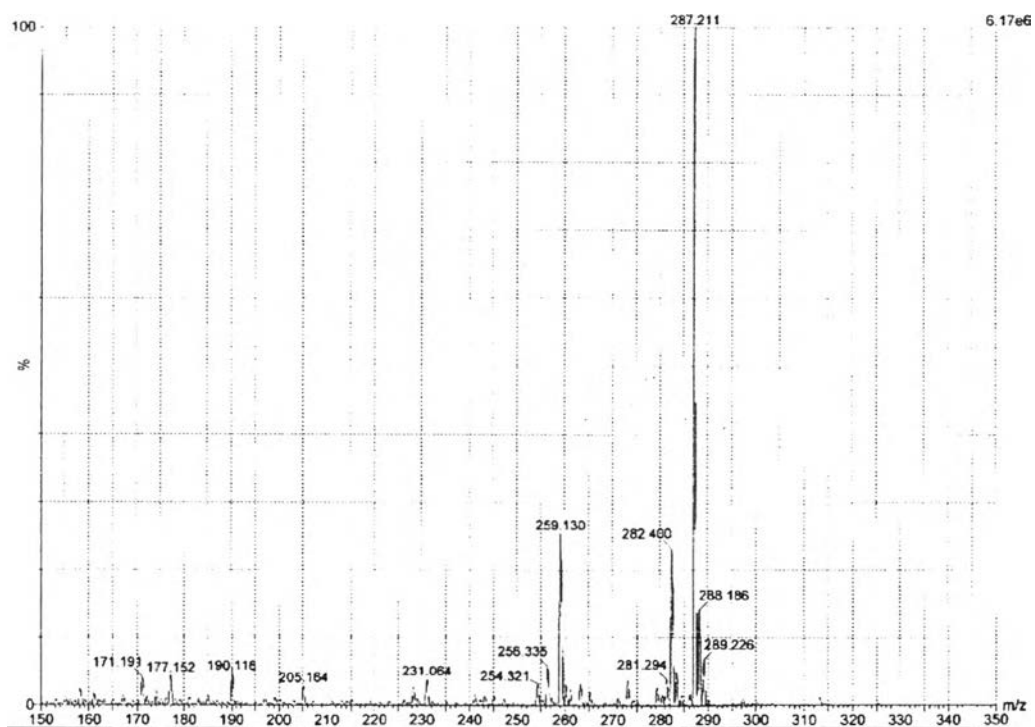


Figure A.16 Mass spectrum of compound 3b

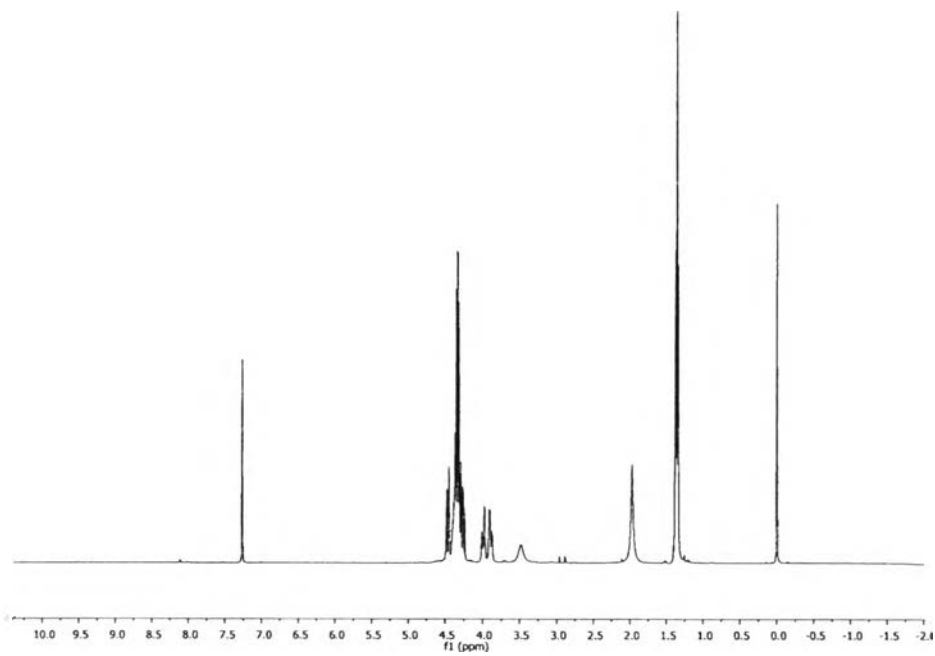


Figure A.17 ^1H NMR (CDCl_3) spectrum of compound 3c

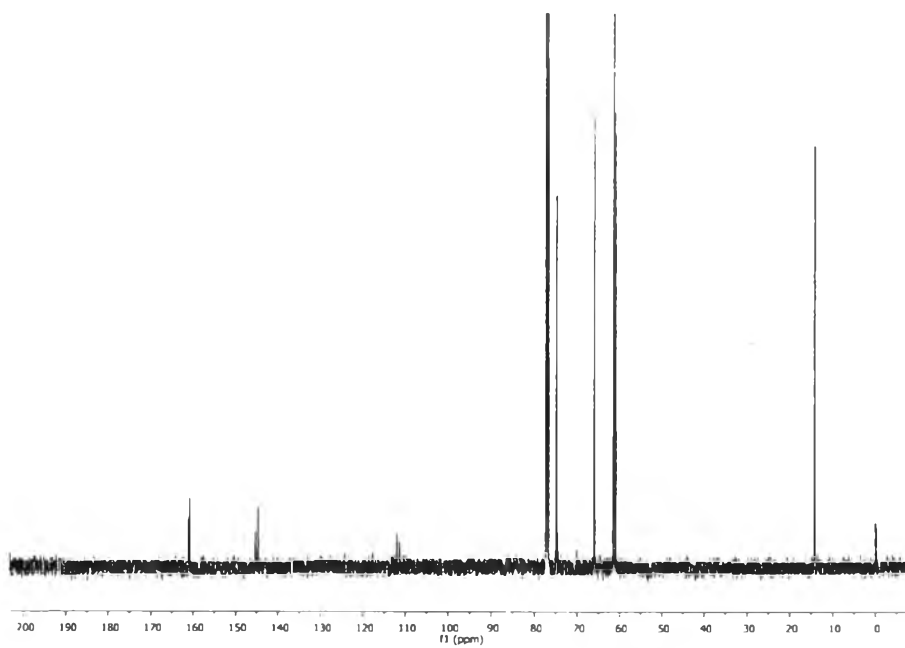


Figure A.18 ^{13}C NMR (CDCl_3) spectrum of compound 3c



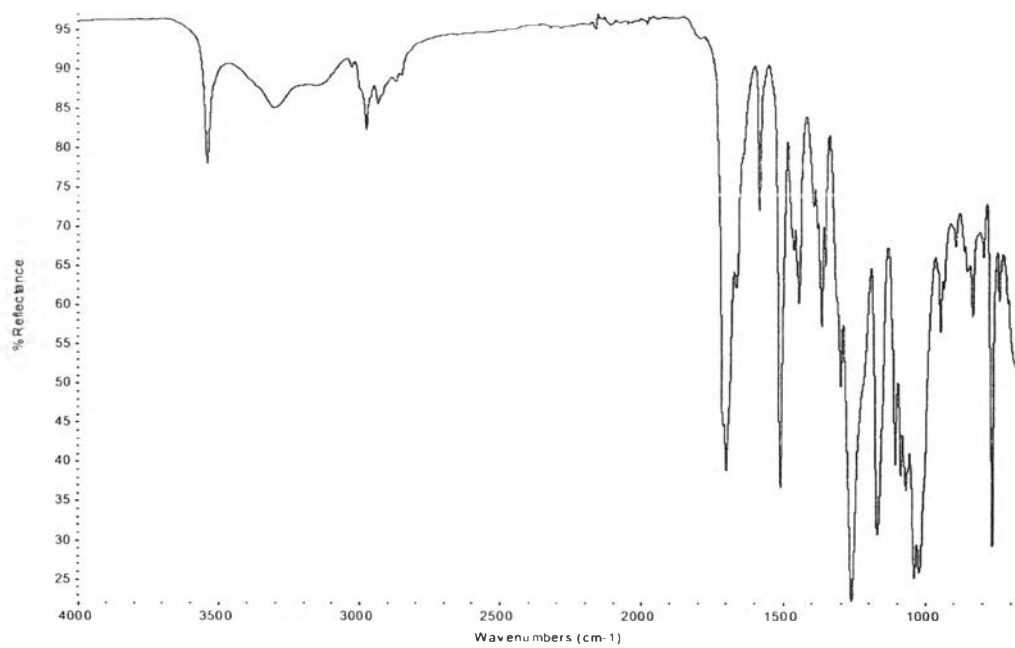


Figure A.19 IR spectrum of compound 3c



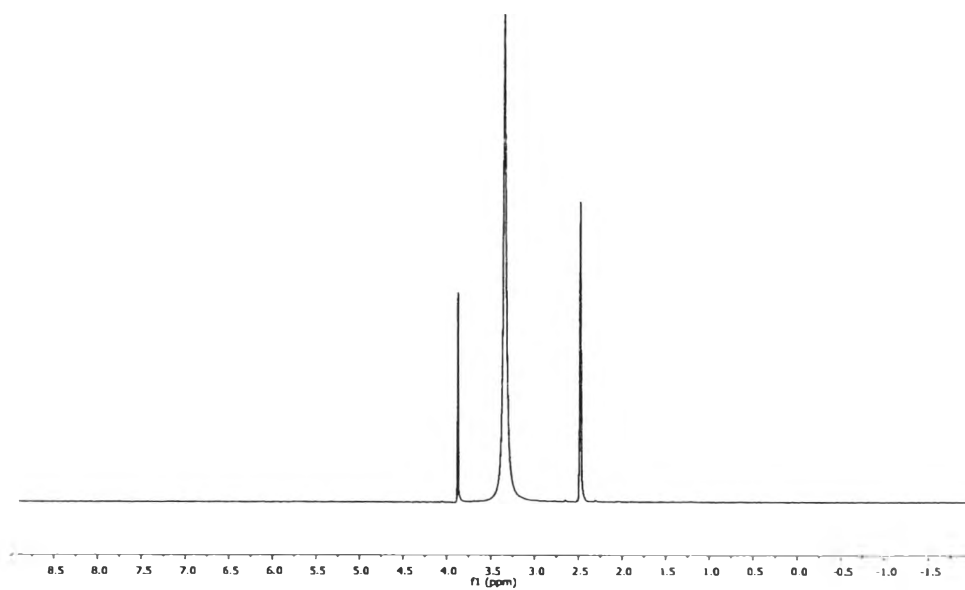


Figure A.20 ^1H NMR ($\text{DMSO-}d_6$) spectrum of compound 4a

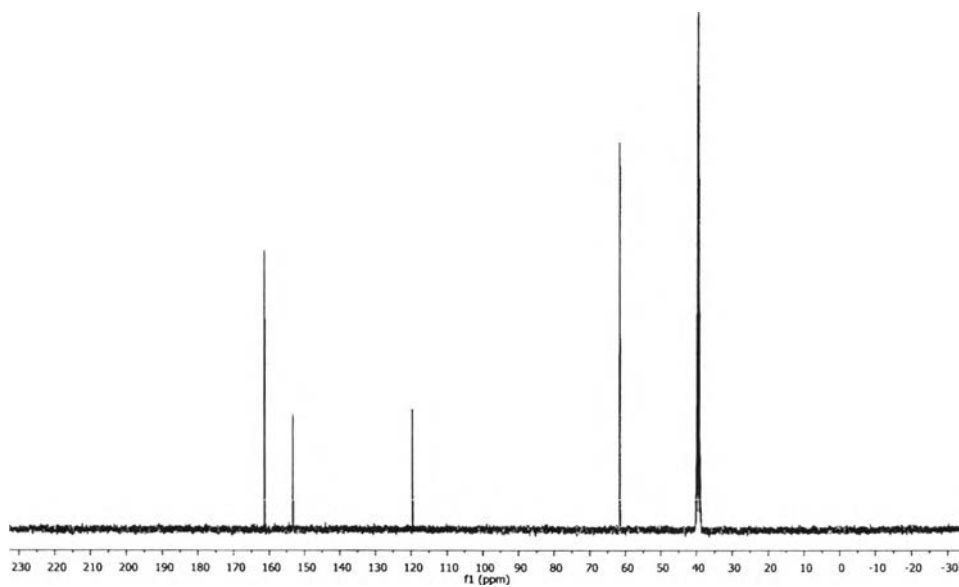


Figure A.21 ^{13}C NMR ($\text{DMSO-}d_6$) spectrum of compound 4a



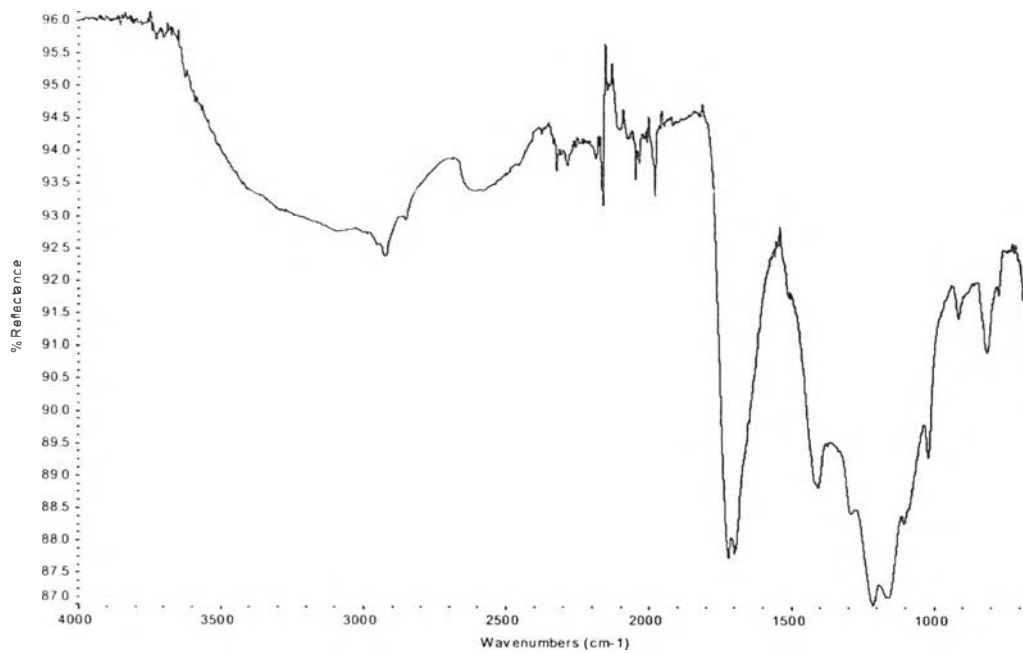


