Supplementary Information for

Novel Spiroketal-Based Diphosphites Ligands for Hydroformylation of Terminal and Internal Olefins

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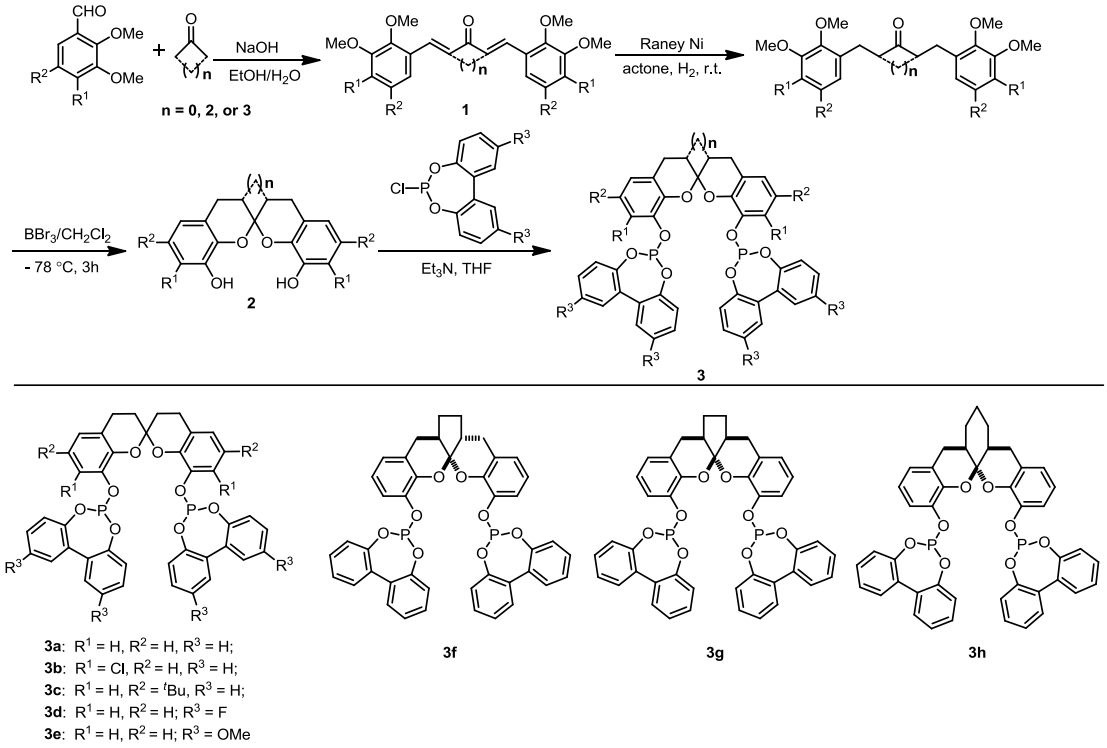
1. General methods

Unless otherwise noted, all manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. Melting points were measured on a RY-I apparatus and uncorrected. ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR spectra were recorded on a Varian Mercury 300 MHz or 400 MHz spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^{1}H NMR), $CDCl_3$ (^{13}C NMR), external 85% H_3PO_4 (^{31}P NMR), or external CF3CO2H (19F NMR) references, respectively. EI (70 eV) and ESI mass spectra were obtained on HP5989 A and Mariner LC-TOF spectrometers, respectively. HRMS (EI) and HRMS (ESI) were determined on Waters Micromass GCT Premier and APEX III 7.0 TESLA FTMS spectrometers, respectively. The IR spectra were measured on a NICOLET AVATAR 330 or a Bruker Tensor 27 spectrometer. GC analyses were measured on an Agilent 7820A system.

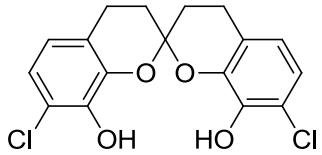
2. Ligand synthesis and characterization



2.1. Synthesis of the diphenols 2.

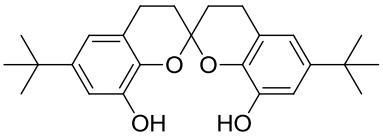
Diphenols **2a,** were synthesized by following a literature procedure.[1]

7,7'-Dichloro-2,2'-spirobi[chroman]-8,8'-diol (2b)



White solid, 32% yield, M.P. 189 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.90 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 5.16 (*br* s, 2H), 3.05-2.97 (m, 4H), 2.42-2.35 (m, 2H), 2.12-2.01 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.4, 139.4, 124.2, 121.9, 120.2, 113.7, 96.8, 30.4, 19.3 ppm. FTIR (neat): 3455, 2924, 2853, 1586, 1470, 1452, 1186, 1143, 943, 798 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{17}H_{13}Cl_2O_4^-$: 351.0196, Found: 351.0183 $(M - H)^-$.

6,6'-Di-*tert*-butyl-2,2'-spirobi[chroman]-8,8'-diol (2c)



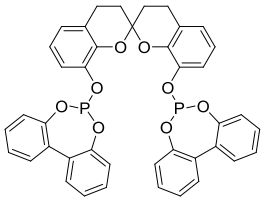
White solid, 50% yield, M.P. 182 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.81 (s, 2H), 6.67 (s, 2H), 5.16 (s, 2H), 3.18-3.11 (m, 2H), 2.81-2.76 (m, 2H), 2.31-2.28 (m, 2H), 2.06-2.00 (m, 2H), 1.27 (s, 18H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.5, 143.9, 136.8, 1120.6, 116.7, 110.6, 97.3, 34.2, 31.4, 31.3, 20.9 ppm. FTIR (neat): 3027, 2950, 1676, 1597, 1495, 1448, 1432, 1327, 1221, 1181, 908 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{25}H_{33}O_4^+$: 397.2373, Found: 397.2366 $(M + H^+)$.

2.2 Preparation and characterization of Ligand 3a-3h, general procedure.

PCl_3 (4.0 mmol) was added dropwise to a solution of (1,1'-biphenyl)-2,2'-diol (2.0 mmol) in toluene (3 mL) at room temperature. The resulting mixture was then heated to reflux for 12 h. The solvent and the excessive PCl_3 was removed under vacuum. A solution of diol **2** (0.3 mmol) in THF was then added dropwise to a solution of phosphorochloridites and triethylamine (4.0 mmol) in THF (1 mL) at 0 °C. After

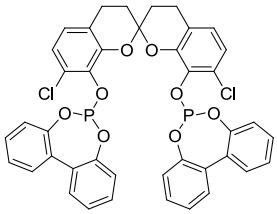
stirring at room temperature for 12 h, the precipitated $Et_3N{\cdot}HCl$ salt were filtered off, and the solvent of the filtrate was removed under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EA = 10/1) to afford the product ligand **3**.

8,8'-Bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin-6-yloxy)-2,2'-spirobi[chroman] (3a)



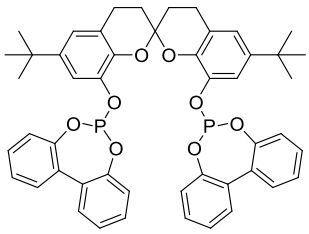
White solid, 50% yield, m.p. 90 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.39 (m, 4H), 7.35-7.31 (m, 2H), 7.26-7.14 (m, 9H), 6.91-6.85 (m, 5H), 6.79-6.76 (m, 2H), 3.67-3.58 (m, 2H), 2.82-2.77 (m, 2H), 2.36-2.32 (m, 2H), 2.09-2.01 (m, 2H) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): 146.6 ppm. FTIR (neat): 2958, 2866, 1593, 1473, 1438, 1180, 1013, 930, 902, 755 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{41}H_{31}O_8P_2^+$: 713.1489, Found: 713.1480 ($M + H^+$).

6,6'-(7,7'-Dichloro-2,2'-spirobi[chroman]-8,8'-diyl)bis(oxy)didibenzo[*d,f*][1,3,2]dioxaphosphepine (3b)



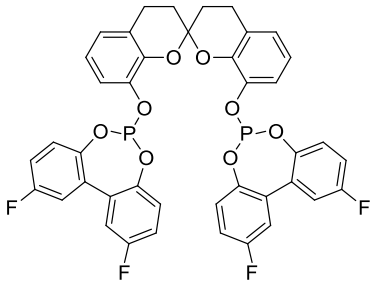
White solid, 86% yield, m.p. 105 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.21 (m, 14H), 6.96-6.84 (m, 6H), 3.42-3.34 (m, 2H), 3.06-3.00 (m, 2H), 2.42-2.37 (m, 2H), 2.07-2.00 (m, 2H) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): 145.9 ppm. FTIR (neat): 3064, 2976, 2898, 1589, 1497, 1471, 1435, 1244, 1182, 903, 766 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{41}H_{29}Cl_2O_8P_2^+$: 781.0709, Found: 781.0705 ($M + H^+$).

6,6'-(6,6'-di-*tert*-butyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(oxy)didibenzo[*d,f*][1,3,2]dioxaphosphepine (3c)



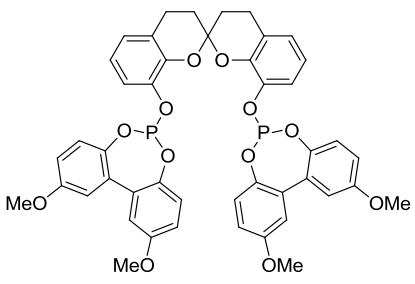
White solid, 81% yield, m.p. 95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.26 (m, 8H), 7.22-7.17 (m, 6H), 6.89-6.86 (m, 4H), 6.79-6.77 (m, 2H), 3.71-3.62 (m, 2H), 2.83-2.77 (m, 2H), 2.39-2.34 (m, 2H), 2.15-2.05 (m, 2H), 1.16 (s, 18H) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): 147.0 ppm. FTIR (neat): 2958, 2864, 1593, 1487, 1435, 1202, 1181, 904, 730 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{49}H_{47}O_8P_2^+$: 825.2741, Found: 825.2749 ($M + H^+$).

8,8'-Bis(2,10-difluorodibenzo[*d,f*][1,3,2]dioxaphosphepin-6-yloxy)-2,2'-spirobi[chroman] (3d)



White solid, 89% yield, m.p. 109 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.12-7.00 (m, 8H), 6.90-6.74 (m, 8H), 6.60-6.55 (m, 2H), 3.55-3.49 (m, 2H), 2.82-2.75 (m, 2H), 2.36-2.30 (m, 2H), 2.09-2.01 (m, 2H), ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): ^{31}P NMR (121 MHz, $CDCl_3$): 147.3 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.5, -117.9 ppm; FTIR (neat): 2983, 2891, 1588, 1473, 1431, 1182, 861, 769 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{41}H_{27}F_4O_8P_2^+$: 785.1112, Found: 785.1102 ($M + H^+$).

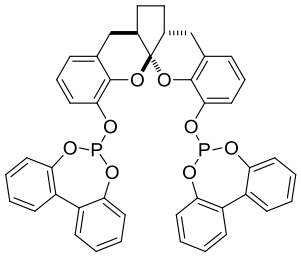
8,8'-Bis(2,10-dimethoxydibenzo[*d,f*][1,3,2]dioxaphosphepin-6-yloxy)-2,2'-spirobi[chroman] (3e)



White solid, 76% yield, M.P. 120 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.08 (d, *J* = 8.7

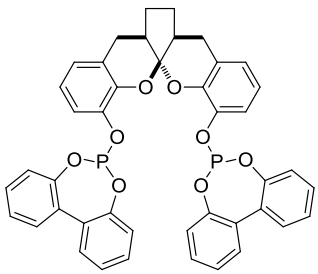
Hz, 2H), 6.95-6.85 (m, 10H), 6.82-6.74 (m, 6H), 3.81 (s, 6H), 3.78 (s, 6H), 3.69-3.58 (m, 2H), 2.84-2.77 (m, 2H), 2.38-2.32 (m, 2H), 2.12-2.01 (m, 2H) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): 146.7 ppm. FTIR (neat): 3057, 2952, 2836, 1595, 1480, 1436, 1201, 1034, 934, 904, 735 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{45}H_{39}O_{12}P_2^+$: 833.1911, Found: 833.1910 ($M + H^+$).

