ANODIC CYLCIZATION REACTIONS: REVERSING THE POLARITY OF KETENE DITHIOACETAL GROUPS

Yongmao Sun, Bin Liu, Jeff Kao, D. Andre' d'Avignon and Kevin D. Moeller*

Department of Chemistry, Washington University, St. Louis, MO 63130

Supporting Information

A. General Procedure for Electrolysis Reaction

In a flame dried three-neck round bottom flask, under Argon atmosphere was placed a 0.03M mixture of the electrolysis substrate in 30% methanol / tetrahydrofuran. To this mixture was added the tetraethylammonium p-toluenesulfonate electrolyte (0.1M) and 2,6-lutidine (6.0 equivalent). A reticulated vitreous carbon anode and a platinum wire cathode were inserted into the reaction mixture, and then the resulting solution sonicated under Argon atmosphere for 10 minutes. The electrolysis was carried out at constant current of 8.0 mA until 2.2 F/mol of electricity had been passed. The solvent mixture was then removed under reduced pressure. The residue was diluted with ether, the electrolyte removed by filtration, and the resulting solution concentrated *in vacuo*. The crude product was immediately chromatographed through a silica gel column that had been slurry packed using a 1% triethylamine in hexane solution with eluting solvent with range from pure hexane to 50% ether in hexane.

B. Spectral data

Compound 5a: ^{1}HNMR ($CDCl_3$/300MHz) δ 6.29 (d, J=12.6Hz, 0.5H), 5.97 and 5.95 (t and t, J=7.5Hz, 1H), 5.88 (dt, J_d=6.3Hz, J_t=1.5Hz, 0.5H), 4.71 (d t, J_d=12.6Hz, J_t=7.5Hz, 0.5H), 4.33 (q, J_q=6.9Hz, 0.5H), 3.58 (s, 1.5H), 3.50 (s, 1.5H), 2.86 (m, 4H), 2.23 (m, 4H), 2.07(dq, J_q=7.5Hz, J_d=1.2Hz, 1H), 1.94 (dq, J_q=7.5Hz, J_d=0.9Hz, 1H), 1.43 (p, J=7.5Hz, 2H); ^{13}C NMR ($CDCl_3$/75MHz) δ 147.4, 146.5, 135.1, 134.8, 125.7, 106.6, 102.7, 59.8, 56.2, 45.0, 37.9, 36.1, 35.2, 30.8, 30.4, 30.0, 29.5, 29.1, 27.6, 26.0, 25.8, 25.7, 23.9, 21.4, 15.6; IR (neat/NaCl) 2930, 2847, 1655, 1585, 1209, 1110 cm^{-1}; HRMS m/z calculated for $[M+H]^+$ 231.0877, found 231.0868.

Compound 5b: ^{1}HNMR ($CDCl_3$/300MHz) δ 6.28 (d, J=12.6Hz, 0.5H), 5.96 and 5.95 (t and t, J_t=7.5Hz, 1H), 5.86 (dt, J_d=6.3Hz, J_t=1.5Hz, 0.5H), 4.71 (dt, J_d=12.6Hz, J_t=7.5Hz, 0.5H), 4.34 (q, J_q=7.5Hz, 0.5H), 3.57 (s, 1.5H), 3.50 (s, 1.5H), 2.85 (m, 4H), 2.25-2.14 (m, 4H), 2.05(dq, J_q=7.5Hz, J_d=1.5Hz, 1H), 1.94 (dq, J_q=7.2Hz, J_d=2.4Hz, 1H), 1.43-1.31 (m, 4H); ^{13}C NMR ($CDCl_3$/75MHz) δ 147.3, 146.3, 135.3, 135.1, 125.5 125.3, 106.9, 103.1, 59.7, 56.1, 30.7, 30.6, 30.4, 30.0, 29.5, 29.4, 29.3, 29.2, 28.8, 28.5, 27.6, 25.6, 25.5, 23.8; IR (neat/ NaCl) 2929, 2852, 1661, 1654, 1459, 1420, 1107 cm^{-1}; HRMS m/z calculated for $[M+H]^+$ 245.1034, found 245.1034.

Compound 6a: ^{1}HNMR ($CDCl_3$/300MHz) δ 4.24 (d, J=5.1Hz, 1H), 3.41(s, 3H), 3.40(s, 3H), 3.39 (s, 3H), 3.10(m, 2H), 2.67-2.47 (m, 4H), 2.09-2.01 (m, 1H), 1.95-1.86(m, 2H), 1.83-1.66(m, 4H), 1.64-1.53(m, 1H); ^{13}C NMR ($CDCl_3$/75MHz) δ 108.2, 97.4, 55.7, 54.7, 51.5, 47.8, 43.9, 28.5, 27.8, 26.8, 26.7, 26.0, 25.3; IR (neat/ NaCl) 2936, 2823, 1446, 1420, 1119, 1071, 1049 cm^{-1}; HRMS m/z calculated for $[M+Li]^+$ 299.1327, found 299.1310.

Compound 6b: ^{1}HNMR ($CDCl_3$/300MHz) δ 5.00 (d, J=2.7Hz, 1H), 3.58 (s, 3H), 3.50 (s, 3H), 3.47 (s, 3H), 3.33-3.00 (broad, m, 2H), 2.66-2.57 (broad, m, 2H), 2.10-1.85 (m, 6H), 1.79-1.63 (broad, m, 2H), 1.44-1.31 (broad, m, 4H); ^{13}C NMR ($CDCl_3$/75MHz) δ 106.4, 97.3, 56.5, 55.2, 51.2, 50.3, 43.7, 42.1, 42.0, 28.9, 27.1, 27.0, 26.3, 25.6, 25.4, 24.0; IR (neat/ NaCl) 2933, 2856, 2252, 1073, 909, 734cm^{-1}; HRMS m/z calculated for $[M+H]^+$ 307.1402, found 307.1407.

Compound 11a: ^{1}H NMR ($CDCl_3$/300MHz) δ 5.95 (t, J=7.2Hz, 1H), 3.63 (t, J=6.3Hz, 2H), 2.86 (m, 4H), 2.34 (dq, J_q=7.5Hz, J_d=1.2Hz, 3H), 2.28-2.12 (m, 2H), 1.65 (m, J=7.2Hz, 2H); ^{13}C NMR ($CDCl_3$/75MHz) δ 133.7, 126.5, 62.1, 31.9, 30.6, 29.9, 25.8, 25.4; IR (neat/ NaCl) 3368, 2930, 1583, 1420, 1276, 1056 cm^{-1}; HRMS m/z calculated for $[M+Li]^+$ 197.0646, found 197.0647.

Compound 11b: ^{1}H NMR ($CDCl_3$/300MHz) δ 5.95 (t, J=7.5Hz, 1H), 3.65 (t, J=7.2Hz, 2H), 2.86 (t, J=6.0Hz, 4H), 2.29-2.13 (m, 4H), 1.66-1.44 (m, 5H); ^{13}C NMR ($CDCl_3$/75MHz) δ 134.4, 126.0, 62.9, 32.3, 30.6, 29.8, 29.2, 25.5, 25.3; IR (neat/ NaCl) 3401, 2936, 2094, 1654, 1638 cm^{-1}; HRMS m/z calculated for $[M+Li]^+$ 211.0803, found 211.0799

Compound 11c: ^{1}H NMR ($CDCl_3$/300MHz) δ 3.46-3.56 (m, 2H), 3.38-3.30 (m, 1H), 2.89-2.85 (m, 4H), 2.15-2.07 (m, 2H), 1.97(dd, J=7.5, 4.8 Hz, 1H), 1.76 (s, 1H), 1.65-1.49 (m, 2H), 1.00 (d, J=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$/75MHz) δ 142.4, 119.5, 61.0, 37.3, 33.7, 30.0, 29.9, 24.9, 18.9, 14.5; IR (neat/ NaCl) 3361, 2952, 2930,2868, 1418, 1272, 1049, 909 cm^{-1}; HRMS m/z calculated for $[M+H]^+$ 219.0877, found 219.0868.

