Supplementary Materials for

Novel Chiral Dendritic Diphosphine Ligands for Rh(I)-Catalyzed Asymmetric Hydrogenation: Remarkable Structural Effects on Catalytic Properties

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1. General Information

Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques, or performed in a nitrogen-

filled glovebox. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 300 Spectrometer (^{1}H 300 MHz, ^{31}P 121 MHz and ^{13}C 75 MHz respectively). Chemical shift (δ) are given in ppm and are referenced to residual solvent peaks (^{1}H and ^{13}C NMR) or to an external standard (85% H_3PO_4, ^{31}P NMR). Infrared spectra were recorded on a Bruker Tensor 27 spectrophotometer. MALDI-TOF mass spectra were obtained on a BIFLEX _ instrument with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. High resolution mass spectra were recorded on a GCT or a APEX _ spectrometer. Elemental analyses were performed on a Flash EA 1112 Elemental Analyzer. Optical rotations were measured on a AA-10R automatic polarimeter in the solvent indicated. Melting points were uncorrected. All enantiomeric excess values were obtained from GC analysis with a Chrompack CHIR-L-VAL chiral column. All solvents were dried using standard, published methods and were distilled under a nitrogen atmosphere before use. Pyrphos **2** ((R,R)-3,4-bis(diphenylphosphino)pyrrolidine) was prepared according to the reported procedures. [1] All other chemicals were used as received from Aldrich or Acros without further purification.

2. General procedure for synthesis of chiral dendrimer ligands and their characterisation

Typical procedure: Generation 1 acid (103 mg, 0.308 mmol), (3*R*,4*R*)-pyrphos hydrochloride (147 mg, 0.308 mmol), DCC (63 mg, 0.308 mmol), and DAMP (26 mg, 0.210 mmol) were combined in dry, degassed CH_2Cl_2 (10 ml) at ambient temperature. The mixture was stirred for 10 h at the same temperature (TLC monitoring), and the hydrated DCC adduct dicyclohexylurea (DCU) precipitate was removed by filtration .

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After the filtrate was evaporated under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate 2:1,v/v) to afford **1-G$_1$** as a white powder. (202 mg, 87%); m.p.: 78-79_; R_f=0.24 (1:1 petroleum ether / dichloromethane); [_]$_D^{20}$ = +108.0 (c 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.45-7.29 (m, 18H), 7.25-7.04 (m, 12H), 6.70- 6.62 (m, 3H), 5.02 (s, 4H), 4.25-4.08 (m, 1H), 3.99-3.84 (m, 1H), 3.67 (pseudo-t, *J* = 13.8 Hz, 1H), 3.29 (pseudo-t, *J* = 12.0 Hz, 1H), 2.99-2.92 (m, 1H), 2.80-2.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):_ 169.3, 159.7, 138.7, 136.7, 133.6 (m), 133.3, 129.3 (m), 128.7 (m), 128.1, 127.5, 106.2, 104.0, 70.2, 51.1 (m), 48.5 (m), 39.5 (m), 37.5 (m); ^{31}P NMR (121 MHz, $CDCl_3$): _ -11.4, -11.8 (*J* = 12 Hz); IR (KBr): *v*(cm^{-1}) 1633, 1590; MALDI-TOF MS: m/z 756.5 ([M+H]$^+$); HRMS (FAB) m/z found: 756.2795, $C_{49}H_{43}NO_3P_2$ ([M+H]$^+$) requires: 756.2791.

1-G$_2$: A procedure similar to that for the preparation of **1-G$_1$** was used to prerare **1-G$_2$** from generation 2 acid and (3*R*,4*R*)-Pyrphos hydrochloride. The resulting residue was purified by flash chromatography on silica gel to afford **1-G$_2$** as a white powder, yield 82%; m.p.: 70-71_; R_f =0.27 (1:2 petroleum ether / dichloromethane); [_]$_D^{20}$ = +65.0 (c 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.47-7.28 (m, 28H), 7.23-7.01 (m, 12H), 6.67- 6.57 (m, 9H), 5.02 (s, 8H), 4.95-4.86 (m, 4H), 4.24-3.94 (m, 2H), 3.66 (pseudo-t, *J* = 13.5 Hz, 1H), 3.34 (pseudo-t, *J* = 11.7 Hz, 1H), 2.97-2.88 (m, 1H), 2.81-2.77 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):_ 169.4, 160.3, 159.8, 139.0, 138.7, 136.8, 133.6 (m), 133.3, 129.3 (m), 128.8 (m), 128.7, 128.1, 127.6, 106.5, 106.3, 103.8, 101.8, 70.2, 51.3 (m), 48.6 (m), 39.5 (m), 37.5 (m); ^{31}P NMR (121 MHz, $CDCl_3$): _ -11.3, -11.6 (*J* = 12 Hz); IR (KBr): *v*(cm^{-1}) 1634, 1595; MALDI-TOF MS: m/z 1180.8 ([M+H]$^+$); Anal. Calcd for $C_{77}H_{67}NO_7P_2$: C 78.35, H 5.72, N 1.19;

found: C 78.07, H 5.73, N 1.28.

1-G$_3$: A procedure similar to that for the preparation of **1-G$_1$** was used to prerare **1-G$_3$** from generation 3 acid and (3*R*,4*R*)-Pyrphos hydrochloride. The resulting residue was purified by flash chromatography on silica gel to afford **1-G$_3$** as a white powder, yield 87%; m.p.: 68-69_; R_f =0.20 (1:2 petroleum ether / dichloromethane); [_]$_D^{20}$ = +48.0 (c 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.42-7.28 (m, 48H), 7.23-7.01 (m, 12H), 6.69-6.56 (m, 21H), 5.02 (s, 16H), 4.97 (s, 8H), 4.91 (s, 4H), 4.26-3.95 (m, 2H), 3.67 (pseudo-t, *J* = 13.5 Hz 1H), 3.35 (pseudo-t, *J* = 11.7 Hz, 1H), 2.98-2.87 (m, 1H), 2.83-2.79 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):_ 169.3, 160.1, 159.7, 139.1, 138.9, 138.6, 136.7, 133.7 (m), 133.1, 129.2 (m), 128.5, 127.9, 127.5, 106.8, 106.3 (m), 103.7, 101.6, 70.0, 51.3 (m), 48.5 (m), 39.4 (m), 37.4 (m); ^{31}P NMR (121 MHz, $CDCl_3$): _ -11.7, -11.9 (brs); IR (KBr): ν(cm^{-1}) 1634, 1595; MALDI-TOF MS: m/z 2028.7 ($[M+H]^+$); Anal. Calcd for $C_{133}H_{115}NO_{15}P_2$: C 78.72, H 5.71, N 0.69; found: C 78.52, H 5.76, N 0.85.

1-G$_4$: A procedure similar to that for the preparation of **1-G$_1$** was used to prerare **1-G$_4$** from generation 4 acid and (3*R*,4*R*)-Pyrphos hydrochloride. The resulting residue was purified by flash chromatography on silica gel to afford **1-G$_4$** as a white powder, yield 92 %; m.p.: 69-70_; R_f =0.30 (1:4 petroleum ether / dichloromethane); [_]$_D^{20}$ = +20.0 (c 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.38-7.26 (m, 88H), 7.21-6.99 (m, 12H), 6.64-6.53 (m, 45H), 4.97 (s, 32H), 4.91 (s, 16H), 4.87 (s, 8H), 4.83 (s, 4H), 4.23-4.09 (m, 1H), 4.03-3.92 (m, 1H), 3.65 (pseudo-t, *J* = 13.2 Hz 1H), 3.32 (pseudo-t, *J* = 11.7 Hz, 1H), 2.94-2.92 (m, 1H), 2.78-2.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):_ 169.3, 160.2, 160.1, 159.7, 139.2, 139.1, 136.8, 133.6 (m), 129.3 (m), 128.6,

128.0 (m), 127.6, 127.1, 106.4, 103.7, 101.6, 70.1, 69.9, 51.3 (m), 48.5 (m), 39.5 (m), 37.2 (m); ^{31}P NMR (121 MHz, $CDCl_3$): _ -11.3, -11.4 (brs); IR (KBr): ν(cm^{-1}) 1635, 1595; MALDI-TOF MS: m/z 3766.0 ($[M+K]^+$); Anal. Calcd for $C_{245}H_{211}NO_{31}P_2$: C 78.95, H 5.71, N 0.38; found: C 79.21, H 6.00, N 0.48.

