Supplementary Material (ESI) for Chemical Communications

-Supporting Information-

One-pot synthesis of a shape-persistent endo-functionalised nano-sized adamantoid compound

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Synthetic procedures

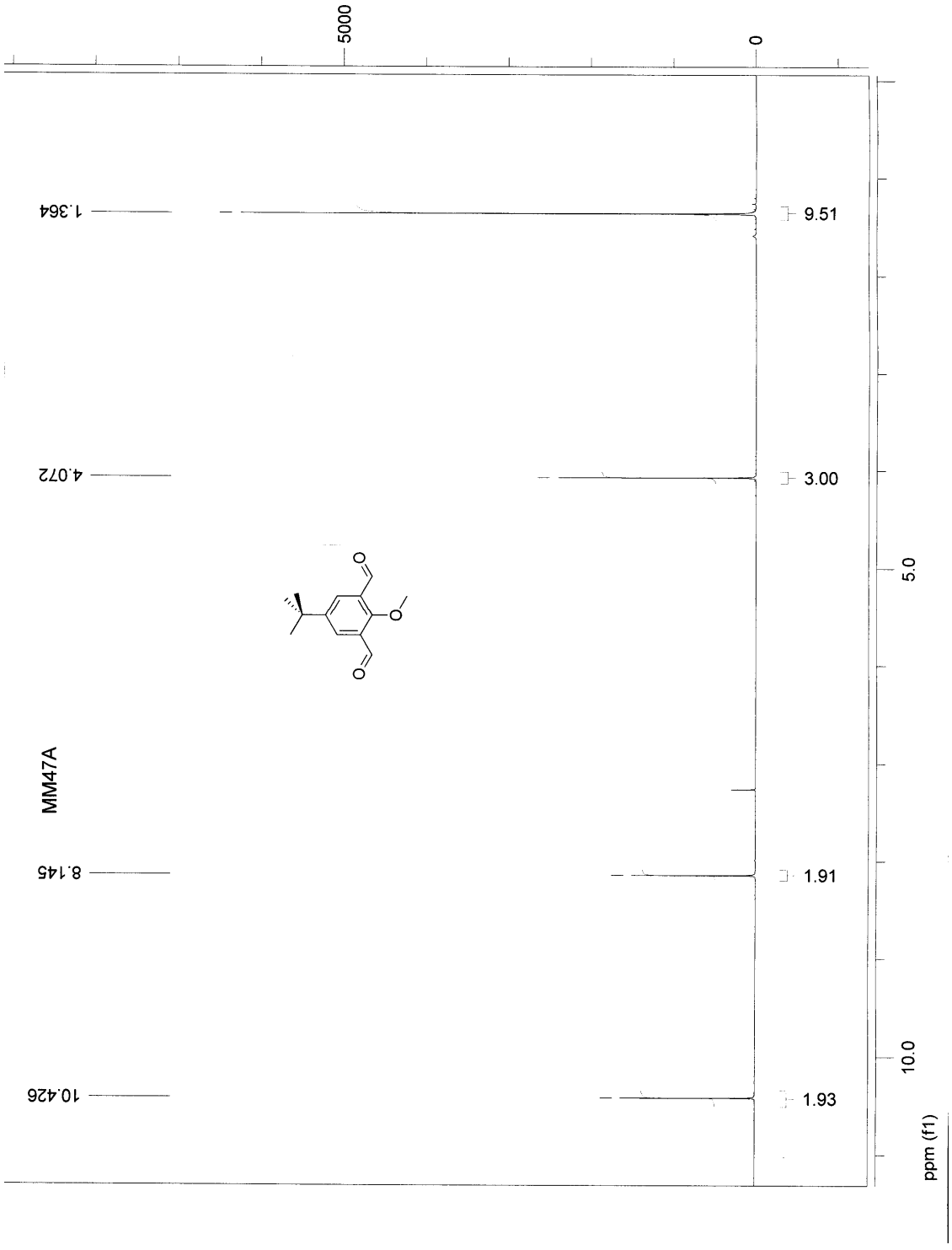
General remarks: Melting points (not corrected) were measured with a *Büchi Melting Point B-545*. IR- Spectra were recorded as KBr-pellets on a *Perkin Elmer Spectrum 2000* FT-IR spectrometer. The UV/Vis spectrum was taken on a *Perkin-Elmer Lambda 19*. NMR spectra were recorded on a *Bruker DRX 400* at 278 K at 400 MHz (^{1}H) and 100 MHz (^{13}C). MALDI-TOF experiments were carried out on a *Bruker Daltonik Reflex III*. ESI/MS were taken on a *micromass ZMD* (solvent: acetonitrile/formic acid) and GC-MS (EI) were measured on a *Varian Saturn 2000*. Elemental analyses were determined with a *Elementar Vario EL*. THF and methanol were purchased from Prolabo and dried prior to use. Salicylbisadehyde **2** (Aldrich), Isophthalaldehyde **4** (Merck VWR) are commercial available and used without further purification. Triamine **1** was synthesized by a procedure published before.

Synthesis of 5-tert-butyl-2-methoxyisophthalaldehyde (**5**):

To a suspension of salicyldialdehyde **2** (200 mg, 1.0 mmol) and potassium carbonate (770 mg, 5.57 mmol) in DMF (10 mL) iodomethane (0.06 mL, 0.97 mmol) were added and heated at 60-70 ºC for 6h. After cooling to room temperature, water (20 mL) and dichloromethane (20 mL) was added and the layers separated. The organic layer was washed with water (3 x 25 mL), aqueous ammonium chloride solution (1N, 25 mL), and brine (25 mL) and dried over sodium sulphate. The solvents were removed by rotary evaporation and the oily orange residue purified by flash chromatography (SiO_2, petrol ether/ethylacetate 4:1) to give after drying in vacuo 180 mg (82%) of a pale yellow solid. M.p. 82-84 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.36 ppm (s, 9H, tBu-*H*), 4.07 (s, 3H, O*CH*$_3$), 8.15 (s, 2H, Ar-*H*), 10.43 (s, 2H, C*H*O). ^{13}C NMR ($CDCl_3$, 133 MHz): δ = 31.1 ppm (q,-C(*C*H$_3$)$_3$), 34.82 (s, -*C*(CH$_3$)$_3$), 66.69 (s, O*C*H$_3$), 129.45 (s), 132.00 (d), 148.29 (s), 163.56 (s, all Ar-*C*), 188.71 (*C*HO). IR (KBr): nu-tilde: 3360 (s) (cm^{-1}), 3072 (s), 3004 (s), 2959 (s), 2888 (m), 2871 (m), 2851 (m), 2755 (m), 1686 (vs), 1651 (w), 1576 (s), 1478 (s), 1431 (w), 1412 (s), 1396 (s), 1366 (m), 1293 (w), 1244 (s), 1216 (s), 1109 (m), 1007 (w), 991 (s), 959 (m), 909 (w), 811 (w), 794 (w), 765 (w), 723 (m), 643 (m), 616 (m), 552 (m), 520 (w), 471 (w). MS (EI): *m/z* = 220, 206, 205, 176, 175, 147, 133, 121, 91, 77. Elemental analysis: calcd. for $C_{13}H_{16}O_3$ (M = 220.26 g/mol): C 70.89, H 7.32; found: C 70.76, H 7.37.

*Reaction of isophtaldehyde **4** with triamine **1**:*
A solution of **1** (51 mg, 0.17 mmol) and **4** (35 mg, 0.26 mmol) in dry THF (10 mL) was stirred at room temperature for 5 days. The formed yellow precipitate was filtered, washed with THF and dried in vacuo to give 70 mg of a pale yellow solid.

