Supporting Information

Copper-Catalyzed Addition of H-Phosphine Oxides to Alkynes Forming Alkenylphosphine Oxides

Mingyu Niu,[a] Hua Fu,*[a] Yuyang Jiang,[a,b] Yufen Zhao[a]

[a]*Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology, Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China*

[b]*Key Laboratory of Chemical Biology, Guangdong Province, Graduate School of Shenzhen, Tsinghua University, Shenzhen 518057, P. R. China*

E-mail: fuhua@mail.tsinghua.edu.cn; Fax: 86-10-62781695

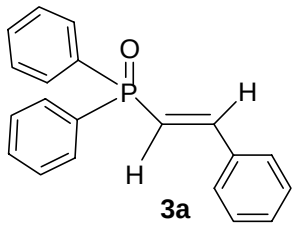
Table of contents

General Experimental Section

All reactions were performed under nitrogen atmosphere. Unless otherwise noted, all reagents were purchased from commercial sources and were used without further purification. Dibenzylphosphine oxide was prepared according to a reported procedure.[1] Solvents were dried and purified before use by standard procedure. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with tetramethylsilane or solvent resonance as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm). 85% H_3PO_4 was used as the external reference of ^{31}P NMR spectra.

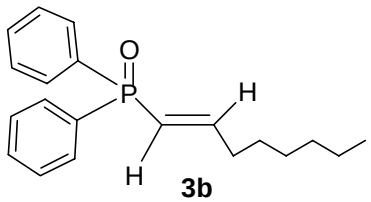
General procedure for copper-catalyzed additions of P(O)H compounds to alkynes. Organophosphorus reagent containing P-H bond (0.5 mmol), alkyne (0.75 mmol), CuI (0.05 mmol) and ligand (0.075 mmol) were dissolved in 1.0 mL of solvent under nitrogen. The reaction was performed in the corresponding reaction time and temperature as shown in Tables 1 and 2. The resulting solution was cooled to room temperature, and then 10 mL of chloroform and 10 mL of brine were added to the solution, the organic layer was washed with brine (10 mL × 2) and was dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo to give a pale yellow semisolid. The crude product was then purified by silica gel column chromatography using EtOAc/ hexane (1:1) (sometimes, a small amount of ethanol was used to adjust polarity of the solvent) as the eluent to provide the pure target product as a white solid or colorless oil.

Characterization data for compounds **3 - 5**



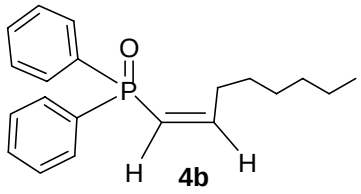
3a

(*E*)-1-Diphenylphosphinyl-2-phenylethene (3a).[2] White solid, mp 169-170 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.79 (m, 16H), 6.84 (dd, J_{P-H} = 22.3 Hz, J_{H-H} = 17.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 135.0 (d, J_{P-C} = 17.9 Hz), 132.9 (d, J_{P-C} = 104.7 Hz), 131.8, 131.3 (d, J_{P-C} = 10.0 Hz), 130.1, 128.7 (d, J_{P-C} = 11.5 Hz), 128.5, 127.7, 119.1 (d, J_{P-C} = 103.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.2. HRMS m/z calcd. for $C_{20}H_{18}OP$ $[M+H]^+$: 305.1095, found: 305.1089.



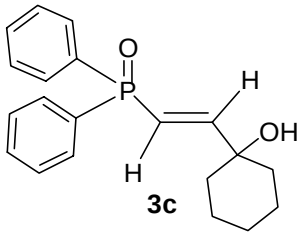
3b

(*E*)-1-Diphenylphosphinyl-1-octene (3b).[2] White solid, mp 69-70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.73 (m, 10H), 6.65-6.82 (m, 1H), 6.22 (dd, J_{P-H} = 24.4 Hz, J_{H-H} = 16.8 Hz, 1H), 2.26-2.33 (m, 2H), 1.43-1.52 (m, 2H), 1.21-1.37 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 133.2 (d, J_{P-C} = 103.9 Hz), 131.6, 131.3 (d, J_{P-C} = 10.0 Hz), 128.4 (d, J_{P-C} = 12.2 Hz), 121.5 (d, J_{P-C} = 102.5 Hz), 34.5 (d, J_{P-C} = 17.2 Hz), 31.5, 28.8, 27.8, 22.5, 14.0. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.2. HRMS m/z calcd. for $C_{20}H_{26}OP$ $[M+H]^+$: 313.1721, found: 313.1725.



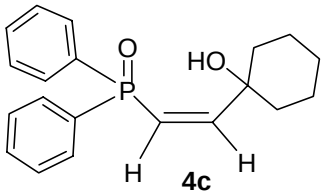
4b

(*Z*)-1-Diphenylphosphinyl-1-octene (4b).[3] White solid, mp 66-67 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.78 (m, 10H), 6.57-6.80 (m, 1H), 6.11 (dd, $J_{P\text{-}H}$ = 25.4 Hz, $J_{H\text{-}H}$ = 12.7 Hz, 1H), 2.49-2.56 (m, 2H), 1.17-1.36 (m, 8H), 0.83 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 134.6 (d, $J_{P\text{-}C}$ = 102.5 Hz), 131.4, 130.9 (d, $J_{P\text{-}C}$ = 10.0 Hz), 128.5 (d, $J_{P\text{-}C}$ = 11.5 Hz), 121.2 (d, $J_{P\text{-}C}$ = 99.7 Hz), 31.5, 30.9 (d, $J_{P\text{-}C}$ = 7.9 Hz), 28.8, 22.5, 13.9. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.6. HRMS m/z calcd. for $C_{20}H_{26}OP$ $[M+H]^+$: 313.1721, found: 313.1727.



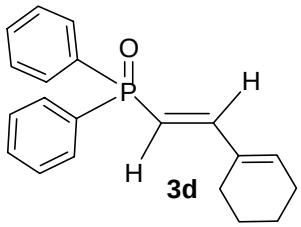
3c

(*E*)-1-(1-hydroxy)cyclohexyl -2-(diphenylphosphinyl)ethene (3c). White solid, mp 208-210 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.70 (m, 10H), 6.85 (dd, $J_{P\text{-}H}$ = 19.9 Hz, $J_{H\text{-}H}$ = 16.8 Hz, 1H), 6.57 (dd, $J_{P\text{-}H}$ = 25.1 Hz, $J_{H\text{-}H}$ = 16.8 Hz, 1H), 2.78 (br, 1H), 1.26-1.63 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 132.9 (d, $J_{P\text{-}C}$ = 103.9 Hz), 131.6, 131.2 (d, $J_{P\text{-}C}$ = 9.3 Hz), 128.5 (d, $J_{P\text{-}C}$ = 11.5 Hz), 118.1 (d, $J_{P\text{-}C}$ = 101.1 Hz), 72.7 (d, $J_{P\text{-}C}$ = 14.3 Hz), 36.9, 25.2, 21.4. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.8. HRMS m/z calcd. for $C_{20}H_{24}O_2P$ $[M+H]^+$: 327.1514, found: 327.1518.



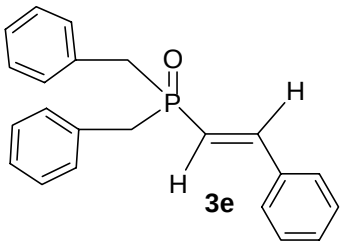
4c

(*Z*)-1-(1-hydroxy)cyclohexyl -2-(diphenylphosphinyl)ethene (4c). White solid, mp 132-134 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.75 (m, 10H), 6.87 (dd, $J_{P\text{-}H}$ = 40.5 Hz, $J_{H\text{-}H}$ = 14.1 Hz, 1H), 5.94 (dd, $J_{P\text{-}H}$ = 24.7 Hz, $J_{H\text{-}H}$ = 14.1 Hz, 1H), 1.20-1.82 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 133.0 (d, $J_{P\text{-}C}$ = 106.1 Hz), 131.8, 131.2 (d, $J_{P\text{-}C}$ = 10.0 Hz), 128.6 (d, $J_{P\text{-}C}$ = 12.2 Hz), 118.0 (d, $J_{P\text{-}C}$ = 97.5 Hz), 71.7 (d, $J_{P\text{-}C}$ = 6.5 Hz), 37.9, 25.4, 21.6. ^{31}P NMR (121 MHz, $CDCl_3$) δ 27.4. HRMS m/z calcd. for $C_{20}H_{24}O_2P$ $[M+H]^+$: 327.1514, found: 327.1517.



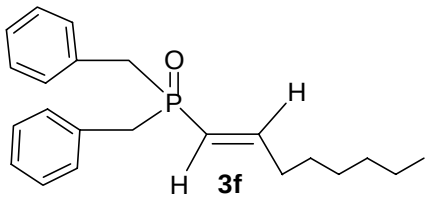
3d

(*E*)-1-(Cyclohexen-1-yl)-2-(diphenylphosphinyl)ethene (3d).[2] White solid, mp 137-138 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.74 (m, 10H), 7.04 (dd, $J_{P\text{-}H}$ = 19.6 Hz, $J_{H\text{-}H}$ = 17.2 Hz, 1H), 6.10 (dd, $J_{P\text{-}H}$ = 22.7 Hz, $J_{H\text{-}H}$ = 17.2 Hz, 1H), 6.08 (s, 1H), 2.18-2.19 (m, 4H), 1.61-1.72 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 137.9, 135.3 (d, $J_{P\text{-}C}$ = 17.9 Hz), 133.5 (d, $J_{P\text{-}C}$ = 104.7 Hz), 131.6, 131.3 (d, $J_{P\text{-}C}$ = 10.0 Hz), 128.4 (d, $J_{P\text{-}C}$ = 12.2 Hz), 114.6 (d, $J_{P\text{-}C}$ = 105.4 Hz), 26.2, 24.1, 22.0. ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.8. HRMS m/z calcd. for $C_{20}H_{22}OP$ $[M+H]^+$: 309.1408, found: 309.1401.



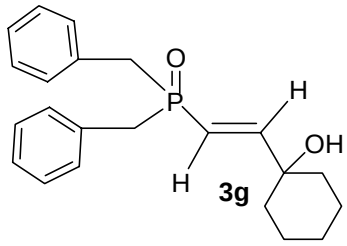
3e

(*E*)-1-Dibenzylphosphinyl-2-phenylethene (3e). White solid, mp 170-171 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.39 (m, 16H), 6.22 (dd, $J_{P\text{-}H}$ = 25.7 Hz, $J_{H\text{-}H}$ = 17.2 Hz, 1H), 3.23 (d, $J_{P\text{-}H}$ = 14.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 135.2 (d, $J_{P\text{-}C}$ = 16.5 Hz), 131.8 (d, $J_{P\text{-}C}$ = 7.2 Hz), 129.9 (d, $J_{P\text{-}C}$ = 5.0 Hz), 129.8, 128.7 (d, $J_{P\text{-}C}$ = 2.1 Hz), 127.5, 126.9 (d, $J_{P\text{-}C}$ = 2.9 Hz), 117.5(d, $J_{P\text{-}C}$ = 96.1 Hz), 37.4(d, $J_{P\text{-}C}$ = 64.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 34.1. HRMS m/z calcd. for $C_{22}H_{22}OP$ $[M+H]^+$: 333.1408, found: 333.1402.



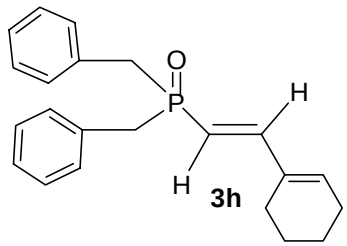
3f

(*E*)-1-Dibenzylphosphinyl-1-octene (3f). White solid, mp 109-110 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.33 (m, 10H), 6.49-6.61 (m, 1H), 5.58 (dd, $J_{P\text{-}H}$ = 28.8 Hz, $J_{H\text{-}H}$ = 17.2 Hz, 1H), 3.09-3.16 (m, 4H), 2.09-2.16 (m, 2H), 1.18-1.36 (m, 8H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 131.9 (d, $J_{P\text{-}C}$ = 7.2 Hz), 129.8 (d, $J_{P\text{-}C}$ = 5.0 Hz), 128.6 (d, $J_{P\text{-}C}$ = 2.3 Hz), 126.8 (d, $J_{P\text{-}C}$ = 2.9 Hz), 119.5 (d, $J_{P\text{-}C}$ = 95.4 Hz), 37.3 (d, $J_{P\text{-}C}$ = 63.8 Hz), 34.4 (d, $J_{P\text{-}C}$ = 15.8 Hz), 31.5, 28.6, 27.8, 22.5, 14.1. ^{31}P NMR (121 MHz, $CDCl_3$) δ 33.1. HRMS m/z calcd. for $C_{22}H_{30}OP$ $[M+H]^+$: 341.2034, found: 341.2026.



3g

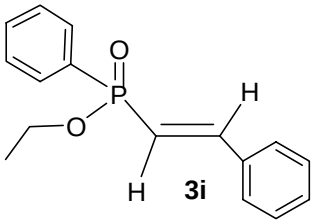
(*E*)-1-(1-hydroxy)cyclohexyl -2-(dibenzylphosphinyl)ethene (3g). White solid, mp 115-116 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.28 (m, 10H), 6.56 (dd, $J_{P\text{-}H}$ = 17.2 Hz, $J_{H\text{-}H}$ = 17.2 Hz, 1H), 5.94 (dd, $J_{P\text{-}H}$ = 26.1 Hz, $J_{H\text{-}H}$ = 17.2 Hz, 1H), 3.12 (d, $J_{P\text{-}H}$ = 12.0 Hz, 4H), 2.31 (br, 1H), 1.18-1.54 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 131.7 (d, $J_{P\text{-}C}$ = 6.5 Hz), 129.9 (d, $J_{P\text{-}C}$ = 2.9 Hz), 128.5, 126.7, 116.6 (d, $J_{P\text{-}C}$ = 99.6 Hz), 72.4 (d, $J_{P\text{-}C}$ = 13.6 Hz), 37.2 (d, $J_{P\text{-}C}$ = 68.1 Hz), 36.7, 25.1, 21.4. ^{31}P NMR (121 MHz, $CDCl_3$) δ 33.9. HRMS m/z calcd. for $C_{20}H_{28}OP$ $[M+H]^+$: 355.1827, found: 355.1822.



3h

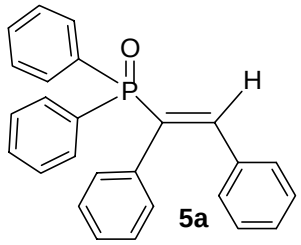
(*E*)-1-(Cyclohexen-1-yl)-2-(dibenzylphosphinyl)ethene (3h). White solid, mp 158-160 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.32 (m, 10H), 6.93 (dd, $J_{P\text{-}H}$ = 17.7 Hz, $J_{H\text{-}H}$ = 17.7 Hz, 1H), 6.01 (bs, 1H), 5.47 (dd, $J_{P\text{-}H}$ = 26.4 Hz, $J_{H\text{-}H}$ = 17.7 Hz, 1H), 3.13 (d, $J_{P\text{-}H}$ = 14.8 Hz, 4H), 2.15 (bs, 2H), 2.00 (bs, 2H), 1.58-1.70 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 137.4, 135.1 (d, $J_{P\text{-}C}$ = 17.2 Hz), 132.0 (d, $J_{P\text{-}C}$ = 7.2 Hz), 129.9 (d, $J_{P\text{-}C}$ = 5.0 Hz), 128.6, 126.8, 112.8 (d, $J_{P\text{-}C}$ = 97.5 Hz), 37.5 (d, $J_{P\text{-}C}$ = 63.8 Hz), 26.1, 23.9, 22.0. ^{31}P NMR (121 MHz, $CDCl_3$) δ 34.6. HRMS m/z calcd. for $C_{22}H_{26}OP$ $[M+H]^+$:

337.1721, found: 337.1715.



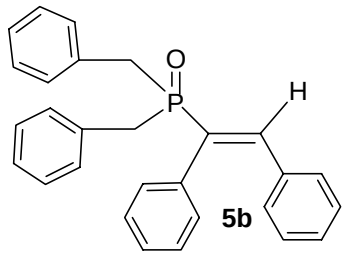
3i

(*E*)-1-Ethoxylphenylphosphinyl-2-phenylethene (3i).[4] Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.86 (m, 11H), 6.49 (dd, $J_{P\text{-}H}$ = 20.3 Hz, $J_{H\text{-}H}$ = 17.2 Hz, 1H), 4.07-4.20 (m, 2H), 1.37 (t, $J_{P\text{-}H}$ = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7 (d, $J_{P\text{-}C}$ = 5.7 Hz), 134.9 (d, $J_{P\text{-}C}$ = 20.1 Hz), 132.2, 131.4 (d, $J_{P\text{-}C}$ = 136.9 Hz), 131.3 (d, $J_{P\text{-}C}$ = 10.0 Hz), 130.1, 128.8, 128.5 (d, $J_{P\text{-}C}$ = 12.9 Hz), 127.7, 117.9 (d, $J_{P\text{-}C}$ = 138.4 Hz), 60.8 (d, $J_{P\text{-}C}$ = 5.7 Hz), 16.5 (d, $J_{P\text{-}C}$ = 6.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.3. HRMS m/z calcd. for $C_{16}H_{18}O_2P$ $[M+H]^+$: 273.1044, found: 273.1036.



5a

(*E*)-1-Diphenylphosphinyl-1,2-diphenylethene (5a).[3] White solid, mp 150-151 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92-7.70 (m, 21H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1 (d, $J_{P\text{-}C}$ = 9.3 Hz), 135.5 (d, $J_{P\text{-}C}$ =9.3 Hz), 135.3 (d, $J_{P\text{-}C}$ = 90.4 Hz), 134.8 (d, $J_{P\text{-}C}$ = 17.2 Hz), 132.4 (d, $J_{P\text{-}C}$ = 9.3 Hz), 131.8, 131.0 (d, $J_{P\text{-}C}$ = 102.5 Hz), 130.3, 129.9 (d, $J_{P\text{-}C}$ = 4.3 Hz), 128.9, 128.7, 128.3 (d, $J_{P\text{-}C}$ = 11.5 Hz), 128.1, 127.7. ^{31}P NMR (121 MHz, $CDCl_3$) δ 29.4. HRMS m/z calcd. for $C_{26}H_{22}OP$ $[M+H]^+$: 381.1408, found: 381.1401.



5b

(*E*)-1-Dibenzylphosphinyl-1,2-diphenylethene (5b). White solid, mp 164-166 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88-7.44 (m, 21H), 3.11 (d, J_{P-H} = 12.7 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5 (d, J_{P-C} = 6.5 Hz), 136.3 (d, J_{P-C} =10.0 Hz), 134.6, 134.2 (d, J_{P-C} = 98.9 Hz), 131.7 (d, J_{P-C} = 7.2 Hz), 130.0, 129.4, 129.2 (d, J_{P-C} = 3.6 Hz), 128.7, 128.5, 128.0, 126.8, 35.0 (d, J_{P-C} = 64.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.5. HRMS m/z calcd. for $C_{28}H_{26}OP$ $[M+H]^+$: 409.1721, found: 409.1726.

