Supporting Information

for

Cyclization of Bisphosphines to Phosphacycles via the Cleavage of Two Carbon–Phosphorus Bonds by Nickel Catalysis

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CONTENTS

I. General Information

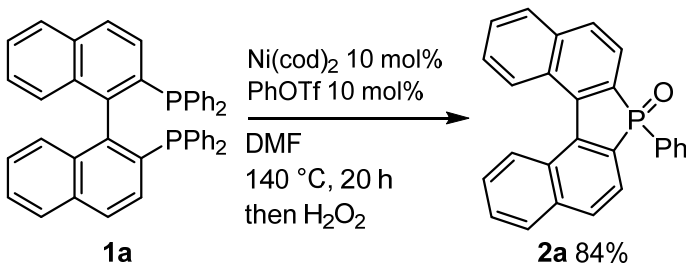
^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$. The data is reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-700 spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 (Silicycle SilicaFlash F60 (230-400 mesh)). Gel permeation chromatography (GPC) was performed using a LC-9210NEXT HPLC or LC9225NEXT HPLC system. Data collection for X-ray crystal analysis were performed on a Rigaku/XtaLAB Pro P200 Hybrid Photon Counting diffractometer (Cu-Kα, λ = 1.54184 Å for **3** and Mo-Kα, λ = 0.71075 Å for **4**). The structures were solved with direct methods and refined with full-matrix least squares.

II. Materials

All reagents were obtained from commercial suppliers and were used as received. $Ni(cod)_2$ was purchased from Strem Chemicals. Phenyl trifluoromethanesulfonate (CAS: 17763-67-6), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (**1a**, CAS: 98327-87-8), (*S*)-Tol-BINAP (**1b**, CAS: 100165-88-6), (*S*)-Xyl-BINAP (**1c**, CAS: 135139-00-3), 2,2'-bis(diphenylphosphino)-1,1'-biphenyl (**1d**, CAS: 84783-64-2), (*R*)-SEGPHOS (**1f**, CAS: 244261-66-3), DPEPHOS (**1j**, CAS: 166330-10-5), (*R*)-DTBM-SEGPHOS (**1k**, CAS: 566940-03-2) and DPPB (**1l**, 7688-25-7) were purchased from Tokyo Chemical Industry Co., Ltd. (*R*)-H_8-BINAP (**1e**, CAS: 139139-86-9), (*R*)-C_3-TUNEPHOS (**1g**, CAS: 301847-89-2), (*R*)-Ph-GARPHOS (**1h**, CAS: 1365531-75-4) and (*R*)-P-PHOS (**1i**, CAS: 221012-82-4) were purchased from Sigma-Aldrich Co. $NiCl(2\text{-Np})(PCy_3)_2$ was prepared according to literature procedure.[1]

III. A Typical Procedure for Nickel-Catalyzed Cyclization via the Cleavage of Two Carbon–Phosphorus Bonds

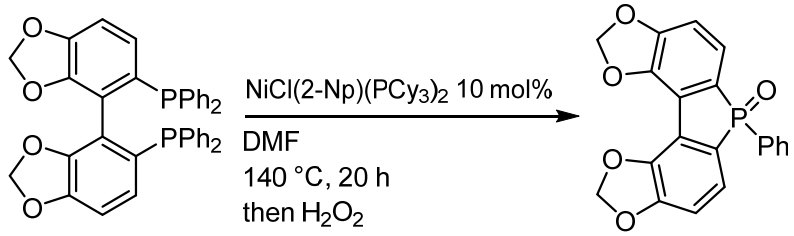
Run on a 0.20 mmol scale.



1a **2a** 84%

In a glovebox filled with nitrogen, $Ni(cod)_2$ (5.5 mg, 0.02 mmol), PhOTf (4.5 mg, 0.020 mmol), **1a** (125 mg, 0.20 mmol) and DMF (1 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The vessel was heated at 140 °C for 20 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with EtOAc. The filtrate was evaporated, and the residue was purified by GPC to give **2a** (63 mg, 84%) as a pale yellow solid.

Run on a 3.0 mmol scale.

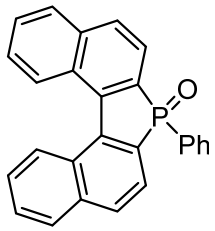


1f **2f** 93%
1.05 g

$NiCl(2\text{-}Np)(PCy_3)_2$ (234 mg, 0.30 mmol), **1f** (1.86 g, 3.0 mmol) and DMF (30 mL) were added to a 100 mL two-necked flask. The solution was heated at 140 °C for 20 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, 3 mL) was added, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with EtOAc. The filtrate was evaporated, and the residue was purified by flash column chromatography using EtOAc as eluent to give **2a** (1.05 g, 93%) as a white solid.

IV. Spectroscopic Data of Products

7-Phenylbenzo[*e*]naphtho[2,1-*b*]phosphindole 7-oxide (2a) [CAS:159211-70-8]



Pale yellow solid (60.9 mg, 84%). R_f 0.34 (SiO_2, EtOAc).

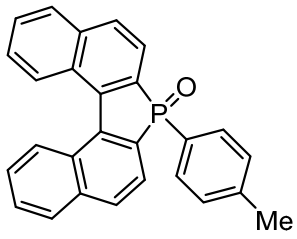
^1H NMR ($CDCl_3$, 399.78 MHz) δ: 7.35 (td, J = 7.6, 3.2 Hz, 2H), 7.47 (td, J = 7.6, 1.6 Hz, 1H), 7.54–7.66 (m, 6H), 7.83 (dd, J = 9.2, 8.2 Hz, 2H), 7.98 (d, J = 7.8 Hz, 4H), 8.21 (d, J = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 124.4 (d, J = 9.6 Hz), 125.8, 127.6, 128.1, 128.7, 128.8, 128.9, 130.2 (d, J = 102.6 Hz), 130.5 (br), 131.0, 131.1, 132.3 (d, J = 2.9 Hz), 137.3, 141.5 (br).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 35.1.

HRMS (EI+, M^+) Calcd for $C_{26}H_{17}OP$: 376.1017. Found: 376.1015.

7-(4-Methylphenyl)benzo[*e*]naphtho[2,1-*b*]phosphindole 7-oxide (2b)



Pale yellow solid (74.3 mg, 95%). R_f 0.50 (SiO_2, EtOAc).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 2.33 (s, 3H), 7.16 (dd, *J* = 2.3, 8.0 Hz, 2H), 7.49–7.65 (m, 6H), 7.81 (t, *J* = 9.2 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 4H), 8.20 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 21.6, 124.4 (d, *J* = 10.5 Hz), 125.8, 126.6 (d, *J* = 105.4 Hz), 127.6, 128.1, 128.8, 129.5, 129.7, 130.5 (br), 131.1, 131.2, 137.3, 142.89, 142.92.

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 35.5.

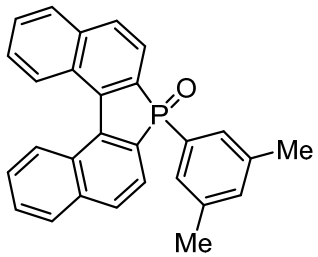
HRMS (EI+, M^+) Calcd for $C_{27}H_{19}OP$: 390.1174. Found: 390.1169.

IR (KBr): 3443 w, 3050 w, 2953 w, 2925 w, 2870 w, 2359 w, 2343 w, 1734 w, 1700 w, 1676 w, 1600 w, 1578 w, 1559 w, 1542 w, 1507 w, 1499 w, 1444 w, 1396 w, 1377 w, 1359 w, 1337 m, 1308 w, 1284 w, 1254 w, 1202 s, 1189 s, 1151 m, 1108 s, 1025 w, 984 w, 961 w, 952 w, 878 w, 839 w, 815 m, 773 w, 749 s, 709 w, 677 m, 667 s, 657 m, 643 m, 634 w, 623 w, 604 w, 592 w, 584 w, 561 m, 526 s, 508 w.

MS, *m/z* (relative intensity, %): 391 (27), 390 (M^+, 100), 389 (54), 327 (12), 326 (18), 298 (14), 297 (39), 281 (15), 252 (24), 250 (14).

m.p. 160 ºC

7-(3,5-Dimethylphenyl)benzo[*e*]naphtho[2,1-*b*]phosphindole 7-oxide (2c)



Pale yellow solid (77.0 mg, 96%). R_f 0.59 (SiO_2, EtOAc).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 2.22 (s, 6H), 7.10 (s, 1H), 7.22–7.29 (m, 2H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 6.9 Hz, 2H), 7.82 (t, *J* = 7.83 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 4H), 8.22 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 21.2, 124.4 (d, *J* = 9.6 Hz), 125.7, 127.5, 128.1, 128.5, 128.6, 128.8, 129.58 (d, *J* = 102.6 Hz), 129.60 (d, *J* = 9.6 Hz), 130.1 (br), 134.3 (d, *J* = 2.9 Hz), 137.3,

138.6, 138.7.

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 35.9.

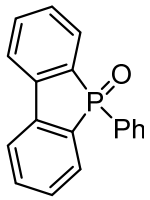
HRMS (EI+, M^+) Calcd for $C_{28}H_{21}OP$: 404.1330. Found: 404.1329.

IR (KBr): 3443 m, 2323 w, 2138 w, 1992 w, 1847 w, 1733 w, 1688 w, 1631 w, 1599 w, 1508 w, 1449 m, 1417 m, 1397 w, 1337 w, 1312 w, 1286 w, 1234 m, 1204 s, 1151 m, 1124 s, 1101 m, 1024 m, 993 m, 887 w, 870 m, 850 m, 815 m, 750 m, 727 w, 704 m, 689 s, 650 m, 626 w, 594 w, 583 m, 569 m, 553 m, 541 m, 530 m, 524 m.

MS, *m/z* (relative intensity, %): 405 (31), 404 (M^+, 100), 403 (51), 341 (10), 340 (12), 298 (17), 297 (43), 281 (17), 252 (25), 250 (14).

m.p. 155 ºC

5-Phenylbenzo[*b*]phosphindole 5-oxide (2d) [CAS:1031-13-6]



White solid (67.1 mg, 99%). R_f 0.34 (SiO_2, EtOAc).

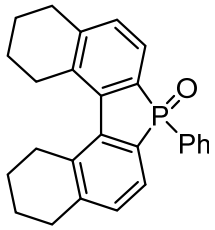
^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.39 (td, *J* = 7.8, 3.7 Hz, 4H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 7.57–7.74 (m, 6H), 7.83 (dd, *J* = 7.6, 3.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 121.2 (d, *J* = 9.6 Hz), 128.7 (d, *J* = 12.5 Hz), 129.5 (d, *J* = 11.5 Hz), 129.9 (d, *J* = 9.6 Hz), 130.1 (d, *J* = 103.5 Hz), 131.0 (d, *J* = 10.5 Hz), 132.2 (d, *J* = 2.9Hz), 132.2, 133.3 (d, *J* = 1.9 Hz), 141.8 (d, *J* = 22.0 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 34.3.

HRMS (EI+, M^+) Calcd for $C_{18}H_{13}PO$: 276.0704. Found: 276.0706.

7-Phenyl-2,3,4,7,10,11,12,13-octahydro-1H-benzo[*e*]naphtho[2,1-*b*]phosphindole 7-oxide (2e) [CAS:2148300-95-0]



White solid (35.1 mg, 93%). R_f 0.31 (SiO_2, EtOAc).

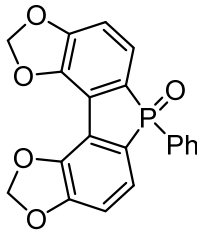
^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.63 (quint, *J* = 6.9 Hz, 4H), 1.87 (quint, *J* = 6.9 Hz, 4H), 2.77 (t, *J* = 6.0 Hz, 4H), 2.86 (t, *J* = 6.0 Hz, 4H), 7.16 (dd, *J* = 7.3, 3.7 Hz, 2H), 7.33–7.58 (m, 7H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 21.4, 22.1, 28.8, 30.3, 127.3 (d, J = 9.6 Hz), 128.5 (d, J = 12.5 Hz), 129.4 (d, J = 12.5 Hz), 131.0 (d, J = 10.5 Hz), 131.6 (d, J = 97.8 Hz), 131.7 (d, J = 2.9 Hz), 132.7 (d, J = 6.7 Hz), 137.3 (d, J = 10.5 Hz), 142.2 (d, J = 22.0 Hz), 145.0 (d, J = 1.9 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 33.5.

HRMS (EI+, M^+) Calcd for $C_{26}H_{25}OP$: 384.1643. Found: 384.1640.

6-Phenyl-9,10-dihydro-[1,3]dioxolo[4",5":3',4']benzo[1',2':2,3]phosphindolo[4,5-*b*][1,4]dioxole 6-oxide (2f) [CAS:2127850-05-7]



White solid (66.9 mg, 90%). R_f 0.29 (SiO_2, EtOAc).

Isolated by flash column chromatography using EtOAc as eluent.

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.13 (s, 4H), 6.82 (dd, J = 7.8, 2.8 Hz, 2H), 7.23 (dd, J = 10.8, 7.8 Hz, 2H), 7.36–7.40 (m, 2H), 7.45–7.49 (m, 1H), 7.63 (ddd, J = 12.9, 7.8, 1.4 Hz, 2H).

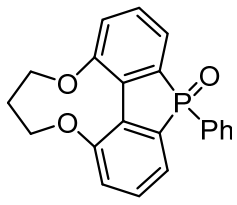
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 101.7, 109.2 (d, J = 14.4 Hz), 119.5 (d, J = 25.0 Hz), 125.1 (d, J = 10.5 Hz), 126.9 (d, J = 110.2 Hz), 128.6 (d, J = 12.5 Hz), 130.9 (d, J = 10.5 Hz), 131.8 (d, J = 107.4 Hz), 131.9, 142.8 (d, J = 15.3 Hz), 152.6.

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 32.2.

HRMS (EI+, M^+) Calcd for $C_{20}H_{13}O_5P$: 364.0501. Found: 364.0506.

Anal. Calcd for $C_{20}H_{13}O_5P$: C, 65.94; H, 3.60, Found: C, 66.21; H, 3.93.

4-Phenyl-10,11-dihydro-9H-8,12-dioxa-4-phosphacyclonona[*def*]fluorene 4-oxide (2g) [CAS:2127850-04-6]



White solid (59.2 mg, 91%). R_f 0.20 (SiO_2, EtOAc).

Isolated by flash column chromatography using EtOAc as eluent.

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.73 (s, 1H), 2.01 (s, 1H), 4.32 (d, J = 11.5 Hz, 2H), 4.60 (t, J = 9.6 Hz, 2H), 7.33–7.43 (m, 6H), 7.47–7.55 (m, 3H), 7.63 (dd, J = 12.8, 6.9 Hz, 2H).

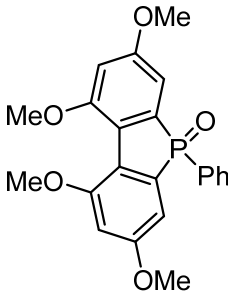
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 25.9, 76.9, 126.3 (d, J = 9.6 Hz), 128.7 (d, 12.5 Hz), 130.6 (d, J

= 104.5 Hz), 130.9 (d, *J* = 1.9 Hz), 131.1 (d, *J* = 10.5 Hz), 131.4 (d, *J* = 13.4 Hz), 132.2 (d, *J* = 2.9 Hz), 134.8 (d, *J* = 2.9 Hz), 135.2 (d, *J* = 127.5 Hz), 155.4 (d, *J* = 13.4 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 33.1.

HRMS (EI+, M^+) Calcd for $C_{21}H_{17}O_3P$: 348.0915. Found: 348.0908.

1,3,7,9-Tetramethoxy-5-phenylbenzo[*b*]phosphindole 5-oxide (2h)



Pale yellow solid (74.2 mg, 99%). R_f 0.41 (SiO_2, EtOAc).

Isolated by flash column chromatography using EtOAc as eluent.

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.78 (s, 6H), 3.92 (s, 6H), 6.66 (d, *J* = 2.3 Hz, 2H), 6.83 (dd, *J* = 11.9, 2.3 Hz, 2H), 7.36–7.40 (m, 2H), 7.48 (td, *J* = 7.3, 1.6 Hz, 1H), 7.63 (ddd, *J* = 12.8, 7.6, 1.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 55.7, 56.8, 106.0, 106.1, 123.1 (d, *J* = 23.0 Hz), 128.7 (d, *J* = 12.5 Hz), 131.0 (d, *J* = 10.5 Hz), 131.1 (d, *J* = 103.5 Hz), 132.0 (d, *J* = 2.9 Hz), 135.9 (d, *J* = 104.5 Hz), 156.4 (d, *J* = 17.3 Hz), 161.0 (d, *J* =16.3 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 34.8.

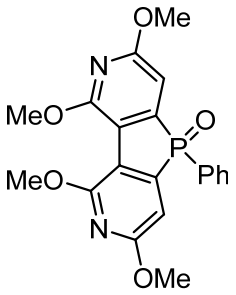
HRMS (EI+, M^+) Calcd for $C_{22}H_{21}O_5P$: 396.1127. Found: 396.1120.

IR (KBr): 3054 w, 3007 w, 2992 m, 2964 m, 2937 m, 2837 m, 1599 s, 1565 s, 1456 s, 1431 s, 1407 m, 1341 s, 1303 s, 1231 s, 1219 m, 1200 s, 1178 s, 1160 s, 1137 s, 1115 m, 1065 s, 1047 s, 998 w, 988 m, 957 w, 945 w, 934 w, 862 s, 849 s, 836 m, 822 s, 760 m, 752 m, 722 s, 707 m, 697 s, 661 m, 629 w, 613 w, 590 m, 569 m, 541 m, 501 m, 491 m, 447 w, 426 w, 419 w.

MS, *m/z* (relative intensity, %): 397 (22), 396 (M^+, 100), 381 (21).

m.p. 200 ºC

1,3,7,9-Tetramethoxy-5-phenylphospholo[3,2-*c*:4,5-*c*′]dipyridine 5-oxide (2i)
[CAS:2127850-07-9]



Yellow solid (74.8 mg, 95%). R_f 0.76 (SiO_2, EtOAc).

Isolated by flash column chromatography using EtOAc as eluent.

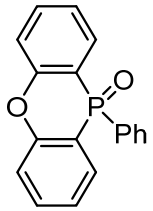
^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.94 (s, 6H), 4.08 (s, 6H), 6.60 (s, 1H), 6.63 (s, 1H), 7.38–7.43 (m, 2H), 7.50–7.54 (m, 1H), 7.58–7.63 (m, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 53.9, 54.1, 101.9 (d, J = 10.5 Hz), 113.0 (d, J = 22.0 Hz), 128.9 (d, J = 12.5 Hz), 129.1 (d, J = 104.5 Hz), 130.8 (d, J = 10.5 Hz), 132.7 (d, J = 1.9 Hz), 146.5 (d, J = 100.6 Hz), 157.2 (d, J = 15.3 Hz), 162.5 (d, J = 17.3 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 31.1.

HRMS (EI+, M^+) Calcd for $C_{20}H_{19}N_2O_5P$: 398.1032. Found: 398.1024.

10-Phenyl-10H-phenoxaphosphinine 10-oxide (2j) [CAS:1091-27-6]



White solid. R_f 0.34 (SiO_2, EtOAc).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.23–7.25 (m, 2H), 7.34–7.49 (m, 5H), 7.57–7.67 (m, 4H), 7.74 (ddd, J = 13.1, 7.8, 1.6 Hz, 2H).

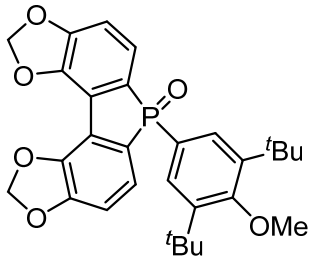
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 115.3 (d, J = 103.5 Hz), 118.3 (d, J = 5.6 Hz), 124.1 (d, J = 10.5 Hz), 128.5 (d, J = 3.4 Hz), 131.3 (d, J = 5.6 Hz), 131.6 (d, J = 10.5 Hz), 131.8 (d, J = 2.9 Hz), 133.8, 134.0 (d, J = 118.9 Hz), 155.6 (d, J = 2.9 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -0.1.

HRMS (EI+, M^+) Calcd for $C_{18}H_{13}O_2P$: 292.0653. Found: 292.0655.

Anal. Calcd for $C_{18}H_{13}O_2P$: C, 73.97; H, 4.48, Found: C, 74.10; H, 4.54.

6-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-9,10-dihydro-[1,3]dioxolo[4'',5'':3',4']benzo[1',2':2,3]phosphindolo[4,5-*b*][1,4]dioxole 6-oxide (2k)



White solid (34.0mg, 76%). R_f 0.74 (SiO_2, EtOAc).

Isolated by flash column chromatography using EtOAc as eluent.

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.34 (s, 18H), 3.67 (s, 3H), 6.15 (dd, *J* = 6.9, 1.4 Hz, 4H), 6.85 (dd, *J* = 7.7, 3.0 Hz, 2H), 7.29 (dd, *J* = 10.5, 7,7 Hz, 2H), 7.50 (d, *J* = 13.7 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 31.8, 35.9, 64.3, 101.6, 109.1 (d, *J* = 13.4 Hz), 119.5 (d, *J* = 24.0 Hz), 125.1 (d, *J* = 10.5 Hz), 125.1 (d, *J* = 112.1 Hz), 127.3 (d, *J* = 110.2 Hz), 129.5 (d, *J* = 12.5 Hz), 142.8 (d, *J* = 15.3 Hz), 144.4 (d, *J* = 12.5 Hz), 152.4 (d, *J* = 1.9 Hz), 163.0 (d, *J* = 2.9 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 33.8.

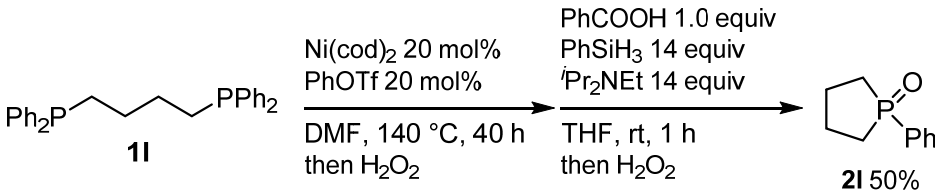
HRMS (EI+, M^+) Calcd for $C_{29}H_{31}O_6P$: 506.1858. Found: 506.1864.

IR (KBr): 3648 w, 3423 w, 2962 m, 1621 w, 1506 w, 1477 s, 1428 m, 1410 w, 1394 w, 1362 w, 1340 w, 1265 s, 1190 s, 1161 m, 1145 w, 1007 m, 927 w, 905 w, 886 w, 845 w, 818 w, 750 w, 706 w, 618 m, 553 w, 541 w, 494 w, 479 w, 464 w, 449 w, 439 w, 426 w, 404 w.

MS, *m/z* (relative intensity, %): 507 (28), 506 (88, M^+), 492 (31), 491 (100), 461 (34), 449 (14), 435 (11), 288 (13), 287 (72), 271 (13).

m.p. 305 ºC

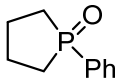
V. Synthesis of 1-Phenylphospholane Oxide (2l).



In a glovebox filled with nitrogen, $Ni(cod)_2$ (5.5 mg, 0.020 mmol), PhOTf (4.5 mg, 0.020 mmol), **1l** (43 mg, 0.10 mmol) and DMF (5 mL) were added to a 10 mL vial with a Teflon-sealed screwcap. The vessel was heated at 140 °C for 40 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was then stirred at room temperature for 1 h. The reaction mixture was dried in vacuo and then subjected to column chromatography but **2l**, triphenylphosphine oxide and oxidized **1l** could not be separated by flash column chromatography. O'Brien and co-workers reported on a method for the selective reduction of **2l** in the presence of non-cyclic tertiary phosphine oxides.[2] We used this method for selective reduction of **2l** in the

presence of triphenylphosphine oxide and oxidized **1l**, which would allow us to isolate **2l** from the reaction mixture. Thus, the reaction mixture containing **2l**, $PhCO_2H$ (12 mg, 0.10 mmol), $^{i}Pr_2NEt$ (180 mg, 1.4 mmol) and THF (3 mL) were added to a 10 mL vial and the solution was stirred for 1 min. $PhSiH_3$ (152 mg, 1.4 mmol) was then added and the solution was stirred at room temperature for 1 h. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through a short pad of silica gel, and the pad was further washed with THF. The filtrate was evaporated to give **2l** as a mixture with triphenylphosphine oxide (20 mg, **2l**:$Ph_3P(=O)$ = 1.0:1.4 by ^{31}P NMR). The yield of **2l** was estimated to be 50%.

1-Phenylphospholane 1-oxide (2l) [CAS:4963-91-1]



White solid. R_f 0.20 (SiO_2, 3% NEt_3, EtOAc).

