Supporting Information
For

Substituent controlled reactivity switch: selective synthesis of α-diazoalkylphosphonates or vinylphosphonates *via* nucleophilic substitution of alkyl bromides with Bestmann-Ohira reagent

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Experimental Section

General

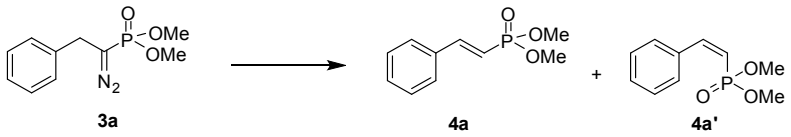
All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (Merck, 100-200 mesh). Melting points were recorded on a Precision melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer's RX I FTIR spectrophotometer. NMR spectra were recorded on a Brucker Avance spectrometer at 400 MHz (^{1}H), 100 MHz (^{13}C), and 162 MHz (^{31}P). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for ^{1}H and ^{13}C and phosphoric acid as the external standard for ^{31}P. To describe spin multiplicity, standard abbreviations such as s, d, t, q, m, dd referring to singlet, doublet, triplet, quartet, multiplet and doublet of doublet respectively, are used. The coupling constants (*J*) are given in Hz. The ESI-HRMS spectra were recorded on Agilent 6520- Q-TofLC/MS system.

All reactions were conducted in oven-dried glasswares under Nitrogen. Dimethyl oxopropyl phosphonate was purchased from Sigma Aldrich and used as received for the synthesis of the Bestmann-Ohira reagent **2**.[1,2] All other reagents were purchased from local suppliers and used without purification. Alkyl bromides were either commercially available or prepared from respective aldehydes *via* sodium borohydride reduction followed by bromination with PBr_3.[3] The brominated Morita-Baylis-Hillman product **1v** was synthesized following literature procedure.[4]

General procedure for the reaction of alkyl bromides 1 with BOR 2

To a stirred solution of alkyl bromide **1** (1 mmol) in dry MeOH (5 mL) was added Bestmann-Ohira reagent **2** (1.2 mmol, 230 mg) followed by KOH (1.2 mmol, 67 mg) and the reaction mixture was stirred at room temperature until the completion of the reaction (TLC monitoring). Methanol was distilled off under reduced pressure and crude residue was directly subjected to column chromatograpy on silica gel using 0-60% (0-80% in case of **5**) hexane/ethyl acetate as eluent to afford the products **3/4** or **5**. (Amount of BOR and KOH was doubled in case of **1q-r** & **1v**).

Table S1. Various conditions screened for the conversion of diazomethyl benzylphosphonate 3a into dimethyl styrylphosphonate 4a/4a'



Entry	Condition	Yield of **4a : 4a'**(%)[a]
1	NaOMe, THF, -78 °C - rt	–[b]
2	DCC, BF_3.OEt, DCM, 0 °C – 5 °C	80:0
3	Cu powder, MeOH, reflux, 4h	76:0
4	Cu powder, 1,4-dioxan, reflux, 1h	80:0
5	Cu powder, Toluene, reflux, 20 min	98:0

[a]ratio of isomers assigned on the basis of crude 1H NMR, [b]Intractable mixture.

Condition 1: NaOMe mediated reaction

To a stirred solution of diazomethyl benzylphosphonate **3a** (240 mg, 1 mmol) in anhydrous THF (5 mL) was added NaOMe (81 mg, 1.5 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. However, no product could be isolated as **3a** underwent decomposition resulting into an intractable mixture.

Condition 2: BF_3OEt/DCC mediated reaction

To a stirred solution of diazomethyl benzylphosphonate **3a** (240 mg, 1 mmol) and DCC (247 mg, 1.2 mmol) in DCM (5 mL) was added BF_3OEt (0.15 mL, 1.2 mmol in 2 mL DCM) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. After the completion of reaction, the reaction mixture was diluted with DCM and washed with $NaHCO_3$ and water. The solvent was distilled off under reduced pressure and crude residue was submitted for proton NMR. The crude product was purified by column chromatograpy on silica gel using 0-60% hexane/ethyl acetate as eluent to afford the product **4a**.

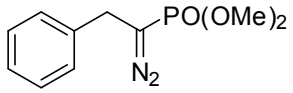
Condition 3: Cu powder mediated reaction

To a stirred solution of diazomethyl benzylphosphonate **3a** (240 mg, 1 mmol) in solvent (5 mL) was added Cu powder (6.3 mg, 10 mol %) and the reaction mixture was refluxed until the completion of the reaction (TLC monitoring). Solvent was distilled off under reduced pressure and crude residue was directly subjected to column chromatograpy on silica gel using 0-60% hexane/ethyl acetate as eluent to afford the product **4a**.

General procedure for the conversion of dimethyl diazoethyl phosphonates 3 into corresponding vinylphosphonates 4

To a stirred solution of dimethyl diazoethylphosphonate **3** (1 mmol) in toluene (5 mL) was added Cu powder (6.3 mg, 10 mol %) and the reaction mixture was refluxed until the completion of the reaction (TLC monitoring). Toluene was distilled off under reduced pressure and crude residue was directly subjected to column chromatograpy on silica gel using 0-60% hexane/ethyl acetate as eluent to afford the product **4**.

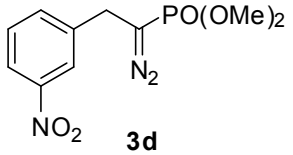
Dimethyl 1-diazo-2-phenylethylphosphonate (3a)[5]



3a

Yellow oil; isolated yield 87% (209 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2358, 2081, 1496, 1249, 1030; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.28 (m, 2H), 7.17 – 7.21 (m, 3H), 3.63 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.36 (d, $J_{H\text{-}P}$ = 10.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.2 (d, $J_{C\text{-}P}$ = 3.1 Hz, C_{Ar}), 128.8 (C_{Ar}H x 2), 128.3 (C_{Ar}H x 2), 127.2 (C_{Ar}H), 52.8 (d, $J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 x 2), 30.0 (d, $J_{C\text{-}P}$ = 8.6 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 24.19; **HRMS** for $C_{10}H_{13}N_2O_3P$: calcd. (MH^+): 241.0742, found: 241.0729

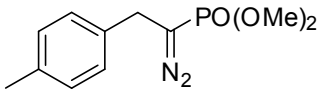
Dimethyl 1-diazo-2-(3-nitrophenyl)ethylphosphonate (3d)



3d

Yellow oil; isolated yield 80% (231 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2373, 2081, 1531, 1455, 1257, 1028; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 8.06 (m, 2H), 7.53 – 7.55 (m, 1H), 7.42 – 7.46 (m, 1H), 3.65 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.48 (d, $J_{H\text{-}P}$ = 10.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5 (C_{Ar}), 139.6 (C_{Ar}, $J_{C\text{-}P}$ = 2.1 Hz), 134.4 (C_{Ar}H), 129.8 (C_{Ar}H), 123.1 (C_{Ar}H), 122.3 (C_{Ar}H), 53.1 (d, $J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2), 30.0 (d, $J_{C\text{-}P}$ = 8.7 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 23.12; **HRMS** for $C_{10}H_{12}N_3O_5P$: calcd. (MH^+): 286.0593, found: 286.0578.

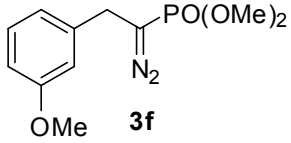
Dimethyl 1-diazo-2-*p*-tolylethylphosphonate (3e)



3e

Yellow oil; isolated yield 78% (198 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2371, 2081, 1525, 1254, 1031; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 (s, 4H), 3.64 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.32 (d, $J_{H\text{-}P}$ = 9.8 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.9 (C_{Ar}), 134.1 (d, $J_{C\text{-}P}$ = 2.3 Hz, C_{Ar}), 129.5 (C_{Ar}H x 2), 128.3 (C_{Ar}H x 2), 52.9 (d, $J_{C\text{-}P}$ = 5.2 Hz, {PO}OCH_3 x 2), 29.6 (d, $J_{C\text{-}P}$ = 8.9 Hz, CH_2), 21.1 (CH_3); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 24.41; **HRMS** for $C_{11}H_{15}N_2O_3P$: calcd. (MH^+): 255.0899, found: 255.0891

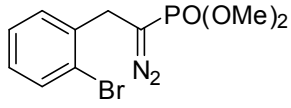
Dimethyl 1-diazo-2-(3-methoxyphenyl)ethylphosphonate (3f)



3f

Yellow oil; isolated yield 79% (213 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2081, 1599, 1489, 1257, 1036; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.20 (m, 1H), 6.73 – 6.77 (m, 3H), 3.73 (s, 3H), 3.64 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.33 (d, $J_{H\text{-}P}$ = 10.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5 (CO), 159.9 (C_{Ar}), 138.8 (d, $J_{C\text{-}P}$ = 3.4 Hz, C_{Ar}), 129.9 (C_{Ar}H), 120.6 (C_{Ar}H), 114.1 (C_{Ar}H), 112.6 (C_{Ar}H), 55.2 (OCH_3), 52.9 (d, $J_{C\text{-}P}$ = 5.3 Hz, {PO}OCH_3 x 2), 30.1 (d, $J_{C\text{-}P}$ = 8.5 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 24.29; **HRMS** for $C_{11}H_{15}N_2O_4P$: calcd. (MH^+): 271.0848, found: 271.0839.

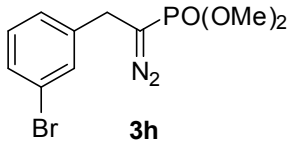
Dimethyl 2-(2-bromophenyl)-1-diazoethylphosphonate (3g)



3g

Yellow oil; isolated yield 76% (241 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2373, 1603, 1248, 1034; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 8.0, 1.0 Hz, 1H), 7.20 – 7.26 (m, 2H), 7.04 – 7.08 (m, 1H), 3.59 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.52 (d, $J_{H\text{-}P}$ = 10.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.6 (d, $J_{C\text{-}P}$ = 2.8 Hz, C_{Ar}), 133.1 (C_{Ar}H), 130.9 (C_{Ar}H), 128.9 (C_{Ar}H), 127.7 (C_{Ar}H), 124.4 (C_{Ar}), 52.9 (d, $J_{C\text{-}P}$ = 5.2 Hz, {PO}OCH_3 x 2), 30.7 (d, $J_{C\text{-}P}$ = 8.9 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 23.88; **HRMS** for $C_{10}H_{12}BrN_2O_3P$: calcd. (MH^+): 318.9847, found: 318.9836.

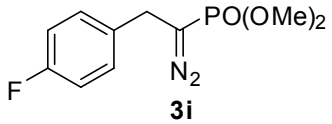
Dimethyl 2-(3-bromophenyl)-1-diazoethylphosphonate (3h)



3h

Yellow oil; isolated yield 75% (238 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2371, 1617, 1455, 1250, 1032; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.34 (m, 2H), 7.10 – 7.16 (m, 2H), 3.64 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.33 (d, $J_{H\text{-}P}$ = 10.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4 (C=N_2), 139.5 (d, $J_{C\text{-}P}$ = 2.0 Hz, C_{Ar}), 131.3 (C_{Ar}H), 130.3 (C_{Ar}H x 2), 126.9 (C_{Ar}H), 122.7 (C_{Ar}), 53.0 (d, $J_{C\text{-}P}$ = 5.2 Hz, {PO}OCH_3 x 2), 29.6 (d, $J_{C\text{-}P}$ = 8.7 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 23.68; **HRMS** for $C_{10}H_{12}BrN_2O_3P$: calcd. (MH^+): 318.9847, found: 318.9853.

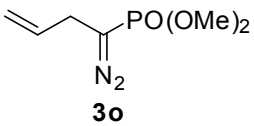
Dimethyl 1-diazo-2-(4-fluorophenyl)ethylphosphonate (3i)



3i

Yellow oil; isolated yield 78% (201 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2369, 1602, 1230, 1035; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 7.16 (m, 2H), 6.91 – 6.96 (m, 2H), 3.62 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.33 (d, $J_{H\text{-}P}$ = 10.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 244.1 Hz, C_{Ar}F), 132.9 (dd appearing as t, $J_{C\text{-}P}$ = 3.3 Hz, $J_{C\text{-}F}$ = 3.2 Hz, C_{Ar}), 129.9 (C_{Ar}H), 129.8 (C_{Ar}H), 115.7 (C_{Ar}H), 115.5 (C_{Ar}H), 52.8 (d, $J_{C\text{-}P}$ = 5.3 Hz, {PO}OCH_3 x 2), 29.3 (d, $J_{C\text{-}P}$ = 8.5 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 23.89; **HRMS** for $C_{10}H_{12}FN_2O_3P$: calcd. (MH^+): 259.0648, found: 259.0643.

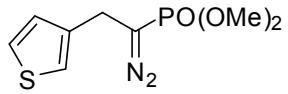
Dimethyl 1-diazobut-3-enylphosphonate (3o)



3o

Yellow oil; isolated yield 76% (144 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2084, 1252, 1035; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.67 – 5.77 (m, 1H), 5.05 – 5.10 (m, 2H), 3.65 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 2.73 – 2.77 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.5 (d, $J_{C\text{-}P}$ = 3.1 Hz, CH), 117.8 (δ-CH_2), 52.9 (d, $J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 x 2), 28.0 (d, $J_{C\text{-}P}$ = 8.3 Hz, β-CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 21.46; **HRMS** for $C_6H_{11}N_2O_3P$: calcd. (MH^+): 191.0586, found: 191.0580

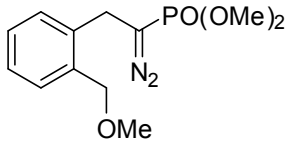
Dimethyl 1-diazo-2-(thiophen-3-yl)ethylphosphonate (3p)



3p

Yellow oil; isolated yield 78% (192 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2374, 1458, 1247, 1034; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 4.9 Hz, J = 3.0 Hz, 1H), 7.02 (t, J = 0.8 Hz, 1H), 6.93 (dd, J = 4.9 Hz, J = 1.2 Hz, 1H), 3.63 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.38 (d, $J_{H\text{-}P}$ = 9.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.5 (d, $J_{C\text{-}P}$ = 3.4 Hz, C_{Ar}), 127.6 ($C_{Ar}H$), 126.6 ($C_{Ar}H$), 122.2 ($C_{Ar}H$), 52.9 (d, $J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 x 2), 24.8 (d, $J_{C\text{-}P}$ = 8.8 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 24.06; **HRMS** for $C_8H_{11}N_2O_3PS$: calcd. (MH^+): 247.0306, found: 247.0301.

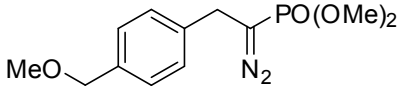
Dimethyl 1-diazo-2-(2-(methoxymethyl)phenyl)ethylphosphonate (3q)



3q

Yellow oil; isolated yield 86% (244 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2370, 1617, 1249, 1032; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.26 (m, 4H), 4.41 (s, 2H), 3.63 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.46 (d, $J_{H\text{-}P}$ = 9.3 Hz, 2H), 3.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.1 (C_{Ar}), 135.8 (d, $J_{C\text{-}P}$ = 3.4 Hz, C_{Ar}), 129.9 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 128.5 ($C_{Ar}H$), 127.4 ($C_{Ar}H$), 72.9 (CH_2), 58.1(OCH_3), 52.9 (d, $J_{C\text{-}P}$ = 5.3 Hz, {PO}OCH_3 x 2), 26.5 (CH_2, $J_{C\text{-}P}$ = 8.8 Hz); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 24.44; **HRMS** for $C_{12}H_{17}N_2O_4P$: calcd. (MH^+): 285.1004, found: 285.0995.

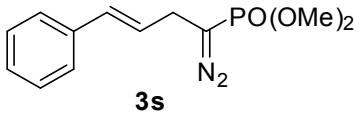
Dimethyl 1-diazo-2-(4-(methoxymethyl)phenyl)ethylphosphonate (3r)



3r

Yellow oil; isolated yield 88% (250 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2370, 1654, 1247, 1036; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 4.36 (s, 2H), 3.63 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.35 (d, $J_{H\text{-}P}$ = 10.0 Hz, 2H), 3.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.3 (C_{Ar}), 136.6 (d, $J_{C\text{-}P}$ = 3.1 Hz, C_{Ar}), 128.4 ($C_{Ar}H$ x 2), 128.2 ($C_{Ar}H$ x 2), 74.3 (CH_2), 58.1(OCH_3), 52.9 (d, $J_{C\text{-}P}$ = 5.3 Hz, {PO}OCH_3 x 2), 29.7 (CH_2, $J_{C\text{-}P}$ = 8.6 Hz); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 24.28; **HRMS** for $C_{12}H_{17}N_2O_4P$: calcd. (MH^+): 285.1004, found: 285.0998.

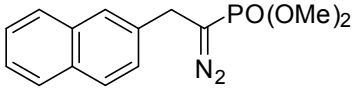
(E)-Dimethyl 1-diazo-4-phenylbut-3-enylphosphonate (3s)



3s

Yellow oil; isolated yield 79% (210 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2369, 1456, 1250, 1035; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.28 (m, 4H), 7.13 – 7.17 (m, 1H), 6.42 (d, $J_{H\text{-}P}$ = 15.7 Hz, 1H), 6.05 – 6.13 (m, 1H), 3.68 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 2.91 – 2.95 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.6 (C_{Ar}), 132.9 ($C_{ali}H$), 128.6 ($C_{Ar}H$ x 2), 127.8 ($C_{Ar}H$), 126.3 ($C_{Ar}H$ x 2), 124.1 (d, $J_{C\text{-}P}$ = 3.1 Hz, $C_{ali}H$), 53.0 (d, $J_{C\text{-}P}$ = 5.2 Hz, {PO}OCH_3 x 2), 27.6 (d, $J_{C\text{-}P}$ = 8.6 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 24.24; **HRMS** for $C_{12}H_{15}N_2O_3P$: calcd. (MH^+): 267.0899, found: 267.0879.

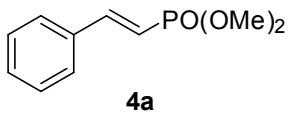
Dimethyl 1-diazo-2-(naphthalene-2-yl)ethylphosphonate (3t)



3t

Yellow oil; isolated yield 87% (252 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2373, 1687, 1339, 1238, 1037; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.76 (m, 3H), 7.60 (br s, 1H), 7.36 – 7.42 (m, 2H), 7.31 (dd, J = 8.4 Hz, J = 1.8 Hz, 1H), 3.63 (d, $J_{H\text{-}P}$ = 11.6 Hz, 6H), 3.52 (d, $J_{H\text{-}P}$ = 10.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.7 (d, $J_{C\text{-}P}$ = 3.2 Hz, C_{Ar}), 133.5 (C_{Ar}), 132.6 (C_{Ar}), 128.8 ($C_{Ar}H$), 127.7 ($C_{Ar}H$), 127.6 ($C_{Ar}H$), 126.9 ($C_{Ar}H$), 126.5 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 125.9 ($C_{Ar}H$), 53.0 (d, $J_{C\text{-}P}$ = 4.9 Hz, {PO}OCH_3 x 2), 30.3 (d, $J_{C\text{-}P}$ = 8.6 Hz, CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 24.15; **HRMS** for $C_{14}H_{15}N_2O_3P$: calcd. (MH^+): 291.0899, found: 291.0893.

(*E*)-Dimethyl styrylphosphonate (4a)[6]

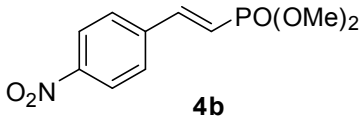


4a

Colorless oil; isolated yield 98% (208 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2402, 1525, 1216, 1036, 927; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.50 (m, 3H), 7.30 – 7.31 (m, 3H), 6.14 (t, $J_{H\text{-}P}$ = 17.8 Hz, 1H), 3.69 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7 (d, $J_{C\text{-}P}$ = 6.7 Hz, β-CH), 134.7 (d, $J_{C\text{-}P}$ = 23.3 Hz, C_{Ar}), 130.4 ($C_{Ar}H$), 128.9 ($C_{Ar}H$ x 2), 127.8 ($C_{Ar}H$ x 2), 112.3 (d, $J_{C\text{-}P}$ = 191.5 Hz, α-CH), 52.5 (d, $J_{C\text{-}P}$ = 5.5 Hz,

{PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 22.41; **HRMS** for $C_{10}H_{13}O_3P$, calcd (MH^+): 213.0681, found: 213.0689.

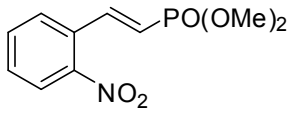
(*E*)-Dimethyl 4-nitrostyrylphosphonate (4b)[7]



4b

Yellow solid; isolated yield 85% (218 mg). R_f 0.30 (70% EtOAc/hexane); Mp 97-100 °C; **IR** (Film, cm^{-1}): 1526, 1217, 1038; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.46 (dd, $J_{H\text{-}P}$ = 22.2 Hz, J = 17.7 Hz, 1H), 6.31 (dd appearing as t, $J_{H\text{-}P}$ = 17.0 Hz, J = 17.0 Hz, 1H), 3.71 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.6 (C_{Ar}), 146.4 (d, $J_{C\text{-}P}$ = 6.0 Hz, β-CH), 140.6 (d, $J_{C\text{-}P}$ = 21.5 Hz, C_{Ar}), 128.4 (C_{Ar}H x 2), 124.2 (C_{Ar}H x 2), 117.9 (d, $J_{C\text{-}P}$ = 190.1 Hz, α-CH), 52.6 (d, $J_{C\text{-}P}$ = 5.1 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 20.01; **HRMS** for $C_{10}H_{12}NO_5P$, calcd (MH^+): 258.0531, found: 258.0526.

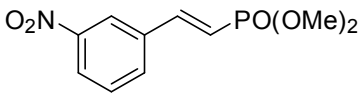
(*E*)-Dimethyl 2-nitrostyrylphosphonate (4c)



4c

Colorless oil; isolated yield 88% (226 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2371, 1525, 1347, 1252, 1030; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.4 Hz, 1H), 7.81 (dd appearing as t, $J_{H\text{-}P}$ = 20.9 Hz, J = 18.1 Hz, 1H), 7.47 – 7.59 (m, 3H), 6.11 (dd appearing as t, $J_{H\text{-}P}$ = 17.7 Hz, J = 17.4 Hz, 1H), 3.75 (d, $J_{H\text{-}P}$ = 10.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9 (C_{Ar}), 144.6 (d, $J_{C\text{-}P}$ = 7.8 Hz, β-CH), 133.7 (C_{Ar}H), 131.5 (d, $J_{C\text{-}P}$ = 24.6 Hz, C_{Ar}), 130.4 (C_{Ar}H), 129.2 (C_{Ar}H), 124.9 (C_{Ar}H), 118.7 (d, $J_{C\text{-}P}$ = 188.8 Hz, α-CH), 52.8 (d, $J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 19.20; **HRMS** for $C_{10}H_{12}NO_5P$, calcd (MH^+): 258.0531, found: 258.0534.

(*E*)-Dimethyl 3-nitrostyrylphosphonate (4d)

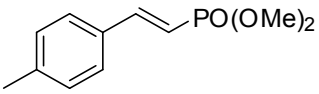


4d

Colorless oil; isolated yield 88% (226 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2402, 1532, 1035, 909; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (t, $J_{H\text{-}P}$ = 1.7 Hz, 1H), 8.16 (dd, J

= 8.2 Hz, J = 1.3 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.44 – 7.54 (m, 2H), 6.32 (dd, $J_{H\text{-}P}$ = 16.4 Hz, J = 17.5 Hz, 1H), 3.73 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5 (d, $J_{C\text{-}P}$ = 6.7 Hz, β-CH), 146.4 (C_{Ar}), 136.4 (d, $J_{C\text{-}P}$ = 23.8 Hz, C_{Ar}), 133.5 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 124.7 ($C_{Ar}H$), 122.0 ($C_{Ar}H$), 116.6 (d, $J_{C\text{-}P}$ = 190.5 Hz, α-CH), 52.7 (d, $J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 20.3; **HRMS** for $C_{10}H_{12}NO_5P$, calcd (MH^+): 258.0531, found: 258.0530.

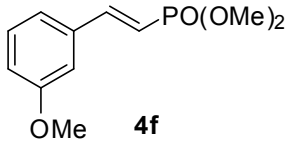
(*E*)-Dimethyl 4-methylstyrylphosphonate (4e)



4e

Colorless oil; isolated yield 98% (221 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1216, 1156, 1035, 867; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, $J_{H\text{-}P}$ = 22.6 Hz, J = 17.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.08 (t, $J_{H\text{-}P}$ = 17.8 Hz, 1H), 3.69 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7 (d, $J_{C\text{-}P}$ = 6.7 Hz, β-CH), 140.9 (C_{Ar}),132.0 (d, $J_{C\text{-}P}$ = 23.5 Hz, C_{Ar}), 129.6 ($C_{Ar}H$ x 2), 127.8 ($C_{Ar}H$ x 2), 110.9 (d, $J_{C\text{-}P}$ = 192.1 Hz, α-CH), 52.4 (d, $J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2), 21.4 (CH_3); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 22.92; **HRMS** for $C_{11}H_{15}O_3P$, calcd (MH^+): 228.0837, found: 228.0830.

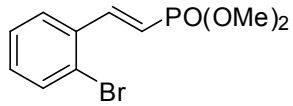
(*E*)-Dimethyl 3-methoxystyrylphosphonate (4f)[8]



4f

Colorless oil; isolated yield 96% (232 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1216, 1156, 1034, 836; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, $J_{H\text{-}P}$ = 22.5 Hz, J = 17.5 Hz, 1H), 7.21 (t, J = 7.9 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 2.1 Hz, 1H), 6.85 (dd, J = 8.2 Hz, J = 2.4 Hz, 1H), 6.12 (t, $J_{H\text{-}P}$ = 17.6 Hz, 1H), 3.74 (s, 3H), 3.69 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9 (C_{Ar}), 149.5 (d, $J_{C\text{-}P}$ = 6.6 Hz, β-CH), 136.1 (d, $J_{C\text{-}P}$ = 23.3 Hz, C_{Ar}), 129.9 ($C_{Ar}H$), 120.4 ($C_{Ar}H$), 116.2 ($C_{Ar}H$), 112.7 ($C_{Ar}H$), 112.7 (d, $J_{C\text{-}P}$ = 190.9 Hz, α-CH), 55.3 (OCH_3), 52.5 (d, $J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 22.22; **HRMS** for $C_{11}H_{15}O_4P$, calcd (MH^+): 243.0786, found: 243.0780.

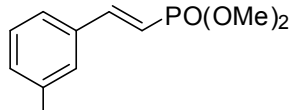
(*E*)-Dimethyl 2-bromostyrylphosphonate (4g)[9]



4g

Colorless oil; isolated yield 95% (276 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2402, 1463, 1247, 1036; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, $J_{H\text{-}P}$ = 22.5 Hz, J = 17.5 Hz, 1H), 7.48 – 7.54 (m, 2H), 7.23 – 7.27 (m, 1H), 7.13 – 7.17 (m, 1H), 6.13 (t, $J_{H\text{-}P}$ = 17.8 Hz, 1H), 3.72 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5 (d, $J_{C\text{-}P}$ = 7.9 Hz, β-CH), 134.9 (d, $J_{C\text{-}P}$ = 23.9 Hz, C_{Ar}), 133.4 ($C_{Ar}H$), 131.3 ($C_{Ar}H$), 127.7 ($C_{Ar}H$), 127.6 (d, $J_{C\text{-}P}$ = 1.1 Hz, $C_{Ar}H$), 124.9 (C_{Ar}), 116.1 (d, $J_{C\text{-}P}$ = 190.0 Hz, α-CH), 52.7 (d, $J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 20.74; **HRMS** for $C_{10}H_{12}BrO_3P$, calcd (MH^+): 290.9786, found: 290.9785.

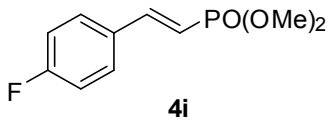
(*E*)-Dimethyl 3-bromostyrylphosphonate (4h)



4h

Colorless oil; isolated yield 91% (264 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1620, 1216, 1155, 1035, 856; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (t, J = 1.6 Hz, 1H), 7.41 – 7.43 (br m, 1H), 7.31 – 7.37 (m, 2H), 7.16 – 7.23 (m, 1H), 6.15 (t, $J_{H\text{-}P}$ = 17.3 Hz, 1H), 3.69 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8 (d, $J_{C\text{-}P}$ = 7.0 Hz, β-CH), 136.8 (d, $J_{C\text{-}P}$ = 23.6 Hz, C_{Ar}), 133.2 ($C_{Ar}H$), 130.4 ($C_{Ar}H$), 130.3 ($C_{Ar}H$), 126.5 ($C_{Ar}H$), 123.1 (C_{Ar}), 114.4 (d, $J_{C\text{-}P}$ = 190.7 Hz, α-CH), 52.6 (d, $J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 21.30; **HRMS** for $C_{10}H_{12}BrO_3P$, calcd (MH^+): 290.9786, found: 290.9785.

(*E*)-Dimethyl 4-fluorostyrylphosphonate (4i)

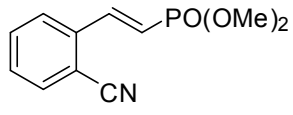


4i

Colorless oil; isolated yield 98% (225 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 3411 (br m), 3021 (m), 1657 (m), 1428 (w), 1216 (s), 1039 (m), 932 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.44 (m, 3H), 6.98 (t, J = 8.7 Hz, 2H), 6.04 (t, $J_{H\text{-}P}$ = 17.5 Hz, 1H), 3.68 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9 (d, $J_{C\text{-}F}$ = 249.9 Hz, $C_{Ar}F$), 148.3 (d, $J_{C\text{-}P}$ = 6.8 Hz, β-CH), 130.9 (dd, $J_{C\text{-}P}$ = 23.9 Hz, $J_{C\text{-}F}$ = 3.5 Hz, C_{Ar}), 129.7 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 116.1 ($C_{Ar}H$), 115.9 ($C_{Ar}H$), 112.2 (dd, $J_{C\text{-}P}$ = 192.0 Hz, $J_{C\text{-}F}$ = 2.2 Hz, α-CH), 52.5

(d, $J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 22.15; **HRMS** for $C_{10}H_{12}FO_3P$, calcd (MH^+): 231.0586, found: 231.0582.

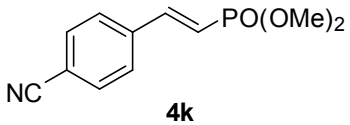
(*E*)-Dimethyl 2-cyanostyrylphosphonate (4j)



4j

Colorless oil; isolated yield 86% (204 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2226, 1622, 1254, 1032; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.70 (m, 3H), 7.54 – 7.58 (m, 1H), 7.39 – 7.43 (m, 1H), 6.43 (dd, $J_{H\text{-}P}$ = 17.5 Hz, J = 16.8 Hz, 1H), 3.75 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7 (d, $J_{C\text{-}P}$ = 6.7 Hz, *β*-CH), 137.6 (d, $J_{C\text{-}P}$ = 23.7 Hz, C_{Ar}), 133.5 ($C_{Ar}H$), 133.0 ($C_{Ar}H$), 130.1 ($C_{Ar}H$), 127.1 ($C_{Ar}H$), 118.8 (d, $J_{C\text{-}P}$ = 189.7 Hz, *α*-CH), 117.0 (CN), 112.2 (C_{Ar}), 52.8 (d, $J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 19.46; **HRMS** for $C_{11}H_{12}NO_3P$: calcd. (MH^+): 238.0633, found: 238.0626.

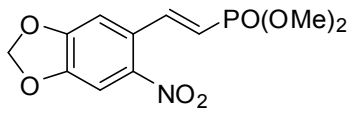
(*E*)-Dimethyl 4-cyanostyrylphosphonate (4k)



4k

Colorless oil; isolated yield 83% (197 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2370, 1596, 1347, 1247, 1032; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.41 (dd, $J_{H\text{-}P}$ = 22.4 Hz, J = 17.6 Hz, 1H), 6.25 (dd, $J_{H\text{-}P}$ = 17.5 Hz, J = 16.6 Hz, 1H), 3.69 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0 (d, $J_{C\text{-}P}$ = 6.7 Hz, *β*-CH), 138.8 (d, $J_{C\text{-}P}$ = 23.5 Hz, C_{Ar}), 132.7 ($C_{Ar}H$ x 2), 128.1 ($C_{Ar}H$ x 2), 118.3 (CN), 116.9 (d, $J_{C\text{-}P}$ = 190.3 Hz, *α*-CH), 113.5 (C_{Ar}), 52.7 (d, $J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 20.34; **HRMS** for $C_{11}H_{12}NO_3P$: calcd. (MH^+): 238.0633, found: 238.0628.

(*E*)-Dimethyl 2-(6-nitrobenzo[d][1,3]dioxol-5-yl)vinylphosphonate (4l)

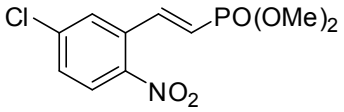


4l

Yellow solid; isolated yield 78% (235 mg). R_f 0.30 (70% EtOAc/hexane); Mp 116-118 °C; **IR** (KBr, cm^{-1}): 2375, 1516, 1261, 1032; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, $J_{H\text{-}P}$ = 21.8 Hz, J = 17.3 Hz, 1H), 7.46 (s, 1H), 6.87 (s, 1H), 6.08 (s, 2H), 5.98 (dd appearing as t, $J_{H\text{-}P}$ =

35.0 Hz, J = 17.5 Hz, 1H), 3.73 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.2 (C_{Ar}), 148.9 (C_{Ar}), 144.9 (d, $J_{C\text{-}P}$ = 8.3 Hz, β-CH), 142.5 (C_{Ar}), 128.1 (d, $J_{C\text{-}P}$ = 25.2 Hz, C_{Ar}), 117.4 (d, $J_{C\text{-}P}$ = 189.4 Hz, α-CH), 107.4 ($C_{Ar}H$), 105.5 ($C_{Ar}H$), 103.4 (CH_2), 52.7 (d, $J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 19.50; **HRMS** for $C_{11}H_{12}NO_7P$, calcd (MH^+): 302.0430, found: 302.0430.

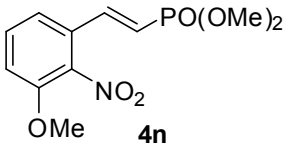
(*E*)-Dimethyl 5-chloro-2-nitrostyrylphosphonate (4m)



4m

Colorless oil; isolated yield 80% (233mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2358, 1496, 1247, 1029; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 1H), 7.78 (dd, $J_{H\text{-}P}$ = 21.8 Hz, J = 17.4 Hz, 1H), 7.48 (d, J = 2.2 Hz, 1H), 7.43 (dd, J = 8.8 Hz, J = 2.2 Hz, 1H), 6.11 (dd appearing as t, $J_{H\text{-}P}$ = 17.3 Hz, 1H), 3.74 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.8 (C_{Ar}), 143.5 (d, $J_{C\text{-}P}$ = 8.2 Hz, β-CH), 140.3 (C_{Ar}), 133.3 (d, $J_{C\text{-}P}$ = 29.9 Hz, C_{Ar}), 130.2 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 119.9 (d, $J_{C\text{-}P}$ = 188.6 Hz, α-CH), 52.8 (d, $J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 18.53; **HRMS** for $C_{10}H_{11}ClNO_5P$, calcd (MH^+): 292.0142, found: 292.0136.

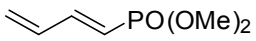
(*E*)-Dimethyl 3-methoxy-2-nitrostyrylphosphonate (4n)



4n

Colorless oil; isolated yield 79% (227 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1536, 1386, 1217, 1058; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, J = 8.2 Hz, 1H), 7.21 (dd, $J_{H\text{-}P}$ = 22.2 Hz, J = 17.4 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 6.21 (dd appearing as t, $J_{H\text{-}P}$ = 17.2 Hz, 1H), 3.83 (s, 3H), 3.69 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1 (C_{Ar}), 140.9 (d, $J_{C\text{-}P}$ = 7.2 Hz, β-CH), 140.7 (C_{Ar}), 131.2 ($C_{Ar}H$), 128.6 (d, $J_{C\text{-}P}$ = 24.3 Hz, C_{Ar}), 119.6 (d, $J_{C\text{-}P}$ = 188.7 Hz, α-CH), 118.6 ($C_{Ar}H$ merged with α-CH peak), 113.8 ($C_{Ar}H$), 56.6 (OCH_3), 52.8 (d, $J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 18.93; **HRMS** for $C_{11}H_{14}NO_6P$, calcd (MH^+): 288.0637, found: 288.0631.

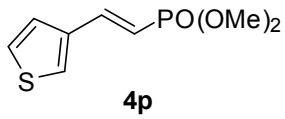
(*E*)-Dimethyl buta-1,3-dienylphosphonate (4o)[10]



4o

Colorless oil; isolated yield 85% (138 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2241, 1585, 1245, 1035; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 – 7.01 (m, 1H), 6.23 – 6.30 (m, 1H), 5.50 – 5.59 (m, 1H), 5.42 (d, $J_{H\text{-}P}$ = 16.9 Hz, 1H), 5.31 – 5.35 (m, 1H), 3.58 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6 (d, $J_{C\text{-}P}$ = 5.8 Hz, γ-CH), 135.4 (d, $J_{C\text{-}P}$ = 26.9 Hz, *β*-CH), 125.2 (CH_2), 116.3 (d, $J_{C\text{-}P}$ = 190.0 Hz, *α*-CH), 52.2 (d, $J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 21.46; **HRMS** for $C_6H_{11}O_3P$, calcd (MH^+): 163.0524, found: 163.0522.

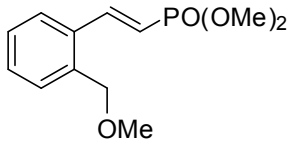
(*E*)-Dimethyl 2-(thiophen-3-yl)vinylphosphonate (4p)



4p

Colorless oil; isolated yield 95% (207 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1534, 1217, 1061; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.48 (m, 2H), 7.24 – 7.27 (m, 1H), 7.20 (t, dd, *J* = 5.1 Hz, *J* = 1.1 Hz, 1H), 5.93 (t, $J_{H\text{-}P}$ = 17.8 Hz, 1H), 3.69 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2 (d, $J_{C\text{-}P}$ = 6.7 Hz, *β*-CH), 138.2 (d, $J_{C\text{-}P}$ = 25.8 Hz, C_{Ar}), 127.9 ($C_{Ar}H$), 127.0 ($C_{Ar}H$), 124.9 ($C_{Ar}H$), 111.7 (d, $J_{C\text{-}P}$ = 191.9 Hz, *α*-CH), 52.4 (d, $J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 22.68; **HRMS** for $C_8H_{11}O_3PS$, calcd (MH^+): 219.0245, found: 219.0239.

(*E*)-Dimethyl 2-(methoxymethyl)styrylphosphonate (4q)

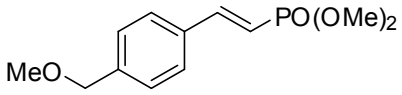


4q

Colorless oil; isolated yield 96% (256 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2226, 1622, 1254, 1032; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (dd, $J_{H\text{-}P}$ = 22.8 Hz, *J* = 17.5 Hz, 1H), 7.49 – 7.52 (m, 1H), 7.25 – 7.34 (m, 3H), 6.12 (dd, $J_{H\text{-}P}$ = 18.8 Hz, *J* = 17.5 Hz, 1H), 4.49 (s, 2H), 3.72 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H), 3.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6 (d, $J_{C\text{-}P}$ = 6.8 Hz, *β*-CH), 136.7 (C_{Ar}), 134.1 (d, $J_{C\text{-}P}$ = 22.8 Hz, C_{Ar}), 129.9 ($C_{Ar}H$), 129.5 ($C_{Ar}H$), 128.4 ($C_{Ar}H$), 126.5 ($C_{Ar}H$), 114.7 (d, $J_{C\text{-}P}$ = 189.8 Hz, *α*-CH), 72.4 (CH_2),

58.3 (OCH_3), 52.5 (d, $J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 21.88; **HRMS** for $C_{12}H_{17}O_4P$: calcd. (MH^+): 257.0943, found: 257.0937.

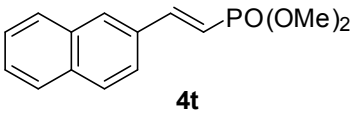
(*E*)-Dimethyl 4-(methoxymethyl)styrylphosphonate (4r)



4r

Colorless oil; isolated yield 96% (256 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2226, 1622, 1254, 1032; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.48 (m, 3H), 7.27 (d, J = 8.1 Hz, 2H), 6.13 (t, $J_{H\text{-}P}$ = 17.7 Hz, 1H), 4.39 (s, 2H), 3.69 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H), 3.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3 (d, $J_{C\text{-}P}$ = 6.6 Hz, *β*-CH), 140.8 (C_{Ar}), 134.0 (d, $J_{C\text{-}P}$ = 23.3 Hz, C_{Ar}), 127.9 (C_{Ar}H x 2), 127.8 (C_{Ar}H x 2), 112.2 (d, $J_{C\text{-}P}$ = 191.5 Hz, *α*-CH), 74.1 (CH_2), 58.3 (OCH_3), 52.5 (d, $J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 22.40; **HRMS** for $C_{12}H_{17}O_4P$: calcd. (MH^+): 257.0943, found: 257.0945.