Figure A.22 IR spectrum of compound 4a



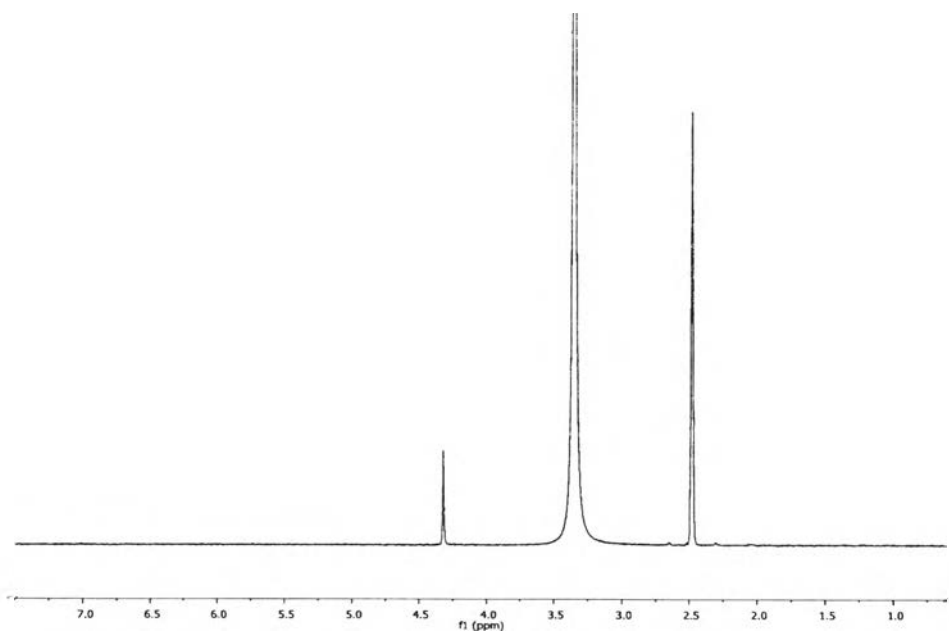


Figure A.23 ^1H NMR ($\text{DMSO-}d_6$) spectrum of compound 4b

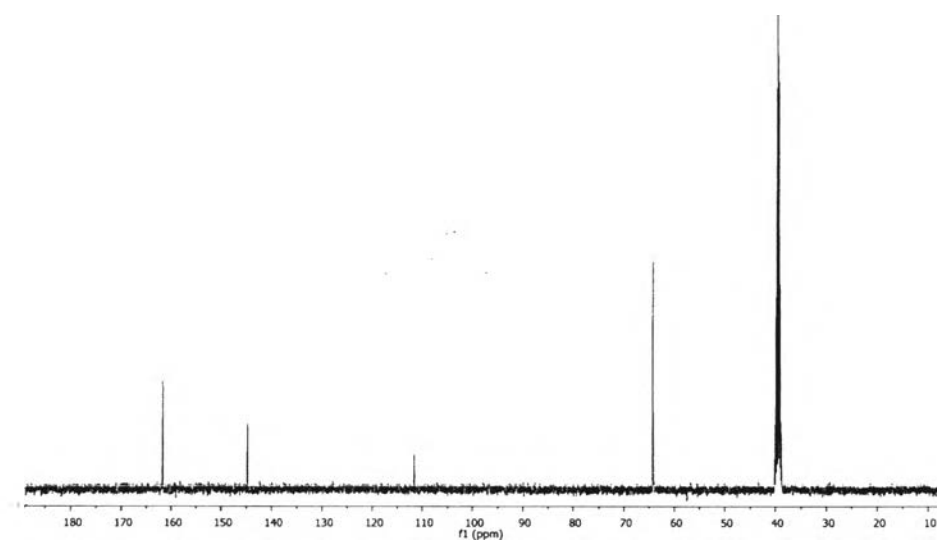


Figure A.24 ^{13}C NMR ($\text{DMSO-}d_6$) spectrum of compound 4b



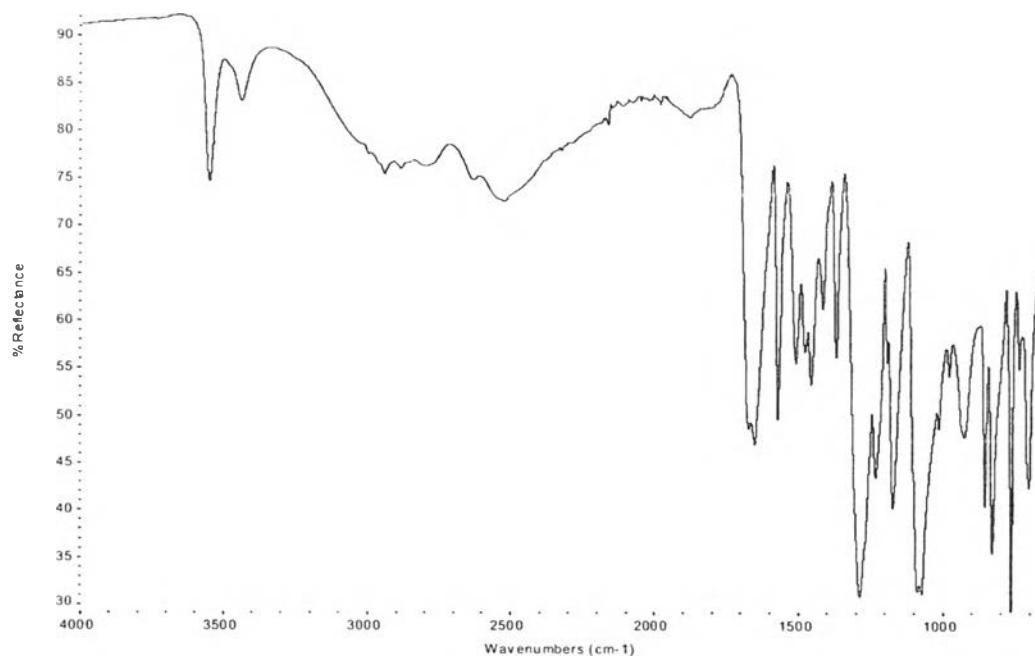


Figure A.25 IR spectrum of compound 4b



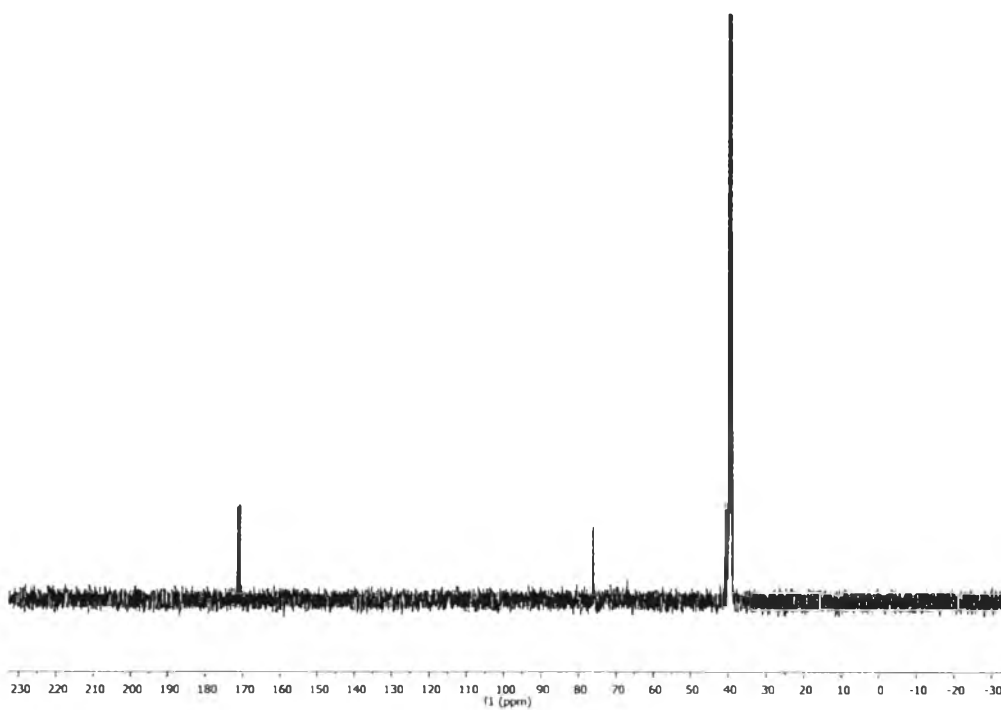


Figure A.26 ^{13}C NMR ($\text{DMSO-}d_6$) spectrum of compound 4d

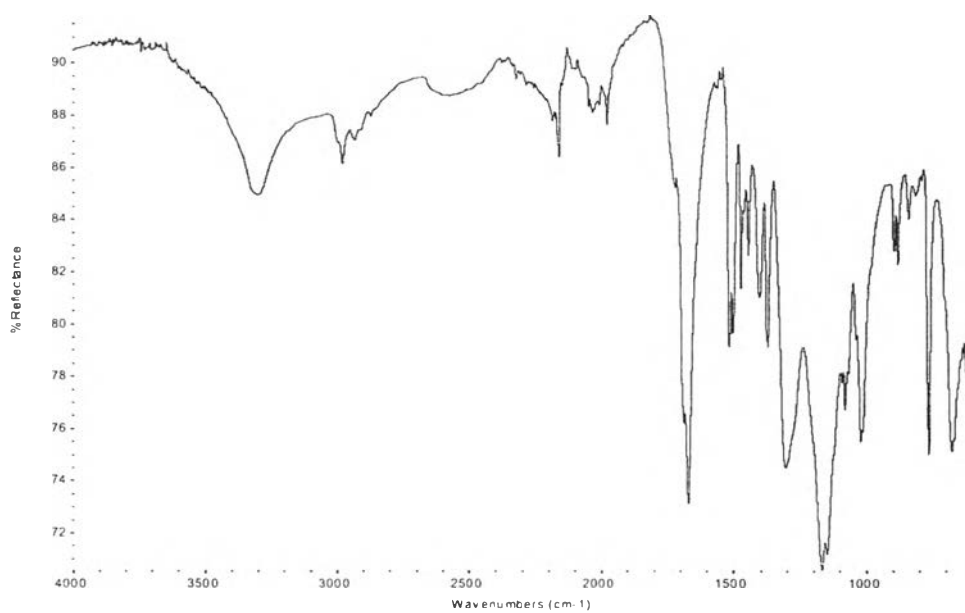


Figure A.27 IR spectrum of compound 4d

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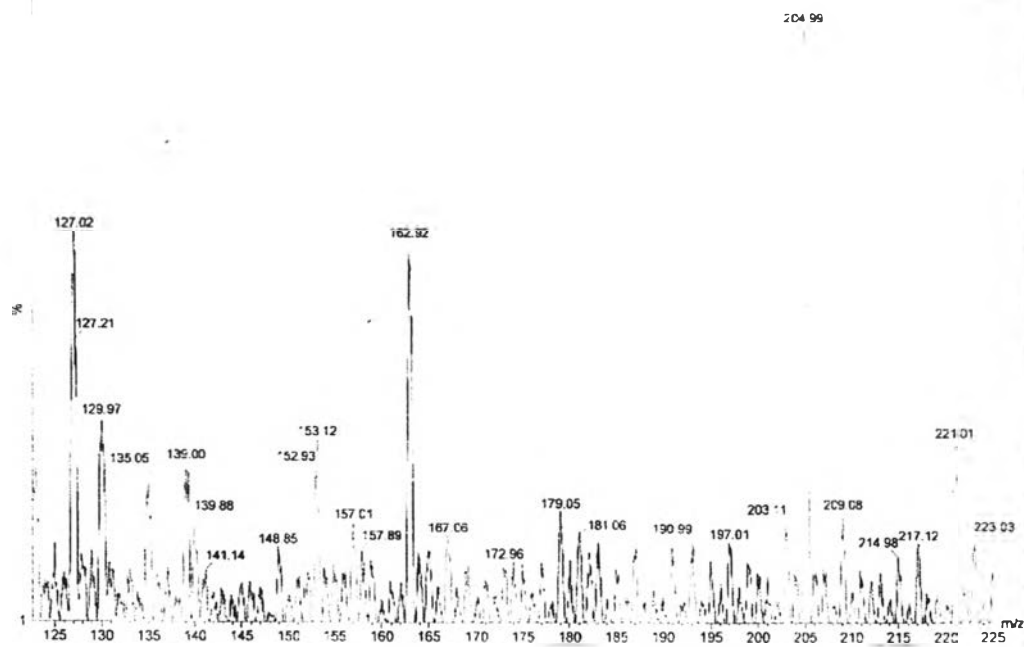


Figure A.28 Mass spectrum of compound 4d



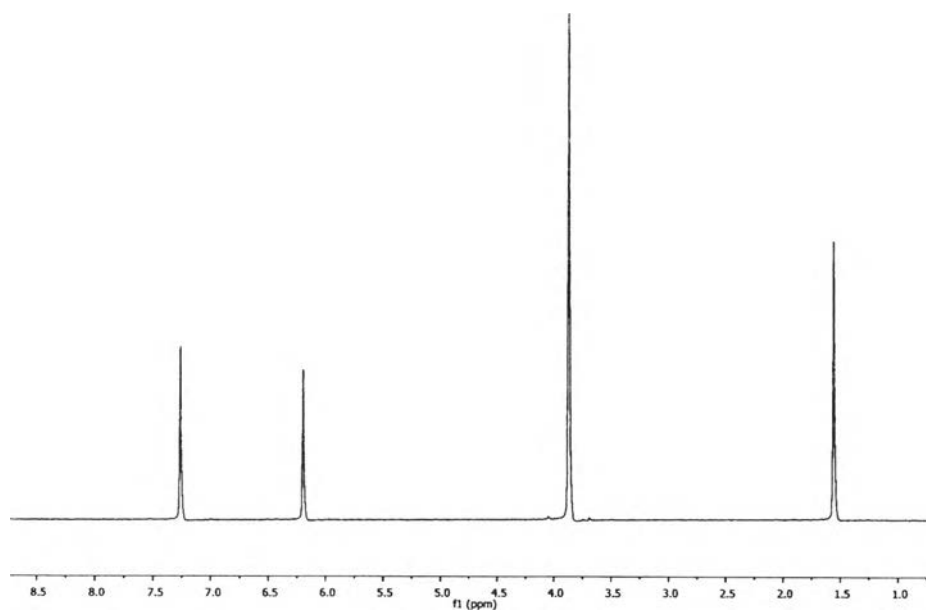


Figure A.29 ^1H NMR (CDCl_3) spectrum of compound 5a

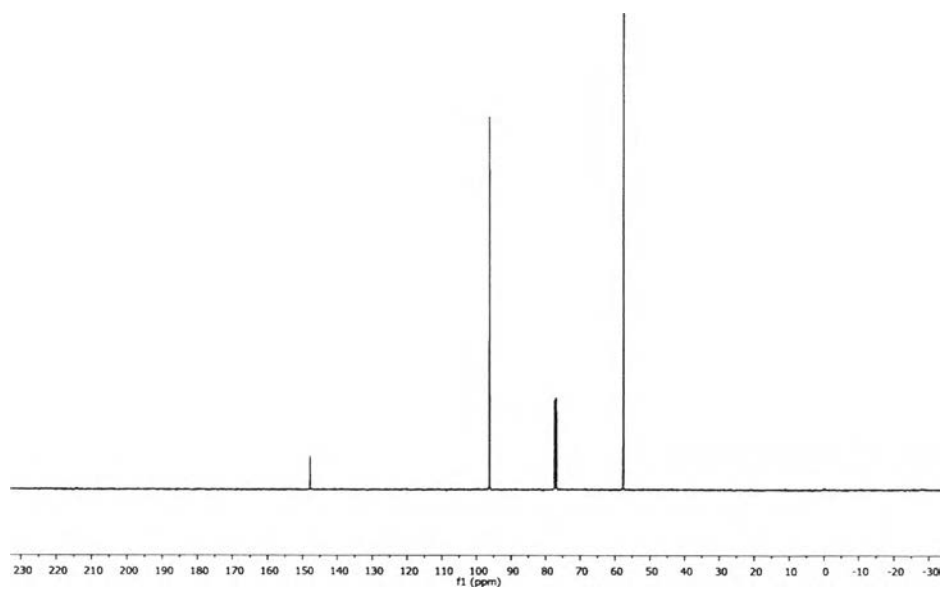


Figure A.30 ^{13}C NMR (CDCl_3) spectrum of compound 5a

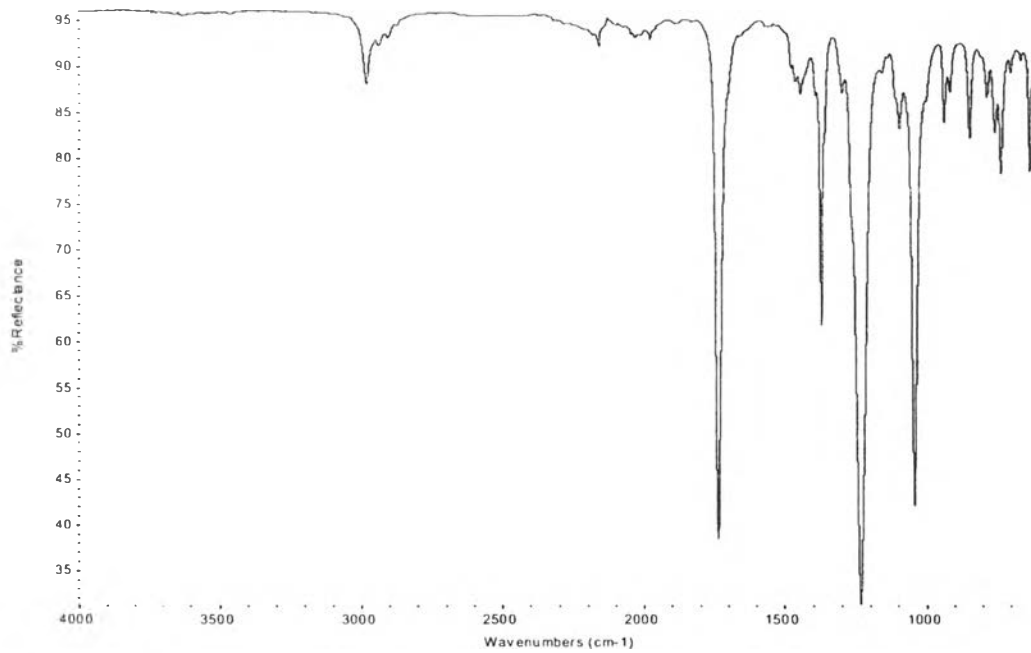


Figure A.31 IR spectrum of compound 5a



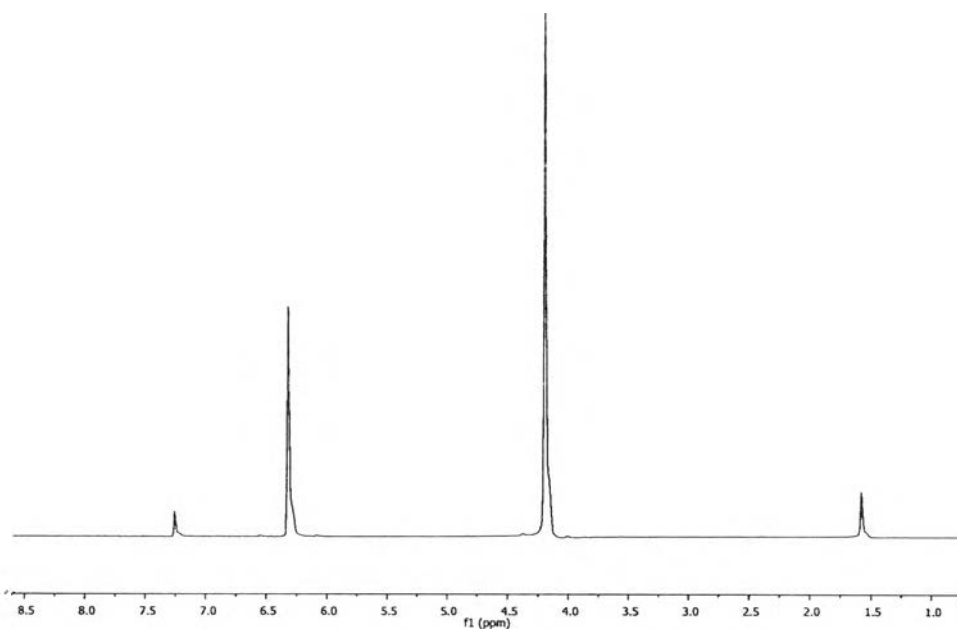


Figure A.32 ^1H NMR (CDCl_3) spectrum of compound 5b

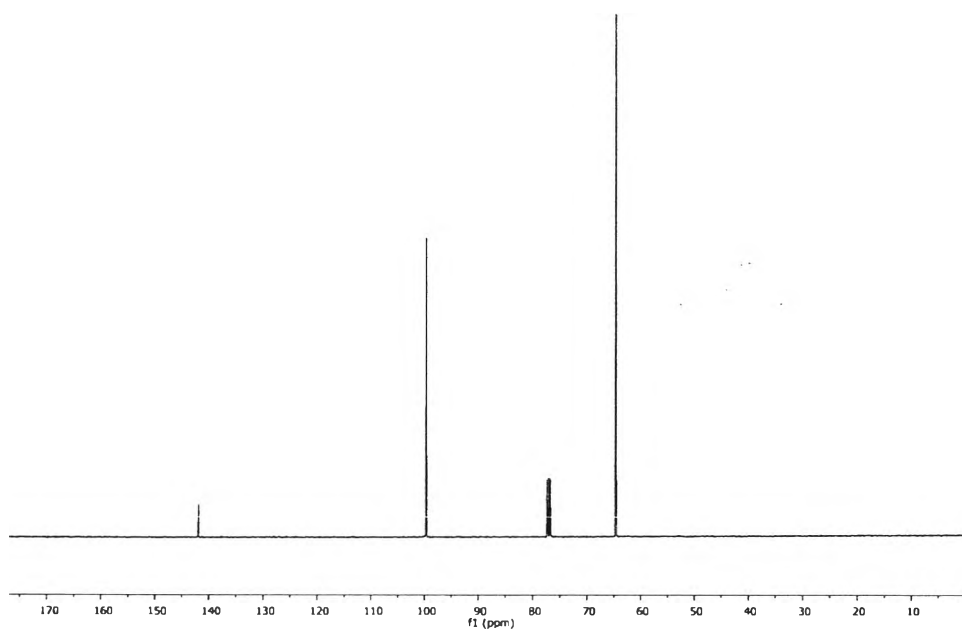


Figure A.33 ^{13}C NMR (CDCl_3) spectrum of compound 5b

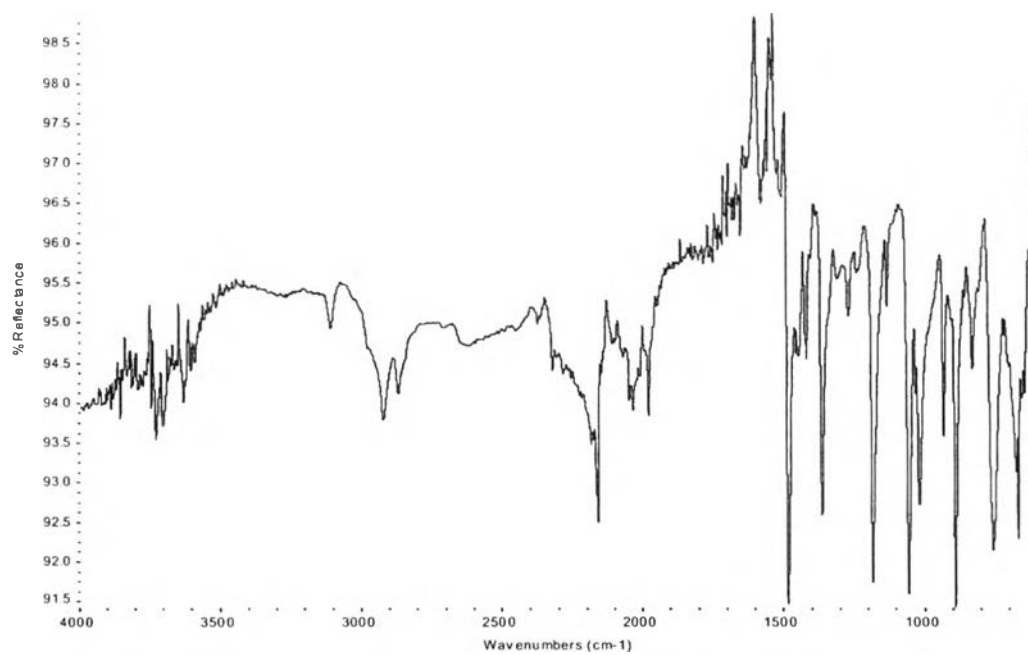


Figure A.34 IR spectrum of compound 5b



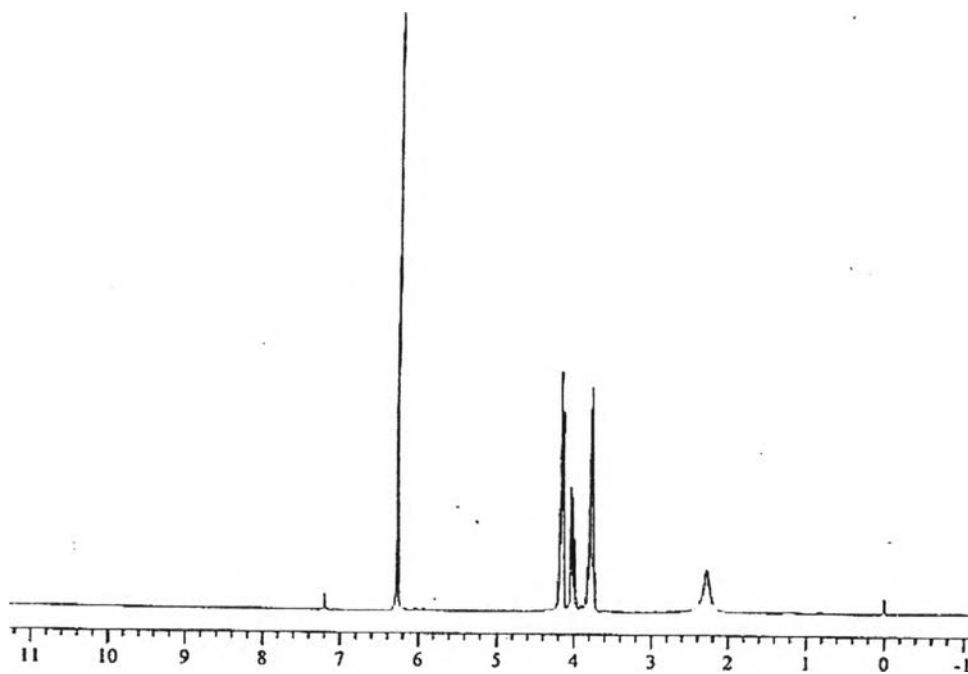


Figure A.35 ^1H NMR (CDCl_3) spectrum of compound 6

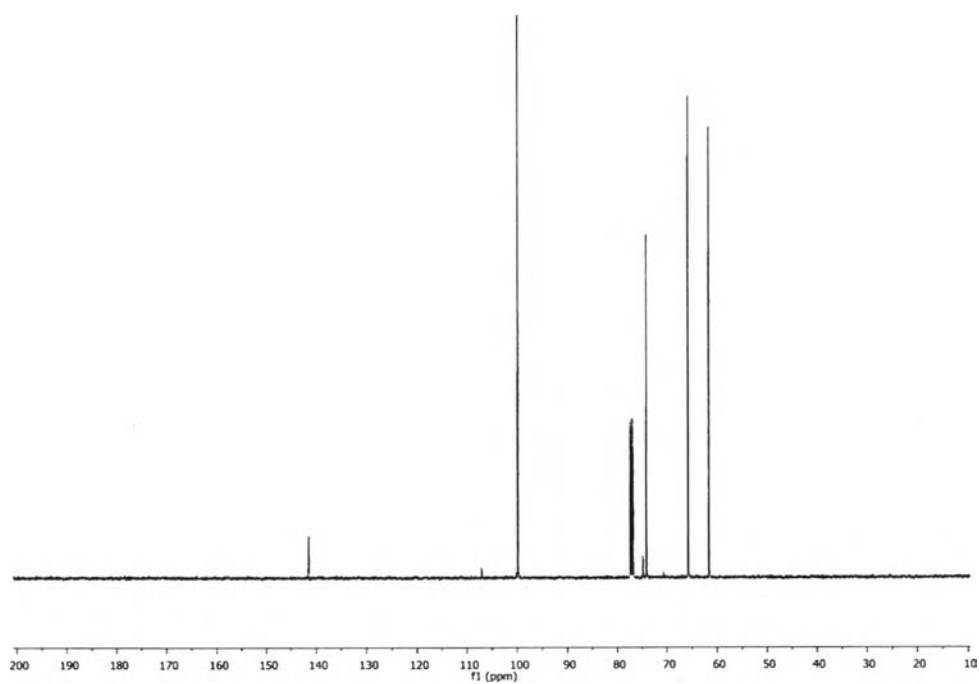


Figure A.36 ^{13}C NMR (CDCl_3) spectrum of compound 6



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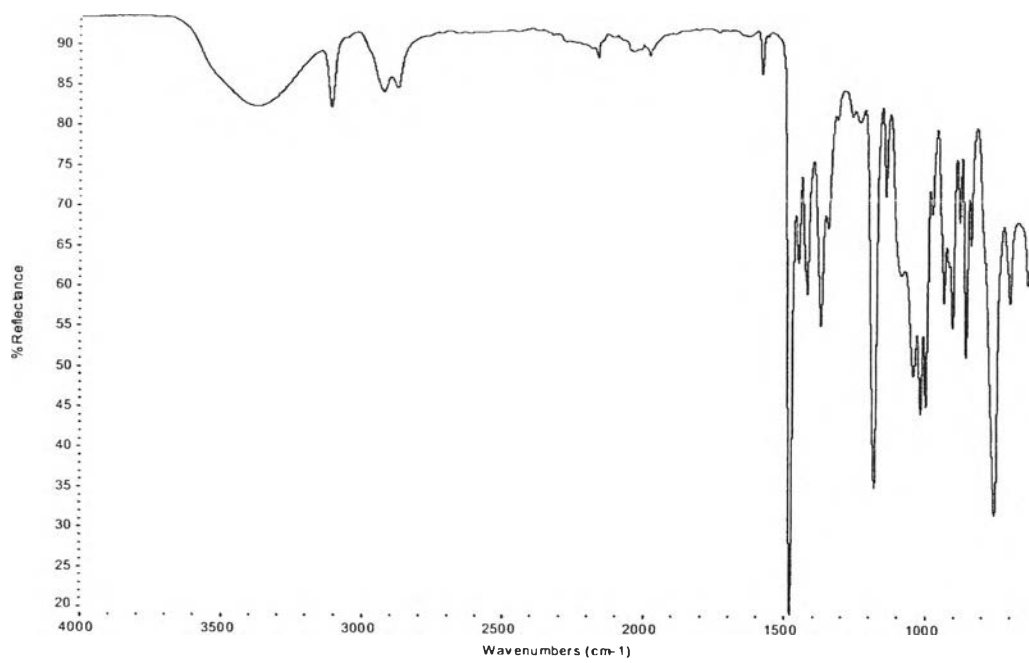


Figure A.37 IR spectrum of compound 6



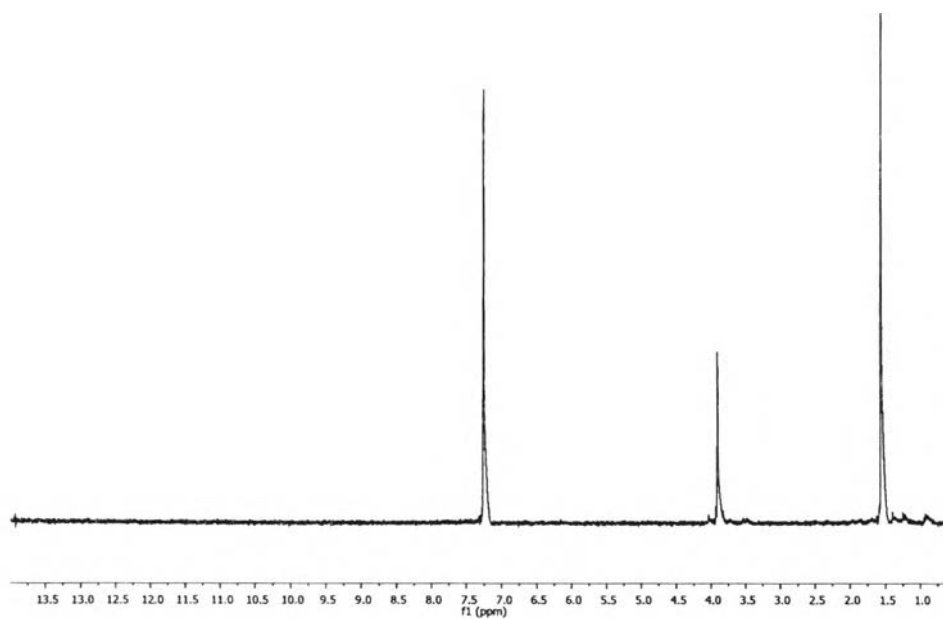


Figure A.38 ^1H NMR (CDCl_3) spectrum of compound 7a

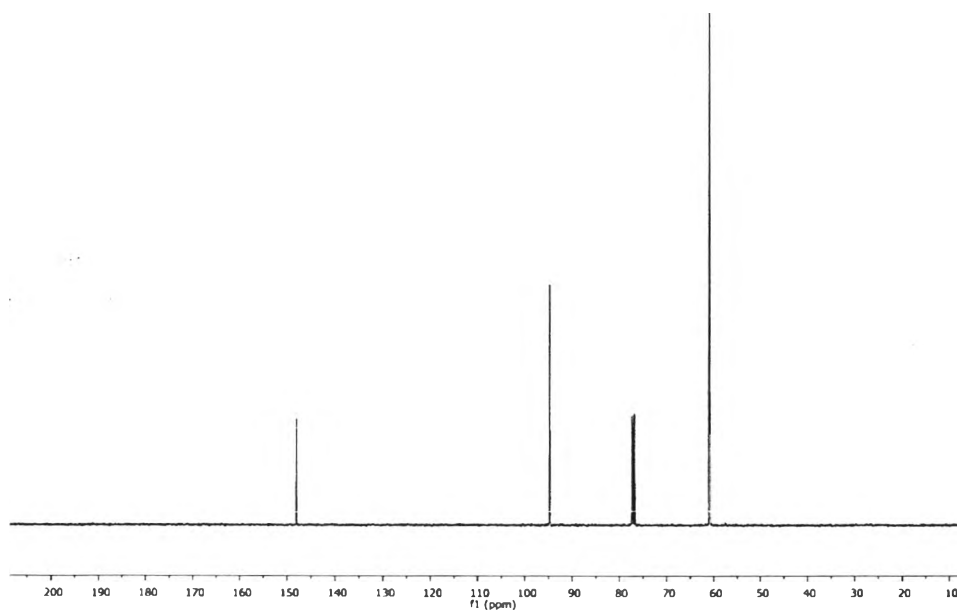


Figure A.39 ^{13}C NMR (CDCl_3) spectrum of compound 7a



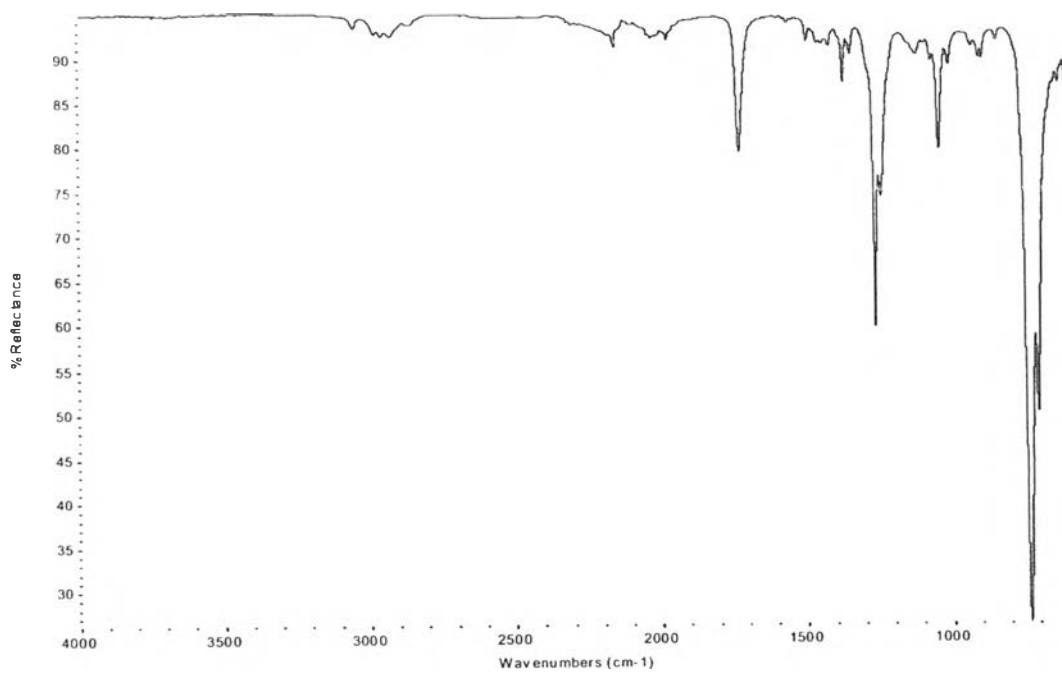


Figure A.40 IR spectrum of compound 7a

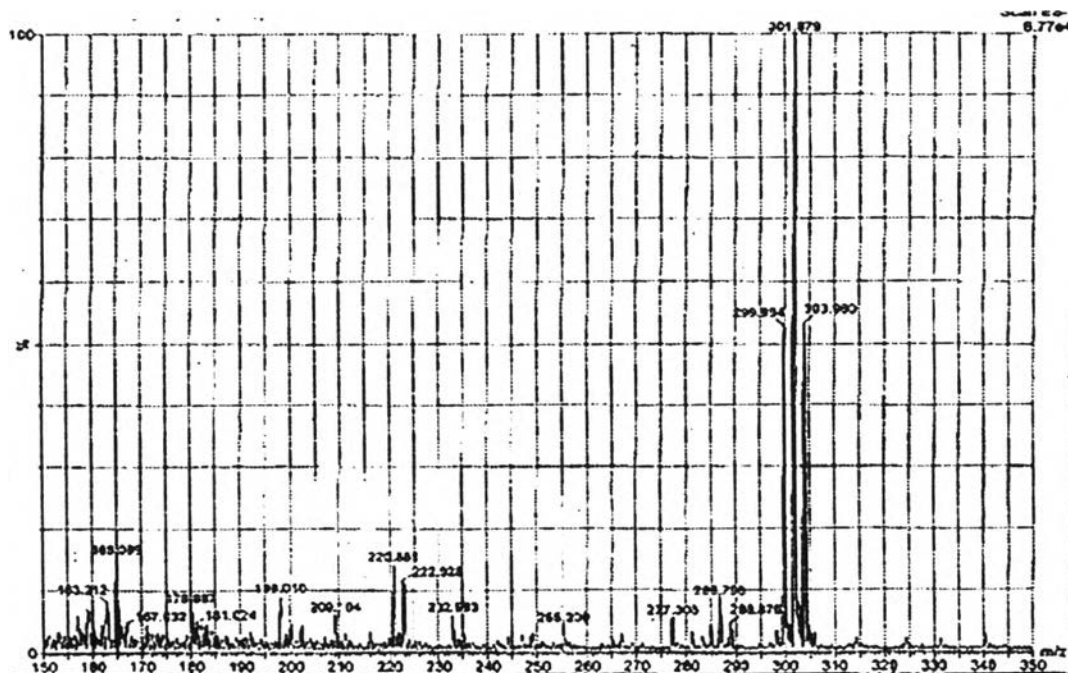


Figure A.41 Mass spectrum of compound 7a



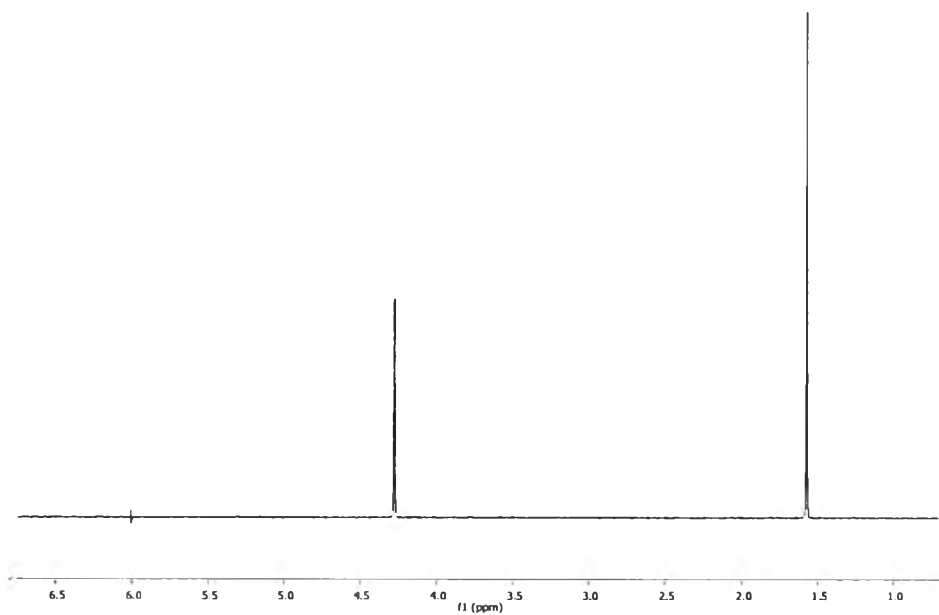


