Electrocyclization of Phosphahexatrienes: An Approach to λ^5-Phosphinines

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General Comments:

All procedures with compounds sensitive to hydrolysis and oxidation were carried out in an atmosphere of dry argon. All solvents were purified and dried by standard methods. ^{1}H spectra were recorded at 300 MHz or 500 MHz; C_6D_6, $CDCl_3$ or DMSO-d_6 as solvents with TMS as an internal standard; ^{31} P NMR spectra were recorded at 121 MHz with 85% H_3PO_4 as an external standard, for all compounds phosphorus spectra were recorded in the same solvent that was used for taking up ^{1}H NMR. ^{13}C NMR spectra.

The peak assignments in the NMR spectra of the compounds **10** and **16a** were confirmed by COSY and HSQC 2D correlations. LC/MS (APCI MS) spectra for compounds **3b**, **7, 8, 10, 18a** and **21a** were recorded using chromatography/mass spectrometric system. Mass spectra (EI, 70 eV) for compounds **13a, 16a-c, 17b, 19b, 20** and **23a,b** were obtained by direct inlet. Compounds **13b,c** and **17a** were oxidized to appropriate phosphorus oxides in mass-spectrometer and mass spectra are shown for their phosphorus oxides. FAB mass spectra for **3a,b**, **14a-c**, **18b**, **22b**, **25a,b**, **26b**, **27a,b** substances were recorded. Microanalyses were obtained using elemental micro-analyzers. Melting points are uncorrected. Yields refer to pure isolated products.

General Procedures:

Synthesis of phosphonium salts 3:

To a solution of pent-2,4-dien-yl bromide **2** (0.87 g, 6 mmol) in hexane (10 mL) hexaalkylphosphorus triamide **1** (6 mmol) was added with stirring. The reaction mixture was left for 3 h with stirring. The precipitated solid was collected by filtration and washed with hexane. (for **1a** toluene at 40°C was used.)

Synthesis of phosphonous diamides 13.

To a stirred solution of (2-ethoxyvinyl)phosphonous dichloride **12** (3 g, 16.8 mmol) in hexane (20 mL) was slowly added a solution of morpholine (33.6 mmol) and Et_3N (33.6 mmol) for **13a** or the corresponding amine (67.2 mmol) for **13b,c** in hexane (20 mL) at 0-5 ºC. The reaction mixture was left for 1 day with stirring at r.t. The precipitated solid was filtred and the filtrate was evaporated *in vacuo*. For **13b,c** the residue was distilled *in vacuo* (0.03 torr, bp 76-81ºC for **13b**, 78ºC for **13c**).

Synthesis of phosphines 17.

To a stirred solution of (2-ethoxyvinyl)phosphonous dichloride **12** (5 g, 28.9 mmol) in Et_2O (20 mL) was slowly added a solution of CH_3MgI for **17a** or PhMgBr for **17b** (57.8 mmol) in Et_2O (40 mL) at -50 ºC. The reaction mixture was stirred for 3 h and was allowed warming to r. t., then the solution of NH_4Cl (4.64 g, 86.7 mmol) in deoxygenated water (30 mL) was added. The reaction mixture was stirred for 1 day at r.t. The organic layer was separated, dried (Na_2SO_4), end evaporated *in vacuo*.

Synthesis of phosphinous amides 21.

To a stirred solution of phosphonamidous chloride **20** (1 g, 5.5 mmol) in THF (30 mL) was slowly added a solution of CH_3Li for **21a** or PhLi for **21b** (5.5 mmol). The reaction mixture was stirred 1 h and then was allowed warming to r. t. and evaporated *in vacuo*. The residue was extracted with pentane and then was distilled using a short path vacuum distillation apparatus.

Synthesis of allyl phosphonium salts 14, 18, 22

To a stirred solution of phosphonous diamide **13** for **14**, phosphine **17** for **18** or phosphinous amide **21** for **22** (6.6 mmol) in CH_2Cl_2 (10 mL) allyl bromide (0.8 g, 6.6

mmol) was added. The reaction mixture was stirred at r.t. 3 h and evaporated *in vacuo*. The residue was washed with hexane.

Synthesis of allyl phosphonium salts 8, 25:

To a stirred solution of phosphine **7** or phosphonite **24** (3.3 mmol) in benzene (for **25b** hexane) (10 mL), a solution of allyl bromide (0.4 g, 3.3 mmol) was added. The reaction mixture was refluxed with stirring for 7 h for **8** or stirred 1 day for **25**. The precipitated solid was collected by filtration and washed with an appropriate solvent.

Synthesis phosphonium salts 27:

To a solution of **26a** for **27a** or **25b** for **27b** (2.9 mmol) in isopropanol (20 mL) DMADMF (3.5 g, 3.91 mL, 0.029 mol) was added with stirring. The reaction mixture was refluxed for 16h for **27a** or 9 days for **27b**. The solvents were evaporated and the residue was triturated with heptane, the solid was collected, washed with heptane and dried.

Synthesis of λ^5-phosphinines 10, 16, 19, 23:

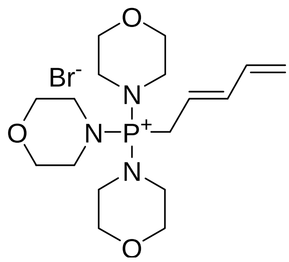
To a suspension of allyl phosphonium salts **8, 14, 18, 22** or salt **27** (2 mmol) in THF (20 mL) cooled to -78°C a solution of n-BuLi (4 mmol, 2,5 M, 1,62 mL) was added with stirring. The reaction mixture was stirred for 1 h and was allowed warming to room temperature and was kept stirring for 12 h.

For **10: T**he reaction mixture was evaporated and the residue was extracted with $CHCl_3$ (3x10 mL). The solution evaporated and the solid was dried.

For **16:** Water (50 mL) was added to the reaction mixture and the phosphinine was extracted with benzene (3x20 mL). The solution was evaporated and the residue dried and crystallized from pentane for **16a** or distilled *in vacuo* (0.03 torr, bp 90-95ºC) **for 16b,c**.

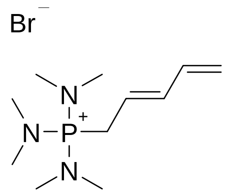
For **19, 23:** Water (50 mL) was added to the reaction mixture and the phosphinine was extracted with Et_2O (3x20 mL). The solution was evaporated and the residue dried.

Compound data:



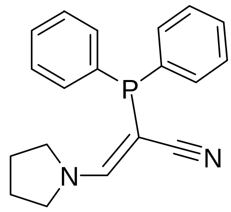
trimorpholin-4-yl(penta-2,4-dien-1-yl)phosphonium bromide (3a).

Yield: 29.4%; amorphous solid (hexane - toluene); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 3.32 (br t, 12H), 3.78 (br t, 12H), 4.46 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{2}J_{PH}$ = 17.4 Hz, 2H), 5.23 (d, $^{3}J_{HH}$ = 9.6 Hz, 1H), 5.36 (d, $^{3}J_{HH}$ = 18 Hz, 1H), 5.43 - 5.55 (m, 1H), 6.27 - 6.39 (m, 1H), 6.68 - 6.78 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 28.2 (d, $^{1}J_{PC}$ = 99.3 Hz, CH_2-P), 45.7 (NCH_2), 66.6 (d, $^{3}J_{PC}$ = 5.0 Hz, OCH_2), 118.0 (d, J = 13.8 Hz, CH), 120.3 (d, $^{5}J_{PC}$ = 3.8 Hz, $\underline{C}H_2$=CH), 135.0 (d, J = 3.8 Hz, CH), 139.9 (d, J = 15.1 Hz, CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 49.3; **MS-FAB,** *m/z* (%)**:** 356 ([M – Br]$^+$, 100) ; **Anal. Calcd for $C_{17}H_{31}BrN_3O_3P$:** C, 46.80; H, 7.16; N, 9.63; P, 7.10. Found C, 46.83; H, 7.17; N, 9.7; P, 7.15.



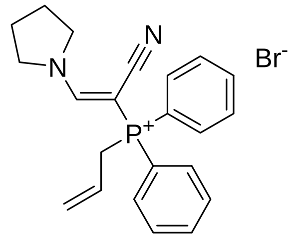
tris(dimethylamino)(penta-2,4-dien-1-yl)phosphonium bromide (3b).

Yield: 96%; amorphous solid (hexane); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.85 (d, $^{3}J_{PH}$= 10.5 Hz, 18H), 3.86 (dd, $^{3}J_{HH}$ = 7.5 Hz, , $^{2}J_{PH}$ = 17.7 Hz, 2H), 5.16 (d, $^{3}J_{HH}$ = 9.6 Hz, 1H), 5.28 (d, $^{3}J_{HH}$ = 16.8 Hz, 1H), 5.48-5.62 (m, 1H), 6.29 - 6.54 (m, 1H), 6.70 -6.79 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 28.9 (d, $^{1}J_{PC}$ = 104.4 Hz, CH_2-P), 37.54 (NCH_3), 118.9 (d, J_{PC} = 10.1 Hz, CH), 119.2 (d, $^{5}J_{PC}$ = 3.8 Hz, $\underline{C}H_2$=CH), 135.4 (d, J_{PC} = 5.0 Hz, CH), 138.8 (d, J_{PC} = 13.8 Hz, CH); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 55.9; **APCI MS**: [M – Br]$^+$ = 230; **Anal. Calcd for $C_{11}H_{25}BrN_3P$:** C, 42.59; H, 8.12; N, 13.55; P, 9.98. Found C, 42.62; H, 8.11; N, 13.57; P, 10.02.



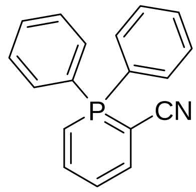
2-(diphenylphosphino)-3-pyrrolidin-1-ylacrylonitrile (7).

To a solution of Ph_2PCl (3,6 g, 16,4 mmol, 2,94 mL) in CH_2Cl_2 (10 mL) a mixture of **14** (2 g, 16,4 mmol) and Et_3N (2,16 g, 21,3 mmol, 2,96 mL) in CH_2CI_2 (30 mL) wa added with stirring. The reaction mixture was kept stirring at room temperature for 3 days. Water (50 mL) was added to the reaction mixture, the reaction mixture was thoroughly shaken, the organic layer was separated, dried over Na_2SO_4. The solvent was evaporated, the residue was recrystallized from isopropanol. **Yield:** 31.1%; **mp** 125-127°C (2-propanol); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.88 (br m, 2H), 1.98 (br m, 2H), 3.51 (br m, 2H), 3.85 (br m, 2H), 7.25 (d, $^3J_{PH}$ = 11.7 Hz, 1H), 7.35 - 7.47 (m, 6H), 7.49 - 7.52 (m, 4H) (This substance exists as a mixture of *Z*/*E* isomers, ^{1}H NMR spectra refer to the major isomer). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 24.6 (b, CH_2), 25.8 (b, CH_2), 47.7 (b, NCH_2), 54.1 (b, NCH_2), 67.3 (d, $^1J_{PC}$ = 11.3 Hz, C(2)), 120.7 (d, $^2J_{PC}$ = 5 Hz, CN), 128.3 (d, $^3J_{PC}$ = 7.5 Hz, PPh_2), 128.6 (PPh_2), 132.5 (d, $^2J_{PC}$ = 20 Hz, PPh_2), 137.8 (d, $^1J_{PC}$ = 6.3 Hz, PPh_2), 155.3 (d, $^2J_{PC}$ = 74.2 Hz, C(3)); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 1.7; **APCI MS**: M^++1 = 307; **Anal. Calcd for $C_{19}H_{19}N_2P$:** C, 74.49; H, 6.25; N, 9.14; P, 10.11. Found C, 74.61; H, 6.13; N, 9.26; P, 10.00.



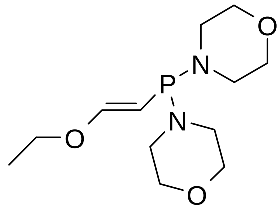
allyl(1-cyano-2-pyrrolidin-1-ylvinyl)diphenylphosphonium bromide (8).

Yield: 24.3%; **mp** 203-205°C (acetone); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.88 – 2.12 (m, 4H), 3.93 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 4.16 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 4.62 (dd, $^3J_{HH}$ = 5.69 Hz, $^2J_{PH}$ = 20.4 Hz, 2H), 5.31-5.36 (m, 1H), 5.51-5.56 (m, 2H), 7.65 - 7.83 (m, 6H), 7.85 - 7.93 (m, 4H), 8.65 (d, $^3J_{PH}$ = 11.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 23.6 (CH_2), 25.0 (CH_2), 27.4 (d, $^1J_{PC}$ = 51.6 Hz, CH_2-P), 48.2 (NCH_2), 55.3 (NCH_2), 117.4 (d, $^2J_{PC}$ = 7.5 Hz, CN), 119.3 (d, $^1J_{PC}$ = 90.2 Hz, PPh_2), 123.3 (d, $^2J_{PC}$ = 10 Hz, CH_2=<u>C</u>H), 125.5 (d, $^3J_{PC}$ = 12.6 Hz, <u>C</u>H_2=CH), 129.9 (d, $^3J_{PC}$ = 12.6 Hz, PPh_2), 133.3 (d, $^2J_{PC}$ = 10 Hz, PPh_2), 134.6 (d, $^4J_{PC}$ = 2.8 Hz. PPh_2), 156.2 (d, $^2J_{PC}$ = 20 Hz, C(2)), the C(1) signal is not observed; **^{31}P NMR** (81 MHz, $CDCl_3$): δ 25.1; **APCI MS**: $[M - Br]^+ = 347$; **Anal. Calcd for $C_{22}H_{24}BrN_2P$:** C, 61.84; H, 5.66; N, 6.56; P, 7.25. Found C, 61.98; H, 5.72; N, 6.40; P, 7.14.



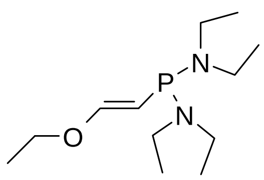
1,1-diphenyl-1λ^5-phosphinine-2-carbonitrile (10):

Yield: 78%; **mp** 132°C ($CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.00 (dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 17.4 Hz, 1H), 5.29 (ddd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 8.7 Hz, $^4J_{PH}$ = 1.5 Hz, 1H), 7.08 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{PH}$ = 26.1 Hz, 1H), 7.27 (ddd, , $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 36.6 Hz, 1H) , 7.45 - 7.63 (m, 10H);**^{13}C NMR** (125 MHz, $CDCl_3$): δ 44.8 (d, $^1J_{PC}$ = 113.2 Hz, C(2)), 78.9 (d, $^1J_{PC}$ = 93 Hz, C(6)), 100.7 (d, $^3J_{PC}$ = 17.6 Hz, C(4)), 122.7 (d, $^2J_{PC}$ = 11.3 Hz, CN), 122.7 (d, $^3J_{PC}$ = 13.8 Hz, PPh_2), 130.8 (d, $^1J_{PC}$ = 90.5 Hz, PPh_2), 131.7 (d, $^2J_{PC}$ = 11.3 Hz, PPh_2), 132.1 (d, $^4J_{PC}$ = 3.8 Hz. PPh_2), 139.0 (d, $^2J_{PC}$ = 3.8 Hz, C(3)), 143.6 (C(5)); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 8.48. **APCI MS**: $M^+ + 1 = 276$; **Anal. Calcd for $C_{18}H_{14}NP$:** C, 78.53; H, 5.13; N, 5.09; P, 11.25. Found C, 78.47; H, 5.05; N, 5.13; P, 11.4.



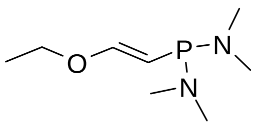
4,4'-((2-ethoxyvinyl)phosphinediyl)dimorpholine (13a):

Yield: 69%; oil; ^{1}**H NMR** (300 MHz, C_6D_6): δ 1.02 (t, $^{3}J_{HH}$ = 6.9 Hz, 3H), 2.75-3.20 (m, 8H), 3.42-3.52 (m, 10H), 4.89 (dd, $^{3}J_{HH}$ =13.8 Hz, $^{2}J_{PH}$ = 12 Hz, 1H), 6.60 (dd, $^{3}J_{HH}$ = 13.8 Hz, $^{3}J_{PH}$ = 5.1 Hz, 1H); ^{13}**C NMR** (125 MHz, C_6D_6): δ 14.4 (CH_3), 49.1 (d, $^{2}J_{PC}$ = 12.6 Hz, NCH_2), 64.6 (O$\underline{CH_2}$$CH_3$), 68.0 (d, $^{3}J_{PC}$ = 7.5 Hz, OCH_2) 97.9 (d, $^{1}J_{PC}$ = 5 Hz, CH-P), 155.7 (d, $^{2}J_{PC}$ = 40.2 Hz, EtO-<u>CH</u>=CH); ^{31}**P NMR** (81 MHz, C_6D_6): δ 87.3.; **MS-EI,** *m/z* (%): 274(M^+,18), 189(11), 188(100), 103(26), 86(19), 85(7), 83(8), 75(12), 56(10), 42(6). **Anal. Calcd for $C_{12}H_{23}N_2O_3P$:**C, 52.55; H, 8.45; N, 10.21; O, 17.50; P, 11.29. Found C, 52.49; H, 8.47; N 10.23; P 11.30.



***P*-(2-ethoxyvinyl)-*N*,*N*,*N*',*N*'-tetraethylphosphonous diamide (13b):**

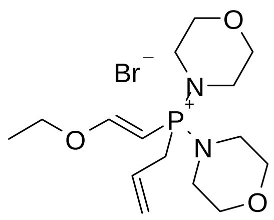
Yield: 69%; bp 76-81ºC (0.03 torr); ^{1}**H NMR** (300 MHz, C_6D_6): δ 0.98-1.03 (m, 15H), 2.96-3.17 (m, 8H), 3.49 (q, $^{3}J_{HH}$ = 6.9 Hz, 2H), 5.09 (dd, $^{3}J_{HH}$ = 13.5 Hz, $^{2}J_{PH}$ = 13.5 Hz, 1H), 6.68 (dd, $^{3}J_{HH}$ = 13.5 Hz, $^{3}J_{PH}$ = 4.5 Hz, 1H); ^{13}**C NMR** (125 MHz, C_6D_6): δ 14.5 ($OCH_2\underline{CH_3}$), 14.9 (d, $^{3}J_{PC}$ = 3.8 Hz, CH_3), 42.4 (d, $^{2}J_{PC}$ = 17.6 Hz, NCH_2), 64.2 (O$\underline{CH_2}$$CH_3$), 101.1 (CH-P), 154.1 (d, $^{2}J_{PC}$ = 39 Hz, EtO-<u>CH</u>=CH); ^{31}**P NMR** (81 MHz, C_6D_6): δ 86.8.; **MS-EI for P=O,** *m/z* (%): 262(M^+, 6), 217(17), 190(77), 136(78),100(24), 73(21), 72(100), 58(78), 44(42), 42(17). **Anal. Calcd for $C_{12}H_{27}N_2OP$:** C, 58.51; H, 11.05; N 11.37; P 12.57. Found C, 58.49; H, 11.07; N 11.41; P 12.55.



***P*-(2-ethoxyvinyl)-*N*,*N*,*N*',*N*'-tetramethylphosphonous diamide (13c):**

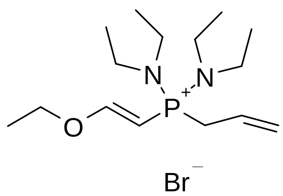
Yield: 85 %; 70°C (0.05 torr); ^{1}**H NMR** (300 MHz, C_6D_6): δ 1.00 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H), 2.63 (d, $^{3}J_{PH}$ = 9.3 Hz, 12H), 3.41 (q, $^{3}J_{HH}$ = 7.2 Hz, 2H), 5.07 (dd, $^{3}J_{HH}$ = 13.8 Hz, $^{2}J_{PH}$ = 10.8 Hz, 1H), 6.64 (dd, $^{3}J_{HH}$ = 13.8 Hz, $^{3}J_{PH}$ = 5.4 Hz, 1H); ^{13}**C NMR** (125 MHz, C_6D_6): δ 14.4 (CH_3), 40.5 (d, $^{2}J_{PC}$ = 15.1 Hz, N-CH_3), 64.3(O-CH_2), 100.1(CH-P), 155.3 (d, $^{2}J_{PC}$

= 42.8 Hz, EtO-CH=CH); ^{31}**P NMR** (81 MHz, C_6D_6) 92.1; **MS-EI for P=O,** *m/z* (%): 206(M^+, 7), 176(1), 161(30), 136(14),119(13), 108(97), 72(40), 58(12), 44(100)**.**; **Anal. Calcd for $C_8H_{19}N_2OP$:** C, 50.51; H 10.07; N, 14.73; P, 16.28. Found C, 50.48; H, 10.06; N, 14.77; P, 16.25.



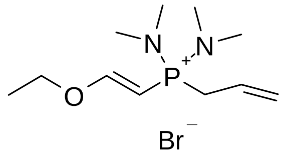
allyl(2-ethoxyvinyl)dimorpholin-4-ylphosphonium bromide (14a):

Yield: 88 %; amorphus solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.39 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 3.28-3.33(m, 8H), 3.74-3.77 (m, 8H), 4.08 (dd, 2H, $^3J_{HH}$ = 6.6 Hz, $^2J_{PH}$ = 16.8 Hz), 4.33 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.07 (dd, $^3J_{HH}$ = 13.2 Hz, $^2J_{PH}$ = 13.2 Hz, 1H), 5.44-5.47 (m, 1H), 5.59-5.69(m, 2H), 7.82 (dd, $^3J_{HH}$ = 13.2 Hz, $^3J_{PH}$ = 10.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.5 ($\underline{CH_3}CH_2O$), 30.1 (d, $^1J_{PC}$ = 81.7 Hz, P-CH_2), 45.4 (NCH_2), 67.2 (d, $^2J_{PC}$ = 5.1, O-CH_2), 69.6 (O-$\underline{CH_2}CH_3$), 79.5 (d, $^1J_{PC}$ = 137 Hz, CH-P), 124.4 (d, $^2J_{PC}$ = 7.5 Hz, CH_2=$\underline{CH}$), 124.5 (d, $^3J_{PC}$ = 11.3 Hz, $\underline{CH_2}$=CH), 168.3 (d, $^2J_{PC}$ = 22.6 Hz, EtO-$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 53.7; **MS-FAB,** *m/z* (%): 315([M-Br]$^+$,100); **Anal. Calcd for $C_{15}H_{28}N_2O_3PBr$:** C, 45.58; H, 7.14; Br, 20.21; N, 7.09; P, 7.84. Found C, 45.54; H, 7.12; Br, 20.1; N, 7.13; P, 7.87.



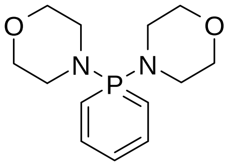
allyl(bis(diethylamino))(2-ethoxyvinyl)phosphonium bromide (14b):

Yield: 100 %; amorphus solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.1 (t, $^3J_{HH}$ = 6.9 Hz, 12H), 1.28 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 3.06-3.17(m, 8H), 3.54 (dd, 2H, $^3J_{HH}$ = 6.9 Hz, $^2J_{PH}$ = 16.2 Hz), 4.21 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 4.95 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 13.5 Hz, 1H), 5.31-42(m, 1H), 5.48-5.61 (m, 1H), 5.62-5.78 (m, 1H), 7.51 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 11.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1 (d, $^3J_{PC}$ = 2.5 Hz, $\underline{CH_3}CH_2N$), 14.5 ($\underline{CH_3}CH_2O$), 31.5 (d, $^1J_{PC}$ = 85.5 Hz, P-CH_2),40.2 (d, $^3J_{PC}$ = 3.8 Hz, CH_2N), 69.2 (O-CH_2), 81.6 (d, $^1J_{PC}$ = 137 Hz, CH-P), 123.9 (d, $^3J_{PC}$ = 13.8 Hz, $\underline{CH_2}$=CH), 124.7 (d, $^2J_{PC}$ = 8.8 Hz, CH_2=$\underline{CH}$), 166.9 (d, $^2J_{PC}$ = 21.4 Hz, EtO-$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 54.8; **MS-FAB,** *m/z* (%): 287([M-Br]$^+$,100); **Anal. Calcd for $C_{15}H_{32}N_2OPBr$:** C, 49.05; H, 8.78; Br, 21.75; N, 7.63; P, 8.43. Found C, 49.00; H, 8.76; Br, 21.69; N, 7.67; P, 8.45.



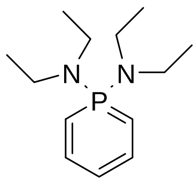
allyl(bis(dimethylamino))(2-ethoxyvinyl)phosphonium bromide (14c):

Yield: 100 %; amorphus solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.32 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.80 (d, $^3J_{PH}$ = 10.2 Hz, 12H), 3.58 (dd, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 16.2 Hz, 2H), 4.25 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 4.97 (dd, $^3J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 13.8 Hz, 1H), 5.35-5.43 (m, 1H), 5.45-5.55 (m, 1H), 5.61-5.80 (m, 1H), 7.59 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 10.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.5 (CH_3), 30.9 (d, $^1J_{PC}$ =84.3 Hz, P-CH_2), 37.4 (N-CH_3), 69.2(O-CH_2), 80.3 (d, $^1J_{PC}$ = 137 Hz, CH-P), 123.9 (d, $^3J_{PC}$ = 12.6 Hz, $\underline{CH_2}$=CH), 124.4 (d, $^2J_{PC}$ = 8.8 Hz, CH_2=$\underline{CH}$), 167.1 (d, $^2J_{PC}$ = 20.1 Hz, EtO-$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 57.4; **MS-FAB,** *m/z* (%): 231([M-Br]$^+$,100); **Anal. Calcd for $C_{11}H_{24}N_2OPBr$:** C, 42.46; H, 7.77; Br, 25.68; N, 9.00; O, 5.14; P, 9.95. Found C, 42.43; H, 7.75; Br, 25.70; N, 8.98; P, 9.93.



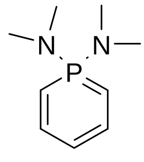
1,1-dimorpholin-4-yl-1λ[5]-phosphinine (16a):

Yield: 46.6%; **mp** 75-80°C (diethyl ether); **^{1}H NMR** (300 MHz, C_6D_6): δ 2.59-2.65 (m, 8H), 3.33 (t, $^3J_{HH}$ = 4.5 Hz, 8H), 4.28 (dd, $^3J_{HH}$ = 11.1 Hz, $^2J_{PH}$ = 6.9 Hz, 2H), 5.66 (dt, $^4J_{PH}$ = 3 Hz, $^3J_{HH}$ = 7.5 Hz, 1H), 7.35 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{PH}$ = 36.9 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 44.7 (NCH_2), 66.9 (d, $^3J_{PC}$ = 8.0 Hz, OCH_2), 72.3 (d, $^1J_{PC}$ = 123 Hz, C(2), C(6)), 99.3 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 140.4 (d, $^2J_{PC}$ = 3.8 Hz, C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ 46.3. **MS-EI,** *m/z* (%): 268 (M^+, 67), 211(14), 183(34), 182(100), 134(8), 126(9), 97(23), 87(99), 86(75), 56(22); **Anal. Calcd for $C_{13}H_{21}N_2O_2P$:** C, 58.20; H, 7.89; N, 10.44; P, 11.54. Found C, 58.24; H, 7.87; N, 10.42; P, 11.53.



***N*[1],*N*[1],*N*[1],*N*[1]-tetraethyl-1λ[5]-phosphinine-1,1-diamine (16b):**

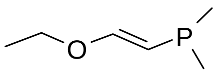
Yield: 48%; **bp** 90-95°C (0.05 torr); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz, 12H), 2.78 - 2.89 (m,8H), 4.54 (dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{PH}$ = 7.5 Hz, 2H), 5.71 (dt, $^4J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 7.5 Hz, 1H), 7.46 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 37 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 38.6 (NCH_2), 75.6 (d, $^1J_{PC}$ = 124.2 Hz, C(2), C(6)), 97.7 (d, $^3J_{PC}$ = 21.3 Hz, C(4)), 138.9 (d, $^2J_{PC}$ = 3.8 Hz, C(3), C(5)); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 49.26. **MS-EI,** *m/z* (%): 240(M^+, 41), 169(37), 168(100), 98(23), 97(27), 72(53), 58(32), 56(18), 44(23), 42(22); **Anal. Calcd for $C_{13}H_{25}N_2P$:** C, 64.97; H, 10.49; N, 11.66; P, 12.89. Found C, 64.96; H, 10.48; N, 11.64; P, 12.91.



***N*[1],*N*[1],*N*[1],*N*[1]-tetramethyl-1λ[5]-phosphinine-1,1-diamine (16c) :**

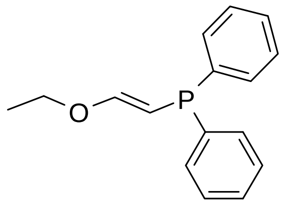
Yield: 44.5%; **bp** 75-80°C (0.05 torr); **^{1}H NMR** (300 MHz, C_6D_6): δ 2.21 (d, $^3J_{PH}$ = 11.7 Hz, 12H), 4.48 (dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{PH}$ = 6.6 Hz, 2H), 5.70 (dtt, $^4J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.6 Hz 1H), 7.45 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 36.6 Hz, 2H);

^{13}C NMR (125 MHz, C_6D_6): δ 35.9 (d, $^2J_{PC}$ = 2.5 Hz, NCH_3), 71.1 (d, $^1J_{PC}$ = 125 Hz, C(2), C(6)), 99.1 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 140.2 (d, $^2J_{PC}$ = 4 Hz, C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ 51.9. **MS-EI,** *m/z* (%): 184(M^+,5), 140(12), 57(3), 45(46), 44(100), 43(8), 41(6), 36(5), 30(3); **Anal. Calcd for $C_9H_{17}N_2P$:** C, 58.68; H, 9.30; N, 15.21; P, 16.18. Found C, 58.67; H, 9.32; N, 15.27; P, 16.22.



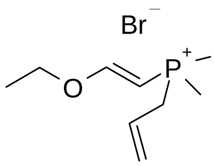
(2-ethoxyvinyl)(dimethyl)phosphine (17a):

Yield: 88 %; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.96 (t, $^3J_{HH}$ = 6.9 Hz) 0.98 (d, $^2J_{PH}$ = 3 Hz, 6H), 3.37 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 4.84 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 3.9 Hz, 1H), 6.82 (dd, $^3J_{HH}$ = 13,5 Hz, $^3J_{PH}$ = 9.9 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.3 (CH_3), 16.1(d, $^1J_{PC}$ = 10 Hz, PCH_3), 64.4 (O-CH_2), 103.6 (d, $^1J_{PC}$ = 10 Hz, CH-P), 155.7 (d, $^2J_{PC}$ = 60.4 Hz, EtO-CH=CH); **^{31}P NMR** (81 MHz, C_6D_6) -57.2. **MS-EI for P=O,** *m/z* (%): 148(M^+, 11), 128(25), 87(89), 86(62), 85(37), 83(51), 72(14), 58(25), 57(100), 56(43). **Anal. Calcd for $C_6H_{13}OP$:** C, 54.54; H 9.92; P, 23.44. Found C, 54.59; H, 9.94; P, 23.38.



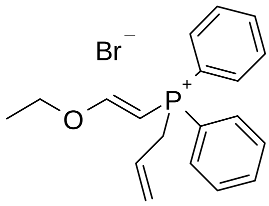
(2-ethoxyvinyl)(diphenyl)phosphine (17b):

Yield: 74.2 %; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.91 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 3.31 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.35 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 4.2 Hz, 1H), 6.92 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 9.9 Hz, 1H), 7.00-7.15 (m, 6H), 7.48-7.53 (m,4H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.3 (CH_3), 64.9 (O-CH_2), 98.3 (d, $^1J_{PC}$ = 3.8 Hz, CH-P), 128.1 (PPh_2), 128.4 (d, $^3J_{PC}$ = 6.3 Hz, PPh_2), 132.5 (d, $^2J_{PC}$ = 18.9 Hz, PPh_2), 141.1 (d, $^1J_{PC}$ = 7.6 Hz, PPh_2),155.7 (d, $^2J_{PC}$ = 69.1 Hz, EtO-CH=CH); **^{31}P NMR** (81 MHz, C_6D_6) δ -19.5; **MS-EI,** *m/z* (%): 256(M^+,100), 241(49), 201(58), 186(25), 183(25), 153(28), 141(31), 108(60), 77(56), 47(24); **Anal. Calcd for $C_{16}H_{17}OP$:** C, 74.99; H 6.69; P, 12.09. Found C, 75.05; H, 6.71; P, 11.99.



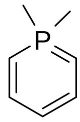
allyl(2-ethoxyvinyl)dimorpholin-4-ylphosphonium bromide (18a):

Yield: 85.5 %; amorphus solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.28 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 2.14 (d, $^2J_{PH}$ = 14.1 Hz, 6H), 3.48 (dd, $^3J_{HH}$ = 7.5 Hz, $^2J_{PH}$ = 16.8 Hz, 2H), 4.07 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.19 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 12.3 Hz, 1H), 5.36-5.47 (m, 2H), 5.52-5.69 (m, 1H), 7.47 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 11.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 9.0 ($^1J_{PC}$ = 57.8 Hz, PCH_3), 14.3 (CH_3), 30.2 (d, $^1J_{PC}$ = 55.3 Hz, P-CH_2), 68.1 (O-CH_2), 80.8 (d, $^1J_{PC}$ = 96.8 Hz, CH-P), 124.2 (d, $^3J_{PC}$ = 12.6 Hz, $\underline{CH_2}$=CH), 124.3 (d, $^2J_{PC}$ = 10 Hz, CH_2=$\underline{CH}$), 164.8 (d, $^2J_{PC}$ = 16.3 Hz, EtO-$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 20.5; **APCI MS**: $[M – Br]^+$ = 173; **Anal. Calcd for $C_9H_{18}OPBr$:** C, 42.71; H, 7.17; Br, 31.57; P, 12.24. Found C, 42.69; H, 7.15; Br, 31.52; P, 12.18.



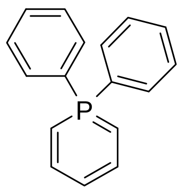
allyl(2-ethoxyvinyl)diphenylphosphonium bromide (18b):

Yield: 79.1 %; amorphus solid (hexane); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.32 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 4.26 (dd, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 15.9 Hz, 2H), 4.36 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.34-5.39 (m, 1H), 5.48-5.53 (m, 1H), 5.62-5.68 (m, 1H), 5.91 (dd, $^3J_{HH}$ = 12 Hz, $^2J_{PH}$ = 13.5 Hz, 1H), 7.15 (dd, $^3J_{HH}$ = 12 Hz, $^3J_{PH}$ = 12.6 Hz, 1H), 7.65-7.88 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 30.0 (d, $^1J_{PC}$ = 54.1 Hz, P-CH_2), 69.3 (O-CH_2), 78.8 (d, $^1J_{PC}$ = 103 Hz, CH-P), 119.4 (d, $^1J_{PC}$ = 89.3 Hz, PPh_2), 123.8 (d, $^2J_{PC}$ = 10 Hz, CH_2=$\underline{CH}$), 125.2 (d, $^3J_{PC}$ = 13.8 Hz, $\underline{CH_2}$=CH), 130.1 (d, $^3J_{PC}$ = 11.3 Hz, PPh_2), 133.3 (d, $^2J_{PC}$ = 10 Hz, PPh_2), 134.6 (d, $^4J_{PC}$ = 2.5 Hz, PPh_2), 167.8 (d, $^2J_{PC}$ = 17.6 Hz, EtO-$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 18.1; **MS-FAB,** *m/z* (%): 298($[M-Br]^+$,42); **Anal. Calcd for $C_{19}H_{22}OPBr$:** C, 60.49; H, 5.88; Br, 21.18; P, 8.21. Found C, 60.52; H, 5.86; Br, 21.02; P, 8.25.



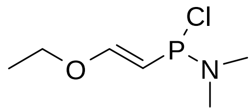
1,1-dimethyl-1λ^5-phosphinine (19a):

Yield: 44.5%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.91 (d, $^2J_{PH}$ =12.6 Hz, 6H), 3.9 (dd, $^3J_{HH}$ = 11.1 Hz, $^2J_{PH}$ = 17.4 Hz, 2H), 5.24 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.14 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{PH}$ = 33.9 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 24.6 (d, $^2J_{PC}$ = 56.6 Hz, PCH_3), 66.4 (d, $^1J_{PC}$ = 96.8 Hz, C(2), C(6)), 96.2 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 140.3 (C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ –3.8. **Anal. Calcd for $C_7H_{11}P$:** C, 66.65; H, 8.79; P, 24.56. Found C, 66.69; H, 8.82; P, 24.51.



