

Supporting Information
For

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

Mukund M. D. Pramanik,^{a, b} Atul Kumar Chaturvedi,^{a, b} Namrata Rastogi*,^{a, b}

^aMedicinal & Process Chemistry Division, CSIR-Central Drug Research Institute, Sector 10, Jankipuram extension, Sitapur Road, P.O. Box 173, Lucknow 226031, India

^bAcademy of Scientific and Innovative Research, New Delhi 110001, India

namrataiit@gmail.com; namrata.rastogi@cdri.res.in

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Experimental Section

General

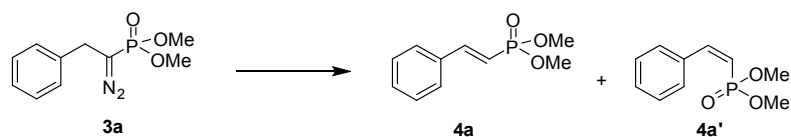
All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (Merck, 100-200 mesh). Melting points were recorded on a Precision melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer's RX I FTIR spectrophotometer. NMR spectra were recorded on a Bruker Avance spectrometer at 400 MHz (^1H), 100 MHz (^{13}C), and 162 MHz (^{31}P). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for ^1H 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-ToF LC/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 chromatography 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

^aratio of isomers assigned on the basis of crude ¹H NMR, ^bIntractable 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: BF₃OEt/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 BF₃OEt (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 NaHCO₃ 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 chromatography on silica gel using 0-60% hexane/ethyl acetate as eluent to afford the product **4a**.

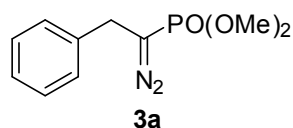
Condition 3: Cu powder mediated reaction

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 chromatography 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**

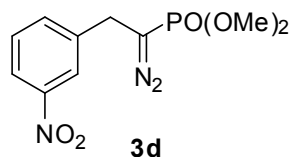
To a stirred solution of dimethyl diazoethylphosphonate **3** (1 mmol) in toluene (5 mL) was added Cu powder (6.3 mg, 10 mol %) and the reaction mixture was refluxed until the completion of the reaction (TLC monitoring). Toluene was distilled off under reduced pressure and crude residue was directly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

Dimethyl 1-diazo-2-phenylethylphosphonate (**3a**)⁵



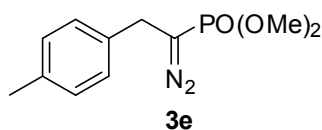
Yellow oil; isolated yield 87% (209 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2358, 2081, 1496, 1249, 1030; **^1H NMR** (400 MHz, CDCl_3) δ 7.24 – 7.28 (m, 2H), 7.17 – 7.21 (m, 3H), 3.63 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.36 (d, $J_{\text{H-P}} = 10.0$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 137.2 (d, $J_{\text{C-P}} = 3.1$ Hz, C_{Ar}), 128.8 ($\text{C}_{\text{ArH}} \times 2$), 128.3 ($\text{C}_{\text{ArH}} \times 2$), 127.2 (C_{ArH}), 52.8 (d, $J_{\text{C-P}} = 5.5$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 30.0 (d, $J_{\text{C-P}} = 8.6$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 24.19; **HRMS** for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_3\text{P}$: calcd. (MH^+): 241.0742, found: 241.0729

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



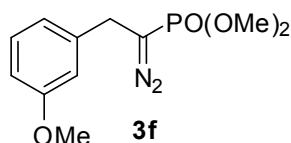
Yellow oil; isolated yield 80% (231 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2373, 2081, 1531, 1455, 1257, 1028; **^1H NMR** (400 MHz, CDCl_3) δ 8.03 – 8.06 (m, 2H), 7.53 – 7.55 (m, 1H), 7.42 – 7.46 (m, 1H), 3.65 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.48 (d, $J_{\text{H-P}} = 10.6$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 148.5 (C_{Ar}), 139.6 (C_{Ar} , $J_{\text{C-P}} = 2.1$ Hz), 134.4 (C_{ArH}), 129.8 (C_{ArH}), 123.1 (C_{ArH}), 122.3 (C_{ArH}), 53.1 (d, $J_{\text{C-P}} = 5.4$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 30.0 (d, $J_{\text{C-P}} = 8.7$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 23.12; **HRMS** for $\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}_5\text{P}$: calcd. (MH^+): 286.0593, found: 286.0578.

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



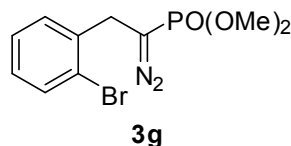
Yellow oil; isolated yield 78% (198 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2371, 2081, 1525, 1254, 1031; **^1H NMR** (400 MHz, CDCl_3) δ 7.07 (s, 4H), 3.64 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.32 (d, $J_{\text{H-P}} = 9.8$ Hz, 2H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 136.9 (C_{Ar}), 134.1 (d, $J_{\text{C-P}} = 2.3$ Hz, C_{Ar}), 129.5 ($\text{C}_{\text{Ar}}\text{H} \times 2$), 128.3 ($\text{C}_{\text{Ar}}\text{H} \times 2$), 52.9 (d, $J_{\text{C-P}} = 5.2$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 29.6 (d, $J_{\text{C-P}} = 8.9$ Hz, CH_2), 21.1 (CH_3); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 24.41; **HRMS** for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_3\text{P}$: calcd. (MH^+): 255.0899, found: 255.0891

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



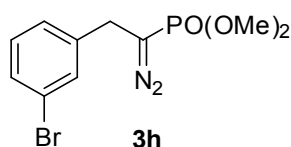
Yellow oil; isolated yield 79% (213 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2081, 1599, 1489, 1257, 1036; **^1H NMR** (400 MHz, CDCl_3) δ 7.16 – 7.20 (m, 1H), 6.73 – 6.77 (m, 3H), 3.73 (s, 3H), 3.64 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.33 (d, $J_{\text{H-P}} = 10.0$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 173.5 (CO), 159.9 (C_{Ar}), 138.8 (d, $J_{\text{C-P}} = 3.4$ Hz, C_{Ar}), 129.9 ($\text{C}_{\text{Ar}}\text{H}$), 120.6 ($\text{C}_{\text{Ar}}\text{H}$), 114.1 ($\text{C}_{\text{Ar}}\text{H}$), 112.6 ($\text{C}_{\text{Ar}}\text{H}$), 55.2 (OCH_3), 52.9 (d, $J_{\text{C-P}} = 5.3$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 30.1 (d, $J_{\text{C-P}} = 8.5$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 24.29; **HRMS** for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_4\text{P}$: calcd. (MH^+): 271.0848, found: 271.0839.

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



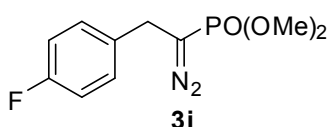
Yellow oil; isolated yield 76% (241 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2373, 1603, 1248, 1034; **^1H NMR** (400 MHz, CDCl_3) δ 7.50 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.20 – 7.26 (m, 2H), 7.04 – 7.08 (m, 1H), 3.59 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.52 (d, $J_{\text{H-P}} = 10.1$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 136.6 (d, $J_{\text{C-P}} = 2.8$ Hz, C_{Ar}), 133.1 ($\text{C}_{\text{Ar}}\text{H}$), 130.9 ($\text{C}_{\text{Ar}}\text{H}$), 128.9 ($\text{C}_{\text{Ar}}\text{H}$), 127.7 ($\text{C}_{\text{Ar}}\text{H}$), 124.4 (C_{Ar}), 52.9 (d, $J_{\text{C-P}} = 5.2$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 30.7 (d, $J_{\text{C-P}} = 8.9$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 23.88; **HRMS** for $\text{C}_{10}\text{H}_{12}\text{BrN}_2\text{O}_3\text{P}$: calcd. (MH^+): 318.9847, found: 318.9836.

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



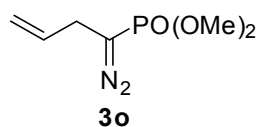
Yellow oil; isolated yield 75% (238 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2371, 1617, 1455, 1250, 1032; **^1H NMR** (400 MHz, CDCl_3) δ 7.32 – 7.34 (m, 2H), 7.10 – 7.16 (m, 2H), 3.64 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.33 (d, $J_{\text{H-P}} = 10.3$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 175.4 ($\text{C}=\text{N}_2$), 139.5 (d, $J_{\text{C-P}} = 2.0$ Hz, C_{Ar}), 131.3 (C_{ArH}), 130.3 ($\text{C}_{\text{ArH}} \times 2$), 126.9 (C_{ArH}), 122.7 (C_{Ar}), 53.0 (d, $J_{\text{C-P}} = 5.2$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 29.6 (d, $J_{\text{C-P}} = 8.7$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 23.68; **HRMS** for $\text{C}_{10}\text{H}_{12}\text{BrN}_2\text{O}_3\text{P}$: calcd. (MH^+): 318.9847, found: 318.9853.

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



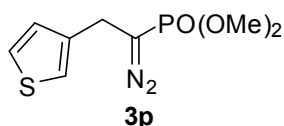
Yellow oil; isolated yield 78% (201 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2369, 1602, 1230, 1035; **^1H NMR** (400 MHz, CDCl_3) δ 7.12 – 7.16 (m, 2H), 6.91 – 6.96 (m, 2H), 3.62 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.33 (d, $J_{\text{H-P}} = 10.1$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 161.9 (d, $J_{\text{C-F}} = 244.1$ Hz, C_{ArF}), 132.9 (dd appearing as t, $J_{\text{C-P}} = 3.3$ Hz, $J_{\text{C-F}} = 3.2$ Hz, C_{Ar}), 129.9 (C_{ArH}), 129.8 (C_{ArH}), 115.7 (C_{ArH}), 115.5 (C_{ArH}), 52.8 (d, $J_{\text{C-P}} = 5.3$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 29.3 (d, $J_{\text{C-P}} = 8.5$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 23.89; **HRMS** for $\text{C}_{10}\text{H}_{12}\text{FN}_2\text{O}_3\text{P}$: calcd. (MH^+): 259.0648, found: 259.0643.

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



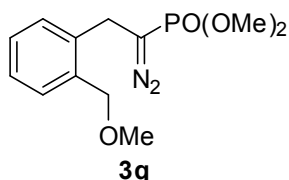
Yellow oil; isolated yield 76% (144 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2084, 1252, 1035; **^1H NMR** (400 MHz, CDCl_3) δ 5.67 – 5.77 (m, 1H), 5.05 – 5.10 (m, 2H), 3.65 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 2.73 – 2.77 (m, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 132.5 (d, $J_{\text{C-P}} = 3.1$ Hz, CH), 117.8 ($\delta\text{-CH}_2$), 52.9 (d, $J_{\text{C-P}} = 5.6$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 28.0 (d, $J_{\text{C-P}} = 8.3$ Hz, $\beta\text{-CH}_2$); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 21.46; **HRMS** for $\text{C}_6\text{H}_{11}\text{N}_2\text{O}_3\text{P}$: calcd. (MH^+): 191.0586, found: 191.0580

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



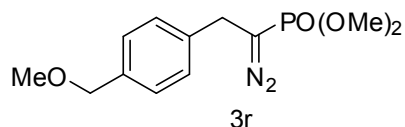
Yellow oil; isolated yield 78% (192 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2374, 1458, 1247, 1034; **^1H NMR** (400 MHz, CDCl_3) δ 7.23 (dd, $J = 4.9$ Hz, $J = 3.0$ Hz, 1H), 7.02 (t, $J = 0.8$ Hz, 1H), 6.93 (dd, $J = 4.9$ Hz, $J = 1.2$ Hz, 1H), 3.63 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.38 (d, $J_{\text{H-P}} = 9.9$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 137.5 (d, $J_{\text{C-P}} = 3.4$ Hz, C_{Ar}), 127.6 (C_{ArH}), 126.6 (C_{ArH}), 122.2 (C_{ArH}), 52.9 (d, $J_{\text{C-P}} = 5.5$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 24.8 (d, $J_{\text{C-P}} = 8.8$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 24.06; **HRMS** for $\text{C}_8\text{H}_{11}\text{N}_2\text{O}_3\text{PS}$: calcd. (MH^+): 247.0306, found: 247.0301.

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



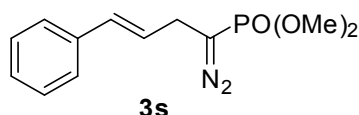
Yellow oil; isolated yield 86% (244 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2370, 1617, 1249, 1032; **^1H NMR** (400 MHz, CDCl_3) δ 7.19 – 7.26 (m, 4H), 4.41 (s, 2H), 3.63 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.46 (d, $J_{\text{H-P}} = 9.3$ Hz, 2H), 3.30 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 136.1 (C_{Ar}), 135.8 (d, $J_{\text{C-P}} = 3.4$ Hz, C_{Ar}), 129.9 (C_{ArH}), 129.8 (C_{ArH}), 128.5 (C_{ArH}), 127.4 (C_{ArH}), 72.9 (CH_2), 58.1 (OCH_3), 52.9 (d, $J_{\text{C-P}} = 5.3$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 26.5 (CH_2 , $J_{\text{C-P}} = 8.8$ Hz); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 24.44; **HRMS** for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_4\text{P}$: calcd. (MH^+): 285.1004, found: 285.0995.

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



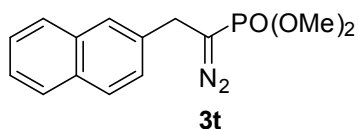
Yellow oil; isolated yield 88% (250 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2370, 1654, 1247, 1036; **^1H NMR** (400 MHz, CDCl_3) δ 7.23 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.1$ Hz, 2H), 4.36 (s, 2H), 3.63 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.35 (d, $J_{\text{H-P}} = 10.0$ Hz, 2H), 3.30 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 137.3 (C_{Ar}), 136.6 (d, $J_{\text{C-P}} = 3.1$ Hz, C_{Ar}), 128.4 ($\text{C}_{\text{ArH}} \times 2$), 128.2 ($\text{C}_{\text{ArH}} \times 2$), 74.3 (CH_2), 58.1 (OCH_3), 52.9 (d, $J_{\text{C-P}} = 5.3$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 29.7 (CH_2 , $J_{\text{C-P}} = 8.6$ Hz); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 24.28; **HRMS** for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_4\text{P}$: calcd. (MH^+): 285.1004, found: 285.0998.

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



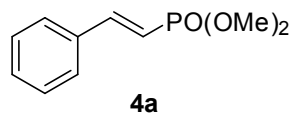
Yellow oil; isolated yield 79% (210 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2369, 1456, 1250, 1035; **^1H NMR** (400 MHz, CDCl_3) δ 7.20 – 7.28 (m, 4H), 7.13 – 7.17 (m, 1H), 6.42 (d, $J_{\text{H-P}} = 15.7$ Hz, 1H), 6.05 – 6.13 (m, 1H), 3.68 (d, $J_{\text{H-P}} = 11.6$ Hz, 6H), 2.91 – 2.95 (m, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 136.6 (C_{Ar}), 132.9 (C_{aliH}), 128.6 ($\text{C}_{\text{ArH}} \times 2$), 127.8 (C_{ArH}), 126.3 ($\text{C}_{\text{ArH}} \times 2$), 124.1 (d, $J_{\text{C-P}} = 3.1$ Hz, C_{aliH}), 53.0 (d, $J_{\text{C-P}} = 5.2$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 27.6 (d, $J_{\text{C-P}} = 8.6$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 24.24; **HRMS** for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}_3\text{P}$: calcd. (MH^+): 267.0899, found: 267.0879.

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



Yellow oil; isolated yield 87% (252 mg). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2373, 1687, 1339, 1238, 1037; **^1H 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, $J_{\text{H-P}} = 11.6$ Hz, 6H), 3.52 (d, $J_{\text{H-P}} = 10.0$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 134.7 (d, $J_{\text{C-P}} = 3.2$ Hz, C_{Ar}), 133.5 (C_{Ar}), 132.6 (C_{Ar}), 128.8 (C_{ArH}), 127.7 (C_{ArH}), 127.6 (C_{ArH}), 126.9 (C_{ArH}), 126.5 (C_{ArH}), 126.4 (C_{ArH}), 125.9 (C_{ArH}), 53.0 (d, $J_{\text{C-P}} = 4.9$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 30.3 (d, $J_{\text{C-P}} = 8.6$ Hz, CH_2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 24.15; **HRMS** for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_3\text{P}$: calcd. (MH^+): 291.0899, found: 291.0893.

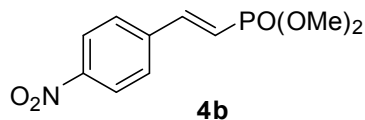
(E)-Dimethyl styrylphosphonate (4a)⁶



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

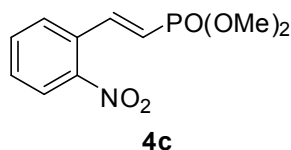
{PO}OCH₃ x 2); **³¹P NMR** (161.9 MHz, CDCl₃) δ 22.41; **HRMS** for C₁₀H₁₃O₃P, calcd (MH⁺): 213.0681, found: 213.0689.

(E)-Dimethyl 4-nitrostyrylphosphonate (4b)⁷



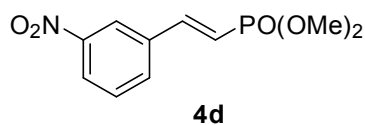
Yellow solid; isolated yield 85% (218 mg). *R_f* 0.30 (70% EtOAc/hexane); Mp 97-100 °C; **IR** (Film, cm⁻¹): 1526, 1217, 1038; **¹H NMR** (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J*_{H-P} = 22.2 Hz, *J* = 17.7 Hz, 1H), 6.31 (dd appearing as t, *J*_{H-P} = 17.0 Hz, *J* = 17.0 Hz, 1H), 3.71 (d, *J*_{H-P} = 11.1 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 148.6 (C_{Ar}), 146.4 (d, *J*_{C-P} = 6.0 Hz, β-CH), 140.6 (d, *J*_{C-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-P} = 190.1 Hz, α-CH), 52.6 (d, *J*_{C-P} = 5.1 Hz, {PO}OCH₃ x 2); **³¹P NMR** (161.9 MHz, CDCl₃) δ 20.01; **HRMS** for C₁₀H₁₂NO₅P, calcd (MH⁺): 258.0531, found: 258.0526.

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



Colorless oil; isolated yield 88% (226 mg). *R_f* 0.30 (70% EtOAc/hexane); **IR** (Film, cm⁻¹): 2371, 1525, 1347, 1252, 1030; **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.4 Hz, 1H), 7.81 (dd appearing as t, *J*_{H-P} = 20.9 Hz, *J* = 18.1 Hz, 1H), 7.47 – 7.59 (m, 3H), 6.11 (dd appearing as t, *J*_{H-P} = 17.7 Hz, *J* = 17.4 Hz, 1H), 3.75 (d, *J*_{H-P} = 10.9 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 147.9 (C_{Ar}), 144.6 (d, *J*_{C-P} = 7.8 Hz, β-CH), 133.7 (C_{Ar}H), 131.5 (d, *J*_{C-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-P} = 188.8 Hz, α-CH), 52.8 (d, *J*_{C-P} = 5.6 Hz, {PO}OCH₃ x 2); **³¹P NMR** (161.9 MHz, CDCl₃) δ 19.20; **HRMS** for C₁₀H₁₂NO₅P, calcd (MH⁺): 258.0531, found: 258.0534.

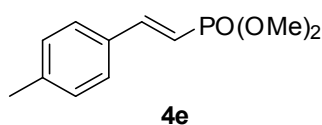
(E)-Dimethyl 3-nitrostyrylphosphonate (4d)



Colorless oil; isolated yield 88% (226 mg). *R_f* 0.30 (70% EtOAc/hexane); **IR** (Film, cm⁻¹): 2402, 1532, 1035, 909; **¹H NMR** (400 MHz, CDCl₃) δ 8.30 (t, *J*_{H-P} = 1.7 Hz, 1H), 8.16 (dd, *J*

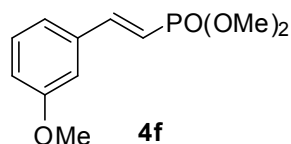
= 8.2 Hz, $J = 1.3$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.44 – 7.54 (m, 2H), 6.32 (dd, $J_{\text{H-P}} = 16.4$ Hz, $J = 17.5$ Hz, 1H), 3.73 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.5 (d, $J_{\text{C-P}} = 6.7$ Hz, β -CH), 146.4 (C_{Ar}), 136.4 (d, $J_{\text{C-P}} = 23.8$ Hz, C_{Ar}), 133.5 (C_{ArH}), 130.0 (C_{ArH}), 124.7 (C_{ArH}), 122.0 (C_{ArH}), 116.6 (d, $J_{\text{C-P}} = 190.5$ Hz, α -CH), 52.7 (d, $J_{\text{C-P}} = 5.7$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); ^{31}P NMR (161.9 MHz, CDCl_3) δ 20.3; HRMS for $\text{C}_{10}\text{H}_{12}\text{NO}_5\text{P}$, calcd (MH^+): 258.0531, found: 258.0530.

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



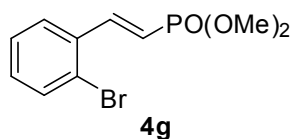
Colorless oil; isolated yield 98% (221 mg). R_f 0.30 (70% EtOAc/hexane); IR (Film, cm^{-1}): 1216, 1156, 1035, 867; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (dd, $J_{\text{H-P}} = 22.6$ Hz, $J = 17.6$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.08 (t, $J_{\text{H-P}} = 17.8$ Hz, 1H), 3.69 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.7 (d, $J_{\text{C-P}} = 6.7$ Hz, β -CH), 140.9 (C_{Ar}), 132.0 (d, $J_{\text{C-P}} = 23.5$ Hz, C_{Ar}), 129.6 ($\text{C}_{\text{ArH}} \times 2$), 127.8 ($\text{C}_{\text{ArH}} \times 2$), 110.9 (d, $J_{\text{C-P}} = 192.1$ Hz, α -CH), 52.4 (d, $J_{\text{C-P}} = 5.4$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$), 21.4 (CH_3); ^{31}P NMR (161.9 MHz, CDCl_3) δ 22.92; HRMS for $\text{C}_{11}\text{H}_{15}\text{O}_3\text{P}$, calcd (MH^+): 228.0837, found: 228.0830.

(E)-Dimethyl 3-methoxystyrylphosphonate (4f)⁸



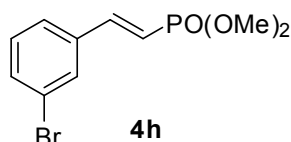
Colorless oil; isolated yield 96% (232 mg). R_f 0.30 (70% EtOAc/hexane); IR (Film, cm^{-1}): 1216, 1156, 1034, 836; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (dd, $J_{\text{H-P}} = 22.5$ Hz, $J = 17.5$ Hz, 1H), 7.21 (t, $J = 7.9$ Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 6.94 (t, $J = 2.1$ Hz, 1H), 6.85 (dd, $J = 8.2$ Hz, $J = 2.4$ Hz, 1H), 6.12 (t, $J_{\text{H-P}} = 17.6$ Hz, 1H), 3.74 (s, 3H), 3.69 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.9 (C_{Ar}), 149.5 (d, $J_{\text{C-P}} = 6.6$ Hz, β -CH), 136.1 (d, $J_{\text{C-P}} = 23.3$ Hz, C_{Ar}), 129.9 (C_{ArH}), 120.4 (C_{ArH}), 116.2 (C_{ArH}), 112.7 (C_{ArH}), 112.7 (d, $J_{\text{C-P}} = 190.9$ Hz, α -CH), 55.3 (OCH_3), 52.5 (d, $J_{\text{C-P}} = 5.4$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); ^{31}P NMR (161.9 MHz, CDCl_3) δ 22.22; HRMS for $\text{C}_{11}\text{H}_{15}\text{O}_4\text{P}$, calcd (MH^+): 243.0786, found: 243.0780.

(E)-Dimethyl 2-bromostyrylphosphonate (4g)⁹



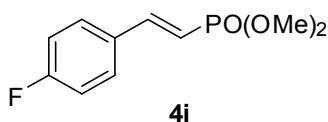
Colorless oil; isolated yield 95% (276 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2402, 1463, 1247, 1036; **^1H NMR** (400 MHz, CDCl_3) δ 7.75 (dd, $J_{\text{H-P}} = 22.5$ Hz, $J = 17.5$ Hz, 1H), 7.48 – 7.54 (m, 2H), 7.23 – 7.27 (m, 1H), 7.13 – 7.17 (m, 1H), 6.13 (t, $J_{\text{H-P}} = 17.8$ Hz, 1H), 3.72 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 147.5 (d, $J_{\text{C-P}} = 7.9$ Hz, β -CH), 134.9 (d, $J_{\text{C-P}} = 23.9$ Hz, C_{Ar}), 133.4 (C_{Ar} H), 131.3 (C_{Ar} H), 127.7 (C_{Ar} H), 127.6 (d, $J_{\text{C-P}} = 1.1$ Hz, C_{Ar} H), 124.9 (C_{Ar}), 116.1 (d, $J_{\text{C-P}} = 190.0$ Hz, α -CH), 52.7 (d, $J_{\text{C-P}} = 5.7$ Hz, {PO}OCH₃ x 2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 20.74; **HRMS** for $\text{C}_{10}\text{H}_{12}\text{BrO}_3\text{P}$, calcd (MH^+): 290.9786, found: 290.9785.

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



Colorless oil; isolated yield 91% (264 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1620, 1216, 1155, 1035, 856; **^1H 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, $J_{\text{H-P}} = 17.3$ Hz, 1H), 3.69 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 147.8 (d, $J_{\text{C-P}} = 7.0$ Hz, β -CH), 136.8 (d, $J_{\text{C-P}} = 23.6$ 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, $J_{\text{C-P}} = 190.7$ Hz, α -CH), 52.6 (d, $J_{\text{C-P}} = 5.6$ Hz, {PO}OCH₃ x 2); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 21.30; **HRMS** for $\text{C}_{10}\text{H}_{12}\text{BrO}_3\text{P}$, calcd (MH^+): 290.9786, found: 290.9785.

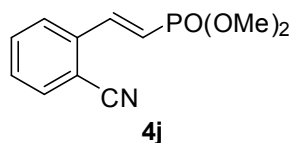
(E)-Dimethyl 4-fluorostyrylphosphonate (4i)



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); **^1H NMR** (400 MHz, CDCl_3) δ 7.34 – 7.44 (m, 3H), 6.98 (t, $J = 8.7$ Hz, 2H), 6.04 (t, $J_{\text{H-P}} = 17.5$ Hz, 1H), 3.68 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 163.9 (d, $J_{\text{C-F}} = 249.9$ Hz, C_{Ar} F), 148.3 (d, $J_{\text{C-P}} = 6.8$ Hz, β -CH), 130.9 (dd, $J_{\text{C-P}} = 23.9$ Hz, $J_{\text{C-F}} = 3.5$ 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, $J_{\text{C-P}} = 192.0$ Hz, $J_{\text{C-F}} = 2.2$ Hz, α -CH), 52.5

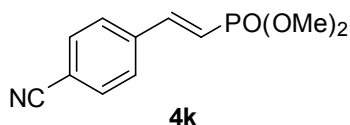
(d, $J_{\text{C-P}} = 5.7$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 22.15; **HRMS** for $\text{C}_{10}\text{H}_{12}\text{FO}_3\text{P}$, calcd (MH^+): 231.0586, found: 231.0582.

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



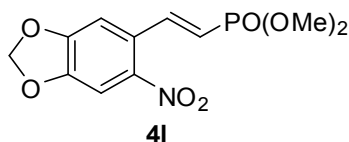
Colorless oil; isolated yield 86% (204 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2226, 1622, 1254, 1032; **^1H NMR** (400 MHz, CDCl_3) δ 7.61 – 7.70 (m, 3H), 7.54 – 7.58 (m, 1H), 7.39 – 7.43 (m, 1H), 6.43 (dd, $J_{\text{H-P}} = 17.5$ Hz, $J = 16.8$ Hz, 1H), 3.75 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 143.7 (d, $J_{\text{C-P}} = 6.7$ Hz, β -CH), 137.6 (d, $J_{\text{C-P}} = 23.7$ Hz, C_{Ar}), 133.5 (C_{ArH}), 133.0 (C_{ArH}), 130.1 (C_{ArH}), 127.1 (C_{ArH}), 118.8 (d, $J_{\text{C-P}} = 189.7$ Hz, α -CH), 117.0 (CN), 112.2 (C_{Ar}), 52.8 (d, $J_{\text{C-P}} = 5.7$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 19.46; **HRMS** for $\text{C}_{11}\text{H}_{12}\text{NO}_3\text{P}$: calcd. (MH^+): 238.0633, found: 238.0626.

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



Colorless oil; isolated yield 83% (197 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2370, 1596, 1347, 1247, 1032; **^1H 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, $J_{\text{H-P}} = 22.4$ Hz, $J = 17.6$ Hz, 1H), 6.25 (dd, $J_{\text{H-P}} = 17.5$ Hz, $J = 16.6$ Hz, 1H), 3.69 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 147.0 (d, $J_{\text{C-P}} = 6.7$ Hz, β -CH), 138.8 (d, $J_{\text{C-P}} = 23.5$ Hz, C_{Ar}), 132.7 ($\text{C}_{\text{ArH}} \times 2$), 128.1 ($\text{C}_{\text{ArH}} \times 2$), 118.3 (CN), 116.9 (d, $J_{\text{C-P}} = 190.3$ Hz, α -CH), 113.5 (C_{Ar}), 52.7 (d, $J_{\text{C-P}} = 5.6$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); **^{31}P NMR** (161.9 MHz, CDCl_3) δ 20.34; **HRMS** for $\text{C}_{11}\text{H}_{12}\text{NO}_3\text{P}$: calcd. (MH^+): 238.0633, found: 238.0628.

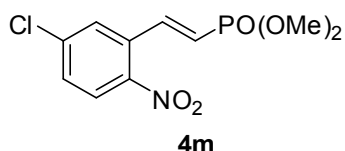
(E)-Dimethyl 2-(6-nitrobenzo[d][1,3]dioxol-5-yl)vinylphosphonate (4l)



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; **^1H NMR** (400 MHz, CDCl_3) δ 7.77 (dd, $J_{\text{H-P}} = 21.8$ Hz, $J = 17.3$ Hz, 1H), 7.46 (s, 1H), 6.87 (s, 1H), 6.08 (s, 2H), 5.98 (dd appearing as t, $J_{\text{H-P}} =$

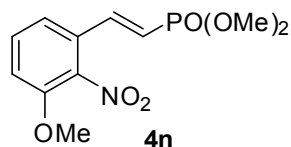
35.0 Hz, $J = 17.5$ Hz, 1H), 3.73 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.2 (C_{Ar}), 148.9 (C_{Ar}), 144.9 (d, $J_{\text{C-P}} = 8.3$ Hz, $\beta\text{-CH}$), 142.5 (C_{Ar}), 128.1 (d, $J_{\text{C-P}} = 25.2$ Hz, C_{Ar}), 117.4 (d, $J_{\text{C-P}} = 189.4$ Hz, $\alpha\text{-CH}$), 107.4 (C_{ArH}), 105.5 (C_{ArH}), 103.4 (CH_2), 52.7 (d, $J_{\text{C-P}} = 5.7$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); ^{31}P NMR (161.9 MHz, CDCl_3) δ 19.50; HRMS for $\text{C}_{11}\text{H}_{12}\text{NO}_7\text{P}$, calcd (MH^+): 302.0430, found: 302.0430.

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



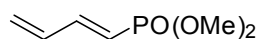
Colorless oil; isolated yield 80% (233mg). R_f 0.30 (70% EtOAc/hexane); IR (Film, cm^{-1}): 2358, 1496, 1247, 1029; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.8$ Hz, 1H), 7.78 (dd, $J_{\text{H-P}} = 21.8$ Hz, $J = 17.4$ Hz, 1H), 7.48 (d, $J = 2.2$ Hz, 1H), 7.43 (dd, $J = 8.8$ Hz, $J = 2.2$ Hz, 1H), 6.11 (dd appearing as t, $J_{\text{H-P}} = 17.3$ Hz, 1H), 3.74 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.8 (C_{Ar}), 143.5 (d, $J_{\text{C-P}} = 8.2$ Hz, $\beta\text{-CH}$), 140.3 (C_{Ar}), 133.3 (d, $J_{\text{C-P}} = 29.9$ Hz, C_{Ar}), 130.2 (C_{ArH}), 129.1 (C_{ArH}), 126.4 (C_{ArH}), 119.9 (d, $J_{\text{C-P}} = 188.6$ Hz, $\alpha\text{-CH}$), 52.8 (d, $J_{\text{C-P}} = 5.7$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); ^{31}P NMR (161.9 MHz, CDCl_3) δ 18.53; HRMS for $\text{C}_{10}\text{H}_{11}\text{ClNO}_5\text{P}$, calcd (MH^+): 292.0142, found: 292.0136.

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



Colorless oil; isolated yield 79% (227 mg). R_f 0.30 (70% EtOAc/hexane); IR (Film, cm^{-1}): 1536, 1386, 1217, 1058; ^1H NMR (400 MHz, CDCl_3) δ 7.34 (t, $J = 8.2$ Hz, 1H), 7.21 (dd, $J_{\text{H-P}} = 22.2$ 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, $J_{\text{H-P}} = 17.2$ Hz, 1H), 3.83 (s, 3H), 3.69 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.1 (C_{Ar}), 140.9 (d, $J_{\text{C-P}} = 7.2$ Hz, $\beta\text{-CH}$), 140.7 (C_{Ar}), 131.2 (C_{ArH}), 128.6 (d, $J_{\text{C-P}} = 24.3$ Hz, C_{Ar}), 119.6 (d, $J_{\text{C-P}} = 188.7$ Hz, $\alpha\text{-CH}$), 118.6 (C_{ArH} merged with $\alpha\text{-CH}$ peak), 113.8 (C_{ArH}), 56.6 (OCH_3), 52.8 (d, $J_{\text{C-P}} = 5.6$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); ^{31}P NMR (161.9 MHz, CDCl_3) δ 18.93; HRMS for $\text{C}_{11}\text{H}_{14}\text{NO}_6\text{P}$, calcd (MH^+): 288.0637, found: 288.0631.

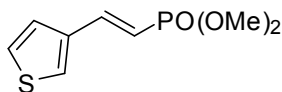
(E)-Dimethyl buta-1,3-dienylphosphonate (4o)¹⁰



4o

Colorless oil; isolated yield 85% (138 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 2241, 1585, 1245, 1035; **¹H 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, $J_{\text{H-P}} = 16.9$ Hz, 1H), 5.31 – 5.35 (m, 1H), 3.58 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); **¹³C NMR** (100 MHz, CDCl_3) δ 149.6 (d, $J_{\text{C-P}} = 5.8$ Hz, γ -CH), 135.4 (d, $J_{\text{C-P}} = 26.9$ Hz, β -CH), 125.2 (CH_2), 116.3 (d, $J_{\text{C-P}} = 190.0$ Hz, α -CH), 52.2 (d, $J_{\text{C-P}} = 5.6$ Hz, {PO}OCH₃ x 2); **³¹P NMR** (161.9 MHz, CDCl_3) δ 21.46; **HRMS** for $\text{C}_6\text{H}_{11}\text{O}_3\text{P}$, calcd (MH^+): 163.0524, found: 163.0522.

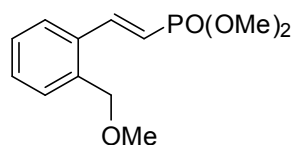
(E)-Dimethyl 2-(thiophen-3-yl)vinylphosphonate (4p)



4p

Colorless oil; isolated yield 95% (207 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1534, 1217, 1061; **¹H 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, $J_{\text{H-P}} = 17.8$ Hz, 1H), 3.69 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); **¹³C NMR** (100 MHz, CDCl_3) δ 143.2 (d, $J_{\text{C-P}} = 6.7$ Hz, β -CH), 138.2 (d, $J_{\text{C-P}} = 25.8$ Hz, C_{Ar}), 127.9 (C_{ArH}), 127.0 (C_{ArH}), 124.9 (C_{ArH}), 111.7 (d, $J_{\text{C-P}} = 191.9$ Hz, α -CH), 52.4 (d, $J_{\text{C-P}} = 5.4$ Hz, {PO}OCH₃ x 2); **³¹P NMR** (161.9 MHz, CDCl_3) δ 22.68; **HRMS** for $\text{C}_8\text{H}_{11}\text{O}_3\text{PS}$, calcd (MH^+): 219.0245, found: 219.0239.

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

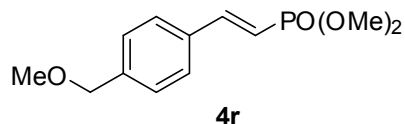


4q

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

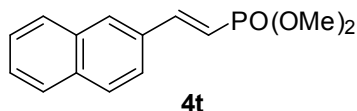
58.3 (OCH₃), 52.5 (d, $J_{\text{C-P}} = 5.4$ Hz, {PO}OCH₃ x 2); **³¹P NMR** (161.9 MHz, CDCl₃) δ 21.88; **HRMS** for C₁₂H₁₇O₄P: calcd. (MH⁺): 257.0943, found: 257.0937.

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



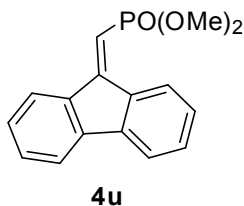
Colorless oil; isolated yield 96% (256 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm⁻¹): 2226, 1622, 1254, 1032; **¹H NMR** (400 MHz, CDCl₃) δ 7.38 – 7.48 (m, 3H), 7.27 (d, $J = 8.1$ Hz, 2H), 6.13 (t, $J_{\text{H-P}} = 17.7$ Hz, 1H), 4.39 (s, 2H), 3.69 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H), 3.31 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 149.3 (d, $J_{\text{C-P}} = 6.6$ Hz, β -CH), 140.8 (C_{Ar}), 134.0 (d, $J_{\text{C-P}} = 23.3$ Hz, C_{Ar}), 127.9 (C_{Ar}H x 2), 127.8 (C_{Ar}H x 2), 112.2 (d, $J_{\text{C-P}} = 191.5$ Hz, α -CH), 74.1 (CH₂), 58.3 (OCH₃), 52.5 (d, $J_{\text{C-P}} = 5.6$ Hz, {PO}OCH₃ x 2); **³¹P NMR** (161.9 MHz, CDCl₃) δ 22.40; **HRMS** for C₁₂H₁₇O₄P: calcd. (MH⁺): 257.0943, found: 257.0945.