(5aR,7aR)-1,12-Bis(dibenzo[d,f][1,3,2]dioxaphosphepin-6-yloxy)-5,5a,6,7,7a,8-hexahydrocyclopenta[1,2-*b*:1,5-*b'*]dichromene (3f)



White solid, 95% yield, M.P. 92 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.35 (m, 4H), 7.22-7.14 (m, 8H), 7.02-6.78 (m, 10H), 3.17-3.12 (m, 2H), 2.73-2.63 (m, 4H), 2.03-1.98 (m, 2H), 1.56-1.48 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): ^{31}P NMR (121 MHz, $CDCl_3$): 148.5 ppm. FTIR (neat): 3059, 2950, 2836, 1590, 1497, 1472, 1435, 1244, 1204, 1182, 903, 766, 738 cm^{-1}. EI-MS (70 eV) m/z: 408 (M^+); HRMS (ESI) m/z: Calcd. For $C_{43}H_{33}O_8P_2^+$: 739.1645, Found: 739.1637 ($M + H^+$).

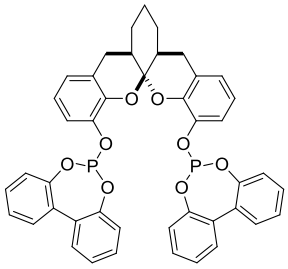
(5aR,7aS,13ar)-1,12-Bis(dibenzo[d,f][1,3,2]dioxaphosphepin-6-yloxy)-5,5a,6,7,7a,8-hexahydrocyclopenta[1,2-b:1,5-b']dichromene (3g)



White solid, 75% yield, M.P. 100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.05 (m, 14H), 6.96-6.67 (m, 8H), 3.46-3.40 (m, 2H), 2.89-2.83 (m, 1H), 2.72-2.68 (m, 2H), 2.39-2.29 (m, 1H), 2.00-1.94 (m, 2H), 1.66-1.42 (m, 2H) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): 147.6 (d, J = 3.1 Hz), 147.2 (d, J = 3.1 Hz) ppm. FTIR (neat): 2982, 2893, 2836, 1590, 1473, 1434, 1244, 1203, 1182, 902, 766 cm^{-1}. HRMS (ESI) m/z: Calcd.

For $C_{43}H_{33}O_8P_2^+$: 739.1645, Found: 739.1639 ($M + H^+$).

(5aR,8aS,14ar)-1,13-Bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin-6-yloxy)-5a,6,7,8,8a, 9-hexahydro-5*H*-chromeno[3,2-d]xanthene (3h)



White solid, 77% yield, M.P. 110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.35 (m, 4H), 7.31-7.28 (m, 2H), 7.22-7.11 (m, 8H), 6.86-6.83 (m, 6H), 6.77-6.74 (m, 2H), 3. 88 (dd, *J* = 16.4, 6.0 Hz, 1H), 3.39 (dd, *J* = 15.6, 13.6 Hz, 1H), 2.65 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.45 (d, *J* = 16.4, 1H), 2.24-2.20 (m, 1H), 2.03-1.97 (m, 1H), 1.81-1.57 (m, 4H), 1.44-1.40 (m, 2H) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): 147.8 (d, *J* = 2.9 Hz), 147.1 (d, *J* = 2.7 Hz) ppm. FTIR (neat): 3066, 2979, 2946, 1589, 1498, 1471, 1435, 1243, 1182, 901, 766 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{44}H_{35}O_8P_2^+$: 753.1802, Found: 753.1795 ($M + H^+$).

3. Hydroformylation of terminal and internal olefins using [Rh(acac)(CO)$_2$]/3 as the catalyst

3.1. Hydroformylation of 1-hexene with ligand 3a, typical procedure:

In a glove box, a glass vial with a magnetic stirring bar was charged with ligand **3a** (2.12 mg, 0.003 mmol) and Rh(acac)(CO)$_2$ (0.26 mg, 0.001mmol) in toluene (1.0 mL). The mixture was stirred for 5 min. 1-Hexene (1.24 mL, 10 mmol) was then added, followed by decane (97 μL, 0.5 mmol) as the internal standard. The resulting mixture was transferred to an autoclave, which was purged with nitrogen three times and subsequently charged with H_2 (10 bar) and CO (5 bar). The autoclave was then heated to 90 °C (oil bath) and stirred thereby for 3 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The reaction mixture was

immediately analyzed by GC to determine the turnover number (TON), percentage of isomerization, and regioselectivity (*l*/*b* ratio).

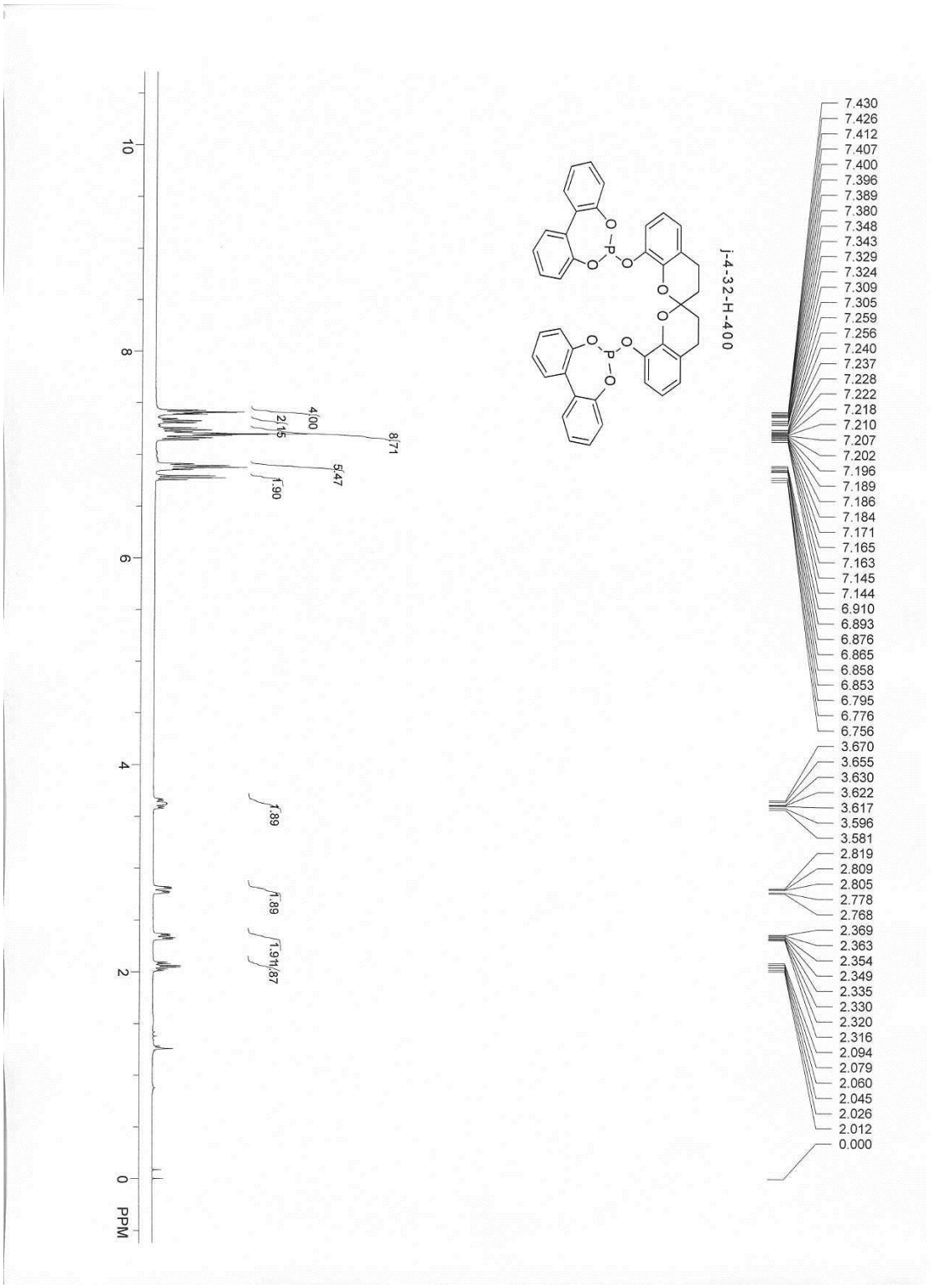
3.2. Typical procedure for the regioselective isomerizing hydroformylation of (*Z*)-2-butene with ligand 3a.

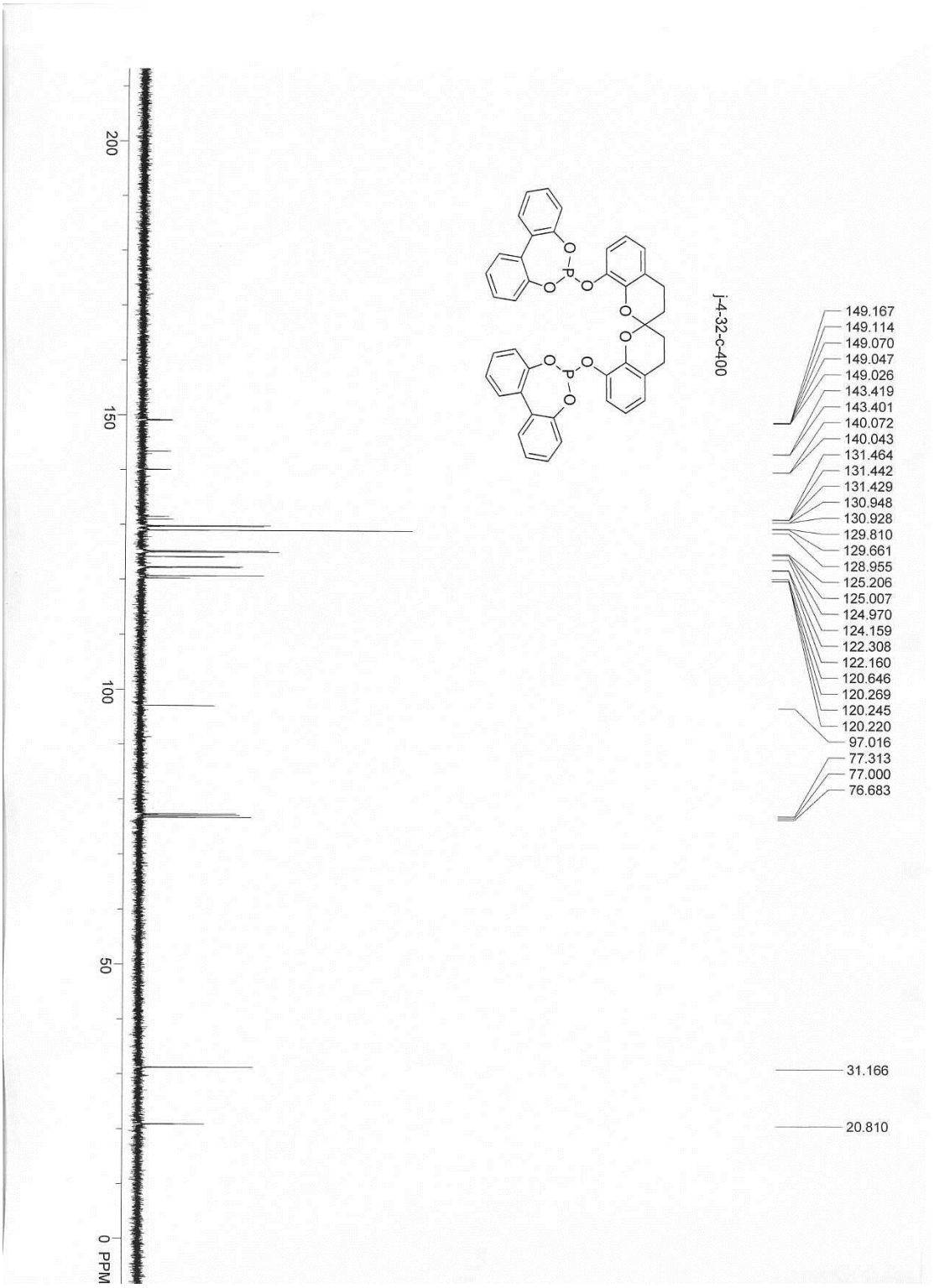
In a glove box, an autoclave with a magnetic stirring bar was charged with ligand **3a** (2.12 mg, 0.003 mmol), $Rh(acac)(CO)_2$ (0.26 mg, 0.001mmol) and decane (97 μL, 0.5 mmol) as internal standard in toluene (1.0 mL). The mixture was stirred for 5 min. The autoclave was cooled to 0 °C, purged with nitrogen for three times, and then charged with (*Z*)-2-butene (2.8 g, 50 mmol). The autoclave was charged with CO (5 bar) and H_2 (10 bar), and then heated to 110 °C (oil bath) for 15 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The reaction mixture was immediately analyzed by GC to determine the turnover number (TON) and regioselectivity (*l*/*b* ratio).

