

Supplementary Information:

Photochemical Studies on Aromatic γ,δ -epoxy Ketones: Efficient Synthesis of Benzocyclobutanones and Indanones

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General and Materials

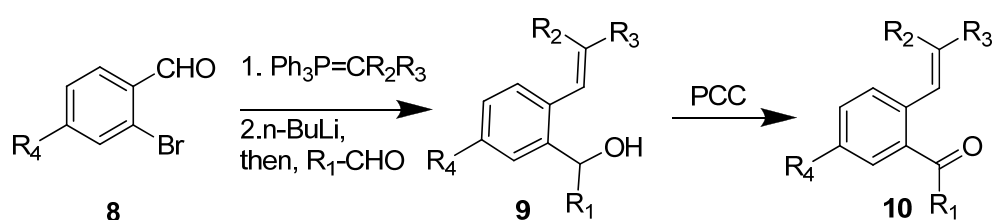
General Procedures. Reactions were carried out under an atmosphere of nitrogen and monitored by thin-layer chromatography (TLC) using UV light visualizing agent and ethanolic solution of Phosphomolybdic acid hydrate. NMR spectra were measured on Bruker AVANCE III 400M NMR in CDCl₃ (7.262 for ¹H, 77.01 for ¹³C) or CD₃COCD₃ (2.05 for ¹H, 29.84 and 206.26 for ¹³C) with tetramethylsilane as the internal reference. When peak multiplicities were reported, the following abbreviations were used: s-singlet, d-doublet, t-triplet, q-quartet,

m-multiplet, br-broadened. IR absorption spectra results were obtained on Nicolet impact 400 FT-IR instrument and using as a film on NaCl single-crystal plate (SPECTRUM100). HRMS (ESI) was recorded using Agilent 6520 accurate-Mass Q-TOF LC/MS system (1200-6520/Agilent). Low-resolution Mass spectra were obtained from GC-MS system (7890A-5975C/Agilent). Silica gel (200-300 mesh, QingDao, China) was used for column chromatography and preparative thin-layer chromatography was performed on commercial available silica gel plates (GF254, QingDao, China).

Materials. Anhydrous tetrahydrofuran (THF), benzene, diethyl ether (Et₂O) were dried with sodium (Na). Anhydrous dichloromethane (DCM) were dealt with CaH₂. Reagents were purchased at the highest commercial quality and used without further purification.

Experimental Procedures

Synthesis of Olefin-Ketone 10.



Entry	R ₁ /C ₆ H ₅	R ₂ /C ₆ H ₅	R ₃	R ₄
a	Ph	H	H	H
b	p-Me-Ph	H	H	H
c	p-CO ₂ Me-Ph	H	H	H
d	p-Me-Ph	H	H	Me

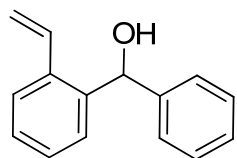
e	i-Pr	H	H	H
f	Ph	Me	H	H
g	Ph	Et	H	H
h	Ph	Ph	H	H
i	p-CO ₂ Me-Ph	Me	H	H
j	Ph	Me	Me	H
k	Me	Ph	H	H

General Procedure for Synthesis of Compound 9.

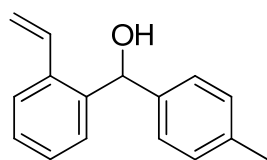
To a stirred solution of $\text{Ph}_3\text{P}^+\text{CH}_2\text{R}_2\text{R}_3\text{Br}^-$ (12.0 mmol) and 80 mL of anhydrous THF was added n-BuLi (5.0 mL, 2.4 M in hexane, 12.0 mmol) dropwise at $-78\text{ }^\circ\text{C}$ under nitrogen protection^[1]. After addition, the mixture was stirred at ambient temperature for one hour. The mixture was cooled to $-78\text{ }^\circ\text{C}$ again before the addition of 2-bromoaldehyde **8** (1.85 g, 10.0 mmol). The reaction was quenched with 15 mL of water at $-30\text{ }^\circ\text{C}$ when 2-bromoaldehyde couldn't be detected by TLC. Then, separated the organic layer and the water layer was extracted with petrol ether (3×50 mL), the combined organic phase was washed with brine (2×50 mL) and dried over MgSO_4 . The solvent was diminished under vacuum to give the crude product, which was used for next step directly without further purification.

The olefin (1.0 equiv) obtained in above step was dissolved in 15 mL of anhydrous THF and cooled to $-78\text{ }^\circ\text{C}$, n-BuLi (2.4 M in hexane, 1.0 equiv) was added dropwise under nitrogen protection^[2], and the mixture was stirred for two hours at the same temperature before the addition of commercial available R_1CHO (1.0 equiv, dissolved

in 3 mL of anhydrous THF) was added. After addition, the reaction was monitored with TLC until the R₁CHO was consumed completely. 5 mL of water was added to the mixture to quench the reaction and stirred until the solid was dissolved completely. Separated the organic layer and the water phase was extracted with diethyl ether (3 × 50 mL), combined the organic solution and dried over Na₂SO₄ before evaporated *in vacuo* to remove the solvent. Then, the crude product was purified by silica gel column chromatography to give the desired alcohols **9** as colorless oil.



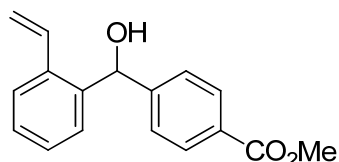
Compound 9a. Yield 74% for two steps. **IR** (neat) ν_{max} : 3408, 3063, 2959, 2871, 1714, 1626, 1454, 1017, 699 cm^{-1} . **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 7.40-7.47 (m, 2H), 7.23-7.30 (m, 7H), 6.96 (dd, $J = 17.2, 11.2$ Hz, 1H), 6.06 (s, 1H), 5.57 (d, $J = 17.6$ Hz, 1H), 5.24 (d, $J = 11.2$ Hz, 1H), 2.31 (br, 1H). **¹³C NMR** (CDCl₃, 100 MHz, ppm): δ 143.1, 140.4, 136.4, 134.4, 128.5, 128.0, 127.9, 127.5, 126.9, 126.4, 116.7, 73.0. **LRMS** (EI): 209 [M-1], 192, 165, 132, 105, 91, 77, 51, 27. **HRMS** (ESI): calcd for C₁₅H₁₅O⁺ 211.1117 [M+H]⁺, found 211.1115.



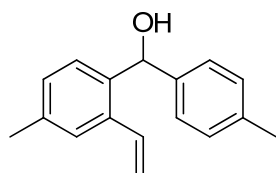
Compound 9b. Yield 82% for two steps. **IR** (neat) ν_{max} : 3435, 2978, 1647, 1513, 1268, 1017, 756 cm^{-1} . **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.51 (dd, $J = 8.8, 2.4$ Hz, 2H), 7.31-7.36 (m, 2 H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.17(d, $J = 8.0$ Hz, 2H), 7.02 (q, $J = 17.2$ Hz, 1H), 5.63 (dd, $J = 17.2, 1.2$ Hz, 1H), 5.30 (dd, $J = 10.8, 1.2$ Hz, 1H), 2.37 (s, 3H), 2.21 (br, 1H). **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 140.5,

140.1, 137.3, 136.2, 134.3, 129.2, 128.0, 127.8, 126.9, 126.7, 126.3, 116.6, 72.9, 21.1.

LRMS (EI): 224 [M], 205, 189, 165, 139, 115, 89, 63, 51, 28, 14. **HRMS** (ESI): calcd for $C_{16}H_{17}O^+$ 225.1274 [M+H]⁺, found 225.1117.

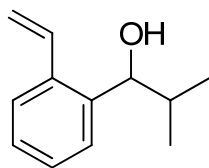


Compound 9c. Yield 77% for two steps. **IR** (neat) ν_{max} : 3445, 3063, 2952, 1713, 1612, 1435, 1104, 754 cm^{-1} . **¹H NMR** ($CDCl_3$, 400 MHz, ppm): δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.45 (t, $J = 9.2$ Hz, 1H), 7.30-7.37 (m, 3H), 7.22-7.26 (m, 2H), 6.96 (dd, $J = 17.4, 10.8/11.2$ Hz, 1H), 6.07 (d, $J = 2.0$ Hz, 1H), 5.57 (dd, $J = 17.2, 0.8/1.2$ Hz, 1H), 5.24 (dd, $J = 10.8, 0.8/1.2$ Hz, 1H), 3.84 (s, 3H), 3.06 (br, 1H). **¹³C NMR** ($CDCl_3$, 100 MHz, ppm): δ 167.1, 148.4, 140.0, 136.4, 134.2, 129.7, 129.0, 128.2, 128.1, 127.2, 126.7, 126.5, 117.0, 72.5, 52.1. **LRMS** (EI): 267 [M-1], 250, 209, 191, 165, 149, 133, 104, 77, 59, 28. **HRMS** (ESI): calcd for $C_{17}H_{17}O_3^+$ 269.1172 [M+H]⁺, found 269.1178.



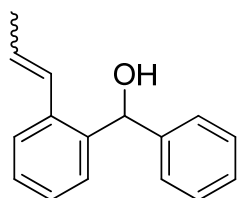
Compound 9d. Yield 77% for two steps. **IR** (neat) ν_{max} : 3367, 2956, 2860, 1901, 1728, 1613, 1456, 1179, 1039, 819 cm^{-1} . **¹H NMR** ($CDCl_3$, 400 MHz, ppm): δ 7.37 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.28 (s, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.09 (m 3H), 6.91 (dd, $J = 17.6/17.2, 11.2/10.8$ Hz, 1H), 6.03 (d, $J = 2.8$ Hz, 1H), 5.54 (d, $J = 17.6$ Hz, 1H), 5.20 (d, $J = 10.8$ Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.24 (br, 1H). **¹³C NMR** ($CDCl_3$, 100 MHz, ppm): δ 140.4, 140.3, 137.8, 137.2, 134.2, 133.4, 129.2, 128.6, 126.2, 115.7, 72.8, 21.4, 21.2. **LRMS** (EI): 239 [M+1], 221, 207, 195,

160, 131, 115, 91, 77, 65, 43, 28, 14. **HRMS** (ESI): calcd for $C_{17}H_{19}O^+$ 239.1430
[M+H]⁺, found 239.1428.



Compound 9e. Yield 55% for two steps. **IR** (neat) ν_{max} : 3400, 3063,

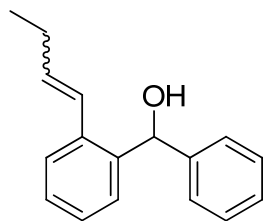
2960, 1625, 1468, 1226, 1004, 756 cm^{-1} . **¹H NMR** ($CDCl_3$, 400 MHz, ppm): δ 7.43-7.47 (m, 2H), 7.23-7.31 (m, 2H), 7.07 (dd, $J = 17.2, 10.8$ Hz, 1H), 5.60 (dd, $J = 17.2, 1.2$ Hz, 1H), 5.34 (dd, $J = 10.8, 1.2$ Hz, 1H), 4.71 (dd, $J = 6.8, 3.2$ Hz, 1H), 1.96-2.04 (m, 1H), 1.01 (d, $J = 2.8$ Hz, 3H), 0.82 (d, $J = 6.8$ Hz, 3H). **¹³C NMR** ($CDCl_3$, 100 MHz, ppm): δ 141.1, 136.2, 134.6, 127.8, 127.4, 126.4, 126.2, 116.2, 76.0, 34.8, 19.6, 17.8. **LRMS** (EI): 176 [M], 158, 133, 115, 103, 91, 77, 63, 55, 39, 27, 15. **HRMS** (ESI): calcd for $C_{12}H_{17}O^+$ 177.1274 [M+H]⁺, found 177.1270.



Compound 9f (Z/E = 1:1). Yield 73% for two steps. **IR** (neat)

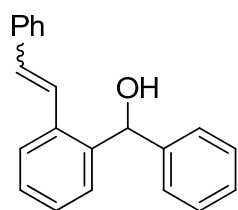
ν_{max} : 3391, 3062, 3028, 2912, 1646, 1449, 1176, 1011, 698 cm^{-1} . **¹H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.51 (d, $J = 8.8$ Hz, 1H), 7.23-7.40 (m, 8H), 6.68 (dd, $J = 7.6, 1.6$ Hz, 0.5H), 6.48 (dd, $J = 7.2, 1.2$ Hz, 0.5H), 6.11 (d, $J = 3.6$ Hz, 0.5H), 5.99 (d, $J = 3.6$ Hz, 0.5H), 6.05 (m, 0.5H), 5.85 (m, 0.5H), 2.25 (m, 1H), 1.85 (dd, $J = 1.6, 6.4$ Hz, 1.3H), 1.63 (dd, $J = 1.6, 5.8$ Hz, 1.6H). **¹³C NMR** ($CDCl_3$, 100 MHz, ppm): δ 143.2, 141.6, 140.0, 136.6, 135.2, 129.8, 128.8, 128.4, 128.4, 127.2, 127.2, 127.1, 126.9, 126.8, 126.8, 126.6, 126.4, 73.3, 72.9, 18.8, 14.3. **LRMS** (EI): 223 [M-1], 208, 196, 182, 167, 147, 131, 105, 97, 89, 79, 65, 43, 29, 15. **HRMS**(ESI): calcd for $C_{16}H_{15}O^+$

223.1128 [M-H]⁻, found 223.1119.



Compound 9g (Z/E = 5:2). Yield 70 % for two steps. **IR** (neat)

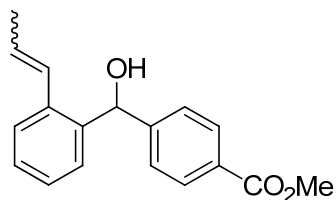
ν_{max} : 3390, 3062, 3028, 2964, 1645, 1453, 1115, 1017, 698 cm^{-1} . **¹H NMR** (400 MHz, CDCl_3 , ppm): δ 7.57 (d, $J = 7.6$ Hz, 1H), 7.44-7.46 (m, 1H), 7.29-7.38 (m, 6H), 7.20 (d, $J = 7.2$ Hz, 1H), 6.69 (d, $J = 14.6$ Hz, 0.3H), 6.47 (d, $J = 11.2$ Hz, 0.7H), 6.15 (s, 0.3H), 6.04 (s, 0.7H), 6.08-6.13 (m, 0.3H), 5.70-5.77 (m, 0.7H), 2.27 (s, 1H), 2.07-2.25 (m, 0.4H), 2.05-2.10 (m, 1.5H), 1.09 (t, $J = 7.6$ Hz, 0.8H), 0.96 (t, $J = 7.6$ Hz, 2.2H). **¹³C NMR** (100 MHz, CDCl_3 , ppm): δ 143.2, 141.5, 135.9, 135.8, 123.0, 128.4, 128.3, 127.4, 127.2, 127.2, 126.9, 126.9, 126.6, 126.3, 73.3, 21.8, 14.1. **LRMS** (EI) : 237 [M-1], 219, 189, 164, 143, 128, 103, 79, 65, 57, 39. **HRMS**(ESI): calcd for $\text{C}_{17}\text{H}_{19}\text{O}^+$ 239.1430 [M+H]⁺, found 239.1370.



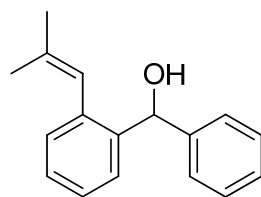
Compound 9h (Z/E = 3:2). Yield 76 % for two steps. **IR** (neat)

ν_{max} : 3565, 3061, 2933, 1667, 1596, 1448, 1267, 1151, 700 cm^{-1} . **¹H NMR** (400 MHz, CDCl_3 , ppm): δ 7.56-7.58 (m, 1H), 7.28-7.41 (m, 10H), 7.15-7.17 (m, 3H), 7.03-7.05 (m, 1H), 6.68 (d, $J = 6.4$ Hz, 1H), 6.24 (d, $J = 3.6$ Hz, 0.4H), 6.10 (d, $J = 3.6$ Hz, 0.6H), 2.25 (d, $J = 4.0$ Hz, 0.4H), 2.11 (d, $J = 3.6$ Hz, 0.6H). **¹³C NMR** (100 MHz, CDCl_3 , ppm): δ 143.1, 141.5, 136.5, 136.1, 131.5, 131.3, 129.5, 129.0, 128.7, 128.6, 128.4, 128.2, 127.8, 127.7, 127.6, 127.4, 127.3, 126.8, 126.8, 126.6, 73.3. **LRMS** (EI):

286 [M], 252, 235, 207, 196, 164, 131, 125, 79, 63, 51. **HRMS**(ESI): calcd for $C_{21}H_{17}O^-$ 285.1285 [M-H], found 285.1261.

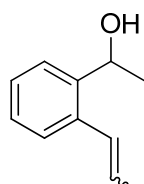


Compound 9i (*Z/E* = 2:1). Yield 74 % for two steps. **IR** (neat) ν_{max} : 3445, 3063, 3023, 2952, 1714, 1610, 1435, 1282, 1113, 762 cm^{-1} . **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.98 (t, *J* = 8.0 Hz, 2H), 7.38-7.42 (m, 3H), 7.17-7.27 (m, 3H), 6.69 (dd, *J* = 1.6, 15.6 Hz, 0.4H), 6.50 (dd, *J* = 1.6, 11.2 Hz, 0.7 H), 6.14 (d, *J* = 4.0 Hz, 0.4H), 6.03 (d, *J* = 3.6 Hz, 0.7H), 6.04-6.08 (m, 0.3H), 5.81-5.87 (m, 0.7H), 3.89 (s, 1H), 3.88 (s, 2H), 2.64 (br, 1H), 1.85 (dd, *J* = 1.6, 6.8 Hz, 1H), 1.62 (dd, *J* = 1.6, 6.8 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 171.4, 167.1, 148.5, 141.1, 135.64, 131.8, 123.0, 129.7, 129.6, 128.1, 127.5, 127.4, 126.7, 126.7, 115.2, 72.8, 72.6, 60.5, 52.1, 21.1, 18.8, 14.3, 14.2. **LRMS** (EI): 281 [M-1], 248, 225, 206, 189, 164, 147, 117, 91, 76, 65, 59, 51, 43, 15. **HRMS**(ESI): calcd for $C_{18}H_{19}O_3^+$ 283.1329 [M+H]⁺, found 283.1322.



Compound 9j. Yield 44 % for two step. **IR** (neat) ν_{max} : 3434, 3063, 2929, 1644, 1448, 1184, 748 cm^{-1} . **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.52-7.54 (m, 1H), 7.27-7.34 (m, 7H), 7.14 (dd, *J* = 2.0, 6.8 Hz, 1H), 6.25 (s, 1H), 6.01 (s, 1H), 2.25 (s, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.56 (d, *J* = 1.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 141.8, 137.0, 136.8, 130.2, 128.3, 127.3, 127.2, 126.9, 126.9, 126.8, 126.1, 123.3, 100.0, 73.4, 25.8, 19.1. **LRMS** (EI): 238 [M], 220,

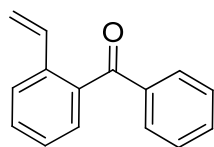
204, 190, 176, 161, 150, 142, 128, 119, 105, 90, 77, 51, 43, 31, 14. **HRMS**(ESI):
calcd for $C_{17}H_{19}O^+$ 239.1430 $[M+H]^+$, found 239.1446.



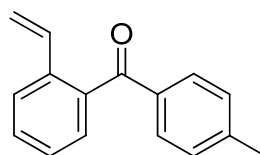
Compound 9k (*Z/E* = 1:1). Yield 82 % for two steps. **IR** (neat) ν_{max} :
3368, 3059, 3025, 2972, 2928, 2627, 1950, 1705, 1631, 1599, 1446, 1367, 1073, 761
 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.24-7.58 (m, 12H), 7.13-7.14 (m, 5H),
7.05-7.07 (m, 2H), 6.97 (d, *J* = 16 Hz, 1H), 6.73 (d, *J* = 12.4 Hz, 1H), 6.63 (d, *J* =
12.4 Hz, 1H), 5.28 (t, *J* = 12.4 Hz, 1H), 5.11 (dd, *J* = 12.8/12.4, 6.4/6.0 Hz, 1H), 1.50
(d, *J* = 6.4 Hz, 3H), 1.40 (d, *J* = 6.4 Hz, 3H), 1.37 (d, *J* = 5.2 Hz, 1H), 1.18 (d, *J* = 6.4
Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 143.6, 143.1, 137.5, 136.6, 135.2,
135.0, 131.3, 131.2, 129.3, 129.1, 128.8, 128.5, 128.2, 128.0, 127.9, 127.8, 127.6,
127.4, 127.3, 126.7, 126.2, 125.7, 125.1, 67.3, 67.1, 24.5, 24.2. **LRMS** (EI): 224 [M],
209, 191, 178, 165, 152, 139, 131, 115, 103, 91, 77, 63, 51, 43, 27, 15. **HRMS**(ESI):
calcd for $C_{17}H_{19}O^+$ 225.1274 $[M+H]^+$, found 225.1270.

Synthesis of Compounds 10. ^[3]

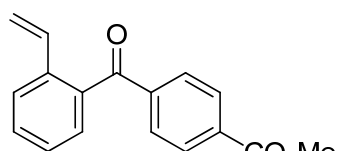
The alcohol **9** prepared above was dissolved in anhydrous CH_2Cl_2 at room temperature, a mixture of PCC (1.5 equiv) and Celite was added. The mixture was allowed to stir at room temperature for four hours and diethyl ether (20 mL) was added. The solution was then filtered through a silica gel column and rinsed with diethyl ether. The solvent was removed *in vacuo* and the residue purified by column chromatography (petrol ether/diethyl ether = 20:1) to yield compound **10** as clear oil.



Compound 10a. Yield 92 %. **IR** (neat) ν_{max} : 3062, 1703, 1667, 1448, 1265, 1152, 774 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.79 (t, $J = 8.4$ Hz, 2H), 7.67 (d, $J = 7.6$ Hz, 1H), 7.57 (d, $J = 7.4$ Hz, 1H), 7.42-7.49 (m, 3H), 7.32-7.35 (m, 2H), 6.77 (dd, $J = 17.4, 10.2/11.2$ Hz, 1H), 5.69 (dd, $J = 17.2, 0.8$ Hz, 1H), 5.21 (dd, $J = 11.2, 0.8$ Hz, 1H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz, ppm): δ 198.2, 138.0, 137.6, 136.7, 134.3, 133.3, 130.4, 130.3, 128.6, 128.5, 127.2, 126.0, 116.2. **LRMS** (EI): 209 [M+1], 206, 191, 180, 165, 152, 139, 130, 115, 102, 89, 77, 51, 27. **HRMS** (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{O}^+$ 209.0961 [M+H] $^+$, found 209.0961.

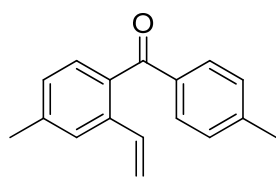


Compound 10b. Yield 91 %. **IR** (neat) ν_{max} : 3060, 2933, 1726, 1651, 1447, 1278, 1074, 702 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.69-7.74 (m, 3H), 7.50 (m, 1H), 7.35 (d, $J = 4.4$ Hz, 2H), 7.26-7.29 (m, 2H), 6.78 (q, $J = 17.6$ Hz, 1H), 5.73 (dd, $J = 17.2, 0.4/0.8$ Hz, 1H), 5.25 (dd, $J = 11.2, 0.4$ Hz, 1H), 2.45 (s, 1H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz, ppm): δ 197.9, 144.3, 138.3, 136.5, 135.1, 134.3, 130.5, 130.1, 129.2, 128.3, 127.1, 125.9, 116.4, 21.7. **LRMS** (EI): 223 [M+1], 208, 193, 165, 151, 134, 119, 105, 91, 77, 51, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{16}\text{H}_{15}\text{O}^+$ 223.1117 [M+H] $^+$, found 223.1112.



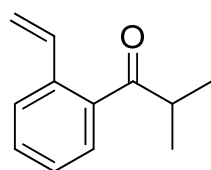
Compound 10c. Yield 95 %. **IR** (neat) ν_{max} : 3064, 2953, 1732, 1652, 1435, 1285, 1108, 770 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 8.09 (t, $J = 8.4$ Hz, 2H), 7.84 (t, $J = 8.4$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.50 (q, $J = 8.4$ Hz,

1H), 7.34 (d, $J = 4.0$ Hz, 2H), 6.77 (q, $J = 8.6$ Hz, 1H), 5.68 (d, $J = 8.8$ Hz, 1H), 5.22 (d, $J = 10.8$ Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 197.4, 166.2, 141.0, 137.2, 137.0, 134.2, 133.9, 130.9, 129.7, 128.8, 127.3, 126.3, 117.1, 52.5. **LRMS** (EI): 266 [M], 251, 235, 207, 178, 163, 131, 103, 77, 51, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{15}\text{O}_3^+$ 267.1016 [M+H] $^+$, found 267.1011.



Compound 10d. Yield 93 %. **IR** (neat) ν_{max} : 2958, 2930, 2857,

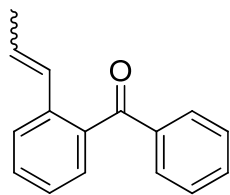
1683, 1607, 1456, 1267, 1180, 1014, 826. ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.70 (d, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.25 (m, 3H), 7.12 (s, 1H), 6.69 (dd, $J = 17.2/17.6$, 10.8/11.2 Hz, 1H), 5.64 (d, $J = 17.2$ Hz, 1H), 5.15 (d, $J = 10.8$ Hz, 1H), 2.41 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 198.2, 144.3, 138.3, 137.2, 135.1, 134.1, 133.6, 131.0, 130.5, 129.2, 128.7, 125.7, 115.5, 21.8, 21.1. **LRMS** (EI): 236 [M], 221, 193, 178, 144, 115, 91, 77, 65, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{17}\text{O}^+$ 237.1274 [M+H] $^+$, found 237.1270.



Compound 10e. Yield 87 %. **IR** (neat) ν_{max} : 3088, 2971, 2328,

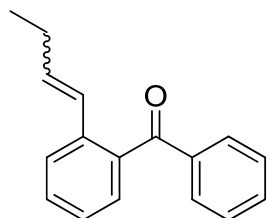
1770, 1693, 1466, 756 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.40-7.46 (m, 2H), 7.31 (t, $J = 7.6$ Hz, 1H), 6.93 (dd, $J = 17.6/17.2$, 11.2/10.8 Hz, 1H), 5.65 (d, $J = 17.2$ Hz, 1H), 5.31 (d, $J = 10.8$ Hz, 1H), 3.31 (m, 1H), 1.16 (d, 6.8 Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 209.7, 138.5, 136.9, 135.2, 130.6, 127.4, 127.2, 126.9, 116.6, 39.4, 18.5. **LRMS** (EI): 174 [M], 131, 103, 77, 63, 51, 43,

28, 14. **HRMS** (ESI): calcd for $C_{12}H_{15}O^+$ 175.1117 $[M+H]^+$, found 175.1112.

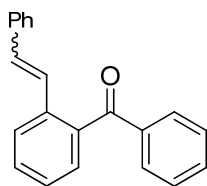


Compound 10f (Z/E = 1:1). Yield 90 %. **IR** (neat) ν_{max} : 3061, 2965, 2874, 1667, 1449, 1286, 1151, 929, 701 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.78-7.84 (m, 2H), 7.57-7.63 (m, 2H), 7.31-7.53 (m, 5H), 6.51 (dd, $J = 1.2, 7.6$ Hz, 0.5H), 6.43 (dd, $J = 1.2, 7.6$ Hz, 0.5H), 6.16-6.25 (m, 0.5H), 5.65-5.74 (m, 0.5H), 1.80 (dd, $J = 1.6, 6.4$ Hz, 1.7H), 1.75 (dd, $J = 1.2, 7.2$ Hz, 1.4H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 198.5, 198.4, 138.8, 137.8, 137.7, 137.3, 137.0, 136.3, 133.2, 133.1, 130.3, 130.1, 129.9, 129.9, 128.9, 128.5, 128.4, 128.3, 128.1, 126.3, 126.1, 126.1, 18.7, 14.5. **LRMS** (EI): 221[M-1], 207, 178, 115, 77, 51, 28, 15.

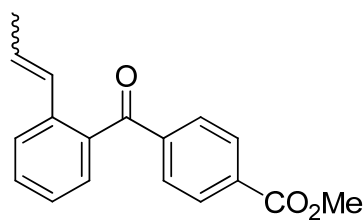
HRMS(ESI) calcd for $C_{16}H_{15}O^+$ 223.1117 $[M+H]^+$, found 223.1112.



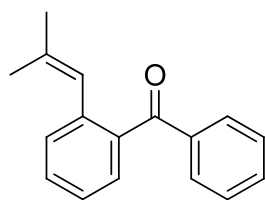
Compound 10g (Z/E = 4:1). Yield 87 %. **IR** (neat) ν_{max} : 2926, 2855, 1769, 1624, 1449, 1293, 1176, 931, 770 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.78-7.81 (m, 2H), 7.56-7.60 (m, 1H), 7.42-7.49 (m, 4H), 7.36-7.38 (m, 2H), 6.47 (d, $J = 15.6$ Hz, 0.2H), 6.38 (d, $J = 11.6$ Hz, 0.8H), 6.17-6.24 (m, 0.2H), 5.53-5.60 (m, 0.8H), 2.15-2.19 (m, 2H), 1.00 (t, $J = 7.2$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 198.4, 190.6, 138.8, 137.7, 136.5, 135.9, 133.1, 130.1, 129.9, 129.8, 128.46, 128.3, 126.4, 126.4, 126.3, 126.2, 126.1, 26.2, 21.9, 14.1. **LRMS** (EI): 236 [M], 220, 193, 164, 151, 139, 115, 91, 77, 63, 51, 39, 27, 18. **HRMS**(ESI): calcd for $C_{17}H_{17}O^+$ 237.1274 $[M+H]^+$, found 237.1254.



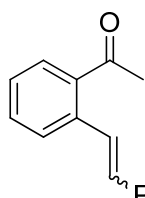
Compound 10h (Z/E = 3:2). Yield 92 %. **IR** (neat) ν_{max} : 3025, 2961, 1964, 1738, 1667, 1447, 1277, 1152, 701 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3 , ppm): δ 7.88 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 7.2$ Hz, 2H), 7.44-7.60 (m, 5H), 7.28-7.36 (m, 2H), 7.14-7.18 (m, 3H), 6.66 (d, $J = 12.4$ Hz, 1H), 6.54 (d, $J = 12.0$ Hz, 1H). **^{13}C NMR** (100 MHz, CDCl_3 , ppm): δ 198.3, 197.8, 138.6, 137.7, 137.0, 136.6, 133.3, 133.0, 132.5, 131.4, 131.3, 130.6, 130.3, 130.3, 130.1, 129.1, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 127.2, 126.9, 126.8, 126.7, 126.0, 125.9. **LRMS** (EI): 284 [M], 265, 252, 239, 225, 206, 194, 178, 165, 151, 142, 126, 115, 105, 91, 77, 63, 28, 14. **HRMS**(ESI): calcd for $\text{C}_{21}\text{H}_{17}\text{O}^+$ 285.1274 [M+H] $^+$, found 285.1277.



Compound 10i (Z/E = 3:1). Yield 87 %. **IR** (neat) ν_{max} : 3062, 2953, 2549, 1943, 1731, 1668, 1435, 1107, 728 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3 , ppm): δ 8.11 (t, $J = 8.4$ Hz, 2H), 7.78-7.85 (m, 2H), 7.35-7.60 (m, 4H), 6.47 (dd, $J = 1.6, 15.6$ Hz, 0.2H), 6.37 (dd, $J = 1.6, 11.6$ Hz, 0.8H), 6.11-6.20 (m, 0.3H), 5.60-5.68 (m, 0.7H), 3.95 (s, 3H), 1.75 (dd, $J = 1.6, 6.4$ Hz, 0.8H), 1.69 (dd, $J = 1.6, 6.8$ Hz, 2.2H). **^{13}C NMR** (100 MHz, CDCl_3 , ppm): δ 197.8, 166.3, 166.3, 141.2, 141.2, 138.1, 137.3, 136.6, 133.8, 130.8, 130.4, 130.1, 130.0, 129.8, 129.6, 129.5, 128.8, 128.7, 128.3, 128.1, 126.6, 126.4, 128.3, 52.5, 18.7, 14.5. **LRMS** (EI): 281 [M+1], 264, 249, 232, 221, 202, 193, 163, 135, 117, 89, 76, 65, 50, 39, 28, 15. **HRMS**(ESI): calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3^+$ 281.1172 [M+H] $^+$, found 281.1169.

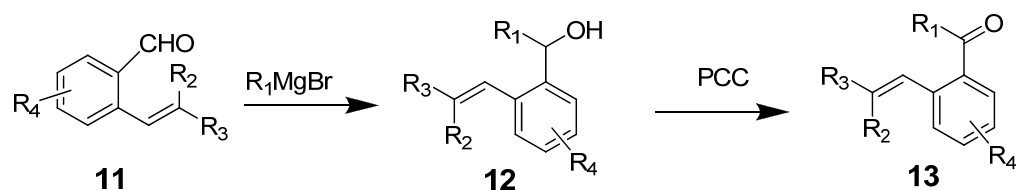


Compound 10j. Yield 74 %. **IR** (neat) ν_{max} : 2967, 1664, 1448, 1263, 929, 702 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3 , ppm): δ 7.77 (d, $J = 7.2$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.42-7.49 (m, 5H), 7.29-7.33 (m, 1H), 6.16 (s, 1H), 1.68 (s, 6H). **^{13}C NMR** (100 MHz, CDCl_3 , ppm): δ 198.77, 132.86, 130.18, 129.92, 129.88, 128.33, 128.22, 125.91, 123.51, 104.24, 25.97, 19.40. **LRMS** (EI): 236 [M], 220, 201, 192, 178, 165, 138, 129, 114, 105, 91, 77, 51, 41, 32, 28, 14. **HRMS**(ESI): calcd for $\text{C}_{17}\text{H}_{17}\text{O}^+$ 237.1274 [M+H] $^+$, found 237.1275.



Compound 10k (Z/E = 1:3). Yield 90 %. **IR** (neat) ν_{max} : 3059, 3023, 2925, 1949, 1682, 1596, 1494, 1355, 1249, 957, 760 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3 , ppm): δ 7.66-7.70 (m, 3H), 7.46-7.54 (m, 3H), 7.24-7.37 (m, 5H), 6.96-7.14 (m, 3H), 6.91 (d, $J = 12.0$ Hz, 0.4 H), 6.64 (d, $J = 12.4$ Hz, 0.38 H), 2.60 (s, 3H), 2.53 (s, 1H). **^{13}C NMR** (100 MHz, CDCl_3 , ppm): δ 202.2, 201.0, 137.8, 137.6, 137.5, 137.4, 137.3, 136.7, 131.7, 131.7, 131.2, 130.5, 130.1, 139.4, 129.3, 129.2, 129.1, 128.7, 128.1, 127.9, 127.6, 127.5, 127.4, 127.3, 127.1, 126.9, 30.0, 29.3. **LRMS** (EI): 222 [M], 207, 189, 178, 165, 152, 145, 131, 115, 103, 88, 76, 63, 51, 43, 28, 15. **HRMS**(ESI): calcd for $\text{C}_{16}\text{H}_{15}\text{O}^+$ 223.1117 [M+H] $^+$, found 223.1120.

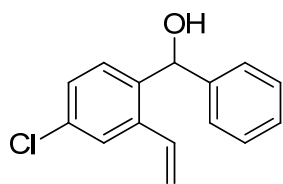
General Procedure for Synthesis of Olefin-Ketone **13**.^[3]



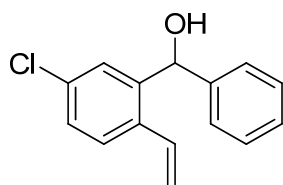
Entry	R ₁ /C ₆ H ₅	R ₂	R ₃	R ₄
a	Ph	H	H	<i>meta</i> -Cl (relative to C=O)
b	Ph	H	H	<i>para</i> -Cl
c	<i>p</i> -CO ₂ Me-Ph	H	H	<i>meta</i> -Cl
d	<i>p</i> -CO ₂ Me-Ph	H	H	<i>para</i> -Cl
e	Ph	Me	H	<i>meta</i> -Cl
f	Ph	Me	H	<i>para</i> -Cl
g	<i>p</i> -CO ₂ Me-Ph	Me	H	<i>para</i> -Cl

Synthesis of Compound **12**.

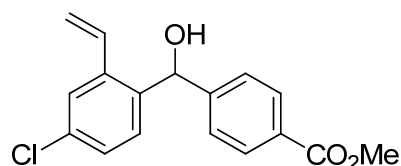
The aldehyde **11** was dissolved in anhydrous THF and cooled to 0 °C, freshly prepared Grignard reagent R₁MgBr (1.5 equiv) was diluted with THF and added dropwise. After addition, the mixture was stirred for another one hour before quenched with 10 mL of saturated NH₄Cl aqueous solution, then extracted with ethyl acetate (3 × 50 mL), washed with brine (50 mL), dried over MgSO₄ and the solvent was diminished under vacuum and the residue was purified by silica gel column chromatography to yield alcohol **12**.



Compound 12a. Yield 91 %. **IR** (neat) ν_{max} : 3350, 2928, 2857, 1754, 1625, 1452, 1192, 1018, 733 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3 , ppm): δ 7.38-7.43 (m, 2H), 7.23-7.35 (m, 6H), 6.88 (dd, $J = 17.2, 10.8$ Hz, 1 H), 6.01 (s, 1H), 5.68 (dd, $J = 17.2, 0.8$ Hz, 1H), 5.29 (dd, $J = 10.8, 0.4/0.8$ Hz, 1H), 2.42 (br, 1H). **^{13}C NMR** (100 MHz, CDCl_3 , ppm): δ 142.6, 138.8, 137.9, 133.7, 133.2, 128.6, 128.4, 127.9, 127.8, 126.9, 126.3, 117.9, 72.6. **LRMS** (EI): 244 [M], 226, 213, 191, 179, 165, 149, 138, 125, 115, 102, 91, 77, 65, 51, 29, 27. **HRMS**(ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{ClO}^+$ 245.0728 [M+H]⁺, found 245.0730.

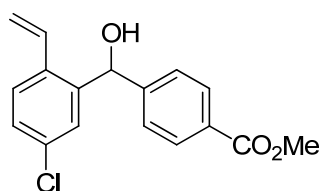


Compound 12b. Yield 90 %. **IR** (neat) ν_{max} : 3030, 2925, 2893, 1762, 1625, 1592, 1452, 1172, 987, 699 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3 , ppm): δ 7.52 (d, $J = 2.4$ Hz, 1H), 7.38 (dd, $J = 8.0$ Hz, 1H), 7.22-7.34 (m, 6 H), 6.83 (dd, $J = 17.2, 10.8$ Hz, 1H), 6.02 (s, 1H), 5.55 (dd, $J = 17.2, 1.2$ Hz, 1H), 5.26 (dd, $J = 11.2/10.8, 1.2/0.8$ Hz, 1H), 2.39 (br, 1H). **^{13}C NMR** (100 MHz, CDCl_3 , ppm): δ 142.3, 142.0, 134.6, 133.9, 133.2, 128.7, 128.5, 127.9, 127.7, 127.0, 126.8, 117.2, 72.7. **LRMS** (EI): 244 [M], 226, 194, 178, 152, 131, 115, 103, 91, 77, 63, 51, 39, 28, 14. **HRMS**(ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{ClO}^+$ 245.0728 [M+H]⁺, found 245.0730.

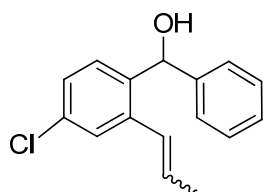


Compound 12c. Yield 86 %. **IR** (neat) ν_{max} : 3441, 2925, 2854, 1935, 1724, 1610, 1437, 1281, 1114, 879 cm^{-1} . **^1H NMR** (400 MHz,

CDCl₃, ppm): δ 7.99 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 2.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.26 (m, 2H), 6.92 (dd, J = 17.2, 10.8 Hz, 1H), 6.11 (s, 1H), 5.62 (d, J = 17.6 Hz, 1H), 5.33 (d, J = 10.8 Hz, 1H), 3.91 (s, 3H), 2.30 (br, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.4, 147.6, 138.1, 134.1, 133.0, 129.9, 129.6, 128.7, 128.1, 126.6, 126.6, 124.5, 118.4, 72.3, 52.2. LRMS (EI): 302 [M], 284, 243, 225, 207, 178, 149, 103, 77, 59, 28, 15. HRMS(ESI): calcd for C₁₅H₁₄ClO⁺ 303.0782 [M+H]⁺, found 303.0730.

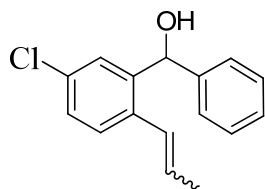


Compound 12d. Yield 86 %. IR (neat) ν_{max} : 3394, 2953, 2854, 2078, 1929, 1720, 1609, 1436, 1283, 1115, 1017, 773 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.00 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.8 Hz, 1H), 7.40-7.44 (m, 4H), 6.89 (dd, J = 17.2/16.8, 11.2/10.8 Hz, 1H), 6.11 (s, 1H), 5.58 (d, J = 17.2 Hz, 1H), 5.30 (d, J = 10.8 Hz, 1H), 3.91 (s, 3H), 2.33 (br, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.8, 146.0, 141.5, 133.0, 131.9, 129.9, 129.6, 128.3, 128.0, 127.1, 126.7, 117.7, 115.2, 72.3, 52.2. LRMS (EI): 303 [M+1], 269, 253, 232, 219, 207, 194, 179, 163, 137, 120, 105, 91, 77, 59, 43, 28, 15. HRMS(ESI): calcd for C₁₅H₁₄ClO⁺ 303.0782 [M+H]⁺, found 303.0730.



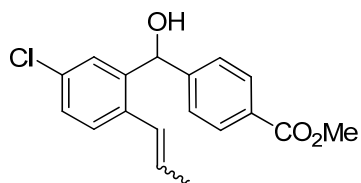
Compound 12e (Z/E = 3:2). Yield 87 %. IR (neat) ν_{max} : 3364, 3063, 2913, 1650, 1592, 1472, 1170, 699 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.50 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.25-7.36 (m, 5H), 7.14-7.25 (m,

1H), 6.59 (dd, $J = 1.6, 15.6$ Hz, 0.4H), 6.38 (d, $J = 11.6$ Hz, 0.6H), 6.05 (s, 0.4H), 5.93 (s, 0.6H), 6.04-6.11 (m, 0.4H), 5.79-5.87 (m, 0.6H), 2.17 (s, 1H), 1.85 (dd, $J = 1.6, 5.6$ Hz, 1H), 1.62 (dd, $J = 1.6, 6.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 148.0, 142.8, 140.1, 137.2, 132.8, 130.1, 129.5, 129.4, 128.5, 128.5, 128.3, 128.2, 127.8, 127.7, 127.7, 127.2, 127.2, 127.1, 127.0, 126.9, 126.8, 126.8, 126.4, 125.8, 72.8, 72.5, 18.7, 14.3. LRMS (EI): 258 [M], 240, 228, 214, 204, 193, 178, 152, 127, 115, 105, 91, 77, 63, 43, 14. HRMS(ESI): calcd for $\text{C}_{16}\text{H}_{16}\text{ClO}^+$ 259.0884 [M+H] $^+$, found 259.0880.



Compound 12f ($Z/E = 4:1$). Yield 87 %. IR (neat) ν_{max} : 3417,

3062, 2964, 1645, 1448, 1024, 699 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.63 (d, $J = 2.4$ Hz, 1H), 7.25-7.44 (m, 6H), 7.13 (d, $J = 8.0$ Hz, 1H), 6.59 (dd, $J = 1.2, 15.6$ Hz, 0.2H), 6.38 (d, $J = 11.6$ Hz, 0.8H), 6.07-6.08 (m, 0.2H), 5.83-5.87 (m, 0.8H), 5.96 (d, $J = 4.0$ Hz, 1H), 2.29 (d, $J = 4.0$ Hz, 1H), 1.87 (dd, $J = 1.6, 6.8$ Hz, 0.5H), 1.63 (dd, $J = 1.6, 7.2$ Hz, 2.6H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 143.4, 142.4, 133.8, 133.1, 129.0, 128.5, 127.8, 127.2, 127.2, 127.0, 126.5, 115.3, 73.0, 14.2. LRMS (EI): 258 [M], 240, 228, 214, 204, 193, 178, 152, 127, 115, 105, 91, 77, 63, 43, 14. HRMS(ESI): calcd for $\text{C}_{16}\text{H}_{16}\text{ClO}^+$ 259.0884 [M+H] $^+$, found 259.0880.



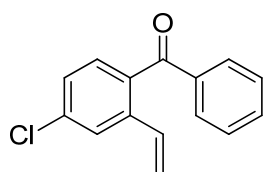
Compound 12g ($Z/E = 2:1$). Yield 89 %. IR (neat) ν_{max} :

3062, 2953, 2850, 1715, 1682, 1435, 1271, 1106, 731 cm^{-1} . ^1H NMR (400 MHz,

CDCl₃, ppm): δ 7.87-7.93 (m, 2H), 7.02-7.43 (m, 5H), 7.04 (d, J = 8.4 Hz, 0.4H), 6.79 (dd, J = 2.0, 6.8 Hz, 0.6H), 6.44-6.50 (m, 0.4H), 5.75-5.80 (m, 0.6H), 6.29-6.32 (m, 0.4H), 5.91-5.99 (m, 0.7H), 3.83 (s, 2H), 3.81 (s, 1H), 2.24 (br, 1H), 1.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 171.3, 167.0, 166.9, 160.3, 147.9, 139.6, 137.3, 131.9, 129.8, 129.7, 129.7, 129.6, 127.4, 126.8, 126.7, 125.2, 72.4, 60.5, 52.1, 21.0, 14.2. LRMS (EI): 315 [M-1], 287, 273, 259, 239, 228, 212, 198, 178, 163, 146, 131, 115, 77, 57, 43, 28, 14. HRMS(ESI): calcd for C₁₈H₁₈ClO₃⁺ 317.0939 [M+H]⁺, found 317.0934.

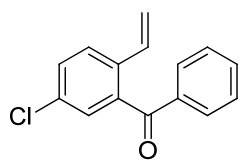
Synthesis of Compounds 13.

The alcohol **12** prepared above was dissolved in anhydrous CH₂Cl₂ at room temperature, a mixture of PCC (1.5 equiv) and Celite was added. The mixture was allowed to stir at room temperature for four hours and diethyl ether (20 mL) was added. The solution was then filtered through a silica gel column and rinsed with diethyl ether. The solvent was removed *in vacuo* and the residue purified by column chromatography (petrol ether/diethyl ether = 20:1) to give the desired products **13**.

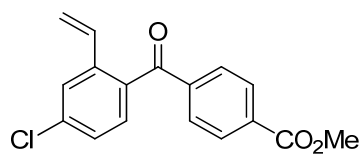


Compound 13a. Yield 85 %. IR (neat) ν_{max} : 2928, 2856, 1774, 1666, 1588, 1448, 1282, 927, 709 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.78 (d, J = 8.0 Hz, 2H), 7.58-7.65 (m, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.31 (m, 1H), 6.73 (dd, J = 17.6/17.2, 11.2/10.8 Hz, 1H), 5.72 (d, J = 17.2 Hz, 1H), 5.28 (d, J = 11.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 197.1, 138.7, 137.3, 136.7, 136.1, 133.6, 133.2, 130.3, 130.1, 128.6, 127.2, 126.1, 118.0. LRMS (EI): 243 [M+1], 221, 207, 193, 178,

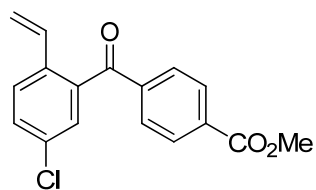
165, 144, 115, 102, 91, 77, 65, 51, 39, 27, 15. **HRMS**(ESI): calcd for $C_{15}H_{12}ClO^+$ 243.0571 $[M+H]^+$, found 243.0565.



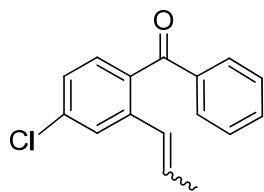
Compound 13b. Yield 85 %. **IR** (neat) ν_{max} : 3086, 2926, 1667, 1449, 1285, 928, 708 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.80 (d, $J = 7.2$ Hz, 2H), 7.58-7.62 (m, 2H), 7.42-7.48 (m, 3H), 7.32 (s, 1H), 6.71 (dd, $J = 11.2/10.8$, 17.6 Hz, 1H), 5.70 (d, $J = 17.6$ Hz, 1H), 5.25 (d, $J = 11.2$ Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 196.6, 139.3, 136.9, 135.0, 133.7, 133.2, 133.1, 130.4, 130.3, 128.7, 128.2, 127.4, 117.2. **LRMS** (EI): 241 $[M-1]$, 224, 208, 189, 175, 136, 126, 103, 89, 76, 63, 51, 39, 27, 14. **HRMS**(ESI): calcd for $C_{15}H_{12}ClO^+$ 243.0571 $[M+H]^+$, found 243.0565.



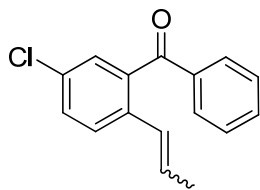
Compound 13c. Yield 85 %. **IR** (neat) ν_{max} : 2952, 2850, 1937, 1726, 1668, 1436, 1279, 1107, 931, 725 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.11 (d, $J = 8.4$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 1.6$ Hz, 1H), 7.25-7.35 (m, 2H), 6.73 (dd, $J = 17.6/17.2$, 11.2/10.8 Hz, 1H), 5.71 (d, $J = 17.2$ Hz, 1H), 5.30 (d, $J = 10.8$ Hz, 1H), 4.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 196.4, 166.1, 140.7, 139.0, 137.2, 135.4, 134.2, 133.2, 130.4, 130.0, 129.8, 127.4, 126.4, 118.4, 52.6. **LRMS** (EI): 300 $[M]$, 285, 269, 243, 212, 178, 165, 135, 120, 102, 88, 76, 50, 28, 15. **HRMS**(ESI): calcd for $C_{17}H_{14}ClO_3^+$ 301.0626 $[M+H]^+$, found 301.0630.



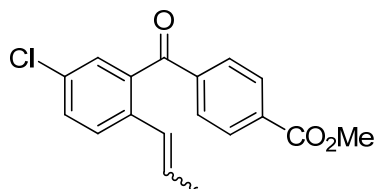
Compound 13d. Yield 87 %. **IR** (neat) ν_{max} : 2952, 2850, 1944, 1727, 1673, 1436, 1280, 1108, 947, 736 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3 , ppm): δ 8.12 (d, $J = 8.4$ Hz, 2H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.47 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.32 (d, $J = 2.0$ Hz, 1H), 6.66 (dd, $J = 17.6/17.2, 11.2/10.8$ Hz, 1H), 5.68 (d, $J = 17.6$ Hz, 1H), 5.30 (d, $J = 10.8$ Hz, 1H), 4.00 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3 , ppm): δ 196.1, 166.1, 140.3, 138.6, 135.3, 134.3, 133.3, 133.0, 130.9, 129.8, 128.4, 127.7, 117.7, 52.6. **LRMS** (EI): 300 [M], 285, 269, 241, 212, 178, 163, 137, 102, 76, 50, 28, 15. **HRMS**(ESI): calcd for $\text{C}_{17}\text{H}_{14}\text{ClO}_3^+$ 301.0626 [M+H] $^+$, found 301.0630.



Compound 13e (Z/E = 3:2). Yield 85 %. **IR** (neat) ν_{max} : 3061, 2937, 1730, 1668, 1449, 1279, 950, 696 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3 , ppm): δ 7.64-7.71 (m, 2H), 7.47-7.49 (m, 2H), 7.34-7.39 (m, 2H), 7.23-7.27 (m, 1H), 7.15-7.17 (m, 1H), 6.36 (dd, $J = 1.6, 15.6$ Hz, 0.4H), 6.26 (dd, $J = 1.6, 11.6$ Hz, 0.6H), 6.08-6.14 (m, 0.4H), 5.57-5.65 (m, 0.6H), 1.68 (dd, $J = 1.6, 6.4$ Hz, 1H), 1.74 (dd, $J = 1.6, 7.2$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3 , ppm): δ 197.2, 138.3, 137.4, 137.1, 135.9, 133.3, 130.2, 130.1, 130.0, 130.0, 129.9, 129.8, 129.5, 128.5, 128.5, 128.4, 128.3, 127.0, 126.5, 18.3, 14.5. **LRMS** (EI): 255 [M-1], 240, 227, 219, 212, 202, 190, 177, 164, 151, 136, 125, 115, 105, 99, 89, 77, 63, 51. **HRMS**(ESI): calcd for $\text{C}_{16}\text{H}_{14}\text{ClO}^+$ 257.0728 [M+H] $^+$, found 257.0712.

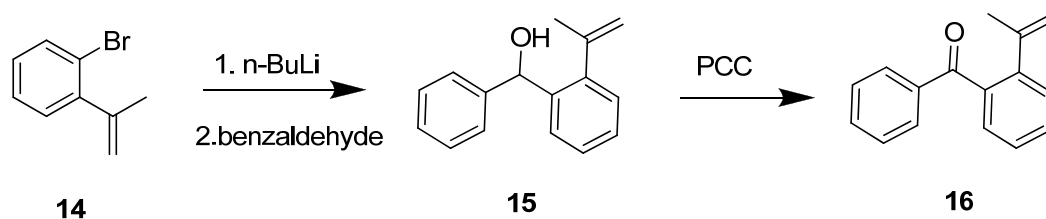


Compound 13f (Z/E = 4:1). Yield 87 %. **IR** (neat) ν_{max} : 3061, 2934, 1775, 1667, 1447, 1280, 925, 707 cm^{-1} . **$^1\text{H NMR}$** (400 MHz, CDCl_3 , ppm): δ 7.77-7.79 (m, 2H), 7.63 (t, $J = 7.6$ Hz, 1H) 7.41-7.49 (m, 4H), 7.29-7.35 (m, 1H), 6.41 (dd, $J = 1.6, 15.6$ Hz, 0.2H), 6.33 (dd, $J = 1.6, 11.6$ Hz, 0.8H), 6.17-6.22 (m, 0.2H), 5.68-5.73 (m, 0.8H), 1.78 (dd, $J = 1.6, 6.4$ Hz, 0.4H), 1.74 (dd, $J = 1.6, 7.2$ Hz, 2.6H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3 , ppm): δ 196.8, 140.3, 137.0, 134.6, 133.5, 132.4, 131.3, 130.0, 129.9, 129.6, 129.2, 128.6, 128.1, 126.9, 18.6, 14.5. **LRMS** (EI): 255 [M-1], 240, 227, 219, 212, 202, 190, 177, 164, 151, 136, 125, 115, 105, 99, 89, 77, 63, 51. **HRMS**(ESI): calcd for $\text{C}_{16}\text{H}_{14}\text{ClO}^+$ 257.0728 [M+H] $^+$, found 257.0712.



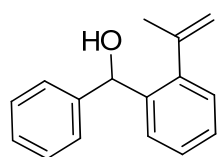
Compound 13g (Z/E = 5:1). Yield 89 %. **IR** (neat) ν_{max} : 3062, 2953, 1943, 1715, 1682, 1435, 1271, 1106, 731 cm^{-1} . **$^1\text{H NMR}$** (400 MHz, CDCl_3 , ppm): δ 8.07-8.13 (m, 2H), 7.76-7.85 (m, 2H), 7.26-7.58 (m, 3H), 6.15-6.43 (m, 1H), 5.62-5.72 (m, 1H), 3.95 (s, 3H), 1.72-1.77 (m, 0.5H), 1.66-1.70 (m, 2.5H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3 , ppm): δ 196.6, 166.2, 140.9, 138.5, 136.6, 136.4, 133.9, 131.4, 130.4, 130.2, 130.0, 129.7, 129.6, 128.7, 128.4, 128.1, 127.0, 126.9, 126.7, 52.5, 18.7, 14.5. **LRMS** (EI): 313 [M-1], 294, 278, 264, 249, 233, 219, 202, 177, 164, 151, 145, 135, 117, 91, 76, 59, 39, 28, 15. **HRMS**(ESI): calcd for $\text{C}_{18}\text{H}_{16}\text{ClO}_3^+$ 315.0782 [M+H] $^+$, found 315.0772.

Synthesis of compounds 16.



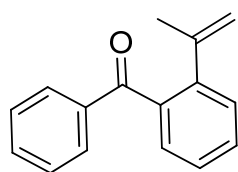
A flame-dried, round-bottomed flask was charged with compound **14**^[4] (1.0 g, 5.07 mmol) and 30 mL of anhydrous THF, the mixture was cooled to -78 °C, n-BuLi (2.1 mL, 2.4 M in hexane, 5.07 mmol) was added dropwise within 10 minutes. After addition, the solution was stirred for 2 hours at the same temperature. Commercial available benzaldehyde (0.56 g, 5.3 mmol) was diluted with 5 mL of anhydrous THF and added into the solution. The reaction was quenched with 20 mL of water before no starting material remaining by TLC analysis. The mixture was extracted with diethyl ether (3 × 50 mL), the combined organic phase was washed with 40 mL of brine, dried over MgSO₄ and chromatographed on a silica gel to give 1.0 g of alcohol **15** as clear oil.

The alcohol **15** (0.9 g, 4.02 mmol) prepared above was oxidized in 25 mL of anhydrous CH₂Cl₂ with a mixture of PCC (1.29 g, 6.03 mmol) and Celite (1.29 g) at room temperature. Upon completion, 5 mL of diethyl ether was added to diluted the mixture before removed the solvent under vacuum. Then, the residue was purified through a silica gel column eluting with petrol ether/ethyl acetate (20:1) to give 0.84 g of products **16** as colorless oil.



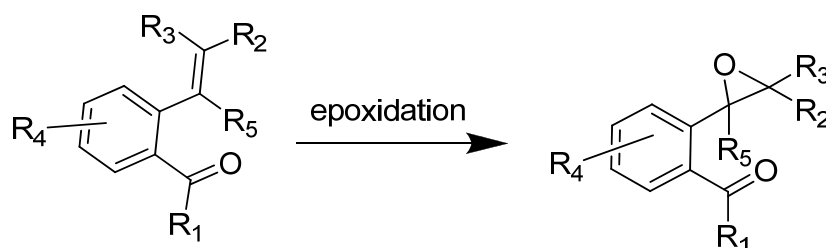
Compound 15. Yield 88 %. IR (neat) ν_{max} : 3401, 3013, 2934, 1699,

1640, 1451, 1182, 1015, 762 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 7.43 (t, $J = 8.0$ Hz, 1H), 7.21-7.34 (m, 7H), 7.12-7.14 (m, 1H), 6.12 (s, 1H), 5.22 (s, 1H), 4.84 (s, 1H), 1.98 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm): δ 144.9, 144.1, 143.1, 140.2, 128.5, 128.3, 128.1, 127.4, 127.4, 127.3, 127.2, 126.8, 125.9, 115.9, 72.5, 25.6. **LRMS** (EI): 223 [M-1], 205, 198, 178, 165, 152, 133, 115, 105, 91, 77, 63, 51, 39, 27. **HRMS**(ESI): calcd for $\text{C}_{16}\text{H}_{17}\text{O}^+$ 223.1128 [M+H] $^+$, found 223.1119.



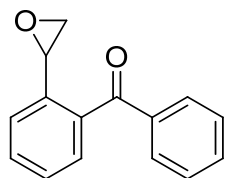
Compound 16. Yield 94 %. **IR** (neat) ν_{max} : 3062, 2965, 1796, 1661, 1597, 1449, 1284, 1152, 710 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 7.72-7.74 (m, 2H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.32-7.48 (m, 6H), 4.95 (s, 1H), 4.85 (s, 1H), 1.94 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm): δ 198.8, 143.9, 142.9, 138.3, 137.9, 132.9, 130.0, 129.9, 128.4, 128.3, 127.9, 126.8, 117.4, 23.7. **LRMS** (EI): 220 [M-2], 203, 173, 145, 115, 91, 77, 51, 43, 27. **HRMS**(ESI): calcd for $\text{C}_{16}\text{H}_{15}\text{O}^+$ 223.1117 [M+H] $^+$, found 223.1125.

General Procedure of Synthesis of Epoxy Ketones. ^[5]

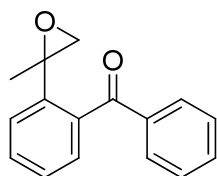


To round-bottomed flask was added olefin prepared above, acetone (20.0 equiv), acetonitrile (1.0 mL/20 mg of substrate), water (1.0 mL/20 mg of substrate), NaHCO_3 (20.0 equiv), 18-crown-6 (0.01 equiv), the mixture was cooled to 0°C , Oxone (4.0

equiv) was dissolved in water and added slowly. After addition, the reaction was stirred at the same temperature until no starting material could be detected by TLC. 30 mL of methylene chloride was added to dilute the mixture, separated the organic layer, the water layer was extracted with methylene chloride (2×40 mL), combined the organic phase and washed with saturated NaHCO_3 aqueous solution (2×40 mL), brine (2×40 mL), dried over Na_2SO_4 . Removed the solvent *in vacuo* and the residue was purified through a flash column chromatography using petral/ethyl acetate (10:1) to give colorless oil.

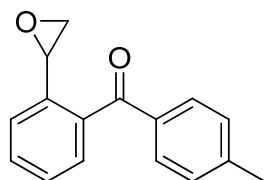


Compound 1a. Yield 64 %. **IR** (neat) ν_{max} : 2927, 1634, 1365, 1231, 1112, 701 cm^{-1} . **^1H NMR** (CDCl_3 , 400 MHz, ppm): δ 7.84 (d, $J = 7.6$ Hz, 2H), 7.36-7.65 (m, 6H), 7.17-7.24 (m, 1H), 4.10 (dd, $J = 3.6, 2.8$ Hz, 1H), 3.12 (t, $J = 4.8$ Hz, 1H), 2.72 (dd, $J = 5.6, 2.4$ Hz, 1H). **^{13}C NMR** (CDCl_3 , 100 MHz, ppm): δ 197.3, 138.2, 137.7, 137.6, 133.3, 131.3, 130.3, 129.4, 128.8, 128.5, 128.2, 127.0, 124.9, 51.6, 50.8. **LRMS** (EI): 203 [M-1], 209, 193, 181, 165, 152, 105, 77, 53, 28. **HRMS** (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2^+$ 225.0910 [M+H] $^+$, found 225.0912.

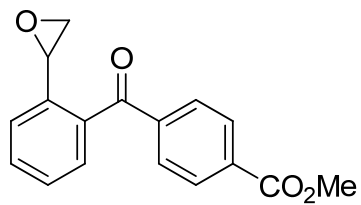


Compound 1b. Yield 70 %. **IR** (neat) ν_{max} : 3060, 2965, 2928, 1667, 1597, 1448, 1267, 929, 705 cm^{-1} . **^1H NMR** (CDCl_3 , 400 MHz, ppm): δ 7.78 (d, $J = 8.4$ Hz, 2H), 7.64-7.68 (m, 2H), 7.52-7.59 (m, 3H), 7.40-7.44 (m, 1H), 7.33 (d, $J = 7.8$ Hz, 1H), 2.77 (d, $J = 5.2$ Hz, 1H), 2.61 (d, $J = 5.2$ Hz, 1H), 1.60 (s, 3H). **^{13}C NMR**

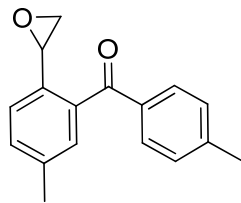
(CDCl₃, 100 MHz, ppm): δ 196.9, 141.3, 137.9, 137.4, 133.1, 130.2, 129.8, 128.5, 128.1, 127.9, 126.9, 57.5, 54.9, 23.8. **LRMS** (EI): 238 [M], 208, 178, 165, 151, 131, 105, 77, 43, 27. **HRMS** (ESI): calcd for C₁₆H₁₅O₂⁺ 239.1067 [M+H]⁺, found 239.1070.



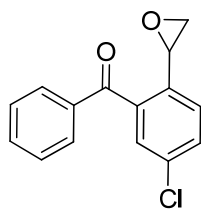
Compound 1c. Yield 61 %. **IR** (neat) ν_{max} : 2850, 1644, 1455, 1260, 1055, 760 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 7.55 (d, J = 8.4 Hz, 2H), 7.41-7.45 (m, 1H), 7.21-7.32 (m, 5H), 3.80 (dd, J = 4.0, 2.8 Hz, 1H), 2.86 (dd, J = 5.6, 4.0 Hz, 1H), 2.53 (dd, J = 5.6, 2.4 Hz, 1H), 2.29 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz, ppm): δ 197.0, 145.1, 139.4, 138.6, 136.2, 131.7, 131.0, 130.1, 129.5, 128.0, 125.6, 51.5, 50.9, 21.6. **LRMS** (EI): 238 [M], 222, 194, 165, 147, 119, 91, 76, 65, 43, 28, 15. **HRMS** (ESI): calcd for C₁₆H₁₅O₂⁺ 239.1067 [M+H]⁺, found 239.1070.



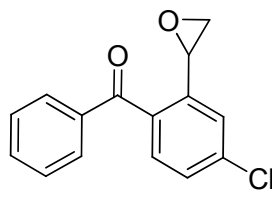
Compound 1d. Yield 60 %. **IR** (neat) ν_{max} : 2953, 1723, 1436, 1281, 1113, 764 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 8.01 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.32 (m, 3H), 3.80 (s, 3H), 2.88 (dd, J = 5.6/5.2, 4.4/4.0 Hz, 1H), 2.53 (dd, J = 5.6/6.0, 2.4/2.8 Hz, 1H), 1.91 (m, 1H). **¹³C NMR** (CDCl₃, 100 MHz, ppm): δ 196.9, 166.6, 142.3, 139.3, 138.2, 134.8, 132.3, 130.8, 130.4, 130.2, 128.2, 126.0, 52.8, 51.6, 51.1. **LRMS** (EI): 283 [M+1], 257, 239, 222, 207, 193, 165, 151, 112, 90, 74, 45, 28, 14. **HRMS** (ESI): calcd for C₁₇H₁₅O₄⁺ 283.0965 [M+H]⁺, found 283.0972.



Compound 1e. Yield 62 %. **IR** (neat) ν_{max} : 3030, 2955, 2930, 1720, 1607, 1556, 1267, 1179, 1010, 839 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.37-7.40 (m, 3H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.23 (s, 1H), 3.90 (dd, $J = 3.6/4.0, 2.4/2.8$ Hz, 1H), 2.98 (dd, $J = 5.6, 4.4$ Hz, 1H), 2.66 (dd, $J = 6.0/5.6, 2.8/2.4$ Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz, ppm): δ 196.3, 144.1, 138.6, 137.0, 135.3, 134.7, 131.3, 130.1, 129.2, 129.0, 124.7, 50.5, 49.9, 20.7, 20.1. **LRMS** (EI): 252, 234, 209, 191, 165, 147, 119, 91, 77, 65, 43, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2^+$ 253.1223 $[\text{M}+\text{H}]^+$, found 253.1220.

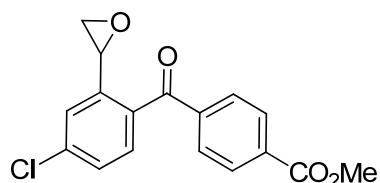


Compound 1f. Yield 63 %. **IR** (neat) ν_{max} : 2961, 2849, 1712, 1663, 1448, 1261, 1021, 840 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.82-7.85 (m, 2H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.58-7.64 (m, 3H), 7.44-7.47 (m, 2H), 3.94 (dd, $J = 2.4, 4.0$ Hz, 1H), 3.02 (dd, $J = 4.4, 5.6$ Hz, 1H), 2.71 (dd, $J = 2.4, 5.6$ Hz, 1H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz, ppm): δ 196.0, 137.5, 134.5, 131.7, 130.8, 129.7, 129.1, 127.8, 51.5, 50.6. **LRMS** (EI): 257 $[\text{M}-1]$, 241, 221, 197, 181, 165, 135, 119, 91, 73, 57, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{ClO}_2^+$ 259.0520 $[\text{M}+\text{H}]^+$, found 259.0527.

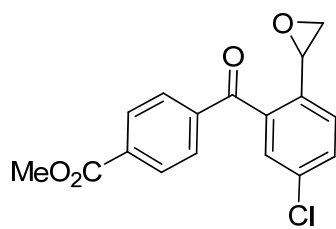


Compound 1g. Yield 66 %. **IR** (neat) ν_{max} : 3050, 2900, 1720, 1662, 1440, 1247, 980, 717 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.82-7.85 (m,

2H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.58-7.64 (m, 3H), 7.44-7.47 (m, 2H), 3.94 (dd, $J = 2.4$, 4.0 Hz, 1H), 3.02 (dd, $J = 4.4$, 5.6 Hz, 1H), 2.71 (dd, $J = 2.4$, 5.6 Hz, 1H). ^{13}C NMR (CDCl₃, 100 MHz, ppm): δ 196.01, 137.51, 134.55, 131.68, 130.81, 129.66, 129.14, 127.81, 51.54, 50.59. **LRMS** (EI): 258 [M], 243, 202, 181, 165, 152, 105, 91, 77, 53, 43, 28, 14. **HRMS** (ESI): calcd for C₁₅H₁₂ClO₂⁺ 259.0520 [M+H]⁺, found 259.0527.

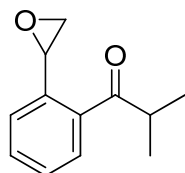


Compound 1h. Yield 59 %. **IR** (neat) ν_{max} : 2953, 2846, 1942, 1726, 1666, 1405, 1281, 1107, 931, 715 cm⁻¹. ^1H NMR (CDCl₃, 400 MHz, ppm): δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.36-7.40 (m, 2H), 7.31 (d, $J = 2.0$ Hz, 1H), 3.92 (dd, $J = 4.4/4.0$, 2.8/2.4 Hz, 1H), 3.81 (s, 3H), 2.92 (dd, $J = 5.6$, 4.4 Hz, 1H), 2.59 (dd, $J = 5.6$, 2.4 Hz, 1H). ^{13}C NMR (CDCl₃, 100 MHz, ppm): δ 196.0, 166.5, 142.1, 142.0, 138.2, 136.7, 134.9, 132.2, 130.8, 130.4, 128.3, 126.0, 52.8, 51.7, 50.8. **LRMS** (EI): 317 [M+1], 301, 285, 257, 214, 181, 163, 135, 103, 76, 59, 43, 28, 15. **HRMS** (ESI): calcd for C₁₇H₁₄ClO₄⁺ 317.0575 [M+H]⁺, found 317.0570.



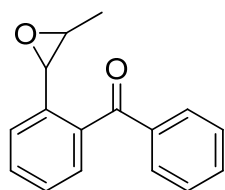
Compound 1i. Yield 62 %. **IR** (neat) ν_{max} : 2923, 2857, 1720, 1650, 1449, 1210, 1110, 911, 723 cm⁻¹. ^1H NMR (CDCl₃, 400 MHz, ppm): δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.50 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.34 (m, 2H), 3.83 (dd, $J = 4.0$, 2.4 Hz, 1H), 3.81 (s, 3H), 2.88 (dd, $J = 10.0/9.2$, 5.6/4.8 Hz, 1H), 2.54 (dd, $J = 5.6/5.2$, 2.8/2.4 Hz, 1H). ^{13}C NMR (CDCl₃, 100 MHz, ppm): δ

195.6, 166.5, 141.6, 140.1, 137.9, 135.2, 132.1, 130.8, 130.5, 129.5, 128.1, 126.0, 52.8, 51.6, 50.7. **LRMS** (EI): 316 [M], 286, 255, 227, 199, 163, 135, 113, 89, 72, 59, 43, 28, 14. **HRMS** (ESI): calcd for $C_{17}H_{14}ClO_4^+$ 317.0575 [M+H]⁺, found 317.0570.



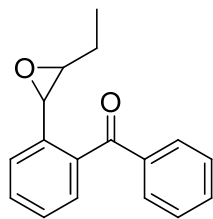
Compound 1. Yield 45 %. **IR** (neat) ν_{max} : 2916, 1790, 1694, 1610,

1461, 1276, 1066, 768 cm^{-1} . **¹H NMR** ($CDCl_3$, 400 MHz, ppm): δ 7.88 (t, $J = 7.4$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 7.2$, 1H), 7.37 (t, $J = 7.4$ Hz, 1H), 4.10 (dd, 3.6, 2.8 Hz, 1H), 3.21 (q, $J = 5.6, 4.8$ Hz, 1H), 3.12 (t, $J = 4.8$ Hz, 1H), 2.72 (dd, $J = 4.6, 2.4$ Hz, 1H), 1.27 (d, $J = 8.0$ Hz, 6H). **¹³C NMR** ($CDCl_3$, 100 MHz, ppm): δ 197.3, 138.2, 133.3, 131.3, 129.4, 127.0, 124.9, 51.6, 50.8, 33.1, 18.1. **LRMS** (EI): 190 [M], 172, 147, 128, 107, 91, 77, 65, 43, 28, 14. **HRMS** (ESI): calcd for $C_{12}H_{15}O_2^+$ [M+H]⁺ 191.1067, found 191.1064.

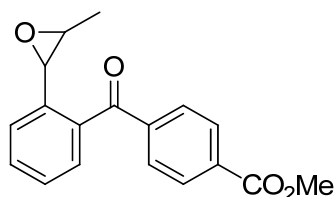


Compound 3a. Yield 67 %. **IR** (neat) ν_{max} : 2927, 2052, 1651,

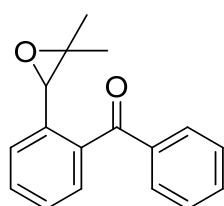
1448, 1269, 928, 700 cm^{-1} . **¹H NMR** ($CDCl_3$, 400 MHz, ppm): δ 7.82 (d, $J = 7.2$ Hz, 2H), 7.61-7.64 (m, 1H), 7.45-7.56 (m, 4H), 7.34-7.38 (m, 2H), 3.75 (d, $J = 2.0$ Hz, 1H), 2.91-2.96 (m, 1H), 1.36 (d, $J = 4.8$ Hz, 3H). **¹³C NMR** ($CDCl_3$, 100 MHz, ppm): δ 197.5, 138.3, 137.9, 137.3, 133.2, 131.4, 129.4, 128.6, 128.5, 128.0, 125.8, 125.0, 59.5, 58.0, 17.7. **LRMS** (EI): 239 [M+1], 226, 209, 194, 164, 150, 126, 97, 77, 63, 43, 32, 28, 14. **HRMS** (ESI): calcd for $C_{16}H_{15}O_2^+$ 239.1067 [M+H]⁺, found 239.1070.



Compound 3b. Yield 67 %. IR (neat) ν_{max} : 2970, 1878, 1658, 1442, 1112, 930, 700 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz, ppm): δ 7.82 (d, $J = 7.2$ Hz, 2H), 7.70 (t, $J = 7.2$ Hz, 1H), 7.56-7.60 (m, 3H), 7.43-7.46 (m, 3H), 3.74 (d, $J = 2.0$ Hz, 1H), 2.82 (m, 1H), 1.52-1.59 (m, 2H), 0.93 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, ppm): δ 184.8, 139.1, 138.8, 134.1, 133.3, 131.9, 130.7, 129.7, 129.5, 127.8, 126.5, 125.7, 100.9, 56.9, 25.8, 9.6. LRMS (EI): 251 [M-1], 222, 209, 192, 164, 152, 115, 95, 77, 63, 39, 28, 14. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2^+$ 253.1223 [M+H] $^+$, found 253.1220.

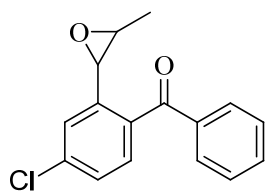


Compound 3c. Yield 67 %. IR (neat) ν_{max} : 3020, 2960, 1715, 1660, 1278, 1105, 700 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz, ppm): δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.45-7.49 (m, 1H), 7.29-7.35 (m, 3H), 3.80 (s, 3H), 3.54 (d, $J = 2.0$ Hz, 2H), 1.90-1.93 (m, 1H), 1.09 (d, $J = 5.2$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, ppm): δ 197.0, 166.6, 142.4, 139.3, 137.9, 134.7, 132.4, 130.7, 130.4, 130.1, 128.0, 125.9, 59.6, 58.3, 52.8, 17.8. LRMS (EI): 297 [M+1], 280, 251, 236, 209, 181, 165, 138, 123, 105, 77, 50, 28, 14. HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{17}\text{O}_4^+$ 297.1121 [M+H] $^+$, found 297.1092.

