Supporting Information

Metal-free site selective cross-coupling of pyridines with secondary phosphine chalcogenides using acylacetylenes as oxidants

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General information

All reactions were carried out under an argon atmosphere. Pyridines **1a**,**b** and diphenylphosphine oxide **2a** are commercial reagents (Alfa Aesar). Diphenylphosphine sulfide **2e** was prepared by oxidation of commercially available diphenylphosphine (Aldrich) with elemental sulfur.[1] Secondary phosphine chalcogenides **2b-d,f-j** were prepared from styrene, 4-chlorostyrene, α-methylstyrene and elemental phosphorus as previously described.[2] Acylacetylenes **3a-d** were prepared by the reported methods.[3] The reaction was monitored using ^{31}P NMR spectra by the disappearance of peaks of the initial secondary phosphine chalcogenides.

The ^{1}H, ^{13}C, ^{15}N, ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometer (400.13, 100.62, 40.56, 161.98 and 76.31 MHz, respectively) in $CDCl_3$ solutions and referenced to HMDS (^{1}H, ^{13}C), $MeNO_2$ (^{15}N), H_3PO_4 (^{31}P) and Me_2Se (^{77}Se). The assignment of signals in ^{1}H spectra was performed using 2D homonuclear correlation method COSY. Resonance signals of ^{13}C were assigned with application of 2D heteronuclear correlation methods HSQC and HMBC. The values of the δ ^{15}N were measured through the 2D ^{1}H–^{15}N HMBC experiment. FT-IR spectra were obtained with a Varian 3100 FT-IR spectrometer. The C, H, N microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The Cl, P, S and Se content were determined by combustion method.

[1] Peters, G. *J. Am. Chem. Soc.* **1960,** *82,* 4751–4751.

[2] (a) Trofimov, B. A.; Brandsma, L.; Arbuzova, S. N.; Malysheva, S. F.; Gusarova, N. K. *Tetrahedron Lett.* **1994,** *35,* 7647–7650. (b) Gusarova, N. K.; Bogdanova, M. V.; Ivanova, N. I.; Chernysheva, N. A.; Sukhov, B. G.; Sinegovskaya, L. M.; Kazheva, O. N.; Alexandrov, G. G.; D'yachenko, O. A.; Trofimov, B. A. *Synthesis* **2005,** 3103–3106. (c) Sukhov, B. G.; Gusarova, N. K.; Ivanova, N. I.; Bogdanova, M. V.; Kazheva, O. N.; Alexandrov, G. G.; Dyachenko, O. A.; Sinegovskaya, L. M.; Malysheva, S. F.; Trofimov, B. A. *J. Struct. Chem.* **2005,** *46,* 1066–1071. (d) Malysheva, S. F.; Artem'ev, A. V.; Gusarova, N. K.; Timokhin, B. V.; Tatarinova, A. A.; Trofimov, B. A. *Russ. J. Gen. Chem.* **2009,** *79,* 1617–1621. (e) Gusarova, N. K.; Arbuzova, S. N.; Trofimov, B. A. *Pure Appl. Chem.* **2012,** *84,* 439–459. (f) Artemrev, A. V.; Malysheva, S. F.; Gusarova, N. K.; Korocheva, A. O.; Timokhina, L. V.; Trofimov, B. A**.** *Russ. Chem. Bull.* **2013,** *62,* 2495–2497.

[3] (a) Zanina, A. S.; Shergina, S. I.; Sokolov, I. E.; Myasnikova, R. N. *Russ. Chem. Bull.* **1995,** *44,* 689–694. (b) Zhang, X.; Lu, Z.; Fu, C.; Ma, S. *Org. Biomol. Chem.* **2009,** *7,* 3258–3263. (c) Whittaker, R. E.; Dermenci, A.; Dong, G. *Synthesis* **2016,** *48,* 161–183.

Typical procedure

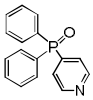
Synthesis of 4-chalcogenophosphoryl pyridines 4a-j, 6a-d: General procedure. A solution of pyridine **1a**,**b** (1.1 mmol), secondary phosphine chalcogenide **2a-j** (1.0 mmol) and acylacetylene **3a-d** (1.1 mmol) in MeCN (3 mL) was stirred under an argon atmosphere at 70–75 °C for 20–70 h (see also Table 1, Schemes 2 and 3). After completion of the reaction (^{31}P NMR monitoring), the solvent was removed under the reduced pressure. The obtained residue was purified by column chromatography on SiO_2 (for pyridines **4a-d, 6a-d**: ethylacetate; for pyridines **4e-j**: toluene/Et_2O, 1:2) to yield the target 4-chalcogenophosphoryl pyridine **4a-j, 6a-d** and a mixture of the unreacted acetylene **3a-d** and ethene **5a-d**.

Ethenes **5a,b** were characterized (^{1}H NMR) in a mixture with **3a,b** (10–15%), whereas **5c,d** were isolated individually by recrystallization of the crude product from hexane. For secondary phosphine selenides **2i,j**, divinyl selenides **7**[4] were also identified in the reaction mixture. Therefore the fraction of acetylene **3a-d** and ethene **5a-d,** obtained from SiO_2 column, was purified by column chromatography on neutral Al_2O_3 via consecutive washing with a mixture of hexane/Et_2O (9:1) to separate acetylene **3a-d** and ethene **5a-d**, then with chloroform to collect divinyl selenides **7**.

[4] Volkov, P. A.; Gusarova, N. K.; Khrapova, K. O.; Telezhkin, A. A.; Ivanova, N. I.; Albanov, A. I.; Trofimov, B. A. *J. Organomet. Chem.* **2017,** DOI: 10.1016/j.jorganchem.2017.09.031.

Analytical data

4-(Diphenylphosphoryl)pyridine (4a).[5]



Yield: 159 mg (57%); beige powder, mp 150–151 °C (published data[5]: 153–155 °C) (reprecipitated from CCl_4 to hexane).

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 7.57 (m, 12H, Ph; $H_{3,5}$, Py), 8.74 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 125.8 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 7.7 Hz), 128.9 (d, C_m, $^3J_{CP}$ = 12.3 Hz), 131.0 (d, C_i, $^1J_{CP}$ = 105.3 Hz), 132.0 (d, C_o, $^2J_{CP}$ = 10.0 Hz), 132.6 (C_p), 142.2 (d, C_4, Py, $^1J_{CP}$ = 96.7 Hz), 150.0 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 9.5 Hz).

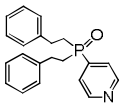
^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -58.9.

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 27.6.

IR (neat): ν_{max} = 3056, 2980, 1674, 1584, 1540, 1484, 1437, 1402, 1316, 1256, 1196, 1123, 1073, 1025, 996, 812, 751, 727, 697, 546 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}NOP$: C, 73.11; H, 5.05; N, 5.02; P, 11.09. Found: C, 73.02; H, 5.22; N, 4.98; P, 10.93.

4-[Bis(2-phenylethyl)phosphoryl]pyridine (4b).



Yield: 228 mg (68%); yellow powder, mp 81–82 °C (reprecipitated from CCl_4 to hexane).

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.16, 2.33 (m, 4H, CH_2P), 2.71, 2.98 (m, 4H, $PhCH_2$), 7.09 (m, 4H, H_o), 7.15 (m, 2H, H_p), 7.22 (m, 4H, H_m), 7.56 (m, 2H, $H_{3,5}$, Py), 8.73 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 27.4 (d, $PhCH_2$, $^2J_{CP}$ = 3.2 Hz), 31.6 (d, CH_2P, $^1J_{CP}$ = 66.5 Hz), 124.4 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 7.0 Hz), 126.6 (C_p), 128.1 (C_o), 128.7 (C_m), 140.3 (d, C_i, $^3J_{CP}$ = 13.5 Hz), 141.8 (d, C_4, Py, $^1J_{CP}$ = 84.8 Hz), 150.1 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 8.8 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -60.2.

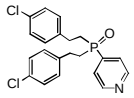
^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 37.2.

IR (neat): ν_{max} = 3028, 2949, 2864, 1668, 1589, 1542, 1495, 1450, 1404, 1321, 1181, 1127, 1072, 1025, 997, 941, 913, 810, 754, 701, 669, 588, 518 cm^{-1}.

Anal. Calcd for $C_{21}H_{22}NOP$: C, 75.21; H, 6.61; N, 4.18; P, 9.24. Found: C, 75.42; H, 6.56; N, 4.03; P, 9.11.

[5] Weiner, M. A.; Schxartr, P. *Inorg. Chem.* **1975,** *14,* 1714–1716.

4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}pyridine (4c).



Yield: 194 mg (48%); light-yellow powder, mp 132–133 °C (hexane-MeCN).

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.14, 2.31 (m, 4H, CH_2P), 2.69, 2.96 (m, 4H, $PhCH_2$), 7.04 (d, 4H, H_o, $^3J_{HH}$ = 8.4 Hz), 7.20 (d, 4H, H_m, $^3J_{HH}$ = 8.4 Hz), 7.55 (m, 2H, $H_{3,5}$, Py), 8.77 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 25.2 (d, $PhCH_2$, $^2J_{CP}$ = 2.2 Hz), 29.9 (d, CH_2P, $^1J_{CP}$ = 66.5 Hz), 122.7 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 6.8 Hz), 127.2 (C_o), 127.9 (C_m), 130.9 (C_p), 137.1 (d, C_i, $^3J_{CP}$ = 13.3 Hz), 139.9 (d, C_4, Py, $^1J_{CP}$ = 85.3 Hz), 148.6 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 8.9 Hz).

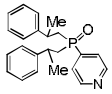
^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -59.6.

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 37.4.

IR (neat): n_{max} = 3036, 2925, 2862, 1663, 1641, 1587, 1491, 1446, 1405, 1320, 1268, 1209, 1181, 1127, 1093, 1012, 928, 844, 809, 774, 731, 653, 516 cm^{-1}.

Anal. Calcd for $C_{21}H_{20}Cl_2NOP$: C, 62.39; H, 4.99; Cl, 17.54; N, 3.46; P, 7.66. Found: C, 62.34; H, 4.85; Cl, 17.87; N, 3.35; P, 7.47.

4-[Bis(2-phenylpropyl)phosphoryl]pyridine (4d).



Yield: 200 mg (55%); waxy product. The product is a mixture of three stereoisomers in a ratio of 10:5:3 (^{1}H and ^{31}P NMR data).

IR (neat): n_{max} = 3056, 3029, 2963, 2927, 2871, 1734, 1713, 1625, 1589, 1492, 1452, 1404, 1317, 1288, 1189, 1123, 1093, 1027, 911, 839, 814, 767, 700, 598, 526 cm^{-1}.

Anal. Calcd for $C_{23}H_{26}NOP$: C, 76.01; H, 7.21; N, 3.85; P, 8.52. Found: C, 75.85; H, 7.10; N, 3.90; P, 8.37.

***R,R(S,S)*-stereoisomer (major)**.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.20, 1.23 (d, 6H, Me, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 7.1 Hz), 1.84, 2.07, 2.15 (m, 4H, CH_2P), 2.92, 3.38 (m, 2H, PhC<u>H</u>(Me)), 6.78–7.20 (m, 10H, Ph), 7.05 (m, 2H, $H_{3,5}$, Py), 8.50 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 23.82, 24.09 (2d, Me, $^3J_{CP}$ = 8.7 Hz, $^3J_{CP}$ = 9.2 Hz), 33.98, 34.14 (2d, Ph<u>C</u>H(Me), $^2J_{CP}$ = 3.2 Hz, $^2J_{CP}$ = 3.7 Hz), 38.66, 39.92 (2d, CH_2P, $^1J_{CP}$ = 66.3 Hz, $^1J_{CP}$ = 67.1 Hz), 124.29 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 7.2 Hz), 126.56, 126.84 (C_p), 126.69, 126.90 (C_o), 128.30, 128.77 (C_m), 143.51 (d, C_4, Py, $^1J_{CP}$ = 84.6 Hz), 145.32, 146.05 (2d, C_i, $^3J_{CP}$ = 7.5 Hz, $^3J_{CP}$ = 7.1 Hz), 149.12 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 9.0 Hz).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 35.3.

***R,S(S,R)R*$_p$- and *R,S(S,R)S*$_p$-stereoisomers:**

Medium. ^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.10 (d, 6H, Me, $^3J_{HH}$ = 6.9 Hz), 1.95, 2.07 (m, 4H, CH_2P), 3.17 (m, 2H, PhC<u>H</u>(Me)), 7.45 (m, 2H, $H_{3,5}$, Py), 8.66 (m, 2H, $H_{2,6}$, Py). The signals of the phenyl ring were overlapped with those of other stereoisomers.

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 23.54 (d, Me, $^3J_{CP}$ = 7.5 Hz), 34.01 (d, Ph<u>C</u>H(Me), $^2J_{CP}$ = 3.9 Hz), 37.91 (d, CH_2P, $^1J_{CP}$ = 66.6 Hz), 124.11 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 7.6 Hz), 126.68 (C_o), 126.75 (C_p), 128.62 (C_m), 144.85 (d, C_4, Py, $^1J_{CP}$ = 75.9 Hz), 145.98 (d, C_i, $^3J_{CP}$ = 9.9 Hz), 149.65 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 9.0 Hz).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 34.4.

M**inor**. ^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.33 (d, 6H, Me, $^3J_{HH}$ = 6.9 Hz), 2.07, 2.26 (m, 4H, CH_2P), 3.05 (m, 2H, PhC<u>H</u>(Me)), 7.03 (m, 2H, $H_{3,5}$, Py), 8.32 (m, 2H, $H_{2,6}$, Py). The signals of the phenyl ring were overlapped with those of other stereoisomers.

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 24.02 (d, Me, $^3J_{CP}$ = 8.9 Hz), 34.06 (d, Ph<u>C</u>H(Me), $^2J_{CP}$ = 3.9 Hz), 39.41 (d, CH_2P, $^1J_{CP}$ = 67.3 Hz), 124.57 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 6.8 Hz), 126.64 (C_p), 126.75 (C_o), 128.36 (C_m), 142.30 (d, C_4, Py, $^1J_{CP}$ = 85.1 Hz), 145.24 (d, C_i, $^3J_{CP}$ = 7.1 Hz), 148.44 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 8.5 Hz).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 35.9.

4-(Diphenylphosphorothioyl)pyridine (4e).[6]

Yield: 133 mg (45%); beige powder, mp 127–128 °C (reprecipitated from CCl_4 to hexane).

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 7.60 (m, 12H, Ph; $H_{3,5}$, Py), 8.72 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 125.9 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 7.8 Hz), 128.9 (d, C_m, $^3J_{CP}$ = 12.7 Hz), 131.3 (d, C_i, $^1J_{CP}$ = 86.0 Hz), 132.2 (C_p), 132.3 (d, C_o, $^2J_{CP}$ = 10.8 Hz), 143.4 (d, C_4, Py, $^1J_{CP}$ = 78.3 Hz), 149.9 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 9.5 Hz).

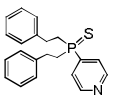
^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -59.7.

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 42.8.

IR (neat): n_{max} = 3054, 2955, 2925, 2857, 1677, 1578, 1541, 1480, 1436, 1401, 1313, 1183, 1107, 1074, 1026, 995, 913, 810, 720, 696, 641, 519 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}NPS$: C, 69.13; H, 4.78; N, 4.74; P, 10.49; S, 10.86. Found: C, 69.24; H, 4.65; N, 4.69; P, 10.37; S, 10.72.

4-[Bis(2-phenylethyl)phosphorothioyl]pyridine (4f).



[6] Burns, M. J.; Rayner, P. J.; Green, G. G. R.; Highton, L. A. R.; Mewis, R. E.; Duckett, S. B. *J. Phys. Chem. B.* **2015,** *119,* 5020−5027.

Yield: 250 mg (71%); brown powder, mp 83–84 °C (reprecipitated from CCl_4 to hexane).

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.38 (m, 4H, CH_2P), 2.68, 3.02 (m, 4H, $PhCH_2$), 7.09 (m, 4H, H_o), 7.16 (m, 2H, H_p), 7.21 (m, 4H, H_m), 7.69 (m, 2H, $H_{3,5}$, Py), 8.72 (br s, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 28.3 (d, $PhCH_2$, $^2J_{CP}$ = 1.9 Hz), 34.4 (d, CH_2P, $^1J_{CP}$ = 51.6 Hz), 124.8 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 7.1 Hz), 126.7 (C_p), 128.3 (C_o), 128.7 (C_m), 140.1 (d, C_i, $^3J_{CP}$ = 14.5 Hz), 140.7 (d, C_4, Py, $^1J_{CP}$ = 66.7 Hz), 150.1 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 8.7 Hz).

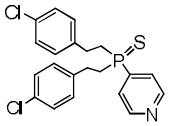
^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -59.5.

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 45.8.

IR (neat): n_{max} = 3057, 3028, 2931, 2862, 1640, 1582, 1541, 1494, 1449, 1402, 1317, 1216, 1121, 1074, 1006, 946, 912, 808, 758, 700, 610, 560, 507 cm^{-1}.

Anal. Calcd for $C_{21}H_{22}NPS$: C, 71.77; H, 6.31; N, 3.99; P, 8.81; S, 9.12. Found: C, 71.70; H, 6.42; N, 3.87; P, 8.58; S, 8.93.

4-{Bis[2-(4-chlorophenyl)ethyl]phosphorothioyl}pyridine (4g).



Yield: 168 mg (40%); light-yellow powder, mp 101–102 °C (hexane-MeCN).

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.28 (m, 4H, CH_2P), 2.59, 2.95 (m, 4H, $PhCH_2$), 6.97 (d, 4H, H_o, $^3J_{HH}$ = 8.1 Hz), 7.13 (d, 4H, H_m, $^3J_{HH}$ = 8.1 Hz), 7.63 (m, 2H, $H_{3,5}$, Py), 8.69 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 27.6 (d, $PhCH_2$, $^2J_{CP}$ = 2.0 Hz), 34.2 (d, CH_2P, $^1J_{CP}$ = 51.9 Hz), 124.6 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 7.6 Hz), 128.7 (C_o), 129.6 (C_m), 132.4 (C_p), 138.4 (d, C_i, $^3J_{CP}$ = 14.4 Hz), 140.4 (d, C_4, Py, $^1J_{CP}$ = 67.1 Hz), 150.0 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 9.2 Hz).

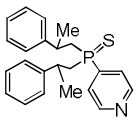
^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -60.4.

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 45.5.

IR (neat): n_{max} = 3047, 2913, 2854, 1655, 1581, 1542, 1489, 1438, 1403, 1316, 1215, 1120, 1089, 1011, 970, 912, 807, 777, 747, 654, 597, 517 cm^{-1}.

Anal. Calcd for $C_{21}H_{20}Cl_2NPS$: C, 60.01; H, 4.80; Cl, 16.87; N, 3.33; P, 7.37; S, 7.63. Found: C, 59.80; H, 4.85; Cl, 16.69; N, 3.25; P, 7.24; S, 7.48.

4-[Bis(2-phenylpropyl)phosphorothioyl]pyridine (4h).



Yield: 220 mg (58%); light-yellow powder, mp 103–104°C (hexane). The product is a mixture of three stereoisomers in a ratio of 3.2:1.6:1 (^{1}H and ^{31}P NMR data).

IR (neat): n_{max} = 3058, 3026, 2964, 2925, 2874, 1659, 1622, 1583, 1539, 1491, 1452, 1402, 1313, 1219, 1114, 1087, 1017, 913, 848, 801, 763, 702, 610, 515 cm^{-1}.

Anal. Calcd for $C_{23}H_{26}NPS$: C, 72.79; H, 6.91; N, 3.69; P, 8.16; S, 8.45. Found: C, 72.71; H, 6.81; N, 3.73; P, 8.03; S, 8.63.

***R,R(S,S)*-stereoisomer (major)**.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.12, 1.15 (d, 6H, Me, $^3J_{HH}$ = 7.0 Hz), 1.56, 2.07, 2.12, 2.37 (m, 4H, CH_2P), 3.11, 3.56 (m, 2H, PhC<u>H</u>(Me)), 6.89 (m, 6H, H_m, H_p), 7.31 (m, 4H, H_o), 7.36 (dd, 2H, $H_{3,5}$, Py, $^3J_{PH}$ = 12.3 Hz, $^3J_{3(5)\text{-}2(6)}$ = 5.0 Hz), 8.42 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 23.49, 24.40 (2d, Me, $^3J_{CP}$ = 10.4 Hz, $^3J_{CP}$ = 11.5 Hz), 34.31, 34.59 (2d, Ph<u>C</u>H(Me), $^2J_{CP}$ = 1.0 Hz, $^2J_{CP}$ = 2.0 Hz), 39.92, 42.29 (2d, CH_2P, $^1J_{CP}$ = 51.5 Hz, $^1J_{CP}$ = 41.1 Hz), 124.45 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 6.8 Hz), 126.47, 128.83 (C_p), 127.19, 127.04 (C_o), 128.03, 128.73 (C_m), 141.89 (d, C_4, Py, $^1J_{CP}$ = 67.0 Hz), 144.33, 145.98 (2d, C_i, $^3J_{CP}$ = 7.0 Hz, $^3J_{CP}$ = 4.0 Hz), 149.12 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 8.8 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -62.0.

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 44.1.

***R,S(S,R)R*$_p$- and *R,S(S,R)S*$_p$-stereoisomers:**

Medium. ^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.35 (d, 6H, Me, $^3J_{HH}$ = 7.0 Hz), 2.34, 2.49 (m, 4H, CH_2P), 3.25 (m, 2H, PhC<u>H</u>(Me)), 7.05 (dd, 2H, $H_{3,5}$, Py, $^3J_{PH}$ = 12.4 Hz, $^3J_{3(5)\text{-}2(6)}$ = 5.0 Hz), 8.17 (m, 2H, $H_{2,6}$, Py). The signals of the phenyl ring were overlapped with those of other stereoisomers.

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 24.40 (d, Me, $^3J_{CP}$ = 11.5 Hz), 34.37 (d, Ph<u>C</u>H(Me), $^2J_{CP}$ = 2.0 Hz), 41.76 (d, CH_2P, $^1J_{CP}$ = 41.5 Hz), 124.71 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 7.6 Hz), 126.52 (C_p), 127.01 (C_o), 128.11 (C_m), 139.95 (d, C_4, Py, $^1J_{CP}$ = 67.1 Hz), 144.50 (d, C_i, $^3J_{CP}$ = 5.0 Hz), 148.46 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 9.2 Hz).

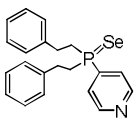
^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 43.9.

Minor. ^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 0.99 (d, 6H, Me, $^3J_{HH}$ = 7.0 Hz), 2.15, 2.48 (m, 4H, CH_2P), 3.27 (m, 2H, PhC<u>H</u>(Me)), 6.79 (m, 6H, H_m, H_p), 7.24 (m, 4H, H_o), 7.73 (dd, 2H, $H_{3,5}$, Py, $^3J_{PH}$ = 12.5 Hz, $^3J_{3(5)\text{-}2(6)}$ = 5.0 Hz), 8.71 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 22.95 (d, Me, $^3J_{CP}$ = 8.4 Hz), 34.43 (d, Ph<u>C</u>H(Me), $^2J_{CP}$ = 1.6 Hz), 40.79 (d, CH_2P, $^1J_{CP}$ = 50.3 Hz), 124.45 (d, $C_{3,5}$, Py, $^2J_{CP}$ = 6.8 Hz), 126.59 (C_p), 126.86 (C_o), 128.51 (C_m), 143.75 (d, C_4, Py, $^1J_{CP}$ = 65.5 Hz), 145.76 (d, C_i, $^3J_{CP}$ = 10.0 Hz), 149.84 (d, $C_{2,6}$, Py, $^3J_{CP}$ = 8.8 Hz).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 43.7.

4-[Bis(2-phenylethyl)phosphoroselenoyl]pyridine (4i).



Yield: 159 mg (40%); light-yellow powder, mp 85–86 °C (reprecipitated from CCl_4 to hexane).

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.50 (m, 4H, CH_2P), 2.68, 3.03 (m, 4H, $PhCH_2$), 7.09 (m, 4H, H_o), 7.15 (m, 2H, H_p), 7.22 (m, 4H, H_m), 7.73 (m, 2H, $H_{3,5}$, Py), 8.71 (br s, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 28.9 (d, $PhCH_2$, $^{2}J_{CP}$ = 1.9 Hz), 33.9 (d, CH_2P, $^{1}J_{CP}$ = 44.5 Hz), 125.2 (d, $C_{3,5}$, Py, $^{2}J_{CP}$ = 7.6 Hz), 126.5 (C_p), 128.1 (C_o), 128.5 (C_m), 138.9 (d, C_4, Py, $^{1}J_{CP}$ = 59.1 Hz), 139.7 (d, C_i, $^{3}J_{CP}$ = 14.8 Hz), 149.9 (d, $C_{2,6}$, Py, $^{3}J_{CP}$ = 8.8 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -58.1.

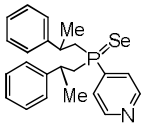
^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 37.4 (+d-satellites, $^{1}J_{PSe}$ = 740.7 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): *d* -421.5 (d, $^{1}J_{PSe}$ = 740.7 Hz).

IR (neat): n_{max} = 3056, 3028, 2928, 28606, 1596, 1579, 1489, 1494, 1449, 1402, 1316, 1216, 1118, 1073, 1021, 1000, 945, 911, 854, 808, 753, 701, 576, 506, 482 cm^{-1}.

Anal. Calcd for $C_{21}H_{22}NPSe$: C, 63.32; H, 5.57; N, 3.52; P, 7.78; Se, 19.82. Found: C, 63.26; H, 5.48; N, 3.47; P, 7.66; Se, 19.63.

4-[Bis(2-phenylpropyl)phosphoroselenoyl]pyridine (4j).



Yield: 158 mg (37%); light-yellow powder, mp 82–83°C (hexane). The product is a mixture of three stereoisomers in a ratio of 10.8:8.3:1 (^{1}H and ^{31}P NMR data).

IR (neat): n_{max} = 3056, 3029, 2962, 2925, 2873, 1658, 1626, 1602, 1579, 1536, 1491, 1452, 1402, 1314, 1219, 1161, 1111, 1085, 1016, 913, 847, 805, 761, 700, 535, 505, 457 cm^{-1}.

Anal. Calcd for $C_{23}H_{26}NPSe$: C, 64.79; H, 6.15; N, 3.28; P, 7.26; Se, 18.52. Found: C, 64.70; H, 6.12; N, 3.22; P, 7.02; Se, 18.33.

***R,R(S,S)*-stereoisomer (major)**.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.00, 1.09 (d, 6H, Me, $^{3}J_{HH}$ = 7.0 Hz), 1.56, 2.29, 2.27, 2.62 (m, 4H, CH_2P), 3.10, 3.56 (m, 2H, PhC<u>H</u>(Me)), 6.86, 7.29 (m, 4H, H_m), 6.85, 7.30 (m, 6H, H_o, H_p), 7.35 (m, 2H, $H_{3,5}$, Py), 8.37 (br s, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 23.39, 24.42 (2d, Me, $^{3}J_{CP}$ = 10.6 Hz, $^{3}J_{CP}$ = 14.7 Hz), 34.98, 35.44 (2d, Ph<u>C</u>H(Me), $^{2}J_{CP}$ = 2.3 Hz, $^{2}J_{CP}$ = 1.5 Hz), 39.34, 41.69 (2d, CH_2P, $^{1}J_{CP}$ = 44.7 Hz), 125.18 (br s, $C_{3,5}$, Py), 126.52, 126.88 (C_p), 127.13, 127.27 (C_o), 128.03, 128.73 (C_m), 139.93 (d, C_4, Py, $^{1}J_{CP}$ = 59.7 Hz), 143.95, 145.74 (2d, C_i, $^{3}J_{CP}$ = 4.2 Hz, $^{3}J_{CP}$ = 7.3 Hz), 149.18 ($C_{2,6}$, Py).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 36.8 (+d-satellites, $^{1}J_{PSe}$ = 738.7 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): *d* -430.7 (d, $^{1}J_{PSe}$ = 738.7 Hz).

***R,S(S,R)R*$_p$- and *R,S(S,R)S*$_p$-stereoisomers:**

Medium. ^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.31 (d, 6H, Me, $^3J_{HH}$ = 7.0 Hz), 2.25, 2.62 (m, 4H, CH_2P), 3.30 (m, 2H, PhC<u>H</u>(Me)), 6.83 (m, 4H, H_m), 6.85 (m, 2H, H_p), 6.95 (m, 4H, H_o), 7.00 (m, 2H, $H_{3,5}$, Py), 8.10 (br s, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 24.41 (d, Me, $^3J_{CP}$ = 12.6 Hz), 35.06 (d, Ph<u>C</u>H(Me), $^2J_{CP}$ = 2.2 Hz), 41.34 (d, CH_2P, $^1J_{CP}$ = 45.9 Hz), 125.33 ($C_{3,5}$, Py), 126.57 (C_p), 127.09 (C_o), 128.09 (C_m), 137.91 (d, C_4, Py, $^1J_{CP}$ = 58.5 Hz), 144.15 (d, C_i, $^3J_{CP}$ = 7.3 Hz), 148.44 ($C_{2,6}$, Py).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 36.1 (+d-satellites, $^1J_{PSe}$ = 738.7 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): *d* -421.3 (d, $^1J_{PSe}$ = 738.7 Hz).

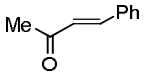
Minor. ^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 0.91 (d, 6H, Me, $^3J_{HH}$ = 7.0 Hz), 2.16, 2.47 (m, 4H, CH_2P), 3.29 (m, 2H, PhC<u>H</u>(Me)), 8.65 (br s, 2H, $H_{2,6}$, Py). The signals of the phenyl and pyridine ($H_{3,5}$) rings were overlapped with those of other stereoisomers.

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 22.85 (d, Me, $^3J_{CP}$ = 9.1 Hz), 35.30 (d, Ph<u>C</u>H(Me), $^2J_{CP}$ = 2.1 Hz), 40.16 (d, CH_2P, $^1J_{CP}$ = 42.8 Hz), 125.33 ($C_{3,5}$, Py), 126.64 (C_p), 126.90 (C_o), 128.51 (C_m), 142.15 (d, C_4, Py, $^1J_{CP}$ = 57.1 Hz), 145.70 (d, C_i, $^3J_{CP}$ = 9.2 Hz), 149.18 ($C_{2,6}$, Py).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 36.3 (+d-satellites, $^1J_{PSe}$ = 736.8 Hz).

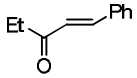
^{77}Se NMR (76.31 MHz, $CDCl_3$): *d* -421.4 (d, $^1J_{PSe}$ = 736.8 Hz).

(3*E*)-4-Phenylbut-3-en-2-one (5a).[7]



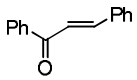
^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.37 (s, 3H, Me), 6.71 (d, 1H, PhC<u>H</u>=, $^3J_{HH}$ = 16.3 Hz), 7.38, 7.53 (m, 5H, Ph), 7.50 (d, 1H, =CH(C=O), $^3J_{HH}$ = 16.3 Hz).

(1*E*)-1-Phenylpent-1-en-3-one (5b).[8]



^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.18 (t, 1H, Me, $^3J_{HH}$ = 7.1 Hz), 2.71 (q, 1H, C<u>H</u>$_2$Me, $^3J_{HH}$ = 7.1 Hz), 6.73 (d, 1H, PhC<u>H</u>=, $^3J_{HH}$ = 16.3 Hz), 7.37, 7.57 (m, 5H, Ph; 1H, =C<u>H</u>(C=O)).

(2*E*)-1,3-Diphenylprop-2-en-1-one (5c).[9]



Yield: 73 mg (35%); white powder, mp 78–79 °C (hexane).

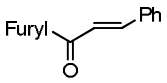
[7] Gottumukkala, A. L.; Teichert, J. F.; Heijnen, D.; Eisink, N.; van Dijk, S.; Ferrer, C.; van den Hoogenband, A.; Minnaard, A. J. *J. Org. Chem.* **2011,** *76,* 3498–3501.
[8] Li, X.; Li, L.; Tang, Y.; Zhong, L.; Cun, L.; Zhu, J.; Liao, J.; Deng, J. *J. Org. Chem.* **2010,** *75,* 2981–2988.
[9] Arbuzova, S. N.; Glotova, T. E.; Dvorko, M. Yu.; Ushakov, I. A.; Gusarova, N. K.; Trofimov, B. A. *Arkivoc* **2011,** *xi,* 183–188.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 7.40, 7.49, 7.56, 7.63 (m, 5H, H_o, H_m, H_p, PhCH=; 3H, H_m, H_p, PhC=O; 1H, =CH(C=O)), 7.80 (d, 1H, PhCH=, $^3J_{HH}$ = 15.7 Hz), 8.01 (d, 2H, H_o, PhC=O, $^3J_{HH}$ = 7.2 Hz).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 122.1 (=CH(C=O)), 128.3 (C_o, PhCH=), 128.4 (C_o, PhC=O), 128.6 (C_m, PhCH=), 128.9 (C_m, PhC=O), 130.5 (C_p, PhCH=), 132.7 (C_p, PhC=O), 134.9 (C_i, PhC=O), 138.2 (C_i, PhCH=), 144.7 (PhCH=), 190.4 (C=O).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.39; H, 5.76.

(2*E*)-1-(Furan-2-yl)-3-phenylprop-2-en-1-one (5d).[9]



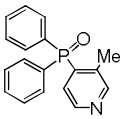
Yield: 89 mg (45%); beige powder, mp 79–80 °C (hexane).

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 6.58, 7.31, 7.40, 7.63 (m, 8H, Ph, Furyl), 7.44 (d, 1H, =CH(C=O), $^3J_{HH}$ = 15.8 Hz), 7.87 (d, 1H, PhCH=, $^3J_{HH}$ =15.8 Hz).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 112.5 (C_4, Furyl), 117.4 (C_3, Furyl), 121.2 (=CH(C=O)), 128.5 (C_m, PhCH=), 128.9 (C_o, PhCH=), 130.6 (C_p, PhCH=), 134.7 (C_i, PhCH=), 143.9 (PhCH=), 146.5 (C_5, Furyl), 153.7 (C_2, Furyl), 178.0 (C=O).

Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C 78.66; H 5.14.

4-(Diphenylphosphoryl)-3-methylpyridine (6a).



Yield: 123 mg (42%); waxy product.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.38 (s, 3H, Me-C_3), 6.85 (dd, 1H, H_5, Py, $^3J_{PH}$ = 13.4 Hz, $^3J_{5\text{-}6}$ = 4.7 Hz), 7.46, 7.57 (m, 10H, Ph), 8.40 (br t, 1H, H_6, Py, $^4J_{PH}$ = 5.1 Hz, $^3J_{5\text{-}6}$ = 4.7 Hz), 8.50 (d, 1H, H_2, Py, $^4J_{PH}$ = 4.5 Hz).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 18.3 (d, Me-C_3, $^3J_{CP}$ = 4.8 Hz), 126.0 (d, C_5, Py, $^2J_{CP}$ = 10.8 Hz), 128.7 (d, C_m, $^3J_{CP}$ = 12.4 Hz), 131.0 (d, C_i, $^1J_{CP}$ = 104.6 Hz), 131.7 (d, C_o, $^2J_{CP}$ = 9.9 Hz), 132.3 (C_p), 136.9 (d, C_3, Py, $^2J_{CP}$ = 4.8 Hz), 139.7 (d, C_4, Py, $^1J_{CP}$ = 95.6 Hz), 147.0 (d, C_6, Py, $^3J_{CP}$ = 10.4 Hz), 152.3 (d, C_2, Py, $^3J_{CP}$ = 8.4 Hz).

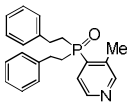
^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -59.9.

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 30.5.

IR (neat): n_{max} = 3055, 2957, 2923, 2855, 1627, 1582, 1476, 1438, 1398, 1298, 1195, 1115, 1068, 1031, 923, 830, 718, 547 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}NOP$: C, 73.71; H, 5.50; N, 4.78; P, 10.56. Found: C, 73.58; H, 5.41; N, 4.69; P, 10.34.

4-[Bis(2-phenylethyl)phosphoryl]-3-methylpyridine (6b).



Yield: 223 mg (64%); waxy product.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.30 (m, 4H, CH_2P), 2.56 (3H, Me-C_3), 2.74, 2.98 (m, 4H, $PhCH_2$), 7.10 (m, 4H, H_o), 7.17 (m, 2H, H_p), 7.23 (m, 4H, H_m), 7.57 (dd, 1H, H_5, Py, $^{3}J_{PH}$ = 11.9 Hz, $^{3}J_{5\text{-}6}$ = 5.0 Hz), 8.49 (d, 1H, H_2, Py, $^{4}J_{PH}$ = 4.8 Hz) 8.56 (br t, 1H, H_6, Py, $^{4}J_{PH}$ = 4.8 Hz, $^{3}J_{5\text{-}6}$ = 5.0 Hz).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 18.6 (Me-C_3), 27.6 (d, $PhCH_2$, $^{2}J_{CP}$ = 2.8 Hz), 31.8 (d, CH_2P, $^{1}J_{CP}$ = 65.5 Hz), 125.5 (d, C_5, Py, $^{2}J_{CP}$ = 7.8 Hz), 126.7 (C_p), 128.1 (C_o), 128.7 (C_m), 135.1 (d, C_3, Py, $^{2}J_{CP}$ = 6.4 Hz), 139.7 (d, C_4, Py, $^{1}J_{CP}$ = 81.5 Hz), 140.4 (d, C_i, $^{3}J_{CP}$ = 13.6 Hz), 147.1 (d, C_6, Py, $^{3}J_{CP}$ = 8.8 Hz), 152.0 (d, C_2, Py, $^{3}J_{CP}$ = 8.4 Hz).

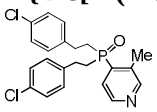
^{15}N NMR (40.56 MHz, $CDCl_3$): *d* -64.8.

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 39.8.

IR (neat): n_{max} = 3027, 2926, 2856, 1739, 1649, 1530, 1496, 1449, 1400, 1294, 1178, 1094, 1078, 1036, 940, 834, 751, 702, 587, 534 cm^{-1}.

Anal. Calcd for $C_{22}H_{24}NOP$: C, 75.62; H, 6.92; N, 4.01; P, 8.86. Found: C, 75.44; H, 6.85; N, 4.12; P, 8.71.

4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}-3-methylpyridine (6c).



Yield: 213 mg (51%); waxy product.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.26 (m, 4H, CH_2P), 2.56 (3H, Me-C_3), 2.72, 2.95 (m, 4H, $PhCH_2$), 7.03 (d, 4H, H_o, $^{3}J_{HH}$ = 8.3 Hz), 7.20 (d, 4H, H_m, $^{3}J_{HH}$ = 8.3 Hz), 7.52 (dd, 1H, H_5, Py, $^{3}J_{PH}$ = 11.7 Hz, $^{3}J_{5\text{-}6}$ = 4.5 Hz), 8.51 (d, 1H, H_2, Py, $^{4}J_{PH}$ = 4.5 Hz), 8.58 (m, 1H, H_6, Py).

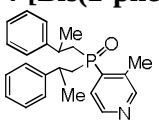
^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 18.5 (Me-C_3), 26.8 (d, $PhCH_2$, $^{2}J_{CP}$ = 2.4 Hz), 31.6 (d, CH_2P, $^{1}J_{CP}$ = 65.9 Hz), 125.2 (d, C_5, Py, $^{2}J_{CP}$ = 6.8 Hz), 128.7 (C_o), 129.4 (C_m), 132.3 (C_p), 134.7 (d, C_3, Py, $^{2}J_{CP}$ = 6.4 Hz), 138.6 (d, C_i, $^{3}J_{CP}$ = 13.2 Hz), 138.7 (d, C_4, Py, $^{1}J_{CP}$ = 82.3 Hz), 147.5 (d, C_6, Py, $^{3}J_{CP}$ = 8.4 Hz), 152.5 (d, C_2, Py, $^{3}J_{CP}$ = 7.2 Hz).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 39.4.

IR (neat): n_{max} = 3022, 2926, 2864, 1663, 1635, 1581, 1540, 1491, 1446, 1405, 1293, 1273, 1206, 1176, 1093, 1012, 919, 810, 768, 730, 653, 545, 513, 487 cm^{-1}.

Anal. Calcd for $C_{22}H_{22}Cl_2NOP$: C, 63.17; H, 5.30; Cl, 16.95; N, 3.35; P, 7.40. Found: C, 63.32; H, 5.21; Cl, 16.81; N, 3.31; P, 7.25.

4-[Bis(2-phenylpropyl)phosphoryl]-3-methylpyridine (6d).



Yield: 165 mg (44%); waxy product. The product is a mixture of three stereoisomers in a ratio of 2.6:1.6:1 (^{1}H and ^{31}P NMR data).

IR (neat): n_{max} = 3059, 3028, 2962, 2925, 2872, 1707, 1663, 1600, 1491, 1452, 1400, 1290, 1189, 1095, 1029, 913, 843, 766, 732, 703, 646, 598, 537, 489, 445 cm^{-1}.

Anal. Calcd for $C_{24}H_{28}NOP$: C, 76.37; H, 7.48; N, 3.71; P, 8.21. Found: C, 76.12; H, 7.40; N, 3.59; P, 8.07.

***R,R(S,S)*-stereoisomer (major)**.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.20, 1.26 (d, 6H, PhCH(Me), $^3J_{HH}$ = 7.0 Hz), 1.81, 1.95, 2.16, 2.25 (m, 4H, CH_2P), 2.33 (s, 3H, Me-C_3), 2.92, 3.41 (m, 2H, PhCH(Me)), 6.80–7.34 (m, 10H, Ph), 7.40 (m, 1H, H_5, Py), 8.26 (d, 1H, H_2, Py, $^3J_{PH}$ = 5.3 Hz), 8.39 (dd, 1H, H_6, Py, $^3J_{6\text{-}5}$ = 4.7 Hz, $^3J_{PH}$ = 3.1 Hz).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 18.47 (d, Me-C_3, $^3J_{CP}$ = 2.4 Hz), 23.82, 24.19 (2d, PhCH(Me), $^3J_{CP}$ = 9.5 Hz, $^3J_{CP}$ = 9.1 Hz), 34.09 (d, PhCH(Me), $^2J_{CP}$ = 3.7 Hz), 37.79, 39.87 (2d, CH_2P, $^1J_{CP}$ = 45.7 Hz, $^1J_{CP}$ = 45.0 Hz), 125.49 (d, C_5, Py, $^2J_{CP}$ = 7.7 Hz), 126.45, 126.50 (C_o), 126.67, 128.52 (C_p), 128.16, 128.22 (C_m), 133.82 (d, C_3, Py, $^2J_{CP}$ = 7.3 Hz), 140.45 (d, C_4, Py, $^1J_{CP}$ = 81.2 Hz), 145.25, 146.01 (2d, C_i, $^3J_{CP}$ = 7.2 Hz, $^3J_{CP}$ = 6.7 Hz), 146.96 (d, C_6, Py, $^3J_{CP}$ = 8.9 Hz), 151.75 (d, C_2, Py, $^3J_{CP}$ = 8.3 Hz).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 37.6.