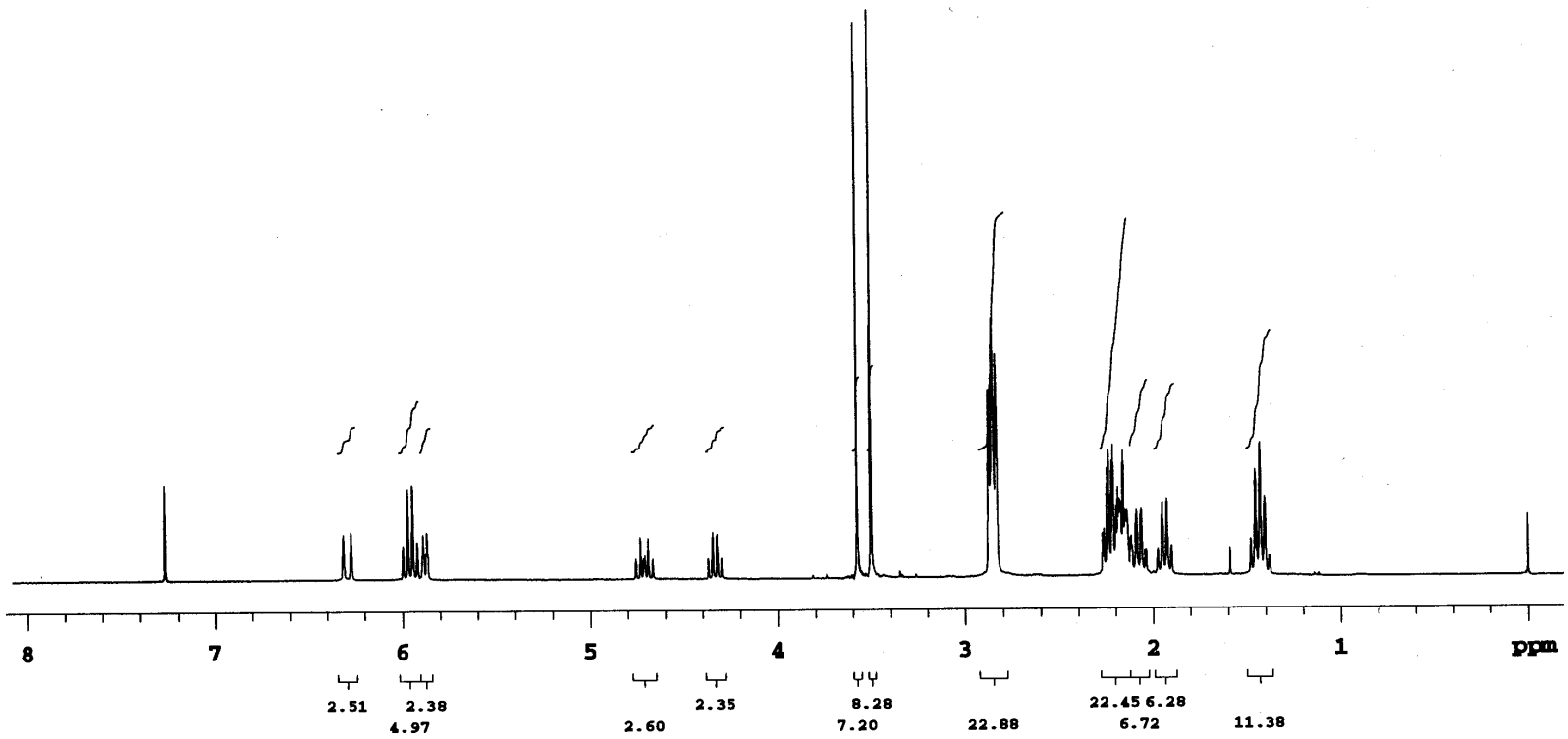
Compound 12a: ^{1}H NMR ($CDCl_3$/300MHz) δ 4.22 (t, J=7.5Hz, 1H), 3.98-3.81 (m, 2H), 3.52 (s, 3H), 3.17-3.00 (m, 2H), 2.76-2.68 (m, 2H), 2.18-1.82 (m, 6H); ^{13}C NMR

($CDCl_3$/75MHz) δ 96.2, 83.5, 69.8, 52.8, 28.0, 26.7, 26.6, 26.4, 24.8; IR (neat/ NaCl) 2934, 2870, 2241, 1726, 1423, 1057 cm^{-1}; HRMS m/z calculated for $[M+Li]^+$ 227.0752, found 227.0750.

Compound 12b: ^1H NMR ($CDCl_3$/300MHz) δ 4.13-4.07 (m, 1H), 3.59-3.48 (m, 1H), 3.47 (s, 3H), 3.46-3.35 (m, 1H), 3.17-3.02 (m, 2H), 2.72-2.62 (m, 2H), 2.09-1.82 (m, 4H), 1.66-1.44 (m, 4H); ^{13}C NMR ($CDCl_3$/75MHz) δ 95.1, 82.1, 69.5, 52.7, 26.7, 26.4, 26.3, 26.0, 25.0, 23.4; IR (neat/ NaCl) 2930, 2846, 1441, 1420, 1206, 1088, 1046cm^{-1}; HRMS m/z calculated for $[M+Li]^+$ 241.0908, found 241.0895.

Compound 12c: ^1H NMR ($CDCl_3$/300MHz) δ 3.87-3.71 (m, 2H), 3.53 (s, 3H), 3.03-2.93 (m, 2H), 2.89-2.70 (m, 3H), 2.07-1.94 (m, 2H), 1.91-1.77 (m, 1H), 1.62-1.50 (m, 1H), 1.18 (s, 1H), 1.08 (d, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$/75MHz) δ 102.6, 90.9, 67.4, 53.3, 39.1, 35.5, 27.2, 26.9, 23.8, 18.2, 16.6; IR (neat/ NaCl) 2960, 2928, 2867, 1088, 1051 cm^{-1}; HRMS m/z calculated for $[M+H]^+$ 249.0983, found 249.0976.