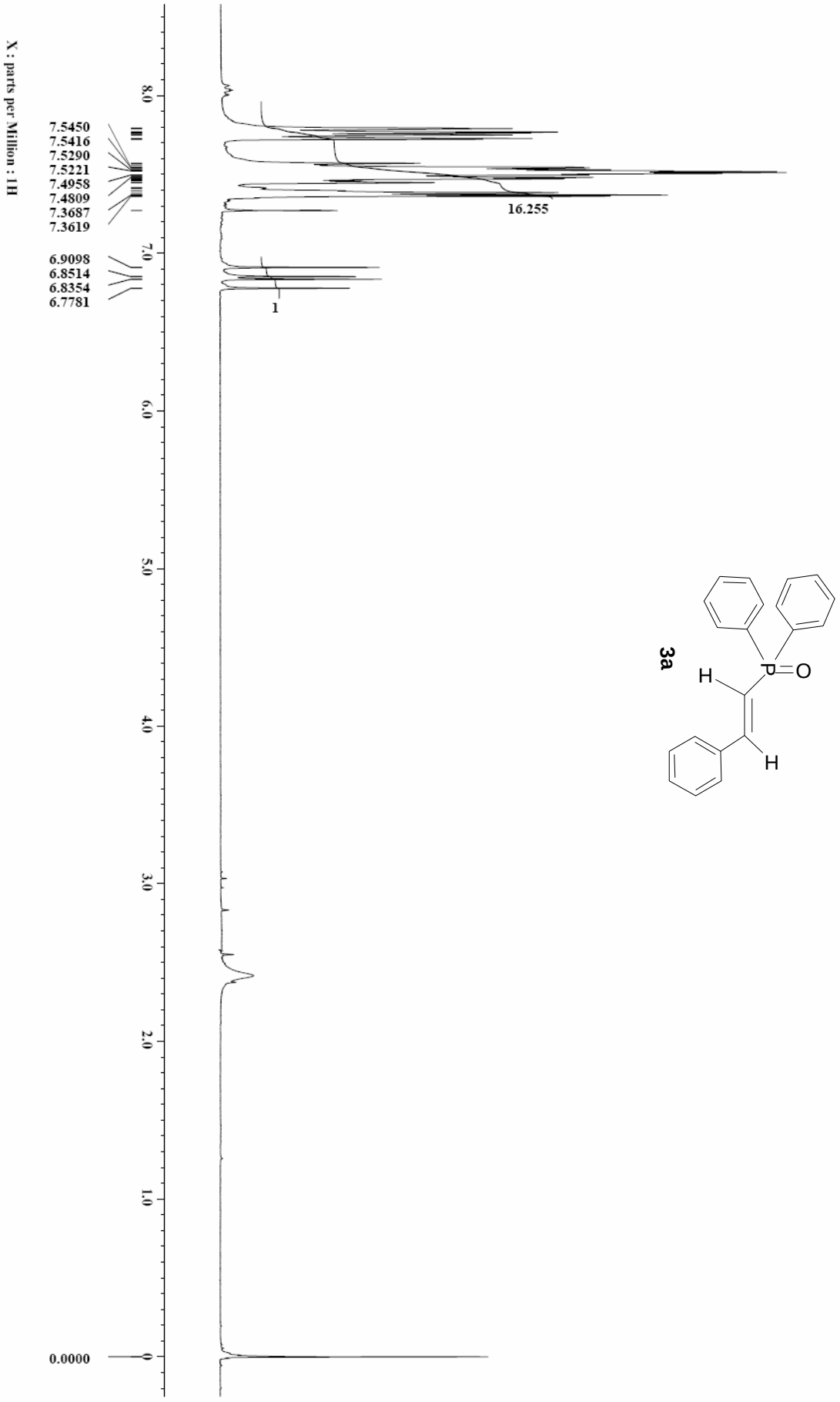
References

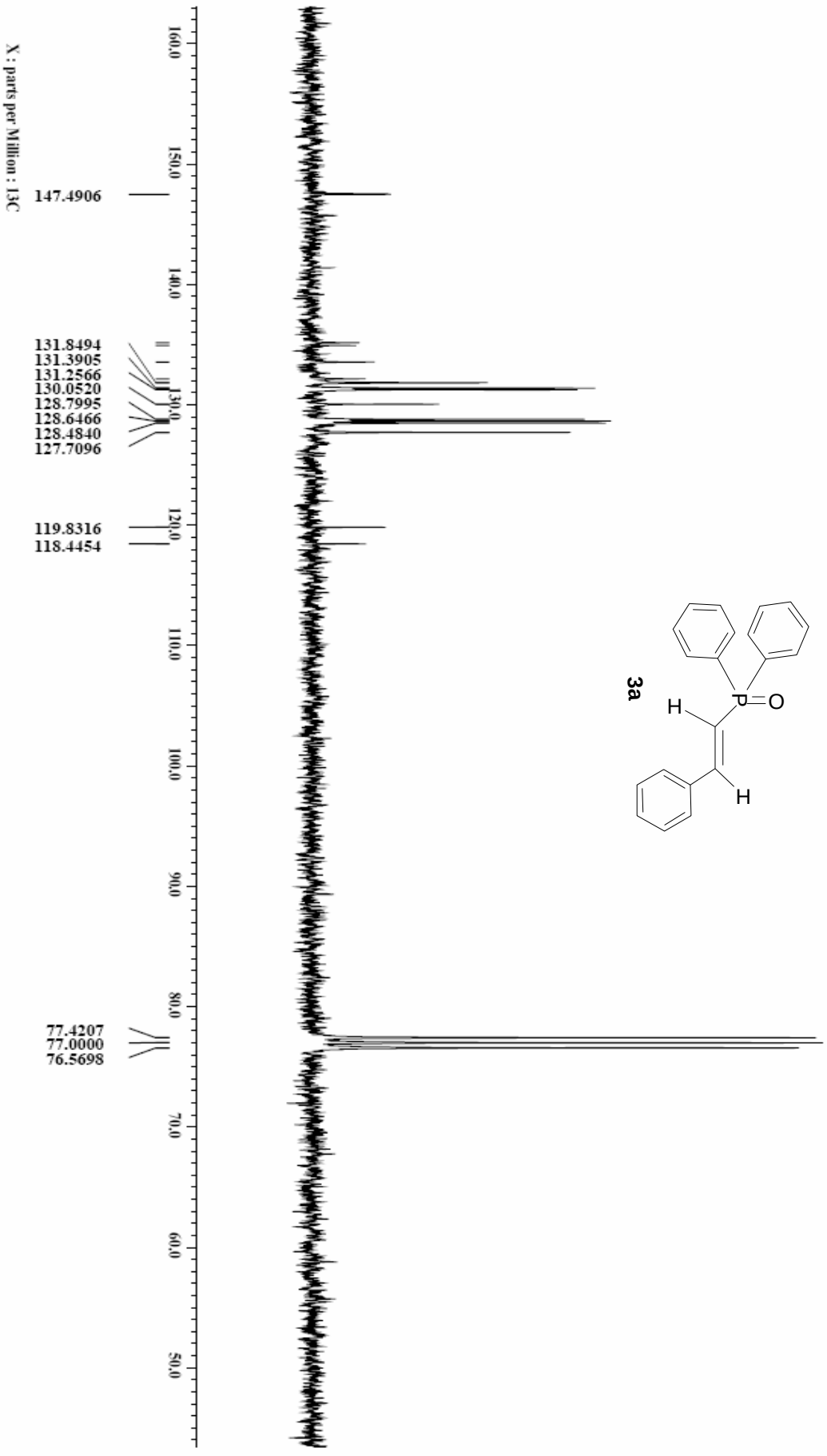
1 H. R.Hays, *J. Org. Chem.* 1968, **33**, 3690.

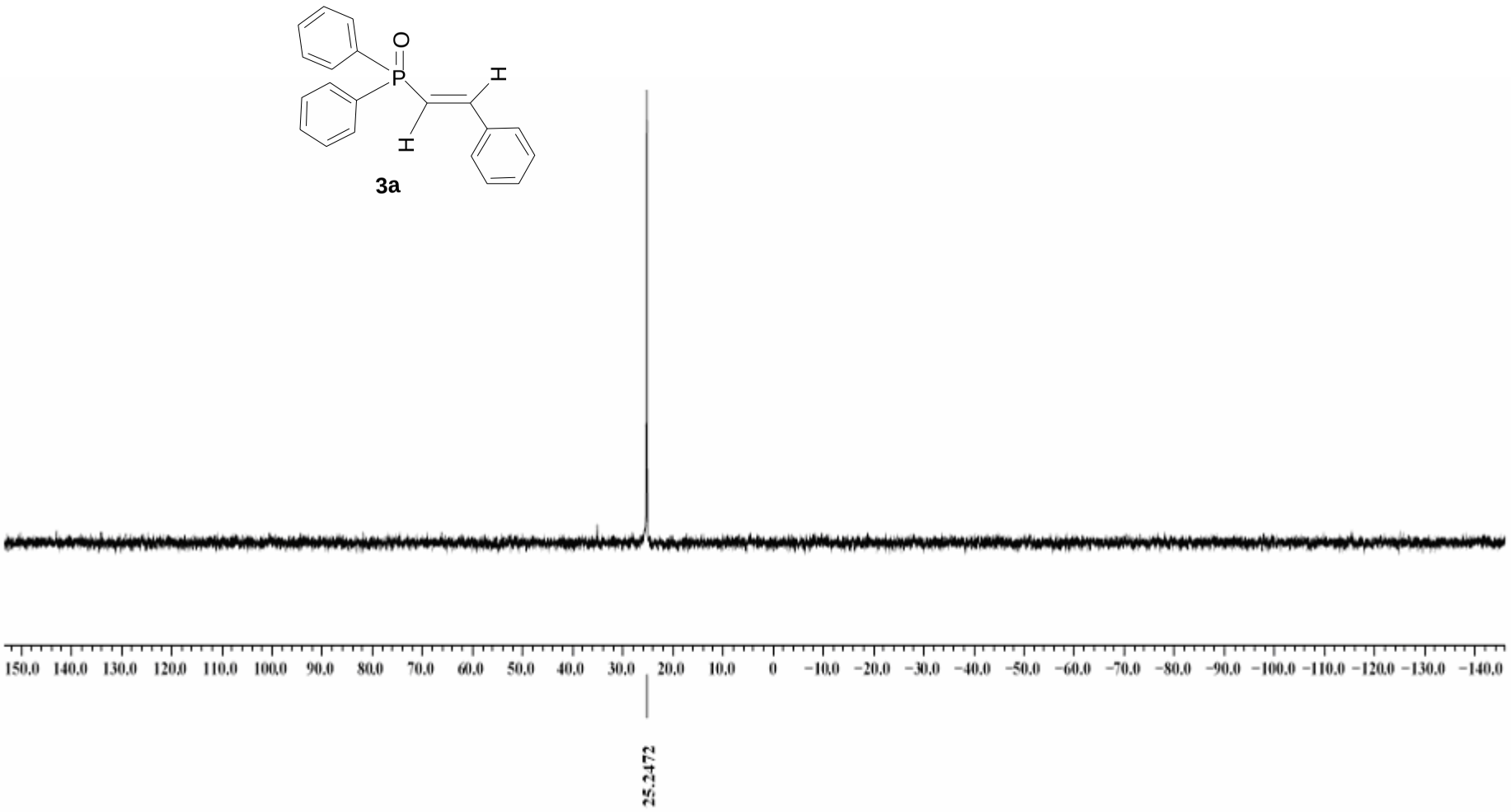
2 L.-B. Han, C.-Q. Zhao and M. Tanaka, *J. Org. Chem*. 2001, **66**, 5929.

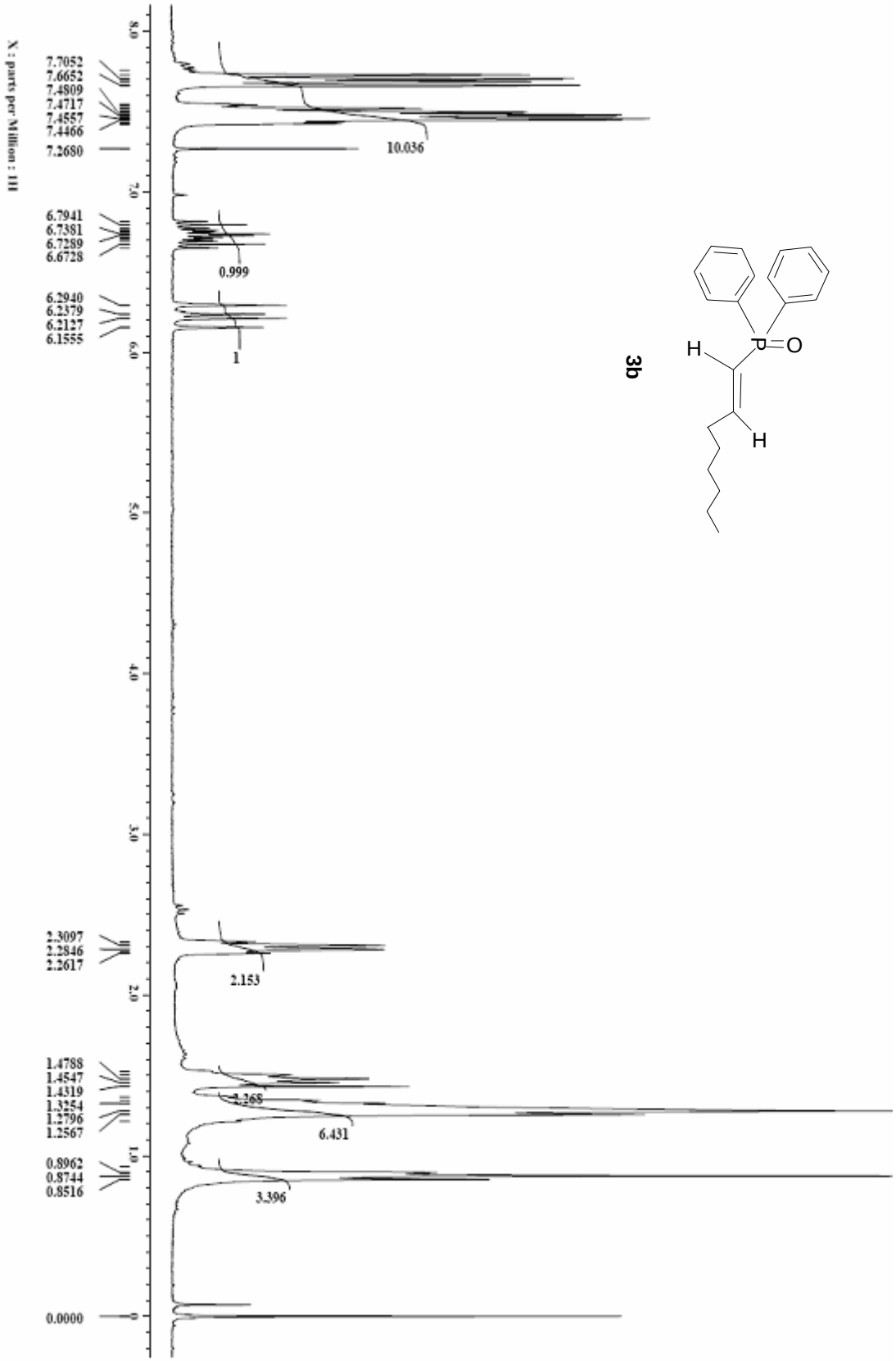
3 K. Takaki, G. Koshoji, K. Komeyama, M. Takeda, T. Shishido, A. Kitani and K. Takehira, *J. Org. Chem.* 2003, **68**, 6554.

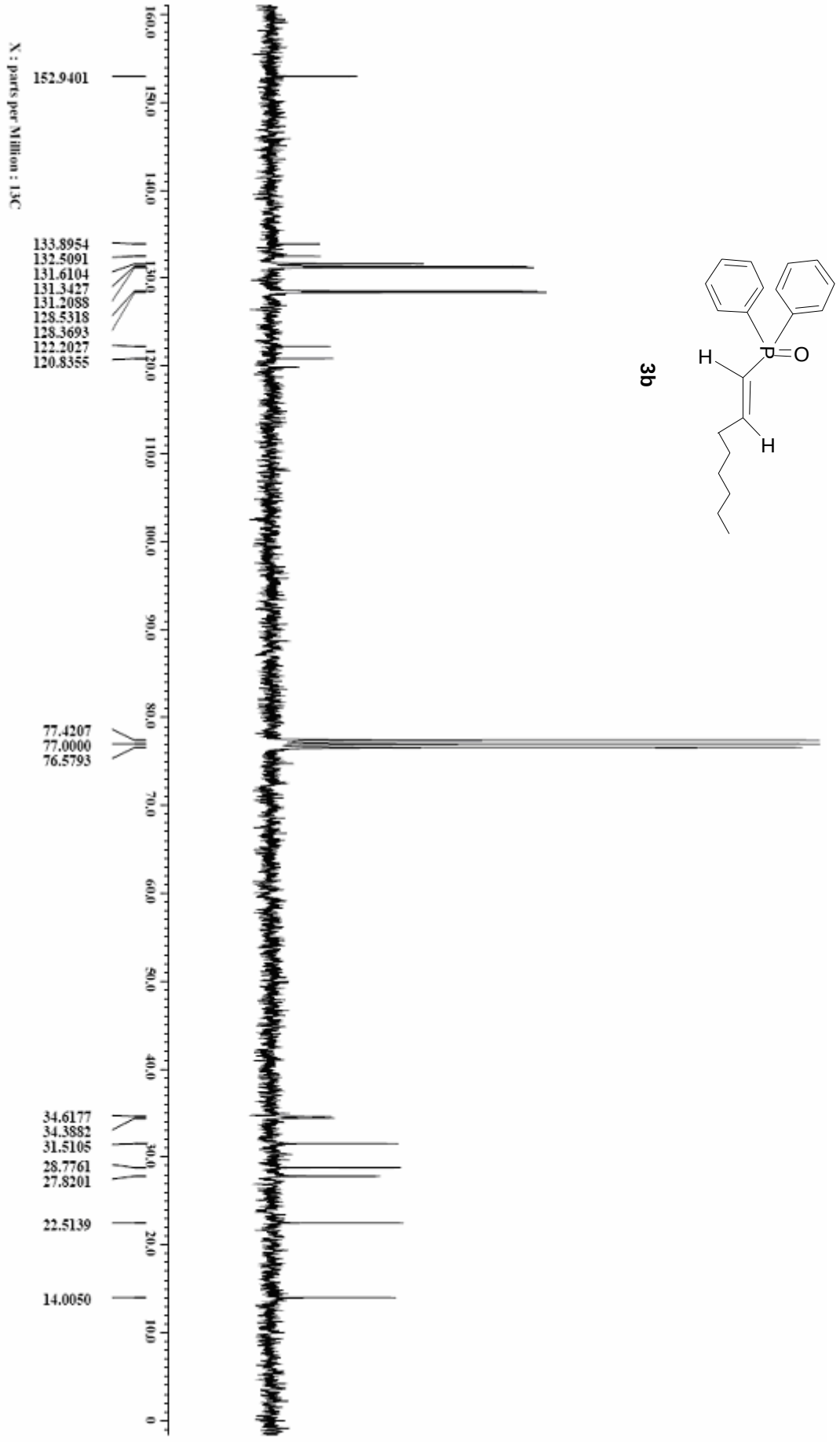
4 L.-B. Han, C. Zhang, H. Yazawa and S. Shimada, *J. Am. Chem. Soc*. 2004, **126**, 5080.

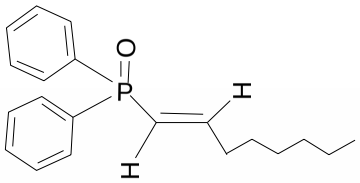

X : parts per Million : 1H
7.5450
7.5416
7.5290
7.5221
7.4958
7.4809
7.3687
7.3619
6.9098
6.8514
6.8354
6.7781
0.0000
16.255
1
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3a
P
O
H
H


X : parts per Million : 13C
147.4906
131.8494
131.3905
131.2566
130.0520
128.7995
128.6466
128.4840
127.7096
119.8316
118.4454
77.4207
77.0000
76.5698
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
3a
H
P
O
H

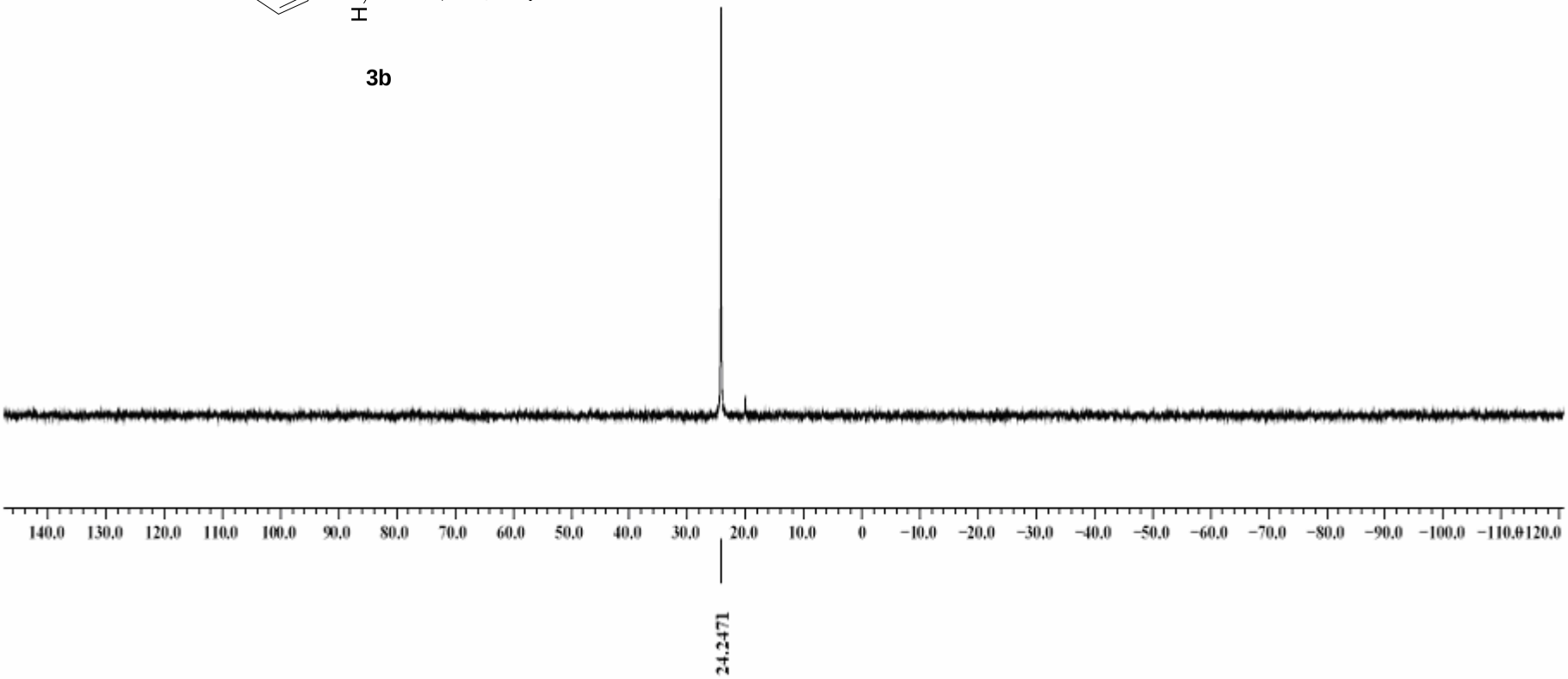

O
P
H
H
3a
150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0 −50.0 −60.0 −70.0 −80.0 −90.0 −100.0 −110.0 −120.0 −130.0 −140.0
25.2472
X : parts per Million : 31P

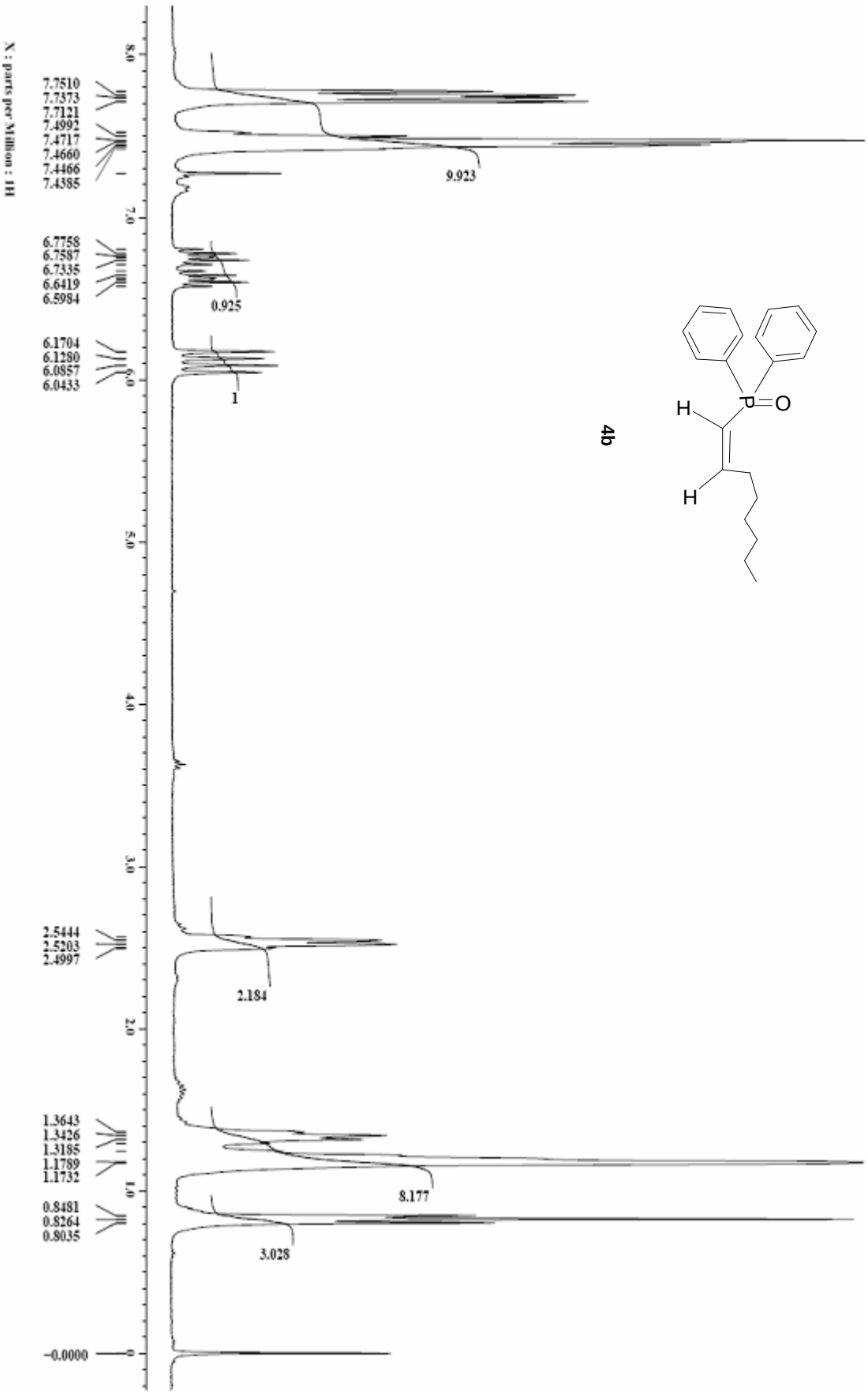

X : parts per Million : 111
7.7052
7.6652
7.4809
7.4717
7.4557
7.4466
7.2680
10.036
6.7941
6.7381
6.7289
6.6728
0.999
6.2940
6.2379
6.2127
6.1555
1
2.3097
2.2846
2.2617
2.153
1.4788
1.4547
1.4319
1.3254
1.2796
1.2567
2.268
6.431
0.8962
0.8744
0.8516
3.396
0.0000
H
P
O
H
3b

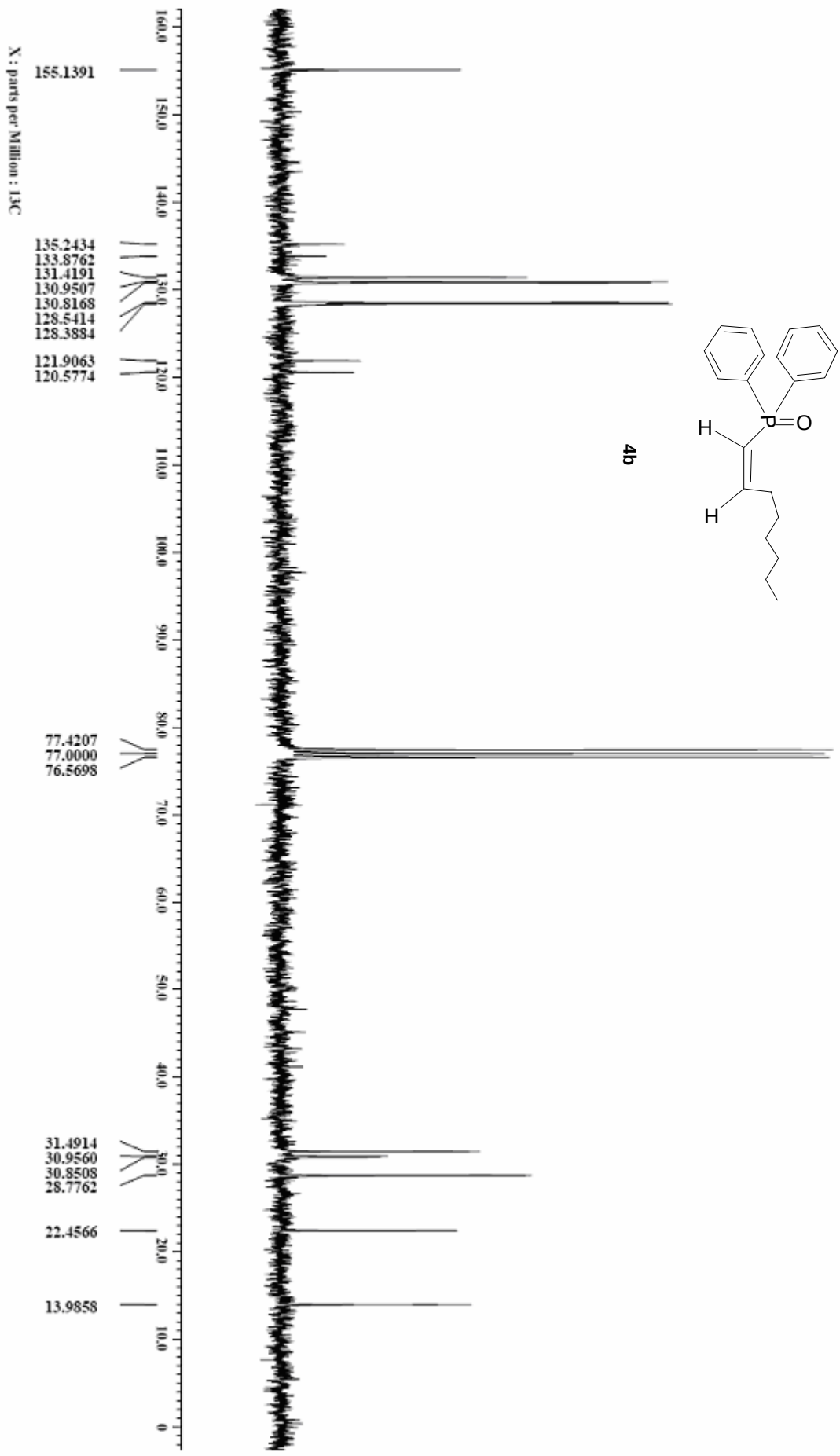

X : parts per Million : 13C
152.9401
133.8954
132.5091
131.6104
131.3427
131.2088
128.5318
128.3693
122.2027
120.8355
77.4207
77.0000
76.5793
34.6177
34.3882
31.5105
28.7761
27.8201
22.5139
14.0050
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
3b
H
P
O
H

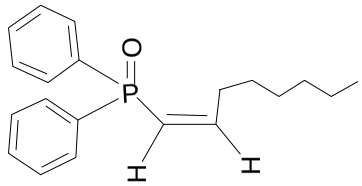

O
P
H
H

3b

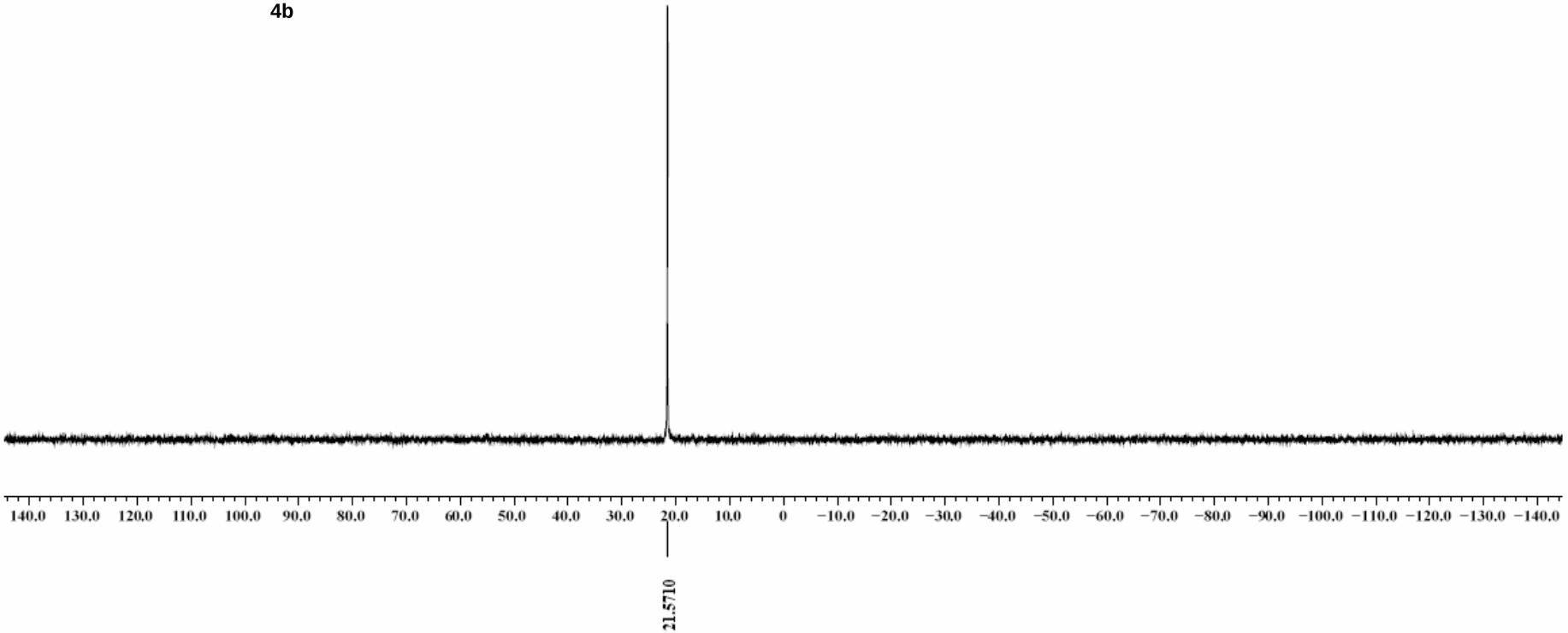

140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0 −50.0 −60.0 −70.0 −80.0 −90.0 −100.0 −110.0 120.0
24.2471
X : parts per Million : 31P


X : parts per Million : 1H
7.7510
7.7373
7.7121
7.4992
7.4717
7.4660
7.4466
7.4385
9.923
6.7758
6.7587
6.7335
6.6419
6.5984
0.925
6.1704
6.1280
6.0857
6.0433
1
4b
H
P
O
H
2.5444
2.5203
2.4997
2.184
1.3643
1.3426
1.3185
1.1789
1.1732
8.177
0.8481
0.8264
0.8035
3.028
-0.0000

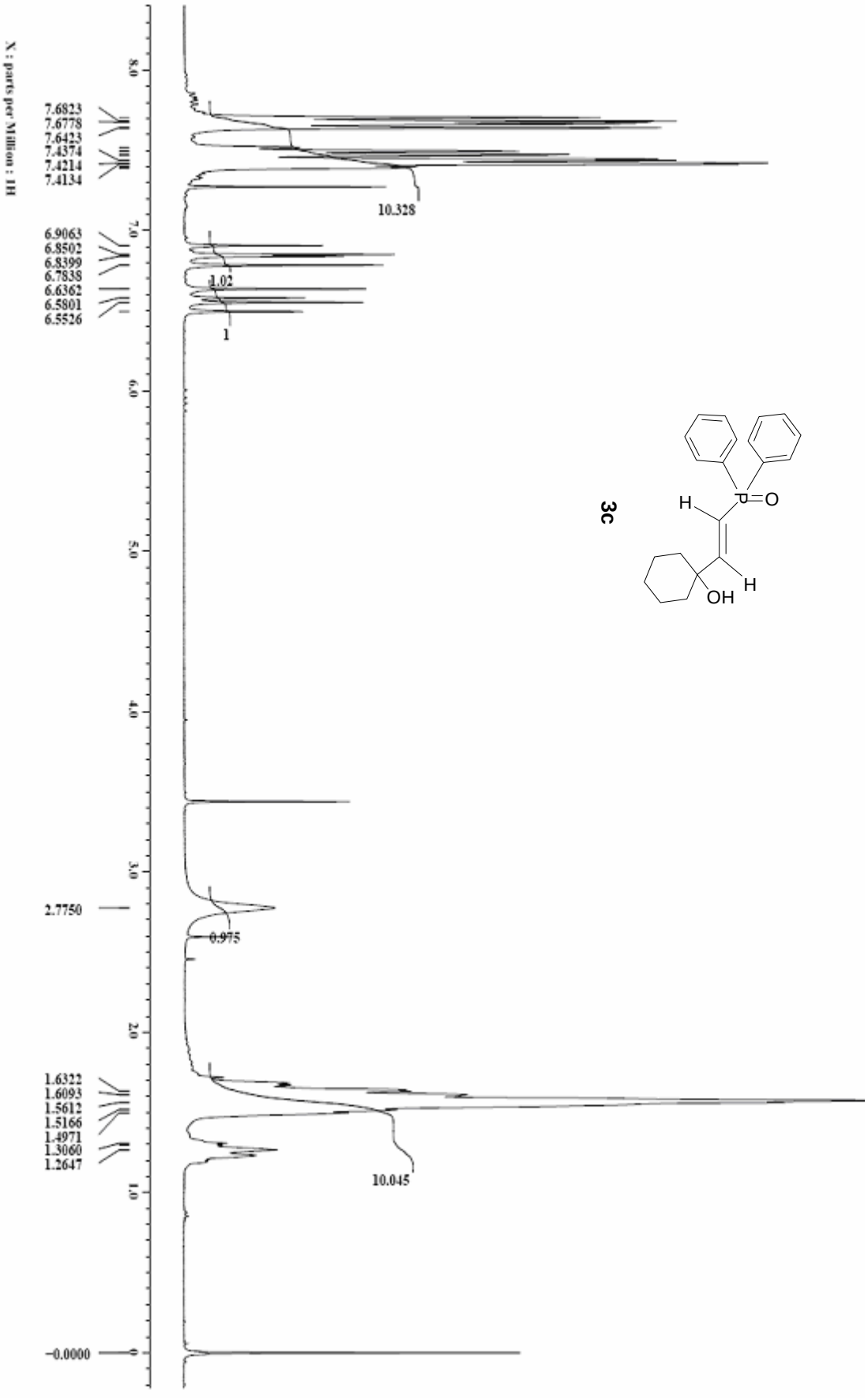

X : parts per Million : 13C
155.1391
135.2434
133.8762
131.4191
130.9507
130.8168
128.5414
128.3884
121.9063
120.5774
77.4207
77.0000
76.5698
31.4914
30.9560
30.8508
28.7762
22.4566
13.9858
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
4b
H
P
O
H

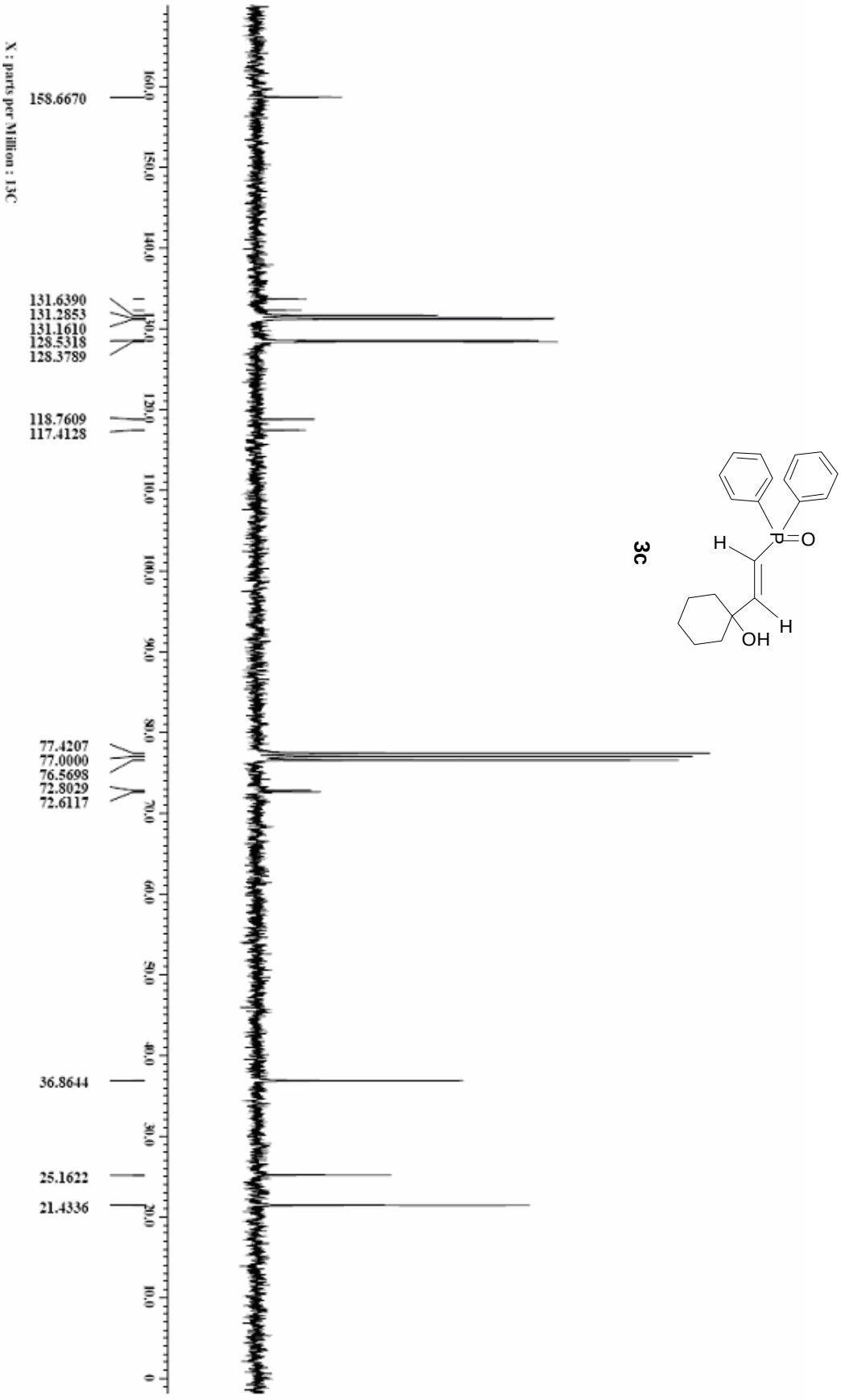


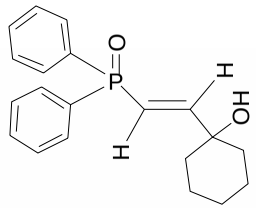
4b



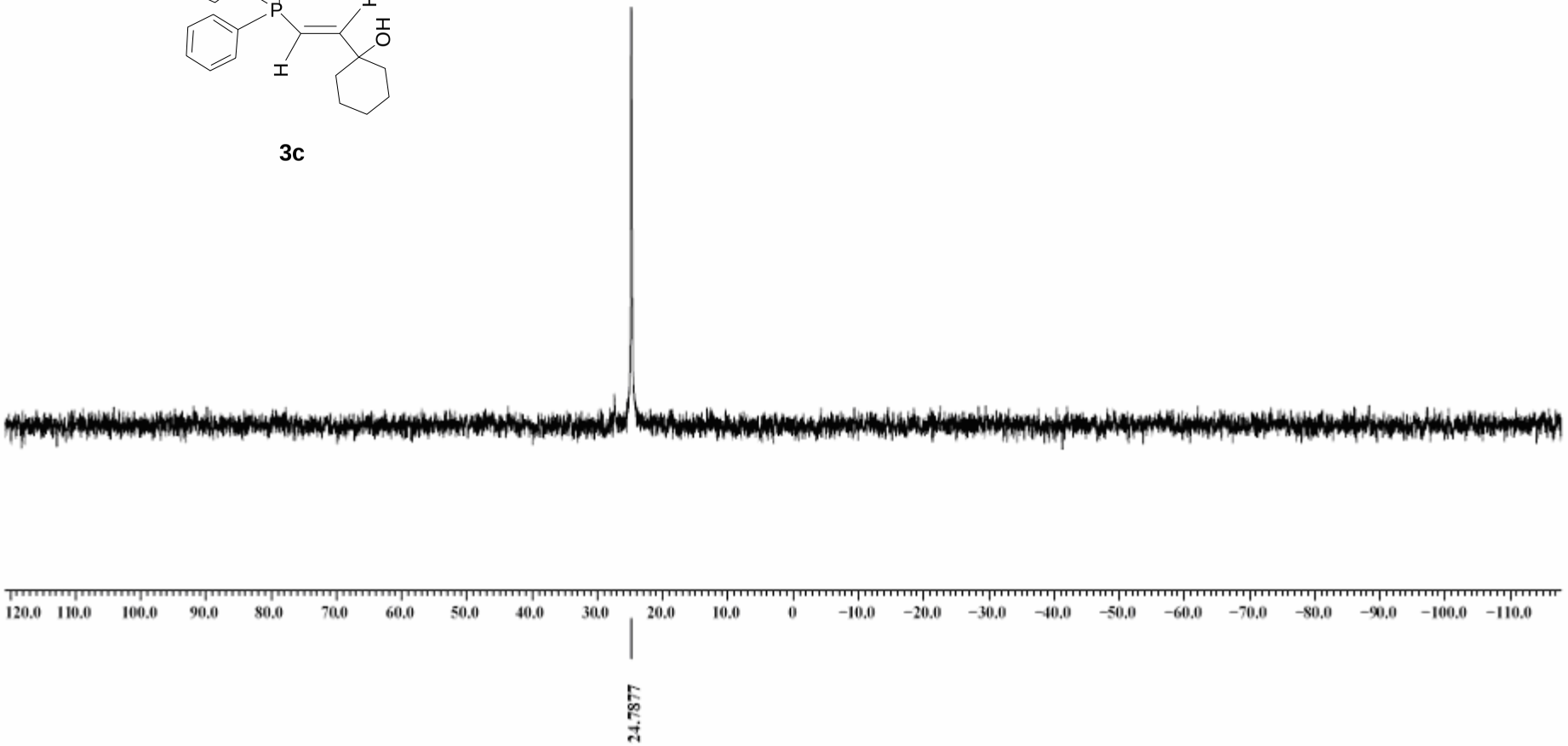
X : parts per Million : 31P


X : parts per Million : 1H
7.6823
7.6778
7.6423
7.4374
7.4214
7.4134
10.328
6.9063
6.8502
6.8399
6.7838
6.6362
6.5801
6.5526
1.02
1
2.7750
0.975
1.6322
1.6093
1.5612
1.5166
1.4971
1.3060
1.2647
10.045
−0.0000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3c
H
O
H
OH

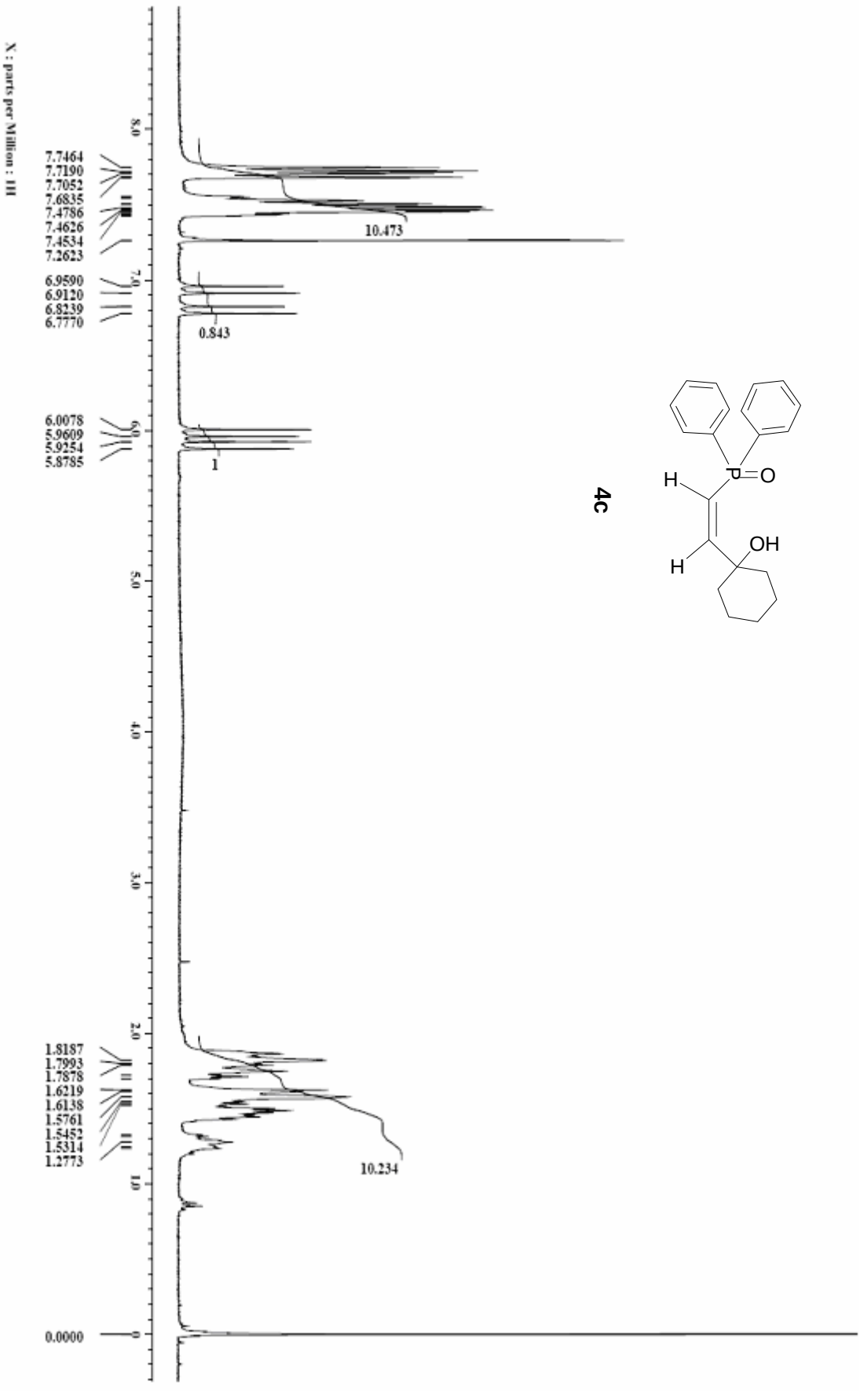

X : parts per Million : 13C
158.6670
131.6390
131.2853
131.1610
128.5318
128.3789
118.7609
117.4128
77.4207
77.0000
76.5698
72.8029
72.6117
36.8644
25.1622
21.4336
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
3c
P
O
H
H
OH

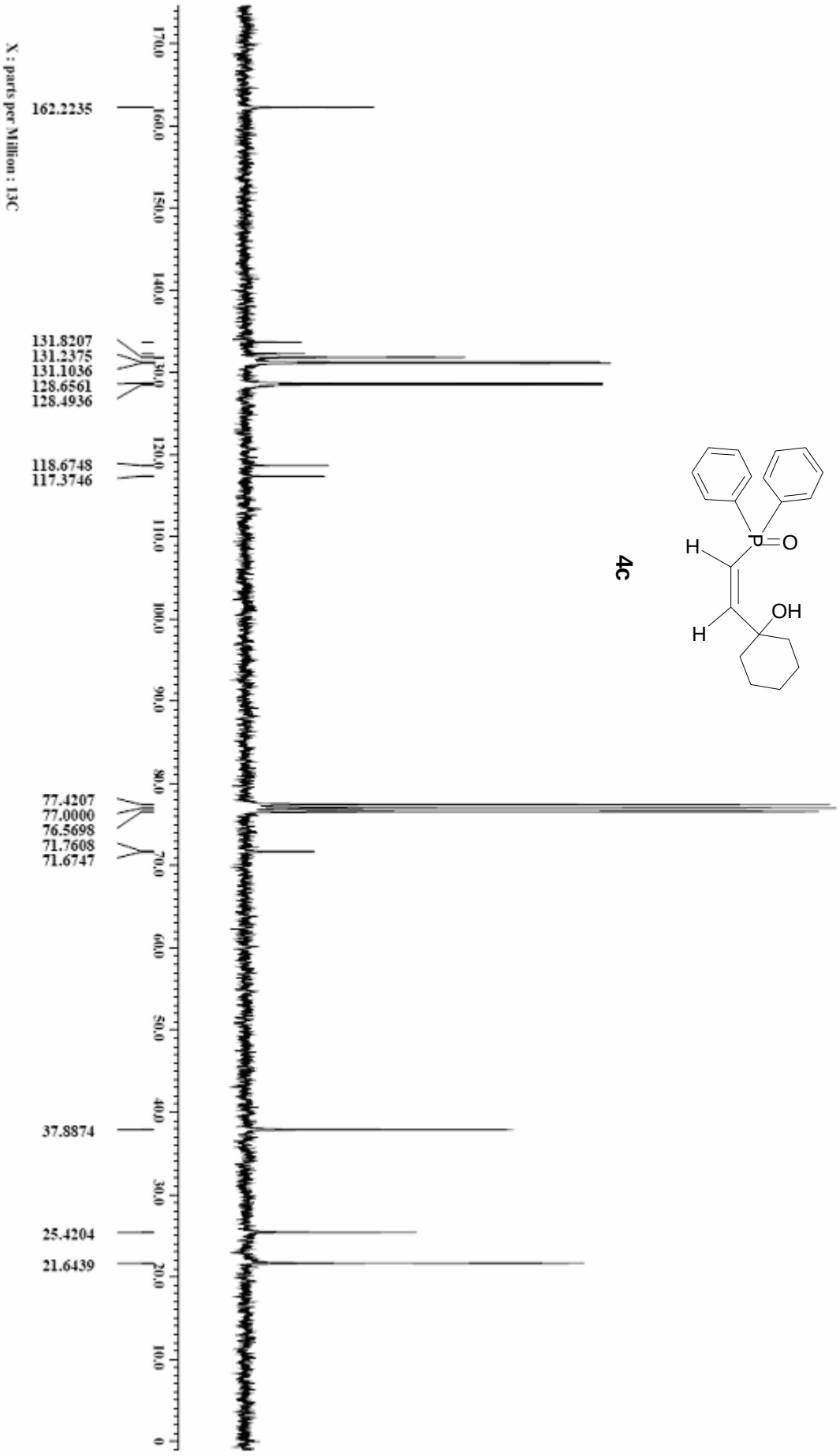


3c



X : parts per Million : 31P

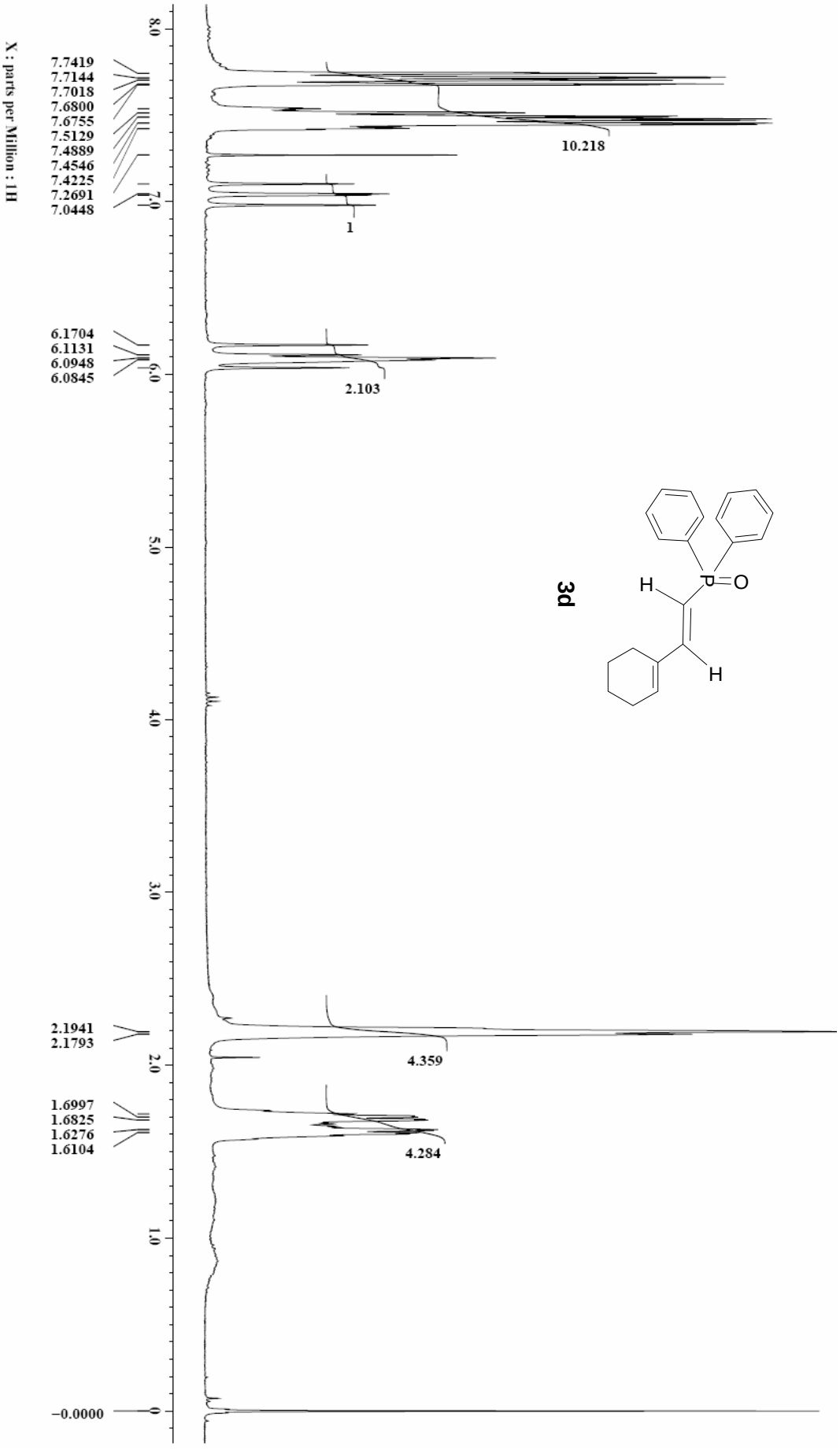

X : parts per Million : 1H
7.7464
7.7190
7.7052
7.6835
7.4786
7.4626
7.4534
7.2623
10.473
6.9590
6.9120
6.8239
6.7770
0.843
6.0078
5.9609
5.9254
5.8785
1
1.8187
1.7993
1.7878
1.6219
1.6138
1.5761
1.5452
1.5314
1.2773
10.234
0.0000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4c
P
O
H
H
OH

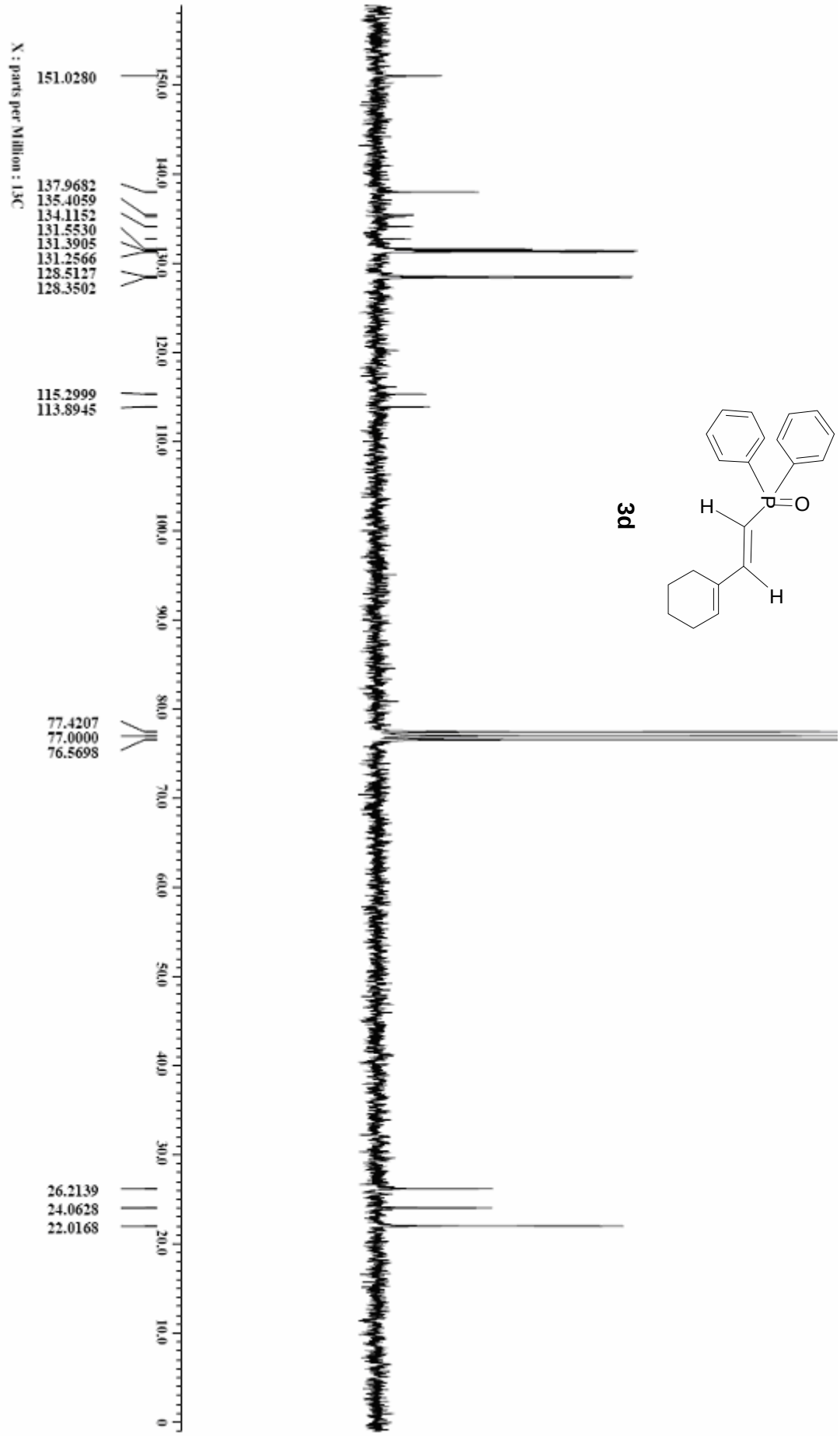

X : parts per Million : 13C
162.2235
131.8207
131.2375
131.1036
128.6561
128.4936
118.6748
117.3746
77.4207
77.0000
76.5698
71.7608
71.6747
37.8874
25.4204
21.6439
4c
H
O
H
OH

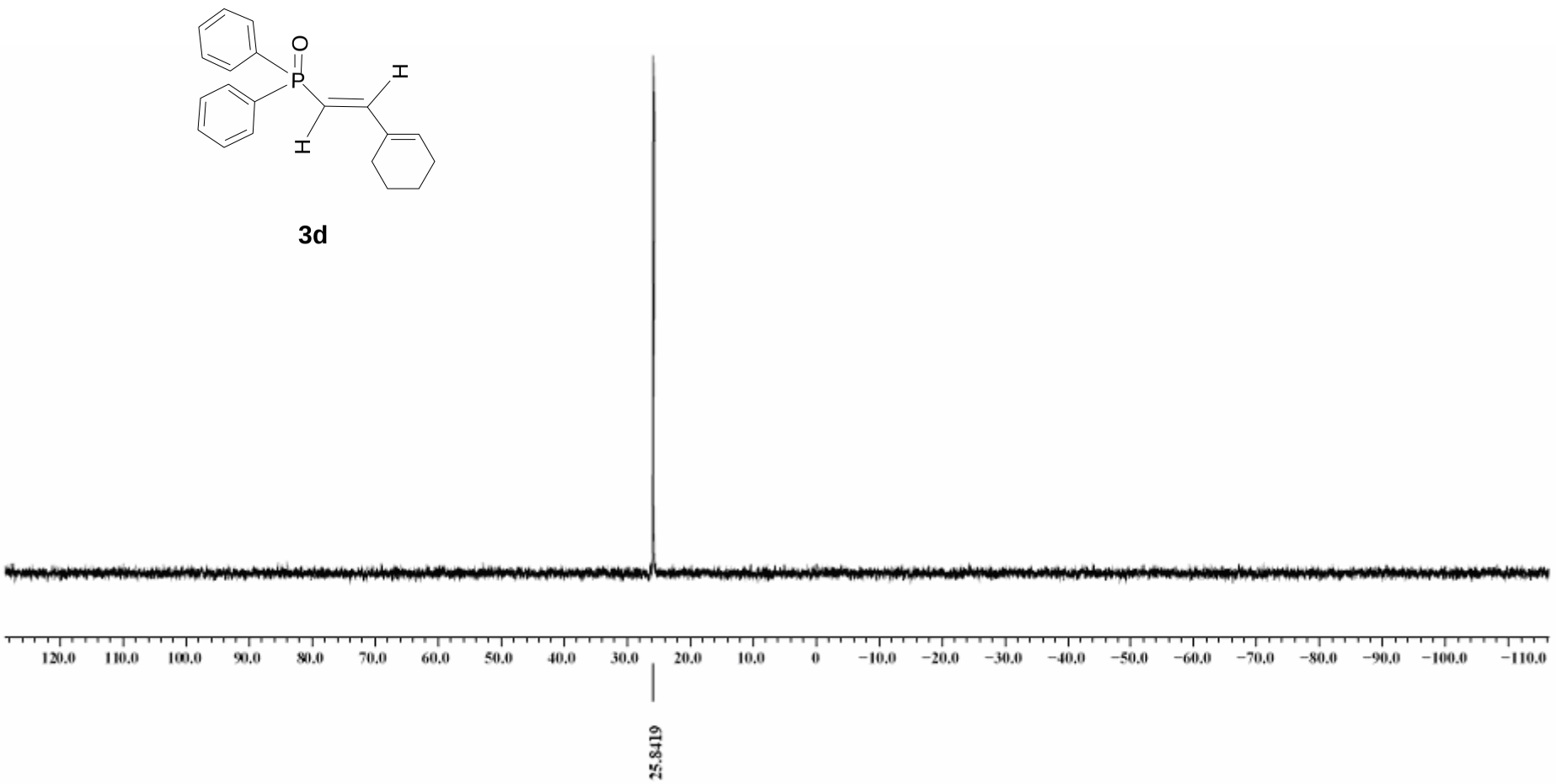
X : parts per Million : 31P
27.3827
110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0

