

Supplementary Information

Green one-pot synthesis of 2*H*-pyrans under solvent-free conditions catalysed by ethylenediammonium diacetate

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Table of Contents

1. General Information	SI-2
2. Experimental Section and Spectroscopic Data	SI-3
3. ¹ H NMR, ¹³ C NMR and DEPT Spectra	SI-10

GENERAL INFORMATION

Chemical reagents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Solvents were analytical grade or were purified by standard procedures prior to use. Yields were calculated for material judged homogeneous by thin layer chromatography and nuclear magnetic resonance (^1H NMR). All reactions were monitored by thin layer chromatography (TLC) performed on silica gel 60 F₂₅₄ pre-coated aluminum sheets, visualized by a 254 nm UV lamp, and stained with an ethanolic solution of 4-anisaldehyde. Column flash chromatography was performed using silica gel 60 (230 – 400 mesh). Melting points (m.p.) were taken on an electrothermal melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were acquired at 300 MHz for ^1H and 75 MHz for ^{13}C using CDCl_3 as solvent. Chemical shifts for proton nuclear magnetic resonance (^1H NMR) spectra are reported in parts per million relative to the signal of tetramethylsilane at 0 ppm (internal standard) and coupling constants (J) are reported in hertz (Hz). Chemical shifts for carbon nuclear magnetic resonance (^{13}C NMR) spectra are reported in parts per million relative to the center line of the CDCl_3 triplet at 76.9 ppm. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, pent = pentet, br = broad. IR spectra were obtained using an FT-IR spectrometer and only partial spectral data are listed. High resolution mass spectra were performed on a mass spectrometer

EXPERIMENTAL SECTION AND SPECTROSCOPIC DATA

Preparation of 1,2-ethylenediammonium diacetate (EDDA)

A 150 ml beaker containing 100 ml of dry ether and 13.37 ml (0.2 mol) of ethylenediamine is placed in an ice-bath and a solution of glacial acetic acid (22.9 ml, 0.4 mol) in 20 ml ether is added with stirring at such a rate as to prevent boiling of the ether. The solution is left to crystallize overnight, then filtered with suction, the crystals washed with ether and recrystallised from approximately 50 ml methanol. Yield after drying in a vacuum desiccator is around 27.5 g (75%) of colourless needles, mp 114 °C.

General procedure for the preparation of 2*H*-pyrans

A mixture of 1,3-dicarbonyl compound (1 mmol), α,β -unsaturated aldehyde (1 mmol), and EDDA (0.1 mmol) was mixed in a mortar under solvent-free conditions. After completion of the reaction indicated by thin layer chromatography (TLC), the residues were purified by silica gel column chromatography (hexanes:ethyl acetate) to afford the desired products.

2,7,7-Trimethyl-2-(4-methylpent-3-en-1-yl)-2,6,7,8-tetrahydro-5*H*-chromen-5-one. (4a)

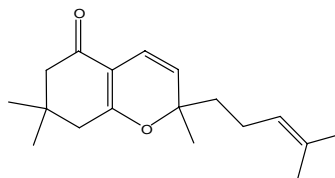
Pale yellow oil. IR (film): $\nu_{\text{max}}/\text{cm}^{-1}$ 2961, 2926, 1651, 1595,

1069. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 6.44 (d, J = 10.2

Hz, 1H), 5.17 (d, J = 10.0 Hz, 1H), 5.08 (tm, J = 7.0 Hz, 1H),

2.27 (bs, 2H), 2.24 (s, 2H), 2.08-1.98 (m, 2H), 1.76-1.66 (m, 1H), 1.67 (s, 3H), 1.62-1.52 (m,

1H), 1.58 (s, 3H), 1.36 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ =



194.1 (s), 170.2 (s), 131.7 (s), 123.5 (d), 121.2 (d), 116.1 (d), 108.9 (s), 82.2 (s), 50.2 (t), 42.2 (t), 41.5 (t), 32.0 (s), 28.4 (q), 28.0 (q), 27.3 (q), 25.5 (q), 22.3 (t), 17.4 (q).

2-Methyl-2-(4-methyl-pent-3-enyl)-2,6,7,8-tetrahydro-chromen-5-one. (4b)

Pale yellow oil. IR (film): $\nu_{\max}/\text{cm}^{-1}$ 2966, 2926, 1651, 1589, 1452,

1348, 1070. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 6.46 (d, J =

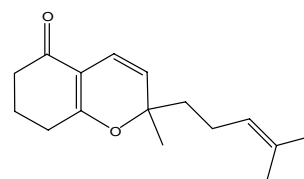
10.1 Hz, 1H), 5.18 (d, J = 10.1 Hz, 1H), 5.08 (tm, J = 7.0 Hz, 1H),

2.40 (t, J = 6.3 Hz, 2H), 2.38 (t, J = 6.7 Hz, 2H), 2.08-2.01 (m, 2H), 1.97 (p, J = 6.6 Hz, 2H),

1.78-1.52 (m, 2H), 1.68 (bs, 3H), 1.59 (bs, 3H), 1.36 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ =

194.5 (s), 171.7 (s), 131.7 (s), 123.5 (d), 121.5 (d), 116.3 (d), 110.1 (s), 82.1 (s), 41.5 (t), 36.3

(t), 28.4 (t), 27.2 (q), 25.5 (q), 22.4 (t), 20.5 (t), 17.4 (q).



2-Methyl-2-(4-methylpent-3-en-1-yl)-2H,5H-pyrano[3,2-c]chromen-5-one. (4c)

Colourless oil. IR (film): $\nu_{\max}/\text{cm}^{-1}$ 3073, 2970, 2924, 2853, 1716,

1607, 1362, 1036. ^1H NMR (CDCl_3 , 300 MHz): δ = 7.80 (dd, J =

7.5, 1.2 Hz, 1H), 7.52 (ddd, J = 8.6, 7.3, 1.8 Hz, 1H), 7.32-7.25 (m,

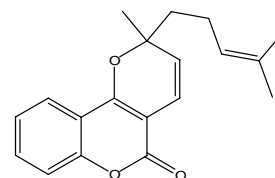
2H), 6.59 (d, J = 10.2 Hz, 1H), 5.48 (d, J = 10.0 Hz, 1H), 5.09 (tm, J = 7.0 Hz, 1H), 2.18-2.10

(m, 2H), 1.94-1.68 (m, 2H), 1.61 (bs, 3H), 1.55 (bs, 3H), 1.52 (s, 3H). ^{13}C NMR (CDCl_3 , 75

MHz): δ = 160.8 (s), 158.9 (s), 153.0 (s), 132.1 (s), 131.9 (d), 124.9 (d), 123.8 (d), 123.2 (d),

122.5 (d), 117.1 (d), 116.6 (d), 115.3 (s), 99.8 (s), 83.0 (s), 41.6 (t), 27.4 (q), 25.4 (q), 22.4 (t),

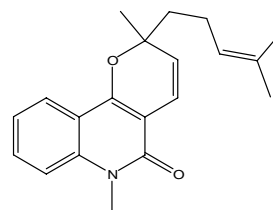
17.5 (q).



2,6-Dimethyl-2-(4-methyl-pent-3-enyl)-2,6-dihydro-pyrano[3,2-c]quinolin-5-one.

(zanthosimuline, 2)

Colourless oil. IR (film): $\nu_{\max}/\text{cm}^{-1}$ 3079, 3058, 2970, 2925, 1656, 1587, 1326, 1121. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): $\delta = 7.96$ (dd,

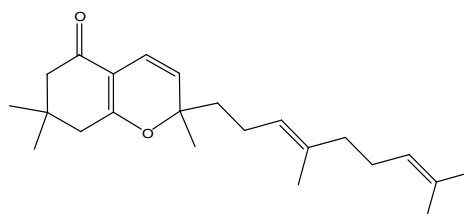


$J = 7.9, 1.4$ Hz, 1H), 7.54 (ddd, $J = 10.1, 7.3, 1.6$ Hz, 1H), 7.31 (bd, $J = 8.2$ Hz, 1H), 7.22 (td, $J = 7.9, 0.8$ Hz, 1H), 6.79 (d, $J = 10.0$ Hz, 1H), 5.48 (d, $J = 10.0$ Hz, 1H), 5.09 (tm, $J = 7.0$ Hz, 1H), 3.69 (s, 3H), 2.18-2.10 (m, 2H), 1.90-1.69 (m, 2H), 1.63 (bs, 3H), 1.55 (bs, 3H), 1.48 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 160.6$ (s), 155.0 (s), 139.0 (s), 131.5 (s), 130.5 (d), 124.9 (d), 123.4 (d), 122.7 (d), 121.3 (d), 118.1 (d), 115.6 (s), 113.6 (d), 105.2 (s), 80.9 (s), 41.2 (t), 28.9 (q), 26.7 (q), 25.3 (q), 22.2 (t), 17.3 (q).

2-(4,8-Dimethyl-nona-3,7-dienyl)-2,7,7-trimethyl-2,6,7,8-tetrahydro-chromen-5-one. (4d)

Colourless to pale yellow oil. IR (film): $\nu_{\max}/\text{cm}^{-1}$

2963, 2926, 1643, 1593, 1420, 1065. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): $\delta = 6.44$ (d, $J = 10.1$ Hz,



1H), 5.18 (d, $J = 10.1$ Hz, 1H), 5.13-5.04 (m, 2H), 2.27 (bd, $J = 1.4$ Hz, 2H), 2.24 (s, 2H), 2.10-1.93 (m, 6H), 1.77-1.52 (m, 2H), 1.68 (bs, 3H), 1.60 (bs, 3H), 1.58 (bs, 3H), 1.37 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 194.1$ (s), 170.2 (s), 135.3 (s), 131.1 (s), 124.0 (d), 123.3 (d), 121.2 (d), 116.1 (d), 108.9 (s), 82.2 (s), 50.2 (t), 42.2 (t), 41.5 (t), 39.4 (t), 31.9 (s), 28.4 (q), 28.0 (q), 27.2 (q), 26.4 (t), 25.5 (q), 22.2 (t), 17.4 (q), 15.7 (q).

2-(4,8-Dimethyl-nona-3,7-dienyl)-2-methyl-2H-pyrano[3,2-c]chromen-5-one. (ferprenin, 4e)

Pale yellow oil. IR (film): $\nu_{\max}/\text{cm}^{-1}$ 2968, 2922, 1715, 1607, 1362,

1036. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 7.80 (dd, J = 7.8, 1.2

Hz, 1H), 7.52 (ddd, J = 8.7, 7.0, 1.6 Hz, 1H), 7.31-7.24 (m, 2H), 6.59

(d, J = 10.3 Hz, 1H), 5.49 (d, J = 10.3 Hz, 1H), 5.11 (tm, J = 7.0 Hz,

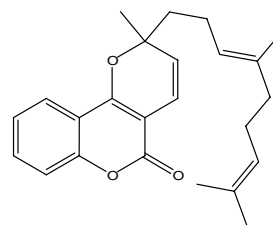
1H), 5.05 (tm, J = 7.0 Hz, 1H), 2.19-2.12 (m, 2H), 2.06-1.98 (m, 2H), 1.95-1.71 (m, 4H), 1.67

(bs, 3H), 1.58 (bs, 3H), 1.56 (bs, 3H), 1.52 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 160.6 (s),

158.8 (s), 152.9 (s), 135.7 (s), 131.8 (d), 131.1 (s), 124.9 (d), 123.9 (d), 123.7 (d), 122.9 (d),

122.4 (d), 117.0 (d), 116.5 (d), 115.2 (s), 99.7 (s), 82.9 (s), 41.5 (t), 39.3 (t), 27.2 (q), 26.3 (t),

25.4 (q), 22.2 (t), 17.4 (q), 15.7 (q).



2,2,7,7-Tetramethyl-2,6,7,8-tetrahydro-chromen-5-one. (4f)

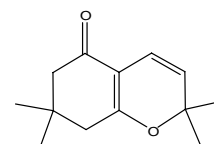
Pale yellow crystals. Mp.: 39.0-40.0 °C. IR (KBr): $\nu_{\max}/\text{cm}^{-1}$ 3049, 2976,

2963, 1635, 1585, 1132, 1090. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ =

6.40 (d, J = 9.9 Hz, 1H), 5.23 (d, J = 9.9 Hz, 1H), 2.27 (bs, 2H), 2.25 (bs, 2H), 1.40 (s, 3H),

1.07 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 194.3 (s), 169.9 (s), 122.5 (d), 115.6 (d), 109.4

(s), 79.6 (s), 50.3 (t), 42.3 (t), 32.0 (s), 28.3 (q), 28.2 (q).

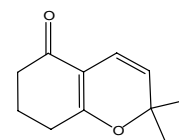


2,2-Dimethyl-2,6,7,8-tetrahydro-chromen-5-one. (4g)

Pale yellow oil. IR (film): $\nu_{\max}/\text{cm}^{-1}$ 2982, 2943, 1637, 1589, 1410, 1094. ^1H

NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 6.41 (d, J = 9.9 Hz, 1H), 5.24 (d, J =

9.9 Hz, 1H), 2.40 (t, J = 6.0 Hz, 2H), 2.38 (t, J = 6.0 Hz, 2H), 1.97 (p, J = 6.2 Hz, 2H), 1.402

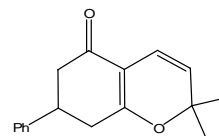


(s, 3H), 1.396 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 194.6 (s), 171.3 (s), 122.7 (d), 115.6 (d), 110.4 (s), 79.5 (s), 36.2 (t), 28.4 (t), 28.2 (2 \times q), 20.4 (t).

2,2-Dimethyl-7-phenyl-2,6,7,8-tetrahydro-chromen-5-one. (4h)

Pale yellow oil. IR (film): $\nu_{\text{max}}/\text{cm}^{-1}$ 3086, 3061, 3028, 2976, 2934, 1643,

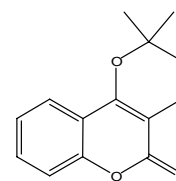
1591, 1412, 1138. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 7.37-7.30 (m, 2H), 7.28-7.21 (m, 3H), 6.44 (d, J = 10.1 Hz, 1H), 5.27 (d, J = 9.9 Hz, 1H), 3.40-3.27 (m, 1H), 2.72-2.55 (m, 4H), 1.45 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 193.5 (s), 170.4 (s), 142.5 (s), 128.5 (2 \times d), 126.8 (d), 126.4 (2 \times d), 122.9 (d), 115.5 (d), 110.1 (s), 79.9 (s), 43.4 (t), 38.6 (d), 35.9 (t), 28.5 (q), 28.0 (q).