*Reaction of bisaldehyde **5** with triamine **1**:*
A solution of **1** (50 mg, 0.17 mmol) and **5** (55 mg, 0.25 mmol) in dry THF (10 mL) was stirred at room temperature. After three and twelve days the rection mixture was analysed by MALDI-TOF mass spectroscopy.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1.93
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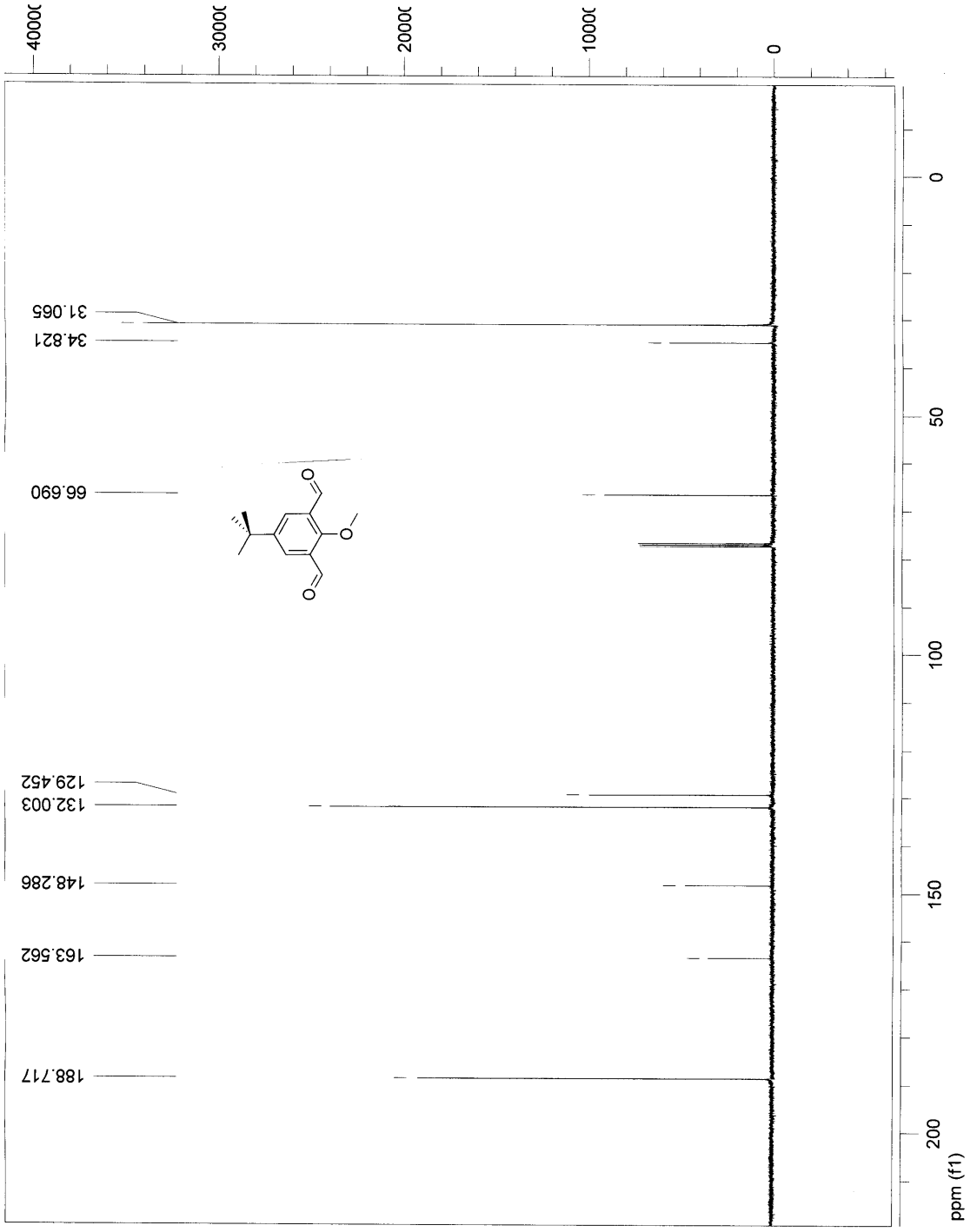
10.0
ppm (f1)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2000
1000
0
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66.690
129.452
132.003
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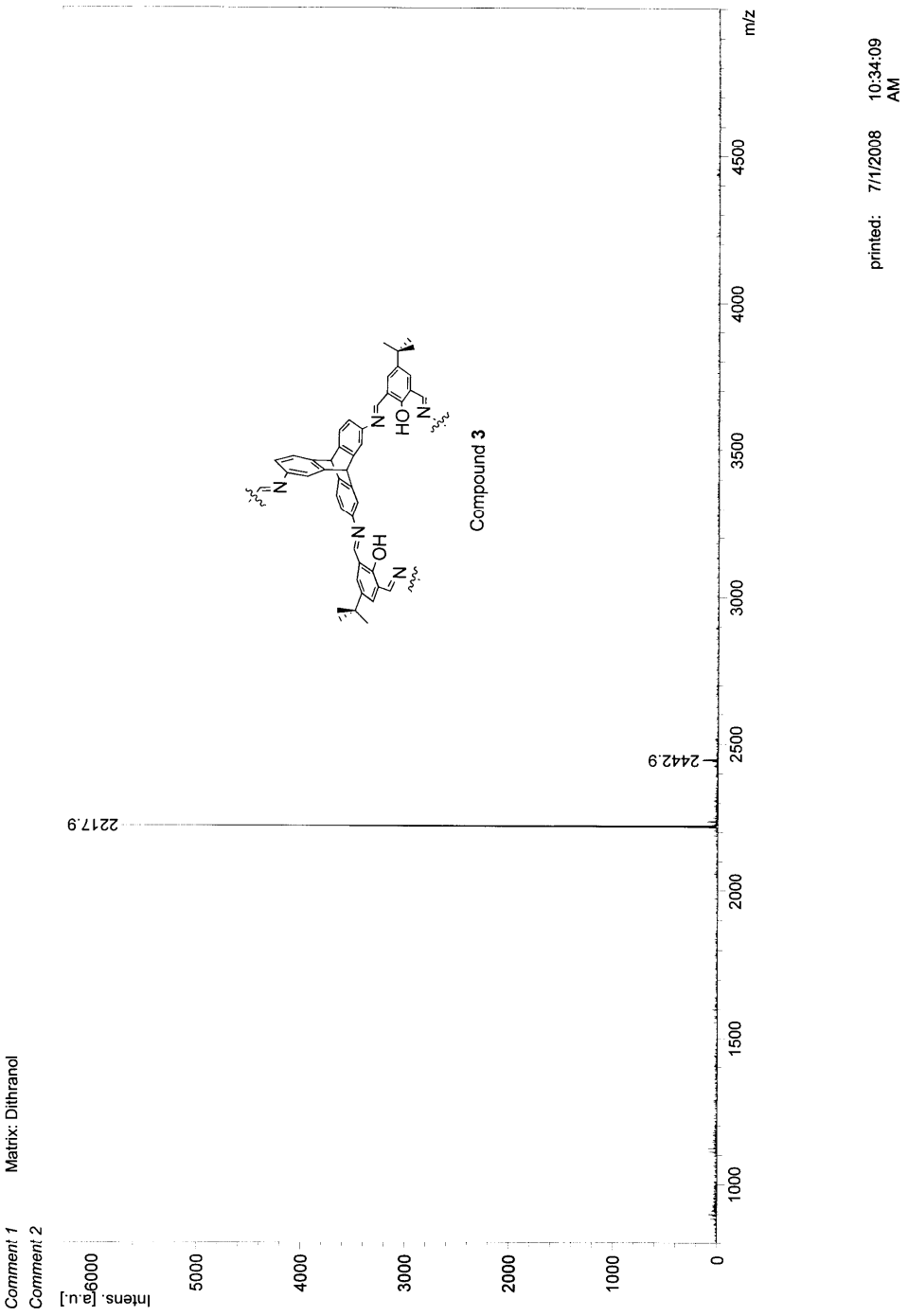
163.562
188.717
0
50
100
150
200
ppm (f1)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5000