***R,S(S,R)R*$_p$- and *R,S(S,R)S*$_p$-stereoisomers:**

Medium. ^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.35 (d, 6H, PhCH(Me), $^3J_{HH}$ = 7.0 Hz), 2.15 (s, 3H, Me-C_3), 2.24, 2.27 (m, 4H, CH_2P), 3.08 (m, 2H, PhCH(Me)), 6.80–7.34 (m, 10H, Ph), 7.30 (m, 1H, H_5, Py), 8.08 (d, 1H, H_2, Py, $^3J_{PH}$ = 5.3 Hz), 8.29 (dd, 1H, H_6, Py, $^3J_{6\text{-}5}$ = 4.7 Hz, $^3J_{PH}$ = 3.0 Hz).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 18.37 (d, Me-C_3, $^3J_{CP}$ = 2.8 Hz), 24.01 (d, PhCH(Me), $^3J_{CP}$ = 8.7 Hz), 34.13 (d, PhCH(Me), $^2J_{CP}$ = 3.8 Hz), 39.18 (d, CH_2P, $^1J_{CP}$ = 37.6 Hz), 126.14 (d, C_5, Py, $^2J_{CP}$ = 7.2 Hz), 126.75 (C_p), 126.97 (C_o), 128.68 (C_m), 133.56 (d, C_3, Py, $^2J_{CP}$ = 7.5 Hz), 138.93 (d, C_4, Py, $^1J_{CP}$ = 81.2 Hz), 145.30 (d, C_i, $^3J_{CP}$ = 7.4 Hz), 146.64 (d, C_6, Py, $^3J_{CP}$ = 9.1 Hz), 151.33 (d, C_2, Py, $^3J_{CP}$ = 8.3 Hz).

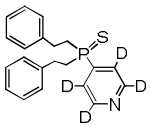
^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 37.8.

Minor. ^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 1.14 (d, 6H, PhCH(Me), $^3J_{HH}$ = 7.0 Hz), 2.04, 2.14 (m, 4H, CH_2P), 2.50 (s, 3H, Me-C_3), 3.17 (m, 2H, PhCH(Me)), 6.80–7.34 (m, 10H, Ph), 7.39 (m, 1H, H_5, Py), 8.41 (d, 1H, H_2, Py, $^3J_{PH}$ = 5.3 Hz), 8.46 (dd, 1H, H_6, Py, $^3J_{6\text{-}5}$ = 4.4 Hz, $^3J_{PH}$ = 3.6 Hz).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 18.47 (d, Me-C_3, $^3J_{CP}$ = 2.4 Hz), 23.66 (d, PhCH(Me), $^3J_{CP}$ = 8.6 Hz), 33.98 (d, PhCH(Me), $^2J_{CP}$ = 3.5 Hz), 38.44 (d, CH_2P, $^1J_{CP}$ = 37.5 Hz), 124.73 (d, C_5, Py, $^2J_{CP}$ = 7.9 Hz), 126.60 (C_p), 126.68 (C_o), 128.68 (C_m), 134.32 (d, C_3, Py, $^2J_{CP}$ = 6.8 Hz), 141.71 (d, C_4, Py, $^1J_{CP}$ = 81.3 Hz), 145.79 (d, C_i, $^3J_{CP}$ = 7.8 Hz), 147.15 (d, C_6, Py, $^3J_{CP}$ = 9.0 Hz), 152.14 (d, C_2, Py, $^3J_{CP}$ = 8.3 Hz).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 37.1.

4-[Bis(2-phenylethyl)thiophosphoryl]pyridine-d$_4$



Yield: 149 mg (42%); waxy product.

^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.41 (m, 4H, CH_2P), 2.72, 3.04 (m, 4H, $PhCH_2$), 7.11, 7.19, 7.25 (m, 10H, Ph).

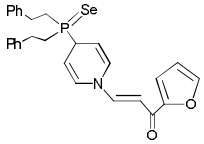
^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 28.1 (d, $PhCH_2$, $^2J_{CP}$ = 2.4 Hz), 34.3 (d, CH_2P, $^1J_{CP}$ = 51.9 Hz), 124.3 (br m, $C_{3,5}$, Py), 126.5 (C_p), 128.1 (C_o), 128.5 (C_m), 139.9 (d, C_i, $^3J_{CP}$ = 14.8 Hz), 140.4 (d, C_4, Py, $^1J_{CP}$ = 67.1 Hz), 149.3 (br m, $C_{2,6}$, Py).

^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 45.1.

Anal. Calcd for $C_{21}H_{18}D_4NPS$: C, 70.96; H, 5.10; N, 3.94. Found: C, 71.25; H, 6.69; N, 3.84.

Reaction of pyridine 1a, bis(2-phenylethyl)phosphine selenide 2i and 2-furoylacetylene 8. A solution of pyridine **1a** (1.1 mmol), bis(2-phenylethyl)phosphine selenide **2i** (1.0 mmol) and 2-furoylacetylene **8** (1.1 mmol) in MeCN (3 mL) was stirred under an argon atmosphere at 20–25 °C for 3 h. After completion of the reaction (^{31}P NMR monitoring), the solvent was removed under the reduced pressure. The reaction mixture contained phosphorylated *N*-ethenyl-1,4-dihydropyridine **9** and 4-selenophosphoryl pyridine **4i** in a 4:1 ratio (^{1}H and ^{31}P NMR data). 1,4-Dihydropyridine **9** was almost completely converted to the corresponding phosphoryl pyridine **4i** for 8–10 days in a $CDCl_3$ solution.

(*E*)-3-[4-(diphenethylphosphoroselenoyl)-1(4*H*)-pyridinyl]-1-(2-furyl)-2-propen-1-one (9).



^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.46 (m, 4H, CH_2P), 2.92 (m, 4H, $PhCH_2$), 3.65 (dt, 1H, H_4, Py, $^3J_{P\text{-}4}$ = 18.3 Hz, $^3J_{4\text{-}3}$ = 4.1 Hz), 5.15 (m, 2H, $H_{3,5}$, Py), 6.20 (d, 1H, =C<u>H</u>C=O, $^3J_{HH}$ = 13.4 Hz), 6.47 (m, 2H, $H_{2,6}$, Py), 6.56 (dd, 1H, H_4, Furyl, $^3J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 1.4 Hz), 7.08 (m, 1H, H_3, Furyl), 7.08-7.24 (m, 10H, Ph), 7.39 (d, 1H, >NC<u>H</u>=, $^3J_{HH}$ = 13.4 Hz), 7.48 (m, H_5, Furyl).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 28.8 (d, $PhCH_2$, $^2J_{CP}$ = 1.9 Hz), 33.4 (d, CH_2P, $^1J_{CP}$ = 46.2 Hz), 39.7 (d, C_4, Py, $^1J_{PC}$ = 41.4 Hz), 96.9 (=<u>C</u>HC=O), 103.6 ($C_{3,5}$, Py), 112.2 ($C_{2,6}$, Py), 112.82 (C_4, Furyl), 115.4 (C_3, Furyl), 126.4 (C_p), 128.2, 128.5 ($C_{o,m}$), 139.7, 140.2 (2d, C_i, $^3J_{PC}$ = 13.3 Hz, $^3J_{PC}$ = 14.6 Hz), 143.1 (>NCH=), 145.3 (C_5, Furyl), 153.6 (C_2, Furyl), 177.1 (C=O). ^{31}P NMR (161.98 MHz, $CDCl_3$): *d* 45.7 (+d-satellites, $^1J_{PSe}$ = 711.5 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): *d* -421.1 (d, $^1J_{PSe}$ = 711.5 Hz).

Reduction of phosphine selenide 4k to 4-[bis(2-phenylethyl)phosphino]pyridine (10).

To a solution of phosphine selenide **4i** (0.2 g, 0.5 mmol) in 6.0 mL of toluene, sodium (0.12 g, 5.0 mmol) was added. The reaction mixture was stirred at reflux for 1 h under an argon atmosphere. The precipitated sodium selenide was separated by filtration. The filtrate was evaporated in vacuo to give phosphine **10**.

Yield: 152 mg (95%); waxy product.

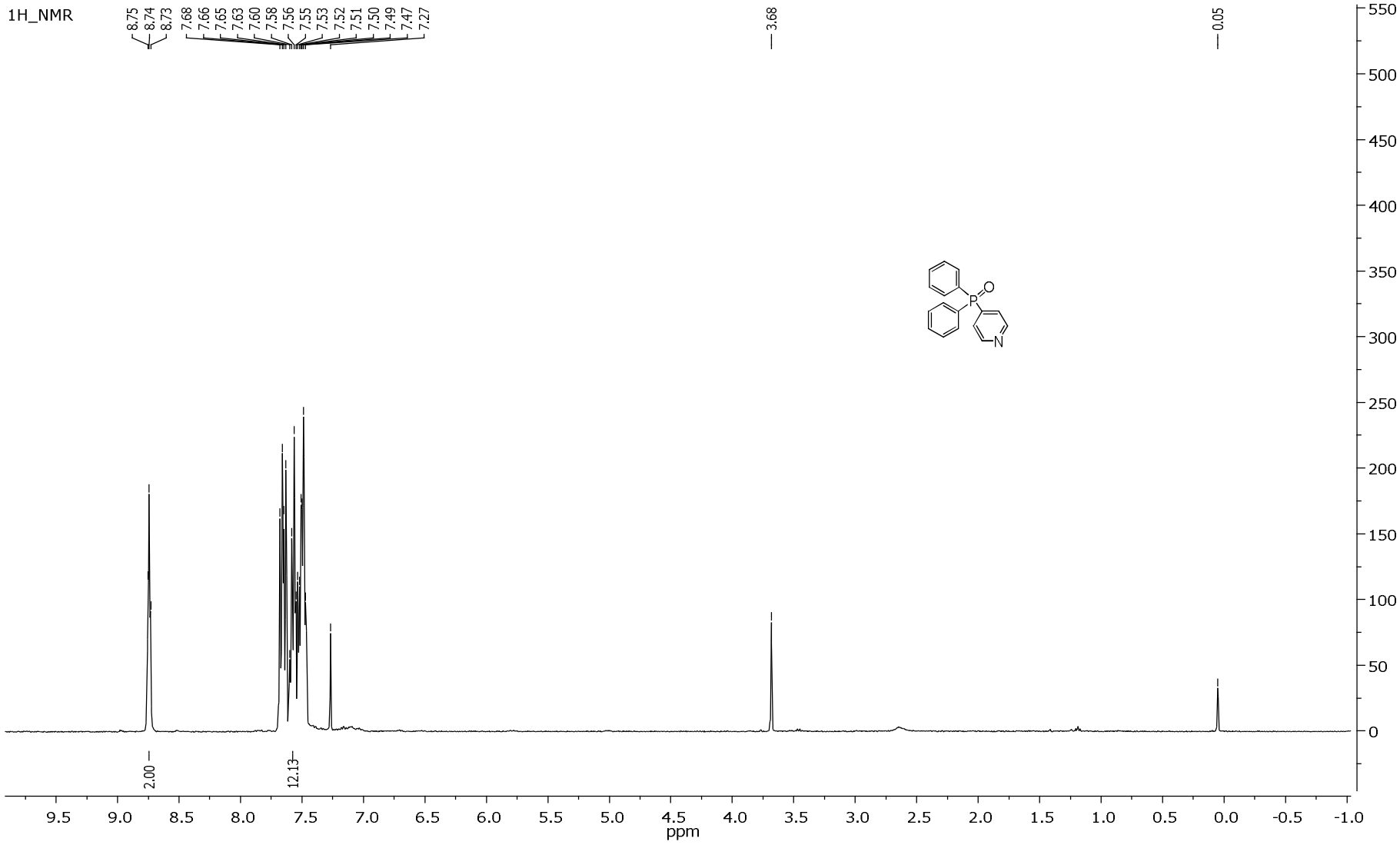
^{1}H NMR (400.13 MHz, $CDCl_3$): *d* 2.08 (m, 4H, CH_2P), 2.70 (m, 4H, $PhCH_2$), 7.17, 7.27 (m, 10H, Ph), 7.37 (m, 2H, $H_{3,5}$, Py), 8.56 (m, 2H, $H_{2,6}$, Py).

^{13}C NMR (100.62 MHz, $CDCl_3$): *d* 28.6 (d, $PhCH_2$, $^{2}J_{CP}$ = 14.4 Hz), 32.0 (d, CH_2P, $^{1}J_{CP}$ = 14.4 Hz), 126.2 (C_p), 126.4 (d, $C_{3,5}$, Py, $^{2}J_{CP}$ = 14.8 Hz), 128.1 (C_o), 128.5 (C_m), 142.0 (d, C_i, $^{3}J_{CP}$ = 10.8 Hz), 149.4 (d, $C_{2,6}$, Py, $^{3}J_{CP}$ = 4.4 Hz), 149.6 (d, C_4, Py, $^{1}J_{CP}$ = 22.4 Hz).

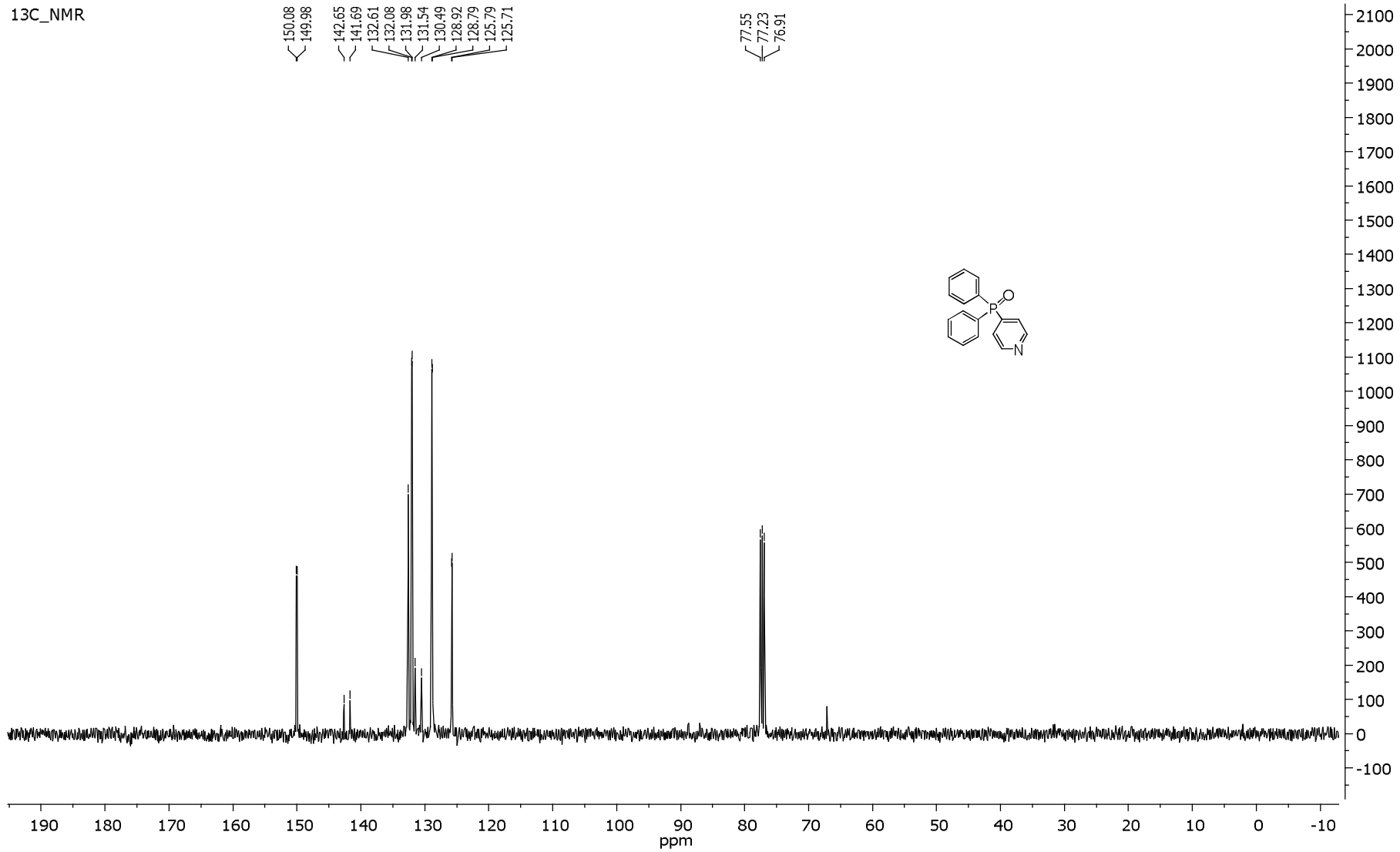
^{31}P NMR (161.98 MHz, $CDCl_3$): *d* -22.9.

Anal. Calcd for $C_{21}H_{22}NP$: C, 78.97; H, 6.94; N, 4.39; P, 9.70. Found: C, 78.85; H, 6.86; N, 4.25; P, 9.62.

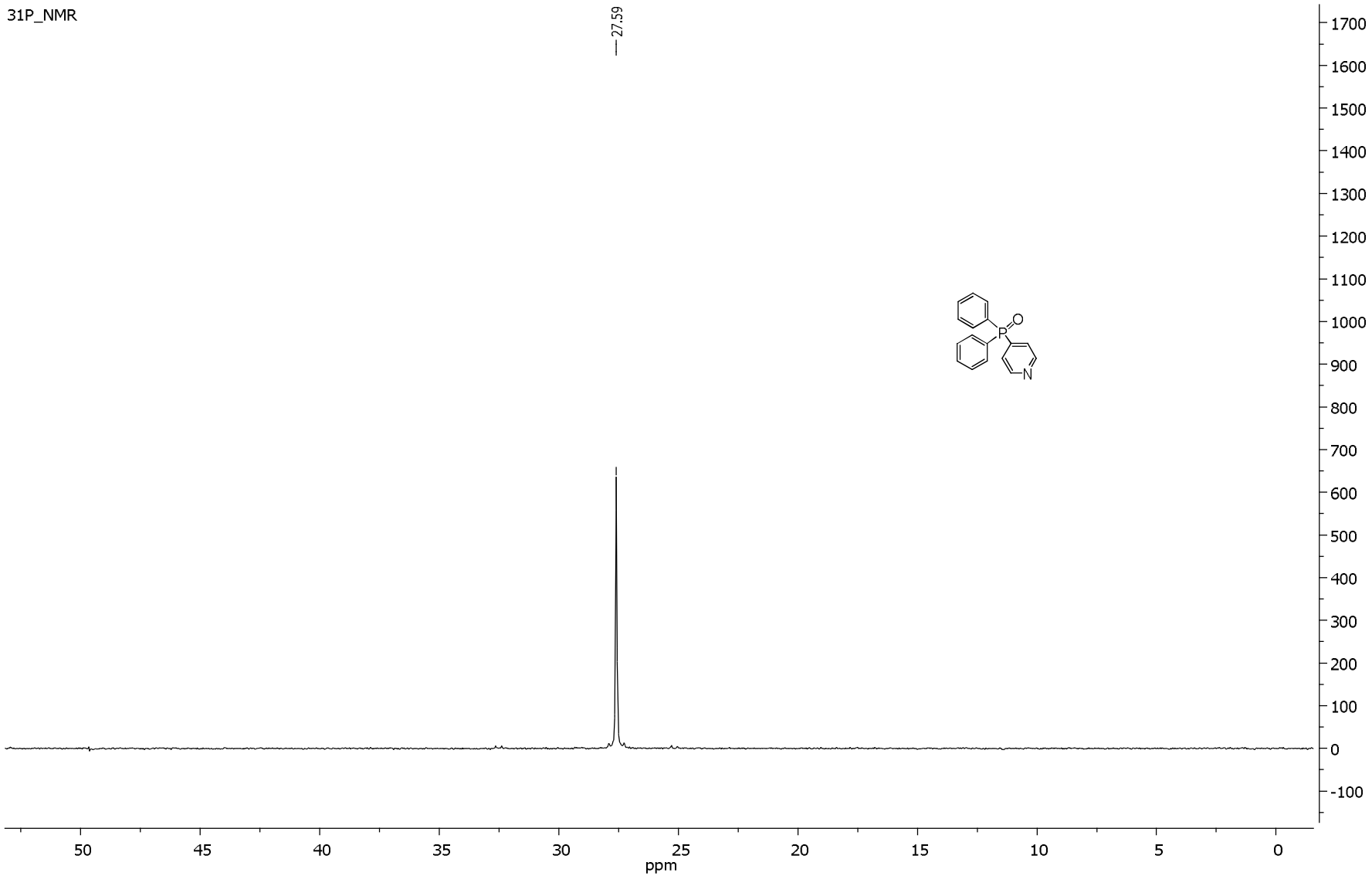
4-(Diphenylphosphoryl)pyridine (4a)



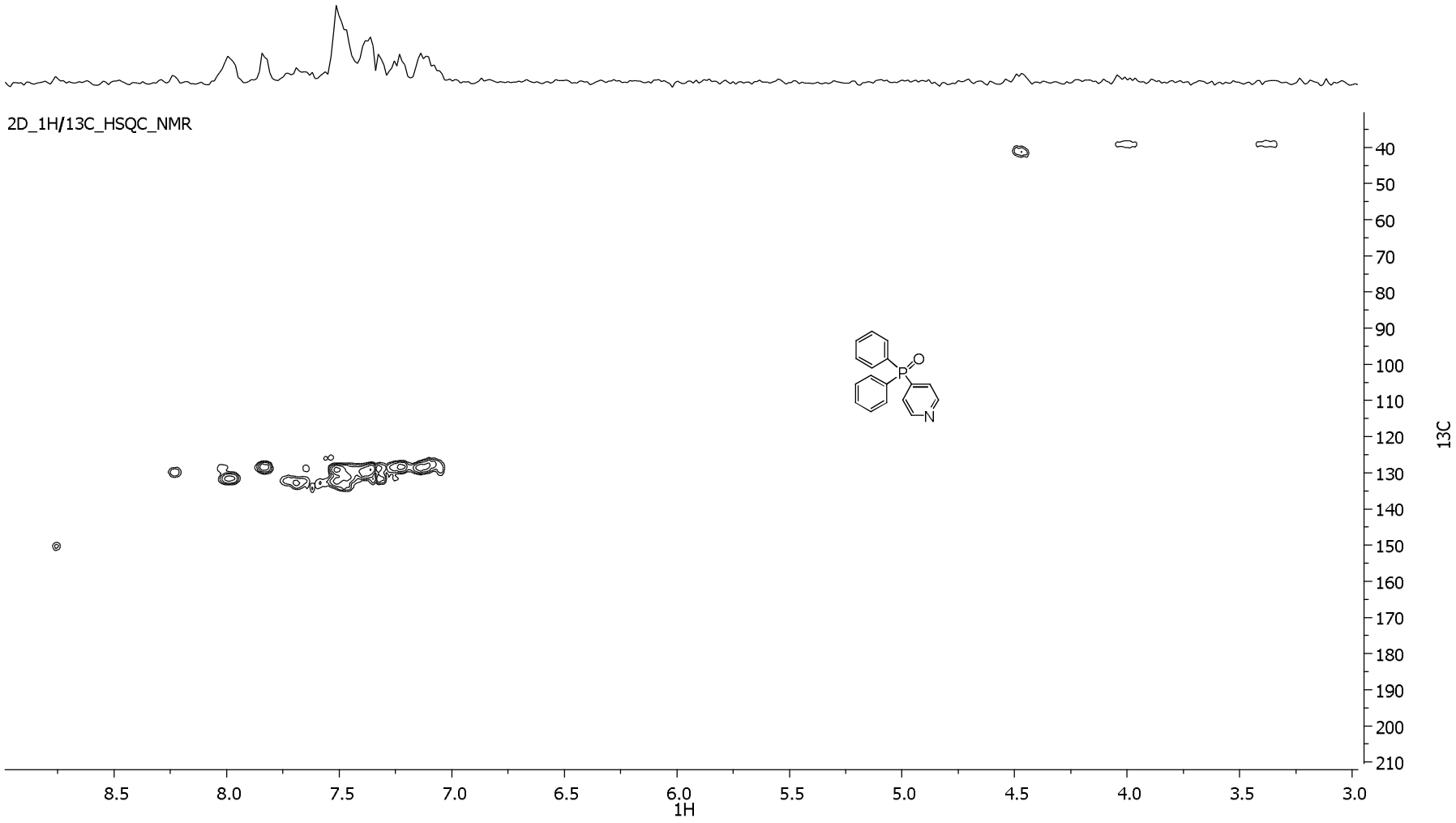
4-(Diphenylphosphoryl)pyridine (4a)



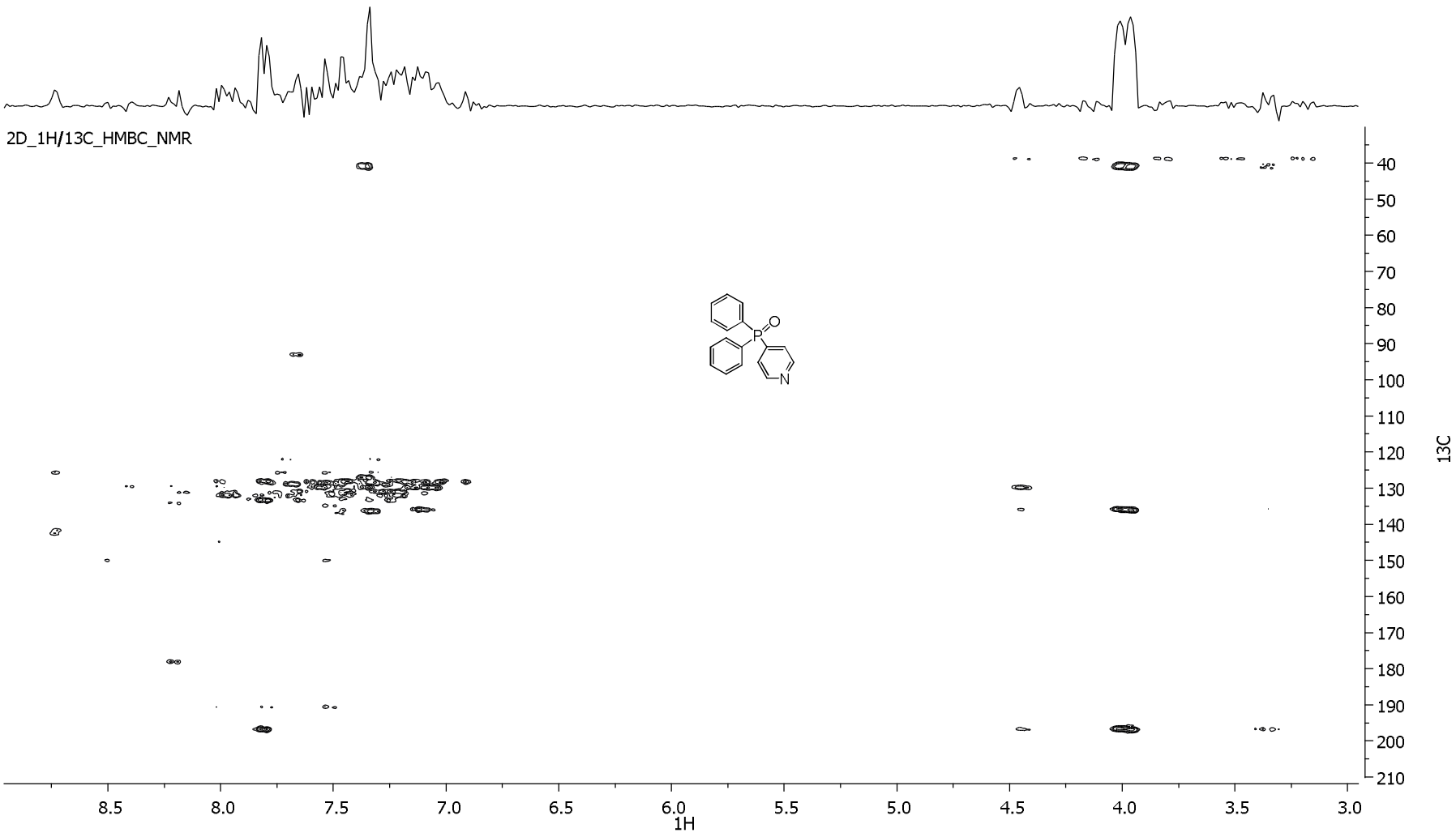
4-(Diphenylphosphoryl)pyridine (4a)



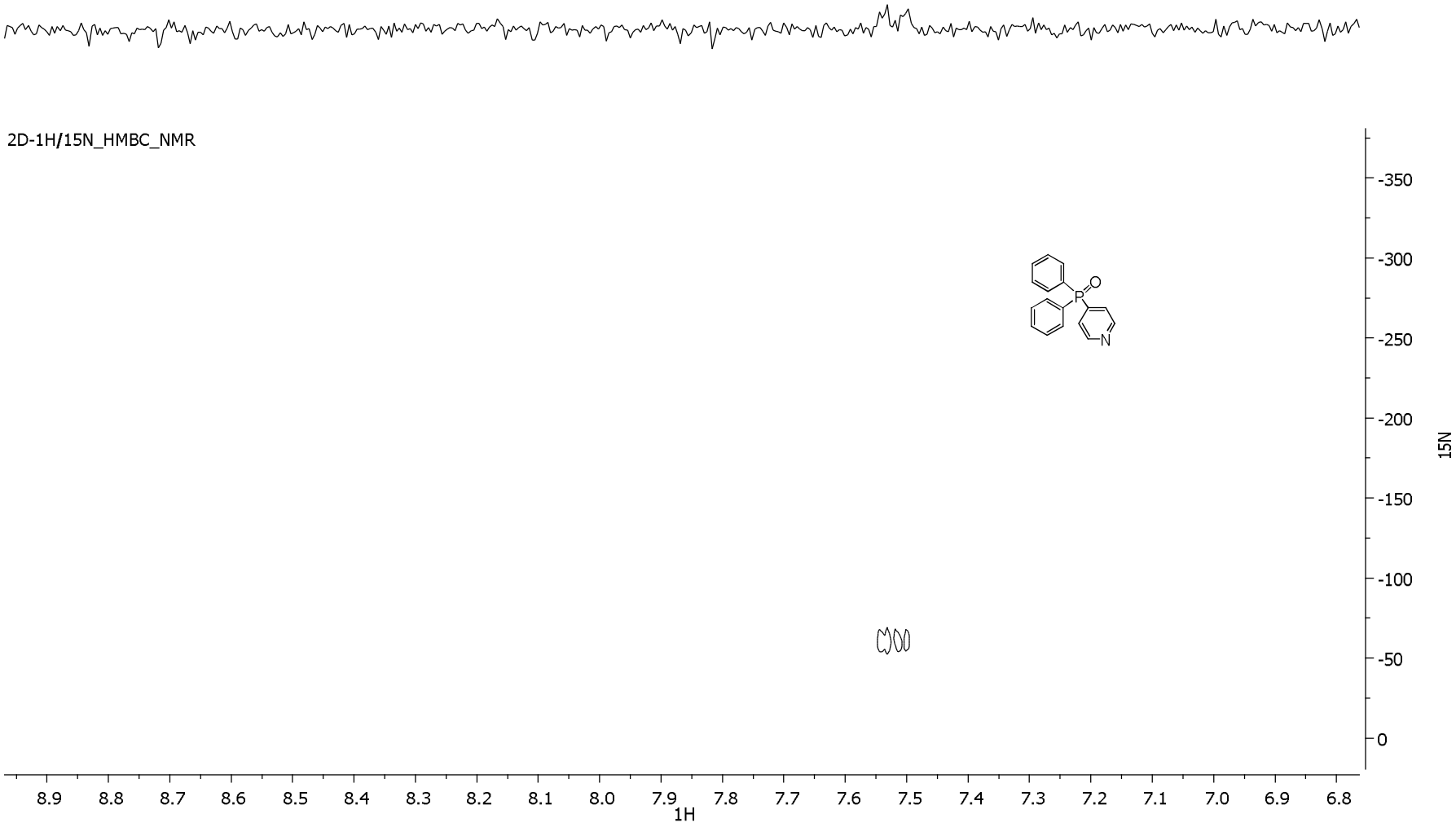
4-(Diphenylphosphoryl)pyridine (4a)



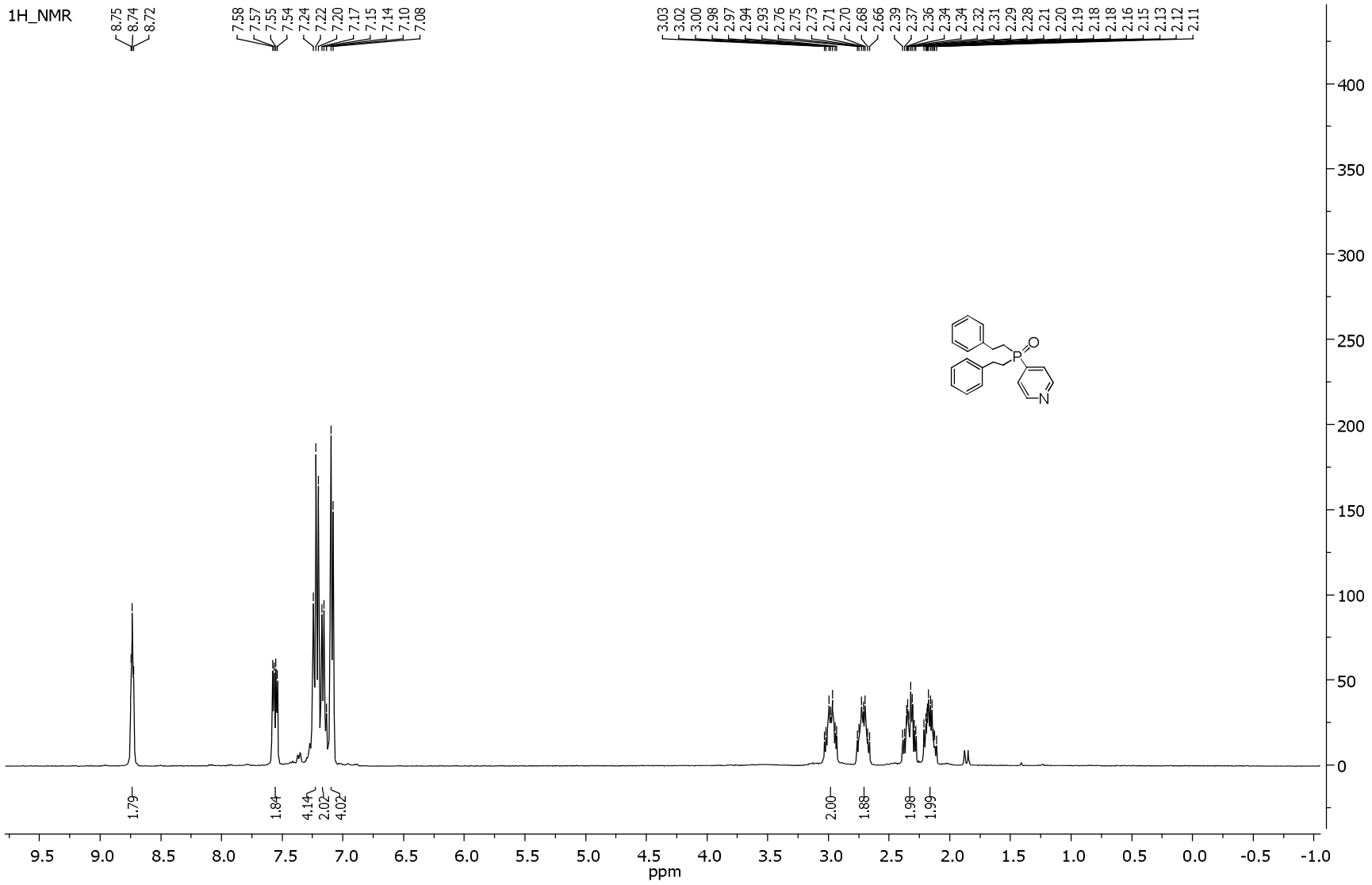
4-(Diphenylphosphoryl)pyridine (4a)



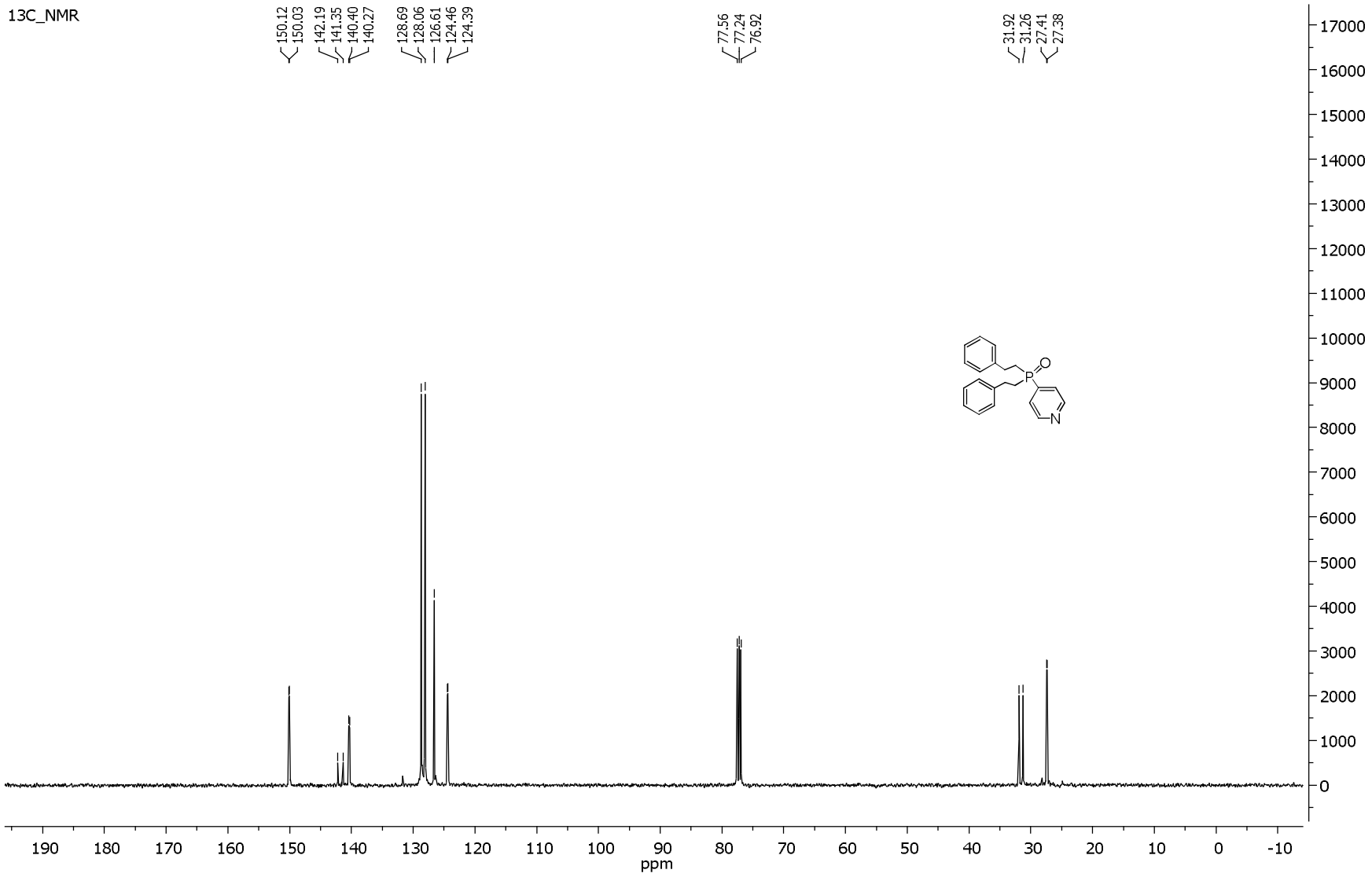
4-(Diphenylphosphoryl)pyridine (4a)



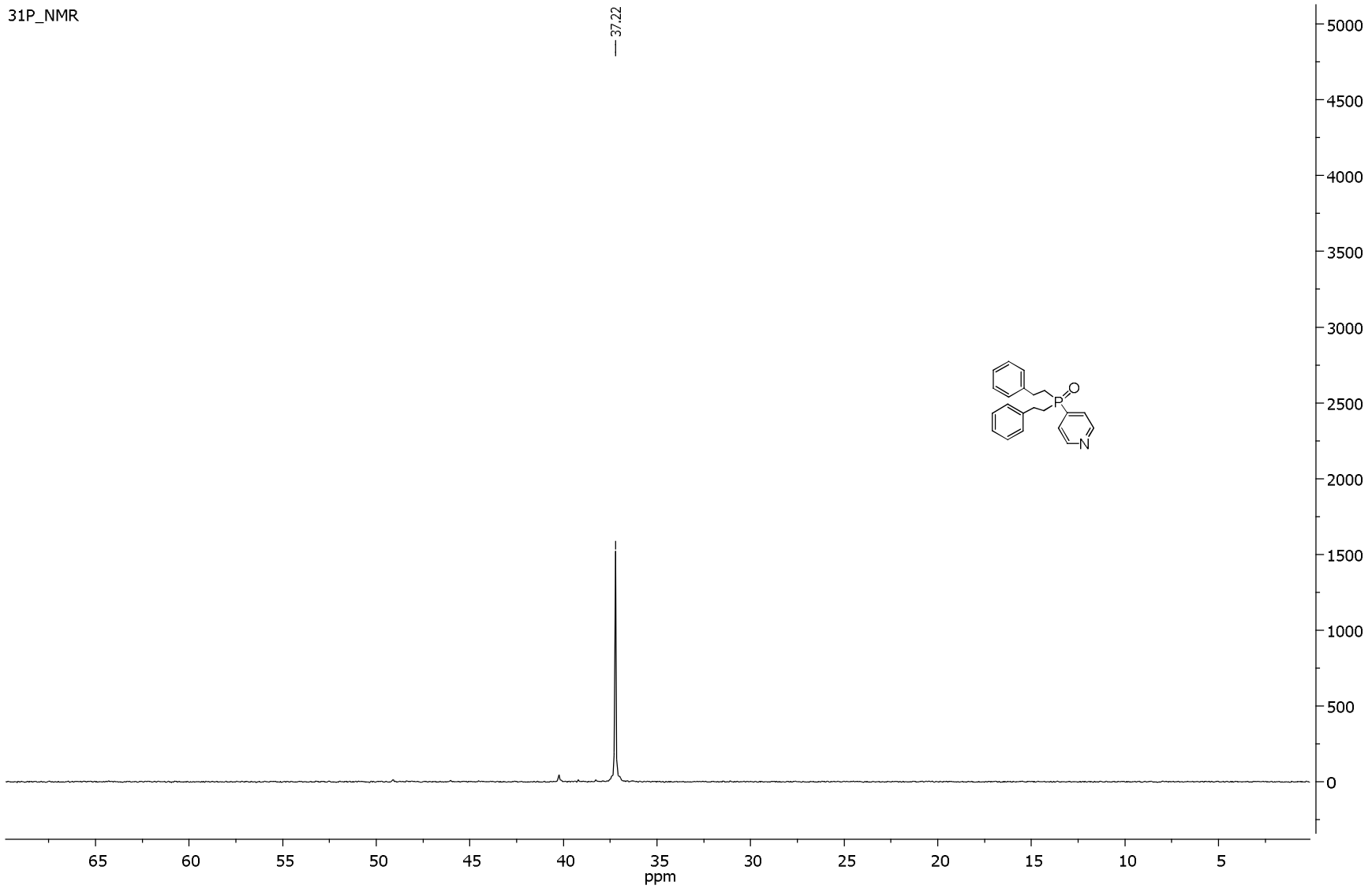
4-[Bis(2-phenylethyl)phosphoryl]pyridine (4b)