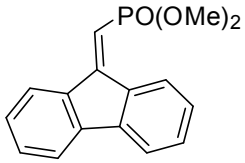
(*E*)-Dimethyl 2-(naphthalene-2-yl)vinylphosphonate (4t)



4t

Colorless oil; isolated yield 96% (251 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2925, 1216, 1155, 1061; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.74 – 7.79 (m, 3H), 7.55 – 7.66 (m, 2H), 7.42 – 7.45 (m, 2H), 6.25 (t, $J_{H\text{-}P}$ = 17.6 Hz, 1H), 3.73 (d, $J_{H\text{-}P}$ = 11.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7 (d, $J_{C\text{-}P}$ = 6.9 Hz, *β*-CH), 134.3 (C_{Ar}), 133.2 (C_{Ar}), 132.1 (d, $J_{C\text{-}P}$ = 23.3 Hz, C_{Ar}), 129.6 (C_{Ar}H), 128.7 (C_{Ar}H), 128.6 (C_{Ar}H), 127.8 (C_{Ar}H), 127.3 (C_{Ar}H), 126.8 (C_{Ar}H), 123.1 (C_{Ar}H), 112.4 (d, $J_{C\text{-}P}$ = 191.4 Hz, *α*-CH), 52.5 (d, $J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 22.49; **HRMS** for $C_{14}H_{16}O_3P$, calcd (MH^+): 263.0837, found: 263.0830.

Dimethyl (9*H*-fluoren-9-ylidene)methylphosphonate (4u)

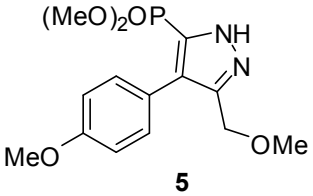


4u

Colorless oil; isolated yield 85% (243 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1537, 1216, 1156, 1033, 929; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, J = 7.8 Hz, 1H), 7.52 –

7.57 (m, 3H), 7.30 – 7.35 (m, 2H), 7.20 – 7.26 (m, 2H), 6.41 (d, $J_{H\text{-}P}$ = 11.6 Hz, 1H), 3.74 (d, $J_{H\text{-}P}$ = 11.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0 (d, $J_{C\text{-}P}$ = 6.4 Hz, *β*-CH), 142.4 (C_{Ar}), 140.7 (C_{Ar}), 138.1 (C_{Ar}), 135.2 (C_{Ar}), 130.9 ($C_{Ar}H$), 130.8 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 127.6 ($C_{Ar}H$), 127.5 ($C_{Ar}H$), 121.4 ($C_{Ar}H$), 119.8 ($C_{Ar}H$), 119.7 ($C_{Ar}H$), 107.4 (d, $J_{C\text{-}P}$ = 192.1 Hz, *α*-CH), 52.6 (d, $J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 19.34; **HRMS** for $C_{16}H_{15}O_3P$: calcd. (MH^+): 287.0837, found: 287.0838.

Dimethyl 3-(methoxymethyl)-4-(4-methoxyphenyl)-1H-pyrazol-5-ylphosphonate (5)



5

Colorless gummy solid; isolated yield 65% (243 mg). R_f 0.40 (90% EtOAc/hexane); **IR** (Film, cm^{-1}): 1219, 1252, 1035, 932; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 4.38 (s, 2H), 3.77 (s, 3H), 3.59 (d, $J_{H\text{-}P}$ = 11.5 Hz, 6H), 3.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2 (C_{Ar}), 130.9 ($C_{Ar}H$ x 2), 128.4 (C_{Ar}), 123.1 (C_{Ar}), 113.7 ($C_{Ar}H$ x 2), 65.4 (CH_2), 58.3 (OCH_3), 55.2 (OCH_3), 53.1 (d, $J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 10.99; **HRMS** for $C_{14}H_{19}N_2O_5P$: calcd. (MH^+): 327.1110, found: 327.1104.

