Supporting Information

Novel regio- and stereoselective phosphonyl radical addition of glycals promoted via Mn(II)/air: syntheses of 1,2-dideoxy 2-*C*-diphenylphosphinylglycopyranosides

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Contents:

1. Experimental Procedures and Characterization Data

(1) General information

Melting points were measured in open capillary tubes. Elemental analyses were carried out on a MOD 1106 analyzer. Infrared spectra were recorded on a Shimadzu IR-435 instrument in the 400–4000 cm^{-1} region. NMR spectra were recorded with a Bruker DPX-400 spectrometer, proton NMR spectra were recorded on a Bruker 400 MHz spectrometer at ambient temperature. Internal reference of proton 7.26 was used for $CDCl_3$. Data were given as follows: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant (J/Hz). ^{13}C NMR spectra were recorded at 100 MHz. Internal references of carbon 77.16 was used for $CDCl_3$. ^{31}P NMR spectra were recorded at 162 MHz. The reactions were detected by thin layer chromatography using GF254 plates. Flash chromatography was performed with silica gel 60.

(2) Experimental procedures and Characterization Data

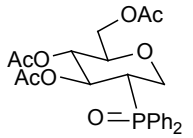
Diphenylphosphine oxide was prepared according to reported methods (K. Shioji, A. Matsumoto, M. Takao, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 743). $Mn(OAc)_3$ was prepared according to reported methods (B. John, Jr Bush, H. Finkbeiner, *J. Am. Chem. Soc.*, 1968, **90**, 5903). Protected glycals were synthesized according to reported methods (N. Chatterjee, P. Pandit, S. Halder, A. Patra, D. K. Maiti, *J. Org. Chem.*, 2008, **73**, 7775)

General procedure for the syntheses of protected 1, 2-dideoxy-2-*C*-diphenyl phosphinylglycopyranoses

To a solution of protected glycals (9.0 mmol) and diphenylphosphine oxide (1.8 mmol) in 20 mL of acetic acid, $Mn(OAc)_2 \cdot 4H_2O$ (2.7 mmol) was added. The mixture was heated at 60 °C with stirring and a clear solution was gradually formed. After TLC (petroleum ether : EtOAc = 1 : 2 - 1 : 3) indicated the reaction was complete, water was added and the solution was extracted with EtOAc. The combined organic layers were washed with $NaHCO_3$ solution and brine, dried over Na_2SO_4 and then evaporated. Flash chromatography (petroleum ether : EtOAc = 1 : 1 - 1 : 3) gave the desired products.

To a solution of protected glycals (0.4 mmol) and diphenylphosphine oxide (0.8 mmol) in 2 mL of acetic acid, $FeCl_3$ or $Cu(OTf)_2$ (1.2 mmol) was added. The mixture was heated at 60 °C with stirring. TLC (petroleum ether : EtOAc = 1 : 2 - 1 : 3) showed no reaction took place. Several hours later, the glycals were gradually destroyed by heated AcOH. TLC showed there was no main spot on the TLC except the starting materials.

3, 4, 6-tri-*O*-acetyl-1, 2-dideoxy-2-*C*-diphenylphosphinyl-D-glucopyranose (2)

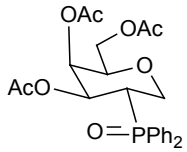


Colorless rod-like crystal, mp 256-257 °C; $[\alpha]_D^{20}$ +19.0^0 (*c* 0.5, $CHCl_3$); IR (KBr) cm^{-1}: 3059, 2913, 1744, 1441, 1376, 1251, 1230, 1138, 1066, 1038, 724, 704; ^1H

NMR ($CDCl_3$, 400 MHz) δ: 7.87-7.76 (4H, m, ArH), 7.47 (br s, 6H, ArH), 5.69-5.66 (m, 1H, H-3), 5.00 (t, 1H, $J_{4,3} = J_{4,5} = 9.6$ Hz, H-4), 4.26 (dd, $J_{6a,5} = 4.8$ Hz, $J_{6a,6b} = 12.4$ Hz, H-6a), 4.04 (dd, 1H, $J_{6b,5} = 1.6$ Hz, $J_{6b,6a} = 12.4$ Hz, H-6b), 3.90-3.86 (m, 1H, H-1a), 3.70 (dt, 1H, $^3J_{P,1b} = 2.0$ Hz, $J_{1b,1a} = J_{1b,2} = 12.0$ Hz, H-1b), 3.63-3.59 (m, 1H, H-5), 3.20-3.12 (m, 1H, H-2), 2.06, 1.96, 1.16 (each 3H, 3 × C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.71, 170.20, 169.22 (3 × CH_3*C*O), 132.26 (d, $J_{C,P} = 99.1$Hz, arom. C-P), 132.28 (d, $J_{Cp,P} = 3.0$ Hz, arom. C$_p$-H), 131.94 (d, $J_{Cp,P} = 3.0$ Hz, arom. C$_p$-H), 131.00 (d, $J_{Co,P} = 9.3$ Hz, arom. C$_o$-H), 130.66 (d, $J_{Co,P} = 8.9$ Hz, arom. C*o*-H), 129.08 (d, $J_{Cm,P} = 11.6$ Hz, arom. C$_m$-H), 128.78 (d, $J_{Cm,P} = 11.8$ Hz, arom. C$_m$-H), 76.55 (C-5), 70.22 (C-4), 70.12 (C-3), 65.93 (C-1), 62.44 (C-6), 41.15 (d, $J_{2,P} = 66.4$ Hz, C-2), 20.81, 20.73, 19.71 (3 × *C*H$_3$CO). ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 24.21; HRESIMS *m/z*: 475.1518 (Calcd for C24H28O8P: M^+ + H, 475.1522); *Anal.*: Calcd for C24H27O8P: C, 60.76; H, 5.74. Found: C, 60.74; H, 5.69.

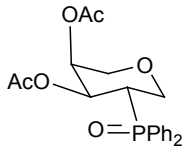
The structure of **2** was definitely characterized by spectroscopic data. The high-resolution ESI-MS spectrum of **2** displays the $[M + Na]^+$ peak at *m/z* 497.1343, indicating its formula to be $C_{24}H_{27}O_8P$. The ^{31}P NMR shows one signal at 24.2 ppm, and the IR spectrum gives one P=O group absorption at 1230 cm^{-1}. The DEPT-135 spectrum gives secondary carbon signals at δ 62.3 ppm and 65.8 ppm, corresponding to C-6 and C-1. In the ^{1}H NMR spectrum, the proton at δ 3.72 (dt, $J_1 = 12.0$ Hz, $J_2 = 2.0$ Hz) is ascribed to the axial one of H-1. These coupling patterns indicate H-2 and newly formed diphenylphosphinyl group are bonded to C-2 in axial and equatorial positions, respectively. The proton that appeared as a multiplet at δ 3.20-3.12 ppm is assigned to H-2. The ^{13}C NMR peak at δ 41.0 ppm as a doublet with coupling constant of 66.0 Hz is assigned to C-2. All the assignments were made on the basis of 2D NMR spectra. The structures of the following new compounds were also definitely characterized by spectroscopic data

3,4,6-tri-*O*-acetyl-1,2-dideoxy-2-*C*-diphenylphosphinyl-D-galactopyranose (3)



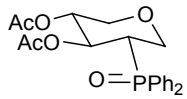
White foam, $[\alpha]_D^{20}$ -24^0 (*c* 0.5, $CHCl_3$); IR (KBr) cm^{-1}: 3091, 3063, 3028, 2943, 2870, 1750, 1440, 1373, 1241, 1166, 1056, 908, 722, 706, 581, 541; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.82-7.77 (m, 4H, ArH), 7.51-7.48 (m, 6H, ArH), 5.53-5.47 (m, 1H, H-3), 5.36 (br s, 1H, H-4), 4.06-4.03 (m, 1H, H-6), 3.94-3.91 (m, 1H, H-1b), 3.81-3.76 (m, 2H, H-1a, H-5), 3.23-3.20 (m, 1H, H-2), 2.14, 2.02, 1.24 (3 × s, each 3H, 3 × C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.54, 170.06, 168.90 (3 × CH_3*C*O), 132.94 ((d, $J_{C,P} = 99.7$ Hz, arom. C-P), 132.24 (arom. C$_p$-H), 131.73 (d, $J_{Cp,P} = 4.8$ Hz, arom. C$_p$-H), 130.64 (d, $J_{Co,P} = 8.9$ Hz, arom. C$_o$-H), 128.99 (d, $J_{Cm,P} = 11.6$ Hz, arom. C$_m$-H), 128.61 (d, $J_{Cm,P} = 11.9$ Hz, arom. C$_m$-H), 74.99 (C-5), 68.52 (d, $J_{3,P} = 5.5$ Hz, C-3), 66.39 (d, $J_{4,P} = 7.5$ Hz, C-4), 65.86 (C-1), 62.26 (C-6), 36.28 (d, $J_{2,P} = 68.0$ Hz, C-2), 20.76, 19.65 (3 × *C*H$_3$CO); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 26.19; HRESIMS *m/z*: 497.1341 (Calcd for $C_{24}H_{27}NaO_8P$: M^+ + Na, 497.1340).

3,4-di-*O*-acetyl-1,2-dideoxy-2-*C*-diphenylphosphinyl-L-arabinopyranose (4)



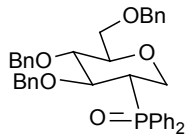
White foam, $[\alpha]_D^{20}$ -4.0^0 (*c* 1.0, $CHCl_3$); IR (KBr) cm^{-1}: 3057, 2978, 2855, 1746, 1438, 1374, 1244, 1190, 1162, 1062, 1023, 755, 722, 703, 547; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.82-7.78 (m, 4H, ArH), 7.49 (br s, 6H, ArH), 5.52-5.46 (m, 1H, H-3), 5.25 (br s, 1H, H-4), 3.94 (br d, 1H, J = 12.8 Hz, H-5a), 3.86 (br d, 1H, J = 12.0 Hz, H-1a), 3.72-3.59 (m, 2H, H-1b, H-5b), 3.29-3.23 (m, 1H, H-2), 2.14, 1.26 (2 × s, each 3H, 2 × CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.20, 169.00 (2 × CH_3*C*O), 132.84 (d, $J_{C,\,P}$ = 99.8 Hz, arom. C-P), 132.20 (d, $J_{Cp,\,P}$ = 2.2 Hz, arom. C$_p$-H), 131.93 (d, $J_{C,\,P}$ = 81.6 Hz, arom. C-P), 131.74 (d, $J_{Cp,\,P}$ = 2.2 Hz, arom. C$_p$-H), 130.69 (d, $J_{Co,\,P}$ = 2.8 Hz, arom. C$_o$-H), 130.60 (d, $J_{Co,\,P}$ = 3.3 Hz, arom. C$_o$-H), 128.98 (d, $J_{Cm,\,P}$ = 12.0 Hz, arom. C$_m$-H), 128.59 (d, $J_{Cm,\,P}$ = 12.0 Hz, arom. C$_m$-H), 68.63 (C-5), 68.00 (d, $J_{3,\,P}$ = 5.2 Hz, C-3), 66.35 (d, $J_{4,P}$ = 7.0 Hz, C-4), 65.82 (d, $J_{1,\,P}$ = 2.1 Hz, C-1), 36.74 (d, $J_{2,\,P}$ = 68.0 Hz, C-2), 21.08, 19.73 (2 × *C*H_3CO); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 26.84; HRESIMS *m/z*: 403.1329 (Calcd for $C_{21}H_{24}O_6P$: M^+ + H, 403.1311); *Anal.*: Calcd for $C_{21}H_{23}O_6P$: C, 62.68; H, 5.76. Found: C, 62.65; H, 5.71.

3,4-di-*O*-acetyl-1,2-dideoxy-2-*C*-diphenylphosphinyl-D-xylopyranose (5)



Yellow syrup, $[\alpha]_D^{20}$ +9.8^0 (*c* 0.5, $CHCl_3$); IR (film) cm^{-1}: 3053, 2924, 2853, 1750, 1439, 1369, 1243, 1185, 1054, 723, 700, 550; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.88-7.76 (m, 4H, ArH), 7.51 (br s, 6H, ArH), 5.64 (dd, 1H, J_1 = 8.8 Hz, J_2 = 19.2 Hz, H-3), 5.00-4.94 (m, 1H, H-4), 3.99 (dd, 1H, $J_{5a,\,4}$ = 5.2 Hz, $J_{5a,\,5b}$ = 10.8 Hz, H-5a), 3.83 (br d, 1H, J = 12.0 Hz, H-1a), 3.61 (t, 1H, $J_{1b,\,1a}$ = $J_{1b,\,2}$ = 11.6 Hz, H-1b), H-1b, H-5b), 3.28 (t, 1H, $J_{5b,\,4}$ = $J_{5b,\,5a}$ = 10.8 Hz, H-5b), 3.12-3.04 (m, 1H, H-2), 1.96, 1.18 (2 × s, each 3H, 2 × CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.40, 169.20 (2 × CH_3*C*O), 132.23 (d, $J_{C,\,P}$ = 98.9 Hz, arom. C-P), 132.22 (d, $J_{Cp,\,P}$ = 2.6 Hz, arom. C$_p$-H), 131.90 (d, $J_{Cp,\,P}$ = 2.7 Hz, arom. C$_p$-H), 130.99 (d, $J_{Co,\,P}$ = 9.2 Hz, arom. C$_o$-H), 130.65 (d, $J_{Co,\,P}$ = 9.1 Hz, arom. C$_o$-H), 129.00 (d, $J_{Cm,\,P}$ = 11.7 Hz, arom. C$_m$-H), 128.74 (d, $J_{Cm,\,P}$ = 11.9 Hz, arom. C$_m$-H), 70.81 (d, $J_{4,P}$ = 10.2 Hz, C-4), 69.61 (d, $J_{3,\,P}$ = 5.2 Hz, C-3), 67.86 (C-5), 66.31 (d, $J_{1,\,P}$ = 2.9 Hz, C-1), 41.11 (d, $J_{2,\,P}$ = 66.5 Hz, C-2), 20.86, 19.76 (2 × *C*H_3CO); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 24.40; HRESIMS *m/z*: 402.1230 (Calcd for $C_{21}H_{23}O_6P$: M^+, 402.1232); *Anal.*: Calcd for $C_{21}H_{23}O_6P$: C, 62.68; H, 5.76. Found: C, 62.73; H, 5.79.

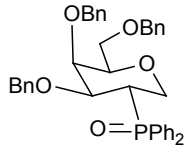
3,4,6-tri-*O*-benzyl-1,2-dideoxy-2-*C*-diphenylphosphinyl-D-glucopyranose (6)



Yellow syrup, $[\alpha]_D^{20}$ -32^0 (c = 0.5 in $CHCl_3$); IR (film) cm^{-1}: 3056, 2901, 2856,

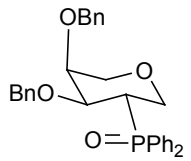
1443, 1359, 1180, 1123, 1089, 1021, 917, 860, 744, 696, 546, 516; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.93-7.88 (m, 2H, ArH), 7.73-7.68 (m, 2H, ArH), 7.45-7.26 (m, 15H, ArH), 7.11-7.02 (m, 4H, ArH), 6.54 (d, 2H, J = 6.8 Hz, ArH), 4.77-4.71 (m, 3H, $PhCH_2$, PhCH), 4.60 (d, 1H, J = 12.0 Hz, PhCH), 4.50 (d, 1H, B of AB, J = 11.2 Hz, $PhCH_B$), 4.48 (d, 1H, A of AB, J = 12.0 Hz, $PhCH_A$), 4.34-4.27 (m, 1H, H-3), 3.79 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.6 Hz, H-4), 3.70-3.60 (m, 4H, H-6, H-1), 3.45-3.42 (m, 1H, H-5), 3.10-3.07 (m, 1H, H-2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 138.20, 137.99, 137.87 (arom. *C*-CH_2O), 133.73 (d, $J_{C,P}$ = 100.4 Hz, arom. C-P), 132.74 (d, $J_{C,P}$ = 96.9 Hz, arom. C-P), 131.69 (d, $J_{Cp,P}$ = 2.5 Hz, arom. C_p-H), 131.37 (d, $J_{Cp,P}$ = 2.7 Hz, arom. C_p-H), 130.64 (d, $J_{Co,P}$ = 3.8 Hz, arom. C_o-H), 130.55 (d, $J_{Co,P}$ = 4.0 Hz, arom. C*o*-H), 128.79 (d, $J_{Cm,P}$ = 11.5 Hz, arom. C_m-H), 128.58 (d, $J_{Cm,P}$ = 12.1 Hz, arom. C_m-H), 128.47, 128.42, 128.06, 127.83, 127.81, 127.69, 127.56, 127.32, 127.01 (arom. C-H), 80.15 (d, $J_{4,P}$ = 10.0 Hz, C-4), 79.87 (d, $J_{3,P}$ = 6.0 Hz, C-3), 79.62 (C-5), 74.97, 74.66, 73.66 (3 × Ph*C*H_2O), 68.80 (C-6), 66.30 (d, $J_{1,P}$ = 4.1 Hz, C-1), 42.42 (d, $J_{2,P}$ = 67.9 Hz, C-2); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 30.09; HRESIMS *m/z*: 641.2429 (Calcd for $C_{39}H_{39}NaO_5P$: M^++Na, 641.2433).

3,4,6-tri-*O*-benzyl-1,2-deoxy-2-*C*-diphenylphosphinyl-D-galactopyranose (7)



Yellow syrup, $[\alpha]_D^{20}$ +25.5^0 (*c* 0.5, $CHCl_3$); IR (film) cm^{-1}: 3056, 2977, 2855, 1439, 1374, 1438, 1243, 1190, 1161, 1023, 756, 706, 550; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.90-7.85 (m, 2H, ArH), 7.74-7.70 (m, 2H, ArH), 7.44-7.09 (m, 19H, ArH), 7.11-7.02 (m, 4H, ArH), 6.76 (d, 2H, J = 7.2 Hz, ArH), 4.81 (d, 1H, B of AB, J = 11.6 Hz, $PhCH_B$), 4.61 (d, 1H, B' of AB', J = 11.2 Hz, $PhCH_{B'}$), 4.54-4.47 (d, 3H, A of AB, $PhCH_A$, $PhCH_2$), 4.44 (d, 1H, A' of AB', J = 11.2 Hz, $PhCH_{A'}$), 4.28 (br t, 1H, J = 8.0 Hz, H-3), 4.00 (br s, 1H, H-4), 3.67-3.50 (m, 6H, H-1, H-6, H-2, H-5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 138.38, 137.74, 137.32 (arom. *C*-CH_2O), 133.33 (d, $J_{C,P}$ = 102.9 Hz, arom. C-P), 131.68 (br s, arom. C_p-H), 131.22 (d, $J_{Cp,P}$ = 1.9 Hz, arom. C_p-H), 130.58 (d, $J_{Co,P}$ = 7.8 Hz, arom. C_o-H), 130.49 (d, $J_{Co,P}$ = 7.9 Hz, arom. C*o*-H), 128.65 (d, $J_{Cm,P}$ = 11.7 Hz, arom. C_m-H), 128.24 (d, $J_{Cm,P}$ = 11.6 Hz, arom. C_m-H), 128.36, 128.33, 127.88, 127.84, 127.73, 127.68, 127.18, 127.04 (arom. C-H), 78.79 (d, $J_{3,P}$ = 5.9 Hz, C-3), 77.70 (C-5), 74.77, 73.43 (2 × Ph*C*H_2O), 72.12 (d, $J_{4,P}$ = 7.3 Hz, C-4), 71.25 (Ph*C*H_2O), 69.17 (C-6), 65.93 (d, $J_{1,P}$ = 3.4 Hz, C-1), 37.07 (d, $J_{2,P}$ = 72.0 Hz, C-2); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 31.25; HRESIMS *m/z*: 641.2431 (Calcd for $C_{39}H_{39}NaO_5P$: M^++Na, 641.2433).

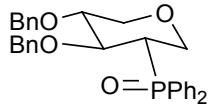
3,4-di-*O*-benzyl-1,2-deoxy-2-*C*-diphenylphosphinyl-L-arabinopyranose (8)



White solid, mp 73-75 ^{0}C; $[\alpha]_D^{20}$ +41^0 (*c* 0.5, $CHCl_3$); IR (KBr) cm^{-1}: 3057, 3031,

2977, 2856, 1437, 1404, 1357, 1168, 1119, 1027, 748, 719, 695, 553, 537; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.86-7.81 (m, 2H, ArH), 7.75-7.70 (m, 2H, ArH), 7.45-7.12 (m, 14H, ArH), 6.80 (d, 2H, J = 6.8 Hz, ArH), 4.67 (s, 2H, $PhCH_2$), 4.43 (d, 1H, B of AB, J = 11.2 Hz, $PhCH_B$), 4.31 (d, 1H, A of AB, J = 11.2 Hz, $PhCH_A$), 4.18-4.14 (m, 1H, H-3), 4.01 (br d, 1H, J = 12.0 Hz, H-1a), 3.78 (br s, 1H, H-4), 3.71-3.66 (m, 1H, H-5a), 3.58 (dt, J_1 = 2.8 Hz, J_2 = 11.6 Hz, H-5b), 3.48-3.42 (m, 1H, H-2), 3.37 (br d, J = 11.6 Hz, H-1b); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 138.42, 137.67 (arom. *C*-CH_2O), 132.53 (d, $J_{C,\,P}$ = 48.9 Hz, arom. C-P), 131.82 (d, $J_{Cp,\,P}$ = 2.4 Hz, arom. C$_p$-H), 131.40 (d, $J_{Cp,\,P}$ = 2.7 Hz, arom. C$_p$-H), 130.81 (d, $J_{Co,\,P}$ = 8.9 Hz, arom. C$_o$-H), 130.72 (d, $J_{Co,\,P}$ = 9.1 Hz, arom. C*o*-H), 128.82 (d, $J_{Cm,\,P}$ = 11.7 Hz, arom. C$_m$-H), 128.40 (d, $J_{Cm,\,P}$ = 12.1 Hz, arom. C$_m$-H), 128.43, 128.00, 127.93, 127.74, 127.42, 127.20 (arom. C-H), 76.80 (d, $J_{3,\,P}$ = 5.0 Hz, C-3), 72.0 (Ph*C*H_2O), 71.32 (d, $J_{4,\,P}$ = 6.8 Hz, C-4), 71.01 (Ph*C*H_2O), 68.54 (C-1), 66.02 (C-5), 37.69 (d, $J_{2,\,P}$ = 70.3 Hz, C-2); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 30.68; HRESIMS *m/z*: 499.2039 (Calcd for $C_{31}H_{32}O_4P$: M^++H, 499.2038).

3,4-di-*O*-benzyl -1,2-deoxy-2-*C*-diphenylphosphinyl-D-xylopyranose (9)

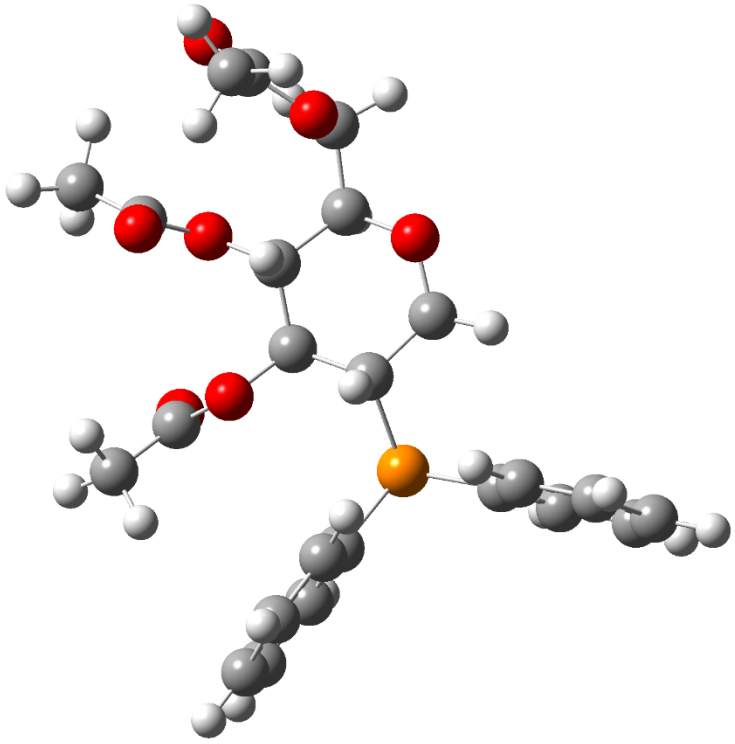


White solid, mp 99-101 ^{0}C; $[\alpha]_D^{20}$ +9.1^0 (*c* 0.5, $CHCl_3$); IR (KBr) cm^{-1}: 3056, 3029, 2968, 2905, 2853, 1589, 1437, 1359, 1262, 1181, 1116, 1072, 1002, 936, 905, 745, 720, 696, 546, 524; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.89-7.84 (m, 2H, ArH), 7.74-7.69 (m, 2H, ArH), 7.43-7.03 (m, 14H, ArH), 6.60 (d, 2H, J = 7.2 Hz, ArH), 4.80 (d, 1H, B of AB, J = 10.8 Hz, $PhCH_B$), 4.64 (d, 1H, B' of AB', J = 12.0 Hz, $PhCH_{B'}$), 4.57 (d, 1H, A' of AB', J = 12.0 Hz, $PhCH_{A'}$), 4.51 (d, 1H, A of AB, J = 10.4 Hz, $PhCH_A$), 4.21 (dd, 1H, J_1 = 8.4 Hz, J_2 = 18.8 Hz, H-3), 3.98 (dd, 1H, $J_{5a,\,4}$ = 5.2 Hz, $J_{5a,\,5b}$ = 11.2 Hz, H-5a), 3.70-3.64 (m, 1H, H-4), 3.56-3.50 (m, 1H, H-1), 3.18 (t, 1H, $J_{5b,\,5a}$ = $J_{5b,\,4}$ = 11.2 Hz, H-5b), 3.00-2.93 m, 1H, H-2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 138.22, 138.04 (arom. *C*-CH_2O), 133.42 (d, $J_{C,\,P}$ = 91.7 Hz, arom. C-P), 132.44 (d, $J_{C,\,P}$ = 87.4 Hz, arom. C-P), 131.71 (d, $J_{Cp,\,P}$ = 2.4 Hz, arom. C$_p$-H), 131.40 (d, $J_{Cp,\,P}$ = 2.5 Hz, arom. C$_p$-H), 130.70 (d, $J_{Co,\,P}$ = 2.7 Hz, arom. C$_o$-H), 130.61 (d, $J_{Co,\,P}$ = 2.5 Hz, arom. C*o*-H), 128.80 (d, $J_{Cm,\,P}$ = 11.6 Hz, arom. C$_m$-H), 128.49 (d, $J_{Cm,\,P}$ = 11.9 Hz, arom. C$_m$-H), 128.46, 127.83, 127.81, 127.69, 127.64, 127.05 (arom. C-H), 80.50 (d, $J_{4,\,P}$ = 10.1 Hz, C-4), 78.60 (d, $J_{3,\,P}$ = 5.7 Hz, C-3), 74.78, 73.05 (2 × Ph*C*H_2O), 69.00 (C-5), 66.75 (d, $J_{1,\,P}$ = 3.7 Hz, C-1), 42.17 (d, $J_{2,\,P}$ = 68.0 Hz, C-2); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 27.98; HRESIMS *m/z*: 521.1856 (Calcd for $C_{31}H_{31}NaO_4P$: M^++Na, 521.1858).