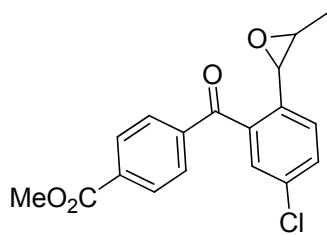


Compound 3d. Yield 57 %. IR (neat) ν_{max} : 3060, 2968, 2860,

1660, 1447, 1067, 928, 702 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz, ppm): δ 7.78-7.81 (m, 2H), 7.64-7.72 (m, 1H), 7.56-7.62 (m, 3H), 7.47-7.51 (m, 3H), 3.86 (s, 1H), 1.24 (s, 3H), 0.99 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, ppm): δ 197.7, 139.0, 138.3, 138.0, 133.9, 133.6, 130.9, 130.1, 129.6, 129.5, 129.5, 129.1, 128.2, 127.9, 127.7, 64.2, 61.8, 24.4, 18.5. **LRMS** (EI): 252 [M], 237, 208, 180, 164, 152, 128, 105, 91, 78, 65, 43, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2^+$ 253.1223 [M+H] $^+$, found 253.1224.

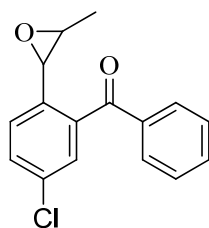


Compound 3e. Yield 57 %. **IR** (neat) ν_{max} : 2950, 2890, 1651, 1448, 1281, 927, 702 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz, ppm): δ 7.79-7.81 (m, 2H), 7.70-7.72 (m, 1H), 7.63-7.66 (m, 1H), 7.57-7.61 (m, 3H), 7.48-7.50 (m, 1H), 4.04 (d, $J = 4.0$ Hz, 1H), 3.21 (m, 1H), 0.98 (d, $J = 6.4$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, ppm): δ 196.2, 140.5, 138.1, 135.4, 134.5, 133.3, 131.2, 130.7, 130.3, 129.7, 129.7, 129.4, 56.7, 55.8, 13.2. **LRMS** (EI): 272 [M], 256, 211, 189, 164, 113, 77, 60, 39, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{16}\text{H}_{14}\text{ClO}_2^+$ 273.0677 [M+H] $^+$, found 273.0673.

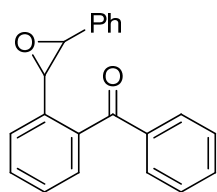


Compound 3f. Yield 59 %. **IR** (neat) ν_{max} : 2994, 2954, 1726, 1664, 1436, 1279, 1107, 729 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz, ppm): δ 8.00-8.03 (m, 2H), 7.73-7.77 (m, 2H), 7.36-7.40 (m, 3H), 4.02 (d, $J = 4.8$ Hz, 1H), 3.80 (s, 3H), 3.16 (m, 1H), 0.74 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, ppm): δ 195.9, 166.5, 142.1, 140.0, 134.9, 133.5, 132.5, 131.6, 130.8, 130.7, 130.5, 130.4, 130.3, 128.6, 127.9, 69.5, 56.9, 52.8, 19.4. **LRMS** (EI): 329 [M-1], 312, 285,

253, 217, 188, 175, 163, 109, 94, 76, 59, 44, 28, 14. **HRMS** (ESI): calcd for $C_{18}H_{16}ClO_4^+$ 331.0732 $[M+H]^+$, found 331.0744.

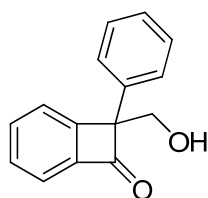
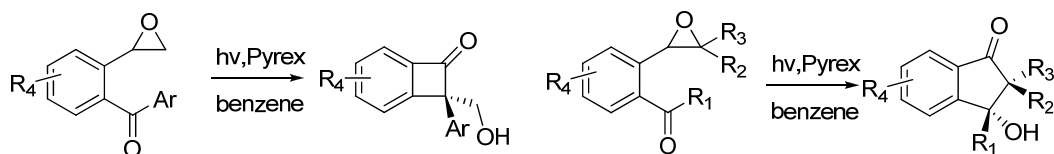


Compound 3g. Yield 56 %. **IR** (neat) ν_{max} : 2960, 2900, 1634, 1259, 1100, 790 cm^{-1} . **1H NMR** ($CDCl_3$, 400 MHz, ppm): δ 7.80-7.83 (m, 2H), 7.67-7.74 (m, 1H), 7.58-7.61 (m, 3H), 7.49 (s, 2H), 3.67 (d, $J = 1.6$ Hz, 1H), 2.95 (m, 1H), 1.24 (d, $J = 4.8$ Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, ppm): δ 196.5, 141.6, 138.6, 137.7, 137.2, 134.2, 133.3, 131.8, 130.7, 130.6, 129.6, 129.3, 128.0, 125.7, 59.9, 57.8, 17.7. **LRMS** (EI): 272 [M], 256, 211, 189, 164, 113, 77, 60, 39, 28, 14. **HRMS** (ESI): calcd for $C_{16}H_{14}ClO_2^+$ 273.0677 $[M+H]^+$, found 273.0663.

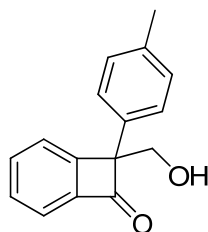


Compound II'. Yield 67 %. **IR** (neat) ν_{max} : 2926, 1726, 1449, 1280, 1019, 699 cm^{-1} . **1H NMR** ($CDCl_3$, 400 MHz, ppm): δ 7.79 (d, $J = 7.2$ Hz, 2H), 7.61-7.62 (m, 4H), 7.32-7.59 (m, 8H), 4.10 (d, $J = 1.6$ Hz, 1H), 3.82 (d, $J = 2.0$ Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz, ppm): δ 197.2, 137.7, 137.6, 137.5, 136.6, 133.1, 131.1, 130.1, 129.4, 128.5, 128.4, 128.3, 127.2, 125.8, 125.1, 63.1, 60.6. **LRMS** (EI): 301 [M+1], 283, 269, 255, 233, 213, 178, 150, 128, 105, 91, 77, 51, 39, 28, 14. **HRMS** (ESI): calcd for $C_{21}H_{17}O_2^+$ 301.1223 $[M+H]^+$, found 301.1233.

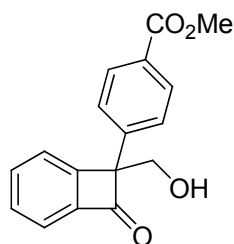
Irradiation of epoxy ketone in benzene.^[6]



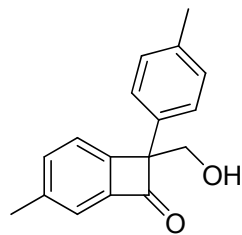
Compound 2a. Yield 73 %. **IR** (neat) ν_{max} : 3417, 2065, 1633, 1364, 1233, 1046, 750 cm^{-1} . **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 7.67 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.32 (d, $J = 7.8$ Hz, 1H), 7.17-7.25 (m, 5H), 5.21 (br, 1H), 3.05 (s, 2H). **¹³C NMR** (CDCl_3 , 100 MHz, ppm): δ 203.7, 145.3, 138.9, 135.8, 129.5, 128.5, 127.4, 125.3, 125.1, 123.2, 78.4, 56.1. **LRMS** (EI): 224 [M], 207, 195, 178, 165, 152, 133, 118, 105, 91, 77, 65, 51, 39, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{ClO}_2^+ 225.0910$ [M+H]⁺, found 225.0912.



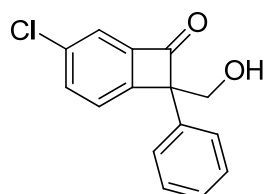
Compound 2c. Yield 72.7 %. **IR** (neat) ν_{max} : 3440, 2926, 1750, 1658, 1262, 1074, 747 cm^{-1} . **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 7.90 (t, $J = 8.8$ Hz, 1H), 7.76 (dd, $J = 8.8, 4.4/5.2$ Hz, 2H), 7.58-7.67 (m, 2H), 7.38 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.09 (t, $J = 8.8$ Hz, 2H), 4.31 (t, $J = 13.6$ Hz, 1H), 4.12 (dd, $J = 14.4, 7.2$ Hz, 1H), 2.54 (s, 3H), 2.04 (br, 1H). **¹³C NMR** (CDCl_3 , 100 MHz, ppm): δ 203.4, 158.3, 142.3, 137.2, 136.0, 135.7, 129.5, 129.2, 128.7, 125.1, 125.0, 123.2, 78.5, 56.2, 21.0. **LRMS** (EI): 238 [M], 222, 209, 181, 165, 147, 119, 104, 91, 76, 65, 43, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{16}\text{H}_{15}\text{ClO}_2^+ 239.1067$ [M+H]⁺, found 239.1070.



Compound 2d. Yield 66 %. **IR** (neat) ν_{max} : 3445, 2925, 1776, 1607, 1436, 1283, 1112, 765 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 8.03 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.70 (q, J = 7.4 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.40-7.47 (m, 3H), 3.94 (s, 3H), 2.70 (br, 1H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz, ppm): δ 202.8, 166.7, 157.7, 150.2, 136.0, 135.9, 129.9, 129.9, 129.3, 25.2, 125.1, 123.4, 78.5, 56.0, 52.2. **LRMS** (EI): 282 [M], 251, 222, 195, 165, 133, 105, 76, 59, 29, 15. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{15}\text{O}_4^+$ 283.0965 [M+H] $^+$, found 283.0969.

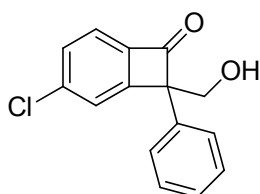


Compound 2e. Yield 67 %. **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.72 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.17-7.26 (m, 5H), 3.18 (s, 3H), 2.46 (br, 1H), 2.44 (s, 3H), 2.37 (s, 3H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz, ppm): δ 206.9, 147.1, 142.5, 138.2, 137.2, 130.8, 129.2, 128.8, 125.2, 125.0, 123.1, 78.4, 56.4, 30.9, 29.7. **LRMS** (EI): 252 [M], 234, 209, 192, 165, 147, 132, 119, 105, 91, 77, 65, 51, 39, 28, 15. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2^+$ 253.1223 [M+H] $^+$, found 253.1220.

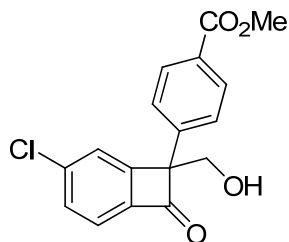


Compound 2f. Yield 62 %. **IR** (neat) ν_{max} : 3386, 2925, 2854, 1713, 1594, 1449, 1232, 1045, 701 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.73 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 1.2, 7.6 Hz, 1H), 7.32-7.42 (m, 6H), 3.19 (s, 2H),

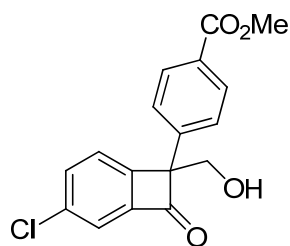
3.04-3.06 (br, 1H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 202.0, 159.7, 144.6, 142.2, 134.2, 130.3, 128.7, 127.7, 125.6, 124.9, 124.5, 78.2, 56.2. LRMS (EI): 259 [M+1], 240, 227, 211, 198, 182, 168, 139, 115, 103, 77, 65, 51, 28, 14. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{ClO}_2^+$ 259.0520 [M+H] $^+$, found 259.0517.



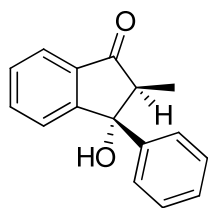
Compound 2g. Yield 63 %. IR (neat) ν_{max} : 2979, 2848, 1634, 1359, 1240, 1052, 740 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.73 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 1.2, 7.6 Hz, 1H), 7.32-7.42 (m, 6H), 3.19 (s, 2H), 3.05 (br, 1H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 202.0, 159.7, 144.6, 142.2, 134.2, 130.3, 128.7, 127.7, 125.6, 124.9, 124.5, 78.2, 56.2. LRMS (EI): 258[M], 240, 229, 212, 194, 178, 167, 152, 138, 105, 91, 77, 63, 51, 39, 28, 14. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{ClO}_2^+$ 259.0520 [M+H] $^+$, found 259.0517.



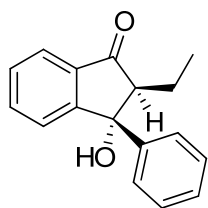
Compound 2h. Yield 46 %. IR (neat) ν_{max} : 3444, 2954, 2855, 1936, 1726, 1610, 1436, 1281, 1108, 777 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.03 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.70 (q, J = 7.4 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.40-7.47 (m, 3H), 3.91 (s, 3H), 3.20 (s, 2H), 2.70 (br, 1H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 202.8, 166.7, 157.7, 150.2, 136.0, 135.9, 129.9, 129.9, 129.3, 25.2, 125.1, 123.4, 78.5, 56.0, 52.2. LRMS (EI): 316 [M], 285, 257, 229, 194, 167, 149, 111, 91, 75, 59, 28, 15. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{14}\text{ClO}_4^+$ 317.0575 [M+H] $^+$, found 317.0570.



Compound 2i. Yield 44 %. **IR** (neat) ν_{max} : 3420, 2920, 2857, 1933, 1720, 1654, 1444, 1280, 1109, 709 cm^{-1} . **^1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.03 (d, $J = 7.8$ Hz, 2H), 7.58 (d, $J = 7.8$ Hz, 2H), 7.44-7.48 (m, 3H), 3.94 (s, 3H), 3.22 (s, 2H), 2.04 (br, 1H). **^{13}C NMR** (CDCl_3 , 100 MHz, ppm): δ 202.7, 166.7, 150.1, 136.0, 130.0, 129.9, 129.1, 128.7, 125.2, 125.2, 123.4, 78.5, 56.0, 52.2. **LRMS** (EI): 316 [M], 279, 242, 227, 199, 169, 123, 95, 76, 58, 43, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{14}\text{ClO}_4^+$ 317.0575 [M+H] $^+$, found 317.0570. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{14}\text{ClO}_4^+$ 317.0575 [M+H] $^+$, found 317.0570.

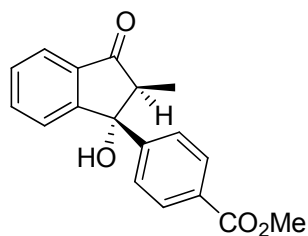


Compound 4a. Yield 62 %. **IR** (neat) ν_{max} : 3444, 3061, 2932, 1714, 1464, 1227, 702 cm^{-1} . **^1H NMR** (CDCl_3 , 400 MHz, ppm): δ 7.83 (d, $J = 7.6$ Hz, 1H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.32-7.45 (m, 6H), 2.94 (q, $J = 7.2$ Hz, 1H), 2.26 (br, 1H), 1.31 (d, $J = 7.2$ Hz, 3H). **^{13}C NMR** (CDCl_3 , 100 MHz, ppm): δ 206.3, 157.3, 144.5, 135.5, 129.7, 128.4, 127.5, 125.5, 125.3, 123.5, 80.0, 57.6, 29.7, 8.4. **LRMS** (EI): 237 [M-1], 208, 189, 181, 160, 143, 105, 91, 76, 51, 43, 27. **HRMS** (ESI): calcd for $\text{C}_{16}\text{H}_{15}\text{O}_2^+$ 239.1067 [M+H] $^+$, found 239.1070.

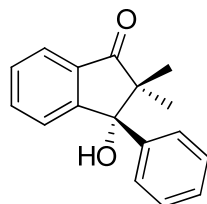


Compound 4b. Yield 61 %. **IR** (neat) ν_{max} : 3444, 2926, 2855, 1715,

1463, 1175, 701 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz, ppm): δ 7.85 (d, $J = 7.6$ Hz, 1H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.29-7.44 (m, 6H), 2.87 (dd, $J = 6.4$, 6.0 Hz, 1H), 2.16 (br, 1H), 1.95-2.03 (m, 1H), 1.83-1.90 (m, 1H), 1.05 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, ppm): δ 205.9, 157.7, 145.4, 135.6, 135.5, 129.7, 128.4, 127.3, 125.4, 125.2, 123.3, 100.0, 80.1, 63.7, 19.2, 12.8. **LRMS** (EI): 252 [M], 237, 223, 209, 195, 181, 152, 128, 105, 91, 77, 51, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2^+$ 253.1223 [M+H] $^+$, found 253.1220.

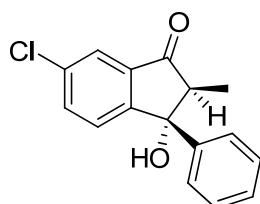


Compound 4c. Yield 84 %. **IR** (neat) ν_{max} : 2979, 2848, 1634, 1359, 1240, 1052, 740 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz, ppm): δ 8.02 (d, $J = 8.8$ Hz, 2H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.62-7.66 (m, 1H), 7.47-7.54 (m, 3H), 7.32 (d, $J = 7.6$ Hz, 1H), 3.91 (s, 3H), 2.90 (q, $J = 7.6$ Hz, 1H), 2.54 (br, 1H), 1.29 (d, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, ppm): δ 205.8, 166.8, 156.8, 149.7, 135.7, 130.0, 129.7, 125.7, 125.3, 123.7, 79.9, 57.6, 52.2, 8.3. **LRMS** (EI): 297 [M+1], 263, 236, 209, 189, 177, 151, 143, 133, 115, 104, 89, 76, 59, 50, 27, 15. **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{17}\text{O}_4^+$ 297.1121 [M+H] $^+$, found 297.1092.



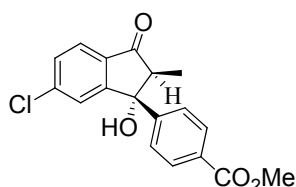
Compound 4d. Yield 80 %. **IR** (neat) ν_{max} : 2979, 2848, 1634, 1359, 1240, 1052, 740 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz, ppm): δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.73 (t, $J = 7.6$ Hz, 1H), 7.54-7.59 (m, 2H), 7.29-7.37 (m, 3H), 7.23-7.25 (m, 2H),

2.52 (br, 1H), 1.33 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 208.9, 155.6, 142.43, 135.4, 134.8, 129.6, 128.0, 127.5, 126.8, 125.4, 123.9, 83.5, 56.1, 23.4, 20.5. **LRMS** (EI): 251 [M-1], 239, 208, 194, 174, 151, 139, 129, 115, 91, 76, 63, 51, 41, 27. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2^+$ 253.1223 [M+H] $^+$, found 253.1220.



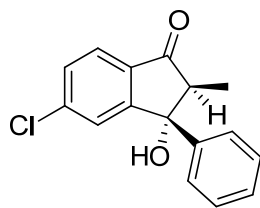
Compound 4e. Yield 62.5 %. **IR** (neat) ν_{max} : 2979, 2848, 1634,

1359, 1240, 1052, 740 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.79 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.37-7.43 (m, 6H), 2.98 (q, $J = 7.2$ Hz, 1H), 2.27 (br, 1H), 1.32 (d, $J = 8.2$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 204.7, 158.7, 143.7, 141.8, 133.8, 130.5, 128.6, 127.7, 125.7, 125.4, 124.8, 79.7, 57.0, 8.4. **LRMS** (EI): 272 [M], 259, 244, 226, 218, 208, 197, 164, 151, 138, 131, 115, 105, 78, 55, 39, 27. **HRMS** (ESI): calcd for $\text{C}_{16}\text{H}_{14}\text{ClO}_2^+$ 273.0677 [M+H] $^+$, found 273.0673.

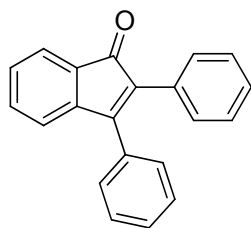


Compound 4f. Yield 66 %. **IR** (neat) ν_{max} : 2979, 2848, 1634,

1359, 1240, 1052, 740 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.03 (dd, $J = 4.4$, 8.4 Hz, 2H), 7.68-7.70 (m, 1H), 7.59 (dd, $J = 2.0$, 6.0 Hz, 1H), 7.46-7.49 (m, 2H), 7.25-7.29 (m, 1H), 3.90 (s, 3H), 2.96 (br, 1H), 2.93 (q, $J = 7.2$ Hz, 1H), 1.28 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 204.6, 166.8, 154.91, 149.0, 142.0, 135.6, 133.8, 130.6, 129.8, 126.8, 125.7, 124.8, 79.5, 58.0, 52.3, 8.2. **LRMS** (EI): 330 [M], 318, 297, 270, 242, 225, 207, 188, 166, 149, 115, 103, 95, 89, 77, 59, 43, 28, 15. **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{16}\text{ClO}_4^+$ 331.0732 [M+H] $^+$, found 331.0744.



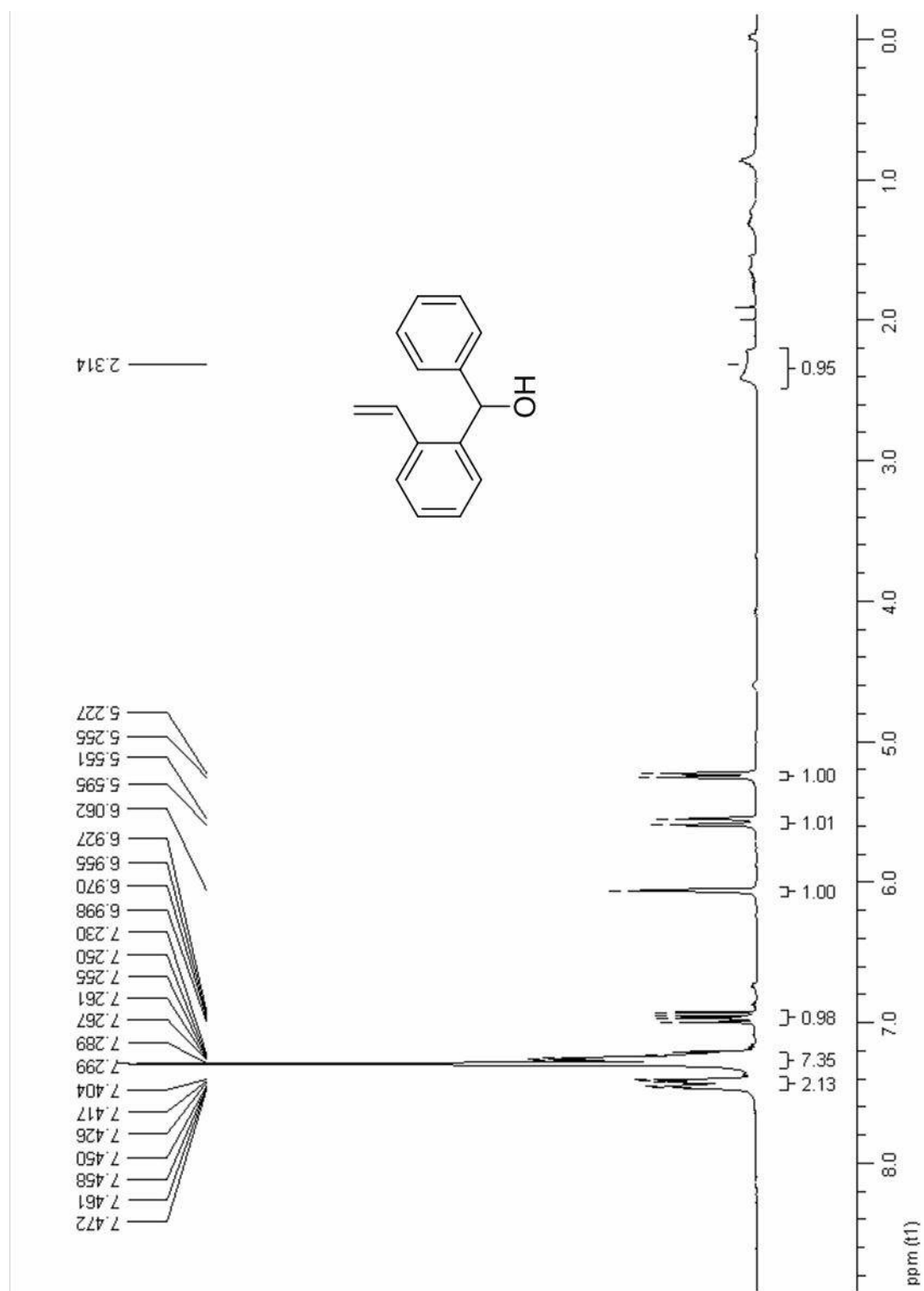
Compound 4g. Yield 62.5 %. **IR** (neat) ν_{max} : 2979, 2848, 1634, 1359, 1240, 1052, 740 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.77 (d, $J = 1.6$ Hz, 1H), 7.62 (dd, $J = 6.0, 2.0$ Hz, 1H), 7.42 (d, $J = 4.4$ Hz, 4H), 7.31-7.38 (m, 2H), 2.97 (q, $J = 7.2$ Hz, 1H), 2.39 (br, 1H), 1.32 (d, $J = 7.2$ Hz, 3H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz, ppm): δ 205.0, 155.4, 143.9, 137.0, 136.2, 135.5, 128.6, 127.7, 126.8, 125.4, 123.4, 79.6, 58.0, 8.3. **LRMS** (EI): 273 [M+1], 268, 256, 243, 226, 208, 193, 165, 152, 138, 115, 105, 91, 83, 78, 67, 55, 43, 28, 14. **HRMS** (ESI): calcd for $\text{C}_{16}\text{H}_{14}\text{ClO}_2^+$ 273.0677 [M+H] $^+$, found 273.0673.

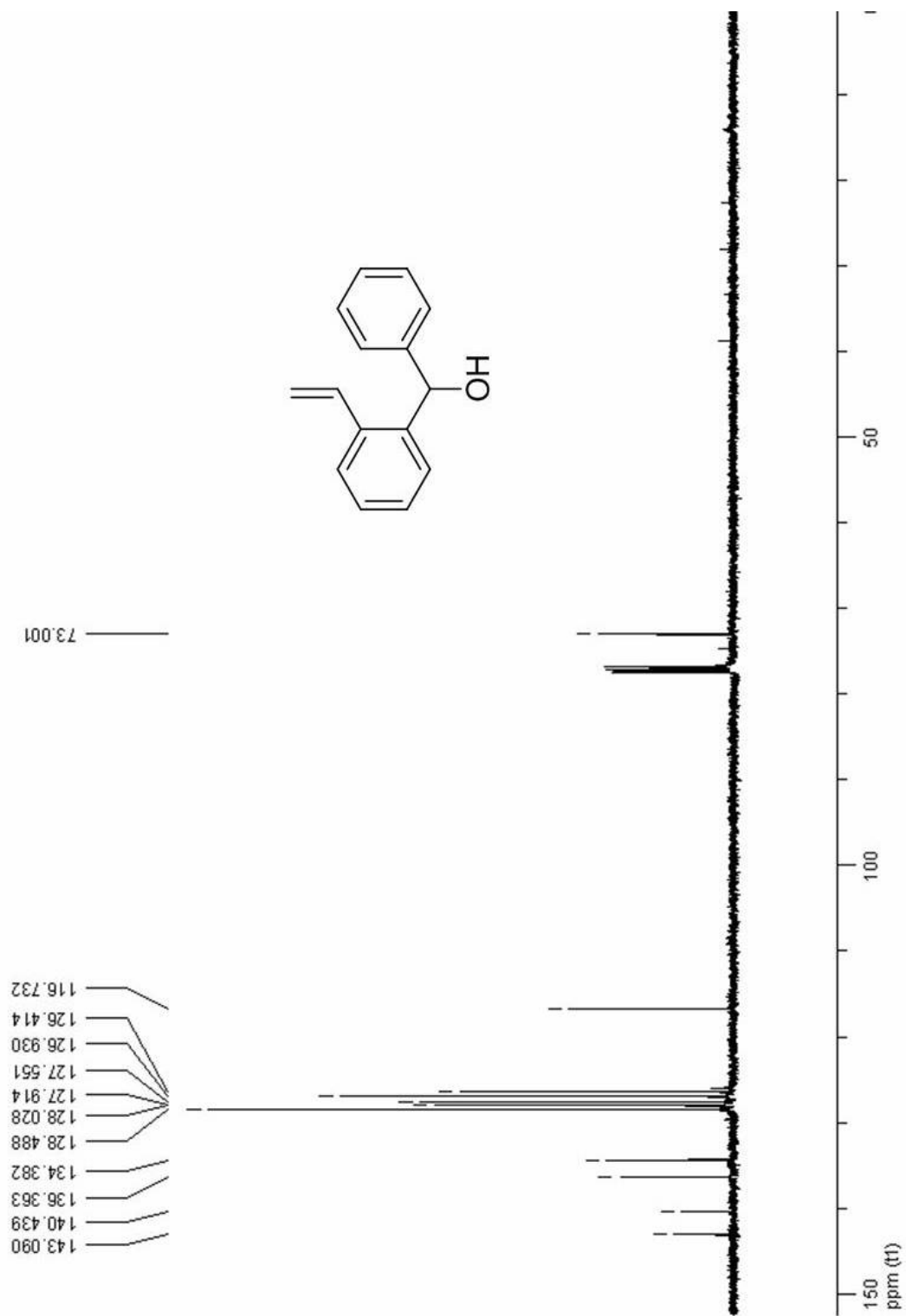


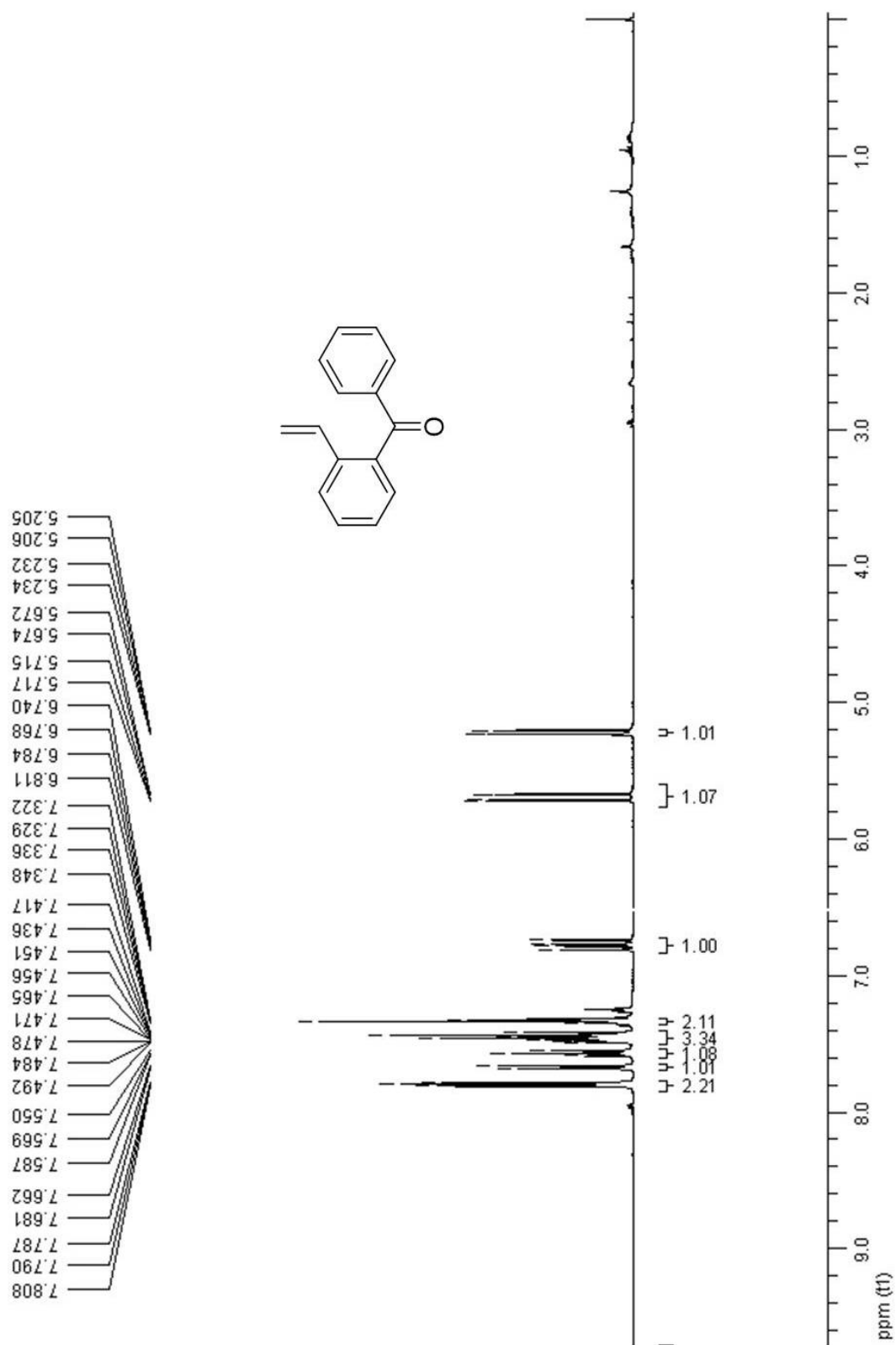
Compound II. Yield 60 %. **IR** (neat) ν_{max} : 2979, 2848, 1634, 1359, 1240, 1052, 740 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz, ppm): δ 7.59 (d, $J = 7.2$ Hz, 2H), 7.31-7.42 (m, 8H), 7.29 (d, $J = 6.4$ Hz, 2H), 7.16 (d, $J = 7.2$ Hz, 2H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz, ppm): δ 196.5, 155.3, 145.3, 133.4, 130.8, 130.8, 130.0, 129.3, 129.0, 128.8, 128.5, 128.1, 127.4, 123.0, 121.8. **LRMS** (EI): 281 [M-1], 252, 225, 200, 176, 150, 126, 99, 77, 51, 22. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{15}\text{O}^+$ 283.1117 [M+H] $^+$, found 283.1122.

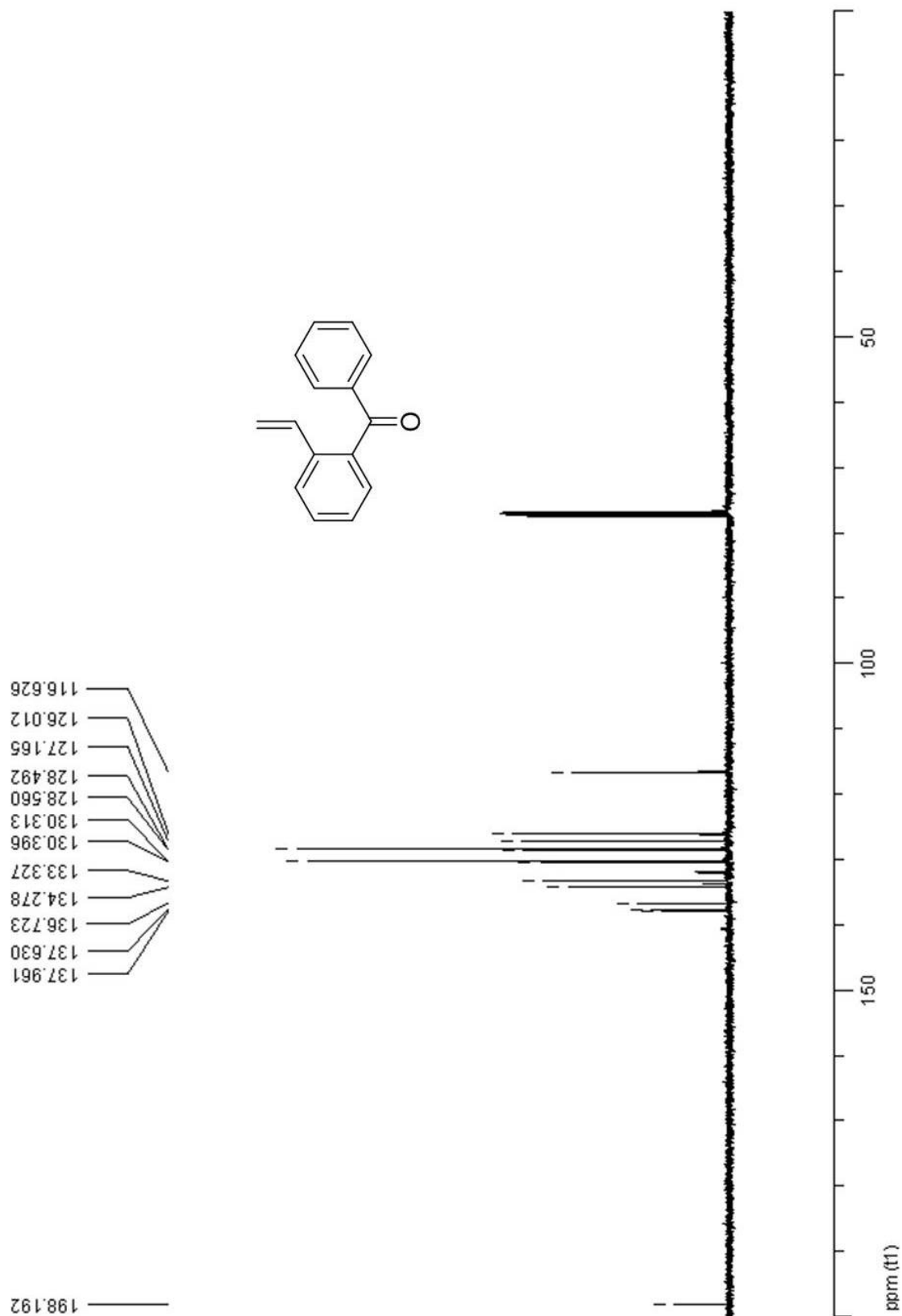
Reference

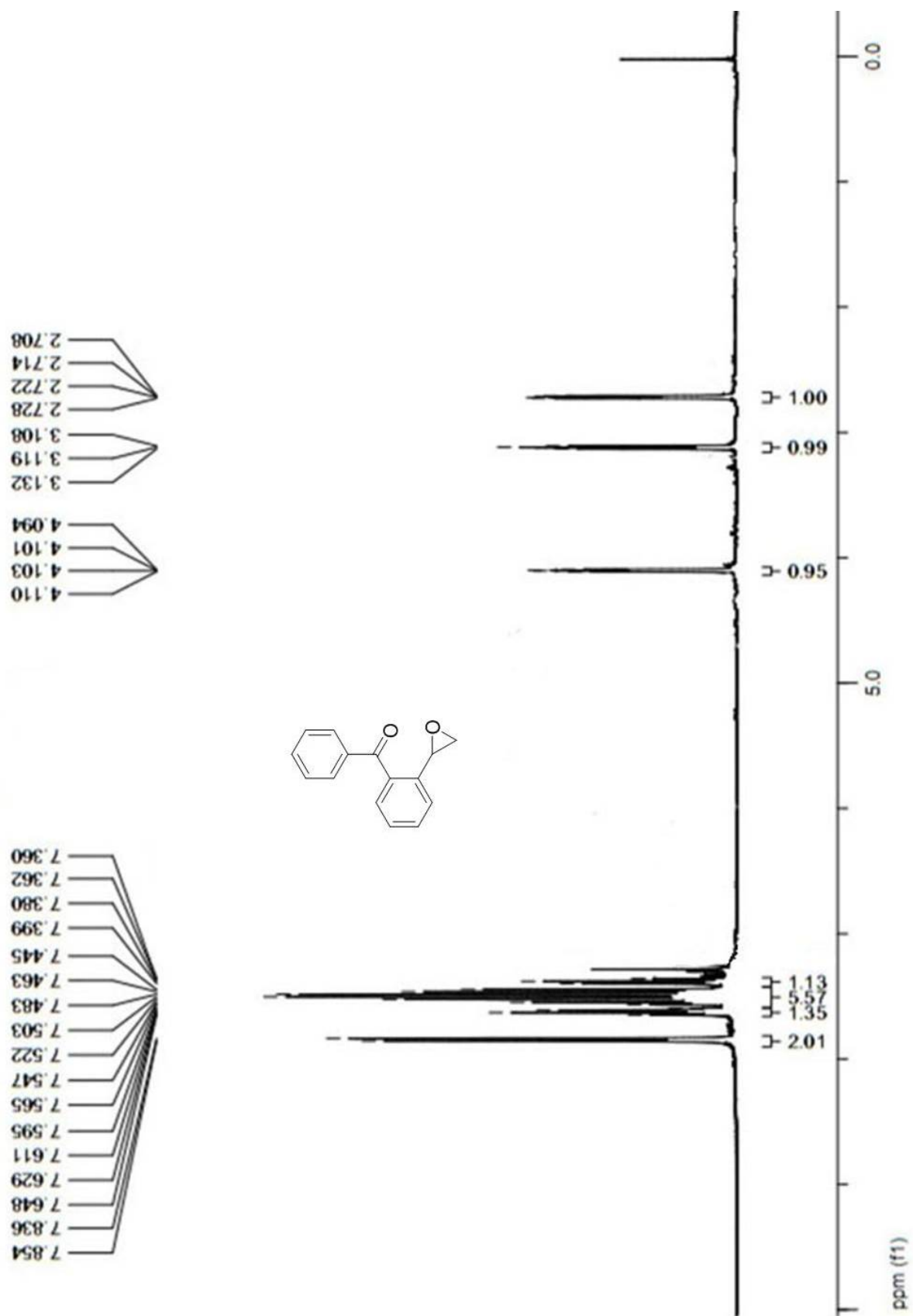
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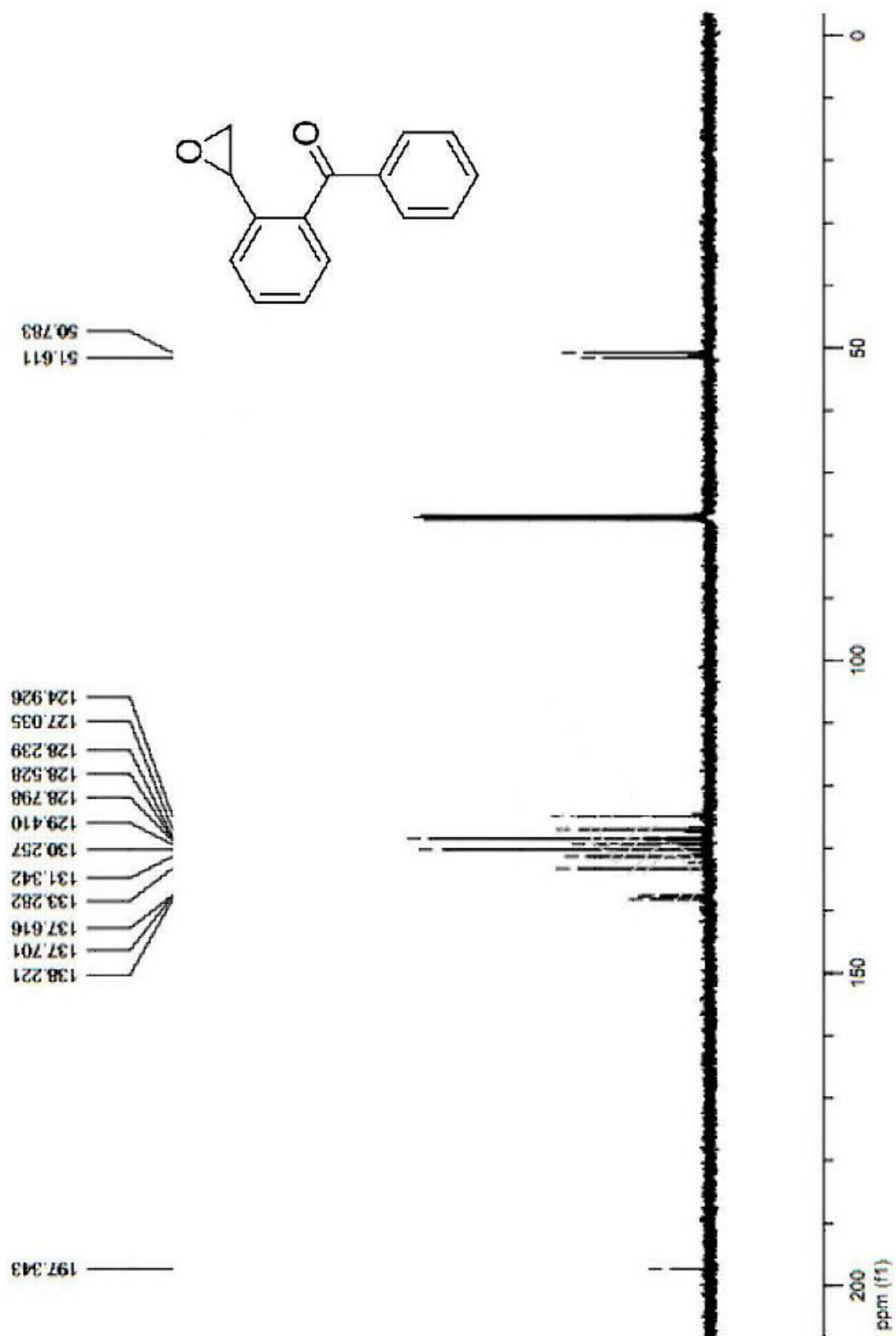