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



Colorless oil; isolated yield 96% (251 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm⁻¹): 2925, 1216, 1155, 1061; **¹H NMR** (400 MHz, CDCl₃) 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, $J_{\text{H-P}} = 17.6$ Hz, 1H), 3.73 (d, $J_{\text{H-P}} = 11.1$ Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 149.7 (d, $J_{\text{C-P}} = 6.9$ Hz, β -CH), 134.3 (C_{Ar}), 133.2 (C_{Ar}), 132.1 (d, $J_{\text{C-P}} = 23.3$ 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, $J_{\text{C-P}} = 191.4$ Hz, α -CH), 52.5 (d, $J_{\text{C-P}} = 5.5$ Hz, {PO}OCH₃ x 2); **³¹P NMR** (161.9 MHz, CDCl₃) δ 22.49; **HRMS** for C₁₄H₁₆O₃P, calcd (MH⁺): 263.0837, found: 263.0830.

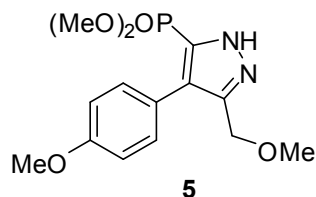
Dimethyl (9H-fluoren-9-ylidene)methylphosphonate (4u)



Colorless oil; isolated yield 85% (243 mg). R_f 0.30 (70% EtOAc/hexane); **IR** (Film, cm⁻¹): 1537, 1216, 1156, 1033, 929; **¹H NMR** (400 MHz, CDCl₃) 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, $J_{\text{H-P}} = 11.6$ Hz, 1H), 3.74 (d, $J_{\text{H-P}} = 11.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.0 (d, $J_{\text{C-P}} = 6.4$ Hz, $\beta\text{-CH}$), 142.4 (C_{Ar}), 140.7 (C_{Ar}), 138.1 (C_{Ar}), 135.2 (C_{Ar}), 130.9 (C_{ArH}), 130.8 (C_{ArH}), 128.1 (C_{ArH}), 127.6 (C_{ArH}), 127.5 (C_{ArH}), 121.4 (C_{ArH}), 119.8 (C_{ArH}), 119.7 (C_{ArH}), 107.4 (d, $J_{\text{C-P}} = 192.1$ Hz, $\alpha\text{-CH}$), 52.6 (d, $J_{\text{C-P}} = 5.5$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); ^{31}P NMR (161.9 MHz, CDCl_3) δ 19.34; HRMS for $\text{C}_{16}\text{H}_{15}\text{O}_3\text{P}$: calcd. (MH^+): 287.0837, found: 287.0838.

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



Colorless gummy solid; isolated yield 65% (243 mg). R_f 0.40 (90% EtOAc/hexane); IR (Film, cm^{-1}): 1219, 1252, 1035, 932; ^1H 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, $J_{\text{H-P}} = 11.5$ Hz, 6H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2 (C_{Ar}), 130.9 ($\text{C}_{\text{ArH}} \times 2$), 128.4 (C_{Ar}), 123.1 (C_{Ar}), 113.7 ($\text{C}_{\text{ArH}} \times 2$), 65.4 (CH_2), 58.3 (OCH_3), 55.2 (OCH_3), 53.1 (d, $J_{\text{C-P}} = 5.4$ Hz, $\{\text{PO}\}\text{OCH}_3 \times 2$); ^{31}P NMR (161.9 MHz, CDCl_3) δ 10.99; HRMS for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}_5\text{P}$: calcd. (MH^+): 327.1110, found: 327.1104.

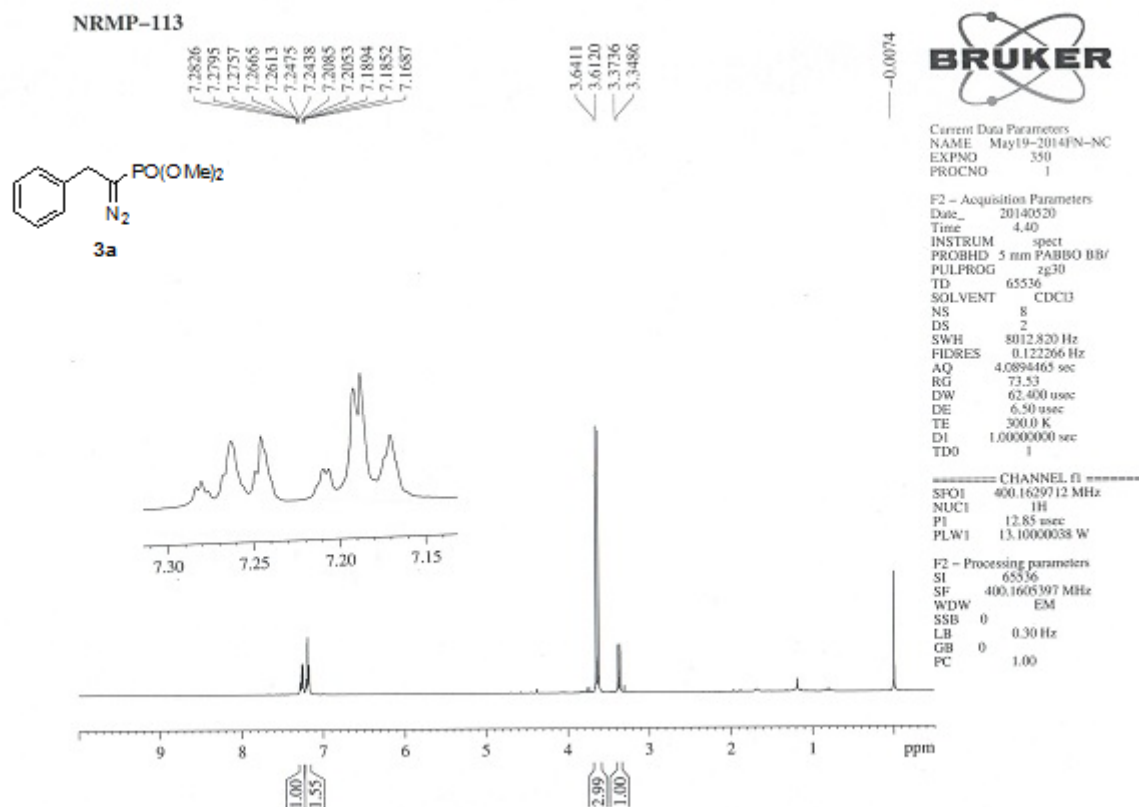


Figure 1: ^1H NMR spectrum of **3a**

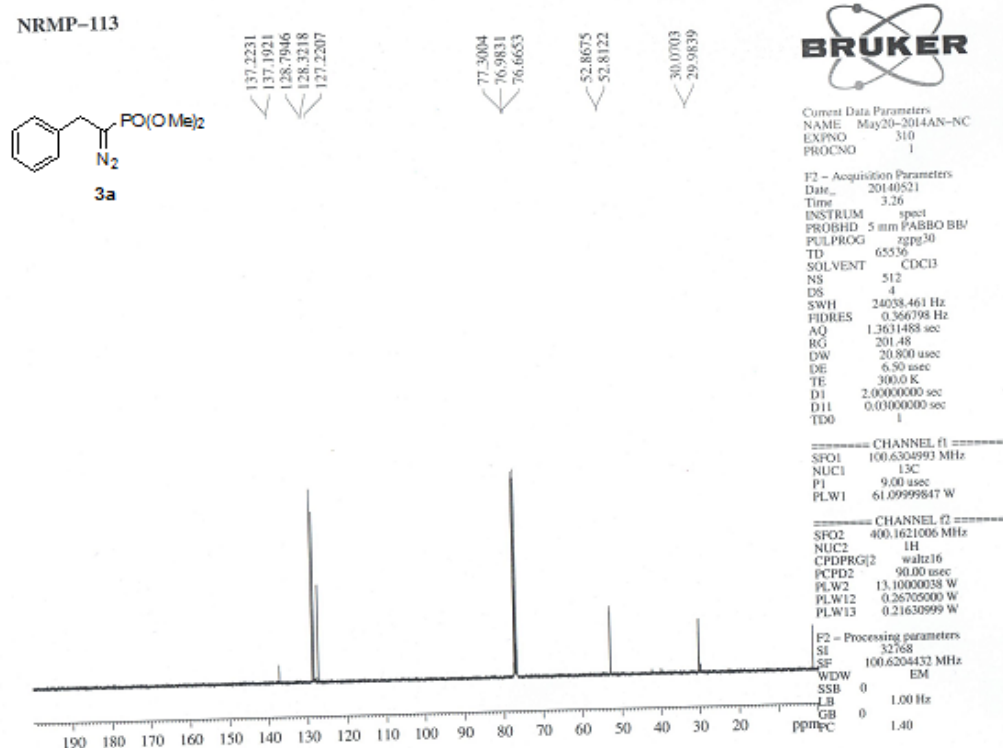
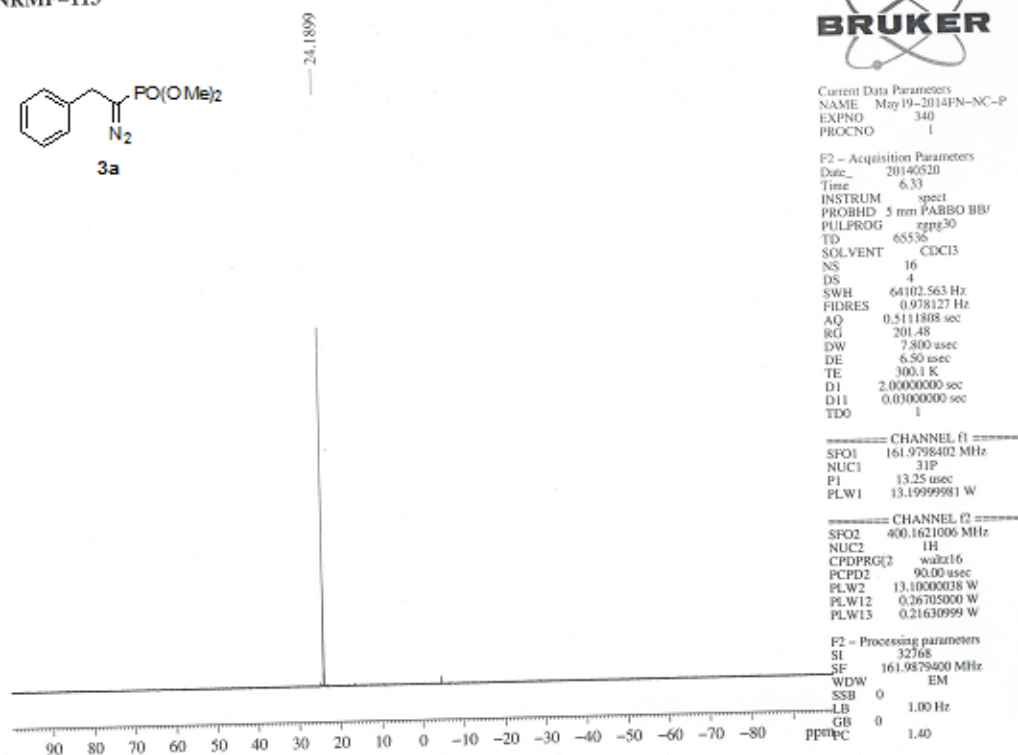
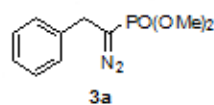
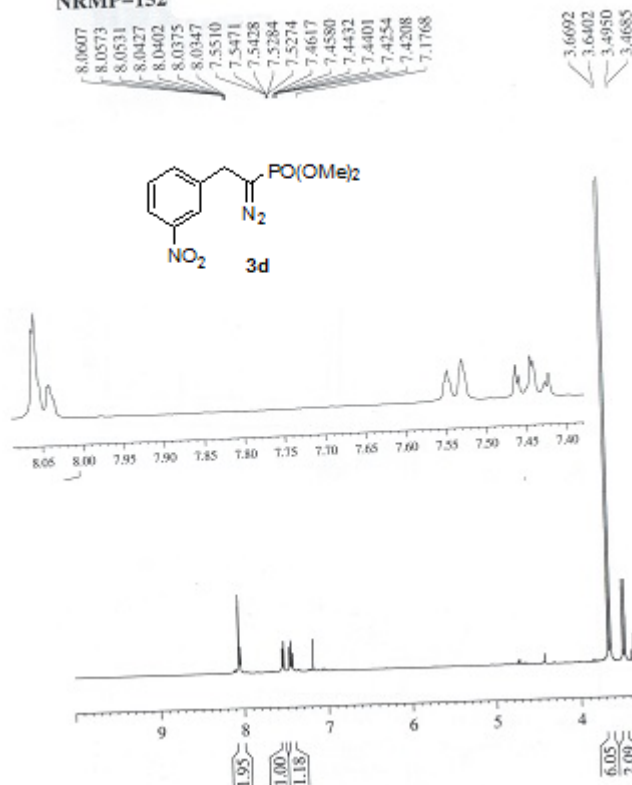


Figure 2: ^{13}C NMR spectrum of **3a**

NRMP-113

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

NRMP-152

Figure 4: ^1H NMR spectrum of 3d

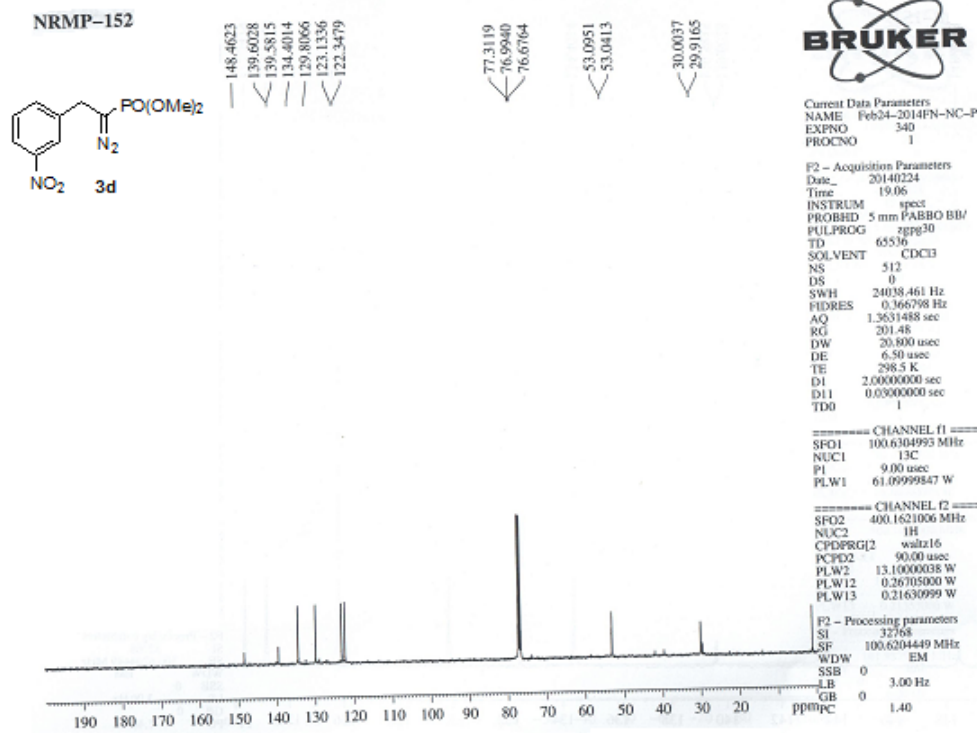


Figure 5: ¹³C NMR spectrum of 3d

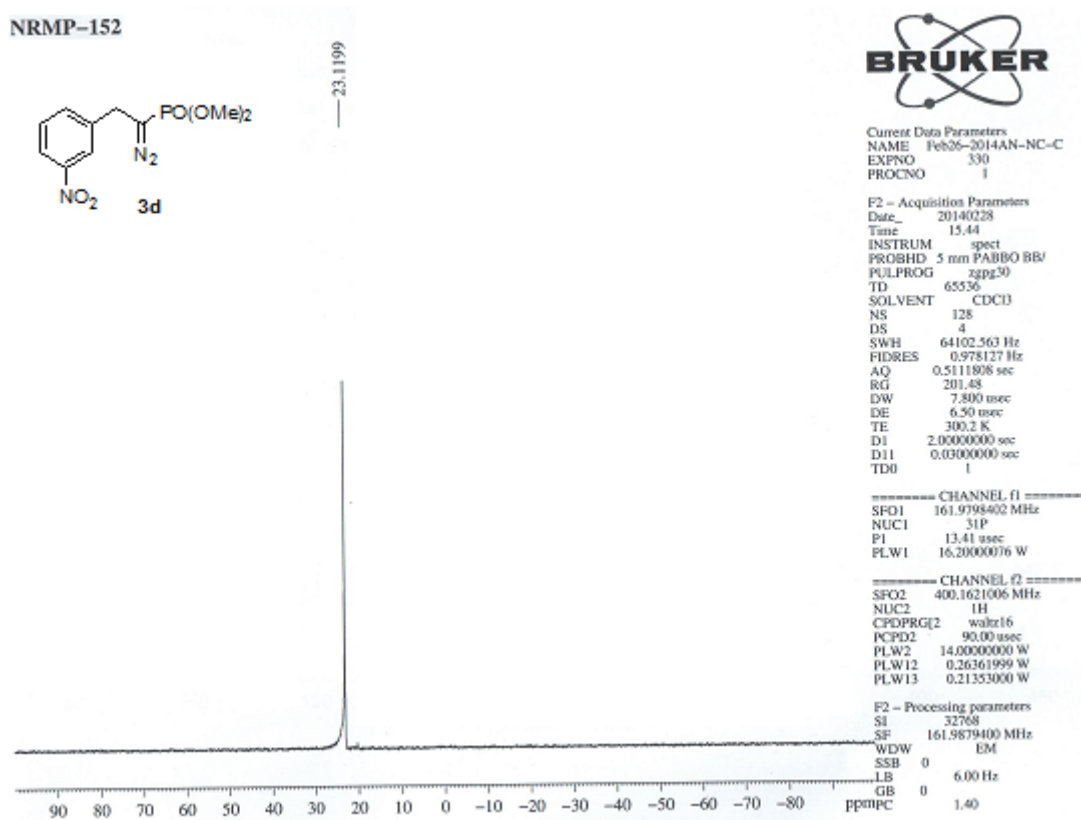


Figure 6: ³¹P NMR spectrum of 3d

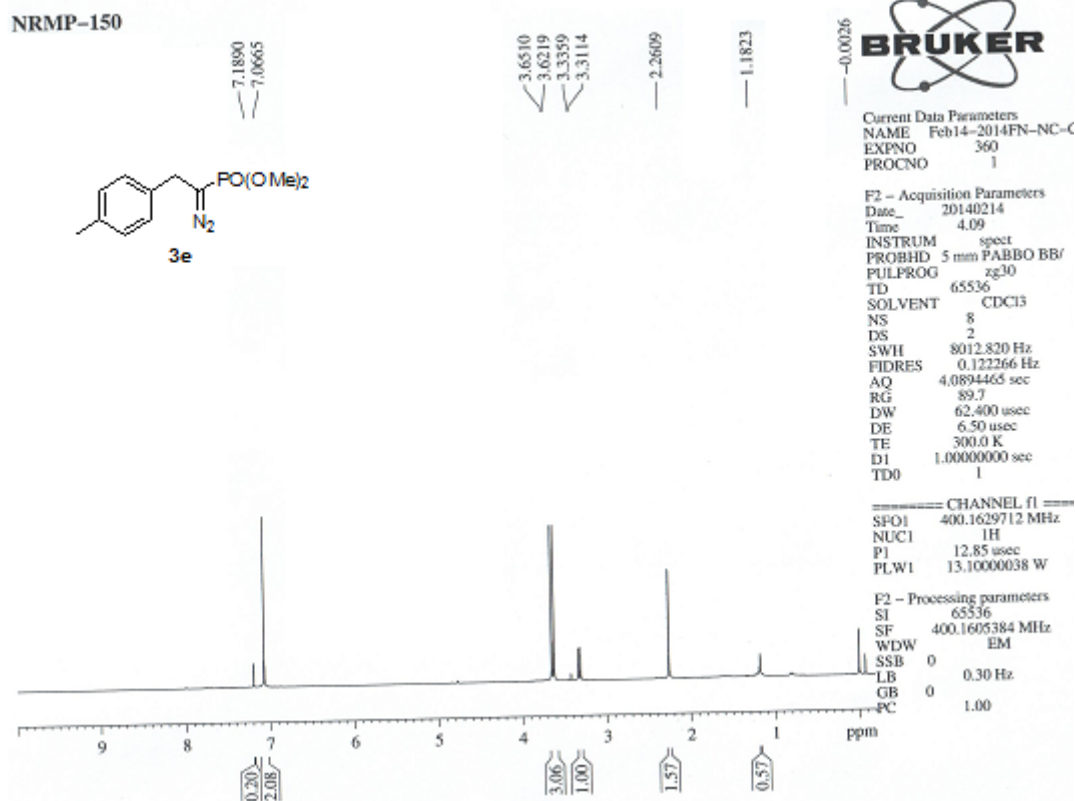


Figure 7: ¹H NMR spectrum of **3e**

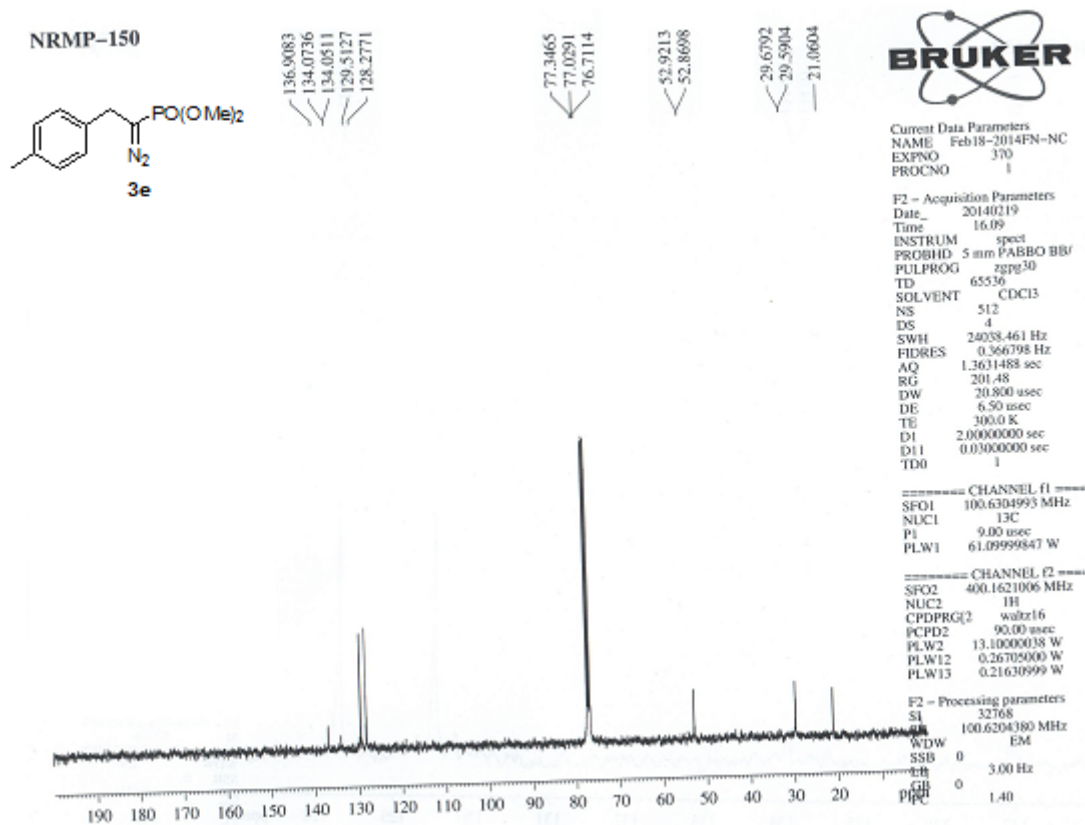
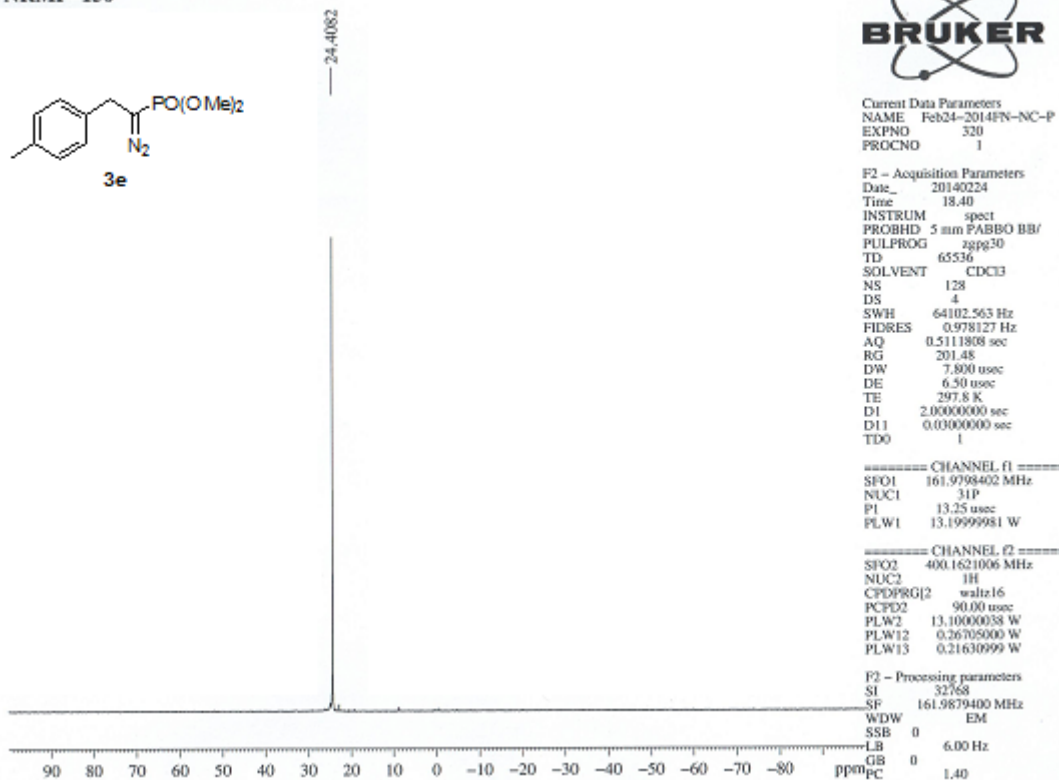
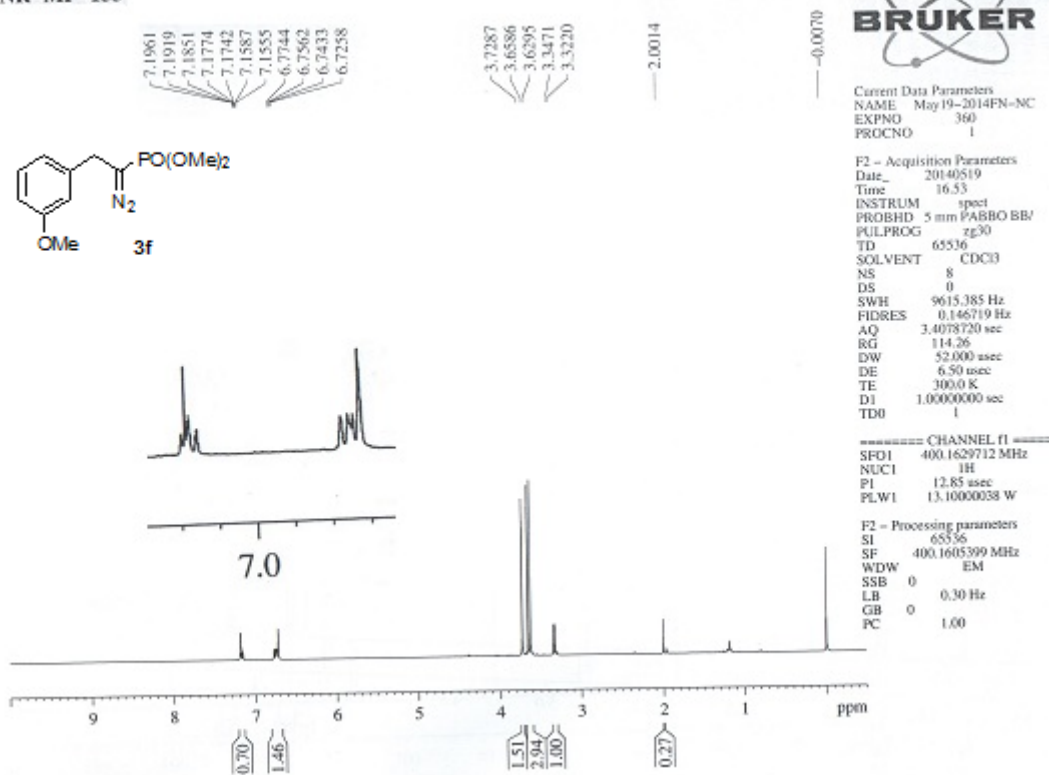


Figure 8: ¹³C NMR spectrum of **3e**

NRMP-150

Figure 9: ³¹P NMR spectrum of **3e**

NR-MP-155

Figure 10: ¹H NMR spectrum of **3f**

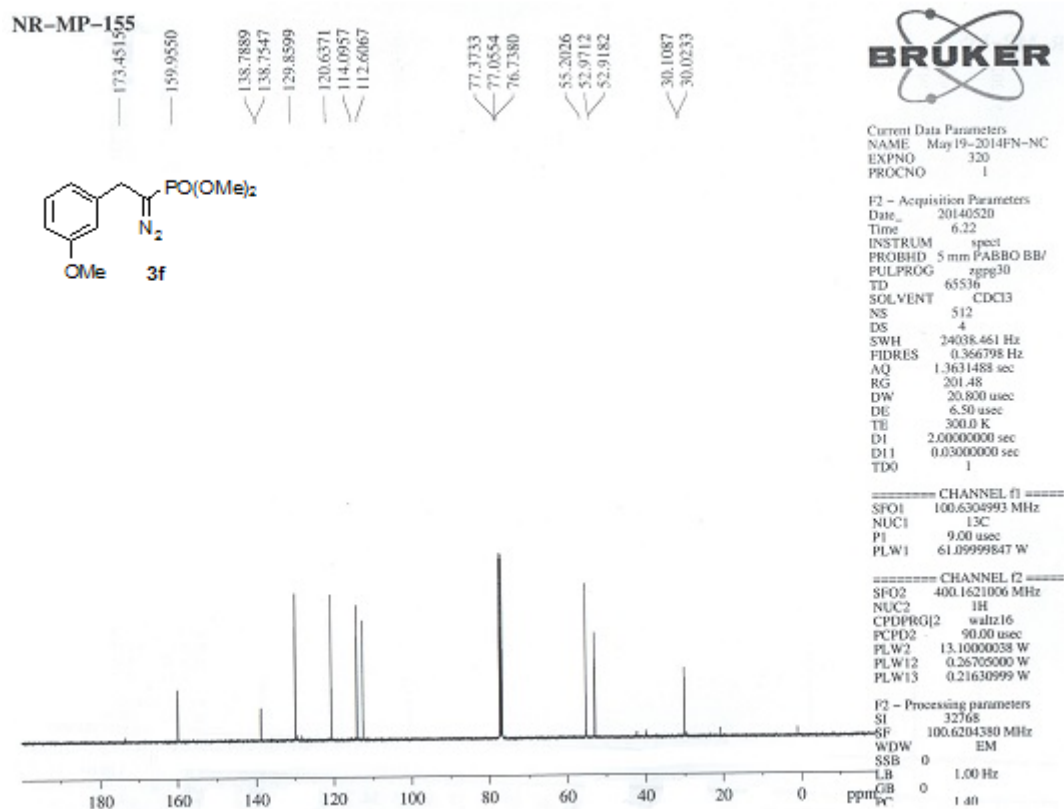


Figure 11: ¹³C NMR spectrum of 3f

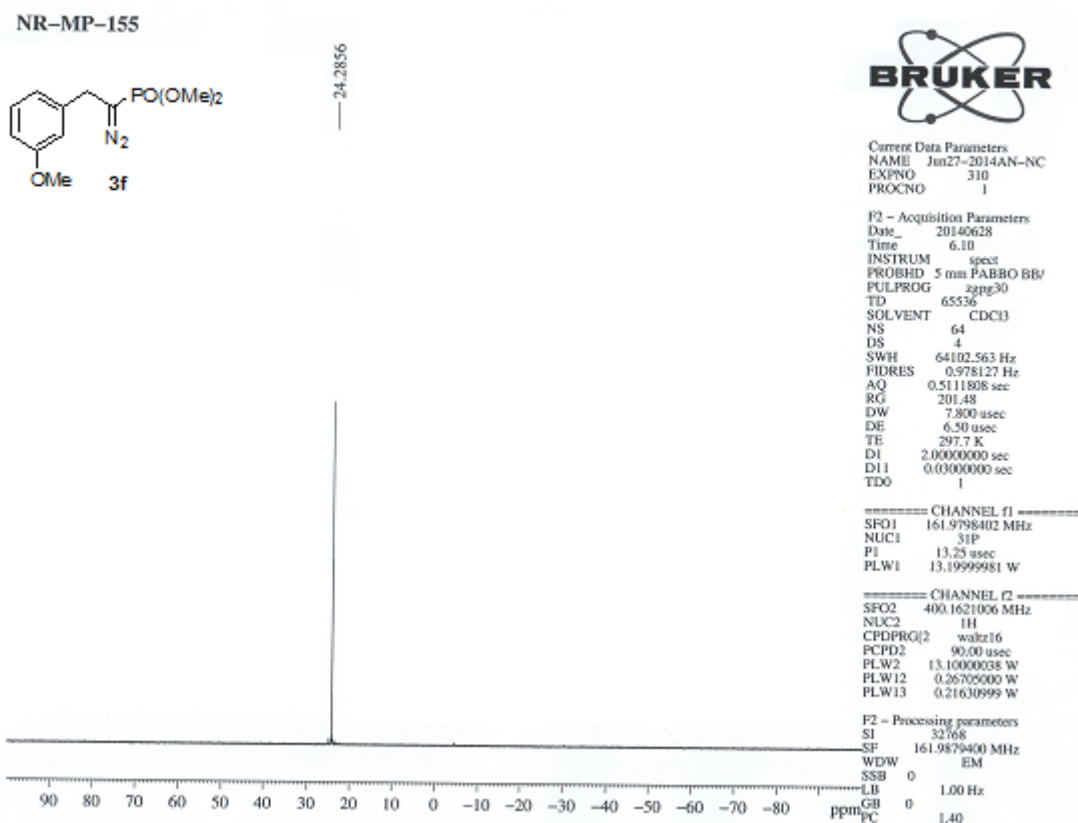


Figure 12: ³¹P NMR spectrum of 3f

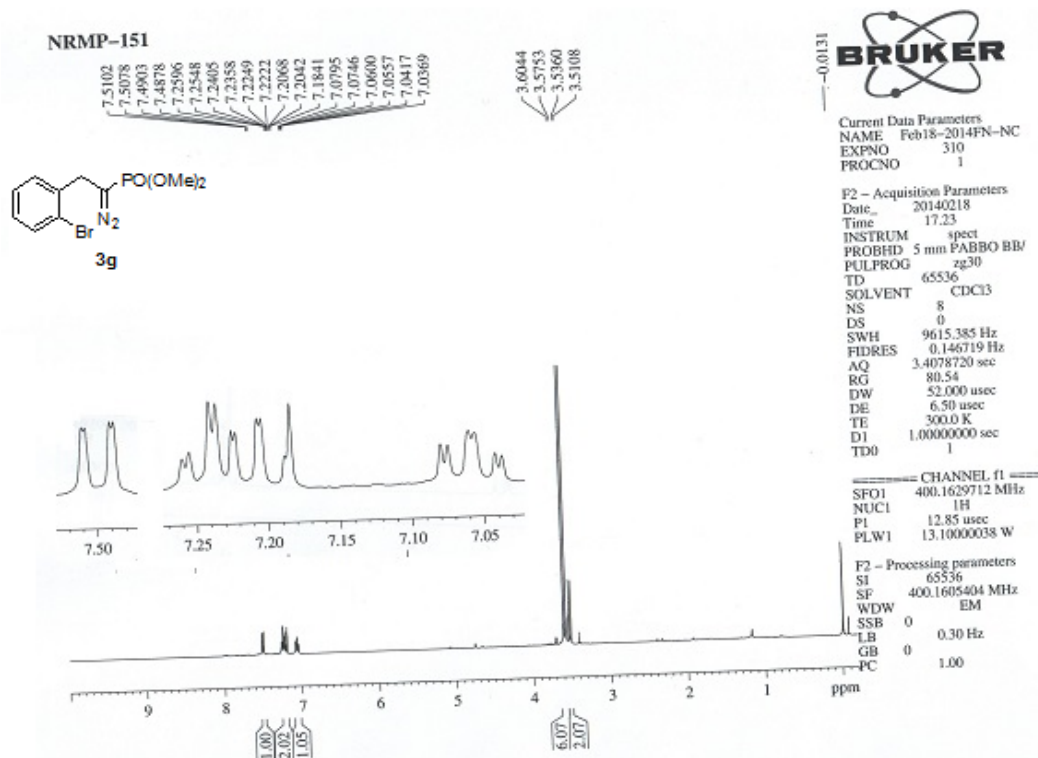


Figure 13: ¹H NMR spectrum of **3g**

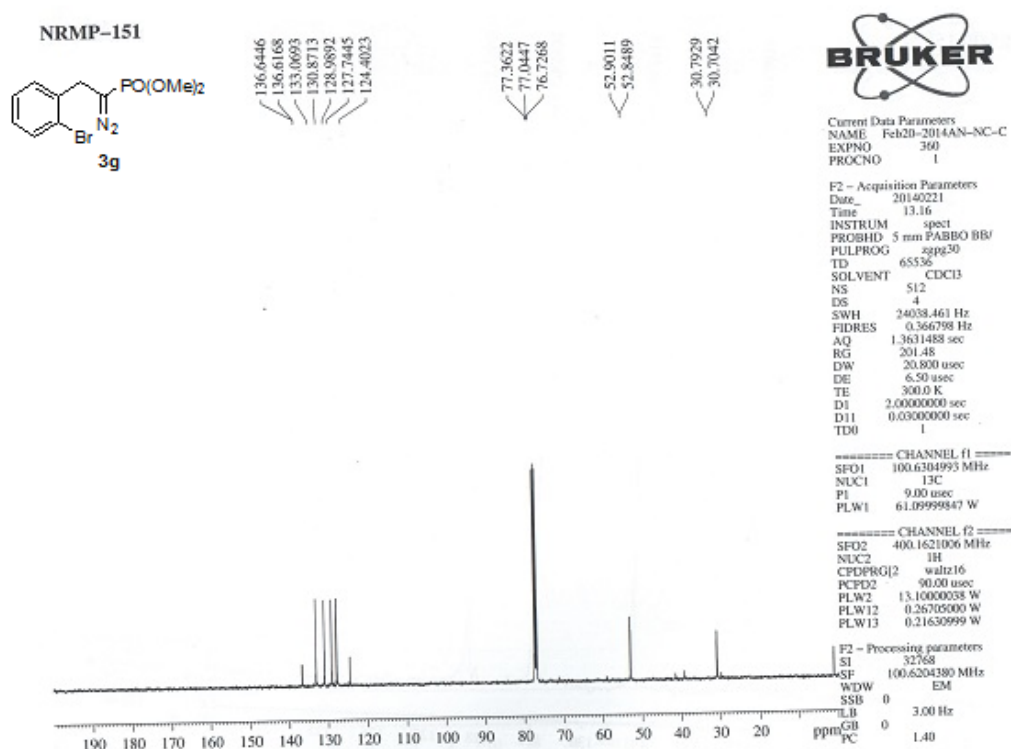
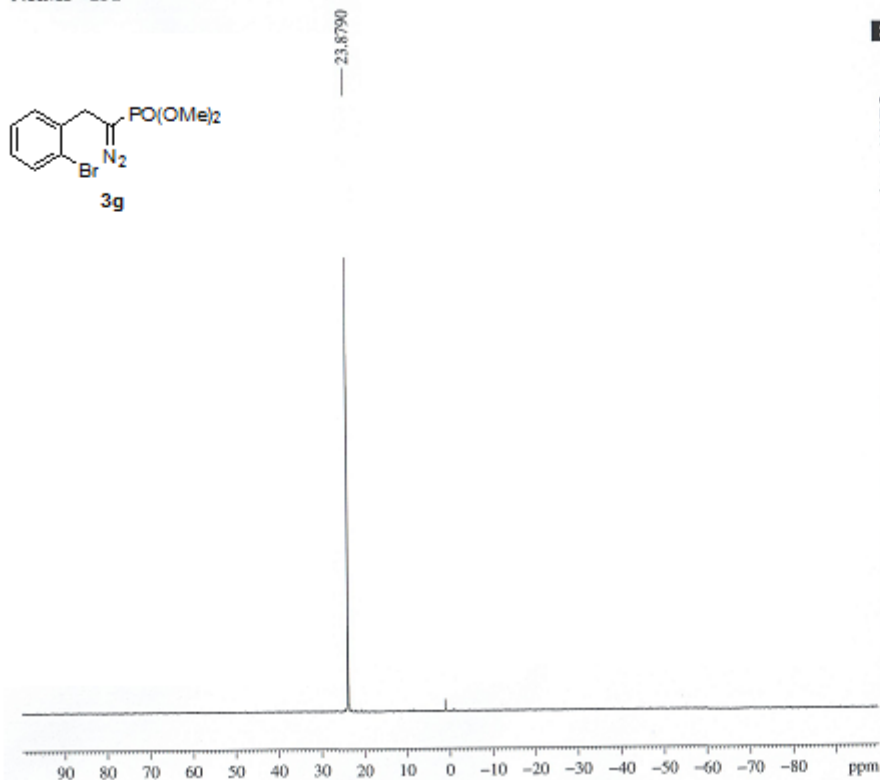


