Supporting Information

Ruthenium-Catalyzed [2+2] Cycloaddition of Allenynes Leading to a Bicyclo[4.2.0]octa-1(8),5-diene Skeleton

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pp. S2 ~ S4: Experimental procedure and spectral data

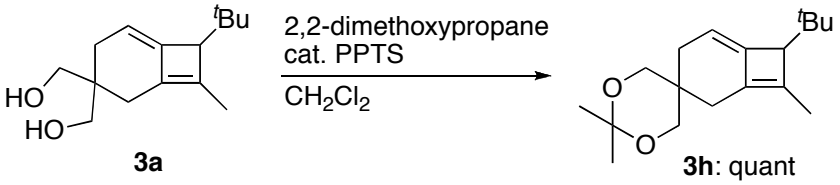
pp. S5 ~ S14: Charts of ^{1}H and ^{13}C NMR spectra of all new compounds

pp. S15 ~ S19: Charts of 2D NMR spectra of compound **3h**

Experimental Section

Compounds 2a and 3a (Scheme 1, eq 1). A mixture of **1a** (72.0 mg, 0.30 mmol) and Cp*RuCl(cod) (11.4 mg, 0.030 mmol) in degassed toluene (3 mL) was stirred at room temperature for 2 h. After removal of volatiles, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 1/1 - 0/1) to give **2a** (20.1 mg, 28%) as a colorless solid and **3a** (45.7 mg, 63%) as a colorless solid, respectively. **2a**: mp. 180-182 °C (recrystallized from toluene); IR (nujor) 3281, 1216 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ 4.82 (d, *J* = 1.5 Hz, 2 H), 3.41 (s, 4 H), 3.70 (s, 4 H), 3.10 (dt, *J* = 1.5, 8.6 Hz , 2 H), 2.00 (dd, *J* = 8.6, 13.2, Hz , 2 H), 1.54 (d, *J* = 14.1 Hz, 2 H), 1.43 (dd, *J* = 8.6, 13.2 Hz, 2 H), 1.33 (d, *J* = 14.1 Hz, 2 H), 0.95 (s, 18 H), 0.92 (s, 6 H); ^{13}C NMR (125 MHz, CD_3OD) δ 147.3 (2C), 133.5 (2C), 67.5 (2C), 65.9 (2C), 55.6 (2C), 54.9 (2C), 53.5 (2C), 49.8 (2C), 42.5 (2C), 34.2 (2C), 32.7 (2C), 31.2 (6C), 16.6 (2C); FAB-LRMS *m/z* 473 [$(M+H)^+$], 277, 263, 185, 93; FAB-HRMS calcd for $C_{30}H_{49}O_4$ 473.3631, found 473.3651. **3**: mp. 118-119 °C (recrystallized from toluene); IR (film, $CHCl_3$) 3268, 1216 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.91 (t, *J* = 3.7 Hz, 1 H), 3.68-3.58 (m, 4 H), 3.00 (s, 1 H), 2.24-1.96 (m, 6 H), 1.80 (s, 3 H), 0.90 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 142.1, 139.4, 101.6, 70.8, 69.4, 62.7, 40.4, 32.5, 29.1, 27.8 (3C), 25.2, 15.0; ESI-LRMS *m/z* 250 [$(M+Na)^+$] , 237, 218, 187; ESI-HRMS calcd for $C_{15}H_{24}O_2Na$ 259.16740, found 259.16778.

The structure of **3a** was elucidated by detailed analyses of various spectral data including 2D-NMR (COSY, NOESY, HMBC, HSQC, and INADEQUATE) of **3h**, which was derived from **3a** as shown in Scheme S1.



Scheme S1.

To a solution of **3a** (17.7 mg, 0.075 mmol) in CH_2Cl_2 (1.0 mL) were added 2,2-dimethoxypropane (50 μL, 0.41 mmol) and PPTS (2.0 mg, 8.0 μmol) at room temperature, and the mixture was stirred at the same temperature for 2 h. To the mixture was added H_2O at 0 °C, and the aqueous layer was washed extracted with Et_2O. The organic layer was washed with saturated NaCl aqueous solution, dried over Na_2SO_4, and concentrate. The residue was purified by flash column chromatography on silica gel (hexane/Et_2O = 20/1) to give **3h** (23.0 mg, quant) as a colorless oil. IR (neat) 1683, 1640, 1075 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.88 (t, *J* = 4.0 Hz, 1 H), 3.67-3.52 (m, 4 H), 2.98 (s, 1 H), 2.35 (d, *J* = 16.0 Hz, 1 H), 2.13 (dd, *J* = 4.0, 16.6 Hz, 1 H), 2.07-2.00 (m, 1 H), 1.96 (d4, *J* = 4.0, 16.6 Hz, 1 H), 1.83 (s, 3 H), 1.43 (s, 6 H), 0.90 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 142.0, 139.4, 101.5, 98.1, 69.5, 68.2, 62.5, 33.9, 32.4, 31.2, 27.8 (3C), 27.1, 24.7, 22.8, 15.0; EI-LRMS m/z 276 (M^+), 261, 218, 187; EI-HRMS calcd for $C_{18}H_{28}O_2$ 276.2089, found 276.2083.

General Procedure for [2+2] Cyclization of Allenyne in MeOH. A mixture of allenyne **1** and Cp*RuCl(cod) (5 mol% to **1**) in degassed MeOH ([**1**] = 0.3 M) was stirred at room temperature under argon atmosphere (1 atm). After removal of volatiles, the residue was purified by column chromatography on silica gel to give **3**.

Compound 3a (Scheme 2, eq 2). According to the general procedure, a crude product, which was

obtained from **1a** (70.8 mg, 0.30 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in MeOH (3.0 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 2/1) to give **3a** (70.3 mg, 99%) as a colorless solid.

Compound 3b. According to the general procedure, a crude product, which was obtained from **1b** (87.6 mg, 0.30 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in MeOH (3.0 mL) for 3 h, was purified by column chromatography on silica gel (hexane/AcOEt = 12/1) to give **3b** (87.5 mg, quant) as a colorless oil. IR (neat) 1737, 1643, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.97 (t, *J* = 4.0 Hz, 1 H), 3.71 (s, 3 H), 3.69 (s, 3 H), 2.98 (s, 1 H), 2.89 (d, *J* = 16.0 Hz, 1 H), 2.79 (dd, *J* = 4.0, 16.0 Hz, 1 H), 2.64 (d, *J* = 16.0 Hz, 1 H), 2.60 (dd, *J* = 4.0, 16.0 Hz, 1 H), 1.80 (s, 3 H), 0.87 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 171.5, 142.9, 141.6, 138.2, 101.8, 62.5, 55.4, 52.7, 52.6, 32.3, 30.9, 27.9, 27.6 (3C), 14.9; EI-LRMS *m/z* 292 (M^+), 261, 233, 217, 173, 131; EI-HRMS calcd for $C_{17}H_{24}O_4$ 292.16746, found 292.16744.

Compound 3c. According to the general procedure, a crude product, which was obtained from **1c** (159.8 mg, 0.30 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in MeOH (3.0 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1) to give **3c** (150.9 mg, 94%) as a colorless amorphous solid. IR (film, $CHCl_3$) 1726, 1530, 1216 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.74-7.60 (m, 8 H), 4.96 (t, *J* = 3.7 Hz, 1 H), 4.34 (dd, *J* = 11.2, 13.8 Hz, 2 H), 4.26 (d, *J* = 2.3 Hz, 2 H), 3.07 (m, 1 H), 2.15 (d, *J* = 16.6 Hz, 1 H), 2.10 (d, *J* = 3.7 Hz, 2 H), 2.06 (d, *J* = 16.6 Hz, 1 H), 1.70 (s, 3 H), 1.00 (s, 9 H); ^{13}C NMR (125 MHz, C_6D_6) δ 164.4, 164.3, 150.70, 150.66, 144.7, 142.4, 138.5, 134.94, 134.92, 130.5 (2C), 130.4 (2C), 123.6 (2C), 123.4 (2C), 101.4, 68.6, 67.7, 63.2, 39.4, 32.7, 29.7, 28.0 (3C), 26.2, 14.9; FAB-LRMS *m/z* 534 (M^+), 518, 305, 199, 166, 152; FAB-HRMS calcd for $C_{29}H_{30}N_2O_8$ 534.2002, found 534.2013.

Compound 3d. According to the general procedure, a crude product, which was obtained from **1d** (106.3 mg, 0.30 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in MeOH (3.0 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 12/1) to give **3d** (100.8 mg, 95%) as a colorless amorphous solid. IR (film, $CHCl_3$) 1739, 1597, 1246 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39-7.29 (m, 4 H), 7.23-7.18 (m, 1 H), 5.23 (t, *J* = 3.7 Hz, 1 H), 3.74 (s, 3 H), 3.71 (s, 3 H), 3.59 (m, 1 H), 3.32 (d, *J* = 16.6 Hz, 1 H), 2.91 (dd, *J* = 3.7, 16.6, Hz, 1 H), 2.88 (dd, *J* = 3.7, 16.6, Hz, 1 H), 2.71 (dd, *J* = 3.7, 16.6 Hz, 1 H), 0.92 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 171.5, 143.3, 141.4, 139.0, 135.6, 128.1 (2C), 127.1 (2C), 126.9, 105.8, 60.3, 55.5, 52.8 (2C), 33.2, 31.0, 29.2, 28.3 (3C); EI-LRMS *m/z* 354 (M^+), 339, 295, 279, 237, 178; EI-HRMS calcd for $C_{22}H_{26}O_4$ 354.18311, found 354.18246.

Compound 3e. According to the general procedure, a crude product, which was obtained from **1e** (118.9 mg, 0.31 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in MeOH (3.0 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 10/1) to give **3e** (111.5 mg, 94%) as a colorless solid. mp. 109-111°C (recrystallized from toluene); IR (film, $CHCl_3$) 1734, 1604, 1249 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6, Hz, 2 H), 7.41 (d, *J* = 8.6, Hz, 2 H), 5.17 (t, *J* = 4.0 Hz, 1 H), 3.81 (s, 3 H), 3.73 (s, 3 H), 3.71 (s, 3 H), 3.56-3.52 (m, 1 H), 3.28 (d, *J* = 16.0 Hz, 1 H), 2.90 (dd, *J* = 3.7, 16.0, Hz, 1 H), 2.85 (dd, *J* = 3.7, 16.0, Hz, 1 H), 2.70 (dd, *J* = 3.7, 16.0 Hz, 1 H), 0.92 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 171.5, 158.6, 142.9, 141.5, 137.0, 128.44 (2C), 128.37, 113.6 (2C), 104.6, 60.3, 55.4, 55.1, 52.7 (2C), 33.1, 31.0, 29.1, 28.3 (3C); EI-LRMS *m/z* 384 (M^+), 327, 309, 267, 208, 165; EI-HRMS calcd for $C_{23}H_{28}O_5$ 384.19367, found 384.19309.