4000
3000
2000
1000
0
1000
1500
2000
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2500
2442.9
3000
3500
4000
4500
m/z
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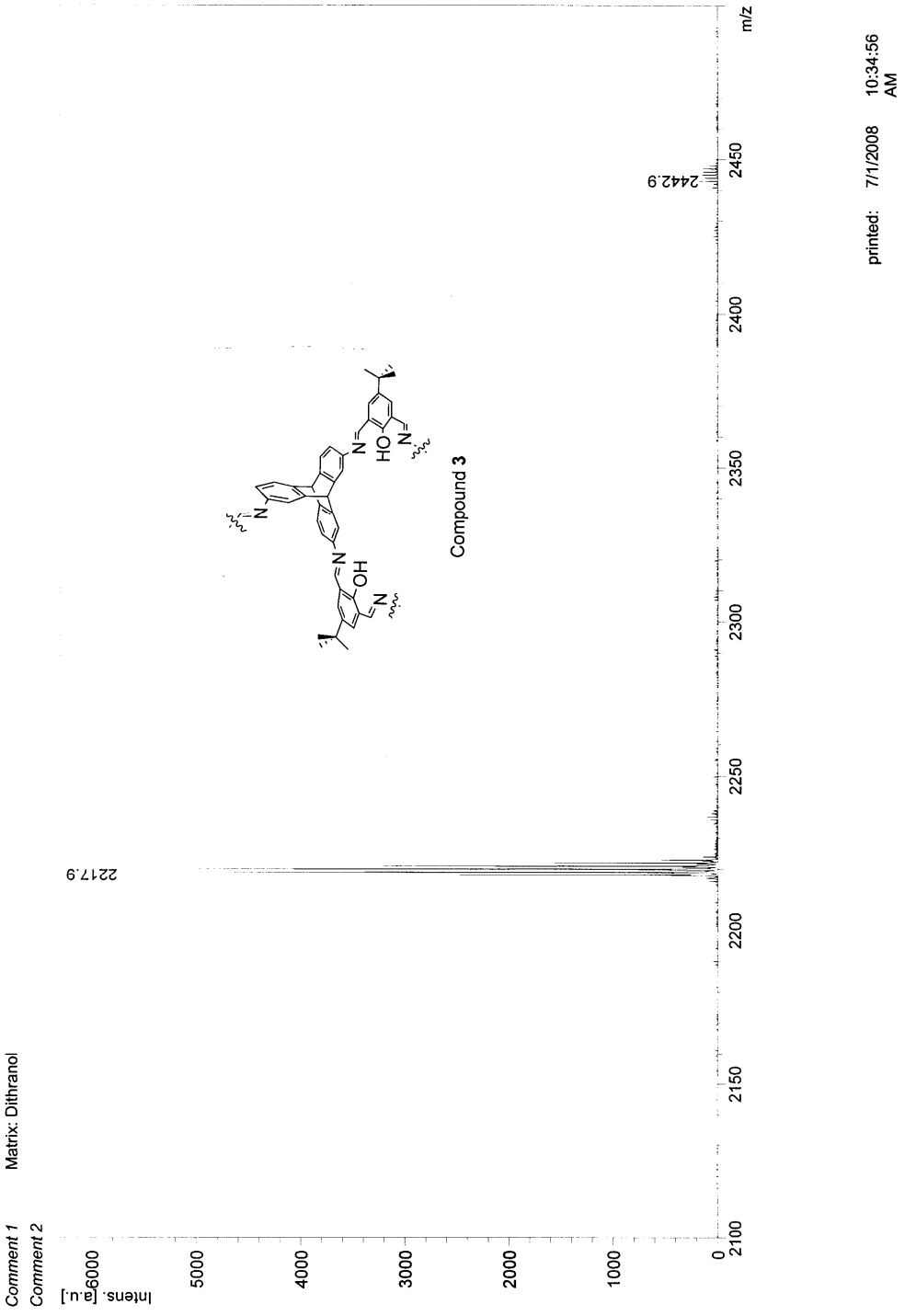
Compound 3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5000
4000
3000
2000
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0
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2200
2250
2300
2350
2400
2450
m/z
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2442.9
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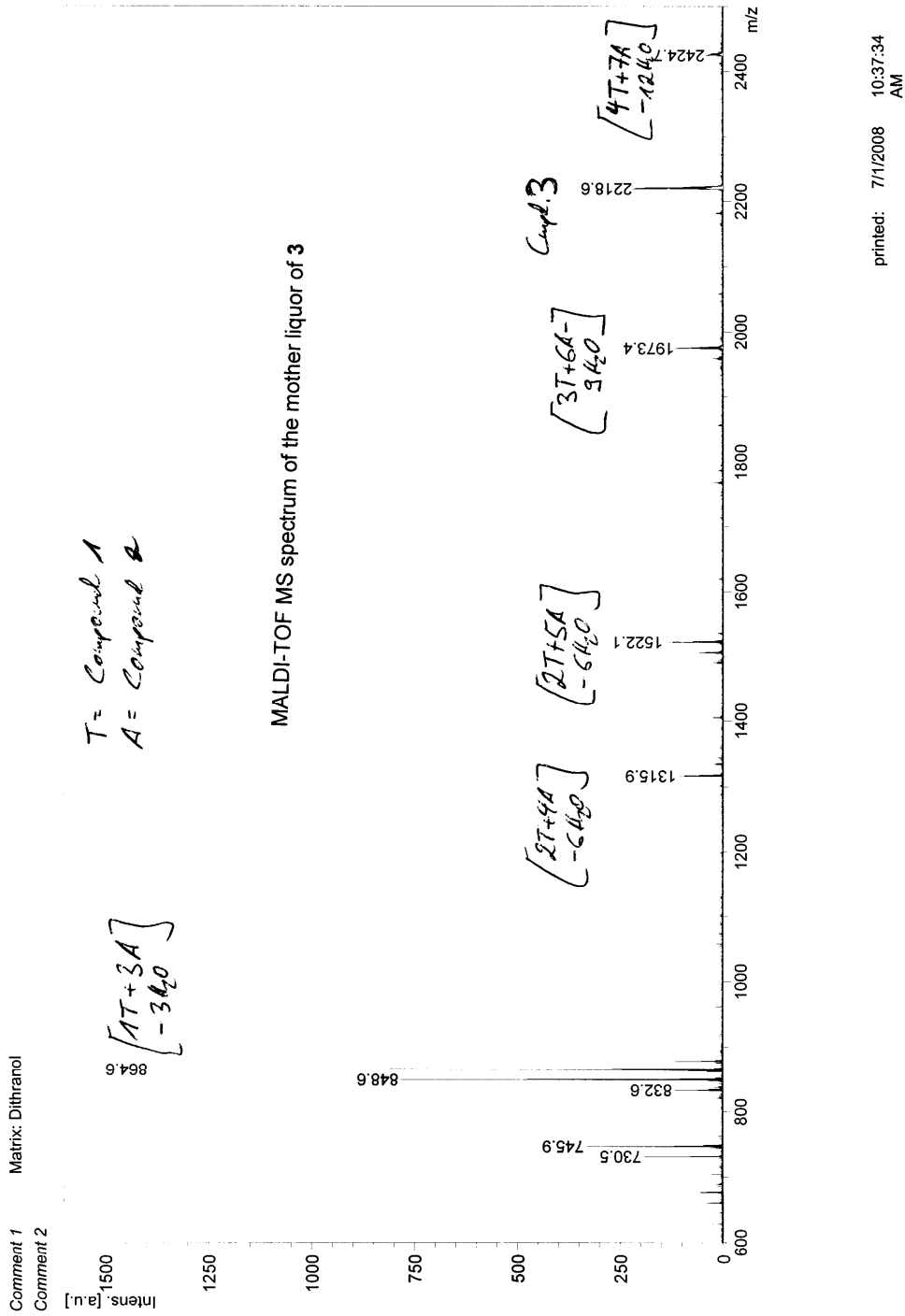
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Comment 1
Comment 2
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Intens. [a.u.]