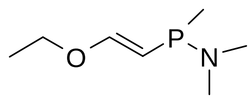
1,1-diphenyl-1λ^5-phosphinine (19b):

Yield: 61.2%; oil; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.36 (dd, $^3J_{HH}$ = 10.8 Hz, $^2J_{PH}$ = 14.4 Hz, 2H), 5.05 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.11 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 10.8 Hz, $^3J_{PH}$ = 34.5 Hz, 2H), 7.43-7.50 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 65.9 (d, $^1J_{PC}$ = 99.4 Hz, C(2), C(6)), 96.0 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 128.6 (d, $^3J_{PC}$ = 11.3 Hz, PPh_2), 130.3 (d, $^4J_{PC}$ = 2.5 Hz, PPh_2), 131.0 (d, $^2J_{PC}$ = 11.3 Hz, PPh_2),136.6 (d, $^1J_{PC}$ = 88.0 Hz, PPh_2), 139.4 (C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ 4.1. **MS-EI,** *m/z* (%): 250(M^+,100), 216(35), 215(81), 202(52), 201(73), 183(35), 173(91), 77(86), 51(55), 47(44); **Anal. Calcd for $C_{17}H_{15}P$:** C, 81.58; H, 6.04; P, 12.38. Found C, 81.56; H, 6.05; P, 12.39.



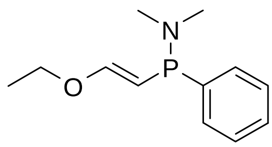
***P*-(2-ethoxyvinyl)-*N*,*N*-dimethylphosphonamidous chloride (20):**

To a stirred phosphonous diamide **13c** (13.2 g, 69.4 mmol) (2-ethoxyvinyl)phosphonous dichloride **12** (12 g, 69.4 mmol) was added at 0ºC. The reaction mixture was allowed warming to r.t. **Yield:** 100 %; oil; **bp** 102-105°C (7 torr); **^{1}H NMR** (300 MHz, C_6D_6): δ 0.85 (t, $^{3}J_{HH}$ = 6.9 Hz, 3H), 2.45 (d, $^{3}J_{PH}$ = 13.8 Hz, 6H), 3.19 (q, $^{3}J_{HH}$ = 6.9 Hz, 2H), 5.48 (dd, $^{3}J_{HH}$ = 13.8 Hz, $^{2}J_{PH}$ = 4.2 Hz, 1H), 6.77 (dd, $^{3}J_{HH}$ = 13.8 Hz, $^{3}J_{PH}$ = 9.6 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.1 (CH_3), 39.2 (d, $^{2}J_{PC}$ = 10.0 Hz, N-CH_3), 65.3(O-CH_2), 103.8(d, $^{1}J_{PC}$ =23.9 Hz, CH-P), 158.1 (d, $^{2}J_{PC}$ = 70.4 Hz, EtO-<u>CH</u>=CH); **^{31}P NMR** (81 MHz, C_6D_6) 142.5; **MS-EI,** *m/z* (%): 181(M^+,45), 146(100), 137(12), 118(20), 109(32), 92(22), 83(18), 75(12), 60(10), 44(69), 32(81).



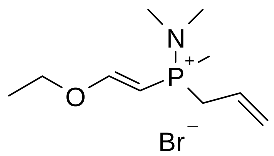
***P*-(2-ethoxyvinyl)-*N*,*N*,*P*-trimethylphosphinous amide (21a):**

Yield: 91.3 %; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.97 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 1.16 (d, $^3J_{HH}$ = 5.4 Hz, 3H,) 2.45 (d, $^3J_{PH}$ = 10.5 Hz, 6H) 3.38 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.14 (dd, $^3J_{HH}$ = 13.8 Hz, 1H), 6.81 (dd, $^3J_{HH}$ = 13,8 Hz, $^3J_{PH}$ = 8.7 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.0 (d, $^1J_{PC}$ =10.0 Hz, PCH_3), 14.3 (CH_3), 39.6 (d, $^2J_{PC}$ = 12.6 Hz, N-CH_3), 64.5(O-CH_2), 100.7 (d, $^1J_{PC}$ =20.1 Hz, CH-P), 156.9 (d, $^2J_{PC}$ = 60.4 Hz, EtO-<u>CH</u>=CH); **^{31}P NMR** (81 MHz, C_6D_6) 38.9; **APCI MS**: M^++1 = 161; **Anal. Calcd for $C_7H_{16}NOP^+$:** C, 52.16; H 10.01; N, 8.69; P, 19.22. Found C, 52.13; H, 9.98; N, 8.63; P, 19.15.



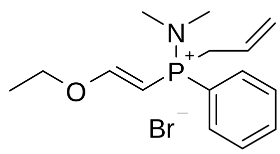
***P*-(2-ethoxyvinyl)-*N*,*N*-dimethyl-*P*-phenylphosphinous amide (21b):**

Yield: 77 %; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.97 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.53 (d, $^3J_{PH}$ = 10.2 Hz, 6H), 3.40 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.36 (dd, $^3J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 3.6 Hz, 1H), 6.95 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 9.6 Hz, 1H), 7.11 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.24 (t, $^3J_{HH}$ = 7.5 Hz, 2H),7.57 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 7.5 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.3 (CH_3), 40.8 (d, $^2J_{PC}$ = 12.6 Hz, N-CH_3), 64.9 (O-CH_2), 98.2 (d, $^1J_{PC}$ = 17.6 Hz, CH-P), 127.3 (PPh_2), 128.1 (d, $^3J_{PC}$ = 3.8 Hz, PPh_2), 130.1 (d, $^2J_{PC}$ = 13.8 Hz, PPh_2), 143.1 (d, $^1J_{PC}$ = 2.5 Hz, PPh_2), 160.0 (d, $^2J_{PC}$ = 71.7 Hz, EtO-<u>CH</u>=CH); **^{31}P NMR** (81 MHz, C_6D_6) δ 54.5. **Anal. Calcd for $C_{12}H_{18}NOP$:** C, 64.56; H 8.13; N, 6.27; P, 13.87. Found C, 64.59; H, 8.15 ; N, 6.24; P, 13.90.



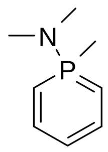
allyl(dimethylamino)(2-ethoxyvinyl)(methyl)phosphonium bromide (22a):

Yield: 100 %; amorphus solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.30 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.20 (d, $^3J_{PH}$ = 13.2 Hz, 3H), 2.76 (d, $^3J_{PH}$ = 10.8 Hz, 6H), 3.33-3.65 (m, 2H), 4.18 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.09 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 12.3 Hz, 1H), 5.35-5.48 (m, 2H), 5.62-5.69 (m, 1H), 7.62 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 11.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 9.55 ($^1J_{PC}$ = 69.1 Hz, PCH_3), 14.5 (CH_3), 30.9 (d, $^1J_{PC}$ = 64.1 Hz, P-CH_2), 37.4 (N-CH_3), 68.9 (O-CH_2), 81.3 (d, $^1J_{PC}$ = 112 Hz, CH-P), 124.1 (d, $^3J_{PC}$ = 12.6 Hz, $\underline{CH_2}$=CH), 124.4 (d, $^2J_{PC}$ = 10 Hz, CH_2=$\underline{CH}$), 166.8 (d, $^2J_{PC}$ = 18.9 Hz, EtO-$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 52.9; **Anal. Calcd for $C_{10}H_{21}NOPBr$:** C, 42.57; H, 7.50; N, 4.96; Br, 28.32; P, 10.98. Found C, 42.59; H, 7.53; N, 4.95; Br, 28.41; P, 11.03.



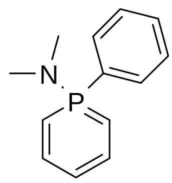
allyl(dimethylamino)(2-ethoxyvinyl)(phenyl)phosphonium bromide (22b):

Yield: 100 %; amorphus solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.38 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.89 (d, $^3J_{PH}$ = 11.1 Hz, 6H), 4.00 (dd, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 16.5 Hz, 2H), 4.35 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.34-5.39 (m, 1H), 5.49-5.53 (m, 2H), 5.62-5.69 (m, 1H), 7.58 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 10.8 Hz, 1H), 7.54-7.89 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.5 (CH_3), 30.9 (d, $^1J_{PC}$ = 66.6 Hz, P-CH_2), 38.4 (N-CH_3), 69.5 (O-CH_2), 79.9 (d, $^1J_{PC}$ = 112 Hz, CH-P), 120.9 (d, $^1J_{PC}$ = 104 Hz, PPh_2), 124.1 (d, $^2J_{PC}$ = 8.8 Hz, CH_2=$\underline{CH}$), 124.5 (d, $^3J_{PC}$ = 15.1 Hz, $\underline{CH_2}$=CH), 130.1(d, $^3J_{PC}$ = 12.6 Hz, PPh_2), 132.5 (d, $^2J_{PC}$ = 11.3 Hz, PPh_2), 134.7 (d, $^4J_{PC}$ = 2.5 Hz, PPh_2), 168.2 (d, $^2J_{PC}$ = 18.9 Hz, EtO-$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 48.4; **MS-FAB,** *m/z* (%): 265($[M-Br]^+$,10); **Anal. Calcd for $C_{15}H_{23}NOPBr$:** C, 52.34; H, 6.73; Br, 23.21; N, 4.07; P, 9.00. Found C, 52.32; H, 6.77; Br, 23.10; N, 4.05; P, 9.08.



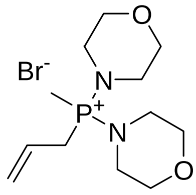
***N*,*N*,1-trimethyl-1λ^5-phosphinin-1-amine (23a):**

Yield: 53.0%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 1.26 (d, $^2J_{PH}$ = 14.4 Hz, 3H), 2.0 (d, $^3J_{PH}$ = 11.4 Hz, 6H), 4.41 (dd, $^3J_{HH}$ = 11.1 Hz, $^2J_{PH}$ = 12 Hz, 2H), 5.64 (dtt, $^4J_{PH}$ = 3 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.39 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{PH}$ = 34.2 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 17.6 (d, $^1J_{PC}$ = 91.8 Hz, PCH_3), 35.6 (NCH_3), 72.4 (d, $^1J_{PC}$ = 108 Hz, C(2), C(6)), 98.6 (d, $^3J_{PC}$ = 22.6 Hz, C(4)), 139.6 (C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ 24.4. **MS-EI,** *m/z* (%): 155(M^+,1), 59(1), 45(75), 44(100), 43(20), 42(20), 41(3), 38(1), 32(12), 30(3); **Anal. Calcd for $C_8H_{14}NP$:** C, 61.92; H, 9.09; N, 9.03; P, 19.96. Found C, 61.90; H, 9.13; N, 9.00; P, 20.03.



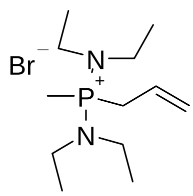
***N*,*N*-dimethyl-1-phenyl-1λ^5-phosphinin-1-amine (23b):**

Yield: 76.0%; oil; **^{1}H NMR** (500 MHz, C_6D_6): δ 2.1 (d, $^3J_{PH}$ = 12.5 Hz, 6H), 4.61 (dd, $^3J_{HH}$ = 11 Hz, $^2J_{PH}$ = 10.5 Hz, 2H), 5.70 (dt, $^4J_{PH}$ = 2.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H), 6.99-7.09 (m, 3H), 7.44 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 11 Hz, $^3J_{PH}$ = 34.5 Hz, 2H), 7.49-7.52(m, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 35.1 (d, $^2J_{PC}$ = 3.8 Hz, NCH_3), 70.7 (d, $^1J_{PC}$ = 110.7 Hz, C(2), C(6)), 99.3 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 128.5 (d, $^3J_{PC}$ = 13.8 Hz, PPh_2), 129.8 (d, $^4J_{PC}$ = 2.5 Hz, PPh_2), 131.3 (d, $^2J_{PC}$ = 10.0 Hz, PPh_2),139.8 (C(3), C(5)), PPh_2 (i) signal are not observed; **^{31}P NMR** (81 MHz, C_6D_6) δ 30.4. **MS-EI,** *m/z* (%): 217(M^+,32), 174(12), 173(100), 171(18), 128(12), 95(17), 83(9), 77(9), 57(11), 44(11). **Anal. Calcd for $C_{13}H_{16}NP$:** C, 71.87; H, 7.42; N, 6.45; P, 14.26. Found C, 71.81; H, 7.43; N, 6.47; P, 14.19.



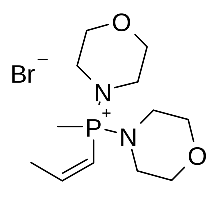
allyl(methyl)dimorpholin-4-ylphosphonium bromide (25a).

Yield: 58.6%; **mp** 180-185°C (2-propanol); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.37 (d, $^2J_{PH}$ = 13 Hz, 3H), 3.26 (br m, 8H), 3.70 (br m, 8H), 3.90 (dd, $^3J_{HH}$ = 6.6 Hz, $^2J_{PH}$ = 17 Hz, 2H), 5.39-5.47 (m, 1H), 5.60-5.71 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 8.9 (d, $^1J_{PC}$ = 80.5 Hz, CH_3-P), 29.3 (d, $^1J_{PC}$ = 76.7 Hz, CH_2-P), 45.1 (NCH_2), 66.7 (d, $^3J_{PC}$ = 5.0 Hz, OCH_2), 123.8 (d, $^2J_{PC}$ = 8.8 Hz, $CH_2{=}\underline{C}H$), 125.2 (d, $^3J_{PC}$ = 13.8 Hz, $\underline{C}H_2{=}CH$); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 60.37. **MS-FAB,** *m/z* (%)**:** 259 ($[M-Br]^+$, 100). **Anal. Calcd for $C_{12}H_{24}BrN_2O_2P$:** C, 42.49; H, 7.13; N, 8.26; P, 9.13. Found C, 42.54; H, 7.12; N, 8.25; P, 9.10.



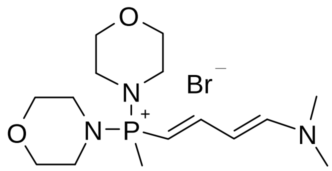
allyl(bis(diethylamino))methylphosphonium bromide (25b):

Yield: 75%; amorphous solid (hexane); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.21 (t, *J* = 6.9 Hz, 12H), 2.26 (d, *J* = 13.2 Hz, 3H), 3.11 - 3.29 (m, 8H), 3.65 (dd, $^3J_{HH}$ = 6 Hz, $^2J_{PH}$ = 16.8 Hz, 2H), 5.44 - 5.49 (m, 1H), 5.69 - 5.75 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 10.0(d, $^1J_{PC}$ = 84.3 Hz, CH_3-P), 14.0 ($NCH_2\underline{C}H_3$), 30.0 (d, $^1J_{PC}$ =77.9 Hz, CH_2-P), 40.0($N\underline{C}H_2CH_3$), 124.3 (d, $^2J_{PC}$ = 7.5 Hz, $CH_2{=}\underline{C}H$), 124.6 (d, $^3J_{PC}$ = 13.8 Hz, $\underline{C}H_2{=}CH$); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 62.1. **MS-FAB,** *m/z* (%)**:** 231 ($[M-Br]^+$, 100). **Anal. Calcd for $C_{12}H_{28}BrN_2P$:** C, 46.31; H, 9.07; N, 9.00; P, 9.95. Found C, 46.33; H, 9.04; N, 8.99; P, 10.00.



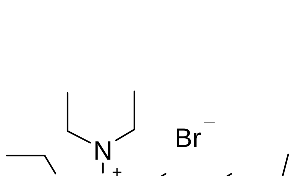
methyl(dimorpholin-4-yl)prop-1-enylphosphonium bromide (26a):

To a solution of **20a** (0,88 g, 2,6 mmol) in pyridine (20 mL) 3 drops of Et_3N was added and the reaction mixture was refluxed for 4 h. The reaction mixture was evaporated, the residue was washed with ether. **Yield: 63.6%;** amorphous solid (diethyl ether); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.05 (d, $^4J_{PH}$ = 6 Hz, 3H), 2.40 (d, $^2J_{PH}$ = 13.5 Hz, 3H), 3.19 (br m, 8H), 3.64 (br m, 8H), 6.3 (dd, $^3J_{HH}$ = 18 Hz, $^2J_{PH}$ = 21 Hz, 1H), 6.93 - 7.05 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 10.5 (d, $^1J_{PC}$ = 85.5 Hz , CH_3-P), 21.3 (d, $^3J_{PC}$ = 21.4 Hz, CH_3), 44.9 (NCH_2), 66.6 (d, $^3J_{PC}$ = 5 Hz, OCH_2), 113.0 (d, $^1J_{PC}$ = 120.7 Hz, CH), 156.8 (d, $^2J_{PC}$ = 6.3 Hz, CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 52.6. **MS-FAB,** *m/z* (%)**:** 259 ([M-Br]$^+$, 100). **Anal. Calcd for $C_{12}H_{24}BrN_2O_2P$:** C, 42.49; H, 7.13; N, 8.26; P, 9.13. Found C, 42.50; H, 7.09; N, 8.25; P, 9.14.



(4-(dimethylamino)buta-1,3-dienyl)(methyl)dimorpholin-4-ylphosphonium bromide (27a):

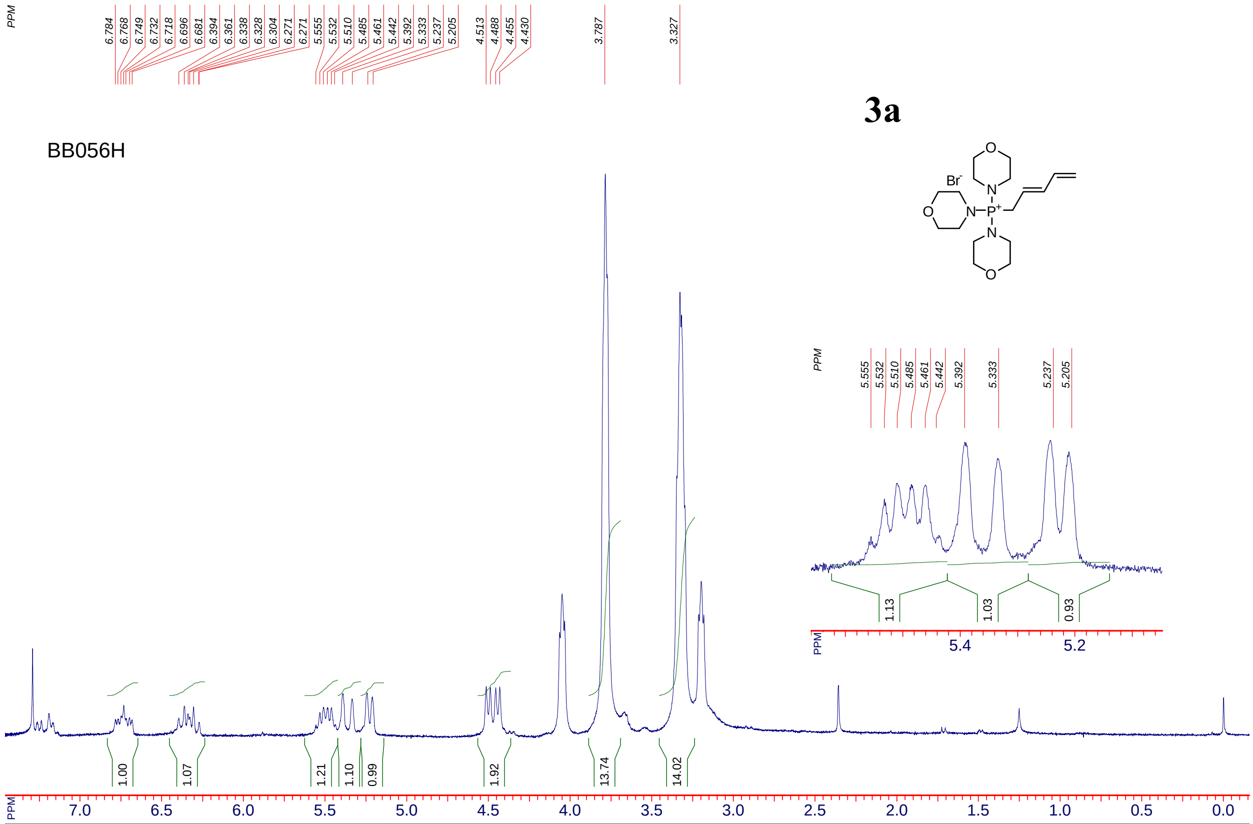
Yield: 70 %; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.33 (d, $^2J_{PH}$ = 12.6 Hz, 3H), 3.0 (br s, 6H), 3.21 (br s, 8H), 3.74 (br s, 8H), 4.75 (dd, $^2J_{PH}$ = 19.2 Hz, $^3J_{HH}$ = 16.5 Hz, 1H), 5.26 (t, $^3J_{HH}$ = 12 Hz, 1H), 7.39 (d, $^3J_{HH}$ = 12 Hz, 1H), 7.46 - 7.61 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 10.6 (d, $^1J_{PC}$ = 86.3 Hz, CH_3-P), 44.8 (NCH_2), 66.7 (d, $^3J_{PC}$ = 5.0 Hz, OCH_2), 83.5 (d, $^1J_{PC}$ = 131.3 Hz, CH-P), 97.6 (d, $^3J_{PC}$ = 26.4 Hz, C(3)), 155.26 (C(4)), 157.2 (d, $^2J_{PC}$ = 12.9 Hz, C(2)), NMe_2 signals are not observed; **^{31}P NMR** (81 MHz, $CDCl_3$) δ 55.2. **MS-FAB,** *m/z* (%)**:** 314 ([M-Br]$^+$, 100). **Anal. Calcd for $C_{15}H_{29}BrN_3O_2P$:** C, 45.69; H, 7.41; N, 10.66; P, 7.86. Found C, 45.67; H, 7.43; N, 10.75; P, 7.89.



bis(diethylamino)(4-(dimethylamino)buta-1,3-dienyl)methylphosphonium bromide (27b):

Yield: 100%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.12-1.21 (m, 12H), 2.10 (d, $^2J_{PH}$ = 12.9 Hz, 3H), 2.96 (br s, 6H), 3.05-3.18 (m, 8H), 4.83 (dd, $^2J_{PH}$ = 20.4 Hz, $^3J_{HH}$ = 16.2 Hz, 1H), 5.20 (t, $^3J_{HH}$ = 9 Hz, 1H), 7.29-7.41 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 12.7 (d, $^1J_{PC}$ = 89.3 Hz, CH_3-P), 14.2 (CH_3), 39.9 (d, $^2J_{PC}$ = 3.8 Hz,

NCH_2), 87.8 (d, $^1J_{PC}$ =137 Hz, CH-P), 97.1 (d, $^3J_{PC}$ = 26.4 Hz, C(3)), 154.6 (C(4)), 155.3 (d, $^2J_{PC}$ = 10.1 Hz, C(2)), NMe_2 signals are not observed; **^{31}P NMR** (81 MHz, $CDCl_3$) δ 55.2. **MS-FAB,** *m/z* (%)**:** 281 ($[M-Br]^+$, 100). **Anal. Calcd for $C_{15}H_{33}BrN_3P$:** C, 49.18; H, 9.08; N, 11.47; P, 8.46. Found C, 49.20; H, 9.11; N, 11.54; P, 8.55.



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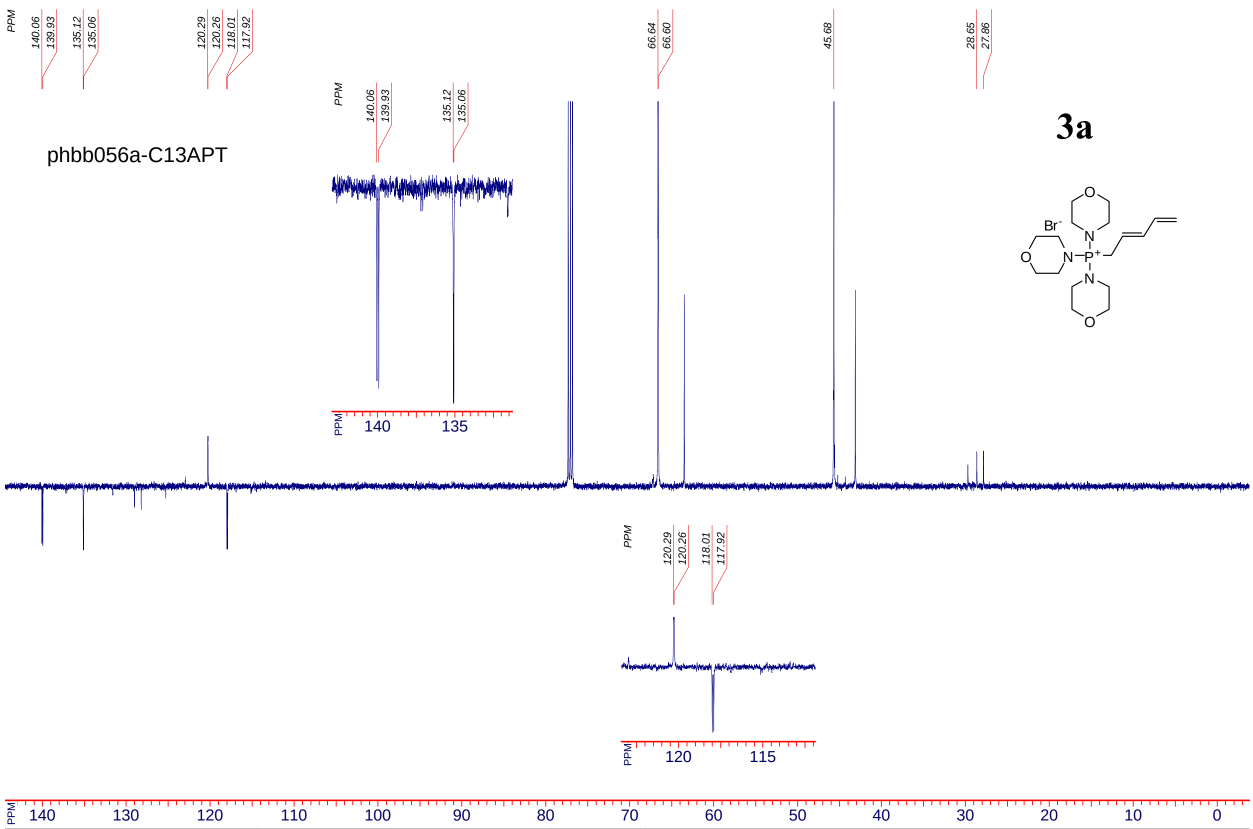
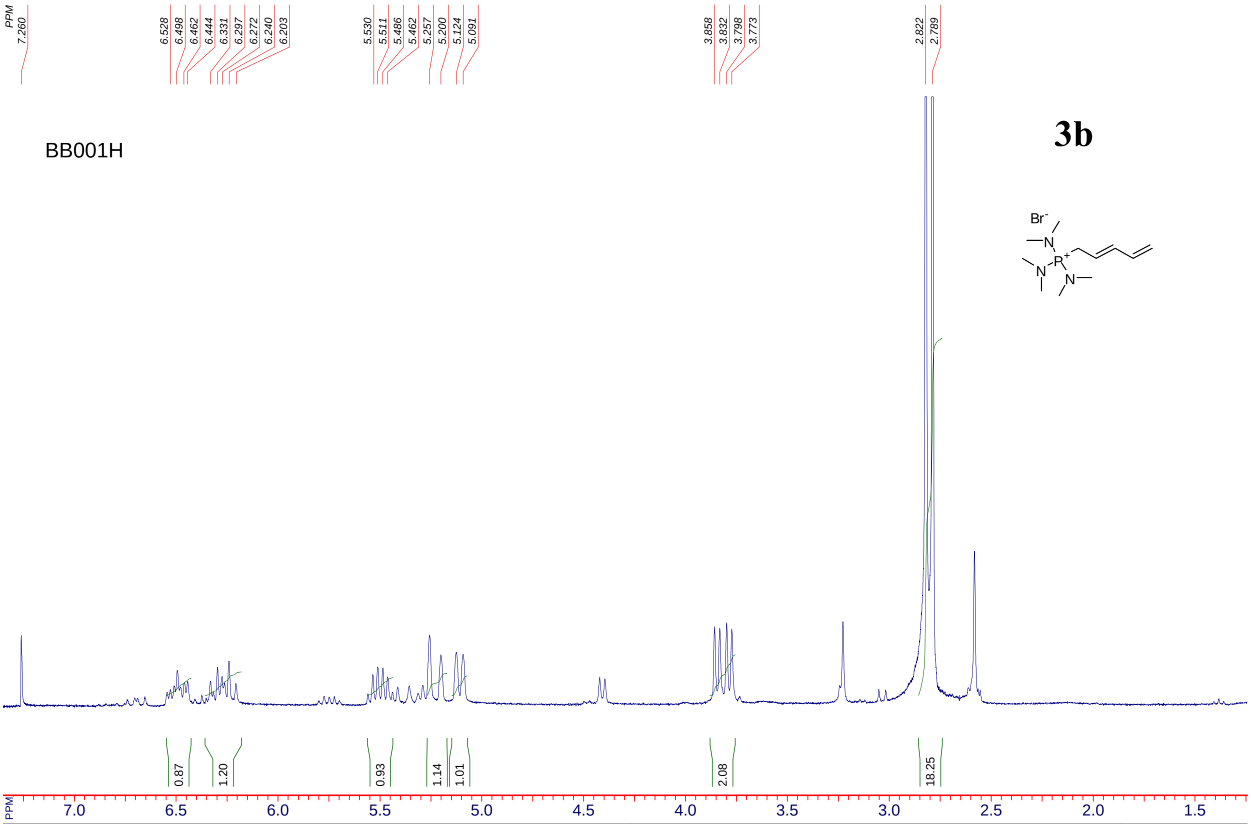
Date: 20-Feb-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.71 sec, RD: 2.00 sec	



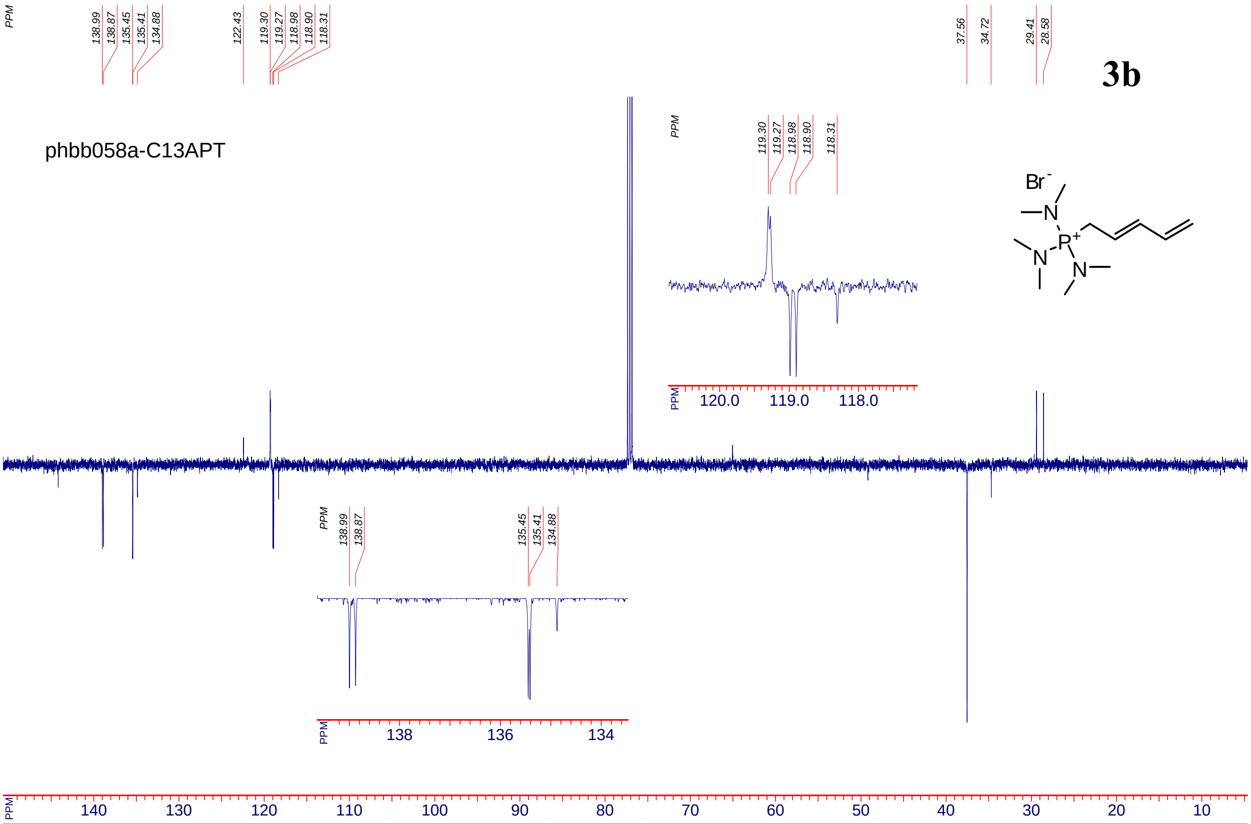
File name: phbb056a-C13APT	Operator: root	SF: 125.7578 MHz	NSC: 5141	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 20-Feb-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

3b



File name: BB001H	Operator:	SF: 299.9430 MHz	NSC: 1	PW: 8.00 usec, RG: 16	SI: 32768
Date: 28-Feb-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.71 sec, RD: 2.00 sec	

3b



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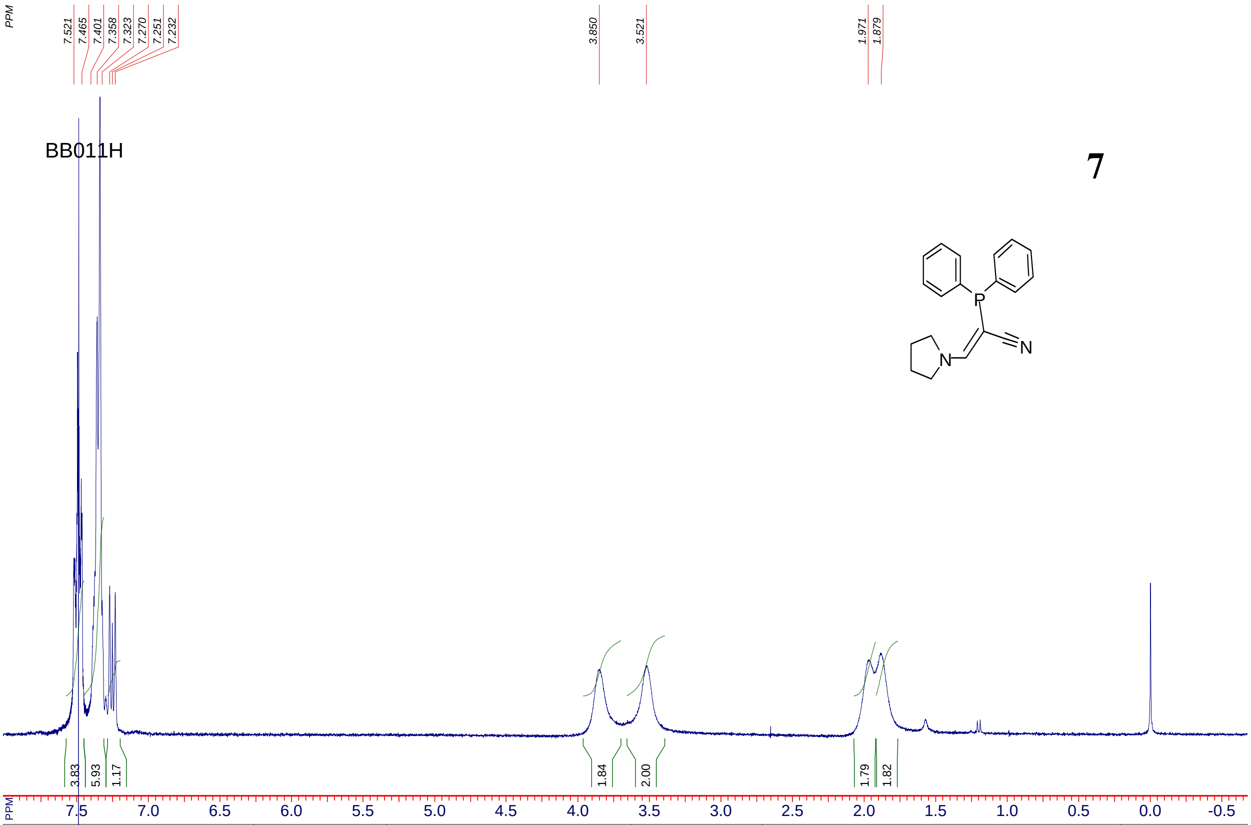