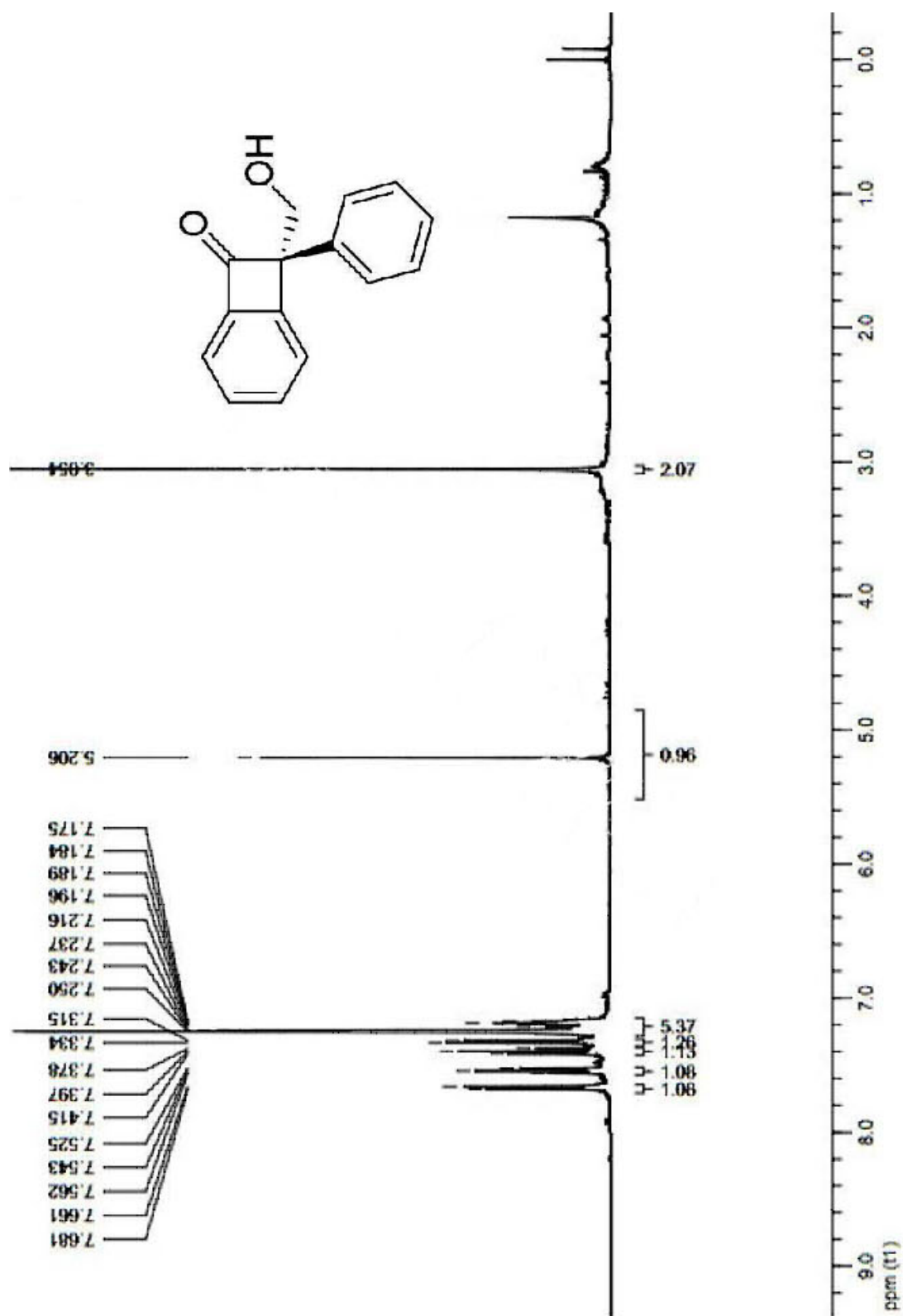


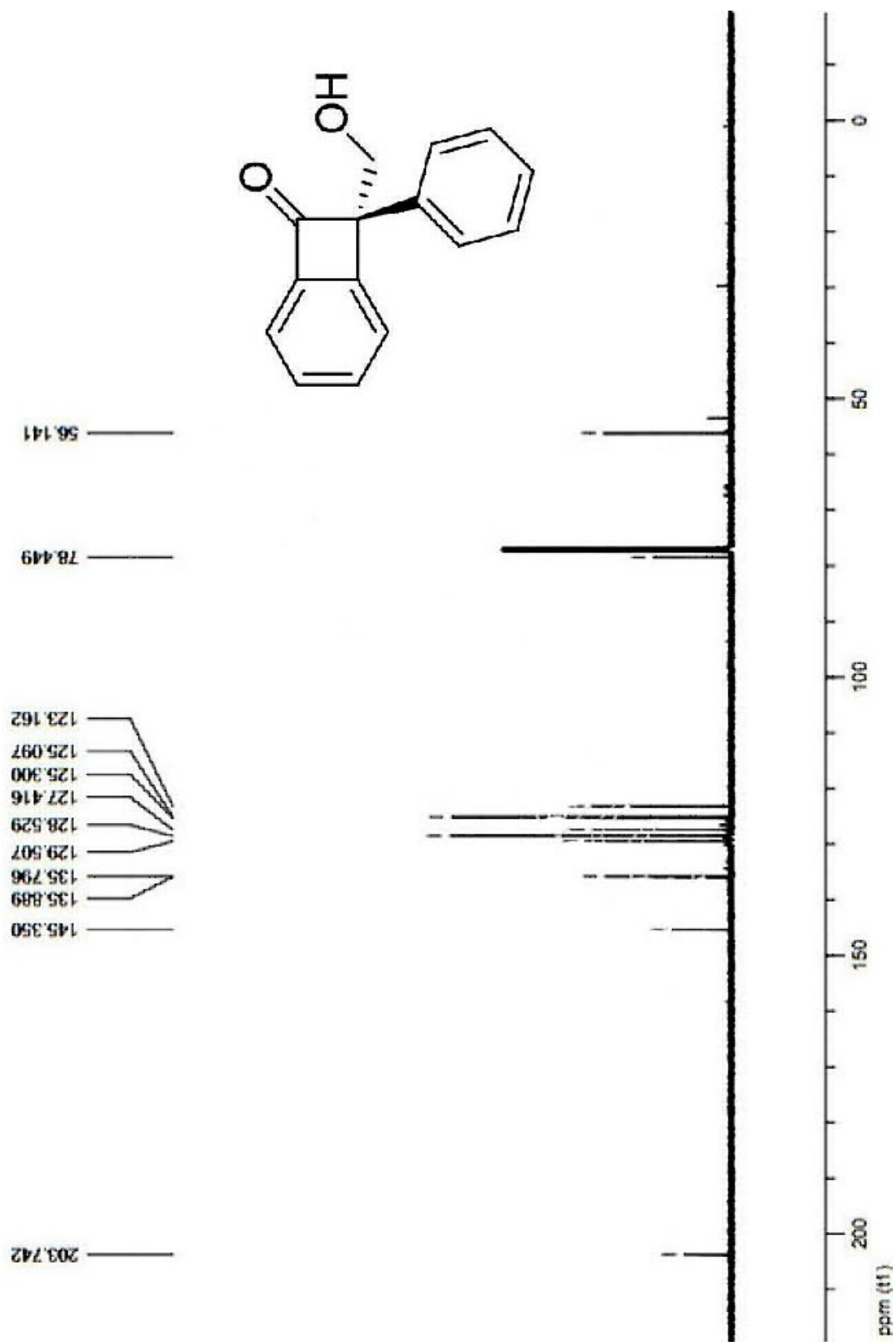


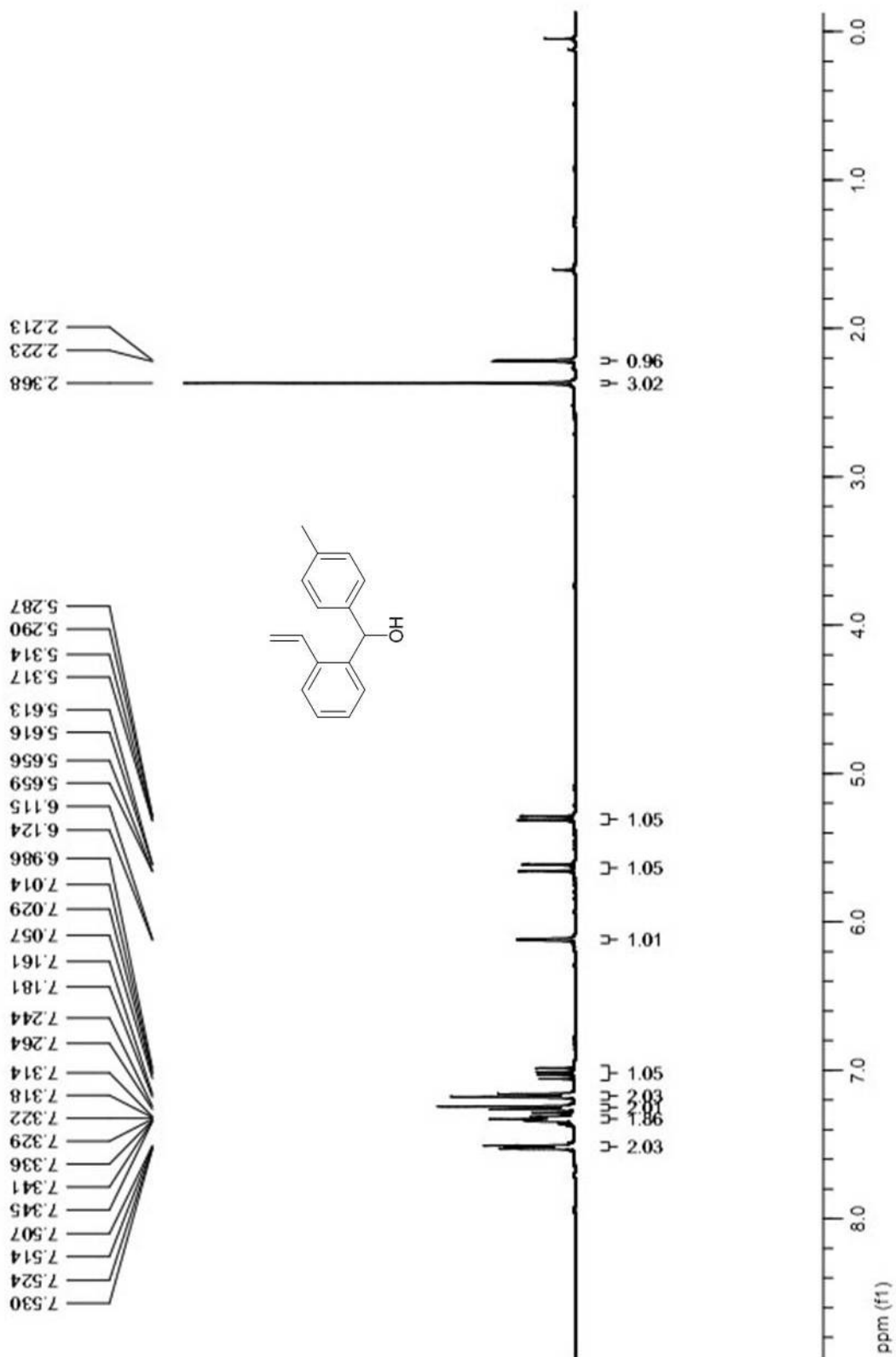


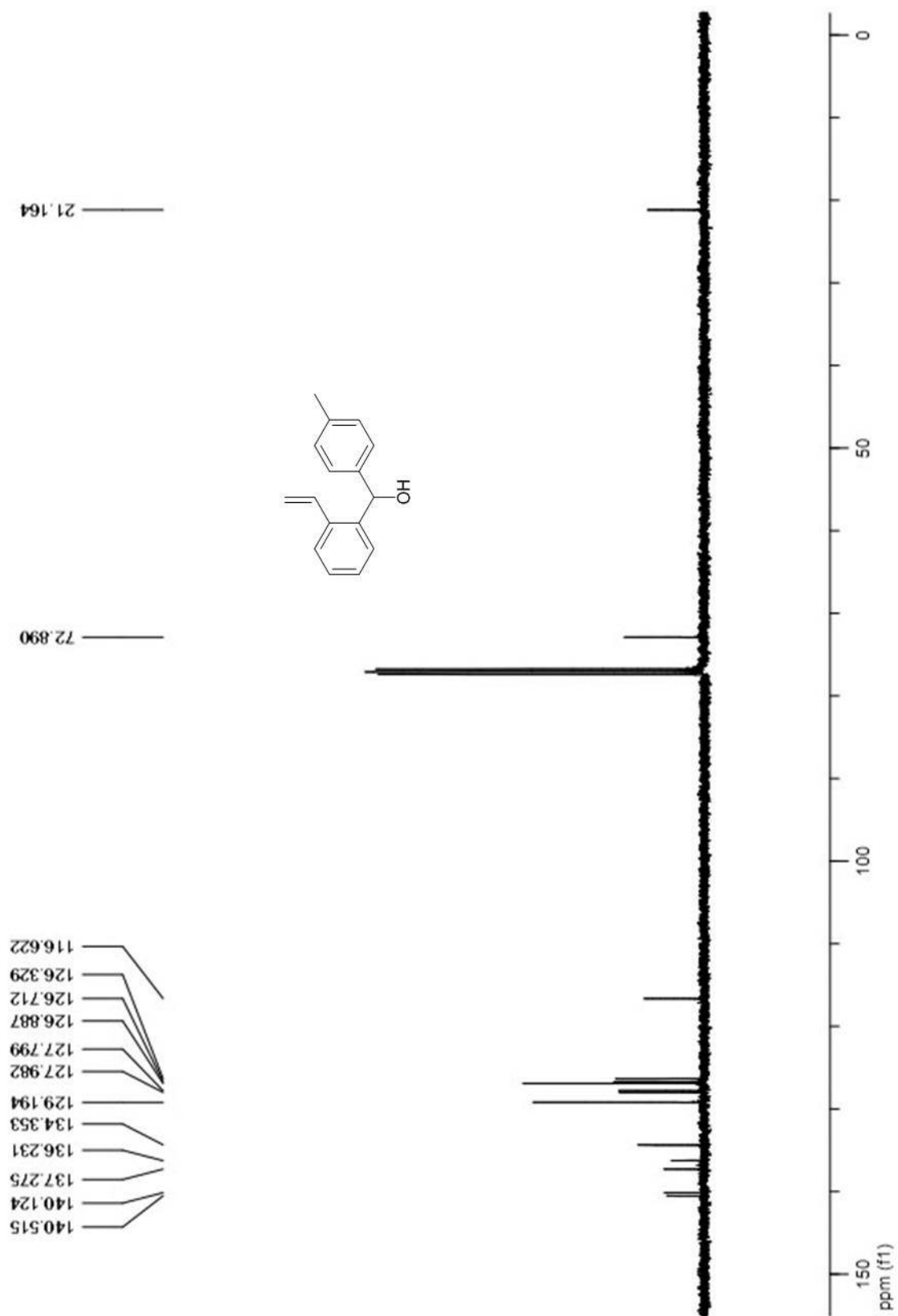


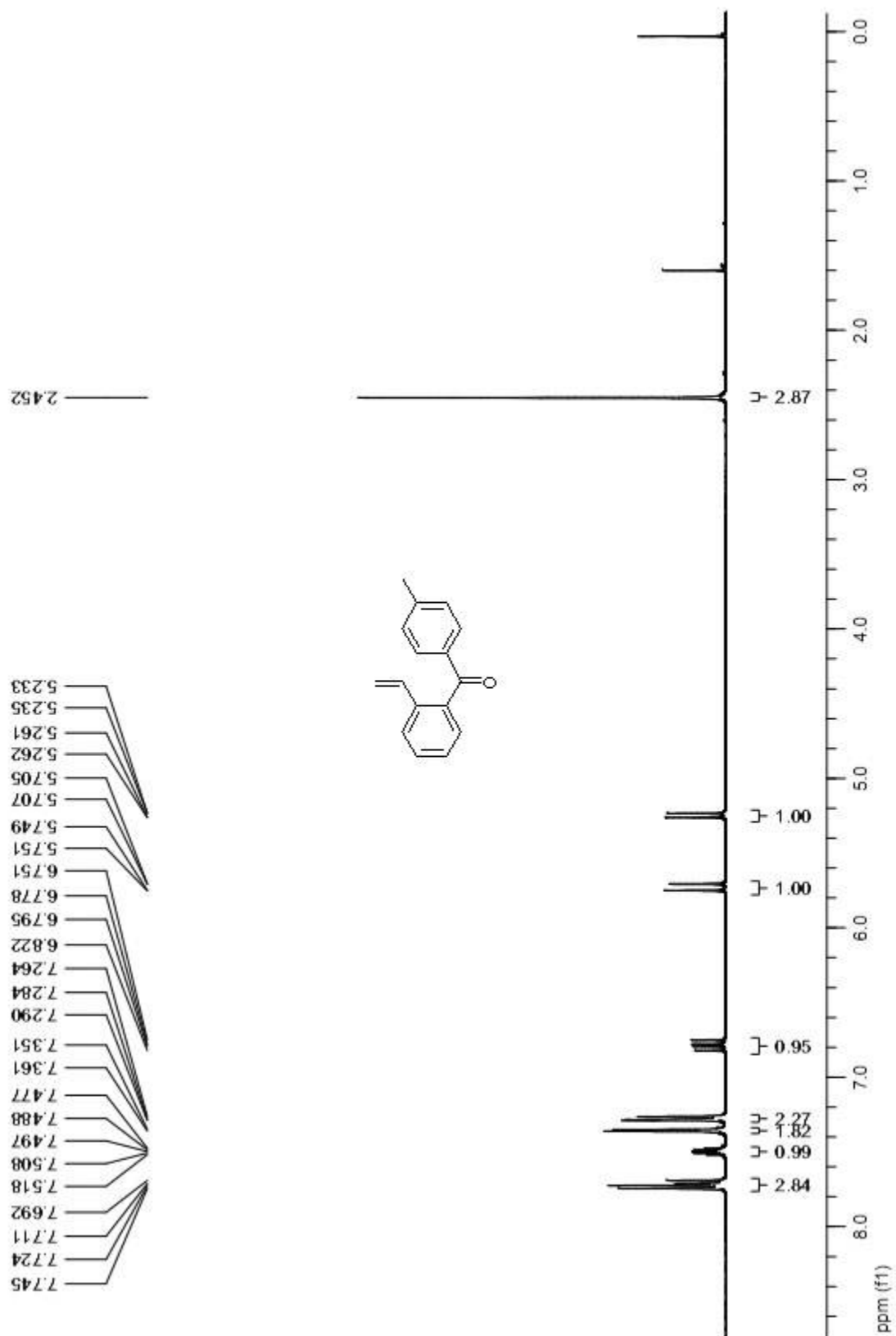


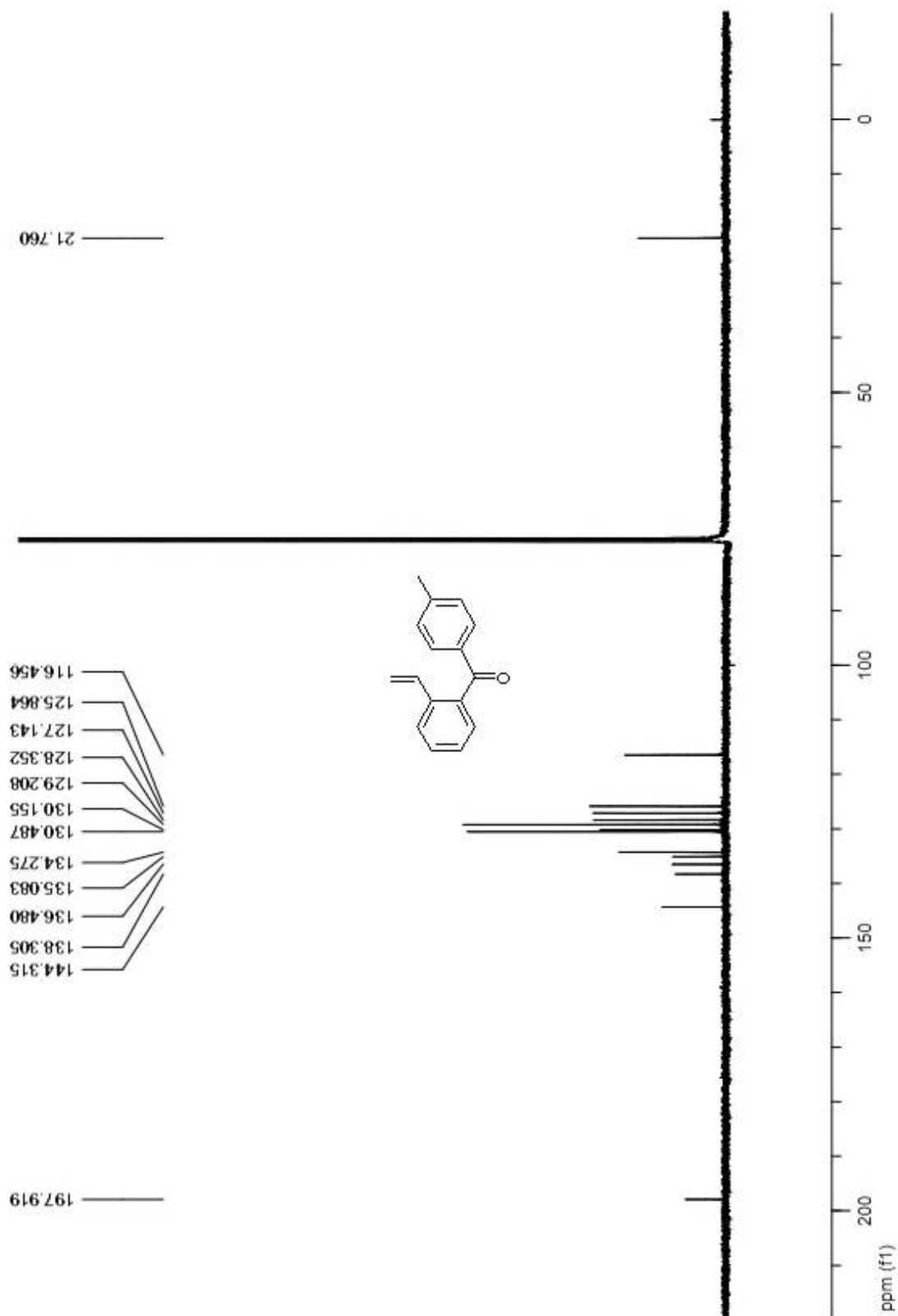


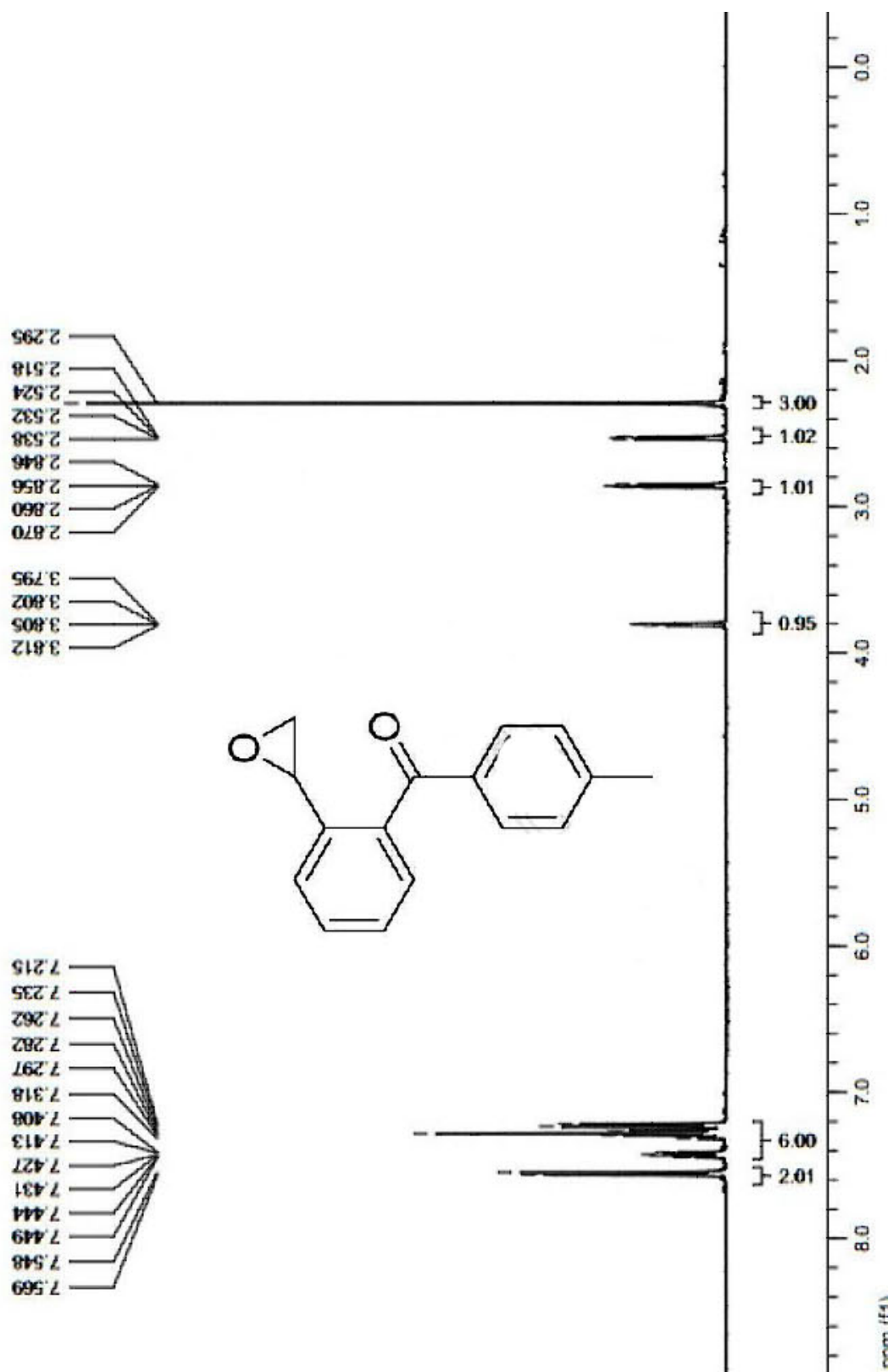


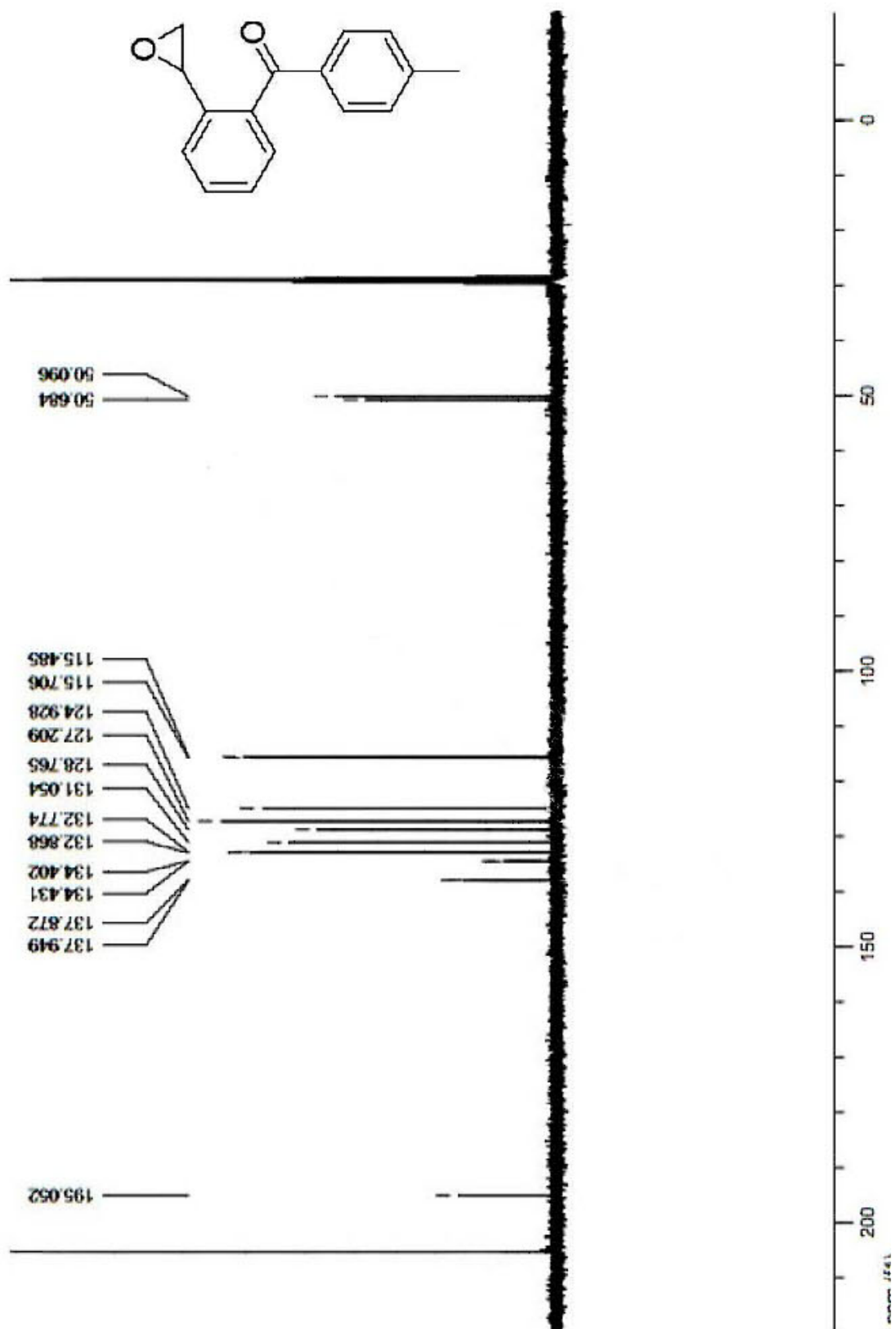


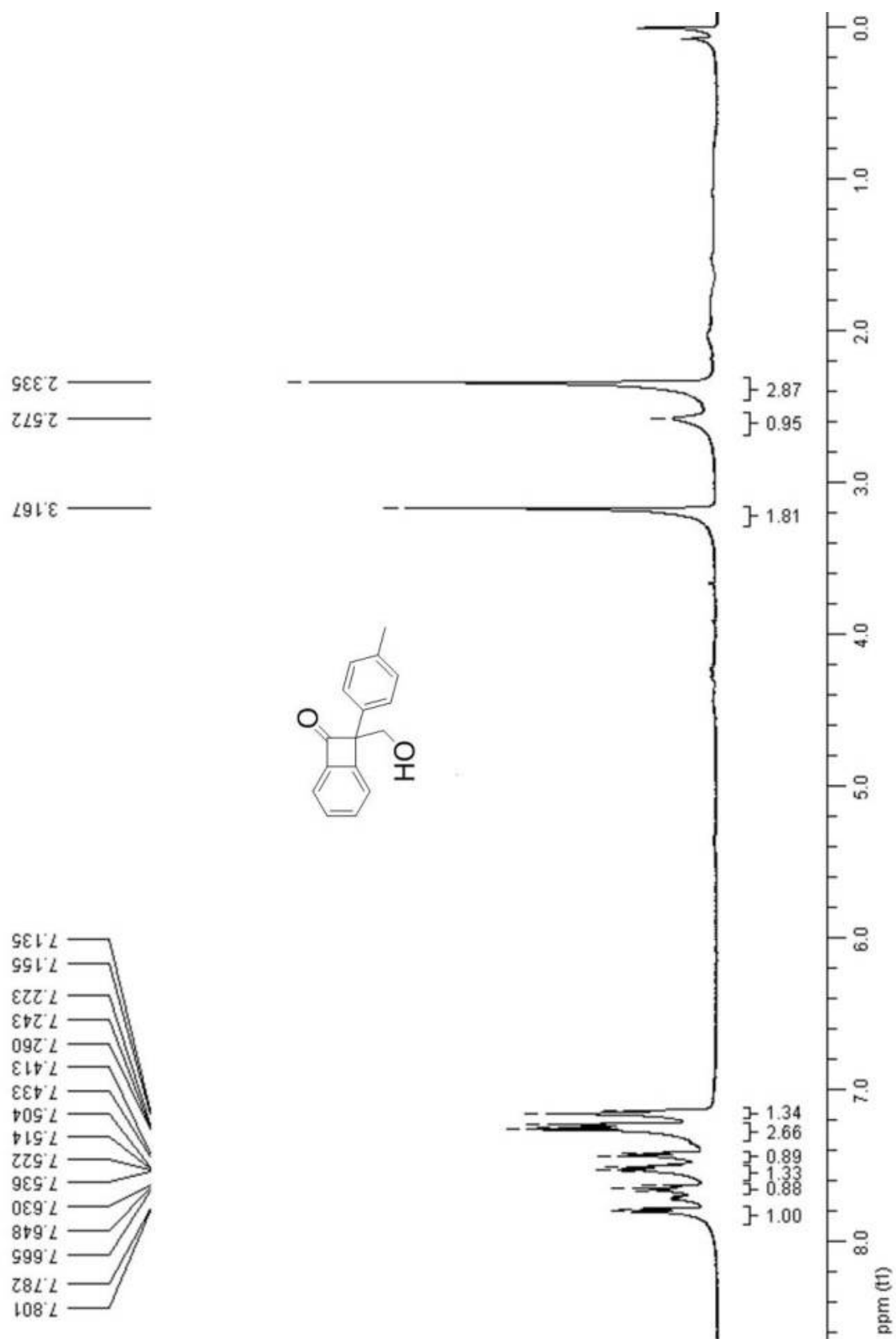


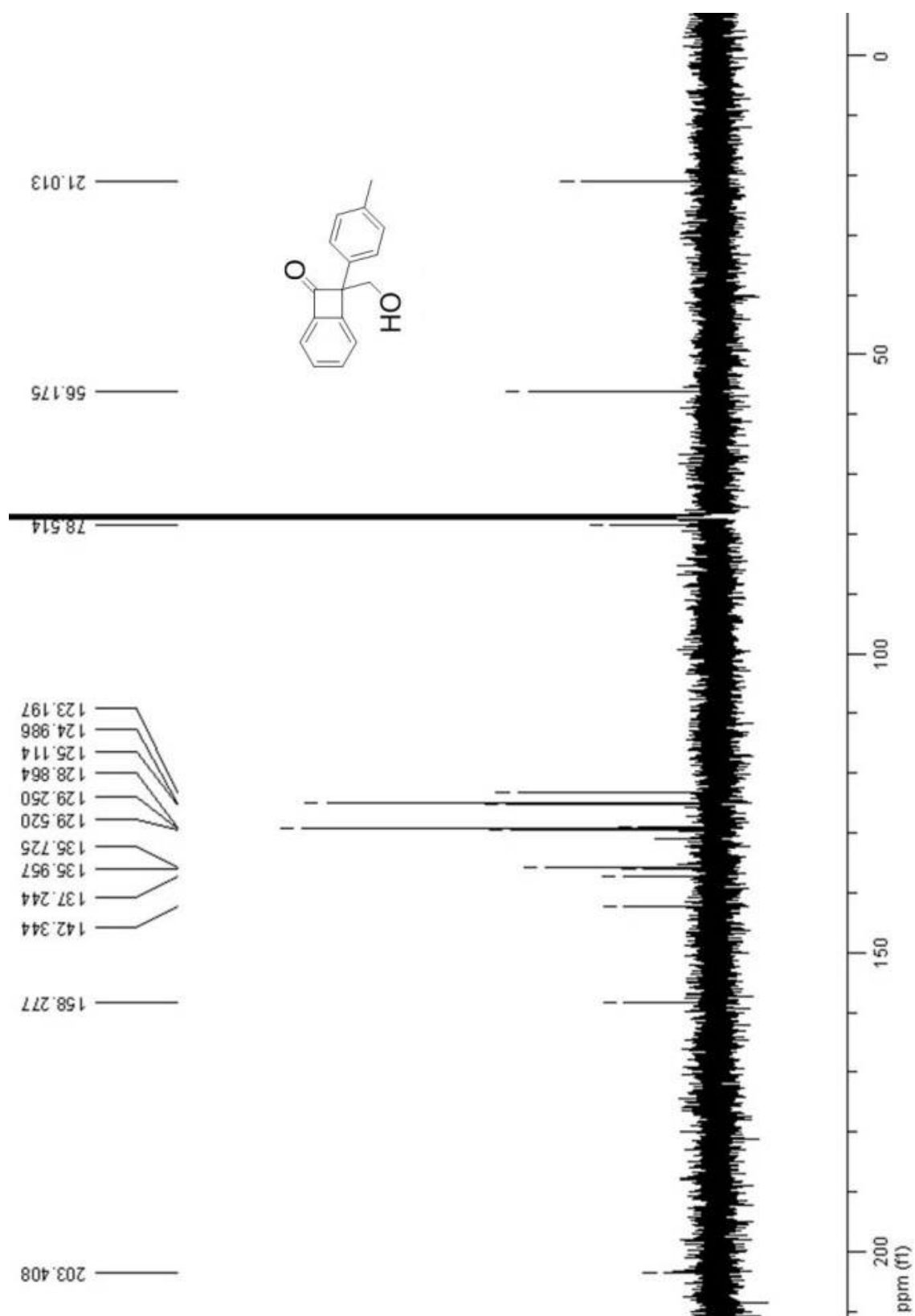


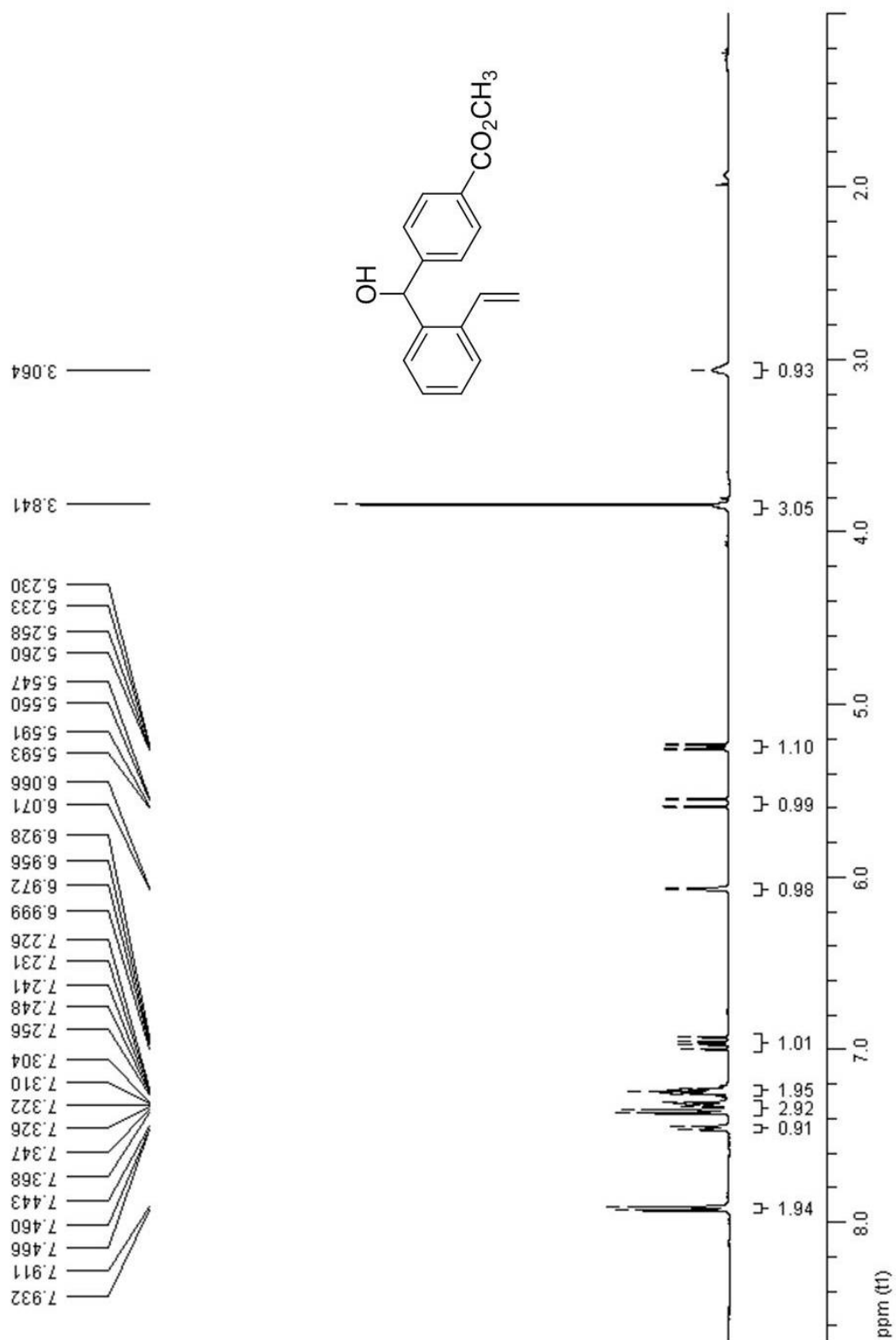


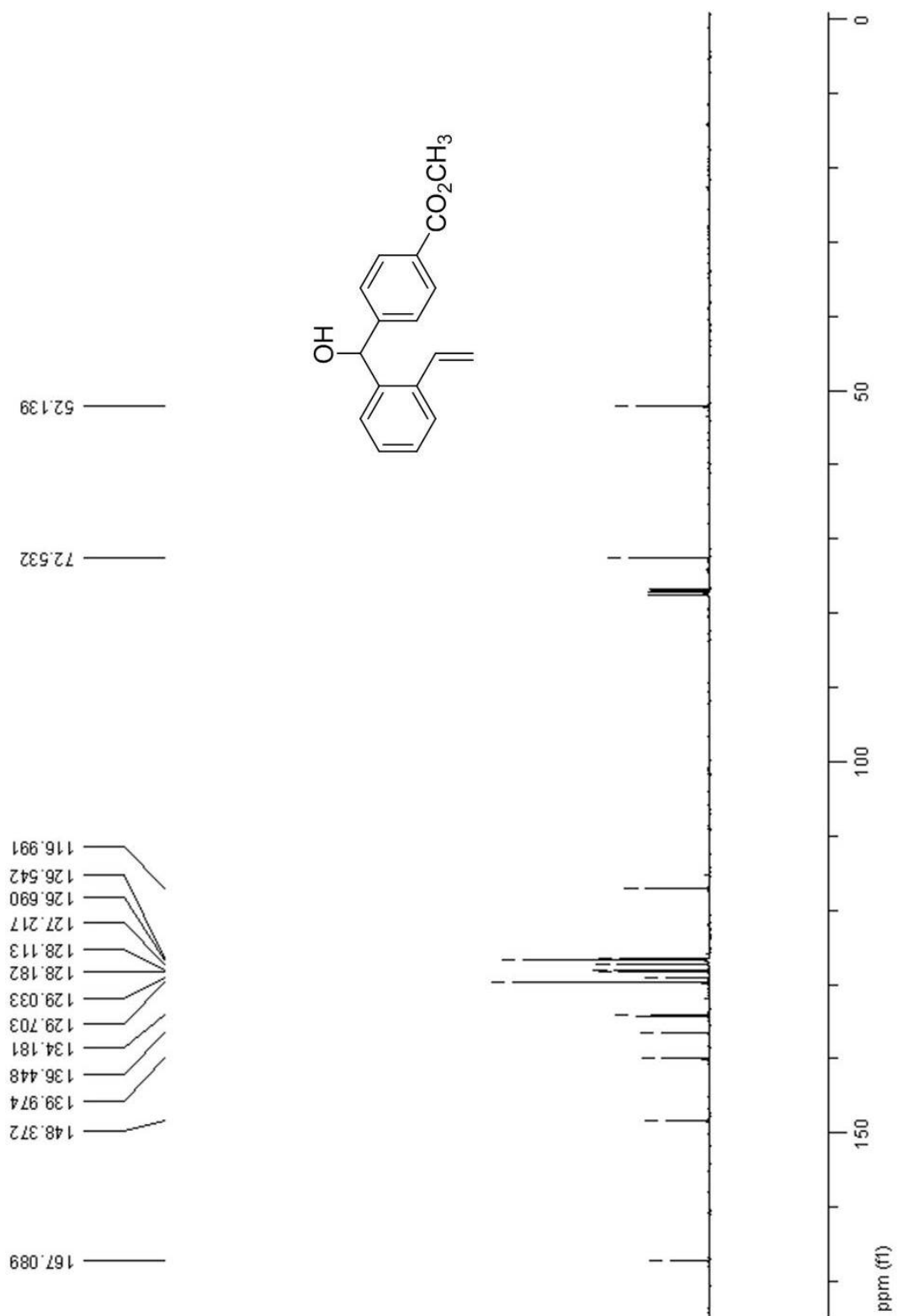


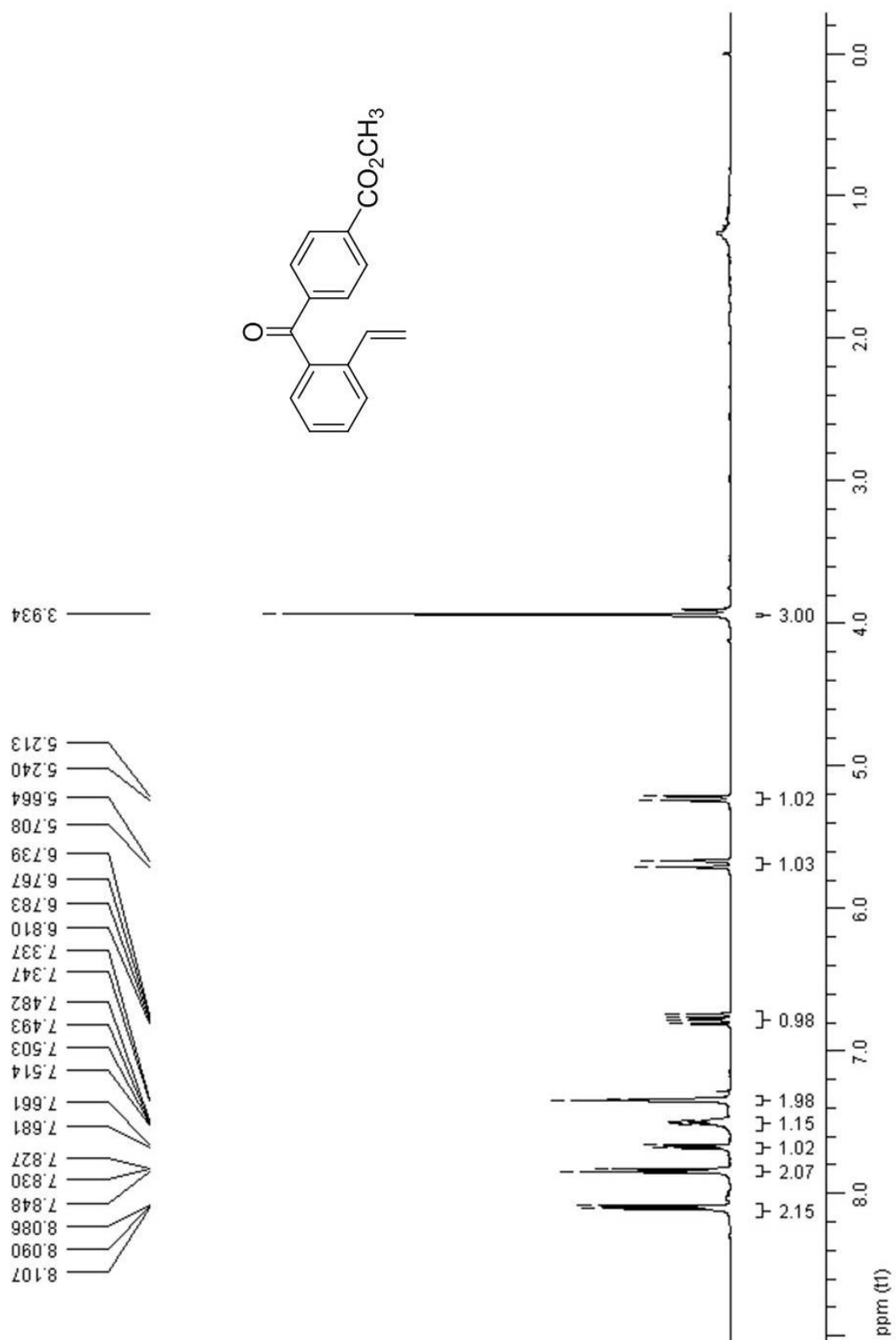


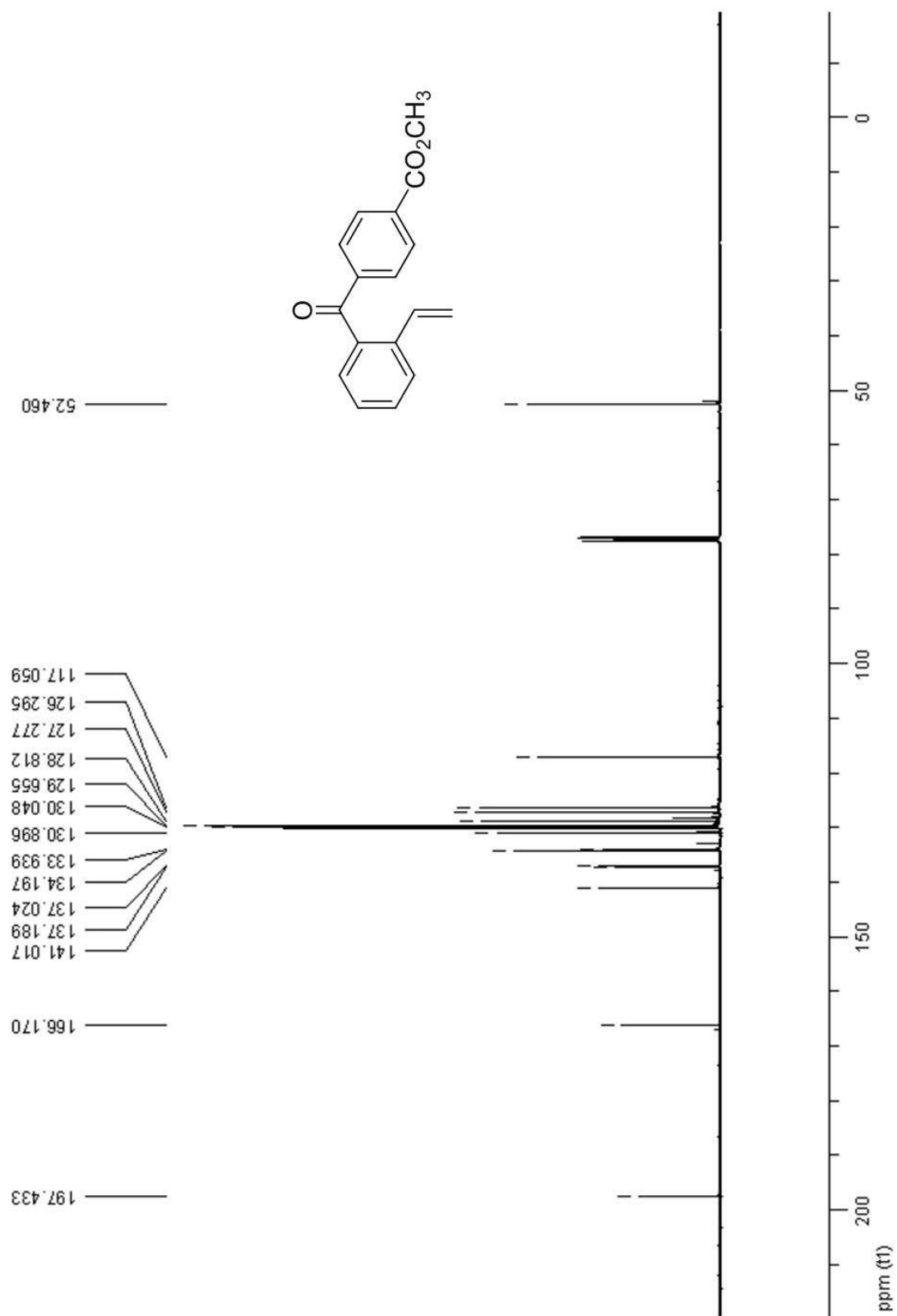


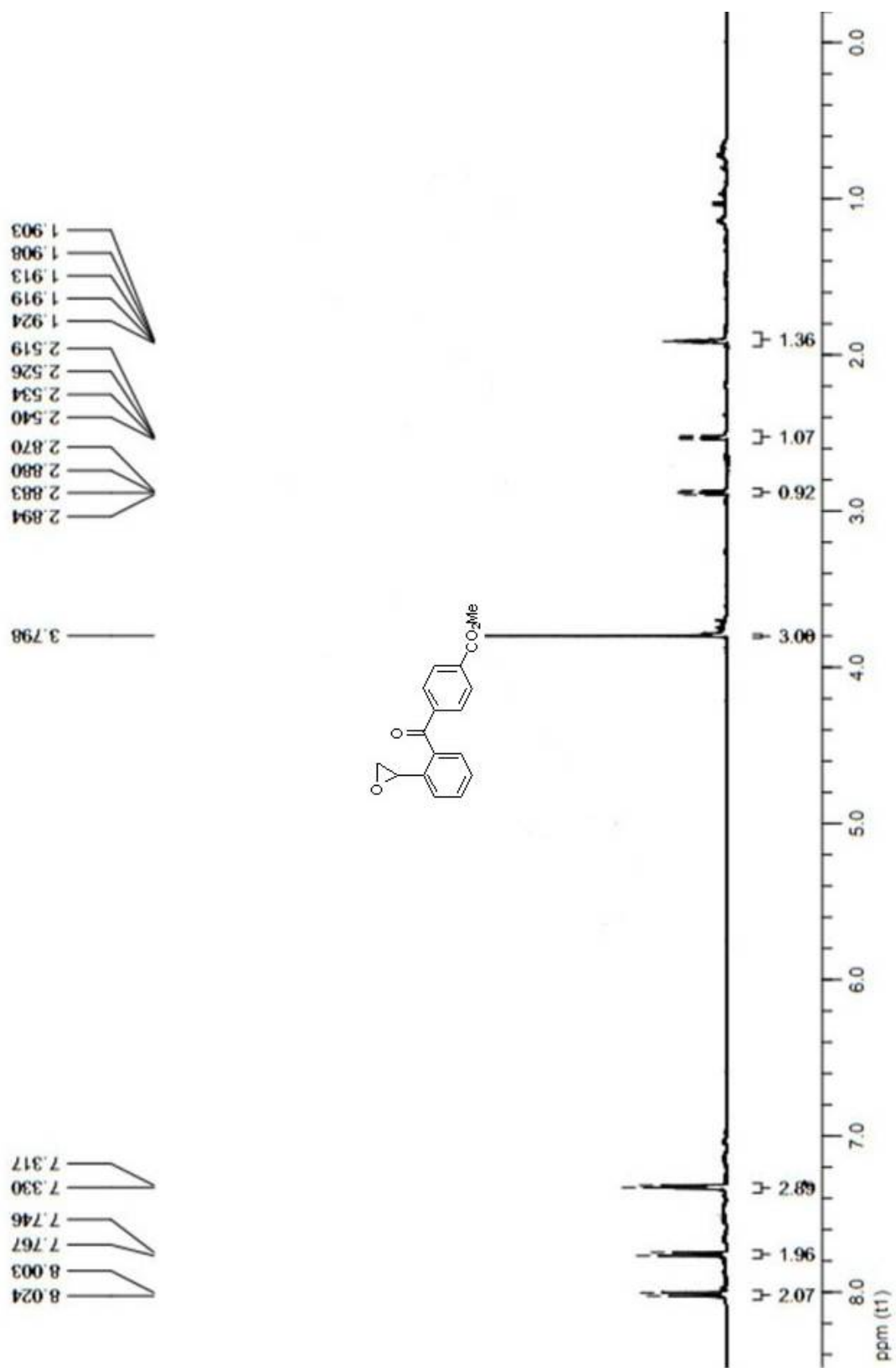


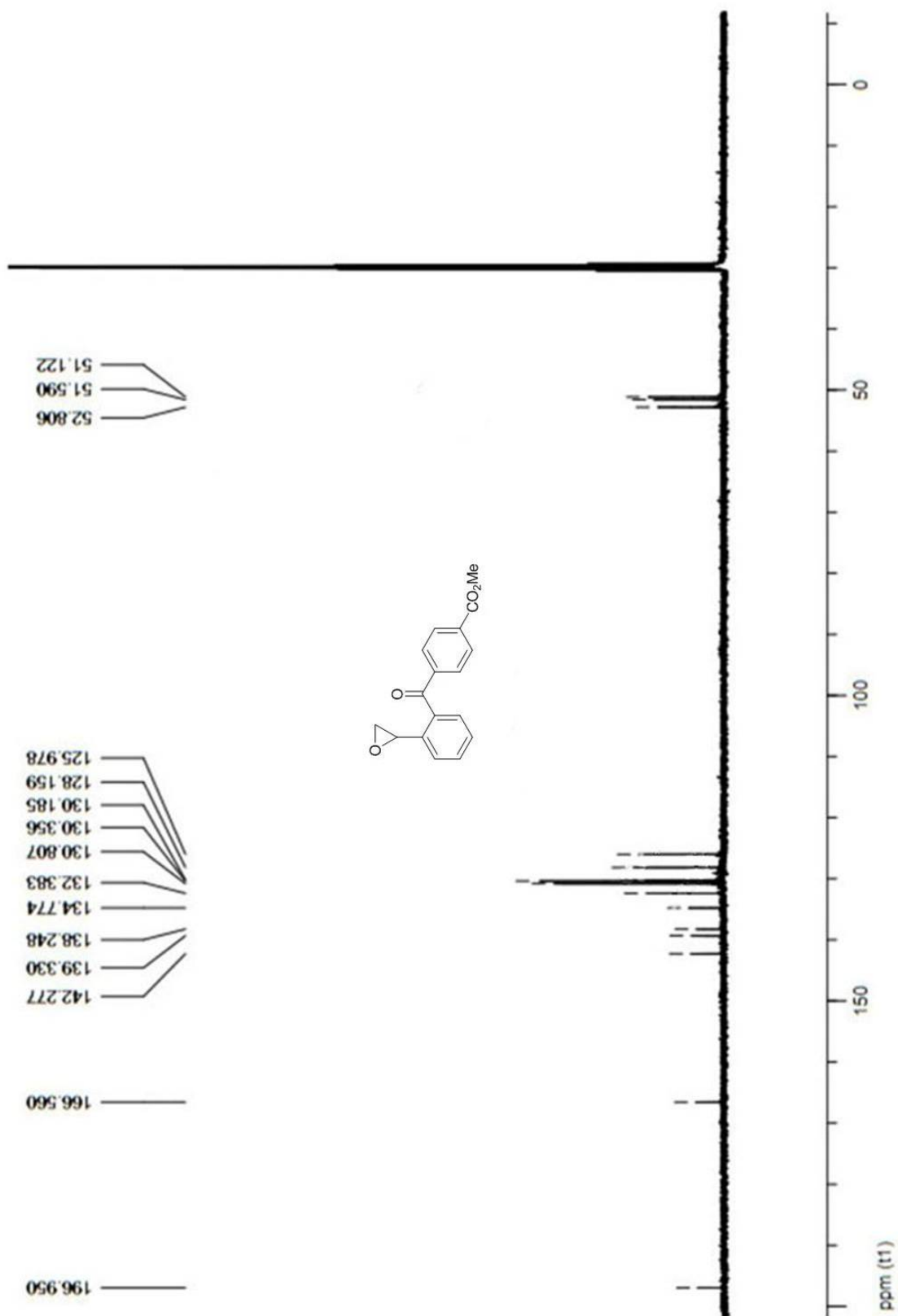


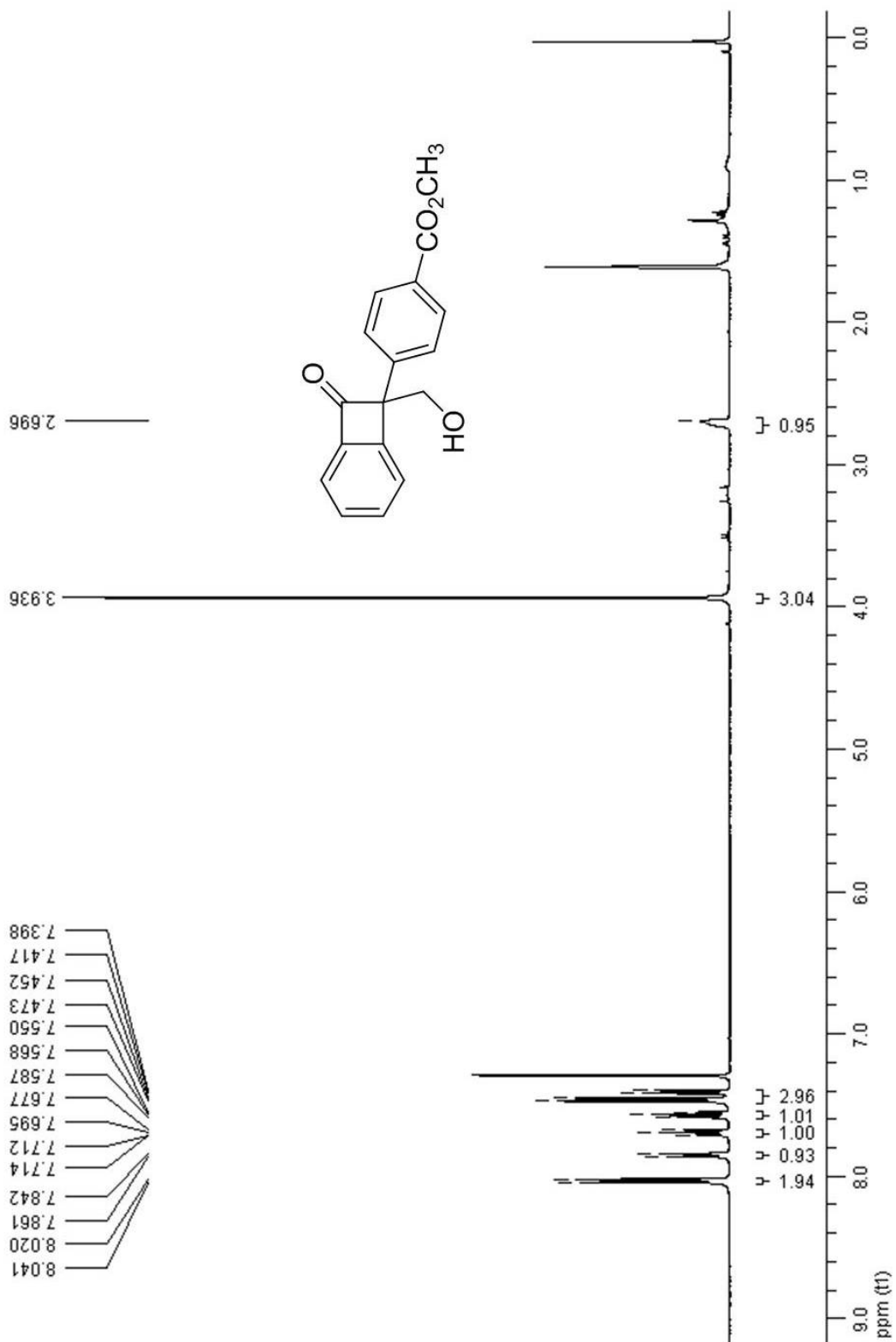


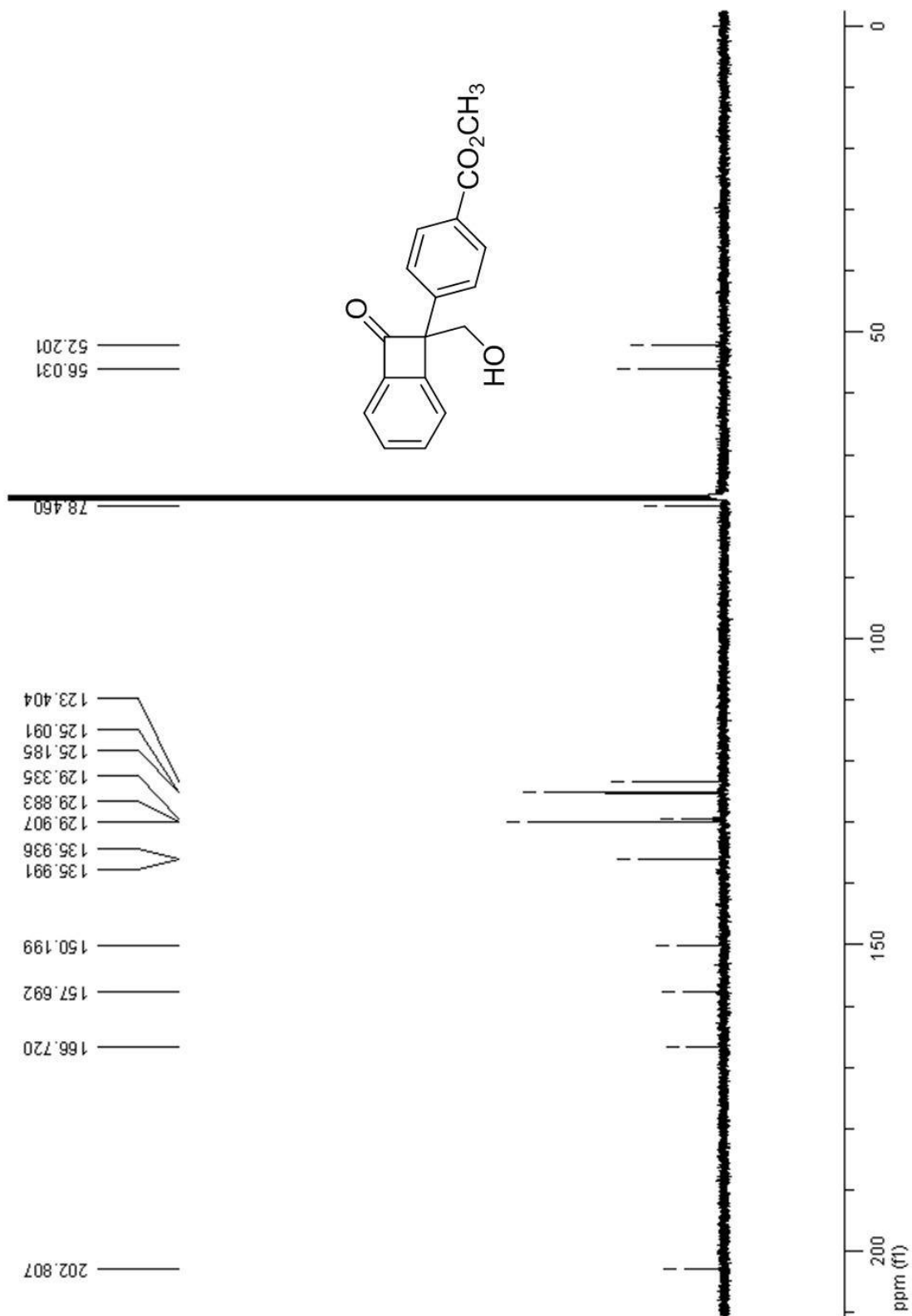


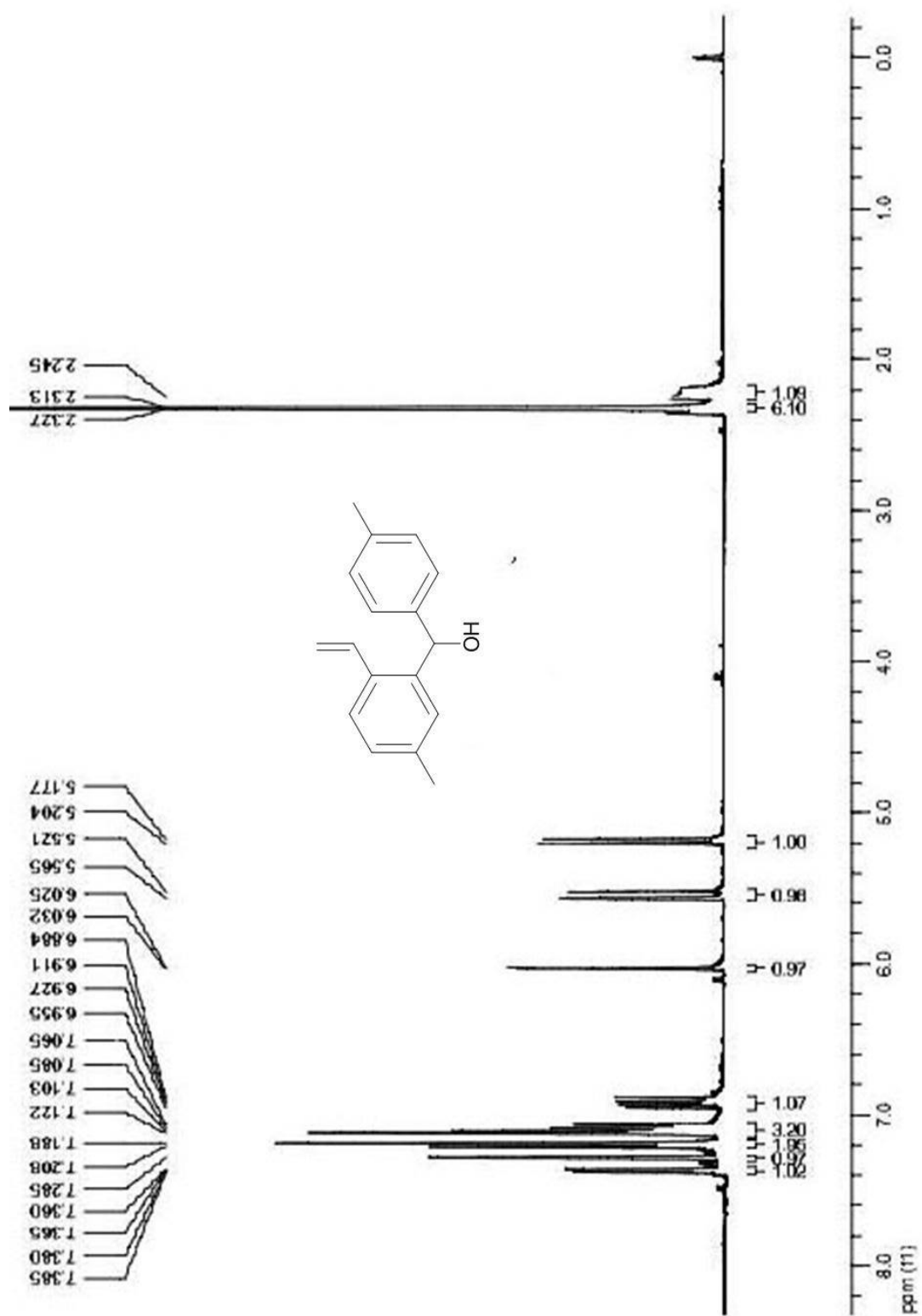


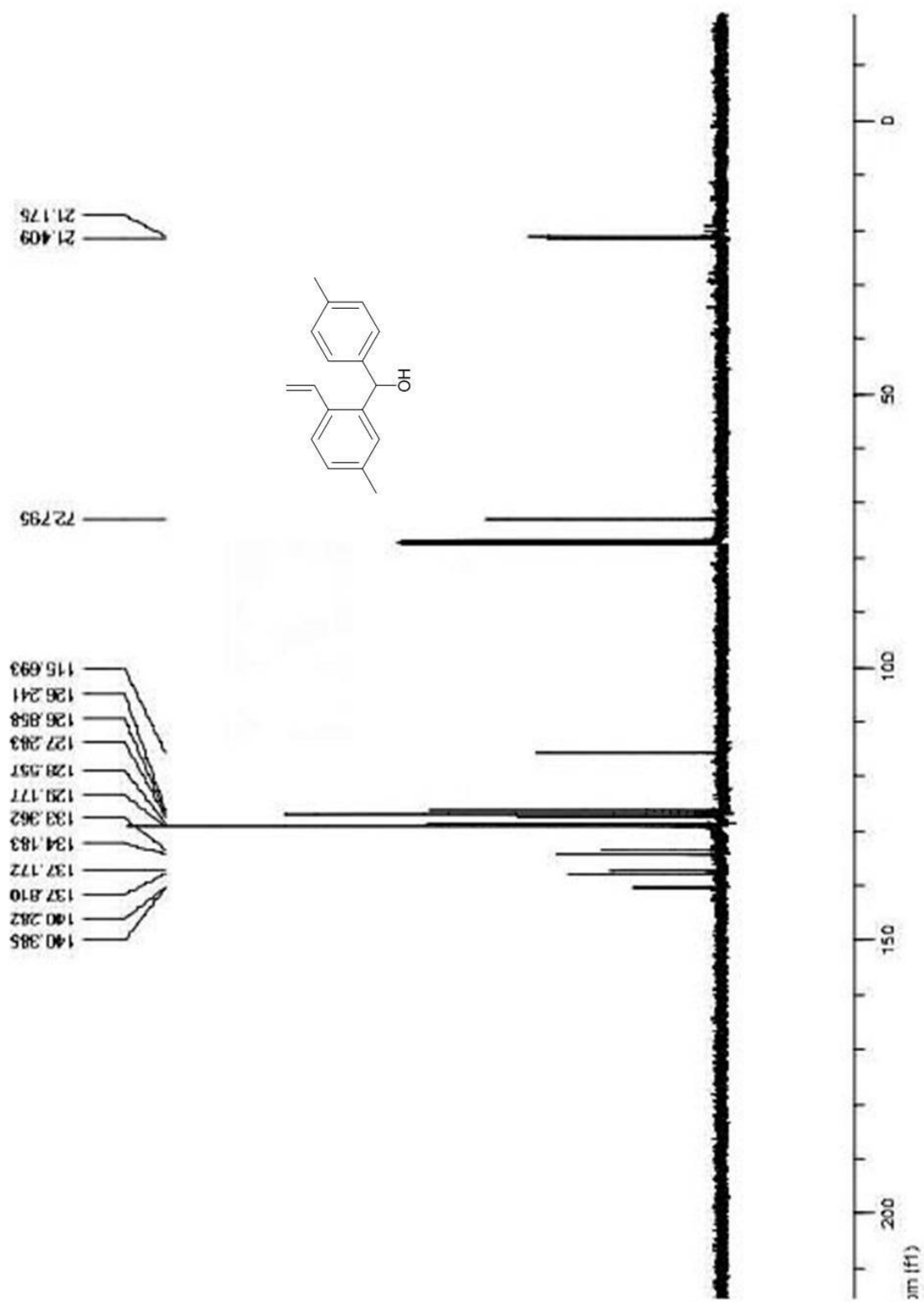


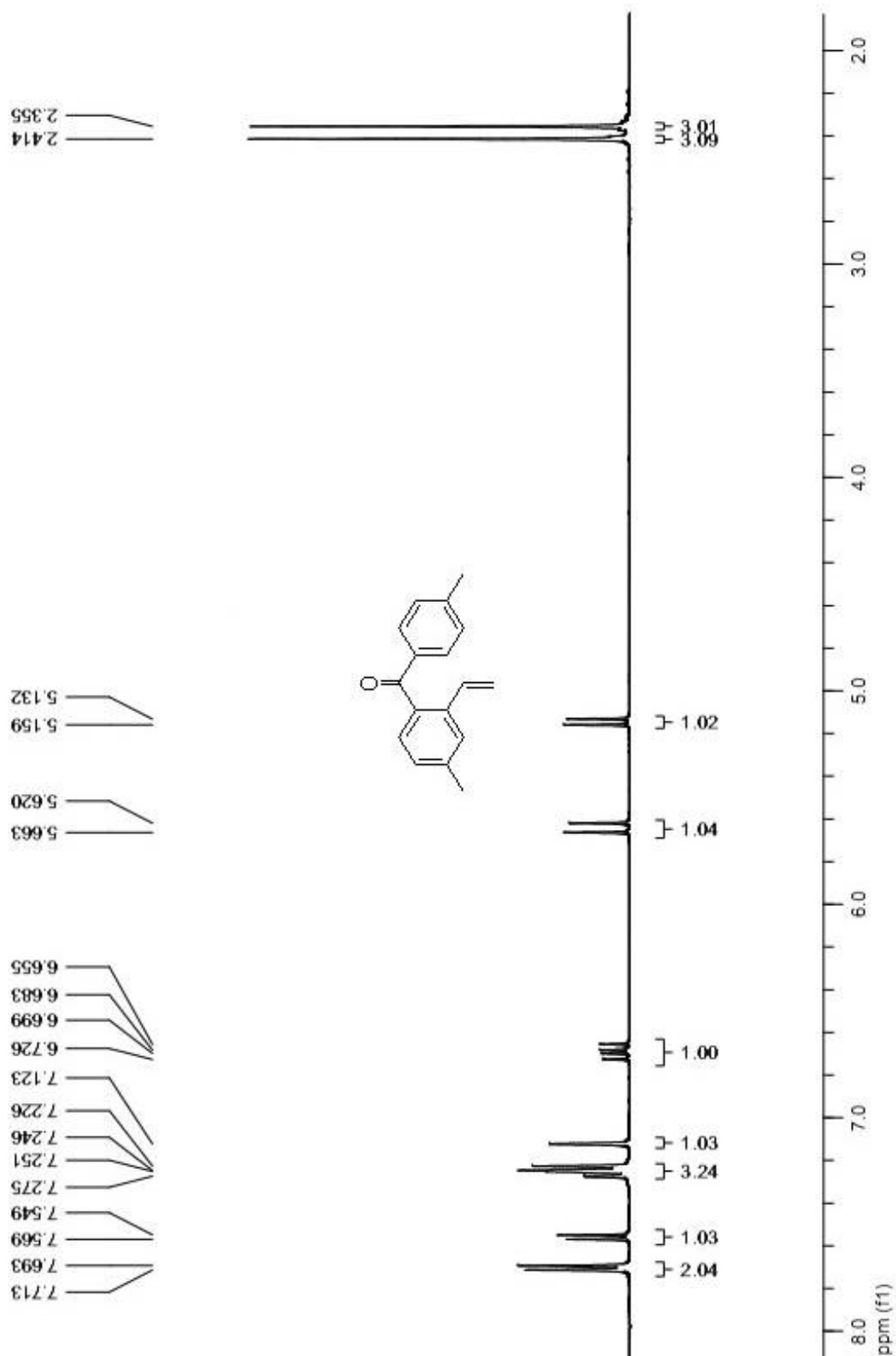


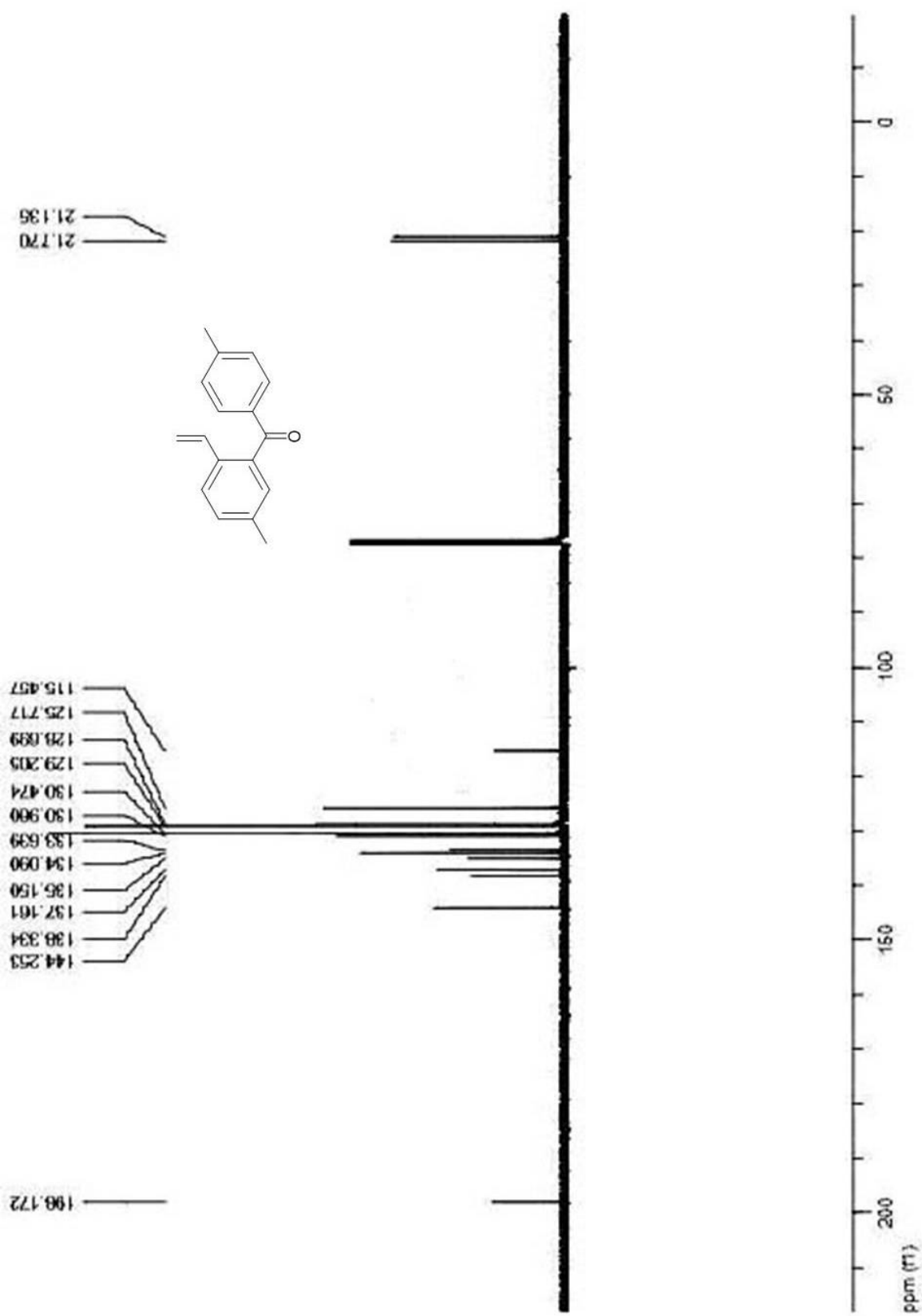


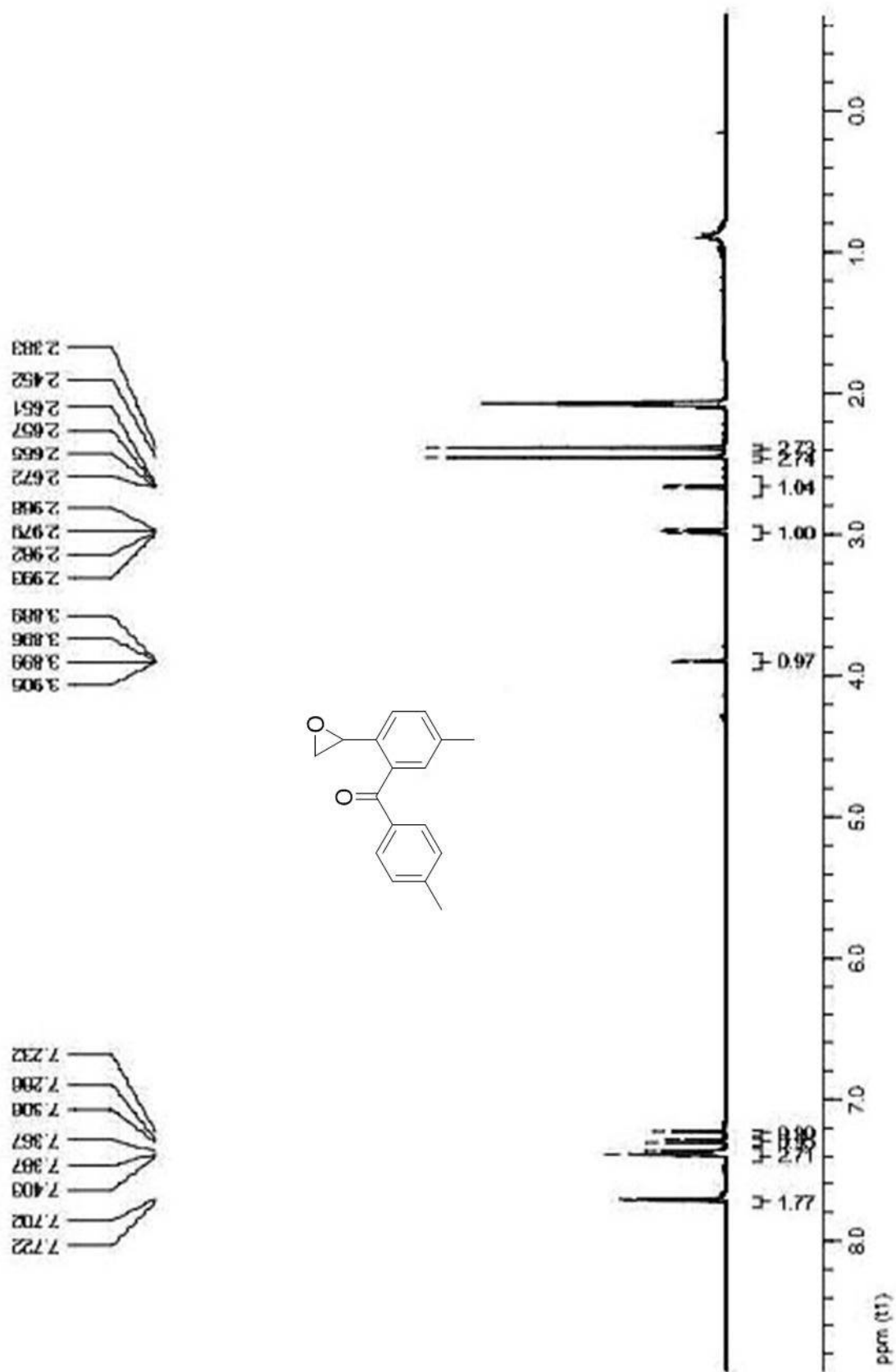


