Furan Ring Opening Reaction for the Synthesis of 2,5-Dicarbonyl-3-ene-phosphates

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I. General procedure for synthesis of 2a

In a sealed tube (25 mL) equipped with a stirring bar, furfuryl phosphonate alcohols (0.2 mmol, 1.0 equiv) and $FeCl_3$ (0.01 mmol, 5 mol %) were combined in THF (2 mL). The mixture was stirred at 60°C for 1 hour. Upon completion, the reaction mixture was quenched with $NaHCO_3$ and extracted three times with dichloromethene (25 mL), followed by washing with brine solution. The organic layer was dried using Na_2SO_4 and concentrated under vacuum. The resulting oily crude product was purified using silica gel and eluted with petroleum ether/ethyl acetate to obtain the corresponding product **2a** in the reported yields.

II. General protocol for synthesizing furfuryl phosphonate alcohol substrates

5-methyl furfuraldehyde (0.91 mmol, 1.0 equiv) and alkyl phosphonates (1.09 mmol, 1.2 equiv) were added dropwise to a round bottom flask (25 mL) equipped with a stirring bar, along with triethylamine (0.045 mmol, 0.05 equiv). The resulting mixture was stirred at room temperature for overnight. After confirming completion via TLC detection, the reaction mixture was quenched with 0.1 N HCl and extracted three times with dichloromethene (25 mL). The organic layer was dried with Na_2SO_4 and concentrated under vacuum. The oily crude product was purified using silica gel and eluted with petroleum ether/ethyl acetate to obtain the corresponding furfuryl phosphonate alcohols in the reported yields.

III. Gram scale synthesis of 2a

A sealed tube (100 mL) equipped with a stirring bar was utilized. Furfuryl phosphonate alcohols (4.02 mmol, 1.0 equiv) and $FeCl_3$ (0.2 mmol, 5 mol %) were combined in THF (10 mL) and stirred at 60°C for 1 hour. Following completion, the reaction mixture was quenched with $NaHCO_3$ and extracted three times with dichloromethene (25 mL), and then washed with brine solution. The organic layer was dried with Na_2SO_4 and concentrated under vacuum. The oily crude product was purified using silica gel and eluted with petroleum ether/ethyl acetate to obtain the corresponding **2a** in the noted yields.

IV. Synthesis of (2a) via one-pot reaction

A sealed tube (25 mL) equipped with a stirring bar was utilized. 5-methyl furfuryldehyde (0.2 mmol, 1.0 equiv), alkyl phosphonates (1.2 equiv), and triethylamine (0.05 equiv) were combined in THF and stirred at room temperature for 8 hours. $FeCl_3$ (5 mol %) was subsequently added, and the mixture was stirred at 60°C for 90 mins. After completion, the reaction mixture was quenched with $NaHCO_3$ and extracted three times with dichloromethene (25 mL), followed by washing with brine solution. The organic layer was dried with Na_2SO_4 and concentrated under vacuum. The resulting oily crude product was purified using silica gel and eluted with petroleum ether/ethyl acetate to obtain the corresponding **2a** in the noted yields.

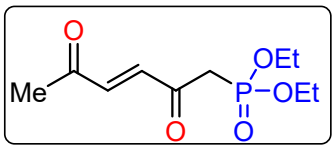
V. Diels-Alder reaction

To a solution of **2a** (0.40 mmol, 100 mg, 1.0 eq) and 2-methylfuran (0.96 mmol, 0.09 mL, 2.3 eq) in dry CH_3CN was added BF_3 Et_2O (0.48 mmol, 0.06 mL, 1.1 eq) in 0 °C under nitrogen atmosphere. The resulting mixture was stirred at the same temperature for 1 hour, and further stirred at the room temperature overnight. The resulting solution was then stirred for 1.5 hours at -20 °C and then quenched with saturated $NaHCO_3$ (5 mL) and extracted three times with dichloromethene (25 mL) and was further washed with brine solution. The organic layer was dried with Na_2SO_4 and concentrated under vacuum. The oily crude product was purified by silica gel with petroleum ether/ethyl acetate as eluent to give the

corresponding 2,5-dioxo phosphonates in noted yields.

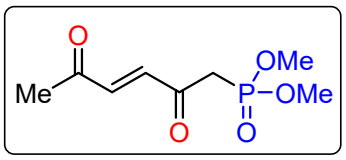
VI. Spectroscopic data of products and substrates

Diethyl (E)-(2, 5-dioxohex-3-en-1-yl)phosphonate (2a)



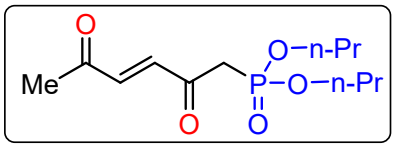
Compound **2a**, a yellow oil, was obtained in a 91% yield (45 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1a**) used as the starting material. **^{1}H NMR** (400 MHz,) δ 6.87 (q, *J* = 16.2 Hz, 2H), 4.14 – 4.05 (m, 4H), 3.25 (d, *J* = 22.9 Hz, 2H), 2.32 (s, 3H), 1.27 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ197.96 (s), 138.33, 136.44, 62.93, 41.48 (d, *J* = 128.0 Hz), 28.33, 16.25 (d, *J* = 6.1 Hz). **^{31}P** NMR (162 MHz, $CDCl_3$) δ 19.99. **HRMS (ESI-TOF) m/z**: calcd for $C_{10}H_{17}O_5PNa$ $[M+Na]^+$ 271.0711 found 271.0713

Dimethyl (E)-(2, 5-dioxohex-3-en-1-yl)phosphonate (2b)



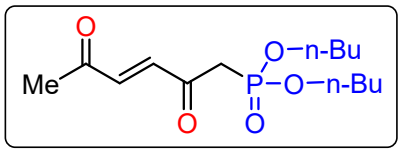
Compound **2b**, a yellow oil, was obtained in a 88% yield (39 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1b**) used as the starting material.**^{1}H NMR** (400 MHz) δ 6.94 (q, *J* = 16.2 Hz, 2H), 3.83 – 3.79 (m, 6H), 3.37 (d, *J* = 22.8 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.78, 191.40 (d, *J* = 6.5 Hz), 138.30, 136.16, 53.03 (d, *J* = 6.5 Hz), 39.99 (d, *J* = 128.8 Hz). **^{31}P** NMR (162 MHz, $CDCl_3$) δ 19.56. **HRMS (ESI-TOF) m/z**: calcd for $C_7H_{10}O_5PNa$ $[M+Na]^+$ 228.0158 found 228.0160

Dipropyl (E)-(2, 5-dioxohex-3-en-1-yl)phosphonate (3c)



Compound **2c**, a yellow oil, was obtained in a 92% yield (51 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1c**) used as the starting material. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 38.0, 16.2 Hz, 2H), 4.05 (m, 4H), 3.33 (d, *J* = 22.8 Hz, 2H), 2.39 (s, 3H), 1.70 (m, 4H), 0.97 – 0.93 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.85, 191.54 (d, *J* = 6.6 Hz), 138.21, 136.40, 68.18 (d, *J* = 6.7 Hz), 41.31 (d, *J* = 127.4 Hz), 28.23, 23.66 (d, *J* = 6.4 Hz), 9.88. **^{31}P** NMR (162 MHz, $CDCl_3$) δ 22.25. **HRMS (ESI-TOF) m/z**: calcd for $C_{12}H_{21}O_5PNa$ $[M+Na]^+$ 299.1024 found 299.1027

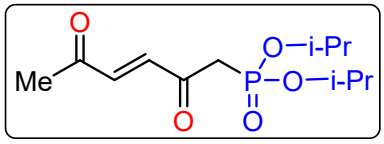
Dibutyl (E)-(2,5-dioxohex-3-en-1-yl)phosphonate(2d)



Compound **2d**, a yellow oil, was obtained in a 90% yield (55 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1d**) used as the starting material. **^{1}H NMR** (400 MHz,) δ 6.95 (dd, *J* = 38.7, 16.2 Hz, 2H), 4.15 – 4.04 (m, 4H), 3.34 (d, *J* = 22.8 Hz, 2H), 2.39 (s, 3H), 1.66 (m, 4H), 1.45 – 1.33 (m, 4H), 0.94 (t, 6H).**^{13}C NMR** (101 MHz,) δ 197.71, 191.43 (d, *J* = 6.6 Hz), 138.07, 136.31, 66.28 (d, *J* = 6.7 Hz), 41.14 (d, *J* =

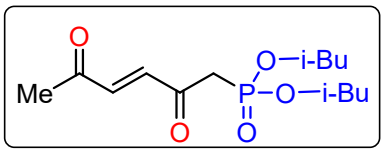
127.3 Hz), 32.14 (d, J = 6.4 Hz), 28.05, 18.43, 13.32. **^{31}P** NMR (162 MHz, $CDCl_3$) δ 22.14. **HRMS (ESI-TOF) m/z**: calcd for $C_{14}H_{25}O_5PNa$ $[M+Na]^+$ 327.1337 found 327.1339

Diisopropyl (E)-(2,5-dioxohex-3-en-1-yl)phosphonate (2e)



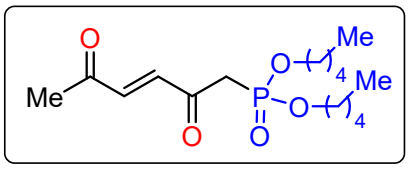
Compound **2e**, a yellow oil, was obtained in a 81% yield (45 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1e**) used as the starting material. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.96 (dd, J = 48.2, 16.2 Hz, 2H), 4.74 (m, 2H), 3.27 (d, J = 22.9 Hz, 2H), 2.38 (s, 3H), 1.35 – 1.32 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ197.98, 191.68 (s), 138.02, 136.54, 71.79 (d, J = 6.6 Hz), 42.97 (d, J = 127.7 Hz), 28.25, 23.84 (dd, J = 11.2, 4.3 Hz). **^{31}P** NMR (162 MHz, $CDCl_3$) δ 19.66. **HRMS (ESI-TOF) m/z**: calcd for $C_{12}H_{21}O_5PNa$ $[M+Na]^+$ 299.1019 found 299.1022

Diisobutyl (E)-(2,5-dioxohex-3-en-1-yl)phosphonate (2f)



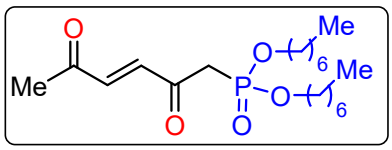
Compound **2f**, a yellow oil, was obtained in a 83% yield (50 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1f**) used as the starting material.· **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (dd, J = 39.2, 16.2 Hz, 2H), 3.82 – 3.75 (m, 4H), 3.26 (d, J = 22.9 Hz, 2H), 2.30 (d, J = 7.6 Hz, 4H), 1.87 (m, 4H), 0.88 – 0.85 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.90, 190.57 (s), 137.28, 135.47, 71.62, 71.59 (d, J = 6.9 Hz), 40.26 (d, J = 127.6 Hz), 28.18, 28.11, 28.15 (d, J = 6.6 Hz). **^{31}P** NMR (162 MHz, $CDCl_3$) δ 20.44. **HRMS (ESI-TOF) m/z** calcd for $C_{14}H_{25}O_5PNa$ $[M+Na]^+$ 327.1332 found 327.1337

Dipentyl (E)-(2,5-dioxohex-3-en-1-yl)phosphonate (2g)



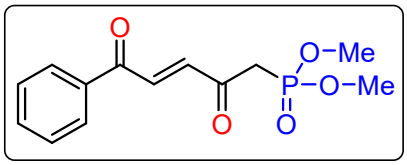
Compound **2g**, a yellow oil, was obtained in a 85% yield (56 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (1a) used as the starting material.· **NMR** (400 MHz,) δ 6.95 (q, J = 16.2 Hz, 2H), 4.14 – 4.04 (m, 4H), 3.32 (d, J = 22.8 Hz, 2H), 2.39 (s, 3H), 1.70 – 1.64 (m, 4H), 1.35 – 1.33 (m, 6H), 0.90 (t, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.81, 191.51, 138.20, 136.40, 66.73 (d, J = 6.7 Hz), 41.33 (d, J = 127.3 Hz), 29.98 (d, J = 6.2 Hz), 27.45, 22.08, 13.84. **^{31}P** NMR (162 MHz, $CDCl_3$) δ 20.98. **HRMS (ESI-TOF) m/z** calcd for $C_{16}H_{29}O_5PNa$ $[M+Na]^+$ 355.1645 found 355.1646

Diheptyl (E)-(2,5-dioxohex-3-en-1-yl)phosphonate (2h)



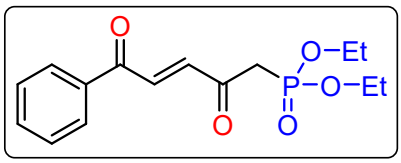
Compound **2h**, a yellow oil, was obtained in a 85% yield (66 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (1h) used as the starting material.· **^{1}H** NMR (400 MHz, $CDCl_3$) δ 6.87 (q, *J* = 16.2 Hz, 2H), 4.00 (m, 4H), 3.24 (d, *J* = 22.8 Hz, 2H), 2.31 (s, 3H), 1.62 – 1.57 (m, 4H), 1.24 (m, 20 H), 0.81 (t, 6H). **^{13}C NMR** (101 MHz,) δ 197.87, 191.63, 138.26, 136.45, 66.78, 41.39 (d, *J* = 127.3 Hz), 31.64, 30.35 (d, *J* = 6.3 Hz), 28.52 (d, *J* = 44.9 Hz), 25.34, 22.52, 14.03. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.23. **HRMS (ESI-TOF) m/z** calcd for $C_{16}H_{29}O_5PNa$ $[M+Na]^+$ 411.2271 found 411. 2274

Dimethyl (E)-(2, 5-dioxo-5-phenylpent-3-en-1-yl)phosphonate (2i)



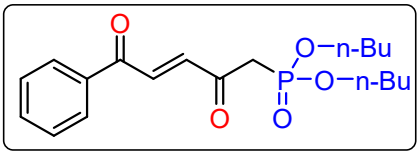
Compound **2i**, a yellow oil, was obtained in a 89% yield (50 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (1i) used as the starting material. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.98 (m, 2H), 7.84 (d, *J* = 15.6 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.50 (t, 2H), 7.18 (t, 1H), 3.80 (d, *J* = 11.3 Hz, 6H), 3.37 (d, *J* = 22.8 Hz, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.22, 189.85, 137.31, 135.68, 134.11, 129.03, 128.99, 53.42, 53.36, 41.60, 40.32. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.50. **HRMS (ESI-TOF) m/z** calcd for $C_{13}H_{15}O_5PNa$ $[M+Na]^+$ 305.0549 found 305.0553

Diethyl (E)-(2,5-dioxo-5-phenylpent-3-en-1-yl)phosphonate (2j)



Compound **4j**, a yellow oil, was obtained in a 87% yield (54 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1j**) used as the starting material.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 15.6 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.53 (t, 2H), 7.27 – 7.19 (m, 1H), 4.22 – 4.12 (m, 4H), 3.37 (d, *J* = 22.8 Hz, 2H), 1.37 – 1.33 (m, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.26, 189.80, 137.41, 136.58, 135.29, 133.96, 128.89 (d, *J* = 3.5 Hz), 62.84, 41.99 (d, *J* = 127.2 Hz), 16.29 (d, *J* = 6.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.88. **HRMS (ESI-TOF) m/z** calcd for $C_{15}H_{19}O_5PNa$ $[M+Na]^+$ 333.0862 found 333.08626

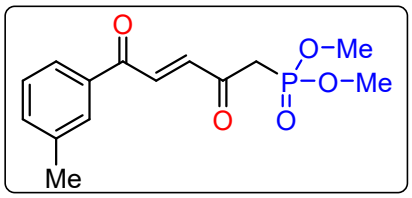
Dibutyl (E)-(2,5-dioxo-5-phenylpent-3-en-1-yl)phosphonate (2k)



Compound **2k**, a yellow oil, was obtained in a 85% yield (62 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1k**) used as the starting material. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.57 (t, 1H), 7.45 (m, 2H), 7.14 (d, *J* = 15.6 Hz, 1H), 4.04 (m, 4H), 3.30 (d, *J* = 22.8 Hz, 2H), 1.63 – 1.55 (m, 4H), 1.32 (m, 4H), 0.85 (t, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ191.15, 189.78,

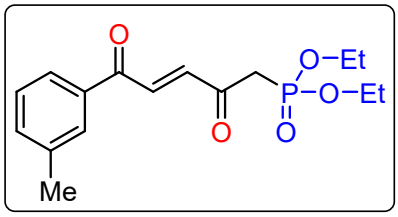
137.43, 136.69, 135.25, 133.95, 128.89 (d, J = 3.9 Hz), 66.52, 41.21 (s), 32.37 (d, J = 6.4 Hz), 18.65, 13.54. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.09. **HRMS (ESI-TOF) m/z** calcd for $C_{19}H_{27}O_5PNa$ $[M+Na]^+$ 389. 1488 found 389. 1489.

Dimethyl (E)-(2,5-dioxo-5-(m-tolyl)pent-3-en-1-yl)phosphonate (2l)



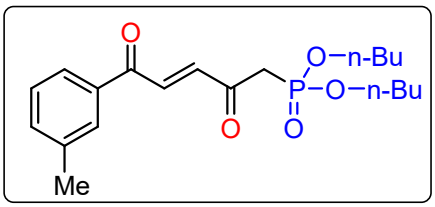
Compound **2l**, a yellow oil, was obtained in a 85% yield (50 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1l**) used as the starting material. **^{1}H** NMR (400 MHz, DMSO) δ 7.99 (d, *J* = 15.8 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 2H), 7.61 – 7.54 (m, 1H), 7.49 (t, 1H), 6.95 (d, *J* = 15.8 Hz, 1H), 3.72 – 3.67 (m, 6H), 2.52 – 2.41 (m, 5H). **^{13}C NMR** (101 MHz, DMSO) δ193.25 (s), 190.49, 139.11, 138.26, 136.78, 136.31, 135.37, 129.62 (d, *J* = 27.3 Hz), 126.70, 53.31 (s), 39.04 (d, *J* = 75.8 Hz), 21.37. **^{31}P NMR** (162 MHz, DMSO) δ 20.21. **HRMS (ESI-TOF) m/z** calcd for $C_{14}H_{17}O_5PNa$ $[M+Na]^+$ 319.0706 found 319.0709

Diethyl (E)-(2,5-dioxo-5-(m-tolyl)pent-3-en-1-yl)phosphonate (2m)



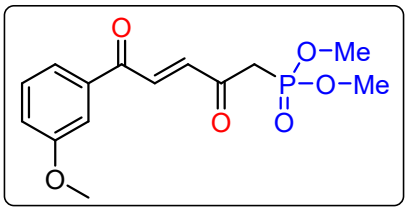
Compound **2m**, a yellow oil, was obtained in a 83% yield (54 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1m**) used as the starting material. **^{1}H** NMR (400 MHz,) δ 7.76 (t, 3H), 7.40 – 7.27 (m, 2H), 7.13 (d, *J* = 15.6 Hz, 1H), 4.14 – 4.07 (m, 4H), 3.30 (d, *J* = 22.8 Hz, 2H), 2.37 (s, 3H), 1.27 (m, 6H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ191.34 (s), 189.87, 138.82, 137.23, 136.61, 135.37, 134.76, 129.29, 128.75, 126.13, 62.91, 62.85, 441.91 (d, *J* = 127.6 Hz), 21.30, 16.26 (d, *J* = 6.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.39. **HRMS (ESI-TOF) m/z** calcd for $C_{16}H_{21}O_5PNa$ $[M+Na]^+$ 347.1019 found 347.1016

Dibutyl (E)-(2,5-dioxo-5-(m-tolyl)pent-3-en-1-yl)phosphonate (2n)



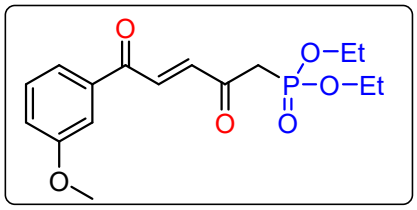
Compound **2n**, a yellow oil, was obtained in a 82% yield (62 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1n**) used as the starting material. **1H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.3 Hz, 3H), 7.40 (d, J = 12.7 Hz, 2H), 7.27 – 7.14 (m, 1H), 4.08 (dt, J = 6.6, 2.6 Hz, 4H), 3.35 (d, J = 22.8 Hz, 2H), 2.42 (s, 3H), 1.67 – 1.60 (m, 4H), 1.37 (dd, J = 15.0, 7.5 Hz, 4H), 0.89 (t, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.27, 189.85, 138.82, 137.26, 136.65, 135.32, 134.74, 129.29, 128.75, 126.13, 66.53 (d, J = 6.7 Hz), 41.83 (d, J = 127.1 Hz), 32.36 (d, J = 6.2 Hz), 21.31, 18.64, 13.52. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.87. **RMS (ESI-TOF) m/z** calcd for $C_{20}H_{29}O_5PNa$ $[M+Na]^+$ 403.1645 found 403.1644

Dimethyl (E)-(5-(3-methoxyphenyl)-2,5-dioxopent-3-en-1-yl)phosphonate (2o)



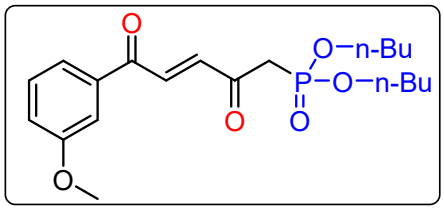
Compound **2o**, a yellow oil, was obtained in a 80% yield (50 mg) through column chromatography over silica gel using a 1:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1a**) used as the starting material.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 15.6 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 1.4 Hz, 1H), 7.36 (t, 1H), 7.14 – 7.07 (m, 2H), 3.82 – 3.74 (m, 9H), 3.33 (t, \2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ191.03 (s), 189.49, 160.04, 137.85, 137.16, 135.63, 129.89, 121.64, 120.77, 112.70, 55.49, 53.26 (d, *J* = 6.3 Hz), 40.83 (d, *J* = 128.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.14. **HRMS (ESI-TOF) m/z** calcd for $C_{14}H_{17}O_6PNa$ $[M+Na]^+$ 335.0655 found 335.0655

Diethyl (E)-(5-(3-methoxyphenyl)-2,5-dioxopent-3-en-1-yl)phosphonate (2p)



Compound **2p**, a yellow oil, was obtained in a 79% yield (54 mg) through column chromatography over silica gel using a 1:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (1a) used as the starting material.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.6 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.40 (t, 1H), 7.26 – 7.18 (m, 1H), 7.15 (m, 1H), 4.18 – 4.10 (m, 4H), 3.85 (s, 3H), 3.37 (m, 2H), 1.34 – 1.30 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ191.24 (s), 189.52, 160.04, 137.90, 137.36, 135.32, 129.87, 121.64, 120.77, 112.62, 62.84 (d, *J* = 6.4 Hz), 55.49, 41.98 (d, *J* = 126.9 Hz), 16.28 (d, *J* = 6.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.24. **HRMS (ESI-TOF) m/z** calcd for $C_{16}H_{21}O_6PNa$ $[M+Na]^+$ 363.0968 found 363.0965

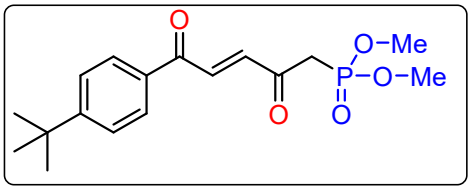
Dibutyl (E)-(5-(3-methoxyphenyl)-2,5-dioxopent-3-en-1-yl)phosphonate (2q)



Compound **2q**, a yellow oil, was obtained in a 77% yield (61 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1q**) used as the starting material.**^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 15.6 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.46 (s, 1H), 7.36 (t, 1H), 7.16 – 7.09 (m, 2H), 4.08 – 3.98 (m, 4H), 3.81 (s, 3H), 3.30 (d, *J* = 22.8 Hz, 2H), 1.61 – 1.57 (m, 4H), 1.34 – 1.28 (m, 4H), 0.84 (d, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ191.22 (s), 189.51, 160.04, 137.92, 137.38, 135.28, 129.87, 121.63, 120.74, 112.63, 66.50 (s), 55.49, 41.17 (s), 32.34 (d, *J* = 6.4 Hz), 18.63, 13.51. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.56. **HRMS (ESI-TOF) m/z** calcd for $C_{20}H_{29}O_6PNa$ $[M+Na]^+$ 419.1594 found 419. 1592

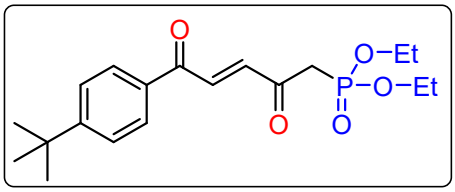
Dimethyl (E)-(5-(4-(tert-butyl)phenyl)-2,5-dioxopent-3-en-1-yl)phosphonate (2r)

Compound **2r**, a yellow oil, was obtained in a 80% yield (54 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (1a) used as



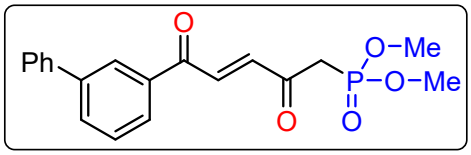
the starting material. **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.83 – 7.76 (m, 1H), 7.45 (t, 2H), 7.10 (d, *J* = 15.6 Hz, 1H), 3.75 (d, *J* = 11.3 Hz, 6H), 3.33 (d, *J* = 16.9, 10.5 Hz, 2H), 1.28 (s, 9H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ191.20 (s), 189.23, 158.05, 136.88, 135.84, 134.00, 128.90, 125.91, 53.27 (d, *J* = 6.4 Hz), 40.82 (d, *J* = 128.3 Hz), 35.27, 30.99. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.32. **HRMS (ESI-TOF) m/z** calcd for $C_{17}H_{23}O_5PNa$ $[M+Na]^+$ 361.1175 found 361.1179

Diethyl (E)-(5-(4-(tert-butyl)phenyl)-2,5-dioxopent-3-en-1-yl)phosphonate (2s)



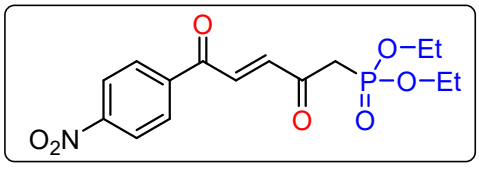
Compound **2s**, a yellow oil, was obtained in a 81% yield (59 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (1a) used as the starting material. **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 15.7 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.12 (t, 1H), 4.15 – 4.05 (m, 4H), 3.30 (d, *J* = 22.8 Hz, 2H), 1.29 – 1.26 (m, 15H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ191.34 (s), 189.30, 157.98, 137.09, 135.56, 134.05, 133.29, 128.90, 125.90, 62.82, 441.97 (d, *J* = 127.3 Hz), 35.26, 31.00, 16.29 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.57. **HRMS (ESI-TOF) m/z** calcd for $C_{20}H_{29}O_5PNa$ $[M+Na]^+$ 403.1645 found 403.1649

Dimethyl (E)-(5-([1,1'-biphenyl]-3-yl)-2,5-dioxopent-3-en-1-yl)phosphonate (2t)



Compound **2t**, a yellow oil, was obtained in a 78% yield (56 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (**1t**) used as the starting material. **^{1}H** NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.54 (m, 3H), 7.45 – 7.39 (m, 2H), 7.33 (t, 1H), 7.20 – 7.12 (m, 1H), 3.75 (d, *J* = 11.3 Hz, 6H), 3.32 (d, *J* = 22.8 Hz, 2H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ191.01 (s), 189.73, 142.13, 139.76, 137.27, 137.08, 135.52, 132.62, 129.38, 128.97, 127.99, 127.70, 127.45, 127.19, 53.28 (d, *J* = 6.5 Hz), 40.95 (d, *J* = 128.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.27. **HRMS (ESI-TOF) m/z** calcd for $C_{19}H_{19}O_5PNa$ $[M+Na]^+$ 381.0862 found 381.0866

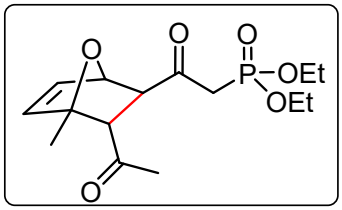
Diethyl (E)-(5-(4-nitrophenyl)-2,5-dioxopent-3-en-1-yl)phosphonate (2u)



Compound **2s**, a yellow oil, was obtained in a 72% yield (49 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.2 mmol of (1a) used as the starting material. **^{1}H** NMR (400 MHz,) δ 8.28 (d, *J* = 18.5, 10.8 Hz, 2H), 8.11 (d, *J* = 11.7, 8.9 Hz, 2H), 7.87 – 7.72 (m, 1H), 7.18 (d, *J* = 14.7 Hz, 1H), 4.15 – 4.05 (m, 4H), 3.31 (d, *J* = 22.9 Hz, 2H), 1.29 (m, 6H).**^{13}C** NMR (101 MHz,) δ190.89, 188.64, 150.65, 140.96, 138.58, 134.17, 129.89, 124.10, 63.02, 41.58 (s), 16.29 (d, *J* = 6.1 Hz). **^{31}P NMR** (162 MHz,) δ

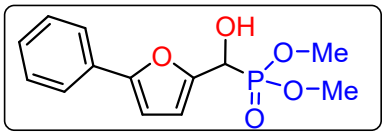
19.81. **HRMS (ESI-TOF) m/z** calcd for C15H18NO7PNa $[M+Na]^+$ 378.0713 found 378.0719.

Diethyl (2-((1R,3S,4R)-3-acetyl-4-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-yl)-2-oxoethyl)phosphonate (3)



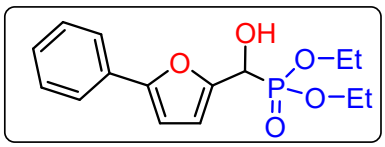
Compound **3**, a yellow oil, was obtained in a 87% yield (86 mg) through column chromatography over silica gel using a 2:1 mixture of petroleum ether and ethyl acetate as the eluent. 0.3 mmol of (**2a**) used as the starting material. **^{1}H** NMR (400 MHz, $CDCl_3$) δ 6.10 – 5.73 (m, 1H), 4.43 (m, 1H), 4.07 (m, 4H), 3.33 – 3.14 (m, 2H), 2.96 (d, *J* = 21.5 Hz, 1H), 2.60 (m, 1H), 2.14 (d, *J* = 23.1 Hz, 6H), 1.25 (dt, *J* = 15.9, 7.1 Hz, 6H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 205.59, 198.20, 152.40, 148.25, 109.13, 106.67, 62.51 (d, *J* = 6.2 Hz), 47.80, 43.05, 39.71 (d, *J* = 132.1 Hz), 29.89, 16.26 (d, *J* = 5.4 Hz), 13.47. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.32. **HRMS (ESI-TOF) m/z** calcd for $C_{15}H_{23}O_6PNa$ $[M+Na]^+$ 353.1124 found 353.1126.

Dimethyl (hydroxy(5-phenylfuran-2-yl)methyl)phosphonate (1i)



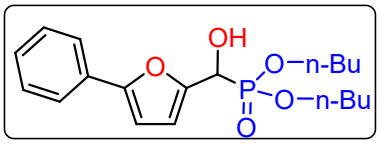
Starting with 0.91 mmol of 5-phenylfuran-2-carbaldehyde and dimethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1i** as a yellow oil (189 mg, 74% yield).**^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.31 (m, 2H), 7.23 – 7.18 (m, 1H), 5.03 (d, *J* = 13.6 Hz, 1H), 3.78 (d, *J* = 10.6 Hz, 3H), 3.70 (d, *J* = 10.5 Hz, 3H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ153.60 – 153.38 (m), 147.94, 129.31, 127.68, 126.70, 122.86, 110.77 (s), 105.04, 63.53 (d, *J* = 167.0 Hz), 53.05 (s). **31P NMR** (162 MHz, $CDCl_3$) δ 22.75. **HRMS (ESI-TOF) m/z** calcd for $C_{13}H_{15}O_5PNa$ $[M+Na]^+$ 305.0549 found 305.0544

Diethyl (hydroxy(5-phenylfuran-2-yl)methyl)phosphonate (1j)



Starting with 0.91 mmol of 5-phenylfuran-2-carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1j** as a yellow oil (240 mg, 85% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.37 (t, 2H), 7.25 (m, 1H), 6.64 (d, *J* = 3.3 Hz, 1H), 6.56 (t, 1H), 4.87 (d, *J* = 26.0 Hz, 1H), 4.16 – 4.02 (m, 4H), 1.25 (t, 6H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 153.53, 146.85 (d, *J* = 6.3 Hz), 130.60, 128.63, 127.30, 123.59, 111.11 (d, *J* = 6.2 Hz), 106.21, 663.25 (d, *J* = 7.0 Hz), 39.70 (d, *J* = 143.3 Hz), 16.35 (d, *J* = 5.8 Hz). **^{31}P NMR** (162 MHz,$CDCl_3$) δ 18.62. **HRMS (ESI-TOF) m/z** calcd for $C_{15}H_{19}O_5PNa$ $[M+Na]^+$ 333.0862 found 333.0862

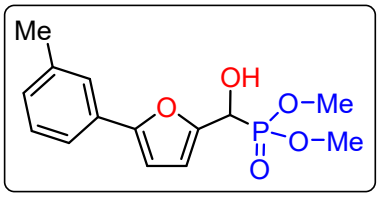
Dibutyl (hydroxy(5-phenylfuran-2-yl)methyl)phosphonate (1k)



Starting with 0.91 mmol of 5-phenylfuran-2-carbaldehyde and

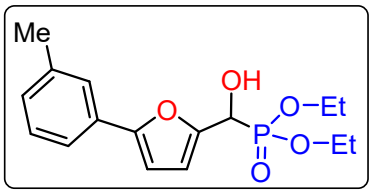
dibutyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1k** as a yellow oil (274 mg, 82% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 2H), 7.50 – 7.26 (m, 2H), 7.23 (t, 1H), 6.62 – 6.59 (m, 2H), 5.06 (m, 1H), 4.14 – 4.00 (m, 4H), 1.67 – 1.50 (m, 4H), 1.43 – 1.19 (m, 4H), 0.91 – 0.75 (m, 6H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 153.94, 149.79, 130.48, 128.53, 127.38, 123.74, 111.28 (d, J = 6.2 Hz), 105.93, 67.06 (dd, J = 34.1, 7.1 Hz), 65.57, 63.91, 32.44, 8.54 (d, J = 4.6 Hz), 13.47 (d, J = 3.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.57. **HRMS (ESI-TOF) m/z** calcd for $C_{19}H_{27}O_5PNa$ $[M+Na]^+$ 389. 1488 found 389.1489

Dimethyl (hydroxy(5-(m-tolyl)furan-2-yl)methyl)phosphonate (1l)



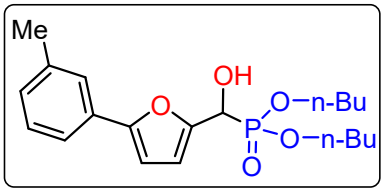
Starting with 0.91 mmol of 5-(p-tolyl)furan-2-carbaldehyde and dimethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1l** as a yellow oil (210 mg, 78% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.6 Hz, 2H), 7.19 (m, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.55 (d, J = 3.4 Hz, 1H), 6.48 (t, 1H), 4.82 (d, J = 26.1 Hz, 1H), 3.65 (d, J = 10.9 Hz, 6H), 2.31 (s, 6H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 153.83, 146.28 (s), 138.27, 130.46, 128.40 (d, J = 35.4 Hz), 124.24, 120.82, 111.26, 111.19, 106.11, 53.84 (d, J = 6.8 Hz), 39.12 (d, J = 143.6 Hz)., 21.48. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.2. **HRMS (ESI-TOF) m/z** calcd for $C_{14}H_{17}O_5PNa$ $[M+Na]^+$ 319. 0706 found 319.0703

Diethyl (hydroxy(5-(m-tolyl)furan-2-yl)methyl)phosphonate (1m)



Starting with 0.91 mmol of 5-(p-tolyl)furan-2-carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1m** as a yellow oil (252 mg, 85% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.18 (m, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.54 (s, 2H), 4.94 (dd, J = 40.6, 13.5 Hz, 1H), 4.26 – 3.96 (m, 4H), 2.30 (s, 3H), 1.29 – 1.22 (m, 3H), 1.18 (t, 3H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 154.26, 149.32, 138.22, 130.35, 128.42 (d, J = 20.1 Hz), 124.40, 120.96, 111.43 (d, J = 6.1 Hz), 105.86, 64.77 (d, J = 166.6 Hz), 63.45 (dd, J = 28.1, 6.8 Hz), 21.41, 16.37 (d, J = 6.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.73. **HRMS (ESI-TOF) m/z** calcd for $C_{16}H_{21}O_5PNa$ $[M+Na]^+$ 347. 1019 found 347.1019

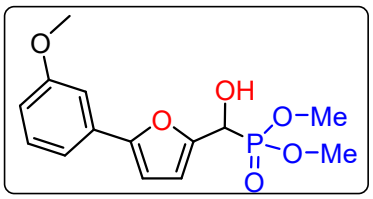
Dibutyl (hydroxy(5-(m-tolyl)furan-2-yl)methyl)phosphonate (1n)



Starting with 0.91 mmol of 5-(p-tolyl)furan-2-carbaldehyde and dibutyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1n** as a yellow oil (285 mg, 82% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 3H), 6.83 – 6.75 (m, 1H), 6.59 (s, 2H), 5.07 (d, J = 13.4 Hz, 1H), 4.15 – 3.97 (m, 4H), 3.80 (s, 3H), 1.67 – 1.44 (m, 4H), 1.27 (m, 4H), 0.84 (m, 6H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 159.73,

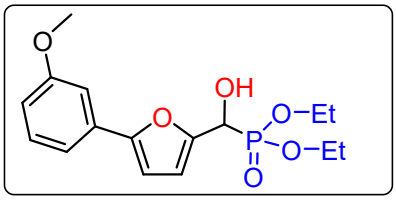
153.72, 149.86, 131.72, 129.58, 116.33, 113.14, 111.27 (d, J = 6.0 Hz), 109.04, 106.25, 67.25, 67.18, 66.90, 66.83, 65.48, 63.82, 55.16, 32.40 (d, J = 2.7 Hz), 18.50 (d, J = 4.4 Hz), 13.44 (d, J = 3.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.33. **HRMS (ESI-TOF) m/z** calcd for $C_{20}H_{29}O_5PNa$ $[M+Na]^+$ 403. 1645 found 403.1646

Dimethyl (hydroxy(5-(3-methoxyphenyl)furan-2-yl)methyl)phosphonate (1o)



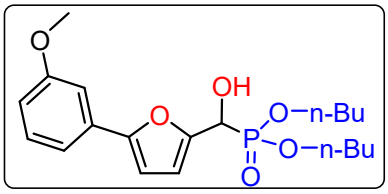
Starting with 0.91 mmol of 5-(4-methoxyphenyl)furan-2-carbaldehyde and dimethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1o** as a yellow oil (205 mg, 72% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 6.27 (m, 3H), 5.83 (m, 2H), 5.65 (m, 1H), 4.17 (d, J = 13.8 Hz, 1H), 2.86 – 2.75 (m, 9H). **^{13}C** NMR (101 MHz) **^{13}C** NMR (101 MHz, $CDCl_3$) δ 159.62, 153.76 (d, J = 2.5 Hz), 149.40, 131.51, 129.55, 116.21, 113.06, 111.38 (d, J = 6.1 Hz), 109.01, 106.21, 64.12 (d, J = 168.4 Hz), 55.03, 553.74 (dd, J = 18.5, 7.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.18. **HRMS (ESI-TOF) m/z** calcd for $C_{14}H_{17}O_6PNa$ $[M+Na]^+$ 335. 0655 found 335.0659

Diethyl (hydroxy(5-(3-methoxyphenyl)furan-2-yl)methyl)phosphonate (1p)