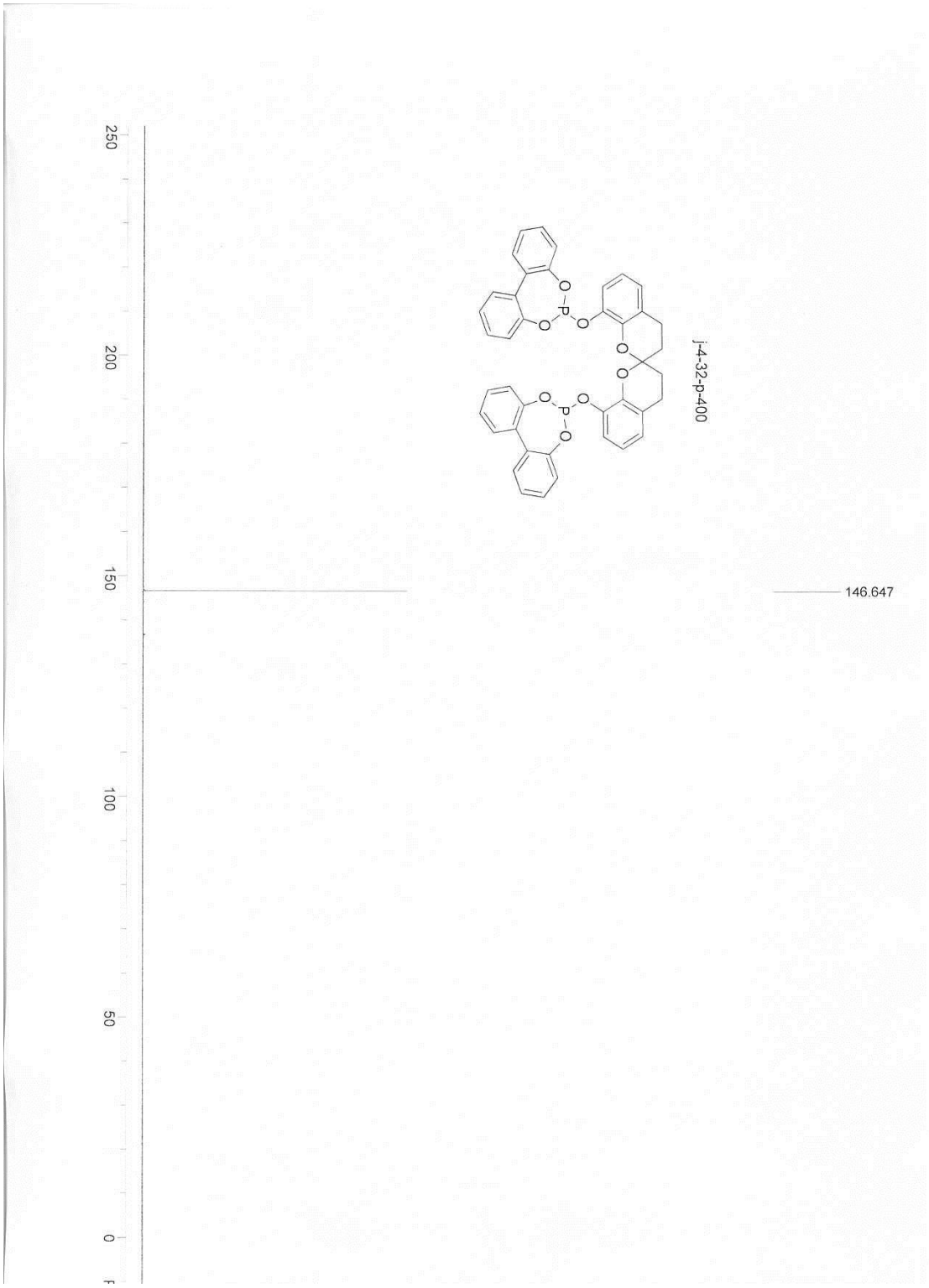
References

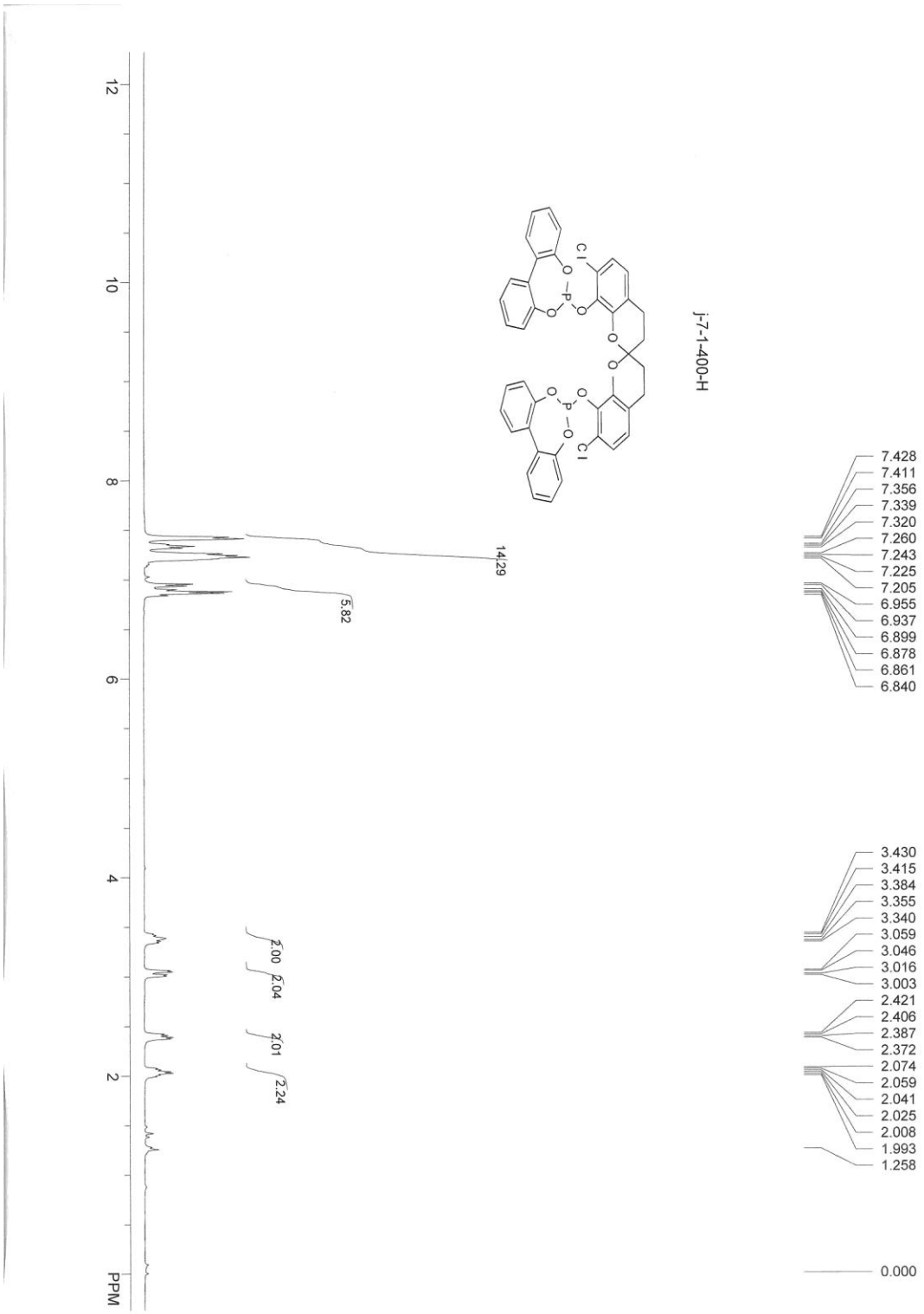
1. Jia, X.; Wang, Z.; Xia, C.; Ding, K. *Chem. Eur. J.* **2012**, *18*, 15288.