compound 5a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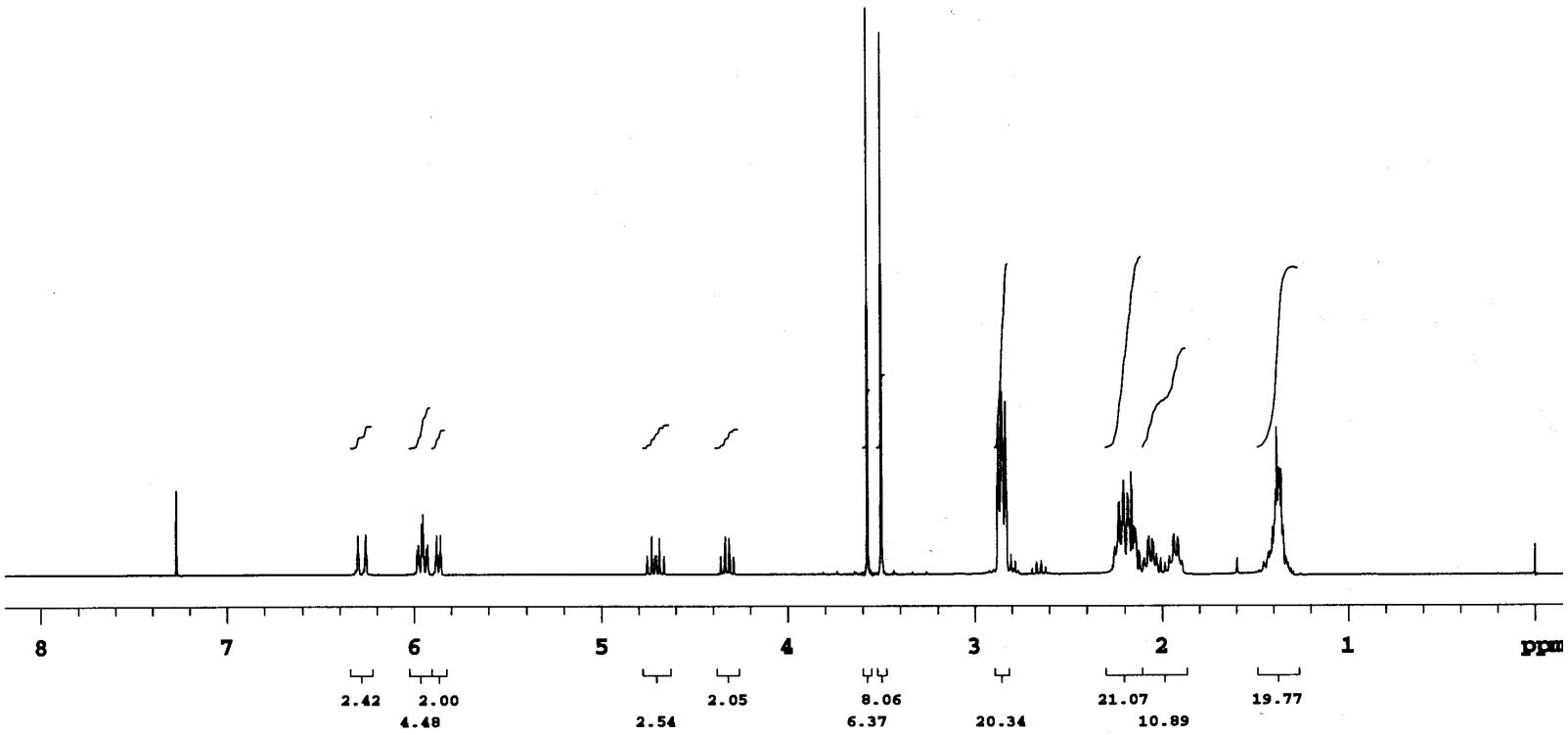
compound 5b



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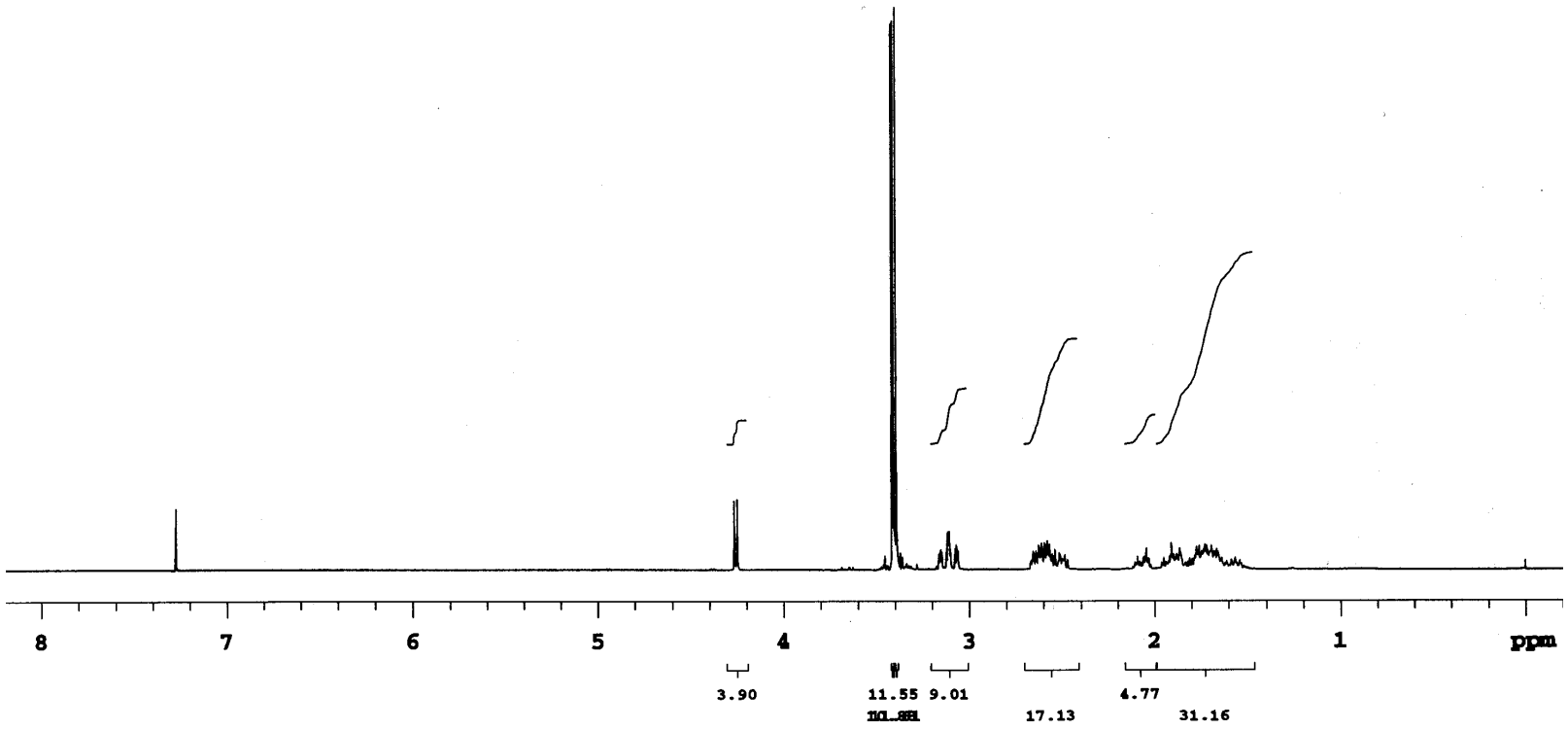

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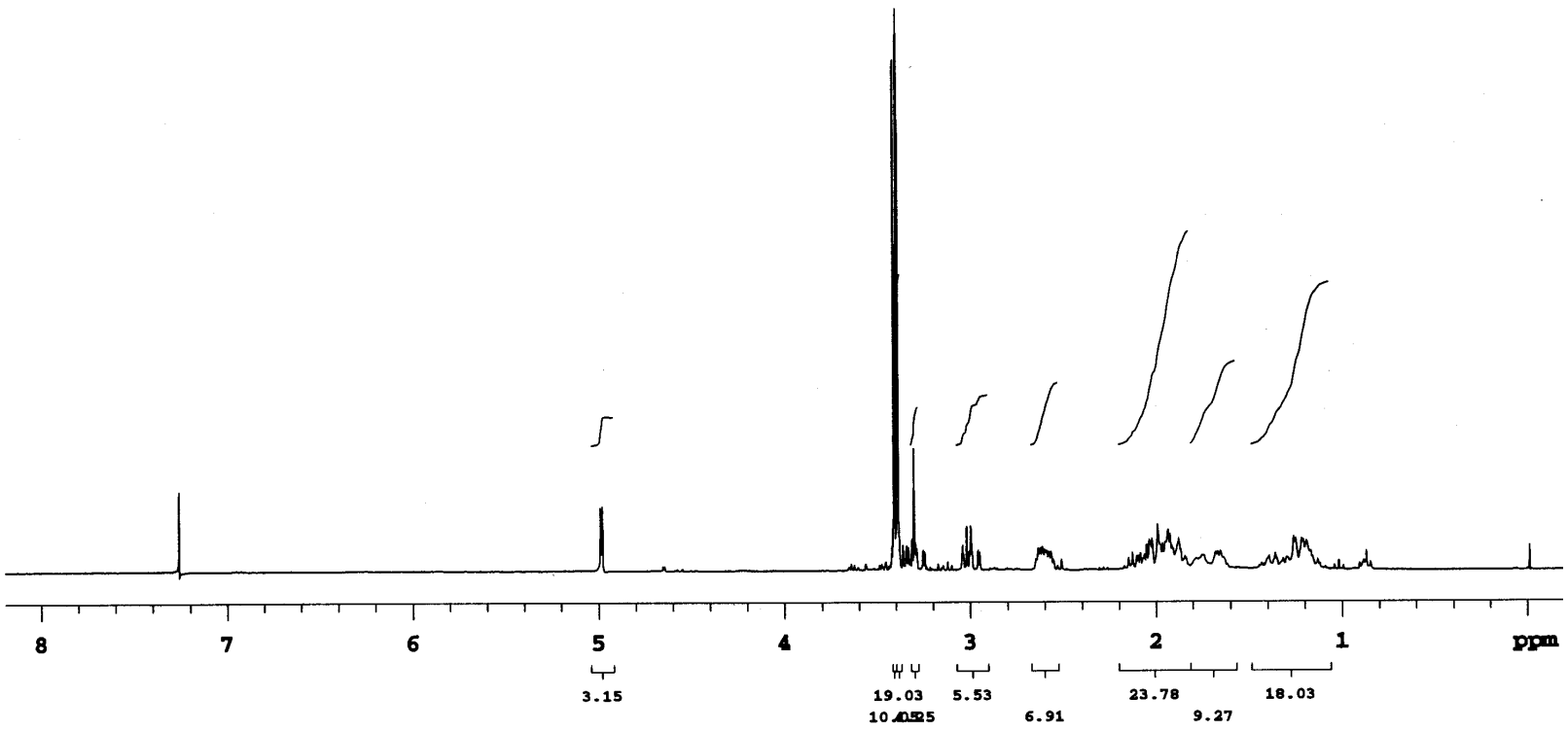