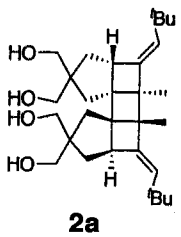
Compound 3f. According to the general procedure, a crude product, which was obtained from **1f** (124.6 mg, 0.30 mmol) and Cp*RuCl(cod) (5.8 mg, 0.015 mmol) in MeOH (3.0 mL) for 2 h, was

purified by column chromatography on silica gel (hexane/AcOEt = 8/1) to give **3f** (122.2 mg, 98%) as a colorless amorphous solid. IR (film, $CHCl_3$) 1726, 1603, 1280 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4, Hz, 2 H), 7.41 (d, *J* = 8.4, Hz, 2 H), 5.31 (t, *J* = 3.6 Hz, 1 H), 3.91 (s, 3 H), 3.74 (s, 3 H), 3.72 (s, 3 H), 3.63-3.60 (m, 1 H), 3.34 (d, *J* = 16.8 Hz, 1 H), 2.94 (dd, *J* = 3.6, 16.8, Hz, 1 H), 2.90 (dd, *J* = 3.6, 16.8, Hz, 1 H), 2.73 (dd, *J* = 3.6, 16.8 Hz, 1 H), 0.92 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 171.2, 166.7, 142.2, 141.7, 141.2, 139.9, 129.5 (2C), 128.0, 126.8 (2C), 107.5, 60.4, 55.4, 52.8 (2C), 52.0, 33.2, 31.0, 29.2, 28.2 (3C); FAB-LRMS *m/z* 435 [$(M+Na)^+$], 412, 381, 176, 154, 136; FAB-HRMS calcd for $C_{24}H_{28}O_6Na$ 435.1783, found 435.1801.

Compound 3g. According to the general procedure, a crude product, which was obtained from **1g** (126.0 mg, 0.30 mmol) and Cp*RuCl(cod) (5.8 mg, 0.015 mmol) in MeOH (3.0 mL) for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt = 14/1) to give **3g** (122.3 mg, 97%) as a colorless oil. IR (neat) 1739, 1254, 1088 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.07 (t, *J* = 4.0 Hz, 1 H), 4.36 (d, *J* = 15.7 Hz, 1 H), 4.25 (d, *J* = 15.7 Hz, 1 H), 3.72 (s, 3 H), 3.68 (s, 3 H), 3.09 (d, *J* = 2.8 Hz, 1 H), 3.06 (d, *J* = 16.6 Hz, 1 H), 2.80 (dd, *J* = 4.0, 16.6, Hz, 1 H), 2.76 (m, 1 H), 2.60 (dd, *J* = 4.0, 16.6 Hz, 1 H), 0.92 (s, 9 H), 0.86 (s, 9 H), 0.08 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 171.4, 144.5, 141.1, 138.3, 103.7, 61.1, 61.0, 55.4, 52.7, 52.6, 32.1, 30.8, 28.6 (3C), 27.7, 25.9 (3C), 18.3, -5.5, -5.5; EI-LRMS *m/z* 422 (M^+), 407, 381, 365, 305, 231, 175, 75; EI-HRMS calcd for $C_{23}H_{38}O_5Si$ 422.2489, found 422.2480.

Compound 3h (Table 1, run 6). According to the general procedure, a crude product, which was obtained from **1h** 83.0 mg, 0.30 mmol) and Cp*RuCl(cod) (5.8 mg, 0.015 mmol) in MeOH (3.0 mL) for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt = 14/1) to give **3h** (81.3 mg, 98%) as a colorless oil.