Starting with 0.91 mmol of 5-(4-methoxyphenyl)furan-2-carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1p** as a yellow oil (252 mg, 82% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 3H), 6.80 – 6.72 (m, 1H), 6.60 – 6.53 (m, 2H), 4.99 (d, J = 13.5 Hz, 1H), 4.18 – 4.01 (m, 4H), 3.78 (s, 3H), 1.23 (m, 6H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 159.83, 154.06 (s), 149.37, 131.68, 129.74, 122.43, 116.44, 113.37, 111.59 (s), 109.15, 106.37, 64.83 (d, J = 166.3 Hz), 63.48 (d, J = 15.5 Hz), 55.29, 16.42. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.62. **HRMS (ESI-TOF) m/z** calcd for $C_{16}H_{21}O_6PNa$ $[M+Na]^+$ 363.0968. found 363.0969

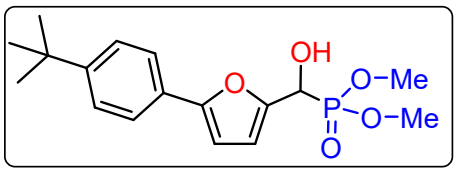
Dibutyl (hydroxy(5-(3-methoxyphenyl)furan-2-yl)methyl)phosphonate (1q)



Starting with 0.91 mmol of 5-(4-methoxyphenyl)furan-2-carbaldehyde and dibutyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1q** as a yellow oil (291 mg, 81% yield). **^{1}H** NMR (400 MHz) δ 7.29 – 7.16 (m, 3H), 6.79 (m, 1H), 6.59 (s, 2H), 5.07 (d, J = 13.4 Hz, 1H), 4.15 – 3.95 (m, 4H), 3.80 (d, J = 5.7 Hz, 3H), 1.66 – 1.49 (m, 4H), 1.28 (m, 4H), 0.84 (m, 6H). **^{13}C** NMR (101 MHz) δ 159.73, 153.72 (s), 149.86, 131.72, 129.58, 116.33, 113.14, 111.27 (d, J = 6.0 Hz), 109.04, 106.25, 67.04 (dd, J = 35.4, 7.3 Hz), 64.65 (d, J = 167.4 Hz), 55.16, 2.40 (d, J = 2.7 Hz), 18.50 (d, J = 4.4 Hz), 13.44 (d, J = 3.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.33. **HRMS (ESI-TOF) m/z** calcd for $C_{20}H_{29}O_6PNa$

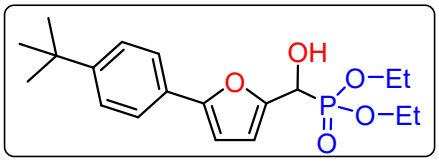
[M+Na]$^+$ 419.1594. found 419.1598

Dimethyl ((5-(4-(tert-butyl)phenyl)furan-2-yl)(hydroxy)methyl)phosphonate (1r)



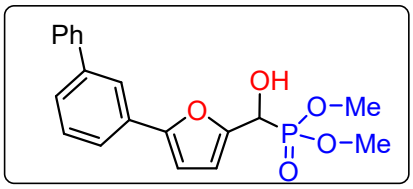
Starting with 0.91 mmol of 5-(4-(tert-butyl)phenyl)furan-2-carbaldehyde and dimethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1r** as a yellow oil (244 mg, 79% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.59 – 6.48 (m, 2H), 5.03 (d, *J* = 13.6 Hz, 1H), 3.77 – 3.63 (m, 6H), 1.25 (s, 9H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 154.60, 150.78, 148.71, 127.67, 125.57, 123.664.51 (d, *J* = 167.2 Hz), 54.23 – 53.72 (m), 34.61, 31.20. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.25. **HRMS (ESI-TOF) m/z** calcd for $C_{17}H_{23}O_5PNa$ [M+Na]$^+$ 361. 1175 found 361.1175

Diethyl ((5-(4-(tert-butyl)phenyl)furan-2-yl)(hydroxy)methyl)phosphonate (1s)



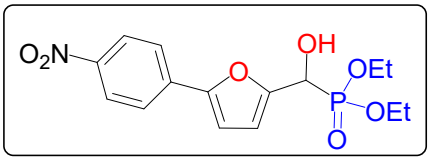
Starting with 0.91 mmol of 5-(4-(tert-butyl)phenyl)furan-2-carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1s** as a yellow oil (287 mg, 86% yield). **^{1}H** NMR NMR (400 MHz) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.65 – 6.49 (m, 2H), 5.07 (d, *J* = 13.5 Hz, 4H), 4.12 (m, 4H), 1.31 (s, 9H), 1.24 (m, 6H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 154.10, 150.44, 149.36, 127.78, 125.43, 123.51, 111.28 (d, *J* = 6.2 Hz), 105.34, 64.69 (d, *J* = 167.3 Hz), 63.35 (dd, *J* = 33.7, 6.8 Hz), 34.50, 31.14, 16.31 (t, *J* = 4.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.56. **HRMS (ESI-TOF) m/z** calcd for $C_{19}H_{27}O_5PNa$ [M+Na]$^+$ 389. 1488 found 389.1486

Dimethyl ((5-([1,1'-biphenyl]-3-yl)furan-2-yl)(hydroxy)methyl)phosphonate (1t)



Starting with 0.91 mmol of 5-([1,1'-biphenyl]-3-yl)furan-2-carbaldehyde and dimethyl phosphonates (1.2 equiv), column chromatography over silica gel (5:1 petroleum ether/ethyl acetate) yielded **1t** as a yellow oil (278 mg, 85% yield). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.61 – 7.53 (m, 3H), 7.45 – 7.36 (m, 4H), 7.30 (t, 1H), 6.64 (d, *J* = 3.4 Hz, 1H), 6.59 (t, 1H), 5.05 (d, *J* = 13.6 Hz, 1H), 3.79 (d, *J* = 10.6 Hz, 3H), 3.73 – 3.69 (m, 3H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 154.12, 149.38, 141.64, 140.75, 130.80, 129.08, 128.74, 127.45, 127.09, 126.41, 122.71, 122.53, 1111.67 (d, *J* = 6.1 Hz), 106.32, 64.39 (d, *J* = 167.3 Hz), 53.98 (d, *J* = 22.4 Hz. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.25. **HRMS (ESI-TOF) m/z** calcd for $C_{19}H_{19}O_5PNa$ [M+Na]$^+$ 381.0862 found 381.0864

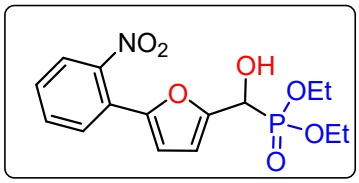
Diethyl (hydroxy(5-(4-nitrophenyl)furan-2-yl)methyl)phosphonate (1u)



Starting with 0.91 mmol of 5-(2-nitrophenyl)furan-2-

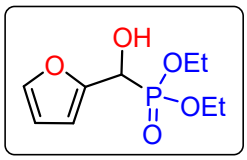
carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (4:1 petroleum ether/ethyl acetate) yielded **1v** as a yellow oil (278 mg, 86% yield). **^{1}H** NMR (400 MHz,) δ 8.14 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 3.4 Hz, 1H), 6.61 (t, 1H), 5.04 (d, 1H), 4.25 – 3.98 (m, 4H), 1.27 (t, 3H), 1.20 (t, 3H). **^{13}C** NMR NMR (101 MHz,) δ 152.08, 151.68, 146.40, 135.99, 124.24, 123.90, 111.79 (d, *J* = 6.3 Hz), 109.90, 65.59, 63.46 (d, *J* = 7.0 Hz), 63.46 (d, *J* = 7.0 Hz), 16.42, 16.37, 16.32. **^{31}P NMR** (162 MHz,) δ 19.42. **HRMS (ESI-TOF) m/z** calcd for C15H18NO7PNa [M+Na]$^{+}$ 378.0713 found 378.0719。

Diethyl (hydroxy(5-(2-nitrophenyl)furan-2-yl)methyl)phosphonate (1v)



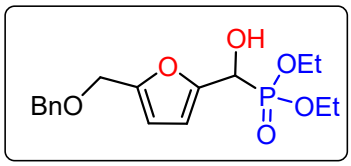
Starting with 0.91 mmol of 5-(2-nitrophenyl)furan-2-carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (4:1 petroleum ether/ethyl acetate) yielded **1v** as a yellow oil (276 mg, 85% yield). **^{1}H** NMR (400 MHz,) δ 7.71 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.63 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.52 (m, 1H), 7.36 (dd, *J* = 11.5, 4.1 Hz, 1H), 6.60 (s, 2H), 5.01 (d, *J* = 13.4 Hz), 4.24 – 3.99 (m, 4H), 1.26 (m, 6H). **^{13}C** NMR (101 MHz,) **^{13}C** NMR (101 MHz,) δ 151.82, 148.04, 147.26, 131.79, 128.85, 128.25, 123.71, 111.22 (d, *J* = 5.9 Hz), 110.80, 65.38, 63.69 (d, *J* = 5.8 Hz), 63.35 (d, *J* = 7.1 Hz), 16.62 – 16.02 (m). **^{31}P NMR** (162 MHz,) δ 19.39. **HRMS (ESI-TOF) m/z** calcd for C15H18NO7PNa [M+Na]$^{+}$ 378.0713 found 378.0717。

Diethyl (furan-2-yl(hydroxy)methyl)phosphonate (1v)



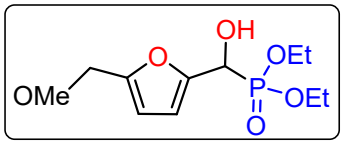
Starting with 0.91 mmol of furan-2-carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (4:1 petroleum ether/ethyl acetate) yielded **1v** as a yellow oil (201 mg, 94% yield). **^{1}H** NMR (400 MHz,) δ 7.36 (s, 1H), 6.45 (t, *J* = 2.8 Hz, 1H), 6.31 (s, 1H), 4.94 (d, *J* = 13.3 Hz, 1H), 4.18 – 3.92 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.22 – 1.15 (m, 3H). **^{13}C** NMR (101 MHz,) δ 149.97, 142.57, 110.55, 109.15 (d, *J* = 6.2 Hz), 63.57 (d, *J* = 5.5 Hz), 63.33 (d, *J* = 7.0 Hz), 16.21 (t, *J* = 5.8 Hz). **^{31}P NMR** (162 MHz,) δ 20.10. **HRMS (ESI-TOF) m/z** calcd for C9H15O5PNa [M+Na]$^{+}$ 257.0549 found 257.0547

Diethyl ((5-((benzyloxy)methyl)furan-2-yl)(hydroxy)methyl)phosphonate （1v）



Starting with 0.91 mmol of 5-((benzyloxy)methyl)furan-2-carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (4:1 petroleum ether/ethyl acetate) yielded **1v** as a yellow oil (271mg, 84% yield). **^{1}H** NMR (400 MHz,) δ 7.33 – 7.18 (m, 5H), 6.43 (t, *J* = 2.9 Hz, 1H), 6.24 (d, *J* = 3.2 Hz, 1H), 4.93 (d, *J* = 13.3 Hz, 1H), 4.46 (s, 2H), 4.39 (s, 2H), 4.12 – 3.97 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C** NMR (101 MHz,) δ 151.92, 150.34, 137.70, 128.32, 127.72 (d, *J* = 14.8 Hz), 110.48, 109.91 (d, *J* = 5.8 Hz), 71.76, 65.48, 63.80 (d, *J* = 5.2 Hz), 63.50 (d, *J* = 6.9 Hz), 63.26 (d, *J* = 6.9 Hz), 16.32 (t, *J* = 5.5 Hz). **^{31}P NMR** (162 MHz,) δ 19.90. **HRMS (ESI-TOF) m/z** calcd for C17H23O6PNa [M+Na]$^{+}$ 377.1124 found 377.1127

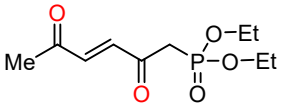
Diethyl (hydroxy(5-(methoxymethyl)furan-2-yl)methyl)phosphonate (1v)



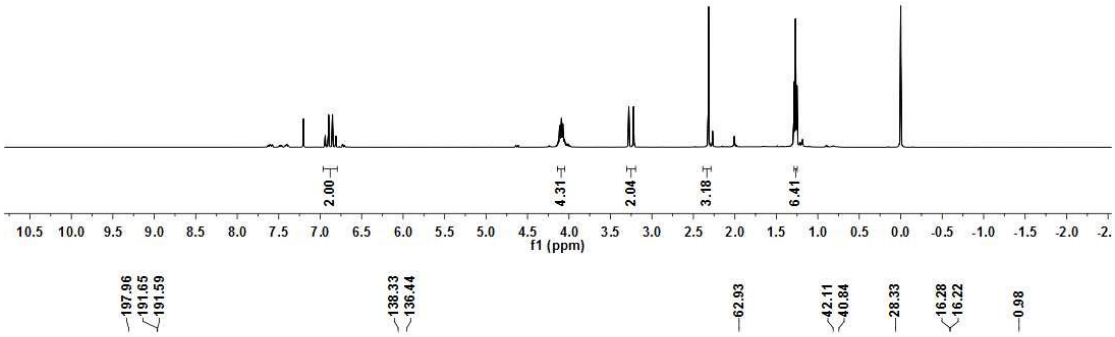
Starting with 0.91 mmol of 5-(methoxymethyl)furan-2-carbaldehyde and diethyl phosphonates (1.2 equiv), column chromatography over silica gel (4:1 petroleum ether/ethyl acetate) yielded **1v** as a yellow oil (231mg, 91% yield). **^{1}H** NMR (400 MHz,) δ 6.43 (t, *J* = 2.9 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 4.93 (d, *J* = 13.3 Hz, 1H), 4.31 (s, 2H), 4.24 – 3.97 (m, 4H), 3.28 (s, 3H), 1.23 (m, 6H). **^{13}C** NMR (101 MHz,) δ 151.88, 151.72, 150.31, 149.37, 110.41, 110.25, 109.94, 109.88, 66.22, 65.47, 63.82, 63.52, 63.46, 63.32, 63.25, 57.72, 16.39, 16.33, 16.27. **^{31}P NMR** (162 MHz,) δ 19.84. **HRMS (ESI-TOF) m/z** calcd for C11H19O6PNa $[M+Na]^+$ 301.0811 found 301.0812.

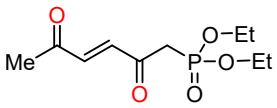
VII. Copies of ^{1}H, ^{13}C and ^{31}P NMR Spectra for products and substrates

^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2a**

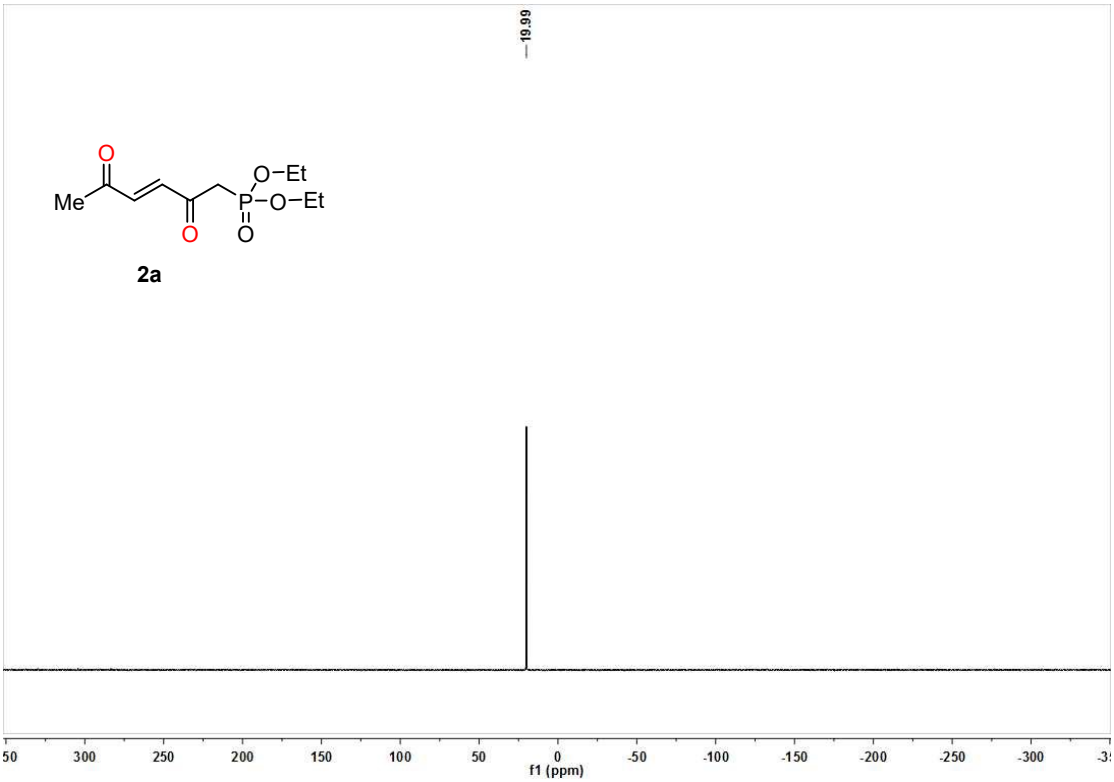


2a



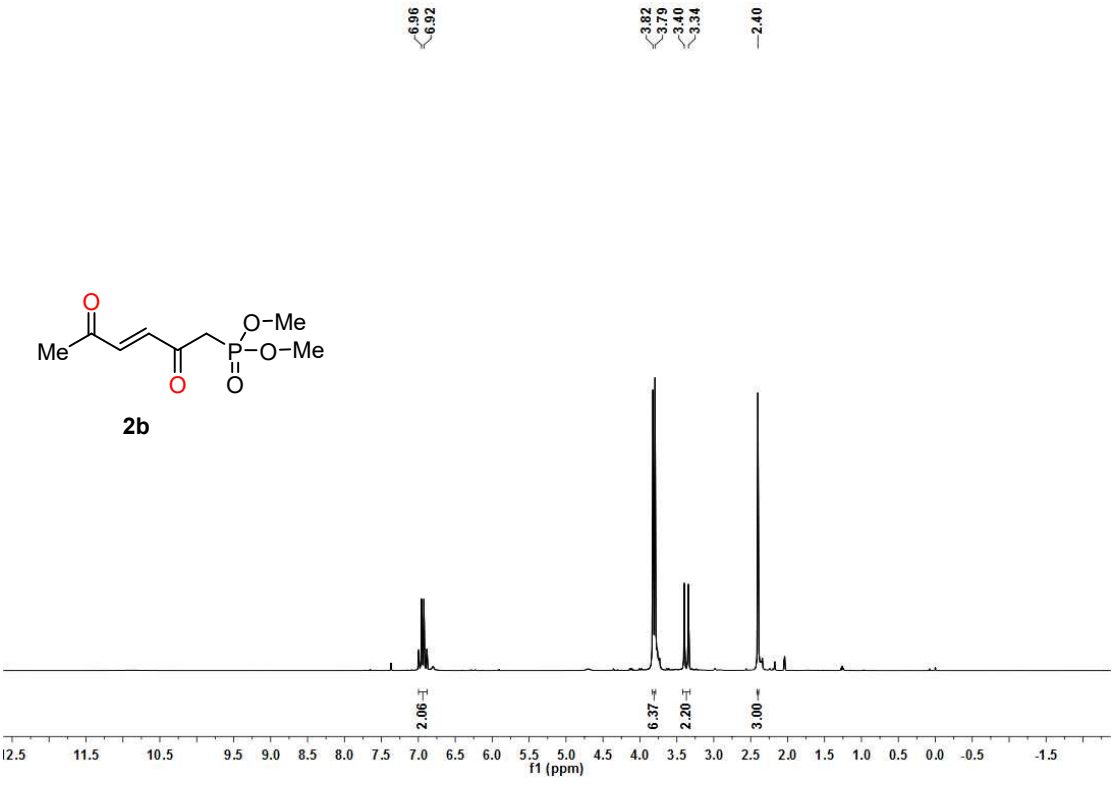


2a

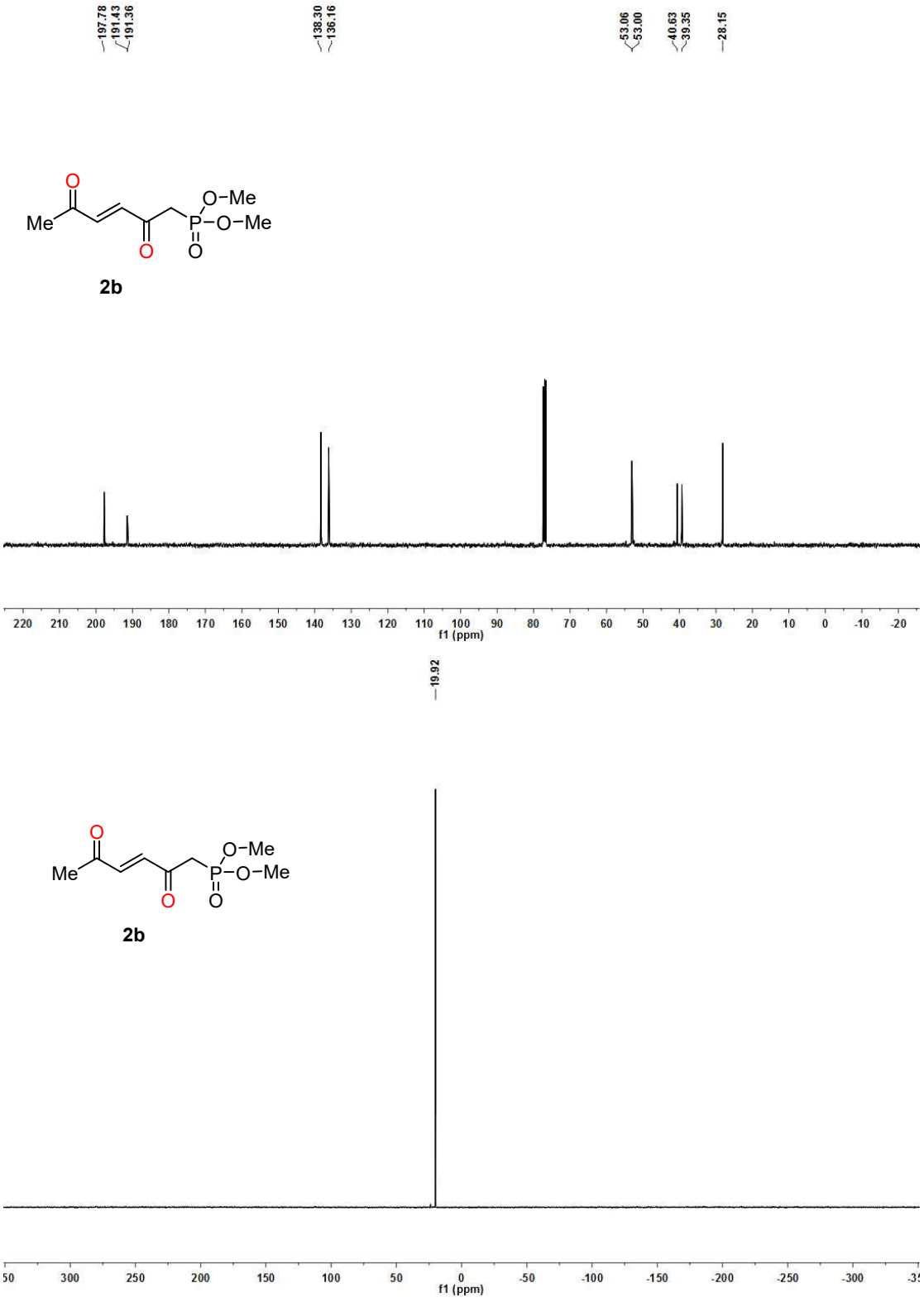


2a

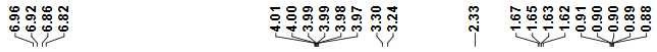
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2b**

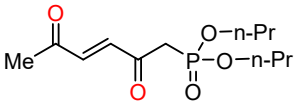


2b

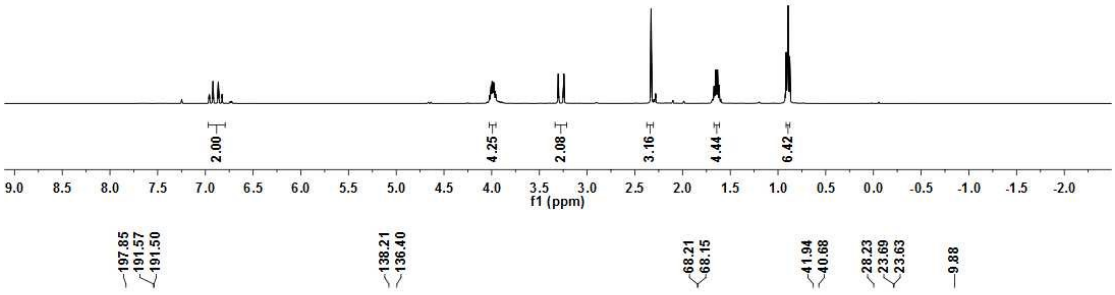

197.78
191.43
191.36
138.30
136.16
53.06
53.00
40.63
39.35
28.15
O
Me
O
O−Me
P−O−Me
O
2b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
19.92
O
Me
O
O−Me
P−O−Me
O
2b
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

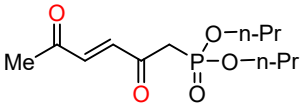
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2c**



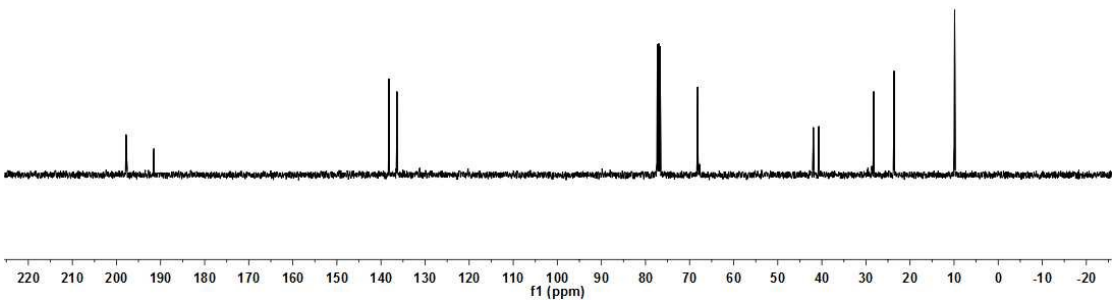


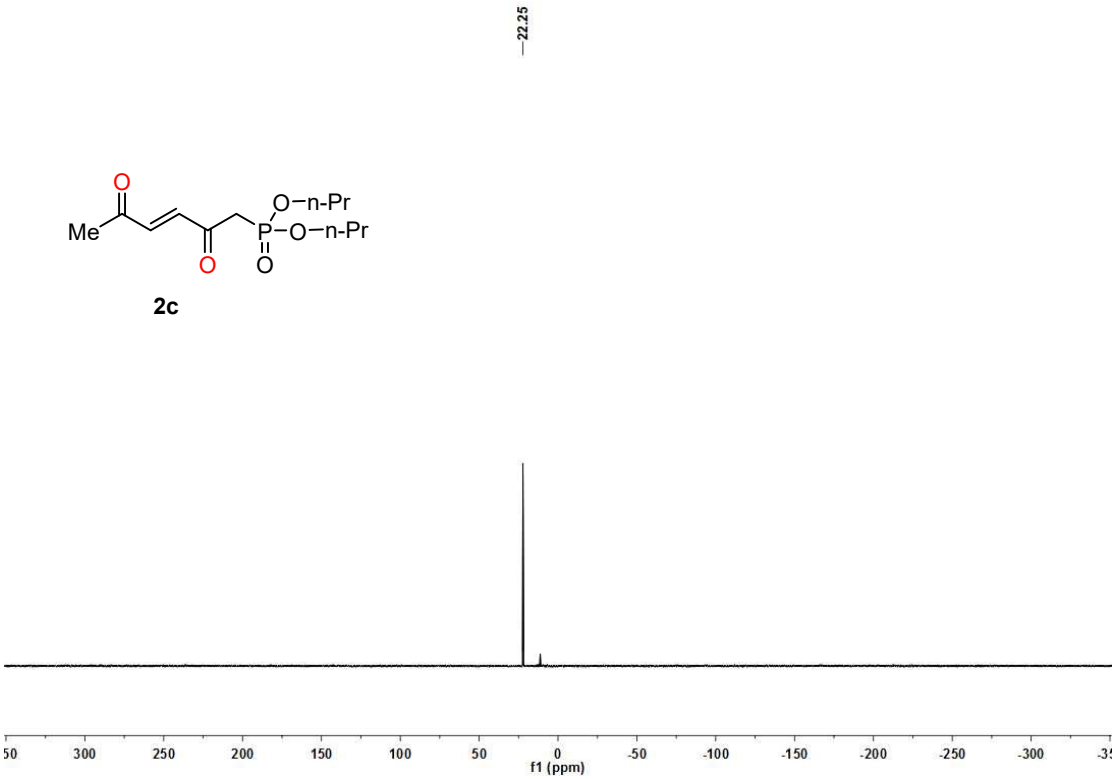
2c





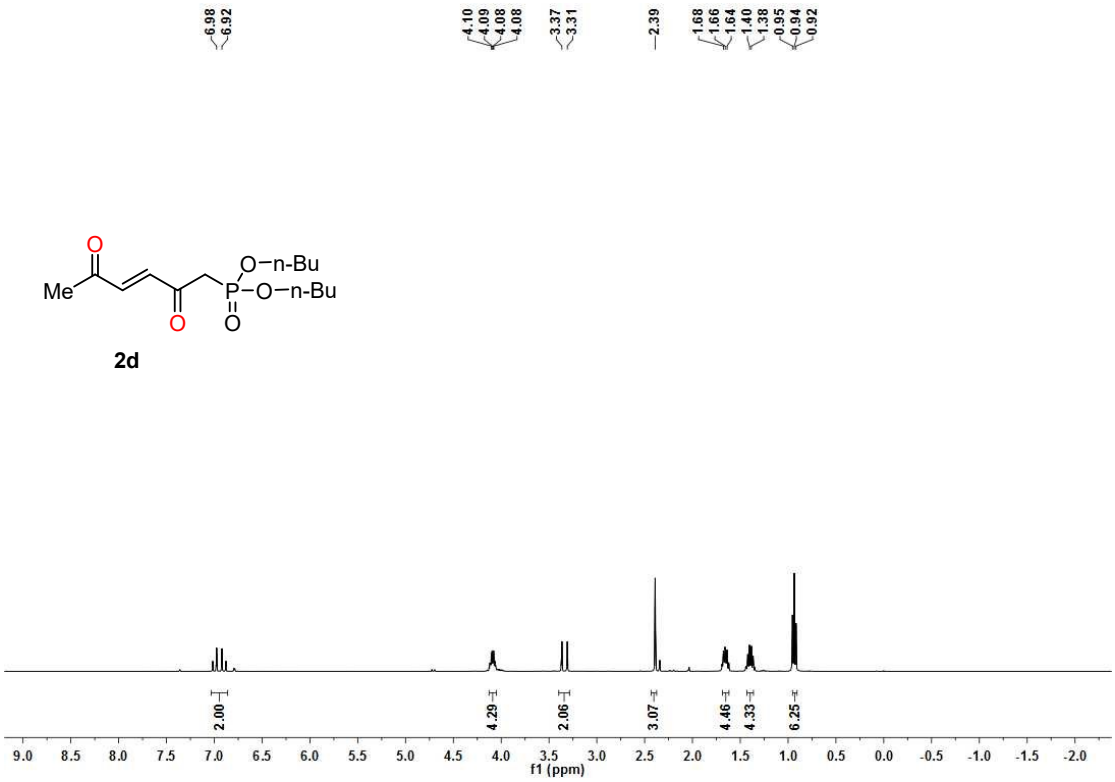
2c



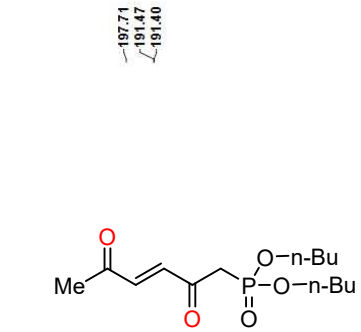


2c

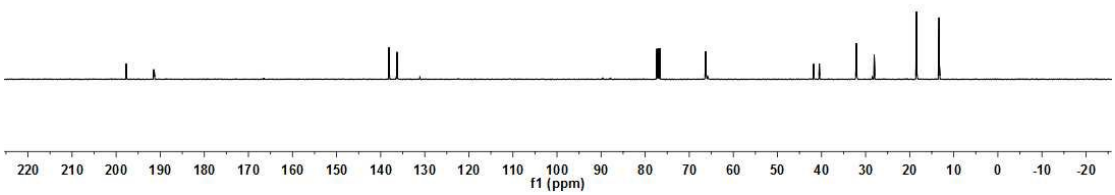
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2d**

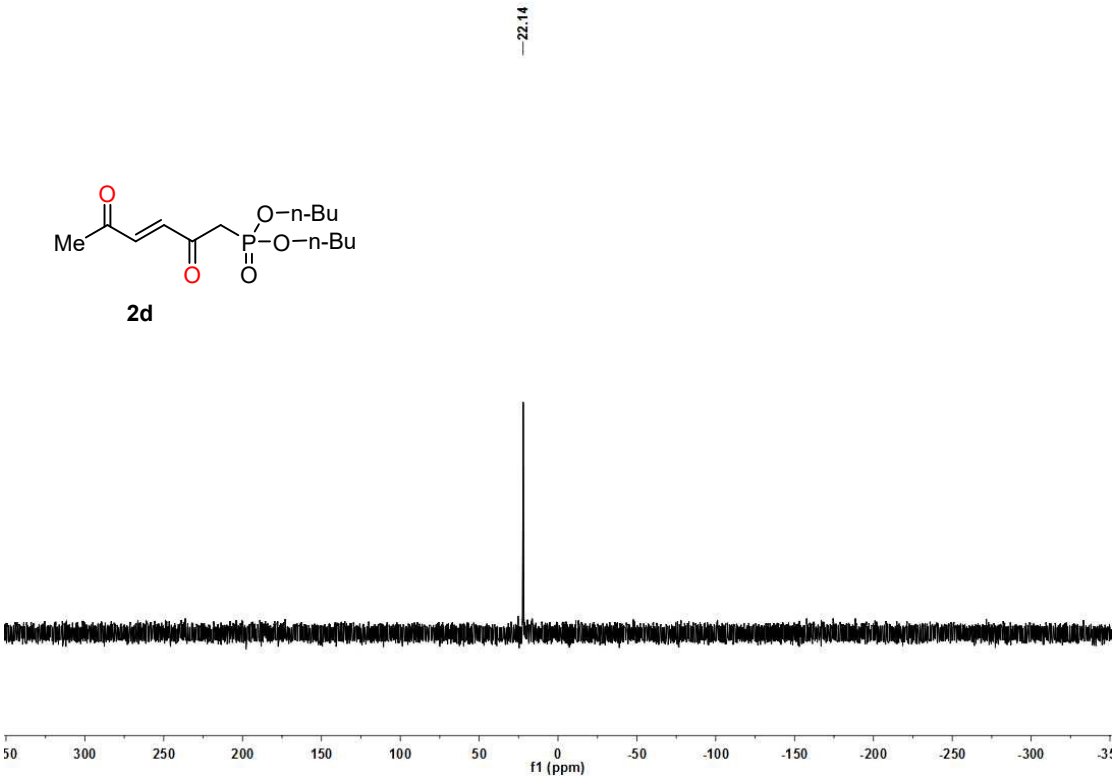


2d


197.71
191.47
191.40
138.07
136.31
66.31
66.25
41.77
40.51
32.17
32.10
28.05
18.43
13.32
O
Me
O
O−n-Bu
P
O−n-Bu
O

