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APPENDICES

Appendix A

A.1 Chromophore substitution calculation from UV Absorption data

- 4-Methoxycinnamoyl-phthaloylchitosan

Since molar absorptivity (ε) of 4-methoxycinnamoyl moiety are 23,000 $M^{-1}cm^{-1}$ (λ_{max} = 310), calculation of degree of substitution can be done as follow:

$$A = \varepsilon bc$$

At concentration of 4-methoxycinnamoyl phthaloylchitosan solution of 20 ppm, the absorbance was 0.60.

Therefore, $0.60 = 23{,}000 \times c$

$c = 2.61 \times 10^{-5}$ M = concentration of chromophore unit

one gram of product contains chromophore = $(2.61 \times 10^{-5}/20 \times 10^{-3}) \times 177$

= 0.231 g

one gram of product contains phthaloylchitosan backbone = 1 – 0.231

= 0.769 g

Since phthaloylchitosan substitution 1.0 gives M.W. of the phthaloylchitosan of 192,160

therefore 192,160 g of phthaloylchitosan will contain 4-methoxycinnamoyl moieties = (0.231/0.769) × 192,160 = 57,723 g = 326 mole equivalents

Therefore degree of substitution = 326/632 = 0.52

With similar calculation procedure, degree of substitution of the 4-methoxycinnamoyl groups on irradiated chitosan was 0.63

- 2,4,5-Trimethoxycinnamoyl-phthaloyl chitosan

Since molar absorptivity (ε) of 2,4,5-trimethoxycinnamoyl moiety is 11,723 and 12,832 $M^{-1}cm^{-1}$ (λ_{max} = 290 and 350, respectively), calculation of degree of substitution can be done as follow:

$$A = \varepsilon bc$$

At concentration of 2,4,5-trimethoxycinnamoyl phthaloylchitosan solution of 20 ppm, the absorbance was 0.30.

Therefore, $0.30 = 12{,}832 \times c$

$c = 2.33 \times 10^{-5}$ M = concentration of chromophore unit

one gram of product contains chromophore = $(2.33\times10^{-5}/20\times10^{-3}) \times 222$

= 0.259 g

one gram of product contains phthaloylchitosan backbone = 1 – 0.259

= 0.741 g

Since phthaloylchitosan substitution 1.0 gives M.W. of the phthaloylchitosan of 192,160

Therefore 192,160 g of phthaloylchitosan will contain 2,4,5-trimethoxycinnamoyl moieties = (0.259/0.741) × 192,160 = 67165 g = 303 mole equivalents.

Degree of substitution = 303/632 = 0.48

-Degree of substitution in double grafted product

The 4-methoxycinnamoyl-phthaloylchitosan of ds 0.52 was used to grafted 2,4,5-trimethoxycinnamoyl moieties onto. Since molar absorptivity (ε) of 2,4,5-trimethoxycinnamoyl moiety at 350 nm is 12,832 $M^{-1}cm^{-1}$, calculation of degree of substitution can be done as follow:

$A = \varepsilon bc$

At concentration of 2,4,5-trimethoxycinnamoyl phthaloylchitosan solution of 20 ppm, the absorbance was 0.50.

Therefore, $0.50 = 12{,}832\times c$

$c = 3.90\times10^{-5}$ M = concentration of chromophore unit

one gram of product contains chromophore = $(3.90\times10^{-5}/20\times10^{-3}) \times 222$

= 0.433 g

one gram of product contains phthaloylchitosan backbone with 4-methoxycinnamoyl moieties = 1 – 0.433 = 0.567 g

Since 4-methoxycinnamoyl-phthaloylchitosan substitution 0.52 gives M.W. of the 4-methoxycinnamoyl-phthaloylchitosan of 249,883 (containing 4-methoxycinnamoyl moiety 57,723),

therefore, 192,160-57,723 = 53,244 g of 4-methoxycinnamoyl-phthaloylchitosan will contain 2,4,5-trimethoxycinnamoyl moieties = (0.433/0.567) × 53244 = 40660 g = 183 mole equivalents.

Degree of substitution = 183/632 = 0.29

A.2 Calculation percent penetration of octyl methoxycinnamate

$$A = \varepsilon bc$$

Where A is absorbance

b is the cell path length (1 cm)

c is the concentration of the adsorbing species in mol per litre

Molar absorptivity (ε) of octyl methoxycinnamate is 23000 $M^{-1}cm^{-1}$

$$c_{OMC} = A/23000$$

$$= X \text{ mole/litre}$$

Receptor volume is 13 mL, and molecular weight of OMC is 290.4:

Weight of penetrated OMC = $X \times (13/1000) \times 290.4$

Weight of initial OMC is 0.005 g:

Percent penetration = (Weight of penetrated OMC/Weight of initial OMC) × 100

APPENDIX B

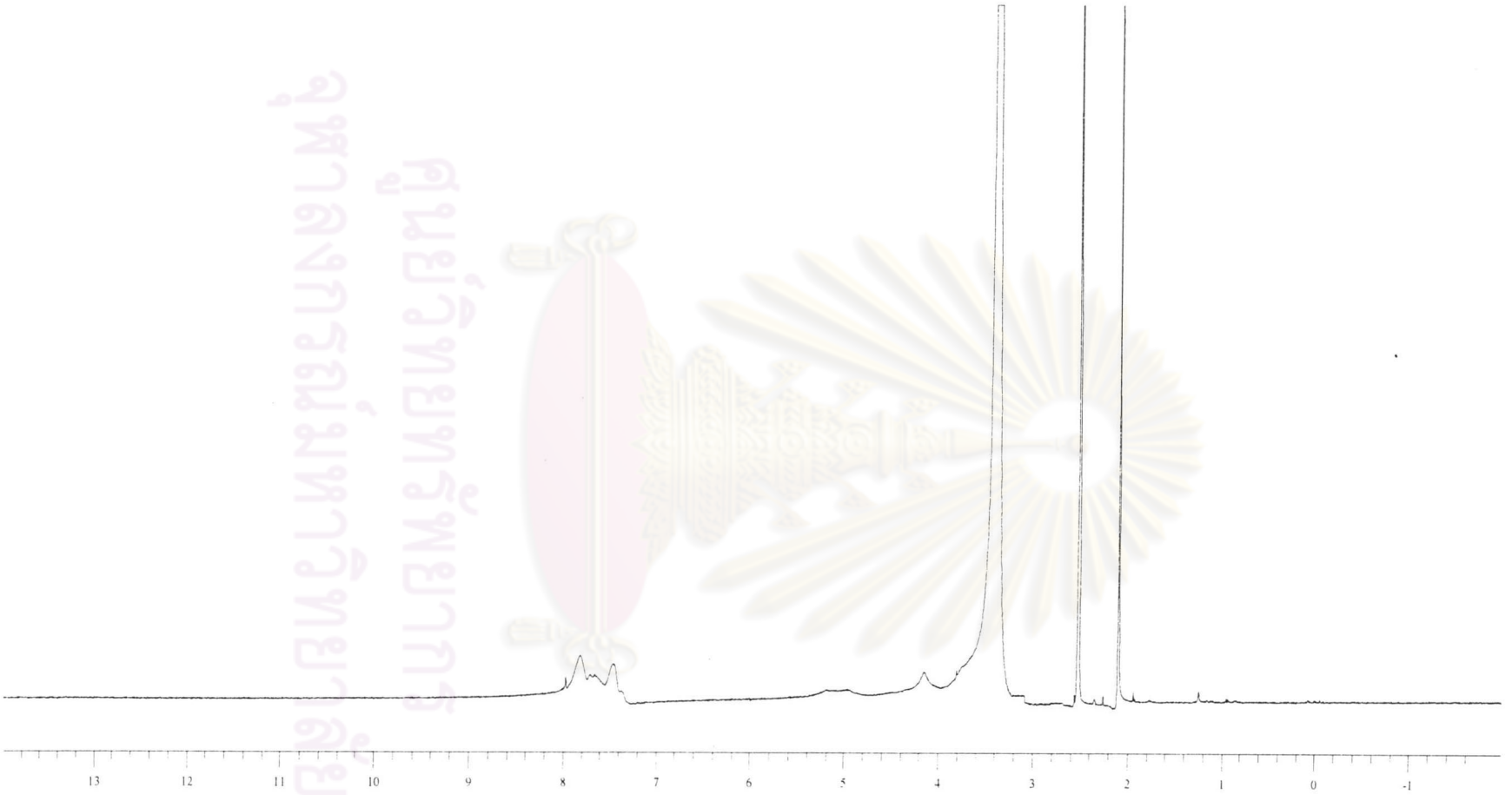

Figure B.1 ^{1}H-NMR spectrum of phthaloylchitosan

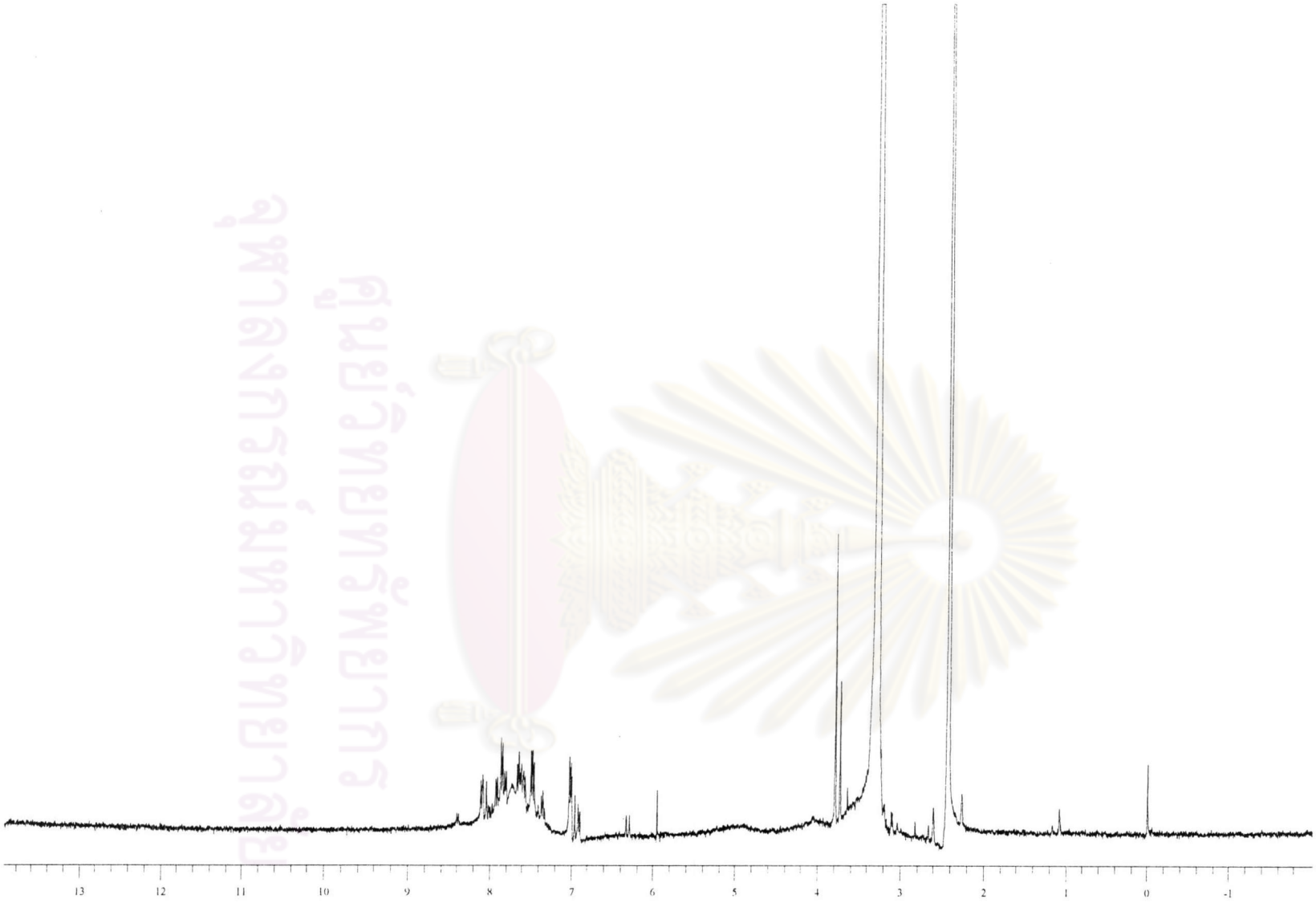