Crystal data and structure refinement for 2.

Empirical formula	C24 H27 O8 P
Formula weight	474.43
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Hexagonal,
Space group	P6(1)
Unit cell dimensions	a = 11.64595(8) Å α = 90^0
	b = 11.64595(8) Å β = 90^0
	c = 31.3727(3) Å γ = 120^0
Volume	3684.96(5) $Å^3$
Z	6
Density (calculated)	1.283 Mg/m^3
Absorption coefficient	1.382 mm^{-1}
F(000)	1500
Crystal size	0.20 x 0.15 x 0.15 mm
Theta range for data collection	4.38 to 67.22°.
Limiting indices	-13<=h<=13, -13<=k<=12, -37<=l<=35
Reflections collected / unique	19381 / 4240 [R(int) = 0.0264]
Completeness to theta = 67.22°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8195 and 0.7696
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4240 / 1 / 300
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0978
R indices (all data)	R1 = 0.0384, wR2 = 0.0995
Absolute structure parameter	0.03(2)
Largest diff. peak and hole	0.207 and -0.172 $e.Å^{-3}$

Optimized structures and Cartesian coordinates of radical **11**



11 Energy = -1872.90898a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	-0.477769	-0.635433	-0.032777
5	1	0	-0.479841	-0.514123	1.065945
6	6	0	0.573214	0.345030	-0.593269
7	1	0	0.428223	0.510554	-1.663240
8	6	0	1.977322	-0.206069	-0.334682
9	1	0	2.167892	-0.265389	0.738374
10	6	0	2.121244	-1.591155	-0.979027
11	1	0	1.930266	-1.510373	-2.058635
12	6	0	3.493149	-2.219753	-0.804468
13	1	0	3.455122	-3.261496	-1.133839
14	1	0	4.235935	-1.679016	-1.390936
15	6	0	5.076659	-1.665211	0.905947
16	6	0	5.281622	-1.660352	2.397801
17	1	0	6.347050	-1.587843	2.621191

18	1	0	4.850386	-2.549894	2.862248
19	1	0	4.775628	-0.778471	2.807469
20	6	0	3.787124	1.360674	-0.120751
21	6	0	4.786568	2.141135	-0.930658
22	1	0	4.314735	2.594901	-1.805480
23	1	0	5.560695	1.448989	-1.281261
24	1	0	5.250118	2.903994	-0.304063
25	6	0	0.459084	2.751088	-0.637993
26	6	0	0.337808	3.947715	0.269899
27	1	0	-0.623778	3.921025	0.792511
28	1	0	0.412025	4.862061	-0.319501
29	1	0	1.127185	3.924221	1.027634
30	6	0	-2.748041	1.265512	0.252625
31	6	0	-2.689354	1.379345	1.650422
32	1	0	-2.267899	0.583500	2.257580
33	6	0	-3.168286	2.526938	2.281957
34	1	0	-3.117059	2.607637	3.364055
35	6	0	-3.710907	3.569952	1.524845
36	1	0	-4.084521	4.462105	2.019718
37	6	0	-3.770914	3.463557	0.134133
38	1	0	-4.189554	4.272459	-0.457970
39	6	0	-3.291170	2.315947	-0.500987
40	1	0	-3.327520	2.227519	-1.582196
41	6	0	-3.267286	-1.591725	-0.174615
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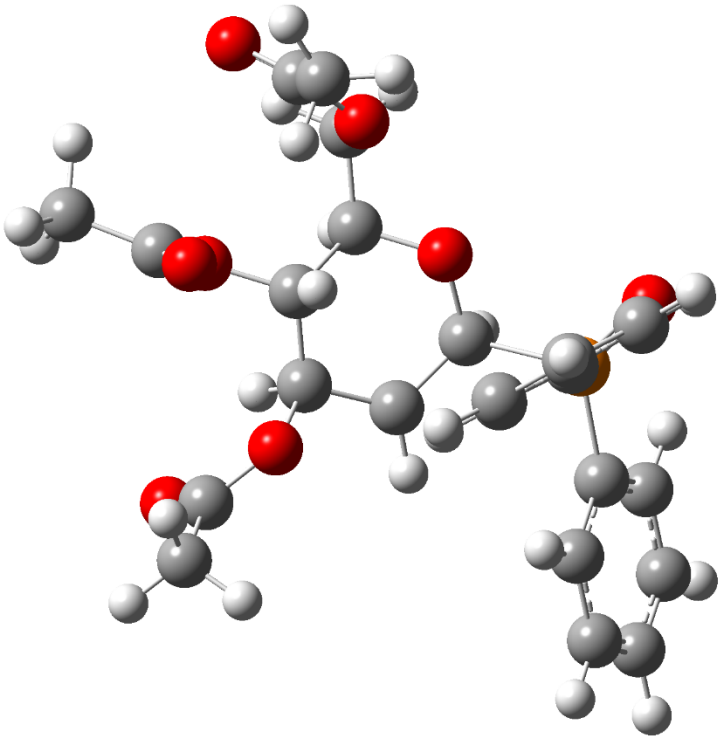
48	6	0	-4.181433	-3.158017	1.437164
49	1	0	-4.206403	-3.558472	2.446631
50	6	0	-3.310876	-2.112885	1.128541
51	1	0	-2.664916	-1.718273	1.907855
52	8	0	-2.204091	0.025181	-2.165538
53	8	0	0.557284	2.781100	-1.844360
54	8	0	0.439690	1.601352	0.096601
55	8	0	2.948853	0.663349	-0.940393
56	8	0	1.152588	-2.481678	-0.406994
57	8	0	3.877131	-2.216202	0.584584
58	8	0	5.852608	-1.211433	0.089801
59	8	0	3.733995	1.317704	1.089843

Optimized structures and Cartesian coordinates of radical **12**



12 Energy = -1872.903415a.u.

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4	6	0	-0.721358	1.249433	-0.810307
5	1	0	-1.547398	1.948142	-0.725429
6	6	0	0.647826	1.758271	-0.511007
7	1	0	0.904450	2.590668	-1.179216
8	6	0	1.722785	0.679151	-0.632404
9	1	0	1.760600	0.072424	0.272607
10	6	0	1.409098	-0.226737	-1.832633
11	1	0	1.307881	0.376952	-2.748987
12	6	0	2.469781	-1.279709	-2.108939
13	1	0	2.096913	-1.974426	-2.866162
14	1	0	3.389042	-0.811573	-2.461689
15	6	0	4.035827	-2.153086	-0.521139
16	6	0	4.135491	-2.908072	0.777998
17	1	0	5.141109	-3.316589	0.888443
18	1	0	3.387837	-3.702177	0.834776

19	1	0	3.949340	-2.202285	1.595710
20	6	0	3.939774	1.200633	0.145522
21	6	0	5.235485	1.833695	-0.285849
22	1	0	5.060105	2.739480	-0.870570
23	1	0	5.770582	1.115159	-0.917502
24	1	0	5.845596	2.053577	0.591302
25	6	0	0.923914	3.614990	1.013461
26	6	0	0.962461	3.963657	2.479829
27	1	0	0.008193	3.707472	2.951132
28	1	0	1.159727	5.029409	2.597866
29	1	0	1.742622	3.381196	2.980132
30	6	0	-3.743588	0.030785	-0.553423
31	6	0	-3.949679	0.773372	0.619372
32	1	0	-3.274213	0.667508	1.462310
33	6	0	-5.039006	1.640032	0.718364
34	1	0	-5.194217	2.207569	1.631595
35	6	0	-5.931243	1.770596	-0.348671
36	1	0	-6.779328	2.444831	-0.267560
37	6	0	-5.738365	1.026863	-1.515106
38	1	0	-6.436381	1.118042	-2.342492
39	6	0	-4.651599	0.158004	-1.617309
40	1	0	-4.512256	-0.438459	-2.513871
41	6	0	-1.771850	-1.705494	0.830047
42	6	0	-2.043577	-3.048049	1.133486
43	1	0	-2.551845	-3.664776	0.399134
44	6	0	-1.651774	-3.585459	2.360133
45	1	0	-1.866673	-4.626071	2.586246
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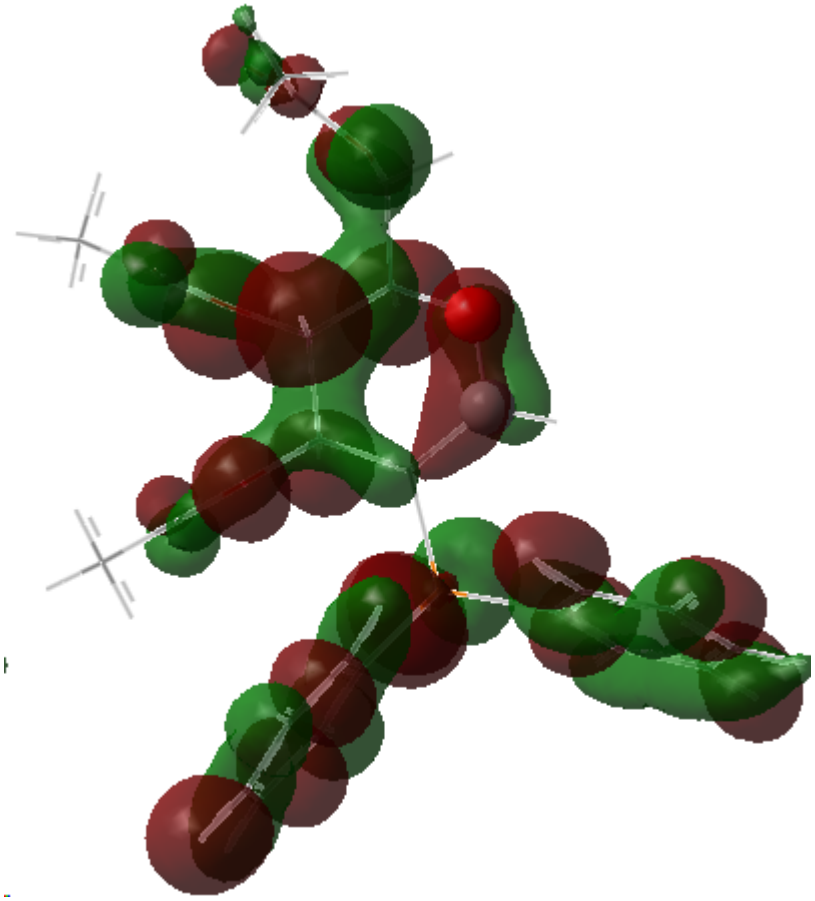
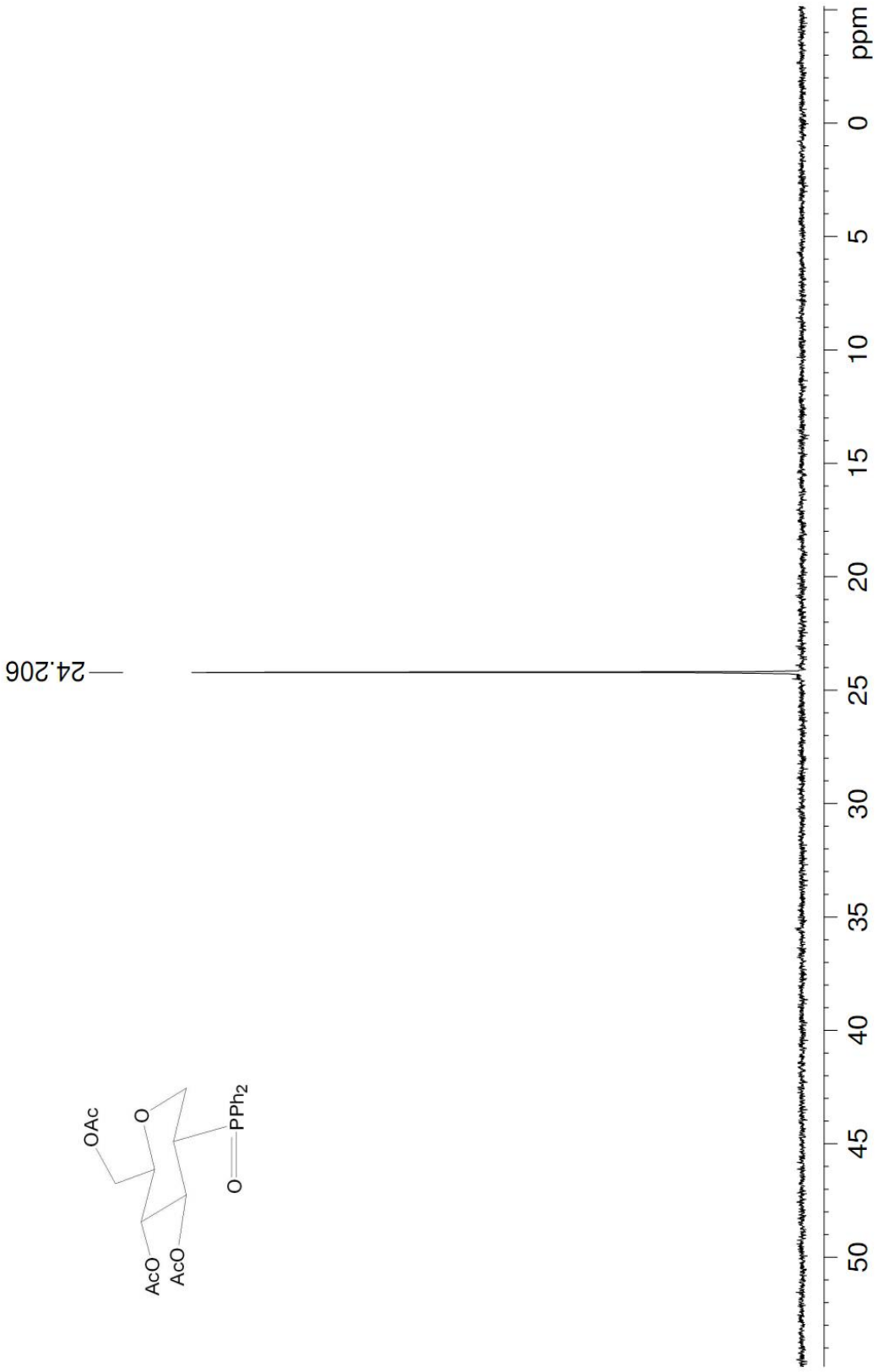
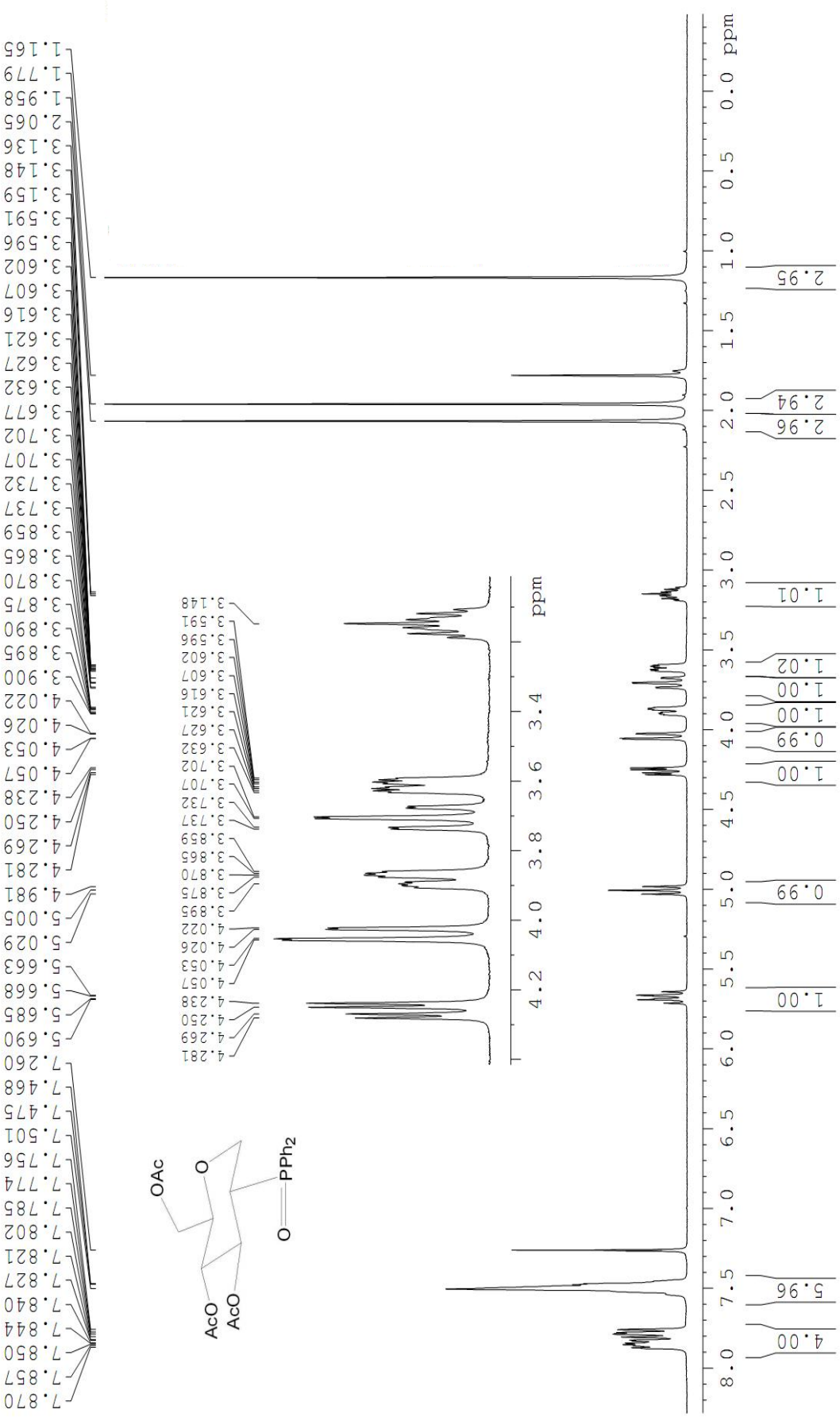
53	8	0	1.080928	4.394715	0.097632
54	8	0	0.684333	2.287318	0.848417
55	8	0	2.999412	1.315622	-0.834089
56	8	0	0.179474	-0.894344	-1.547991
57	8	0	2.742916	-2.041447	-0.917175
58	8	0	4.973089	-1.672306	-1.126533
59	8	0	3.749529	0.631566	1.199457

The C-O *p-p* conjugation of radical **11** calculated at the B3LYP/6-31G(d) level in AcOH.



^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{1}H-^{1}H COSY, HSQC, HMBC of **2**