2,2-Dimethyl-2H-pyrano[3,2-c]chromen-5-one. (4i)

Colourless oil. IR (film): $\nu_{\text{max}}/\text{cm}^{-1}$ 3077, 3054, 2970, 1709, 1674, 1600, 1361,

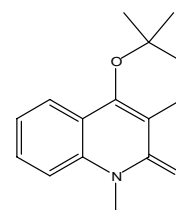
1031. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 7.79 (dd, J = 8.6, 1.8 Hz, 1H), 7.51 (ddd, J = 8.8, 7.9, 1.5 Hz, 1H), 7.29-7.23 (m, 2H), 6.53 (d, J = 9.9 Hz, 1H), 5.54 (d, J = 10.1 Hz, 1H), 1.55 (s, 6H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 160.5 (s), 158.5 (s), 152.8 (s), 131.8 (d), 125.9 (d), 123.7 (d), 122.4 (d), 116.4 (d), 116.3 (d), 115.2 (s), 99.9 (s), 80.3 (s), 28.2 (2 \times q).



2,2,6-Trimethyl-2,6-dihydro-pyrano[3,2-c]quinolin-5-one. (N-methylflindersine, 4j)

Pale yellow crystals. Mp.: 80.0-81.0 $^{\circ}\text{C}$. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 3057, 2972,

1641, 1625, 1325, 1122, 1092. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 7.92 (d, J = 7.8 Hz, 1H), 7.49 (ddd, J = 9.7, 7.3, 1.2 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 9.9 Hz, 1H), 5.52 (d, J = 9.9 Hz, 1H), 3.66 (s, 3H),

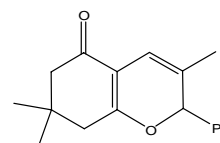


1.50 (s, 6H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 160.5 (s), 154.7 (s), 138.9 (s), 130.4 (d), 125.9 (d), 122.6 (d), 121.3 (d), 117.6 (d), 115.6 (s), 113.6 (d), 105.4 (s), 78.3 (s), 28.8 (s), 27.8 (2 \times q).

3,7,7-Trimethyl-2-phenyl-2,6,7,8-tetrahydro-5H-chromen-5-one. (4k)

Colourless to pale yellow oil. IR (film): $\nu_{\text{max}}/\text{cm}^{-1}$ 3063, 3032, 2959, 1651,

1608, 1047. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 7.34 (bs, 5H), 6.46

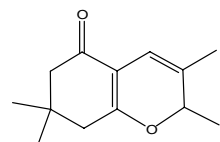


(bs, 1H), 5.66 (s, 1H), 2.26-2.23 (m, 2H), 2.21-2.19 (m, 2H), 1.62 (bs, 3H), 1.04 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 194.4 (s), 167.6 (s), 138.4 (s), 128.9 (d), 128.7 (2 \times d), 127.6 (2 \times d), 124.6 (s), 112.7 (d), 109.9 (s), 82.6 (d), 50.3 (t), 41.8 (t), 32.1 (s), 28.8 (q), 27.6 (q), 19.2 (q). HRMS: m/z calcd. for $\text{C}_{18}\text{H}_{21}\text{O}_2$ ($\text{M} + \text{H}^+$) 269.1536, found 269.1529.

2,3,7,7-Tetramethyl-2,6,7,8-tetrahydro-chromen-5-one. (4l)

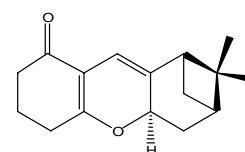
Colourless solid. Mp.: 92.0-93.0 $^\circ\text{C}$. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 2972, 2957, 2918,

1651, 1603, 1398, 1140, 1055. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ =



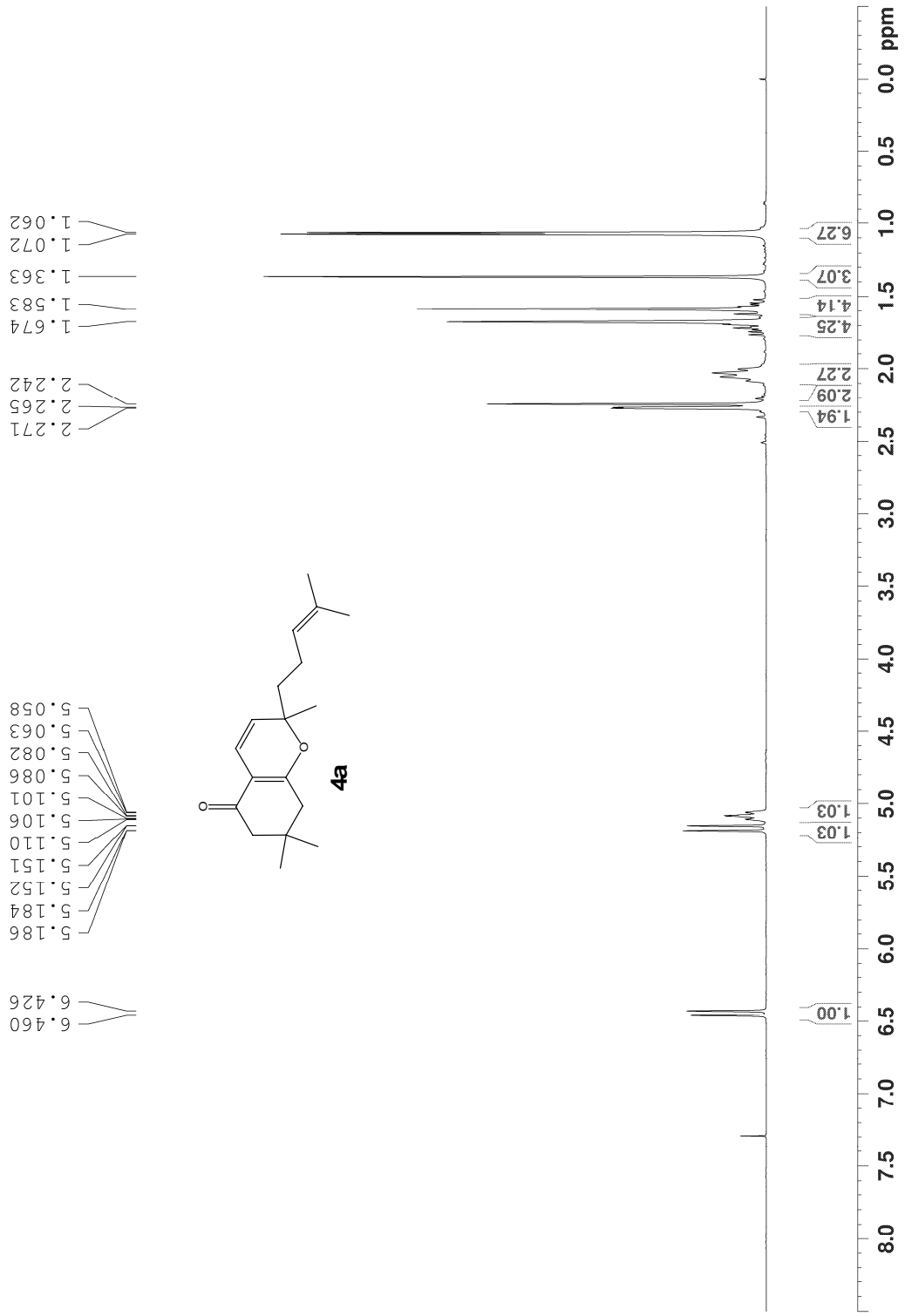
6.18 (d, J = 0.7 Hz, 1H), 4.83 (q, J = 6.5 Hz, 1H), 2.32-2.18 (m, 4H), 1.73 (d, J = 0.8 Hz, 3H), 1.35 (d, J = 6.6 Hz, 3H), 1.08 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 194.2 (s), 167.5 (s), 126.8 (s), 111.5 (d), 110.1 (s), 76.9 (d), 50.2 (t), 41.7 (t), 32.0 (s), 28.7 (q), 27.6 (q), 19.0 (q), 18.5 (q).

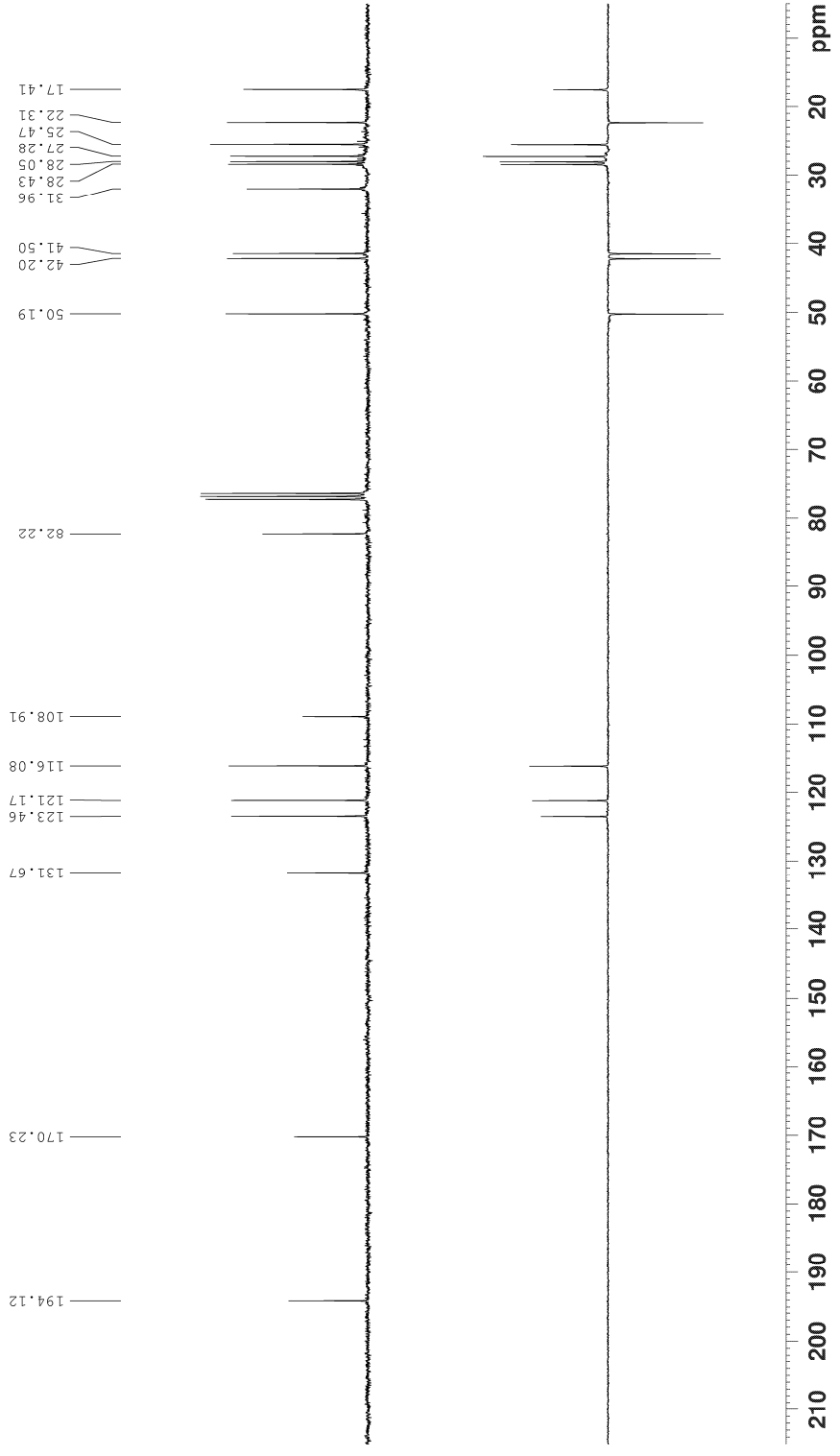
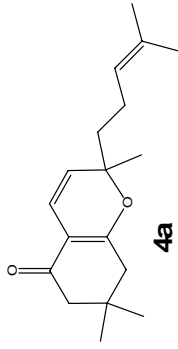
2,3,7,7-Tetramethyl-2,6,7,8-tetrahydro-chromen-5-one. (4m, inseparable mixture of diastereoisomers dr: 9:1)