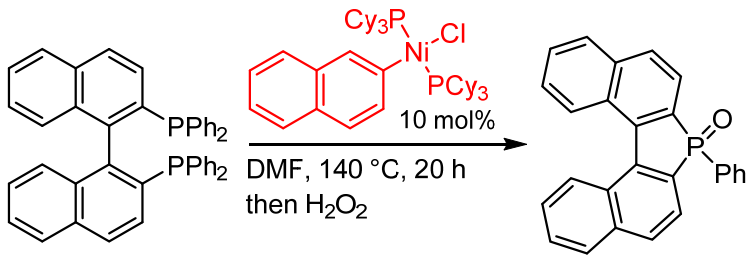
^1H NMR ($CDCl_3$, 399.78 MHz) δ: 1.91–2.24 (m, 8H), 7.47–7.56 (m, 3H), 7.71–7.77 (m, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 25.3 (d, J = 8.6 Hz), 29.7 (d, J = 67.1 Hz), 128.6 (d, J = 11.5 Hz), 129.9 (d, J = 10.5 Hz), 131.6 (d, J = 2.9 Hz), 134.3 (d, J = 90.1 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 61.0.

HRMS (EI+, M^+) Calcd for $C_{10}H_{13}OP$: 180.0704. Found: 180.0701.

VI. Catalytic Experiment Using NiCl(2-Np)(PCy_3)$_2$

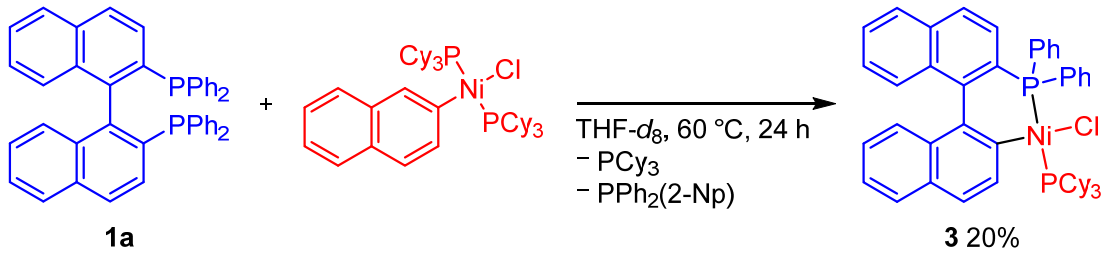


1a **2a** 85%

In a glovebox filled with nitrogen, NiCl(2-Np)(PCy_3)$_2$ (15.6 mg, 0.02 mmol),[1] **1a** (125 mg, 0.20 mmol) and DMF (1 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The vessel was heated at 140 °C for 20 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The yield of **2a** was determined by ^1H NMR using 1,1,2,2,-tetrachloroethane as an internal standard.

VII. Stoichiometric Experiments Using NiCl(2-Np)(PCy_3)$_2$

• **Synthesis of Phospha-Nickelacycle 3 via the Cleavage of Carbon–Phosphorus Bond**



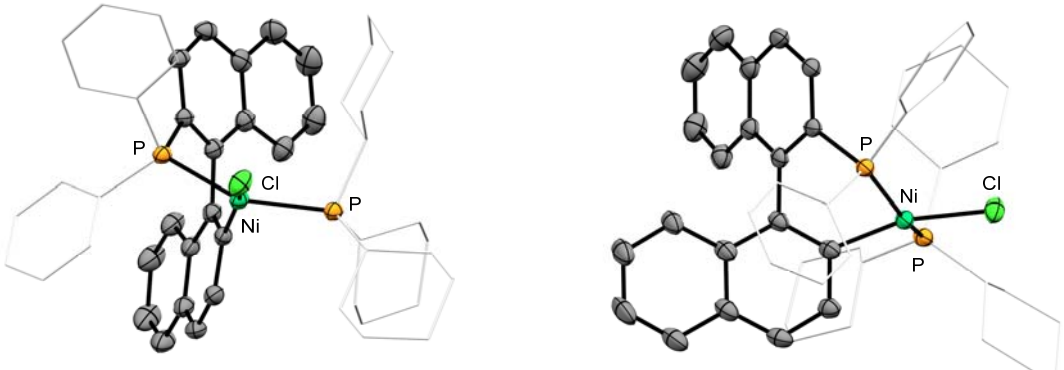
1a **3** 20%

In a glovebox filled with nitrogen, $NiCl(2\text{-}Np)(PCy_3)_2$ (7.8 mg, 0.01 mmol), **1a** (6.3 mg, 0.01 mmol) and THF-d_8 (0.6 mL) were added to a J-Young NMR tube and heated at 60 °C for 24 h. The yield of **3** was determined by ^{31}P NMR using hexamethylphosphoric triamide as an internal standard. The resulting solution was filtered through Celite, and dried in vacuo. Pentane (1.0 mL) was added with vigorous stirring and the resulting red suspension (this precipitate contains complex **4**) was filtrated. The filtrate was dried in vacuo and purified by recrystallization from THF and pentane to afford a red-colored single crystal of **3**. Some of these crystals were suitable for X-ray analysis.

^1H NMR ($CDCl_3$, 399.78 MHz) δ: 0.83–1.94 (m, 33H), 6.73 (br, 1H), 6.87–6.90 (m, 2H), 6.96–7.00 (m, 1H), 7.03–7.06 (m, 1H), 7.09–7.12 (m, 2H), 7.31–7.56 (m, 11H), 7.60 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H).

^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 16.6 (d, J = 318 Hz), 22.8 (d, J = 318 Hz).

HRMS (FAB+, $[M\text{-}Cl]^+$) Calcd for$C_{50}H_{55}NiP_2$: 775.3132. Found: 775.3146.



Front view Side view

Figure S1. ORTEP drawing of **3** with thermal ellipsoids set at the 50% probability (except for the phenyl and cyclohexyl groups) and all the hydrogen atoms are omitted for clarity. CCDC 1907794.

• **NMR Experiments**

In a glovebox filled with nitrogen, $NiCl(2\text{-}Np)(PCy_3)_2$ (7.8 mg, 0.01 mmol), **1a** (6.3 mg, 0.01 mmol) and THF-d_8 (0.6 mL) were added to a J-Young NMR tube and heated. Reaction was monitored by ^{31}P NMR.

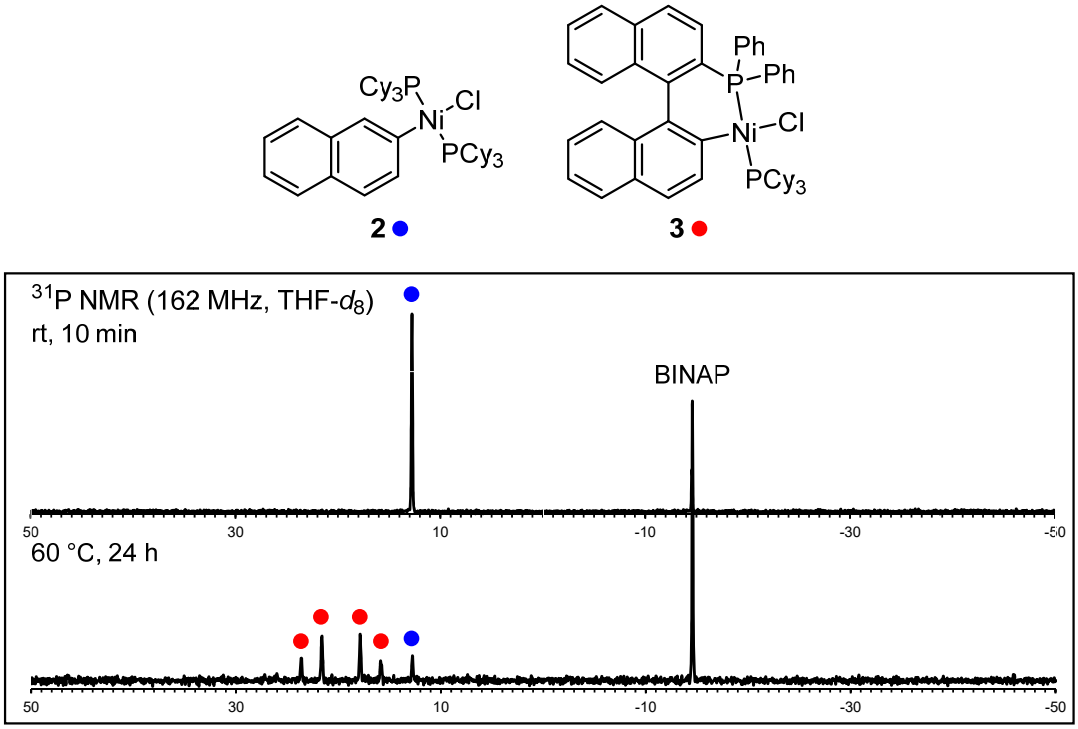
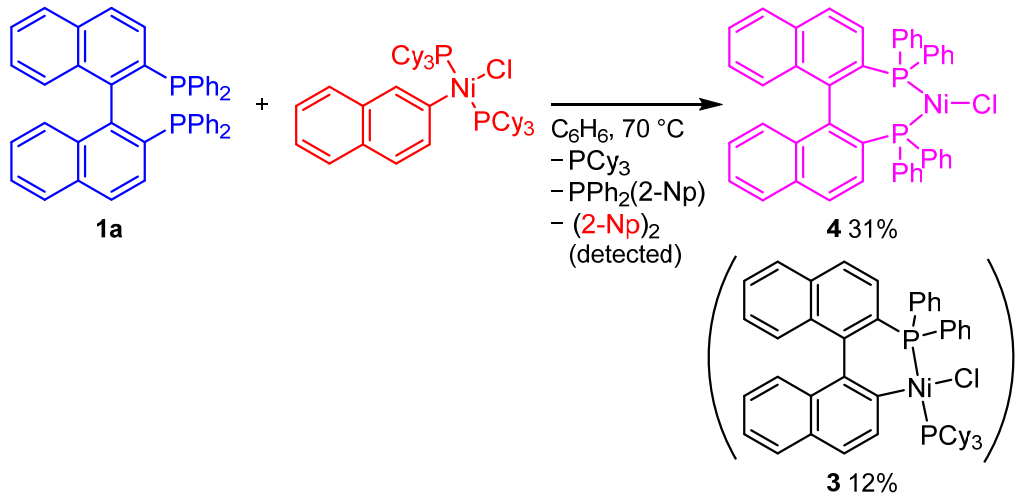


Figure S2. ^{31}P NMR results on the reaction of NiCl(2-Np)(PCy_3)$_2$ with **1a** at 60 °C.

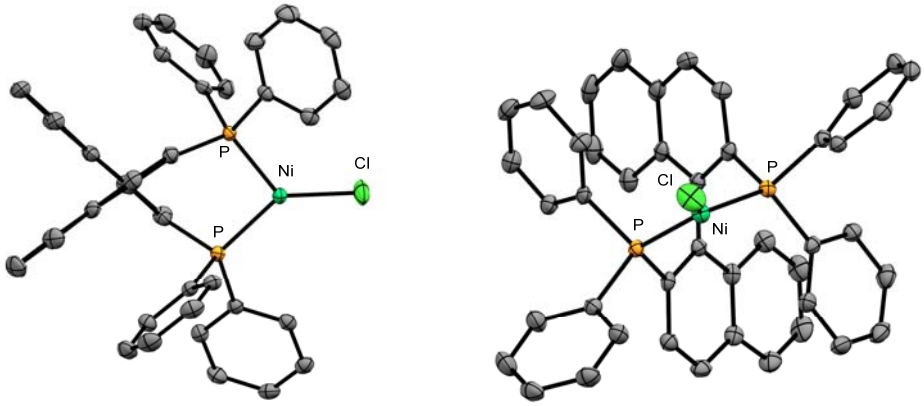
- **Synthesis of Nickel(I) Complex 4**



In a glovebox filled with nitrogen, NiCl(2-Np)(PCy_3)$_2$ (72.9 mg, 0.09 mmol), **1a** (60.8 mg, 0.10 mmol) and benzene (2.5 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The vessel was heated at 70 °C for 40 h without stirring to afford a red precipitate. Complex **4** was isolated as a red solid by filtration. Some of these crystals were suitable for X-ray analysis. During the course of the formation of **4**, 2,2'-binaphthalene [(2-Np)$_2$], which is formed by bimolecular reductive

elimination from BINAP-ligated Ni(II) complex phosphorus residue, was observed by FAB-MS. Hartwig group reported a related binuclear BINAP-ligated Ni(I) complex, which is formed by bimolecular reductive elimination from BINAP-ligated Ni(II) complex.[3] Interestingly, however, we have obtained here a mononuclear BINAP-ligated Ni(I) complex.

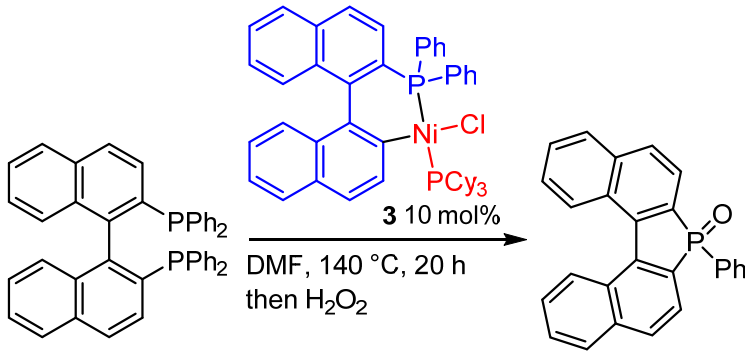
HRMS (FAB+, M^+) Calcd for $C_{44}H_{32}ClNiP_2$: 715.1021. Found: 715.1028.



Top view Front view

Figure S3. ORTEP drawing of **4** with thermal ellipsoids set at the 50% probability and all the hydrogen atoms are omitted for clarity. CCDC 1907915.

VIII. Catalytic Experiment Using Phospha-Nickelacycle 3

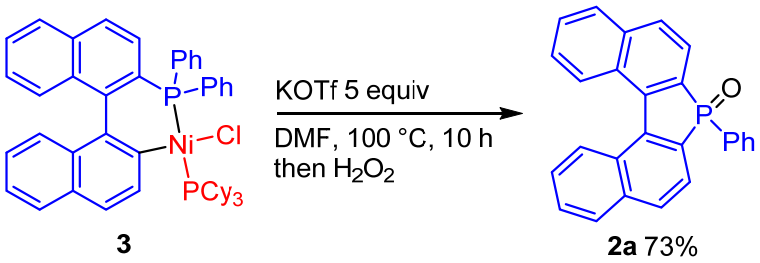


1a **2a** 98%

In a glovebox filled with nitrogen, **3** (16.1 mg, 0.02 mmol), **1a** (126 mg, 0.20 mmol) and DMF (1 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The vessel was heated at 140 °C for 20 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The yield of **2a** was determined by ^{1}H NMR using 1,1,2,2,-tetrachloroethane as an internal standard.

IX. Stoichiometric Experiment Using Phospha-Nickelacycle 3

• **Reductive Elimination of 2a from Phospha-Nickelacycle 3**



3 **2a** 73%

In a glovebox filled with nitrogen, **3** (16.2 mg, 0.02 mmol), KOTf (18.8 mg, 0.10 mmol) and DMF (1 mL) were added to a 5 mL vial with a Teflon-sealed screwcap and heated at 100 °C for 10 h. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The yield of **2a** was determined by ^{1}H NMR using 1,1,2,2,-tetrachloroethane as an internal standard.

• **Effect of KOTf**

In a glovebox filled with nitrogen, **3** (16.2 mg, 0.02 mmol), KOTf (18.8 mg, 0.10 mmol) and DMF (1 mL) were added to a 5 mL vial with a Teflon-sealed screwcap and heated at 100 °C for 1–10 h. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The yield of **2a** was determined by ^{1}H NMR using 1,1,2,2,-tetrachloroethane as an internal standard. Similar experiments were conducted under the condition without addition of KOTf.

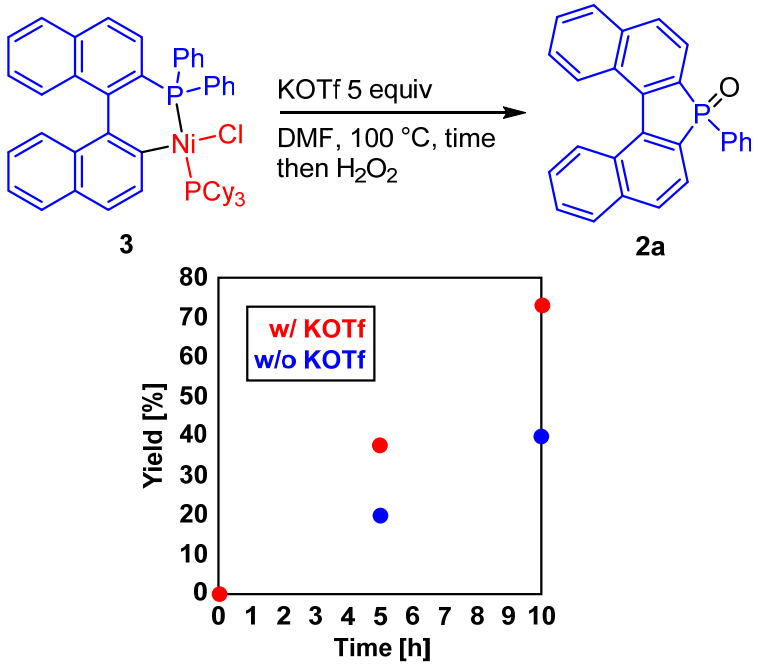
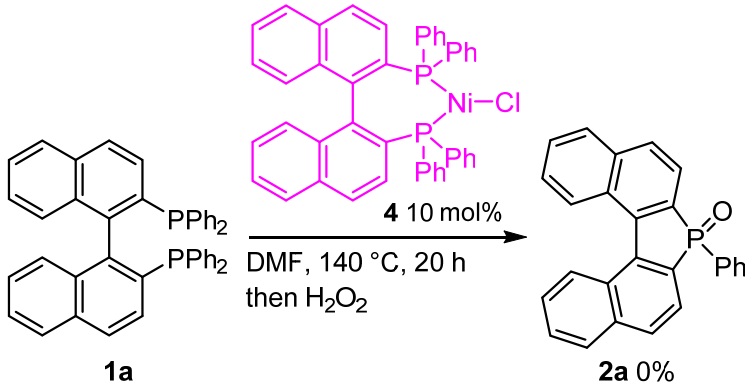


Figure S4. Time course of the reductive elimination of **2a** from **3** in the absence (red)/presence (blue) of KOTf.

X. Catalytic Experiment Using BINAP-ligated Ni(I) Complex 4



In a glovebox filled with nitrogen, **4** (7.2 mg, 0.01 mmol), **1a** (62.3 mg, 0.10 mmol) and DMF (1 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The vessel was heated at 140 °C for 20 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The yield of **2a** was determined by ^{1}H NMR using 1,1,2,2,-tetrachloroethane as an internal standard.

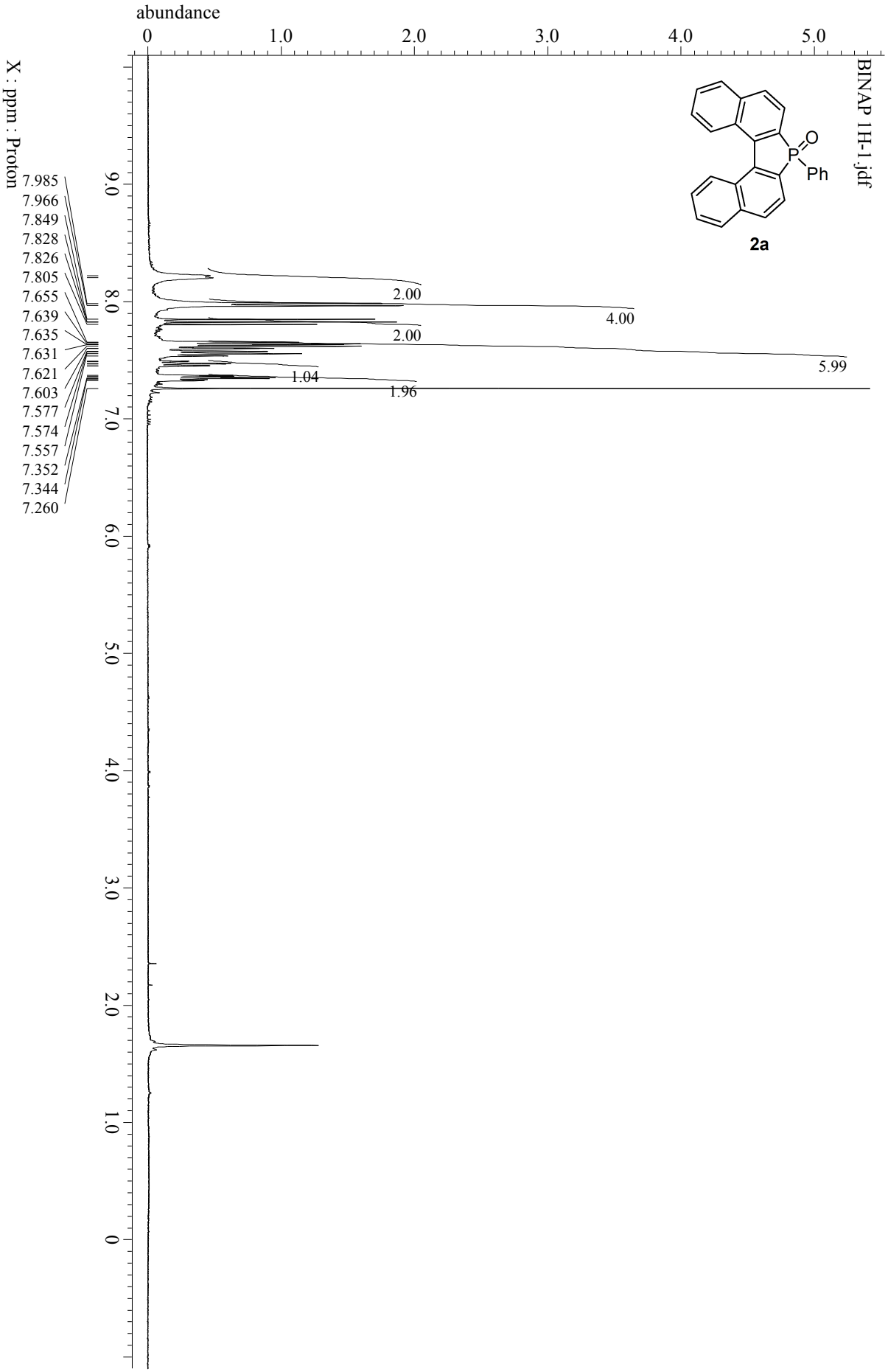
XI. Reference

1 R. L. Jezorek, N. Zhang, P. Leowanawat, M. H. Bunner, N. Gutsche, A. K. R. Pesti, J. T. Olsen, V. Percec, *Org. Lett.* **2014**, *16*, 6326.