6-G$_1$: A procedure similar to that for the preparation of **1-G$_1$** was used to prerare **6-G$_1$** from generation 1 back-folding dendritic acid and (3*R*,4*R*)-Pyrphos hydrochloride. The resulting residue was purified by flash chromatography on silica gel to afford **6-G$_1$** as a white powder, yield 84%; m.p.: 79-80_; R_f =0.21 (dichloromethane); $[\_]_D^{20}$ = +104.0 (c 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.57-7.29 (m, 18H), 7.23-7.06 (m, 13H), 6.61 (d, *J* = 9 Hz, 1H), 6.50 (d, *J* = 9 Hz, 1H), 5.17-4.99 (m, 4H), 4.27-4.13 (m, 1H), 4.09-3.96 (m, 1H), 3.85 (pseudo-t, *J* = 13.1 Hz, 1H), 3.30 (pseudo-t, *J* = 12.0 Hz, 1H), 2.92-2.90 (m, 1H), 2.81-2.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):_ 165.4, 155.8, 155.7, 137.0, 133.7 (m), 133.3, 130.2, 129.1 (m), 128.6 (m), 127.5 (m), 126.7, 117.2, 106.1, 105.8, 70.4, 49.5 (m), 47.9 (m), 38.8 (m), 37.9 (m); ^{31}P NMR (121 MHz, $CDCl_3$): _ -12.6, -12.9 (J = 12 Hz); IR (KBr): ν(cm^{-1}) 1640, 1594; MALDI-TOF MS: m/z 756.6 ($[M+H]^+$); HRMS (EI) m/z found: 755.2703, $C_{49}H_{43}NO_3P_2$ (M^+) requires: 755.2718.

6-G$_2$: A procedure similar to that for the preparation of **1-G$_1$** was used to prerare **6-G$_2$** from generation 2 back-folding dendritic acid and (3*R*,4*R*)-Pyrphos hydrochloride. The resulting residue was purified by flash chromatography on silica gel to afford **6-G$_2$** as a white powder, yield 77%; m.p.: 69-70_; R_f =0.38 (dichloromethane); $[\_]_D^{20}$ = +66.0 (c 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.43-7.29 (m, 31H), 7.22-7.09 (m, 10H), 6.79- 6.53 (m, 8H), 5.13-4.94 (m, 12H), 4.19-3.97 (m, 2H), 3.78

(pseudo-t, *J* = 13.5 Hz, 1H), 3.26 (pseudo-t, *J* = 11.7 Hz, 1H), 2.88-2.86 (m, 1H), 2.80-2.77 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):_ 165.3, 160.1 (m), 156.0, 155.7, 139.5 (m), 136.6 (m), 136.0 (m), 133.8 (m), 130.2, 129.0 (m), 128.5 (m), 127.8 (m), 117.3, 106.3, 106.2, 105.6, 101.7, 71.0, 70.2 (m), 49.3 (m), 47.8 (m), 39.2 (m), 38.0 (m); ^{31}P NMR (121 MHz, $CDCl_3$): _ –12.6, -13.1; IR (KBr): ν(cm^{-1}) 1634, 1596; MALDI-TOF Ms: m/z 1180.8 ($[M+H]^+$). Anal. Calcd for $C_{77}H_{67}NO_7P_2$: C 78.35, H 5.72, N 1.19; found: C 78.40, H 6.02, N 0.95.

6-G$_3$: A procedure similar to that for the preparation of **1-G$_1$** was used to prerare **6-G$_3$** from generation 3 back-folding dendritic acid and (3*R*,4*R*)-Pyrphos hydrochloride. The resulting residue was purified by flash chromatography on silica gel to afford **6-G$_3$** as a white powder, yield 61%; m.p.: 67-68_; R_f =0.39 (dichloromethane); $[\_]_D^{20}$ = +26.0.0 (c 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.39-7.27 (m, 38H), 7.23-6.95 (m, 22H), 6.78-6.50 (m, 21H), 5.15-4.87 (m, 28H), 4.25-3.96 (m, 2H), 3.81 (pseudo-t, *J* = 12.0 Hz 1H), 3.26 (pseudo-t, *J* = 12.0 Hz, 1H), 2.87 (m, 1H), 2.77 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):_ 165.3, 160.1 (m), 156.0, 155.6, 139.5 (m), 136.8, 133.7 (m), 130.3, 129.0 (m), 128.4 (m), 127.6 (m), 117.4, 106.5, 106.2, 105.5, 101.7 (m), 71.1, 70.4 , 70.1, 49.4 (m), 47.9 (m), 39.2 (m), 38.1 (m); ^{31}P NMR (121 MHz, $CDCl_3$): _ –12.9, -13.4; IR (KBr): ν(cm^{-1}) 1637, 1596; MALDI-TOF MS: m/z 2029.0 ($[M+H]^+$); Anal. Calcd for $C_{133}H_{115}NO_{15}P_2$: C 78.72, H 5.71, N 0.69; found: C 78.46, H 5.74, N 0.79.

3. General procedure for hydrogenation reaction and catalyst recycling using Rh(1-G$_3$) as catalyst

In-situ catalyst preparation: Dendritic ligand **1-G$_3$** (11.0mg, 5.4_10^{-3}mmol) and

$[Rh(COD)_2]BF_4$ (2.2mg, 5.4_10^{-3}mmol) were stirred at r.t. for 30 min in CH_2Cl_2 (3ml) under nitrogen. Solvent was removed under reduced pressure to yield an orange-yellow solid. The resulting catalyst was dissolved in toluene (10 ml, 5.4_10^{-4} mmol/ml), which was directly used in the following catalytic reaction without further purification.

Asymmetric hydrogenation: In a 50 ml glass-lined stainless steel reactor with a magnetic stirring bar was charged with substrate **4** (200 mg, 0.975 mmol), the above prepared catalyst Rh(**1**-$\mathbf{G_3}$) (2.26ml, 1.22 x 10^{-3} mmol) and methanol/toluene (20/10 ml). The autoclave was closed and was pressurized with H_2 to 60 atm. The mixture was stirred with magnetic under the H_2 pressure at 20 ^{0}C for 30 min. After carefully venting hydrogen, most of the reaction solvent was removed under reduced pressure. Methanol was then added to this mixture and the catalyst was precipitated and recovered via filtration. The recovered catalyst was reused in the next catalytic cycle. The methanol layer was used to determine the conversion and enantioselectivity of the reduced product by GC with a 25 m Chiralsi L-Val capillary column.

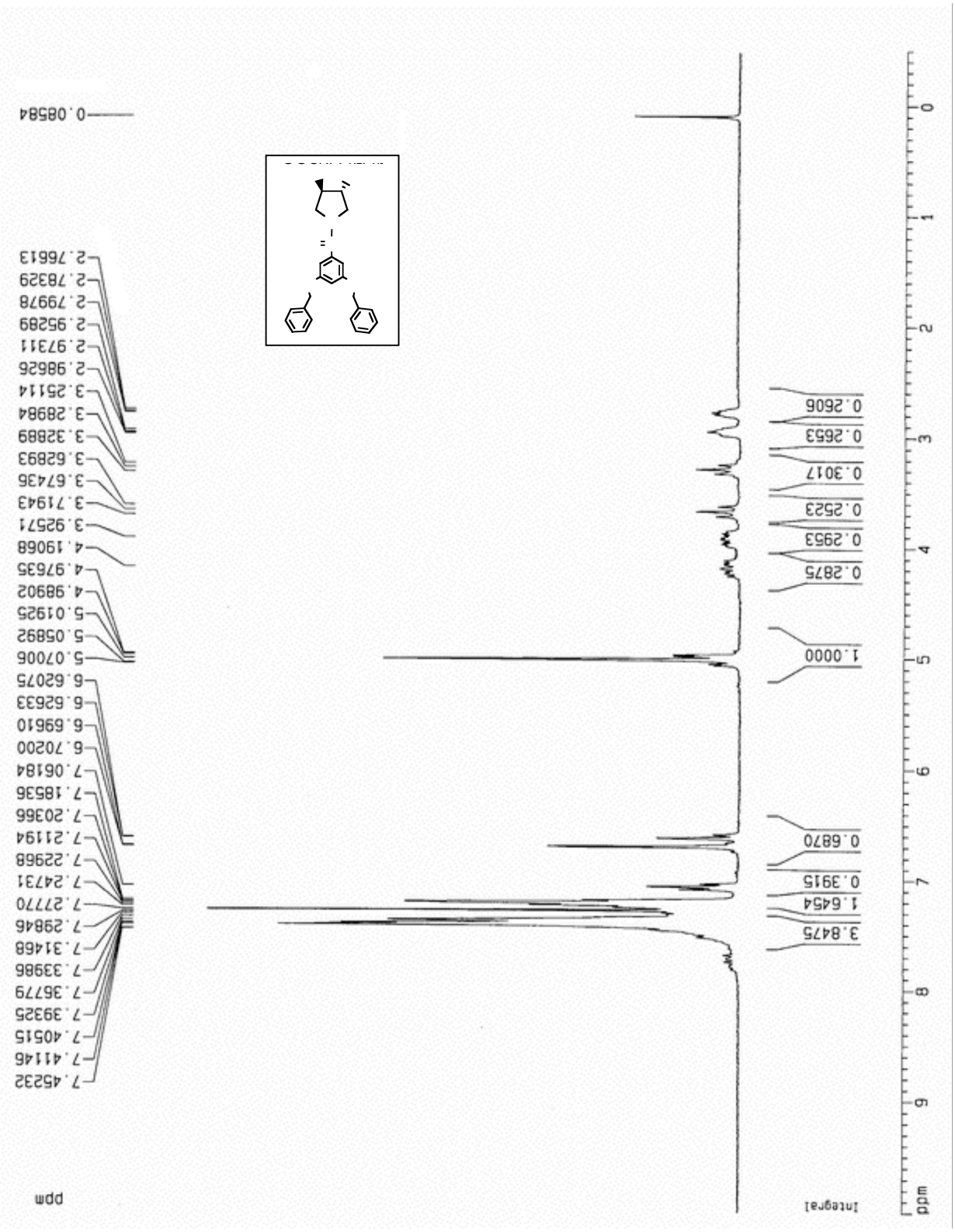
4. General procedure for measurement of conversion-time data with different generation dendrimer catalysts

The catalyst preparation and hydrogenation experiments were carried out by using the above procedures. For sample taking, the stirrer was stopped at distinct times, a small quantity of the reaction mixtures was taken with a dipping tube. The stirrer was then restarted and the pressure reset. The sample was used to determine the ee value and conversion by using ^{1}H NMR and GC.