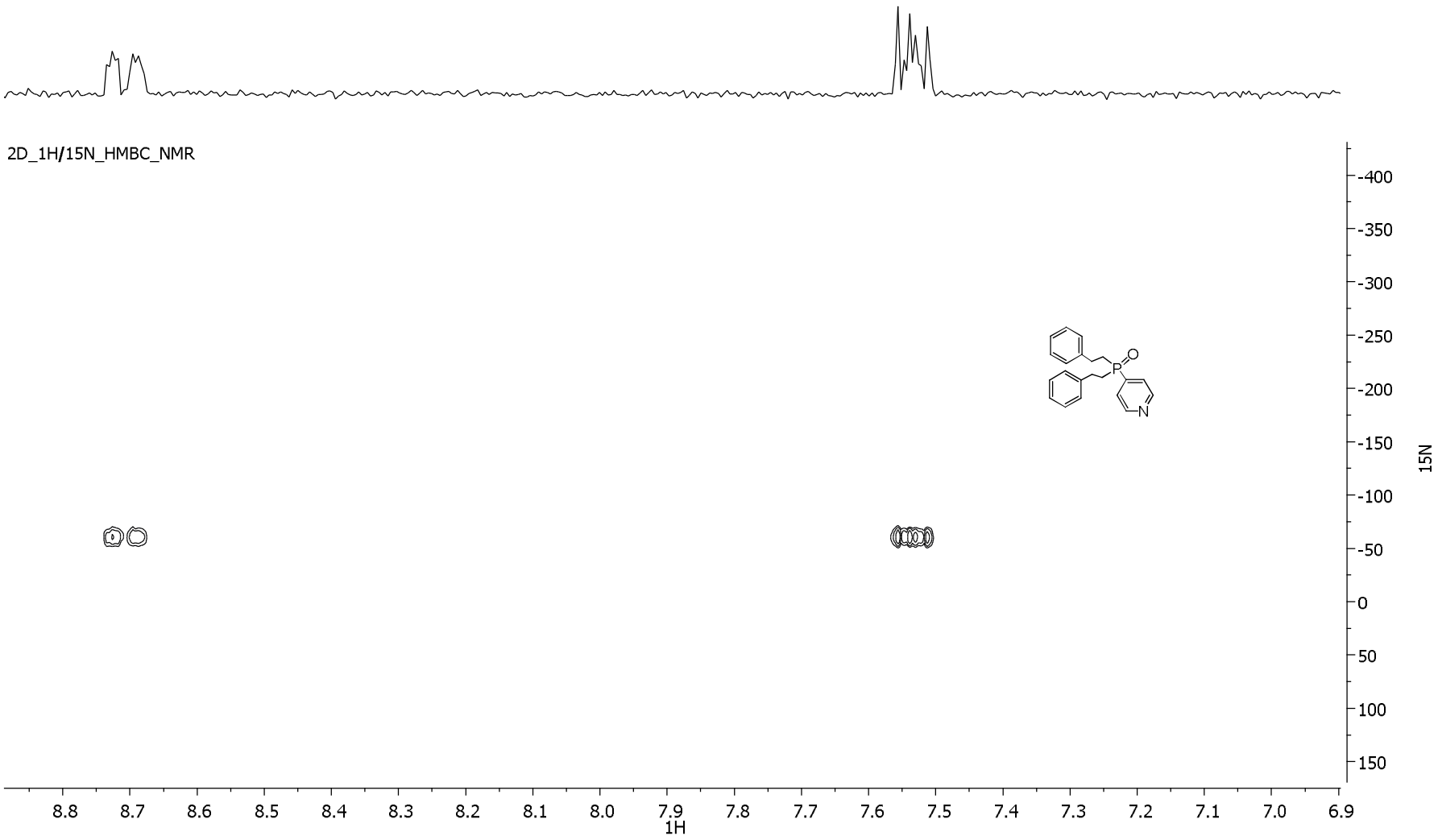
4-[Bis(2-phenylethyl)phosphoryl]pyridine (4b)



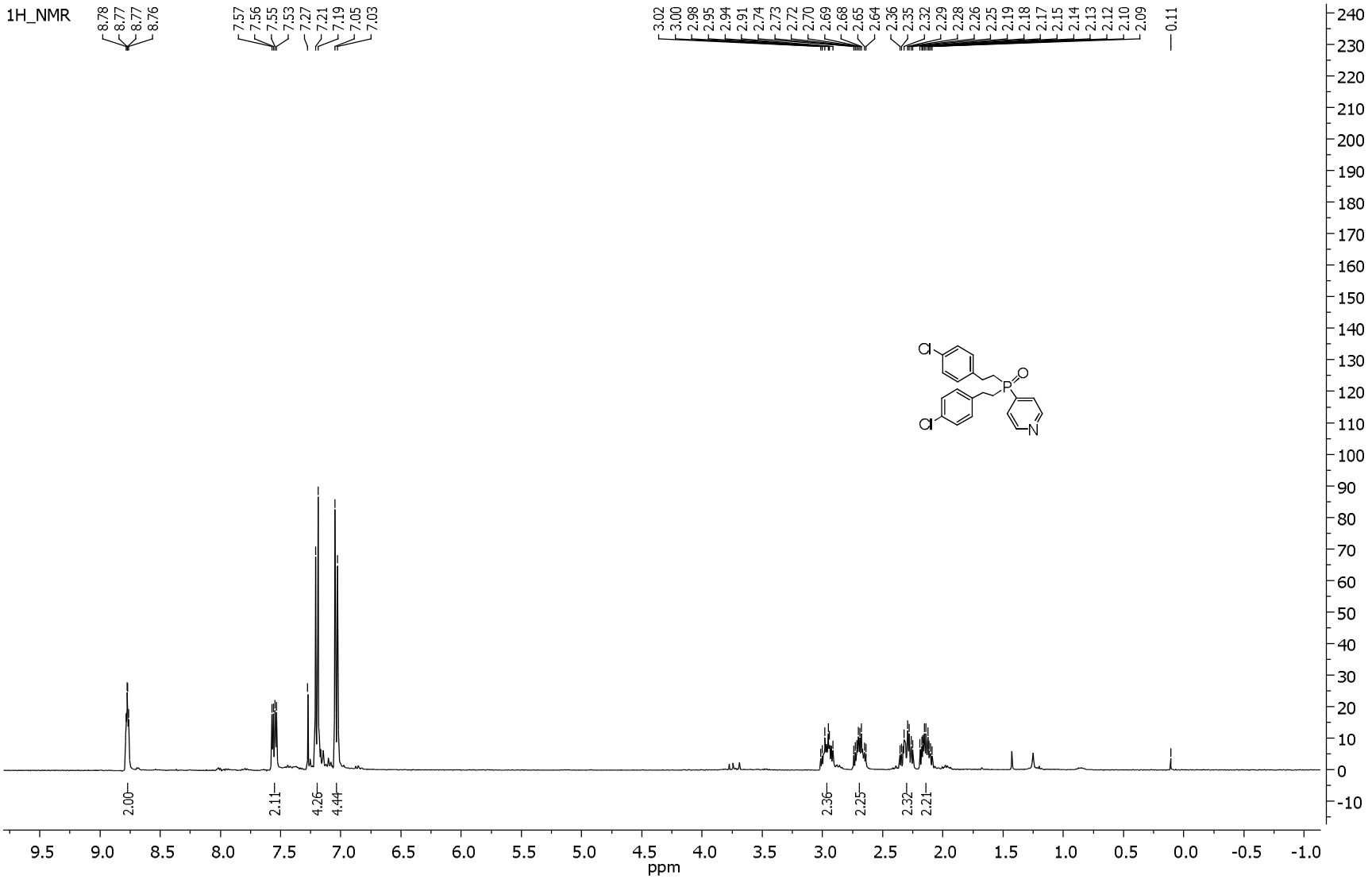
4-[Bis(2-phenylethyl)phosphoryl]pyridine (4b)



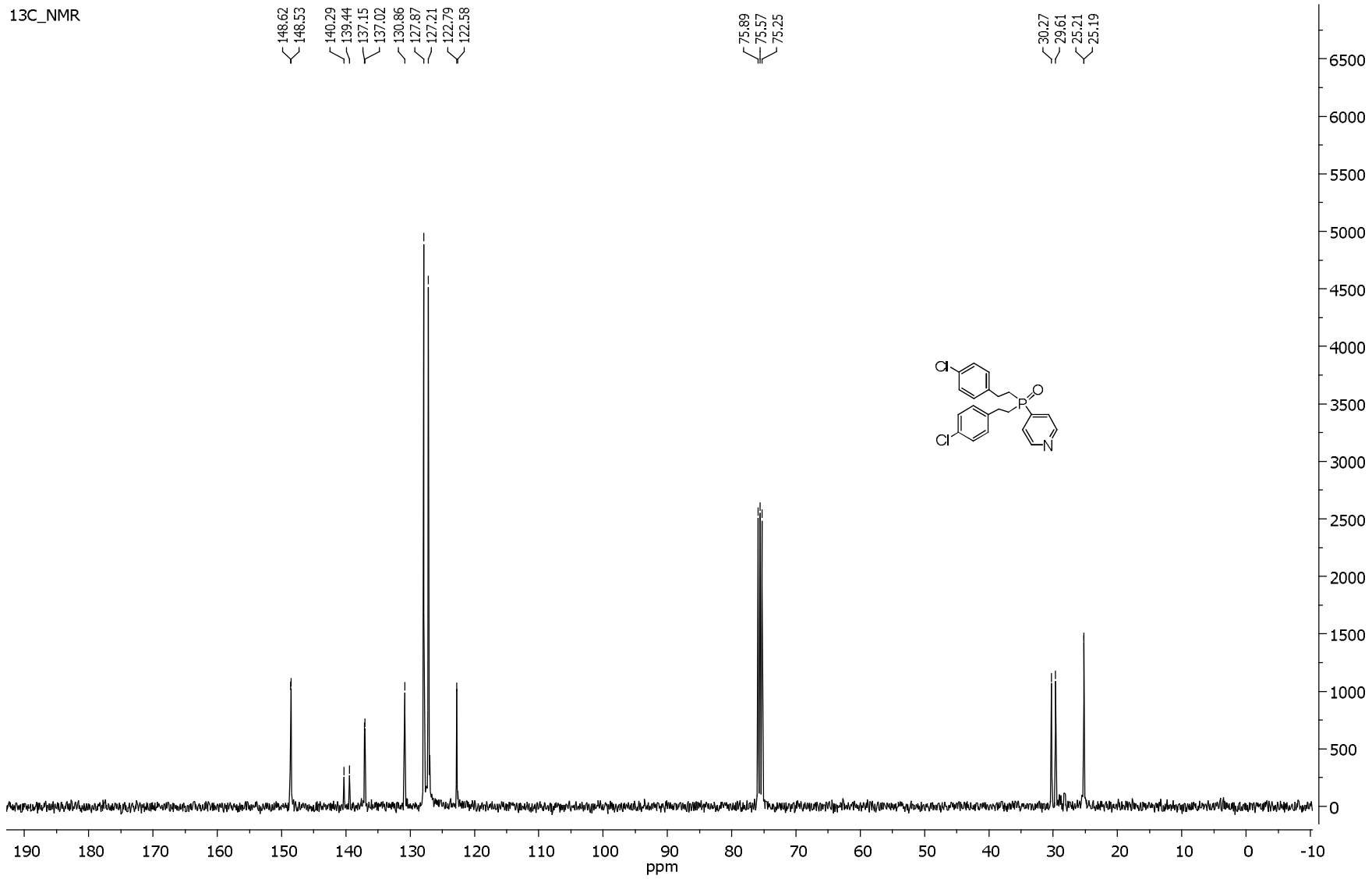
4-[Bis(2-phenylethyl)phosphoryl]pyridine (4b)



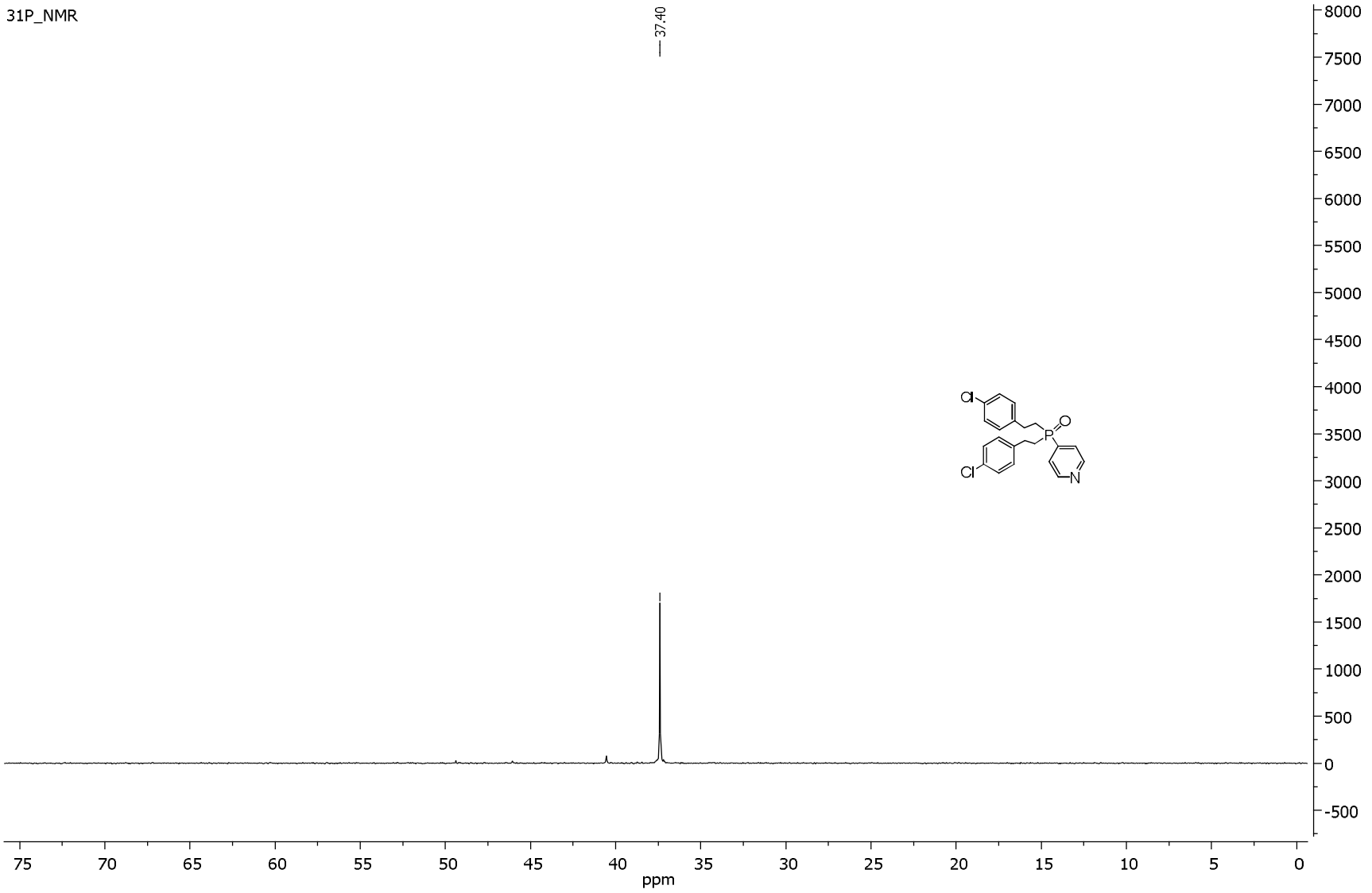
4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}pyridine (4c)



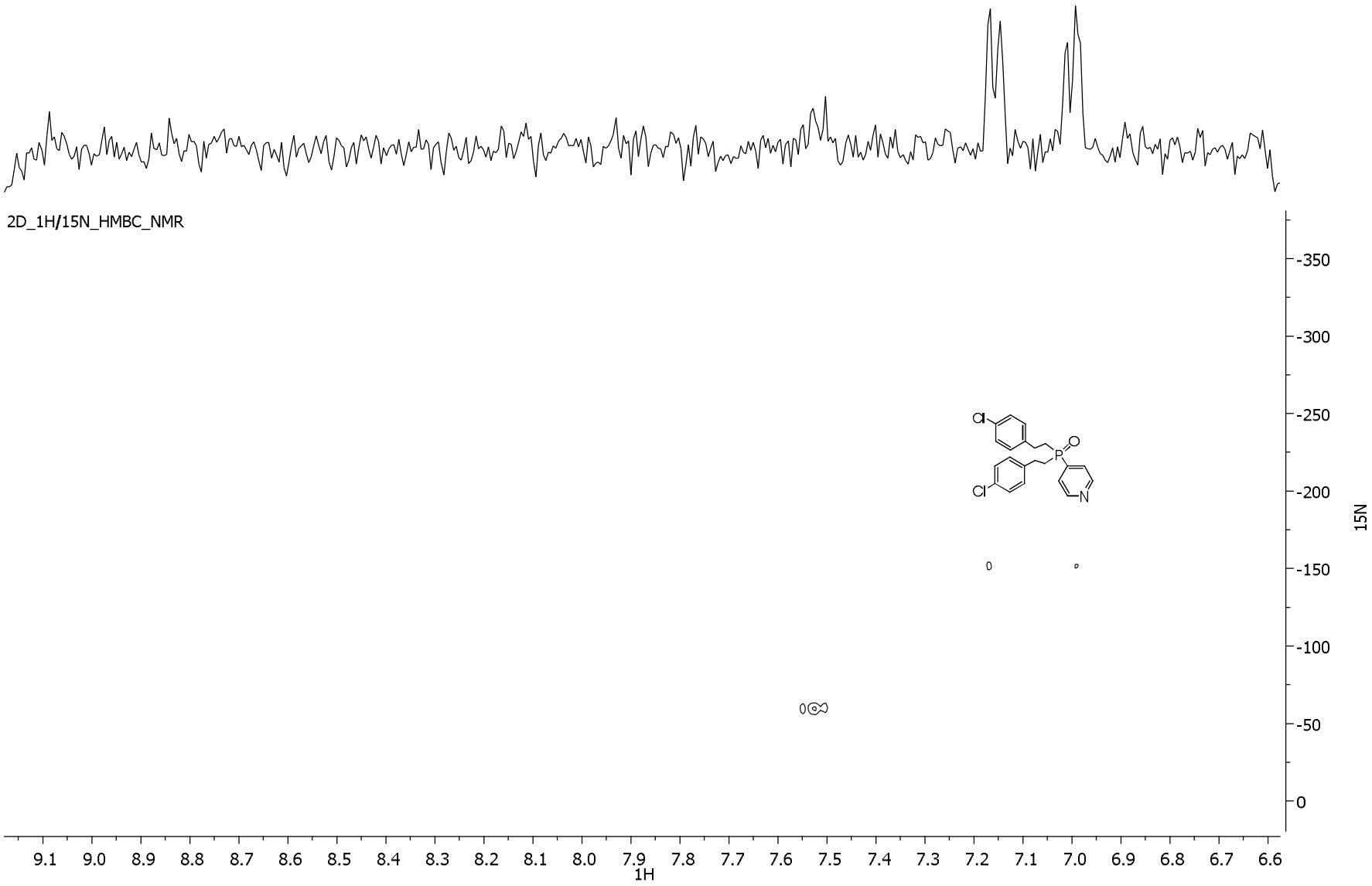
4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}pyridine (4c)



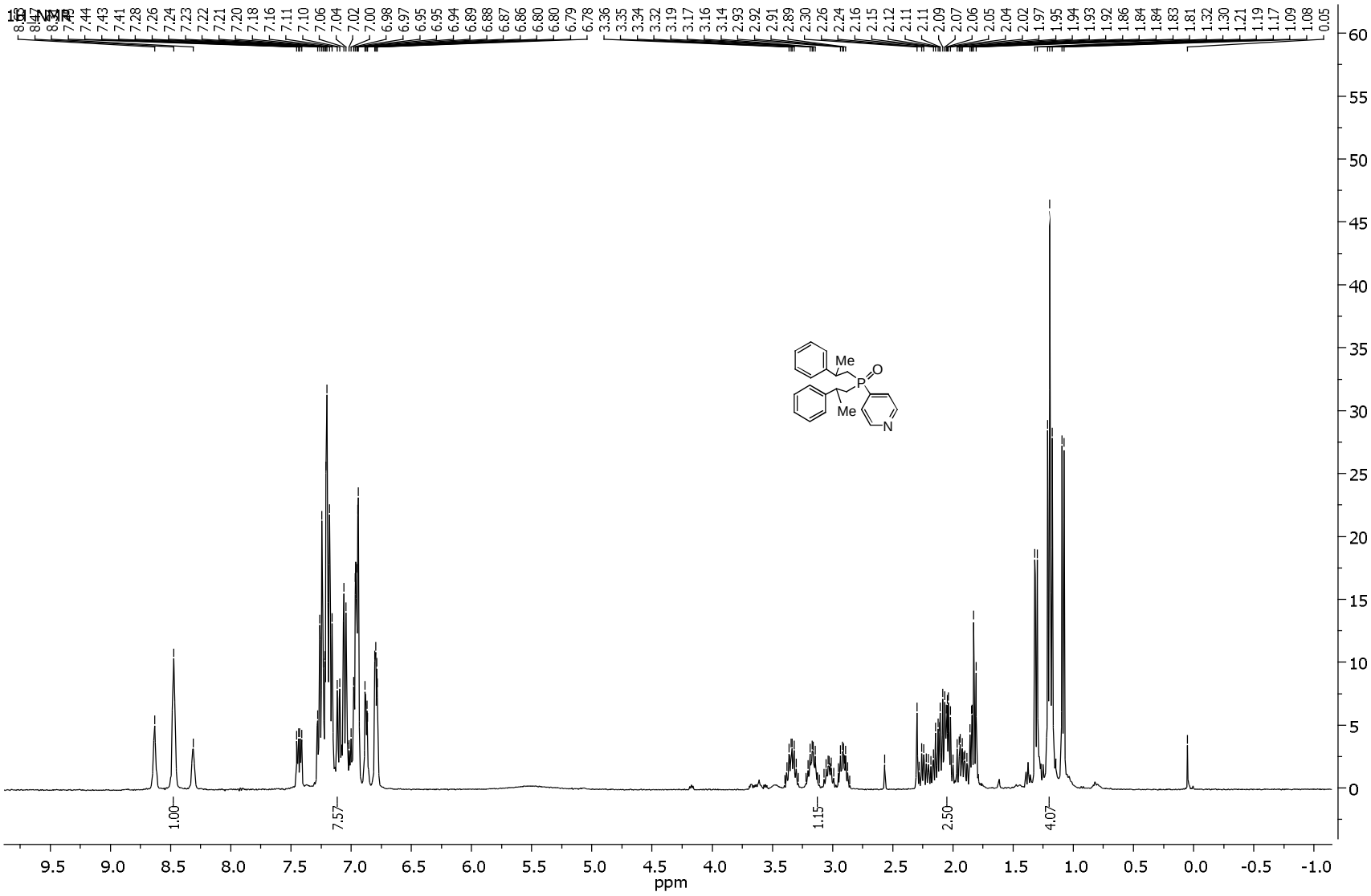
4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}pyridine (4c)



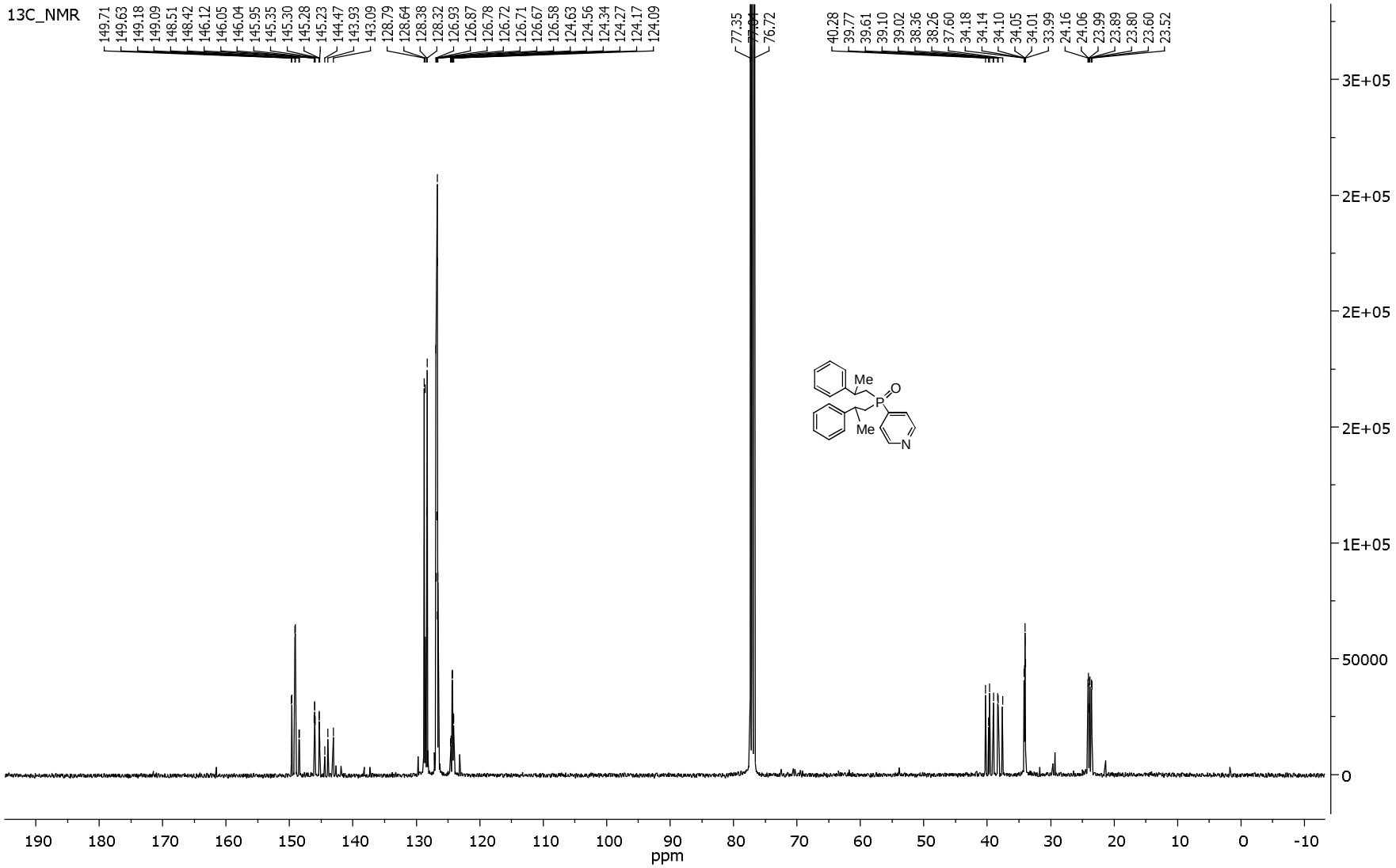
4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}pyridine (4c)



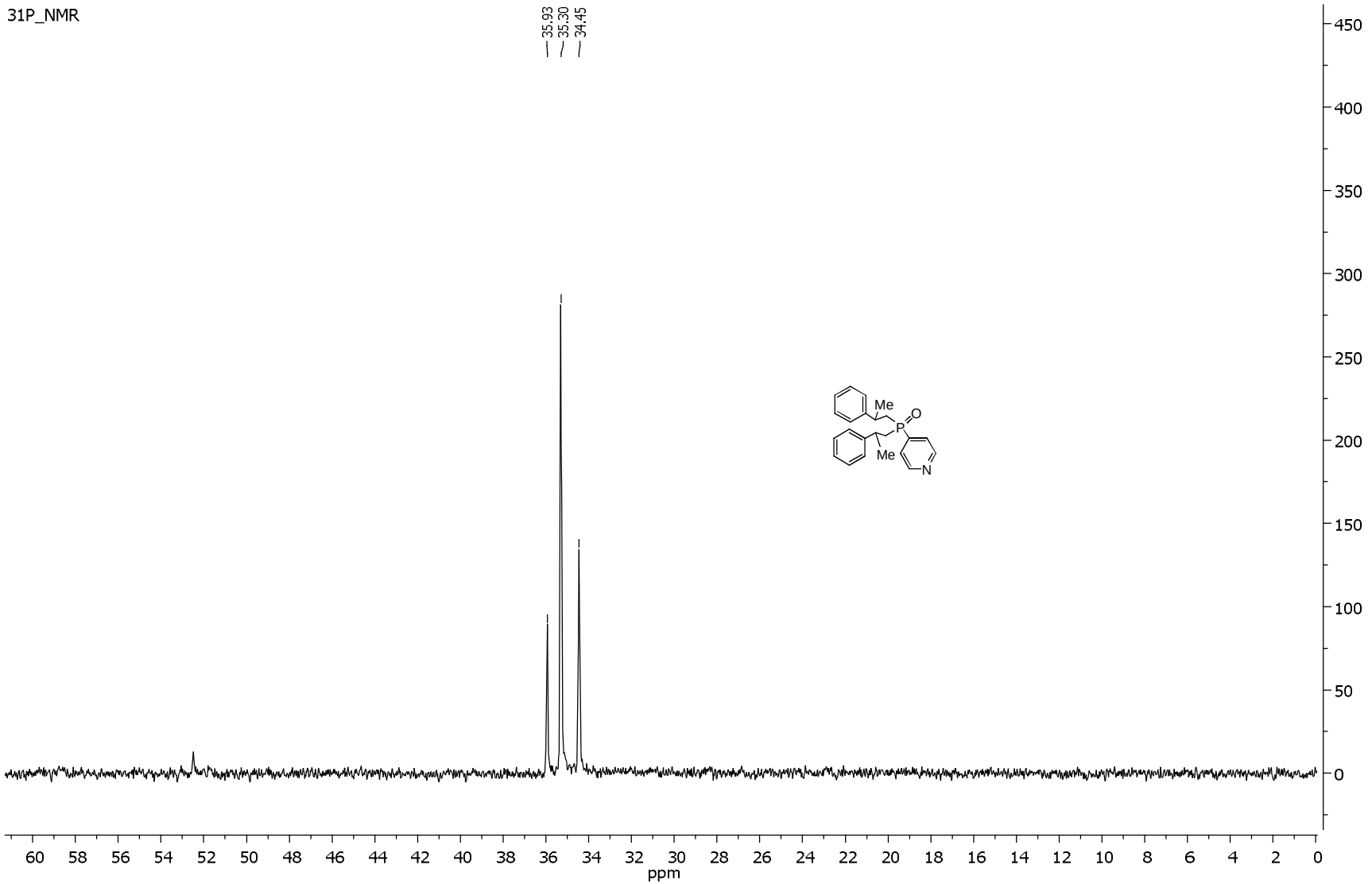
4-[Bis(2-phenylpropyl)phosphoryl]pyridine (4d)



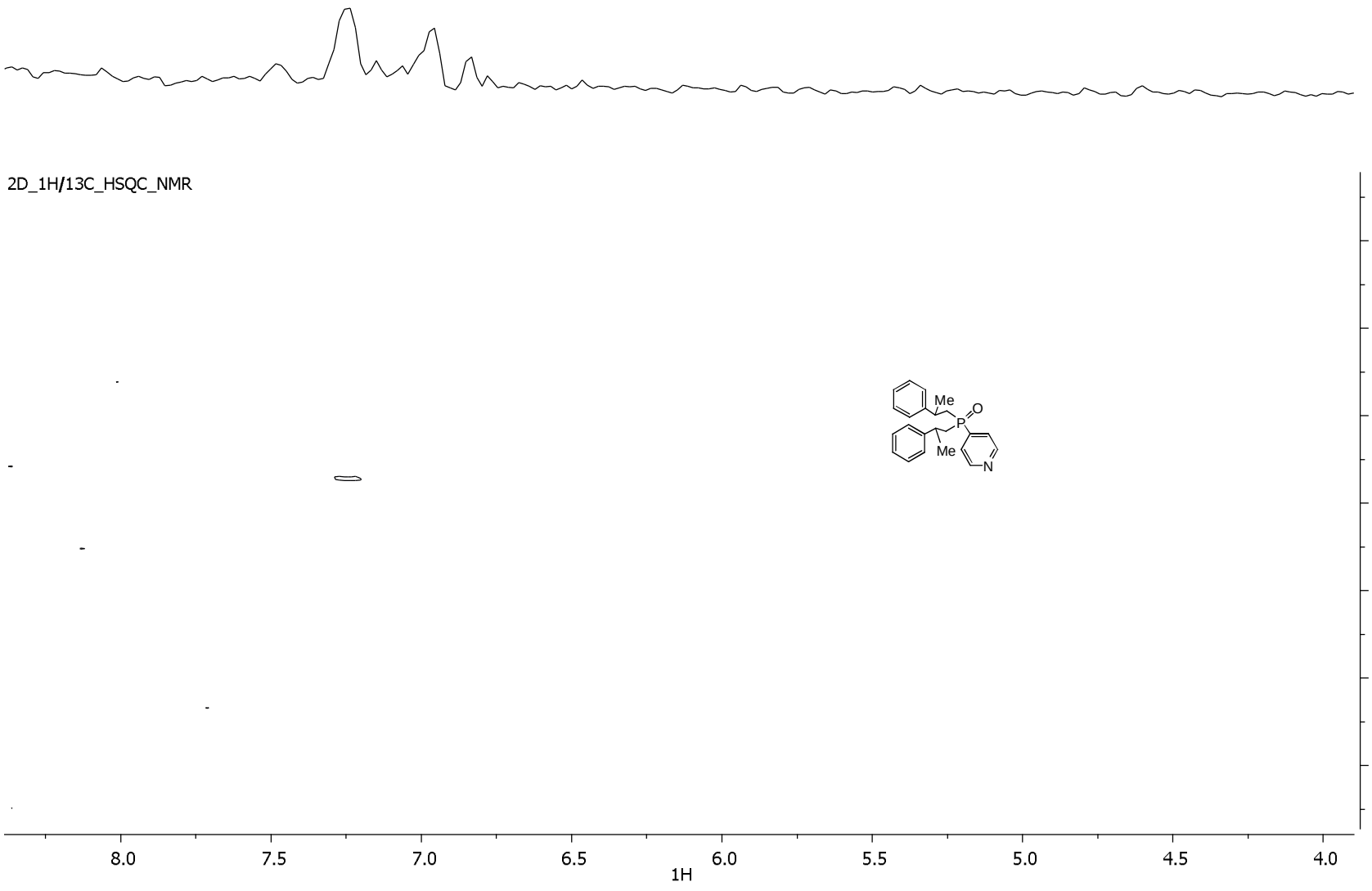
4-[Bis(2-phenylpropyl)phosphoryl]pyridine (4d)



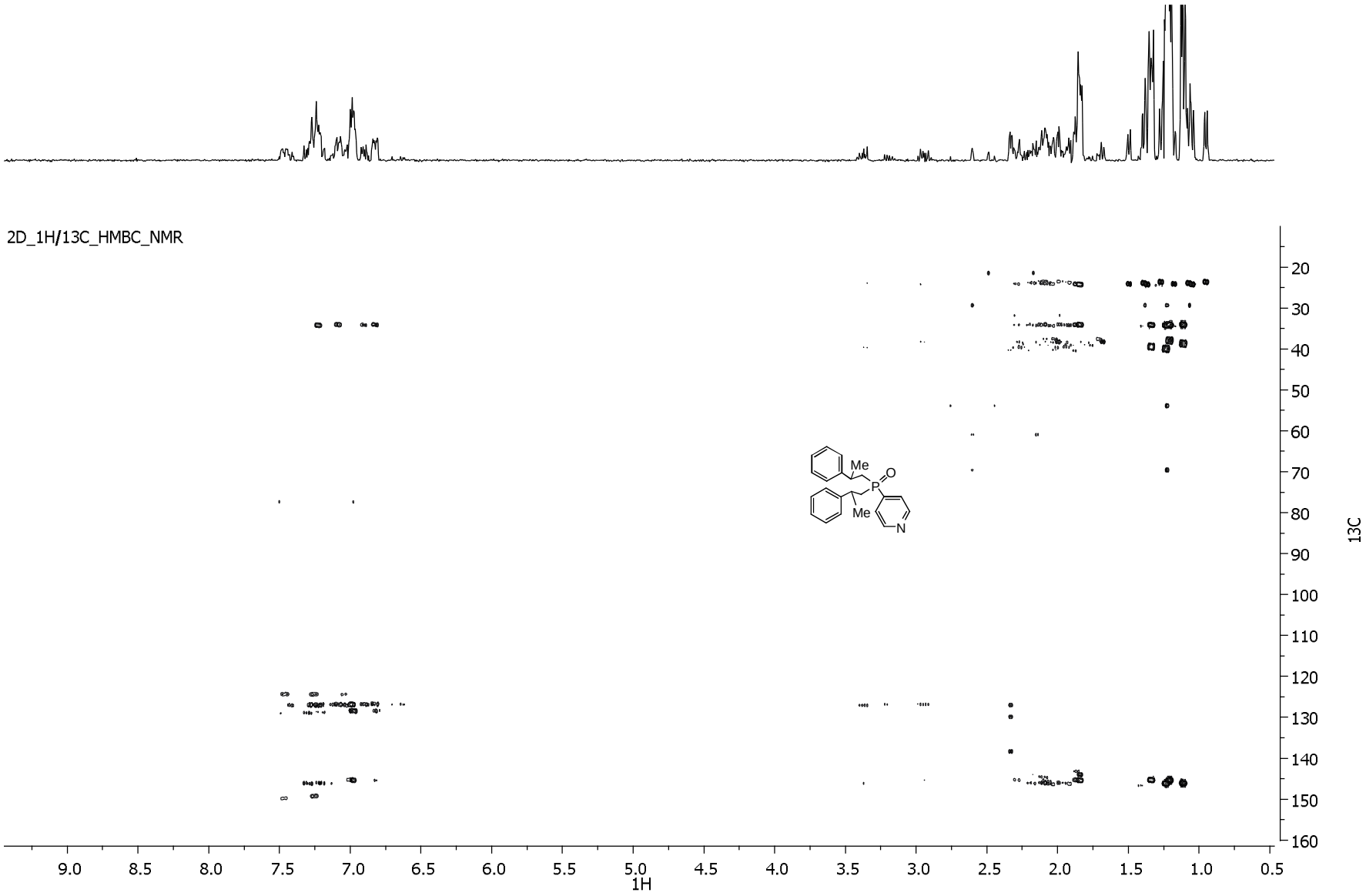
4-[Bis(2-phenylpropyl)phosphoryl]pyridine (4d)



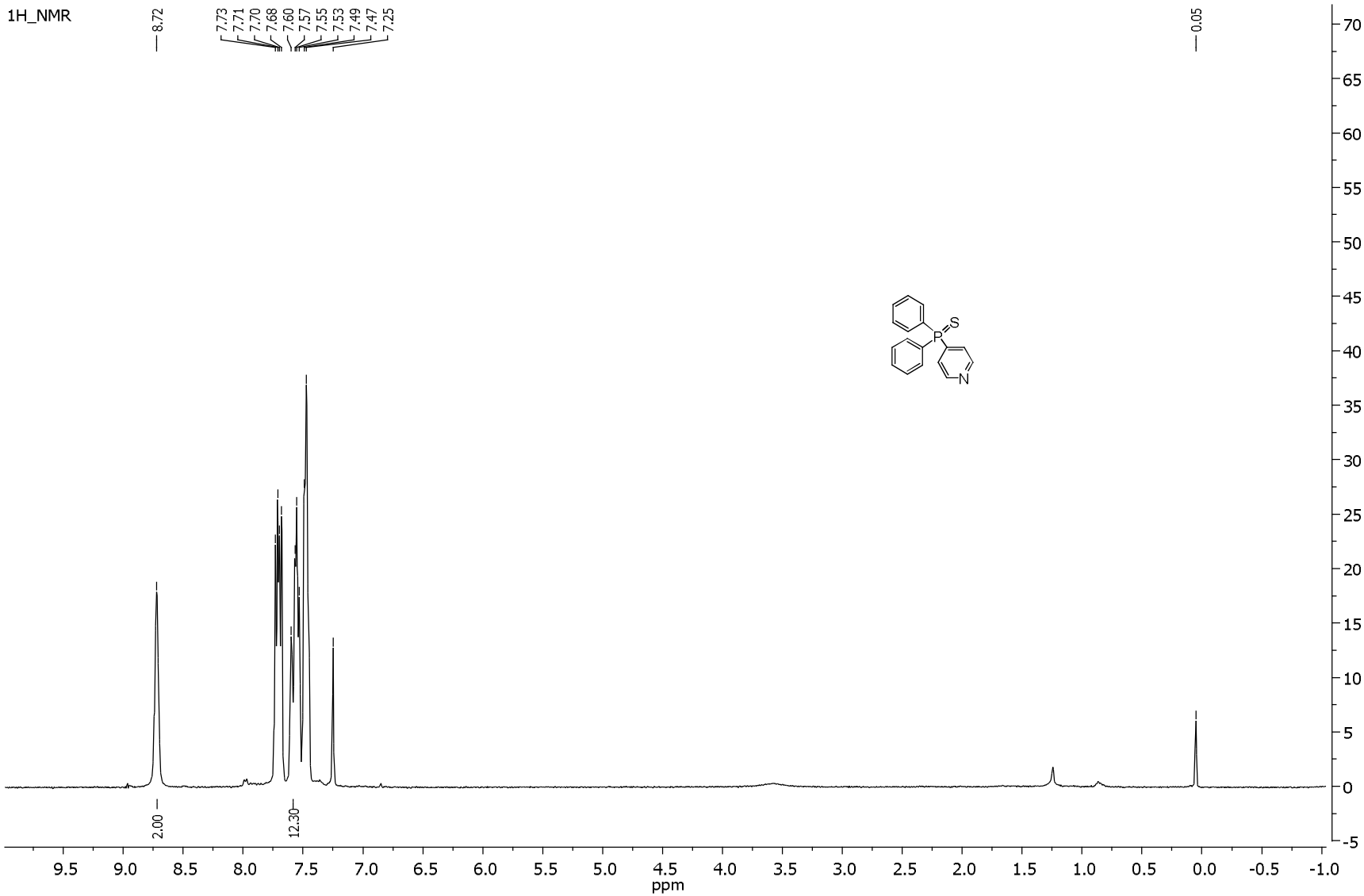
4-[Bis(2-phenylpropyl)phosphoryl]pyridine (4d)