Compound 3i. According to the general procedure, a crude product, which was obtained from **1i** (95.8 mg, 0.29 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in MeOH (3.0 mL) for 3 h, was purified by column chromatography on silica gel (hexane/AcOEt = 12/1) to give **3i** (76.5 mg, 80%) as a colorless solid. mp. 103 °C (recrystallized from $CHCl_3$); IR (film, $CHCl_3$) 1599, 1343, 1163 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 4.96 (t, *J* = 3.8 Hz, 1 H), 3.97-3.86 (m, 2 H), 3.78 (dd, *J* = 3.8, 16.0 Hz, 1 H), 3.74 (dd, *J* = 3.8, 16.0 Hz, 1 H), 2.93 (s, 1 H), 2.42 (s, 3 H), 1.80 (s, 3 H), 0.86 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 142.9, 140.1, 135.3, 134.3, 129.5 (2C), 127.5 (2C), 101.0, 63.3, 44.1, 41.8, 32.2, 27.5 (3C), 21.4, 15.1; EI-LRMS *m/z* 331 (M^+), 316, 274, 175, 160, 120; EI-HRMS calcd for $C_{19}H_{25}O_2S$ 331.1606, found 331.1607.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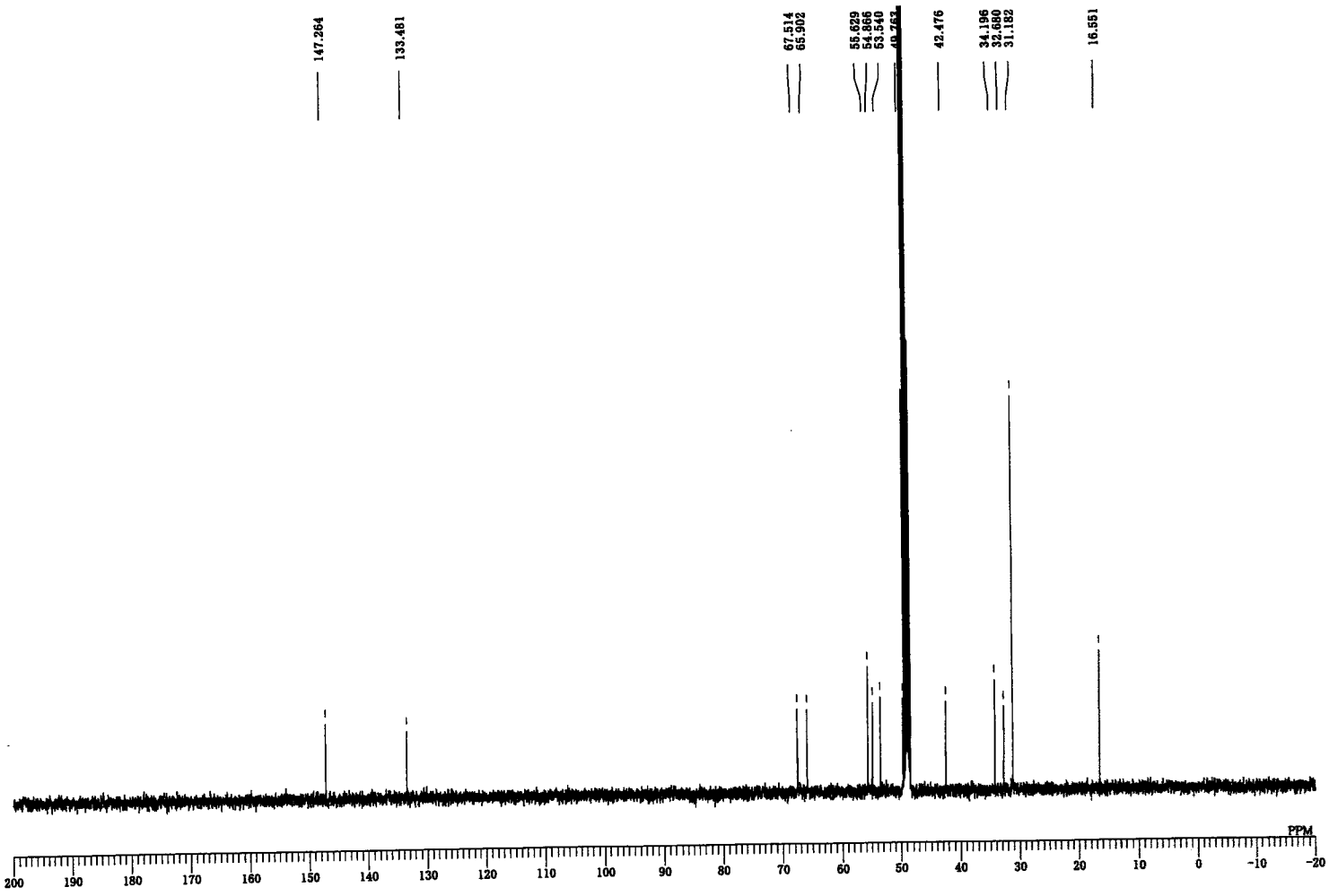
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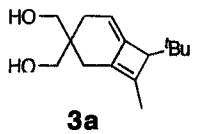
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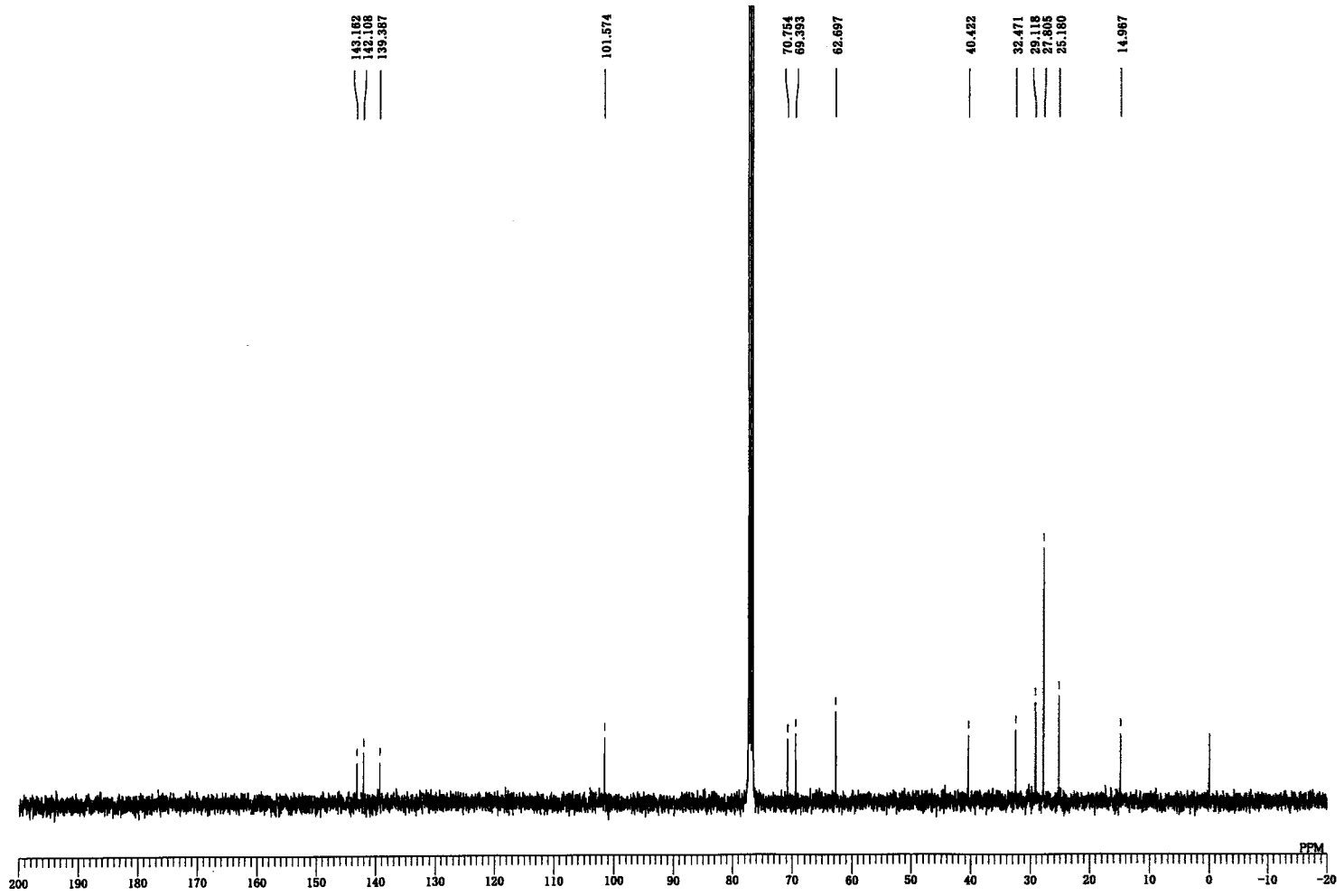
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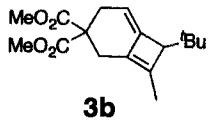
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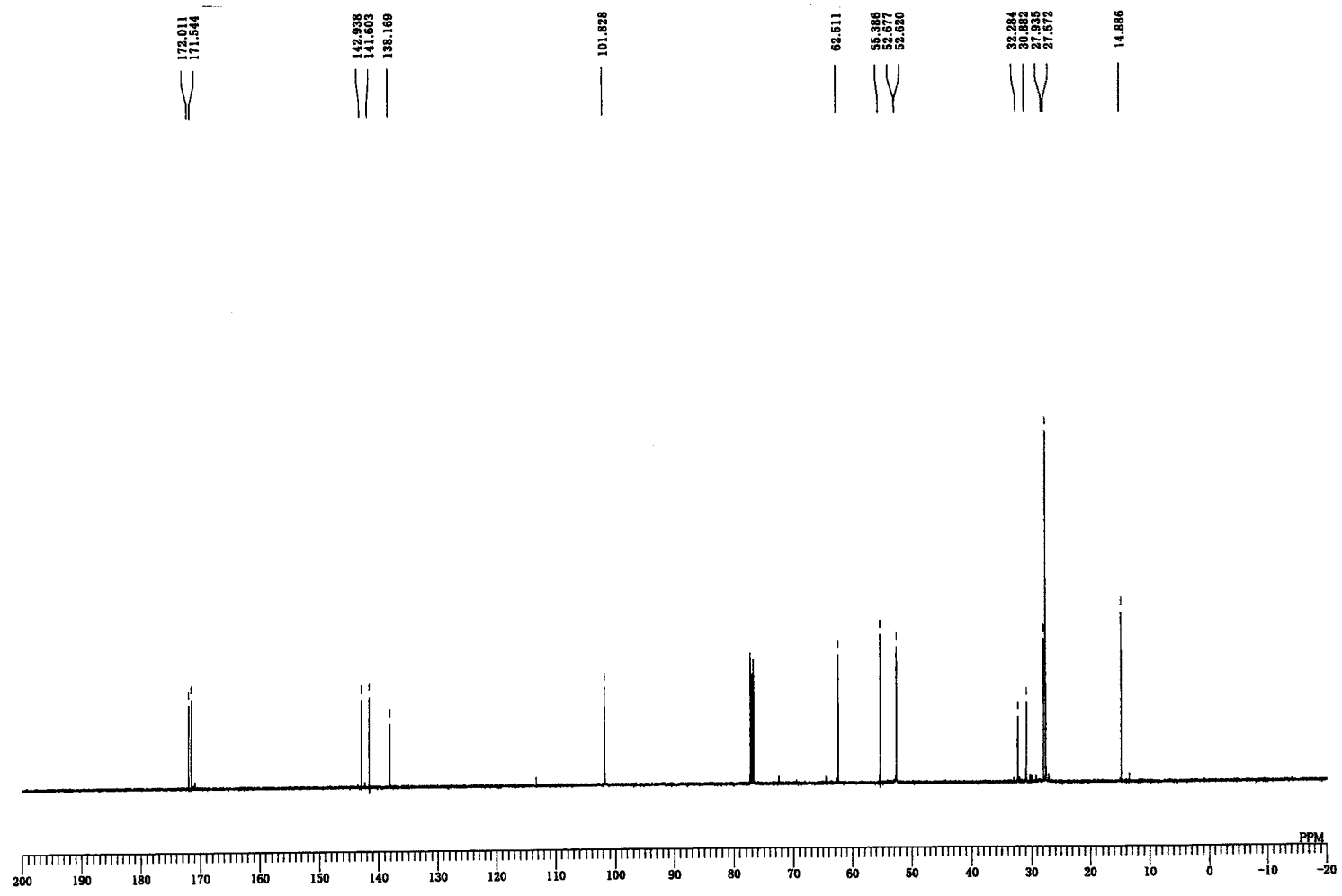
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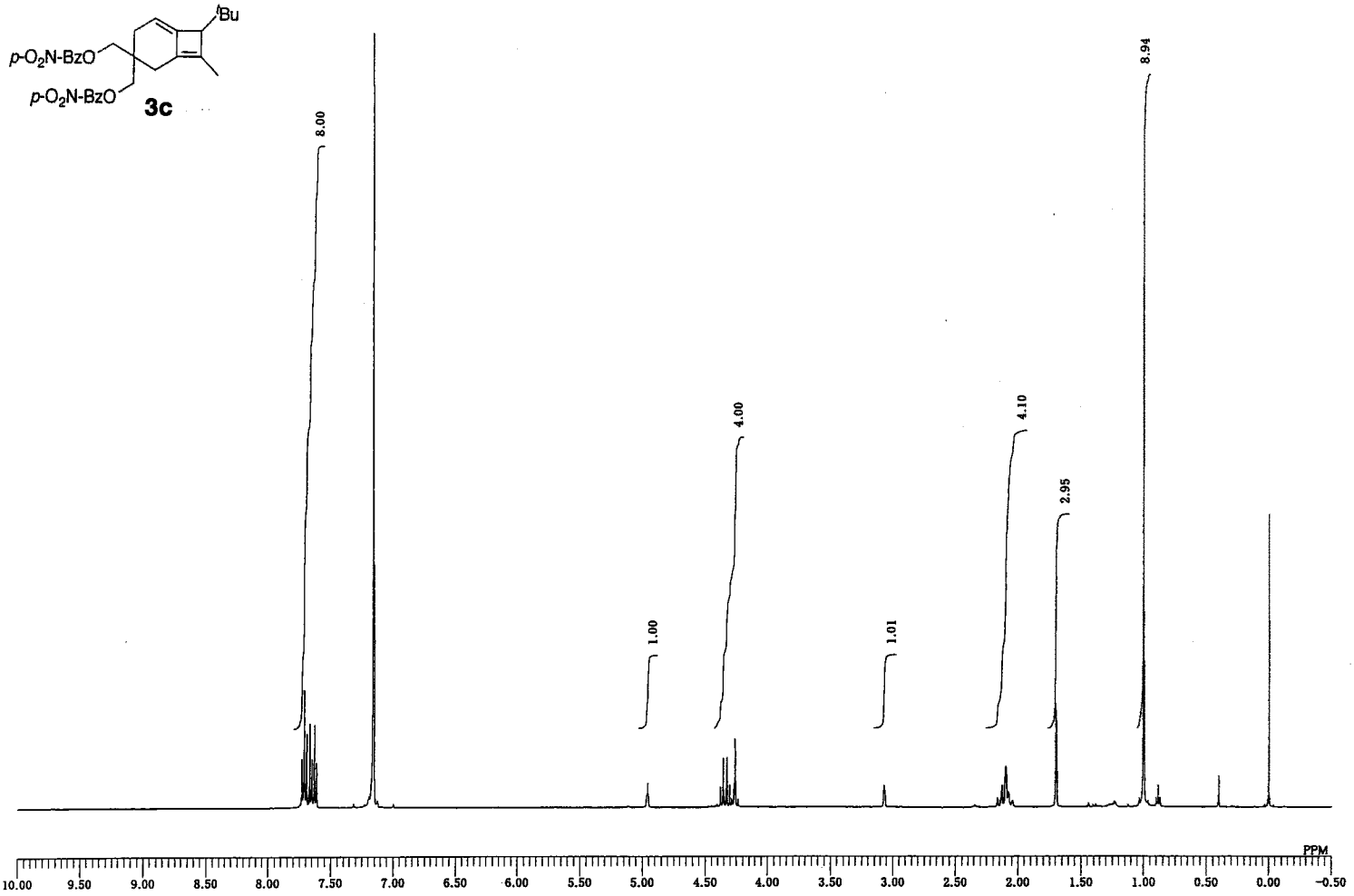
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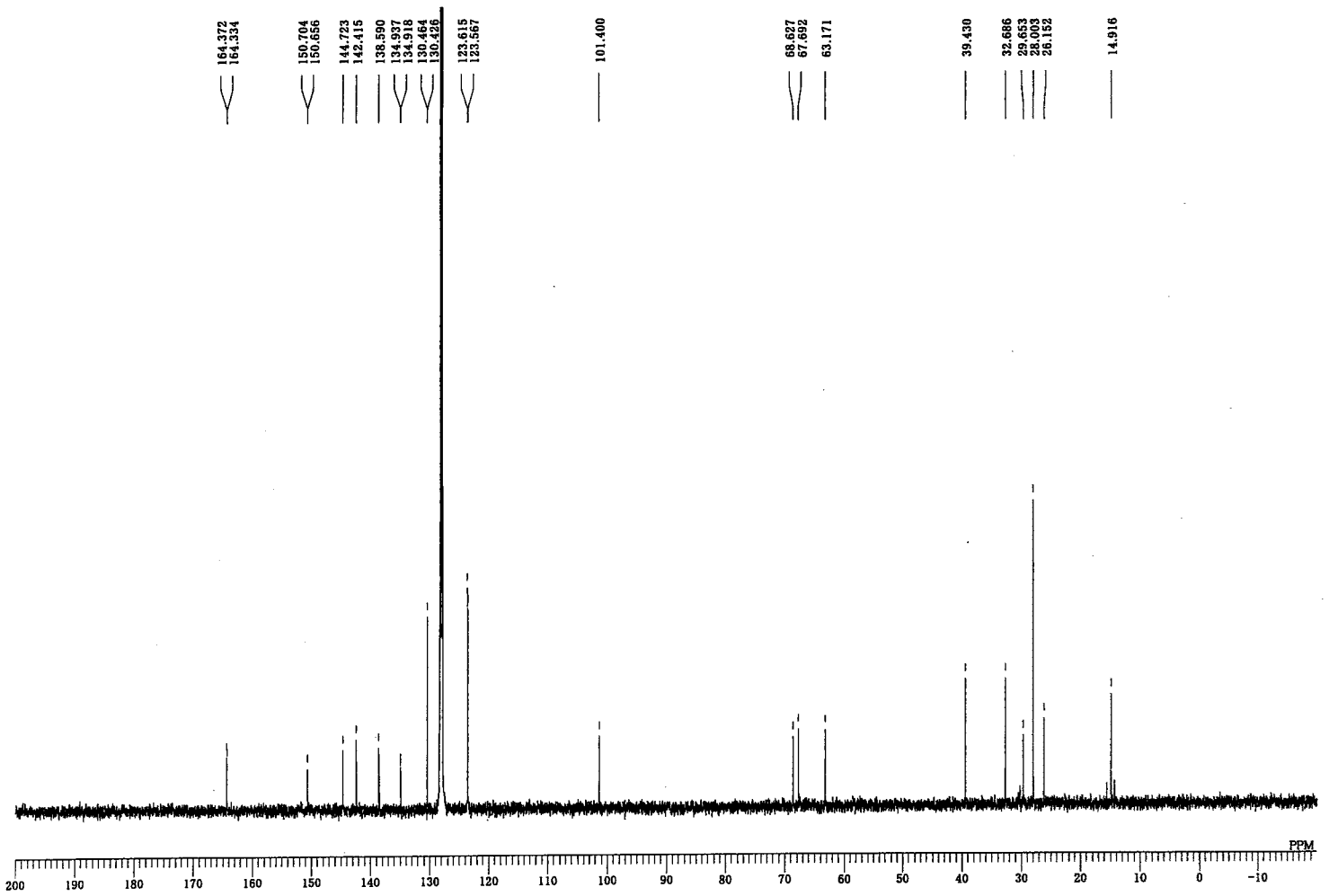
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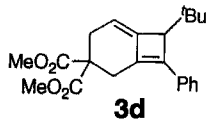
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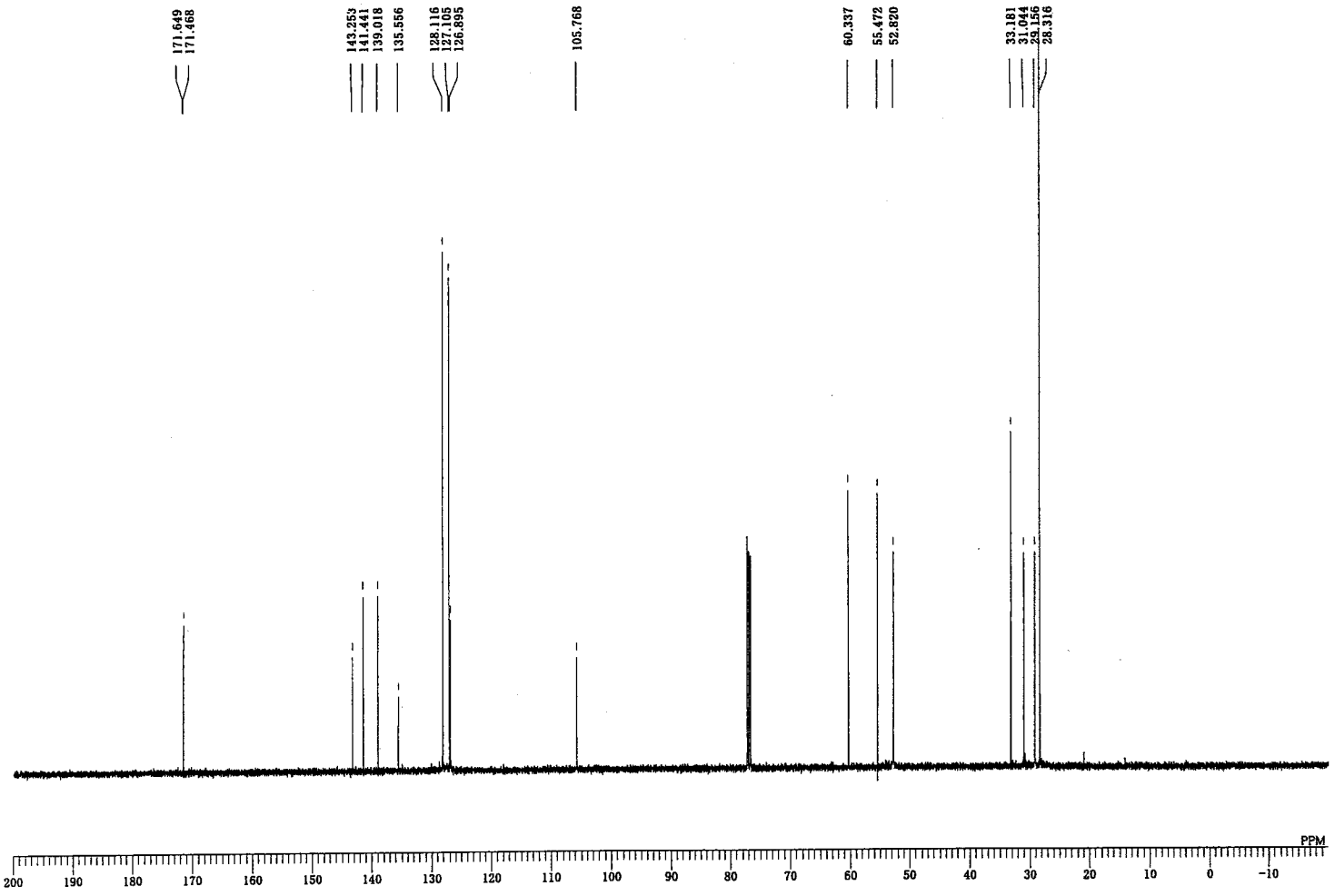
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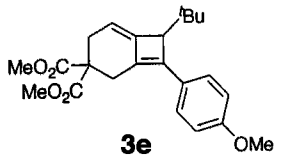
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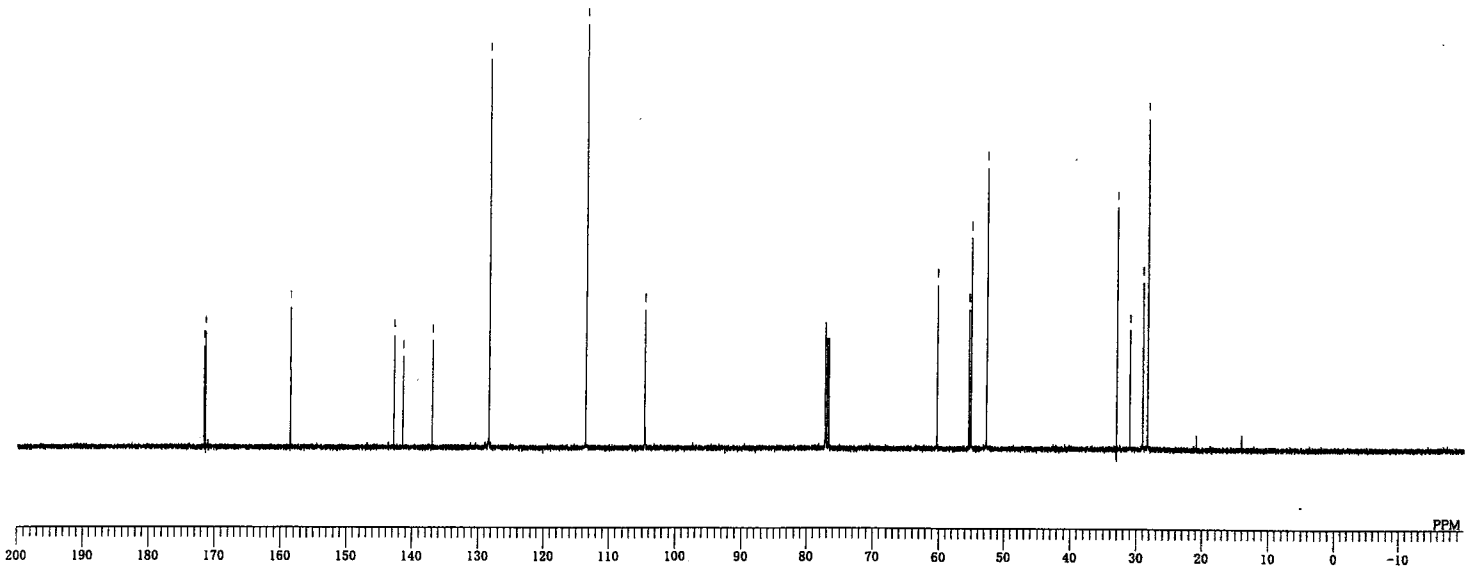
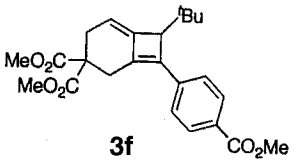
MeO2C
MeO2C
OMe