Figure B.2 ^{1}H-NMR spectrum of 4-methoxycinnamoyl-phthaloylchitosan

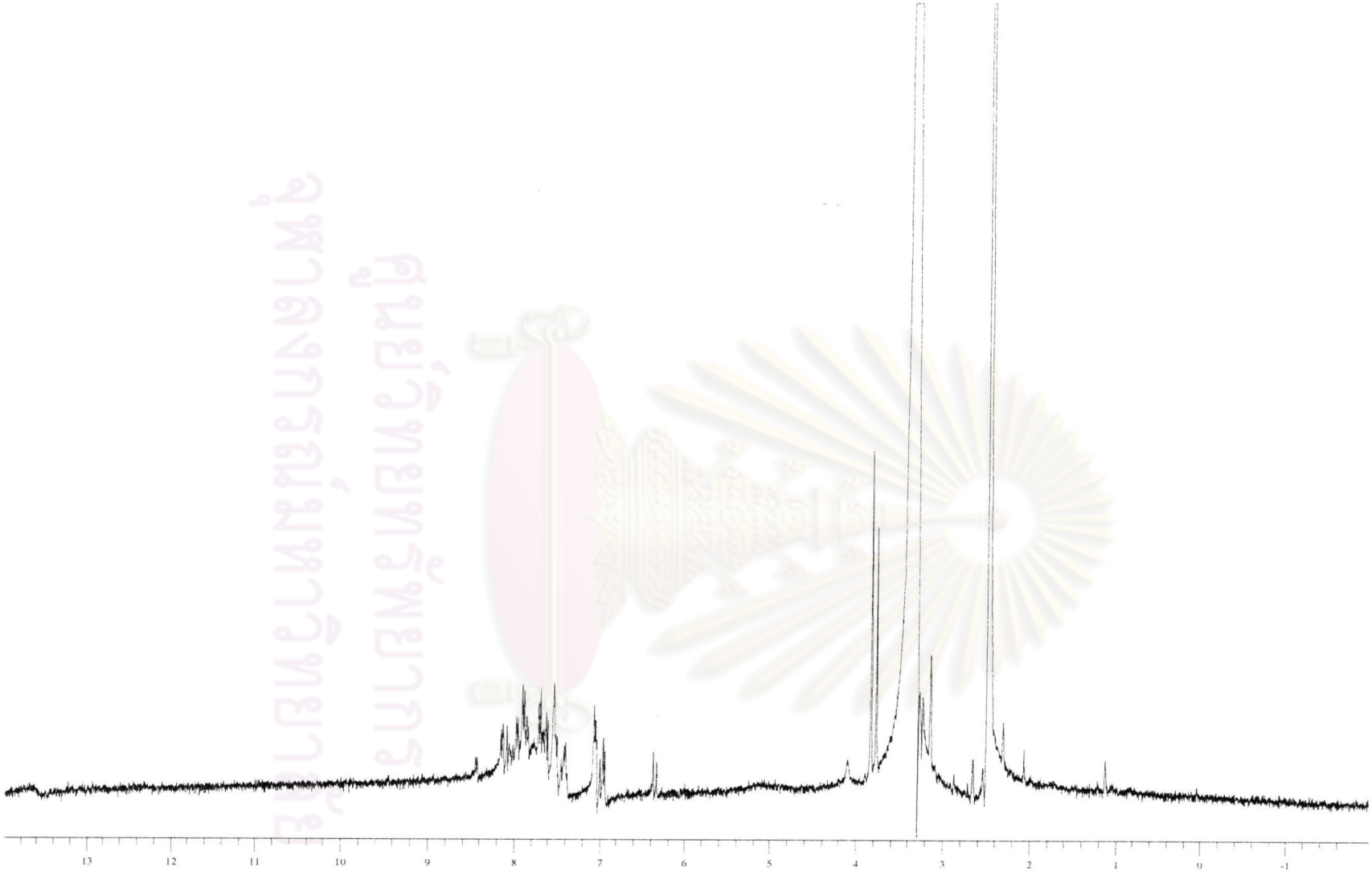

Figure B.3 ^{1}H-NMR spectrum of 4-methoxycinnamoyl-phthaloyl-irradiated chitosan