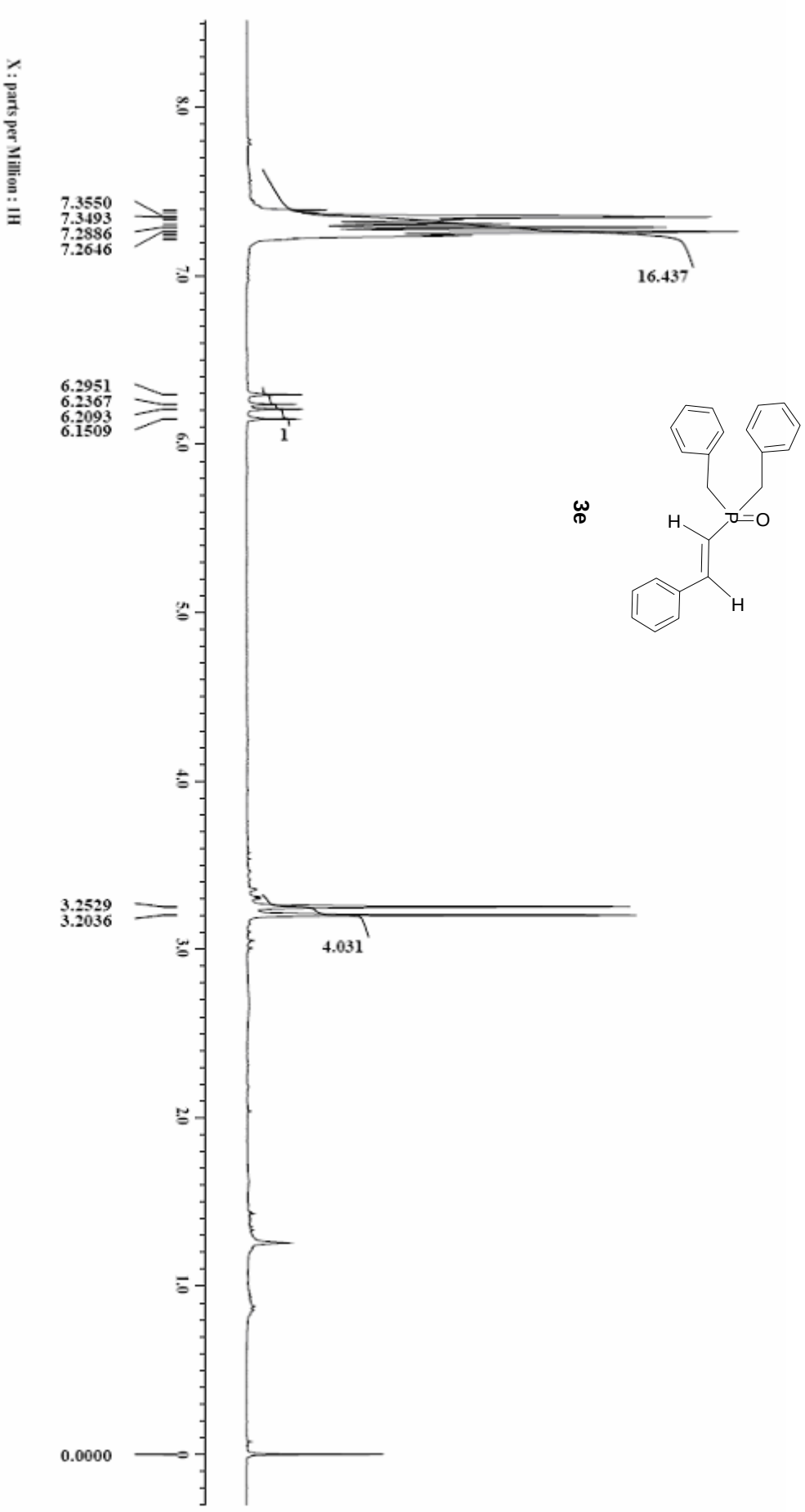
4c

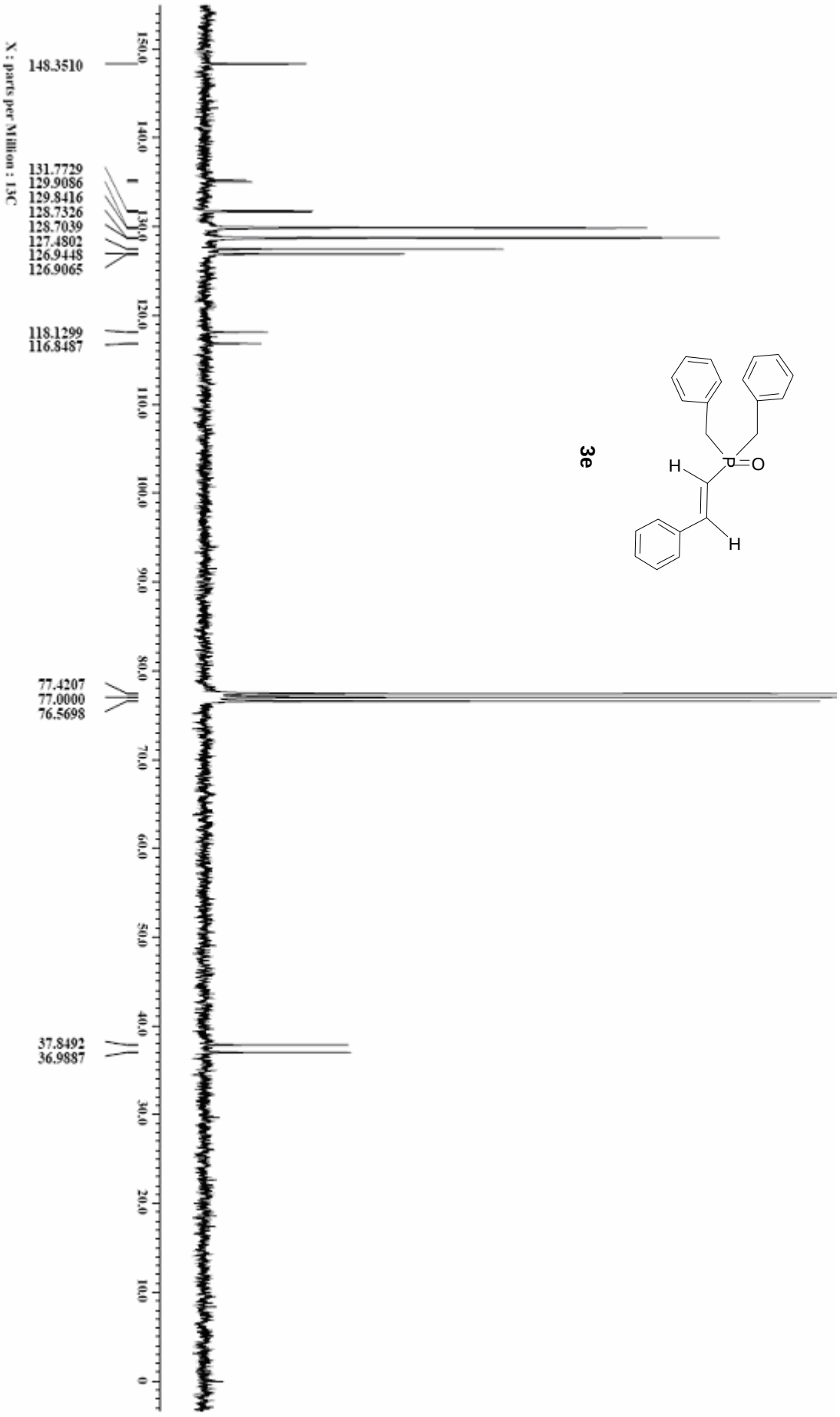
H
P
O
OH
H

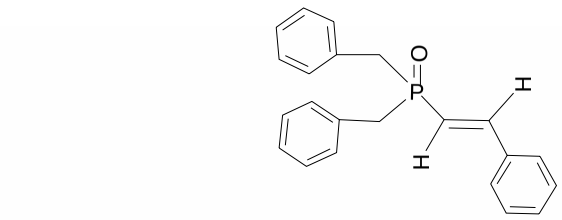

X : parts per Million : 1H
7.7419
7.7144
7.7018
7.6800
7.6755
7.5129
7.4889
7.4546
7.4225
7.2691
7.0448
6.1704
6.1131
6.0948
6.0845
2.1941
2.1793
1.6997
1.6825
1.6276
1.6104
−0.0000
10.218
1
2.103
4.359
4.284
3d
H
P
O
H


X : parts per Million : 13C
151.0280
137.9682
135.4059
134.1152
131.5530
131.3905
131.2566
128.5127
128.3502
115.2999
113.8945
77.4207
77.0000
76.5698
26.2139
24.0628
22.0168
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
3d
H
O
H

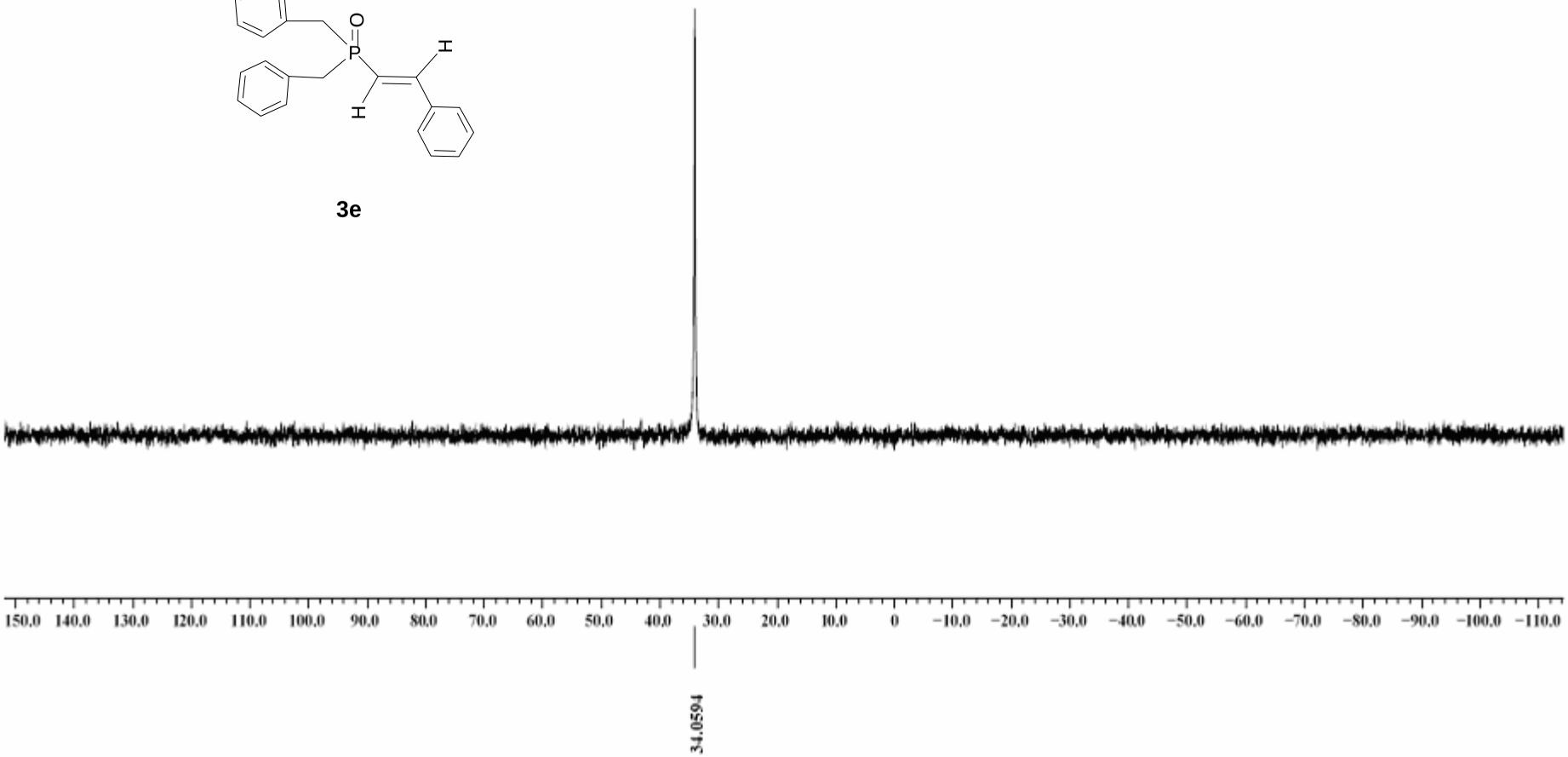

O
P
H
H
3d
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
−60.0
−70.0
−80.0
−90.0
−100.0
−110.0
25.8419
X : parts per Million : 31P

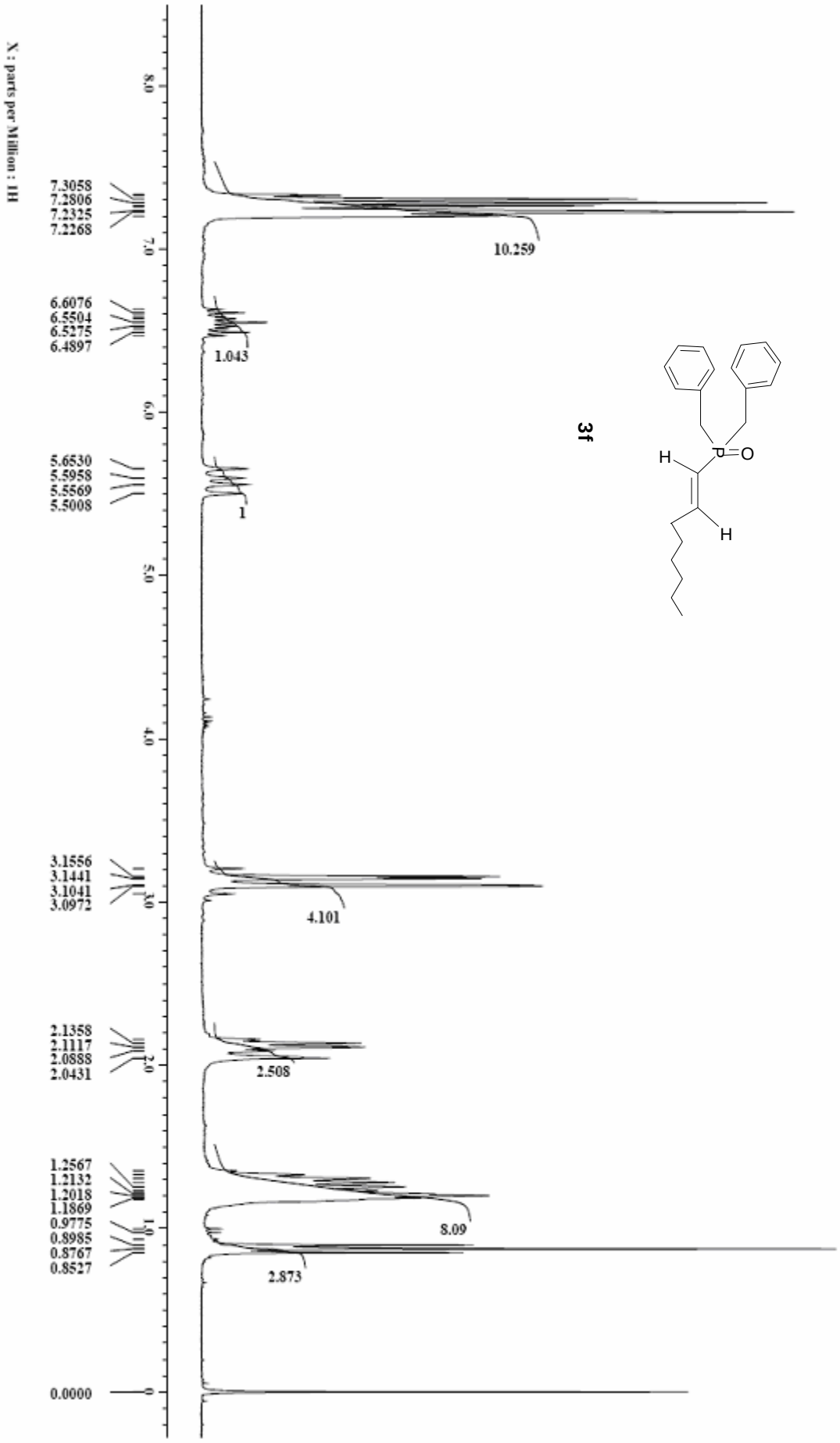

X : parts per Million : 1H
7.3550
7.3493
7.2886
7.2646
6.2951
6.2367
6.2093
6.1509
3.2529
3.2036
0.0000
16.437
1
4.031
3e
P
O
H
H

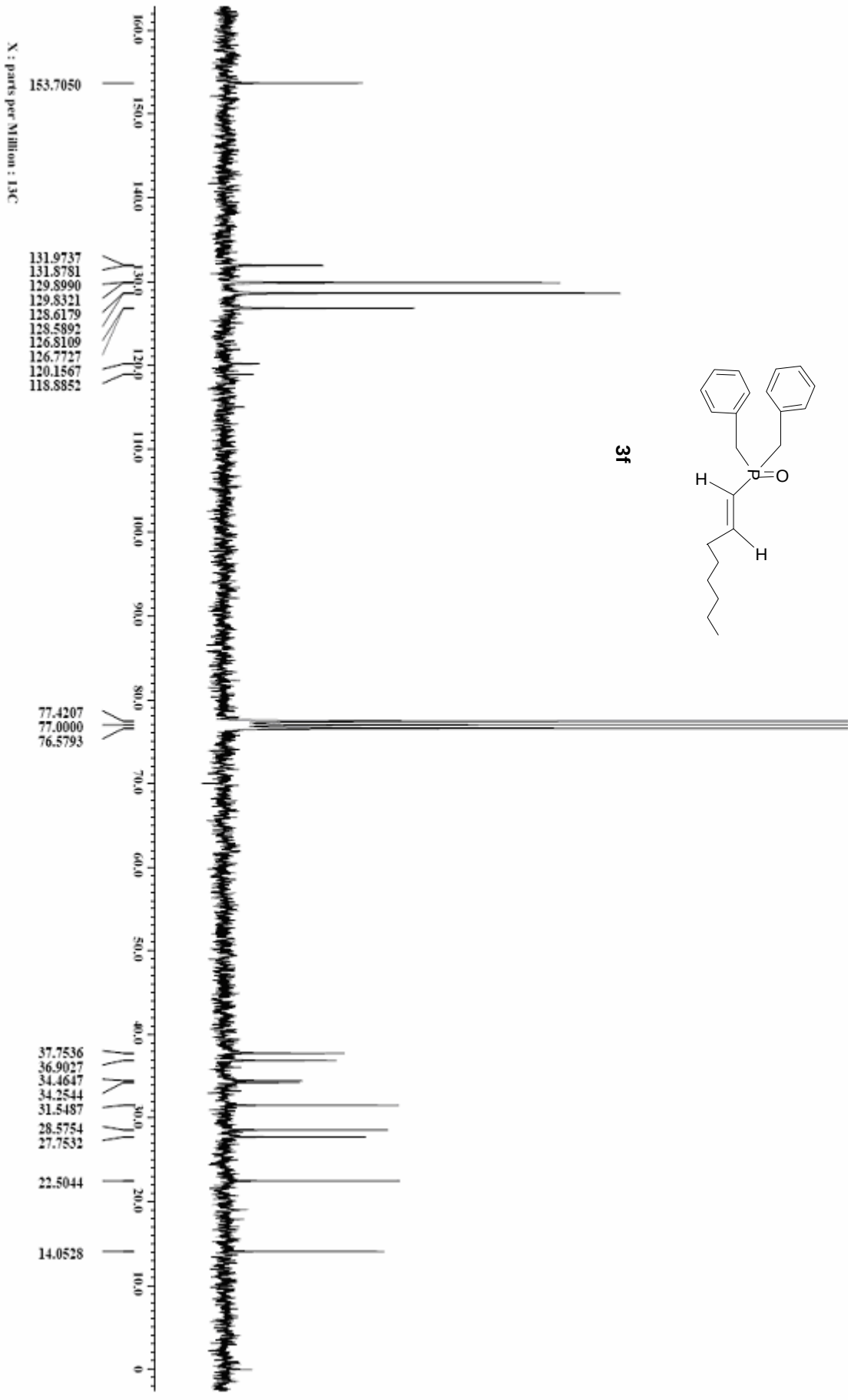

X : parts per Million : 13C
148.3510
131.7729
129.9086
129.8416
128.7326
128.7039
127.4802
126.9448
126.9065
118.1299
116.8487
77.4207
77.0000
76.5698
37.8492
36.9887
3e
H
P
O
H