3e

9.17
6.06
3.32
2.09
2.08
1.00
1.05
1.07
2.07
1.06
PPM
10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00

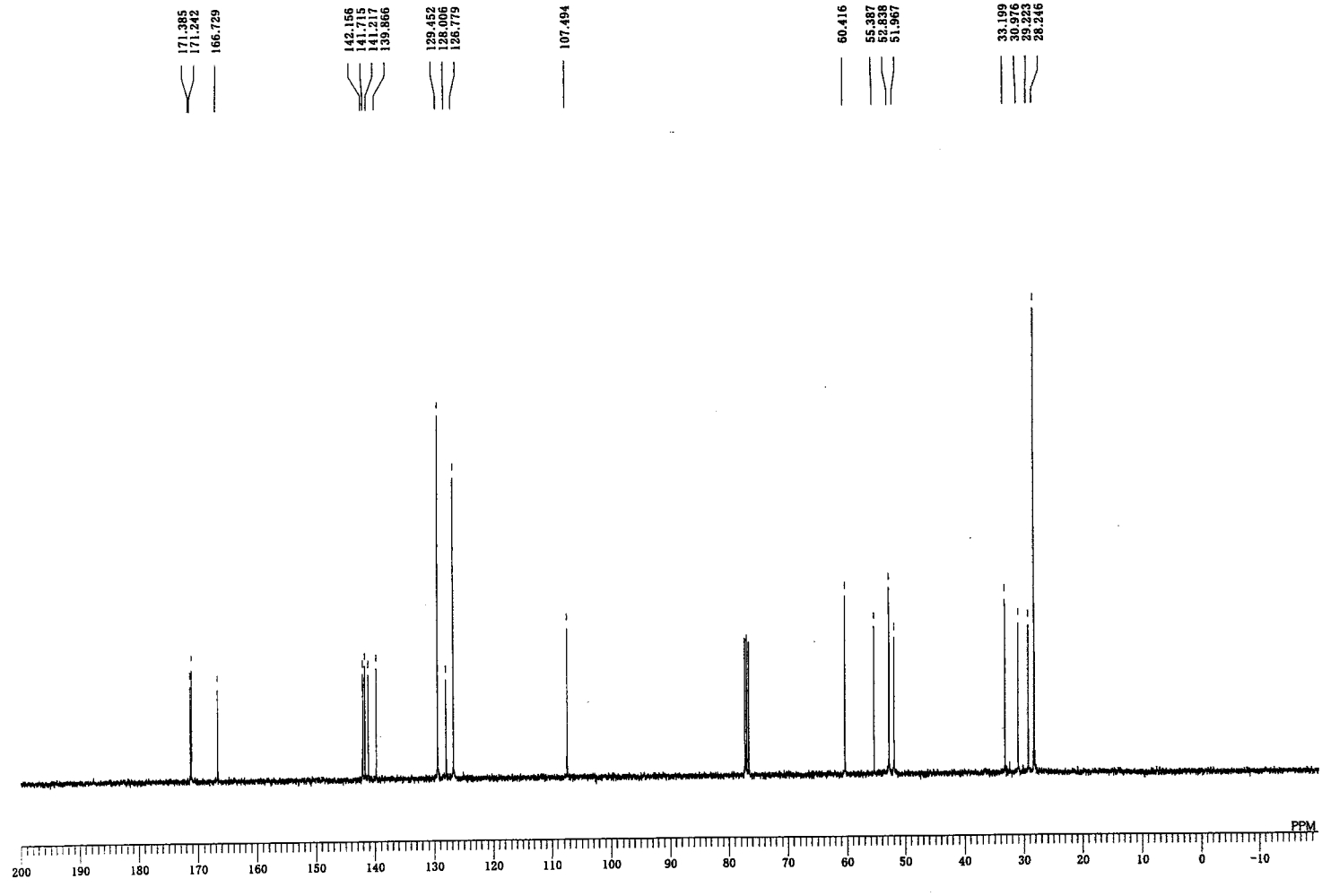

171.696
171.487
158.553
142.872
141.498
136.987
128.440
128.373
113.579
104.604
60.308
55.443
55.138
52.735
33.095
31.016
29.079
28.307