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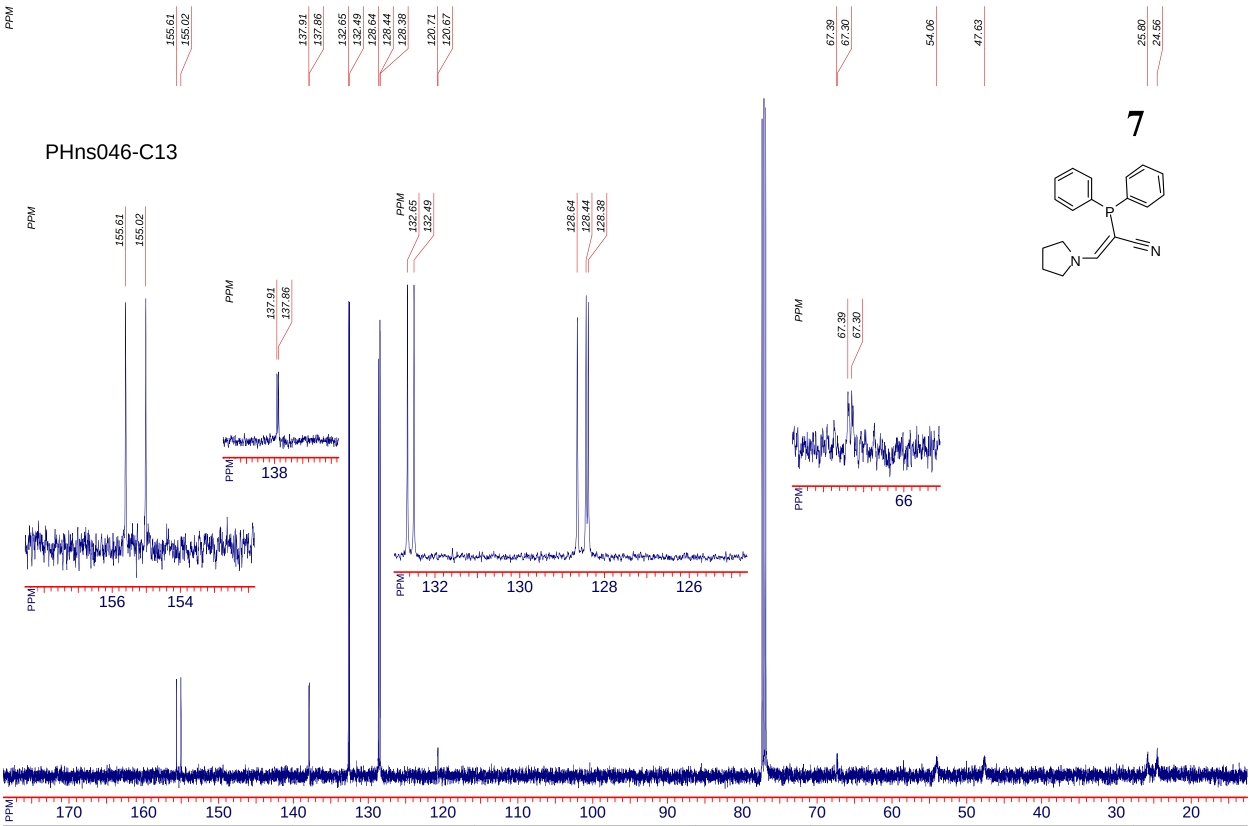

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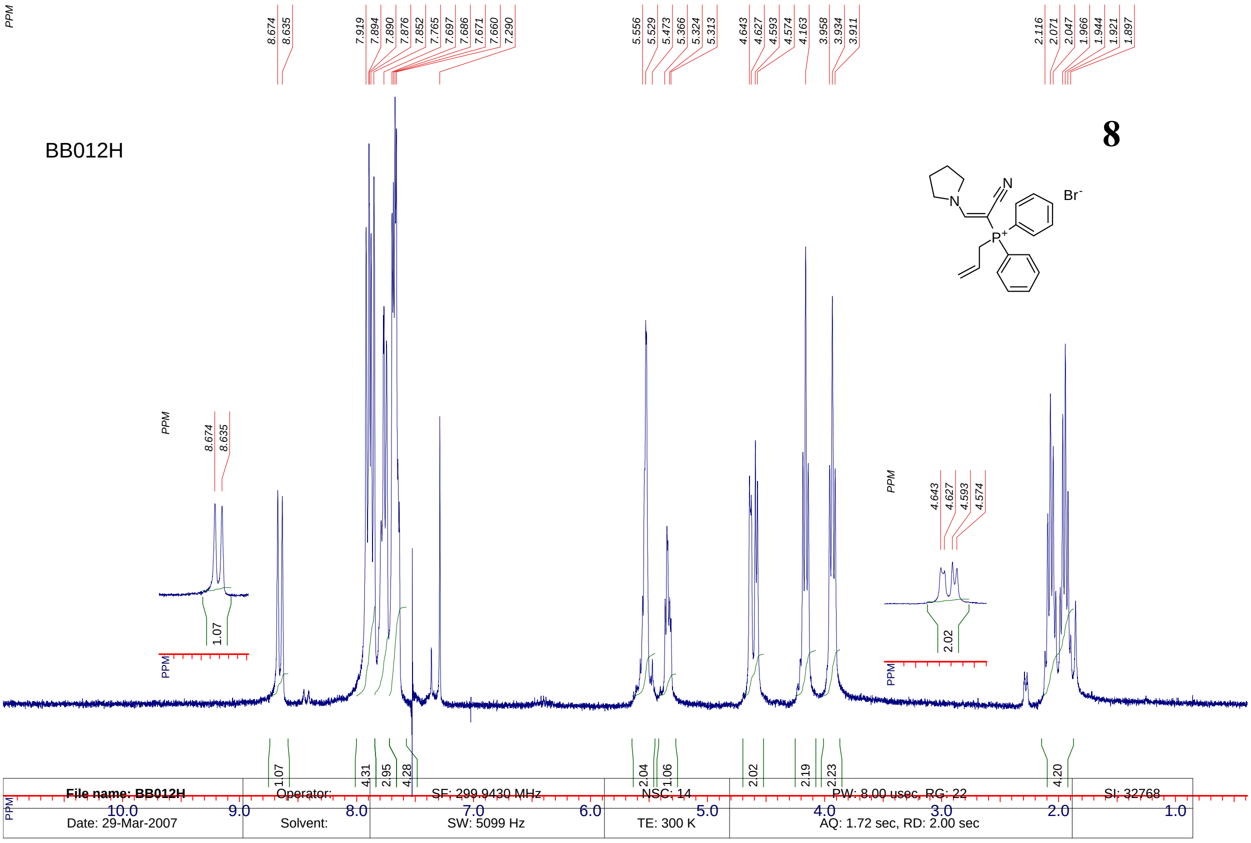

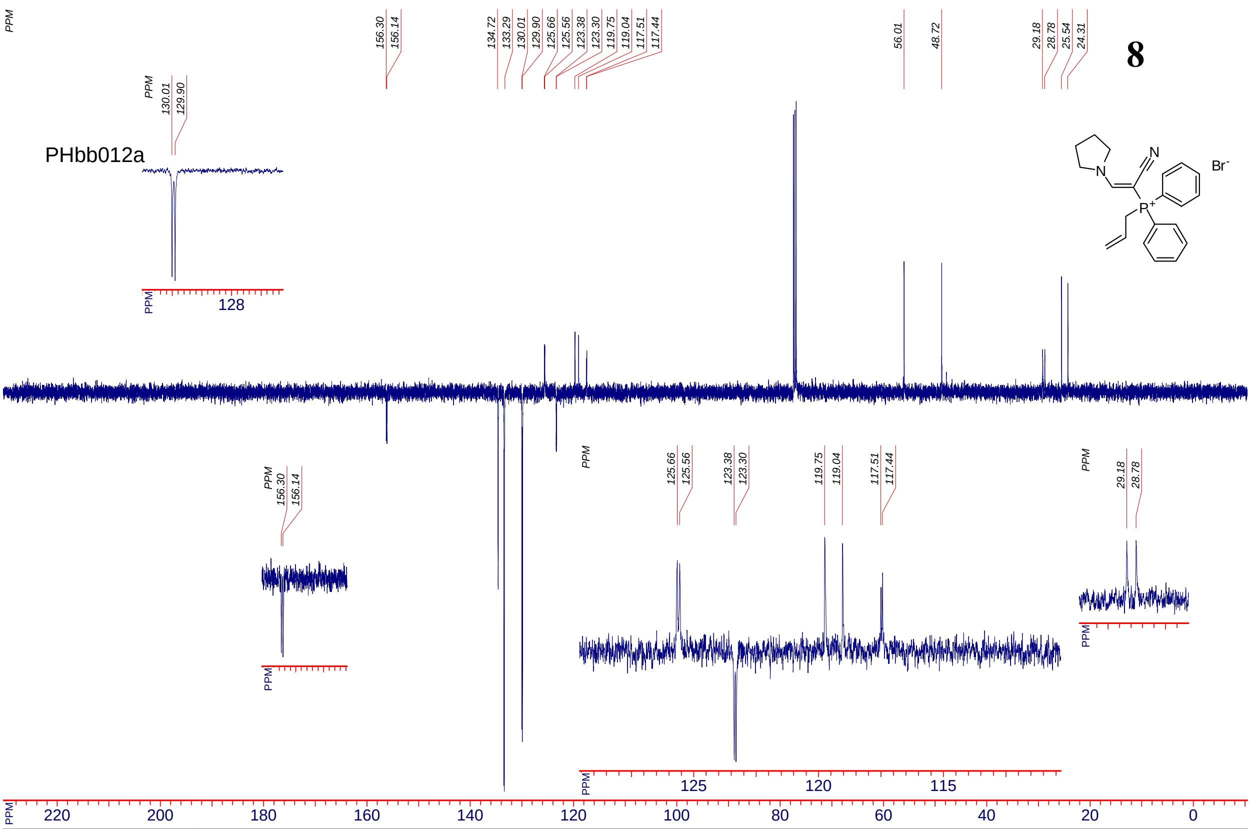

File name: PHbb012a	Operator: root	SF: 125.7578 MHz	NSC: 152	PW: 0.00 usec, RG: 49152	SI: 65536
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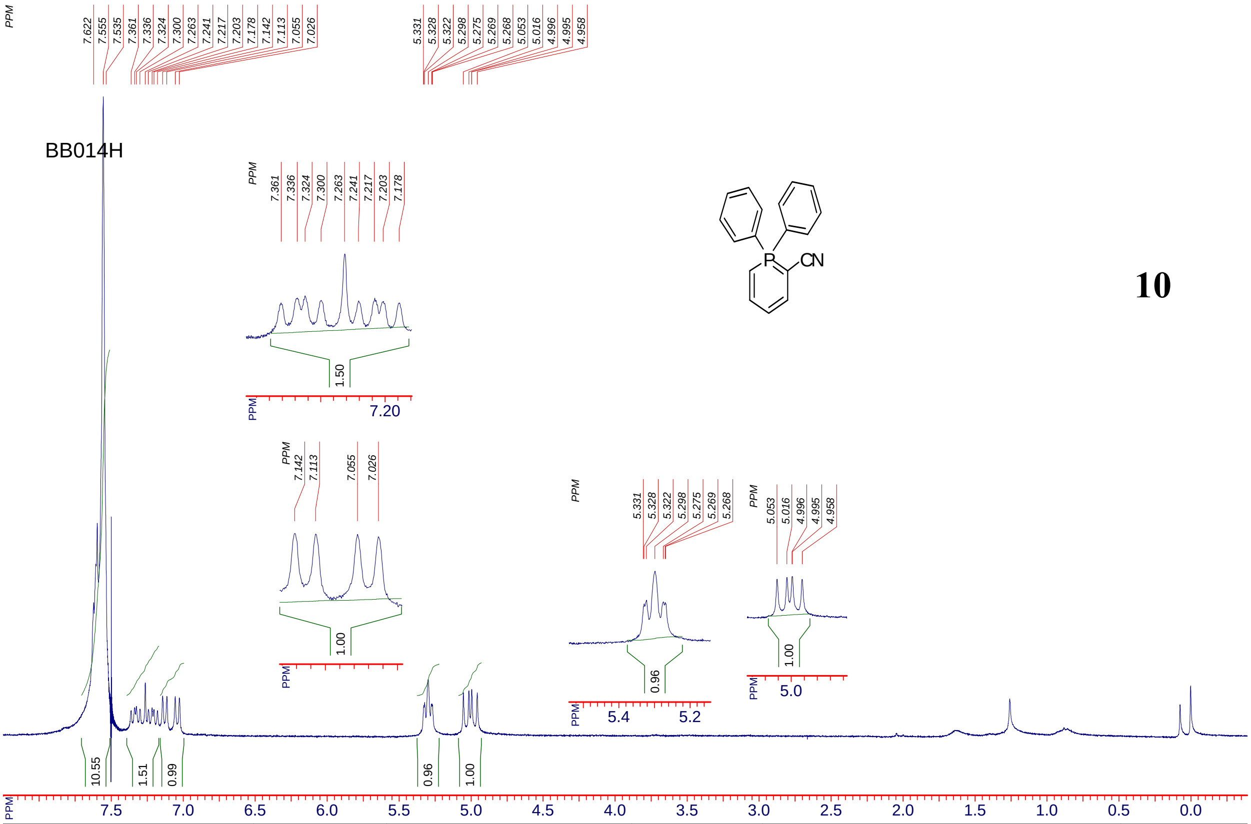
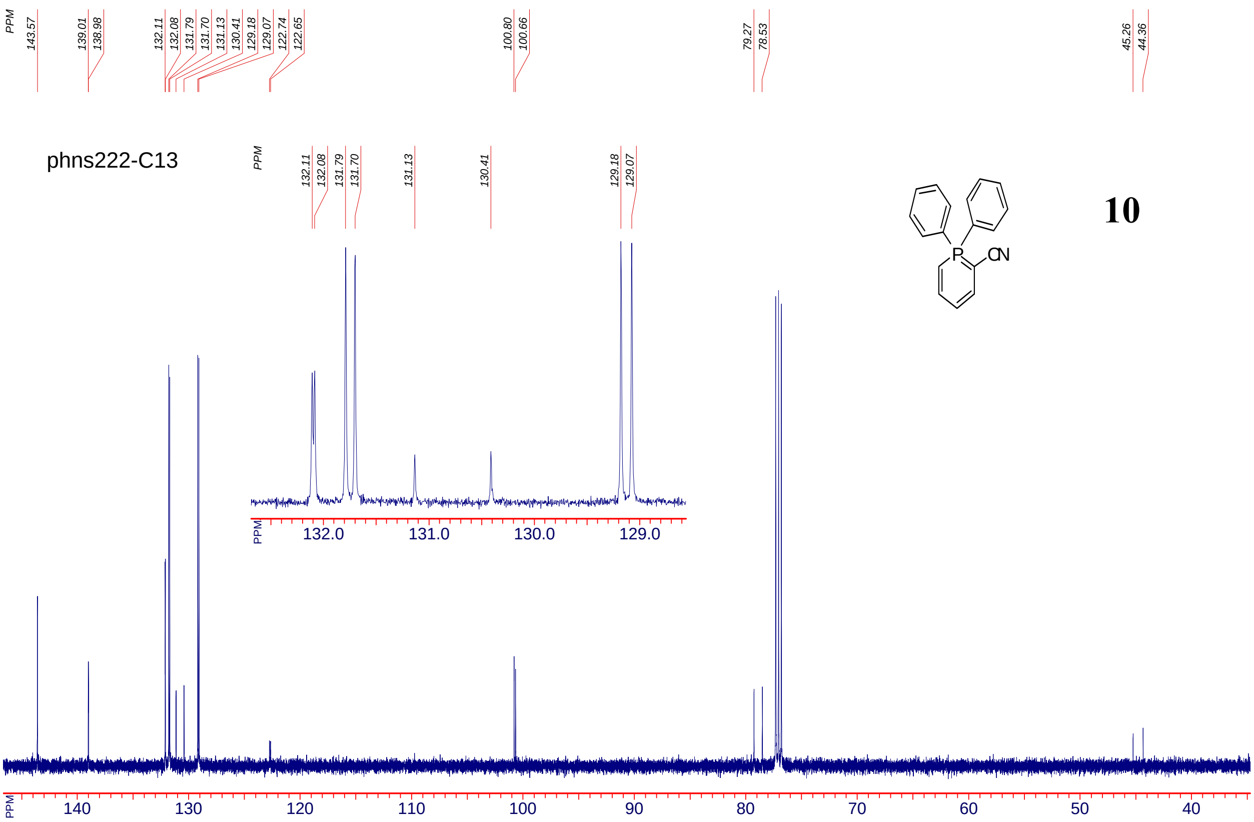


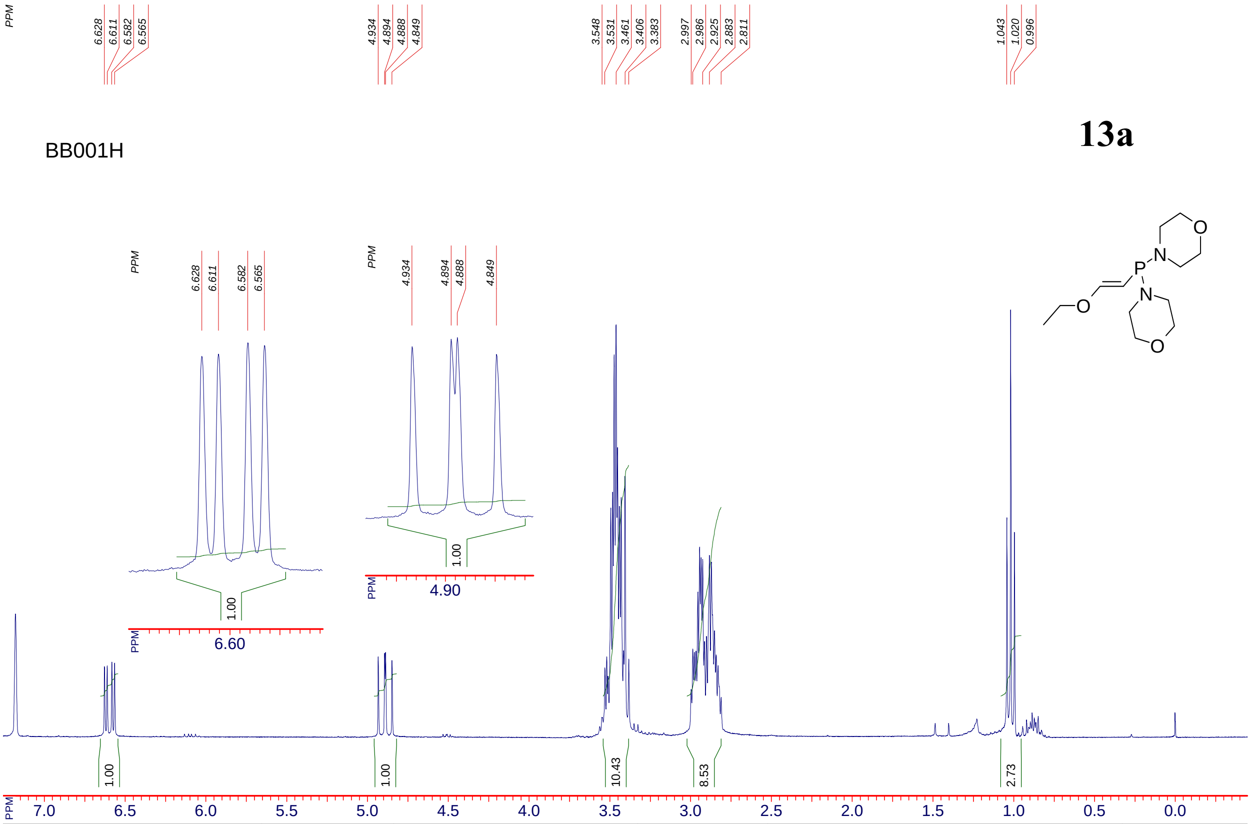
10

File name: BB014H	Operator:	SF: 299.9430 MHz	NSC: 17	PW: 8.00 usec, RG: 18	SI: 32768
Date: 11-Apr-2007	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	

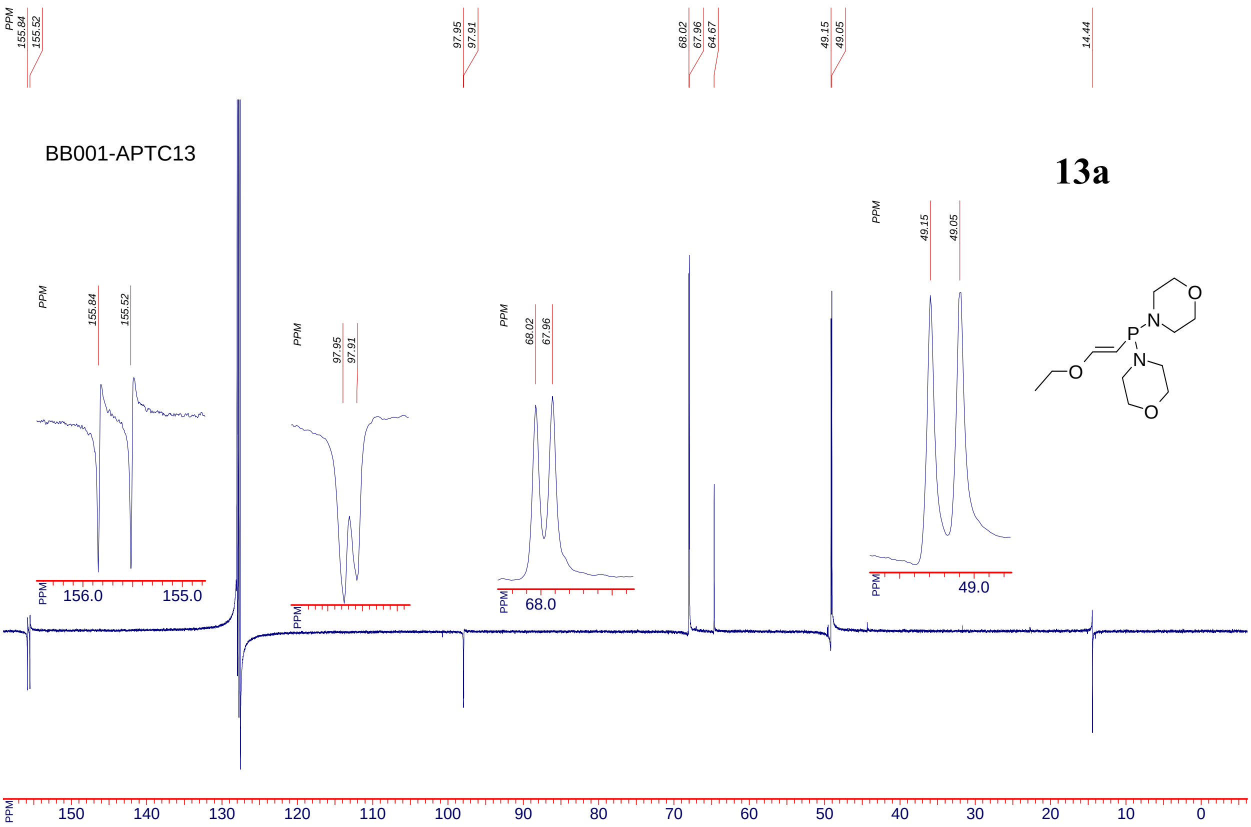


10

File name: phns222-C13	Operator: root	SF: 125.7422 MHz	NSC: 823	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 09-Jul-2010	Solvent: dmso	SW: 32680 Hz	TE: 682 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

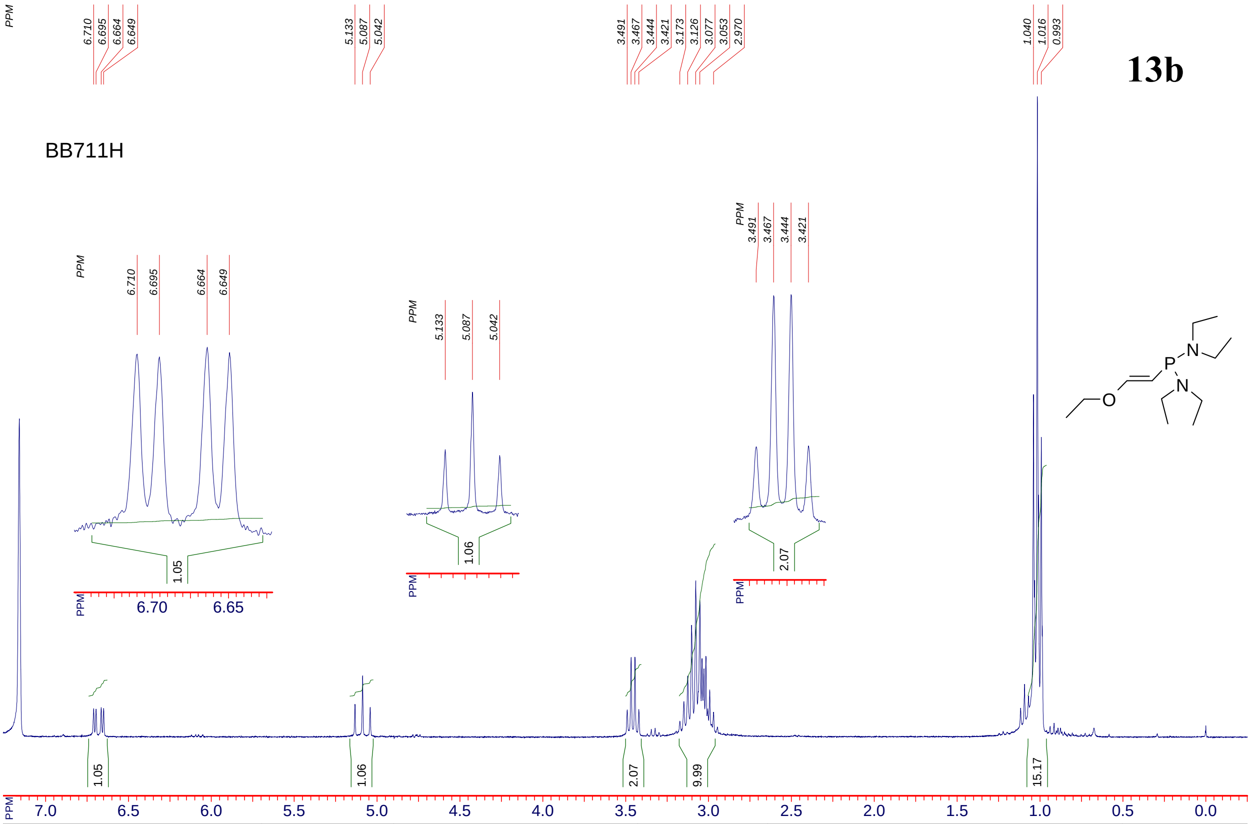


File name: BB001H	Operator:	SF: 299.9430 MHz	NSC: 4	PW: 8.00 usec, RG: 16	SI: 32768
Date: 27-Sep-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	



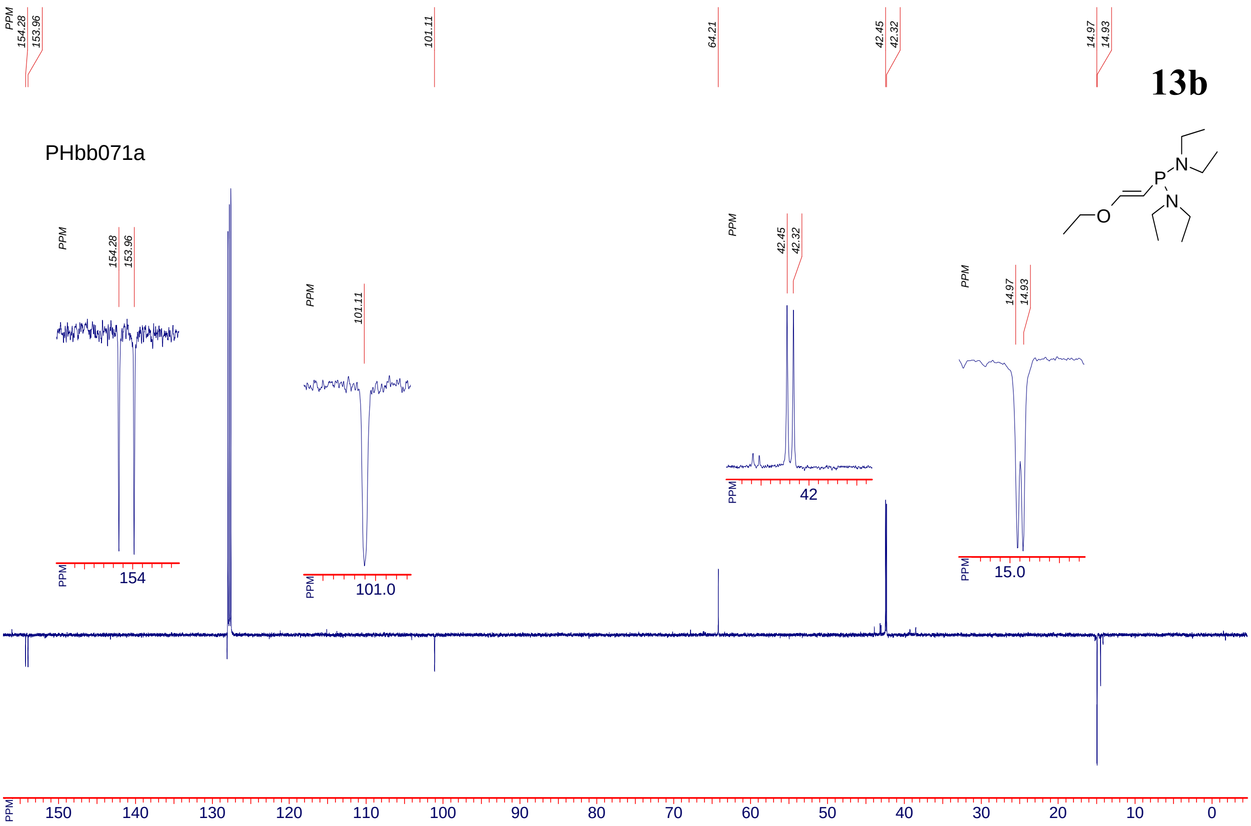
File name: BB001-APTC13	Operator: root	SF: 125.7578 MHz	NSC: 575	PW: 0.00 usec, RG: 32768	SI: 65536
Date: 26-Sep-2008	Solvent: C6D6	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

13b



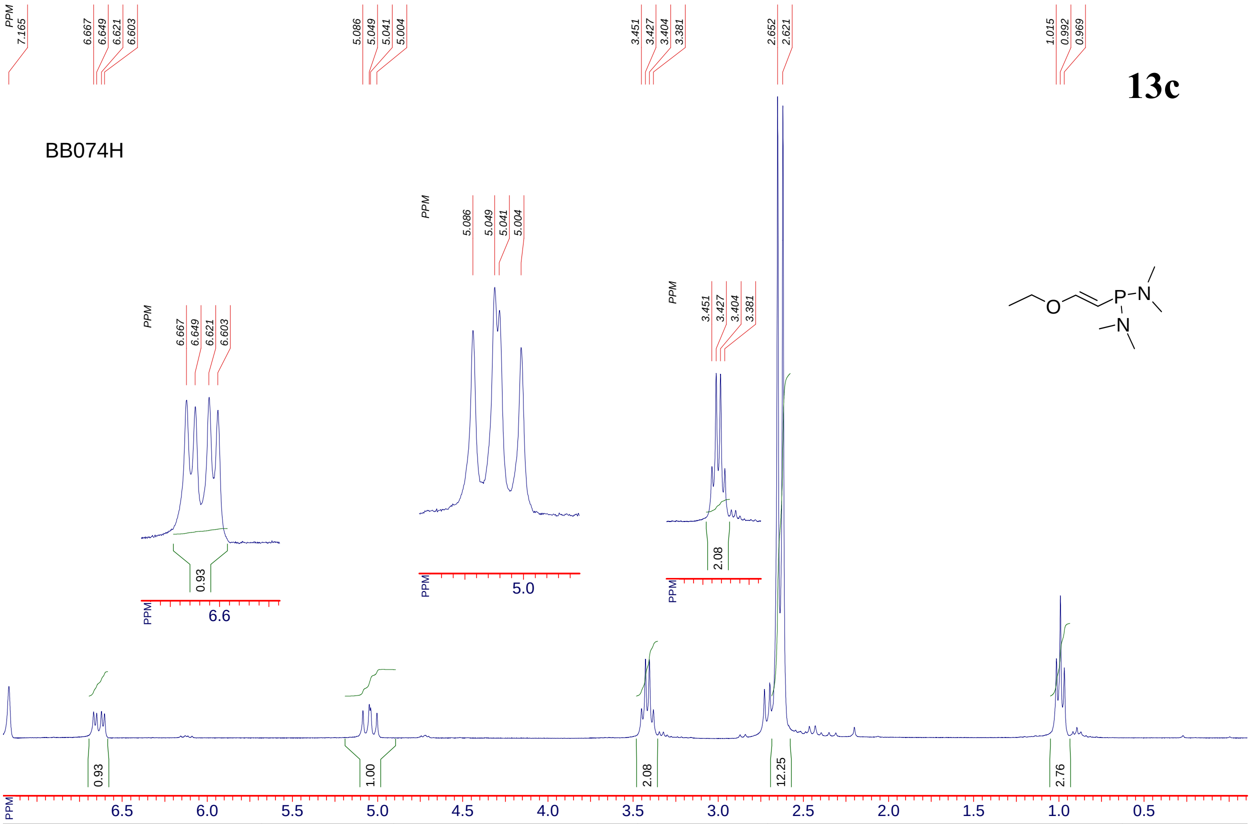
File name: BB711H	Operator:	SF: 299.9430 MHz	NSC: 2	PW: 8.00 usec, RG: 4	SI: 32768
Date: 22-Mar-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	

13b



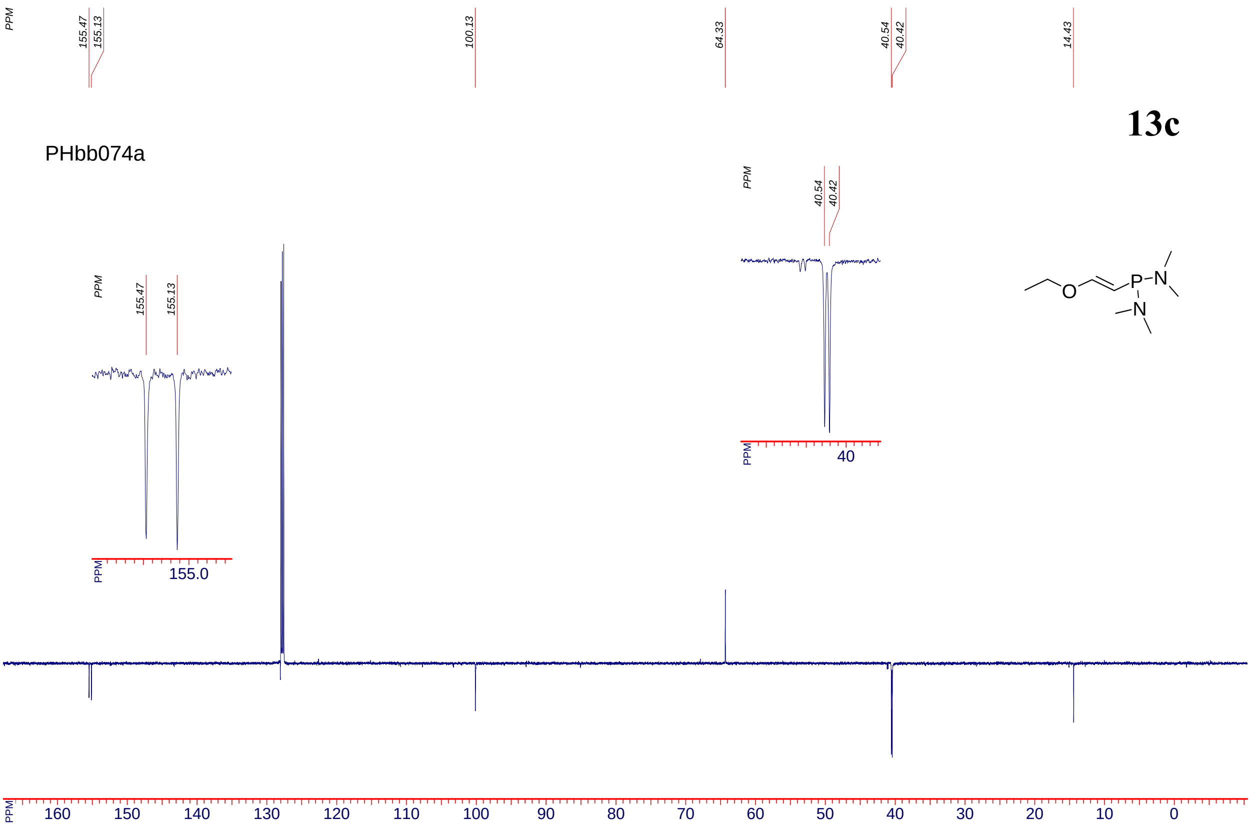
File name: PHbb071a	Operator: root	SF: 125.7578 MHz	NSC: 262	PW: 0.00 usec, RG: 20480	SI: 65536
Date: 24-Mar-2008	Solvent: c6d6	SW: 30303 Hz	TE: 678 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

13c



File name: BB074H	Operator:	SF: 299.9430 MHz	NSC: 7	PW: 8.00 usec, RG: 12	SI: 32768
Date: 27-Mar-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	

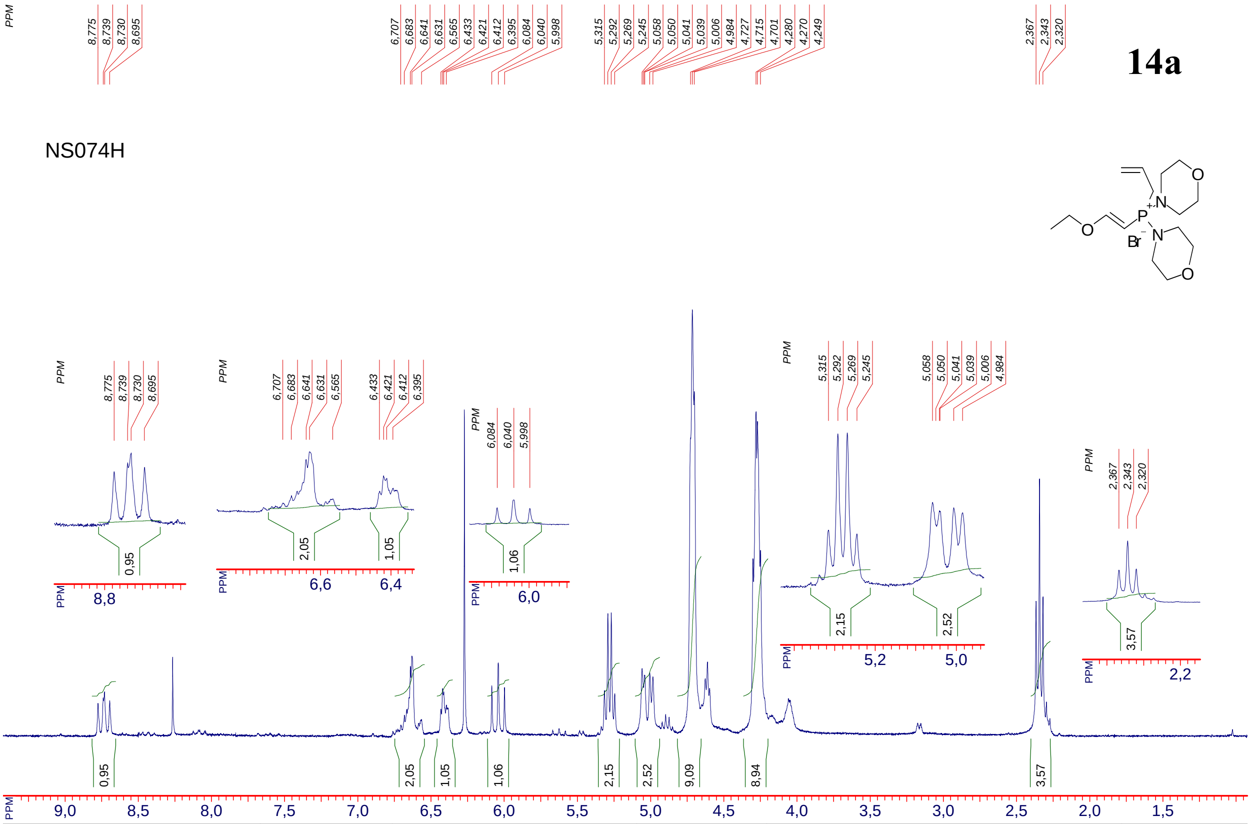
13c



File name: PHbb074a	Operator: root	SF: 125.7578 MHz	NSC: 286	PW: 0.00 usec, RG: 25600	SI: 65536
Date: 26-Mar-2008	Solvent: C6D6	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

14a

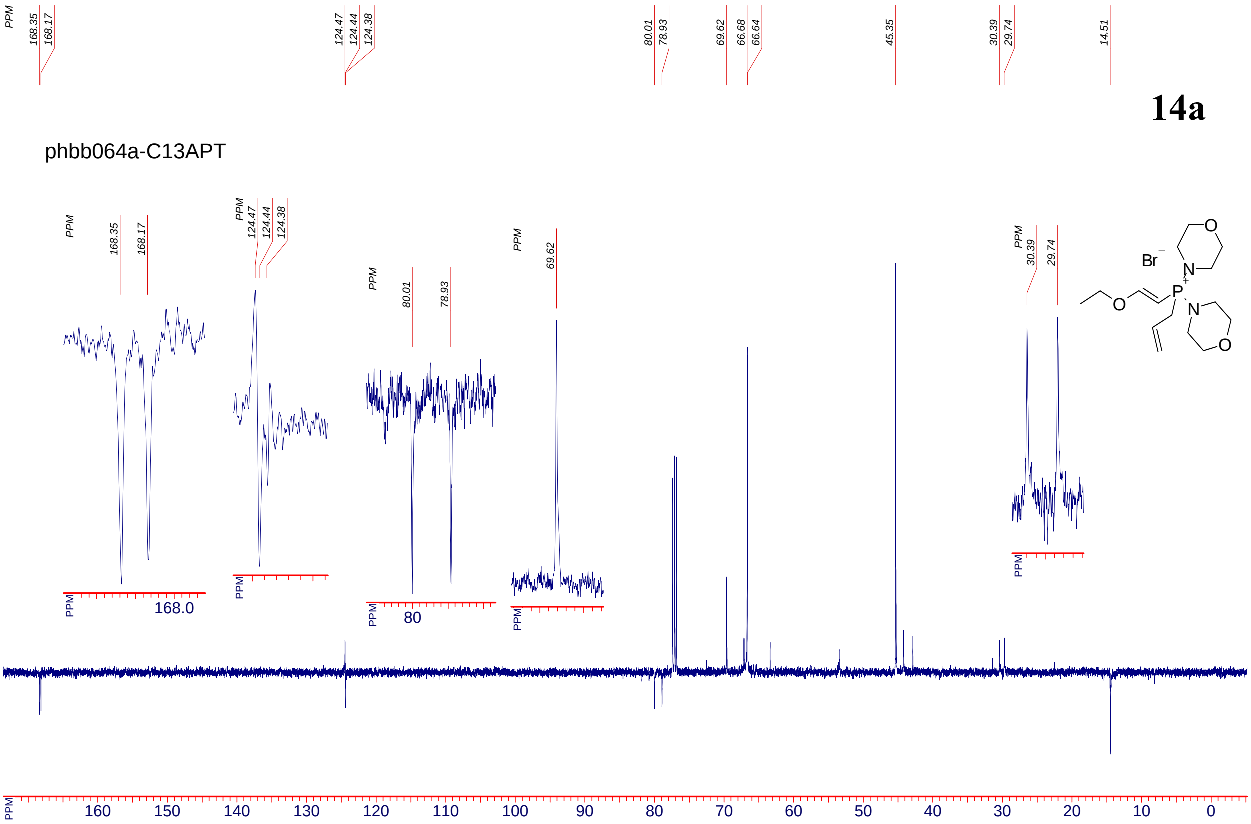
NS074H



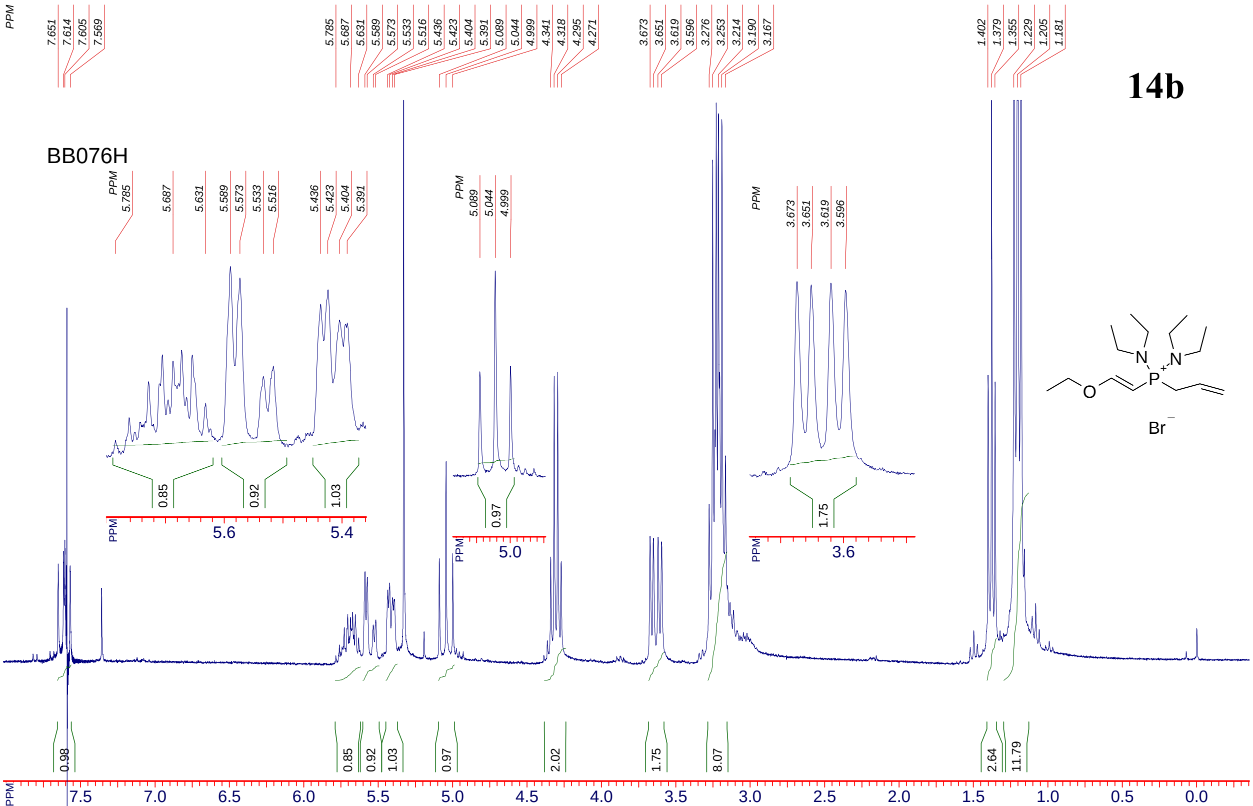
File name: NS074H	Operator:	SF: 299,9430 MHz	NSC: 2	PW: 8,00 usec, RG: 22	SI: 32768
Date: 19-îêò-2010	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1,73 sec, RD: 2,00 sec	

14a

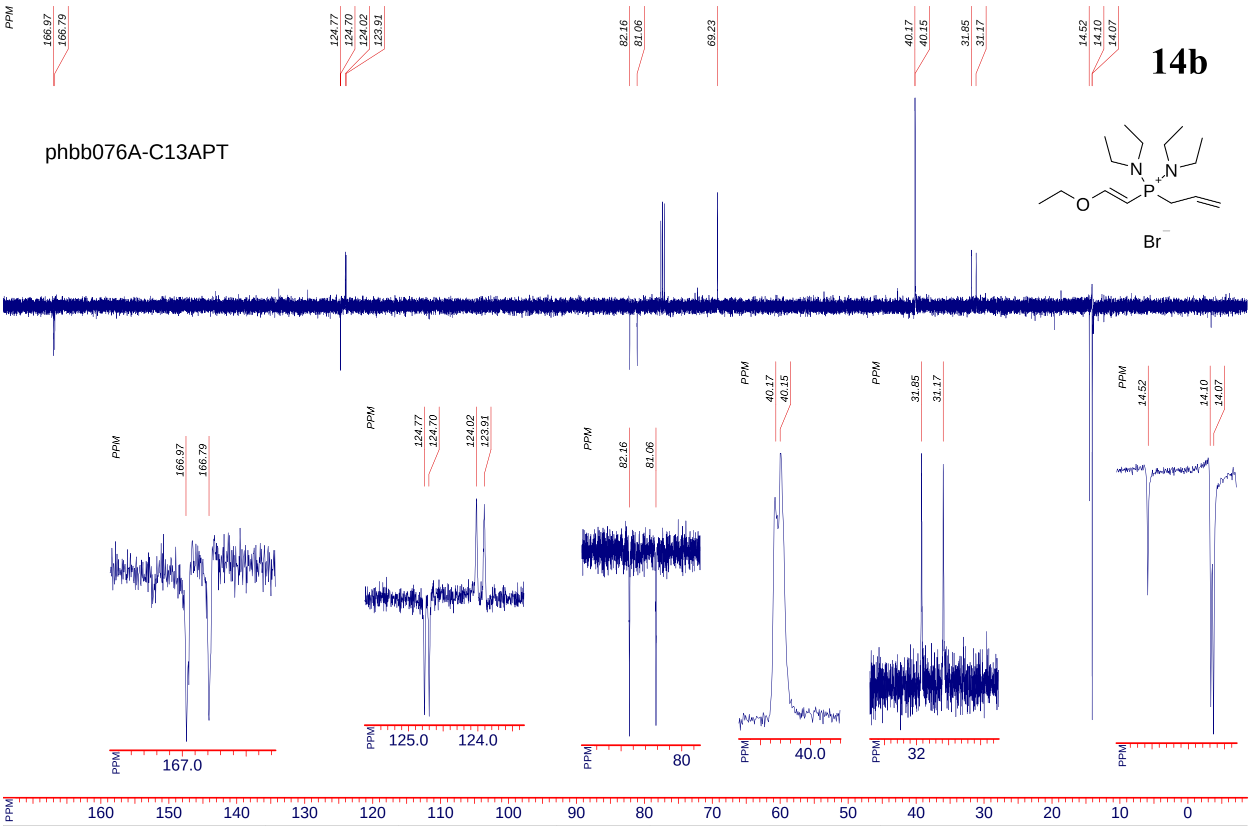
phbb064a-C13APT



File name: phbb064a-C13APT	Operator: root	SF: 125.7578 MHz	NSC: 1130	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 13-Mar-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

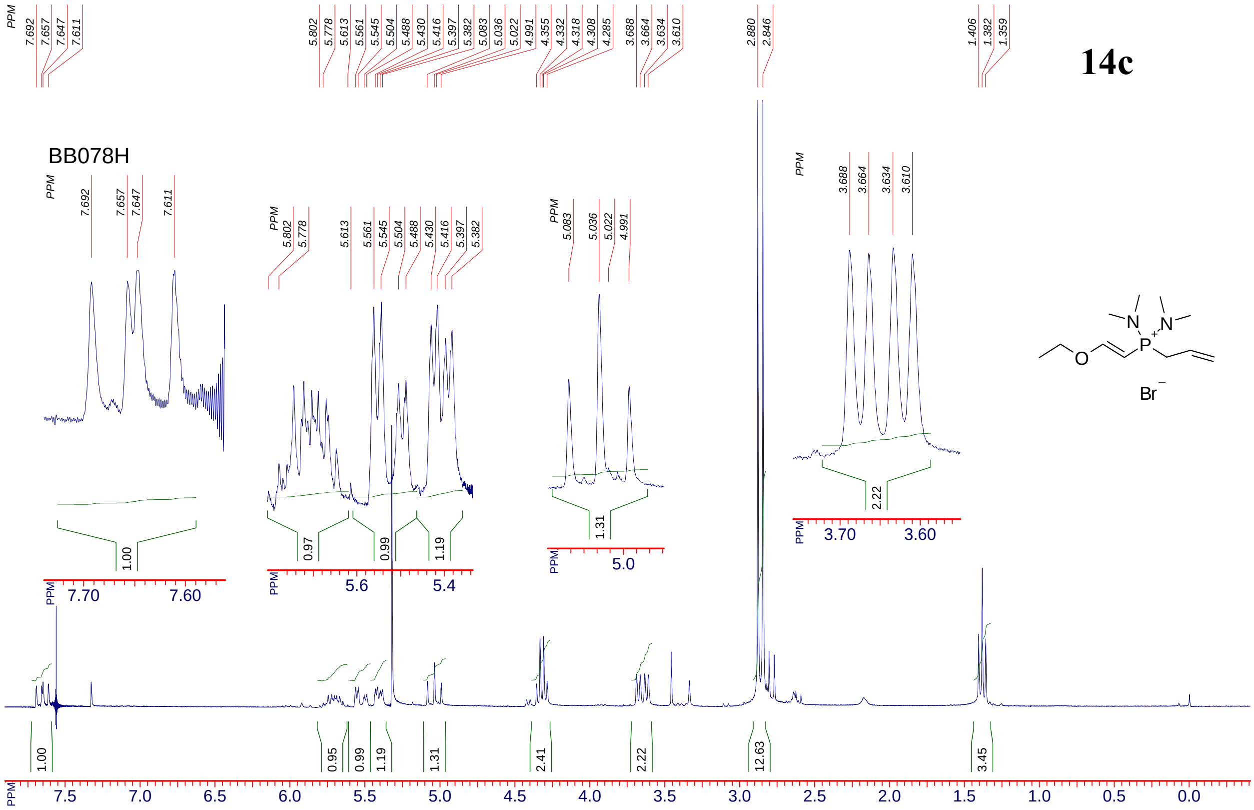


File name: BB076H	IOH	SF: 299.9430 MHz	NSC: 9	PW: 8.00 usec, RG: 16	SI: 32768
Date: 28-Mar-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	*BB076H*



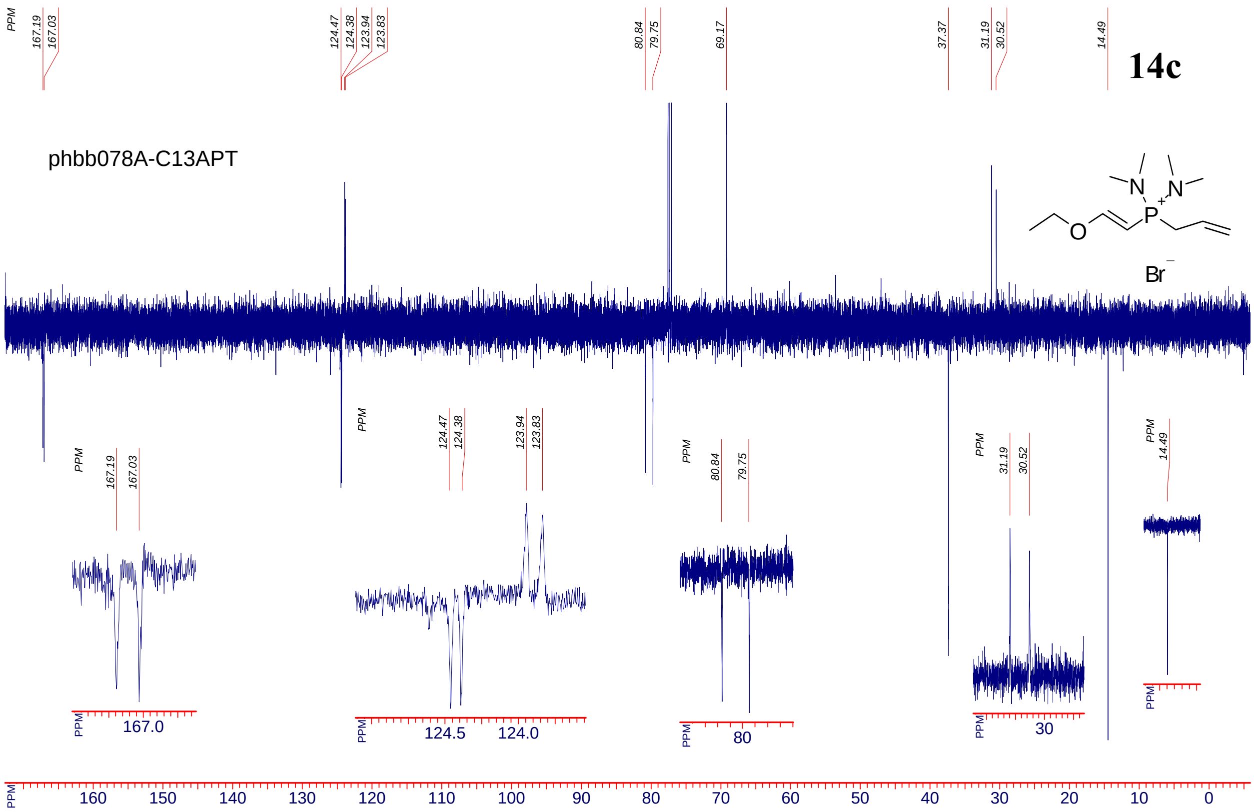
File name: phbb076A-C13APT	Operator: root	SF: 125.7578 MHz	NSC: 1141	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 27-Mar-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

14c



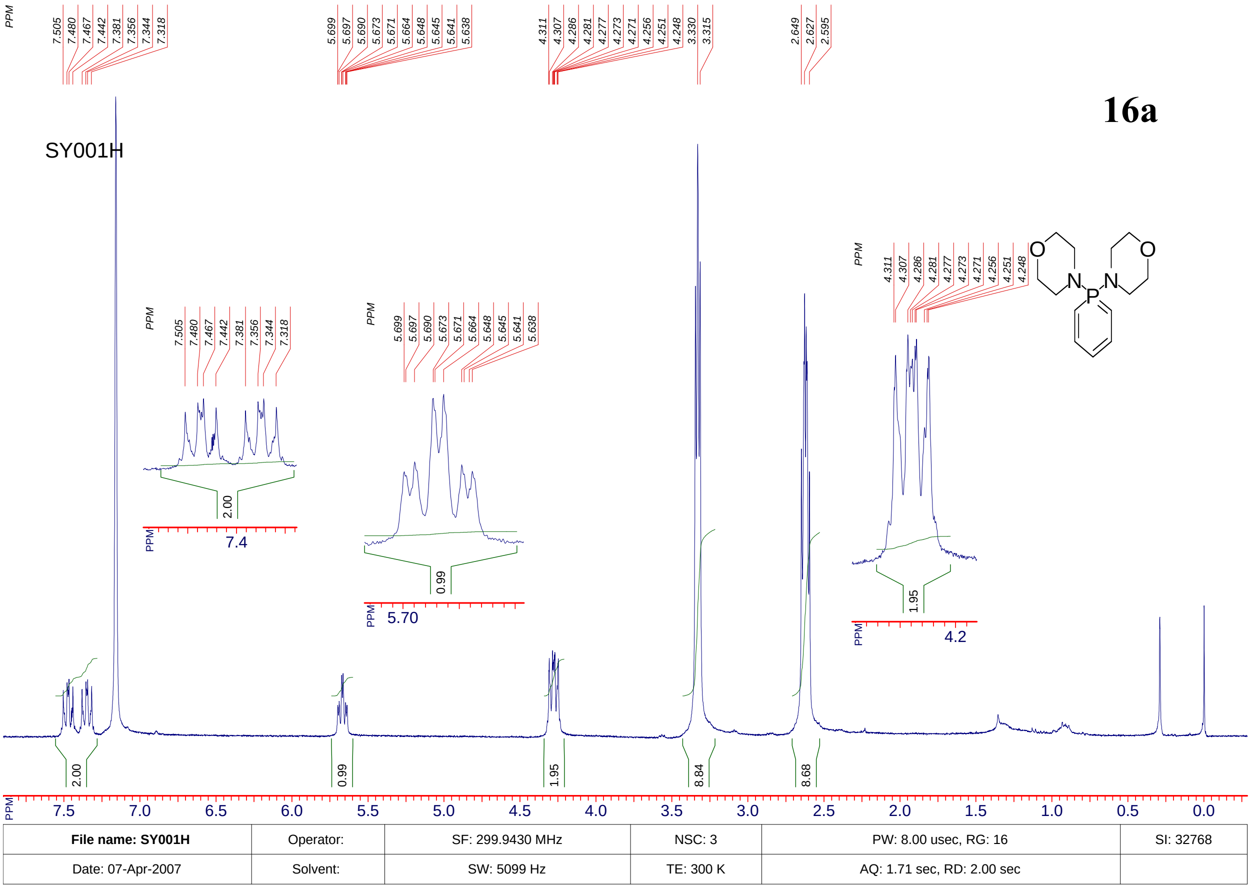
File name: BB078H	IOH	SF: 299.9430 MHz	NSC: 14	PW: 8.00 usec, RG: 16	SI: 32768
Date: 28-Mar-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	*BB078H*

14c

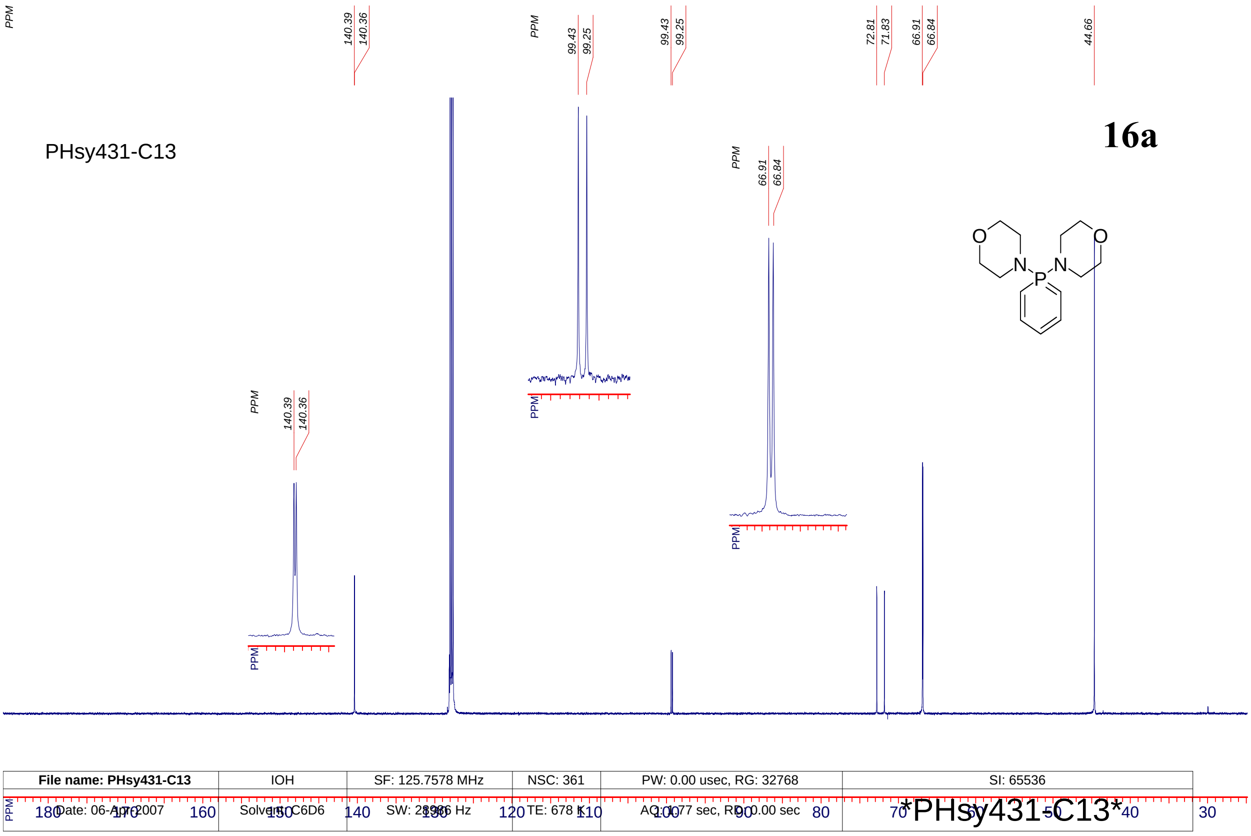


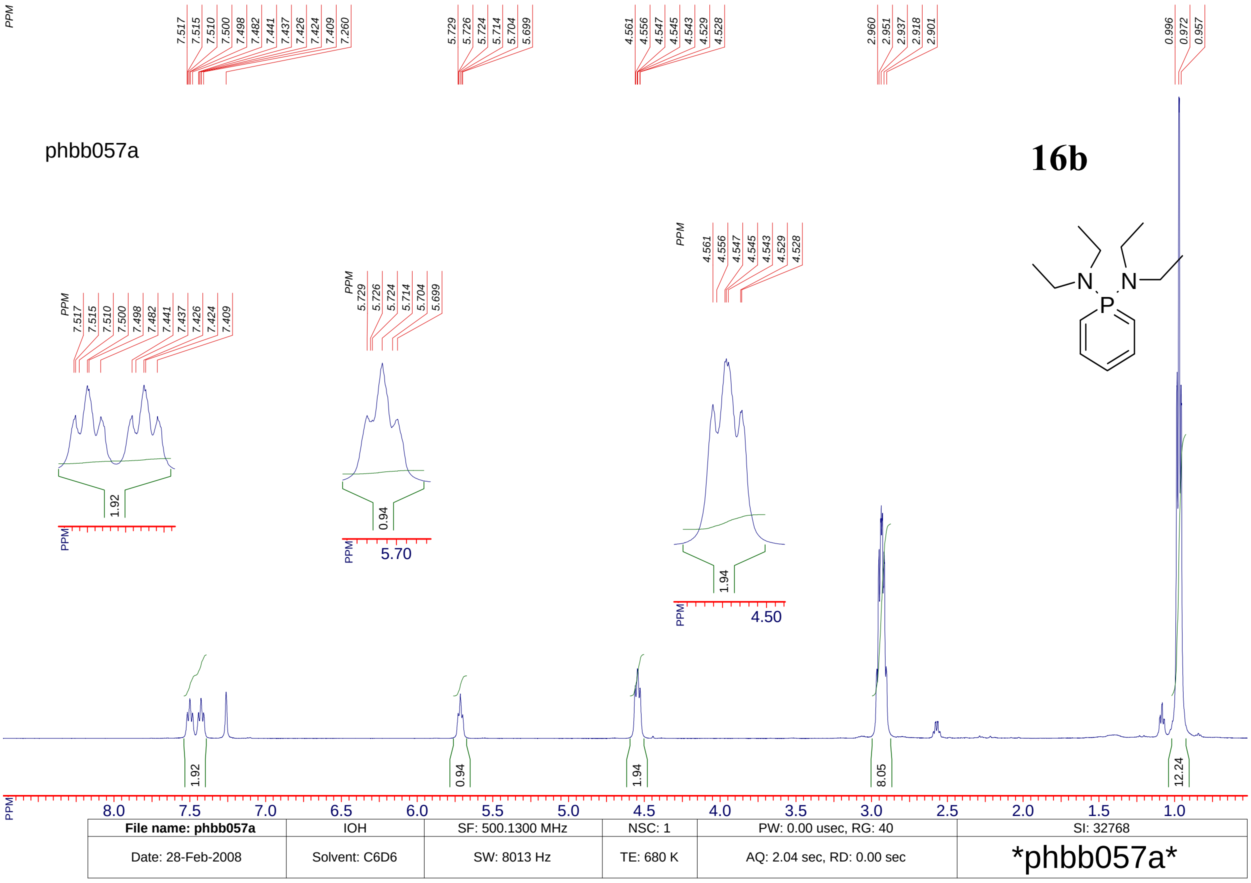
File name: phbb078A-C13APT	IOH	SF: 125.7578 MHz	NSC: 755	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 27-Mar-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	*phbb078A-C13APT*

16a


SY001H
File name: SY001H
Operator:
SF: 299.9430 MHz
NSC: 3
PW: 8.00 usec, RG: 16
SI: 32768
Date: 07-Apr-2007
Solvent:
SW: 5099 Hz
TE: 300 K
AQ: 1.71 sec, RD: 2.00 sec

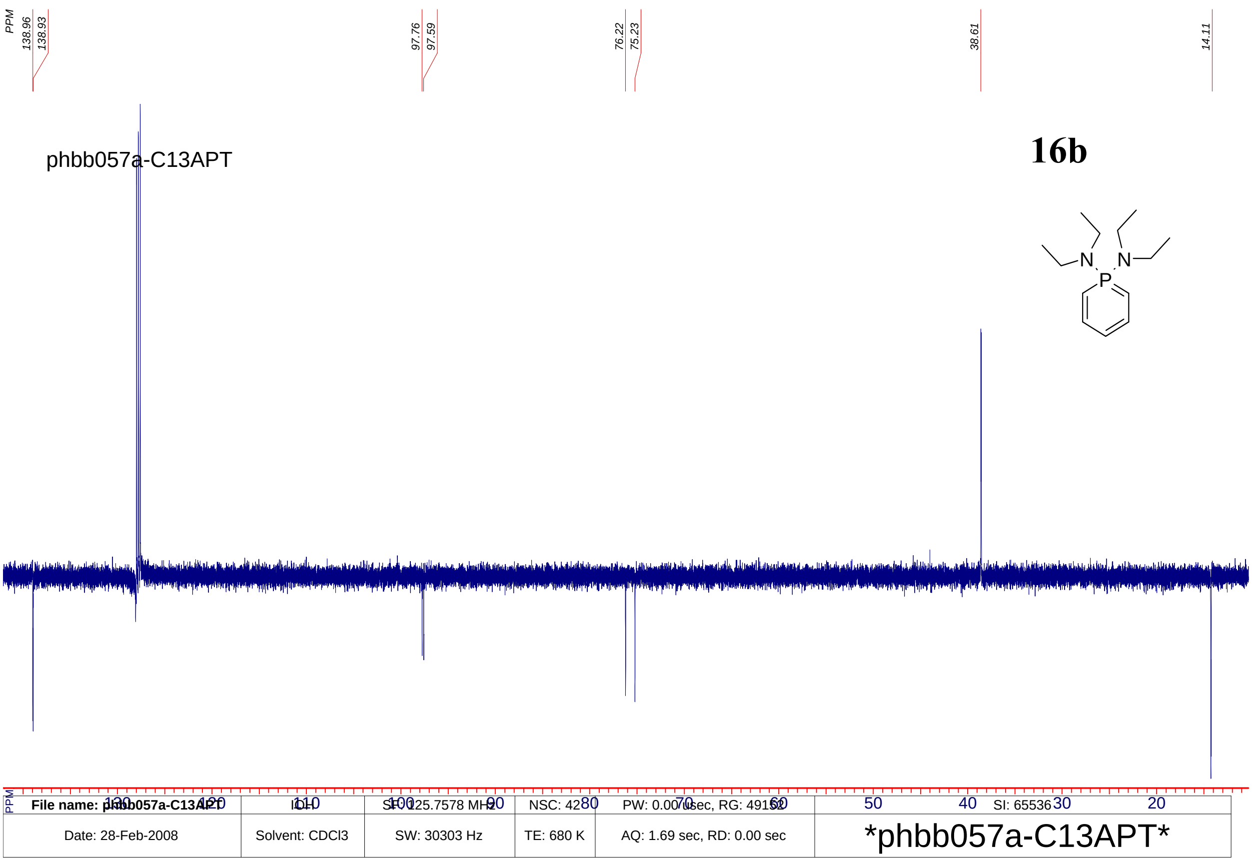
16a


PHsy431-C13
File name: PHsy431-C13
IOH
SF: 125.7578 MHz
NSC: 361
PW: 0.00 usec, RG: 32768
SI: 65536
Solvent: C6D6
PHsy431-C13



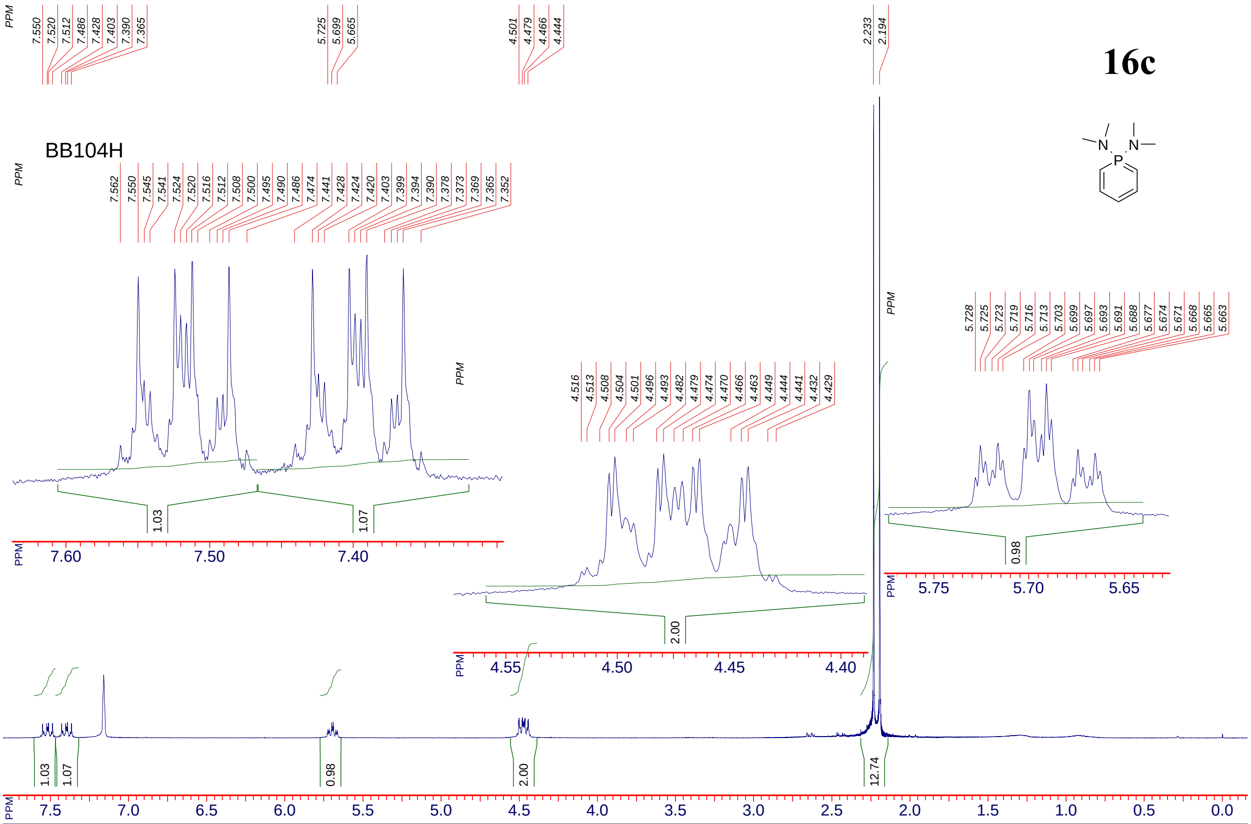
phbb057a
File name: phbb057a
Date: 28-Feb-2008
Solvent: C6D6
SF: 500.1300 MHz
SW: 8013 Hz
NSC: 1
TE: 680 K
PW: 0.00 usec, RG: 40
AQ: 2.04 sec, RD: 0.00 sec
SI: 32768
phbb057a

16b

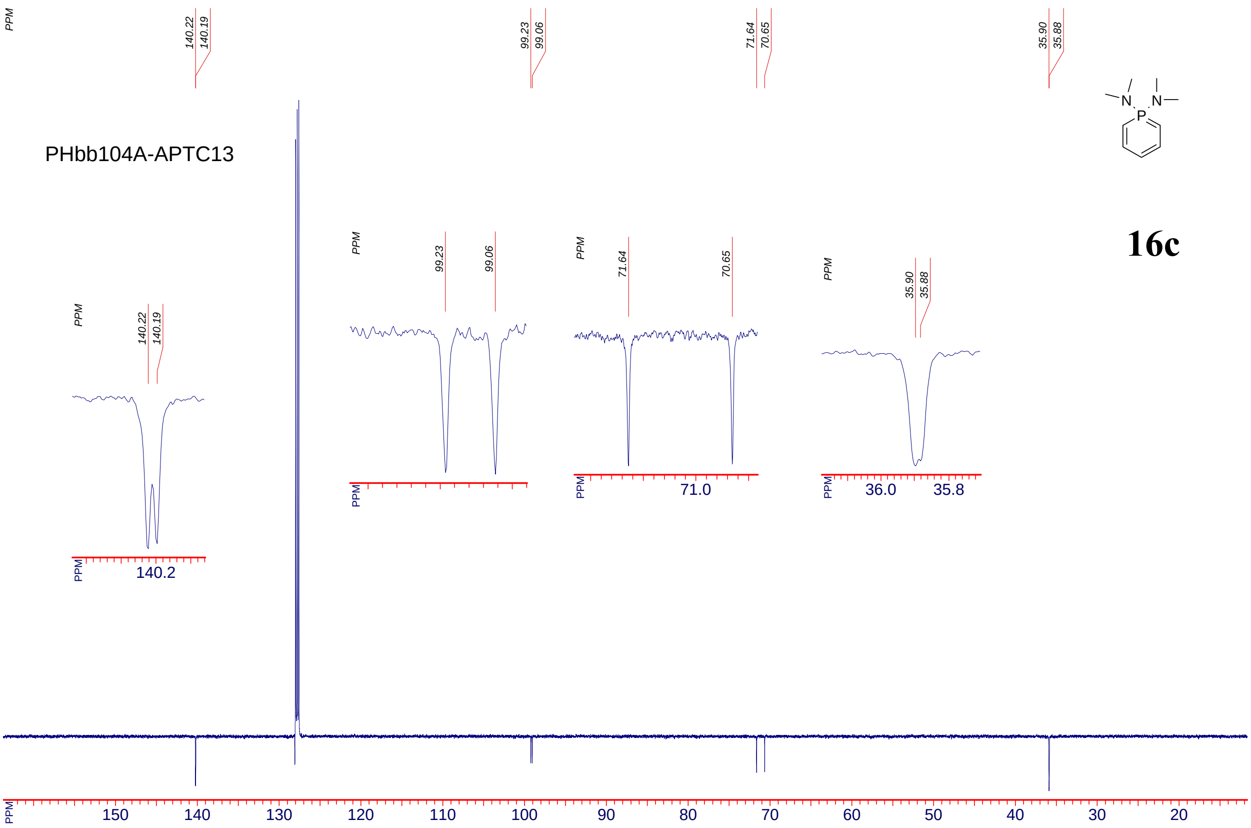


phbb057a-C13APT
File name: phbb057a-C13APT
Date: 28-Feb-2008
Solvent: CDCl3
SW: 30303 Hz
TE: 680 K
AQ: 1.69 sec, RD: 0.00 sec
phbb057a-C13APT

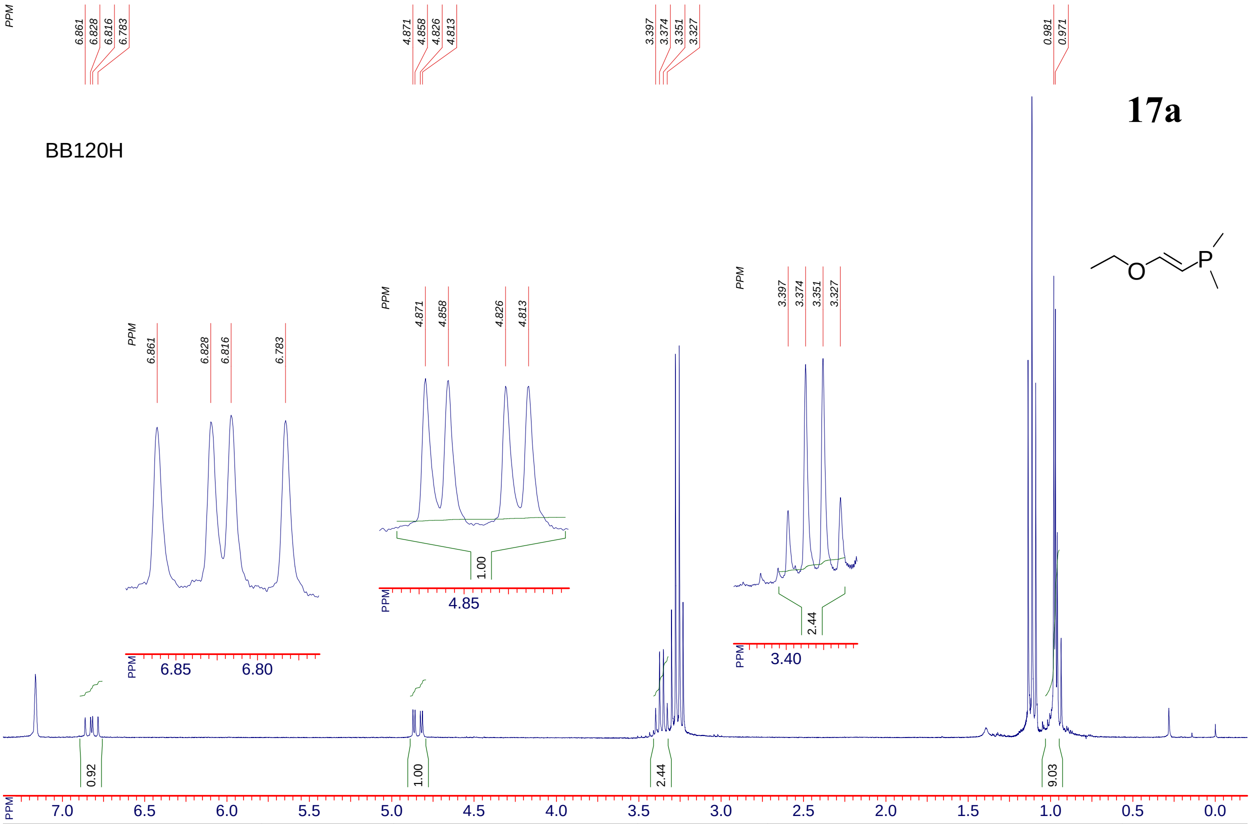
16b



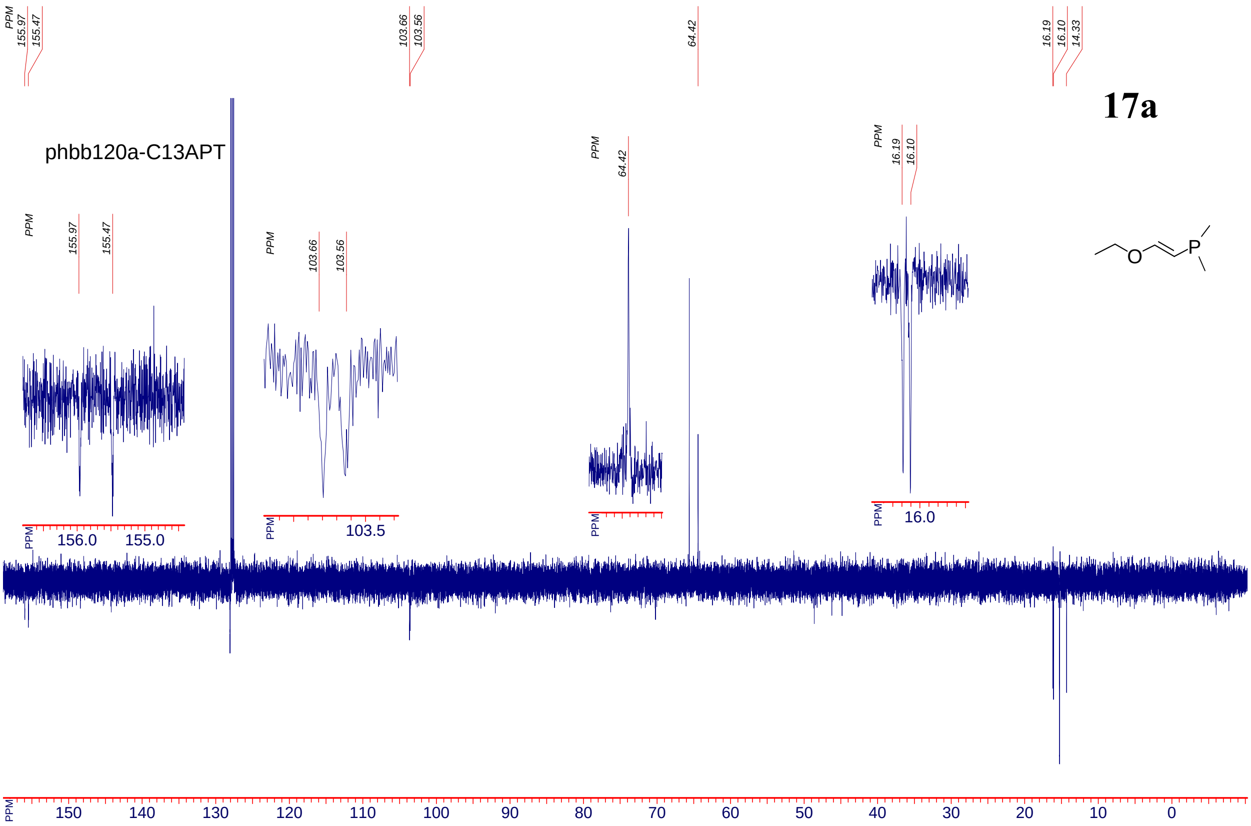
File name: BB104H	Operator:	SF: 299.9430 MHz	NSC: 12	PW: 8.00 usec, RG: 24	SI: 32768
Date: 08-May-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	



File name: PHbb104A-APTC13	Operator: root	SF: 125.7578 MHz	NSC: 378	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 08-May-2008	Solvent: C6D6	SW: 30303 Hz	TE: 678 K	AQ: 1.69 sec, RD: 0.00 sec	

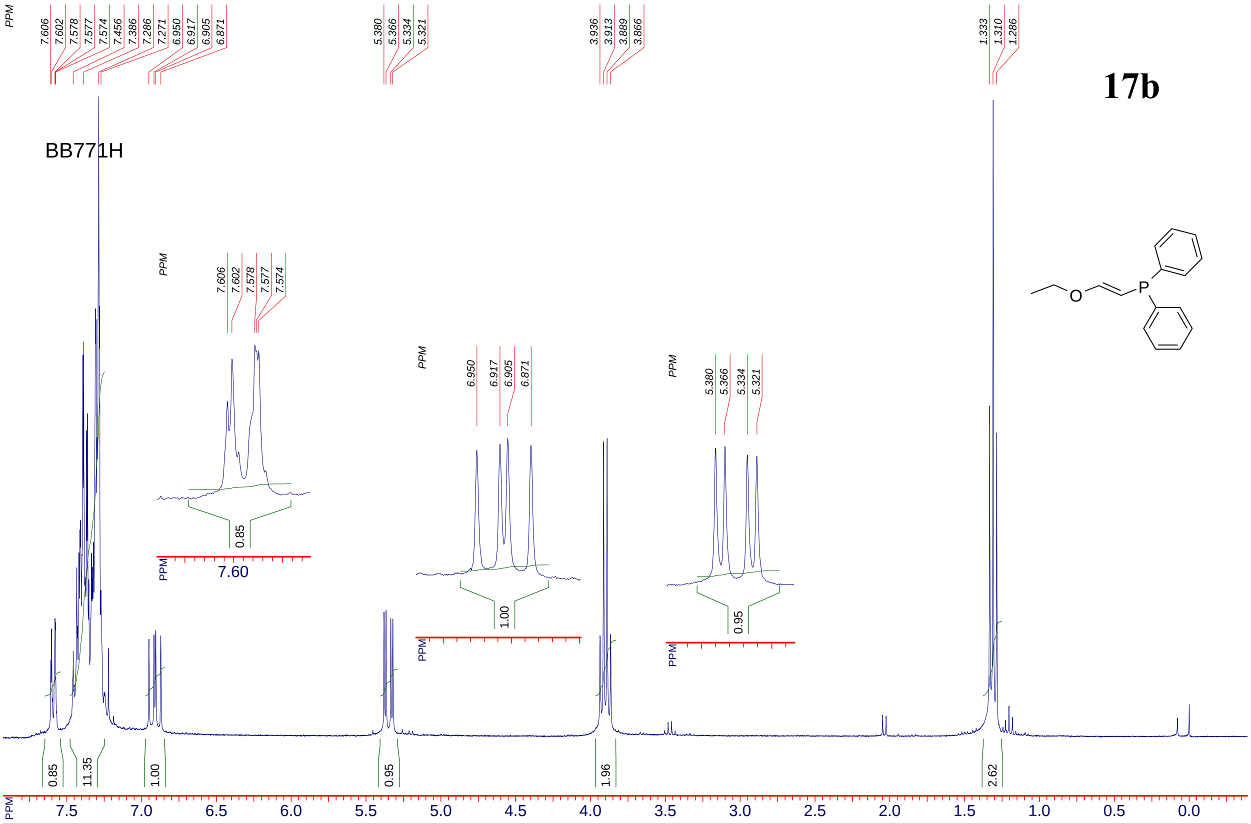


File name: BB120H	Operator:	SF: 299.9430 MHz	NSC: 1	PW: 8.00 usec, RG: 16	SI: 32768
Date: 09-Jul-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.71 sec, RD: 2.00 sec	



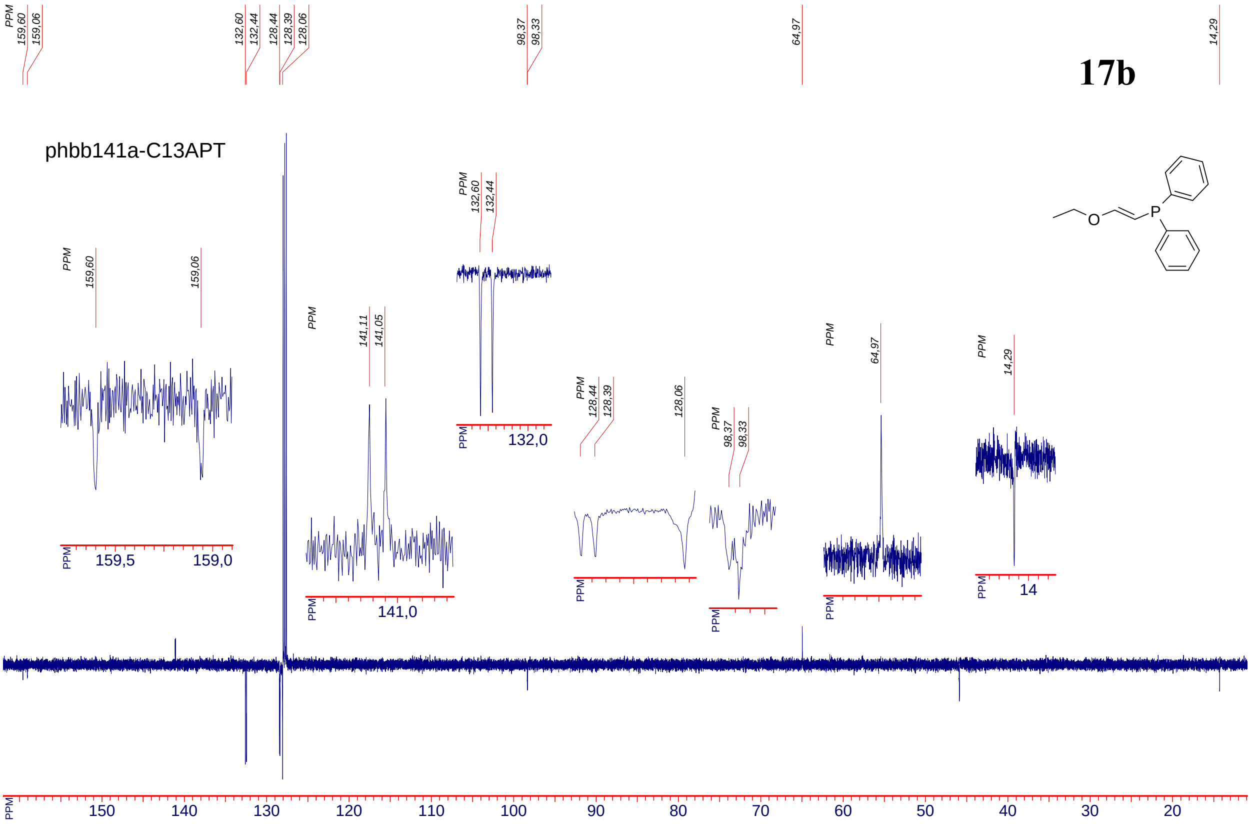
File name: phbb120a-C13APT	Operator: root	SF: 125.7578 MHz	NSC: 135	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 08-Jul-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 0 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

17b

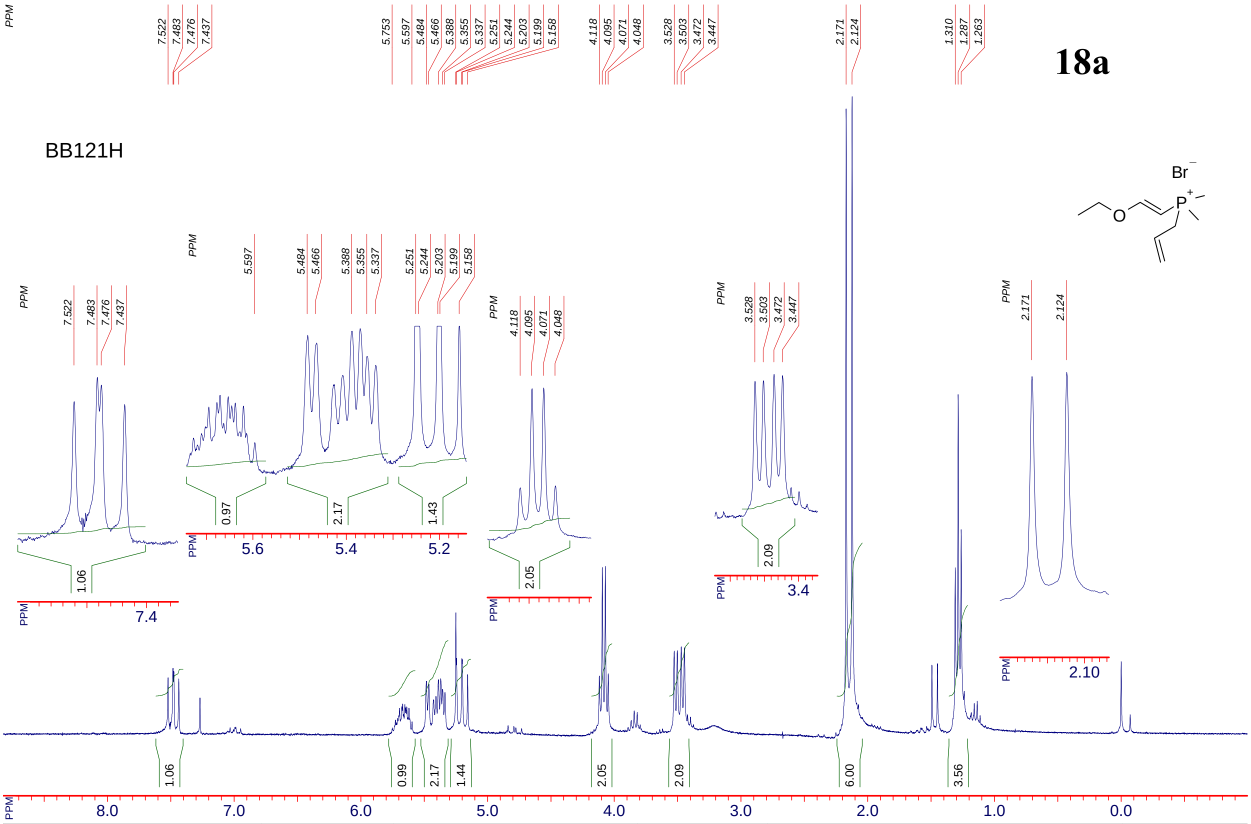


File name: BB771H	Operator:	SF: 299.9430 MHz	NSC: 3	PW: 8.00 usec, RG: 22	SI: 32768
Date: 27-Mar-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	

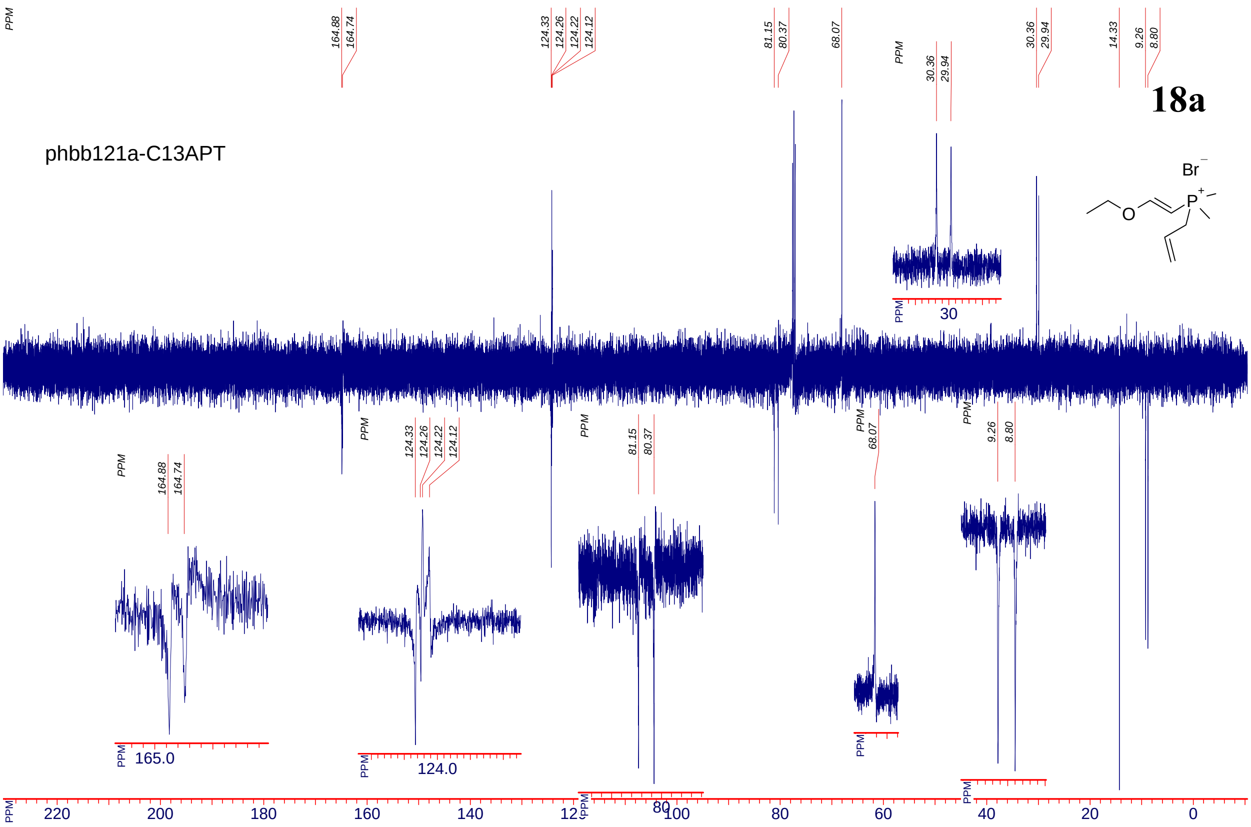
17b



File name: phbb141a-C13APT	Operator: root	SF: 125,7578 MHz	NSC: 160	PW: 0,00 usec, RG: 49152	SI: 65536
Date: 16-ñåí-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 682 K	AQ: 1,69 sec, RD: 0,00 sec	Parameter file, XWIN-NMRVersion 3.5

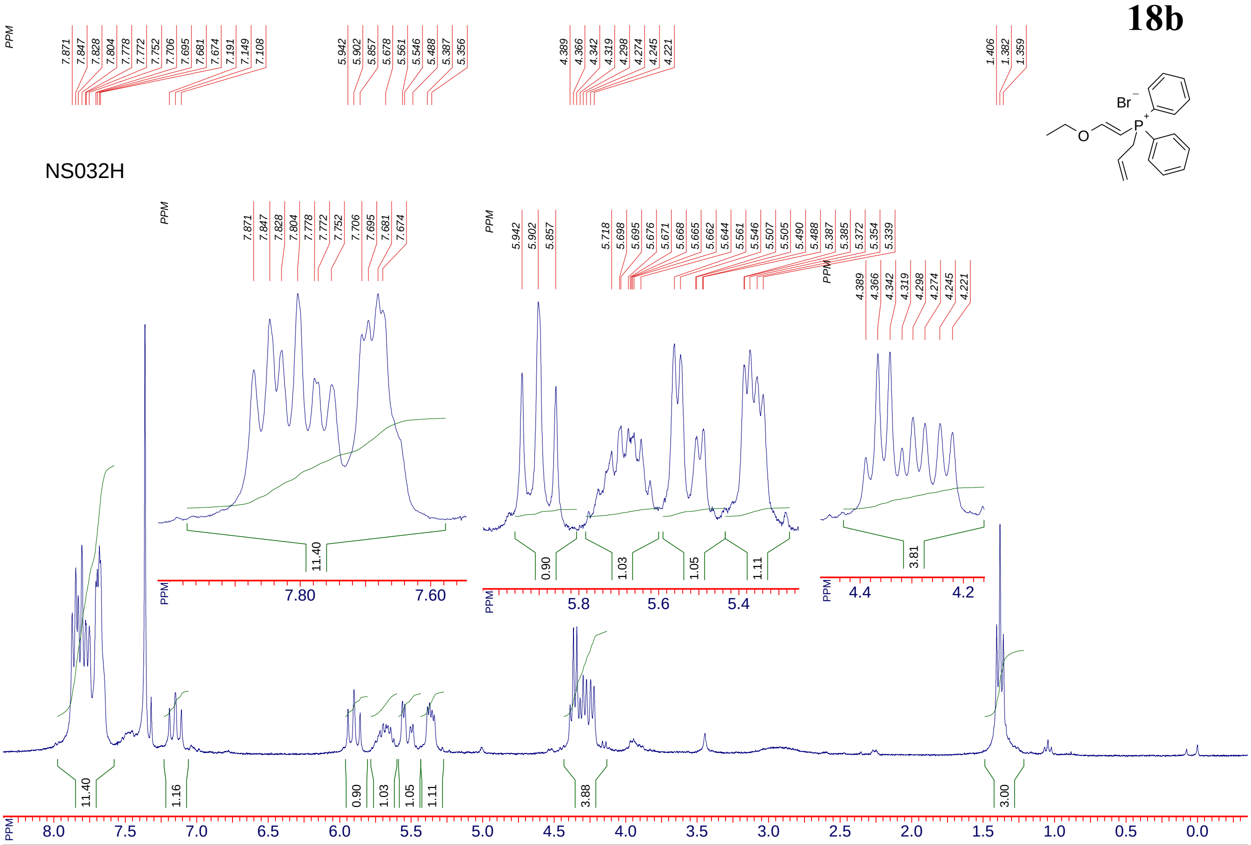


File name: BB121H	Operator:	SF: 299.9430 MHz	NSC: 3	PW: 8.00 usec, RG: 16	SI: 32768
Date: 10-Jul-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	



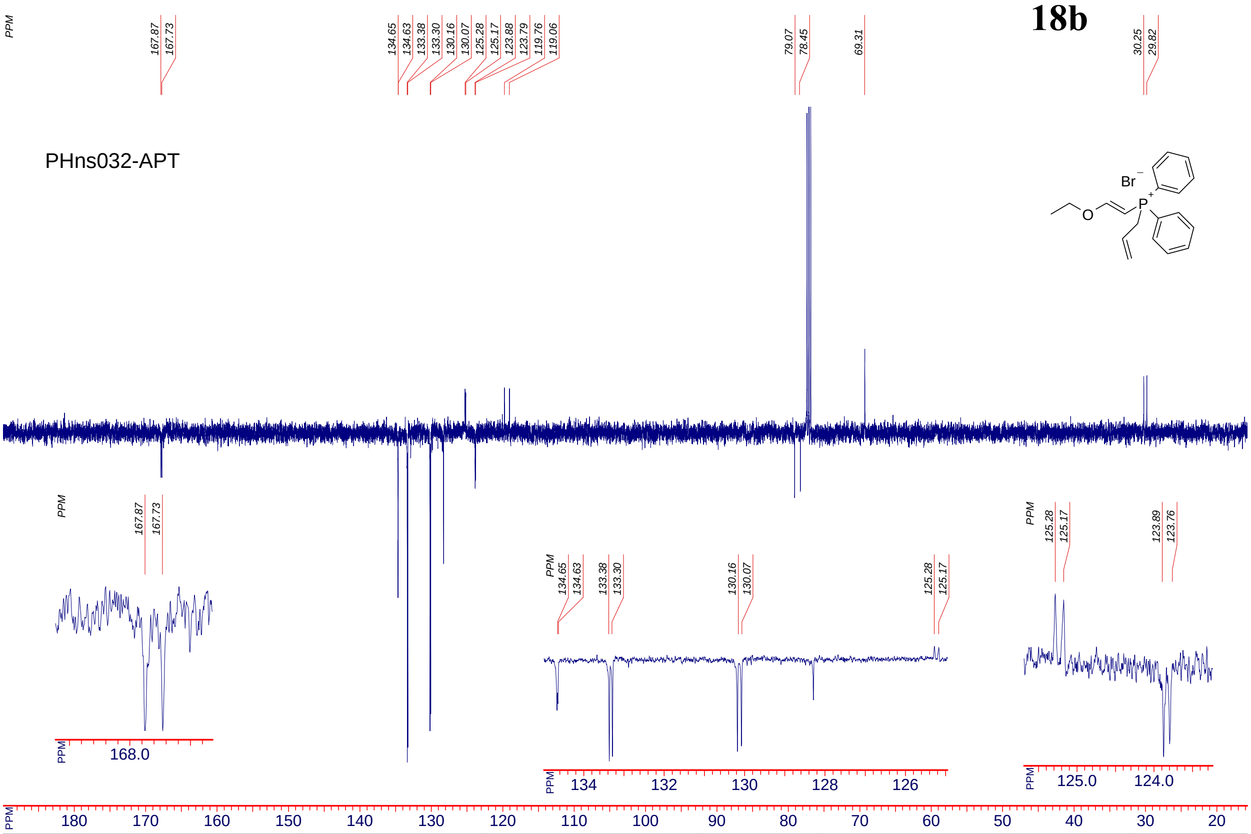
File name: phbb121a-C13APT	Operator: root	SF: 125.7578 MHz	NSC: 191	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 10-Jul-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 0 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

18b



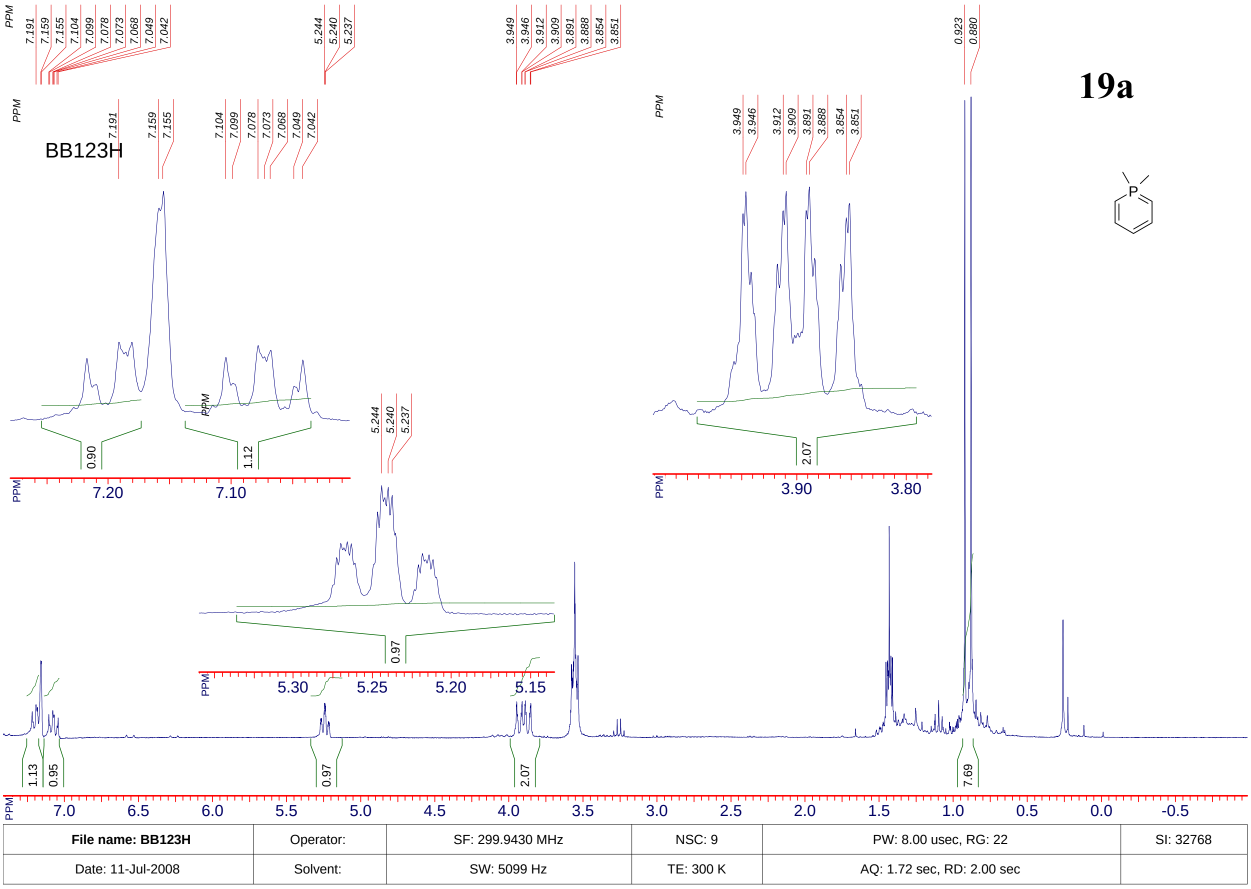
File name: NS032H	Operator:	SF: 299.9430 MHz	NSC: 8	PW: 8.00 usec, RG: 22	SI: 65536
Date: 09-Dec-2009	Solvent: DMSO-d6 + CCl4	SW: 5099 Hz	TE: 300 K	AQ: 1.73 sec, RD: 2.00 sec	

18b

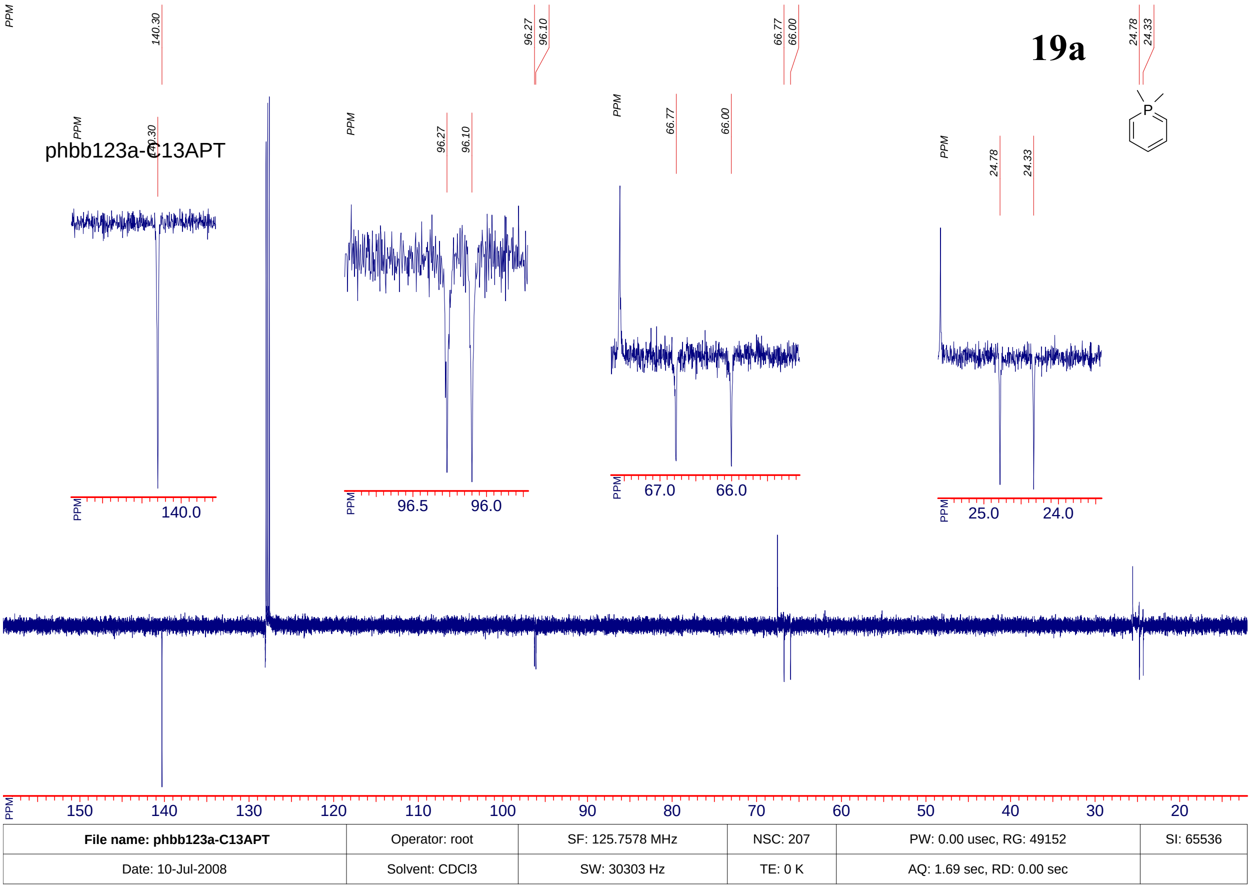


File name: PHns032-APT	Operator: root	SF: 125.7578 MHz	NSC: 176	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 09-Dec-2009	Solvent: CDCl3	SW: 30303 Hz	TE: 681 K	AQ: 1.69 sec, RD: 0.00 sec	

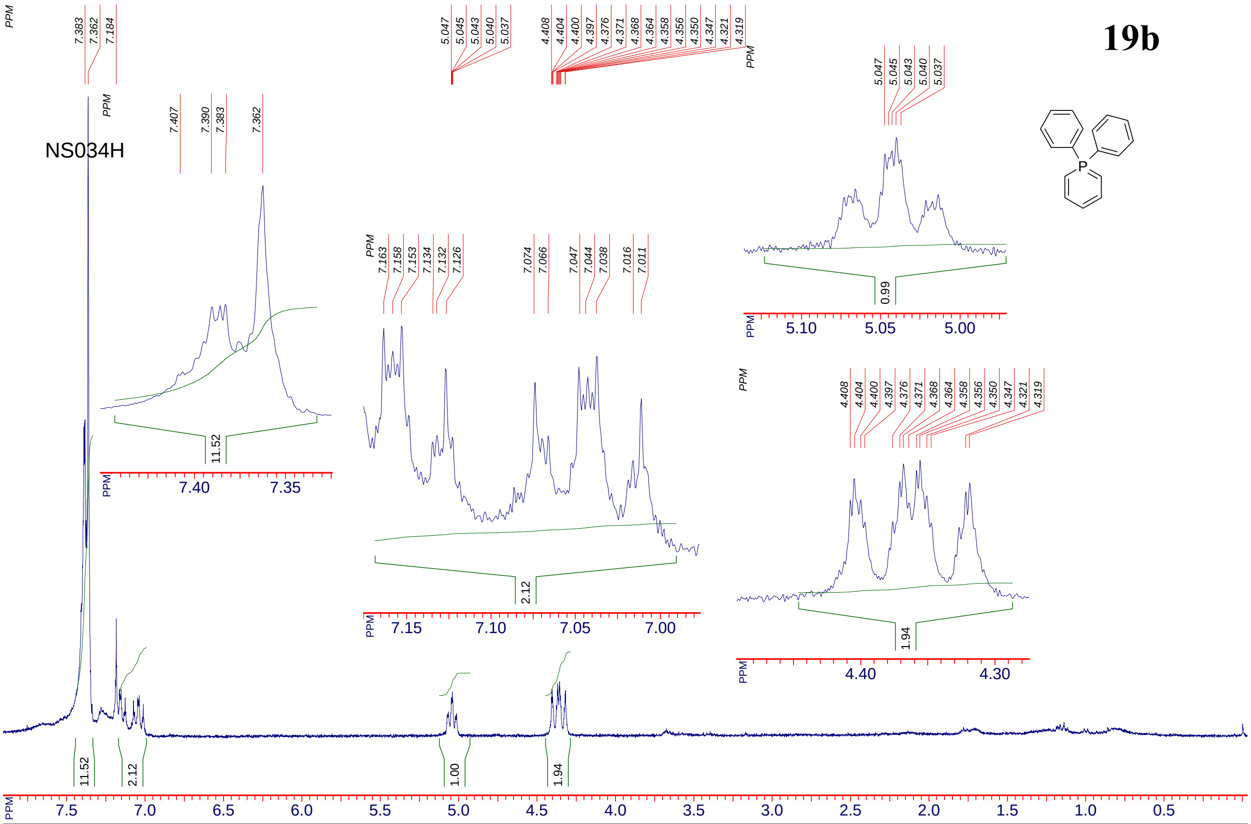
19a


BB123H
File name: BB123H
Date: 11-Jul-2008
Operator:
Solvent:
SF: 299.9430 MHz
SW: 5099 Hz
NSC: 9
TE: 300 K
PW: 8.00 usec, RG: 22
AQ: 1.72 sec, RD: 2.00 sec
SI: 32768

19a

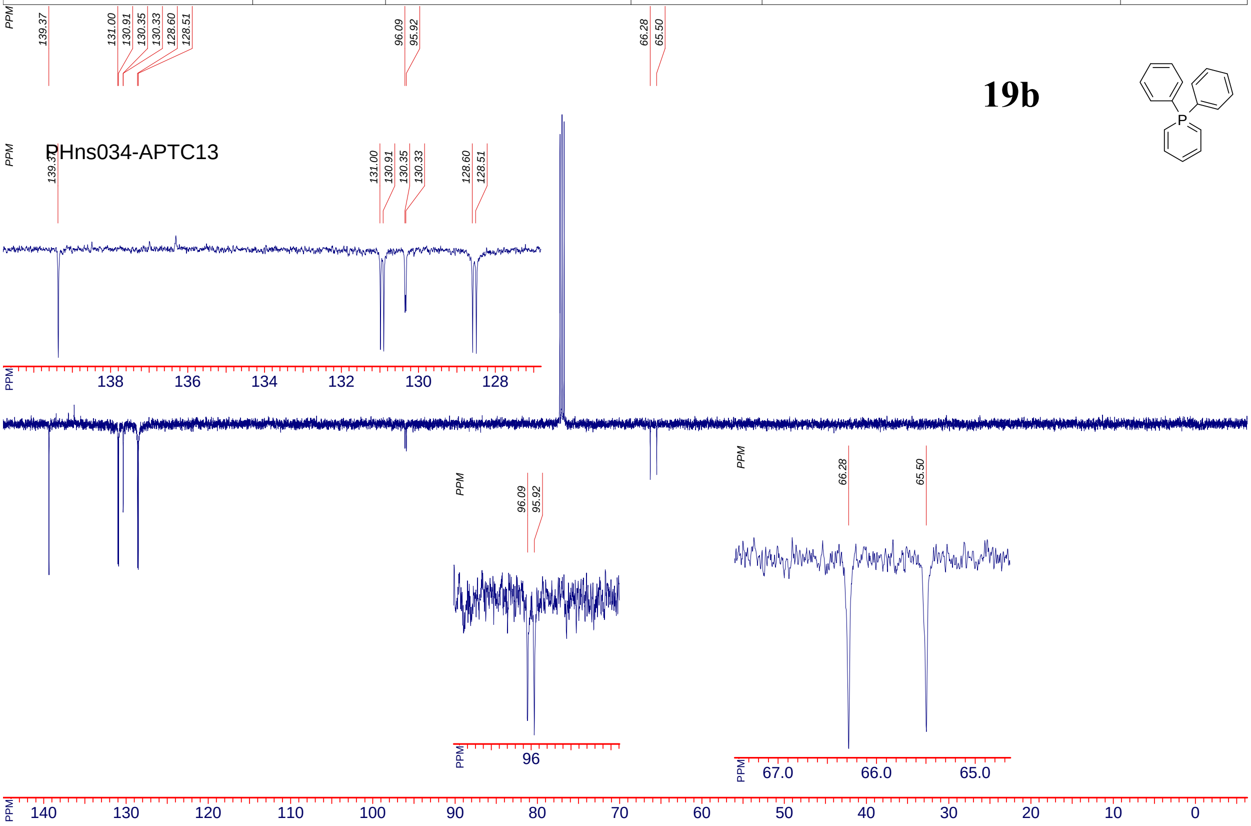

phbb123a-C13APT
File name: phbb123a-C13APT
Date: 10-Jul-2008
Operator: root
Solvent: CDCl3
SF: 125.7578 MHz
SW: 30303 Hz
NSC: 207
TE: 0 K
PW: 0.00 usec, RG: 49152
AQ: 1.69 sec, RD: 0.00 sec
SI: 65536

19b



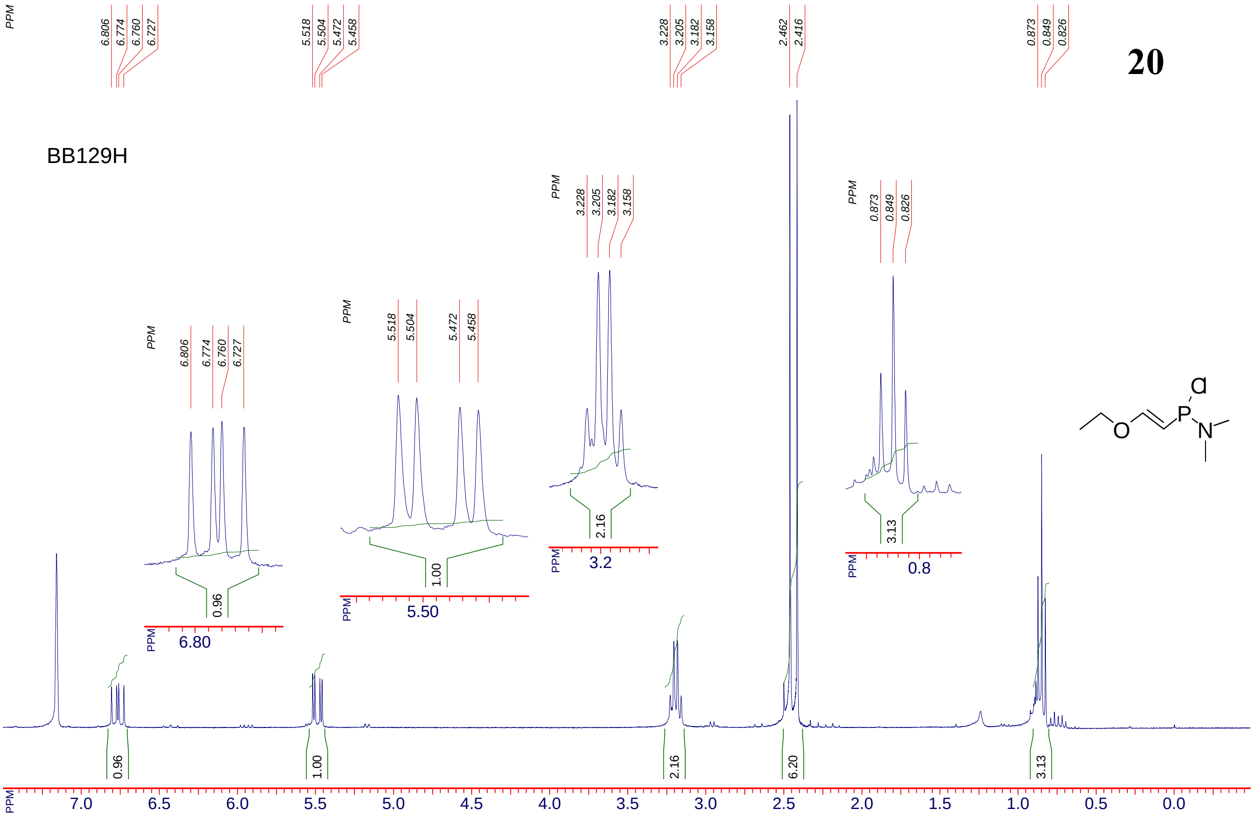
File name: NS034H	Operator:	SF: 299.9430 MHz	NSC: 2	PW: 8.00 usec, RG: 22	SI: 32768
Date: 23-Jan-2010	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.73 sec, RD: 2.00 sec	

19b



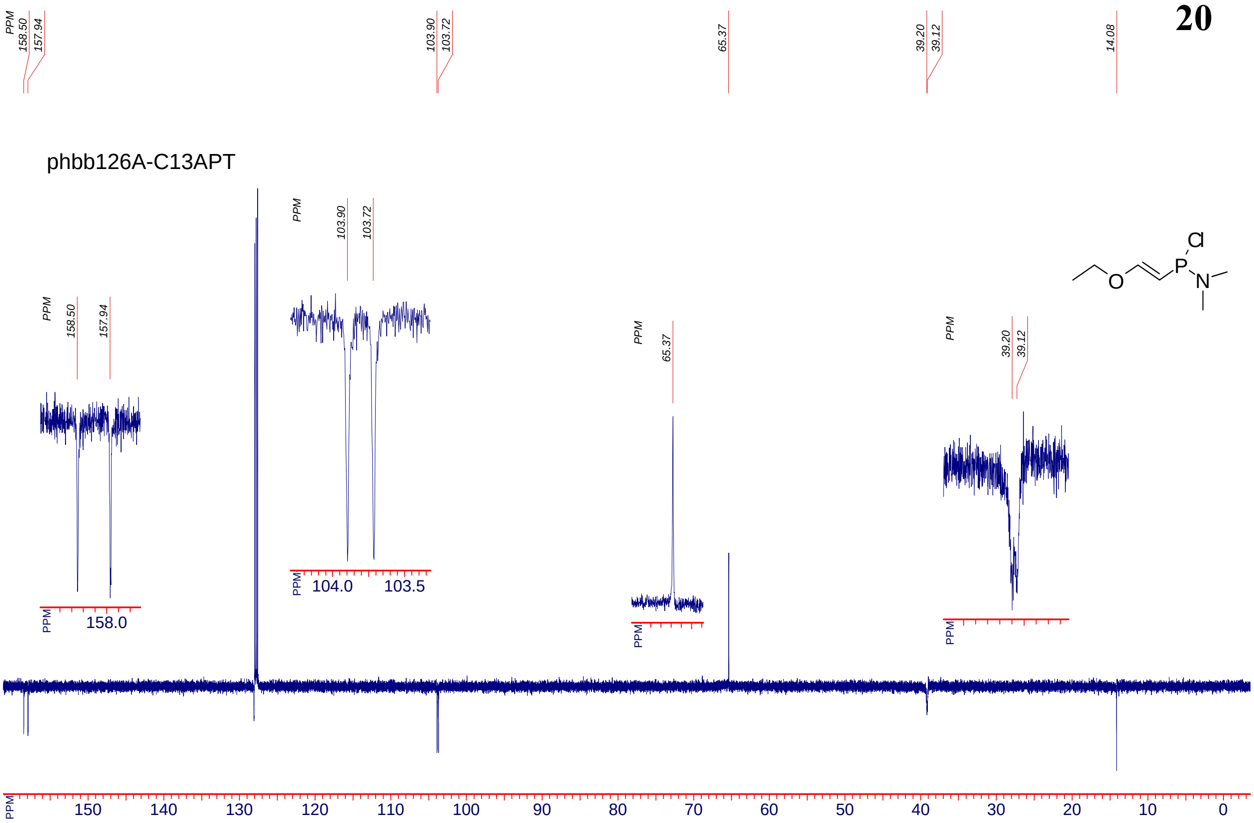
File name: PHns034-APTC13	Operator: root	SF: 125.7578 MHz	NSC: 455	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 22-Jan-2010	Solvent: CDCl3	SW: 30303 Hz	TE: 680 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

20



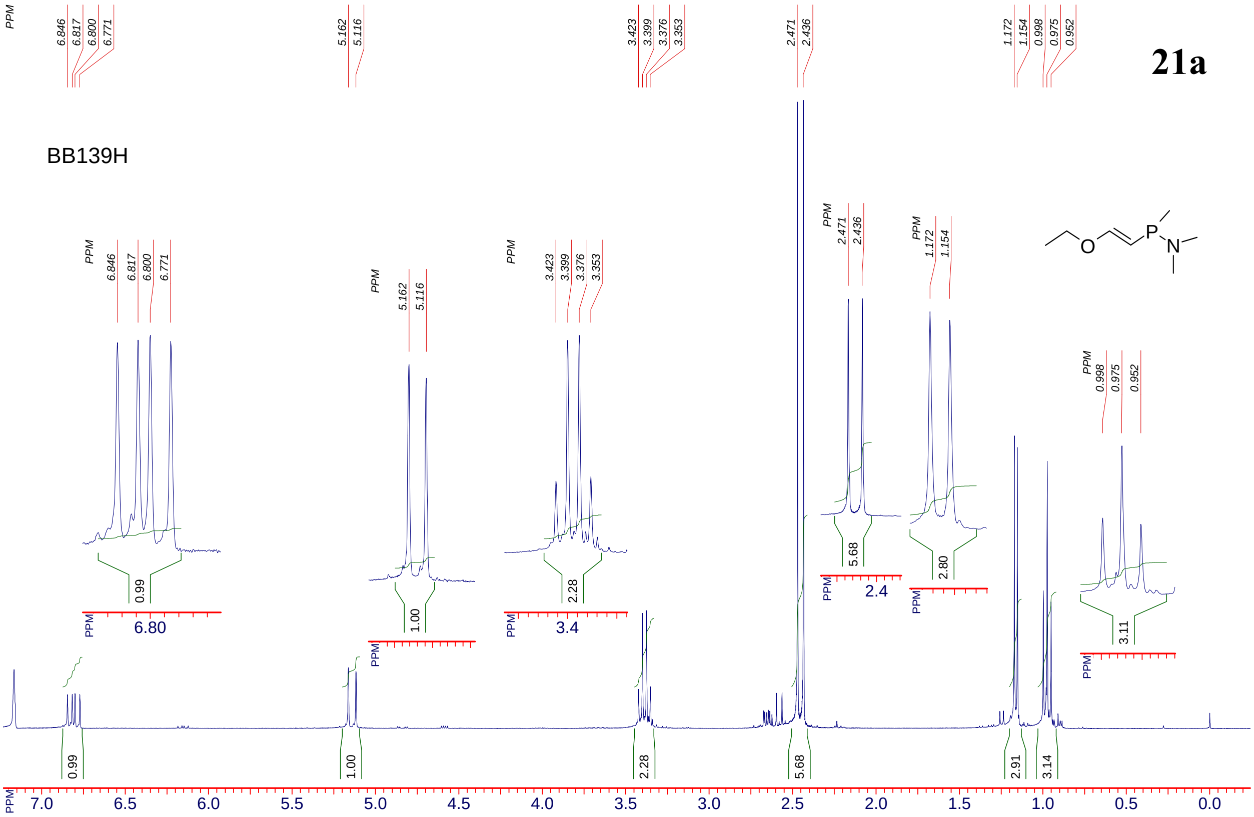
File name: BB129H	Operator:	SF: 299.9430 MHz	NSC: 1	PW: 8.00 usec, RG: 16	SI: 32768
Date: 18-Jul-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	

20



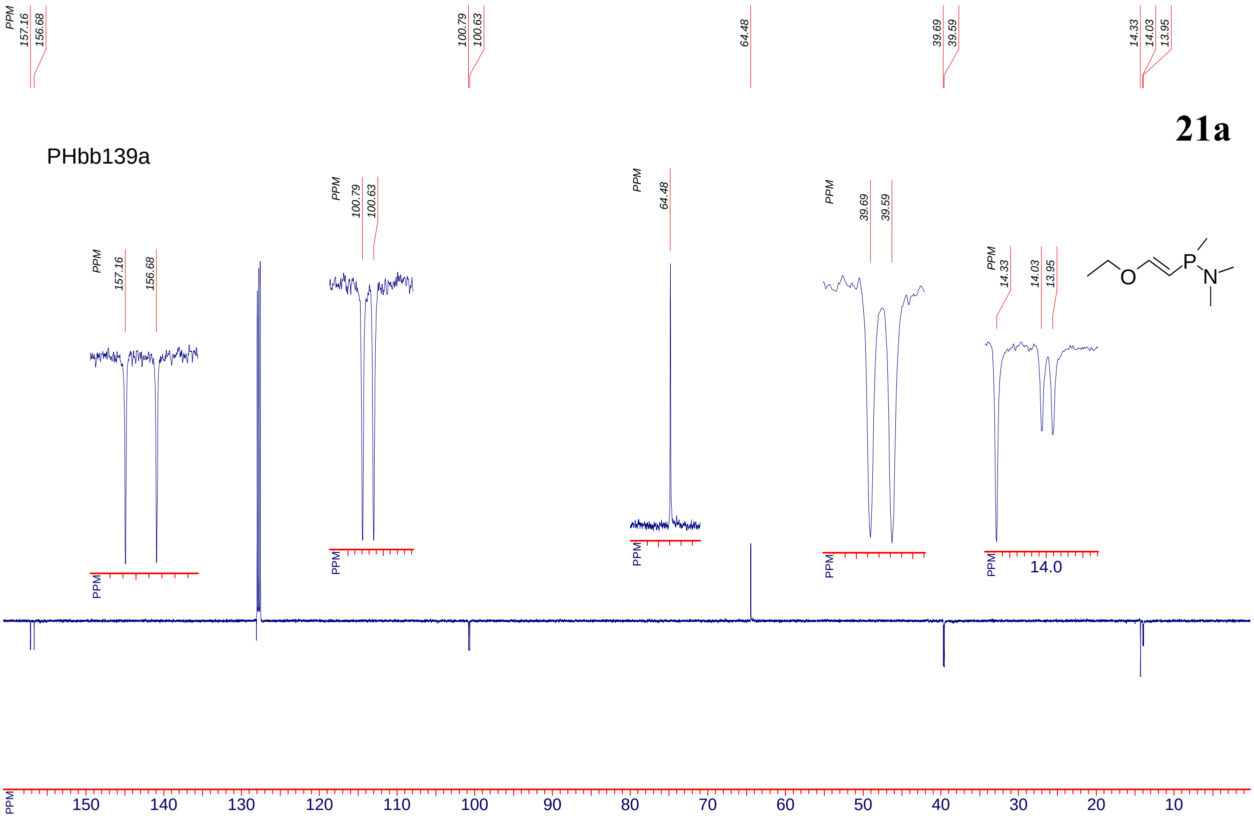
File name: phbb126A-C13APT	Operator: root	SF: 125.7578 MHz	NSC: 429	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 14-Jul-2008	Solvent: DMSO	SW: 30303 Hz	TE: 0 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

21a

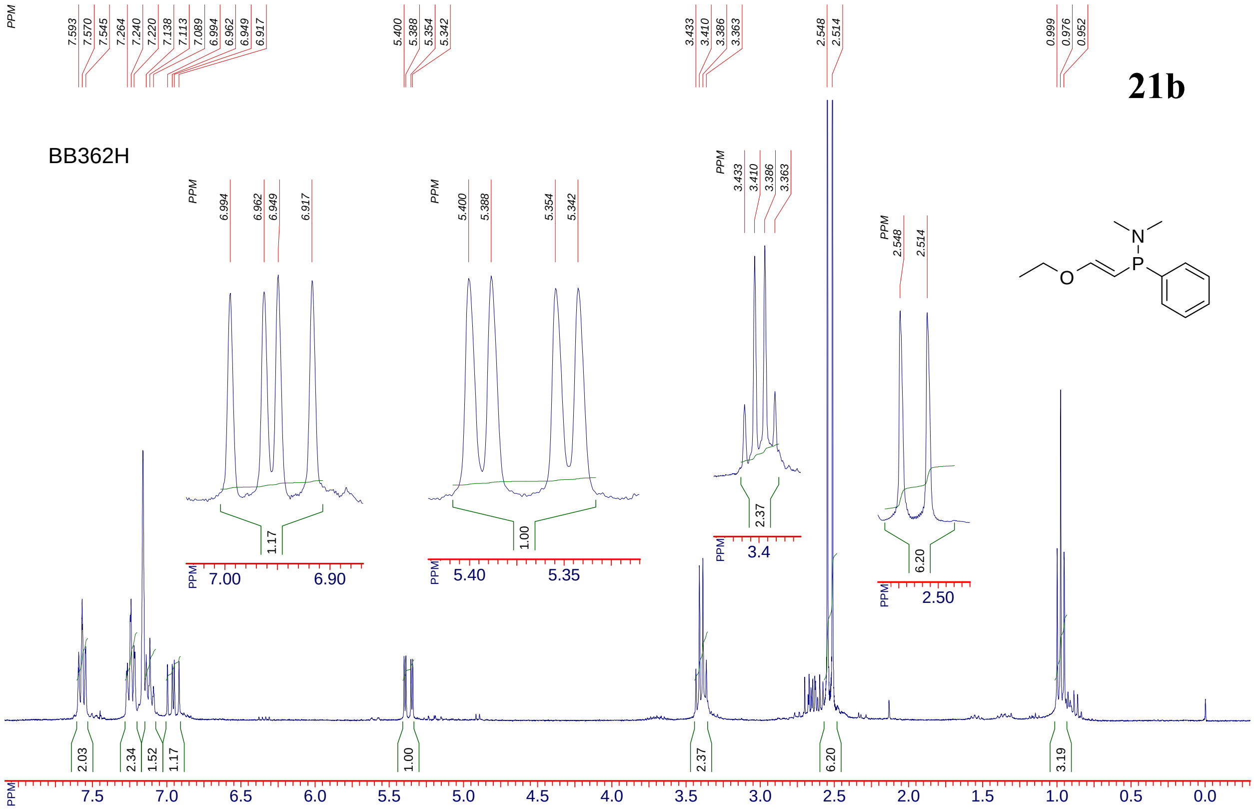


File name: BB139H	Operator:	SF: 299.9430 MHz	NSC: 7	PW: 8.00 usec, RG: 16	SI: 32768
Date: 10-Sep-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	

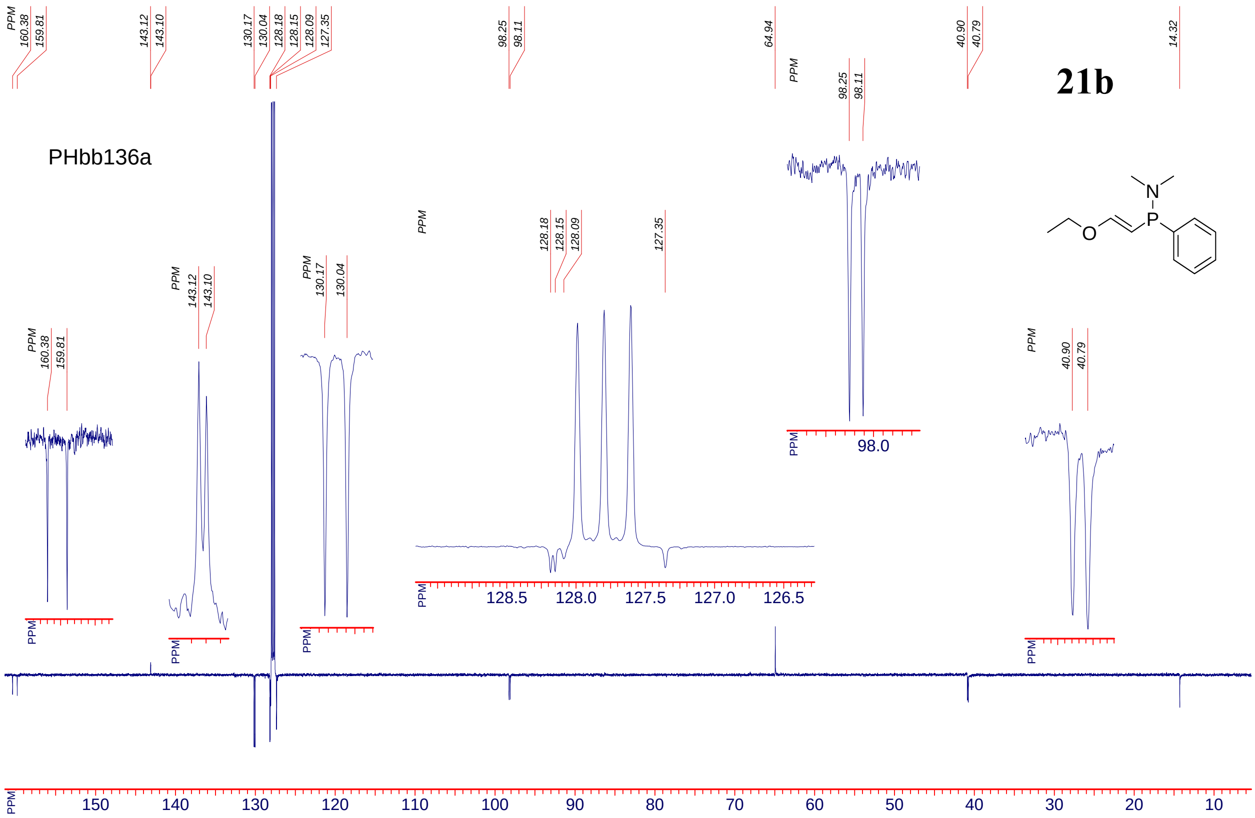
21a



File name: PHbb139a	Operator: root	SF: 125.7578 MHz	NSC: 270	PW: 0.00 usec, RG: 35840	SI: 65536
Date: 10-Sep-2008	Solvent: c6d6	SW: 30303 Hz	TE: 678 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

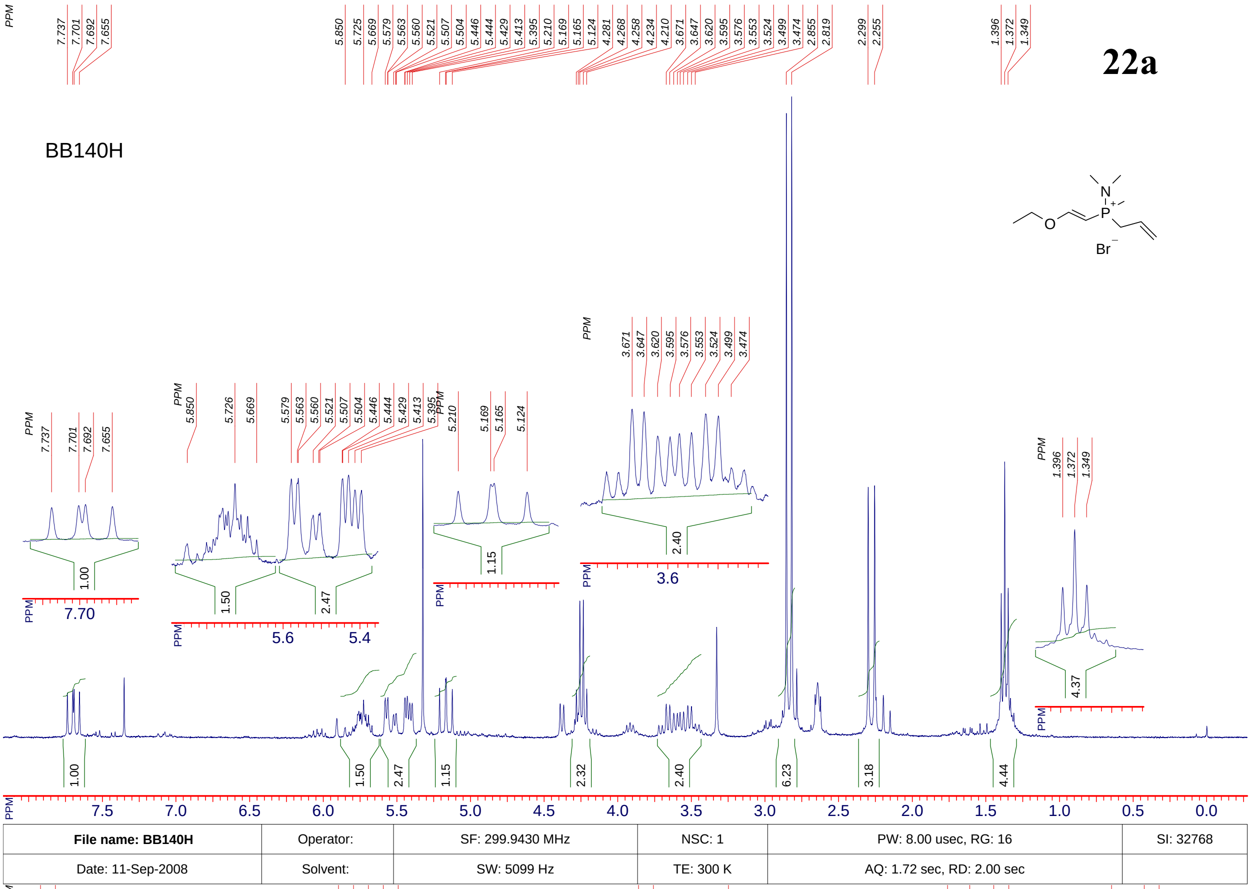


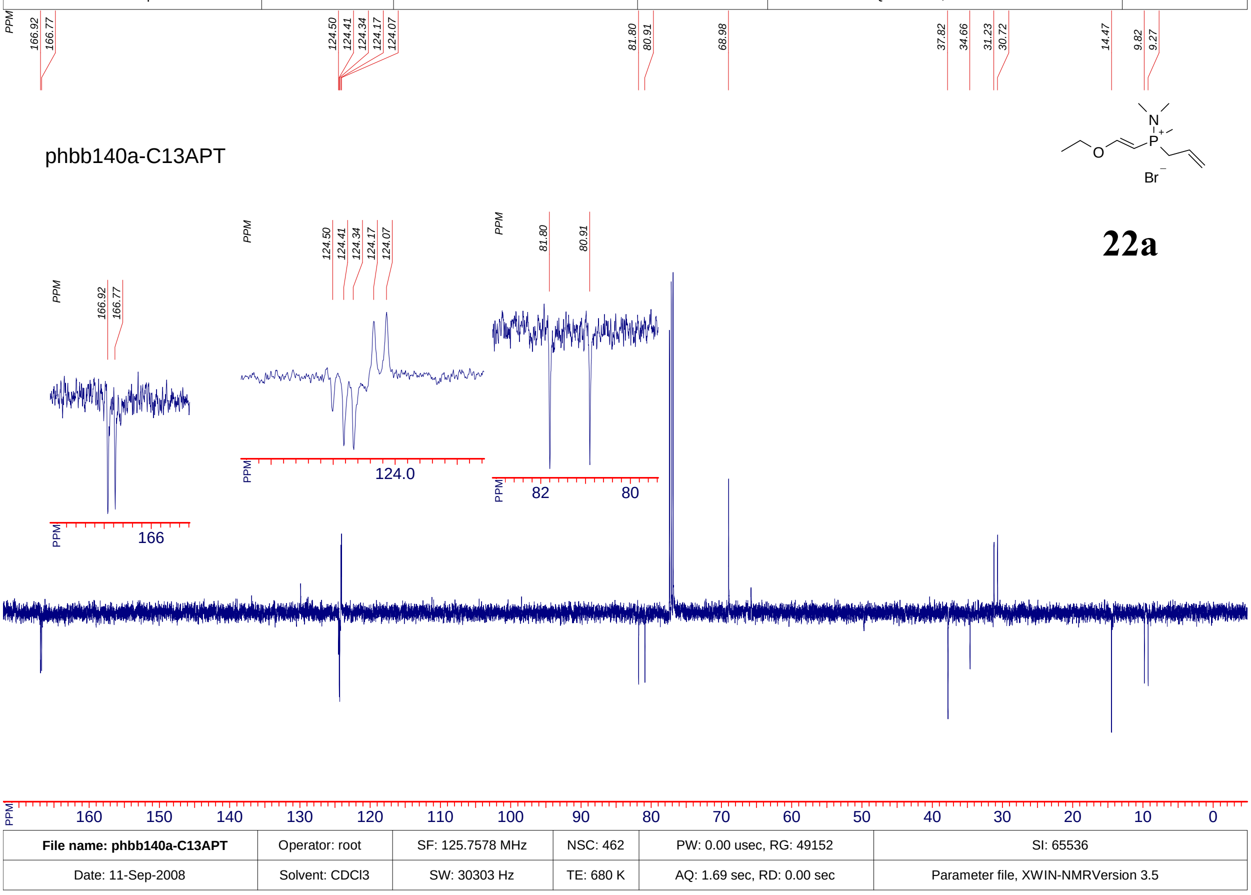
File name: BB362H	IOH	SF: 299.9430 MHz	NSC: 1	PW: 8.00 usec, RG: 16	SI: 32768
Date: 01-Aug-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.71 sec, RD: 2.00 sec	*BB362H*



File name: PHbb136a	Operator: root	SF: 125.7578 MHz	NSC: 692	PW: 0.00 usec, RG: 30720	SI: 65536
Date: 01-Aug-2008	Solvent: C6D6	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

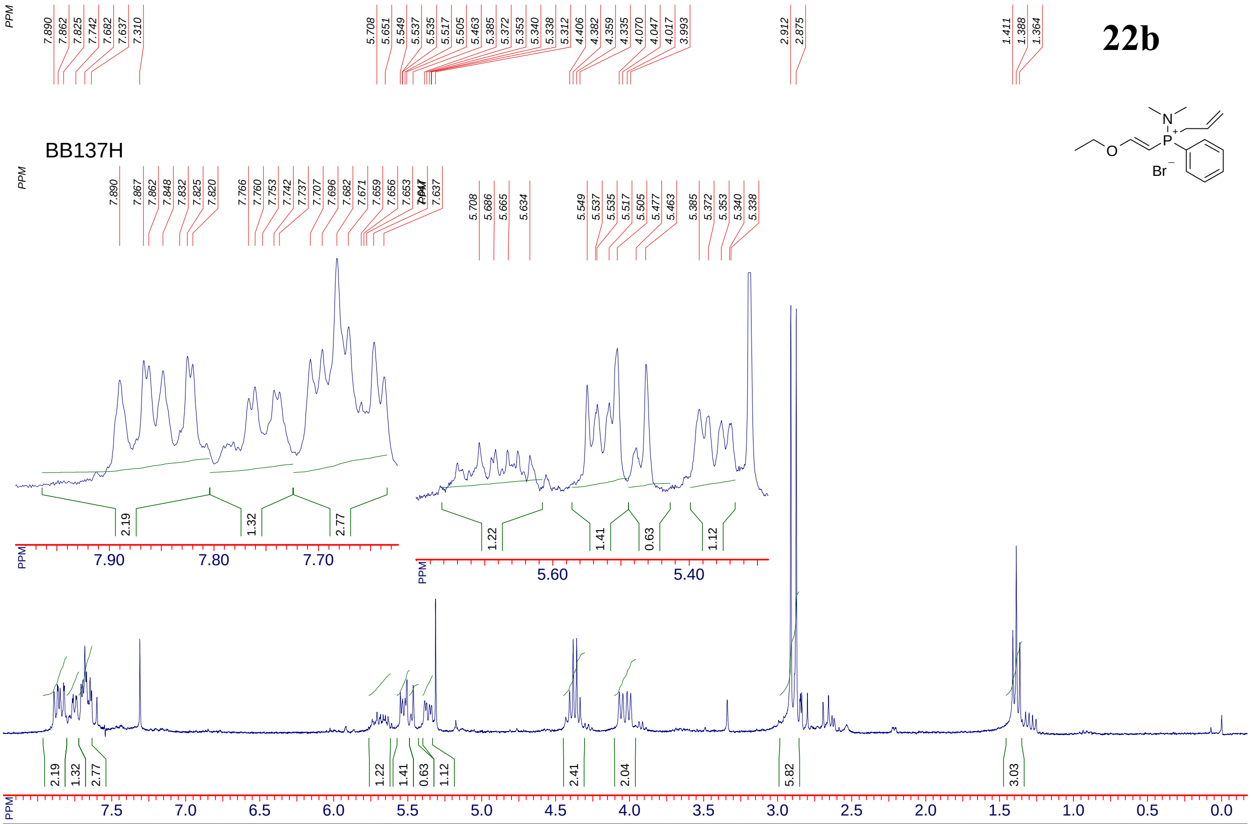
22a


BB140H
File name: BB140H
Operator:
SF: 299.9430 MHz
NSC: 1
PW: 8.00 usec, RG: 16
SI: 32768
Date: 11-Sep-2008
Solvent:
SW: 5099 Hz
TE: 300 K
AQ: 1.72 sec, RD: 2.00 sec


phbb140a-C13APT
File name: phbb140a-C13APT
Operator: root
SF: 125.7578 MHz
NSC: 462
PW: 0.00 usec, RG: 49152
SI: 65536
Date: 11-Sep-2008
Solvent: CDCl3
SW: 30303 Hz
TE: 680 K
AQ: 1.69 sec, RD: 0.00 sec
Parameter file, XWIN-NMRVersion 3.5

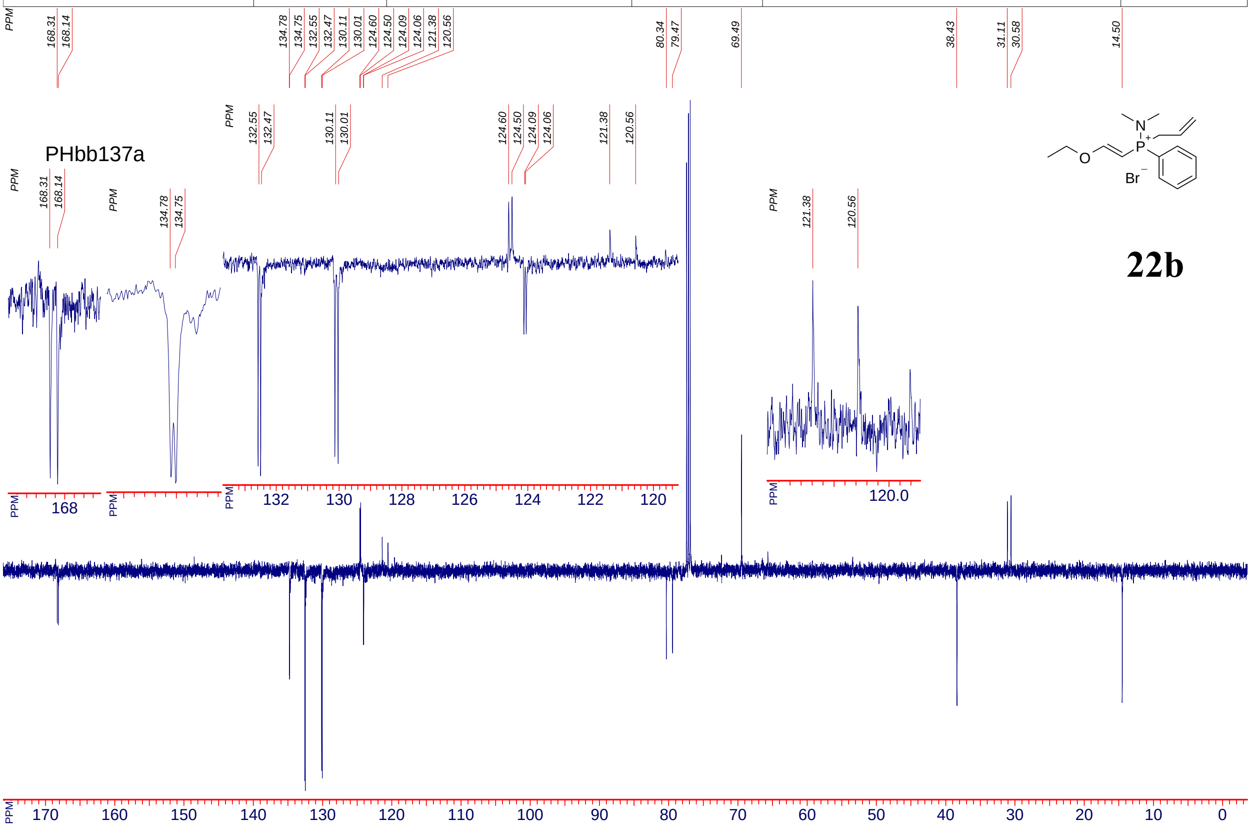
22a

22b

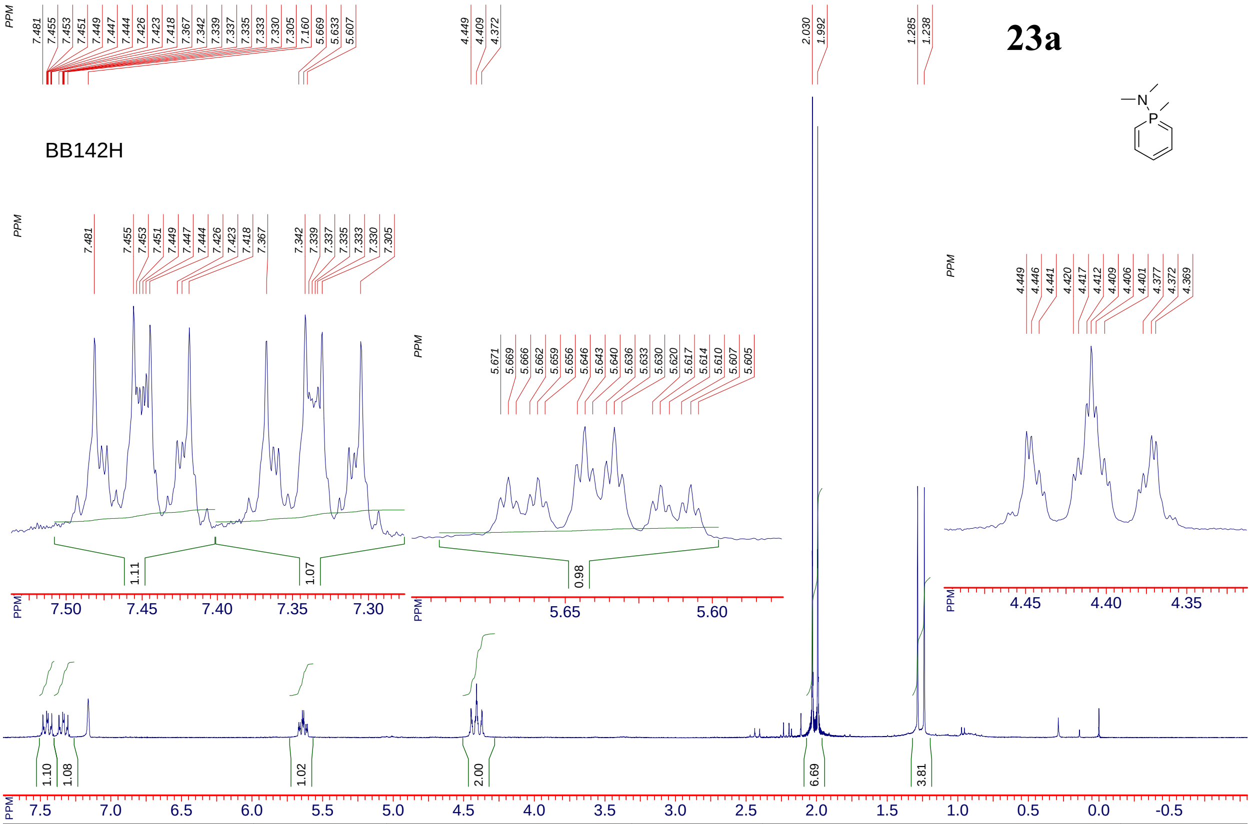


File name: BB137H	Operator:	SF: 299.9430 MHz	NSC: 3	PW: 8.00 usec, RG: 16	SI: 32768
Date: 09-Sep-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.71 sec, RD: 2.00 sec	

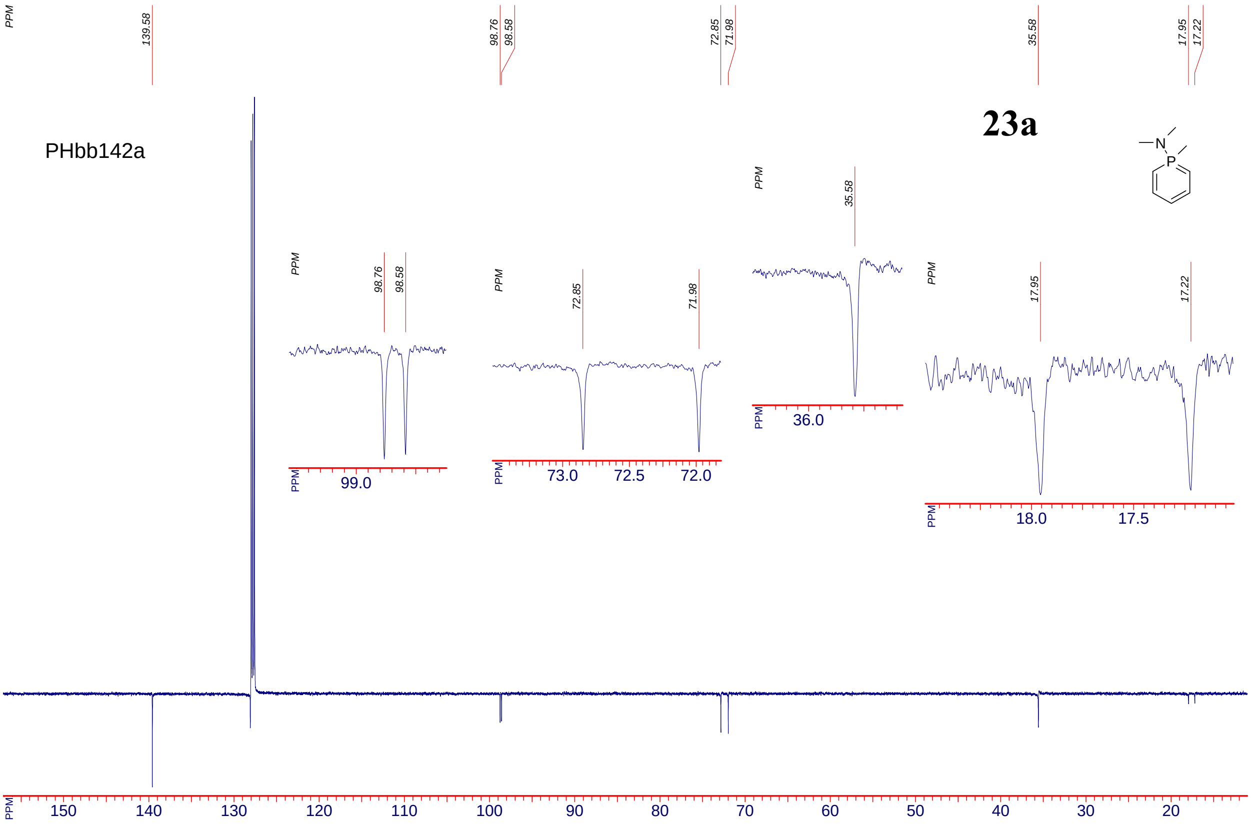
22b



File name: PHbb137a	Operator: root	SF: 125.7578 MHz	NSC: 581	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 01-Aug-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

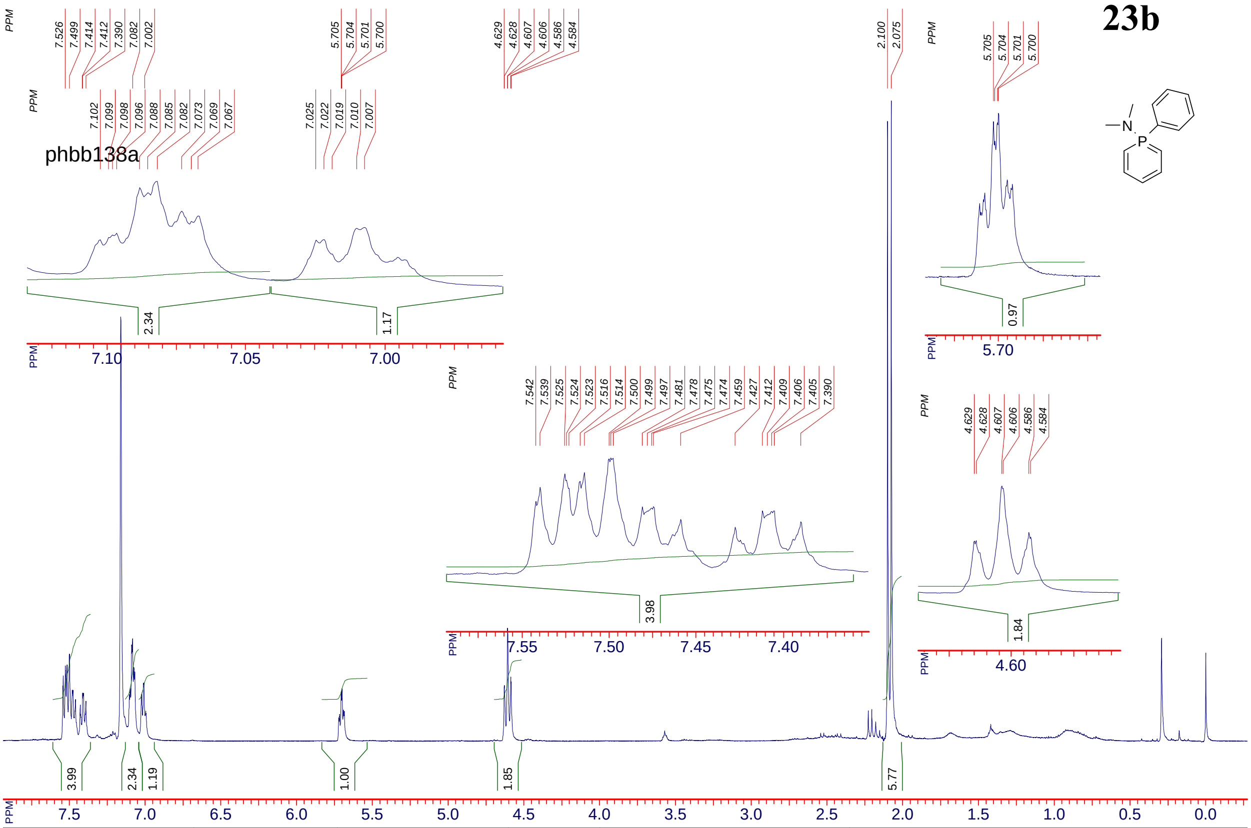


File name: BB142H	Operator:	SF: 299.9430 MHz	NSC: 1	PW: 8.00 usec, RG: 16	SI: 32768
Date: 16-Sep-2008	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.72 sec, RD: 2.00 sec	



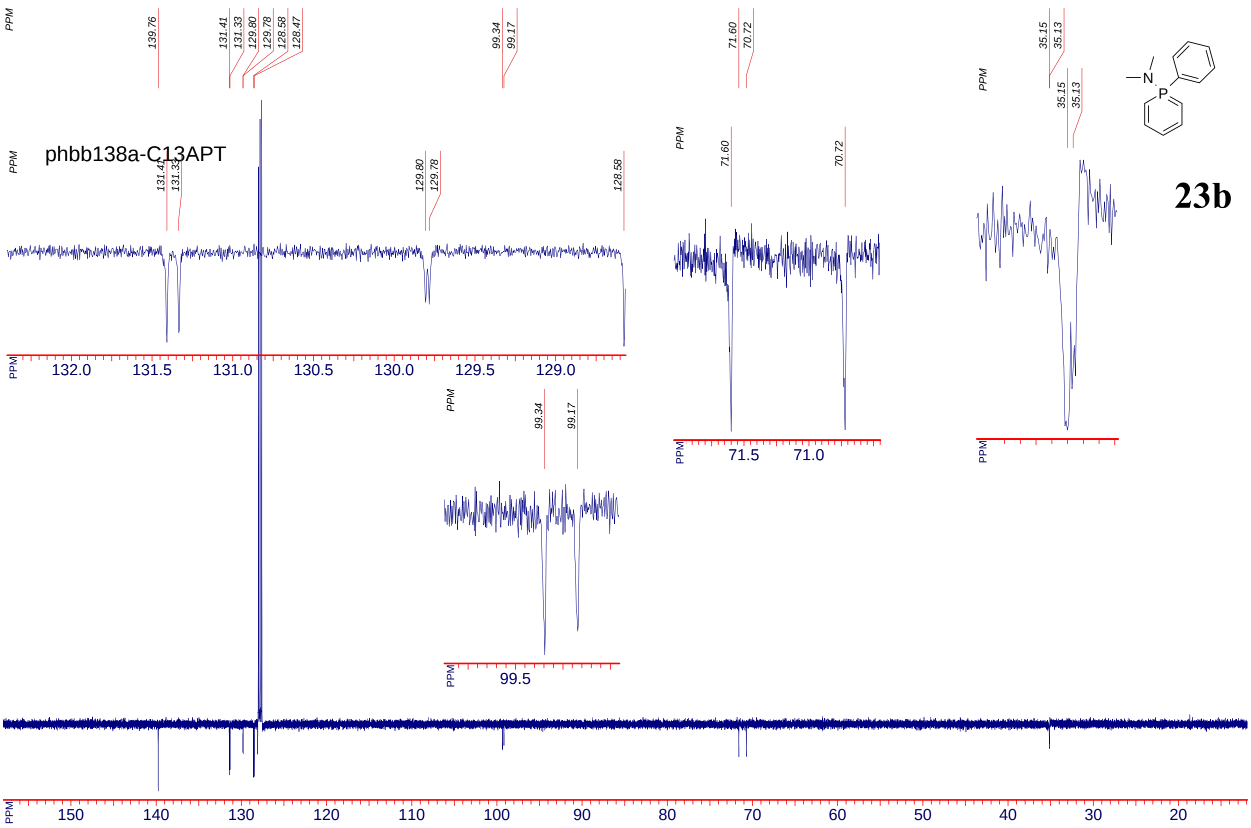
File name: PHbb142a	Operator: root	SF: 125.7578 MHz	NSC: 396	PW: 0.00 usec, RG: 25600	SI: 65536
Date: 15-Sep-2008	Solvent: c6d6	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	

23b

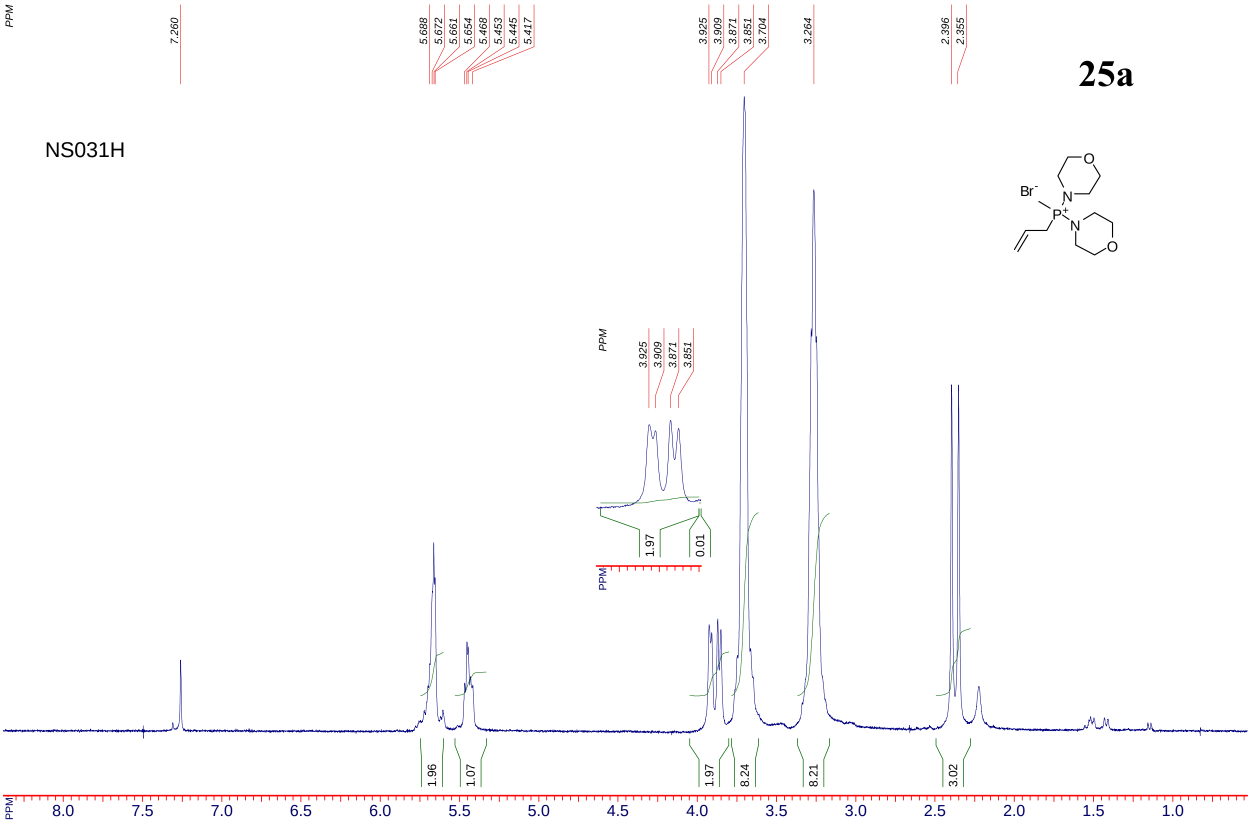


File name: phbb138a	Operator: root	SF: 500.1300 MHz	NSC: 1	PW: 0.00 usec, RG: 40	SI: 32768
Date: 09-Sep-2008	Solvent: C6D6	SW: 8013 Hz	TE: 678 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

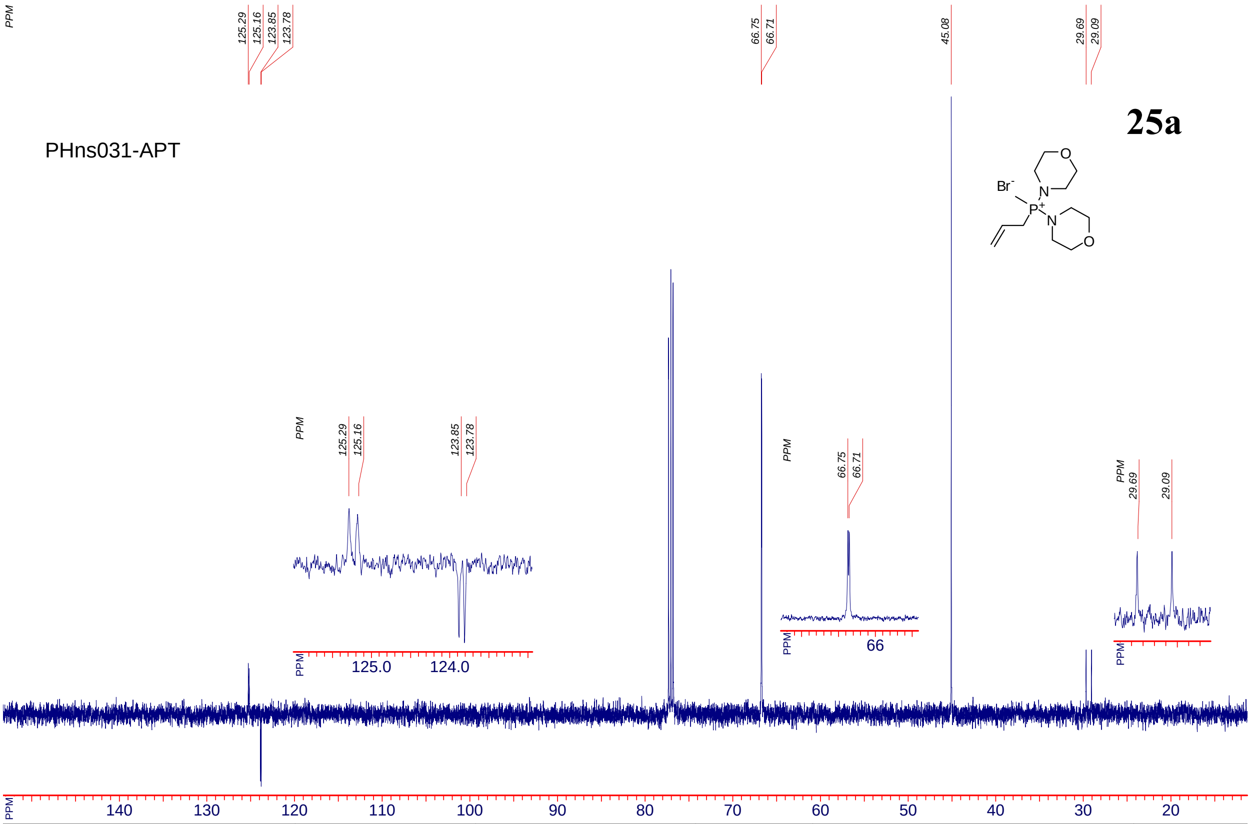
23b



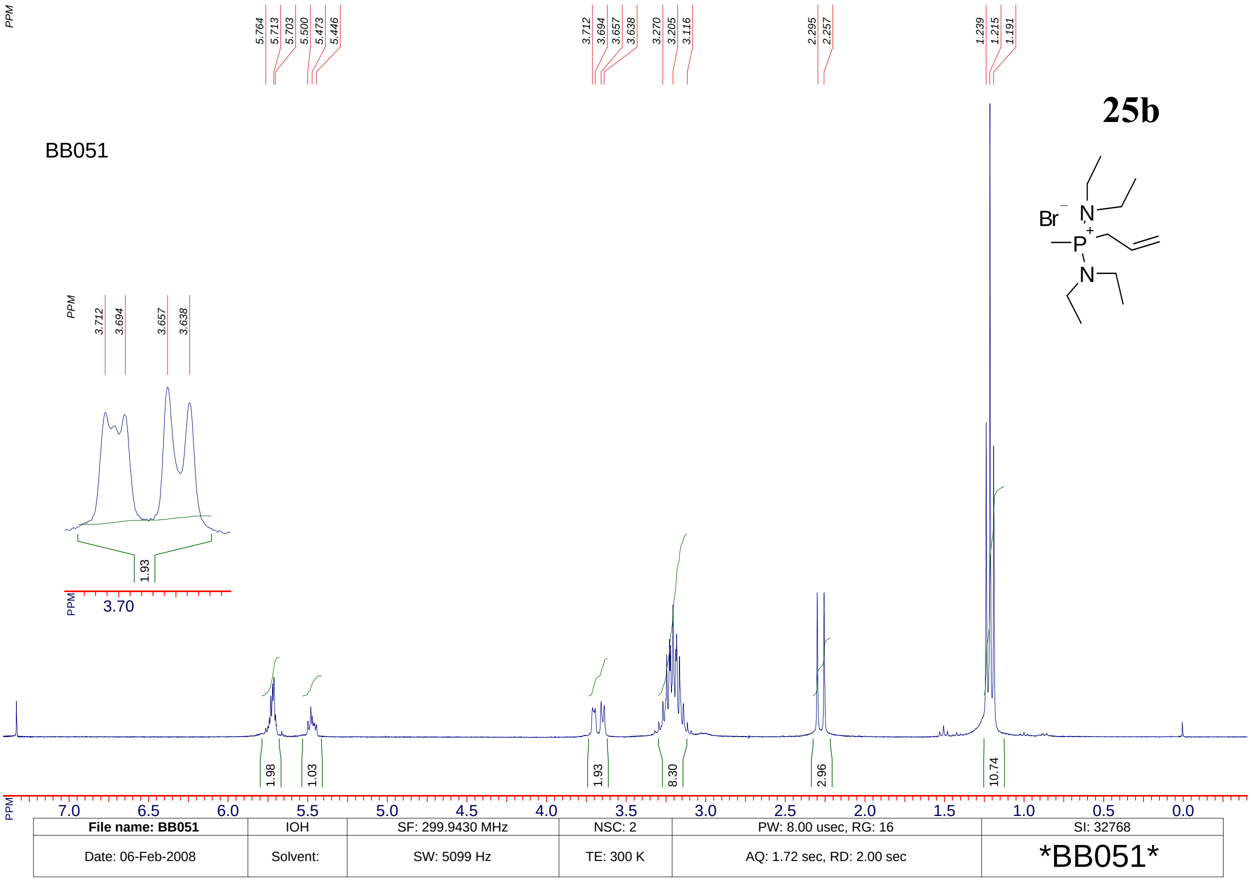
File name: phbb138a-C13APT	Operator: root	SF: 125.7578 MHz	NSC: 376	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 09-Sep-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 678 K	AQ: 1.69 sec, RD: 0.00 sec	

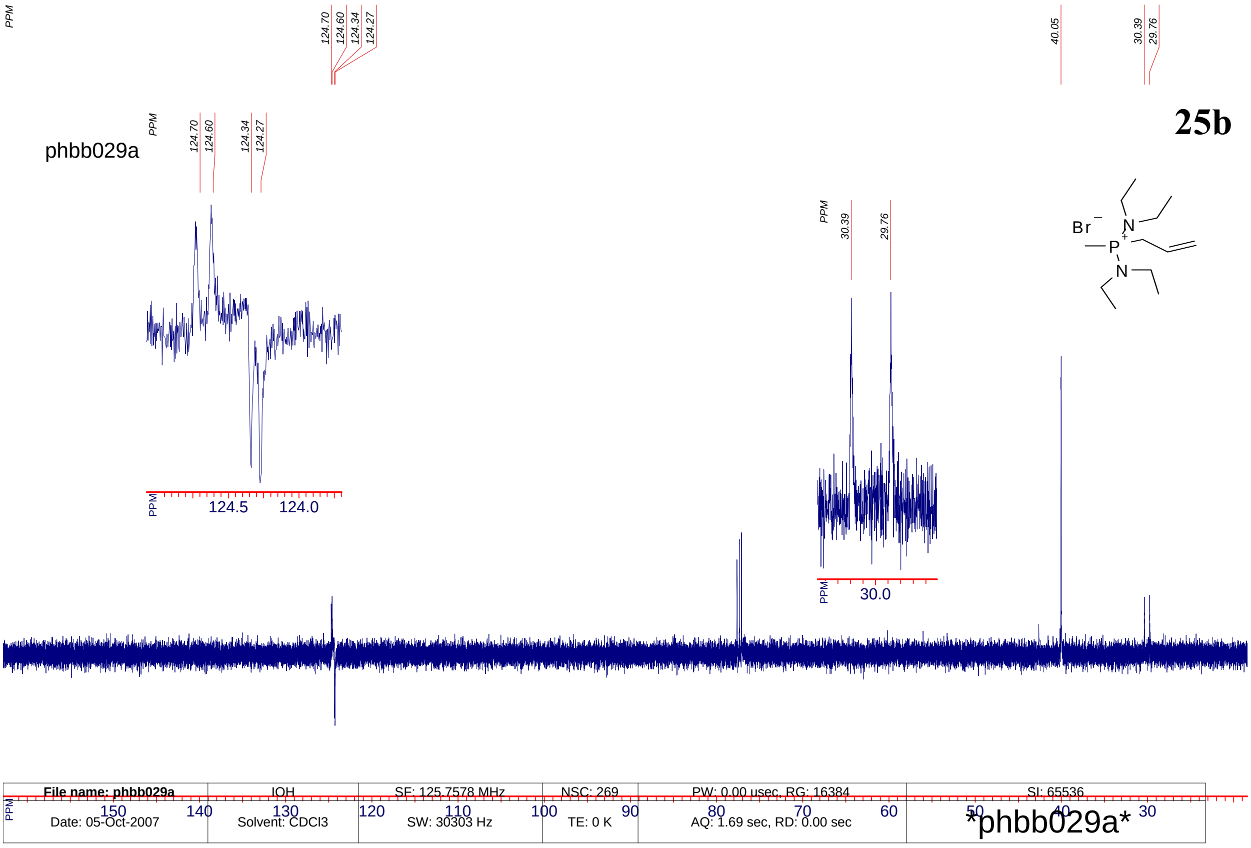


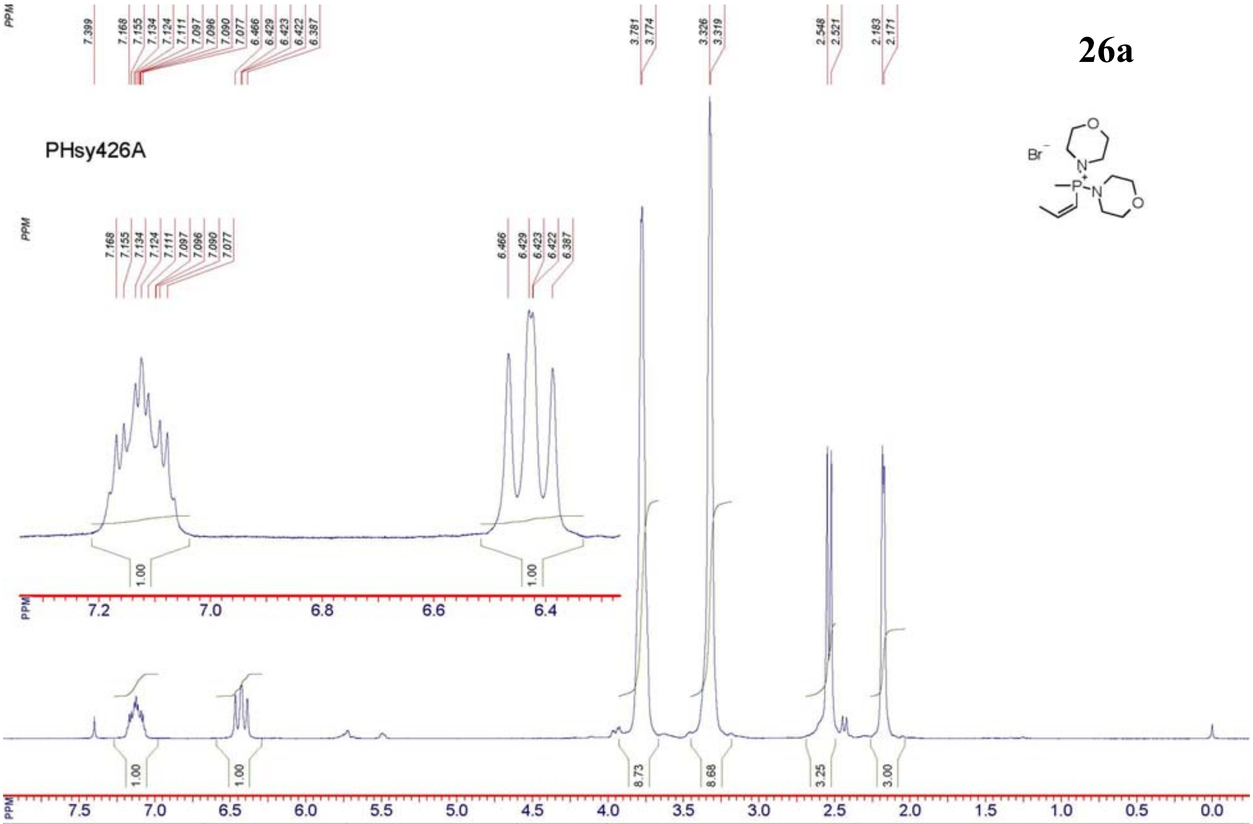
File name: NS031H	Operator:	SF: 299.9430 MHz	NSC: 2	PW: 8.00 usec, RG: 22	SI: 32768
Date: 09-Dec-2009	Solvent:	SW: 5099 Hz	TE: 300 K	AQ: 1.73 sec, RD: 2.00 sec	



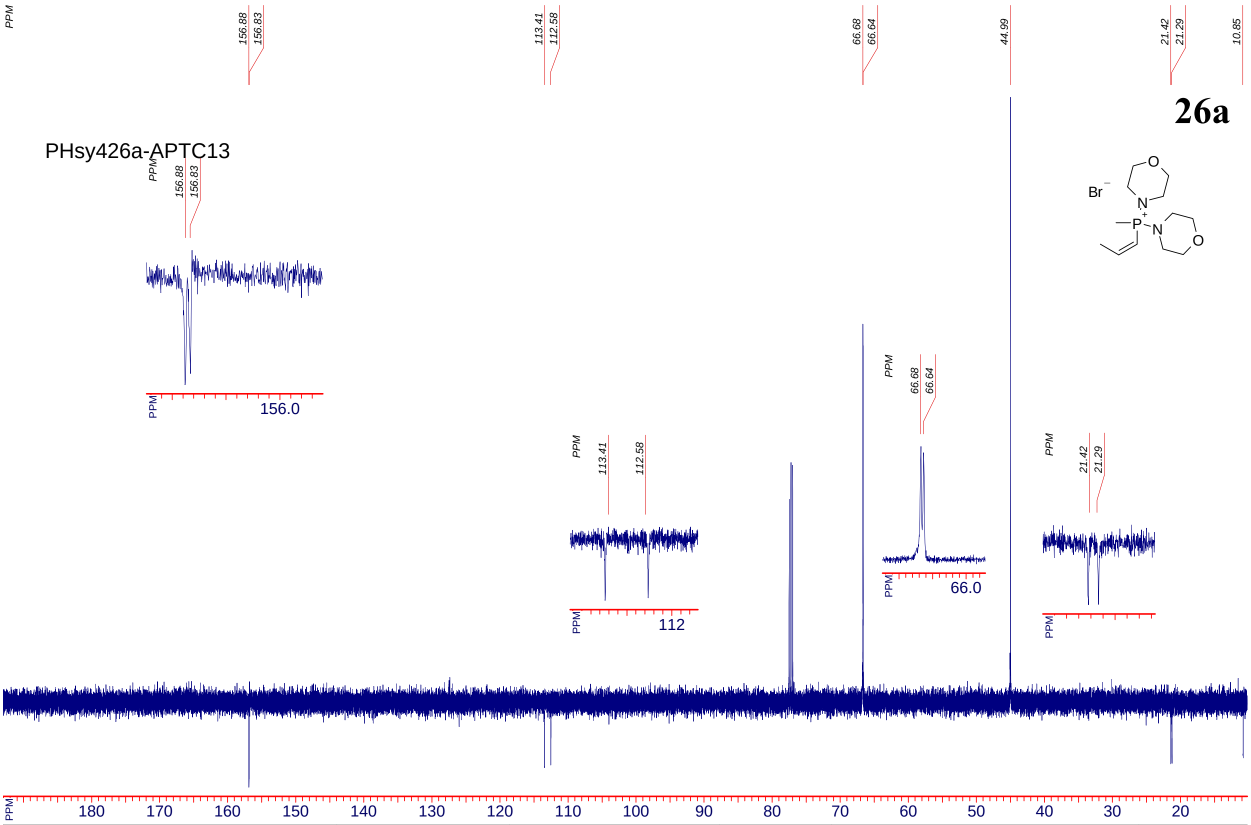
File name: PHns031-APT	Operator: root	SF: 125.7578 MHz	NSC: 214	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 09-Dec-2009	Solvent: CDCl3	SW: 30303 Hz	TE: 681 K	AQ: 1.69 sec, RD: 0.00 sec	


25b
BB051
Br⁻ N P⁺ N
PPM 3.712 3.694 3.657 3.638
1.93
3.70
1.98 1.03 1.93 8.30 2.96 10.74
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
File name: BB051 | IOH | SF: 299.9430 MHz | NSC: 2 | PW: 8.00 usec, RG: 16 | SI: 32768
Date: 06-Feb-2008 | Solvent: | SW: 5099 Hz | TE: 300 K | AQ: 1.72 sec, RD: 2.00 sec | *BB051*


25b
phbb029a
124.70 124.60 124.34 124.27
124.5 124.0
40.05 30.39 29.76
30.0
Br⁻ N P⁺ N
150 140 130 120 110 100 90 80 70 60 50 40 30
File name: phbb029a | IOH | SF: 125.7578 MHz | NSC: 269 | PW: 0.00 usec, RG: 16384 | SI: 65536
Date: 05-Oct-2007 | Solvent: CDCl3 | SW: 30303 Hz | TE: 0 K | AQ: 1.69 sec, RD: 0.00 sec | *phbb029a*

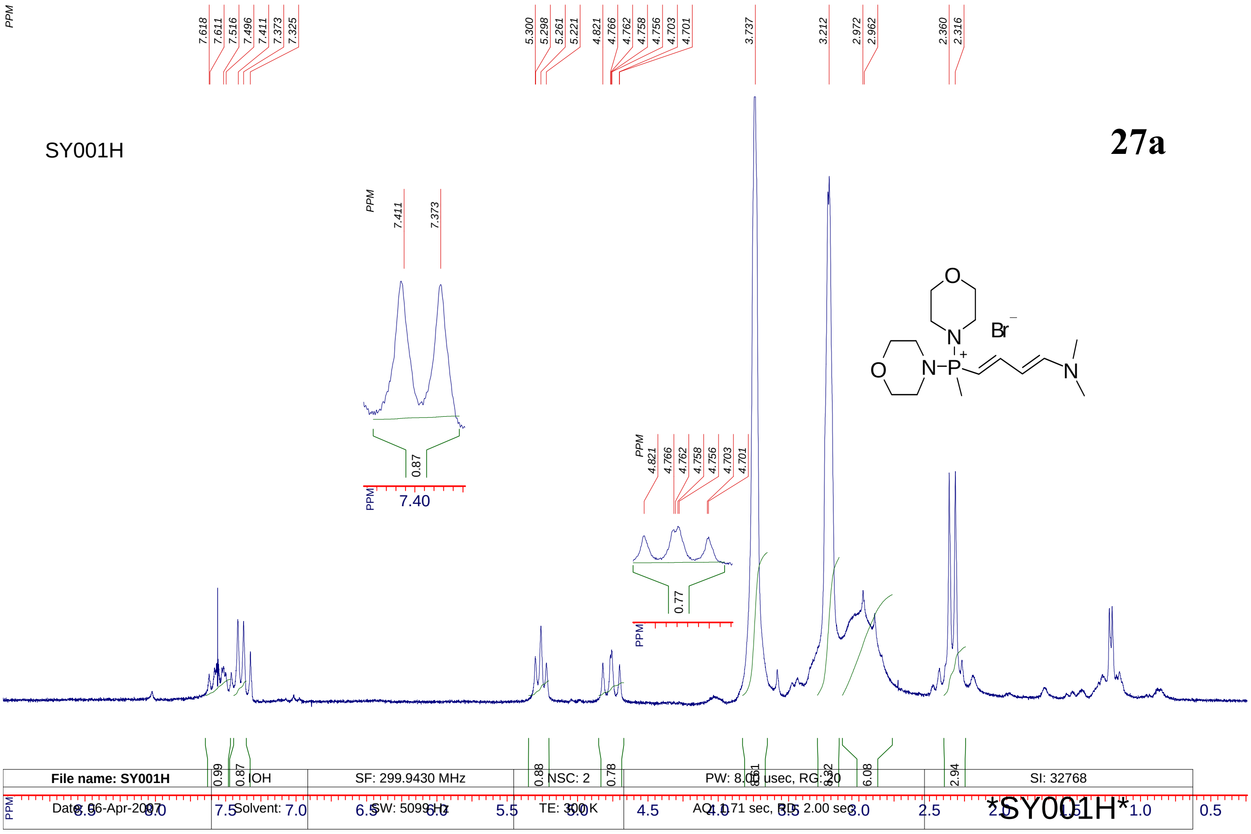


File name: PHsy426A	Operator: root	SF: 500.1300 MHz	NSC: 1	PW: 0.00 usec, RG: 32	SI: 32768
Date: 24-Sep-2008	Solvent: DMSO	SW: 8013 Hz	TE: 679 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

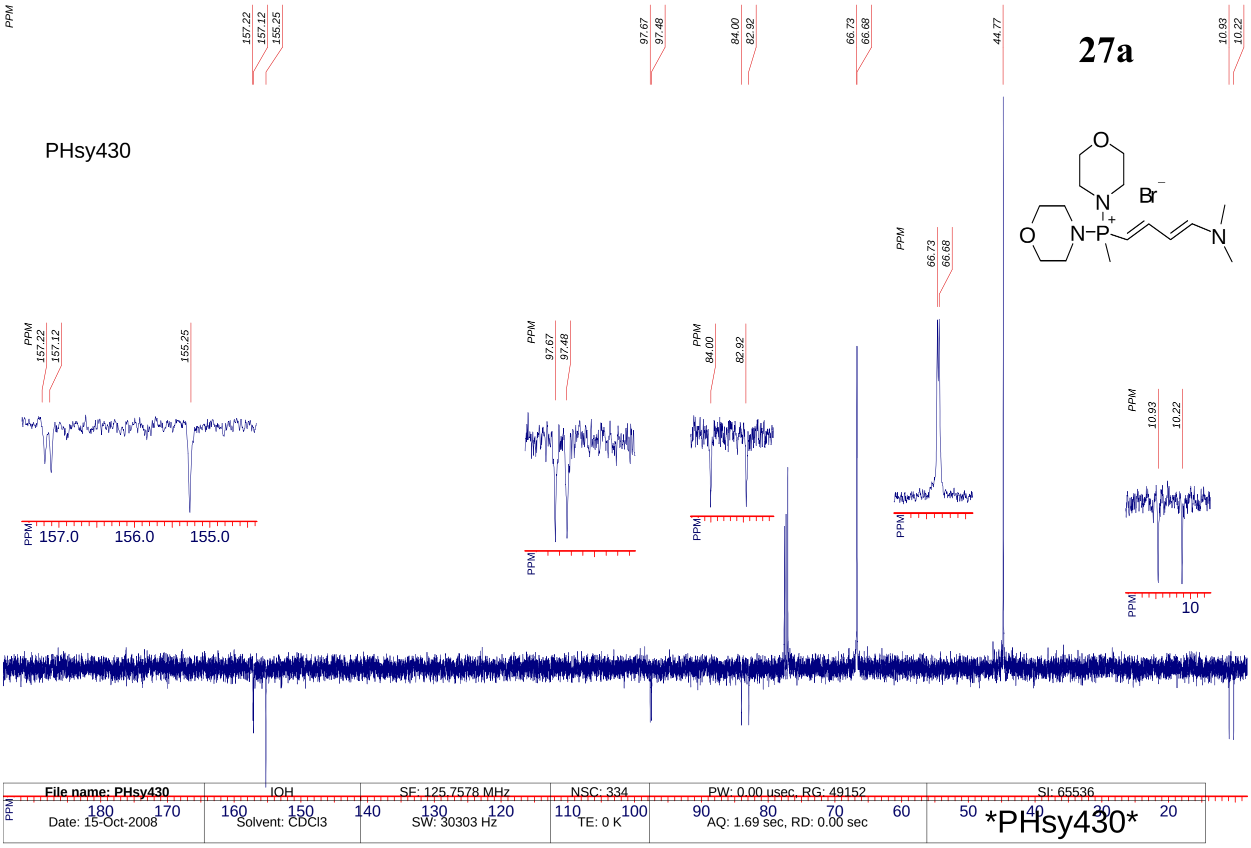


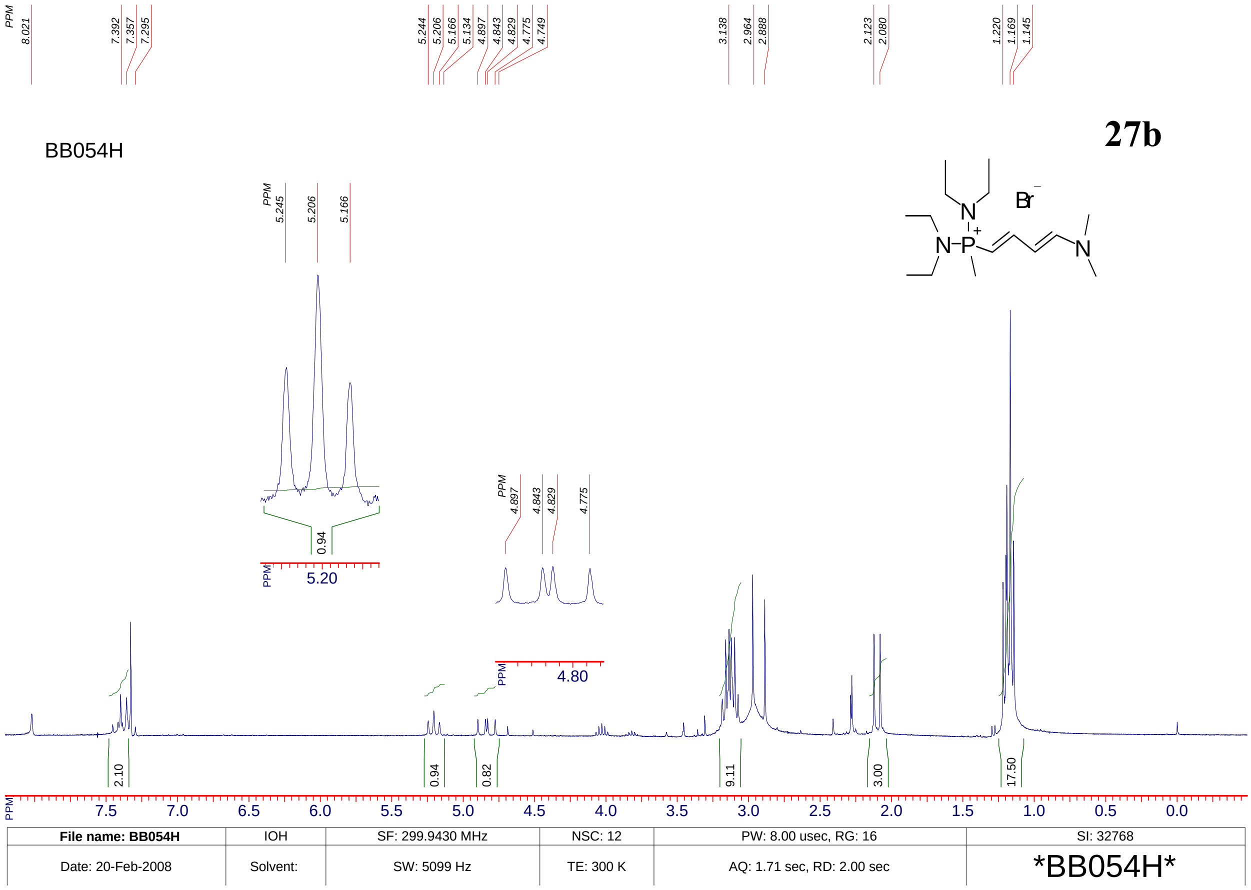
File name: PHsy426a-APTC13	Operator: root	SF: 125.7578 MHz	NSC: 372	PW: 0.00 usec, RG: 49152	SI: 65536
Date: 24-Sep-2008	Solvent: CDCl3	SW: 30303 Hz	TE: 679 K	AQ: 1.69 sec, RD: 0.00 sec	

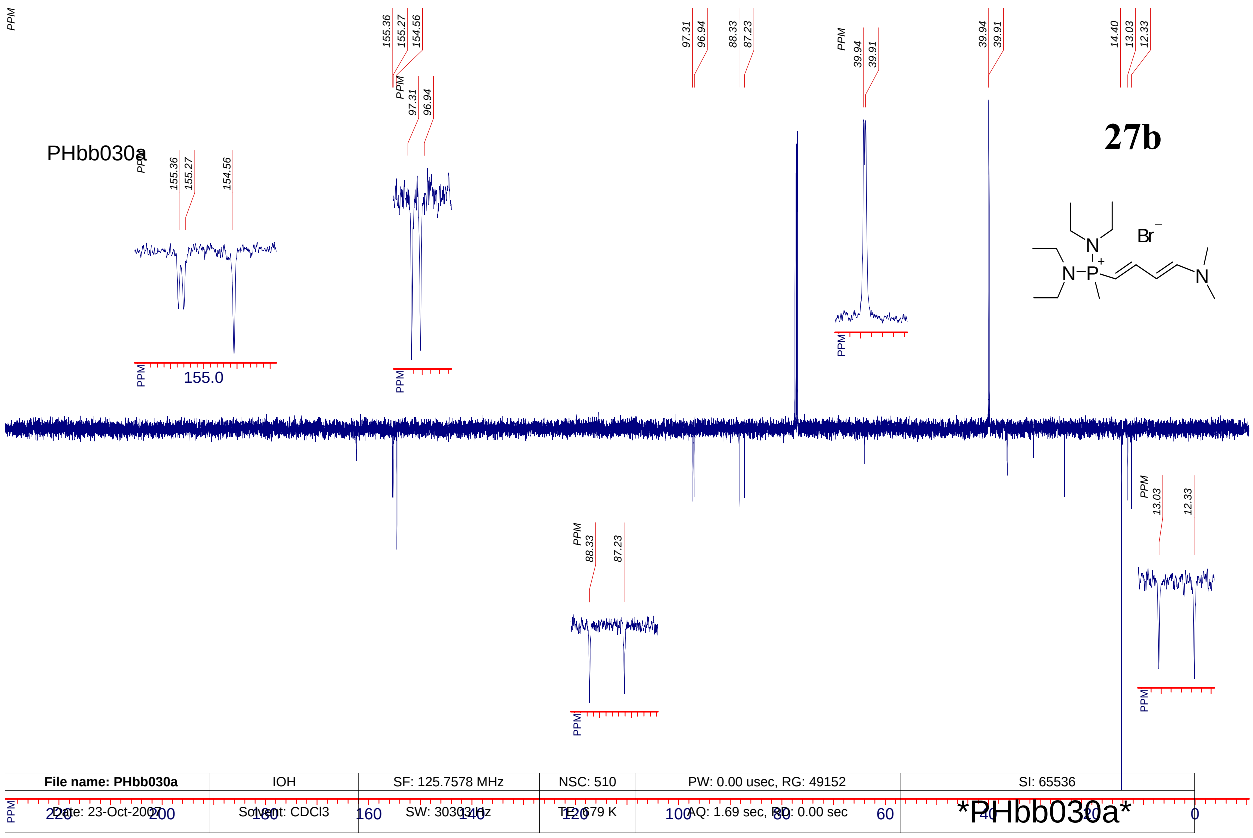
27a


SY001H
File name: SY001H
Date: 06-Apr-2007
IOH
Solvent:
SF: 299.9430 MHz
SW: 5099 Hz
NSC: 2
TE: 300 K
PW: 8.00 usec, RG: 20
AQ: 1.71 sec, RD: 2.00 sec
SI: 32768
SY001H
PPM

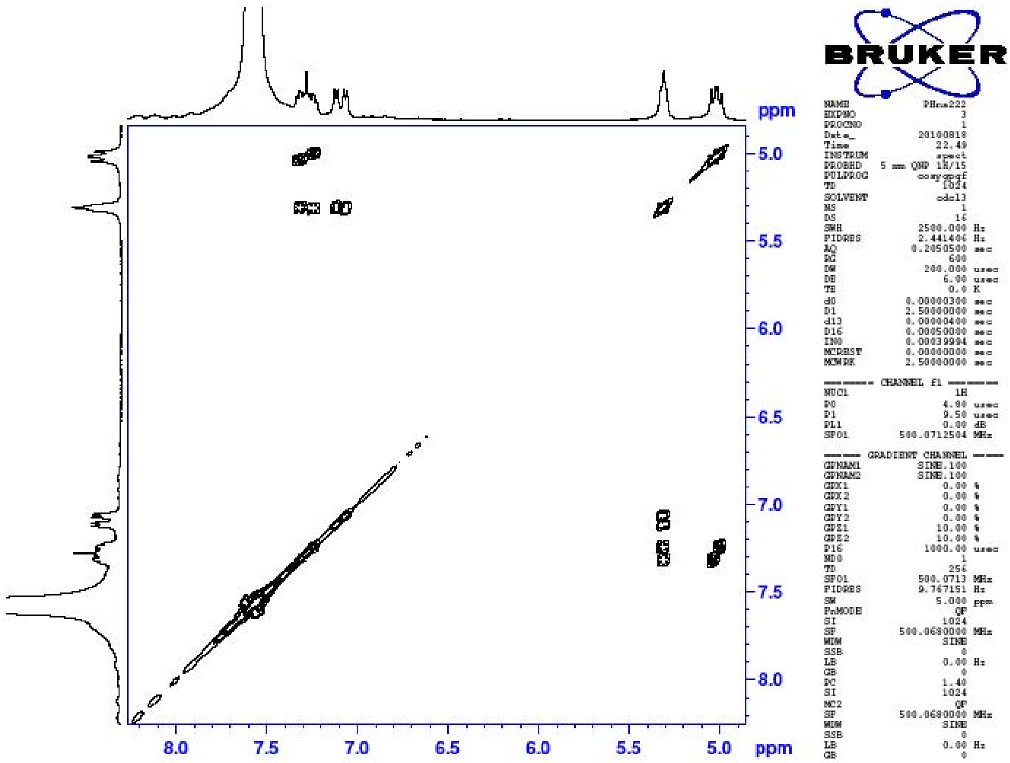
27a


PHsy430
File name: PHsy430
Date: 15-Oct-2008
IOH
Solvent: CDCl3
SF: 125.7578 MHz
SW: 30303 Hz
NSC: 334
TE: 0 K
PW: 0.00 usec, RG: 49152
AQ: 1.69 sec, RD: 0.00 sec
SI: 65536
PHsy430
PPM

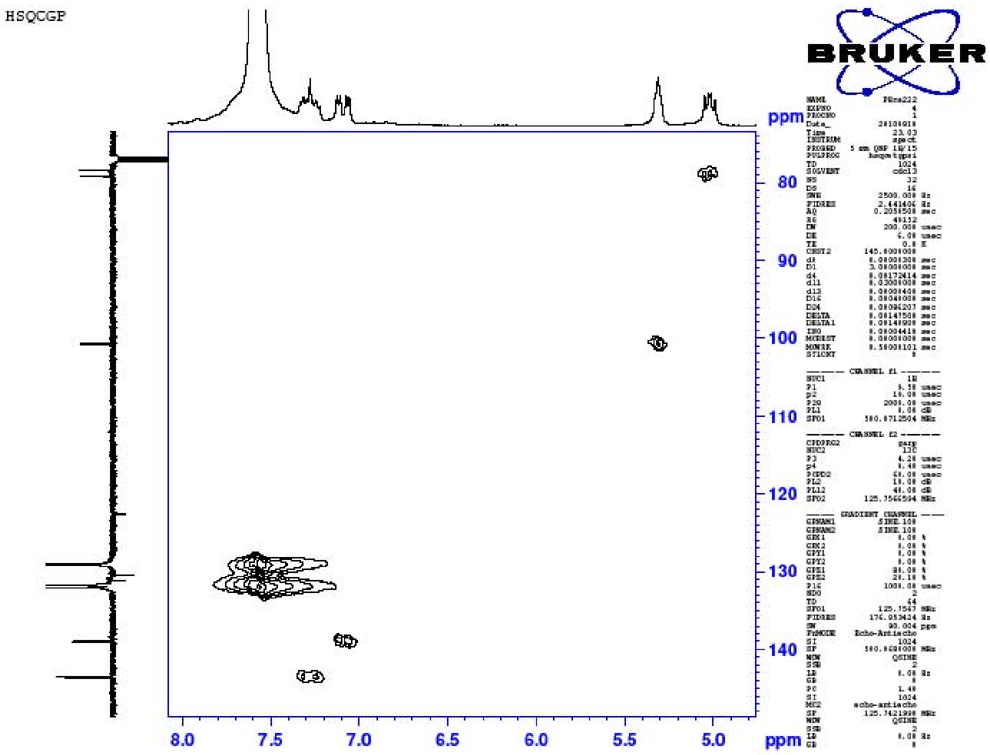

BB054H
27b
Br⁻
File name: BB054H
IOH
SF: 299.9430 MHz
NSC: 12
PW: 8.00 usec, RG: 16
SI: 32768
Date: 20-Feb-2008
Solvent:
SW: 5099 Hz
TE: 300 K
AQ: 1.71 sec, RD: 2.00 sec
BB054H


PHbb030a
27b
Br⁻
File name: PHbb030a
IOH
SF: 125.7578 MHz
NSC: 510
PW: 0.00 usec, RG: 49152
SI: 65536
Date: 23-Oct-2007
Solvent: CDCl3
SW: 30303 Hz
TE: 279 K
AQ: 1.69 sec, RD: 0.00 sec
PHbb030a

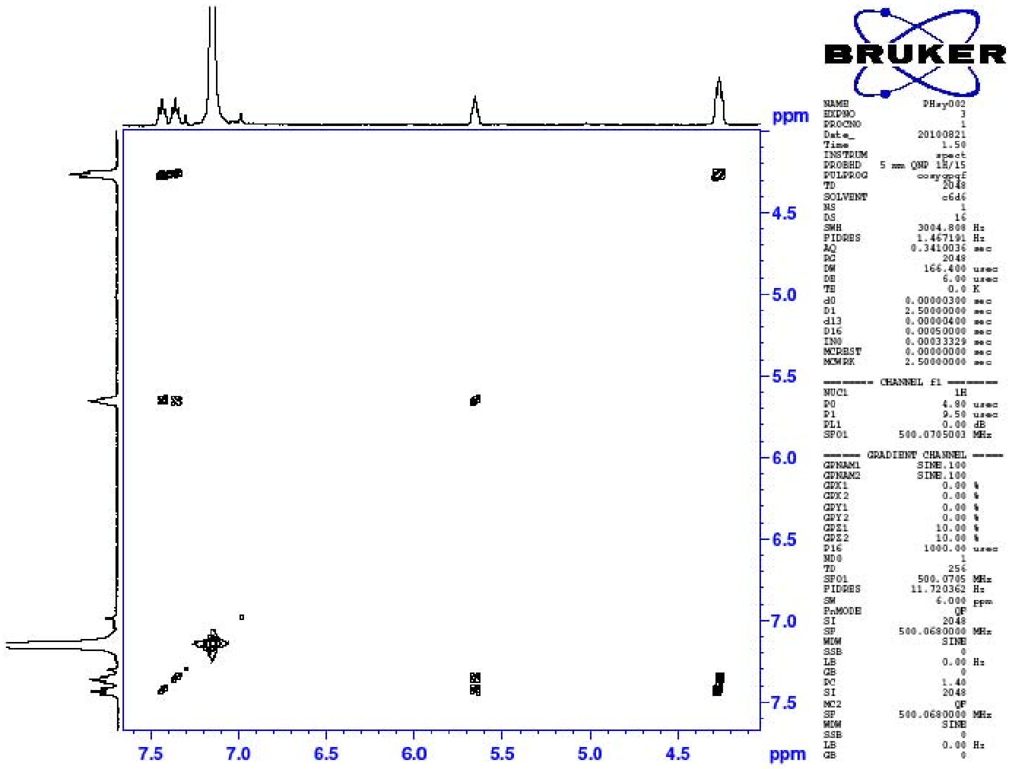
H-H COSY for compound **10**



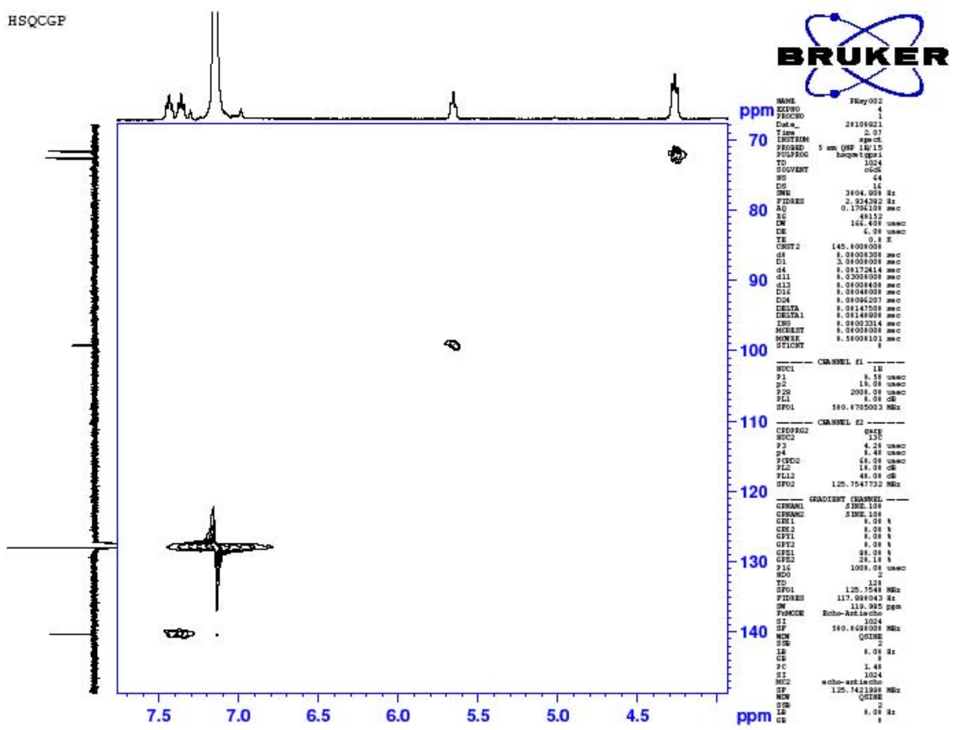
HSQC for compound **10**



H-H COSY for compound **16a** (only significant aromatic region is shown)



HSQC for compound **16a** (only significant aromatic region is shown)



X-ray data for **16a.**

Crystal data: $C_{13}H_{21}N_2O_2P$, M 268.29, orthorhombic, space group $P2_12_12_1$, *a* = 7.65380(10), *b* = 11.5537(2), *c* = 15.5946(3) Å, V = 1379.03(4)Å^3, Z = 4, d_c = 1.292 g·cm^{-3}, μ = 0.196 mm^{-1}, F(000) = 576, crystal size ca. 0.20 × 0.33 × 0.38 mm. All crystallographic measurements were performed at 173K on a Bruker Smart Apex II diffractometer operating in the ω and φ scans mode. The intensity data were collected within the range of 2.19 ≤ θ ≤ 28.59° using Mo-K_α radiation (λ = 0.71078 Å). The intensities of 14886 reflections were collected (3301 unique reflections, R_{merg} = 0.0288). The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the Bruker SHELXTL program package[1]. All hydrogen atoms were refined isotropically. In the refinement 3301 reflections (3124 reflections with I ≥ 2σ(I)) were used. Convergence was obtained at R1 = 0.0320and wR2 = 0.0724, for all reflection and R1 = 0.0292 and wR2 = 0.0706, GOF = 1.052 for observed (247 parameters; observed/variable ratio 12.6; the largest and minimal peaks in the final difference map 0.23 and –0.26 e/Å^3, weighting scheme is as follows: $\omega = 1/[\sigma^2(Fo^2) + (0.044P)^2 + 0.1255P]$, where $P = (Fo^2 + 2Fc^2)/3$)

The molecular structure of compound **16a** was determined by single crystal X-ray diffraction. The perspective view of molecule **16a** is given in the figure below.