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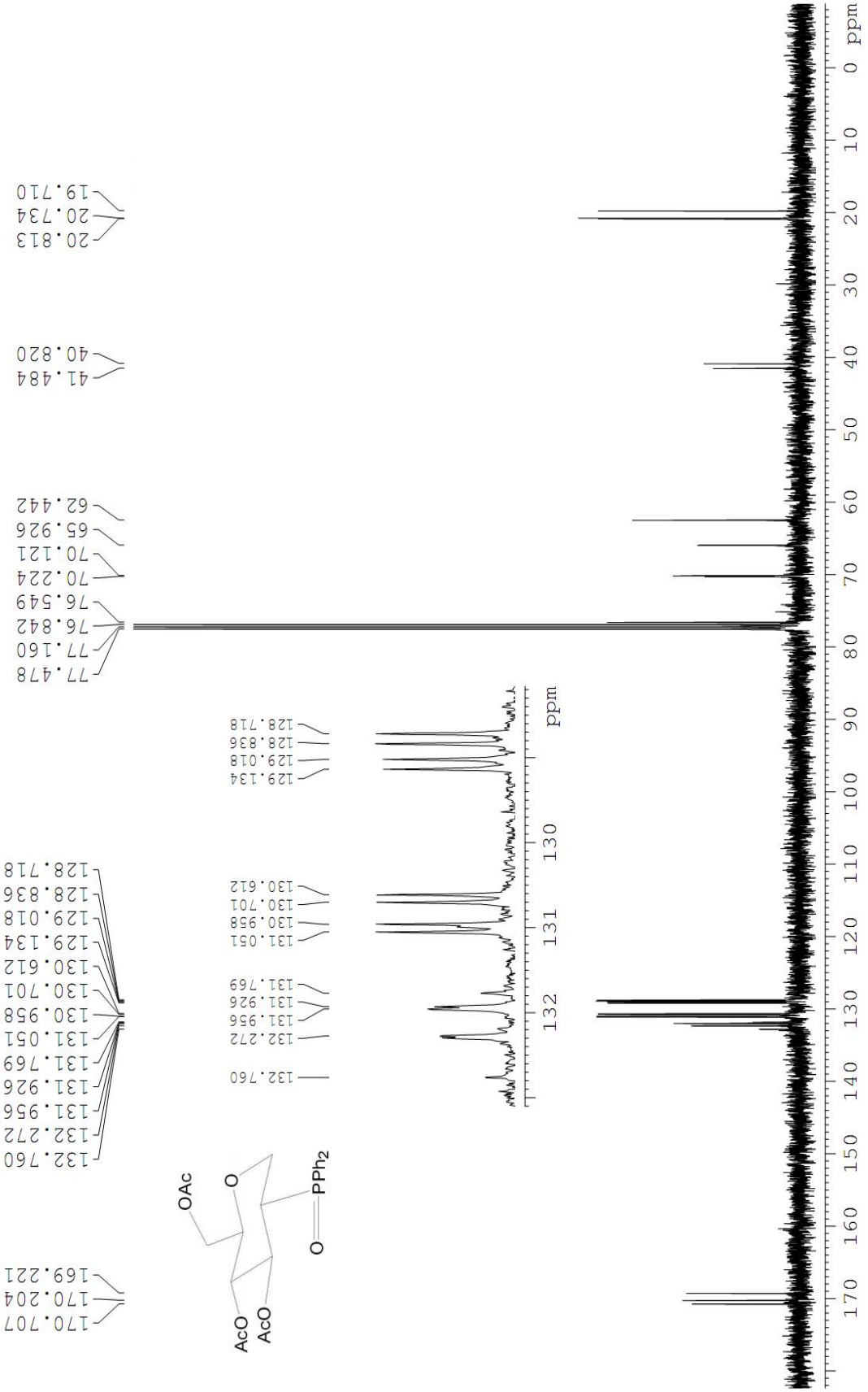
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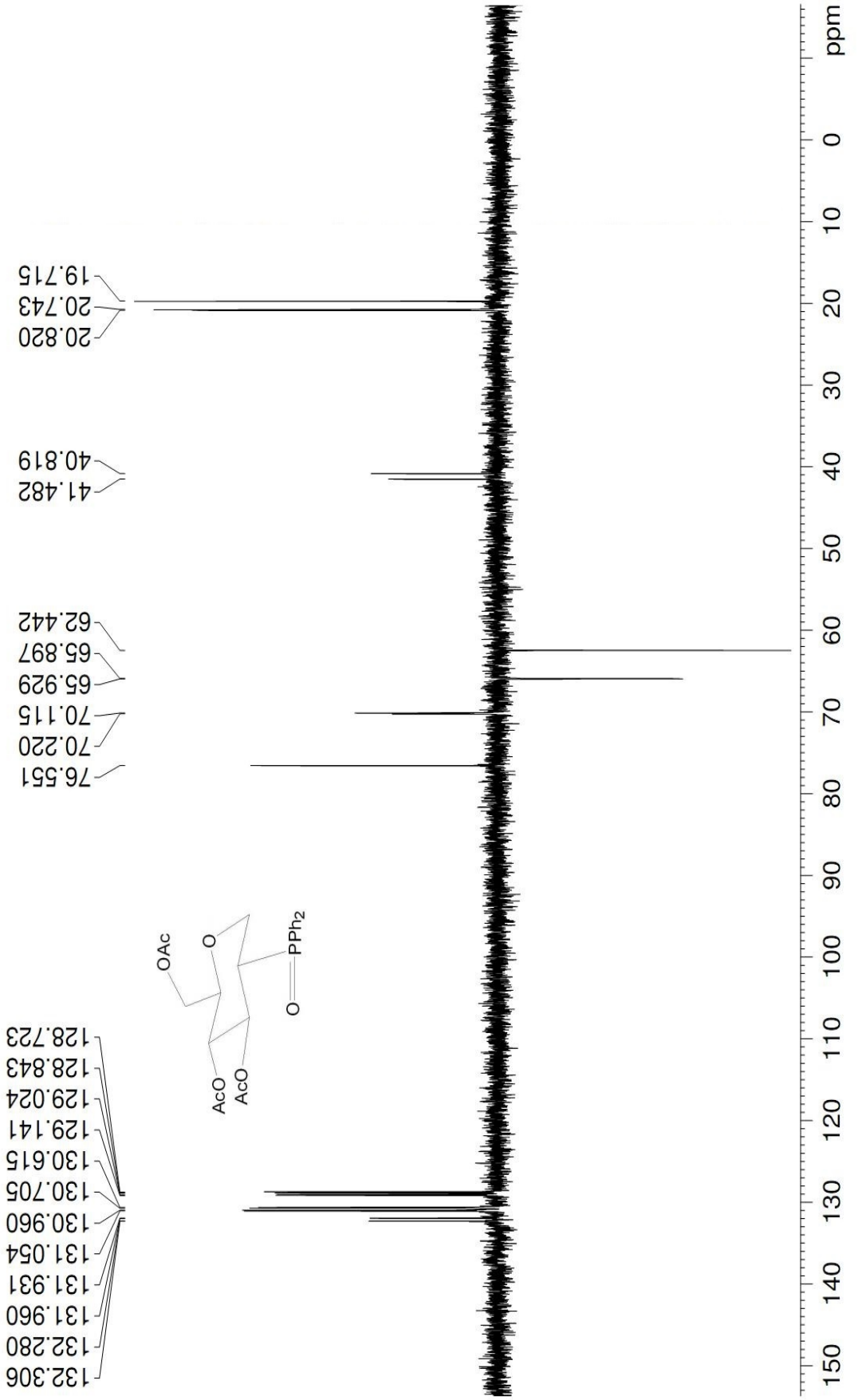
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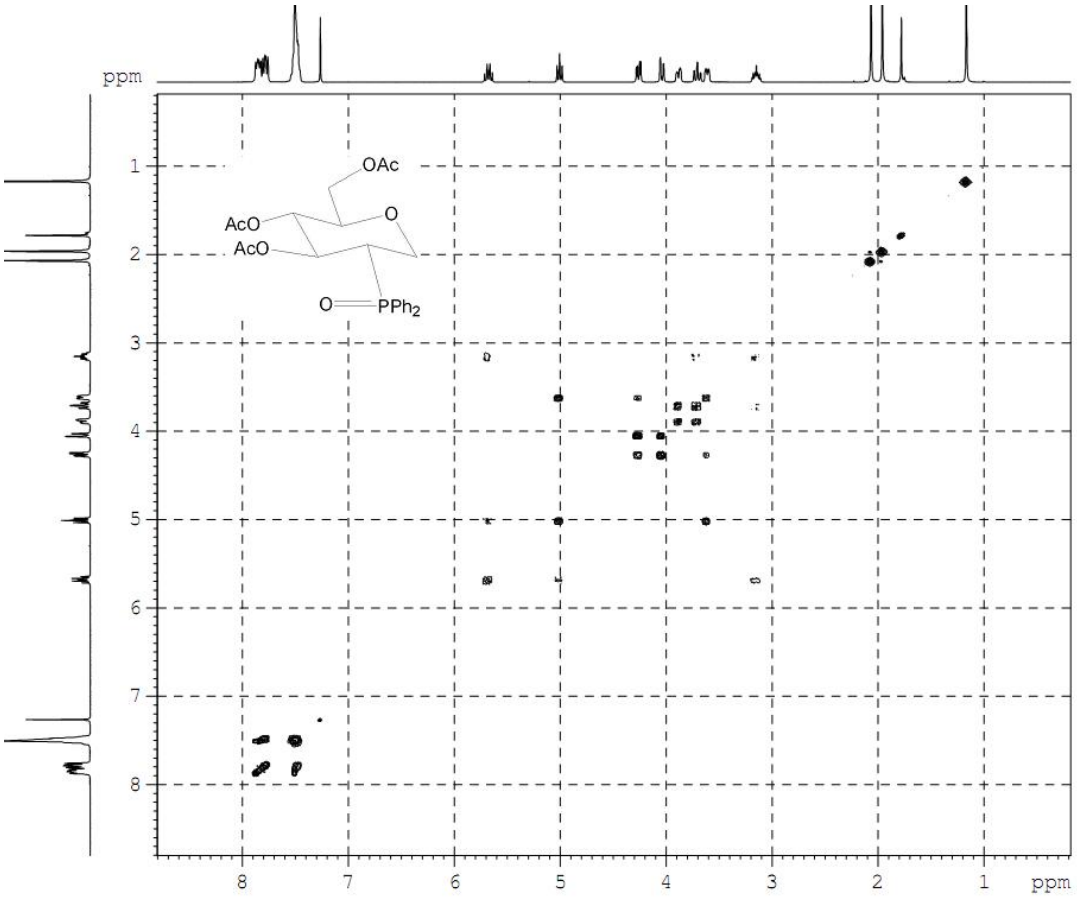
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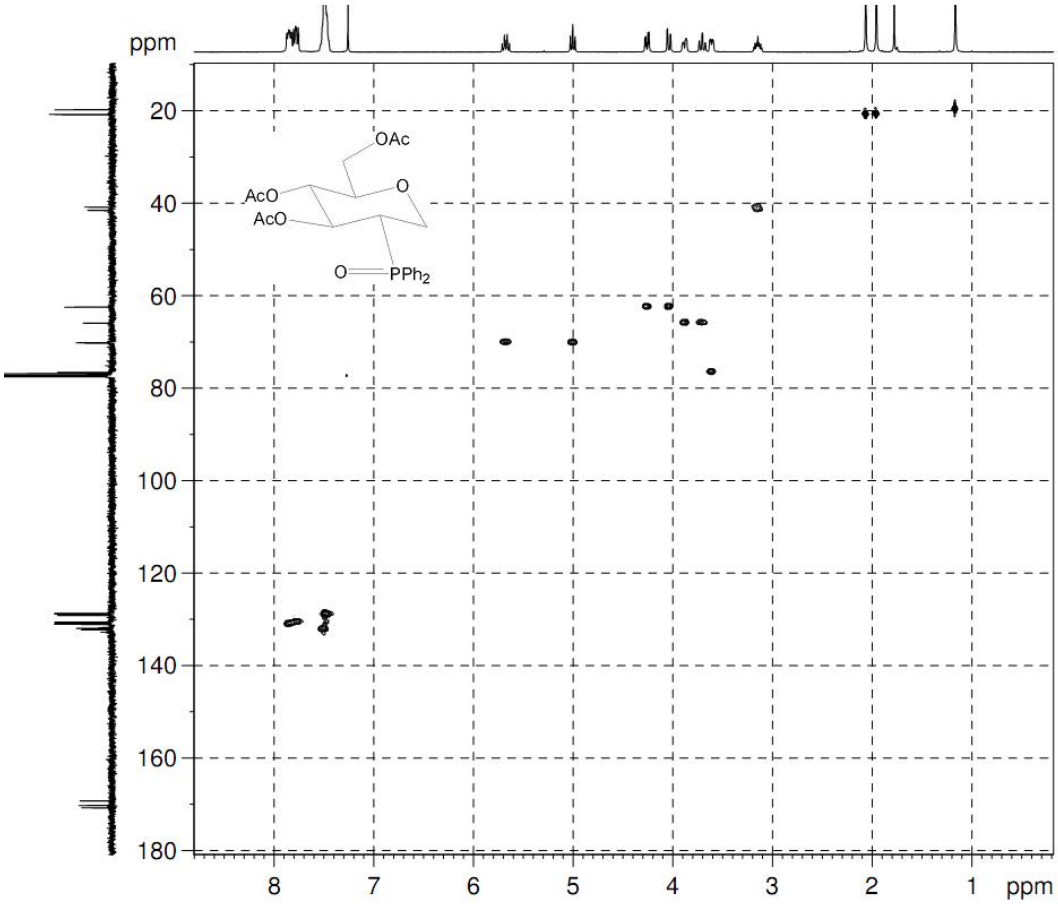
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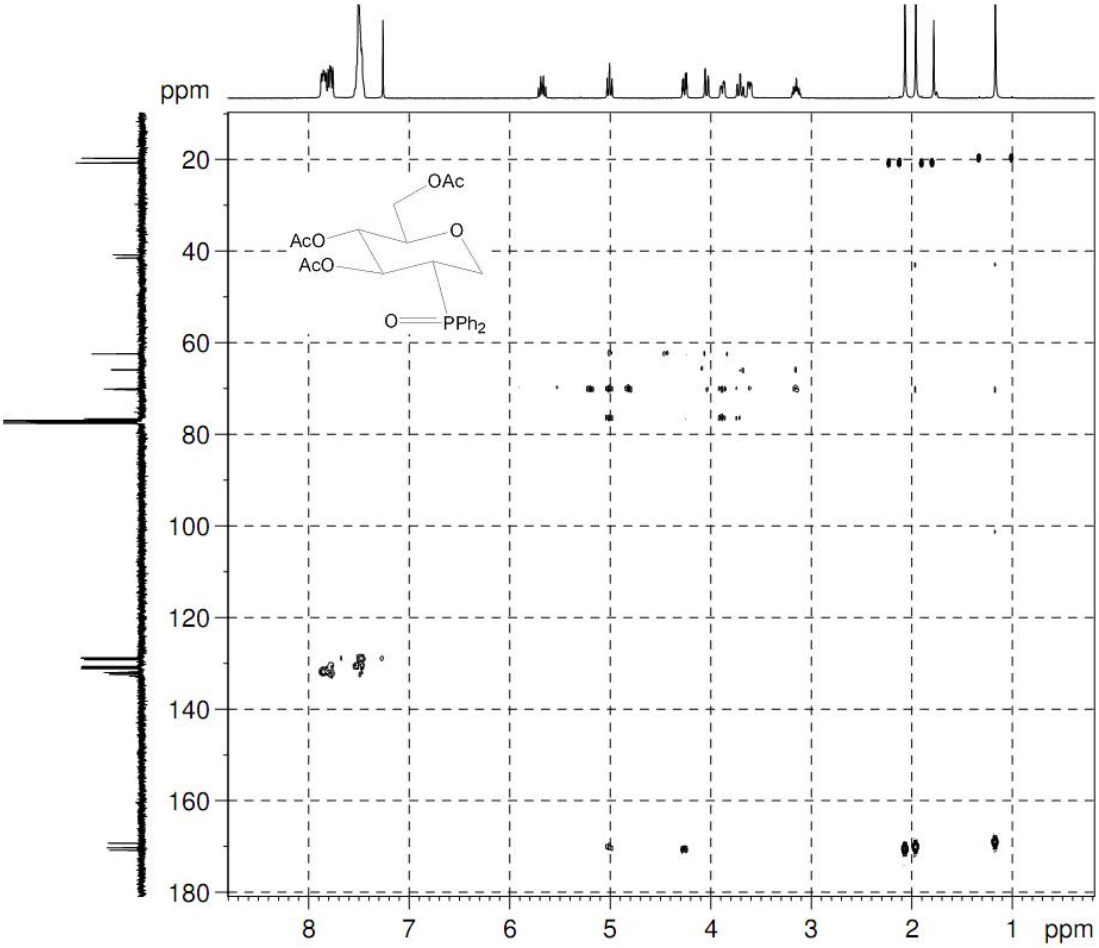
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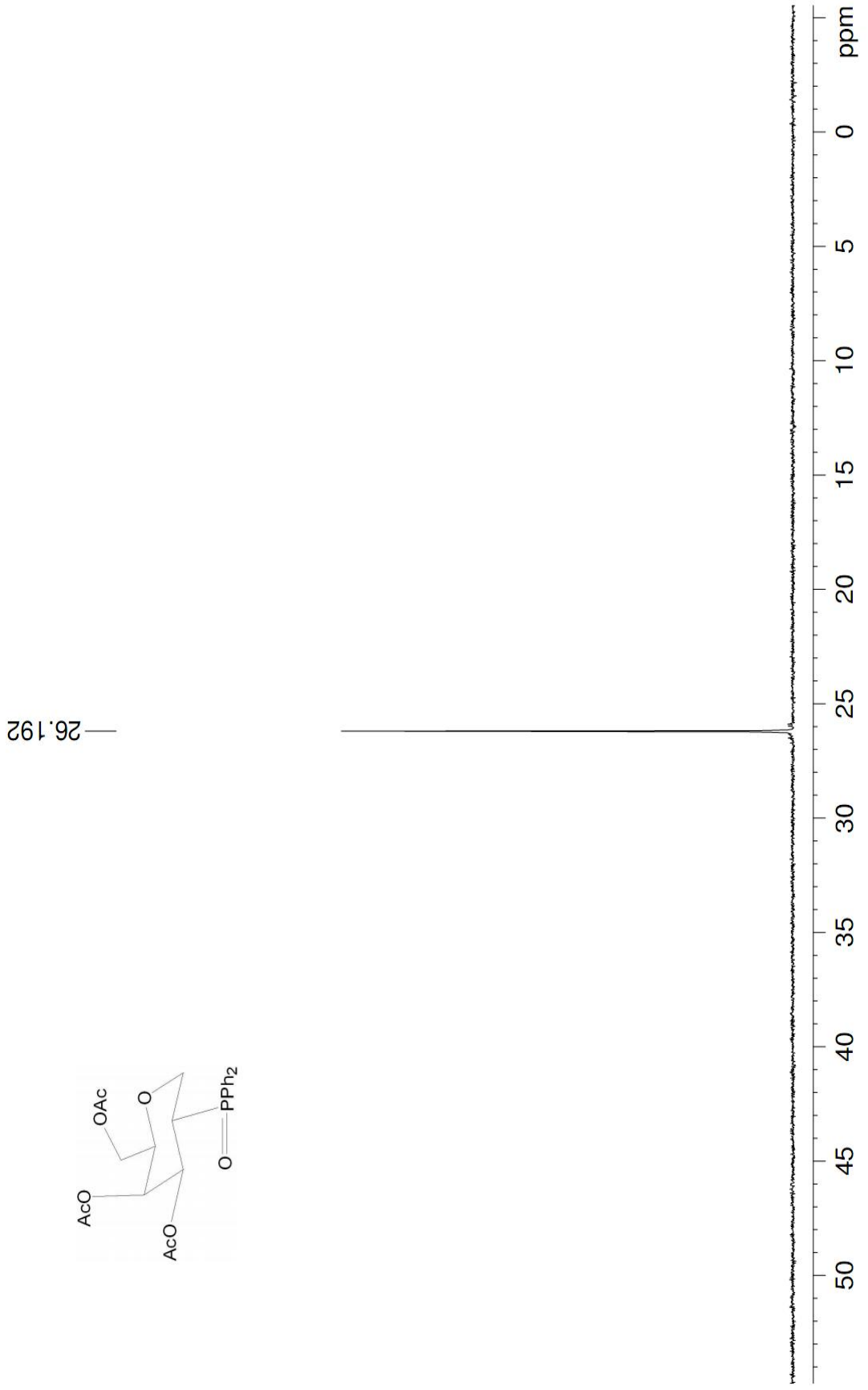
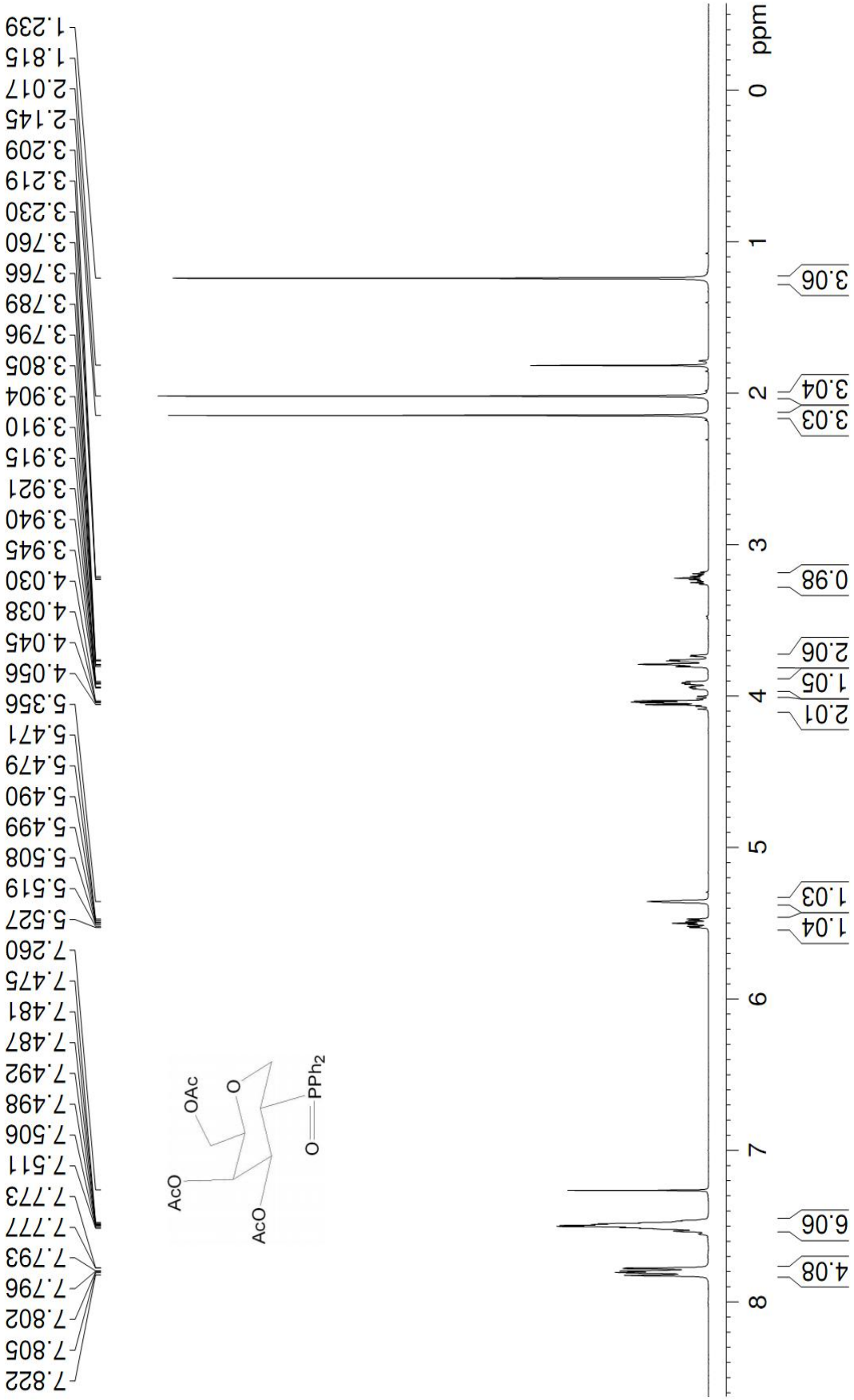
^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{1}H-^{1}H COSY, HSQC of **3**