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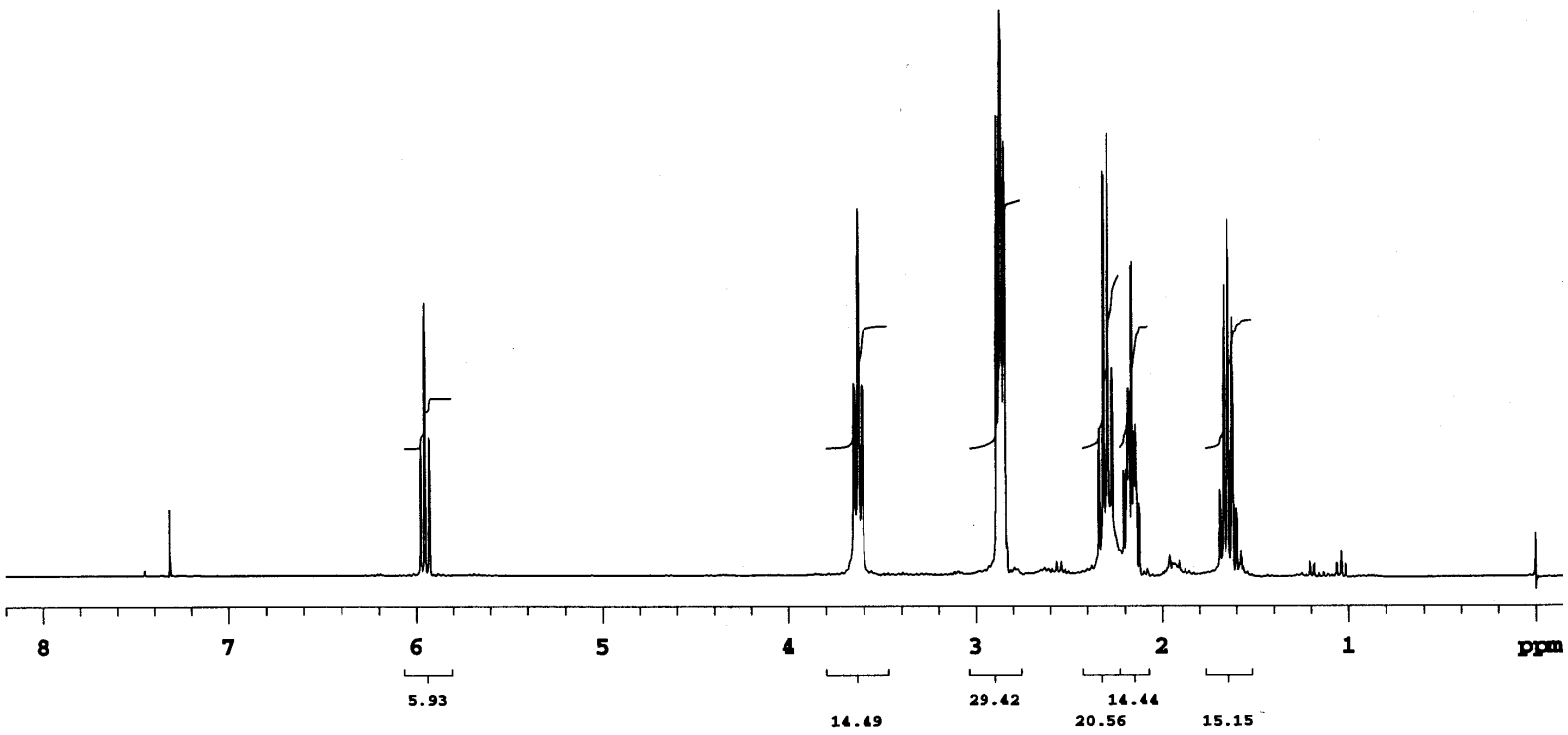

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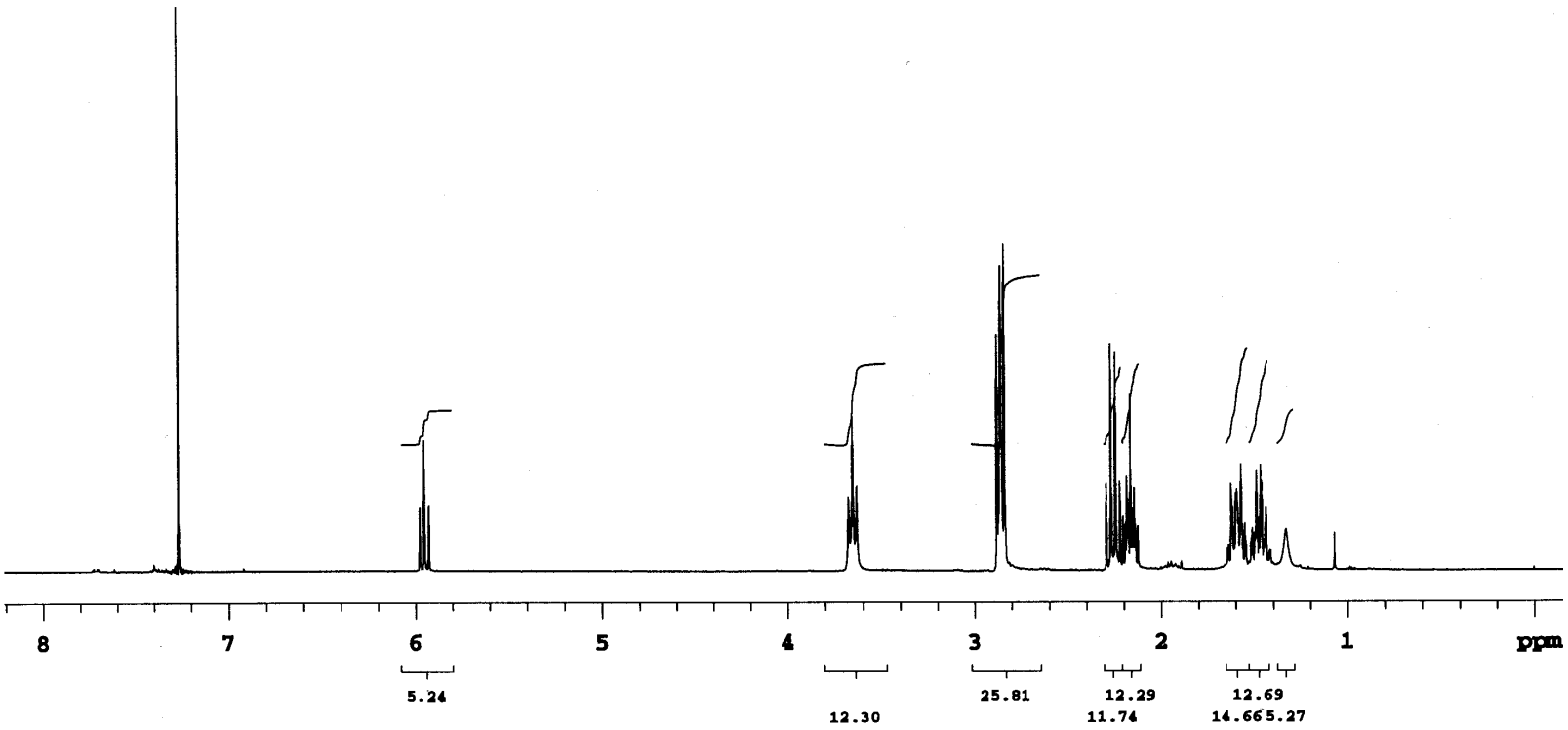