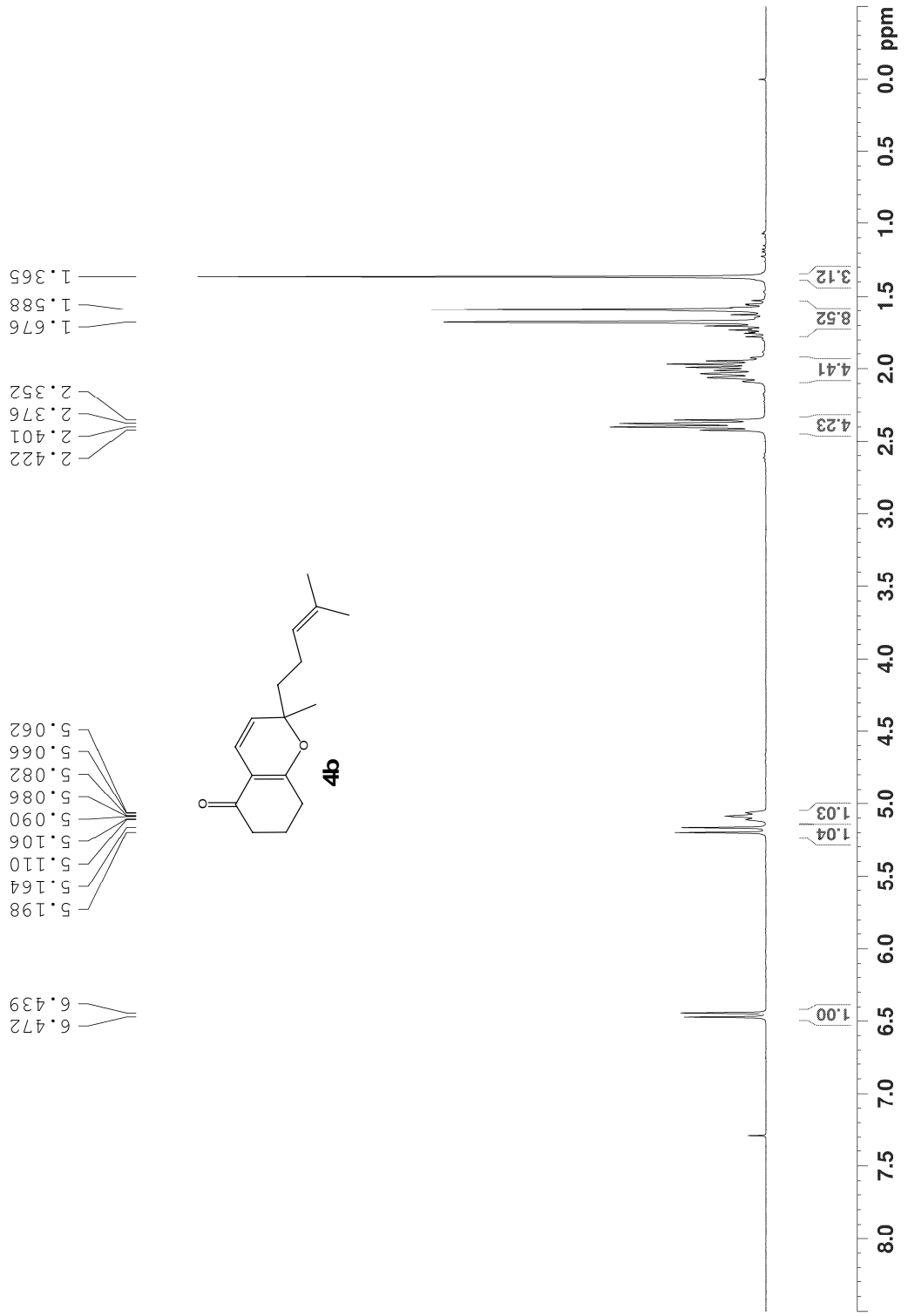


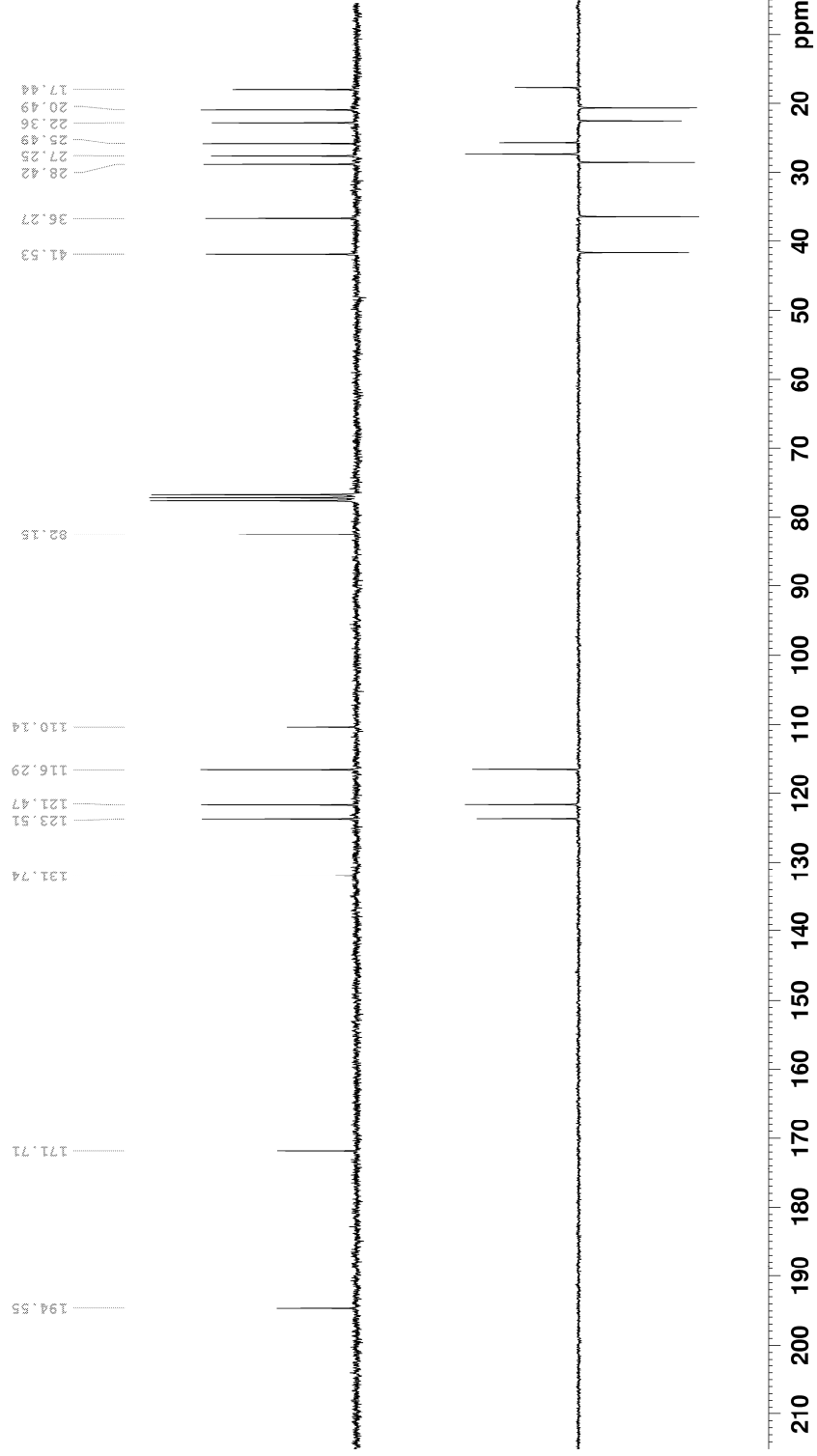
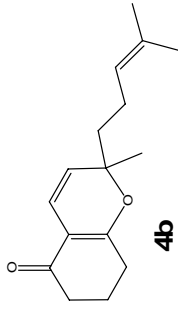
Colourless crystals. Mp.: 92.0-93.0 °C. IR (film): $\nu_{\text{max}}/\text{cm}^{-1}$ 2995, 2920, 1659, 1597, 1398, 1157, 1027. ^1H NMR (CDCl_3 , 300 MHz, Me_4Si): δ = 6.09 (bs, 1H), 5.06-4.98 (m, 1H), 2.62-2.32 (m, 7H), 2.12-1.92 (m, 4H), 1.40-1.25 (m, 1H), 1.28 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 195.3 (s), 171.8 (s), 132.7 (s), 114.2 (s), 110.6 (d), 71.7 (d), 48.2 (d), 41.6 (s), 40.0 (d), 36.4 (t), 31.6 (t), 27.6 (t), 25.28 (t), 25.27 (q), 21.6 (q), 20.6 (t).

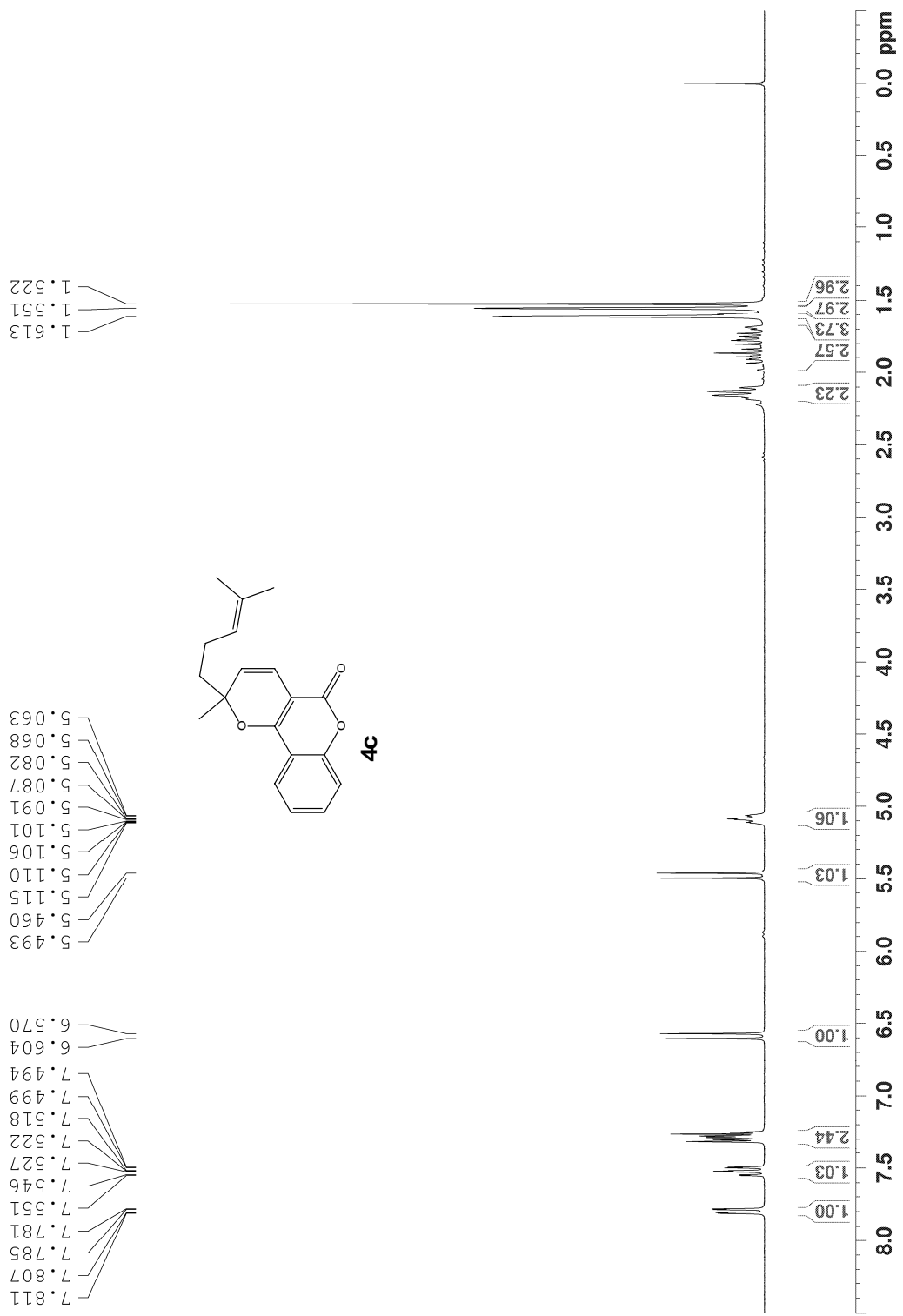
^1H NMR, ^{13}C NMR and other Spectra

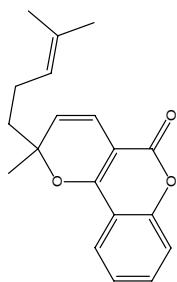




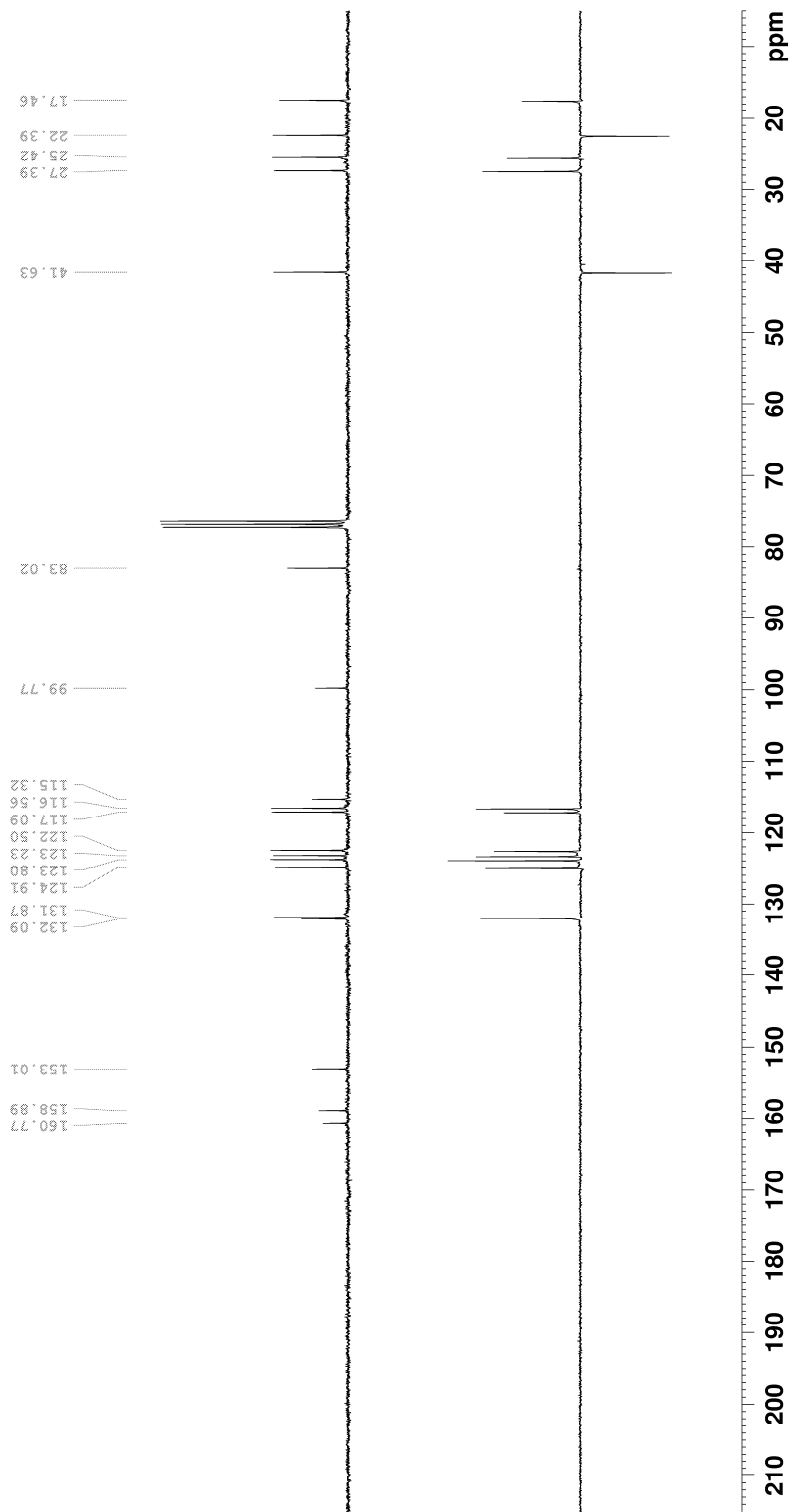


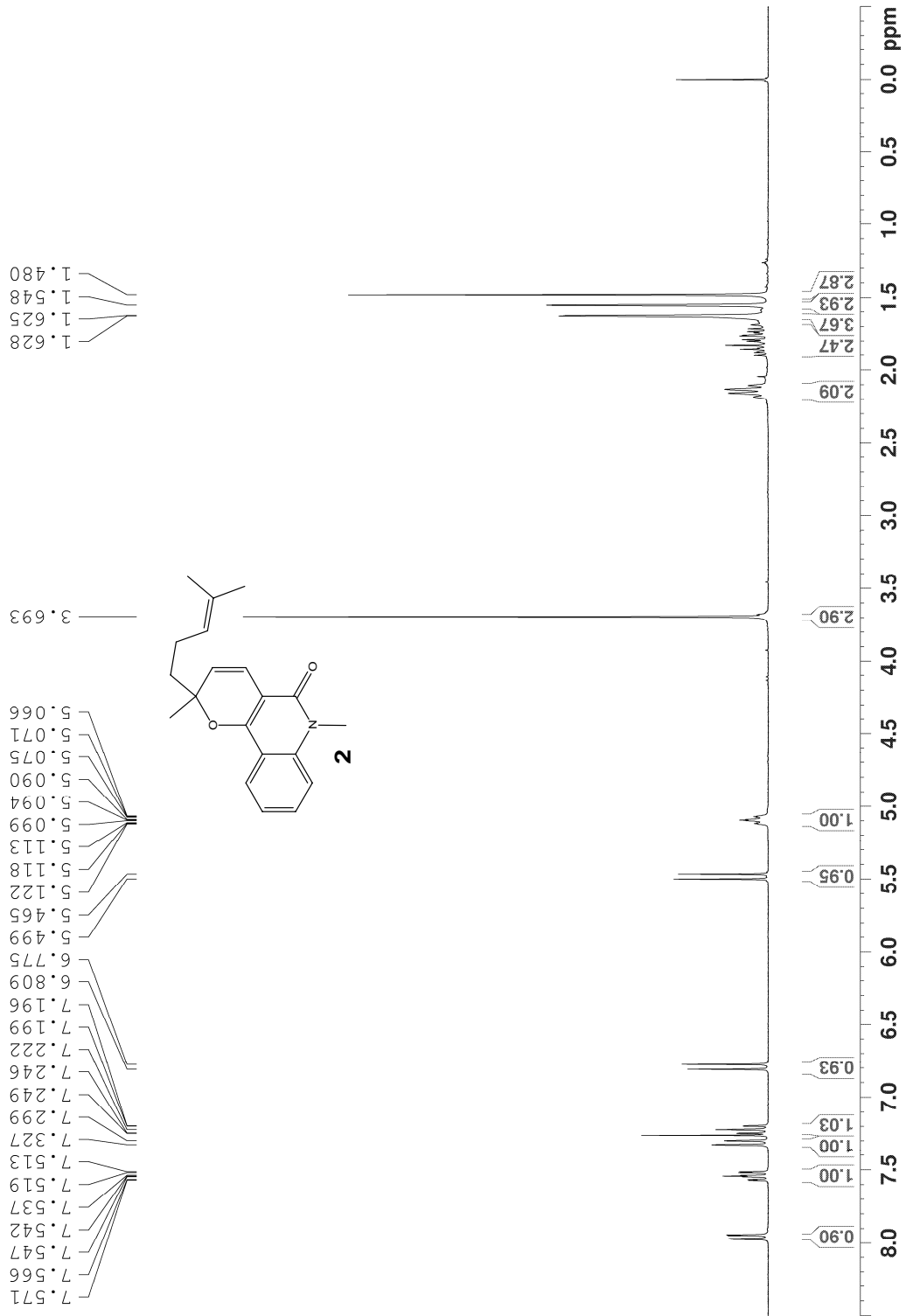


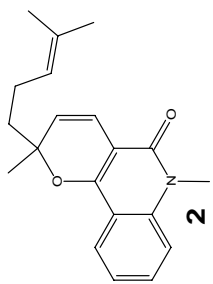




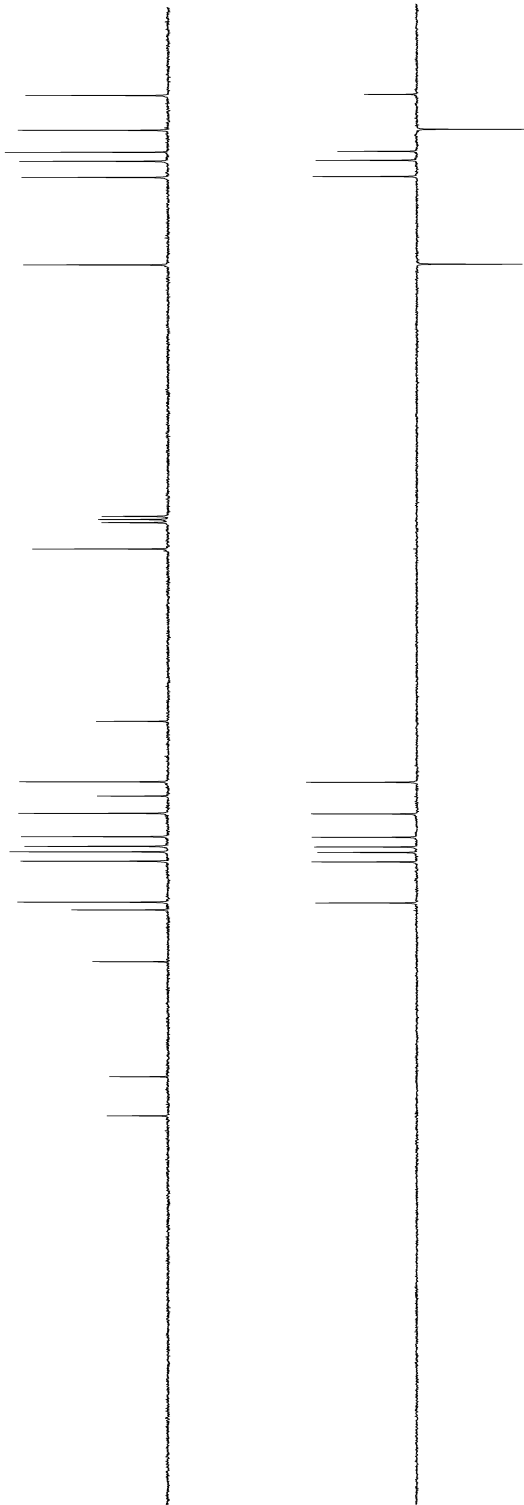
4c



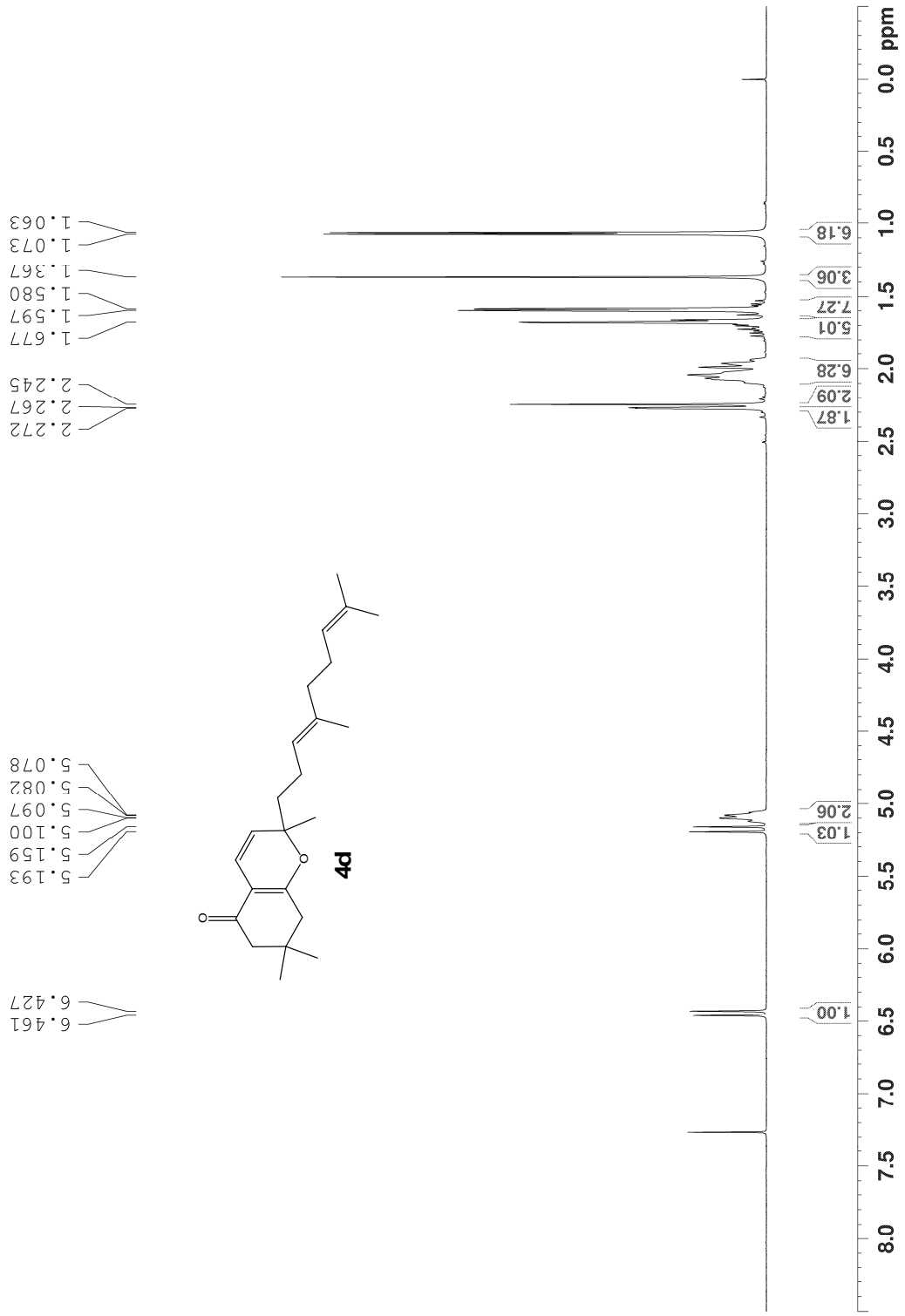


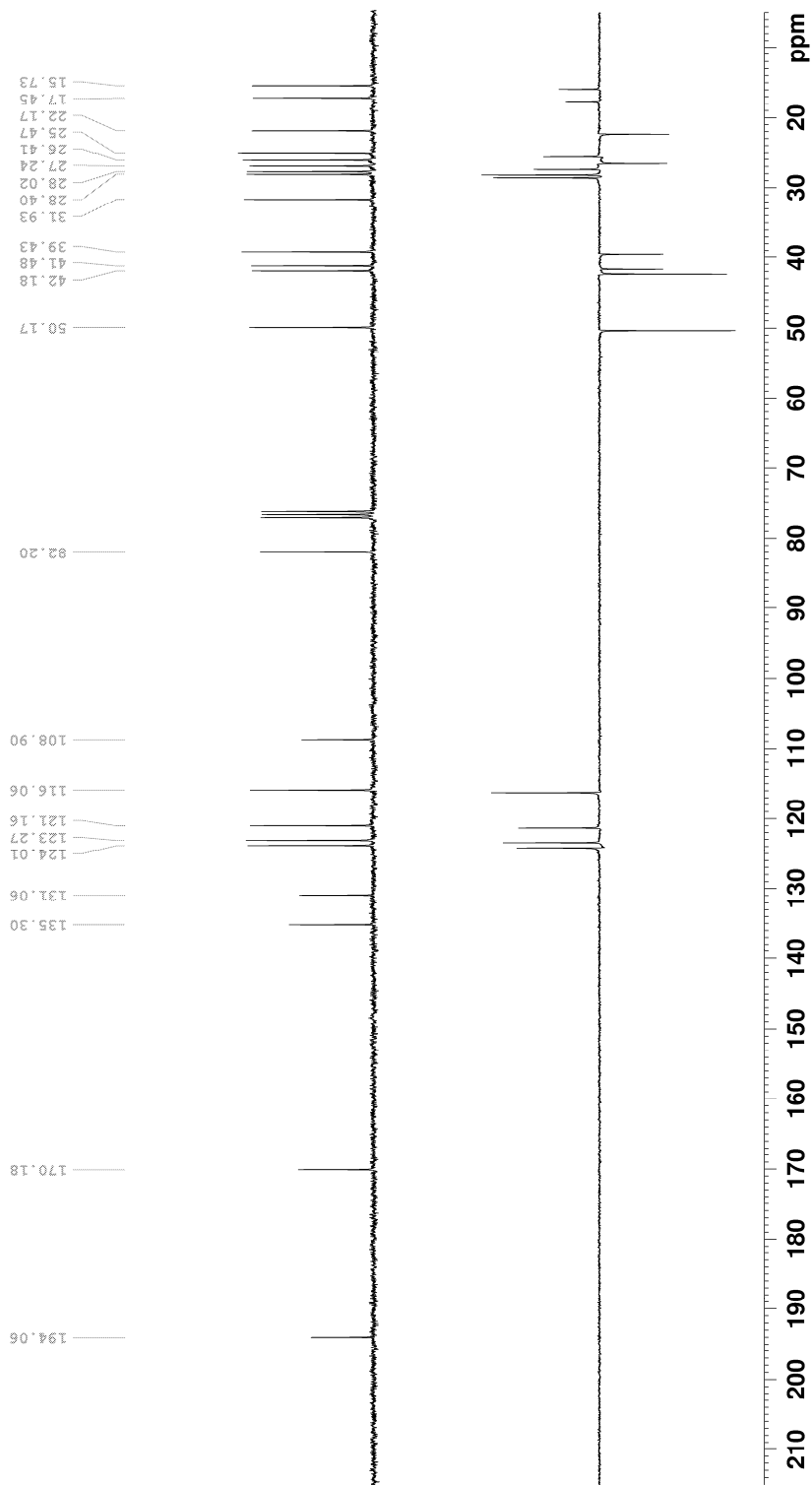
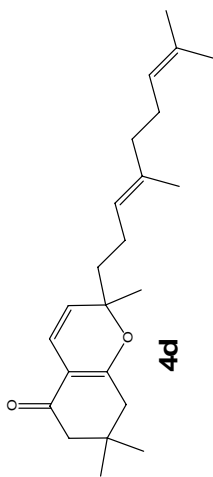