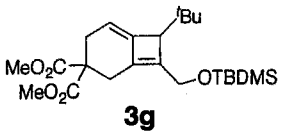

PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


tBu
MeO2C
MeO2C
CO2Me

3f

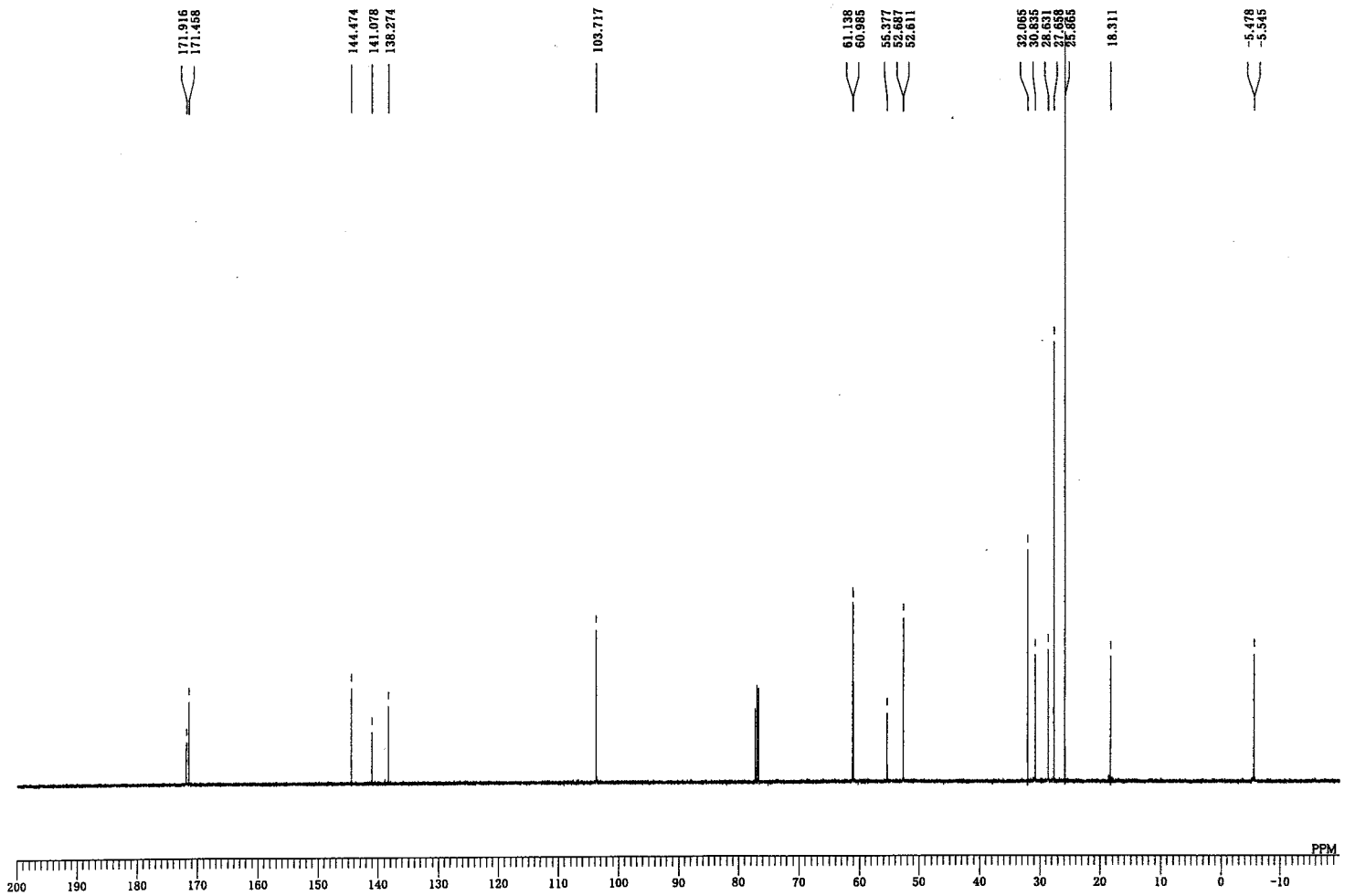
9.52
6.47
3.51
2.18
2.13
1.00
1.05
1.19
2.07
1.15
PPM
10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00

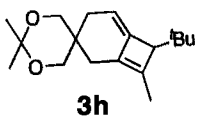

171.385
171.242
166.729
142.156
141.715
141.217
139.866
129.452
128.006
126.779
107.494
60.416
55.387
52.838
51.967
33.199
30.976
29.223
28.246
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


tBu
MeO2C
MeO2C
OTBDMS

3g

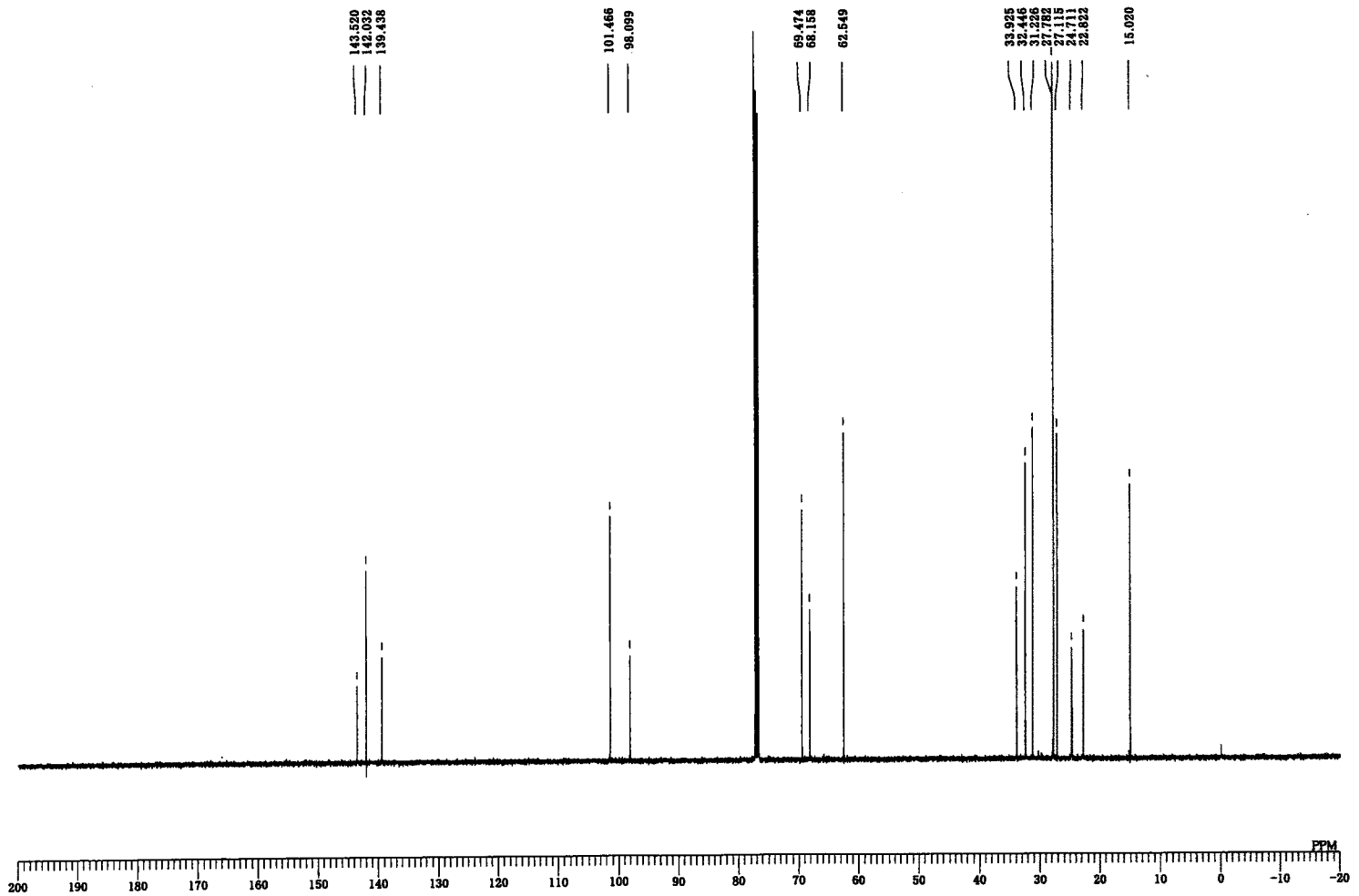
8.84
8.89
5.85
2.85
2.88
2.07
1.99
2.02
1.00
1.03
PPM
10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00

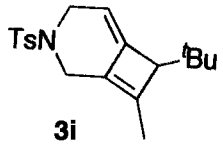

171.916
171.468
144.474
141.078
138.274
103.717
61.138
60.985
55.377
52.687
52.611
32.065
30.835
28.631
27.658
25.665
18.311
-5.478
-5.545
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


tBu

3h

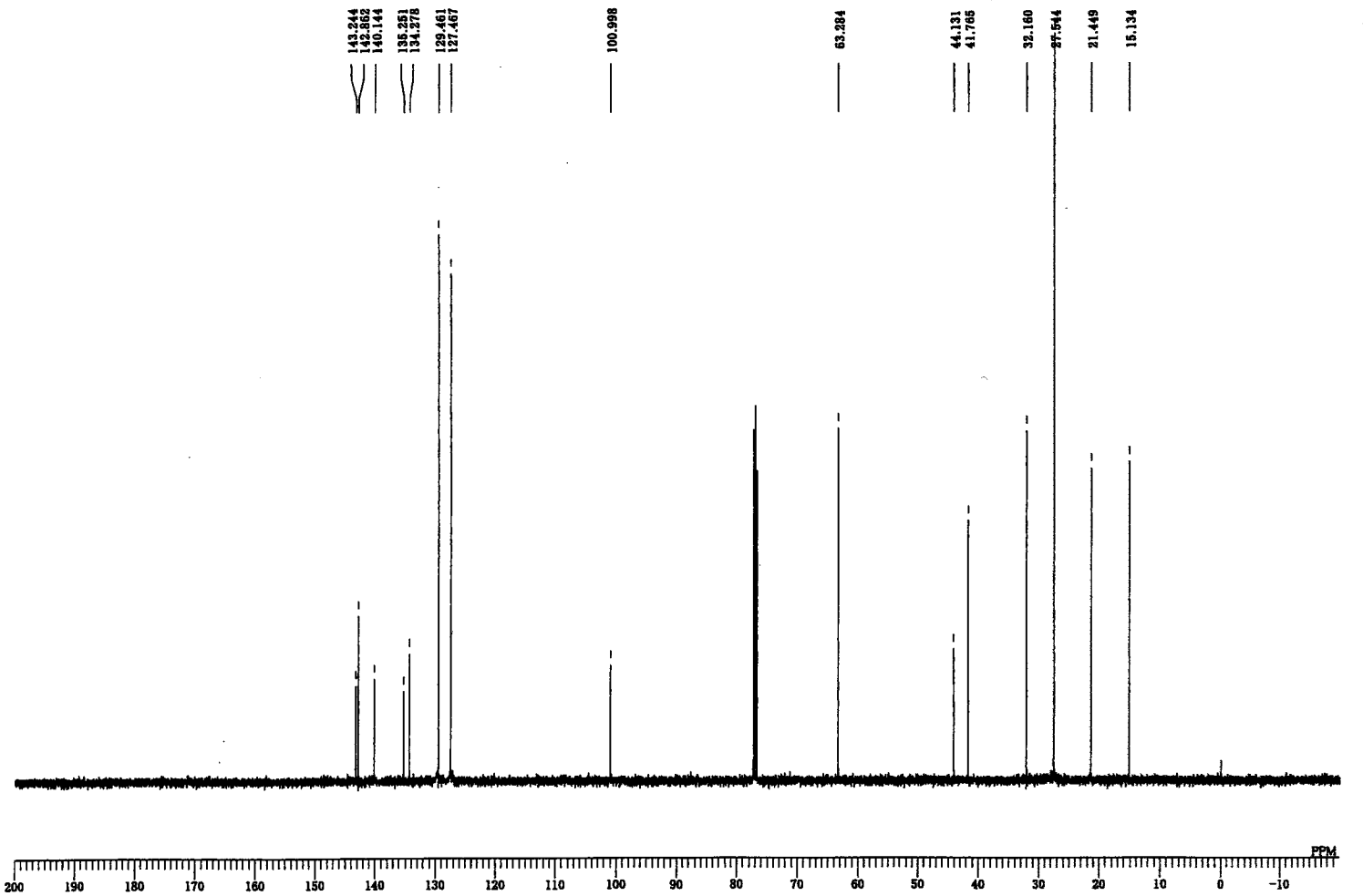
9.78
6.58
4.36
3.15
1.02
1.00
1.06
1.09
1.07
1.08
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