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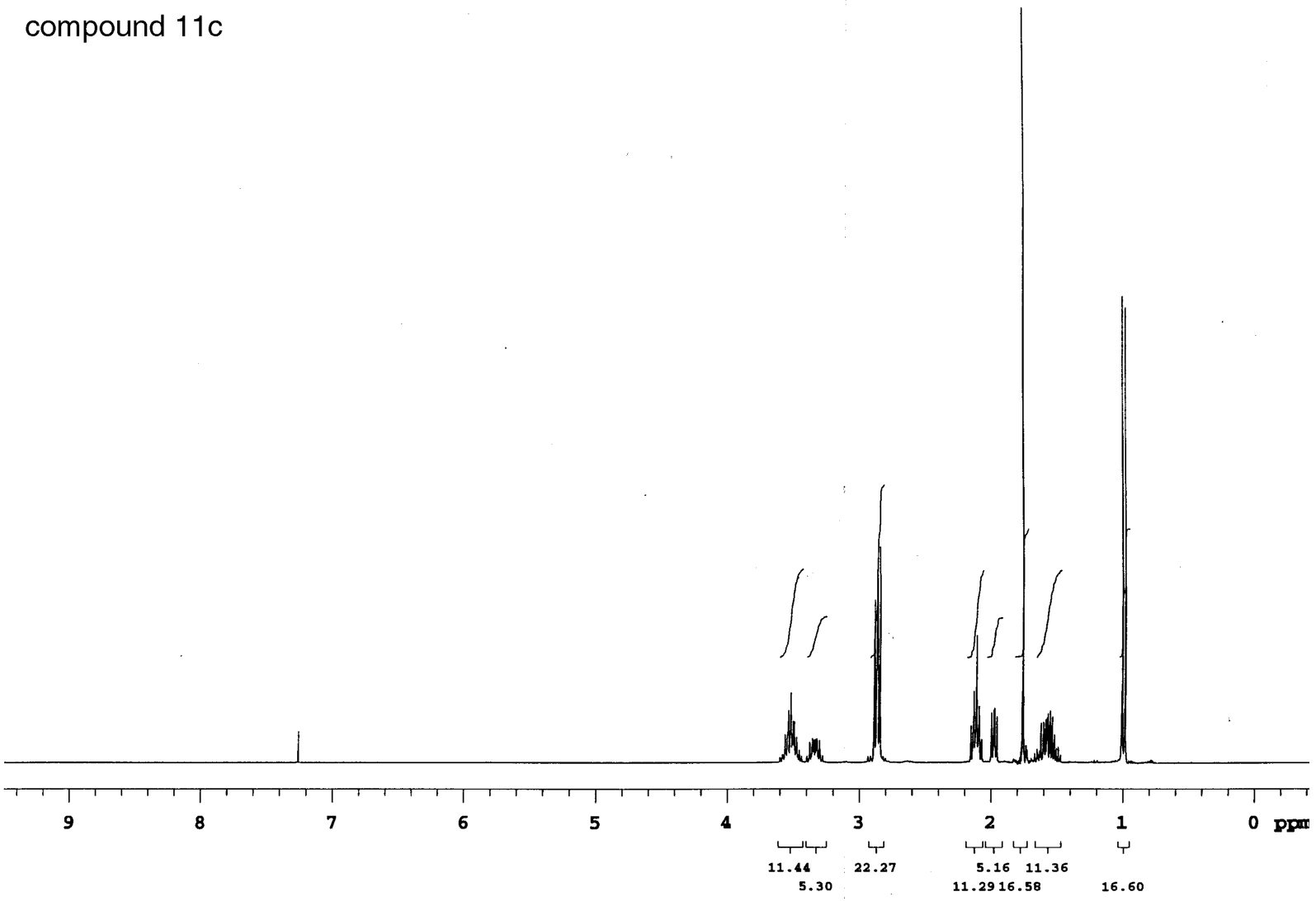
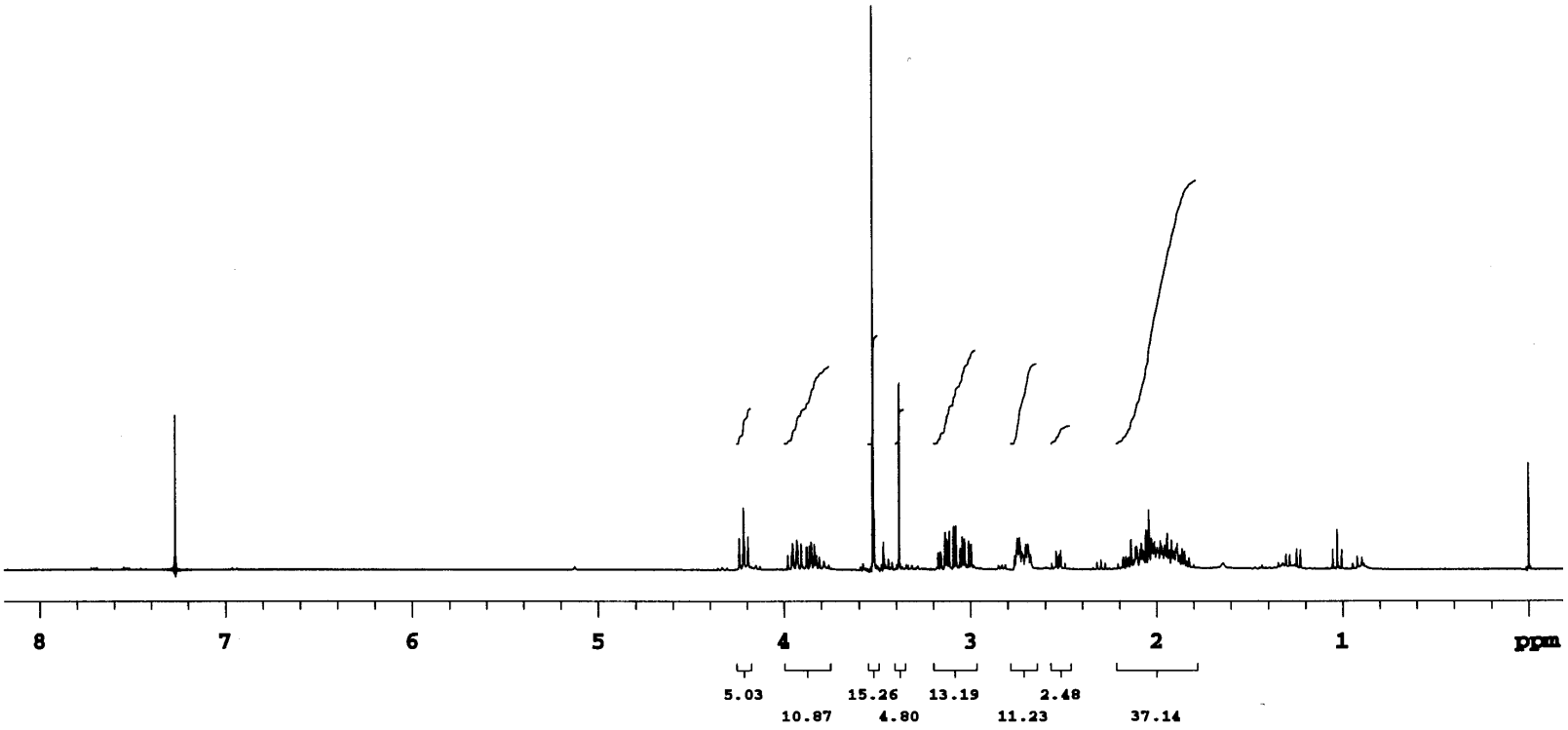