m/z
T = Compound 1
A = Compound 2
Cmpd. 3
[1T+3A -3H2O]
[2T+4A -4H2O]
[2T+5A -6H2O]
[3T+6A -3H2O]
[4T+7A -12H2O]
864.6
848.6
832.6
745.9
730.5
1315.9
1522.1
1973.4
2218.6
2424.7
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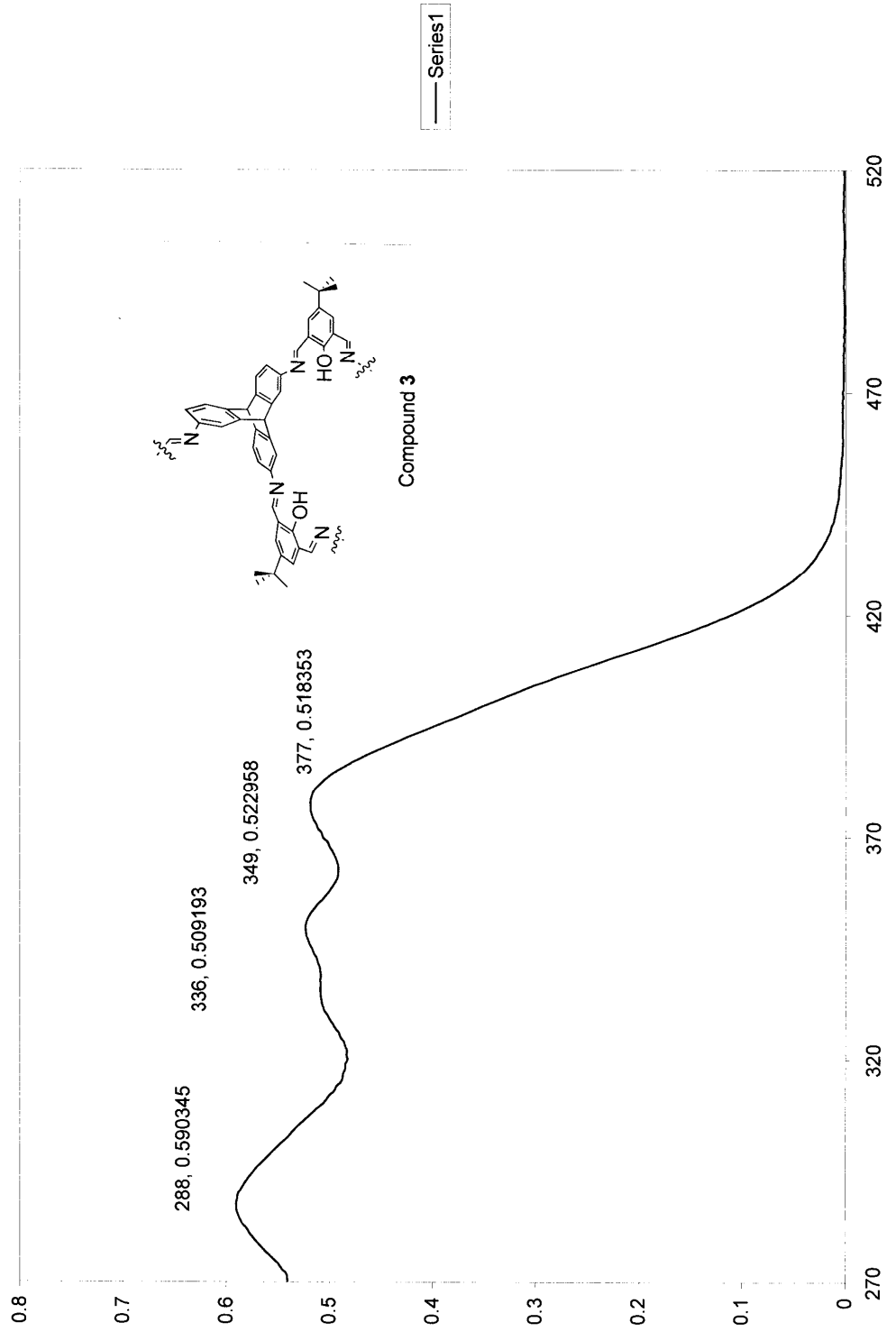
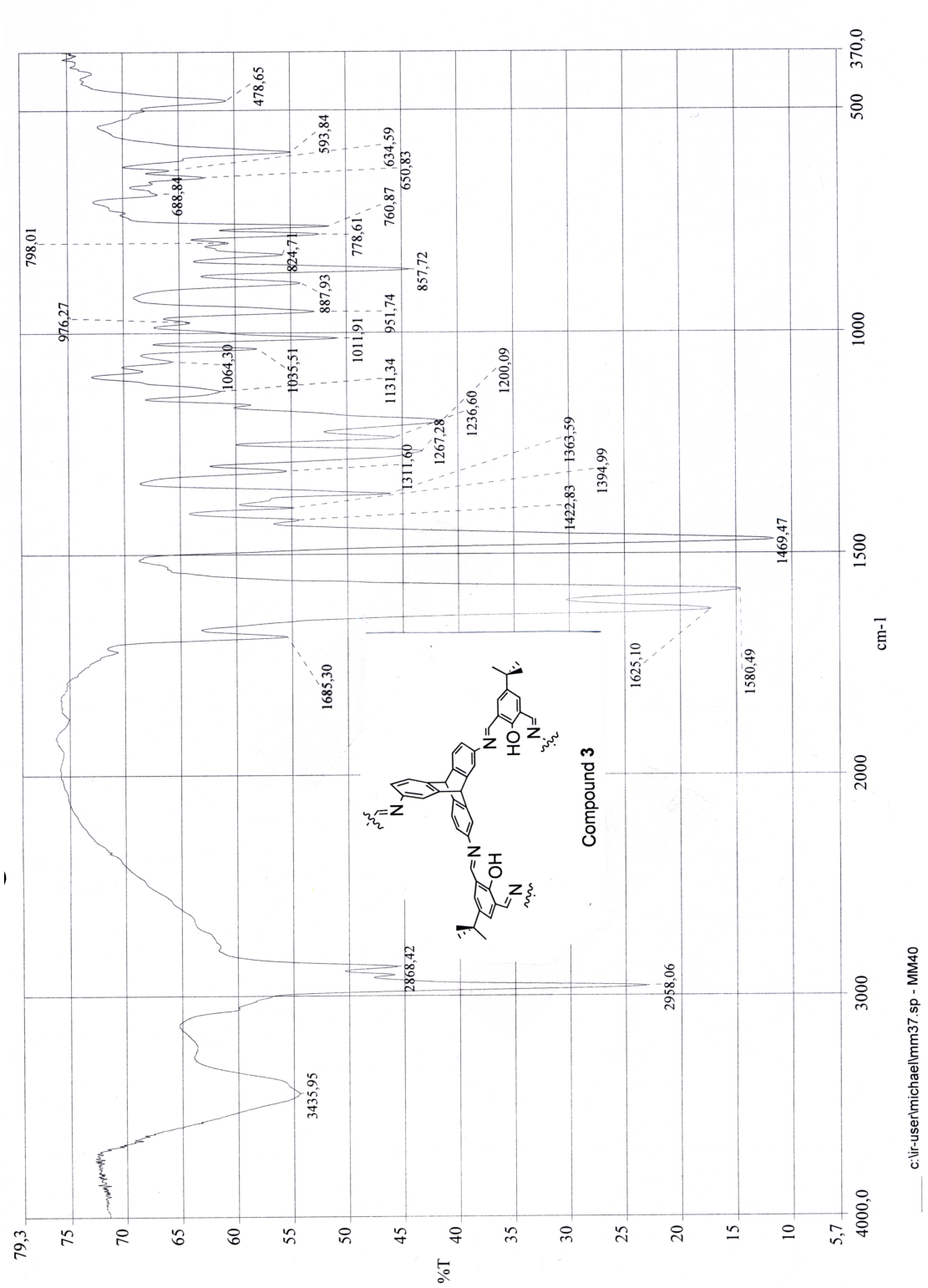

Series1
Compound 3
288, 0.590345
336, 0.509193
349, 0.522958
377, 0.518353
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
270
320
370
420
470
520


Compound 3
%T
cm-1
c:\ir-user\michael\mm37.sp - MM40
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2868,42
2958,06
1685,30
1625,10
1580,49
1469,47
1422,83
1394,99
1363,59
1311,60
1267,28
1236,60
1200,09
1131,34
1064,30
1035,51
1011,91
976,27
951,74
887,93
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824,71
798,01
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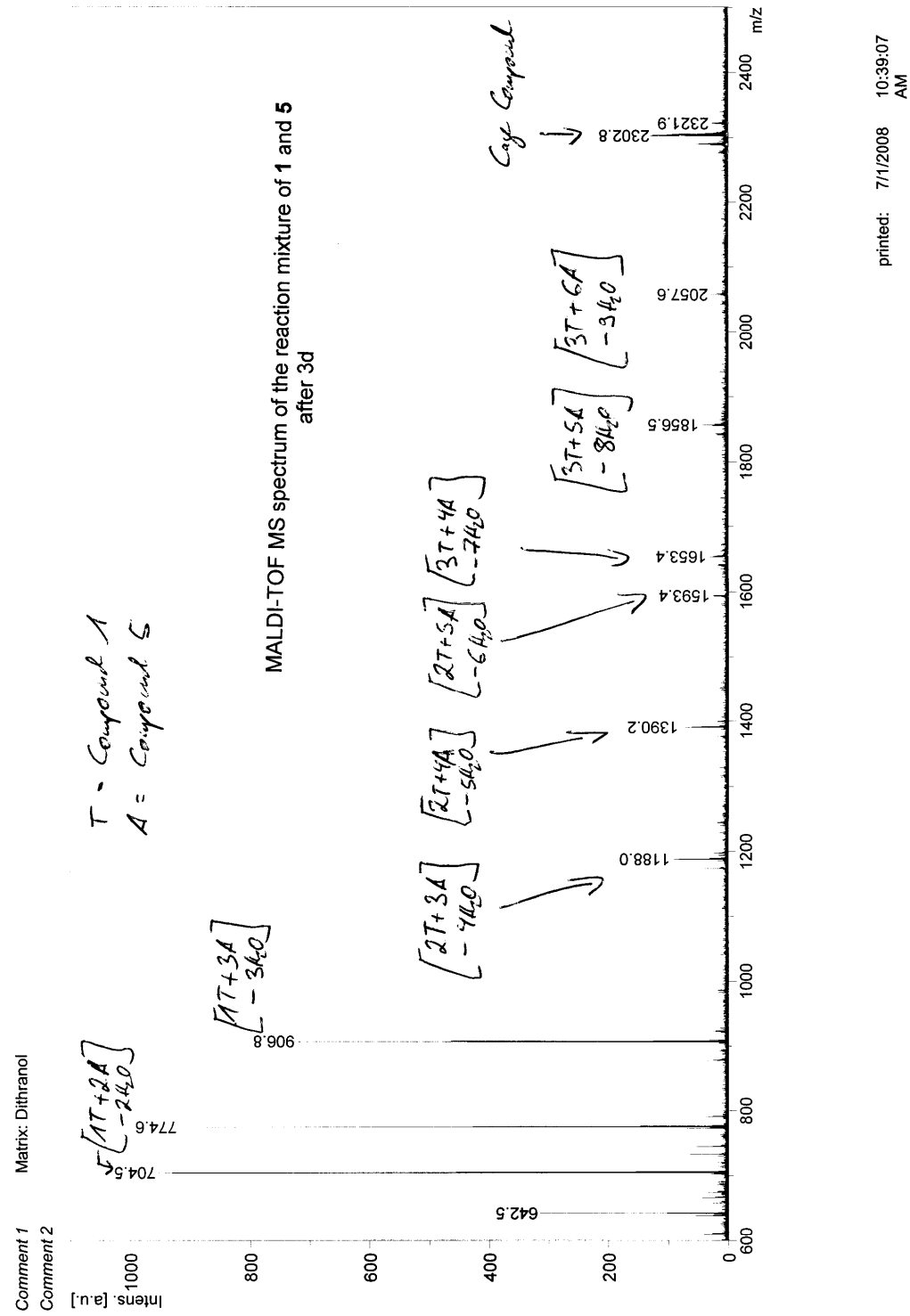