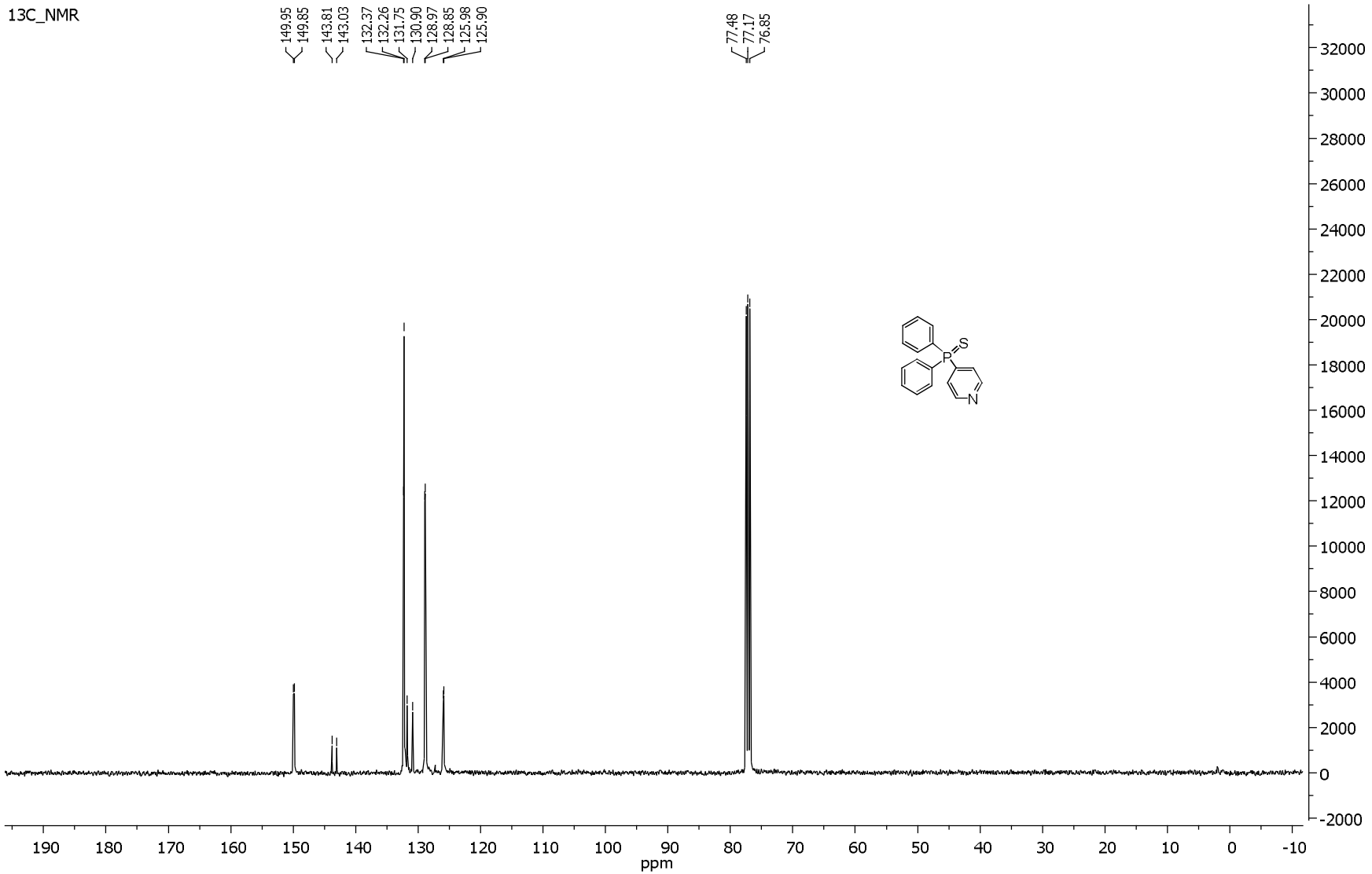
4-[Bis(2-phenylpropyl)phosphoryl]pyridine (4d)



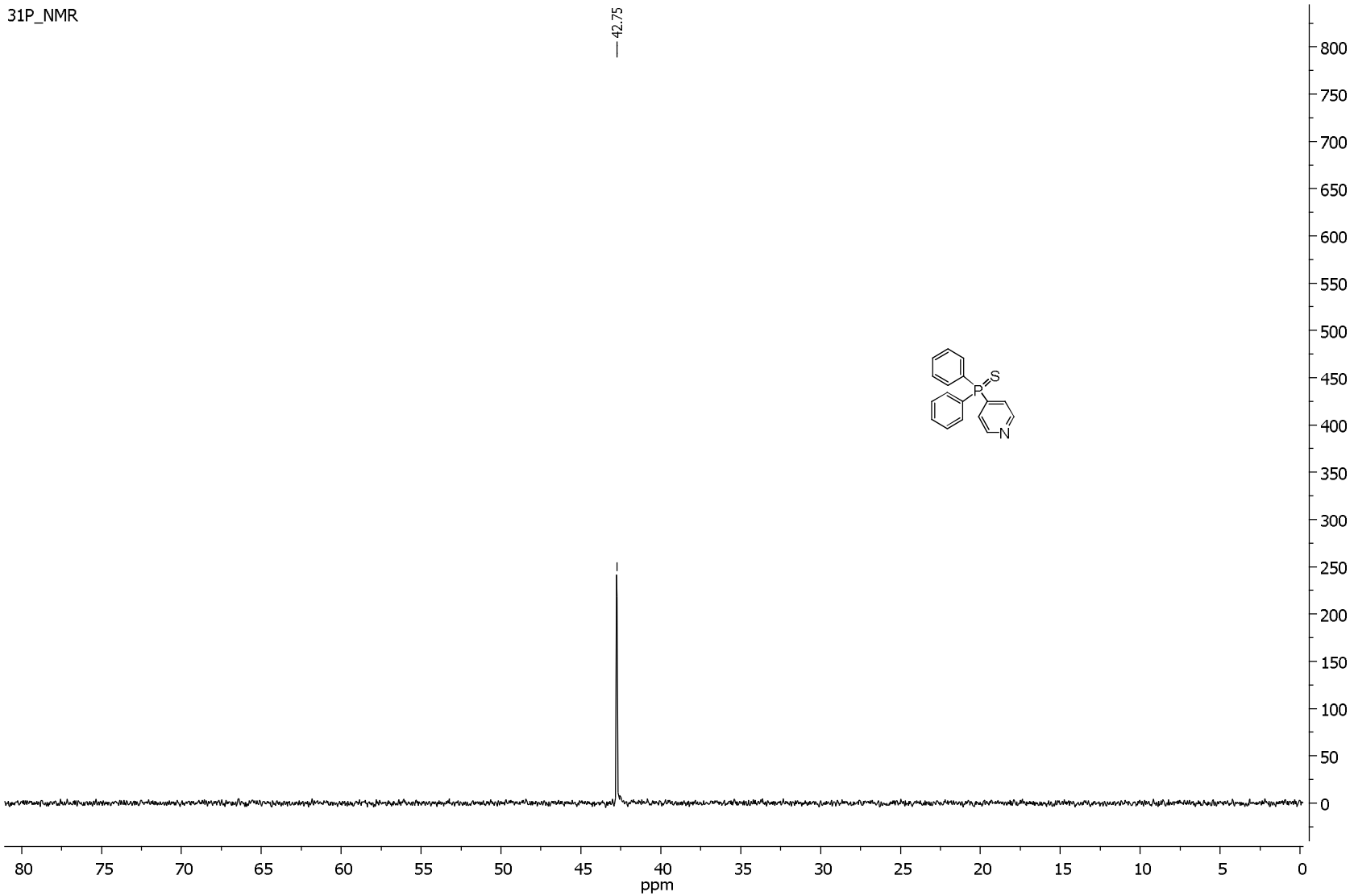
4-(Diphenylphosphorothioyl)pyridine (4e)



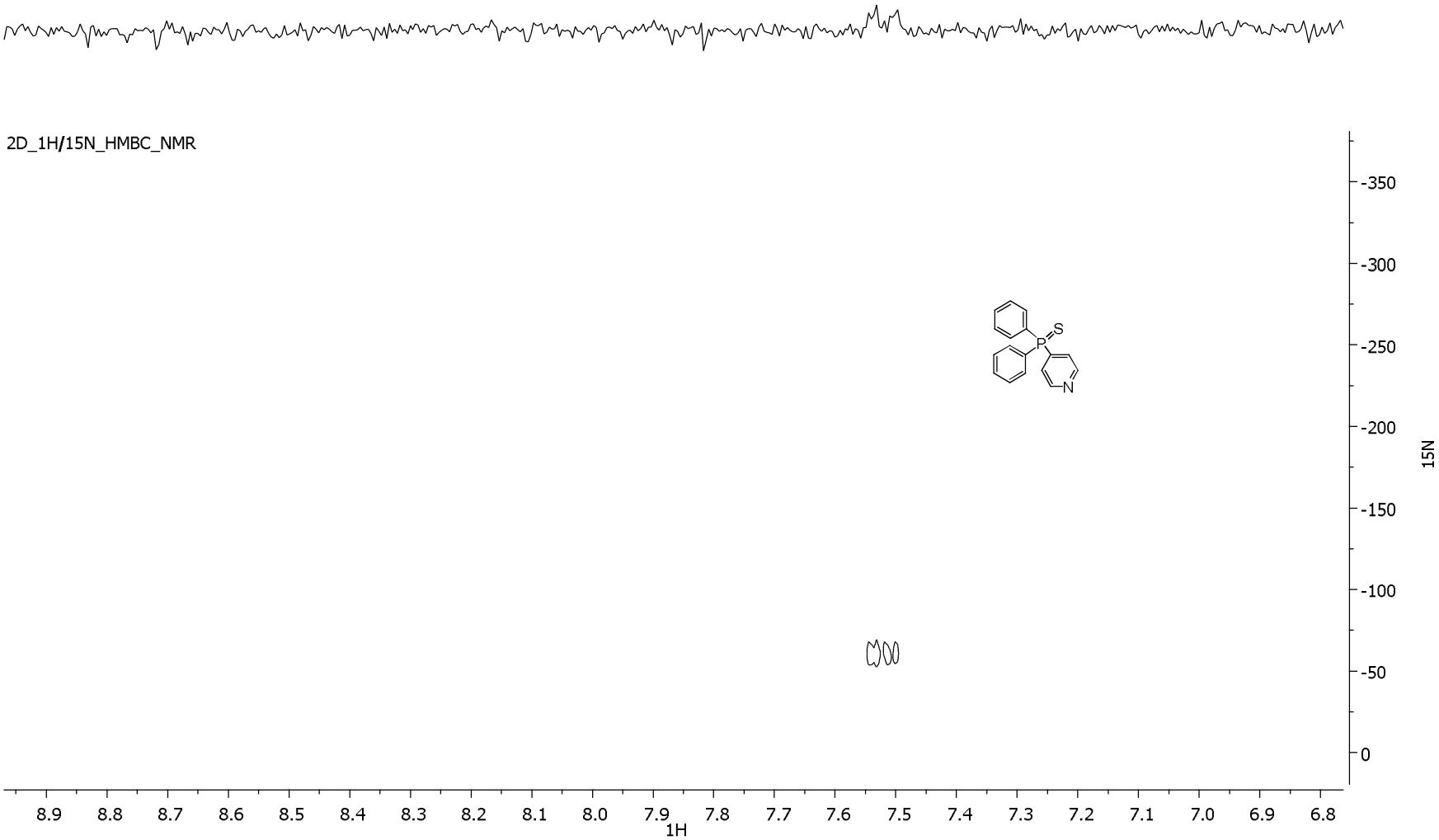
4-(Diphenylphosphorothioyl)pyridine (4e)



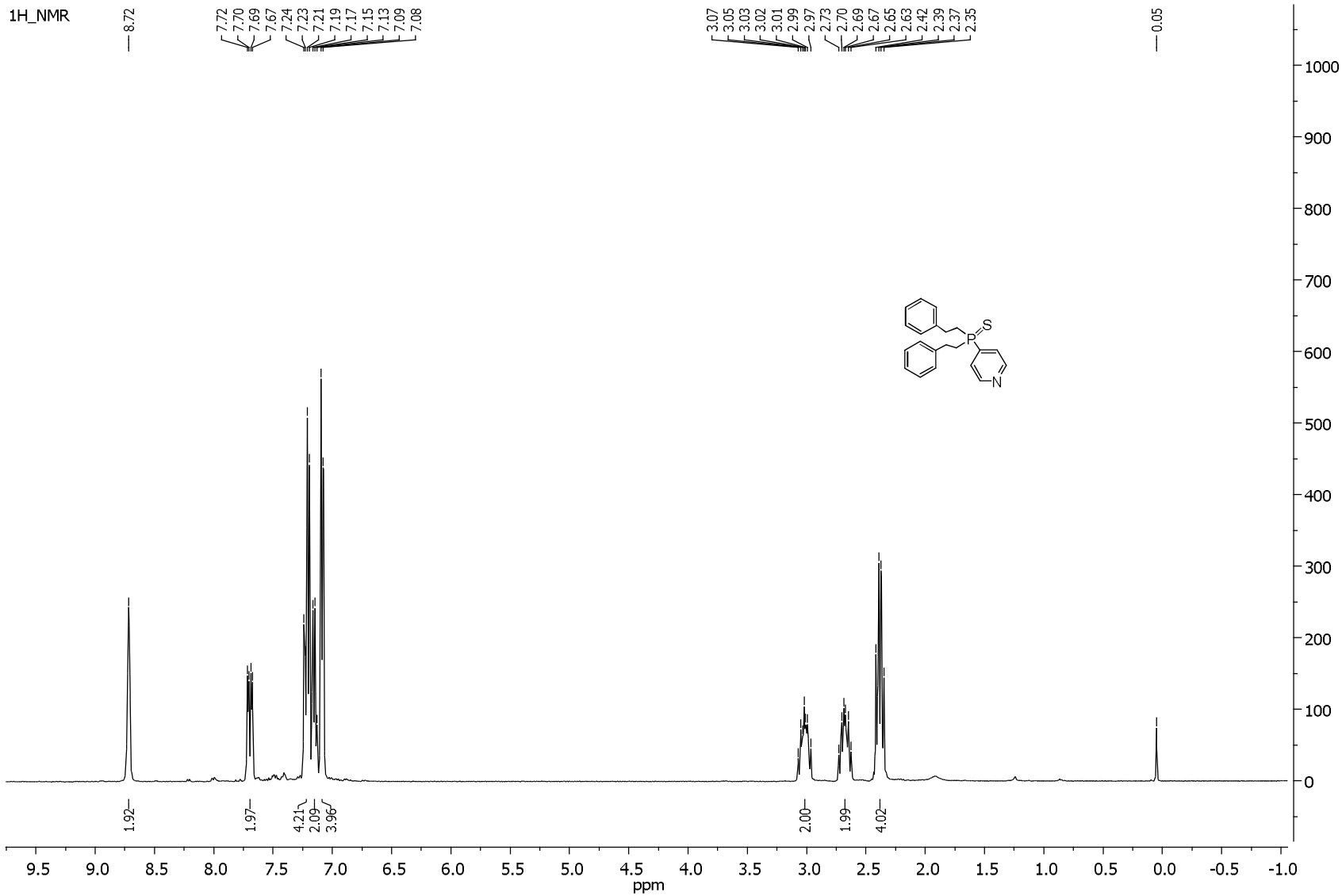
4-(Diphenylphosphorothioyl)pyridine (4e)



4-(Diphenylphosphorothioyl)pyridine (4e)



4-[Bis(2-phenylethyl)phosphorothioyl]pyridine (4f)



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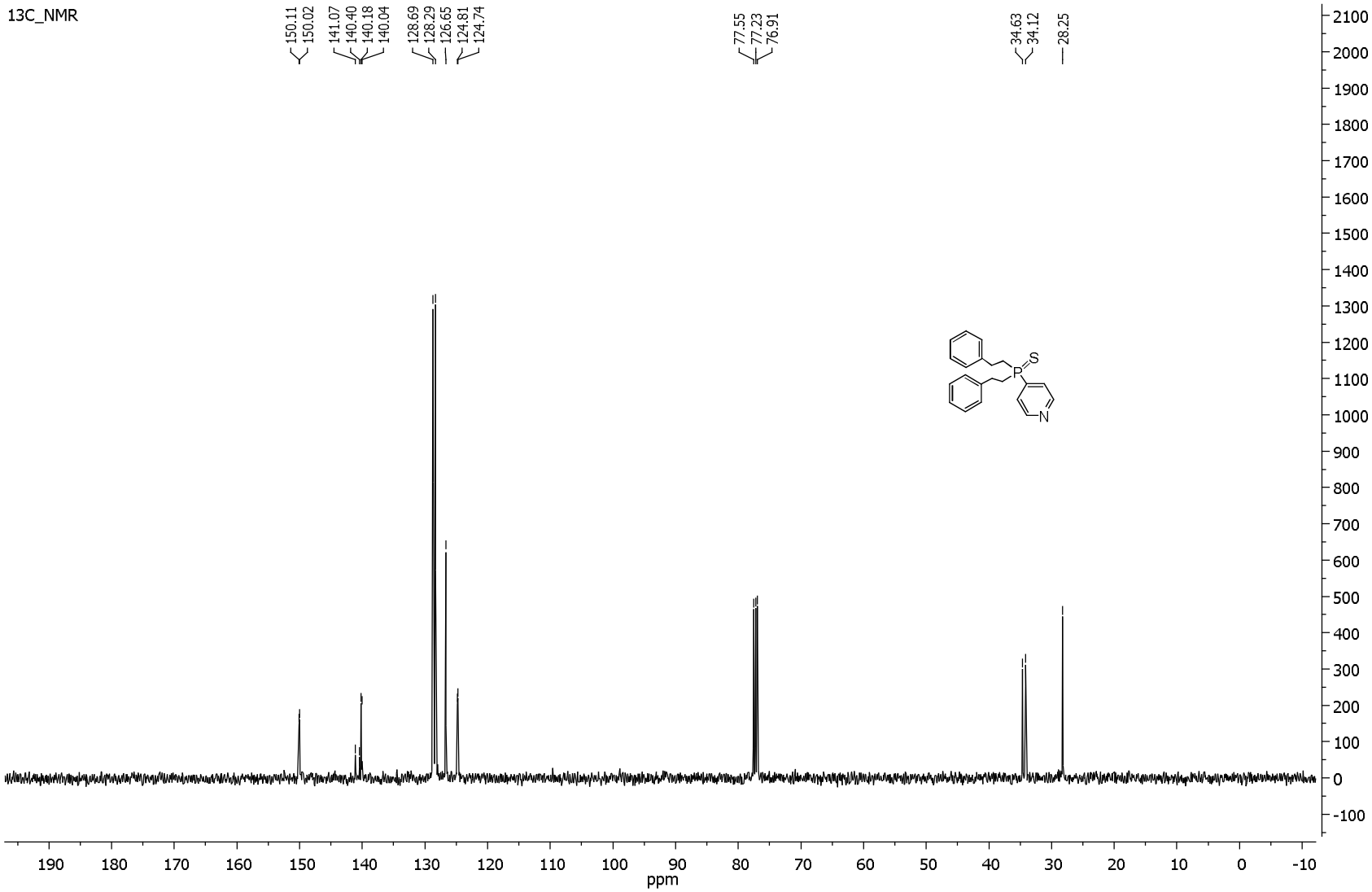

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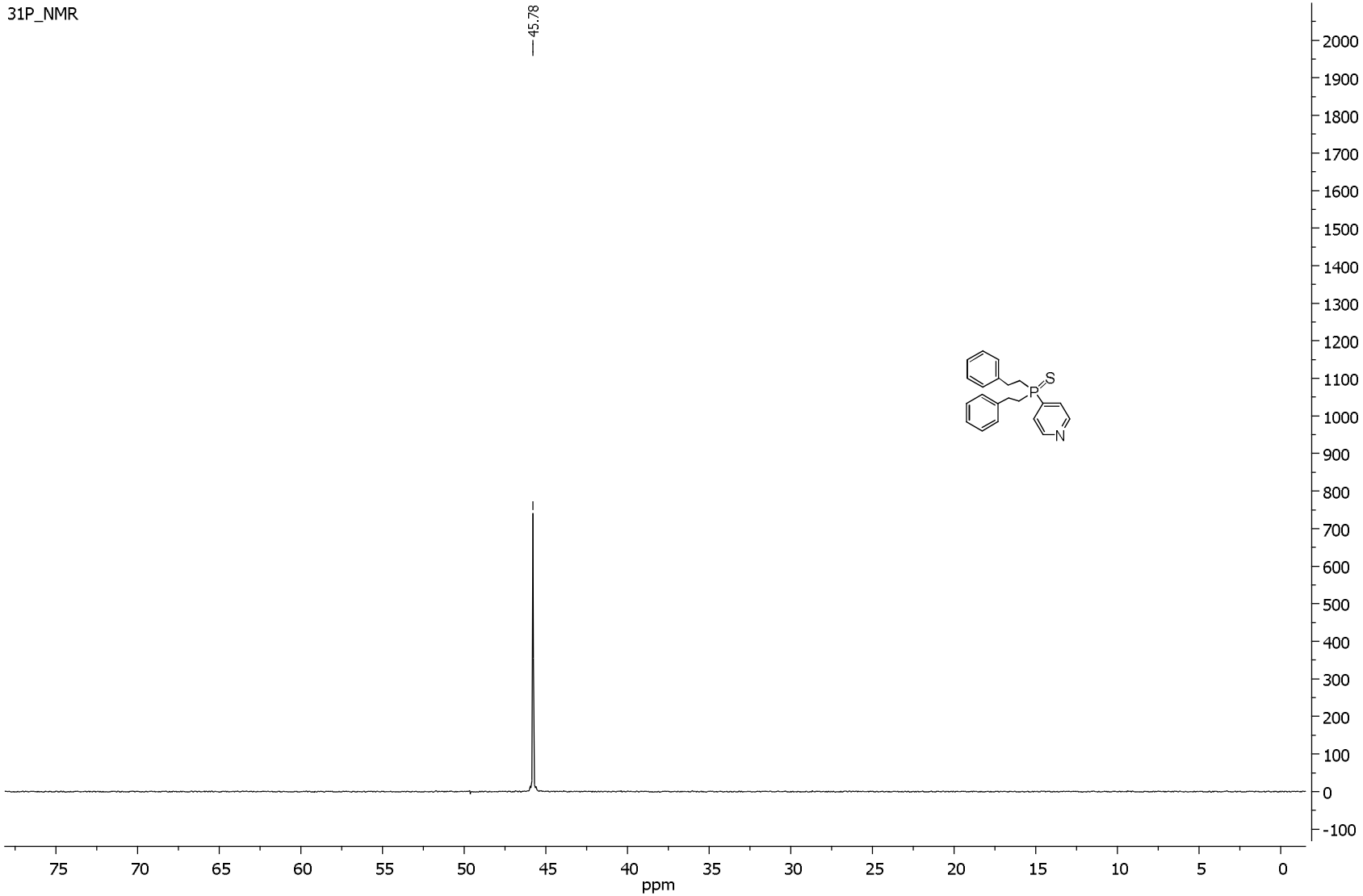

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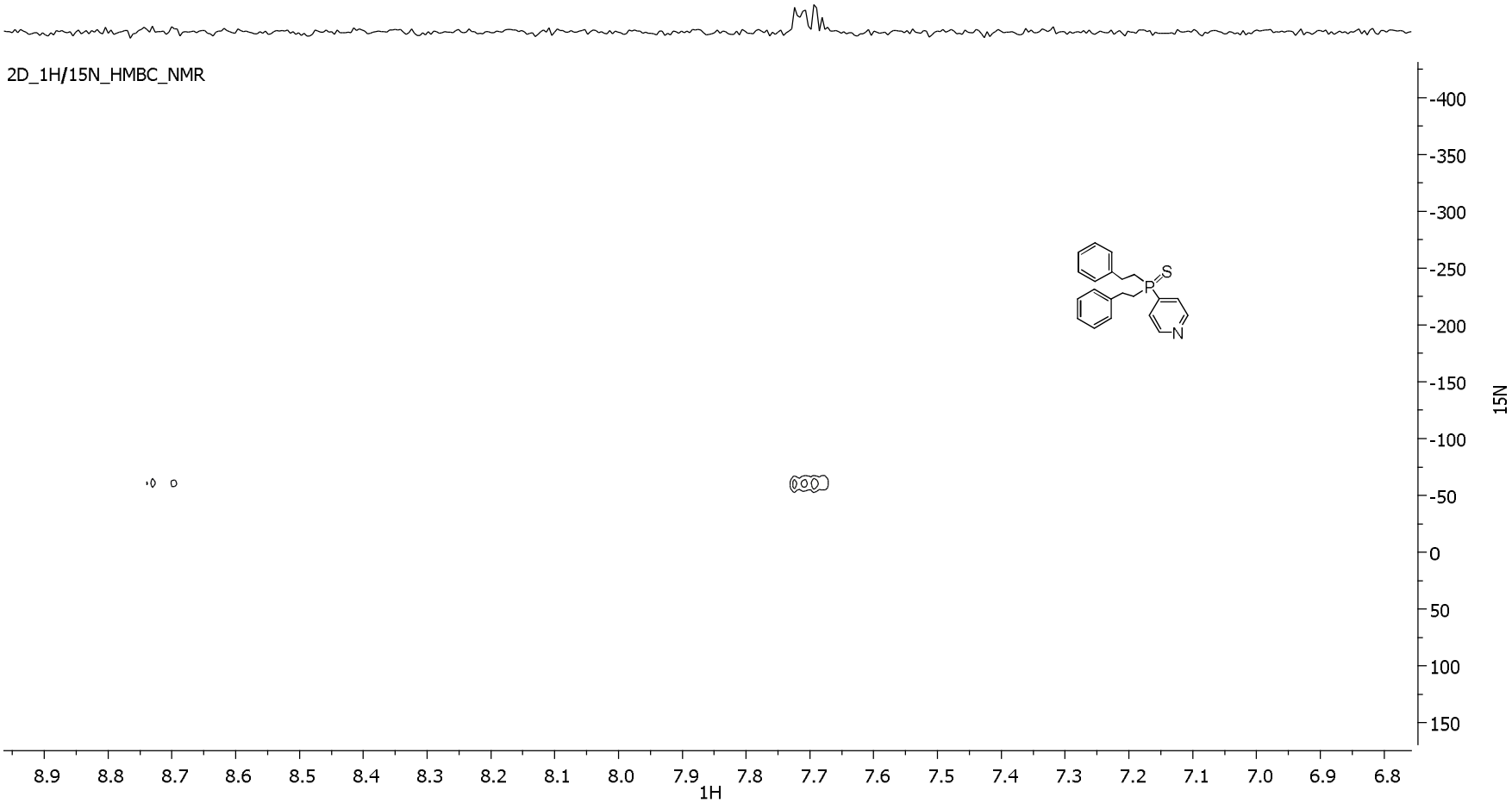
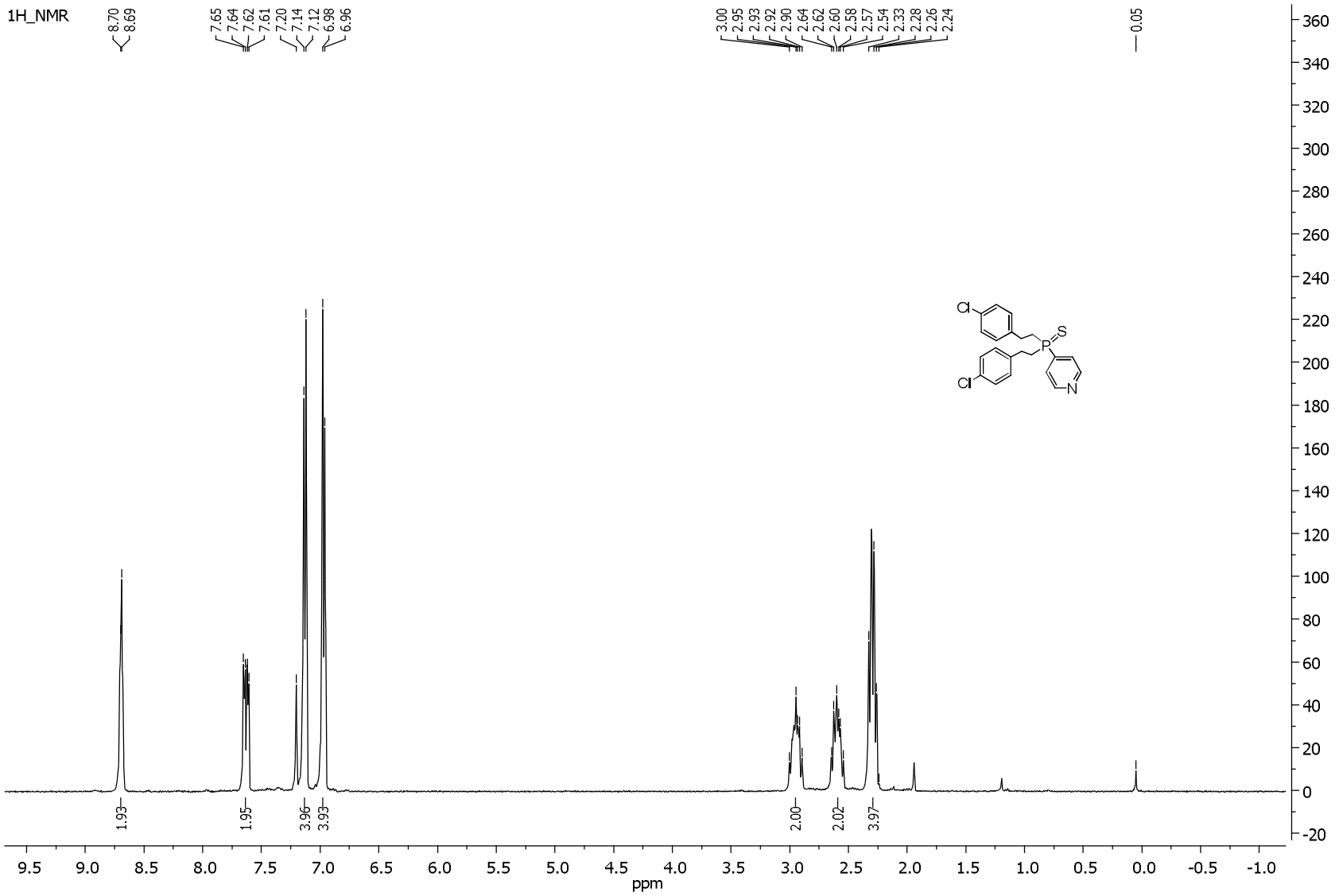


4-{Bis[2-(4-chlorophenyl)ethyl]phosphorothioyl}pyridine (4g)



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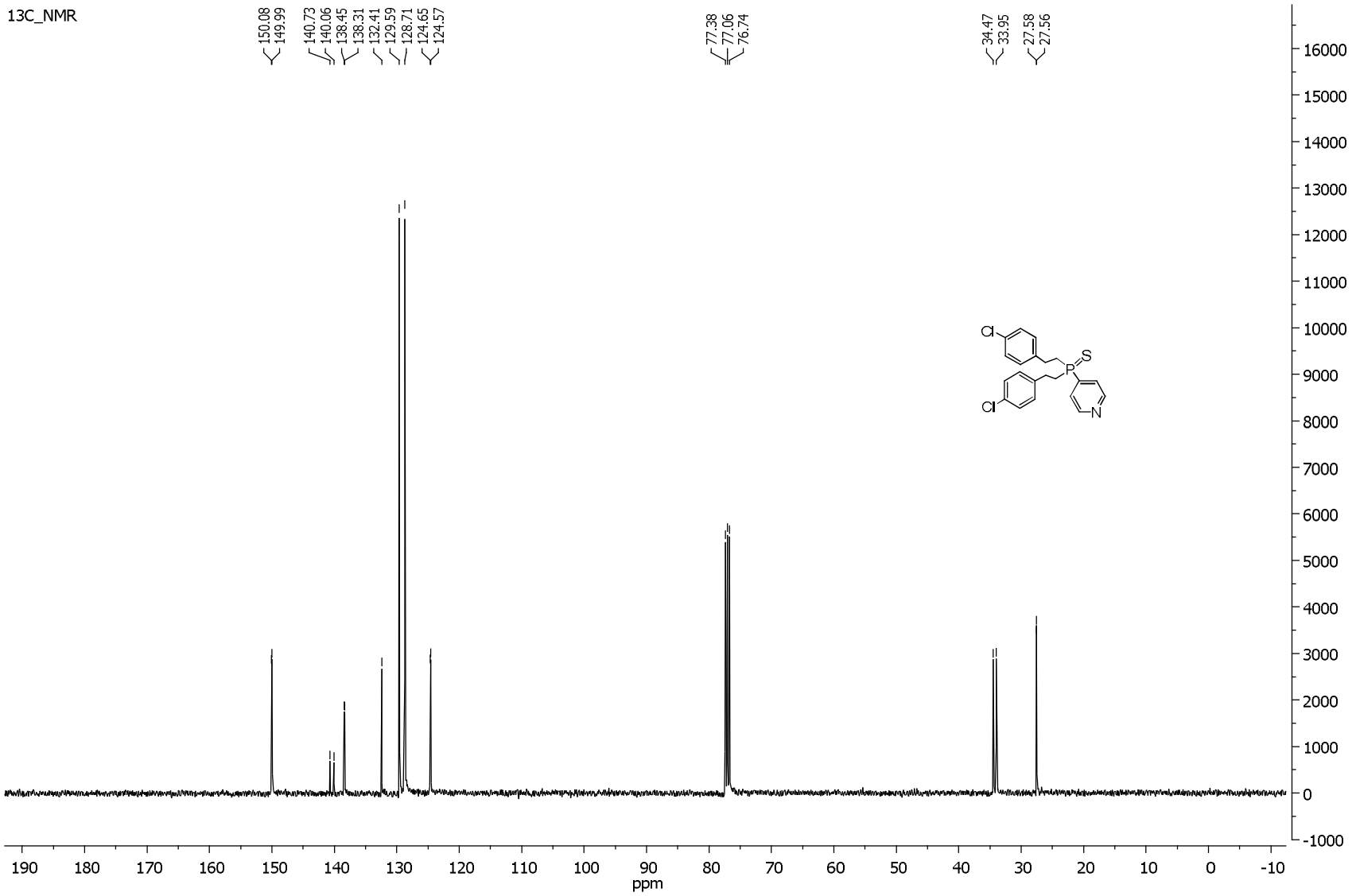

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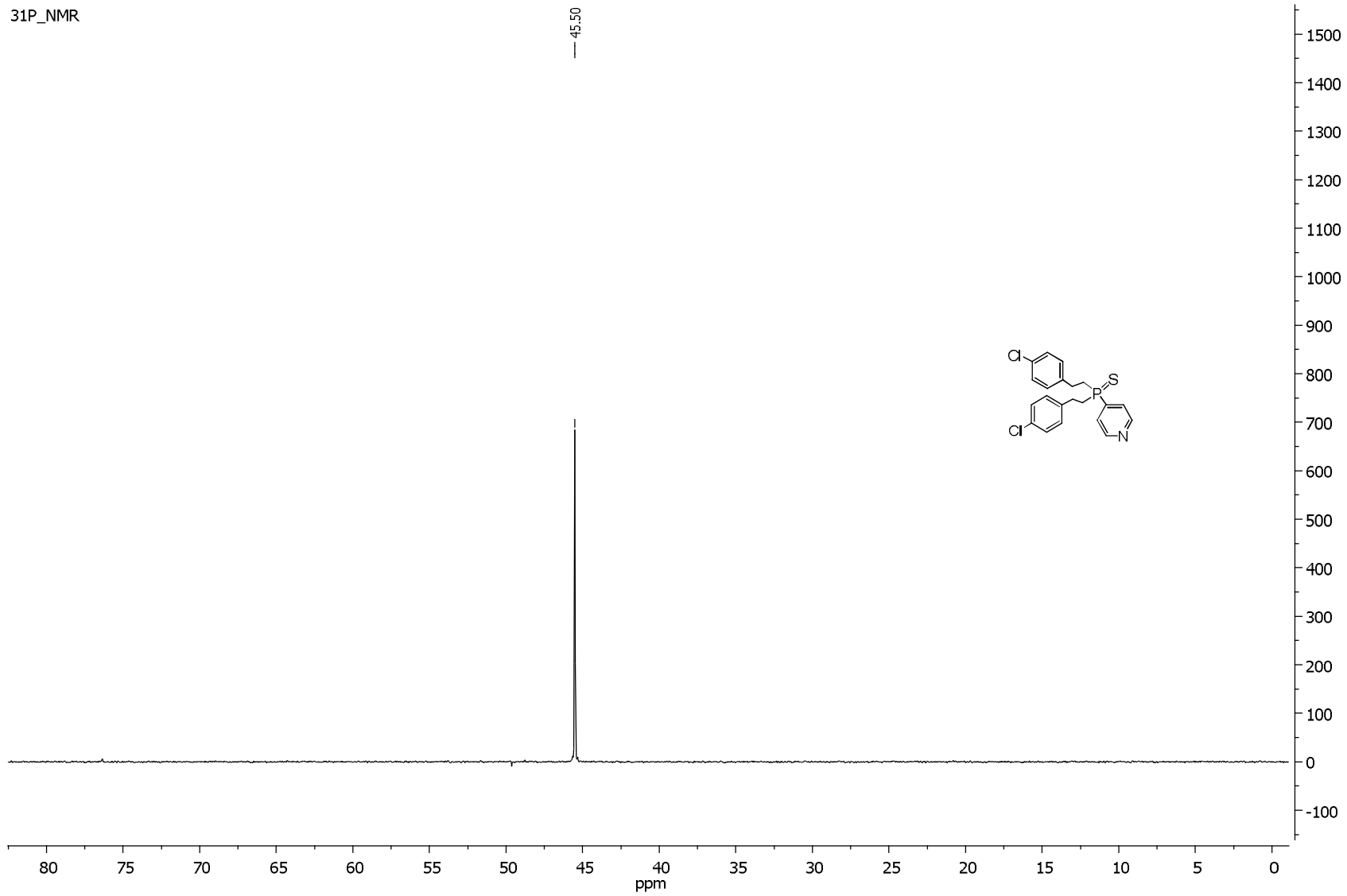

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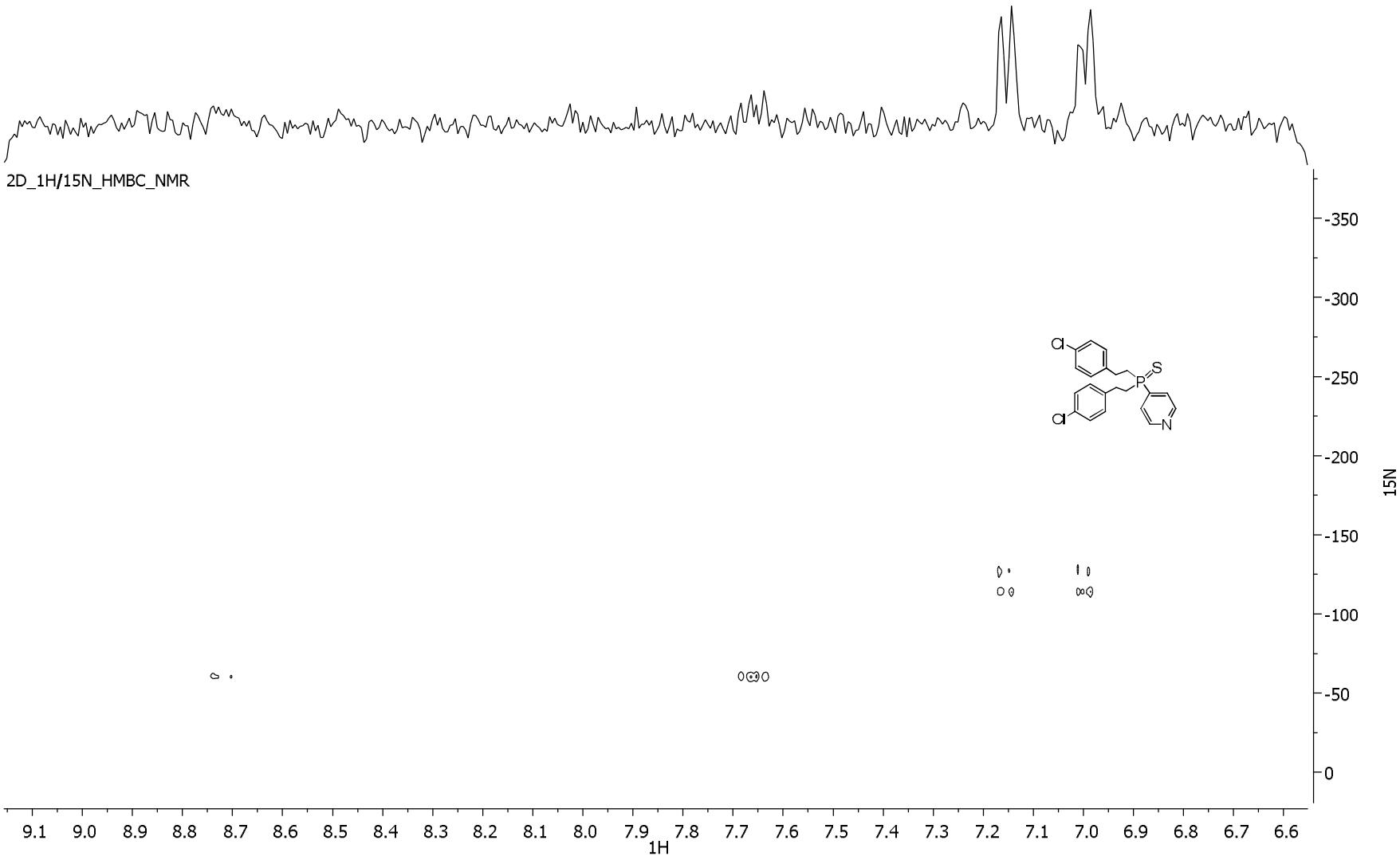
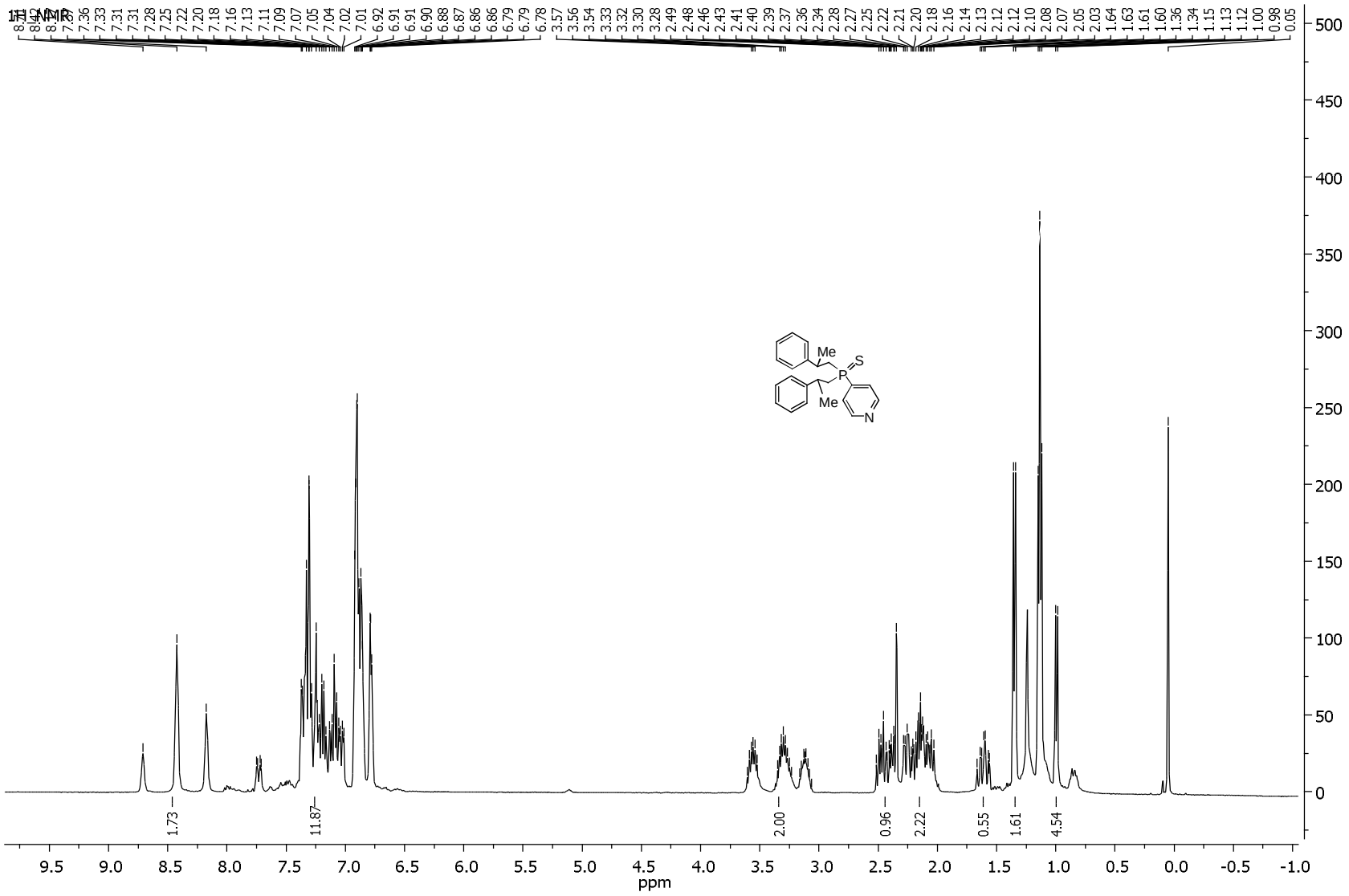