2 C. J. O'Brien, F. Lavigne, E. E. Coyle, A. J. Holohan, B. J. Doonan, *Chem. Eur. J.* **2013**, *19*, 5854.

3 S. Ge, R. A. Green, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 1617.

XII. Copies of ^{1}H, ^{13}C and ^{31}P NMR Spectra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7.603
7.577
7.574
7.557
7.352
7.344
7.260
9.0
8.0
7.0
6.0
5.0
4.0
3.0
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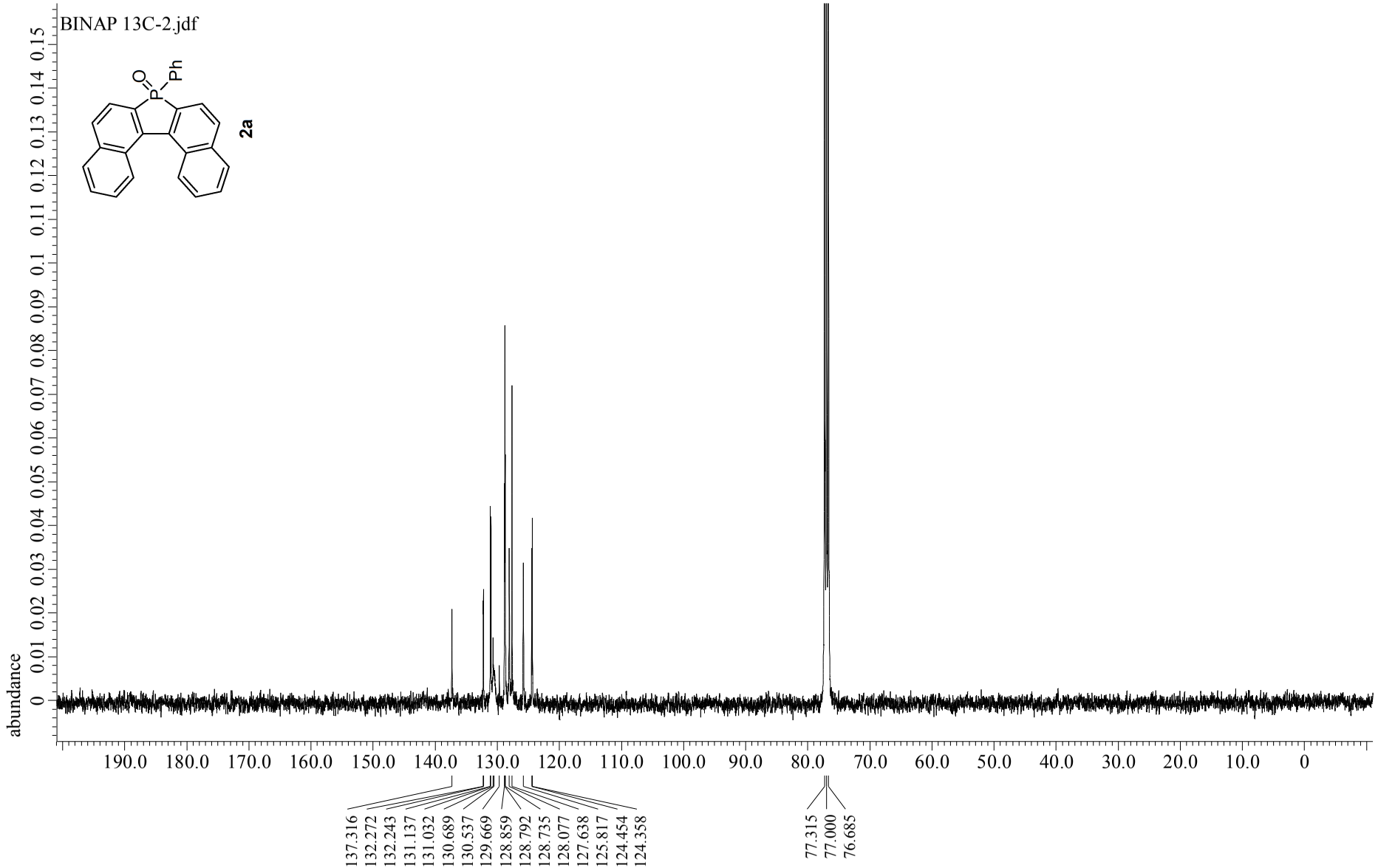
Ph
2a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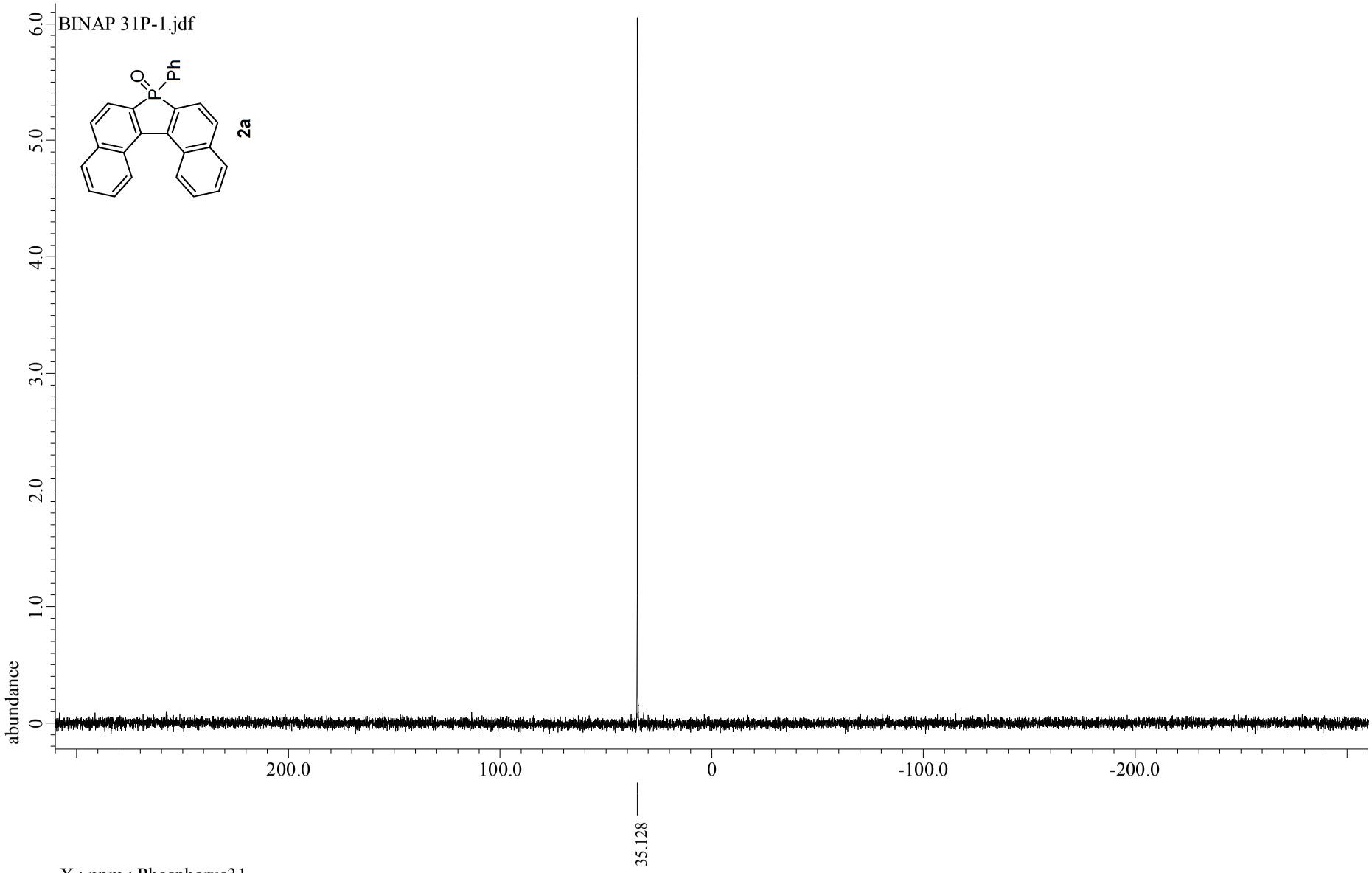
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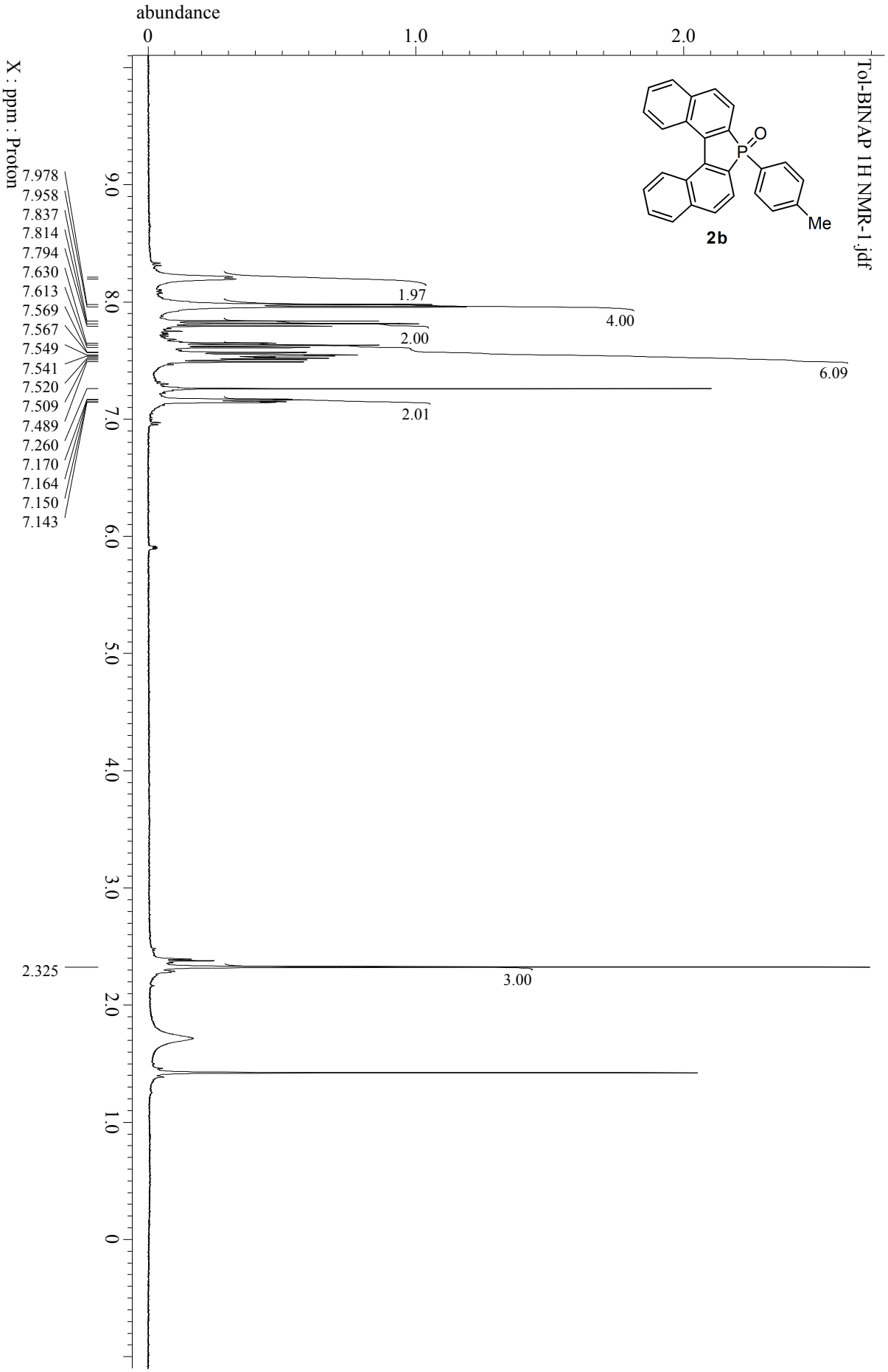
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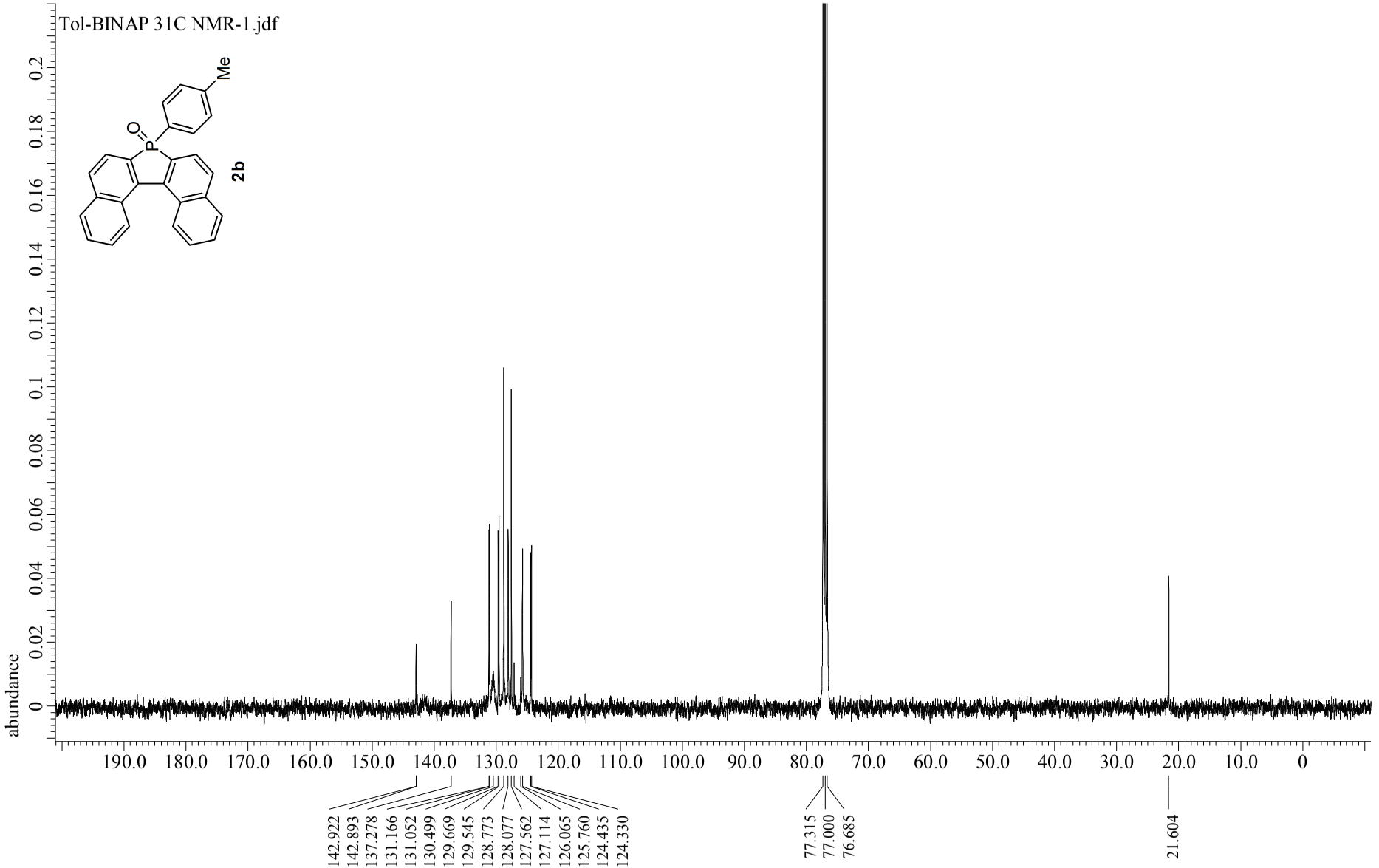
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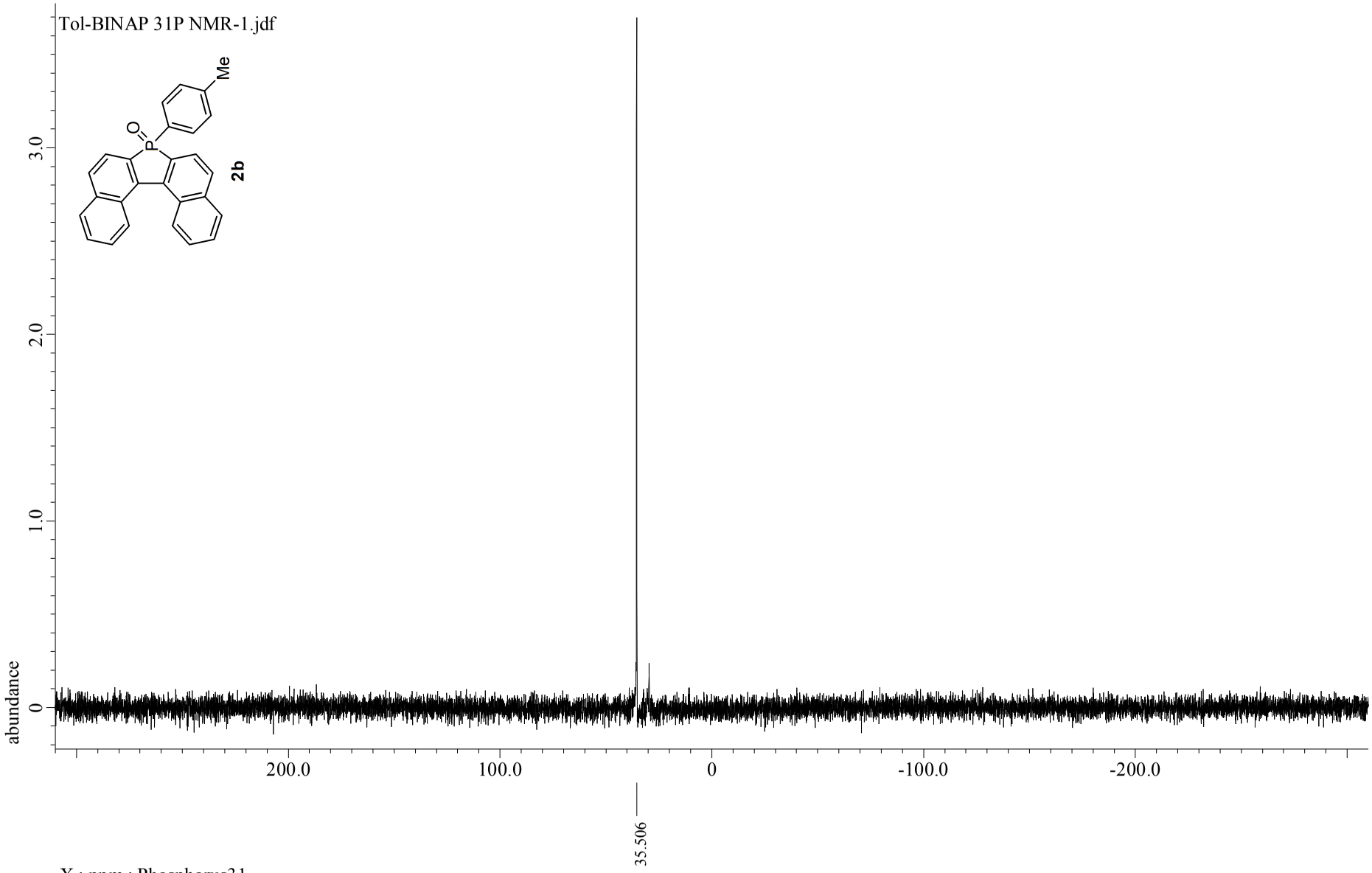
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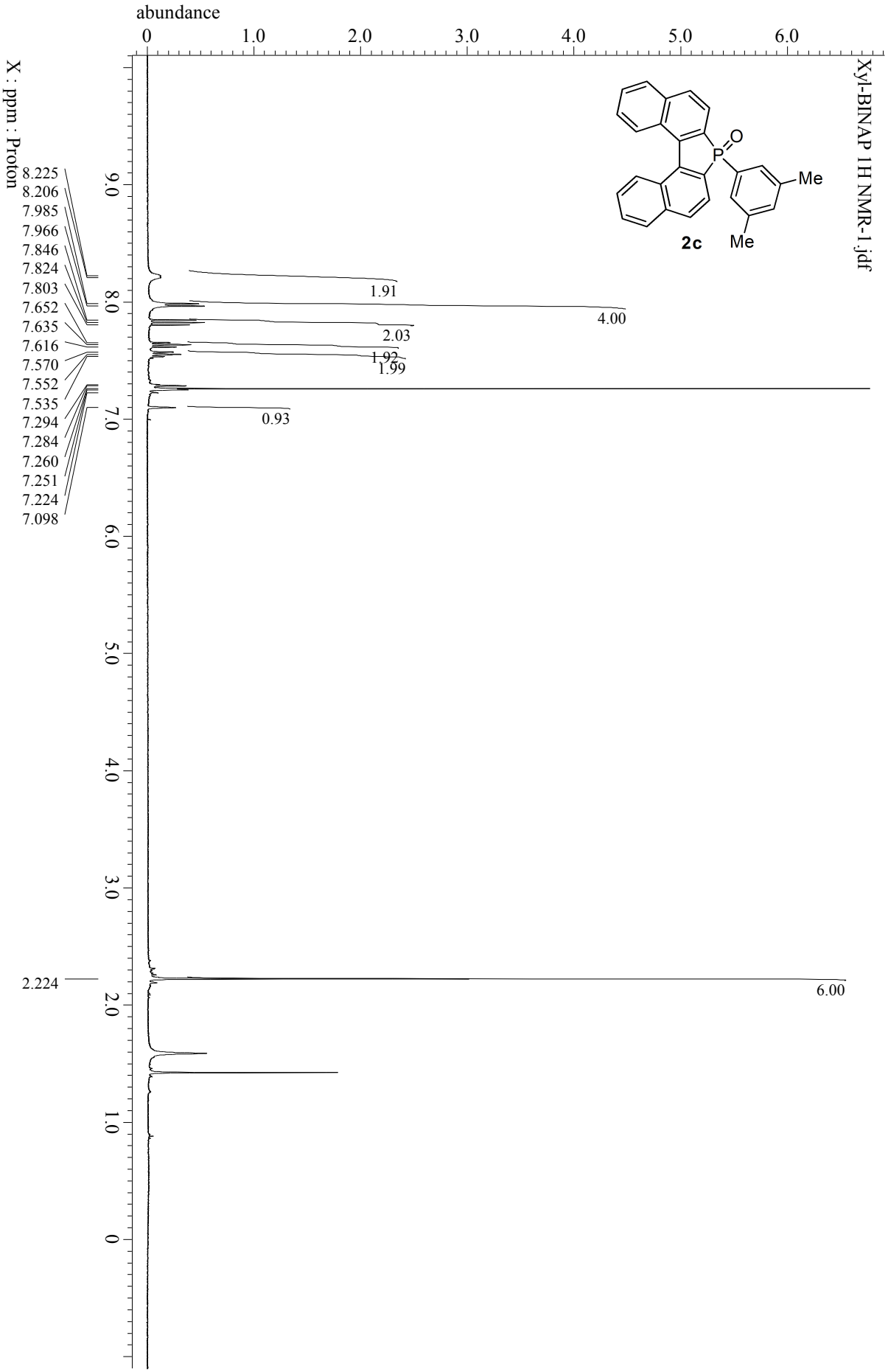
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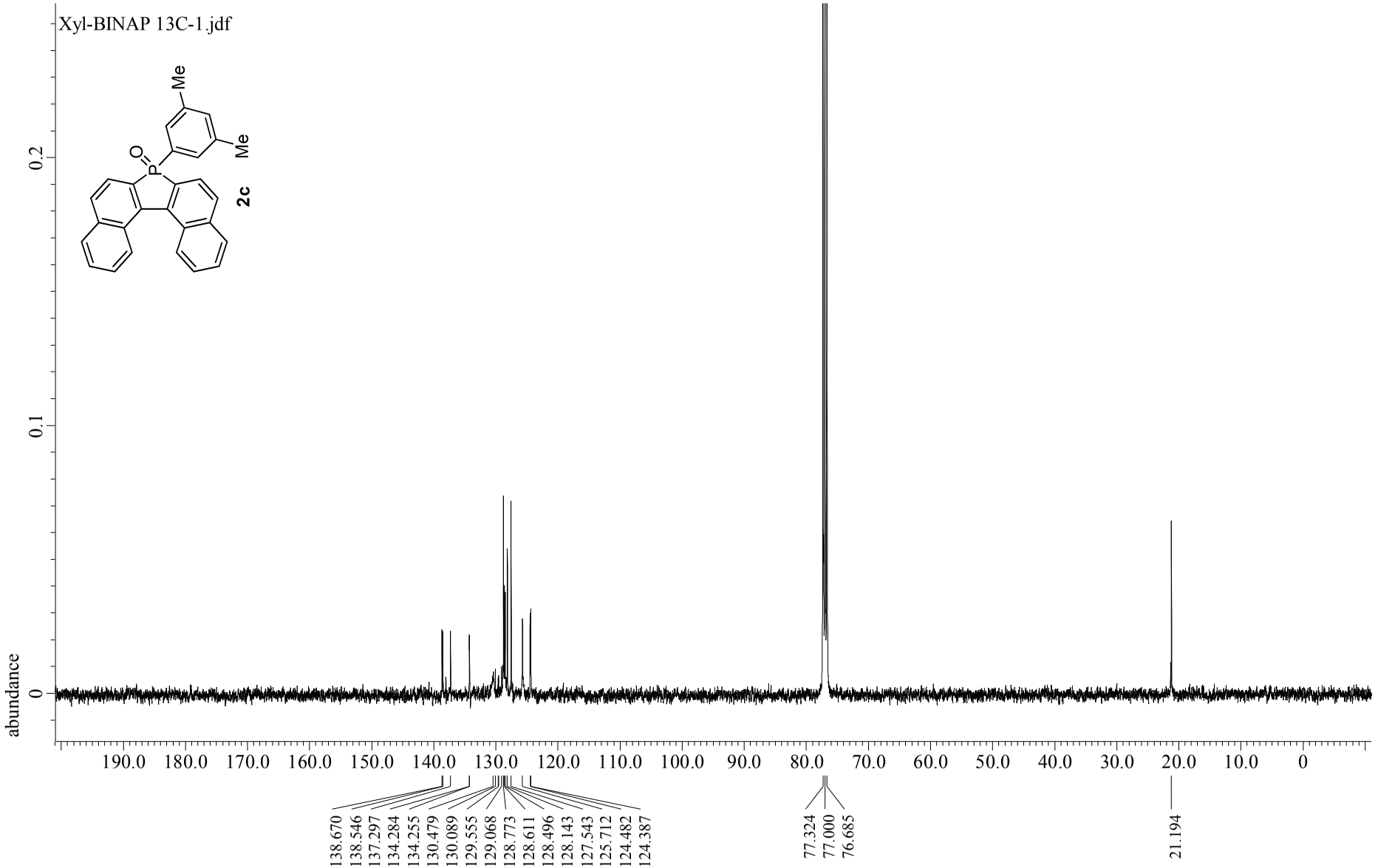
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30.0
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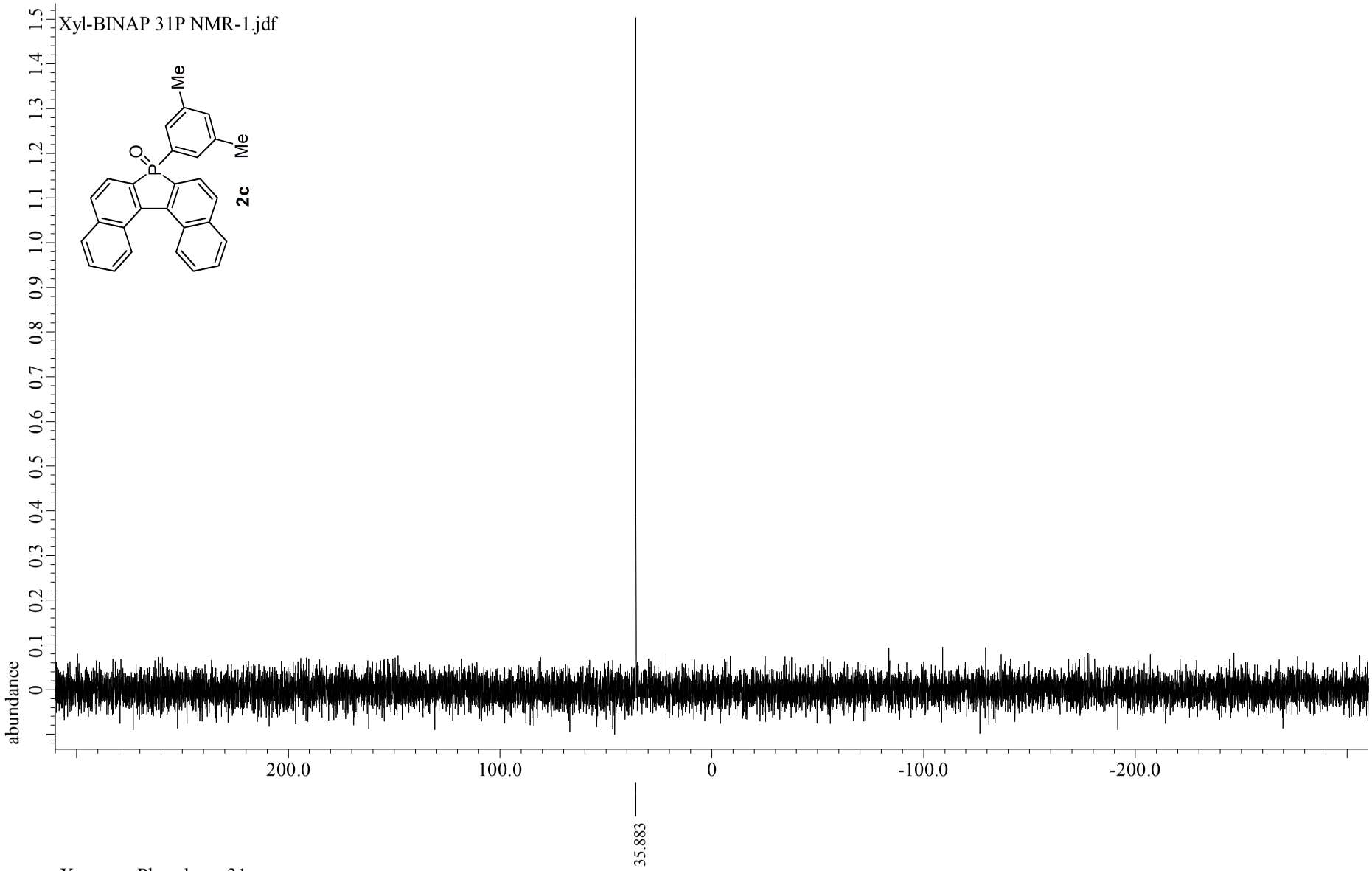
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O
P
2c
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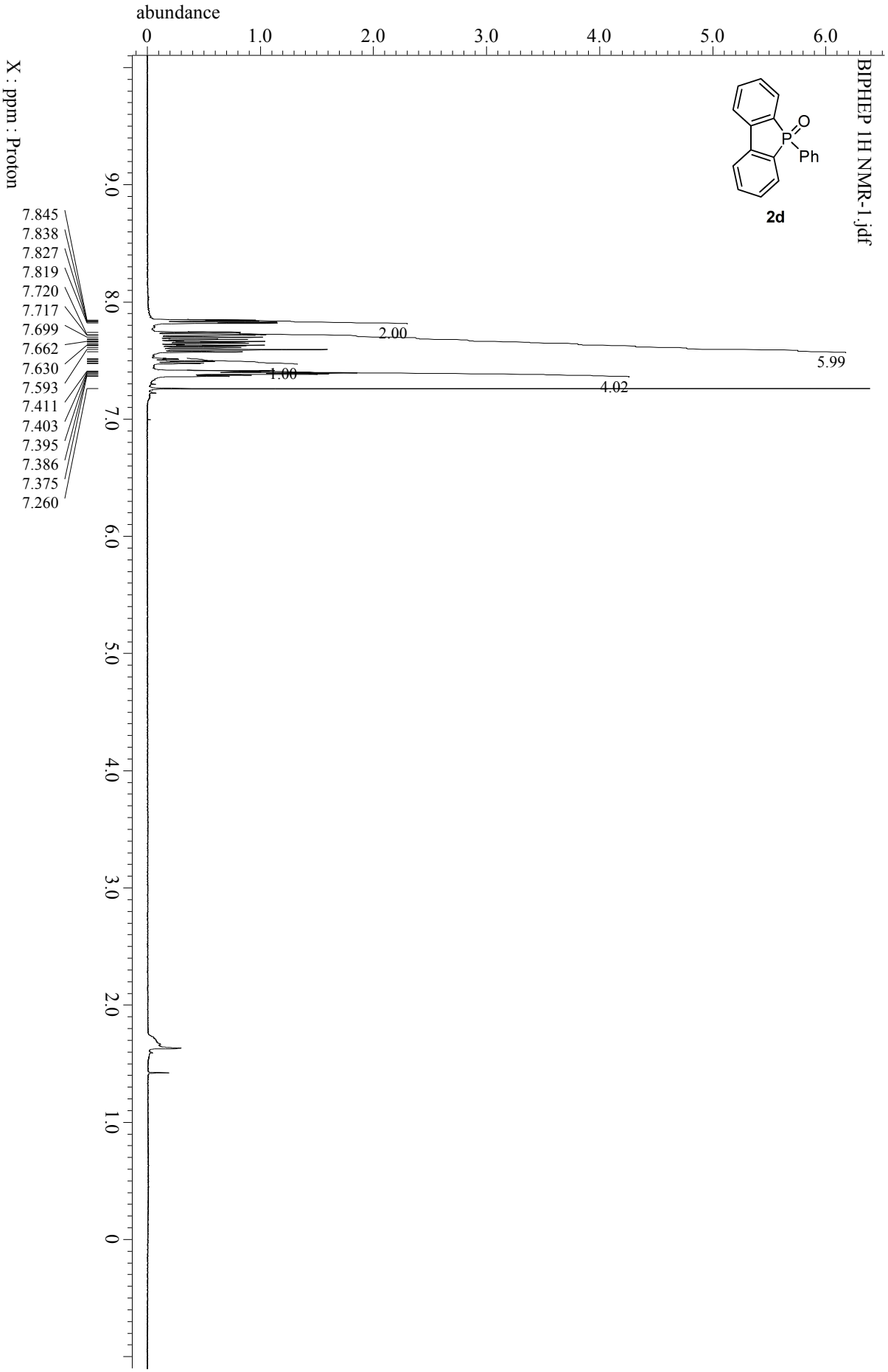
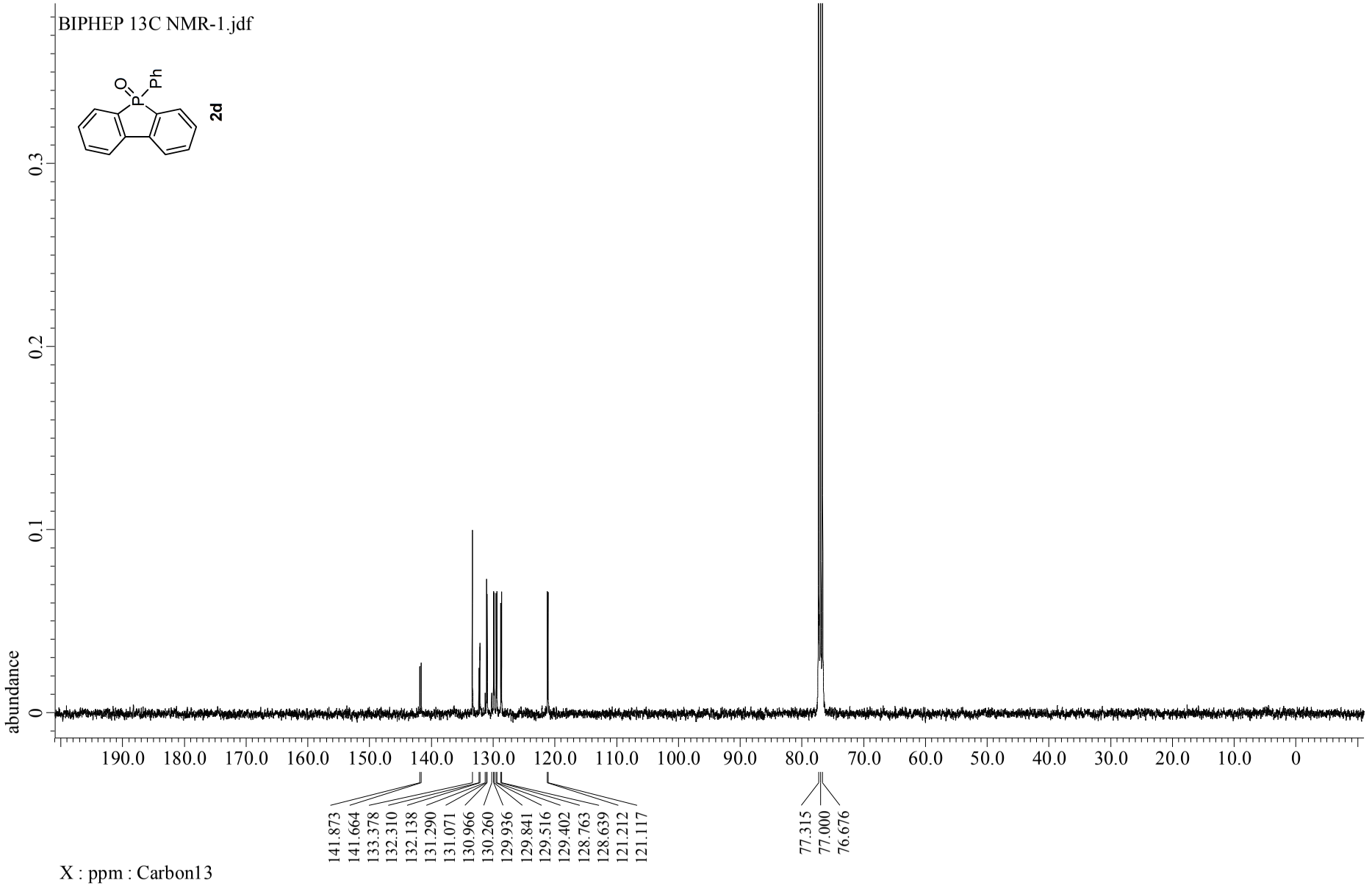
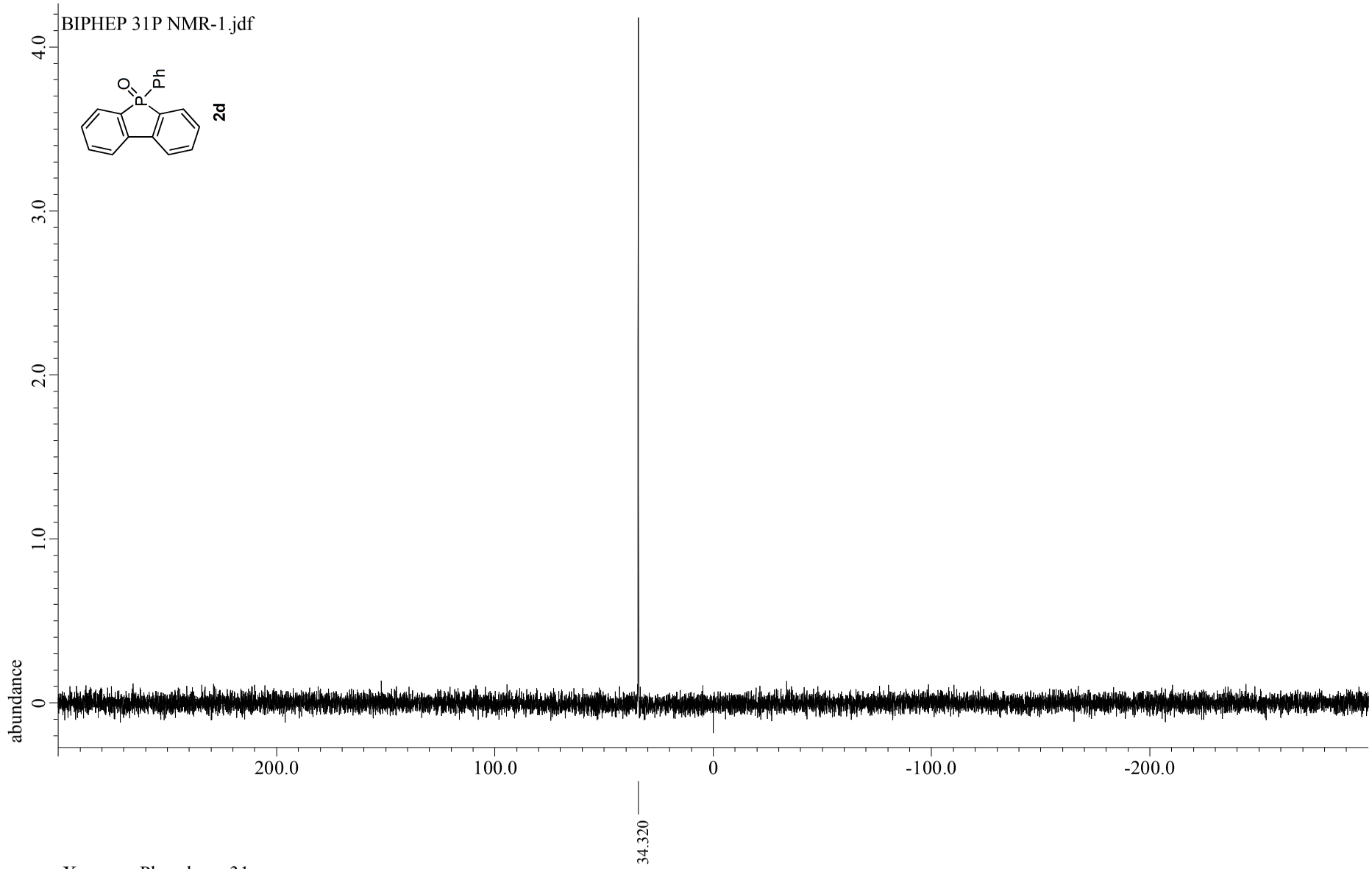
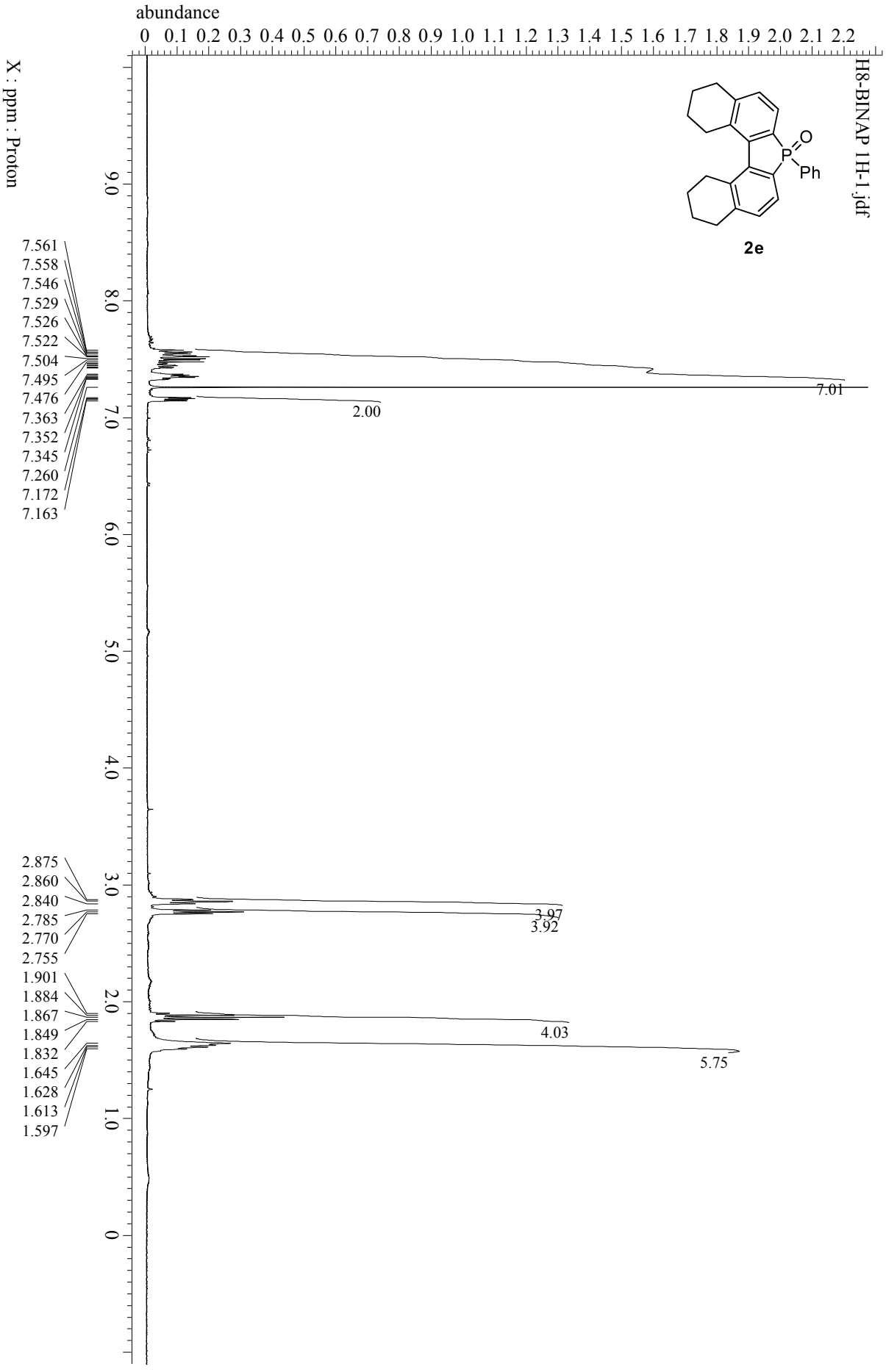
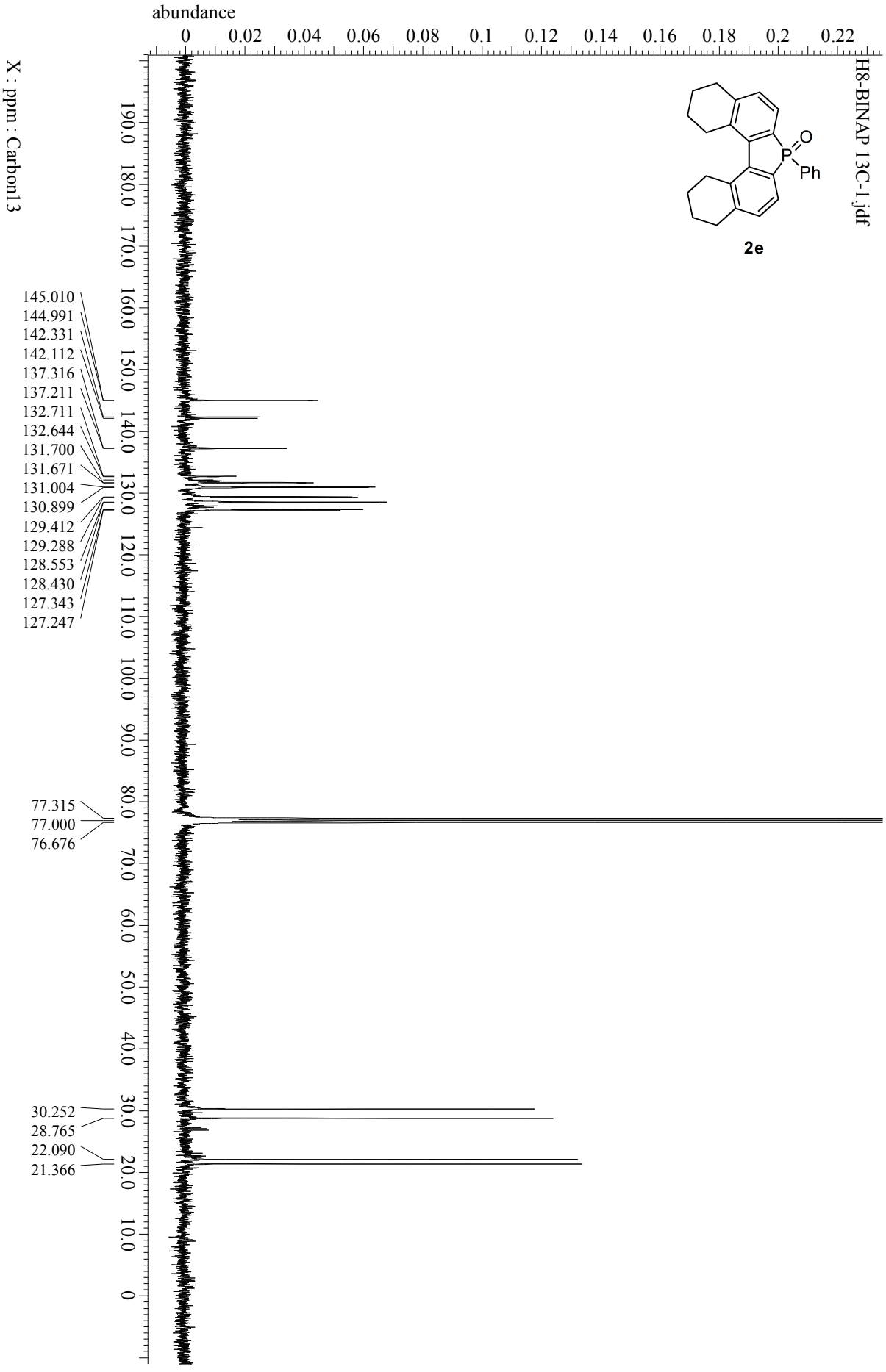
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
200.0
100.0
0
-100.0
-200.0
35.883
X : ppm : Phosphorus31