Figure 14: ¹³C NMR spectrum of **3g**

NRMP-151



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PROCNO 1

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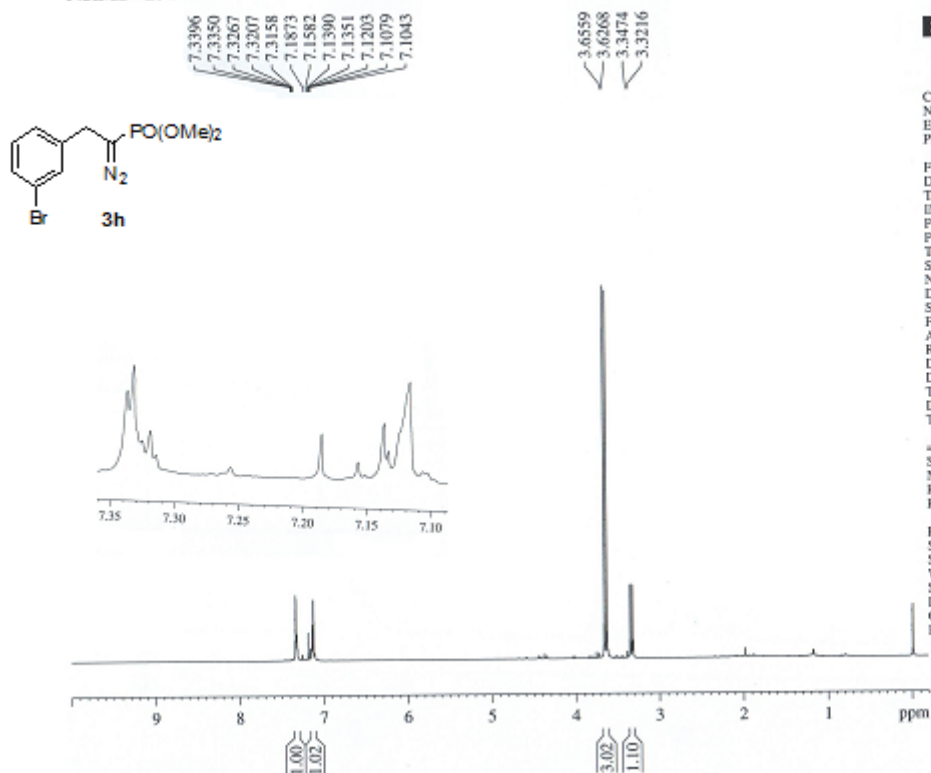
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CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 161.9879400 MHz
WDW EM
SSB 0
LB 6.00 Hz
GB 0
PC 1.40

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

NRMP-154



Current Data Parameters
NAME Jun10-2014FN-NC
EXPNO 390
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140611
Time 11.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 89.7
DW 62.400 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1629712 MHz
NUC1 1H
P1 12.85 usec
PLW1 13.10000038 W

F2 - Processing parameters
SI 65536
SF 400.1605392 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 16: ^1H NMR spectrum of 3h

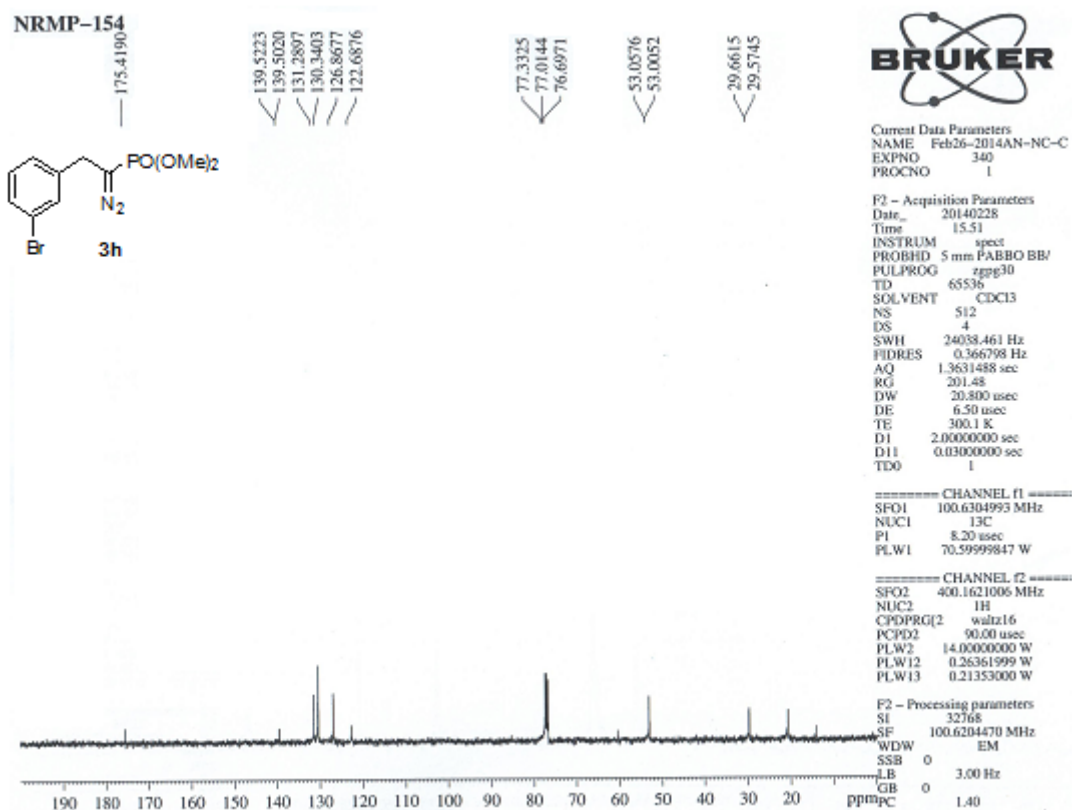


Figure 17: ^{13}C NMR spectrum of 3h

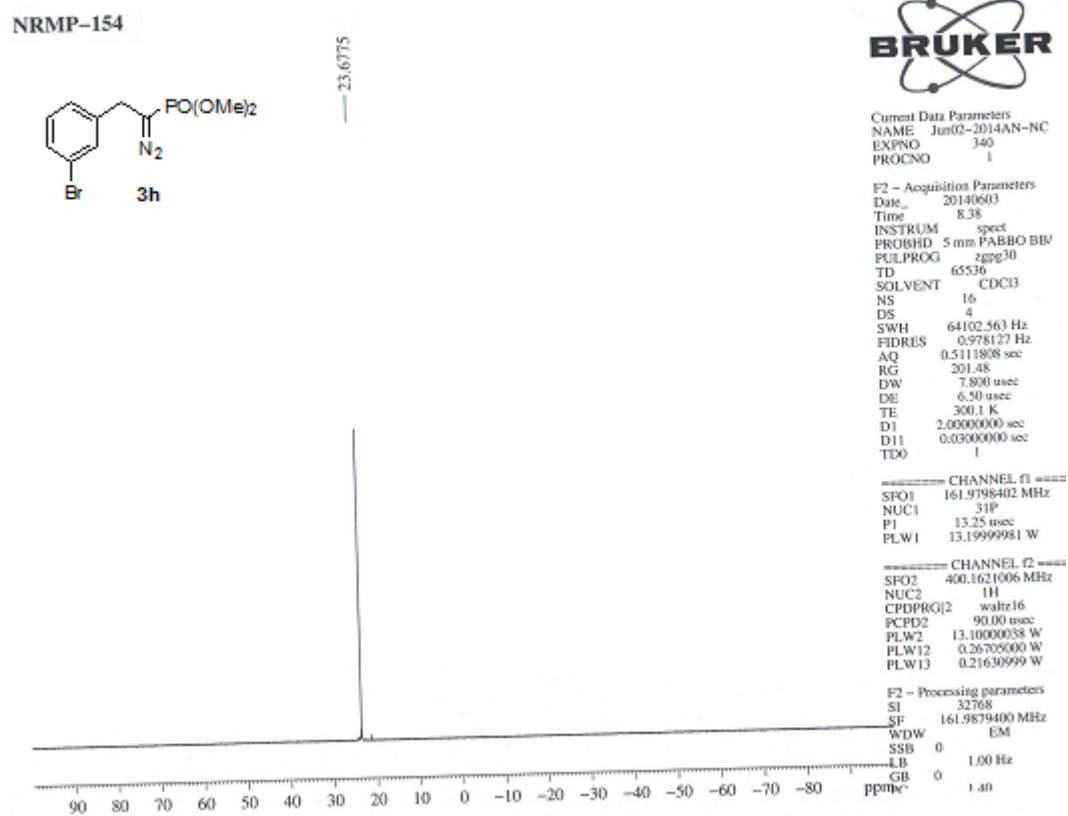


Figure 18: ^{31}P NMR spectrum of 3h

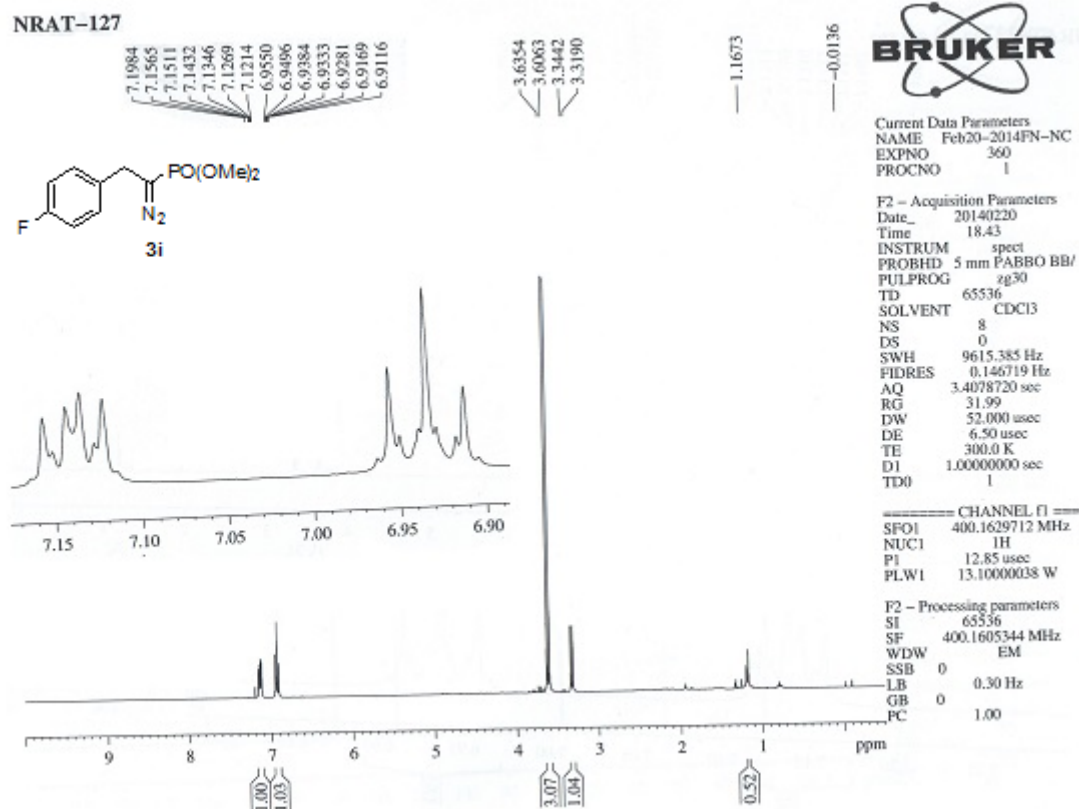


Figure 19: ^1H NMR spectrum of **3i**

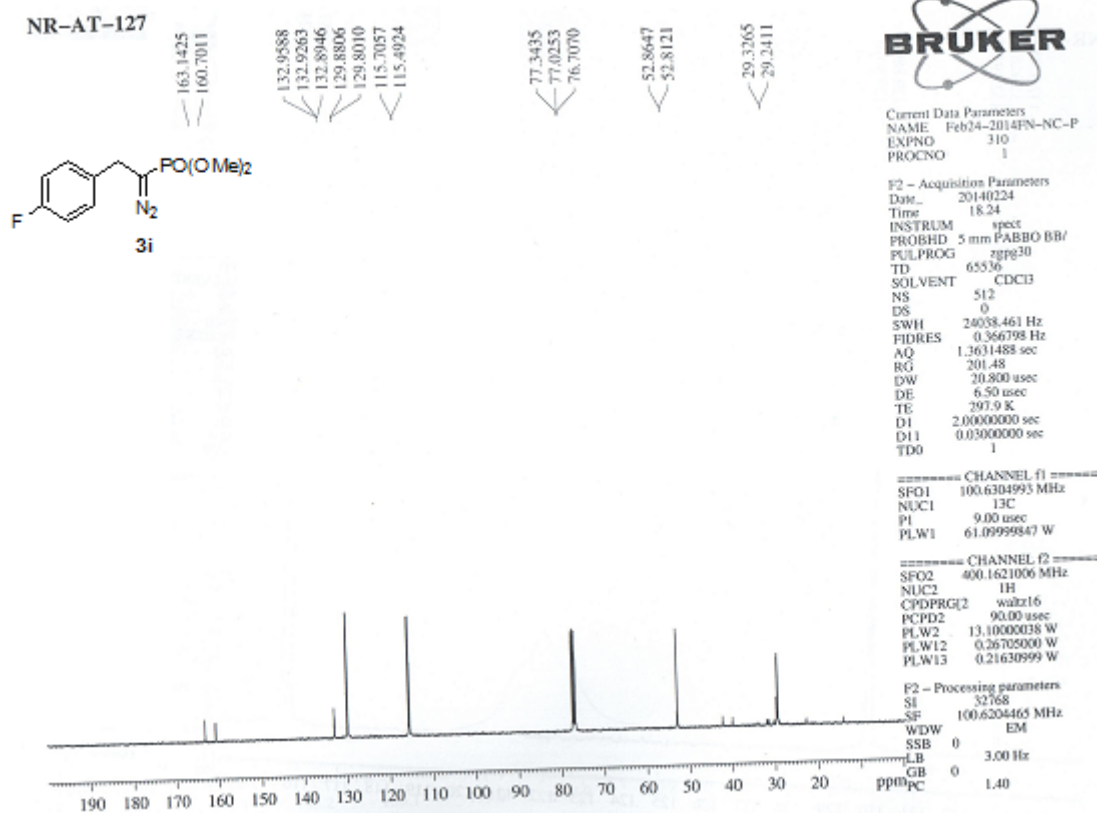
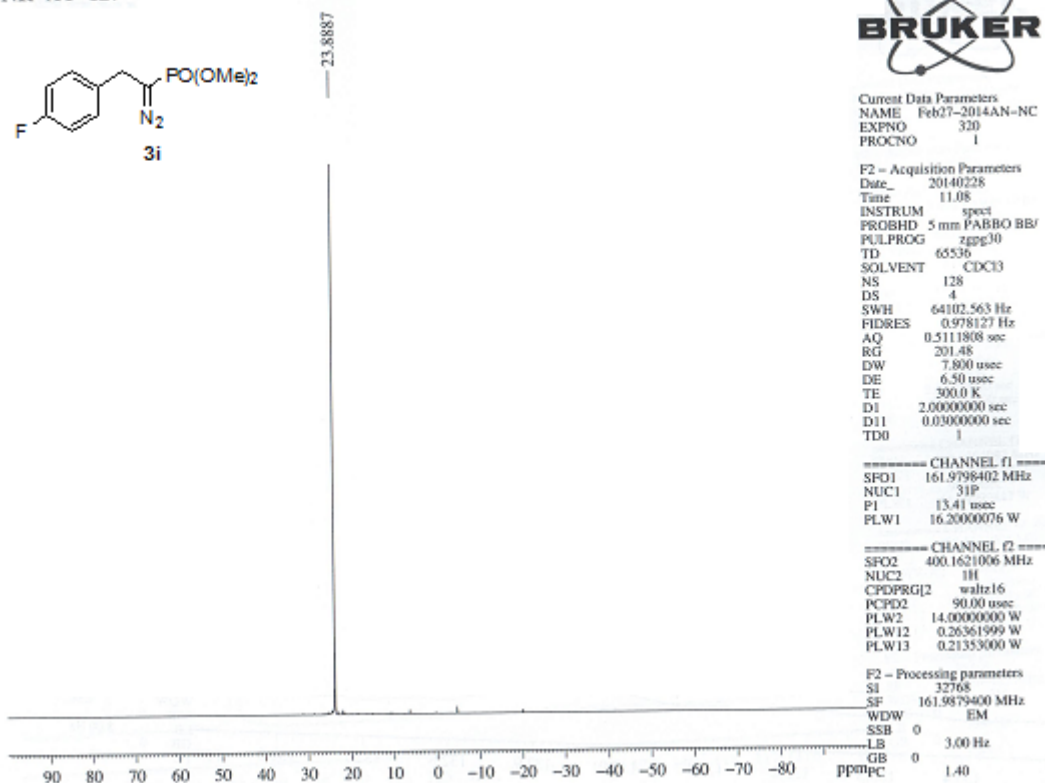
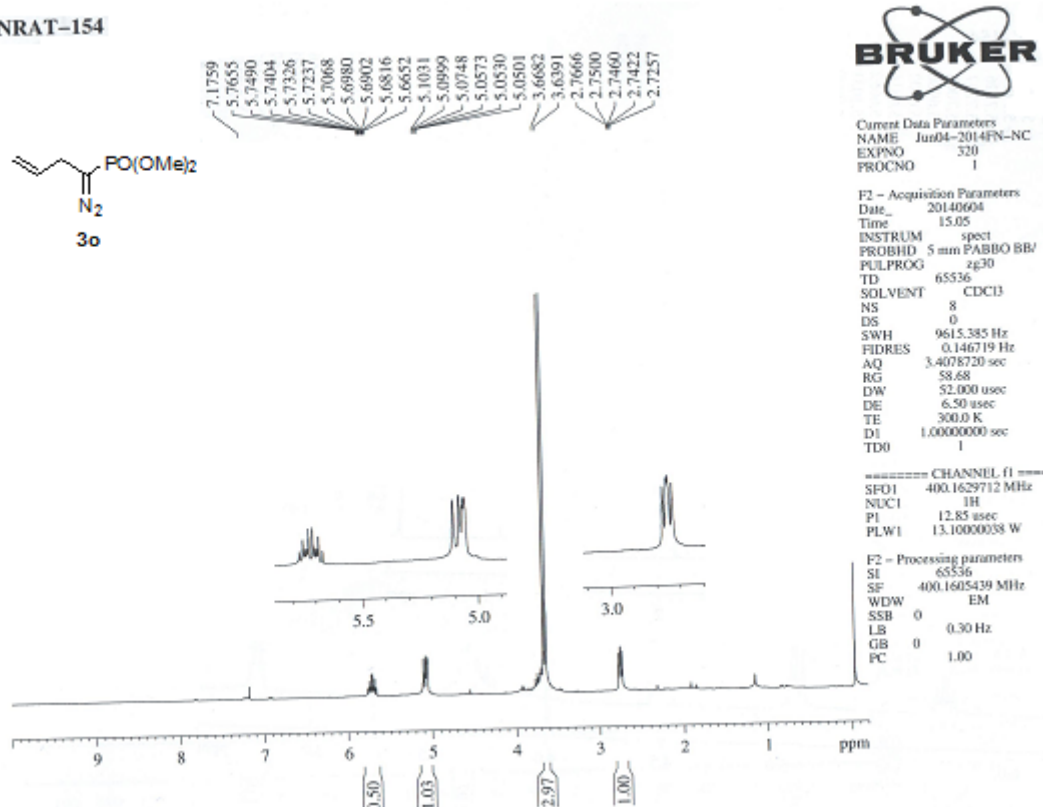


Figure 20: ^{13}C NMR spectrum of **3i**

NR-AT-127

Figure 21: ³¹P NMR spectrum of 3i

NRAT-154

Figure 22: ¹H NMR spectrum of 3o

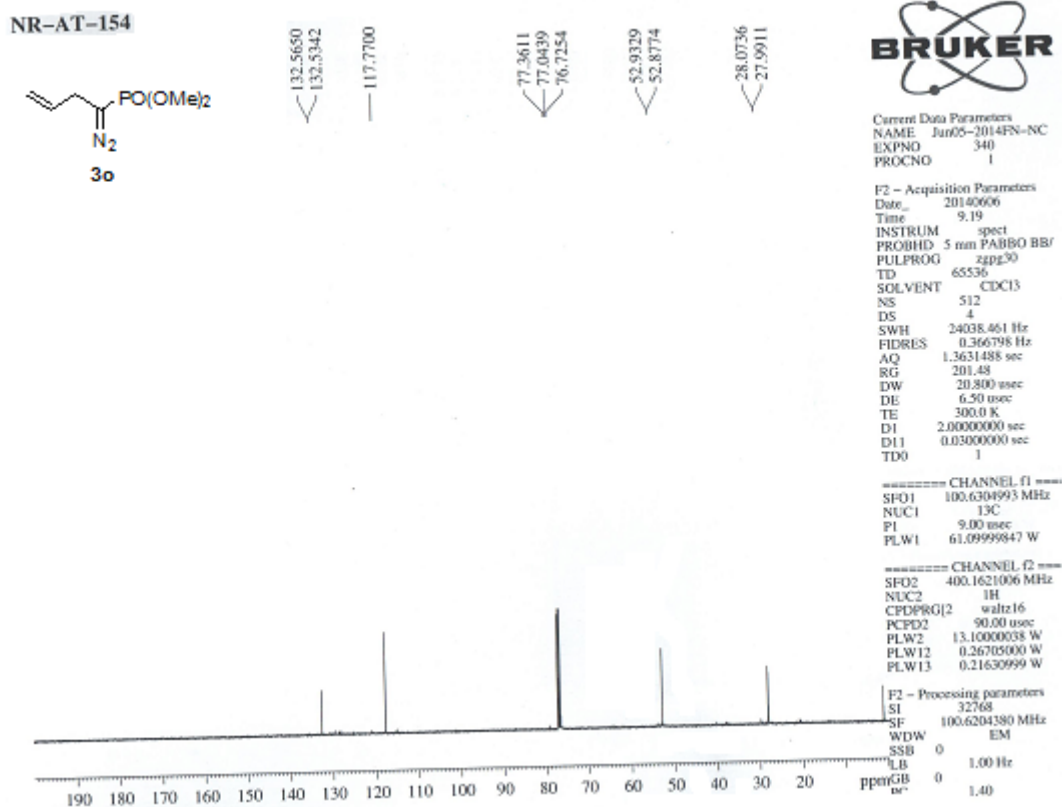


Figure 23: ^{13}C NMR spectrum of **3o**

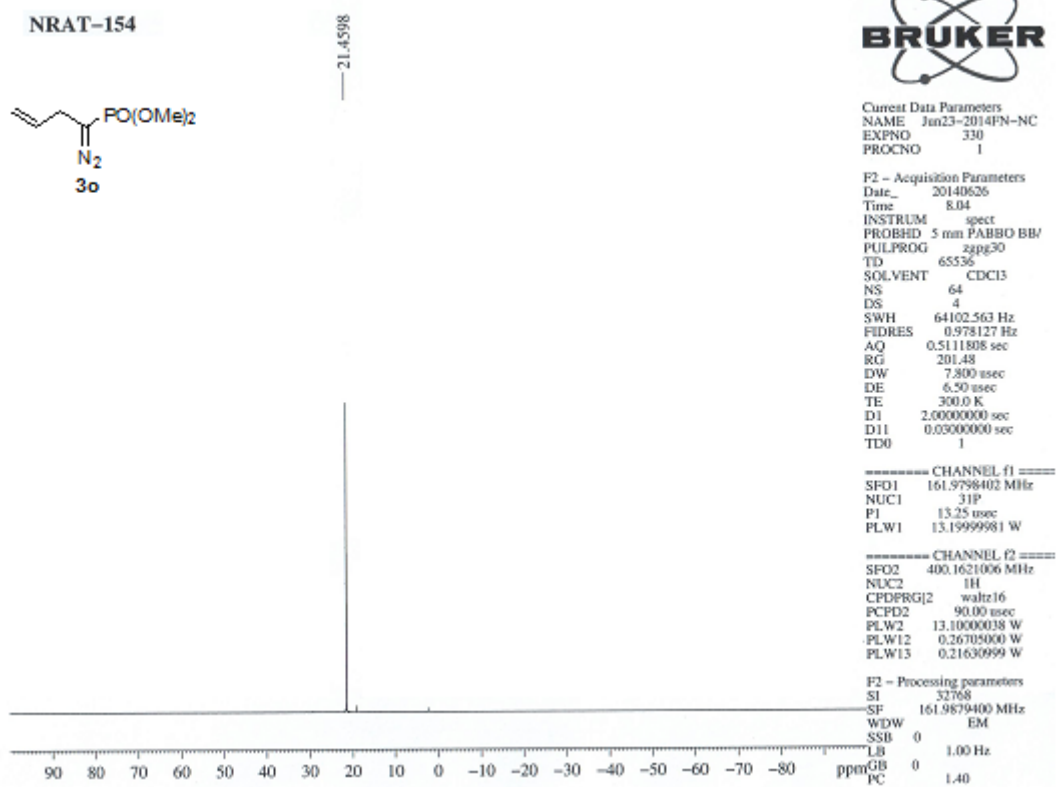


Figure 24: ^{31}P NMR spectrum of **3o**

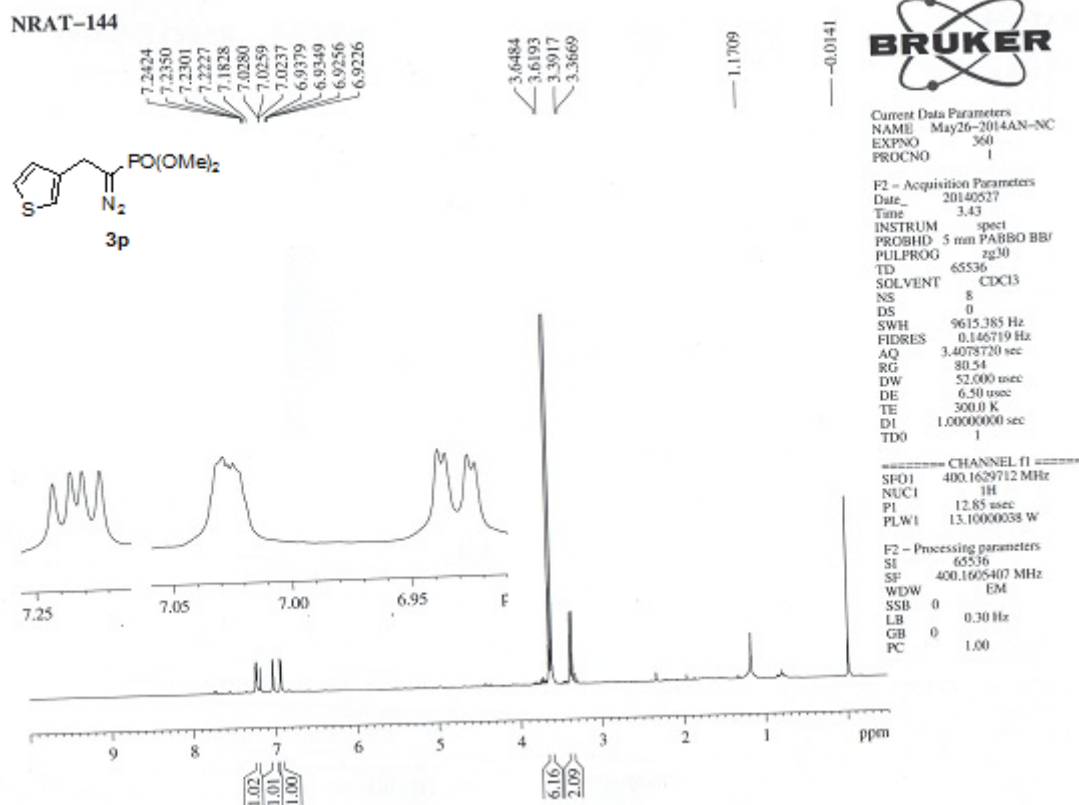


Figure 25: ¹H NMR spectrum of 3p

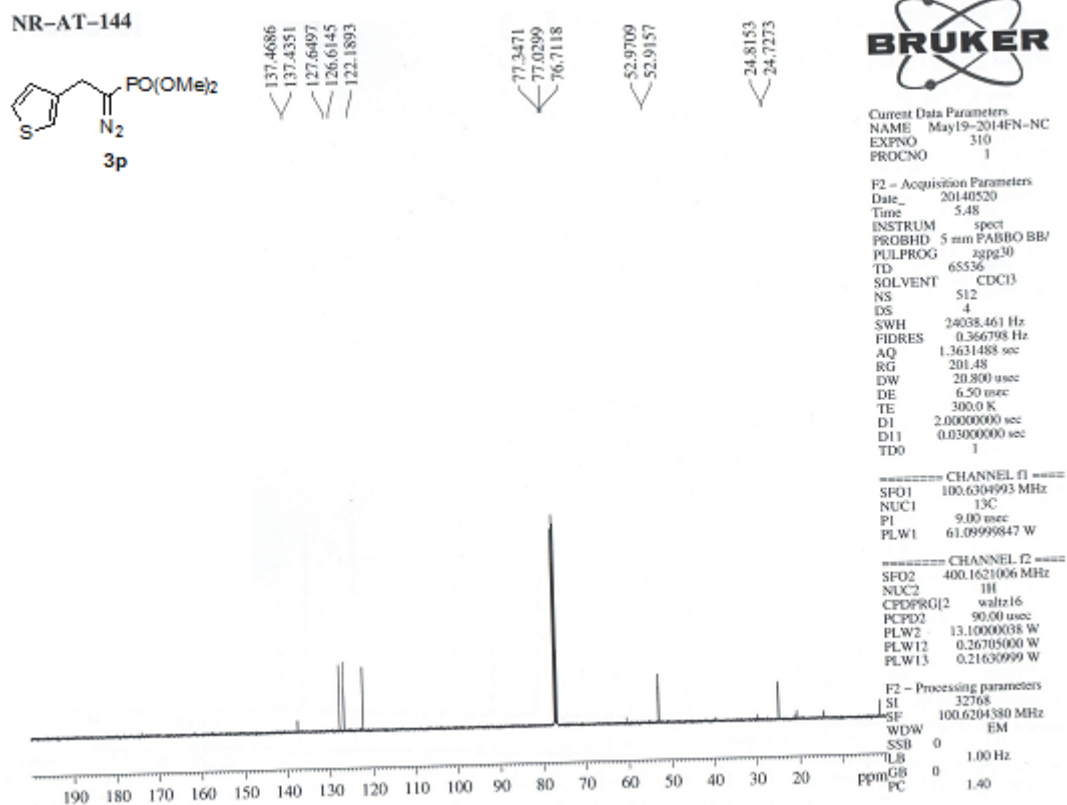
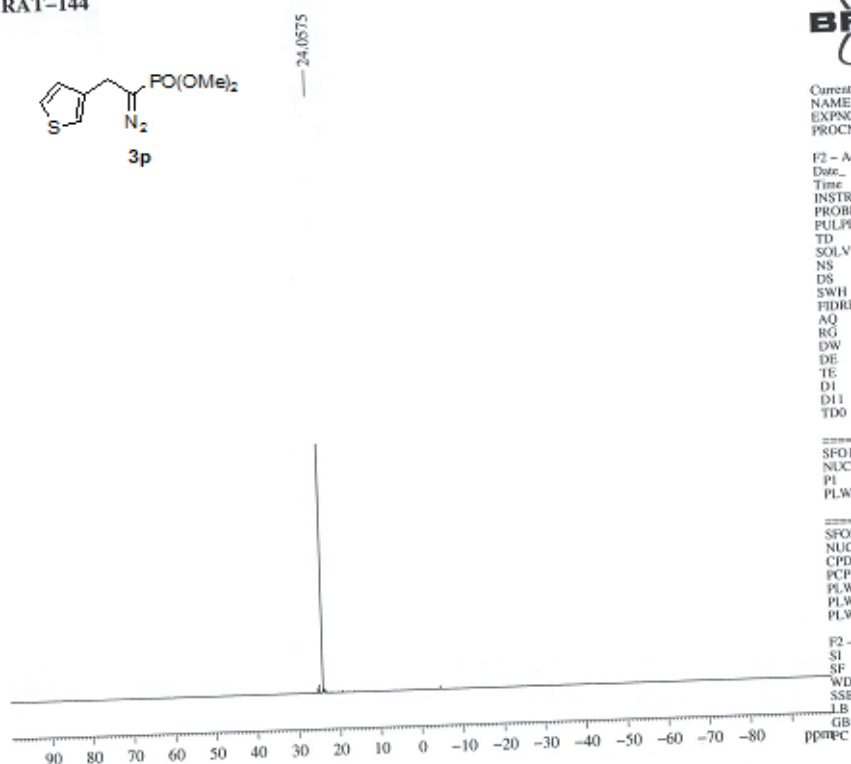
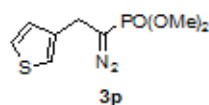


Figure 26: ¹³C NMR spectrum of 3p

NRAT-144



Current Data Parameters
NAME May27-2014AN-NC
EXPNO 350
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140527
Time 23.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 201.48
DW 7.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

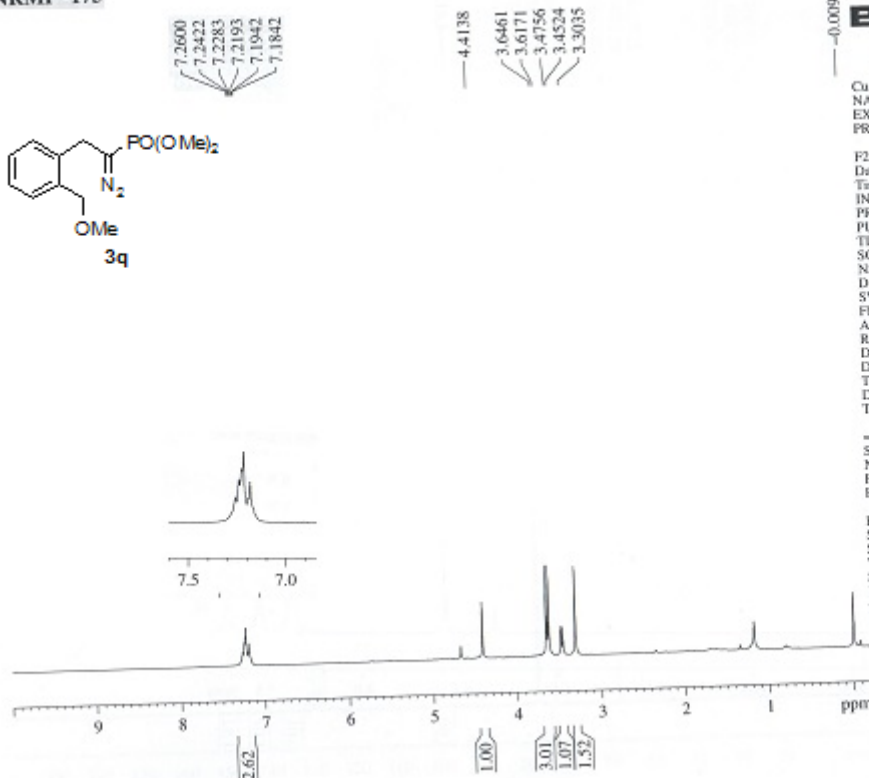
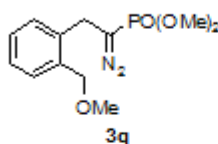
===== CHANNEL f1 =====
SFO1 161.9798402 MHz
NUC1 31P
P1 13.25 usec
PLW1 13.19999981 W