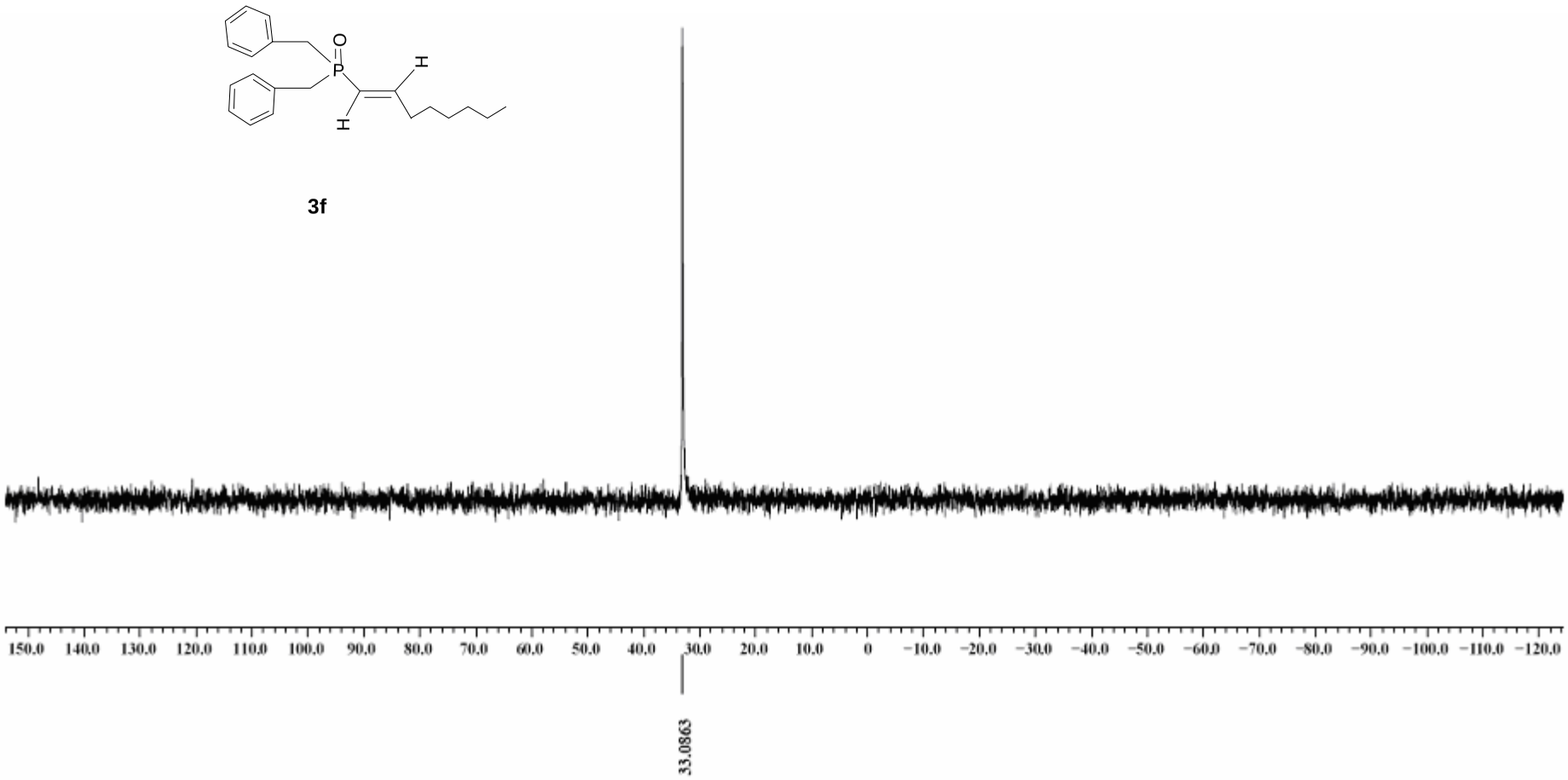


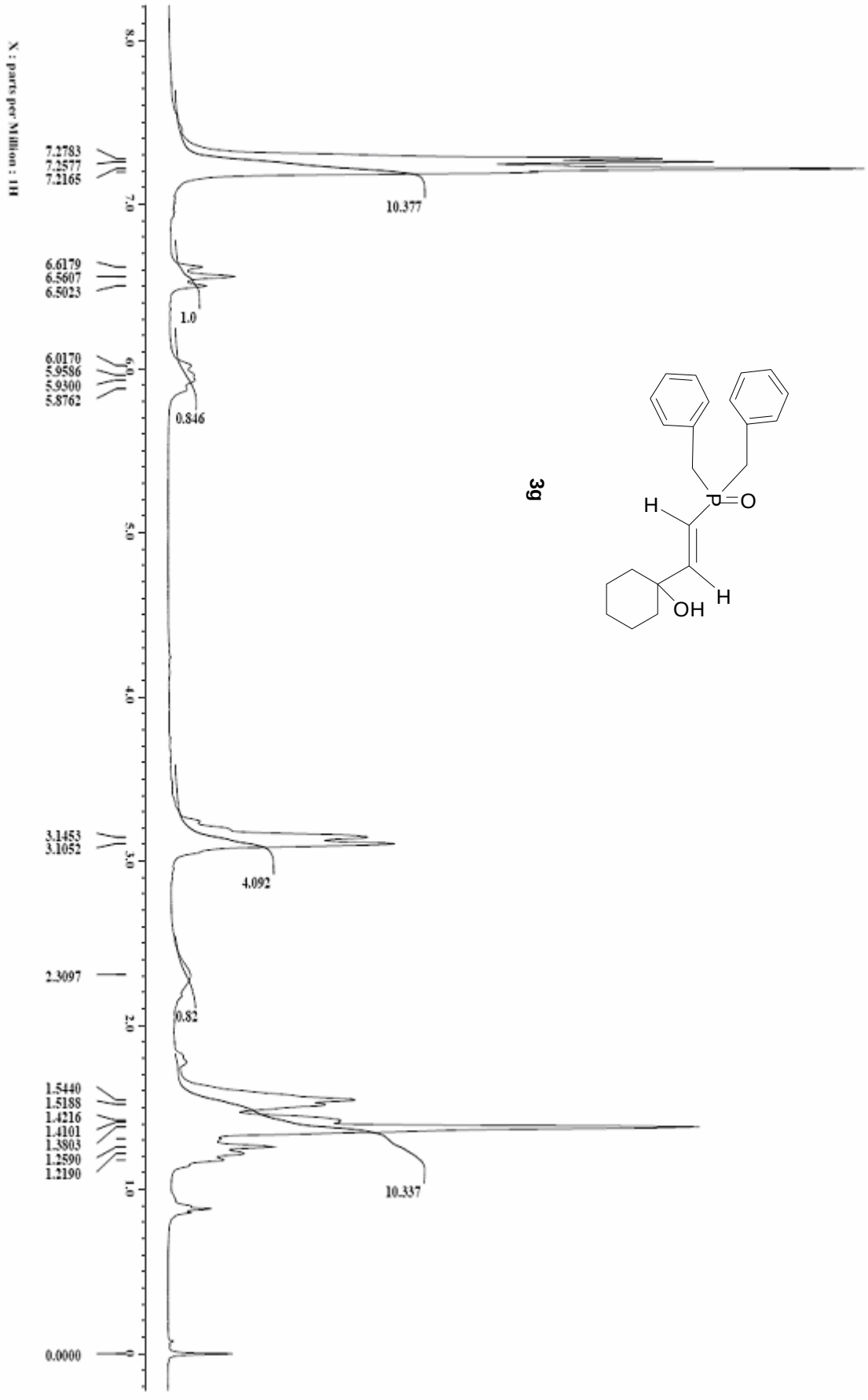
3e

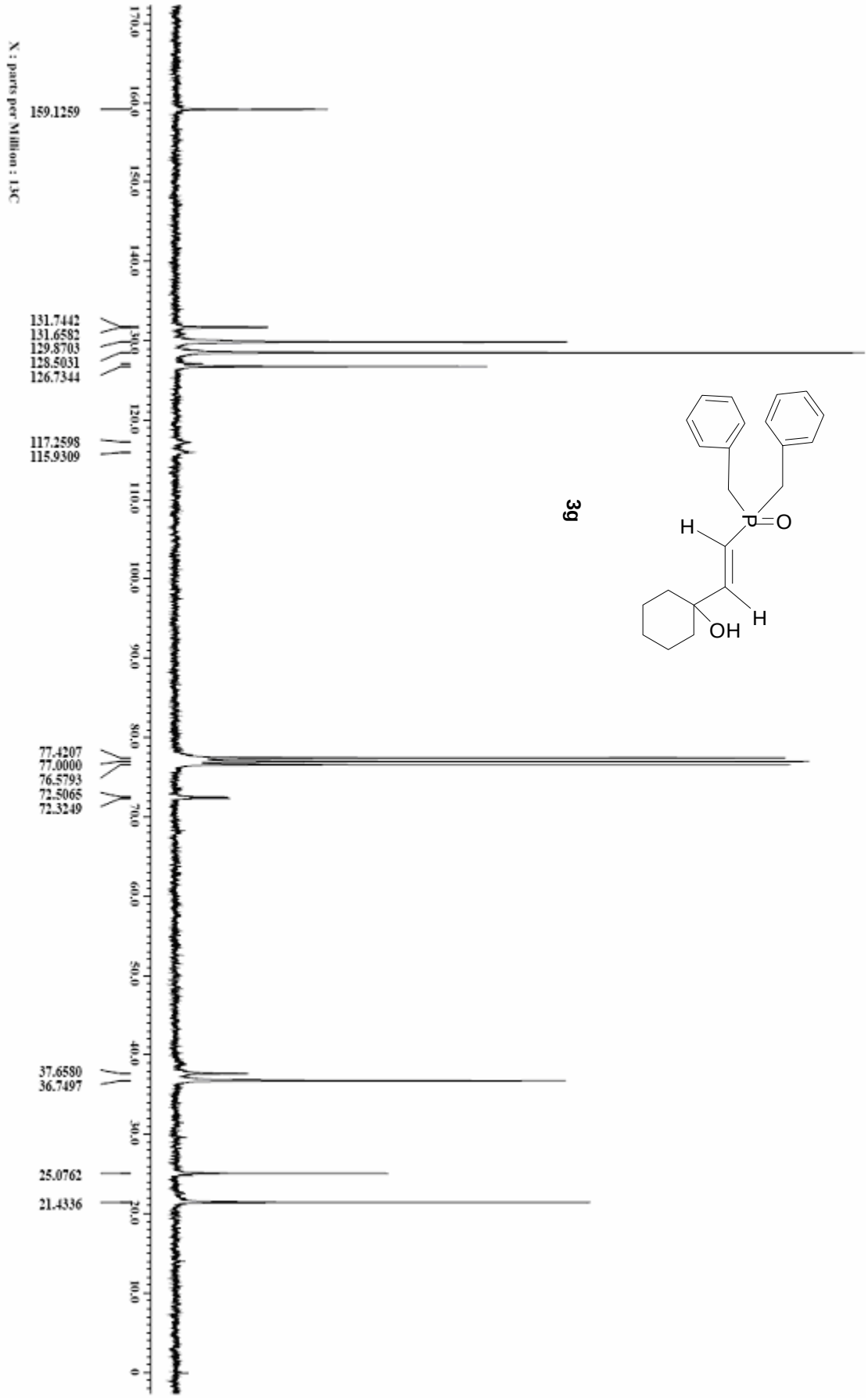

150,0 140,0 130,0 120,0 110,0 100,0 90,0 80,0 70,0 60,0 50,0 40,0 30,0 20,0 10,0 0 −10,0 −20,0 −30,0 −40,0 −50,0 −60,0 −70,0 −80,0 −90,0 −100,0 −110,0
34.0594
X : parts per Million : 31P

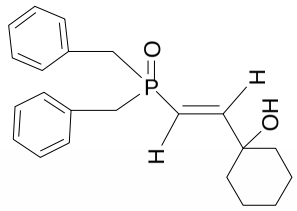

X : parts per Million : 1H
7.3058
7.2806
7.2325
7.2268
10.259
6.6076
6.5504
6.5275
6.4897
1.043
5.6530
5.5958
5.5569
5.5008
1
3.1556
3.1441
3.1041
3.0972
4.101
2.1358
2.1117
2.0888
2.0431
2.508
1.2567
1.2132
1.2018
1.1869
0.9775
0.8985
0.8767
0.8527
8.09
2.873
0.0000
3f
H
O
H


X : parts per Million : 13C
153.7050
131.9737
131.8781
129.8990
129.8321
128.6179
128.5892
126.8109
126.7727
120.1567
118.8852
77.4207
77.0000
76.5793
37.7536
36.9027
34.4647
34.2544
31.5487
28.5754
27.7532
22.5044
14.0528
3f
H
O
H

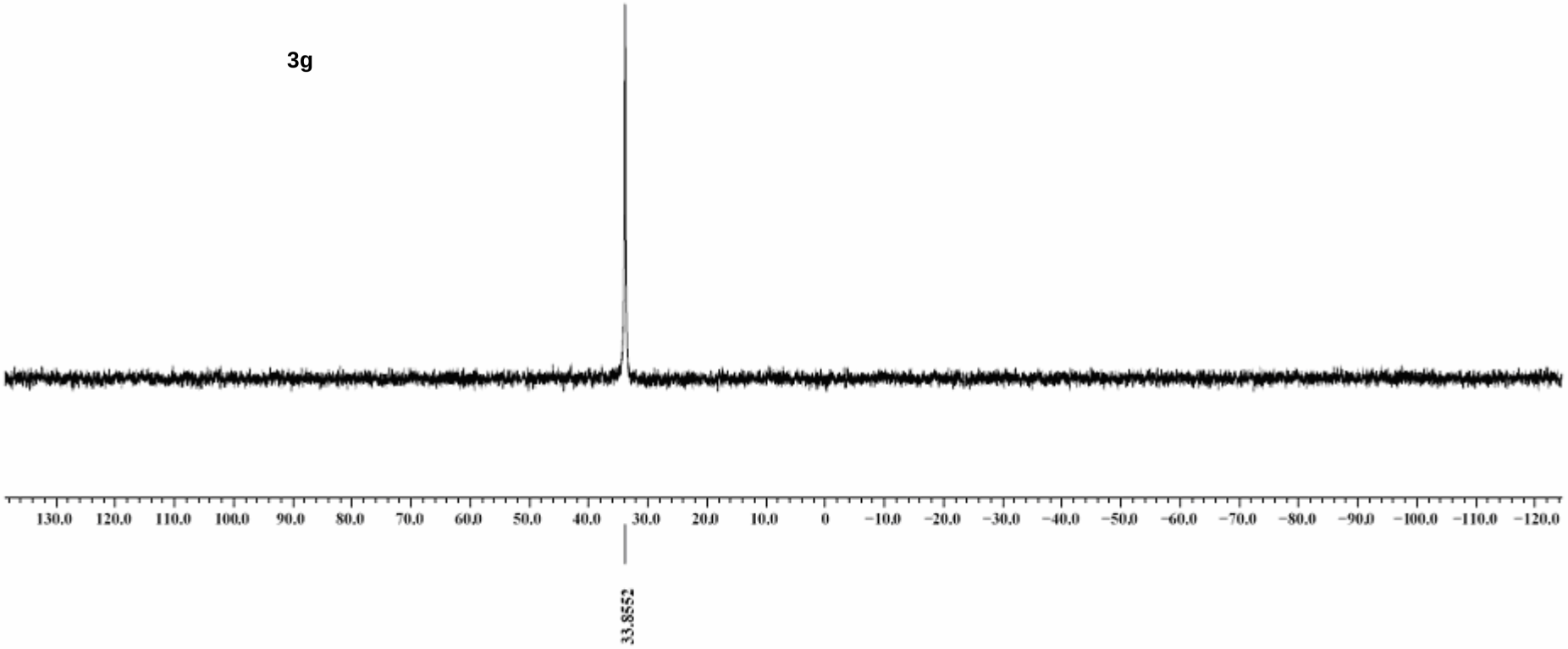

O
P
H
H
3f
150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0 −50.0 −60.0 −70.0 −80.0 −90.0 −100.0 −110.0 −120.0
33.0863
X : parts per Million : 31P


X : parts per Million : 1H
7.2783
7.2577
7.2165
10.377
6.6179
6.5607
6.5023
1.0
6.0170
5.9586
5.9300
5.8762
0.846
3.1453
3.1052
4.092
2.3097
0.82
1.5440
1.5188
1.4216
1.4101
1.3803
1.2590
1.2190
10.337
0.0000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3g
P
O
H
H
OH

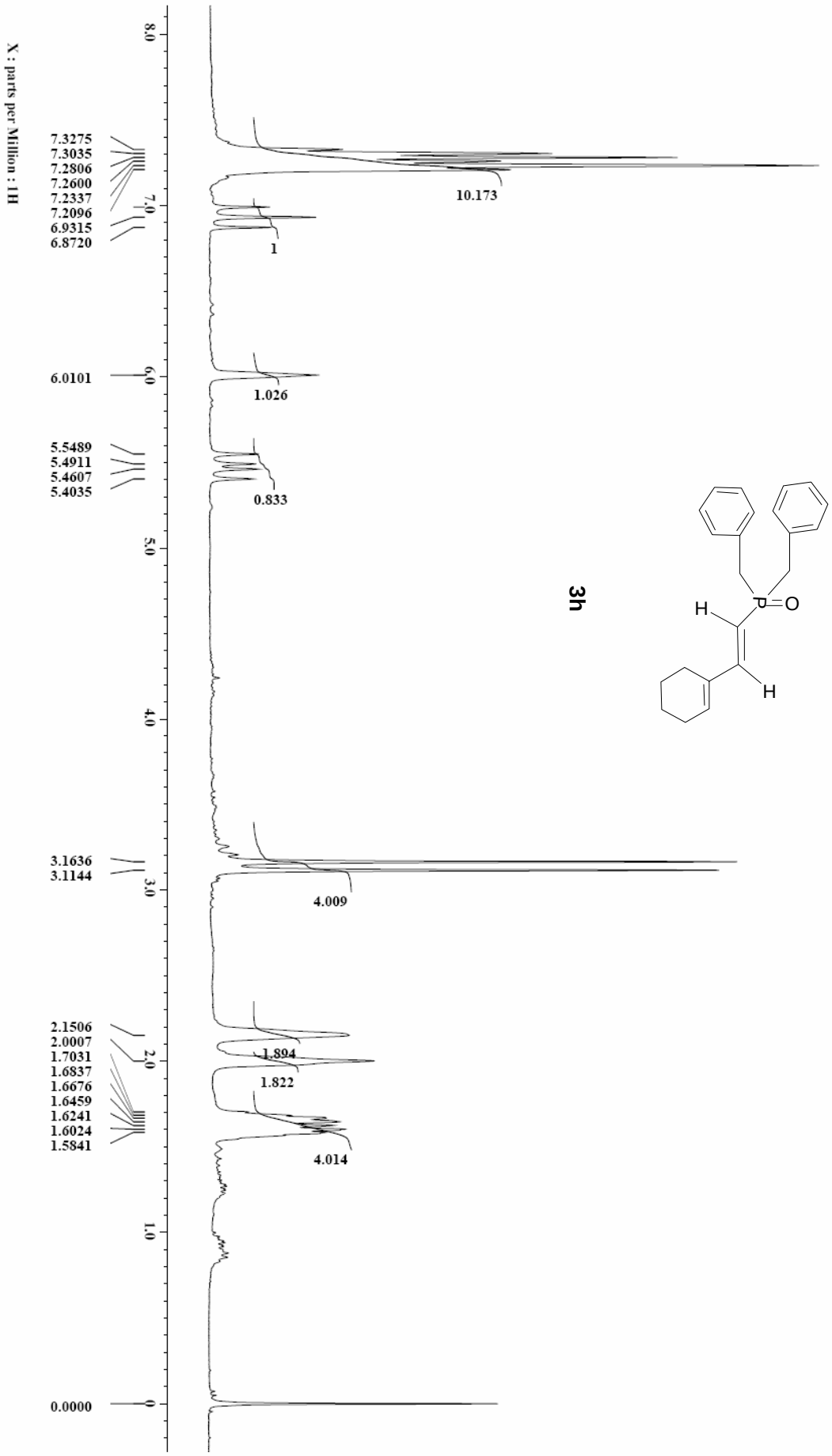

X : parts per Million : 13C
159.1259
131.7442
131.6582
129.8703
128.5031
126.7344
117.2598
115.9309
77.4207
77.0000
76.5793
72.5065
72.3249
37.6580
36.7497
25.0762
21.4336
3g
H
P
O
H
OH