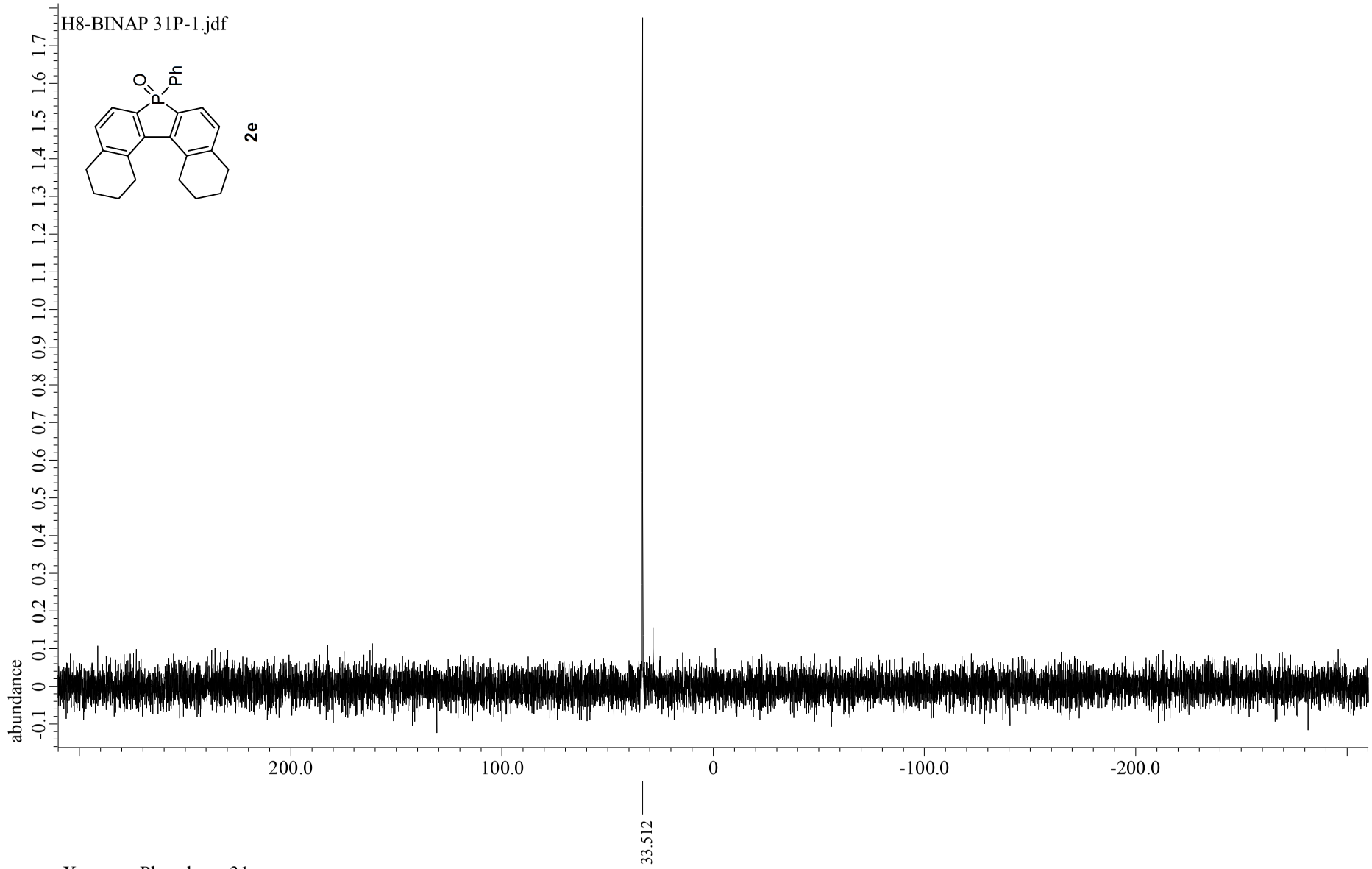

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
BIPHEP 1H NMR-1.jdf
X : ppm : Proton
7.845
7.838
7.827
7.819
7.720
7.717
7.699
7.662
7.630
7.593
7.411
7.403
7.395
7.386
7.375
7.260
2.00
1.00
4.02
5.99
O
P
Ph
2d
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