===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26700000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 161.9879400 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure 27: ³¹P NMR spectrum of 3p

NRMP-175



Current Data Parameters
NAME May09-2014EN-NC
EXPNO 370
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140509
Time 15.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 9615.385 Hz
FIDRES 0.146719 Hz
AQ 3.4078720 sec
RG 80.54
DW 52.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1629712 MHz
NUC1 1H
P1 12.85 usec
PLW1 13.10000038 W

F2 - Processing parameters
SI 65536
SF 400.1605405 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 28: ¹H NMR spectrum of 3q

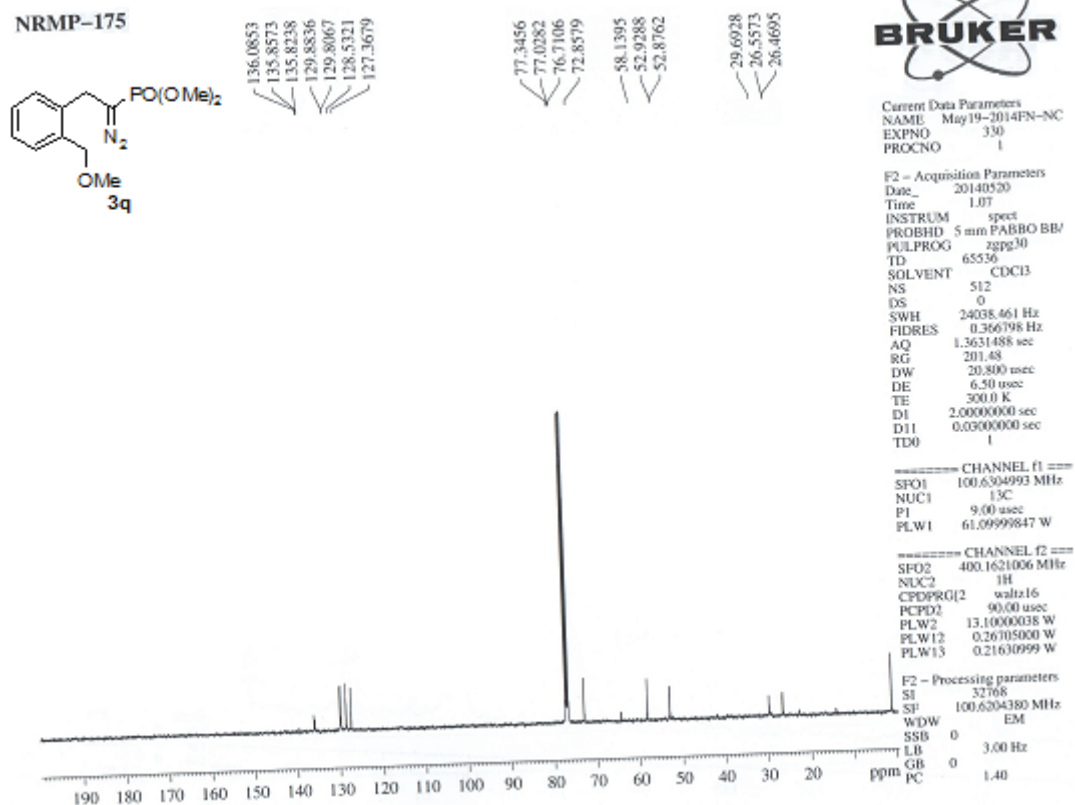


Figure 29: ^{13}C NMR spectrum of 3q

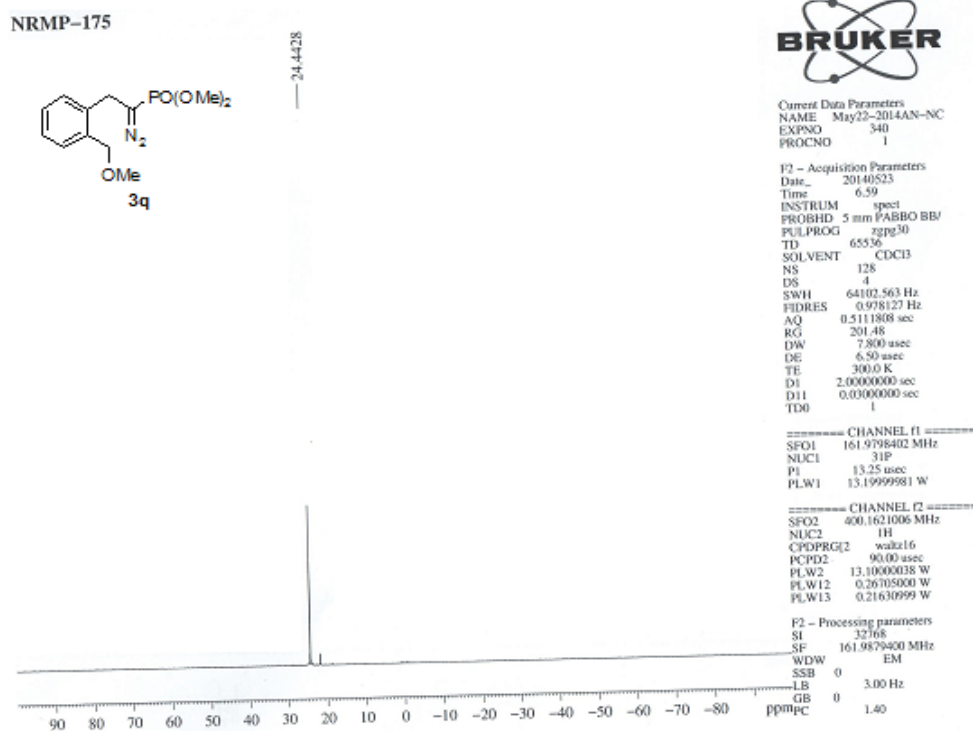


Figure 30: ^{31}P NMR spectrum of 3q

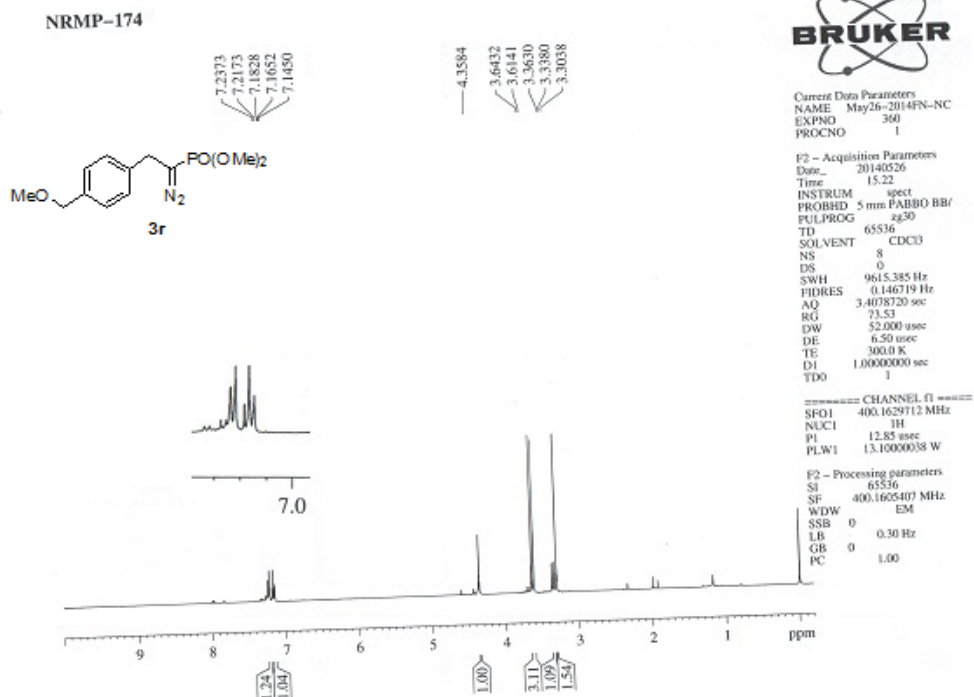


Figure 31: ¹H NMR spectrum of **3r**

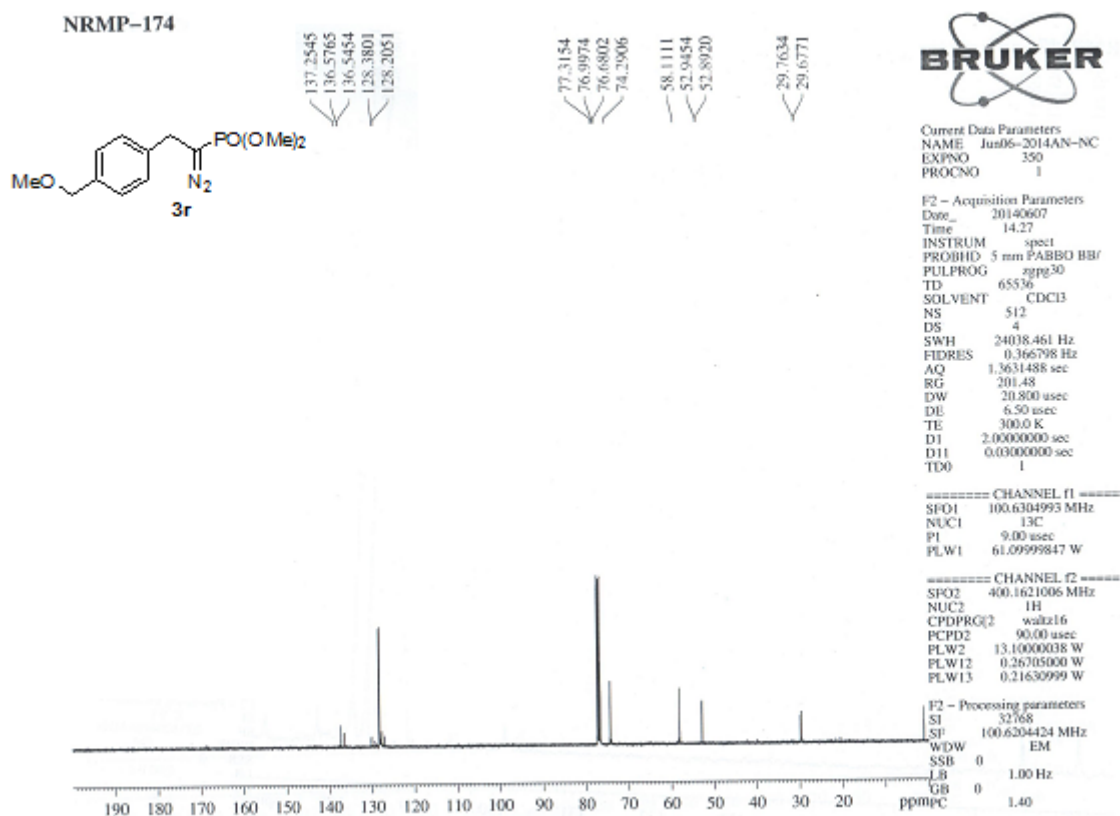
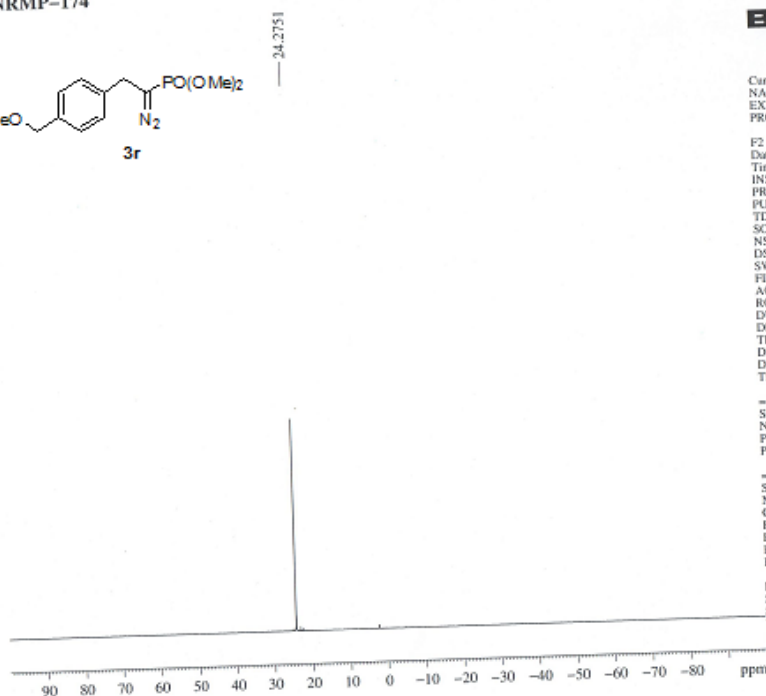
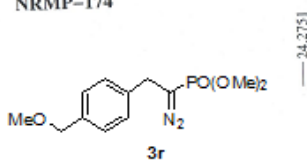


Figure 32: ¹³C NMR spectrum of **3r**

NRMP-174



Current Data Parameters
NAME May27-2014AN-NC
EXPNO 370
PROCNO 1

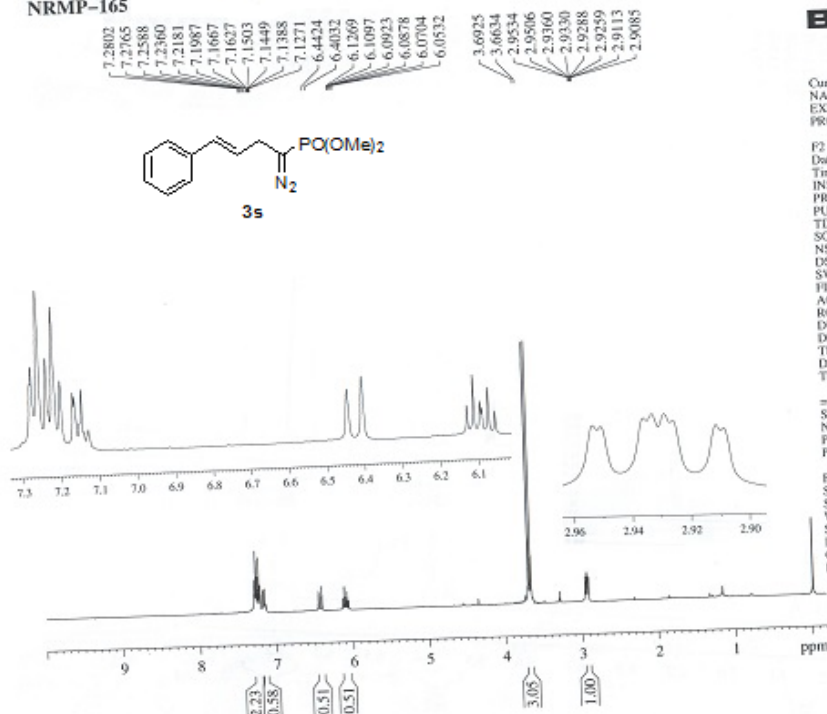
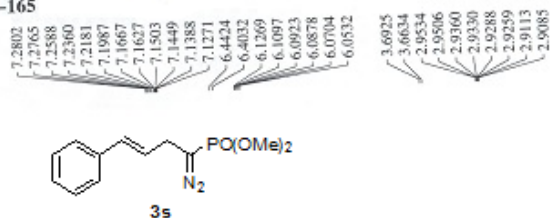
F2 - Acquisition Parameters
Date_ 20140528
Time 8.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 201.48
DW 7.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 161.9798402 MHz
NUC1 31P
P1 13.25 usec
PLW1 13.19999981 W
===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 161.9879400 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

Figure 33: ³¹P NMR spectrum of 3r

NRMP-165



Current Data Parameters
NAME May19-2014AN-NC
EXPNO 360
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140520
Time 4.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 58.68
DW 62.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1629712 MHz
NUC1 1H
P1 12.85 usec
PLW1 13.10000038 W
===== CHANNEL f2 =====
SFO2 101.6251250 MHz
NUC2 13C
P2 12.00 usec
PLW2 1.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1605470 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 34: ¹H NMR spectrum of 3s

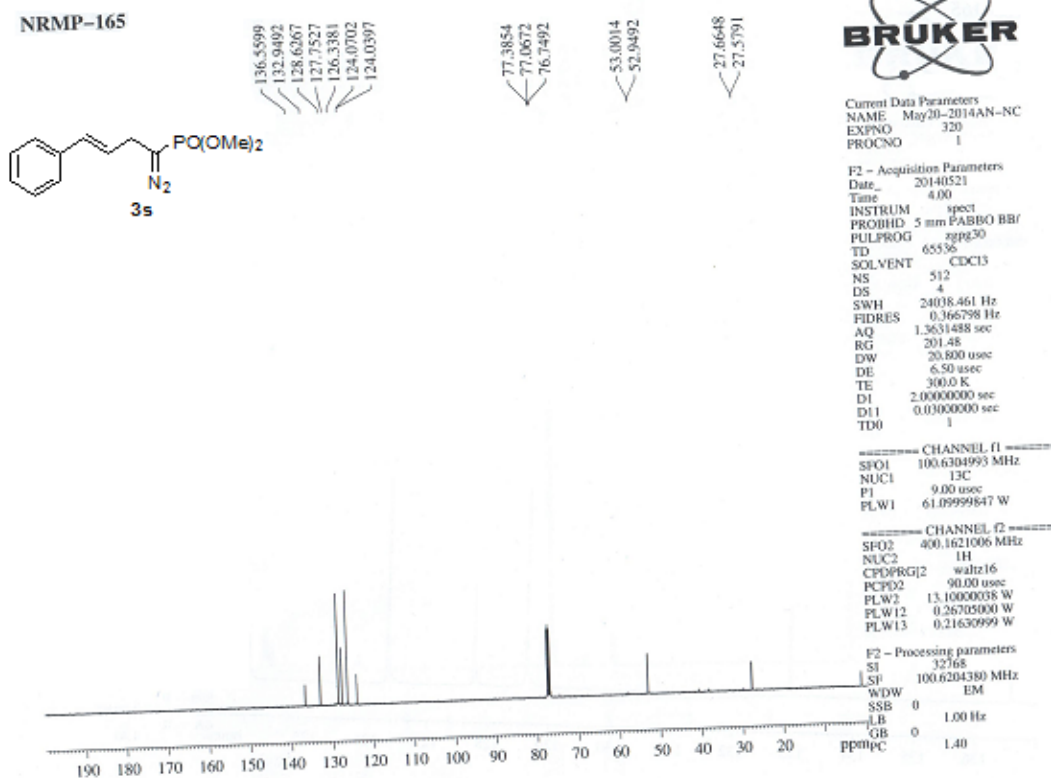


Figure 35: ¹³C NMR spectrum of 3s

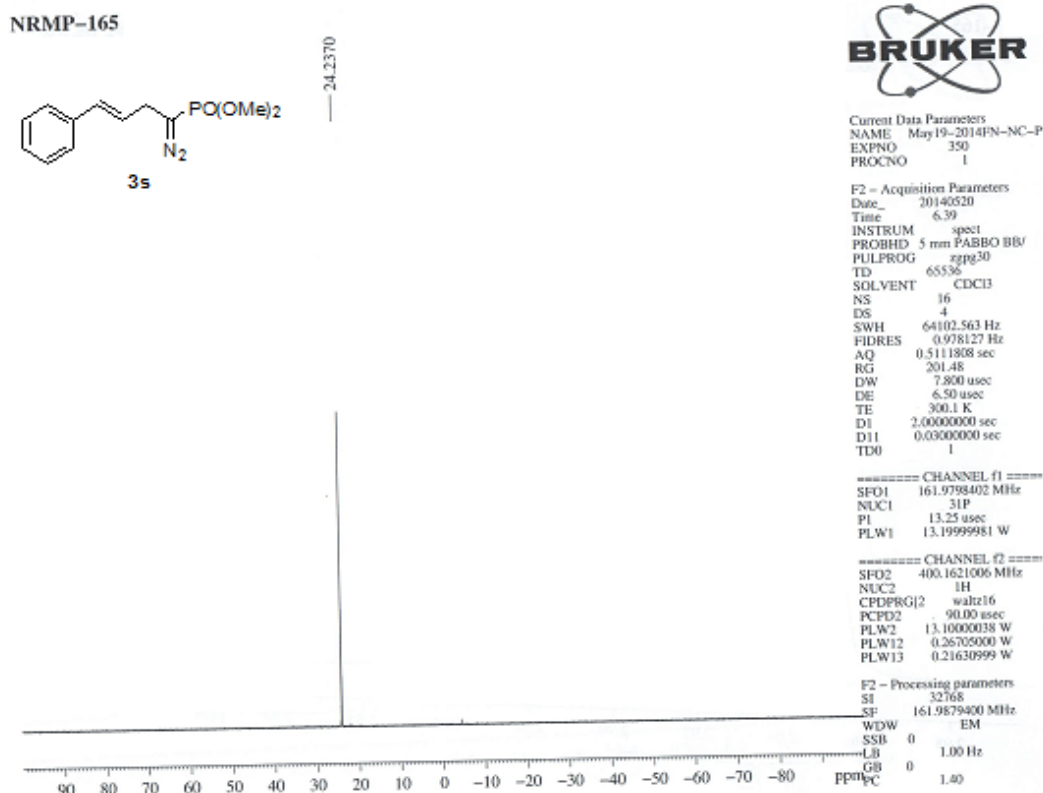


Figure 36: ³¹P NMR spectrum of 3s

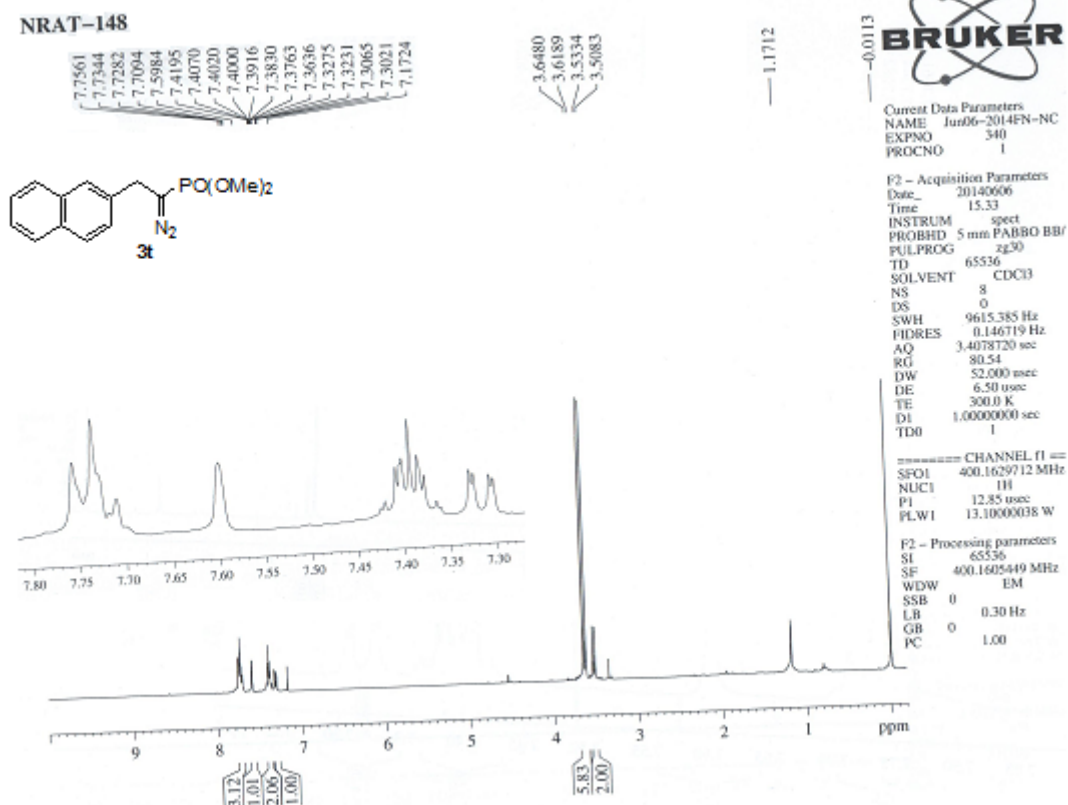


Figure 37: ^1H NMR spectrum of 3t

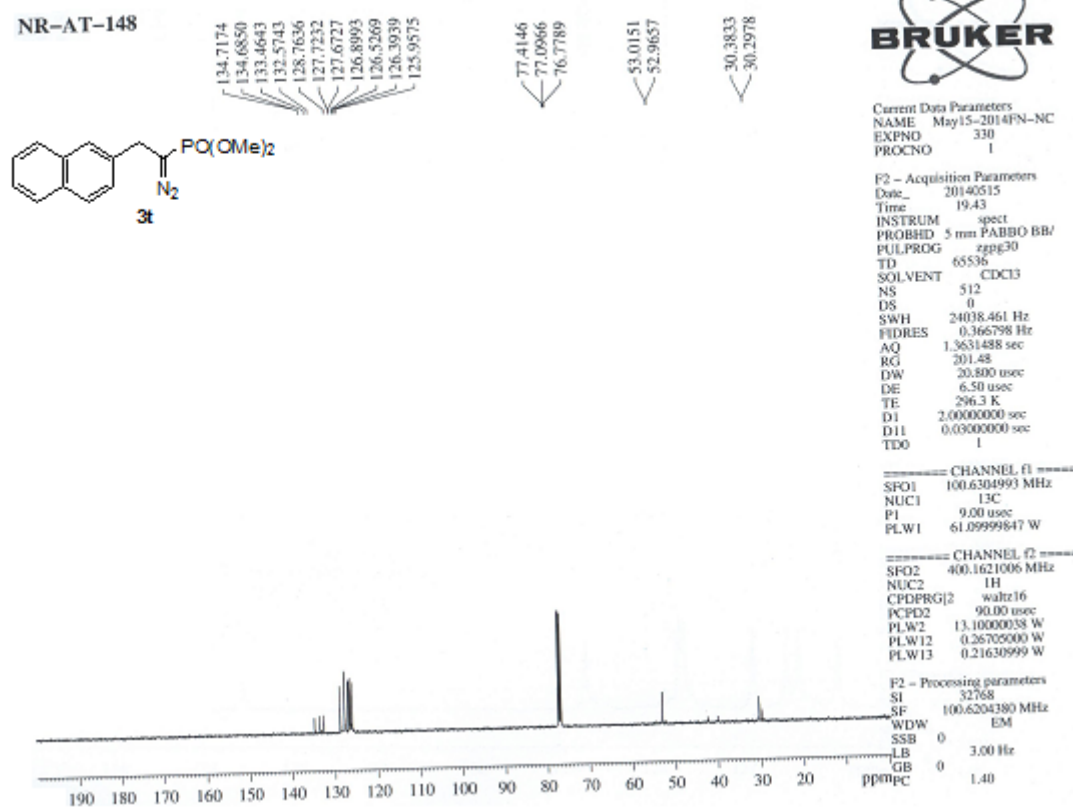
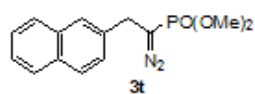


Figure 38: ^{13}C NMR spectrum of 3t

NRAT-148



24.1529



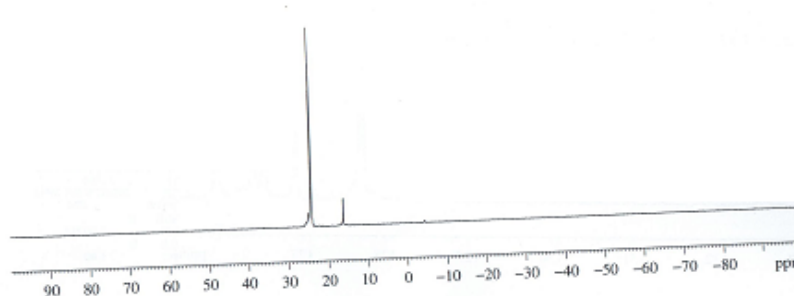
Current Data Parameters
NAME May27-2014AN-NC
EXPNO 340
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140527
Time 22.11
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 201.48
DW 7.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

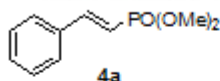
===== CHANNEL f1 =====
SFO1 161.9798402 MHz
NUC1 31P
P1 13.25 usec
PLW1 13.19999981 W

===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 161.9879400 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

Figure 39: ³¹P NMR spectrum of 3t

NRMP-179



7.4975
7.4536
7.4408
7.4332
7.4241
7.4202
7.4155
7.4092
7.3971
7.3113
7.3027
7.2951
7.1850
6.1798
6.1356
6.0911

3.7044
3.6766

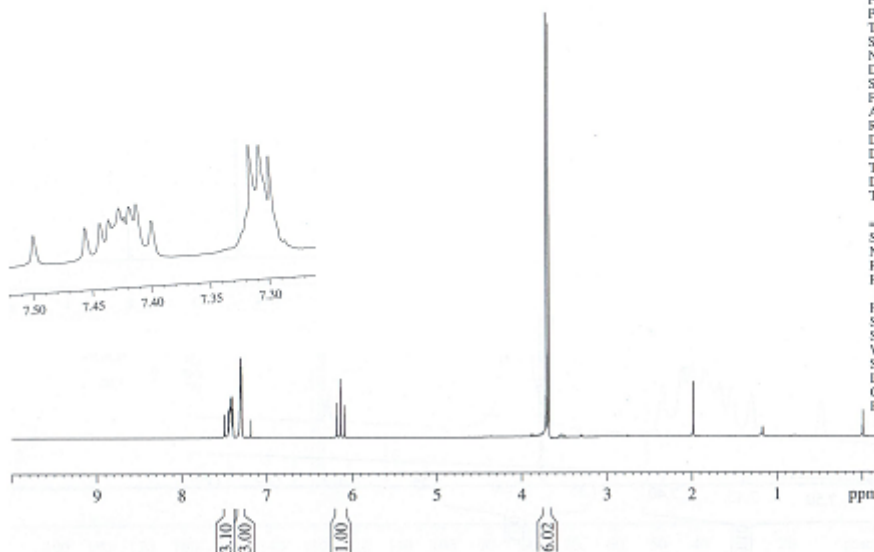


Current Data Parameters
NAME May28-2014FN-NC
EXPNO 340
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140528
Time 15.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 9615.385 Hz
FIDRES 0.146719 Hz
AQ 3.4078720 sec
RG 73.53
DW 52.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1629712 MHz
NUC1 1H
P1 12.85 usec
PLW1 13.10000038 W

F2 - Processing parameters
SI 65536
SF 400.1608398 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 40: ¹H NMR spectrum of 4a

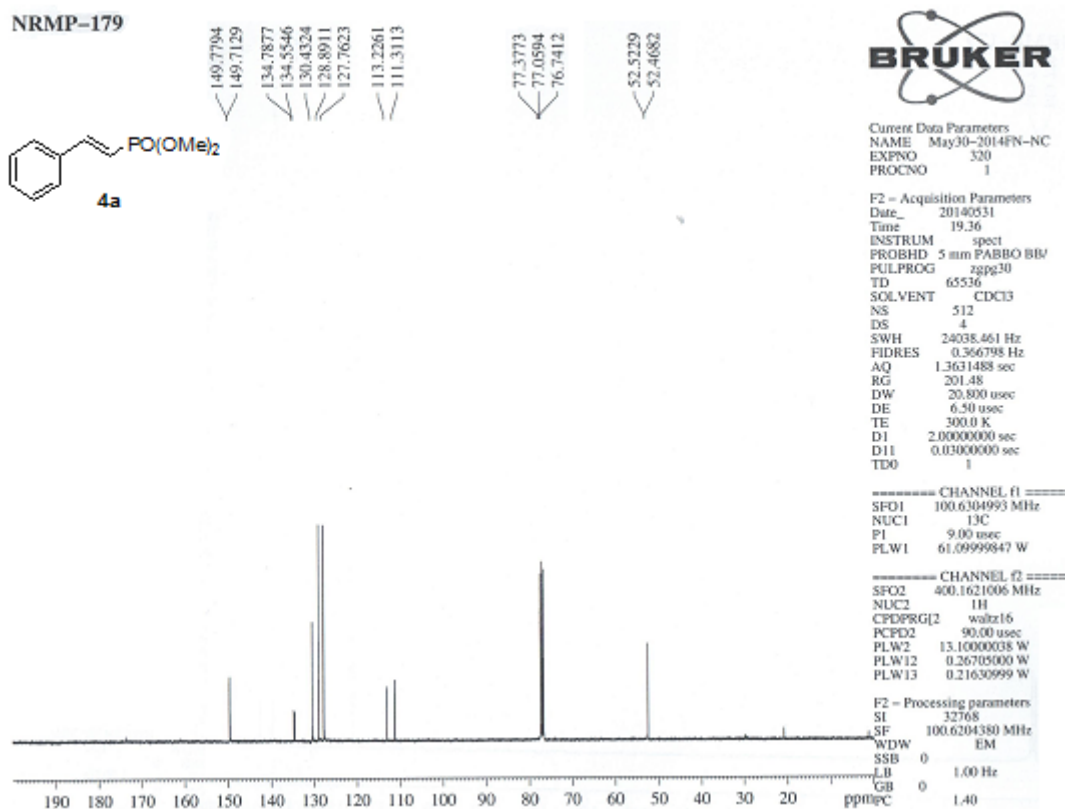


Figure 41: ^{13}C NMR spectrum of **4a**

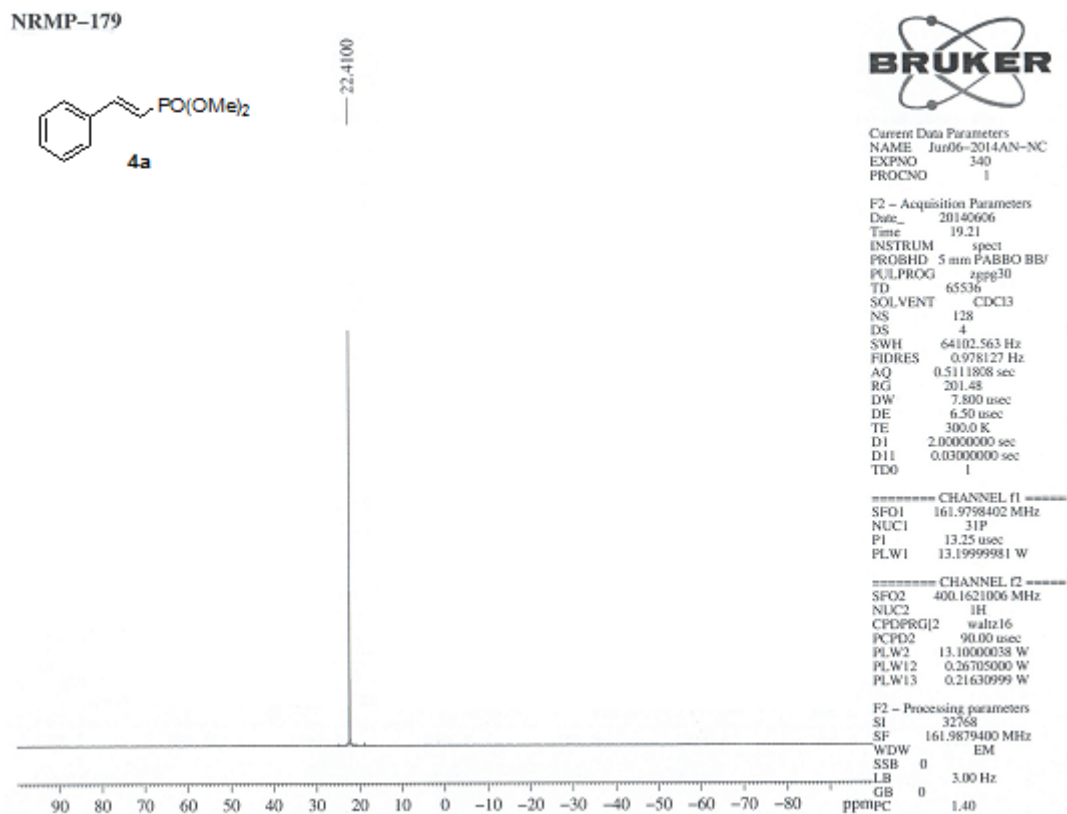


Figure 42: ^{31}P NMR spectrum of **4a**

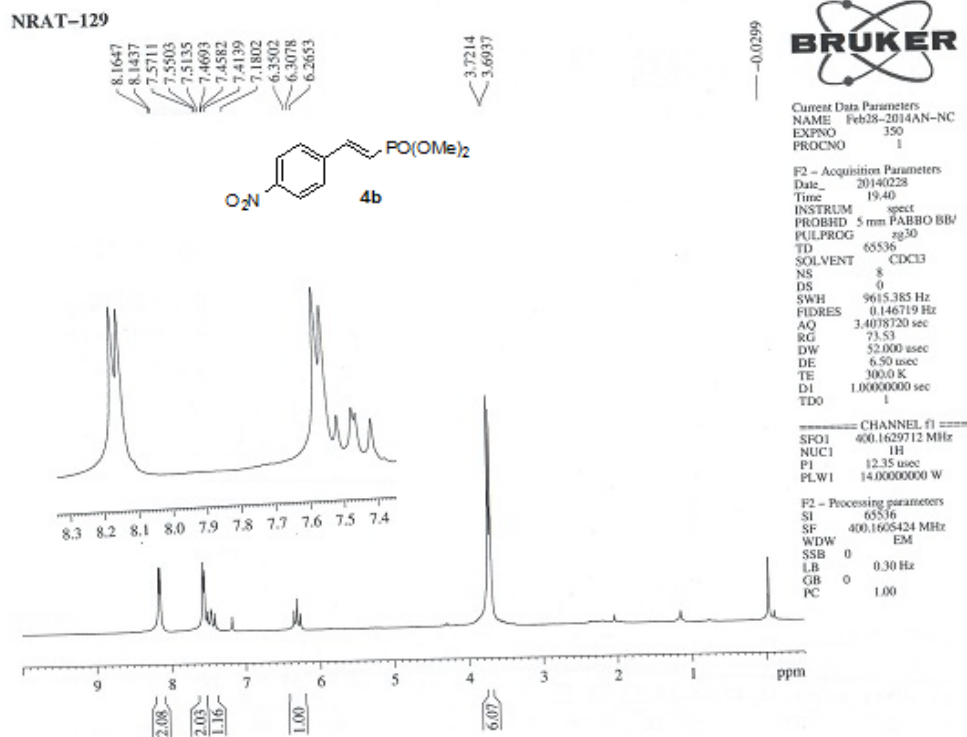


Figure 43: ¹H NMR spectrum of 4b

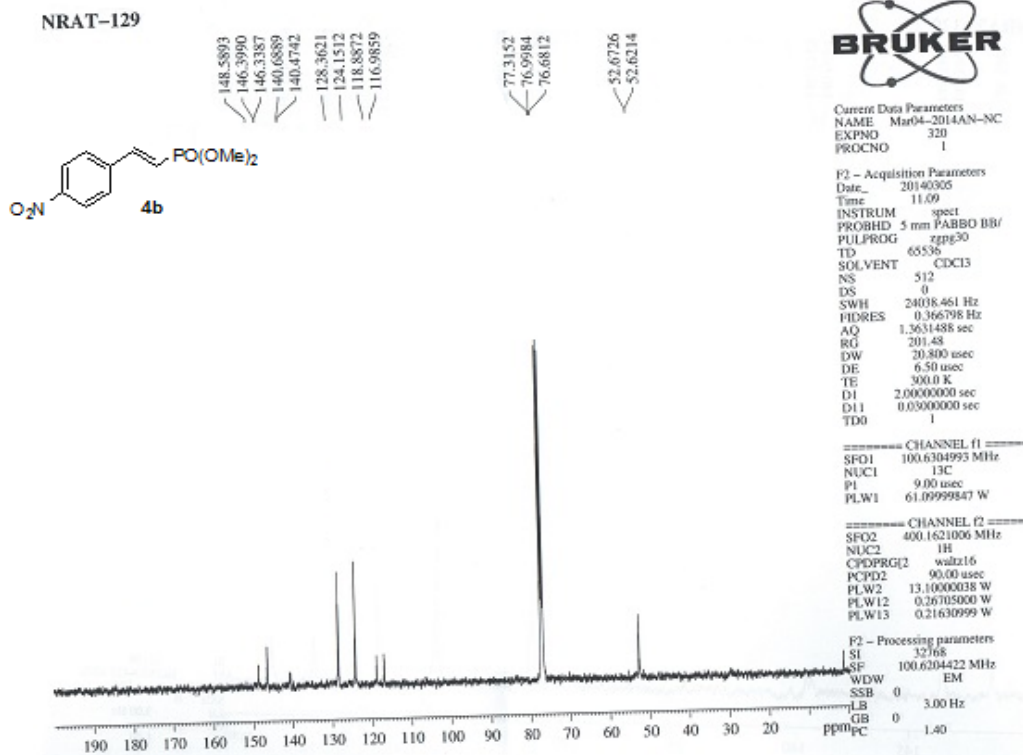
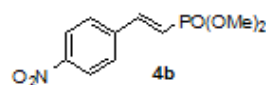
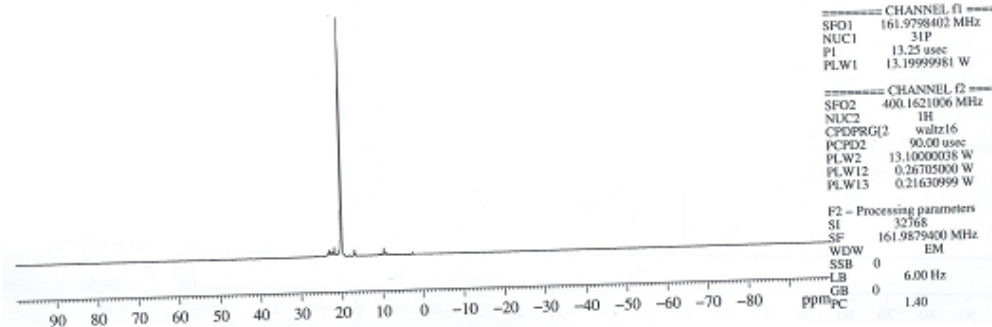