compound 12a



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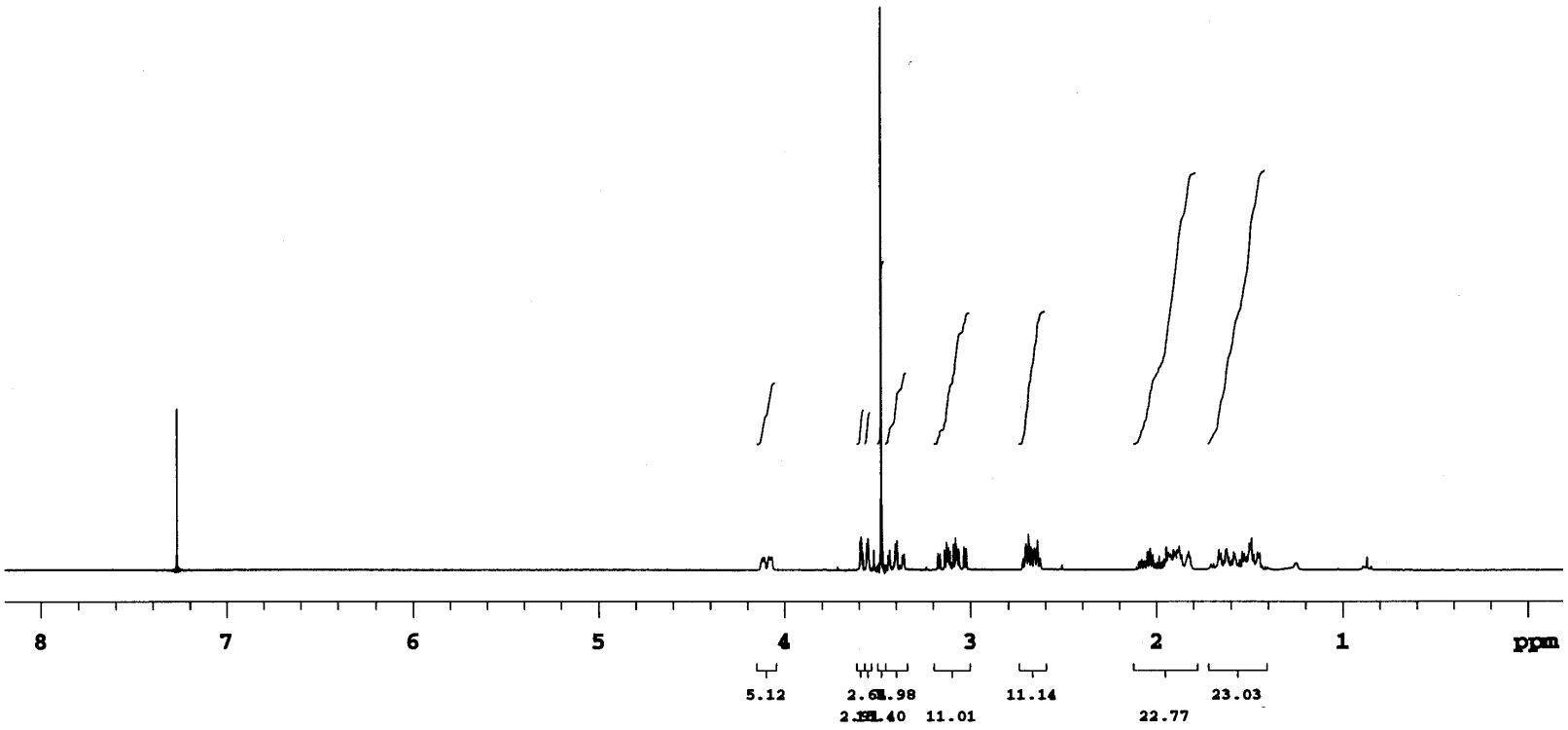