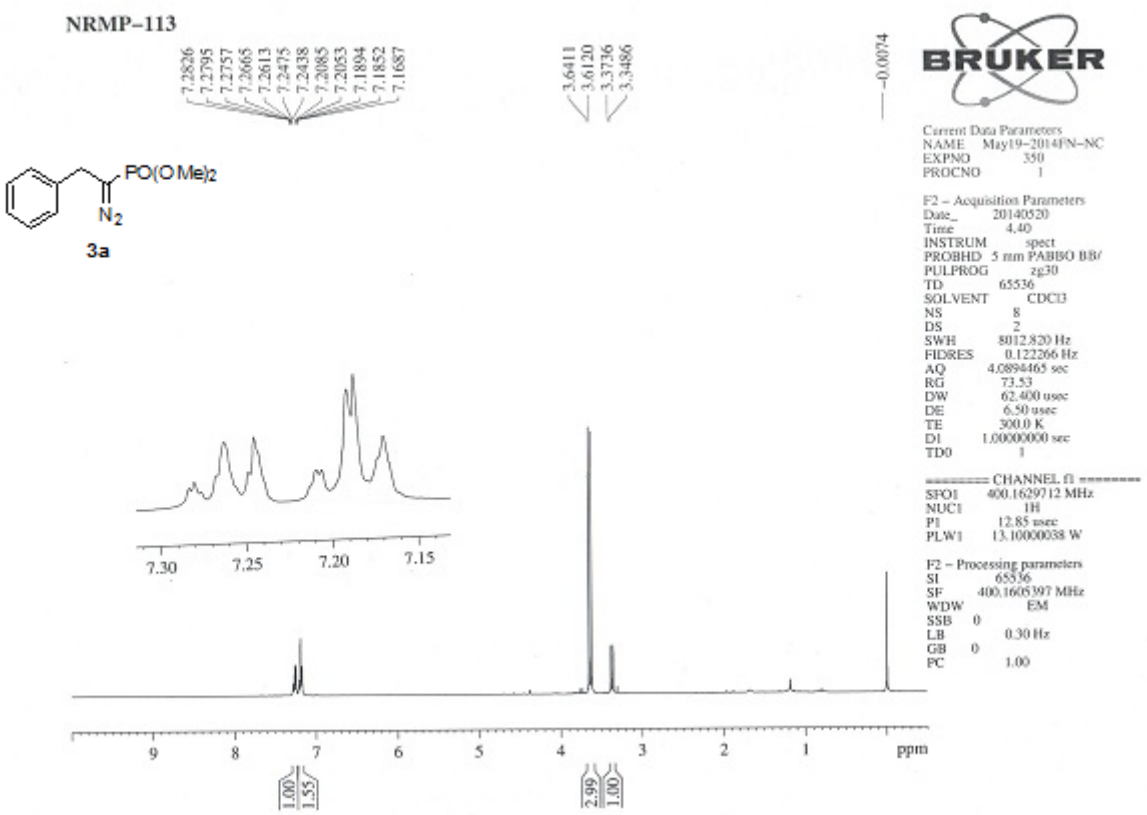


Figure 1: ^{1}H NMR spectrum of 3a

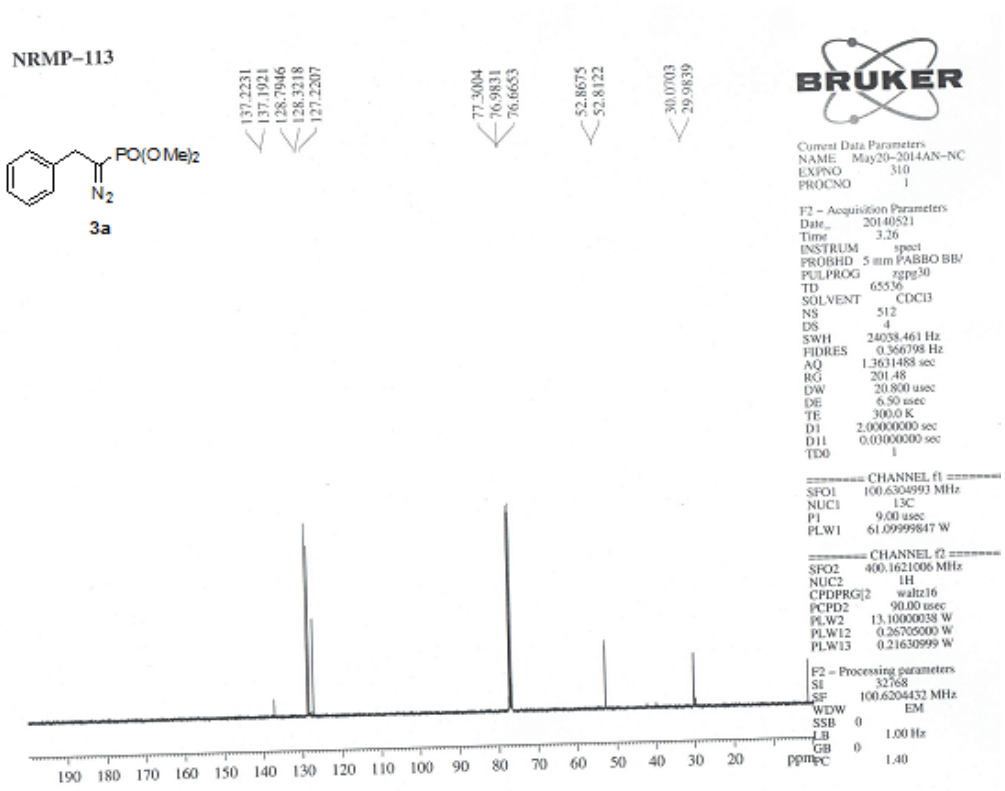


Figure 2: ^{13}C NMR spectrum of 3a

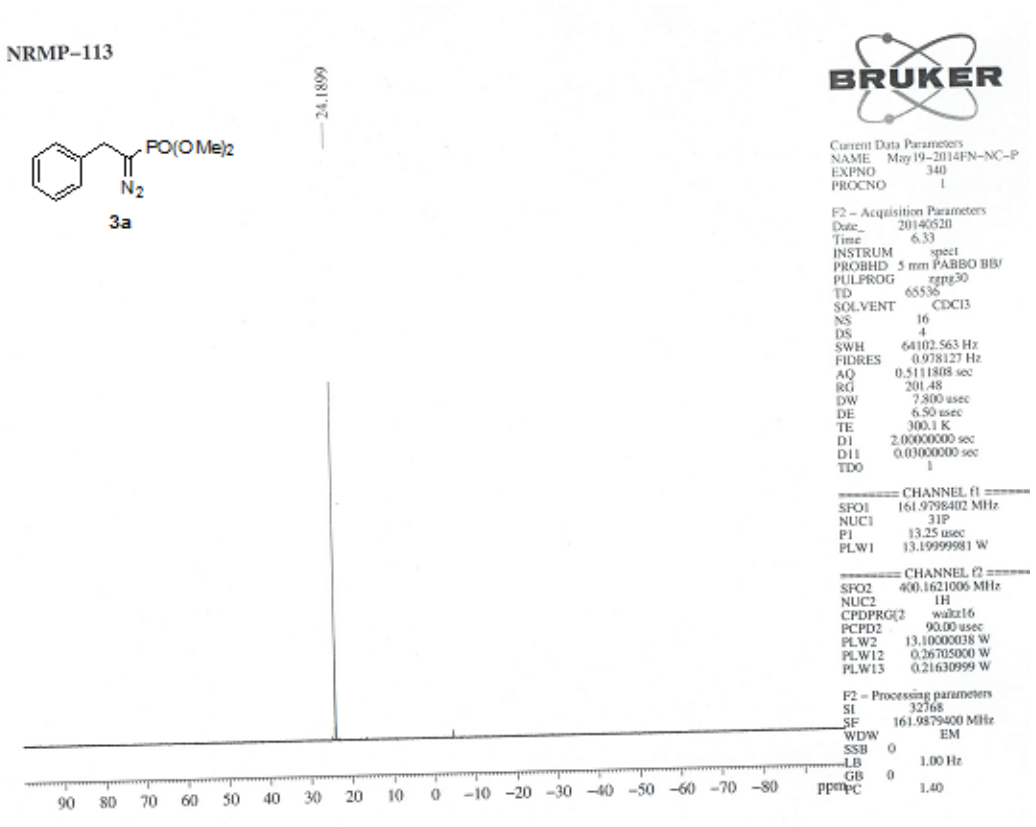


Figure 3: ^{31}P NMR spectrum of 3a

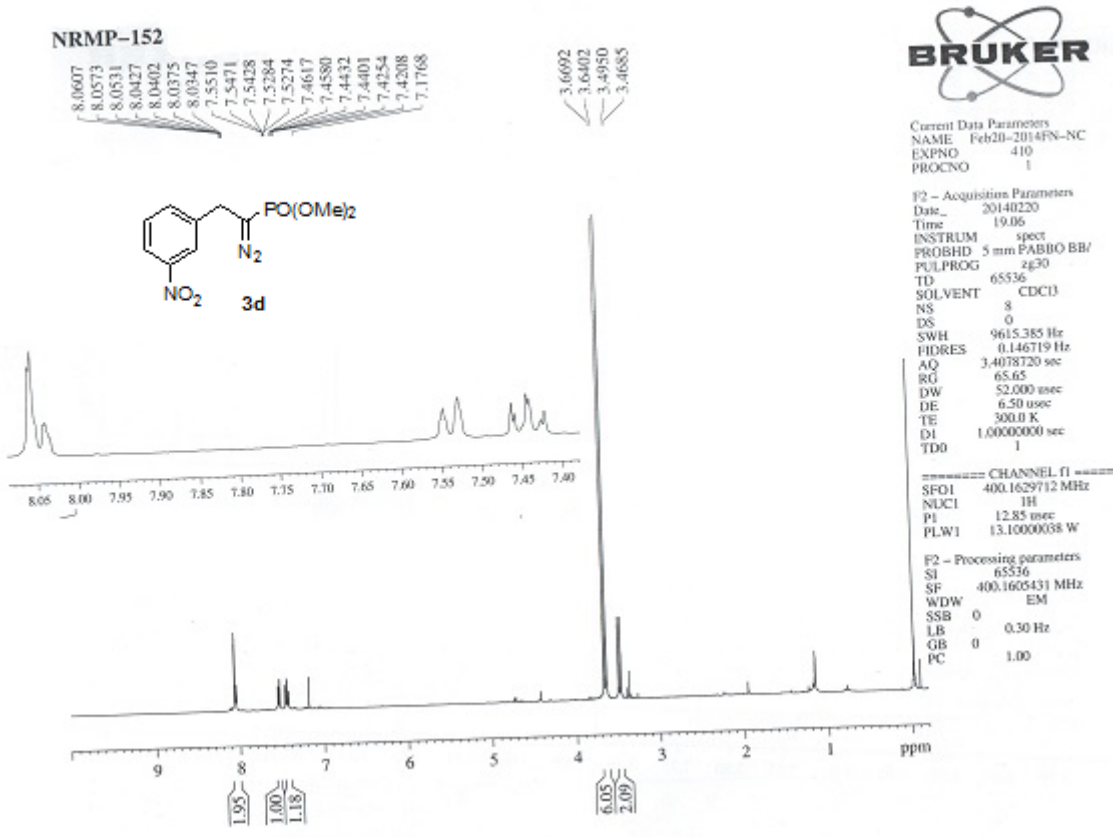


Figure 4: ^{1}H NMR spectrum of 3d

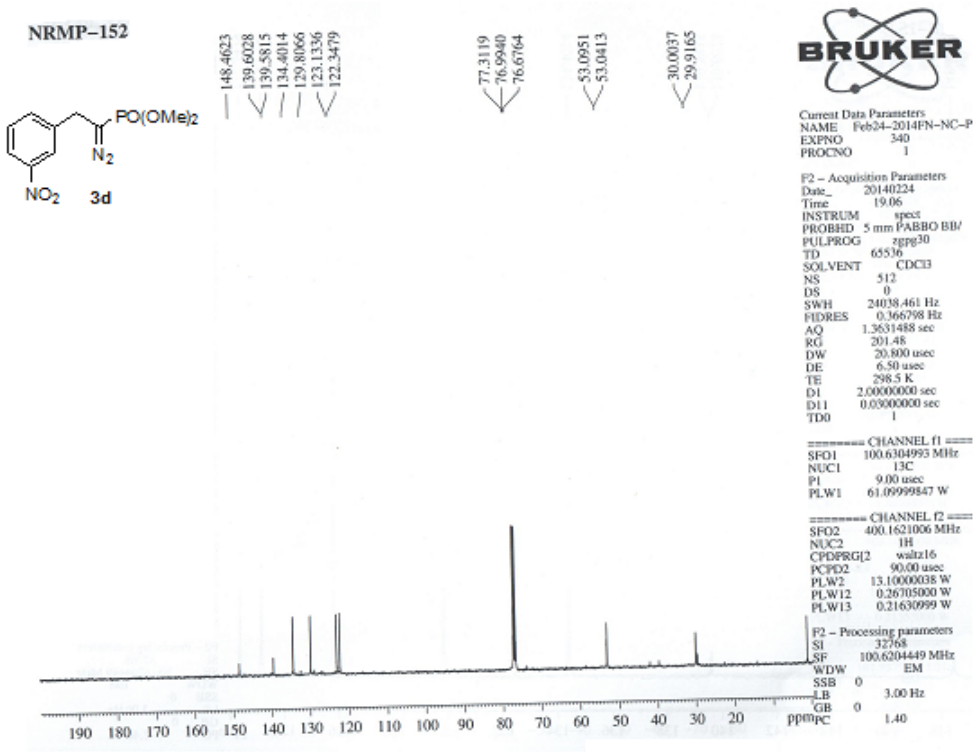


Figure 5: ^{13}C NMR spectrum of 3d

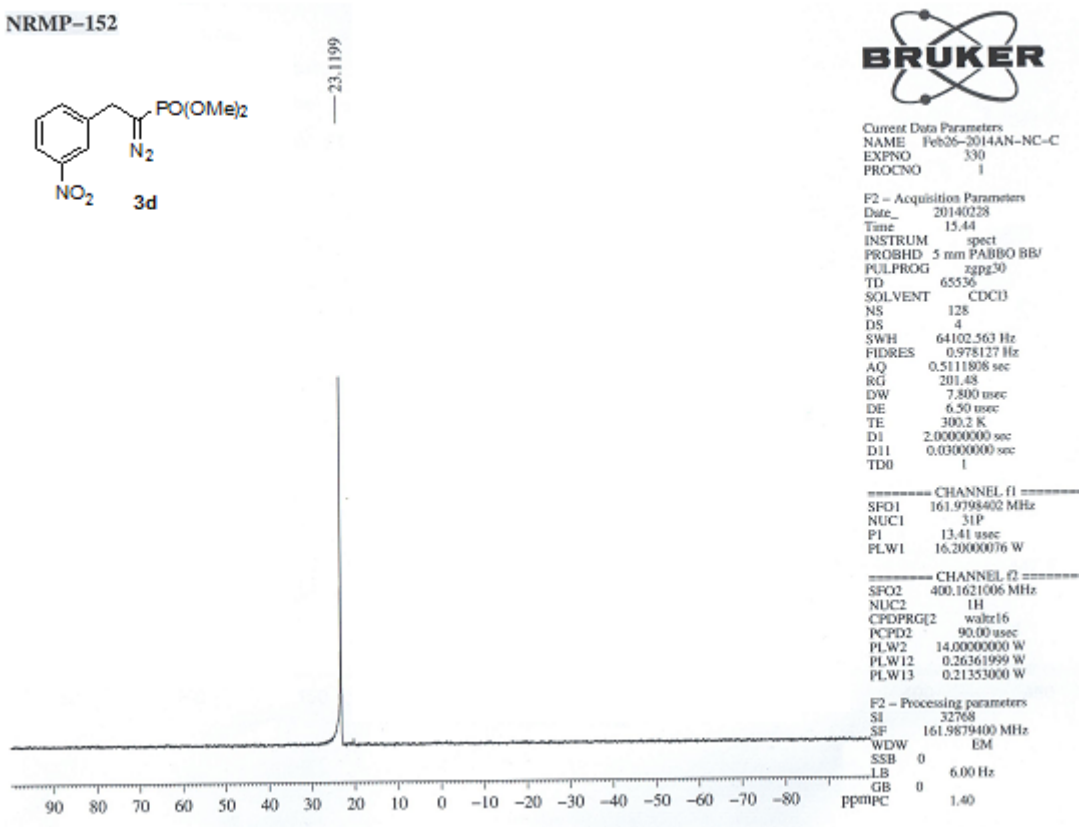


Figure 6: ^{31}P NMR spectrum of 3d

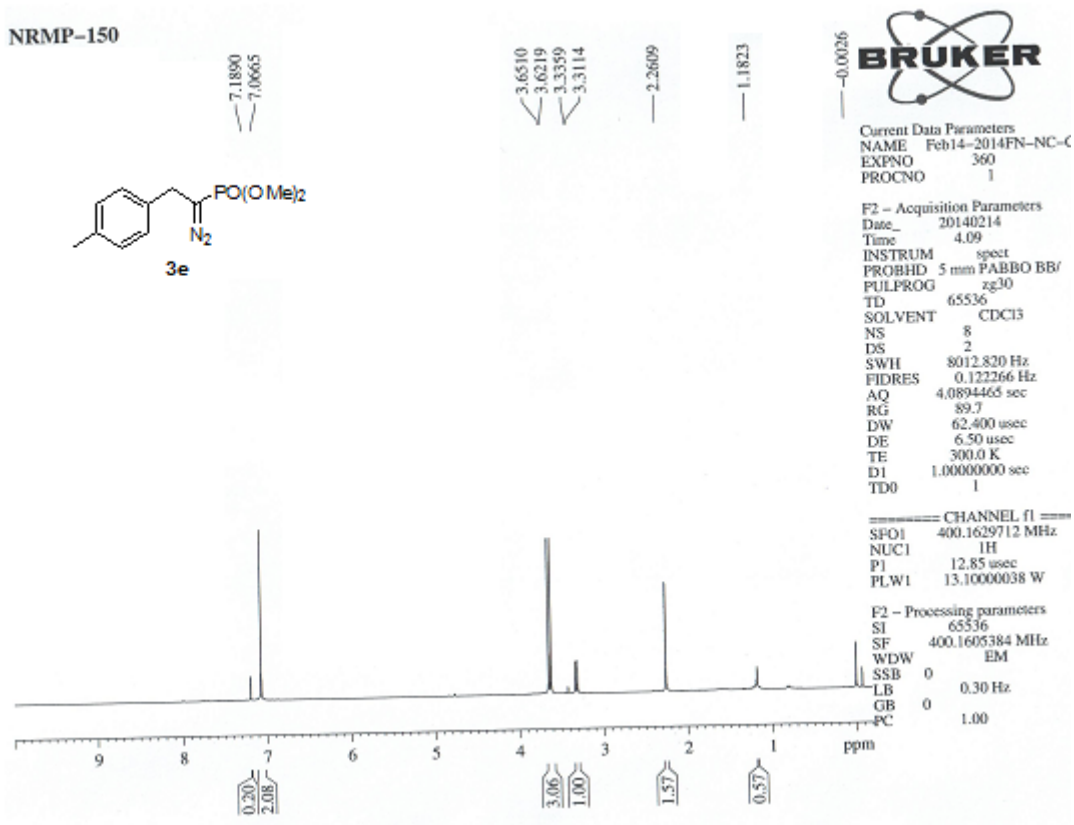


Figure 7: ^{1}H NMR spectrum of 3e

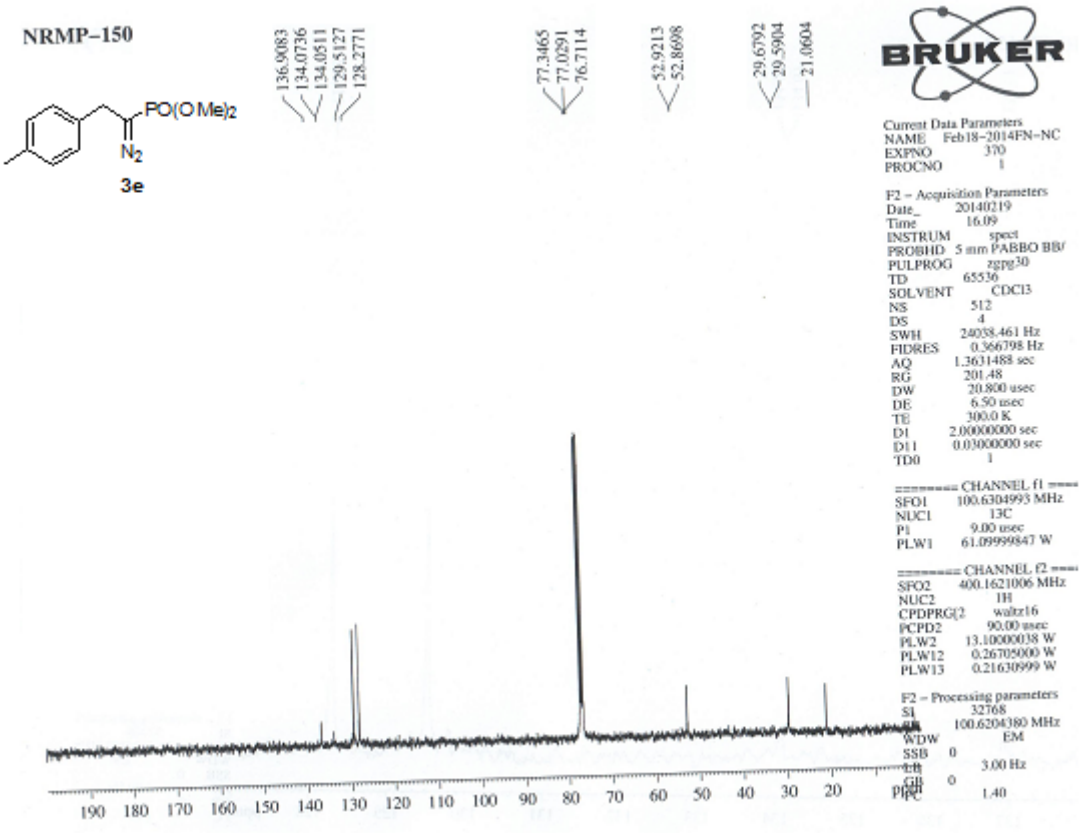


Figure 8: ^{13}C NMR spectrum of 3e

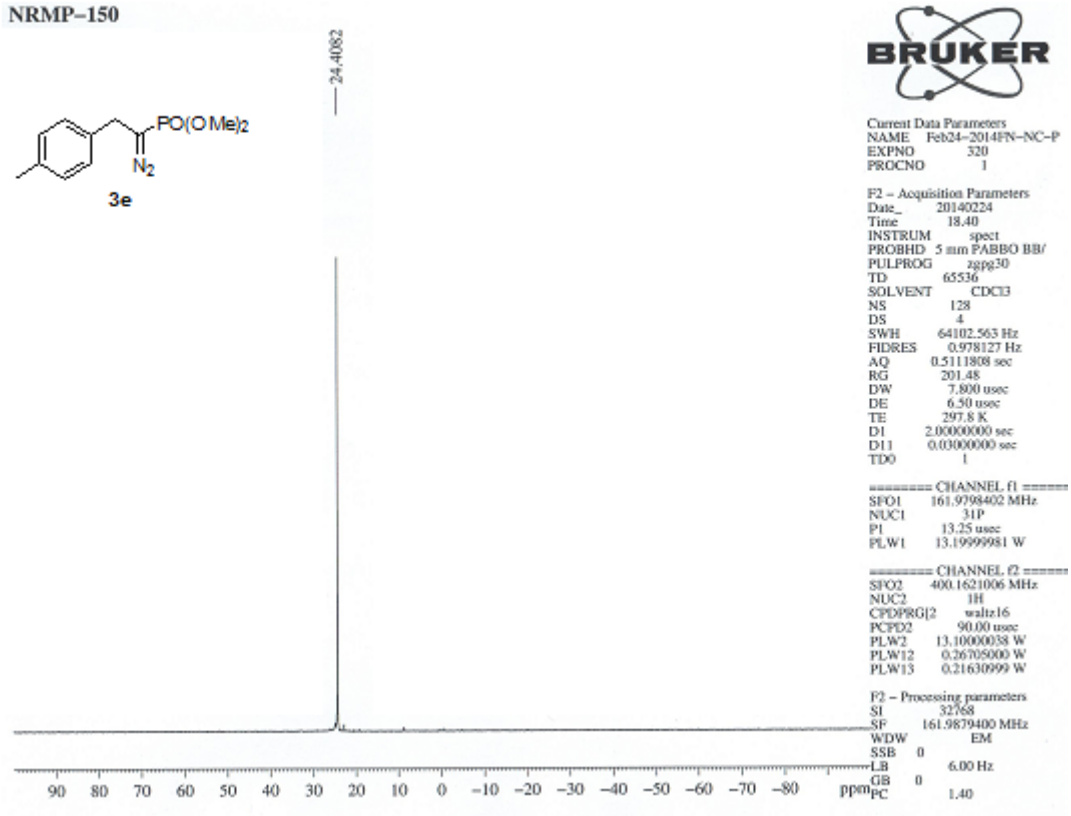


Figure 9: ^{31}P NMR spectrum of 3e

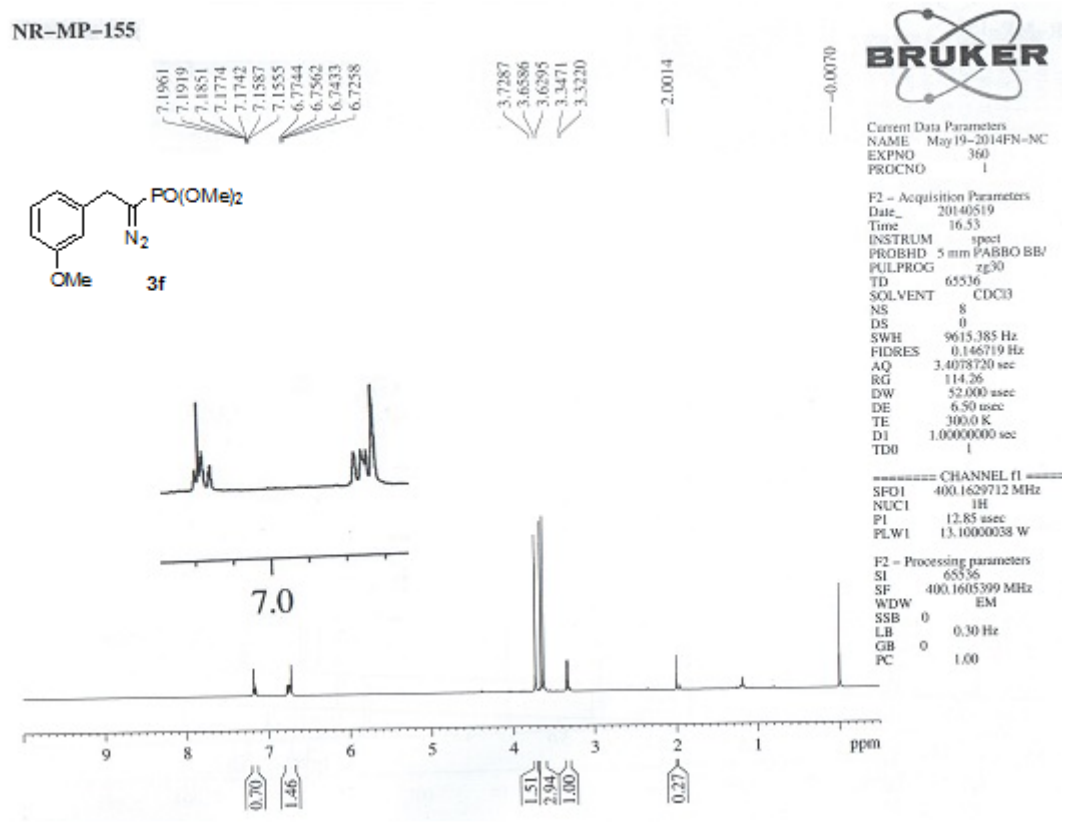


Figure 10: ^{1}H NMR spectrum of 3f

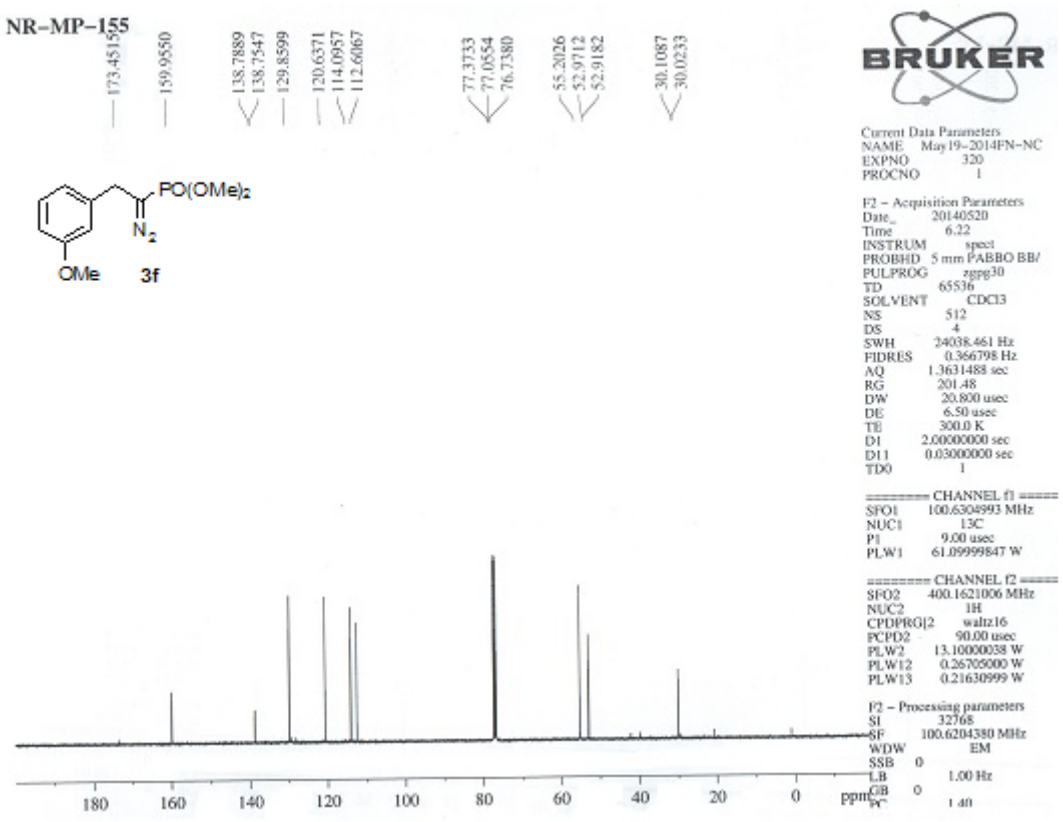


Figure 11: ^{13}C NMR spectrum of 3f

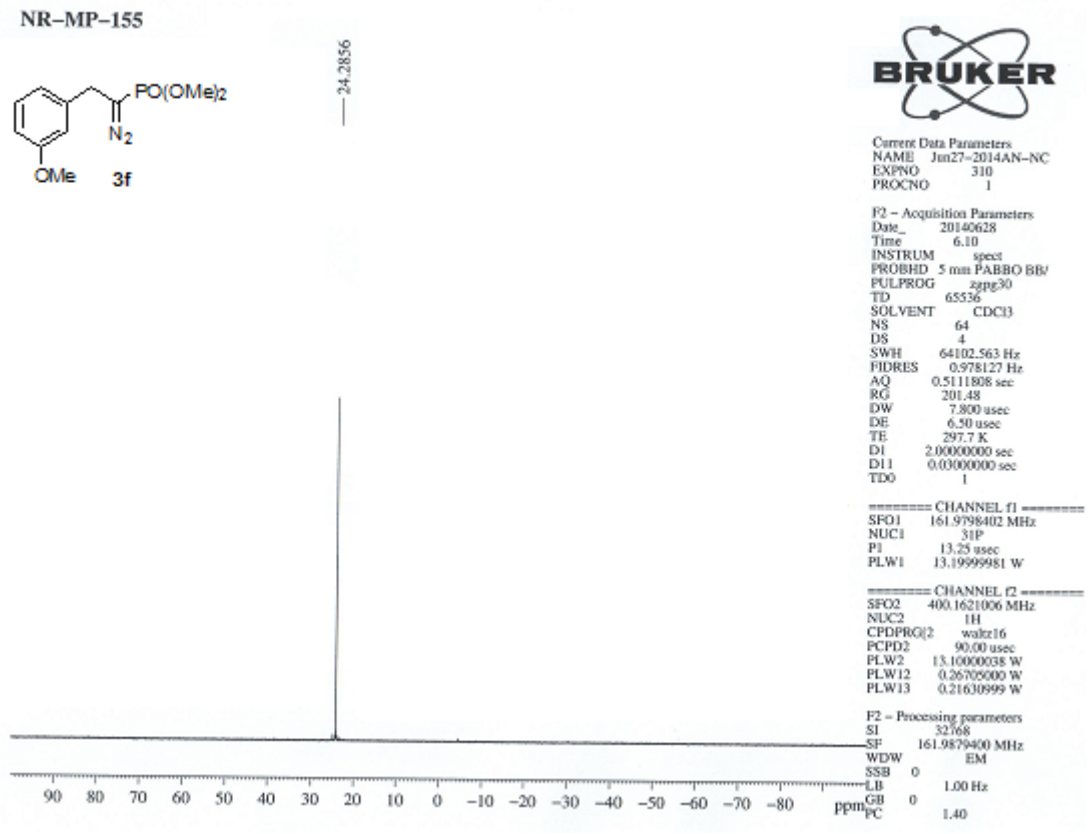


Figure 12: ^{31}P NMR spectrum of 3f

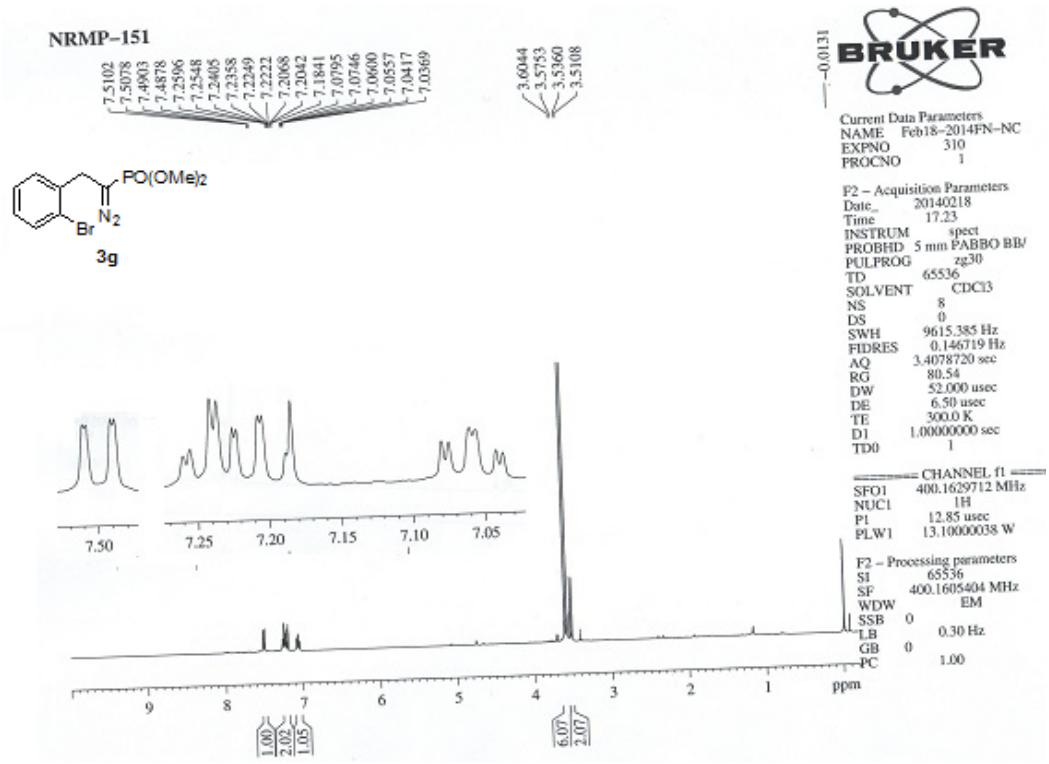


Figure 13: ^{1}H NMR spectrum of 3g

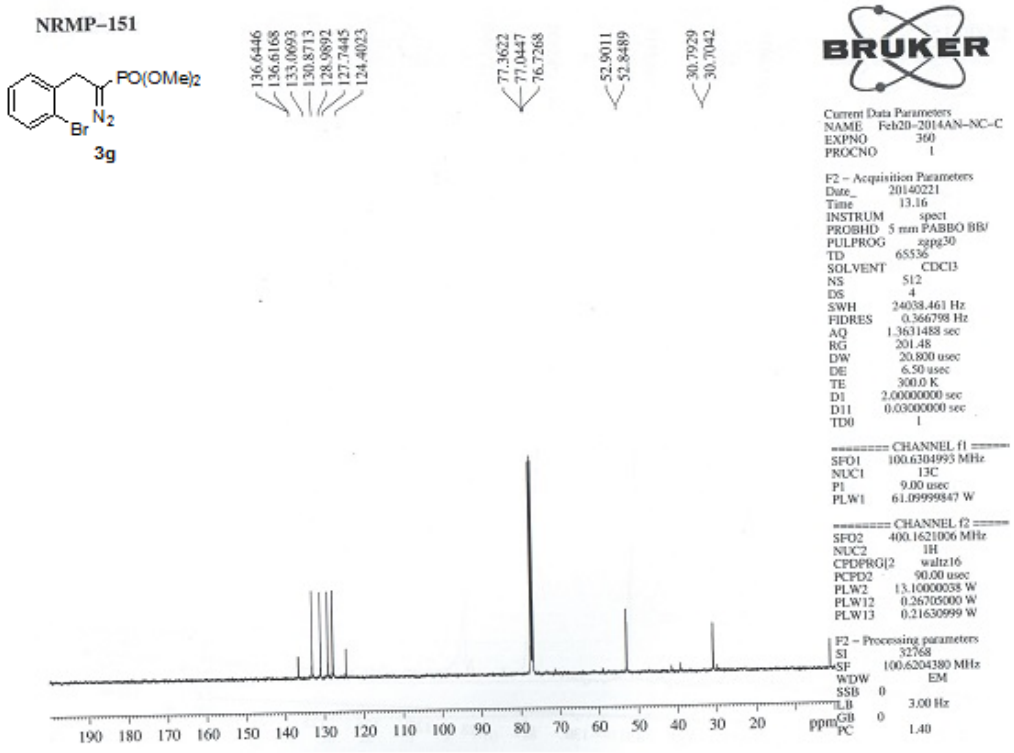


Figure 14: ^{13}C NMR spectrum of 3g

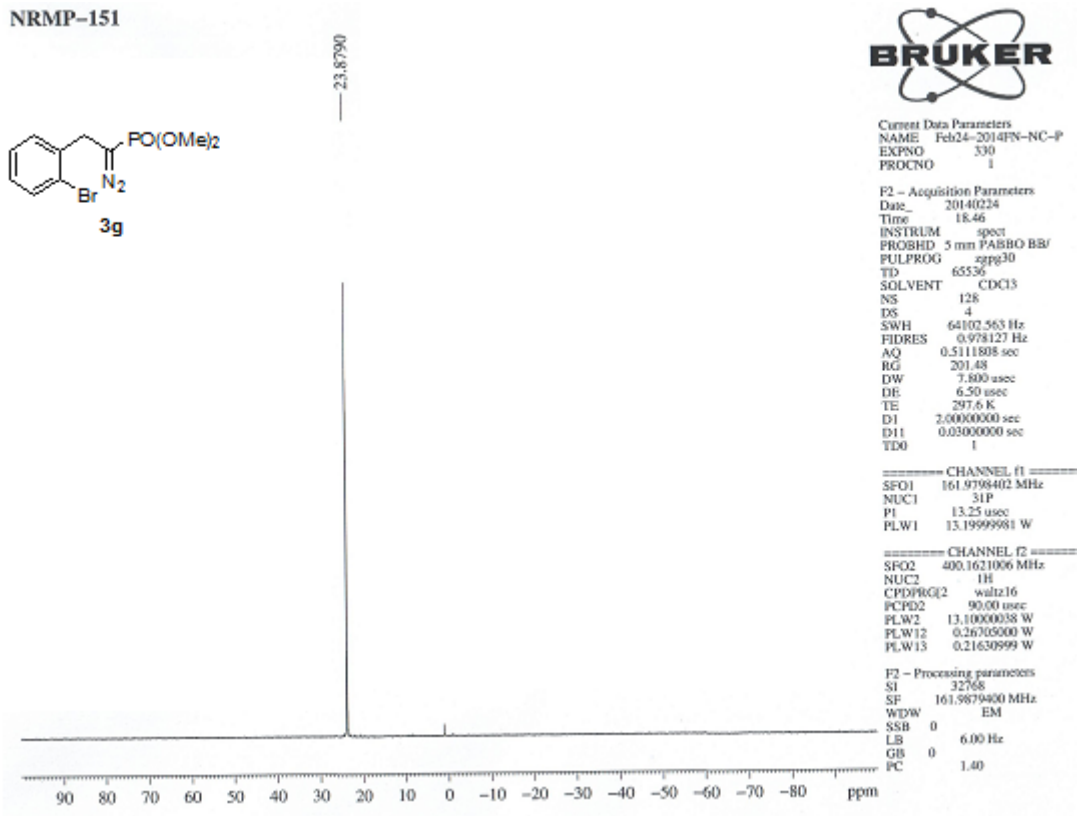


Figure 15: ^{31}P NMR spectrum of 3g

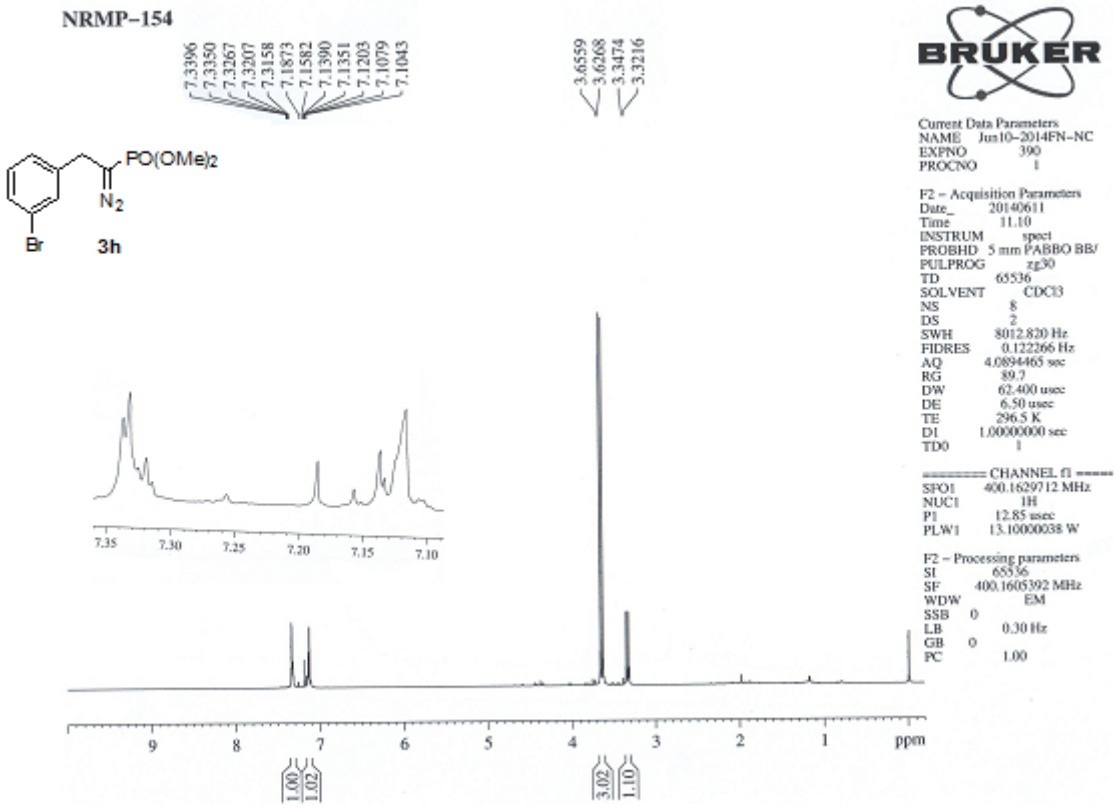


Figure 16: ^{1}H NMR spectrum of 3h

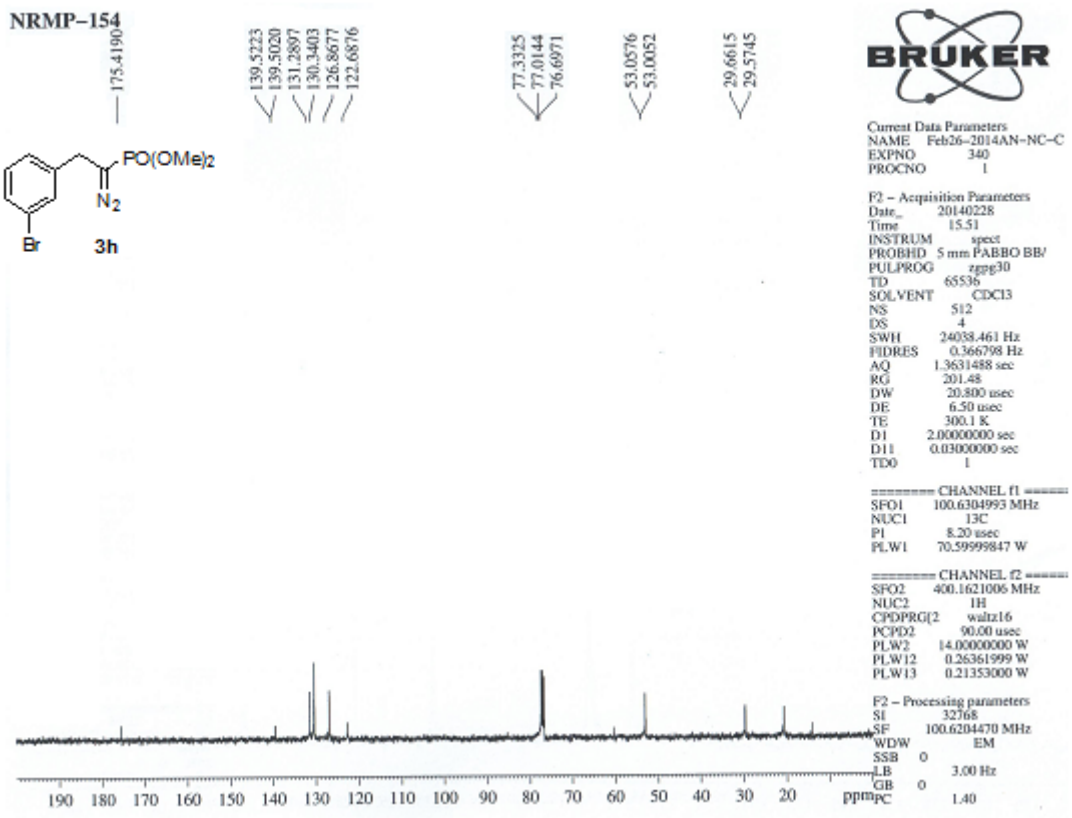


Figure 17: ^{13}C NMR spectrum of 3h