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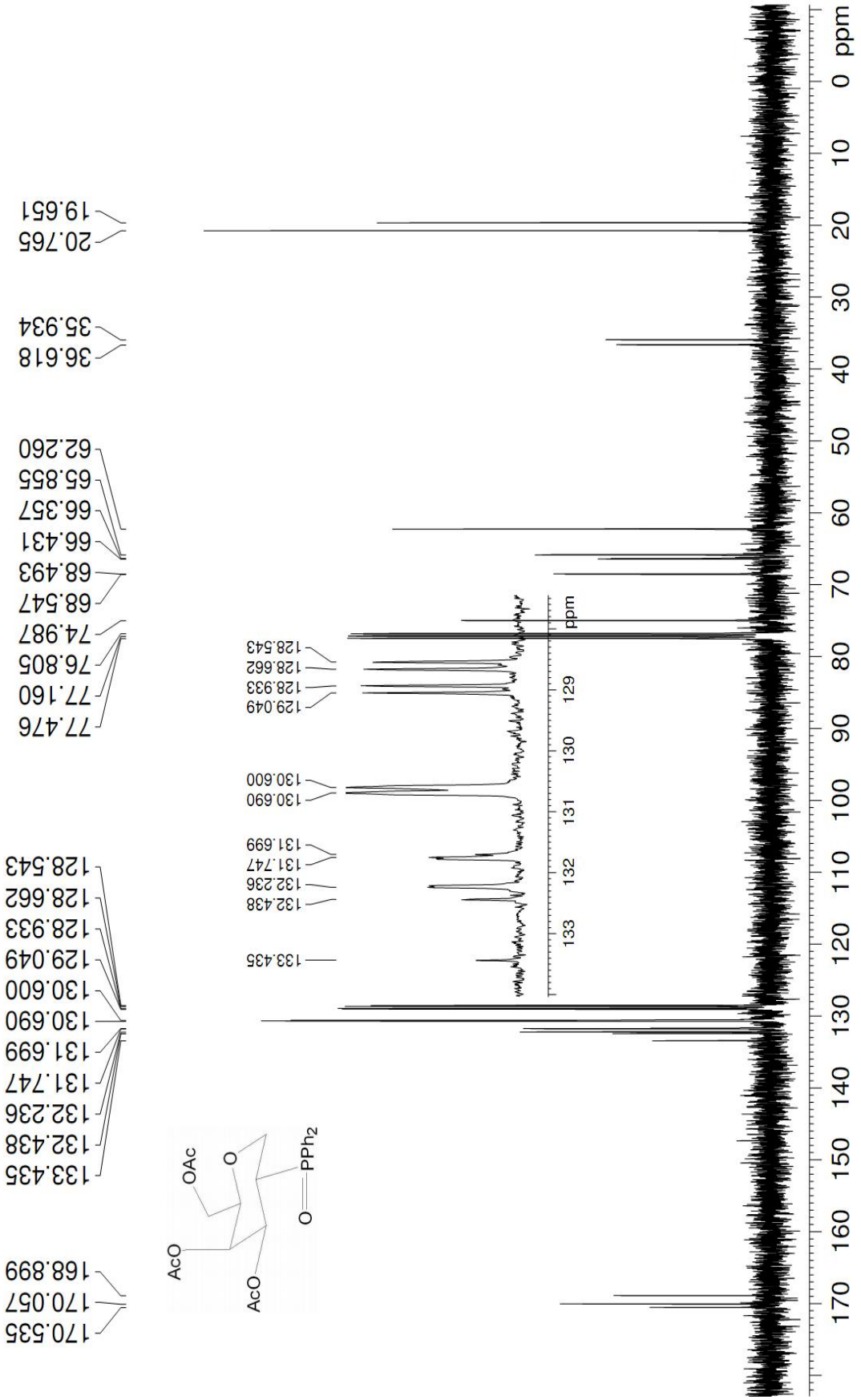
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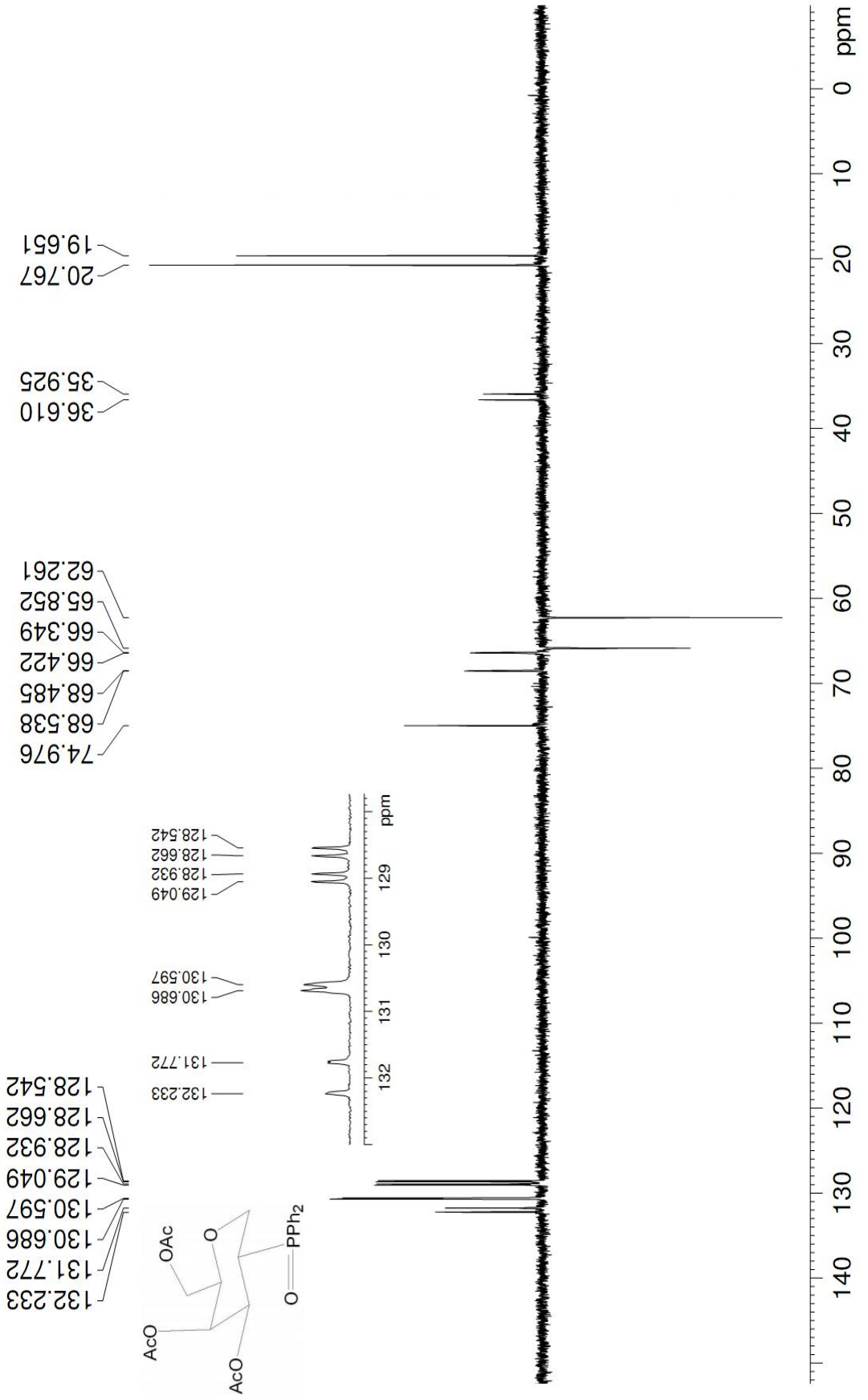
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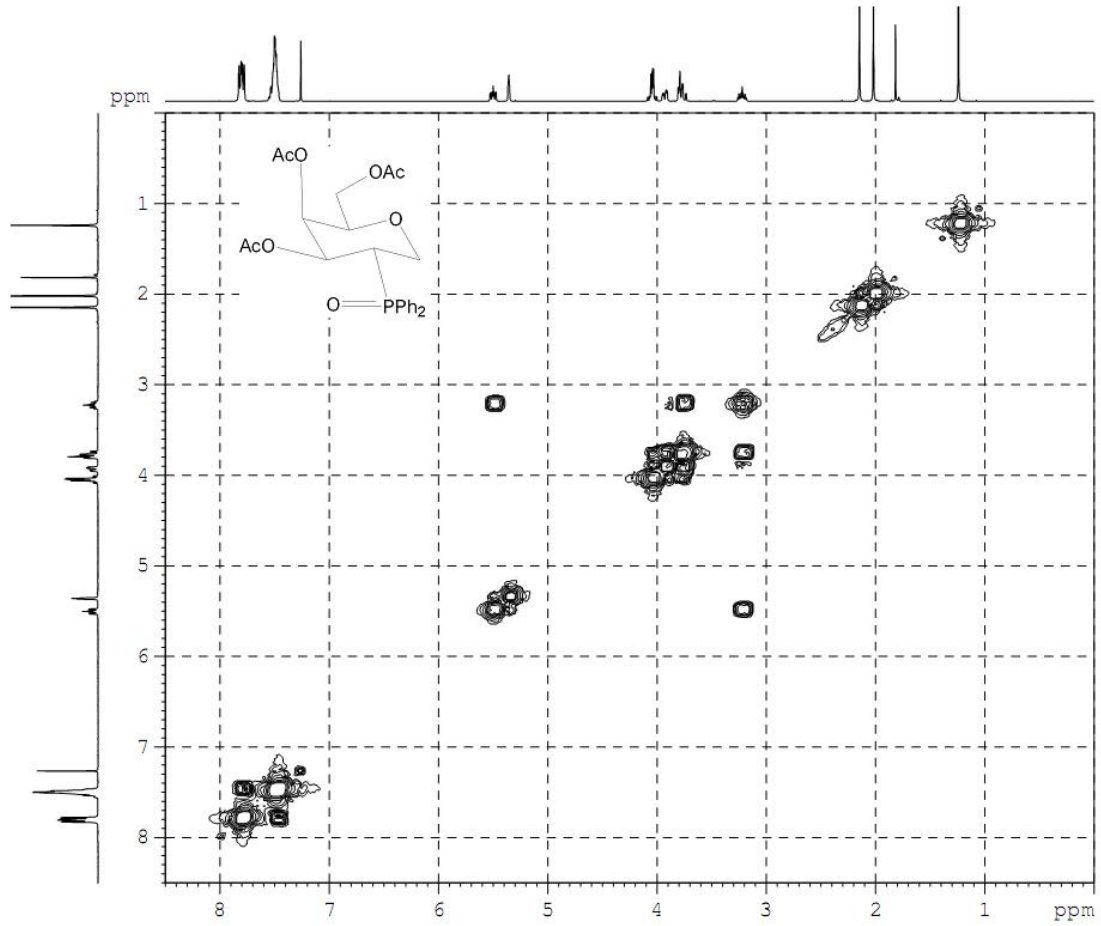
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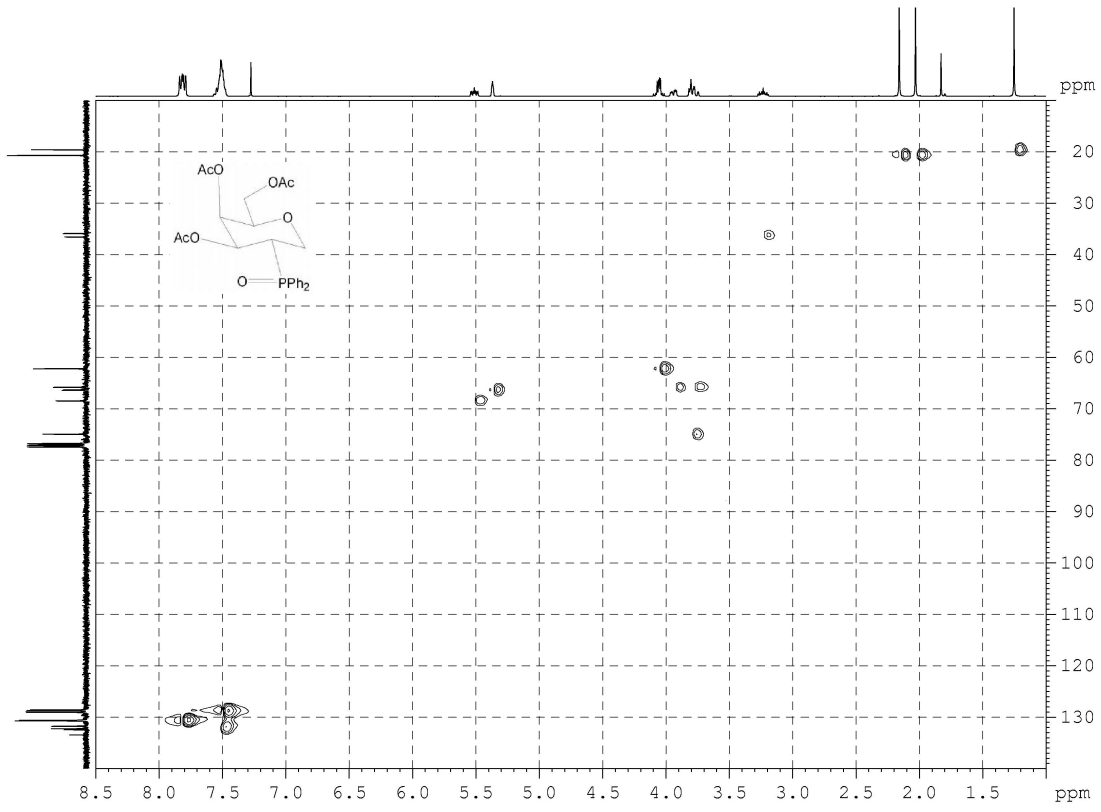
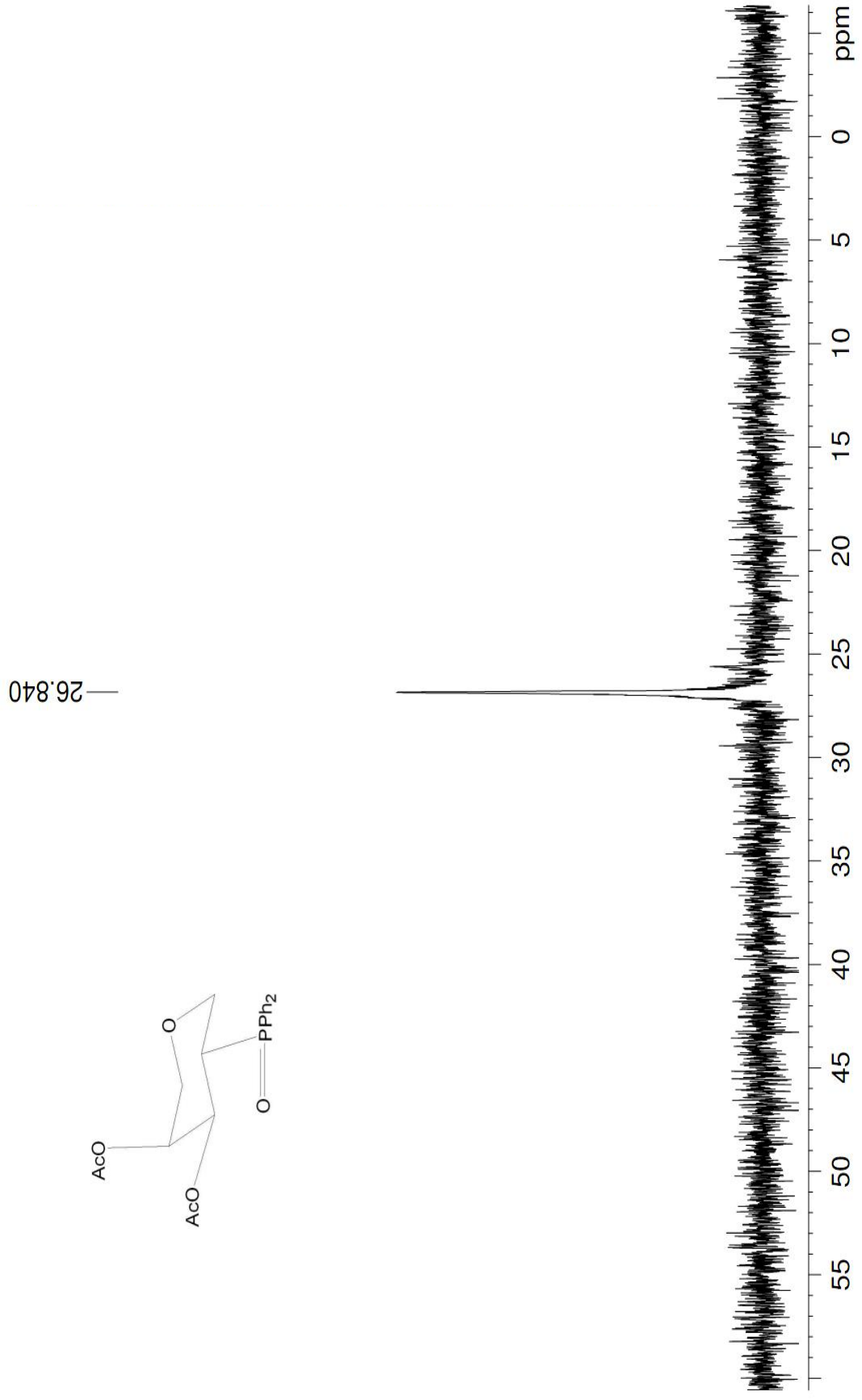
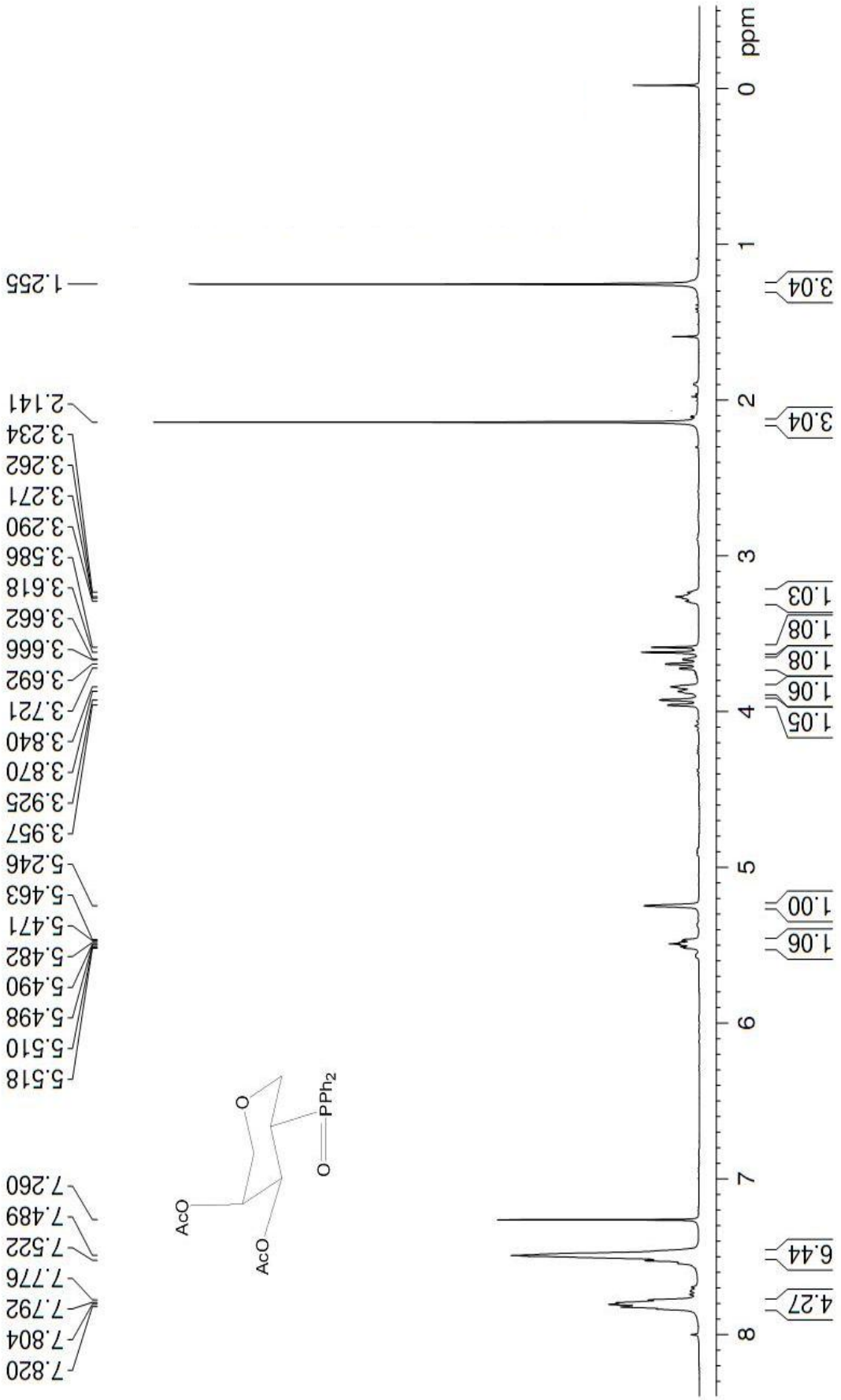
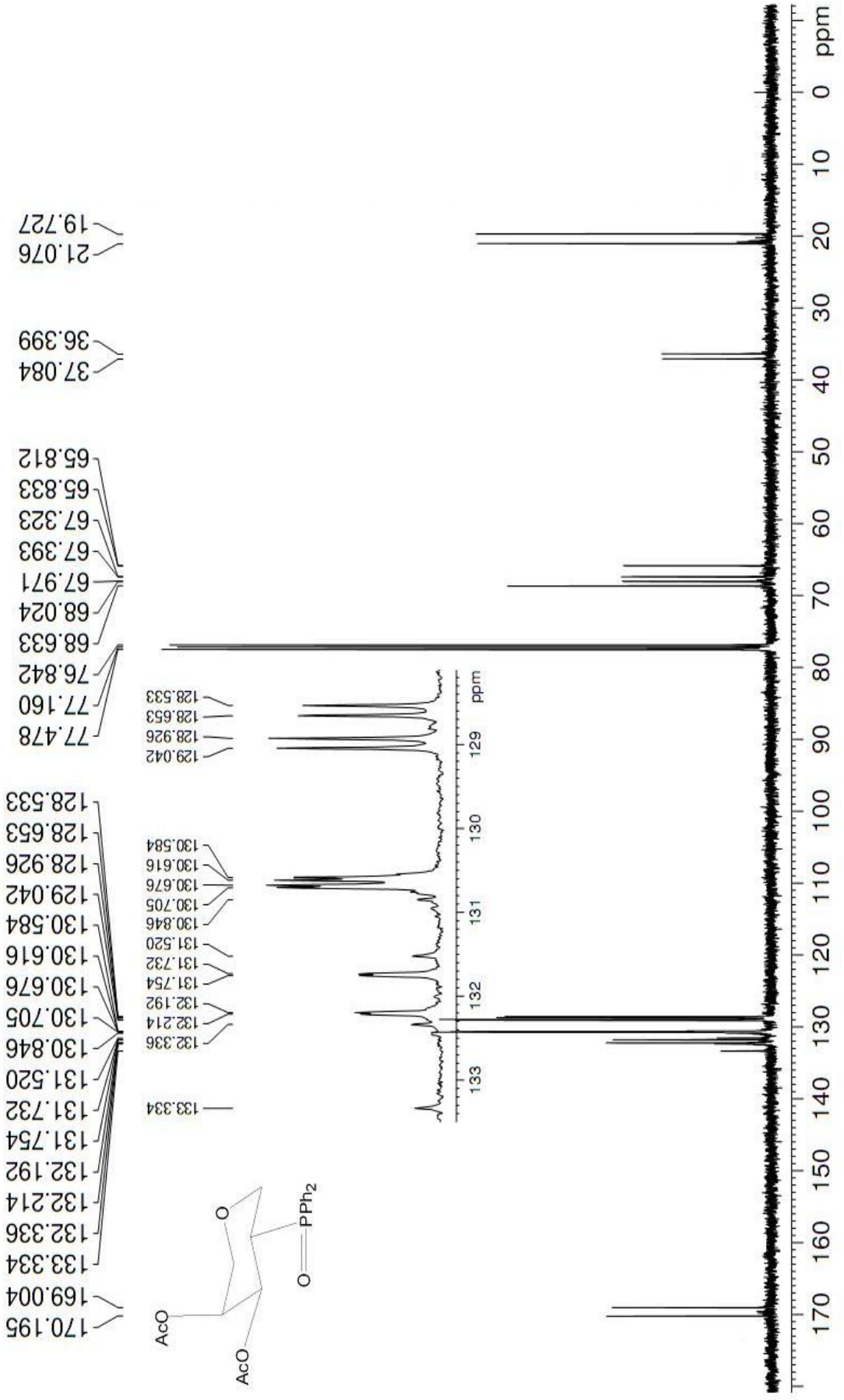
OAc
O
AcO
O
PPh2
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm

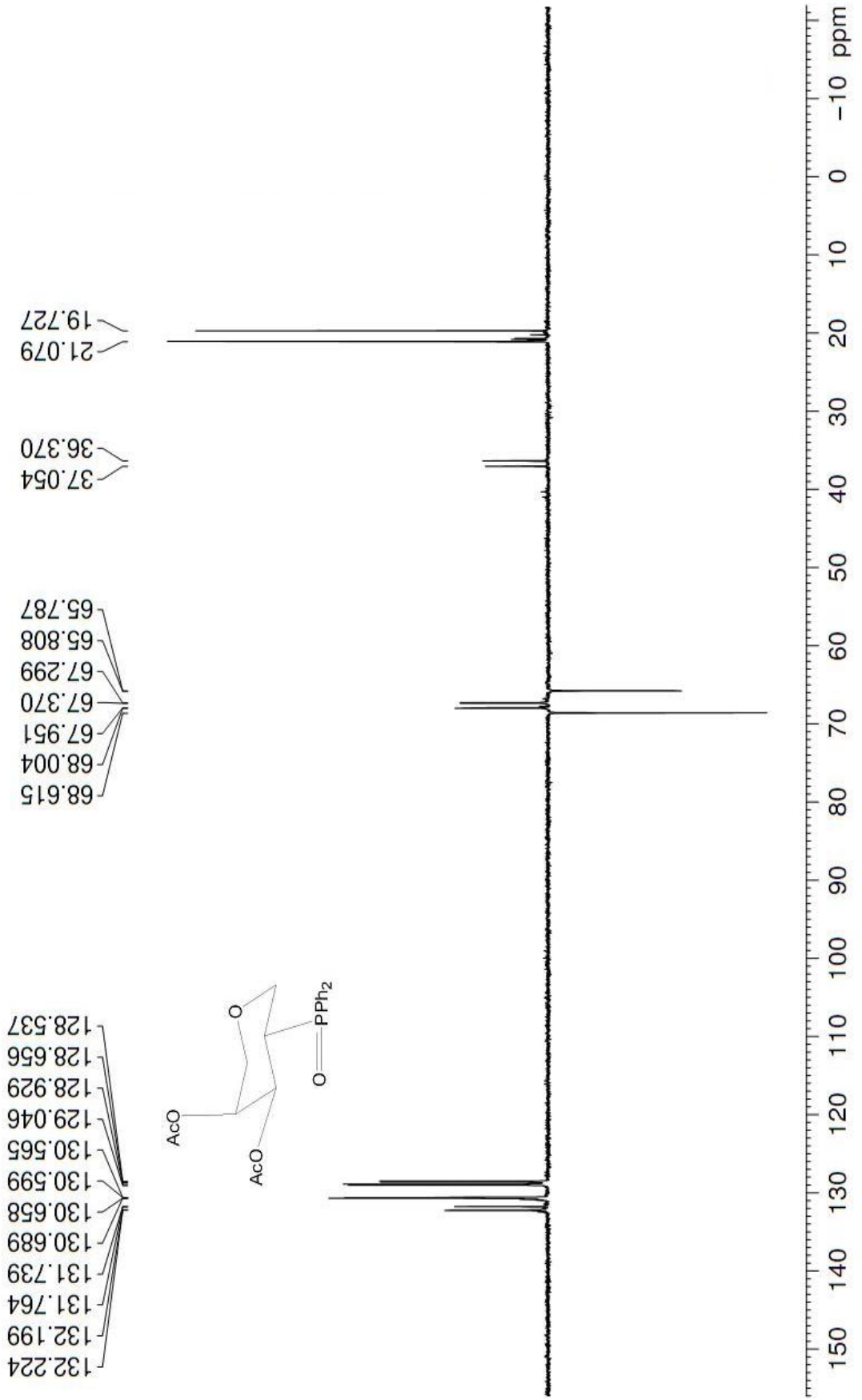

ppm
AcO
OAc
O
AcO
O
PPh2
20
30
40
50
60
70
80
90
100
110
120
130
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

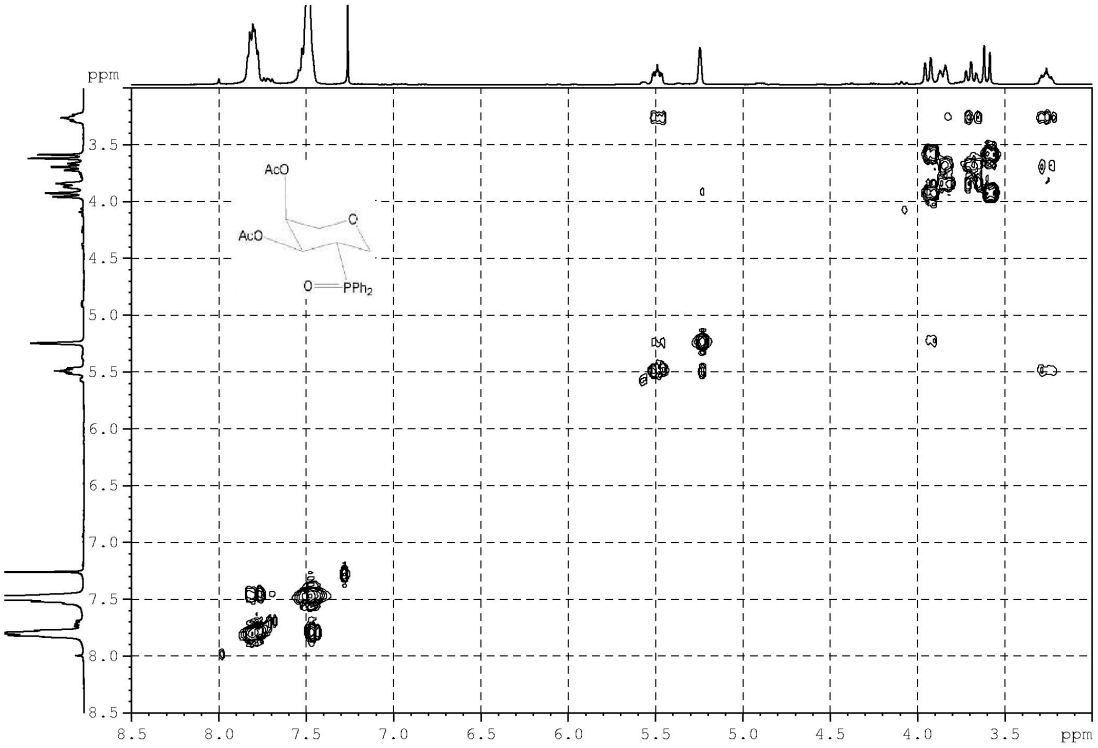
^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{1}H-^{1}H COSY, HSQC of **4**

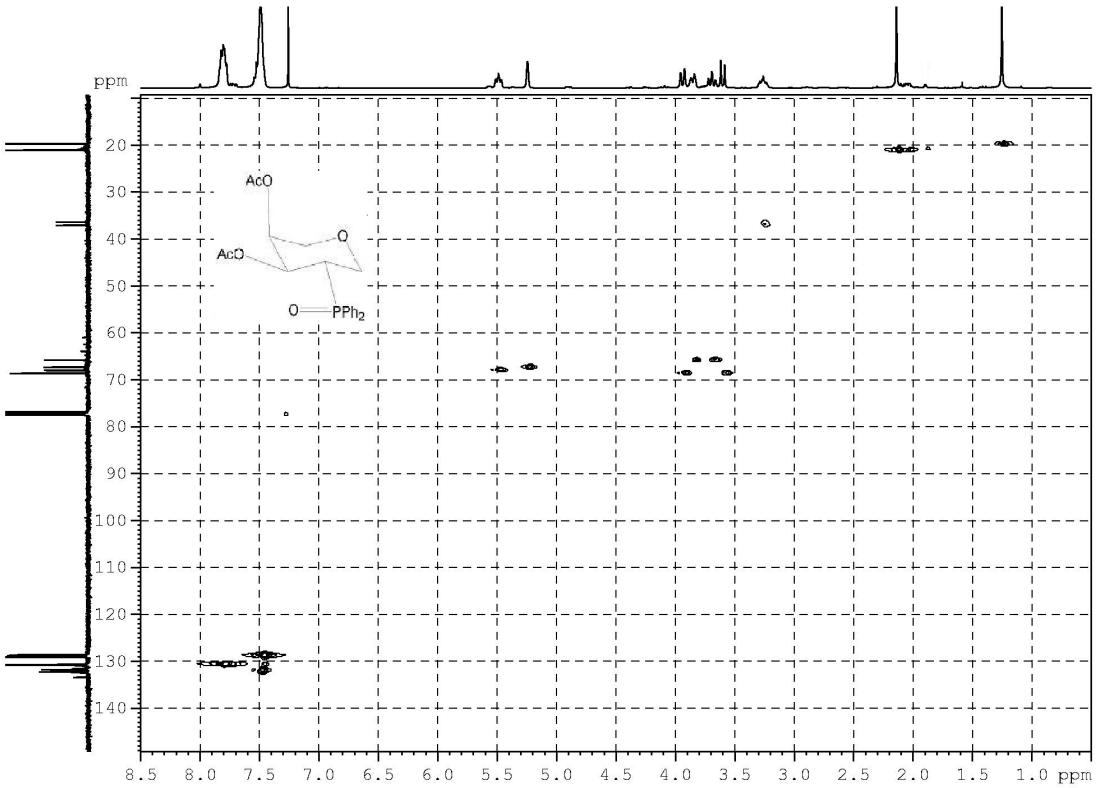



ppm
0
1
2
3
4
5
6
7
8
3.04
3.04
1.03
1.08
1.08
1.06
1.05
1.00
1.06
6.44
4.27
1.255
2.141
3.234
3.262
3.271
3.290
3.586
3.618
3.662
3.666
3.692
3.721
3.840
3.870
3.925
3.957
5.246
5.463
5.471
5.482
5.490
5.498
5.510
5.518
7.260
7.489
7.522
7.776
7.792
7.804
7.820
AcO
AcO
O
O
PPh2

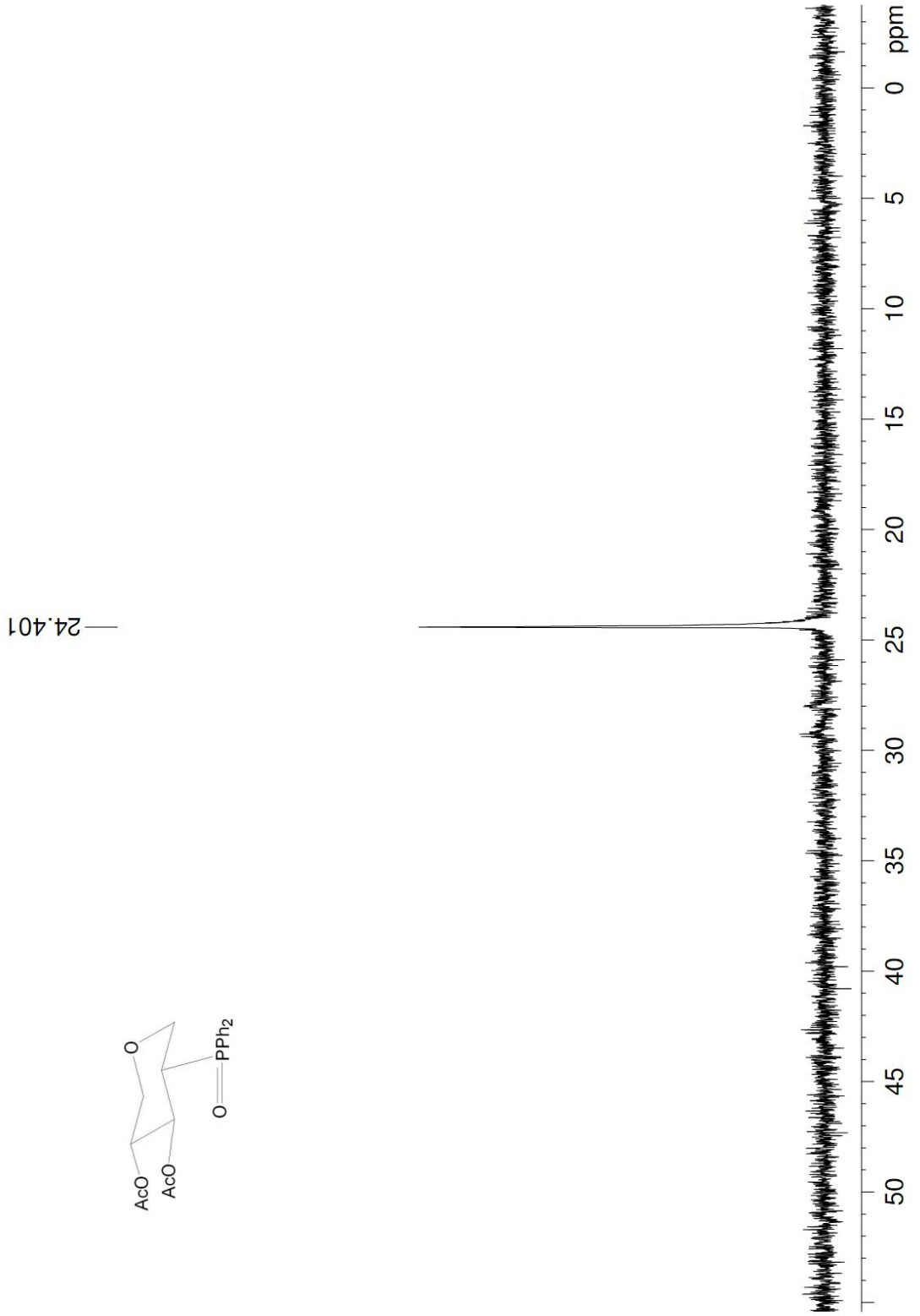

170.195
169.004
133.334
132.336
132.214
132.192
131.754
131.732
131.520
130.846
130.705
130.676
130.616
130.584
129.042
128.926
128.653
128.533
77.478
77.160
76.842
68.633
68.024
67.971
67.393
67.323
65.833
65.812
37.084
36.399
21.076
19.727
AcO
AcO
O
O
PPh2
ppm