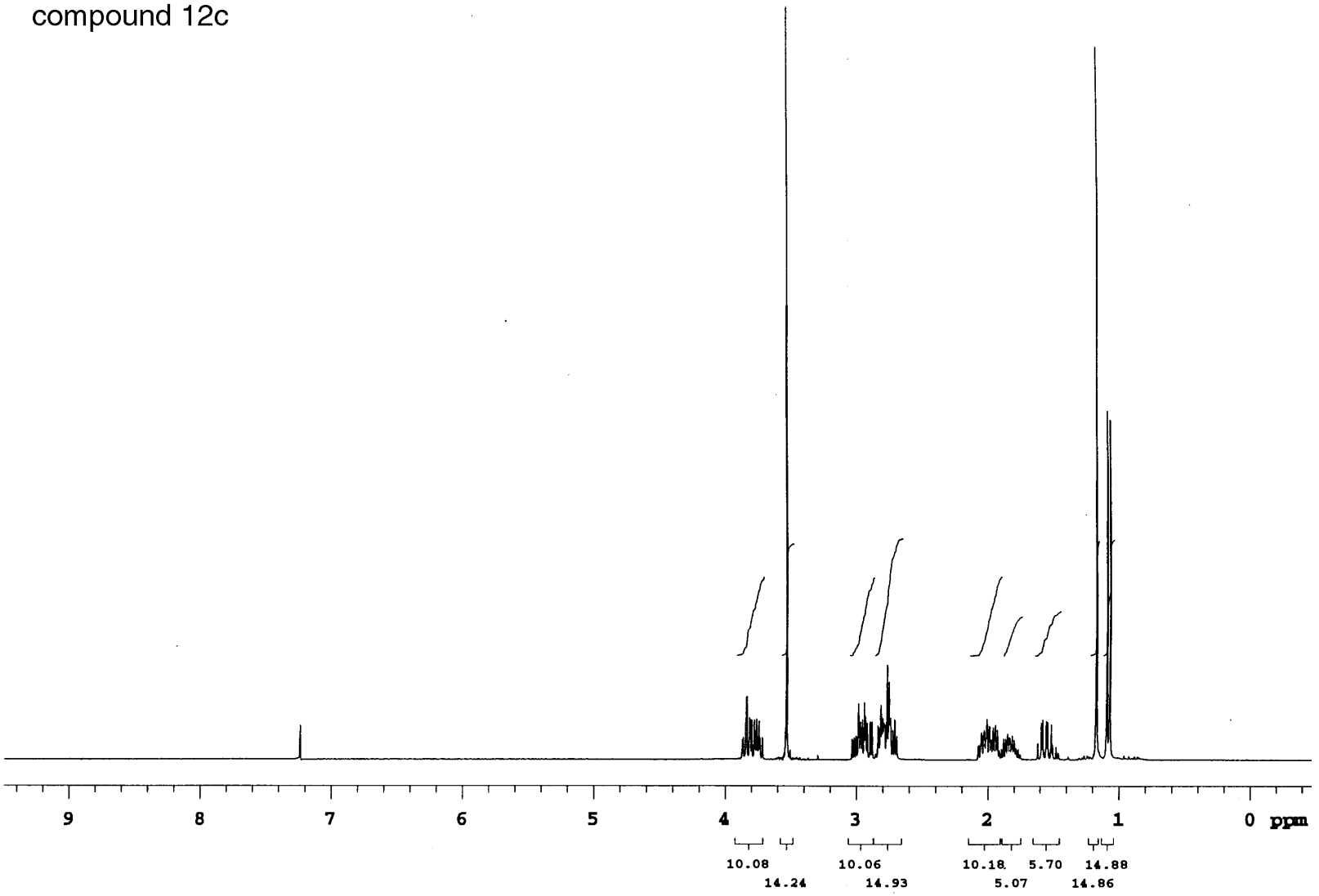
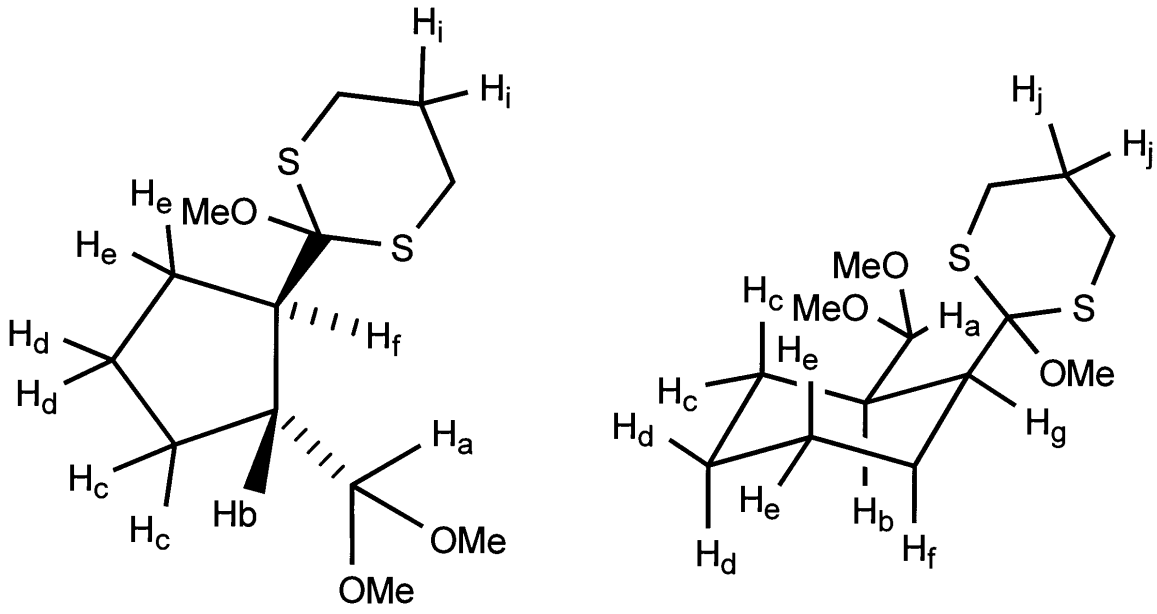
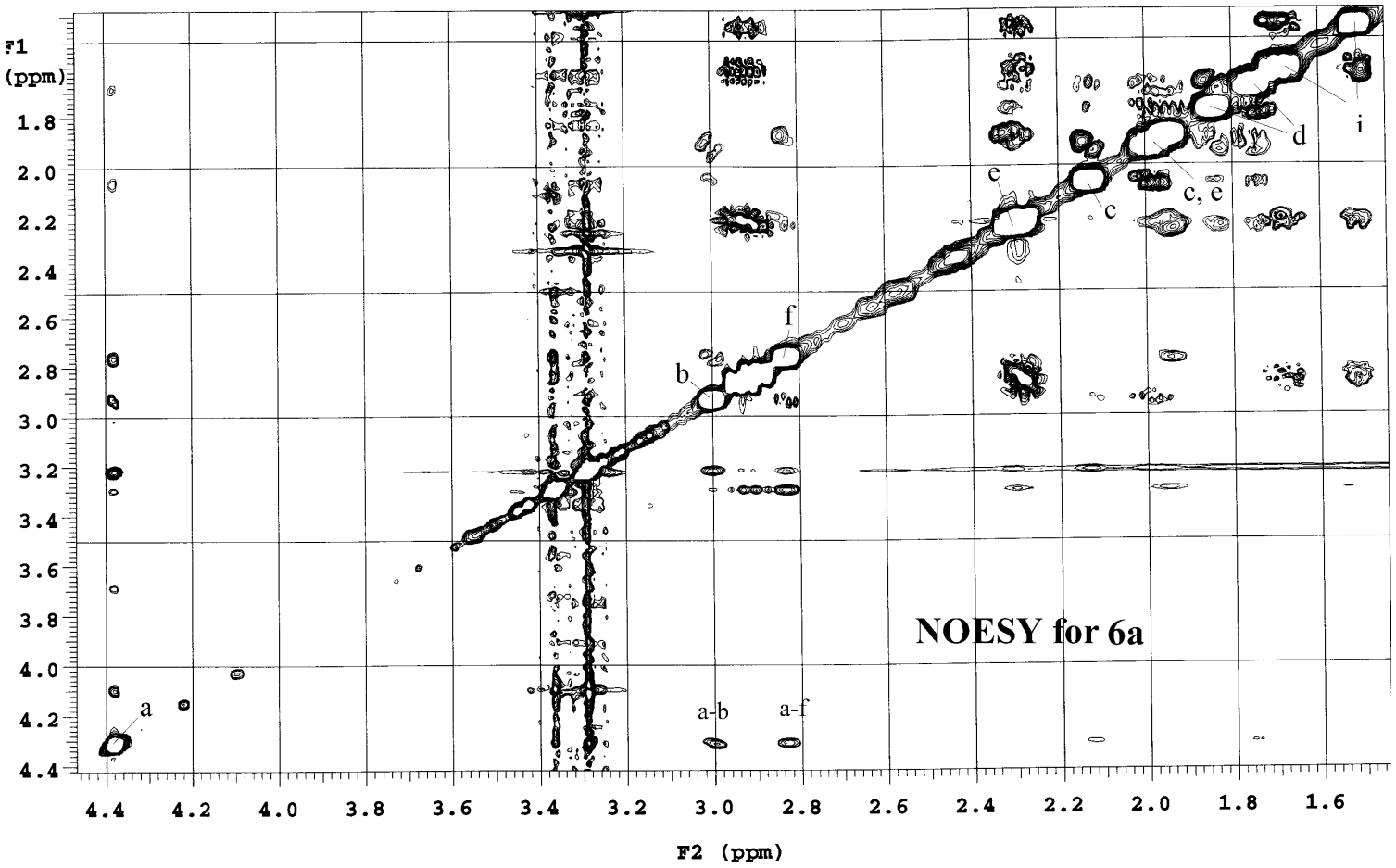