4-[Bis(2-phenylpropyl)phosphorothioyl]pyridine (4h)



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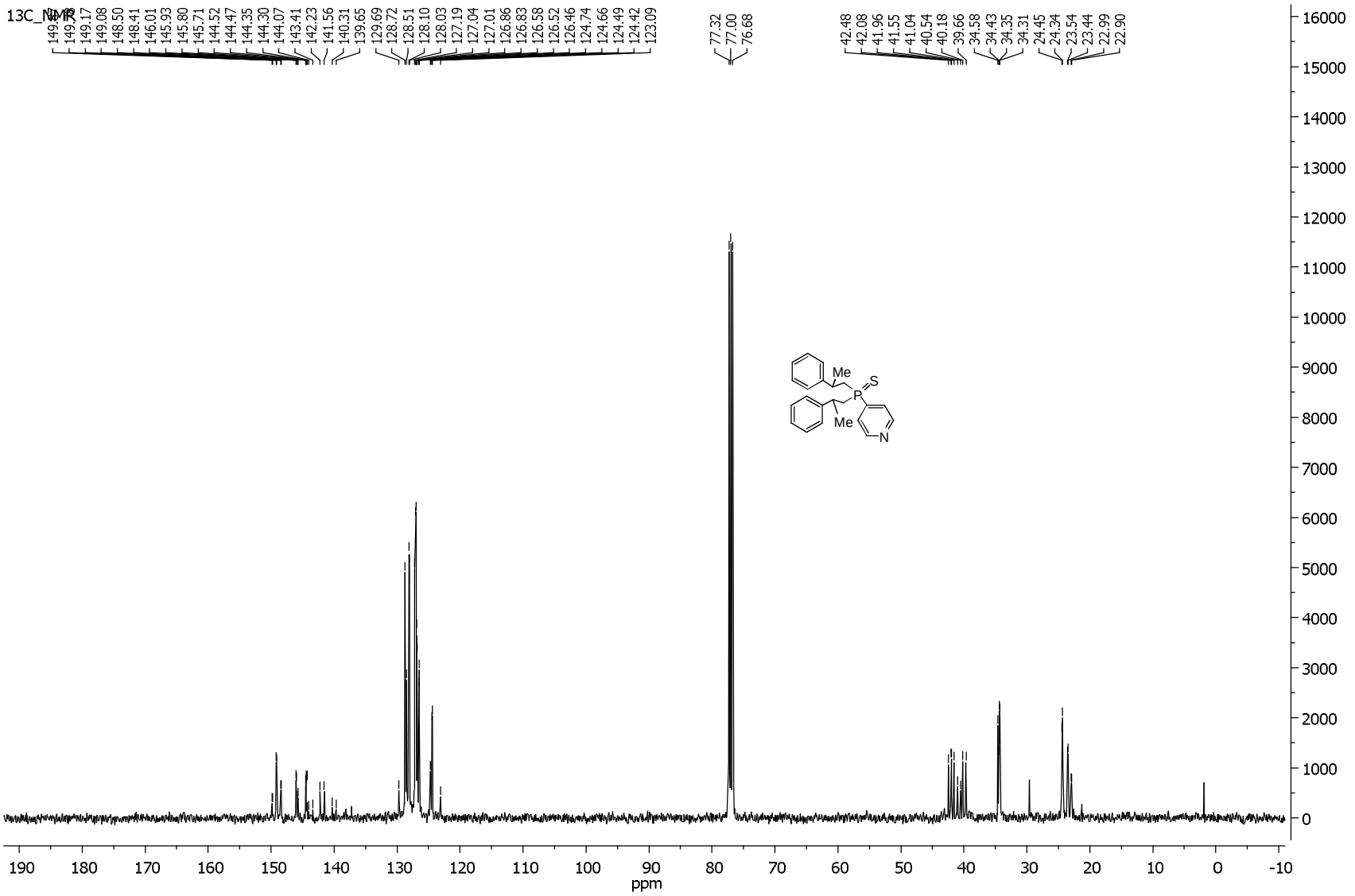

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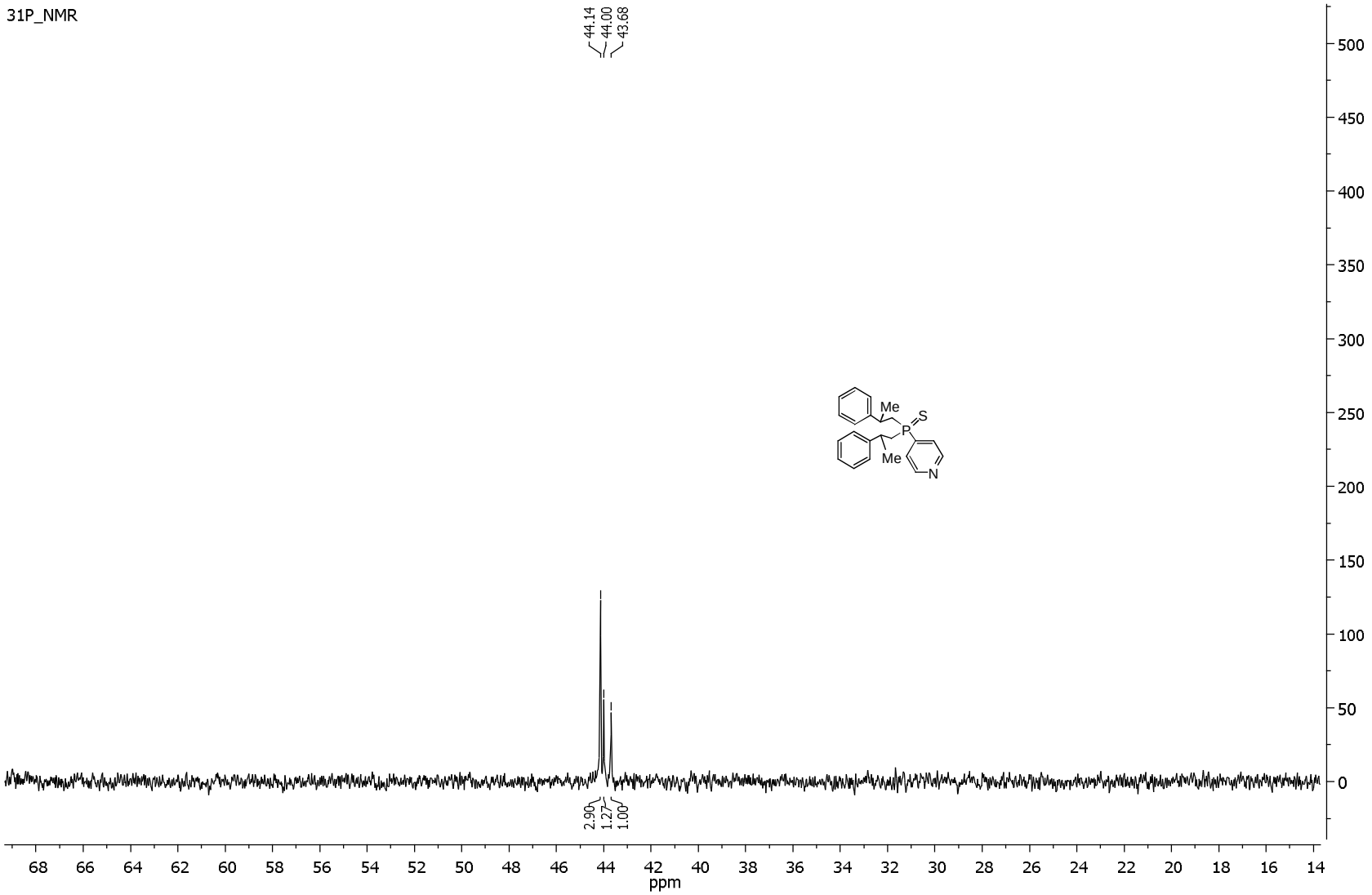

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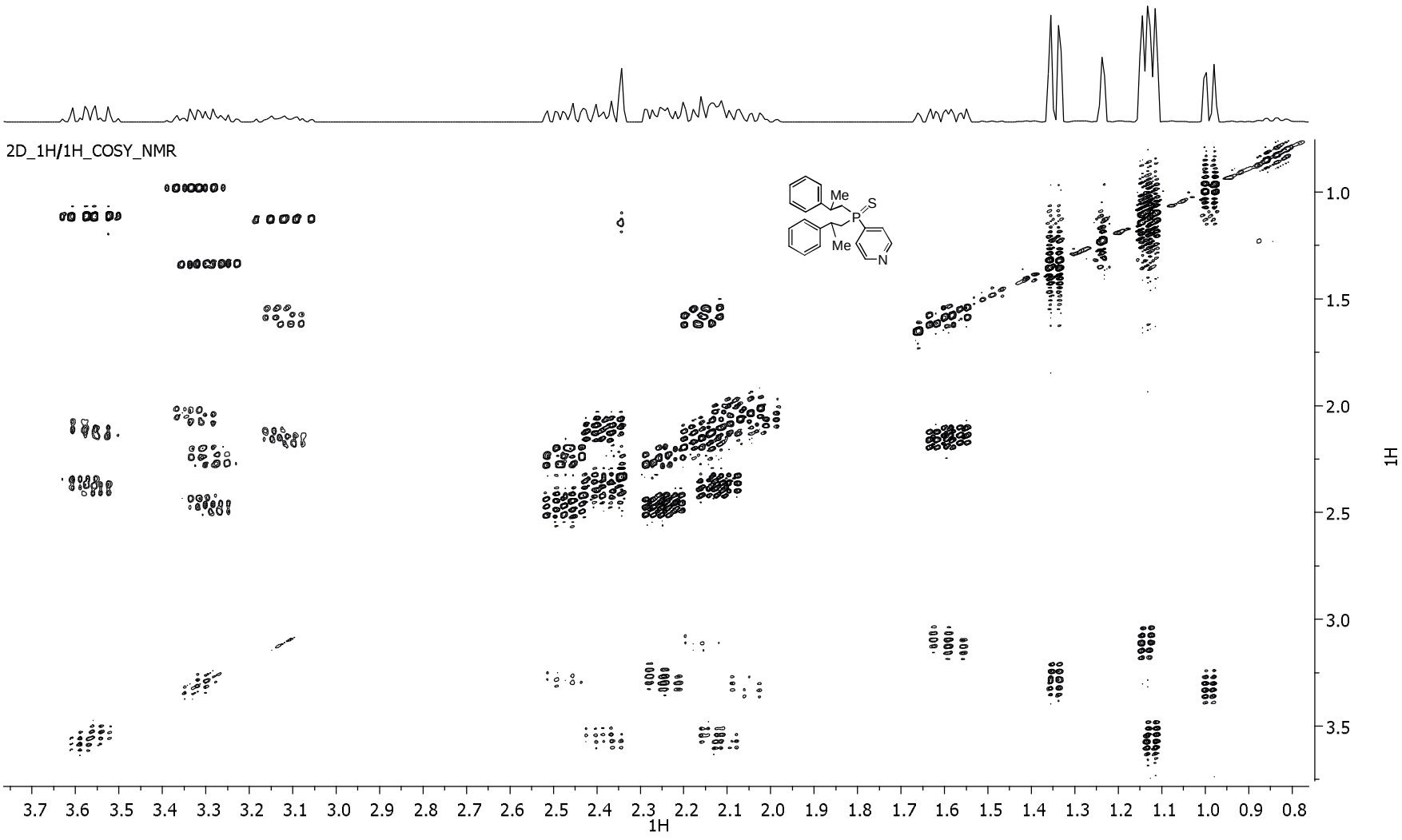

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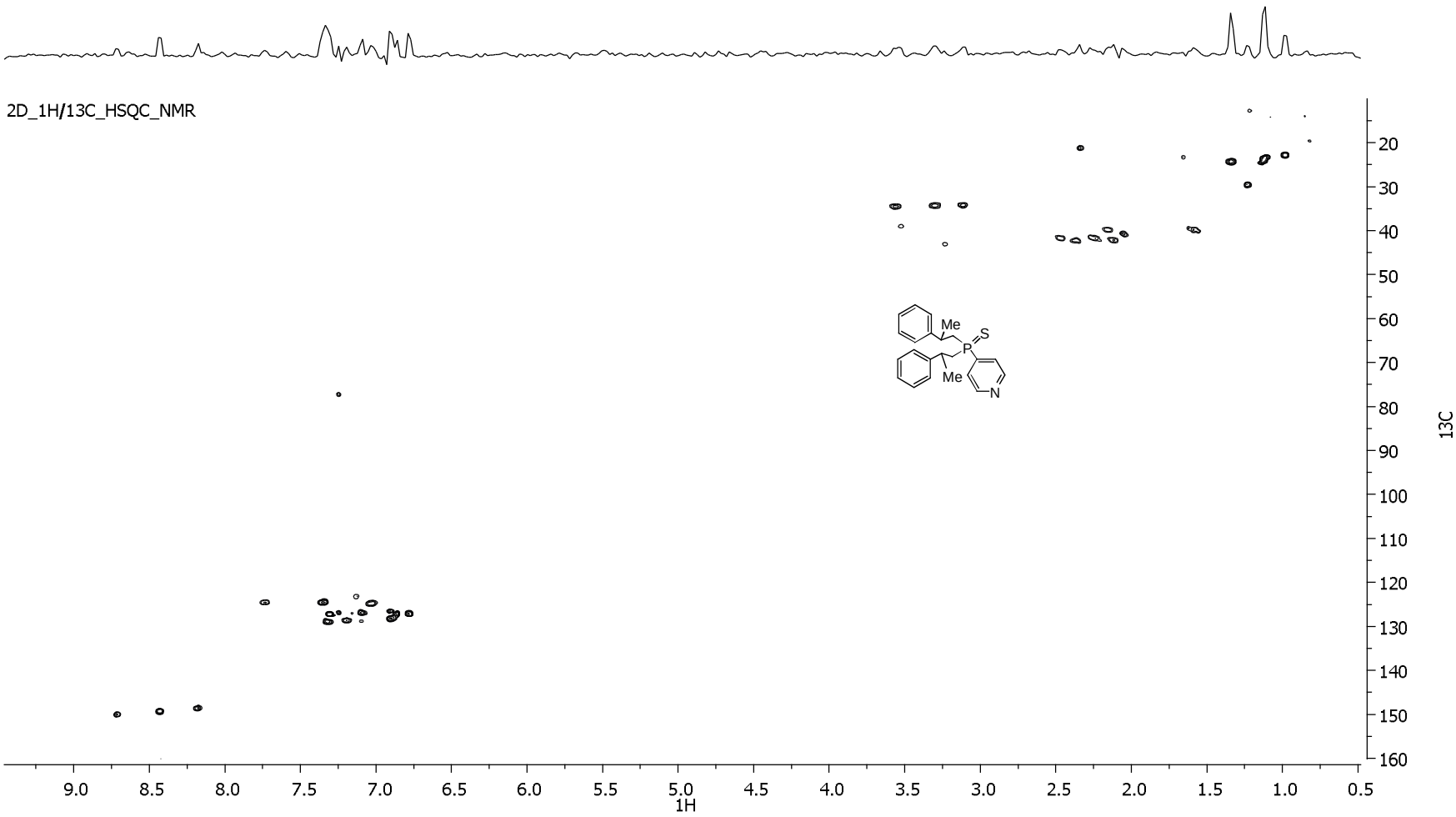

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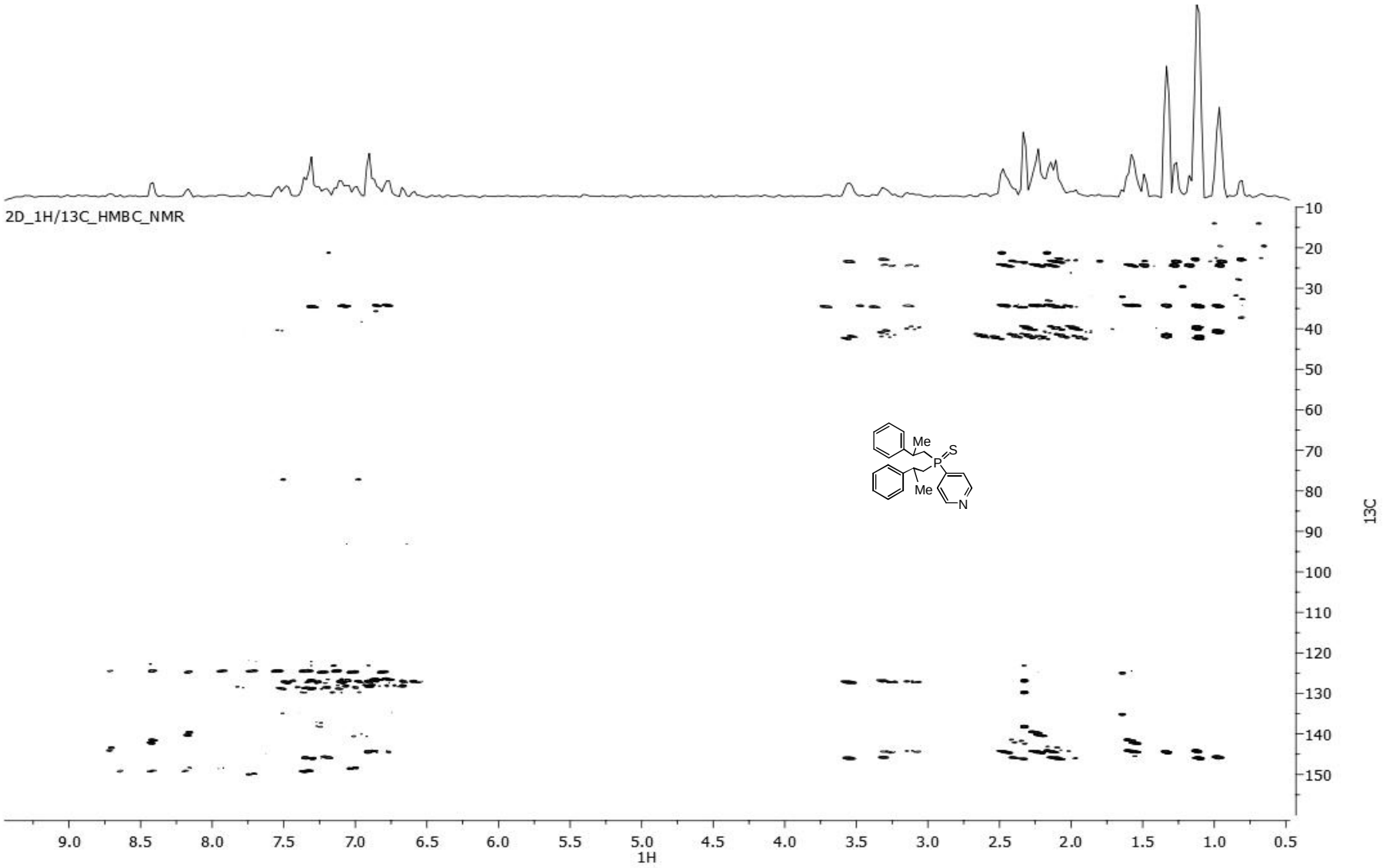
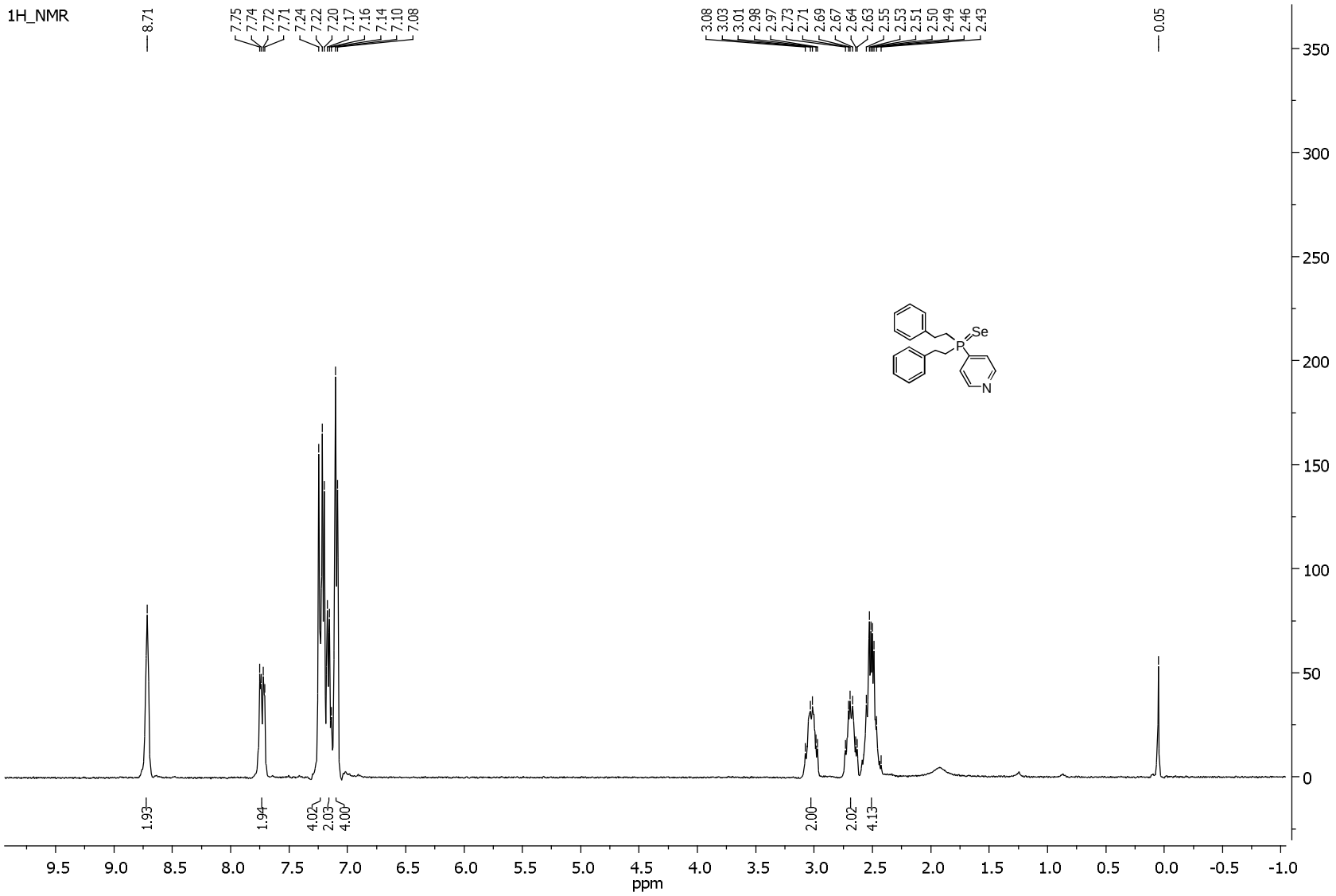
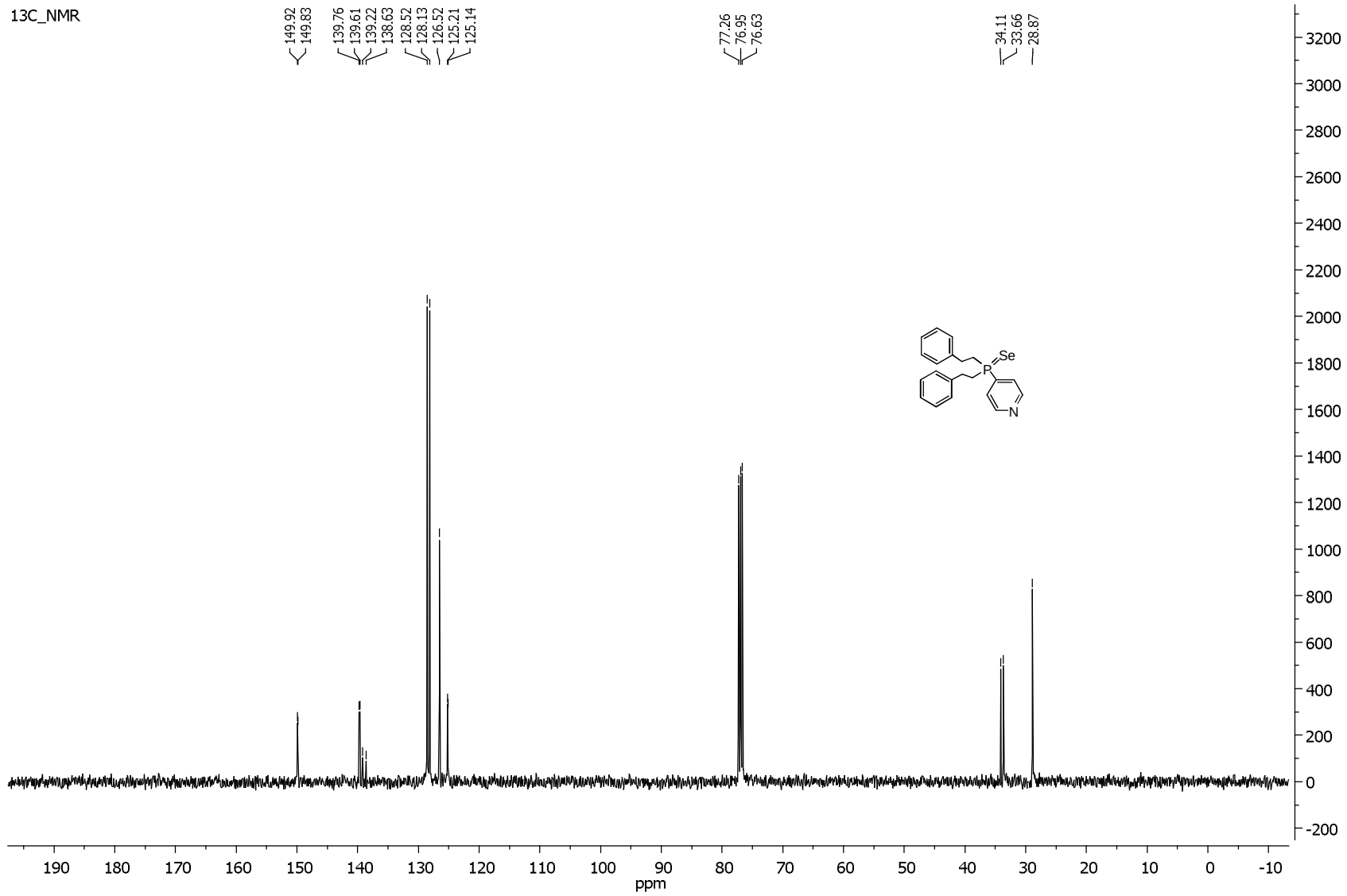


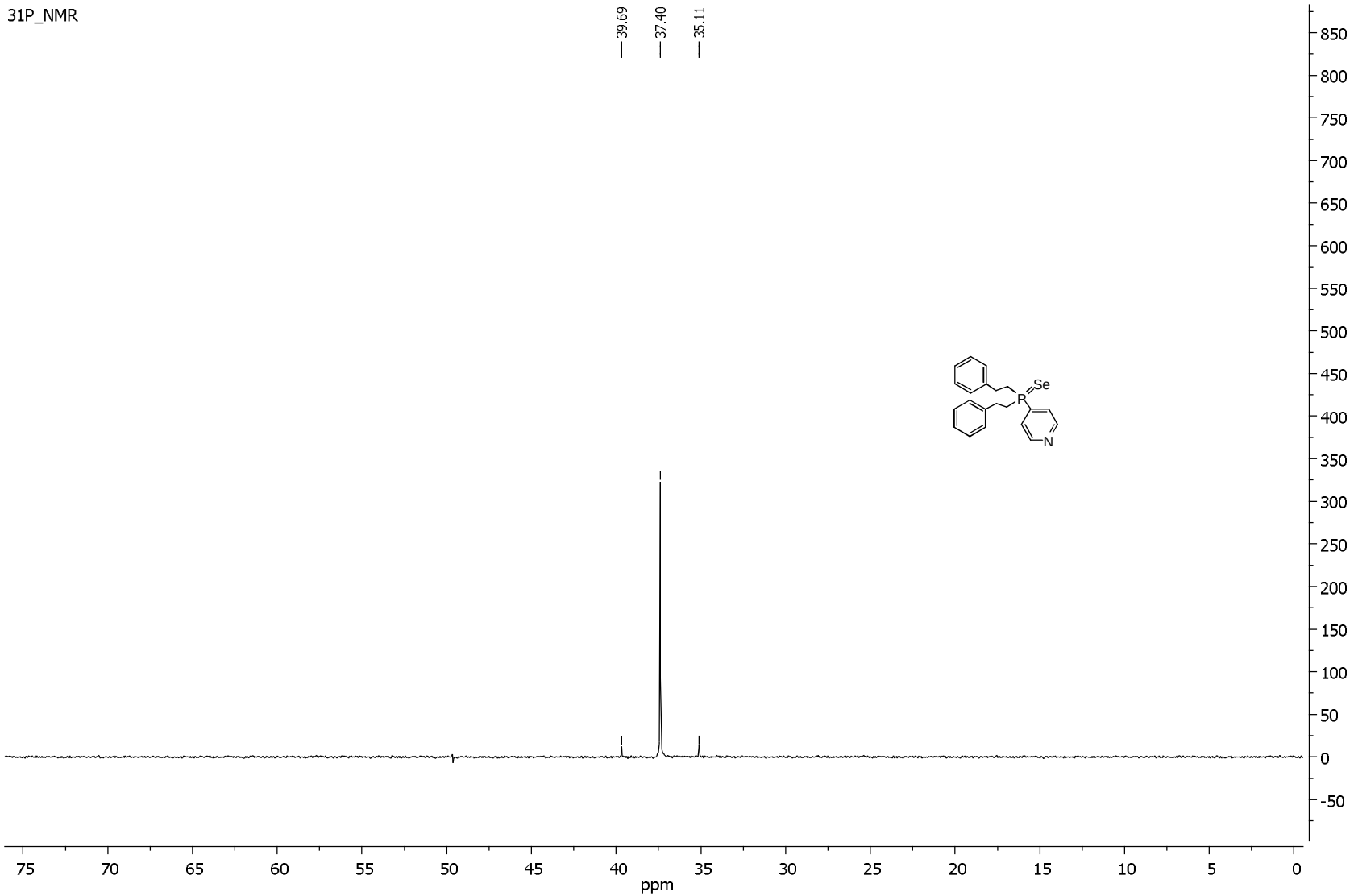
4-[Bis(2-phenylethyl)phosphoroselenoyl]pyridine (4i)



4-[Bis(2-phenylethyl)phosphoroselenoyl]pyridine (4i)



4-[Bis(2-phenylethyl)phosphoroselenoyl]pyridine (4i)



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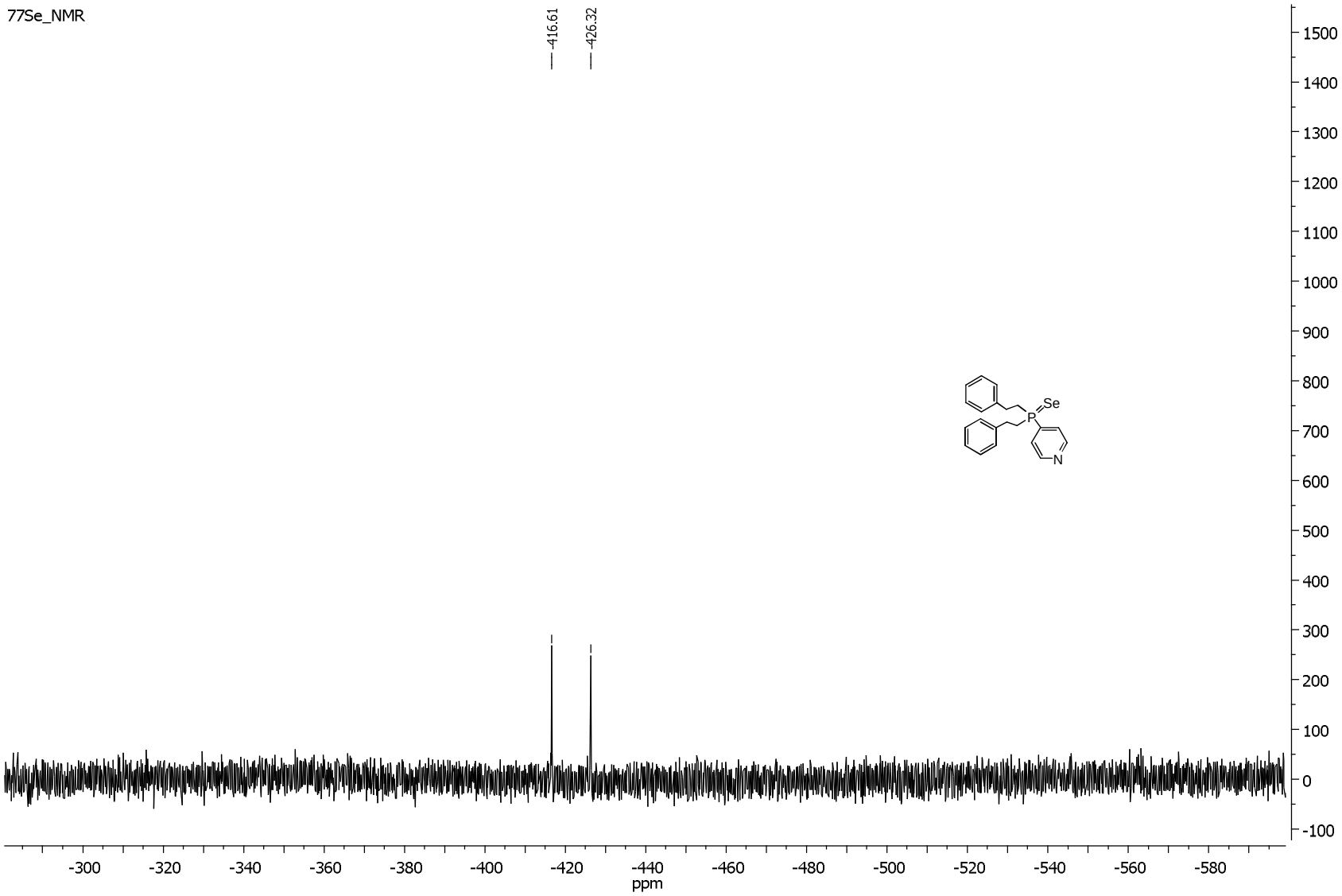

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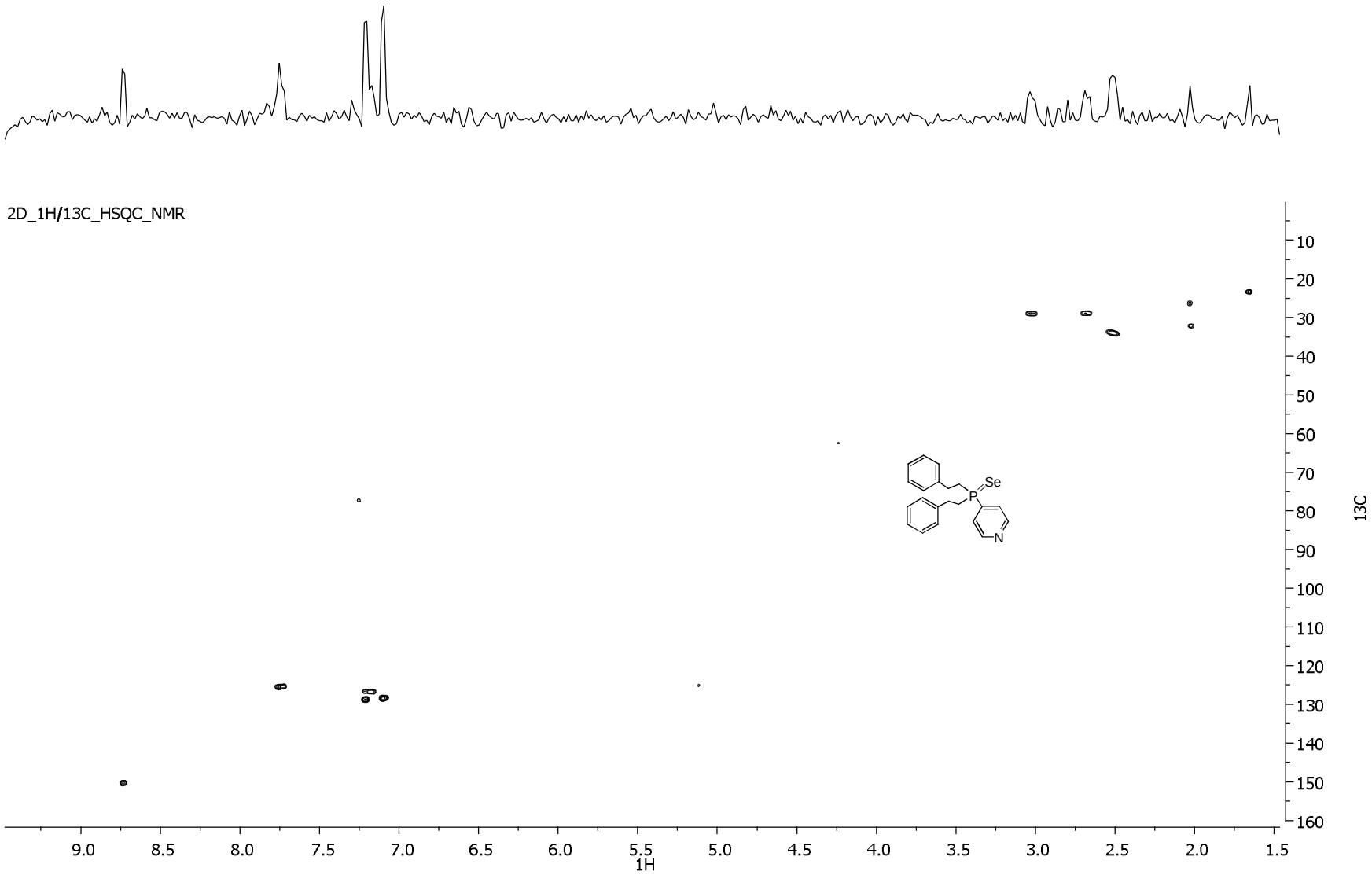
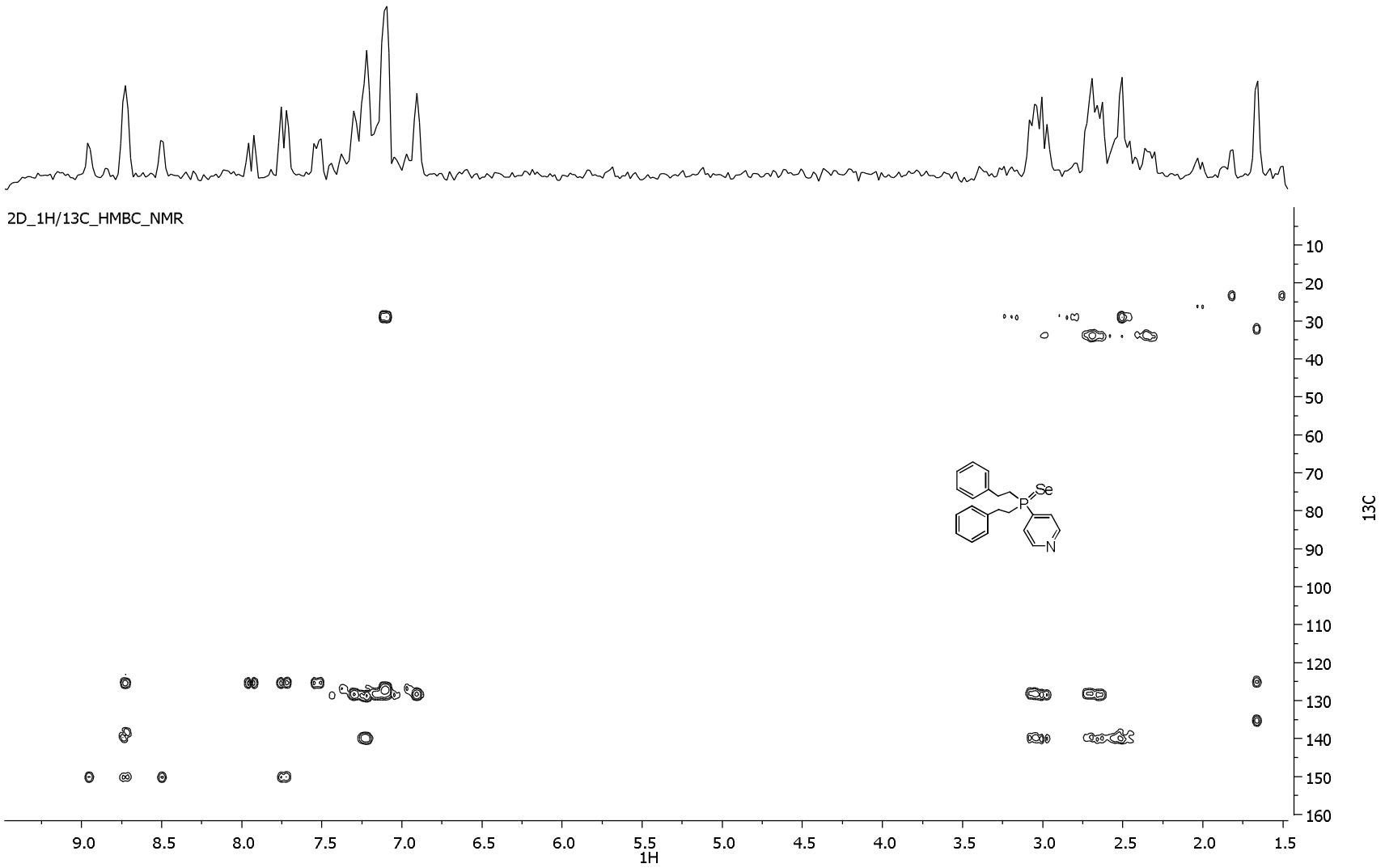