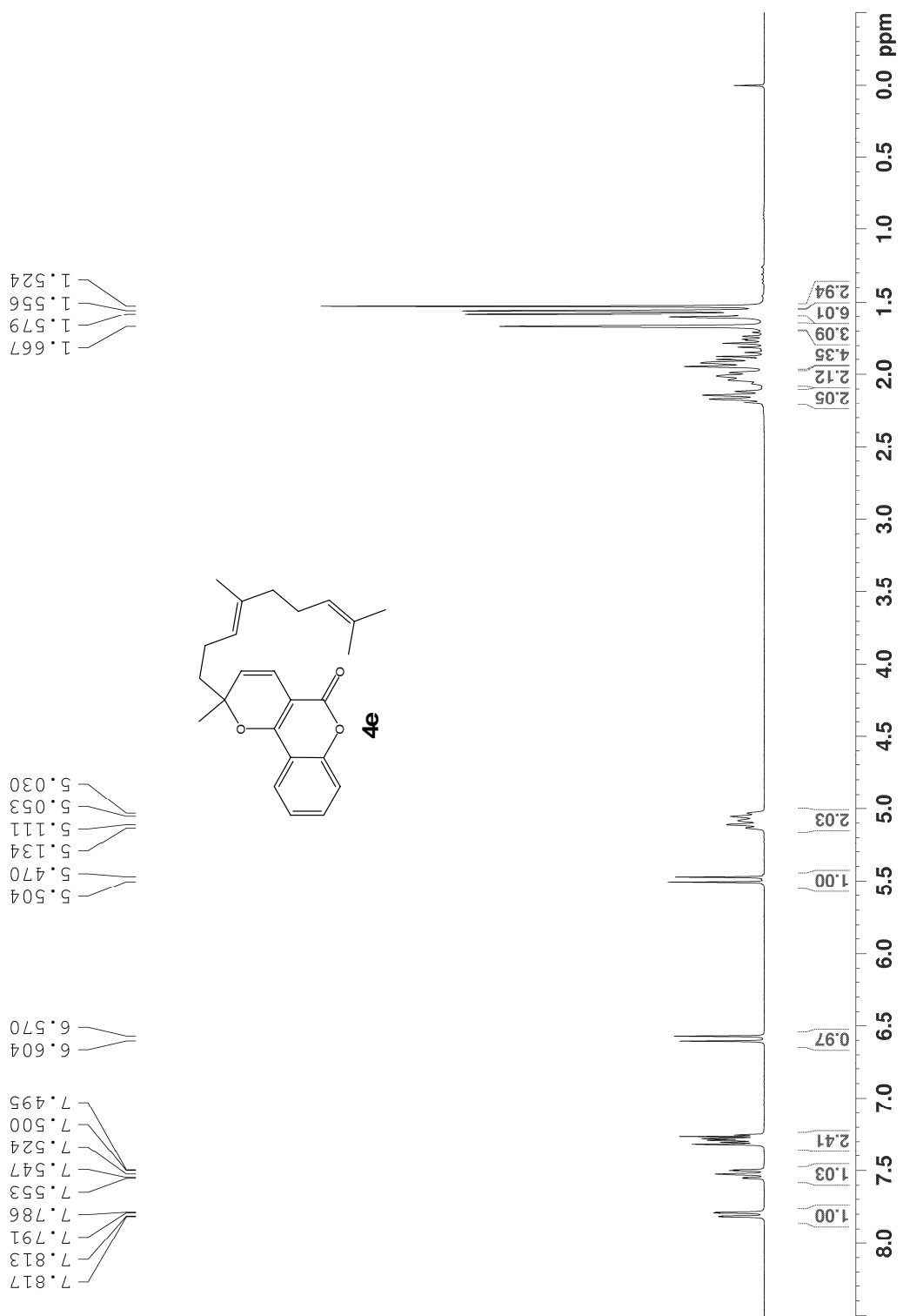
- 160.59
- 155.01
- 139.00
- 131.54
- 130.48
- 124.89
- 123.44
- 122.68
- 121.34
- 118.09
- 115.59
- 113.64
- 105.16
- 80.92
- 41.21
- 28.87
- 26.67
- 25.30
- 22.24
- 17.28

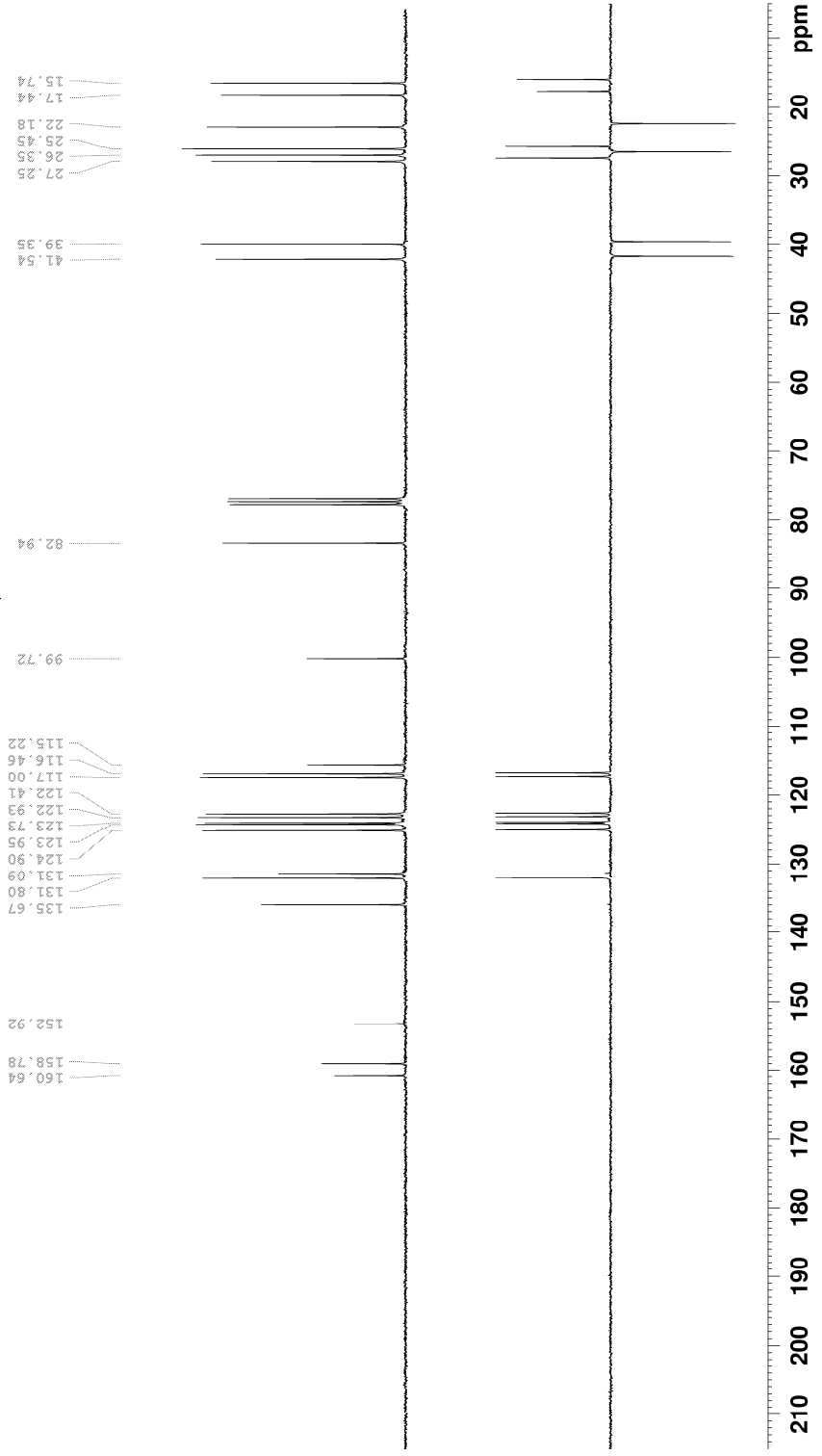
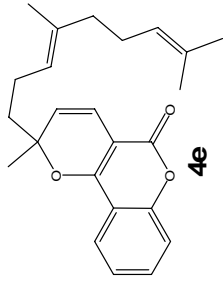


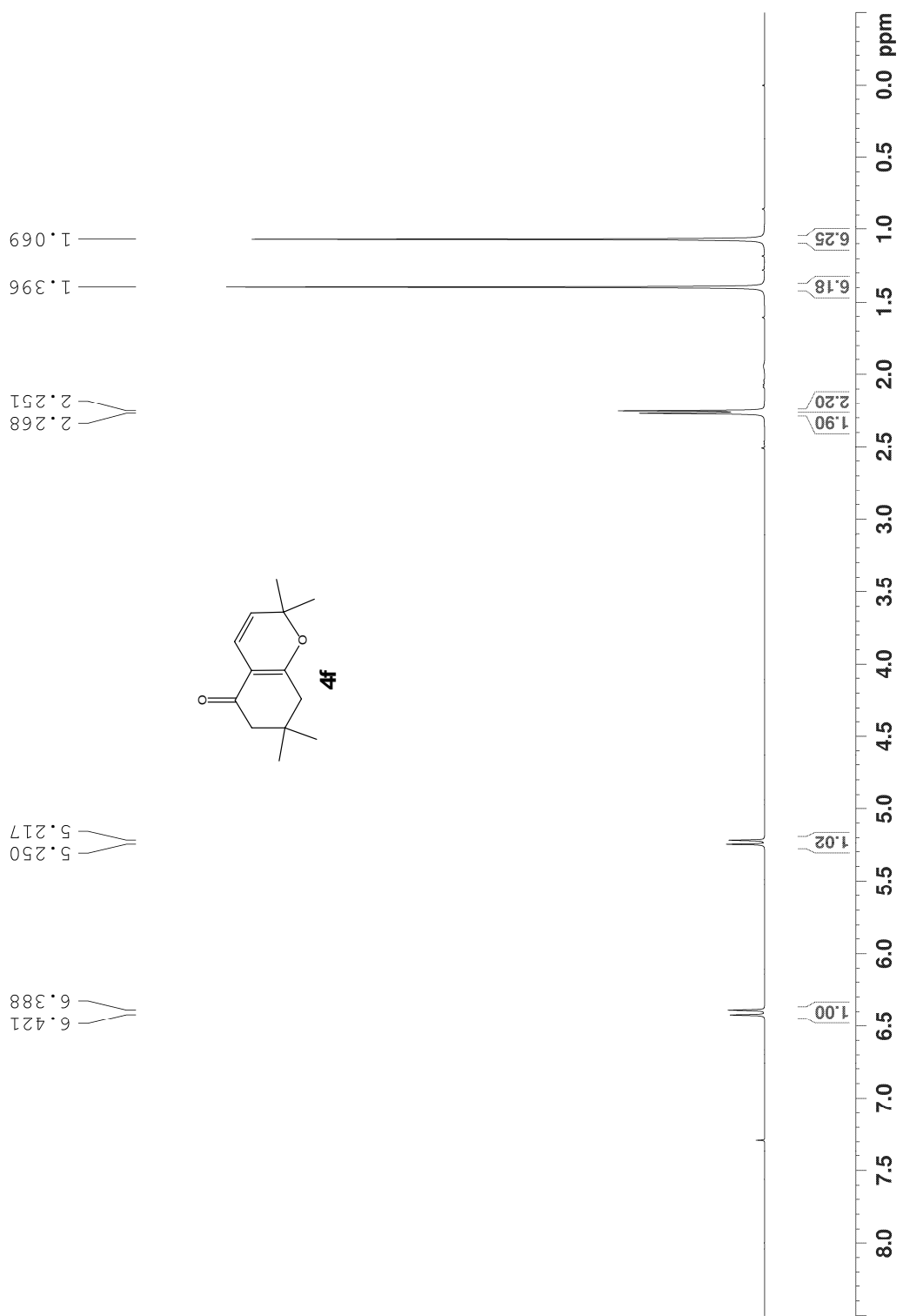
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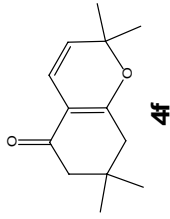