compound 12c





Compounds 6a and 6b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3.6
3.8
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4.2
4.4
a
a-b
a-f
b
c
c, e
d
e
f
i
NOESY for 6a
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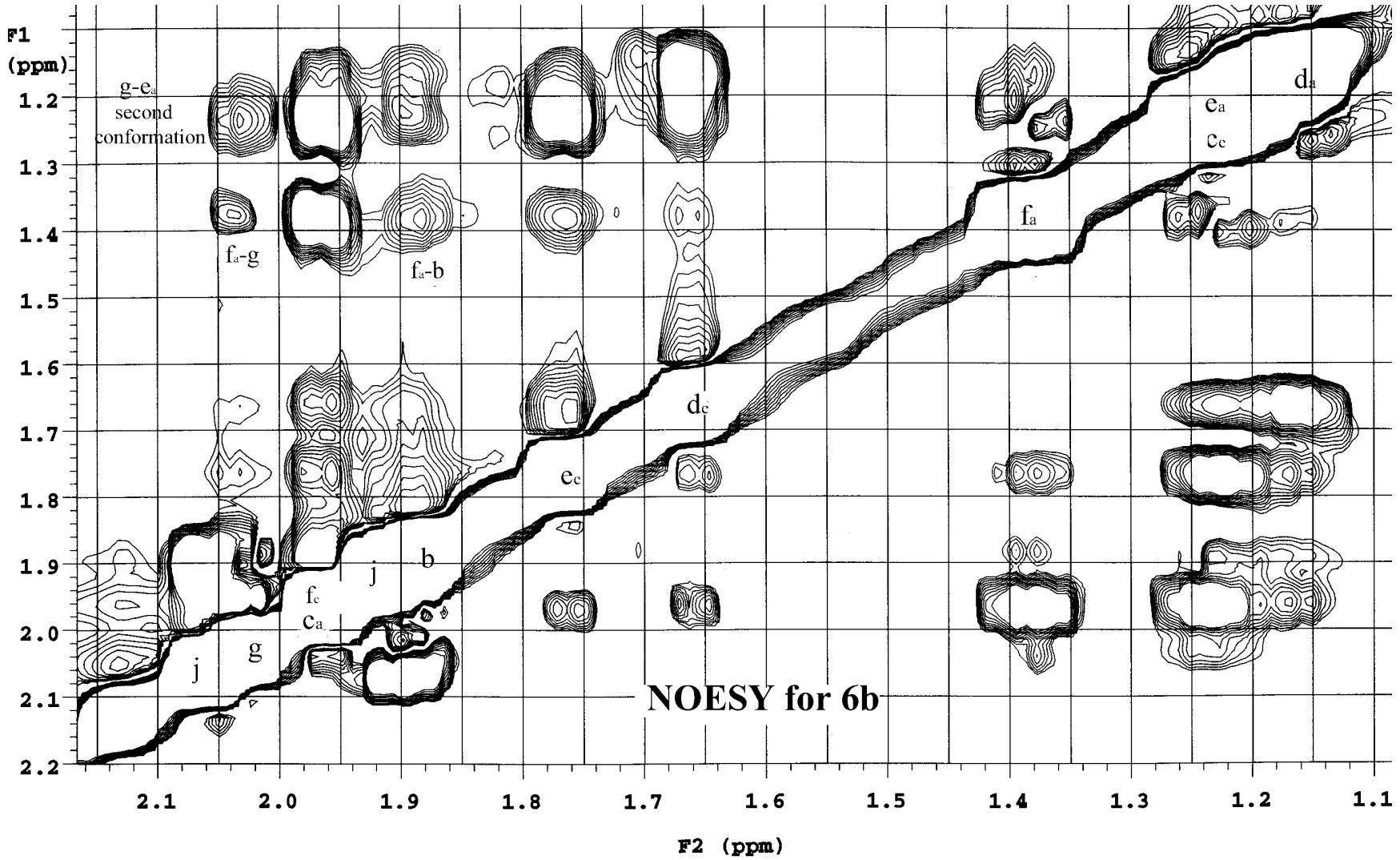
F2 (ppm)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(ppm)
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1.4
1.5
1.6
1.7
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1.9
2.0
2.1
2.2
g-ea
second
conformation
fa-g
fa-b
fa
da
ea
ec
dc
ec
fc
ca
j
g
j
b
NOESY for 6b
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1.6
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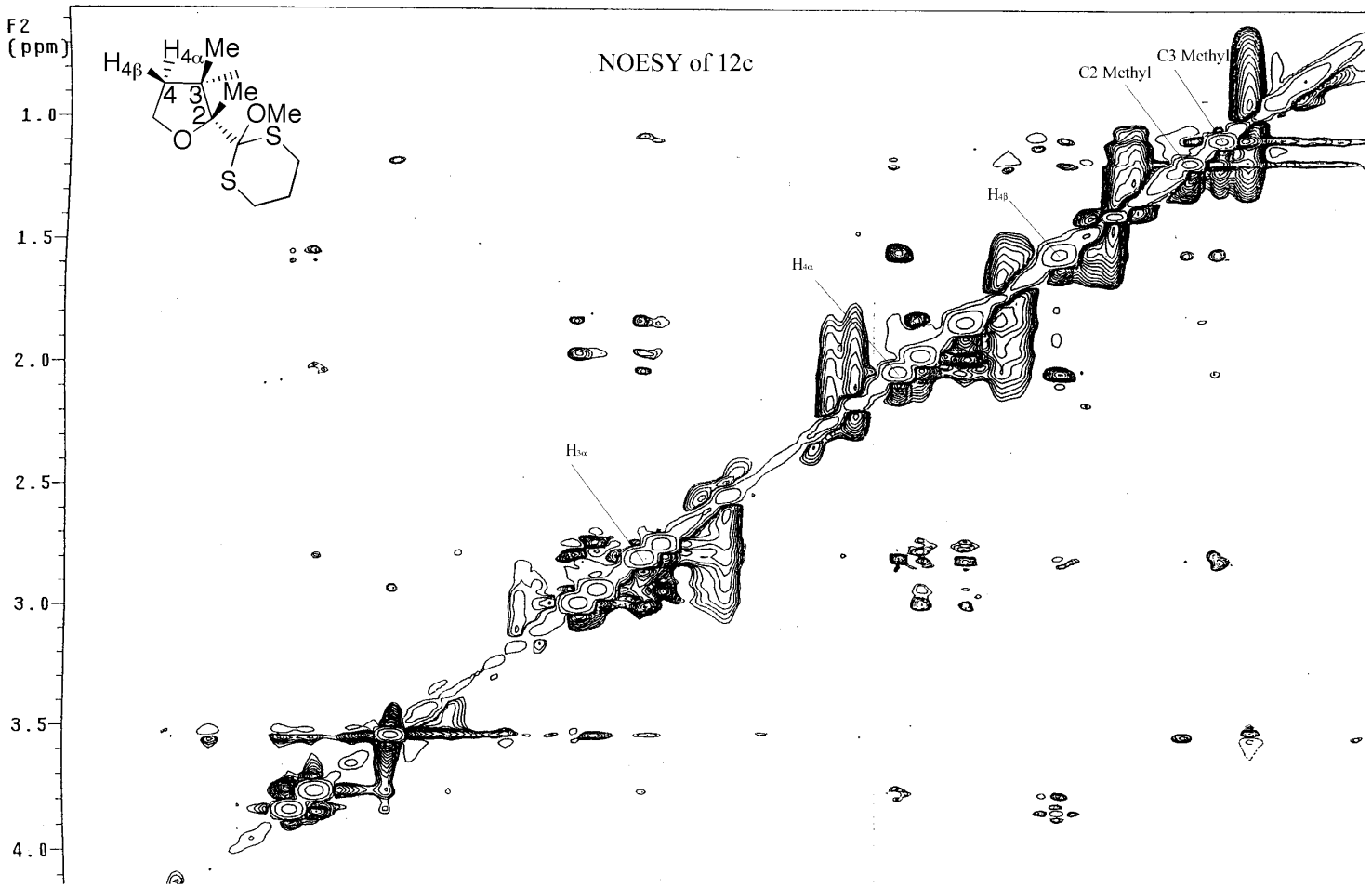
1.4
1.3
1.2
1.1
F2 (ppm)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(ppm)
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3.5
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H4α
Me
4
3
Me
2
OMe
O
S
S
C2 Methyl
C3 Methyl
Hβ
Hαα
Hαα