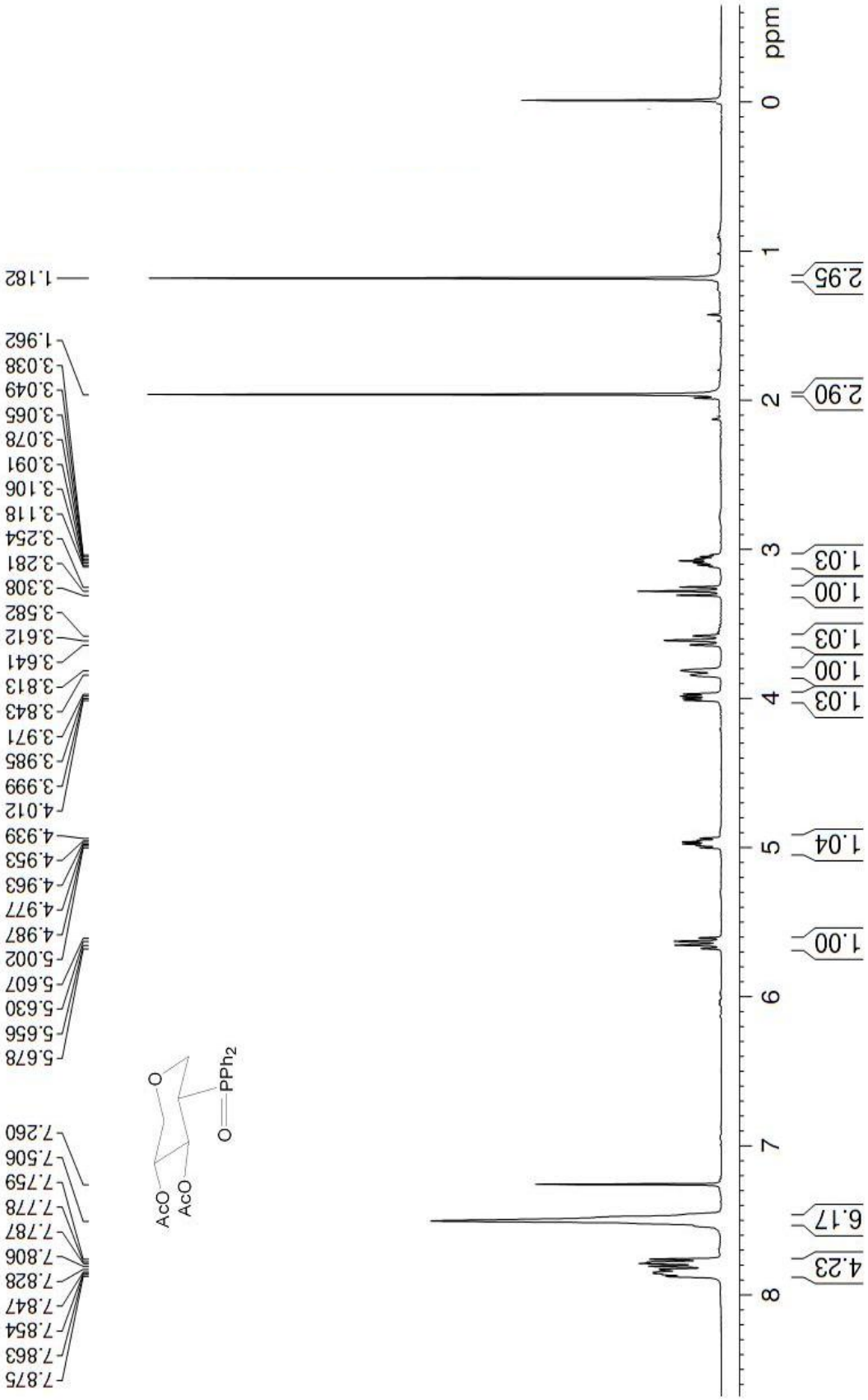

19.727
21.079
36.370
37.054
65.787
65.808
67.299
67.370
67.951
68.004
68.615
128.537
128.656
128.929
129.046
130.565
130.599
130.658
130.689
131.739
131.764
132.199
132.224
AcO
AcO
O
O
PPh2
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

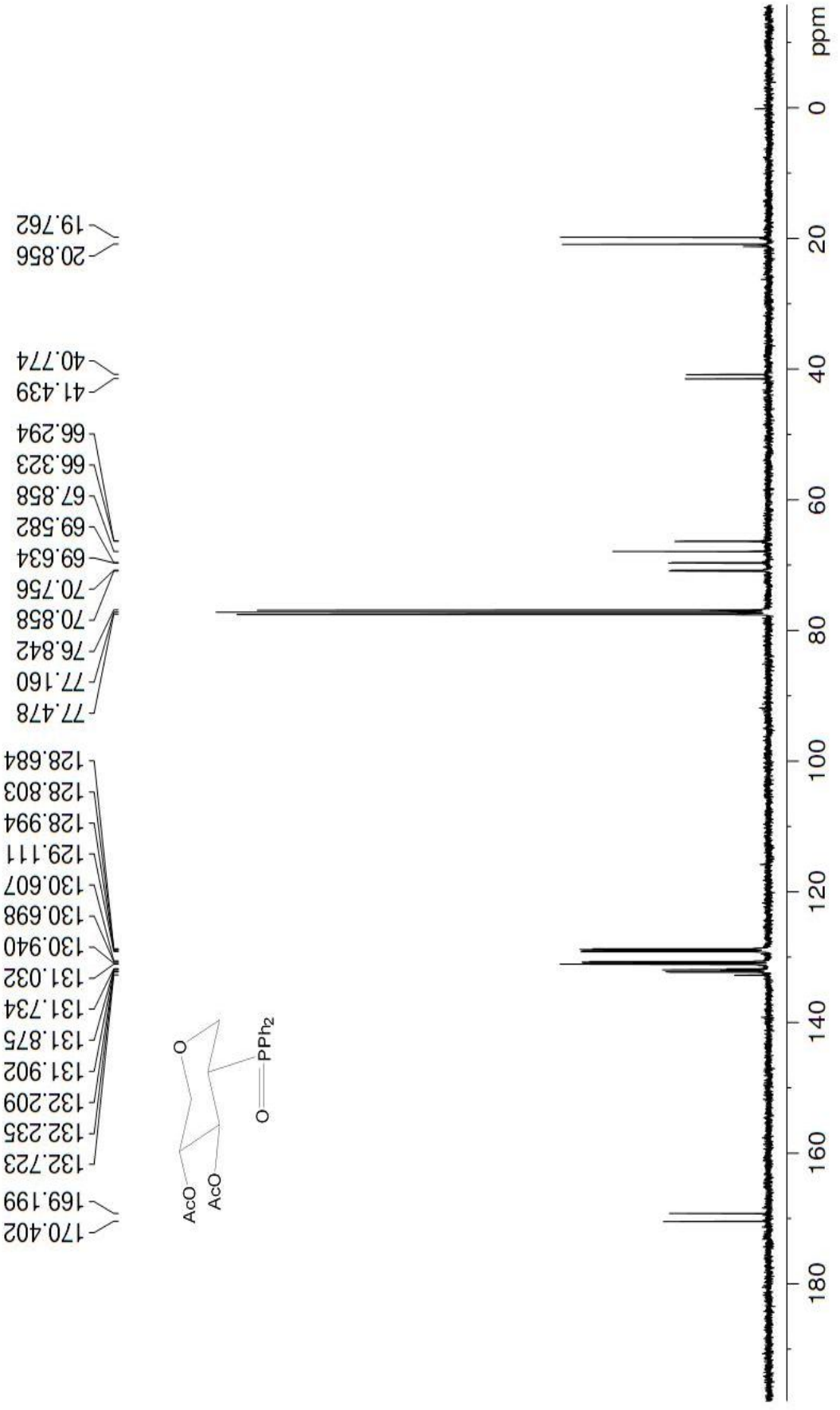

ppm
AcO
AcO
O
O
PPh2
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm

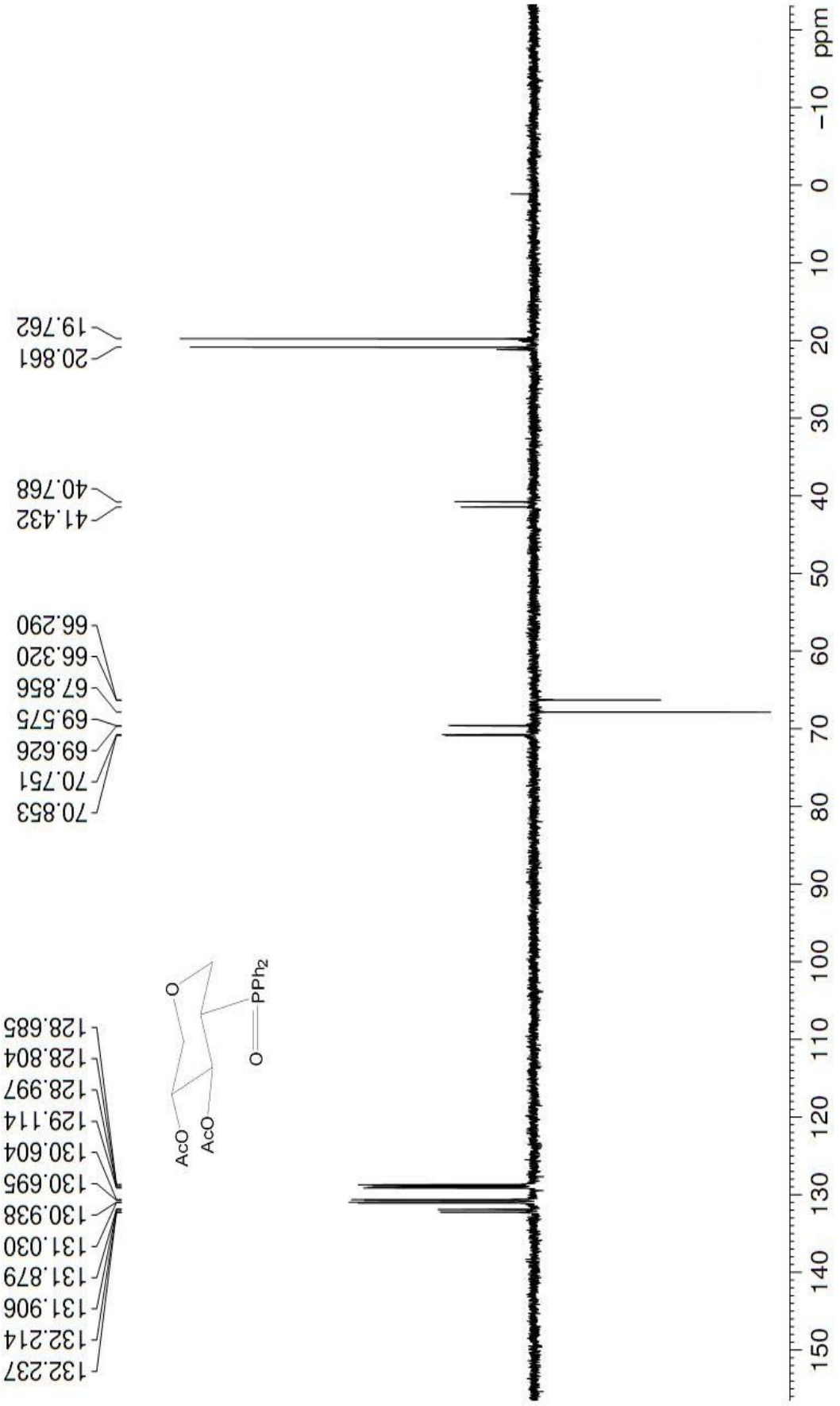

ppm
AcO
AcO
O
O
PPh2
20
30
40
50
60
70
80
90
100
110
120
130
140
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

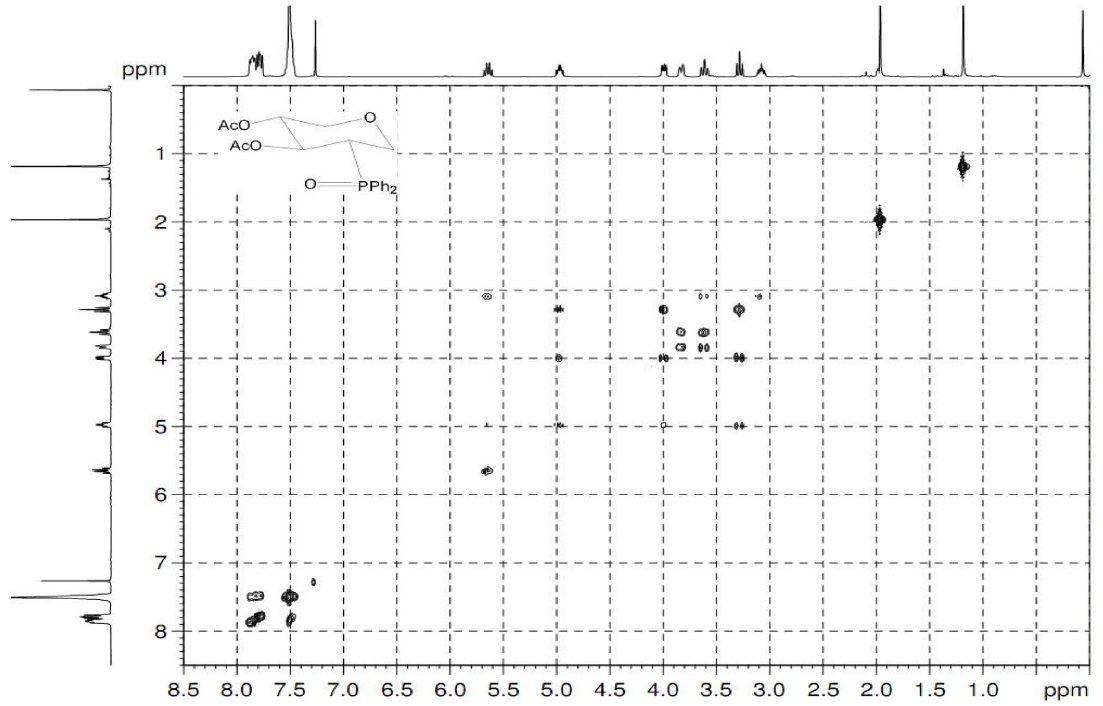
^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{1}H-^{1}H COSY, HSQC of **5**

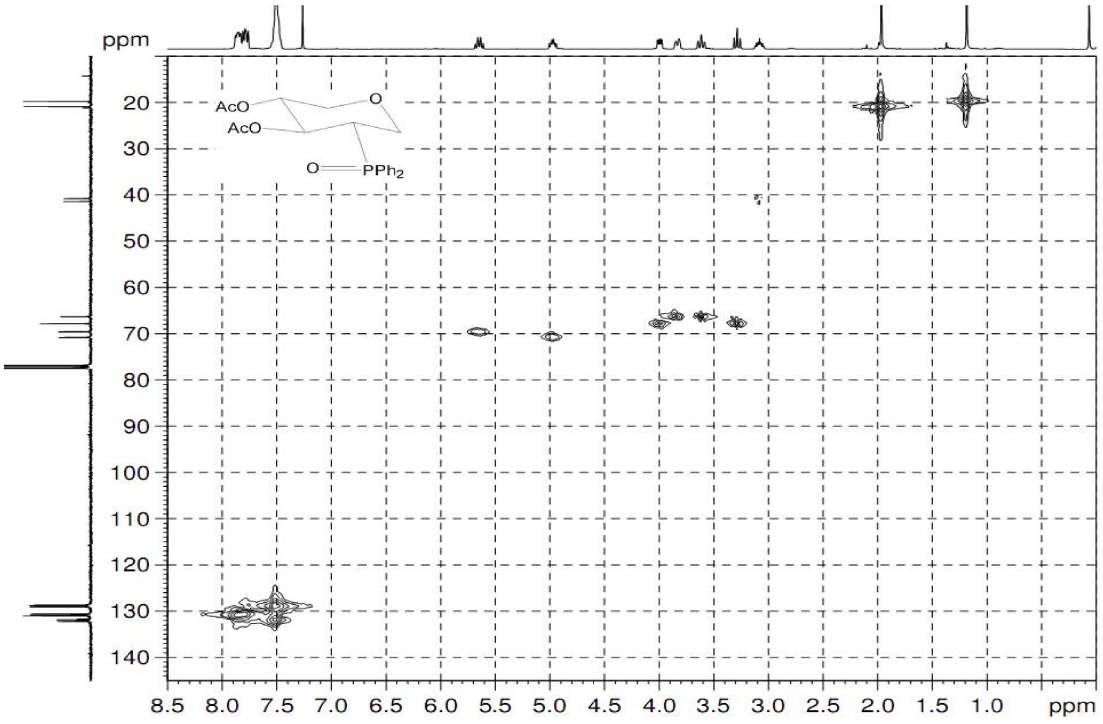



ppm
0
1
2
3
4
5
6
7
8
2.95
2.90
1.03
1.00
1.03
1.00
1.03
1.04
1.00
6.17
4.23
1.182
1.962
3.038
3.049
3.065
3.078
3.091
3.106
3.118
3.254
3.281
3.308
3.582
3.612
3.641
3.813
3.843
3.971
3.985
3.999
4.012
4.939
4.953
4.963
4.977
4.987
5.002
5.607
5.630
5.656
5.678
7.260
7.506
7.759
7.778
7.787
7.806
7.828
7.847
7.854
7.863
7.875
O
PPh2
O
AcO
AcO

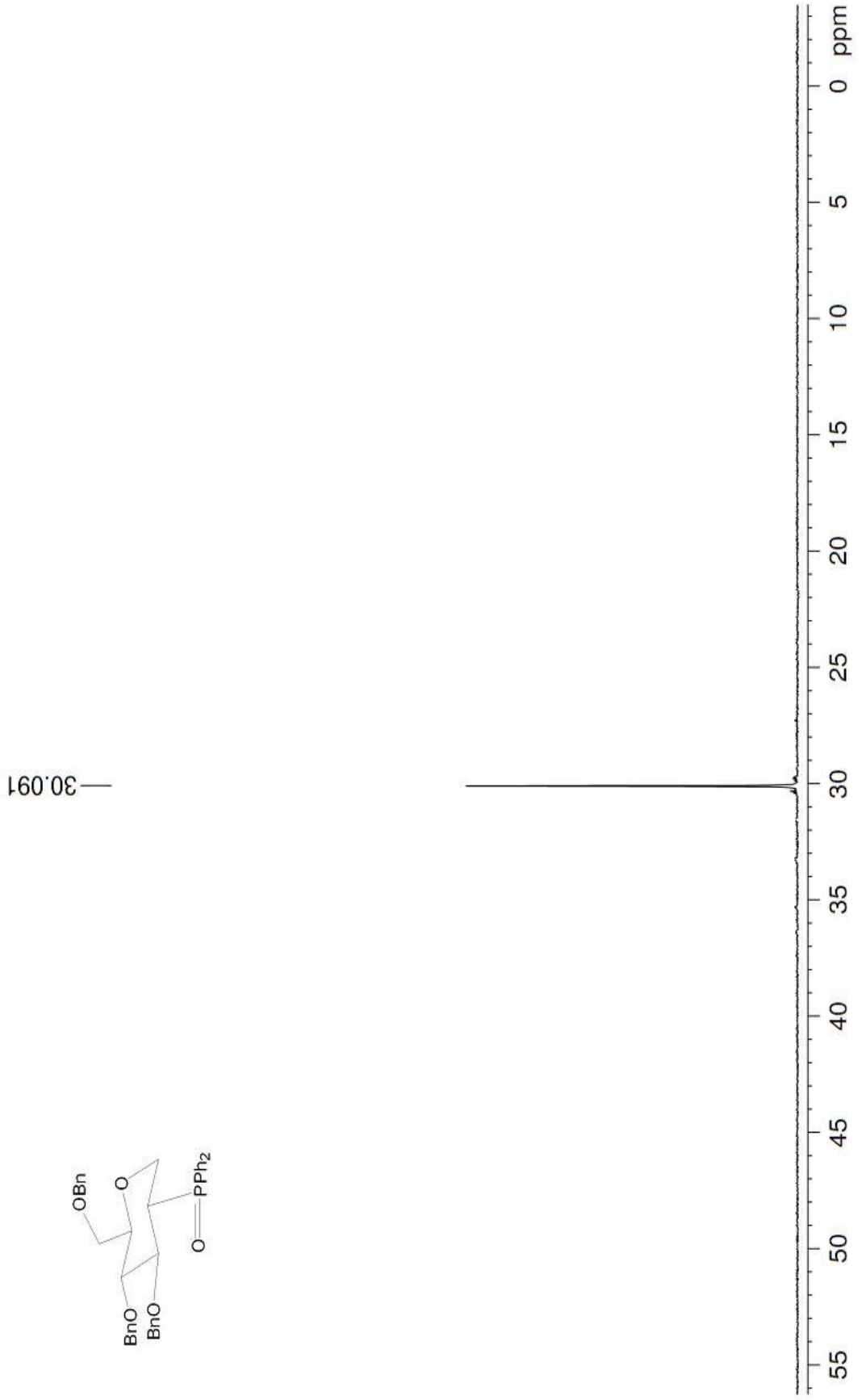

19.762
20.856
40.774
41.439
66.294
66.323
67.858
69.582
69.634
70.756
70.858
76.842
77.160
77.478
128.684
128.803
128.994
129.111
130.607
130.698
130.940
131.032
131.734
131.875
131.902
132.209
132.235
132.723
169.199
170.402
AcO
AcO
O
O
PPh2
ppm
0
20
40
60
80
100
120
140
160
180

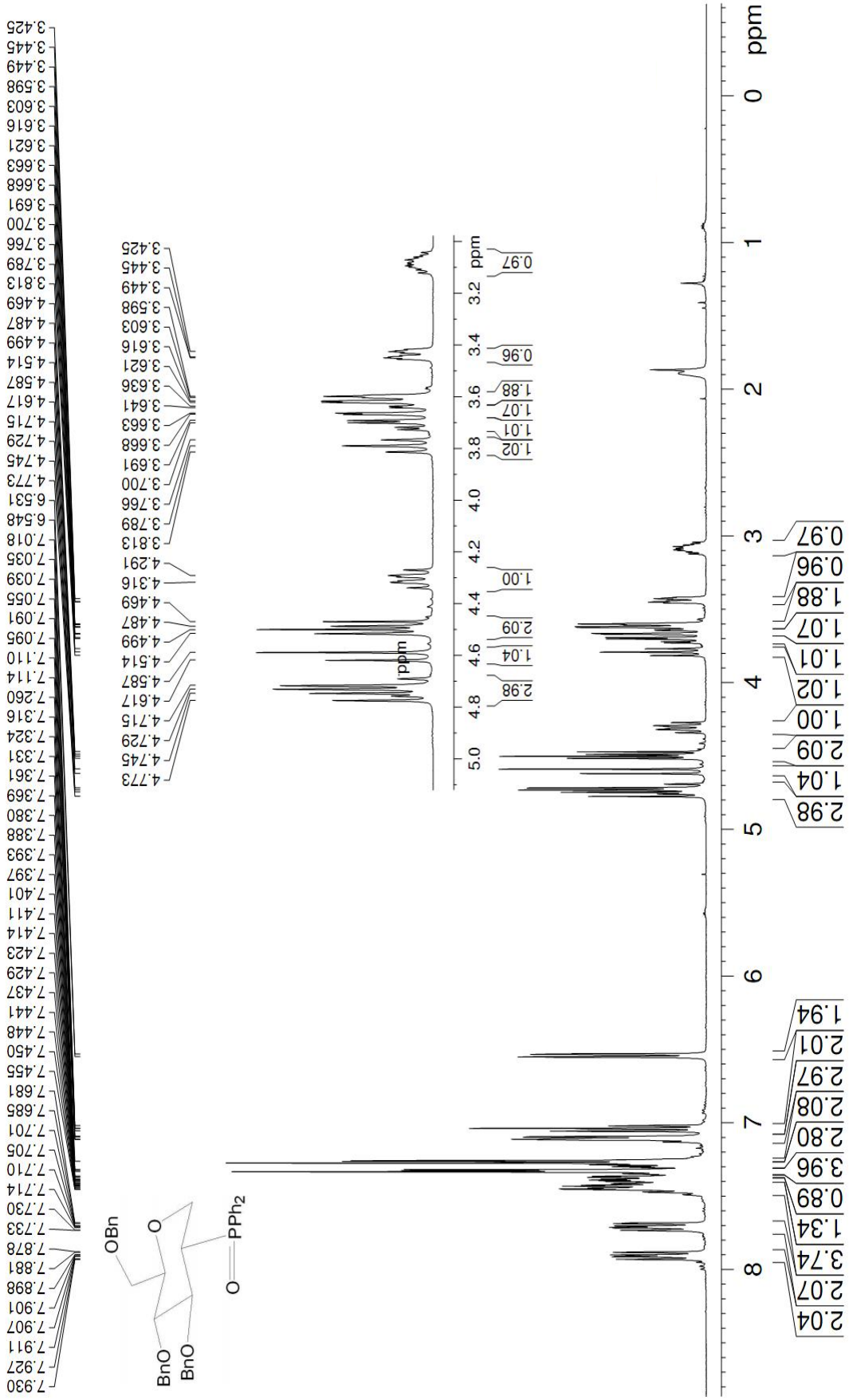

19.762
20.861
40.768
41.432
66.290
66.320
67.856
69.575
69.626
70.751
70.853
128.685
128.804
128.997
129.114
130.604
130.695
130.938
131.030
131.879
131.906
132.214
132.237
AcO
AcO
O
O
PPh2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm

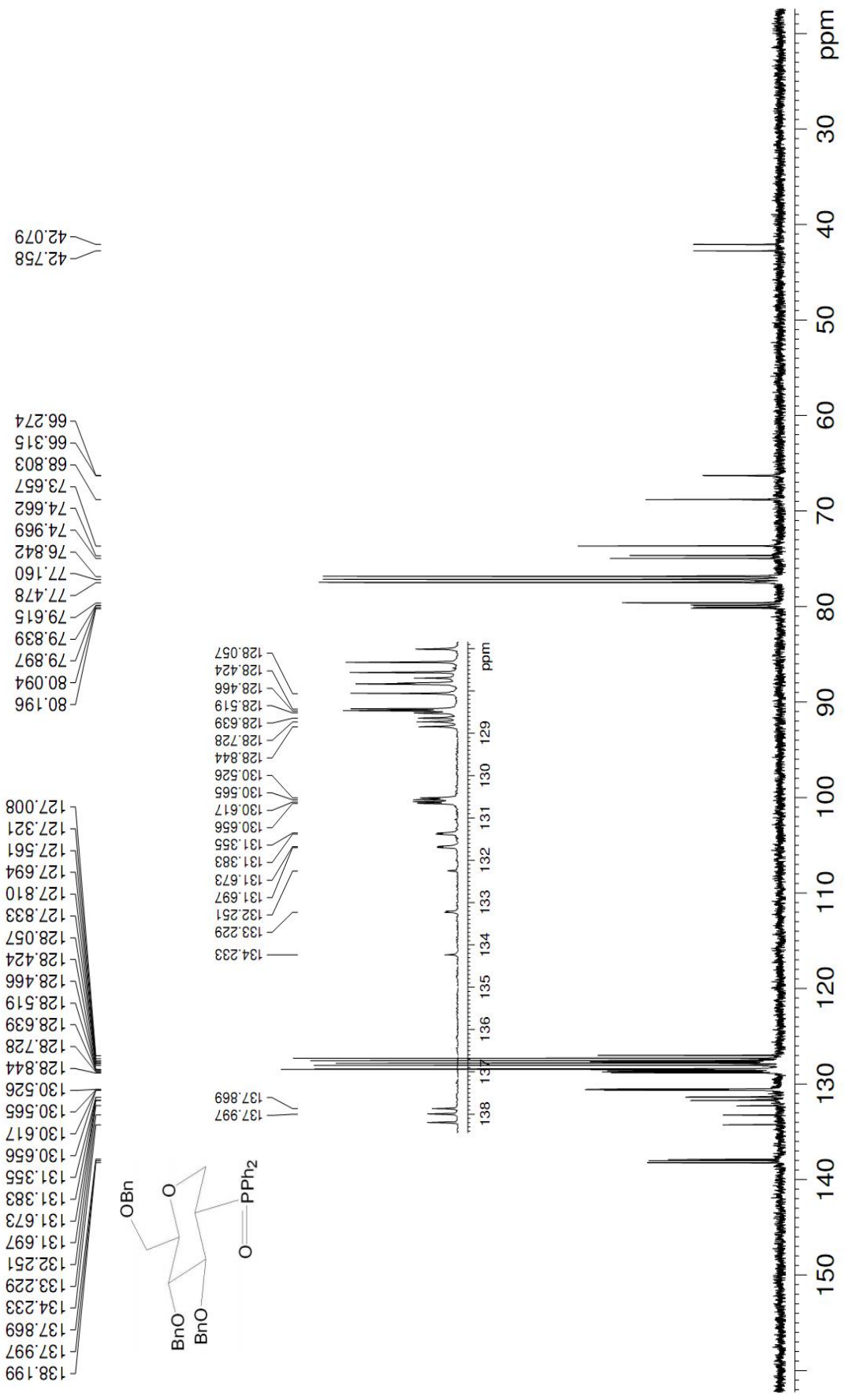

ppm
AcO
AcO
O
O
PPh2
1
2
3
4
5
6
7
8
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

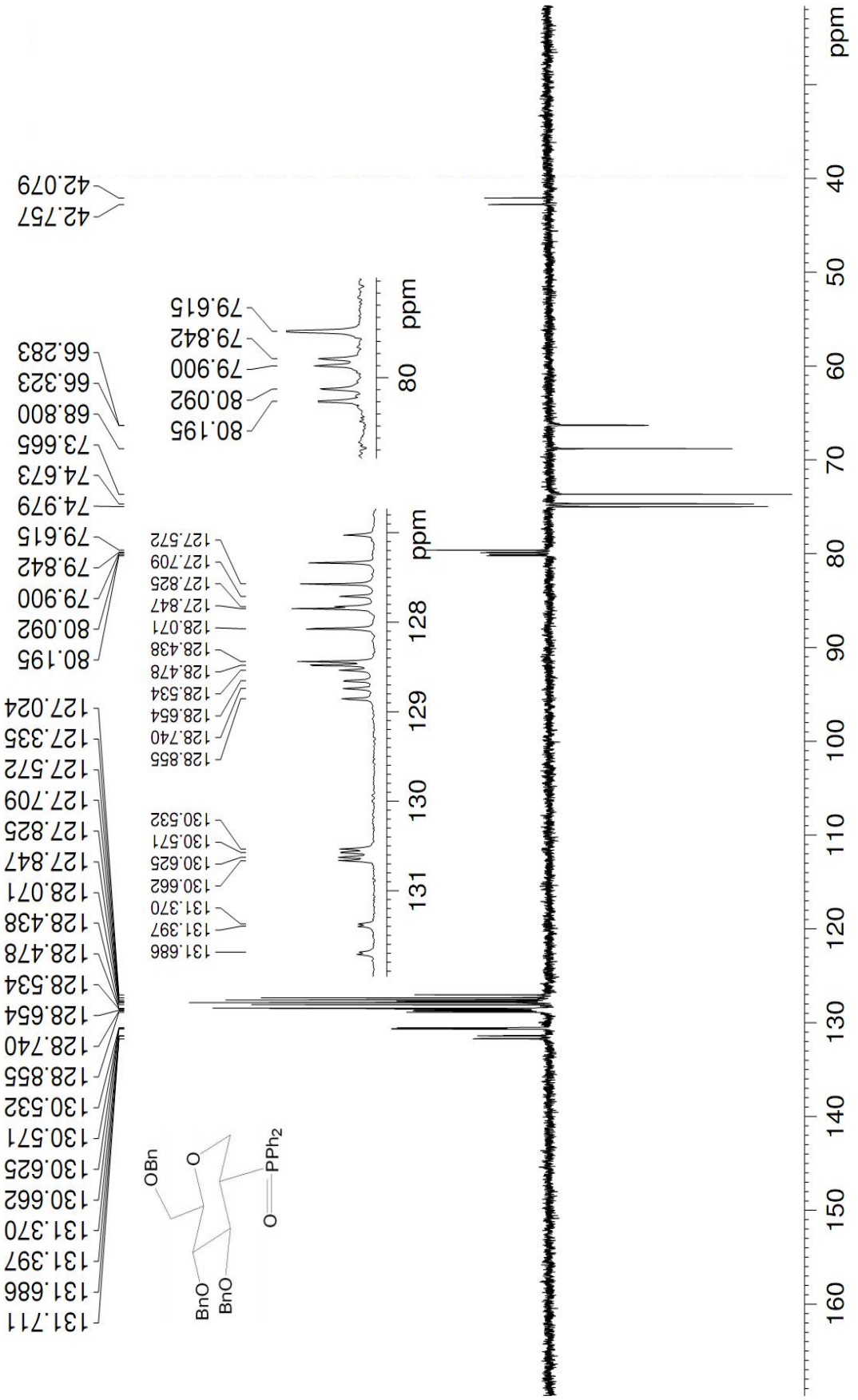

ppm
AcO
AcO
O
O
PPh2
20
30
40
50
60
70
80
90
100
110
120
130
140
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

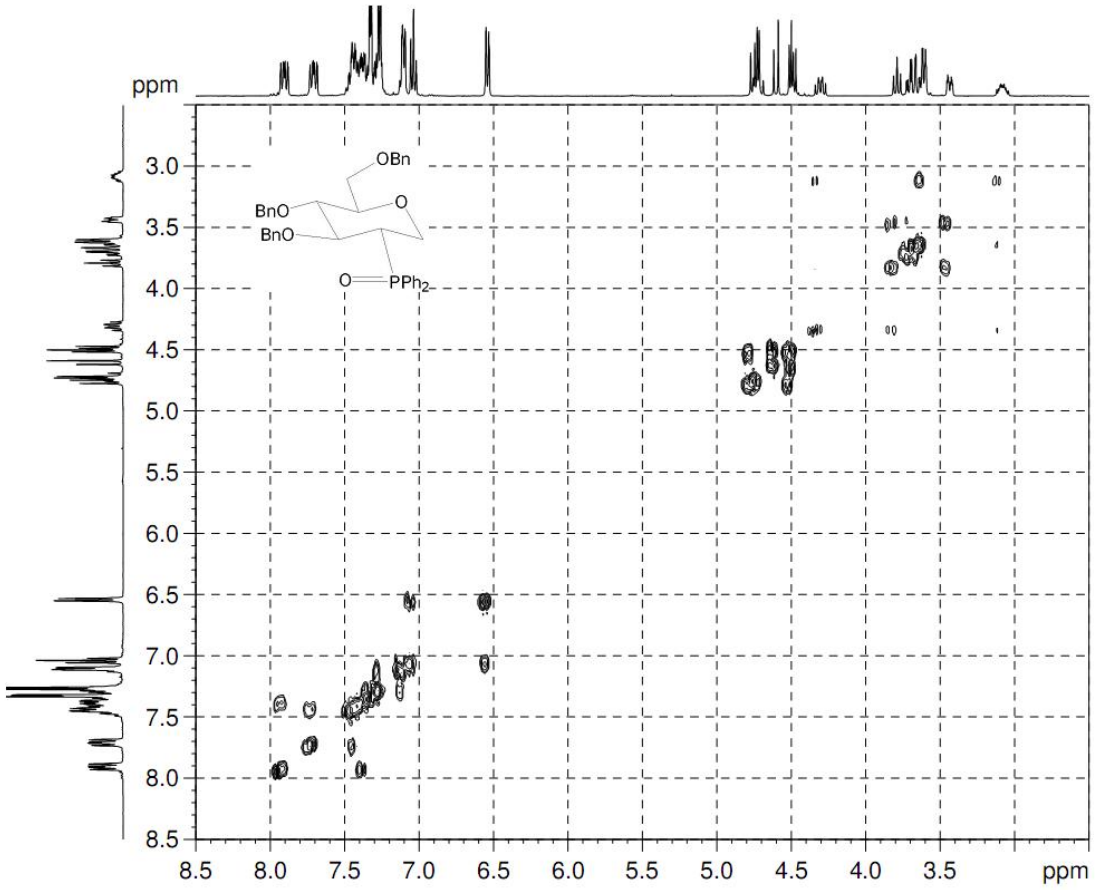
^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{1}H-^{1}H COSY, HSQC of **6**

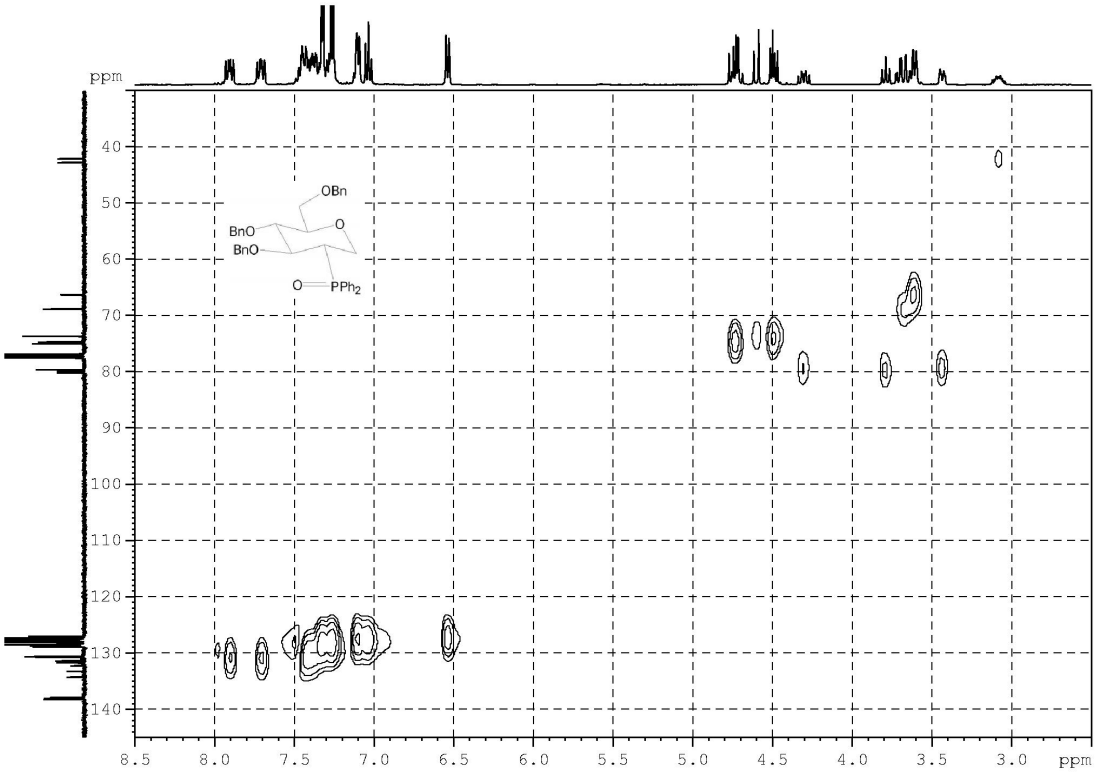



OBn
O
PPh2
O
BnO
BnO
ppm

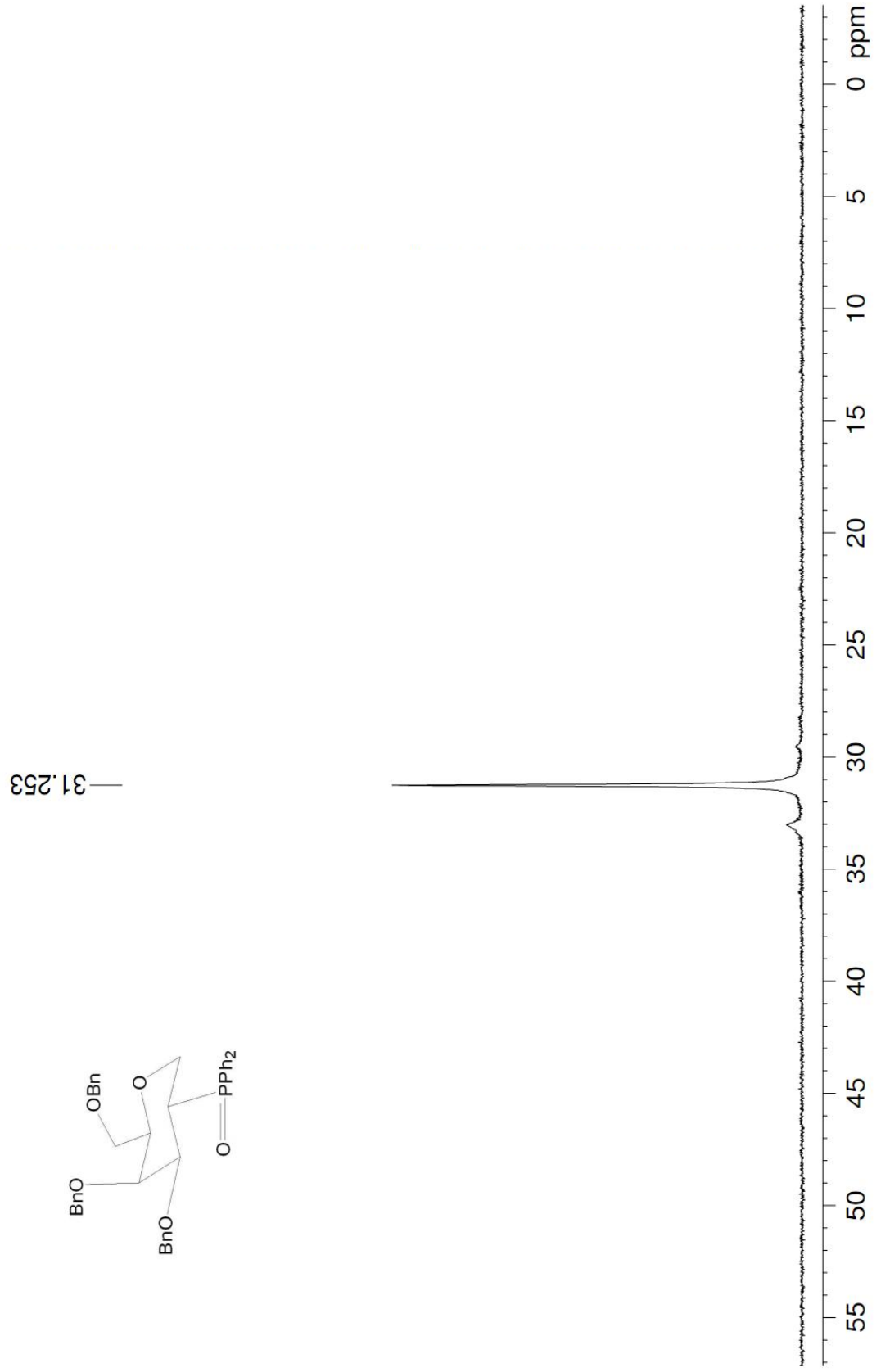

42.758
42.079
66.274
66.315
68.803
73.657
74.662
74.969
76.842
77.160
77.478
79.615
79.839
79.897
80.094
80.196
127.008
127.321
127.561
127.694
127.810
127.833
128.057
128.424
128.466
128.519
128.639
128.728
128.844
130.526
130.565
130.617
130.656
131.355
131.383
131.673
131.697
132.251
133.229
134.233
137.869
137.997
138.199
128.057
128.424
128.466
128.519
128.639
128.728
128.844
130.526
130.565
130.617
130.656
131.355
131.383
131.673
131.697
132.251
133.229
134.233
137.869
137.997
OBn
O
PPh2
O
BnO
BnO
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm
129
130
131
132
133
134
135
136
137
138

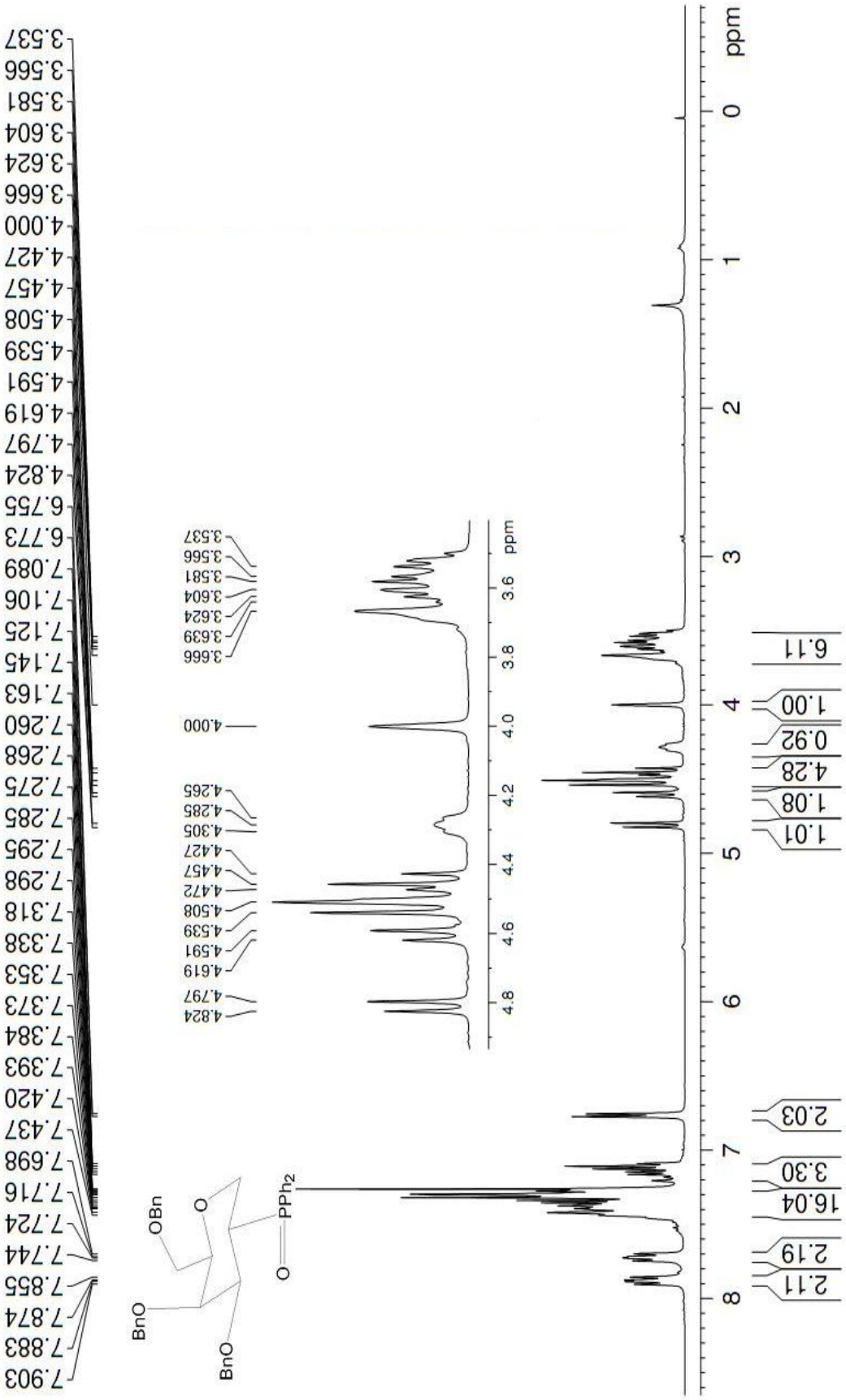

42.757
42.079
66.283
66.323
68.800
73.665
74.673
74.979
79.615
79.842
79.900
80.092
80.195
127.024
127.335
127.572
127.709
127.825
127.847
128.071
128.438
128.478
128.534
128.654
128.740
128.855
130.532
130.571
130.625
130.662
131.370
131.397
131.686
131.711
OBn
O
PPh2
O
BnO
BnO
ppm

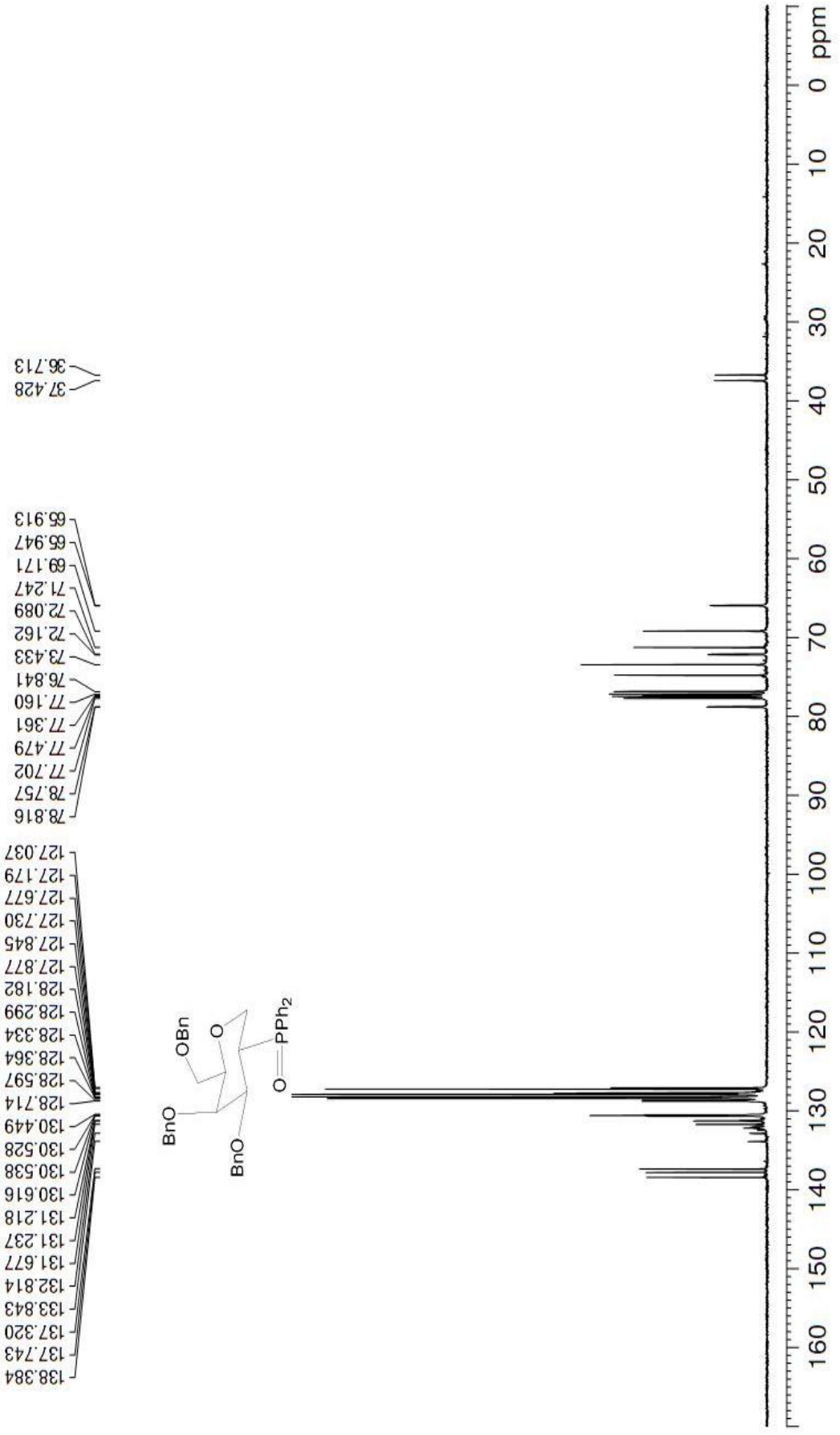

ppm
OBn
BnO
BnO
O
O
PPh2
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
ppm