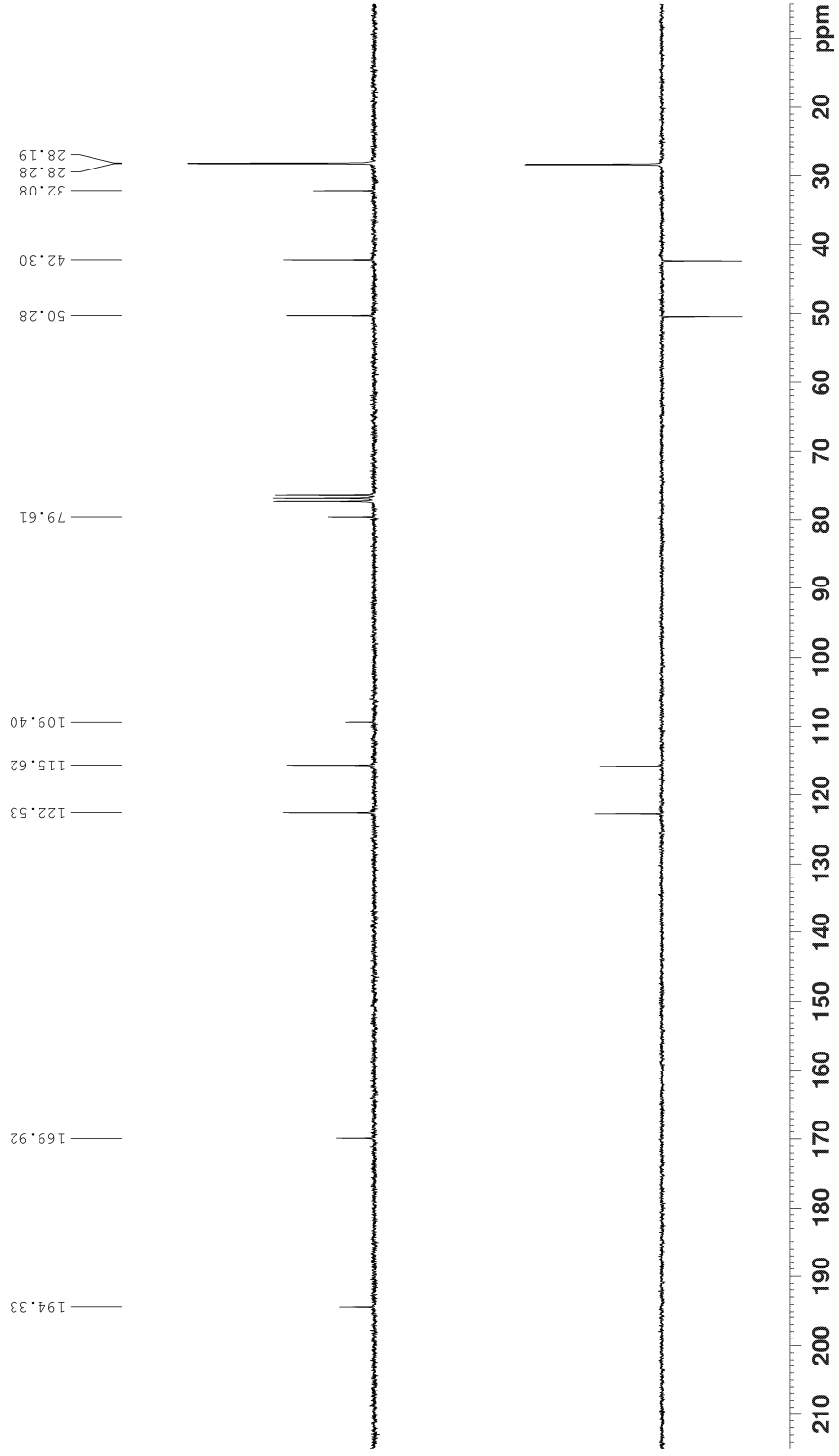


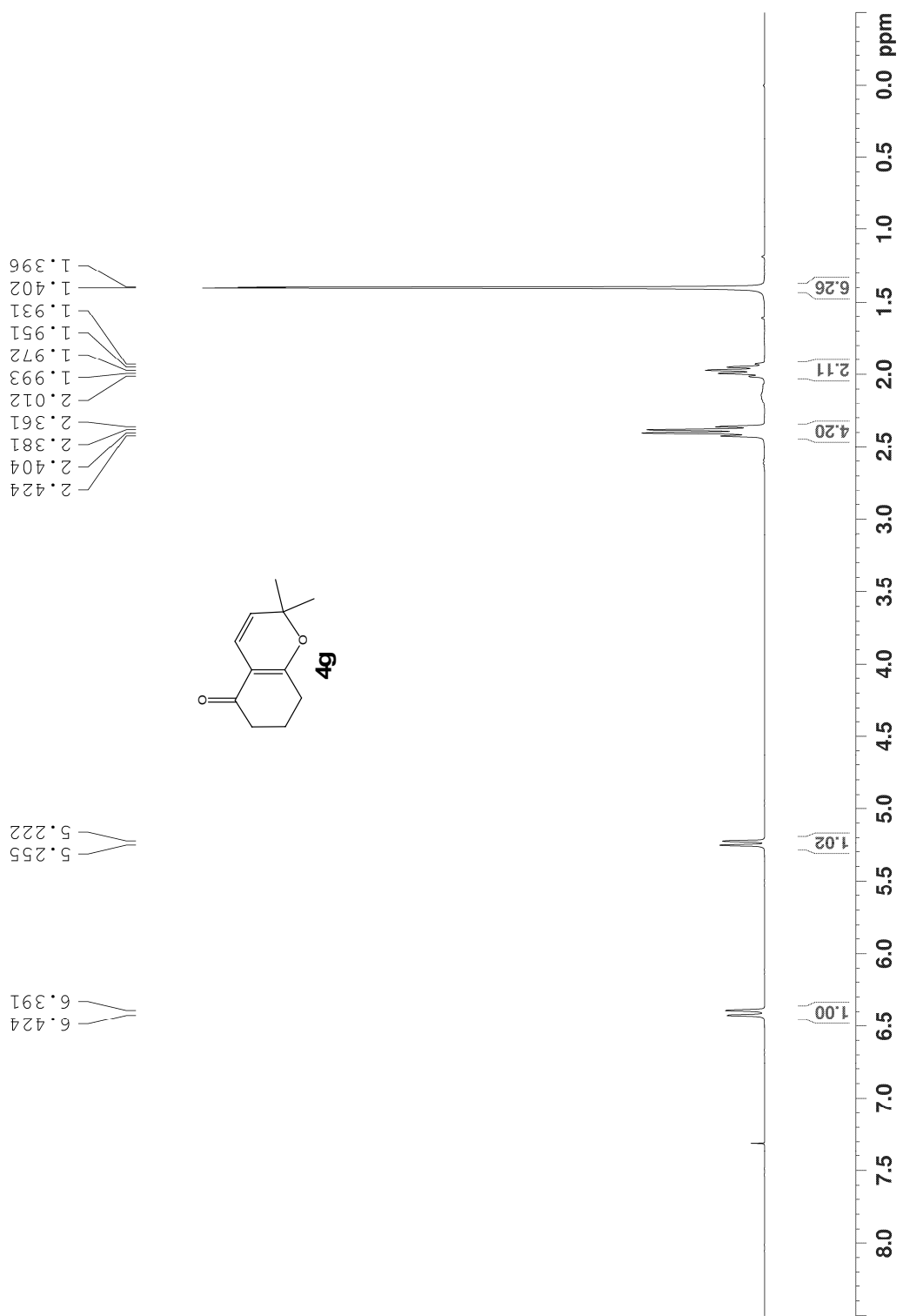


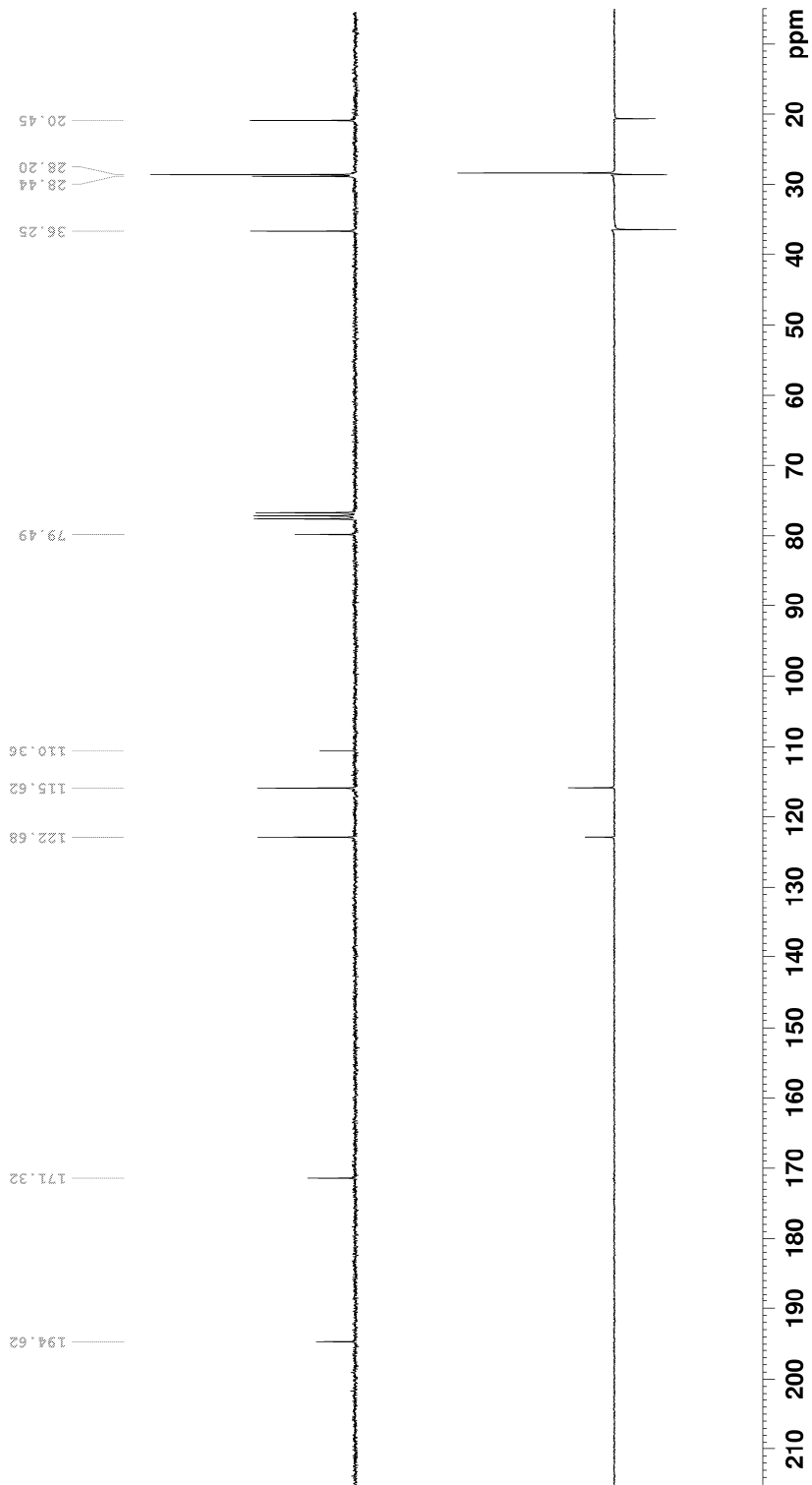
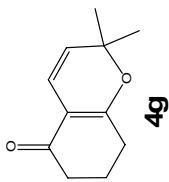


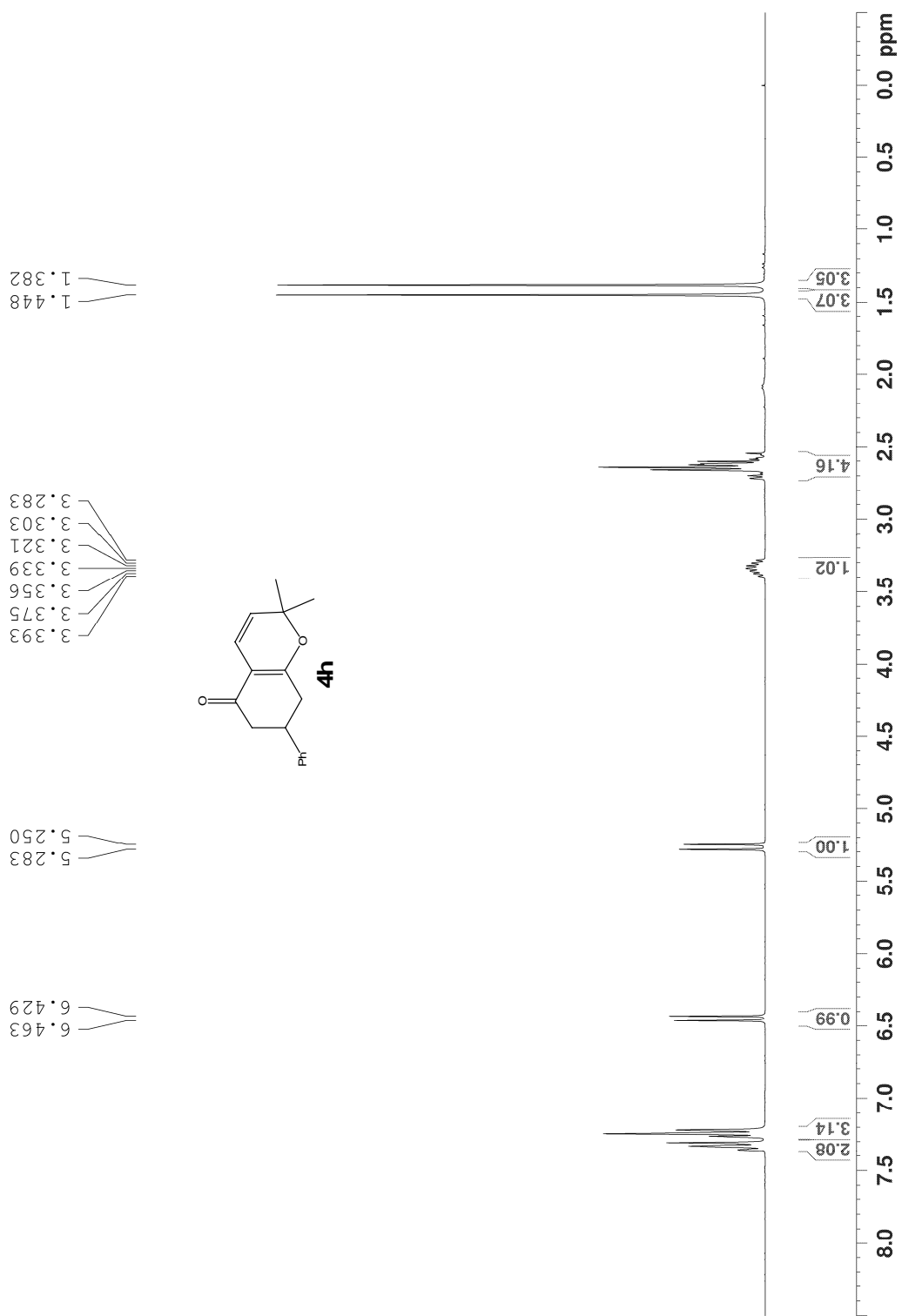


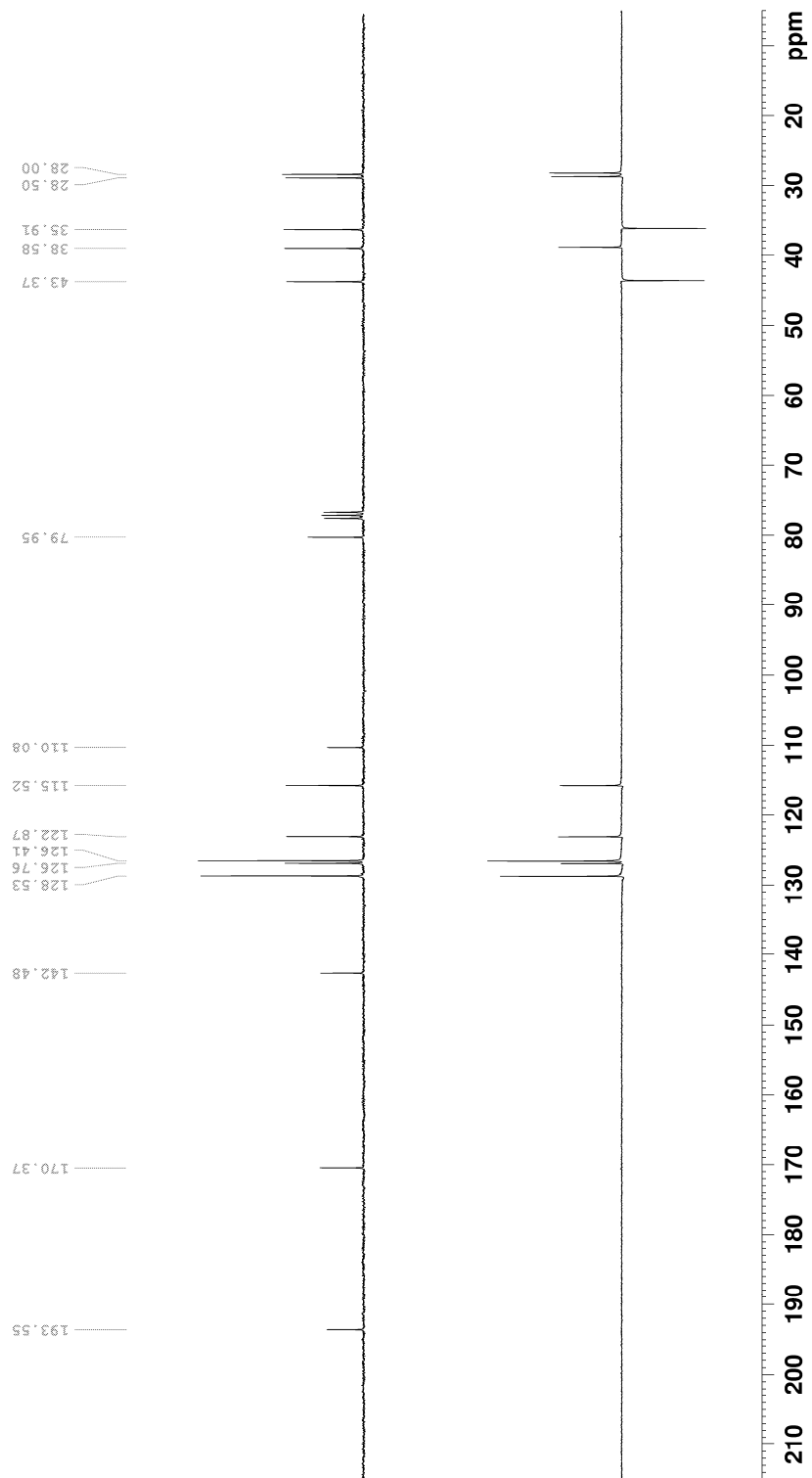
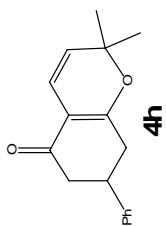
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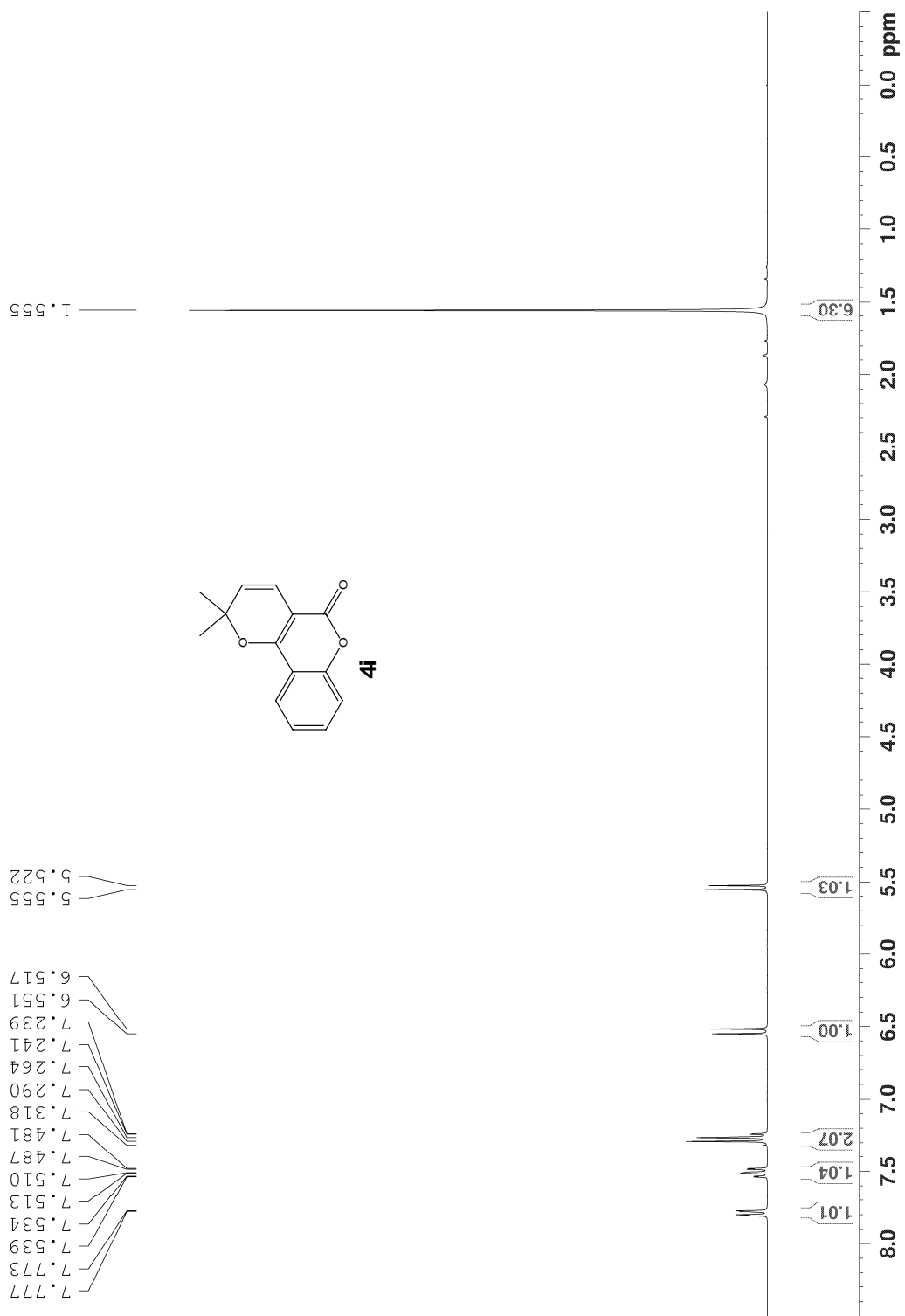