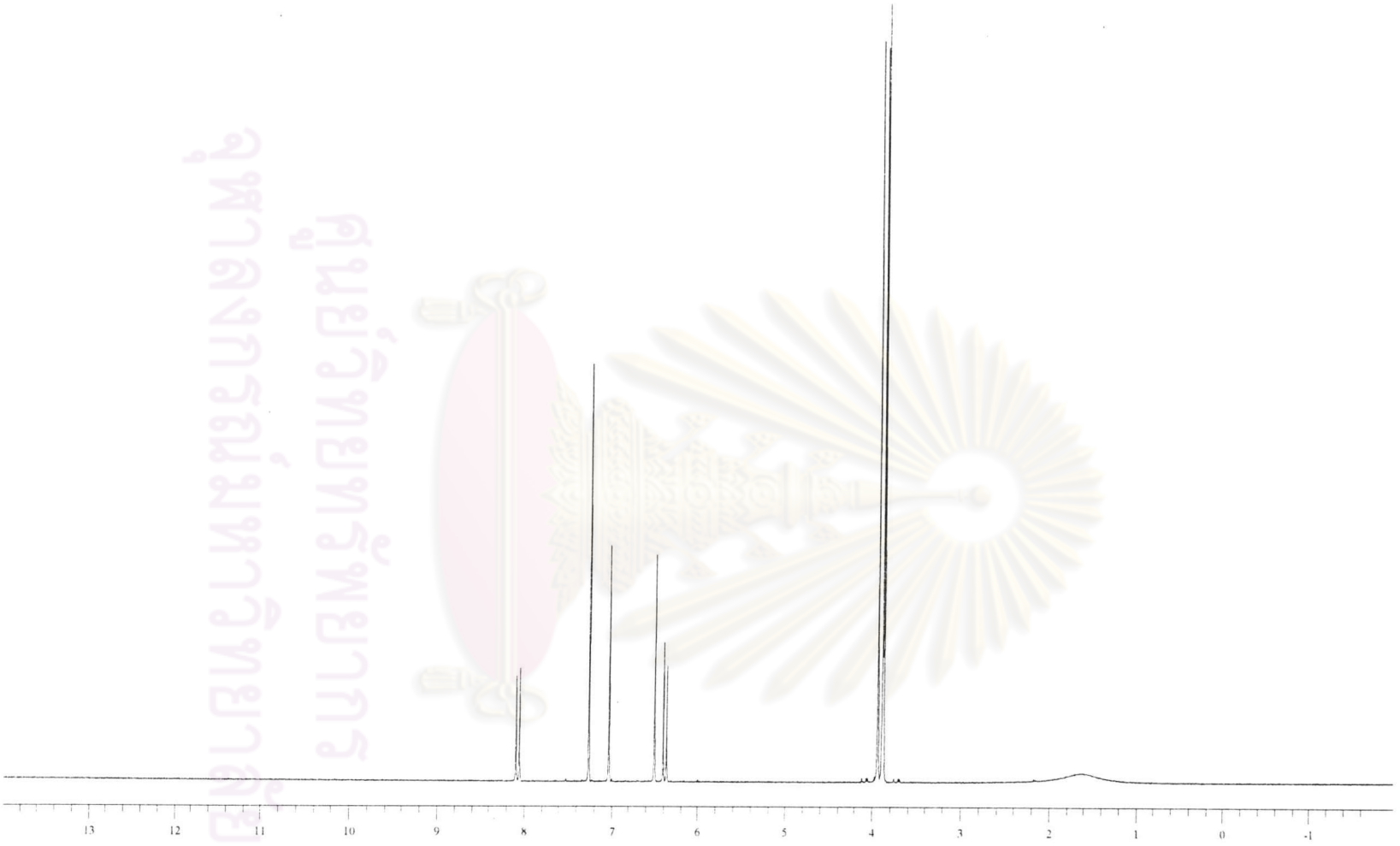

Figure B.4 ^{1}H-NMR spectrum of 2,4,5-trimethoxycinnamic acid

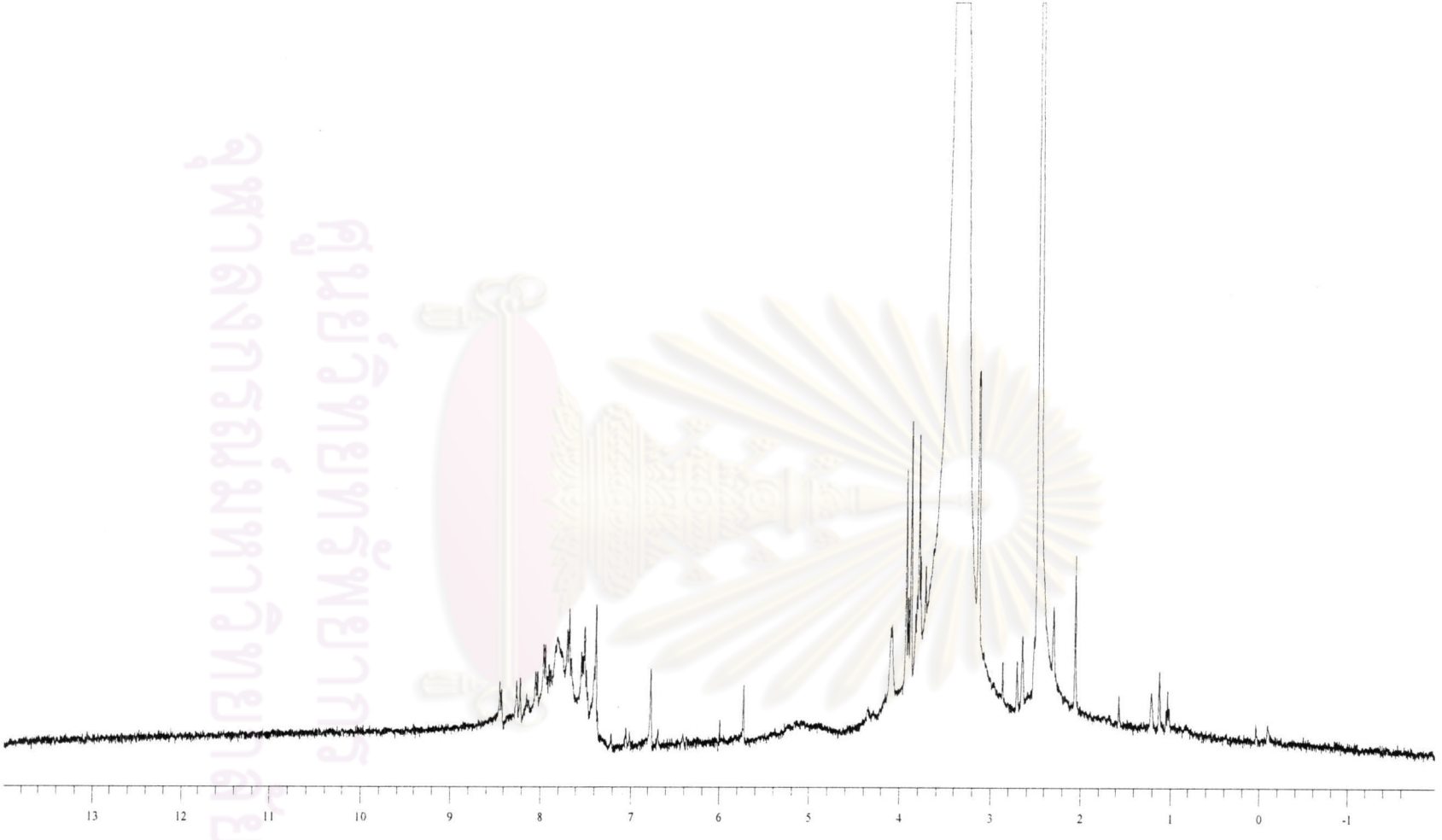

Figure B.5 ^{1}H-NMR spectrum of 