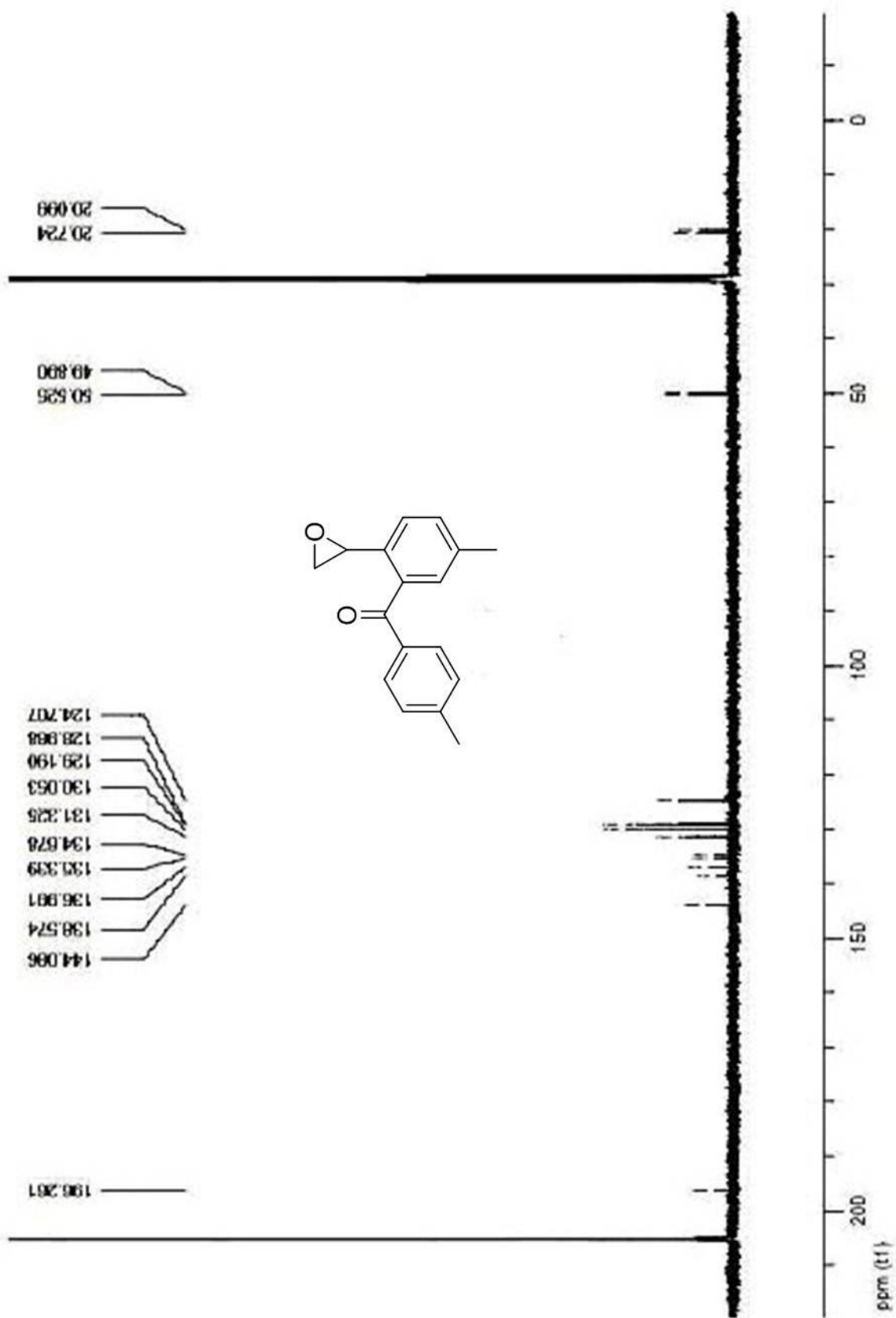


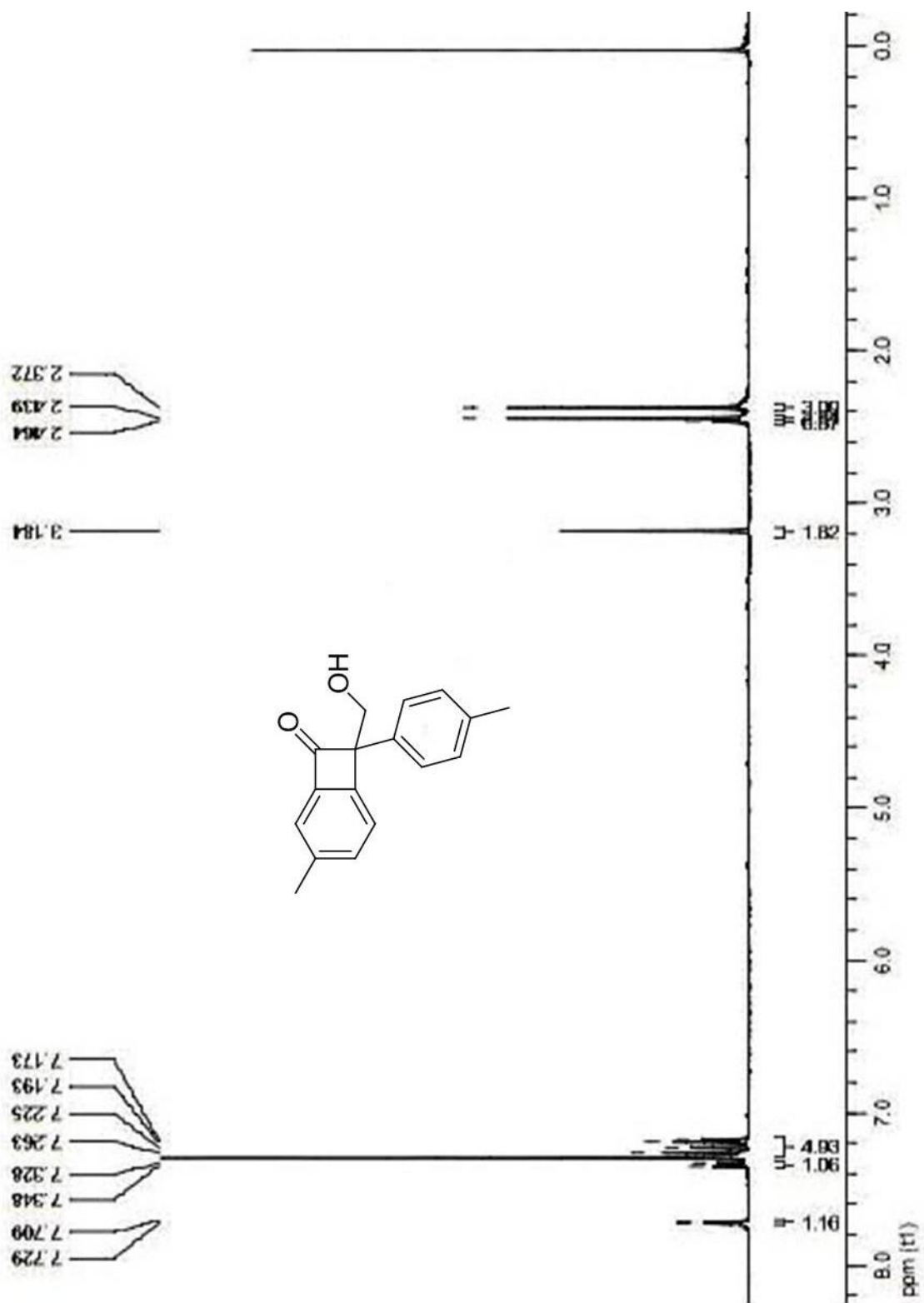


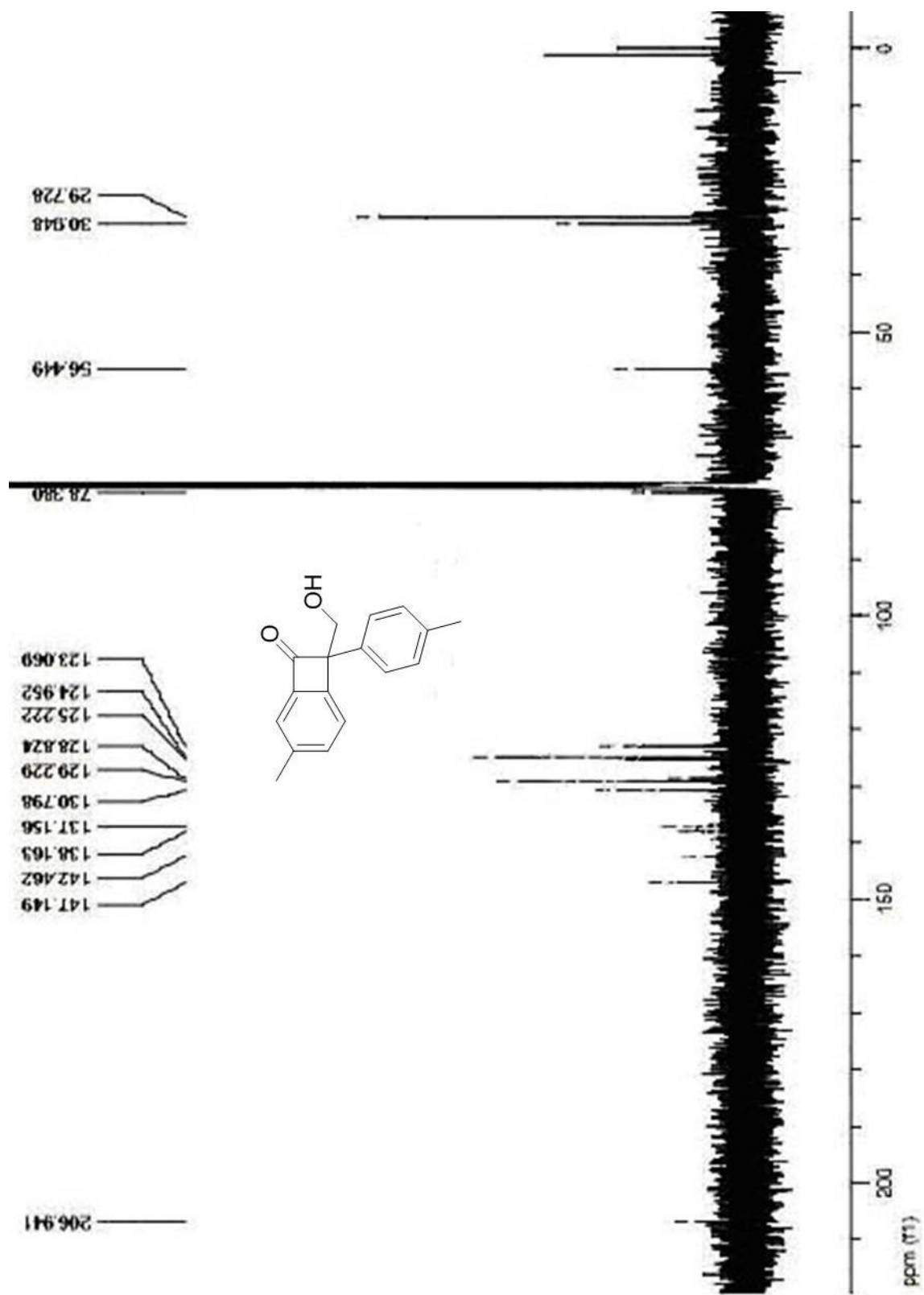


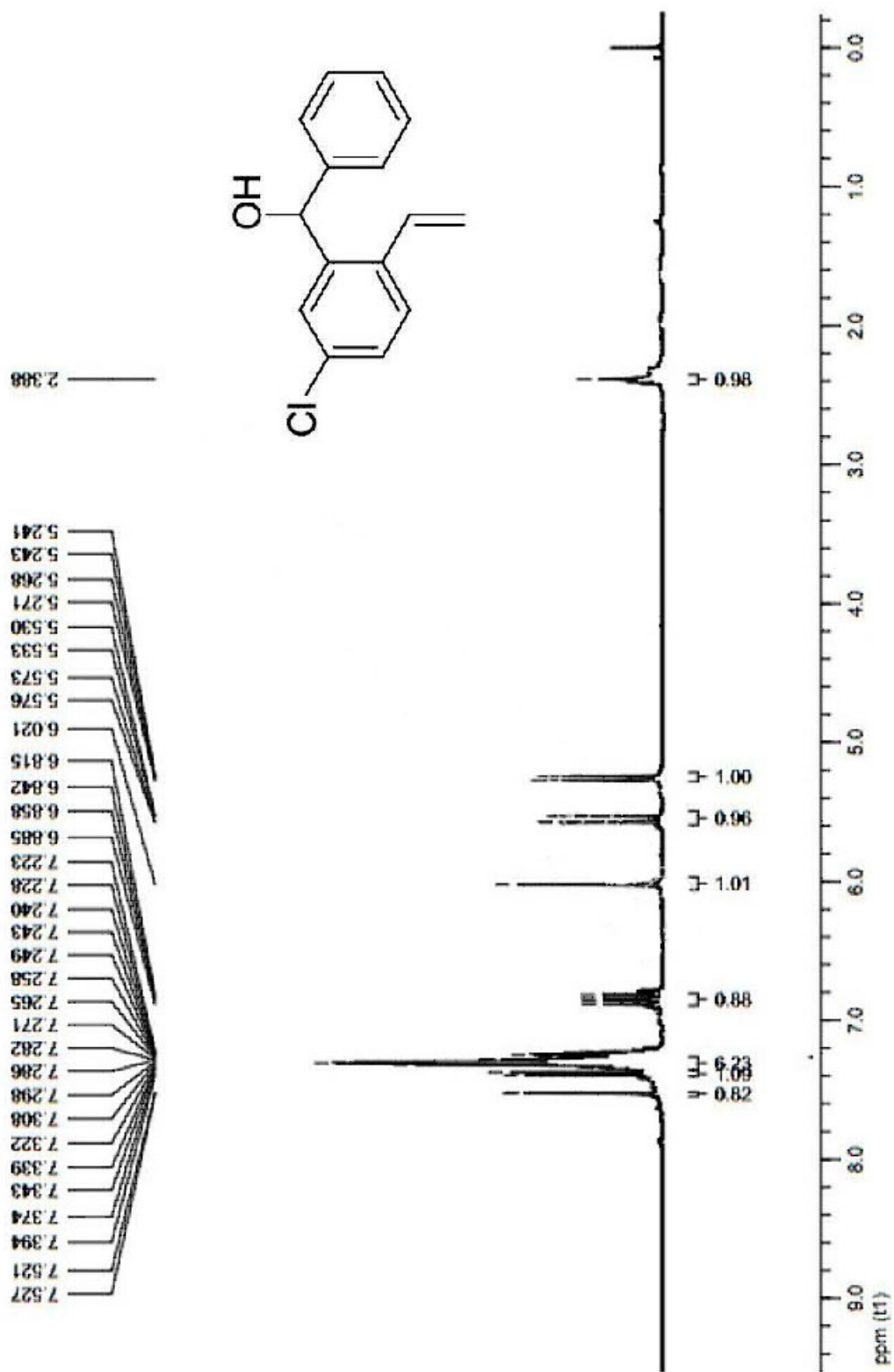


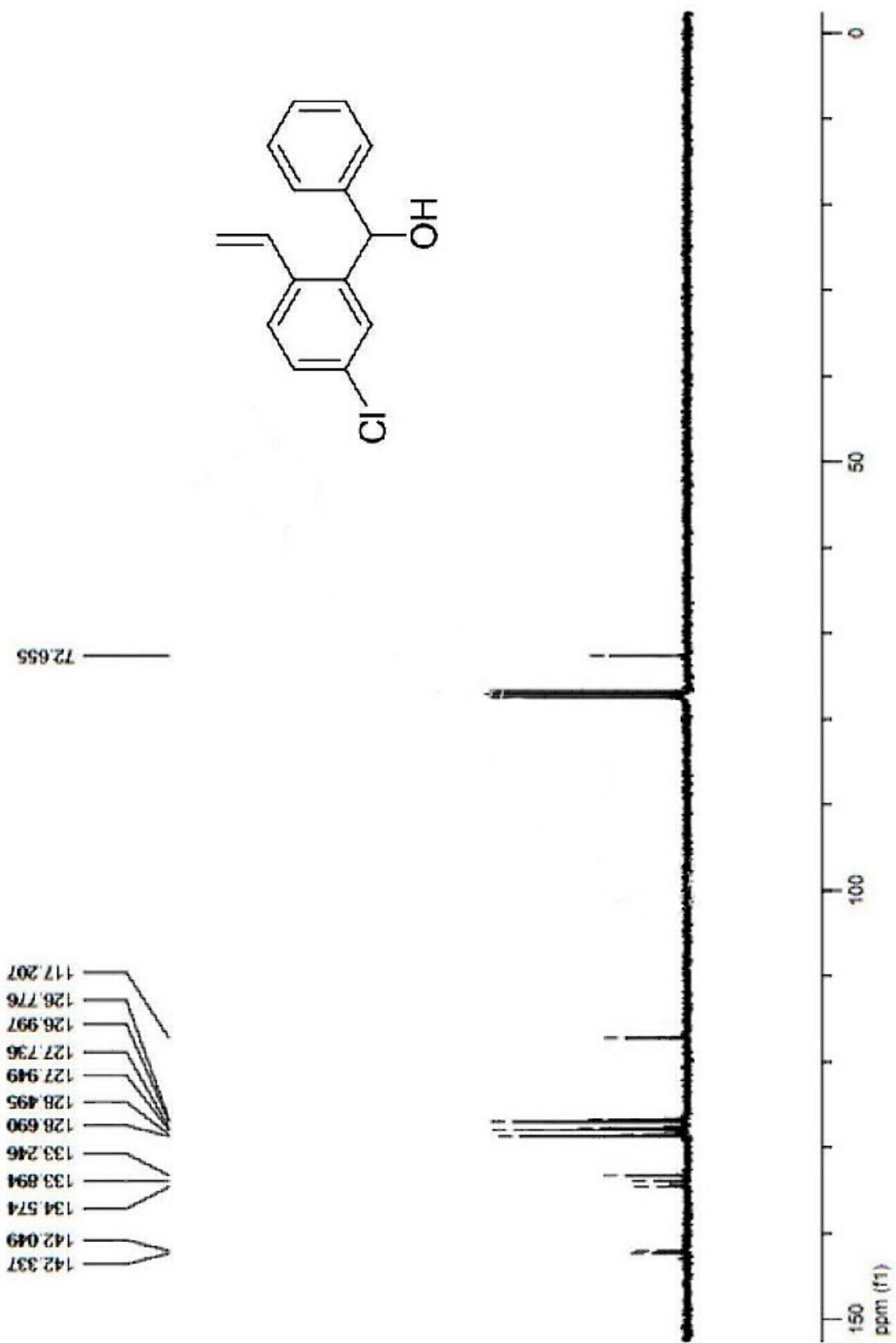


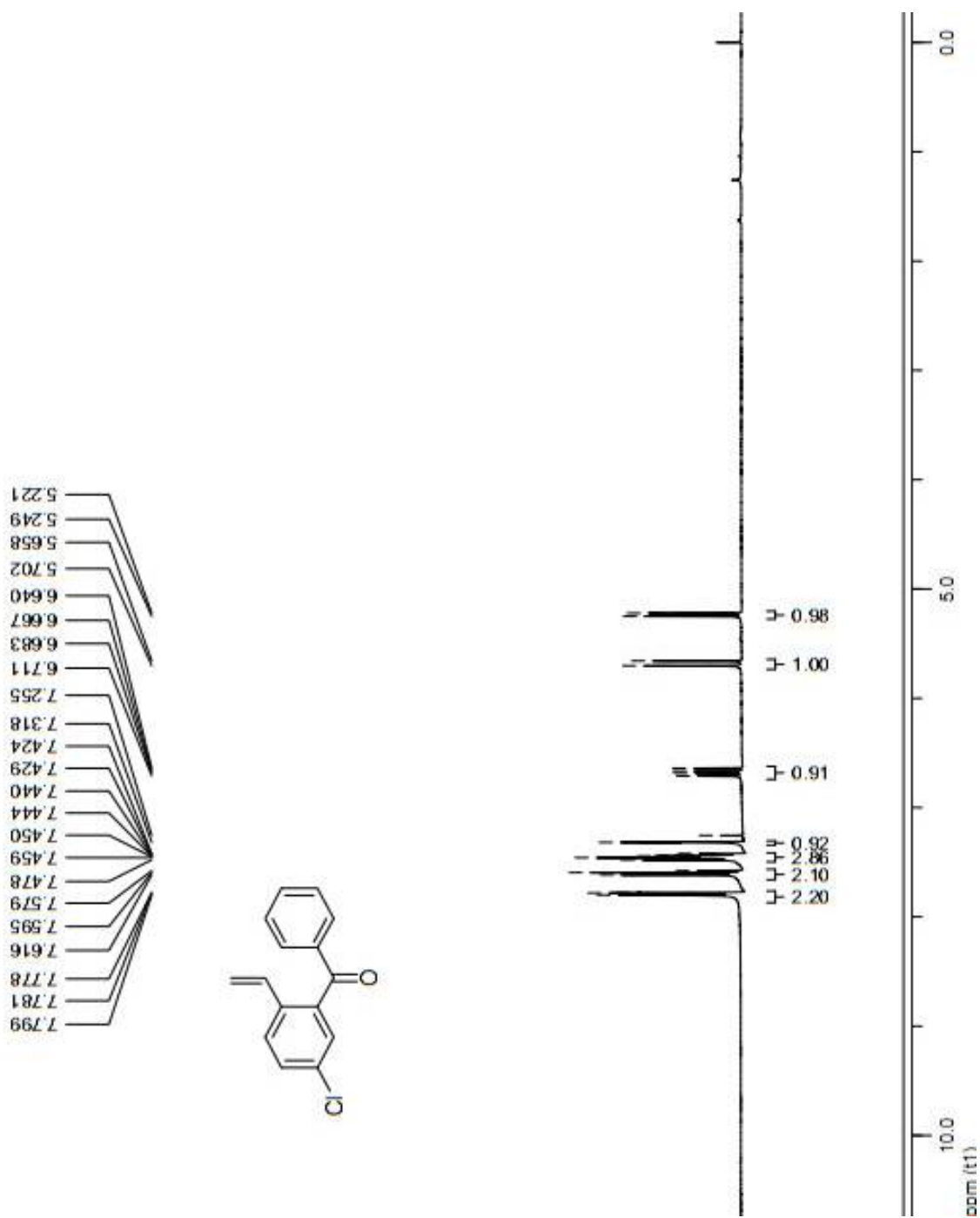


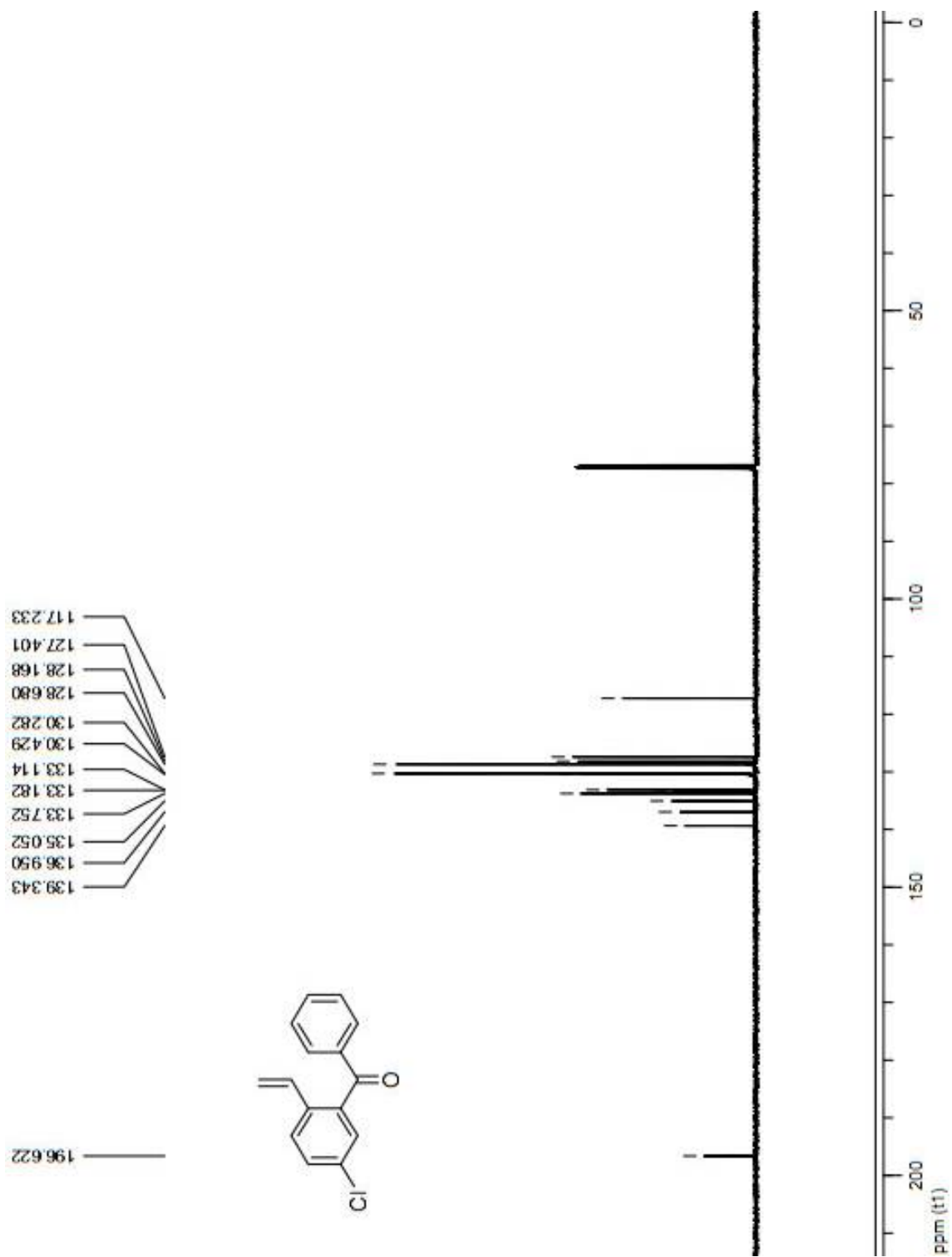


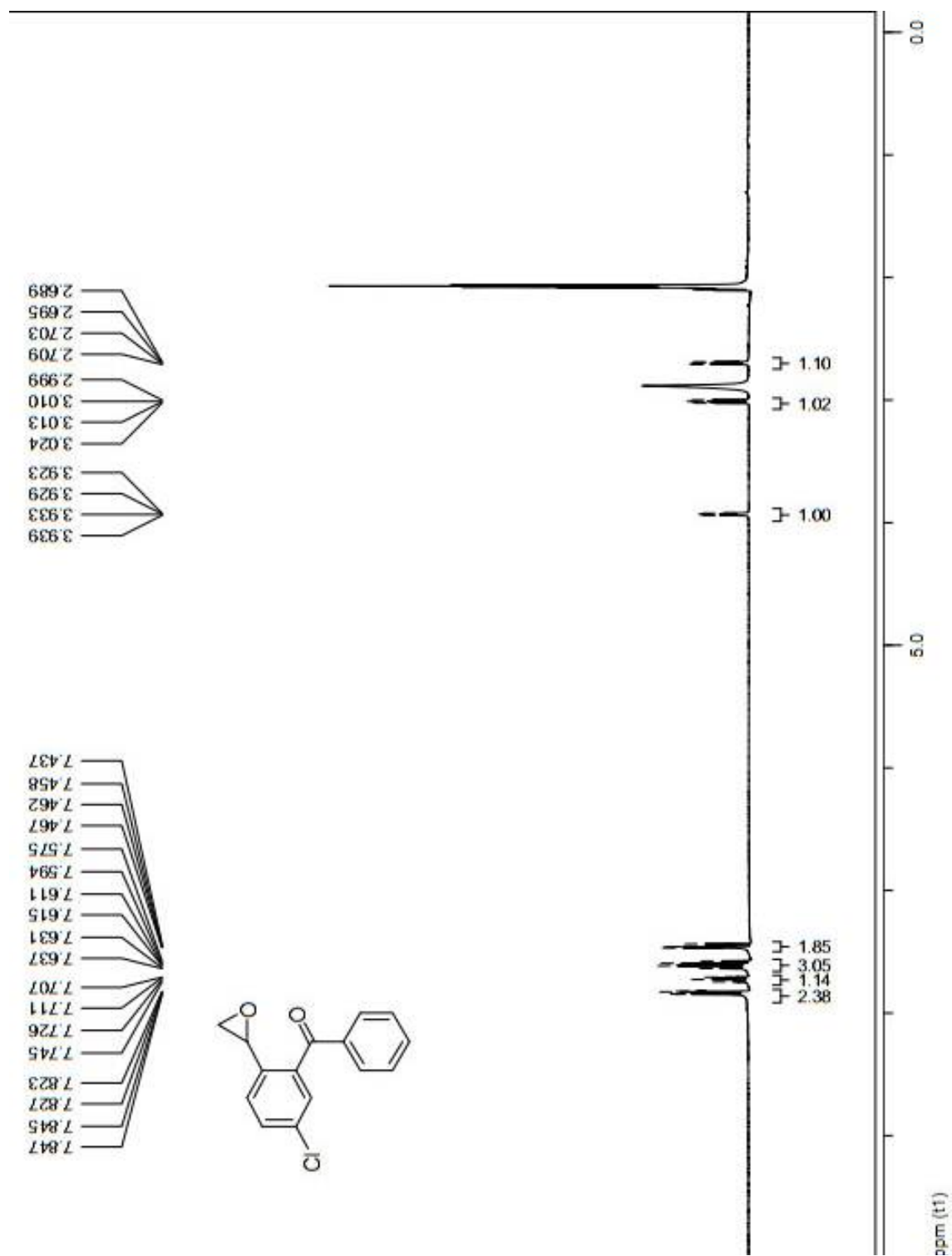


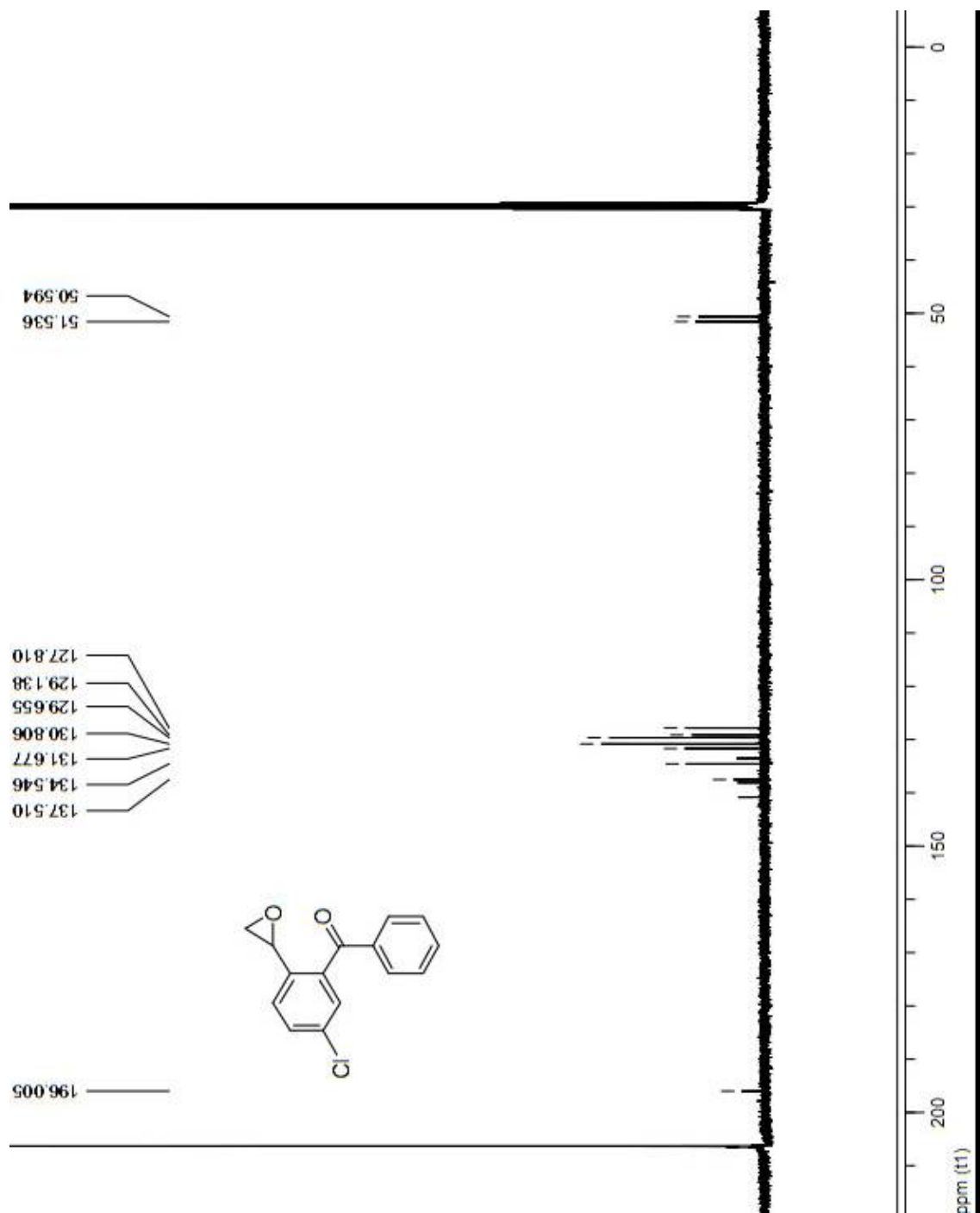


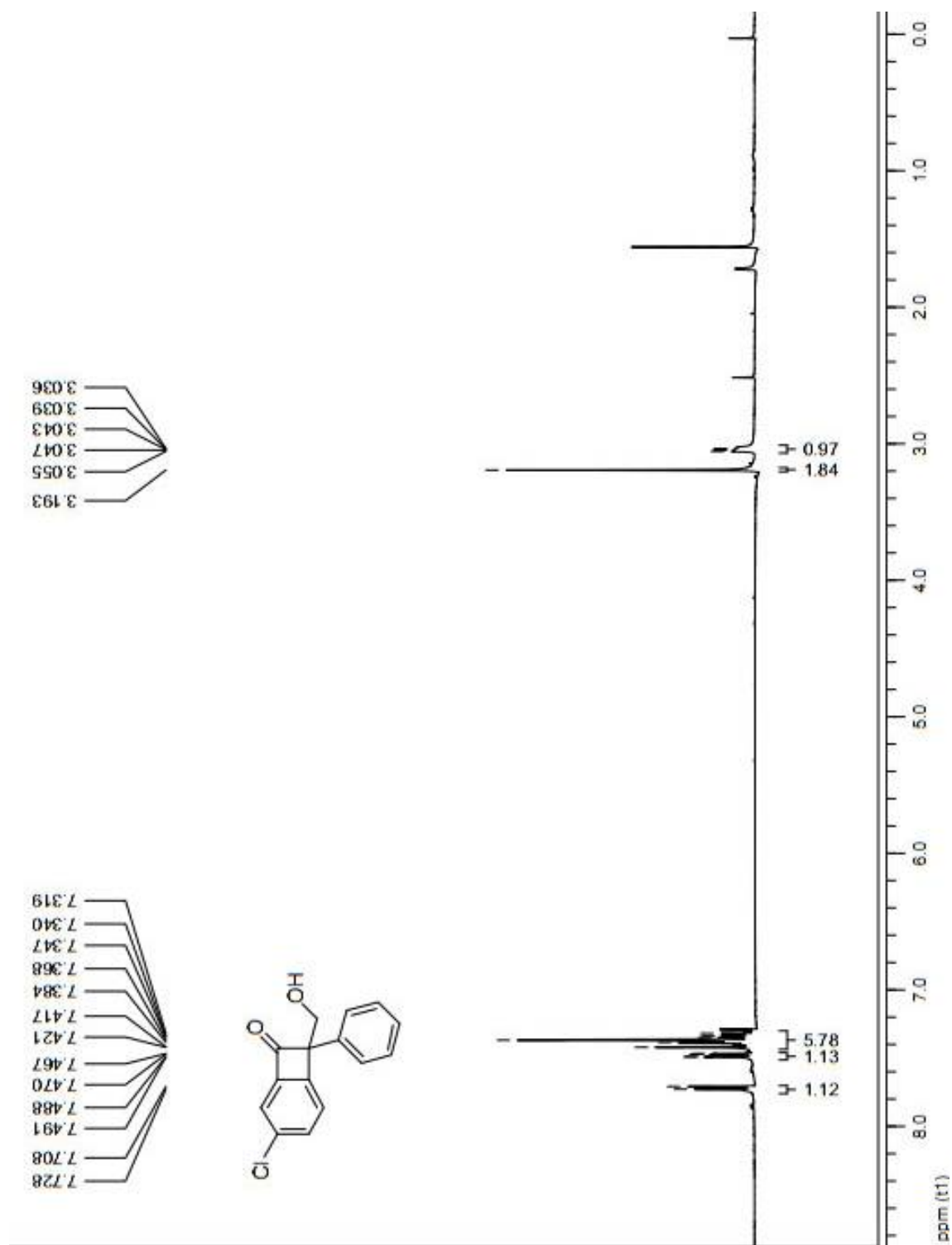


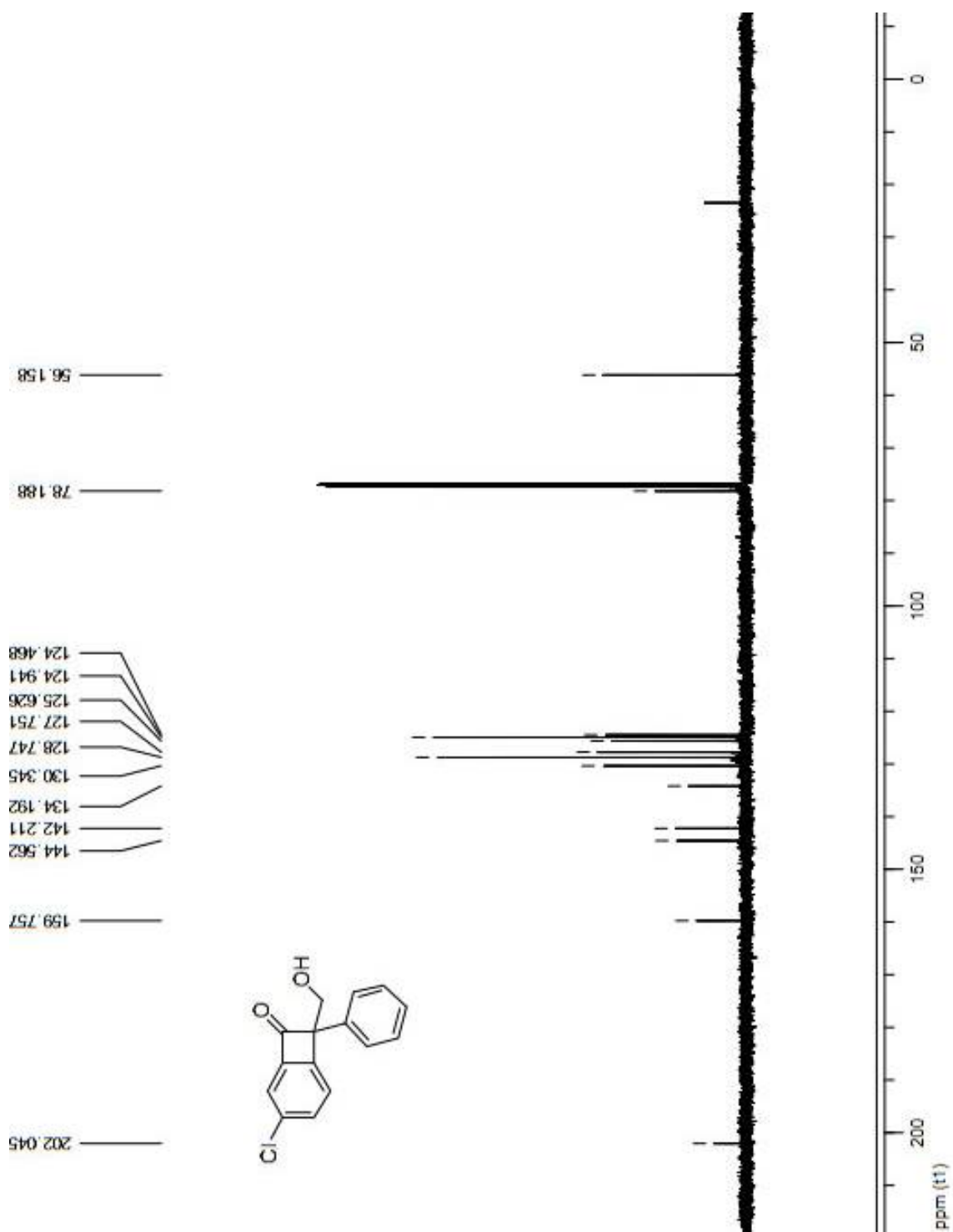


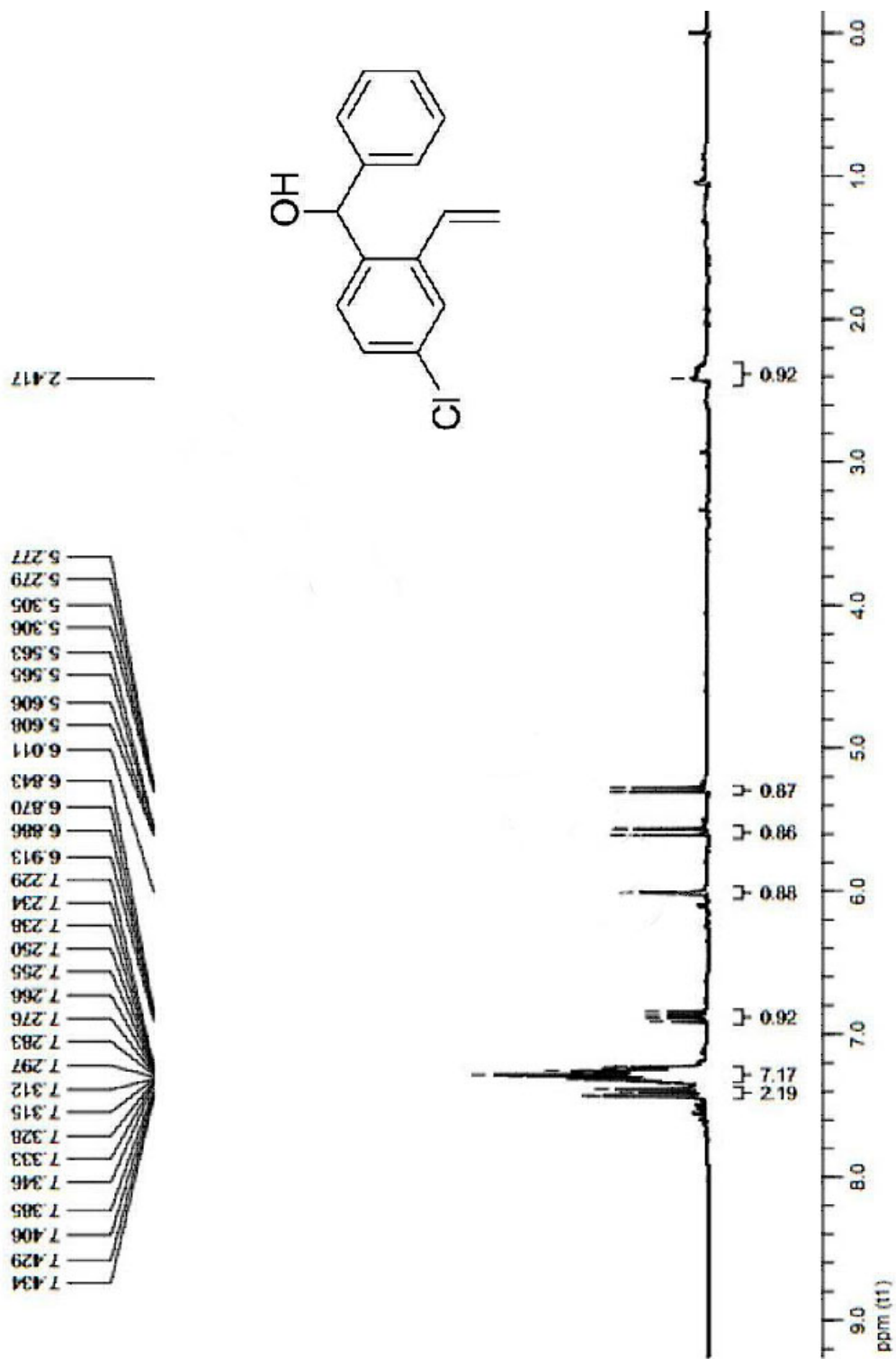




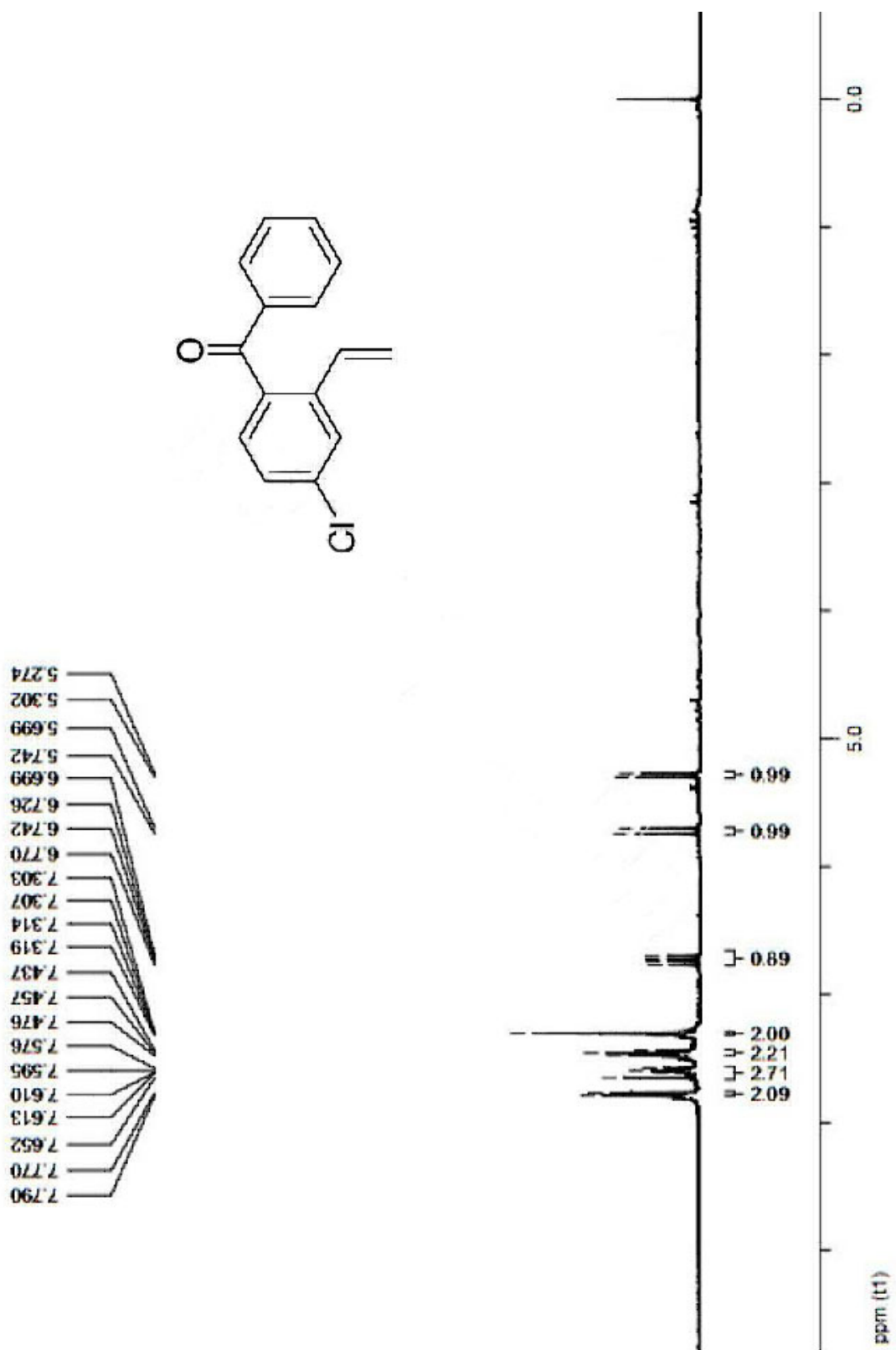


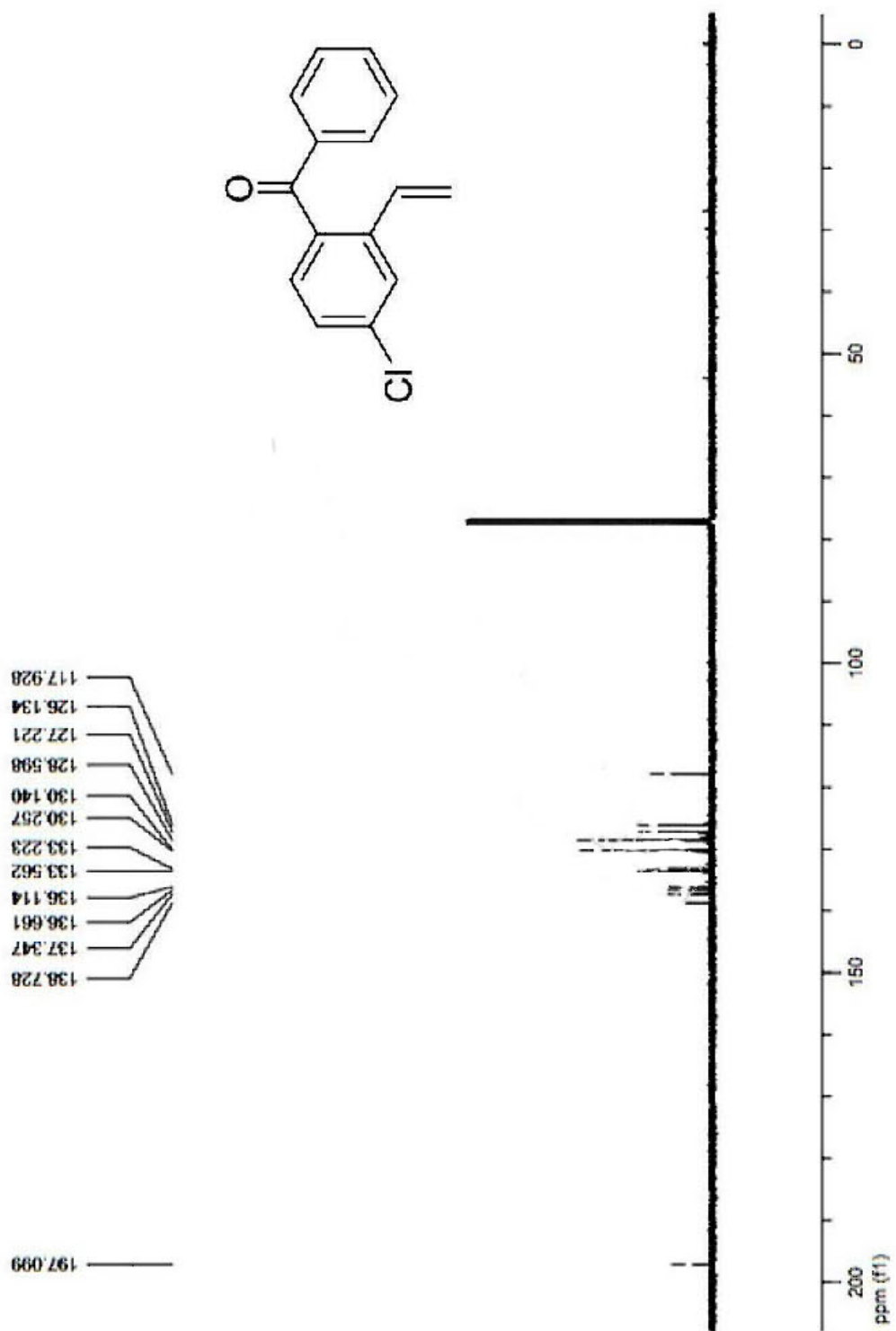


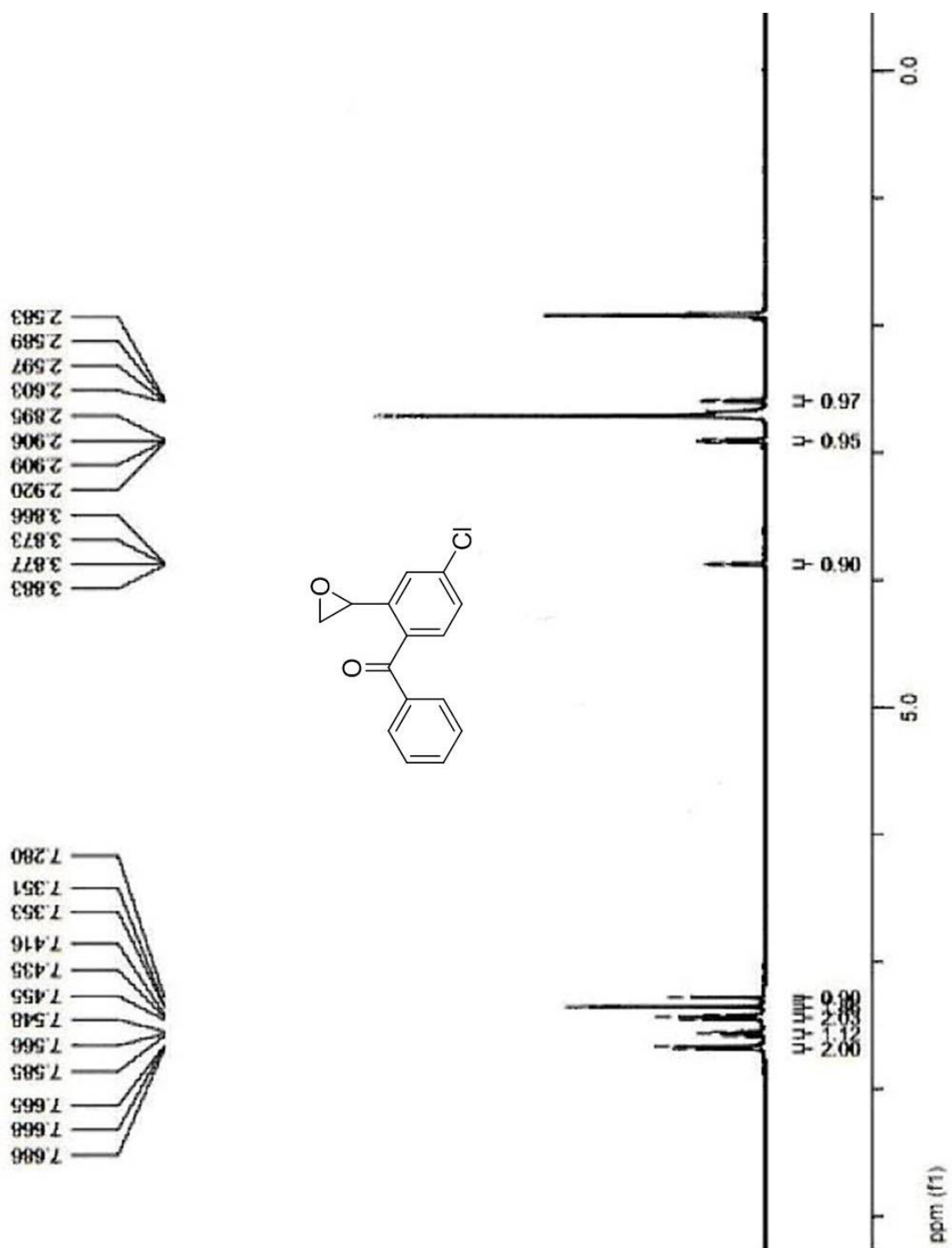


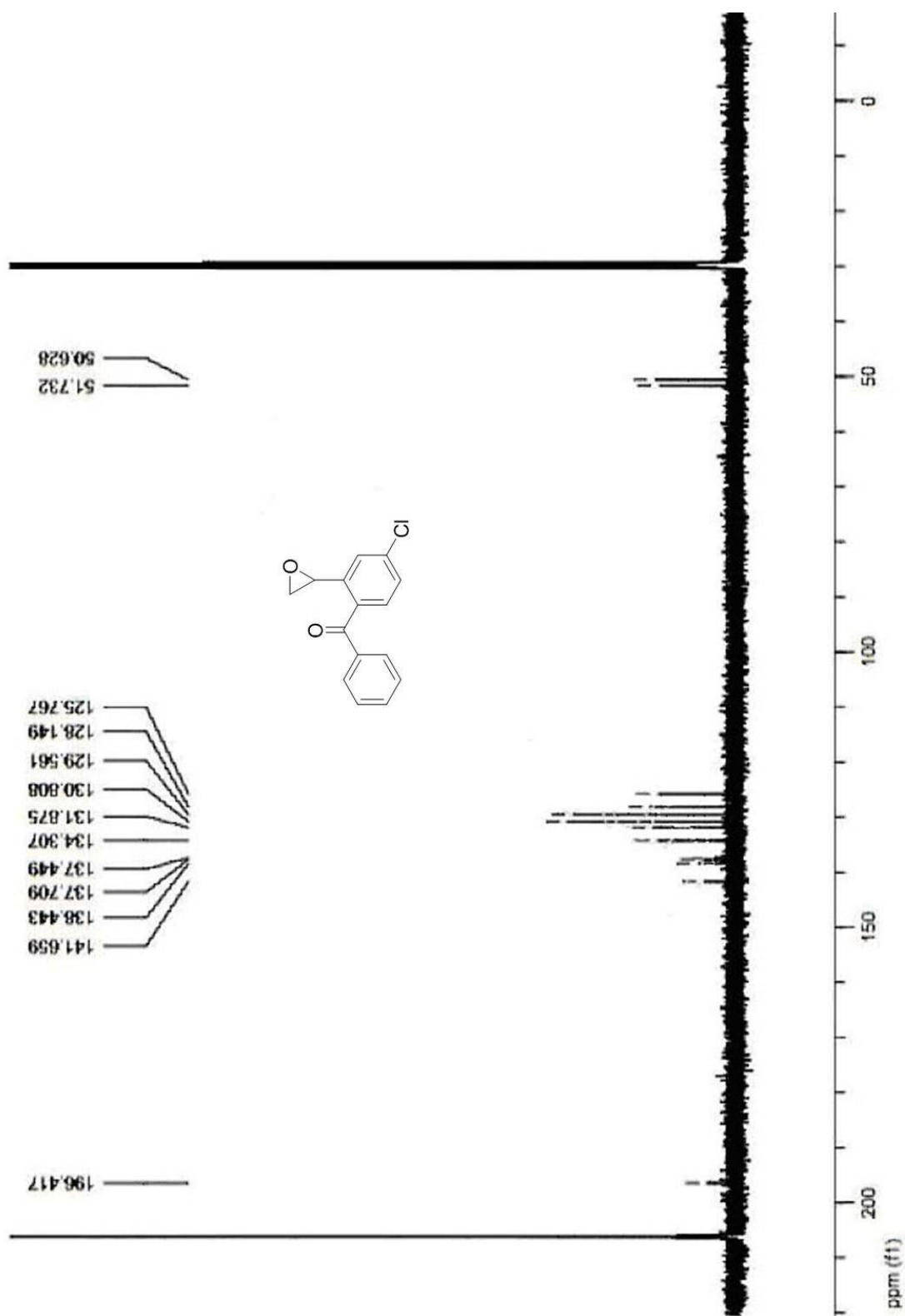


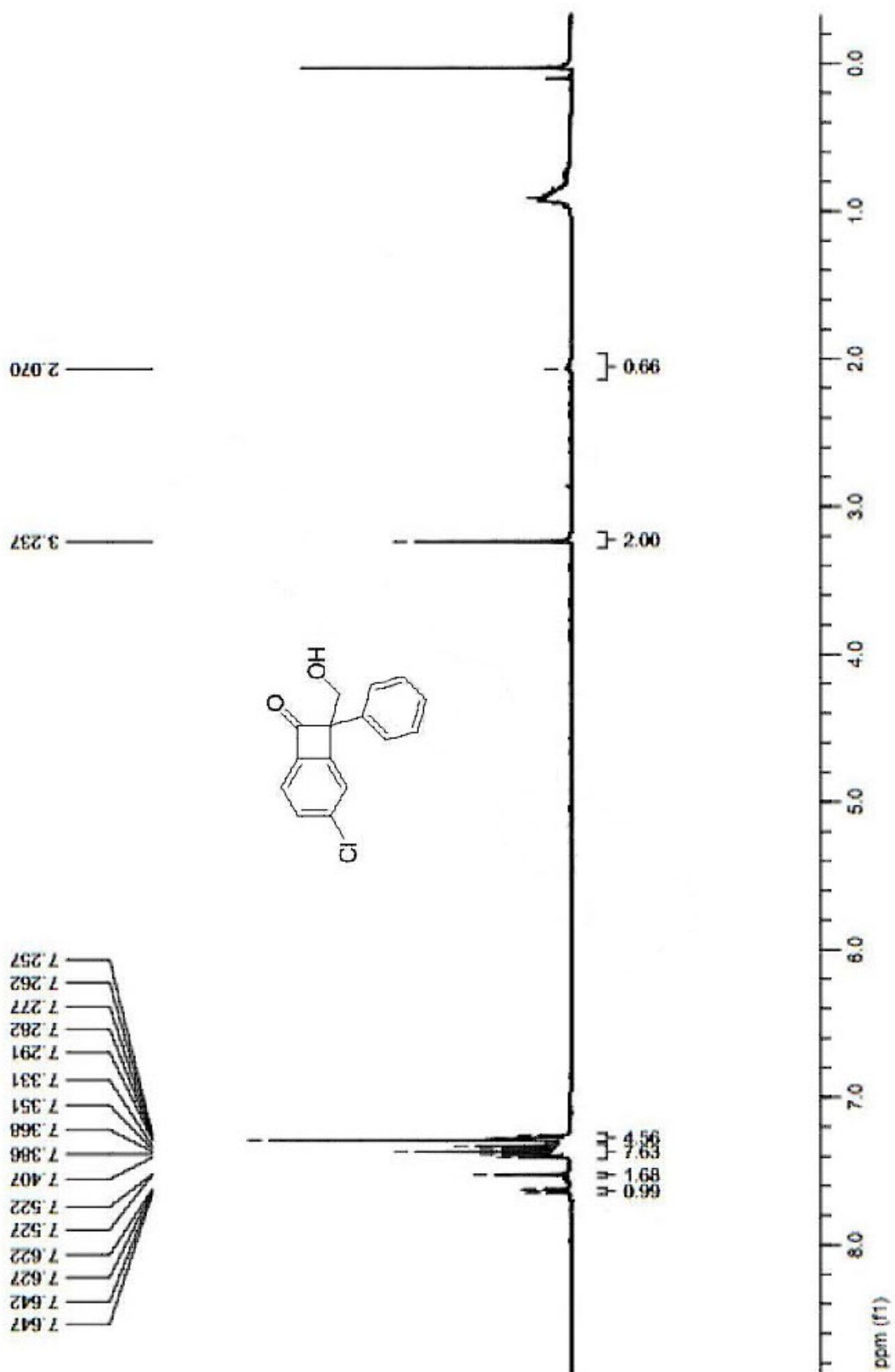


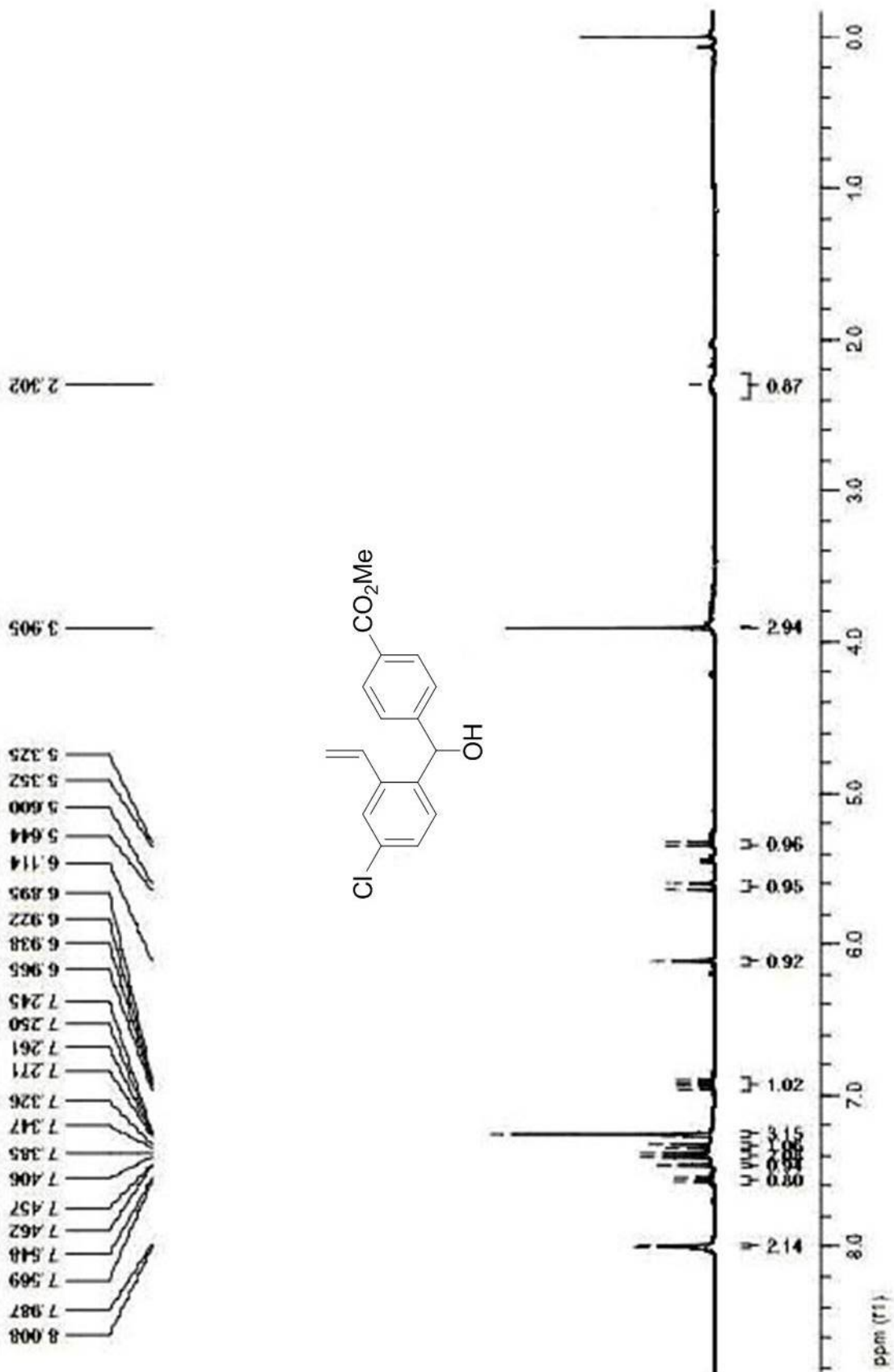


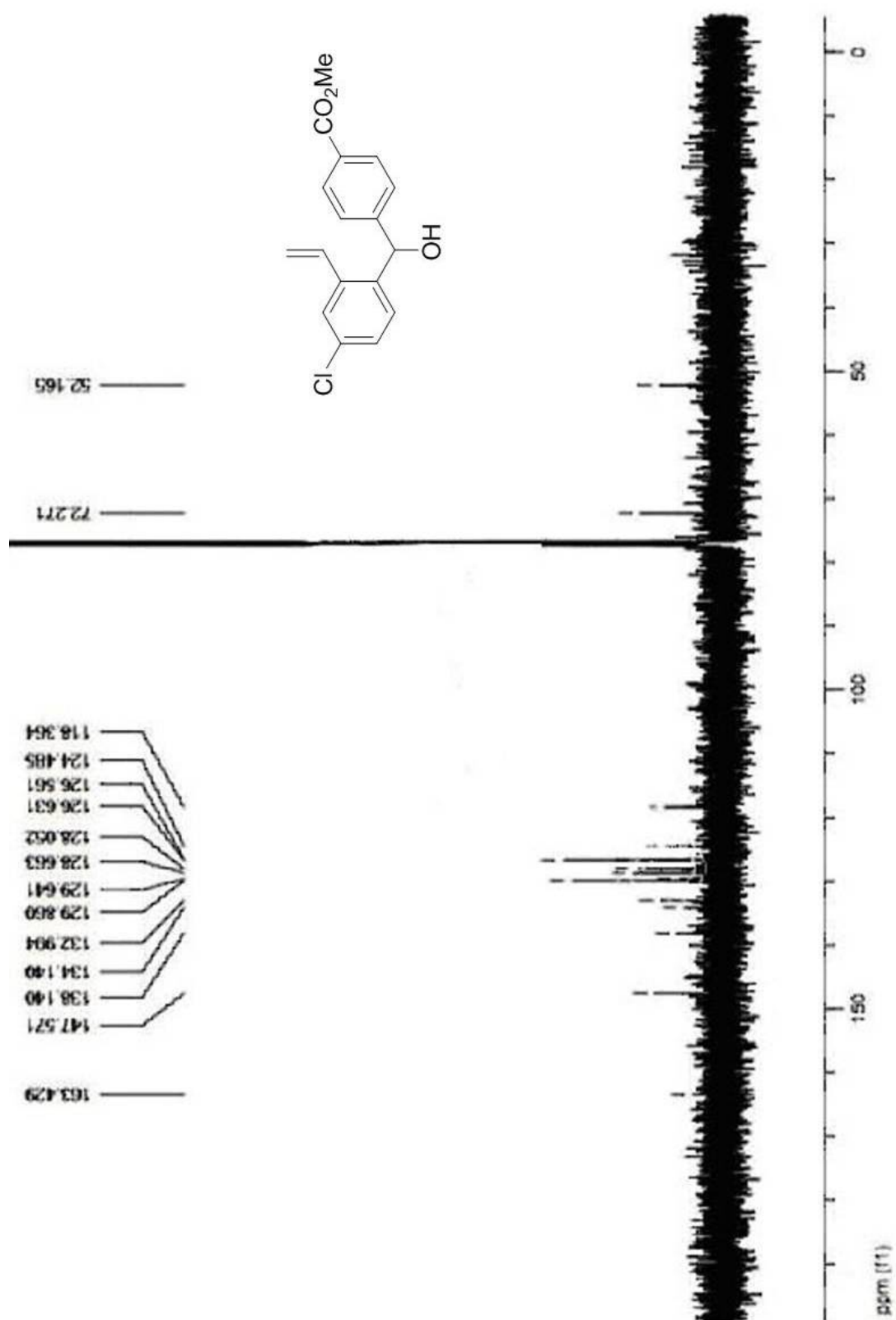


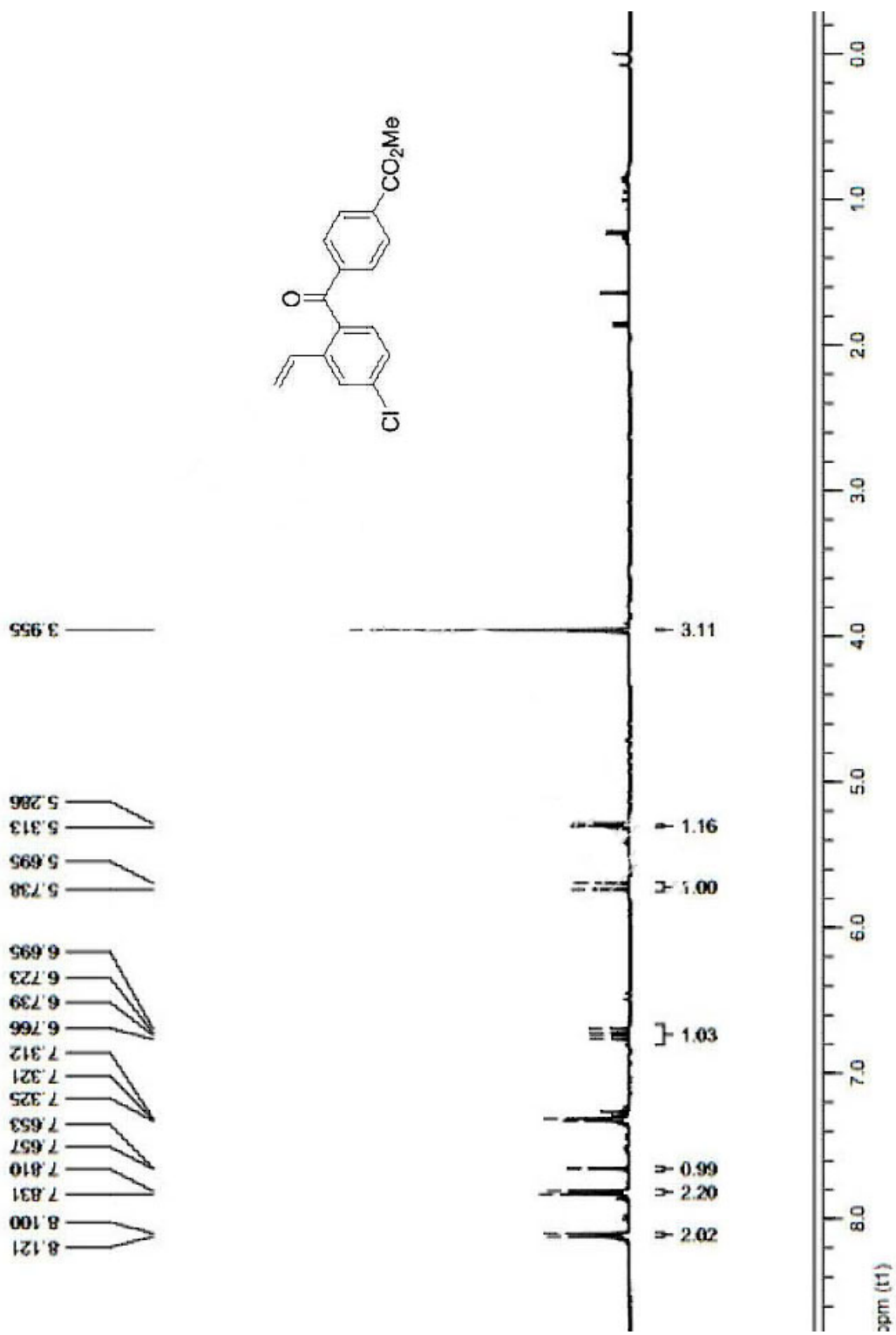


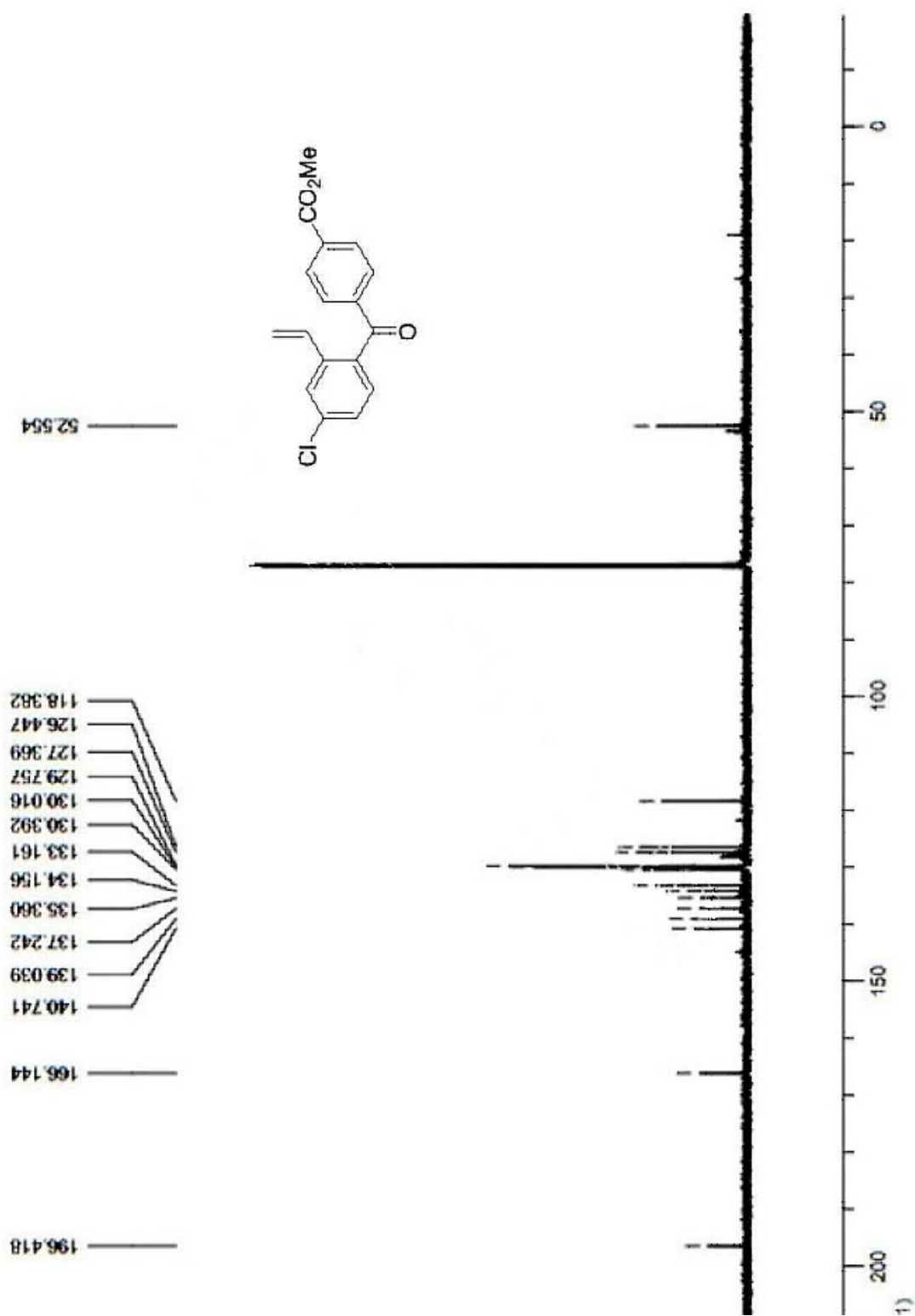


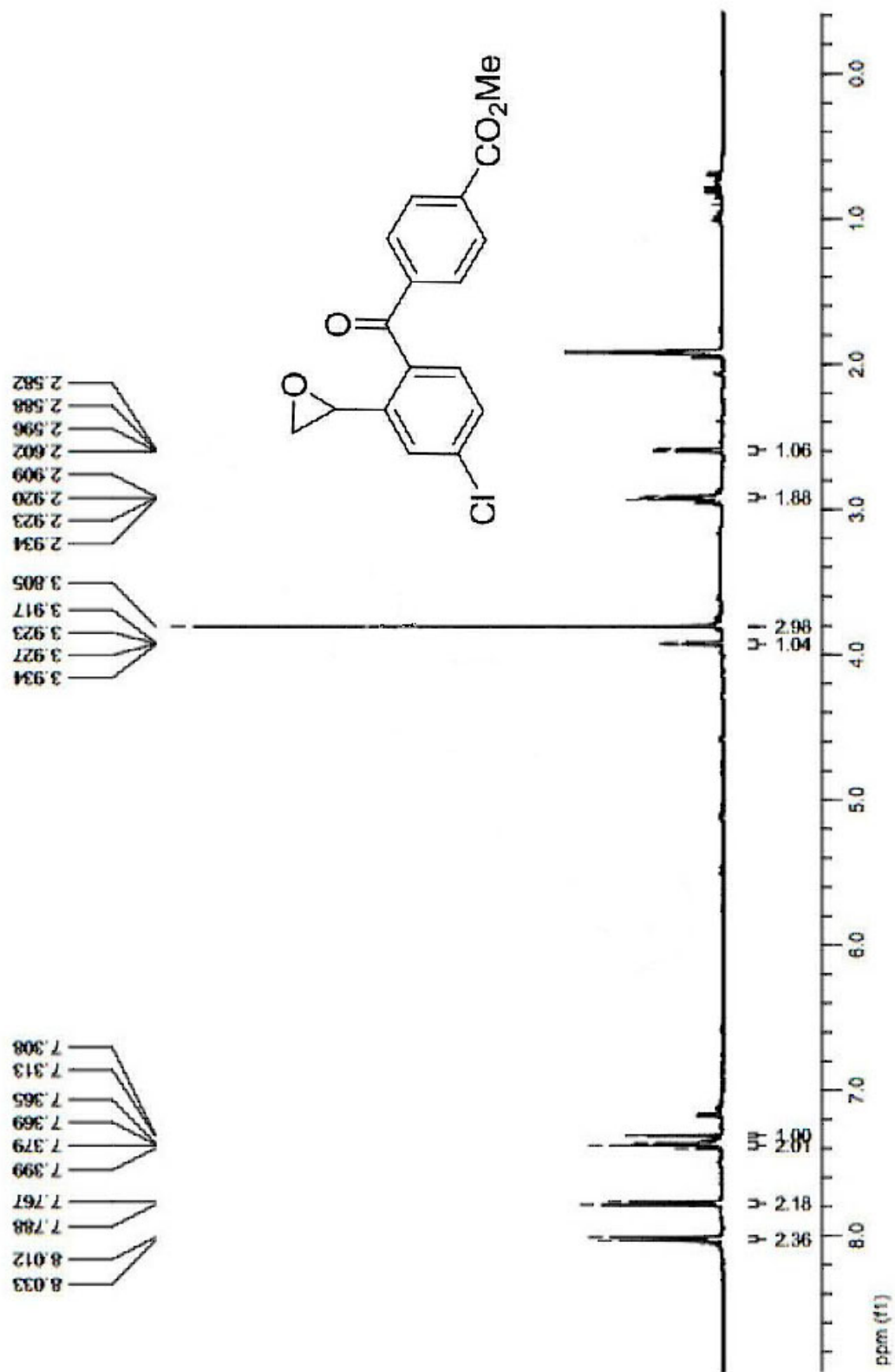