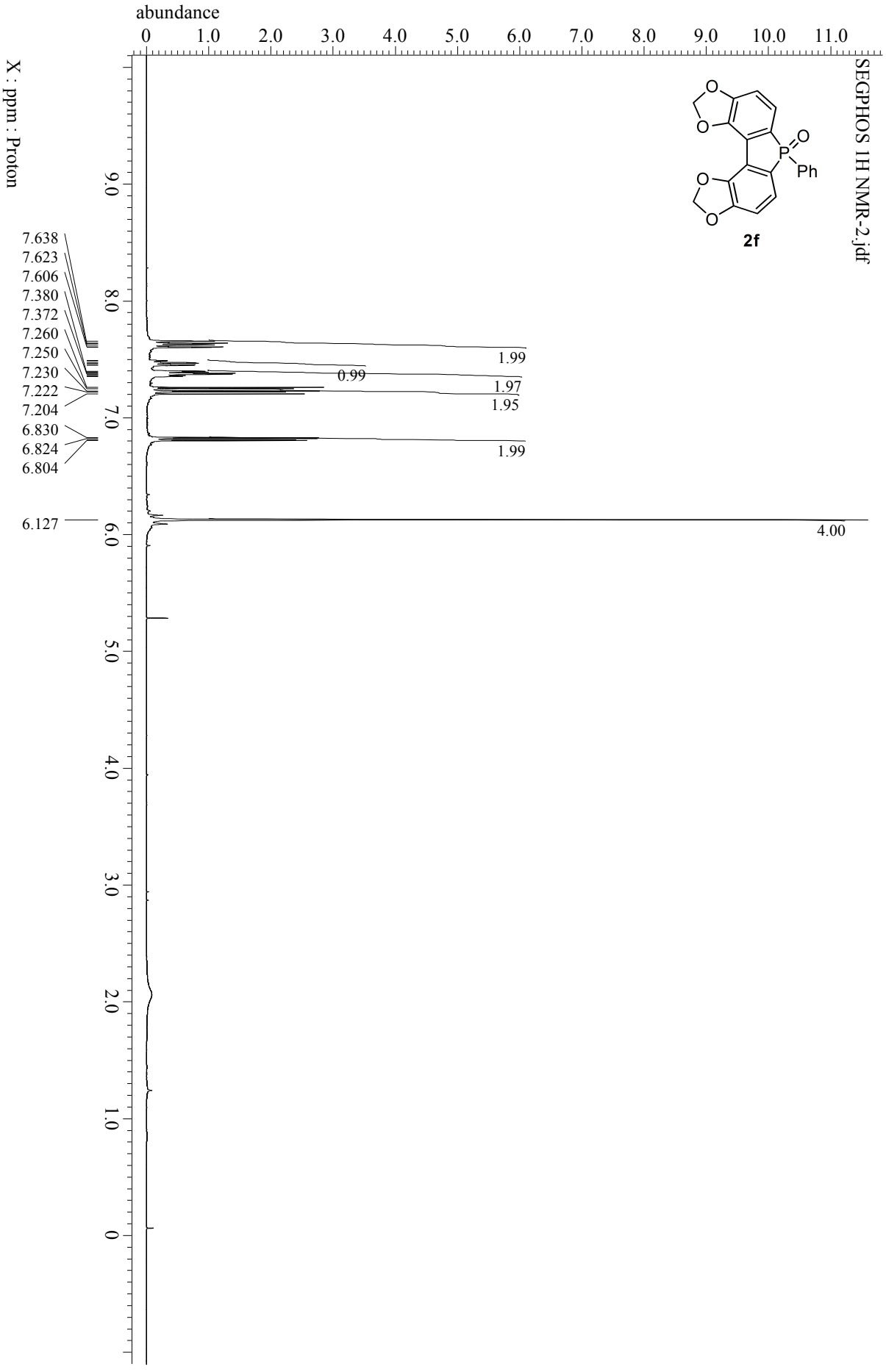

BIPHEP 13C NMR-1.jdf
O
P
Ph
2d
abundance
0
0.1
0.2
0.3
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.873
141.664
133.378
132.310
132.138
131.290
131.071
130.966
130.260
129.936
129.841
129.516
129.402
128.763
128.639
121.212
121.117
77.315
77.000
76.676
X : ppm : Carbon13

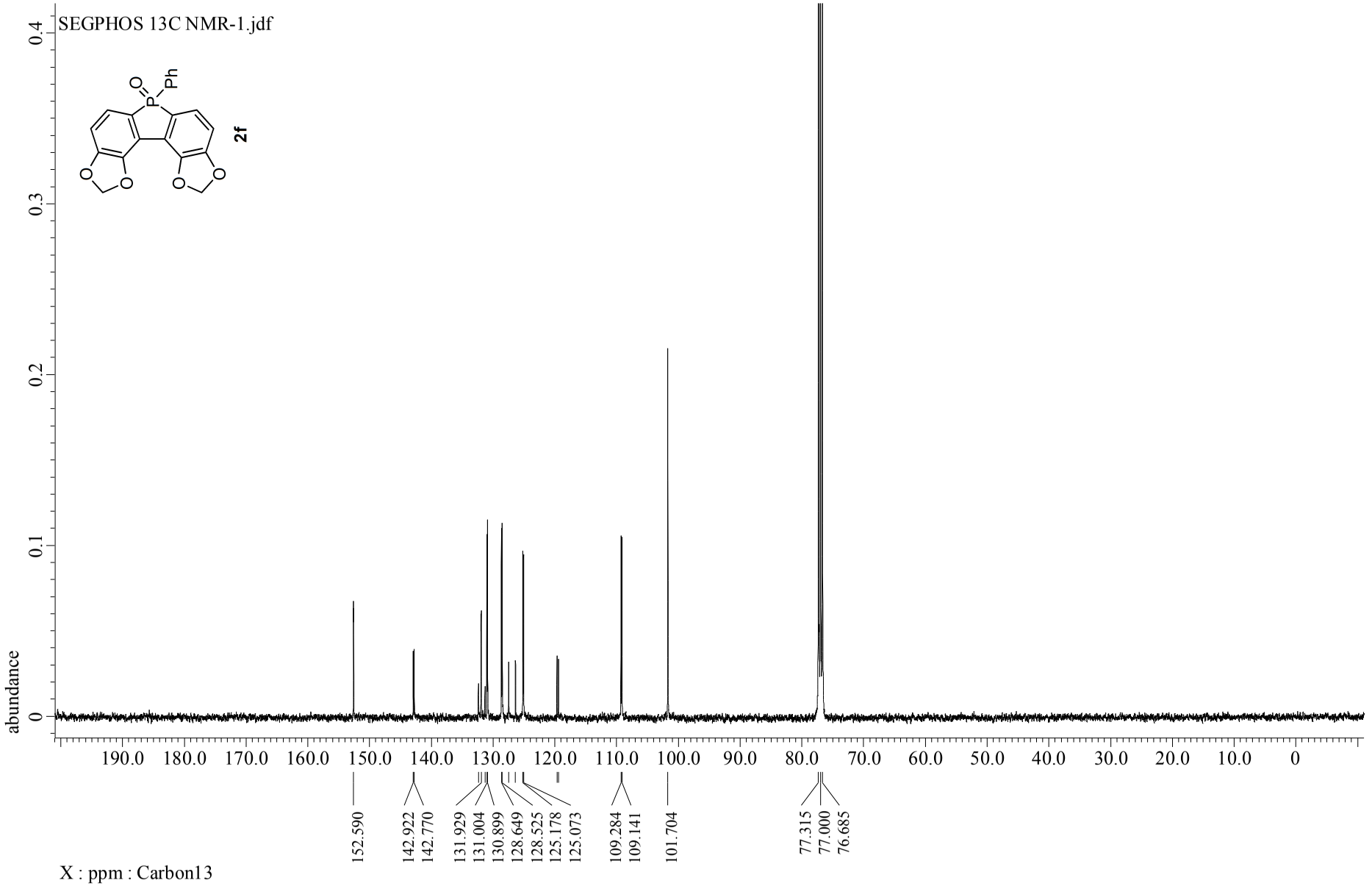

BIPHEP 31P NMR-1.jdf
O
P
Ph
2d
4.0
3.0
2.0
1.0
0
abundance
200.0
100.0
0
-100.0
-200.0
34.320
X : ppm : Phosphorus31

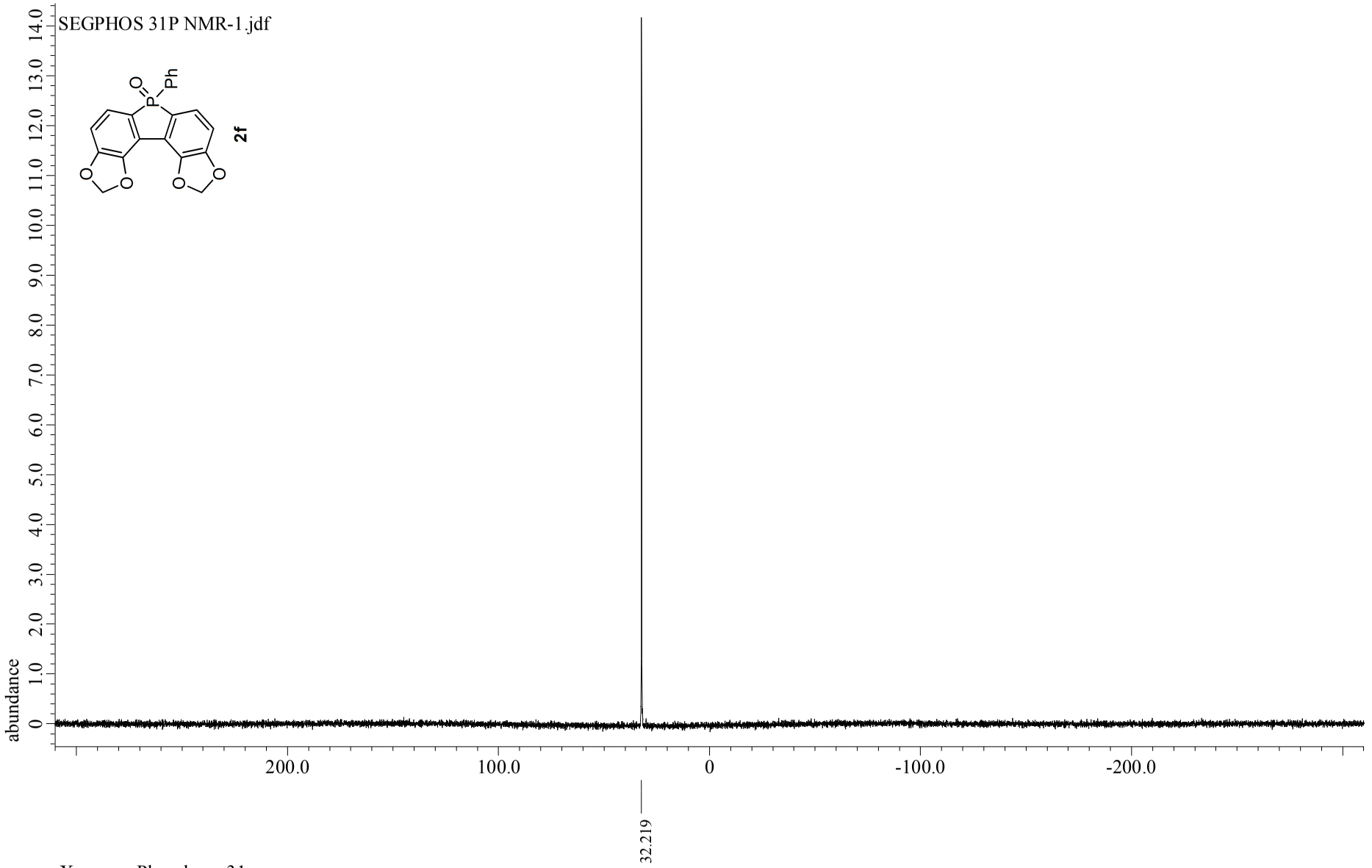

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2
X : ppm : Proton
H8-BINAP 1H-1.jdf
O
P
Ph
2e
7.561
7.558
7.546
7.529
7.526
7.522
7.504
7.495
7.476
7.363
7.352
7.345
7.260
7.172
7.163
2.875
2.860
2.840
2.785
2.770
2.755
1.901
1.884
1.867
1.849
1.832
1.645
1.628
1.613
1.597
7.01
2.00
3.97
3.92
4.03
5.75
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

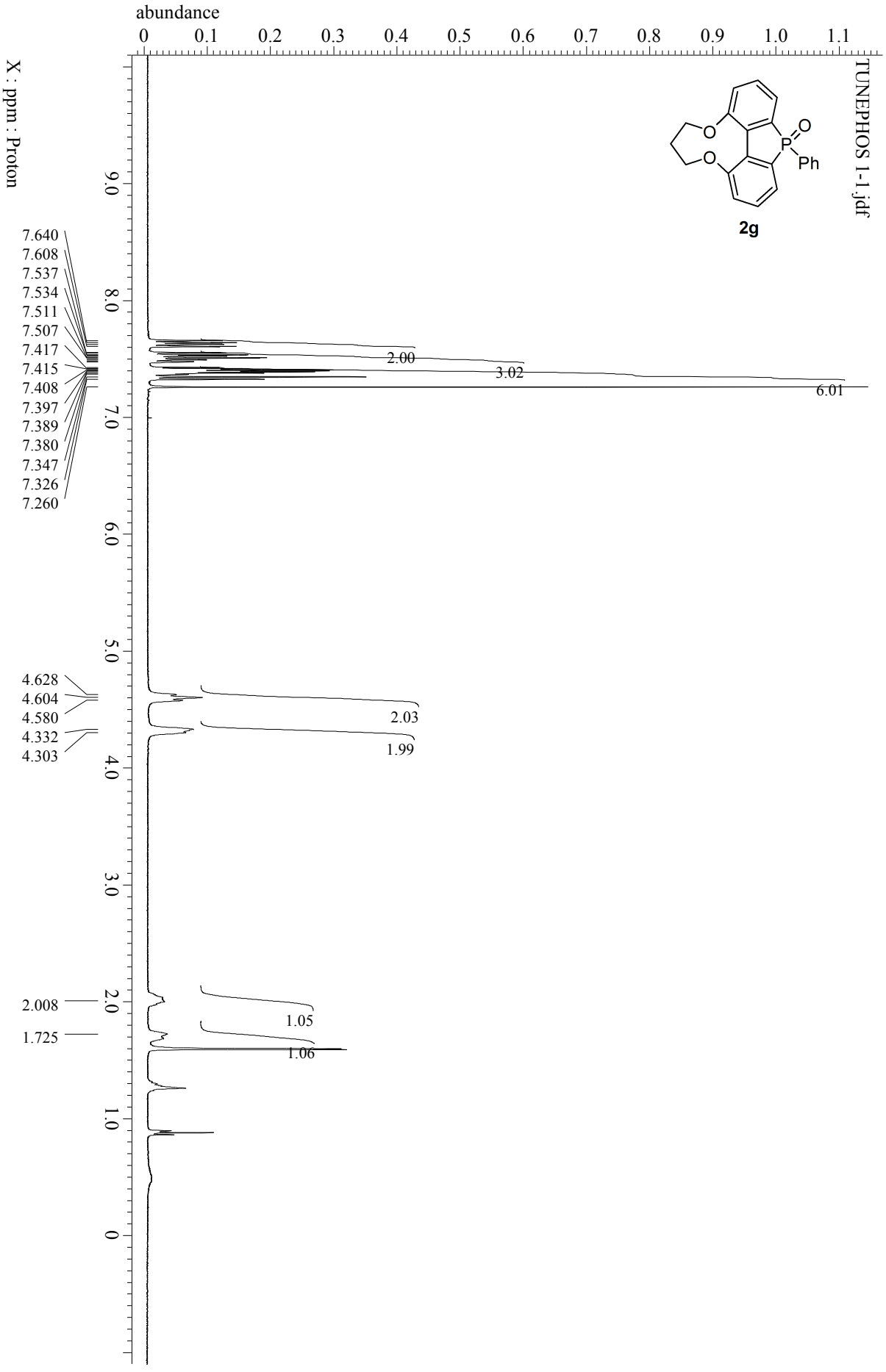

abundance
0 0.02 0.04 0.06 0.08 0.1 0.12 0.14 0.16 0.18 0.2 0.22
H8-BINAP 13C-1.jdf
X : ppm : Carbon13
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
145.010
144.991
142.331
142.112
137.316
137.211
132.711
132.644
131.700
131.671
131.004
130.899
129.412
129.288
128.553
128.430
127.343
127.247
77.315
77.000
76.676
30.252
28.765
22.090
21.366
O
P
Ph
2e

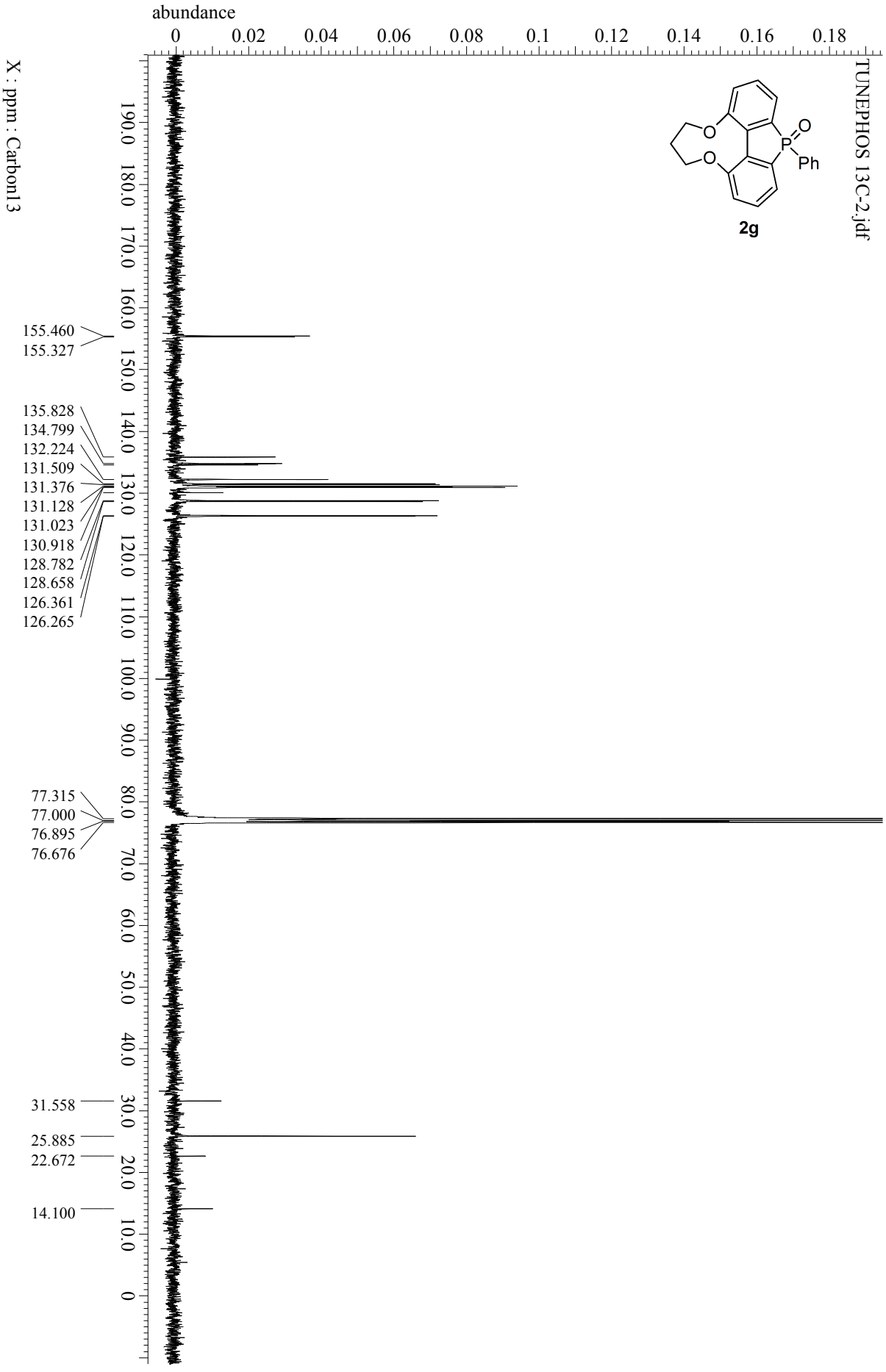

H8-BINAP 31P-1.jdf
O
P
Ph
2e
abundance
-0.1 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7
200.0
100.0
0
-100.0
-200.0
33.512
X : ppm : Phosphorus31