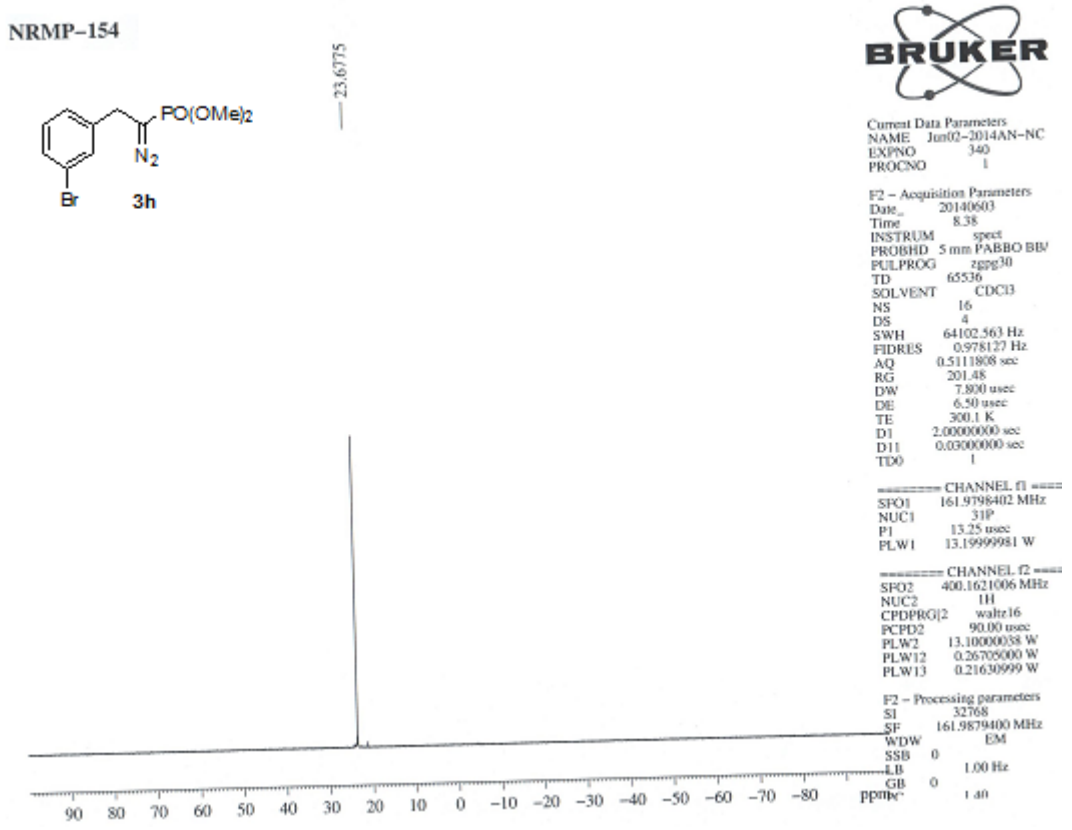


Figure 18: ^{31}P NMR spectrum of 3h

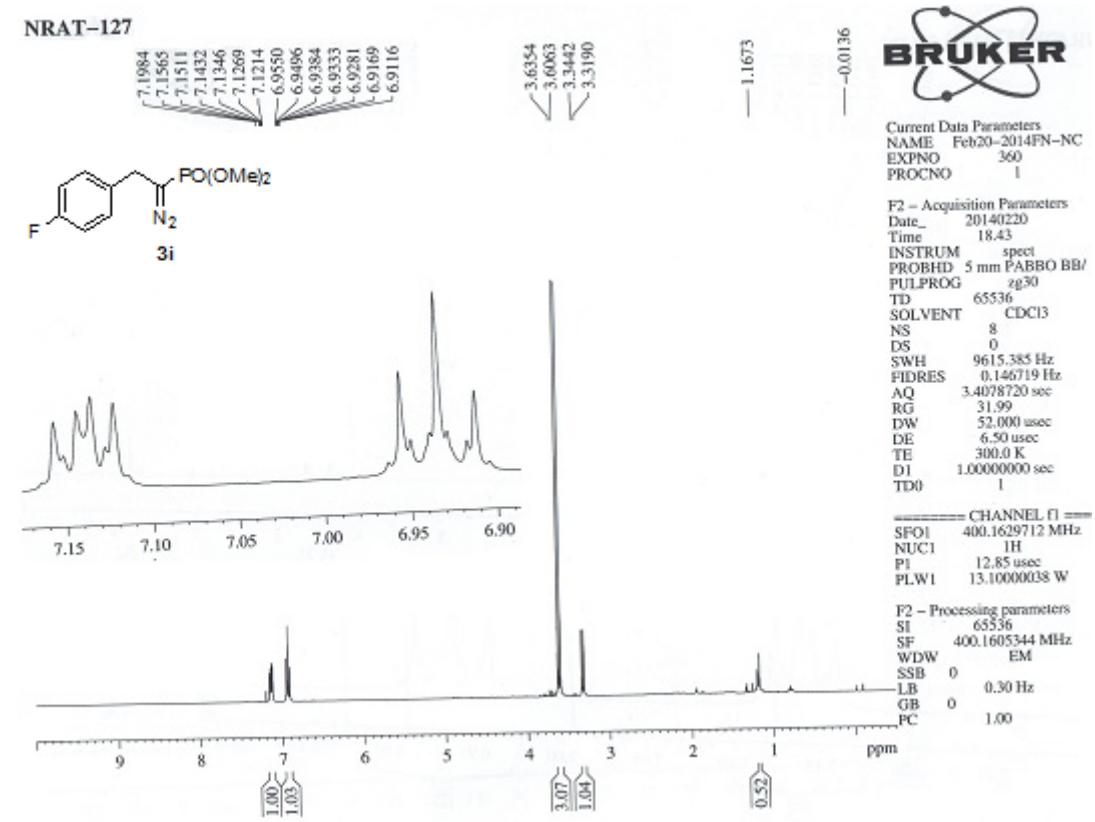


Figure 19: ^{1}H NMR spectrum of 3i

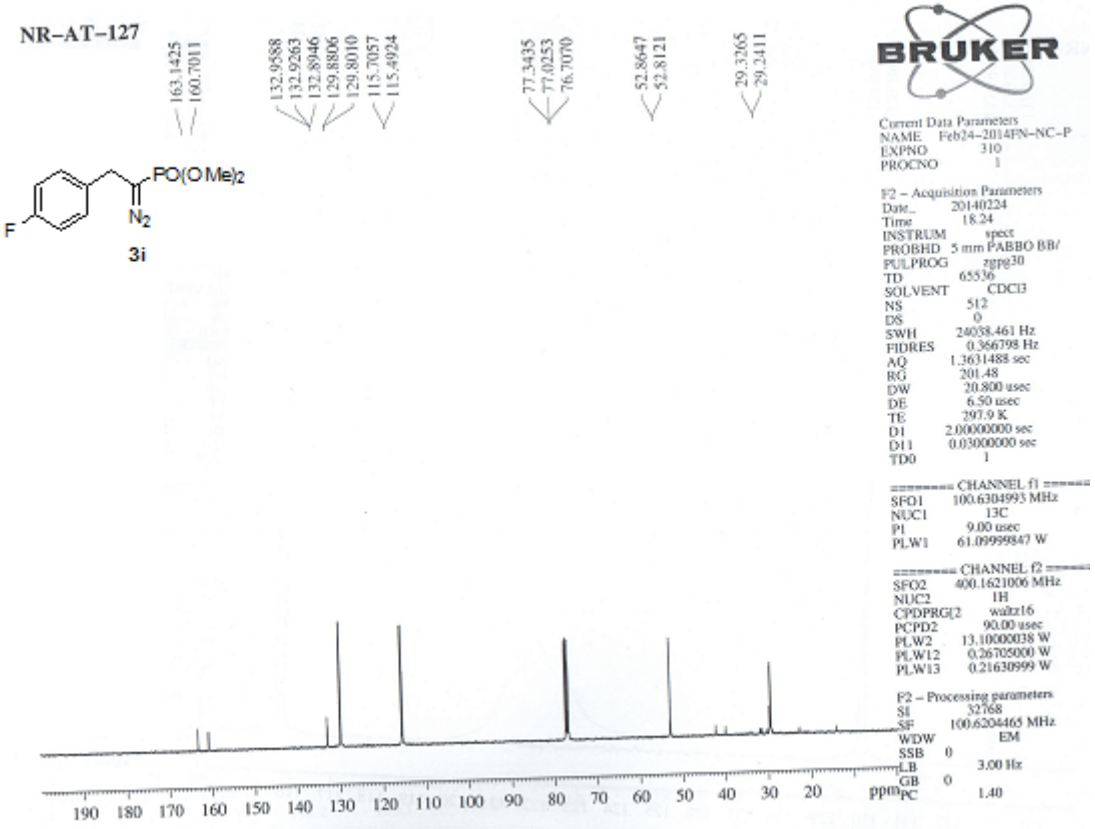


Figure 20: ^{13}C NMR spectrum of 3i

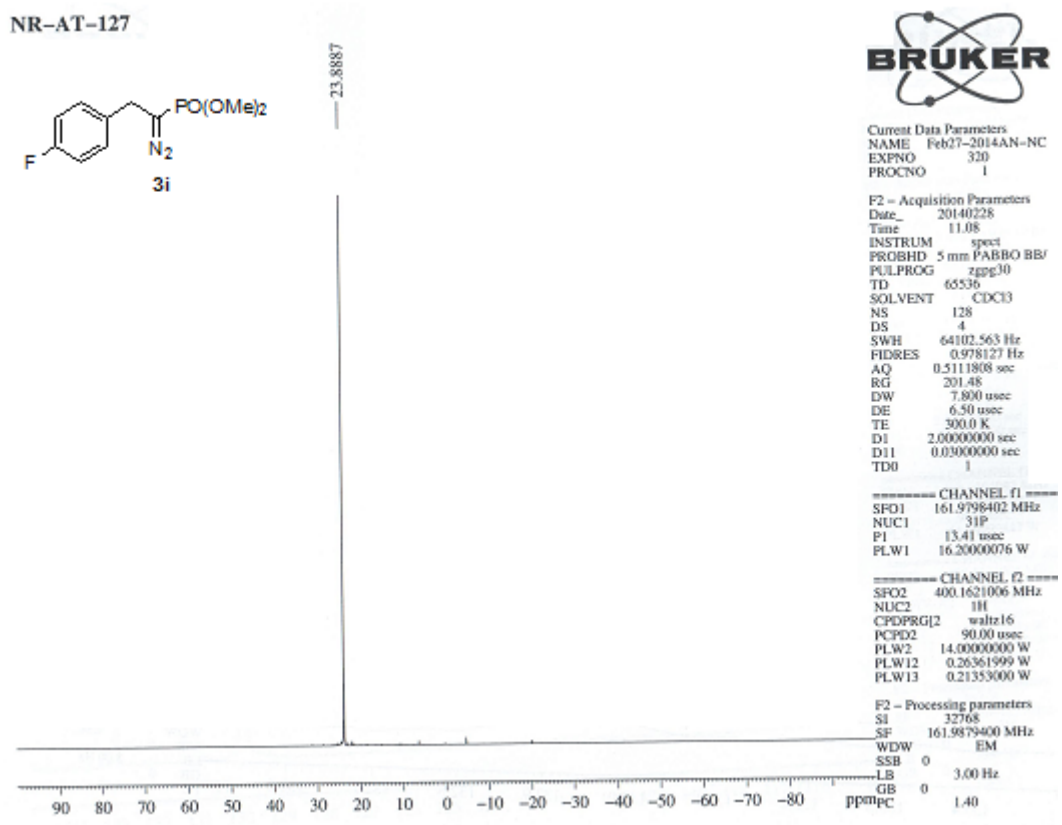


Figure 21: ^{31}P NMR spectrum of 3i

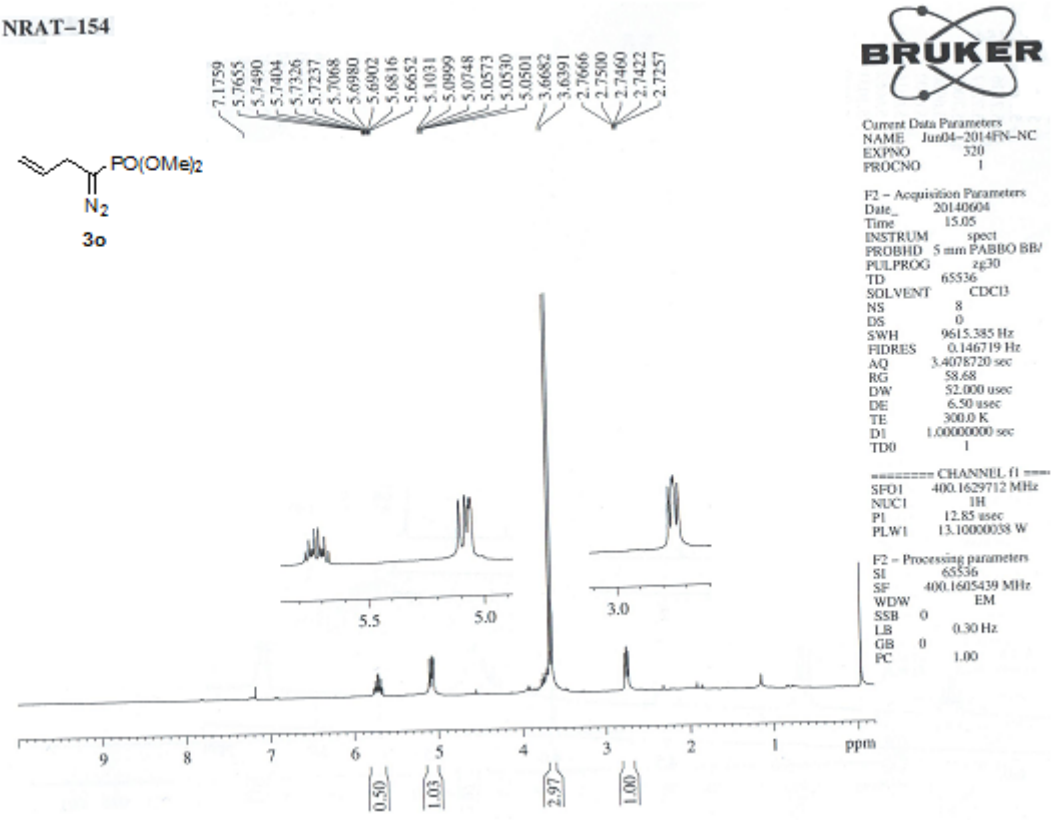


Figure 22: ^{1}H NMR spectrum of 3o

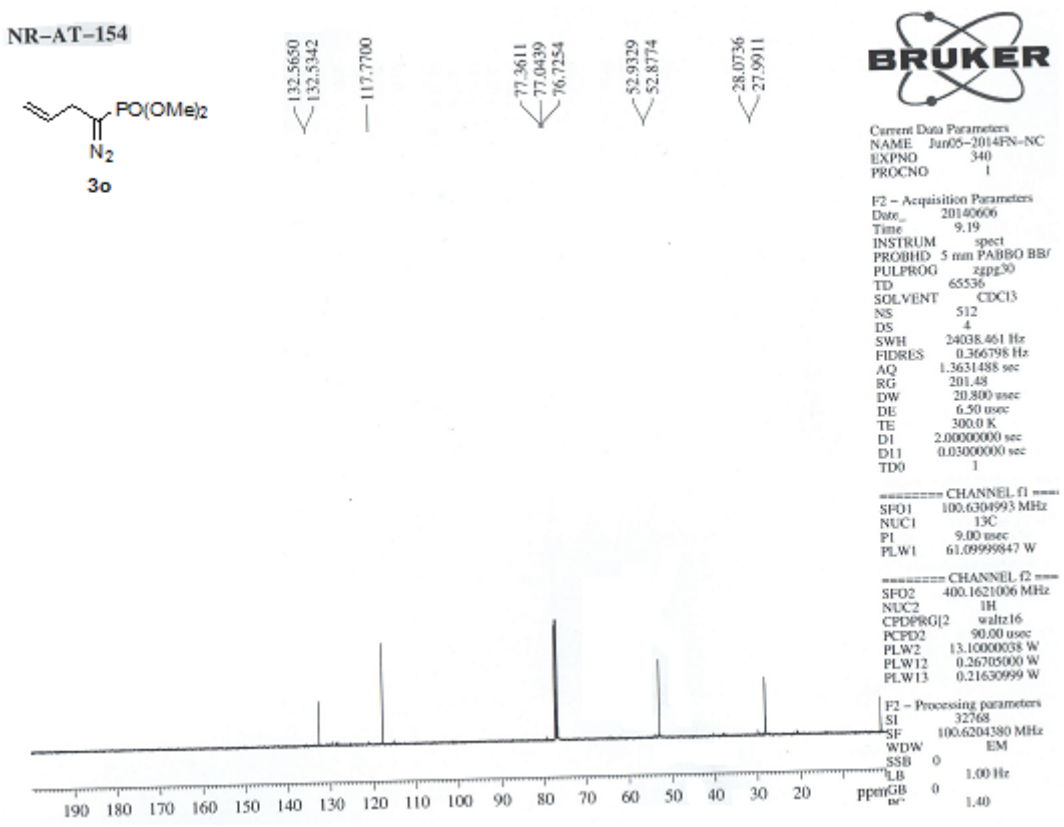


Figure 23: ^{13}C NMR spectrum of 3o

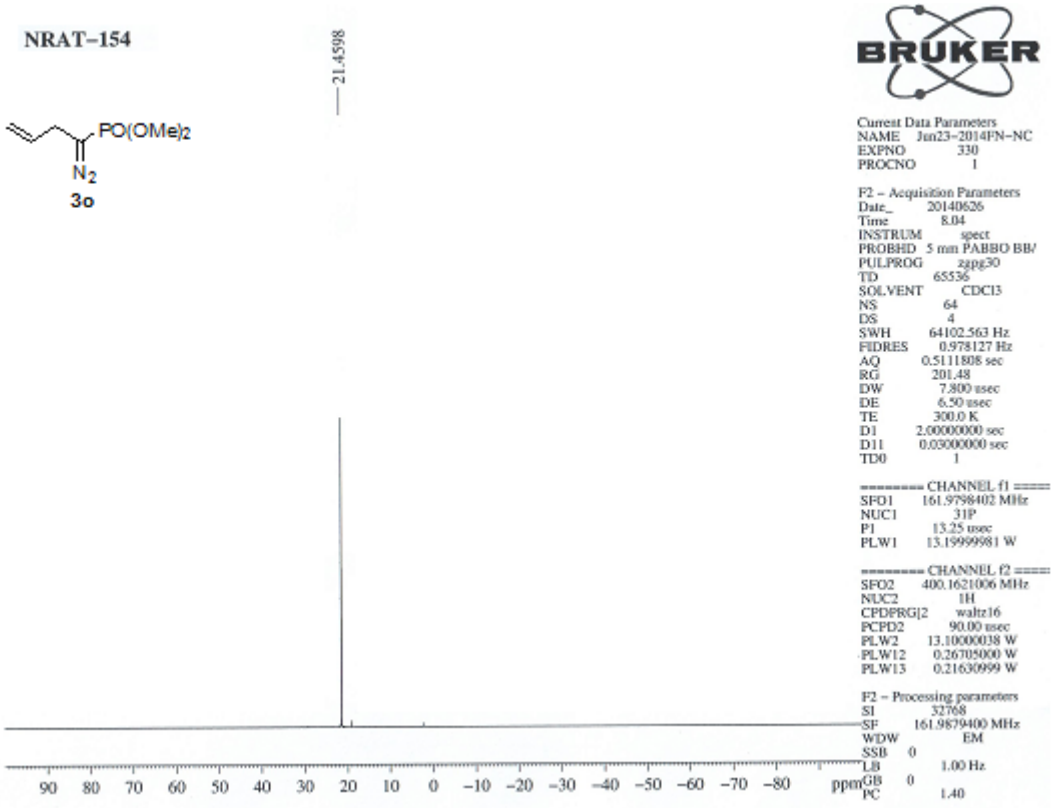


Figure 24: ^{31}P NMR spectrum of 3o

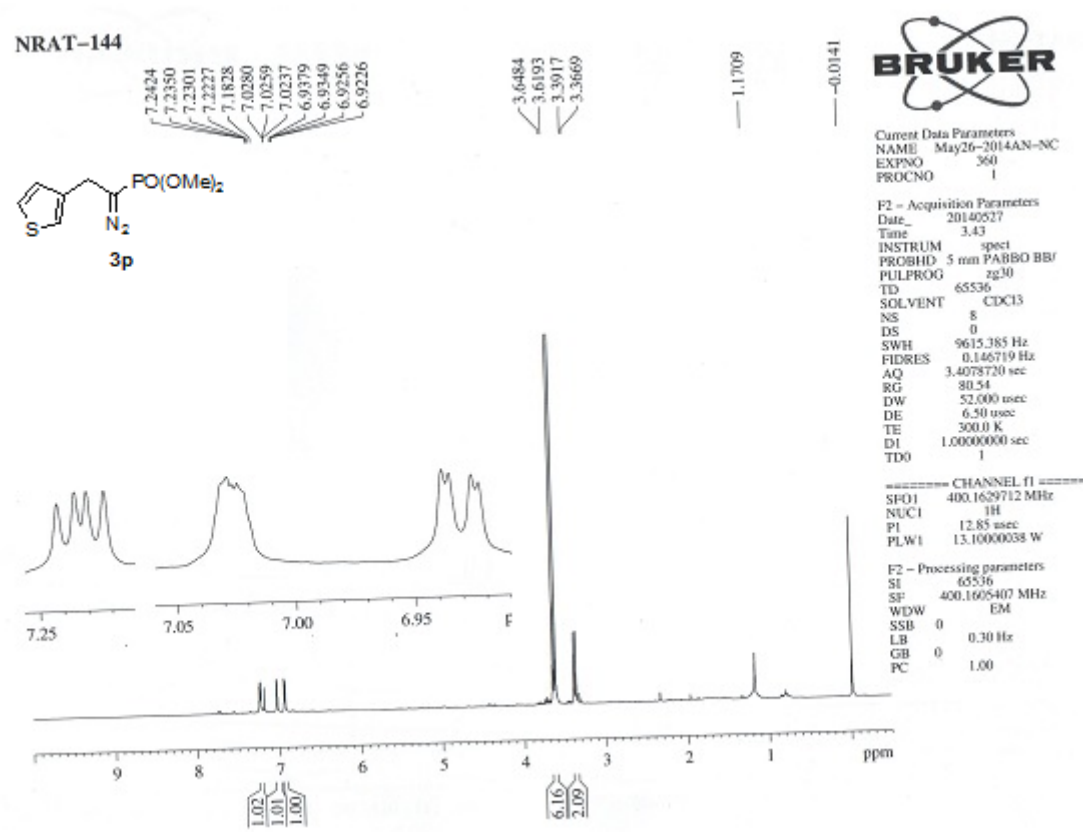


Figure 25: ^{1}H NMR spectrum of 3p

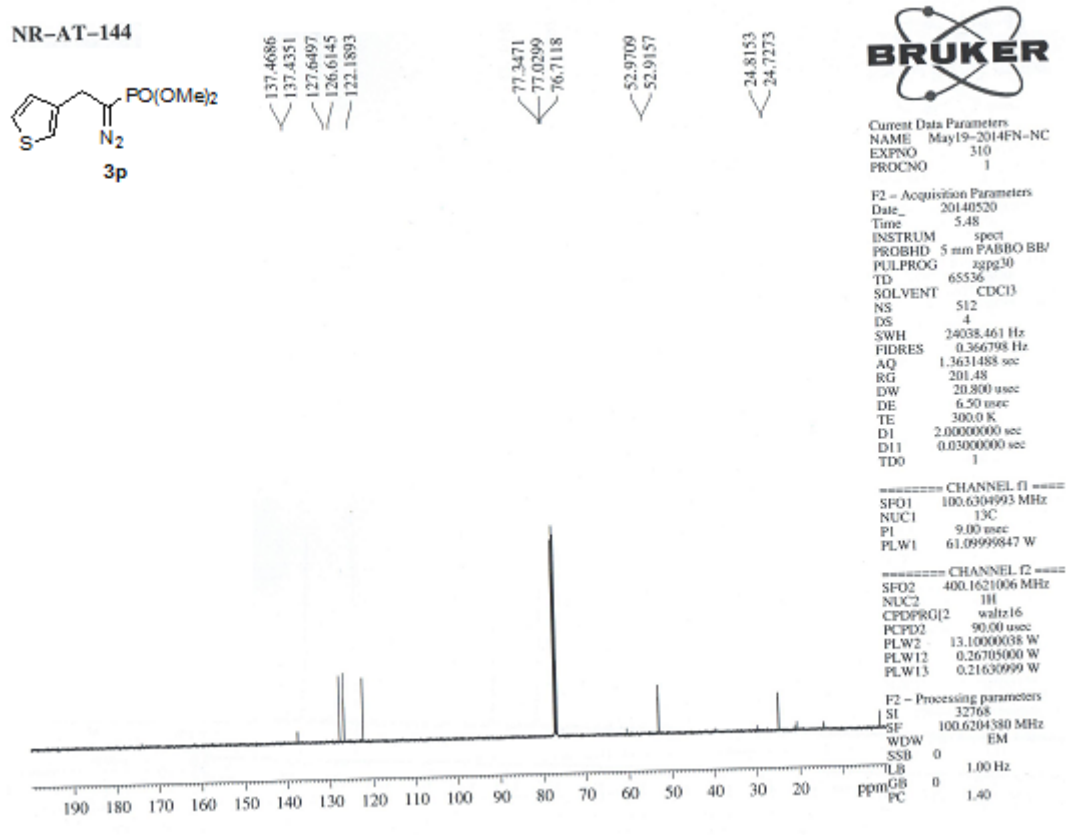


Figure 26: ^{13}C NMR spectrum of 3p

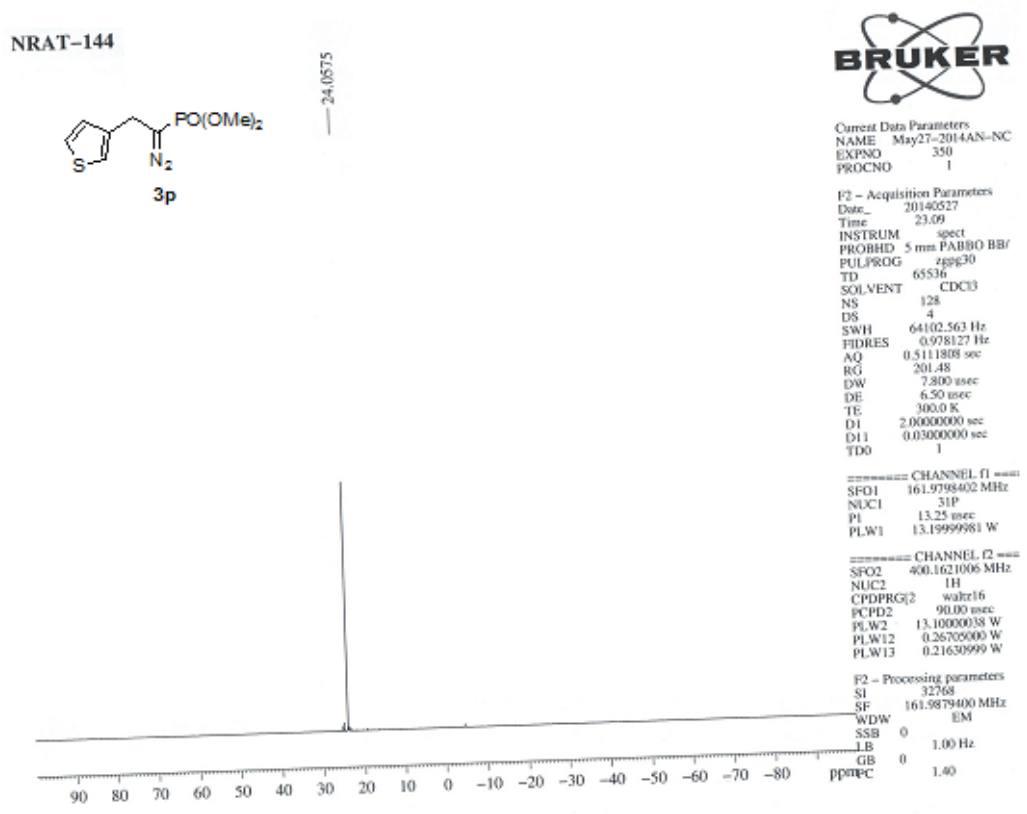


Figure 27: ^{31}P NMR spectrum of 3p

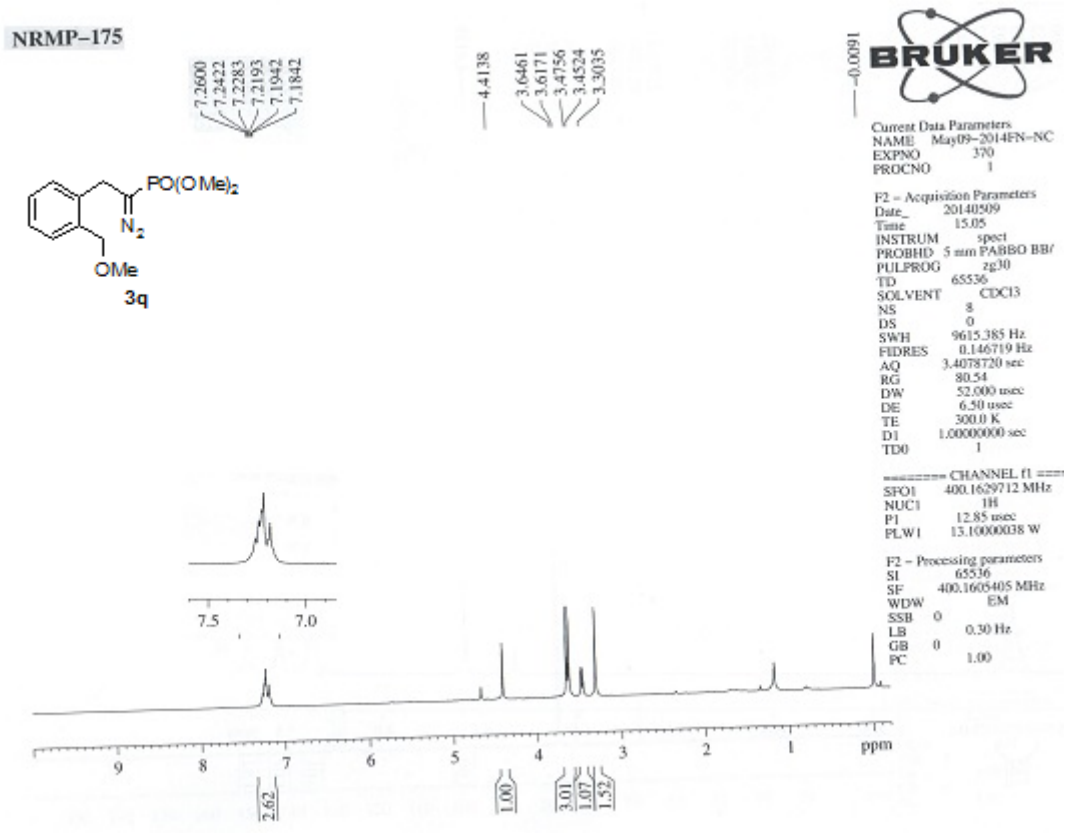


Figure 28: ^{1}H NMR spectrum of 3q

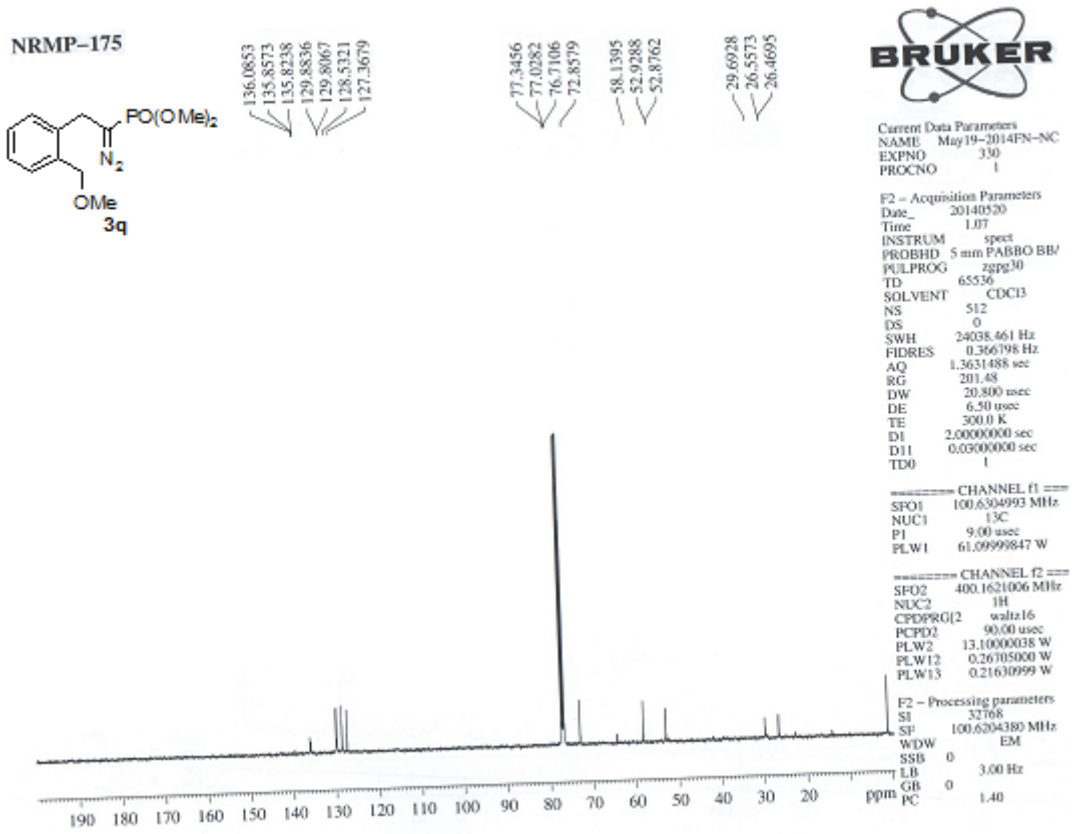


Figure 29: ^{13}C NMR spectrum of 3q

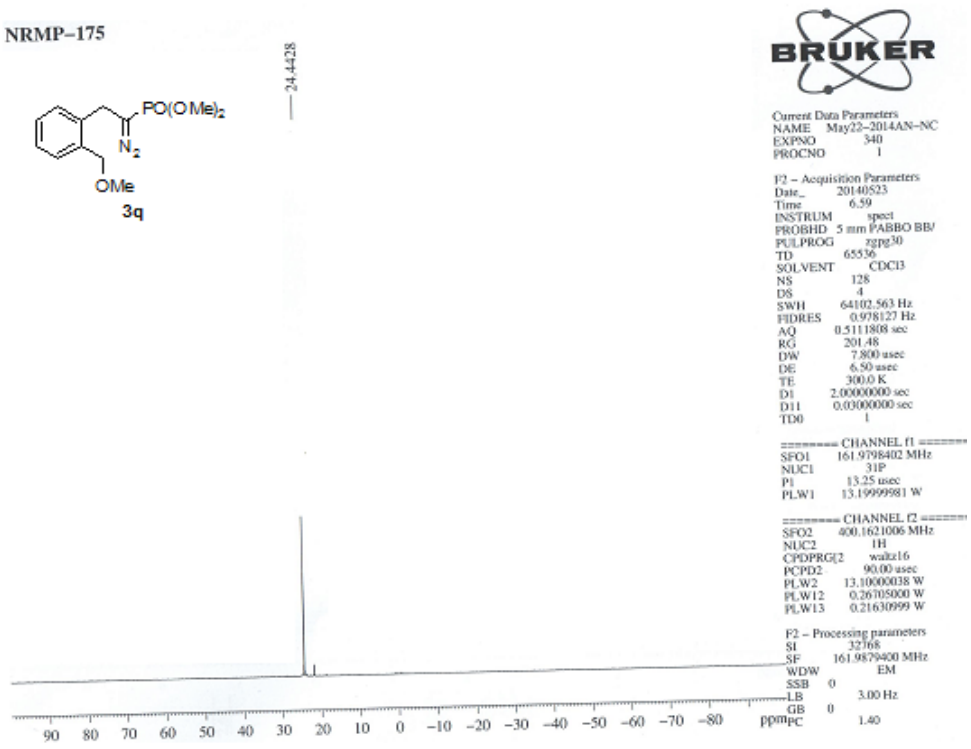


Figure 30: ^{31}P NMR spectrum of 3q

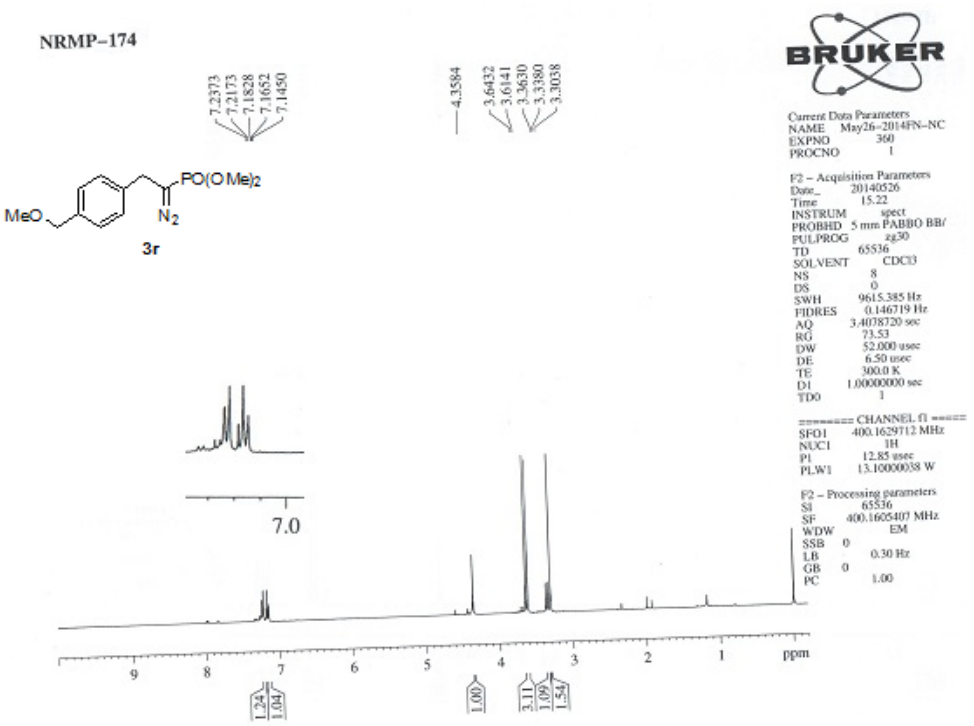


Figure 31: ^{1}H NMR spectrum of 3r

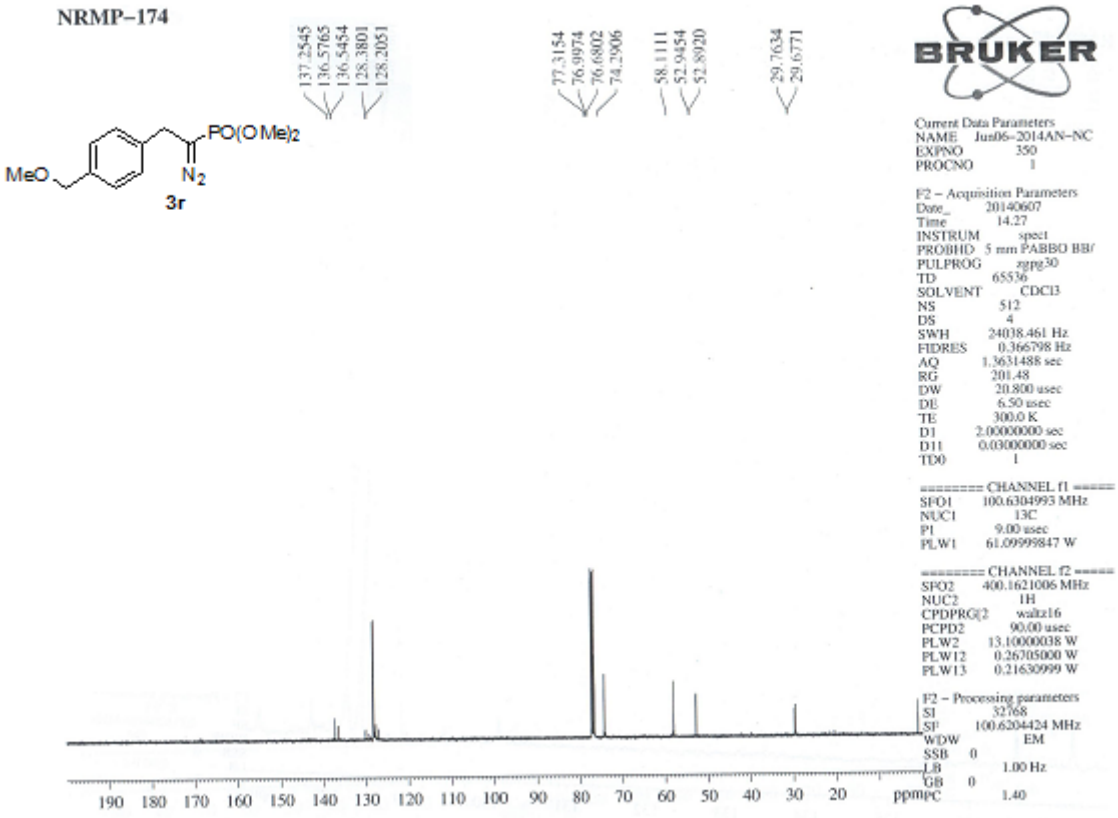


Figure 32: ^{13}C NMR spectrum of 3r

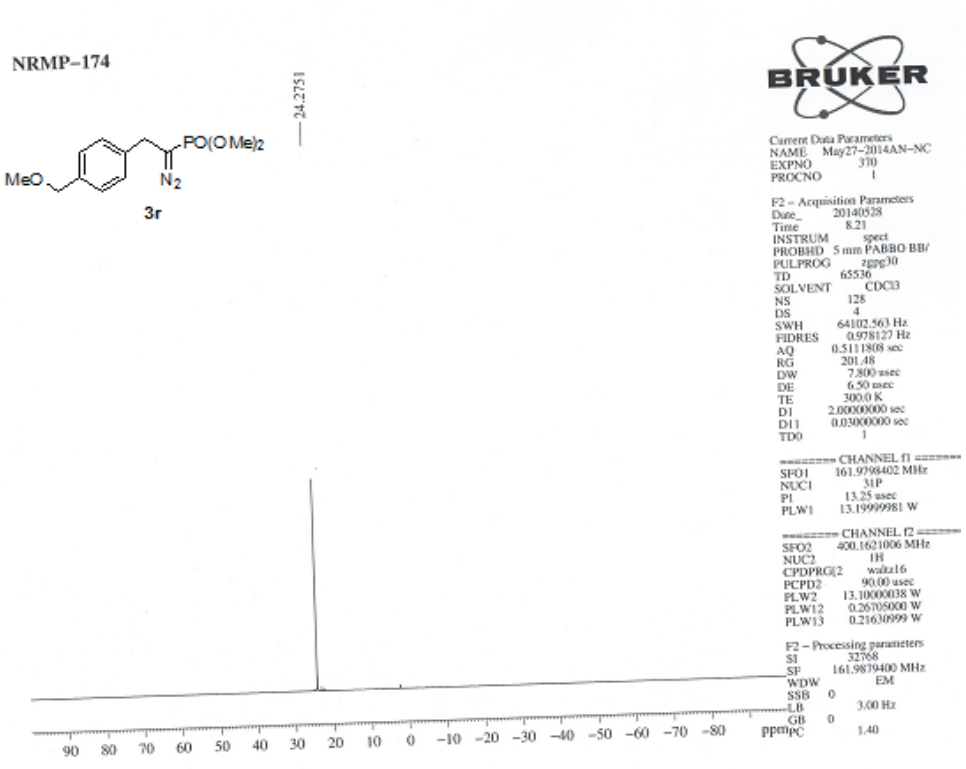


Figure 33: ^{31}P NMR spectrum of 3r

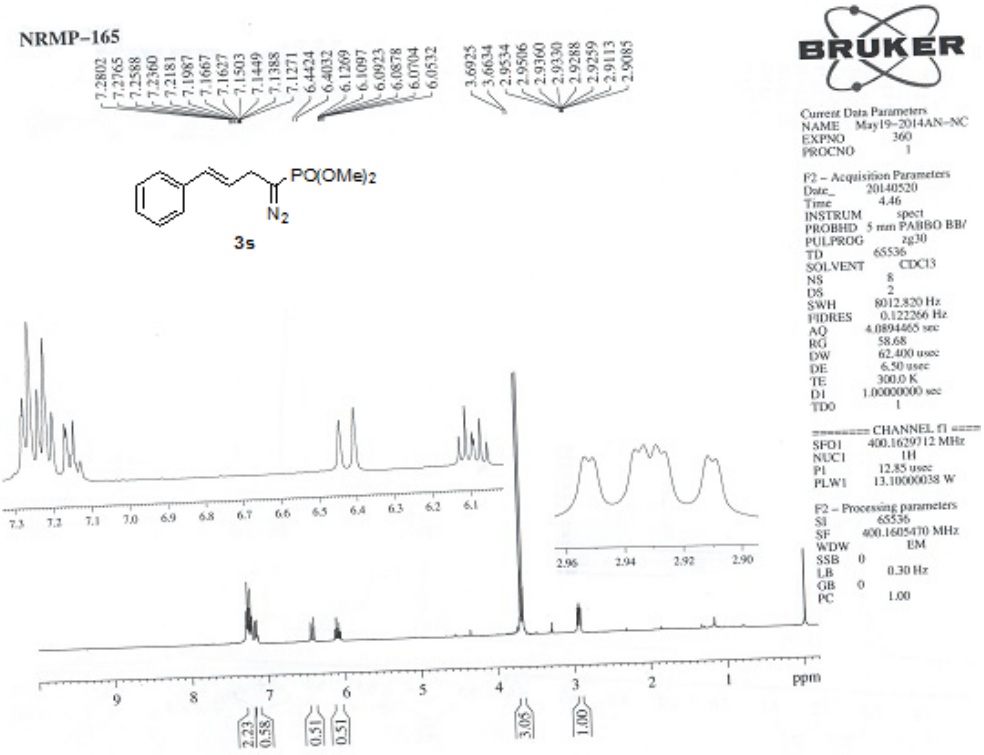


Figure 34: ^{1}H NMR spectrum of 3s

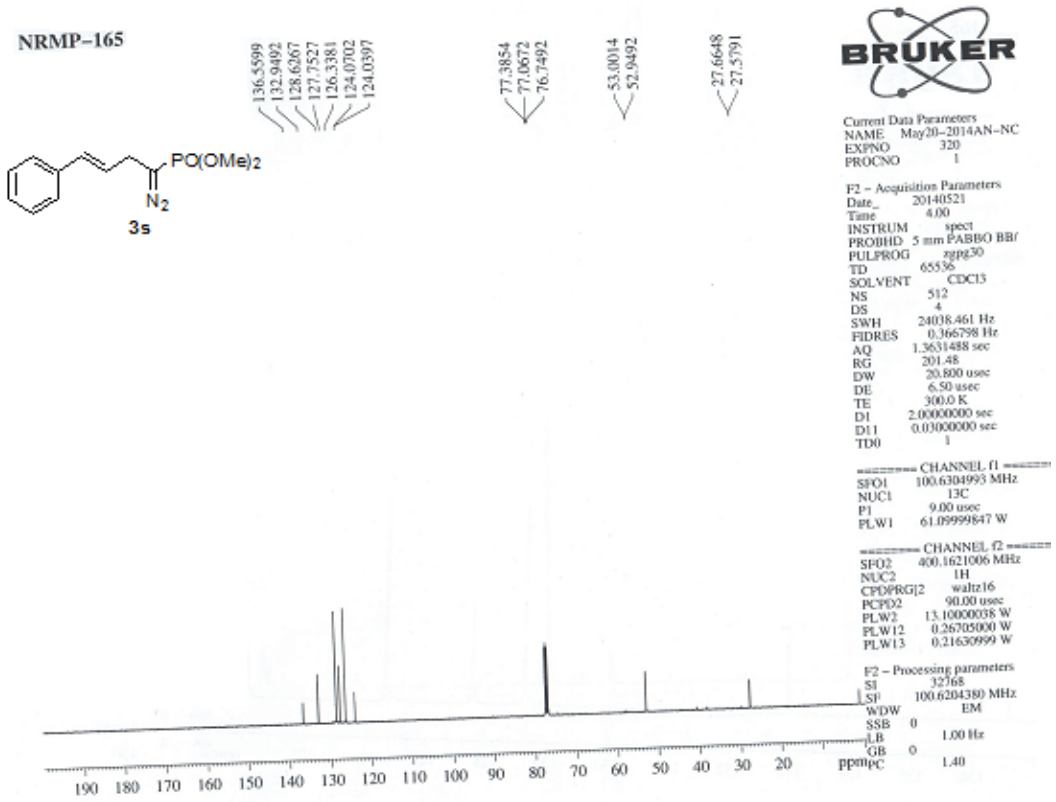