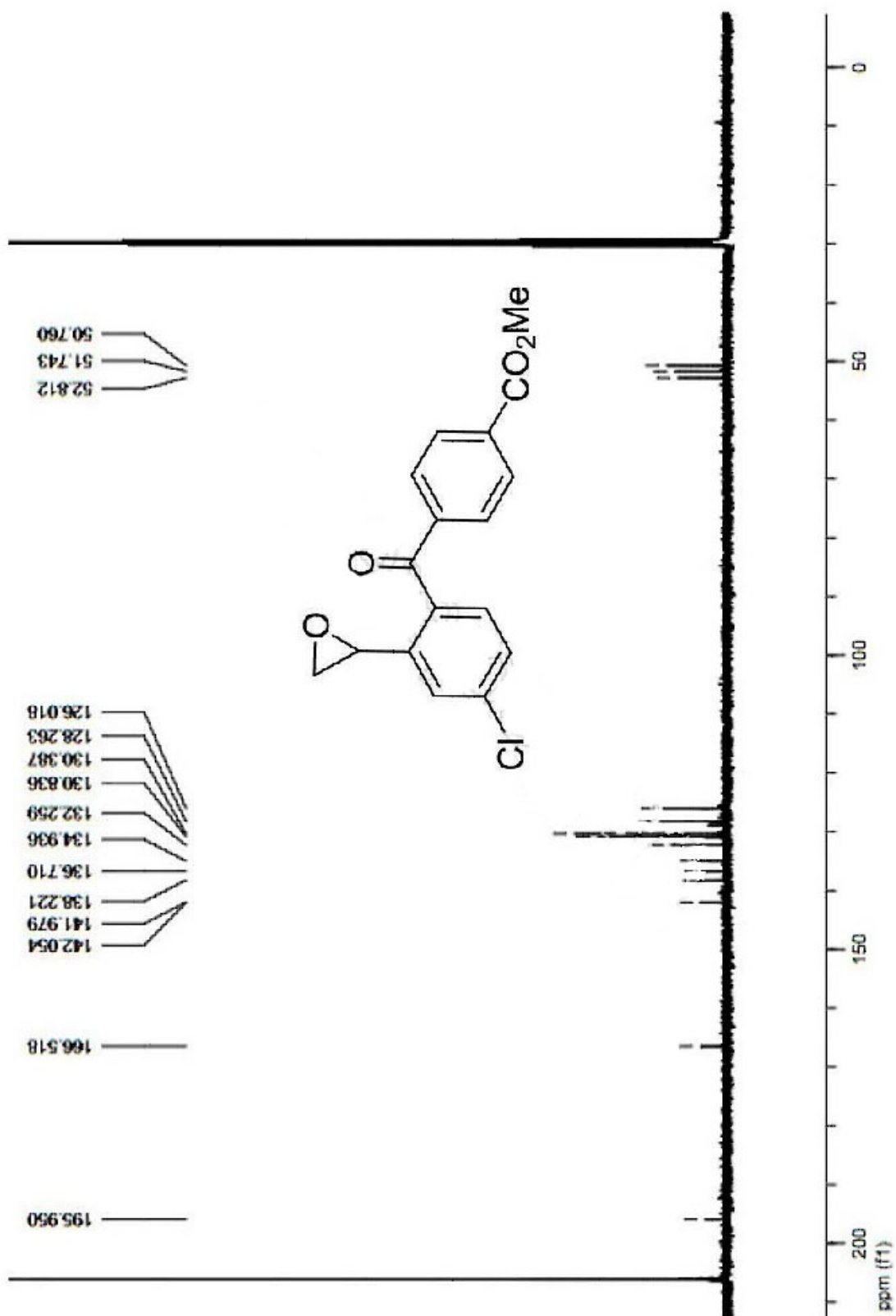


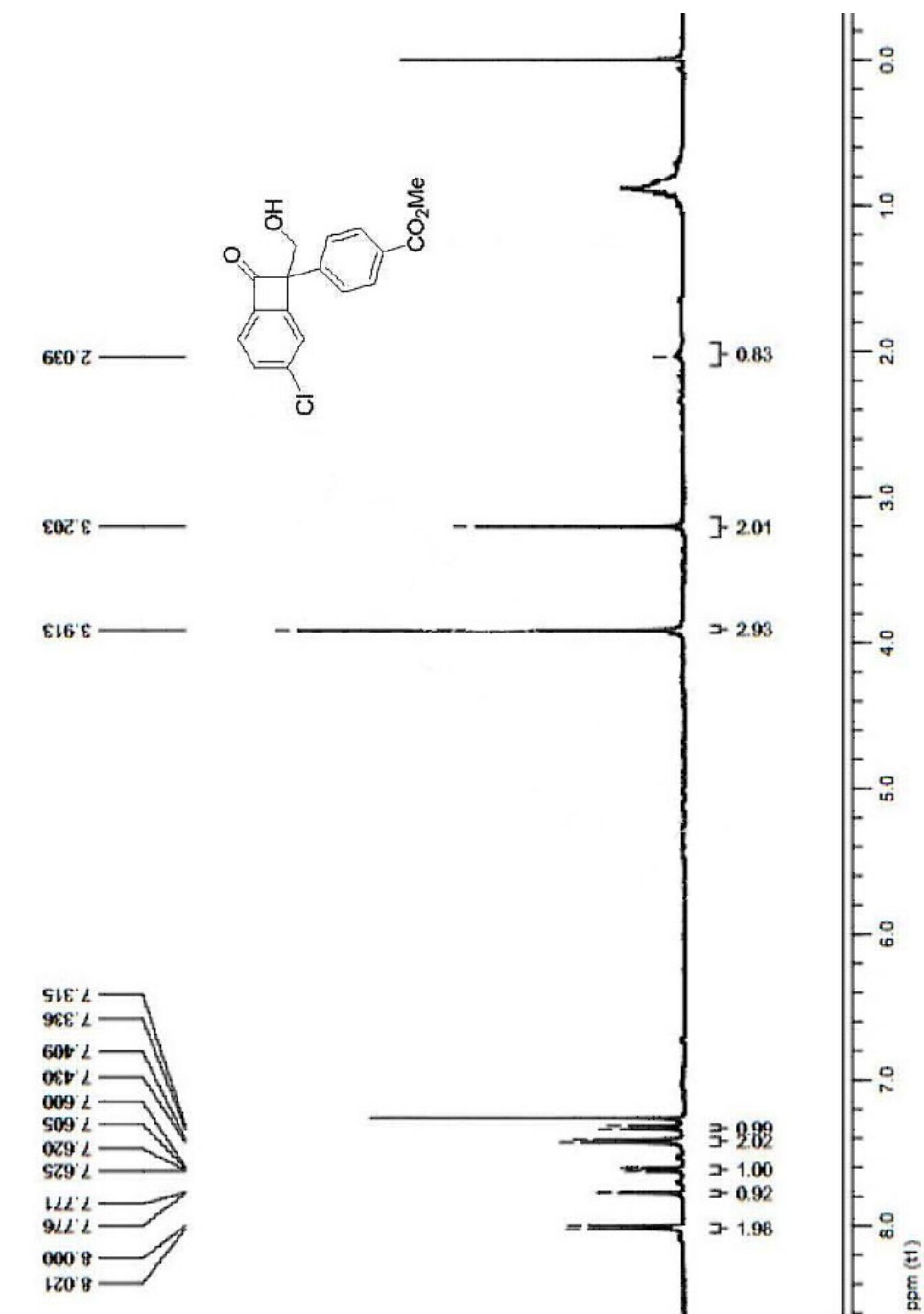


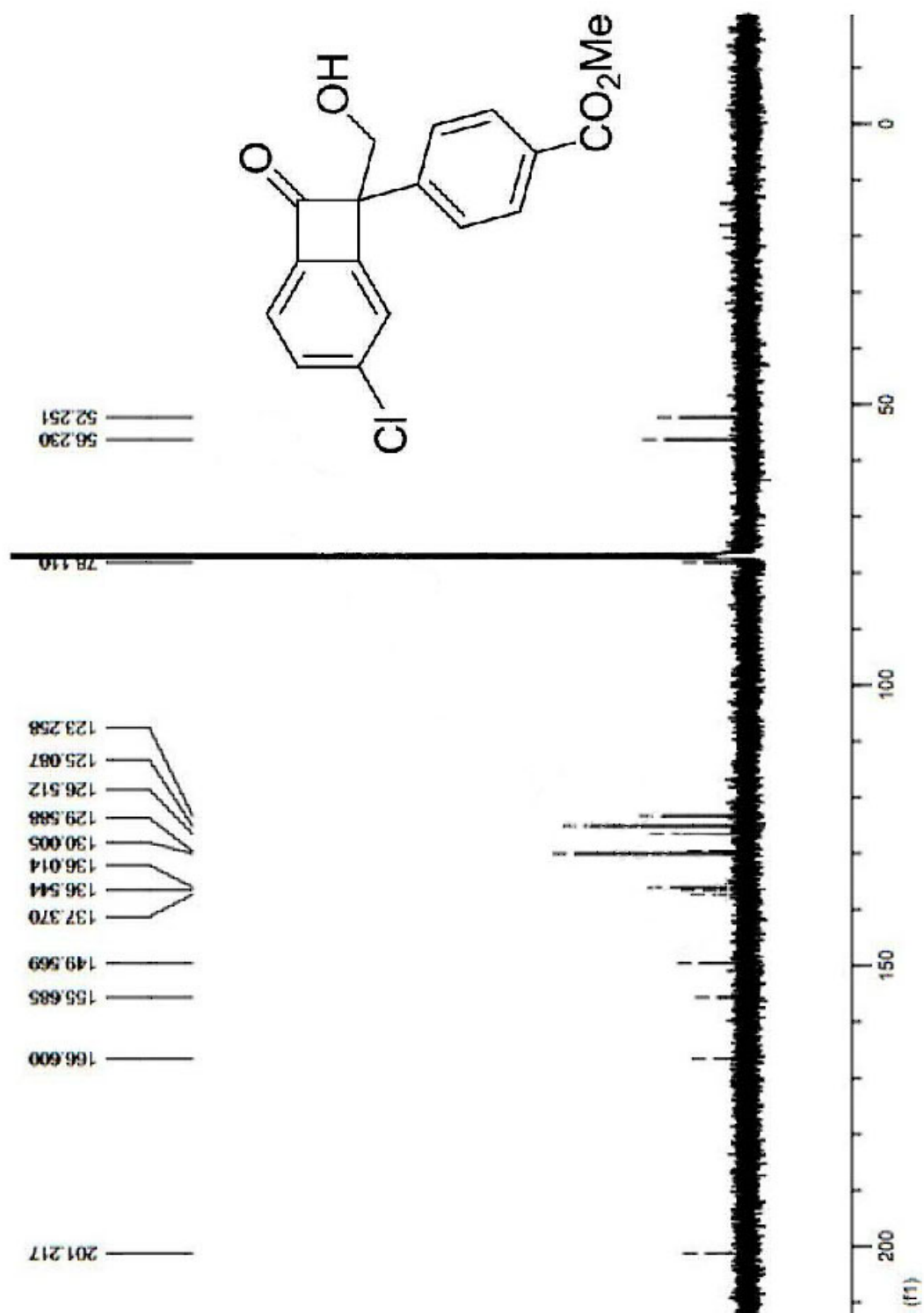


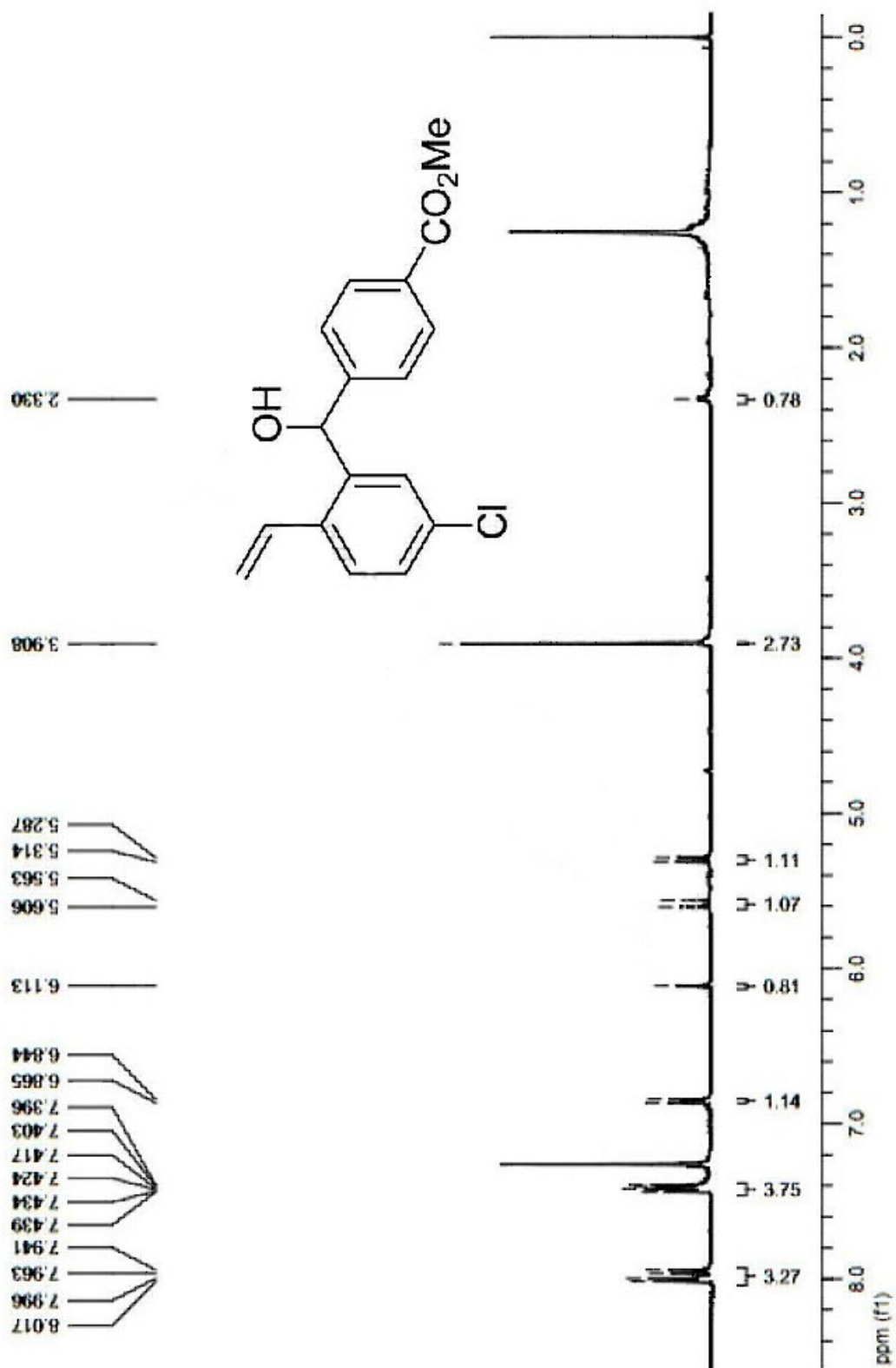


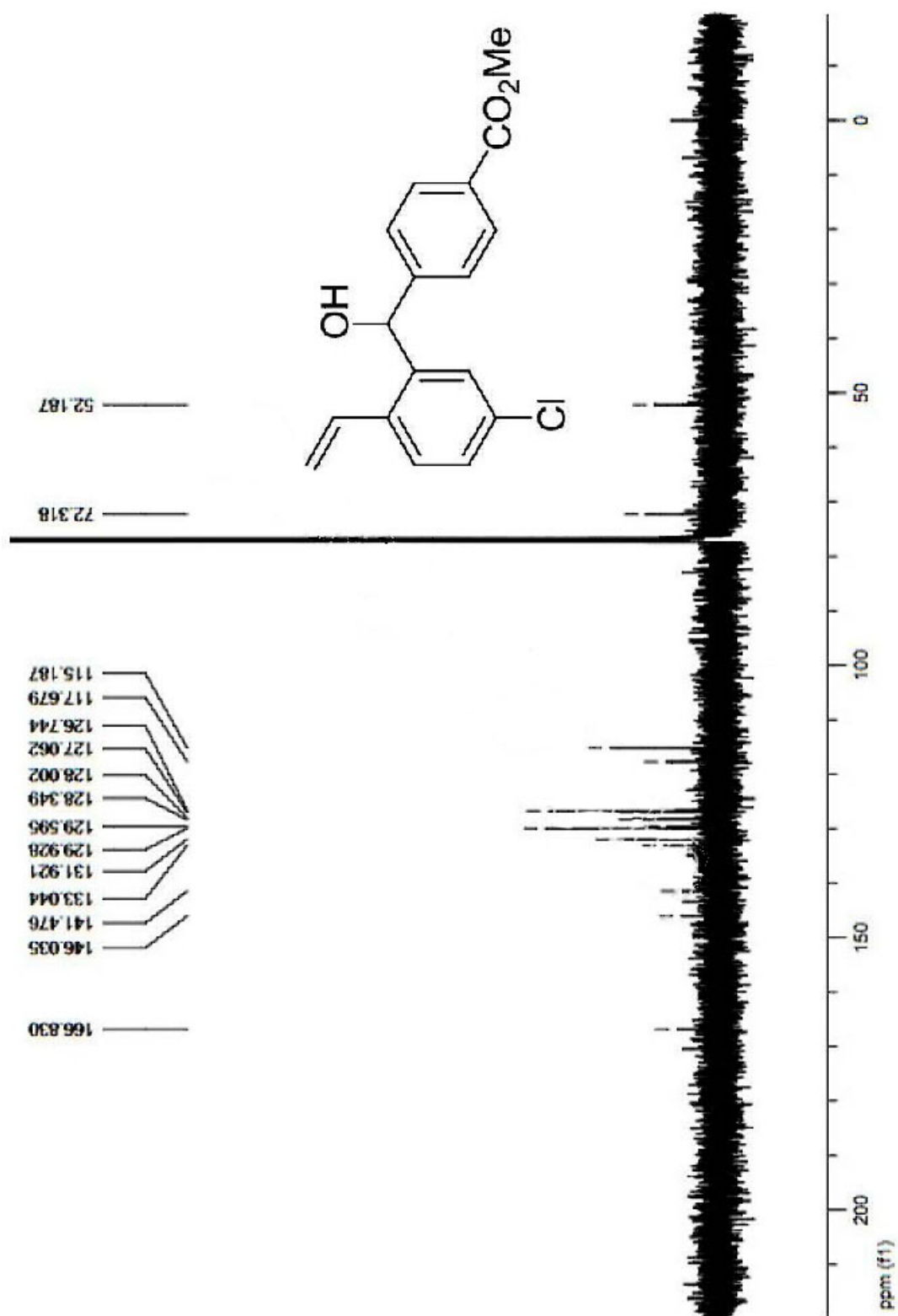


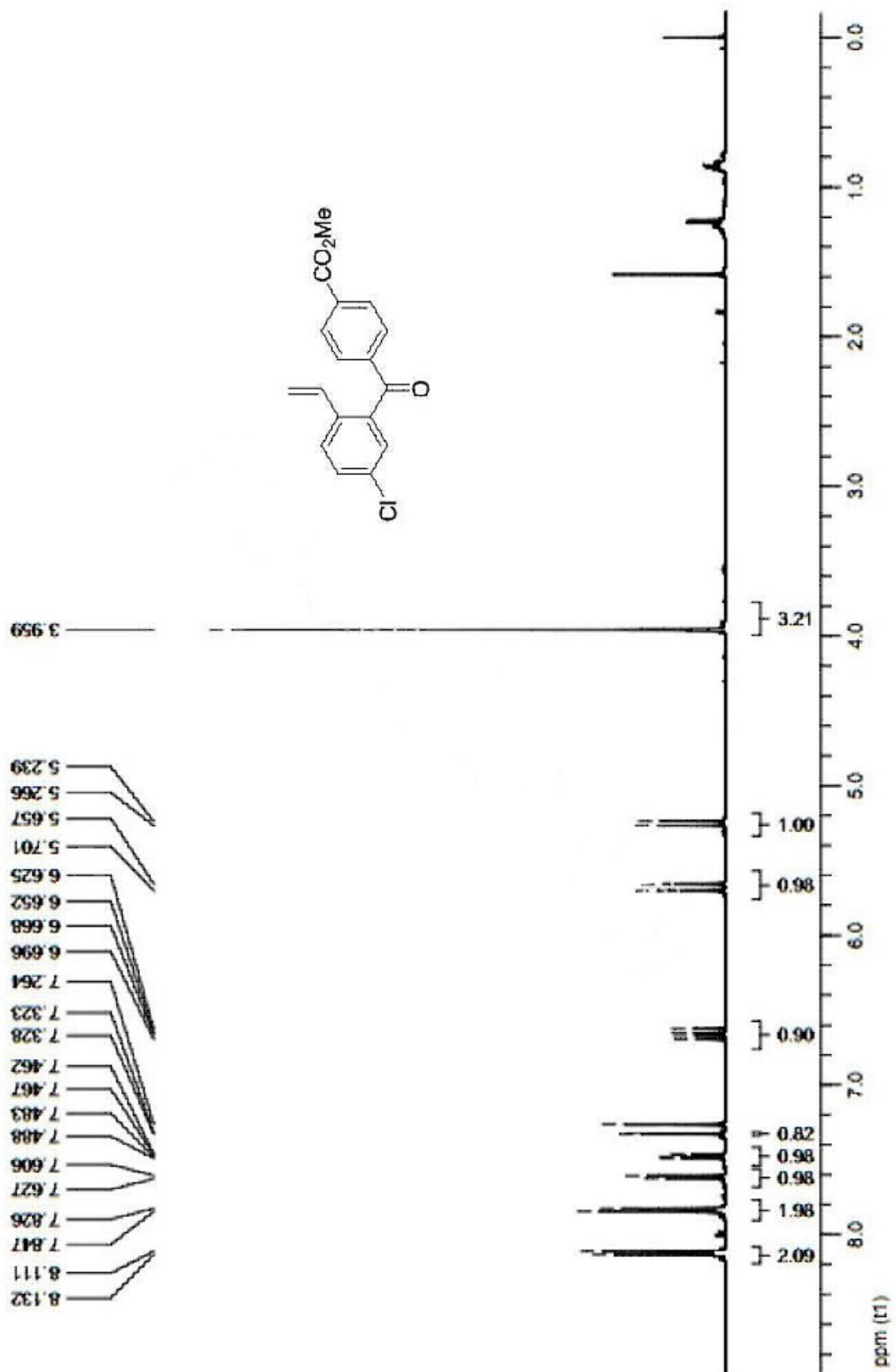


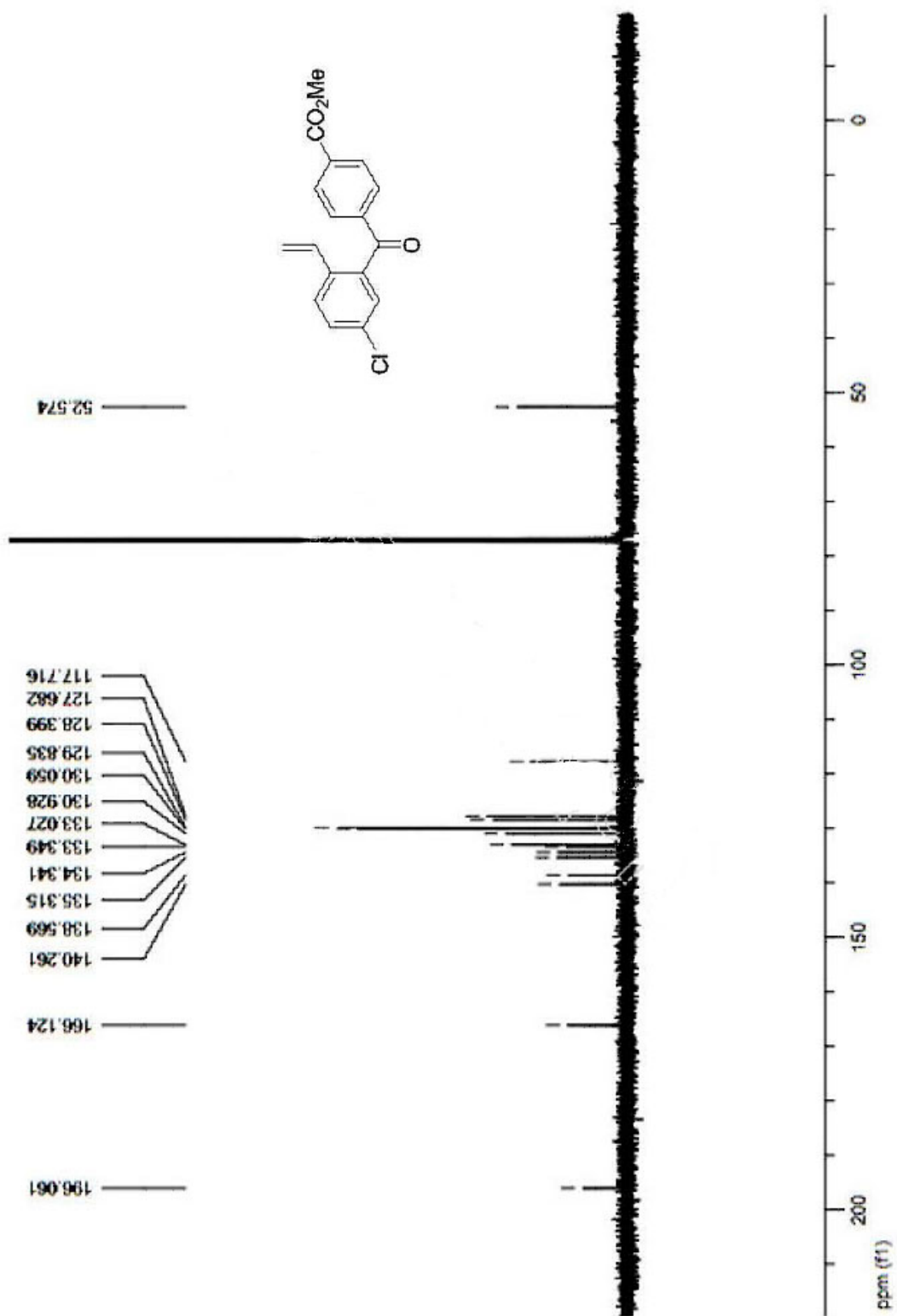


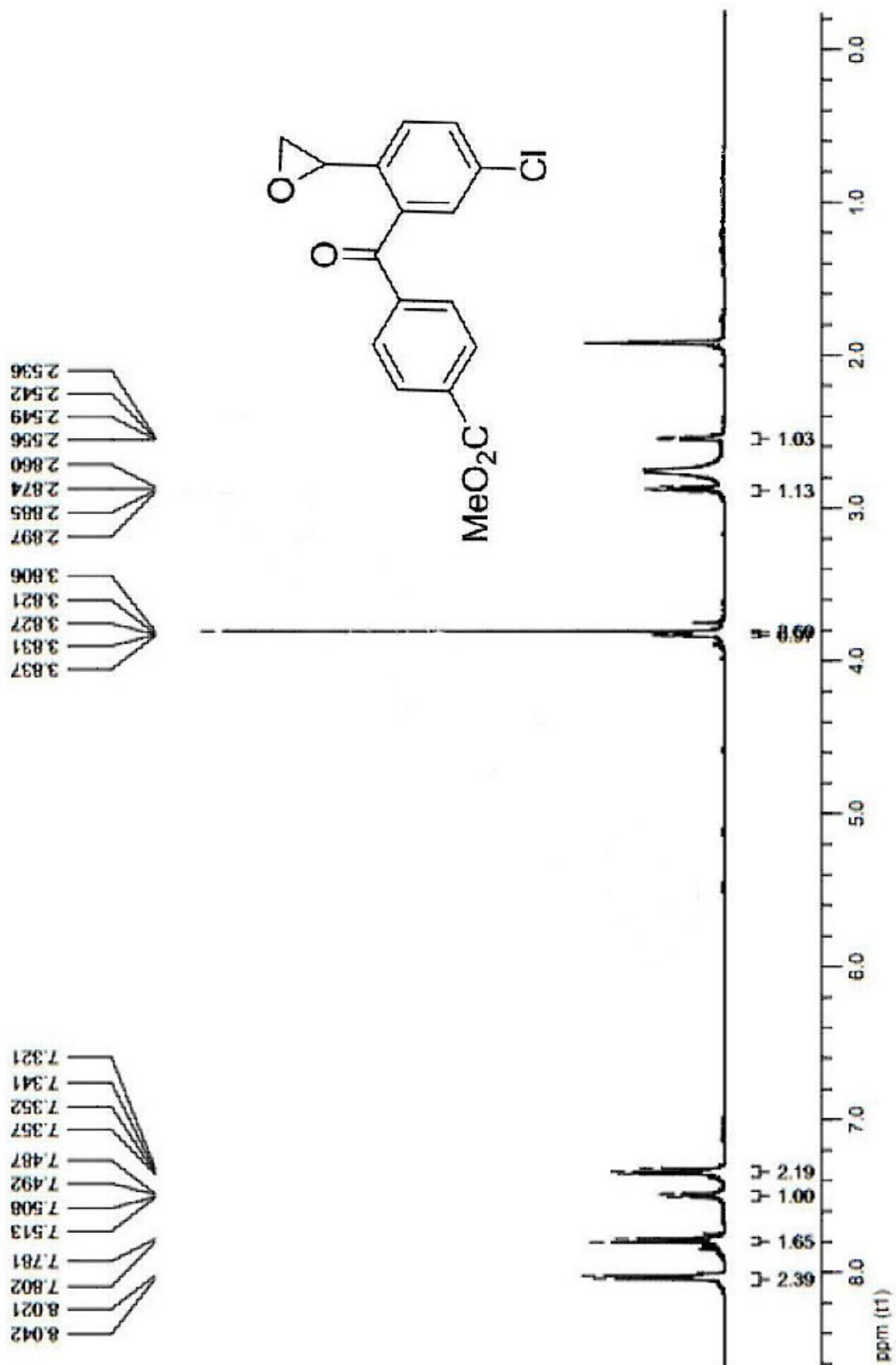


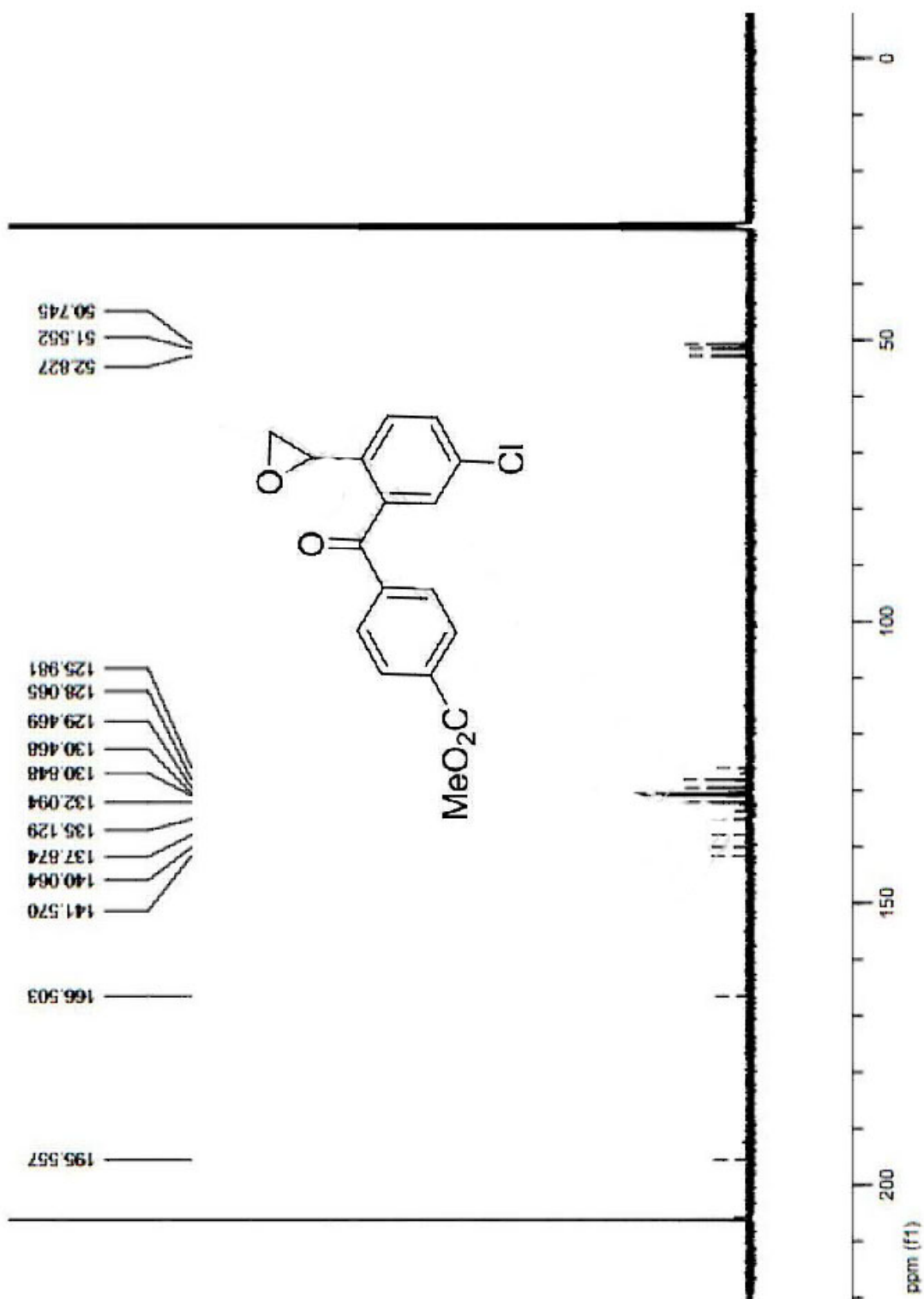


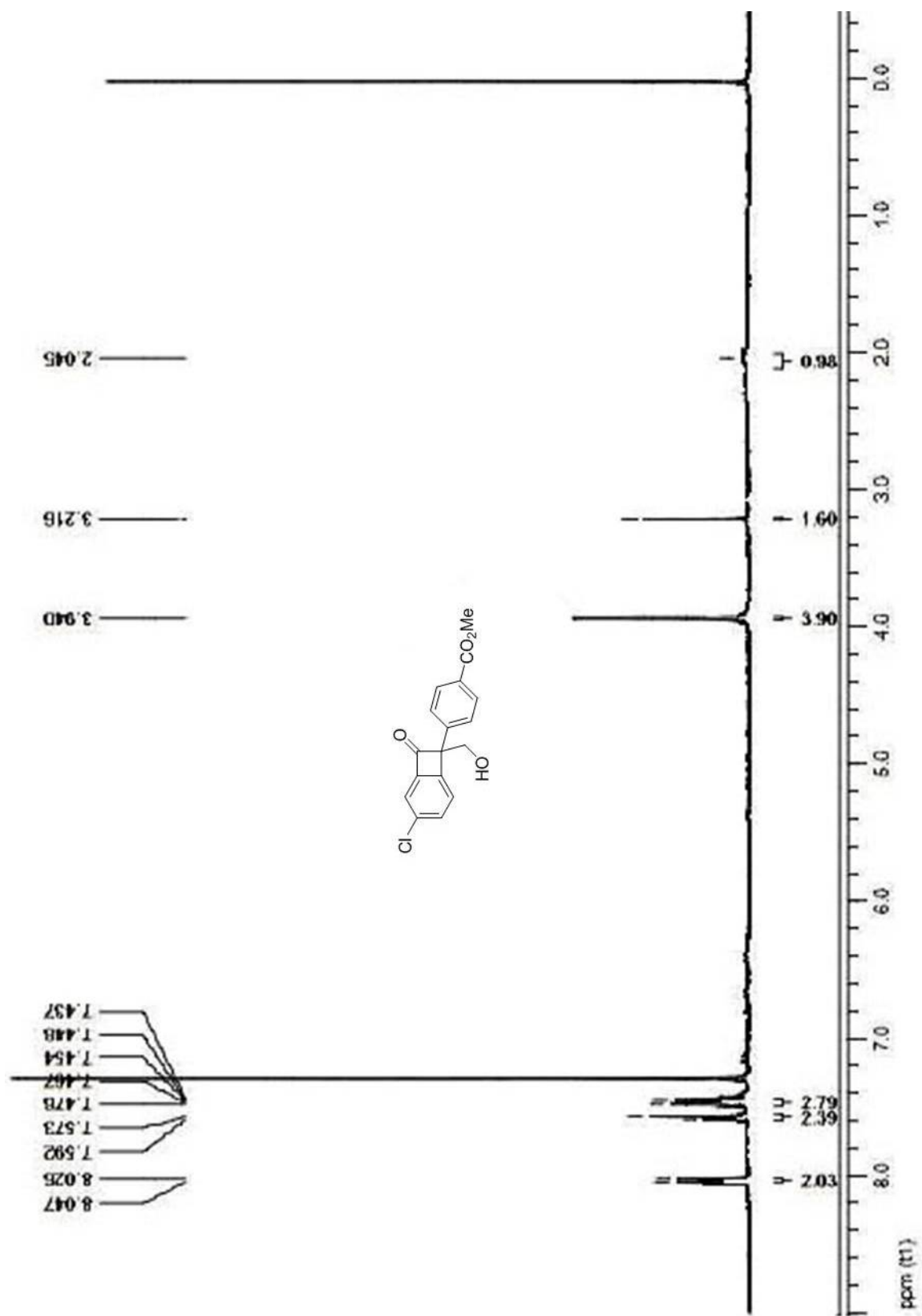


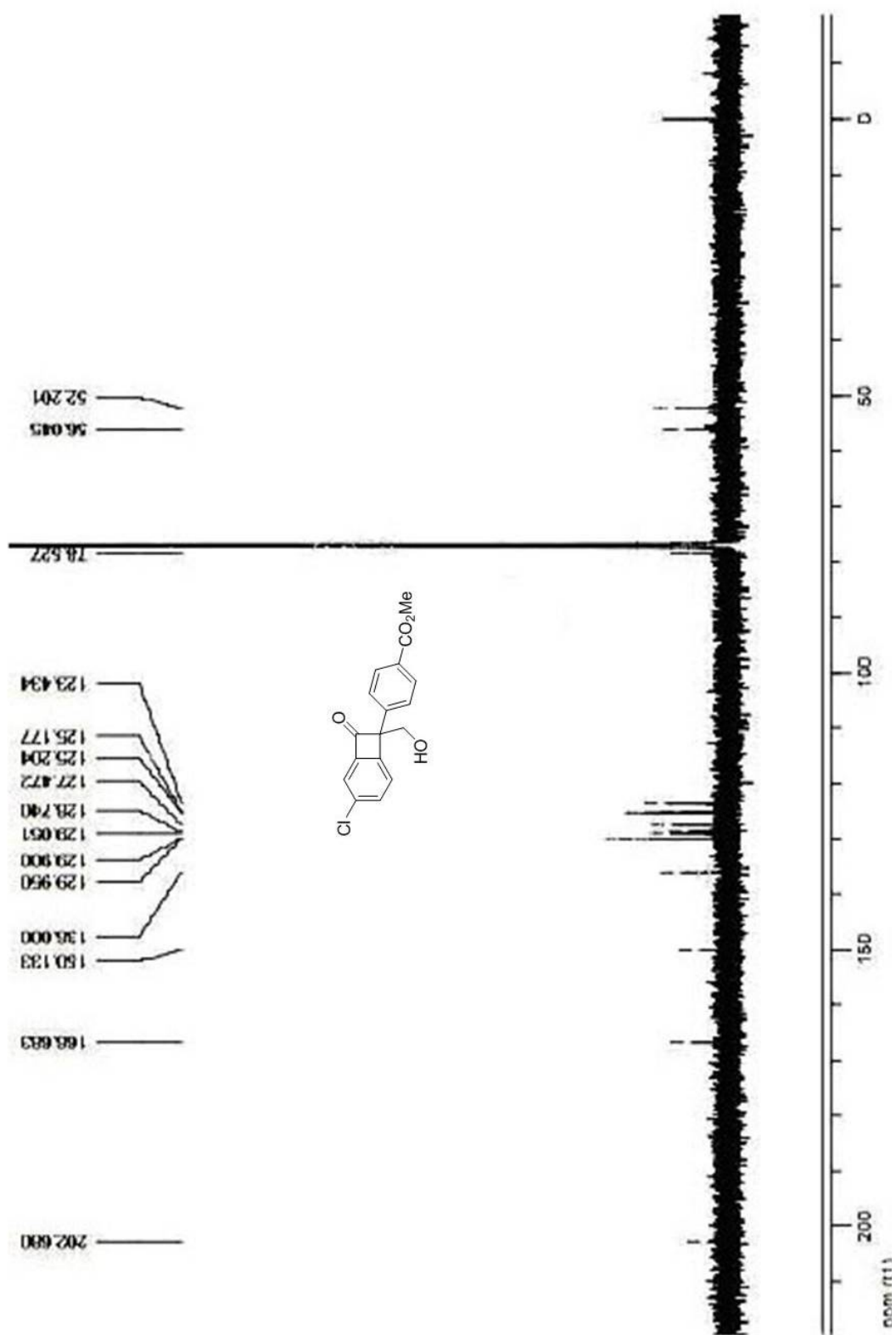


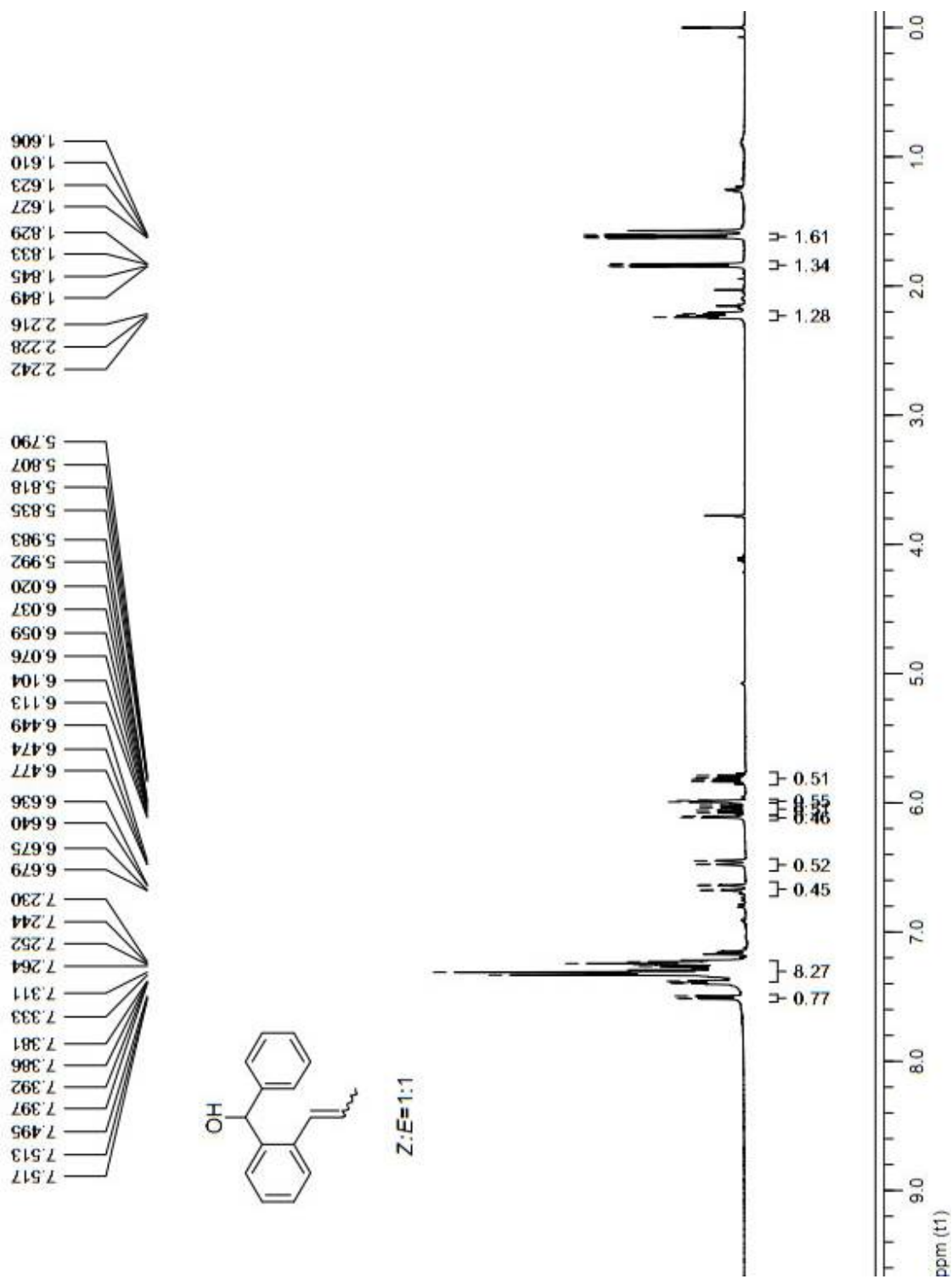


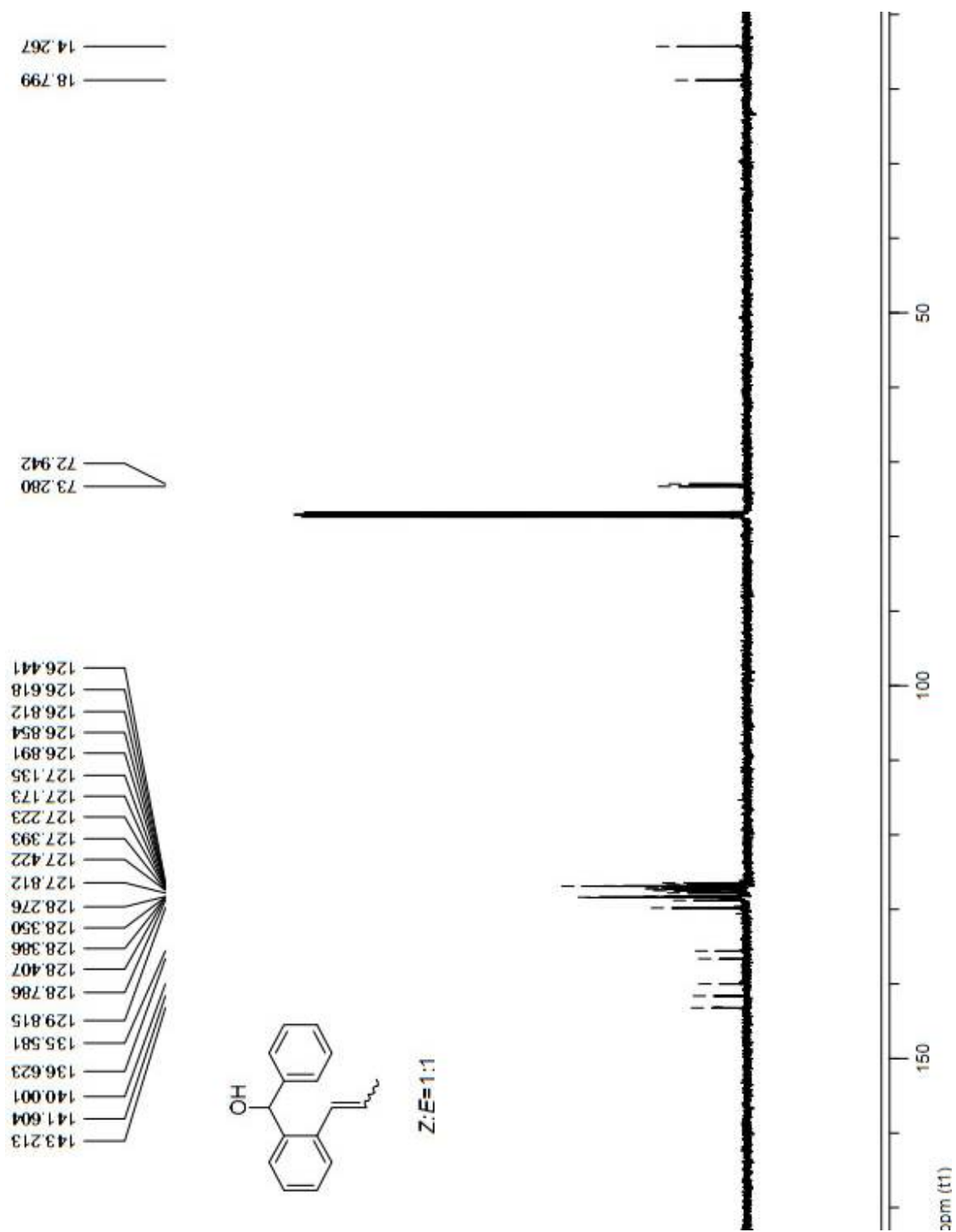


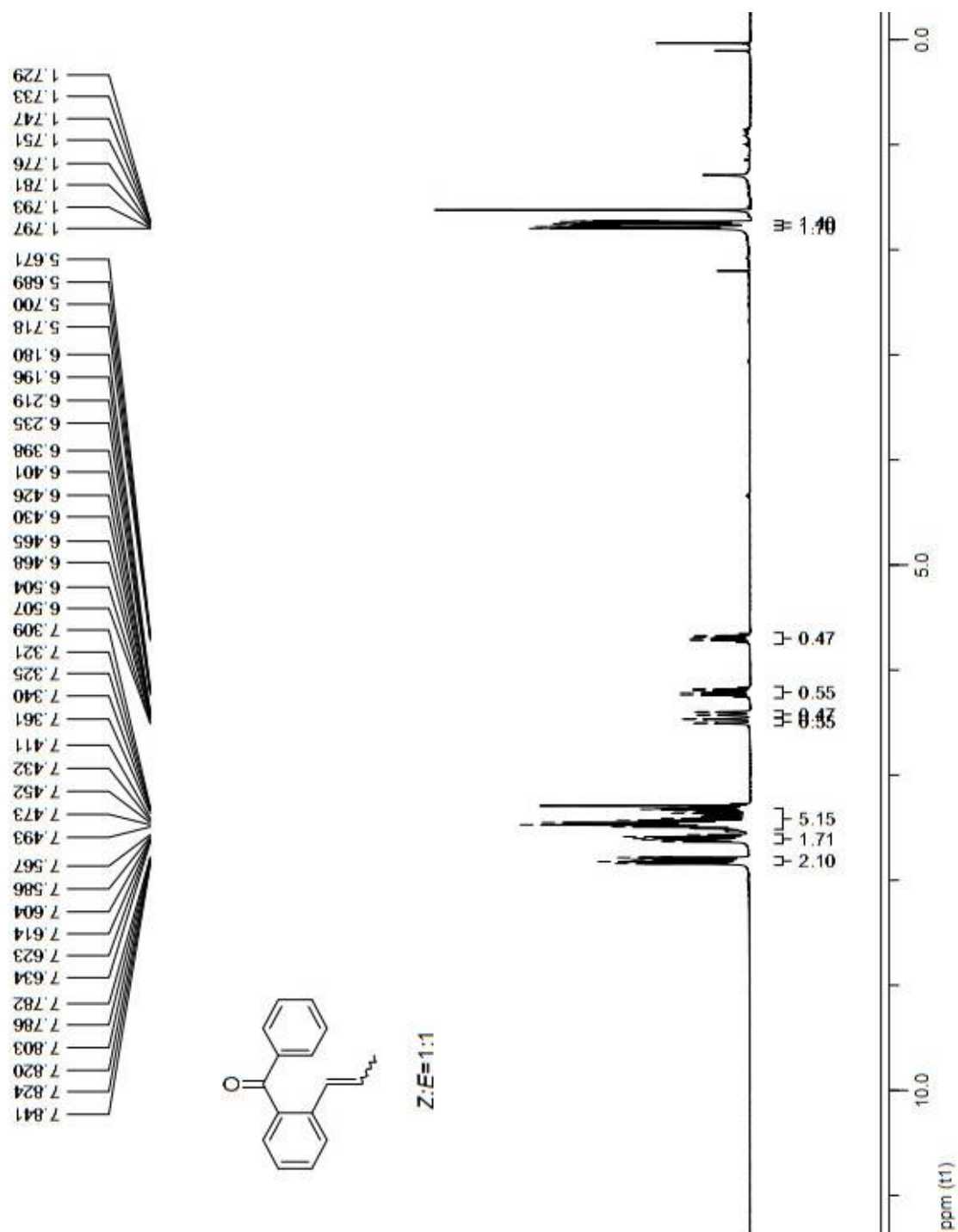


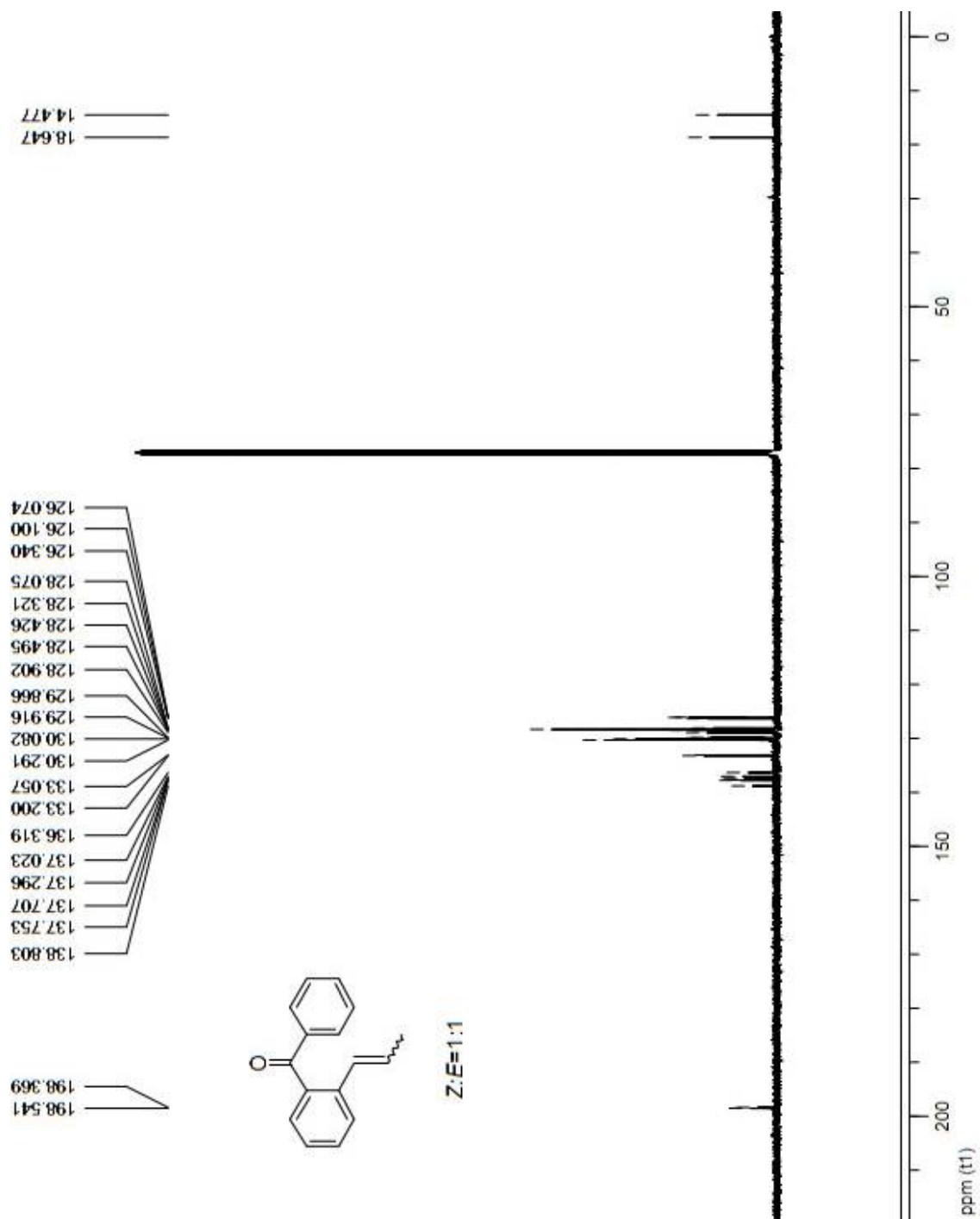


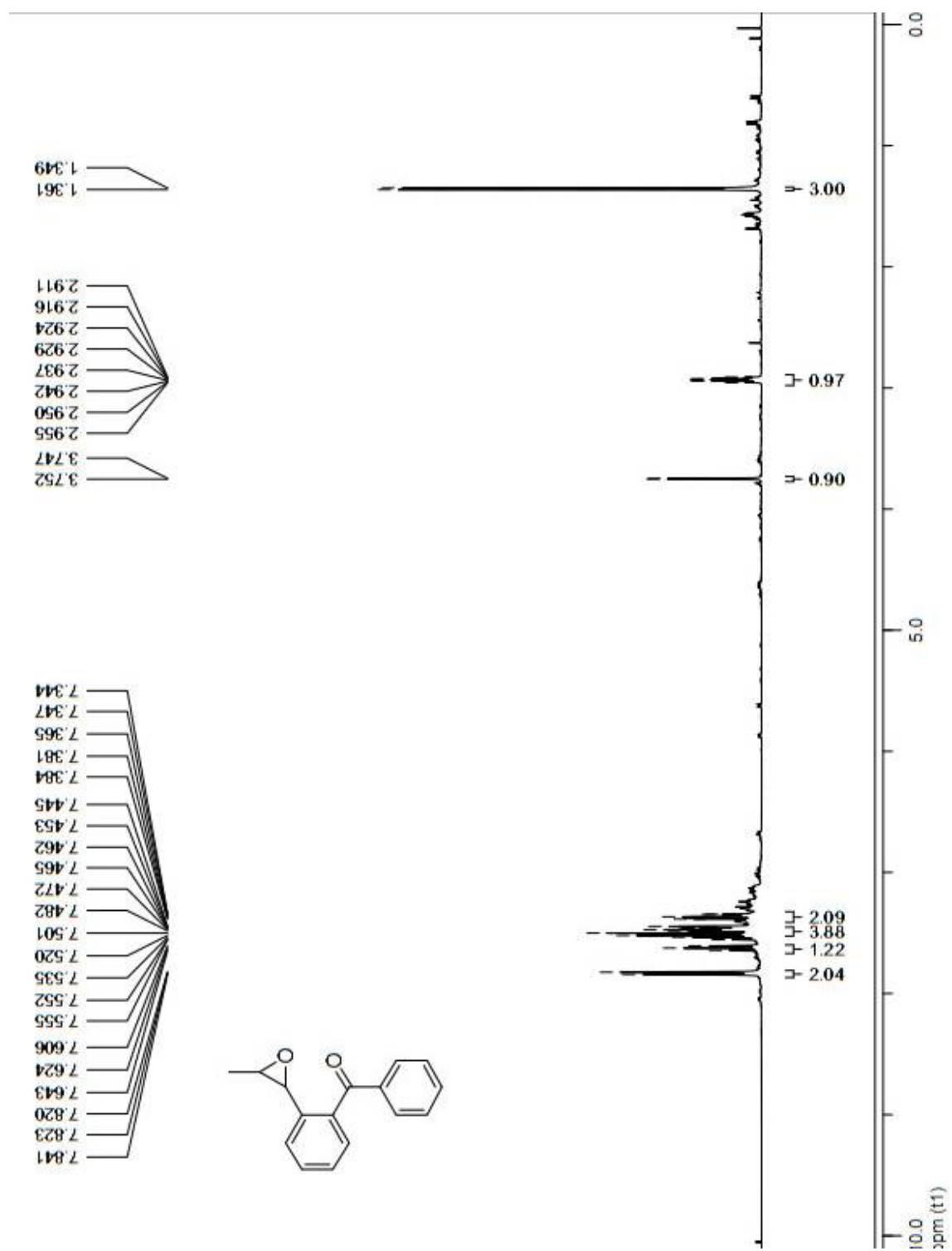


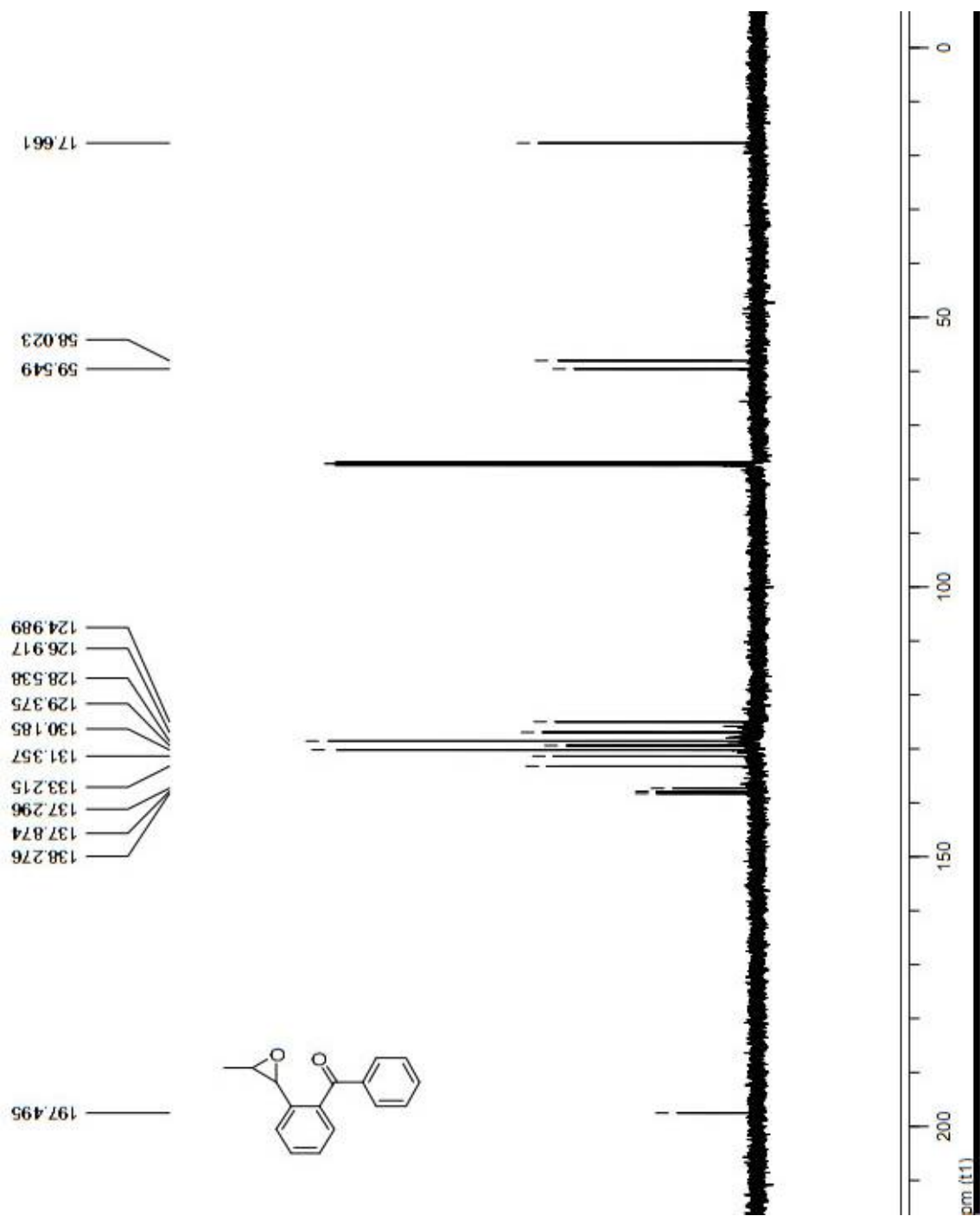


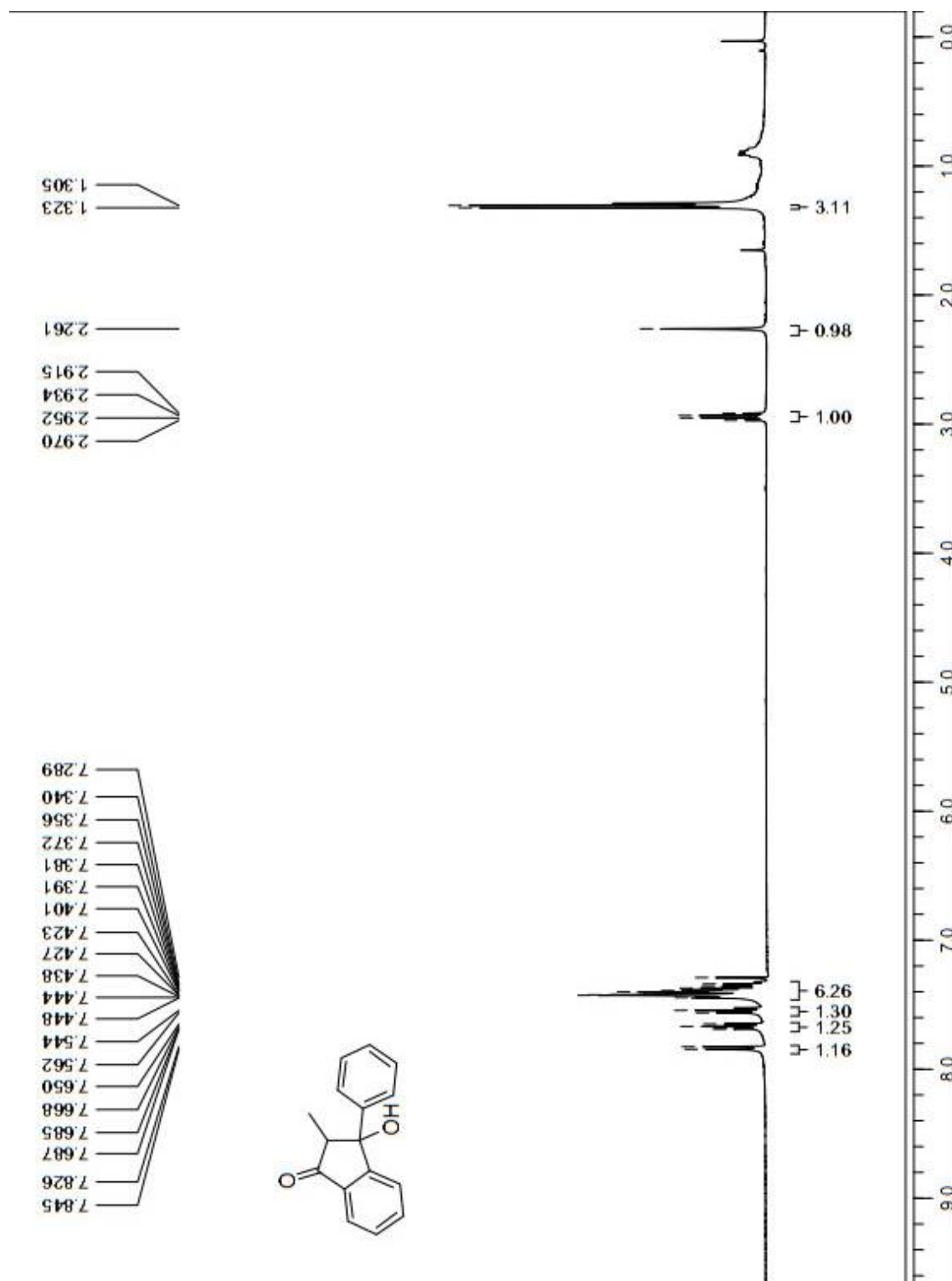


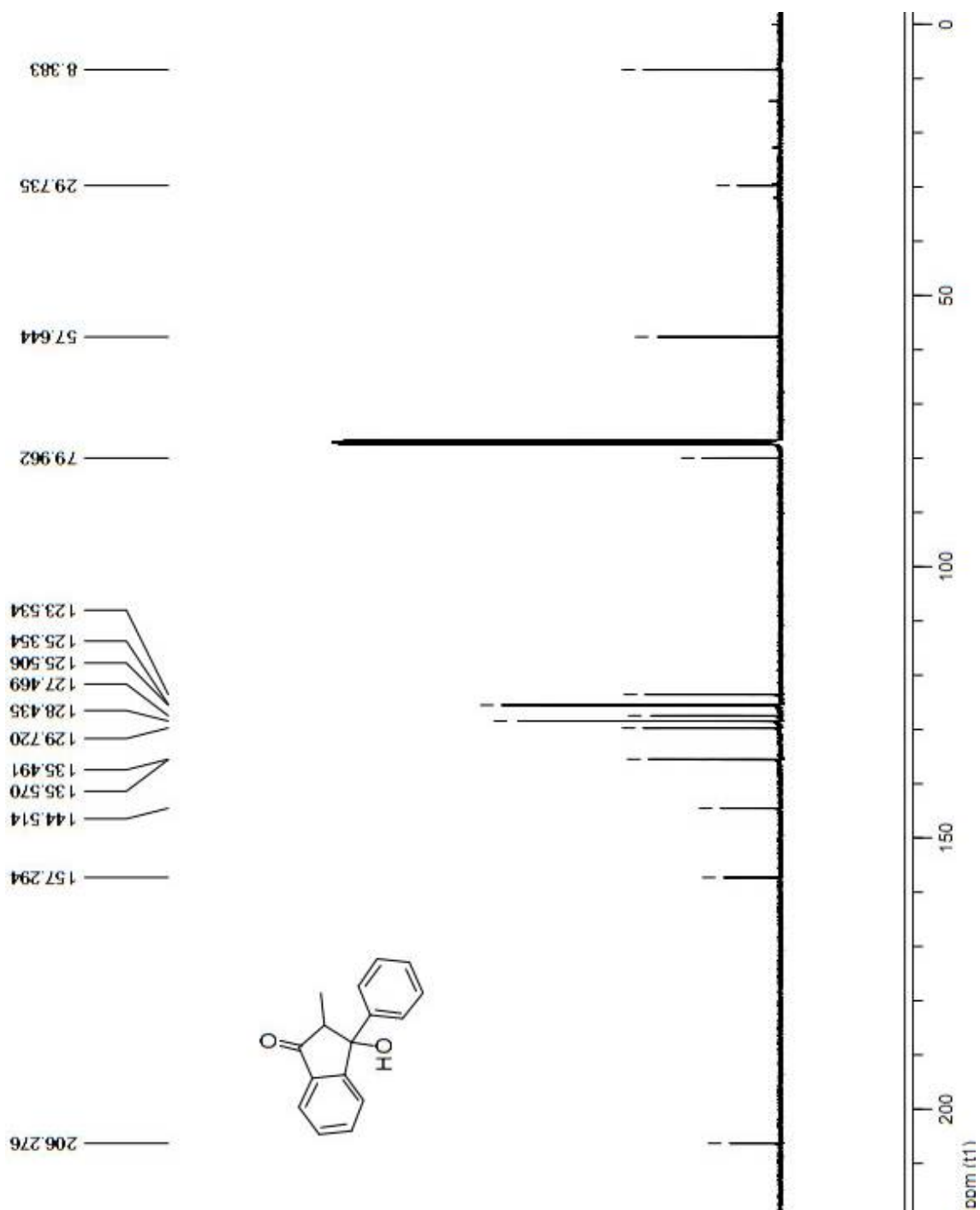


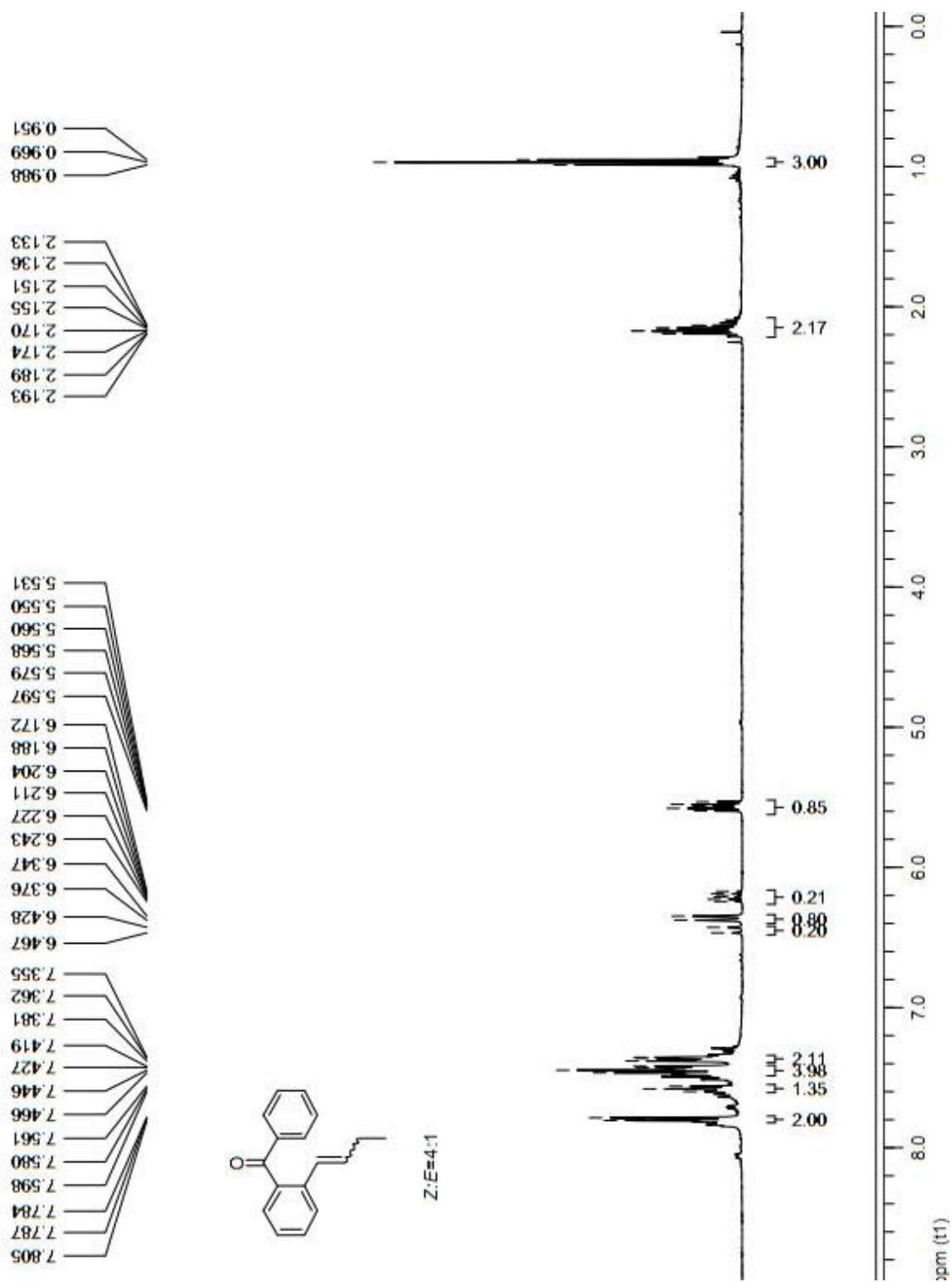


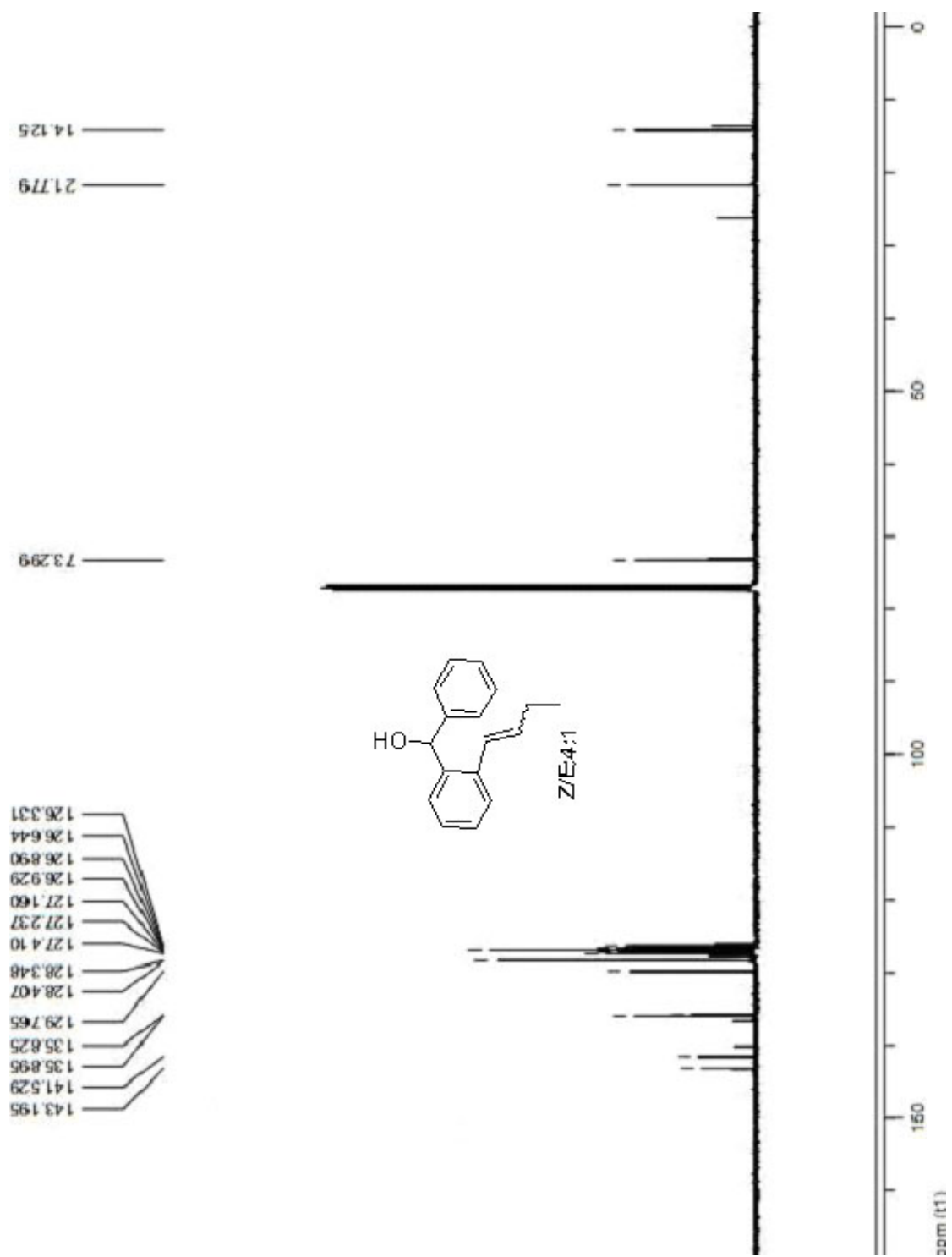


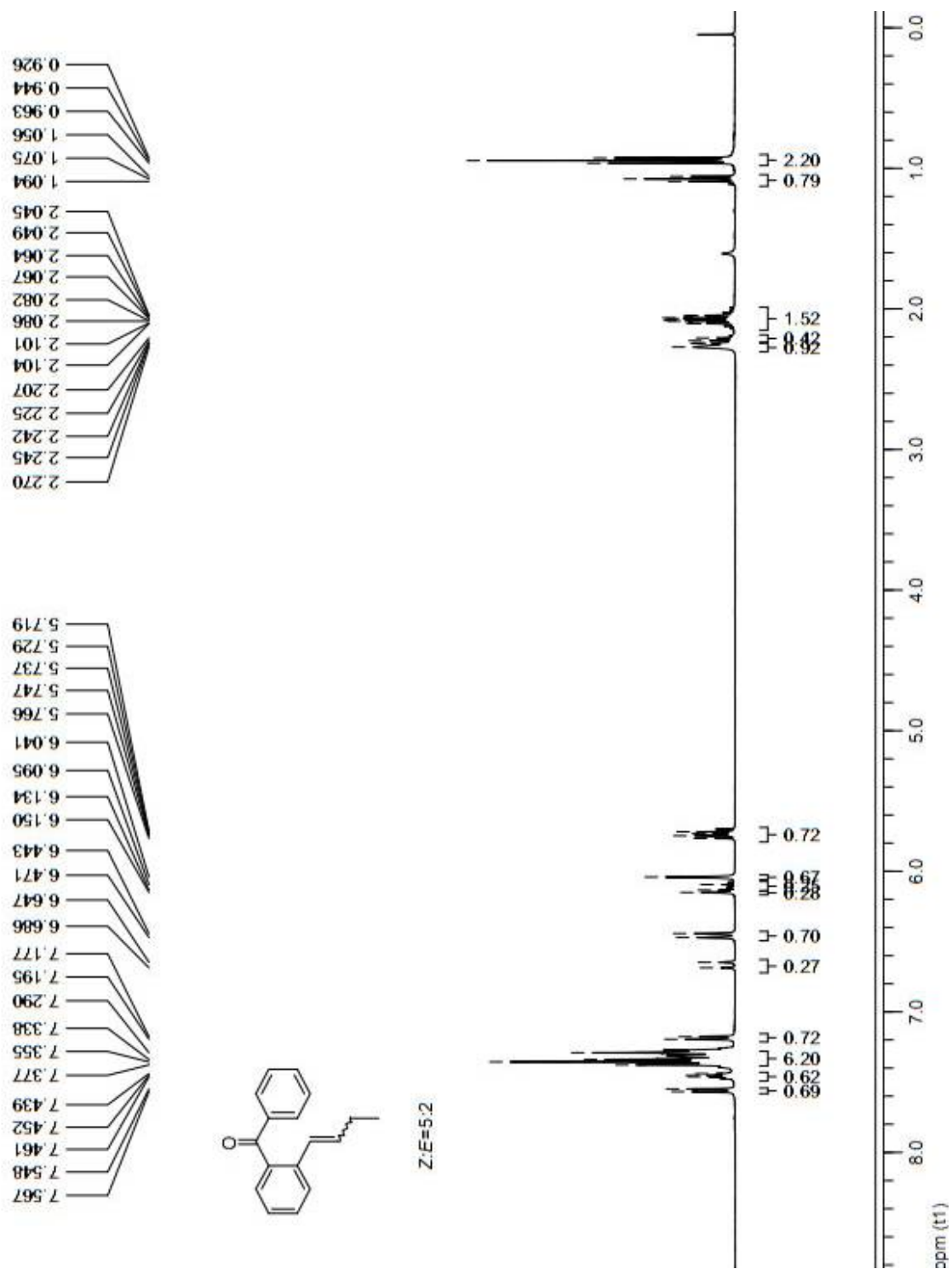


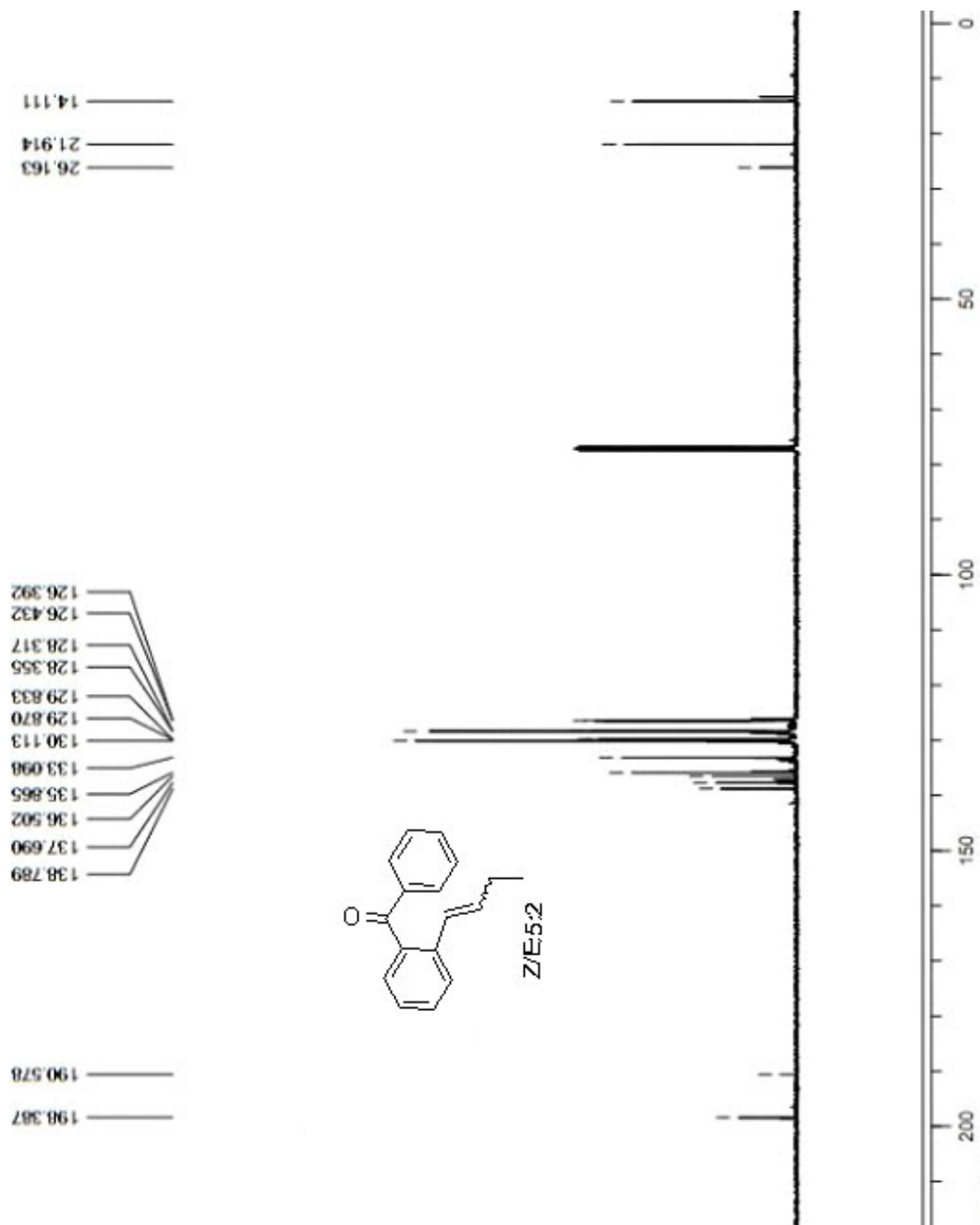