760,87
688,84
650,83
634,59
593,84
478,65


MALDI-TOF MS spectrum of the reaction mixture of 1 and 5
after 3d
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A = Compound 5
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Comment 2
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m/z
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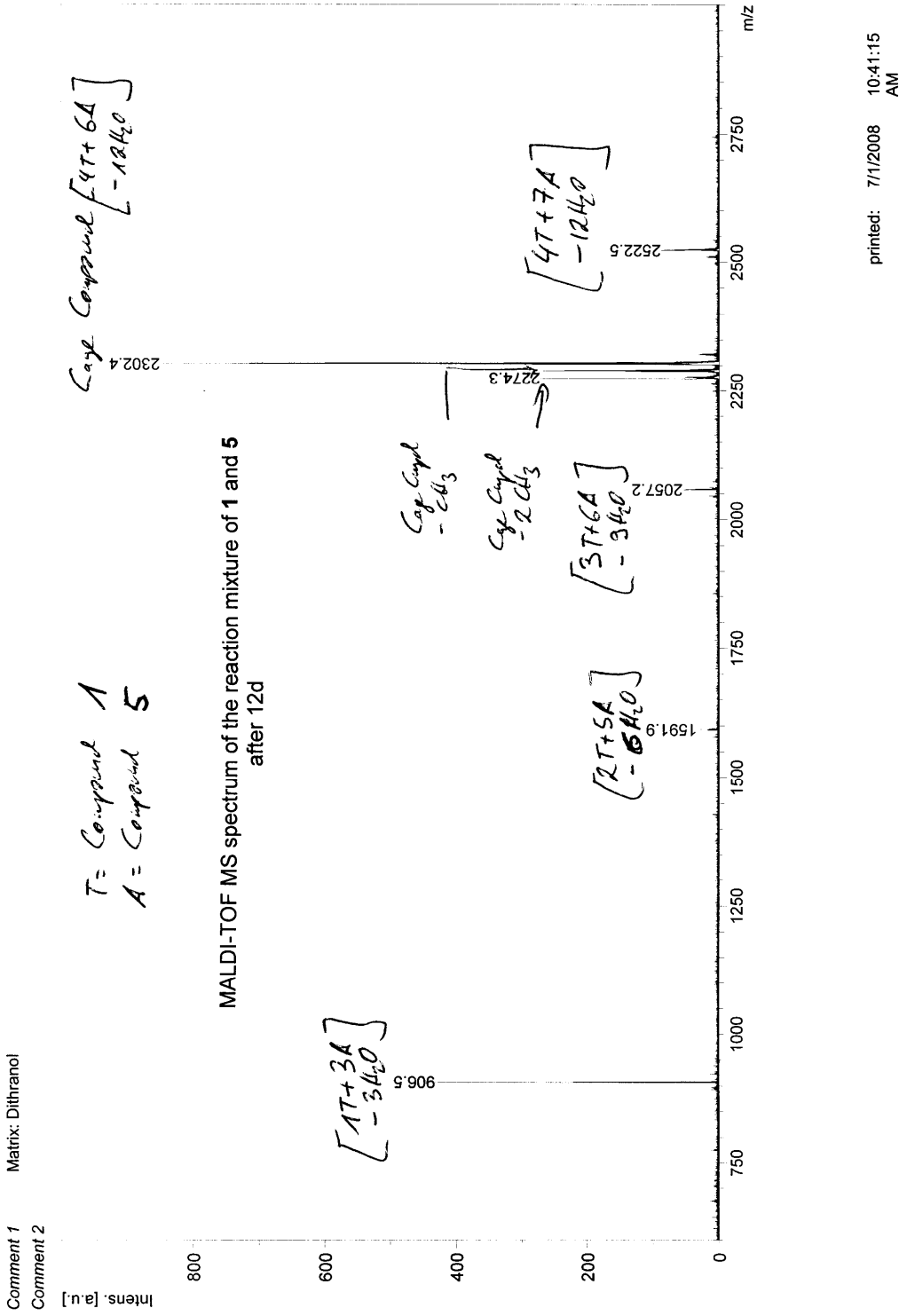
704.5
774.6
906.8
1188.0
1390.2
1593.4
1653.4
1856.5
2057.6
2302.8
2321.9
[1T+2A -2H2O]
[1T+3A -3H2O]
[2T+3A -7H2O]
[2T+4A -5H2O]
[2T+5A -6H2O]
[3T+4A -7H2O]
[3T+5A -8H2O]
[3T+6A -9H2O]
Cyc Compound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after 12d
T = Compound 1
A = Compound 5
Cage Compound [4T+6A -12H2O]
[1T+3A -3H2O]
[2T+5A -6H2O]
[3T+6A -3H2O]
[4T+7A -12H2O]
Cage Cmpd -CH3
Cage Cmpd -2 CH3
906.5
1591.9
2057.2
2274.3
2302.4
2522.5
Intens. [a.u.]