Figure 44: ¹³C NMR spectrum of 4b

NR-AT-129



20.0096



Current Data Parameters
NAME Mar07-2014FN-NC
EXPNO 310
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140307
Time 17.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 201.48
DW 7.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.0000000 sec
D11 0.03000000 sec
TD0 1

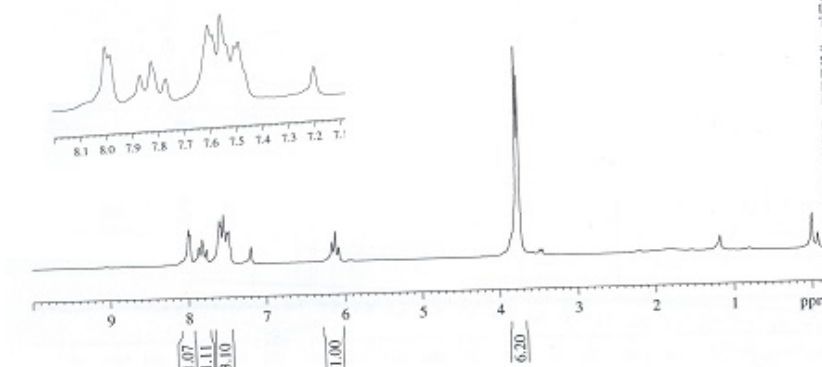
===== CHANNEL f1 =====
SFO1 161.9798403 MHz
NUC1 31P
P1 13.25 usec
PLW1 13.1999981 W

===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
PCPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 161.9879400 MHz
WDW EM
SSB 0
LB 6.00 Hz
GB 0
PC 1.40

Figure 45: ¹³P NMR spectrum of 4b

NRMP-119

3.7609
3.7335

Current Data Parameters
NAME Feb12-2014FN-NC
EXPNO 330
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140212
Time 20.45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 9615.385 Hz
FIDRES 0.146719 Hz
AQ 3.4018720 sec
RG 89.7
DW 52.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1629712 MHz
NUC1 1H
P1 12.85 usec
PLW1 13.10000038 W

F2 - Processing parameters
SI 65536
SF 400.1605389 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

Figure 46: ¹H NMR spectrum of 4c

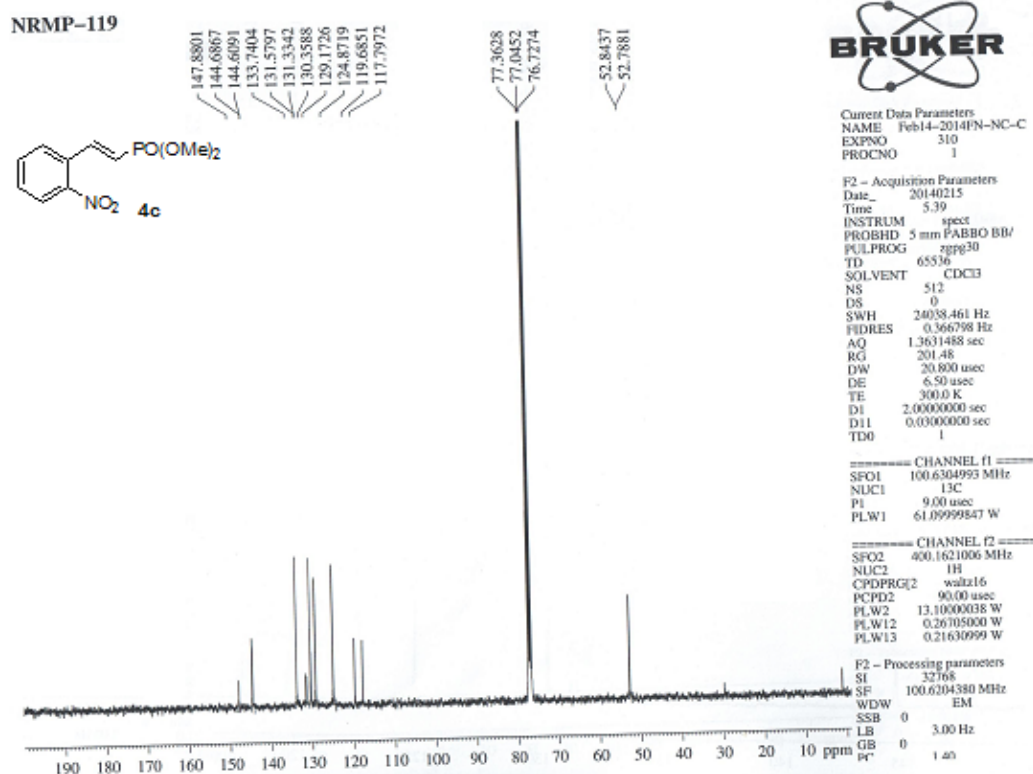


Figure 47: ^{13}C NMR spectrum of **4c**

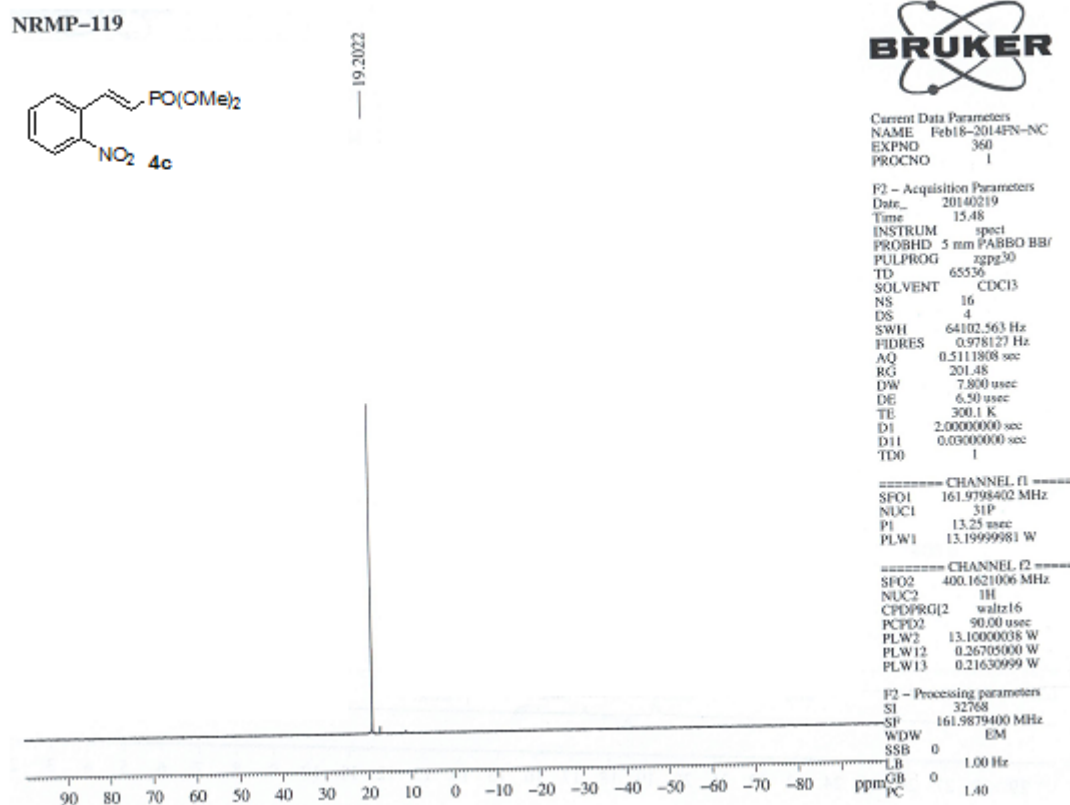


Figure 48: ^{31}P NMR spectrum of **4c**

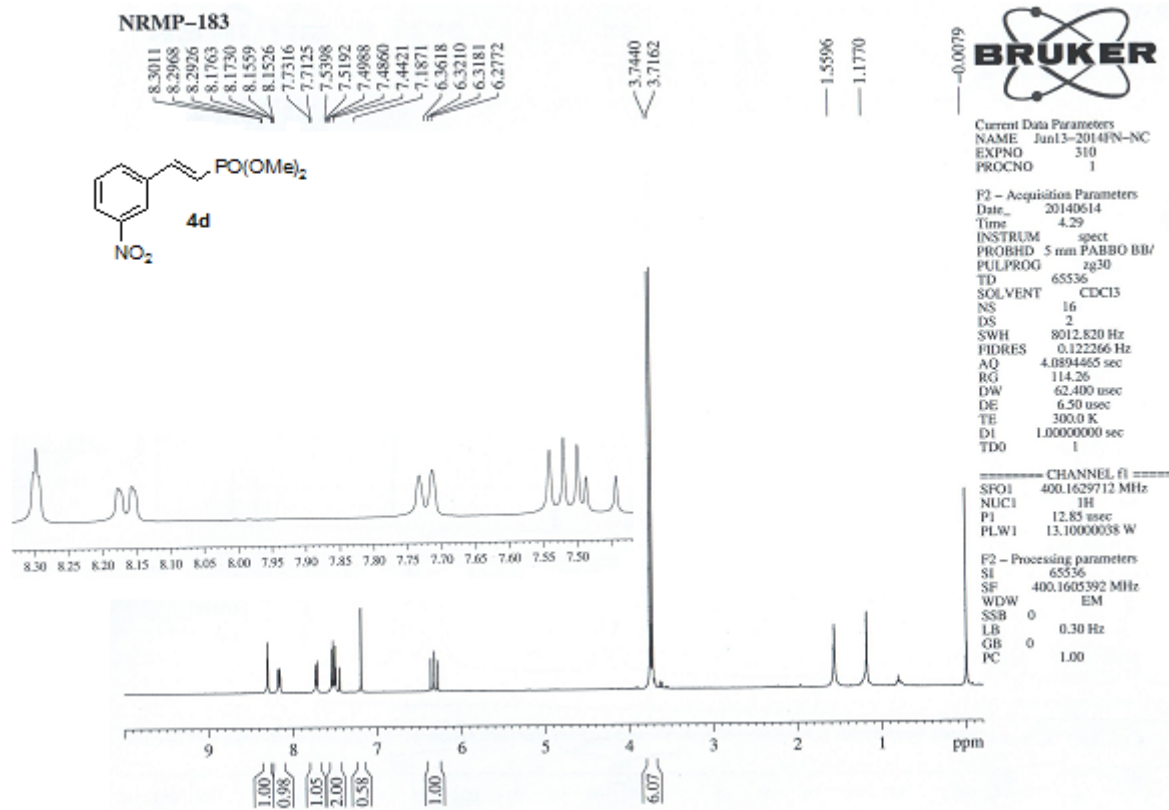


Figure 49: ¹H NMR spectrum of **4d**

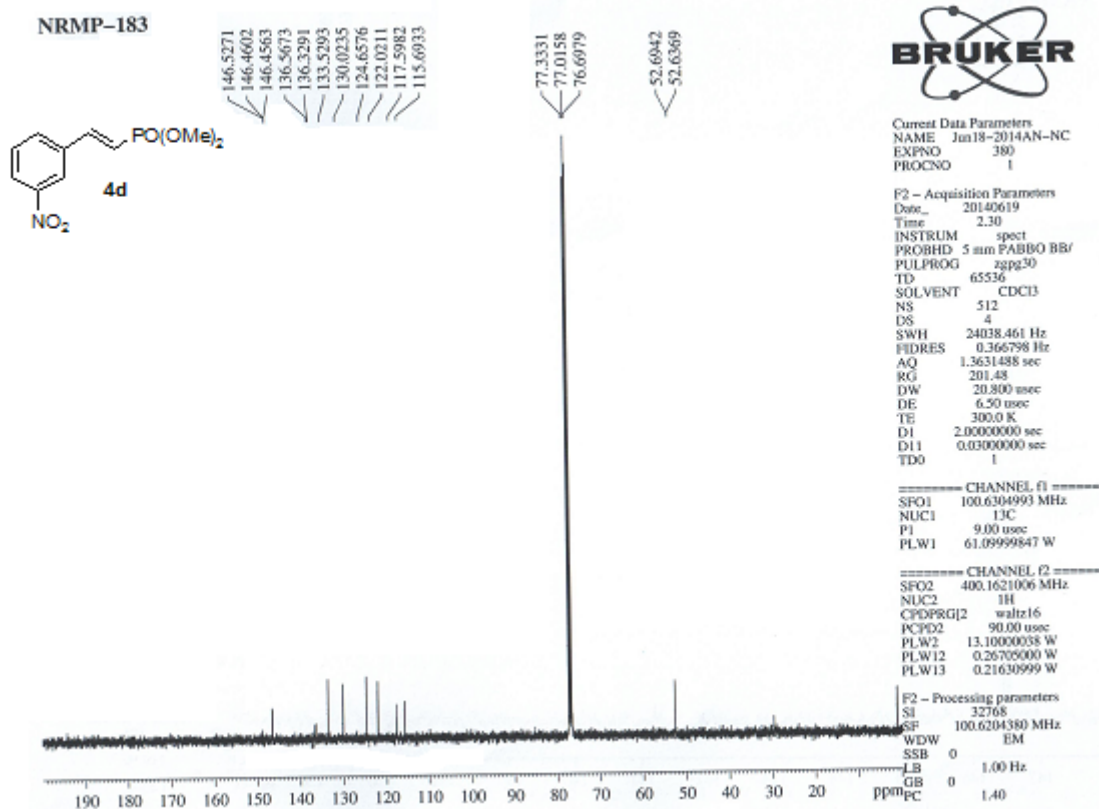
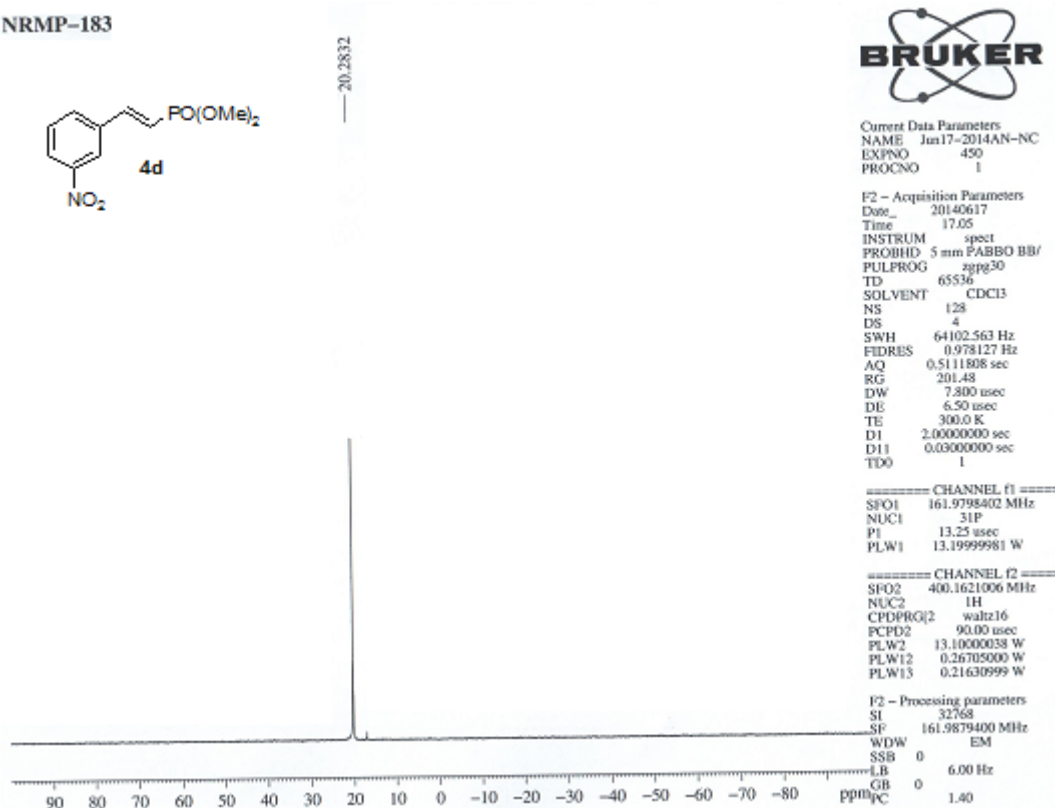
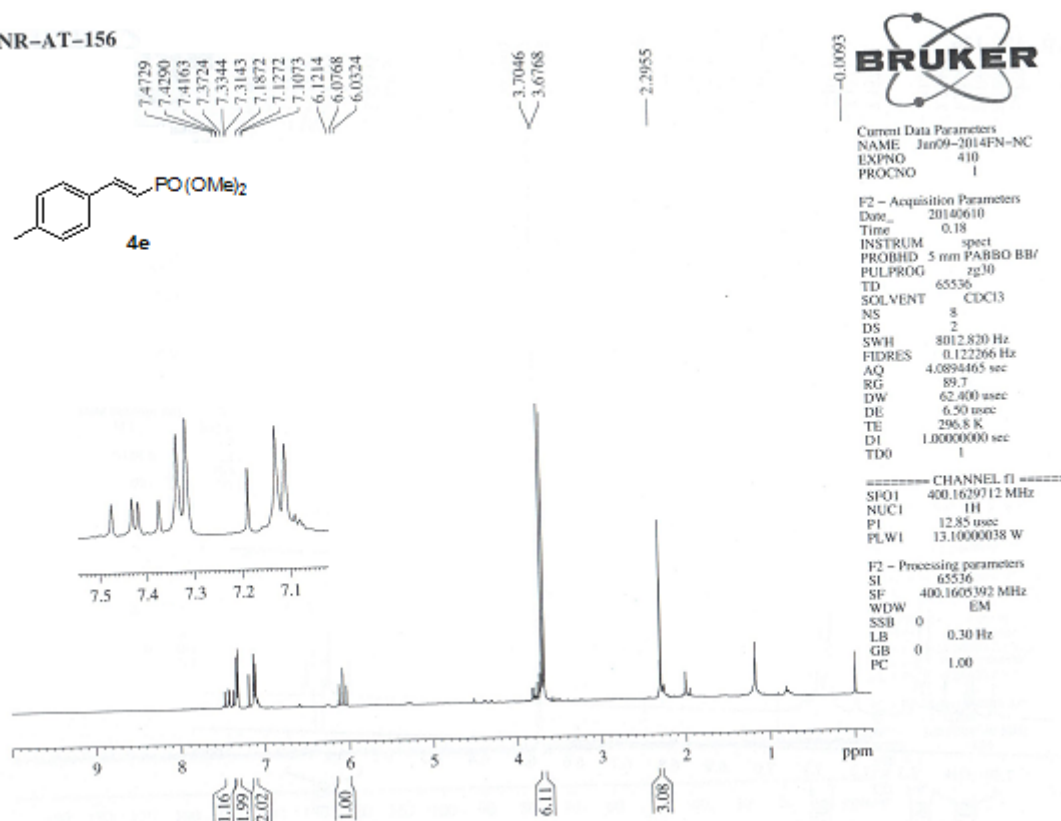


Figure 50: ¹³C NMR spectrum of **4d**

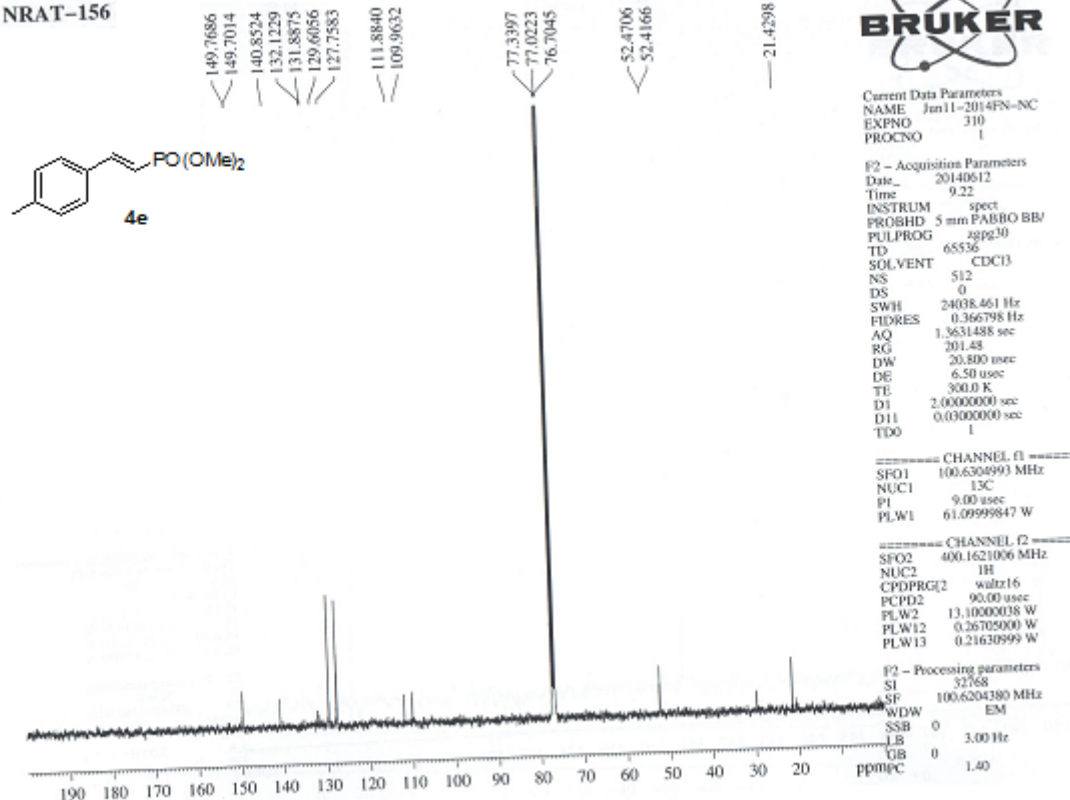
NRMP-183

Figure 51: ³¹P NMR spectrum of 4d

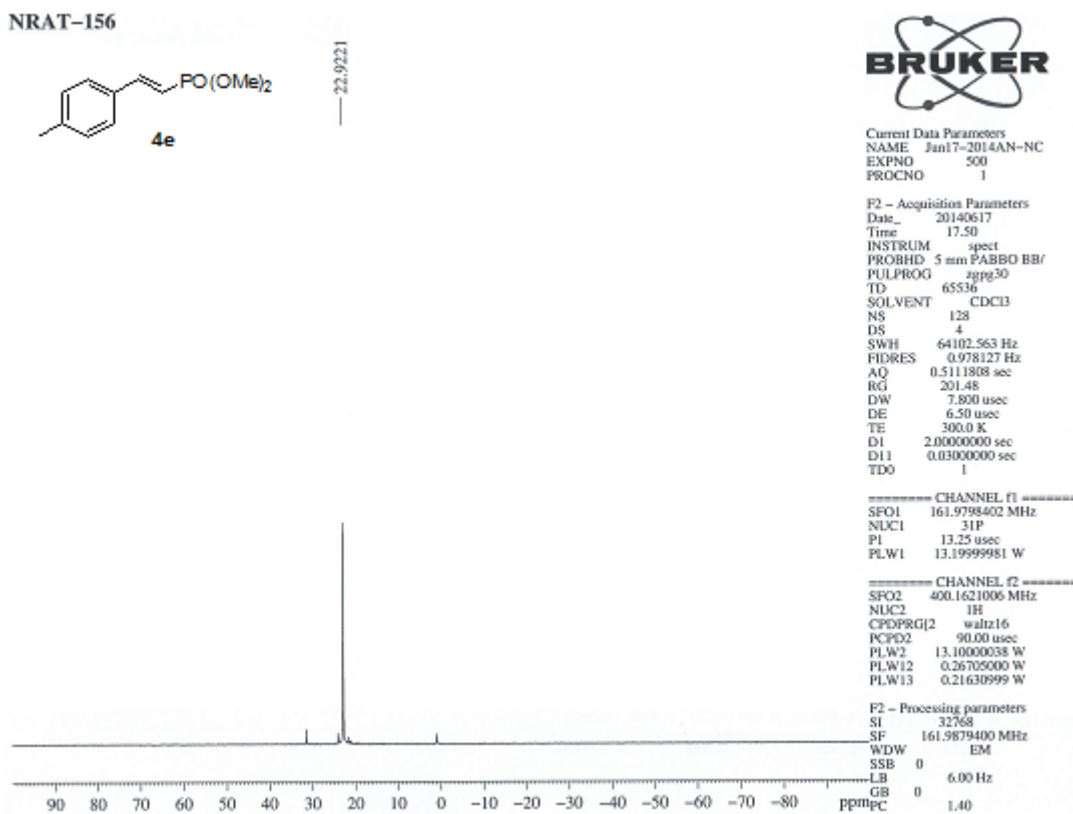
NR-AT-156

Figure 52: ¹H NMR spectrum of 4e

NRAT-156

Figure 53: ¹³C NMR spectrum of **4e**

NRAT-156

Figure 54: ³¹P NMR spectrum of **4e**

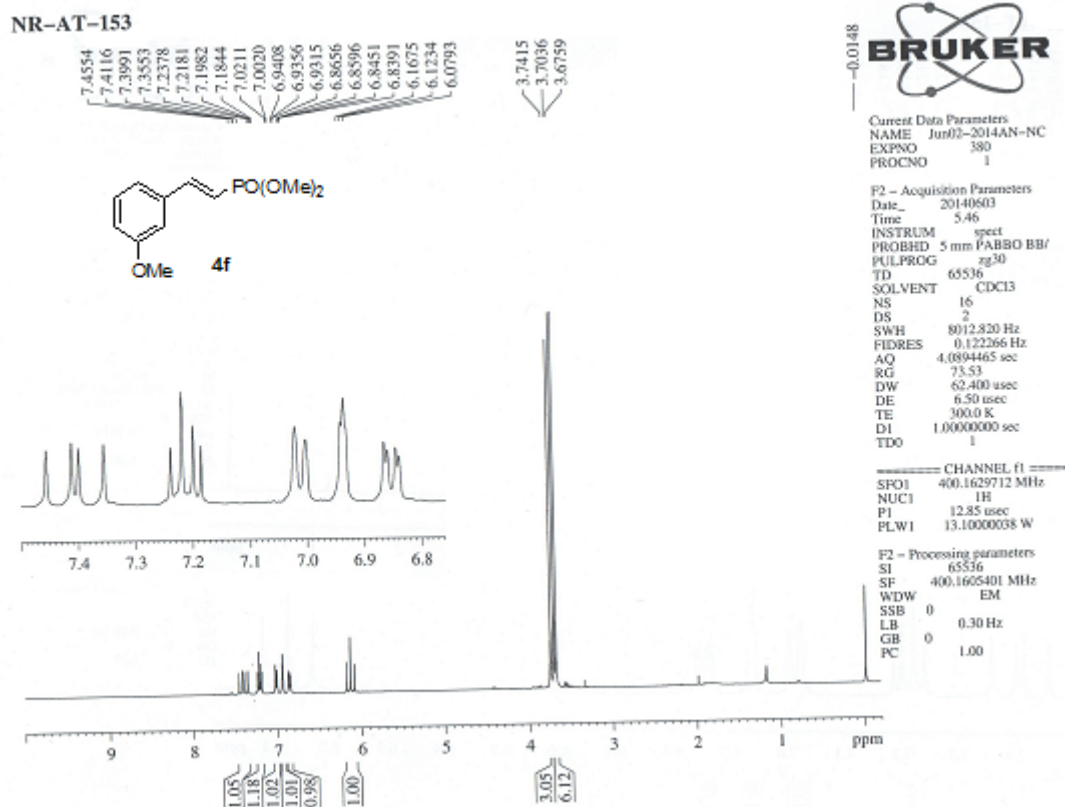


Figure 55: ^1H NMR spectrum of 4f

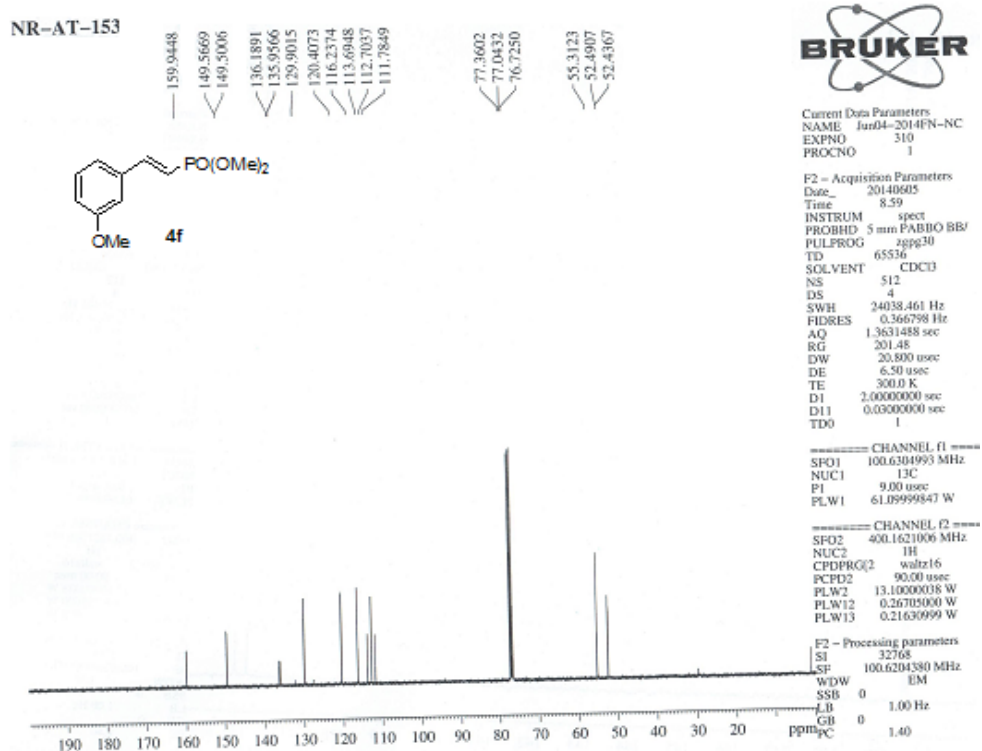
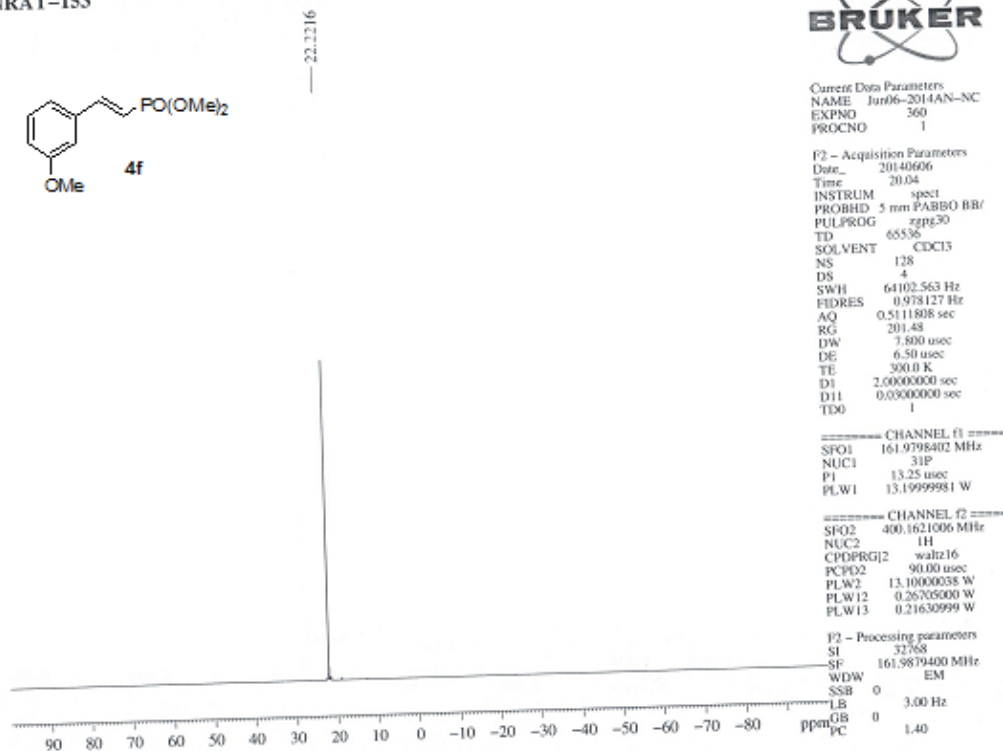
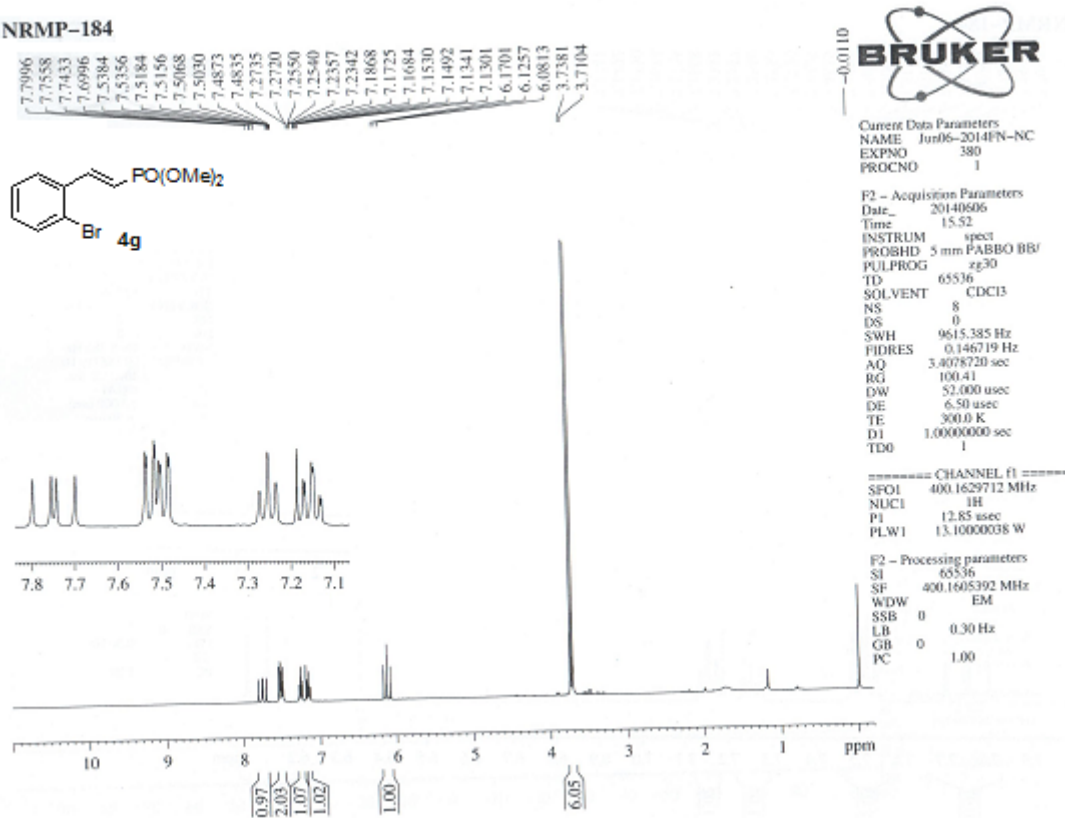