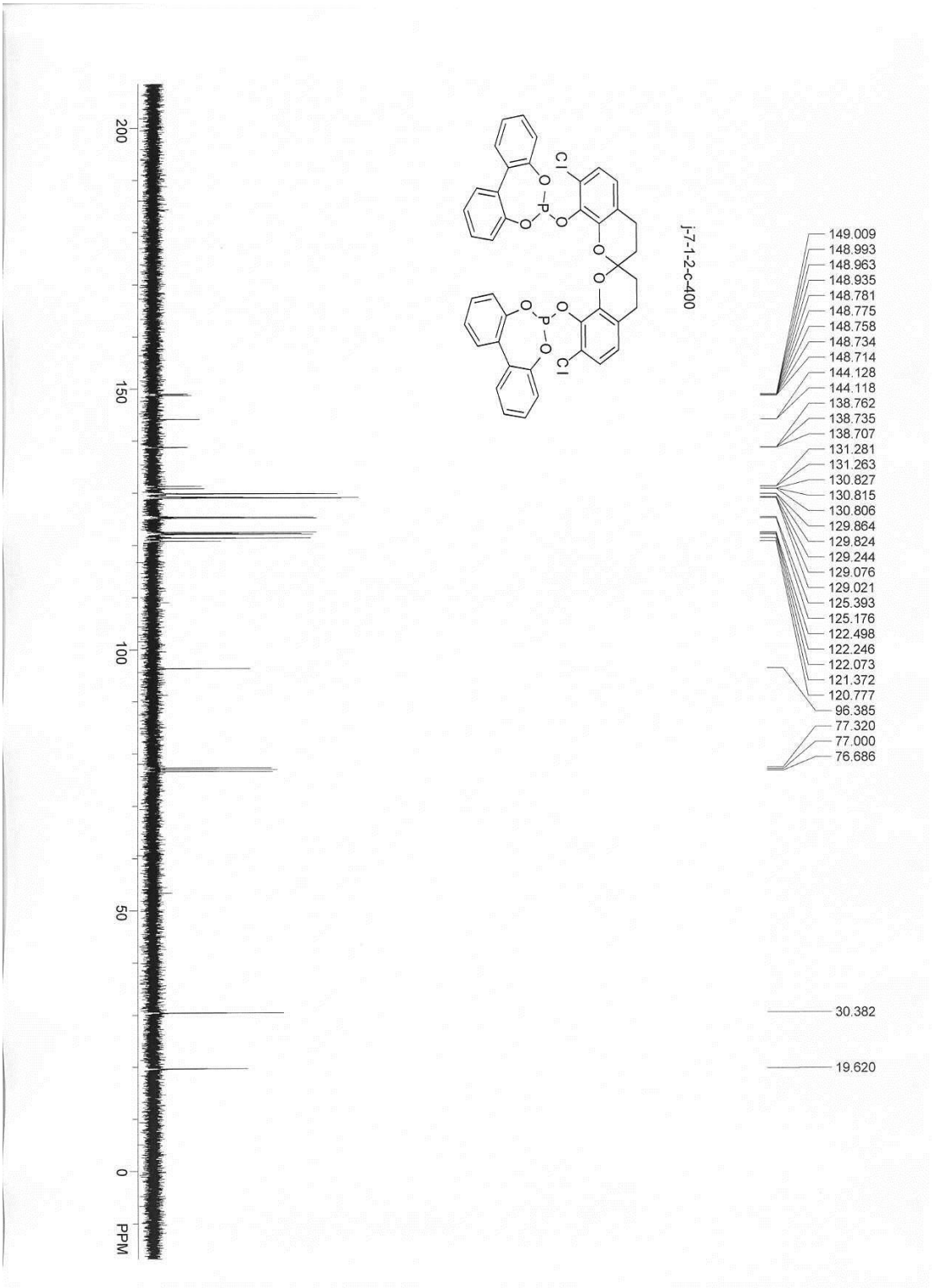
4. NMR spectra of ligands 3a-3h

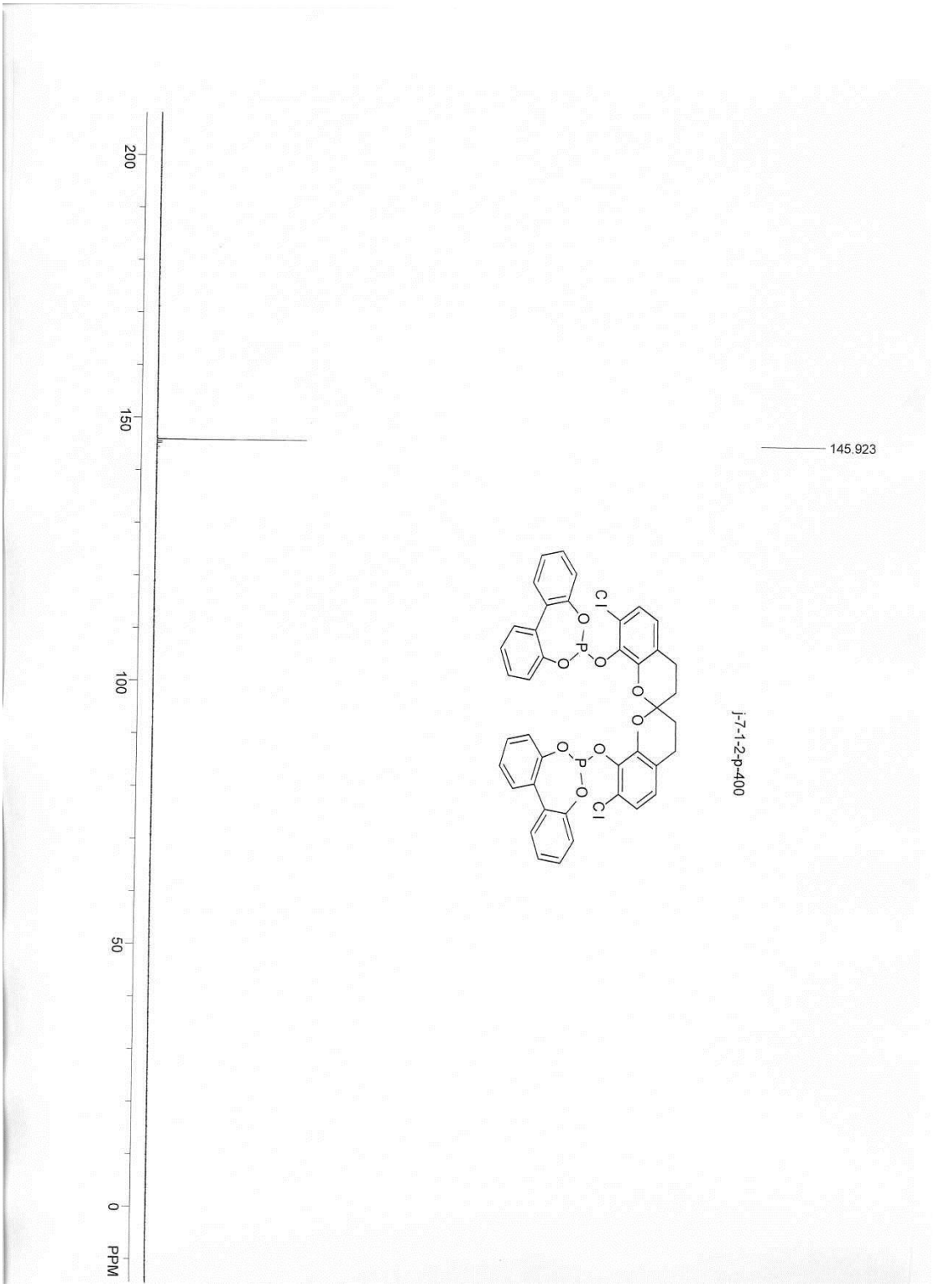


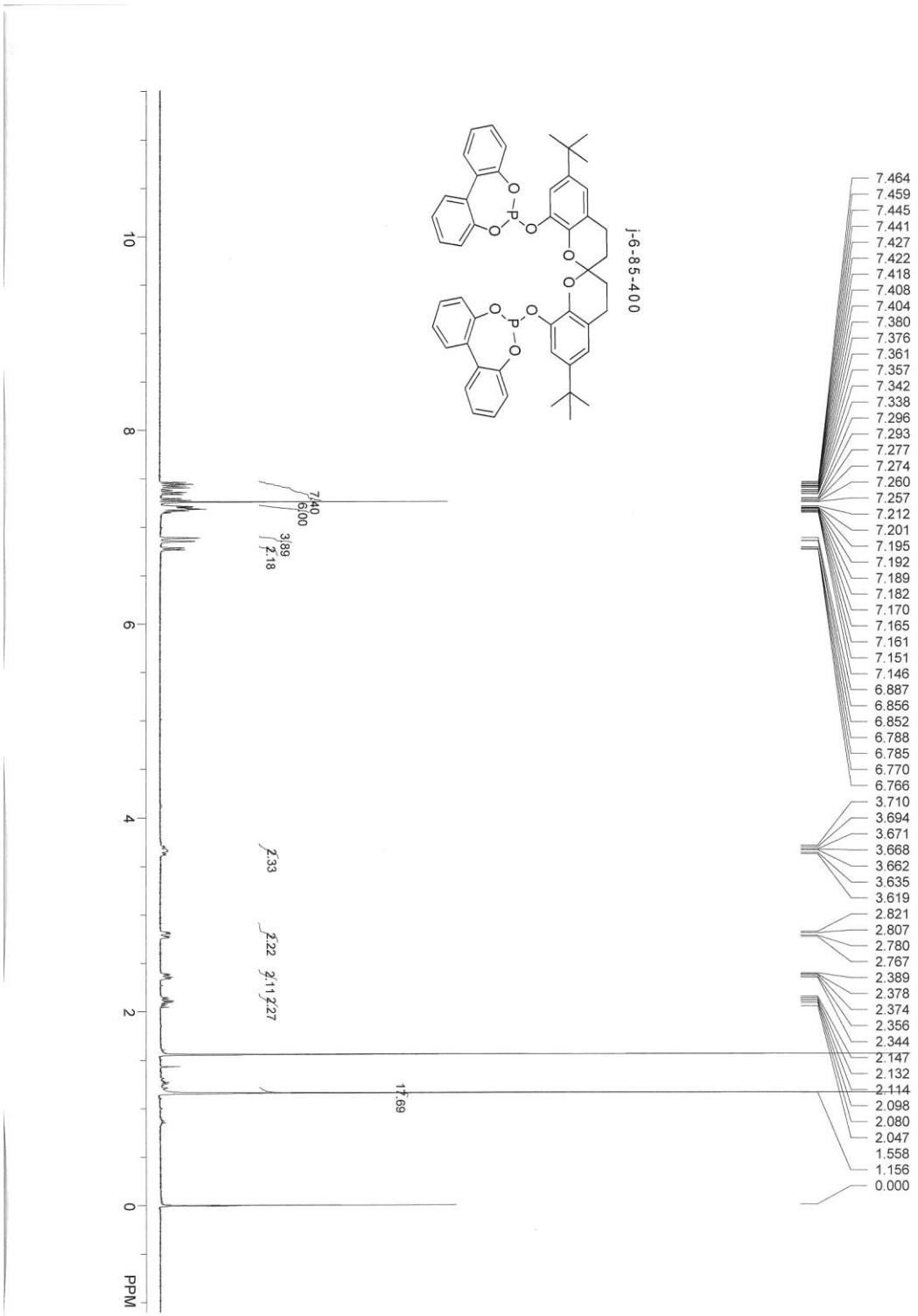