m/z
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Comment 2
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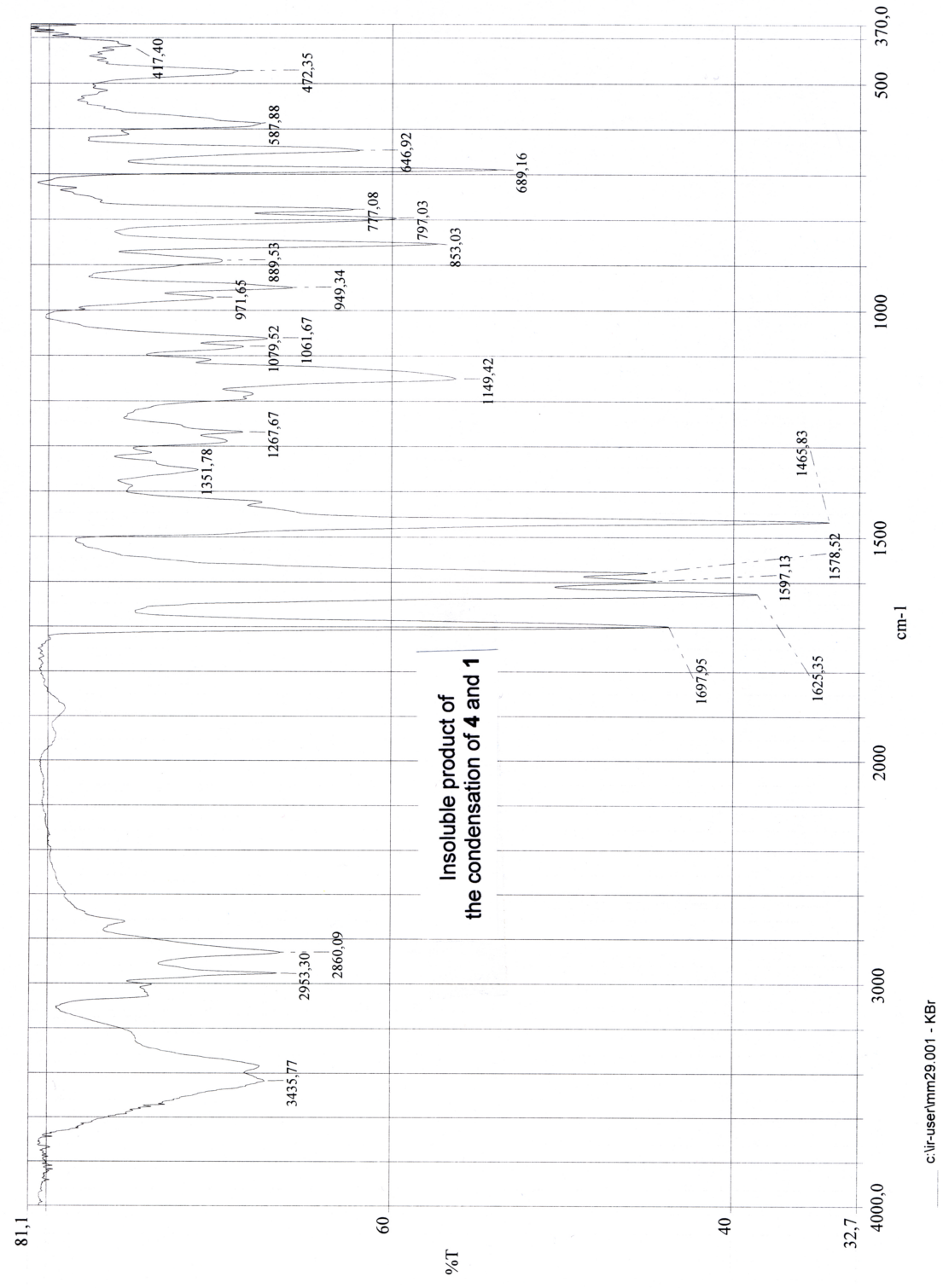
Insoluble product of
the condensation of 4 and 1
%T
cm-1
c:\ir-user\mm29.001 - KBr
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60
40
32,7
4000,0
3000
2000
1500
1000
500
370,0
417,40
472,35
587,88
646,92
689,16
777,08
797,03
853,03
889,53
949,34
971,65
1061,67
1079,52
1149,42
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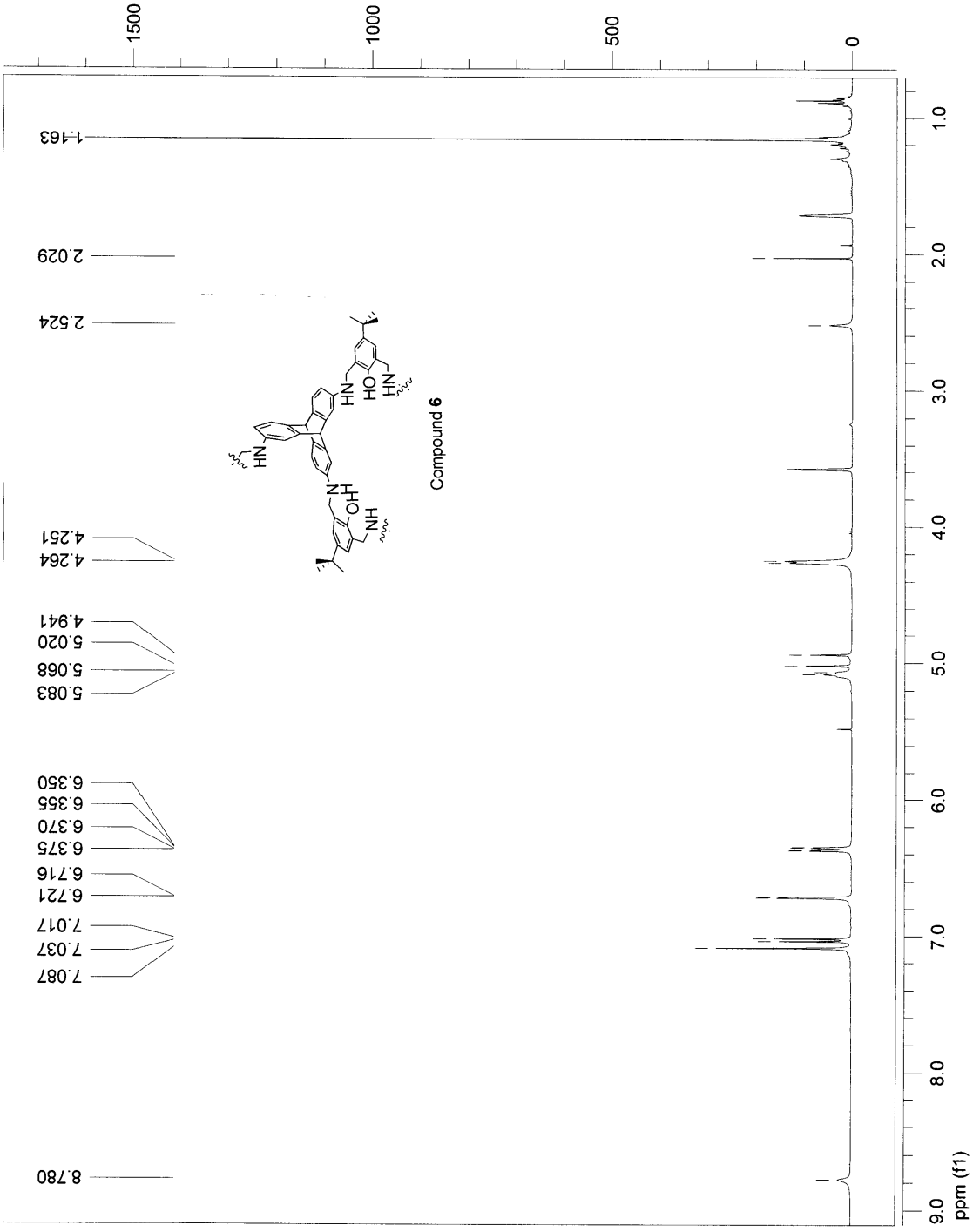
3435,77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1000
500
0