Figure 56: ^{13}C NMR spectrum of 4f

NRAT-153

Figure 57: ³¹P NMR spectrum of 4f

NRMP-184

Figure 58: ¹H NMR spectrum of 4g

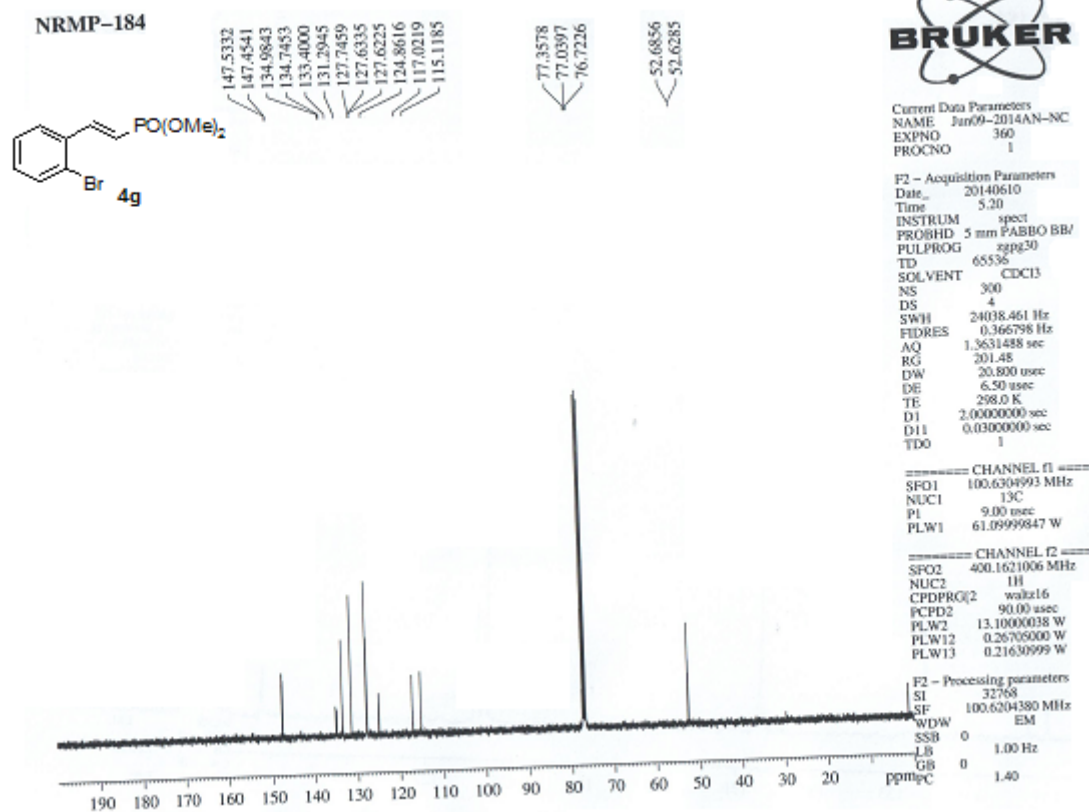


Figure 59: ¹³C NMR spectrum of 4g

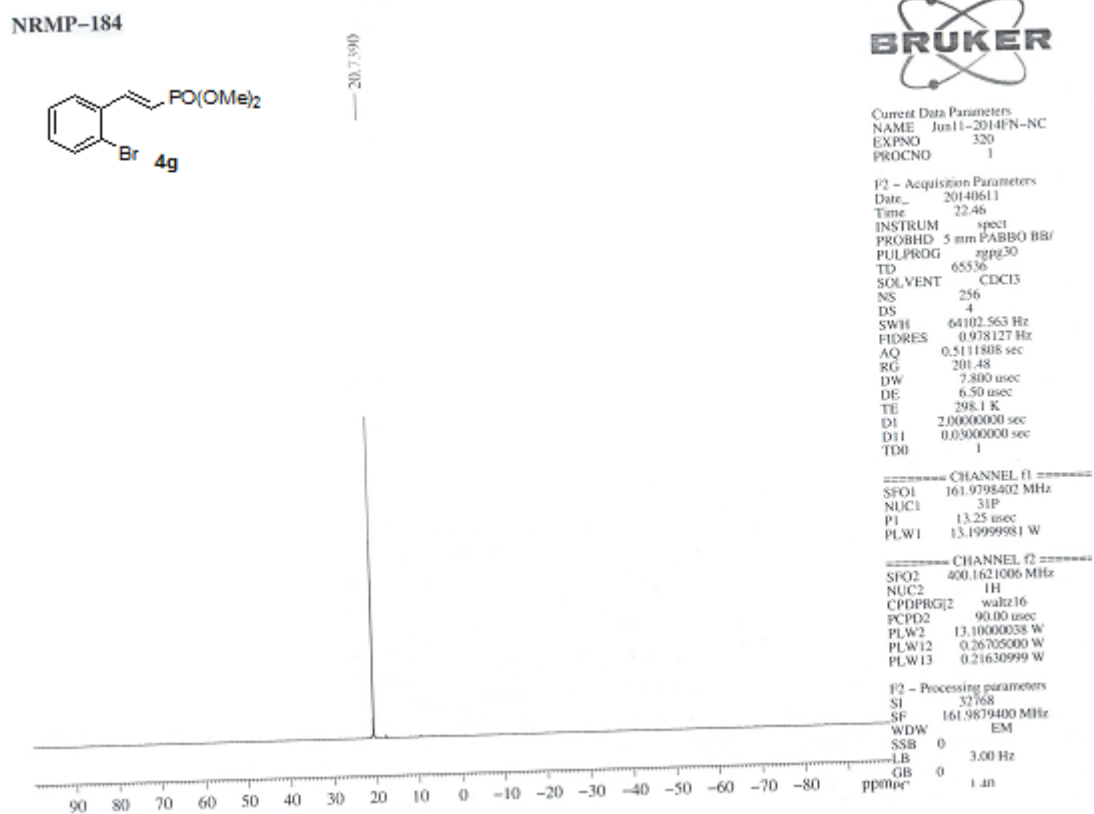


Figure 60: ³¹P NMR spectrum of 4g

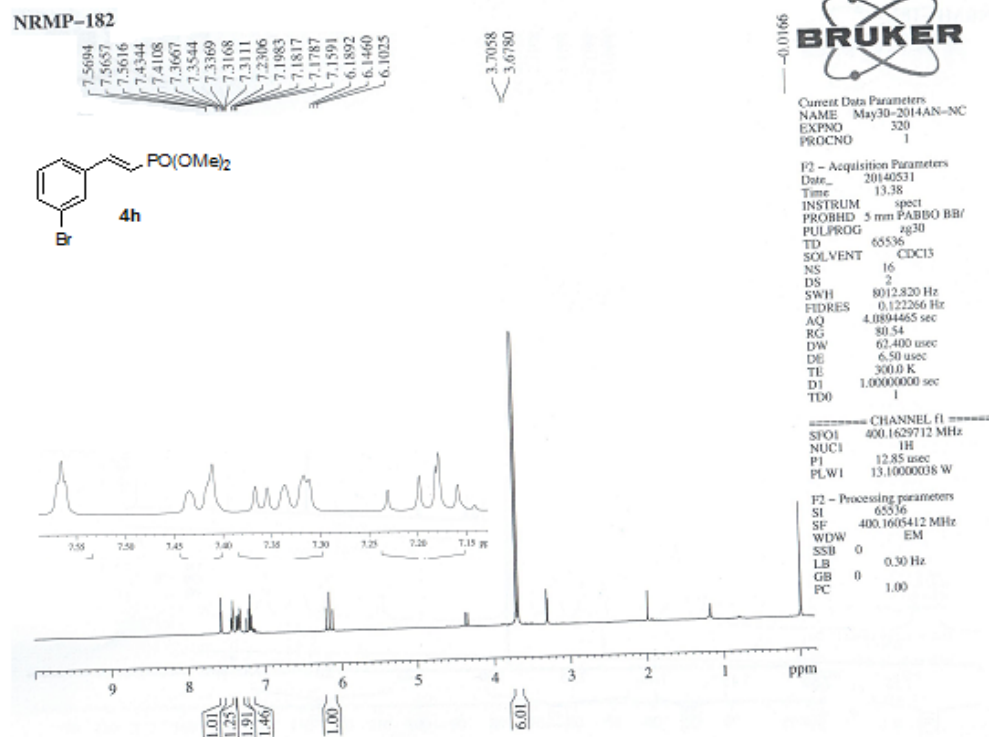


Figure 61: ¹H NMR spectrum of 4h

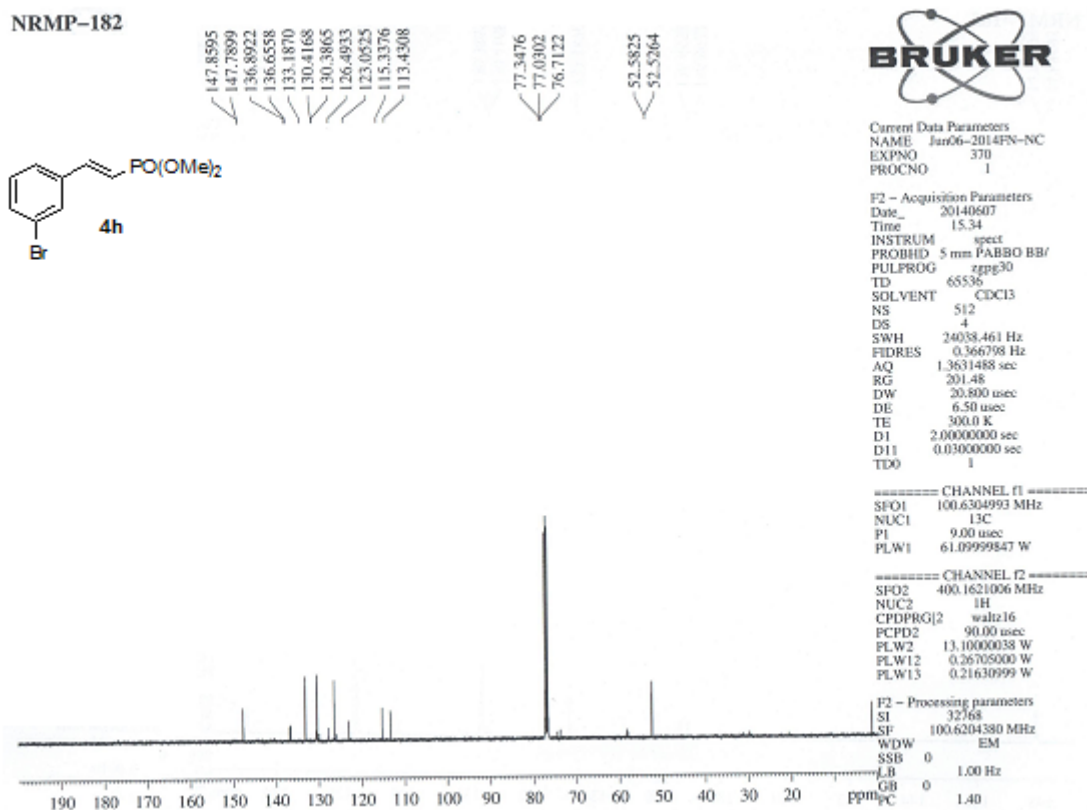
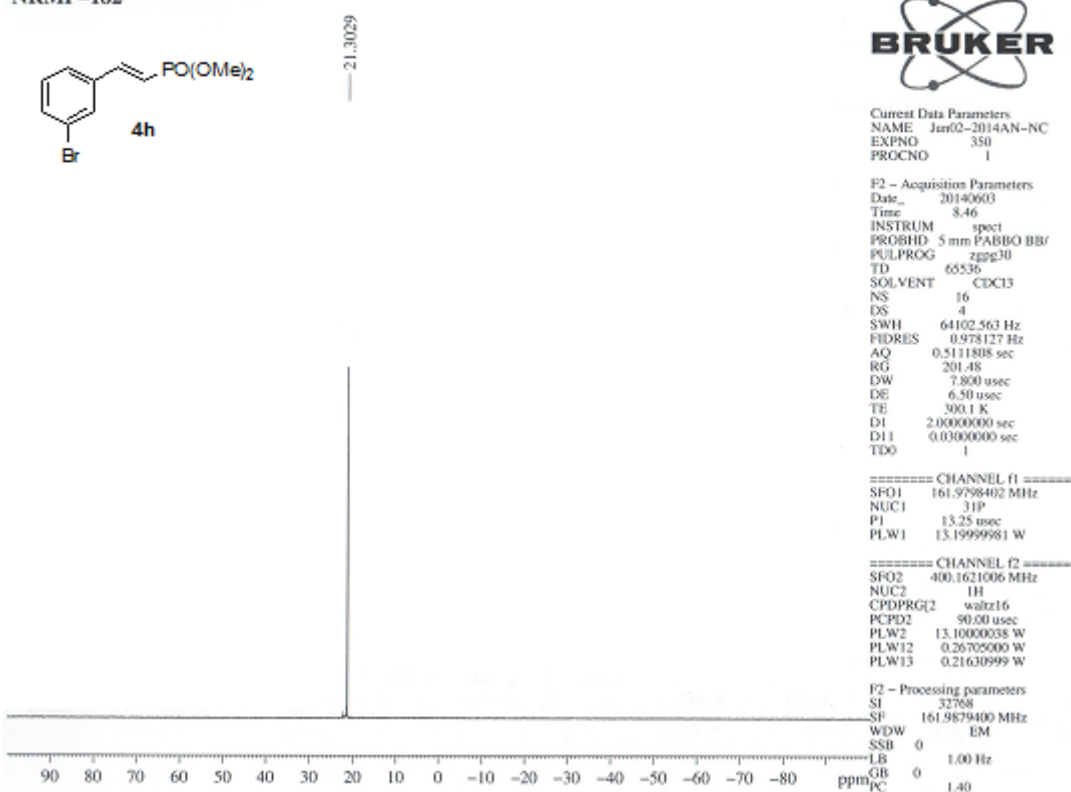
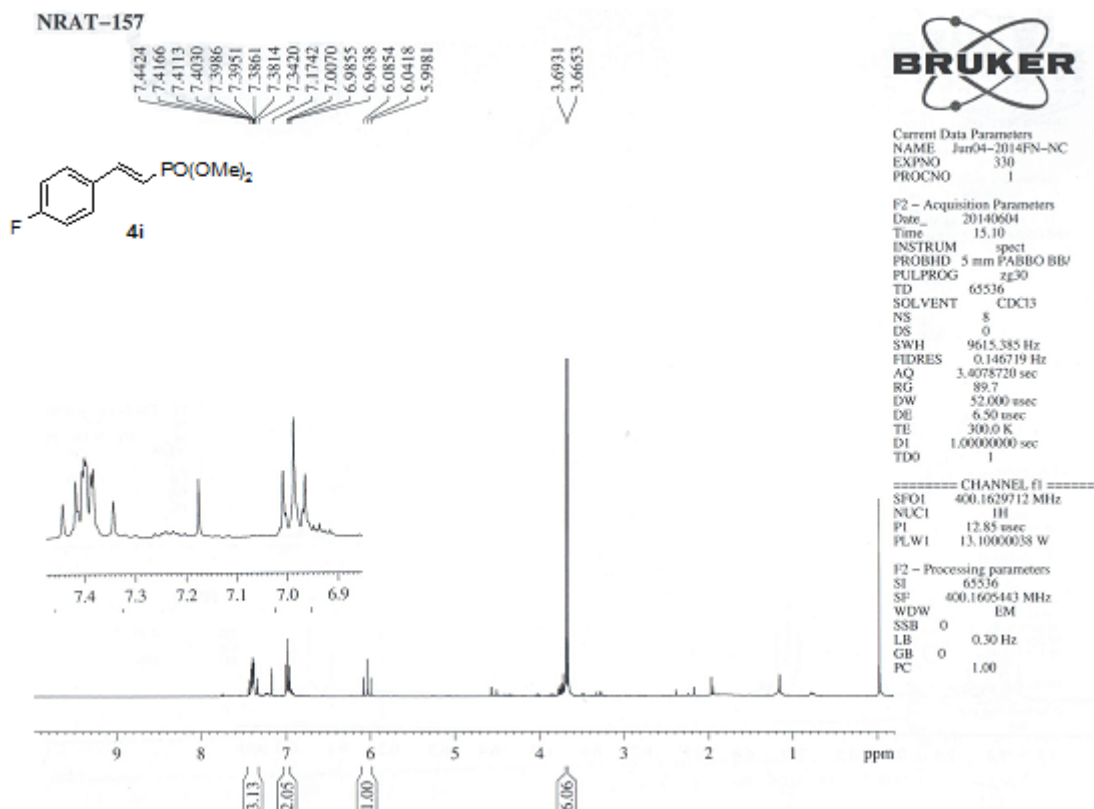


Figure 62: ¹³C NMR spectrum of 4h

NRMP-182

Figure 63: ³¹P NMR spectrum of 4hFigure 64: ¹H NMR spectrum of 4i

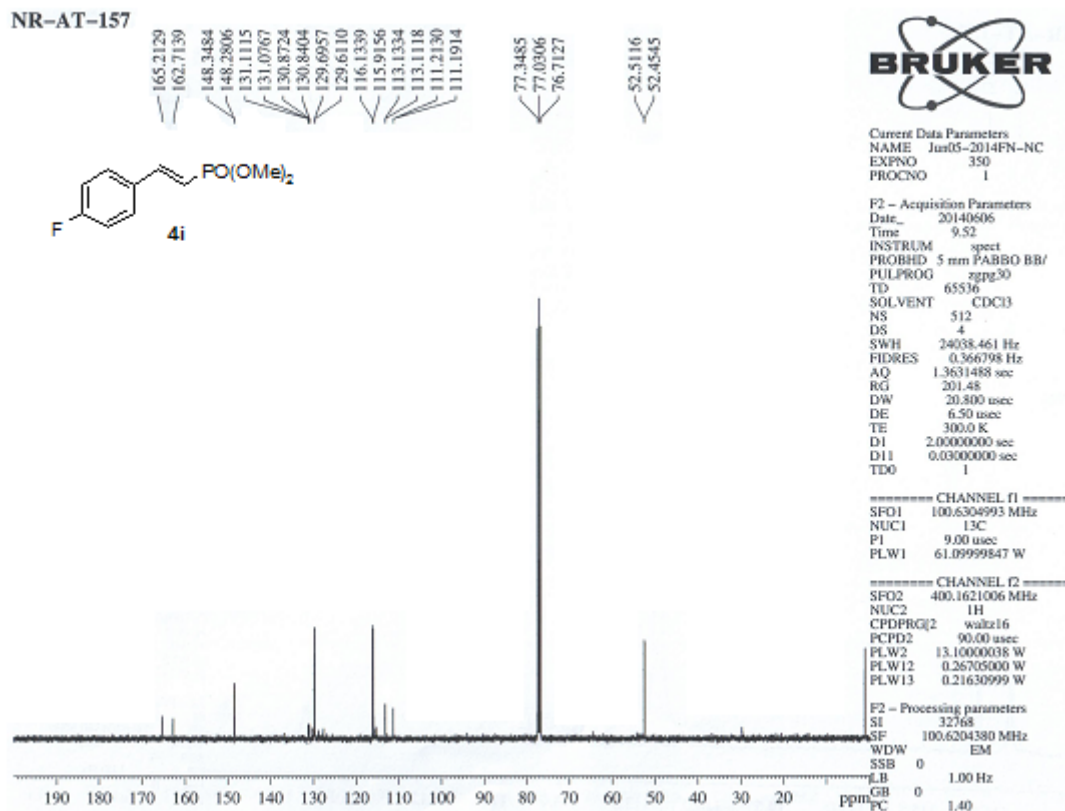


Figure 65: ^{13}C NMR spectrum of **4i**

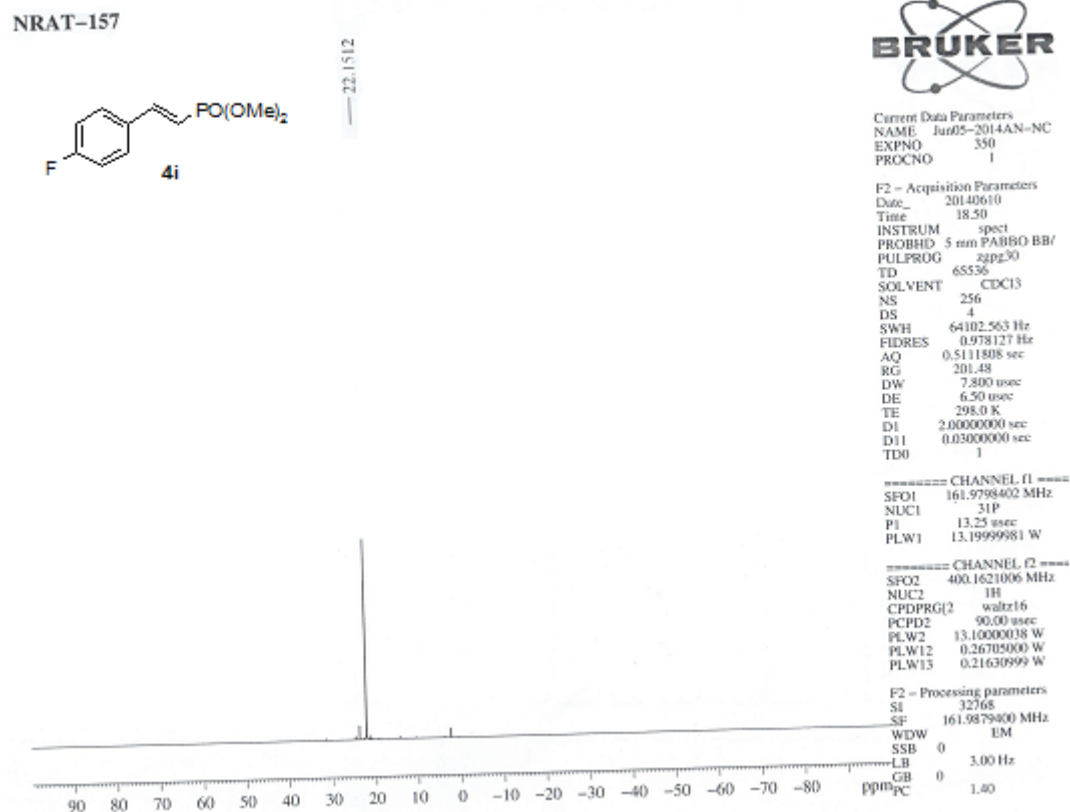


Figure 66: ^{31}P NMR spectrum of **4i**

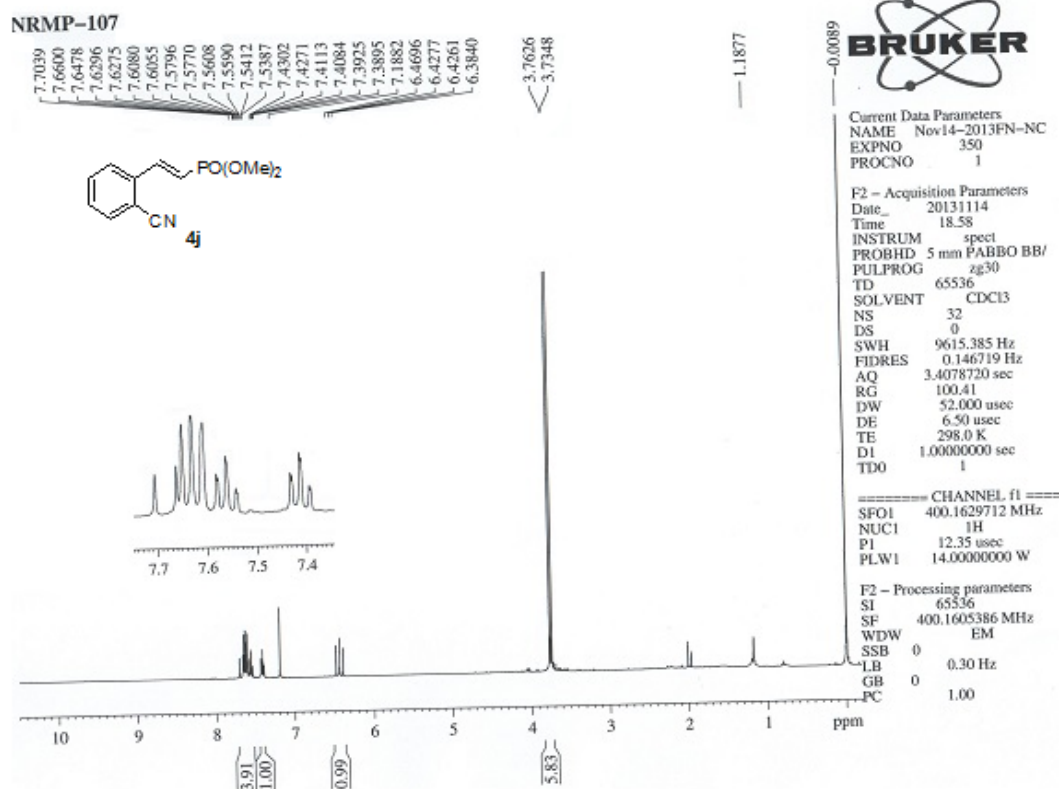


Figure 67: ¹H NMR spectrum of **4j**

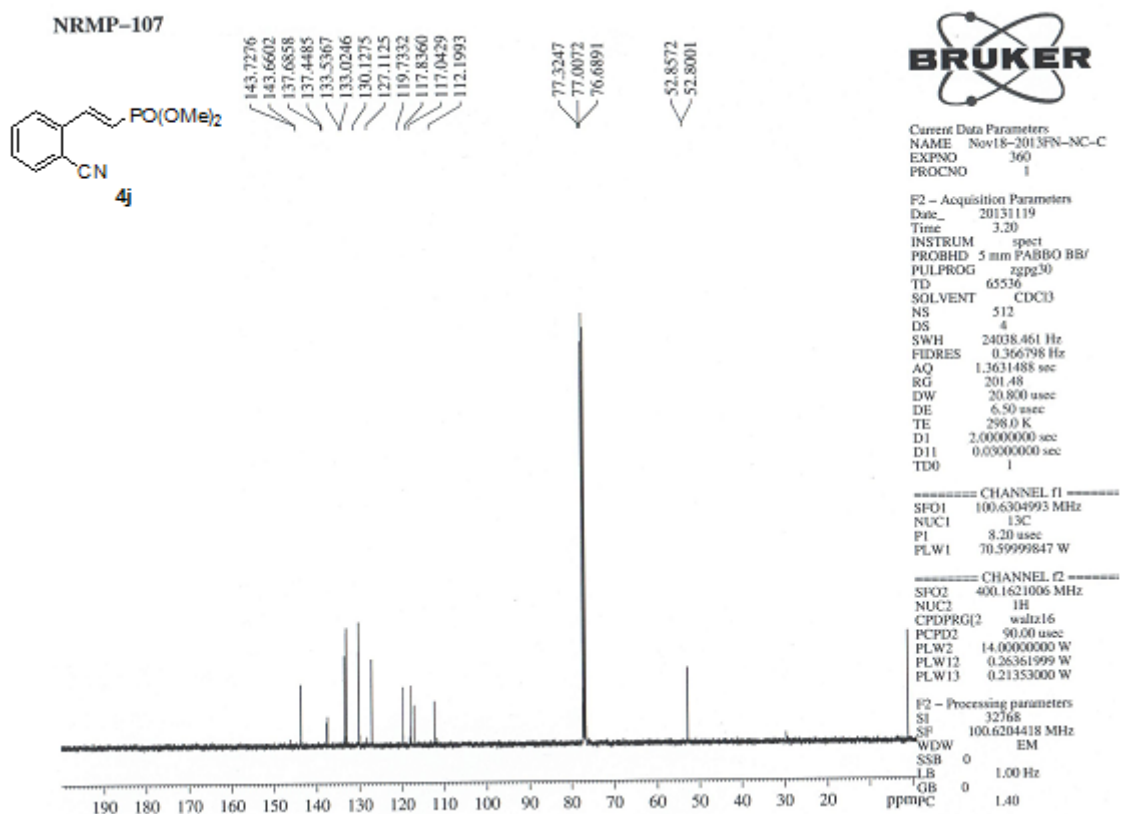
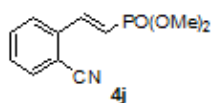


Figure 68: ¹³C NMR spectrum of **4j**

NRMP-107



19.4646

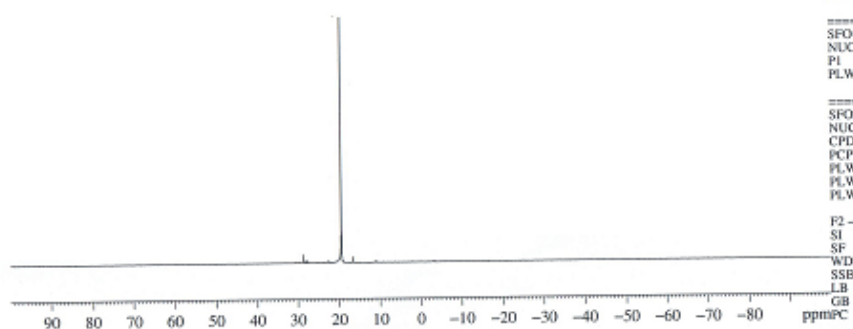


Current Data Parameters
NAME Feb18-2014FN-NC
EXPNO 350
PROCNO 1

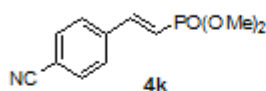
F2 - Acquisition Parameters
Date_ 20140219
Time 15.38
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111868 sec
RG 201.48
DW 7.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 161.9798402 MHz
NUC1 31P
P1 13.25 usec
PLW1 13.19999981 W
===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 161.9879400 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

Figure 69: ³¹P NMR spectrum of 4j

NR-AT-128



7.5946
7.5736
7.5015
7.4804
7.4604
7.4164
7.4045
7.3606
7.1851
6.2972
6.2557
6.2534
6.2119

3.7042
3.6764

1.1477

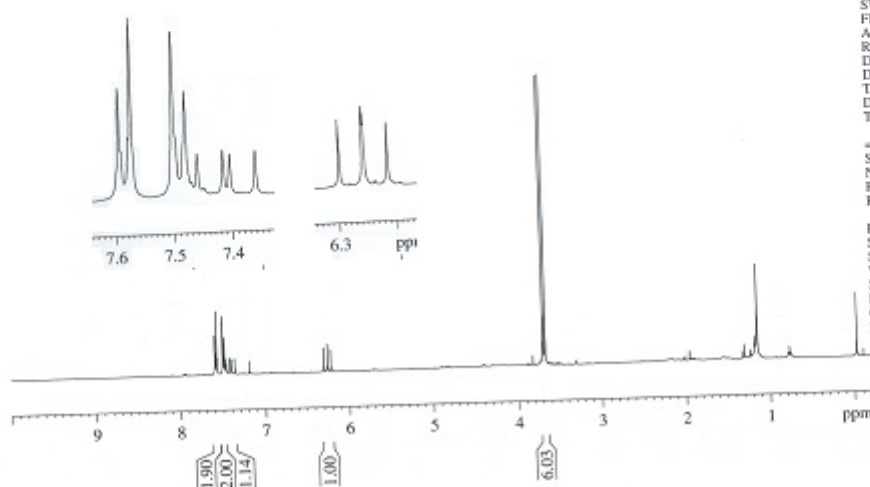


Current Data Parameters
NAME Feb21-2014AN-NC
EXPNO 340
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140221
Time 16.16
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 9615.385 Hz
FIDRES 0.146719 Hz
AQ 3.4078720 sec
RG 31.99
DW 52.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1629712 MHz
NUC1 1H
P1 12.85 usec
PLW1 13.10000038 W

F2 - Processing parameters
SI 65536
SF 400.1605398 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 70: ¹H NMR spectrum of 4k