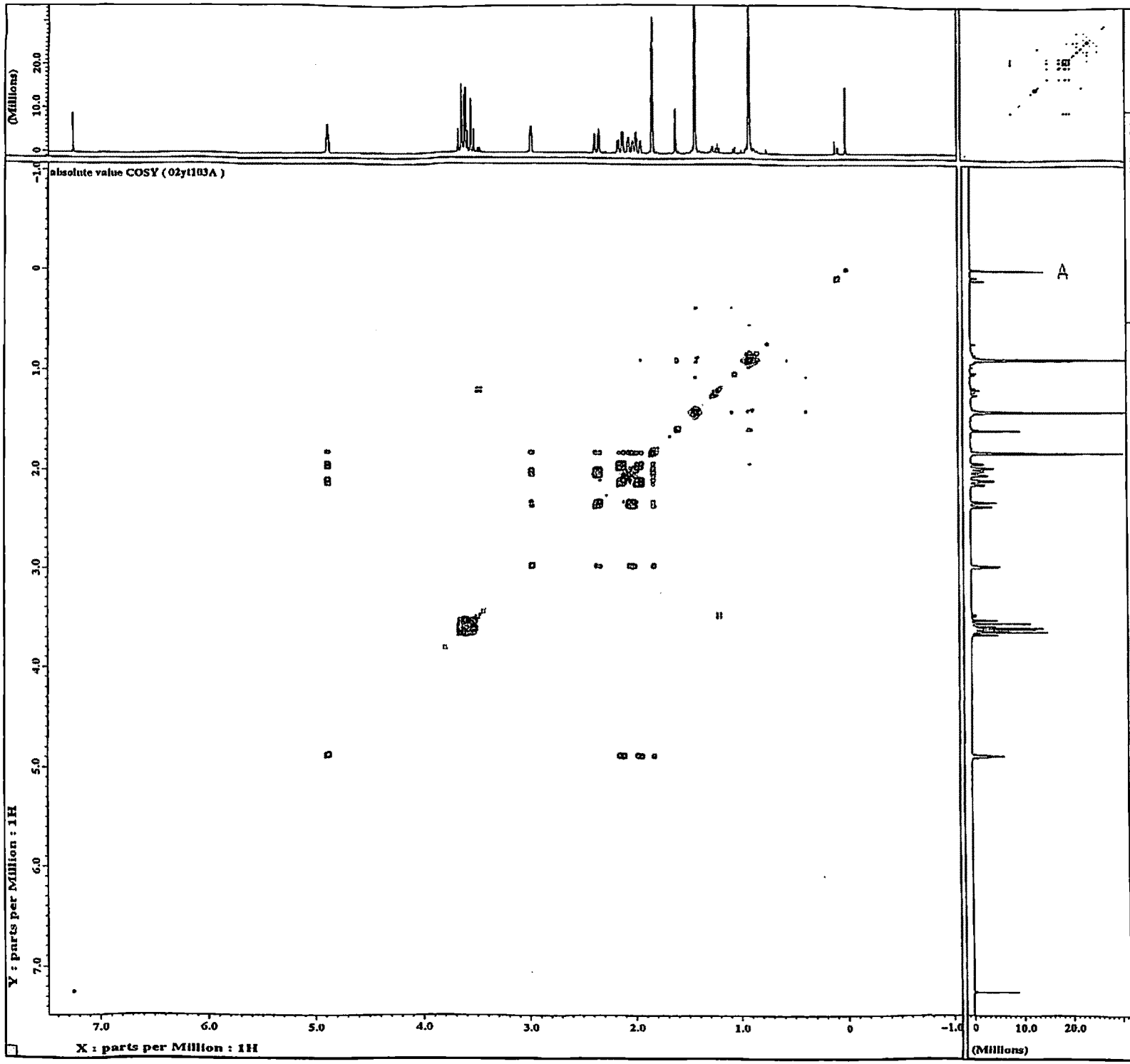

143.520
142.032
139.438
101.466
98.099
69.474
68.158
62.549
33.925
32.446
31.226
27.782
27.115
24.711
22.822
15.020
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20


TsN
tBu

3i

8.73
3.22
2.92
2.02
2.01
1.91
2.06
1.00
1.01
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50


143.244
142.862
140.144
135.251
134.278
129.461
127.467
100.998
63.284
44.131
41.765
32.160
27.544
21.449
15.134
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



JEOL

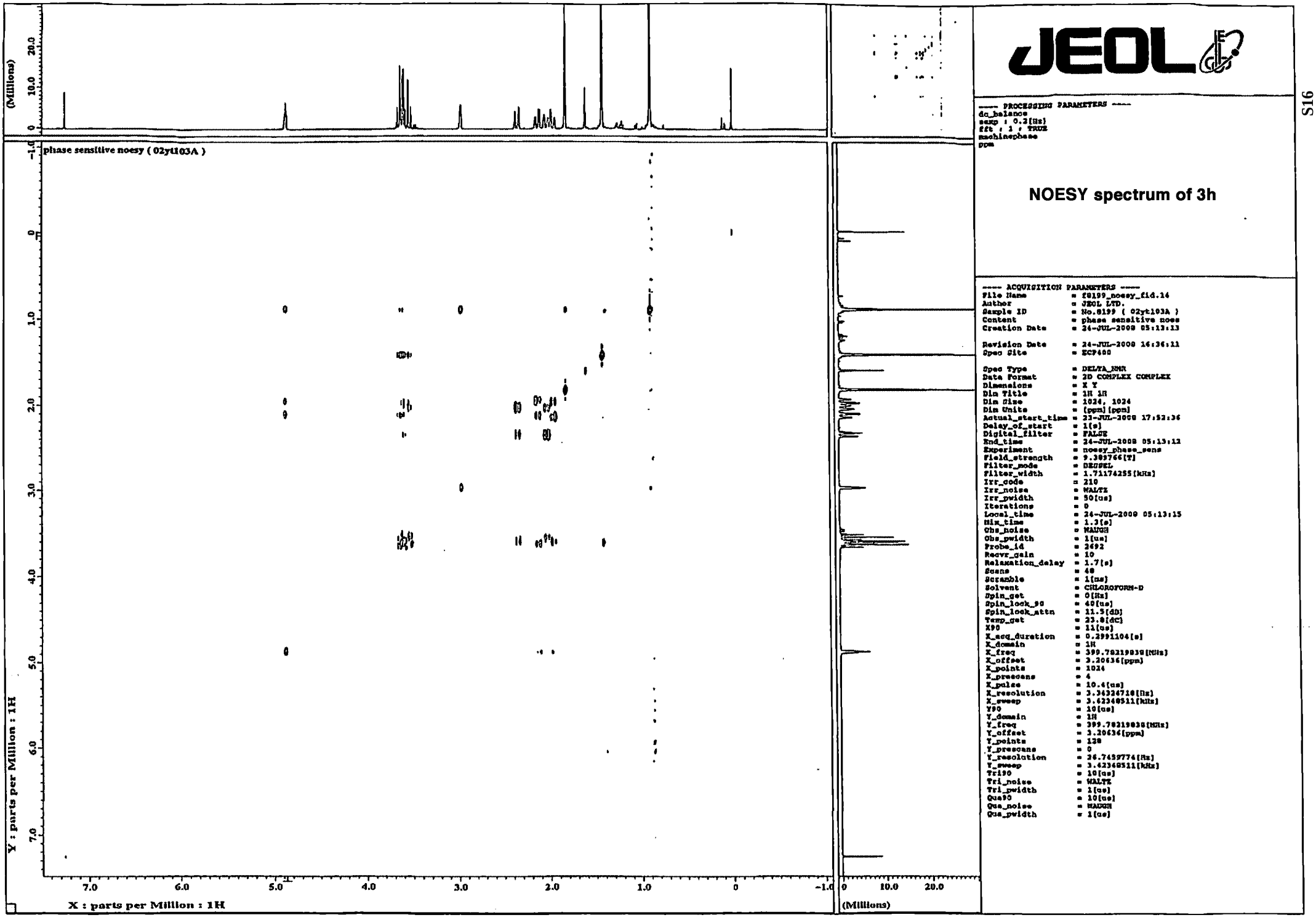
```
----- PROCESSING PARAMETERS -----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
ppm
```