2,4,5-trimethoxycinnamoyl-phthaloylchitosan

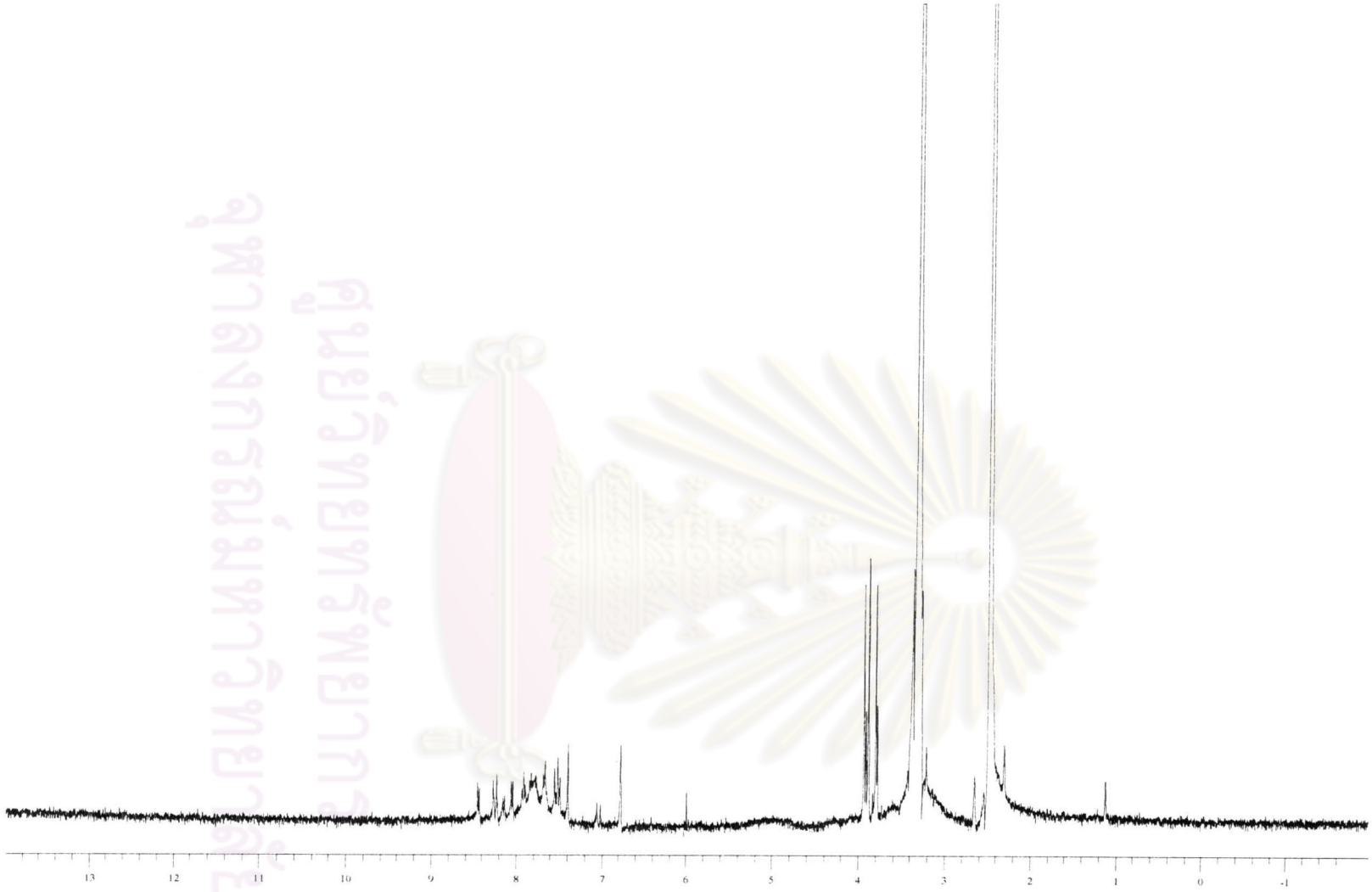

Figure B.6 ^{1}H-NMR spectrum of 2,4,5-trimethoxycinnamoyl-4-methoxycinnamoyl-phthaloylchitosan