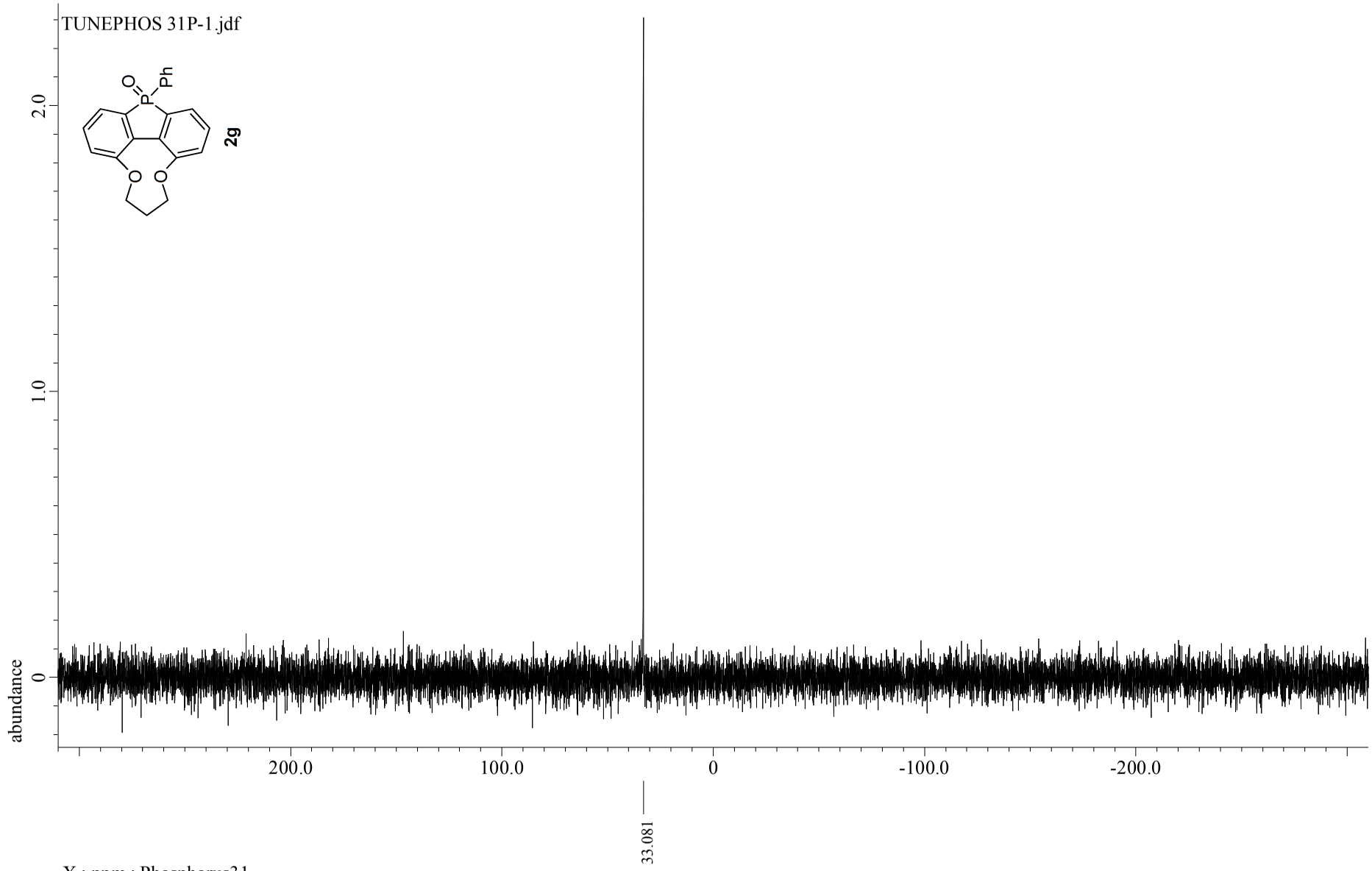

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0
X : ppm : Proton
SEGPHOS 1H NMR-2.jdf
2f
O
O
O
O
P
O
Ph
7.638
7.623
7.606
7.380
7.372
7.260
7.250
7.230
7.222
7.204
6.830
6.824
6.804
6.127
1.99
0.99
1.97
1.95
1.99
4.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

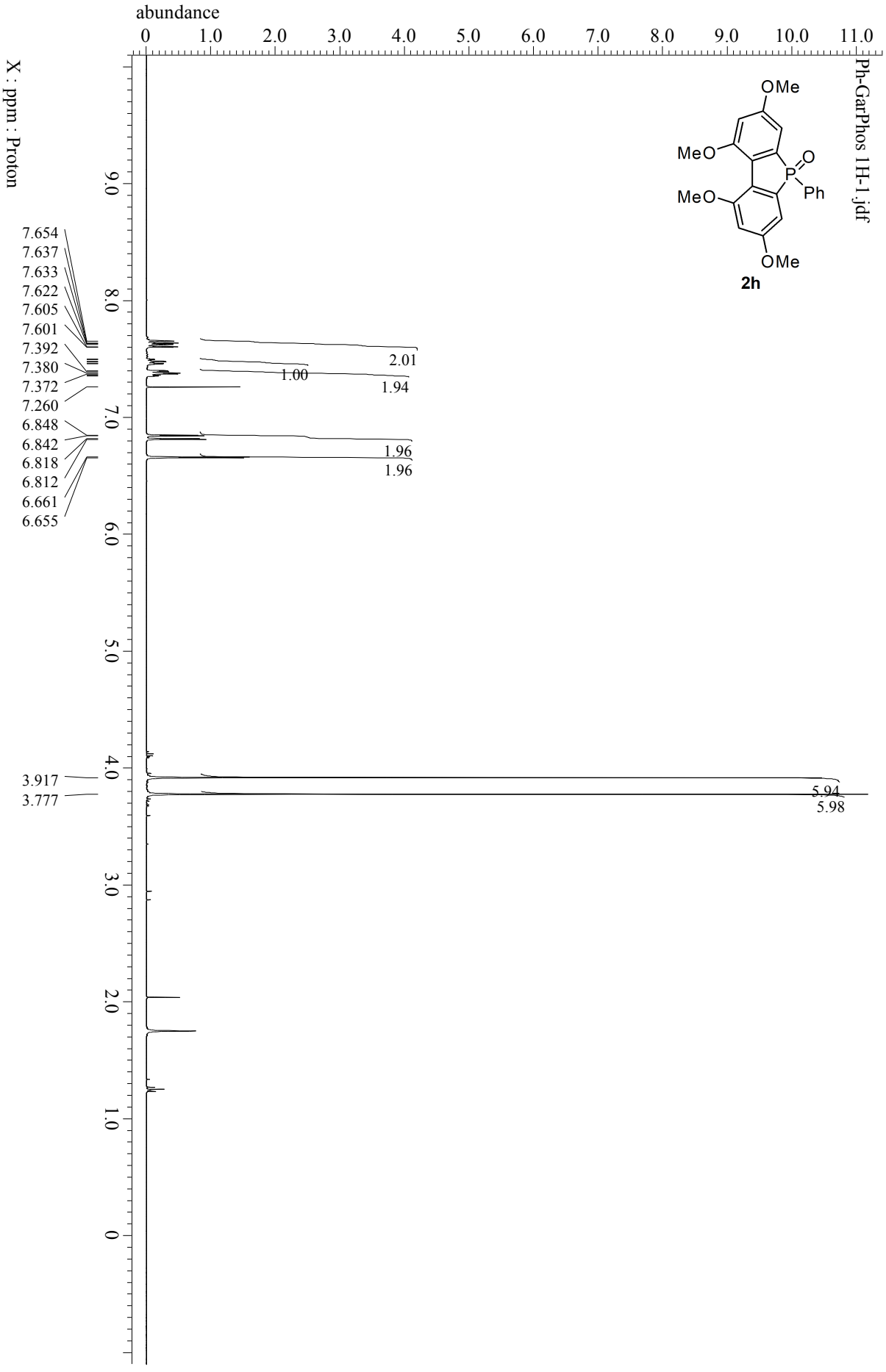

SEGPHOS 13C NMR-1.jdf
O
P
Ph
2f
O
O
O
O
abundance
0
0.1
0.2
0.3
0.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.590
142.922
142.770
131.929
131.004
130.899
128.649
128.525
125.178
125.073
109.284
109.141
101.704
77.315
77.000
76.685
X : ppm : Carbon13

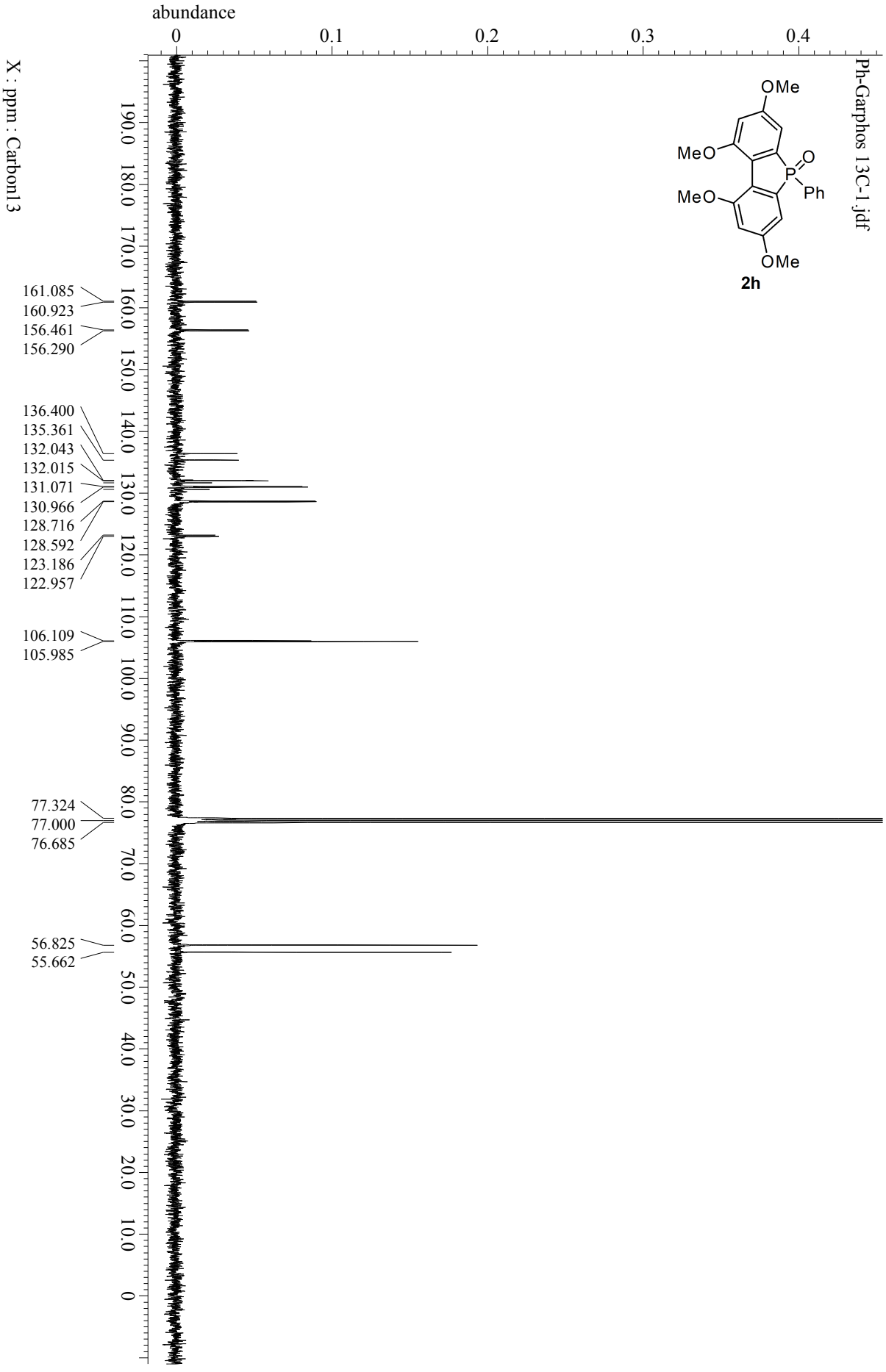

SEGPHOS 31P NMR-1.jdf
O
P
Ph
O
O
O
O
2f
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
200.0
100.0
0
-100.0
-200.0
32.219
X : ppm : Phosphorus31

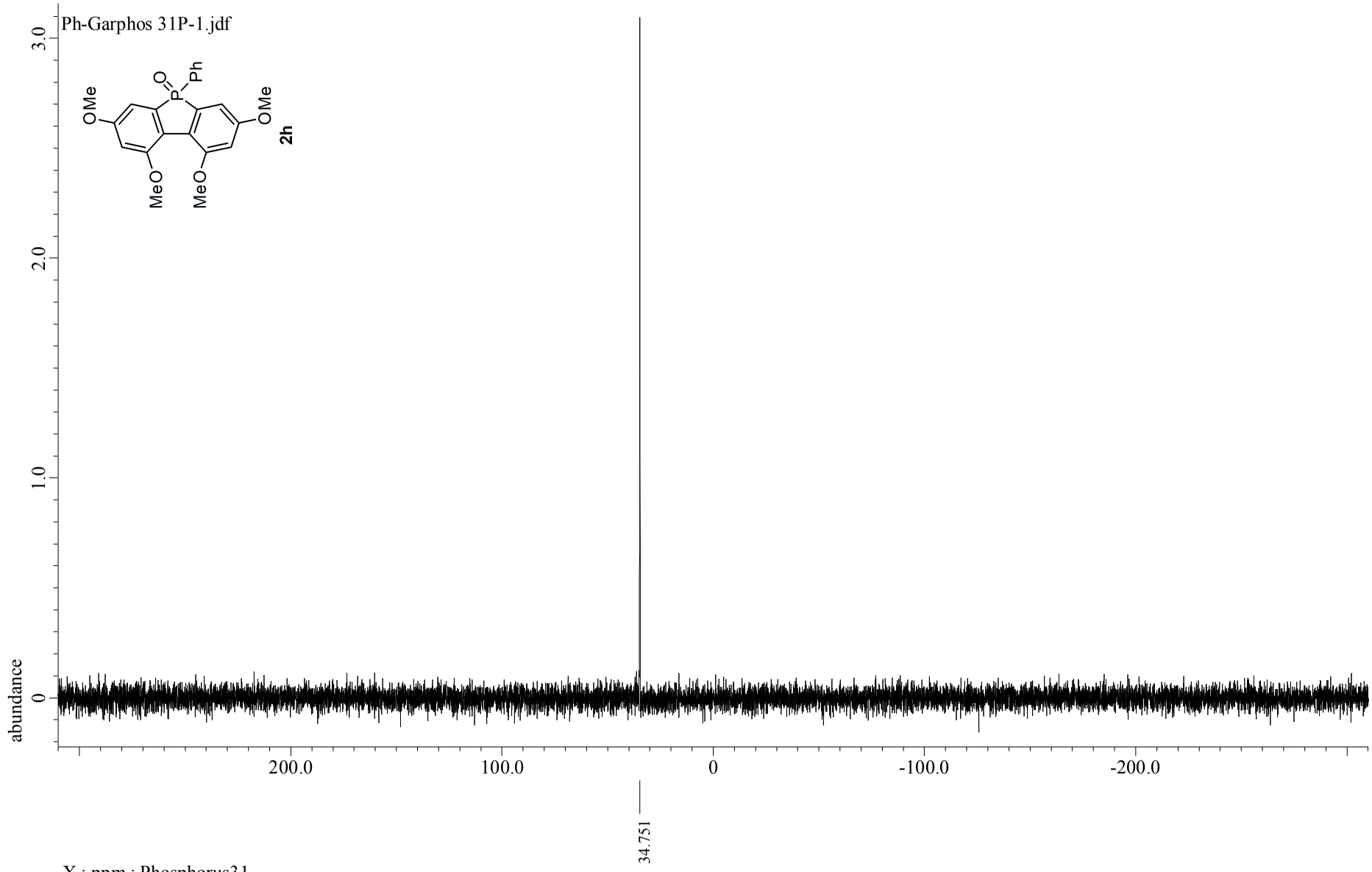

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1
X : ppm : Proton
TUNEPHOS 1-1.jdf
O
O
P
O
Ph
2g
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.640
7.608
7.537
7.534
7.511
7.507
7.417
7.415
7.408
7.397
7.389
7.380
7.347
7.326
7.260
2.00
3.02
6.01
4.628
4.604
4.580
4.332
4.303
2.03
1.99
2.008
1.725
1.05
1.06

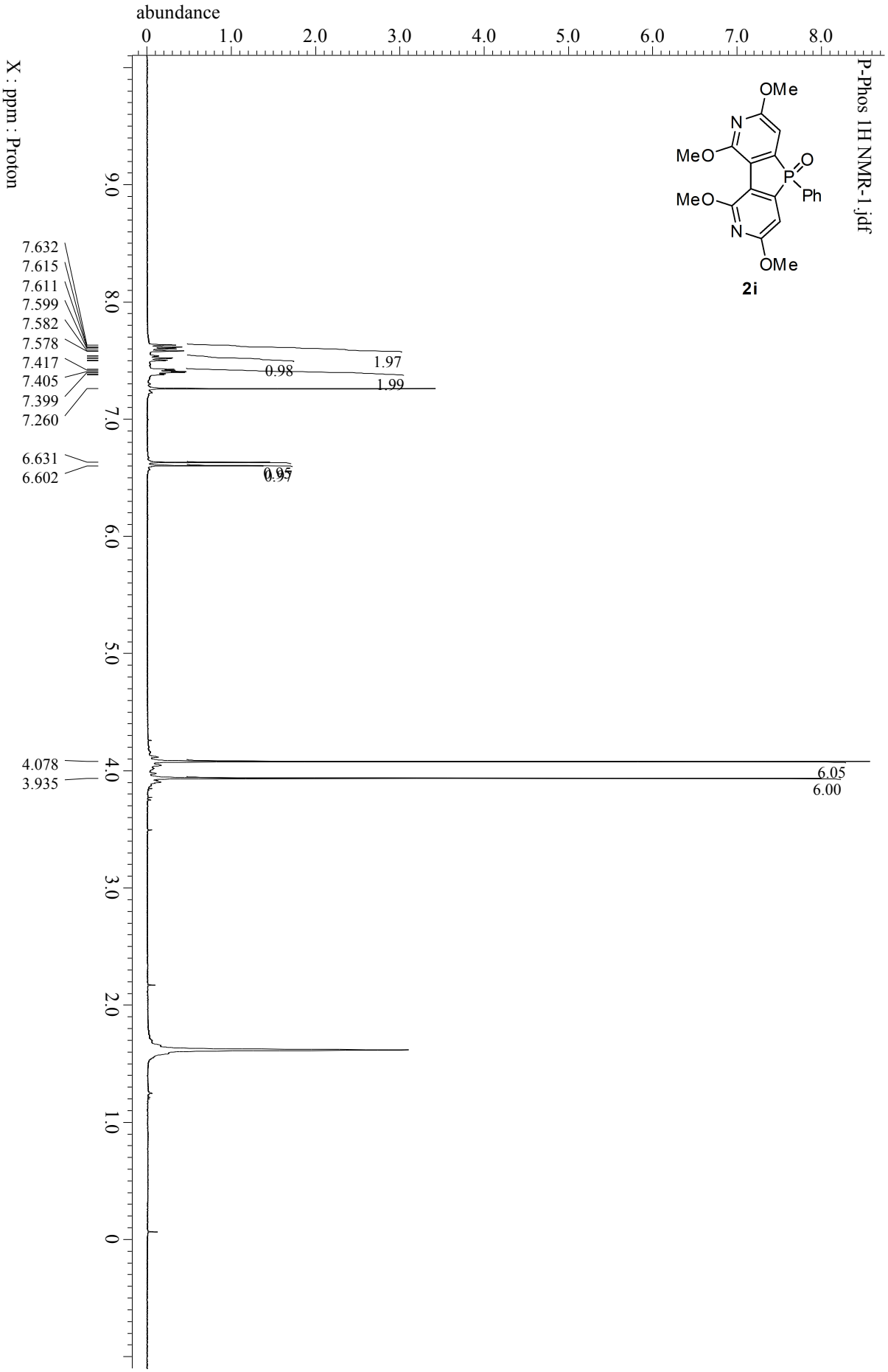

abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
X : ppm : Carbon13
TUNEPHOS 13C-2.jdf
O
O
P
O
Ph
2g
155.460
155.327
135.828
134.799
132.224
131.509
131.376
131.128
131.023
130.918
128.782
128.658
126.361
126.265
77.315
77.000
76.895
76.676
31.558
25.885
22.672
14.100
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0

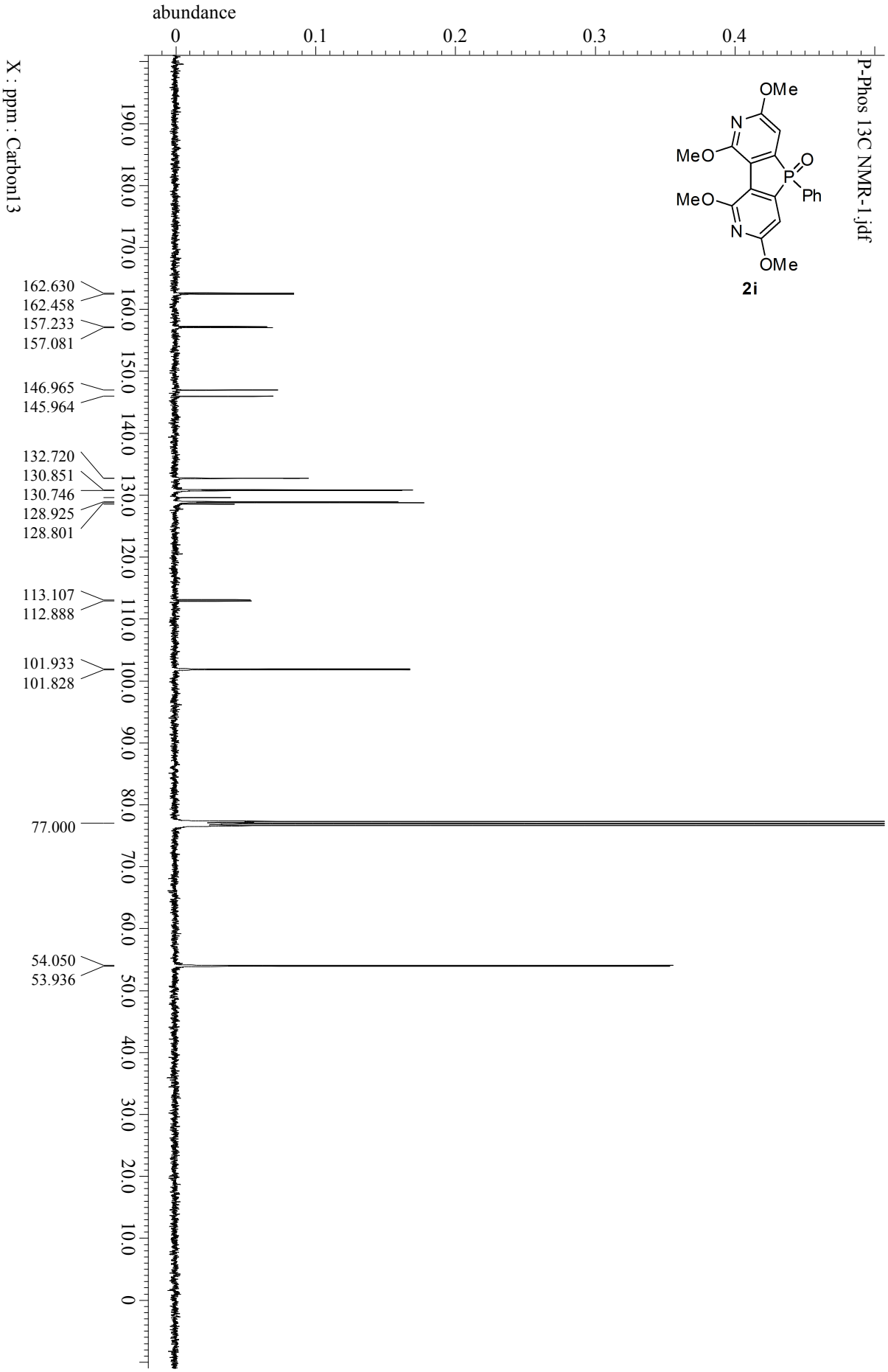

TUNEPHOS 31P-1.jdf
O
P
Ph
O
O
2g
2.0
1.0
0
abundance
200.0
100.0
0
-100.0
-200.0
33.081
X : ppm : Phosphorus31