Figure 35: ^{13}C NMR spectrum of 3s

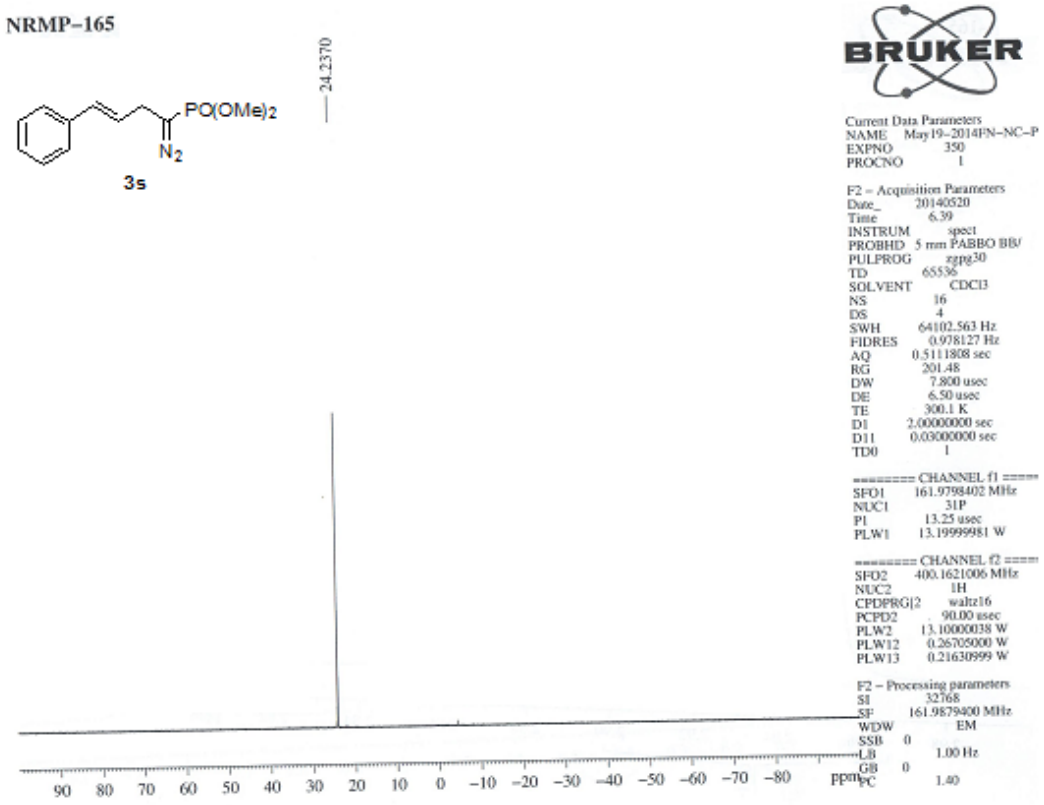


Figure 36: ^{31}P NMR spectrum of 3s

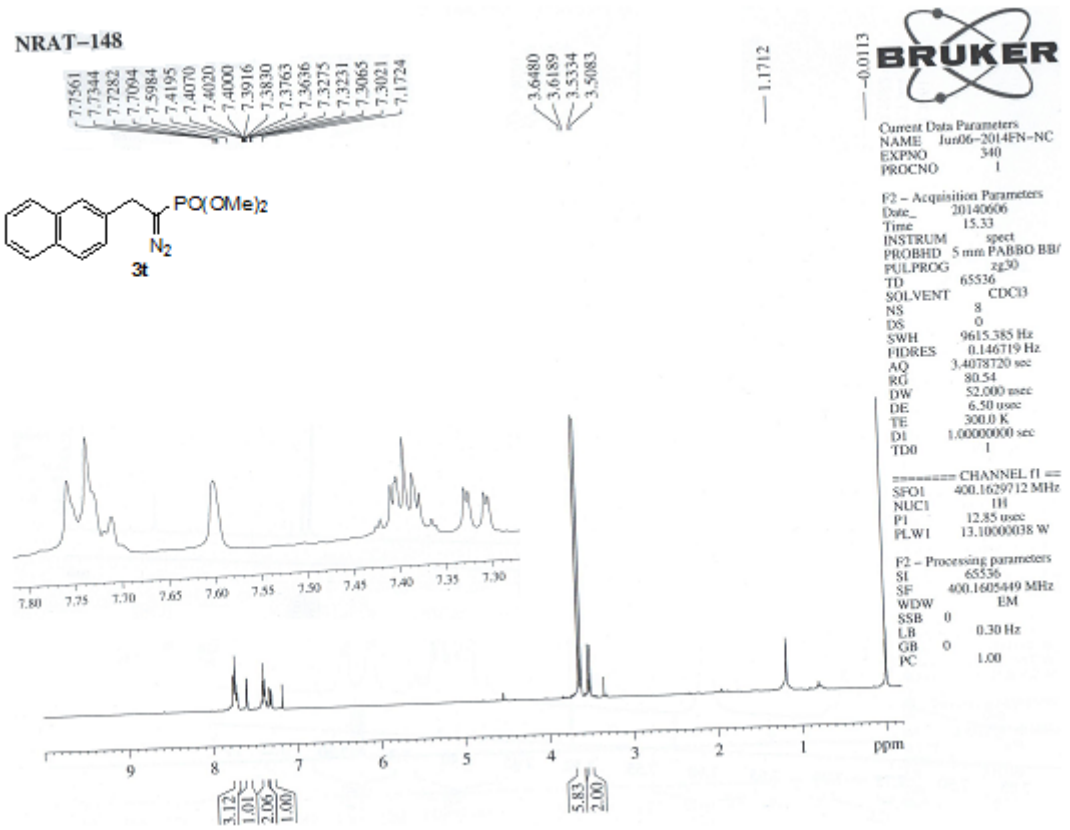


Figure 37: ^{1}H NMR spectrum of 3t

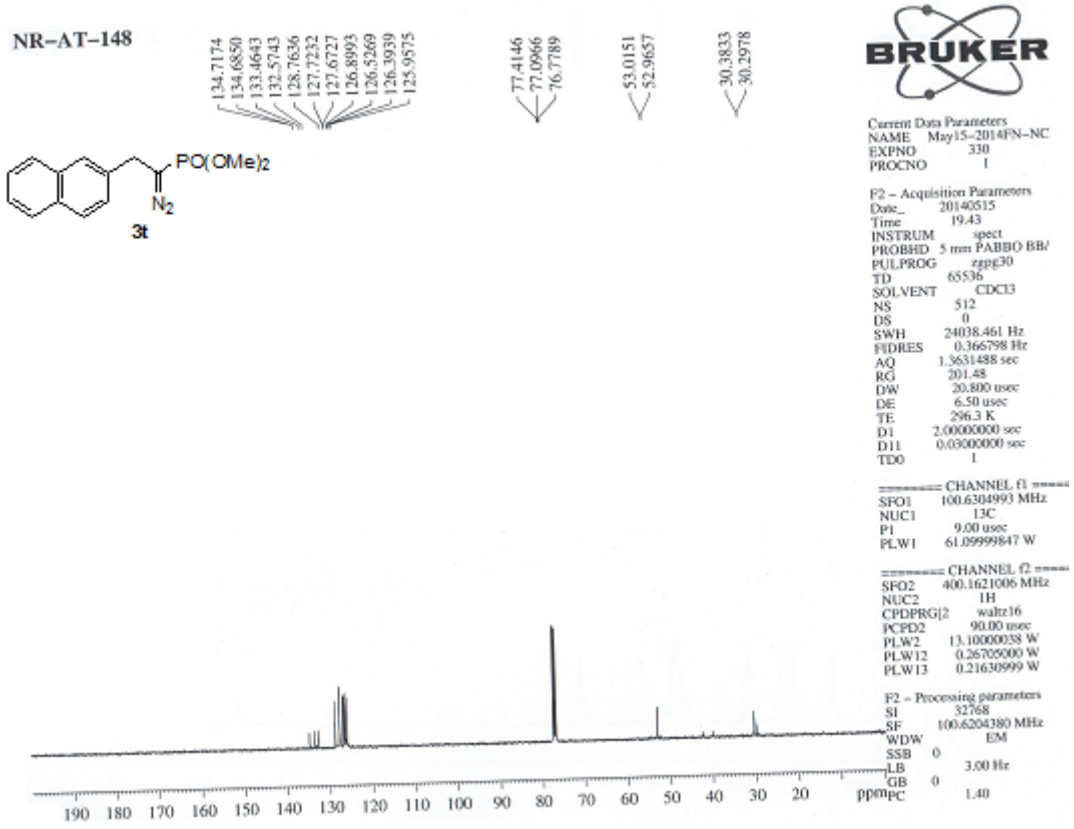


Figure 38: ^{13}C NMR spectrum of 3t

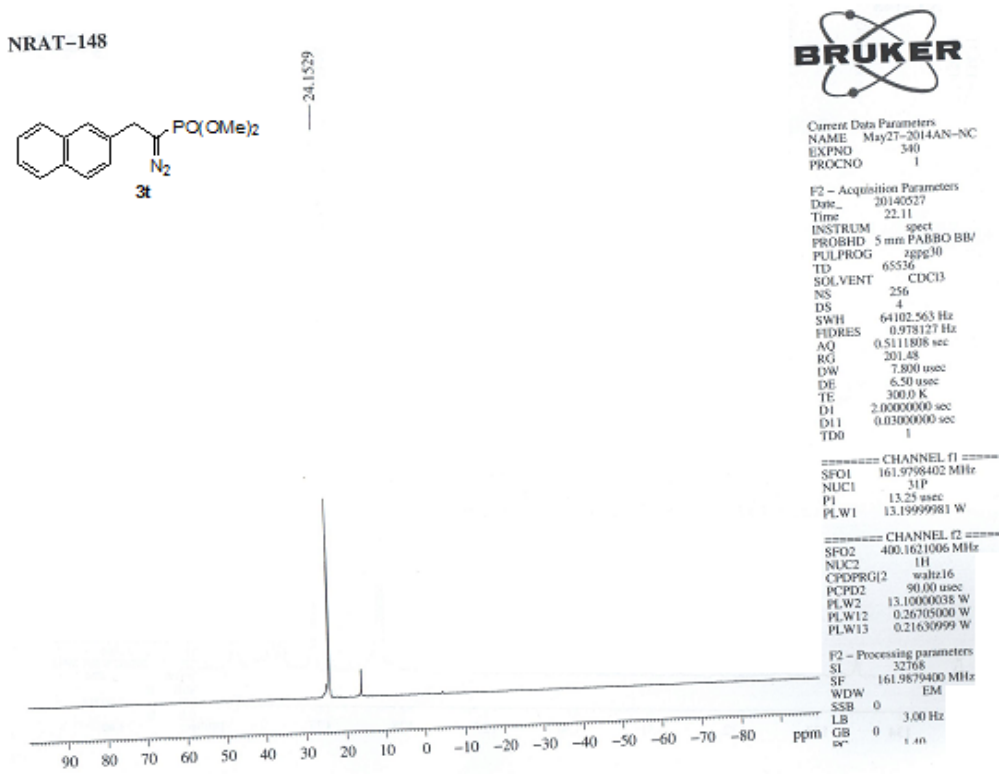


Figure 39: ^{31}P NMR spectrum of 3t

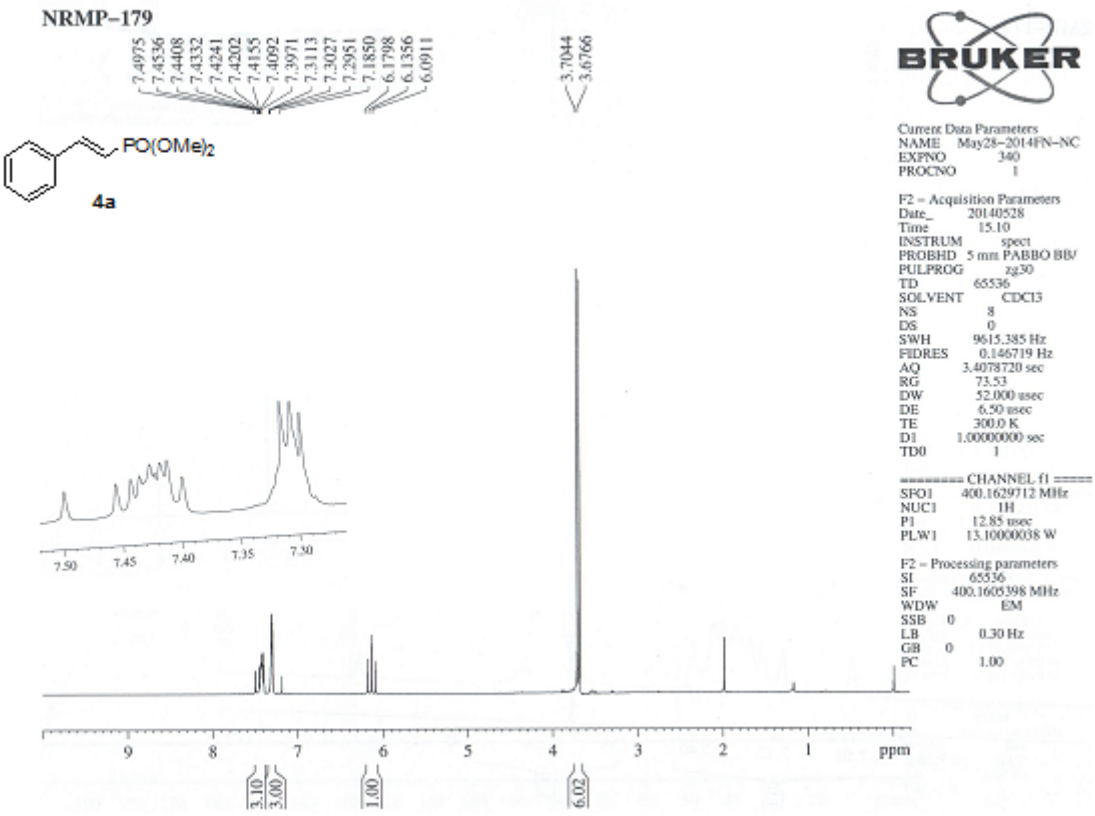


Figure 40: ^{1}H NMR spectrum of 4a

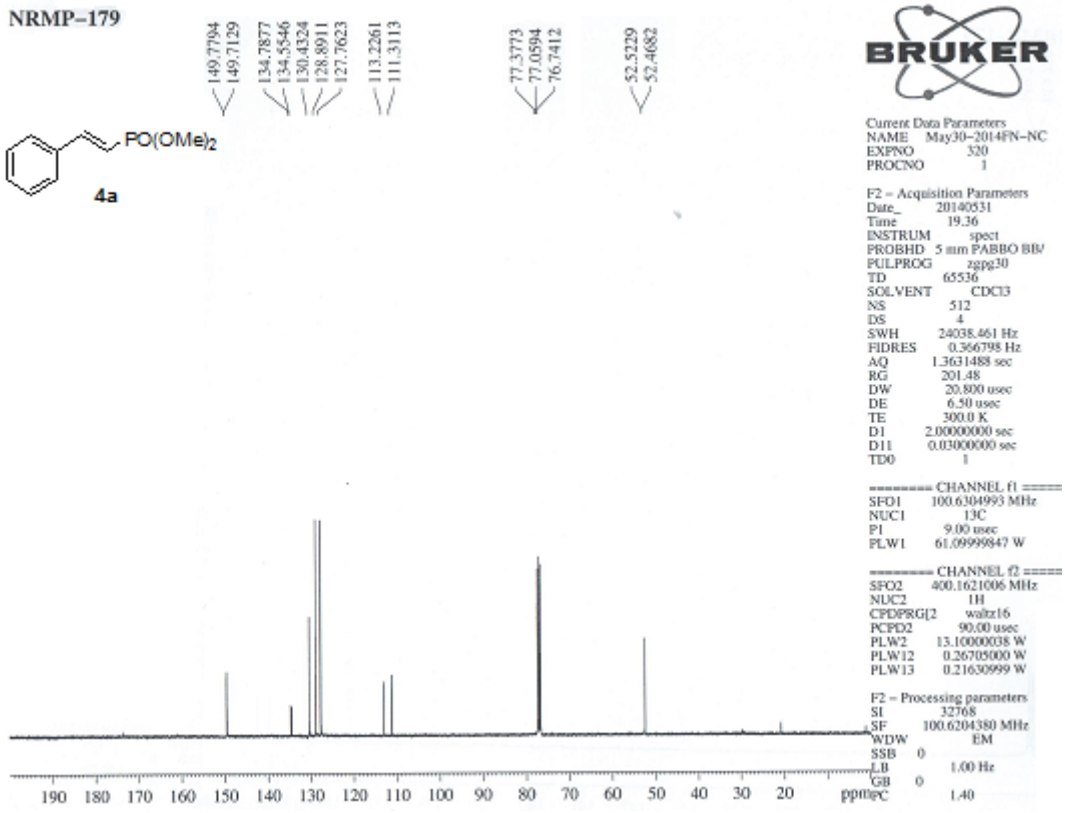


Figure 41: ^{13}C NMR spectrum of 4a

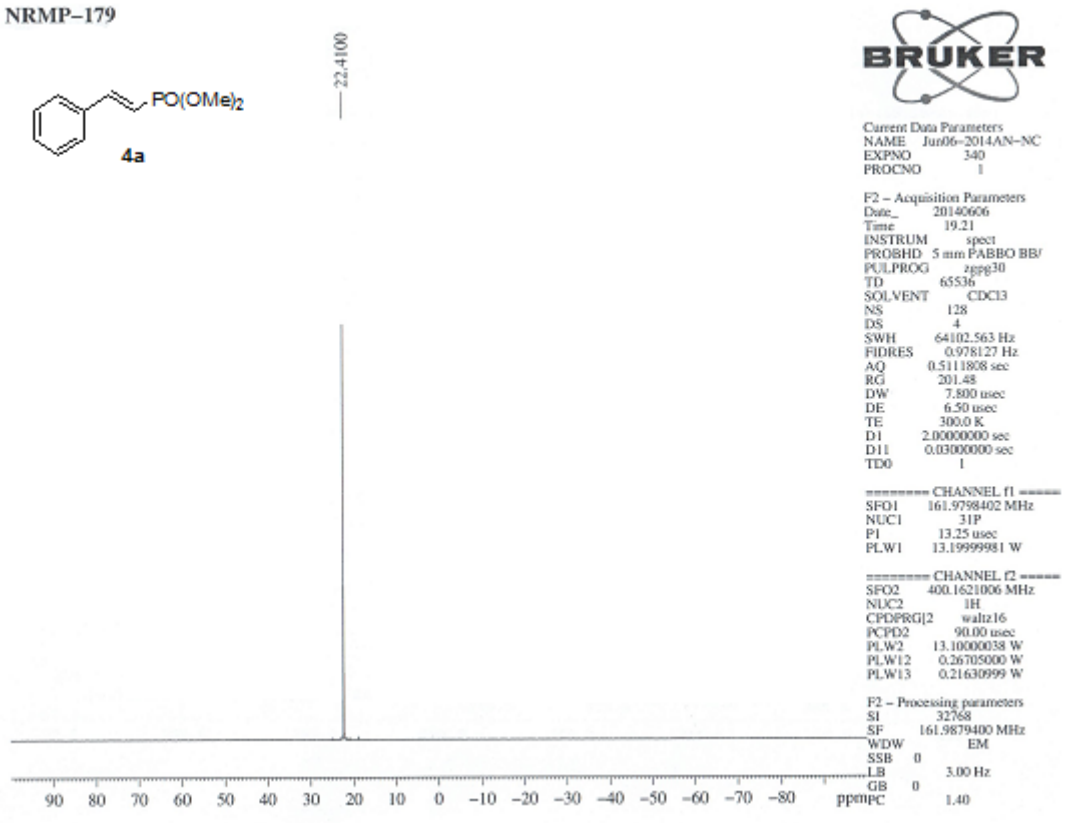


Figure 42: ^{31}P NMR spectrum of 4a

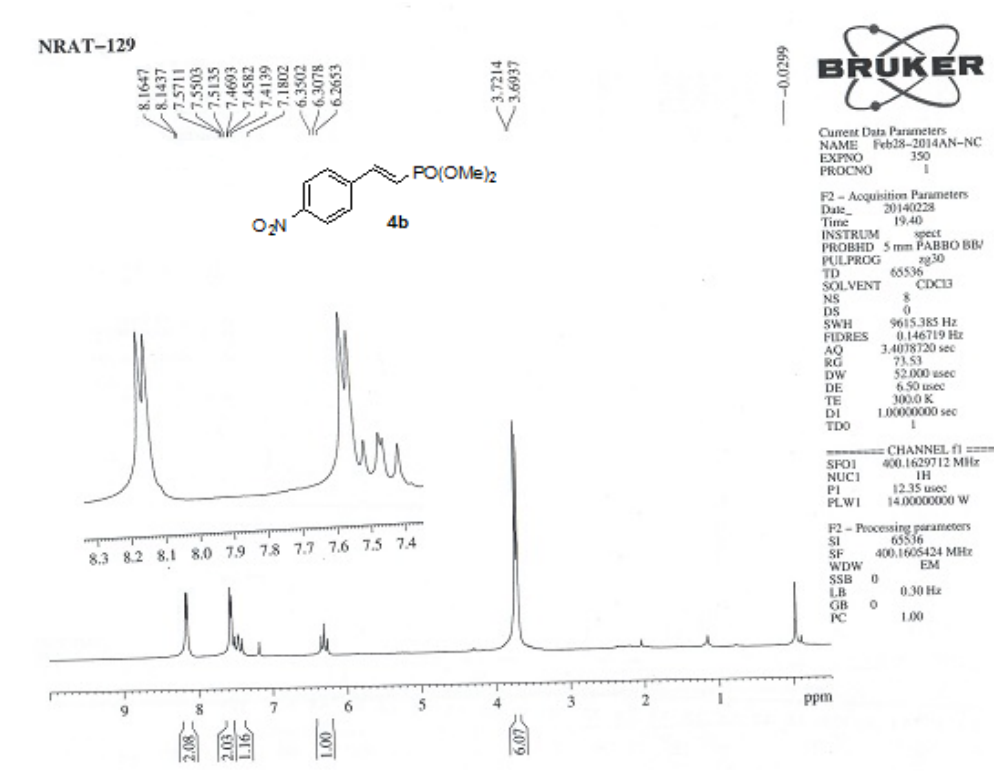


Figure 43: ^{1}H NMR spectrum of 4b

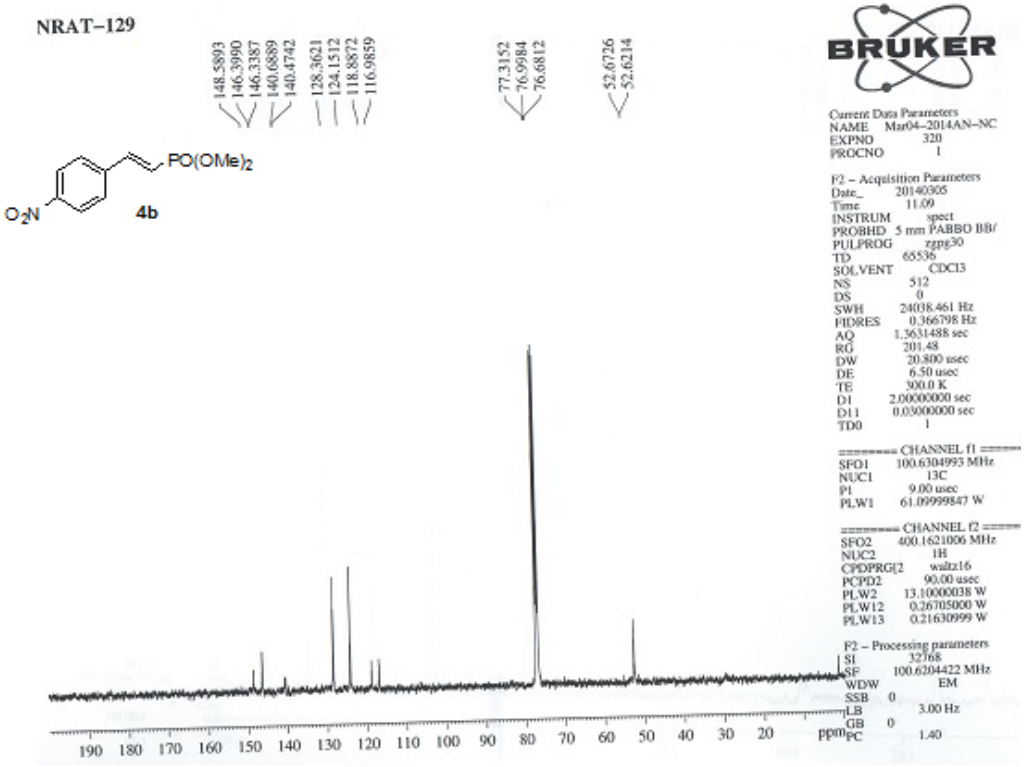


Figure 44: ^{13}C NMR spectrum of 4b

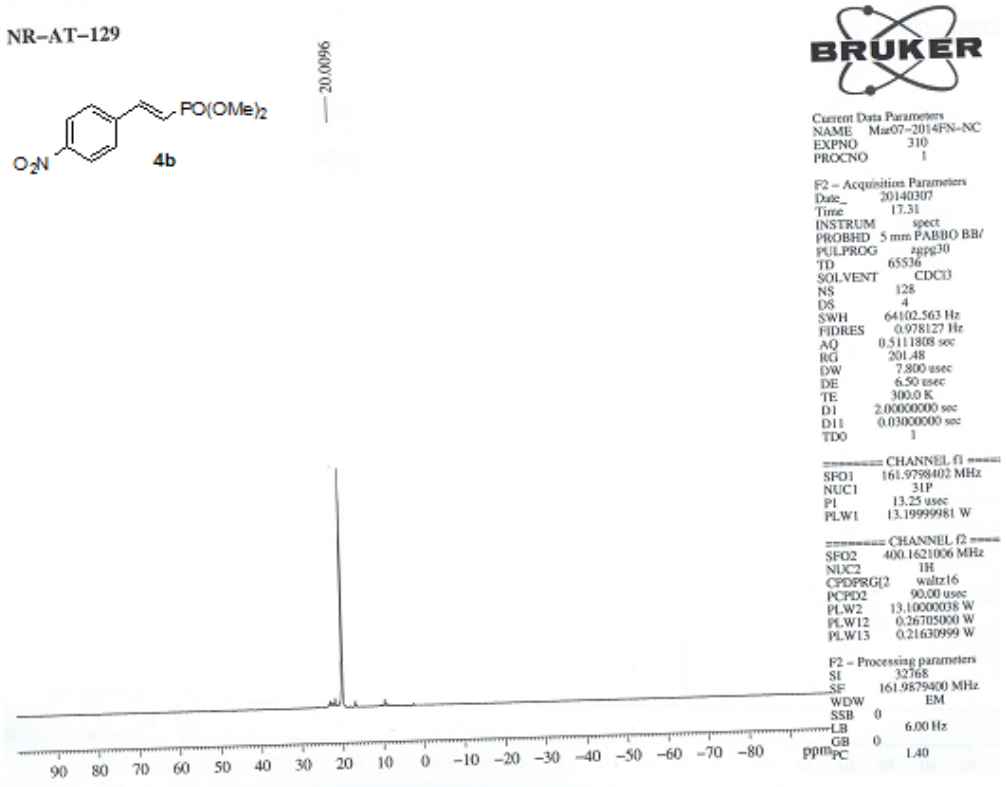


Figure 45: ^{13}P NMR spectrum of 4b

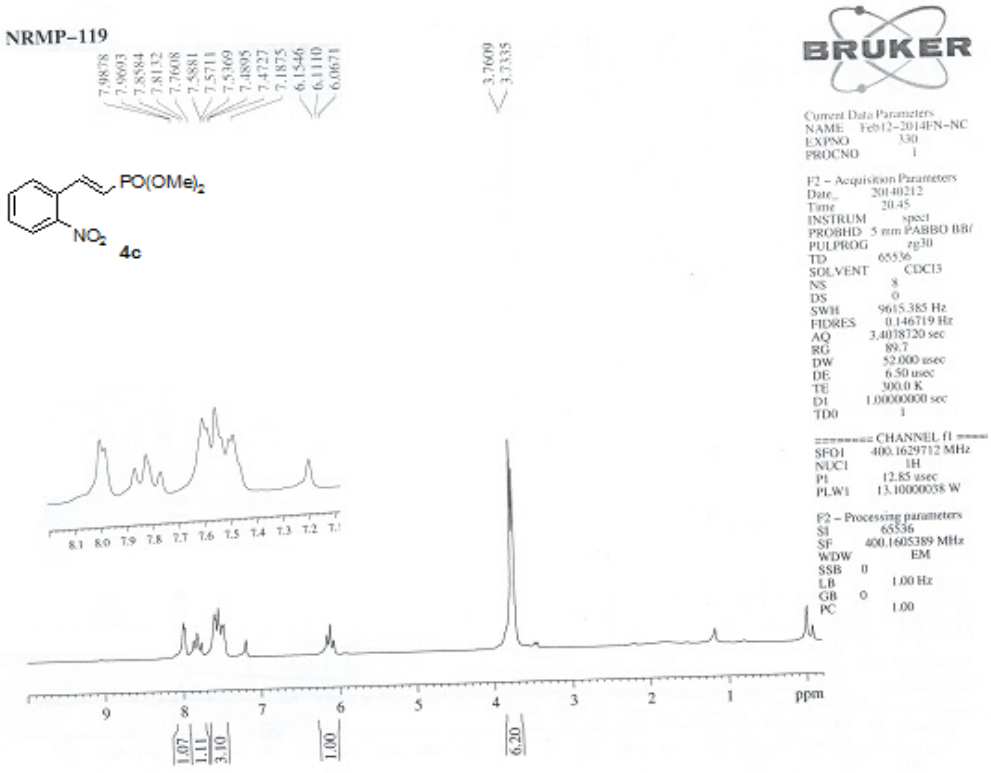


Figure 46: ^{1}H NMR spectrum of 4c

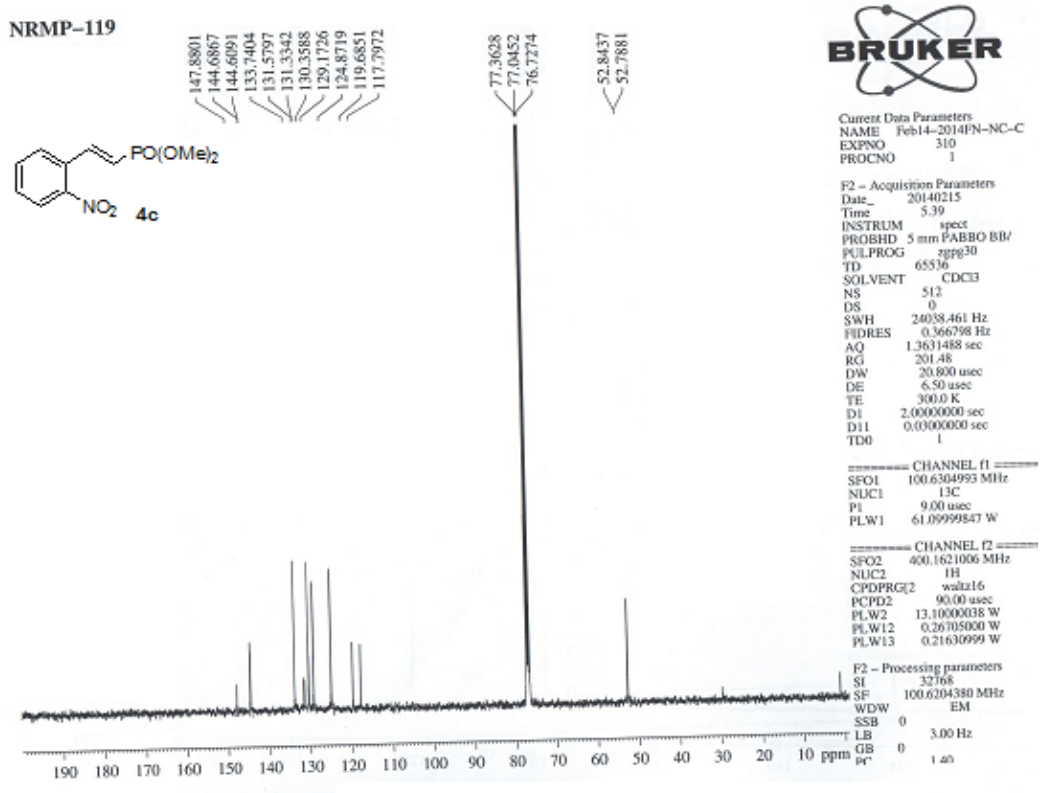


Figure 47: ^{13}C NMR spectrum of 4c

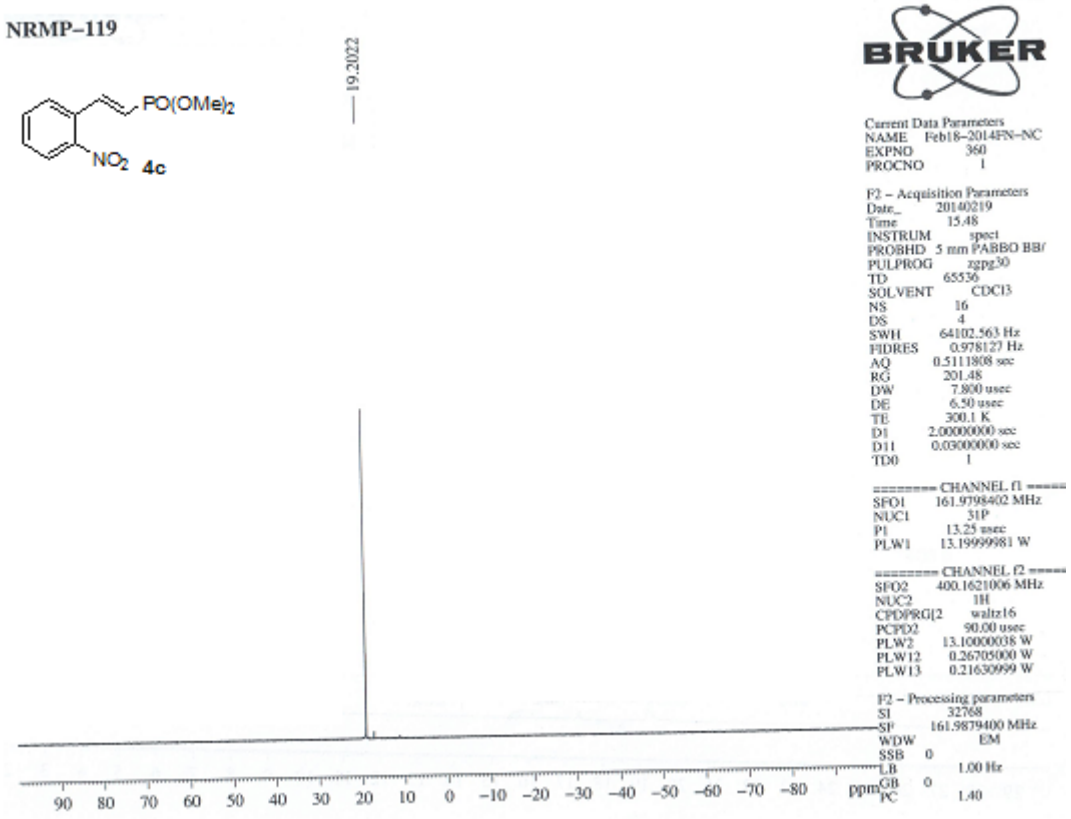


Figure 48: ^{31}P NMR spectrum of 4c

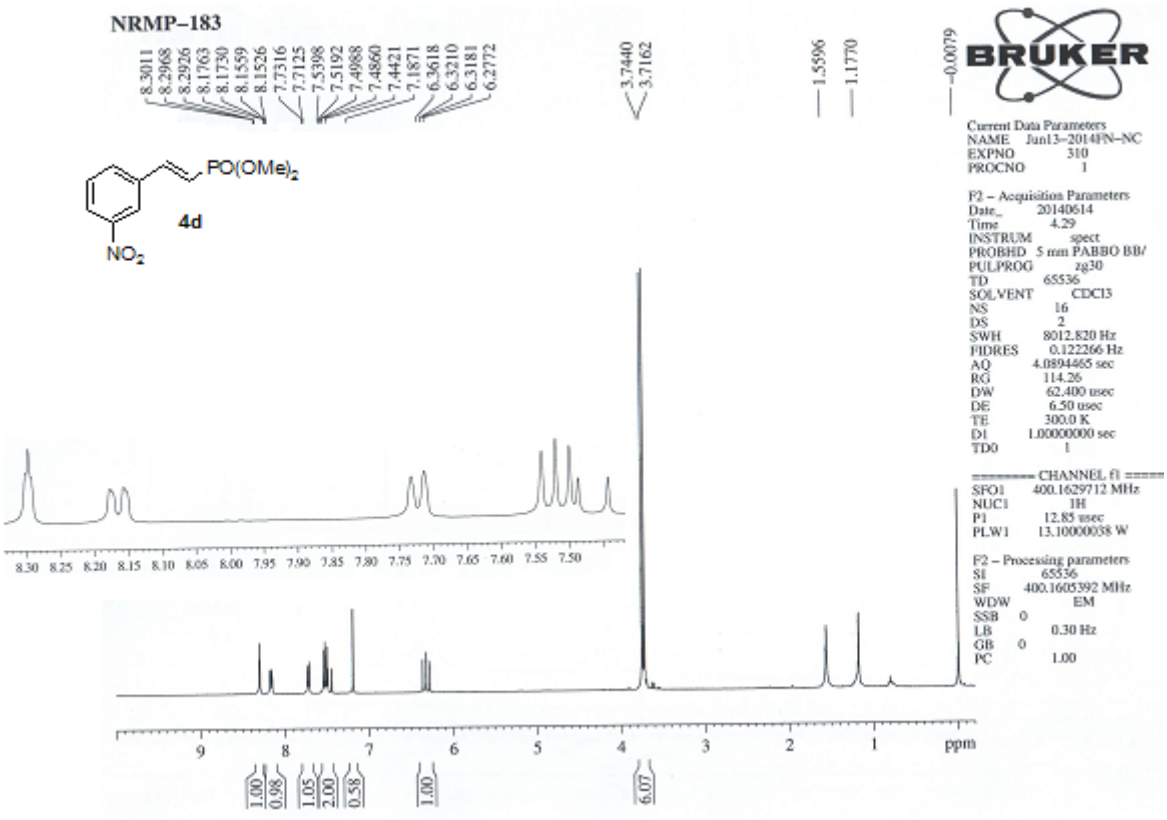


Figure 49: ^{1}H NMR spectrum of 4d

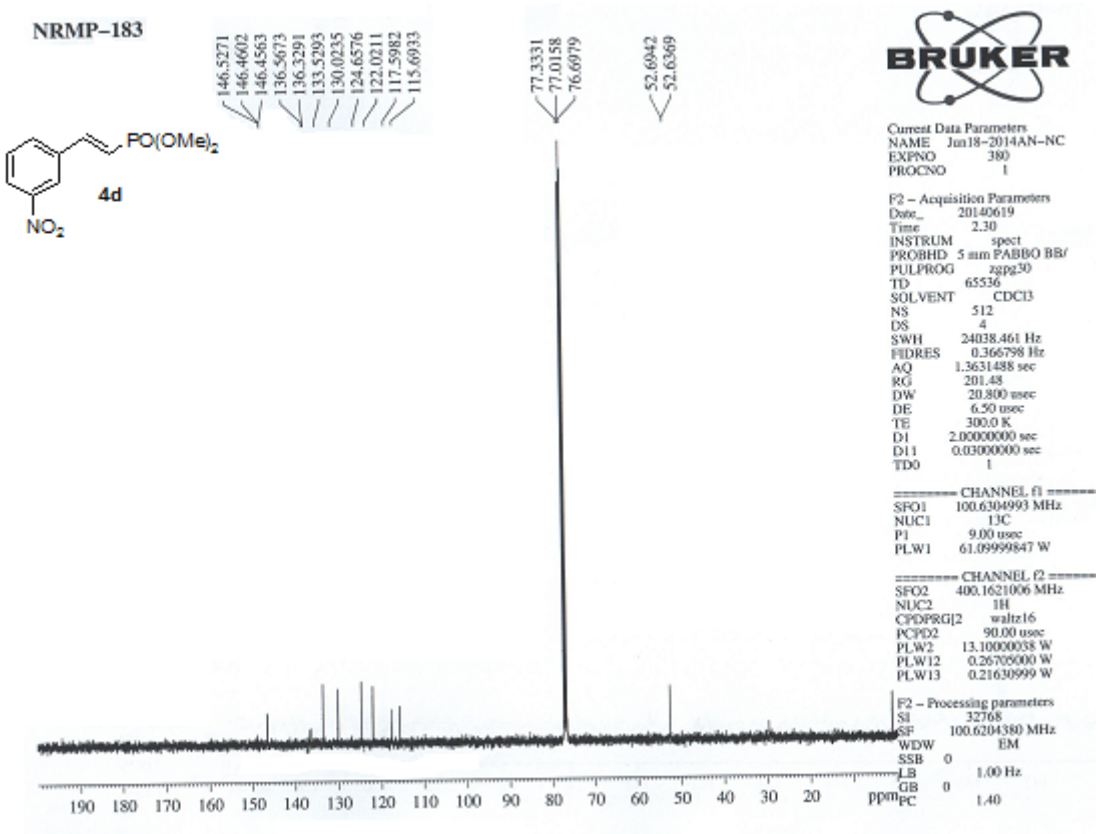


Figure 50: ^{13}C NMR spectrum of 4d

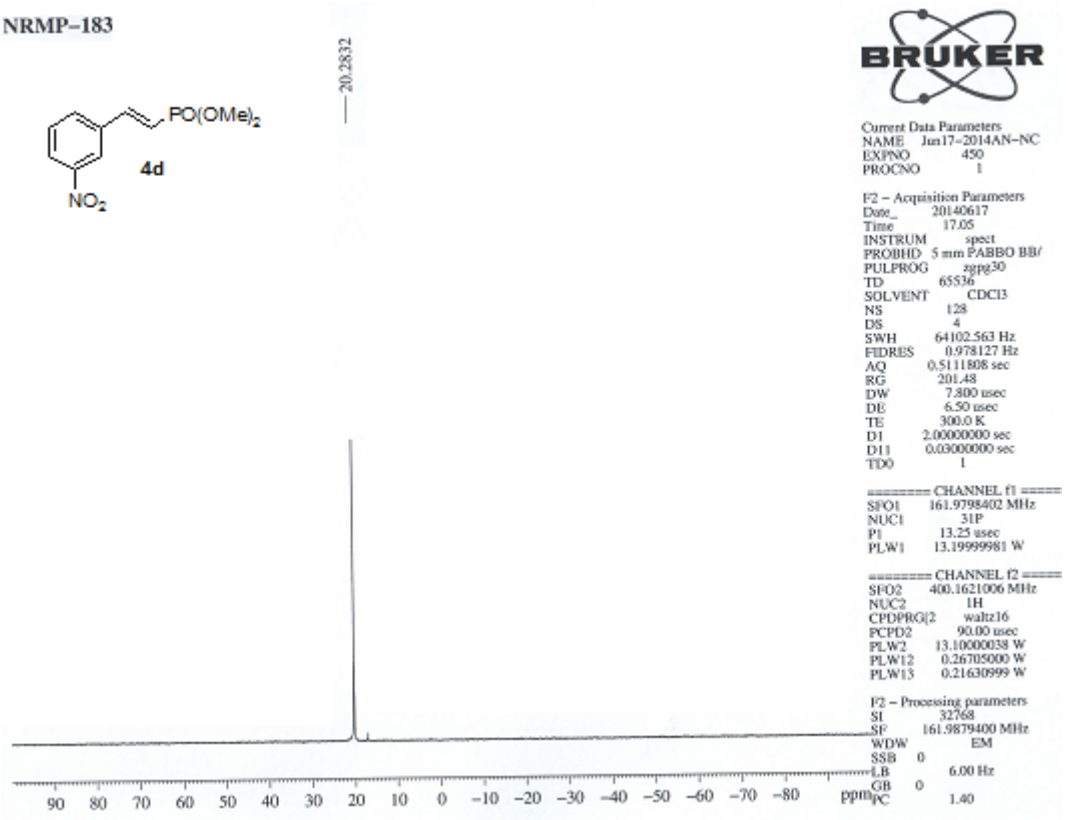


Figure 51: ^{31}P NMR spectrum of 4d

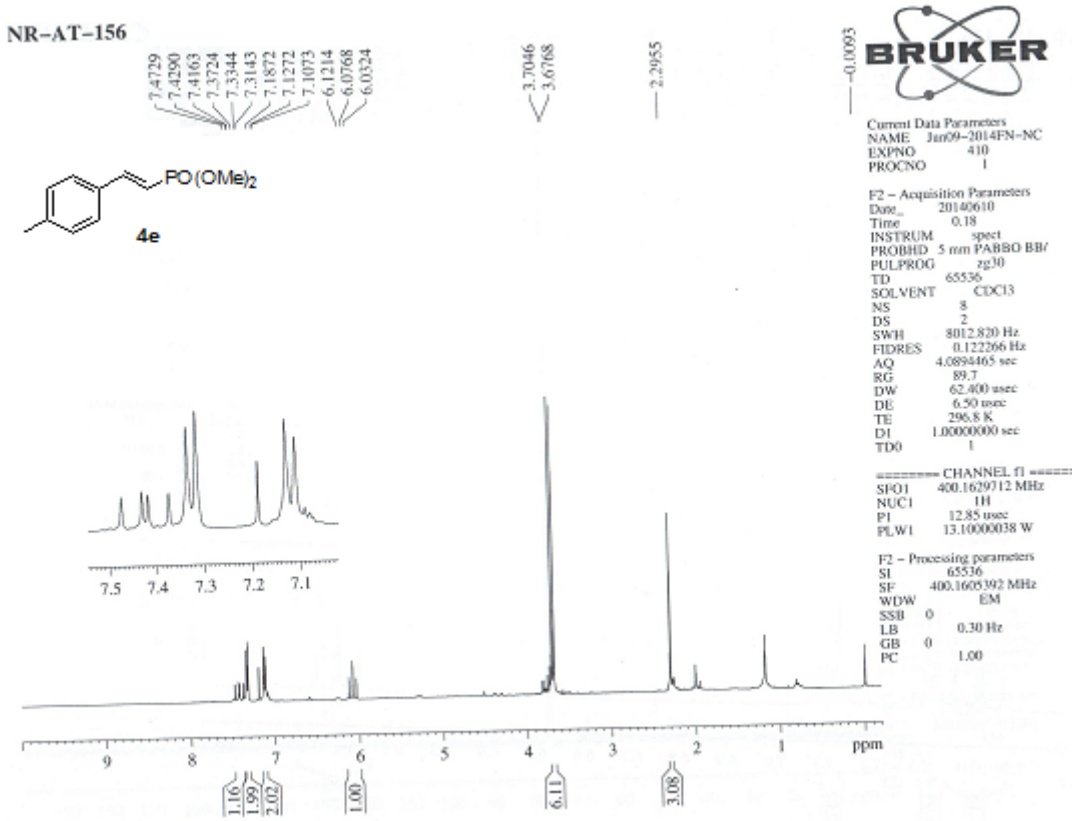


Figure 52: ^{1}H NMR spectrum of 4e

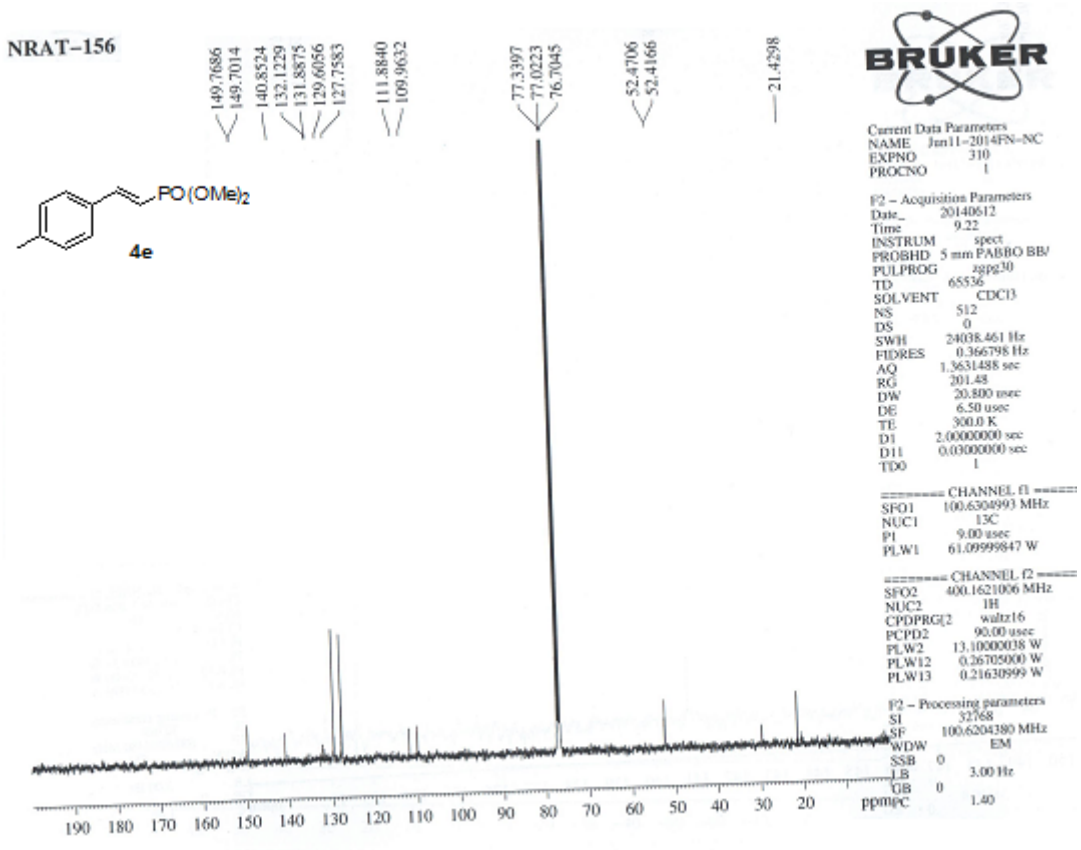


Figure 53: ^{13}C NMR spectrum of 4e

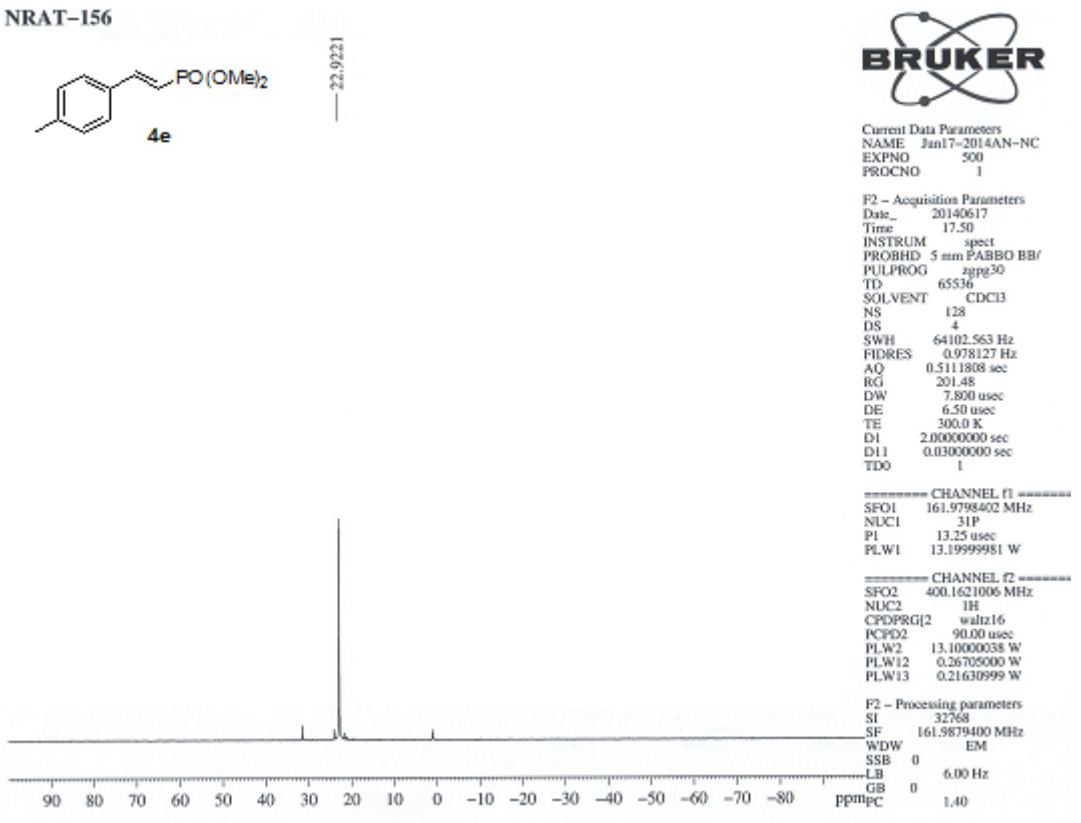


Figure 54: ^{31}P NMR spectrum of 4e

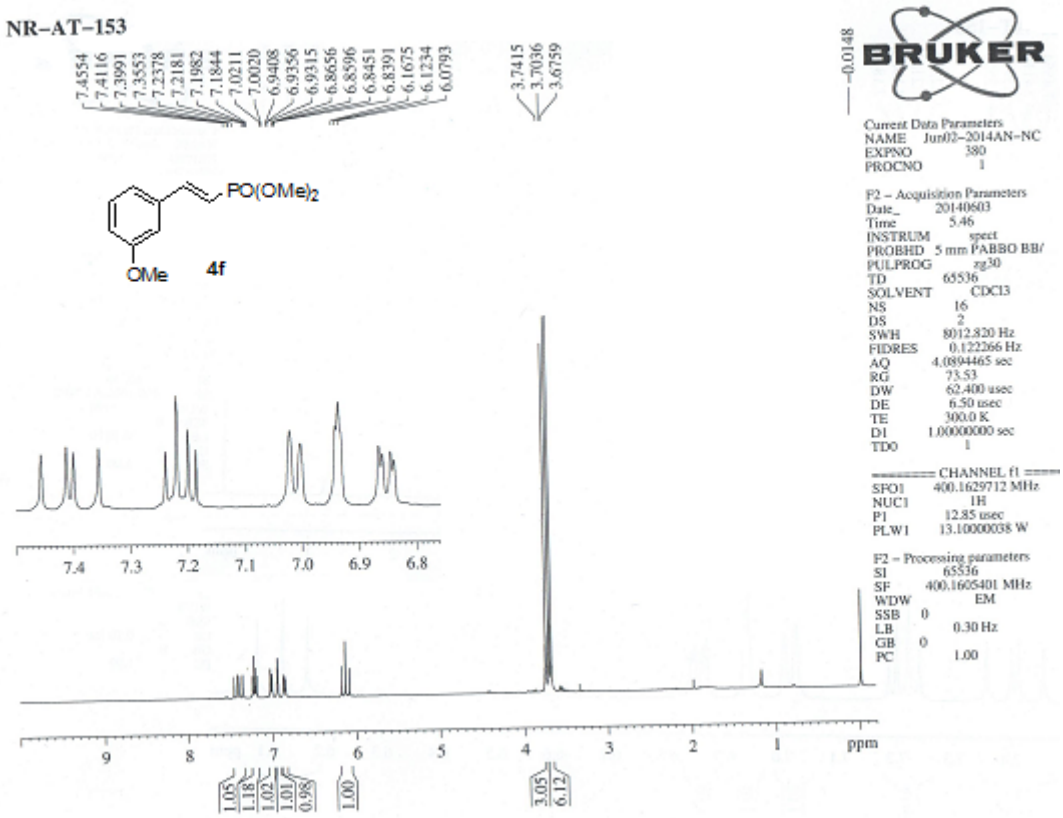


Figure 55: ^{1}H NMR spectrum of 4f

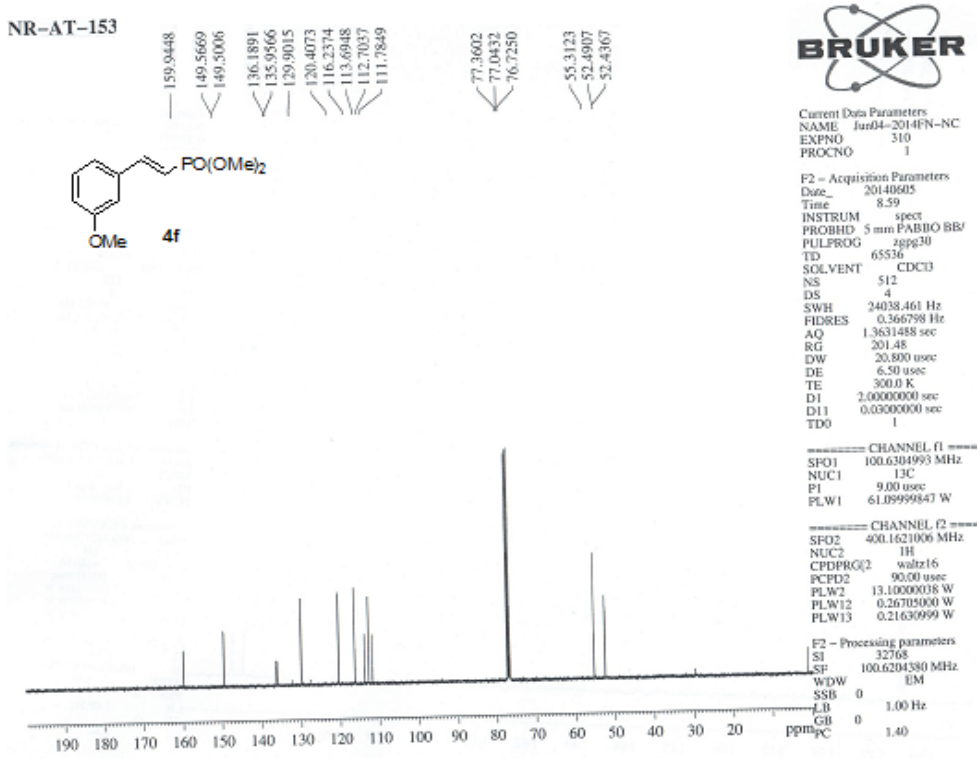


Figure 56: ^{13}CNMR spectrum of 4f

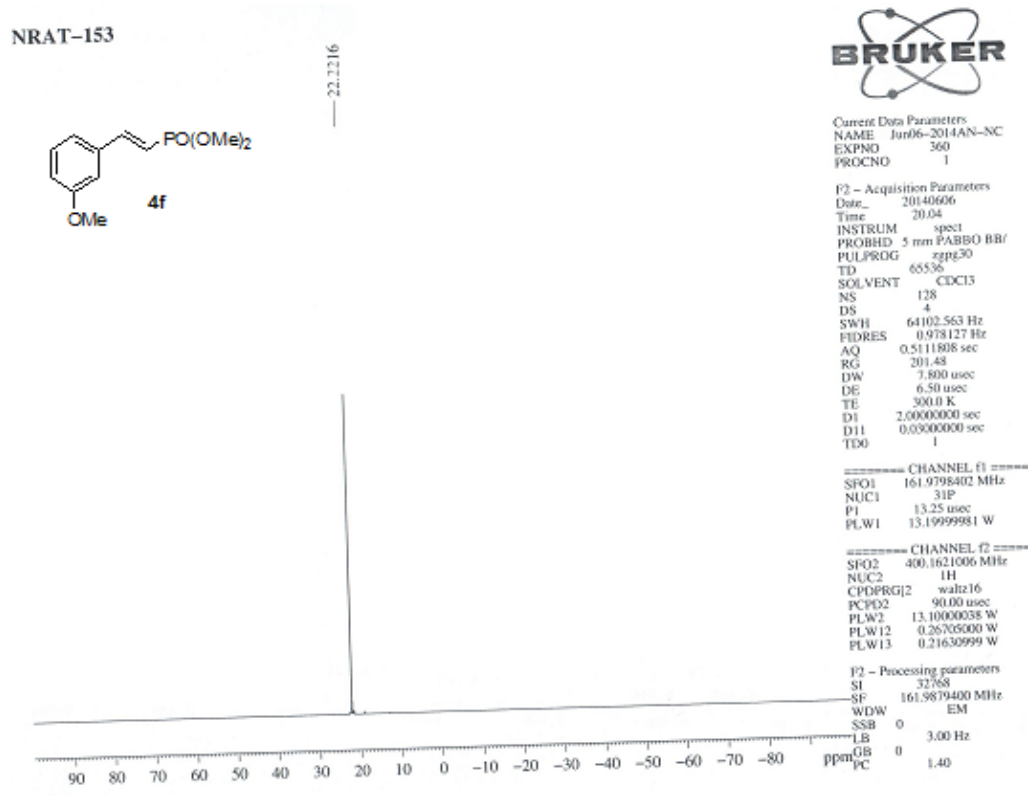


Figure 57: ^{31}P NMR spectrum of 4f

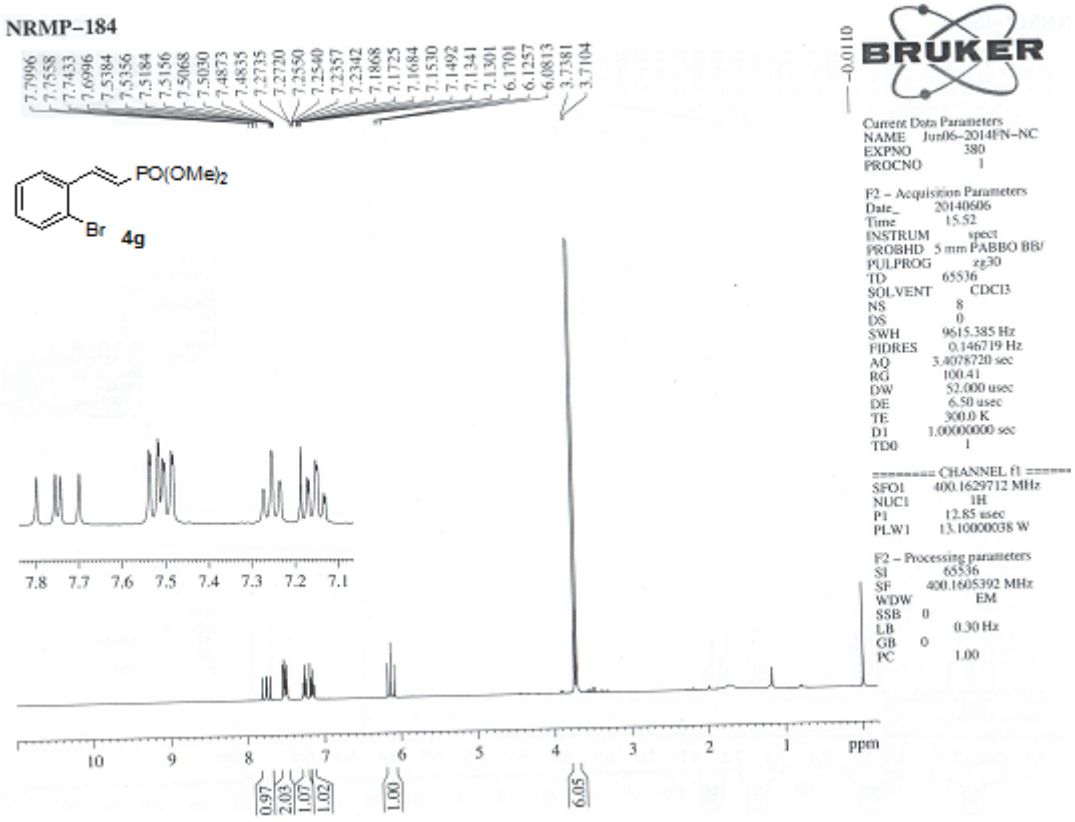


Figure 58: ^{1}H NMR spectrum of 4g

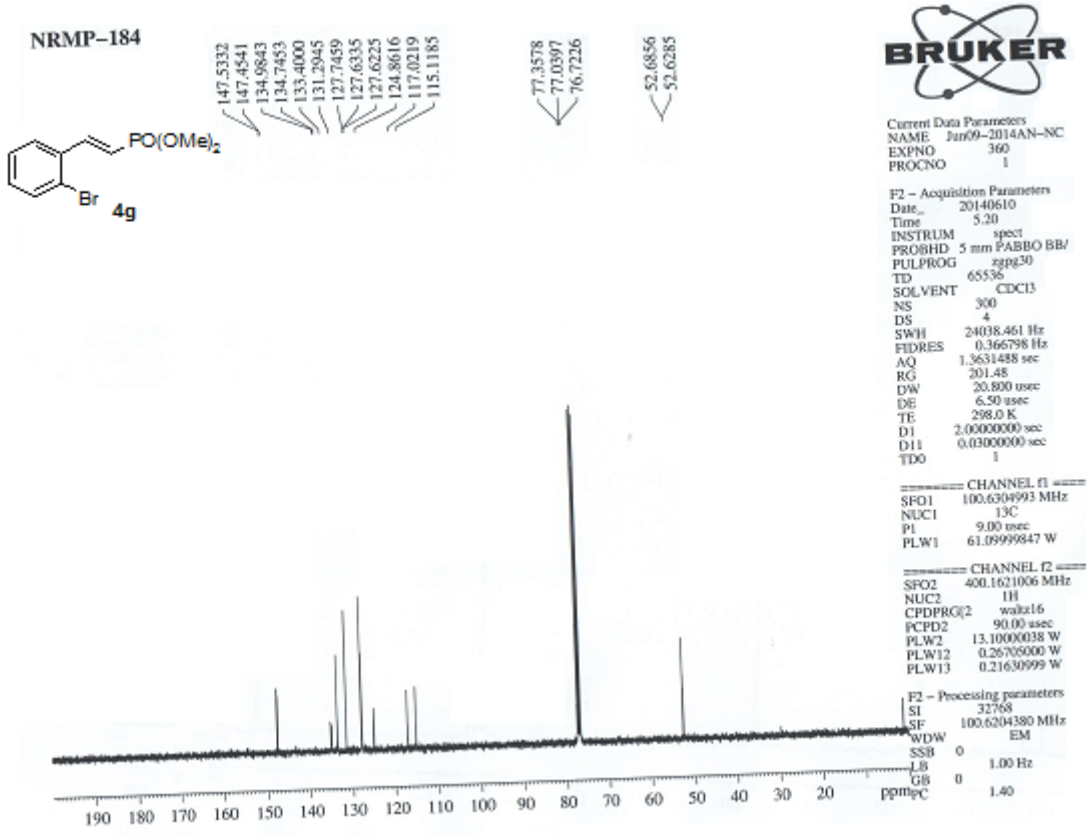


Figure 59: ^{13}C NMR spectrum of 4g

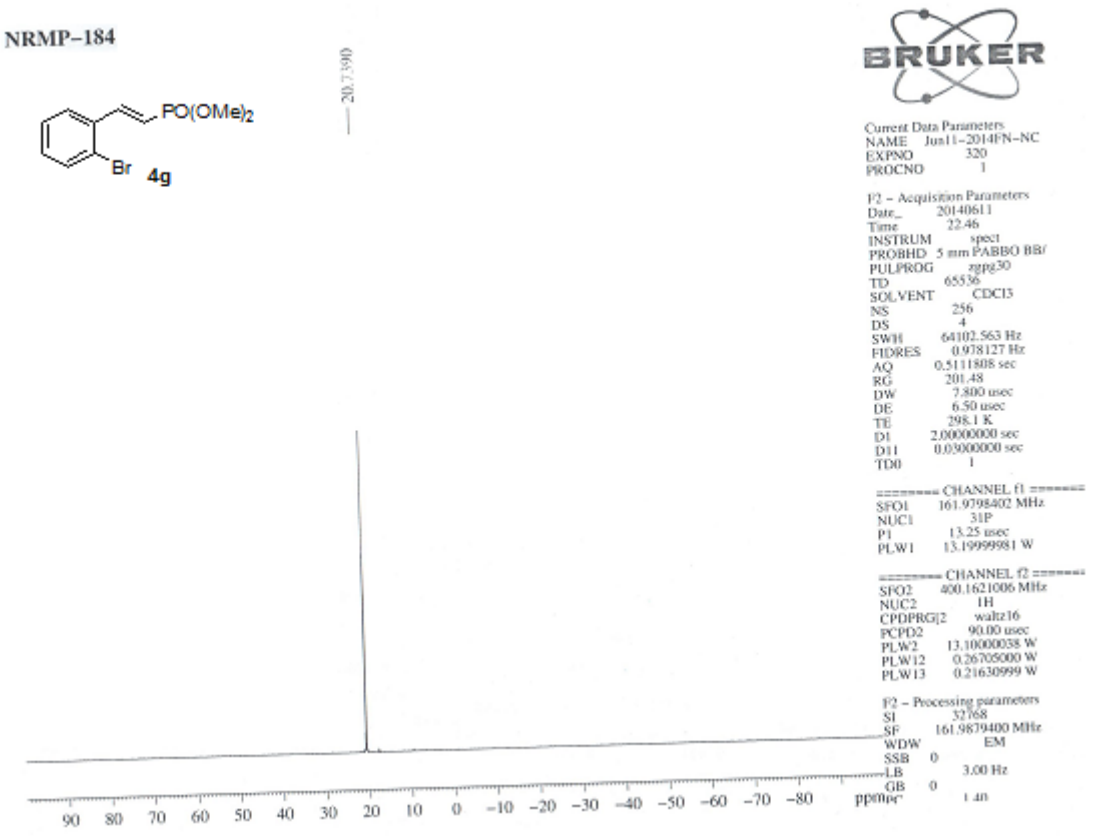


Figure 60: ^{31}P NMR spectrum of 4g

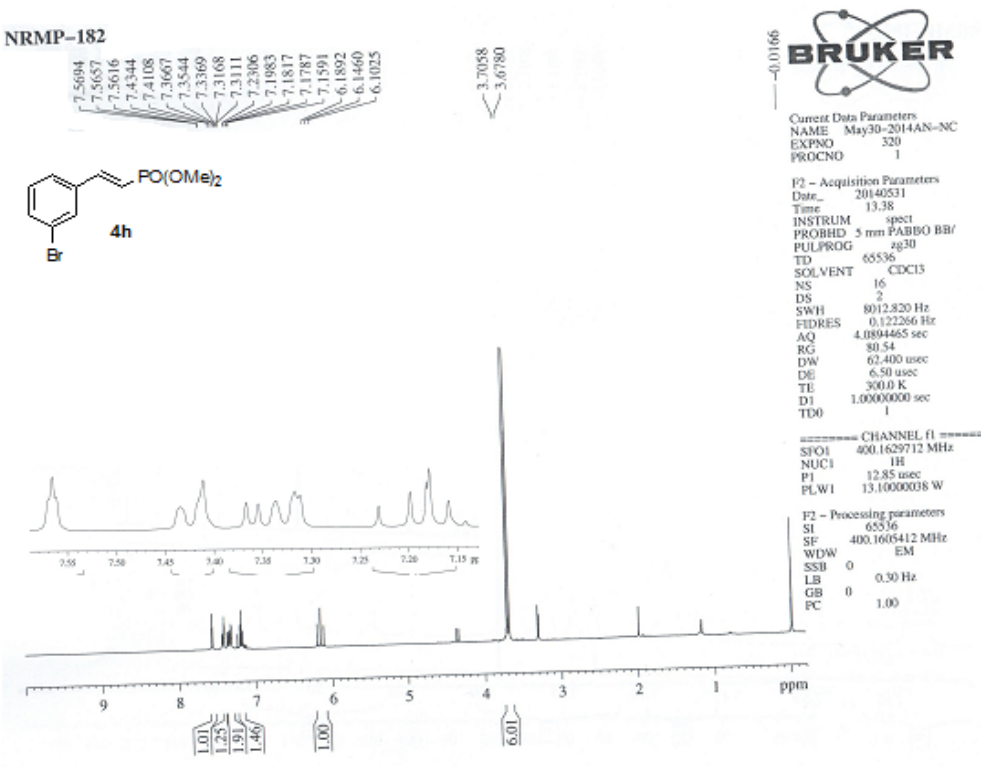


Figure 61: ^{1}H NMR spectrum of 4h

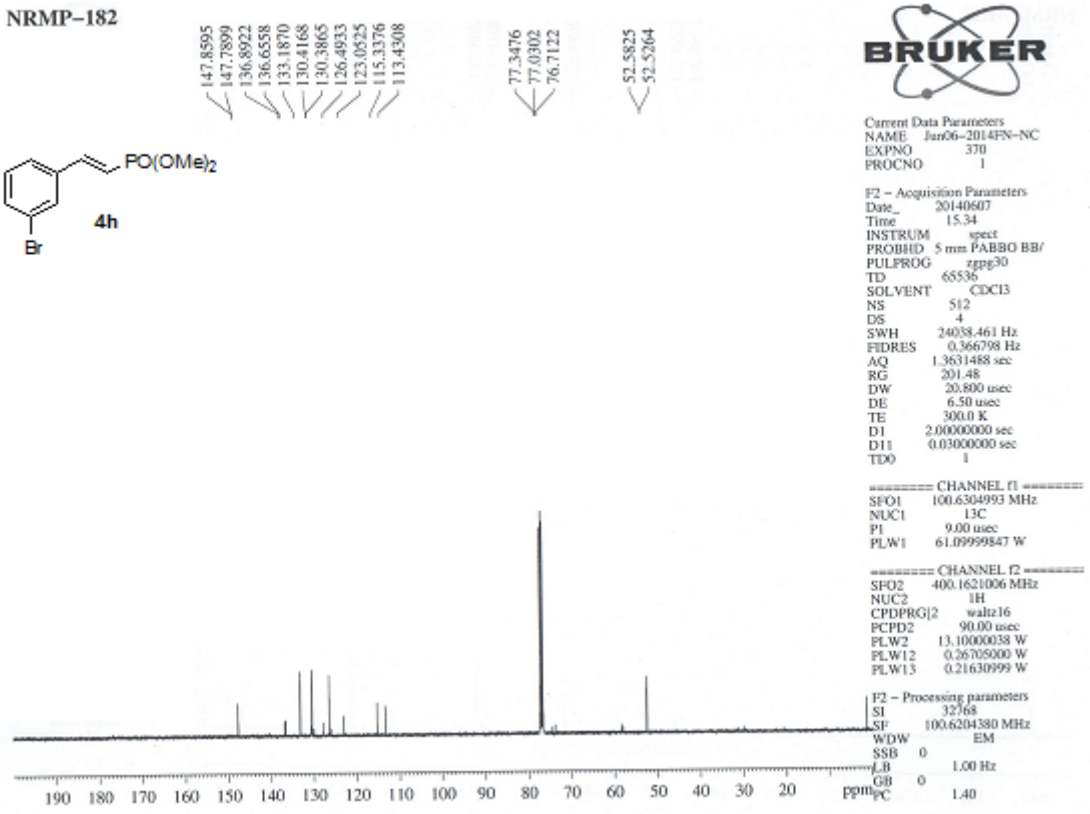


Figure 62: ^{13}C NMR spectrum of 4h

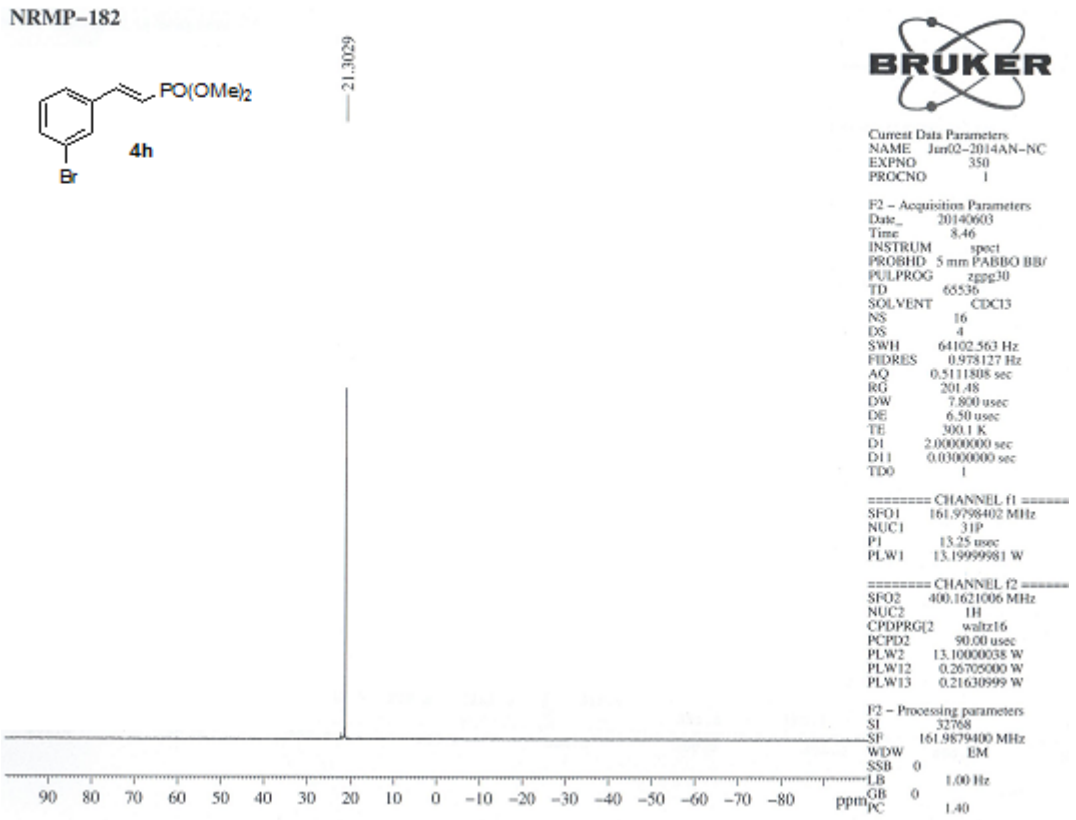


Figure 63: ^{31}P NMR spectrum of 4h

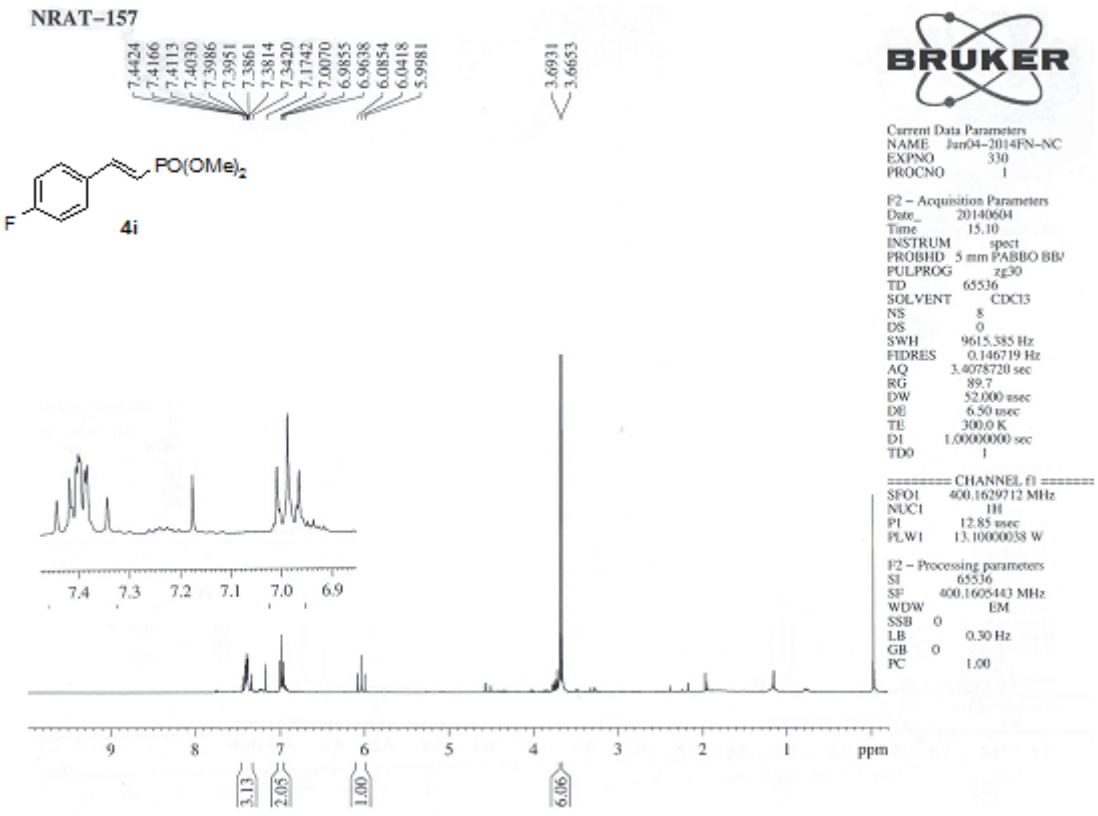


Figure 64: ^{1}H NMR spectrum of 4i

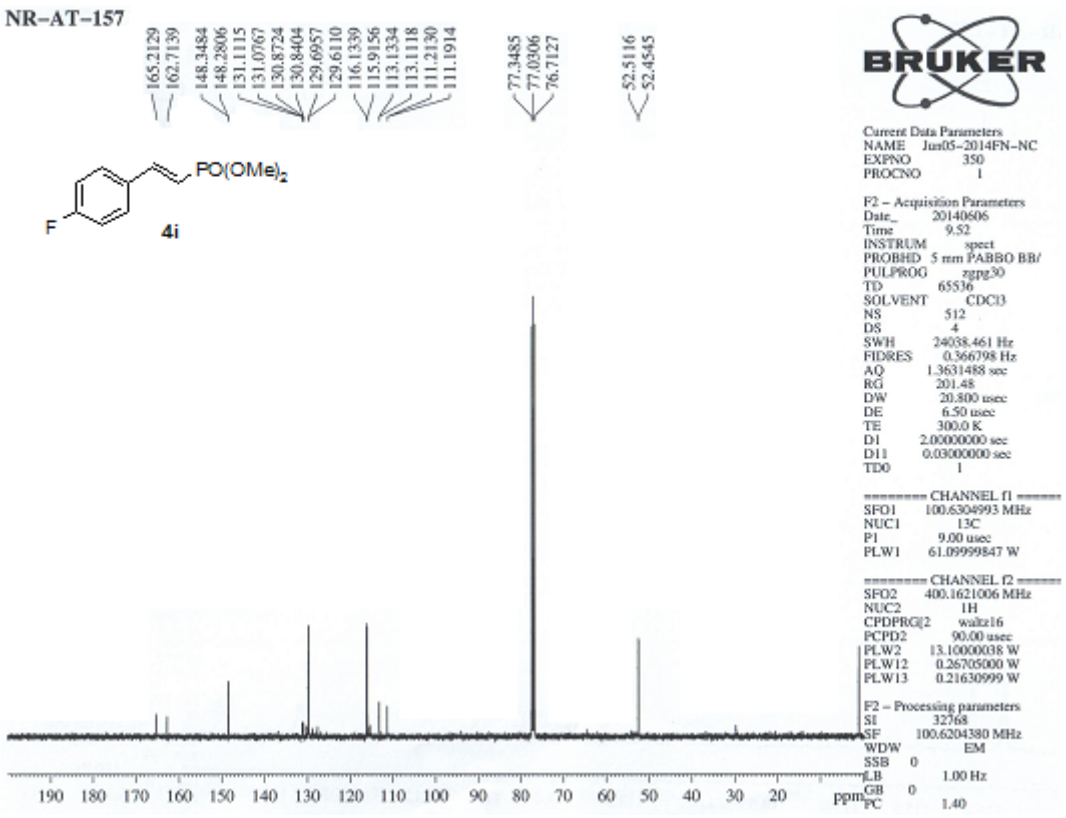


Figure 65: ^{13}C NMR spectrum of 4i

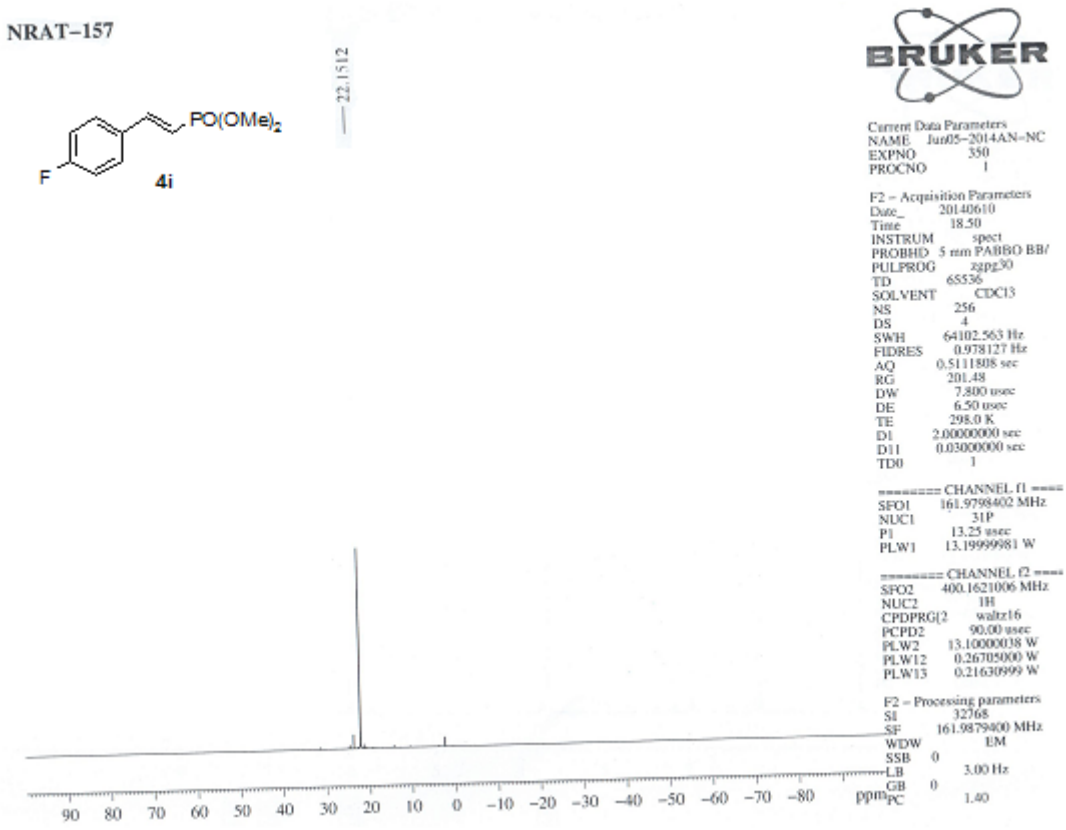


Figure 66: ^{31}P NMR spectrum of 4i

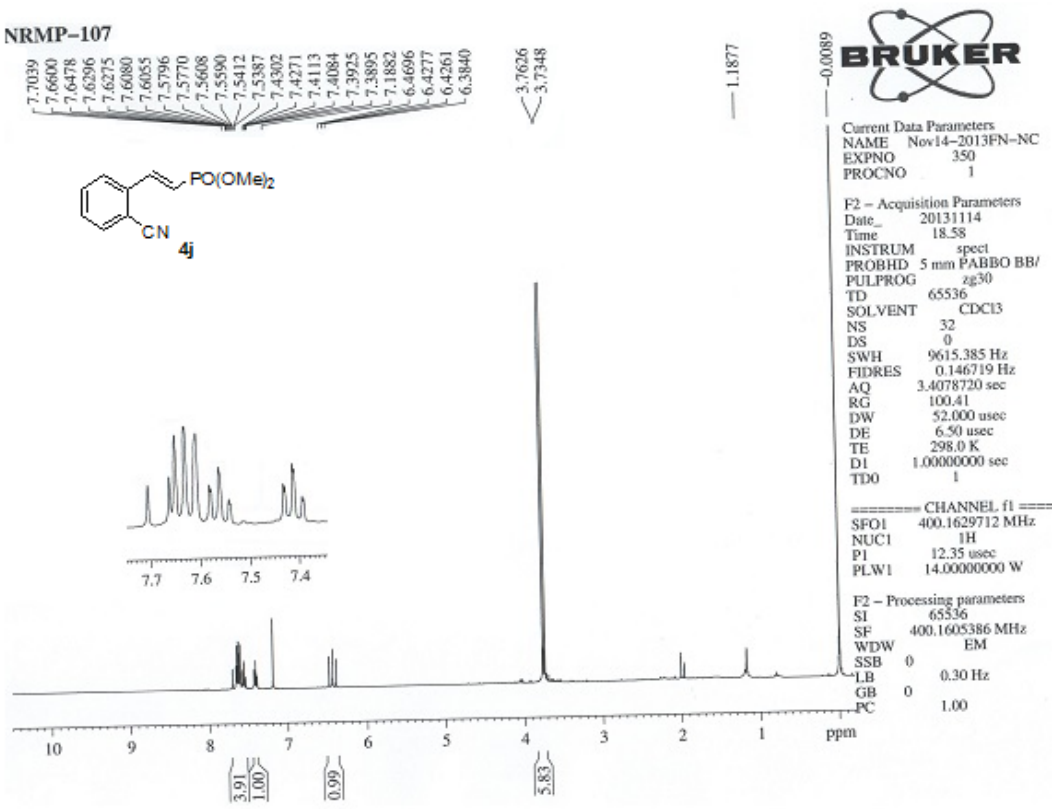


Figure 67: ^{1}H NMR spectrum of 4j

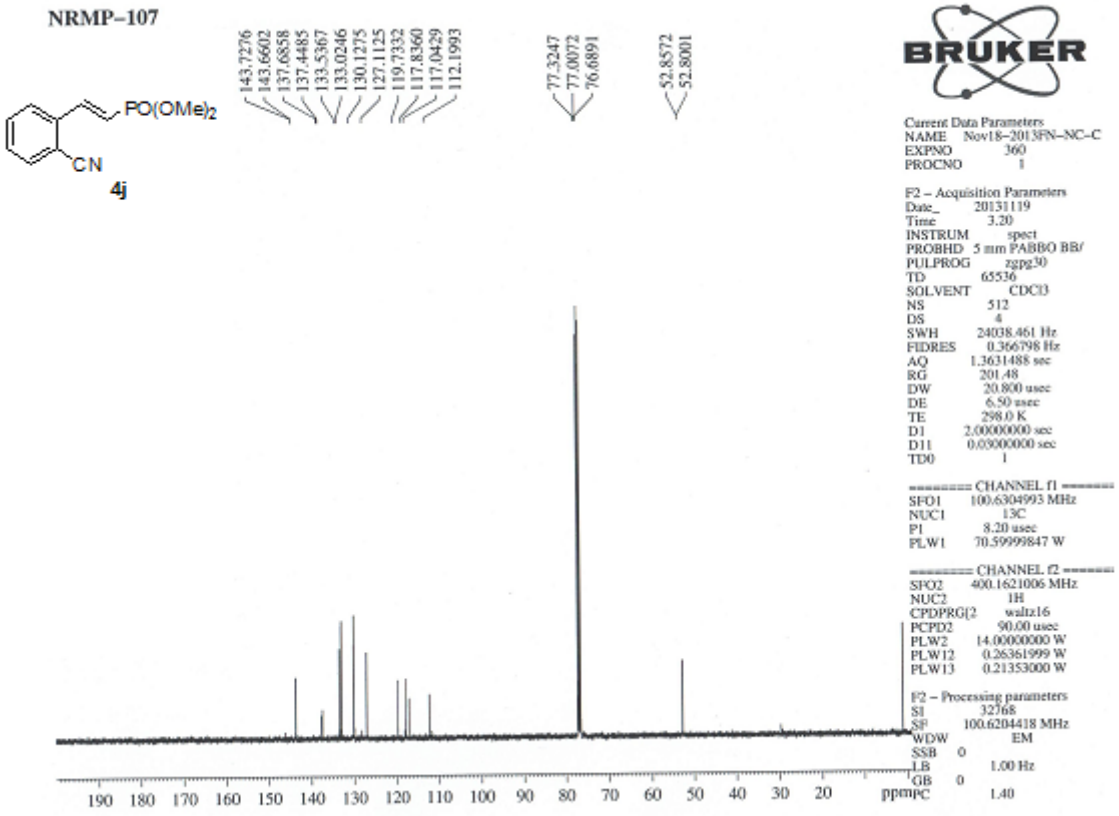


Figure 68: ^{13}C NMR spectrum of 4j

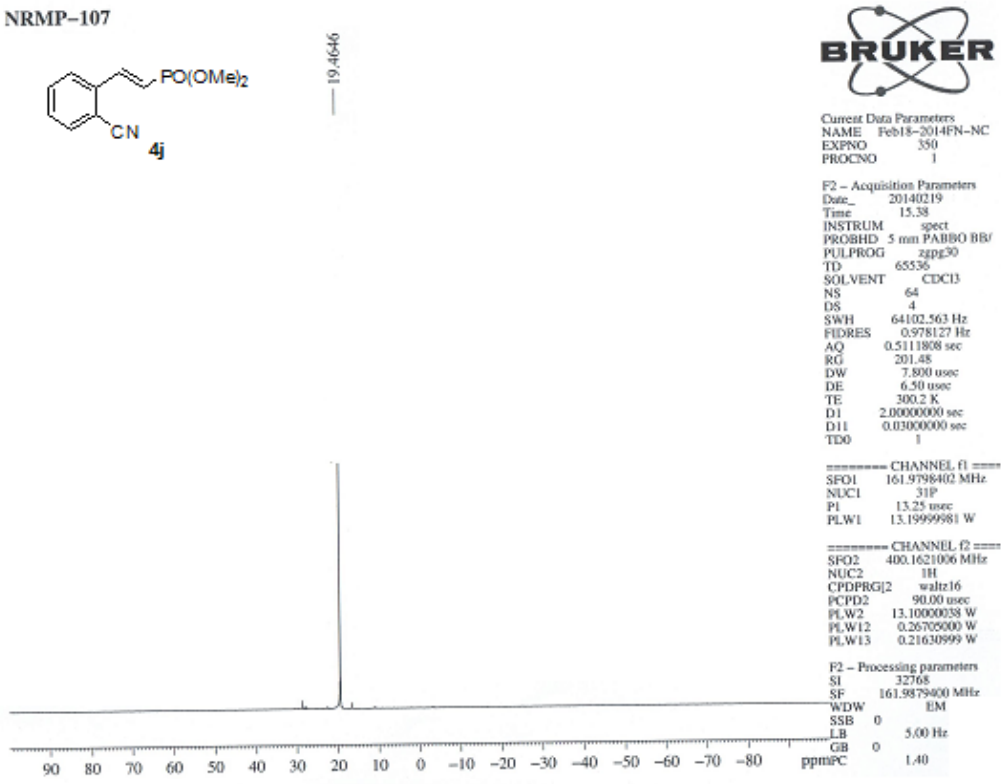


Figure 69: ^{31}P NMR spectrum of 4j

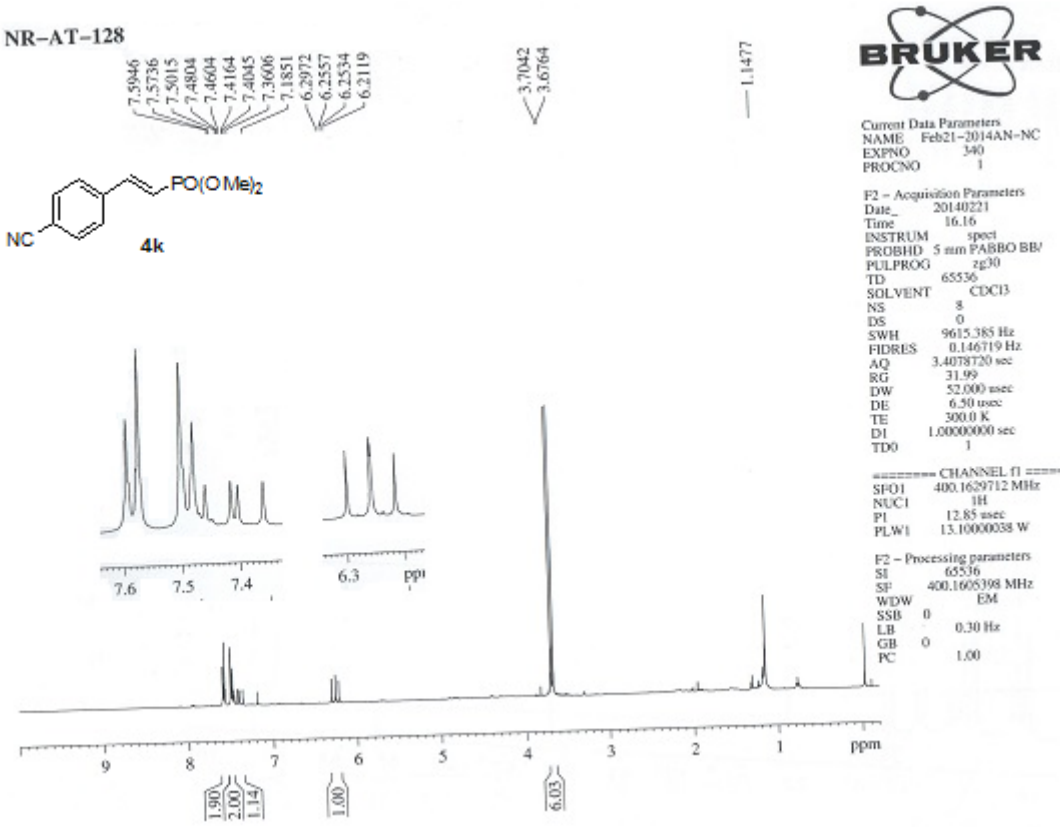


Figure 70: ^{1}H NMR spectrum of 4k

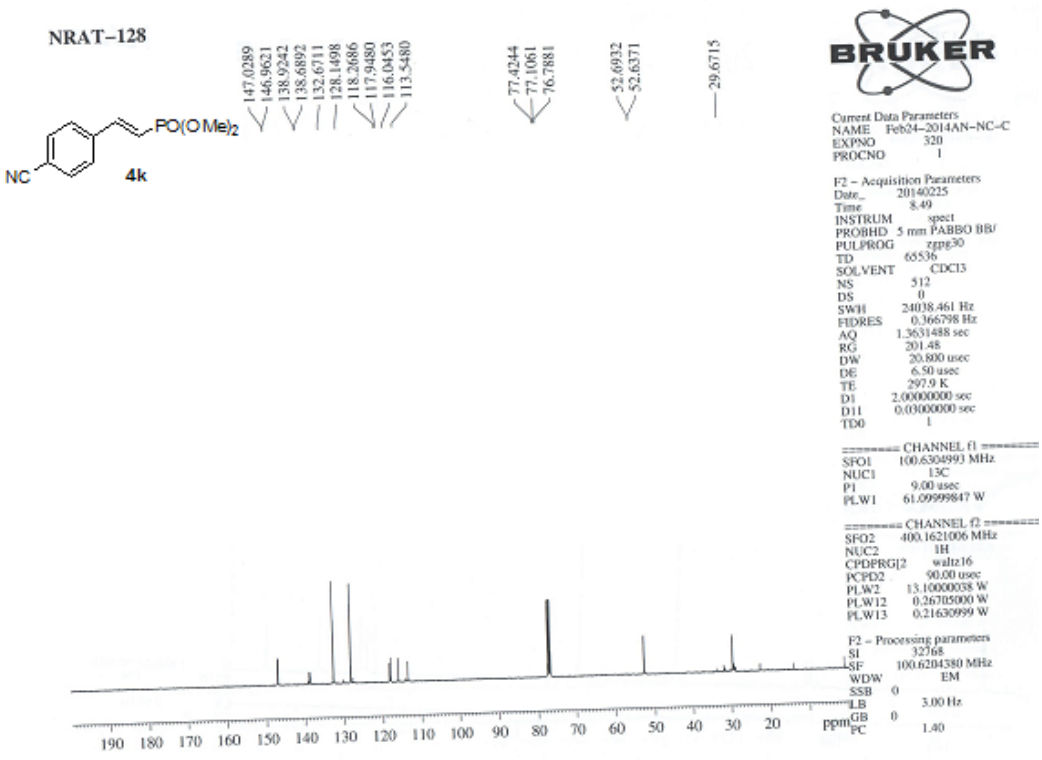


Figure 71: ^{13}C NMR spectrum of 4k

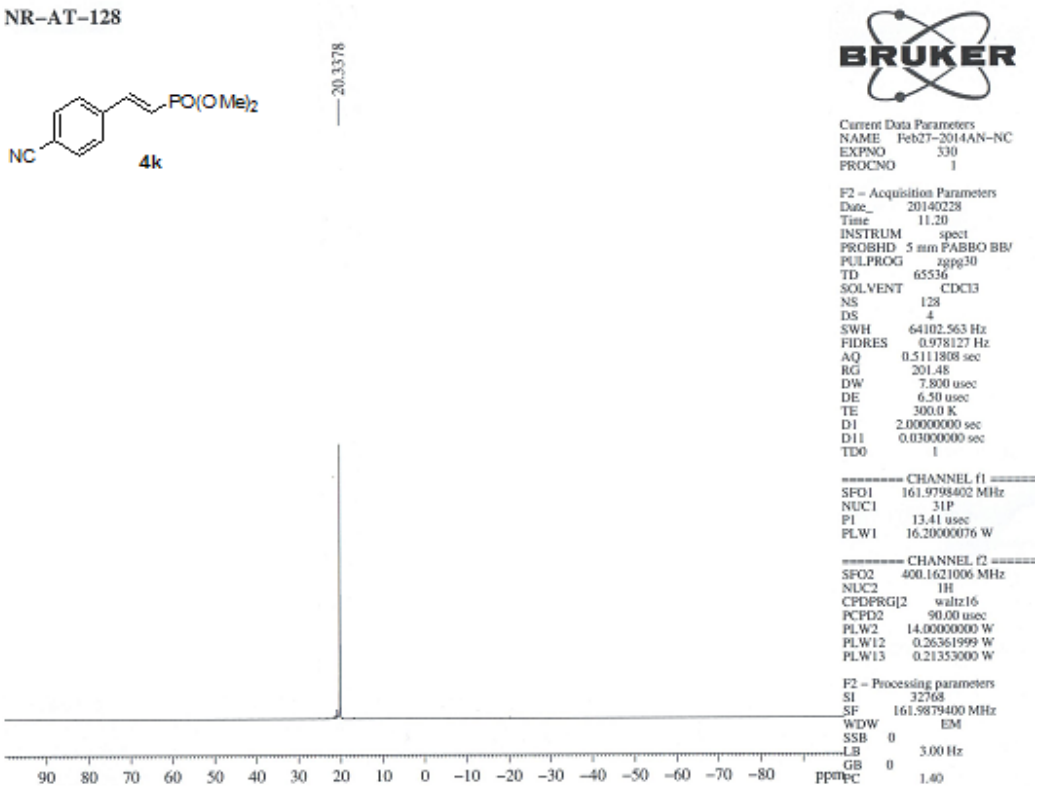


Figure 72: ^{31}P NMR spectrum of 4k

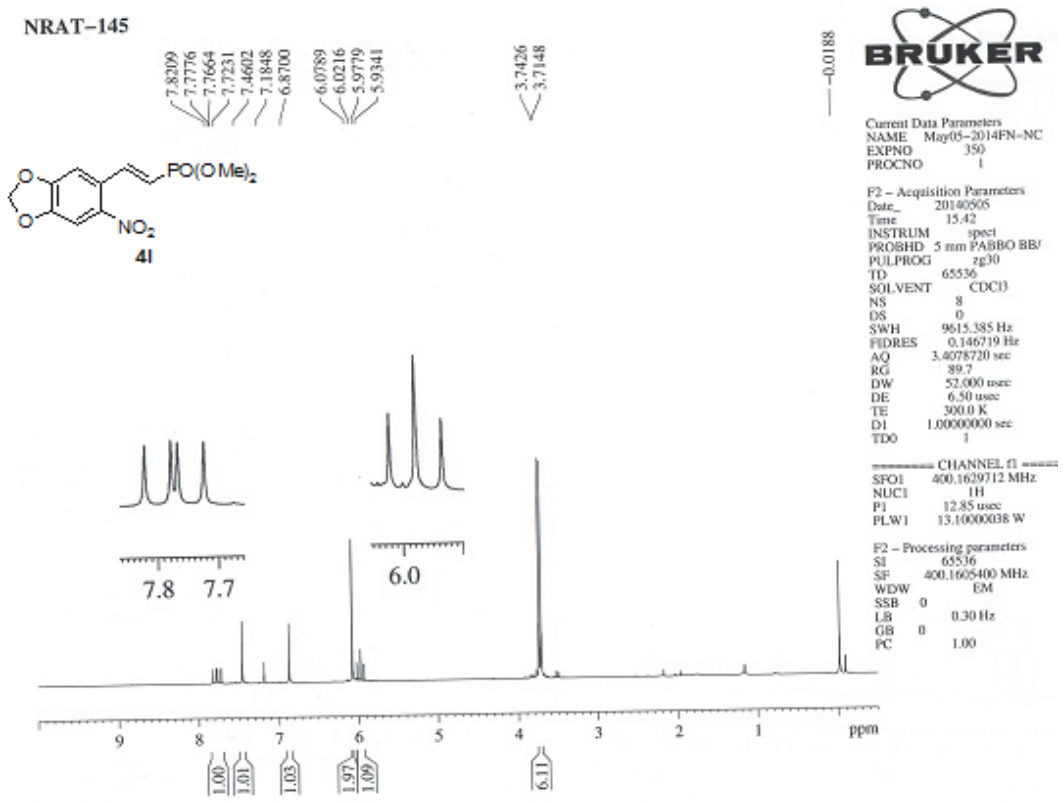


Figure 73: ^{1}H NMR spectrum of 4l

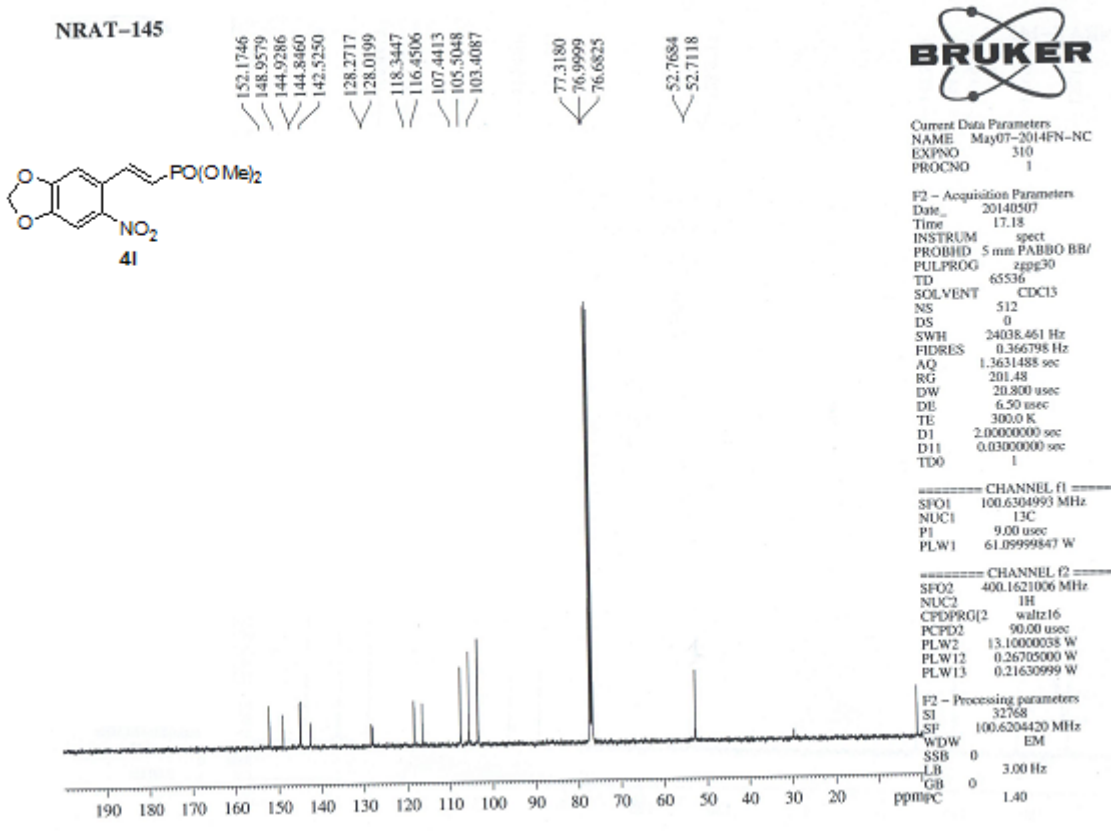


Figure 74: ^{13}C NMR spectrum of 4l

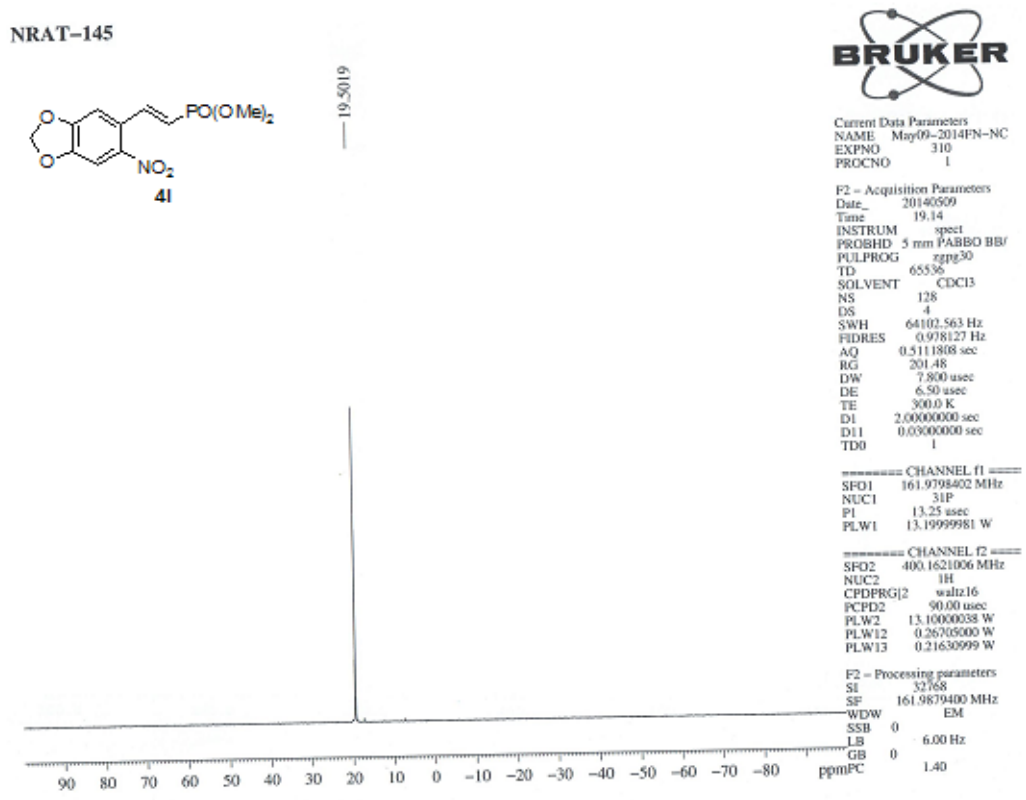


Figure 75: ^{31}P NMR spectrum of 4l

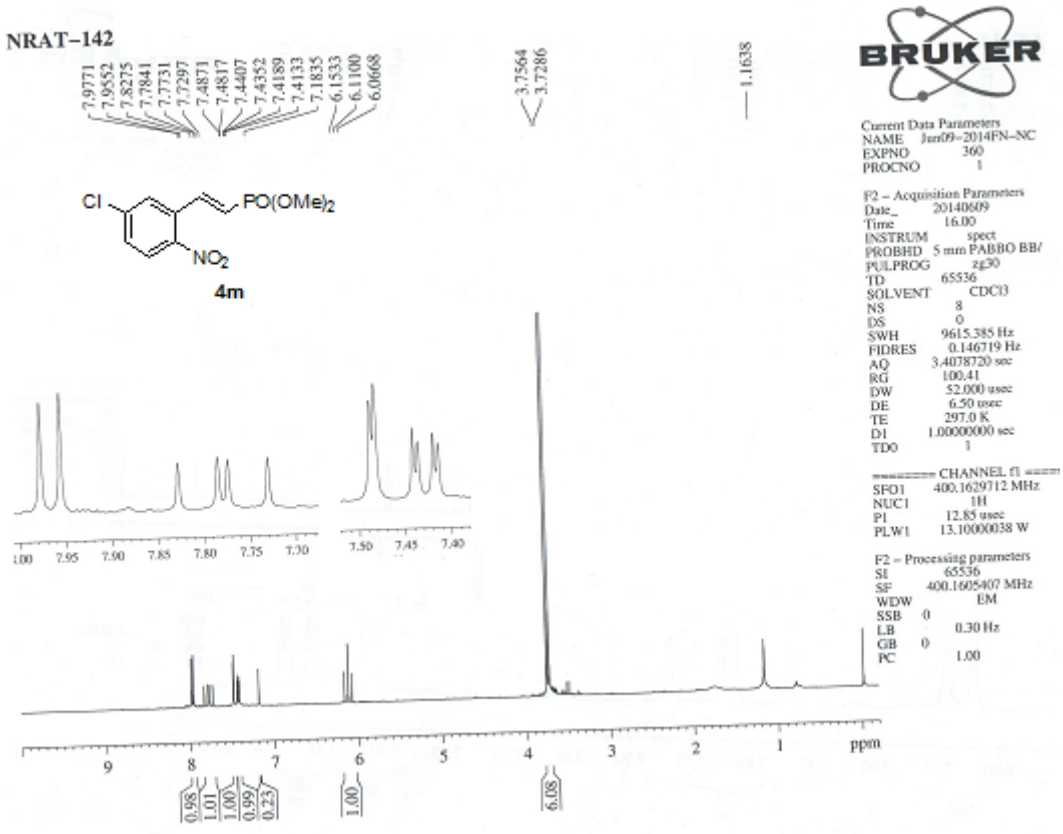


Figure 76: ^{1}H NMR spectrum of 4m

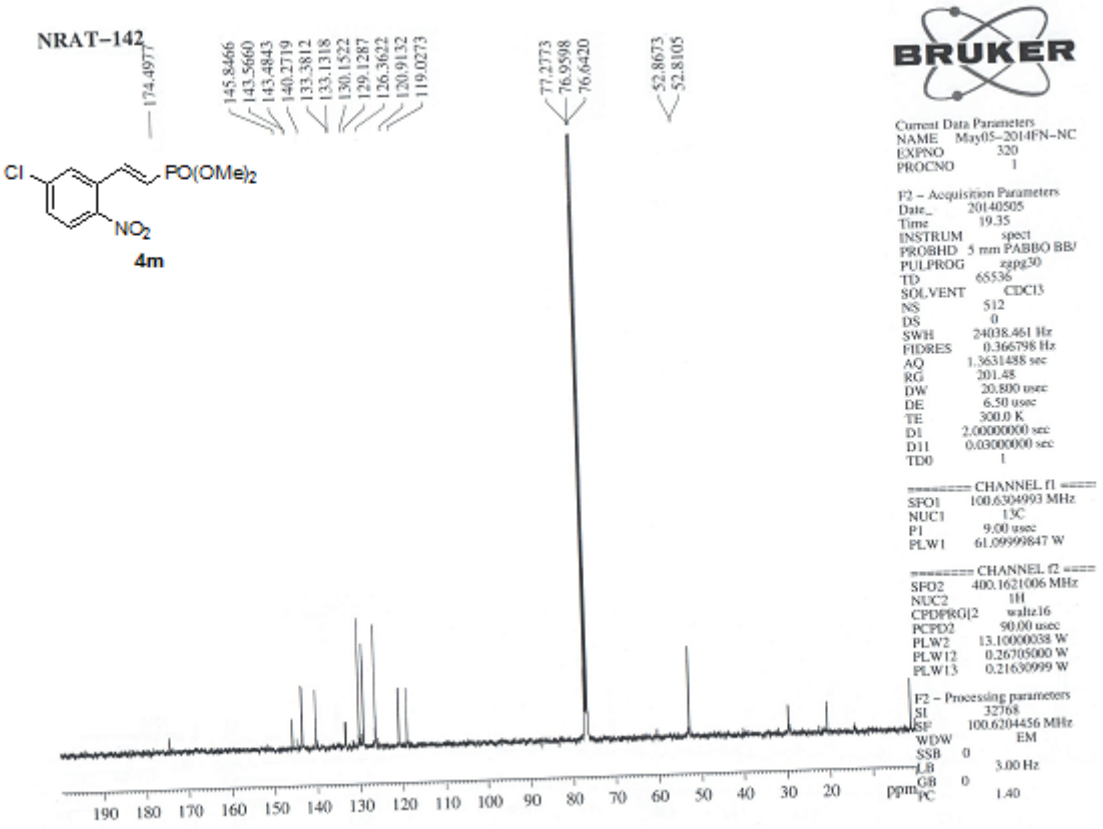


Figure 77: ^{13}C NMR spectrum of 4m

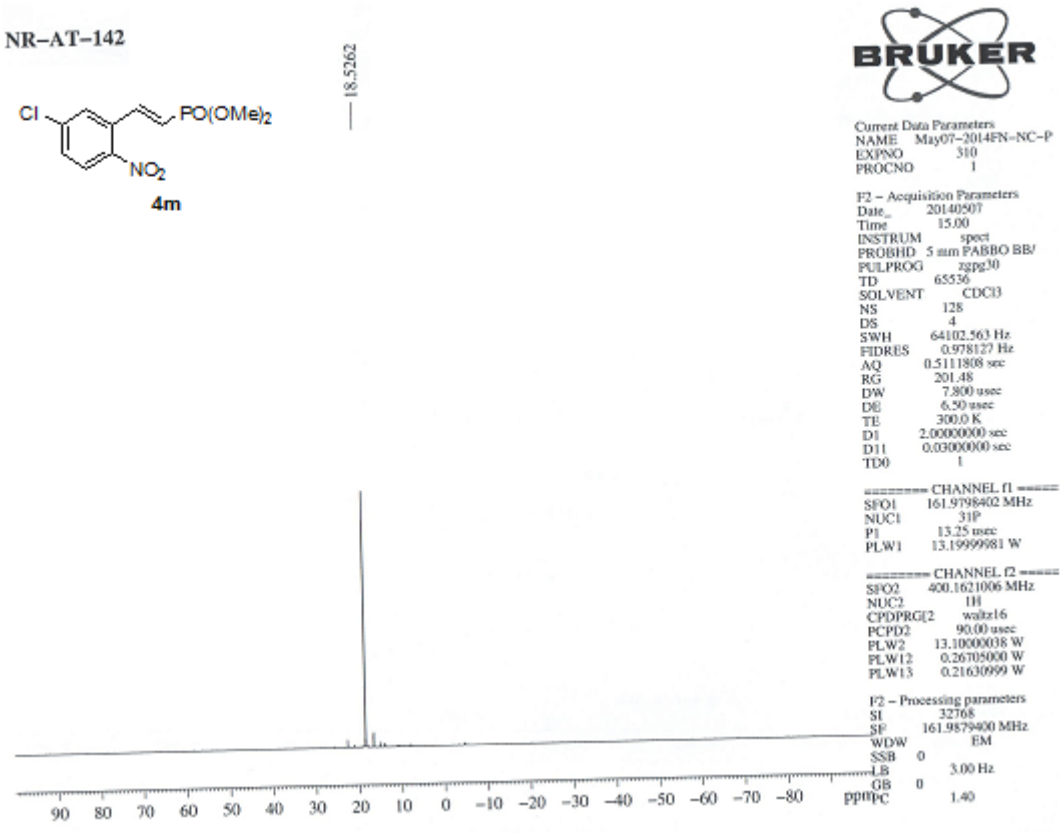


Figure 78: ^{31}P NMR spectrum of 4m

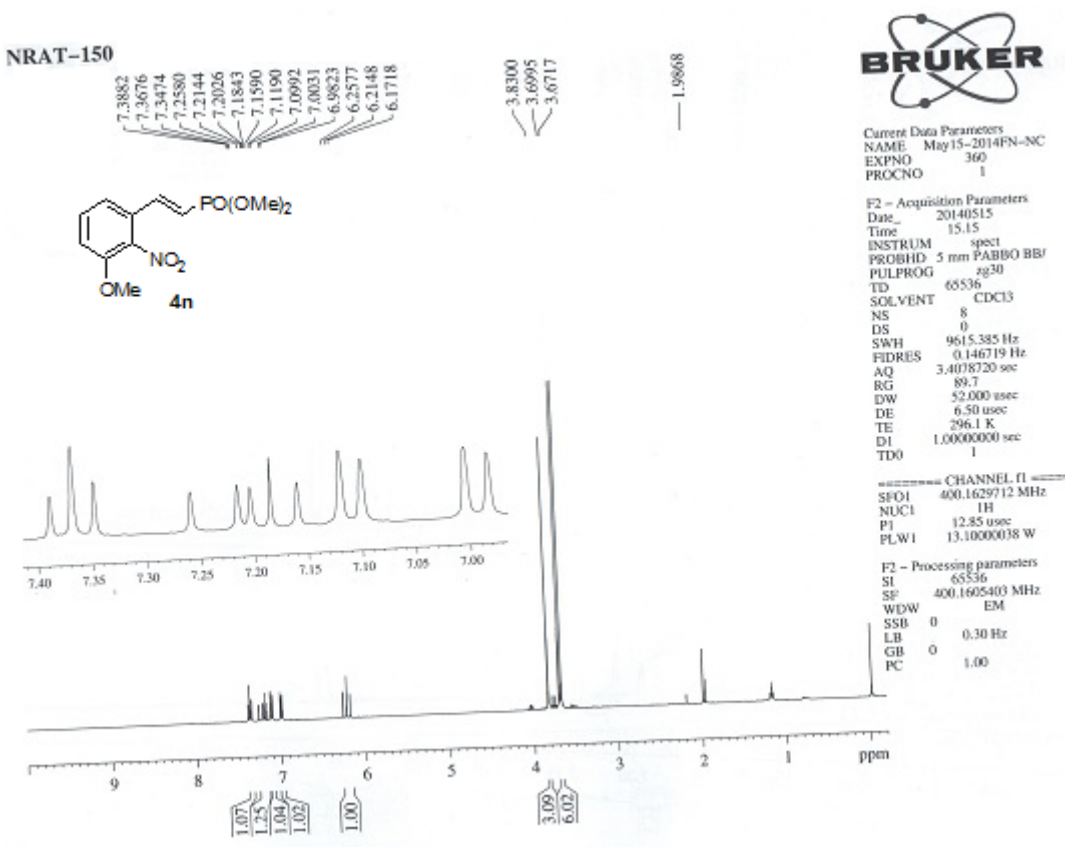


Figure 79: ^{1}H NMR spectrum of 4n

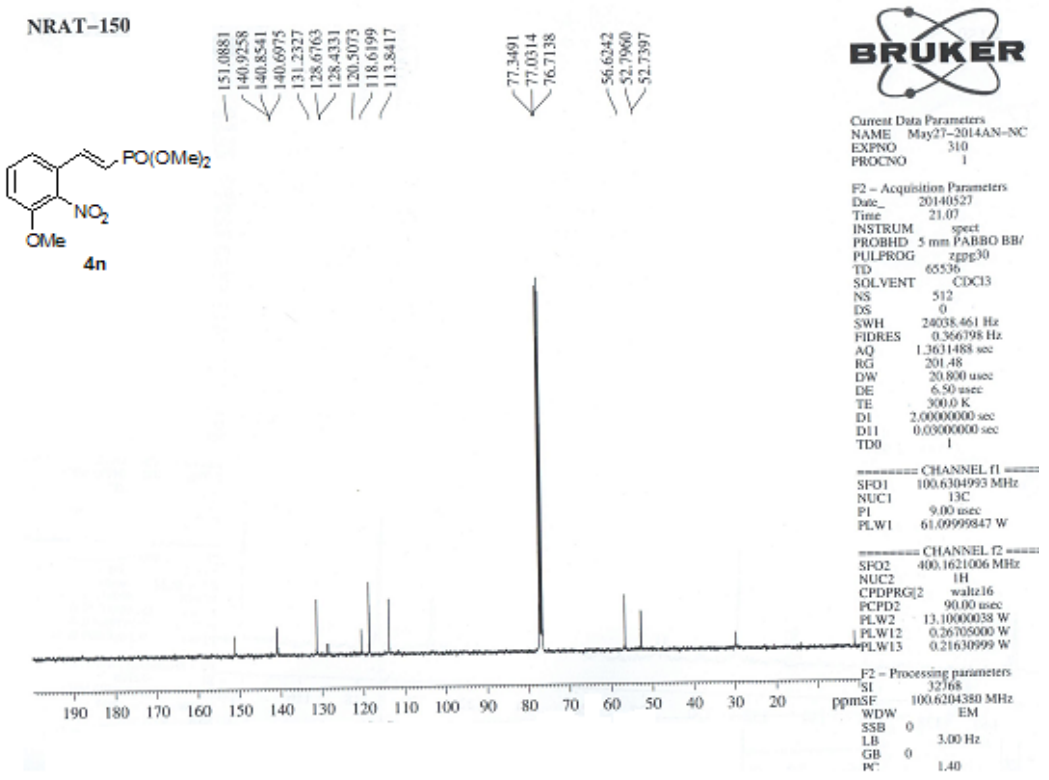


Figure 80: ^{13}C NMR spectrum of 4n

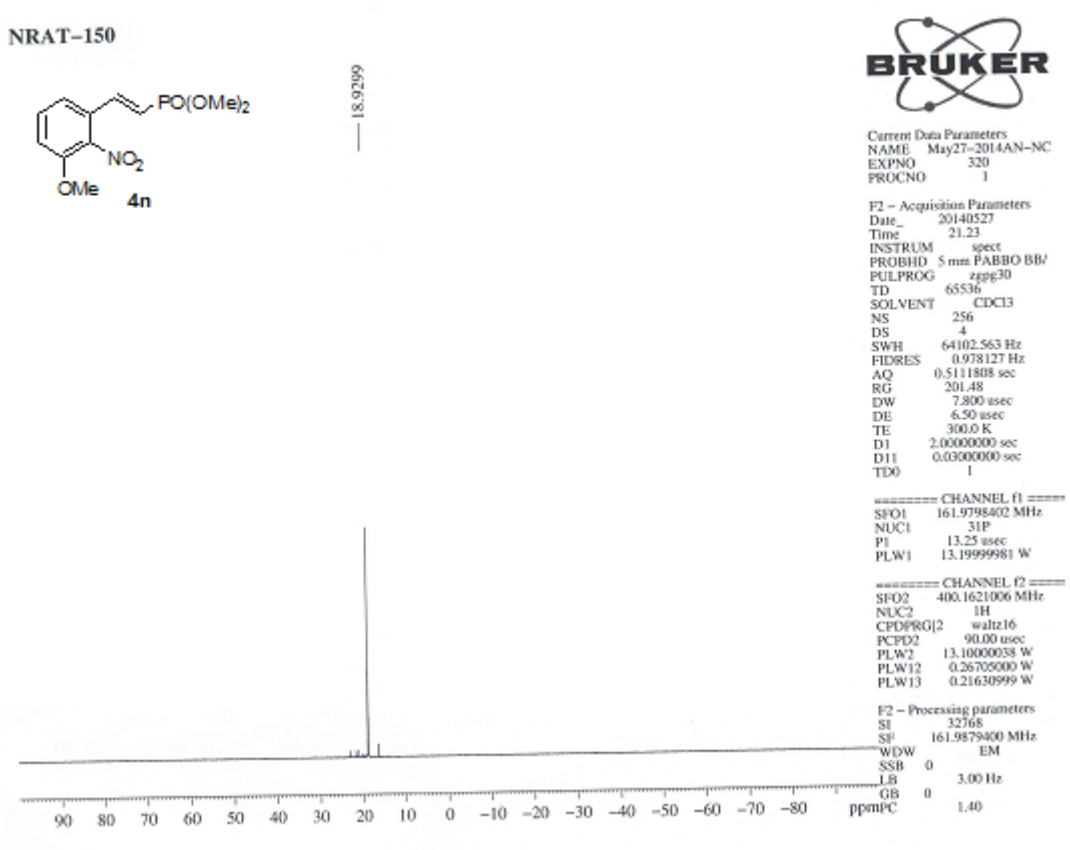


Figure 81: ^{31}P NMR spectrum of 4n

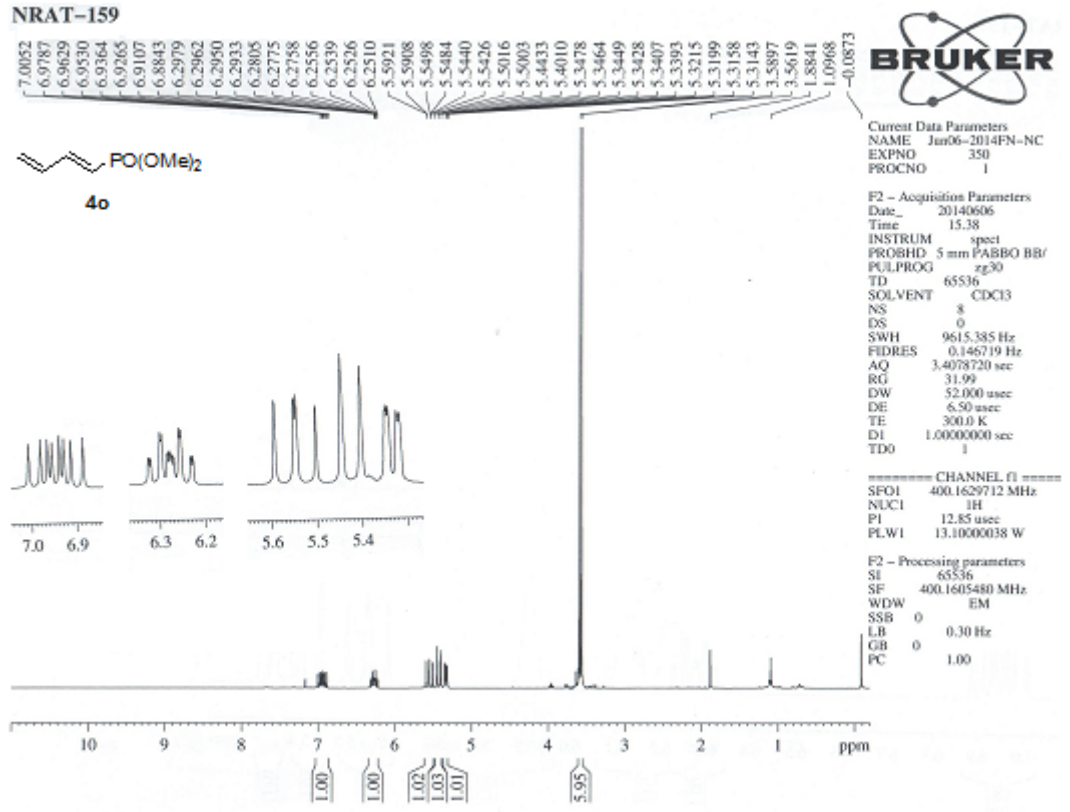


Figure 82: ^{1}H NMR spectrum of 4o

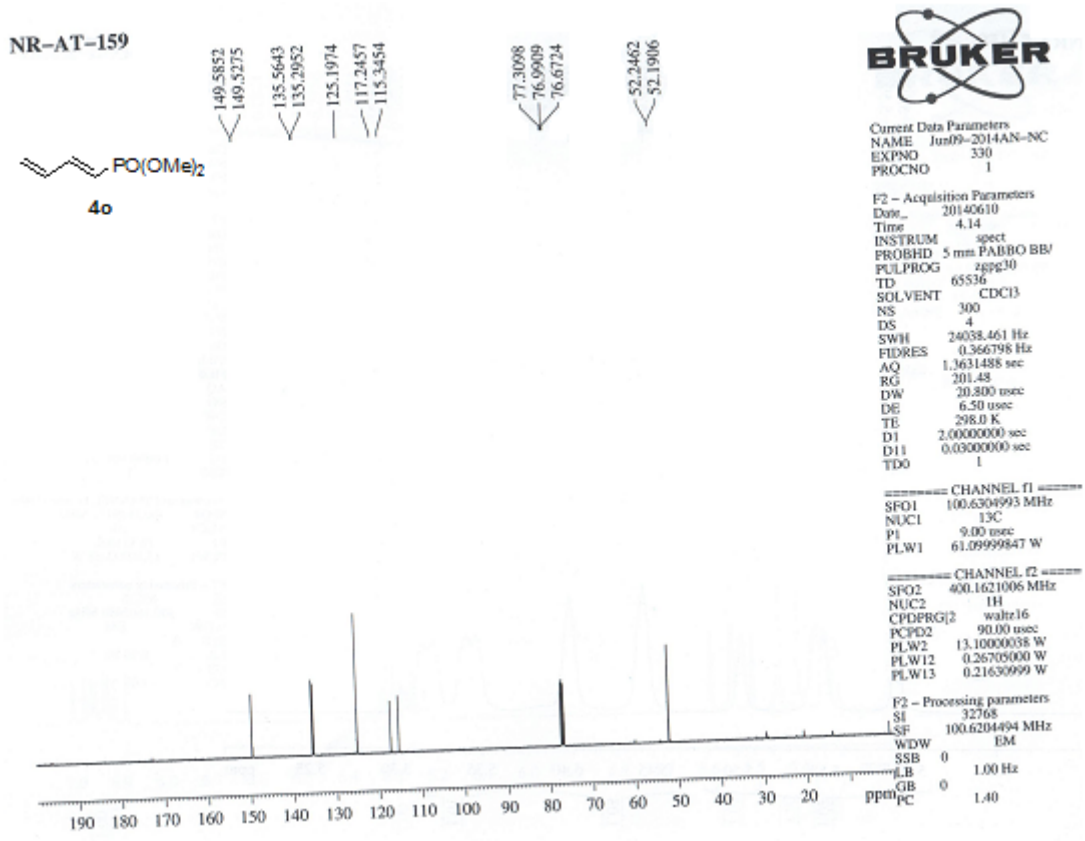


Figure 83: ^{13}C NMR spectrum of 4o

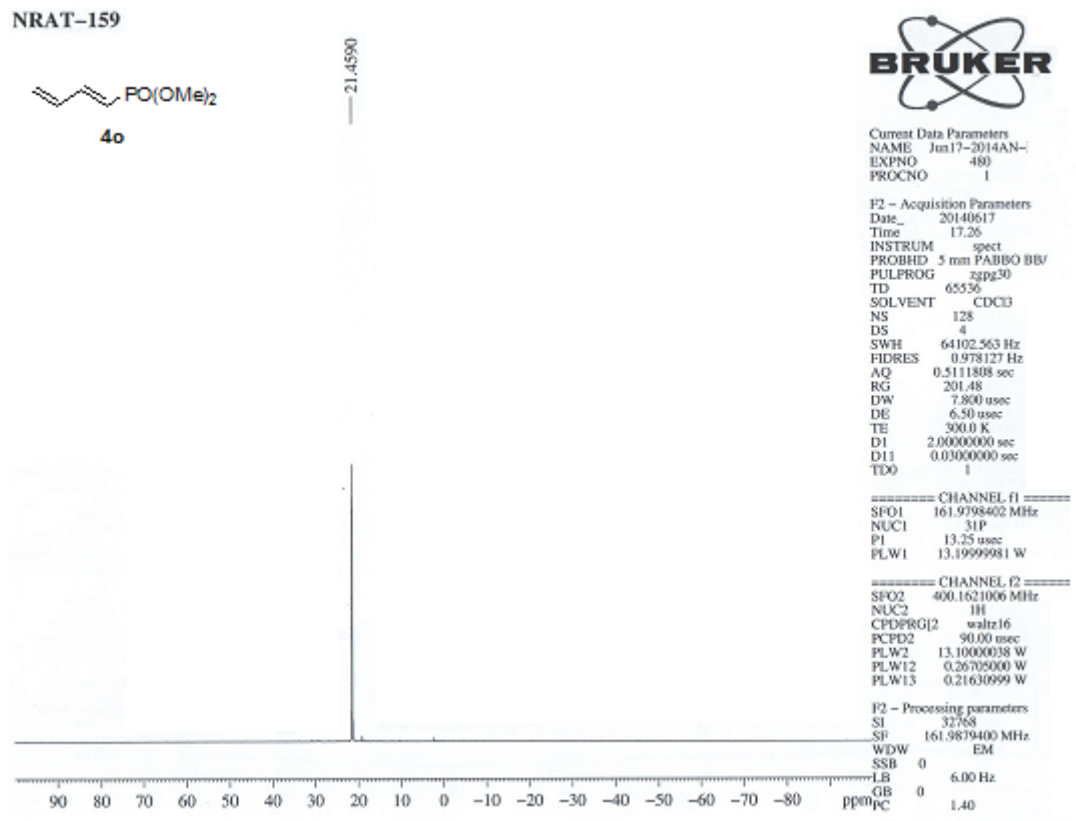


Figure 84: ^{31}P NMR spectrum of 4o

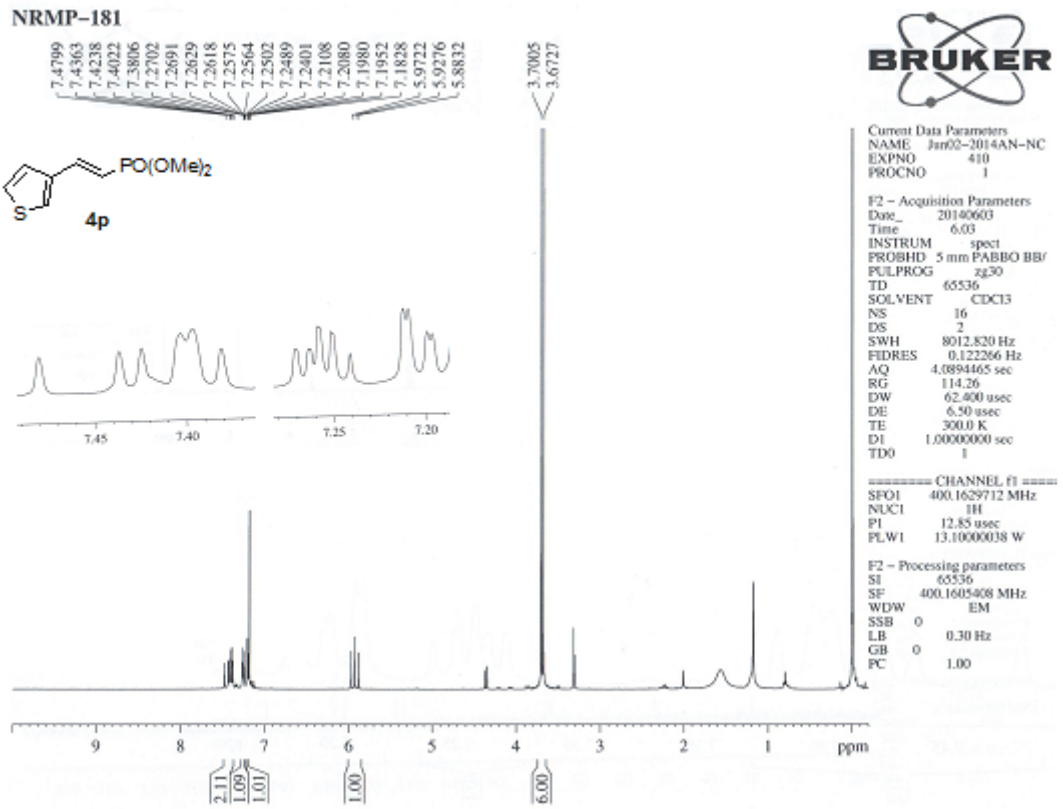


Figure 85: ^{1}H NMR spectrum of 4p

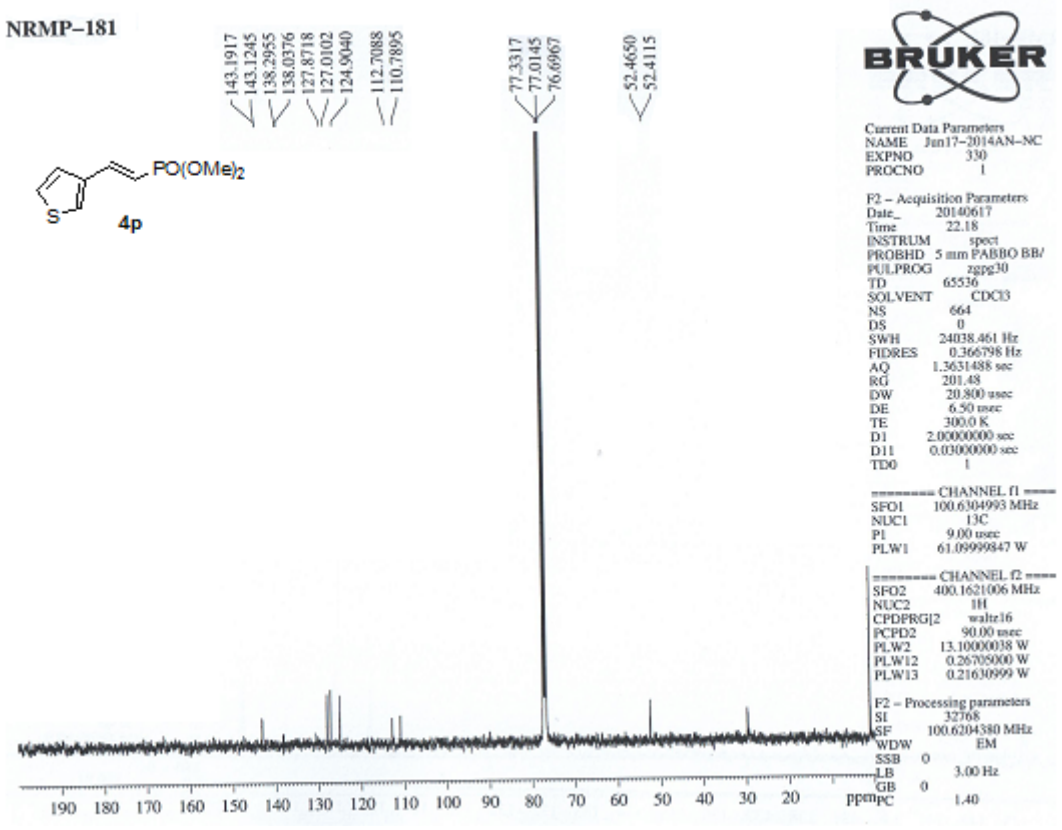