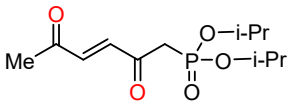
2d


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

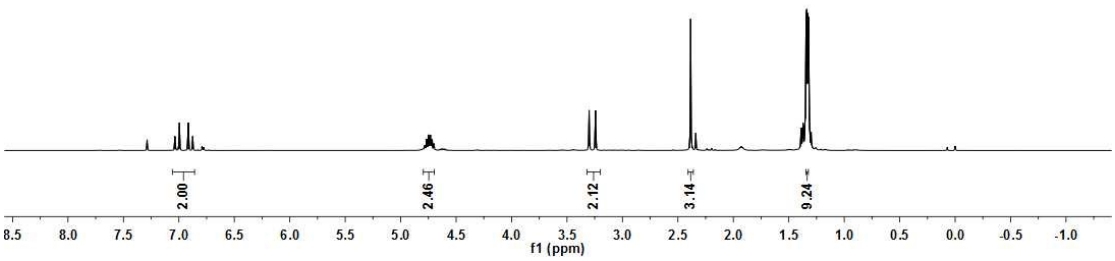

22.14
O
Me
O
O−n-Bu
P
O−n-Bu
O
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

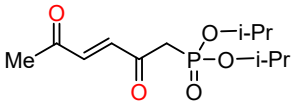
2d

^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2e**

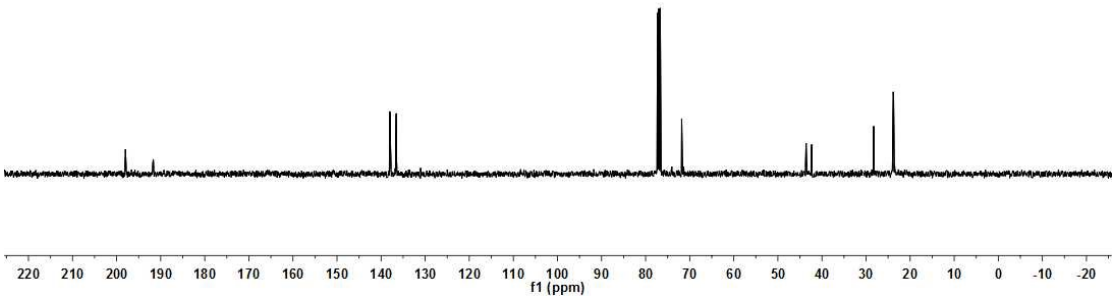


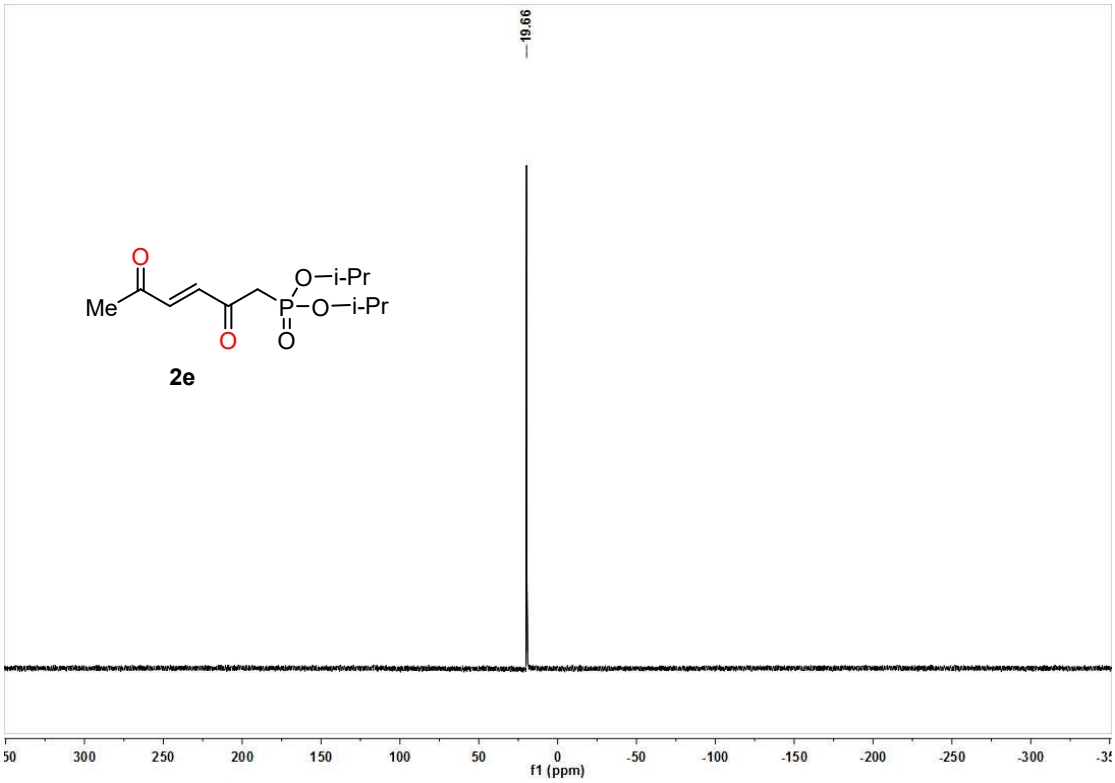
2e





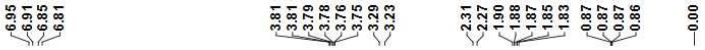
2e

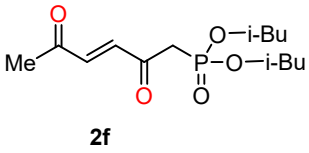




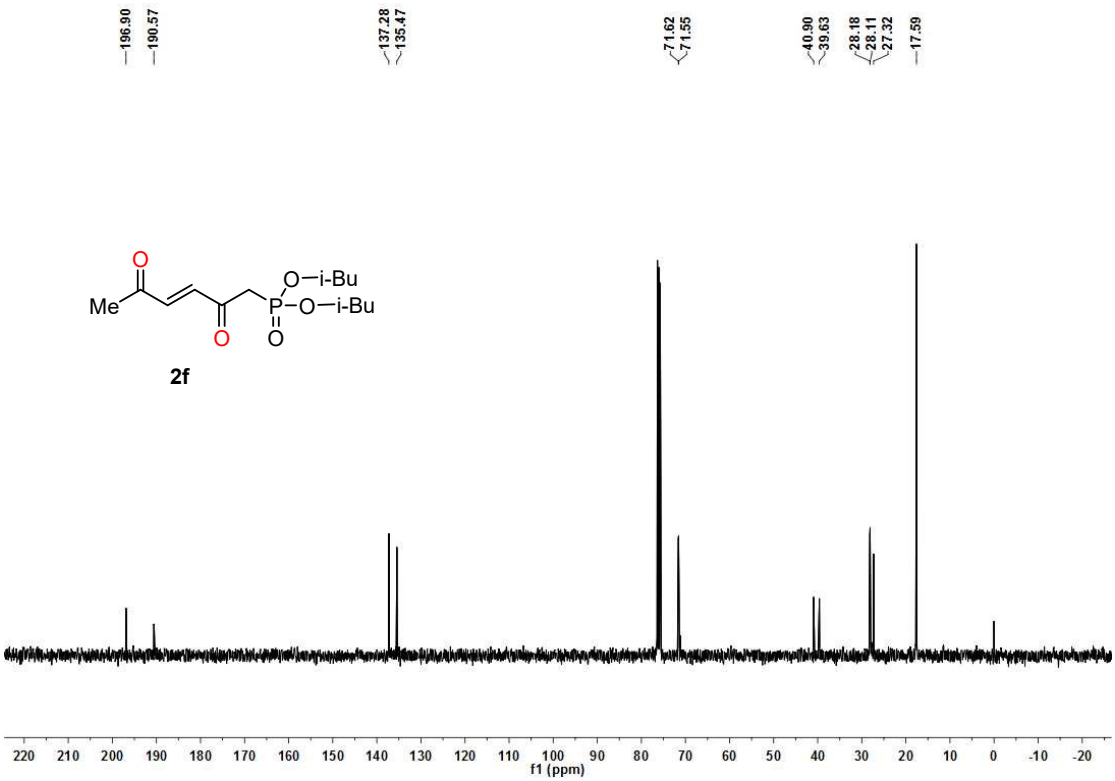
2e

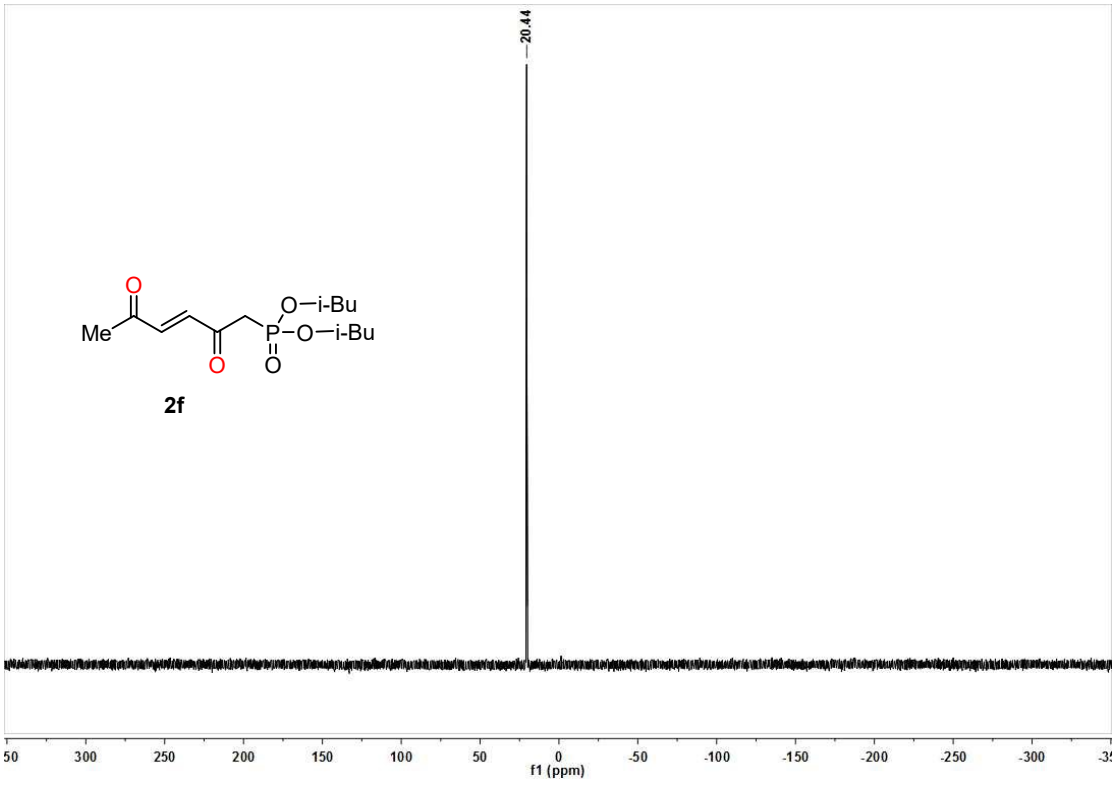
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2f**



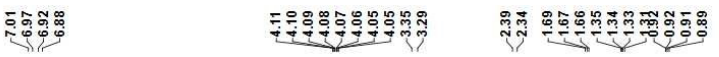


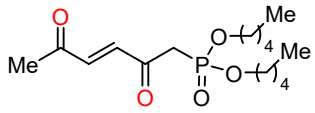
2f


196.90
190.57
137.28
135.47
71.62
71.55
40.90
39.63
28.18
28.11
27.32
17.59
O
Me
O
O—i-Bu
P
O—i-Bu
O
2f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

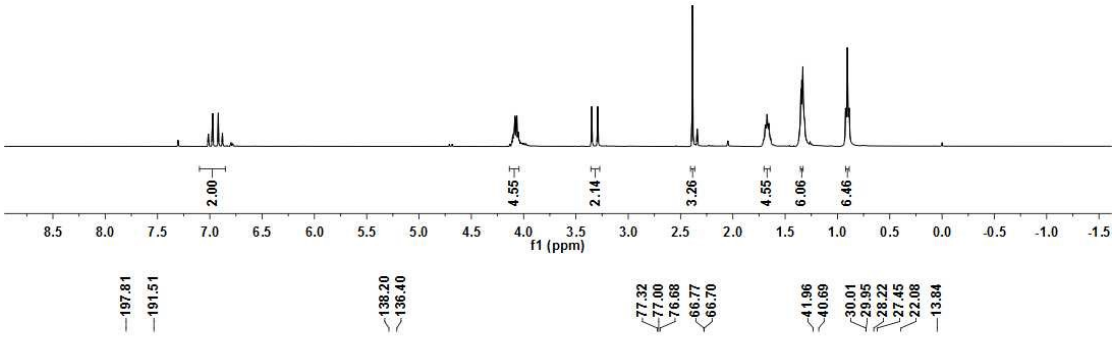

20.44
O
Me
O
O—i-Bu
P
O—i-Bu
O
2f
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

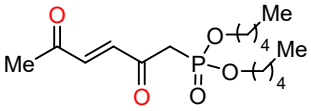
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2g**



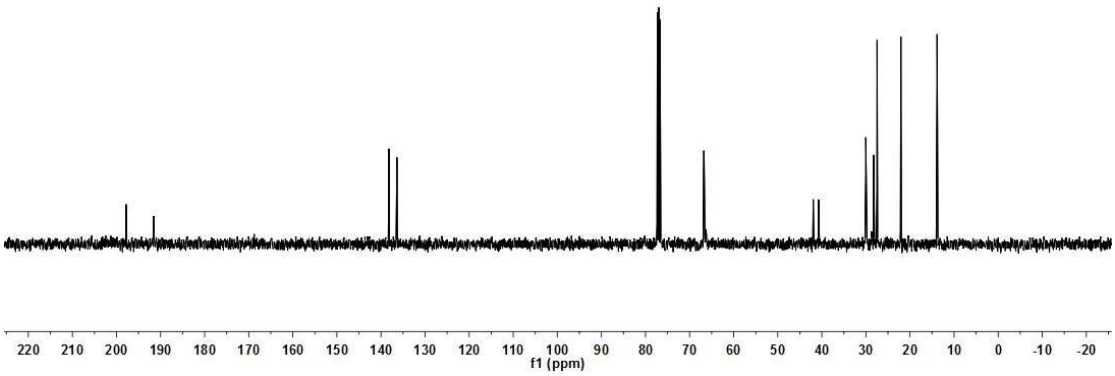


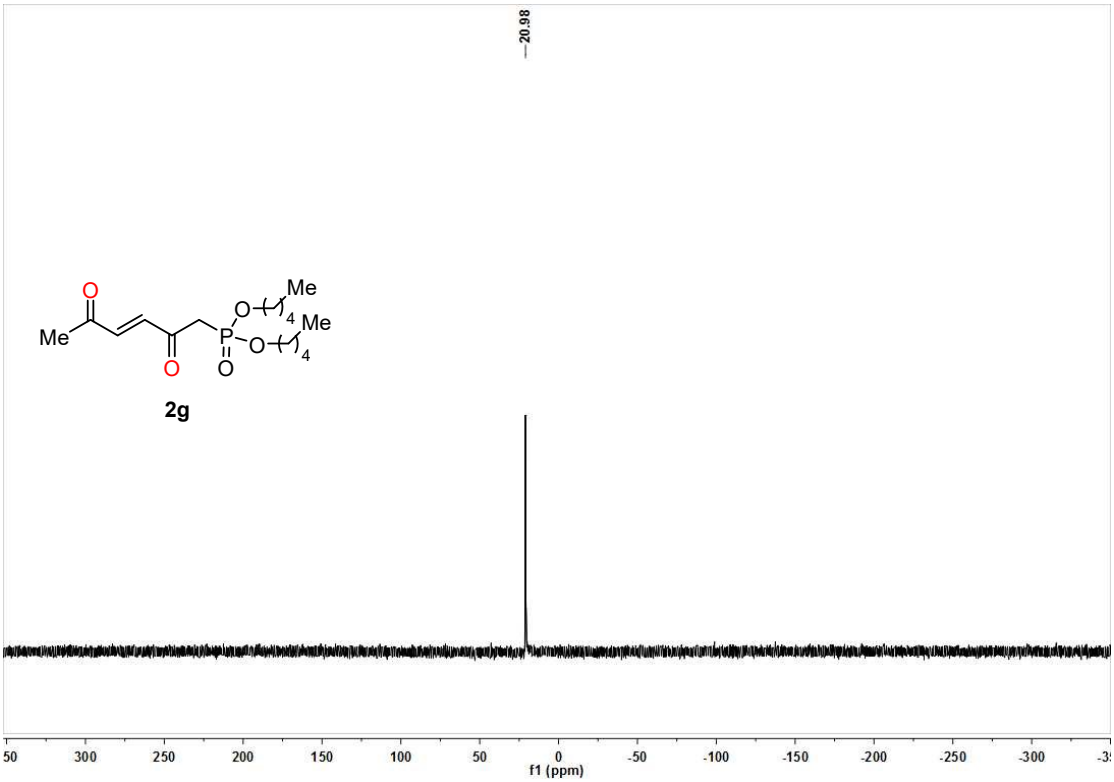
2g



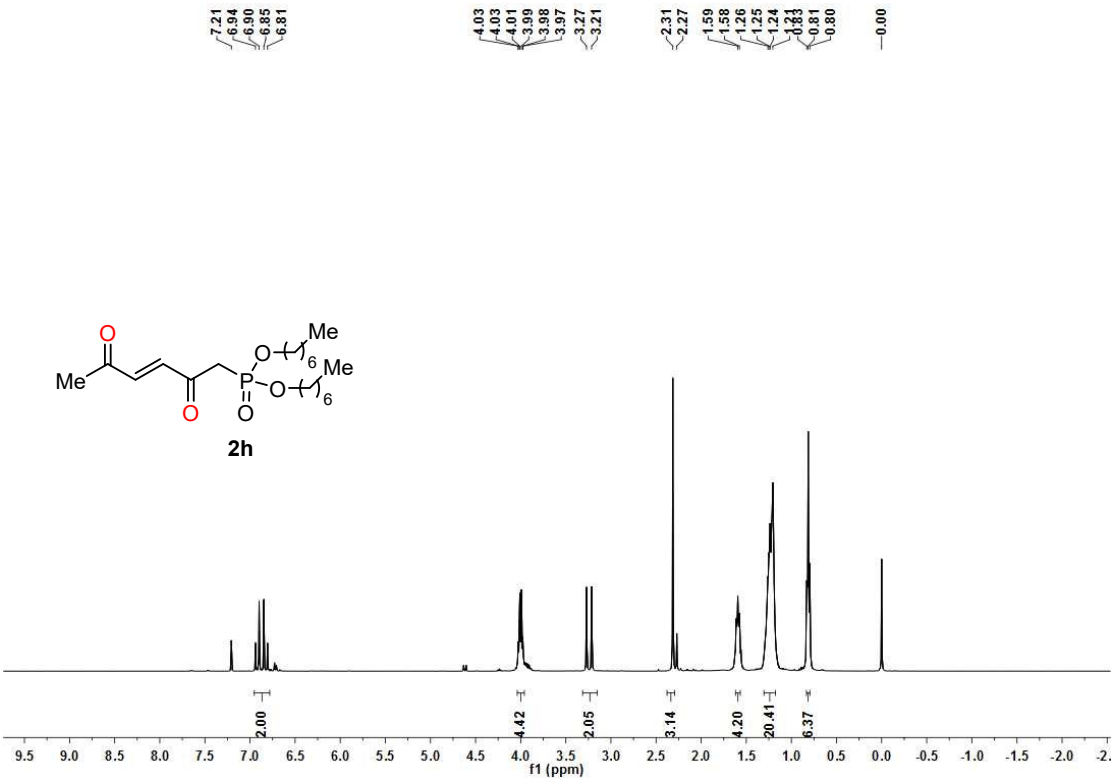


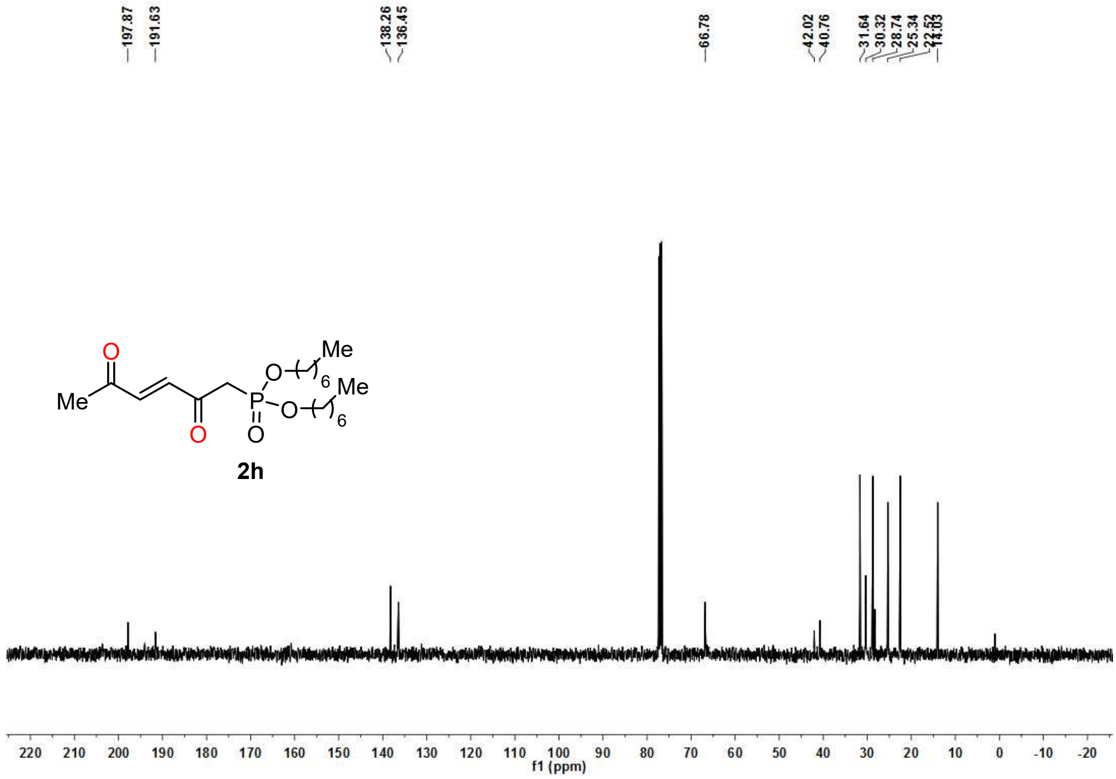
2g

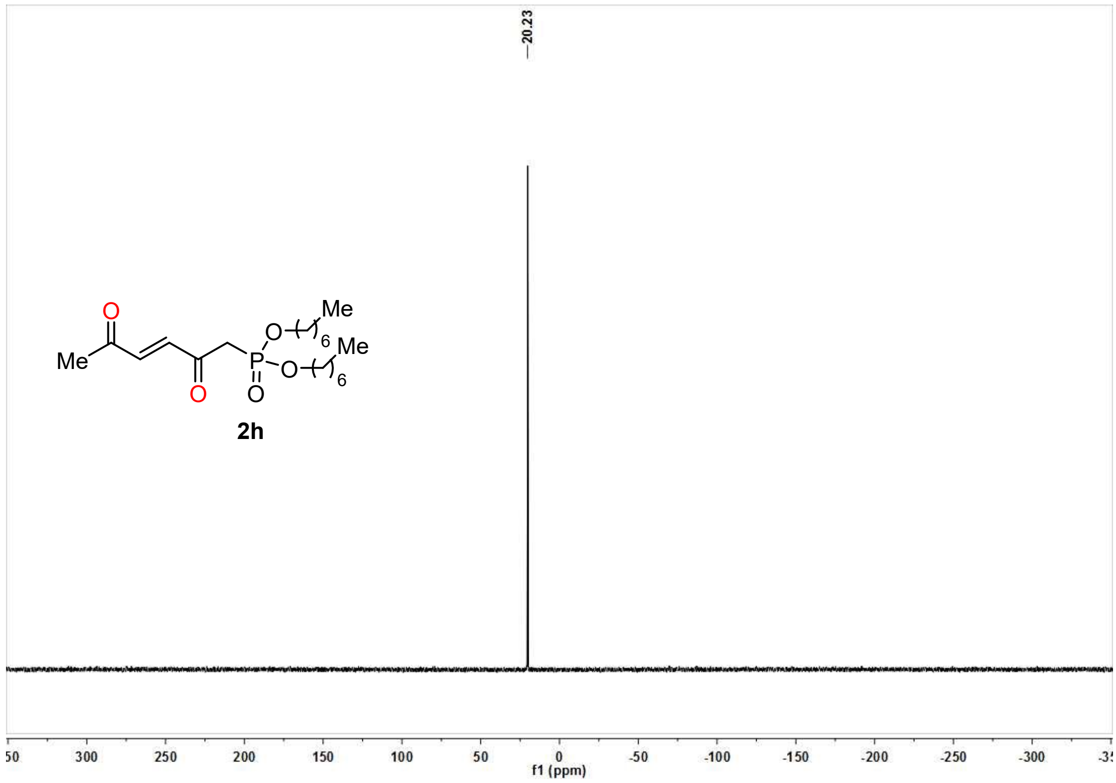




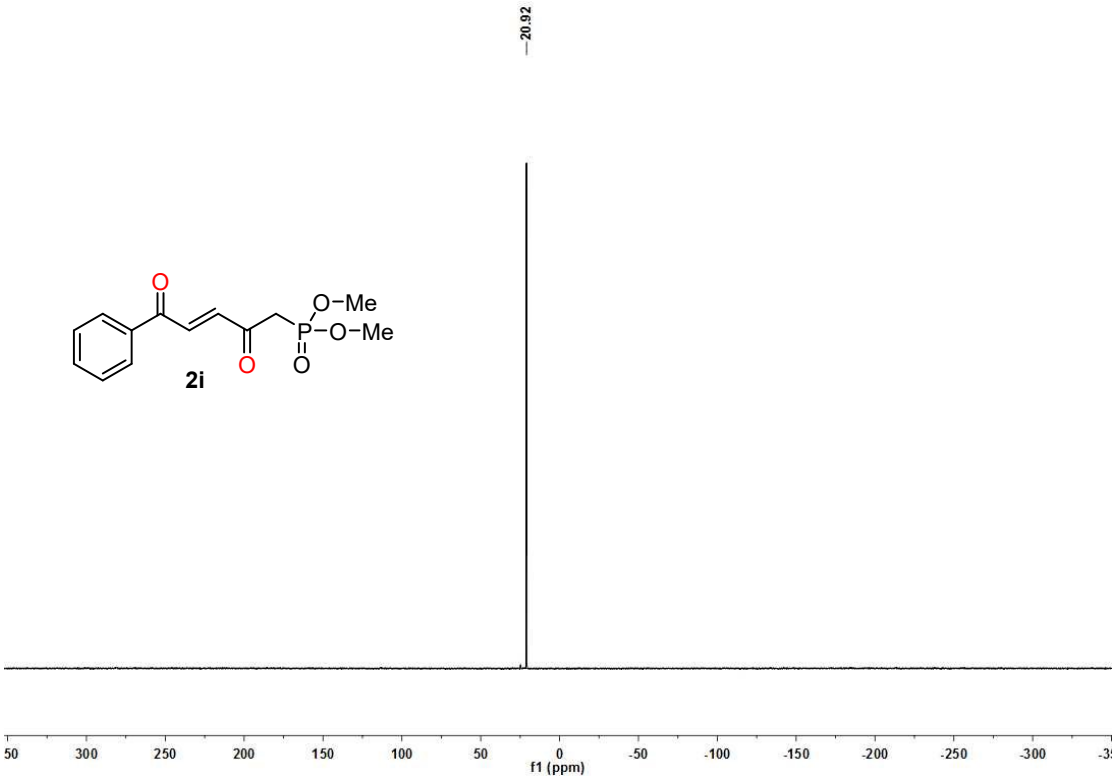
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2h**



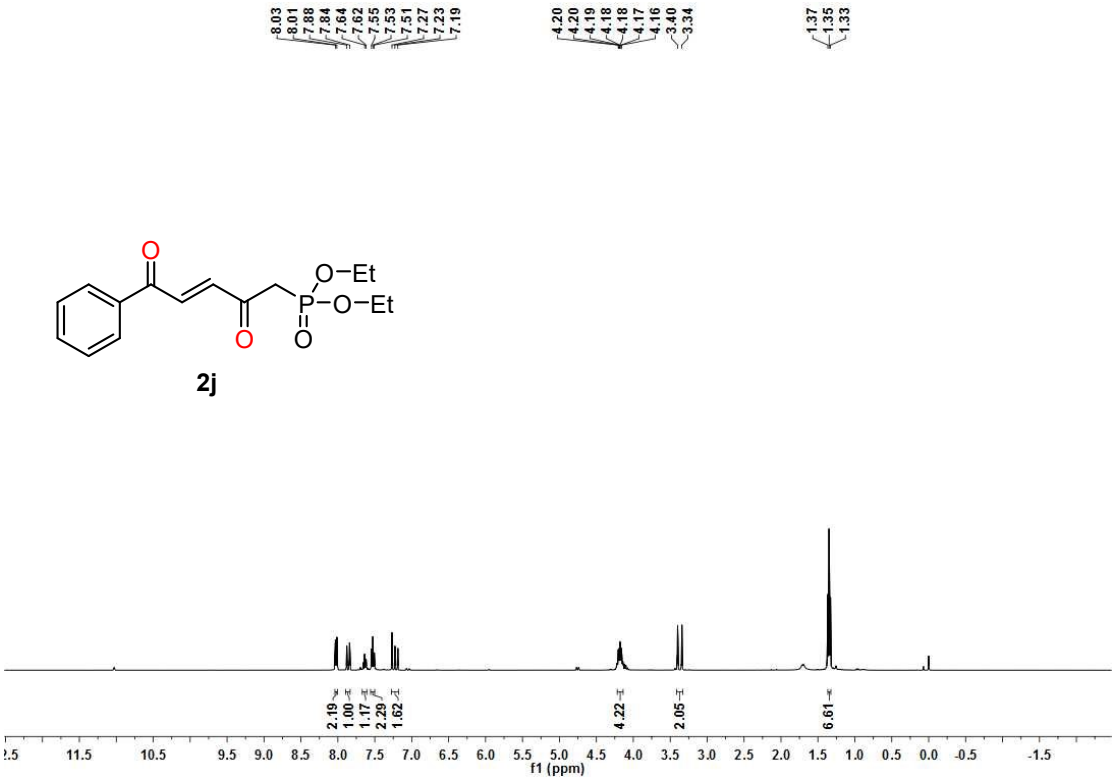

197.87
191.63
138.26
136.45
66.78
42.02
40.76
31.64
30.32
28.74
25.34
22.52
14.03
Me
O
O
Me
O
Me
P
O
O
6
6
2h
f1 (ppm)

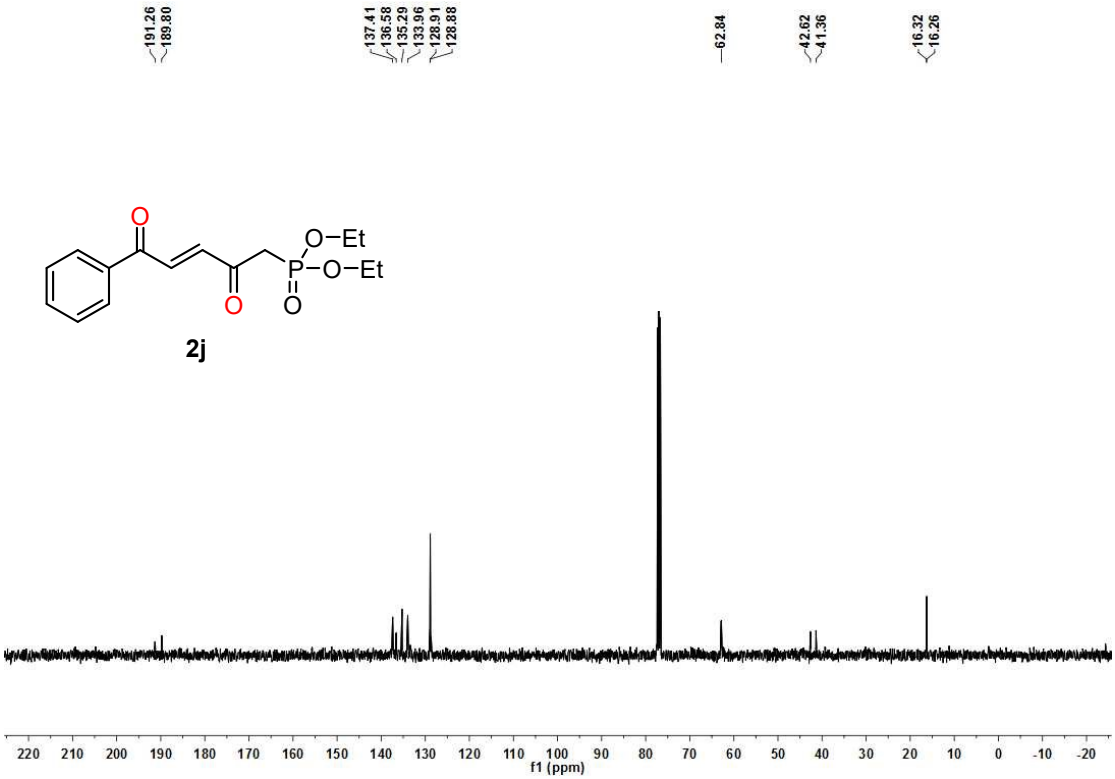

20.23
Me
O
O
Me
O
Me
P
O
O
6
6
2h
f1 (ppm)

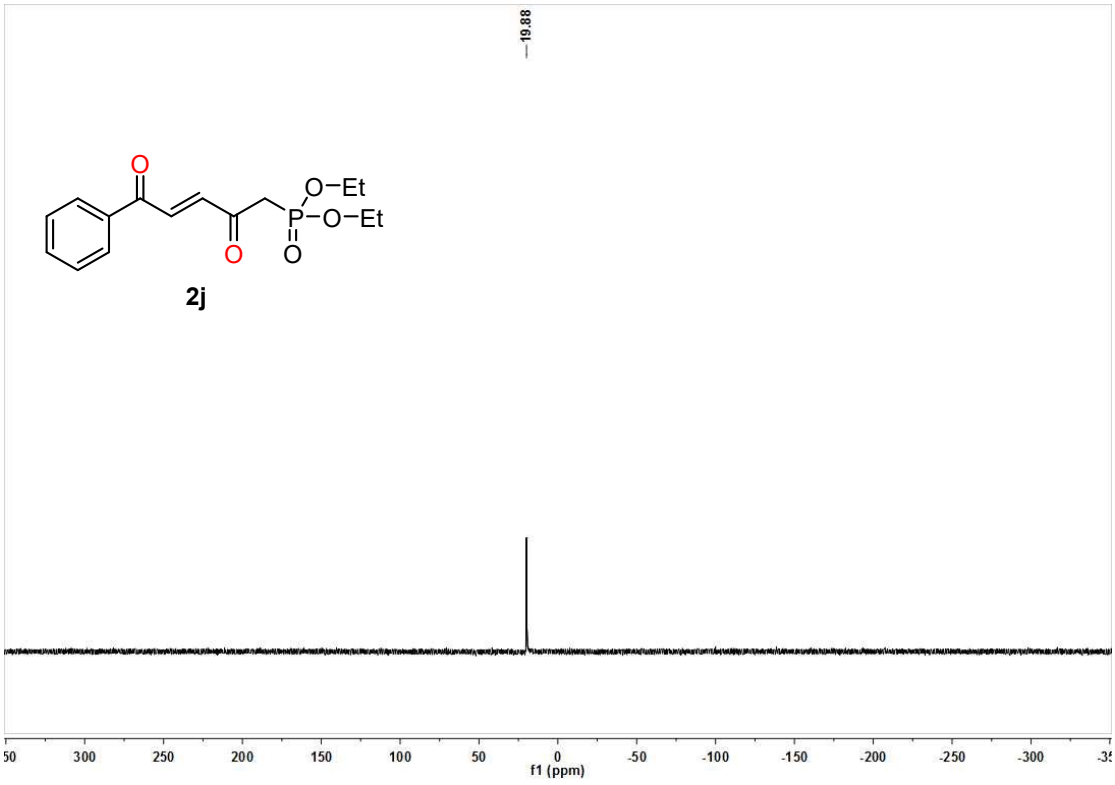
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2i**



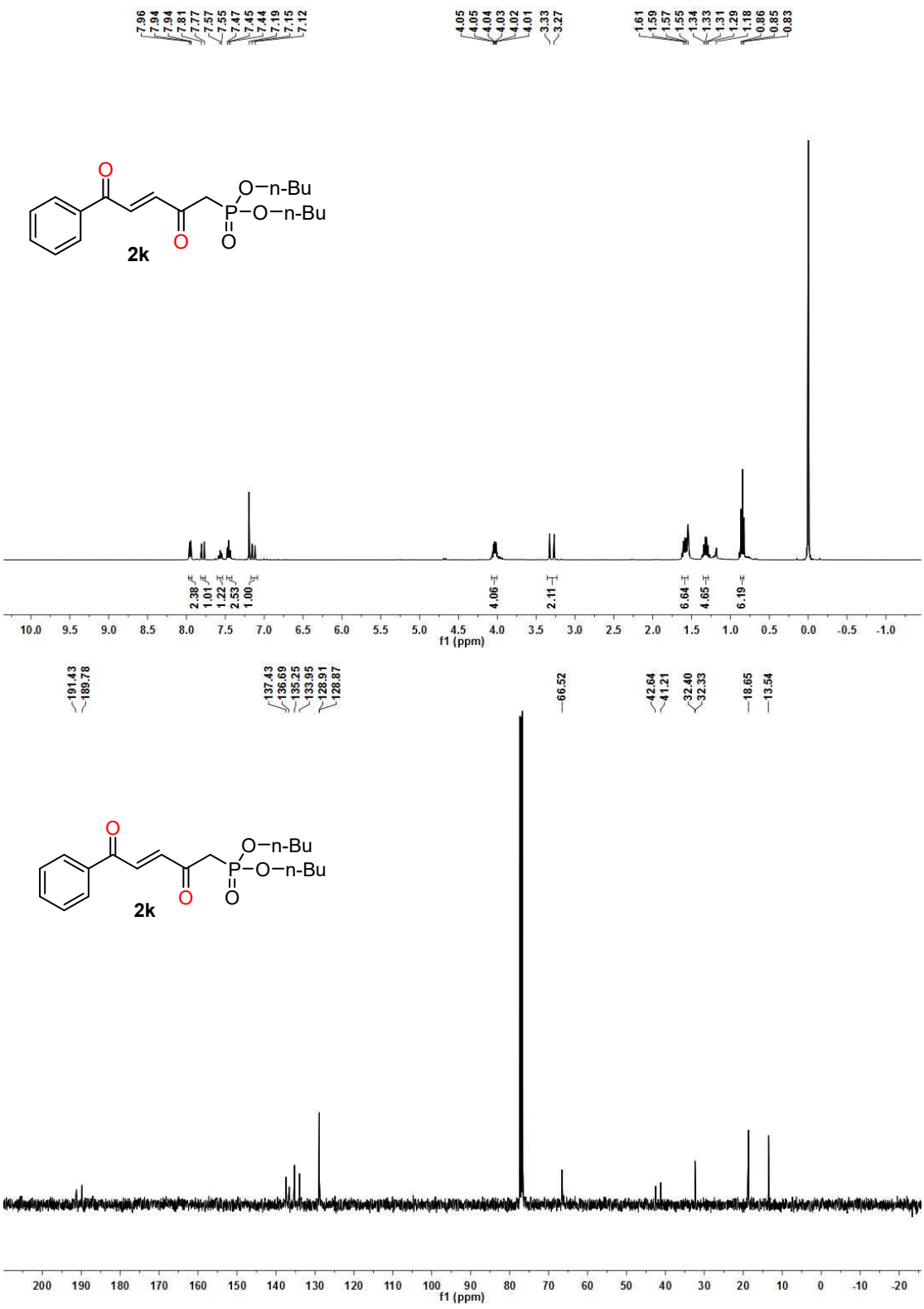
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2j**

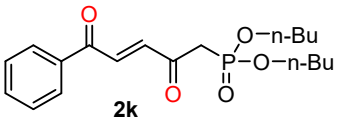



191.26
189.80
137.41
136.58
135.29
133.96
128.91
128.88
62.84
42.62
41.36
16.32
16.26
O
O
O–Et
P–O–Et
O
2j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


19.88
O
O
O–Et
P–O–Et
O
2j
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -35
f1 (ppm)

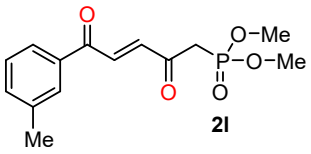
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2k**



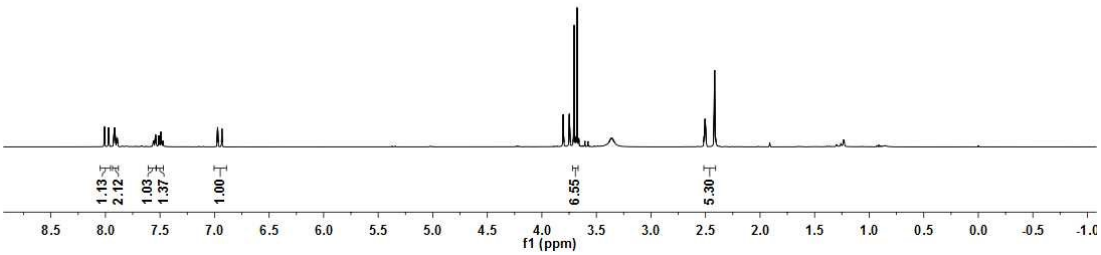


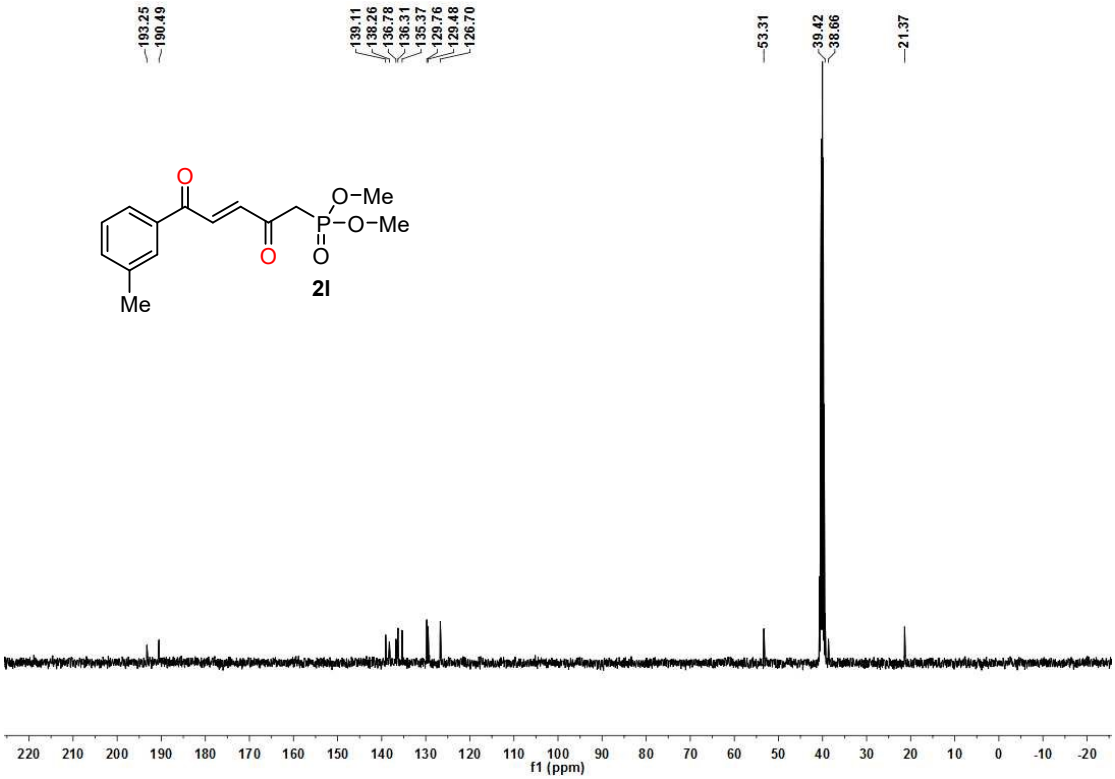
2k

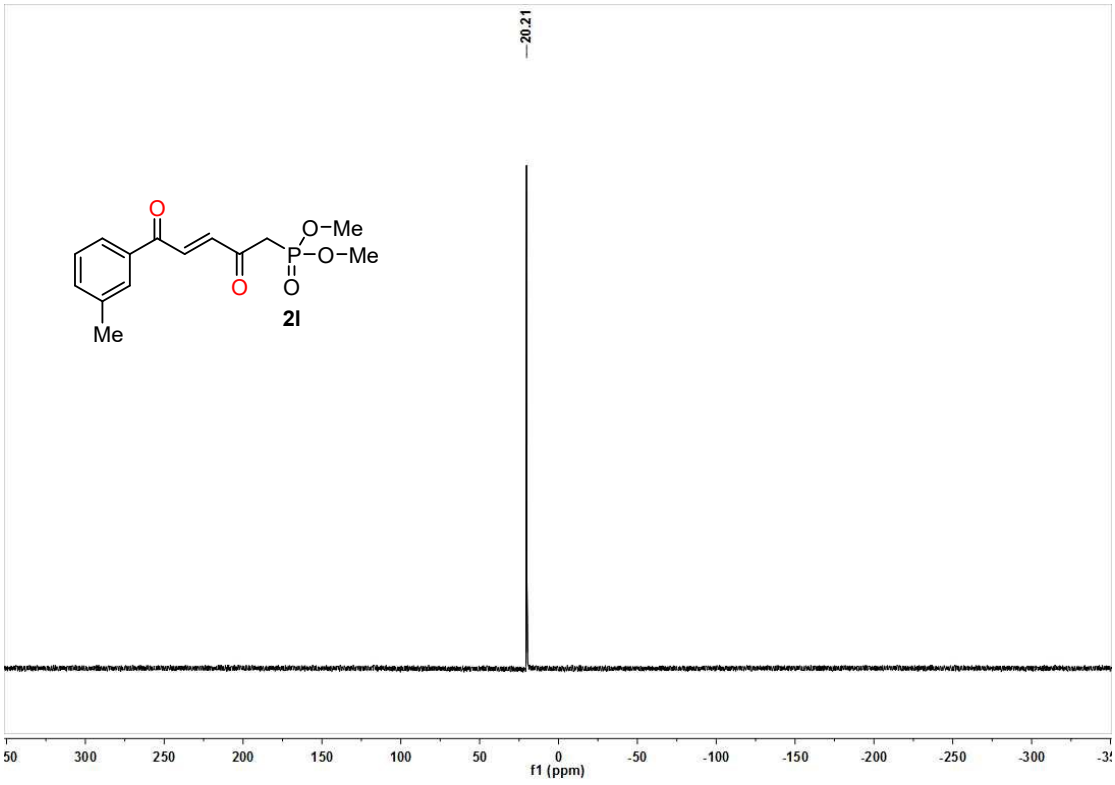
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, DMSO) **and ^{31}P spectra of 2l**



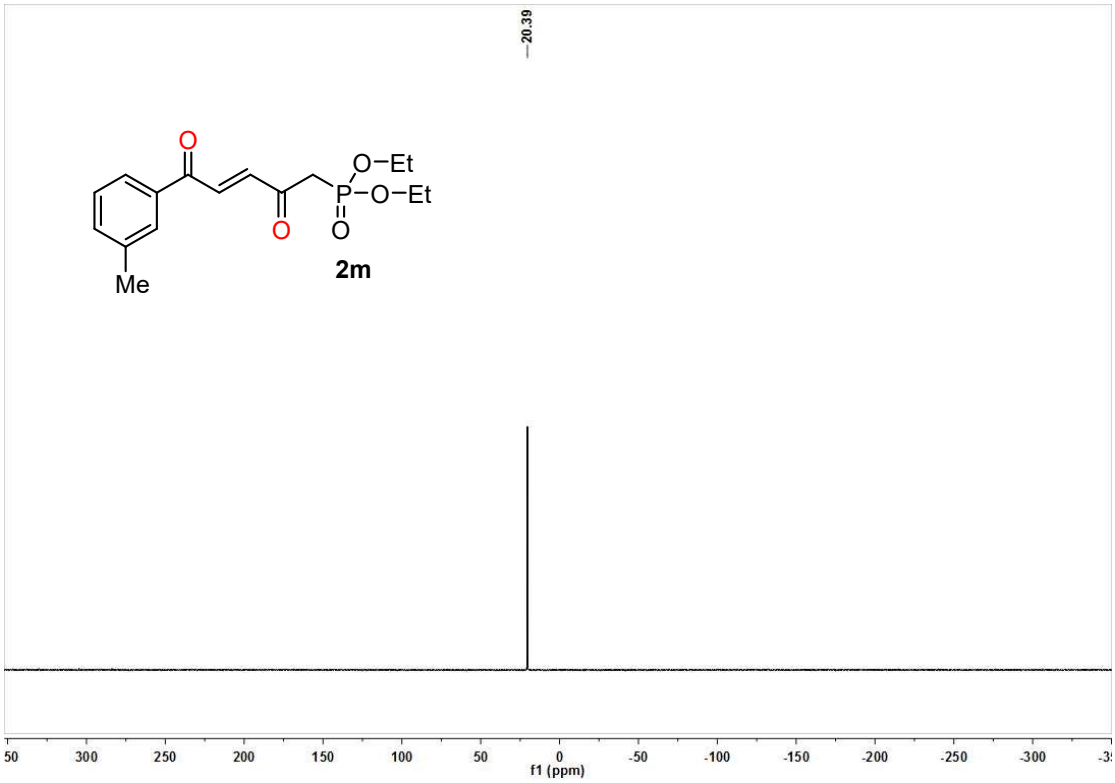
2l



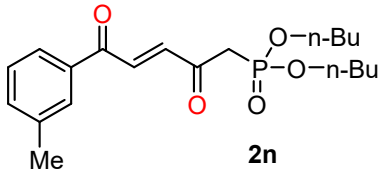

193.25
190.49
139.11
138.26
136.78
136.31
135.37
129.76
129.48
126.70
53.31
39.42
38.66
21.37
O
O
O−Me
P−O−Me
O
Me
2l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

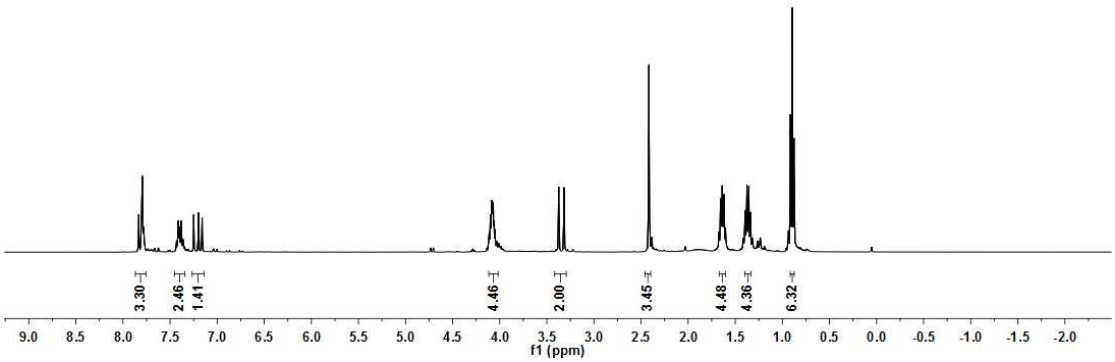

20.21
O
O
O−Me
P−O−Me
O
Me
2l
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

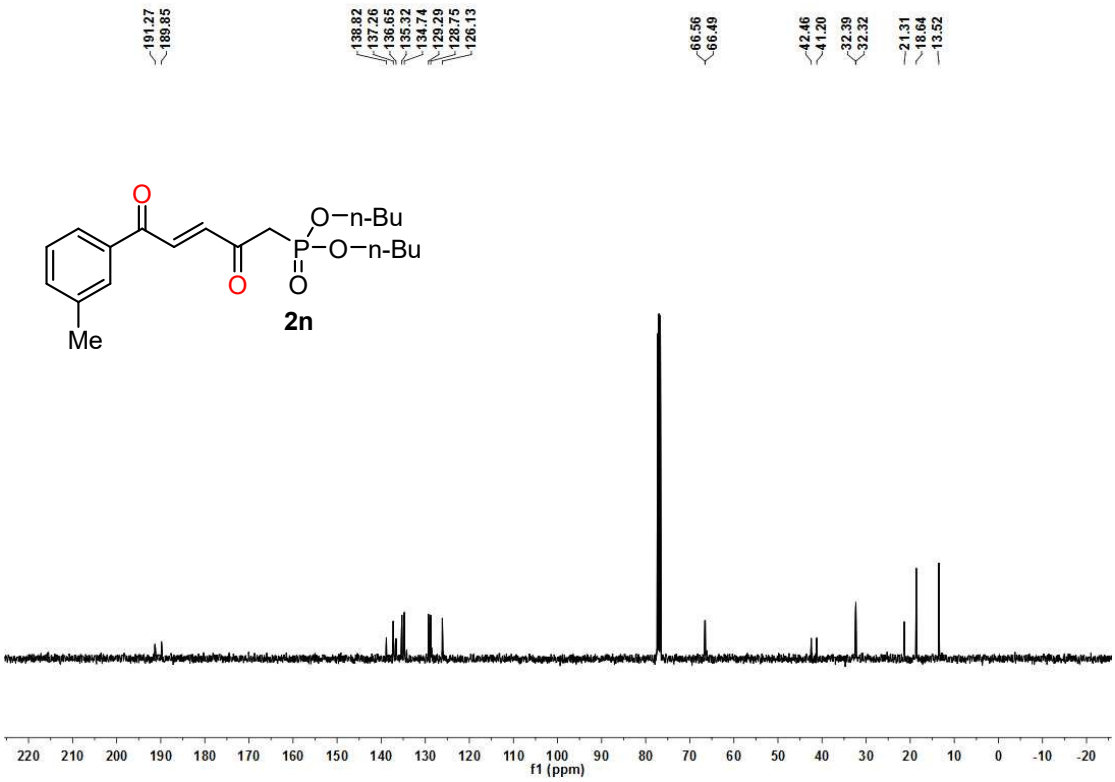
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2m**

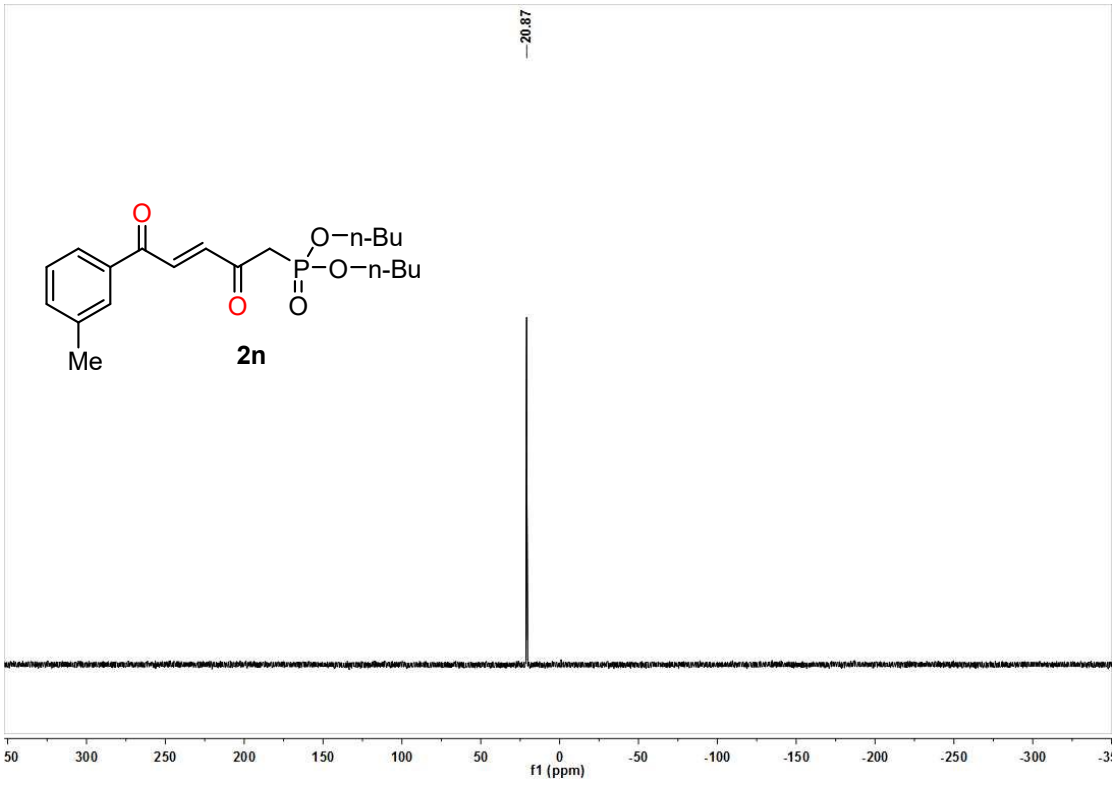


^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2n**

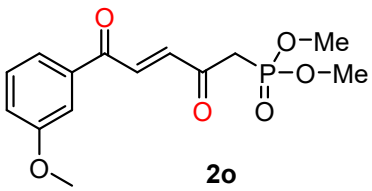




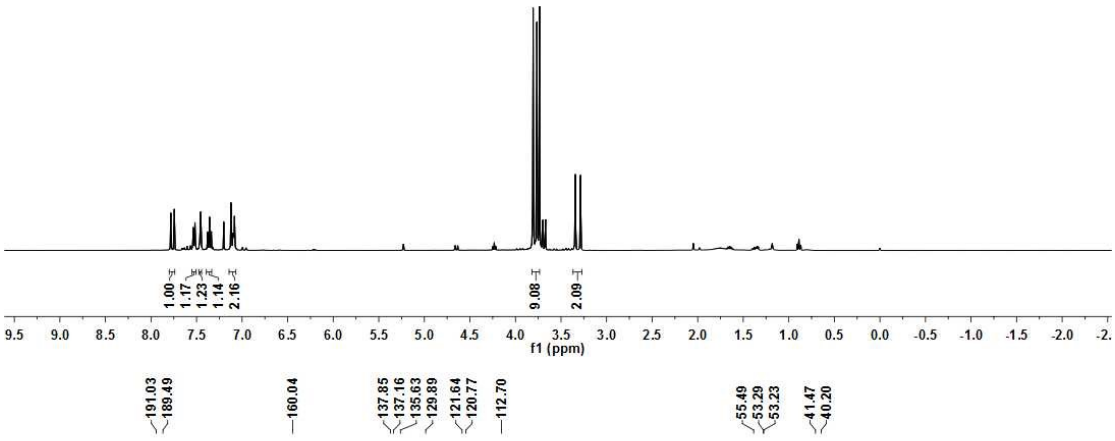

191.27
189.85
138.82
137.26
136.65
135.32
134.74
129.29
128.75
126.13
66.56
66.49
42.46
41.20
32.39
32.32
21.31
18.64
13.52
O
O
O−n-Bu
P−O−n-Bu
O
Me
2n
f1 (ppm)

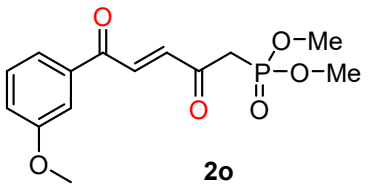

20.87
O
O
O−n-Bu
P−O−n-Bu
O
Me
2n
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2o**

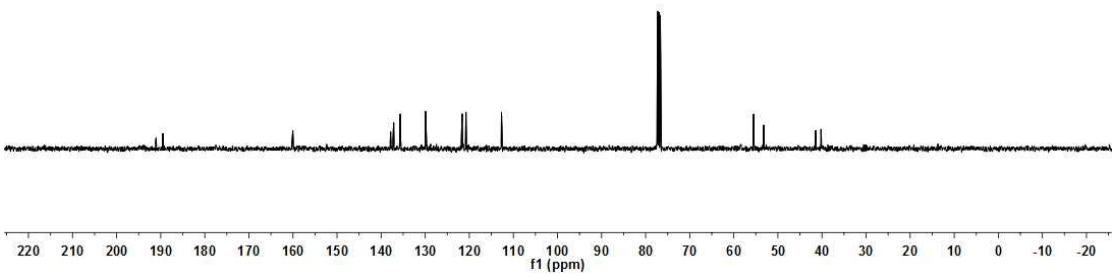


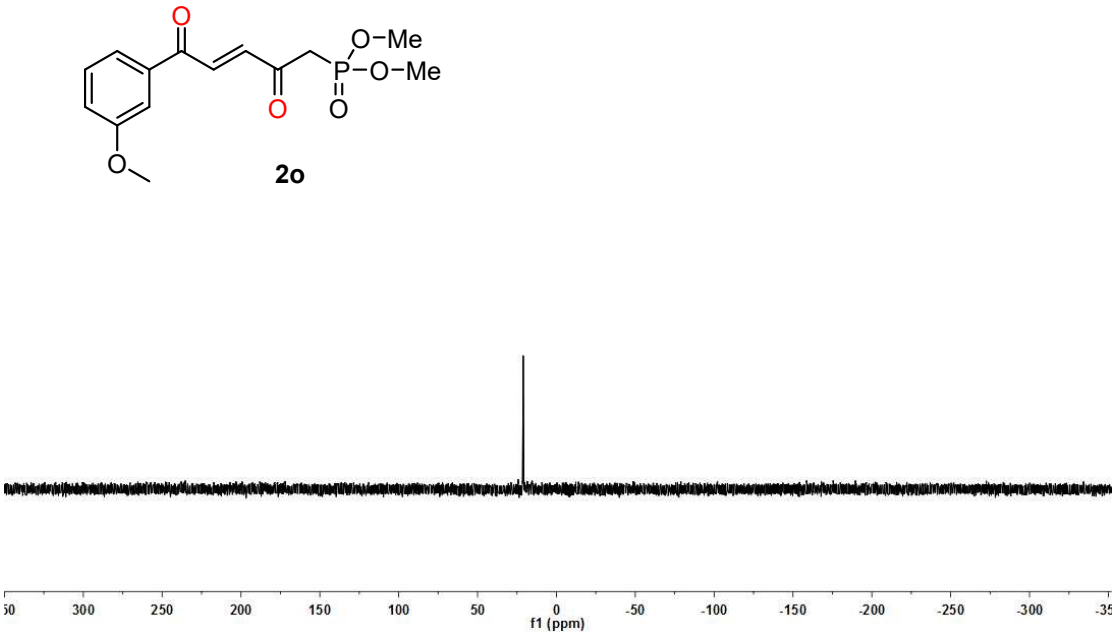
2o





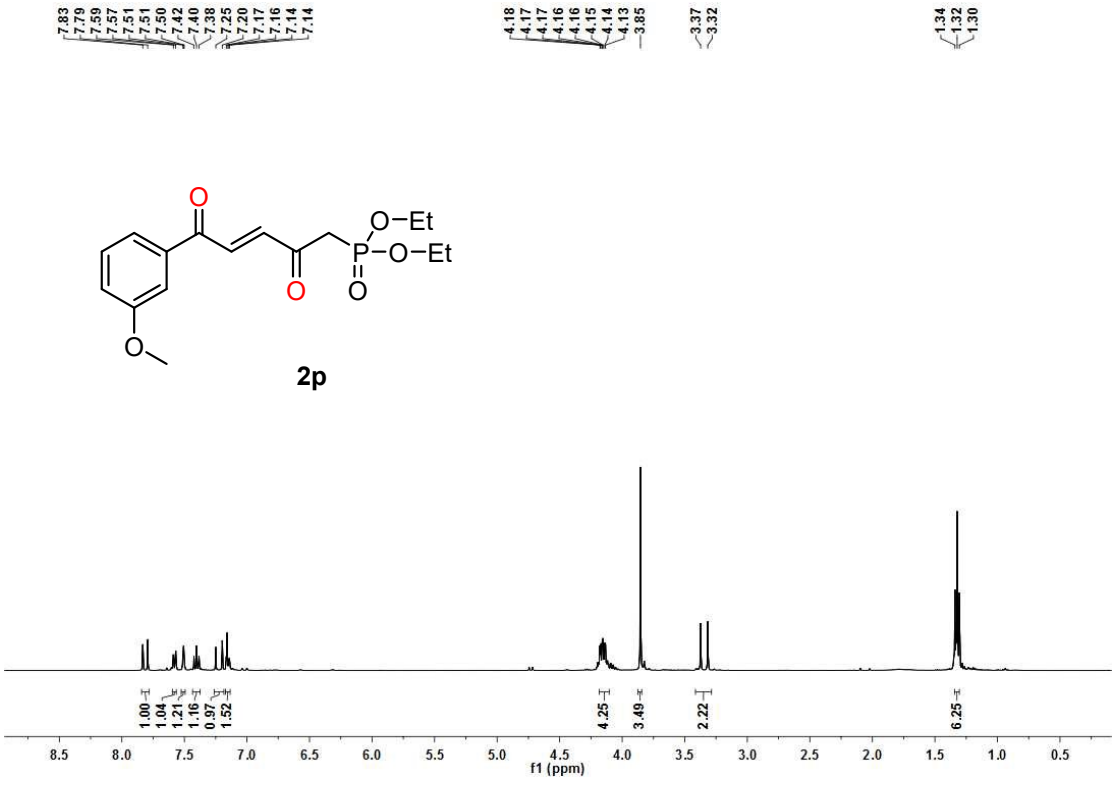
2o



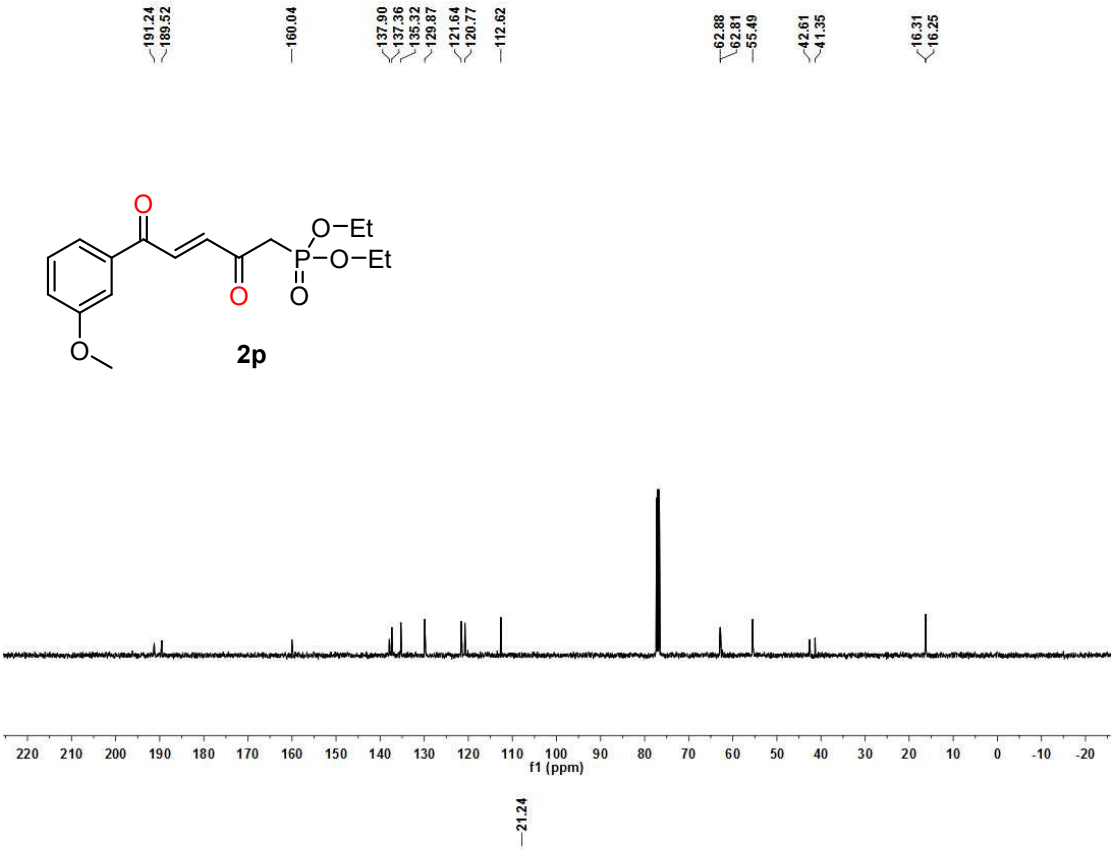


2o

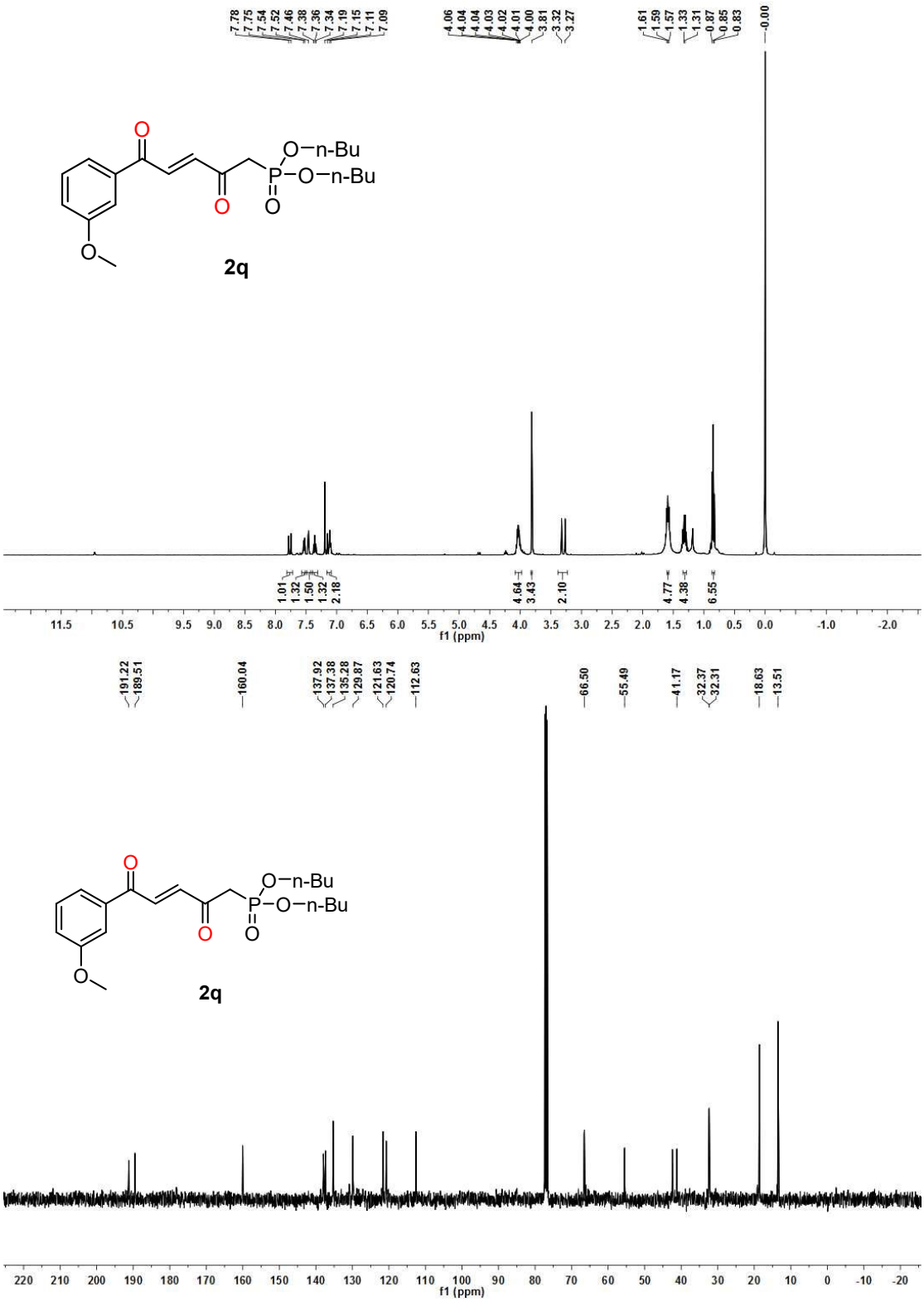
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2p**

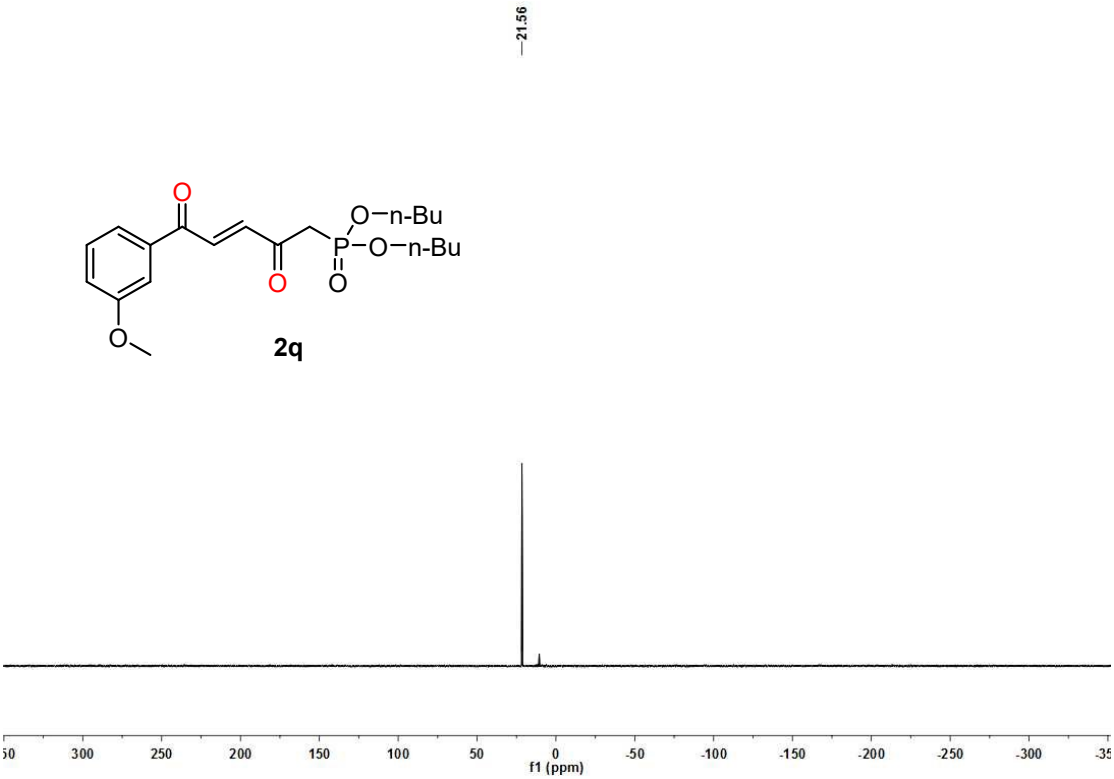


2p


191.24
189.52
160.04
137.90
137.36
135.32
129.87
121.64
120.77
112.62
62.88
62.81
55.49
42.61
41.35
16.31
16.25
O
O
O
O−Et
P−O−Et
O
O
2p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
21.24
O
O
O
O−Et
P−O−Et
O
O
2p
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -35
f1 (ppm)

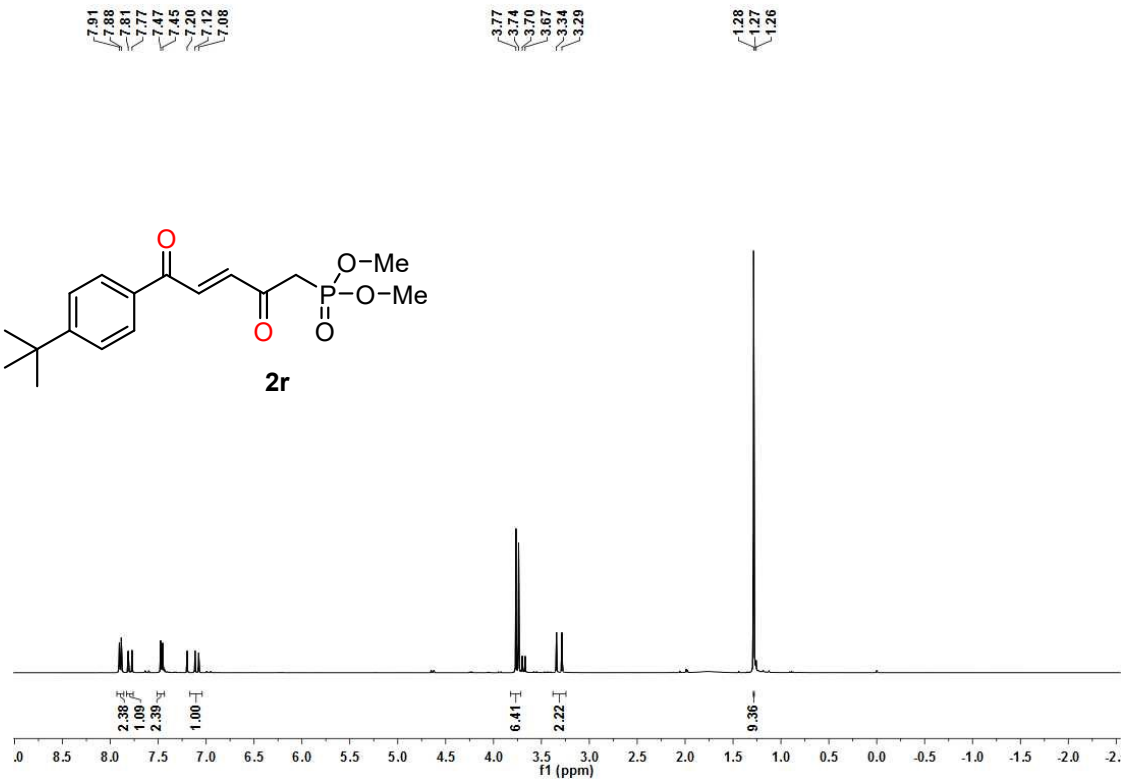
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2q**



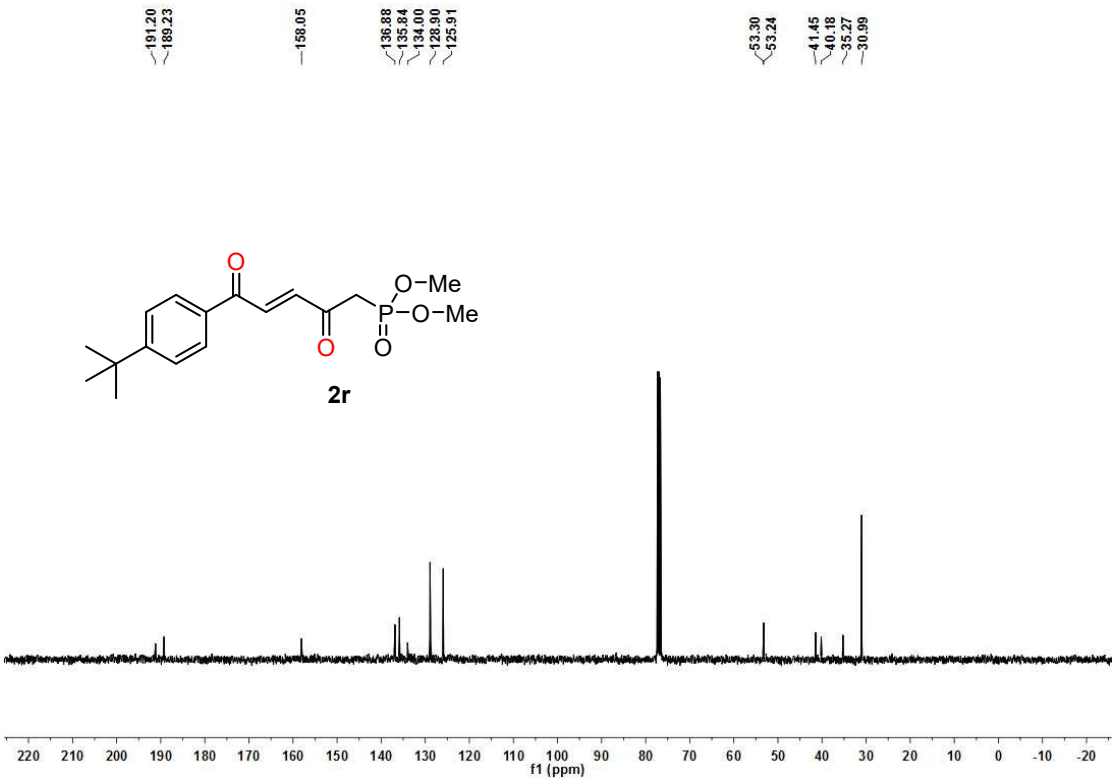


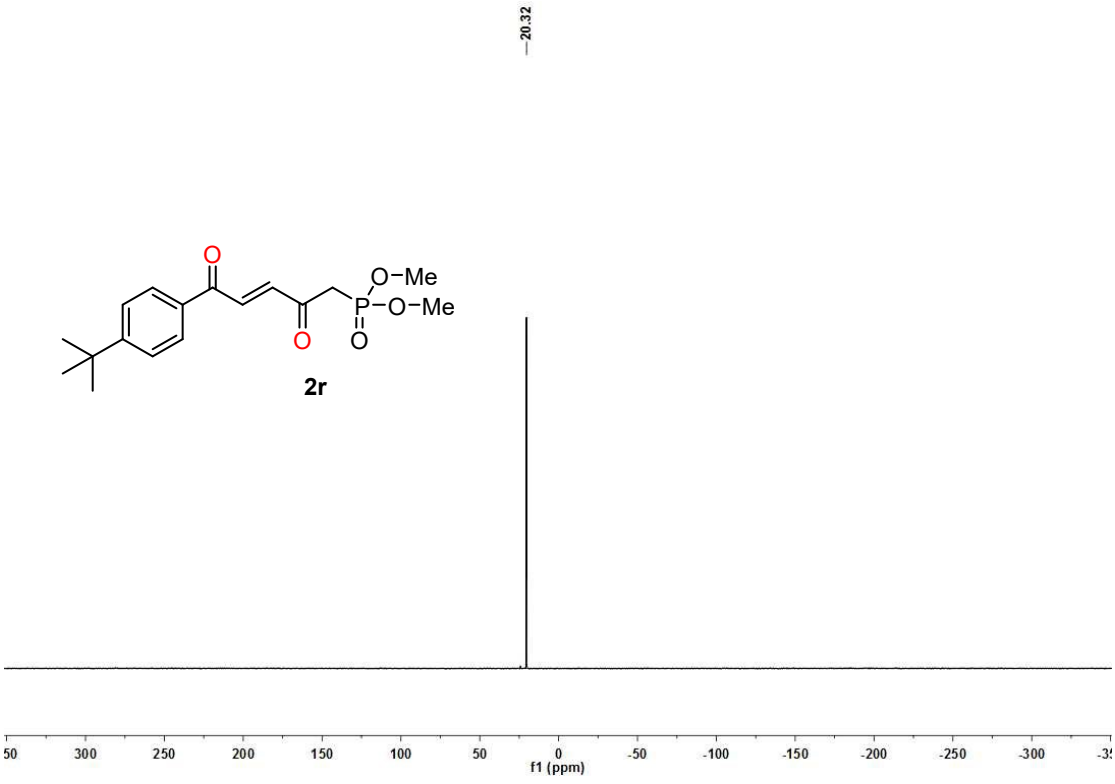
2q

^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2r**

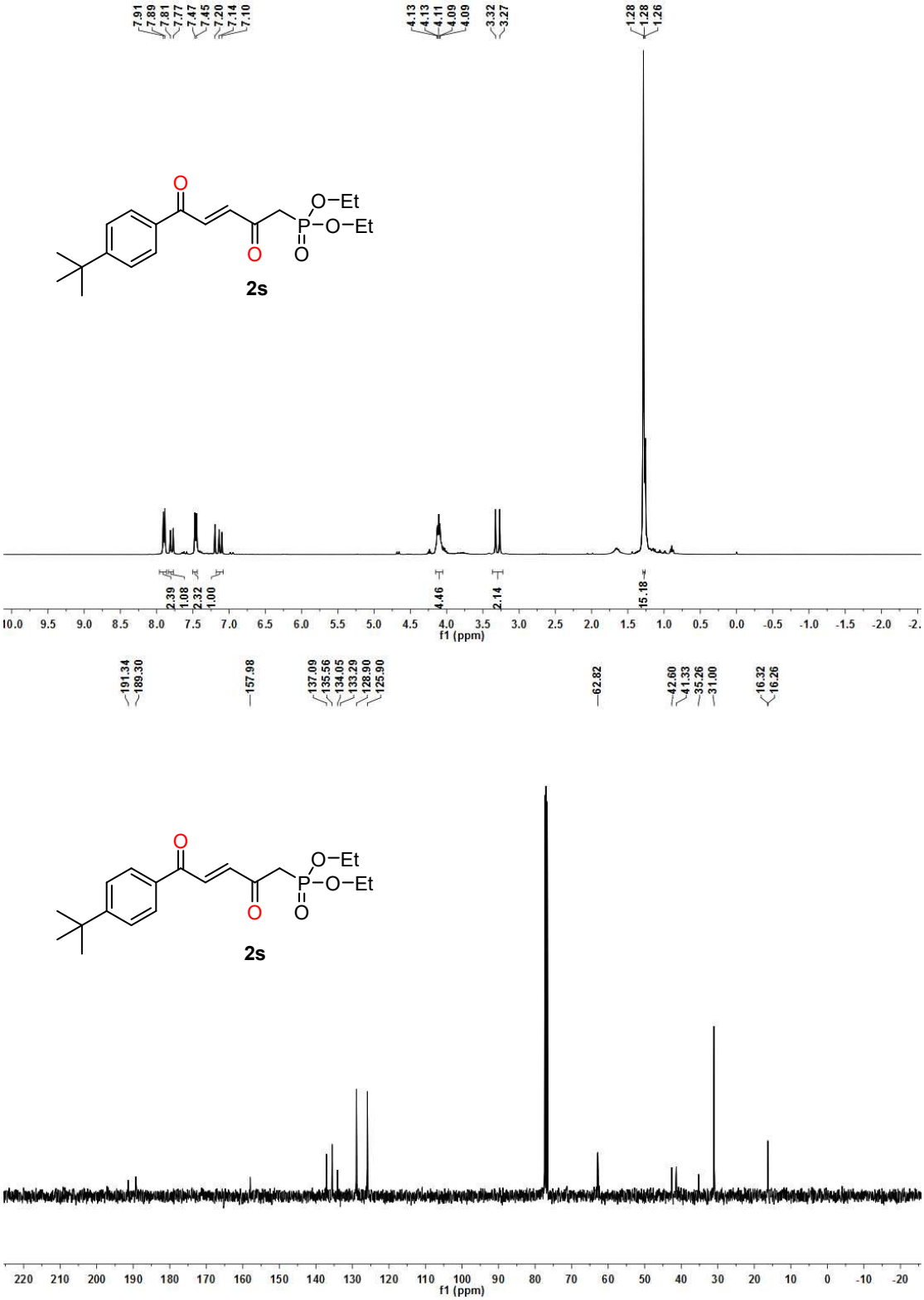


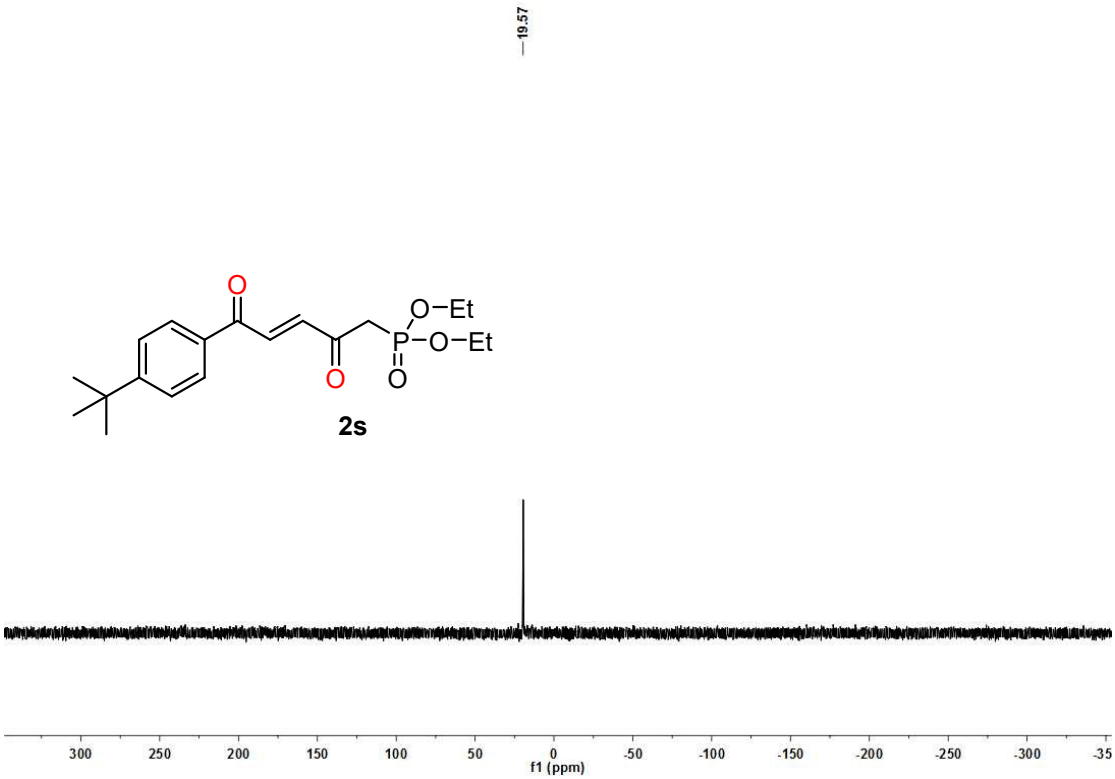
2r


191.20
189.23
158.05
136.88
135.84
134.00
128.90
125.91
53.30
53.24
41.45
40.18
35.27
30.99
O
O−Me
P−O−Me
O
O
2r
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

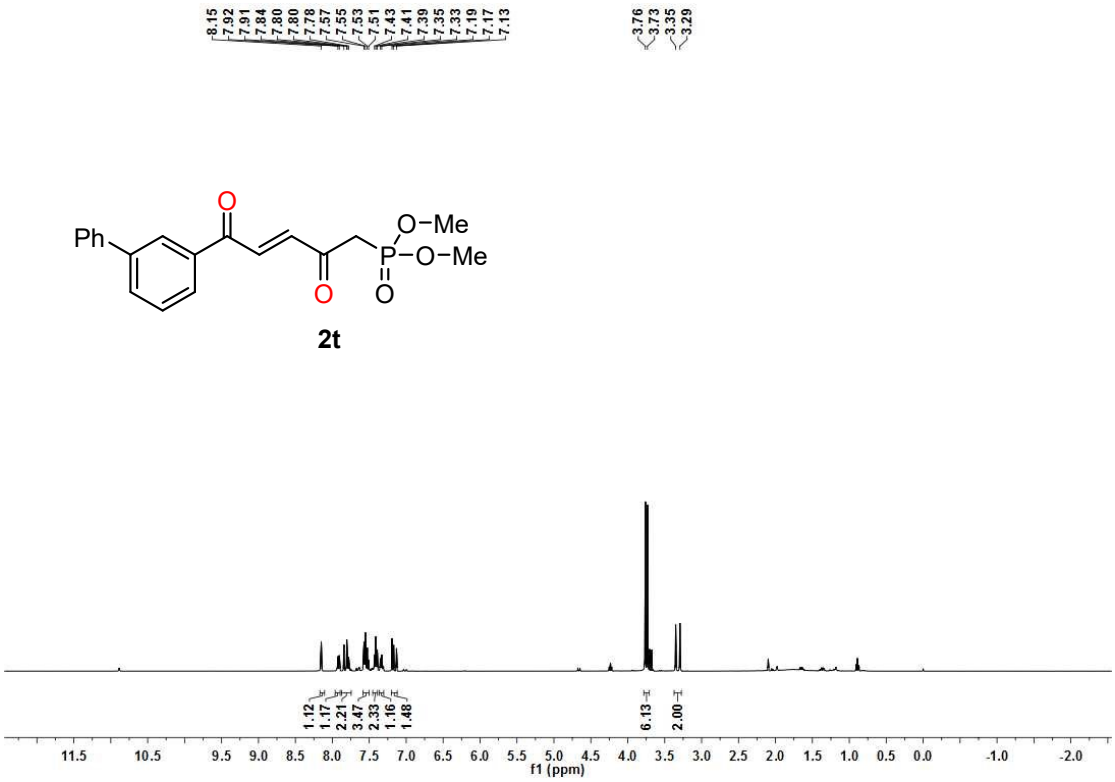

20.32
O
O−Me
P−O−Me
O
O
2r
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

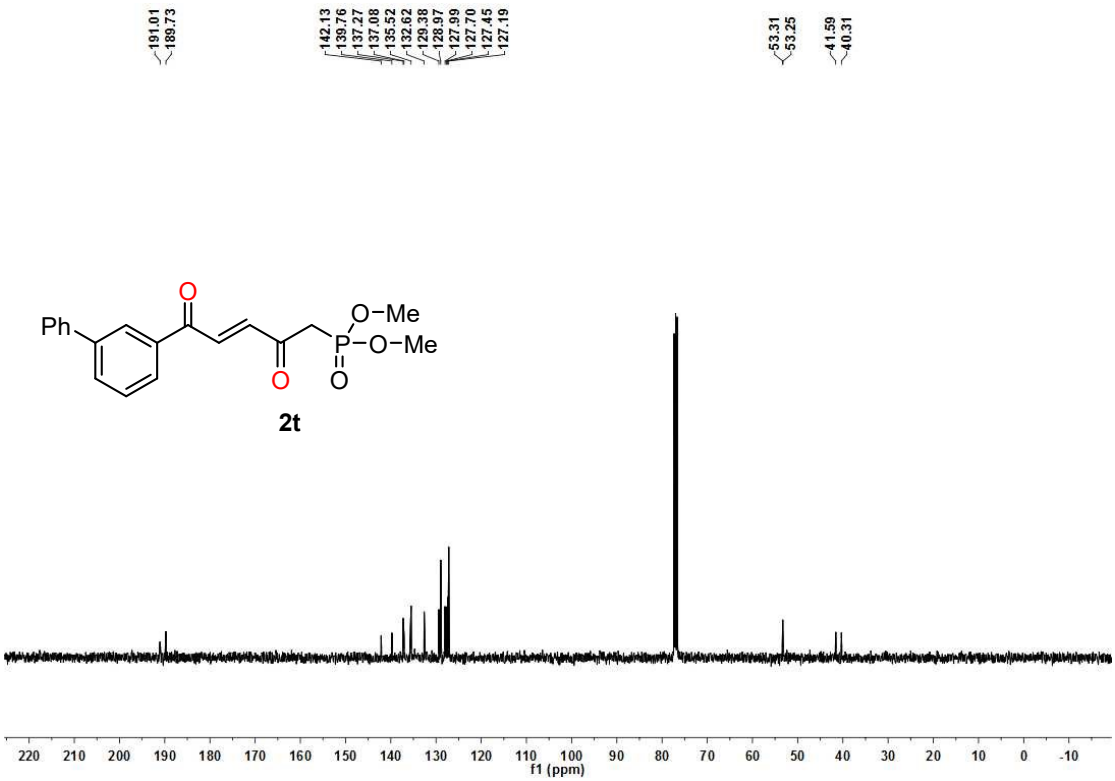
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2s**

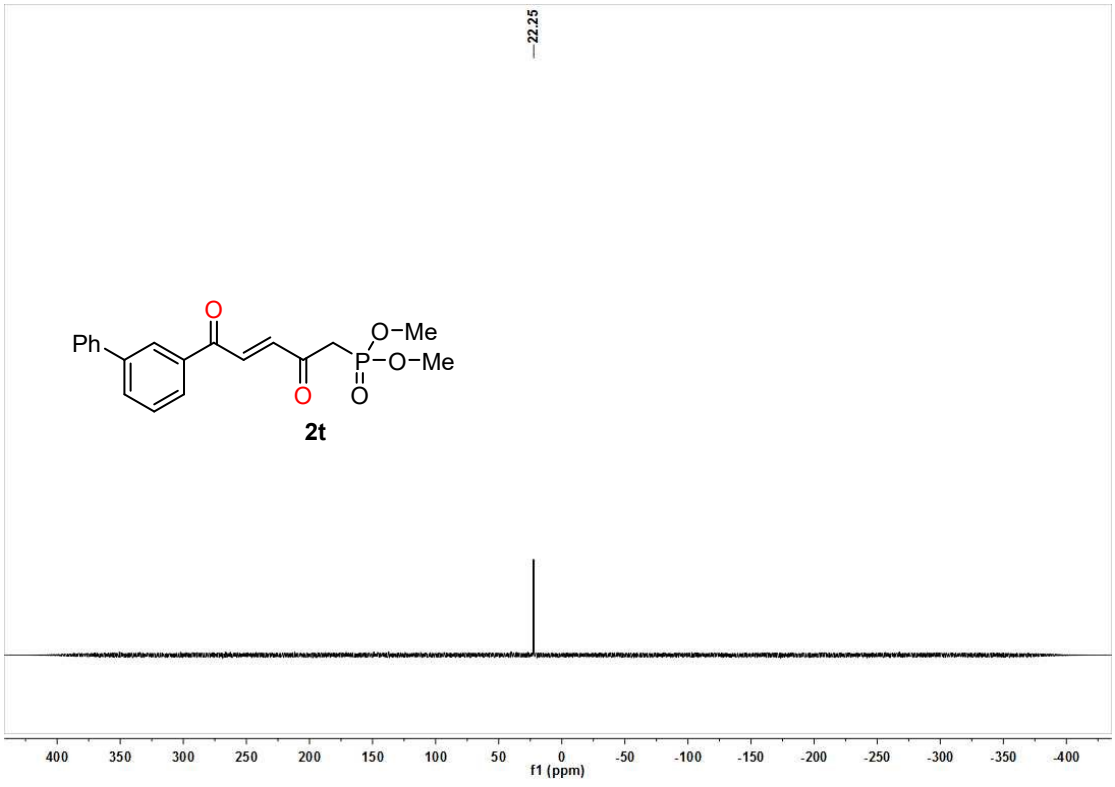




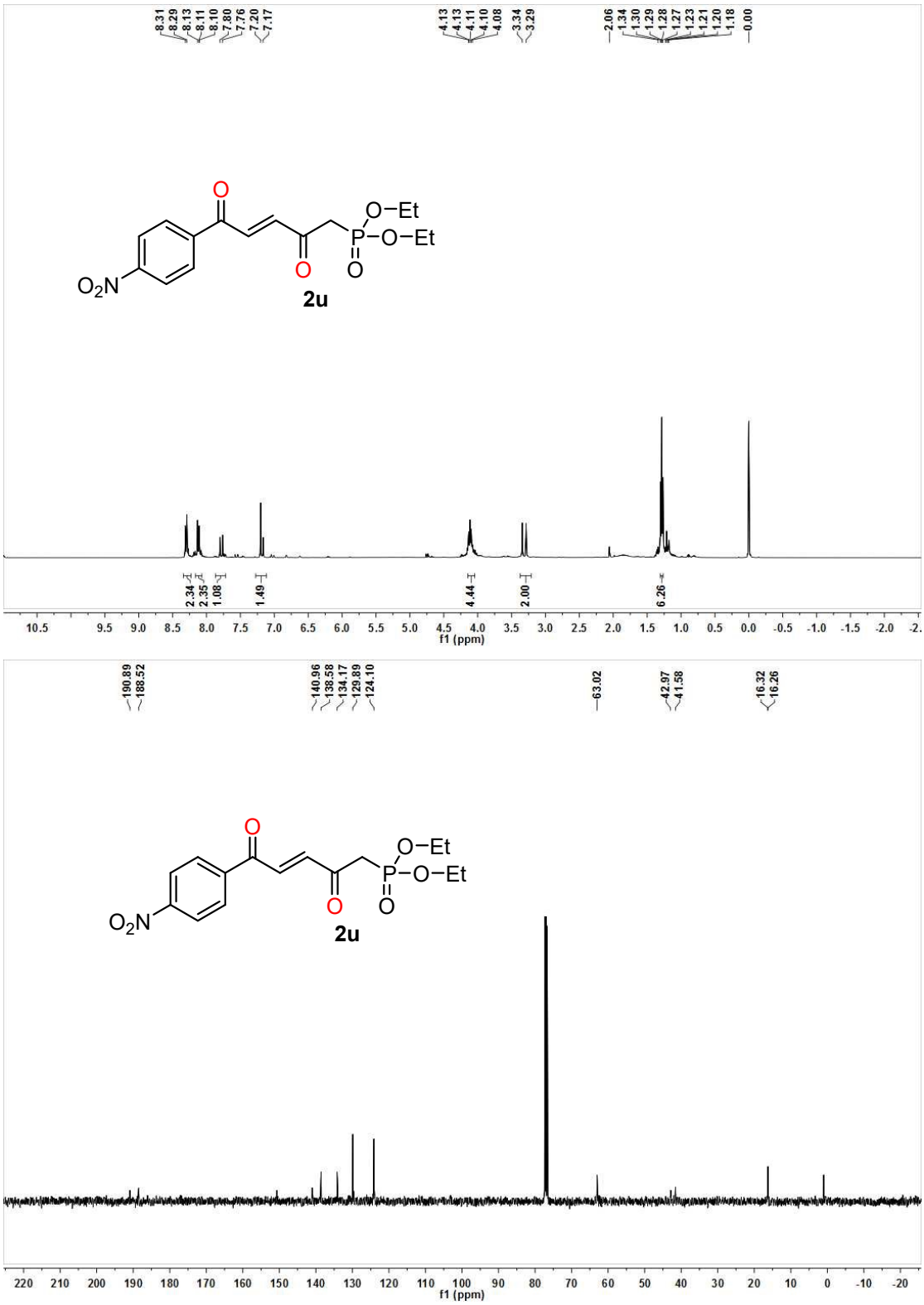
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2t**

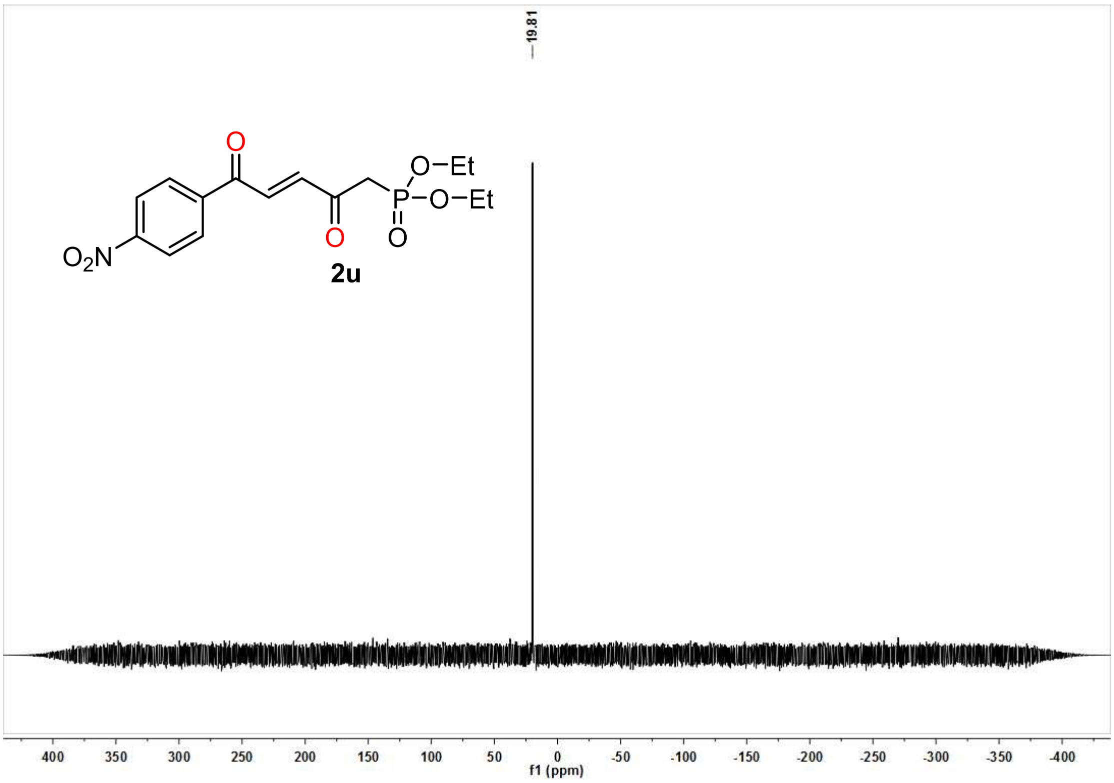



191.01
189.73
142.13
139.76
137.27
137.08
135.52
132.62
129.38
128.97
127.99
127.70
127.45
127.19
53.31
53.25
41.59
40.31
Ph
O
O
O−Me
P−O−Me
O
2t
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

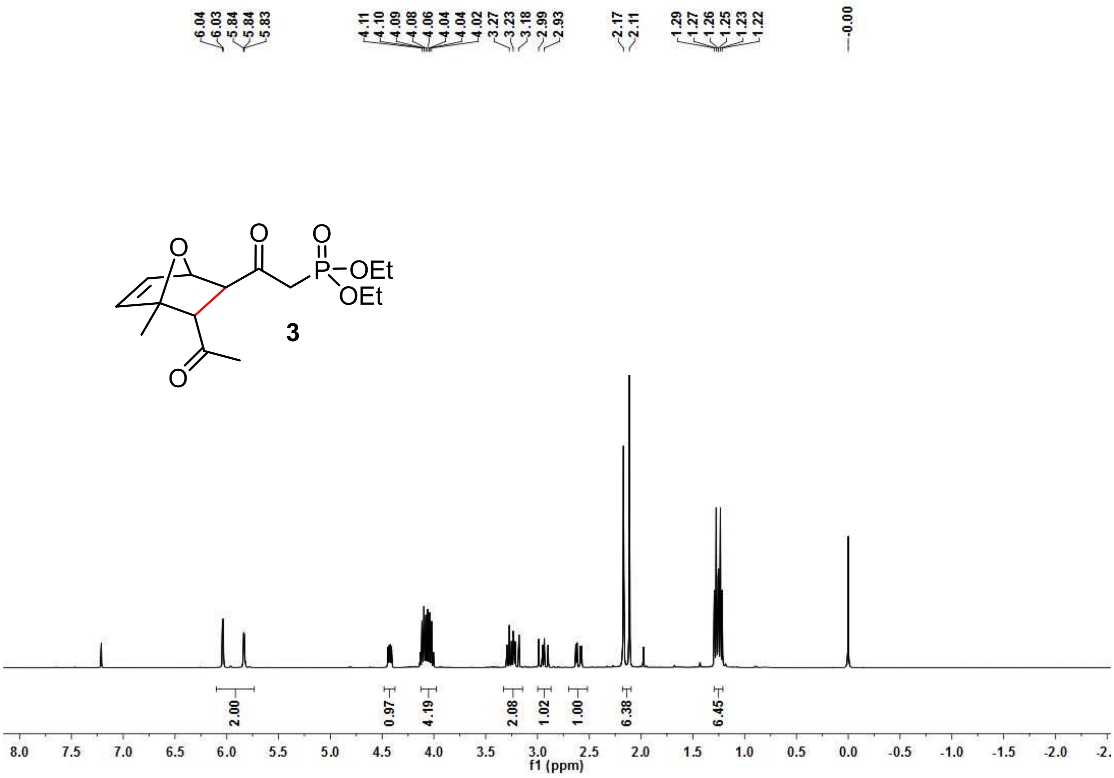

22.25
Ph
O
O
O−Me
P−O−Me
O
2t
400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400
f1 (ppm)

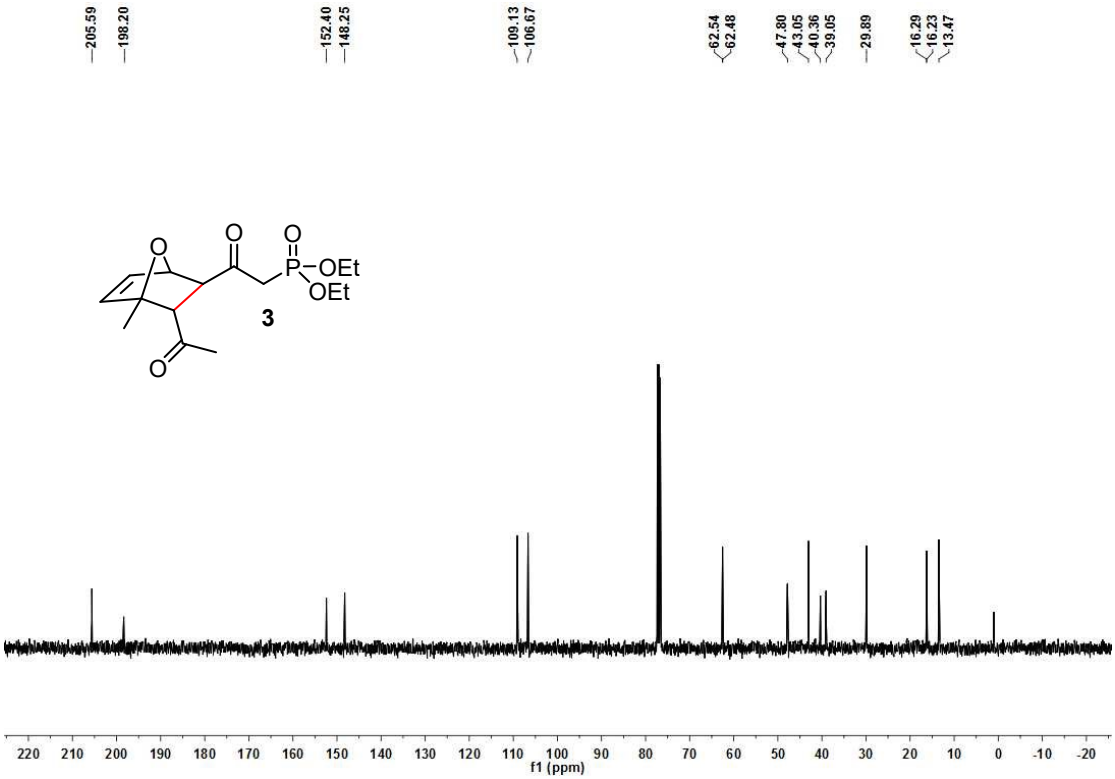
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 2u**

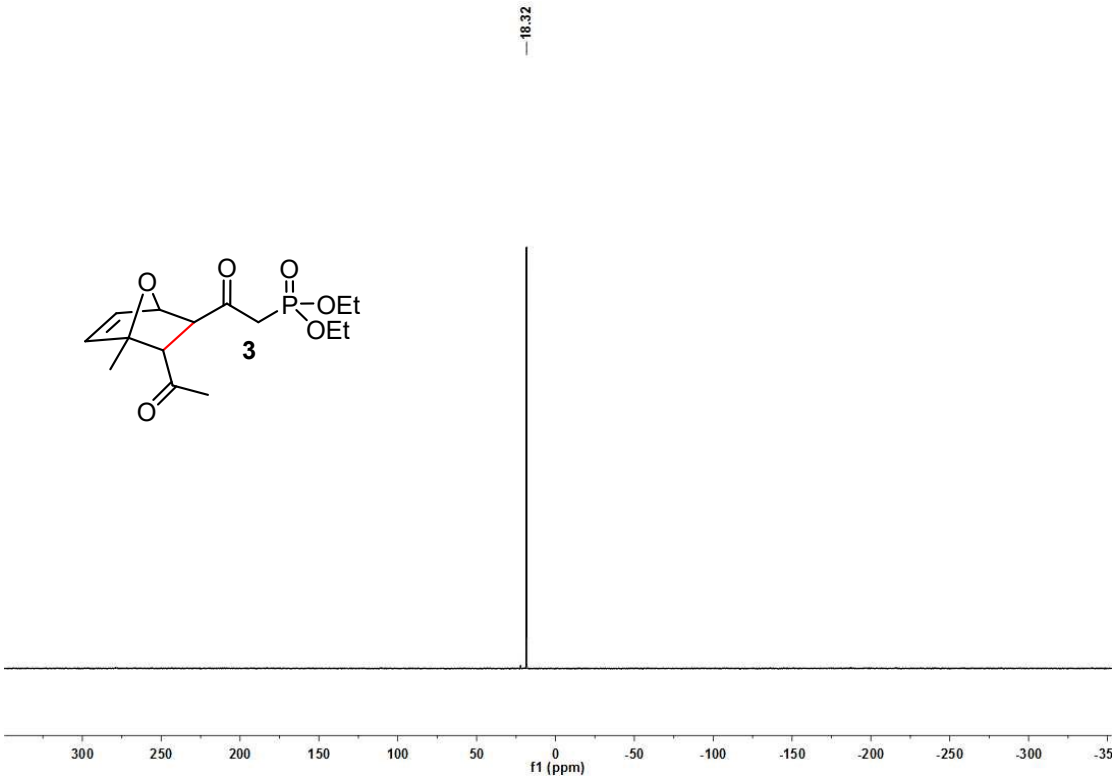




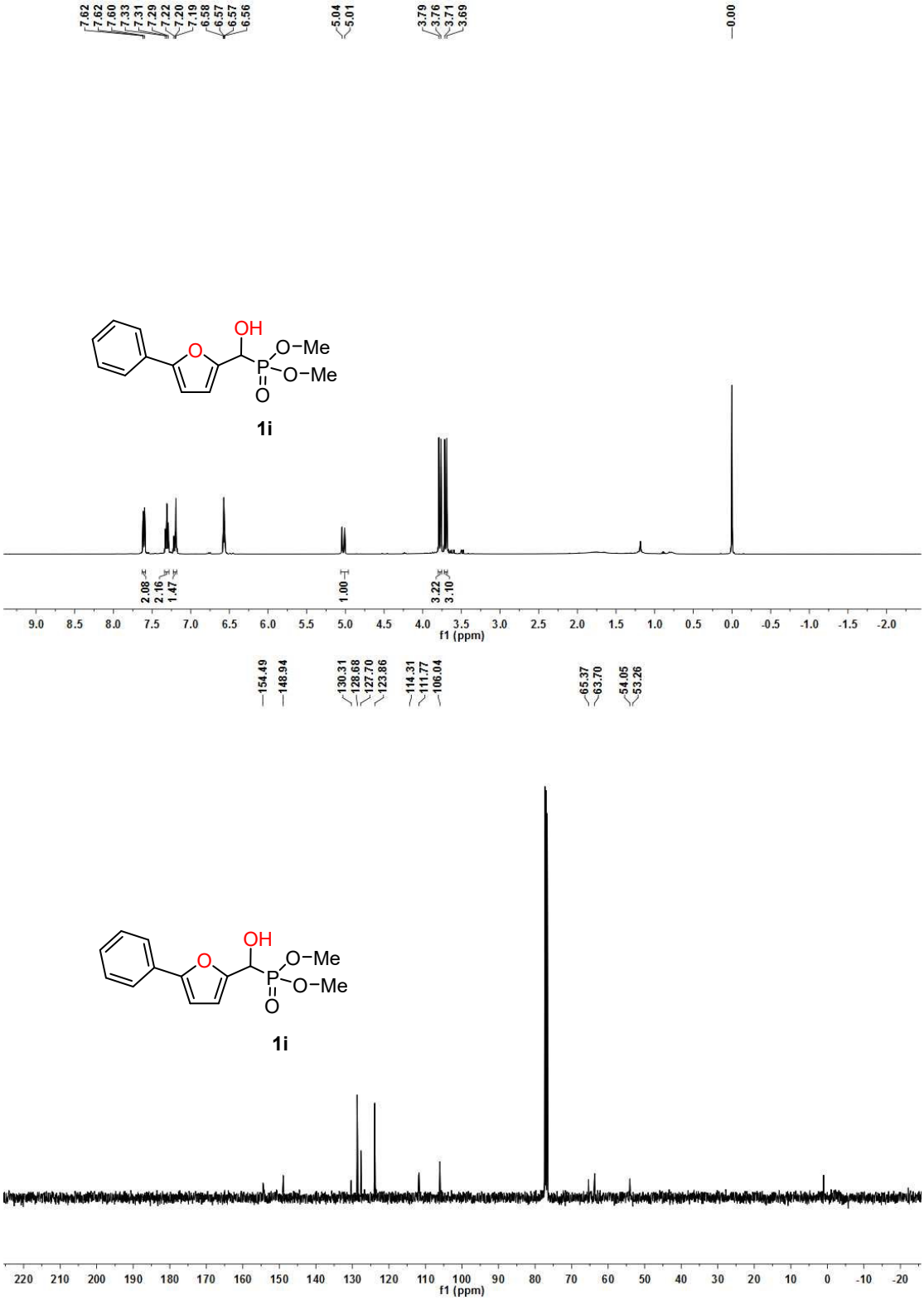
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 3**

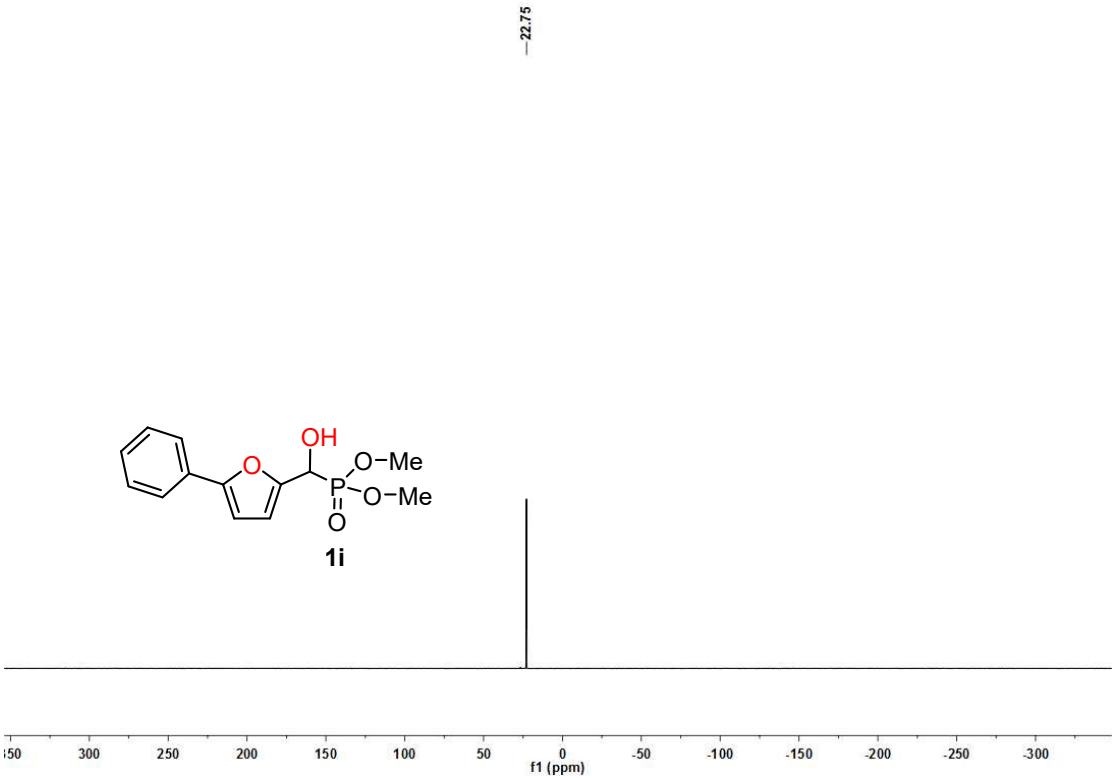



205.59
198.20
152.40
148.25
109.13
106.67
62.54
62.48
47.80
43.05
40.36
39.05
29.89
16.29
16.23
13.47
O
O
O
P
OEt
OEt
3
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

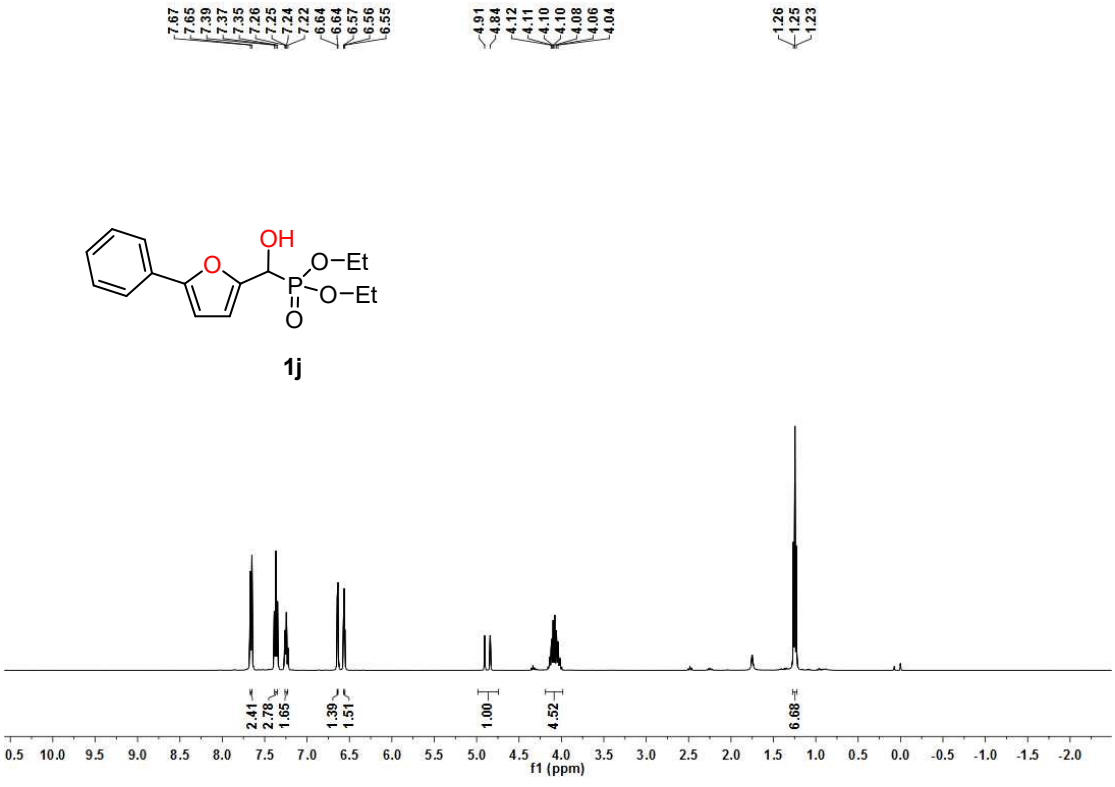

18.32
O
O
O
P
OEt
OEt
3
O
300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -35
f1 (ppm)

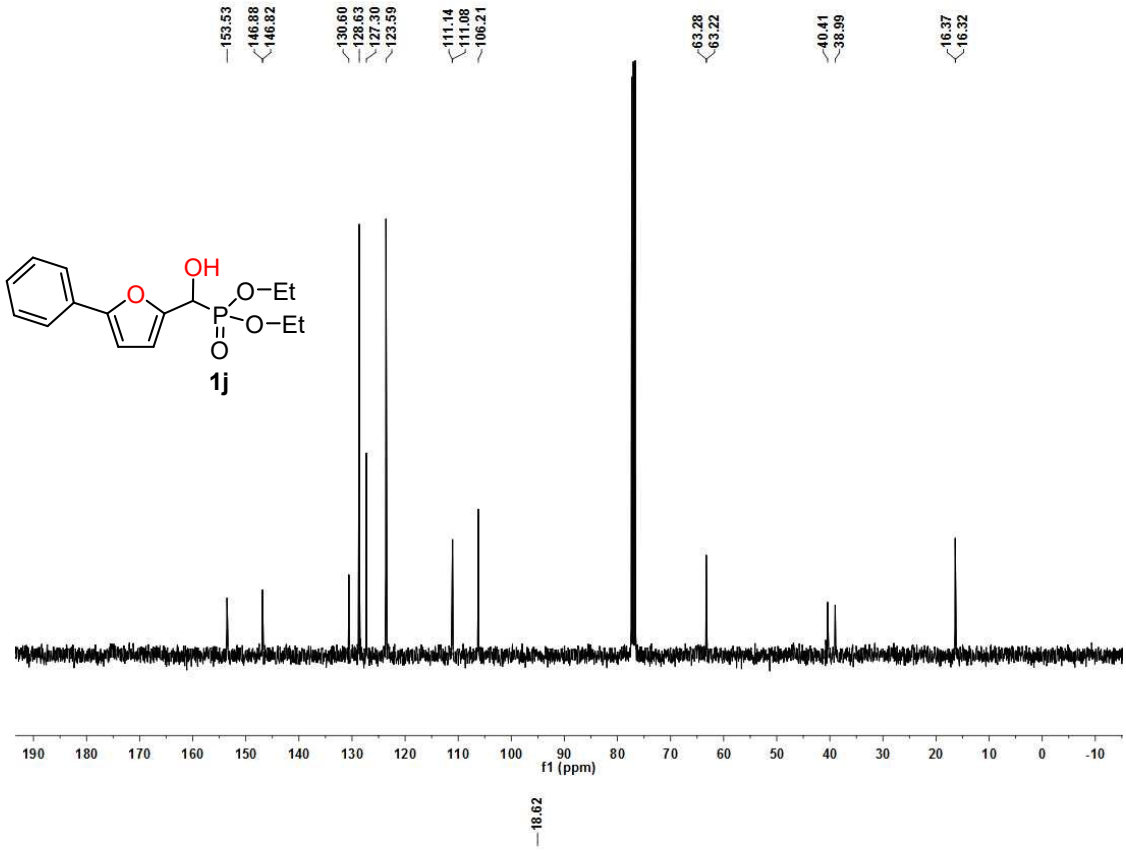
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1i**