5. References

1 Nagel, U.; Kinzel, E. ; Andrade, J.; Prescher, G. *Chem. Ber.*, **1986**,119,3326.

6. **Spectra of dendritic ligands**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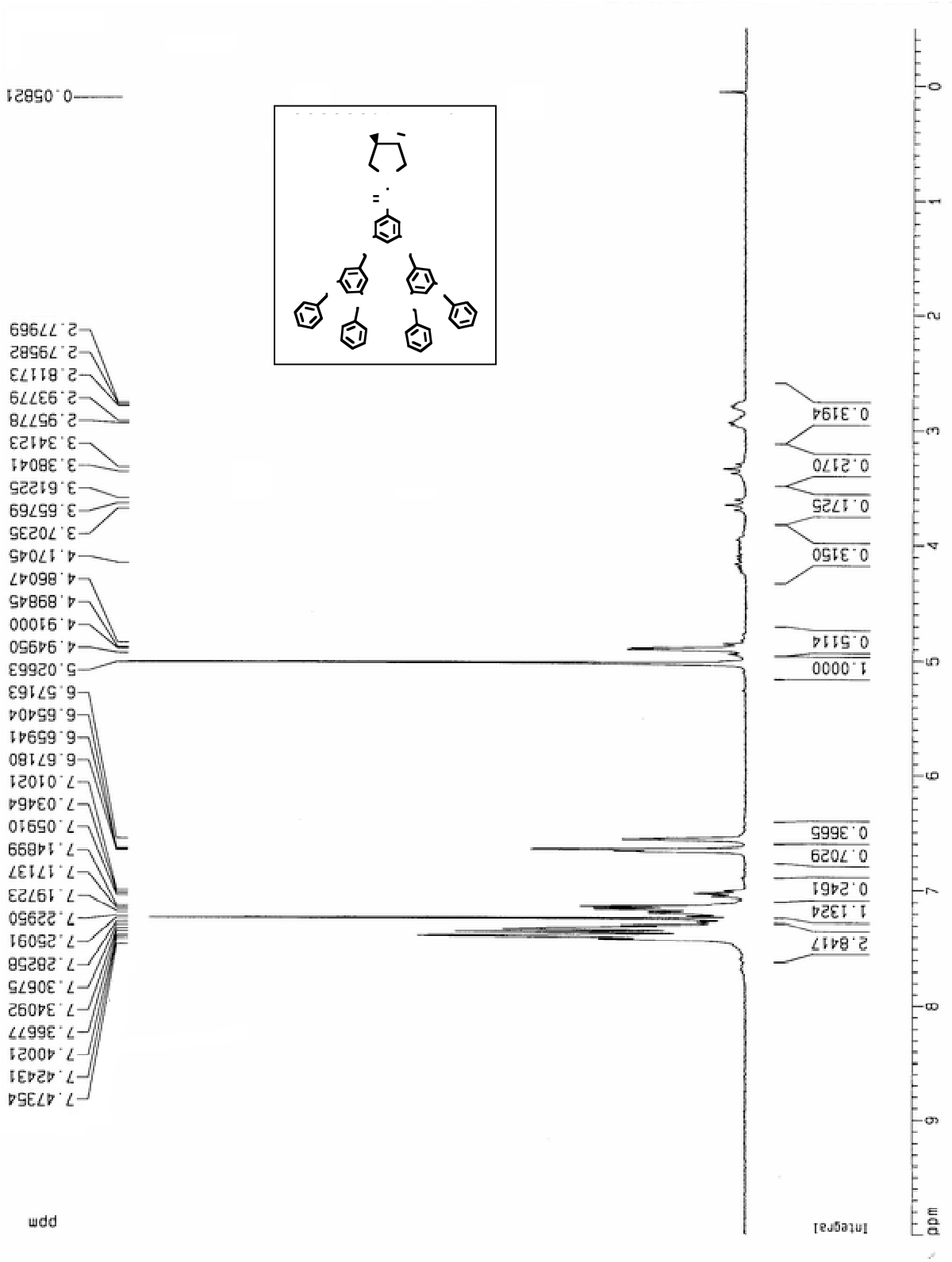
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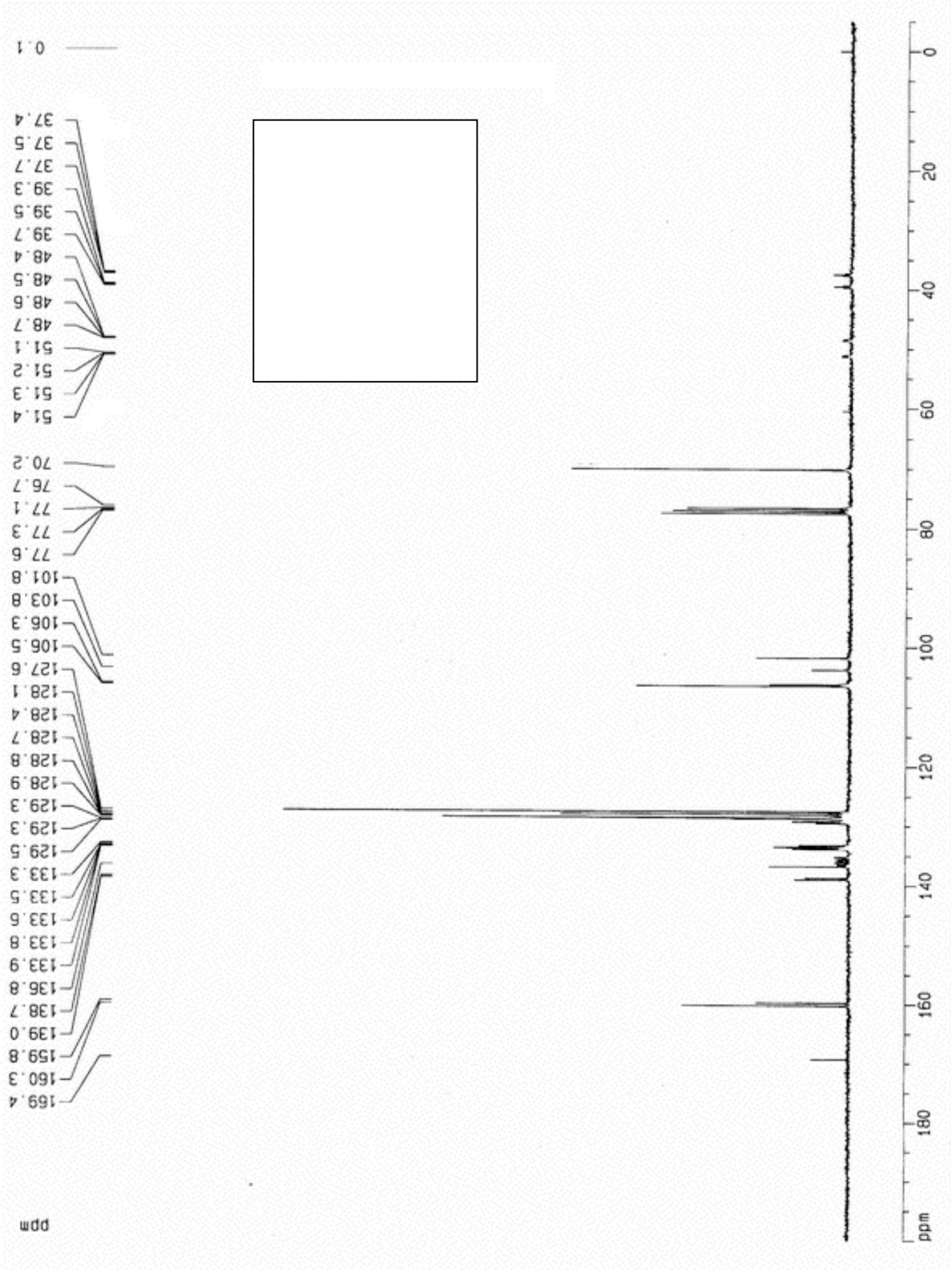
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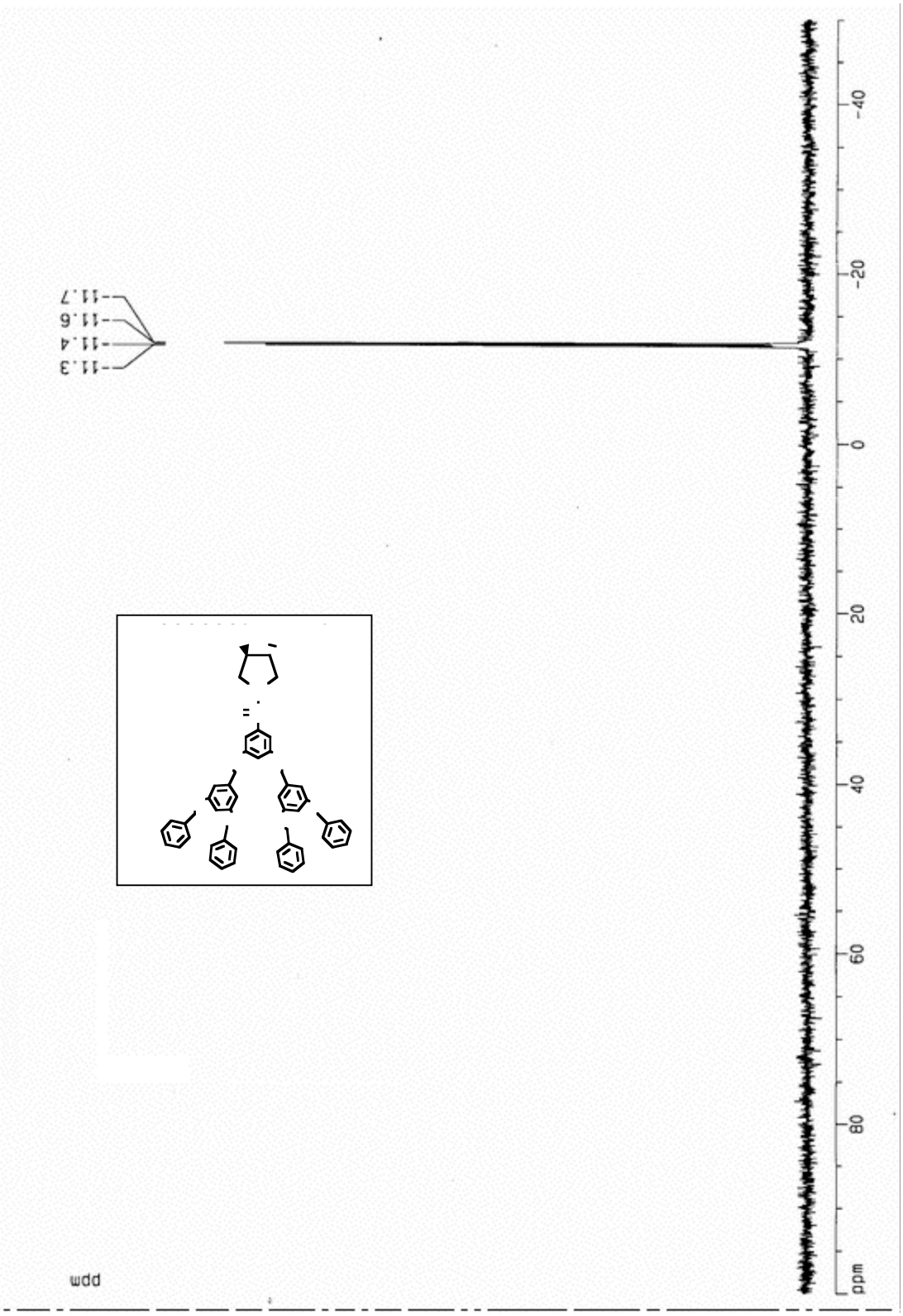
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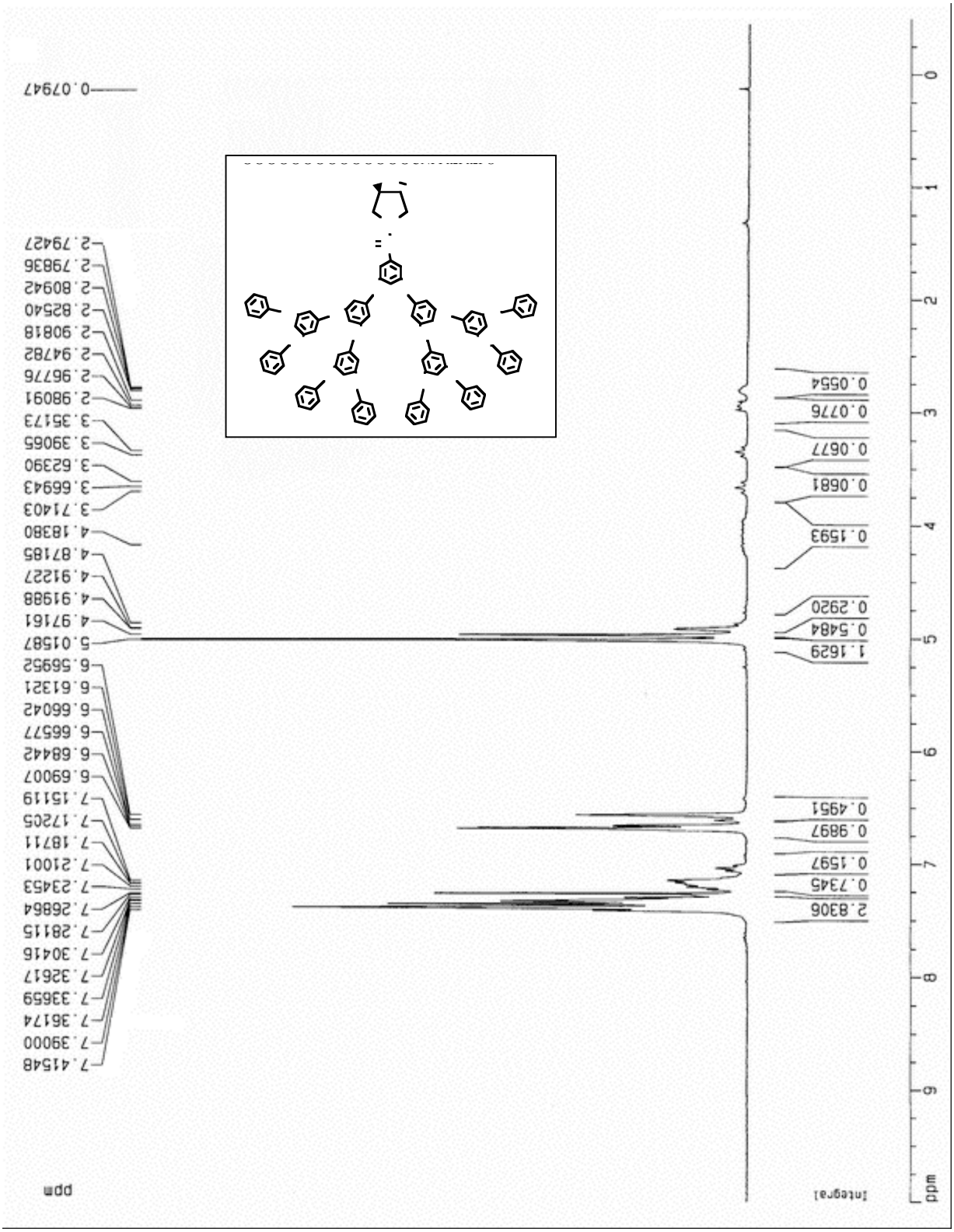
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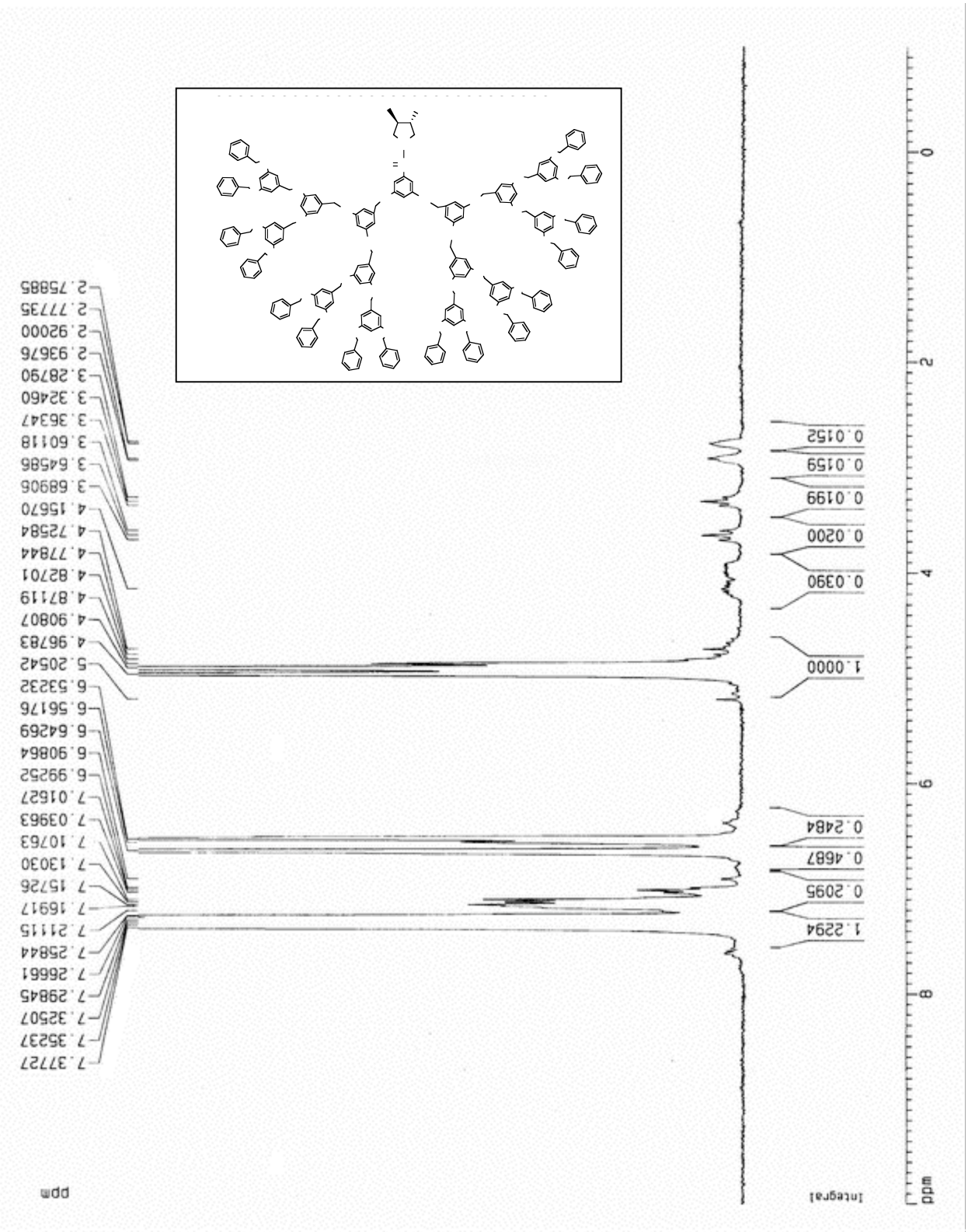