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5.083
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6.355
6.370
6.375
6.716
6.721
7.017
7.037
7.087
8.780
Compound 6
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2.0
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5.0
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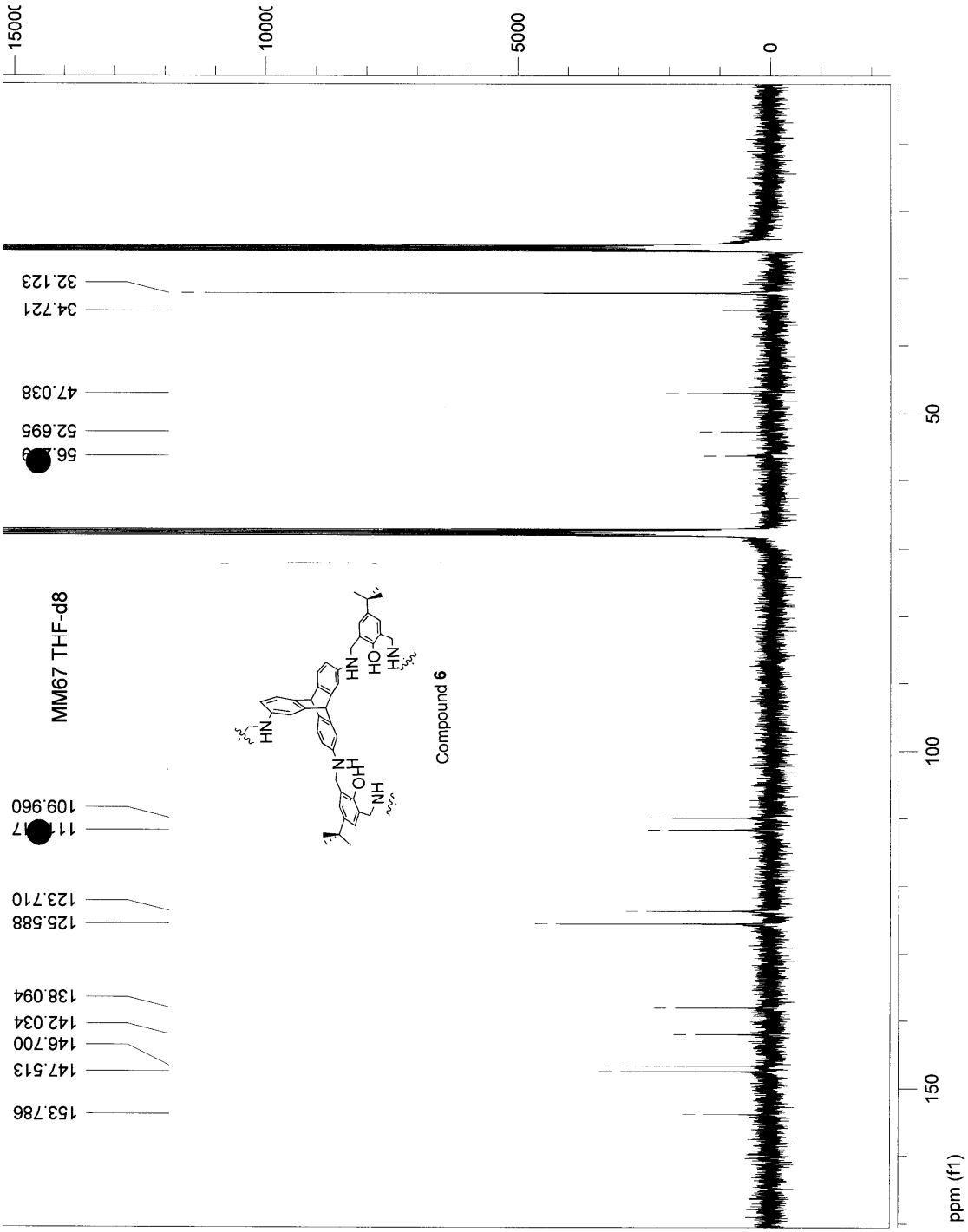
7.0
8.0
9.0
ppm (f1)


MM67 THF-d8
Compound 6
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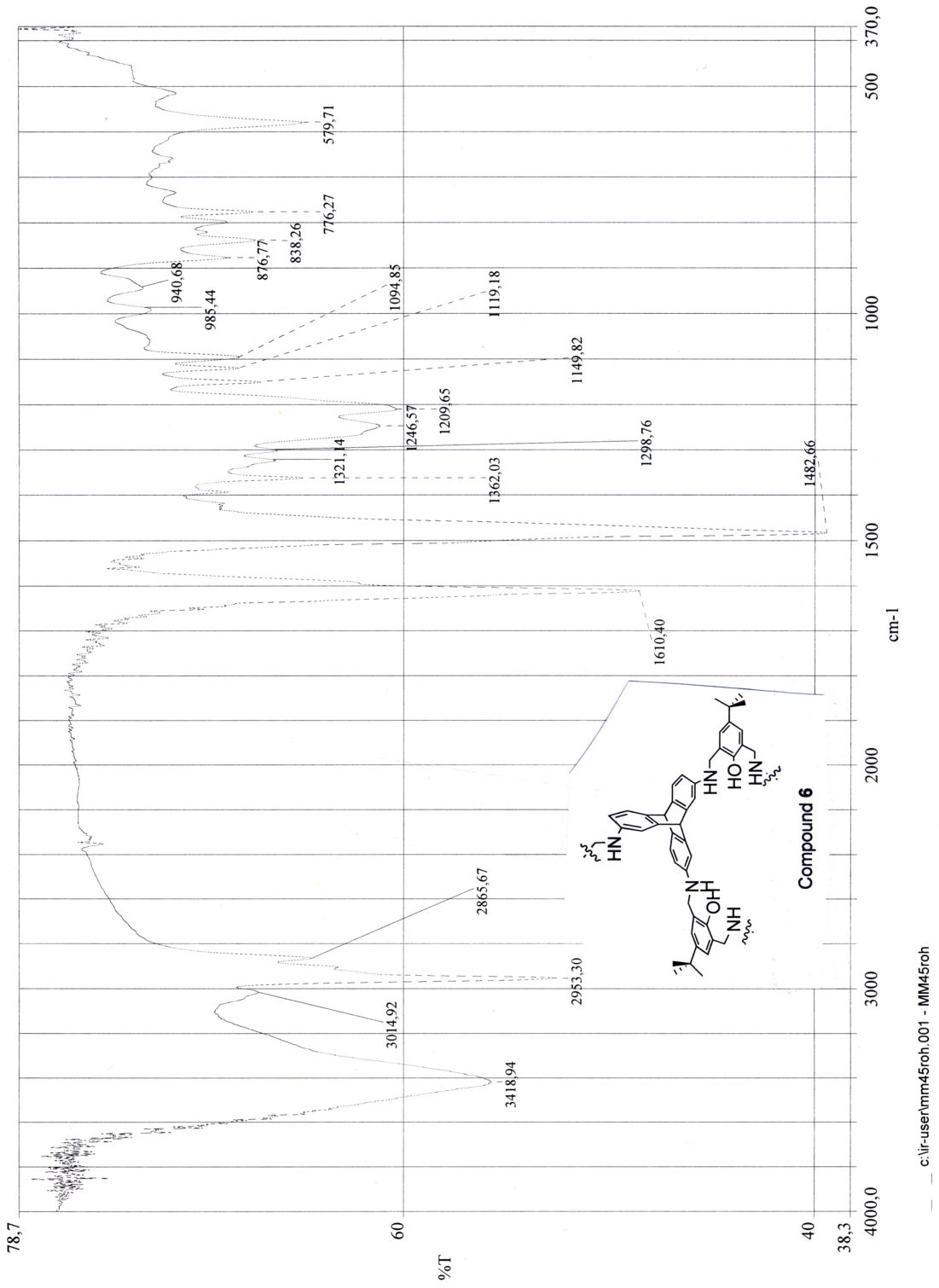
147.513
153.786
ppm (f1)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60
40
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cm-1