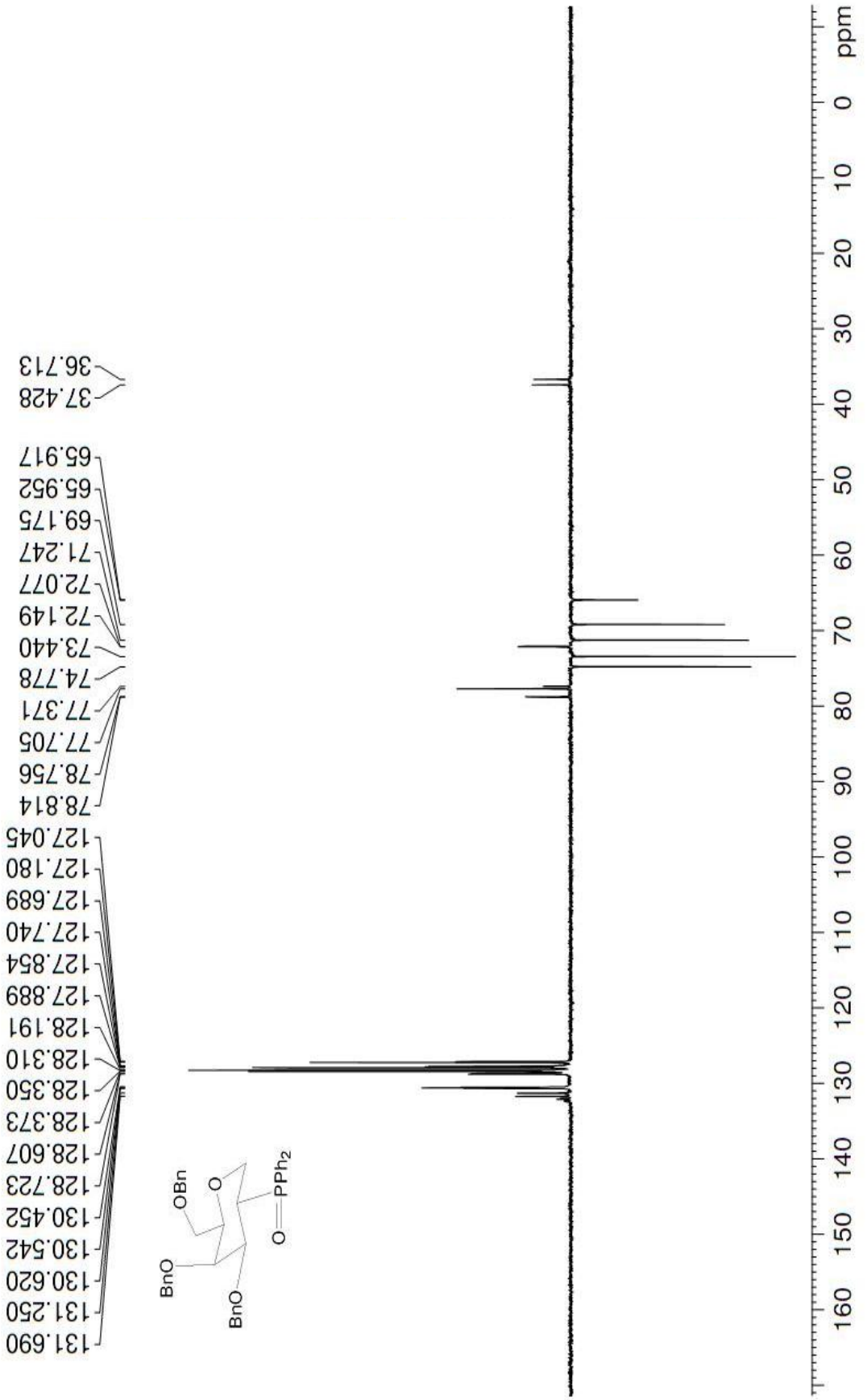

ppm
OBn
BnO
BnO
O
O
PPh2
40
50
60
70
80
90
100
110
120
130
140
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
ppm

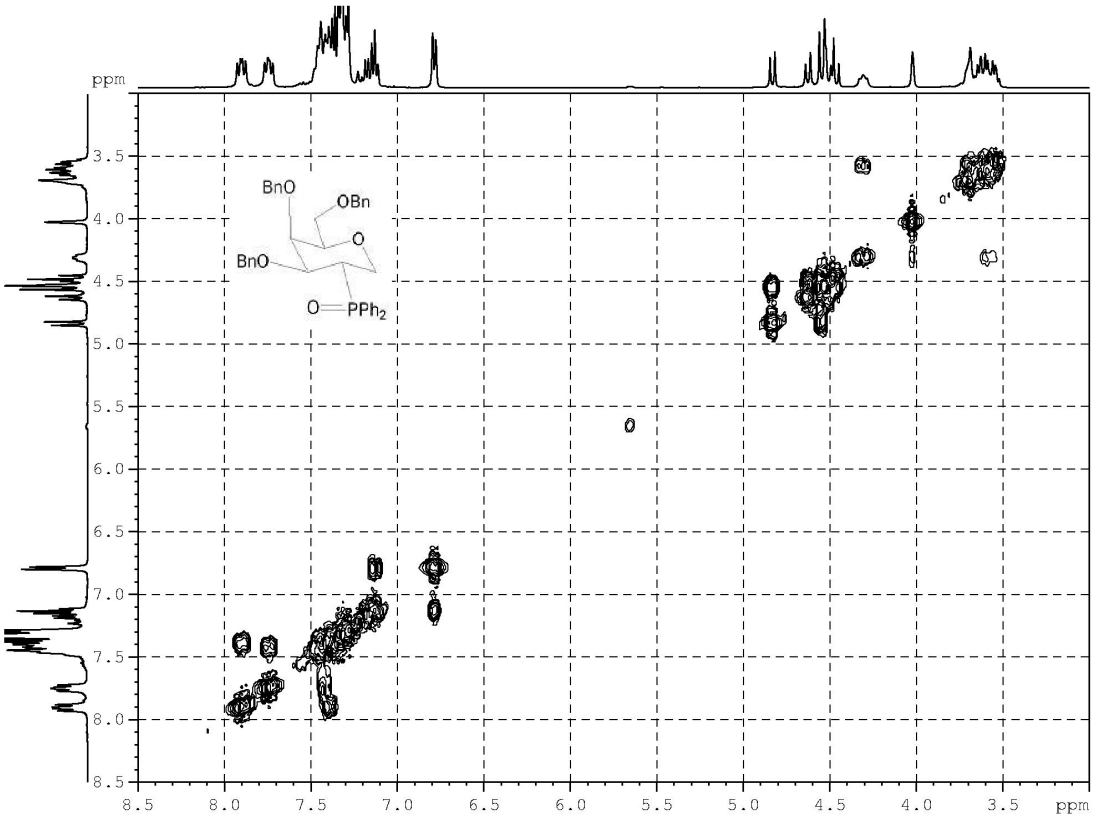
^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{1}H-^{1}H COSY, HSQC of **7**

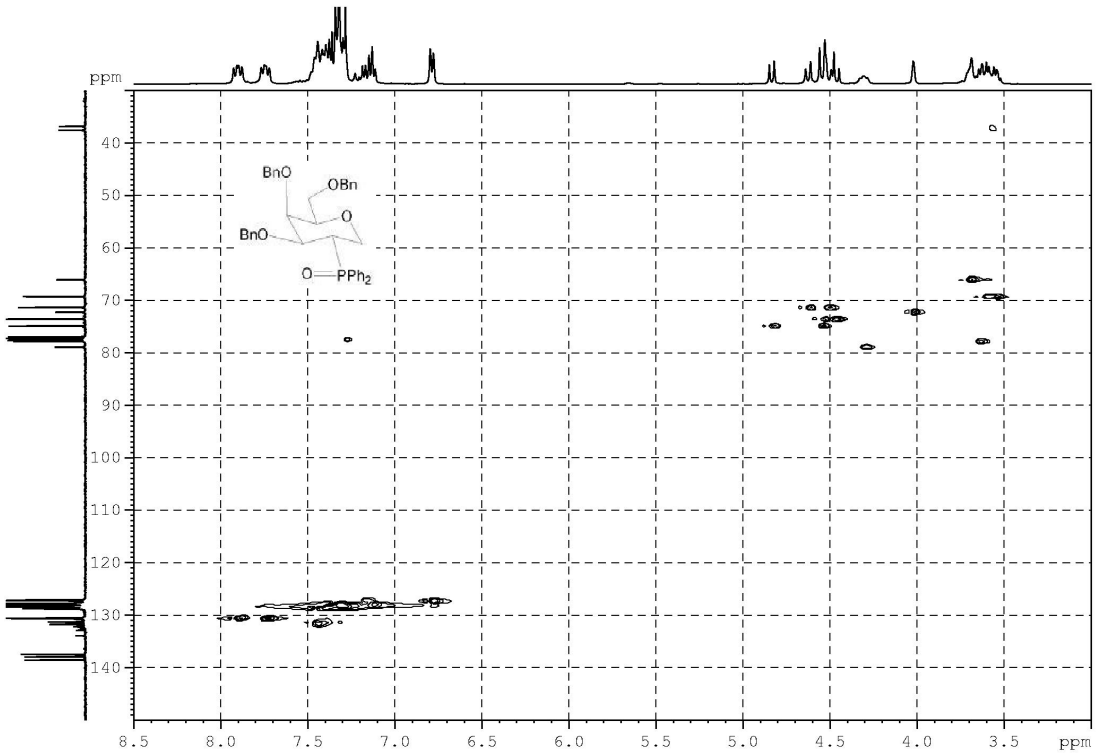



ppm
6.11
1.00
0.92
4.28
1.08
1.01
2.03
3.30
16.04
2.19
2.11
OBn
O
PPh2
O
BnO
BnO

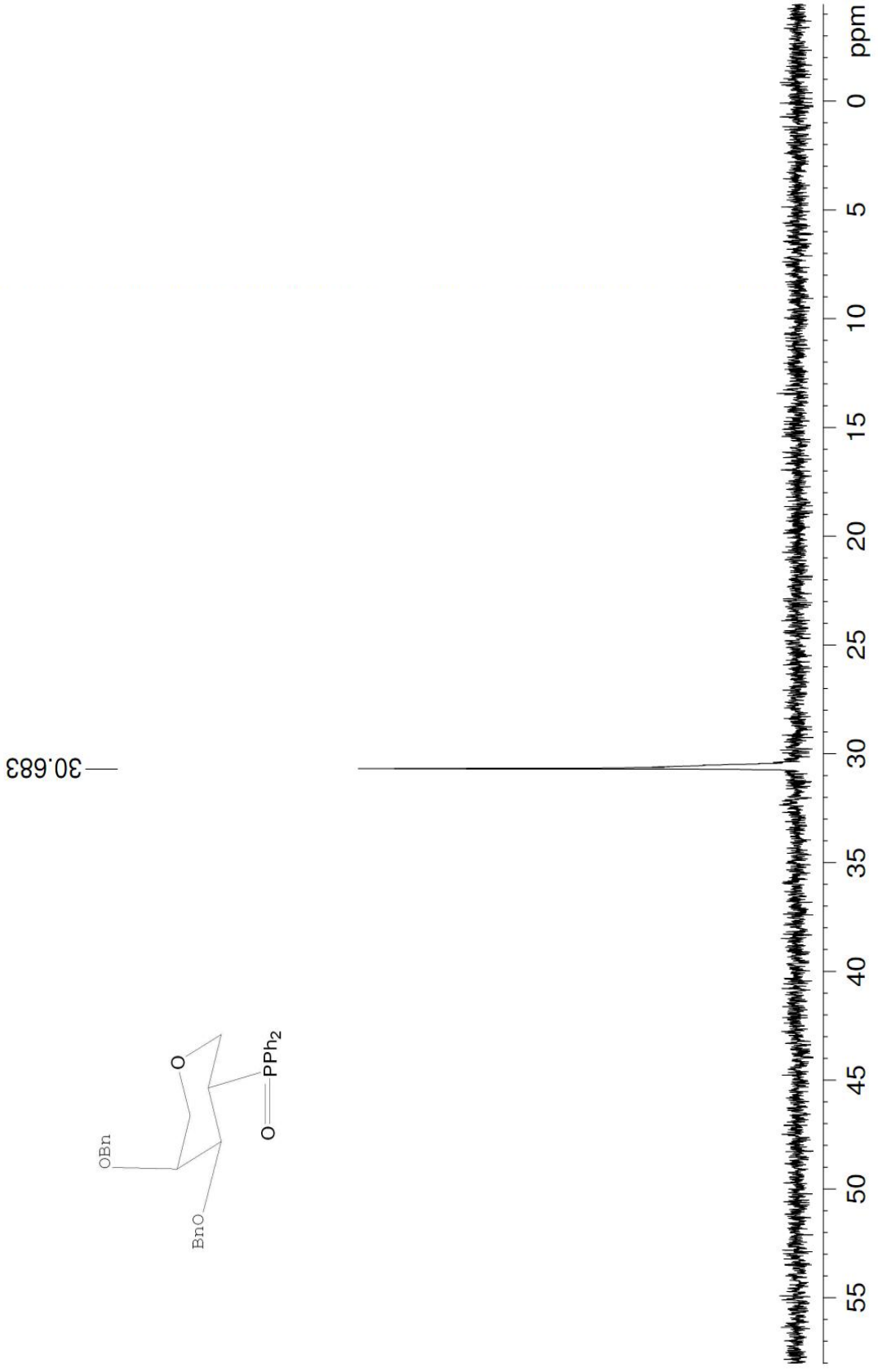

36.713
37.428
65.913
65.947
69.171
71.247
72.089
72.162
73.433
76.841
77.160
77.361
77.479
77.702
78.757
78.816
127.037
127.179
127.677
127.730
127.845
127.877
128.182
128.299
128.334
128.364
128.597
128.714
130.449
130.528
130.538
130.616
131.218
131.237
131.677
132.814
133.843
137.320
137.743
138.384
BnO
OBn
O
BnO
O
PPh2
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 ppm

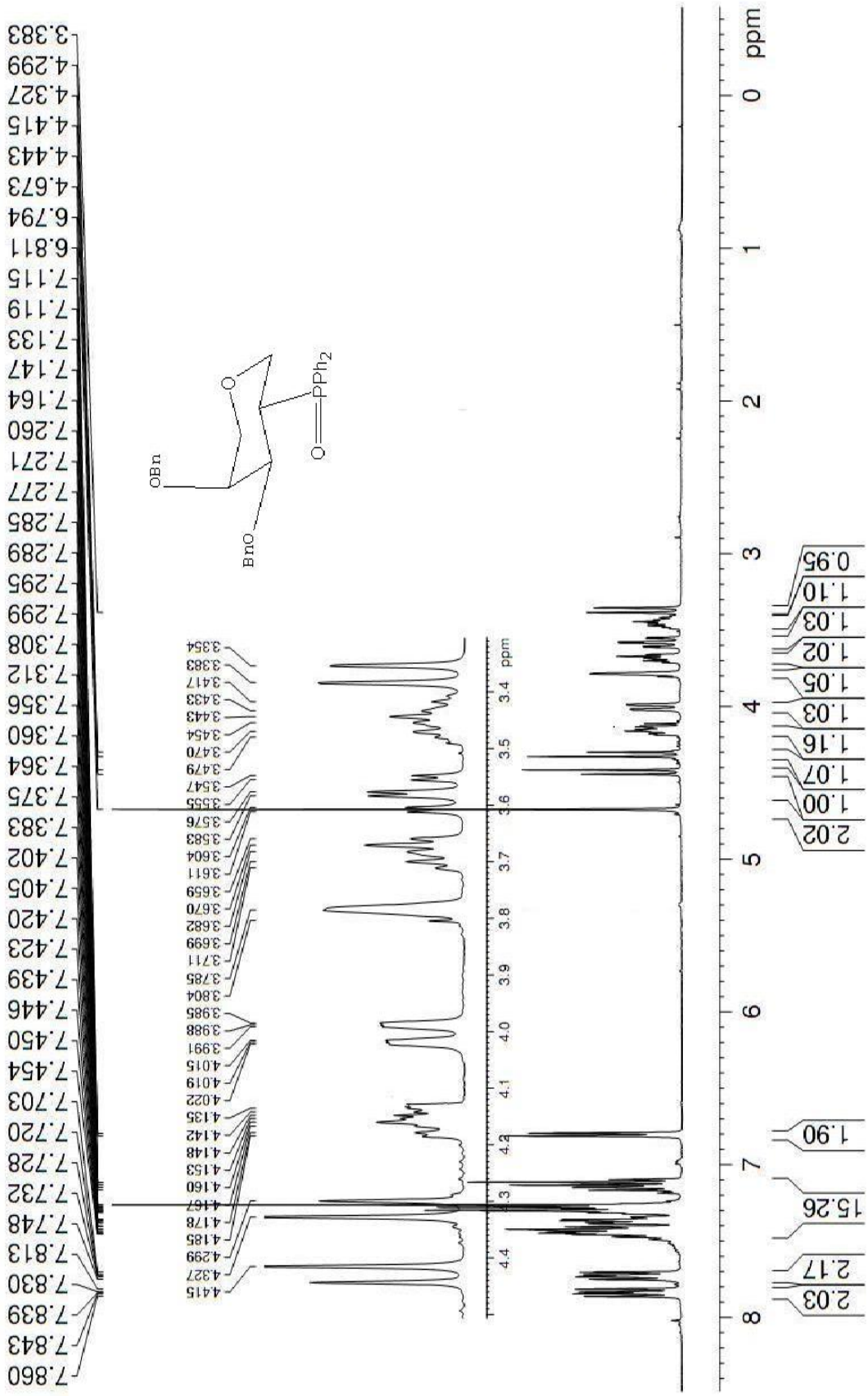

36.713
37.428
65.917
65.952
69.175
71.247
72.077
72.149
73.440
74.778
77.371
77.705
78.756
78.814
127.045
127.180
127.689
127.740
127.854
127.889
128.191
128.310
128.350
128.373
128.607
128.723
130.452
130.542
130.620
131.250
131.690
OBn
O
PPh2
O
BnO
BnO
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

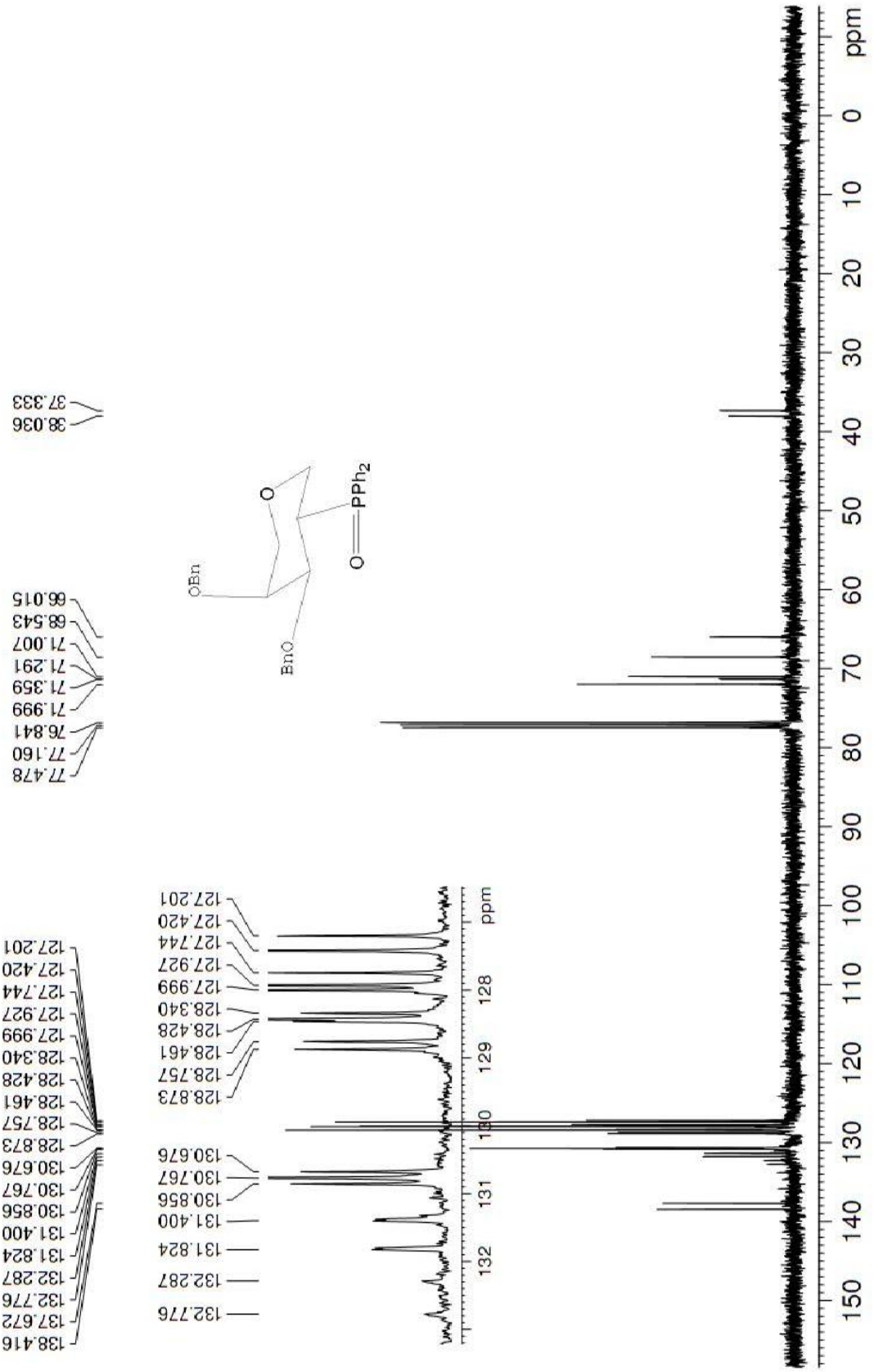

ppm
BnO
OBn
O
BnO
O
PPh2
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

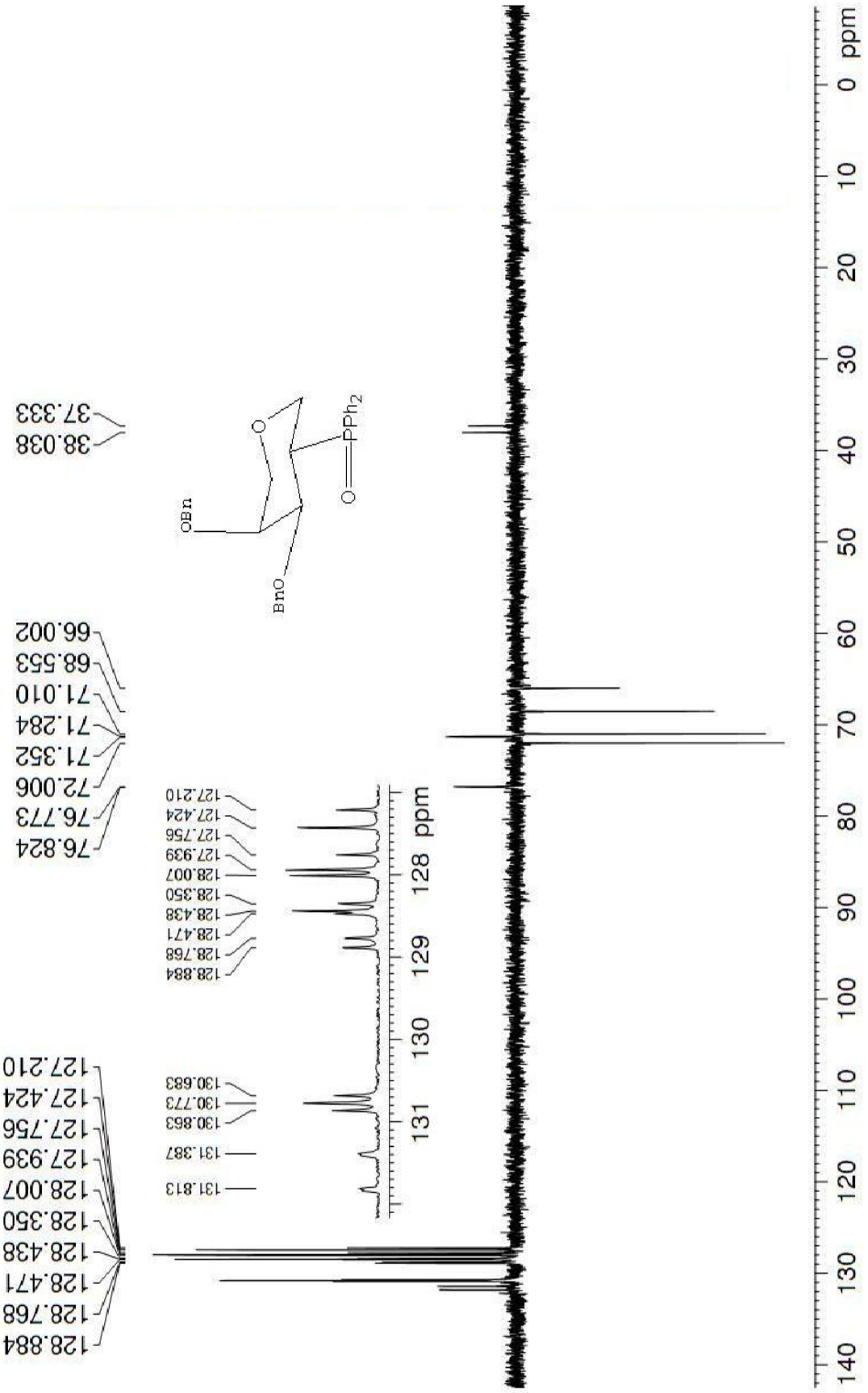

ppm
BnO
OBn
O
BnO
O
PPh2
40
50
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