Figure B.10 IR spectrum of phthaloylchitosan

Figure B.11 IR spectrum of phthaloyl-irradiated chitosan

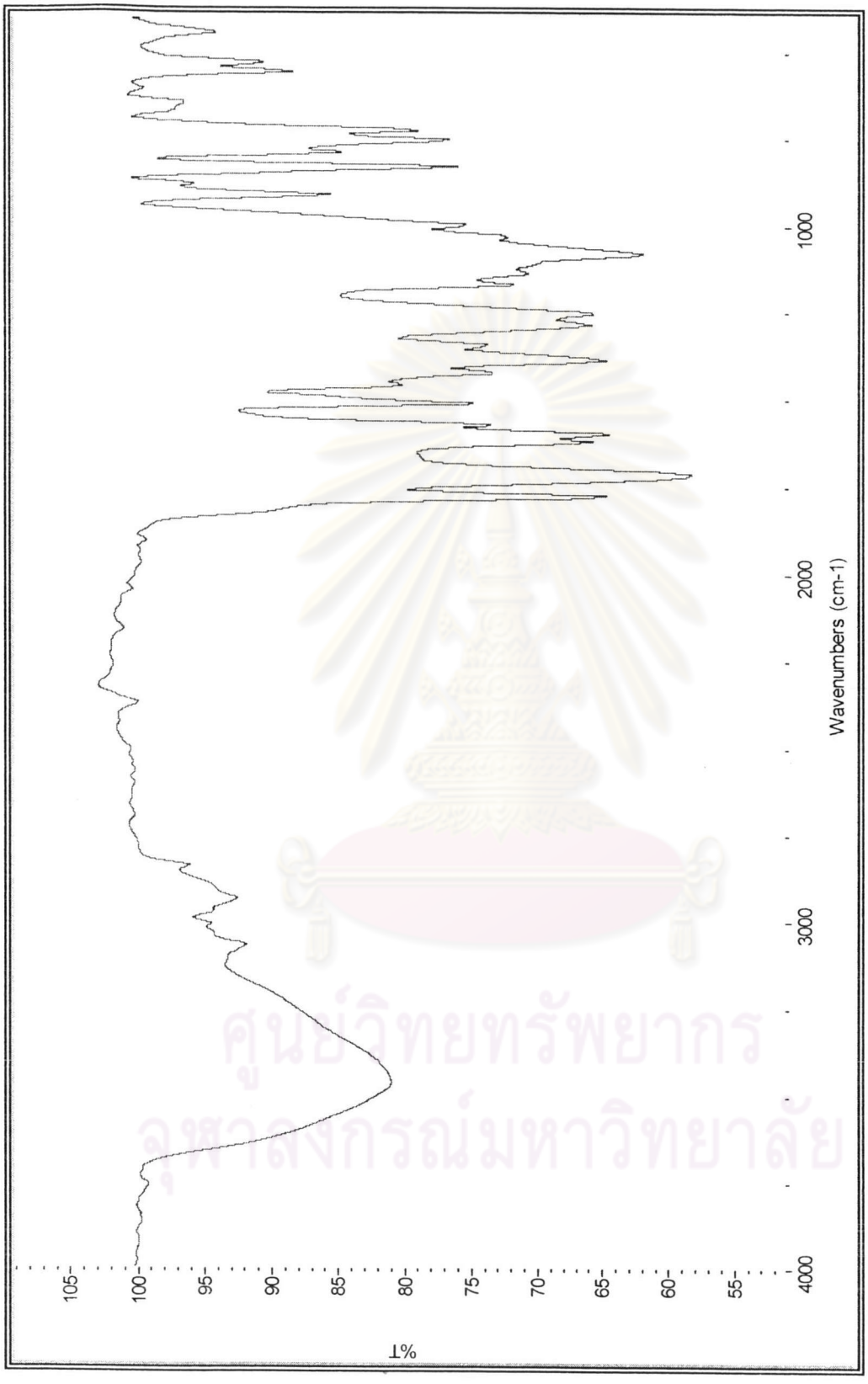

Figure B.12 IR spectrum of 4-methoxycinnamoyl-phthaloylchitosan

Figure B.13 IR spectrum of 4-methoxycinnamoyl-phthaloyl irradiated chitosan

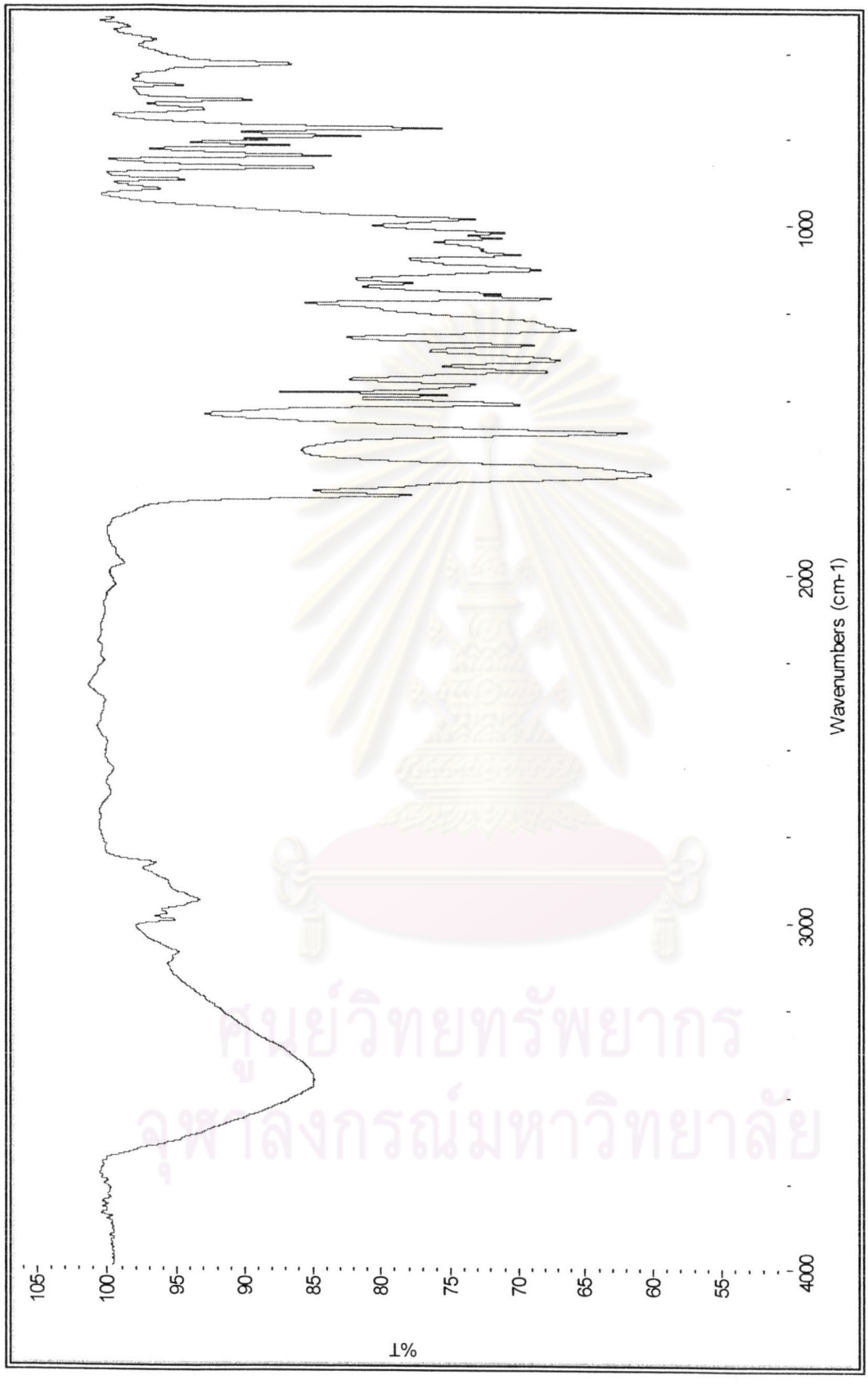

Figure B.14 IR spectrum of 2,4,5-trimethoxycinnamoyl-phthaloylchitosan

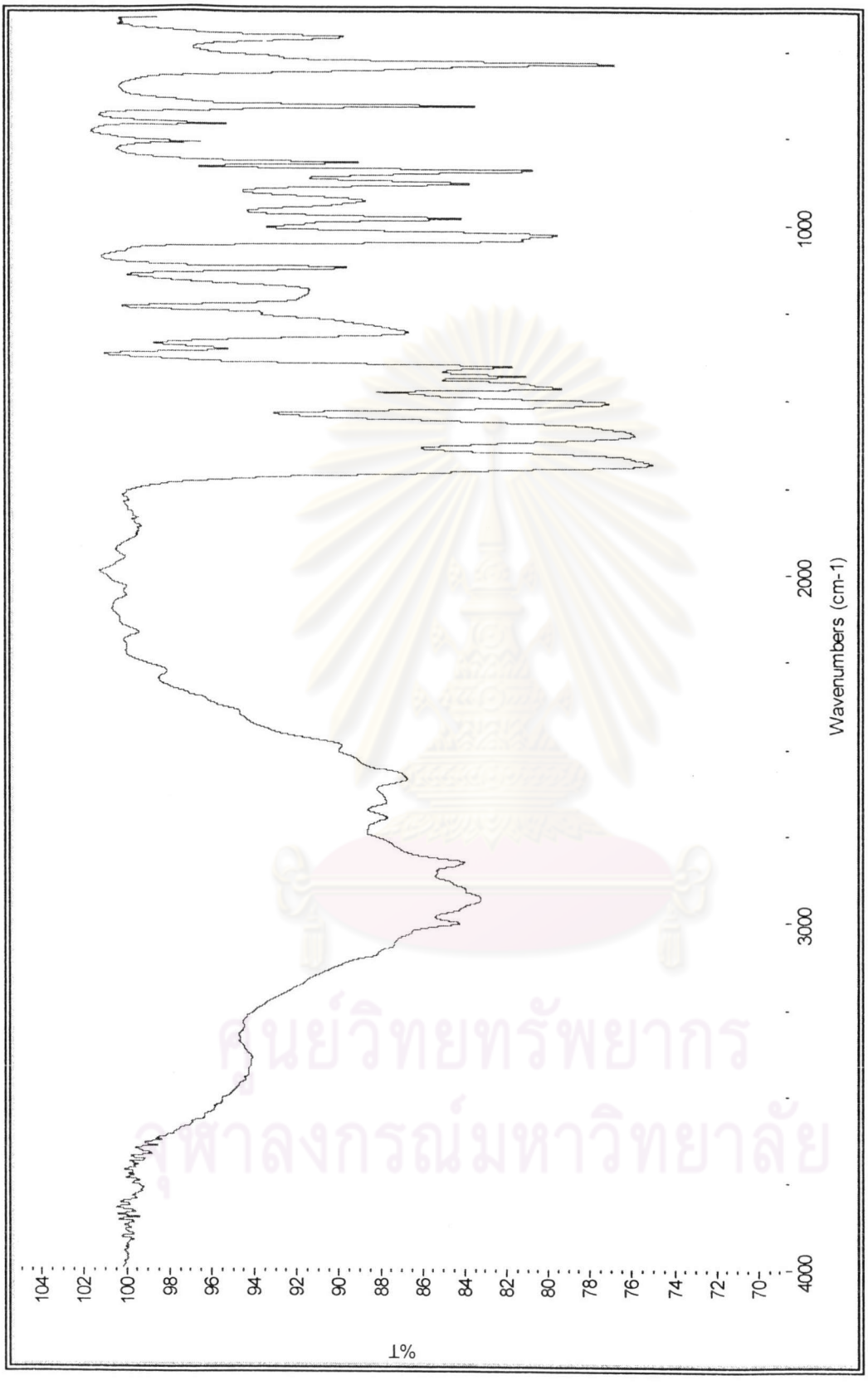