4-[Bis(2-phenylethyl)phosphoroselenoyl]pyridine (4i)



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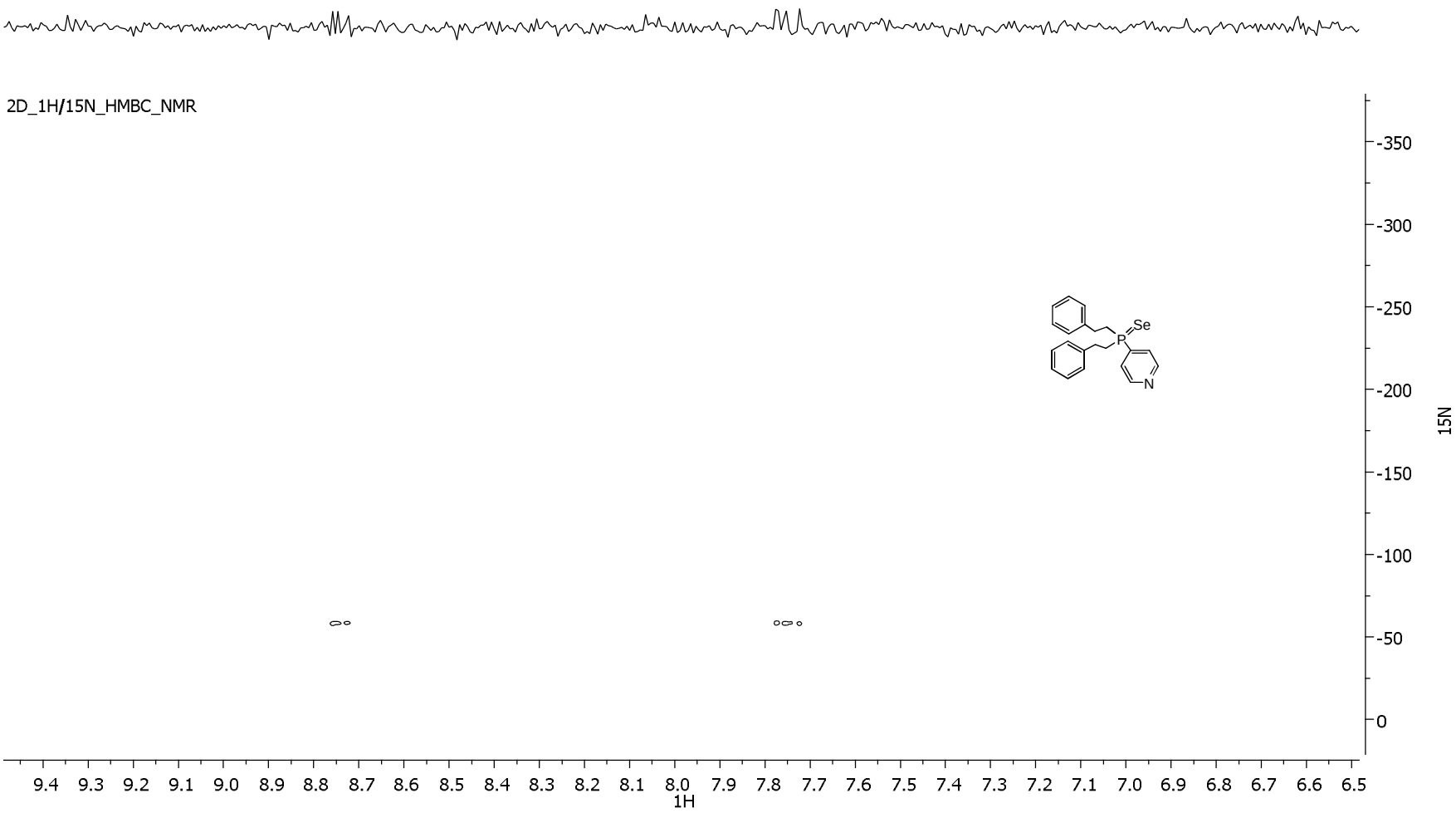

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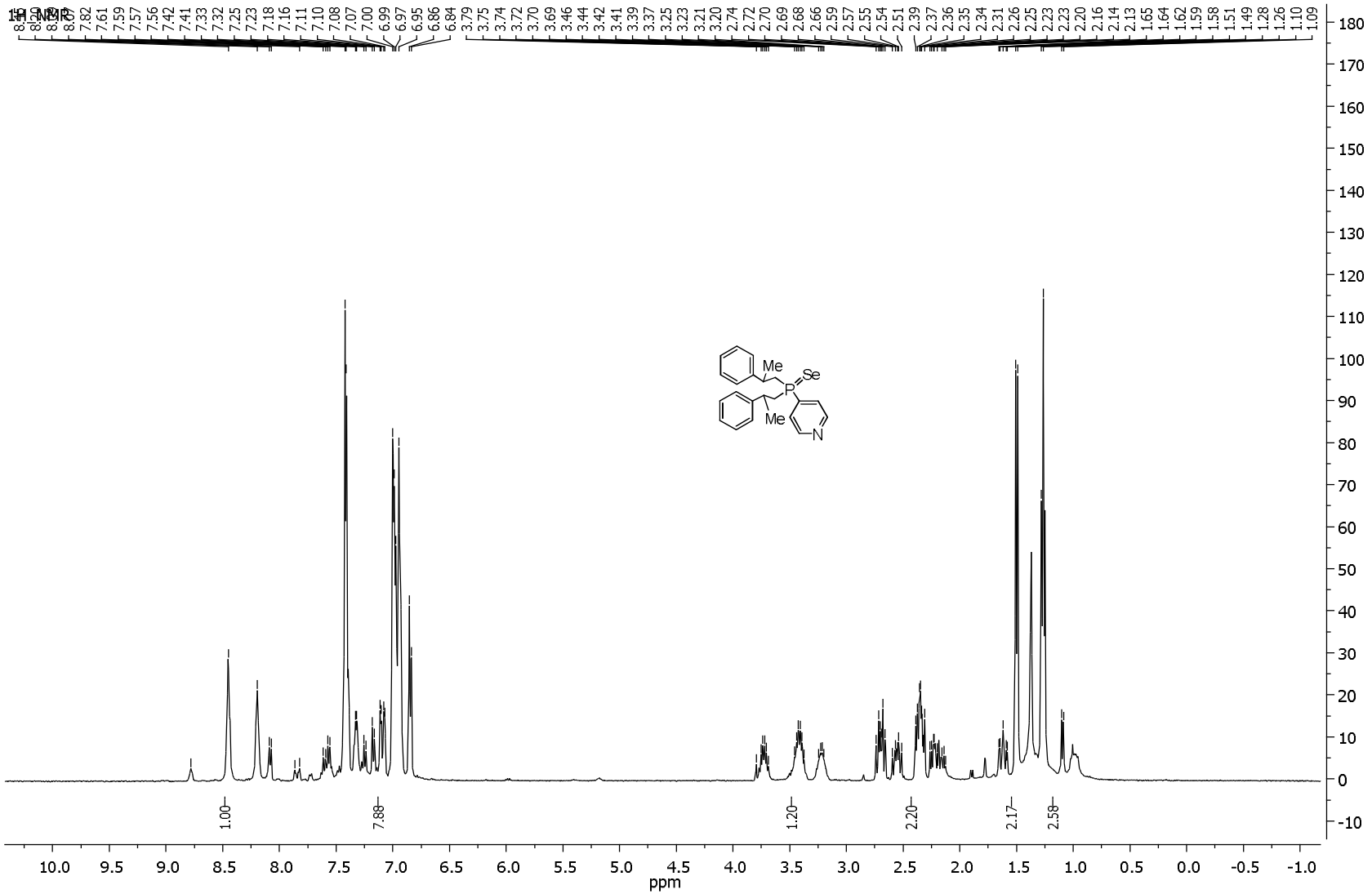

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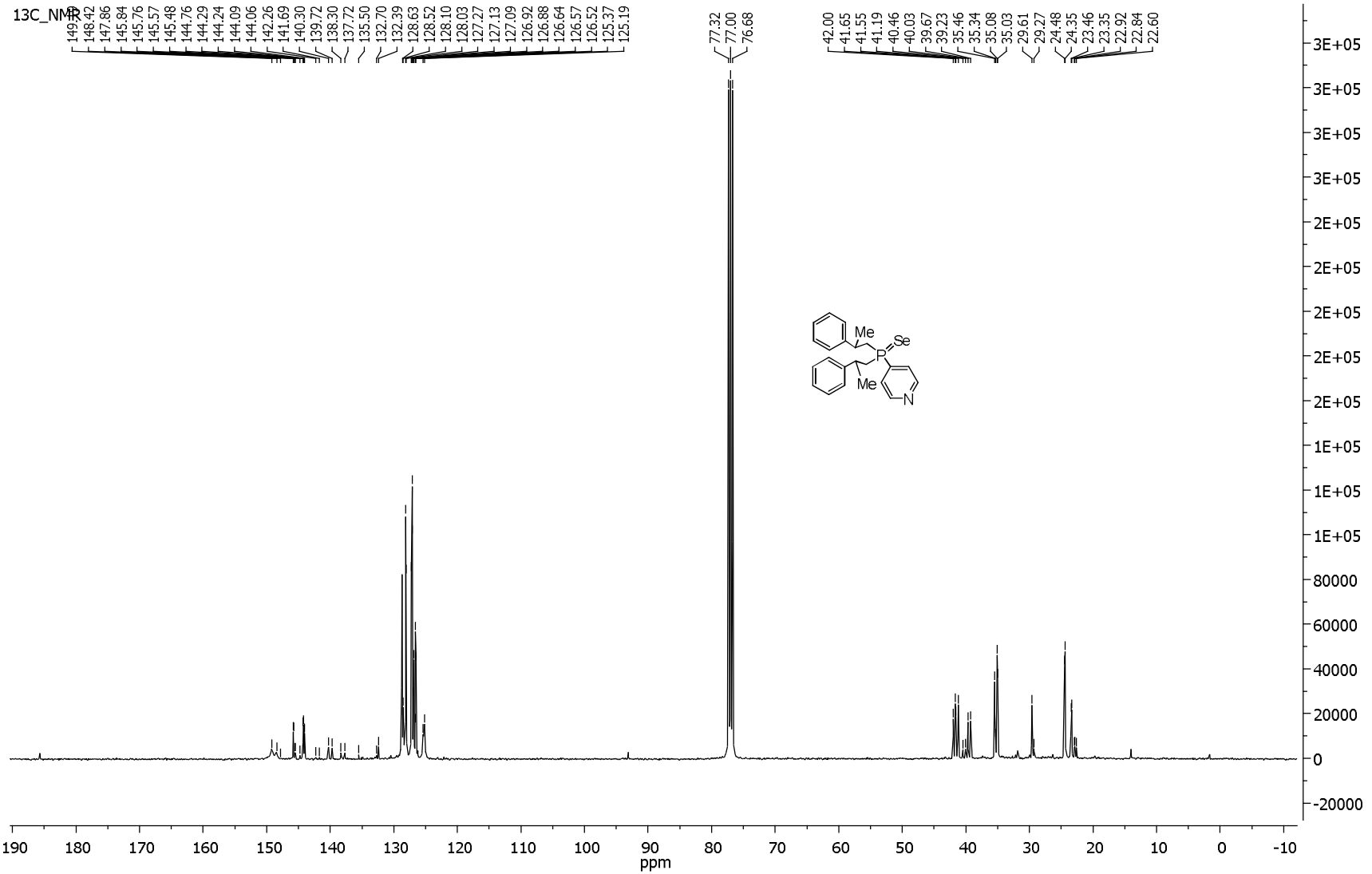

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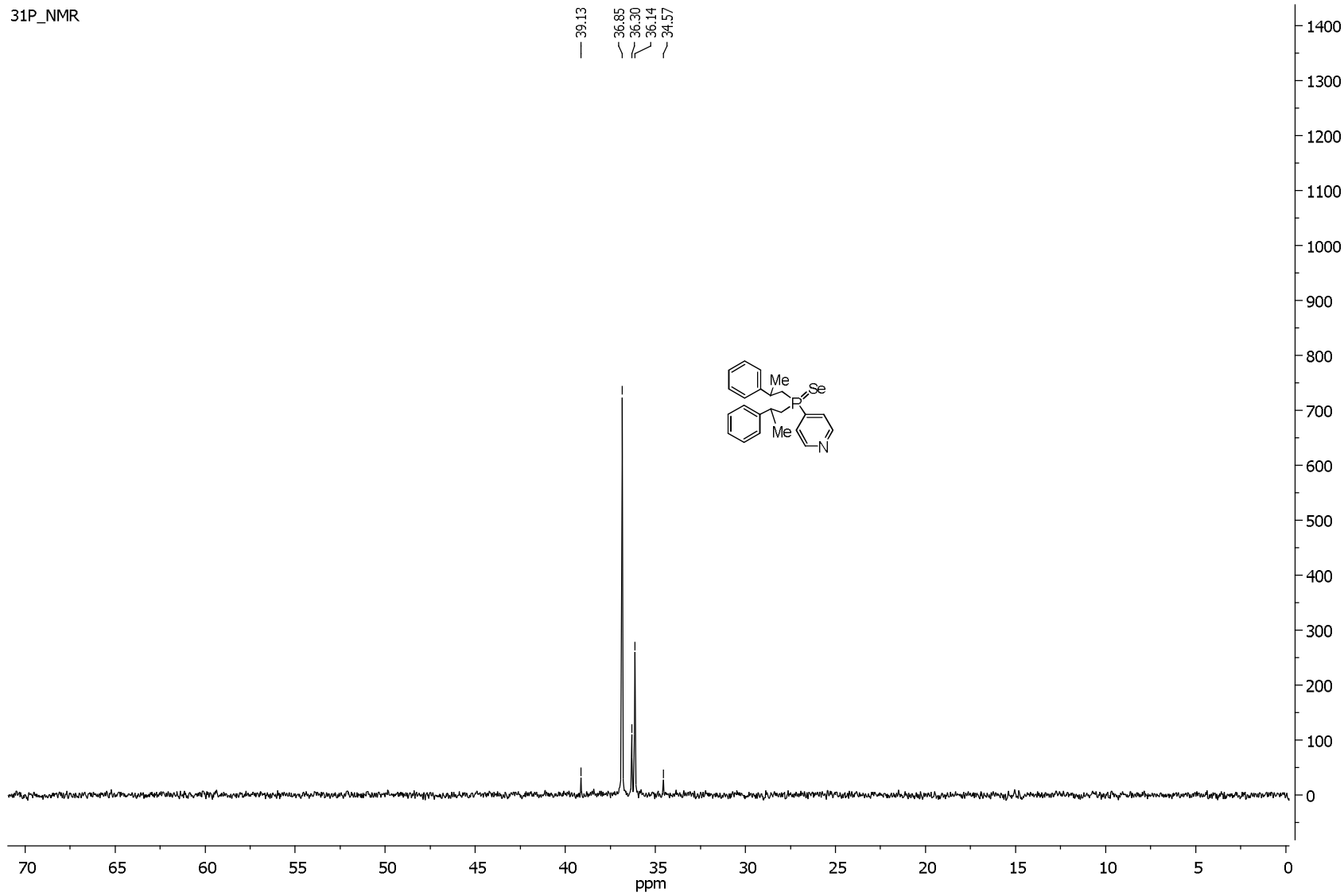

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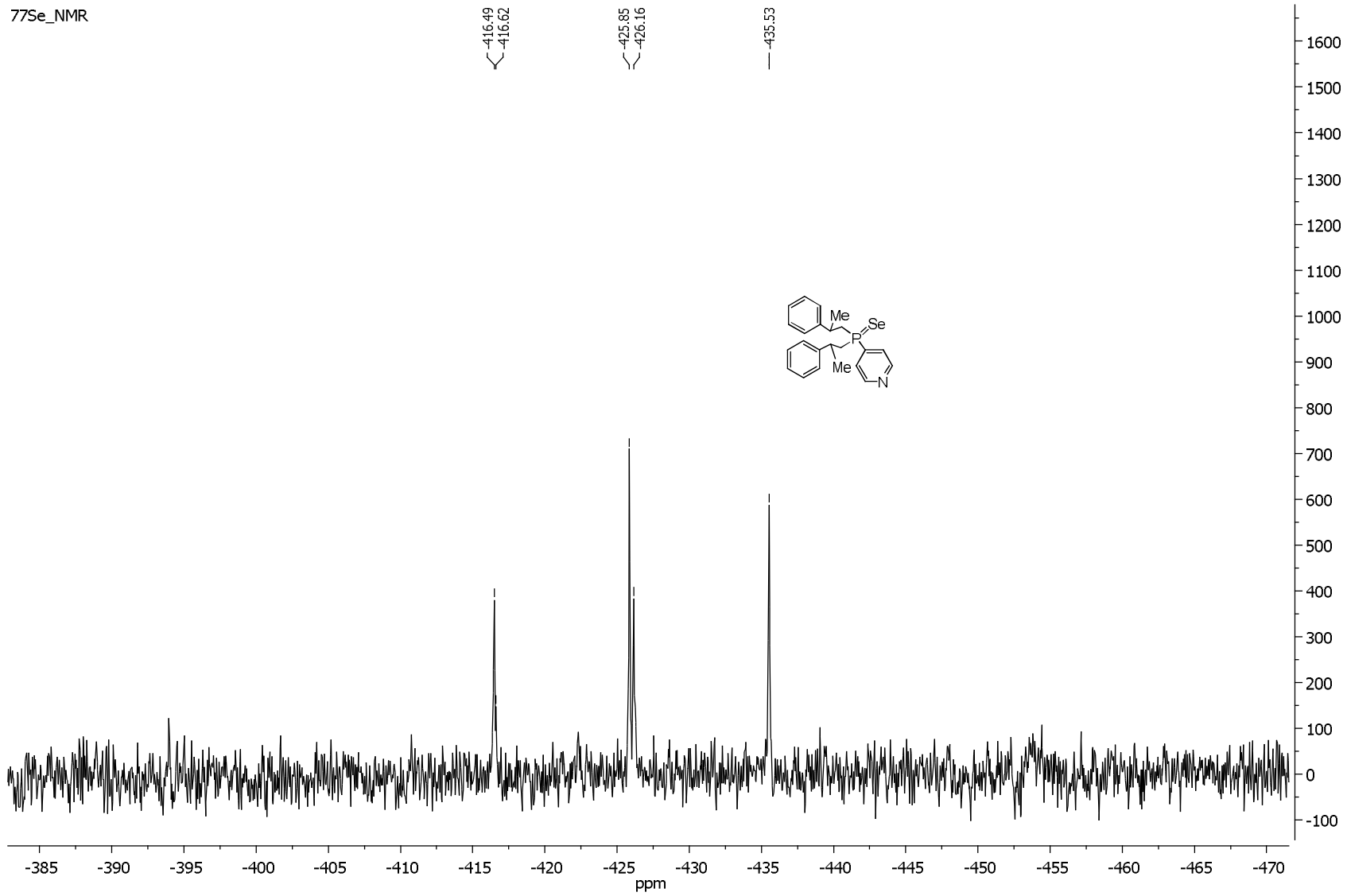

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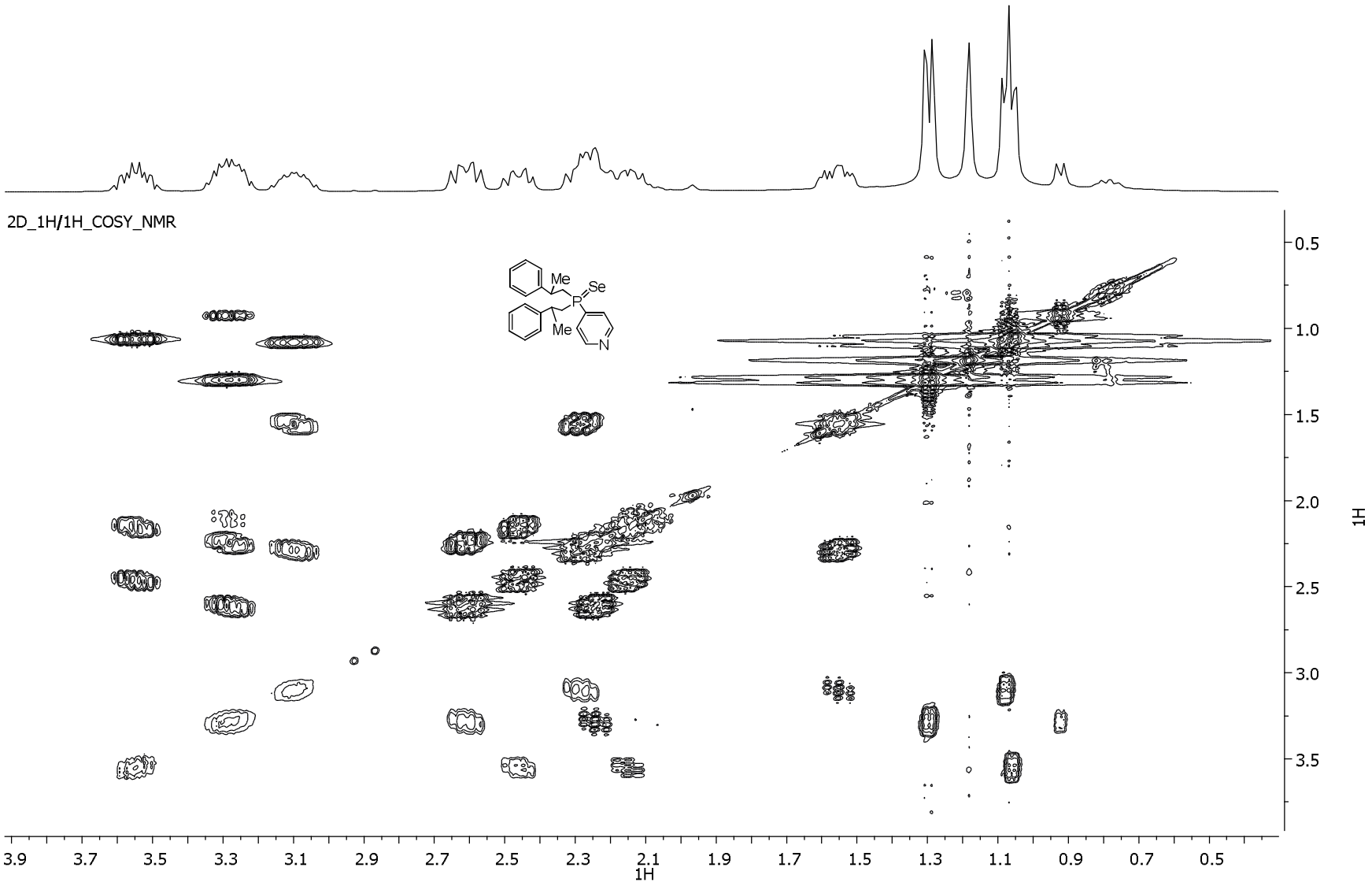
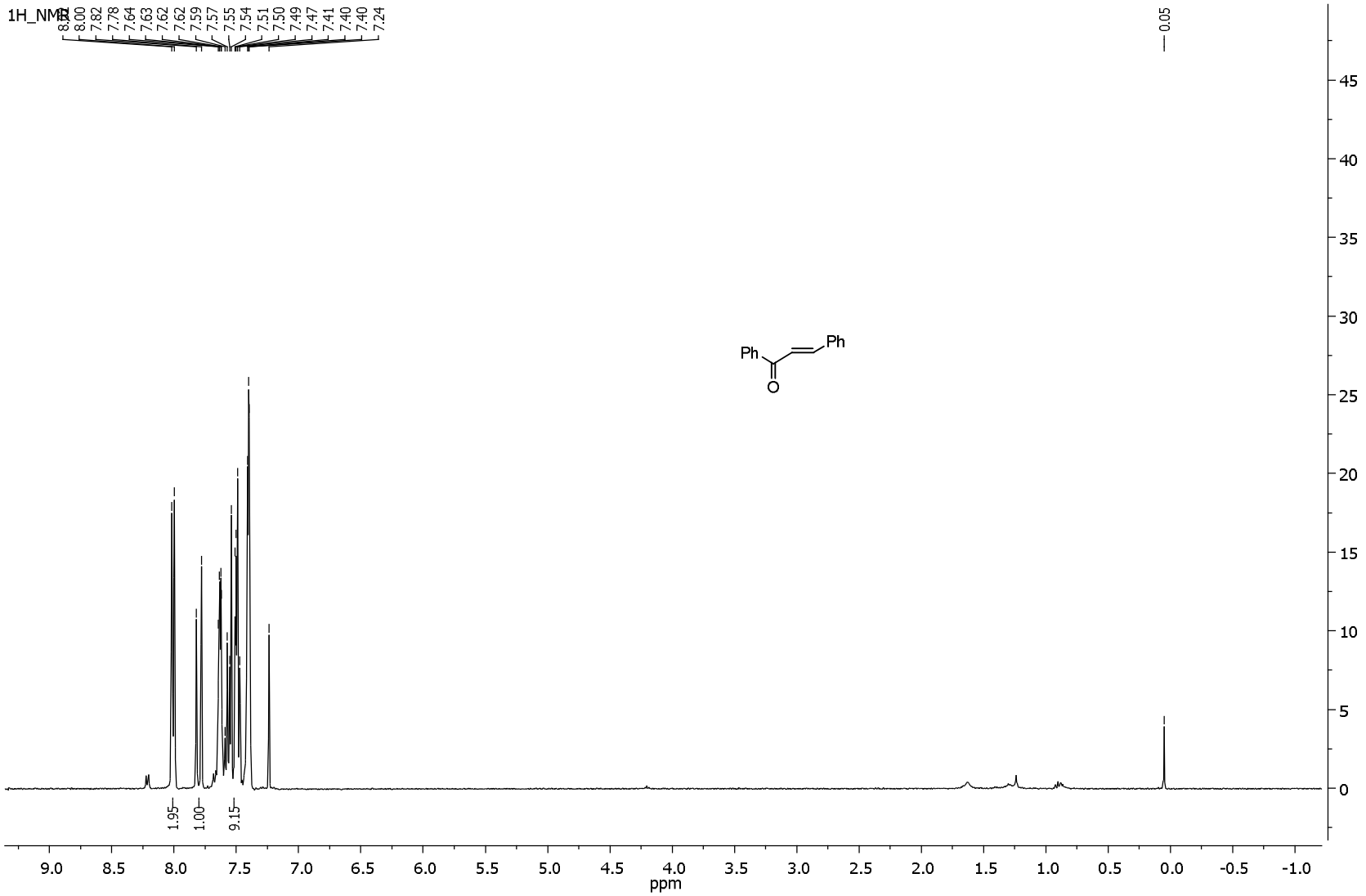
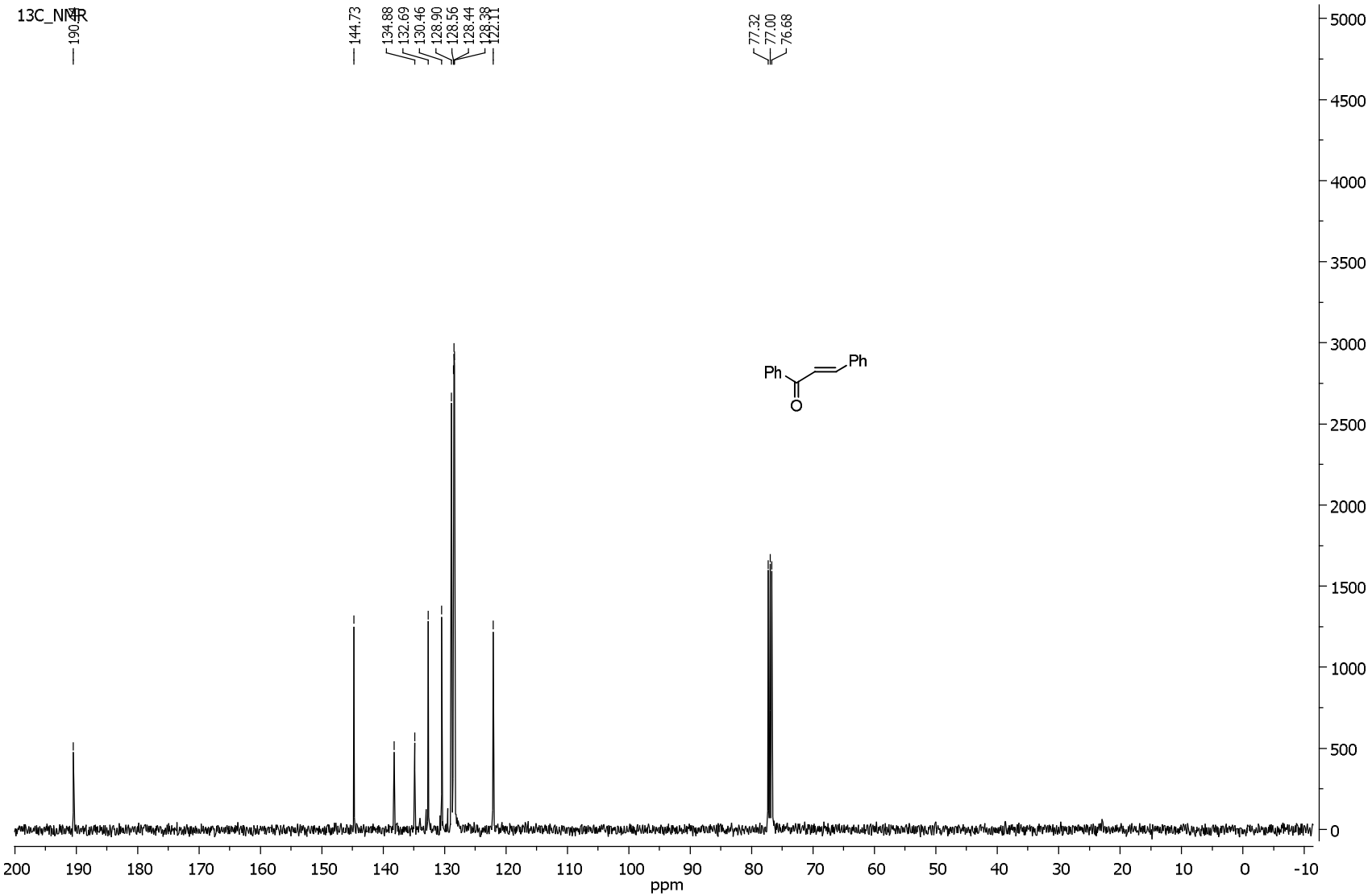


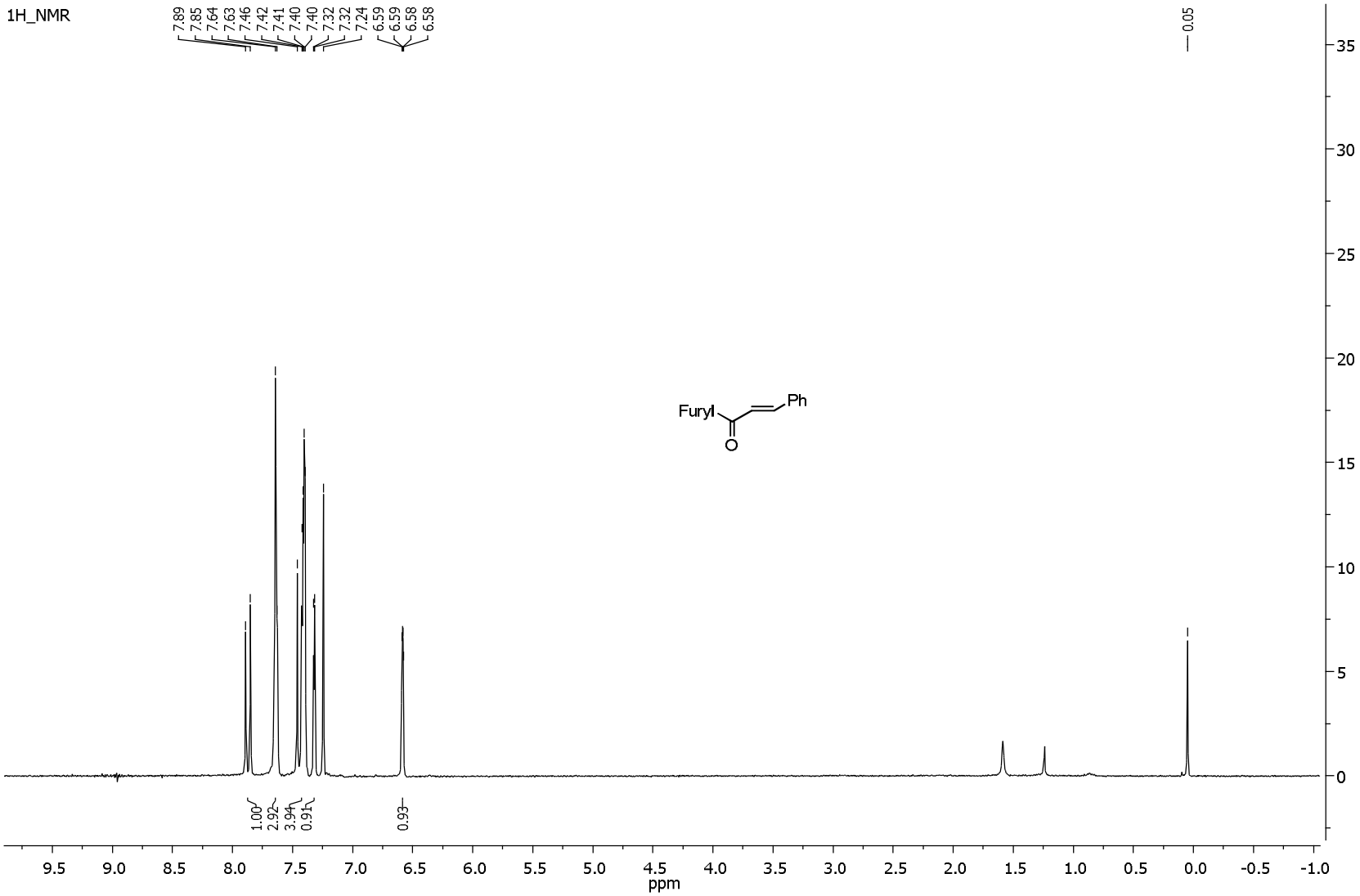
(2*E*)-1,3-Diphenylprop-2-en-1-one (5c)



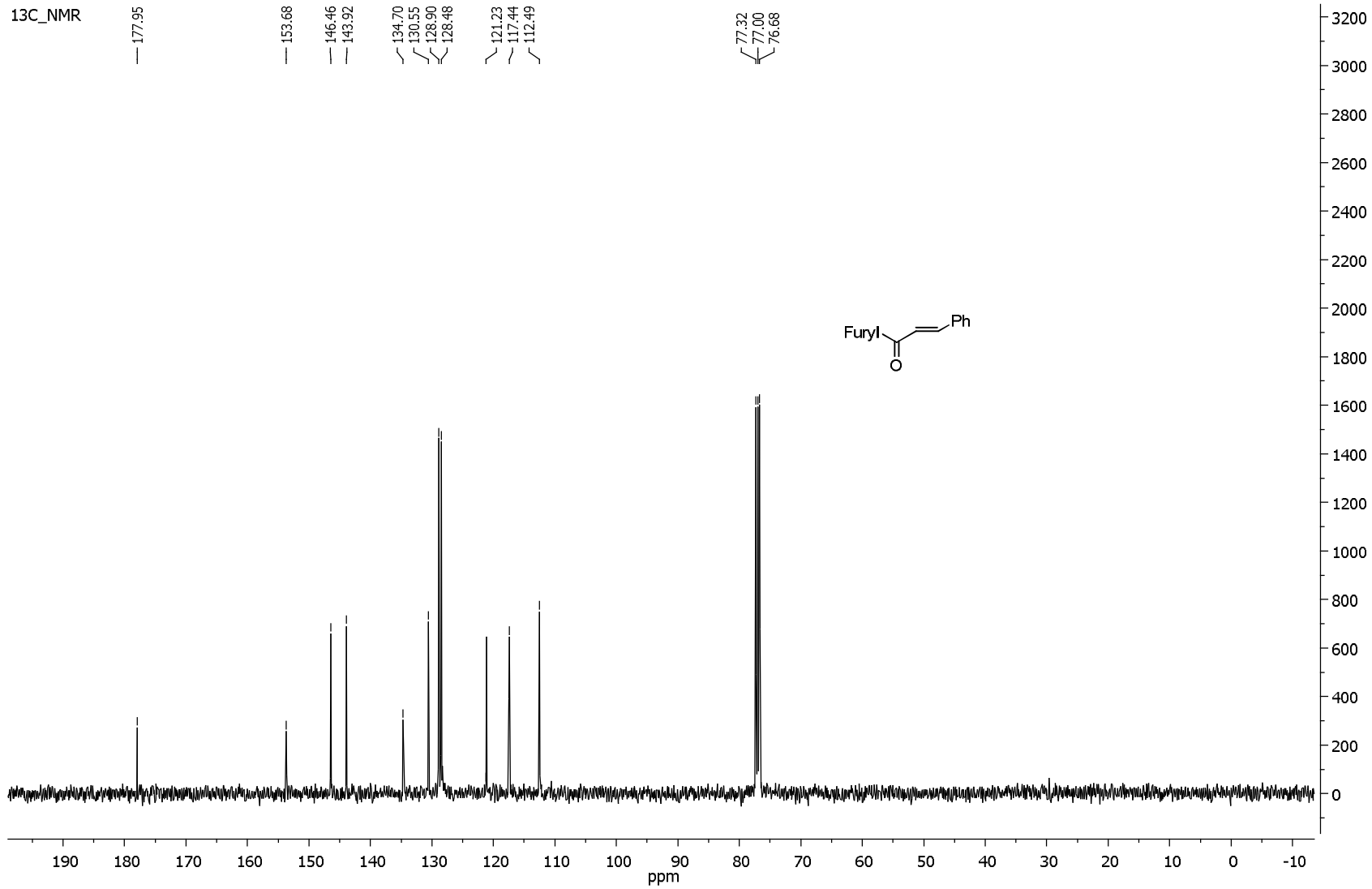
(2*E*)-1,3-Diphenylprop-2-en-1-one (5c)



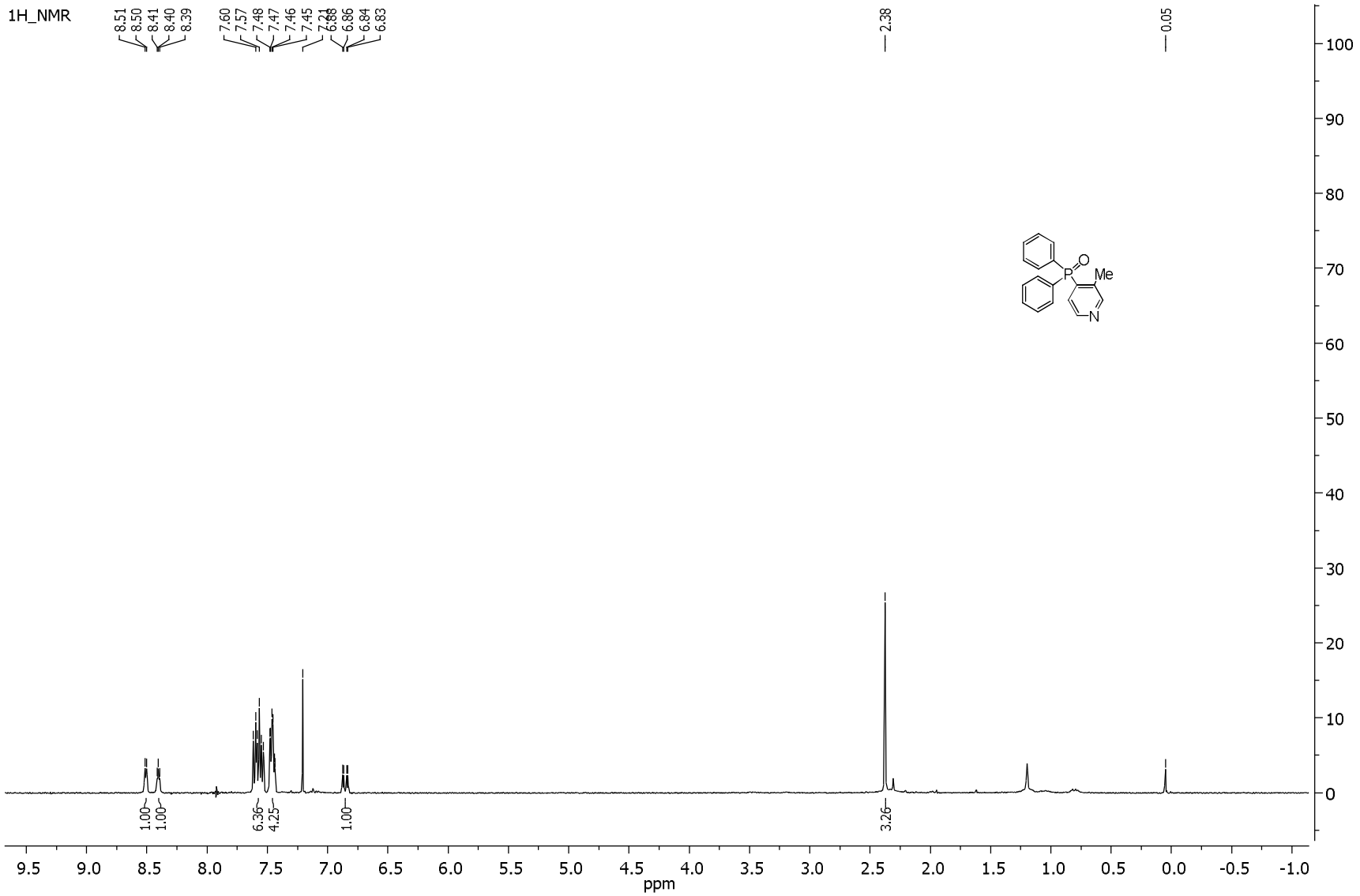
(2*E*)-1-(Furan-2-yl)-3-phenylprop-2-en-1-one (5d)