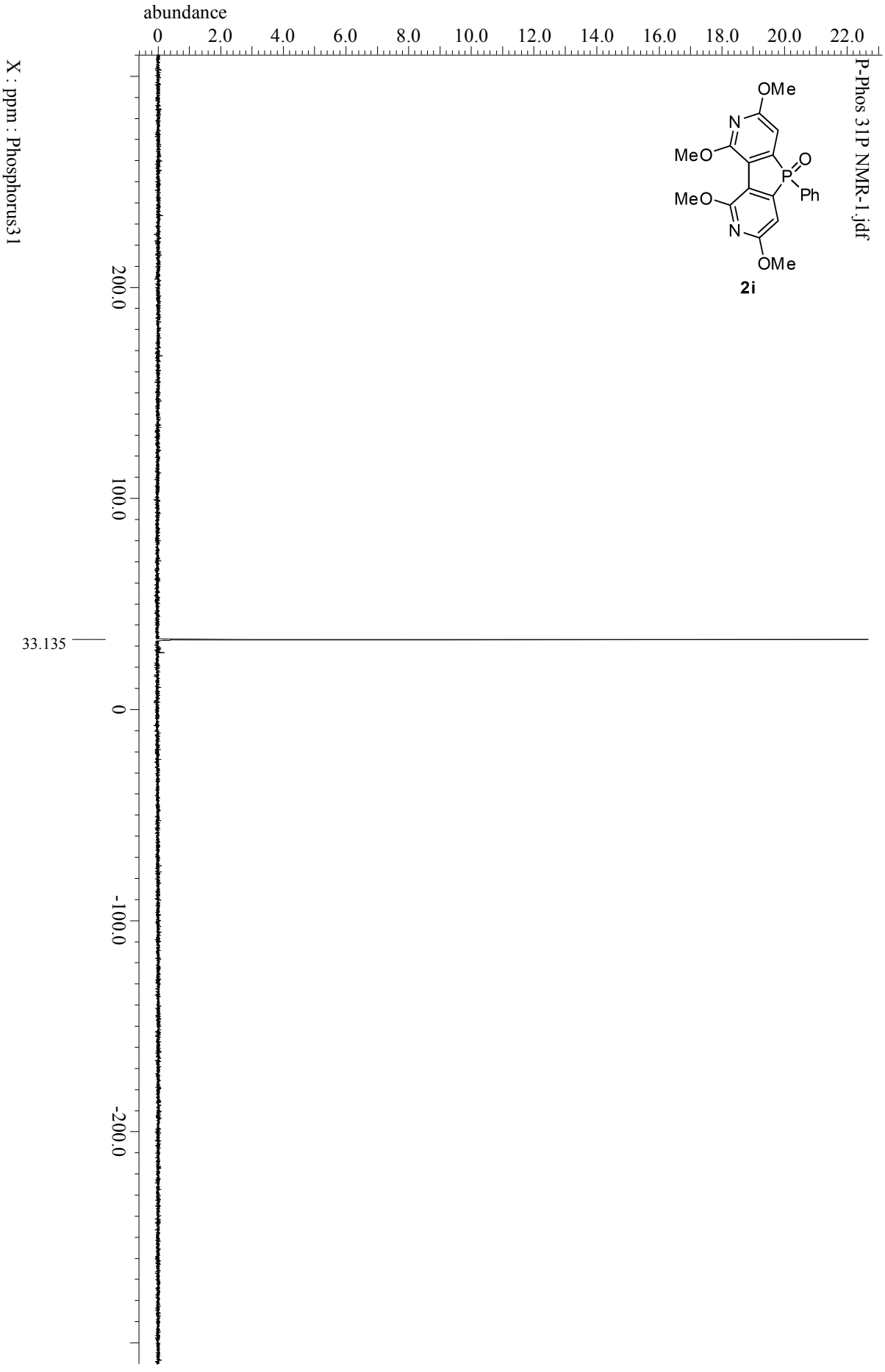

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
X : ppm : Proton
Ph-GarPhos 1H-1.jdf
OMe
MeO
O
P
Ph
MeO
OMe
2h
7.654
7.637
7.633
7.622
7.605
7.601
7.392
7.380
7.372
7.260
6.848
6.842
6.818
6.812
6.661
6.655
3.917
3.777
2.01
1.00
1.94
1.96
1.96
5.94
5.98

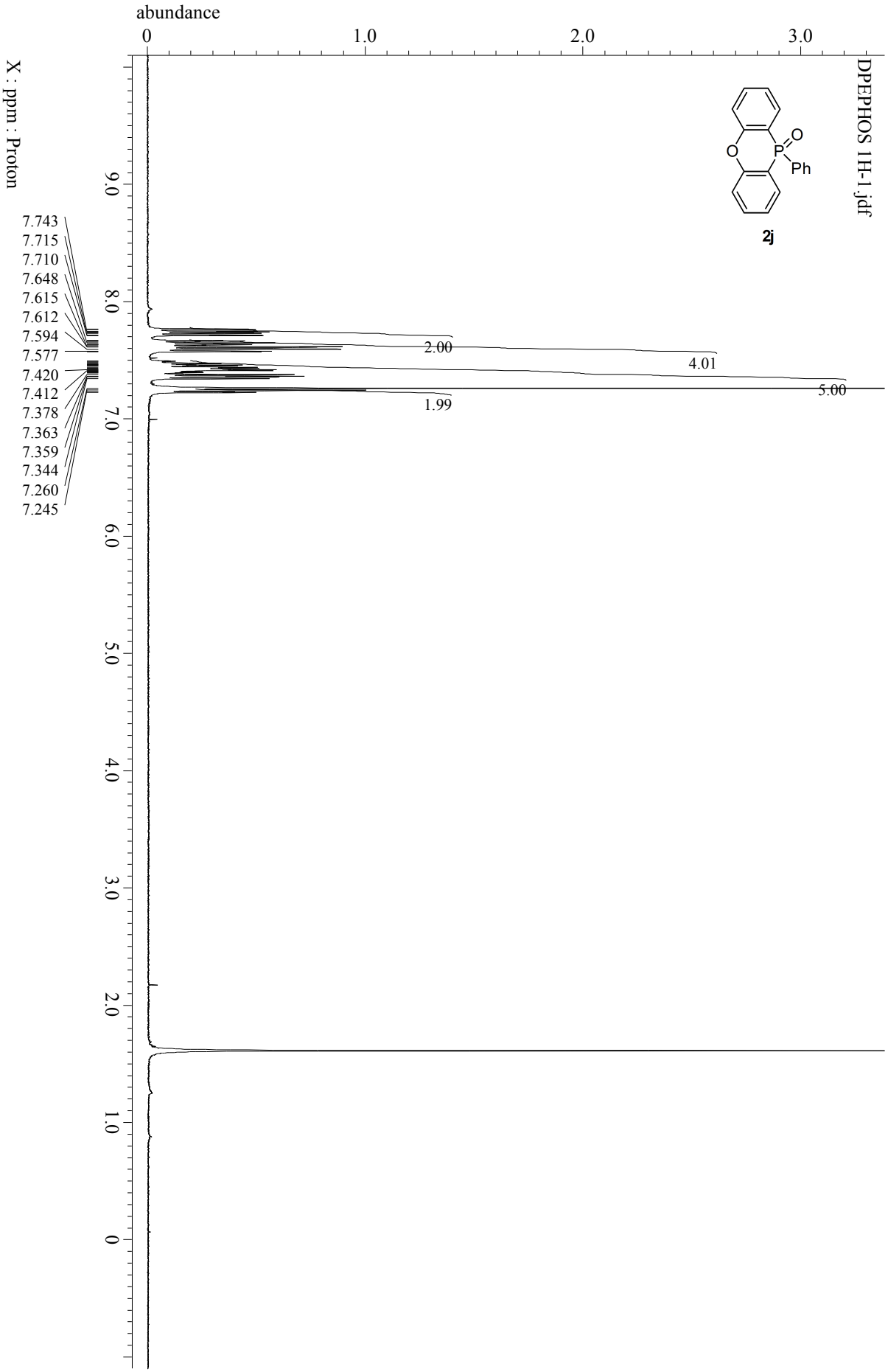

abundance
0
0.1
0.2
0.3
0.4
X : ppm : Carbon13
Ph-Garphos 13C-1.jdf
OMe
MeO
MeO
OMe
O
P
Ph
2h
161.085
160.923
156.461
156.290
136.400
135.361
132.043
132.015
131.071
130.966
128.716
128.592
123.186
122.957
106.109
105.985
77.324
77.000
76.685
56.825
55.662
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0

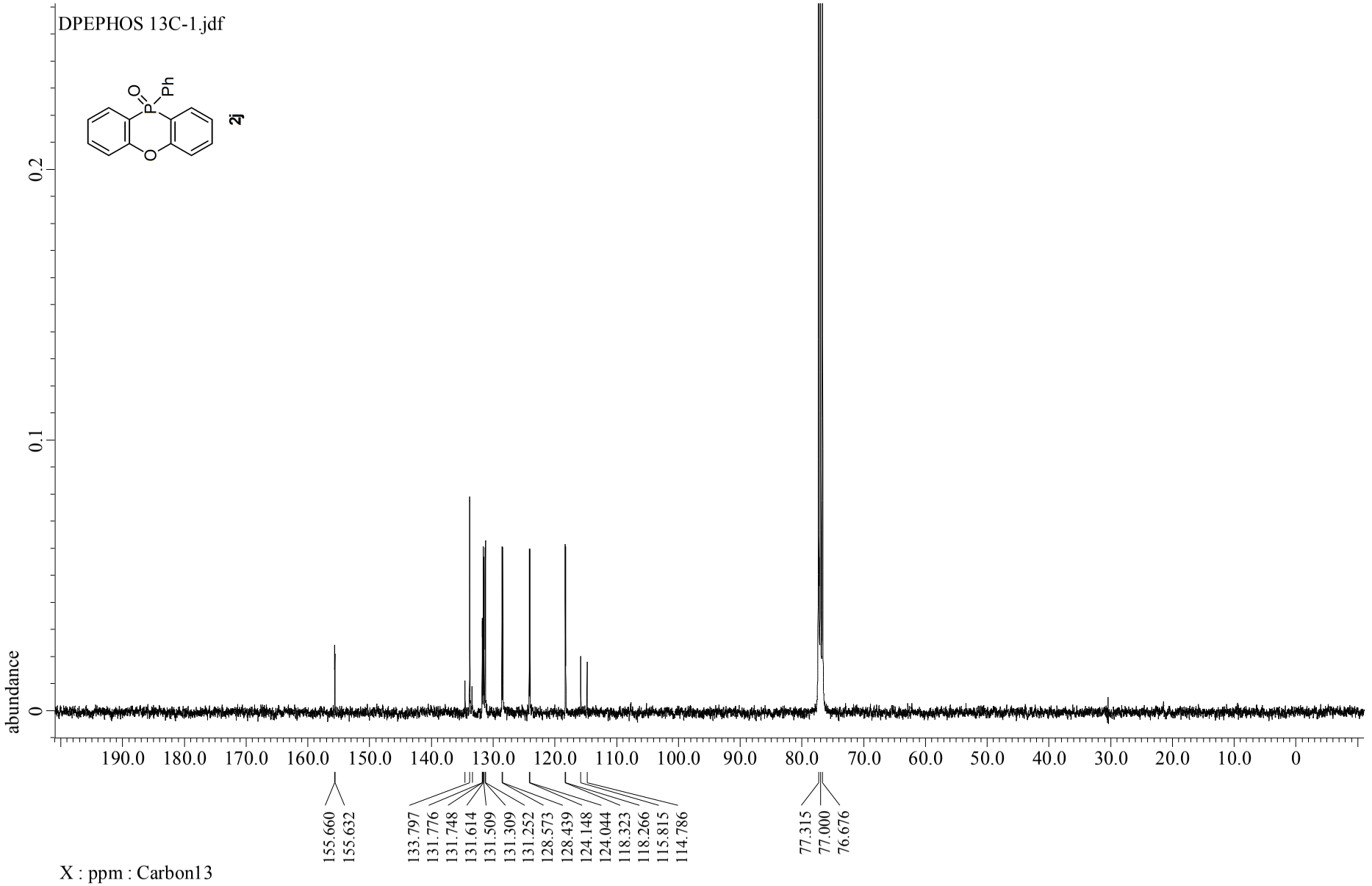

Ph-Garphos 31P-1.jdf
OMe
O
P
Ph
OMe
MeO
MeO
2h
3.0
2.0
1.0
0
abundance
200.0
100.0
0
-100.0
-200.0
34.751
X : ppm : Phosphorus31

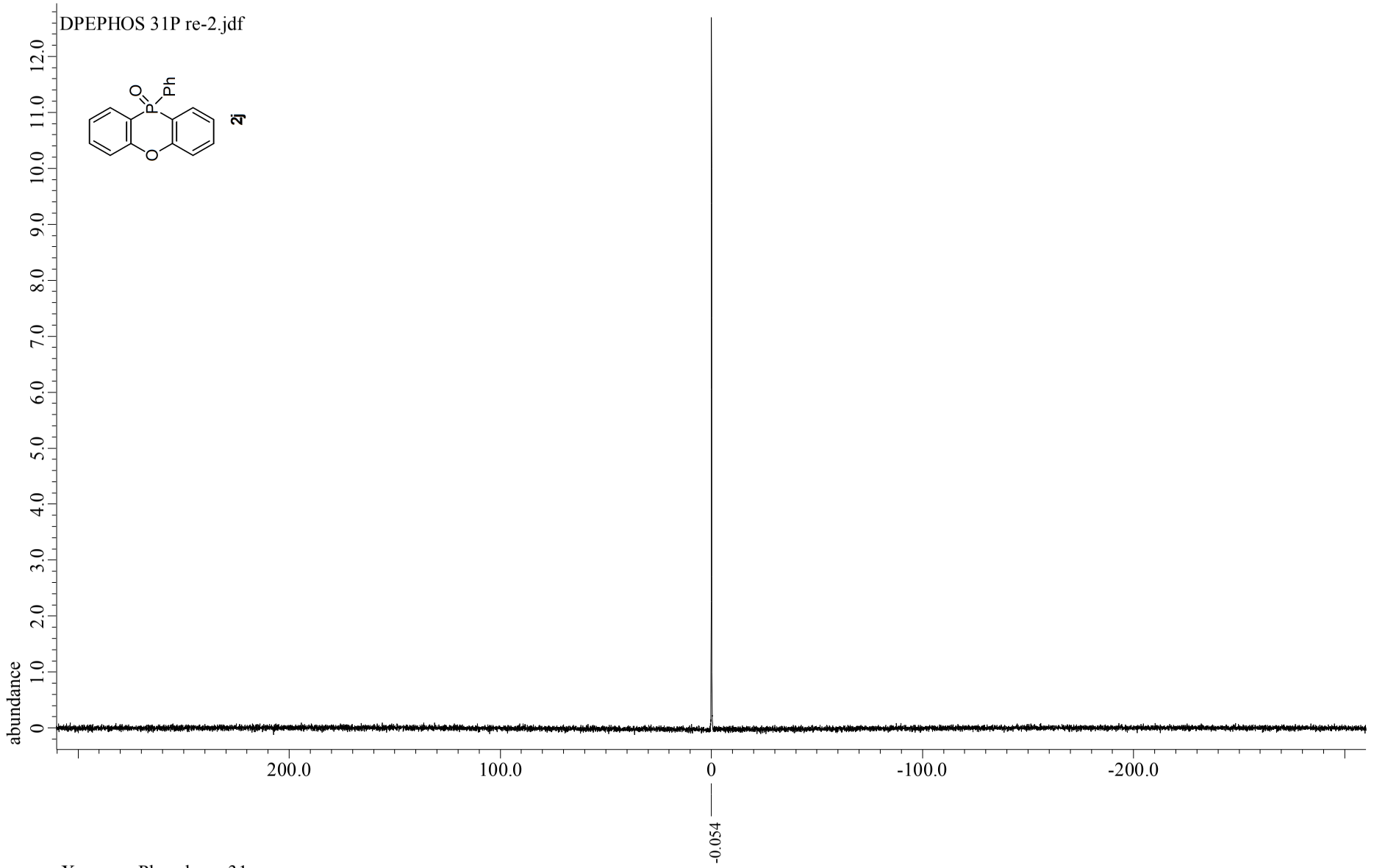

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
X : ppm : Proton
P-Phos 1H NMR-1.jdf
OMe
N
MeO
O
P
Ph
MeO
N
OMe
2i
7.632
7.615
7.611
7.599
7.582
7.578
7.417
7.405
7.399
7.260
6.631
6.602
4.078
3.935
0.98
1.97
1.99
0.95
0.97
6.05
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

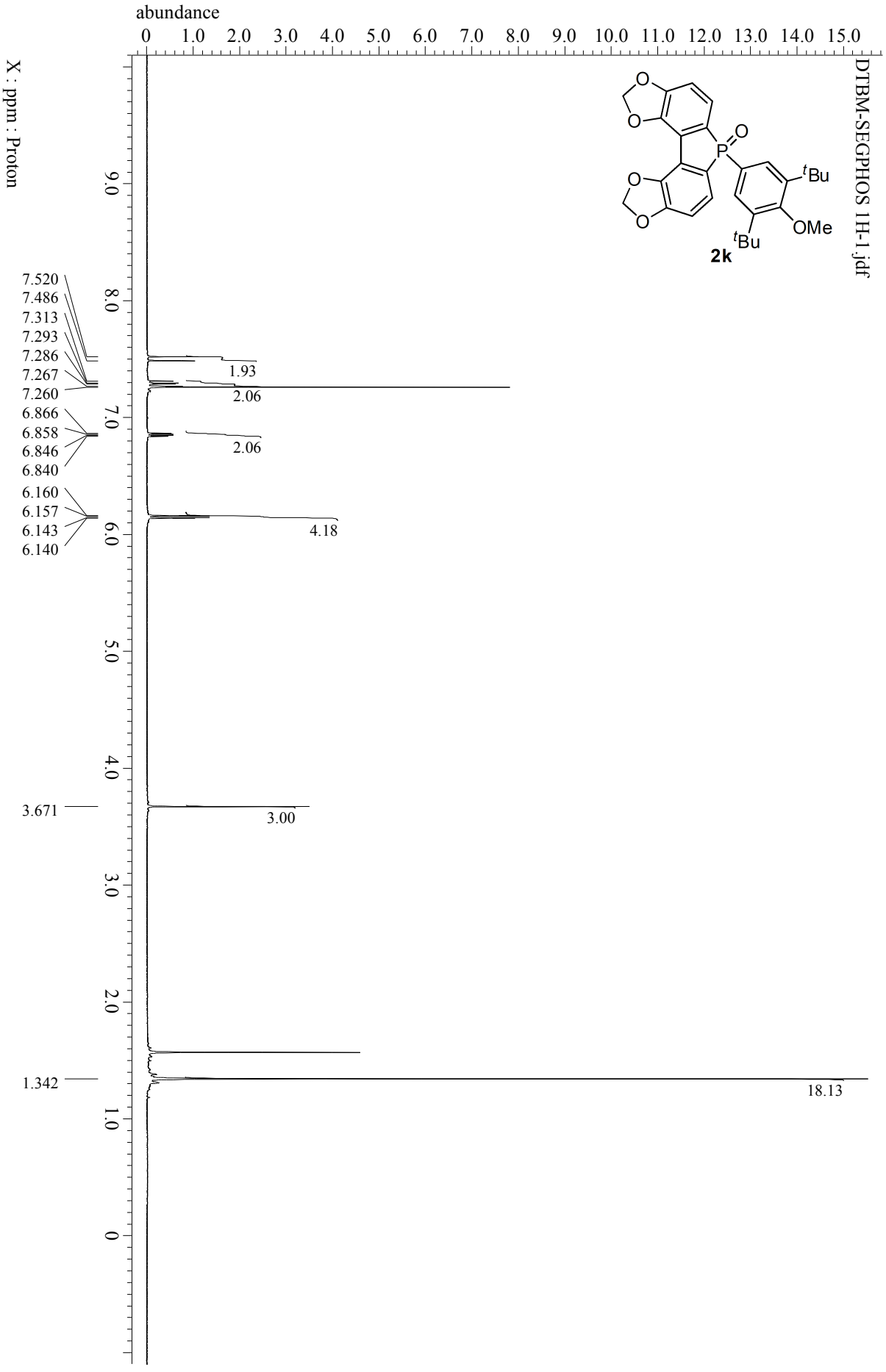

abundance
0
0.1
0.2
0.3
0.4
P-Phos 13C NMR-1.jdf
X : ppm : Carbon13
OMe
N
MeO
O
P
Ph
MeO
N
OMe
2i
162.630
162.458
157.233
157.081
146.965
145.964
132.720
130.851
130.746
128.925
128.801
113.107
112.888
101.933
101.828
77.000
54.050
53.936
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0

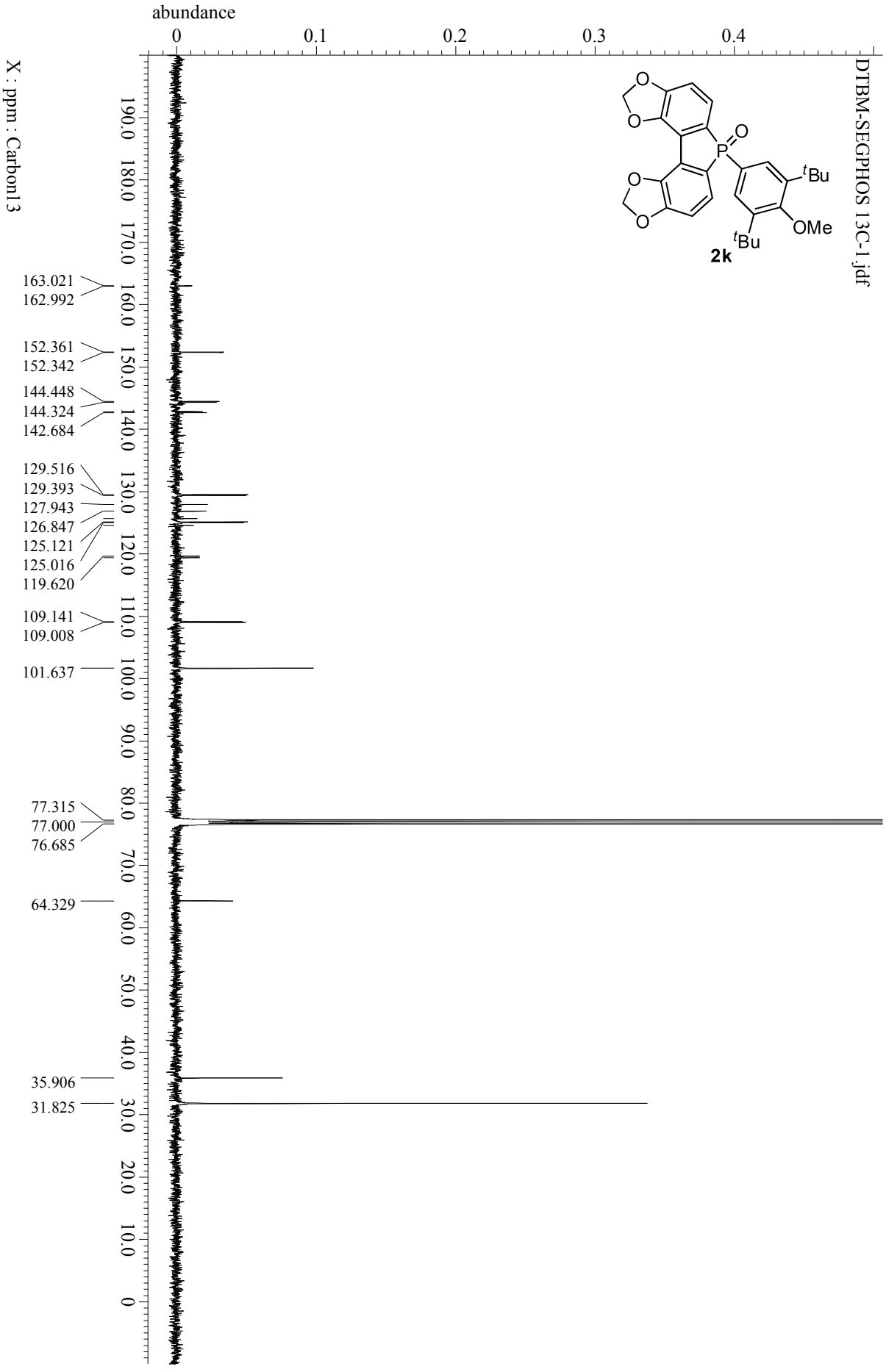

abundance
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
P-Phos 31P NMR-1.jdf
X : ppm : Phosphorus31
200.0
100.0
33.135
0
-100.0
-200.0
OMe
N
MeO
P
O
Ph
MeO
N
OMe
2i