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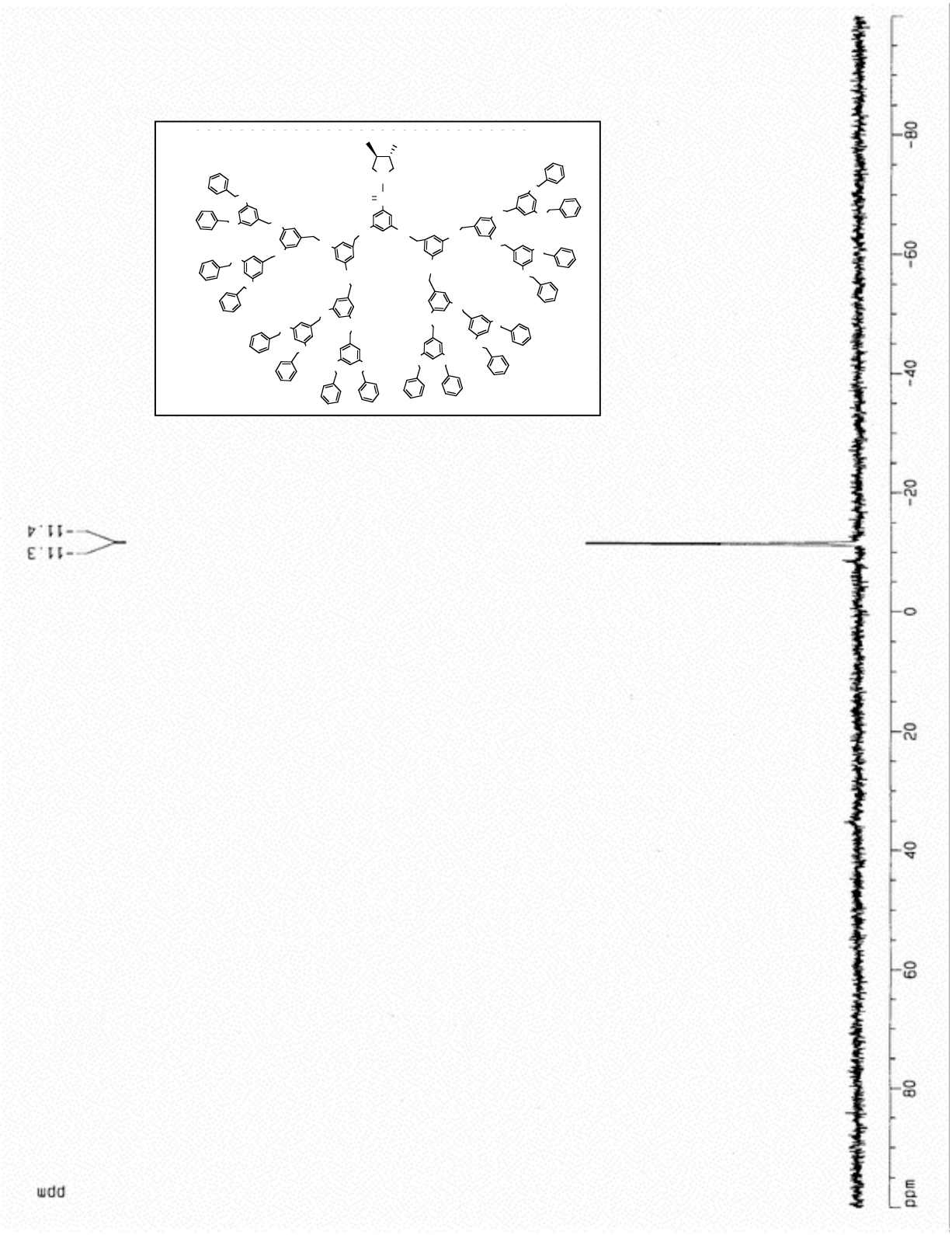
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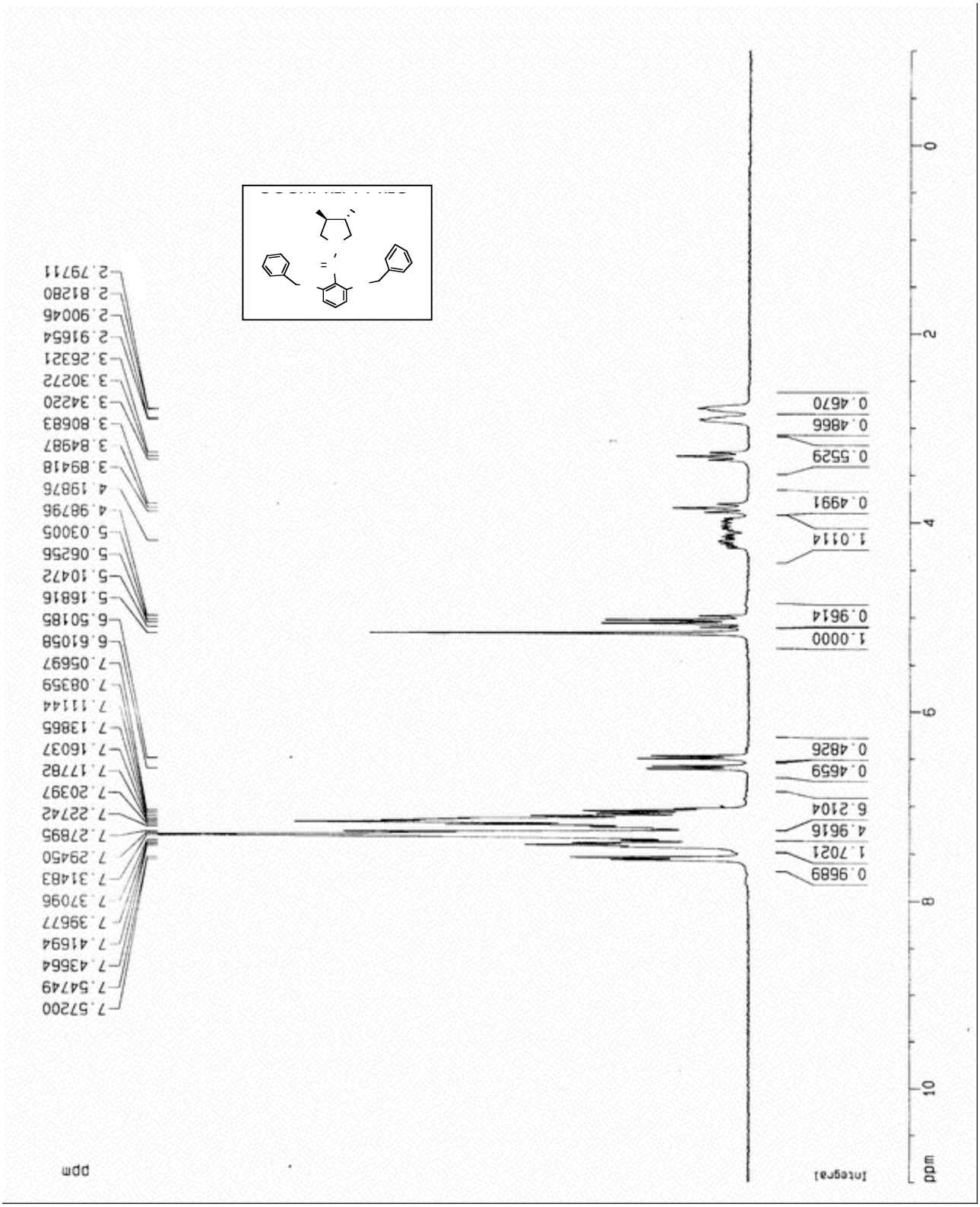
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0.4659
0.4826
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0.9614
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0.5529
0.4866
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7.43564
7.41694
7.39677
7.37096
7.31483
7.29450
7.27895
7.22742
7.20397
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7.16037
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7.11144
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7.05697