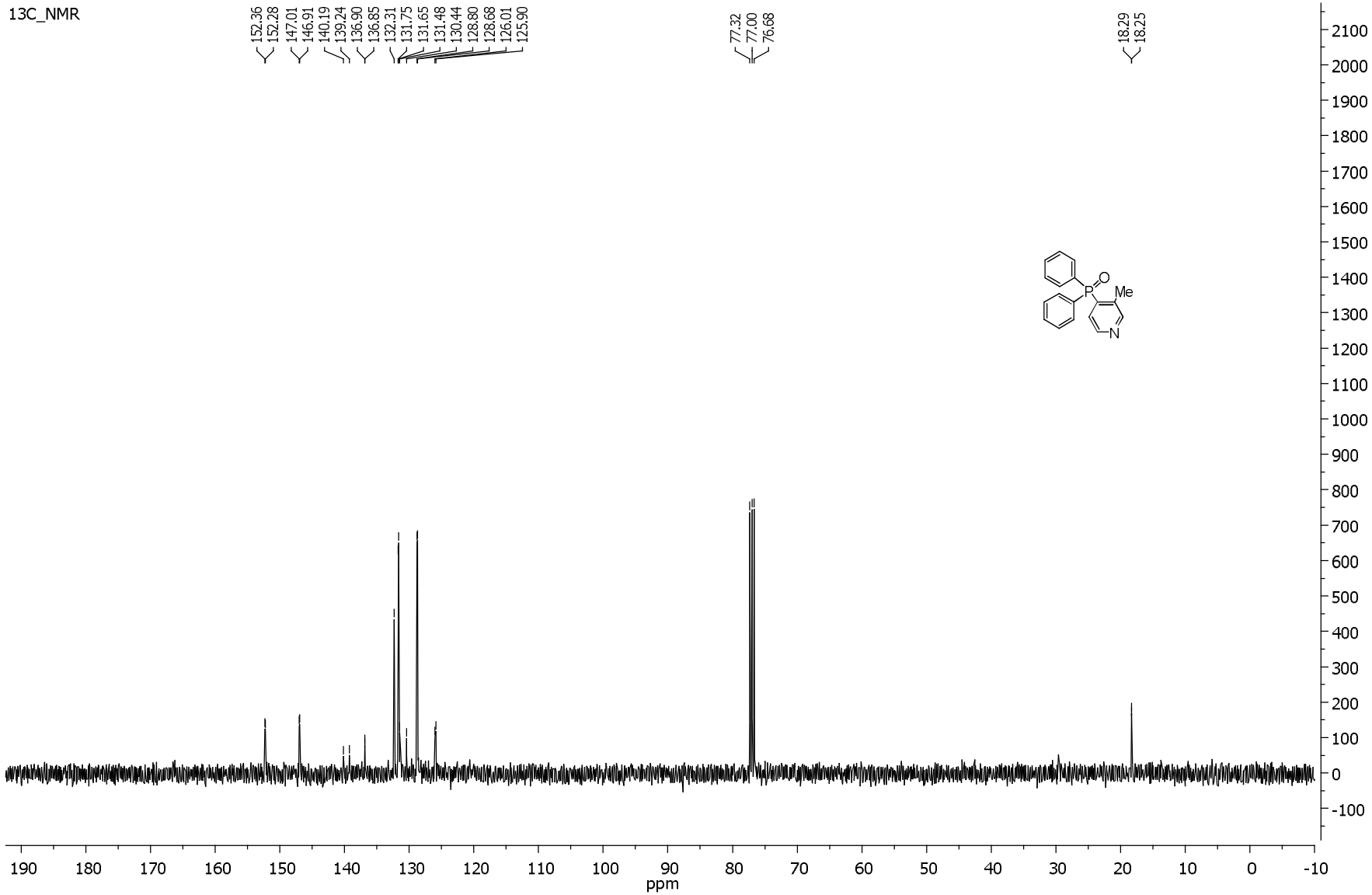
(2*E*)-1-(Furan-2-yl)-3-phenylprop-2-en-1-one (5d)



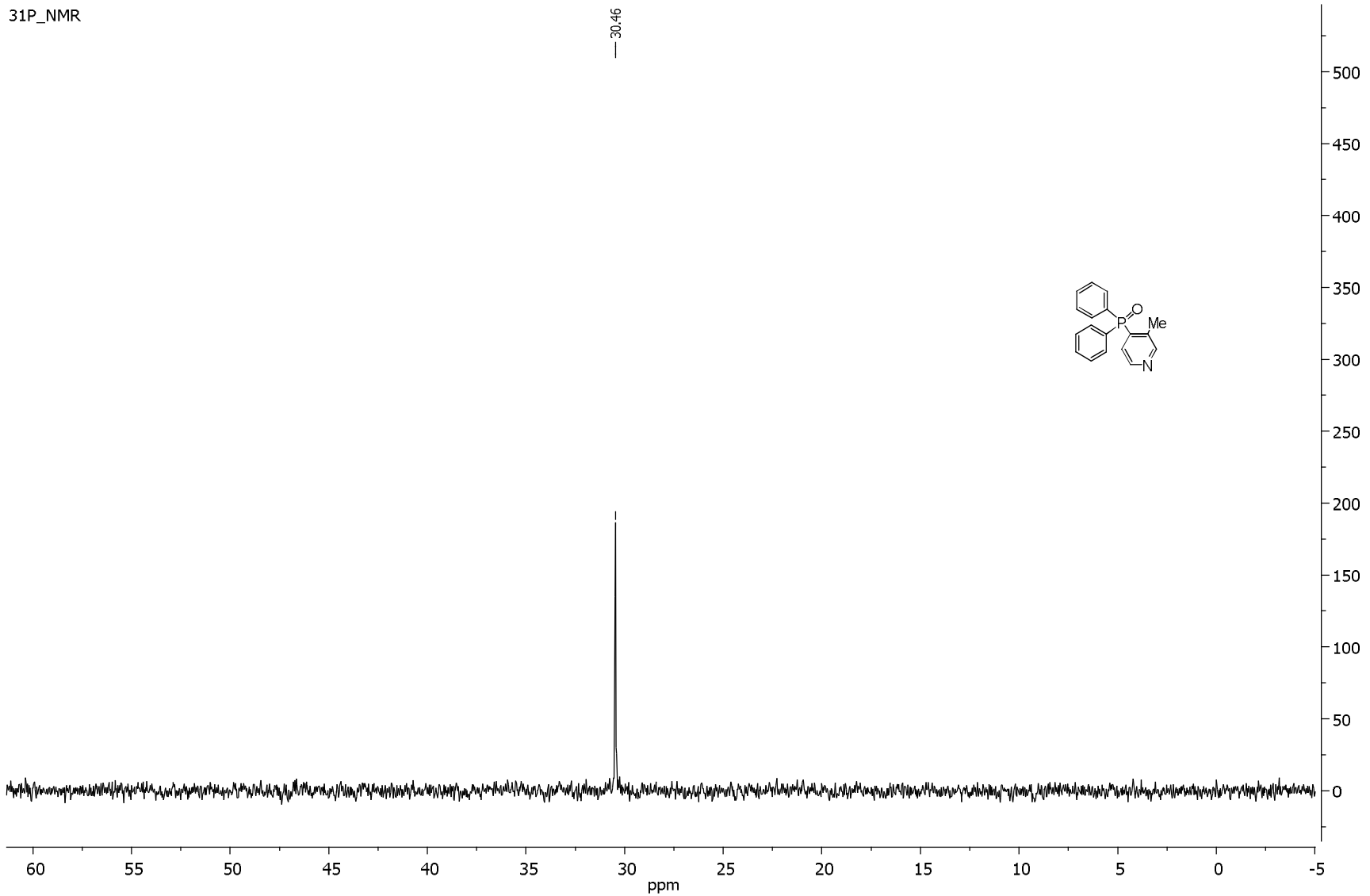
4-(Diphenylphosphoryl)-3-methylpyridine (6a)



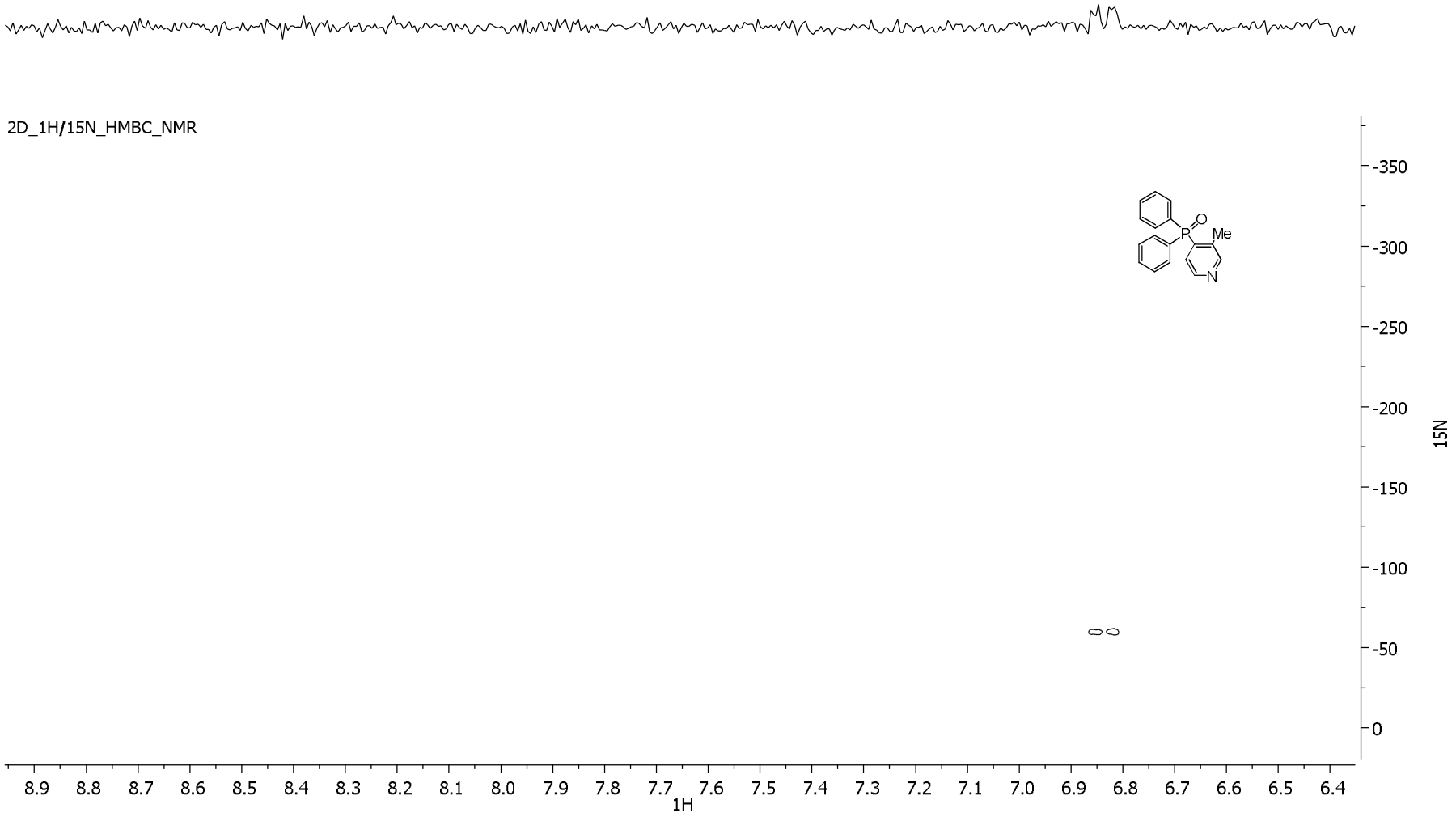
4-(Diphenylphosphoryl)-3-methylpyridine (6a)



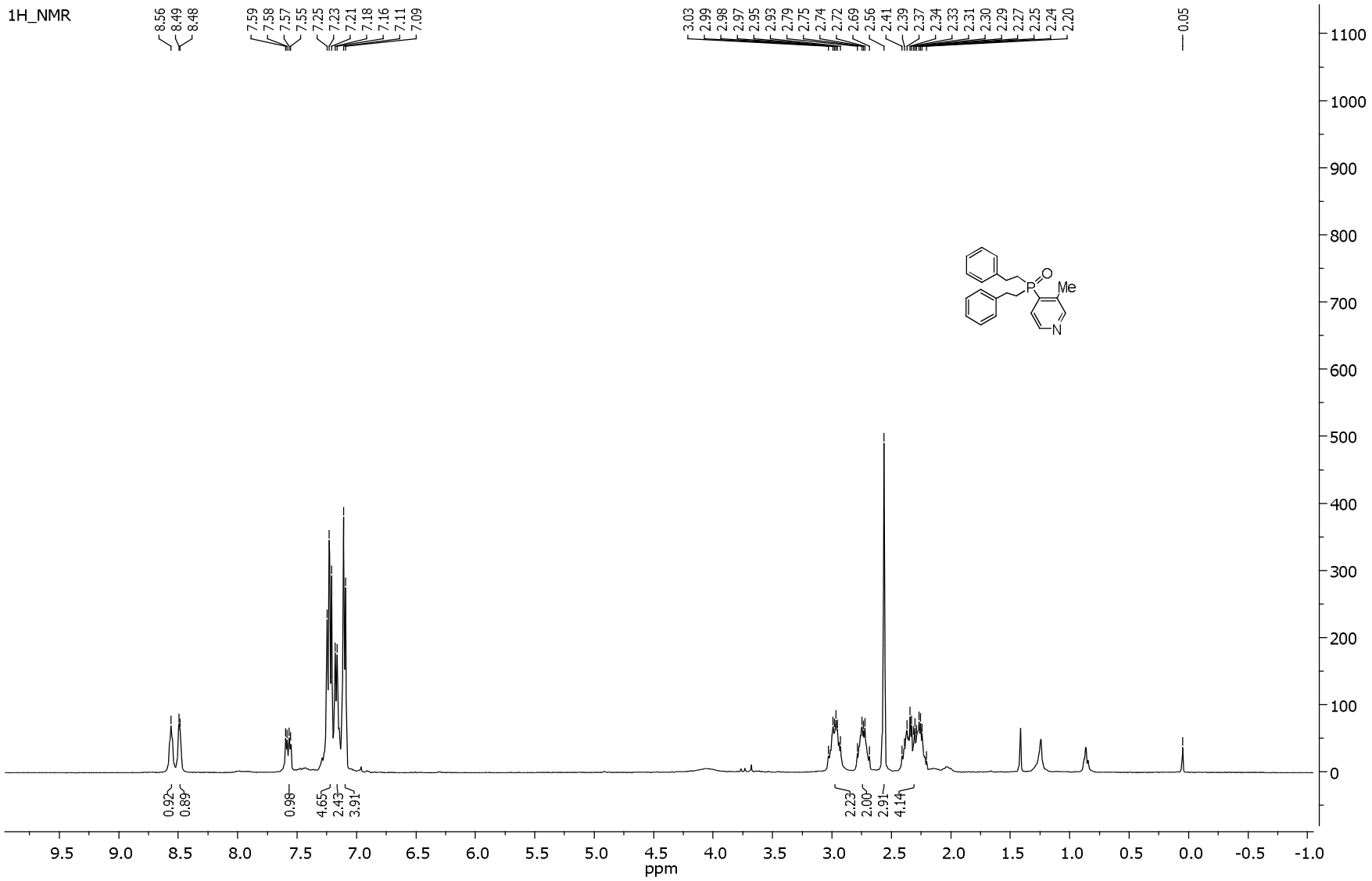
4-(Diphenylphosphoryl)-3-methylpyridine (6a)



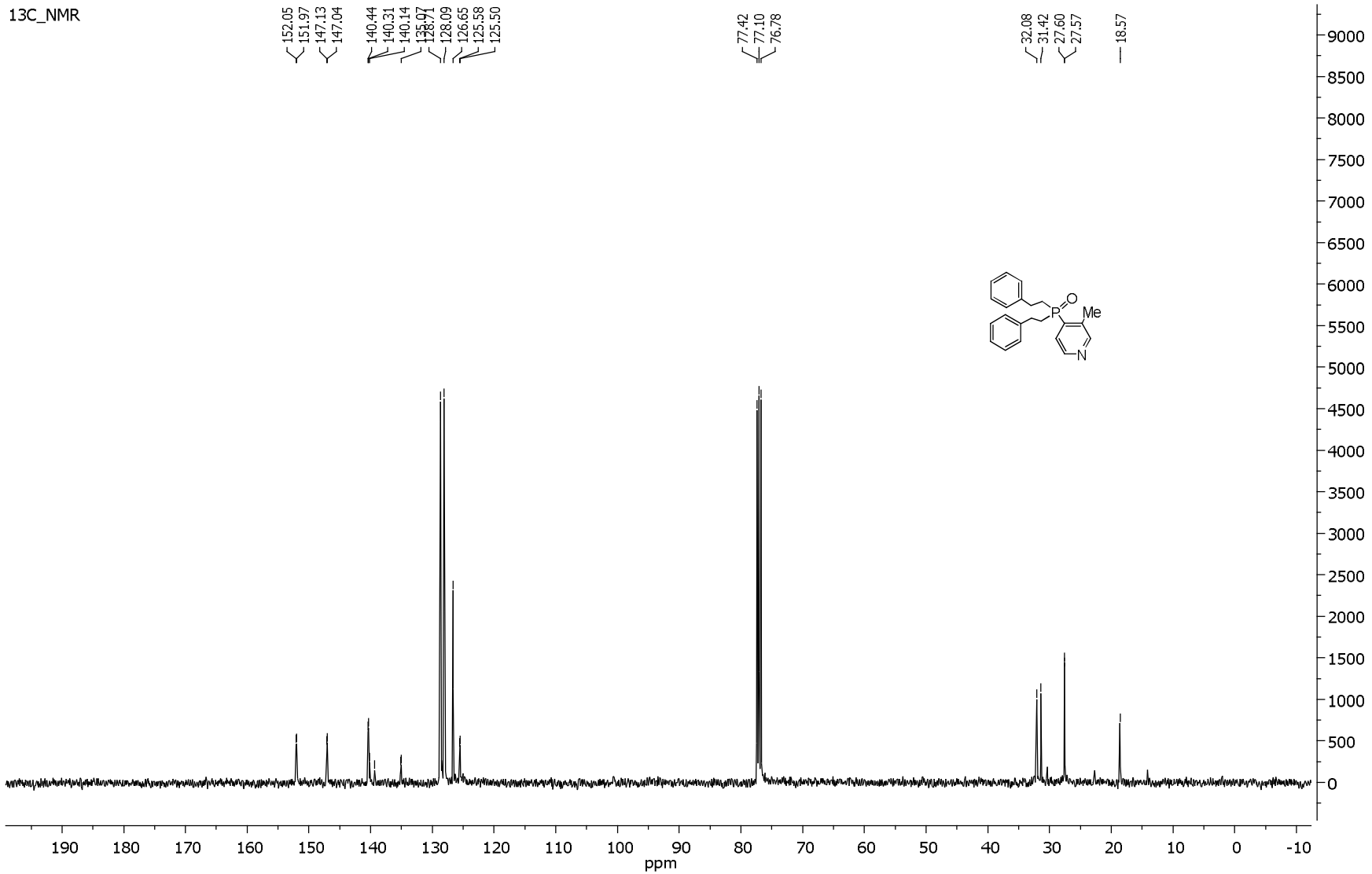
4-(Diphenylphosphoryl)-3-methylpyridine (6a)



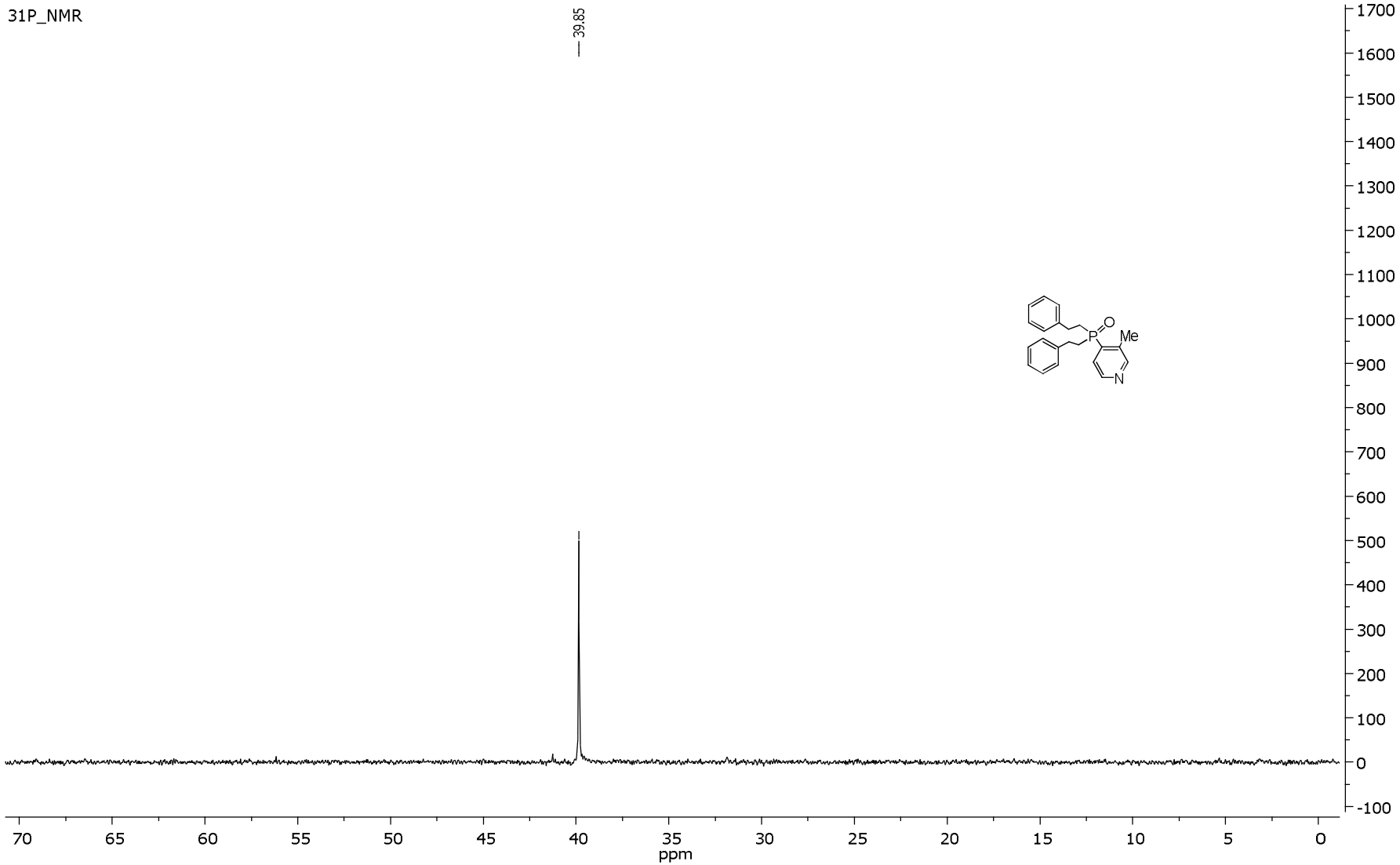
4-[Bis(2-phenylethyl)phosphoryl]-3-methylpyridine (6b)



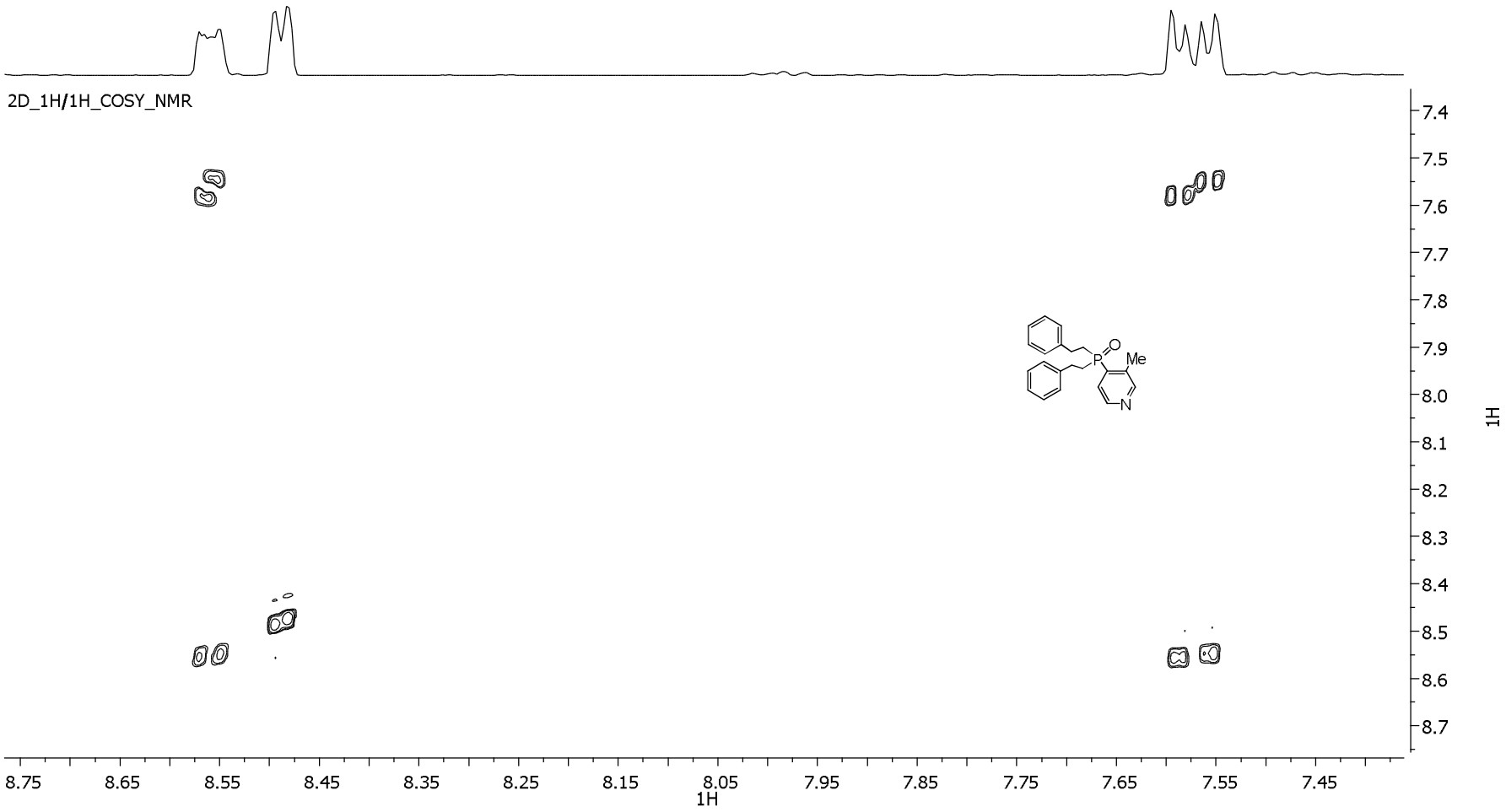
4-[Bis(2-phenylethyl)phosphoryl]-3-methylpyridine (6b)



4-[Bis(2-phenylethyl)phosphoryl]-3-methylpyridine (6b)



4-[Bis(2-phenylethyl)phosphoryl]-3-methylpyridine (6b)



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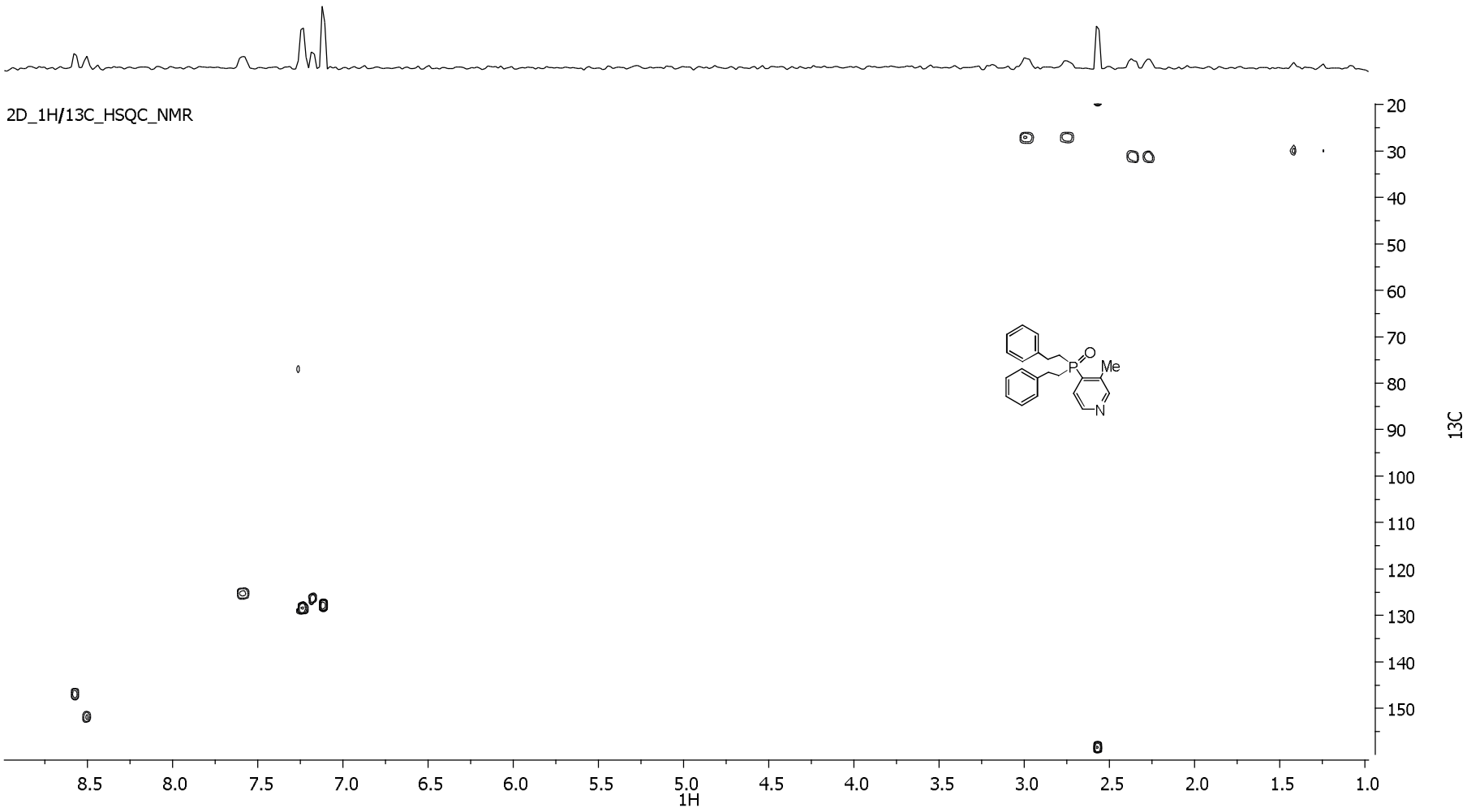

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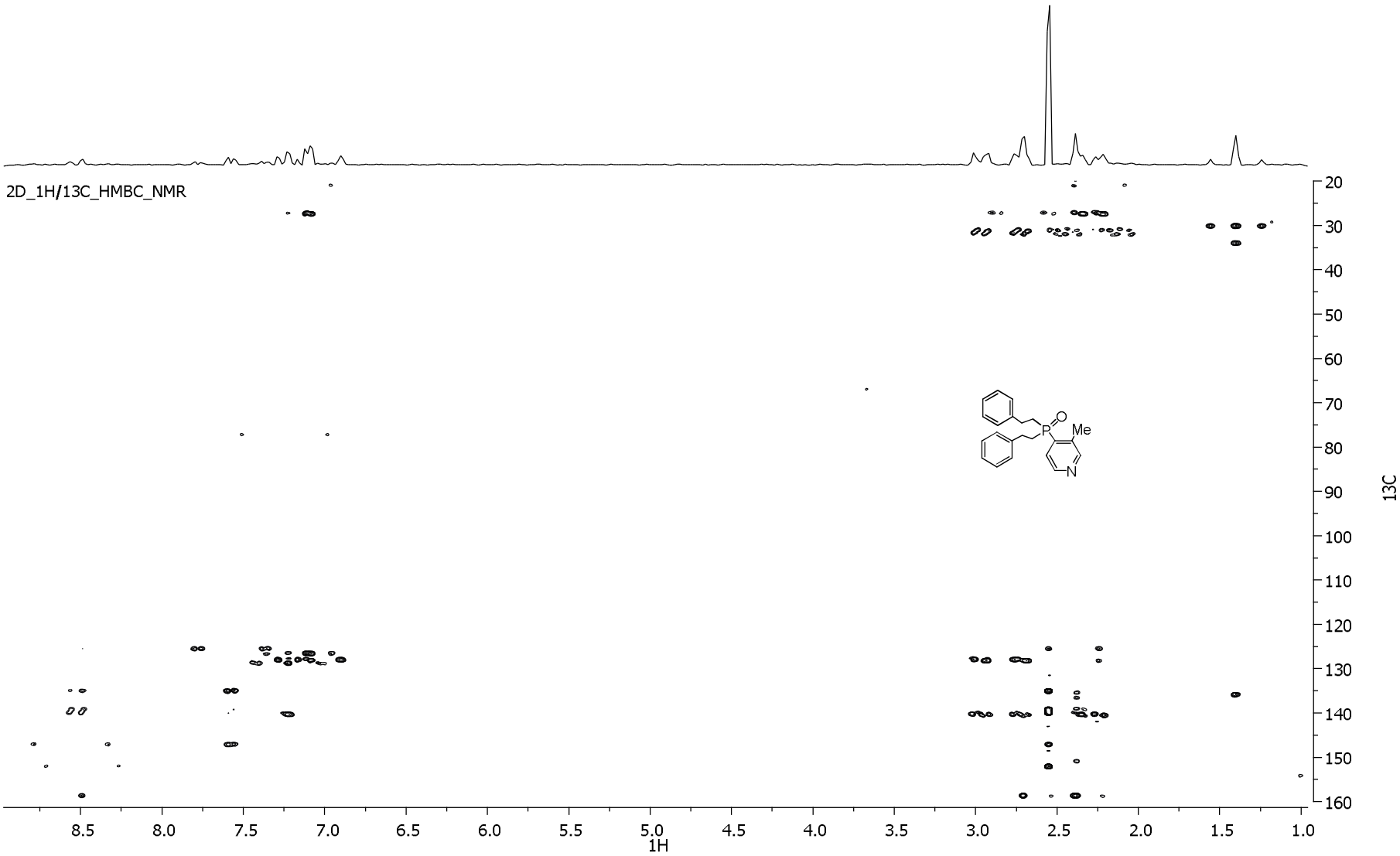

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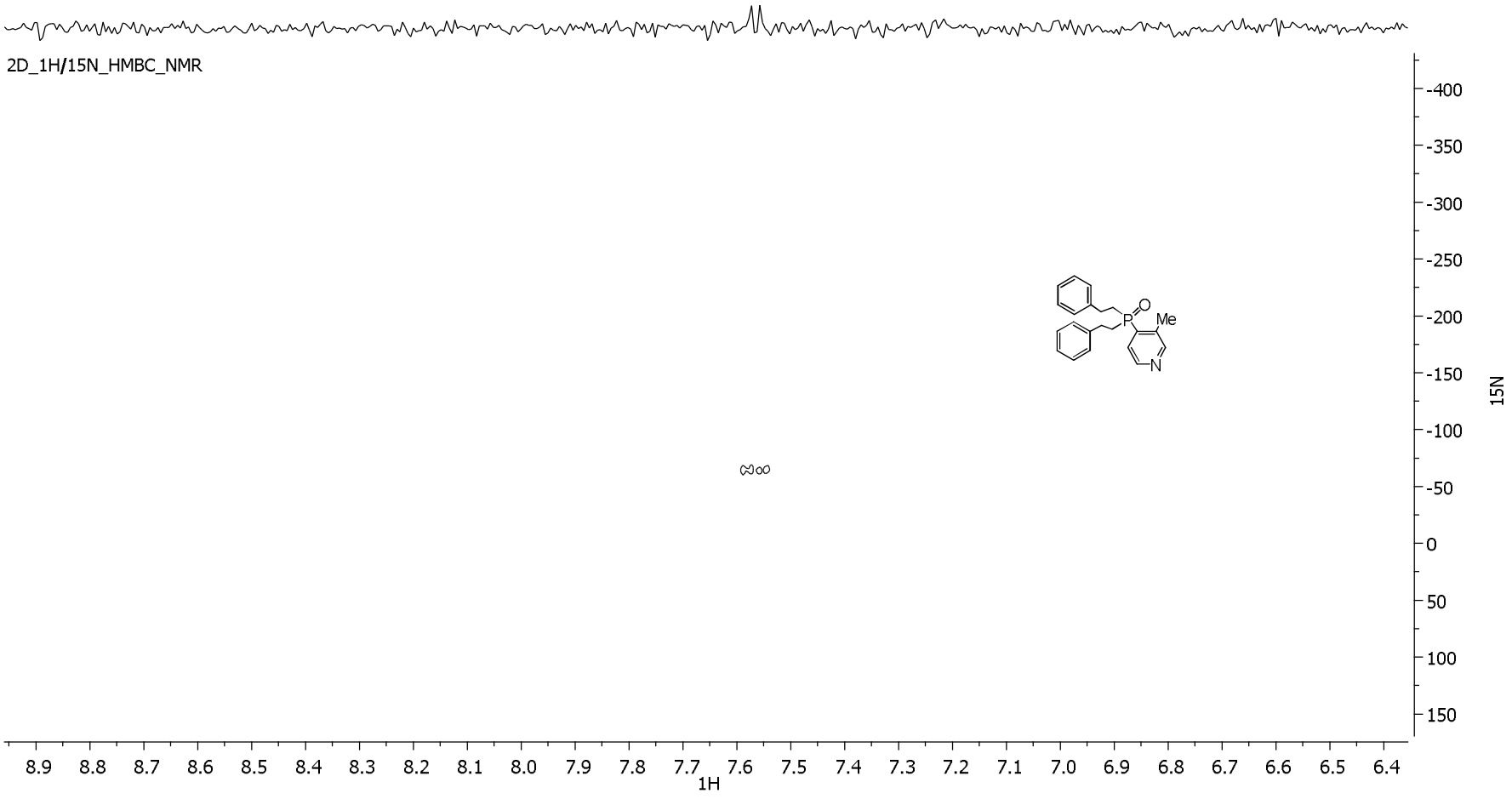
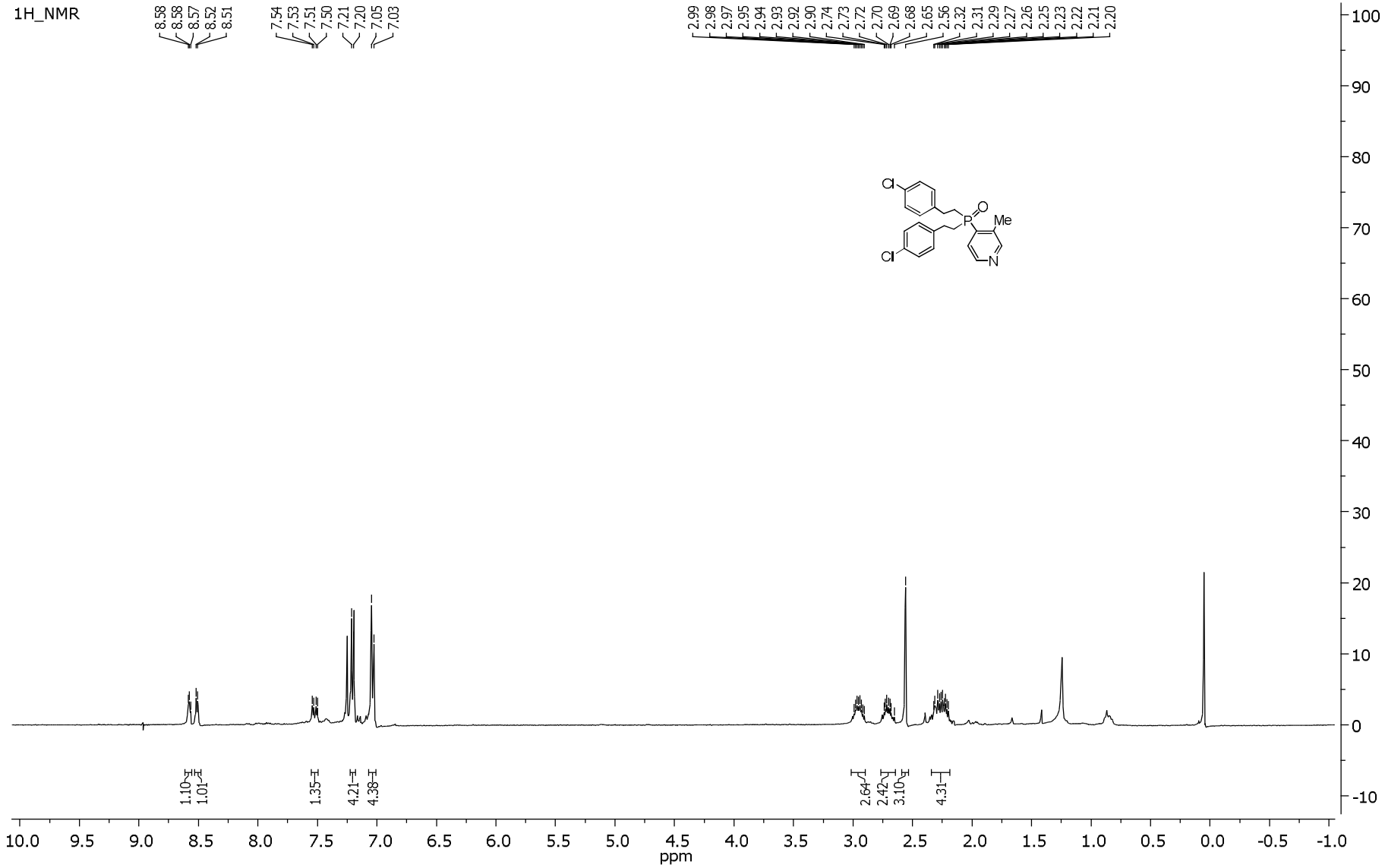
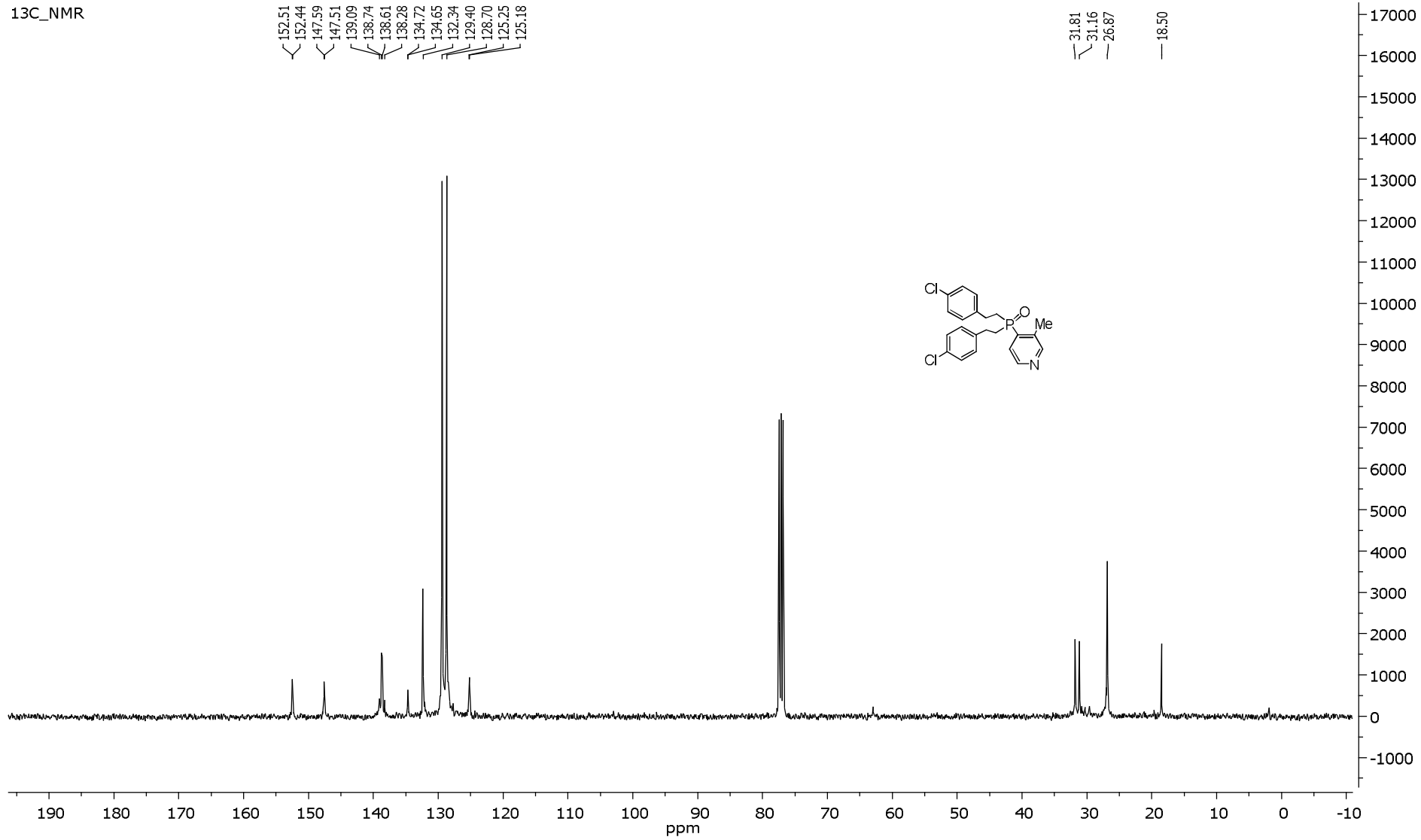