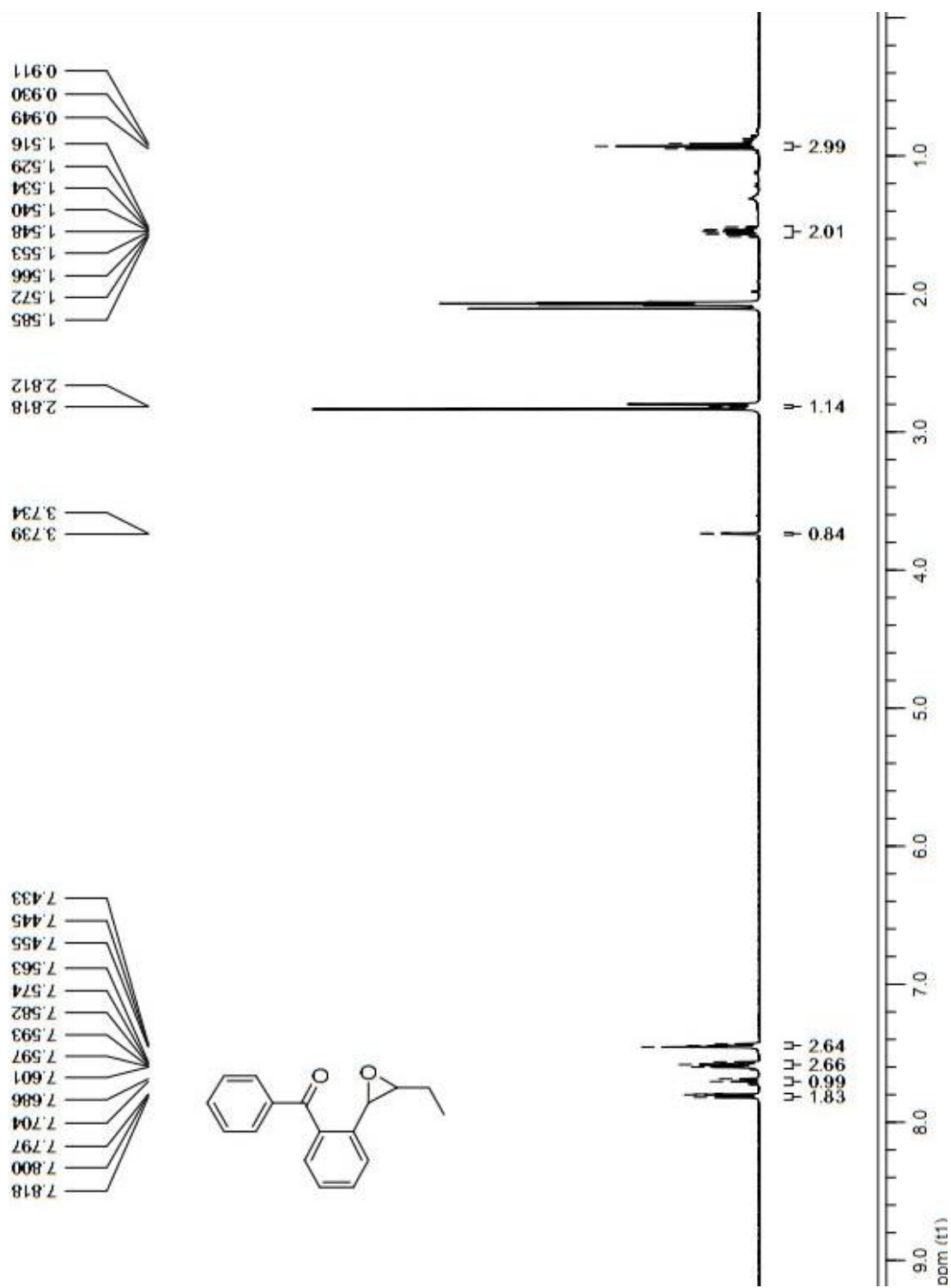


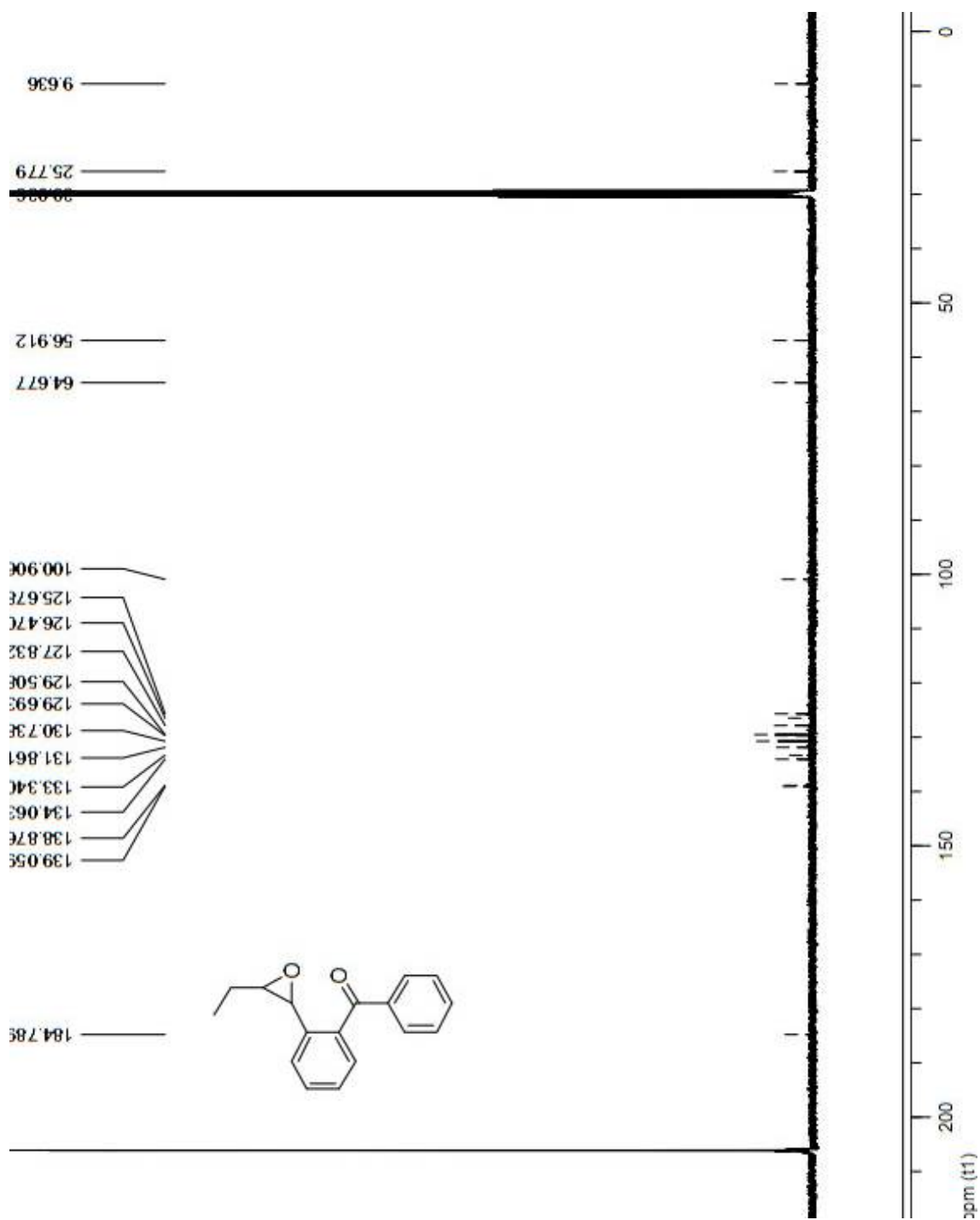


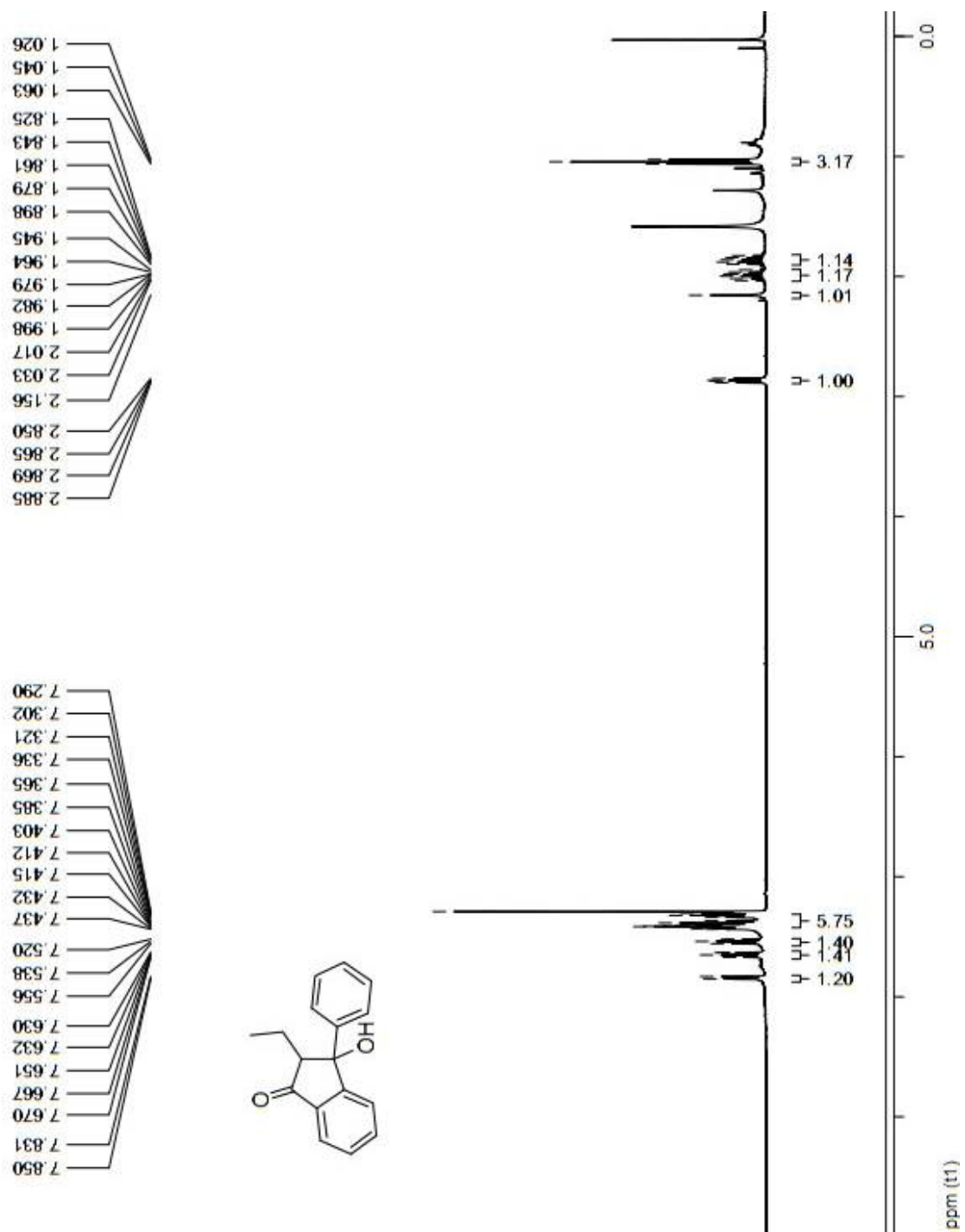


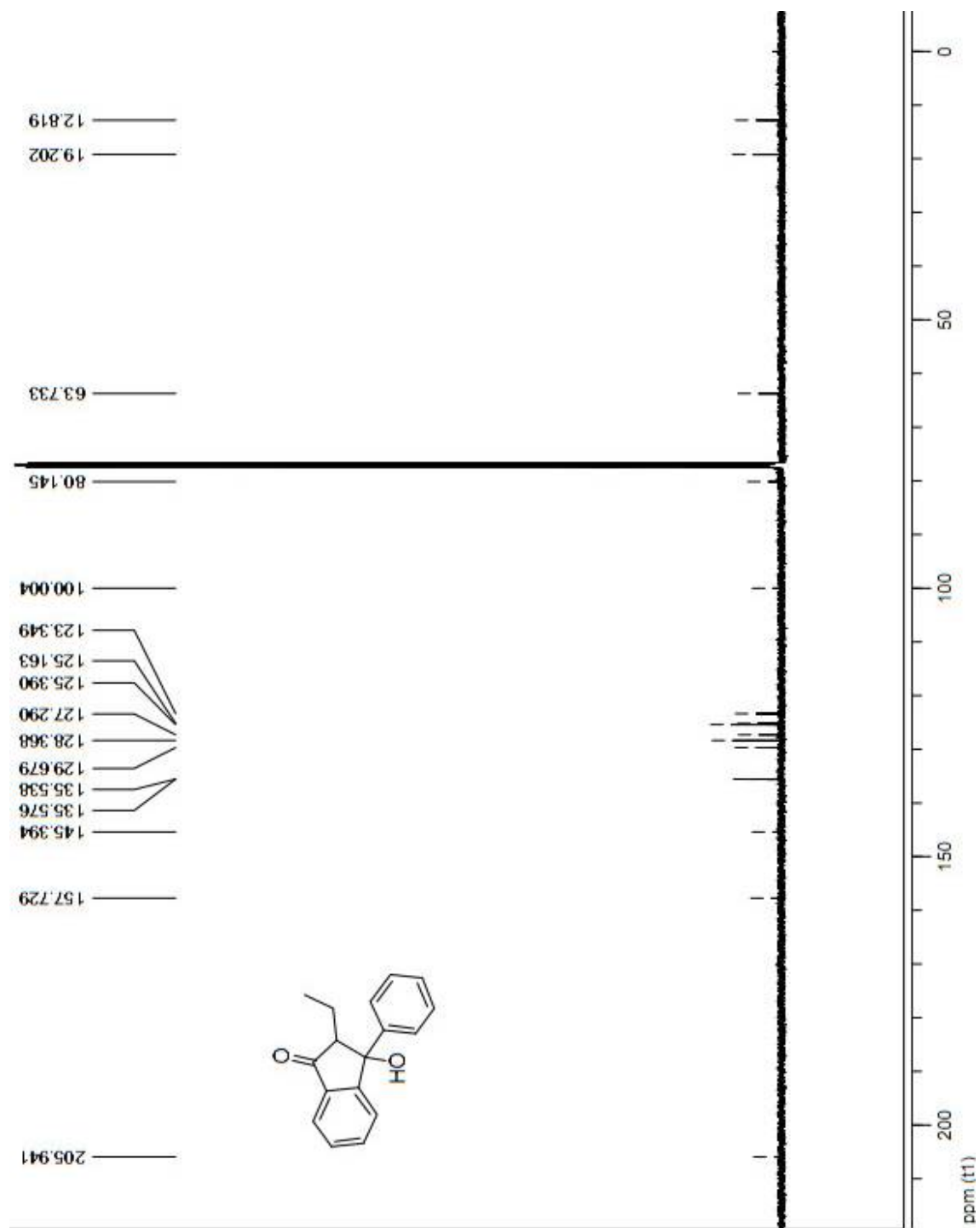


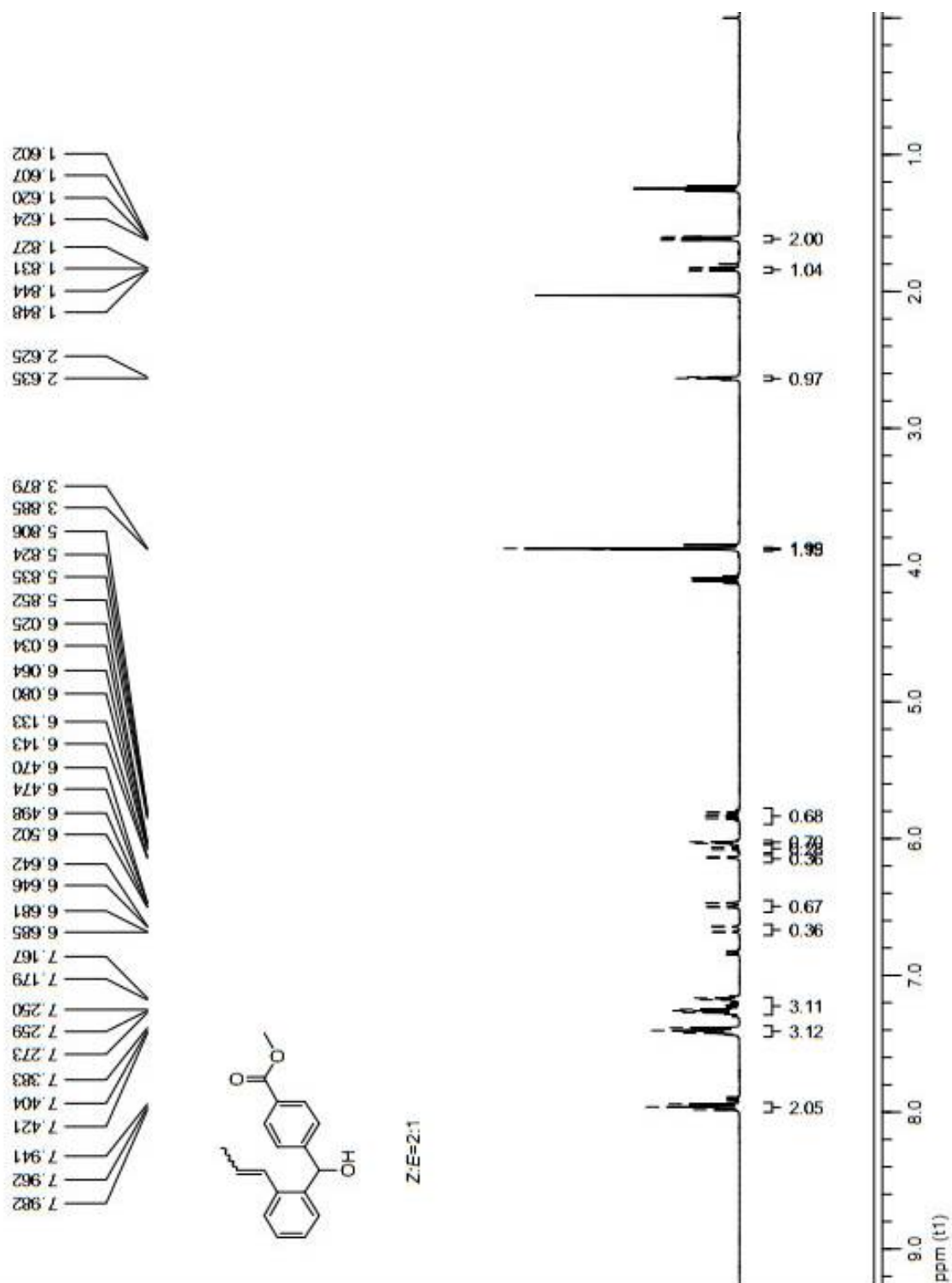


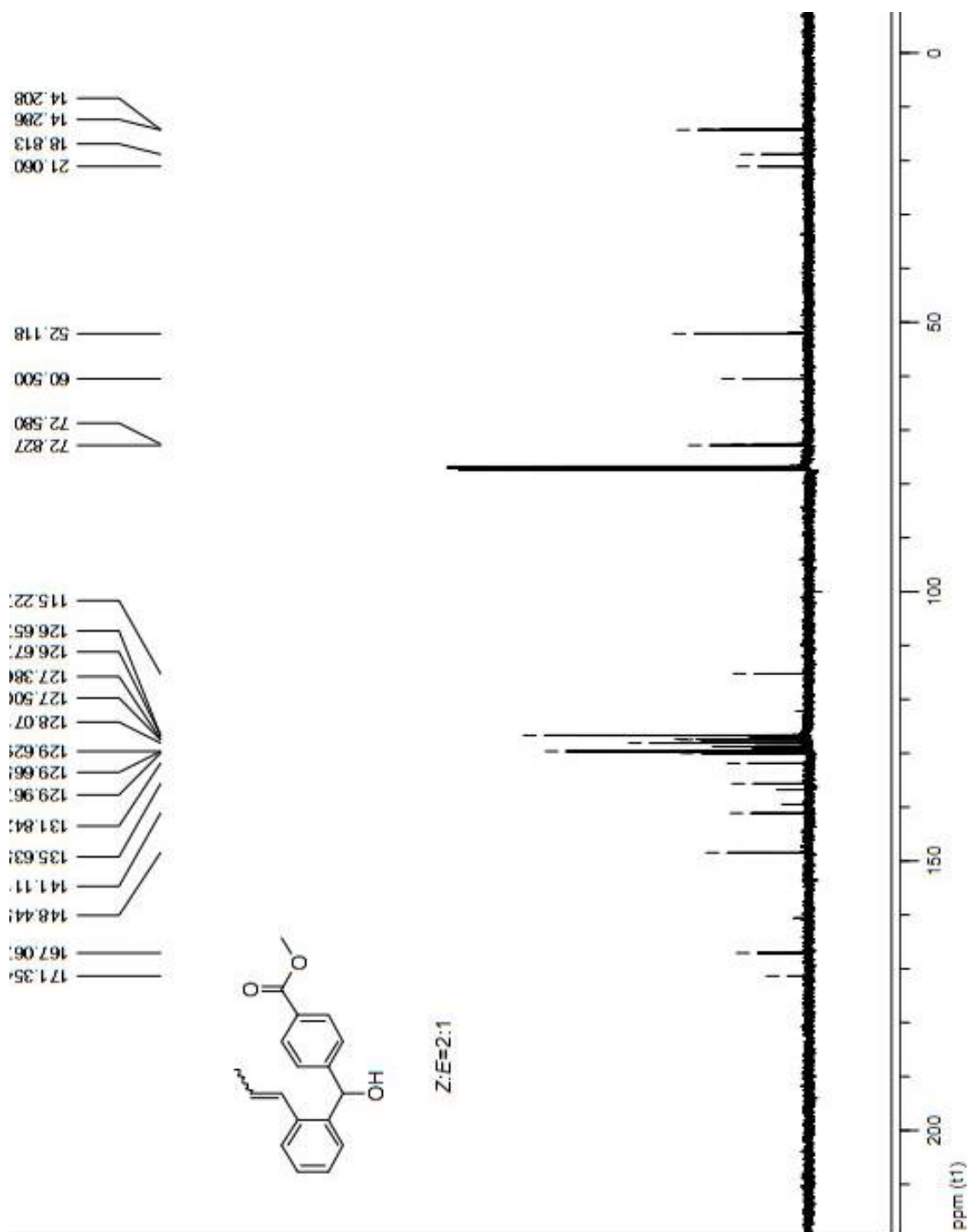


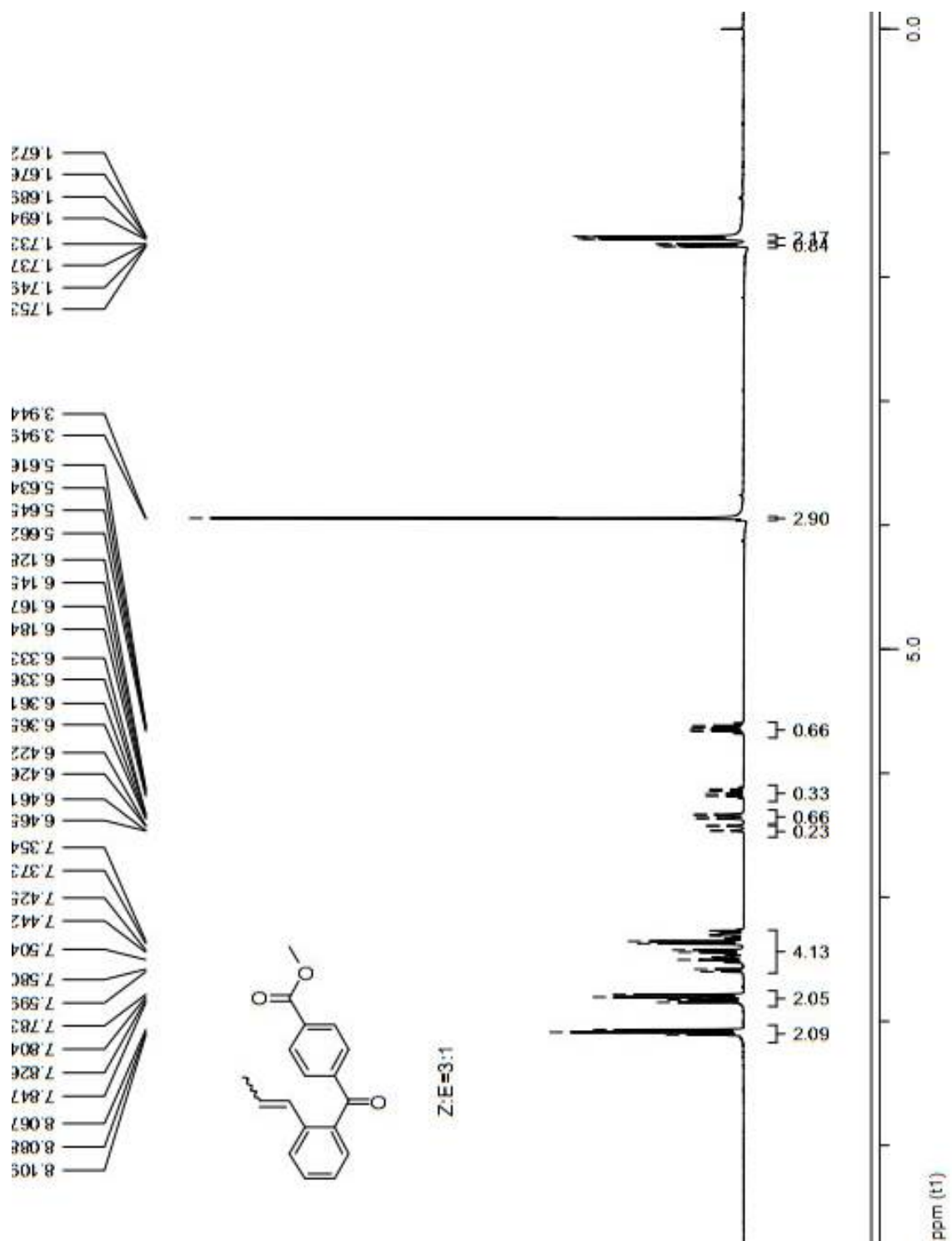


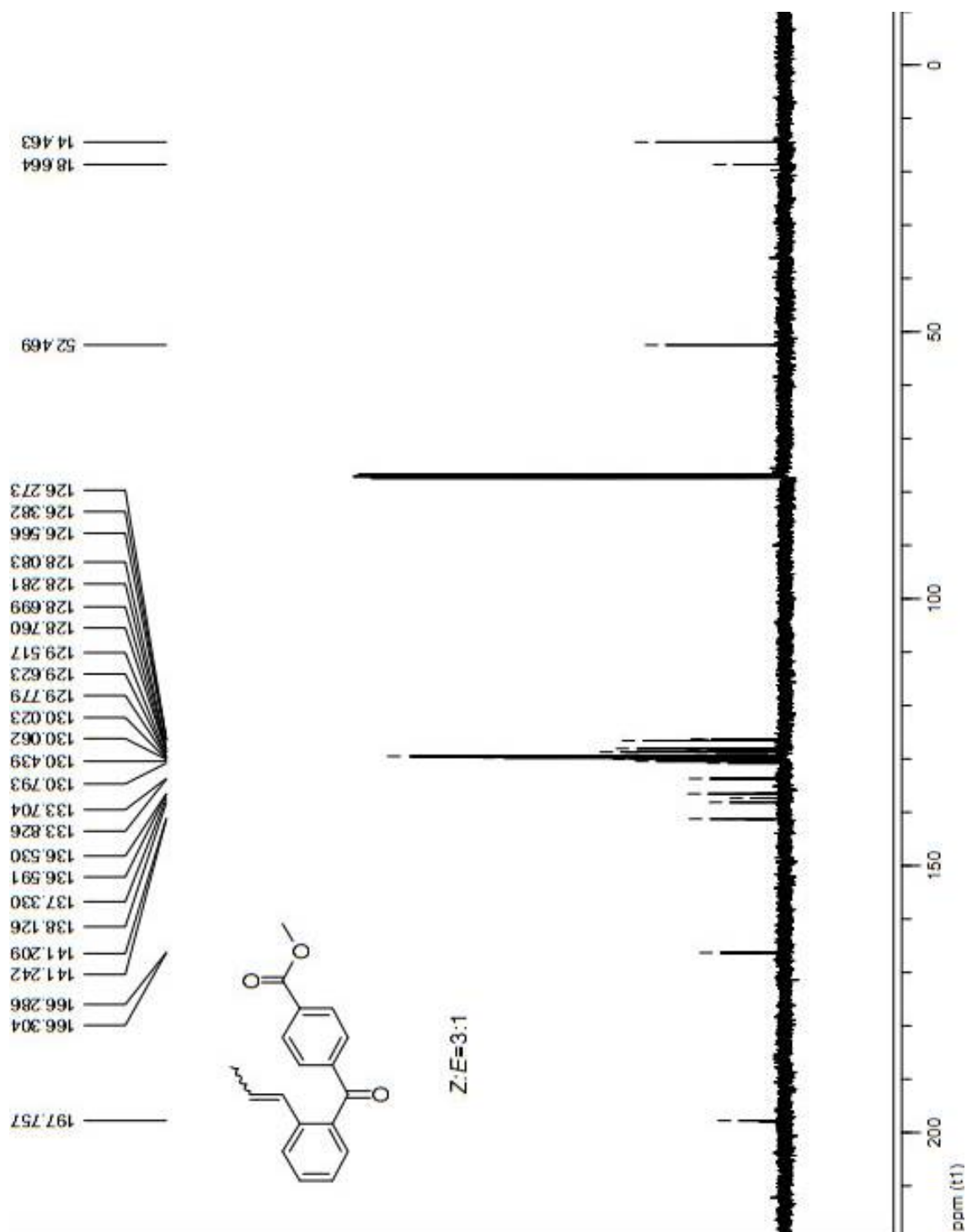


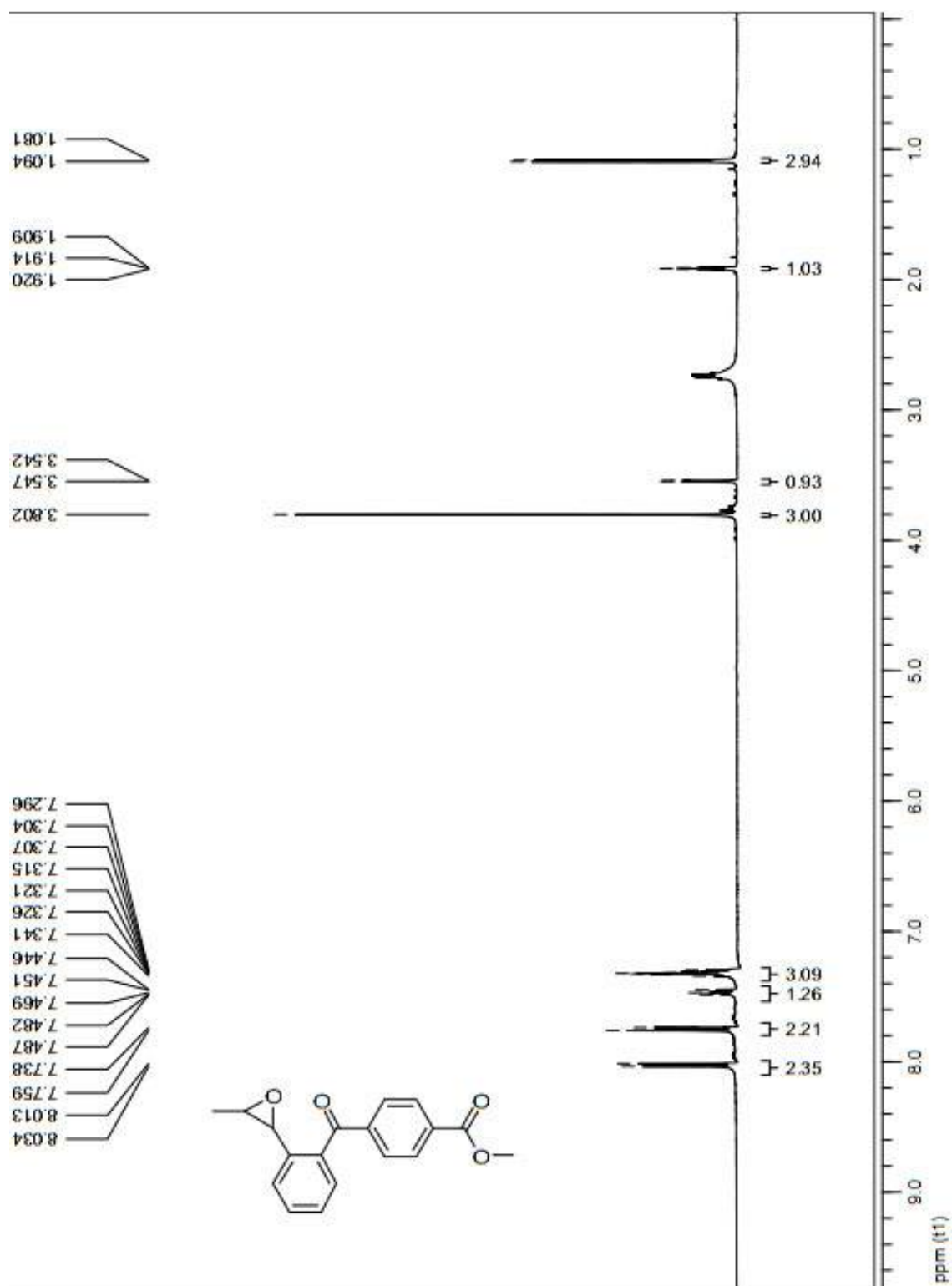


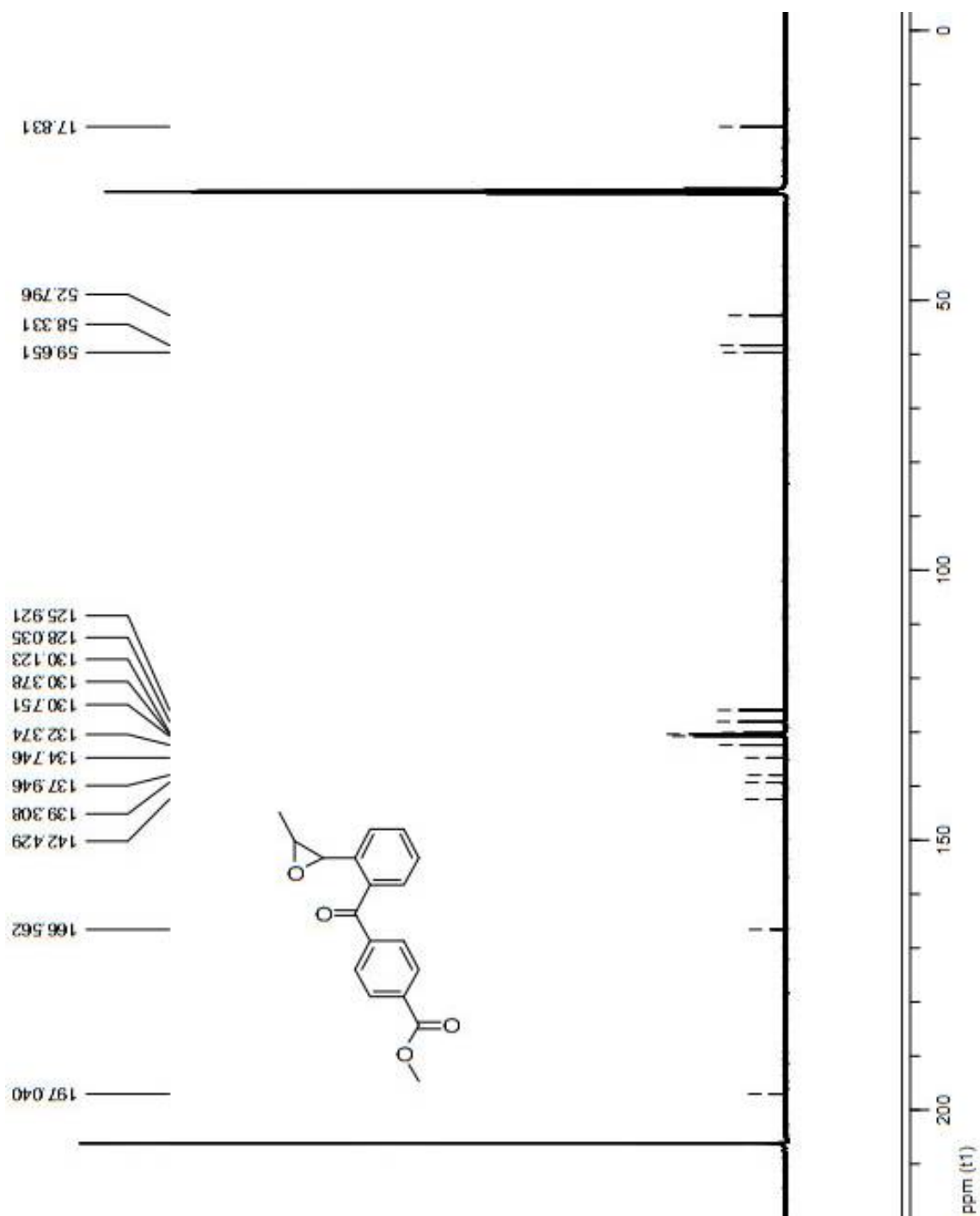


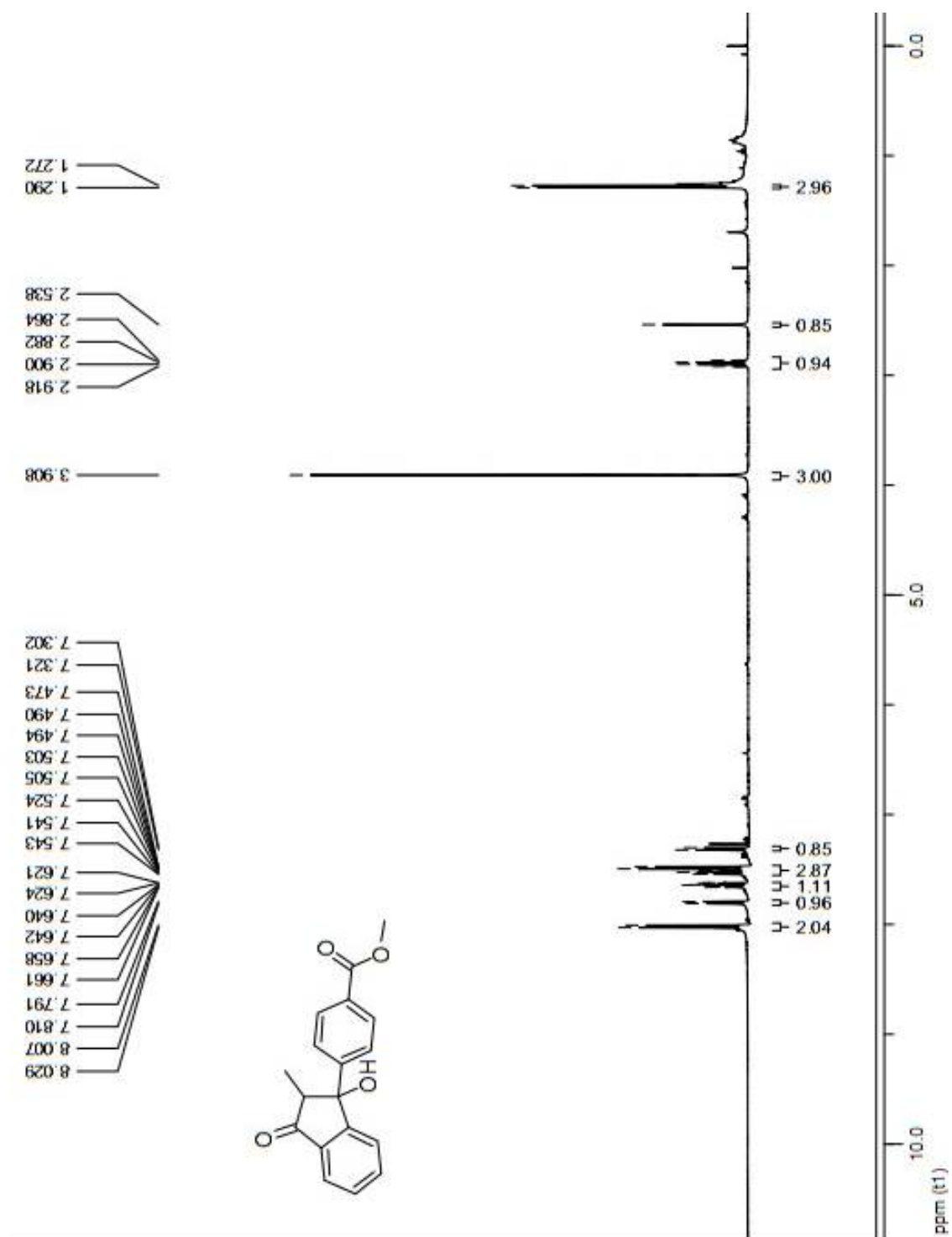


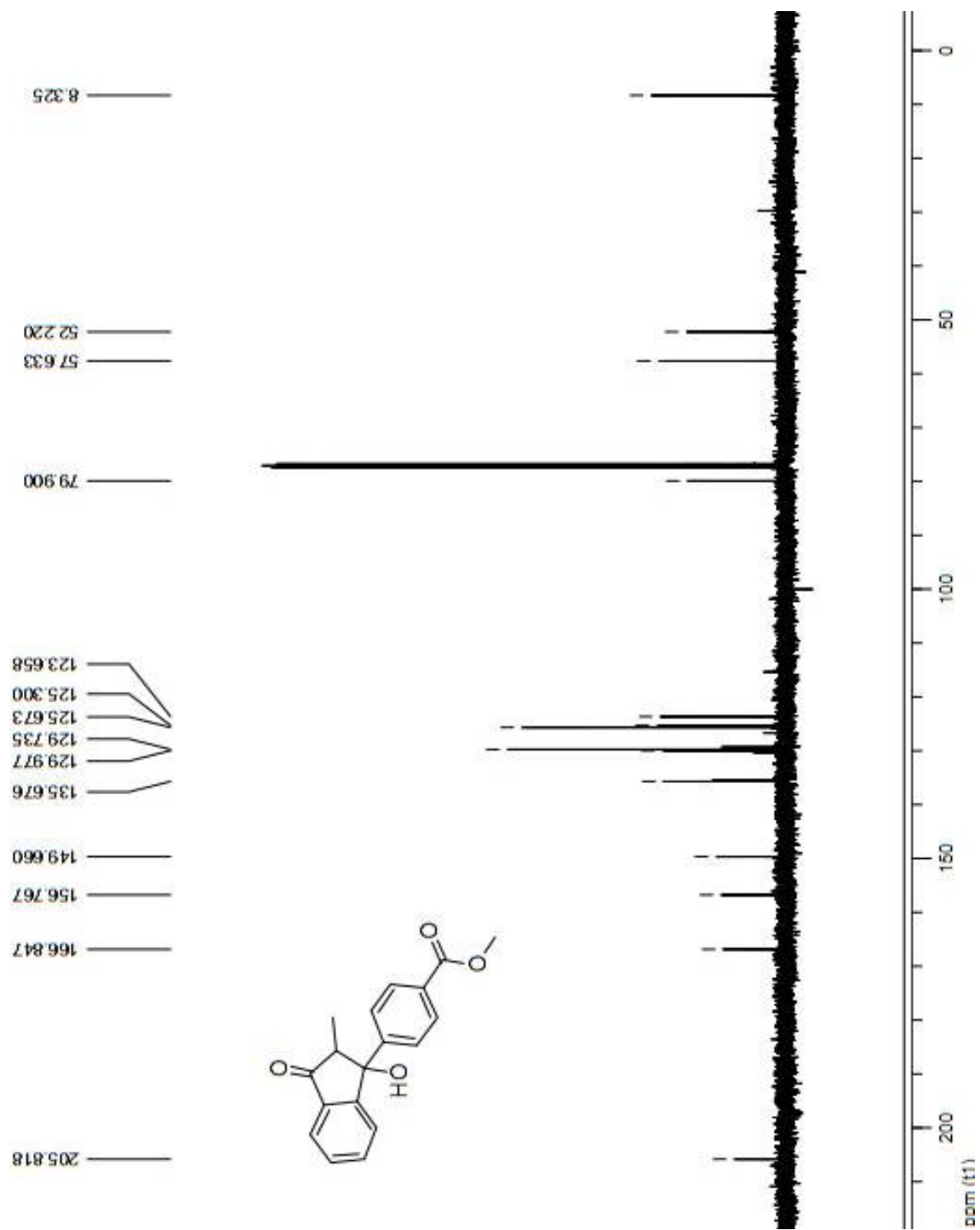


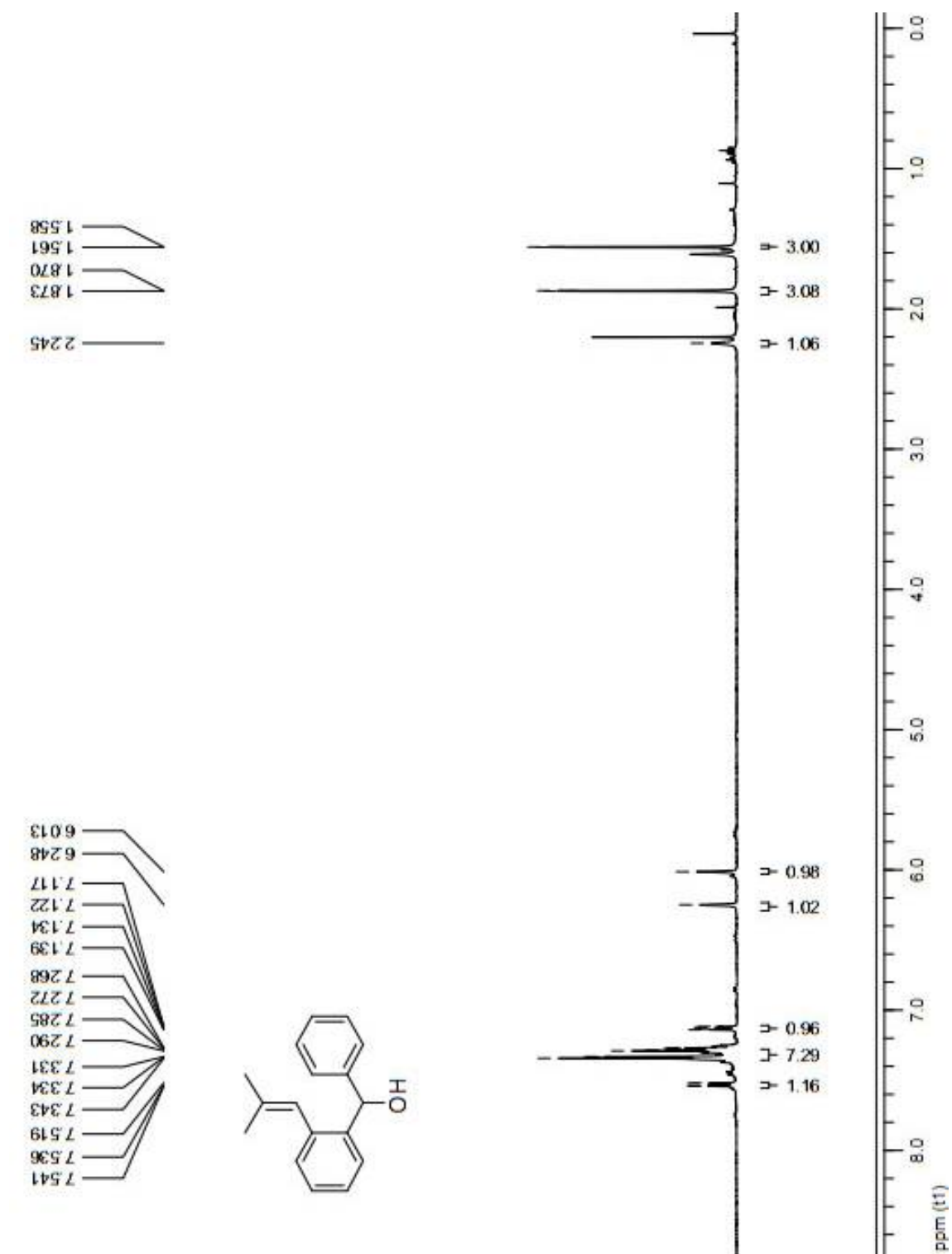


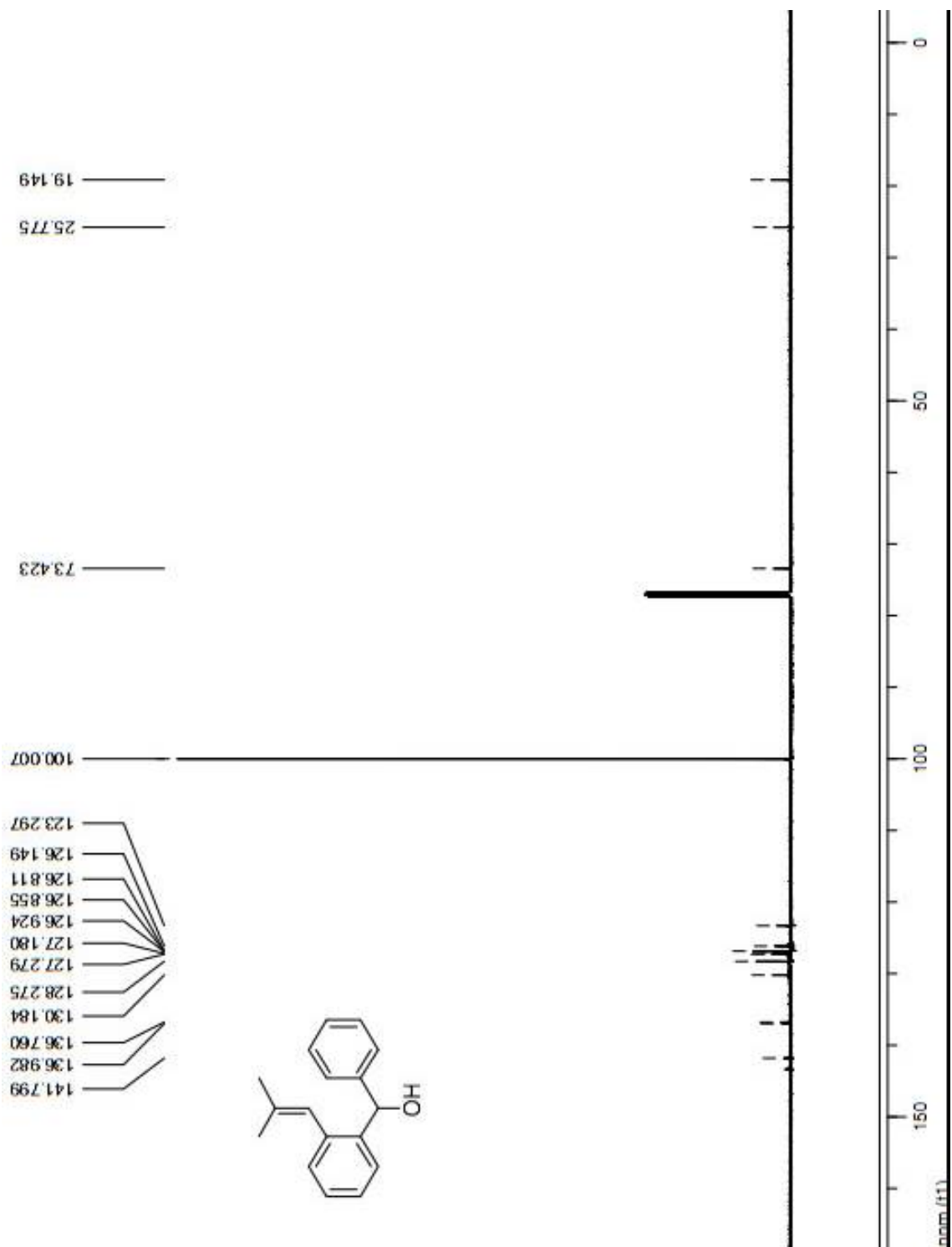


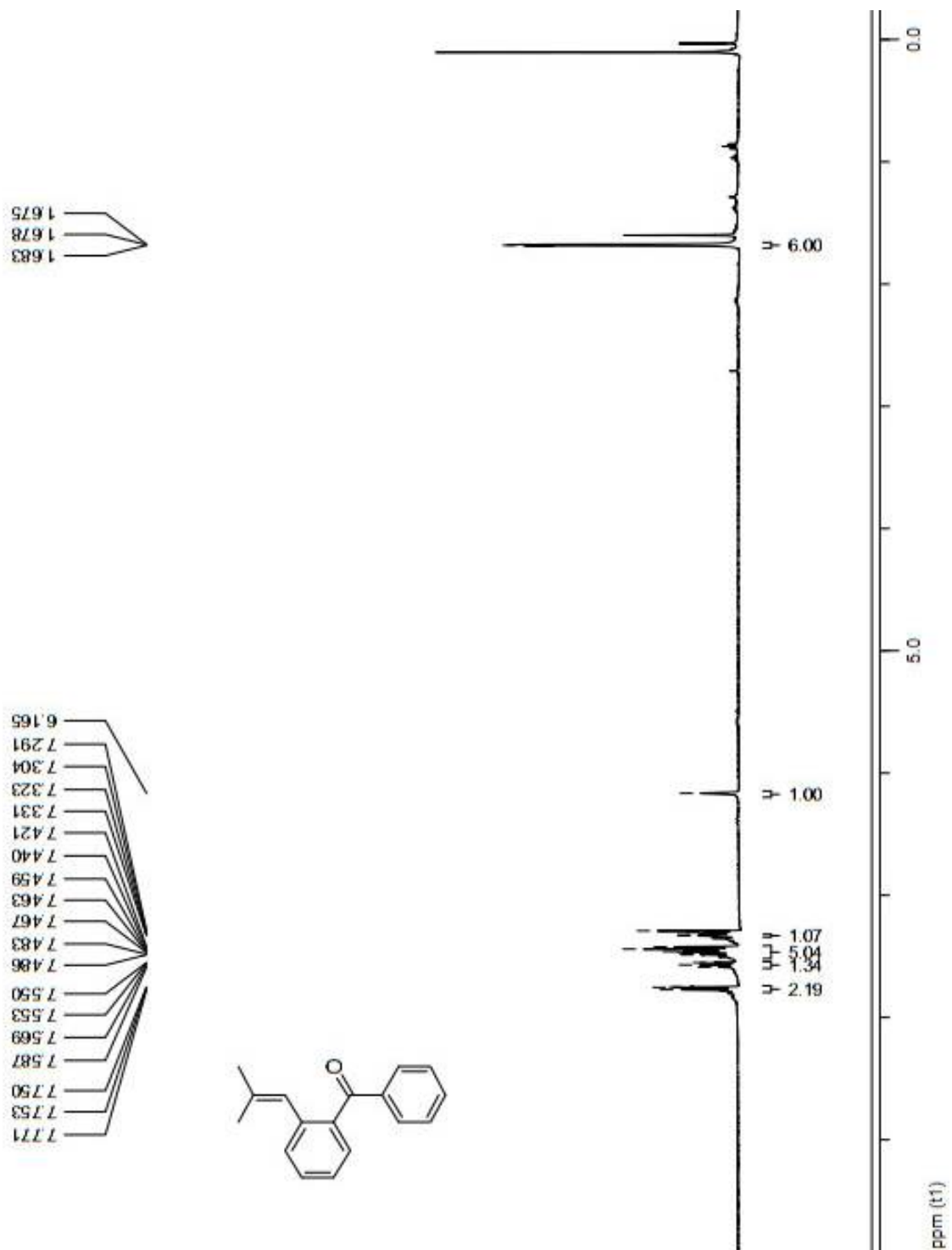


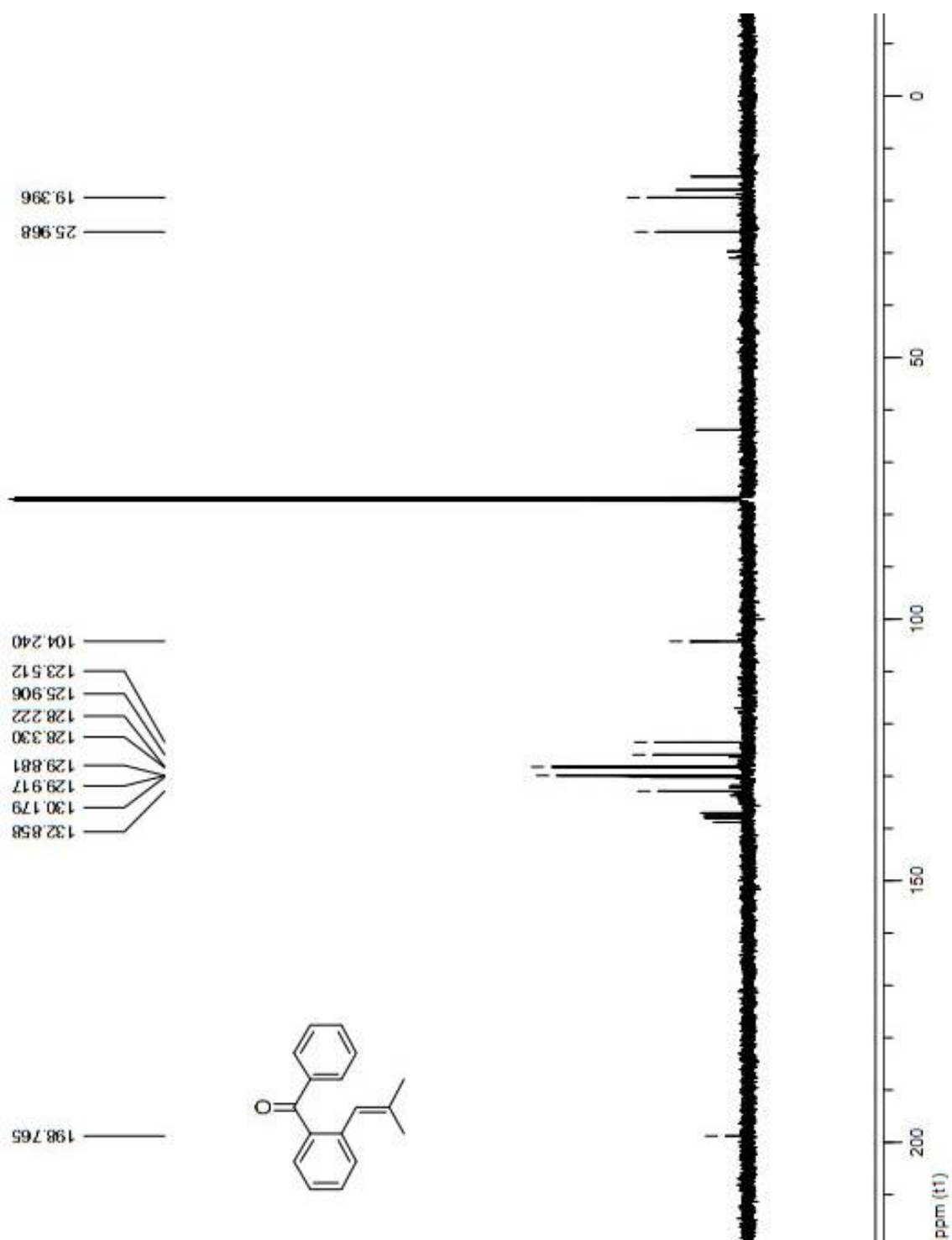


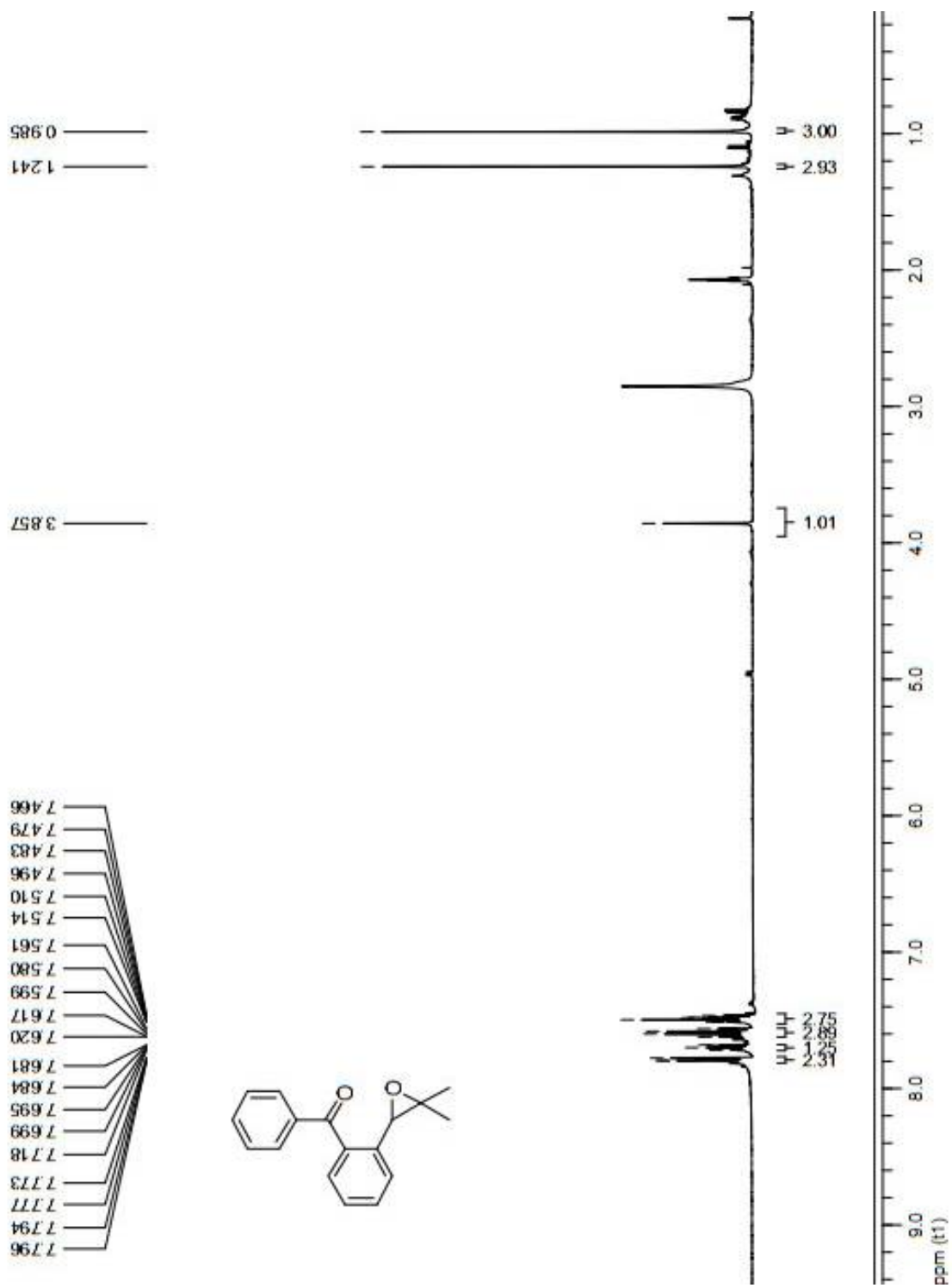


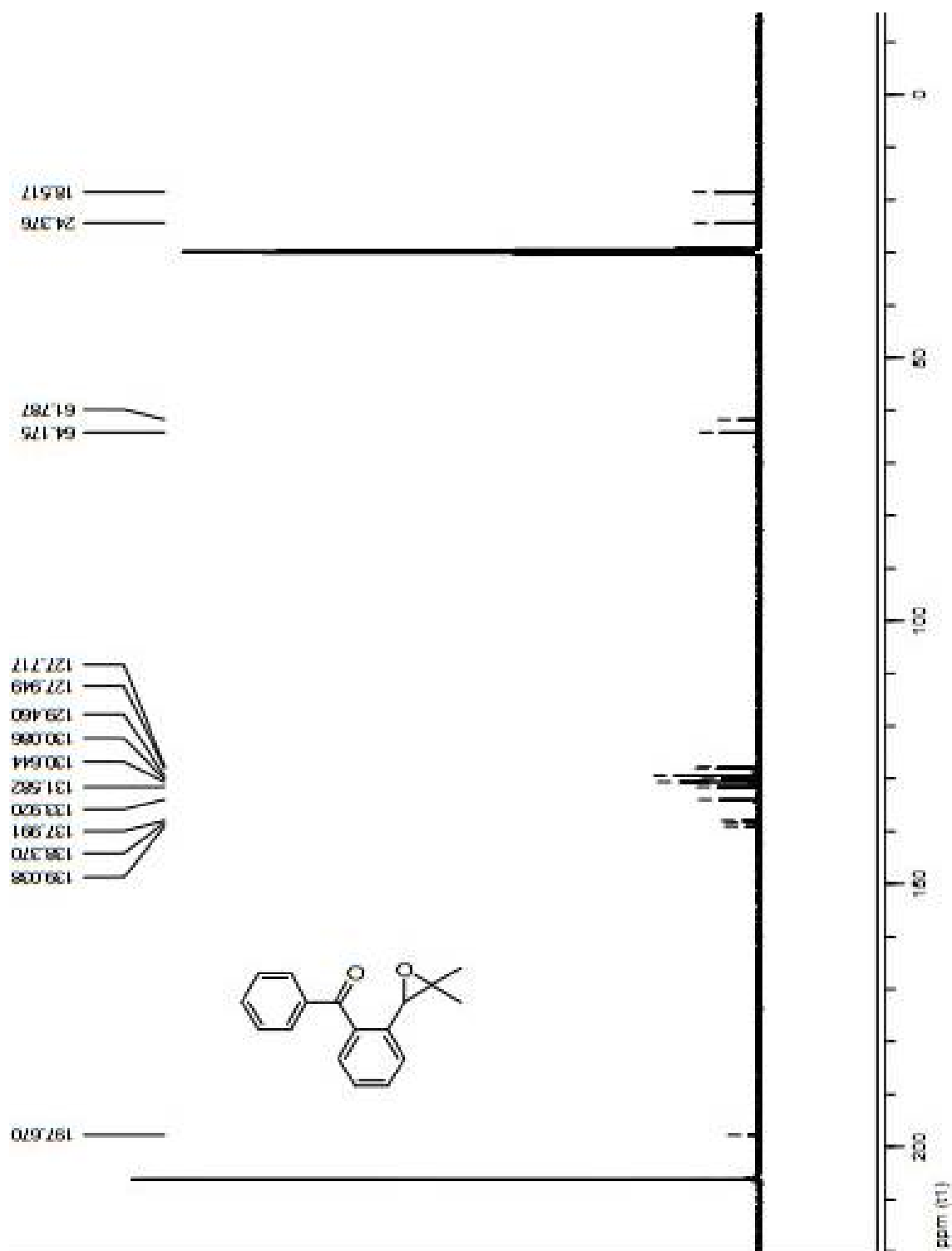


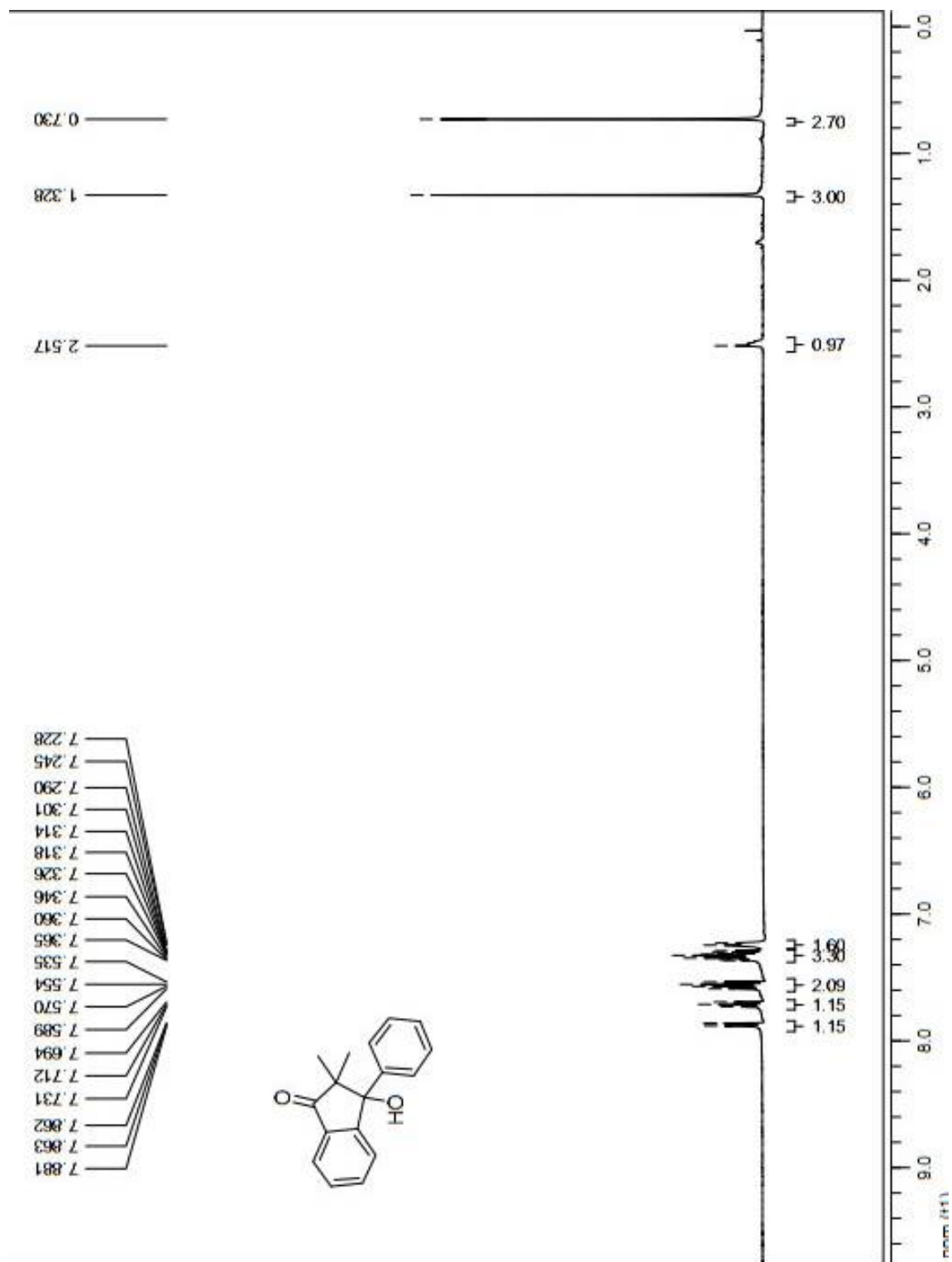


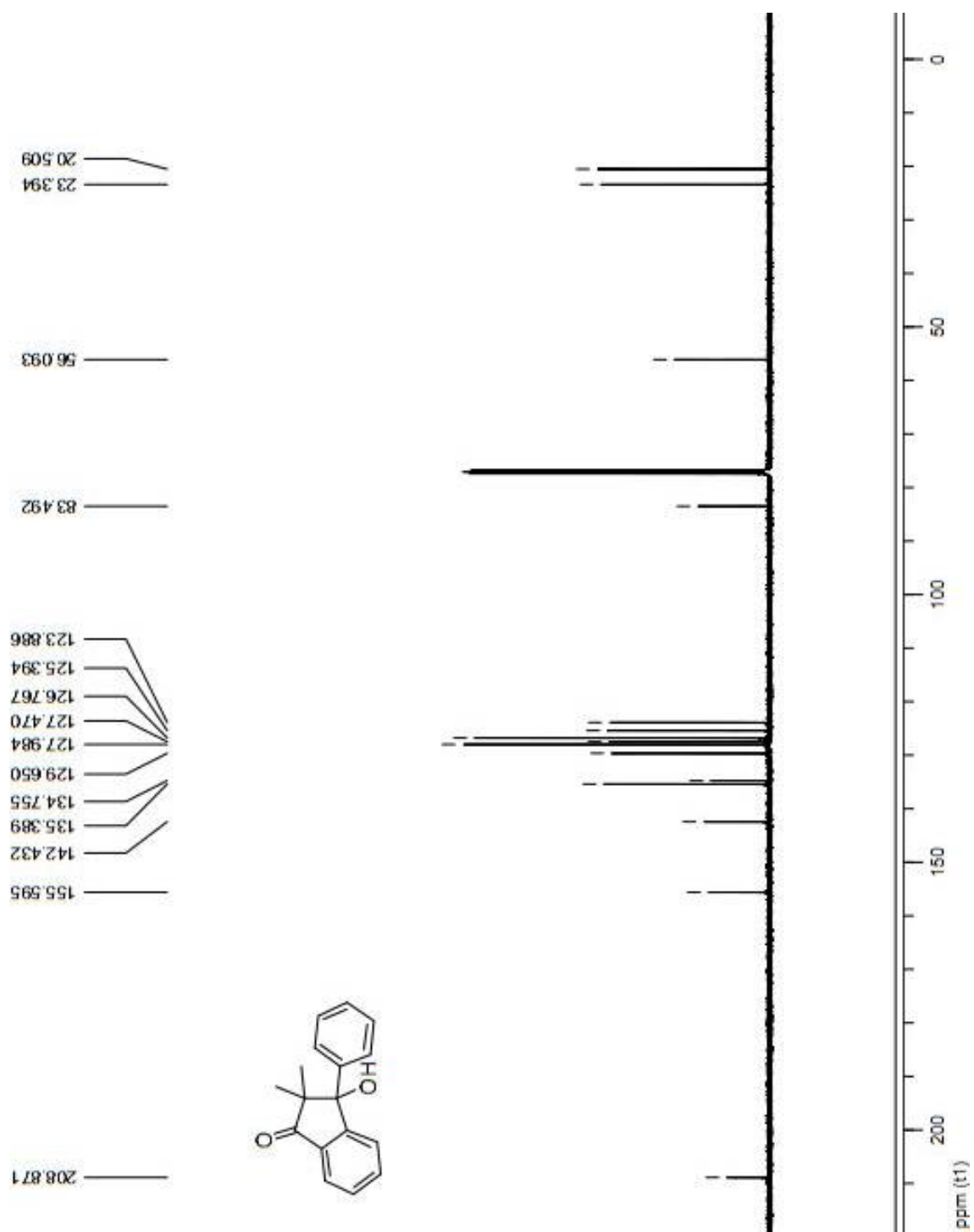


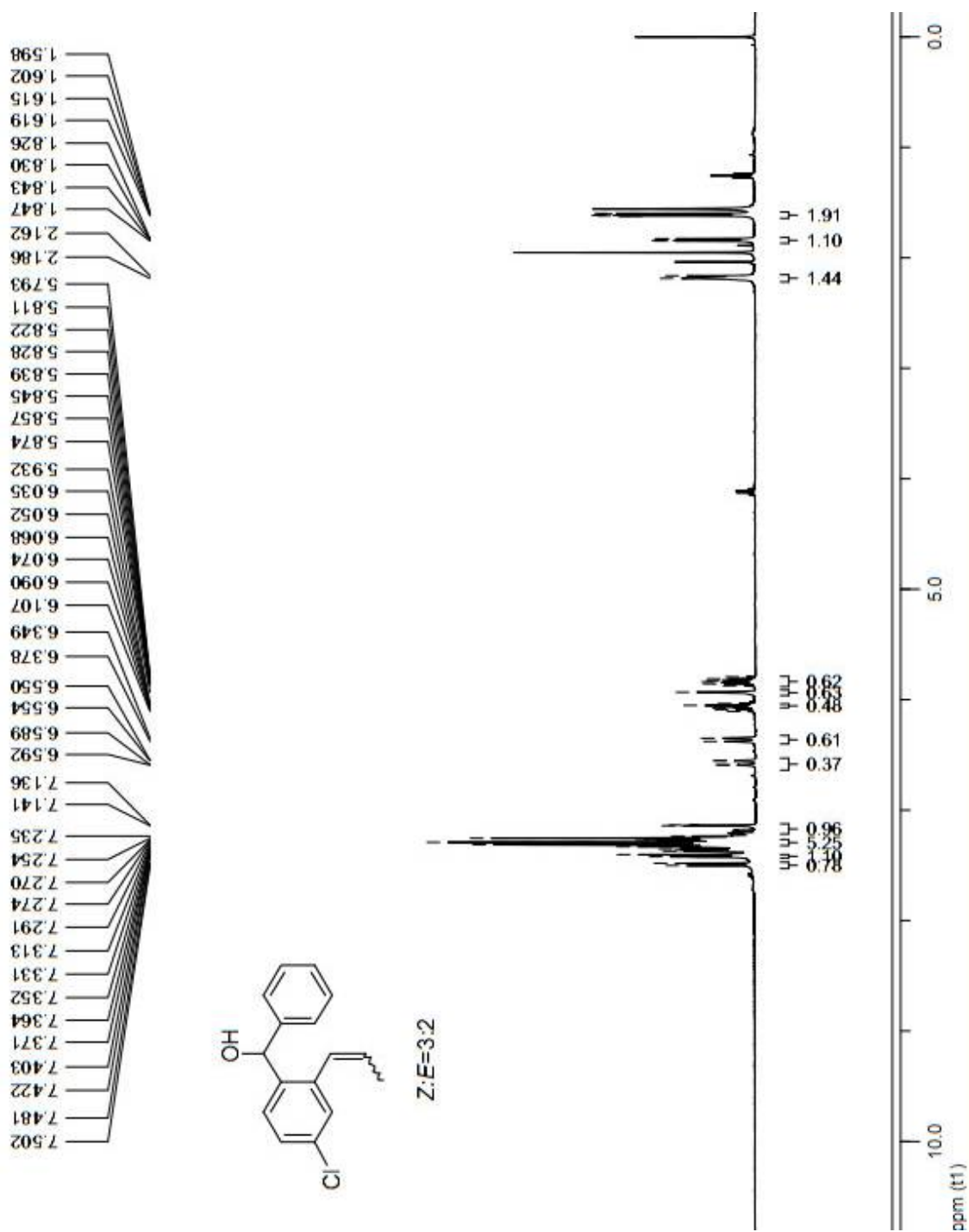


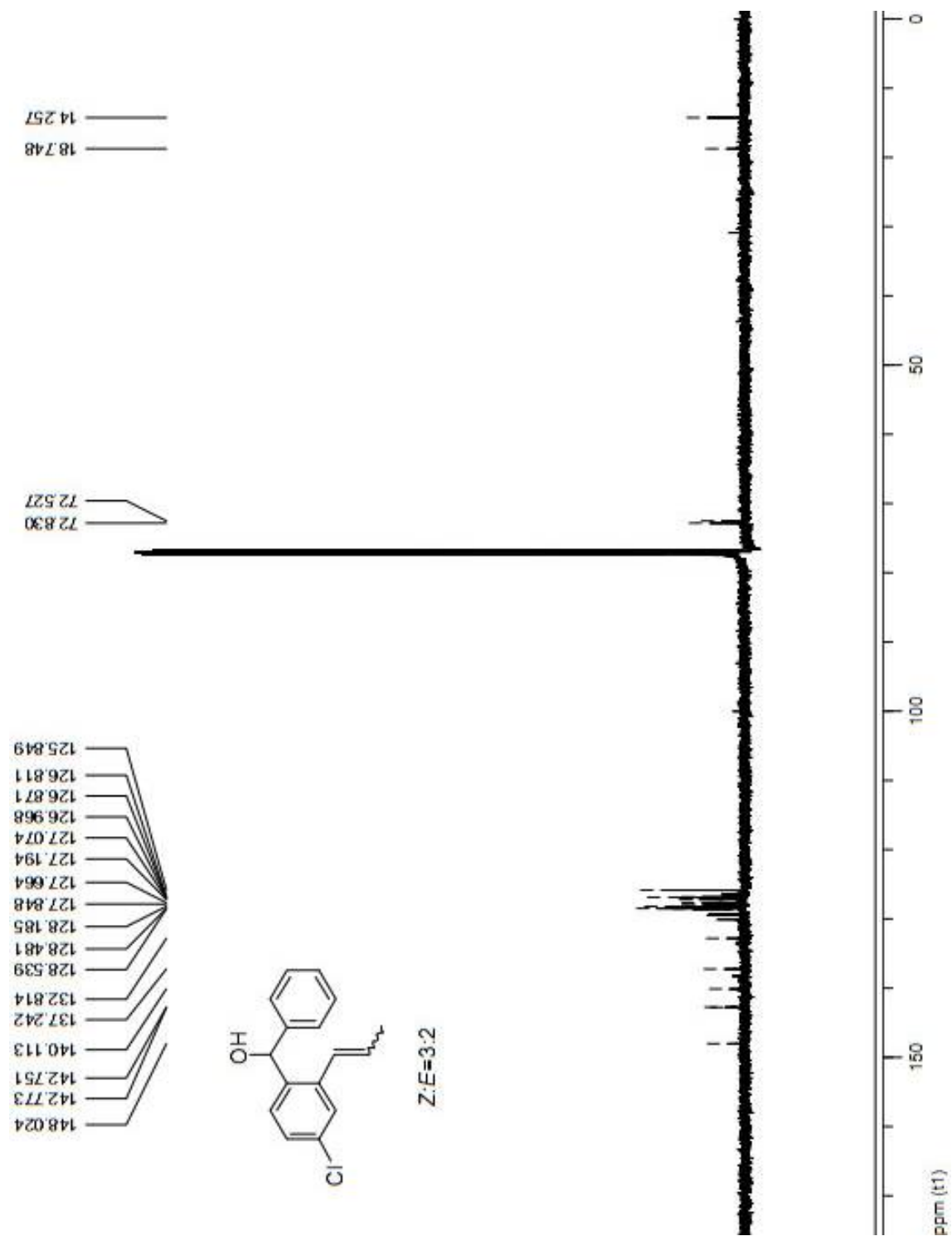


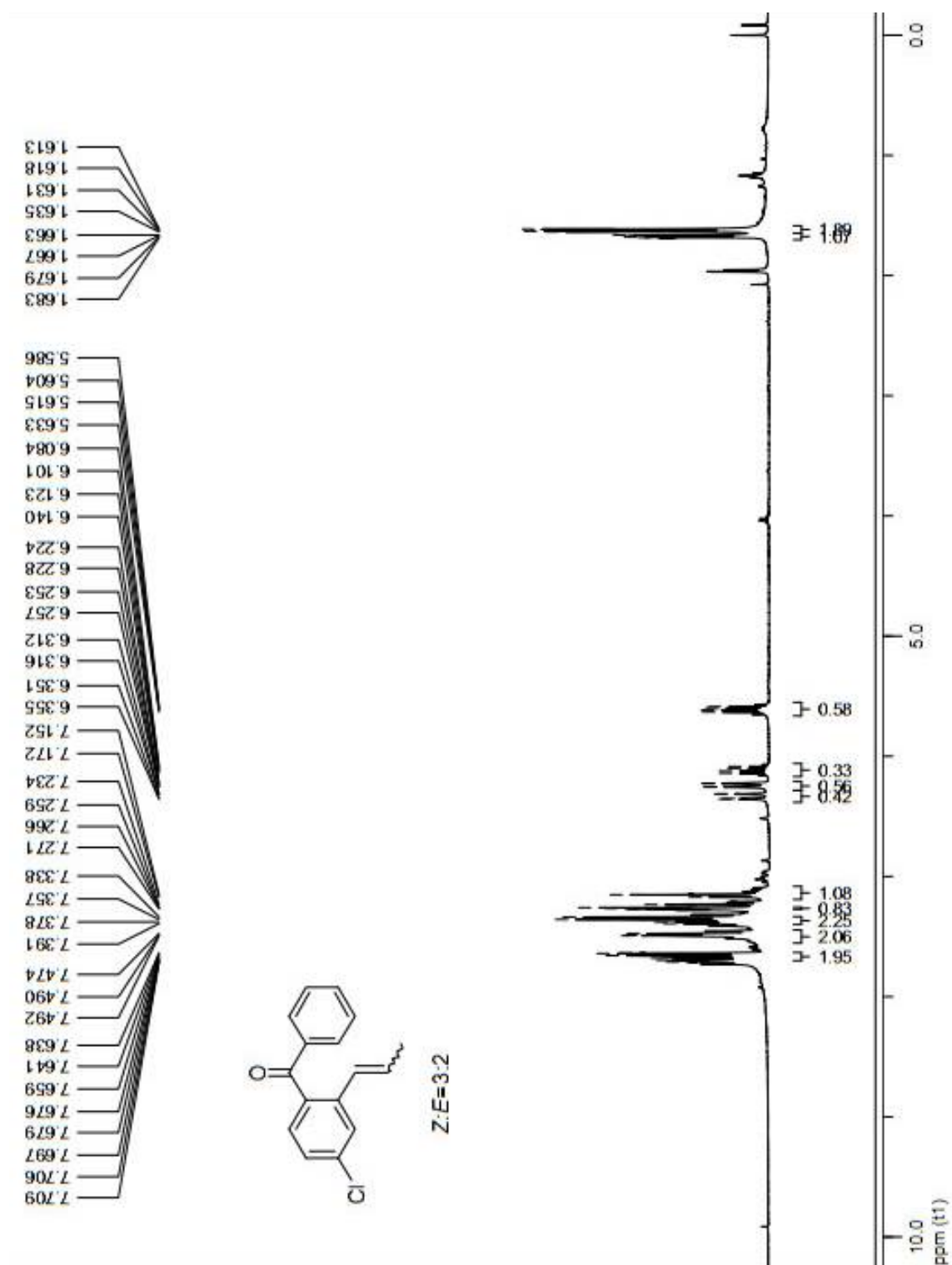