Figure B.15 IR spectrum of 2,4,5-trimethoxycinnamic acid

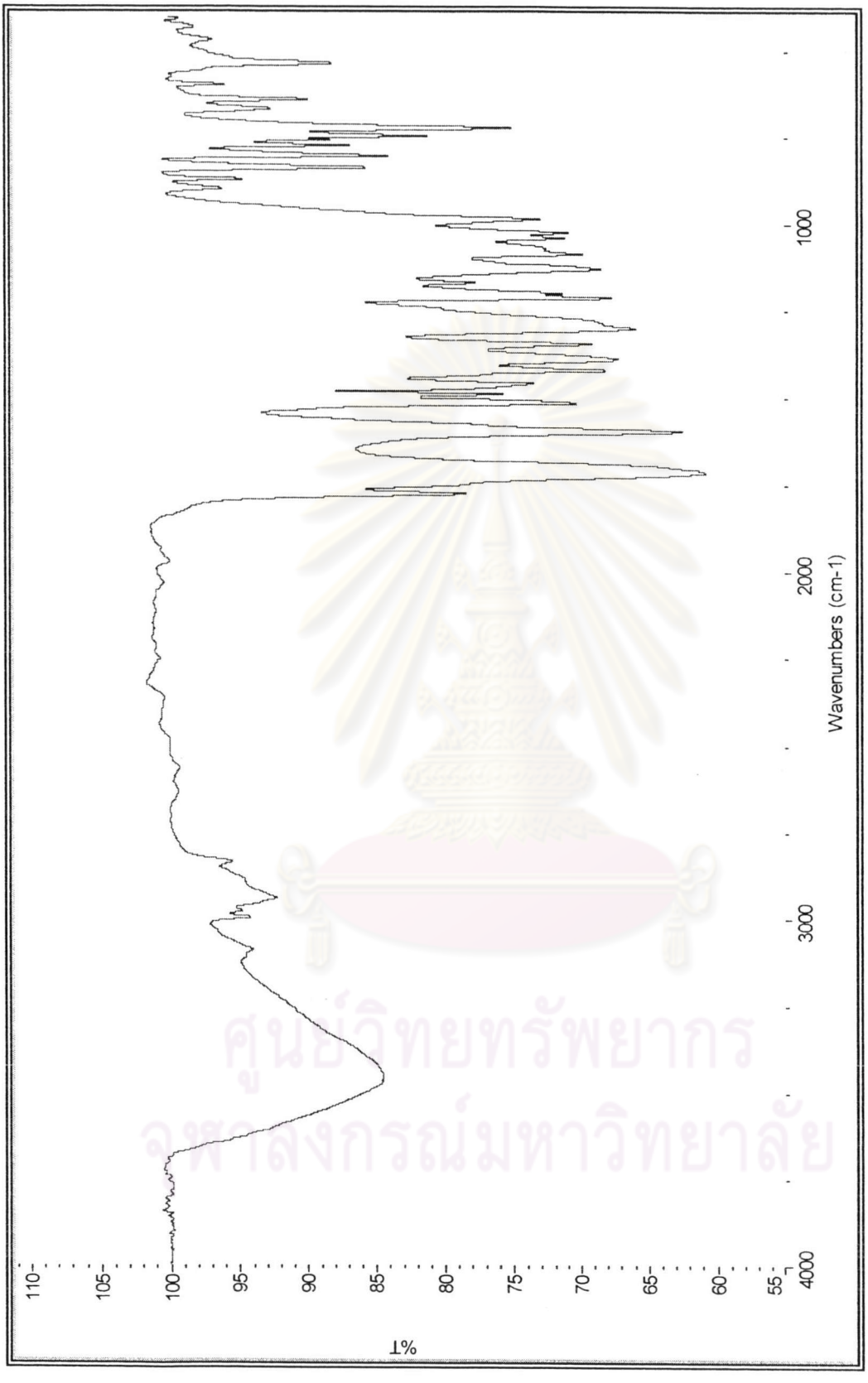

Figure B.16 IR spectrum of 2,4,5-trimethoxycinnamoyl-4-methoxycinnamoyl-phthaloylchitosan

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