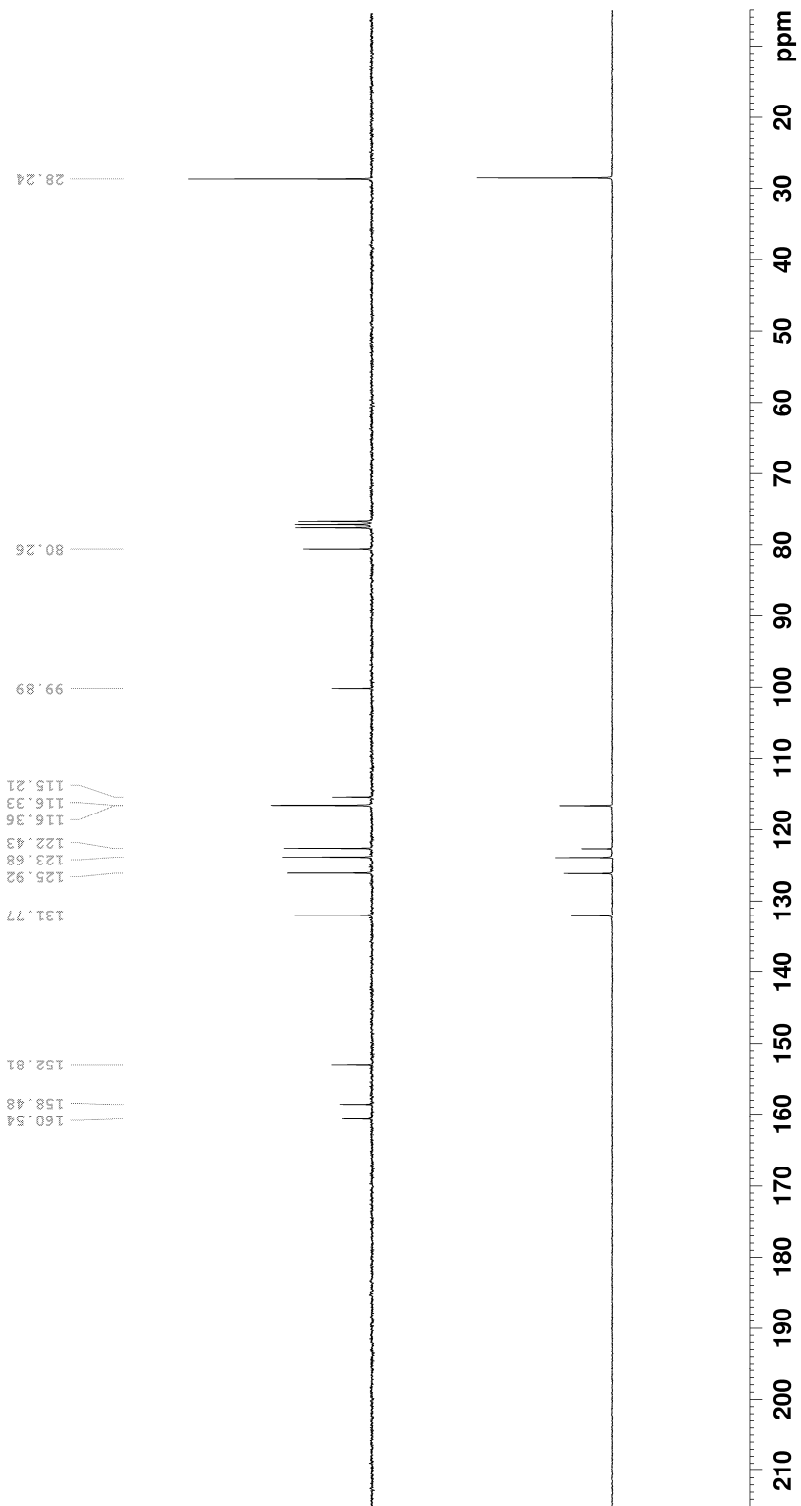
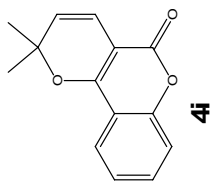


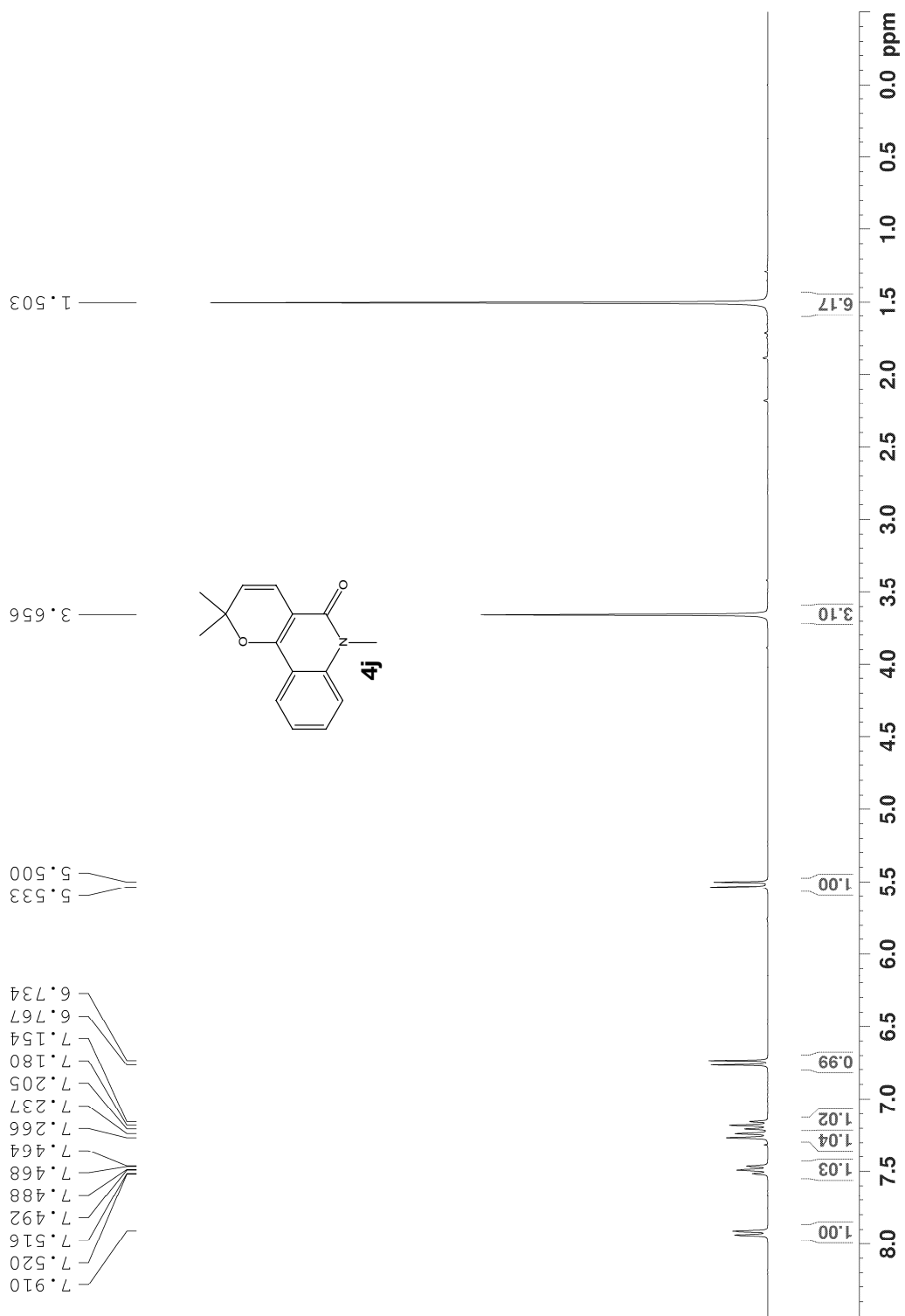


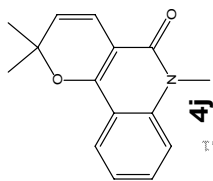




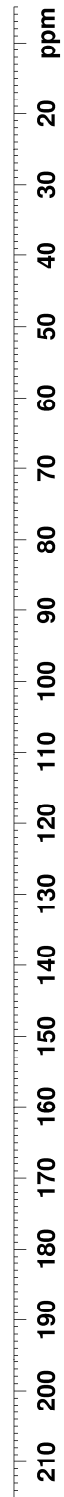
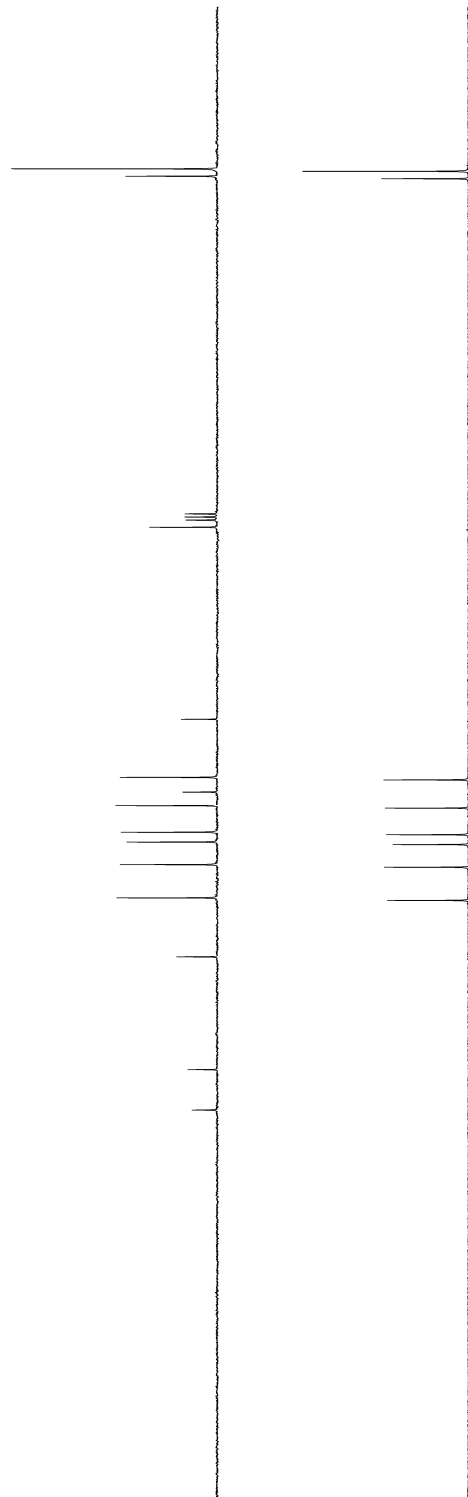