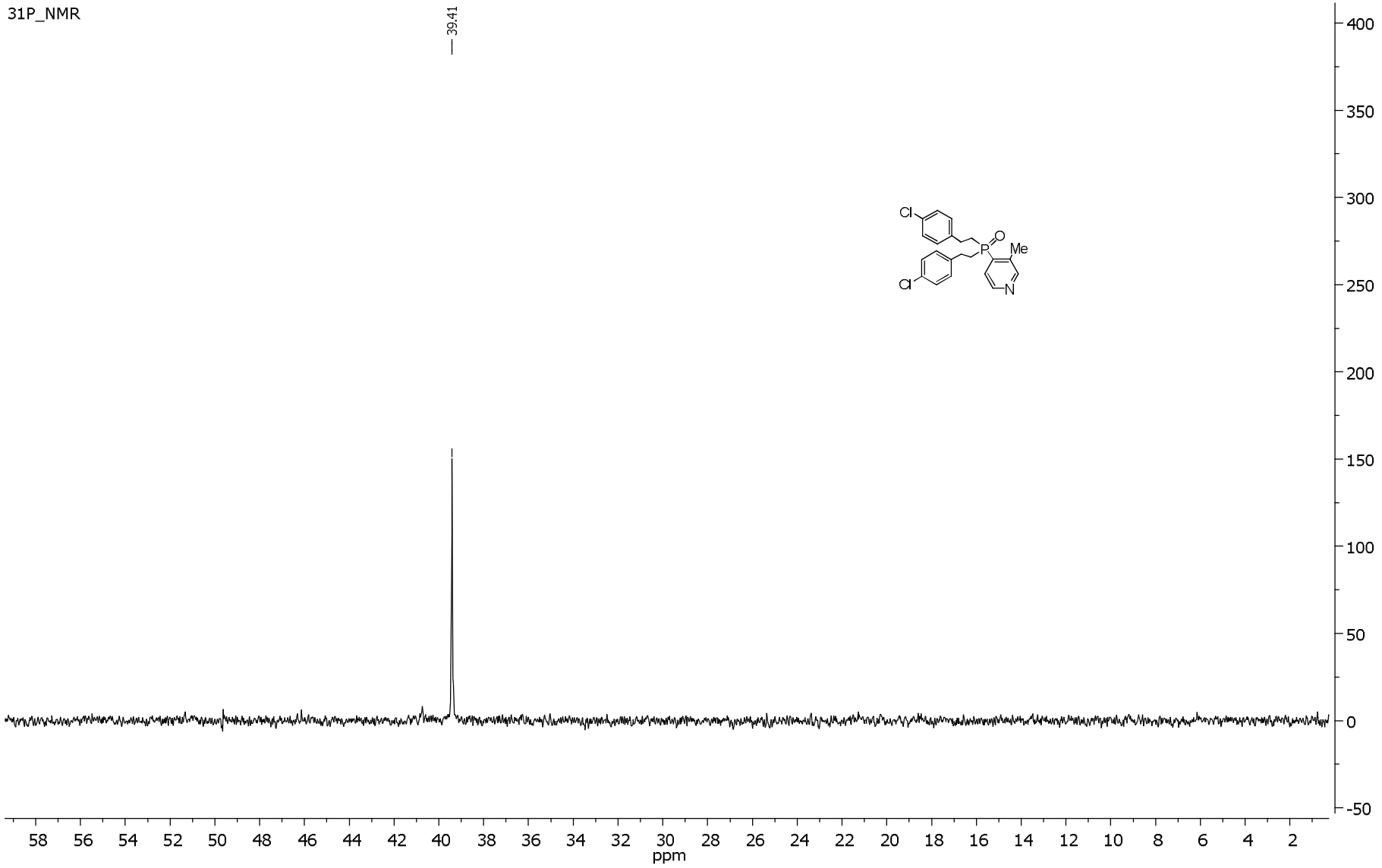
4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}-3-methylpyridine (6c)



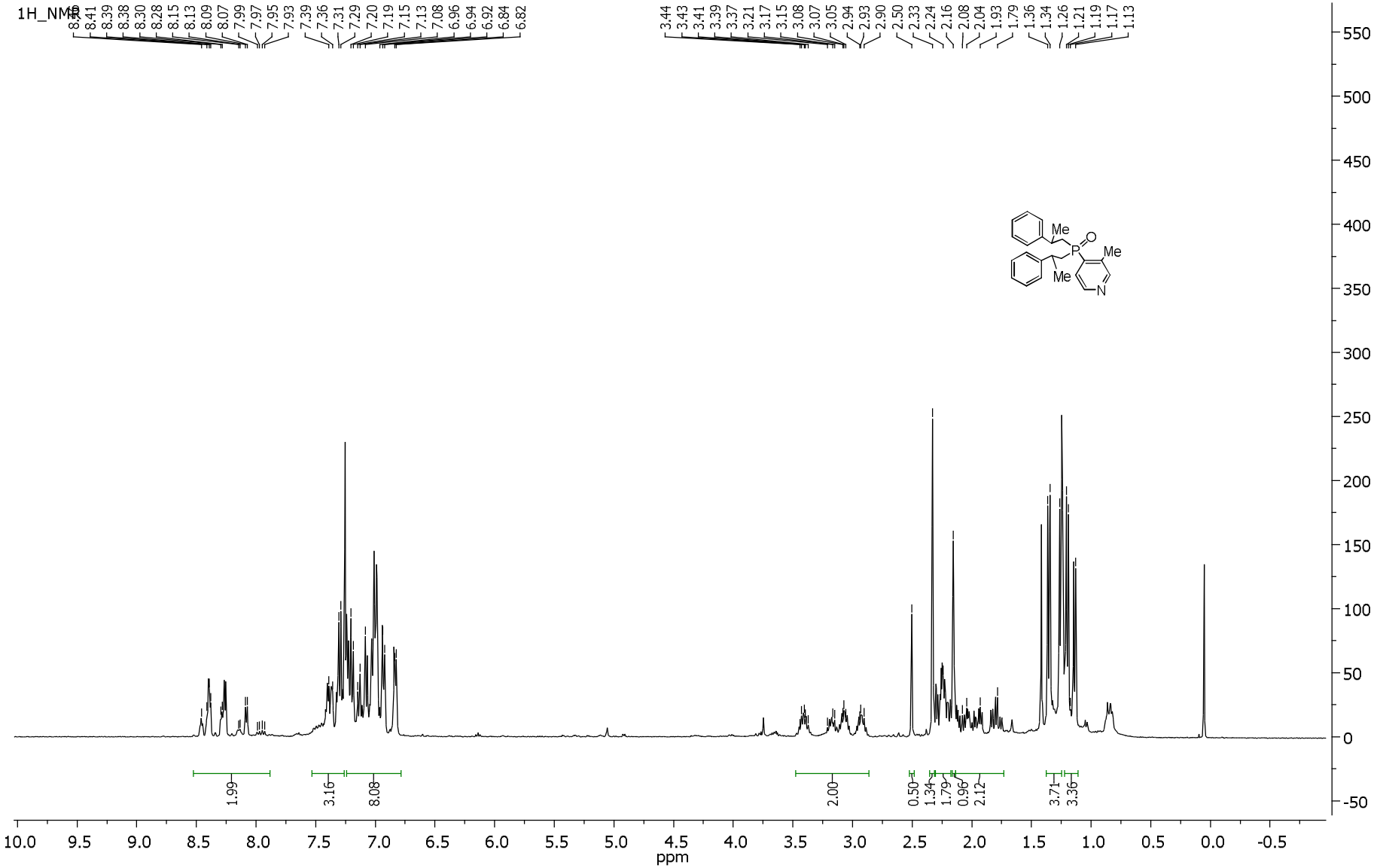
4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}-3-methylpyridine (6c)



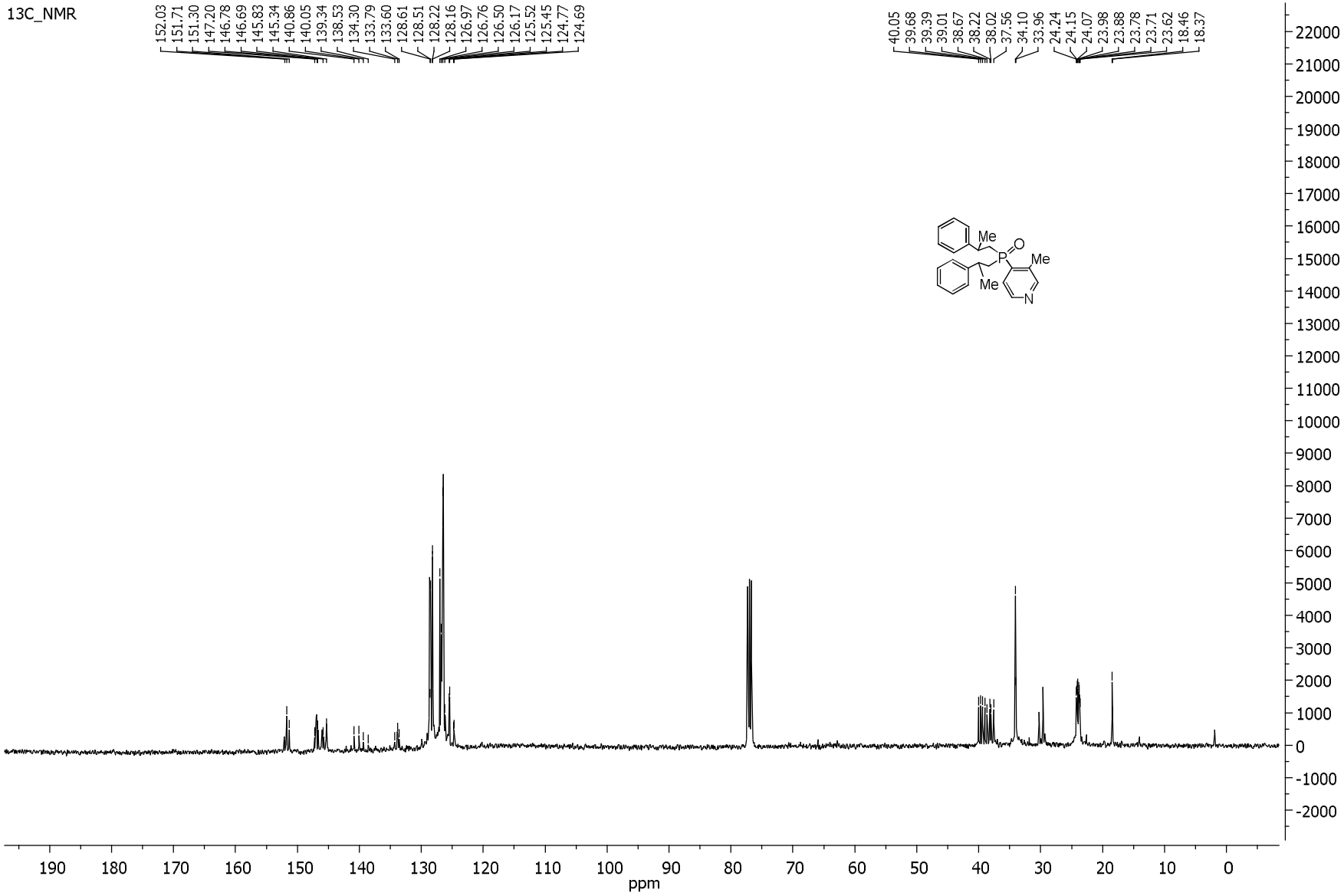
4-{Bis[2-(4-chlorophenyl)ethyl]phosphoryl}-3-methylpyridine (6c)



4-[Bis(2-phenylpropyl)phosphoryl]-3-methylpyridine (6d)



4-[Bis(2-phenylpropyl)phosphoryl]-3-methylpyridine (6d)



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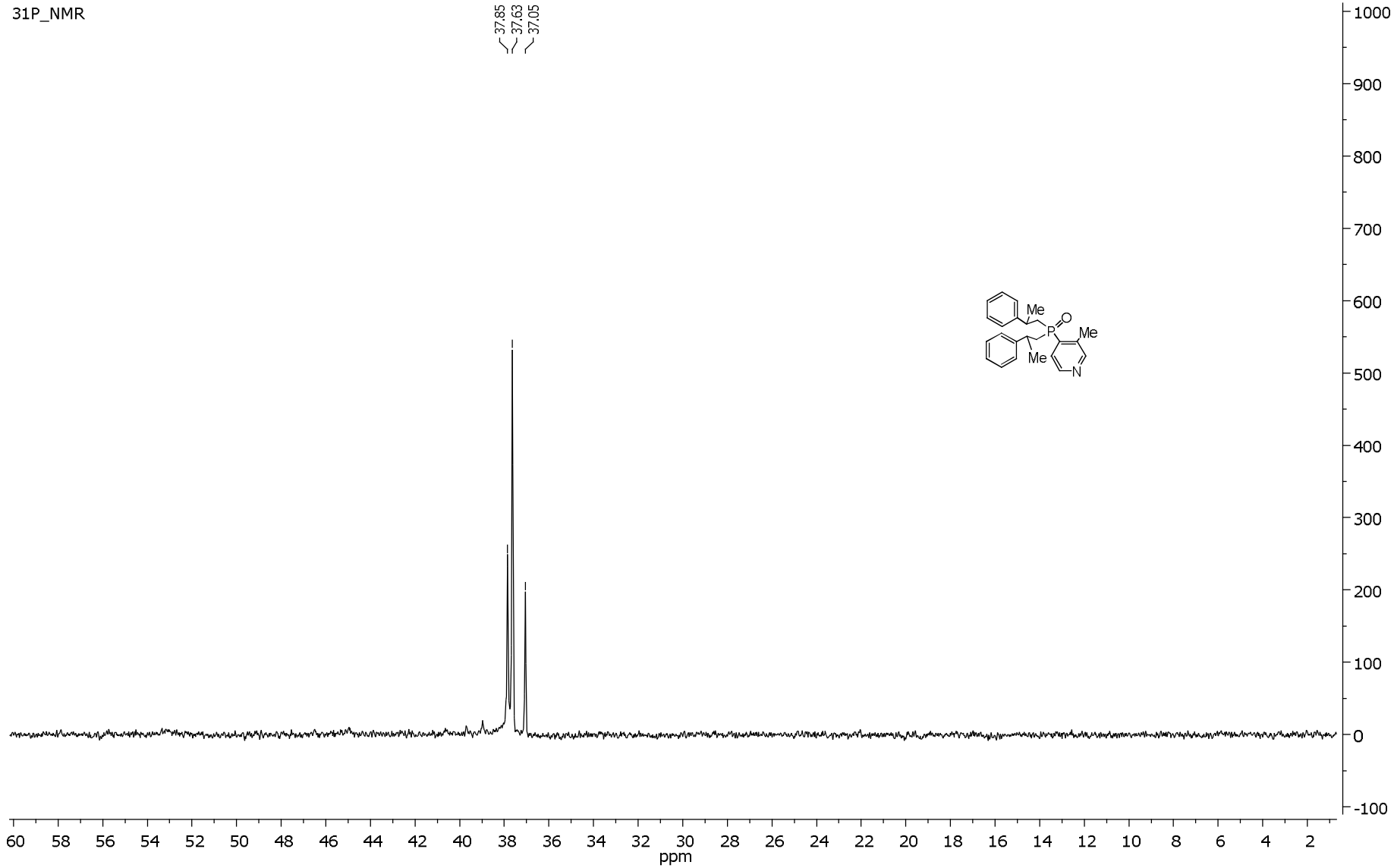
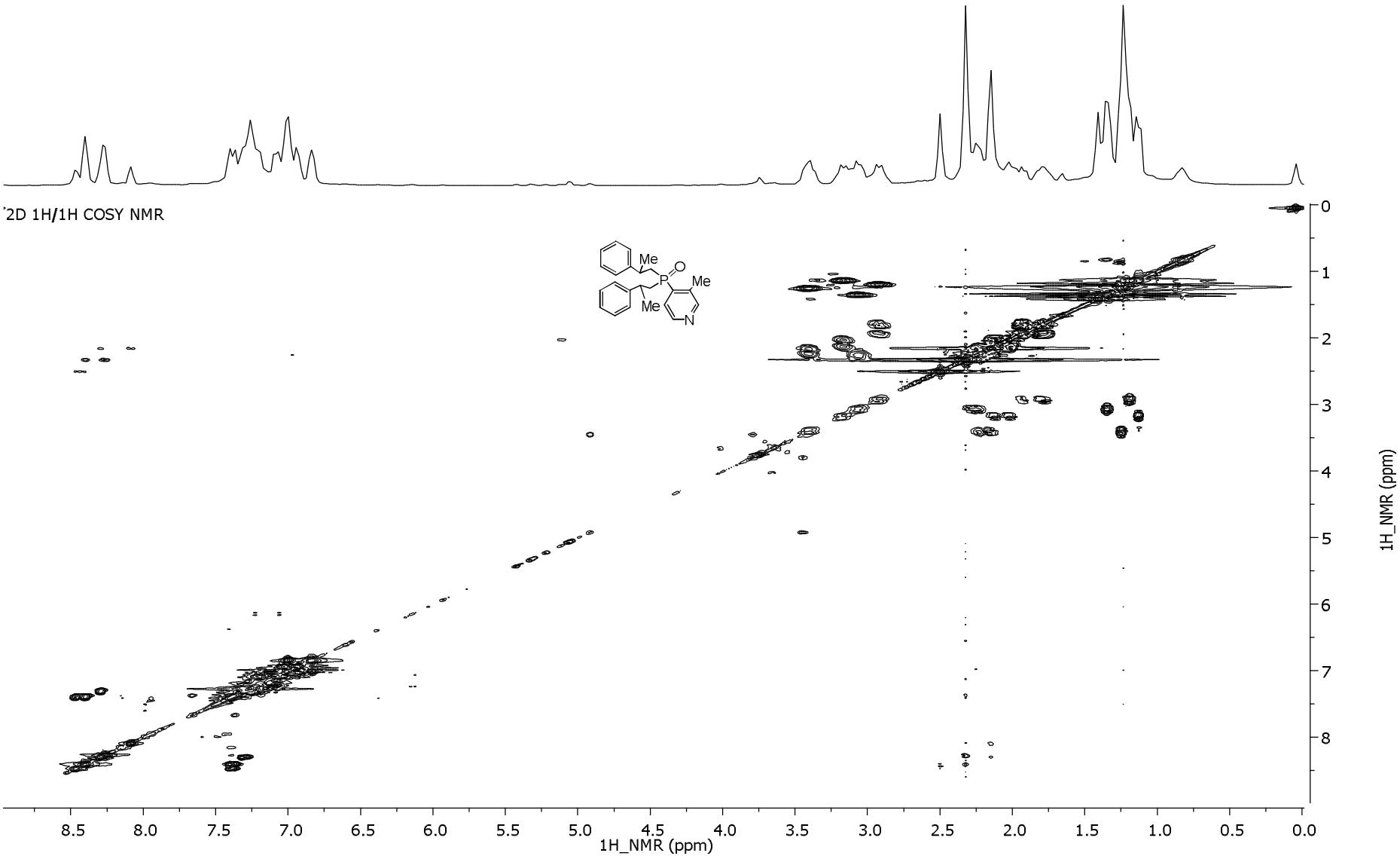
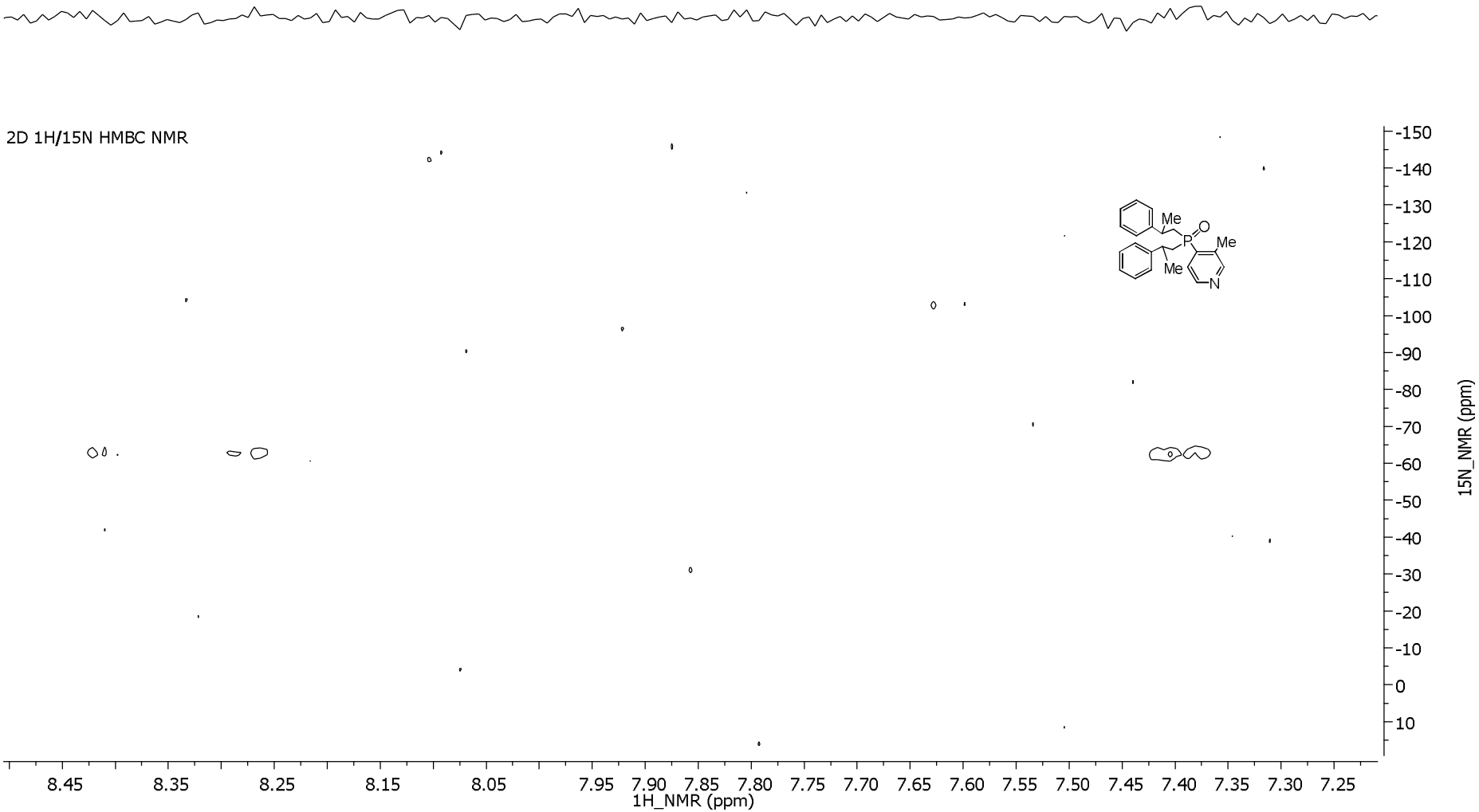


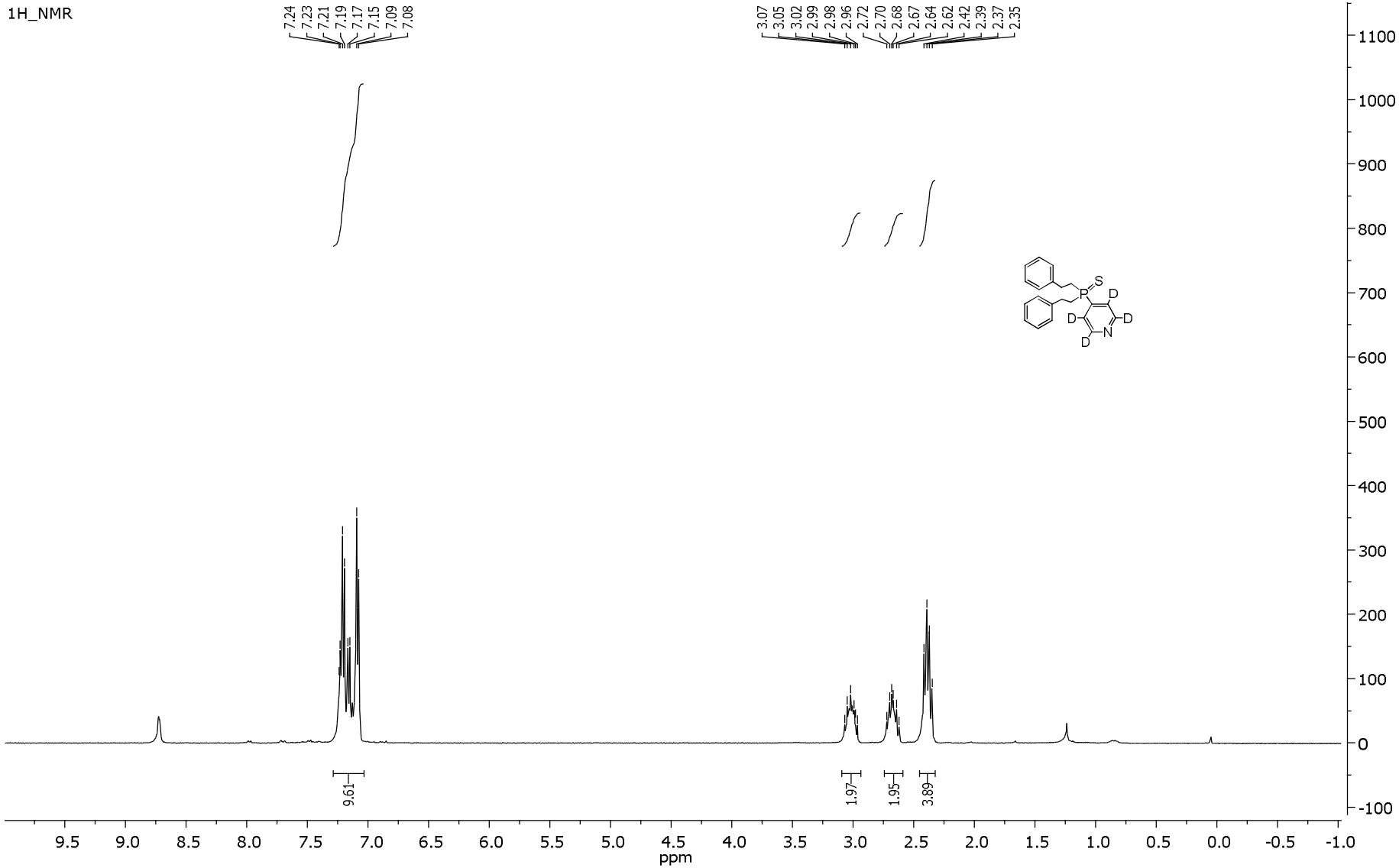
4-[Bis(2-phenylpropyl)phosphoryl]-3-methylpyridine (6d)



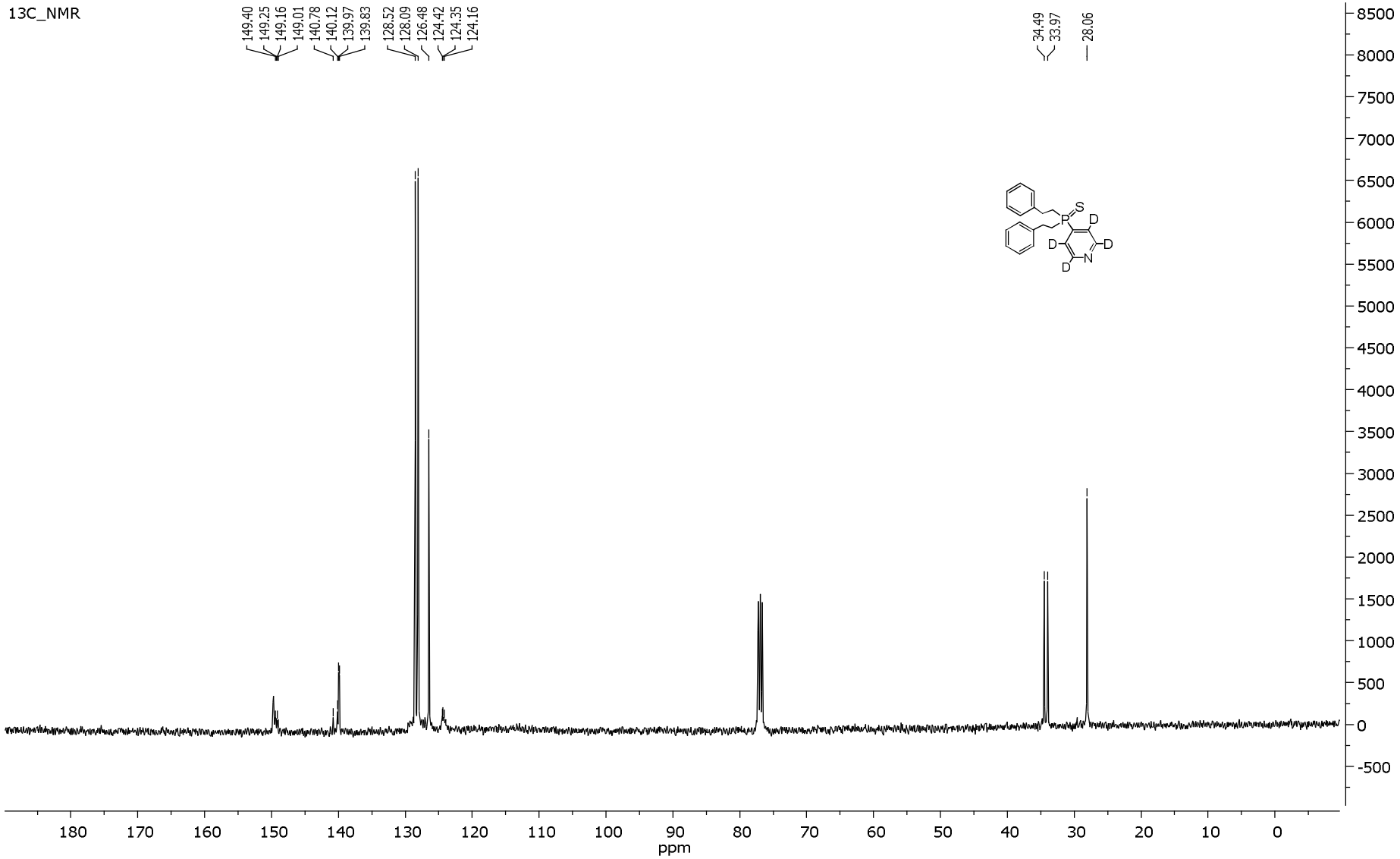
4-[Bis(2-phenylpropyl)phosphoryl]-3-methylpyridine (6d)



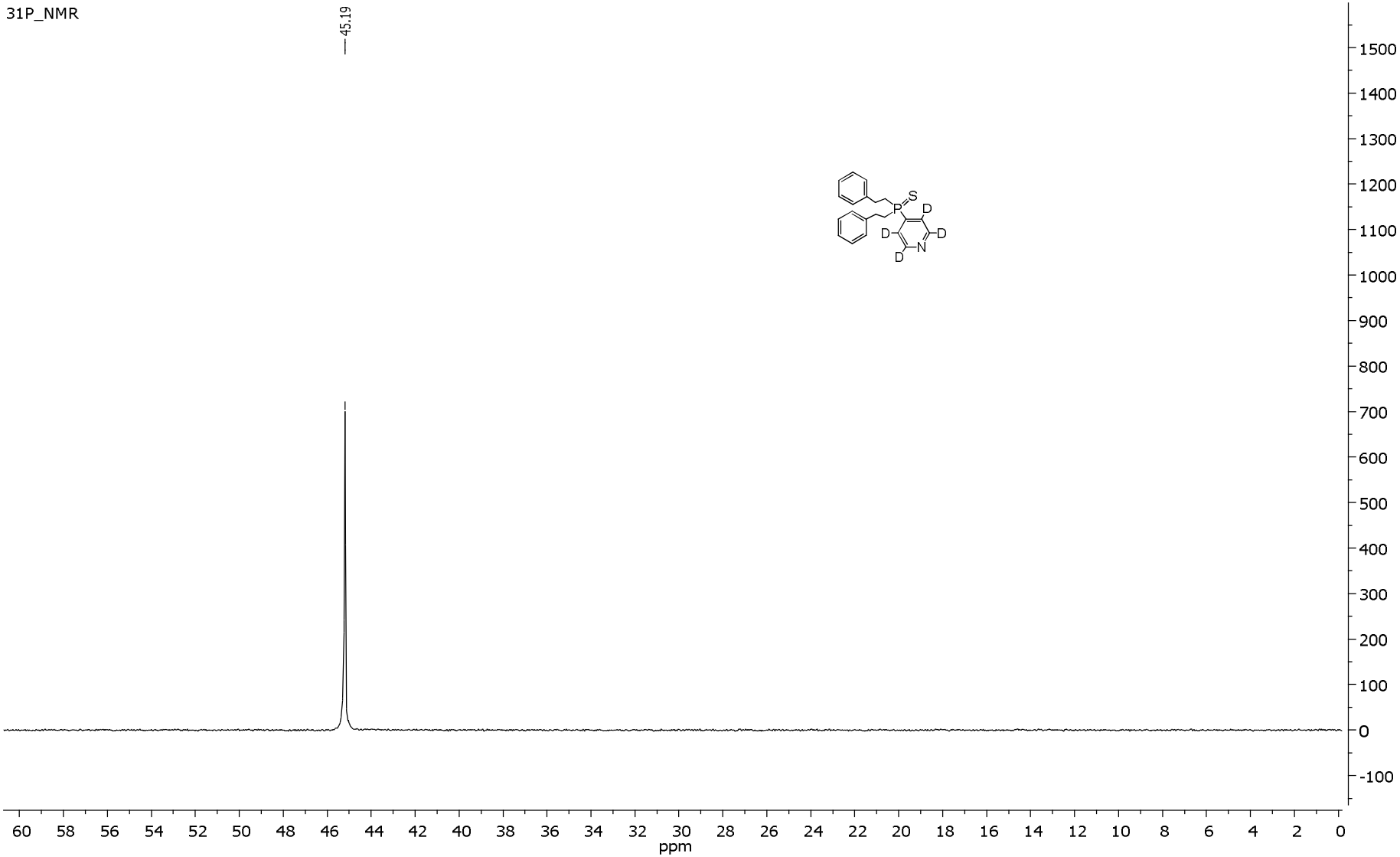
4-[Bis(2-phenylethyl)thiophosphoryl]pyridine-d_4



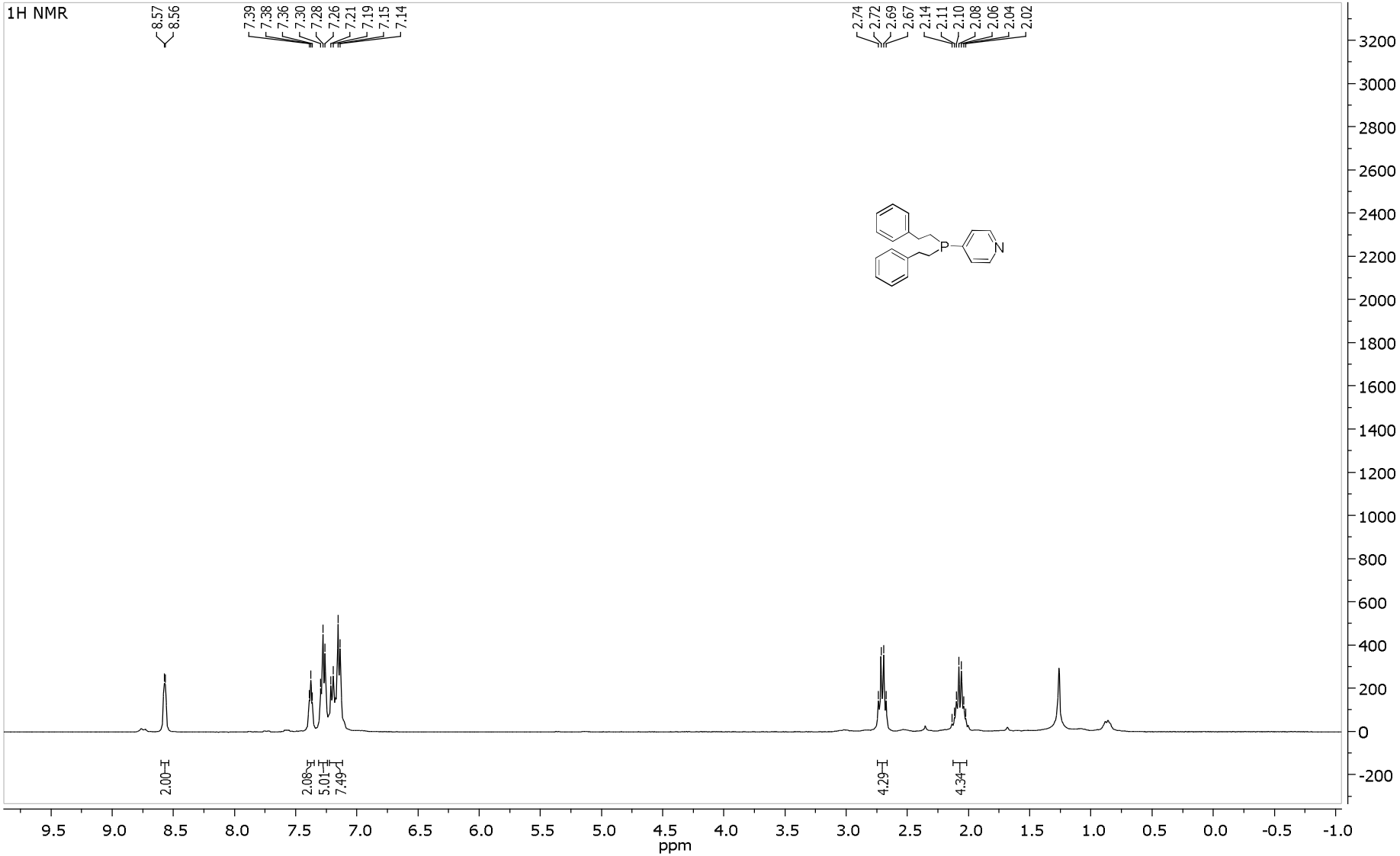
4-[Bis(2-phenylethyl)thiophosphoryl]pyridine-d_4



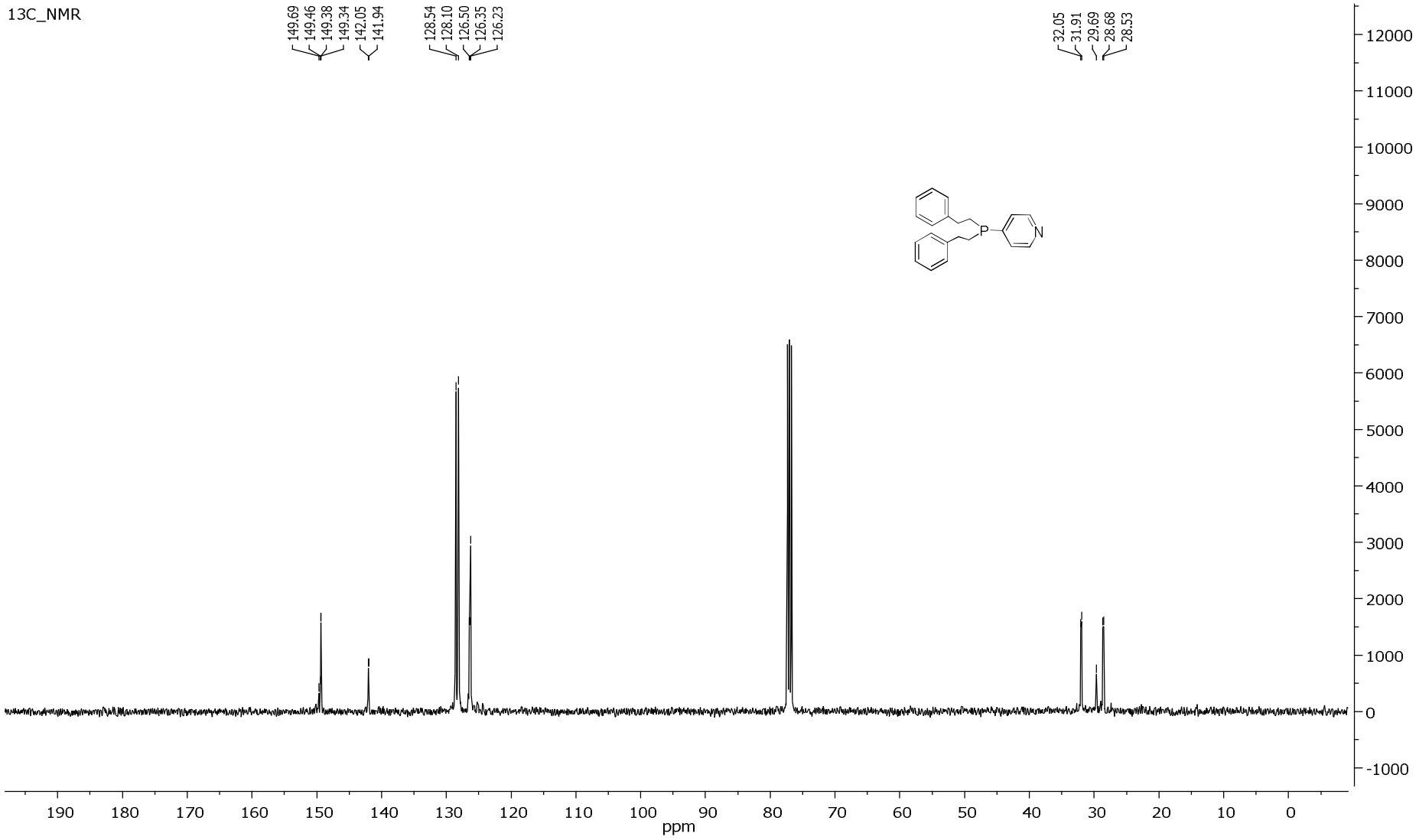
4-[Bis(2-phenylethyl)thiophosphoryl]pyridine-d_4



4-[Bis(2-phenylethyl)phosphino]pyridine (10)



4-[Bis(2-phenylethyl)phosphino]pyridine (10)



4-[Bis(2-phenylethyl)phosphino]pyridine (10)