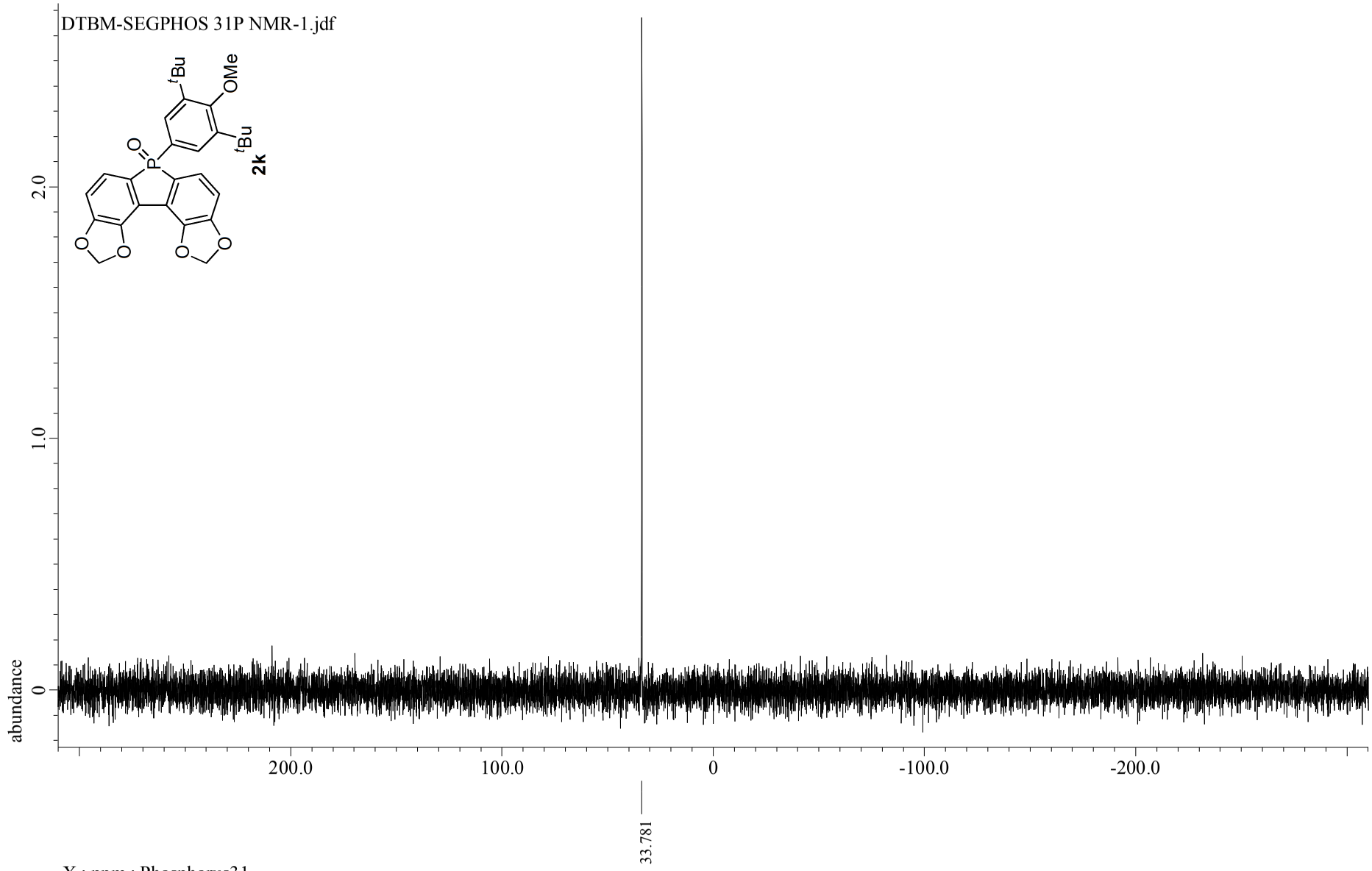

abundance
0
1.0
2.0
3.0
DPEPHOS 1H-1.jdf
X : ppm : Proton
7.743
7.715
7.710
7.648
7.615
7.612
7.594
7.577
7.420
7.412
7.378
7.363
7.359
7.344
7.260
7.245
2.00
4.01
5.00
1.99
O
O
P
Ph
2j
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

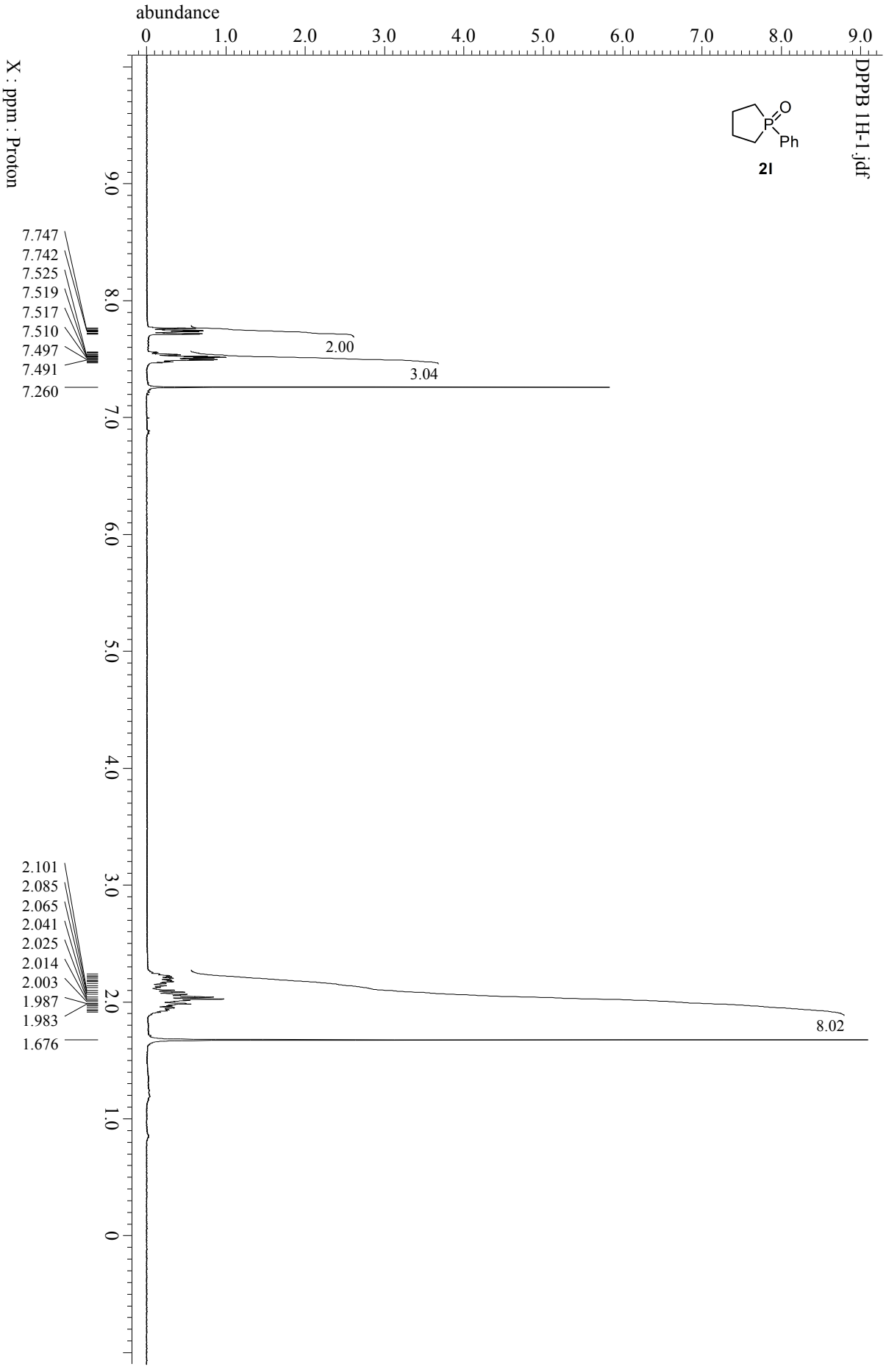

DPEPHOS 13C-1.jdf
O
P
Ph
O
2j
abundance
0
0.1
0.2
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
155.660
155.632
133.797
131.776
131.748
131.614
131.509
131.309
131.252
128.573
128.439
124.148
124.044
118.323
118.266
115.815
114.786
77.315
77.000
76.676
X : ppm : Carbon13

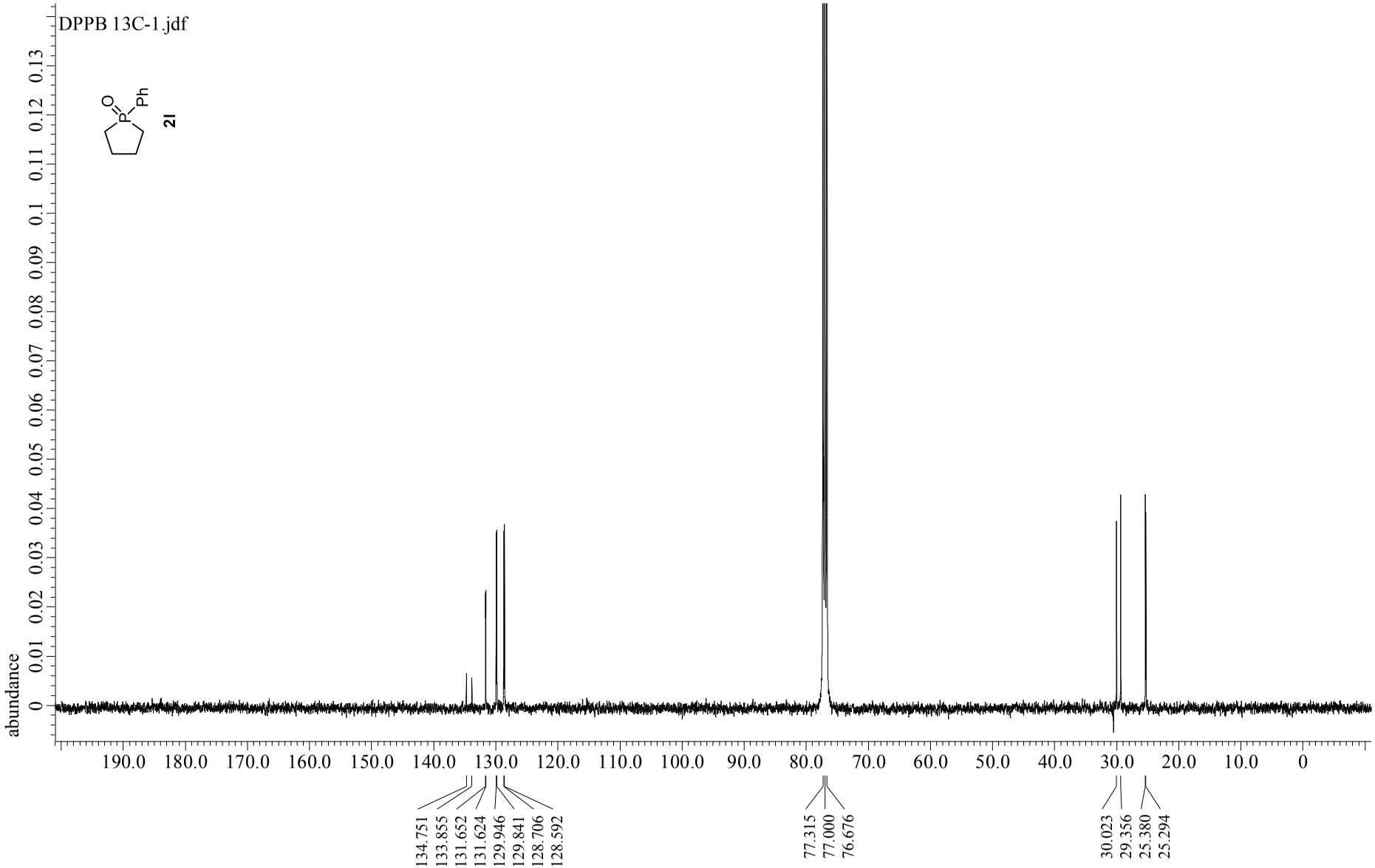

DPEPHOS 31P re-2.jdf
O
P
Ph
O
2j
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
200.0
100.0
0
-100.0
-200.0
-0.054
X : ppm : Phosphorus31

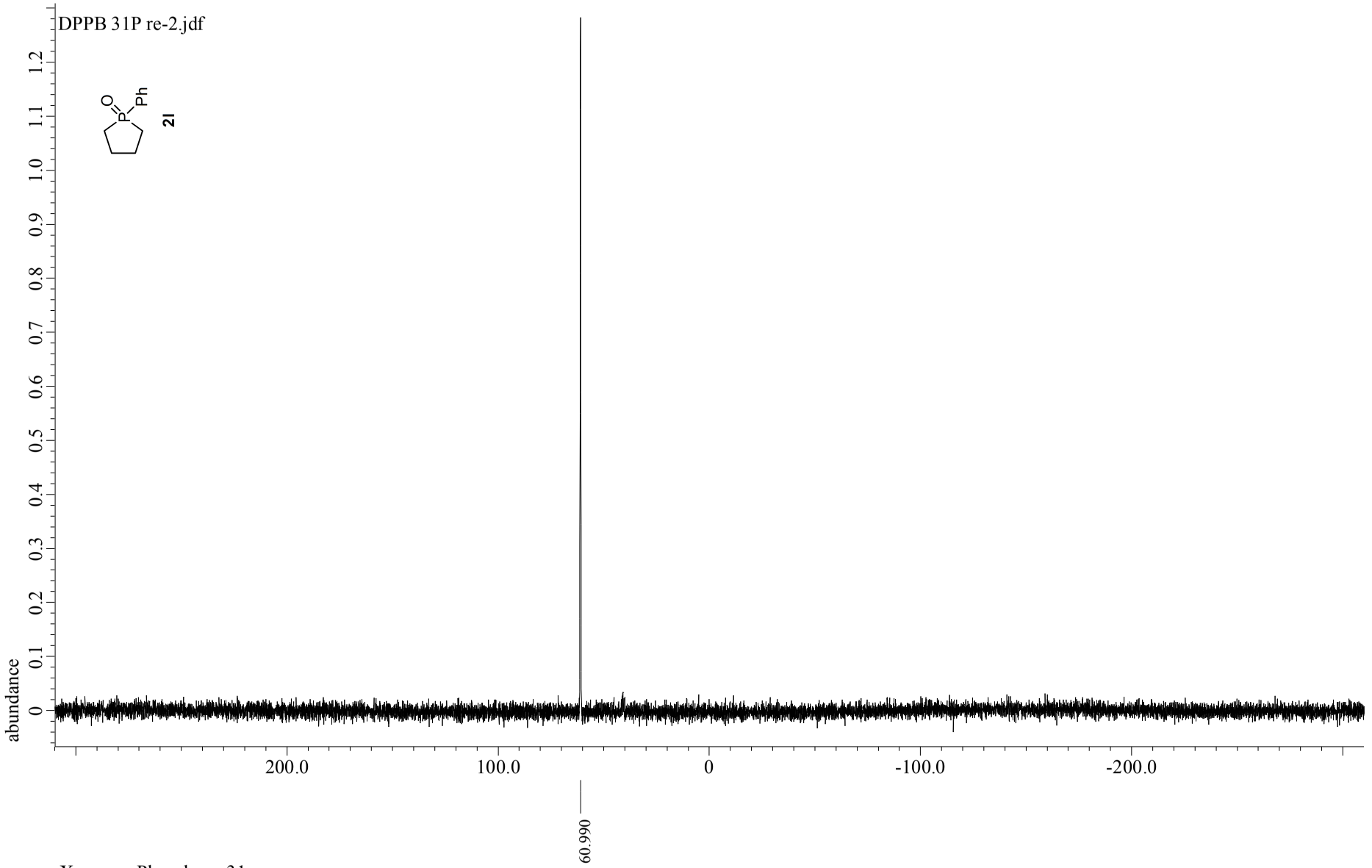

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0
X : ppm : Proton
DTBM-SEGPHOS 1H-1.jdf
2k
7.520
7.486
7.313
7.293
7.286
7.267
7.260
6.866
6.858
6.846
6.840
6.160
6.157
6.143
6.140
3.671
1.342
1.93
2.06
2.06
4.18
3.00
18.13

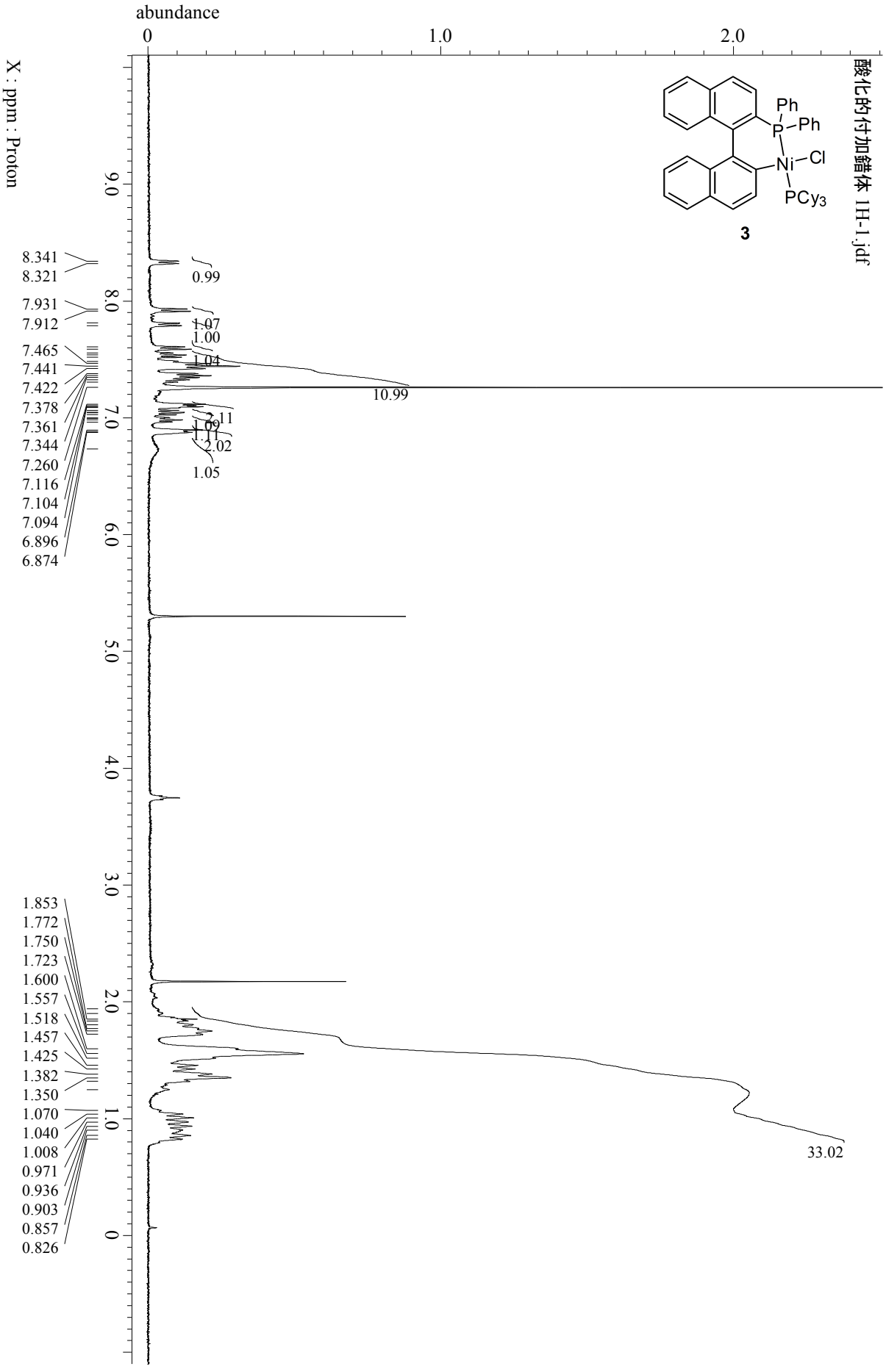

abundance
0
0.1
0.2
0.3
0.4
DTBM-SEGPHOS 13C-1.jdf
X : ppm : Carbon13
2k
163.021
162.992
152.361
152.342
144.448
144.324
142.684
129.516
129.393
127.943
126.847
125.121
125.016
119.620
109.141
109.008
101.637
77.315
77.000
76.685
64.329
35.906
31.825

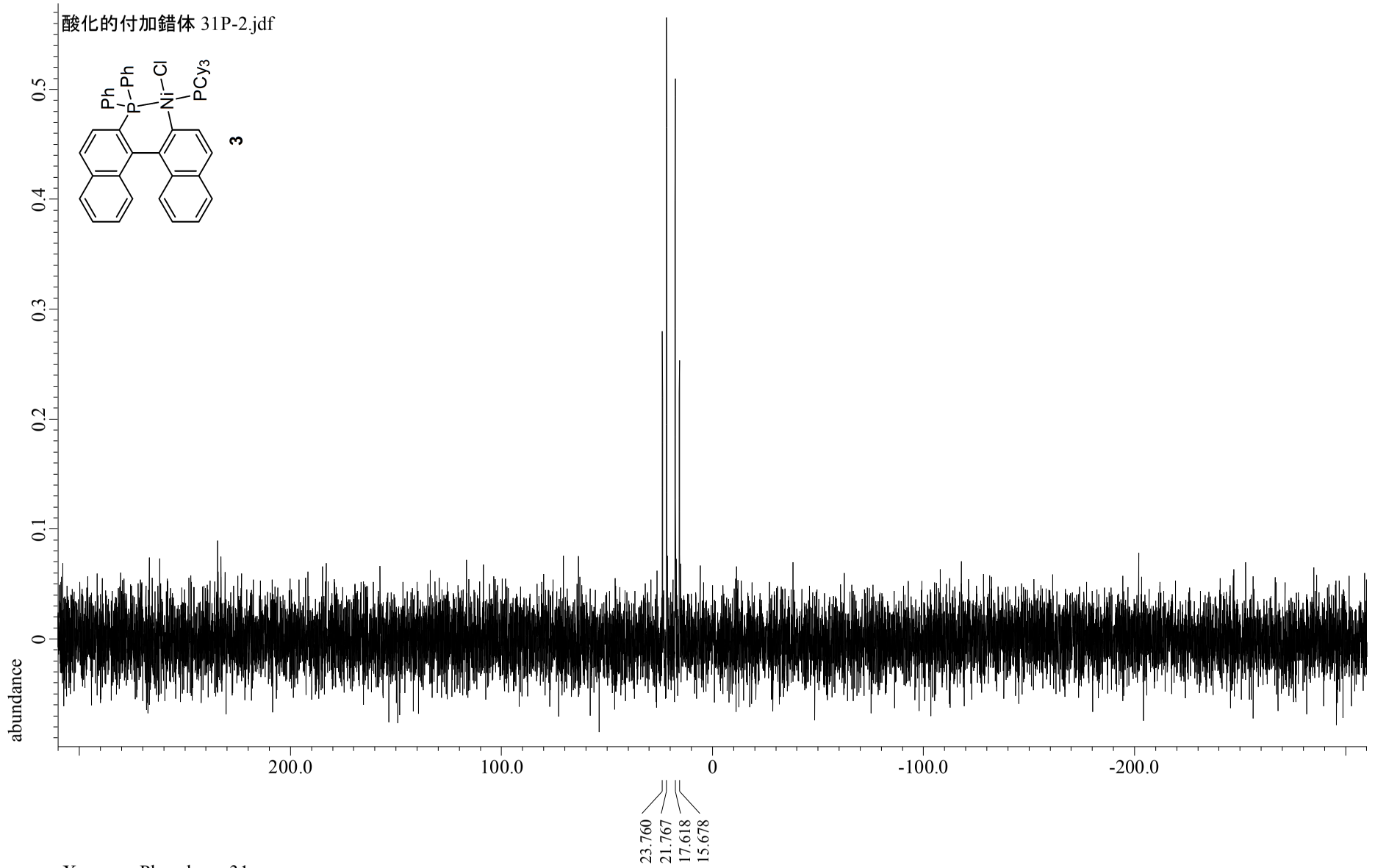

DTBM-SEGPHOS 31P NMR-1.jdf
tBu
OMe
tBu
2k
O
P
O
O
O
O
2.0
1.0
0
abundance
200.0
100.0
0
-100.0
-200.0
33.781
X : ppm : Phosphorus31


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
DPPB 1H-1.jdf
X : ppm : Proton
O
P
Ph
2l
7.747
7.742
7.525
7.519
7.517
7.510
7.497
7.491
7.260
2.00
3.04
2.101
2.085
2.065
2.041
2.025
2.014
2.003
1.987
1.983
1.676
8.02


DPPB 13C-1.jdf
O
P
Ph
2l
abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
134.751
133.855
131.652
131.624
129.946
129.841
128.706
128.592
77.315
77.000
76.676
30.023
29.356
25.380
25.294
X : ppm : Carbon13


DPPB 31P re-2.jdf
O
P
Ph
2l
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
200.0
100.0
0
-100.0
-200.0
60.990
X : ppm : Phosphorus31


abundance
0
1.0
2.0
X : ppm : Proton
酸化的付加錯体 1H-1.jdf
Ph
P
Ph
Ni
Cl
PCy3
3
8.341
8.321
7.931
7.912
7.465
7.441
7.422
7.378
7.361
7.344
7.260
7.116
7.104
7.094
6.896
6.874
0.99
1.07
1.00
1.04
10.99
2.11
1.09
1.11
2.02
1.05
1.853
1.772
1.750
1.723
1.600
1.557
1.518
1.457
1.425
1.382
1.350
1.070
1.040
1.008
0.971
0.936
0.903
0.857
0.826
33.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


酸化的付加錯体 31P-2.jdf
Ph
P
Ph
Ni
Cl
PCy3
3
abundance
0.5
0.4
0.3
0.2
0.1
0
200.0
100.0
0
-100.0
-200.0
23.760
21.767
17.618
15.678
X : ppm : Phosphorus31