6.61058
6.50185
5.16816
5.10472
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4.19876
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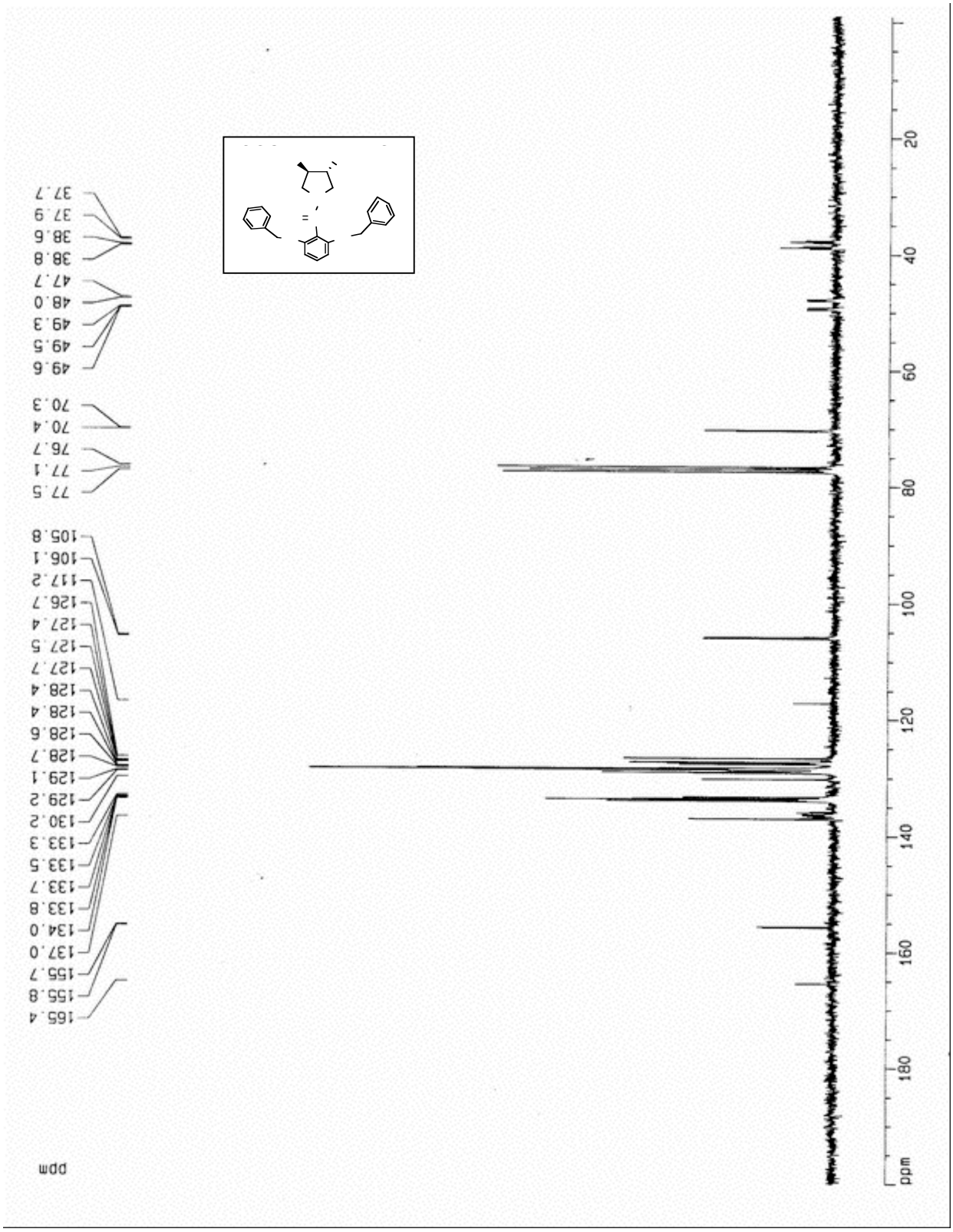
2.81280
2.79711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60
80
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120
140
160
180
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37.9
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38.8
47.7
48.0
49.3
49.5
49.6
70.3
70.4
76.7
77.1
77.5
105.8
106.1
117.2
126.7
127.4
127.5
127.7
128.4
128.4
128.6
128.7
129.1
129.2
130.2
133.3
133.5
133.7
133.8
134.0
137.0
155.7
155.8
165.4

ppm
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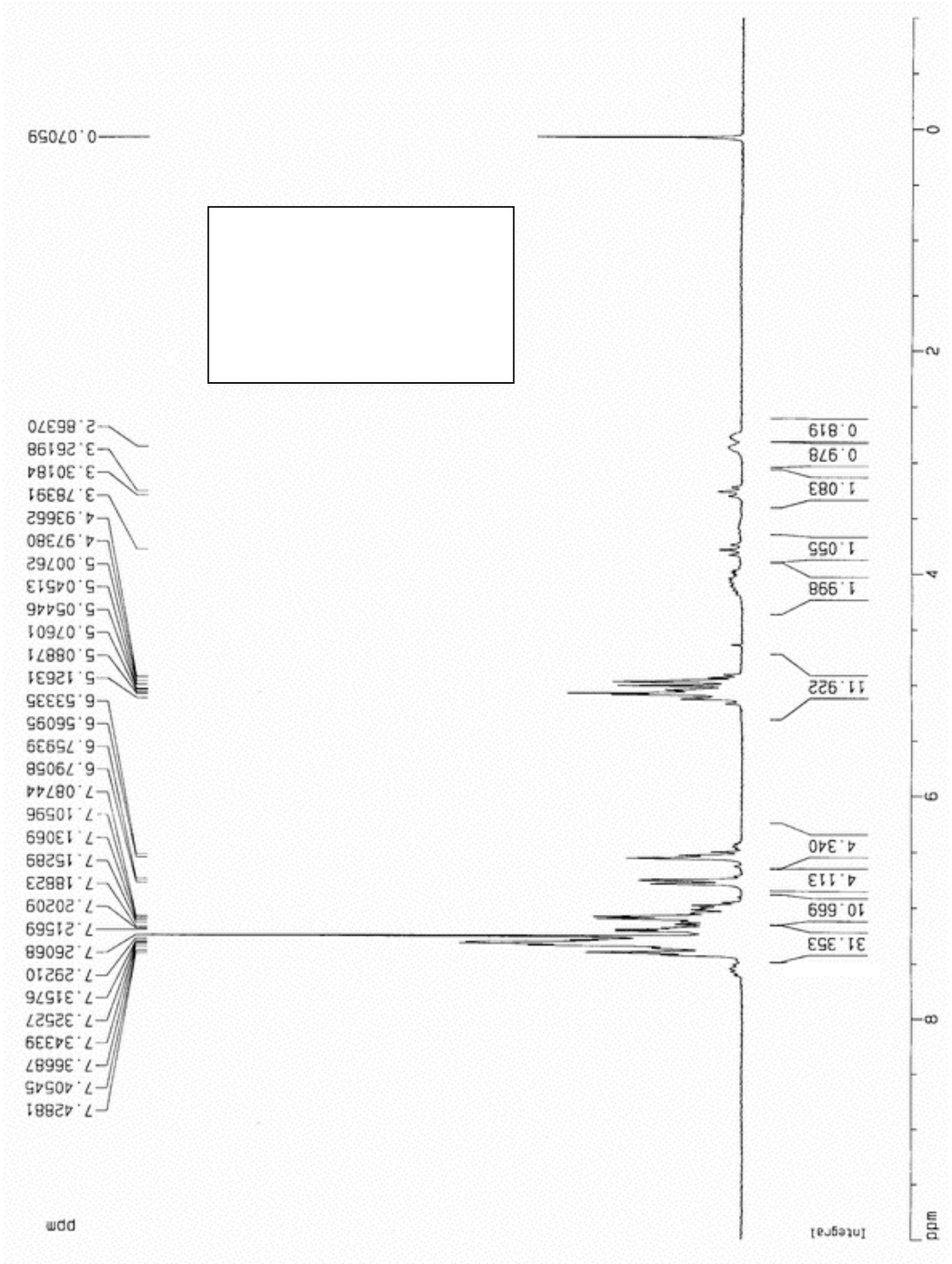
-12.9
-12.7
-12.6
ppm
80
60
40
20
0
-20
-40
-60
-80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5.12631
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6.56095
6.75939
6.79058
7.08744
7.10596
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7.15289
7.18823
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7.42881
ppm
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1.055
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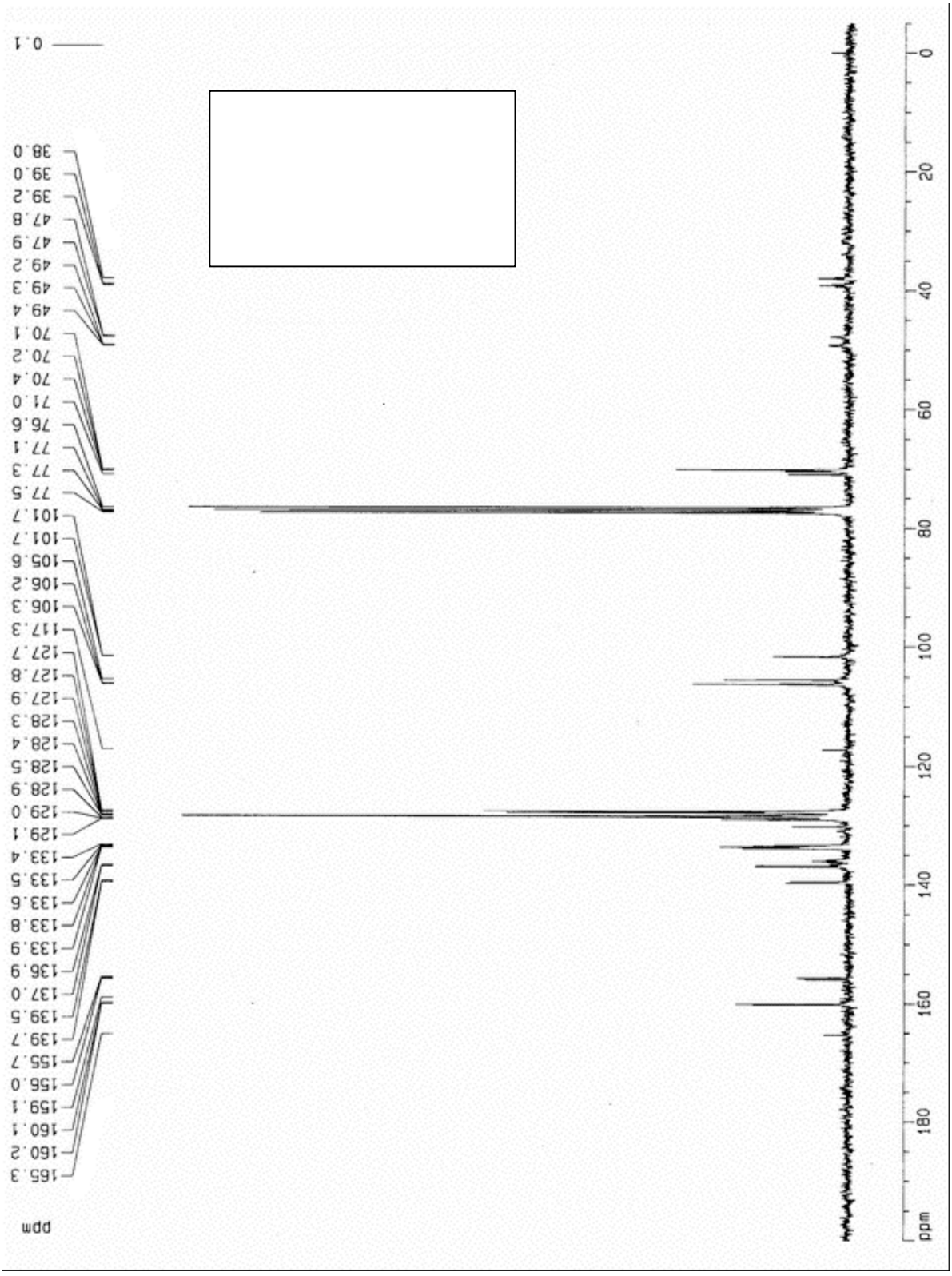
4.113
10.669
31.353
Integral
ppm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49.3
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70.4
71.0
76.6
77.1
77.3
77.5
101.7
101.7
105.6
106.2
106.3
117.3
127.7
127.8
127.9
128.3
128.4
128.5
128.9
129.0
129.1
133.4
133.5
133.6
133.8
133.9
136.9
137.0
139.5
139.7
155.7
156.0
159.1
160.1
160.2
165.3
ppm
0
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40
60
80
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180
ppm