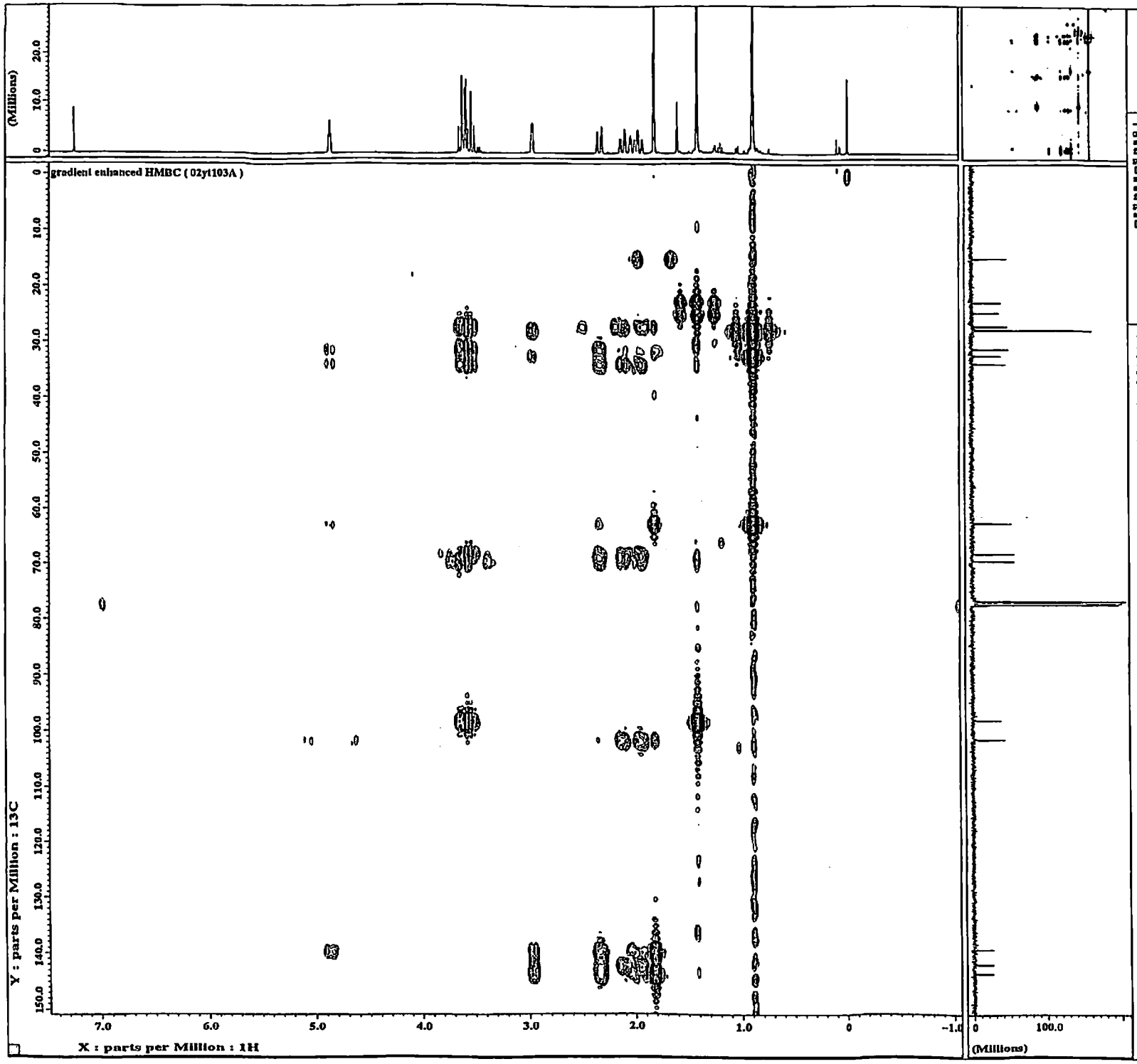
COSY spectrum of 3h

```
---- ACQUISITION PARAMETERS ----
File Name           = f8199_cosy_fid.2
Author              = JEOL LTD.
Sample ID           = No.8199 ( 02yt103A )
Content             = absolute value COSY
Creation Date       = 23-JUL-2008 17:52:29

Revision Date       = 24-JUL-2008 16:19:29
Spec Site           = ECP400

Spec Type           = DELTA_NMR
Data Format         = 2D REAL REAL
Dimensions          = X Y
Dim Title           = 1H 1H
Dim Size            = 1024, 1024
Dim Units           = [ppm][ppm]
Actual_start_time   = 23-JUL-2008 13:41:07
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 23-JUL-2008 17:52:27
Experiment          = cosy.exp
Field_strength      = 9.388766[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 1.71174255[kHz]
Irr_code            = 210
Irr_noise           = WALTZ
Irr_pwidth          = 50[us]
Iterations          = 0
Local_time          = 23-JUL-2008 17:52:30
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 12
Relaxation_delay    = 1.5[s]
Scans               = 32
Solvent             = CHLOROFORM-D
Spin_get            = 0[Hz]
Spin_lock_90        = 40[us]
Spin_lock_attn      = 11.5[dB]
Temp_get            = 24.4[dC]
X90                 = 11[us]
X_acq_duration      = 0.2991104[s]
X_domain            = 1H
X_freq              = 399.78219830[MHz]
X_offset            = 3.20636[ppm]
X_points            = 1024
X_prescans          = 4
X_pulse             = 5.2[us]
X_resolution        = 3.34324710[Hz]
X_sweep             = 3.42348511[kHz]
Y90                 = 10[us]
Y_domain            = 1H
Y_freq              = 399.78219830[MHz]
Y_offset            = 3.20636[ppm]
Y_points            = 256
Y_prescans          = 0
Y_resolution        = 13.3729887[Hz]
Y_sweep             = 3.42348511[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
Tri_pwidth          = 1[us]
Qua90               = 10[us]
Qua_noise           = WAUGH
Qua_pwidth          = 1[us]
```


phase sensitive noesy (02yt103A)
Y : parts per Million : 1H
X : parts per Million : 1H
(Millions)
(Millions)
JEOL
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
ppm
NOESY spectrum of 3h
---- ACQUISITION PARAMETERS ----
File Name = fd199_noesy_fid.14
Author = JEOL LTD.
Sample ID = No.8199 (02yt103A)
Content = phase sensitive noes
Creation Date = 24-JUL-2008 05:13:13
Revision Date = 24-JUL-2008 16:36:11
Spec Site = ECP400
Spec Type = DELTA_NMR
Data Format = 2D COMPLEX COMPLEX
Dimensions = X Y
Dim Title = 1H 1H
Dim Size = 1024, 1024
Dim Units = [ppm][ppm]
Actual_start_time = 23-JUL-2008 17:52:36
Delay_of_start = 1[s]
Digital_filter = FALSE
End_time = 24-JUL-2008 05:13:12
Experiment = noesy_phase_sens
Field_strength = 9.389766[T]
Filter_mode = DECSEL
Filter_width = 1.71174255[kHz]
Irr_code = 210
Irr_noise = WALTZ
Irr_pwidth = 50[us]
Iterations = 0
Local_time = 24-JUL-2008 05:13:15
Mix_time = 1.3[s]
Obs_noise = WALTZ
Obs_pwidth = 1[us]
Probe_id = 2492
Recvr_gain = 10
Relaxation_delay = 1.7[s]
Scans = 48
Scramble = 1[us]
Solvent = CHLOROFORM-D
Spin_rat = 0[Hz]
Spin_lock_90 = 40[us]
Spin_lock_attn = 11.5[dB]
Temp_get = 23.8[dC]
X90 = 11[us]
X_acq_duration = 0.2991104[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 3.20636[ppm]
X_points = 1024
X_prescans = 4
X_pulse = 10.4[us]
X_resolution = 3.34324718[Hz]
X_sweep = 3.42348511[kHz]
Y90 = 10[us]
Y_domain = 1H
Y_freq = 399.78219838[MHz]
Y_offset = 3.20636[ppm]
Y_points = 128
Y_prescans = 0
Y_resolution = 26.7459774[Hz]
Y_sweep = 3.42348511[kHz]
Tri90 = 10[us]
Tri_noise = WALTZ
Tri_pwidth = 1[us]
Qua90 = 10[us]
Qua_noise = WALTZ
Qua_pwidth = 1[us]



JEOL

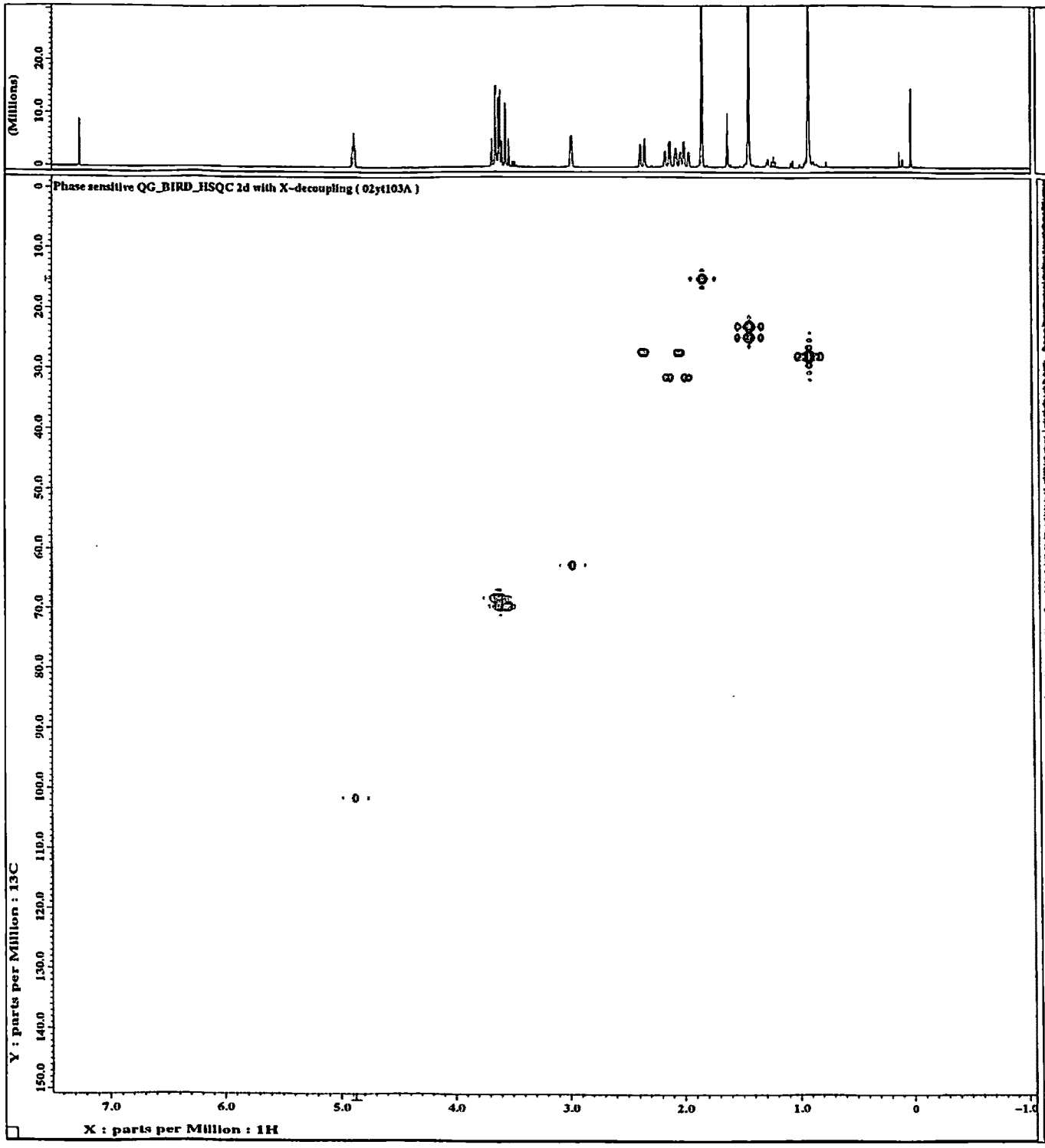
```
---- PROCESSING PARAMETERS ----
gauss : 5[Hz] : 0[s]
sinbell_auto
fft : 1 : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE
ppm
abs
[transpose]
```