Figure 86: ^{13}C NMR spectrum of 4p

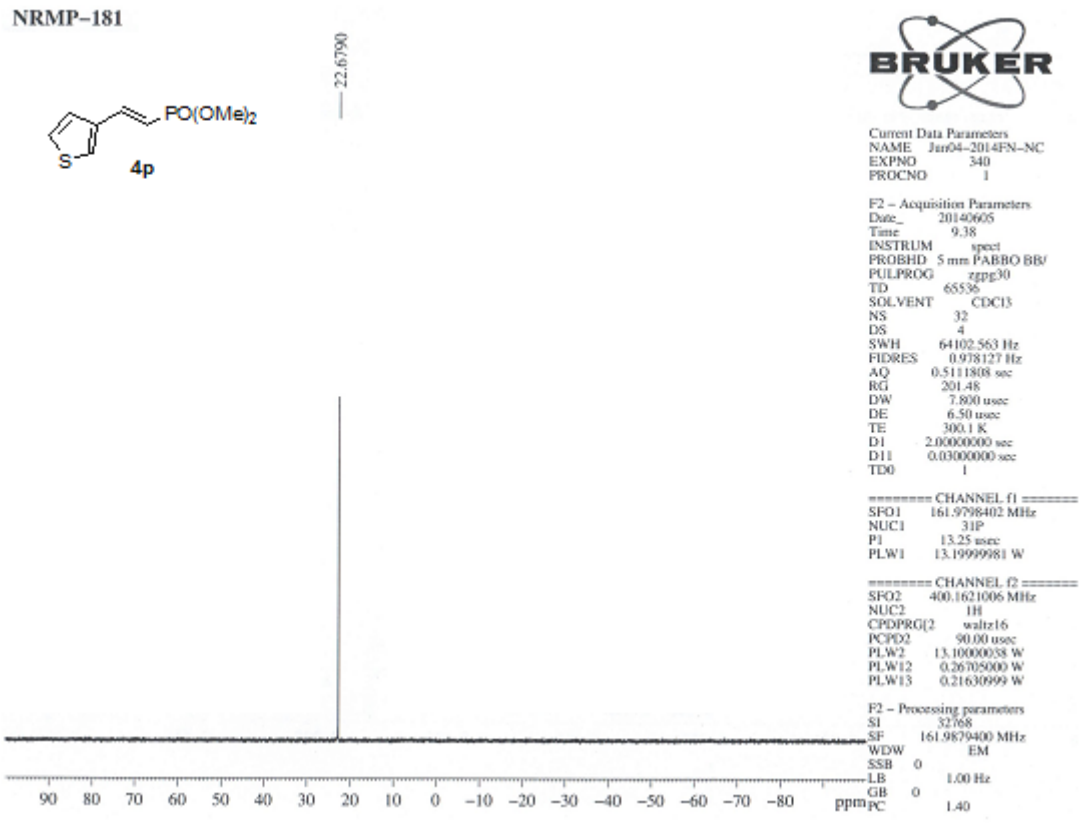


Figure 87: ^{31}P NMR spectrum of 4p

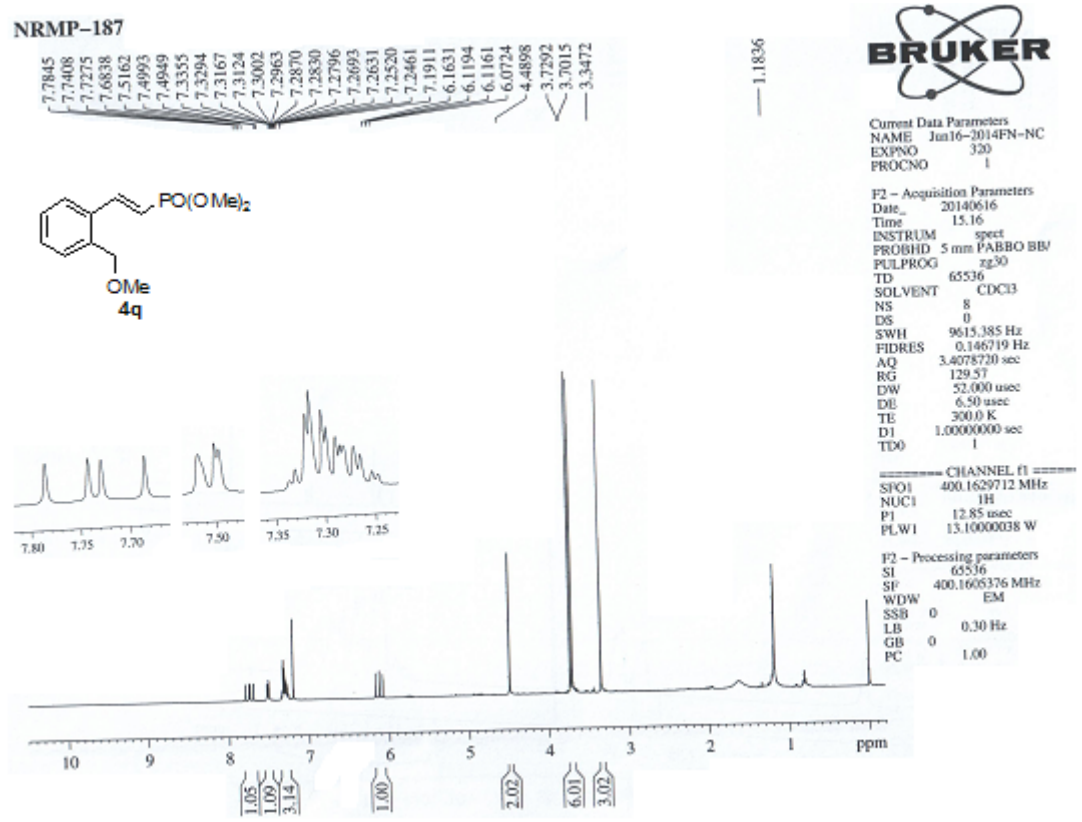


Figure 88: ^{1}H NMR spectrum of 4q

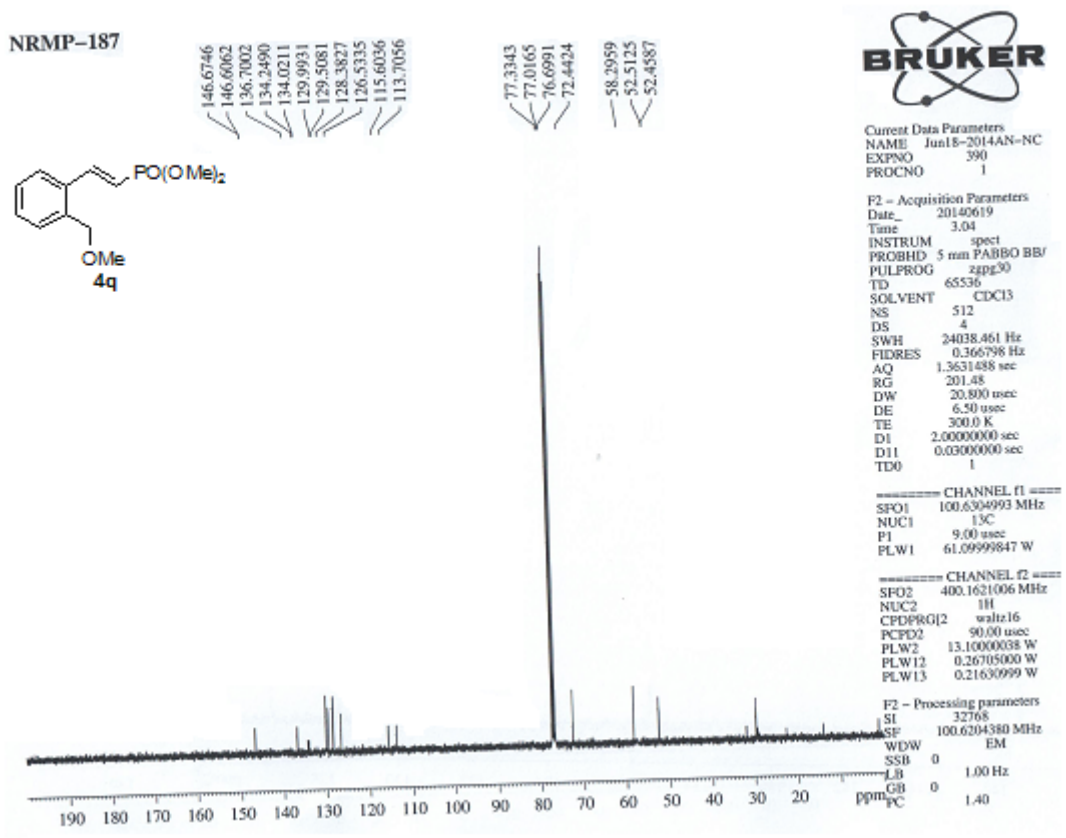


Figure 89: ^{13}C NMR spectrum of 4q

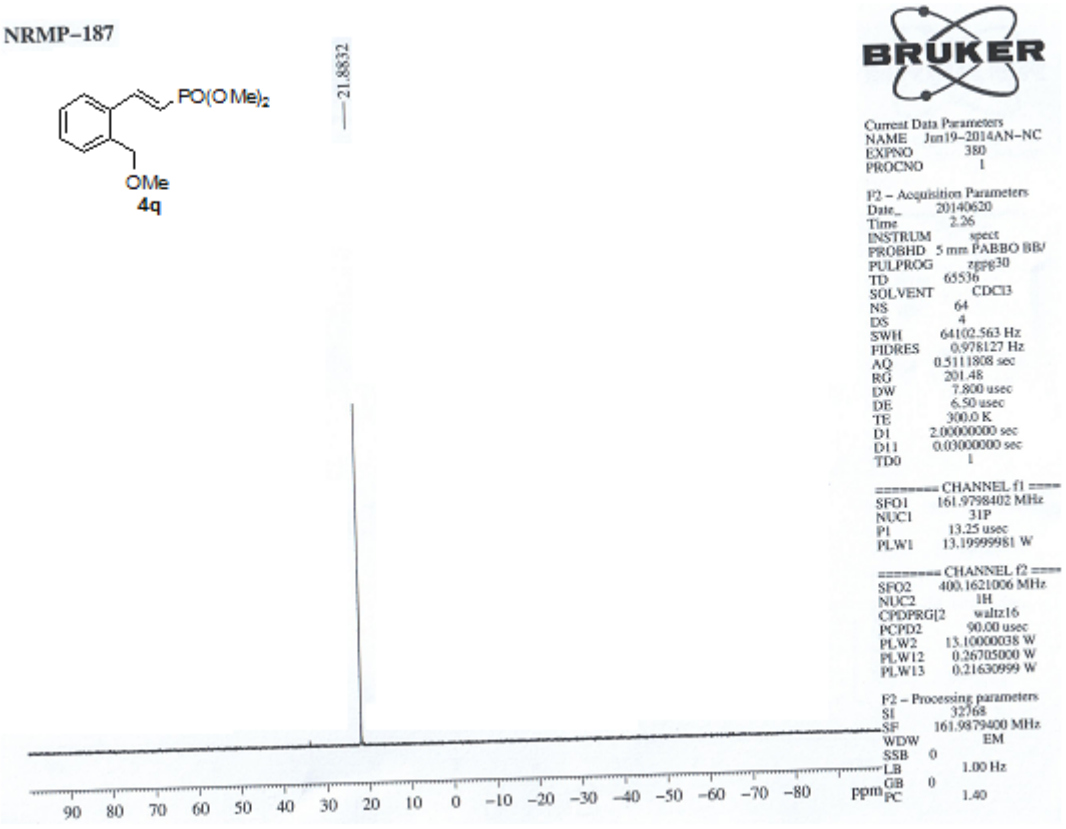


Figure 90: ^{31}P NMR spectrum of 4q

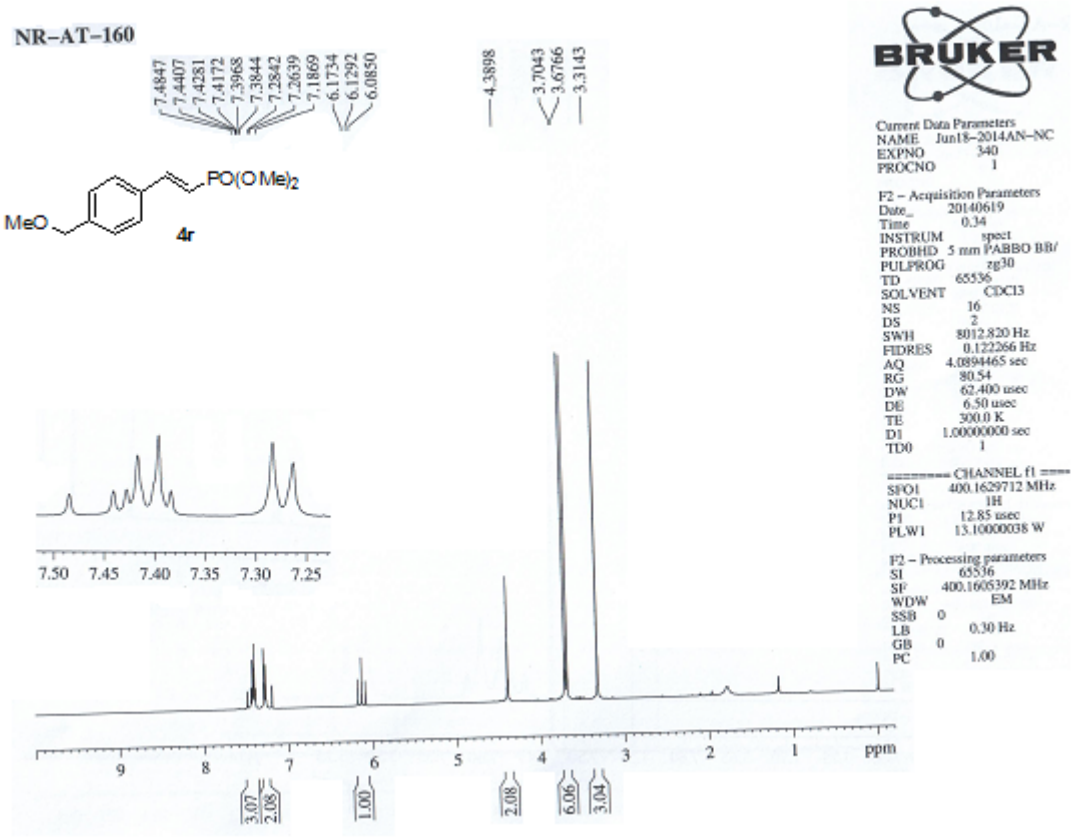


Figure 91: ^{1}H NMR spectrum of 4r

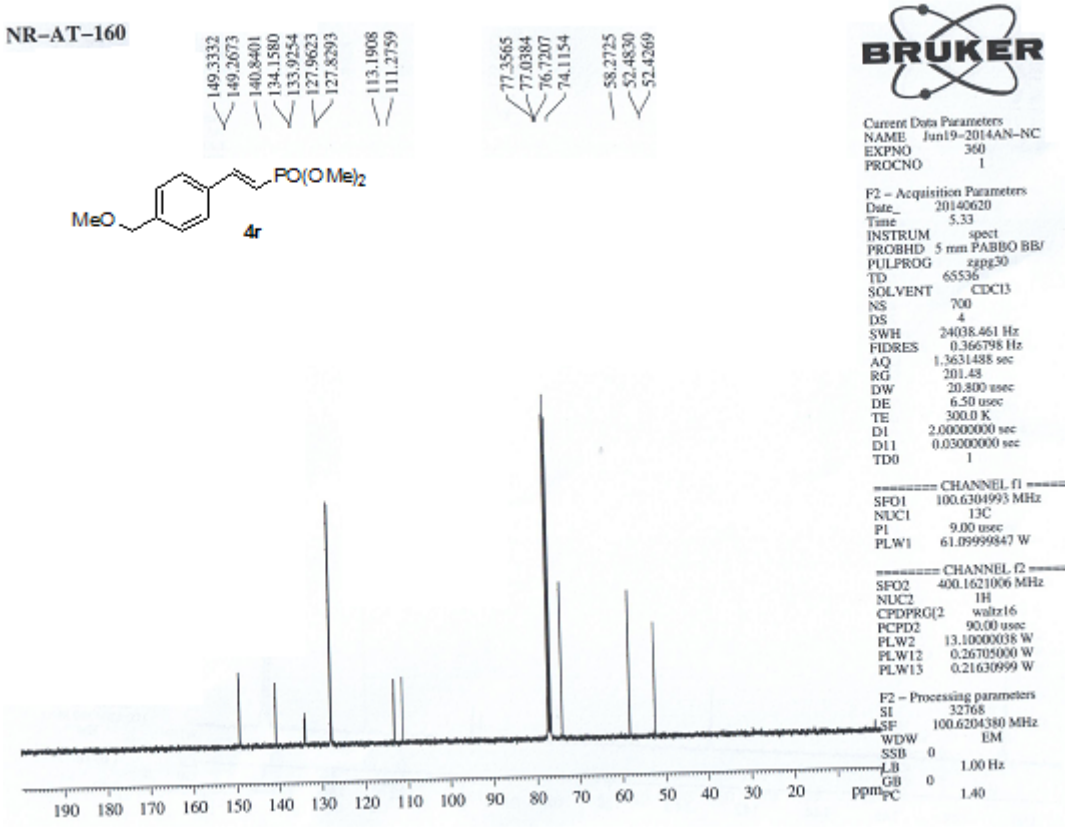


Figure 92: ^{13}C NMR spectrum of 4r

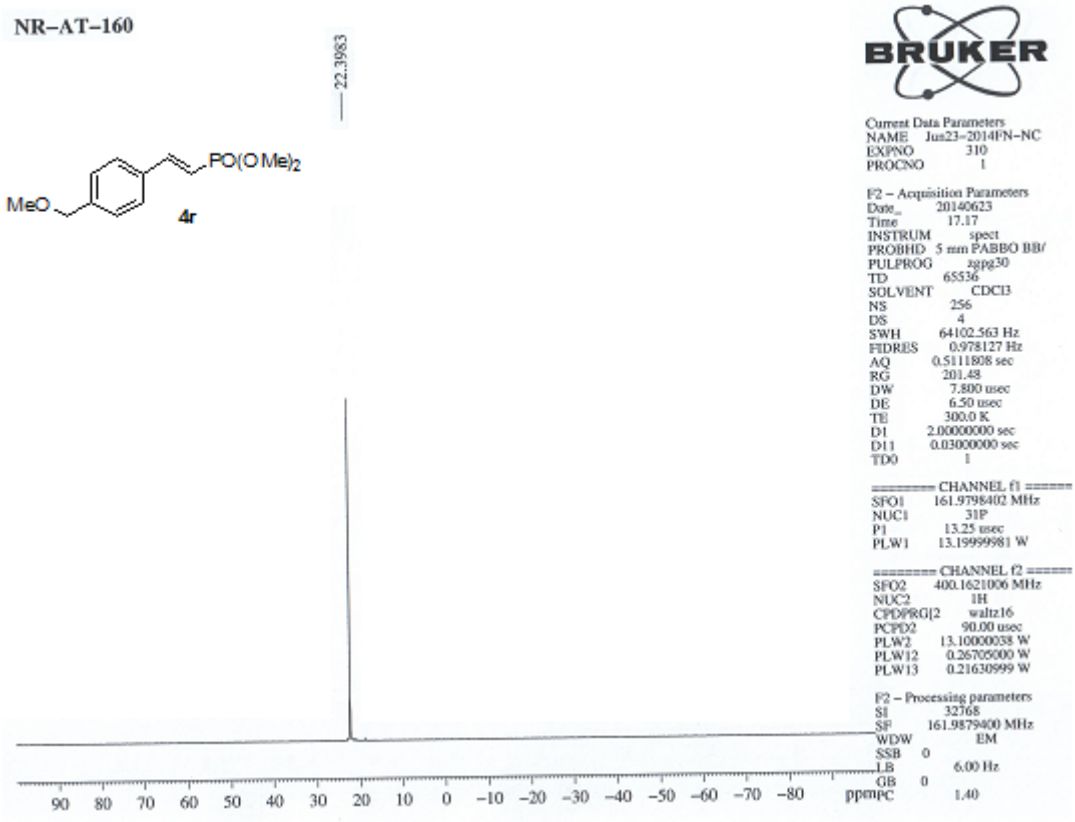


Figure 93: ^{31}P NMR spectrum of 4r

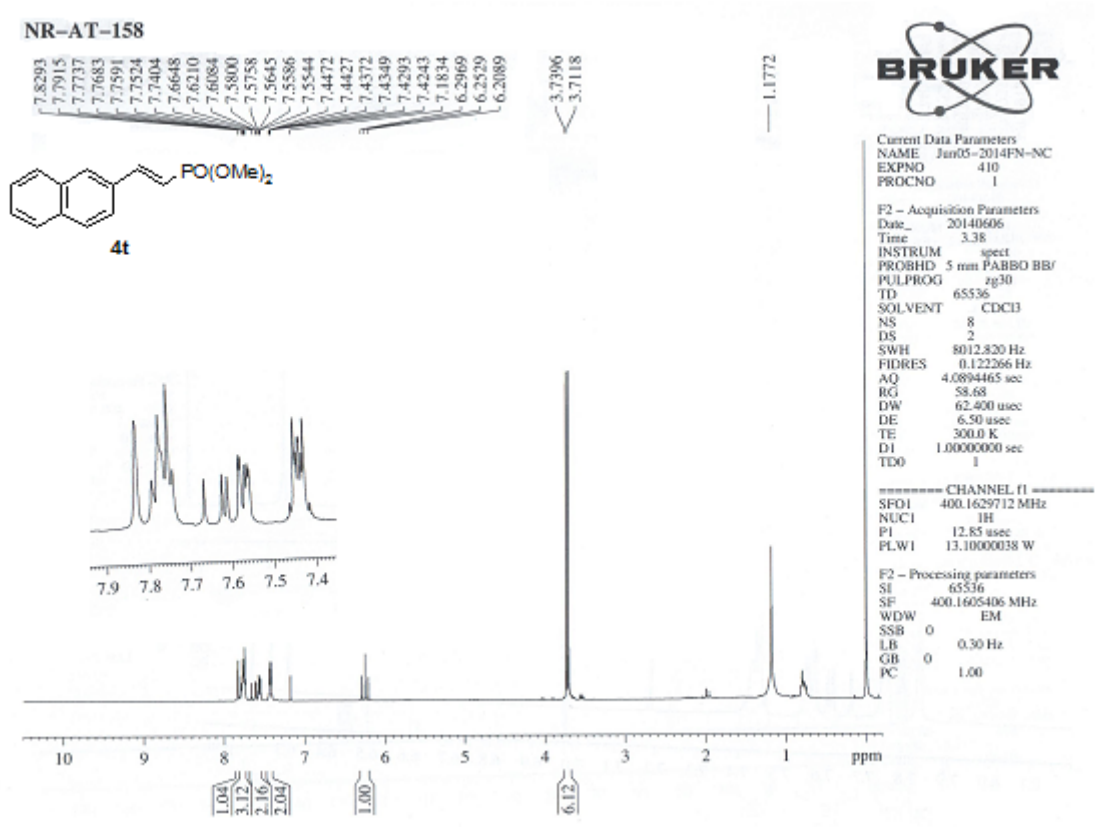


Figure 94: ^{1}H NMR spectrum of 4t

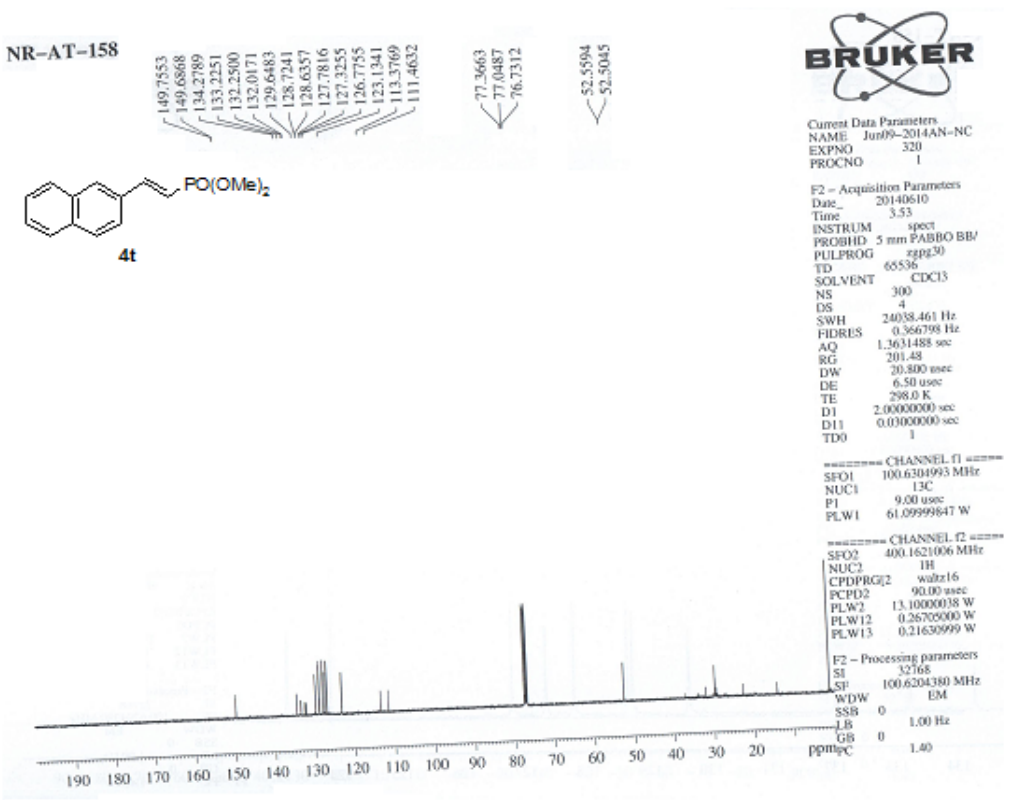


Figure 95: ^{13}C NMR spectrum of 4t

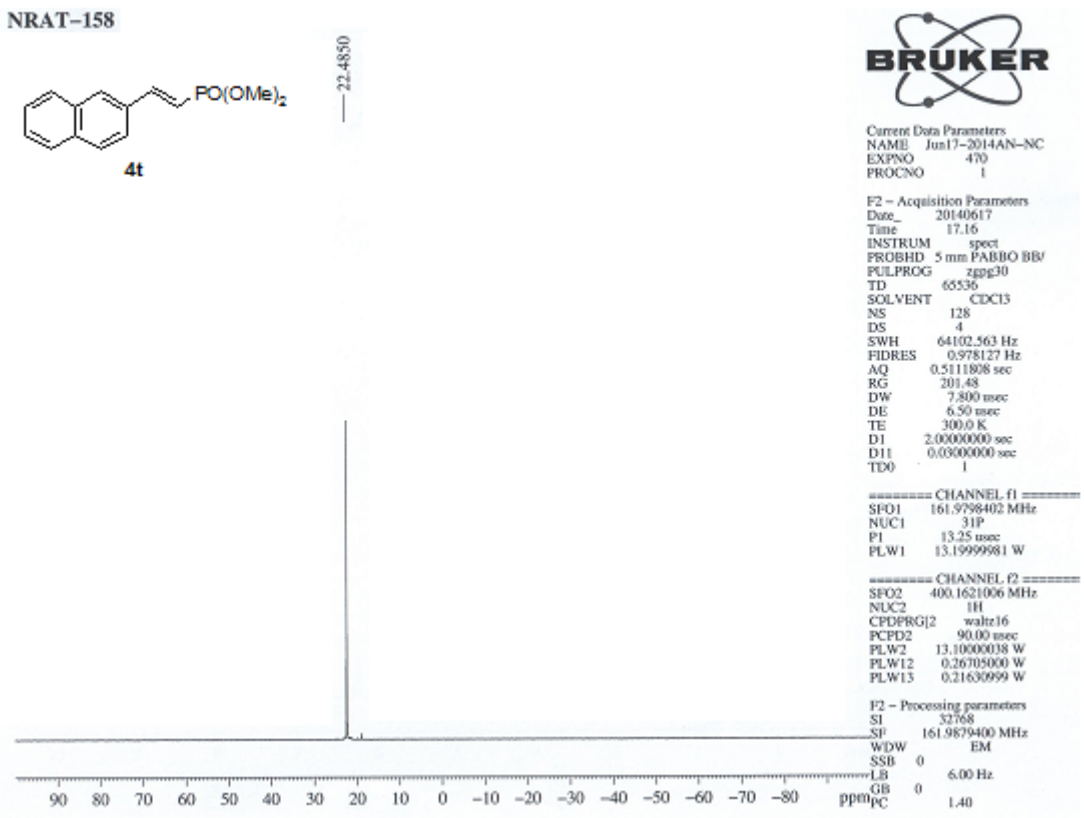


Figure 96: ^{31}P NMR spectrum of 4t

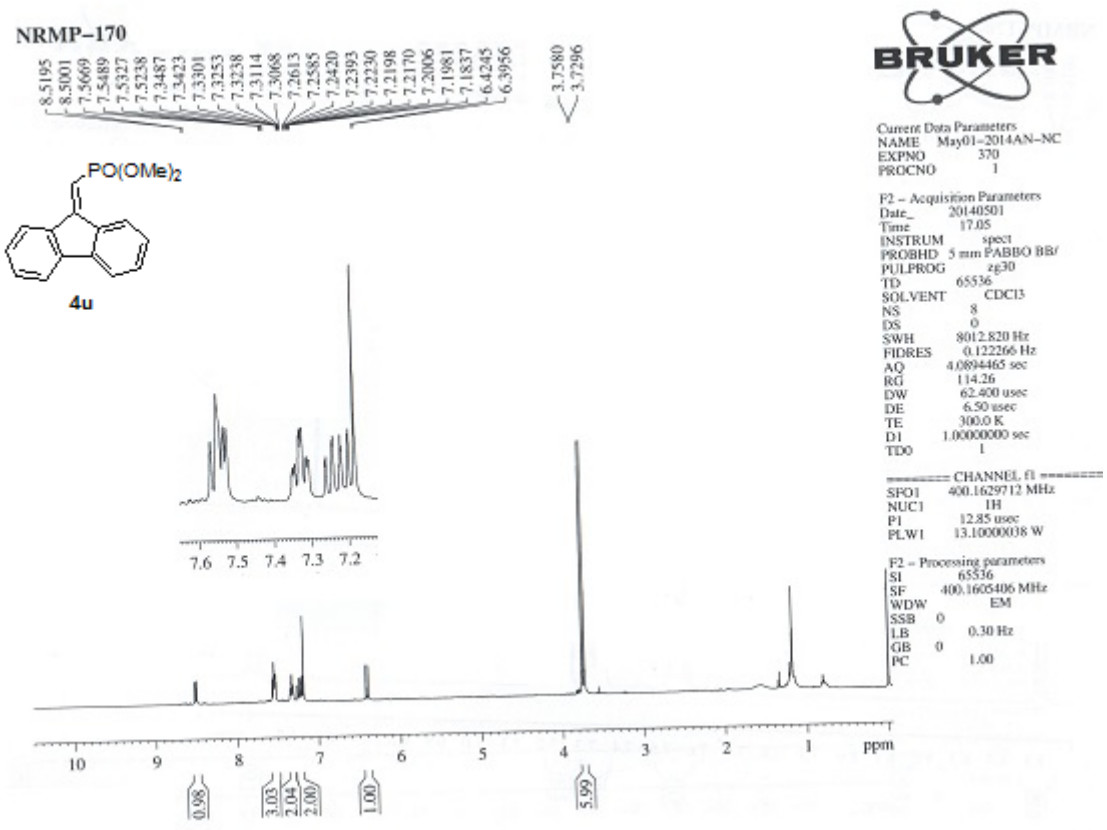


Figure 97: ^{1}H NMR spectrum of 4u

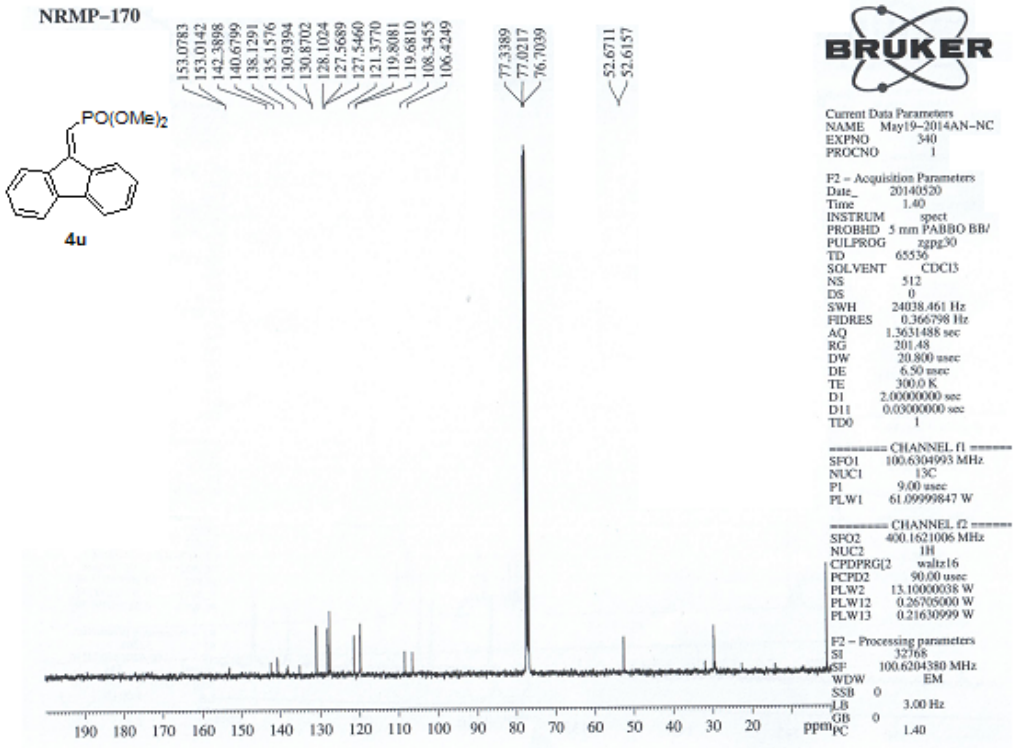


Figure 98: ^{13}C NMR spectrum of 4u

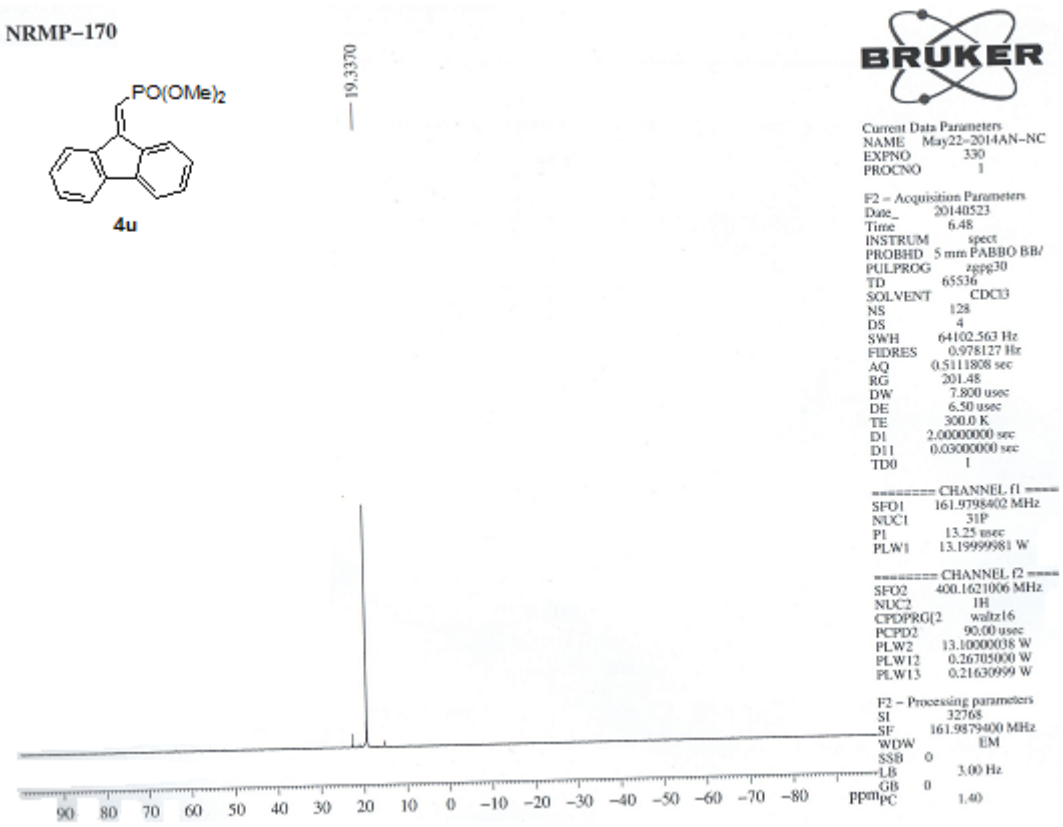


Figure 99: ^{31}P NMR spectrum of 4u

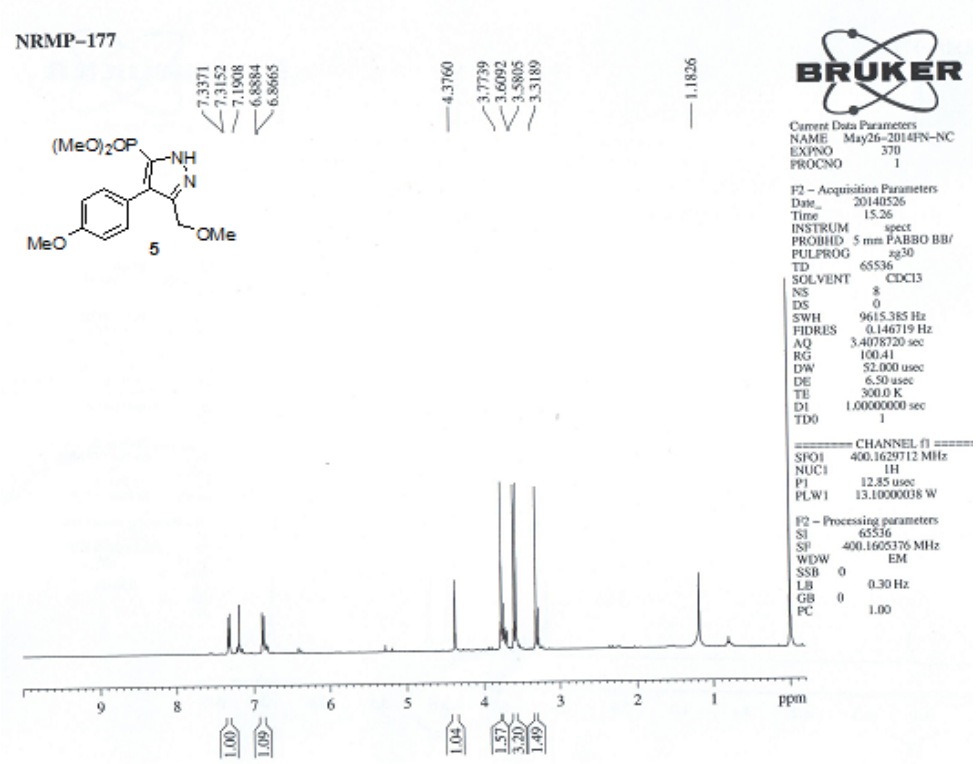


Figure 100: ^{1}H NMR spectrum of 5

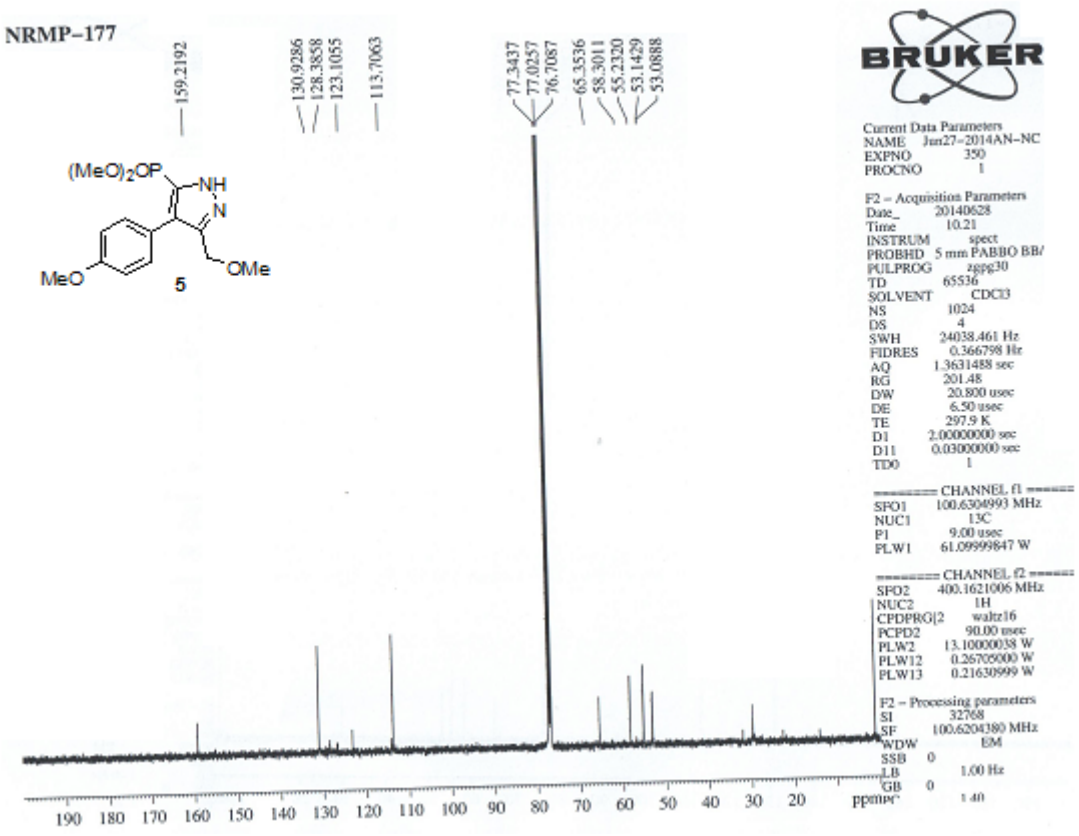


Figure 101: ^{13}C NMR spectrum of 5

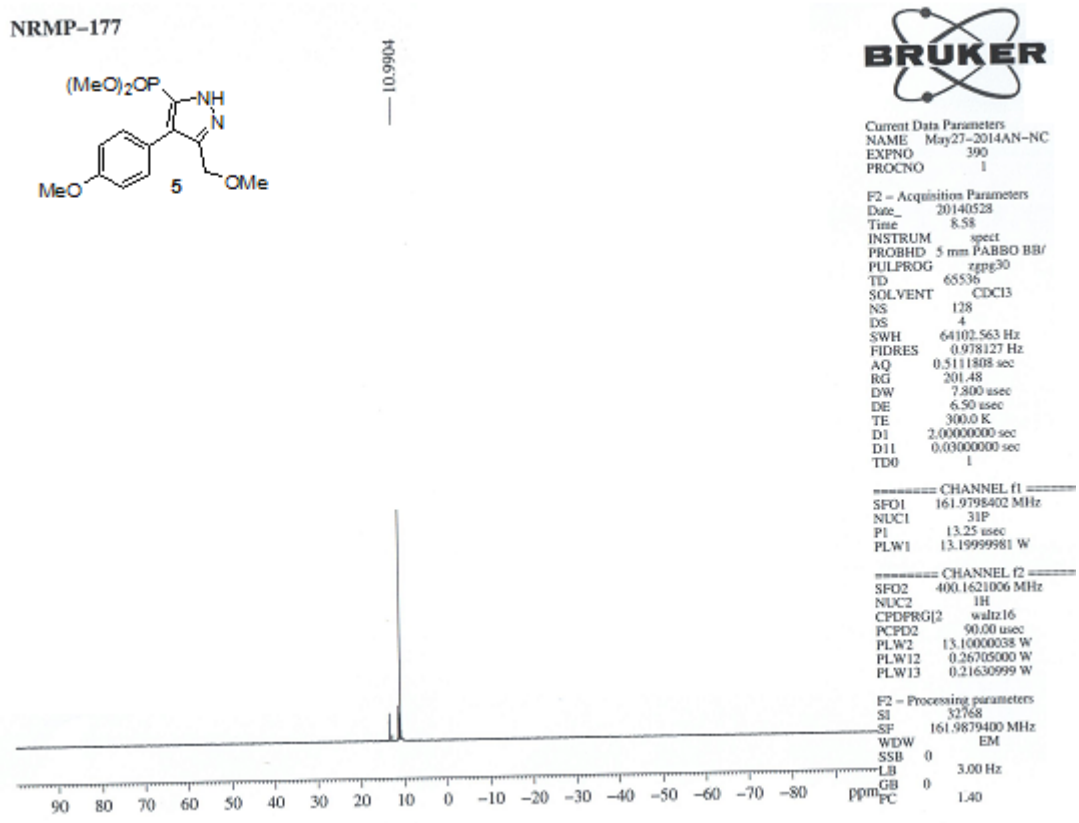


Figure 102: ^{31}P NMR spectrum of 5

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