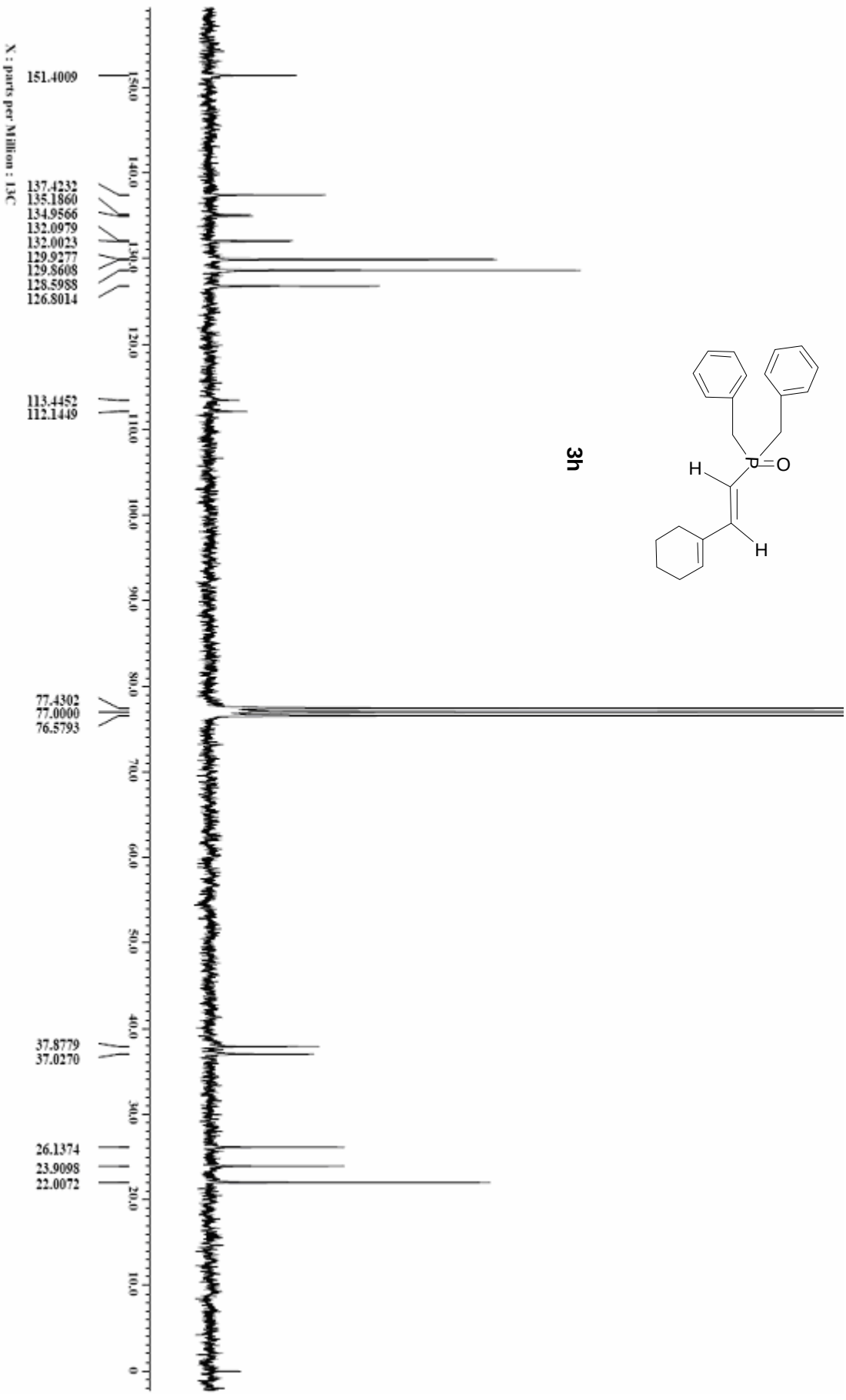


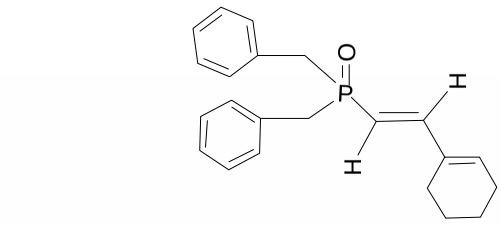
3g



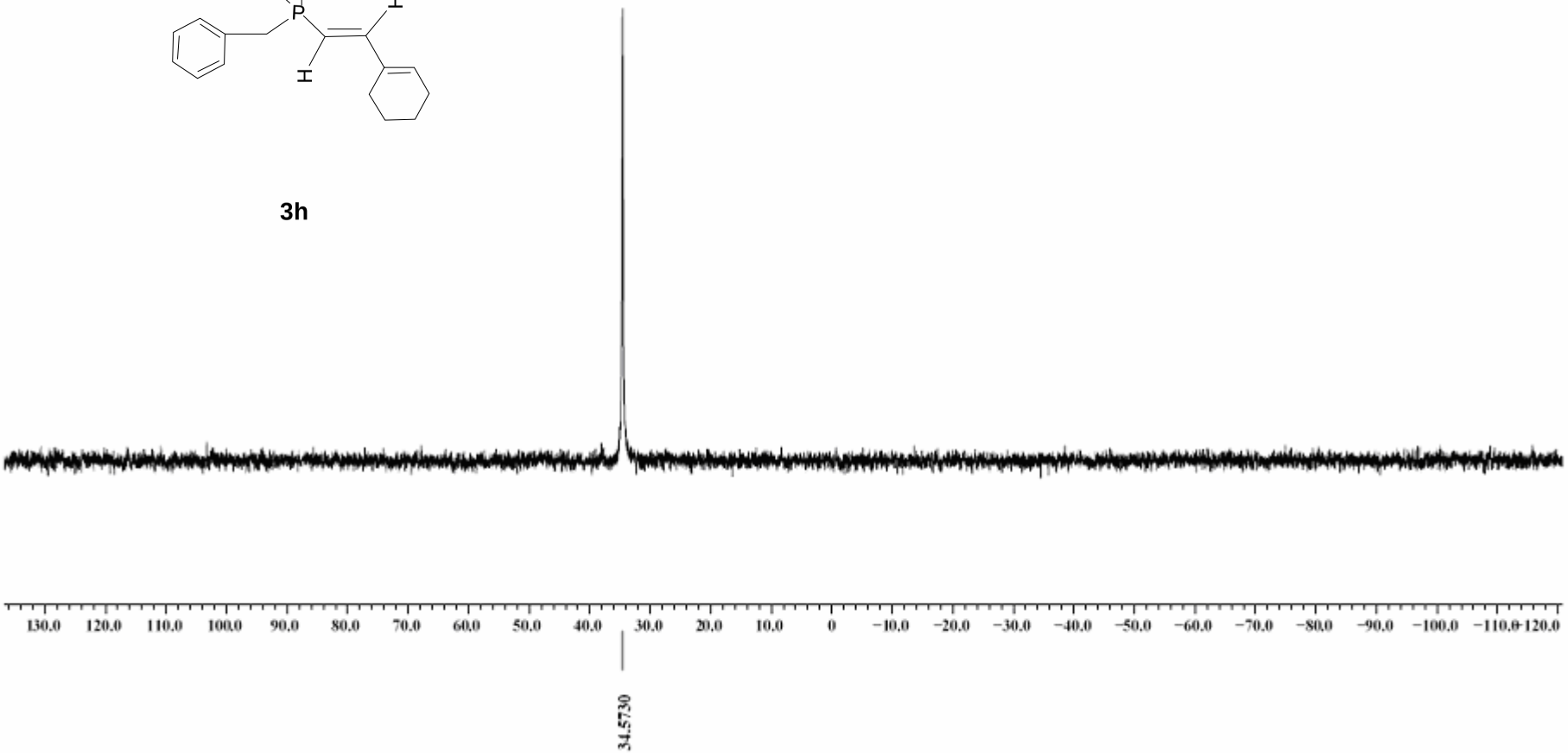
X : parts per Million : 31P

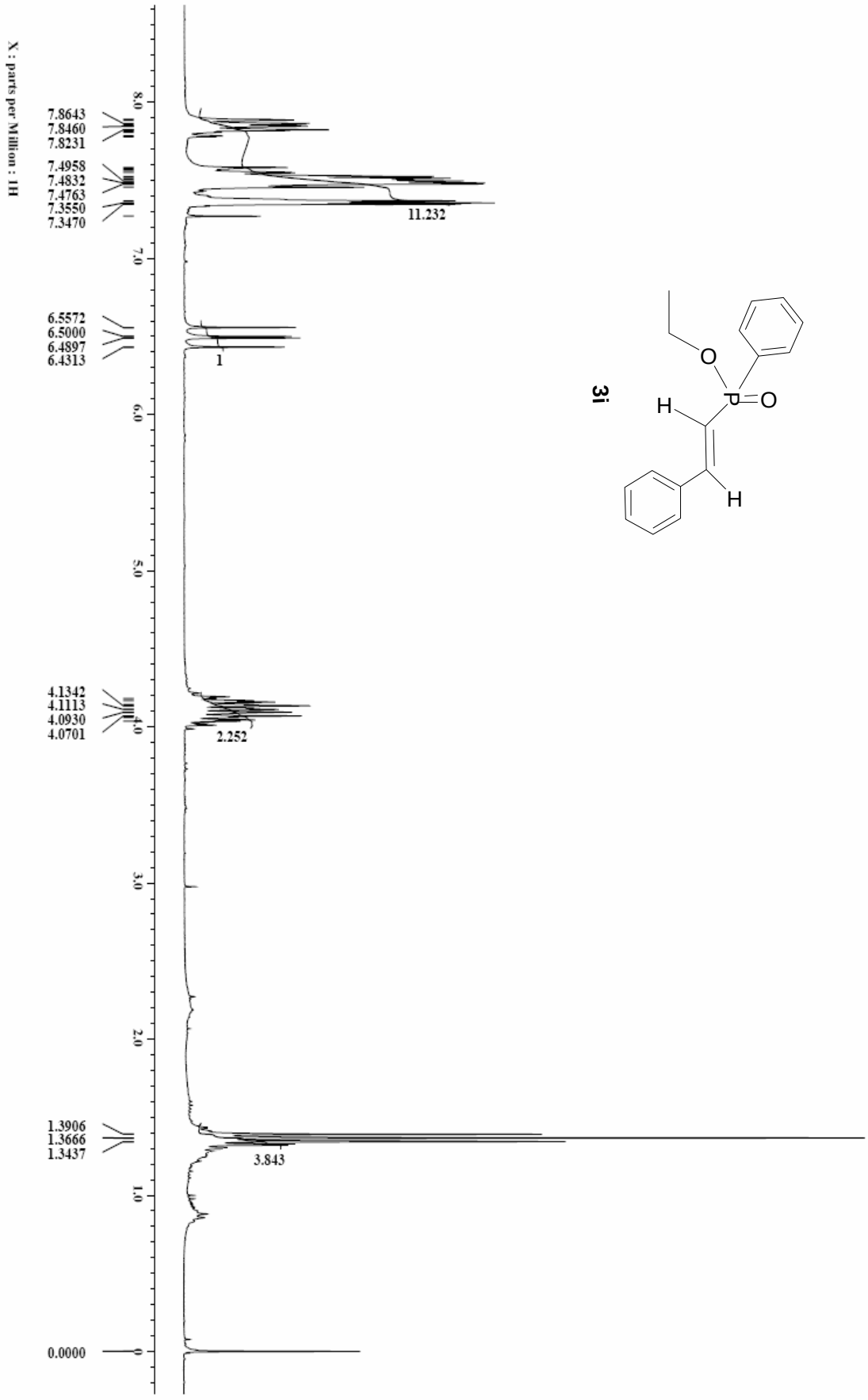

X : parts per Million : 1H
7.3275
7.3035
7.2806
7.2600
7.2337
7.2096
6.9315
6.8720
6.0101
5.5489
5.4911
5.4607
5.4035
3.1636
3.1144
2.1506
2.0007
1.7031
1.6837
1.6676
1.6459
1.6241
1.6024
1.5841
0.0000
10.173
1
1.026
0.833
4.009
1.894
1.822
4.014
3h
H
P
O
H

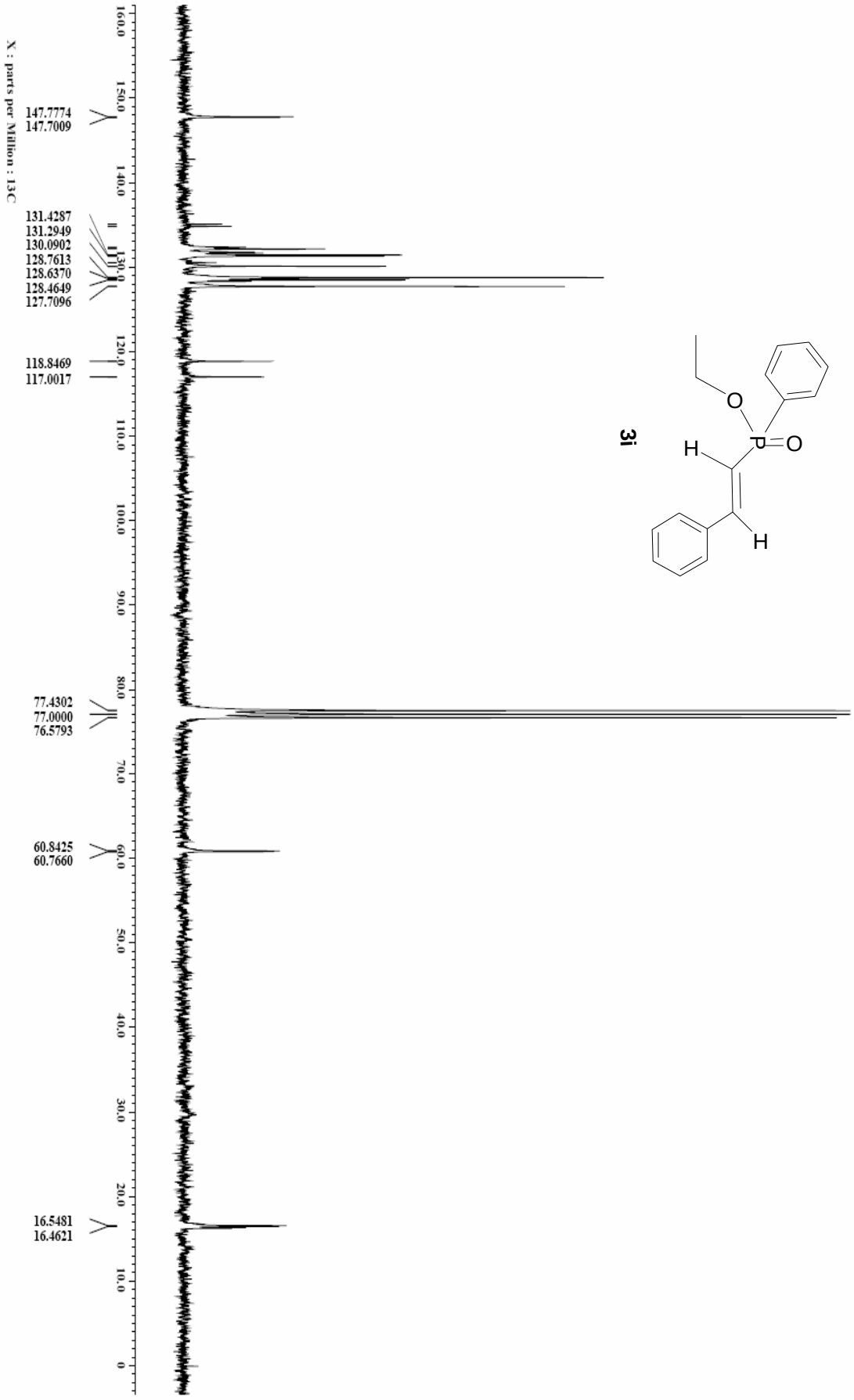

X : parts per Million : 13C
151.4009
137.4232
135.1860
134.9566
132.0979
132.0023
129.9277
129.8608
128.5988
126.8014
113.4452
112.1449
77.4302
77.0000
76.5793
37.8779
37.0270
26.1374
23.9098
22.0072
3h
H
O
H

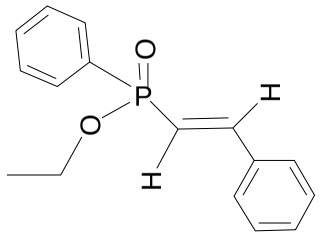

O
P
H
H

3h

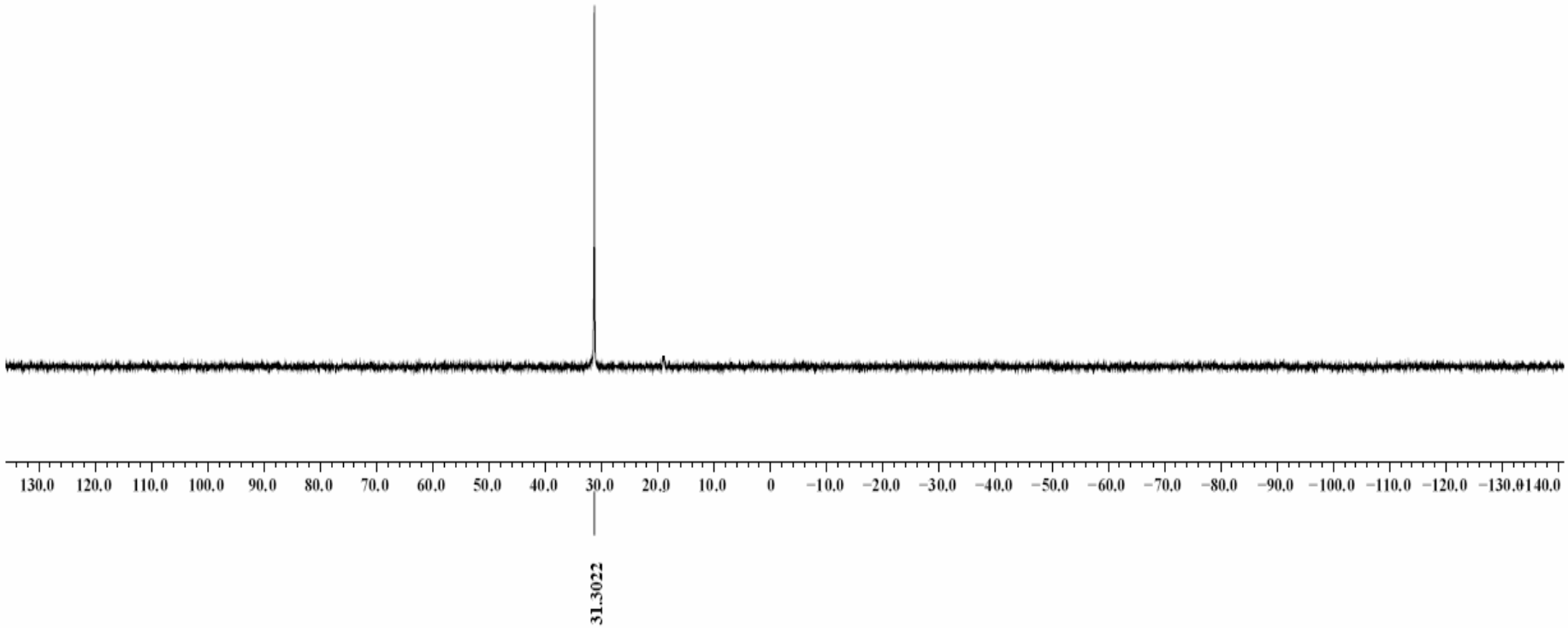

130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
−60.0
−70.0
−80.0
−90.0
−100.0
−110.0
−120.0
34.5730
X : parts per Million : 31P


X : parts per Million : 1H
7.8643
7.8460
7.8231
7.4958
7.4832
7.4763
7.3550
7.3470
11.232
6.5572
6.5000
6.4897
6.4313
1
4.1342
4.1113
4.0930
4.0701
2.252
1.3906
1.3666
1.3437
3.843
0.0000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3i
O
P
O
H
H

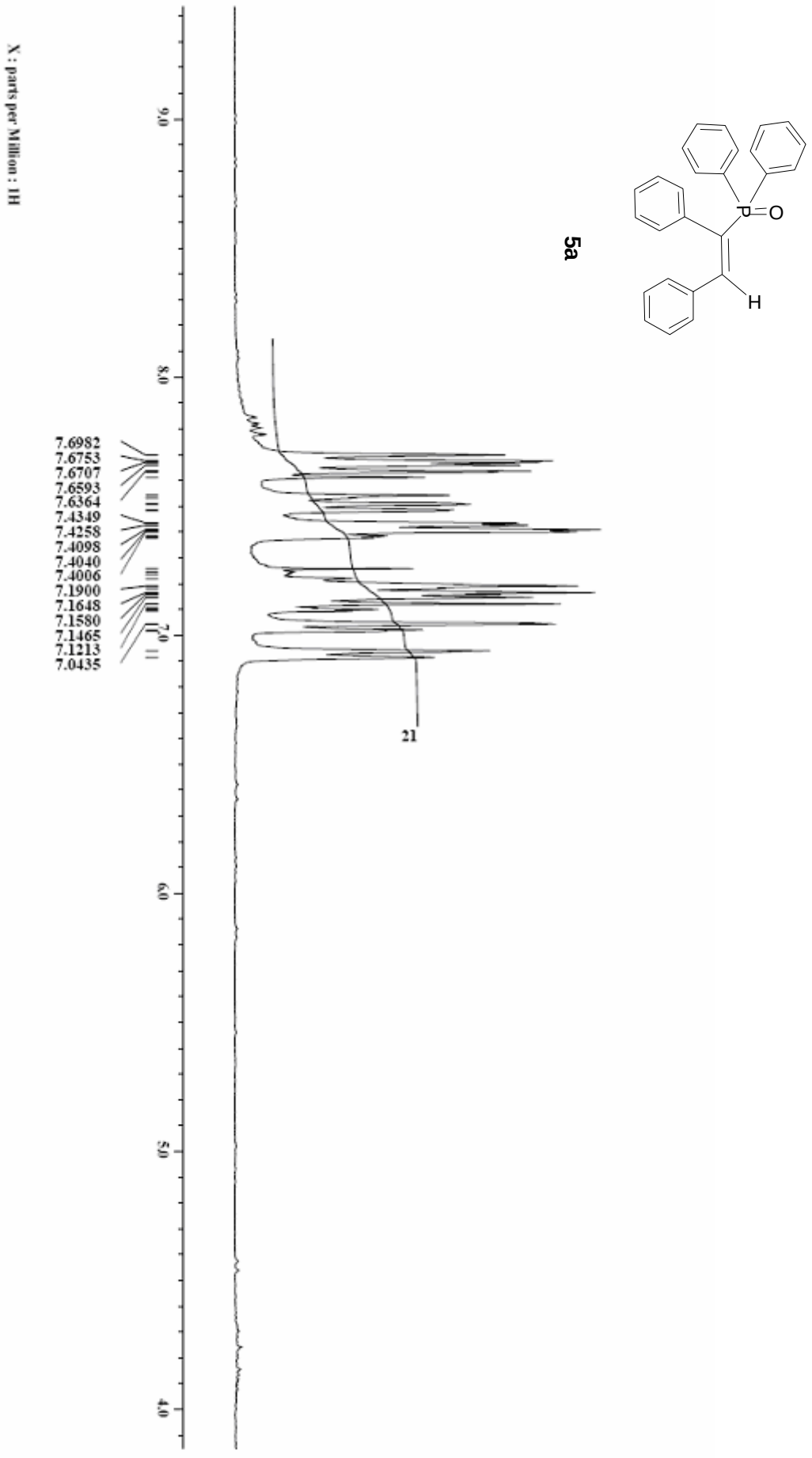

X : parts per Million : 13C
147.7774
147.7009
131.4287
131.2949
130.0902
128.7613
128.6370
128.4649
127.7096
118.8469
117.0017
77.4302
77.0000
76.5793
60.8425
60.7660
16.5481
16.4621
3i
O
P
O
H
H