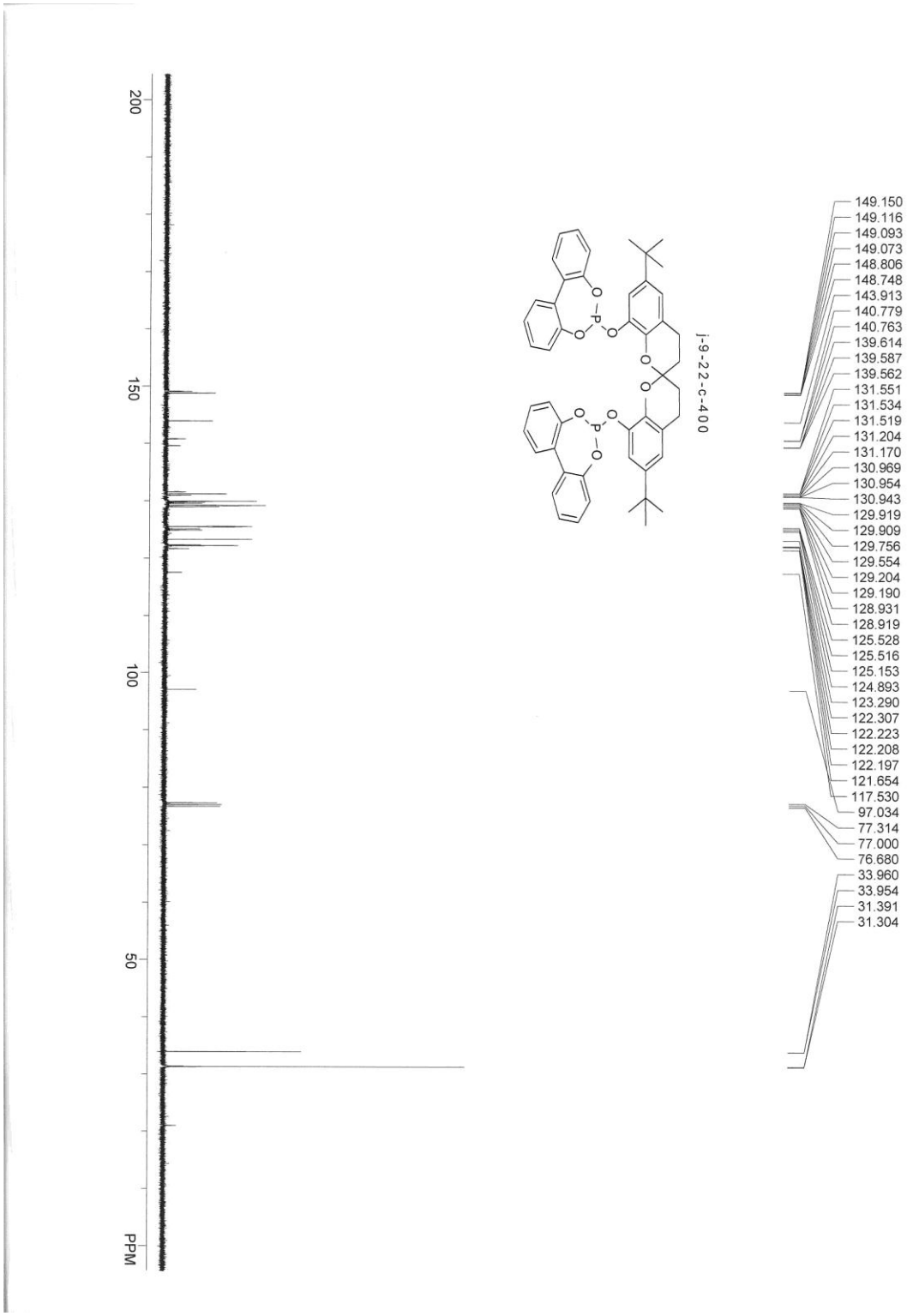


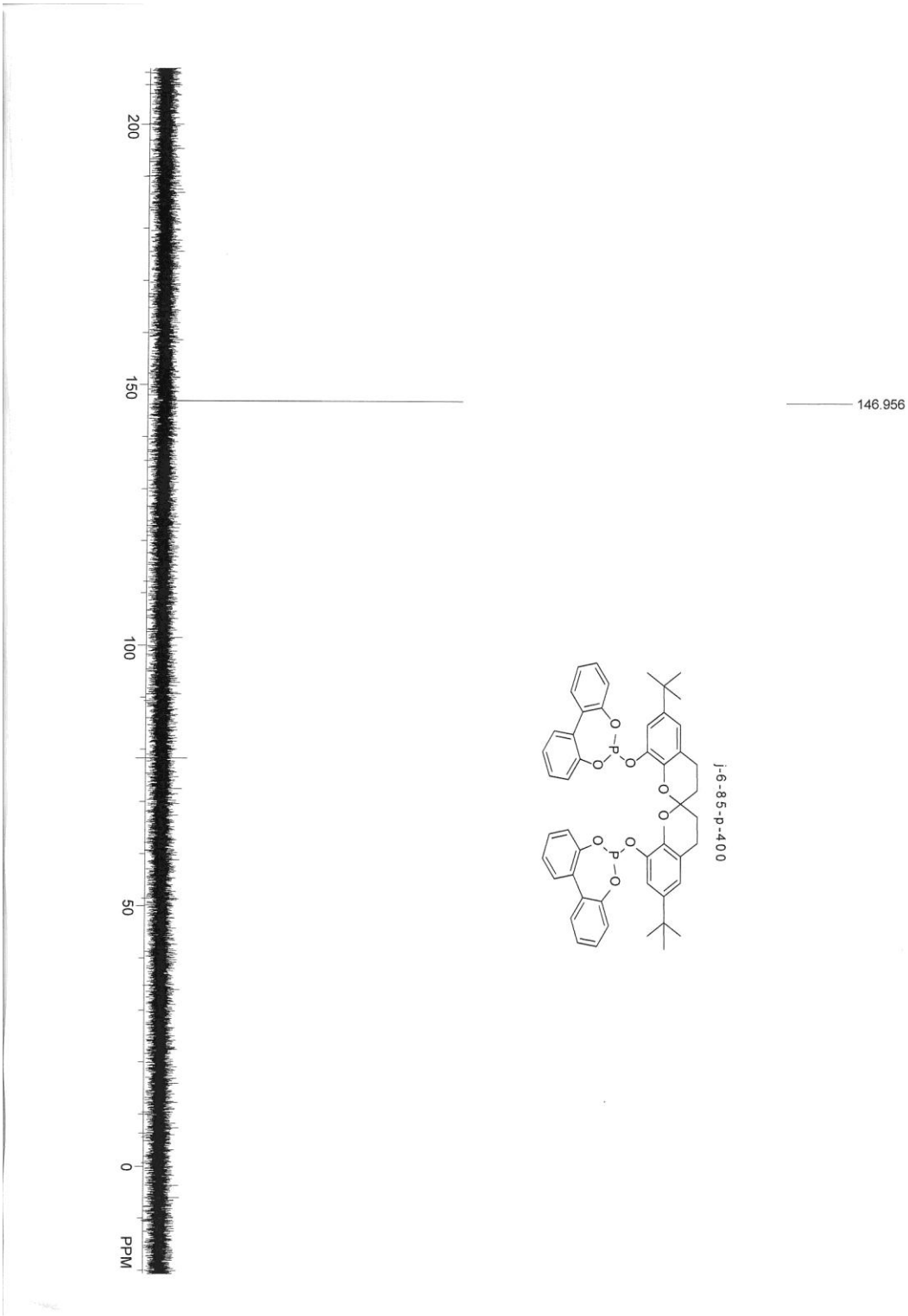


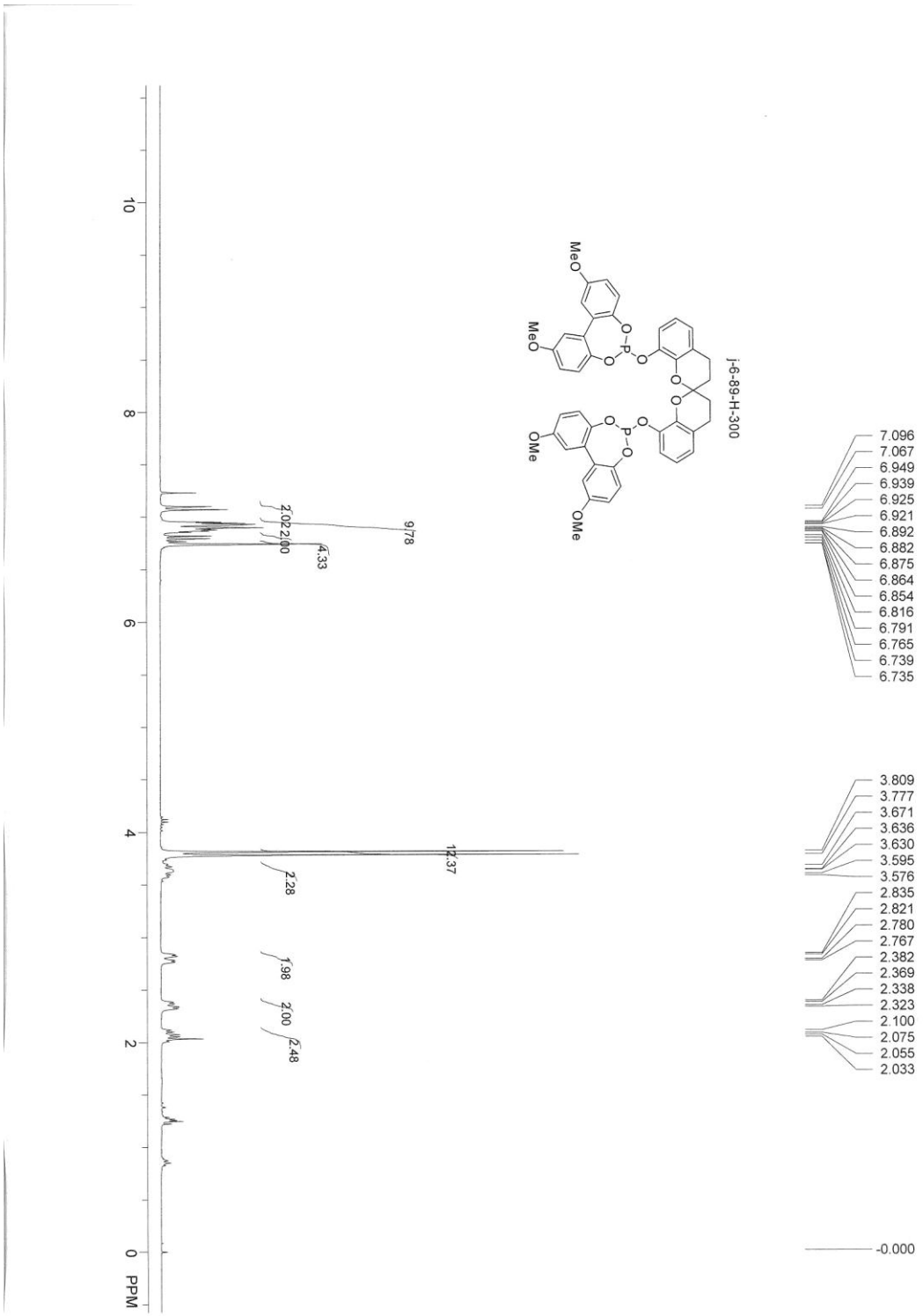


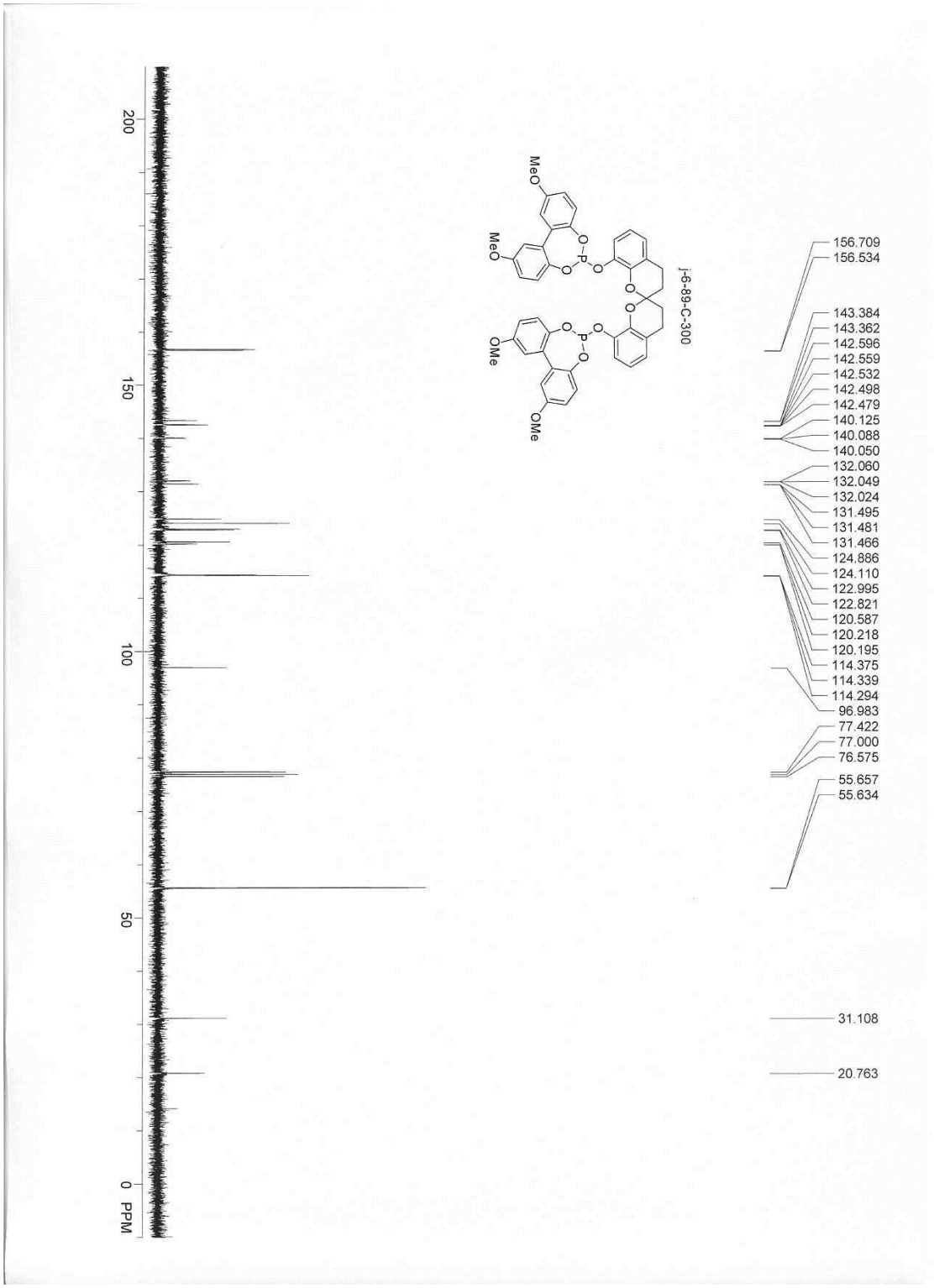