Figure A.42 ^1H NMR (CDCl_3) spectrum of compound 7b

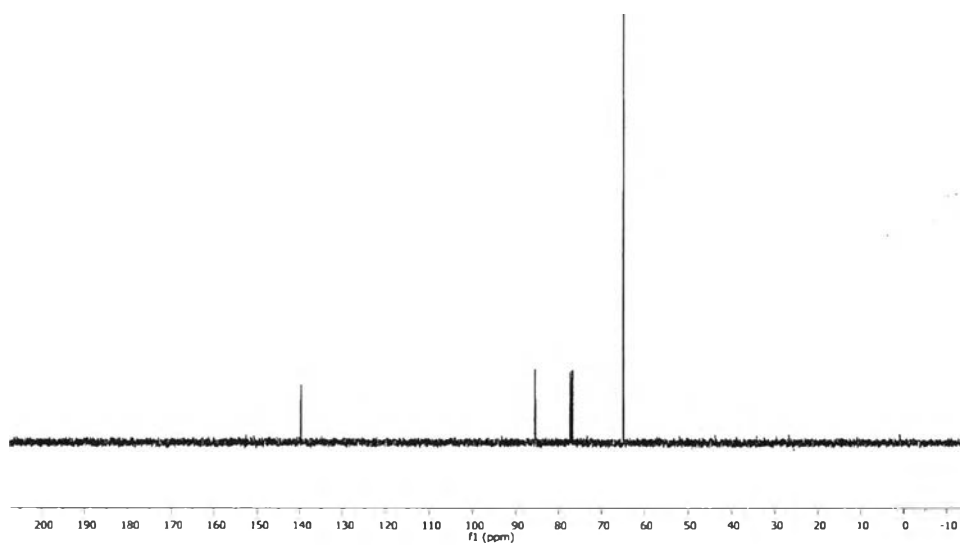


Figure A.43 ^{13}C NMR (CDCl_3) spectrum of compound 7b

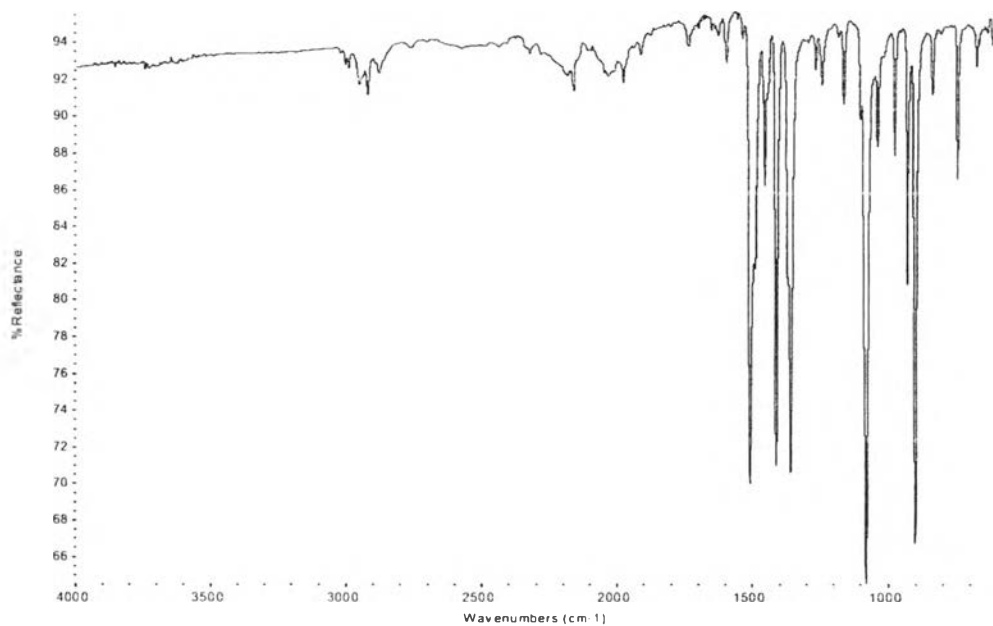


Figure A.44 IR spectrum of compound 7b

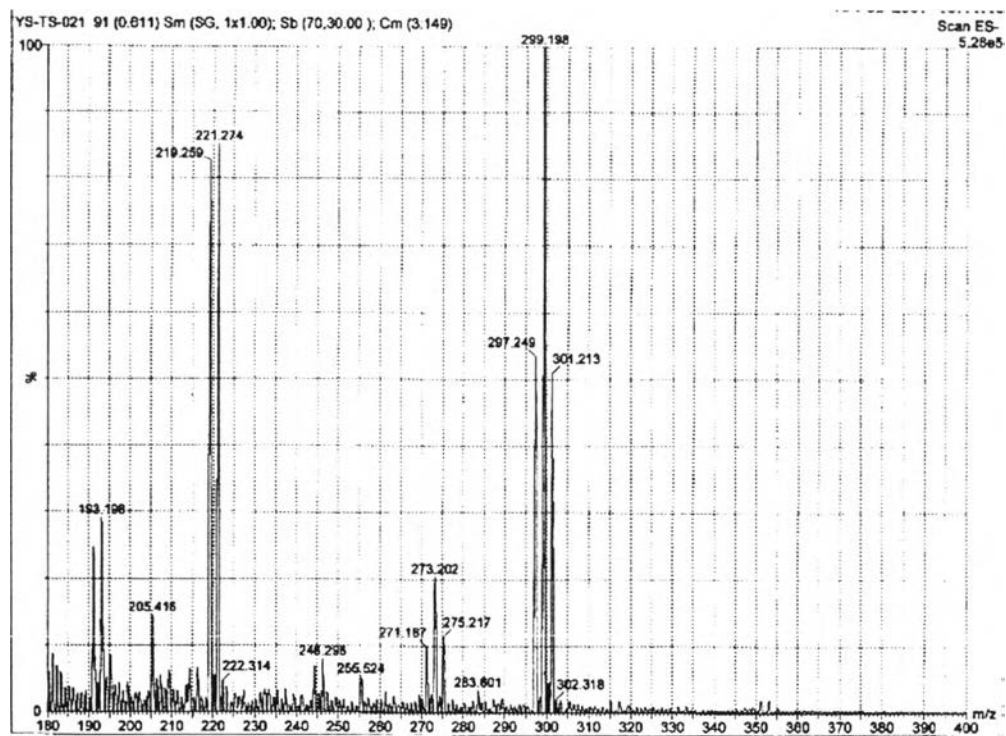


Figure A.45 Mass spectrum of compound 7b

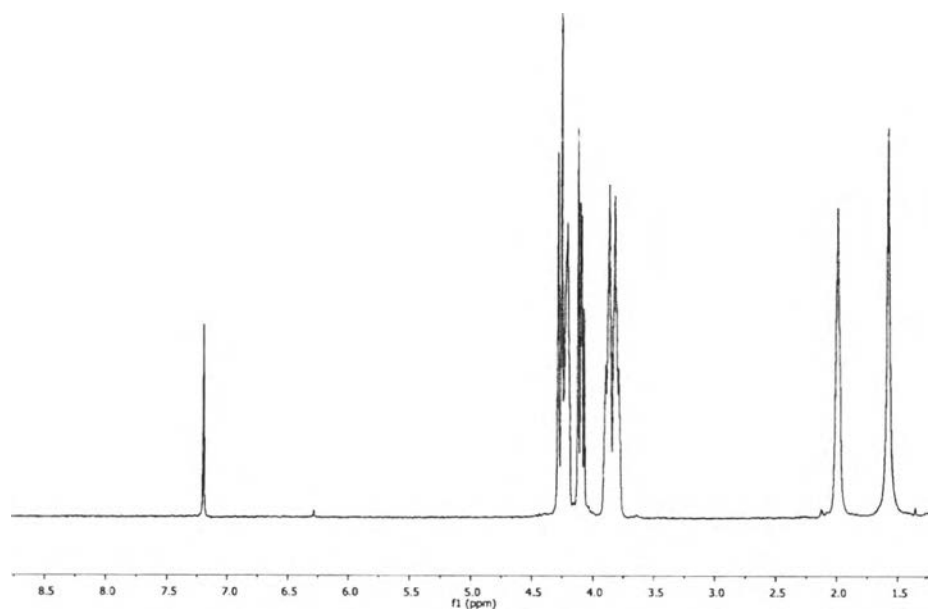


Figure A.46 ^1H NMR (CDCl_3) spectrum of compound 7c

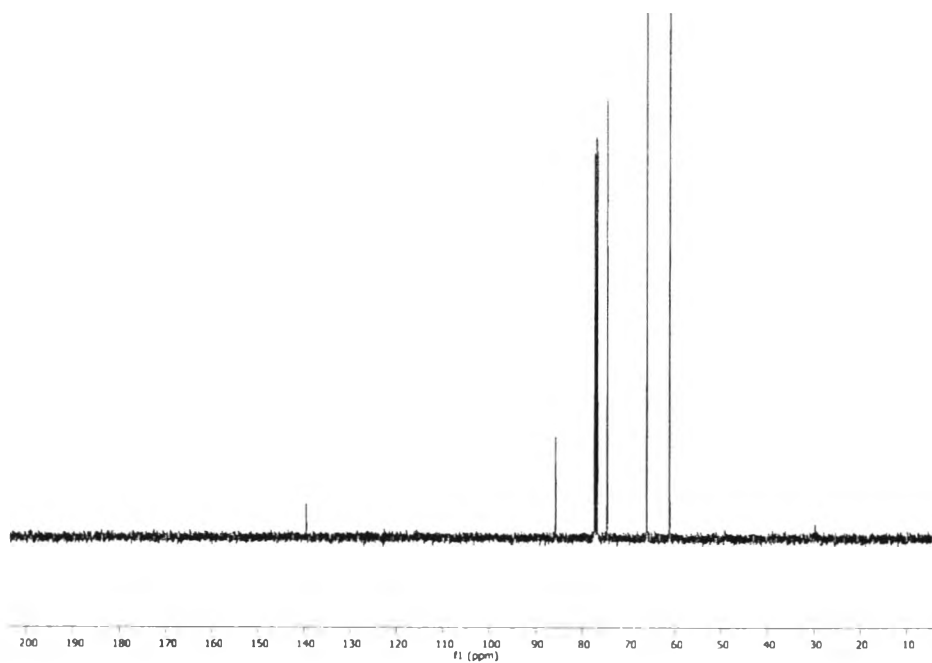


Figure A.47 ^{13}C NMR (CDCl_3) spectrum of compound 7c

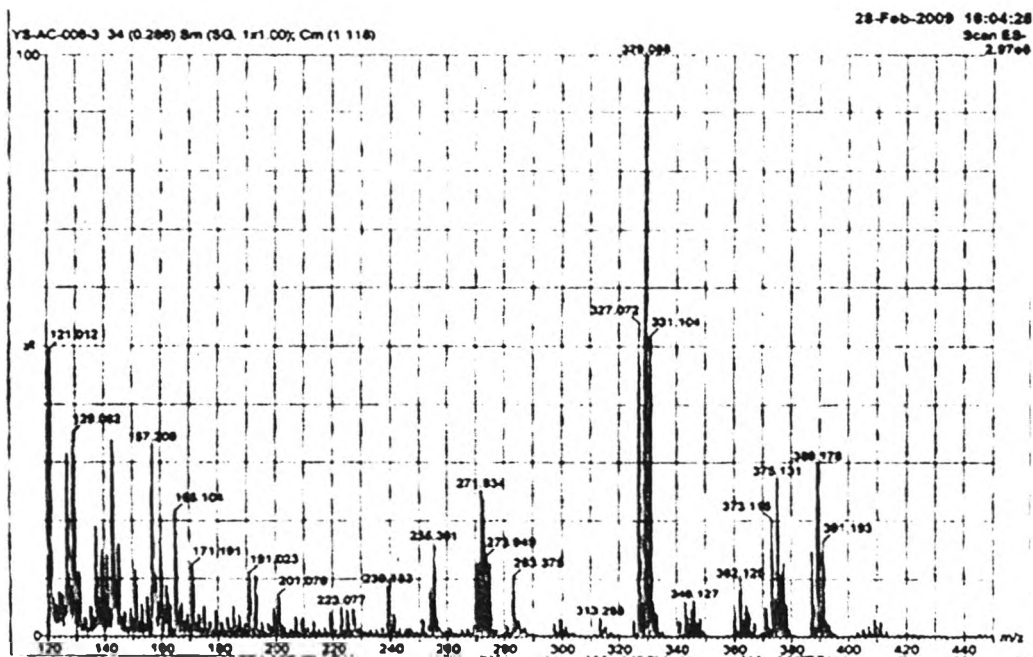


Figure A.48 Mass spectrum of compound 7c



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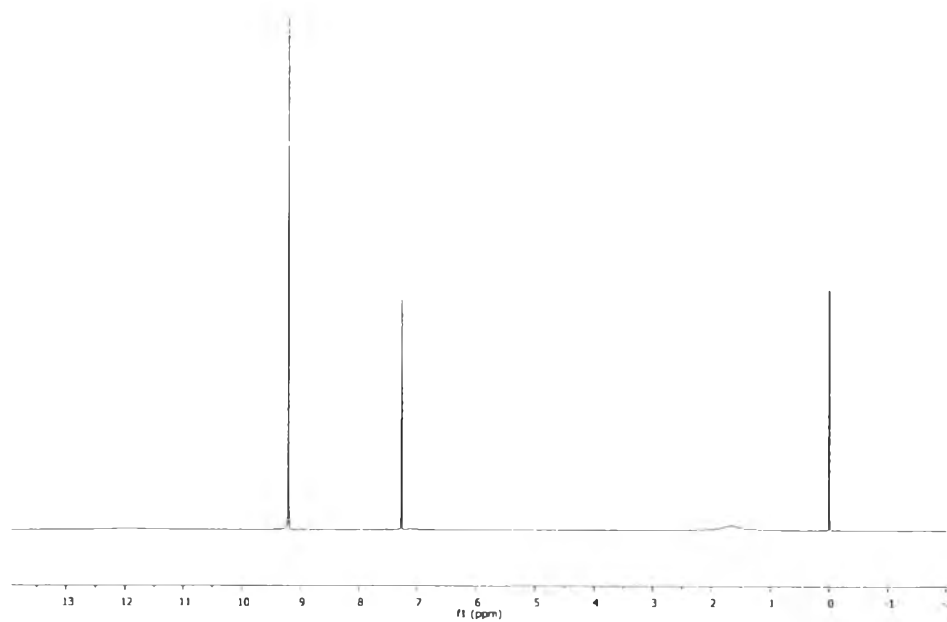


Figure A.49 ^1H NMR (CDCl_3) spectrum of 2,4,6-trinitrophenol (TNP)

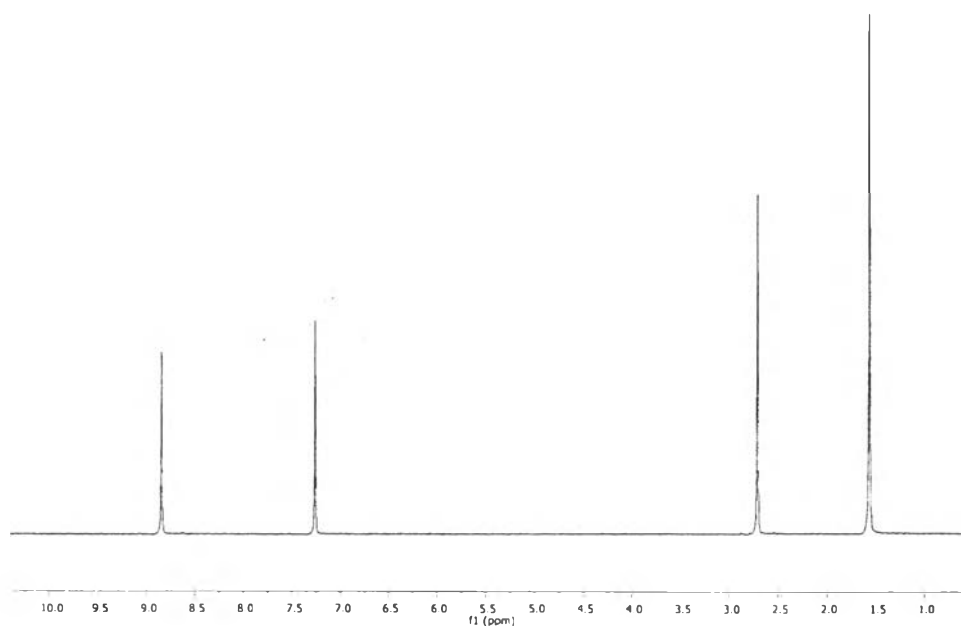


Figure A.50 ^1H NMR (CDCl_3) spectrum of 2,4,6-trinitrotoluene (TNT)