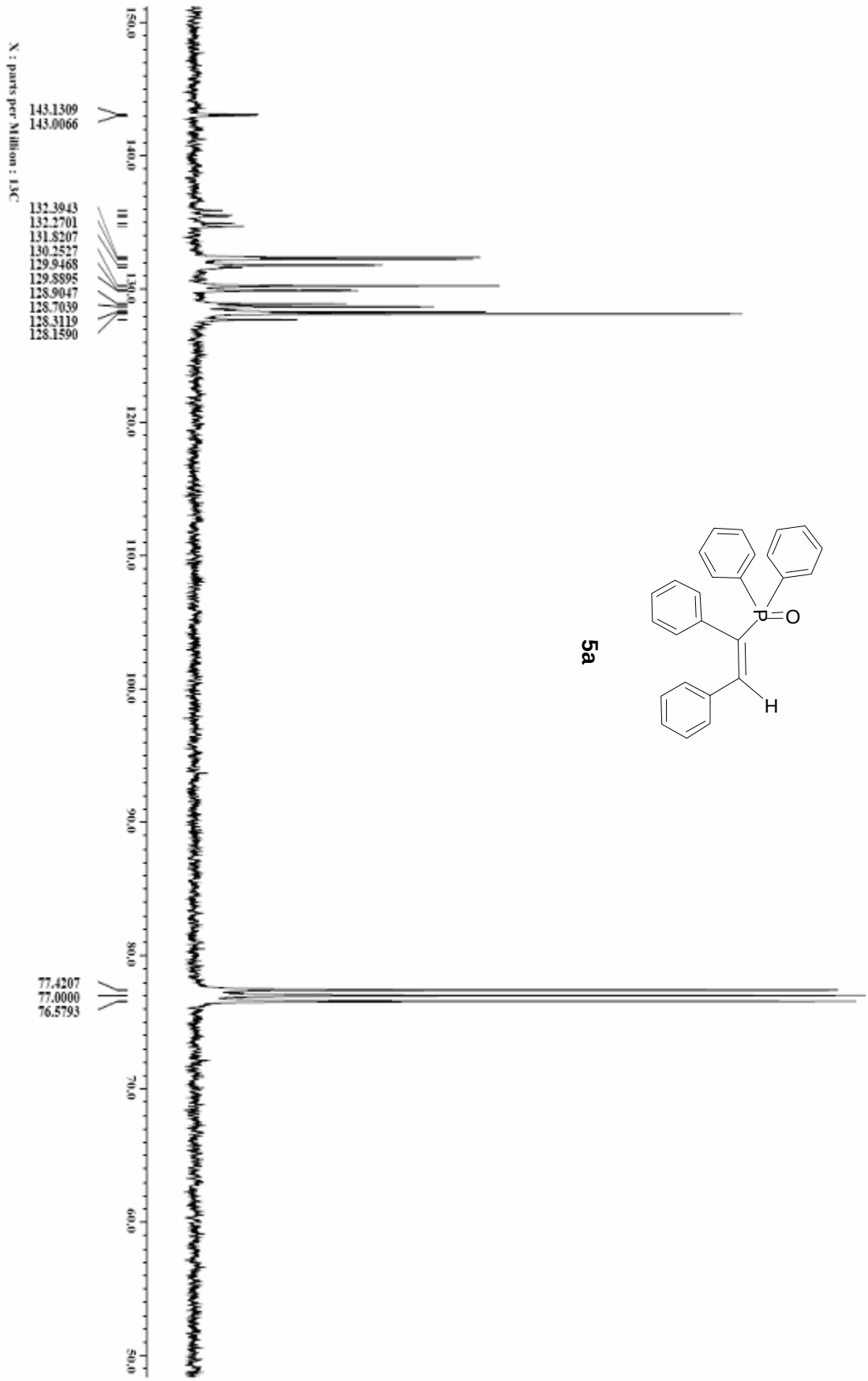


3i

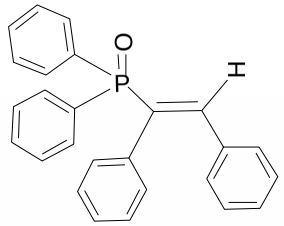


X : parts per Million : 31P

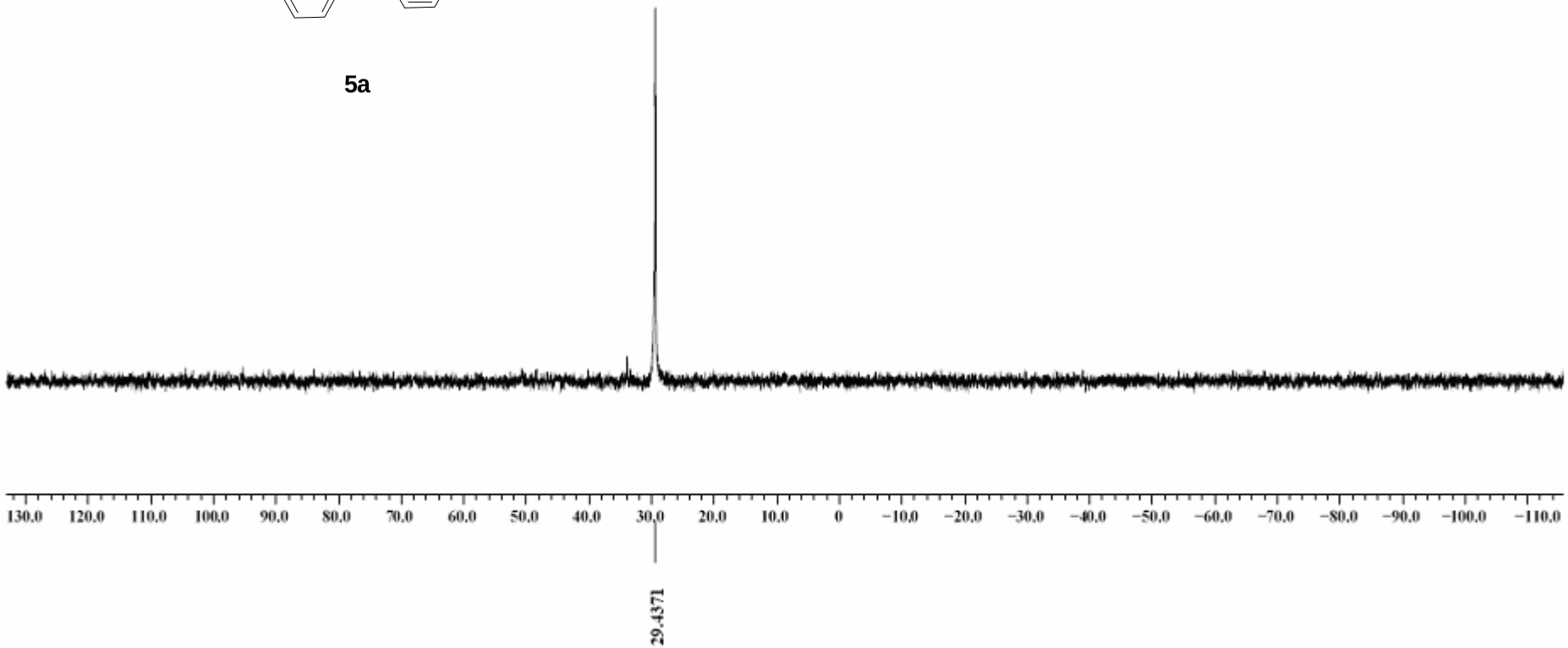

X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
7.6982
7.6753
7.6707
7.6593
7.6364
7.4349
7.4258
7.4098
7.4040
7.4006
7.1900
7.1648
7.1580
7.1465
7.1213
7.0435
21
5a
P
O
H


X : parts per Million : 13C
143.1309
143.0066
132.3943
132.2701
131.8207
130.2527
129.9468
129.8895
128.9047
128.7039
128.3119
128.1590
77.4207
77.0000
76.5793
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
P
O
H

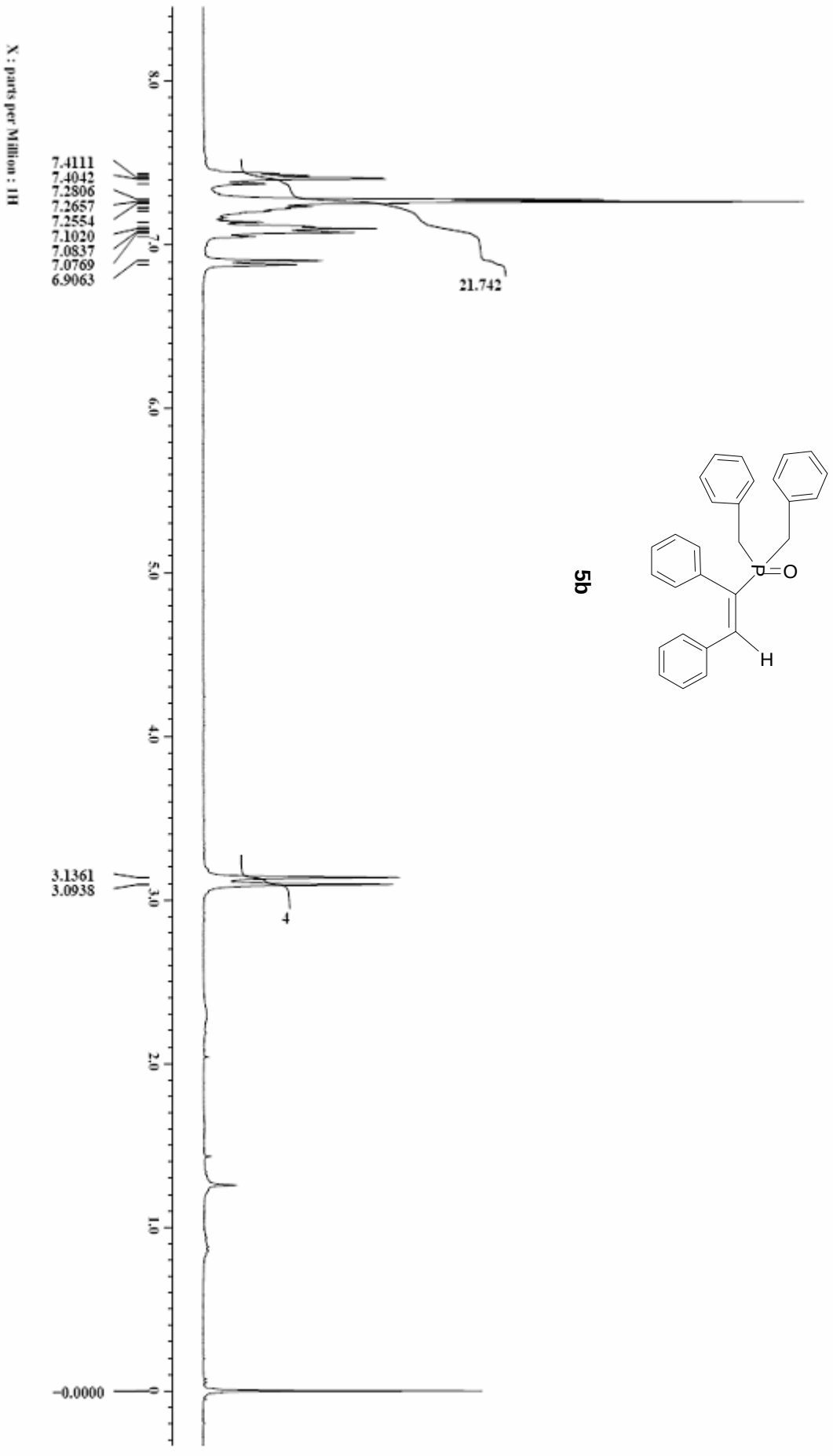
5a



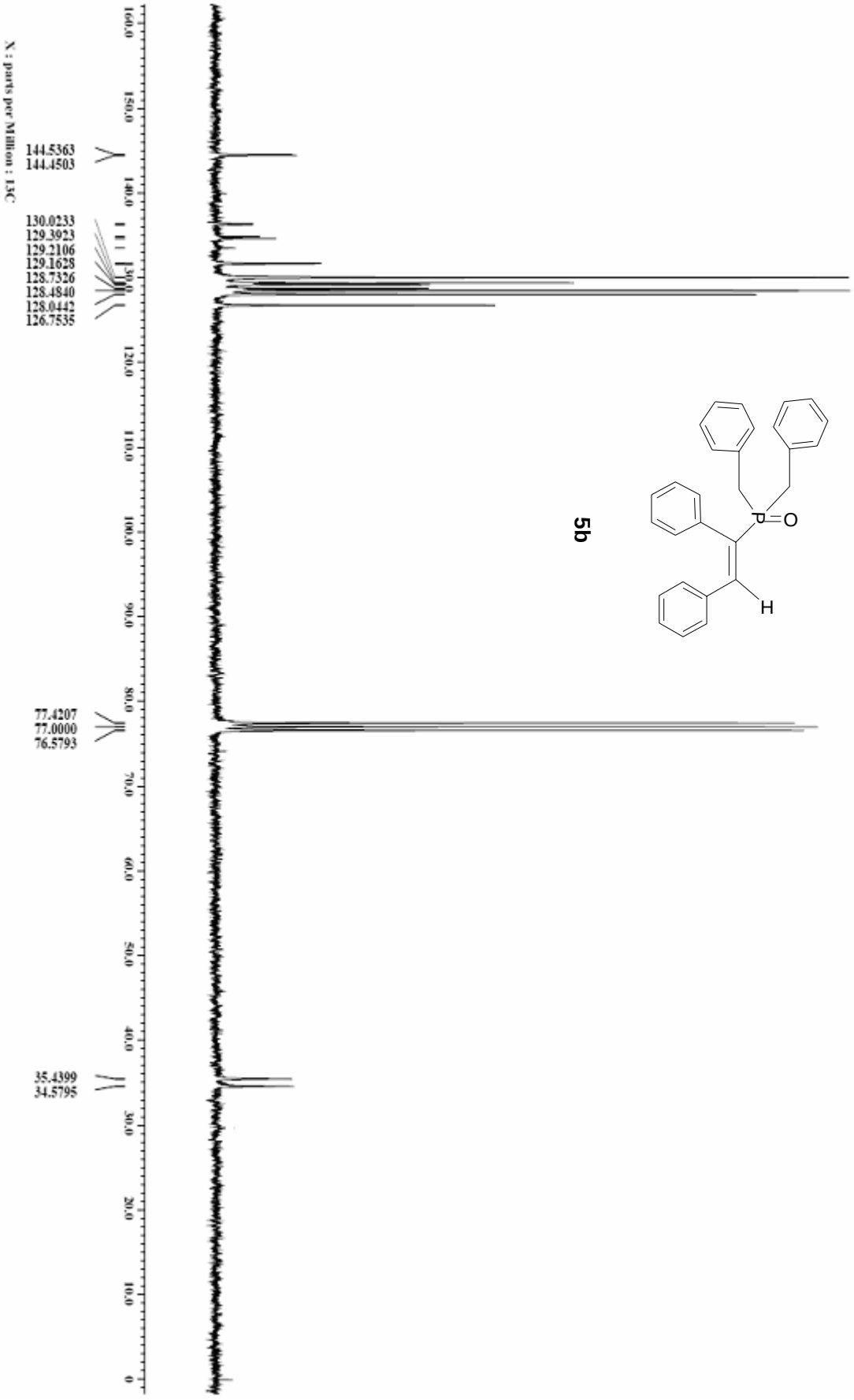
5a



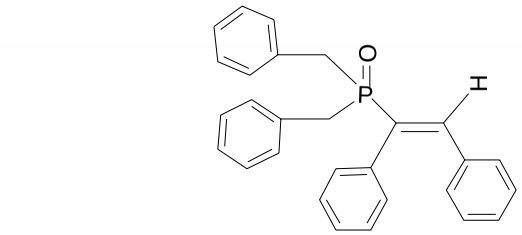
X : parts per Million : 31P


X : parts per Million : 1H
7.4111
7.4042
7.2806
7.2657
7.2554
7.1020
7.0837
7.0769
6.9063
21.742
3.1361
3.0938
4
−0.0000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
P
O
H

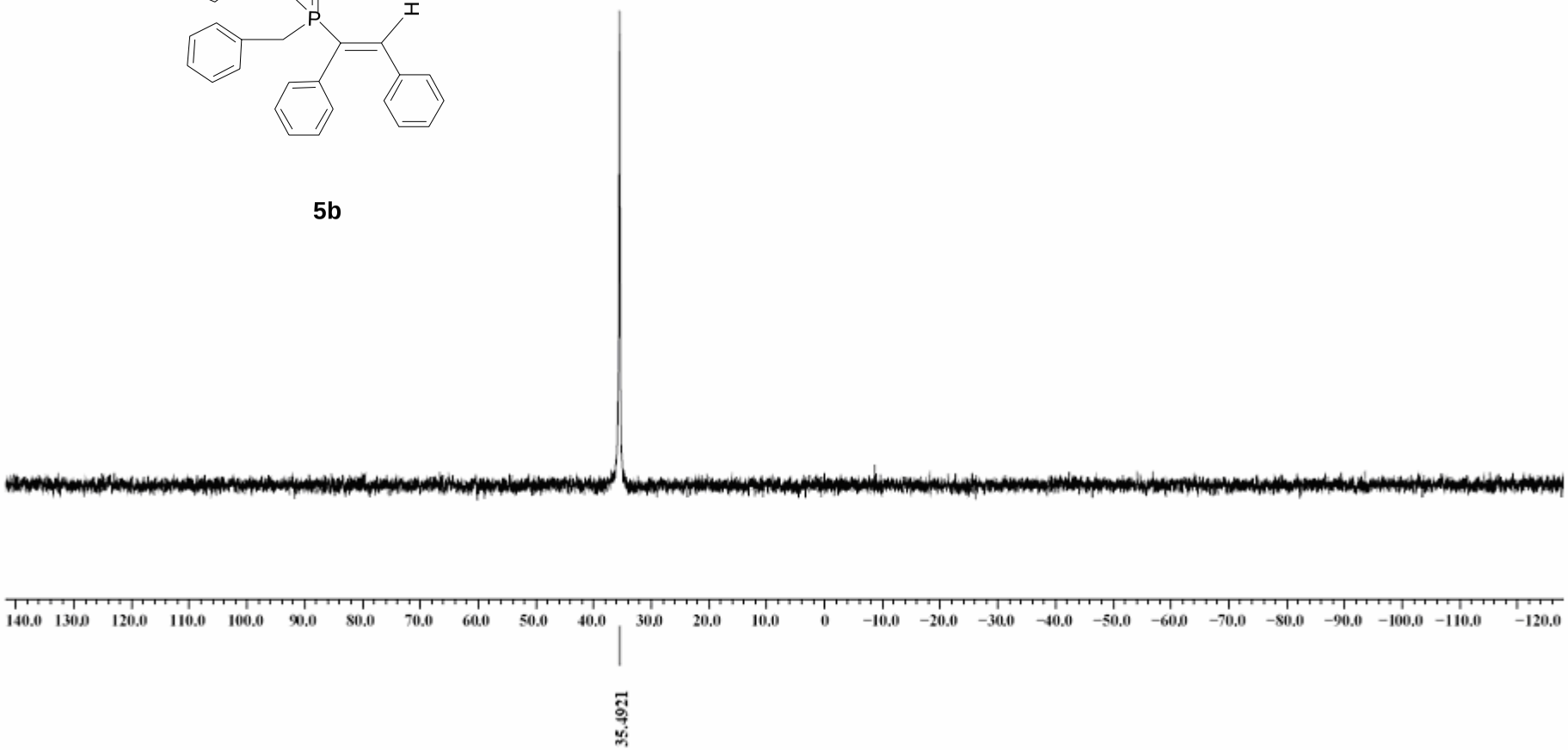
5b


X : parts per Million : 13C
144.5363
144.4503
130.0233
129.3923
129.2106
129.1628
128.7326
128.4840
128.0442
126.7535
77.4207
77.0000
76.5793
35.4399
34.5795
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
P
O
H

5b



5b


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 −10.0 −20.0 −30.0 −40.0 −50.0 −60.0 −70.0 −80.0 −90.0 −100.0 −110.0 −120.0
35.4921
X : parts per Million : 31P