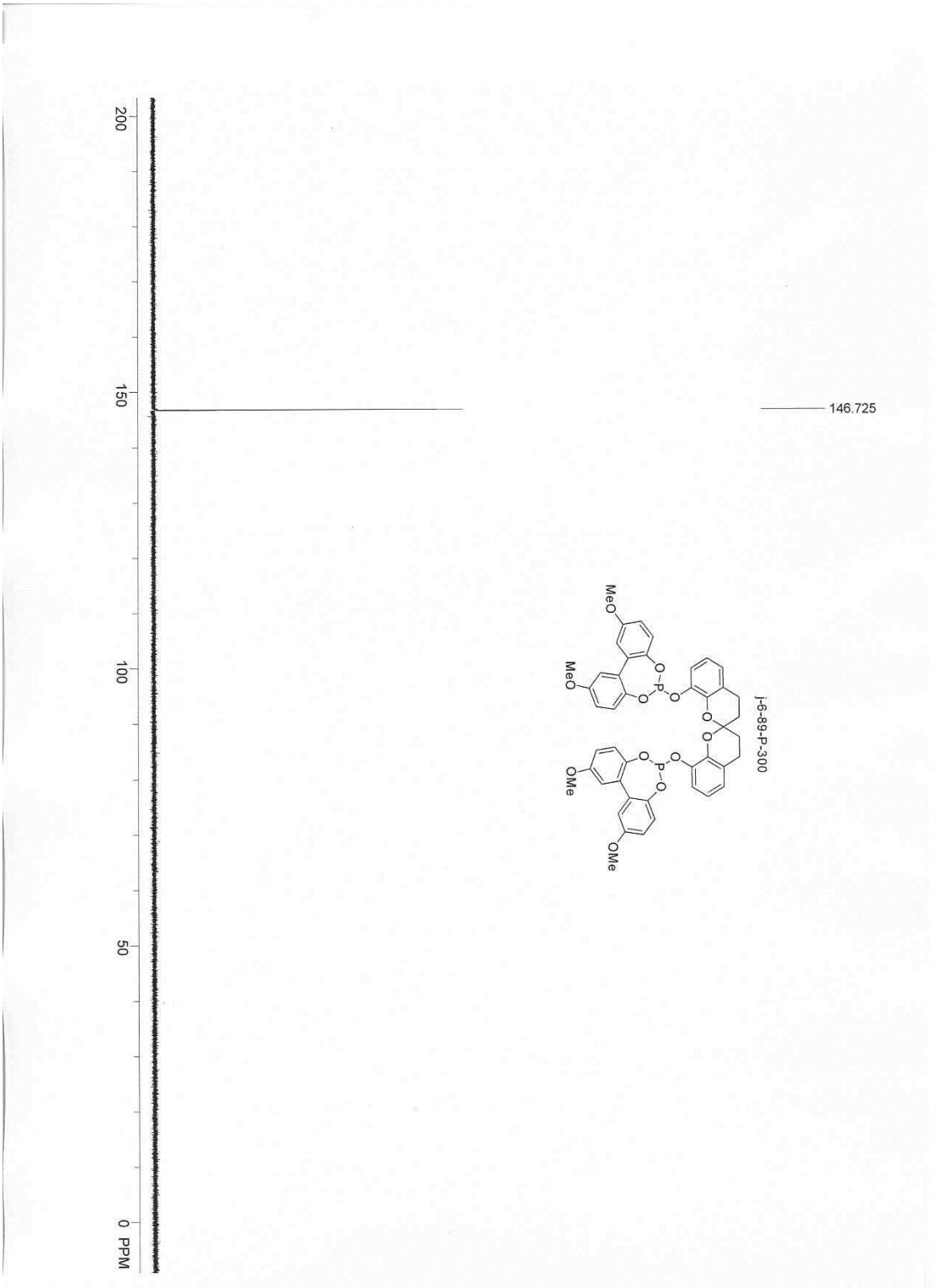








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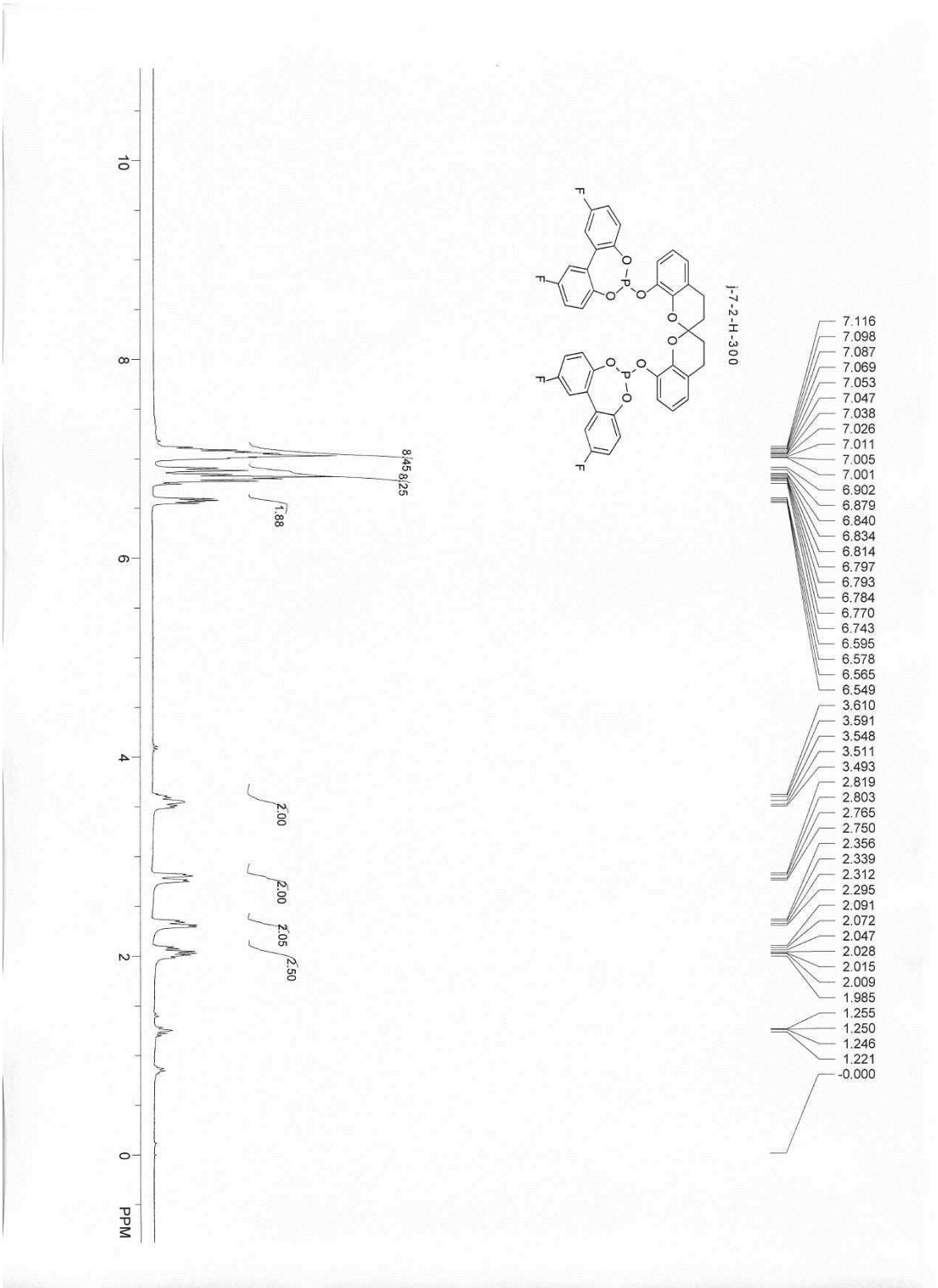