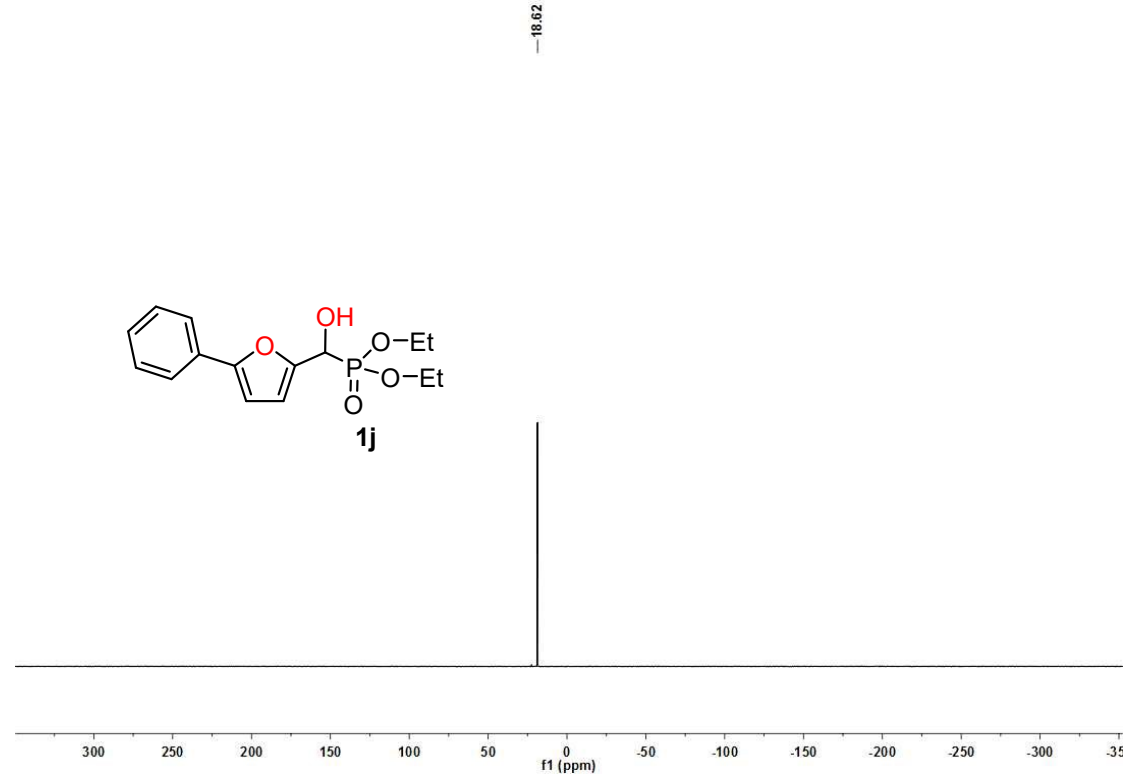




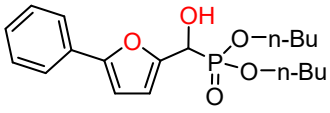
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1j**



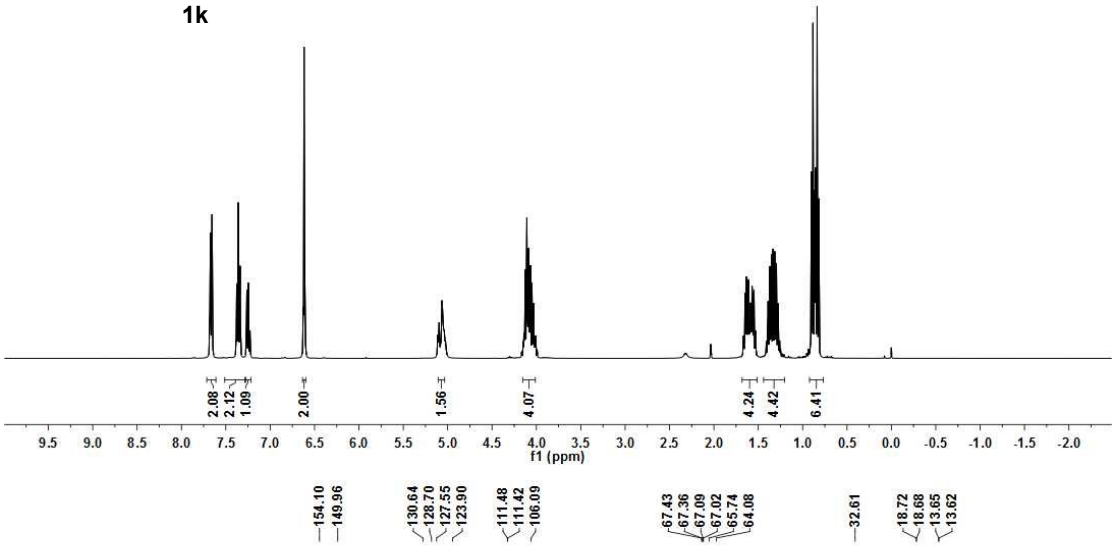

153.53
146.88
146.82
130.60
128.63
127.30
123.59
111.14
111.08
106.21
63.28
63.22
40.41
38.99
16.37
16.32
OH
O
O−Et
P
O−Et
O
1j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

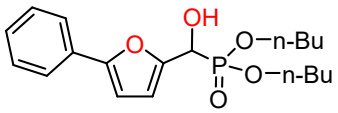

18.62
OH
O
O−Et
P
O−Et
O
1j
300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -35
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1k**

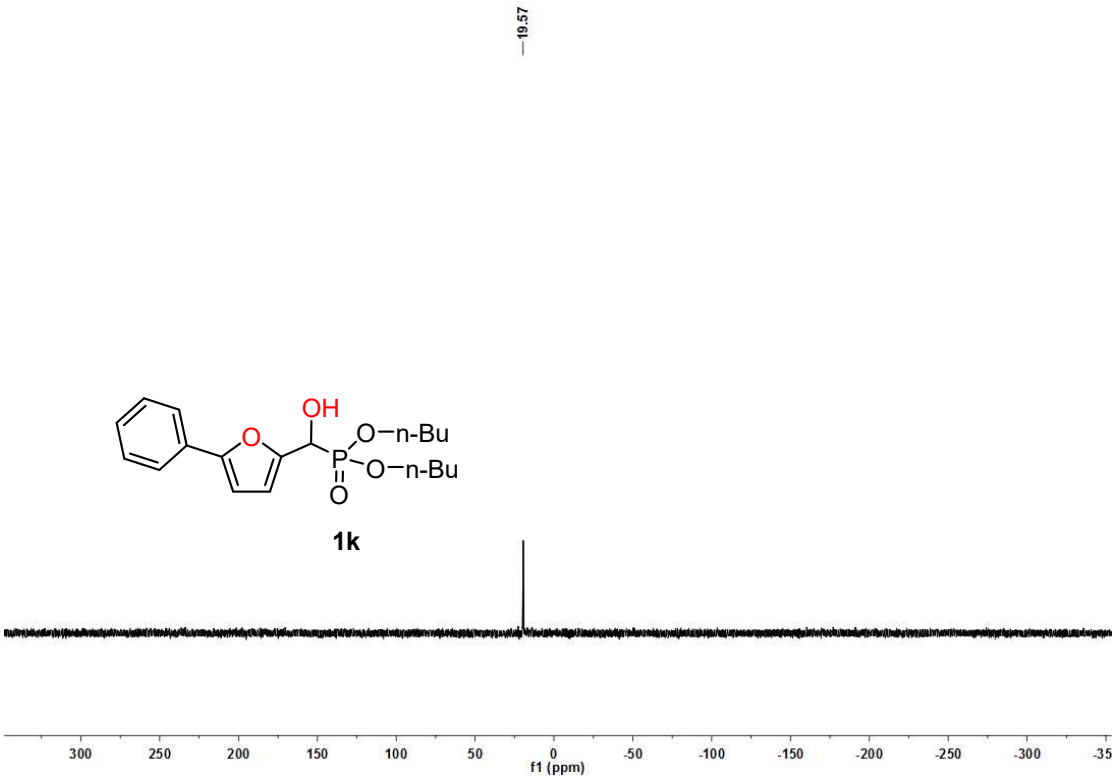


1k

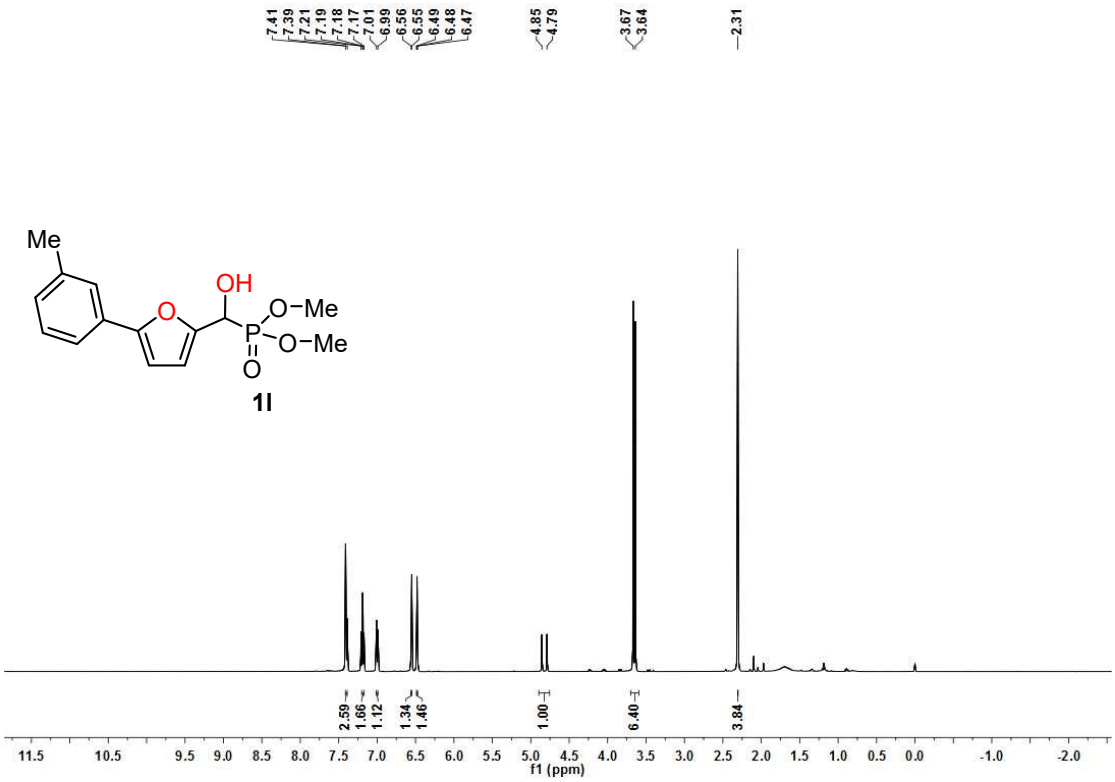


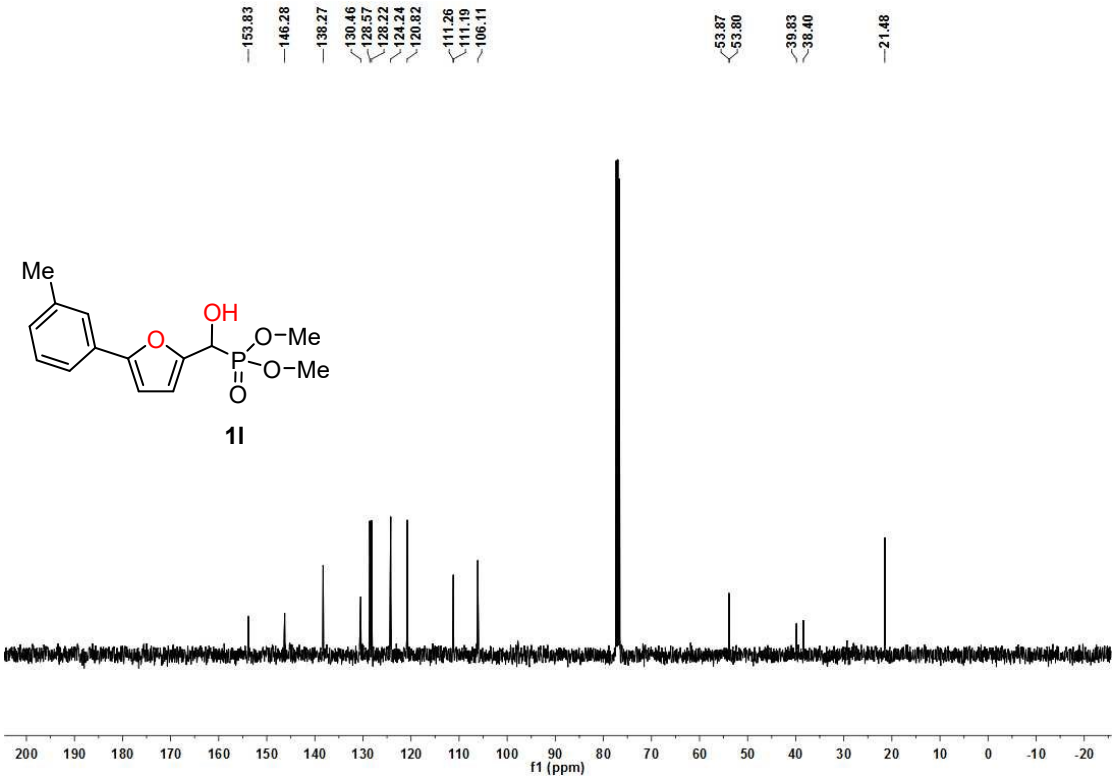


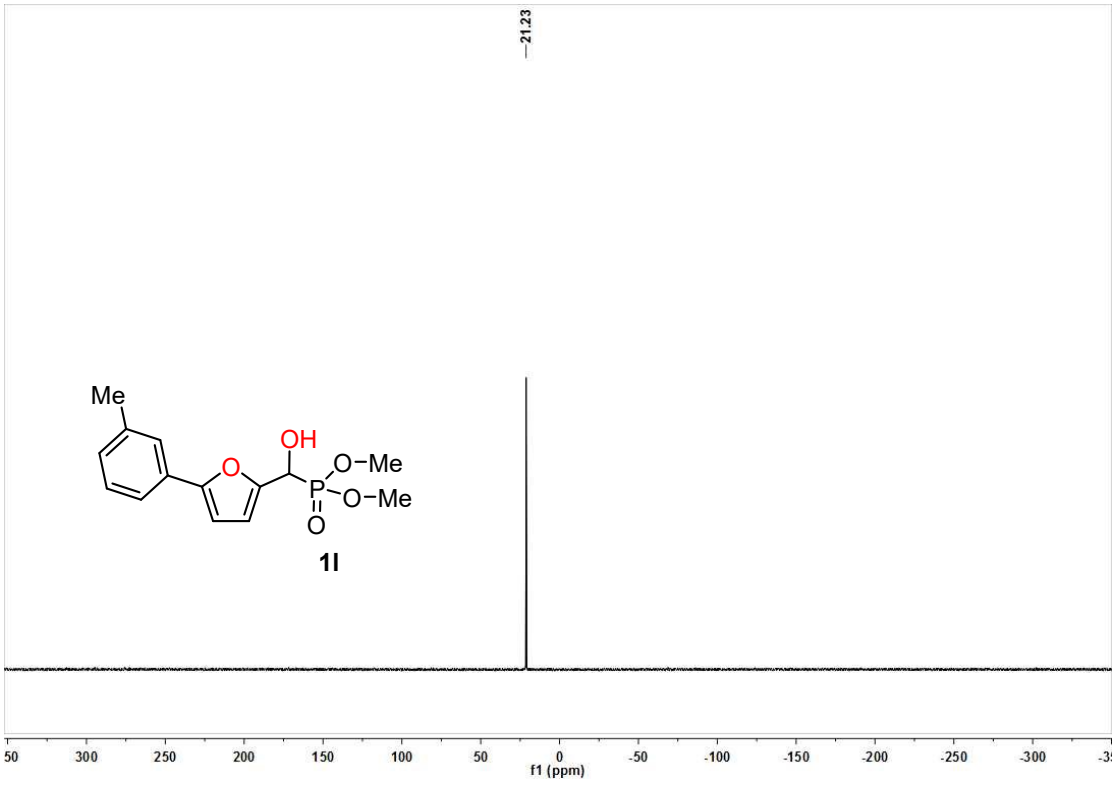
1k



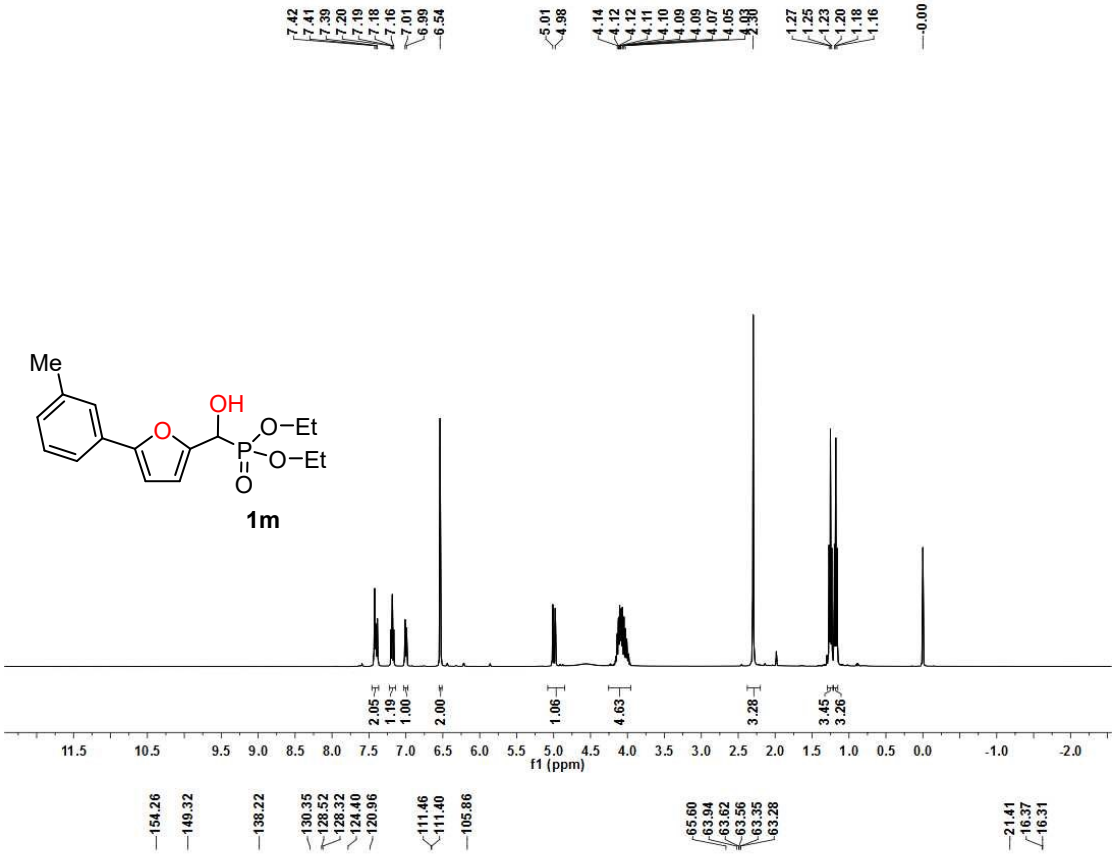
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1l**

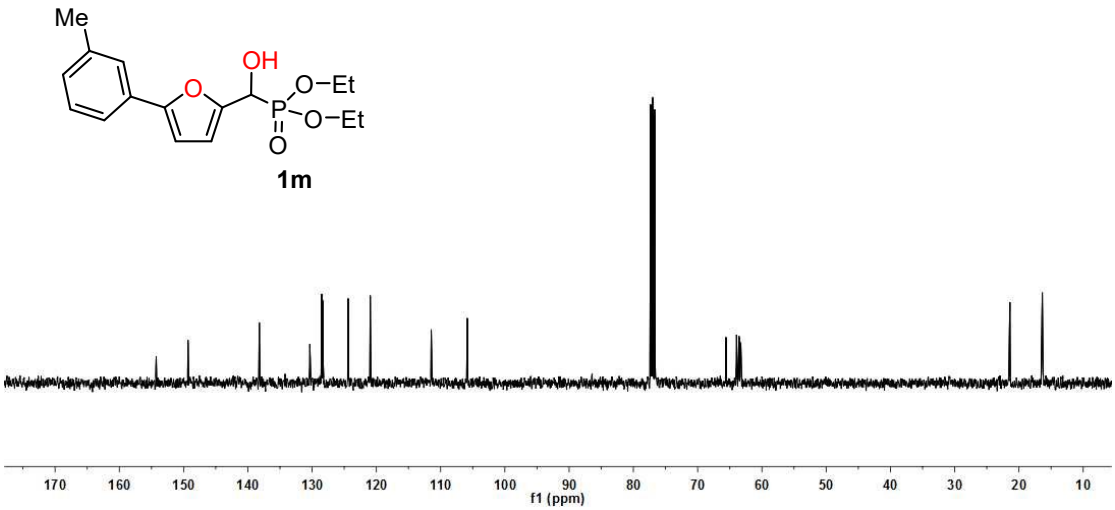


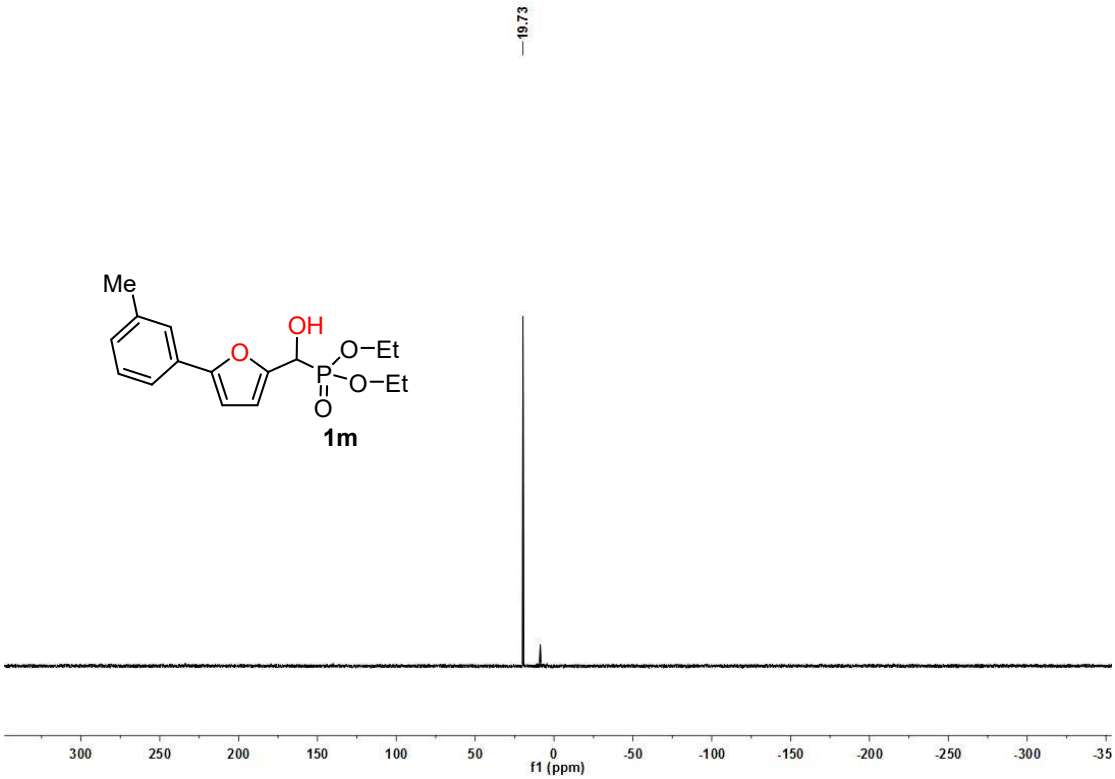

153.83
146.28
138.27
130.46
128.57
128.22
124.24
120.82
111.26
111.19
106.11
53.87
53.80
39.83
38.40
21.48
Me
OH
O
O−Me
P
O−Me
O
1l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


21.23
Me
OH
O
O−Me
P
O−Me
O
1l
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

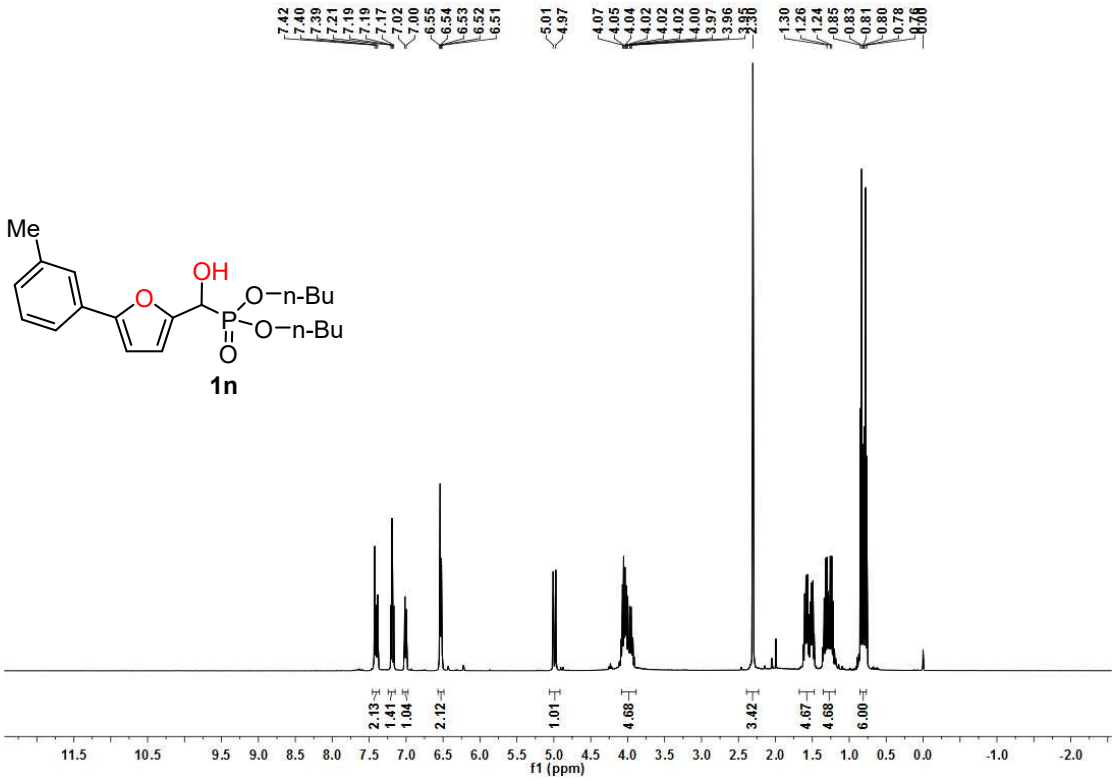
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1m**

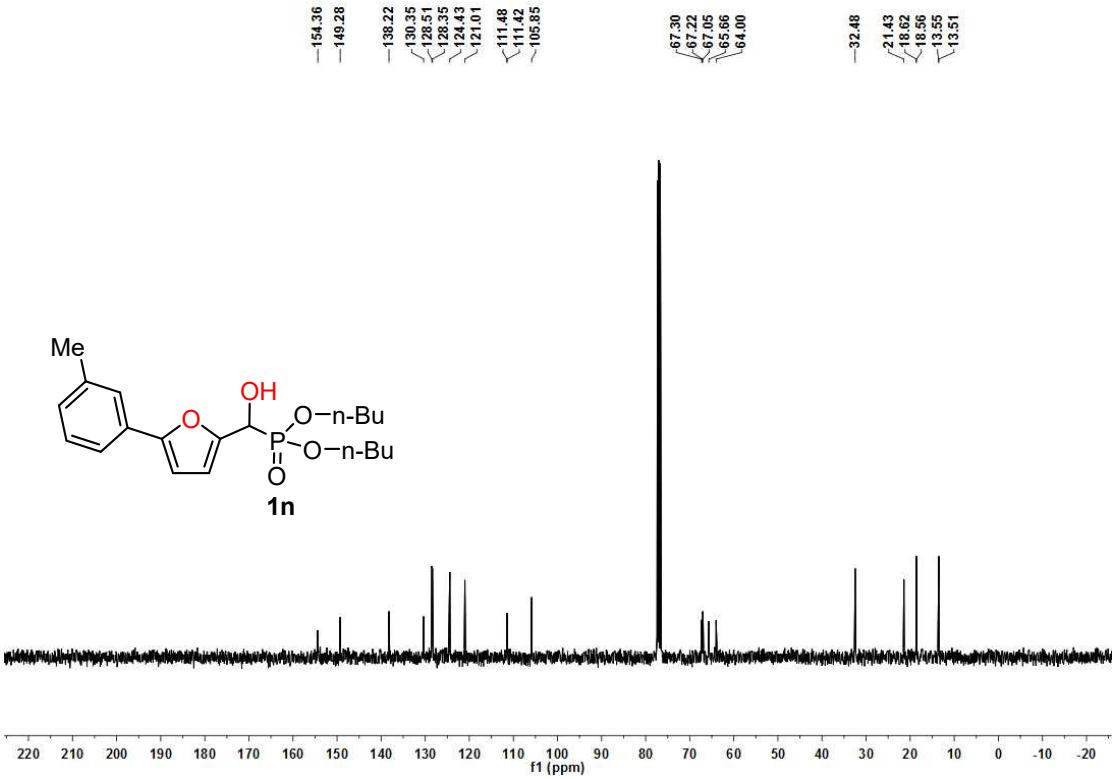


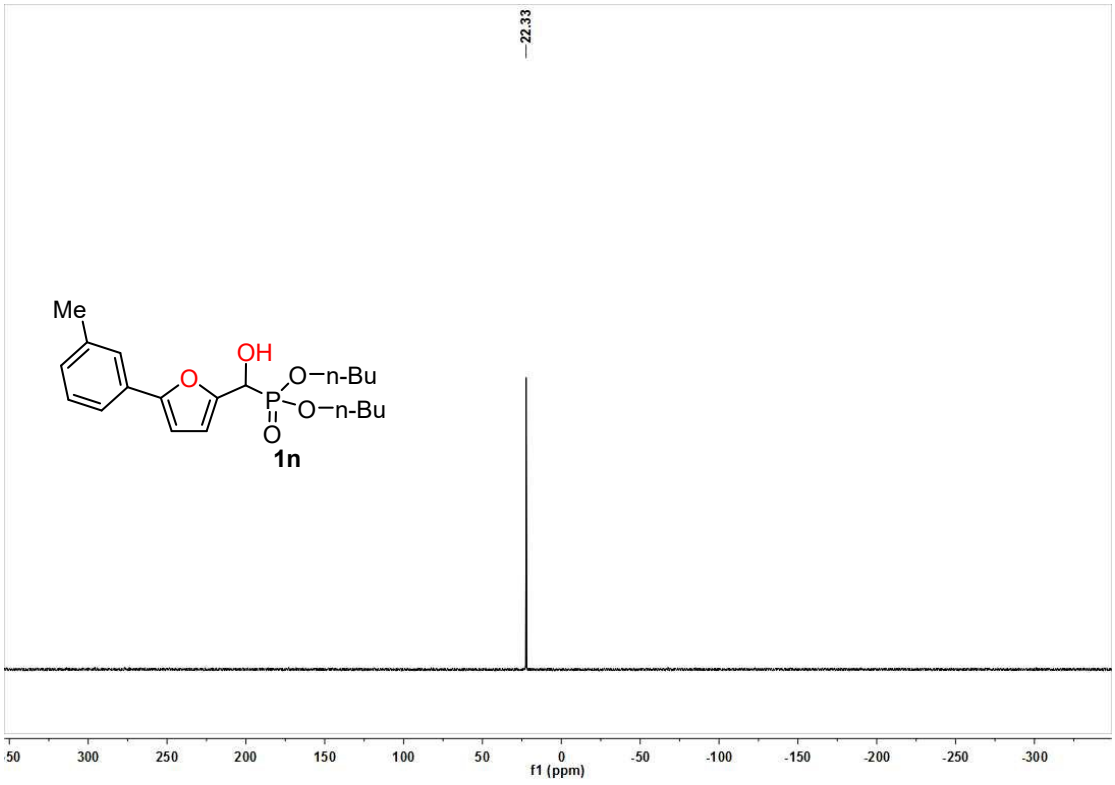




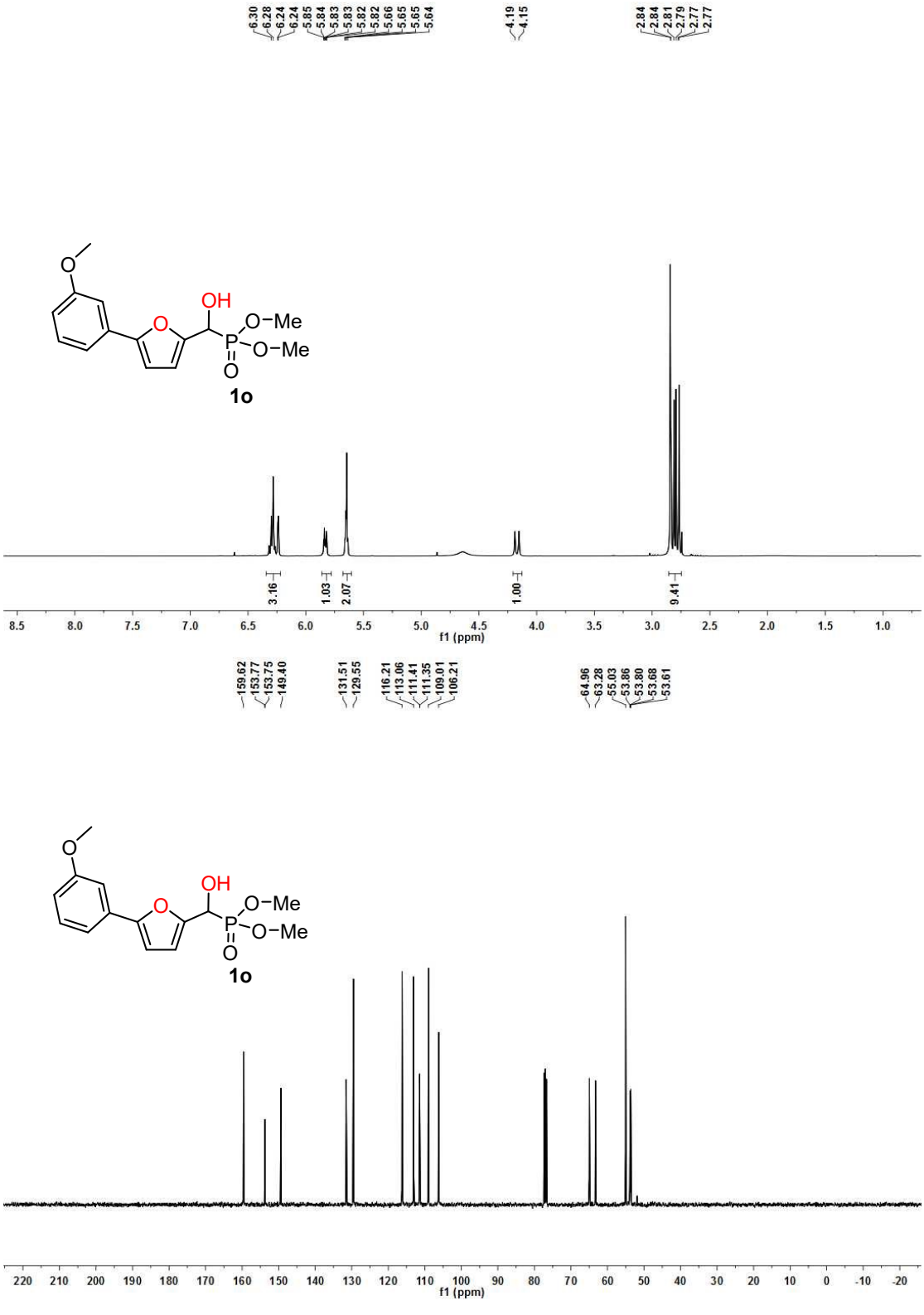
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1n**

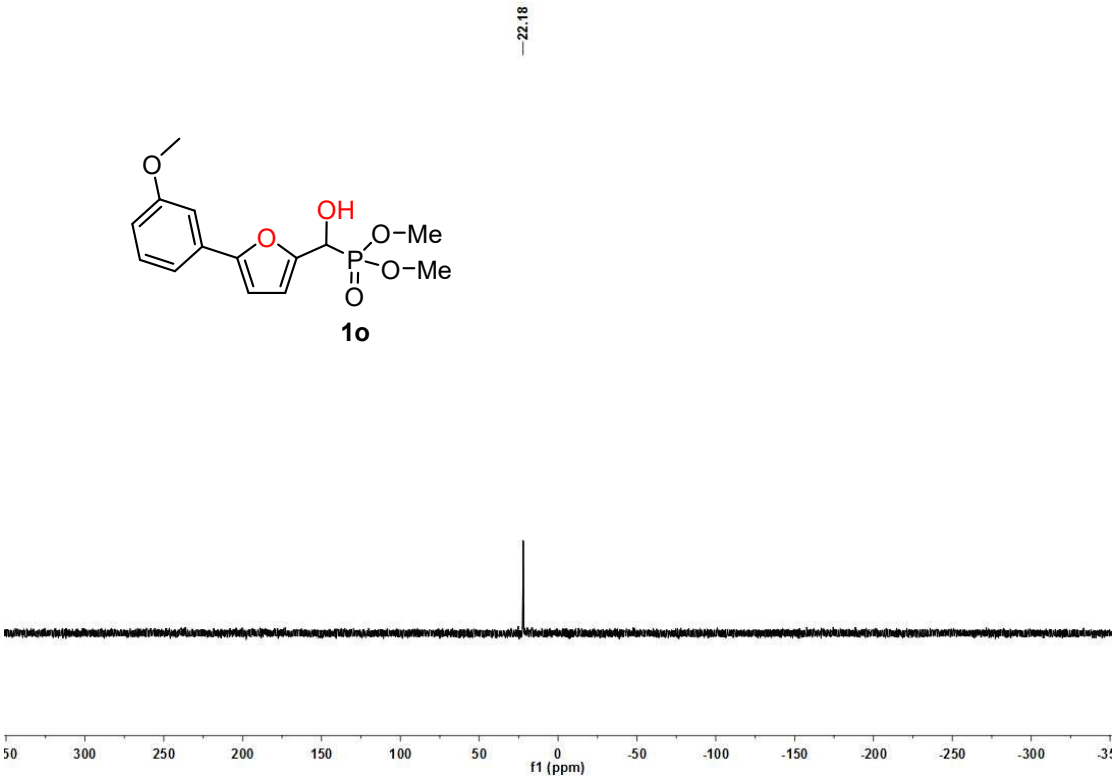



154.36
149.28
138.22
130.35
128.51
128.35
124.43
121.01
111.48
111.42
105.85
67.30
67.22
67.05
65.66
64.00
32.48
21.43
18.62
18.56
13.55
13.51
Me
OH
O
O–n-Bu
O–n-Bu
P
O
1n
f1 (ppm)

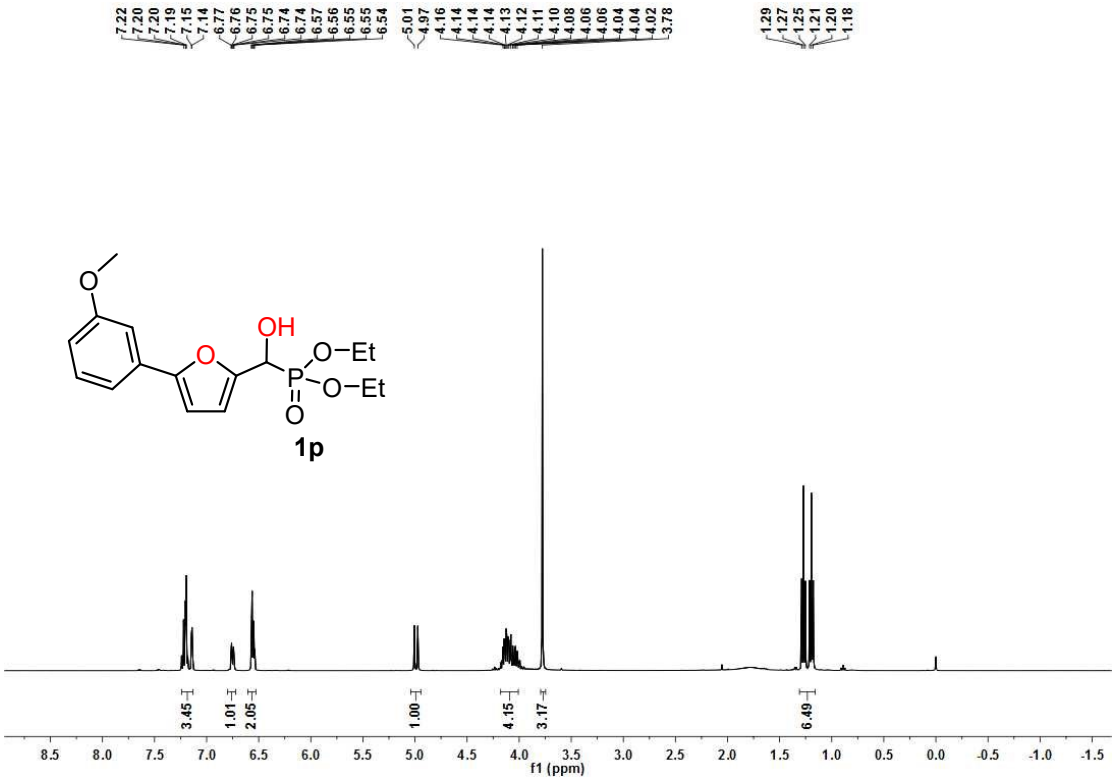

22.33
Me
OH
O
O–n-Bu
O–n-Bu
P
O
1n
f1 (ppm)

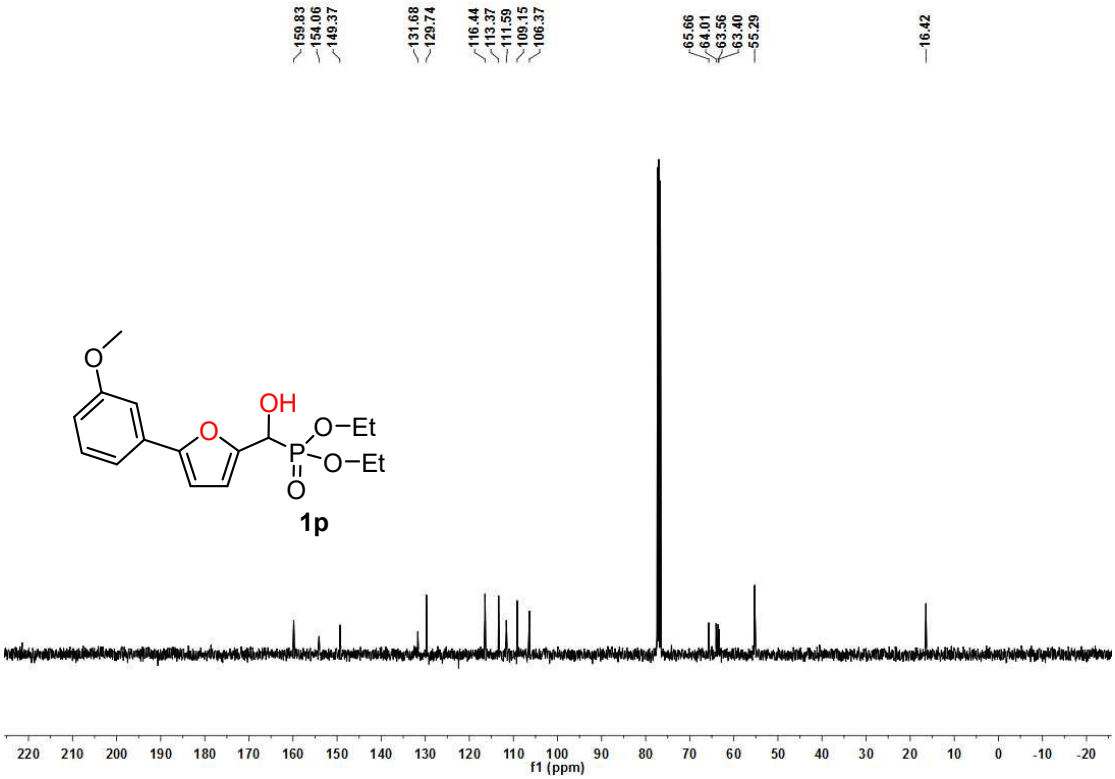
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1o**

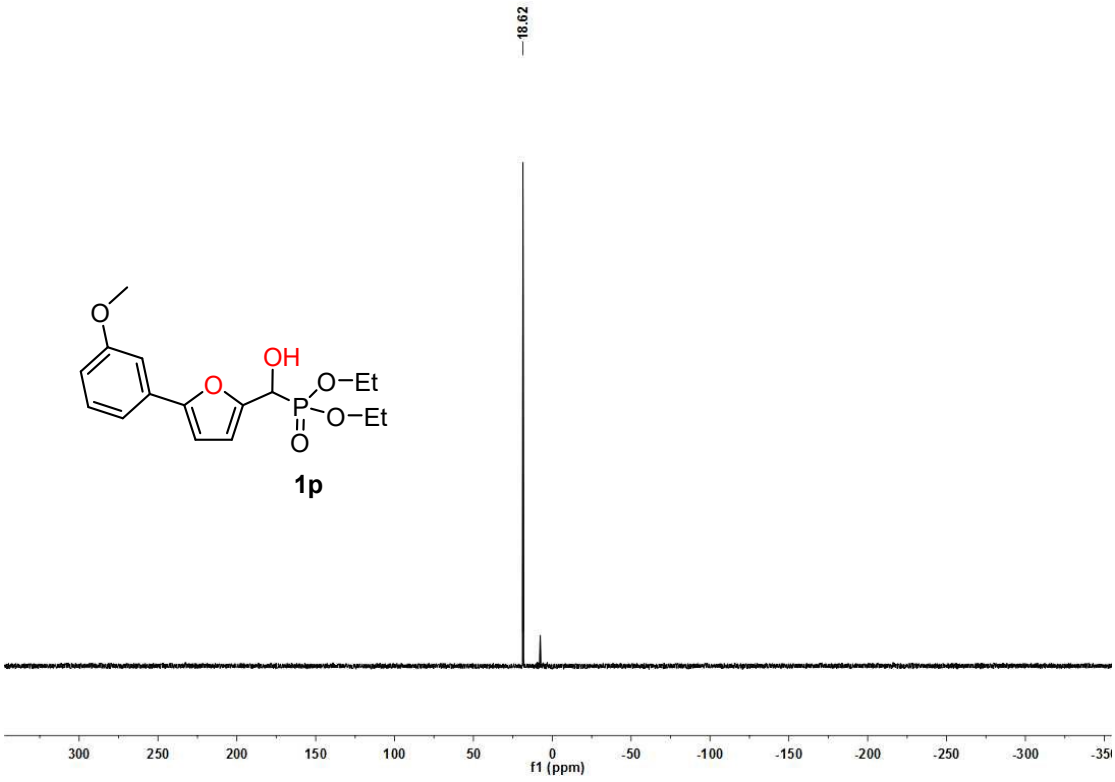




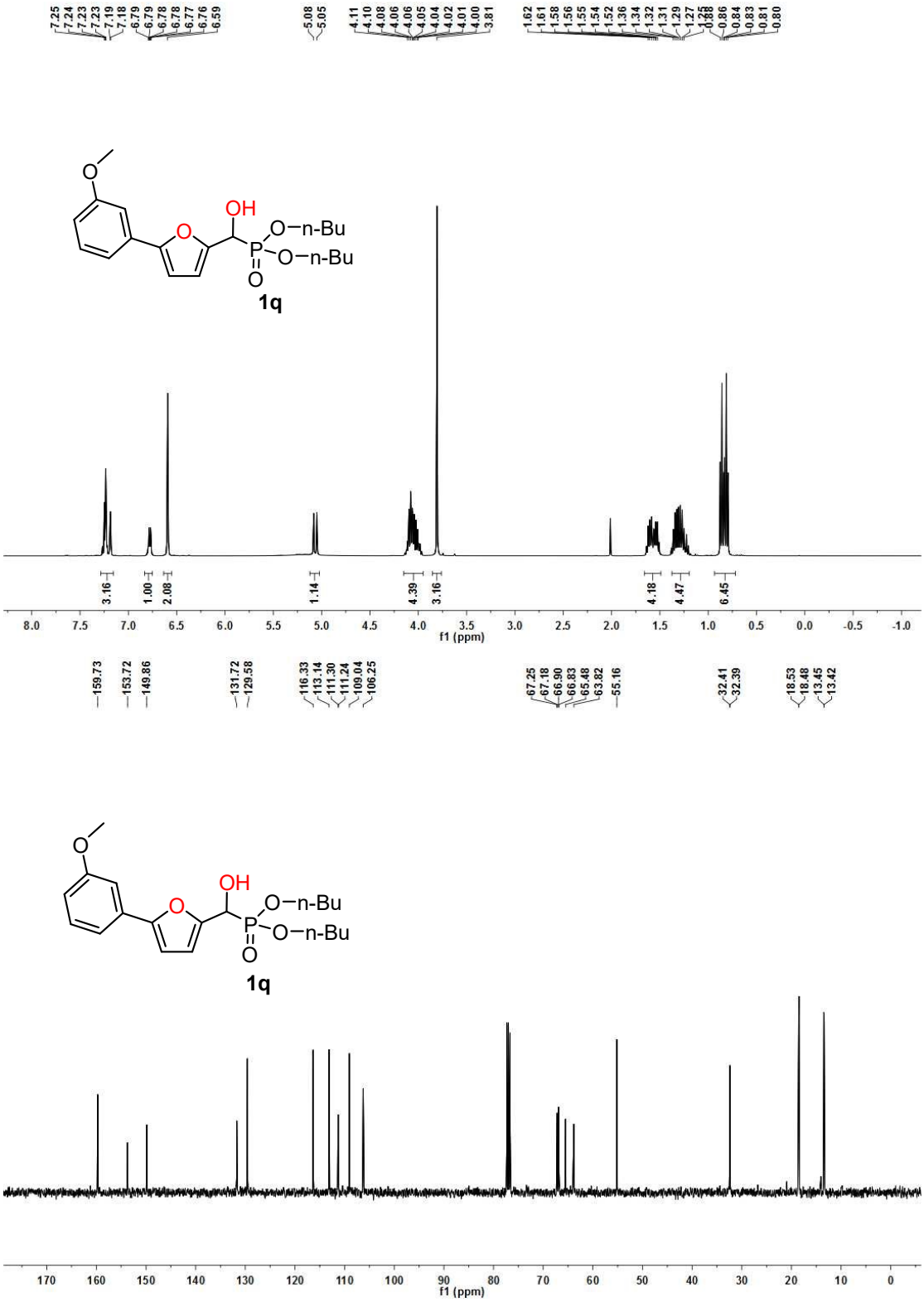
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1p**

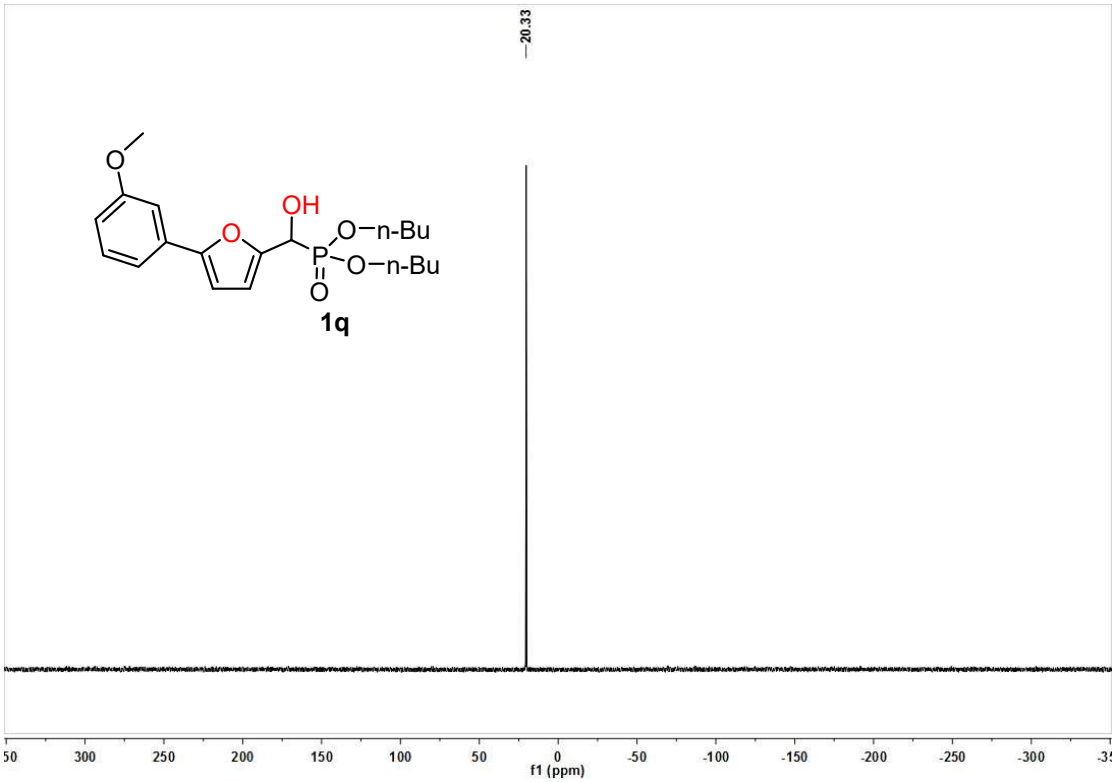



159.83
154.06
149.37
131.68
129.74
116.44
113.37
111.59
109.15
106.37
65.66
64.01
63.56
63.40
55.29
16.42
O
OH
O
O−Et
P
O−Et
O
1p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

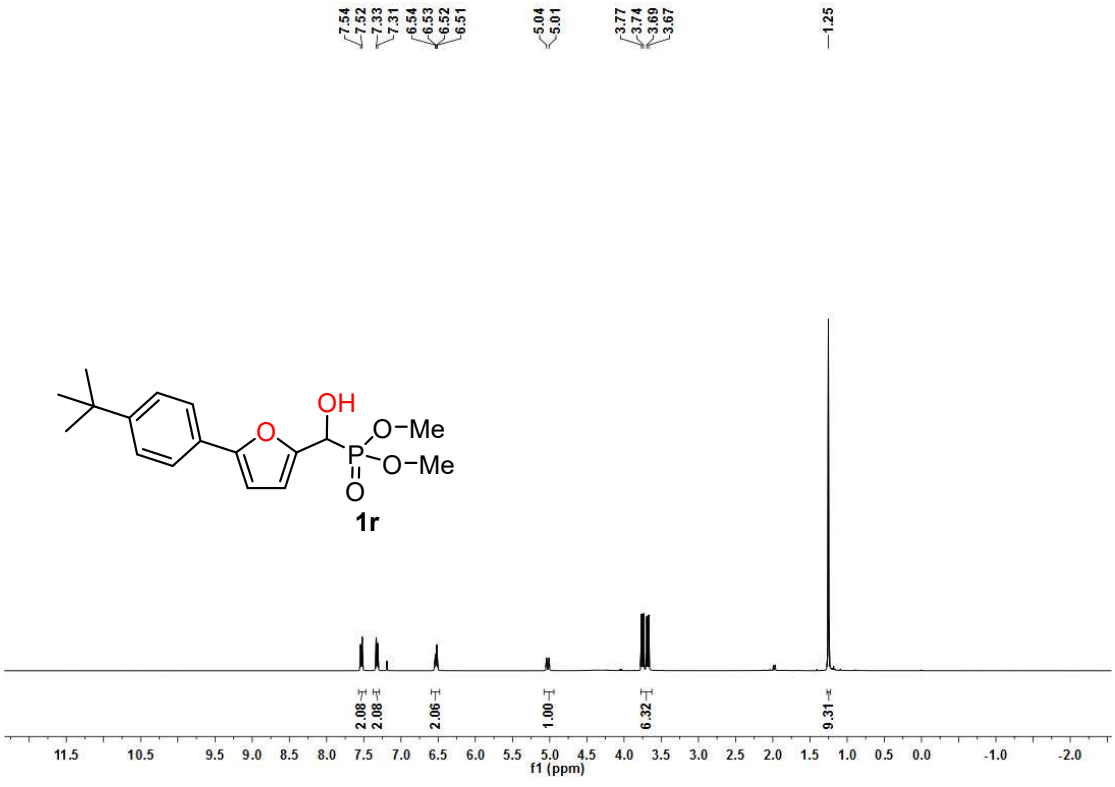

18.62
O
OH
O
O−Et
P
O−Et
O
1p
300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)

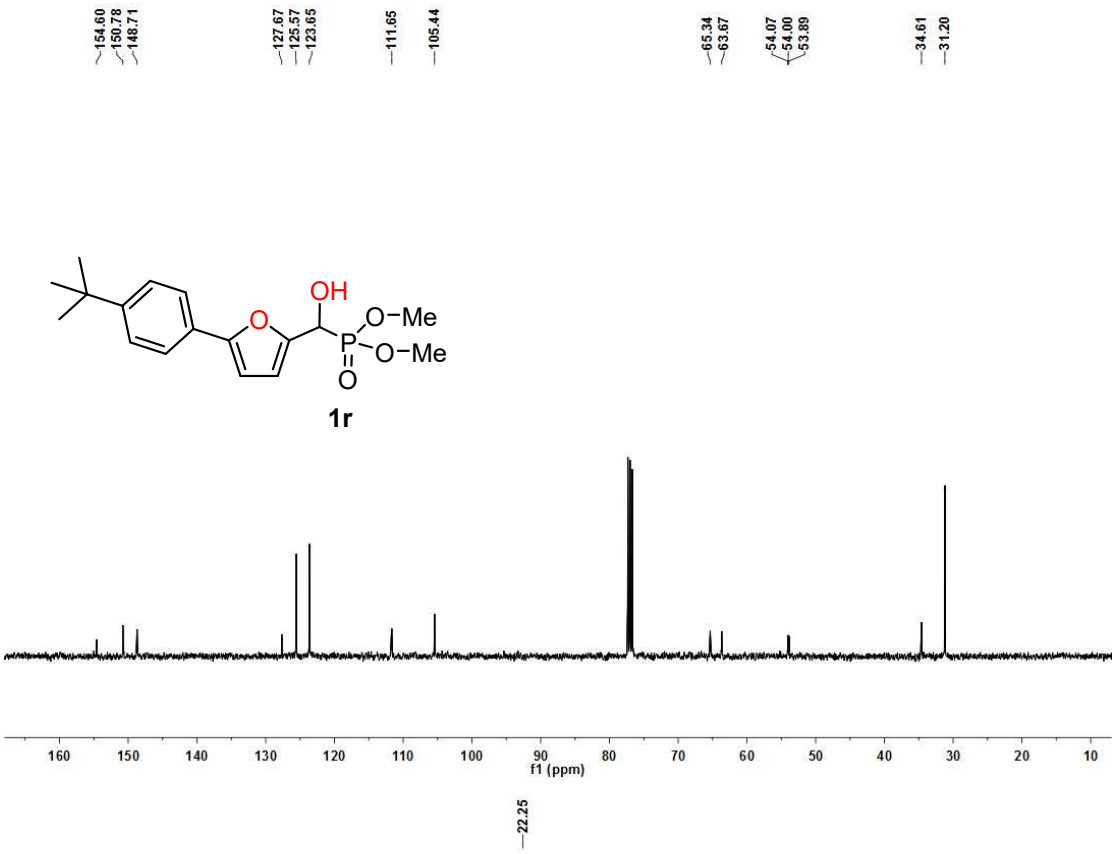
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1q**

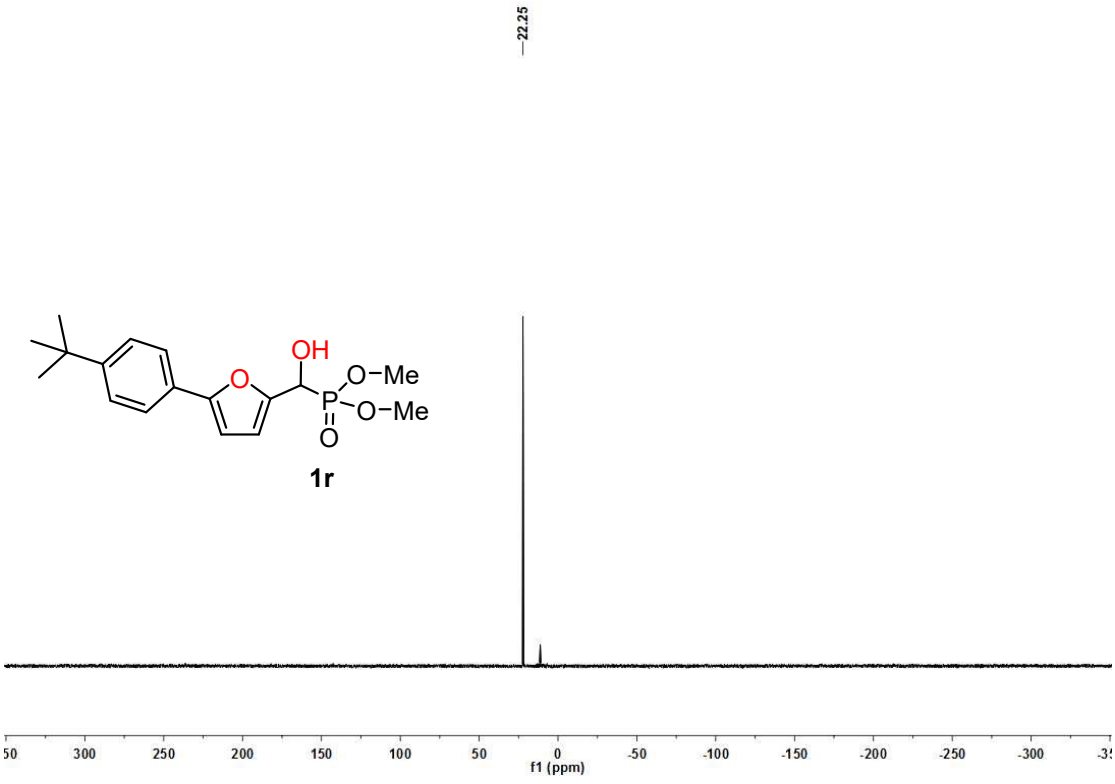




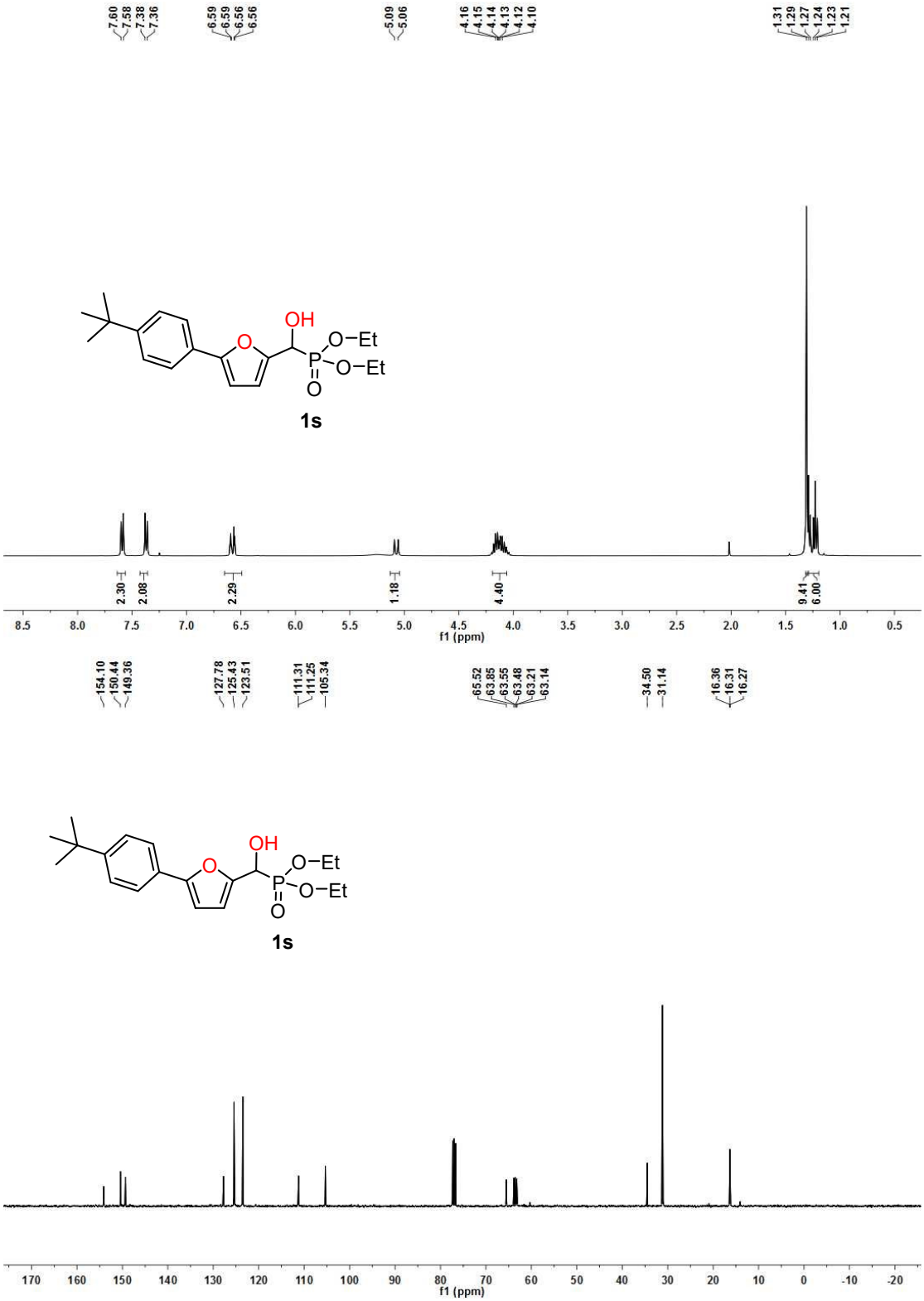
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1r**

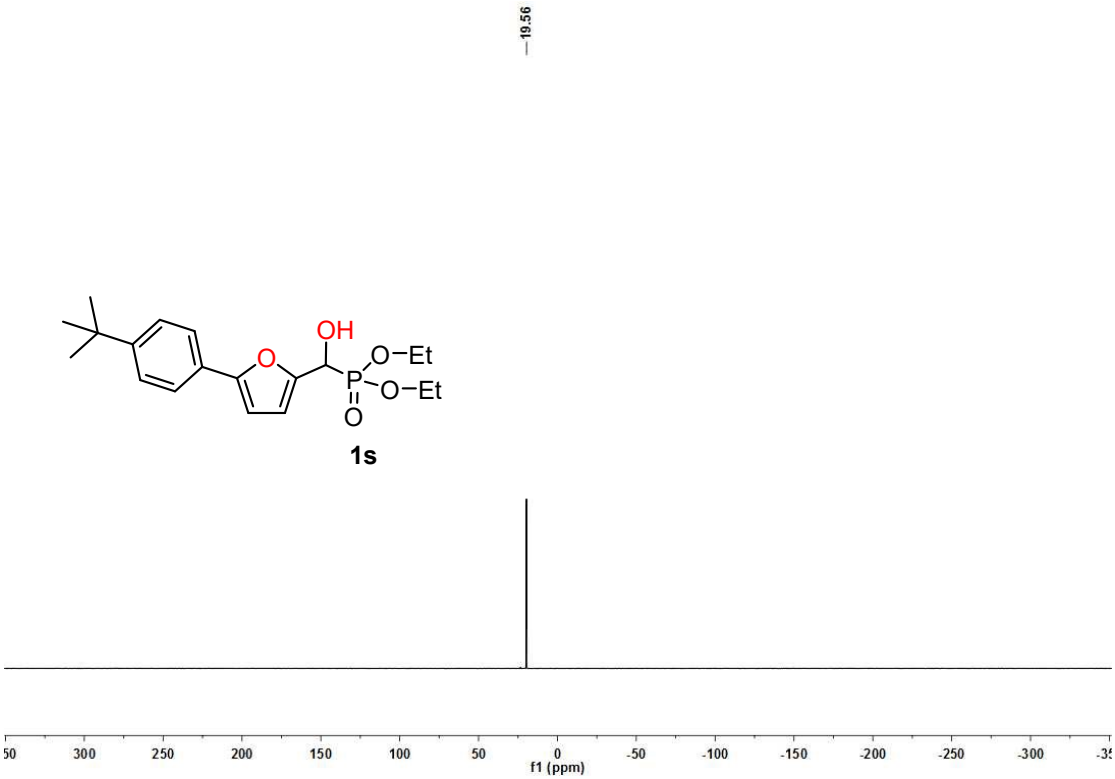



154.60
150.78
148.71
127.67
125.57
123.65
111.65
105.44
65.34
63.67
54.07
54.00
53.89
34.61
31.20
OH
O
O−Me
P
O−Me
O
1r
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

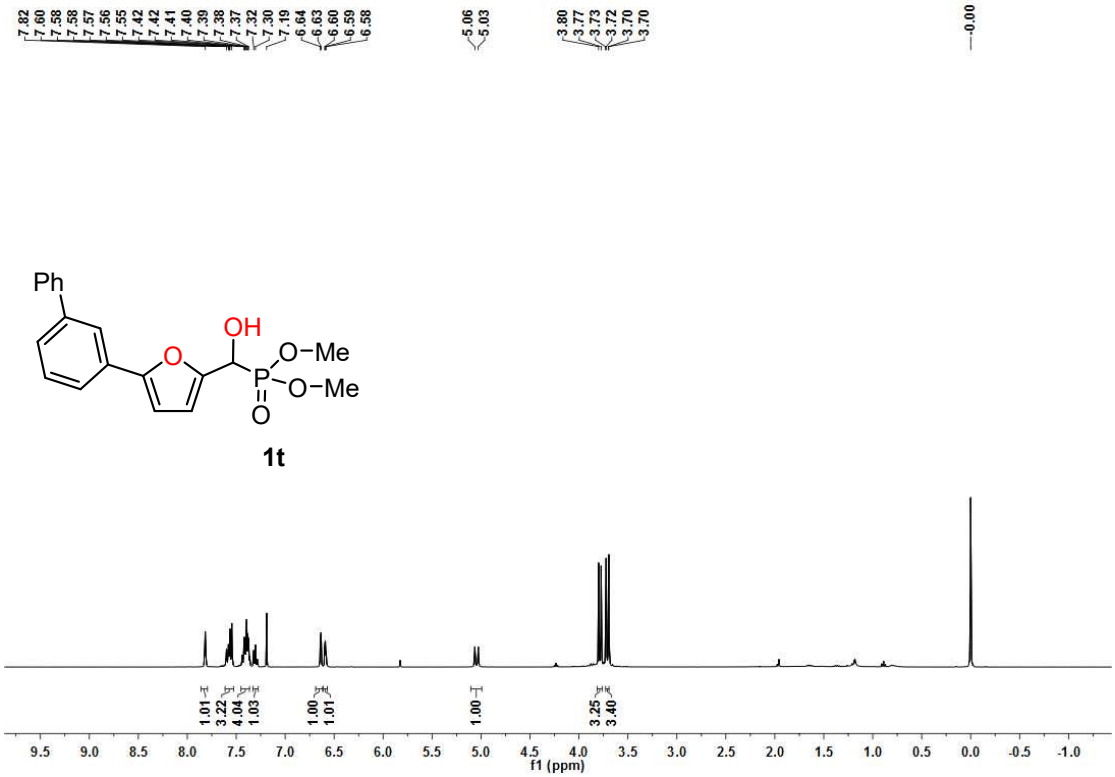

22.25
OH
O
O−Me
P
O−Me
O
1r
50
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

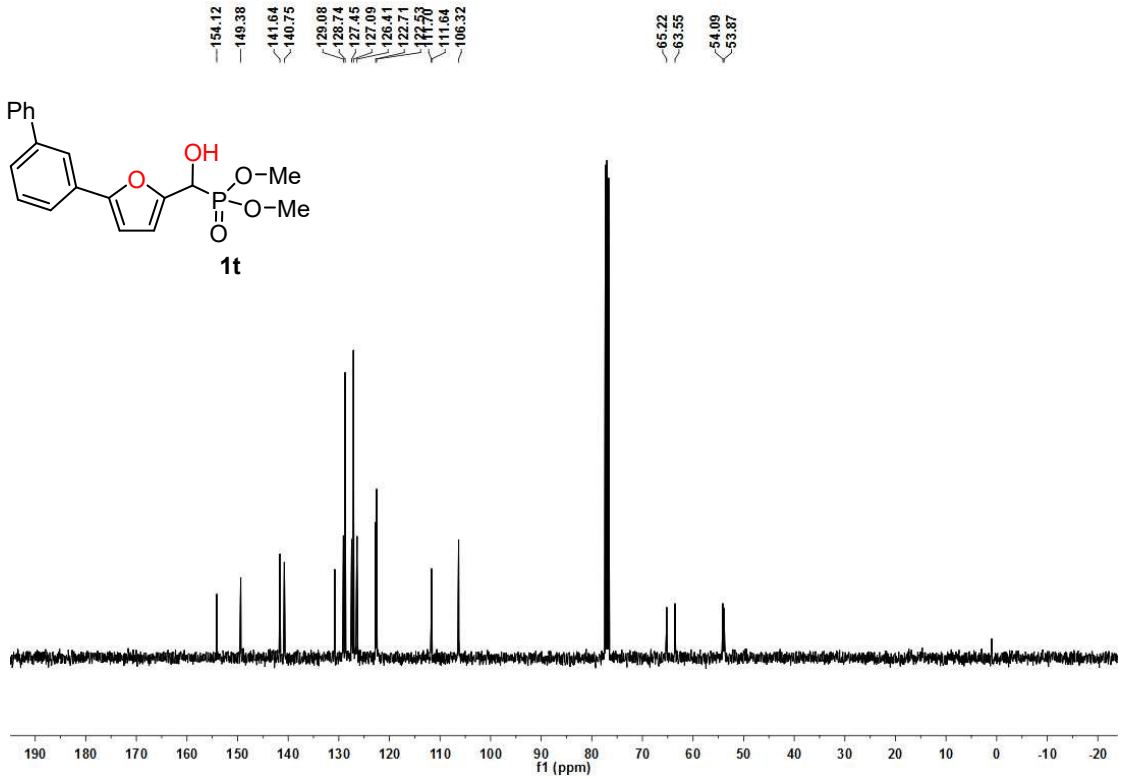
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1s**

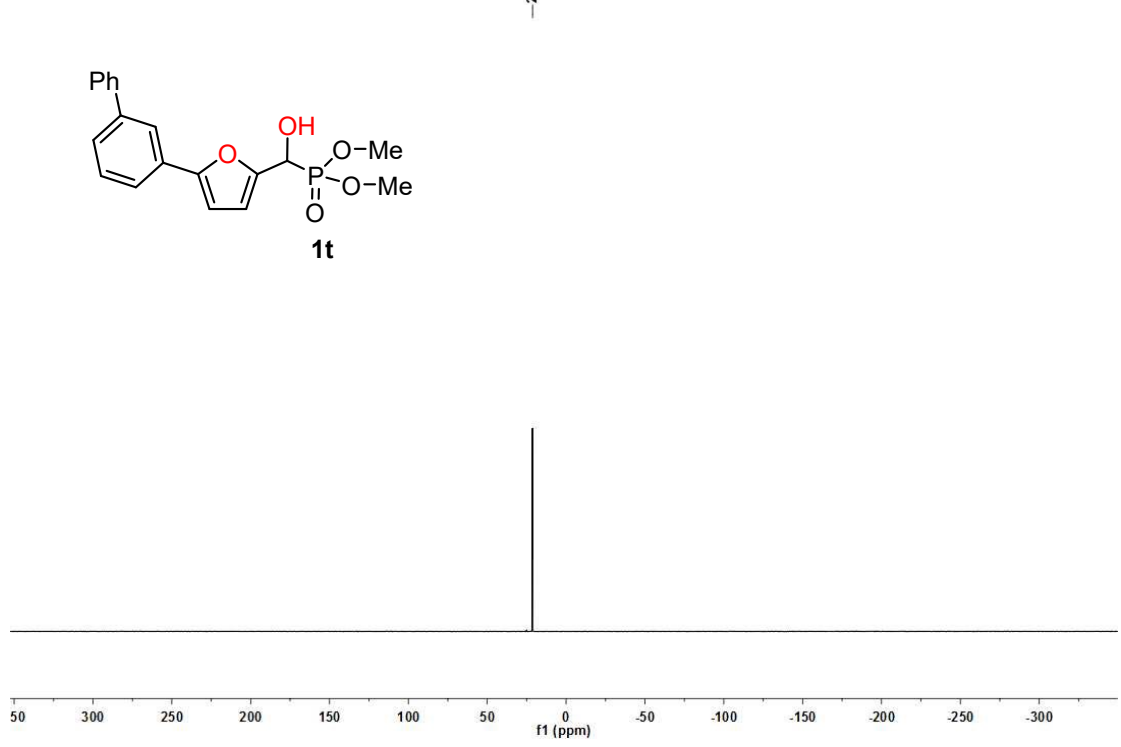




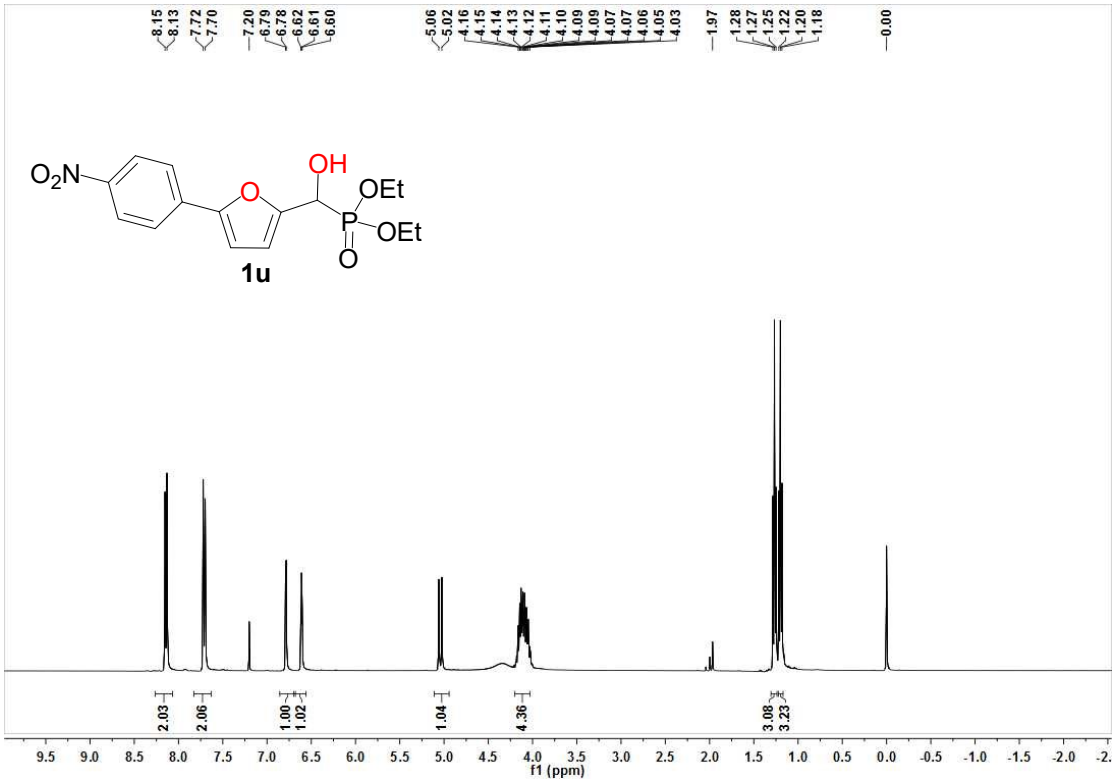
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1t**

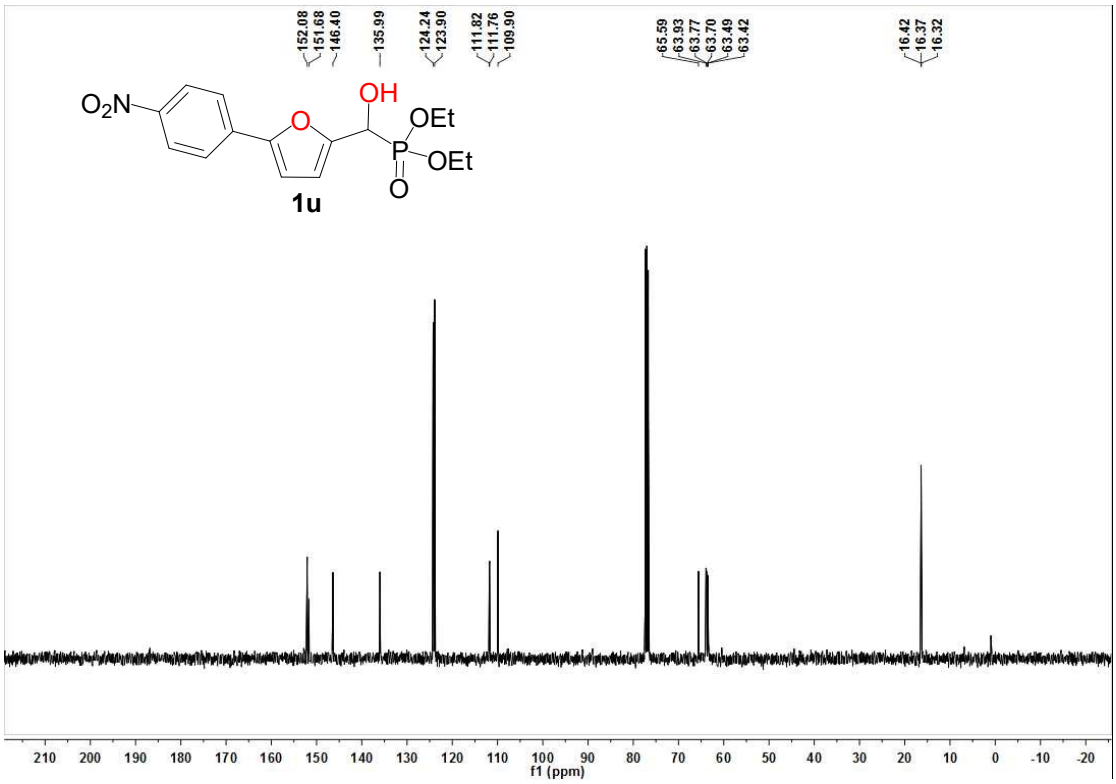


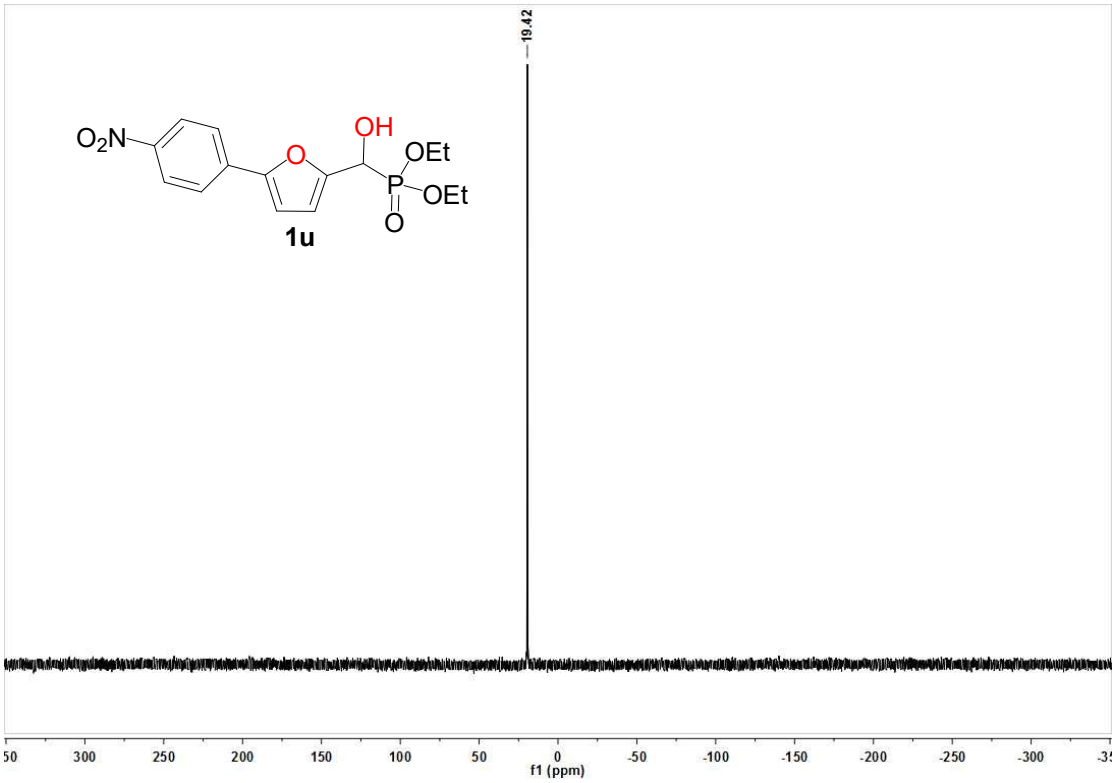

154.12
149.38
141.64
140.75
129.08
128.74
127.45
127.09
126.41
122.71
111.64
106.32
65.22
63.55
54.09
53.87
Ph
OH
O
O−Me
P
O−Me
O
1t
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


21.25
Ph
OH
O
O−Me
P
O−Me
O
1t
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

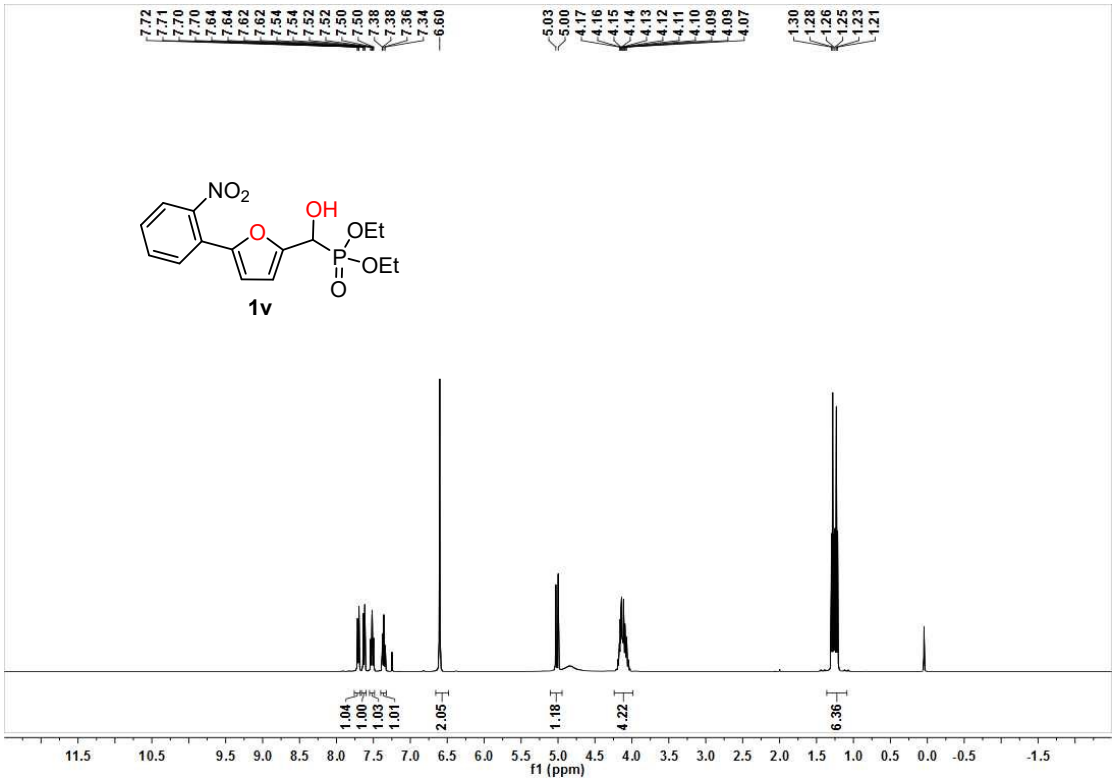
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1u**

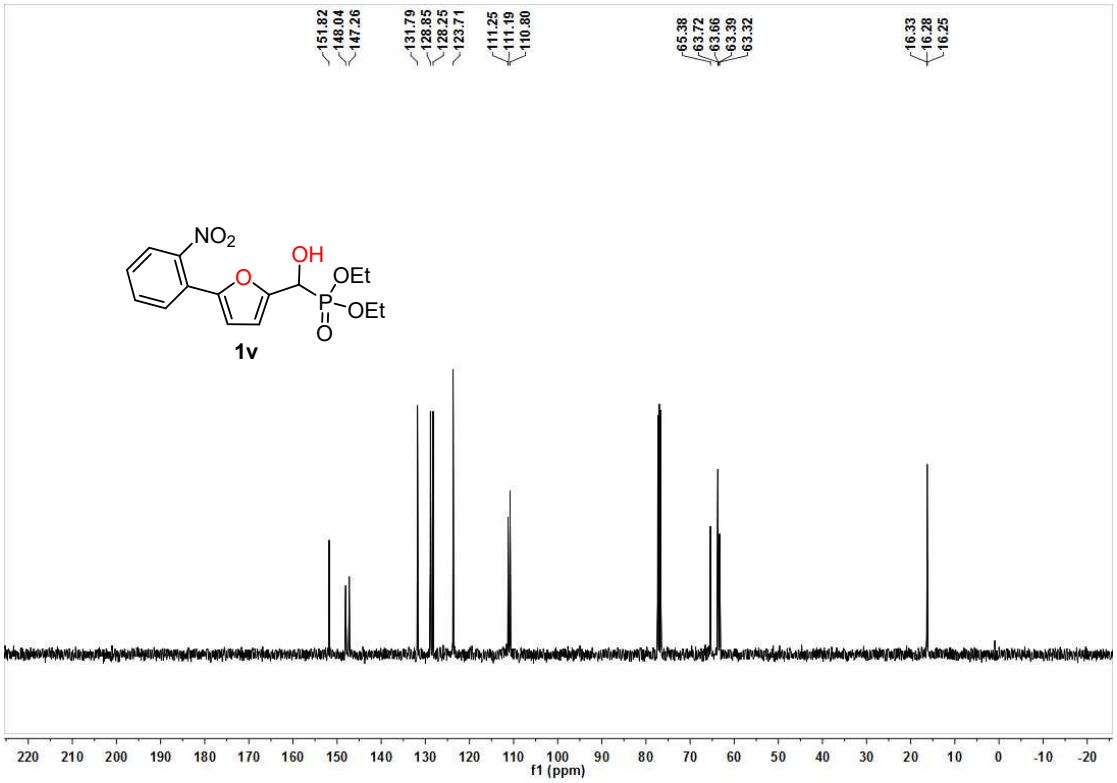


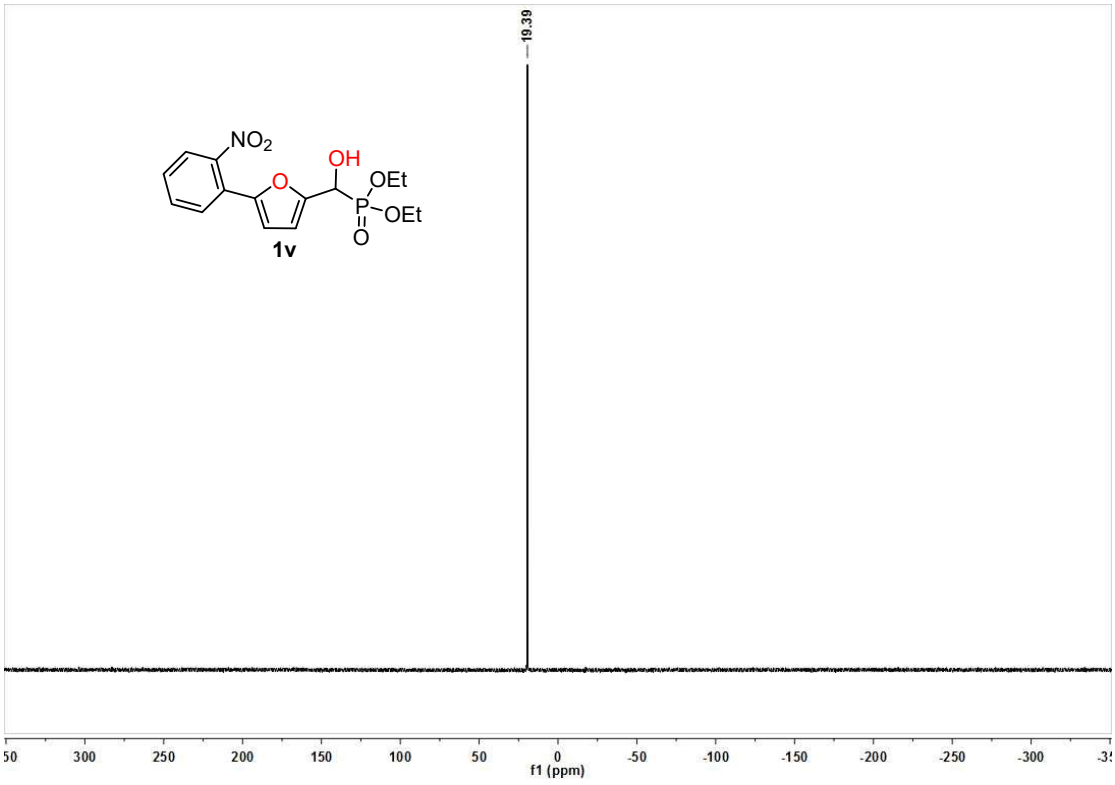




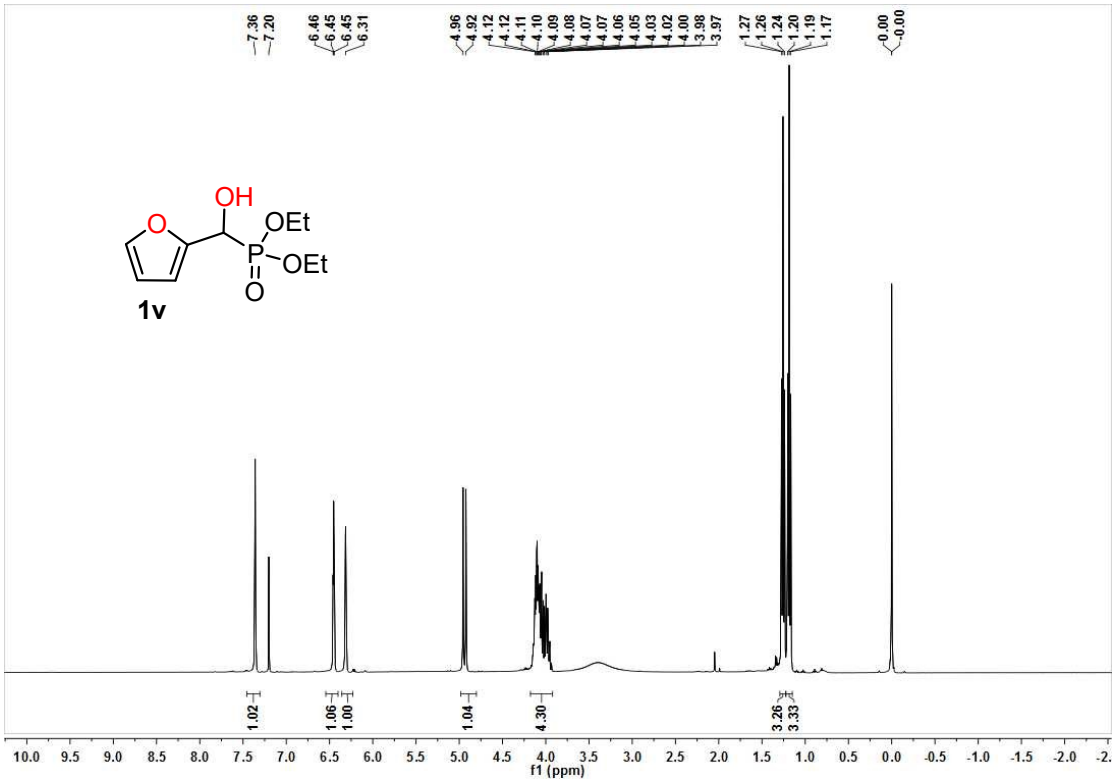
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1v**

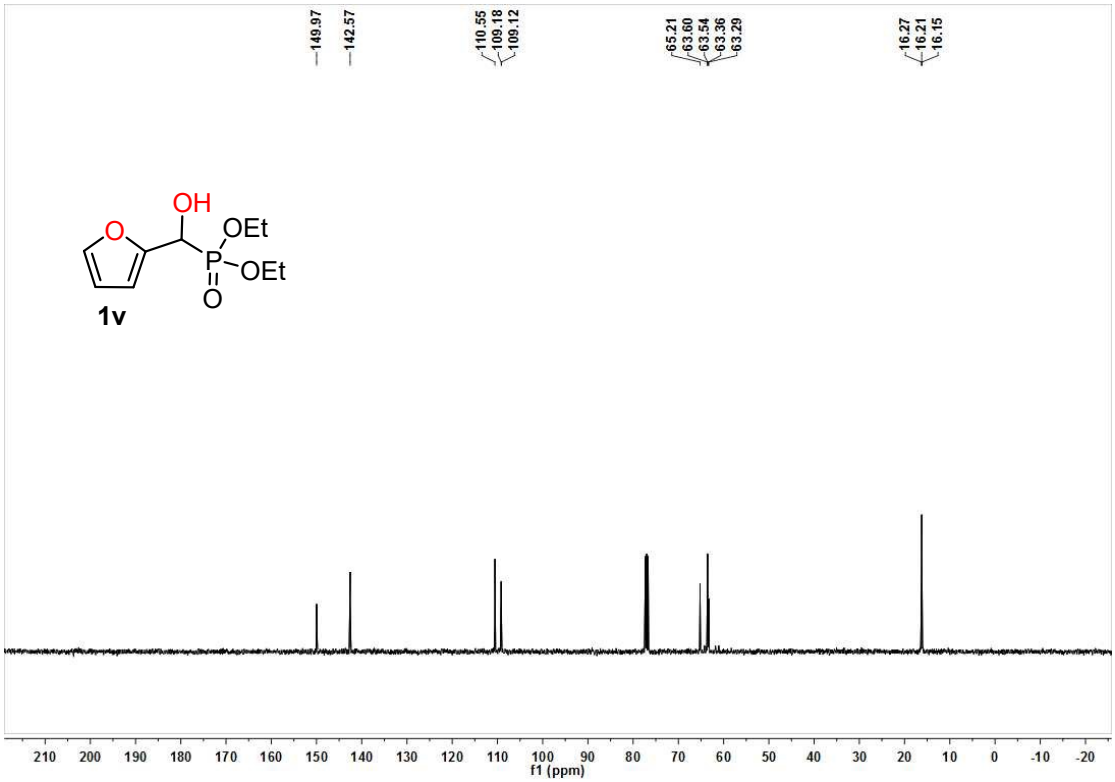


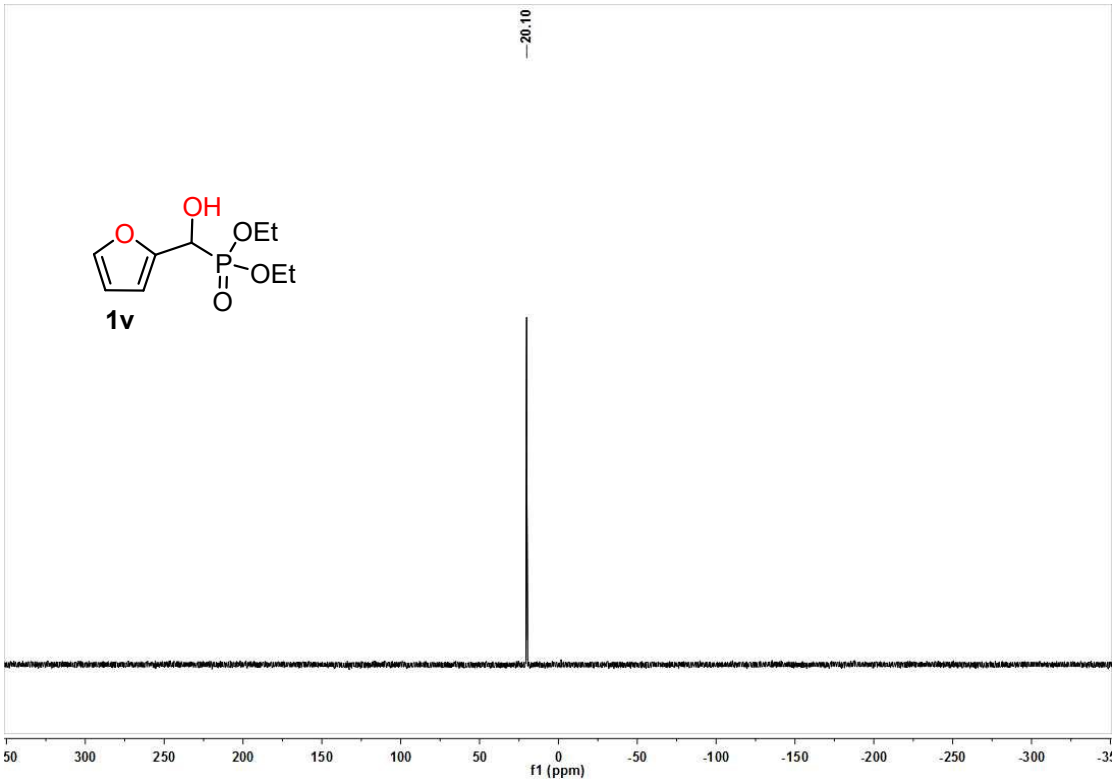

151.82
148.04
147.26
131.79
128.85
128.25
123.71
111.25
111.19
110.80
65.38
63.72
63.66
63.39
63.32
16.33
16.28
16.25
NO2
OH
O
OEt
P
OEt
O
1v
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


19.39
NO2
OH
O
OEt
P
OEt
O
1v
50 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

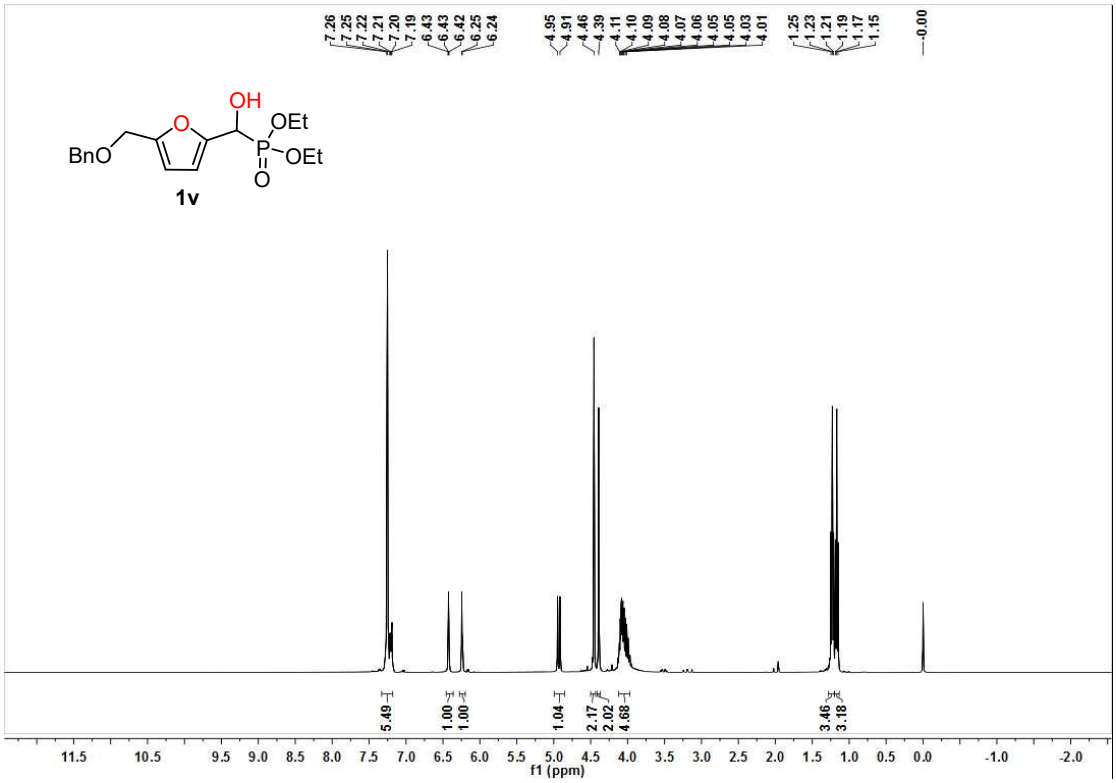
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1v**

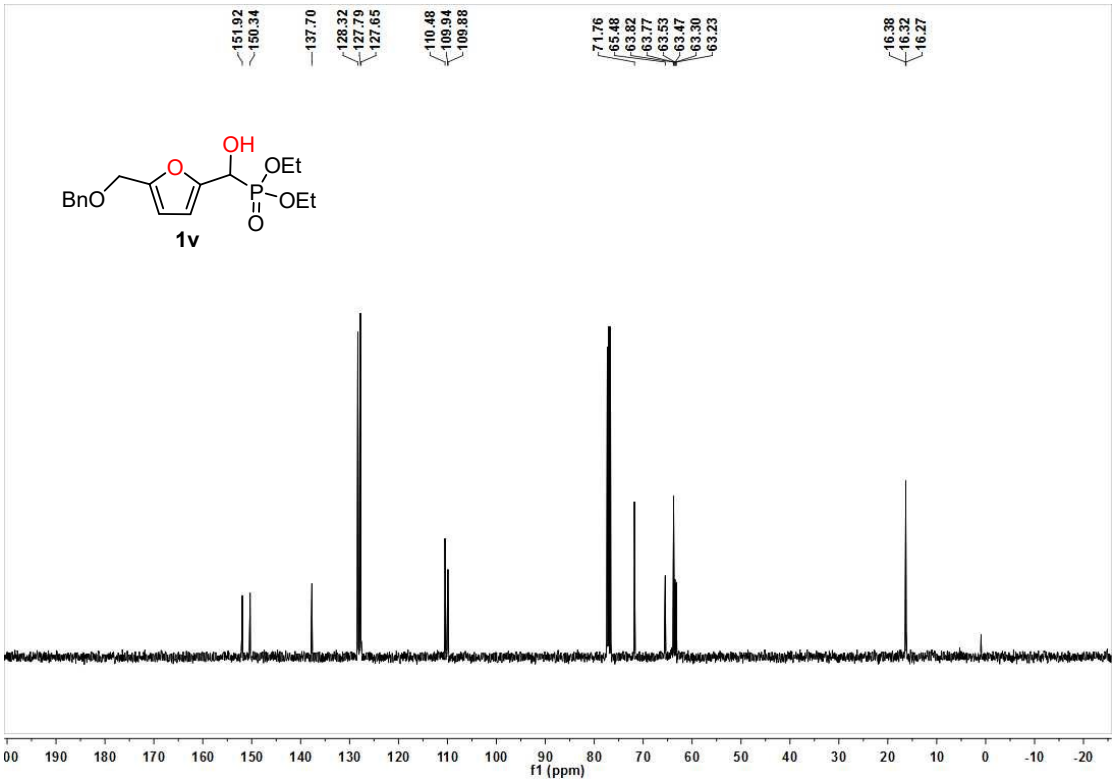


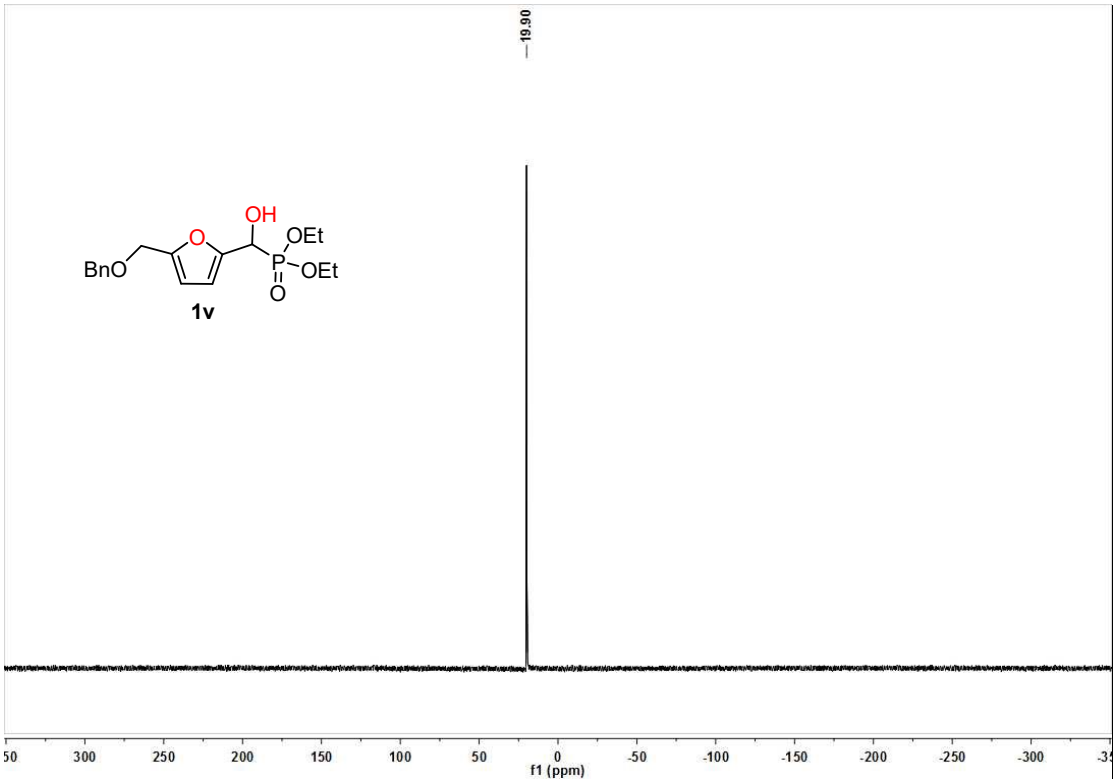




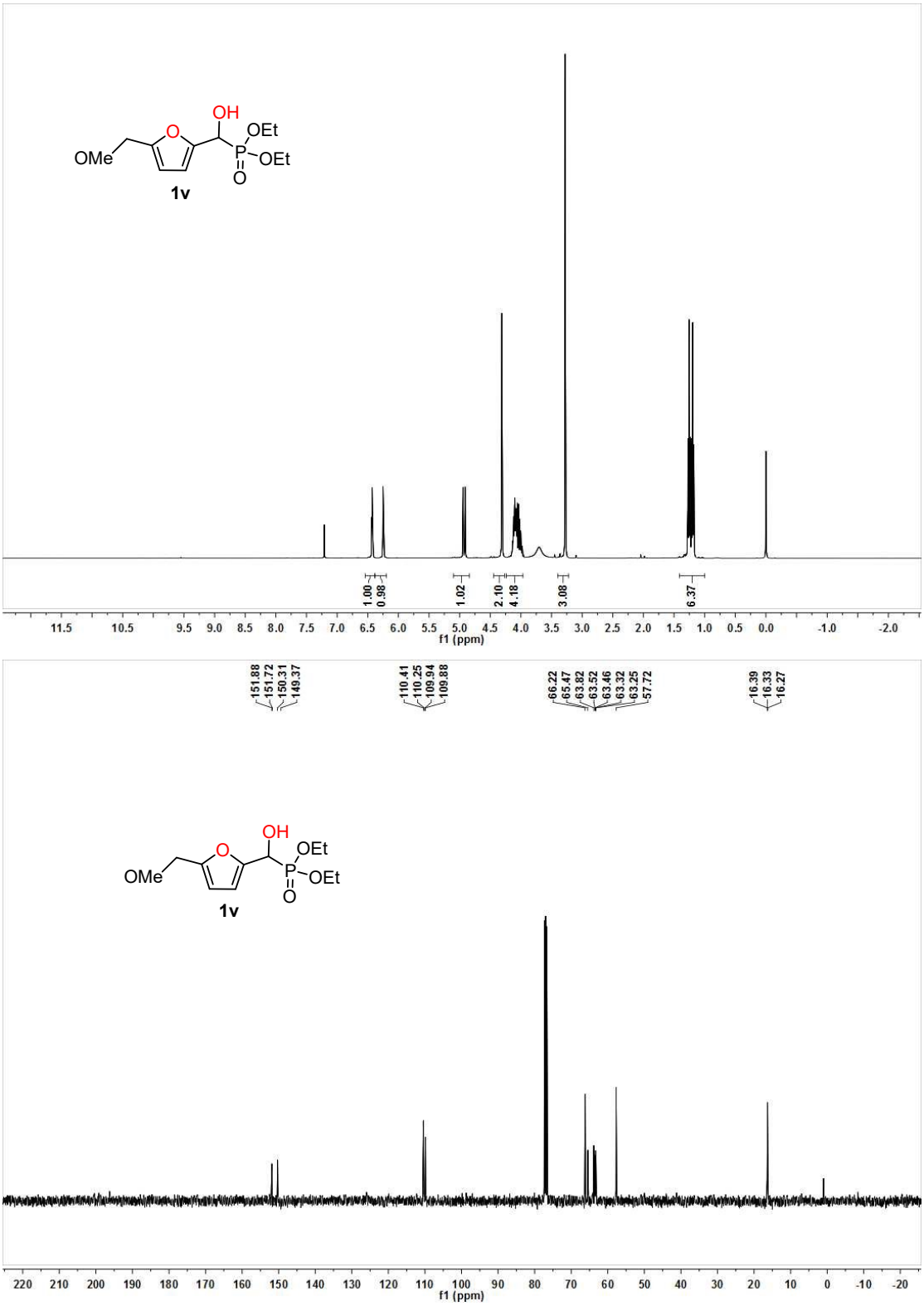
^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1v**

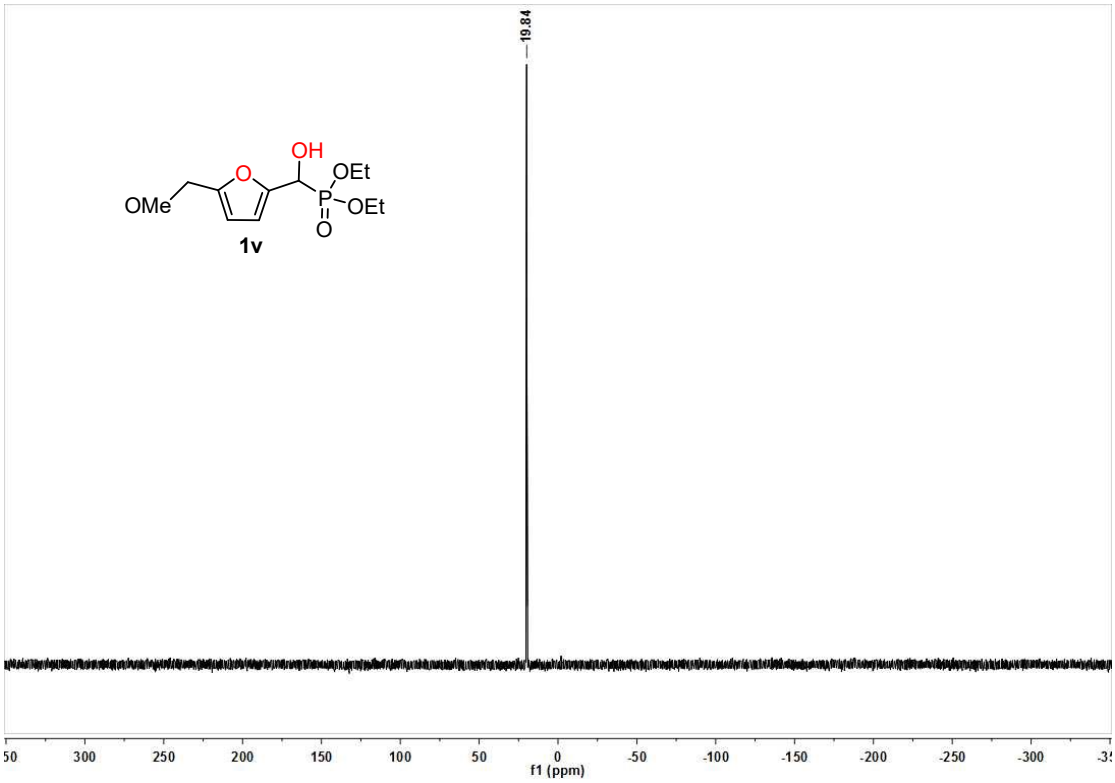



151.92
150.34
137.70
128.32
127.79
127.65
110.48
109.94
109.88
71.76
65.48
63.82
63.77
63.53
63.47
63.30
63.23
16.38
16.32
16.27
OH
O
OEt
BnO
P
OEt
O
1v
f1 (ppm)


19.90
OH
O
OEt
BnO
P
OEt
O
1v
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)**, ^{13}C NMR** (400 MHz, $CDCl_3$) **and ^{31}P spectra of 1v**





VIII.2D NMR spectra for the product 2a