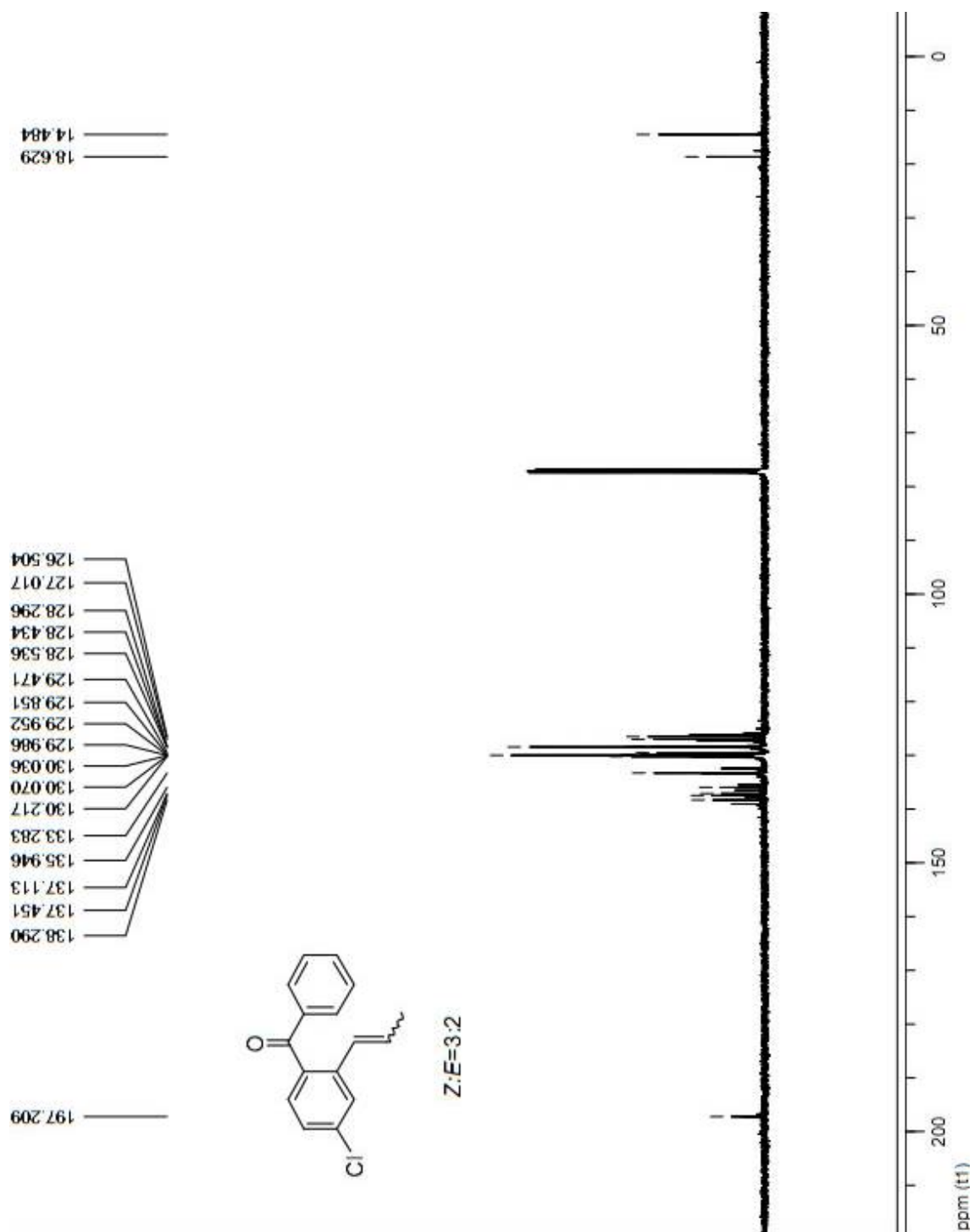


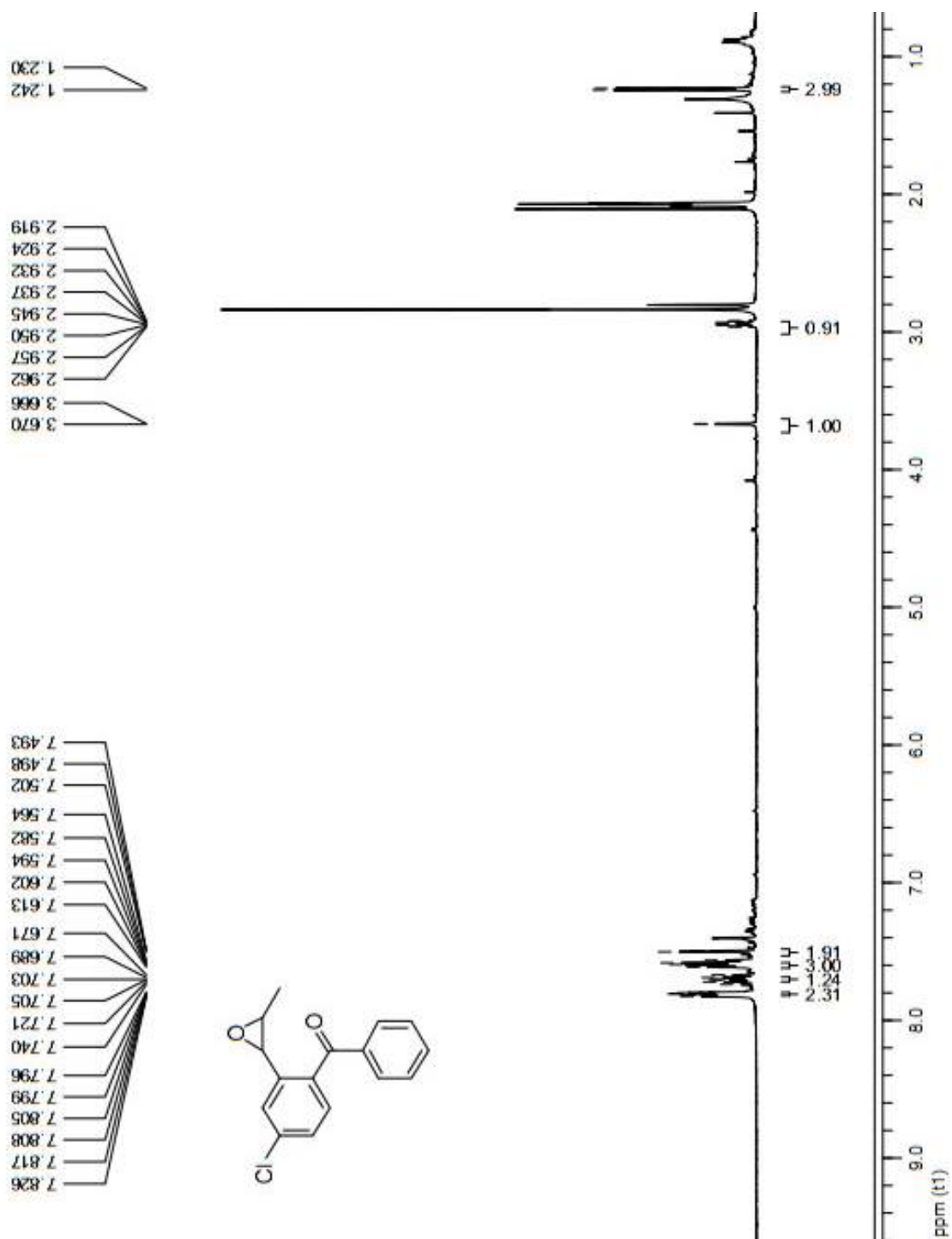


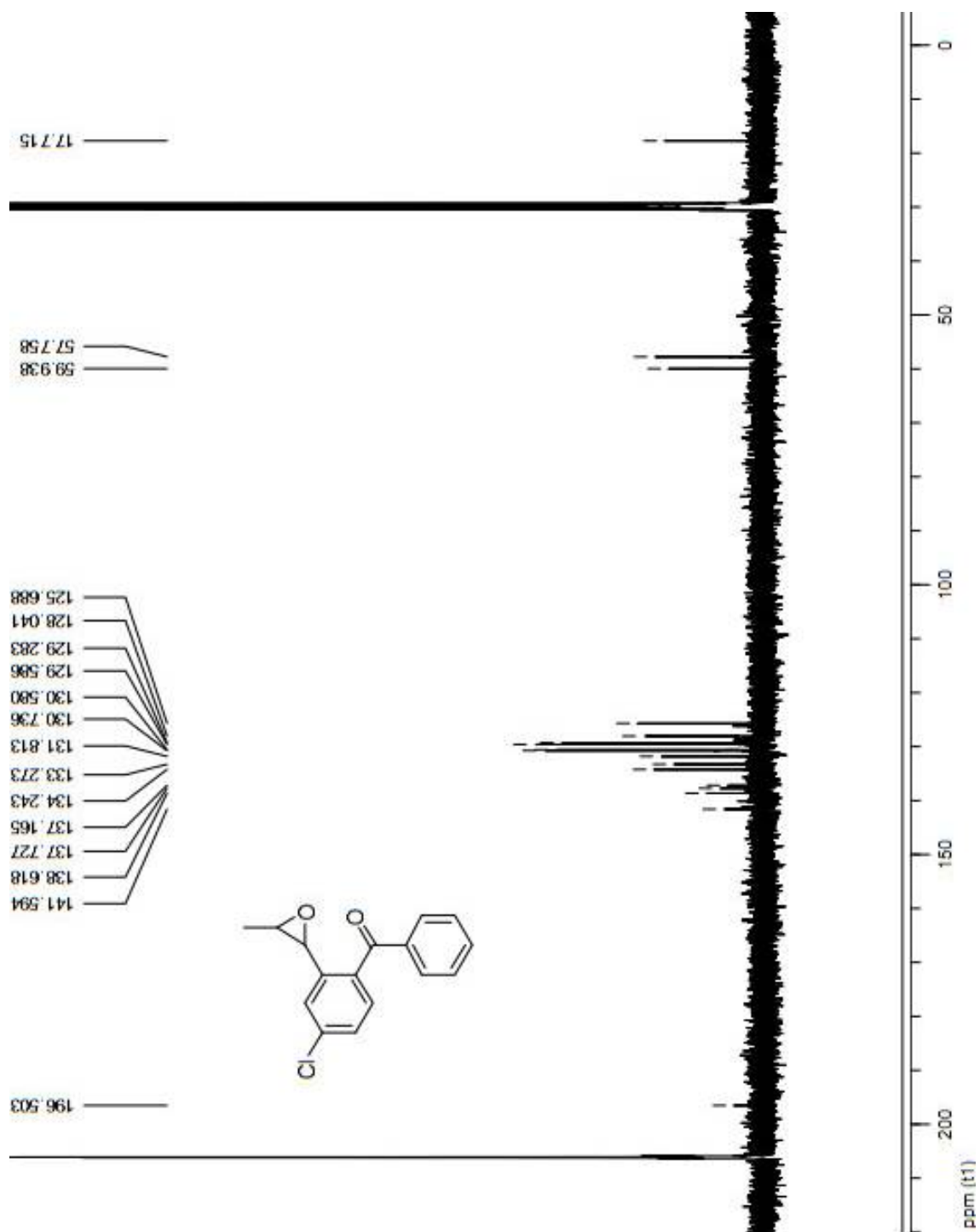


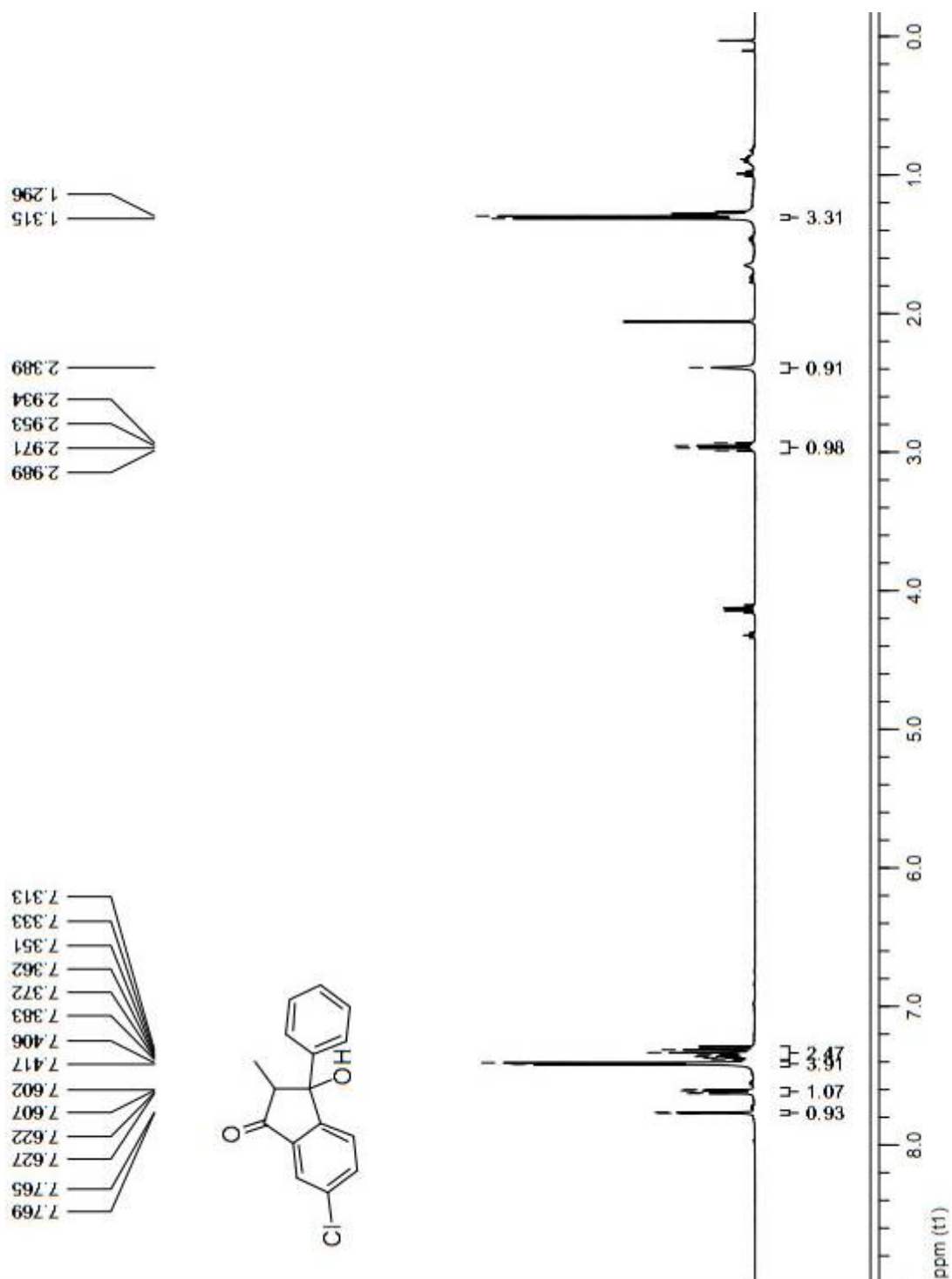


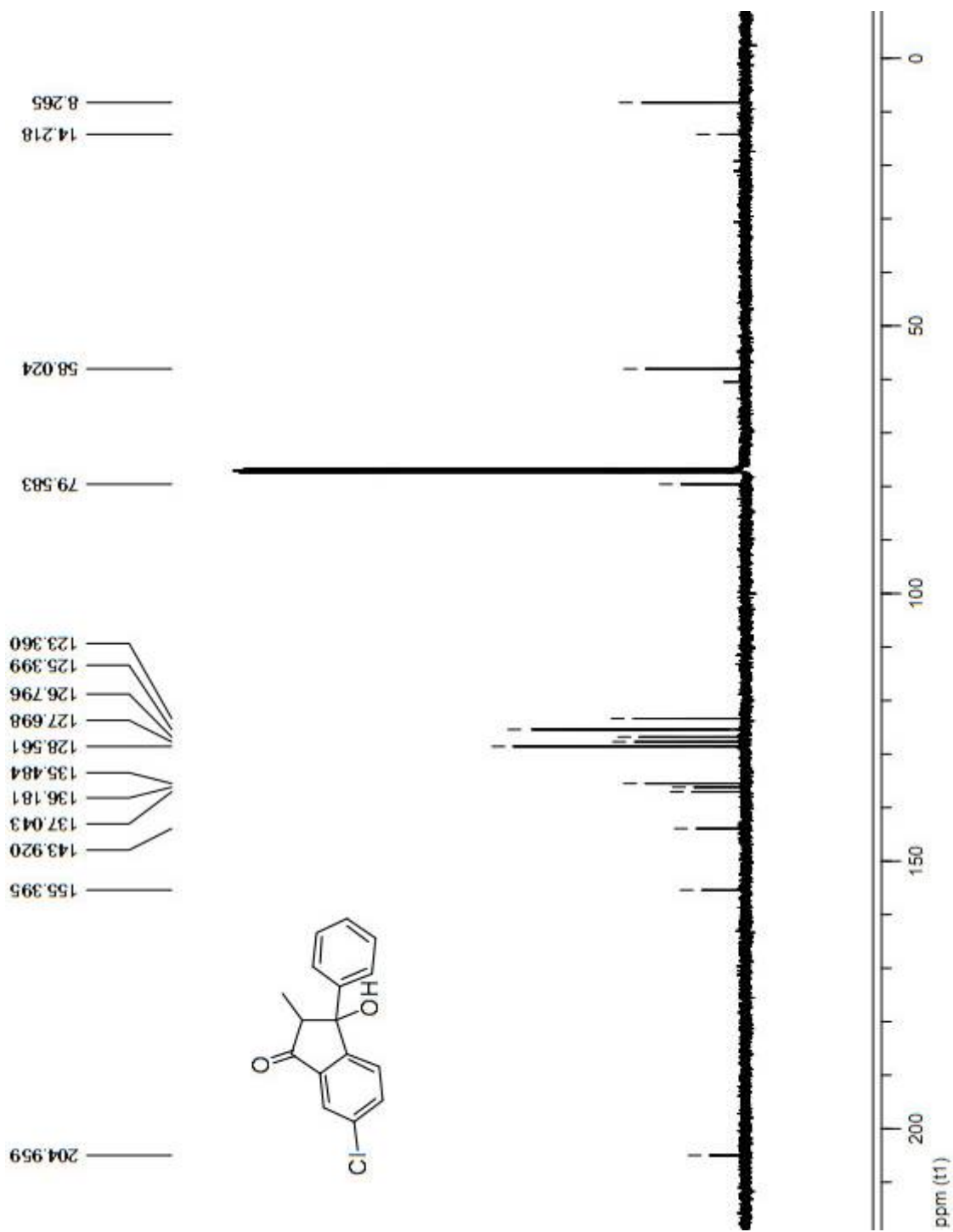


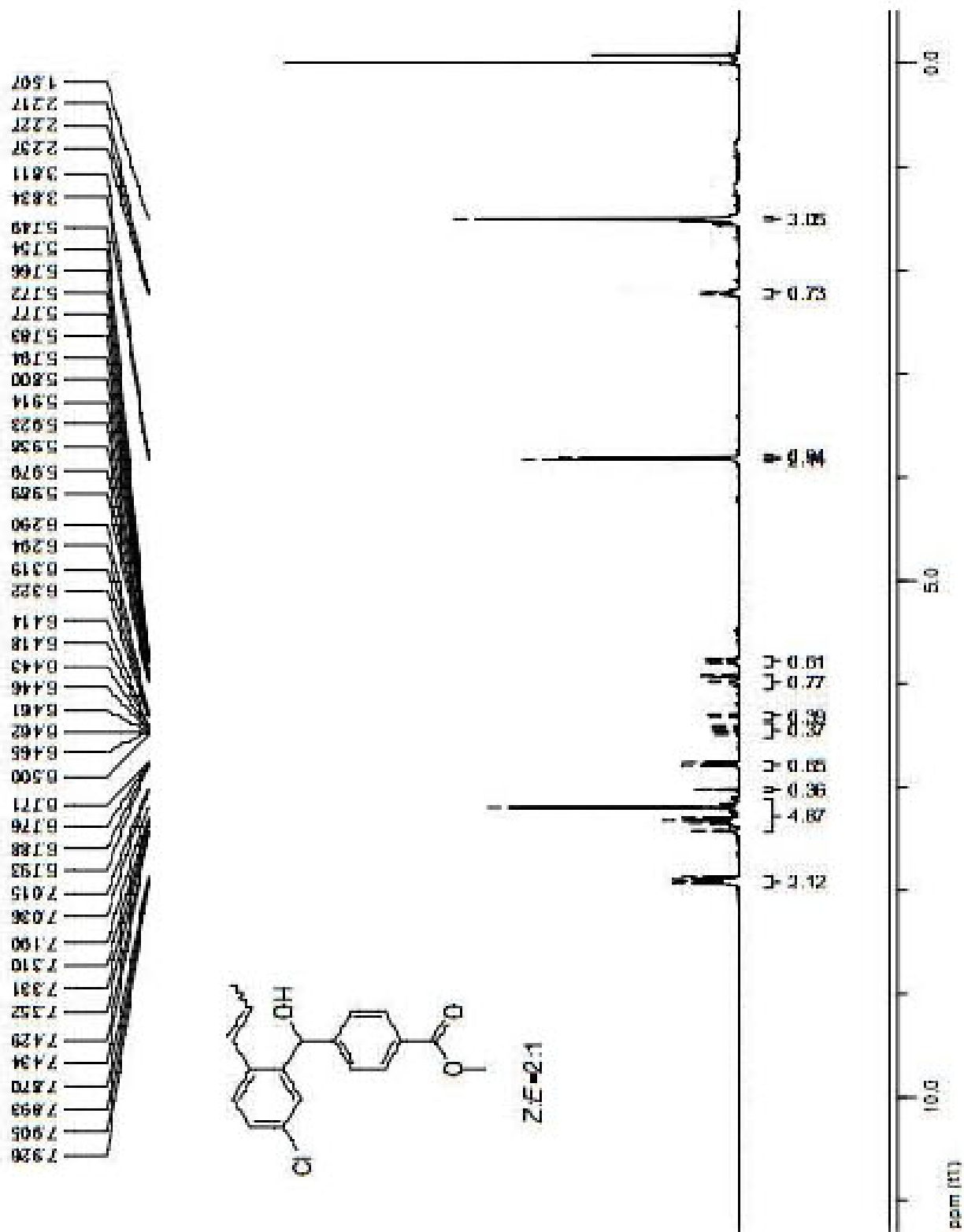


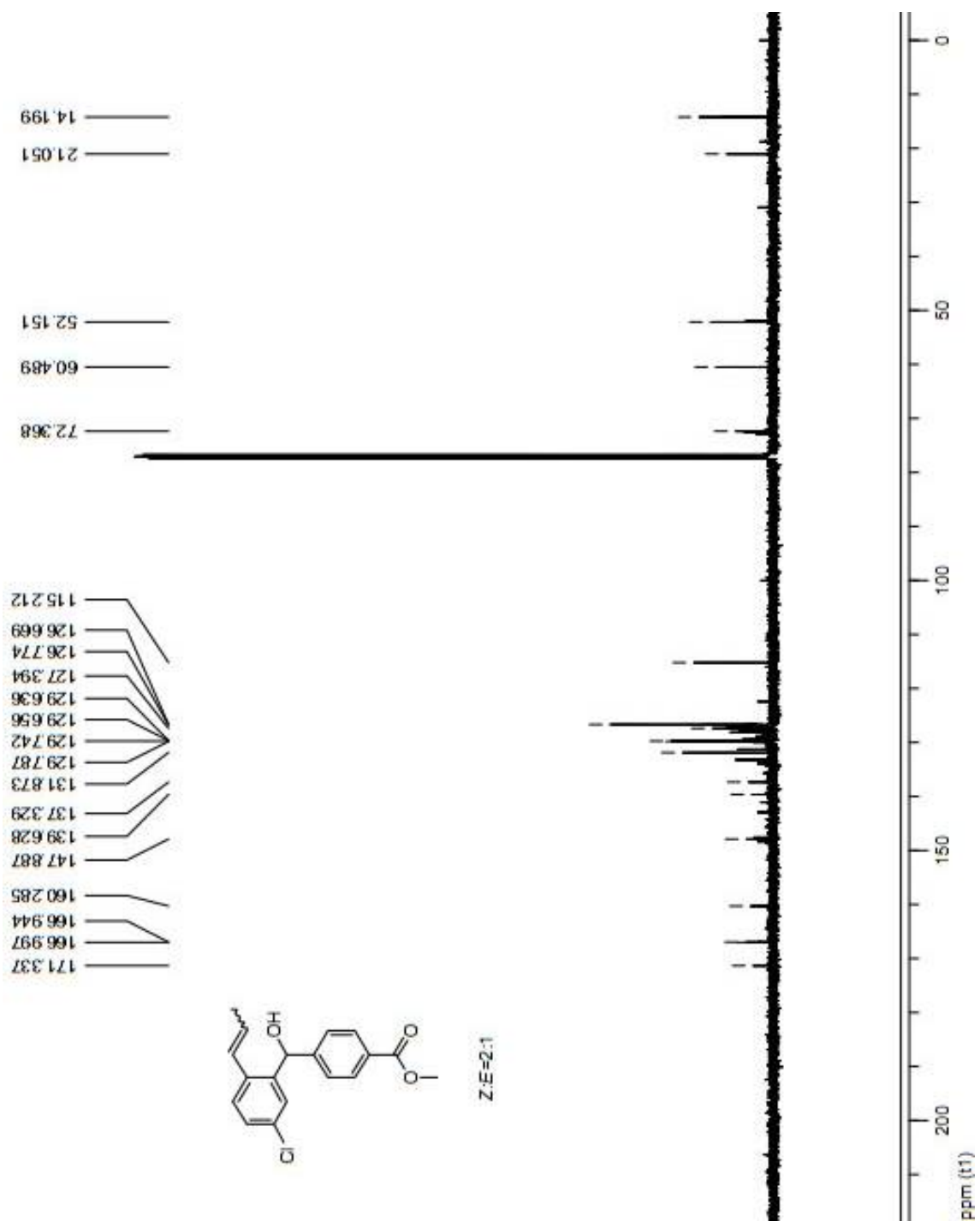


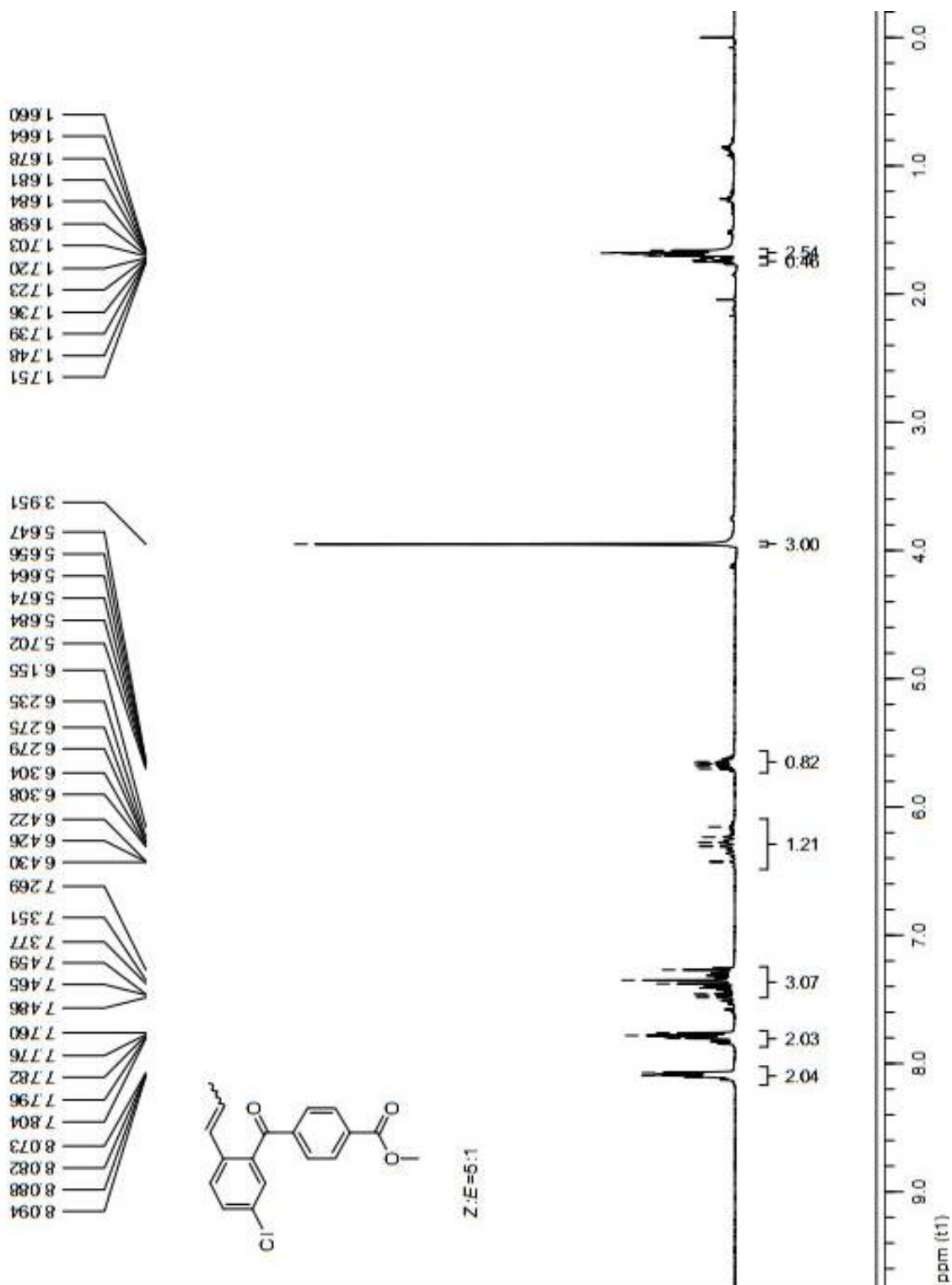


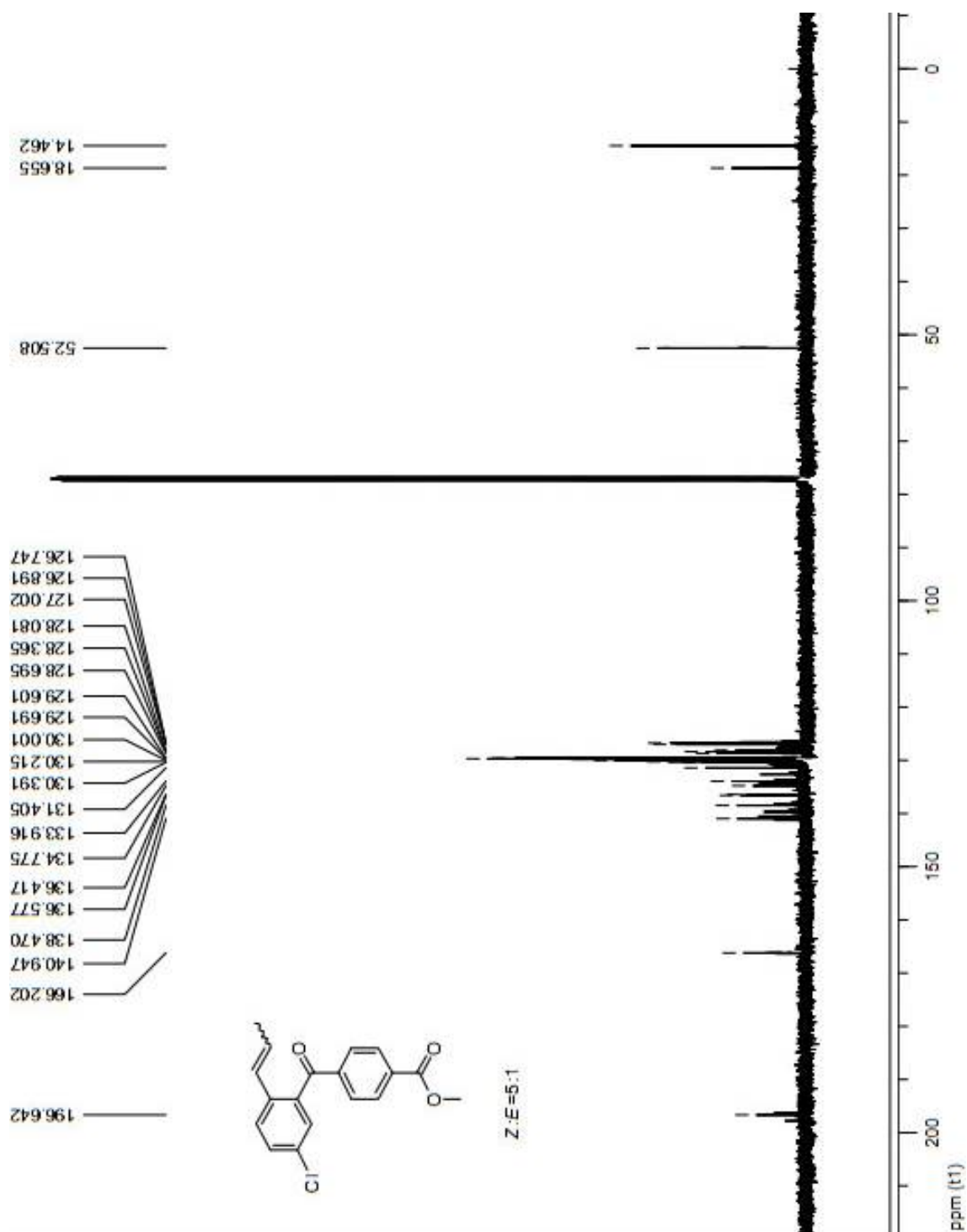


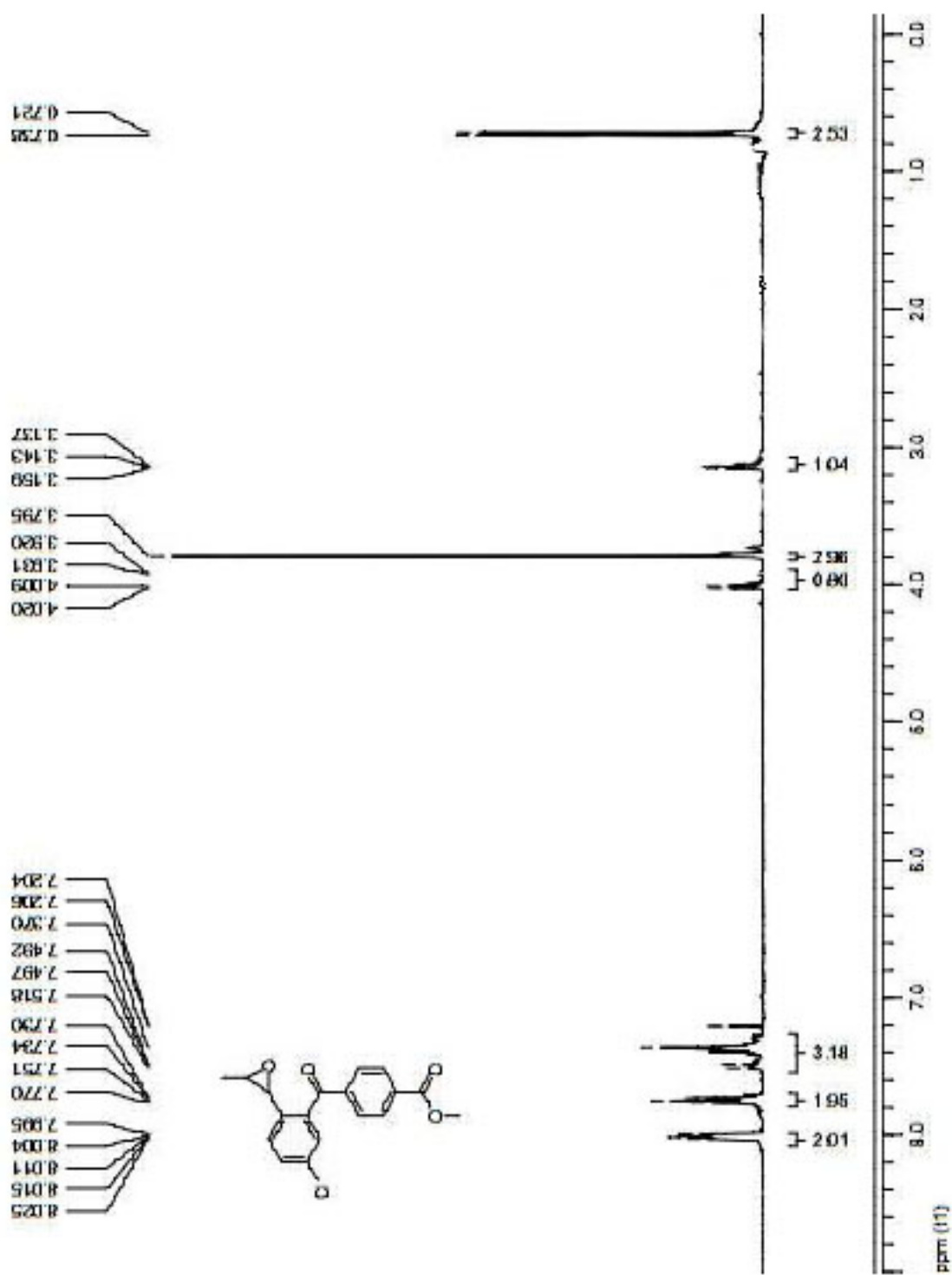


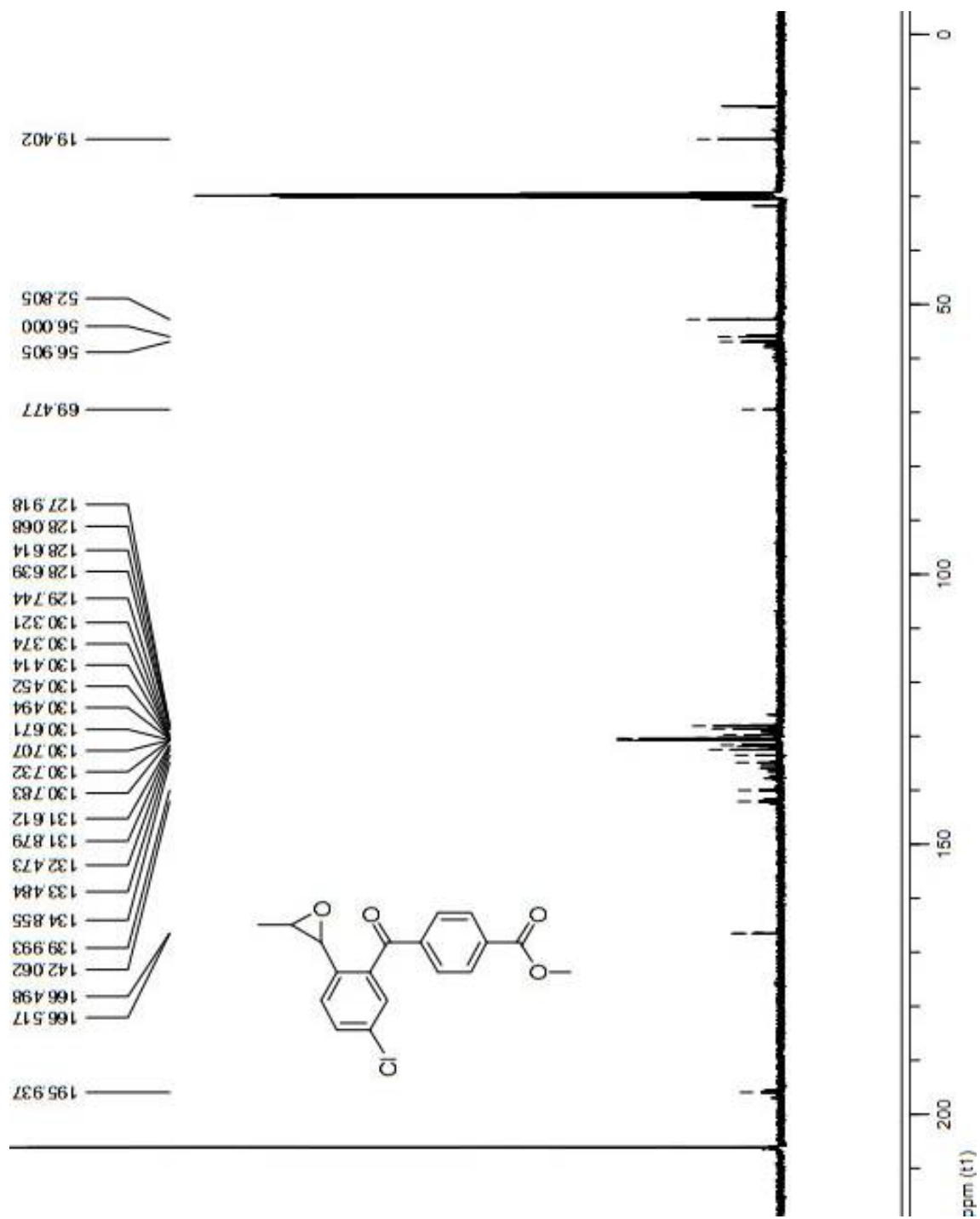


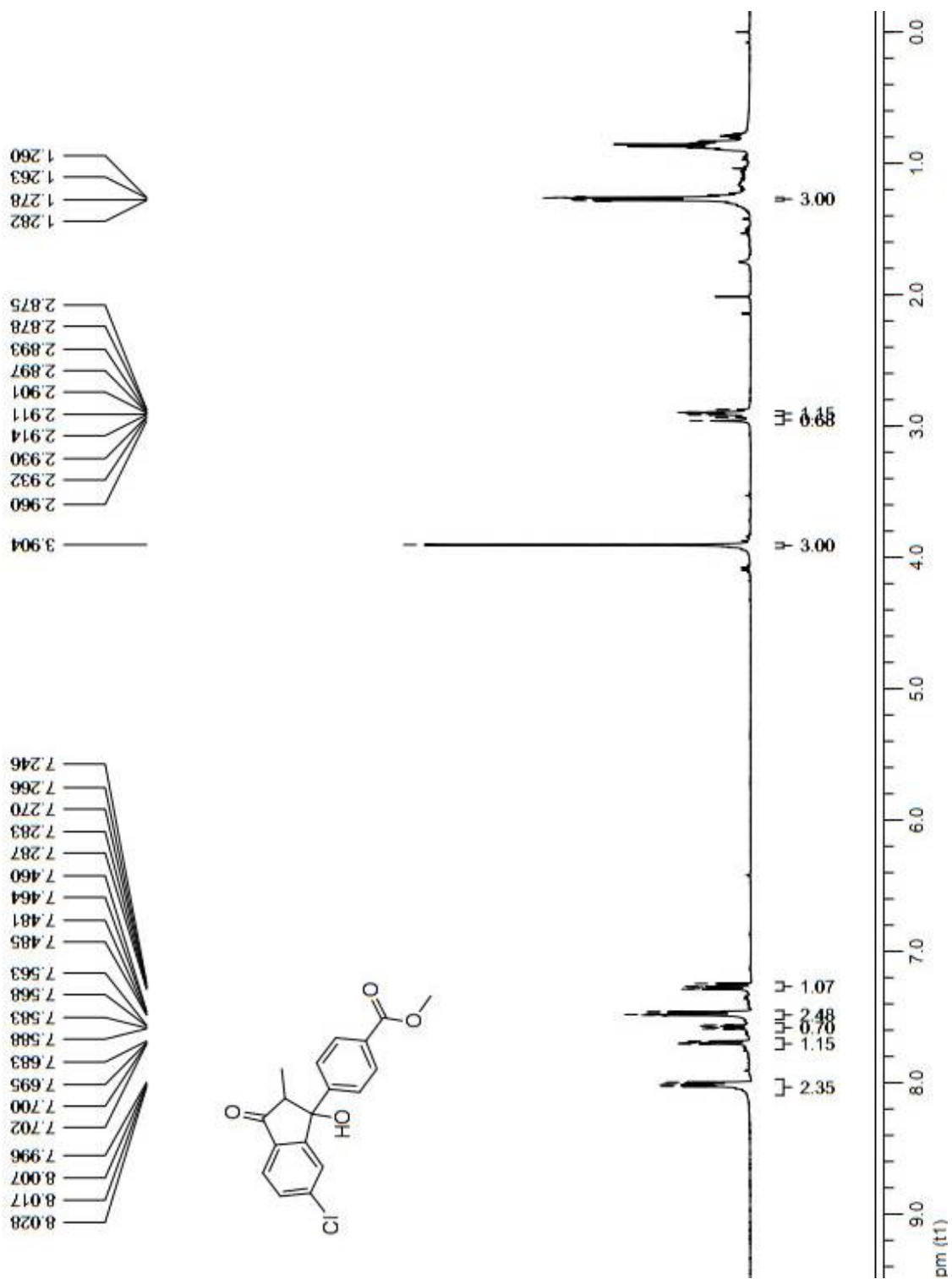


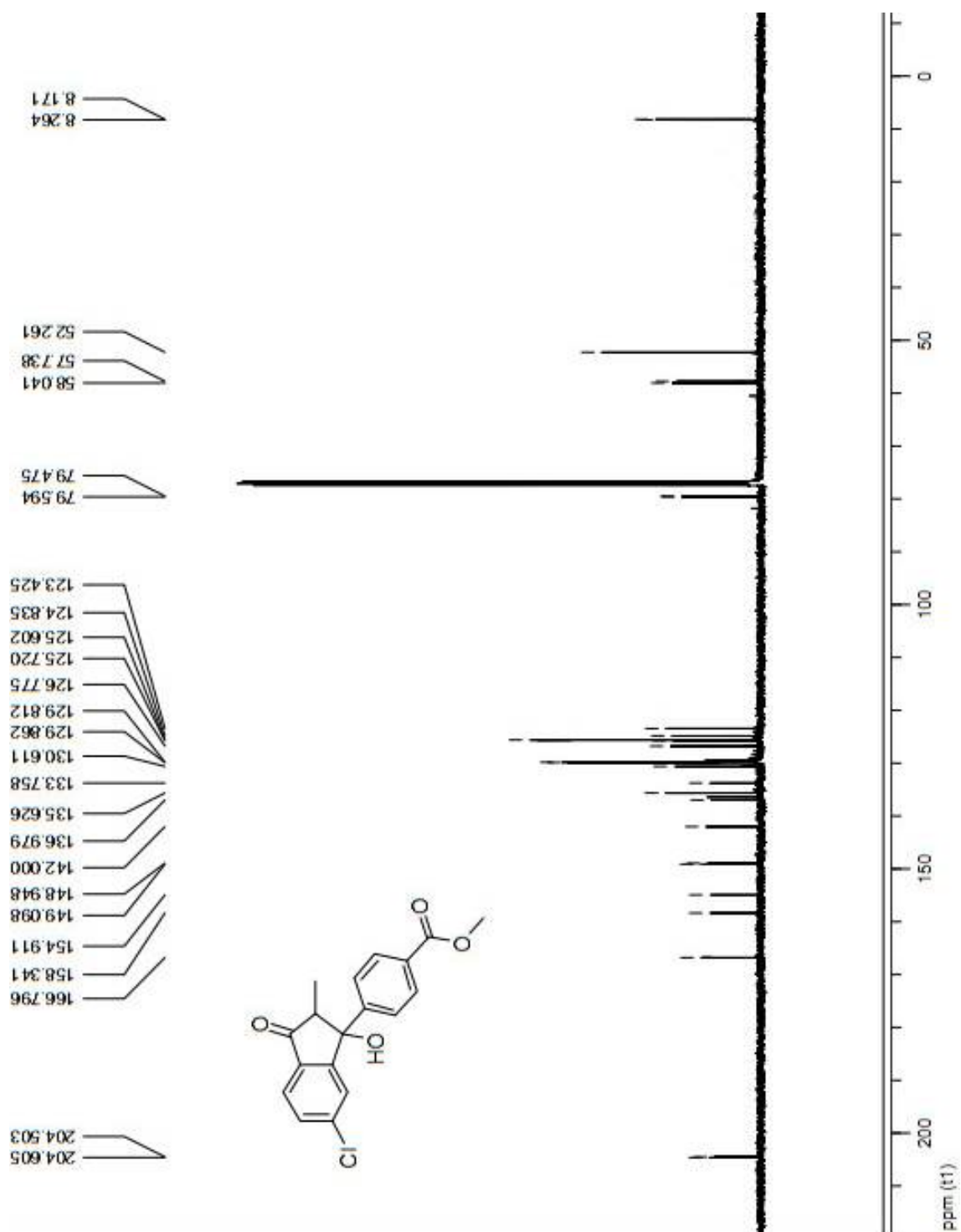


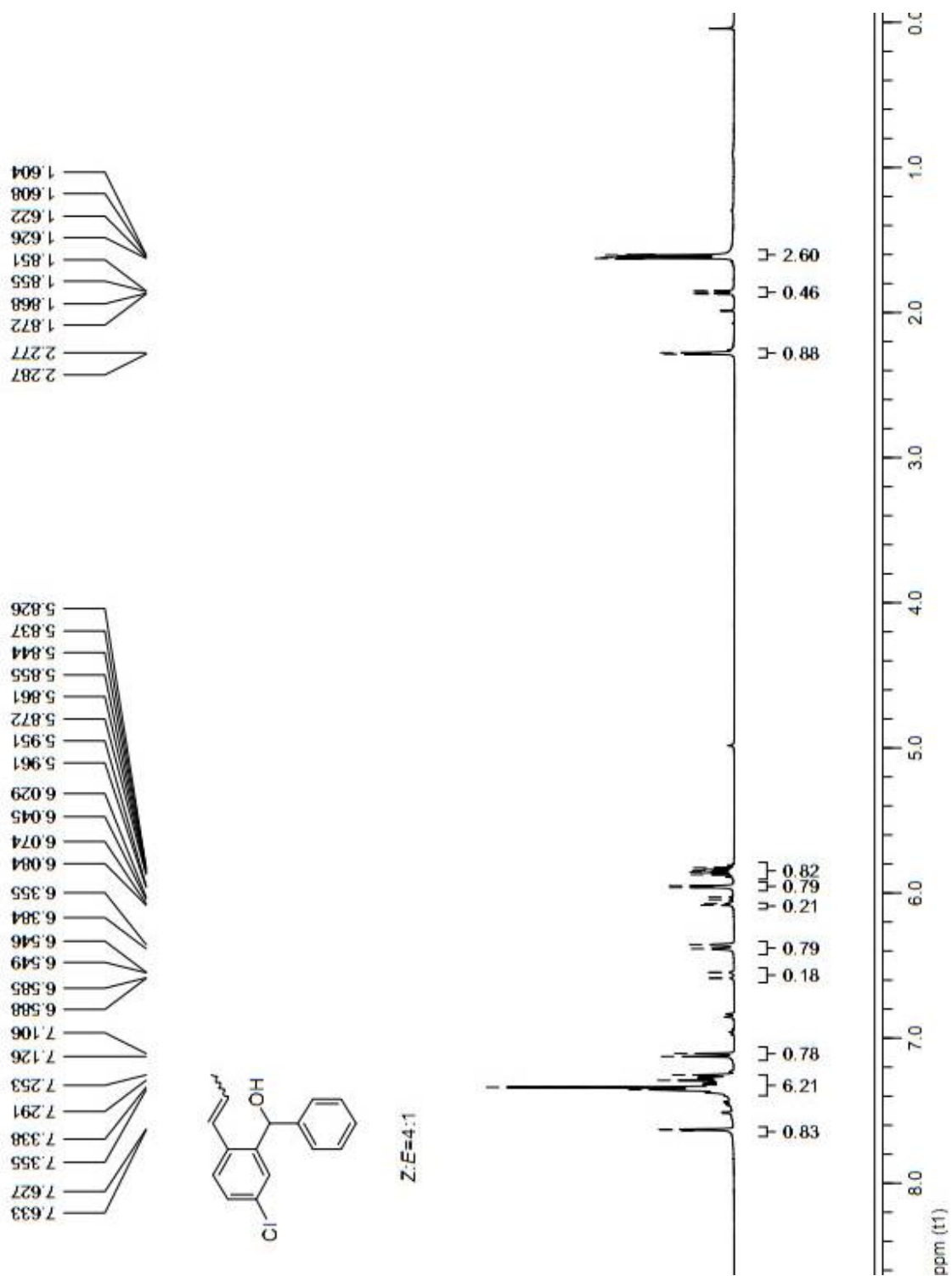


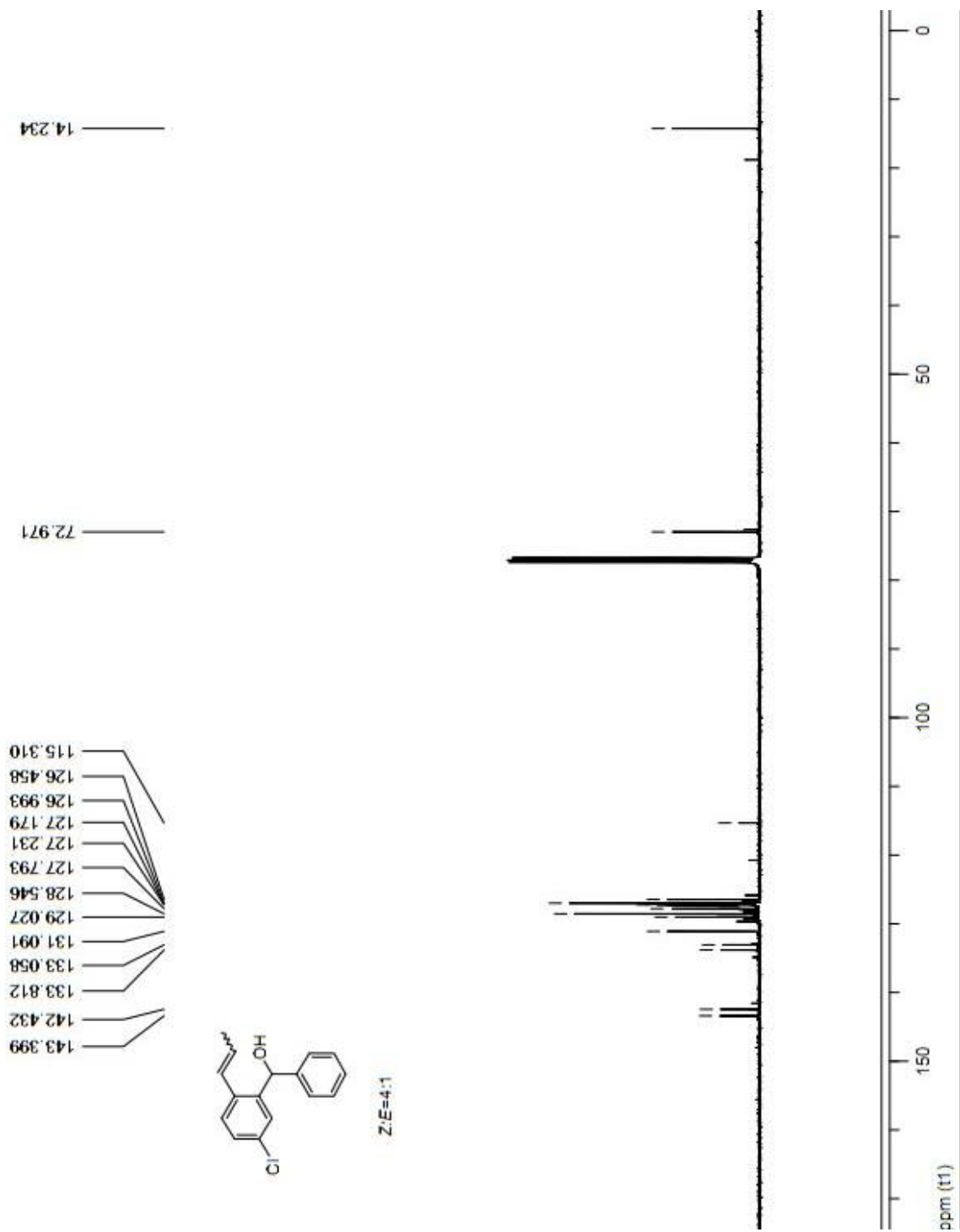


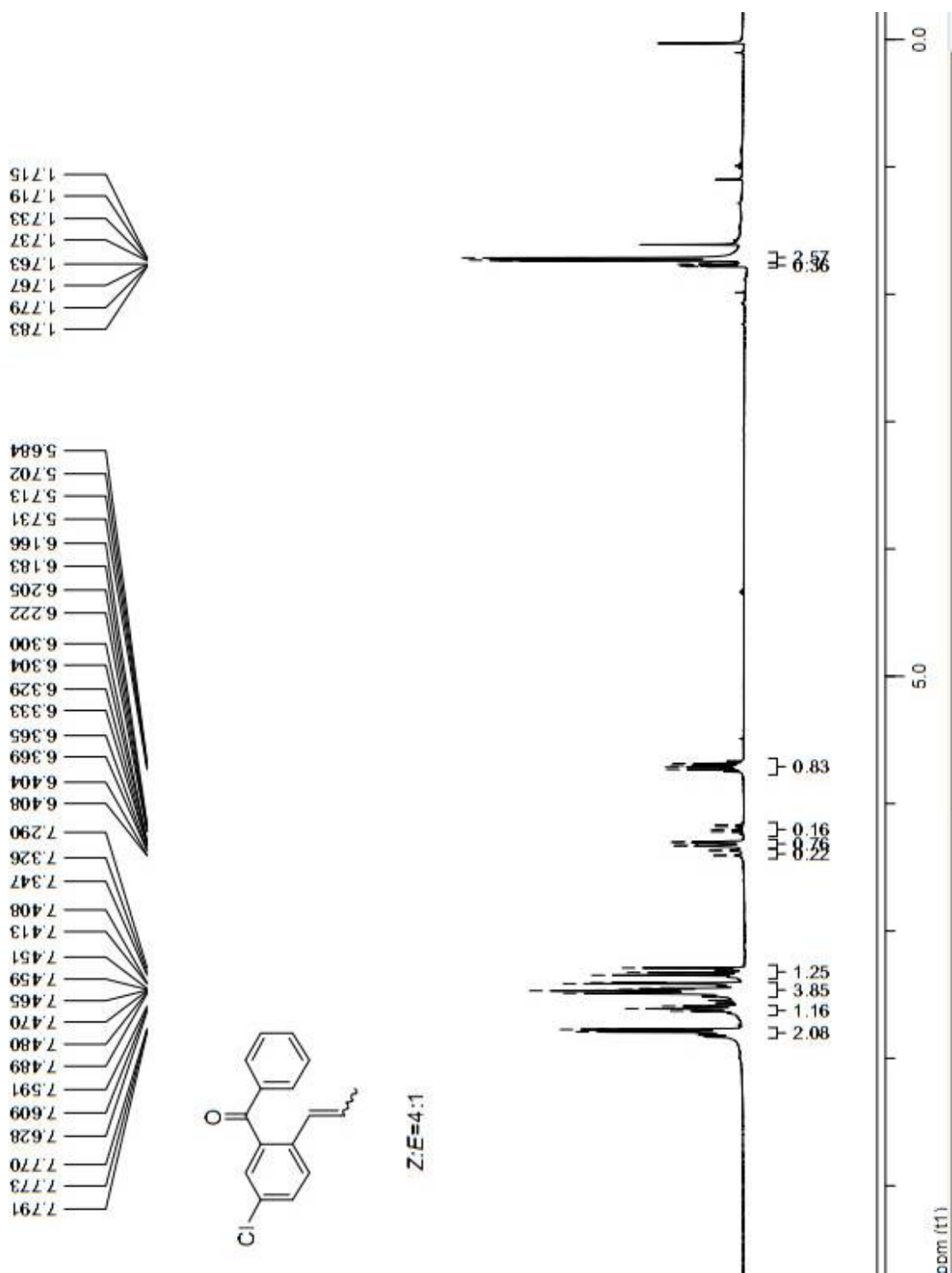


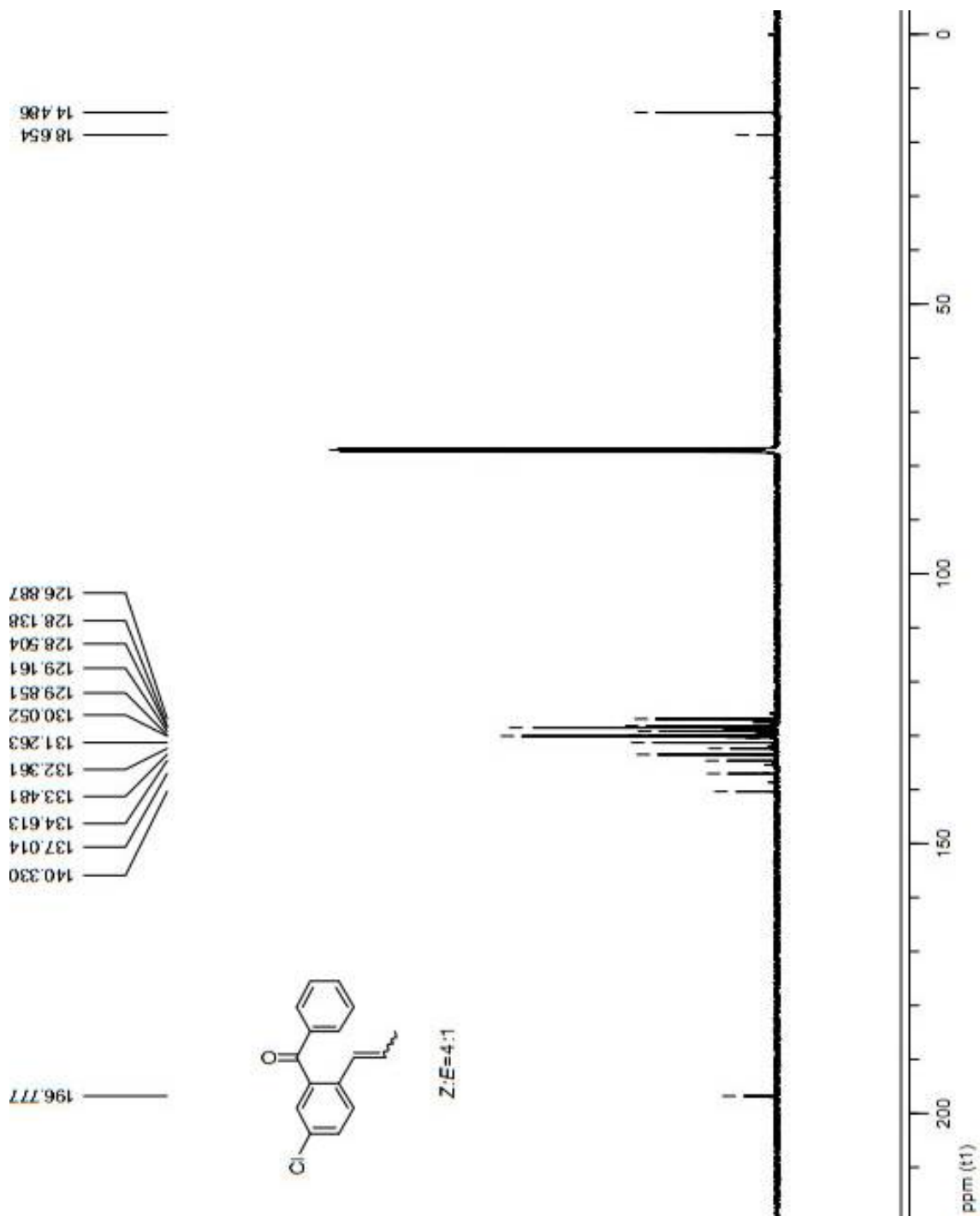


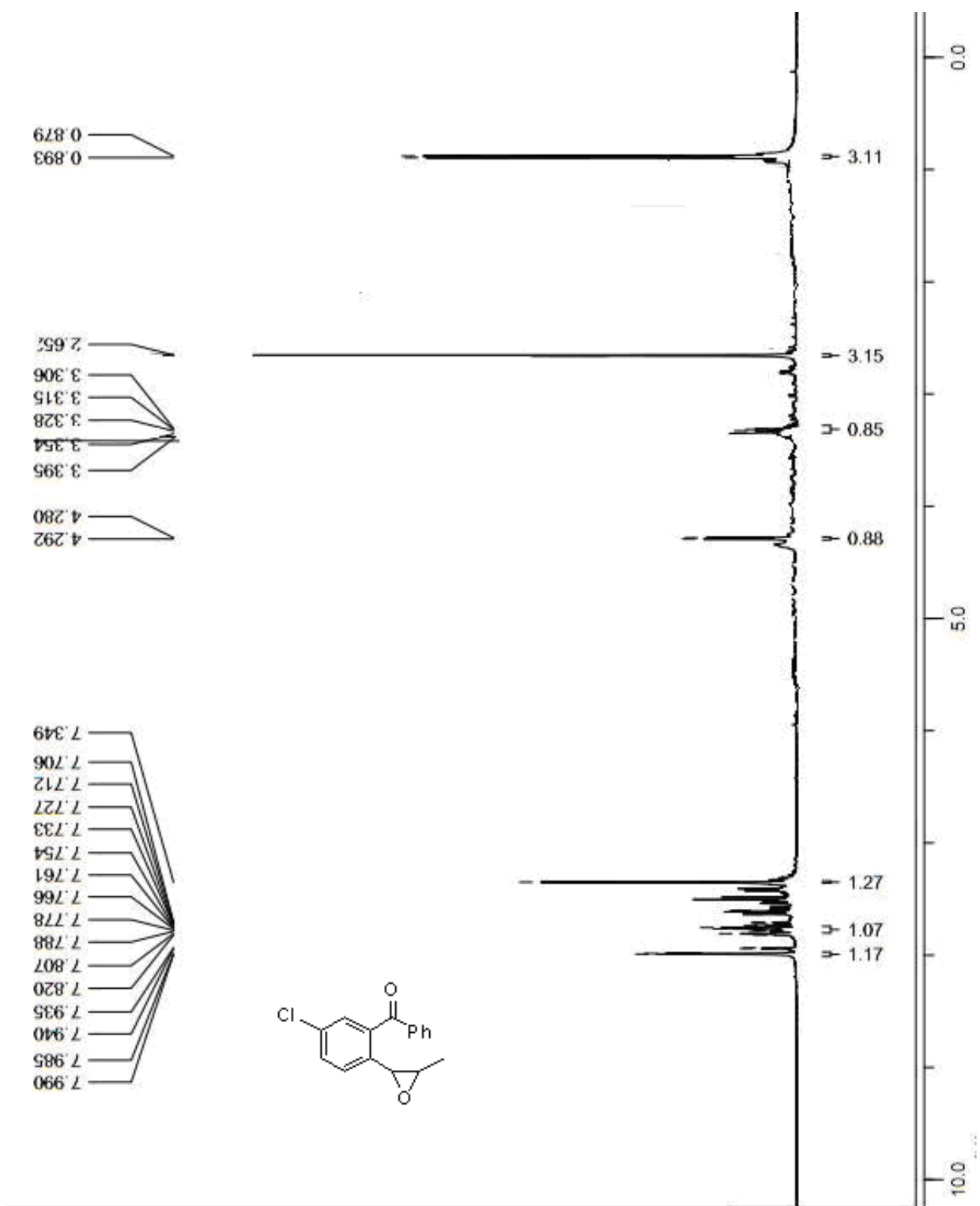


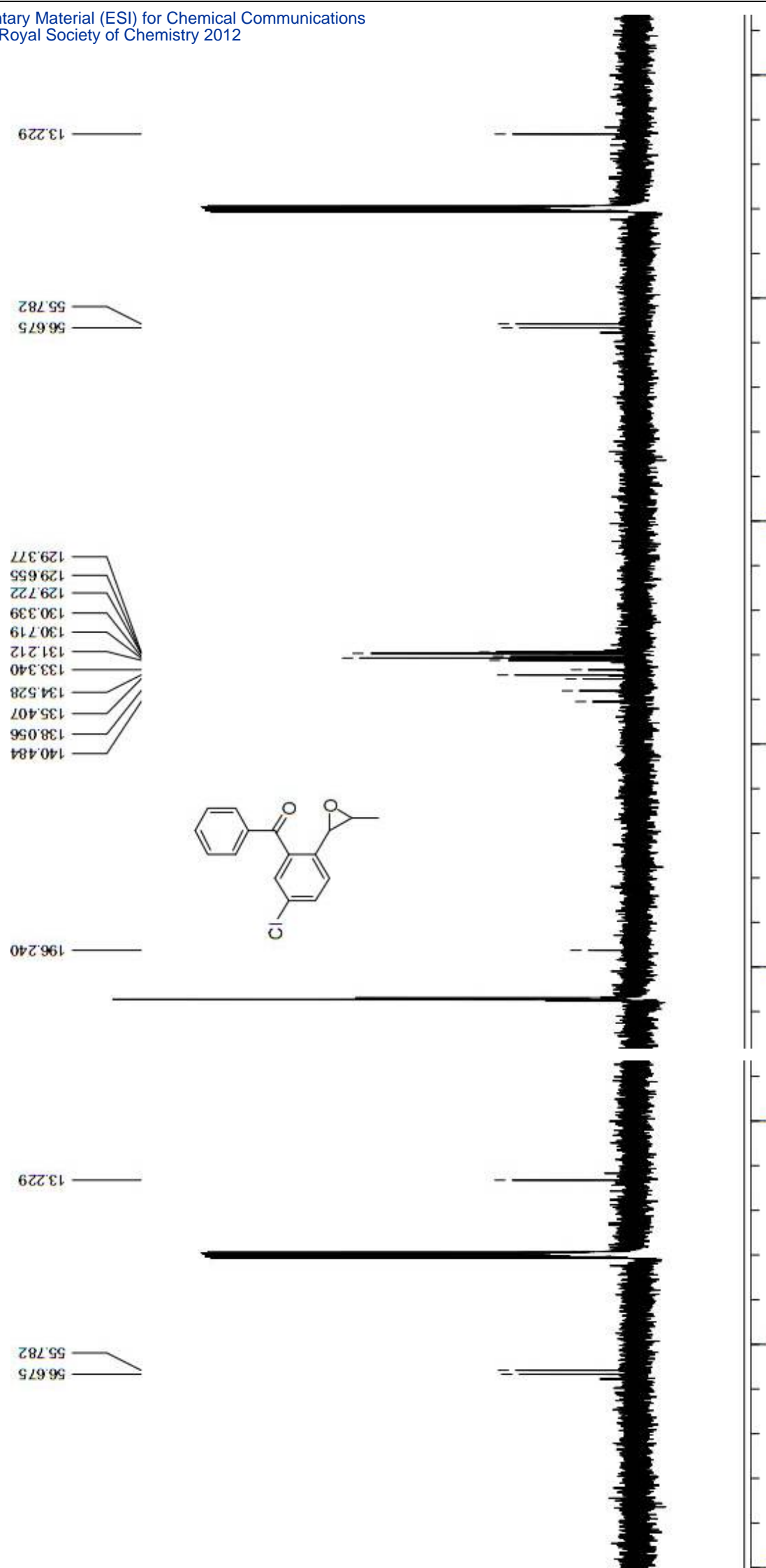


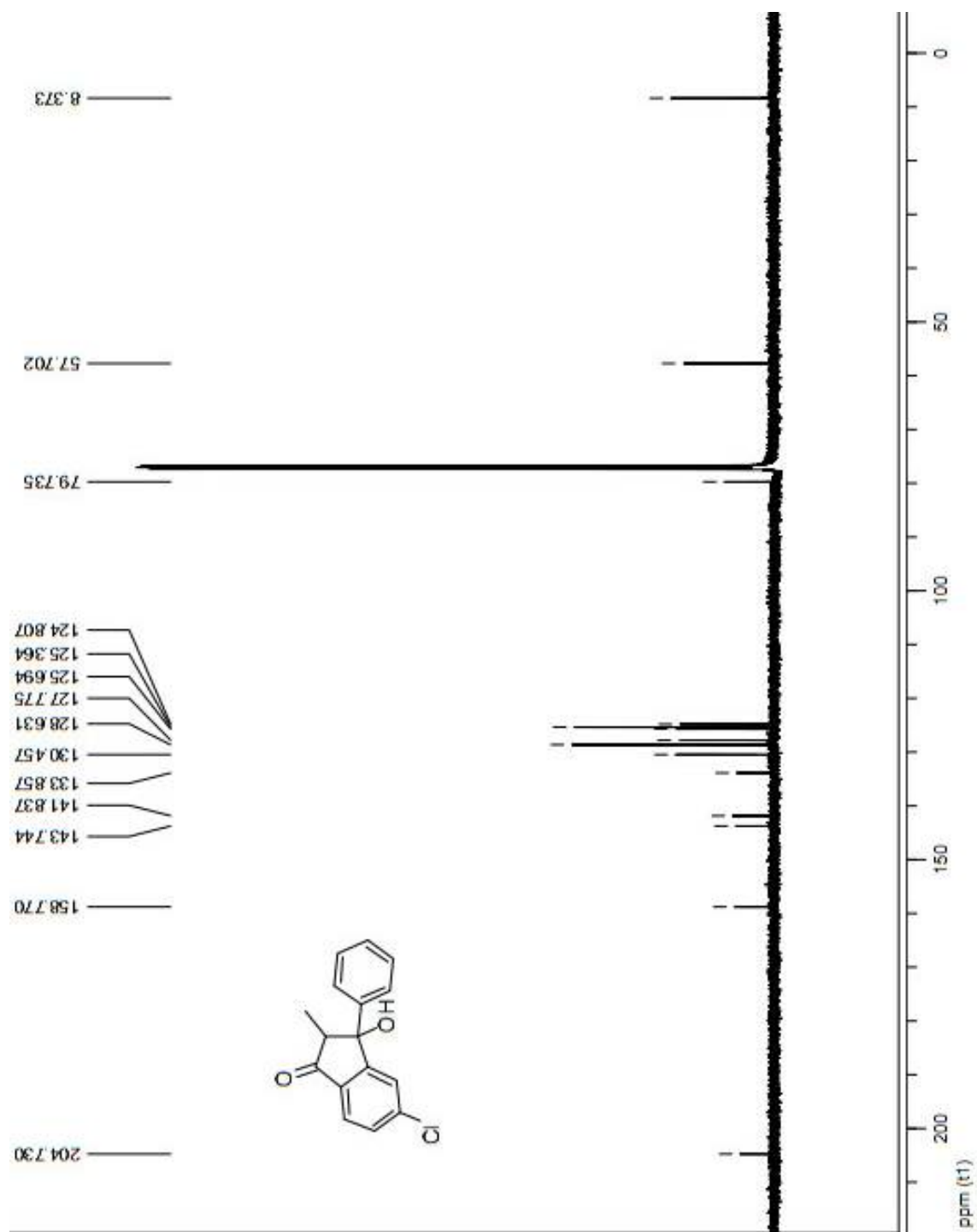


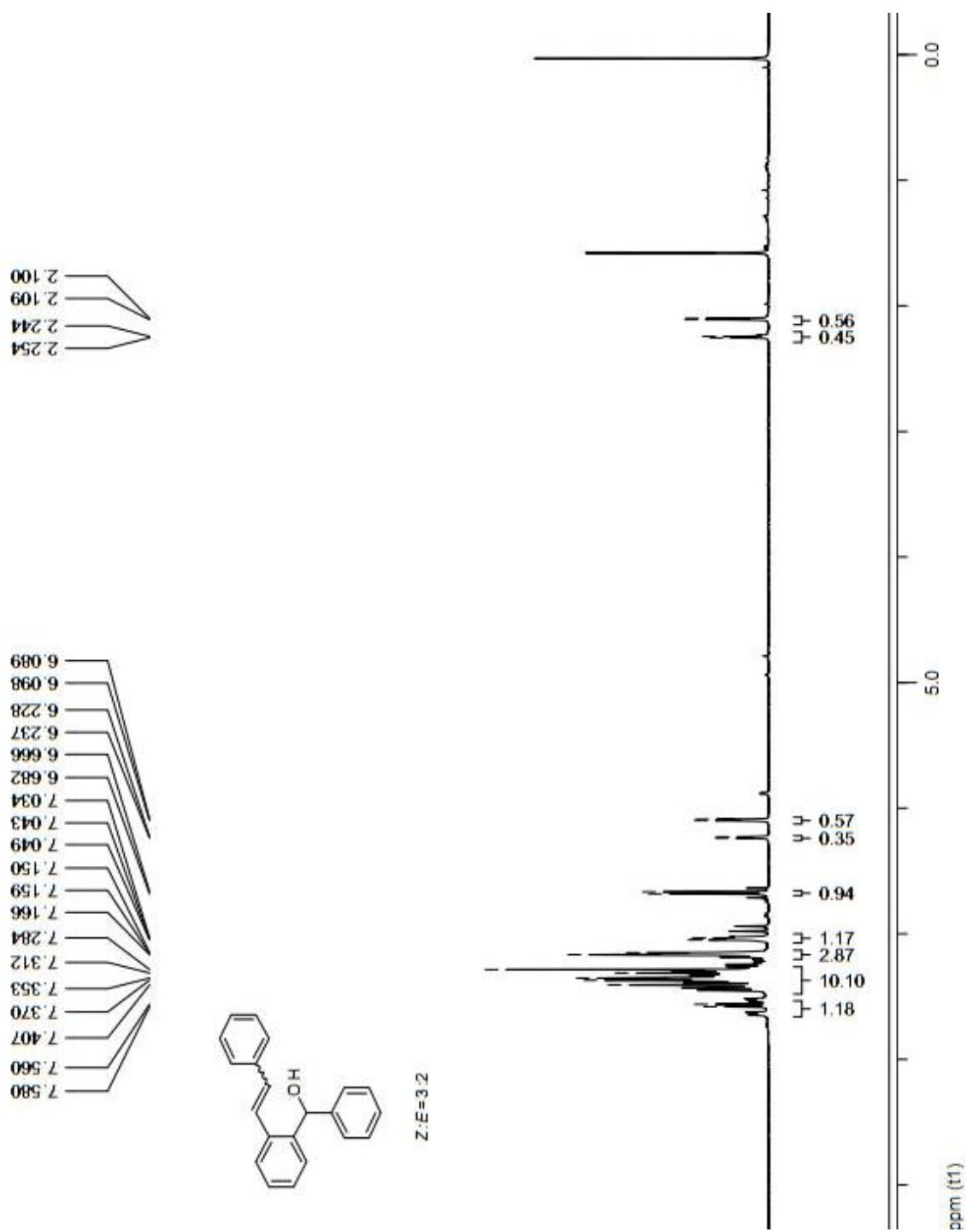


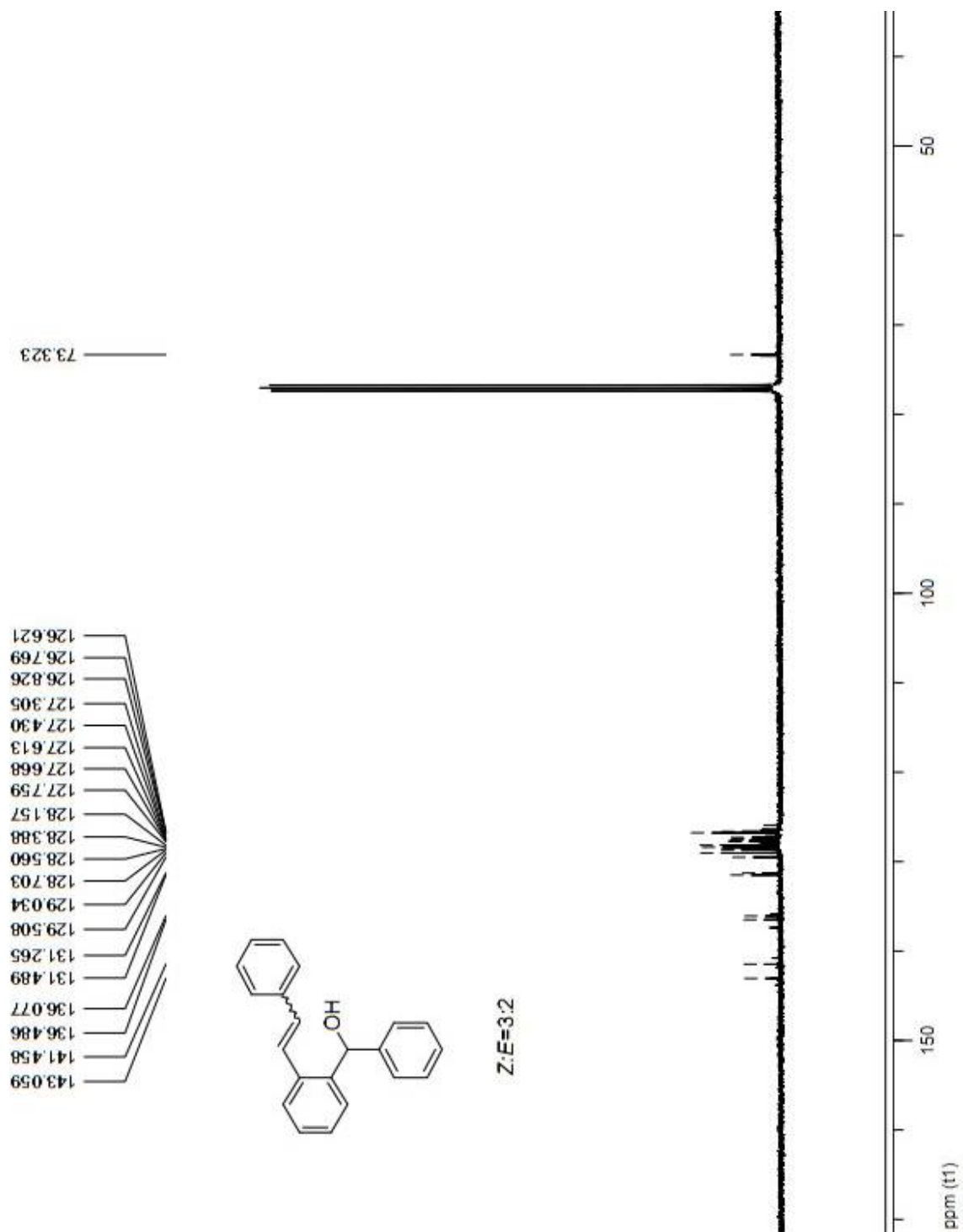