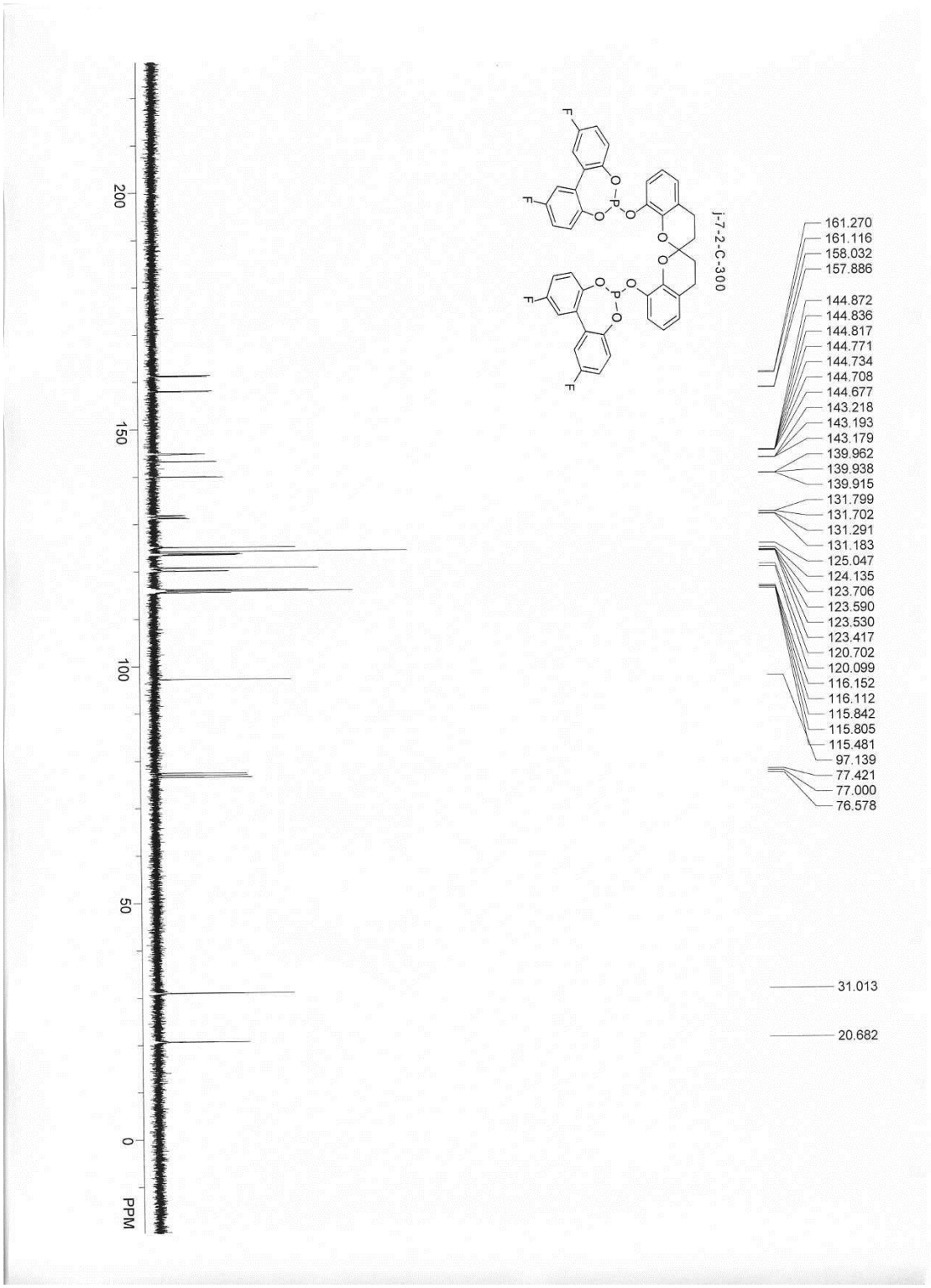

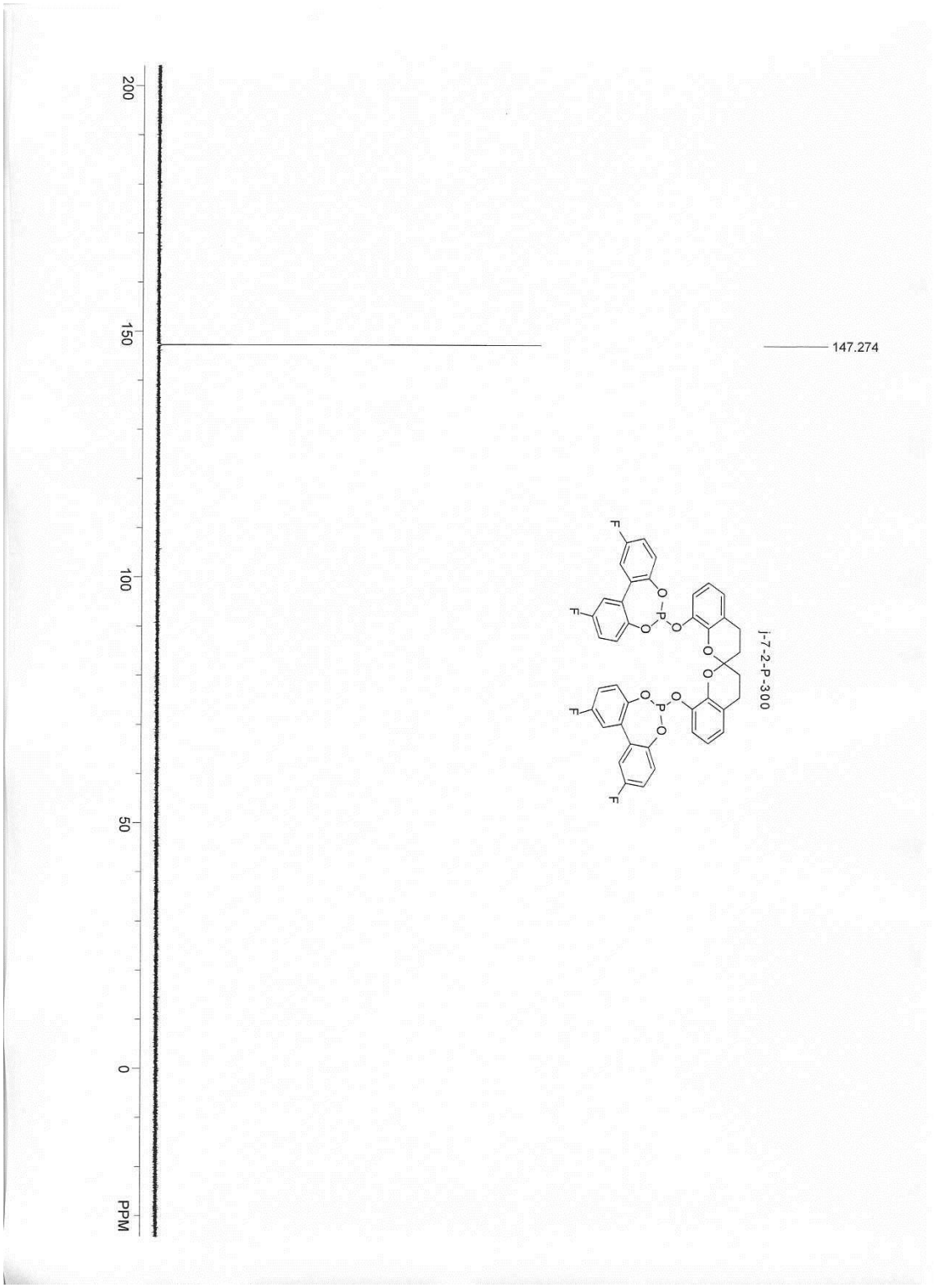
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100
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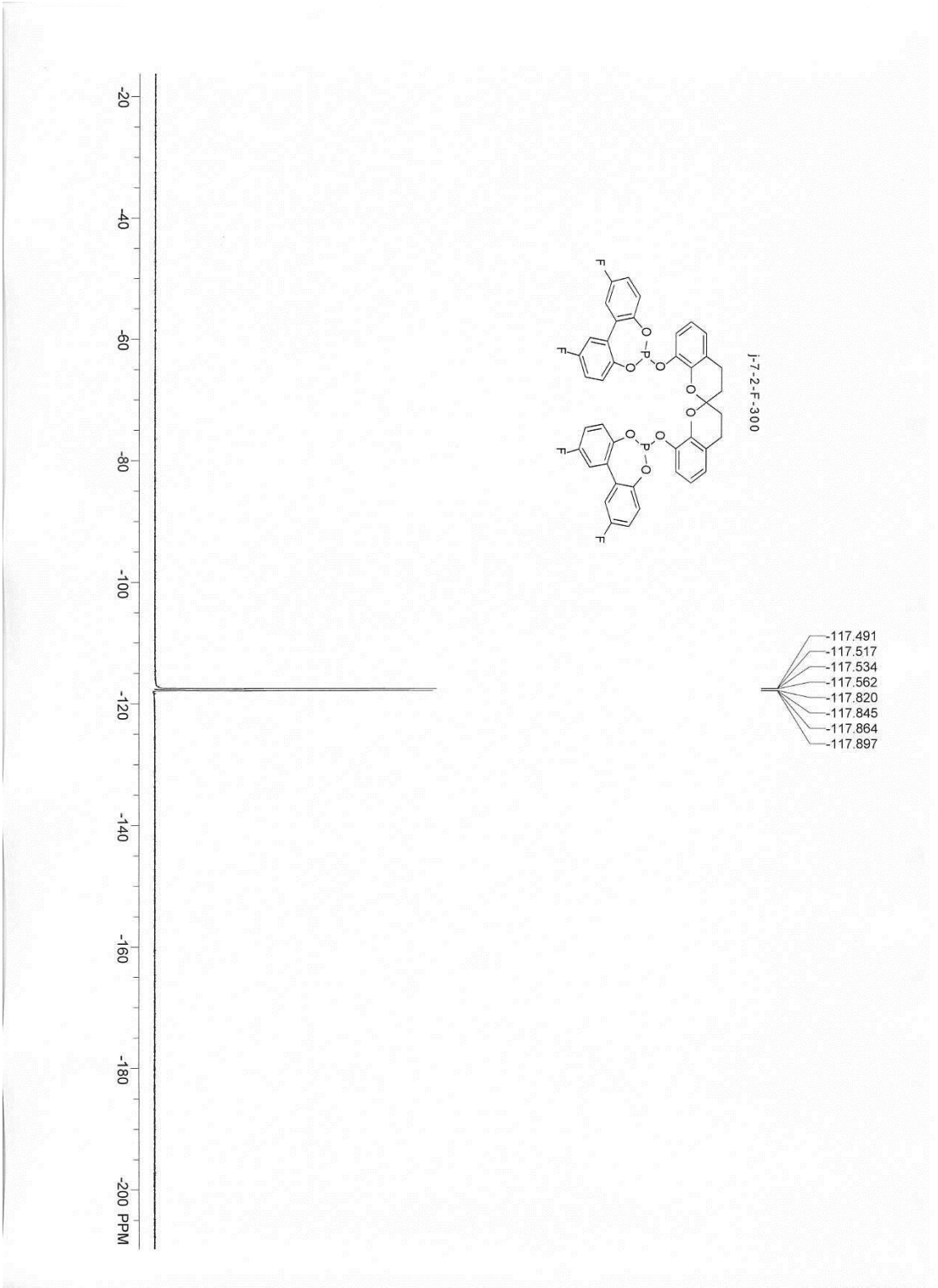
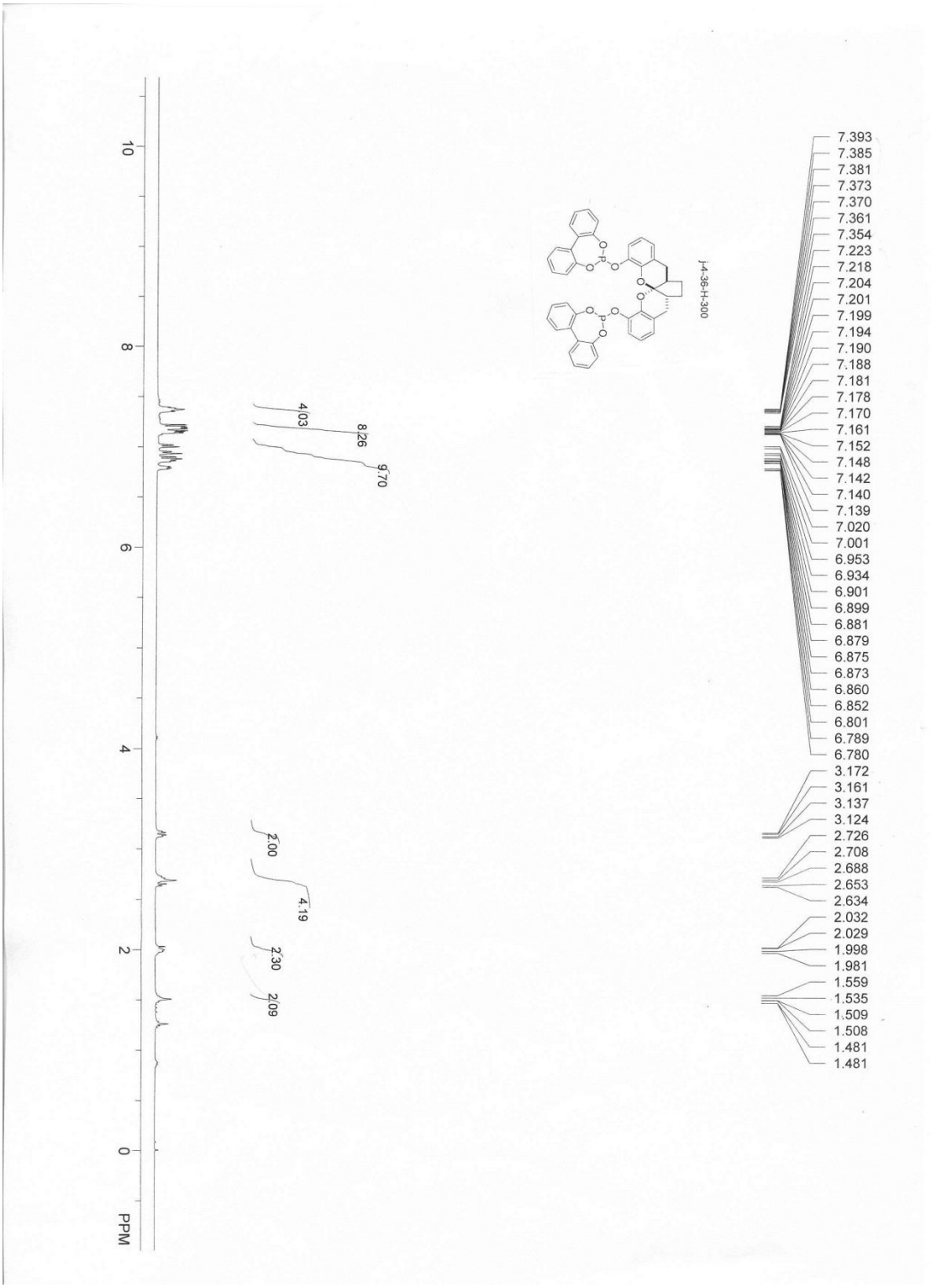
j-7-2-P-300




J-4-36-H-300
7.393
7.385
7.381
7.373
7.370
7.361
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7.223
7.218
7.204
7.201
7.199
7.194
7.190
7.188
7.181
7.178
7.170
7.161
7.152
7.148
7.142
7.140
7.139
7.020
7.001
6.953
6.934
6.901
6.899
6.881
6.879
6.875
6.873
6.860
6.852
6.801
6.789
6.780
3.172
3.161
3.137
3.124
2.726
2.708
2.688
2.653
2.634
2.032
2.029
1.998
1.981
1.559
1.535
1.509
1.508
1.481
1.481
4.03
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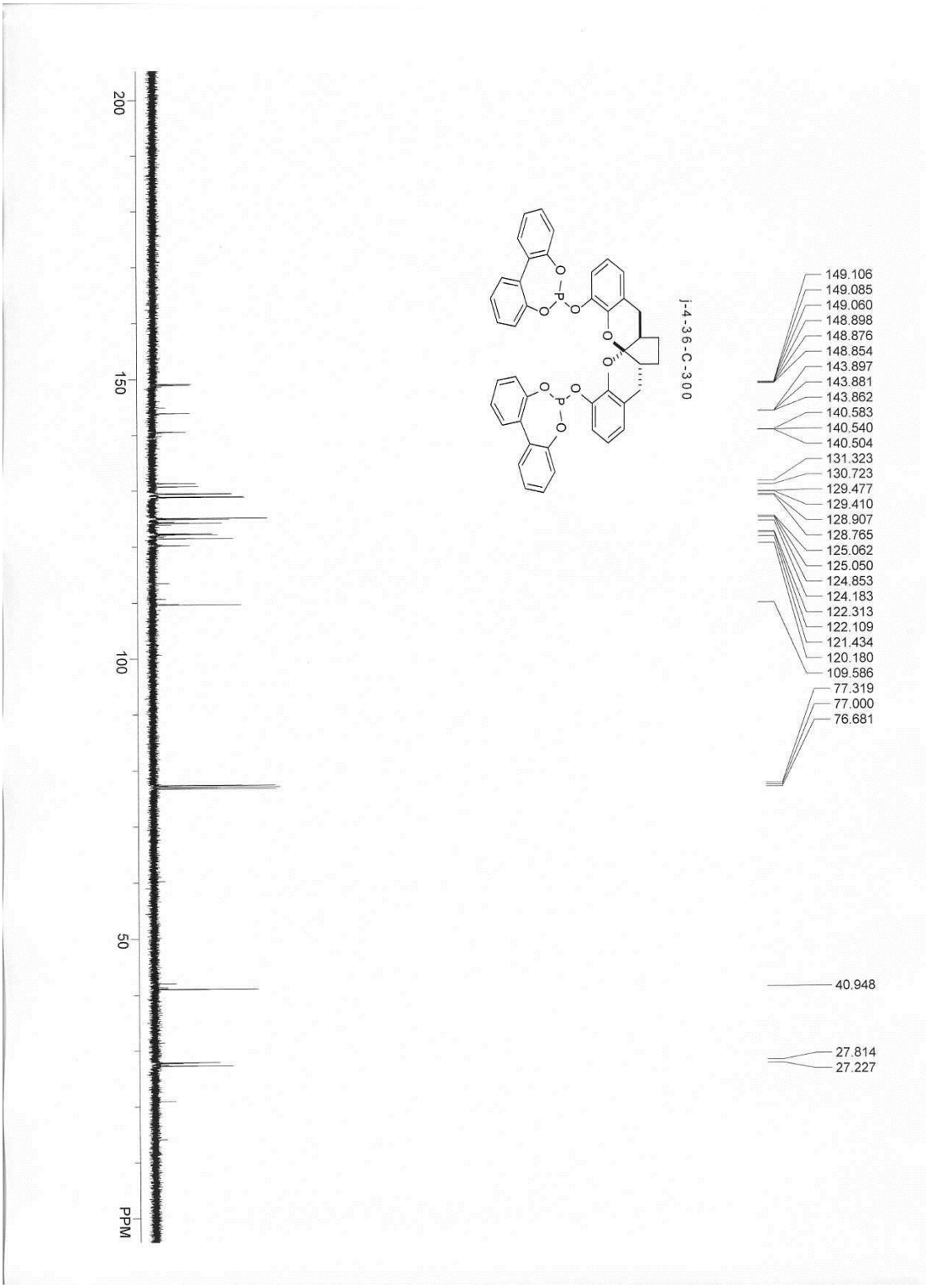
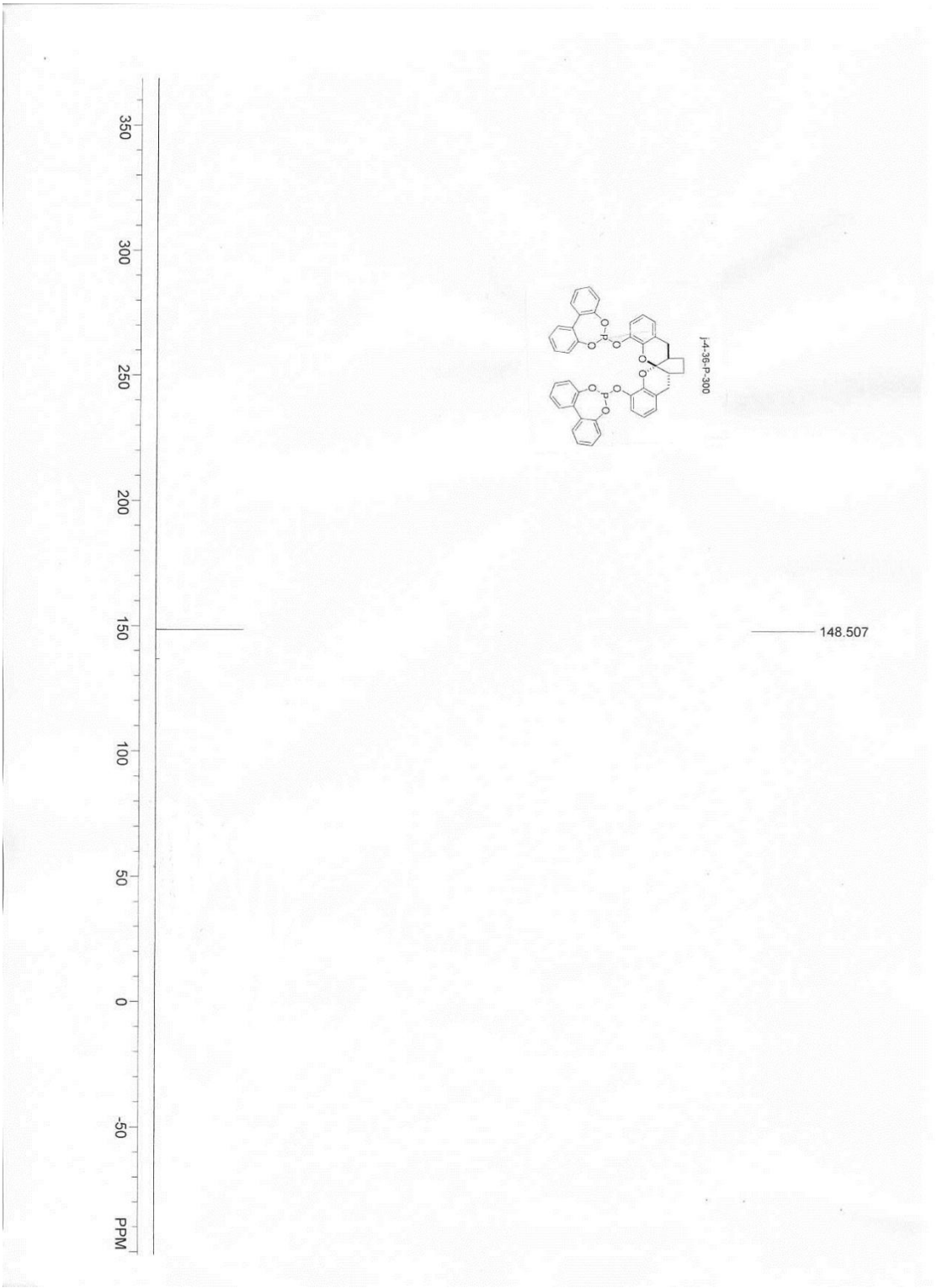
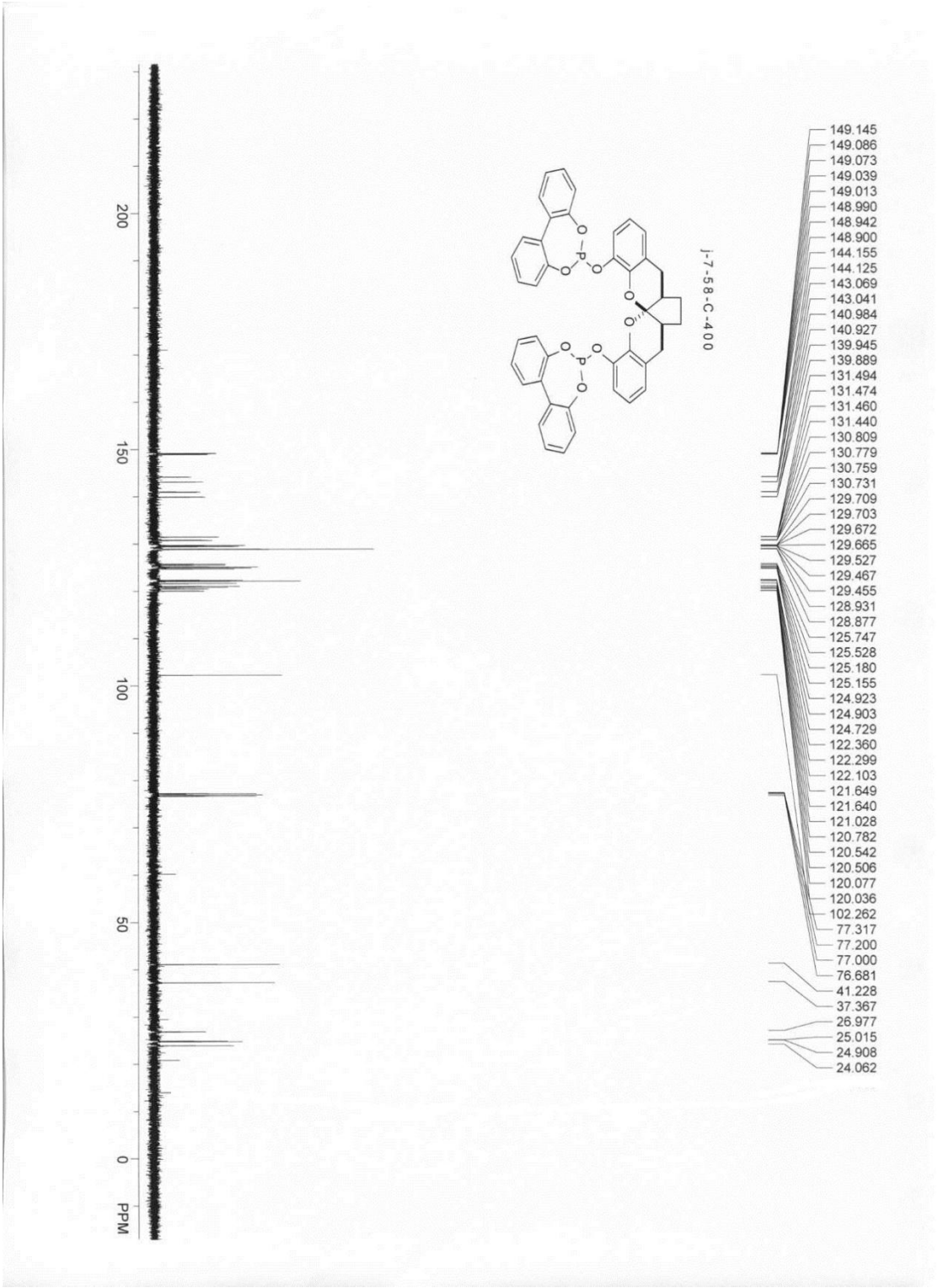
9.70
2.00
4.19
2.30
2.09
10
8
6
4
2
0
PPM






j-7-58-C-400
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148.900
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144.125
143.069
143.041
140.984
140.927
139.945
139.889
131.494
131.474
131.460
131.440
130.809
130.779
130.759
130.731
129.709
129.703
129.672
129.665
129.527
129.467
129.455
128.931
128.877
125.747
125.528
125.180
125.155
124.923
124.903
124.729
122.360
122.299
122.103
121.649
121.640
121.028
120.782
120.542
120.506
120.077
120.036
102.262
77.317
77.200
77.000
76.681
41.228
37.367
26.977
25.015
24.908
24.062
200
150
100
50
0
PPM