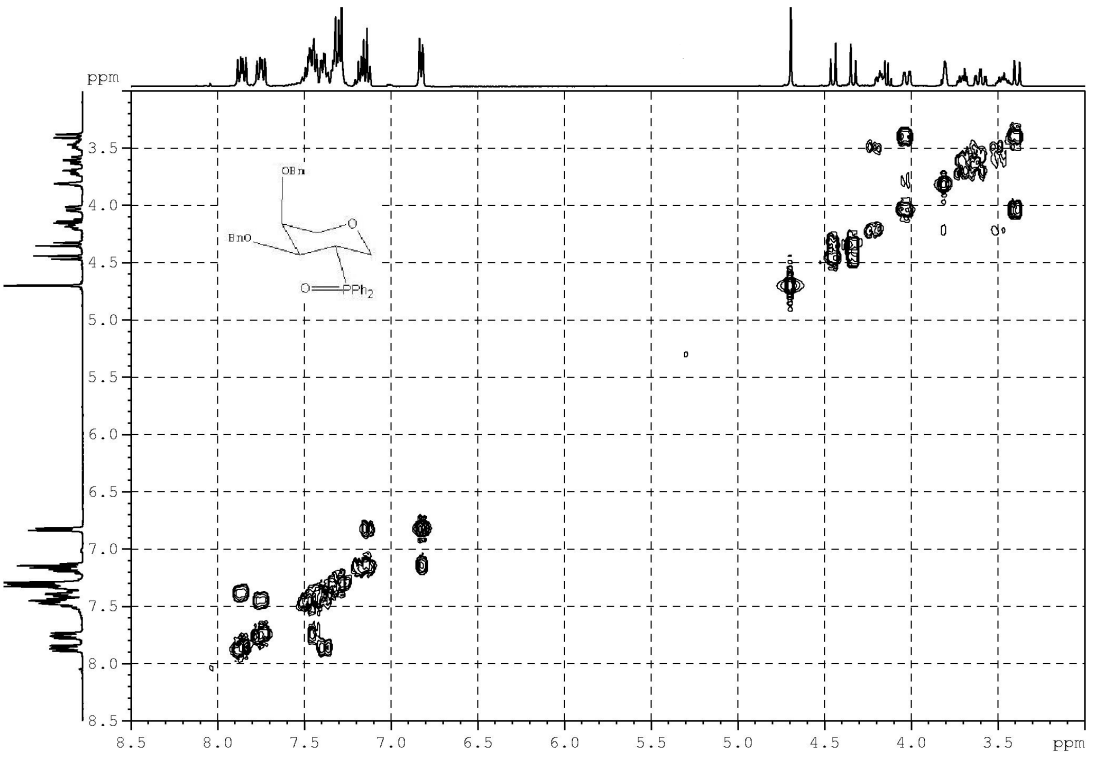
^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{1}H-^{1}H COSY, HSQC of **8**

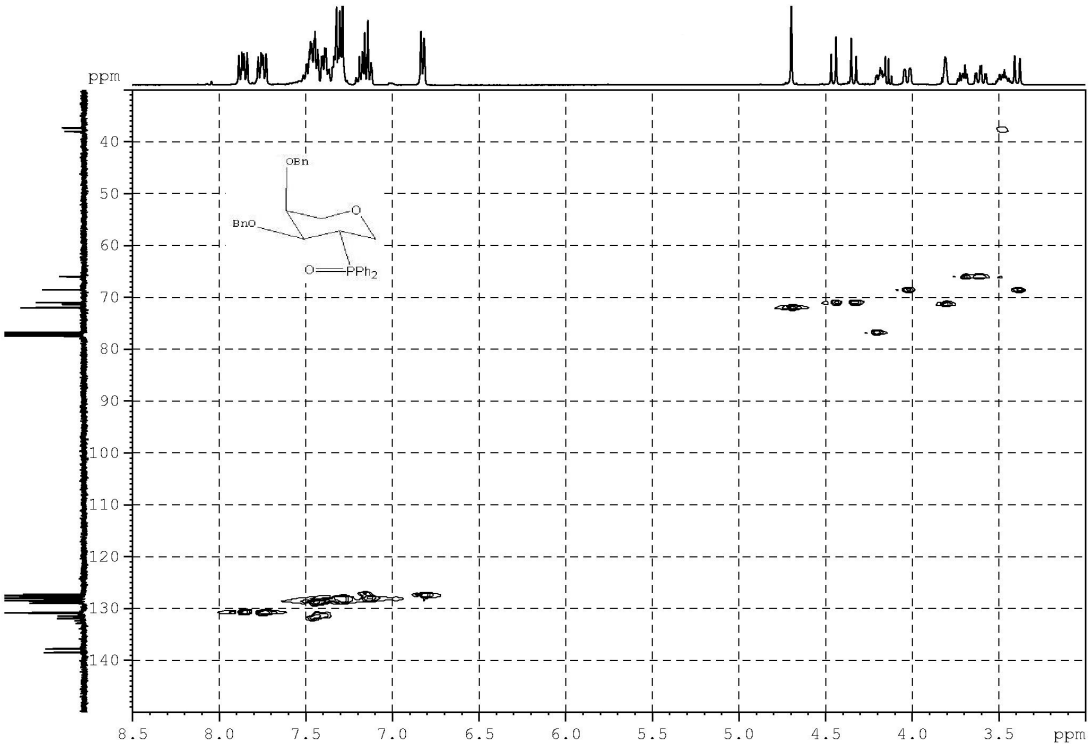



OBn
BnO
O
O=PPh2
ppm

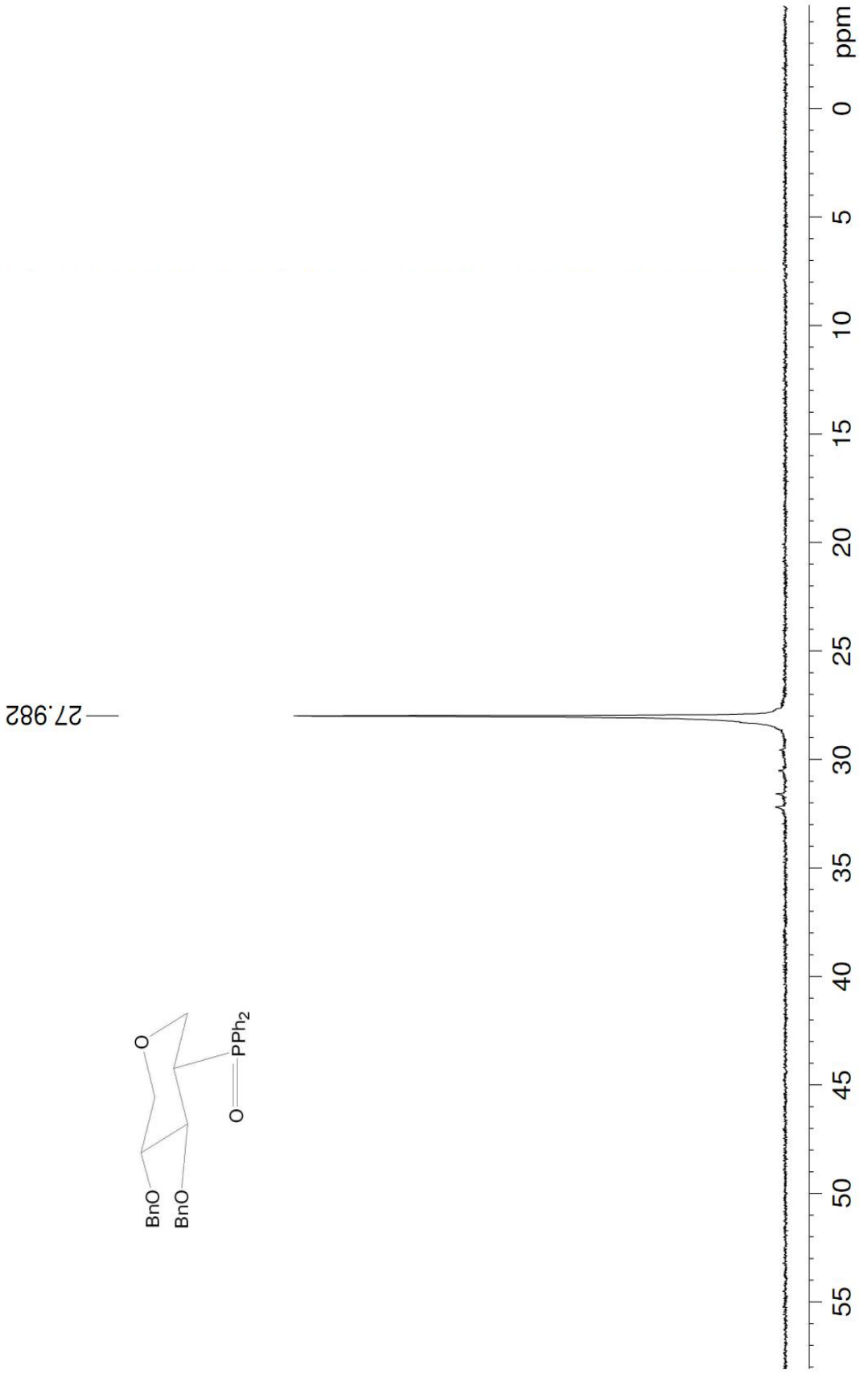

ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
132
131
130
129
128
ppm
OBn
BnO
O
O
PPh2
37.333
38.036
66.015
68.543
71.007
71.291
71.359
71.999
76.841
77.160
77.478
127.201
127.420
127.744
127.927
127.999
128.340
128.428
128.461
128.757
128.873
130.676
130.767
130.856
131.400
131.824
132.287
132.776
137.672
138.416

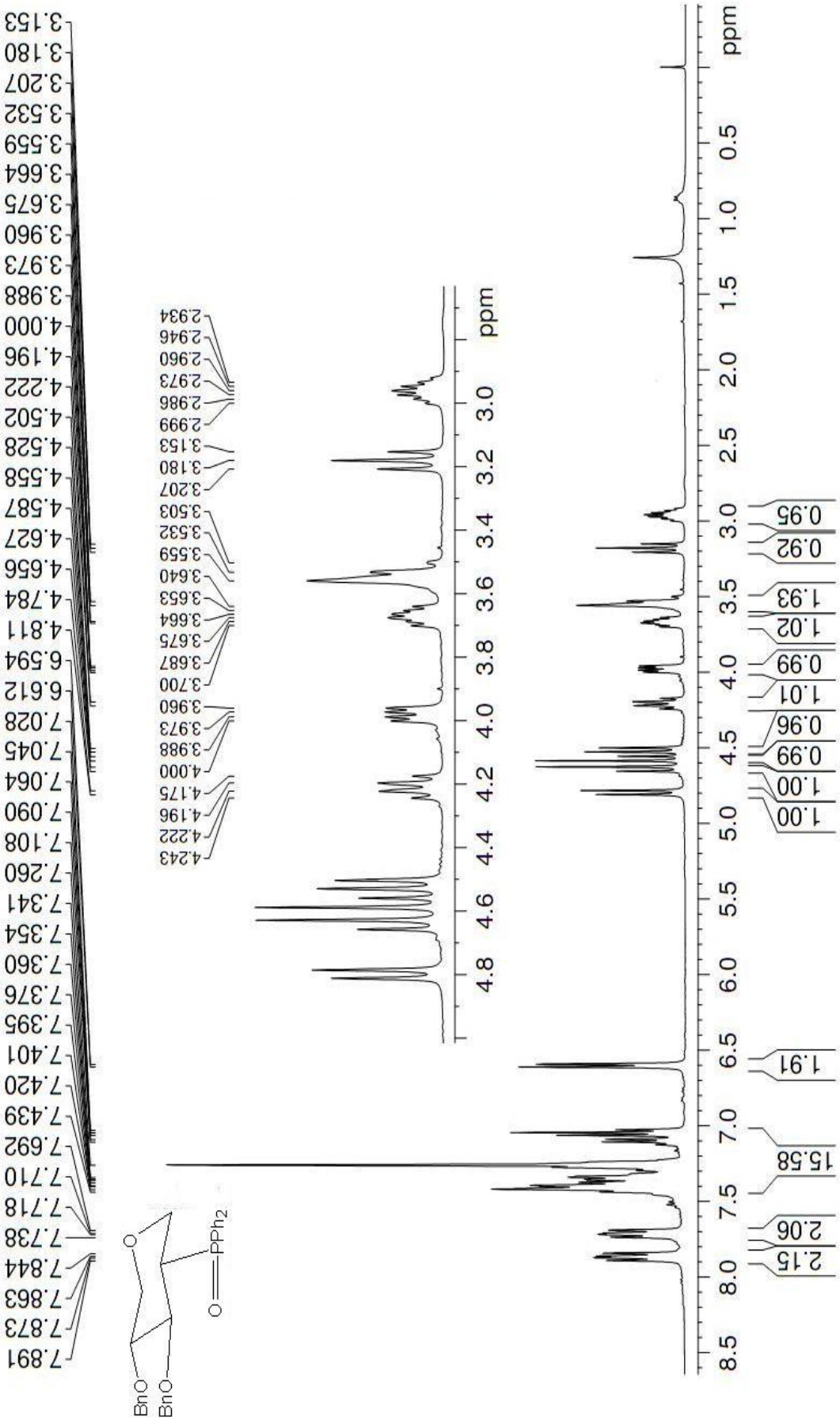

37.333
38.038
66.002
68.553
71.010
71.284
71.352
72.006
76.773
76.824
127.210
127.424
127.756
127.939
128.007
128.350
128.438
128.471
128.768
128.884
130.683
130.773
130.863
131.387
131.813
OBn
BnO
O
O=PPh2
ppm
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140
ppm
128 129 130 131

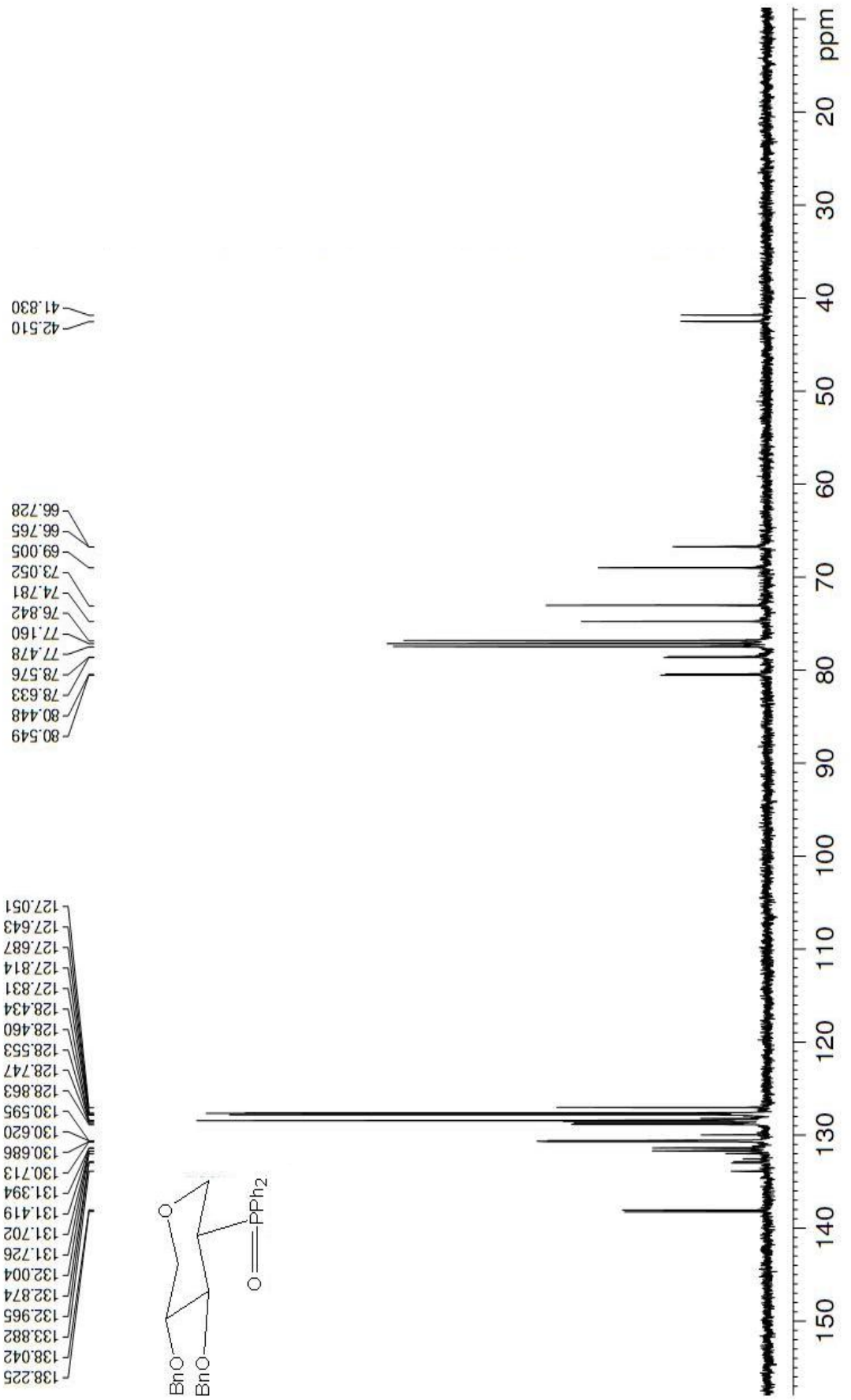

ppm
OBn
BnO
O
O=PPh2
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm

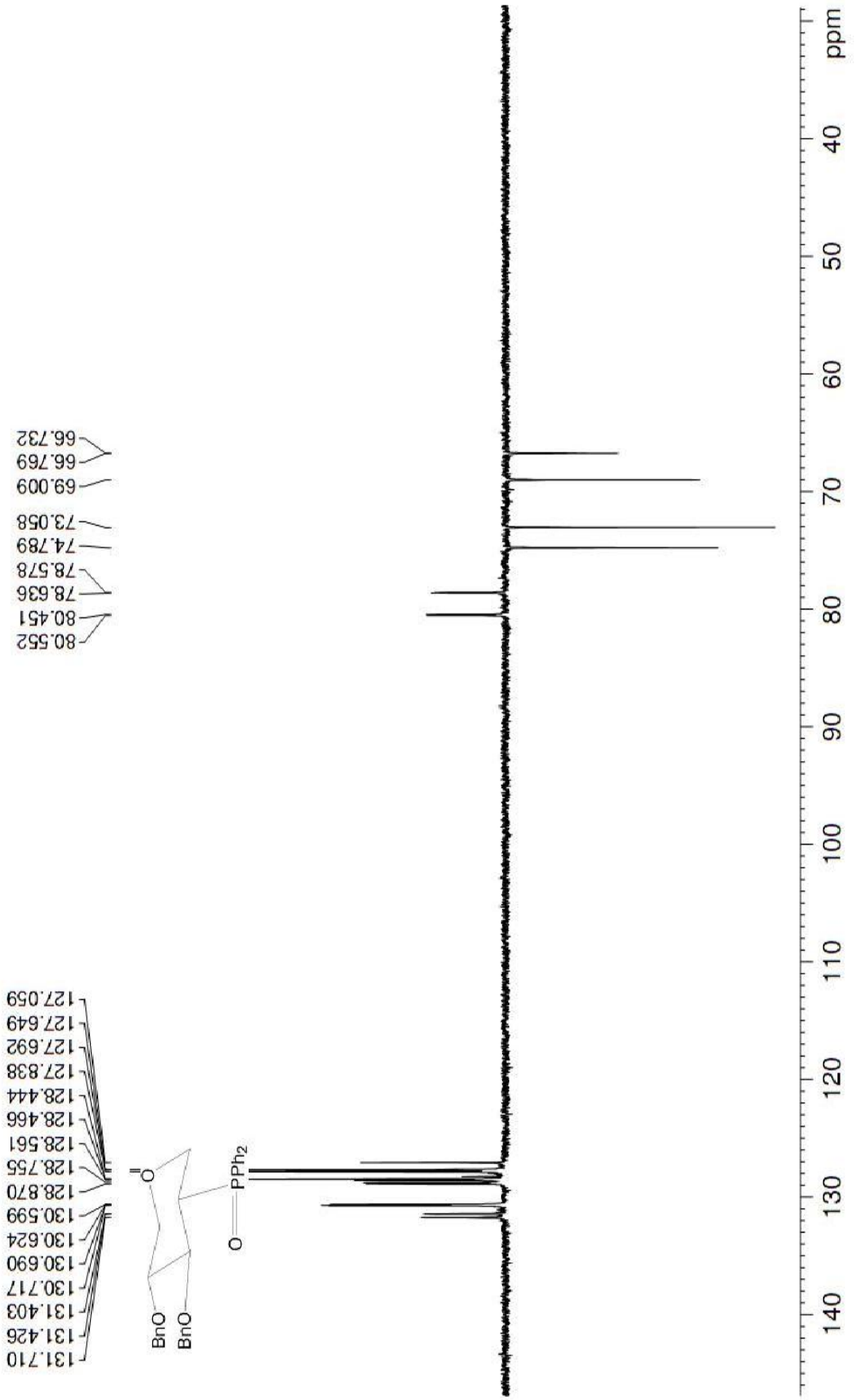

ppm
OBn
BnO
O
O=PPh2
40
50
60
70
80
90
100
110
120
130
140
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm

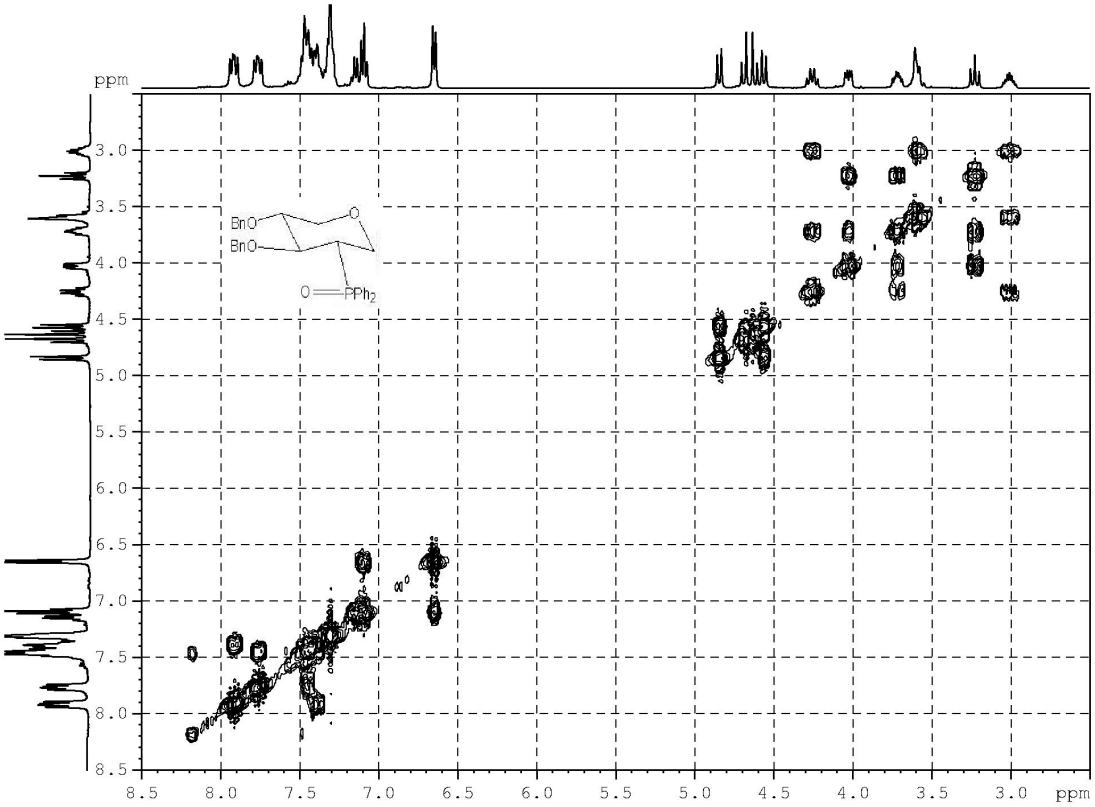
^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{1}H-^{1}H COSY, HSQC of **9**

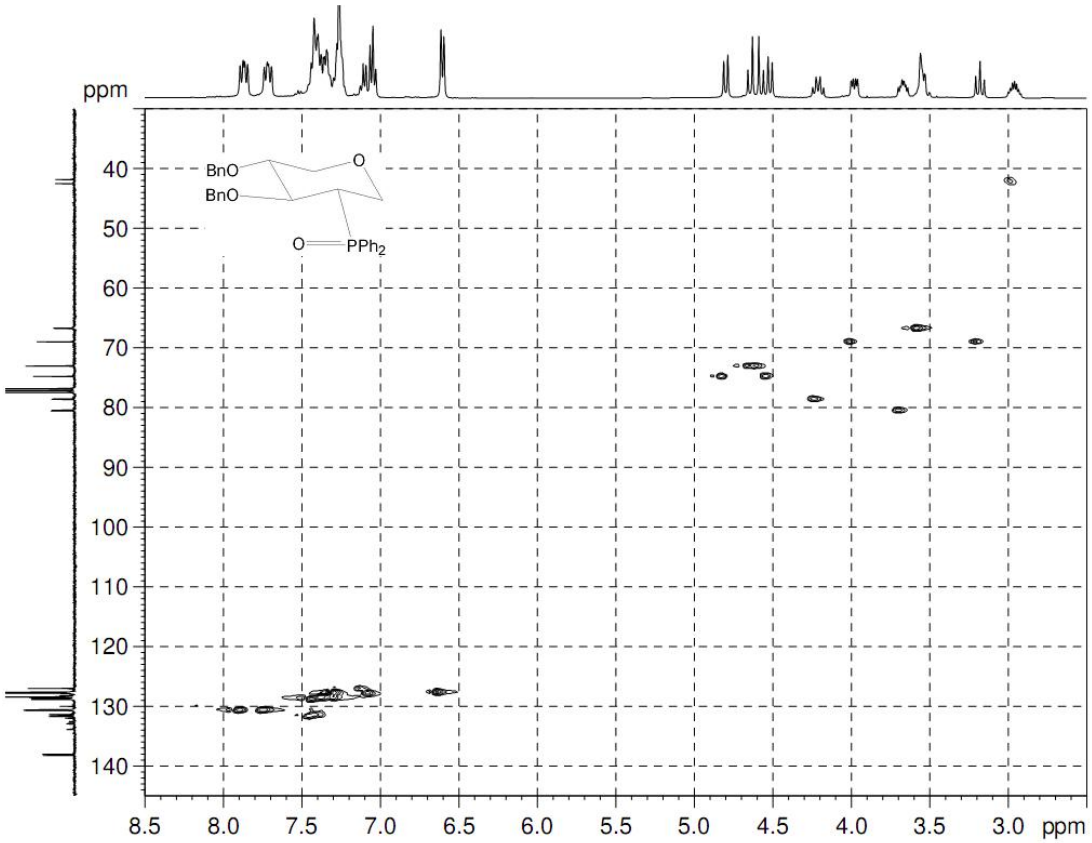



ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.91
15.58
2.06
2.15
1.00
1.00
0.99
0.96
1.01
0.99
1.02
1.93
0.92
0.95
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
ppm
BnO
BnO
O
O=PPh2


ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
138.225
138.042
133.882
132.965
132.874
132.004
131.726
131.702
131.419
131.394
130.713
130.686
130.620
130.595
128.863
128.747
128.553
128.460
128.434
127.831
127.814
127.687
127.643
127.051
80.549
80.448
78.633
78.576
77.478
77.160
76.842
74.781
73.052
69.005
66.765
66.728
42.510
41.830
BnO
BnO
O
O
PPh2


66.732
66.769
69.009
73.058
74.789
78.578
78.636
80.451
80.552
127.059
127.649
127.692
127.838
128.444
128.466
128.561
128.755
128.870
130.599
130.624
130.690
130.717
131.403
131.426
131.710
BnO
BnO
O
O
PPh2
ppm
40
50
60
70
80
90
100
110
120
130
140


ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
BnO
BnO
O
O=PPh2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm


ppm
40
50
60
70
80
90
100
110
120
130
140
BnO
BnO
O
O=PPh2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm