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Catalyst-free addition of secondary phosphine chalcogenides to pyrazolecarbaldehydes

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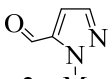
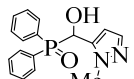
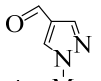
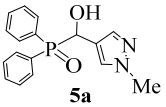
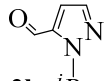
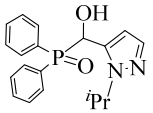
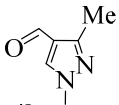
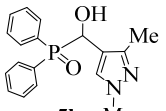
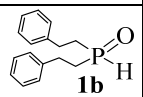
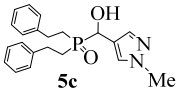
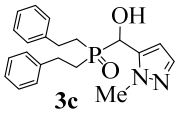
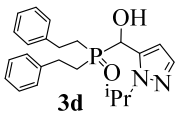
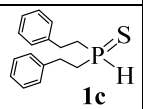
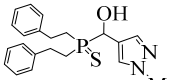
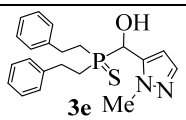
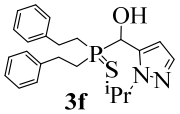
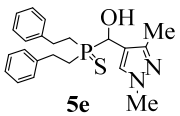
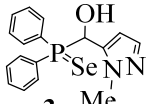
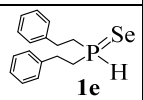
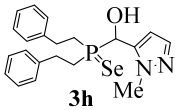
1.1. Materials and apparatus

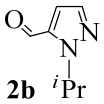
All manipulations with air- and moisture-sensitive compounds were performed in oven dried glassware in an atmosphere of dry argon. Commercially available (Aldrich) diphenylphosphine oxide **1a** was used as received. Diphenylphosphine selenide **1d** was synthesized by oxidation of commercially available diphenylphosphine (Aldrich) with elemental selenium. Secondary phosphine chalcogenides **1b, 1c** and **1e** were prepared from styrene, elemental phosphorus, H_2O_2, sulfur or selenium as previously reported.[S1] Carbaldehydes **2a**, **2b** were new. Carbaldehydes **2c**, **2d** were prepared using a modification of literature routes.[S2] "Pyr" stand for pyrazole moiety. THF was freshly distilled from sodium benzophenone ketyl. Pyrazoles were dried over CaH_2 for 7 days and after that distilled in a stream of dry Ar. DMF was kept over CaH_2 and distilled under reduced pressure and was stored over molecular sieves 4Å. 1-Methyl-, 1,3-dimethyl- and 1-isopropyl-1*H*-pyrazoles were purchased from Art-Chem GmbH, Germany. Solution of *n*-BuLi in *n*-hexane (2.5 *M*) was purchased from Chemetal GmbH, Germany.

The reaction was monitored using ^{31}P NMR spectroscopy by the disappearance of peaks of the initial secondary phosphine chalcogenides **1** (δ_P = 2.2–32.4 ppm) and appearance of new peaks corresponding to chalcogenophosphoryl derivatives **3** (δ_P = ~ 30–58 ppm). The ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P, and ^{77}Se NMR spectra were recorded on Bruker DPX 400 and Bruker AV-400 spectrometers (400.13, 100.61, 40.56, 376.50, 79.49, 161.98, and 76.31 MHz, respectively) in $CDCl_3$ and DMSO-d_6 solutions and referenced to TMS (^{1}H NMR, ^{13}C NMR, ^{29}Si NMR), $MeNO_2$ (^{15}N NMR), $CFCl_3$ (^{19}F NMR), H_3PO_4 (^{31}P NMR), and Me_2Se (^{77}Se NMR). The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment. All 2D NMR spectra were recorded by using a standard gradient Bruker pulse programs. HSQC spectra were recorded via double INEPT transfer in the phasesensitive TPPI mode with GARP decoupling during acquisition.[S3] HMBC spectra were obtained with the inverse technique and processed in the magnitude mode.[S4] IR spectra were recorded on a Bruker Vertex 70 instrument. Melting points were recorded on a Stuart melting point apparatus and are uncorrected. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer, while the P and Se contents were determined by combustion method.

1.2. **Table S1.** Chalcogenophosphoryl hydroxymethyl pyrazoles from pyrazolylcarbaldehydes and secondary phosphine chalcogenides[a]

Entry	$R_2P(X)H$	Aldehyde	*T*/°C	*t*/h	Product	Isolated yield, %
1	$Ph_2P(O)H$ **1a**	 **2a**	45-50 (23-25)	6 (8)	 **3a**	95 (93)
2	**1a**	 **4a**	45-50 (23-25)	6 (12)	 **5a**	90 (90)
3	**1a**	 **2b**	23-25	6	 **3b**	93
4	**1a**	 **4b**	45-50	12	 **5b**	90
5	 **1b**	**4a**	45-50	90	 **5c**	78
6	**1b**	**2a**	45-50	15	 **3c**	93
7	**1b**	**2b**	45-50	13	 **3d**	92
8	 **1c**	**4a**	45-50	65	 **5d**	90
9	**1c**	**2a**	45-50	94	 **3e**	92
10	**1c**	**2b**	45-50	91	 **3f**	87
11	**1c**	**4b**	45-50	94	 **5e**	85
12[b]	$Ph_2P(Se)H$ **1d**	**2a**	23-25	7	 **3g**	80
13[b]	 **1e**	**2a**	45-50 (23-25)	10 (25)	 **3h**	89 (10)

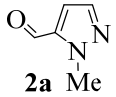
[a]Reaction conditions: secondary phosphine chalcogenide **1** (1.0 mmol), aldehyde **2**,**4** (1.05 mmol) stirring under inert atmosphere for the mentioned time in toluene (2 ml). [b]In Entries 12 and 13, bis(diorganoselenophosphoryl)selenides $(R_2PSe)_2Se$ (where R = Ph, $(CH_2)_2Ph$) are formed in 12% and 5% yield, respectively.



2b ^{i}Pr

1.2.1. 1-Isopropyl-1H-pyrazole-5-carbaldehyde (**2b**)

To a mechanically stirred solution of 1-isopropyl-1*H*-pyrazole (110 g, 1.0 mol) in THF (500 ml), a solution of *n*-BuLi (2.5 *M*, 1.05 mol, 420 ml) was added dropwise at the temperature below -5 °C. After the addition was completed, the cooling bath was removed and the resulted suspension stirred for 2 h. The temperature gradually grew up, and at the end of indicated period of time reached 22 °C. The mixture was stirred at that temperature for additional 2 h, then it was cooled to -15 °C, and DMF (1.1 mol, 80.0 g, 85 ml) was added dropwise. Cooling bath was removed, and the mixture was stirred overnight. The resulted solution was again cooled to -15 °C, and aqueous HCl (3 × 50 ml; 50 ml of 5% solution, 50 ml of 20% solution and finally 50 ml of conc. HCl) was added dropwise with vigorous stirring until pH ~7 was reached. The temperature was kept below 0 °C for this operation. Stirring was continued for additional 1.5 h, the organic phase was separated, the water phase was extracted consistently with CH_2Cl_2 (200 ml) and methyl *tert*-butyl ether (MTBE, 3×150 ml). The combined organic layers were subsequently washed by HCl solution (5%, 100 ml), saturated $NaHCO_3$ solution until pH was ~7, and brine (100 ml), dried over $MgSO_4$ and evaporated under reduced pressure (50 Torr). The residue was purified by distillation with 20-cm Vigreux column to give pure carbaldehyde **2b** (101 g, 73%) as a colorless oil; bp 34-36 °C (2 Torr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, Me), 5.38 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1H, CH), 6.83 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H-4 in Pyr), 7.50 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H-3 in Pyr), 9.82 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.95 (Me), 52.19 (CH), 114.96 (C-4 in Pyr), 137.75 (C-5 in Pyr), 137.96 (C-4 in Pyr), 179.20 (CHO). $C_7H_{10}N_2O$: calcd C 60.85, H 7.30, N 20.28; found: C 60.75, H 7.41, N 20.30.



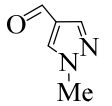
2a Me

1.2.2. 1-Methyl-1H-pyrazole-5-carbaldehyde (**2a**)

The title compound was prepared as it was described earlier from 1-methyl-1*H*-pyrazole (100 g, 1.22 mol), *n*-BuLi (2.5 *M*, 1.27 mol, 506 ml) and DMF (92.3 g, 1.27 mol, 97 ml) in dry THF (700 ml). Extraction was performed with MTBE (3×150 ml). After common work-up, carbaldehyde **2a** was purified by distillation (73 g, 55% yield), colorless oil; bp 55-56 °C at 5 Torr (lit. 67 °C at 16 Torr). [S5] ^{1}H NMR (300 MHz, $CDCl_3$): 4.18 (s, 3H, CH3-N), 6.91 (d, 1H, ^{3}J=2.0 Hz, CHC-N), 7.53 (d, 1H, ^{3}J=2.0 Hz, CHN), 9.87 (s, 1H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 39.31 (CH_3-N), 114.78 (CHC-N), 138.54 (CHN), 138.98 (CHC-N), 179.83 (CHO) ppm. $C_5H_6N_2O$: calcd C 54.54, H 5.49, N 25.44; found: C 54.50, H 4.52; N 25.42.

*1.2.3. Synthesis of pyrazolecarbaldehydes **4a**,**b**; General Procedure*

These compounds were obtained from 1-methyl-1*H*-pyrazole or 1,3-dimethyl-1*H*-pyrazole in $POCl_3$/DMF system (Vilsmeier–Haack's conditions) in 57 or 61% yields, respectively, as colorless oils, which solidified on standing to a white crystalline mass. [S2]



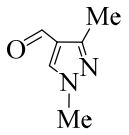
Me

1.2.4. 1-Methyl-1H-pyrazole-4-carbaldehyde (**4a**)

Yield: 57%; colorless fine crystal; bp 87-89 °C (7 Torr) (lit.[S6] 90-92 °C at 10 Torr), mp 27-28 °C (lit.[S7] 30 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H, Me), 7.88 (s, 2H, H-3,5 in Pyr), 9.81 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.96 (Me), 124.05 (C-4 in Pyr), 133.26 (C-5 in Pyr), 140.19

(C-3 in Pyr), 183.59 (CHO). Anal. Calcd for $C_5H_6N_2O$: C 54.54, H 5.49, N 25.44; found: C 54.35, H 5.41, N 25.30.

1.2.5. 1,3-Dimethyl-1H-pyrazole-4-carbaldehyde (**4b**)

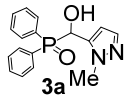


Yield: 61%; colorless fine crystal; bp 100-103 °C (3 Torr) (lit.[S8] 98-100 °C at 2 Torr), mp 50-51 °C (from heptane) (lit. [S9] 49-50 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H, Me), 3.87 (s, 3H, NMe), 7.77 (m, 1H, C-5 Pyr), 9.81 (s, 1H, CHO).^{13}C NMR (100 MHz, $CDCl_3$) δ 12.38 (Me), 38.66 (NMe), 121.11 (C-3 in Pyr), 135.08 (C-5 in Pyr), 150.36 (C-4 in Pyr), 183.69 (CHO).Anal. Calcd for $C_6H_8N_2O$: C 58.05, H 6.50, N 22.57; found: C 58.00, H 6.45, N 22.30.

1.2.6. Synthesis of chalcogenophosphoryl hydroxymethyl pyrazoles **3**,**5***; General Procedure*

A mixture of the corresponding secondary phosphine chalcogenide **1** (1.00 mmol) and carbaldehyde **2** or **4** (1.05 mmol) in toluene (2 ml) was stirred at 23–50 °C for 6 to 94 h in Ar atmosphere (see Table S1). Toluene was removed in vacuum, and the residue was washed with Et_2O (1 ml), dissolved in $CHCl_3$ and precipitated to *n*-hexane. The resulting solid was collected and dried under vacuum to afford the proper chalcogenophosphoryl hydroxymethyl pyrazole **3** or **5**.

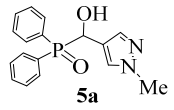
*1.2.7. (Diphenylphosphoryl)(1-methyl-1H-pyrazol-5-yl)methanol (***3a***)*



3a

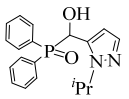
Colorless crystals (148 mg, 95%); mp 69-70 ^{o}C (hexane). IR (KBr): 3430, 3184, 3064, 2948, 2855, 1704, 1635, 1481, 1436, 1397, 1167, 1121, 1065, 1005, 936, 749, 724, 695, 541 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 3H, Me), 5.52 (d, $^2J_{PH}$ = 5.9 Hz, 1H, CHP), 6.05 (br. t, $^3J_{HH}$ = $^4J_{PH}$ = 1.8 Hz, 1H, H-4 in Pyr), 7.23 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H-3 in Pyr), 7.38-7.44 (m, 4H, H$_m$ in Ph), 7.49-7.59 (m, 2H, H$_p$ in Ph), 7.67 and 7.72 (br. d, $^3J_{HH}$ = 8.2 Hz, $^3J_{PH}$ = 10.8 Hz, 4H, H$_o$ in Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.94 (Me), 66.18 (d, $^1J_{PC}$ = 89.4 Hz, CHP), 106.83 (d, $^3J_{PC}$ = 2.1 Hz, C-4 in Pyr), 128.30 and 128.48 (d, $^3J_{PC}$ = 11.5 and 11.7 Hz, C$_m$), 128.44 and 130.27 (d, $^1J_{PC}$ = 97.7 Hz, C$_{ipso}$), 131.63 and 132.30 (d, $^2J_{PC}$ = 9.0 Hz, C$_o$), 132.31 (C$_p$), 137.71 (C-3 in Pyr), 138.35 (C-5 in Pyr). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.37. ^{15}N NMR (40 MHz, $CDCl_3$) δ −180.7 (1-NMe), −76.1 (2-N). Anal. Calcd for $C_{17}H_{17}N_2O_2P$: C 65.38, H 5.49, N 8.97, P 9.92; found: C 65.54, H 5.57, N 8.69, P 10.23.

*1.2.8. (Diphenylphosphoryl)(1-methyl-1H-pyrazol-4-yl)methanol (***5a***)*



5a

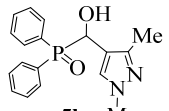
White powder (141 mg, 90%); mp 172-173 ^{o}C (hexane). IR (KBr): 3390, 3239, 3135, 3056, 2916, 1649, 1553, 1482, 1436, 1402, 1340, 1266, 1159, 1053, 1009, 987, 852, 755, 727, 696, 552 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H, Me), 5.45 (d, $^2J_{PH}$ = 2.7 Hz, 1H, CHP), 7.08 (s, 1H, H-3 in Pyr), 7.35 (m, 2H, H$_m$), 7.37 (s, 1H, H-5 in Pyr), 7.45 (m, 2H, H$_m$), 7.53 (m, 2H, H$_p$), 7.66 and 7.83 (br. dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{PH}$ = 10.6 Hz, 4H, H$_o$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.81 (Me), 66.48 (d, $^1J_{PC}$ = 86.4 Hz, PCH), 117.39 (C-4 in Pyr), 128.32 and 128.38 (d, $^3J_{PC}$ = 11.5 Hz, C$_m$), 129.91 (d, $^3J_{PC}$ = 4.6 Hz, C-5 in Pyr), 129.97 and 130.57 (d, $^1J_{PC}$ = 95.6 Hz, C$_{ipso}$), 131.64 and 132.11 (d, $^2J_{PC}$ = 9.0 and 8.7 Hz, C$_o$), 131.92 and 132.03 (d, $^4J_{PC}$ = 2.8 and 3.0 Hz, C$_p$), 138.47 (C-3 in Pyr). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.84. ^{15}N NMR (40 MHz, $CDCl_3$) δ −179.3 (1-NMe), −77.5 (2-N). Anal. Calcd for $C_{17}H_{17}N_2O_2P$: C 65.38, H 5.49, N 8.97, P 9.92; found: C 65.69, H 5.70, N 8.75, P 10.05.



3b

*1.2.9. (Diphenylphosphoryl)(1-isopropyl-1H-pyrazol-5-yl)methanol (***3b***)*

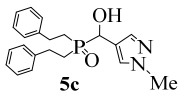
Colorless crystals (158 mg, 93%); mp 84-85 °C (hexane). IR (KBr): 3429, 3190, 3064, 2981, 2936, 2868, 1632, 1438, 1317, 1249, 1166, 1118, 1063, 1024, 935, 745, 697, 532 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 and 1.36 (d, $^3J_{HH}$ = 6.6 Hz, 6H, Me), 4.50 (sept, 1H, CHN), 5.57 (d, $^2J_{PH}$ = 5.3 Hz, 1H, CHP), 6.16 (s, 1H, H-4 in Pyr), 7.27 (d, $^3J_{HH}$ = 1.7 Hz, 1H, H-3 in Pyr), 7.35 and 7.42 (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HP}$ = 3.1 Hz, 4H, H_m), 7.46 and 7.53 (t, $^3J_{HH}$ = 7.8 Hz, 2H, H_p), 7.65 and 7.72 (dd, $^3J_{HH}$ = 7.8 and 11.0 Hz, 4H, H_o). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.34 and 22.92 (Me), 55.57 (CHN), 65.70 (d, $^1J_{PC}$ = 85.3 Hz, CHP), 106.64 (C-4 in Pyr), 128.42 and 128.45 (d, $^3J_{PC}$ = 11.7 Hz, C_m), 129.28 and 130.30 (d, $^1J_{PC}$ = 98.1 and 96.5 Hz, C_{ipso}), 131.61 and 132.12 (d, $^2J_{PC}$ = 9.2 Hz, C_o), 132.19 and 132.24 (d, $^4J_{PC}$ = 2.3 Hz, C_p), 136.70 (d, $^2J_{PC}$ = 3.7 Hz, C-5 in Pyr), 138.10 (C-3 in Pyr). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.05. ^{15}N NMR (40 MHz, $CDCl_3$) δ −157.8 (1-NMe), −84.2 (2-N). Anal. Calcd for $C_{19}H_{21}N_2O_2P$: C 67.05, H 6.22, N 8.23, P 9.10; found: C 66.80, H 6.02, N 8.15, P 9.21.



5b

*1.2.10. (1,3-Dimethyl-1H-pyrazol-4-yl)(diphenylphosphoryl)methanol (***5b***)*

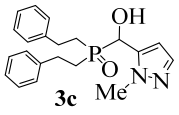
Colorless crystals (147 mg, 90%); mp 149-150 °C (hexane). IR (KBr): 3417, 3136, 3057, 2971, 2926, 1673, 1548, 1479, 1437, 1353, 1255, 1174, 1123, 1017, 951, 751, 728, 697, 552 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 3H, Me), 3.53 (s, 3H, MeN), 5.34 (s, 1H, CHP), 7.08 (s, 1H, H-3 in Pyr), 7.27-7.45 (m, 4H, H_m in Ph), 7.48 (s, 1H, H-5 in Pyr), 7.51-7.55 (m, 2H, H_p), 7.40-7.46 (m, 4H, H_o). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.23 (Me), 38.50 (MeN), 65.34 (d, $^1J_{PC}$ = 85.7 Hz, CHP), 114.14 (C-4 in Pyr), 128.27 and 128.51 (d, $^3J_{PC}$ = 11.3 Hz, C_m), 130.43 and 130.71 (d, $^1J_{PC}$ = 95.1 and 95.6 Hz, C_{ipso}), 131.36 and 132.09 (d, $^2J_{PC}$ = 9.2 Hz, C_o), 131.60 (d, $^3J_{PC}$ = 2.5 Hz, C-5 in Pyr), 131.86 and 132.00 (d, $^4J_{PC}$ = 2.5 Hz, C_p), 146.94 (d, $^3J_{PC}$ = 7.1 Hz C-3 in Pyr). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.31. ^{15}N NMR (40 MHz, $CDCl_3$) δ −184.5 (1-NMe), −83.1 (2-N). Anal. Calcd for $C_{18}H_{19}N_2O_2P$: C 66.25, H 5.87, N 8.58, P 9.49; found: C 66.09, H 5.69, N 8.40, P 9.37.



5c

*1.2.11. (Diphenethylphosphoryl)(1-methyl-1H-pyrazol-4-yl)methanol (***5c***)*

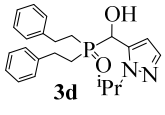
Colorless crystals (144 mg, 78%); mp 133-134 °C (hexane). IR (KBr): 3172, 3027, 2938, 2866, 1604, 1551, 1494, 1448, 1403, 1346, 1267, 1216, 1121, 1052, 1007, 936, 857, 751, 701, 575, 491 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.91-2.12 (m, 4H, CH_2P), 2.76-2.88 (m, 4H, CH_2Ph), 3.73 (s, 3H, Me), 5.07 (d, $^2J_{PH}$ = 3.7 Hz, 1H, CHP), 5.53 (br. s, 1H, OH), 7.10-7.12 (m, 4H, H_o), 7.15-7.19 (m, 2H, H_p), 7.22-7.25 (m, 4H, H_m), 7.49 (s, 1H, H-3 in Pyr), 7.51 (s, 1H, H-5 in Pyr). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.01 and 26.61 (d, $^1J_{PC}$ = 60.4 and 69.0 Hz, CH_2P), 27.24 and 27.35 (d, $^2J_{PC}$ = 2.7 Hz, CH_2Ph), 38.83 (NMe), 66.62 (d, $^1J_{PC}$ = 81.5 Hz, CHP), 117.91 (C-4 in Pyr), 126.32 (C_p), 127.93 (C_o), 128.51 (C_m), 129.09 (d, $^3J_{PC}$ = 2.7 Hz, C-5 in Pyr), 137.56 (d, $^3J_{PC}$ = 2.7 Hz, C-3 in Pyr), 140.77 and 140.82 (d, $^3J_{PC}$ = 13.0 Hz, C_{ipso}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.32. ^{15}N NMR (40 MHz, $CDCl_3$) δ −178.5 (1-NMe), −78.6 (2-N). Anal. Calcd for $C_{21}H_{25}N_2O_2P$: C 68.46, H 6.84, N 7.60, P 8.41; found: C 68.28, H 6.77, N 7.49, P 8.37.



3c

*1.2.12. [Bis(2-phenylethy)lphosphoryl](1-methyl-1H-pyrazol-5-yl)methanol (***3c***)*

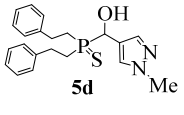
Colorless crystals (171 mg, 93%); mp 140-141 °C (hexane). IR (KBr): 3142, 3111, 3030, 2947, 2858, 2799, 1603, 1493, 1451, 1401, 1279, 1212, 1153, 1136, 1065, 1006, 937, 752, 702, 575, 492 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.99-2.10 and 2.18-2.29 (m, 4H, CH_2P), 2.66-2.77 and 2.85-2.92 (m, 4H, CH_2Ph), 3.81 (s, 3H, Me), 4.98 (d, $^2J_{PH}$ = 8.0 Hz, 1H, CHP), 6.35 (br. t, $^3J_{HH}$ = $^4J_{PH}$ = 1.7 Hz, 1H, H-4 in Pyr), 7.10 and 7.15 (br. d, $^3J_{PH}$ = 7.8 Hz, 4H, H_o), 7.20-7.22 (m, 2H, H_p), 7.25-7.29 (m, 4H, H_m), 7.34 (br. d, $^3J_{HH}$ = 1.7 Hz, 1H, H-3 in Pyr). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.16 and 27.53 (d, $^1J_{PC}$ = 61.4 and 53.3 Hz, CH_2P), 27.18 and 27.22 (d, $^2J_{PC}$ = 2.8 and 2.5 Hz, CH_2Ph), 37.46 (NMe), 66.64 (d, $^1J_{PC}$ = 81.4 Hz, CHP), 105.68 (d, $^3J_{PC}$ = 1.8 Hz, C-4 in Pyr), 126.42 and 126.52 (C_p), 127.94 and 128.03 (C_o), 128.60 and 128.64 (C_m), 138.19 (C-3 in Pyr), 138.97 (C-5 in Pyr), 140.66 and 130.57 (d, $^3J_{PC}$ = 12.0 and 12.9 Hz, C_{ipso}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.92. ^{15}N NMR (40 MHz, $CDCl_3$) δ −181.3 (1-NMe), −74.1 (2-N). Anal. Calcd for $C_{21}H_{25}N_2O_2P$: C 68.46, H 6.84, N 7.60, P 8.41; found: C 68.32, H 6.77, N 7.53, P 8.38.



3d

*1.2.13. [Bis(2-phenylethy)lphosphoryl](1-isopropyl-1H-pyrazol-5-yl)methanol (***3d***)*

Colorless crystals (182 mg, 92%); mp 159-160 °C (hexane). IR (KBr): 3426, 3068, 3036, 2991, 1604, 1495, 1454, 1408, 1324, 1251, 1209, 1144, 1059, 1022, 936, 836, 790, 753, 702, 557 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 and 1.49 (d, $^3J_{PH}$ = 6.6 Hz, 6H, Me), 1.96-2.14 (m, 4H, PCH_2), 2.65-2.84 (m, 4H, $PhCH_2$), 4.61 (sept, 1H, NCH), 4.92 (d, $^2J_{PH}$ = 6.4 Hz, 1H, CHP), 6.36 (br. t, $^3J_{HH}$ = $^4J_{PH}$ = 1.5 Hz, 1H, H-4 in Pyr), 7.05-7.08 (m, 4H, H_o), 7.13-7.16 (m, 2H, H_p), 7.20-7.23 (m, 2H, H_m), 7.40 (d, $^3J_{HH}$ = 1.5 Hz, 1H, H-3 in Pyr). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 and 23.05 (Me), 26.81 and 27.82 (d, $^1J_{PC}$ = 61.2 and 60.2 Hz, CH_2P), 27.38 and 27.42 (d, $^2J_{PC}$ = 3.6 and 3.4 Hz, CH_2Ph), 50.92 (NCH), 64.57 (d, $^1J_{PC}$ = 79.2 Hz, CHP), 105.24 (d, $^3J_{PC}$ = 2.7 Hz, C-4 in Pyr), 126.47 and 126.56 (C_p), 128.02 and 128.07 (C_o), 128.64 and 128.68 (C_m), 137.45 (C-5 in Pyr), 138.55 (C-3 in Pyr), 140.60 and 140.72 (d, $^3J_{PC}$ = 12.2 and 12.8 Hz, C_{ipso}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.53. ^{15}N NMR (40 MHz, $CDCl_3$) δ −158.1 (1-NMe), −81.7 (2-N). Anal. Calcd for $C_{23}H_{29}N_2O_2P$: C 69.68, H 7.37, N 7.07, P 7.81; found: C 69.64, H 7.20, N 6.95, P 7.58.

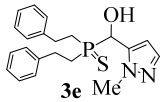


5d

*1.2.14. [Bis(2-phenylethyl)phosphorothioyl](1-methyl-1H-pyrazol-4-yl)methanol (***5d***)*

Colorless crystals (173 mg, 90%); mp 60-61 °C (hexane). IR (film): 3291, 2922, 2853, 1680, 1600, 1550, 1453, 1399, 1343, 1263, 1206, 1133, 1053, 1004, 950, 859, 772, 620, 554, 494 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.95-2.20 (m, 4H, CH_2P), 2.82-2.97 (m, 4H, CH_2Ph), 3.89 (s, 3H, Me), 4.88 (s, 1H, CHP), 7.11-7.13 (m, 4H, H_o), 7.22-7.23 (m, 2H, H-*p*), 7.29-7.30 (m, 4H, H_m), 7.49 (s, 1H, H-3 in Pyr), 7.53 (s, 1H, H-5 in Pyr). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.20 and 28.35 (d, $^2J_{PC}$ = 2.9 and 3.1 Hz, CH_2Ph), 28.97 and 29.29 (d, $^1J_{PC}$ = 45.1 and 45.5 Hz, CH_2P), 39.03 (Me), 66.33 (d, $^1J_{PC}$ = 59.5 Hz, CHP), 117.09 (C-4 in Pyr), 126.44 and 126.49 (C_p in Ph), 128.10 and 128.19 (C_o), 128.58 and 128.61 (C_m), 128.84 (d, $^3J_{PC}$ = 4.0 Hz, C-5 in Pyr), 138.55 (d, $^3J_{PC}$ = 4.0 Hz, C-3 in Pyr), 140.47 (d, $^3J_{PC}$ = 13.6 Hz, C_{ipso}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.73. ^{15}N NMR (40 MHz, $CDCl_3$) δ −178.2 (1-NMe),

−76.7 (2-N). Anal. Calcd for $C_{21}H_{25}N_2OPS$: C 65.60, H 6.55, N 7.29, P 8.06, S 8.34; found: C 65.45, H 6.40, N 7.13, P 7.98, S 8.29.

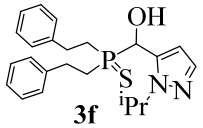


3e

*1.2.15. [Bis(2-phenylethyl)phosphorothioyl](1-methyl-1H-pyrazol-5-yl)methanol (***3e***)*

Colorless crystals (177 mg, 92%); mp 121-122 °C (hexane). IR (KBr): 3119, 3029, 2933, 2865, 1601, 1492, 1440, 1399, 1314, 1278, 1200, 1124, 1050, 1004, 944, 748, 701, 616, 561, 500 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.03-2.10 and 2.17-2.27 (m, 4H, CH_2P), 2.81-2.97 (m, 4H, CH_2Ph), 3.93 (s, 3H, Me), 4.93 (d, $^2J_{PH}$ = 3.7 Hz, 1H, CHP), 6.43 (br. t, $^3J_{HH}$ = $^4J_{PH}$ = 1.8 Hz, 1H, H-4), 7.14-7.20 (m, 4H, H_o), 7.22-7.26 (m, 2H, H_p), 7.27-7.31 (m, 4H, H_m), 7.46 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H-3 in Pyr). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.21 and 28.27 (d, $^2J_{PC}$ = 2.3 Hz, CH_2Ph), 28.85 and 20.08 (d, $^1J_{PC}$ = 45.0 and 45.5 Hz, CH_2P), 38.06 (Me), 65.92 (d, $^1J_{PC}$ = 57.5 Hz, CHP), 105.97 (d, $^3J_{PC}$ = 3.2 Hz, C-4 in Pyr), 126.62 and 126.67 (C_p), 128.22 and 128.33 (C_o), 128.73 (C_m), 138.38 (C-5 in Pyr), 138.47 (d, $^4J_{PC}$ = 1.2 Hz, C-3 in Pyr), 140.30 and 140.40 (d, $^3J_{PC}$ = 13.3 and 13.6 Hz, C_{ipso}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.47. ^{15}N NMR (40 MHz, $CDCl_3$) δ −178.2 (1-NMe), −76.2 (2-N). Anal. Calcd for $C_{21}H_{25}N_2OPS$: C 65.60, H 6.55, N 7.29, P 8.06, S 8.34; found: C 65.49, H 6.40, N 7.13, P 7.98, S 8.14.

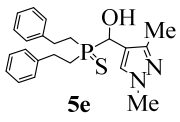
*1.2.16. [Bis(2-phenylethyl)phosphorothioyl](1-isopropyl-1H-pyrazol-5-yl)methanol (***3f***)*



3f

Light-yellow oil (180 mg, 87%); IR (film): 3062, 3028, 2979, 2928, 2863, 1602, 1494, 1451, 1411, 1323, 1249, 1209, 1134, 1065, 1021, 912, 750, 702, 610, 554, 495 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 and 1.50 (d, $^3J_{HH}$ = 6.6 Hz, 6H, Me), 1.97-2.08 and 2.14-2.30 (m, 4H, CH_2P), 2.81-3.00 (m, 4H, CH_2Ph), 4.70 (sept, $^2J_{PH}$ = 6.6 Hz, 1H, CHN), 4.96 (d, $^2J_{PH}$ = 4.7 Hz, 1H, CHP), 5.47 (br. s 1H, OH), 6.36 (br. t, $^3J_{HH}$ = $^4J_{PH}$ = 1.8 Hz, 1H, H-4 in Pyr), 7.10-7.19 (m, 6H, $H_{o,p}$), 7.21-7.25 (m, 4H, H_m), 7.46 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H-3 in Pyr). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.30 and 23.05 (Me), 28.14 and 28.27 (d, $^2J_{PC}$ = 2.8 and 3.0 Hz, CH_2Ph), 29.35 and 29.85 (d, $^1J_{PC}$ = 45.9 and 45.7 Hz, CH_2P), 51.37 (CHN), 65.55 (d, $^1J_{PC}$ = 59.9 Hz, PCH), 105.46 (d, $^3J_{PC}$ = 2.7 Hz, C-4 in Pyr), 126.56 and 126.61 (C_p), 128.19 and 128.30 (C_o), 128.65 and 128.67 (C_m), 137.56 (C-5 in Pyr), 138.44 (d, $^4J_{PC}$ = 1.7 Hz, C-3 in Pyr), 140.25 and 140.38 (d, $^3J_{PC}$ = 11.3 and 10.3 Hz, C_{ipso}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.38. ^{15}N NMR (40 MHz, $CDCl_3$) δ −157.9 (1-NMe), −89.3 (2-N). Anal. Calcd for $C_{23}H_{29}N_2OPS$: C 66.97, H 7.09, N 6.79, P 7.51, S 7.77; found: C 66.75, H 7.01, N 6.59, P 7.48, S 7.60.

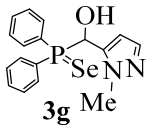
*1.2.17. [Bis(2-phenylethyl)phosphorothioyl](1,3-dimethyl-1H-pyrazol-4-yl)methanol (***5e***)*



5e

Light-yellow oil (169 mg, 85%); IR (film): 3062, 3027, 2926, 2857, 1673, 1602, 1548, 1490, 1448, 1410, 1363, 1271, 1211, 1166, 1024, 948, 833, 751, 702, 616, 557, 494 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.64-1.74 and 1.92-2.01 (m, 4H, CH_2P), 2.00 (s, 3H, Me), 2.45-2.54 and 2.67-2.79 (m, 4H, CH_2Ph), 3.56 (s, 3H, MeN), 4.58 (s, 1H, CHP), 6.80-6.82 (m, 2H, H_o), 6.93-6.96 (m, 4H, $H_{o,p}$), 7.00-7.07 (m, 4H, H_m), 7.39 (s, 1H, H-5 in Pyr). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.18 (Me), 28.71 and 28.80 (d, $^2J_{PC}$ = 2.7 Hz, CH_2Ph), 30.54 and 31.76 (d, $^1J_{PC}$ = 44.2 and 50.5 Hz, CH_2P), 38.95 (NMe), 66.67 (d, $^1J_{PC}$ = 58.3 Hz, CHP), 114.76 (C-4 in Pyr), 126.57 and 126.66 (C_p), 128.18 and 128.28 (C_o), 128.68 and 128.72 (C_m), 129.78 (d, $^3J_{PC}$ = 2.5 Hz, C-5 in Pyr), 140.39 and 140.35 (d, $^3J_{PC}$ = 13.6 Hz,

C_{ipso}), 146.39 (d, $^3J_{PC}$ = 6.1 Hz, C-3 in Pyr). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.67. ^{15}N NMR (40 MHz, $CDCl_3$) δ −182.9 (1-NMe), −79.0 (2-N). Anal. Calcd for $C_{22}H_{27}N_2OPS$: C 66.31, H 6.83, N 7.03, P 7.77, S 8.05; found: C 66.19, H 6.71, N 6.91, P 7.58, S 7.94.

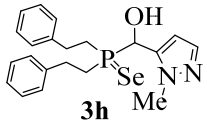


3g

*1.2.18. [Bis(2-phenylethyl)phosphoroselenoyl](1-methyl-1H-pyrazol-5-yl)methanol (**3g**)*

Light-yellow oil (151 mg, 80%); IR (film): 3058, 2969, 2853, 1691, 1586, 1481, 1435, 1396, 1215, 1101, 1037, 934, 762, 897, 568, 512 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 (s, 3H, Me), 4.64. (br. s, 1H, OH), 5.57 (d, $^2J_{PH}$ = 2.3 Hz, 1H, CHP), 6.11 (t, $^3J_{HH}$ = $^4J_{PH}$ = 1.8 Hz, 1H, H-4 in Pyr), 7.27 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H-3 in Pyr), 7.35-7.38 (m, 4H, H_m), 7.48-7.53 (m, 2H, H_p), 7.55-7.58 and 7.82-7.87 (m, 4H, H_o). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 36.98 (Me), 66.39 (d, $^1J_{PC}$ = 53.9 Hz, CHP), 106.83 (d, $^3J_{PC}$ = 3.4 Hz, C-4 in Pyr), 128.55 and 128.74 (d, $^3J_{PC}$ = 11.9 Hz, C_m), 131.08 and 131.17 (d, $^1J_{PC}$ = 101.7 and 96.4 Hz, C_{ipso}), 132.65 and 132.82 (d, $^2J_{PC}$ = 9.9 Hz, C_o), 132.40 and 132.42 (C_p), 137.40 (d, $^2J_{PC}$ = 3.1 Hz, C-5 in Pyr), 137.75 (d, $^4J_{PC}$ = 1.9 Hz, C-3 in Pyr). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.06 (s + d satellites: $^1J_{PSe}$ = 727 Hz). ^{15}N NMR (40 MHz, $CDCl_3$) δ −181.7 (1-NMe), −78.2 (2-N). ^{77}Se NMR (76 Hz, $CDCl_3$) δ −371.88 (d, $^1J_{PSe}$ = 727 Hz). Anal. Calcd for $C_{17}H_{17}N_2OPSe$: C 54.41, H 4.57, N 7.47, P 8.25, Se 21.04; found: C 54.29, H 4.37, N 7.25, P 8.09, Se 20.89.

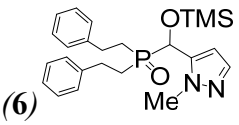
*1.2.19. [Bis(2-phenylethyl)phosphoroselenoyl](1-methyl-1H-pyrazol-5-yl)methanol (**3h**)*



3h

Colorless crystals (193 mg, 89%); mp 135-136 °C (hexane). IR (KBr): 3117, 3029, 2933, 2864, 1603, 1493, 1450, 1399, 1315, 1200, 1125, 1049, 1005, 944, 747, 702, 572, 496, 472 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05-2.07 and 2.25-2.36 (m, 4H, CH_2P), 2.76-2.95 (m, 4H, CH_2Ph), 3.89 (s, 3H, Me), 4.95 (s, $^2J_{PH}$ = 2.5 Hz, 1H, CHP), 6.44 (br. t, $^3J_{HH}$ = $^4J_{PH}$ = 1.7 Hz, 1H, H-4 in Pyr), 7.10-7.12 (m, 2H, H_o), 7.16-7.31 (m, 8H, $H_{o,m,p}$), 7.41 (d, $^4J_{PH}$ = 1.7 Hz, 1H, H-4 in Pyr). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.17 and 29.20 (d, $^2J_{PC}$ = 3.1 Hz, CH_2Ph), 29.31 and 29.68 (d, $^1J_{PC}$ = 34.8 and 35.2 Hz, CH_2P), 38.20 (Me), 64.60 (d, $^1J_{PC}$ = 50.1 Hz, CHP), 106.14 (C-4 in Pyr), 126.75 (C_p), 128.27 and 128.30 (C_o), 128.75 and 128.79 (C_m), 137.59 (C-3 in Pyr), 138.64 (C-5 in Pyr), 139.96 and 140.02 (d, $^3J_{PC}$ = 13.8 Hz, C_{ipso}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.46 (s + d satellites: $^1J_{PSe}$ = 709 Hz). ^{15}N NMR (40 MHz, $CDCl_3$) δ −181.3 (1-N), −71.2 (2-N). ^{77}Se NMR (76 Hz, $CDCl_3$) δ −443.4 (d, $^1J_{PSe}$ = 709 Hz). Anal. Calcd for $C_{21}H_{25}N_2OPSe$: C 58.47, H 5.84, N 6.49, P 7.18, Se 18.30; found: C 58.38, H 5.79, N 6.32, P 7.00, Se 18.15.

1.2.20. 5-{[Bis(2-phenylethyl)phosphoryl](trimethylsilyloxy)methyl}-1-methyl-1H-pyrazole

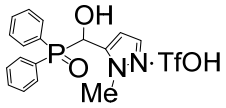


(6)

Pyrazole **3c** (60 mg, 0.2 mmol) was heated in HMDS (1 ml) under reflux during 2 h. HMDS excess was removed in vacuum (1 Torr) at 50 °C to get **6** (79 mg, 95%) as a light beige oil; IR (film): 3141, 3064, 3029, 2948, 2926, 2856, 1673, 1601, 1492, 1451, 1401, 1323, 1256, 1206, 1160, 1077, 1005, 936, 855, 789, 702, 574 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 9H, $SiMe_3$), 1.97-2.17 (m, 4H, CH_2P), 2.63-3.04 (m, 4H, CH_2Ph), 4.01 (s, 3H, NMe), 5.07 (d, $^2J_{PH}$ = 8.2 Hz, 1H, CHP), 6.22 (br. t, $^3J_{HH}$ = $^4J_{PH}$ = 1.7 Hz, 1H, H-4 in Pyr), 7.12 - 7.34 (m, 10H, Ph), 7.44 (d, $^3J_{HH}$ = 1.7 Hz, 1H, H-3 in Pyr).

^{13}C NMR (100 MHz, $CDCl_3$) δ 0.04 ($Si(Me)_3$), 25.92 and 27.56 (d, $^1J_{PC}$ = 61.6 and 60.8 Hz, CH_2P), 27.29 and 27.31 (d, $^2J_{PC}$ = 1.9 Hz, CH_2Ph), 37.98 (NMe), 66.62 (d, $^1J_{PC}$ = 82.5 Hz, CHP), 105.97 (d, $^3J_{PC}$ = 3.4 Hz, C-4 in Pyr), 126.33 and 126.52 (C_p), 127.98 and 128.13 (C_o), 128.57 and 128.69 (C_m), 138.22 (d, $^4J_{PC}$ = 1.5 Hz, C-3 in Pyr), 138.35 (C-5 in Pyr), 140.75 and 141.02 (d, $^3J_{PC}$ = 12.2 and 13.8 Hz, C_{ipso}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.48. ^{15}N NMR (40 MHz, $CDCl_3$) δ −180.9 (1-N), −70.7 (2-N). ^{29}Si NMR (79 MHz, $CDCl_3$) δ 25.04 ($^3J_{PSi}$ = 10.7 Hz). Anal. Calcd for $C_{24}H_{33}N_2O_2PSi$: C 65.43, H 7.55, N 6.36, P 7.03; found: C 65.40, H 7.54, N 6.29, P 6.93.

*1.2.21. 5-[(Diphenylphosphoryl)(hydroxy)methyl]-1-methyl-1*H*-pyrazol-2-ium triflate*



Triflic acid (32 mg, 0.2 mmol) was added to a solution of pyrazole **3a** (67 mg, 0.2 mmol) in THF (1 ml) and stirred during 30 min. Solvent was removed in vacuum (1 Torr) to get **3a**·TfOH (98 mg, 99%) as a light beige very hygroscopic wax. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.20 and 1.30 (d, $^3J_{HH}$ = 6.3 Hz, 6H, Me), 4.83 (sext, 1H, CHN), 5.86 (d, $^2J_{PH}$ = 5.6 Hz, 1H, CHP), 5.99 (s, 1H, H-4 in Pyr), 7.28 (s, 1H, H-3 in Pyr), 7.45-7.91 (m, 10H, Ph). ^{13}C NMR (100 MHz, DMSO-d_6) δ 22.71 and 23.12 (Me), 51.20 (CHN), 64.60 (d, $^1J_{PC}$ = 89.4 Hz, CHOH), 106.94 (d, $^3J_{PC}$ = 2.9 Hz, C-4 in Pyr), 121.08 (q, $^1J_{FC}$ = 321.8 Hz, CF_3), 128.91 and 129.05 (d, $^3J_{PC}$ = 11.4 Hz, C_m), 130.39 and 131.36 (d, $^1J_{PC}$ = 96.9 and 97.0 Hz, C_{ipso}), 131.52 and 132.29 (d, $^2J_{PC}$ = 8.9 and 9.0 Hz, C_o), 132.59 and 132.68 (d, $^4J_{PC}$ = 1.8 and 2.1 Hz, C_p), 137.33 (C-3 in Pyr), 139.49 (C-5 in Pyr). ^{31}P NMR (162 MHz, DMSO-d_6) δ 28.79. ^{15}N NMR (40 MHz, DMSO-d_6) δ −158.1 (1-NMe), −103.1 (2-N^+). ^{19}F NMR (376 Hz, DMSO-d_6) δ −77.57. Anal. Calcd for $C_{18}H_{18}F_3N_2O_5PS$: C 46.76, H 3.92, N 6.06; found: C 46.56, H 3.77, N 6.25.

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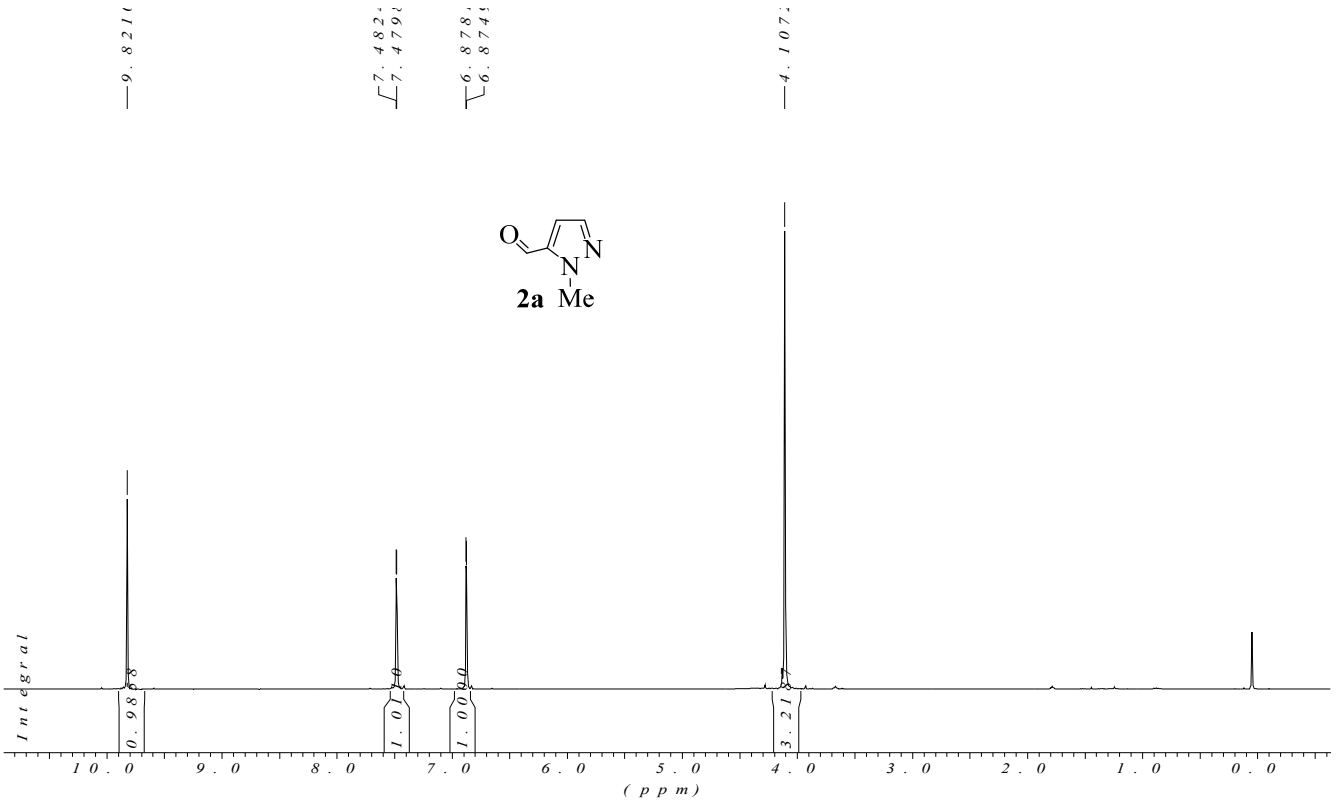
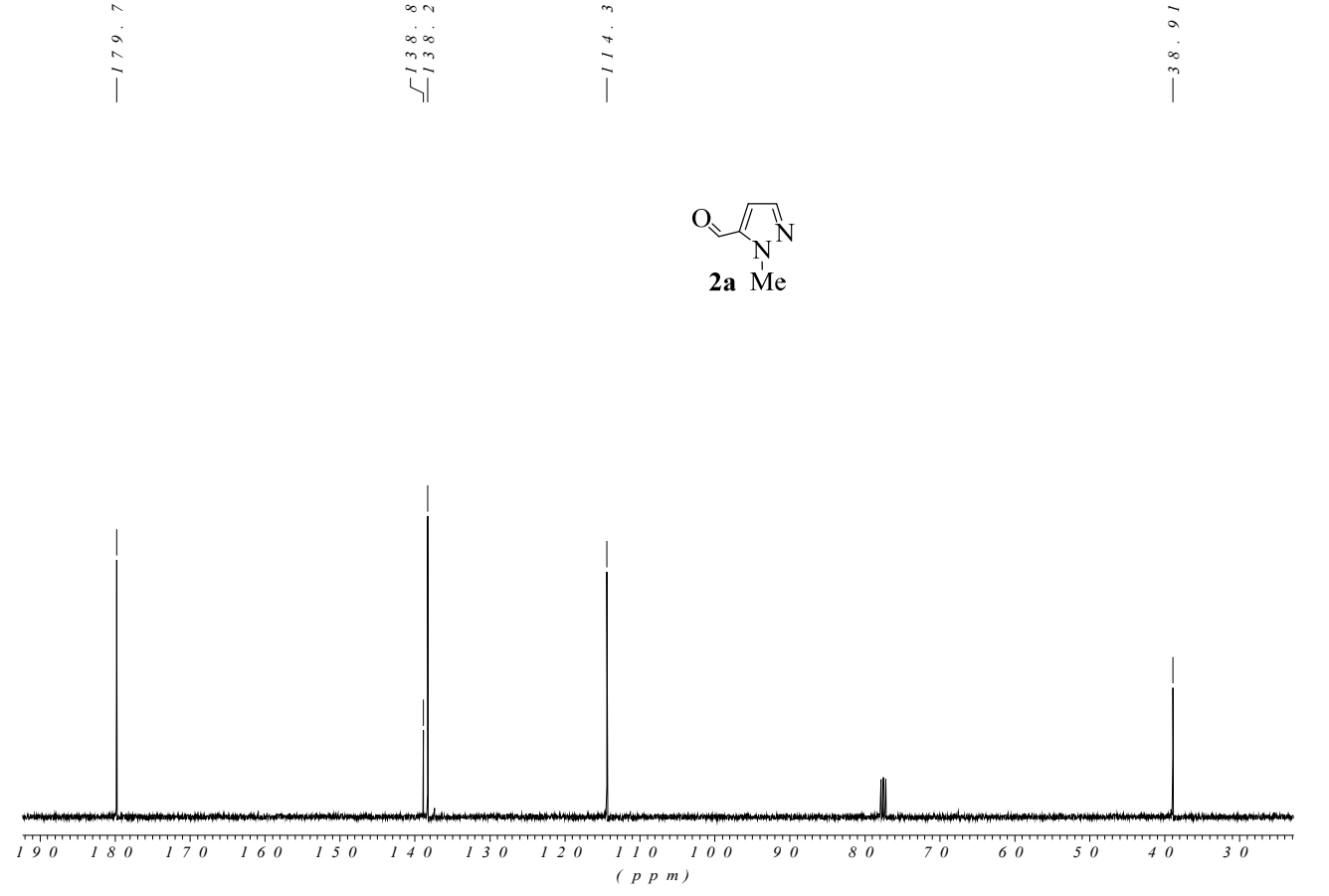
Spectral data of the initial pyrazolecarbaldehydes

^{1}H NMR spectrum of carbaldehyde **2a** ($CDCl_3$)



^{13}C NMR spectrum of carbaldehyde **2a** ($CDCl_3$)



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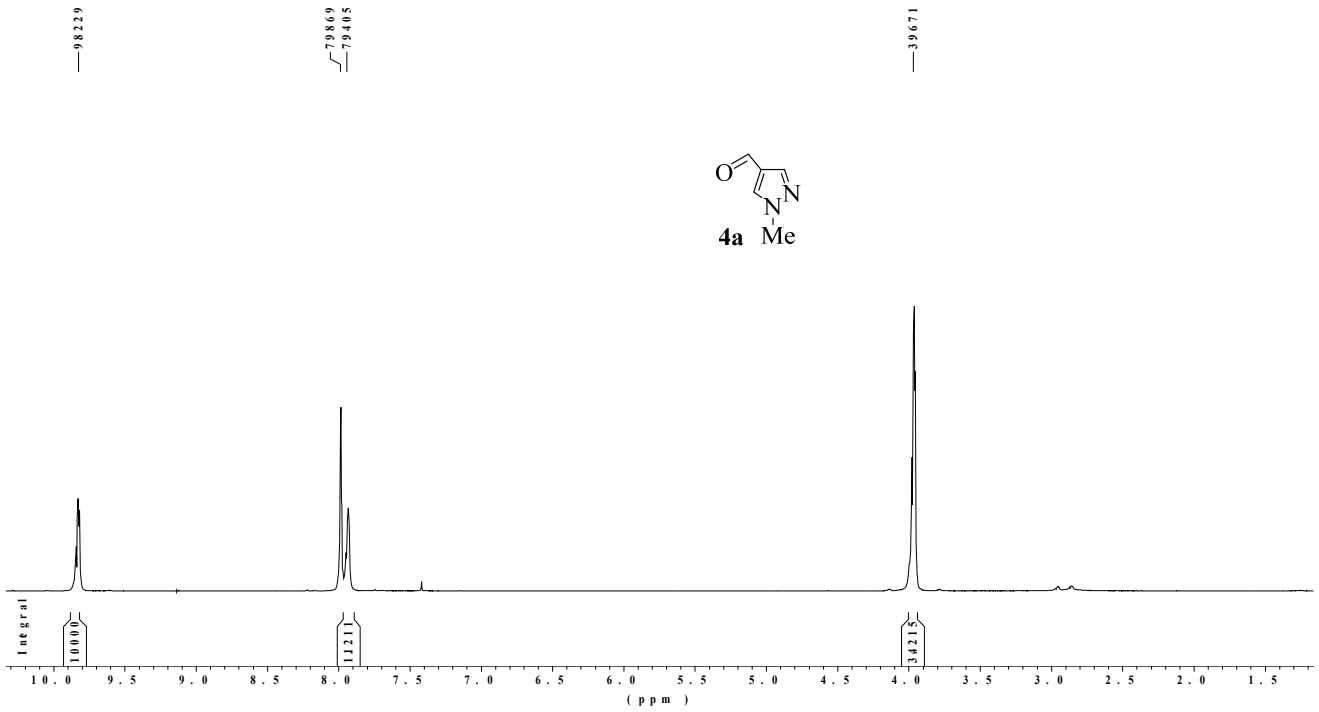
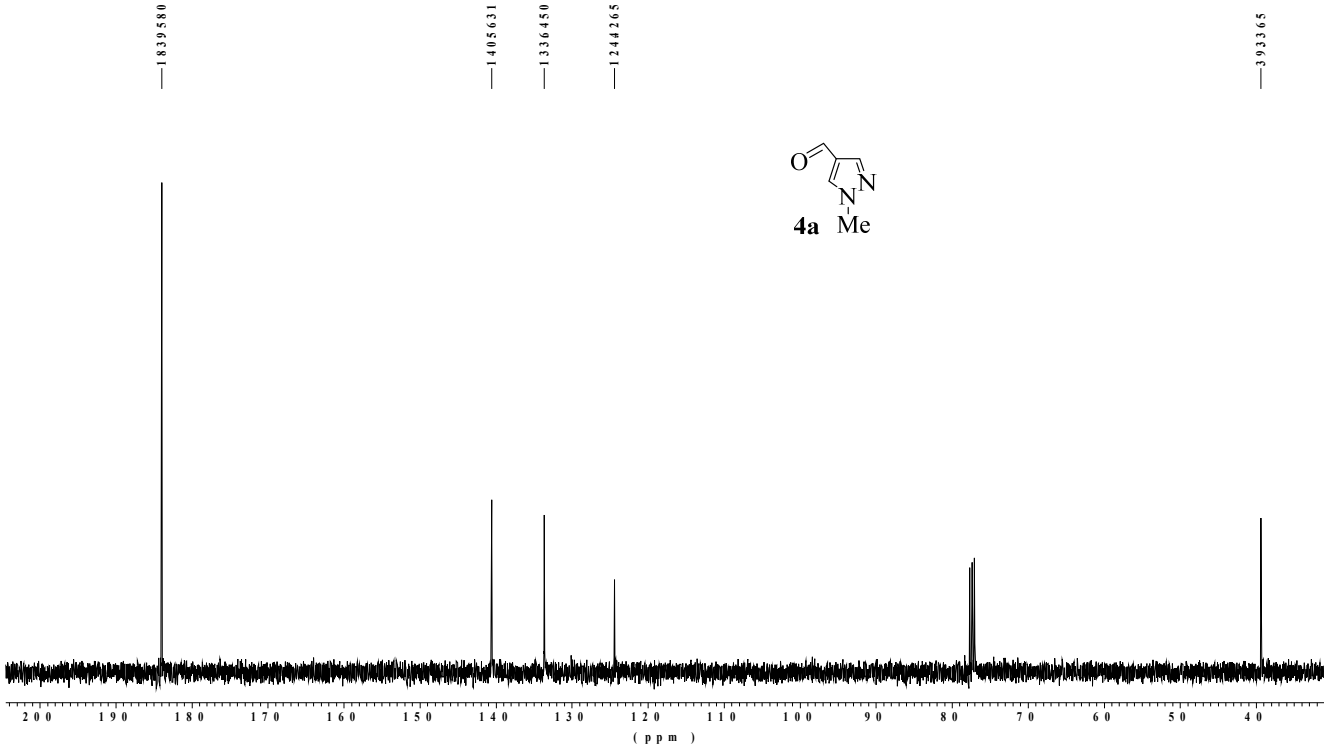
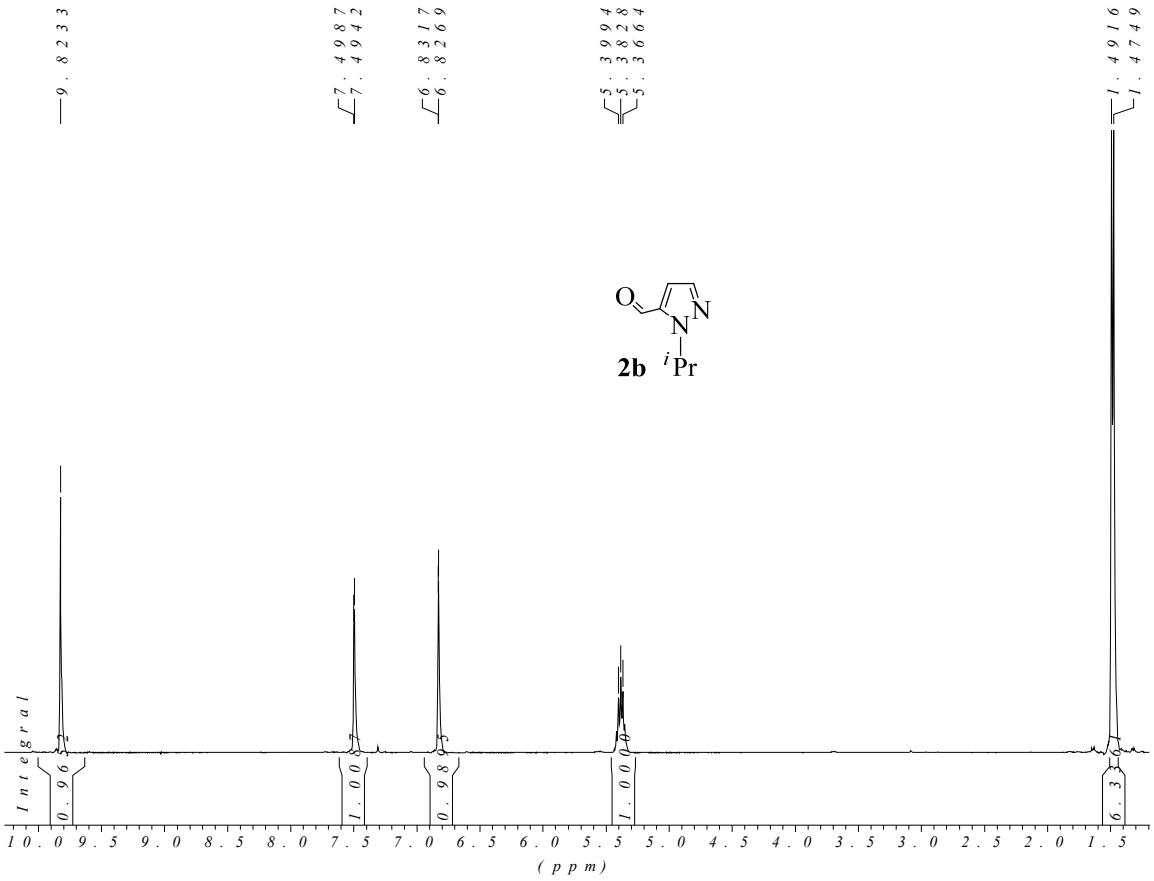


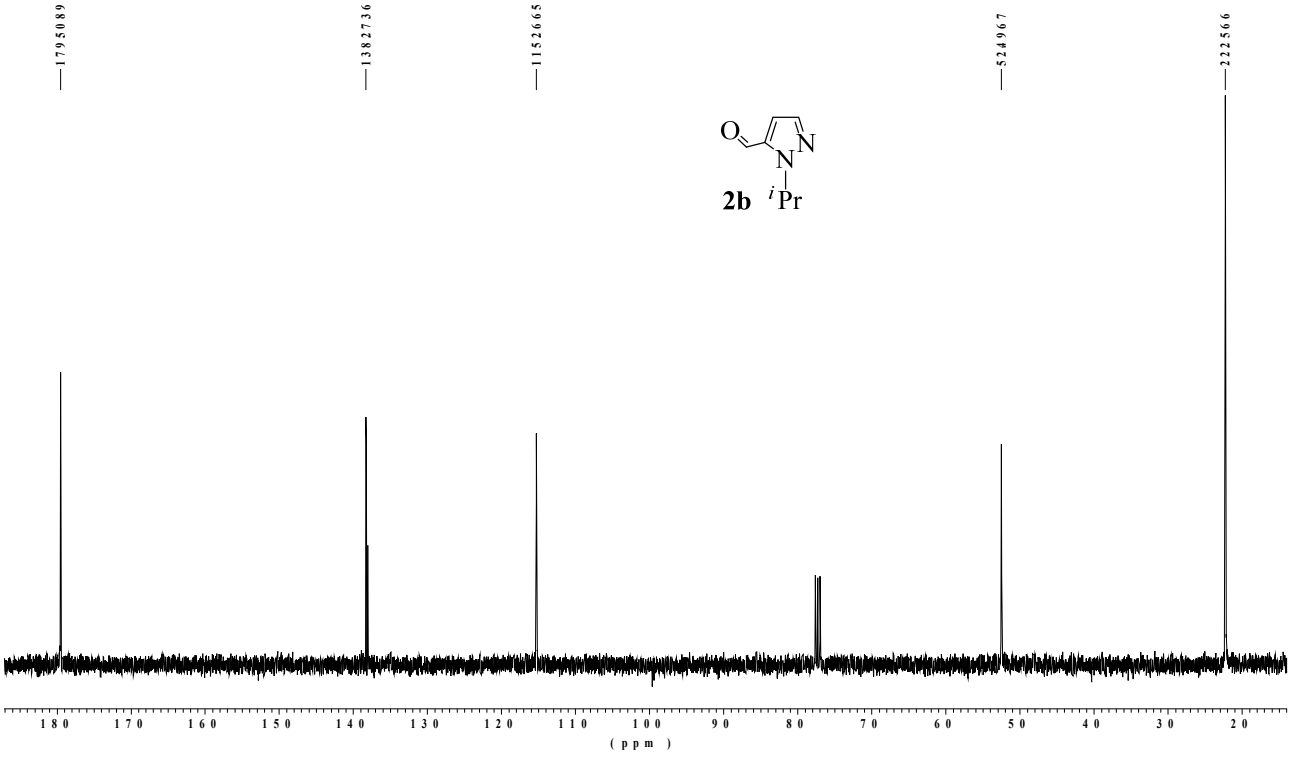
^{13}C NMR spectrum of carbaldehyde **4a** ($CDCl_3$)



^{1}H NMR spectrum of carbaldehyde **2b** ($CDCl_3$)



^{13}C NMR spectrum of carbaldehyde **2b** ($CDCl_3$)



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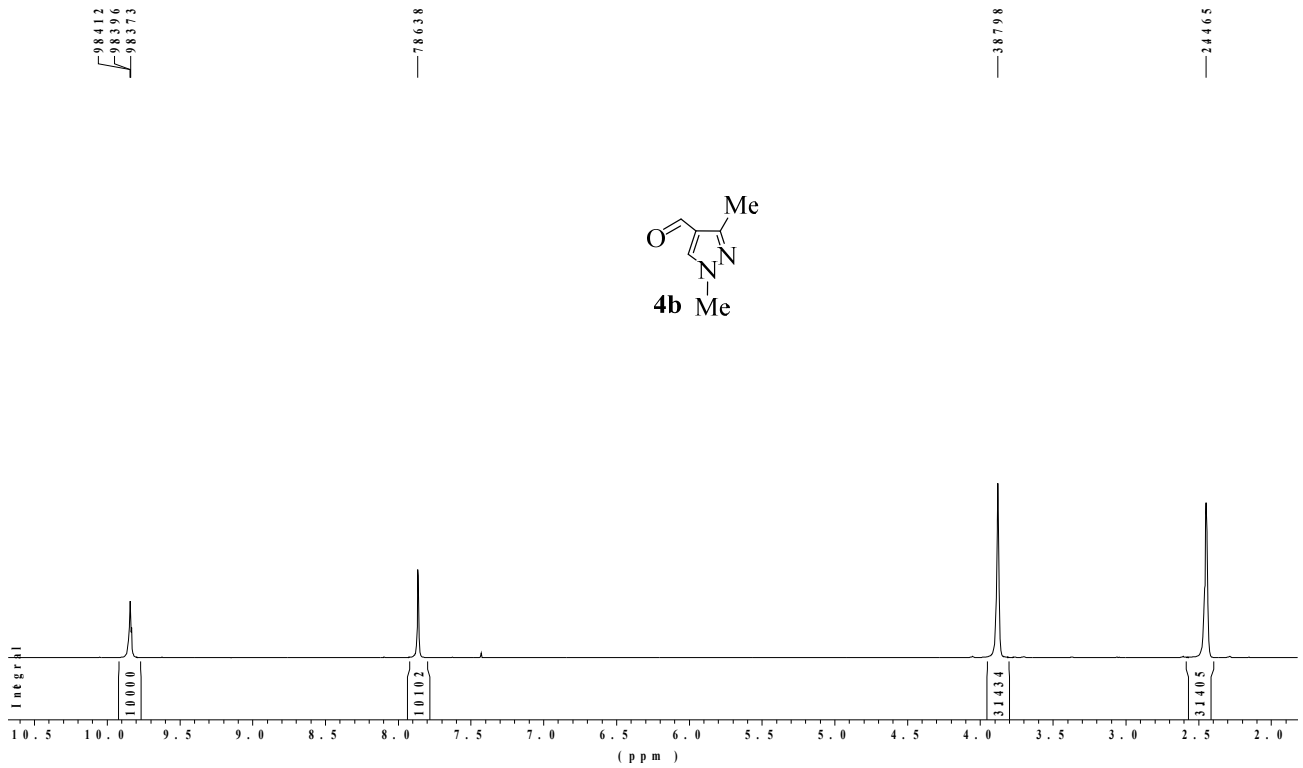

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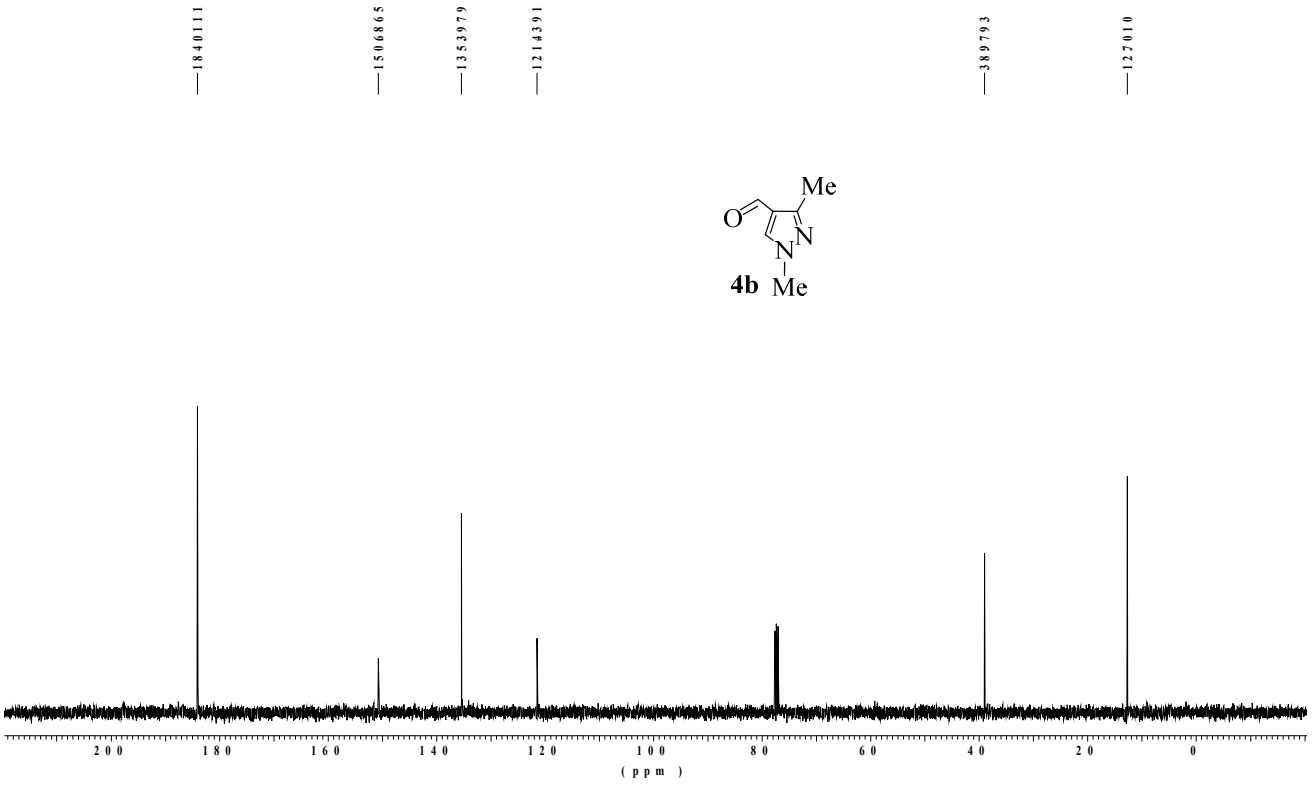
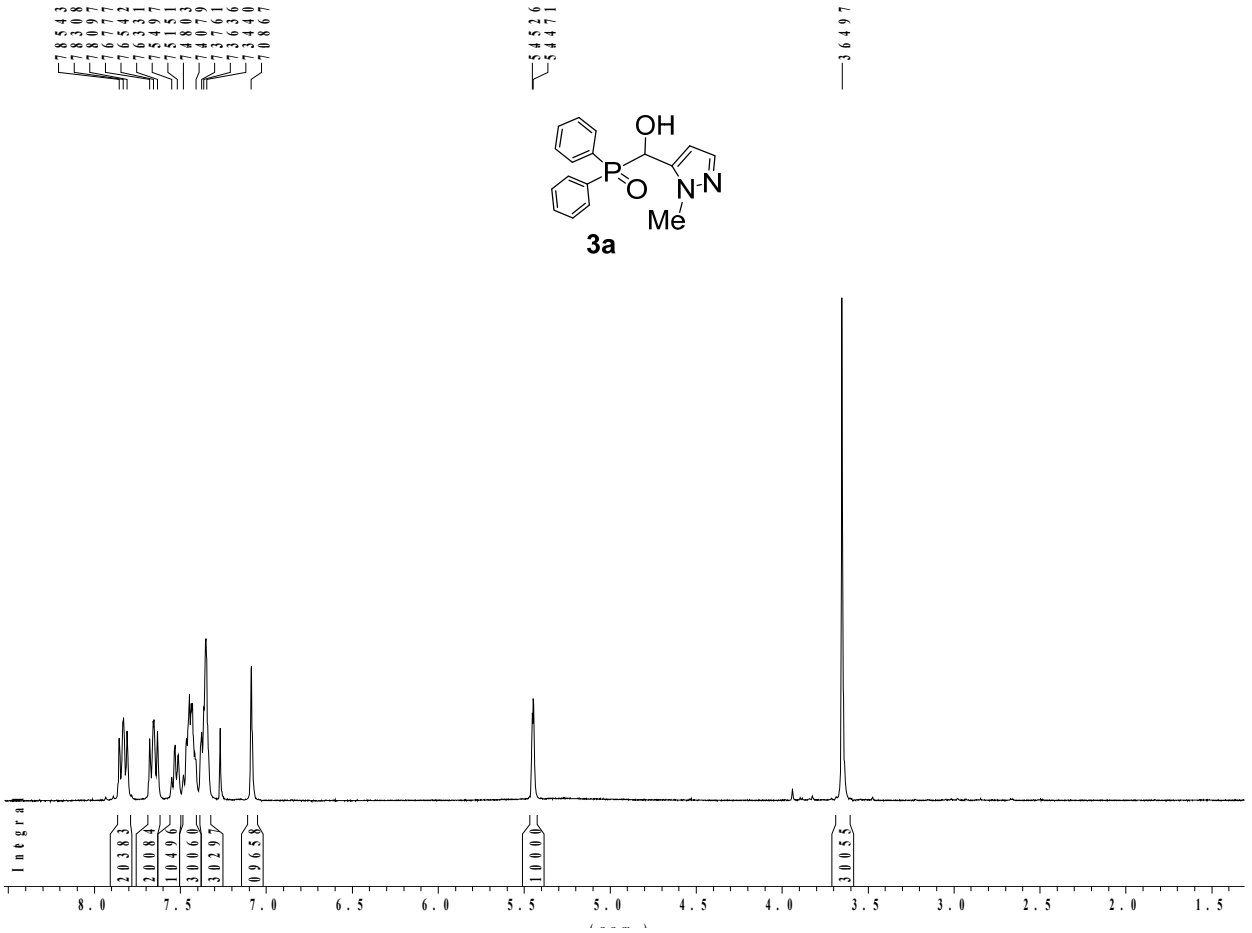
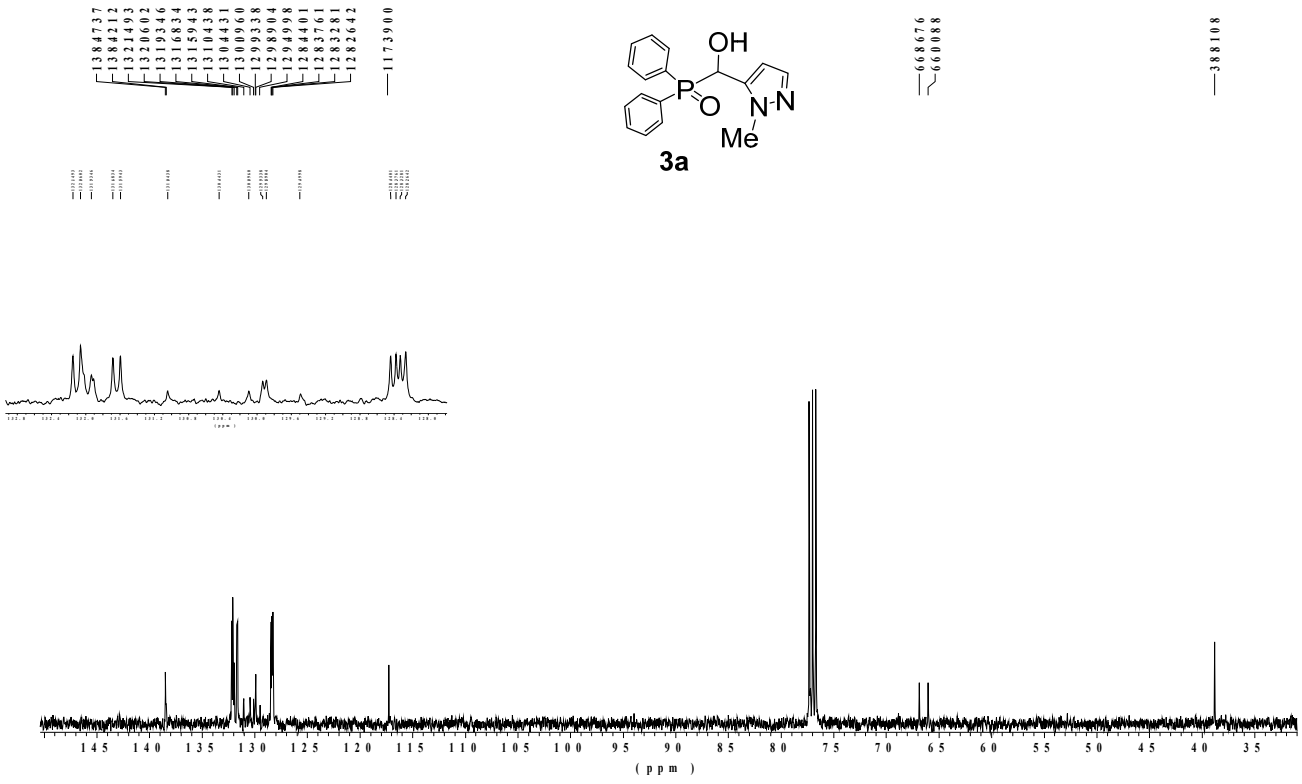


Spectral data of the synthesized products

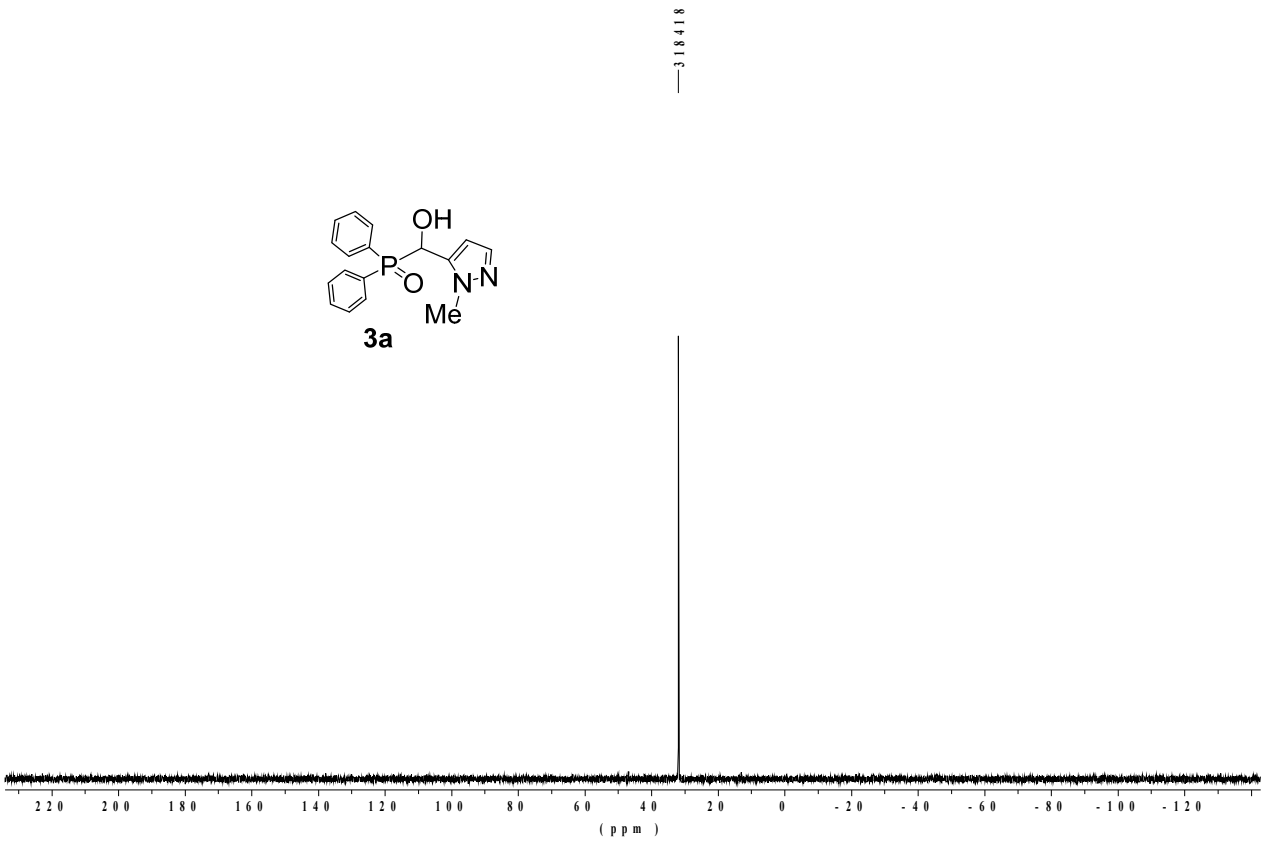
^{1}H NMR spectrum of adduct **3a** ($CDCl_3$)



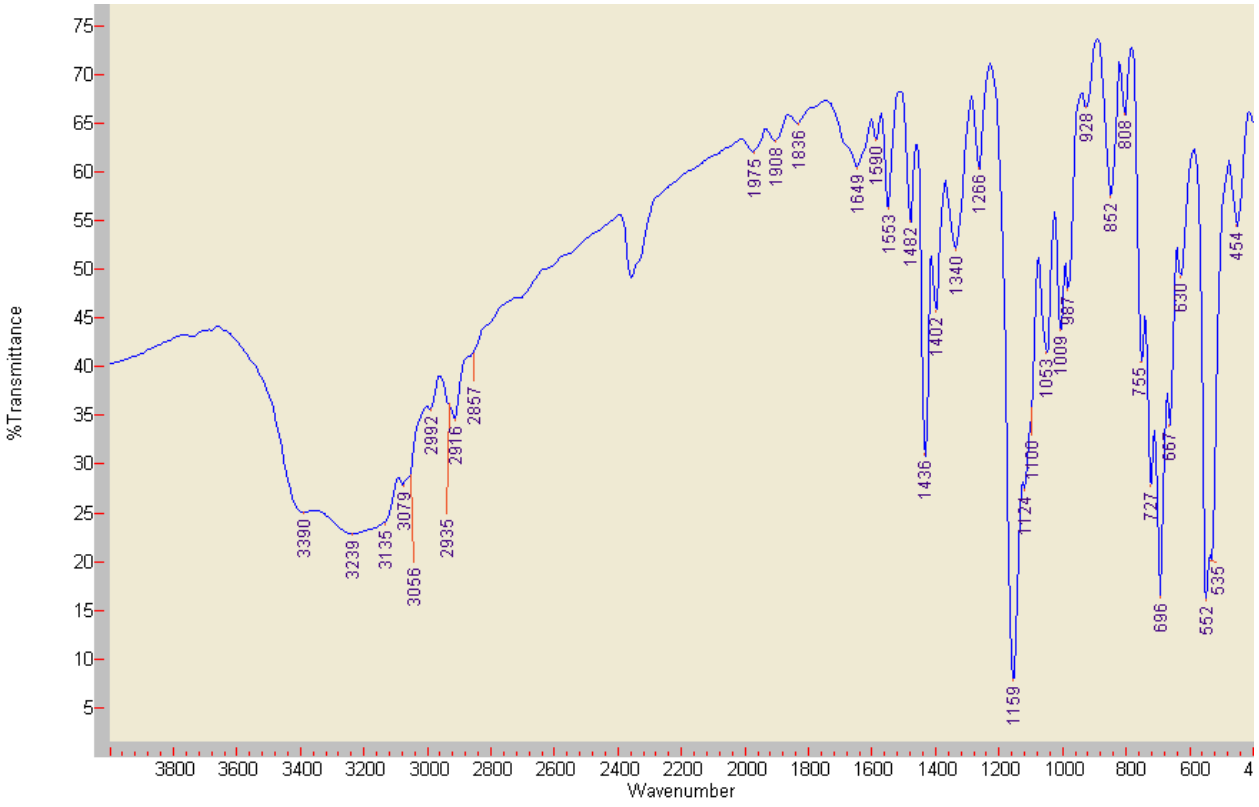
^{13}C NMR spectrum of adduct **3a** ($CDCl_3$)



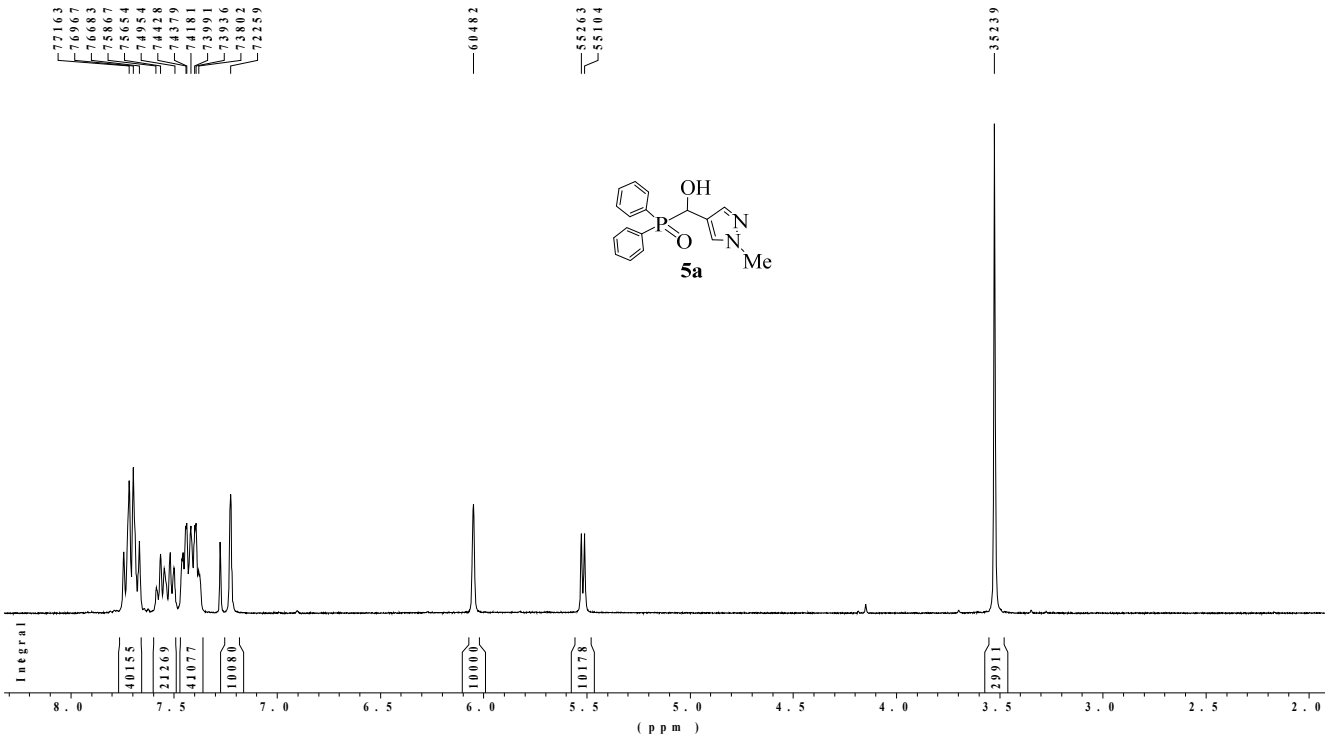
^{31}P NMR spectrum of adduct **3a** ($CDCl_3$)



IR spectrum (cm^{-1}) of adduct **3a**



^{1}H NMR spectrum of adduct **5a** ($CDCl_3$)



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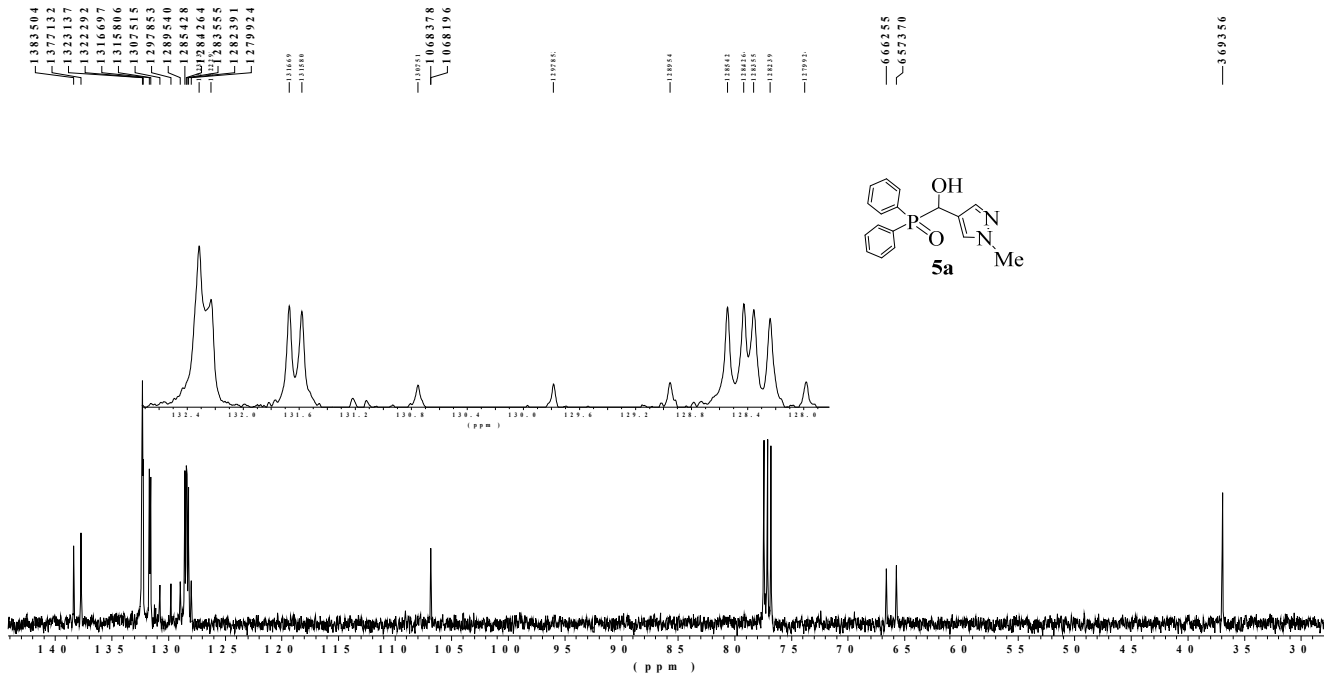

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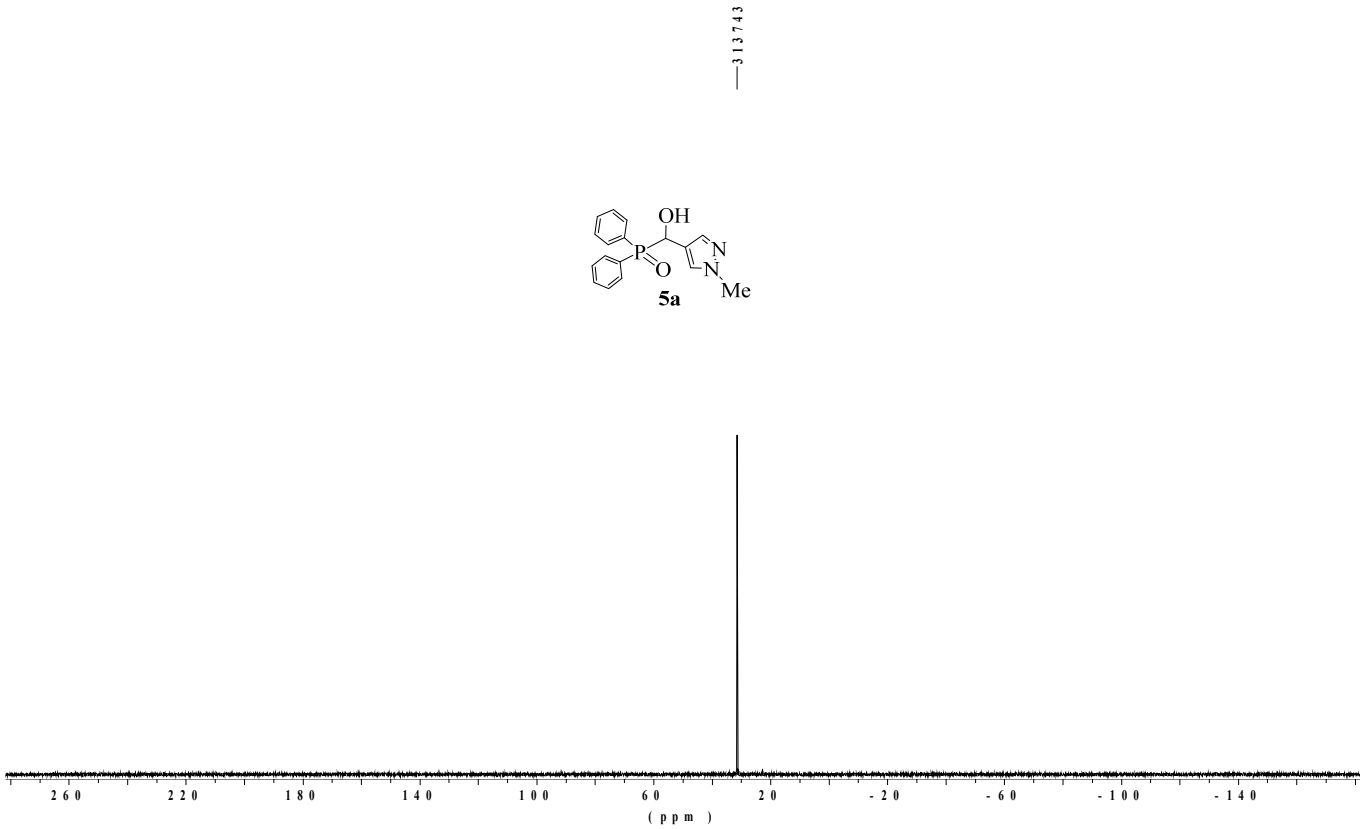
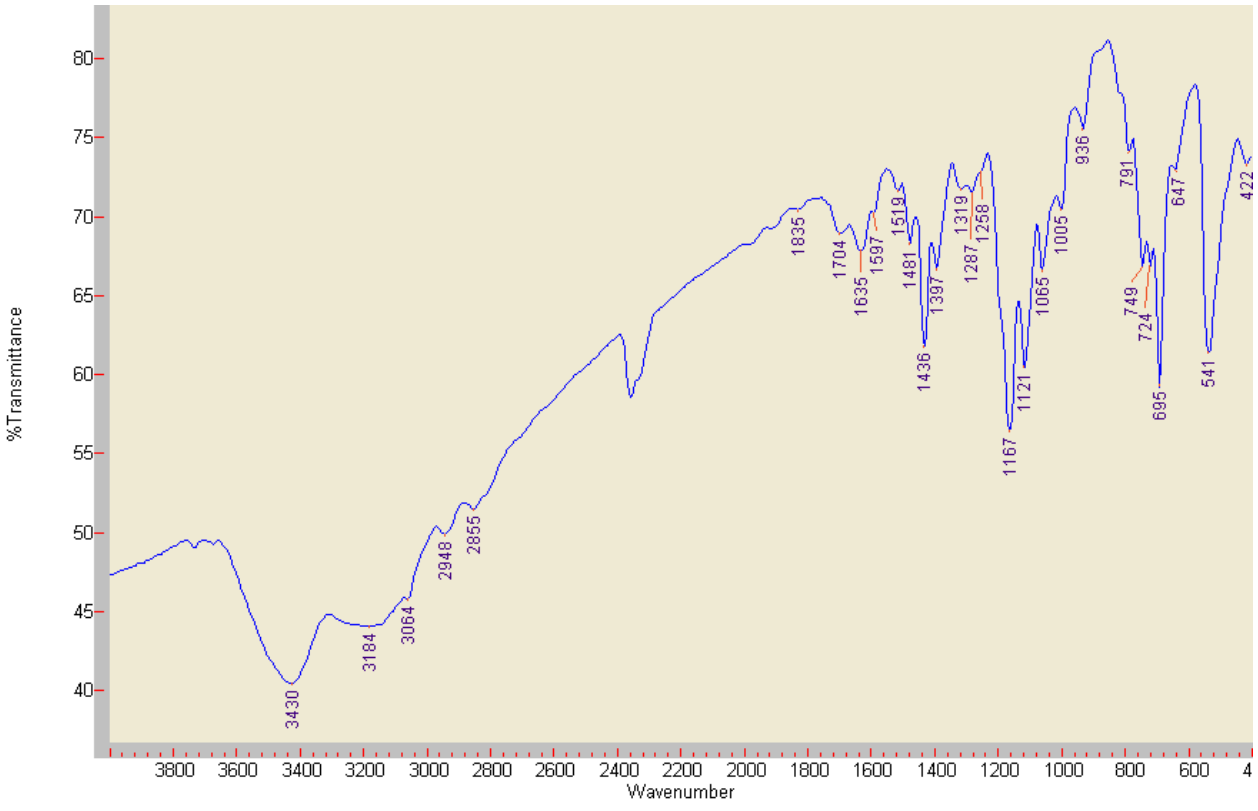
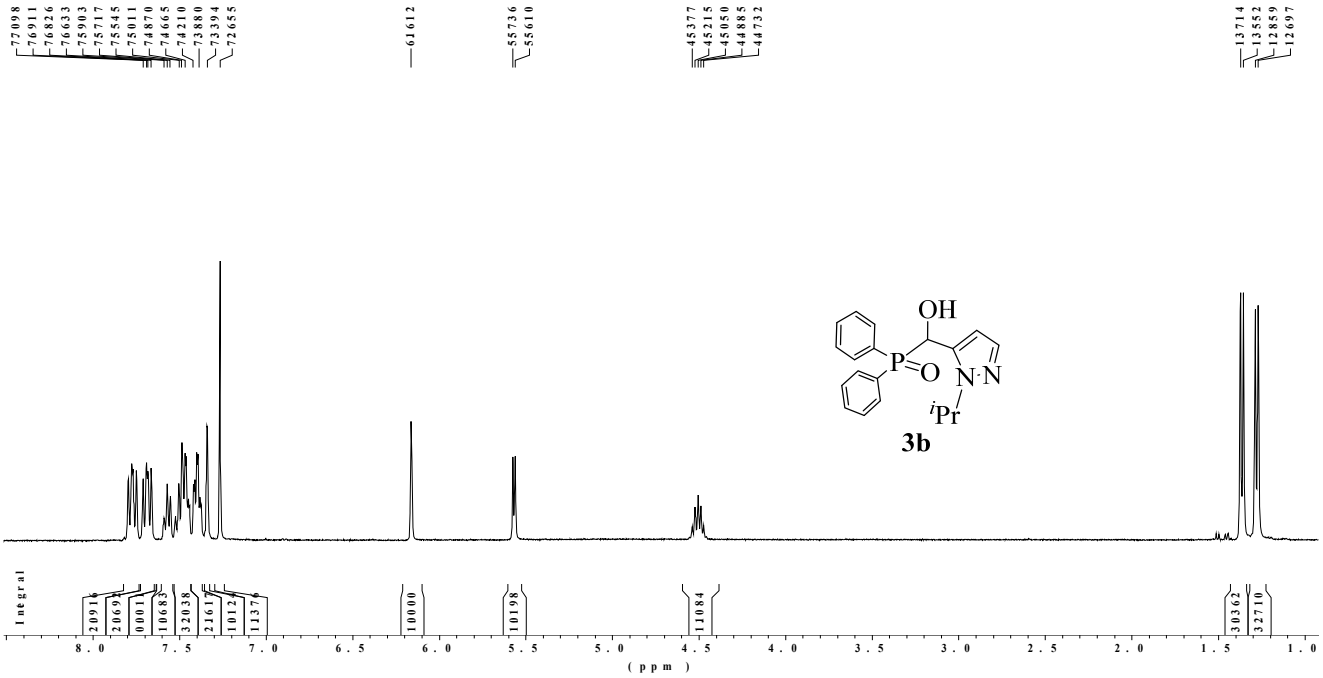


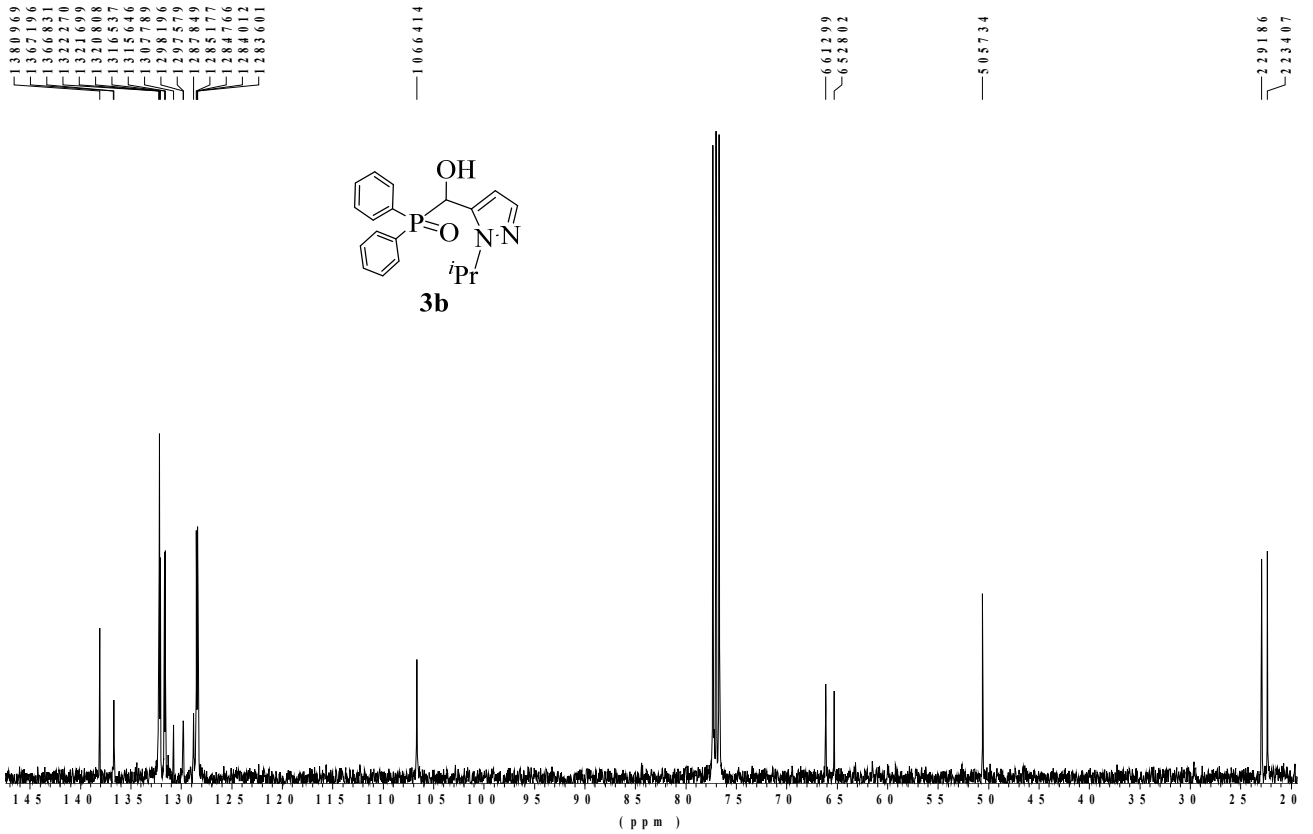
IR spectrum (cm^{-1}) of adduct **5a**



^{1}H NMR spectrum of adduct **3b** ($CDCl_3$)



^{13}C NMR spectrum of adduct **3b** ($CDCl_3$)



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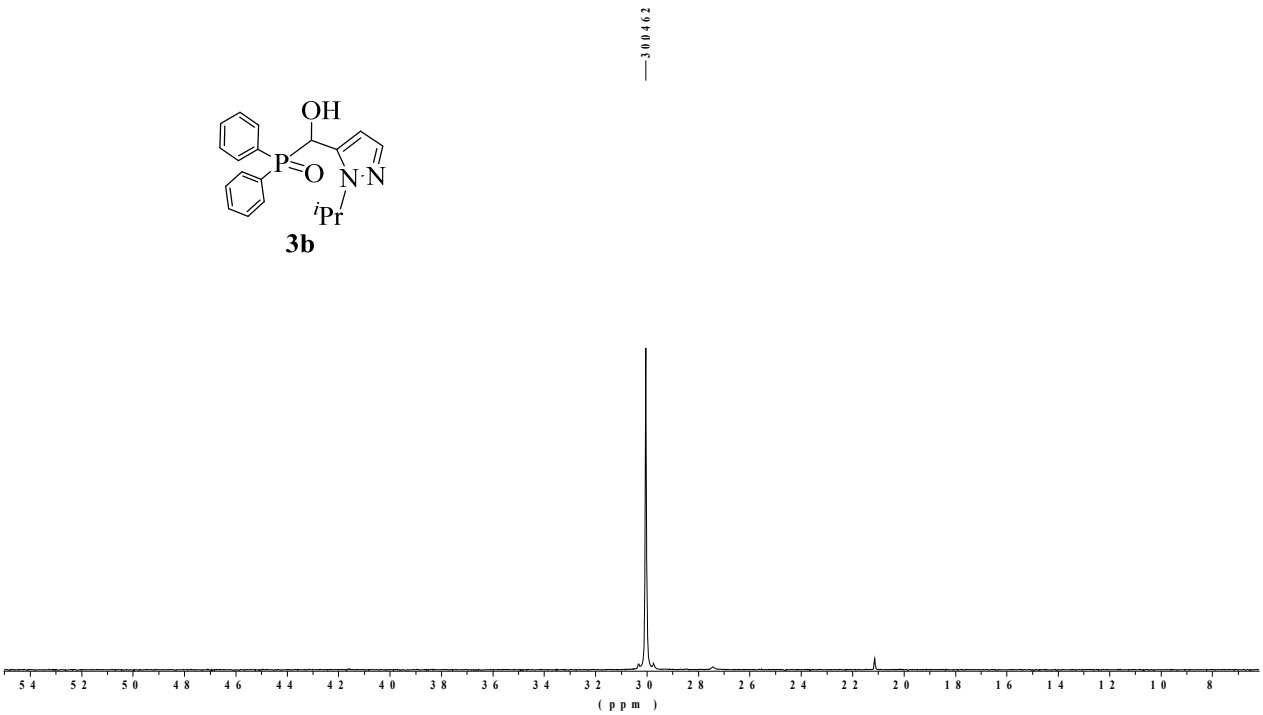
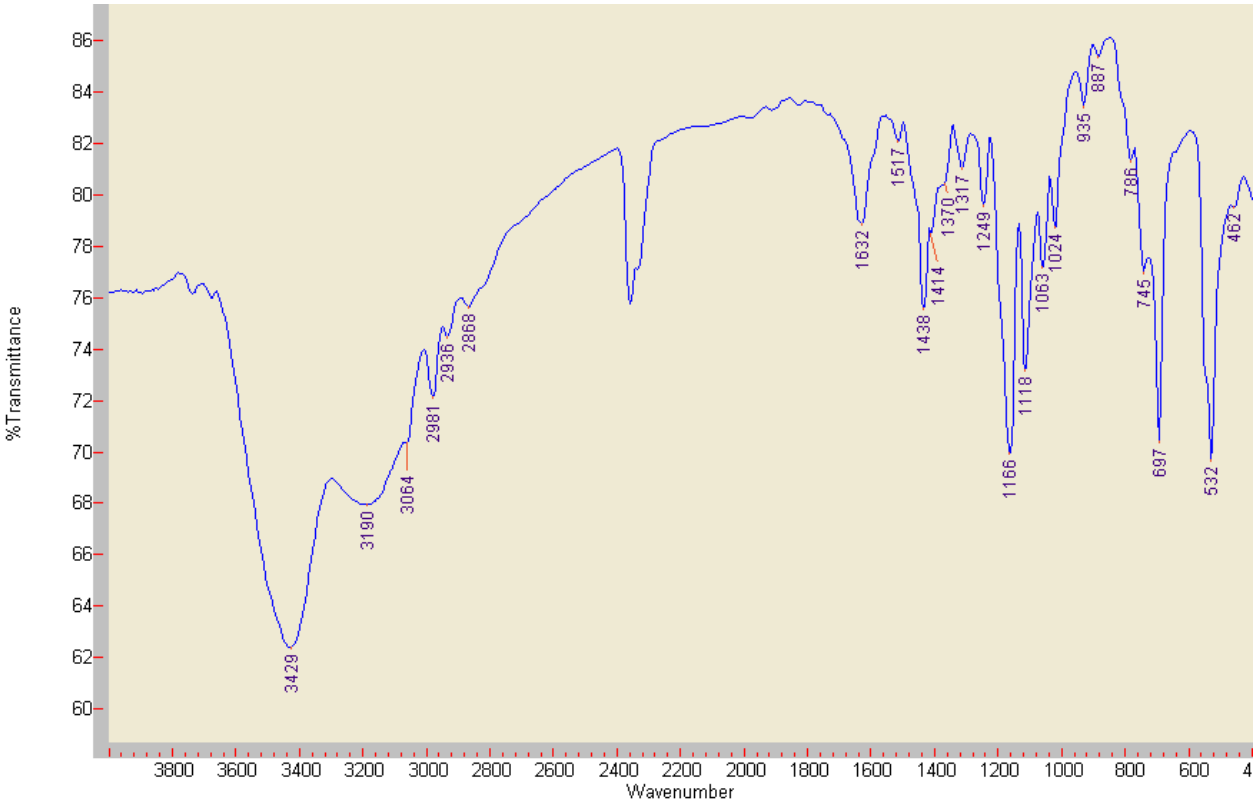


IR spectrum (cm^{-1}) of adduct **3b**



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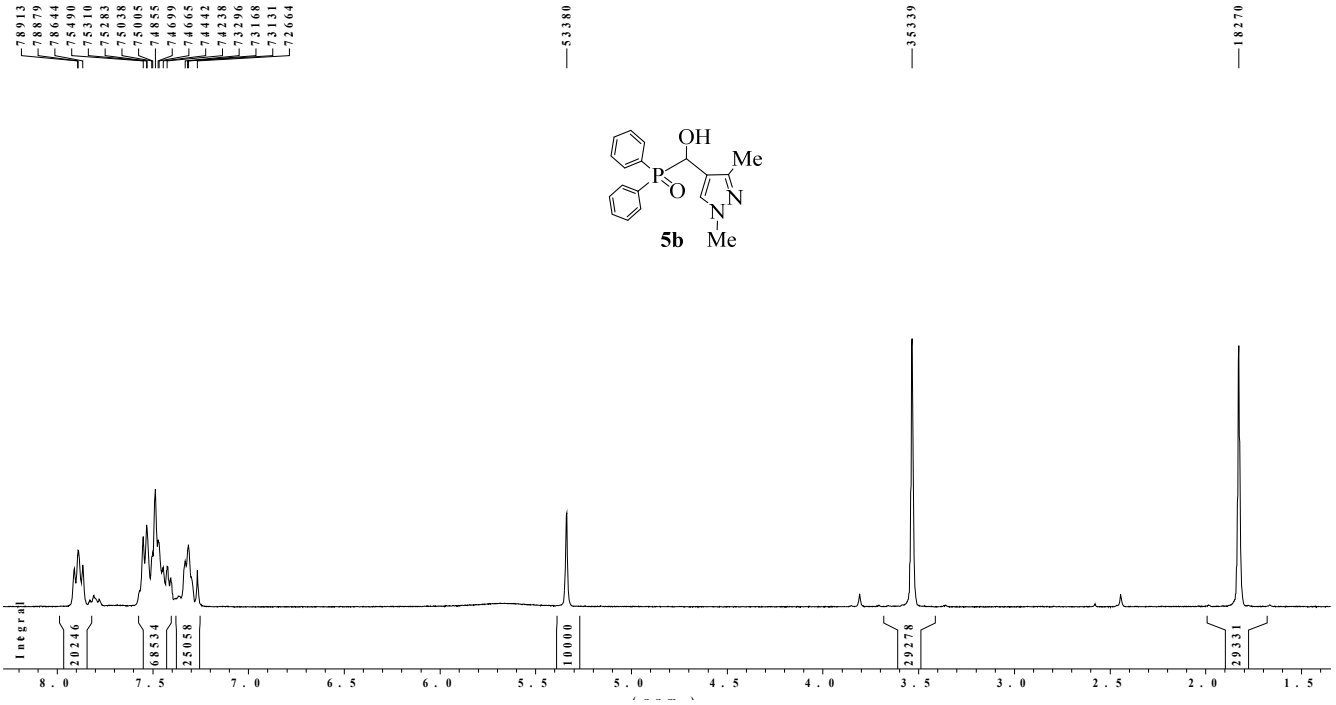

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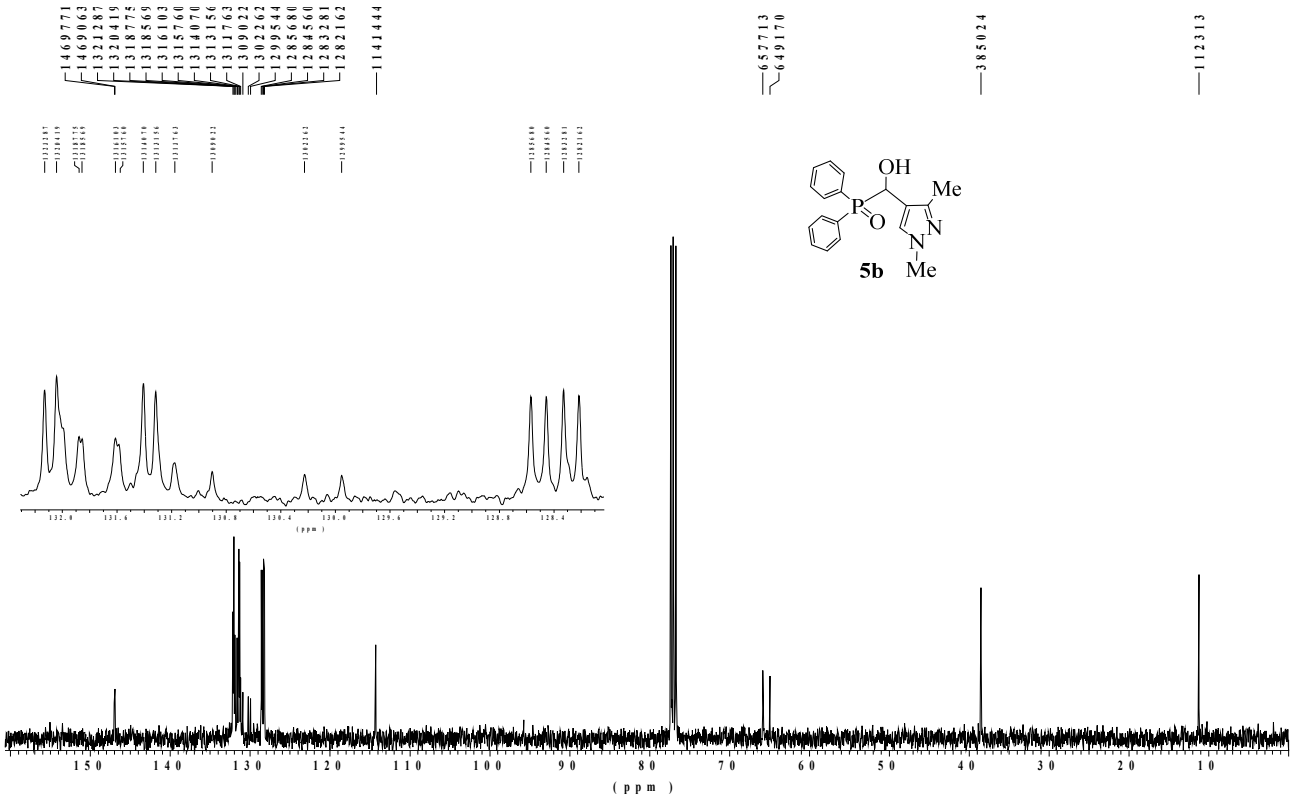

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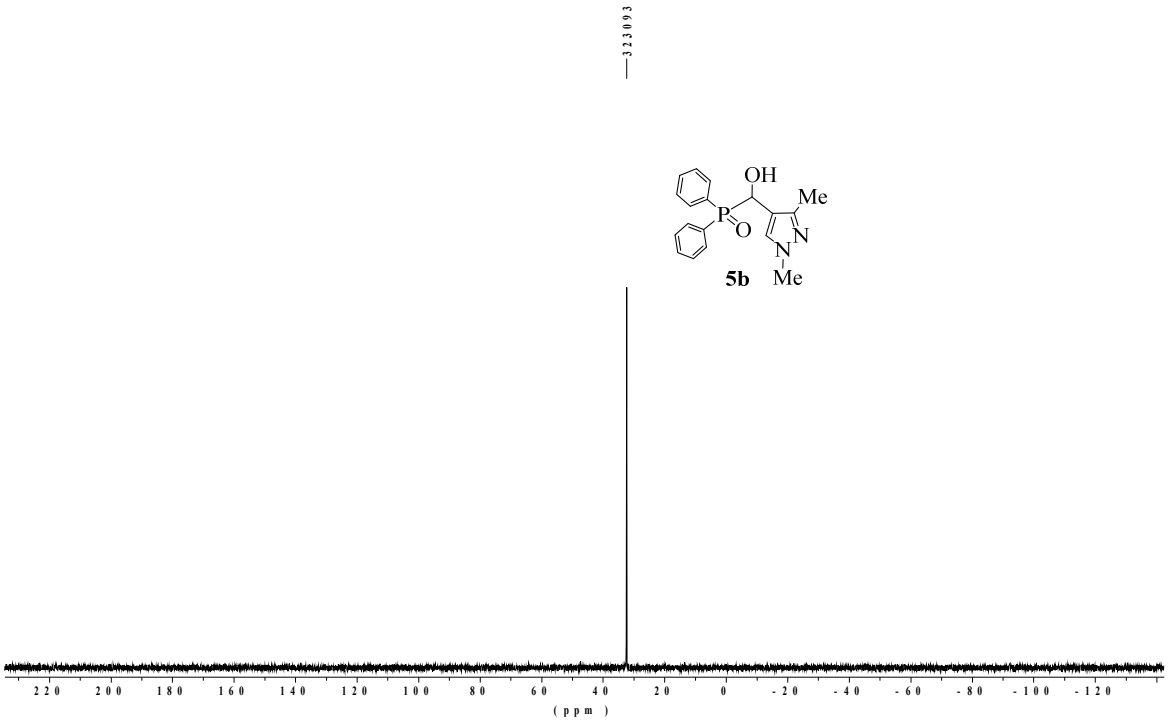
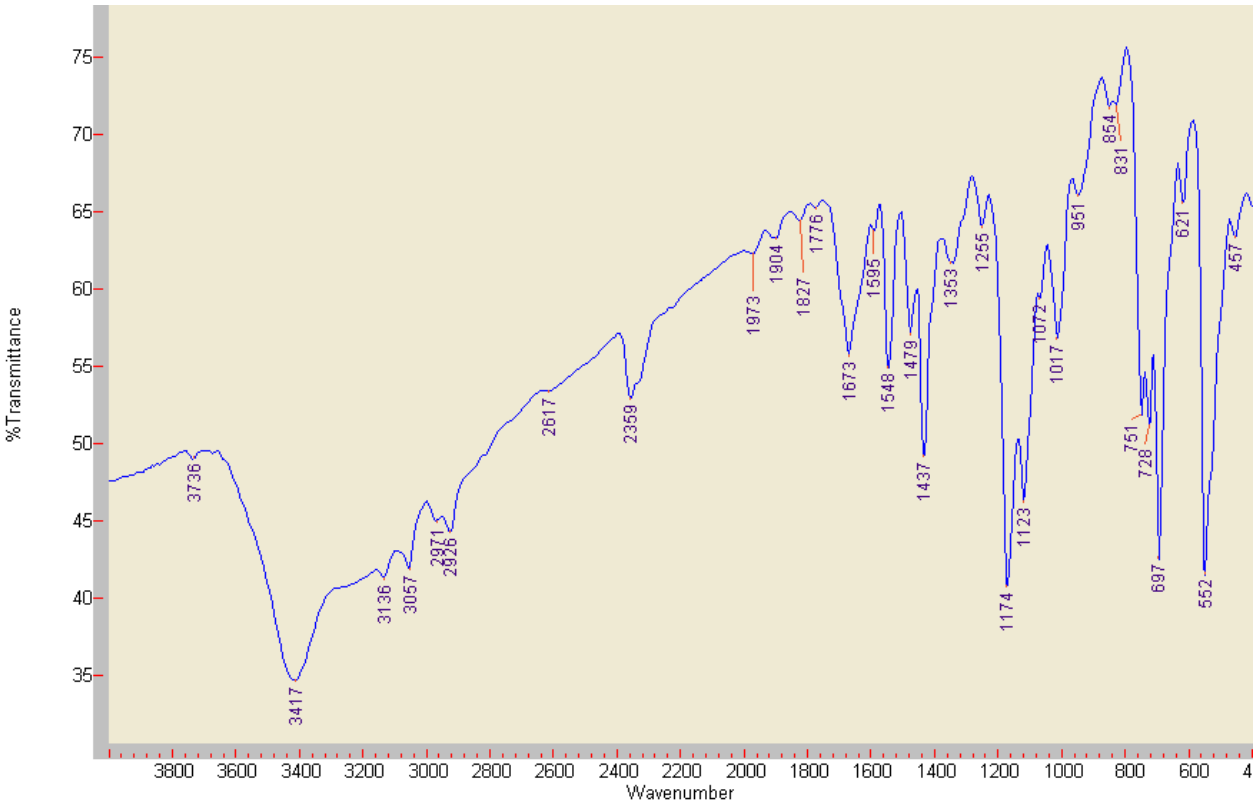
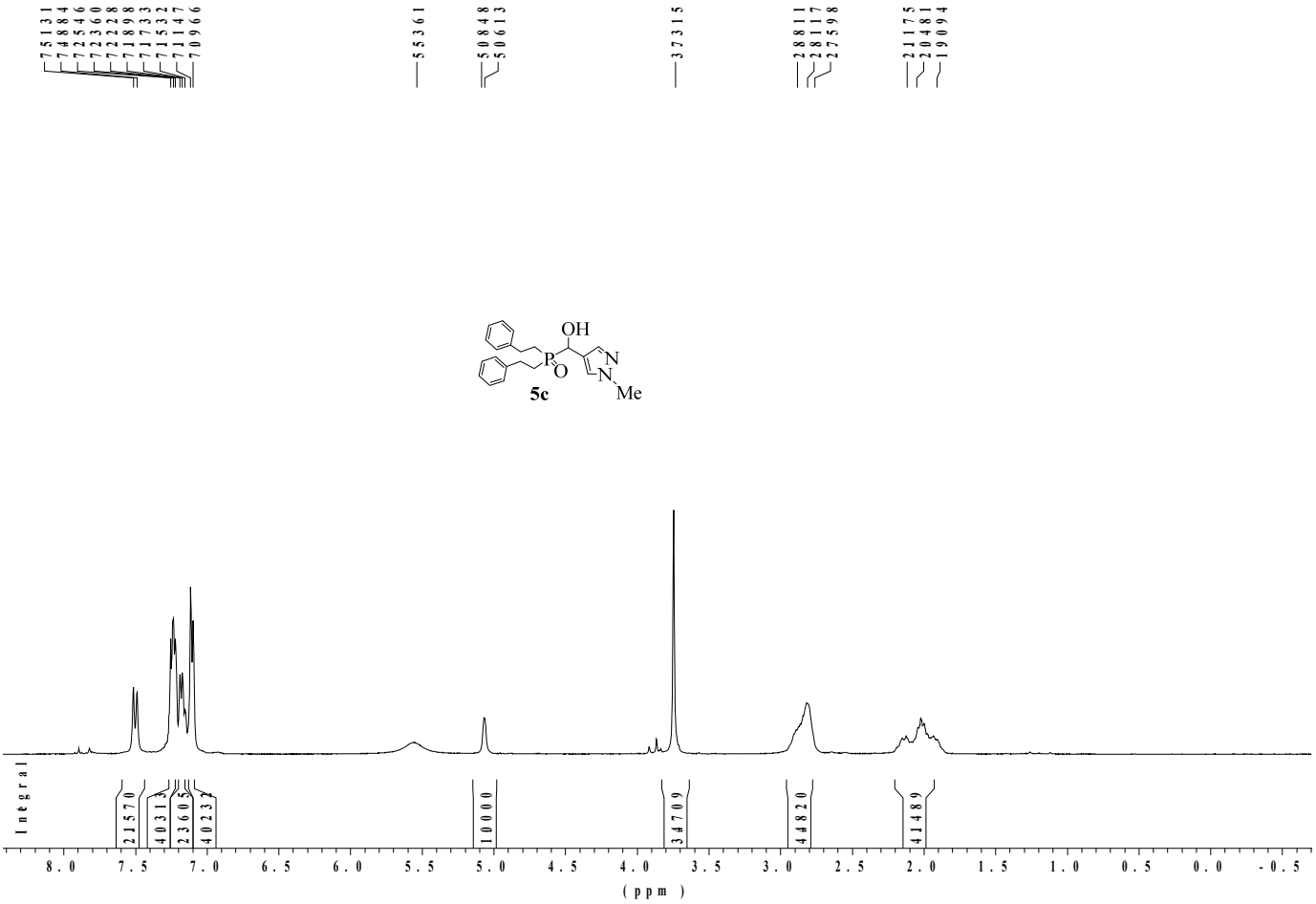


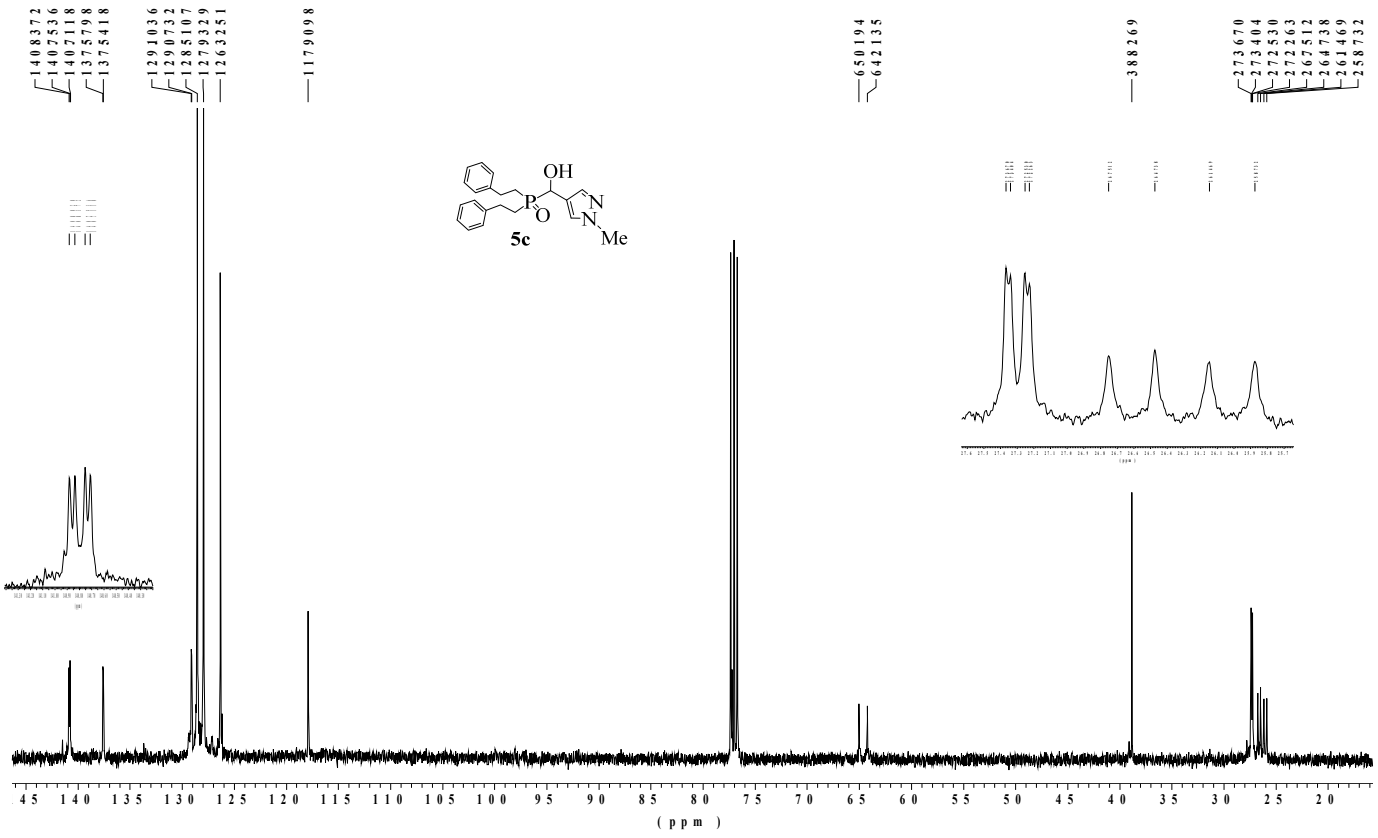
IR spectrum (cm^{-1}) of adduct **5b**



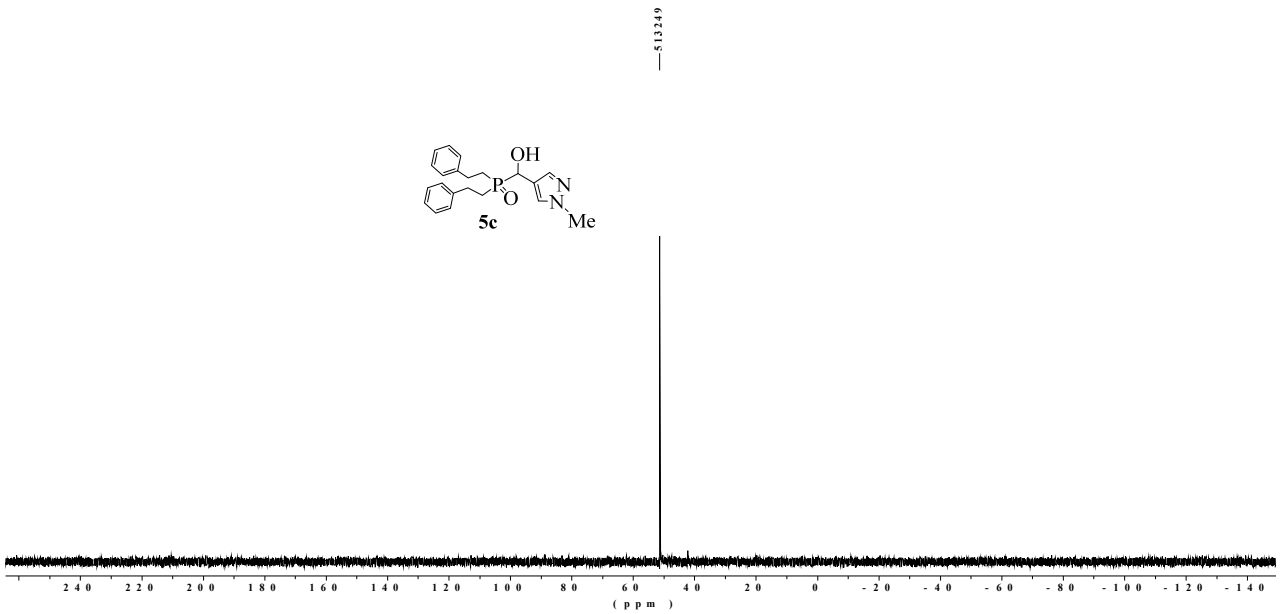
^{1}H NMR spectrum of adduct **5c** ($CDCl_3$)



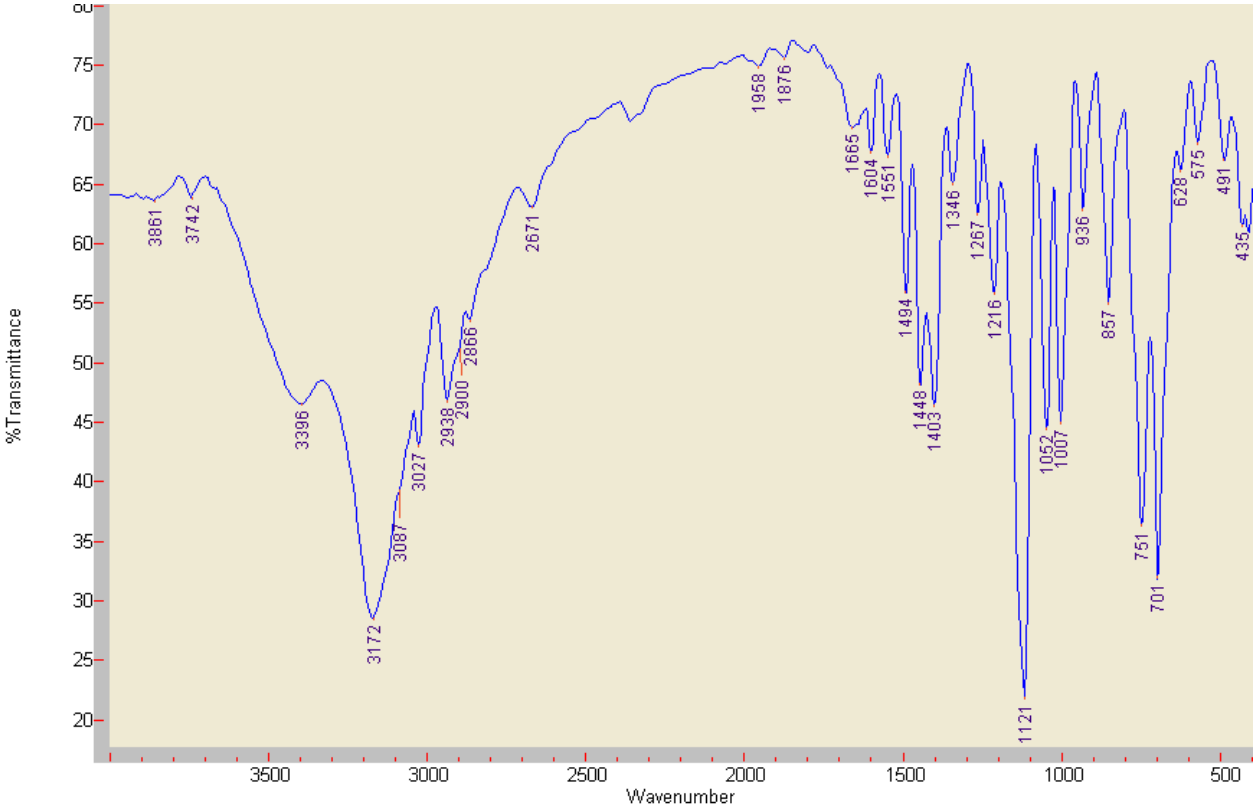
^{13}C NMR spectrum of adduct **5c** ($CDCl_3$)



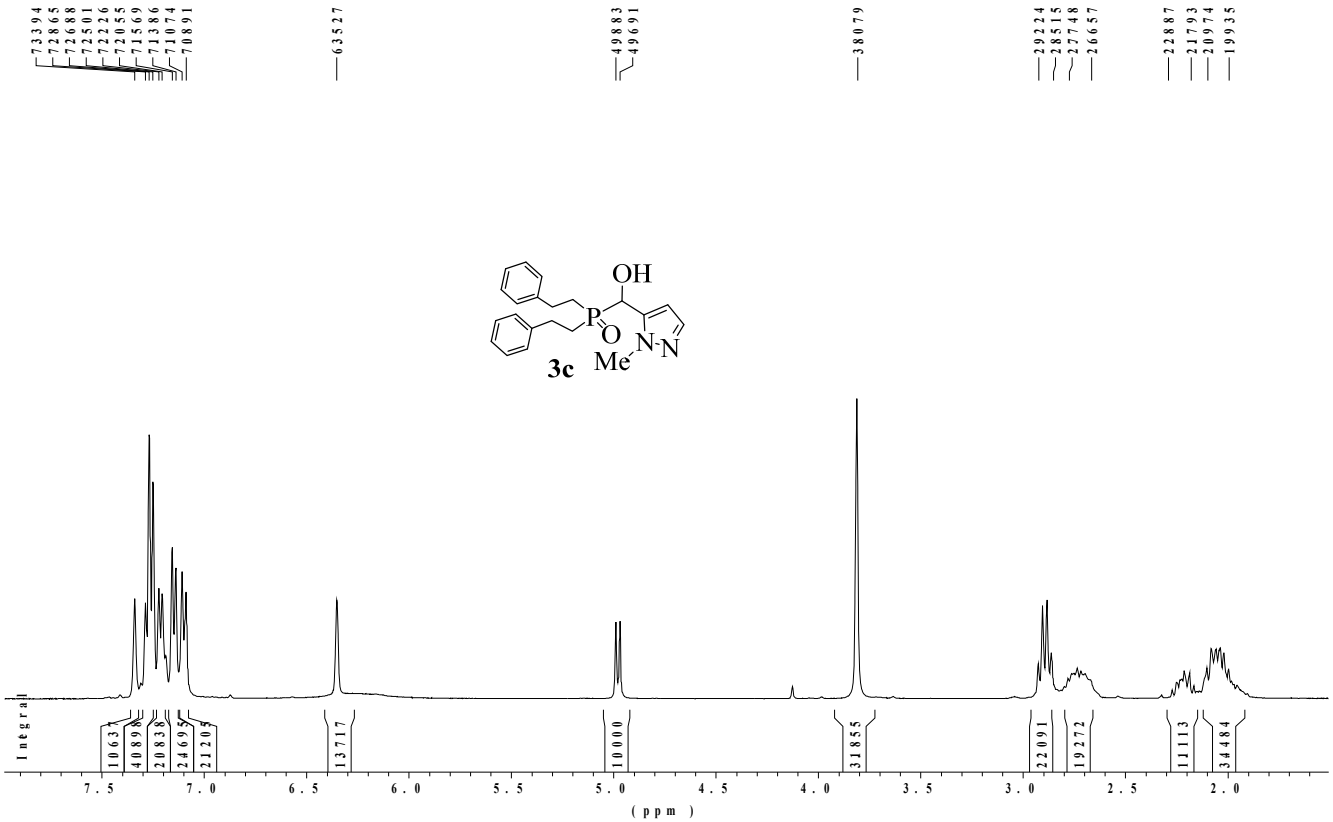
^{31}P NMR spectrum of adduct **5c** ($CDCl_3$)



IR spectrum (cm^{-1}) of adduct **5c**



^{1}H NMR spectrum of adduct **3c** ($CDCl_3$)



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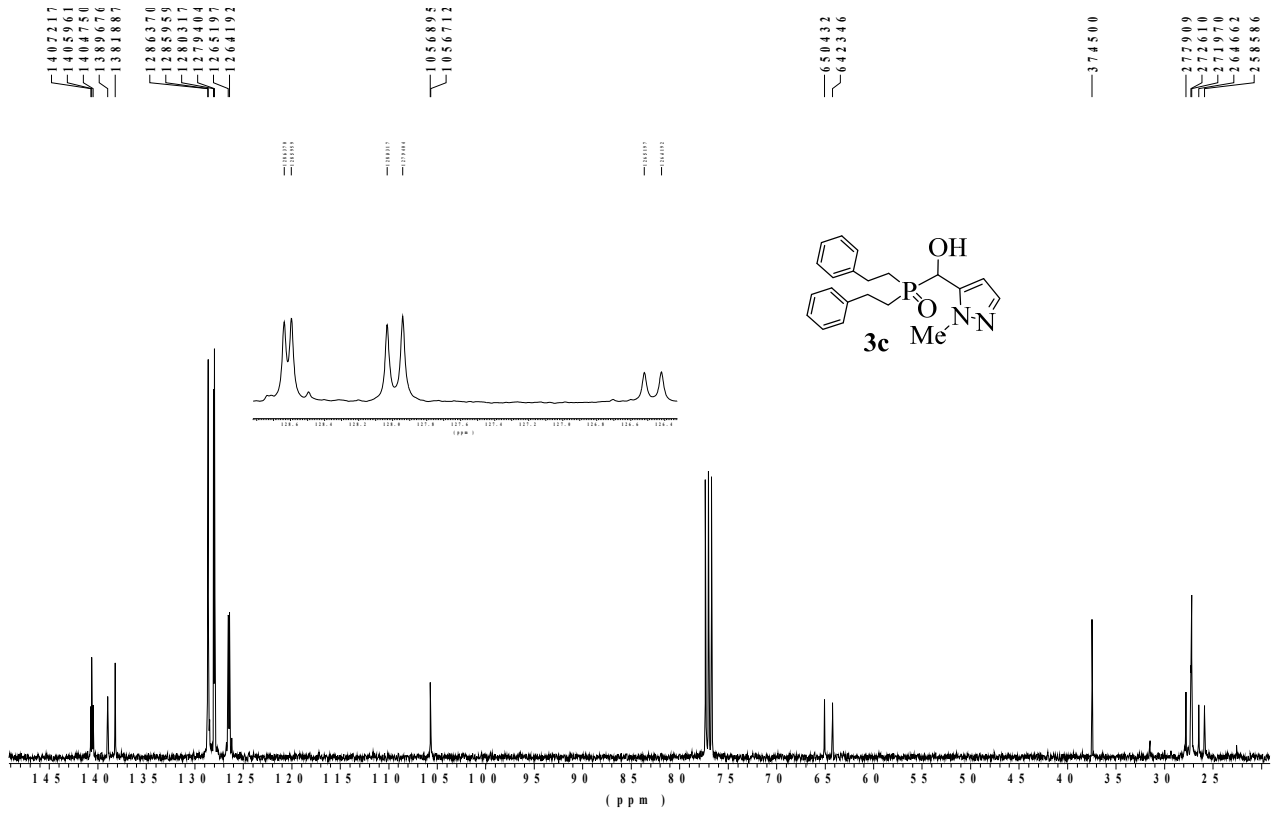

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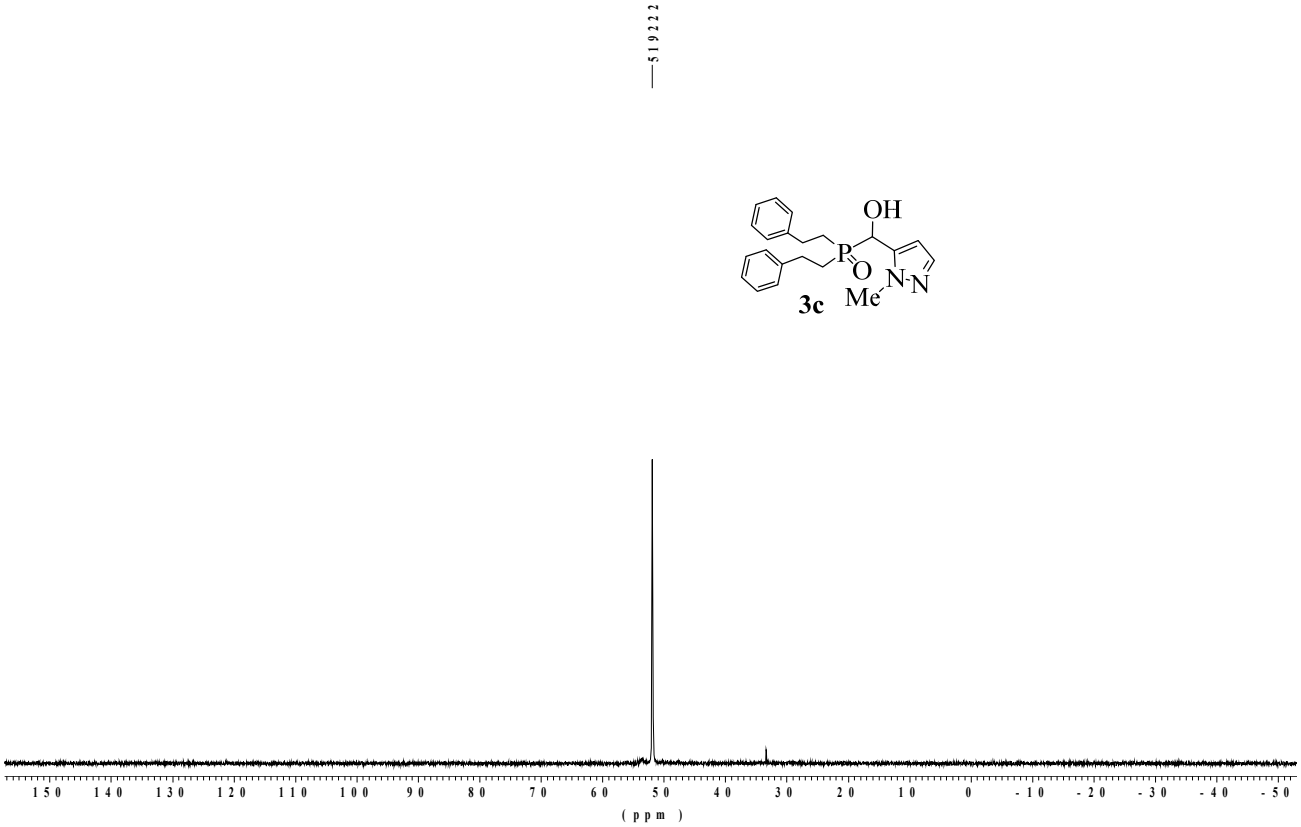
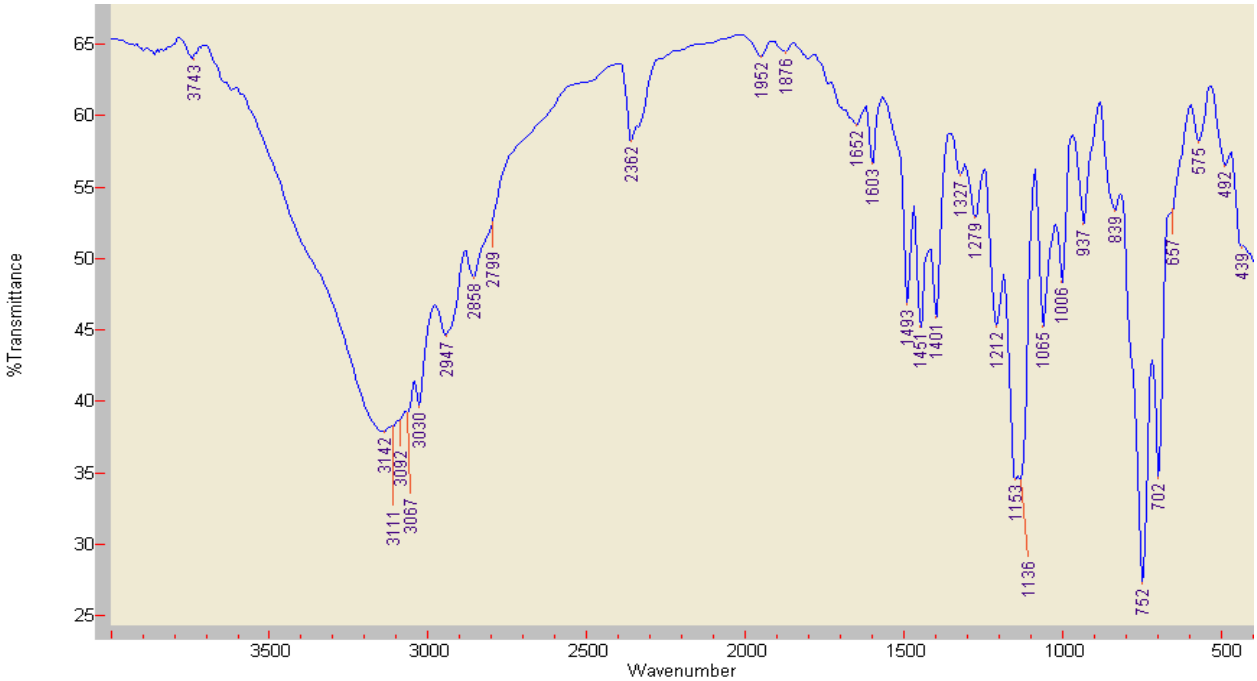
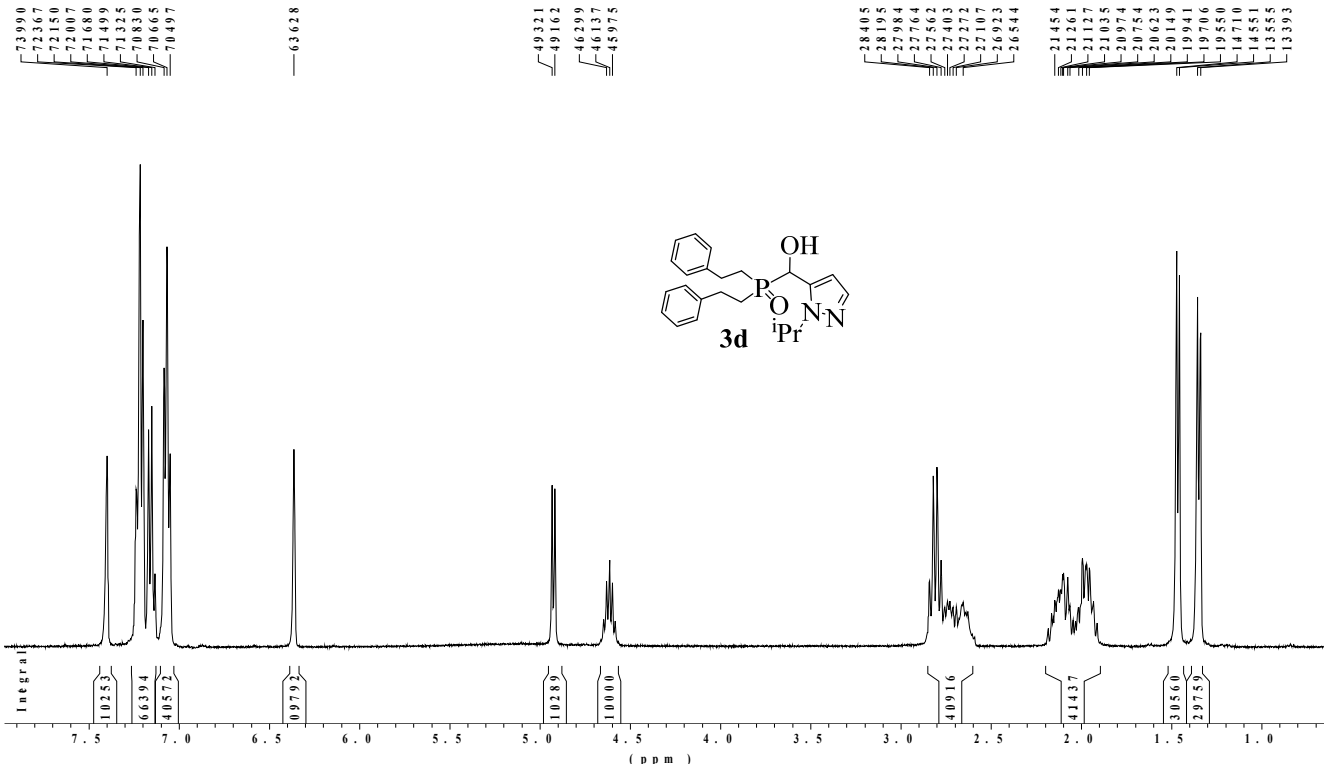


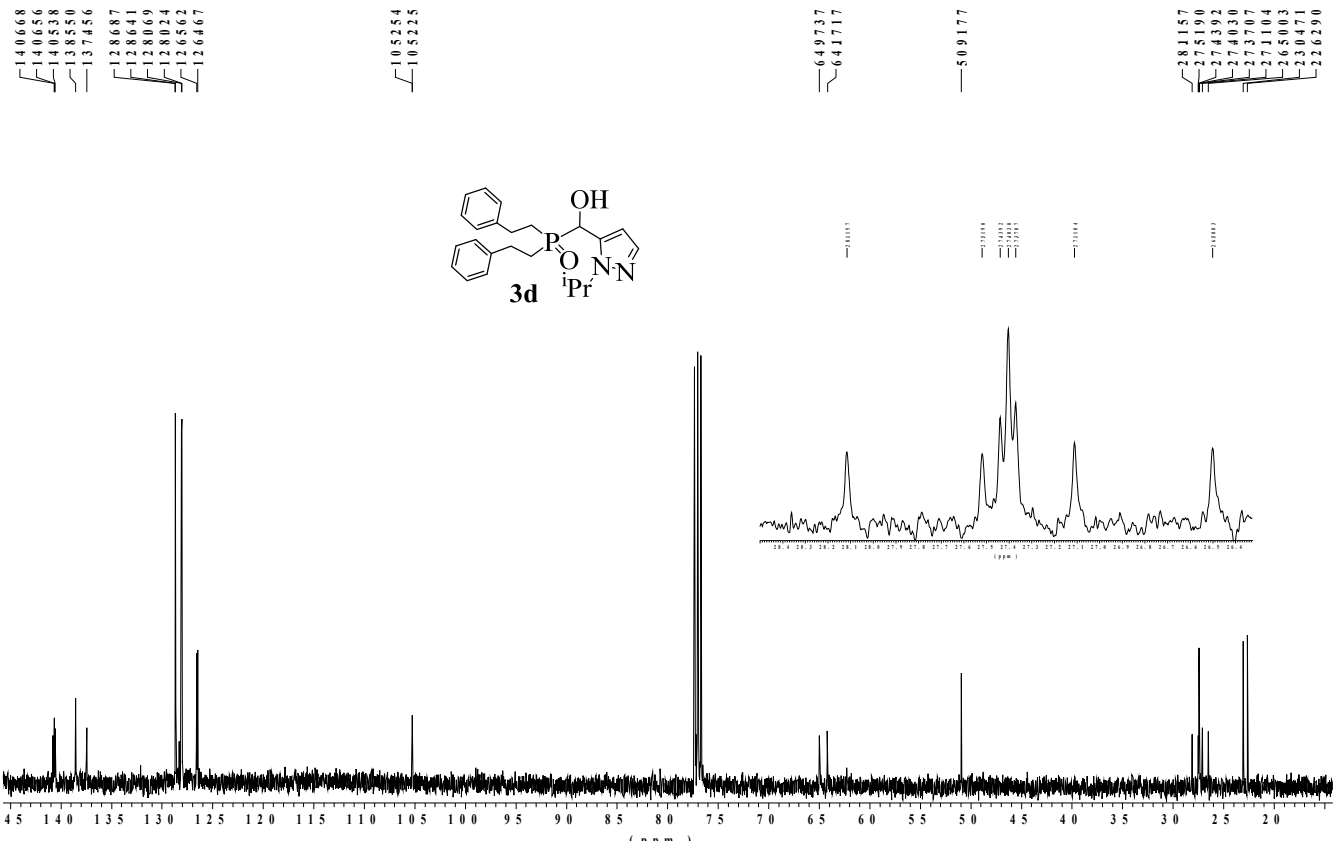
IR spectrum (cm^{-1}) of adduct **3c**



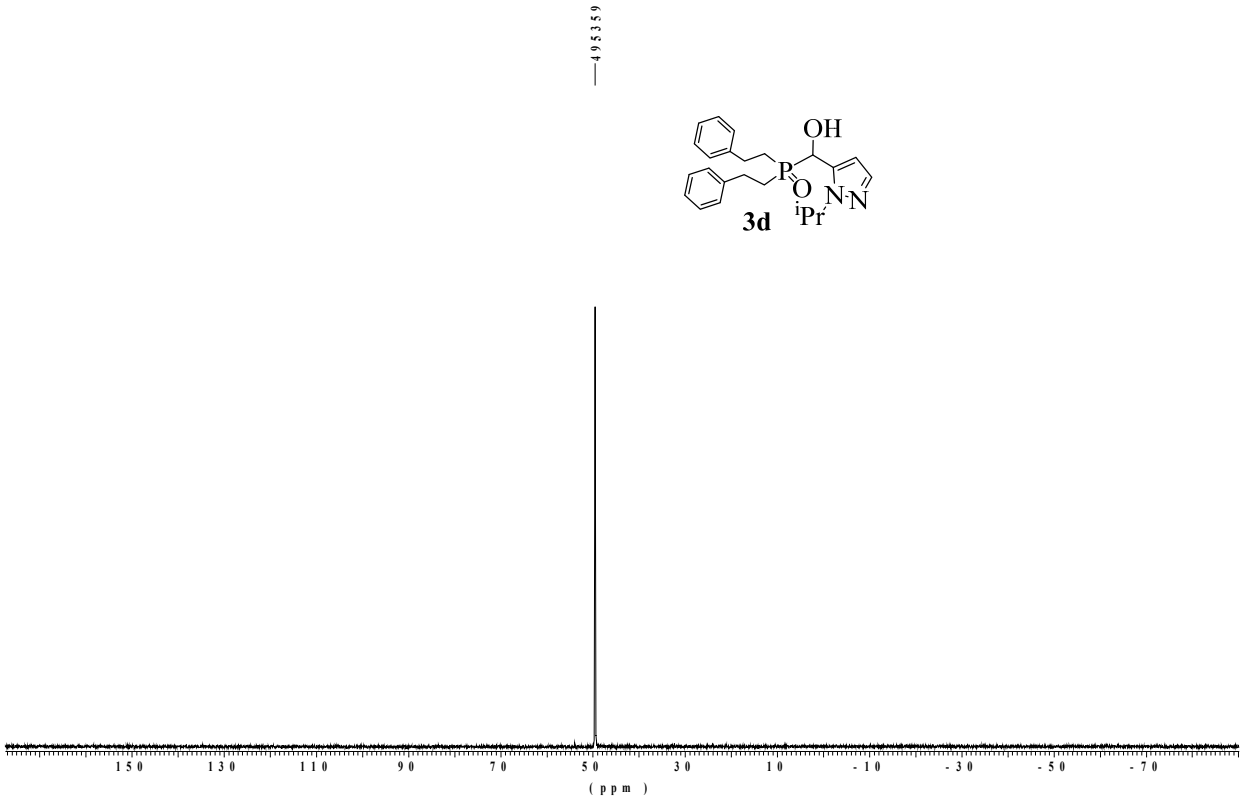
^{1}H NMR spectrum of adduct **3d** ($CDCl_3$)



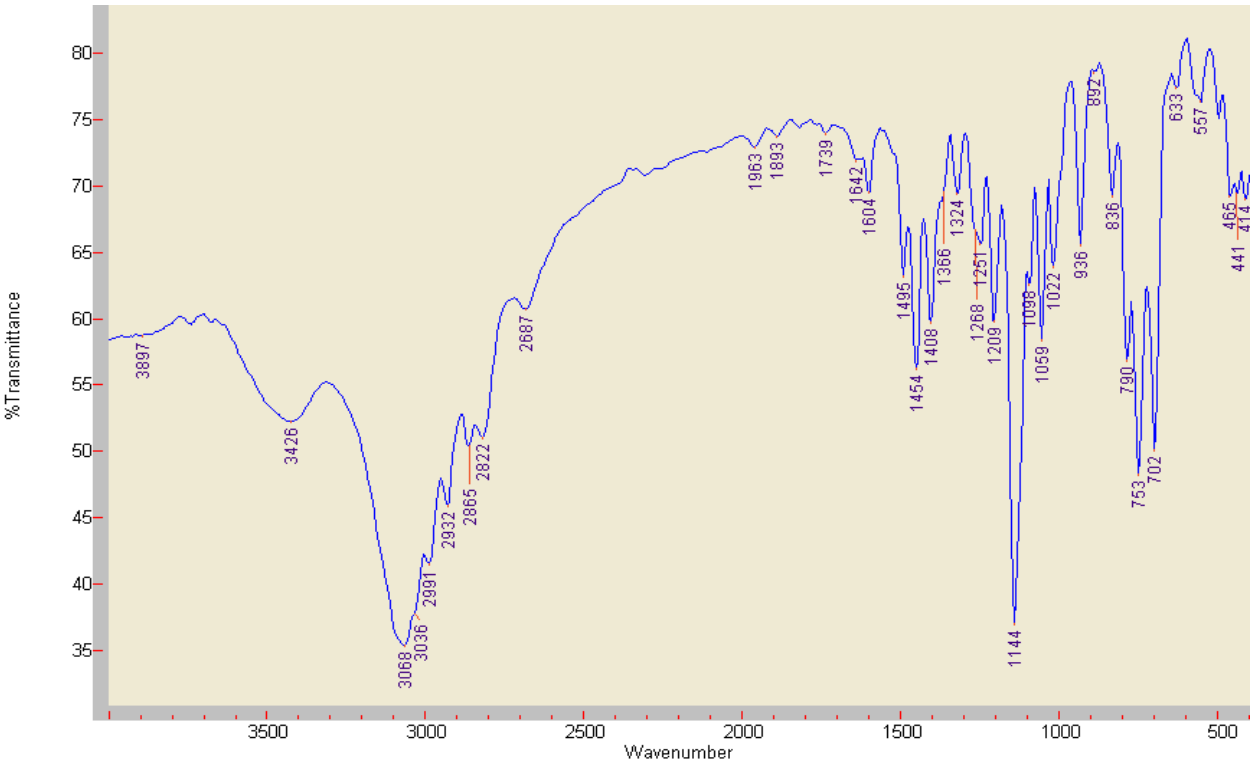
^{13}C NMR spectrum of adduct **3d** ($CDCl_3$)



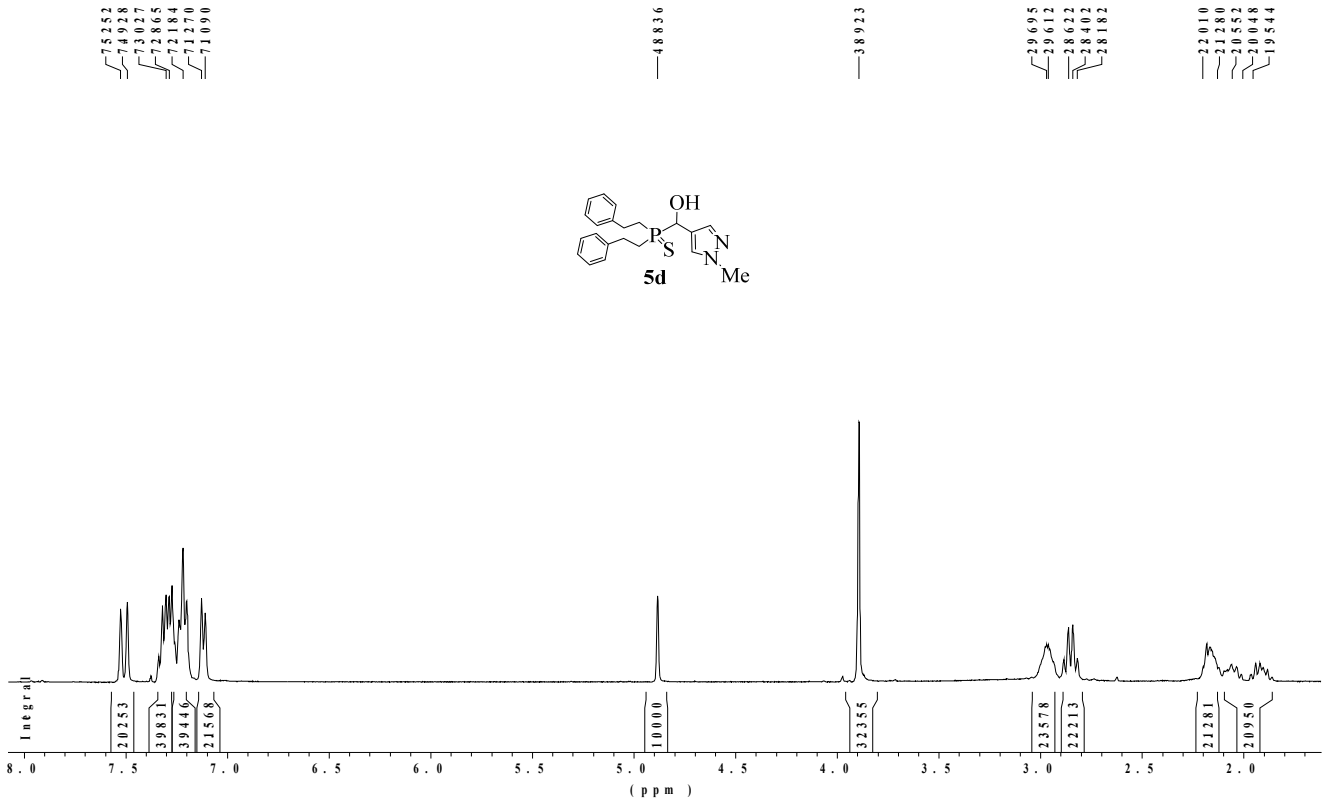
^{31}P NMR spectrum of adduct **3d** ($CDCl_3$)



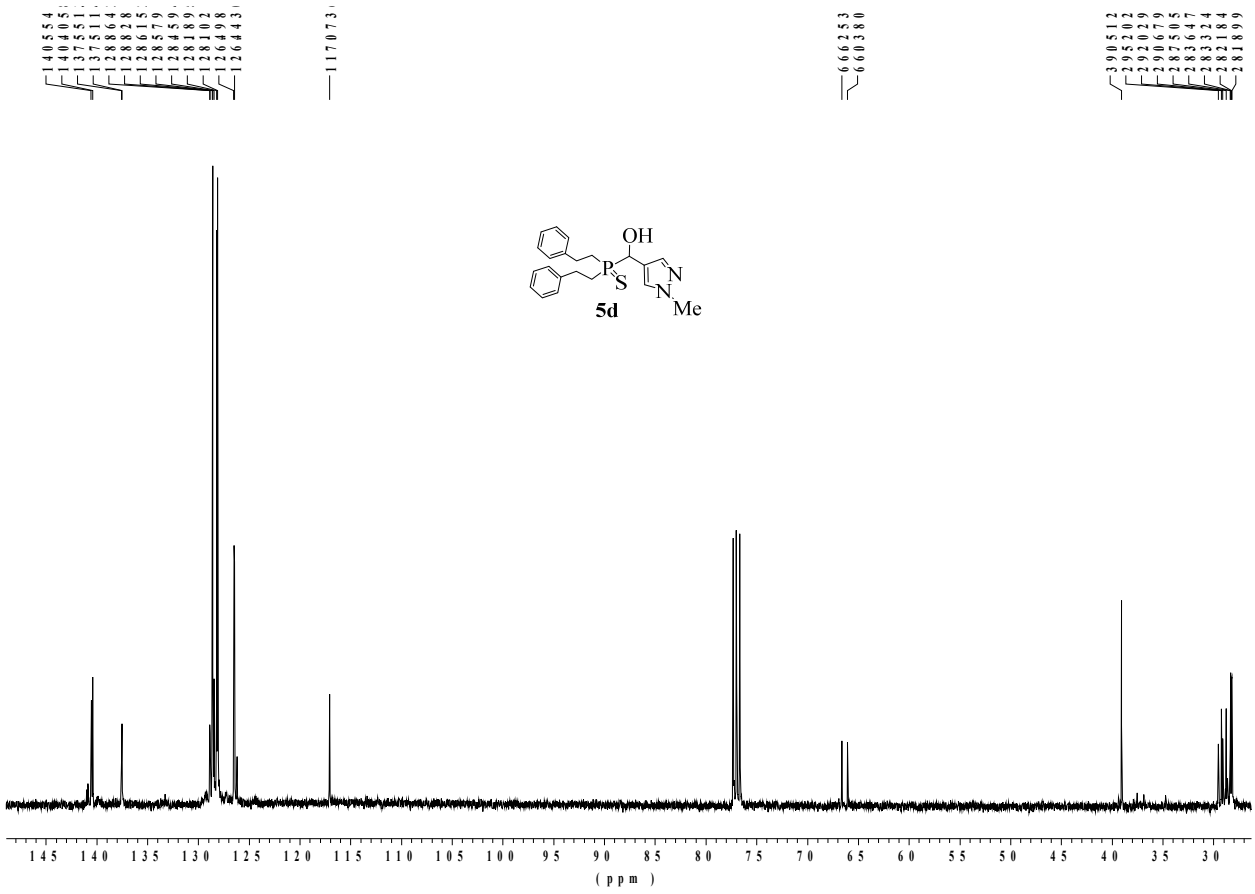
IR spectrum (cm^{-1}) of adduct **3d**



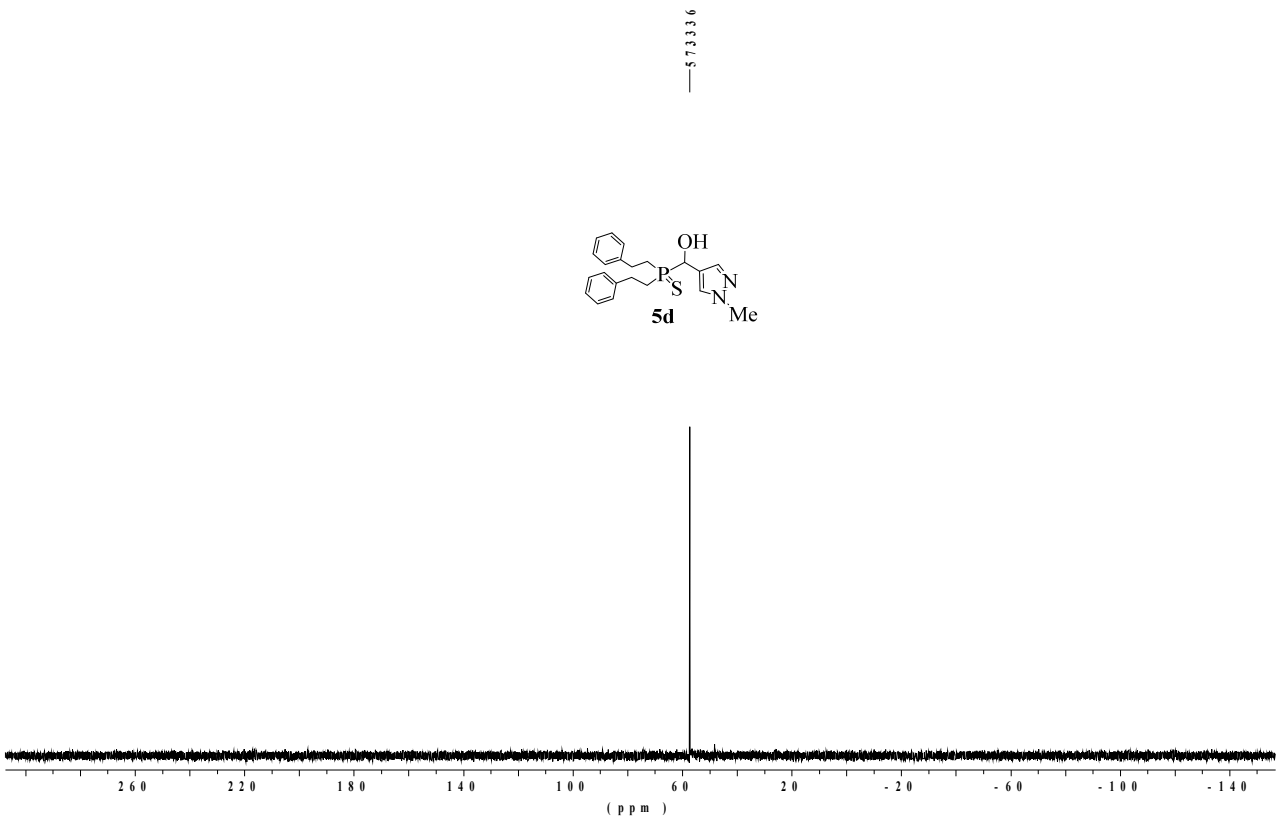
^{1}H NMR spectrum of adduct **5d** ($CDCl_3$)



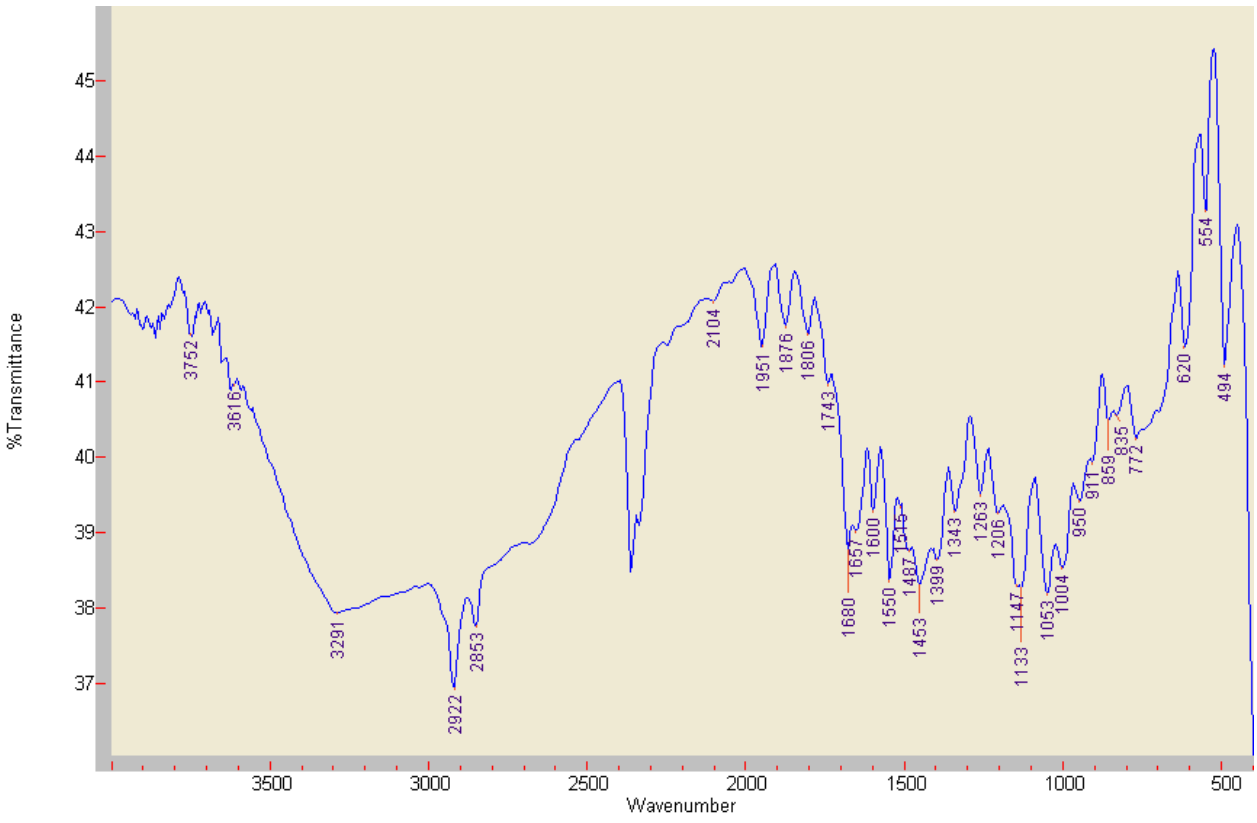
^{13}C NMR spectrum of adduct **5d** ($CDCl_3$)



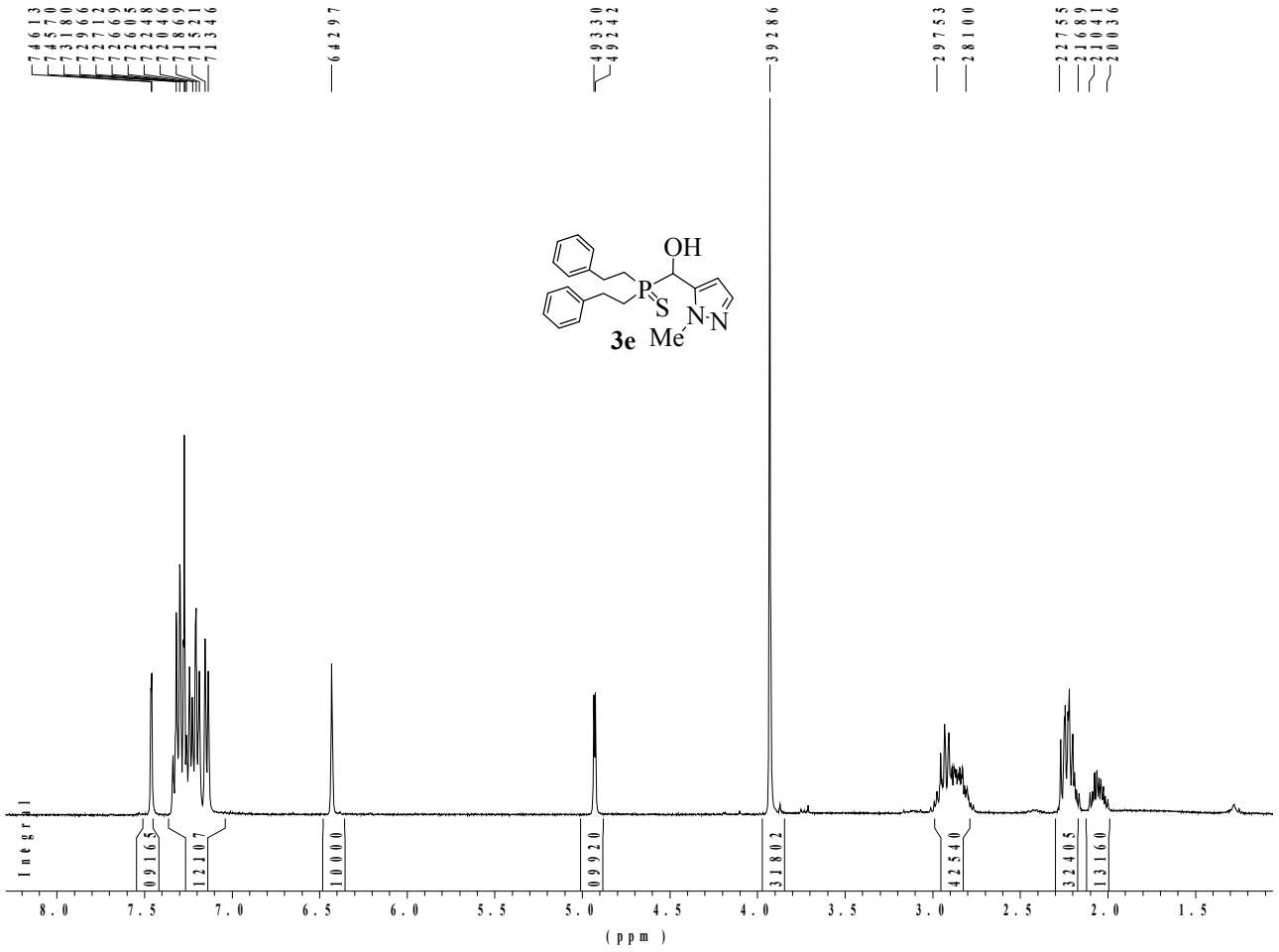
^{31}P NMR spectrum of adduct **5d** ($CDCl_3$)



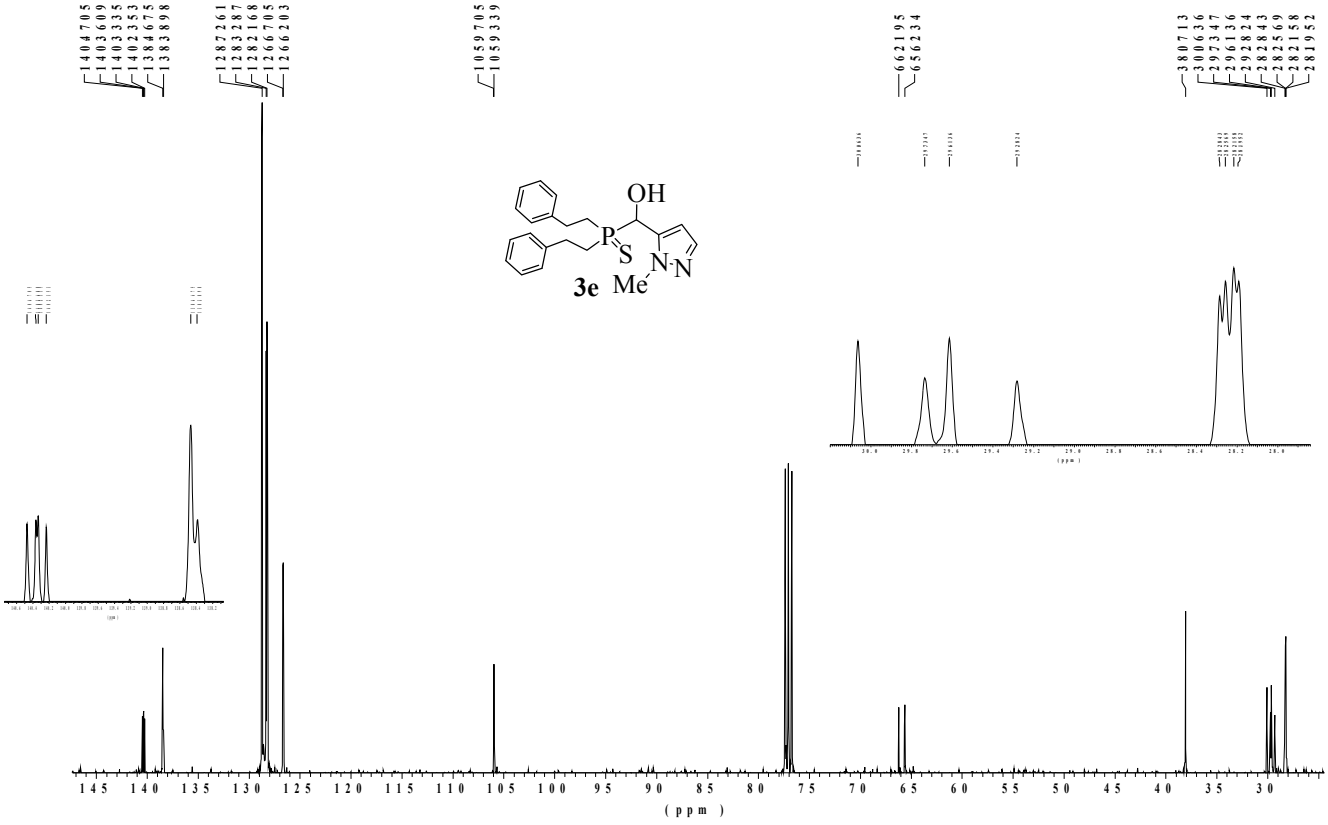
IR spectrum (film, cm^{-1}) of adduct **5d**



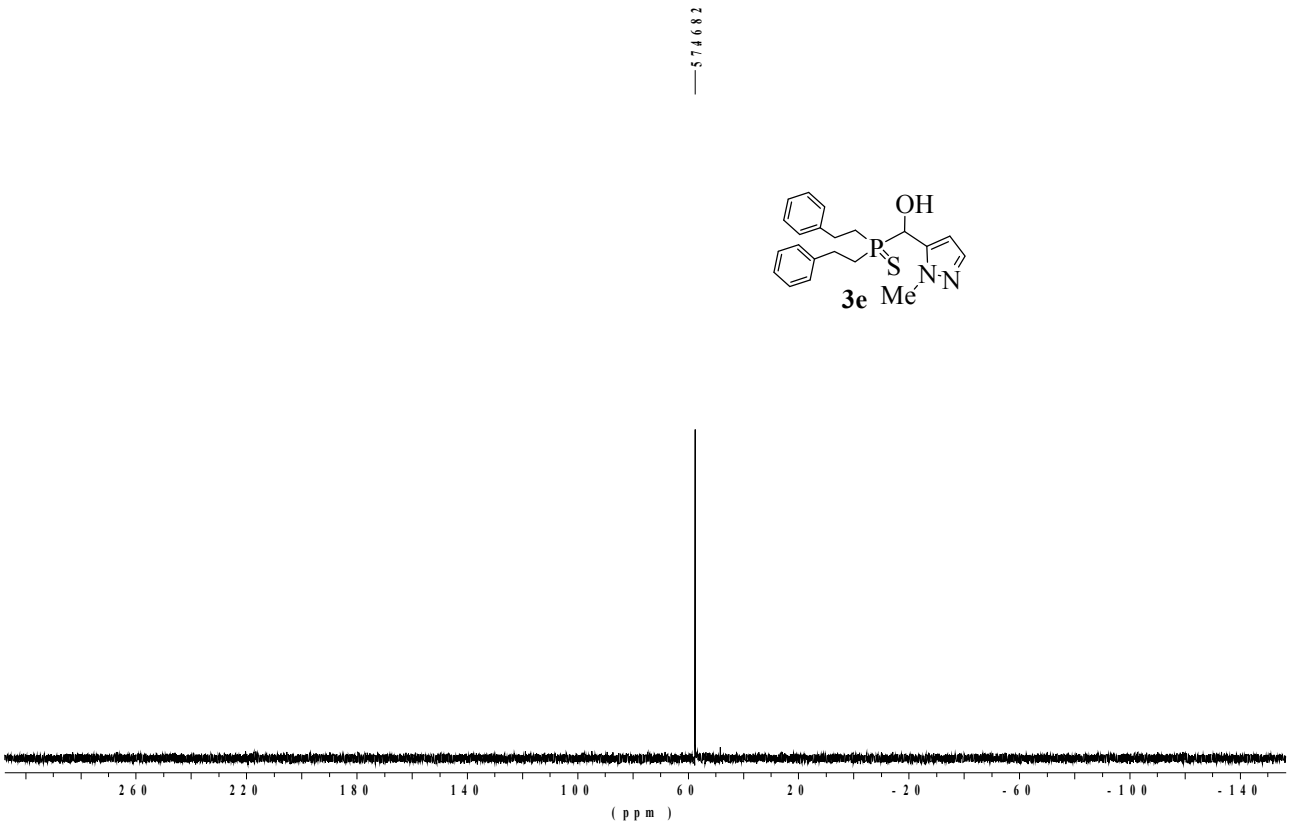
^{1}H NMR spectrum of adduct **3e** ($CDCl_3$)



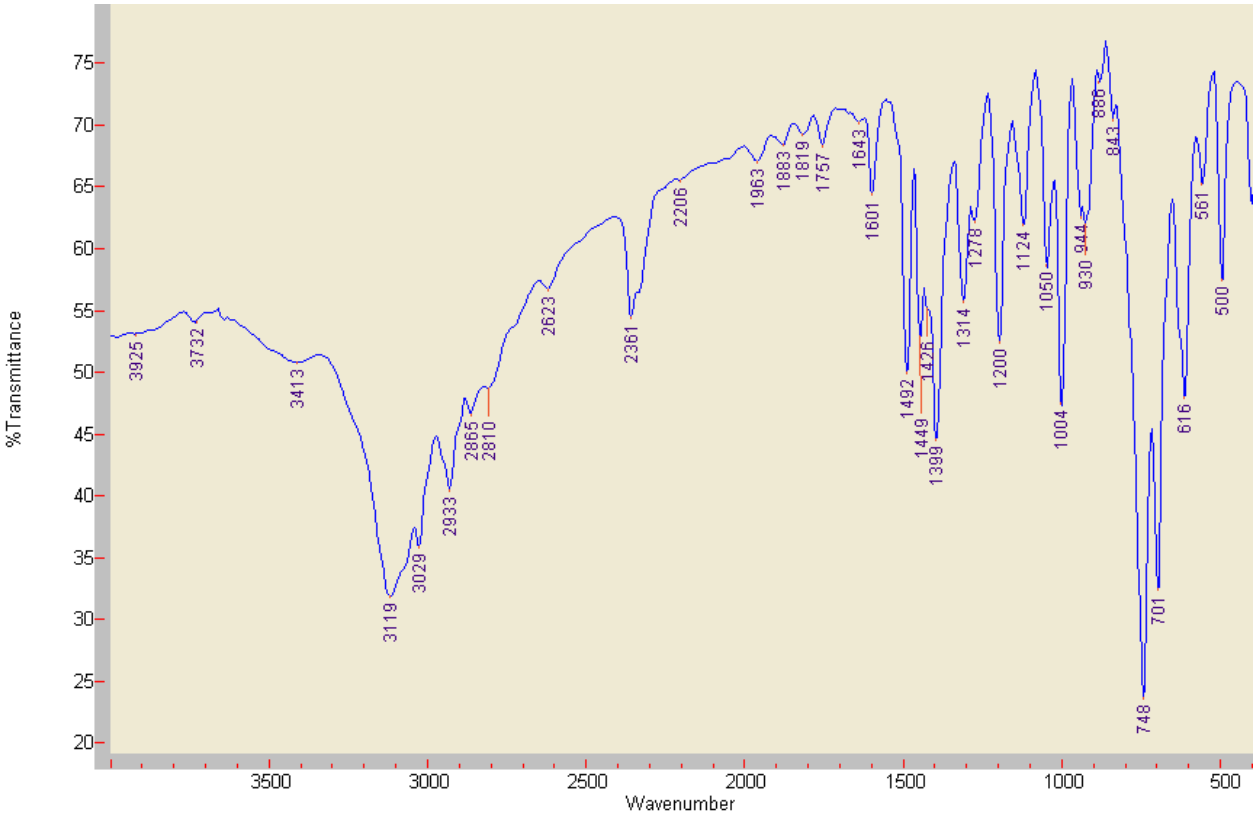
^{13}C NMR spectrum of adduct **3e** ($CDCl_3$)



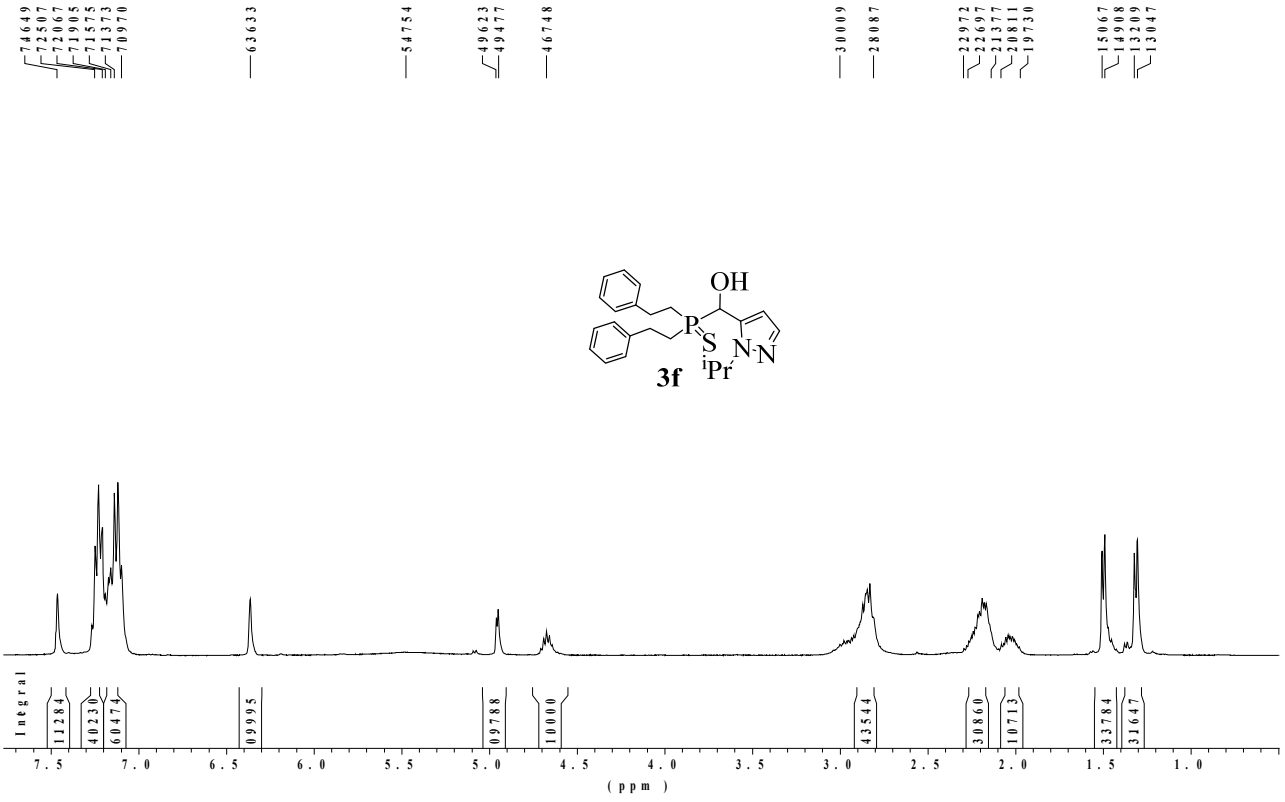
^{31}P NMR spectrum of adduct **3e** ($CDCl_3$)



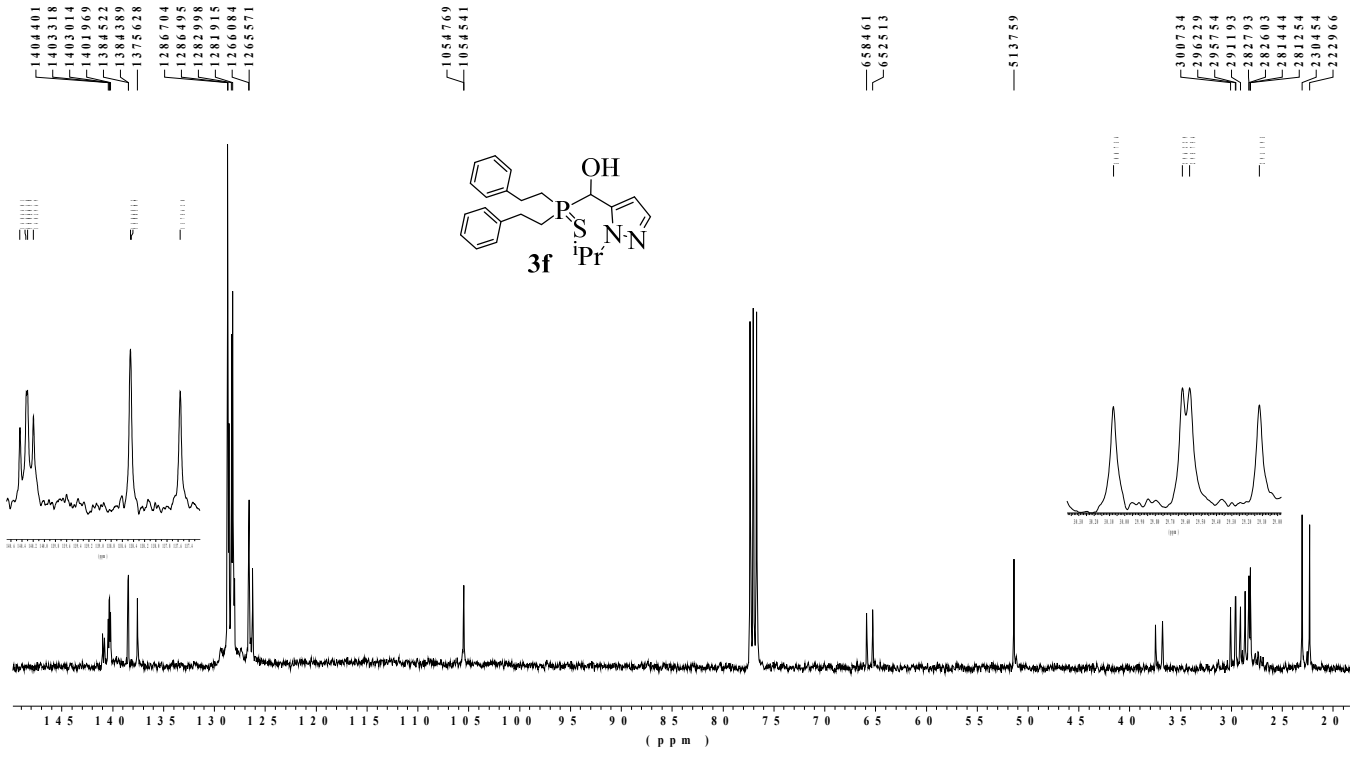
IR spectrum (KBr, cm^{-1}) of adduct **3e**



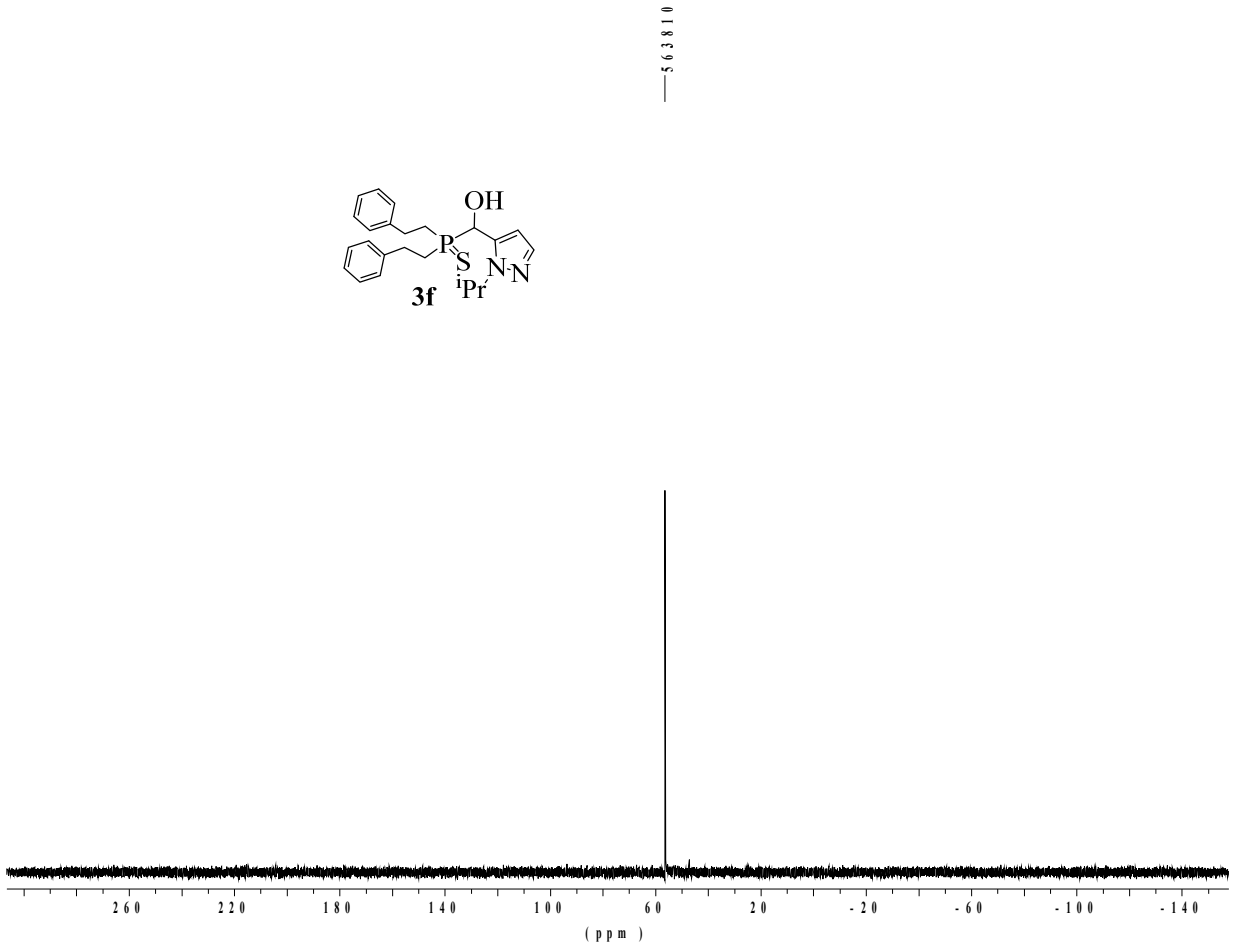
^{1}H NMR spectrum of adduct **3f** ($CDCl_3$)



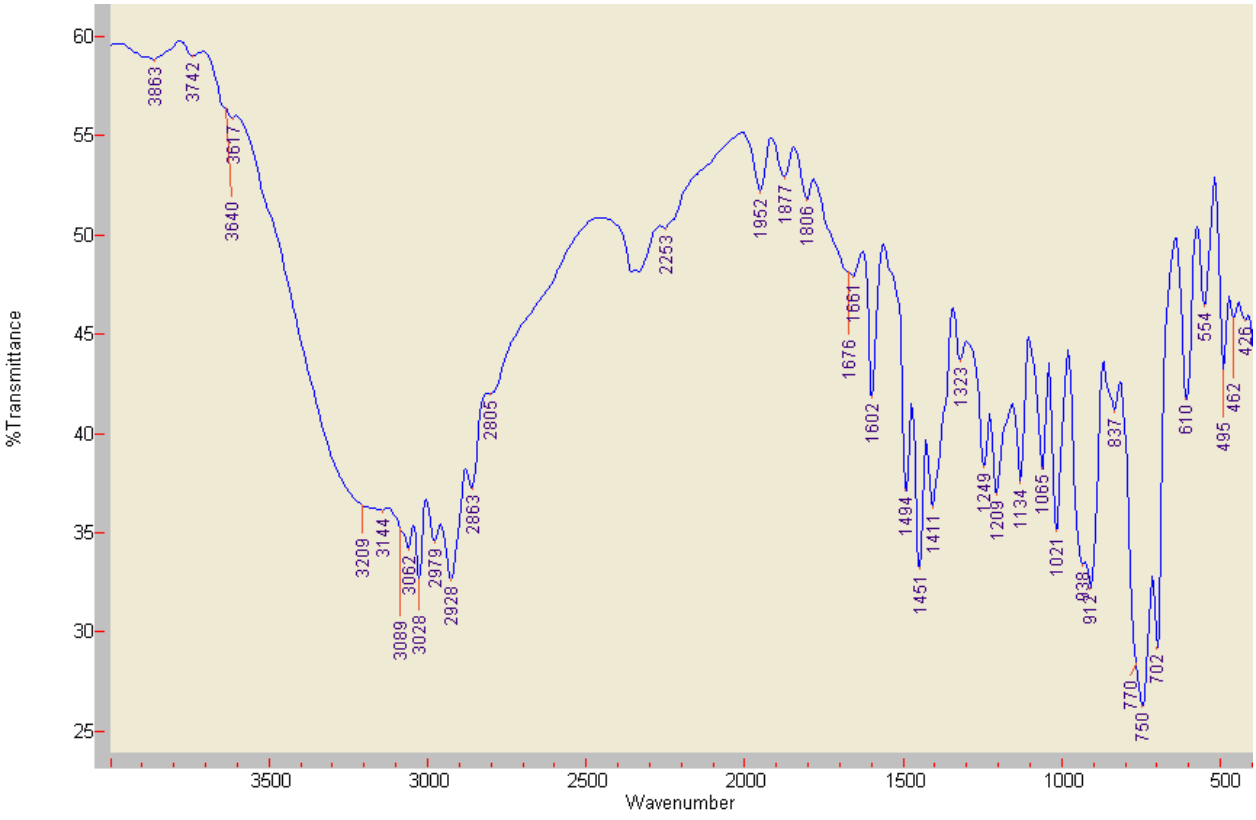
^{13}C NMR spectrum of adduct **3f** ($CDCl_3$)



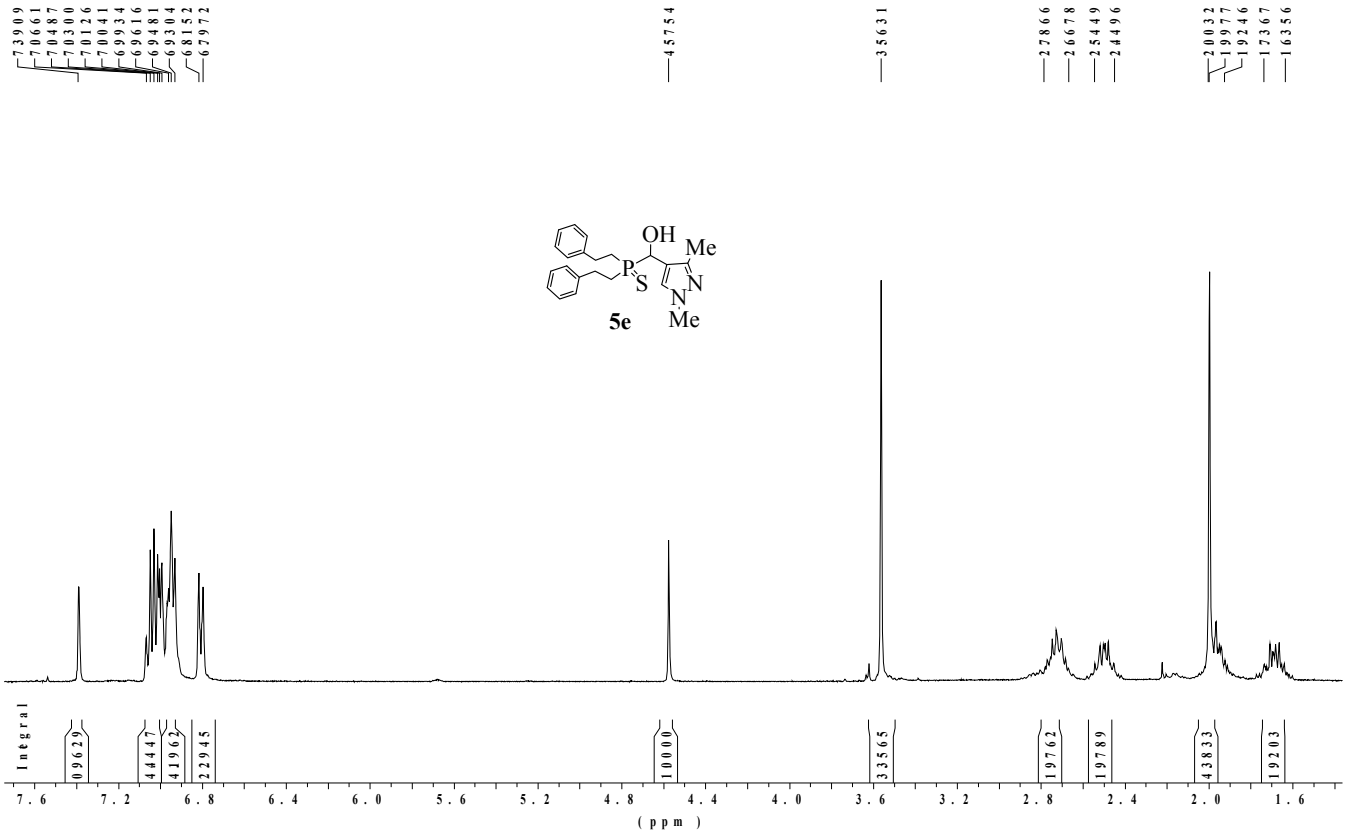
^{31}P NMR spectrum of adduct **3f** ($CDCl_3$)



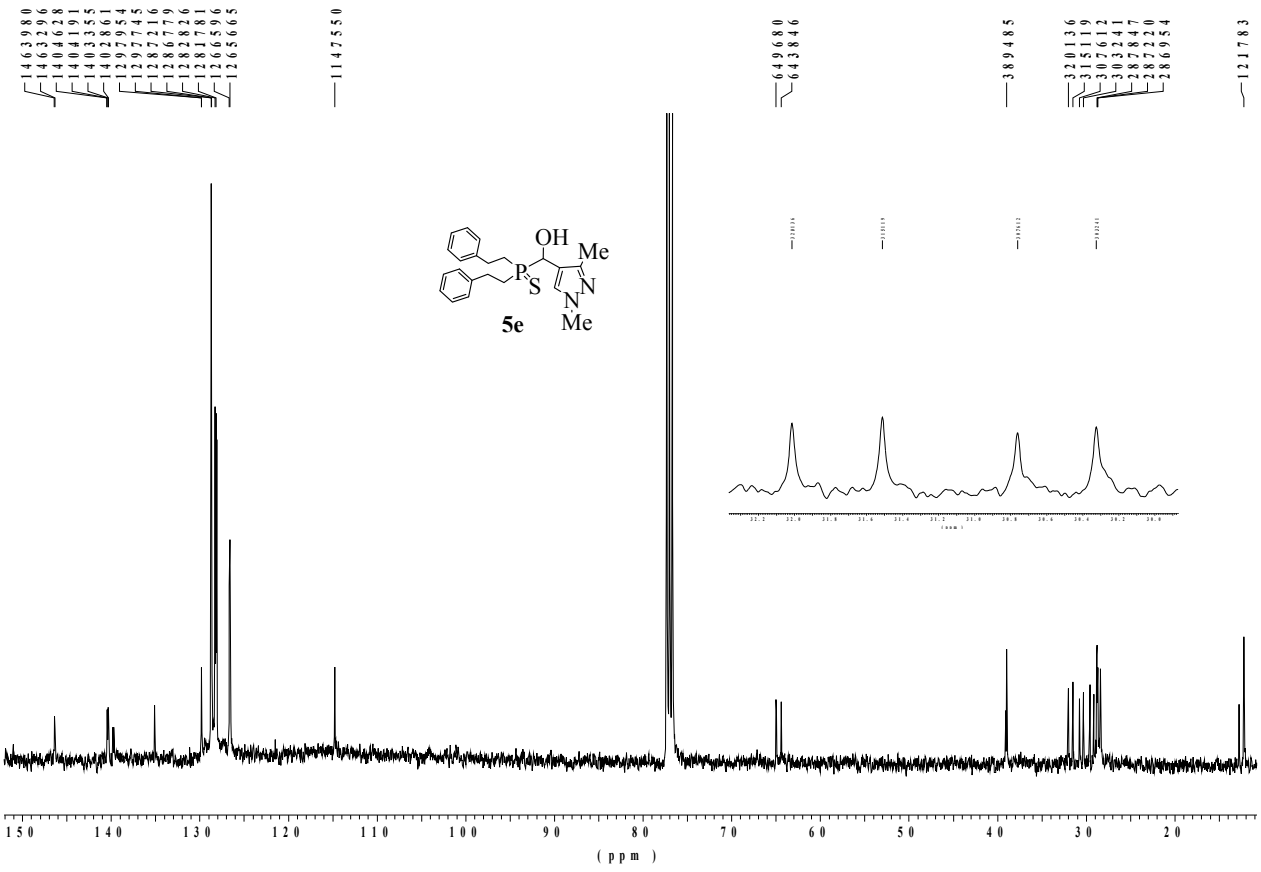
IR spectrum (film, cm^{-1}) of adduct **3f**



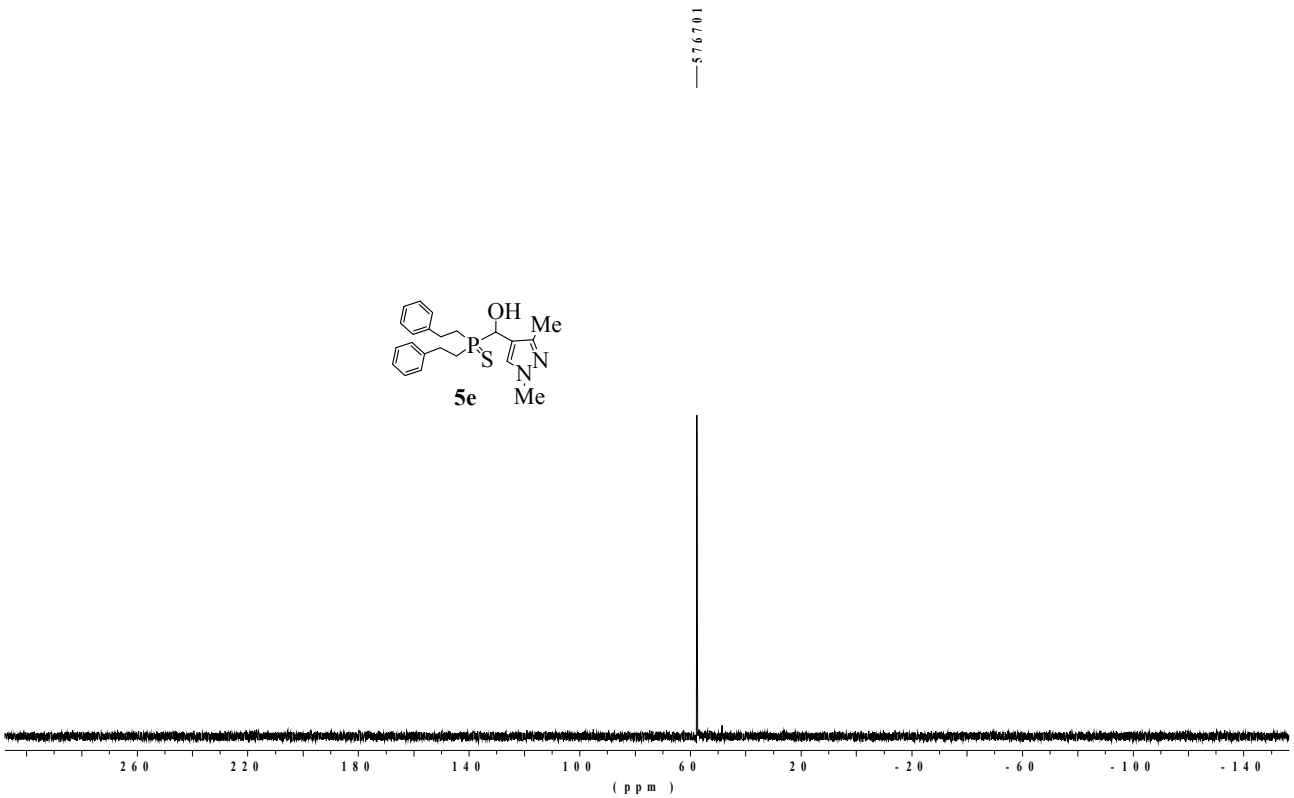
^{1}H NMR spectrum of adduct **5e** ($CDCl_3$)



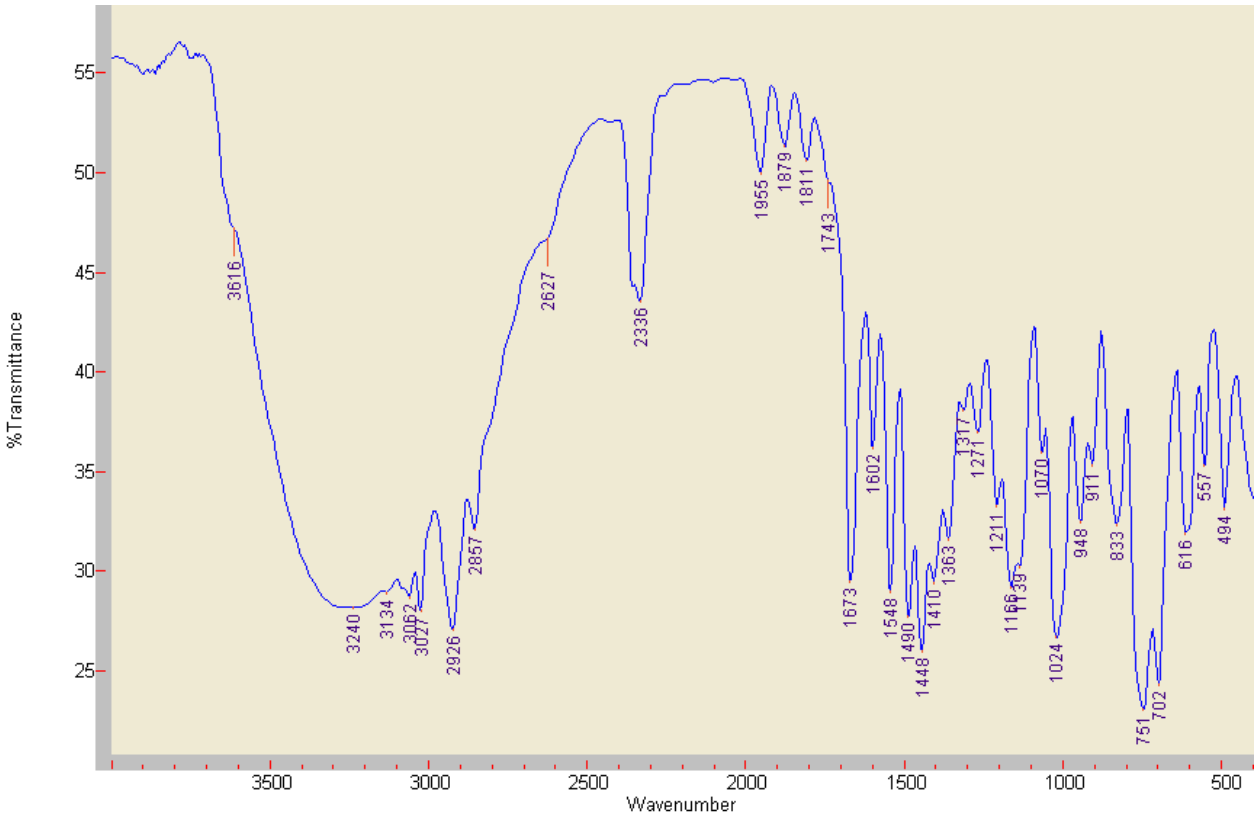
^{13}C NMR spectrum of adduct **5e** ($CDCl_3$)



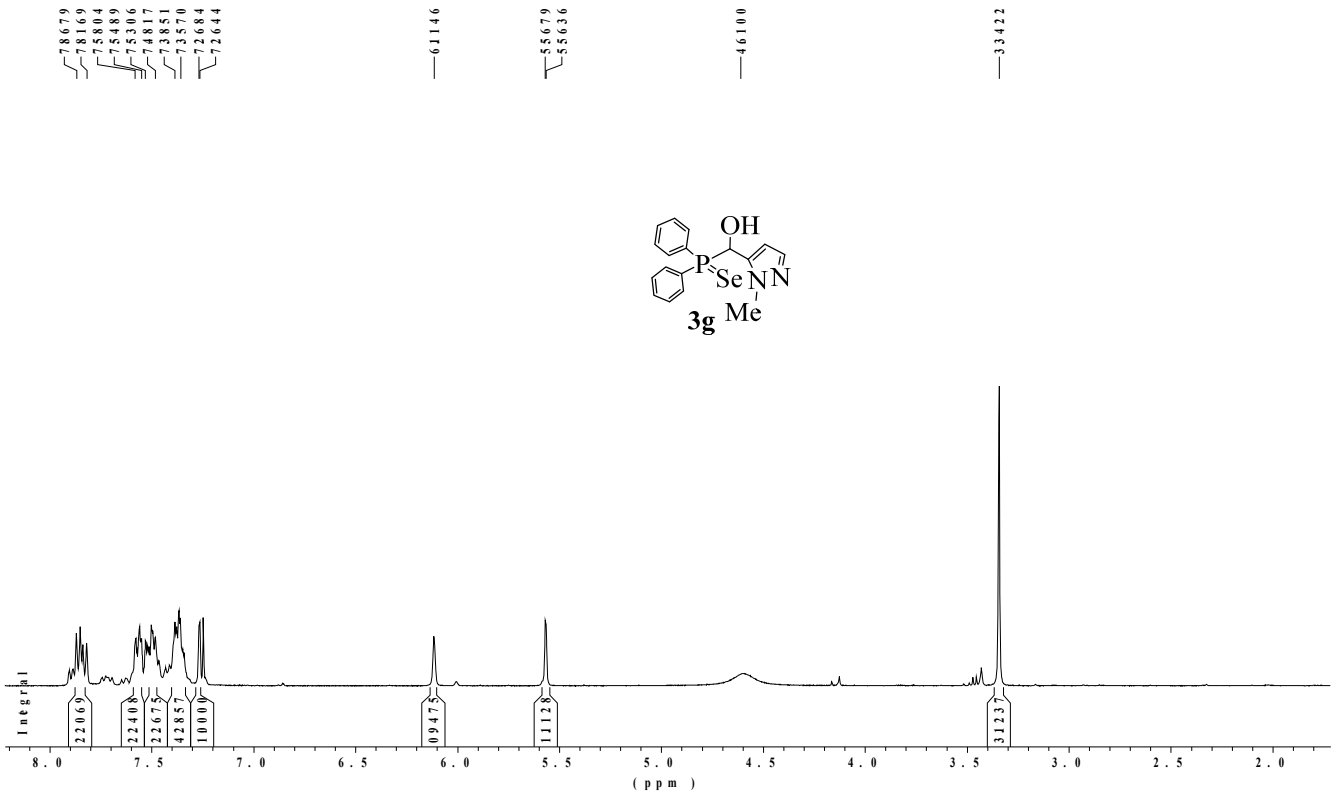
^{31}P NMR spectrum of adduct **5e** ($CDCl_3$)



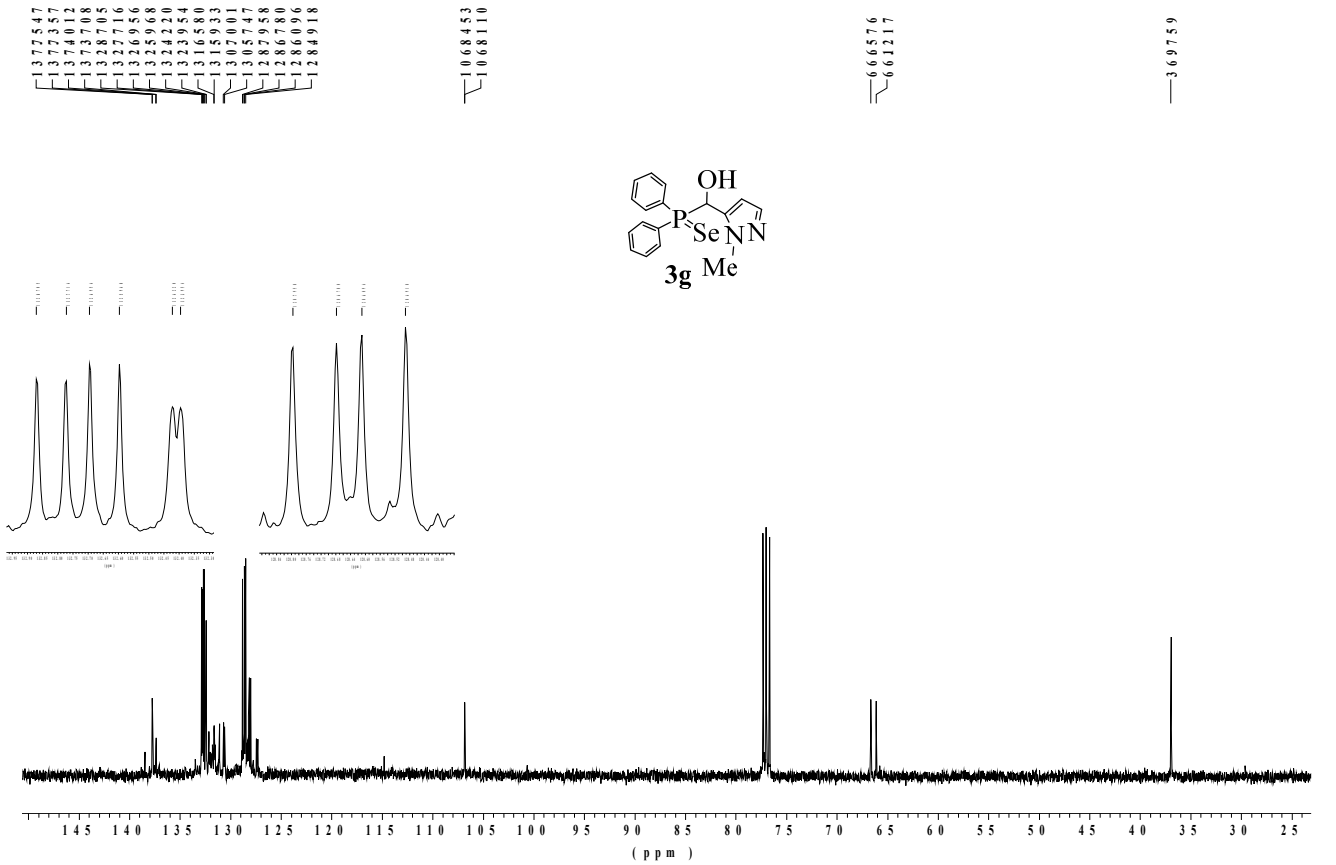
IR spectrum (film, cm^{-1}) of adduct **5e**



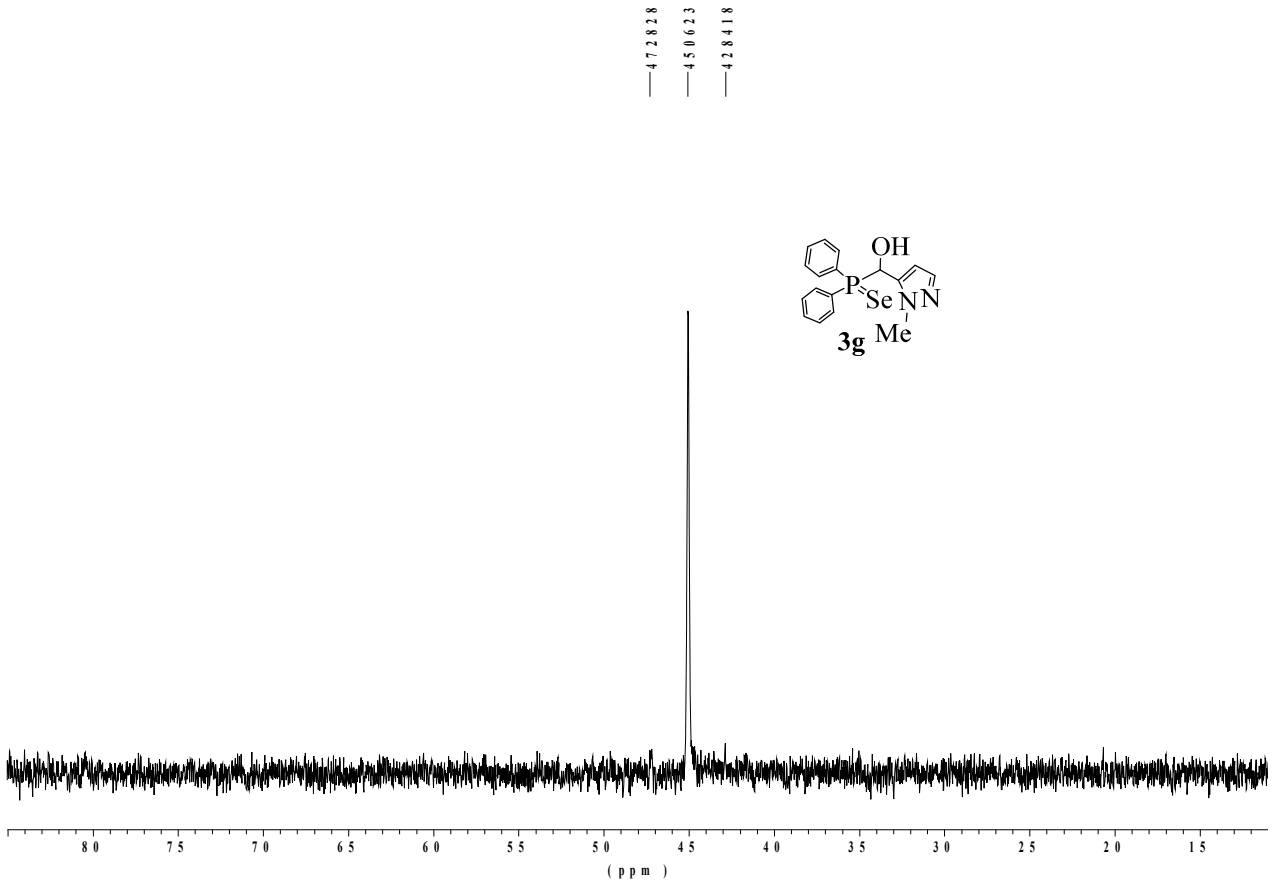
^{1}H NMR spectrum of adduct **3g** ($CDCl_3$)



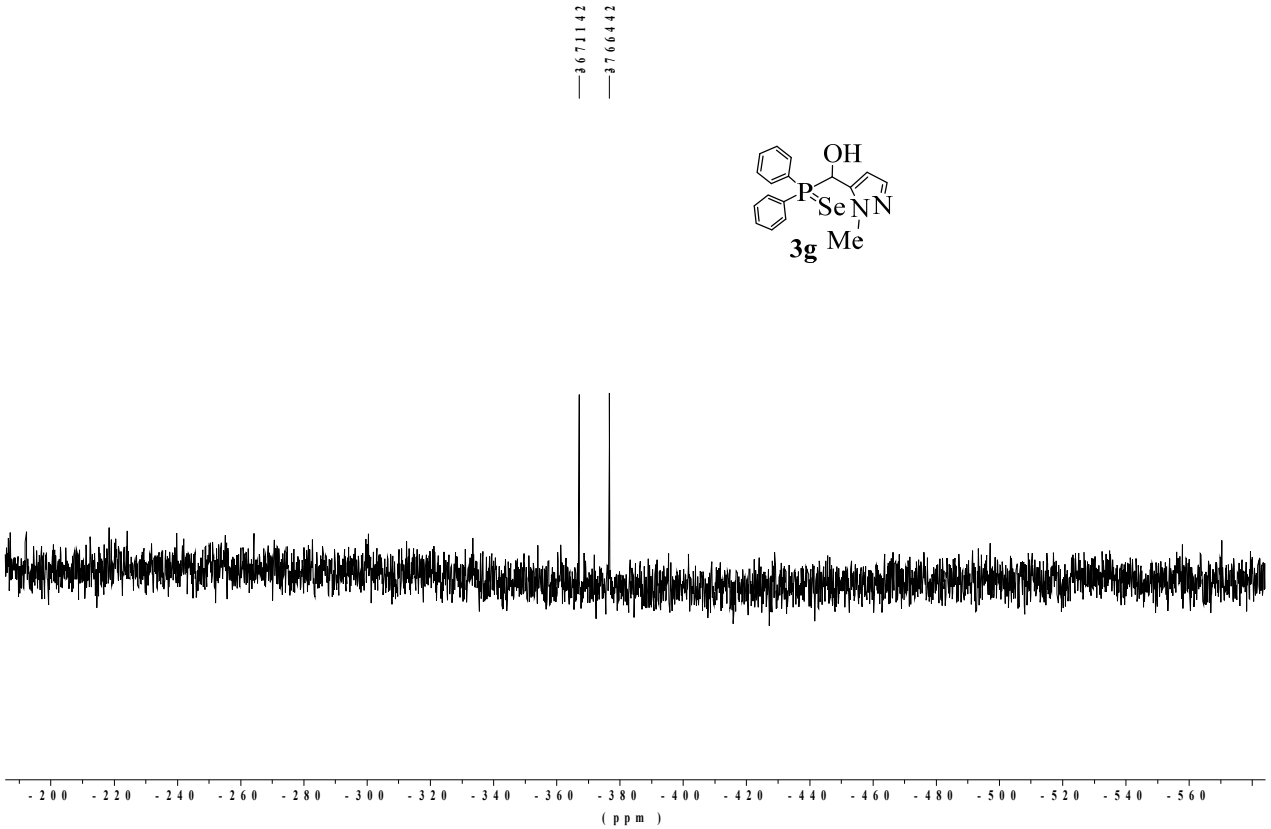
^{13}C NMR spectrum of adduct **3g** ($CDCl_3$)



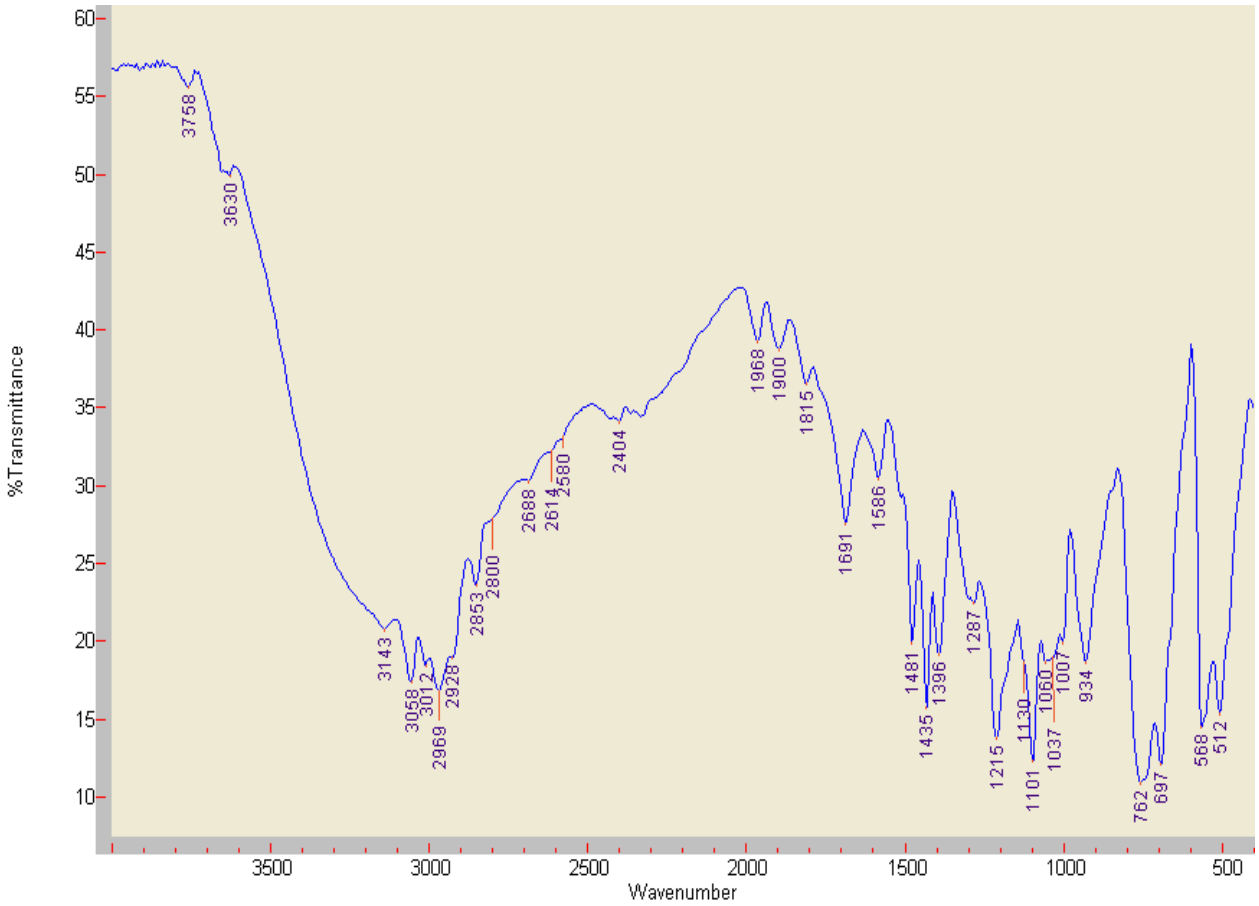
^{31}P NMR spectrum of adduct **3g** ($CDCl_3$)



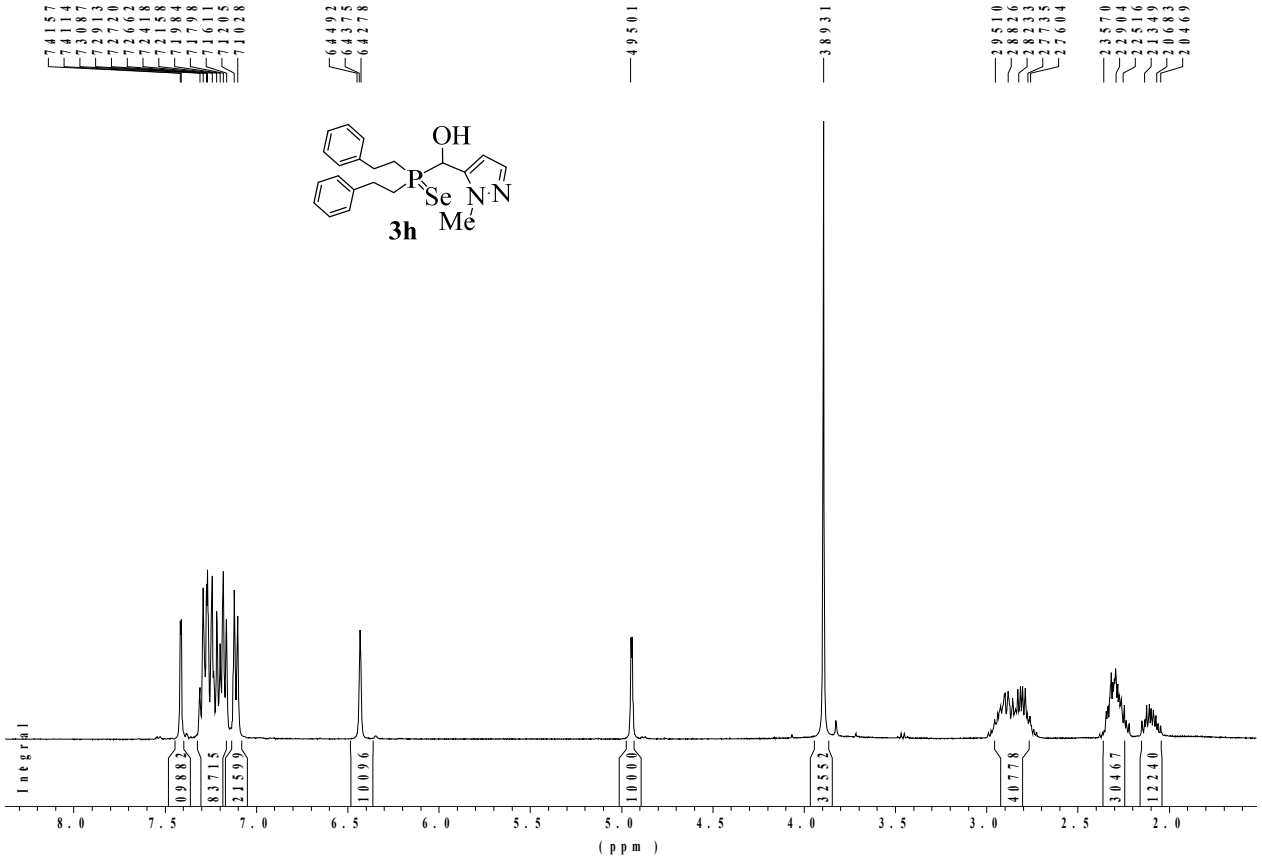
^{77}Se NMR spectrum of adduct **3g** ($CDCl_3$)



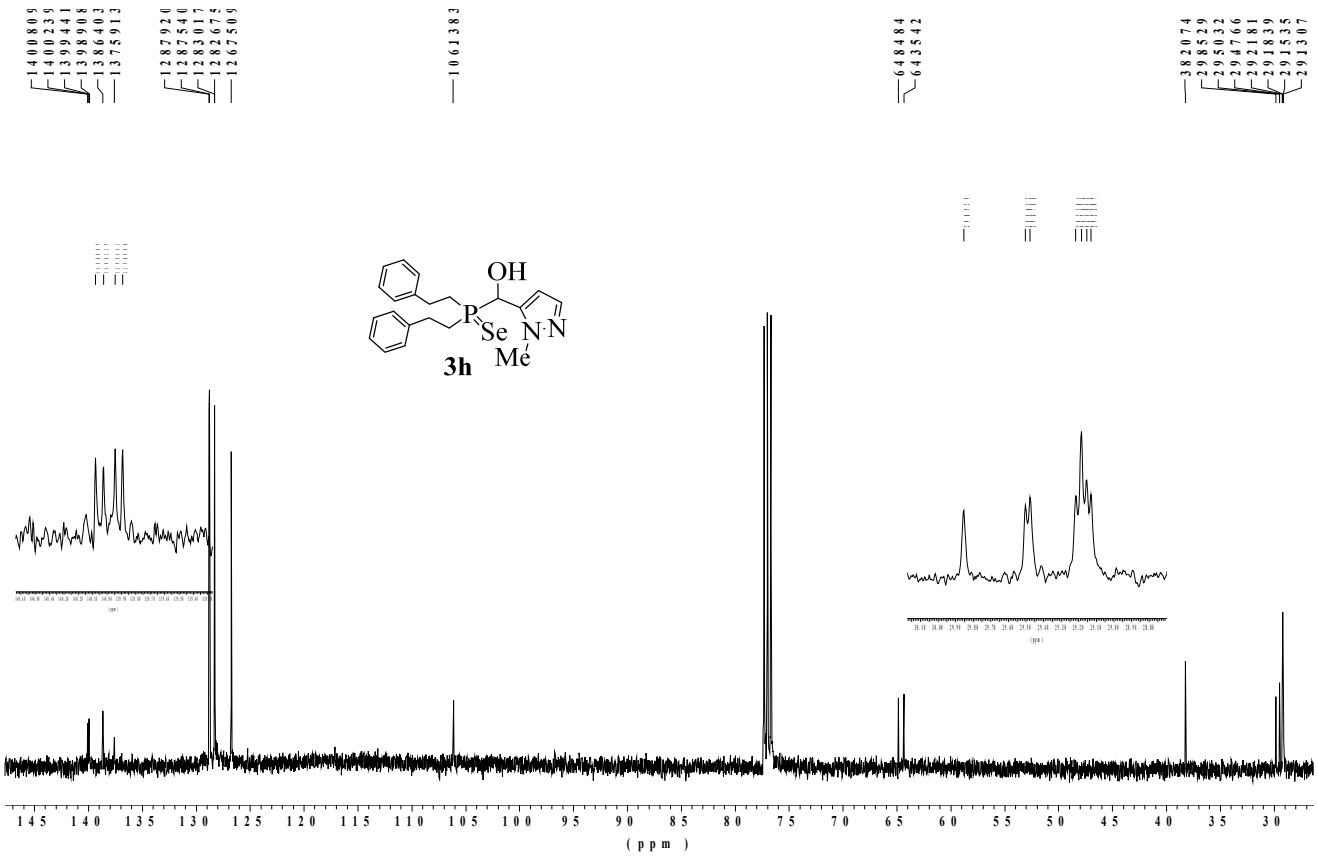
IR spectrum (film, cm^{-1}) of adduct **3g**



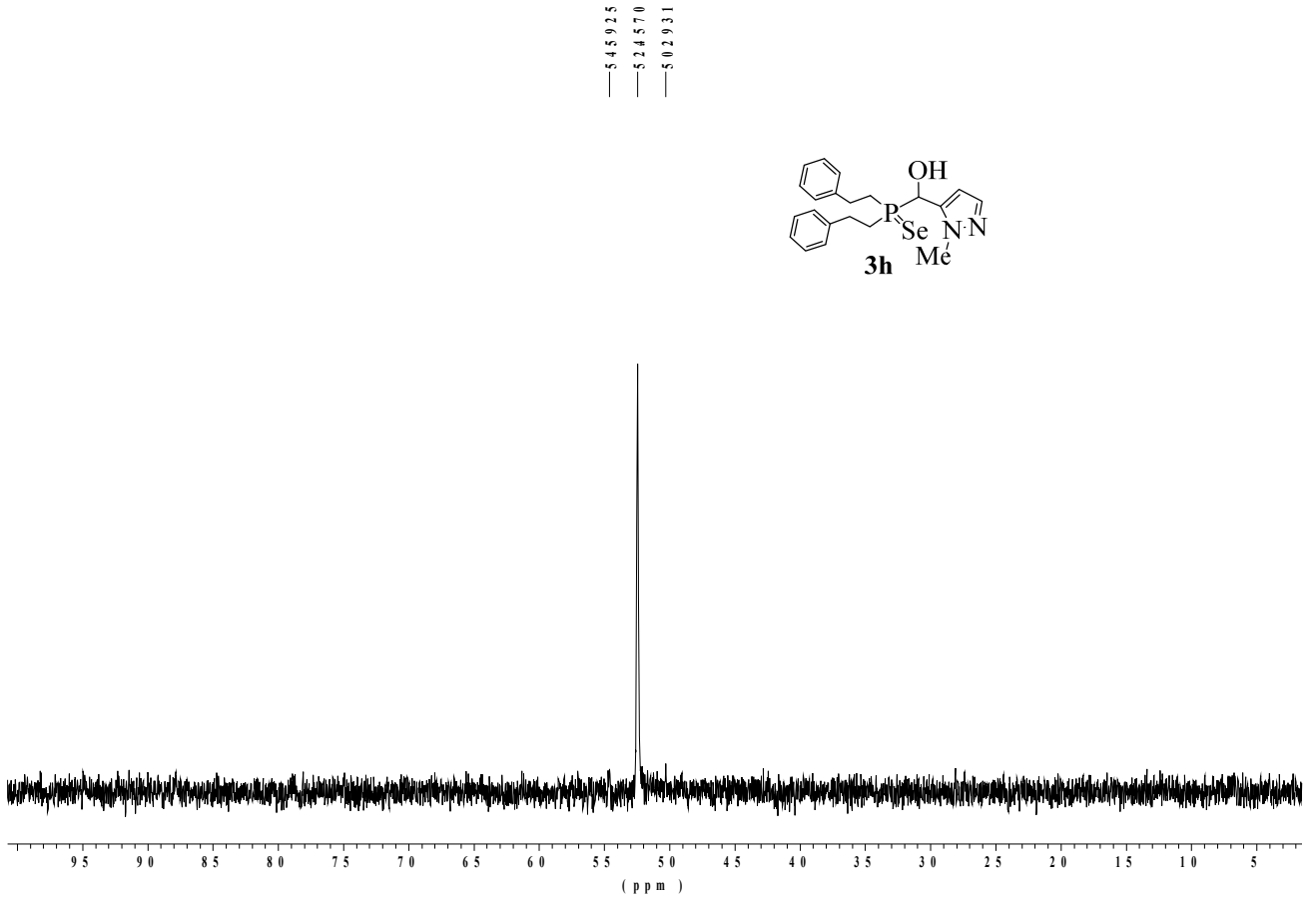
^{1}H NMR spectrum of adduct **3h**
($CDCl_3$)



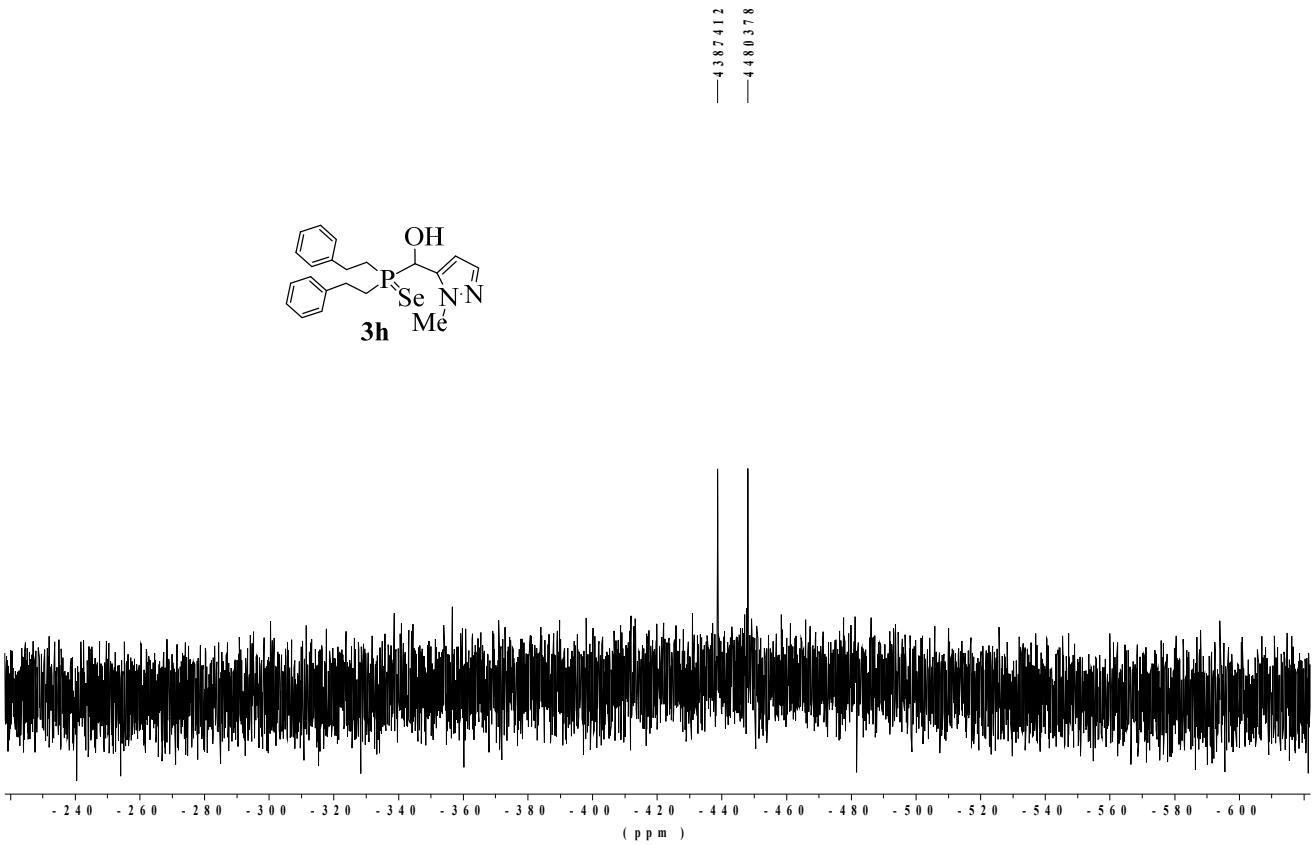
^{13}C NMR spectrum of adduct **3h** ($CDCl_3$)



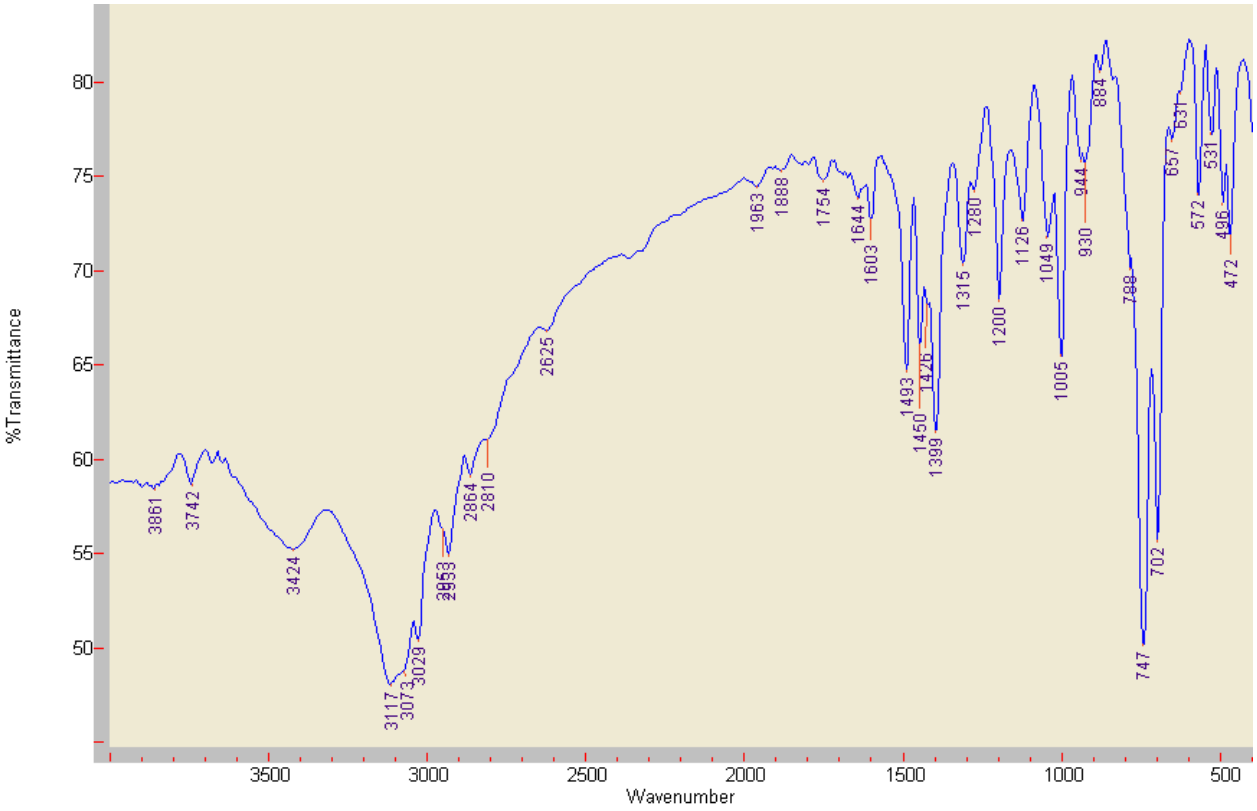
^{31}P NMR spectrum of adduct **3h** ($CDCl_3$)



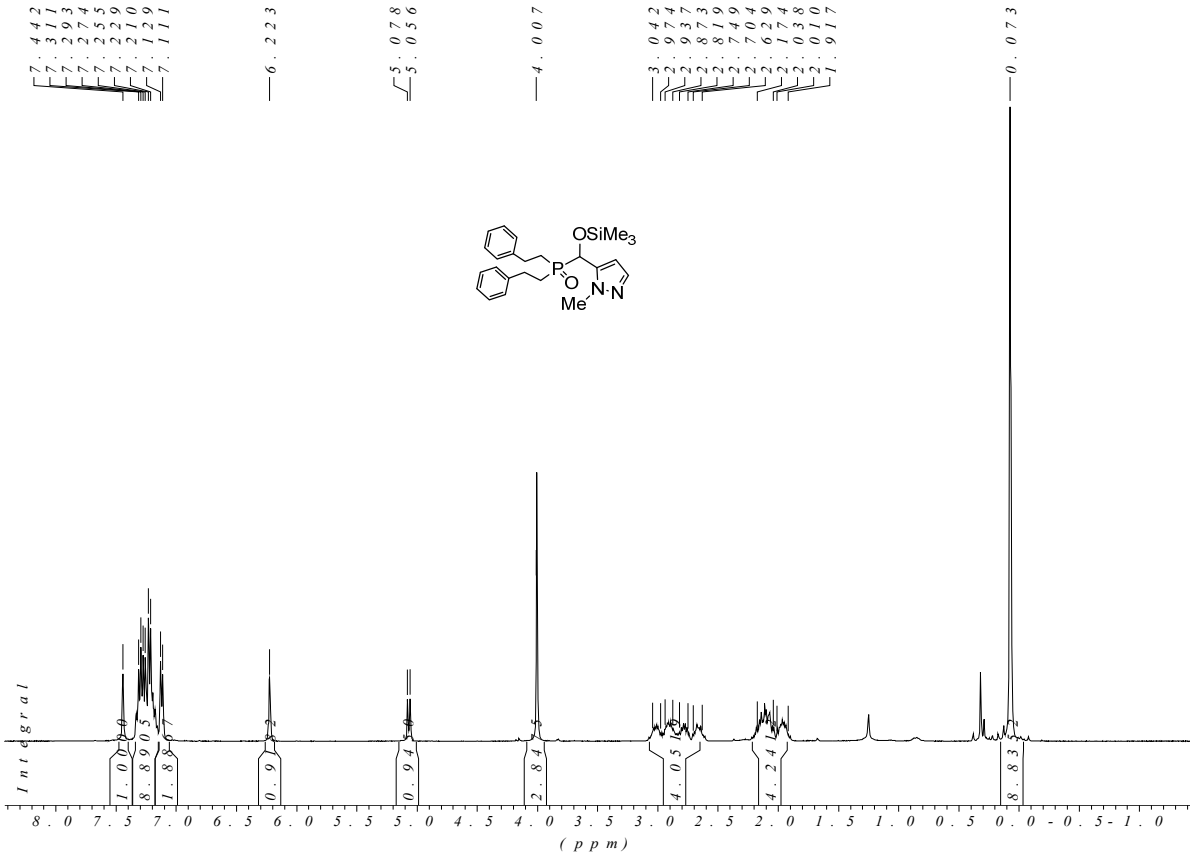
^{77}Se NMR spectrum of adduct **3h** ($CDCl_3$)



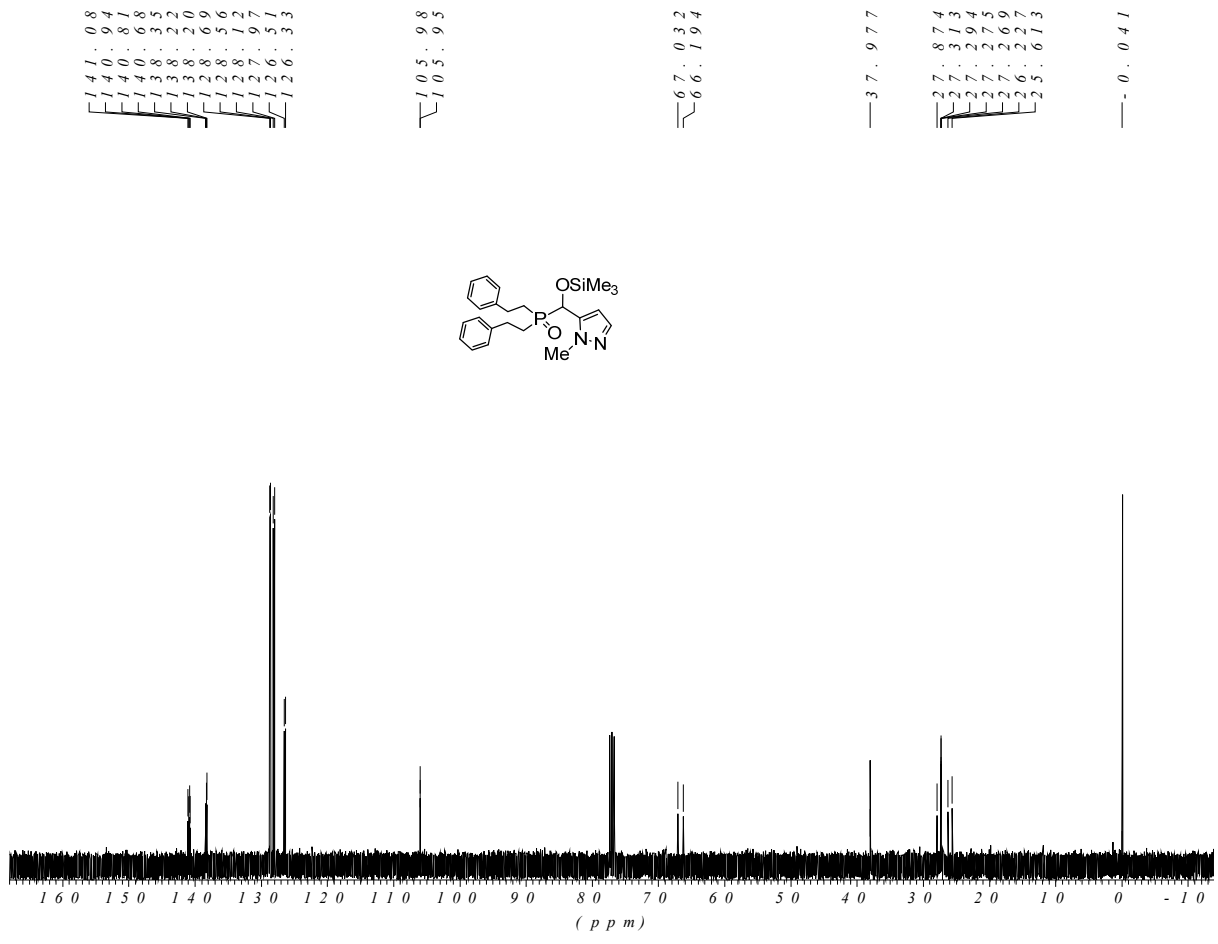
IR spectrum (film, cm^{-1}) of adduct **3h**



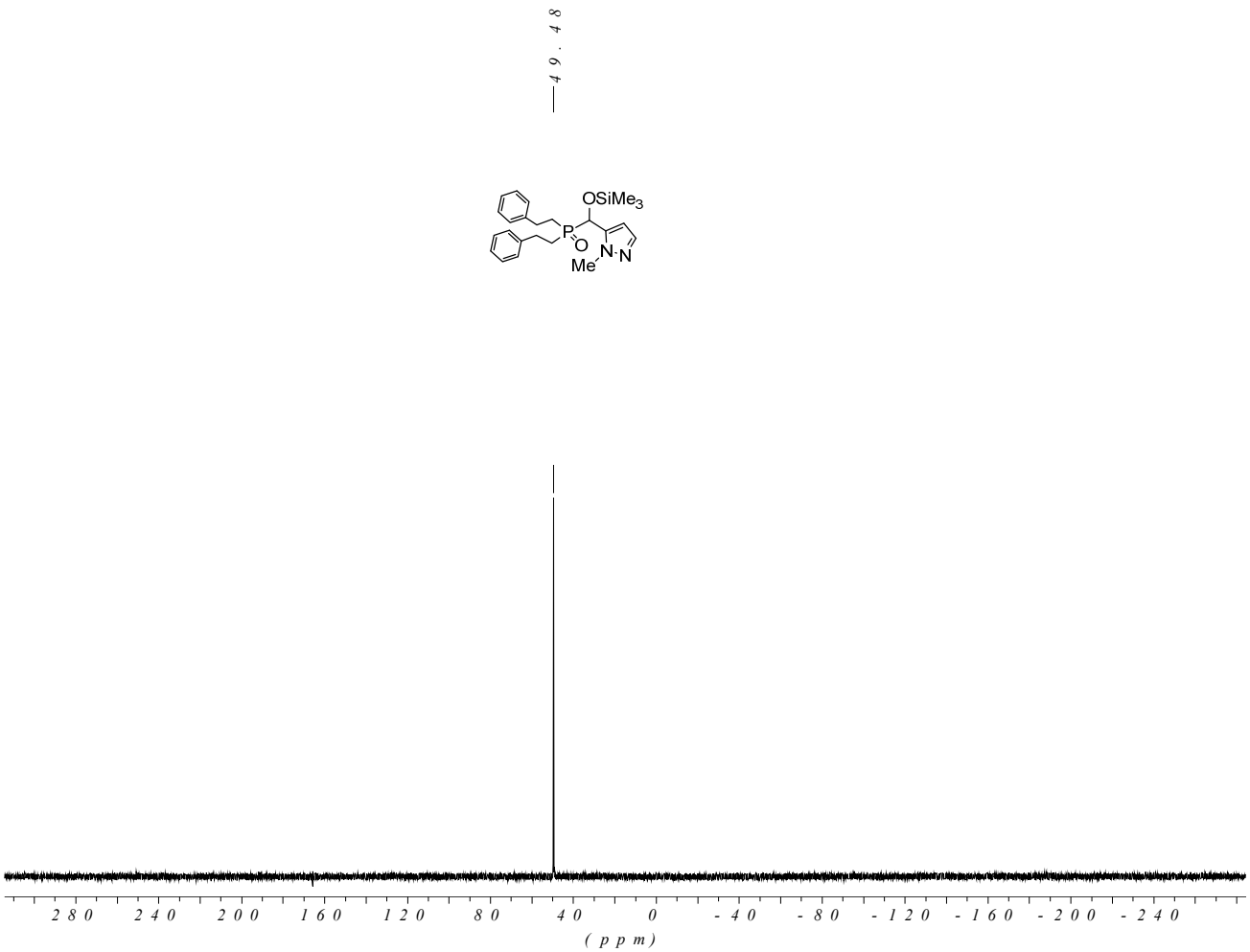
^{1}H NMR spectrum of pyrazole **6** ($CDCl_3$)



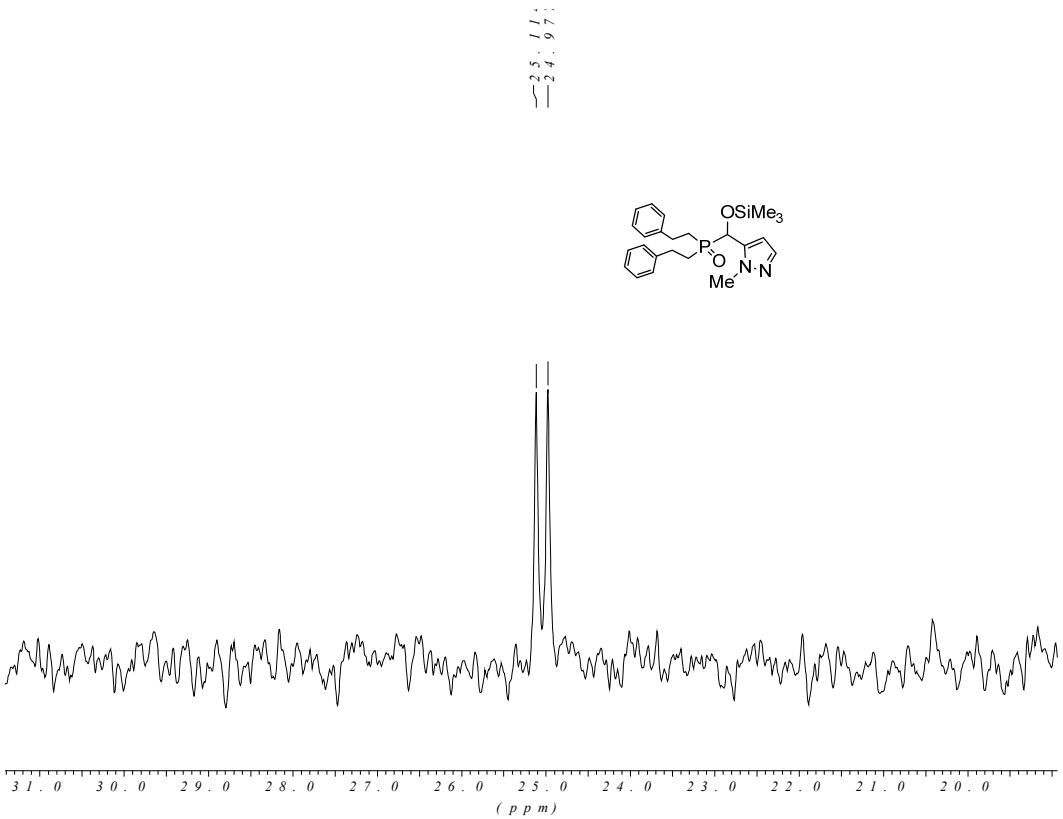
^{13}C NMR spectrum of pyrazole **6** ($CDCl_3$)



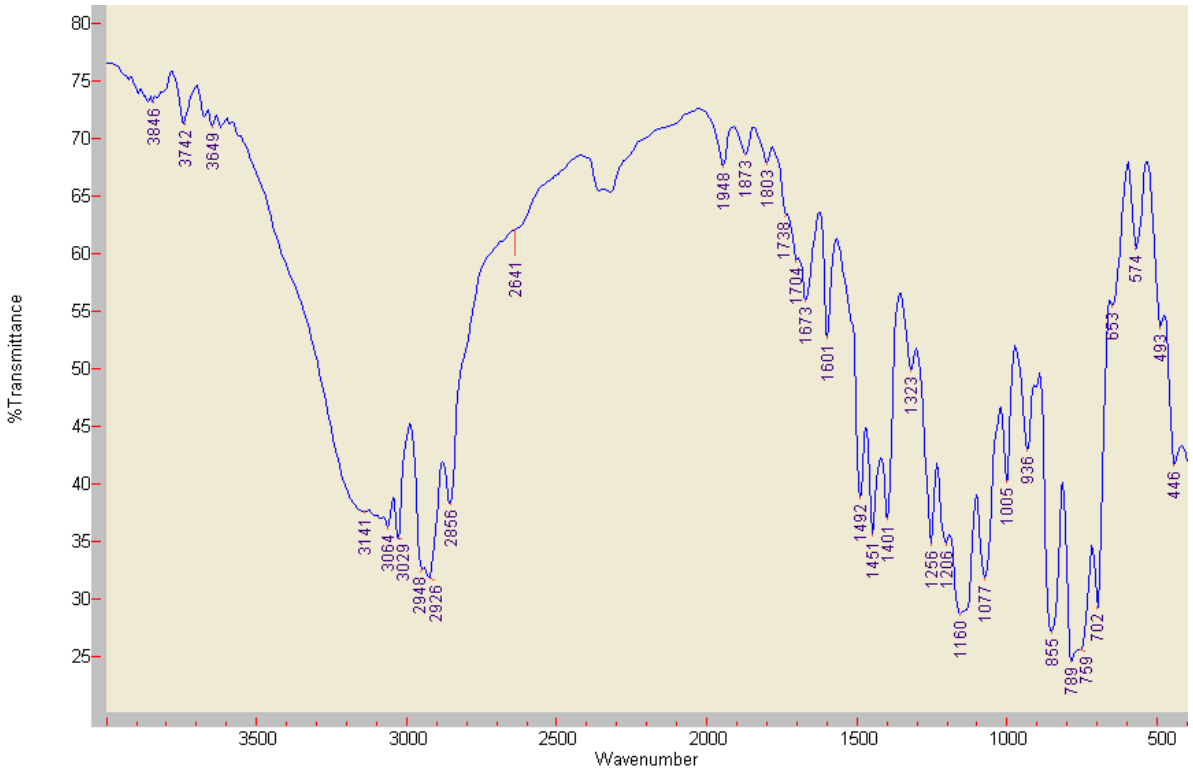
^{31}P NMR spectrum of pyrazole **6** ($CDCl_3$)



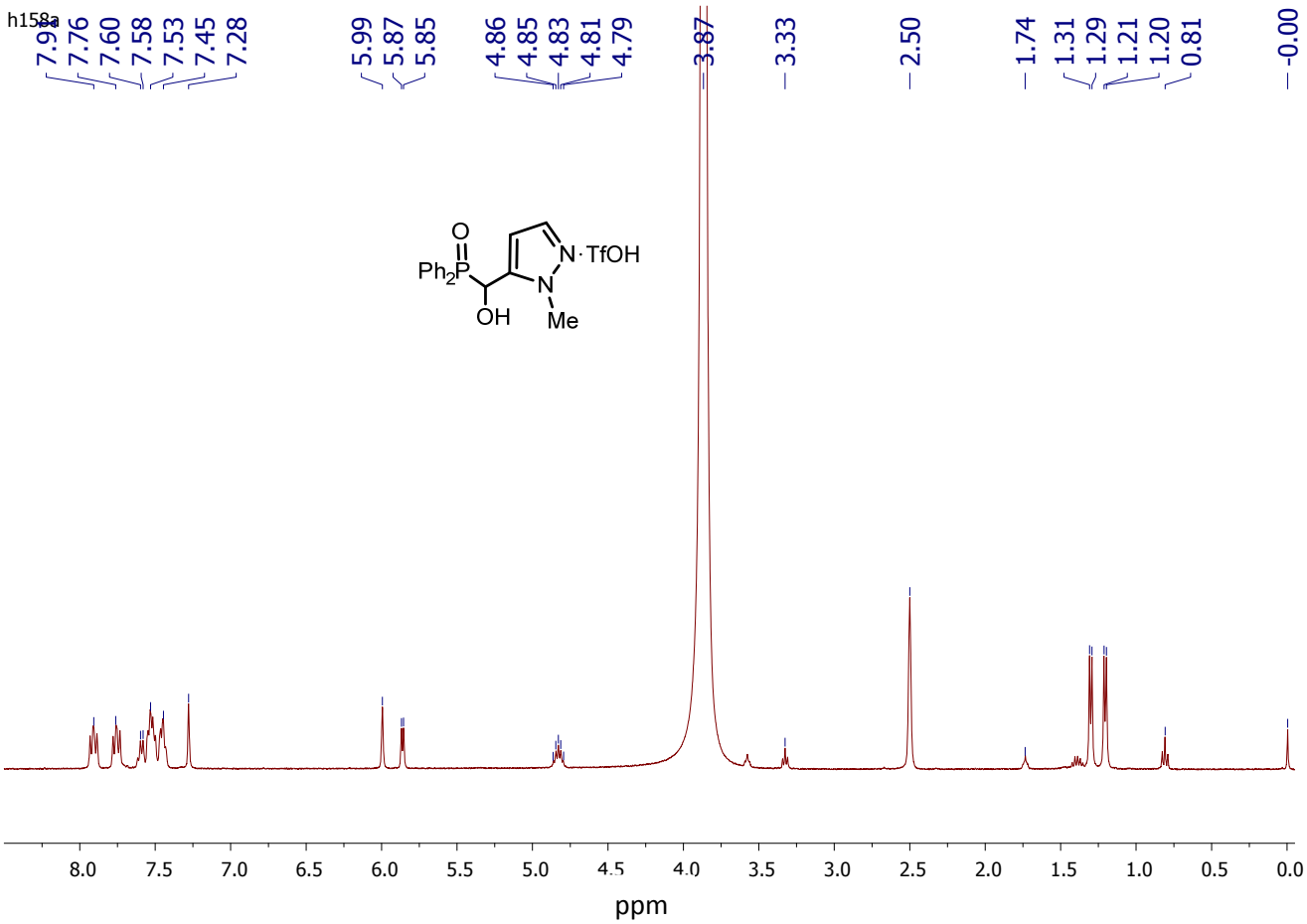
^{29}Si NMR spectrum of pyrazole **6** ($CDCl_3$)



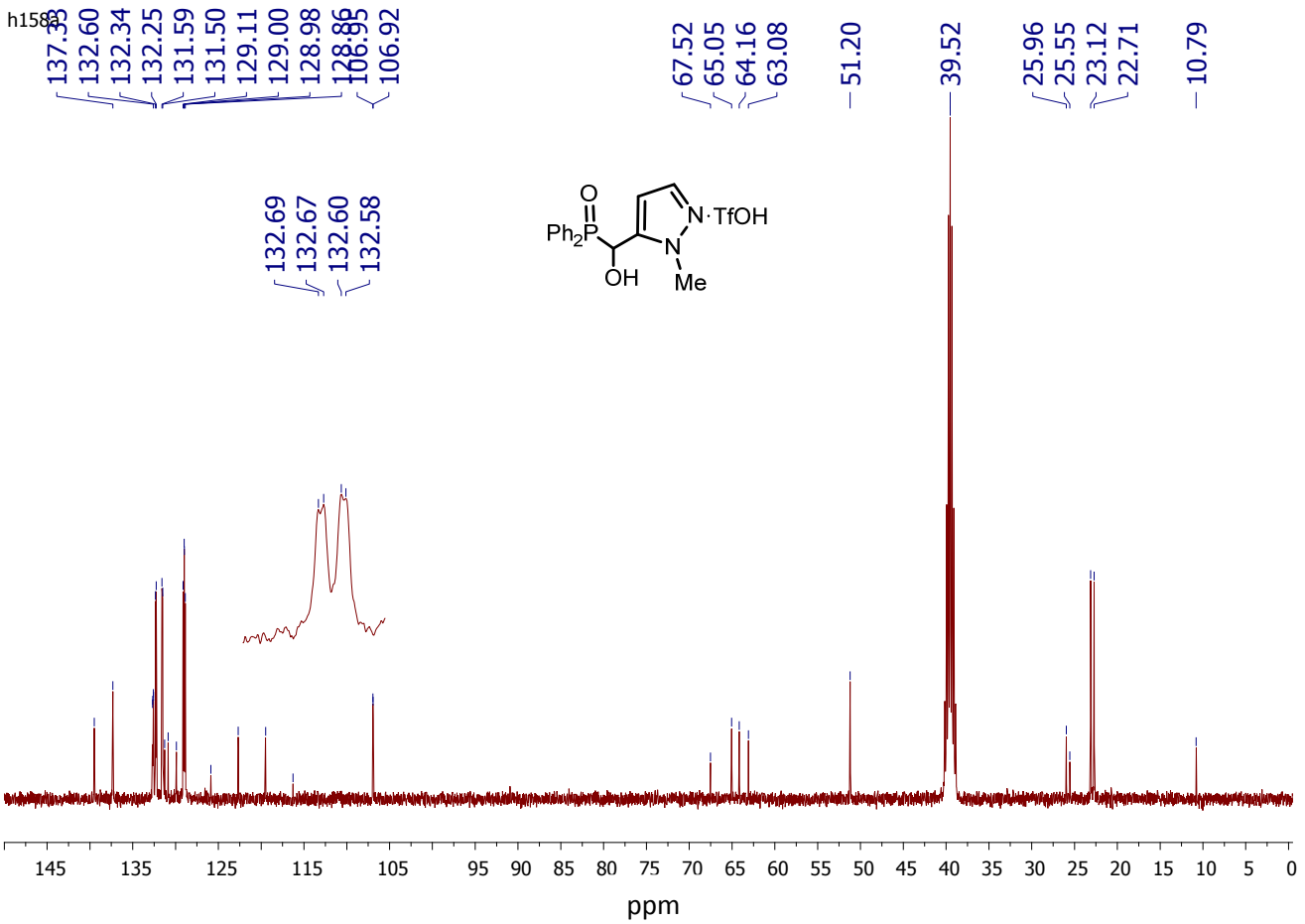
FT-IR spectrum (film, cm^{-1}) of pyrazole **6**



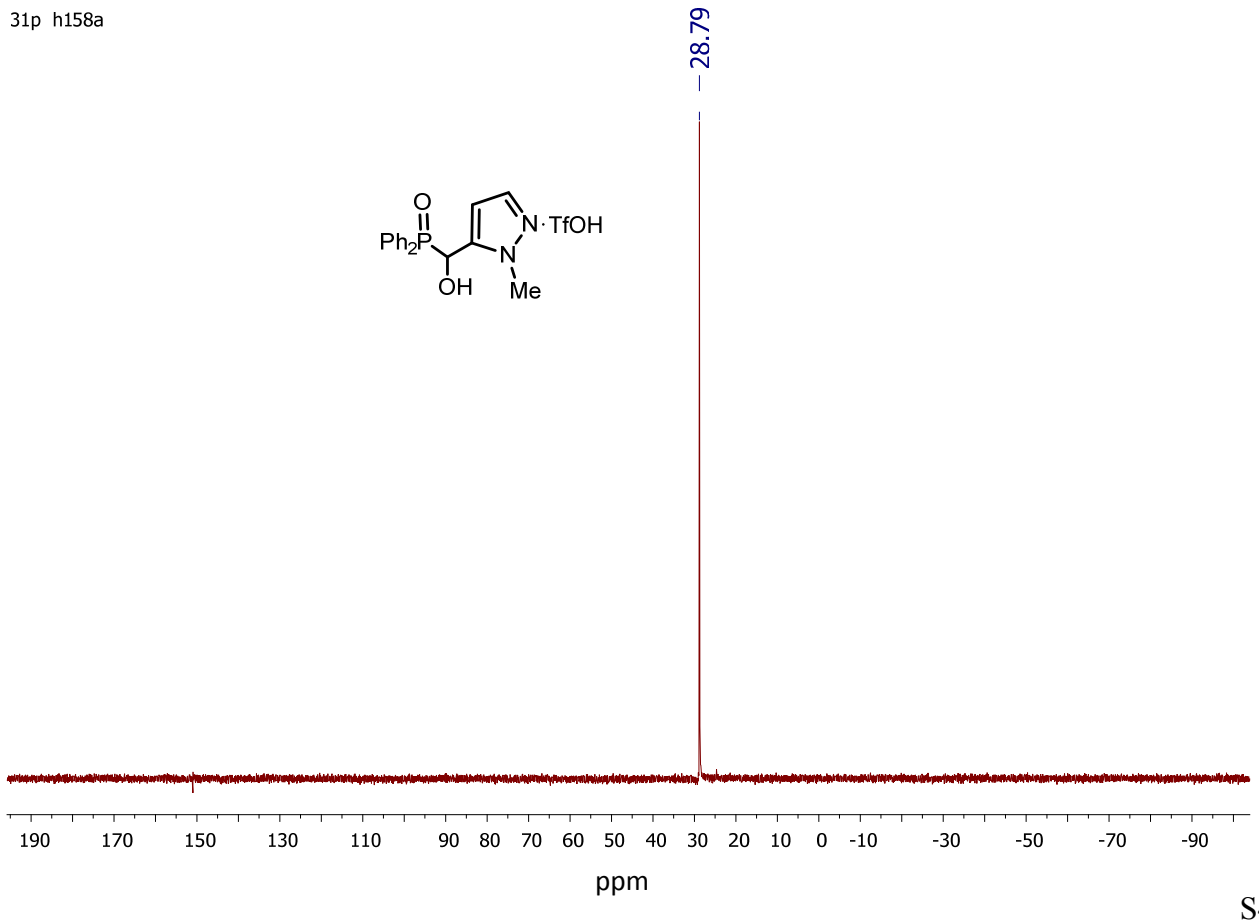
^{1}H NMR spectrum of triflate **3a**·TfOH (DMSO-d_6)



^{13}C NMR spectrum of triflate **3a**·TfOH (DMSO-d_6)



^{31}P NMR spectrum of triflate **3a**·TfOH (DMSO-d_6)



^{19}F NMR spectrum of triflate **3a**·TfOH (DMSO-d_6)