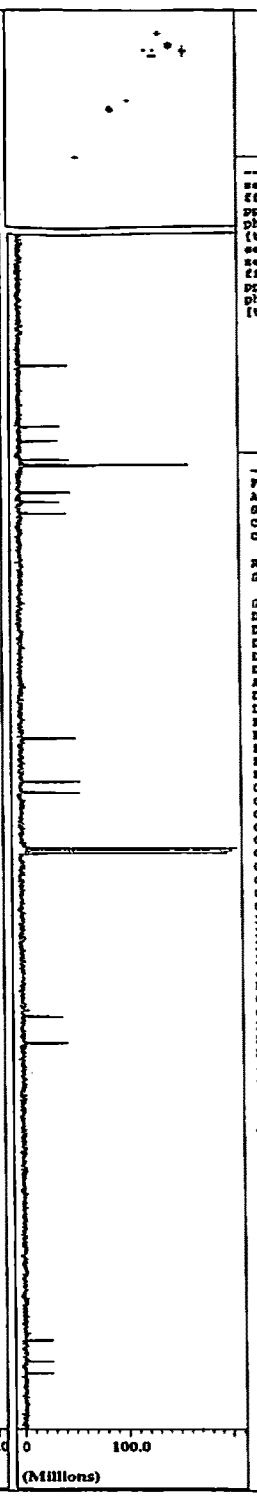
HMBC spectrum of 3h

```
---- ACQUISITION PARAMETERS ----
File Name           = pfg_hmbc.2
Author              = JEOL LTD.
Sample ID           = No.8199 ( 02yt103A )
Content             = gradient enhanced HM
Creation Date       = 24-JUL-2008 17:18:17

Revision Date       = 25-JUL-2008 01:23:05
Spec Site           = EC2400

Spec Type           = DELTA_NMR
Data Format         = 2D REAL REAL
Dimensions          = X Y
Dim Title           = 1H 13C
Dim Size            = 1024, 512
Dim Units           = (ppm)(ppm)
Actual_start_time   = 24-JUL-2008 12:35:11
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 24-JUL-2008 17:18:16
Experiment          = hmbc_pfg_n_c.exp
Field_strength      = 9.389766[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 1.71174255[kHz]
Grad_1              = 1[ms]
Grad_1_amp          = 60[%]
Grad_2              = 1[ms]
Grad_2_amp          = 60[%]
Grad_3              = 1[ms]
Grad_3_amp          = 30[%]
Grad_recover        = 1[ms]
Grad_shape          = square
Irr_code            = 210
Irr_noise           = WALTZ
Irr_pwidth          = 70[us]
Iterations          = 8
J_constant          = 140[Hz]
Local_time          = 24-JUL-2008 17:18:19
Long_range_j        = 8[Hz]
Obs_noise           = WALTZ
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 28
Relaxation_delay    = 1.7[s]
Scans               = 64
Solvent             = CHLOROFORM-D
Spin_get            = 0[Hz]
Spin_lock_90        = 40[us]
Spin_lock_attn      = 11.5[dB]
Temp_get            = 24.6[dC]
X90                 = 11[us]
X_acq_duration      = 0.29911104[s]
X_domain            = 1H
X_freq              = 399.78219838[MHz]
X_offset            = 3.30636[ppm]
X_points            = 1024
X_prescans          = 4
X_pulse             = 11[us]
X_resolution        = 3.34324719[Hz]
X_sweep             = 3.42340511[kHz]
Y90                 = 15[us]
Y_domain            = 13C
Y_freq              = 100.52530333[MHz]
Y_offset            = 74.37406[ppm]
Y_points            = 128
Y_prescans          = 0
Y_pulse             = 11[us]
Y_resolution        = 120.19230769[Hz]
Y_sweep             = 15.38461538[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
Tri_pwidth          = 1[us]
Que90               = 10[us]
Que_noise           = WALTZ
Que_pwidth          = 1[us]
```





JEOL

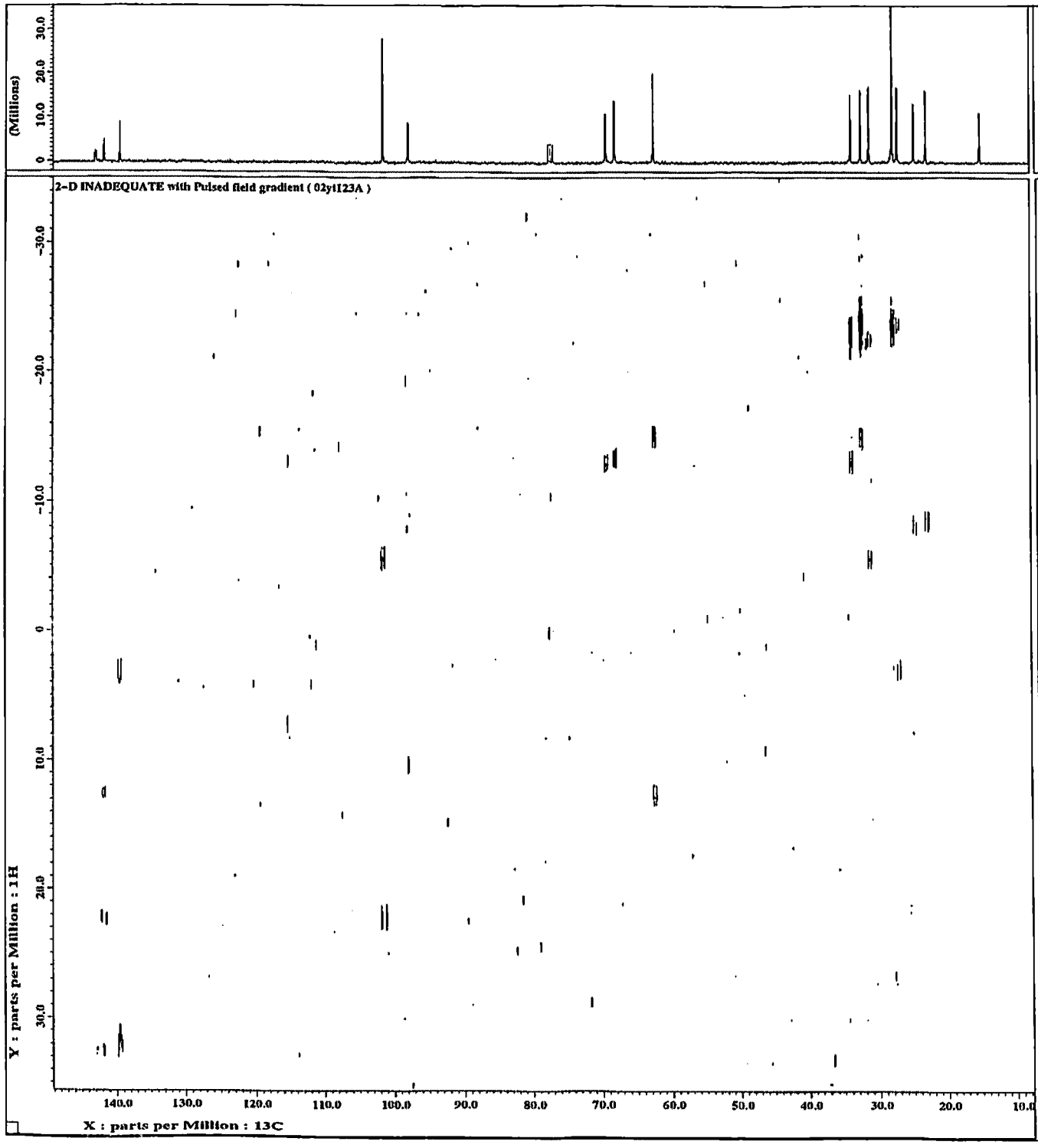
```
---- PROCESSING PARAMETERS ----
sexp : 3[Hz]
fft : 1 : TRUE
ppm
phase : -9 : 205 : 50[%]
[transpose]
sexp : 60[Hz]
zerofill : 4
fft : 0.5 : TRUE
ppm
phase : 0 : 200 : 50[%]
[transpose]
```

HSQC spectrum of 3h

```
---- ACQUISITION PARAMETERS ----
File Name           = f0199_hsqc_fid.16
Author              = JEOL LTD.
Sample ID           = No.0199 ( 02yt103A )
Content             = Phase sensitive QG_B
Creation Date       = 24-JUL-2008 12:35:01

Revision Date       = 25-JUL-2008 01:44:47
Spec Site           = ECP400

Spec Type           = DELTA_NMR
Data Format         = 2D COMPLEX COMPLEX
Dimensions          = X Y
Dim Title           = 1H 13C
Dim Size            = 512, 512
Dim Units           = [ppm][ppm]
Actual_start_time   = 24-JUL-2008 08:13:51
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 24-JUL-2008 12:34:56
Experiment          = hsqc_phase_qgbir
Field_strength      = 9.389766[T]
Filter_mode         = HERMEL
Filter_width        = 1.71174255[kHz]
Grad_1              = 1[ms]
Grad_1_amp          = 11[%]
Grad_2              = 1[ms]
Grad_2_amp          = 20[%]
Grad_3              = 1[ms]
Grad_3_amp          = 35[%]
Grad_4              = 1[ms]
Grad_4_amp          = 26[%]
Grad_recover        = 0.1[ms]
Grad_shape          = square
Irr_code            = 210
Irr_noise           = MPF0
Irr_pwidth          = 70[us]
Iterations          = 0
J_constant          = 140[Hz]
Local_time          = 24-JUL-2008 12:35:00
Obs_noise           = WALTZ8
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 20
Relaxation_delay    = 1.7[s]
Scans               = 32
Solvent             = CHLOROFORM-D
Spin_get            = 0[Hz]
Spin_lock_90        = 40[us]
Spin_lock_attn      = 11.5[dB]
Temp_get            = 24.7[dC]
X90                 = 11[us]
X_acq_duration      = 0.1495552[s]
X_domain            = 1H
X_freq              = 399.78219830[MHz]
X_offset            = 3.20616[ppm]
X_points            = 512
X_prescans          = 4
X_pulse             = 11[us]
X_resolution        = 6.68649435[Hz]
X_sweep             = 3.42340511[kHz]
Y90                 = 15[us]
Y_domain            = 13C
Y_freq              = 100.52330333[MHz]
Y_offset            = 74.37406[ppm]
Y_points            = 128
Y_prescans          = 8
Y_pulse             = 11[us]
Y_resolution        = 120.19230769[Hz]
Y_sweep             = 15.38461538[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
Tri_pwidth          = 1[us]
Qua90               = 10[us]
Qua_noise           = WALTZ8
Que_pwidth          = 1[us]
```



JEOL

```
------ PROCESSING PARAMETERS ------
dc_balance
sexp : 2[Hz]
fft : 1 : TRUE
tmchinephase
ppm
```

INADEQUATE spectrum of 3h

```
---- ACQUISITION PARAMETERS ----
File Name           = 2d_inadequate_pfg_n.
Author              = JEOL LTD.
Sample ID           = No.0249 ( 02yt123A )
Content             = 2-D INADEQUATE with
Creation Date       =  2-SEP-2008 10:20:26

Revision Date       =  3-SEP-2008 16:20:11
Spec Site           = ECP400

Spec Type           = DELTA_NMR
Data Format         = 2D REAL REAL
Dimensions          = X Y
Dim Title           = 13C 1H
Dim Size            = 8192, 128
Dim Units           = [ppm][ppm]
Actual_start_time   =  2-SEP-2008 05:37:16
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  2-SEP-2008 10:20:20
Experiment          = inadequate_2d_pf
Field_strength      = 9.389766[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 7.11237553[kHz]
Grad_1              = 1[ms]
Grad_1_amp          = 20[%]
Grad_2              = 1[ms]
Grad_2_amp          = 40[%]
Grad_recover        = 0.1[ms]
Grad_shape          =
Irr_code            = 210
Irr_domain          = 1H
Irr_freq            = 399.78219030[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 50[us]
Iterations          = 0
J_constant          = 70[Hz]
Local_time          =  2-SEP-2008 18:20:30
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 5[s]
Scans               = 128
Solvent             = CHLOROFORM-D
Spin_get            = 0[Hz]
Spin_lock_90        = 40[us]
Spin_lock_attn      = 11.5[dB]
Temp_get            = 22.9[dC]
X90                 = 15[us]
X_acq_duration      = 0.5758976[s]
X_domain            = 13C
X_freq              = 100.52530333[MHz]
X_offset            = 78.44723[ppm]
X_points            = 8192
X_prescans          = 4
X_pulse             = 20.26666667[us]
X_resolution        = 1.73641981[Hz]
X_sweep             = 14.22675107[kHz]
Y90                 = 11[us]
Y_domain            = 1H
Y_freq              = 399.78219030[MHz]
Y_offset            = 0[ppm]
Y_points            = 64
Y_prescans          = 0
Y_resolution        = 445.15669516[Hz]
Y_sweep             = 28.49002849[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
Tri_pwidth          = 1[us]
Qua90               = 10[us]
Qua_noise           = WAUGH
Qua_pwidth          = 1[us]
```