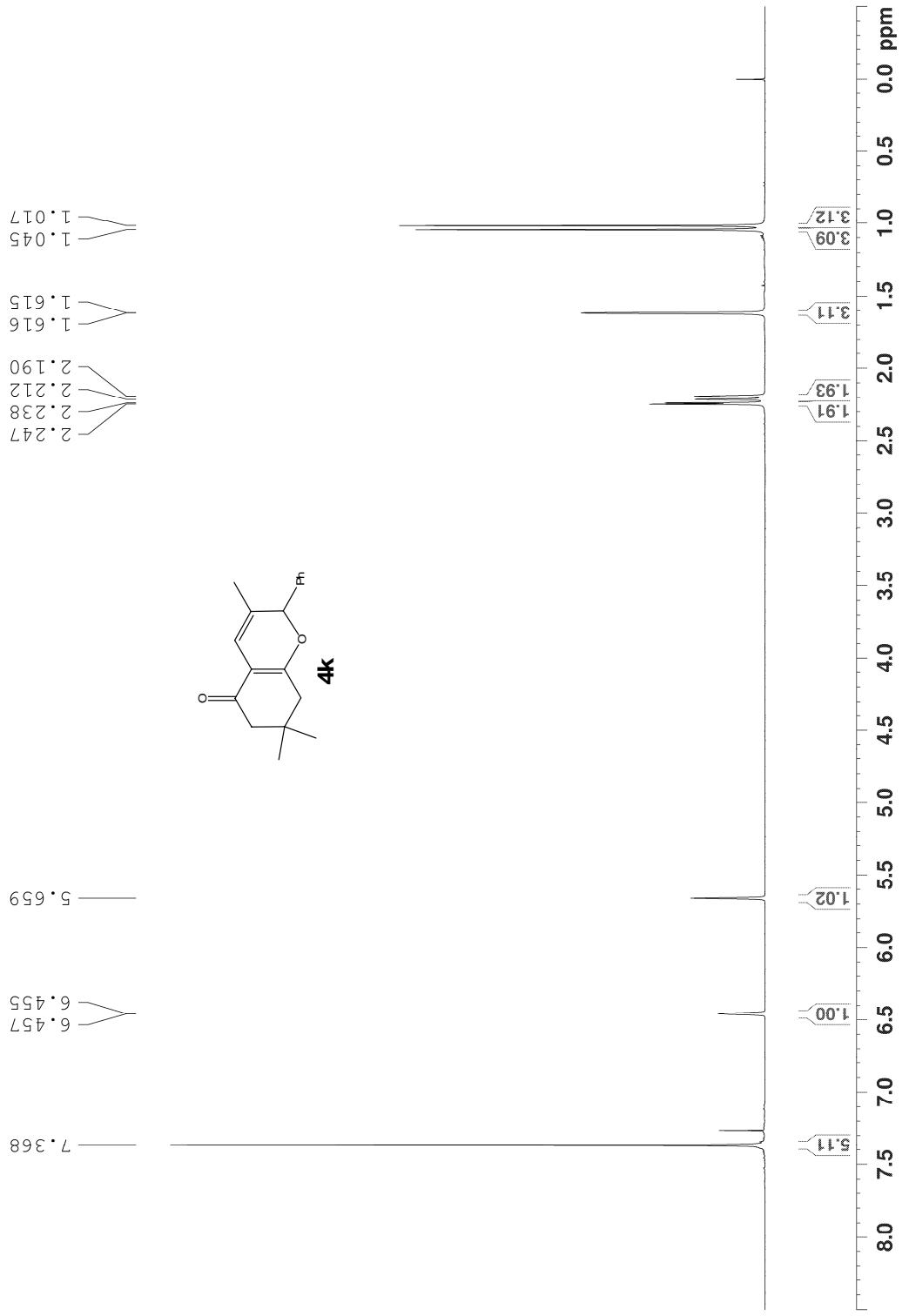


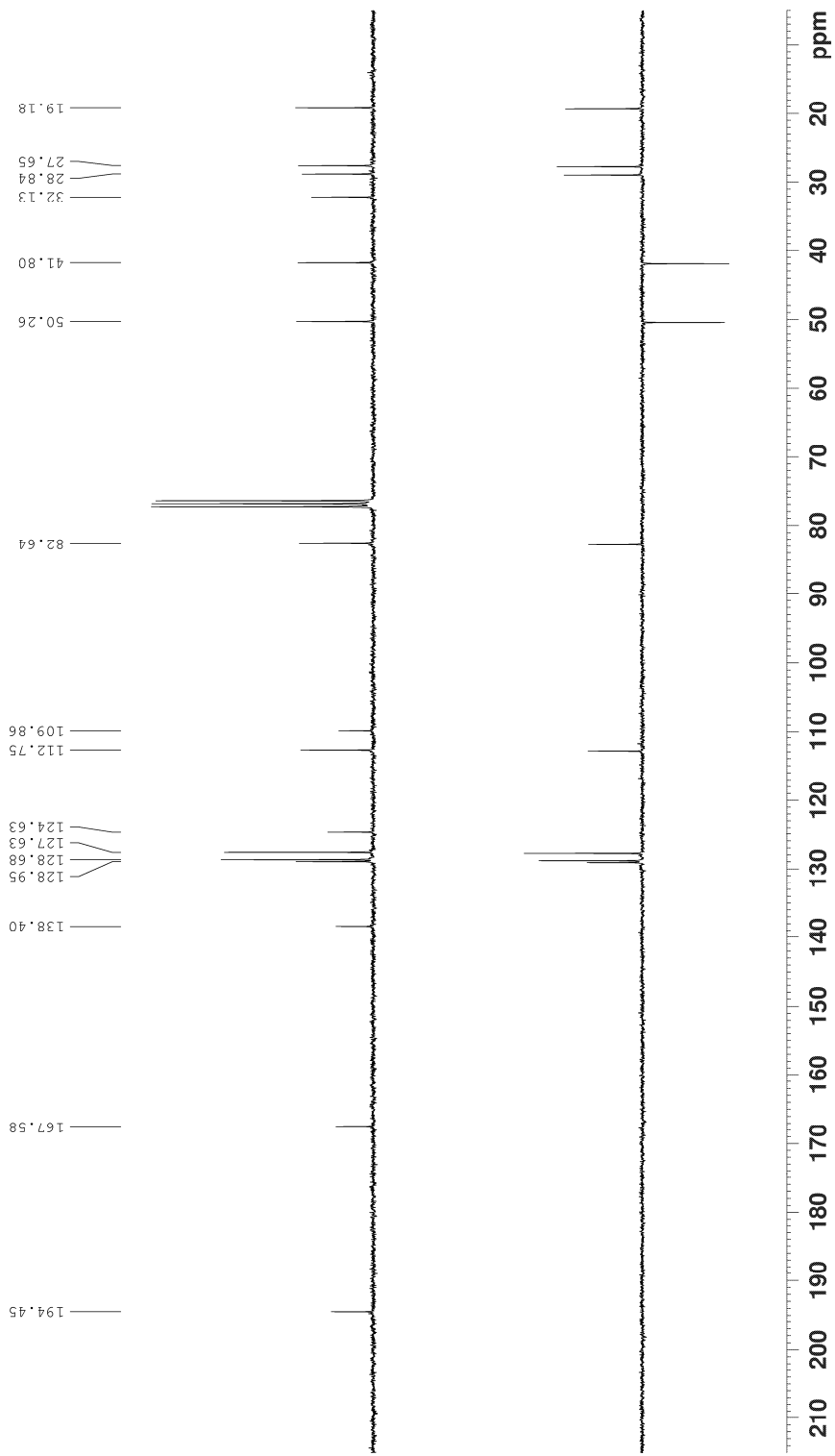
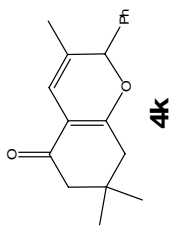


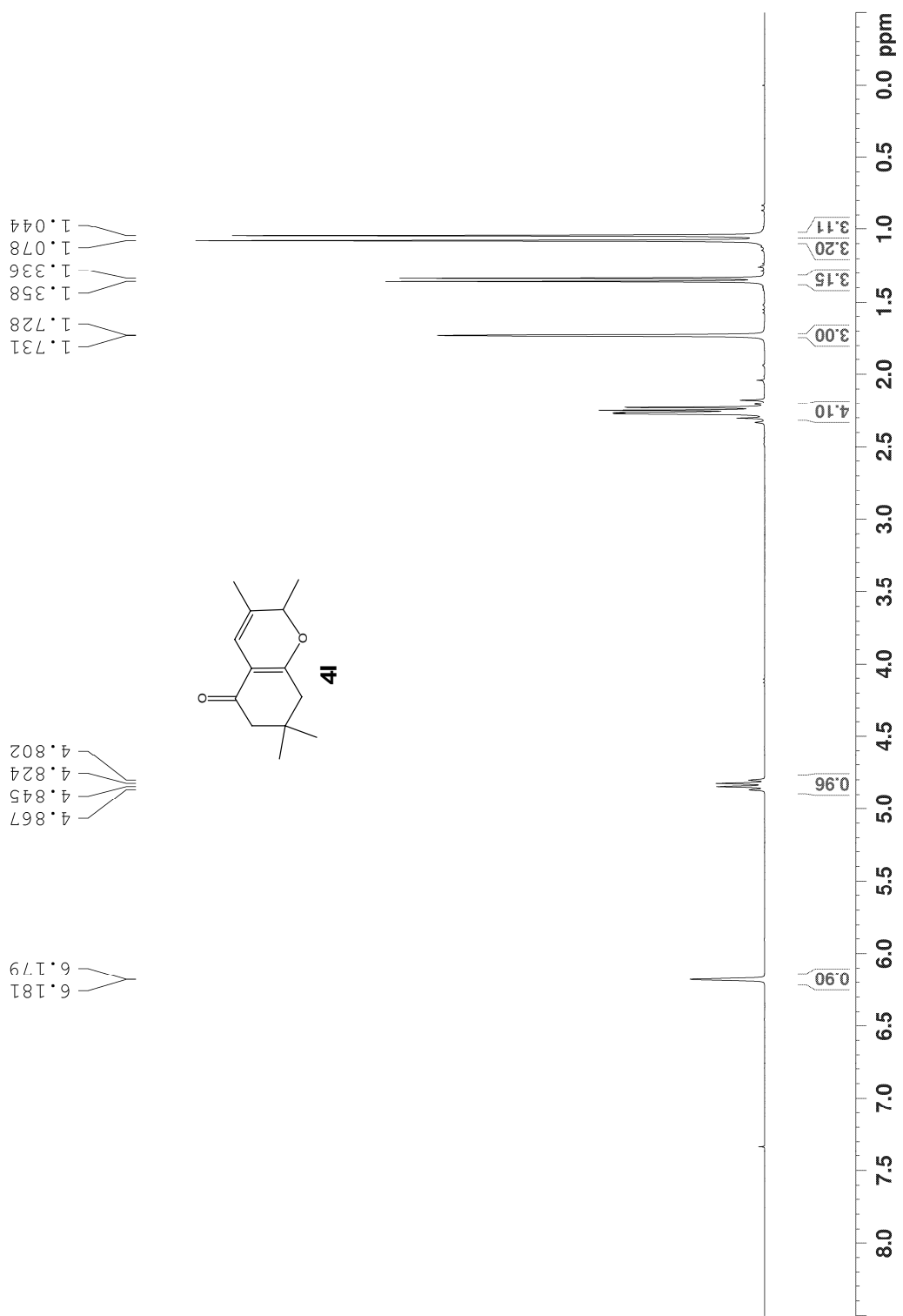


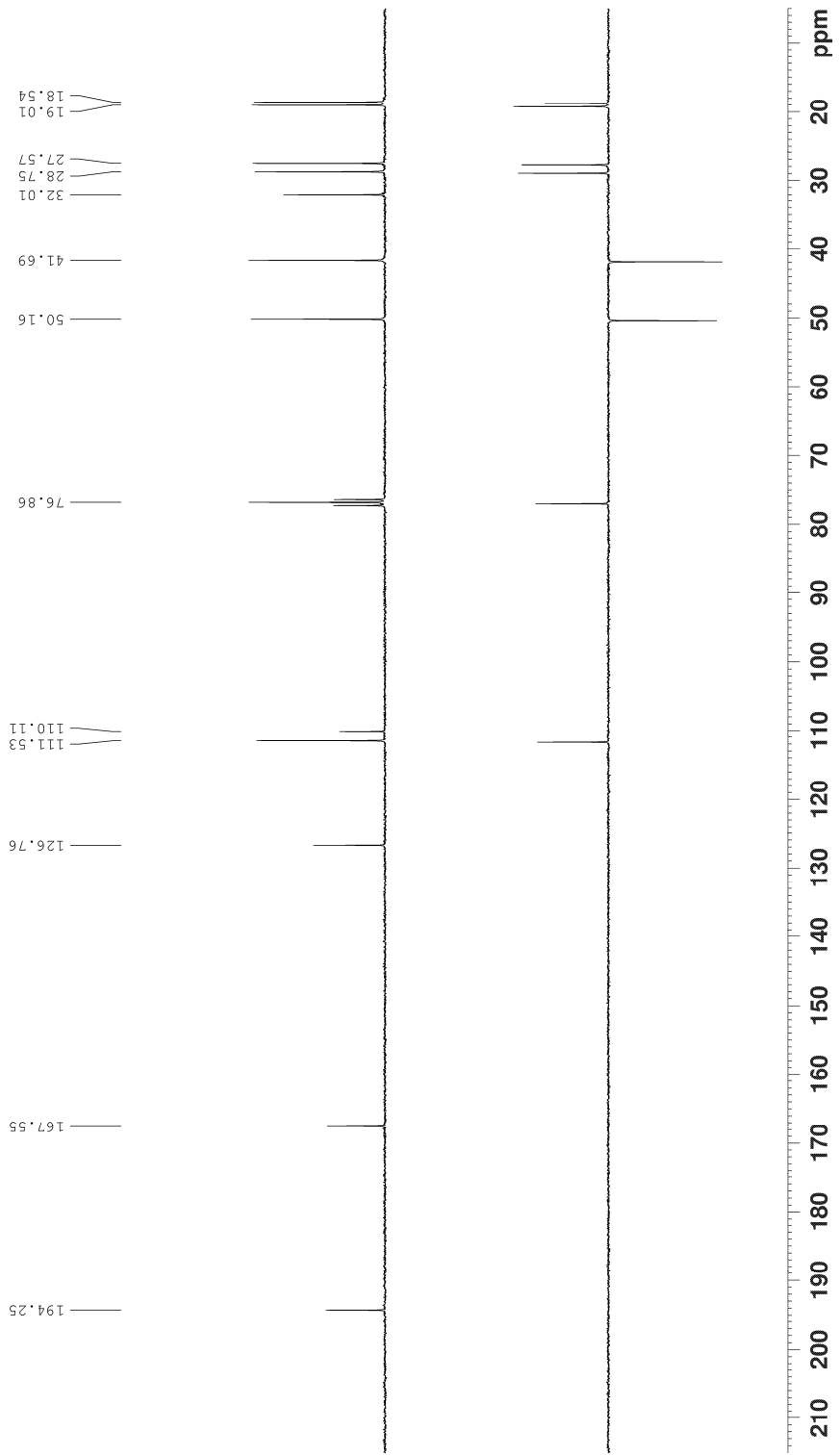
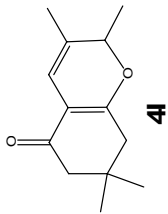
160.51	154.74	138.88	130.45	125.91	122.65	121.28	117.57	115.59	113.58	105.41	78.30	28.83	27.82
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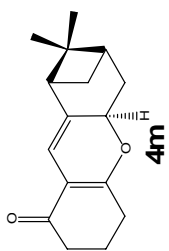












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