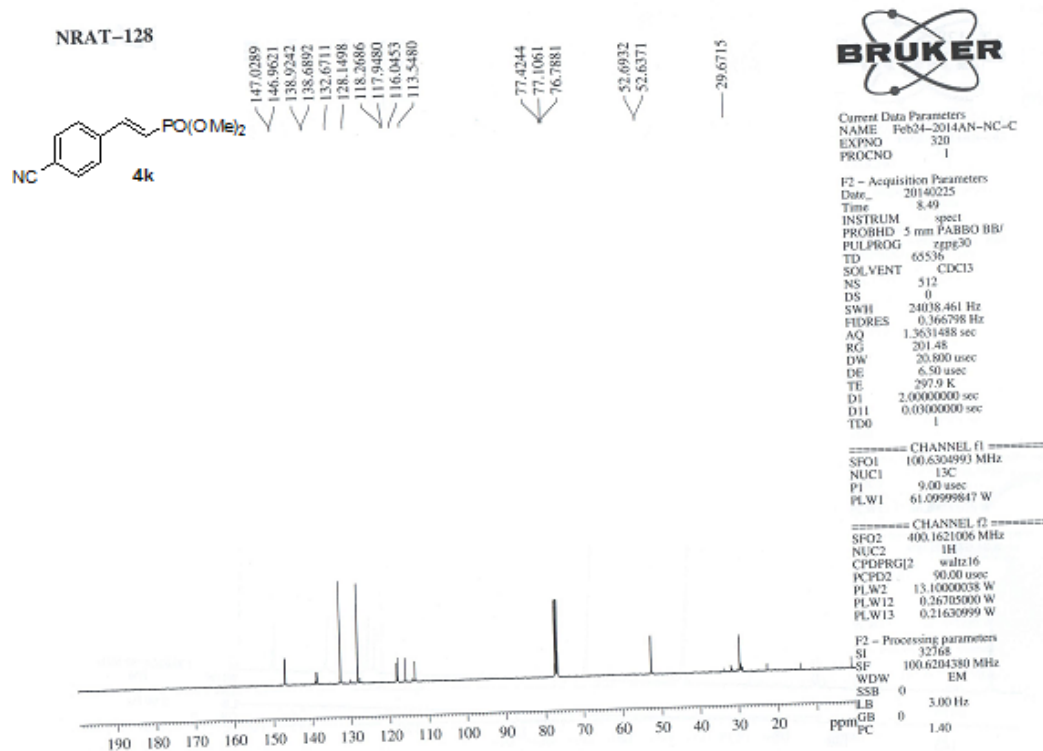


Figure 71: ¹³C NMR spectrum of 4k

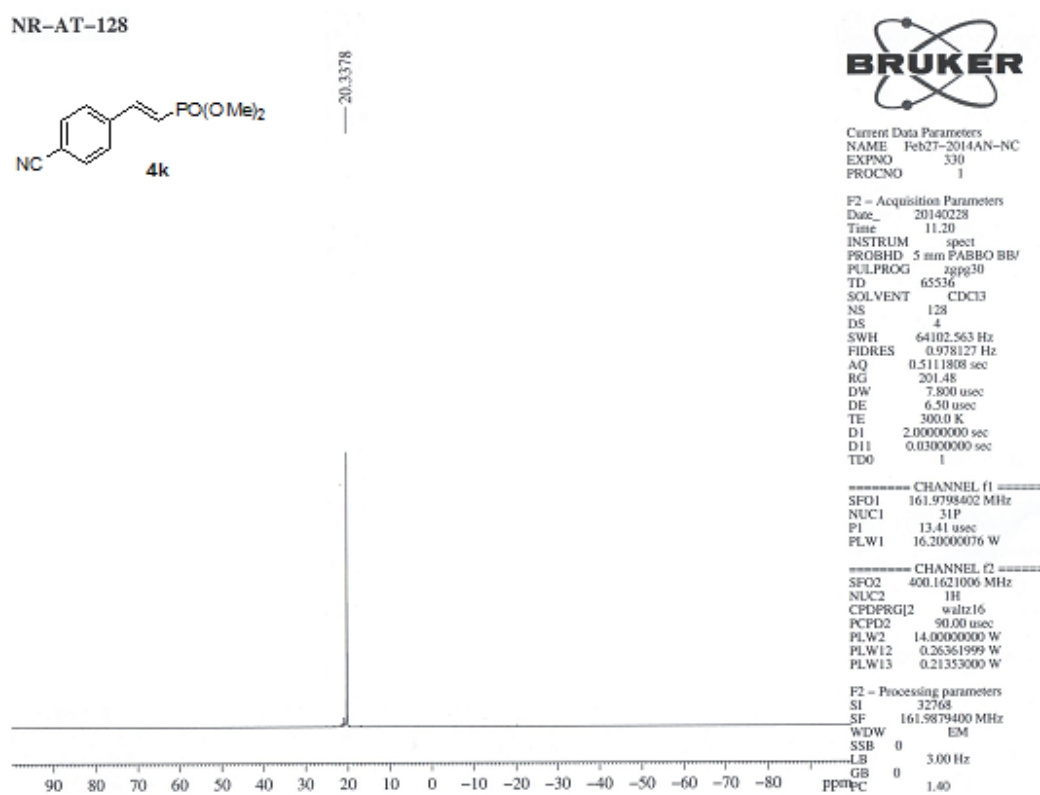


Figure 72: ³¹P NMR spectrum of 4k

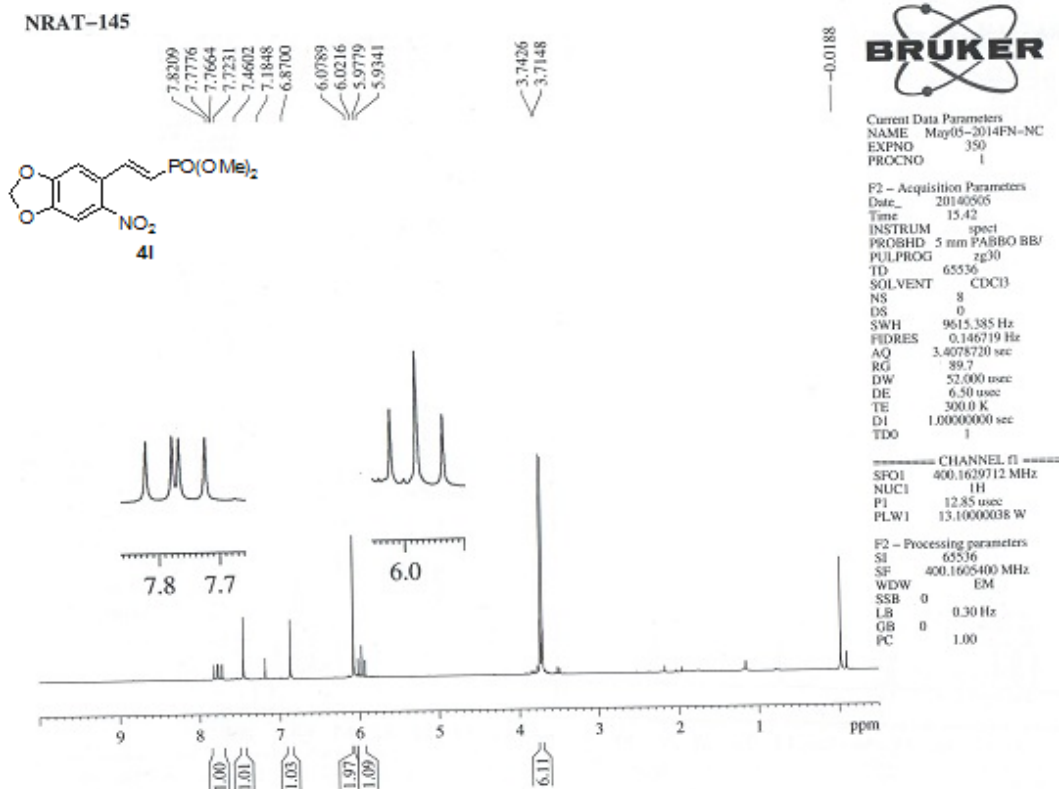


Figure 73: ¹H NMR spectrum of **41**

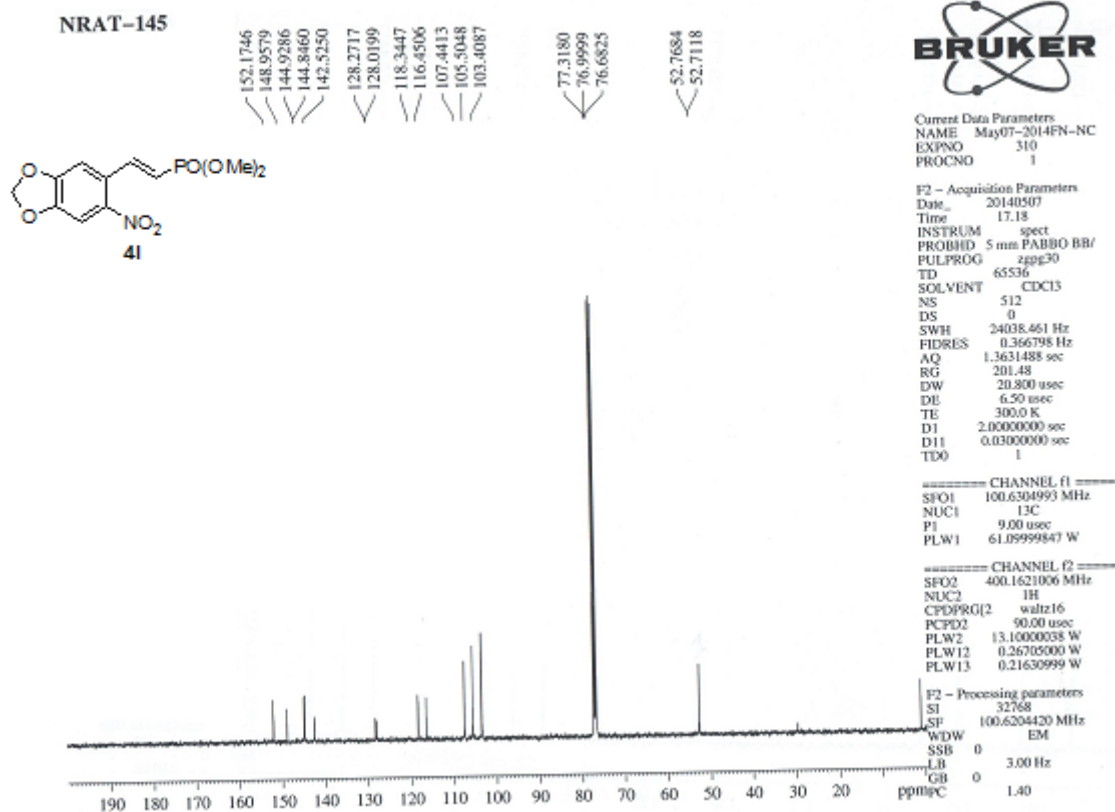
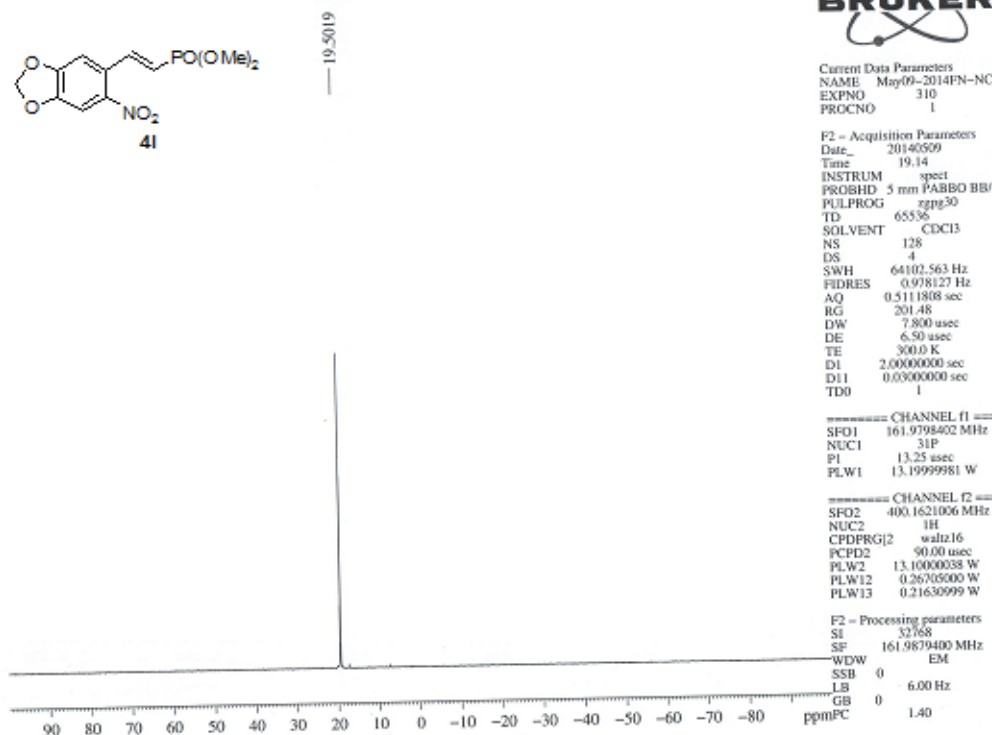
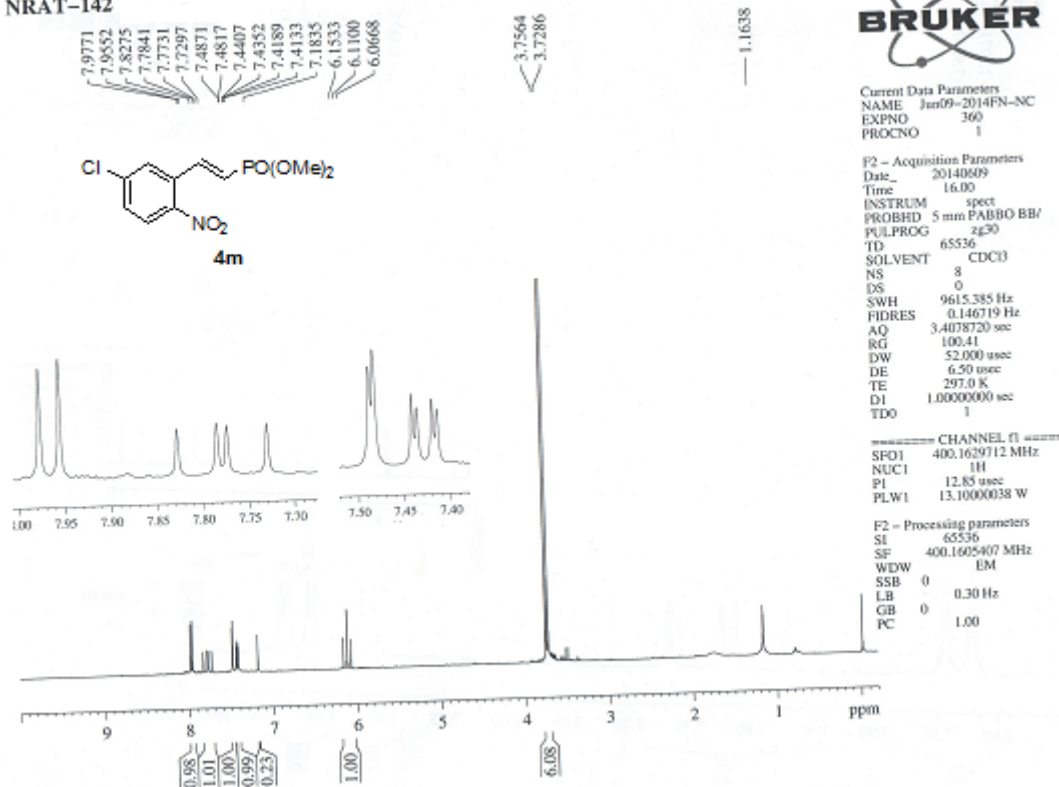


Figure 74: ¹³C NMR spectrum of **41**

NRAT-145

Figure 75: ³¹P NMR spectrum of 4l

NRAT-142

Figure 76: ¹H NMR spectrum of 4m

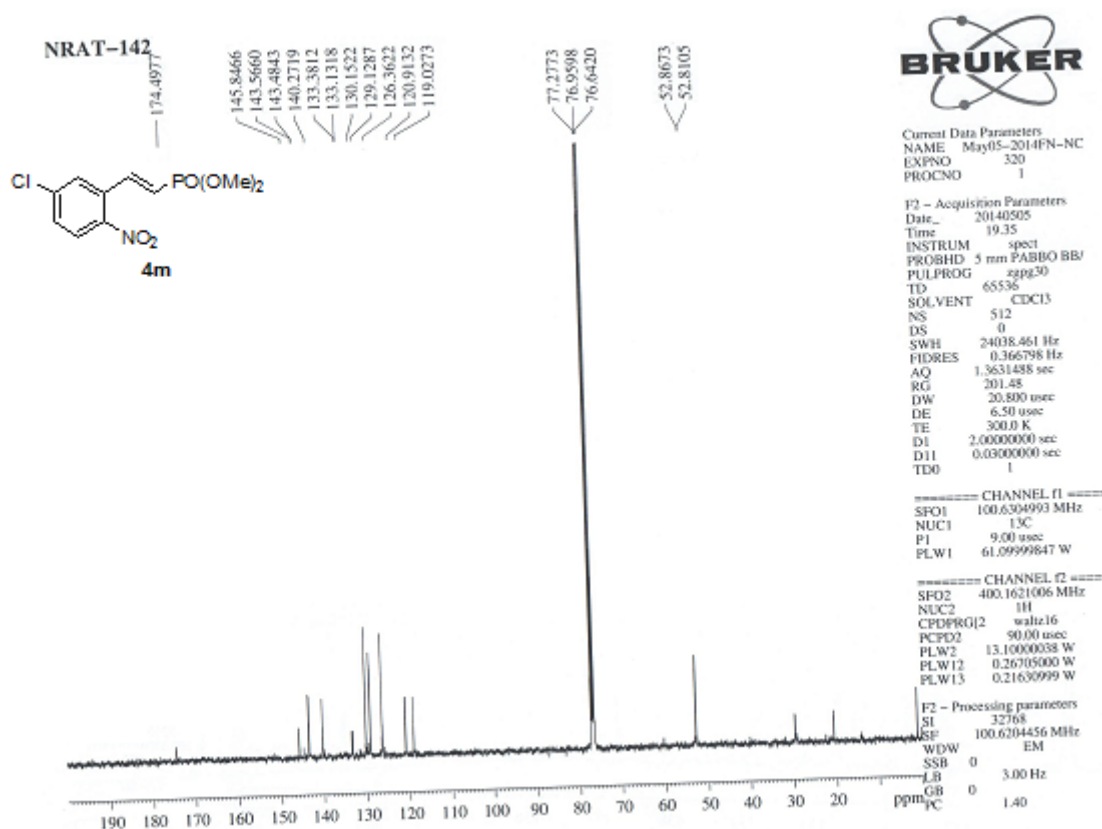


Figure 77: ¹³C NMR spectrum of 4m

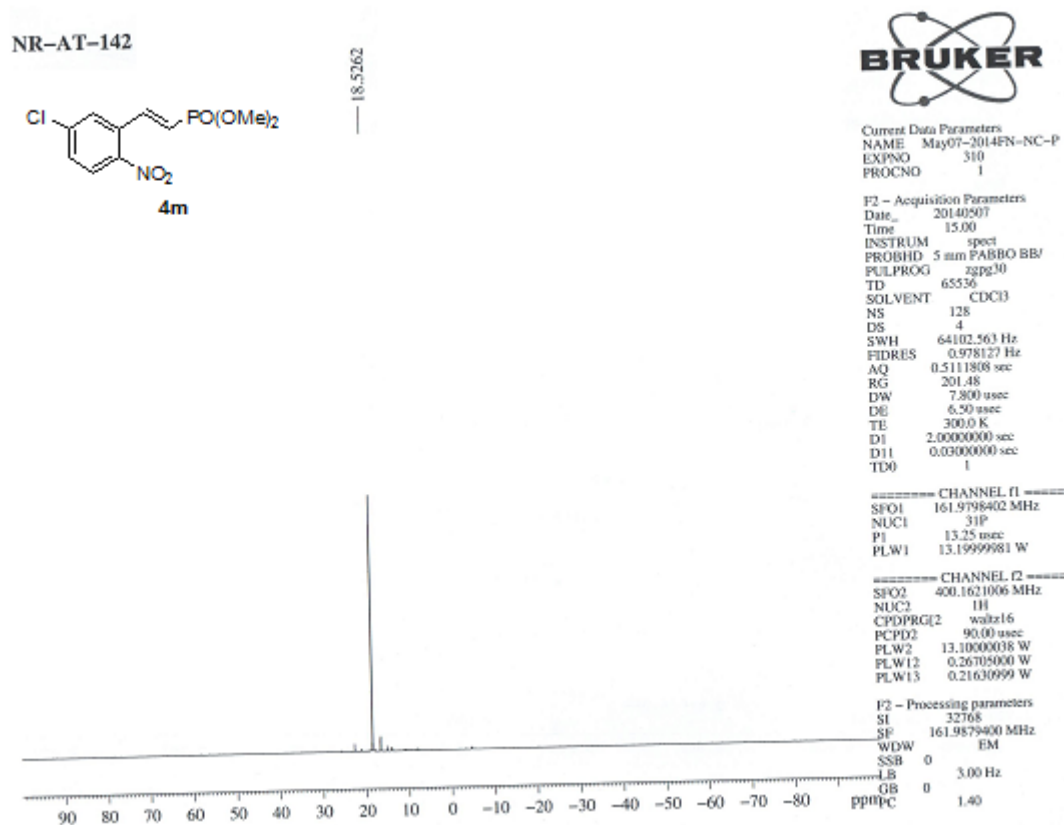


Figure 78: ³¹P NMR spectrum of 4m

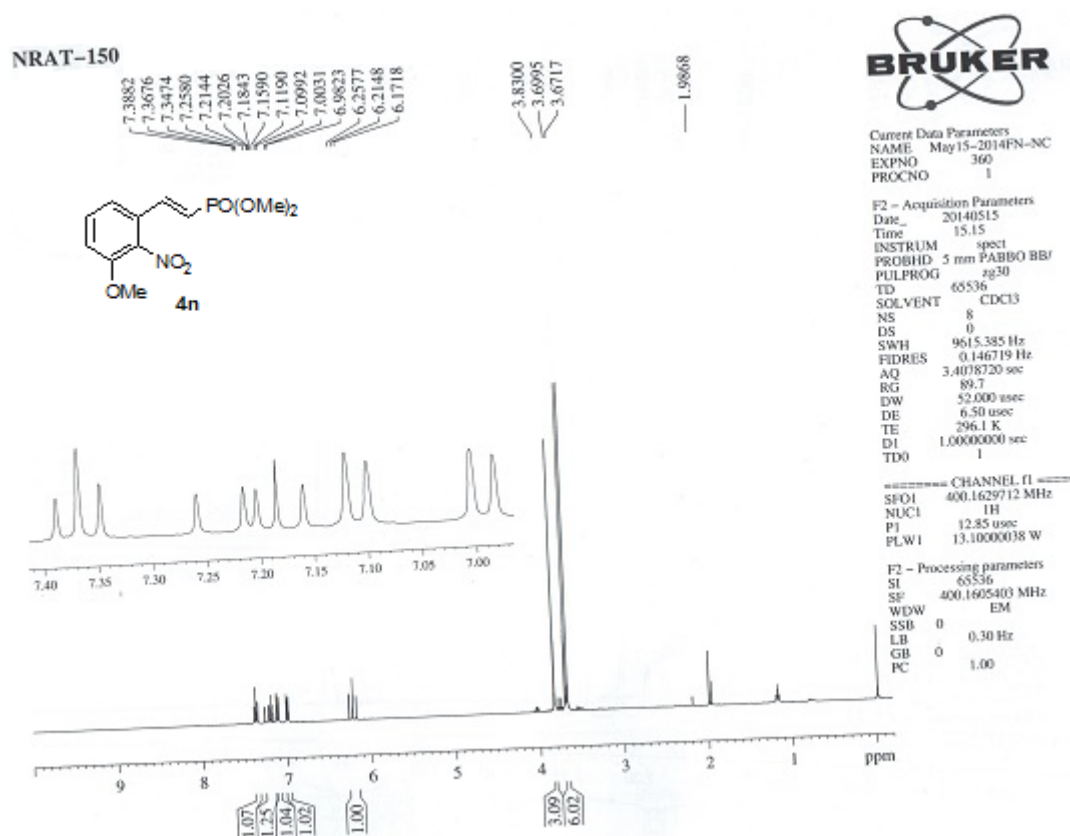


Figure 79: ^1H NMR spectrum of 4n

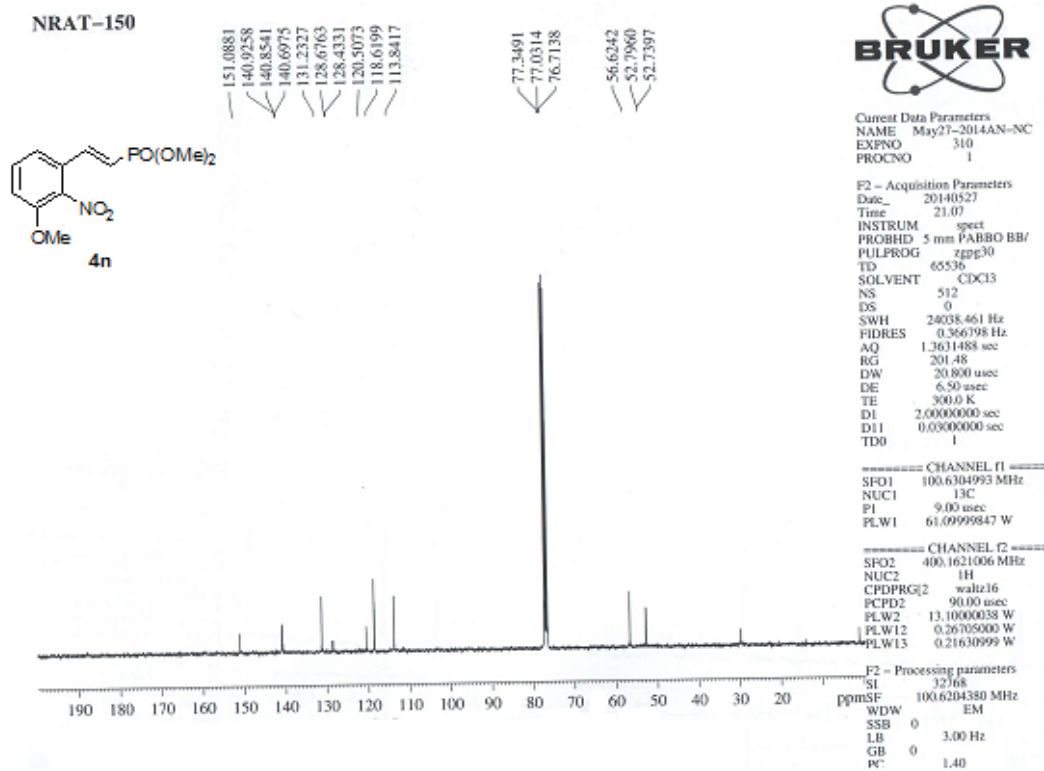
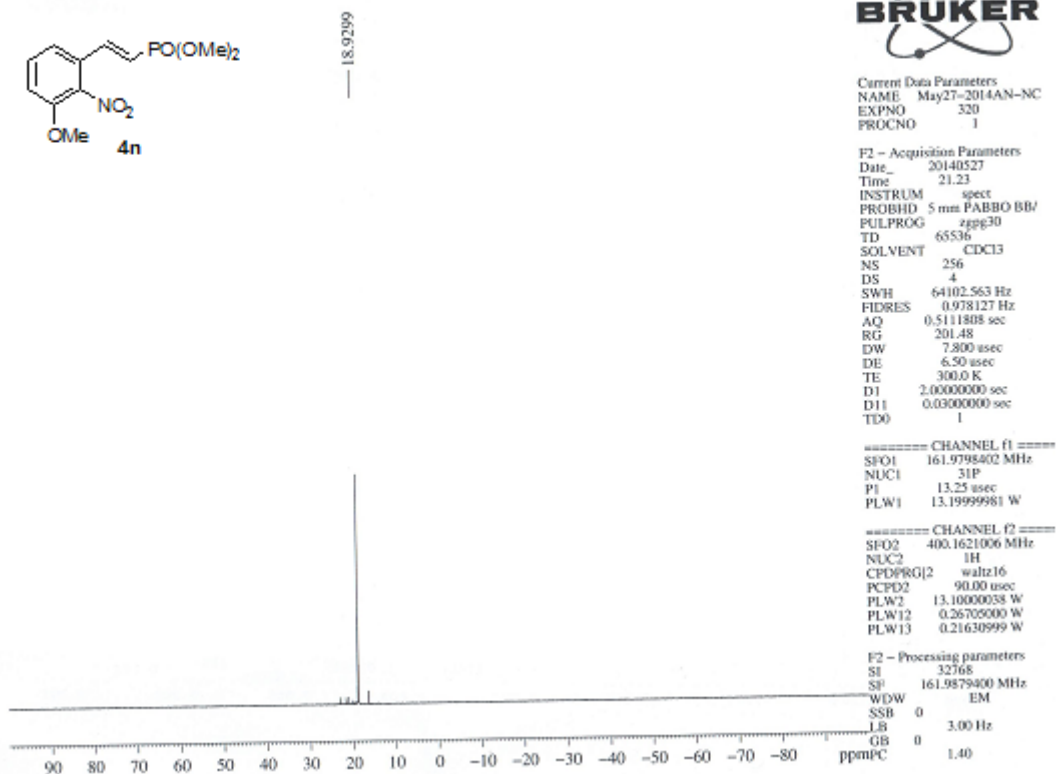
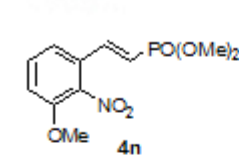
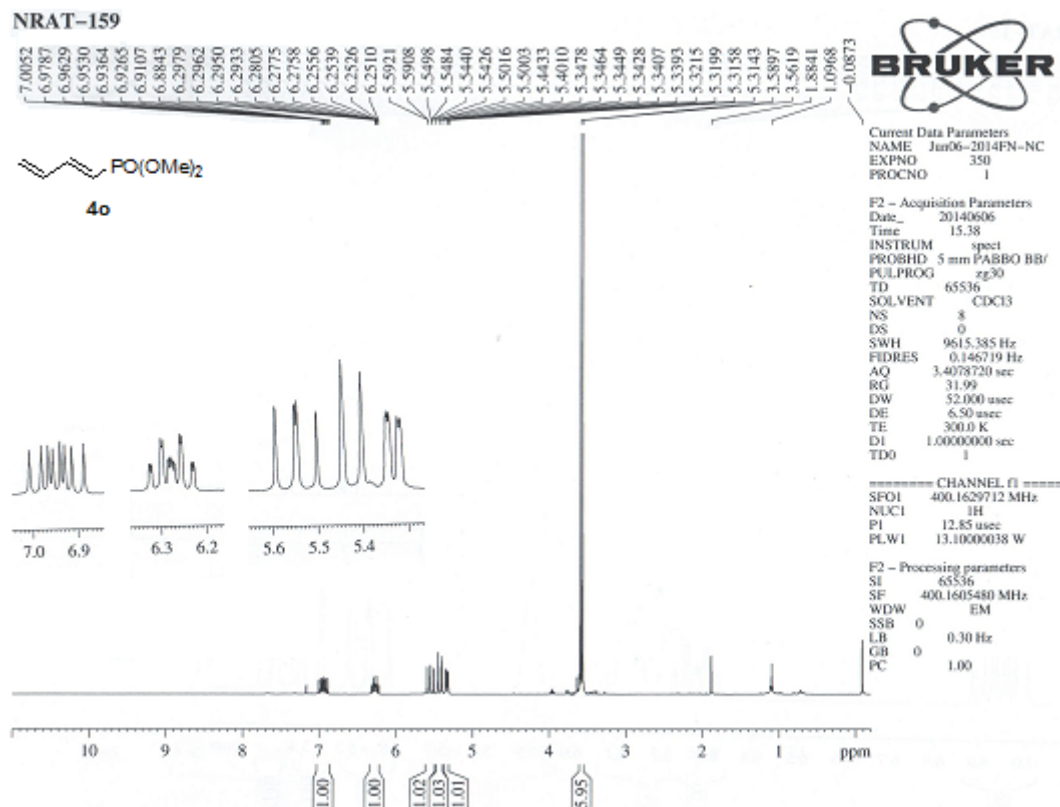
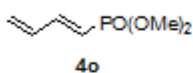


Figure 80: ^{13}C NMR spectrum of 4n

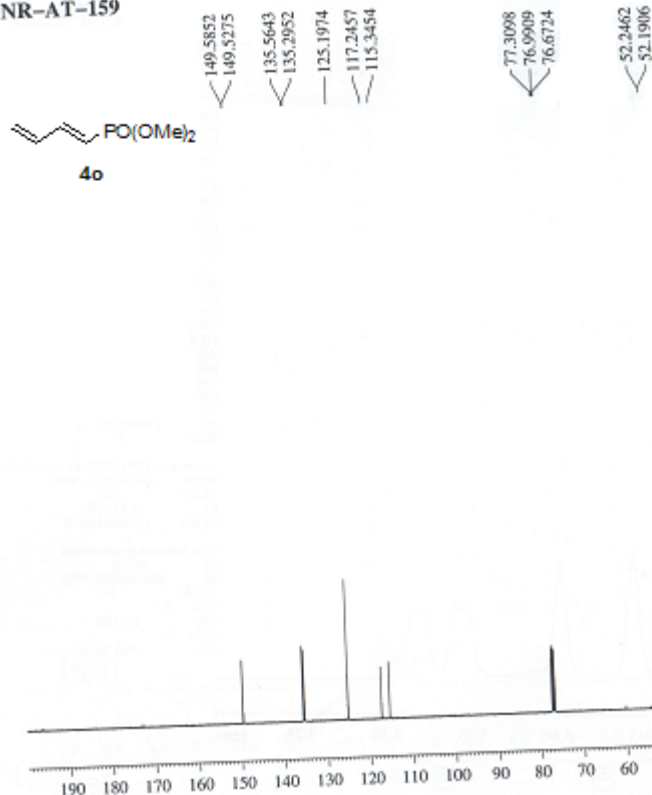
NRAT-150

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

NRAT-159

Figure 82: ^1H NMR spectrum of 4o

NR-AT-159



Current Data Parameters
NAME Jun09-2014AN-NC
EXPNO 330
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140610
Time 4.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 201.48
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 100.6304993 MHz
NUC1 13C
P1 9.00 usec
PLW1 61.09999847 W

===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 100.6204494 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure 83: ¹³C NMR spectrum of **4o**

NRAT-159



Current Data Parameters
NAME Jun17-2014AN-
EXPNO 480
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140617
Time 17.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 201.48
DW 7.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 161.9798402 MHz
NUC1 31P
P1 13.25 usec
PLW1 13.19999981 W

===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 161.9879400 MHz
WDW EM
SSB 0
LB 6.00 Hz
GB 0
PC 1.40

Figure 84: ³¹P NMR spectrum of **4o**

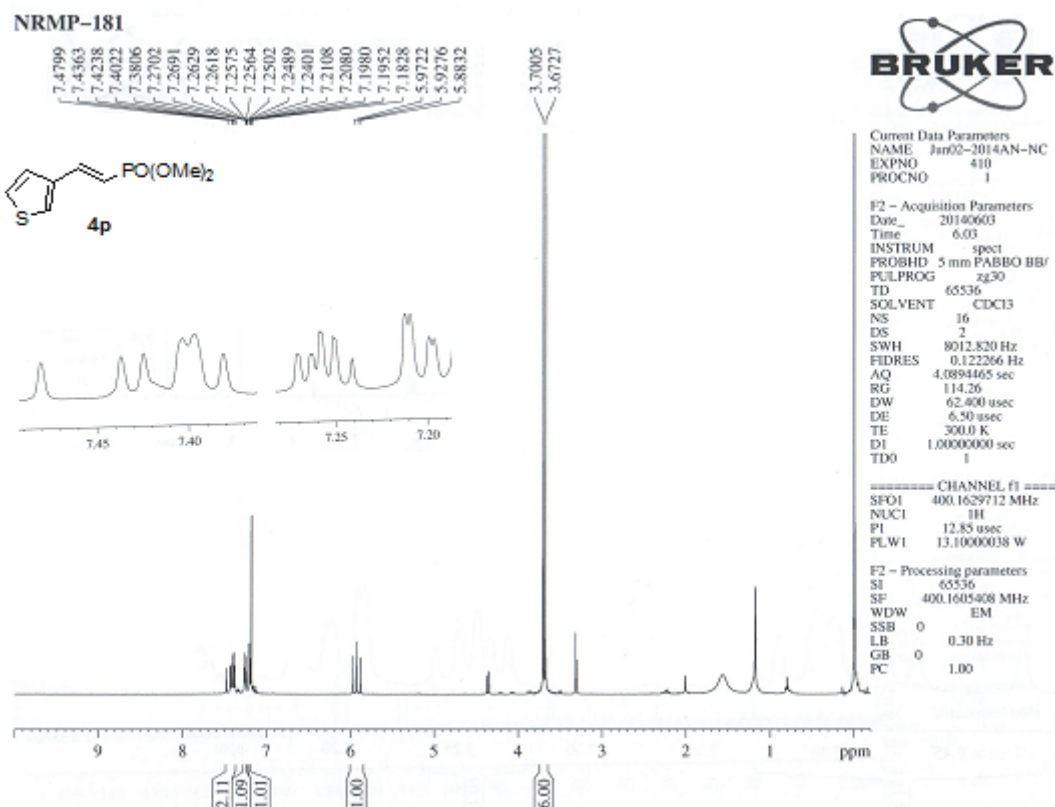


Figure 85: ^1H NMR spectrum of 4p

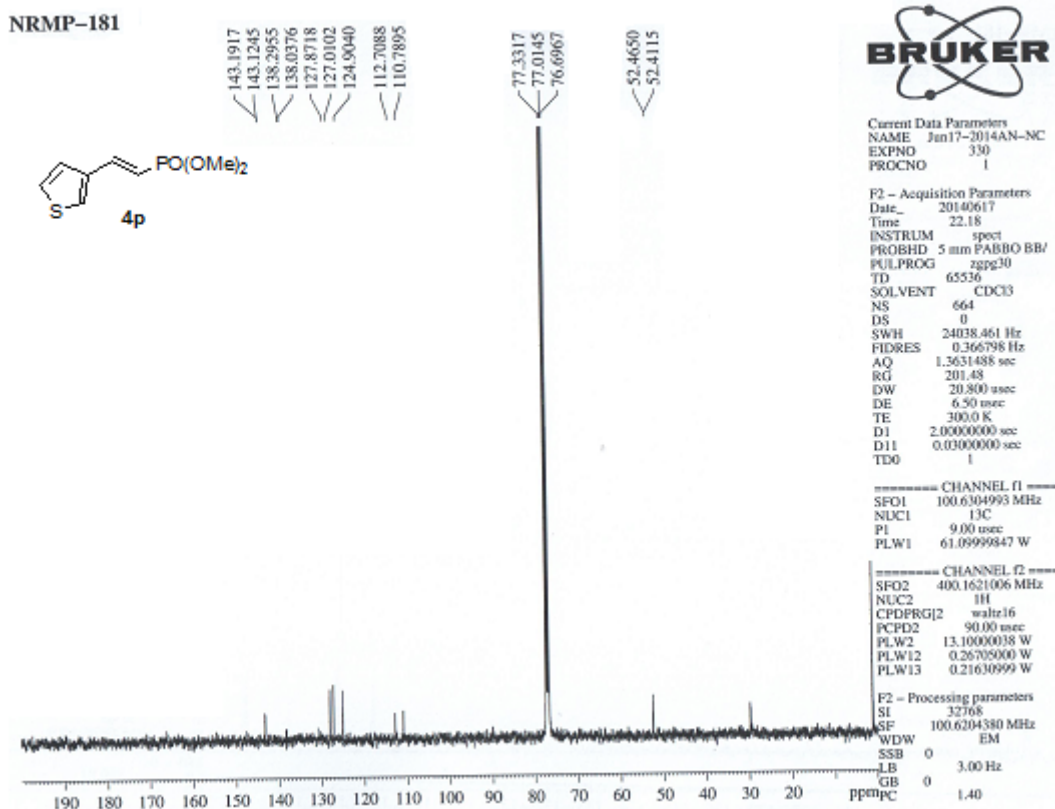
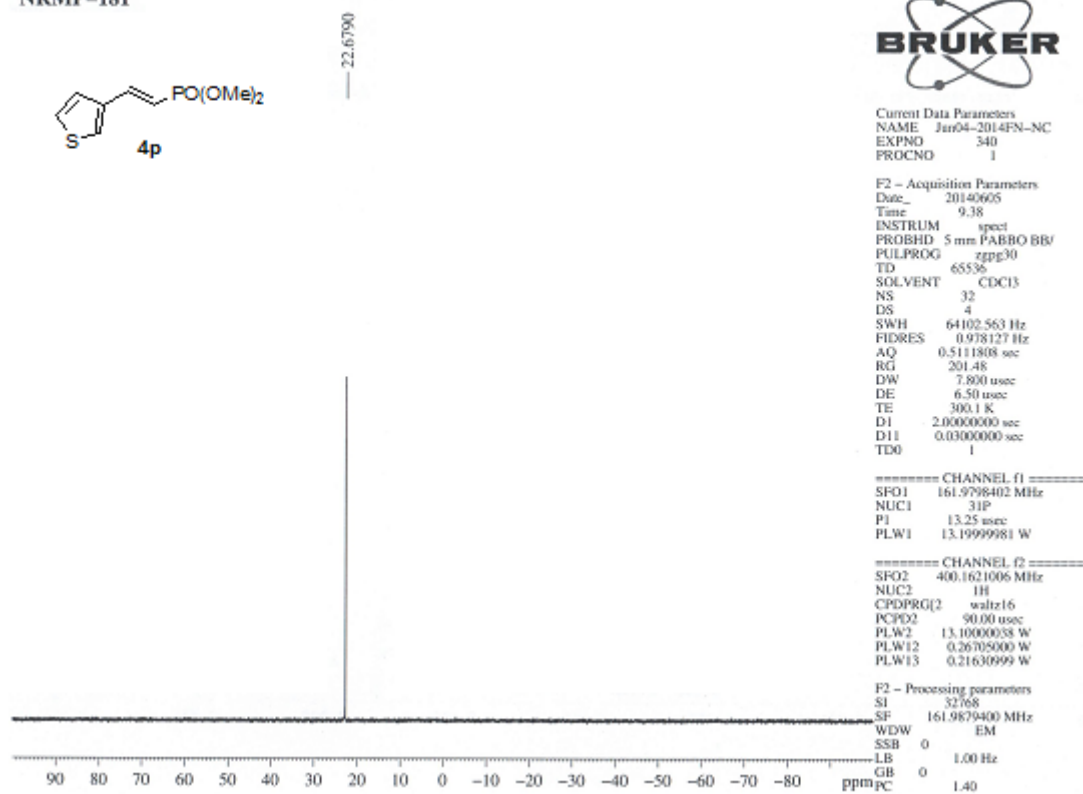
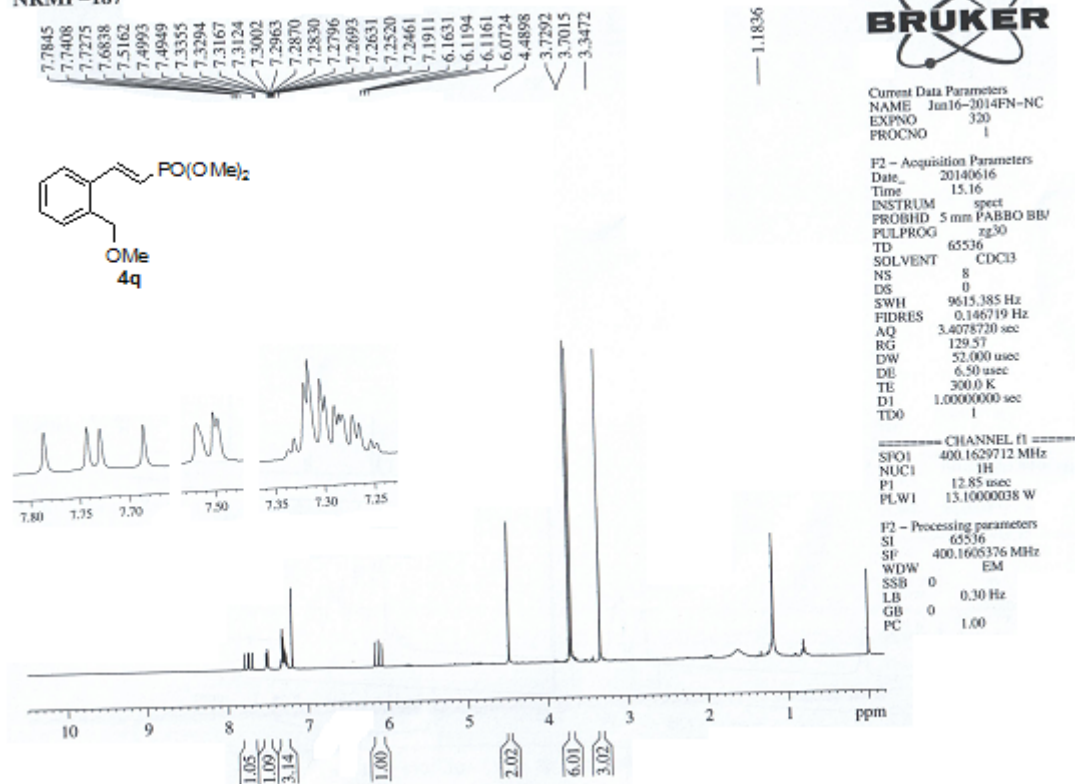