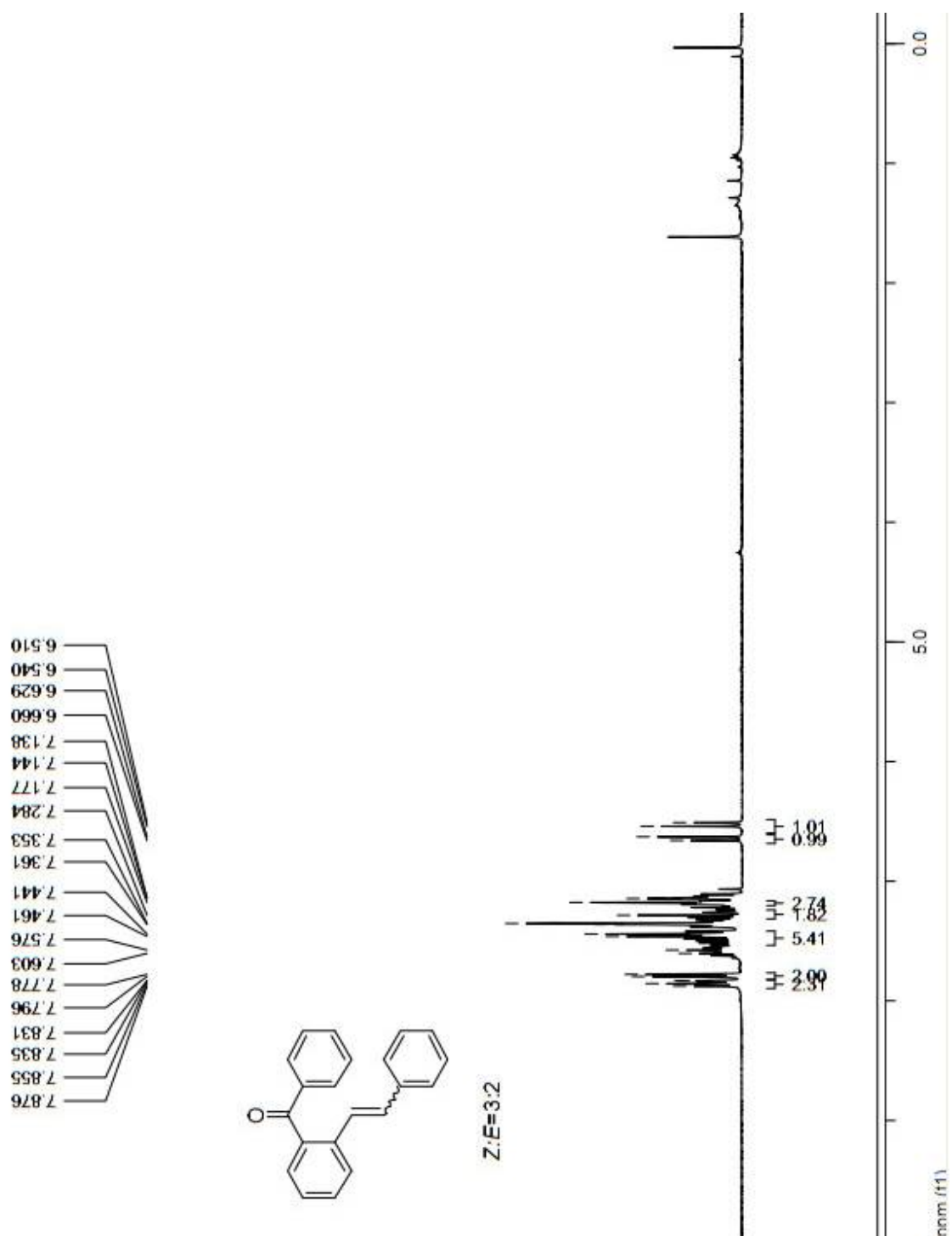


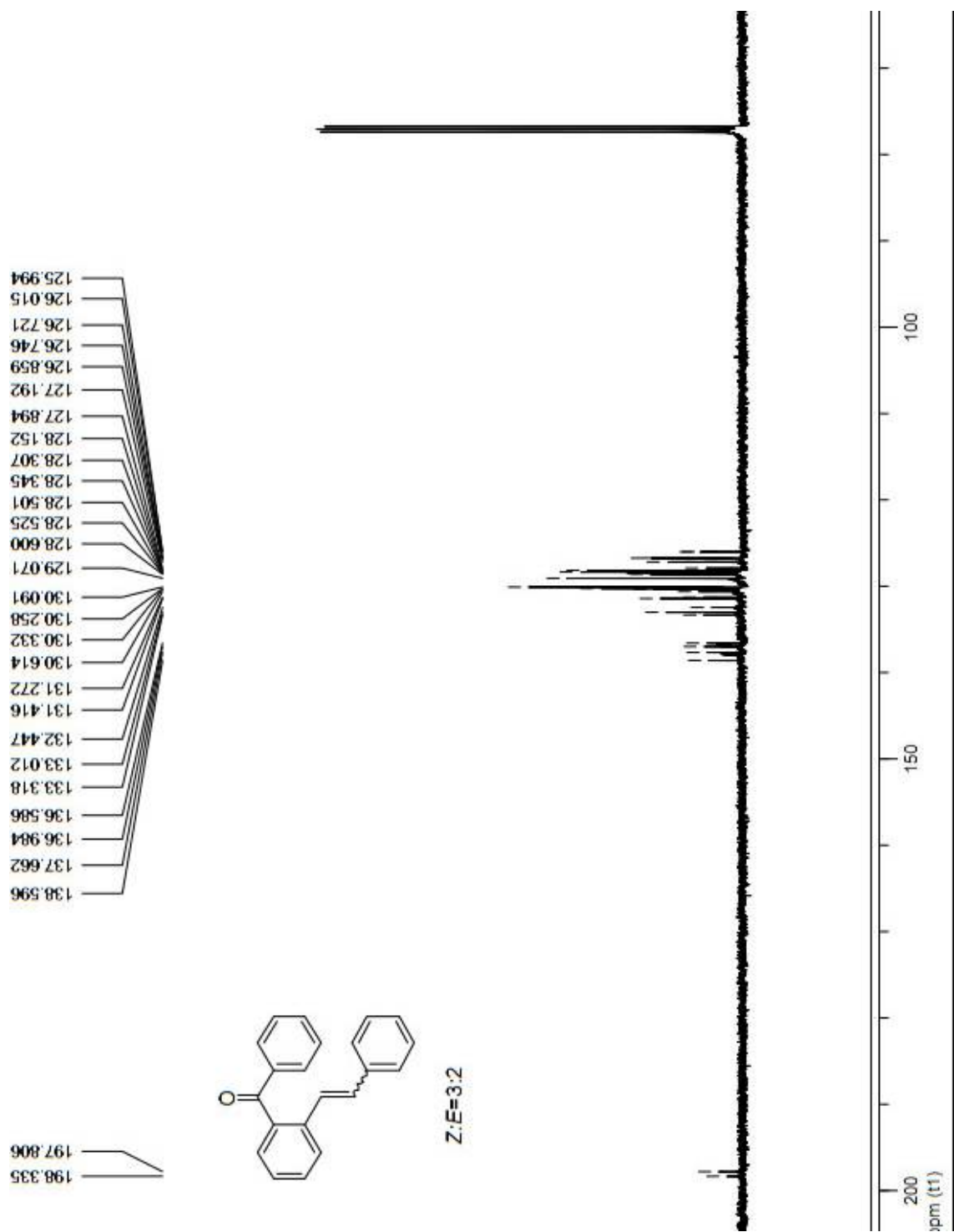


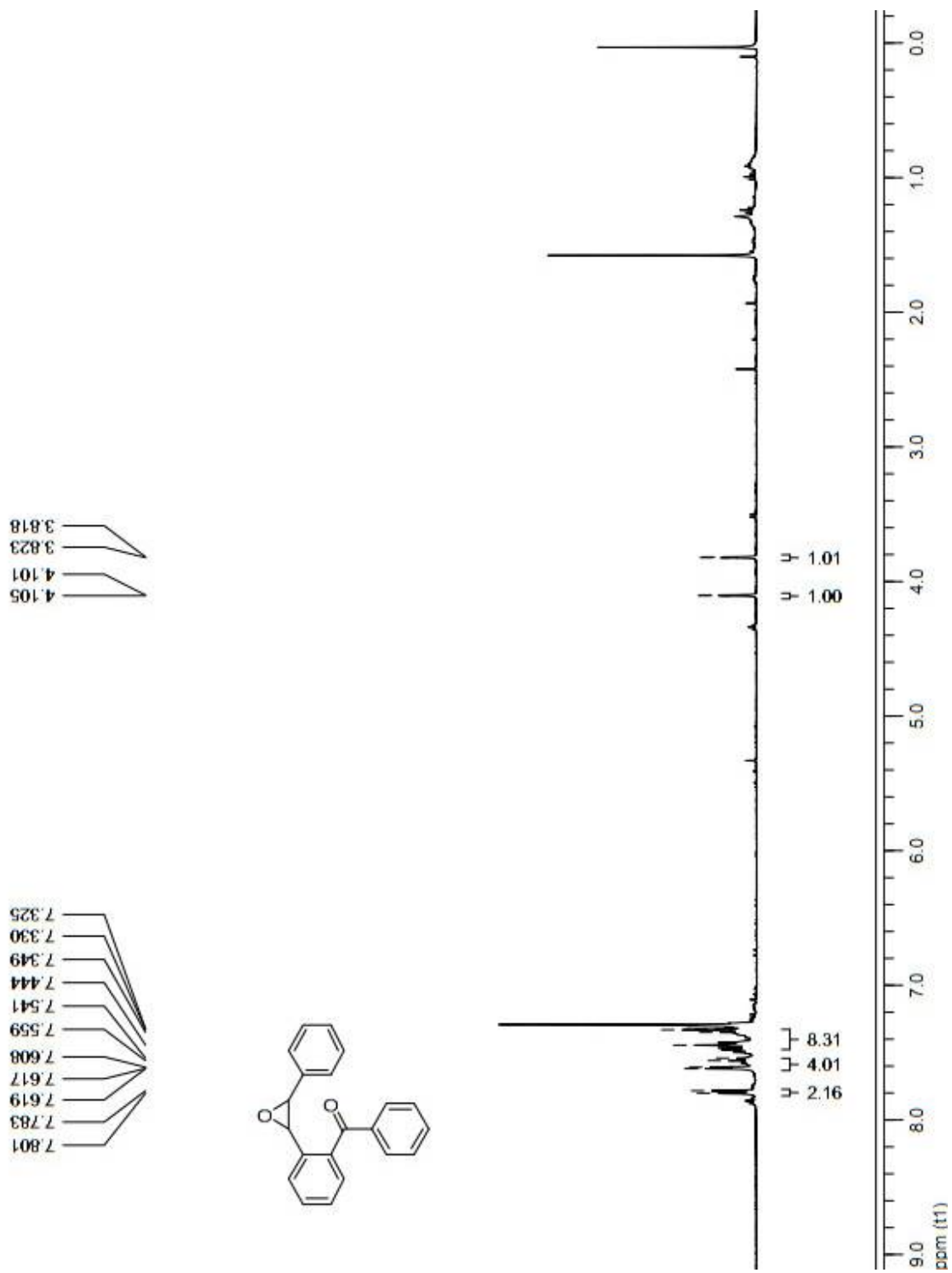


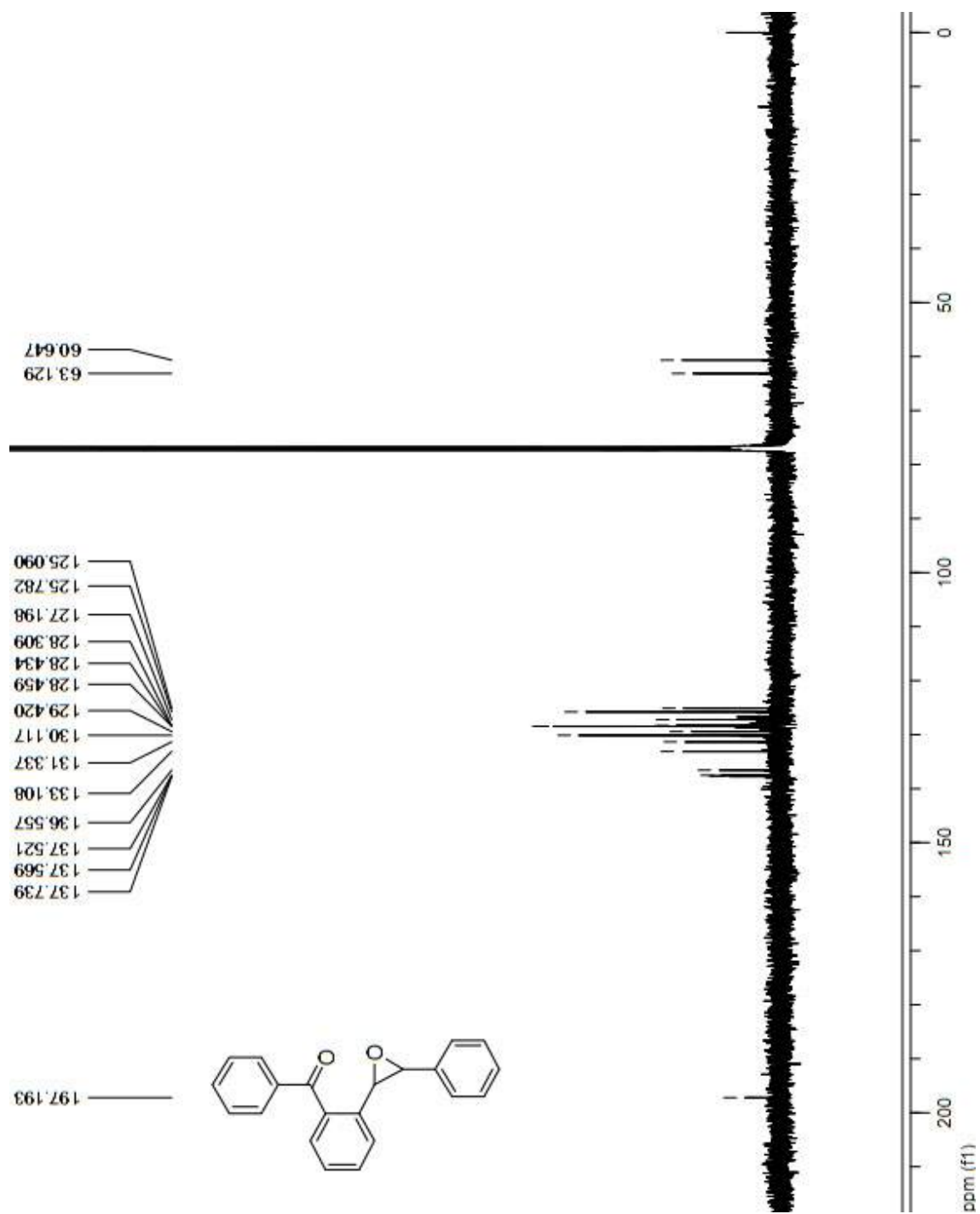


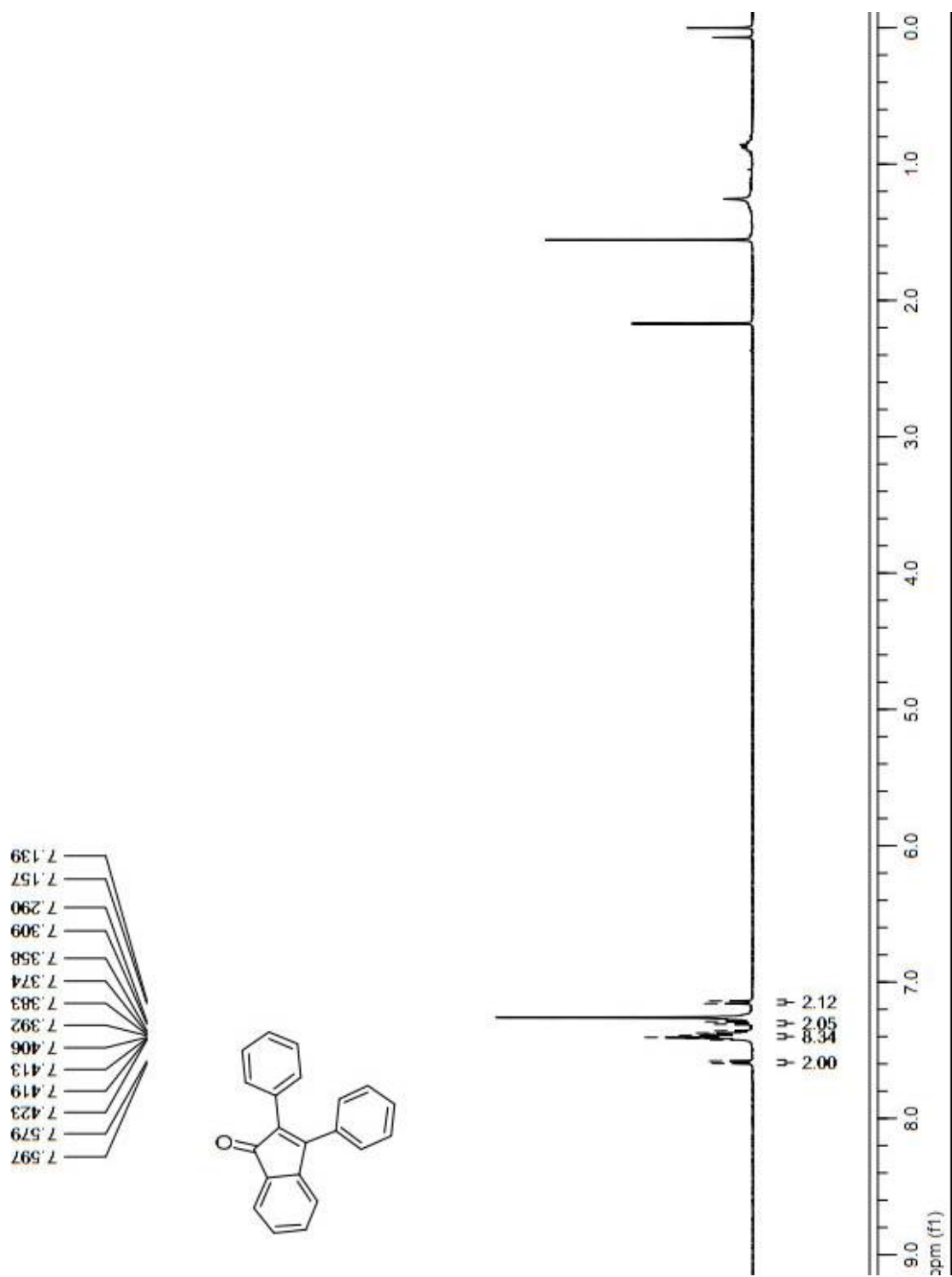


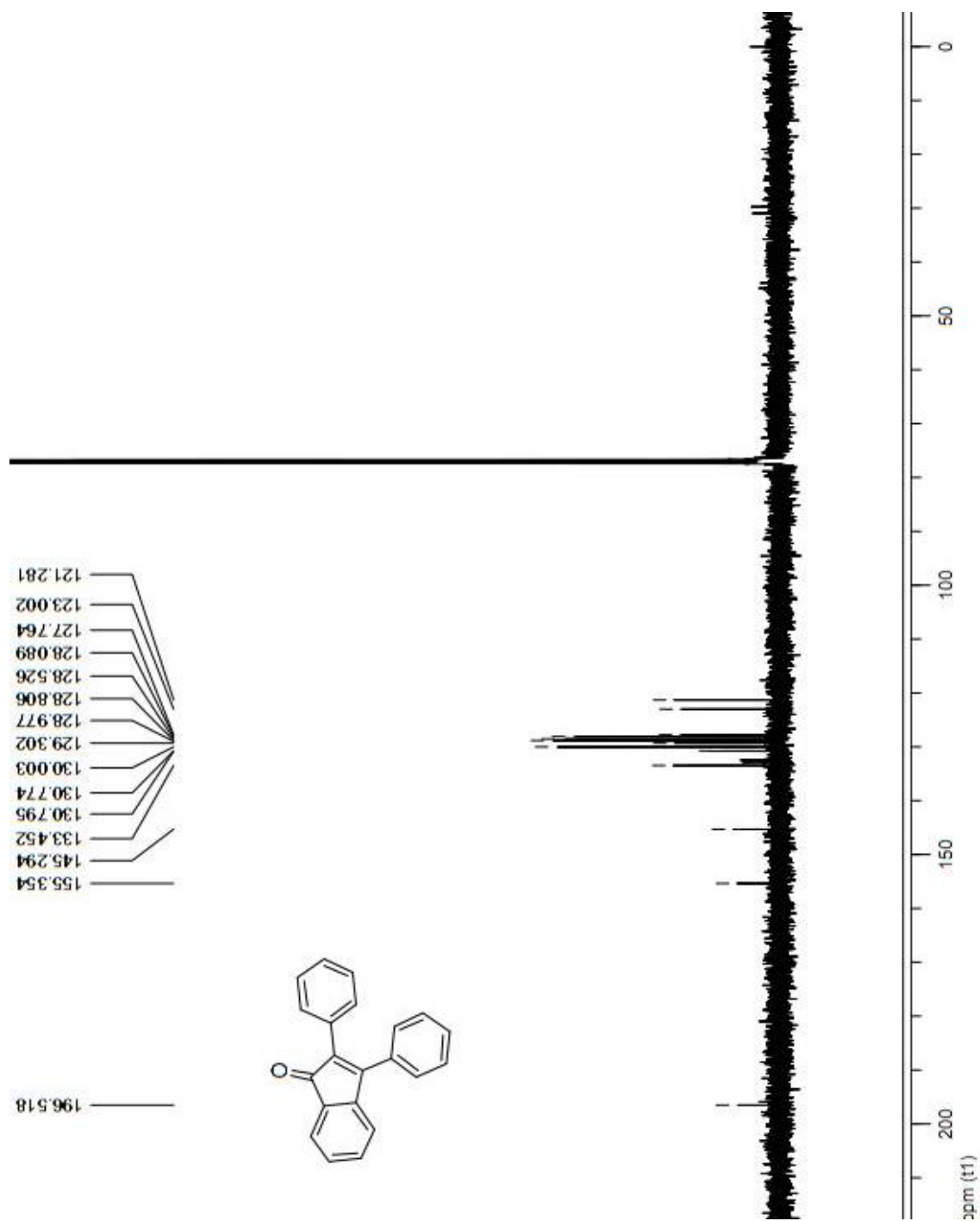


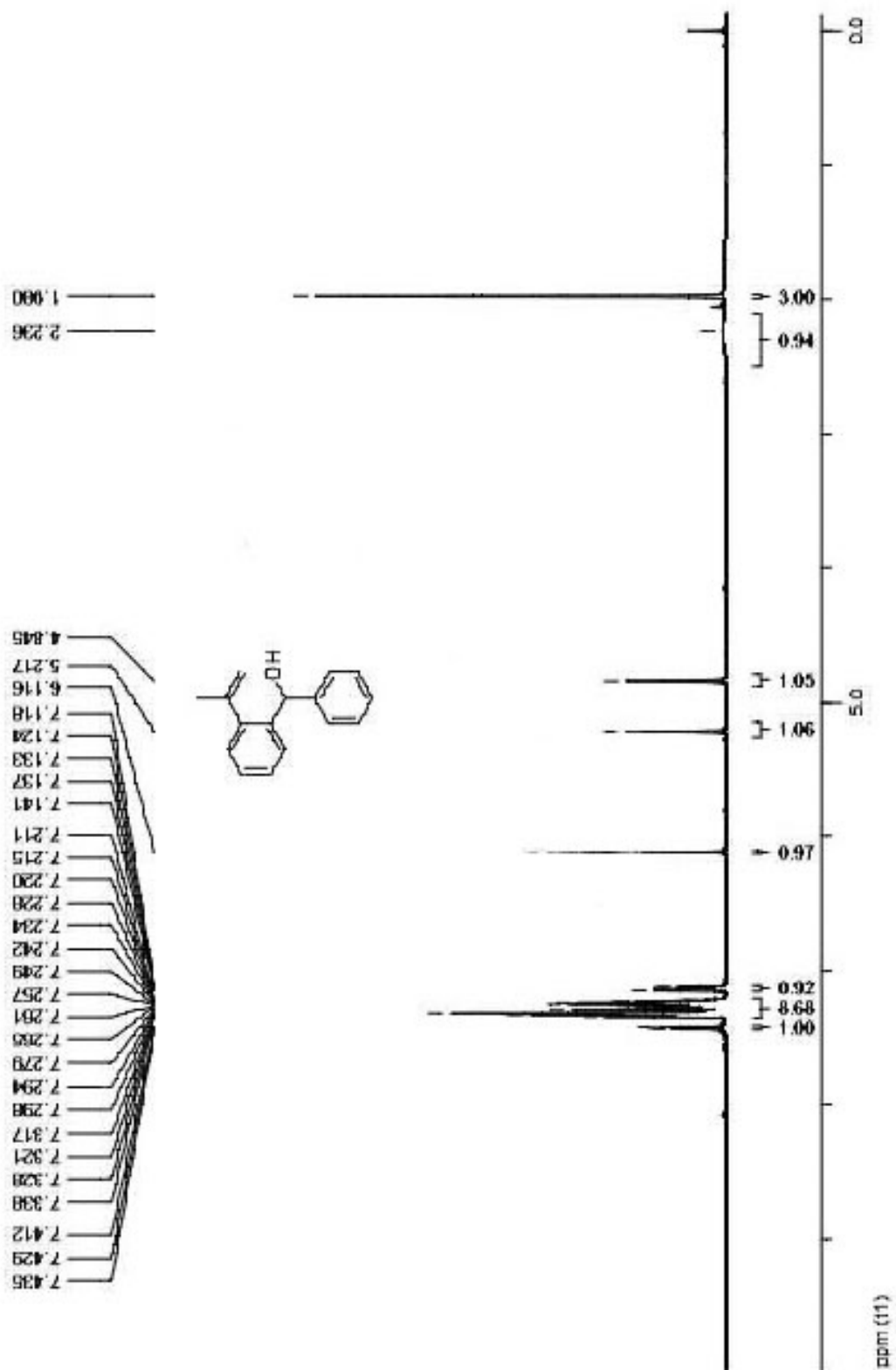


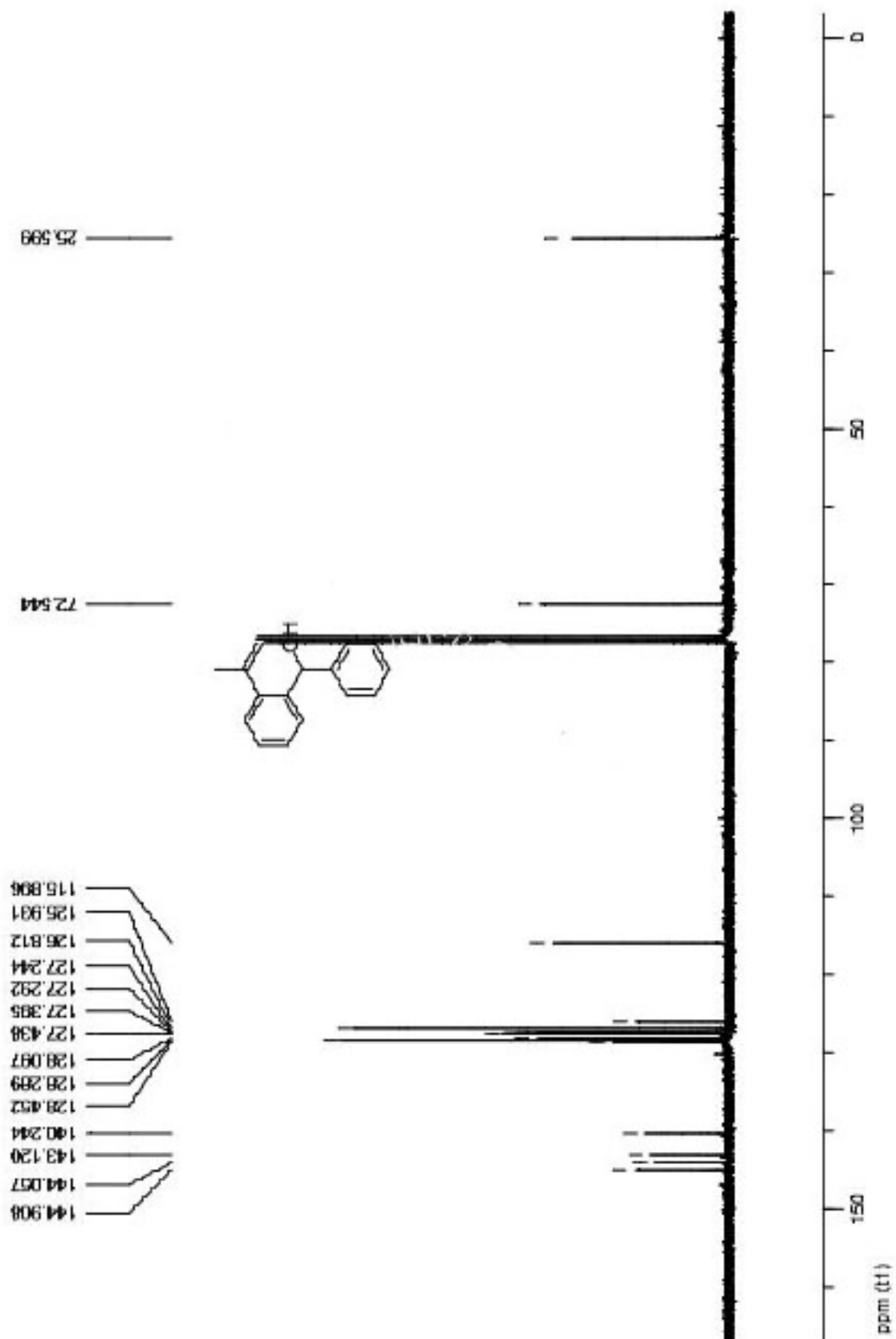


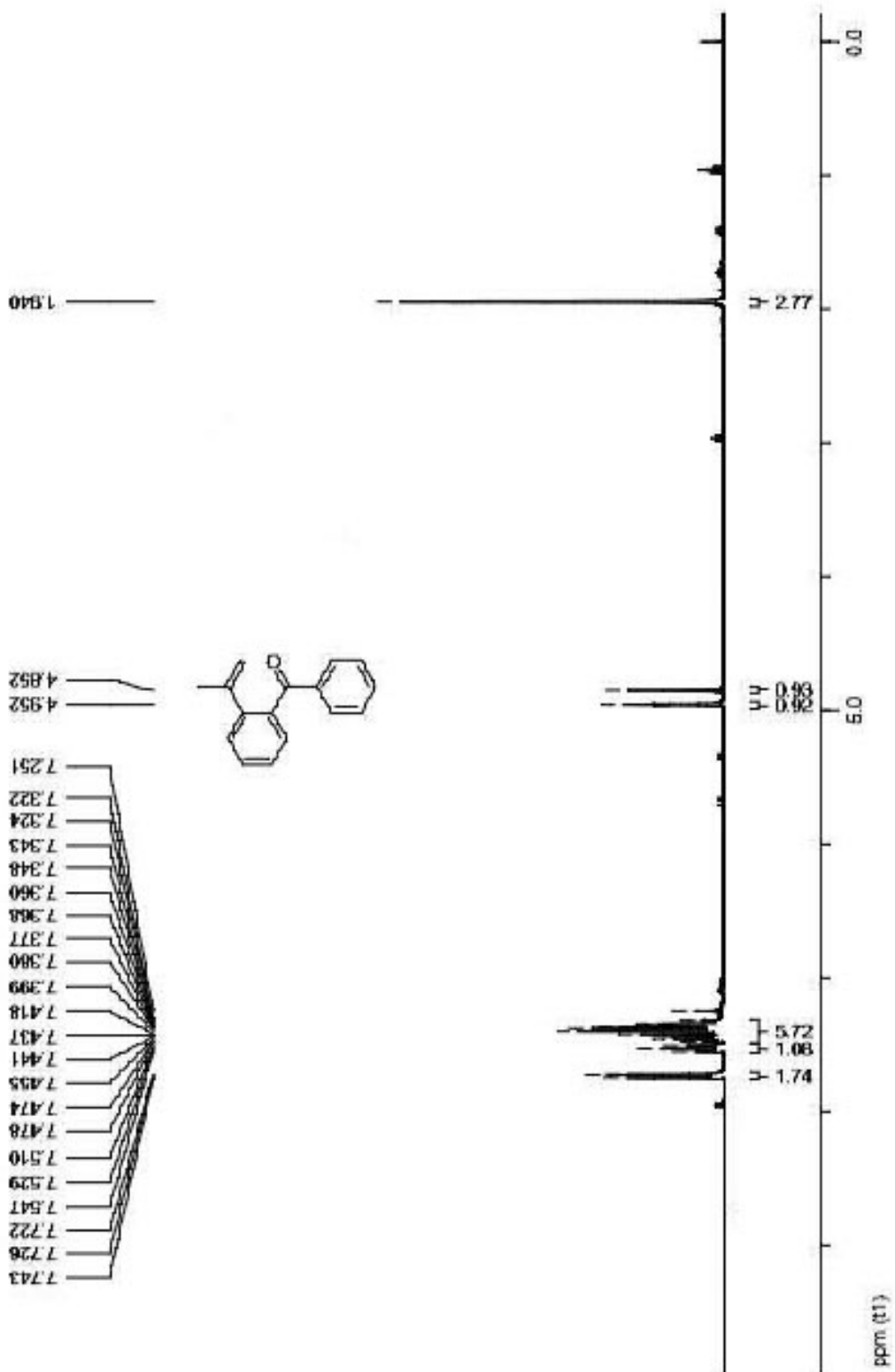


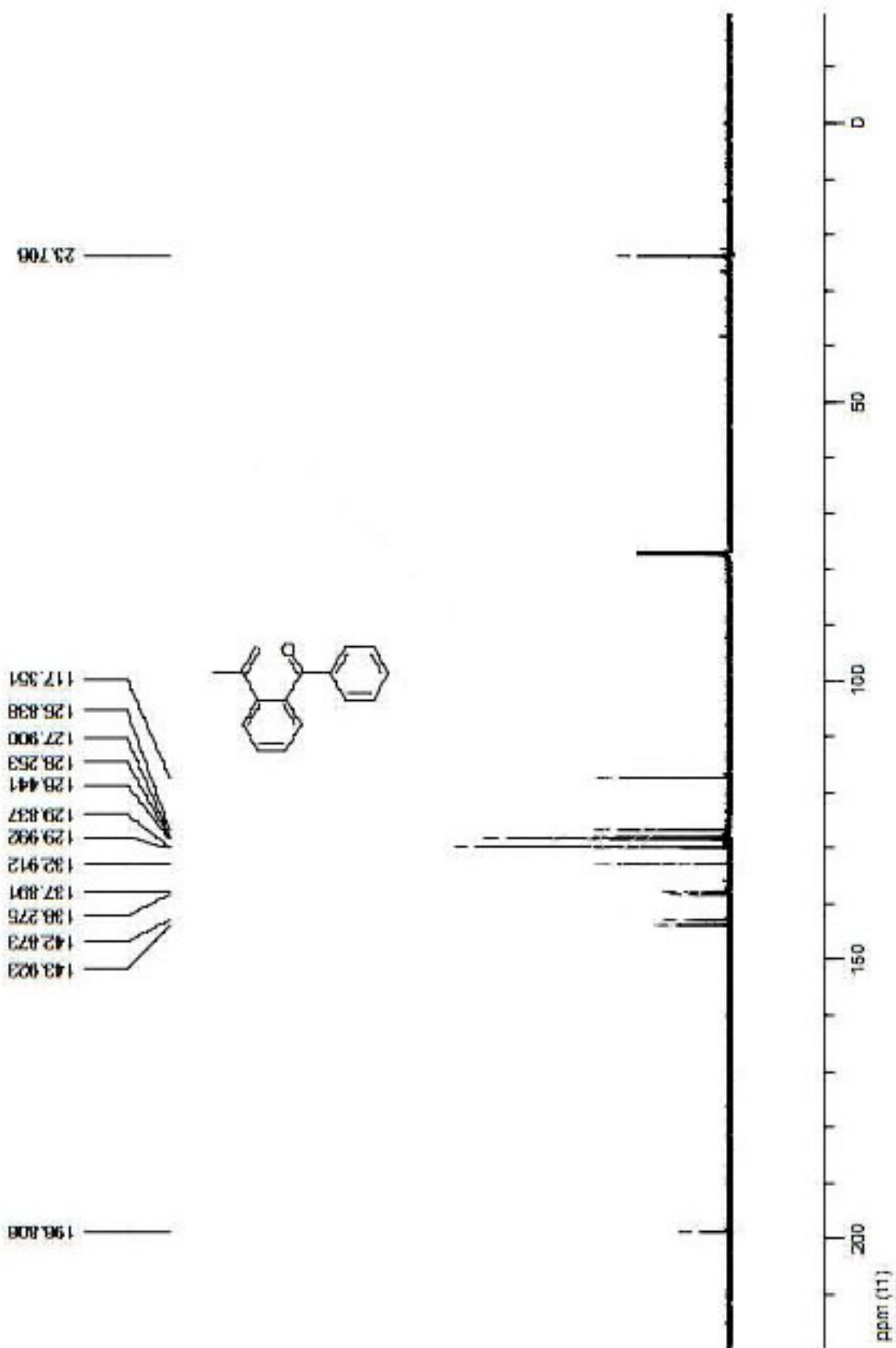


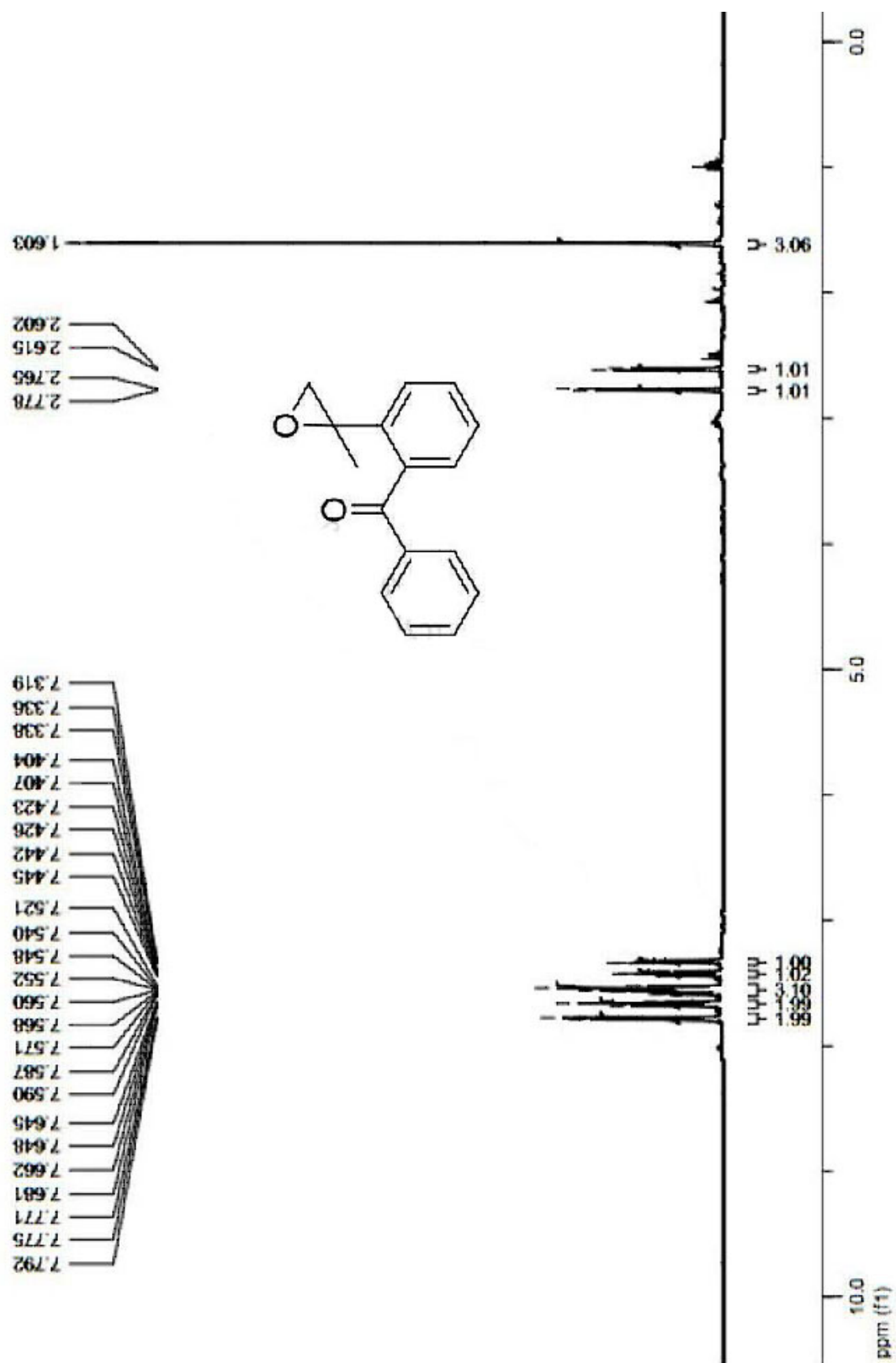


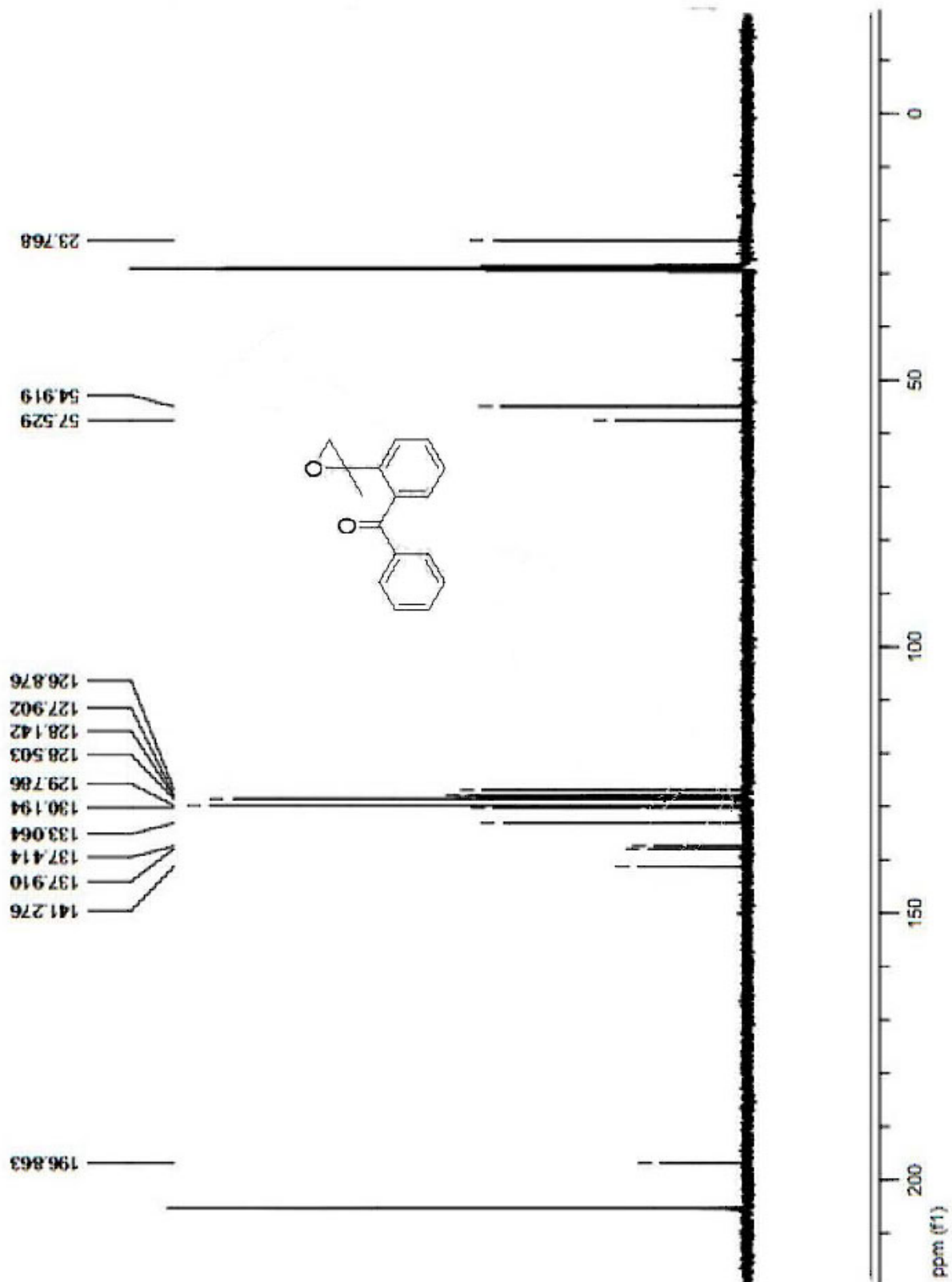


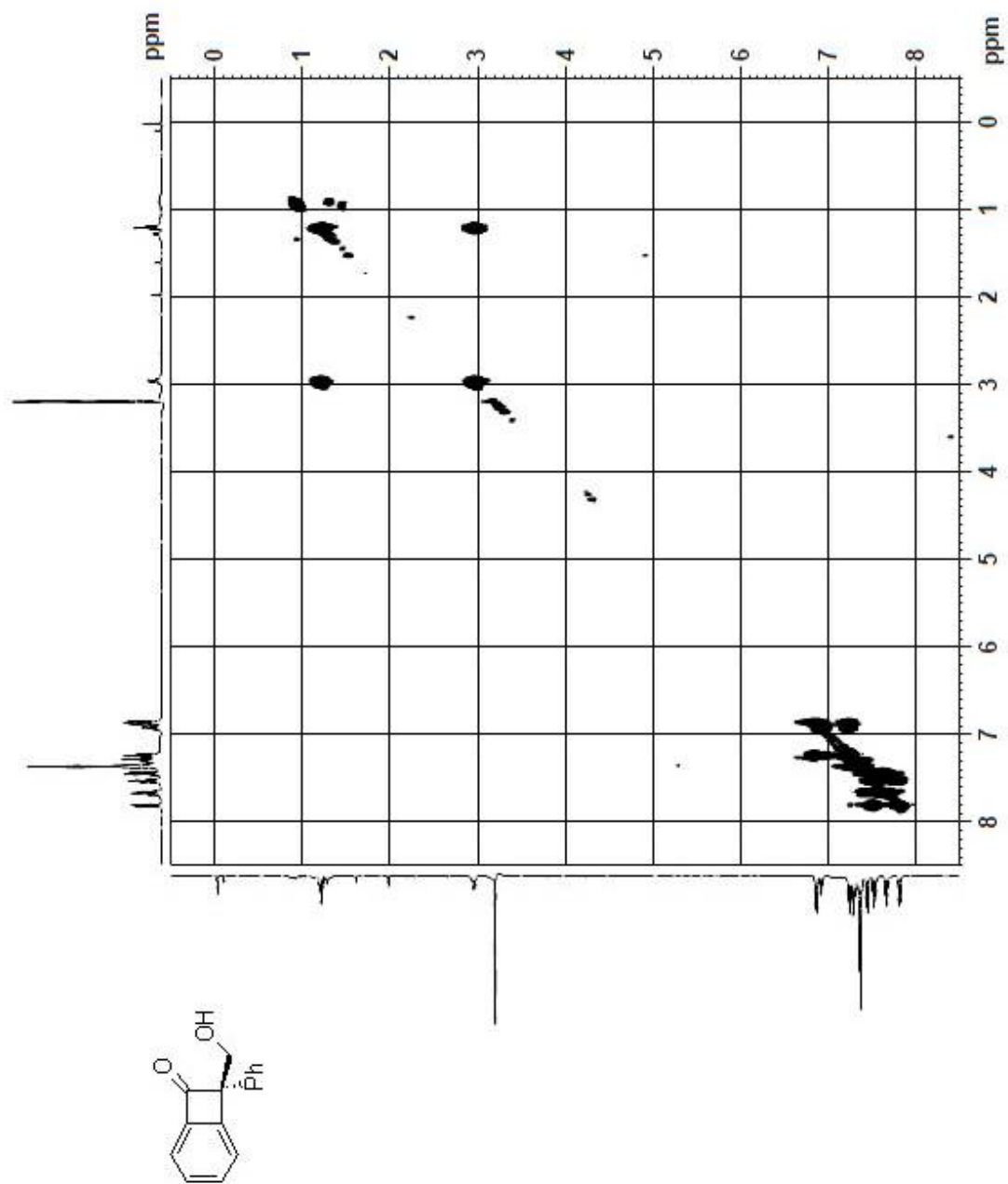


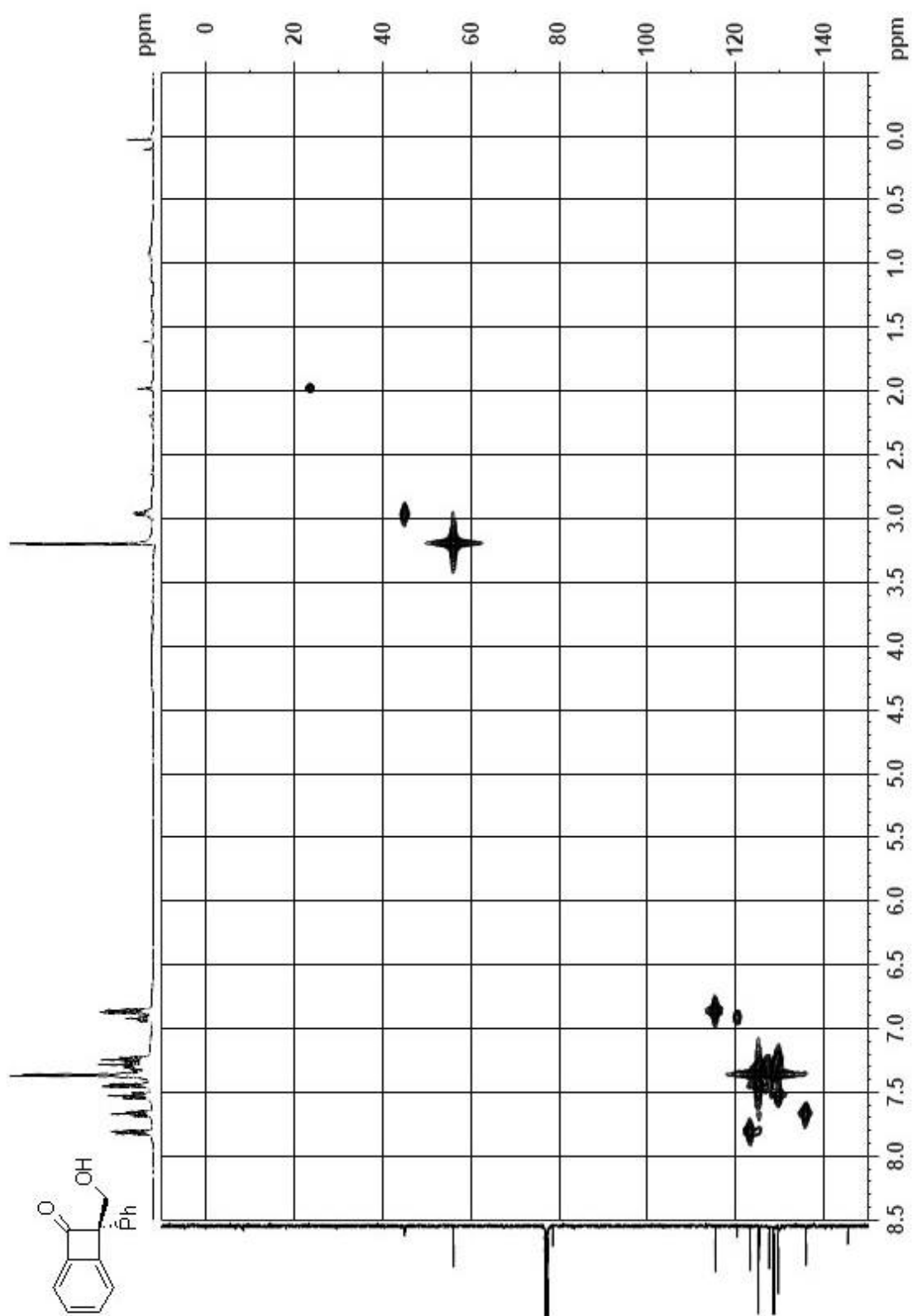


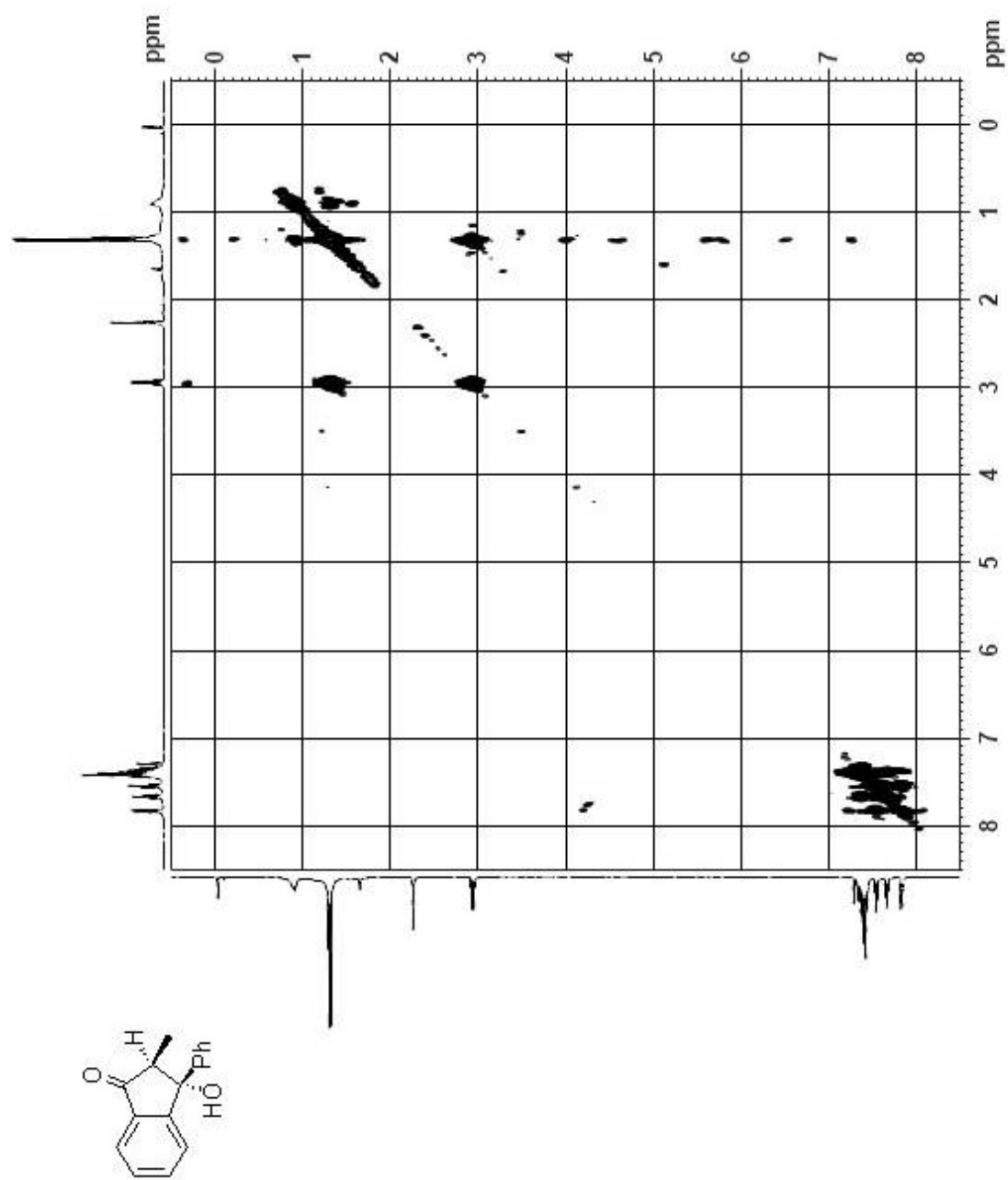


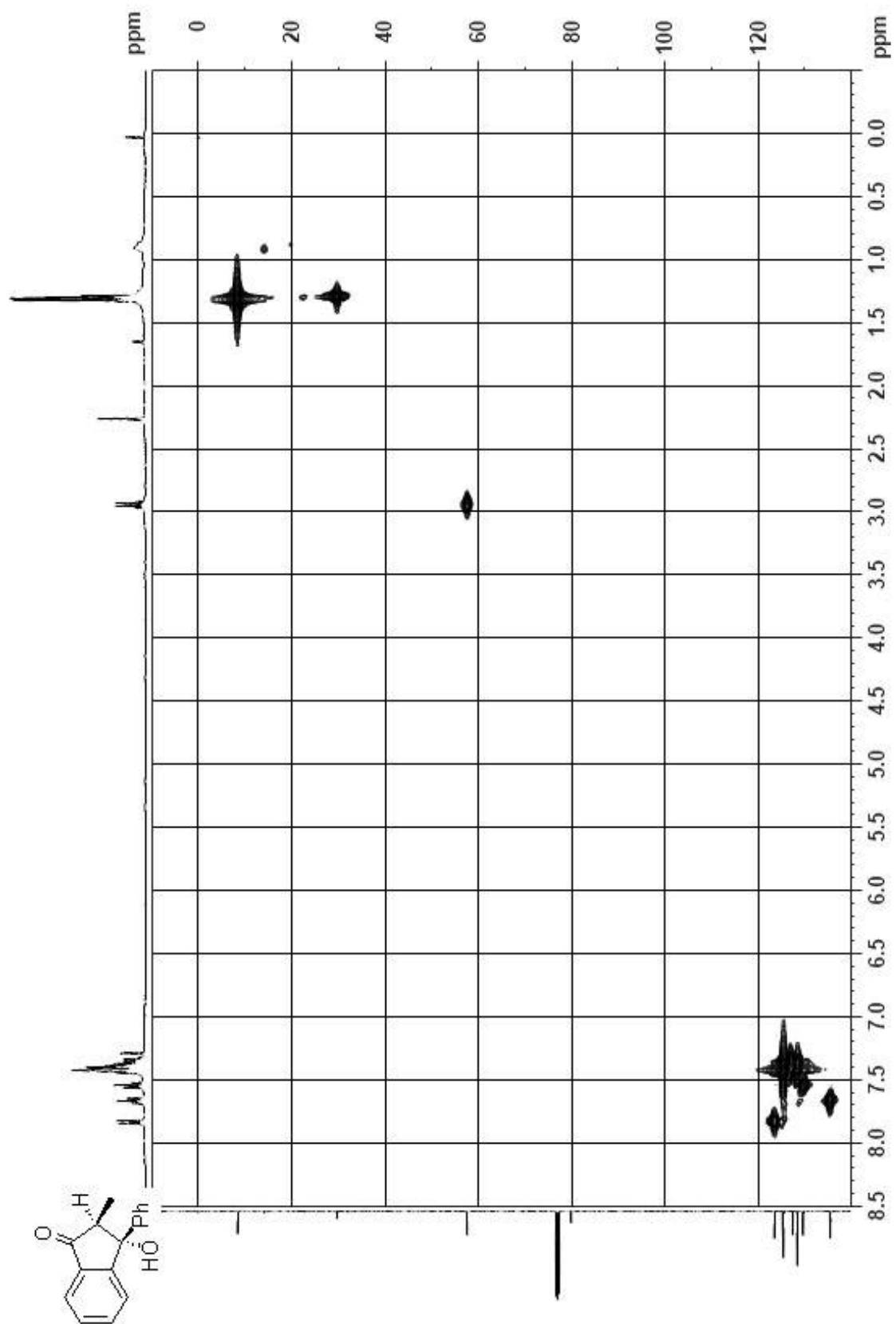


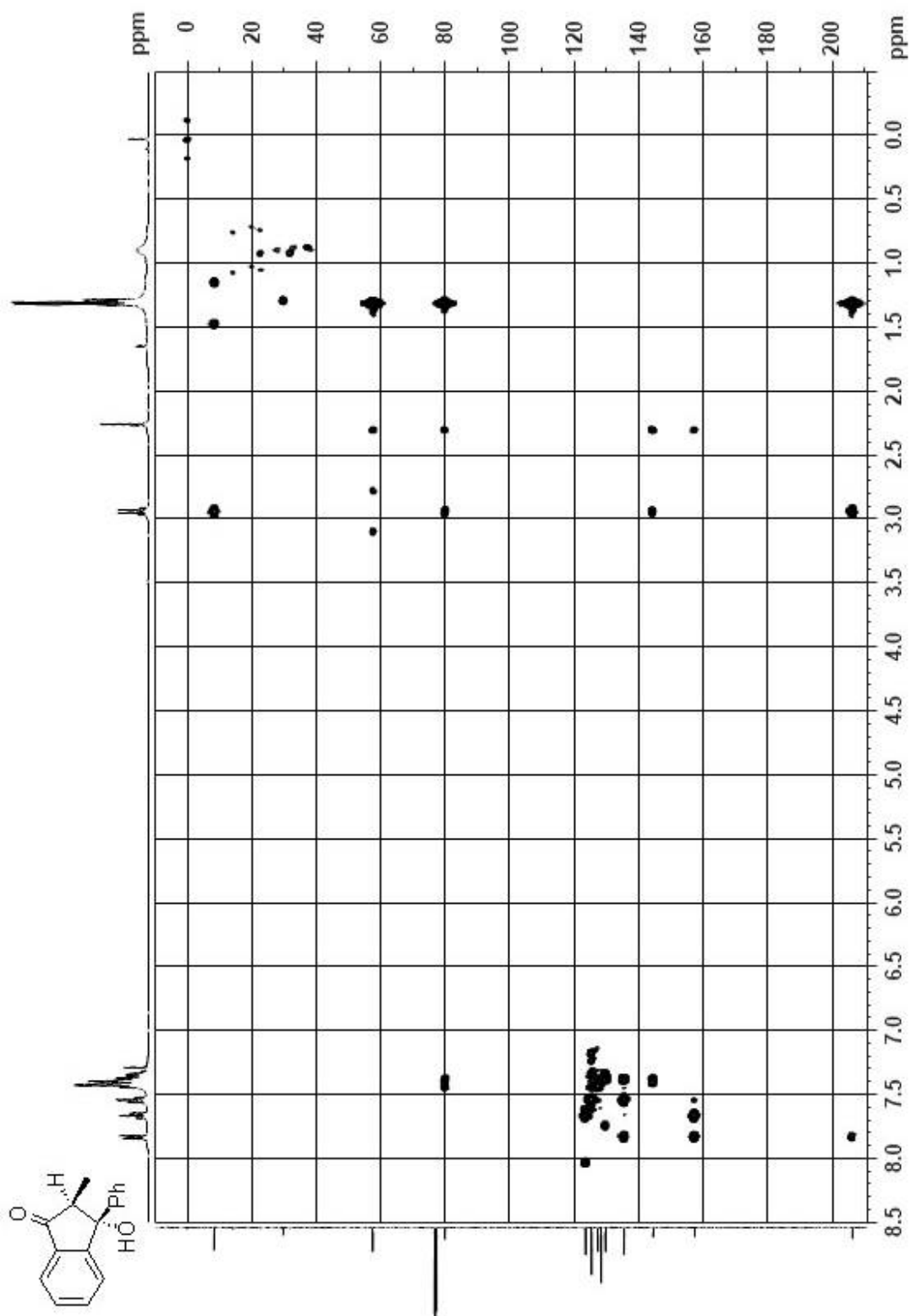


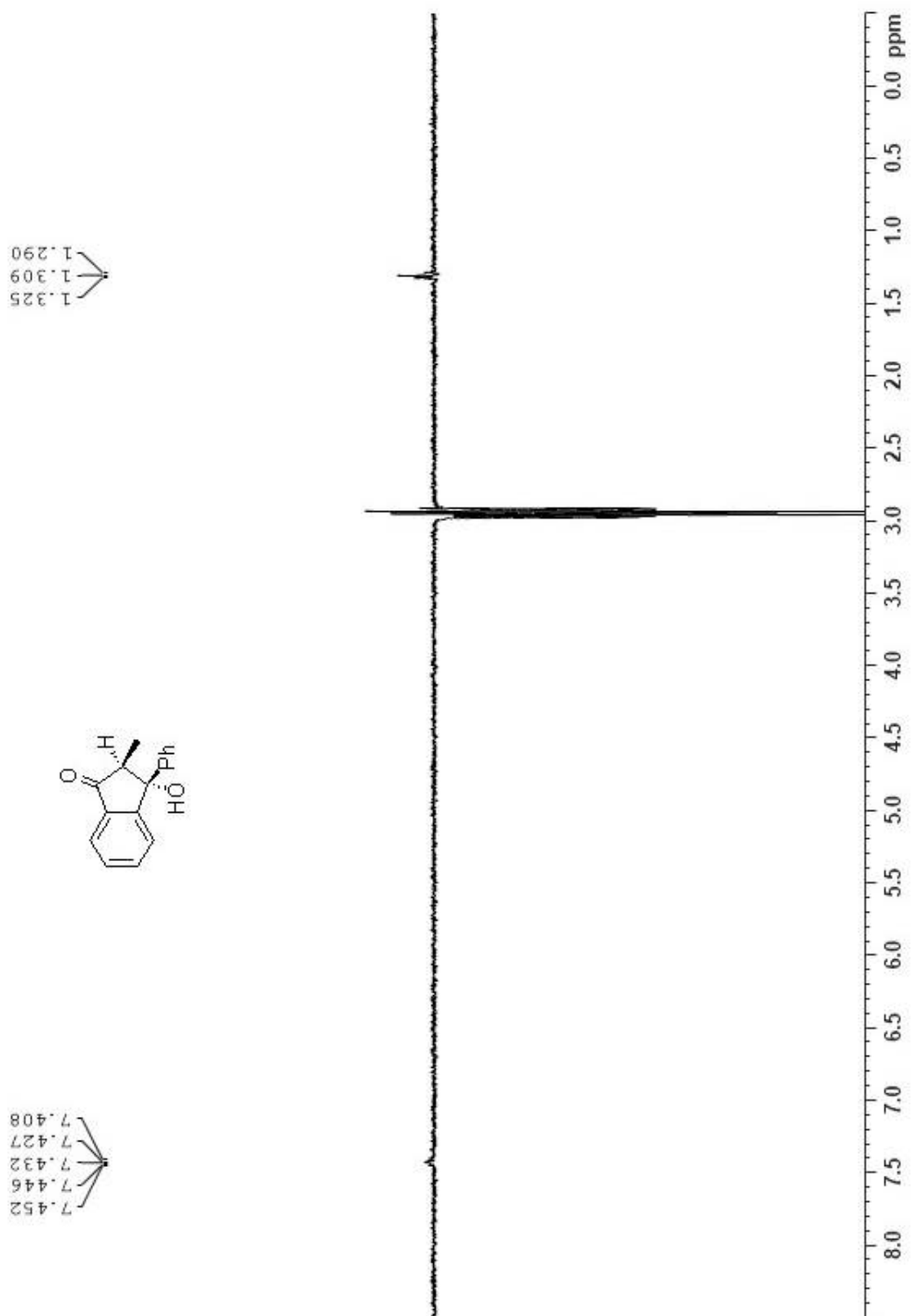


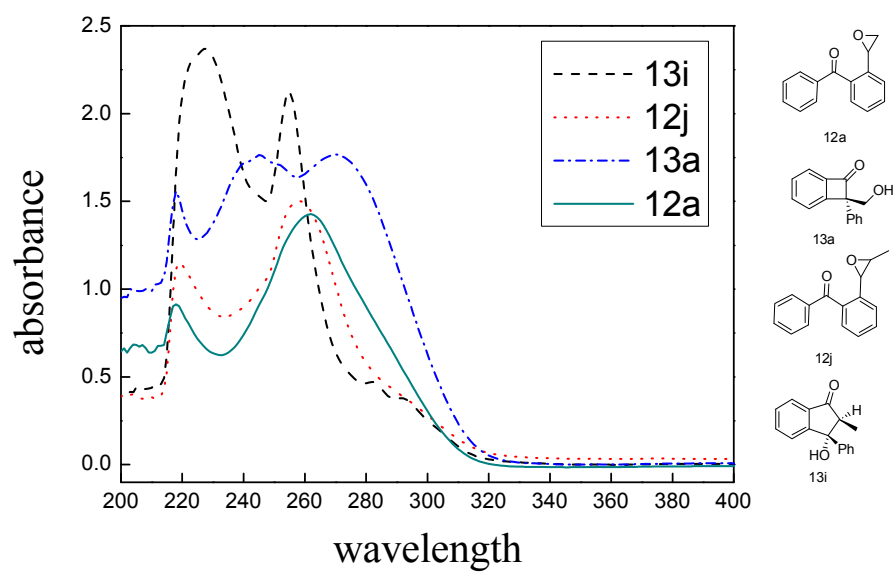












Absorption spectra of substrates **12a** and **12j** in each 1.0×10^{-5} , photoproducts **13a** and **13i** in each 1.0×10^{-4} mol/L concentration in MeOH.