APPENDIX B

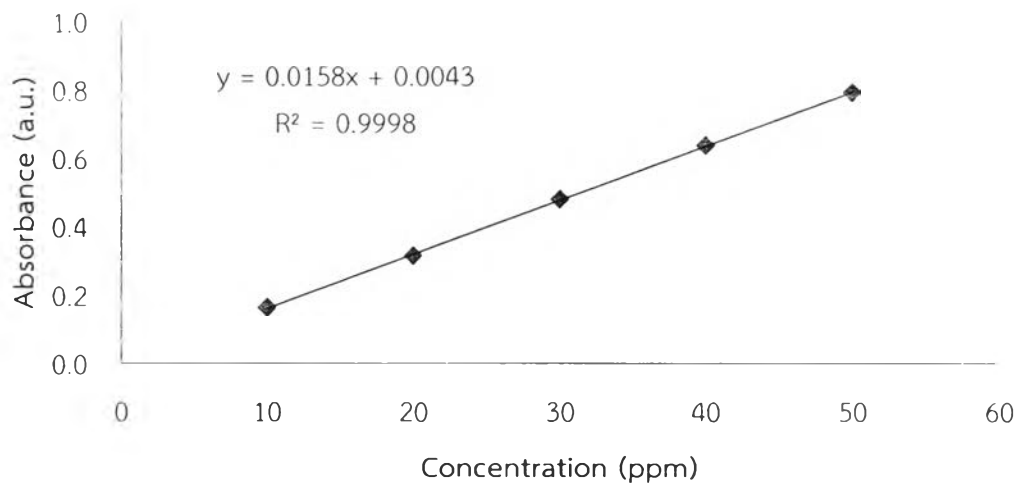


Figure B.1 Calibration curve of TNP in ethyl acetate

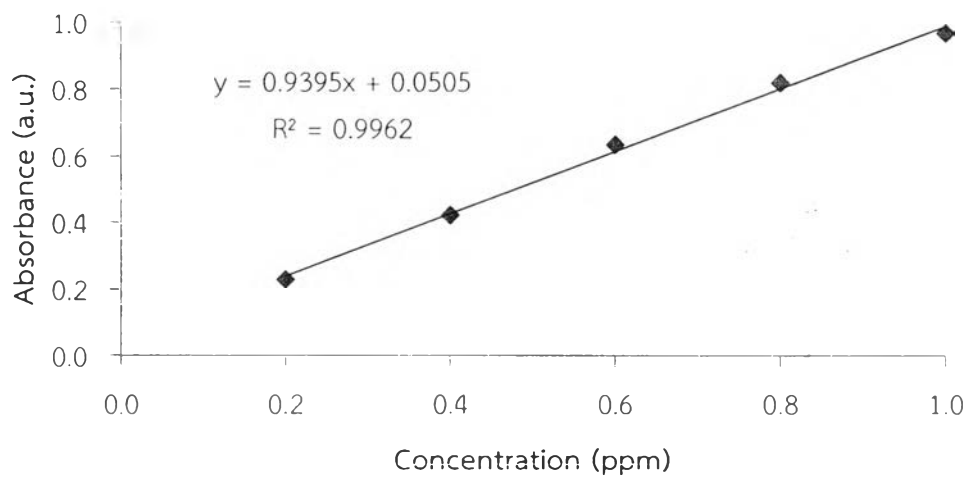


Figure B.2 Calibration curve of TNT in ethyl acetate



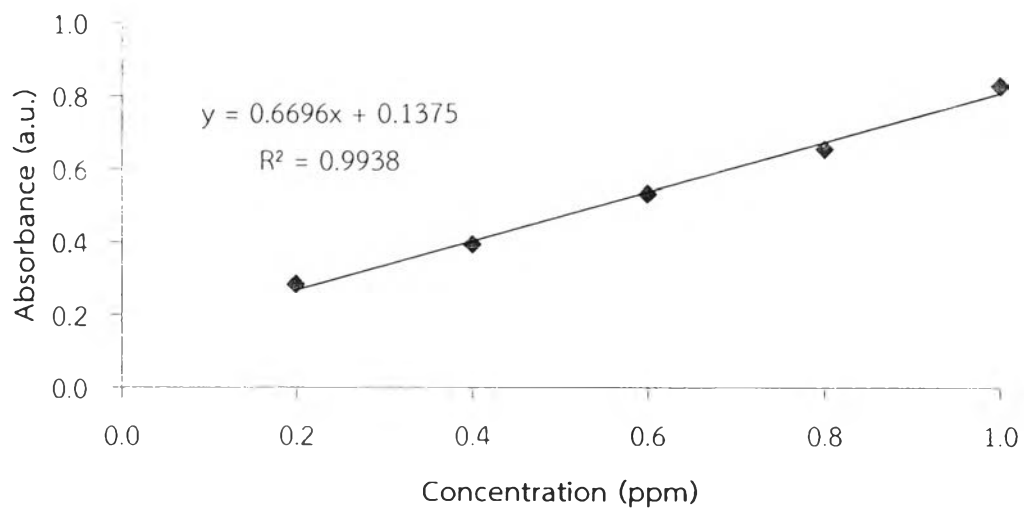


Figure B.3 Calibration curve of TPP in ethyl acetate



- The calculation of Q_{MIPs} , Q_{NIPs} and ΔQ values of TNP-MIPs binding experiment

Note: The weight of all dried TNP-MIPs and NIPs used was 0.1970 g.

From Figure 3.4, at 8 hour;

From equation (2);

$$\begin{aligned} Q_{MIPs} (\mu\text{mol/g}) &= \left(\frac{C_i - C_e}{W \times MW} \right) \times V \\ &= \left(\frac{1022.41 - 680.89}{0.1970 \times 229.10} \right) \times 25 \\ &= 189.18 \mu\text{mol/g} \end{aligned}$$

From Figure 3.4, at 6-15 hour;

From equation (3);

$$\begin{aligned} Q_{NIPs} (\mu\text{mol/g}) &= \left(\frac{C_i - C_e}{W \times MW} \right) \times V \\ &= \left(\frac{1022.41 - 912.71}{0.1970 \times 229.10} \right) \times 25 \\ &= 60.77 \mu\text{mol/g} \end{aligned}$$

From equation (1);

$$\begin{aligned} \Delta Q &= Q_{MIPs} - Q_{NIPs} \\ &= 189.18 - 60.77 \mu\text{mol/g} \\ &= 128.41 \mu\text{mol/g} \end{aligned}$$



- The calculation of Q_{MIPs} , Q_{NIPs} and ΔQ values of TNT-MIPs binding experiment

Note: The weight of all dried TNT-MIPs and NIPs used was 0.1970 g.

From Figure 3.5, at 6 hour;

From equation (2);

$$\begin{aligned} Q_{MIPs} (\mu\text{mol/g}) &= \left(\frac{C_i - C_e}{W \times MW} \right) \times V \\ &= \left(\frac{971.79 - 719.00}{0.1970 \times 227.13} \right) \times 25 \\ &= 141.24 \mu\text{mol/g} \end{aligned}$$

From Figure 3.5, at 3-15 hour;

From equation (3);

$$\begin{aligned} Q_{NIPs} (\mu\text{mol/g}) &= \left(\frac{C_i - C_e}{W \times MW} \right) \times V \\ &= \left(\frac{971.79 - 904.48}{0.1970 \times 227.13} \right) \times 25 \\ &= 37.61 \mu\text{mol/g} \end{aligned}$$

From equation (1);

$$\begin{aligned} \Delta Q &= Q_{MIPs} - Q_{NIPs} \\ &= 141.24 - 37.61 \mu\text{mol/g} \\ &= 103.63 \mu\text{mol/g} \end{aligned}$$



- The calculation of Q_{MIPs} , Q_{NIPs} and ΔQ values of TNP-MIPs rebinding experiment

Note: The weight of all dried TNP-MIPs and NIPs used was 0.1890 g.

From Figure 3.6, at 5 hour;

From equation (2);

$$\begin{aligned} Q_{MIPs}(\mu\text{mol/g}) &= \left(\frac{C_i - C_e}{W \times MW} \right) \times V \\ &= \left(\frac{1025.32 - 880.25}{0.1890 \times 229.10} \right) \times 25 \\ &= 83.76 \mu\text{mol/g} \end{aligned}$$

From Figure 3.6, at 3-10 hour;

From equation (3)

$$\begin{aligned} Q_{NIPs}(\mu\text{mol/g}) &= \left(\frac{C_i - C_e}{W \times MW} \right) \times V \\ &= \left(\frac{1025.32 - 990.68}{0.1890 \times 229.10} \right) \times 25 \\ &= 20.00 \mu\text{mol/g} \end{aligned}$$

From equation (1);

$$\begin{aligned} \Delta Q &= Q_{MIPs} - Q_{NIPs} \\ &= 83.76 - 20.00 \mu\text{mol/g} \\ &= 63.76 \mu\text{mol/g} \end{aligned}$$



- The calculation of Q_{MIPs} , Q_{NIPs} and ΔQ values of TNT-MIPs rebinding experiment

Note: The weight of all dried TNT-MIPs and NIPs used was 0.1890 g.

From Figure 3.7, at 4 hour;

From equation (2);

$$\begin{aligned} Q_{MIPs}(\mu\text{mol/g}) &= \left(\frac{C_i - C_e}{W \times MW} \right) \times V \\ &= \left(\frac{997.45 - 954.98}{0.1890 \times 227.13} \right) \times 25 \\ &= 24.73 \mu\text{mol/g} \end{aligned}$$

From Figure 3.7, at 2-10 hour;

From equation (3)

$$\begin{aligned} Q_{NIPs}(\mu\text{mol/g}) &= \left(\frac{C_i - C_e}{W \times MW} \right) \times V \\ &= \left(\frac{997.45 - 976.22}{0.1890 \times 227.13} \right) \times 25 \\ &= 12.36 \mu\text{mol/g} \end{aligned}$$

From equation (1)

$$\begin{aligned} \Delta Q &= Q_{MIPs} - Q_{NIPs} \\ &= 24.73 - 12.36 \mu\text{mol/g} \\ &= 12.37 \mu\text{mol/g} \end{aligned}$$



- The calculation of binding capacities of TNP-MIPs

The initial amount of TNP in ethyl acetate solution from the binding experiment was 1022.41 ppm or 566.33 $\mu\text{mol/g}$.

The amount of TNP in ethyl acetate solution from extraction off at the end of the binding process was 395.06 ppm or 218.83 $\mu\text{mol/g}$.

$$\begin{aligned}\therefore \text{The binding capacities of the TNP-MIPs} &= \left(\frac{218.83}{566.33} \right) \times 100 \\ &= 38.64 \%\end{aligned}$$

- The calculation of binding capacities of TNT-MIPs

The initial amount of TNT in ethyl acetate solution from the binding experiment was 971.79 ppm or 542.97 $\mu\text{mol/g}$.

The amount of TNT in ethyl acetate solution from extraction off at the end of the binding process was 278.34 ppm or 155.52 $\mu\text{mol/g}$.

$$\begin{aligned}\therefore \text{The binding capacities of the TNT-MIPs} &= \left(\frac{155.50}{542.97} \right) \times 100 \\ &= 28.63 \%\end{aligned}$$



VITA

Miss Supattra Sukrakarn was born on February 22, 1988 in Pathumthani, Thailand. She received a Bachelor's degree of science from Department of Chemistry, Faculty of Science, Chulalongkorn University, Thailand in 2010. She was admitted to a Master's Degree Program in Petrochemical and Polymer science, Faculty of Science, Chulalongkorn University and completed the program in 2014. Her address is 38/4 Moo 8, Tambol Kubangluang, Amphor Ladlumkaew, Pathumthani 12140.