ppm
40
20
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-40
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ppm
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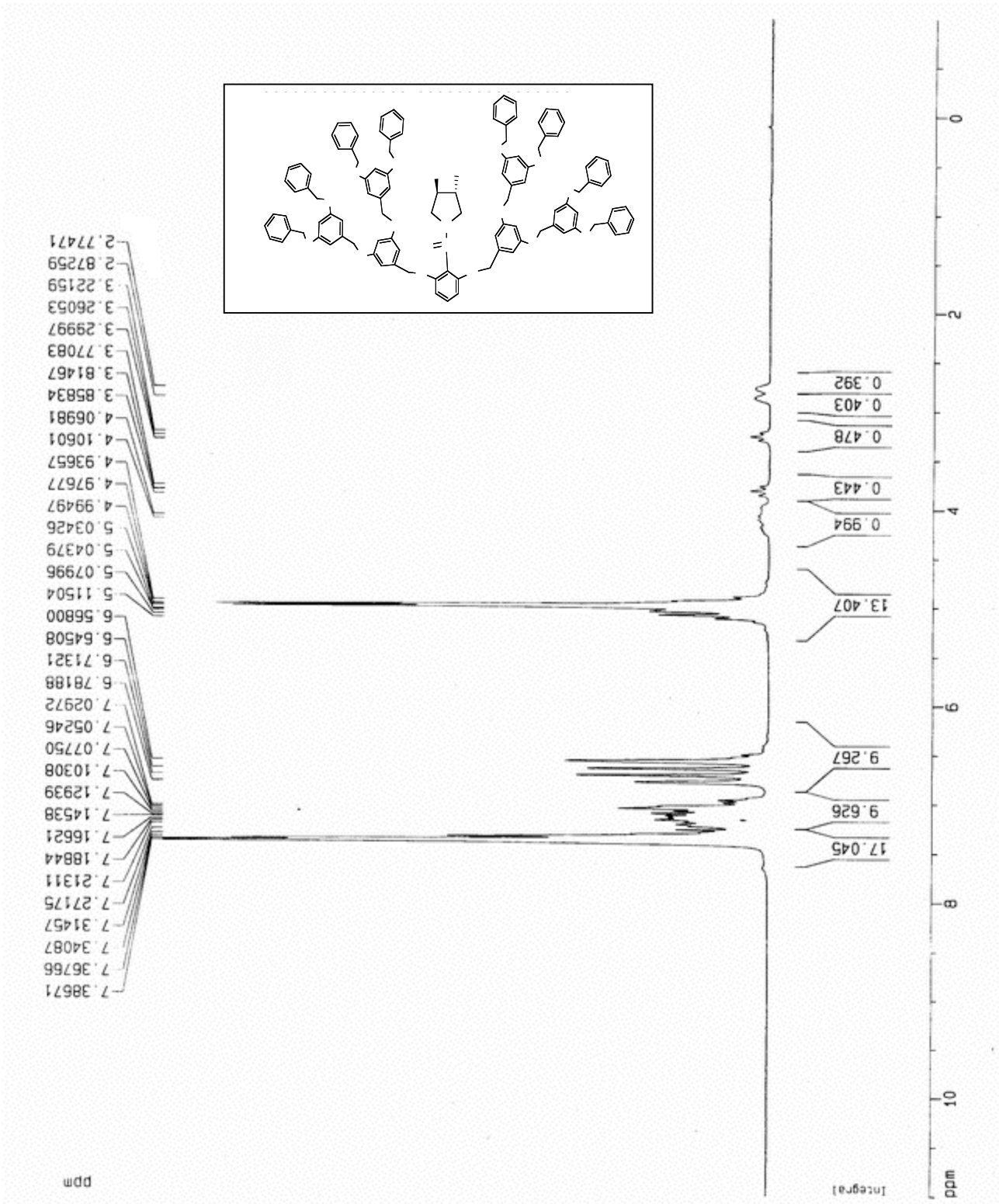
-13.1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3.22159
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3.81467
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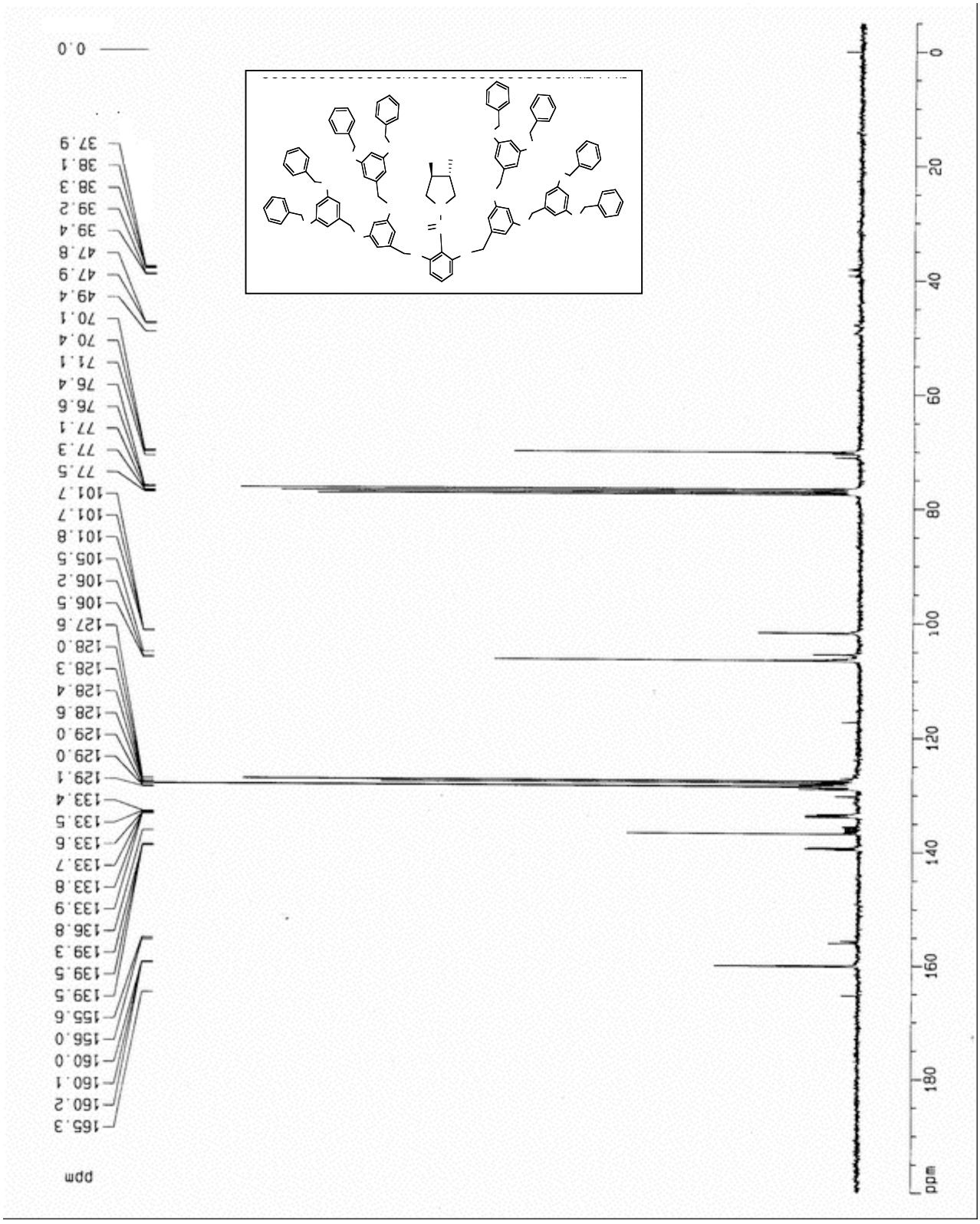
4.10601
4.93657
4.97677
4.99497
5.03426
5.04379
5.07996
5.11504
6.56800
6.64508
6.71321
6.78188
7.02972
7.05246
7.07750
7.10308
7.12939
7.14538
7.16621
7.18844
7.21311
7.27175
7.31457
7.34087
7.36766
7.38671
ppm
0.392
0.403
0.478
0.443
0.994
13.407
9.267
9.626
17.045
Integral
0
2
4
6
8
10
ppm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38.1
38.3
39.2
39.4
47.8
47.9
49.4
70.1
70.4
71.1
76.4
76.6
77.1
77.3
77.5
101.7
101.7
101.8
105.5
106.2
106.5
127.6
128.0
128.3
128.4
128.6
129.0
129.0
129.1
133.4
133.5
133.6
133.7
133.8
133.9
136.8
139.3
139.5
139.5
155.6
156.0
160.0
160.1
160.2
165.3
ppm
0
20
40
60
80
100
120
140
160
180
ppm

ppm
10
0
-10
-20
-30
-40
-50
13.4
13.4
12.9

32.7106
32.8863
33.6310
33.8066
34.2888
34.4644
35.2172
35.3926
ppm
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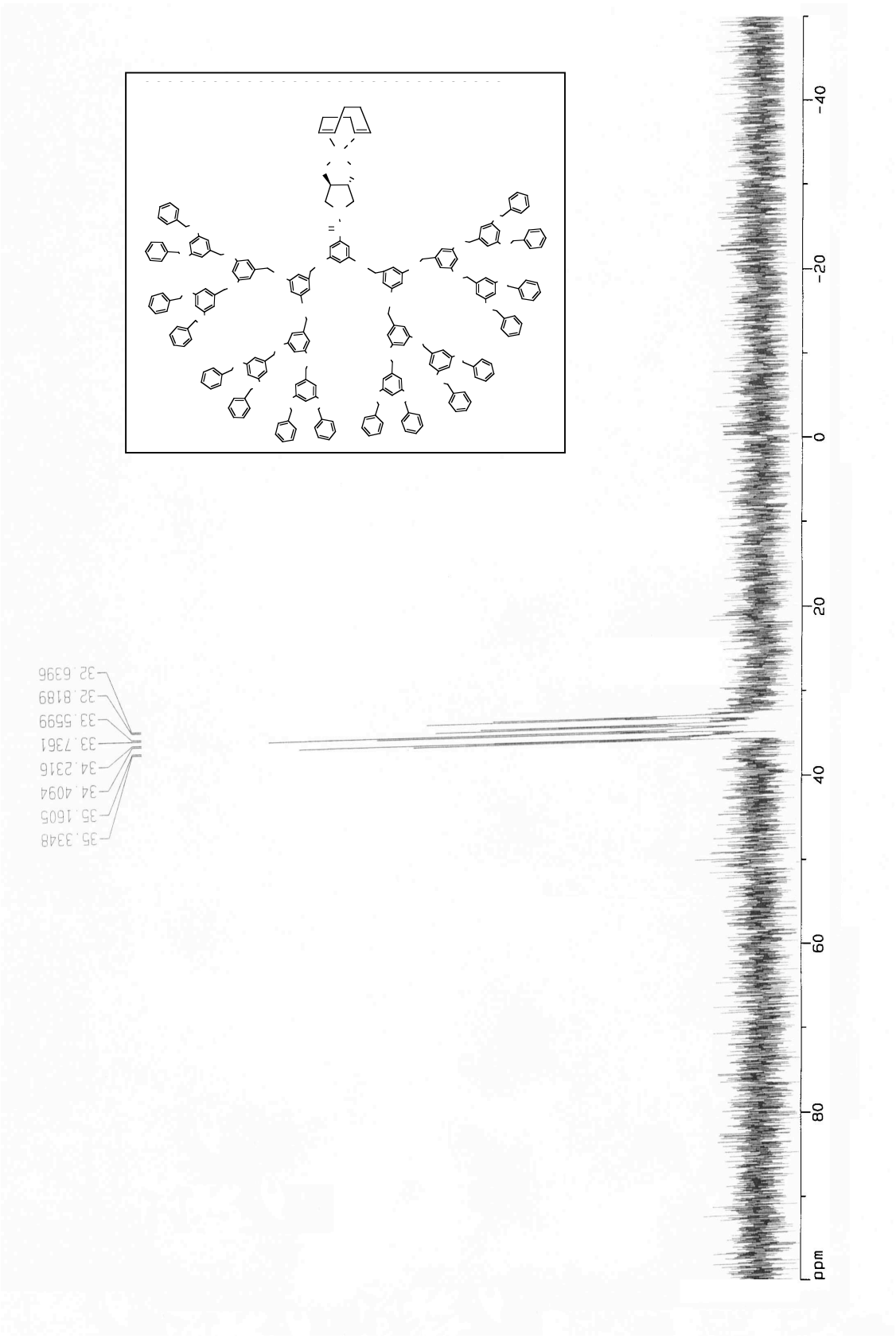
-40
-20
0
20
40
60
80
ppm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35.3348
40
20
0
-20
-40
60
80
ppm