Figure 86: ^{13}C NMR spectrum of 4p

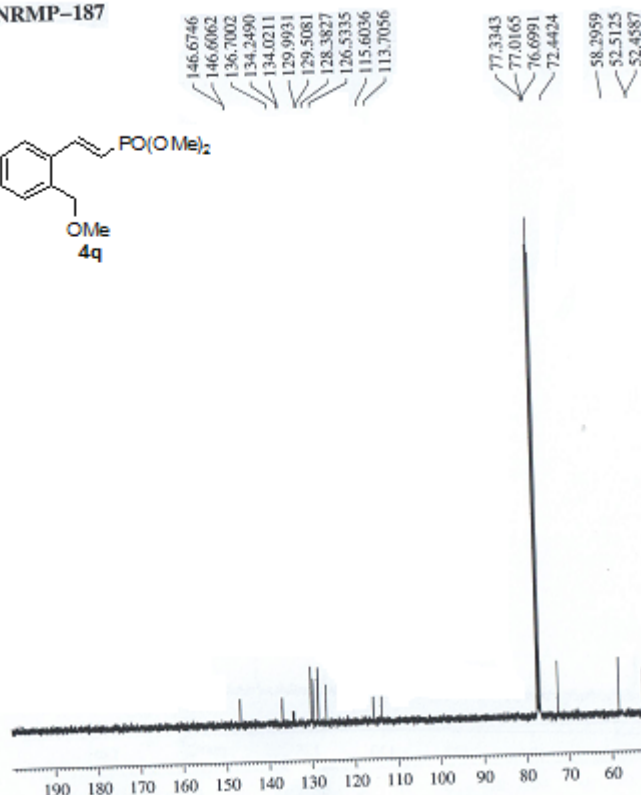
NRMP-181

Figure 87: ³¹P NMR spectrum of 4p

NRMP-187

Figure 88: ¹H NMR spectrum of 4q

NRMP-187



Current Data Parameters
NAME Jun18-2014AN-NC
EXPNO 390
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140619
Time 3.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 201.48
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

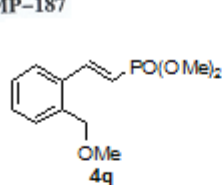
===== CHANNEL f1 =====
SFO1 100.6304993 MHz
NUC1 13C
P1 9.00 usec
PLW1 61.09999847 W

===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 100.6204380 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure 89: ¹³C NMR spectrum of 4q

NRMP-187



Current Data Parameters
NAME Jun19-2014AN-NC
EXPNO 380
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140620
Time 2.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 201.48
DW 7.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 161.9798402 MHz
NUC1 31P
P1 13.25 usec
PLW1 13.19999981 W

===== CHANNEL f2 =====
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 13.10000038 W
PLW12 0.26705000 W
PLW13 0.21630999 W

F2 - Processing parameters
SI 32768
SF 161.9879400 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure 90: ³¹P NMR spectrum of 4q

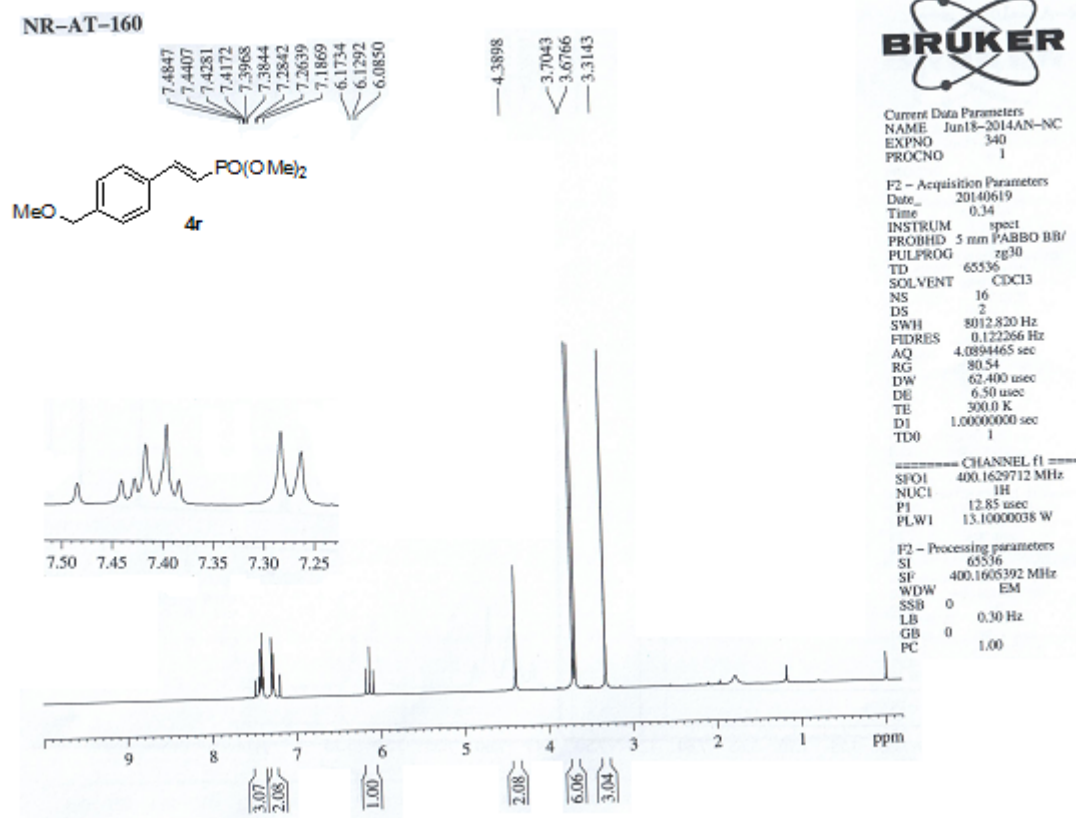


Figure 91: ¹H NMR spectrum of **4r**

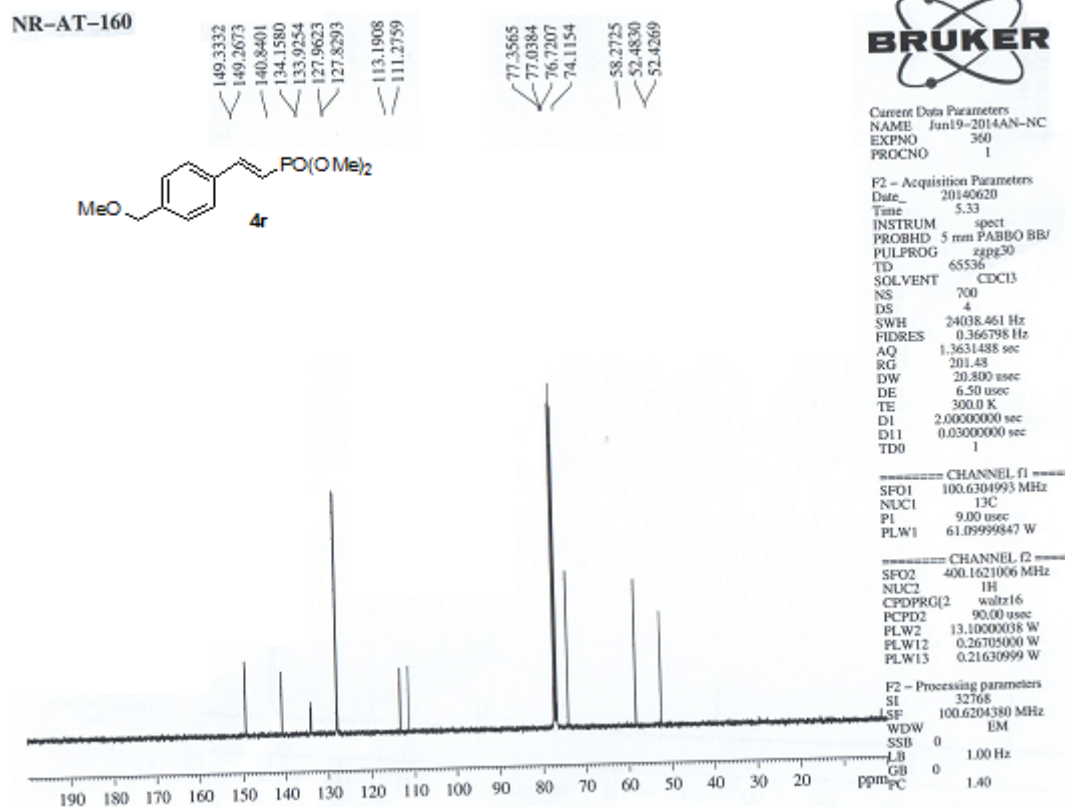


Figure 92: ¹³C NMR spectrum of **4r**

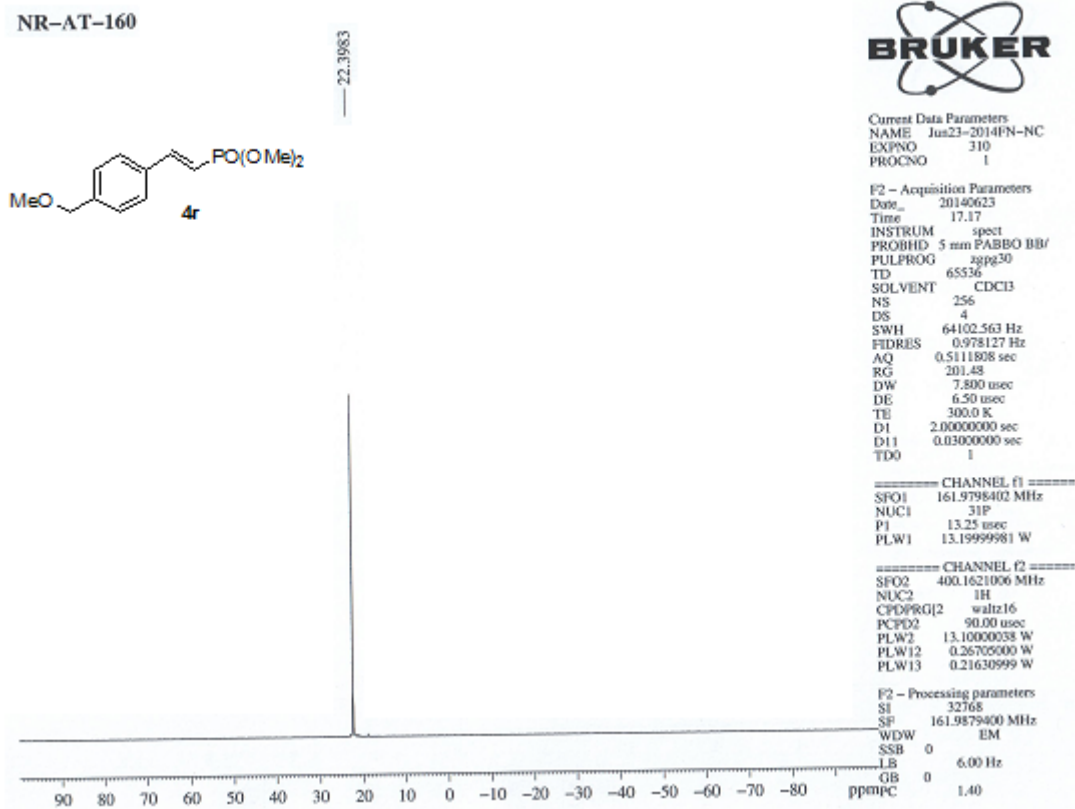


Figure 93: ^{31}P NMR spectrum of **4r**

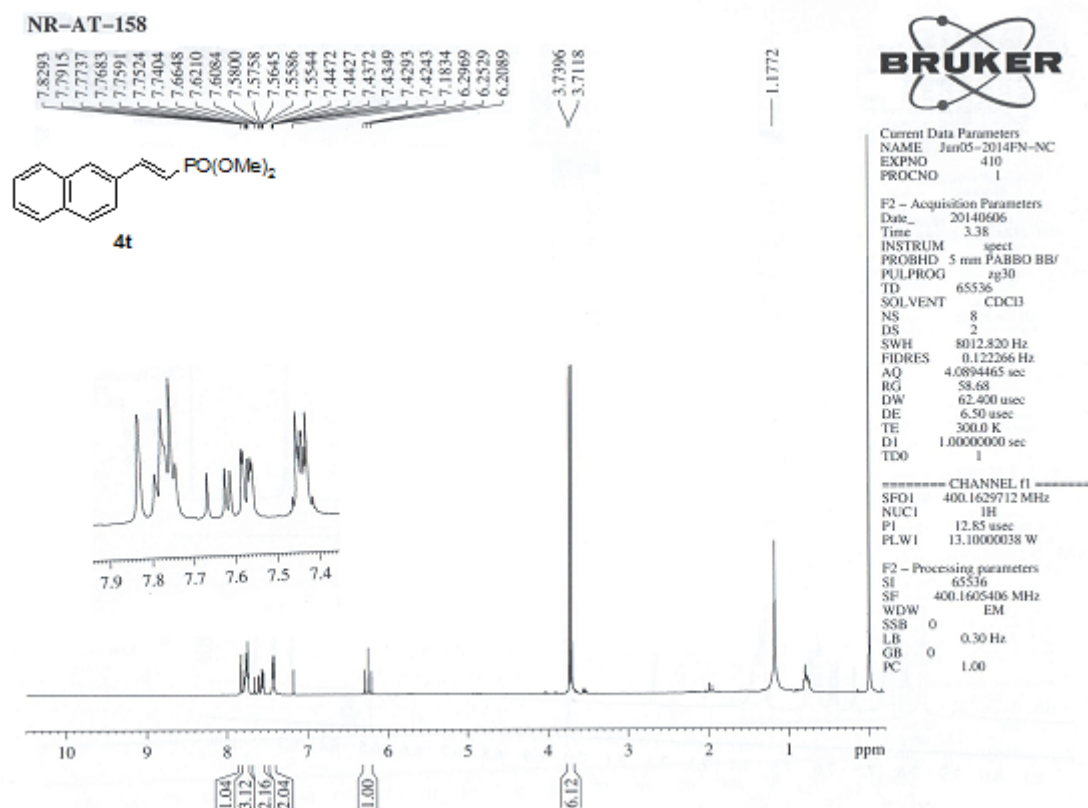


Figure 94: ^1H NMR spectrum of **4t**

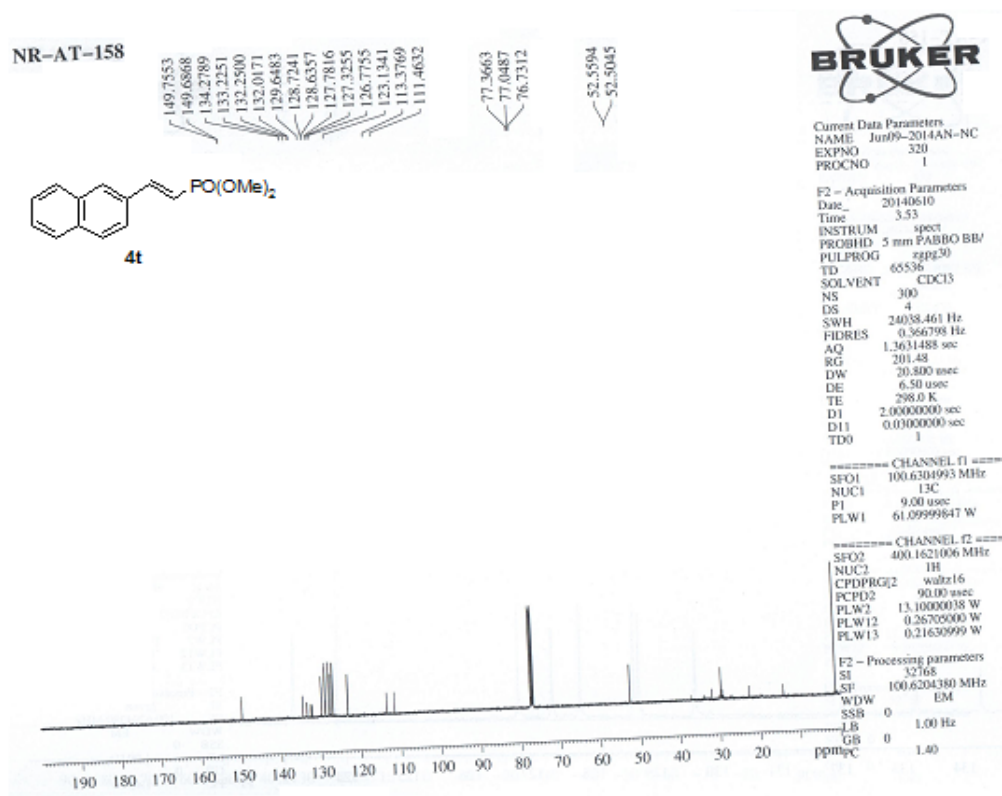


Figure 95: ^{13}C NMR spectrum of **4t**

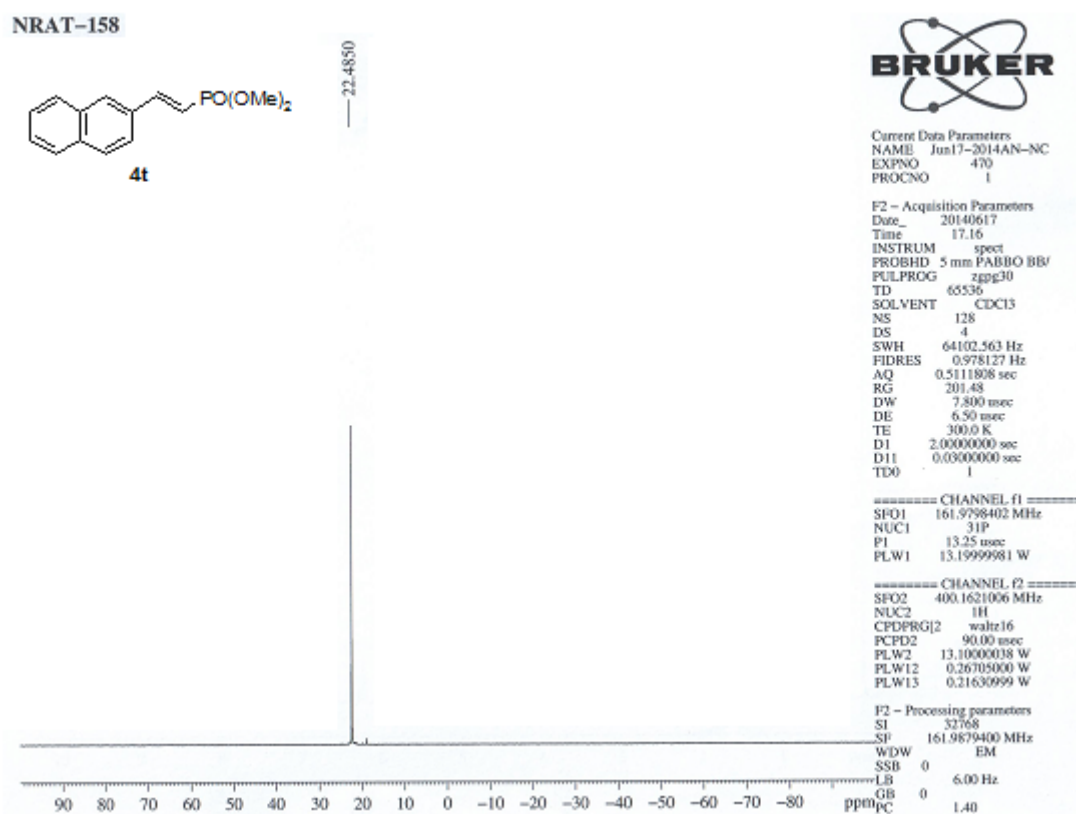


Figure 96: ^{31}P NMR spectrum of **4t**

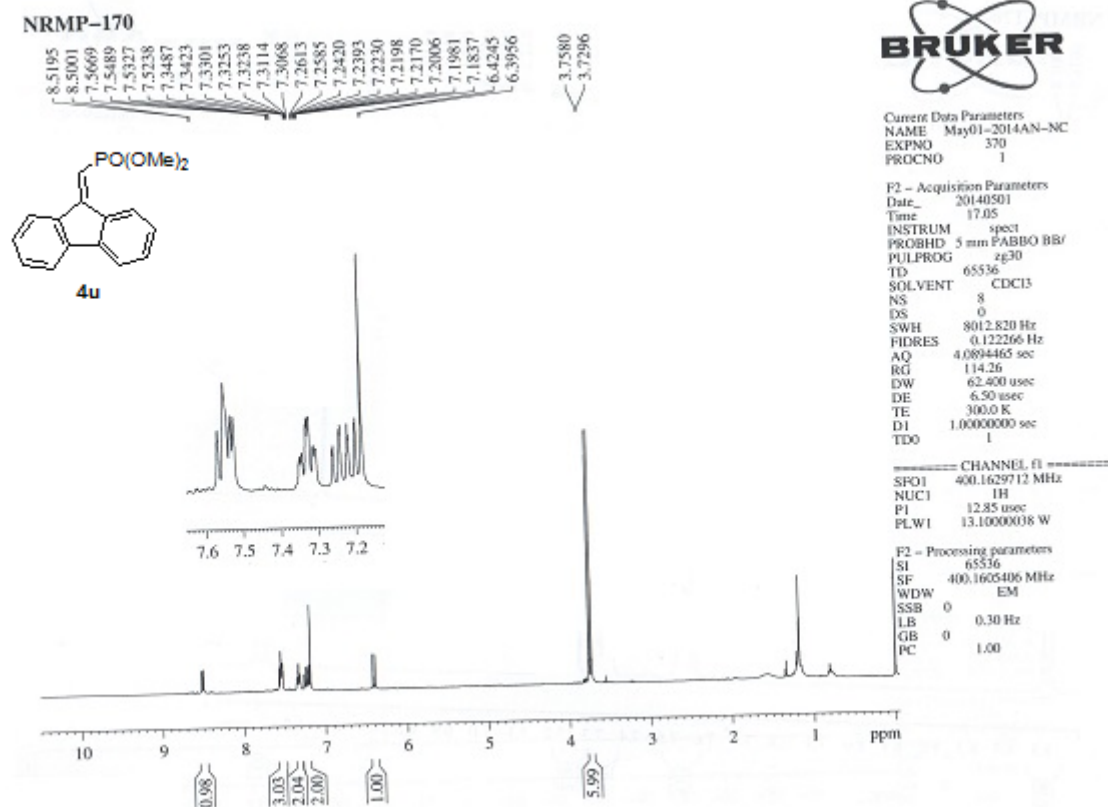


Figure 97: ¹H NMR spectrum of **4u**

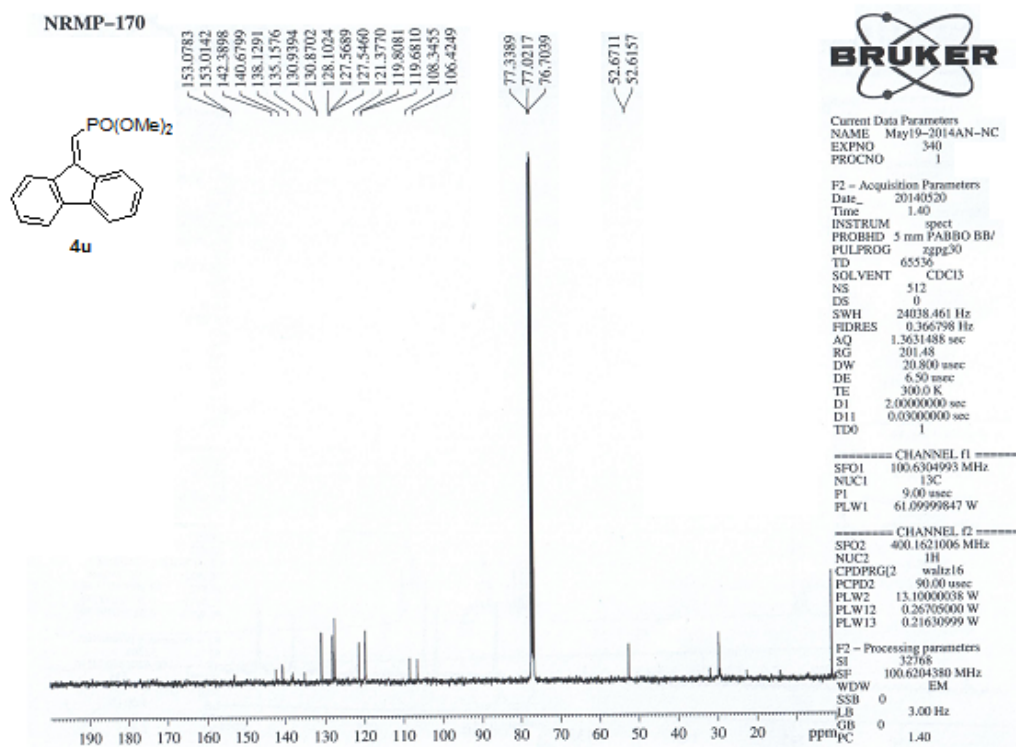
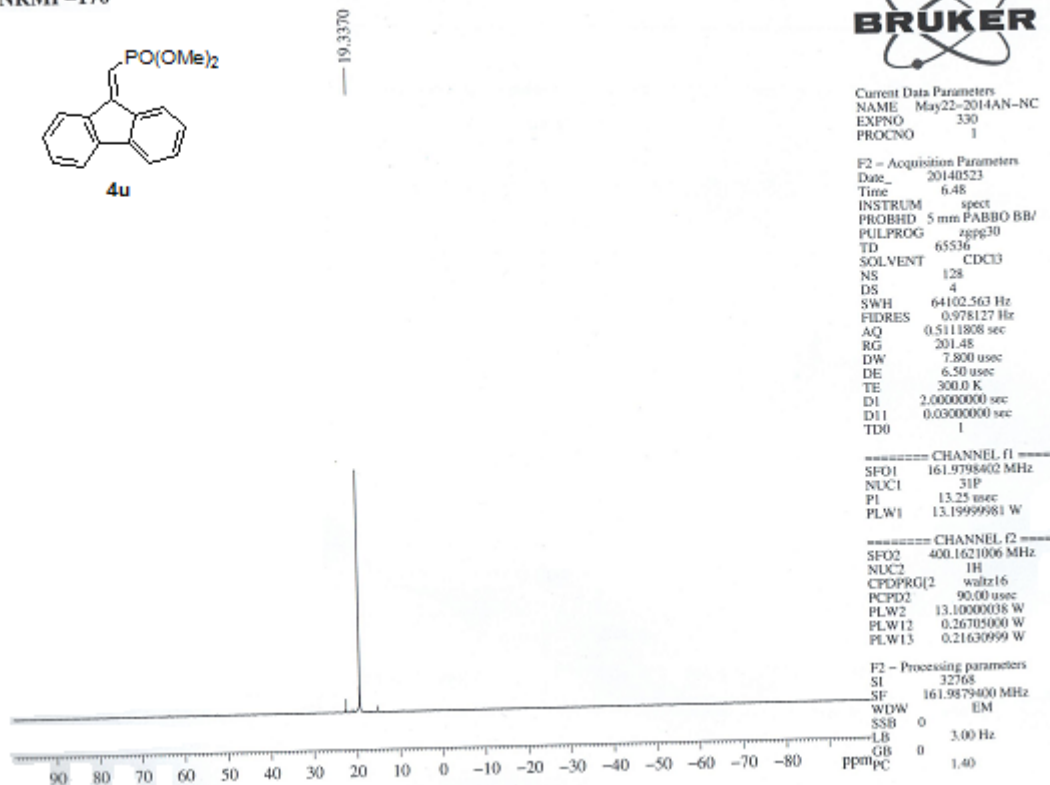
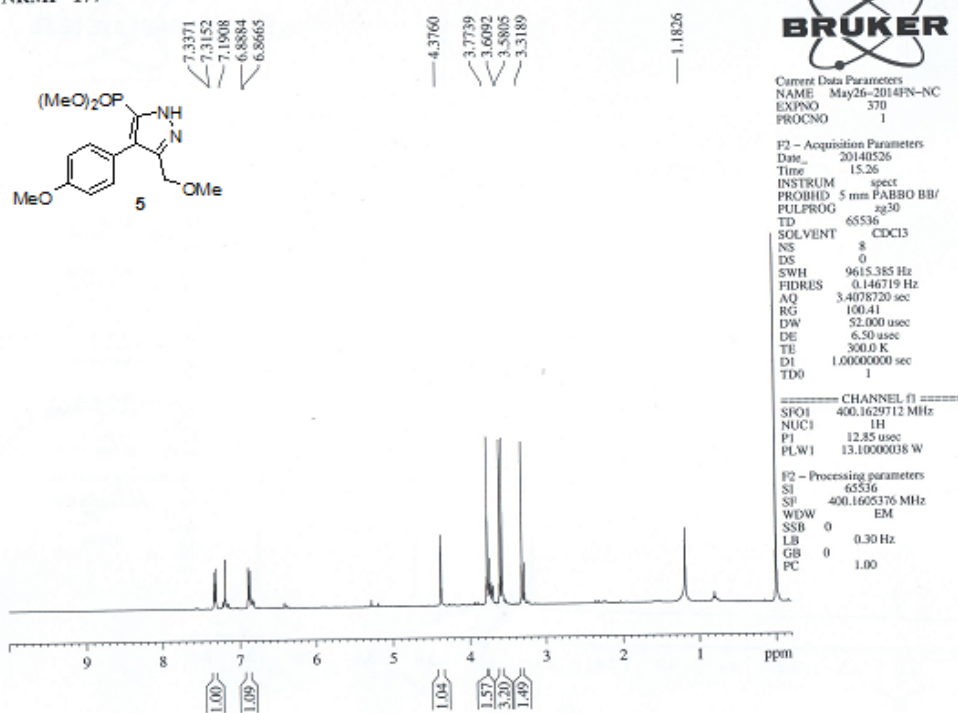


Figure 98: ¹³C NMR spectrum of **4u**

NRMP-170

Figure 99: ³¹P NMR spectrum of 4u

NRMP-177

Figure 100: ¹H NMR spectrum of 5

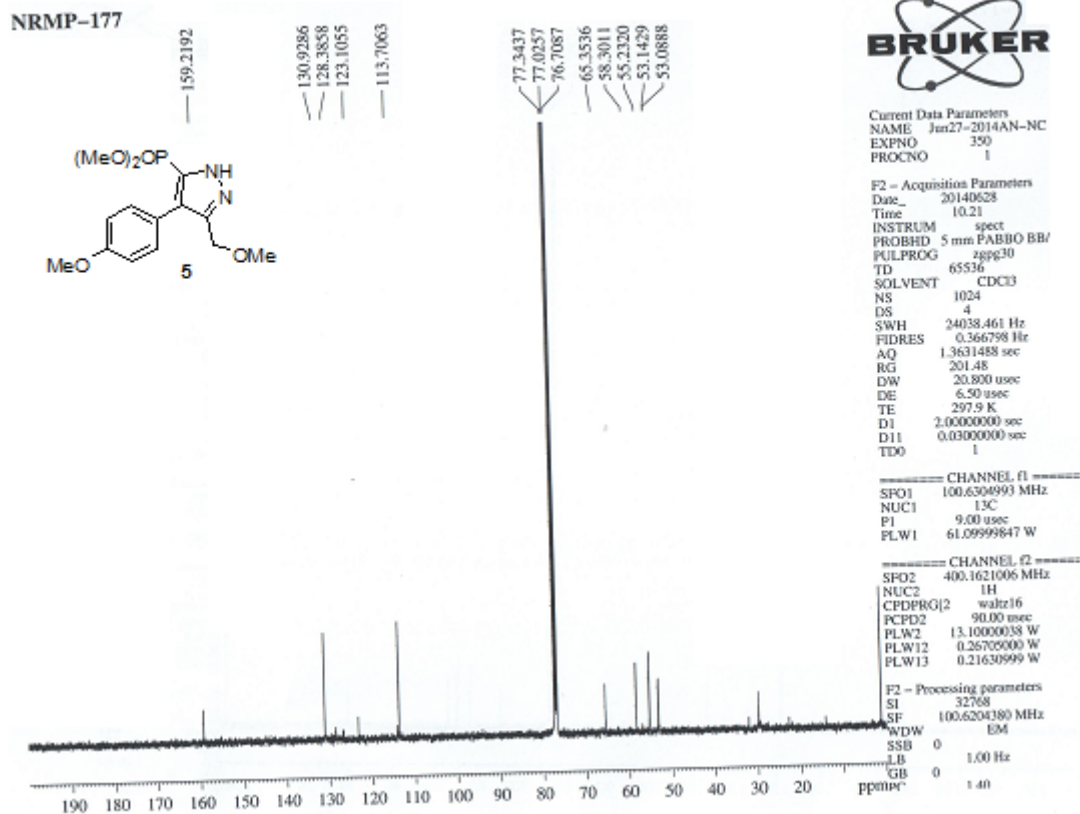


Figure 101: ^{13}C NMR spectrum of 5

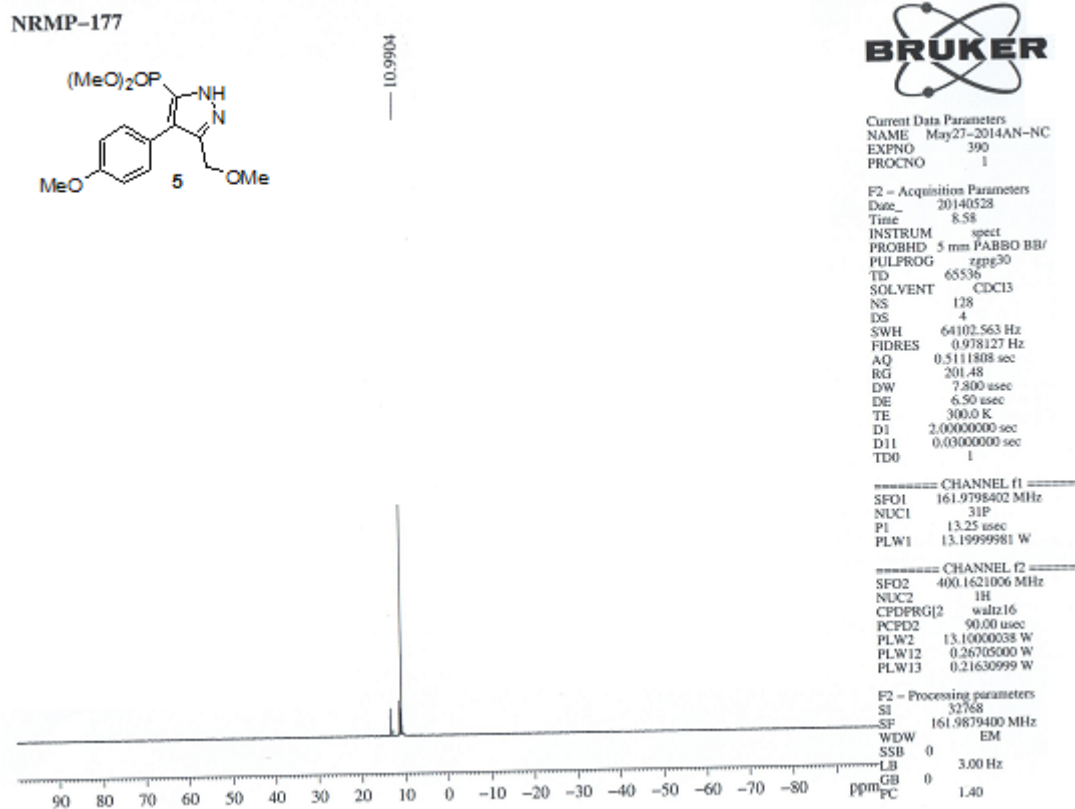


Figure 102: ^{31}P NMR spectrum of 5

References

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