3418,94
3014,92
2953,30
2865,67
1610,40
1482,66
1362,03
1321,14
1298,76
1246,57
1209,65
1149,82
1119,18
1094,85
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Compound 6
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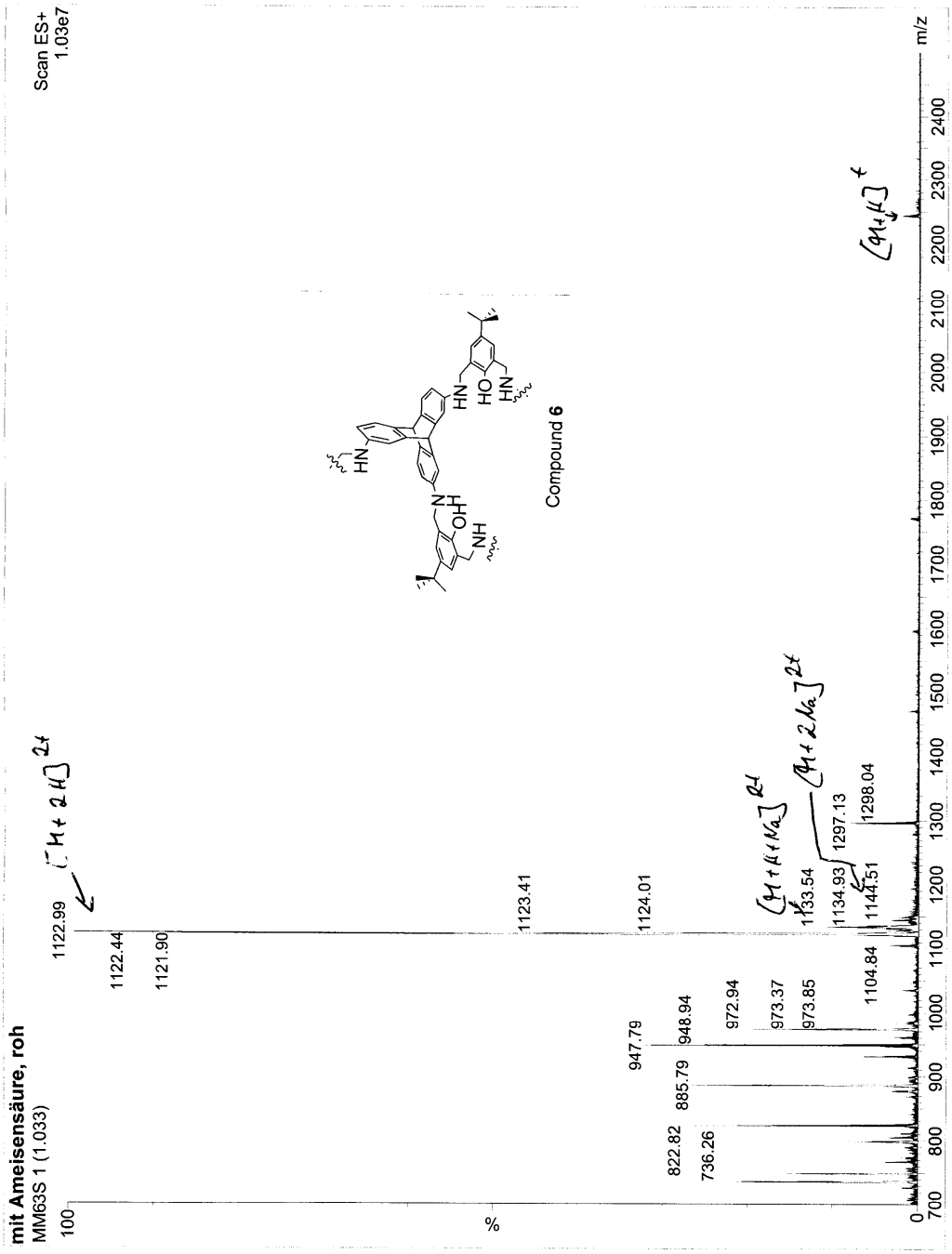
mit Ameisensäure, roh
MM63S 1 (1.033)
Scan ES+
1.03e7
100
%
0
Compound 6
1122.99
1122.44
1121.90
1123.41
1124.01
947.79
948.94
885.79
822.82
736.26
972.94
973.37
973.85
1104.84
1133.54
1134.93
1144.51
1297.13
1298.04
700
800
900
1000
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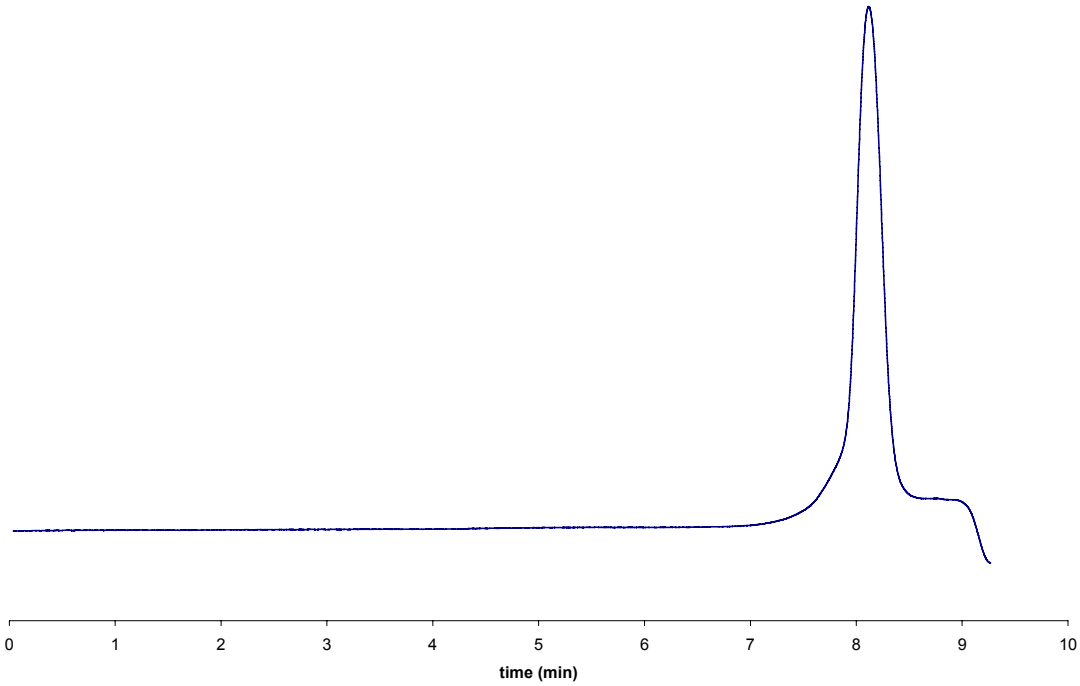
m/z



GPC trace of **6** in THF