

**Highly Diastereoselective Vinylogous Mukaiyama Aldol Reaction
of α -Keto Phosphonates with 2-(Trimethylsilyloxy)furan
Catalyzed by $\text{Cu}(\text{OTf})_2$**

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Supporting Information

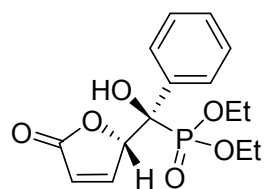
Experimental Section

General Comments.

All reactions were carried out under an inert atmosphere and in heat-dried glassware. Anhydrous CH_2Cl_2 were obtained by standard method. Flash column chromatography was performed on silica gel (particle size 10-40 μm , Ocean Chemical Factory of Qingdao, China). ^1H and ^{13}C NMR spectra were recorded on Bruker-400 (400 MHz for ^1H , 100 MHz for ^{13}C , 121 MHz for ^{31}P). Chemical shifts were reported in ppm downfield from internal $\text{Si}(\text{CH}_3)_4$. The crystal structure was determined on a Bruker SMART 1000 CCD diffractometer. Mass spectra were recorded on a LCQ advantage spectrometer with ESI resource. HR-MS were recorded on APEXII and ZAB-HS spectrometer. Melting points were determined on a T-4 melting point apparatus (uncorrected).

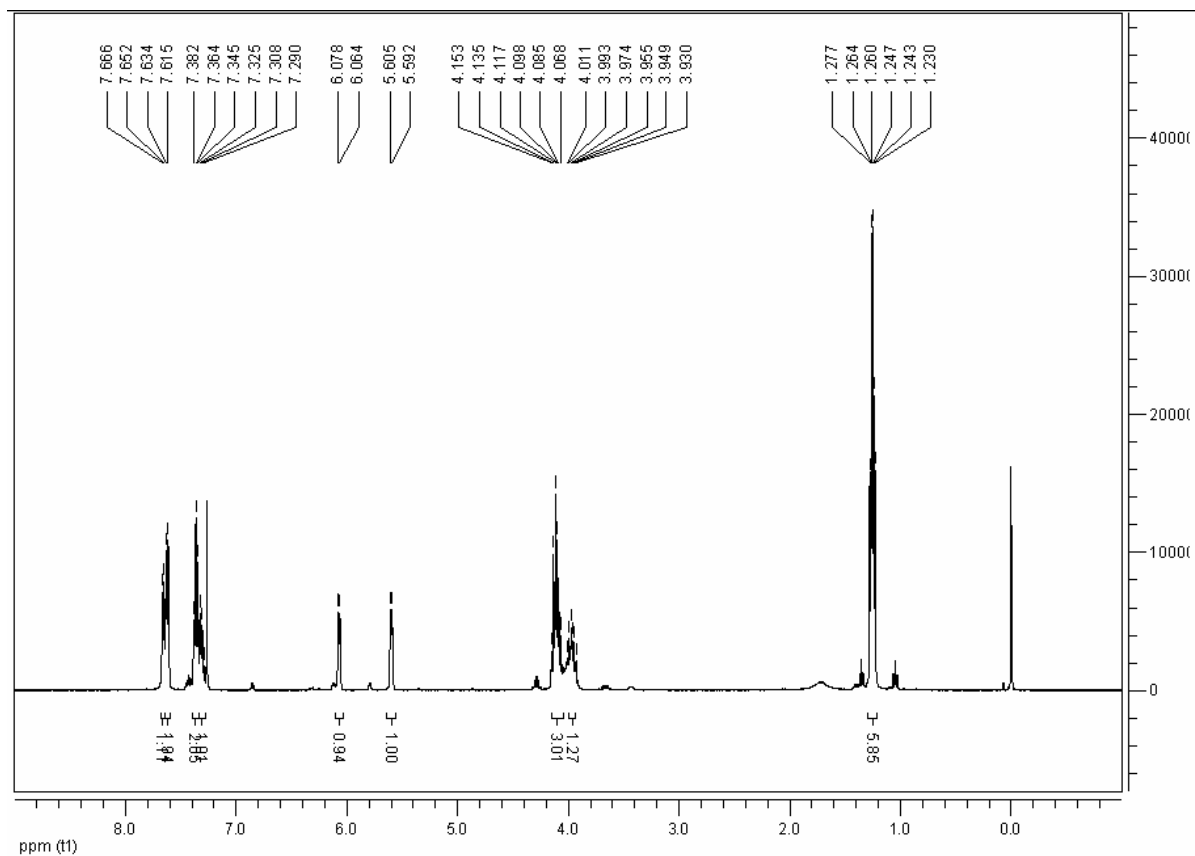
General procedure for the synthesis of dialkyl (2,5-dihydro-5-oxofuran-2-yl)(hydroxy) methylphosphonate 3: A solution of α -keto phosphonate **1** (1.0 mmol) in CH_2Cl_2 (2 mL) was cooled to 0 $^\circ\text{C}$, 2-(trimethylsilyloxy)furan **2** (0.32 g, 2.0 mmol) and $\text{Cu}(\text{OTf})_2$ (0.018 g, 0.05 mmol) were added, subsequently added the TFE (0.12 g, 1.2 mmol). The mixture was stirred for corresponding time at 0 $^\circ\text{C}$. The mixture was hydrolyzed with H_2O (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3×10 mL), and the organic layers were dried with anhydrous MgSO_4 , filtered, and concentrated in vacuo to yield the crude products **3**, which were purified by flash column chromatography on silica gel [petroleum ether/ethyl acetate, 1:1 (V/V)] to provide pure products **3**.

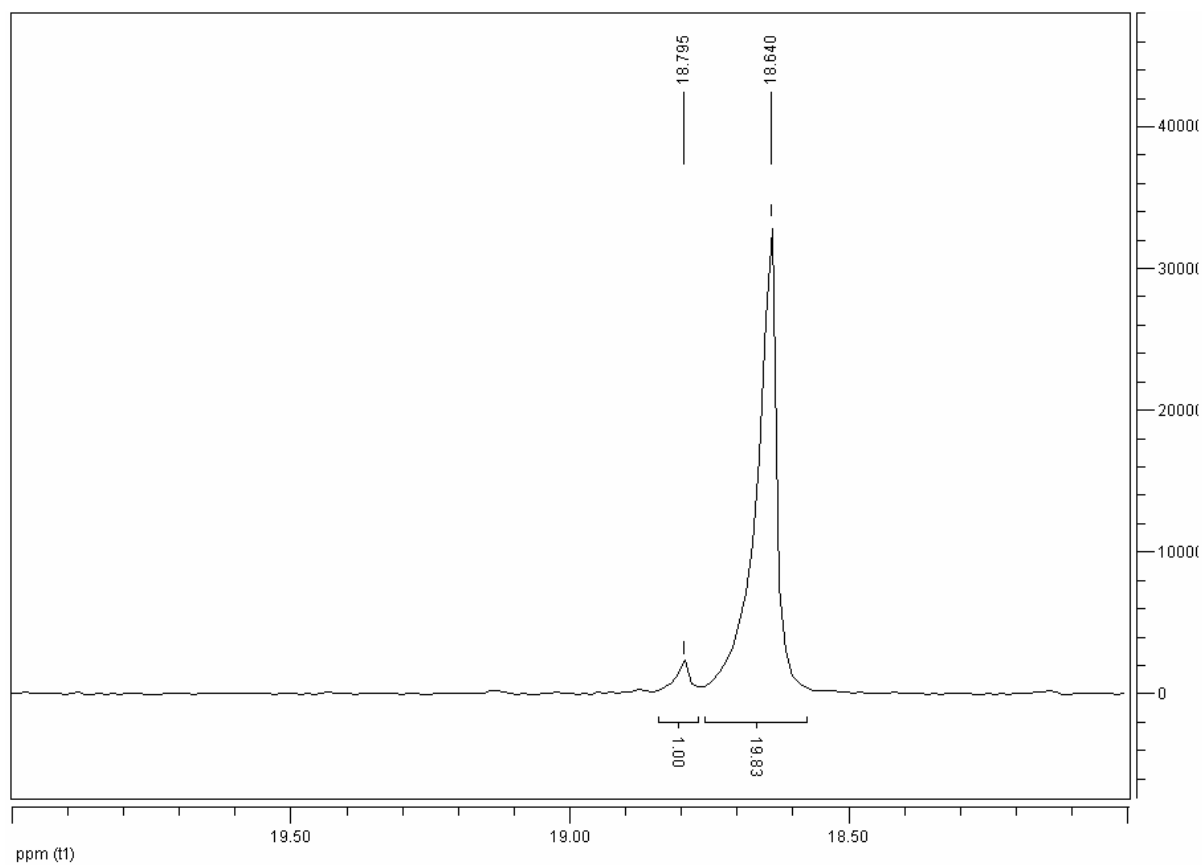
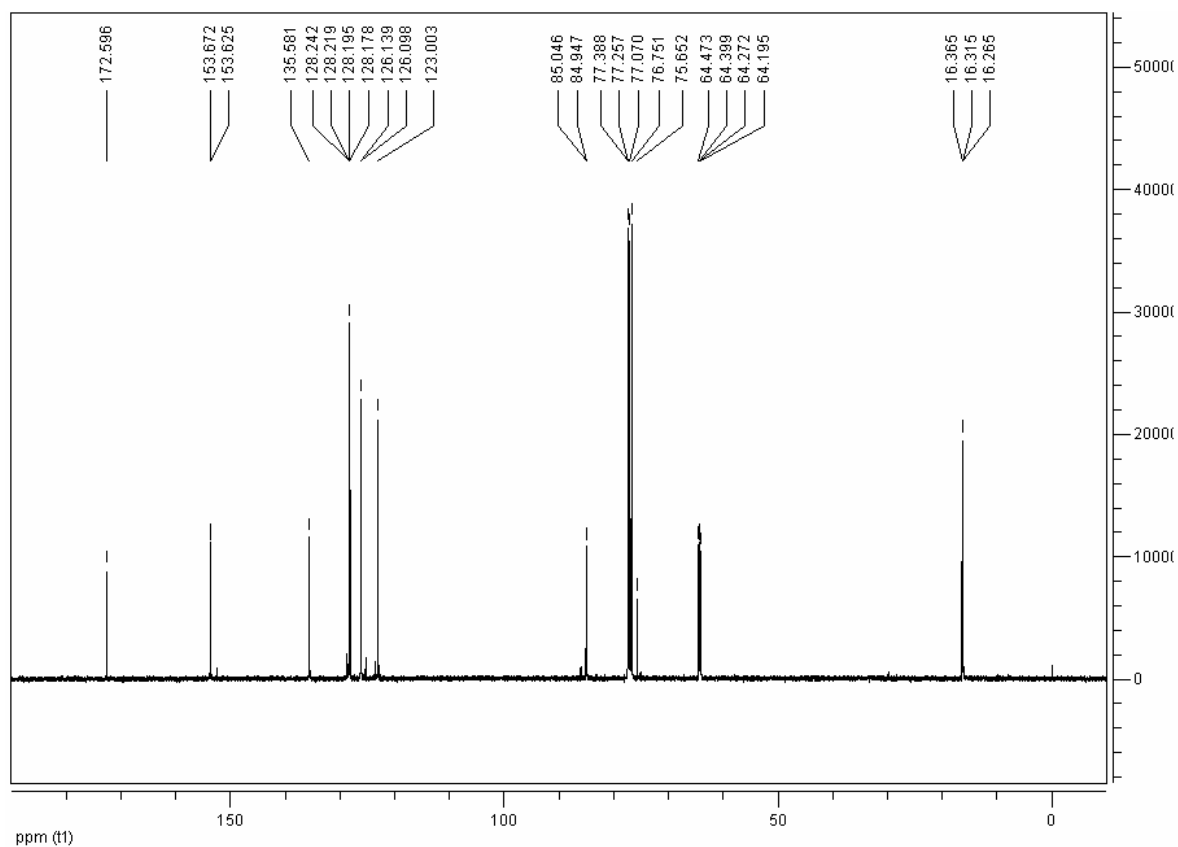
Diethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methylphosphonate (3a):



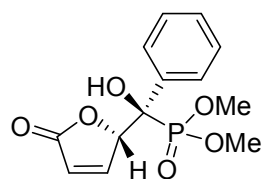
White solid; mp 104-106 $^\circ\text{C}$; ^{31}P -NMR (121 MHz, CDCl_3): δ 18.64, 18.80; ^1H -NMR (400 MHz, CDCl_3): δ 1.25 (td, $^3J_{\text{H-H}} = 7.0$ Hz, $^3J_{\text{P-H}} = 5.0$ Hz, 6H, $(\text{POCH}_2\text{CH}_3)_2$), 3.93-4.15 (m, 4H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 5.60 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.07 (d, $^3J_{\text{H-H}} = 5.7$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.31 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 1H, Ph), 7.36 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 2H, Ph), 7.62 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, Ph), 7.66 (t, $^3J_{\text{H-H}} = 5.7$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 16.32 (t, $^3J_{\text{C,P}} = 5.0$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.23 (d, $^2J_{\text{C,P}} = 7.8$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.44 (d,

$^2J_{C,P} = 7.5$ Hz, $P(OCH_2CH_3)_2$, 76.45 (d, $^1J_{C,P} = 162.5$ Hz, $CP(OCH_2CH_3)_2$), 85.00 (d, $^2J_{C,P} = 10.0$ Hz, $HC=CHCH$), 123.00, 126.12 (d, $^3J_{C,P} = 4.2$ Hz), 128.19 (d, $^4J_{C,P} = 1.7$ Hz), 128.23 (d, $^2J_{C,P} = 9.2$ Hz), 135.58, 153.65 (d, $^3J_{C,P} = 4.7$ Hz), 172.60; ESI-MS: 349.0 ($[M+Na]^+$); HRMS calcd for $C_{15}H_{19}O_6P$: 349.0811 ($M+Na$) $^+$, found: 349.0819.

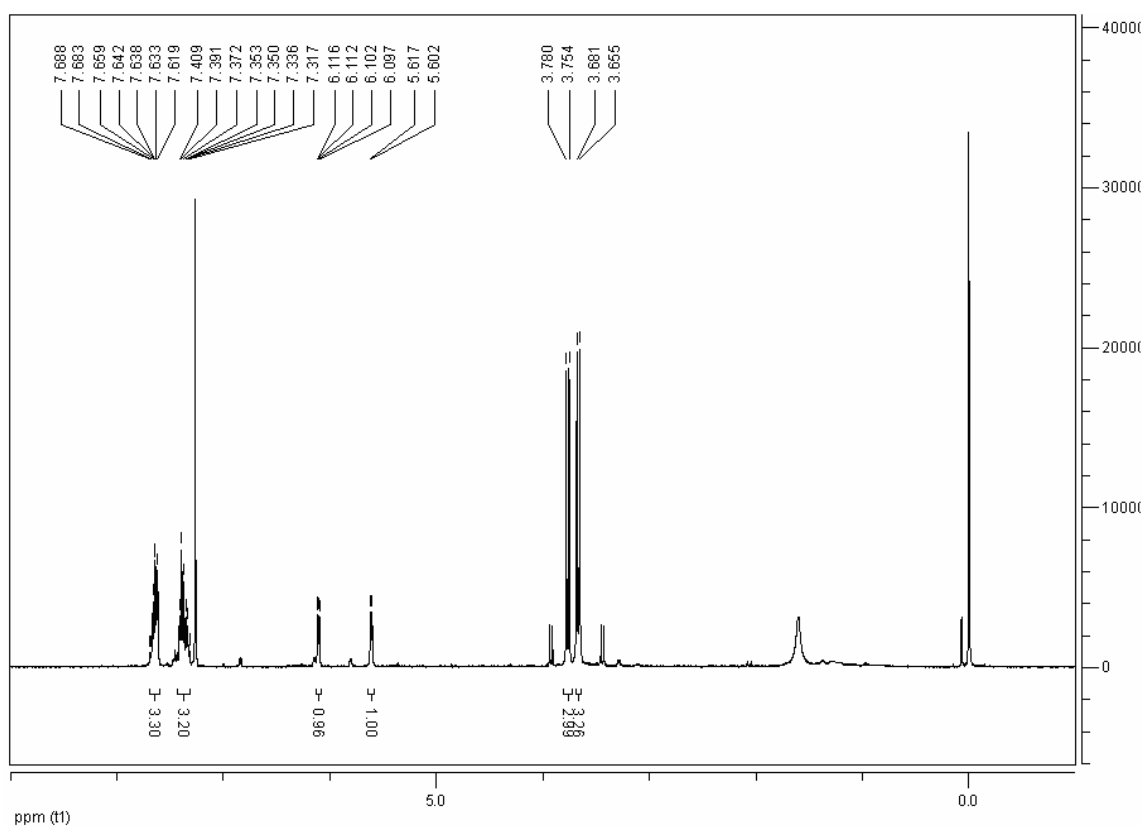


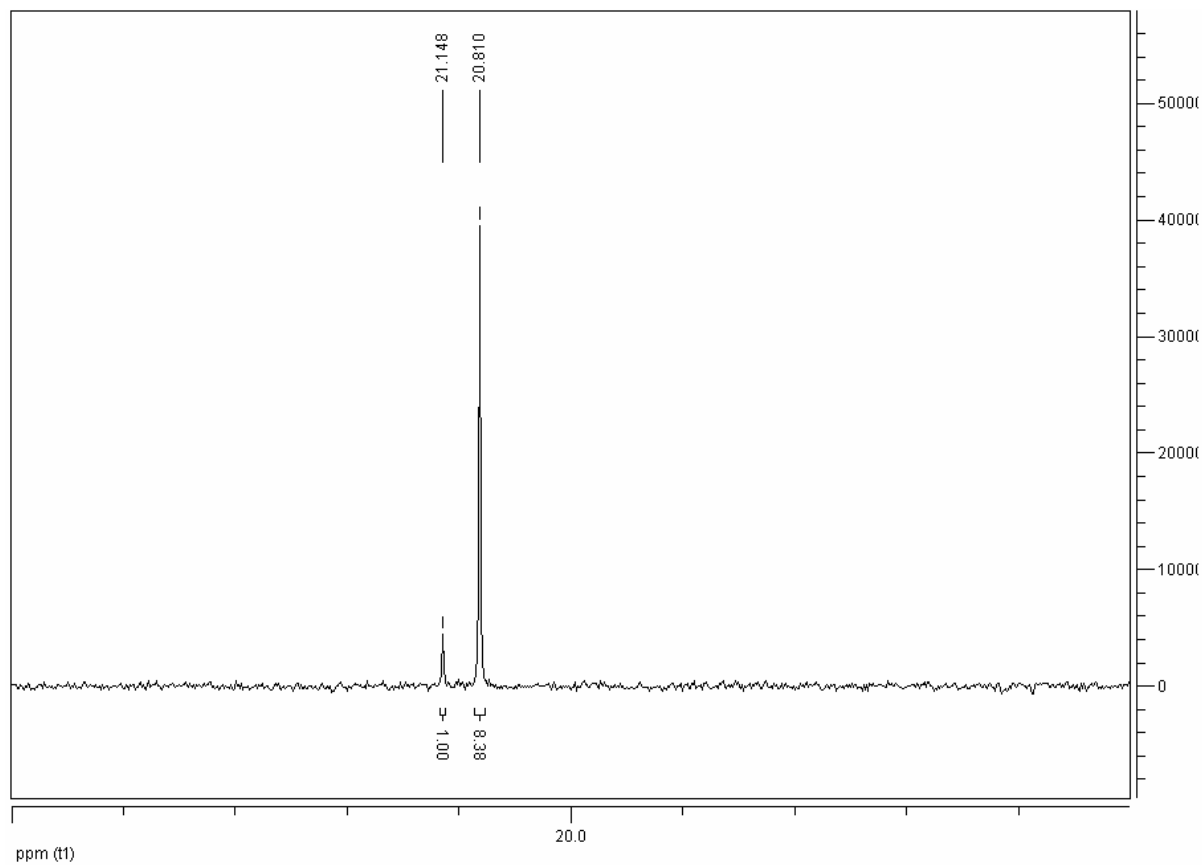
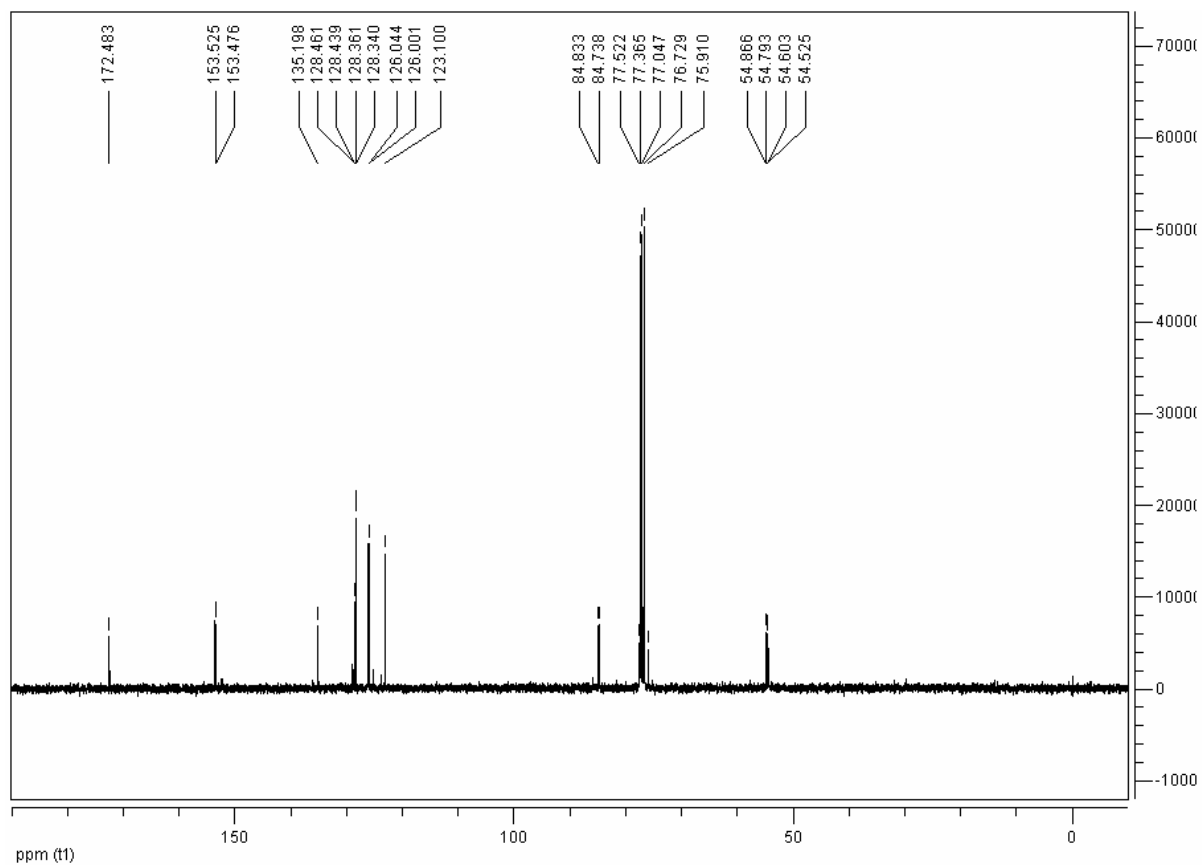


Dimethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methylphosphonate (3b):



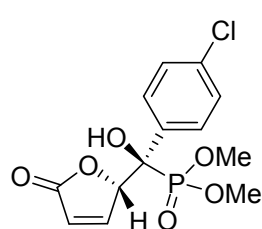
White solid; mp 131-134 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 20.15, 20.81; ^1H -NMR (400 MHz, CDCl_3): δ 3.67 (d, $^3J_{\text{P-H}} = 10.5$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 3.77 (d, $^3J_{\text{P-H}} = 10.5$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 5.61 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.11 (dd, $^3J_{\text{H-H}} = 6.0$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.32-7.41 (m, 3H, Ph), 7.62-7.69 (m, 3H, Ph, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 54.56 (d, $^2J_{\text{C,P}} = 7.8$ Hz, $\text{P}(\text{OCH}_3)_2$), 54.83 (d, $^2J_{\text{C,P}} = 7.3$ Hz, $\text{P}(\text{OCH}_3)_2$), 76.72 (d, $^1J_{\text{C,P}} = 162.2$ Hz, $\text{CP}(\text{OCH}_3)_2$), 84.79 (d, $^2J_{\text{C,P}} = 9.6$ Hz, $\text{HC}=\text{CHCH}$), 123.10, 126.02 (d, $^3J_{\text{C,P}} = 4.4$ Hz), 128.35 (d, $^2J_{\text{C,P}} = 8.4$ Hz), 128.45 (d, $^4J_{\text{C,P}} = 2.2$ Hz), 135.20, 153.50 (d, $^3J_{\text{C,P}} = 4.9$ Hz), 172.48; ESI-MS: 321.0 ($[\text{M}+\text{Na}]^+$); HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{O}_6\text{P}$: 321.0498 ($\text{M}+\text{Na}$) $^+$, found: 321.0507.



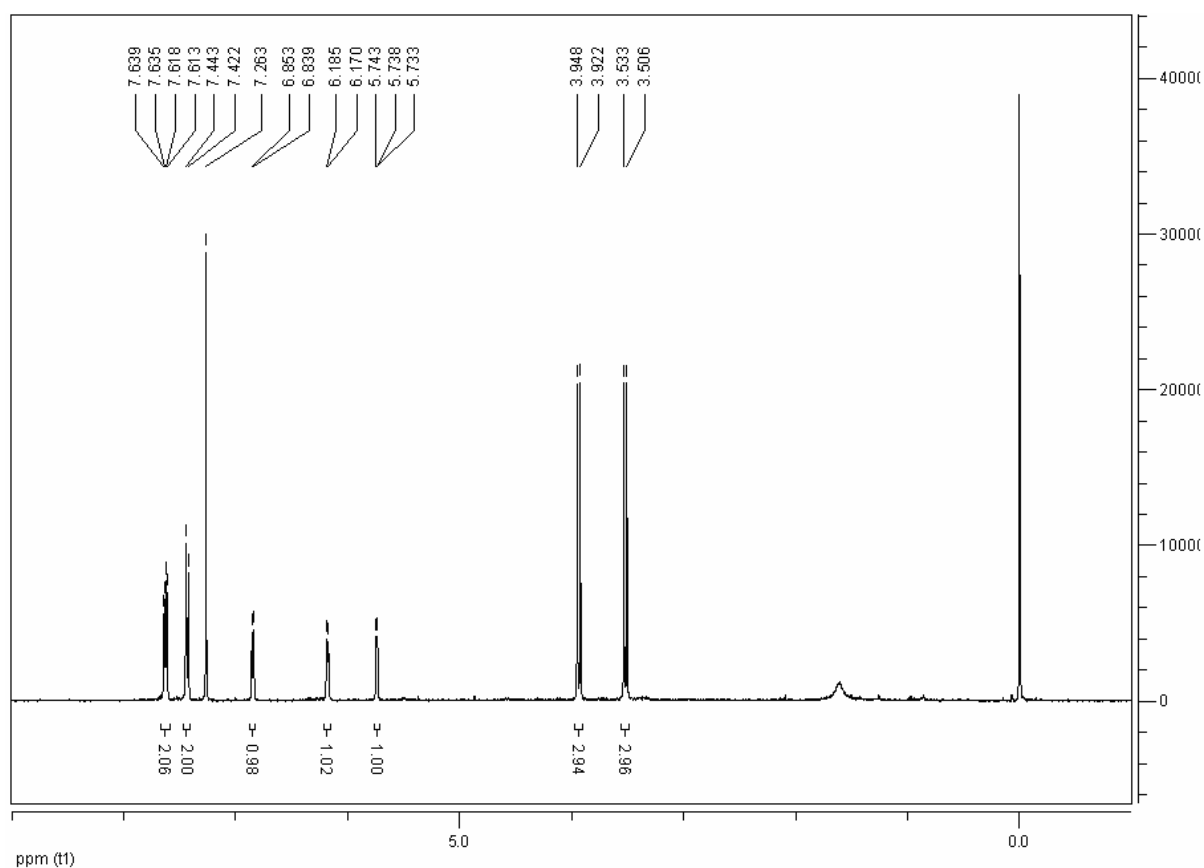


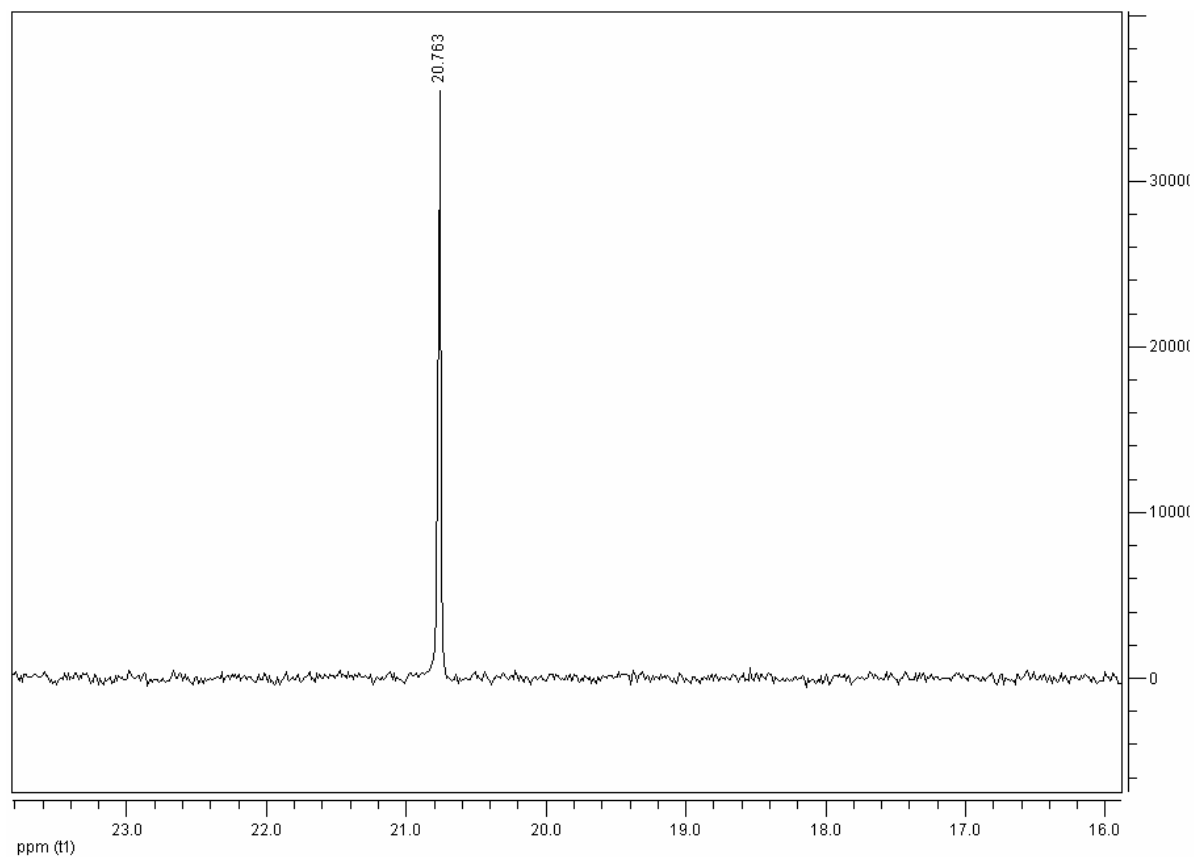
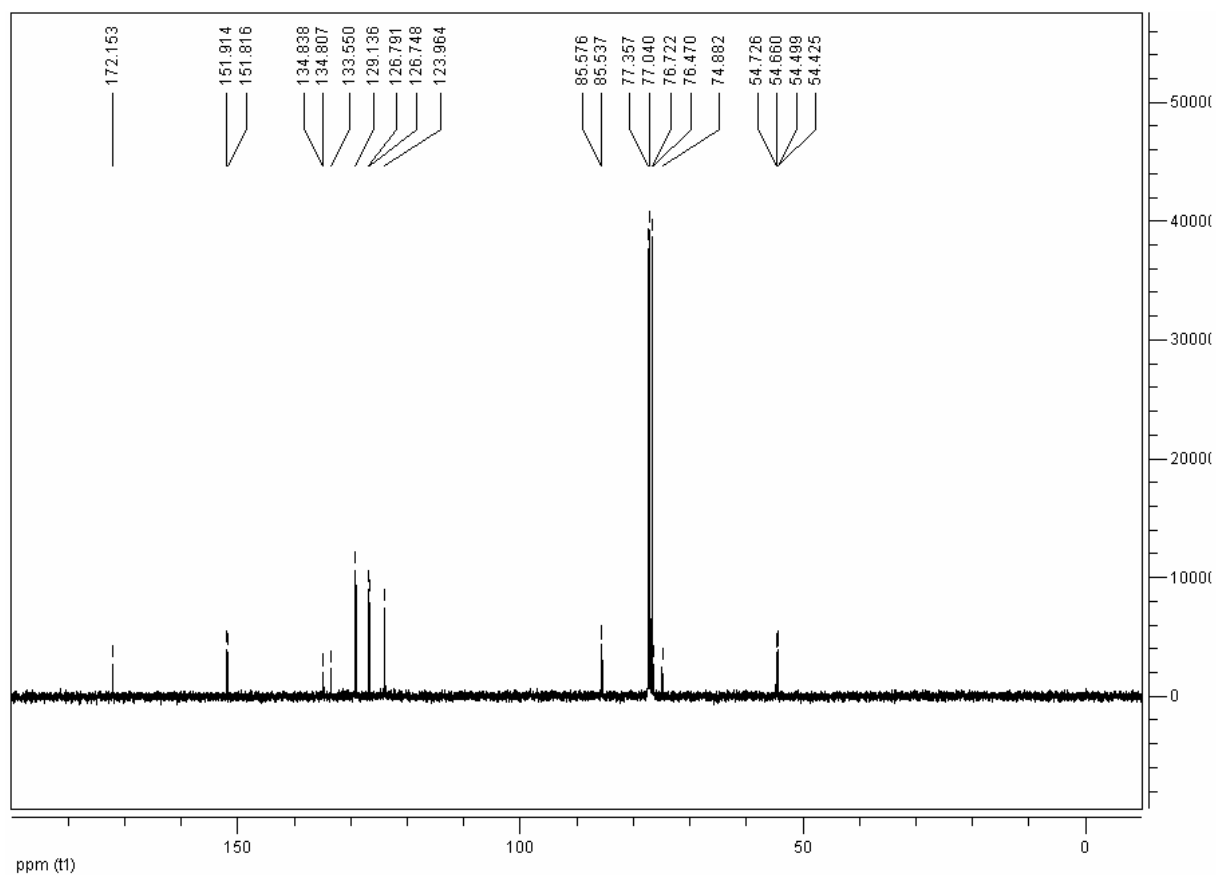
Dimethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*p*-chlorophenyl)methylphosphonate

(3c):

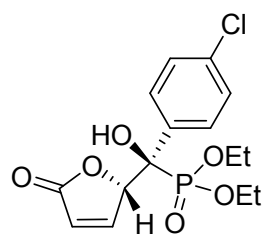


White solid; mp 123-126 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 20.76; ^1H -NMR (400 MHz, CDCl_3): δ 3.52 (d, $^3J_{\text{P-H}} = 10.6$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 3.94 (d, $^3J_{\text{P-H}} = 10.6$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 5.74 (t, $^3J_{\text{H-H}} = 2.0$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.18 (d, $^3J_{\text{H-H}} = 5.8$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.85 (d, $^3J_{\text{H-H}} = 5.8$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.43 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 2H, Ph), 7.63 (dd, $^3J_{\text{H-H}} = 8.7$ Hz, $^4J_{\text{P-H}} = 2.0$ Hz, 2H, Ph); ^{13}C -NMR (100 MHz, CDCl_3): δ 54.46 (d, $^2J_{\text{C,P}} = 7.5$ Hz, $\text{P}(\text{OCH}_3)_2$), 54.69 (d, $^2J_{\text{C,P}} = 6.6$ Hz, $\text{P}(\text{OCH}_3)_2$), 75.68 (d, $^1J_{\text{C,P}} = 159.8$ Hz, $\text{CP}(\text{OCH}_3)_2$), 85.56 (d, $^2J_{\text{C,P}} = 3.9$ Hz, $\text{HC}=\text{CHCH}$), 123.96, 126.77 (d, $^3J_{\text{C,P}} = 4.3$ Hz), 129.14, 133.55, 134.82 (d, $^4J_{\text{C,P}} = 3.1$ Hz), 151.86 (d, $^2J_{\text{C,P}} = 9.9$ Hz), 172.15; ESI-MS: 354.9 ($[\text{M}+\text{Na}]^+$); HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{ClO}_6\text{P}$: 355.0109 ($\text{M}+\text{Na}$) $^+$, found: 355.0116.

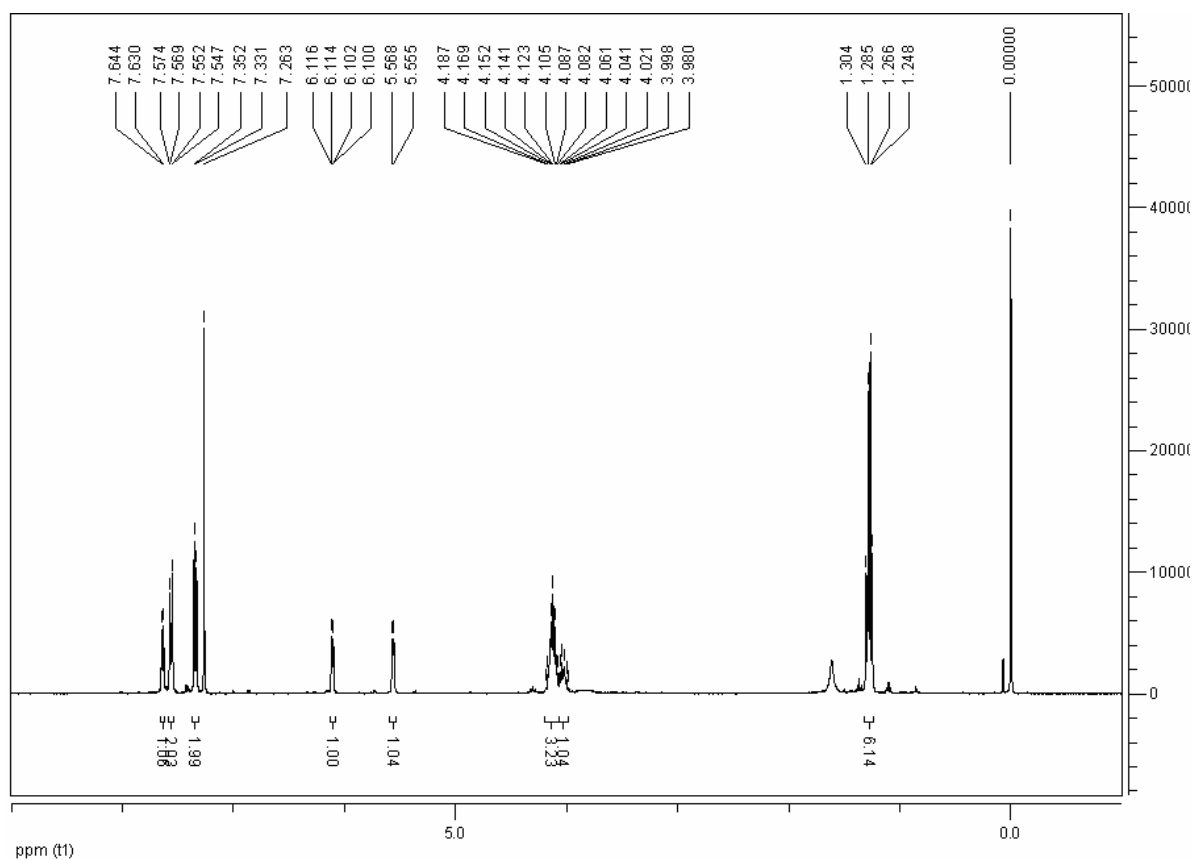


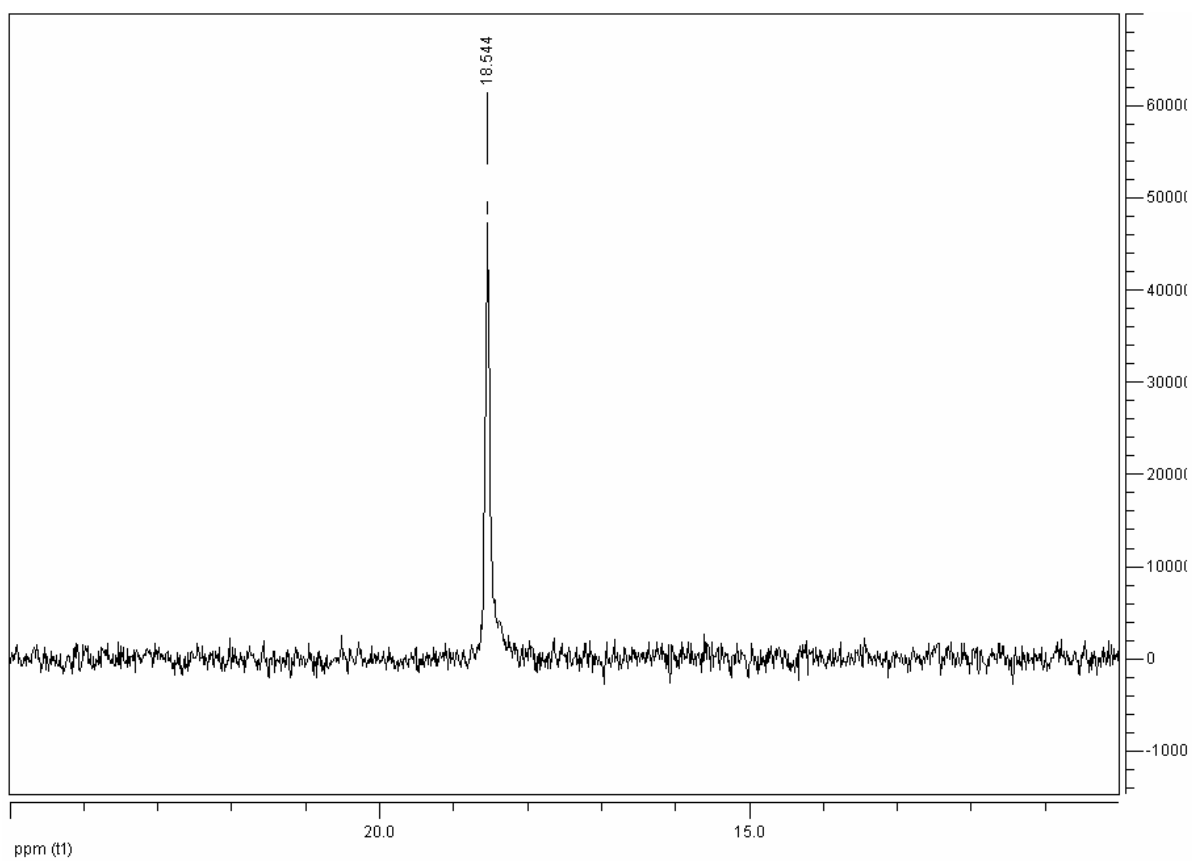
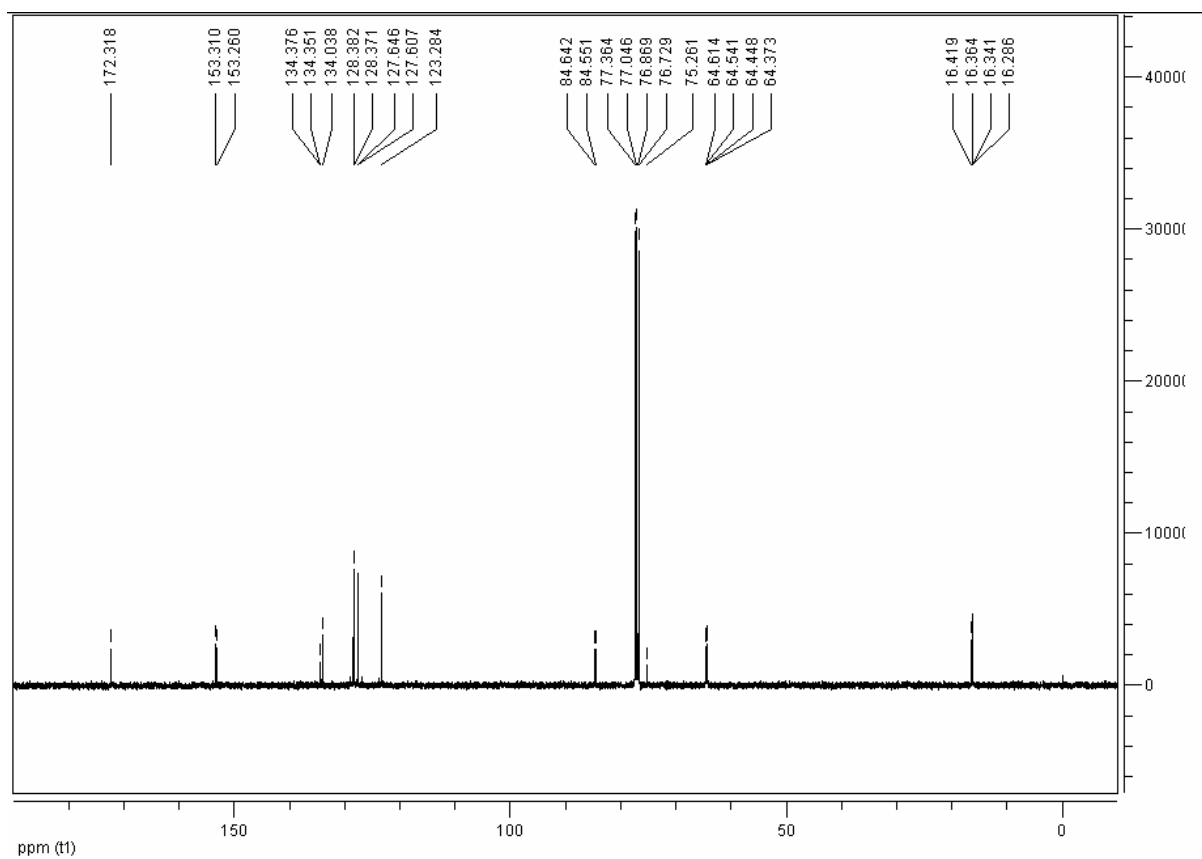


Diethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*p*-chlorophenyl)methylphosphonate (3d):

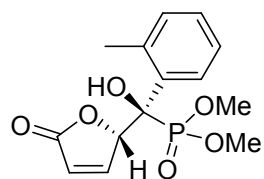


White solid; mp 77-80 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 18.54; ^1H -NMR (400 MHz, CDCl_3): δ 1.28 (q, $^3J_{\text{H-H}} = 7.5$ Hz, 6H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 3.98-4.19 (m, 4H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 5.56 (d, $^3J_{\text{H-H}} = 5.5$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.11 (dd, $^3J_{\text{H-H}} = 5.8$ Hz, $^4J_{\text{H-H}} = 1.0$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.34 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 2H, Ph), 7.57 (dd, $^3J_{\text{H-H}} = 8.7$ Hz, $^4J_{\text{P-H}} = 1.8$ Hz, 2H, Ph), 7.64 (d, $^3J_{\text{H-H}} = 5.8$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 16.31 (d, $^3J_{\text{C,P}} = 5.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 16.39 (d, $^3J_{\text{C,P}} = 5.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.41 (d, $^2J_{\text{C,P}} = 7.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.58 (d, $^2J_{\text{C,P}} = 7.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 76.80 (d, $^1J_{\text{C,P}} = 161.7$ Hz, $\text{CP}(\text{OCH}_2\text{CH}_3)_2$), 84.60 (d, $^2J_{\text{C,P}} = 9.2$ Hz, $\text{HC}=\text{CHCH}$), 123.29, 127.63 (d, $^3J_{\text{C,P}} = 3.9$ Hz), 128.38 (d, $^4J_{\text{C,P}} = 1.1$ Hz), 134.04, 134.36 (d, $^3J_{\text{C,P}} = 2.5$ Hz), 153.28 (d, $^2J_{\text{C,P}} = 5.0$ Hz), 172.32; ESI-MS: 383.0 ($[\text{M}+\text{Na}]^+$); HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{ClO}_6\text{P}$: 383.0422 ($\text{M}+\text{Na})^+$, found: 383.0415.

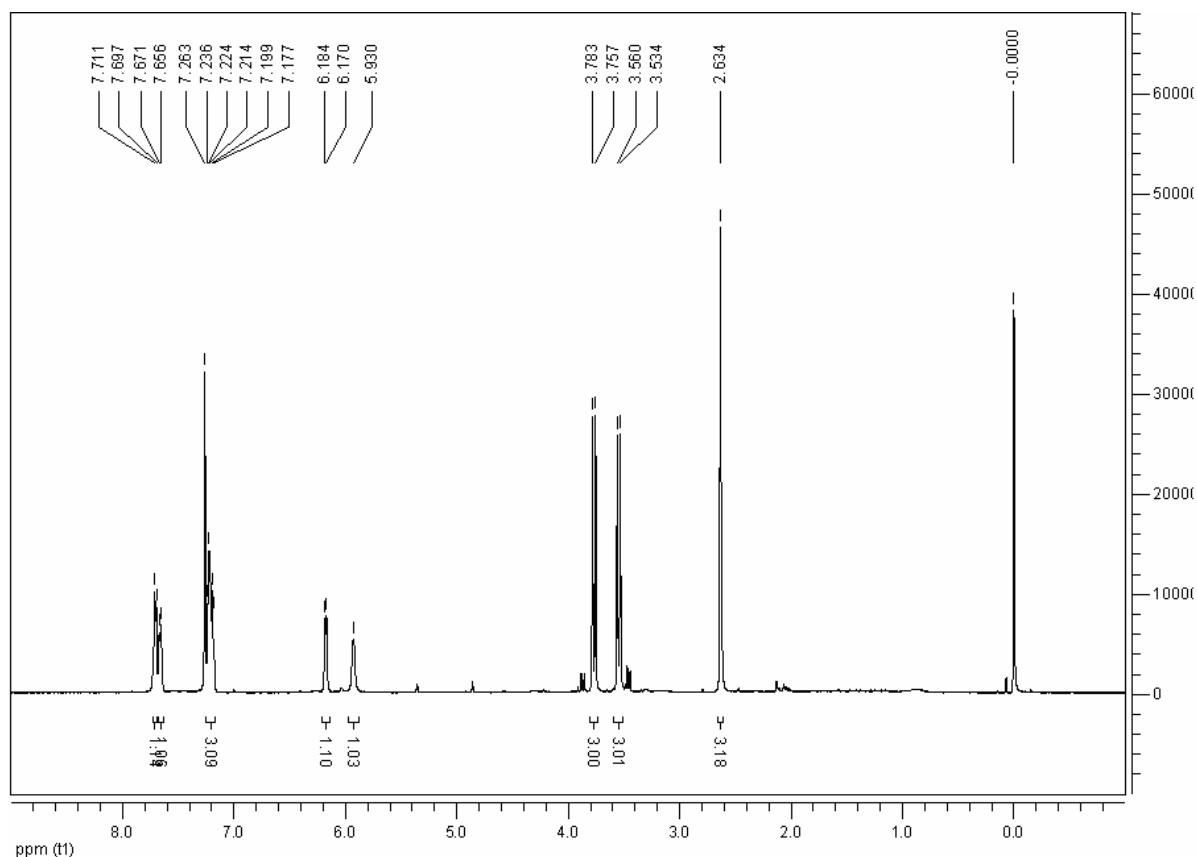


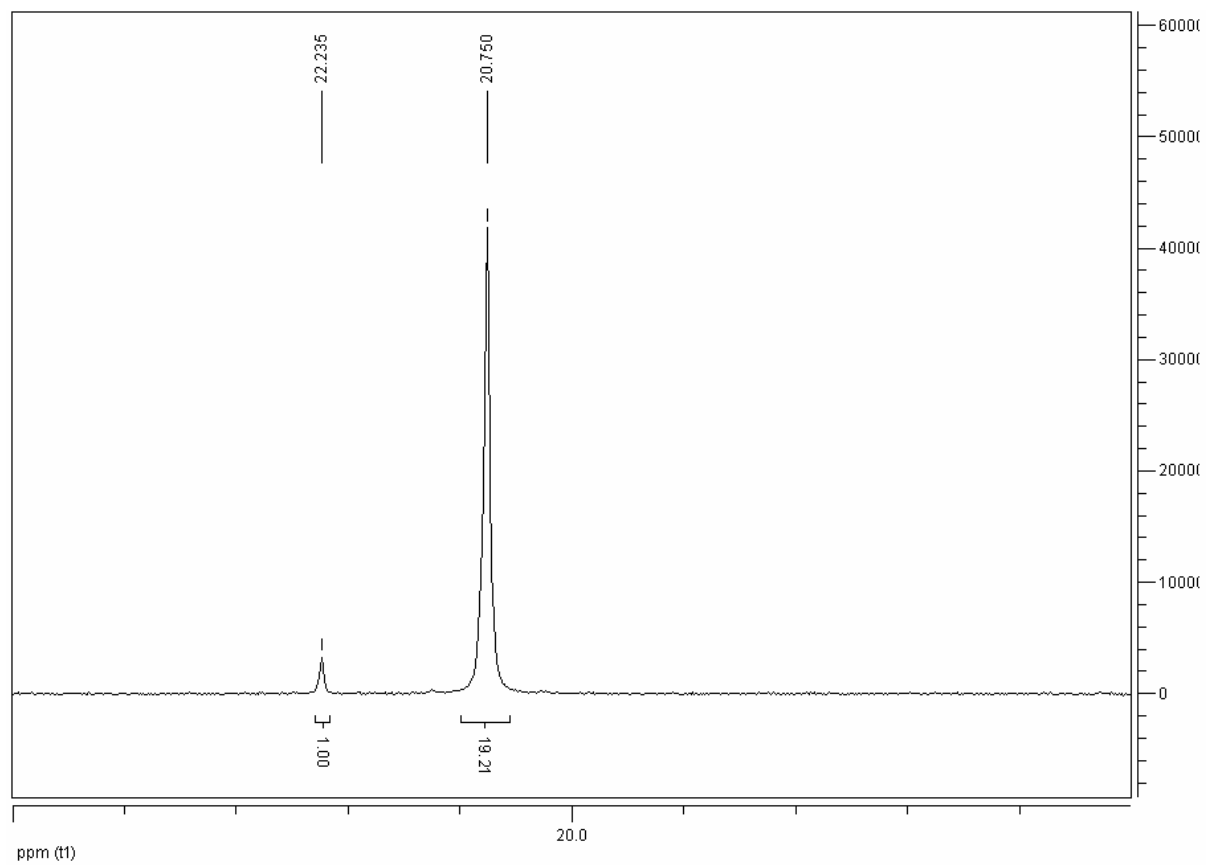
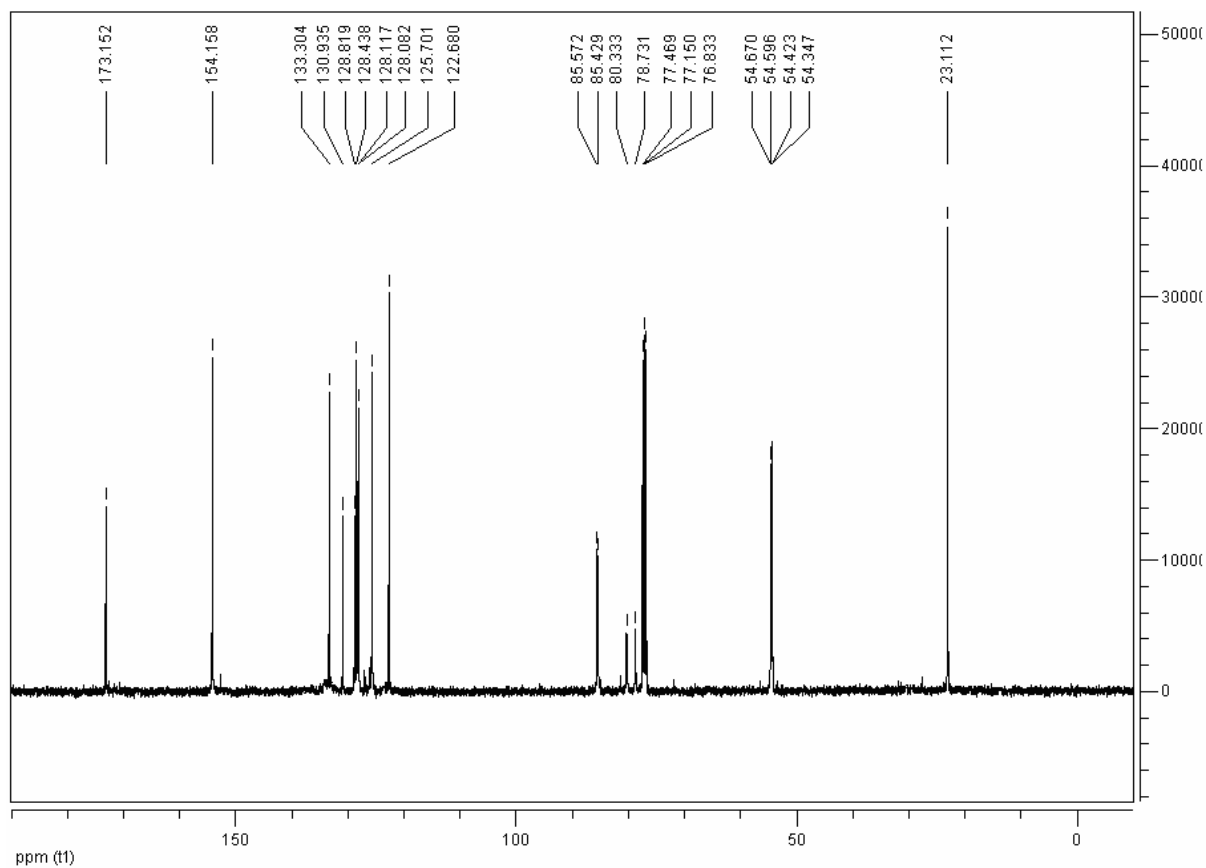


Dimethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*o*-tolyl)methylphosphonate (3e):

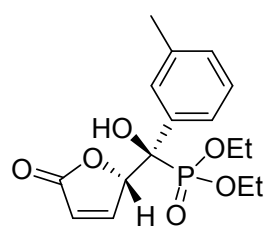


White solid; mp 89-91 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 20.75, 22.24; ^1H -NMR (400 MHz, CDCl_3): δ 2.63 (s, 3H, CH_3), 3.55 (d, $^3J_{\text{P-H}} = 10.5$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 3.78 (d, $^3J_{\text{P-H}} = 10.5$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 5.93 (s, 1H, $\text{HC}=\text{CHCH}$), 6.18 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.18-7.26 (m, 3H, *Ph*), 7.66 (d, $^3J_{\text{H-H}} = 5.9$ Hz, 1H, *Ph*), 7.70 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 23.11, 54.38 (d, $^2J_{\text{C,P}} = 7.7$ Hz, $\text{P}(\text{OCH}_3)_2$), 54.63 (d, $^2J_{\text{C,P}} = 7.7$ Hz, $\text{P}(\text{OCH}_3)_2$), 79.53 (d, $^1J_{\text{C,P}} = 161.1$ Hz, $\text{HCP}(\text{OCH}_3)_2$), 85.50 (d, $^2J_{\text{C,P}} = 14.4$ Hz, $\text{HC}=\text{CHCH}$), 122.68, 125.70, 128.10 (d, $^3J_{\text{C,P}} = 3.5$ Hz), 128.44, 128.82, 130.94, 133.30, 154.16, 173.15; ESI-MS: 312.7 ($[\text{M}+\text{H}]^+$); HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{O}_6\text{P}$: 335.0655 ($\text{M}+\text{Na}$) $^+$, found: 335.0660.

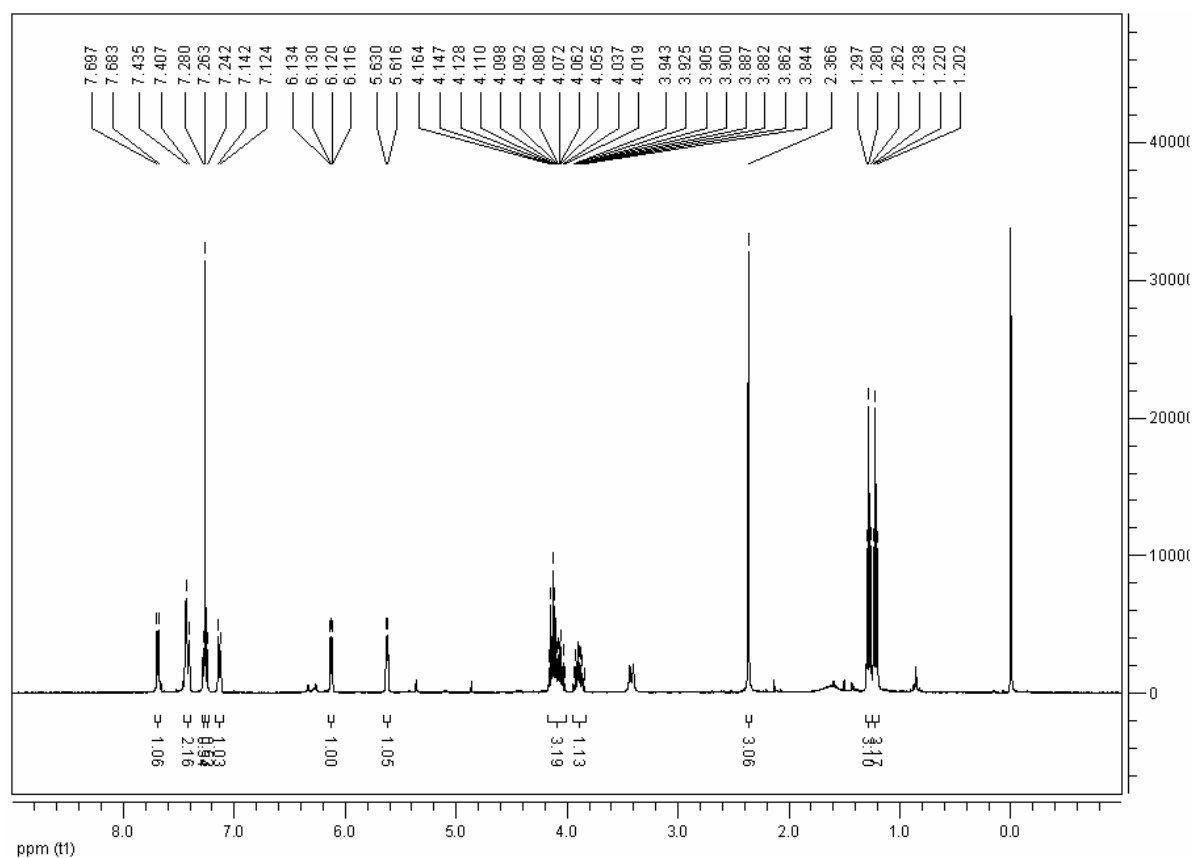


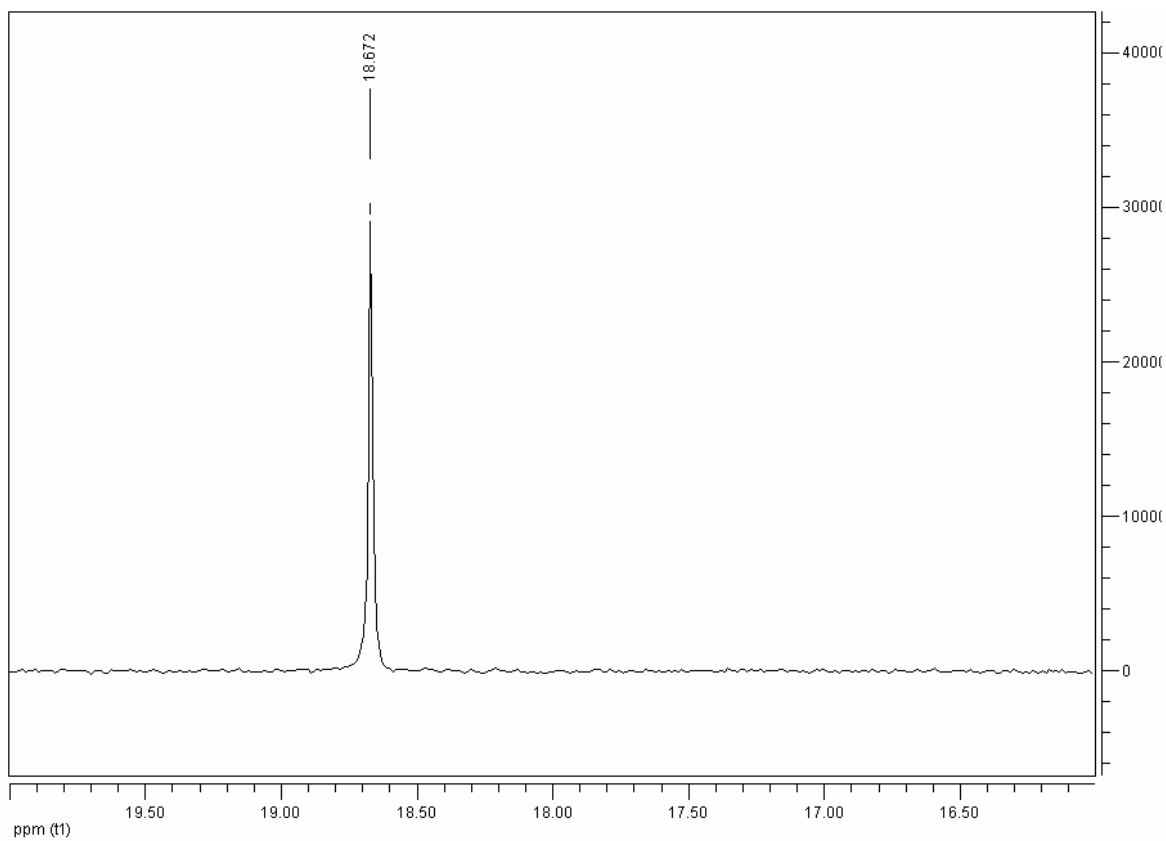
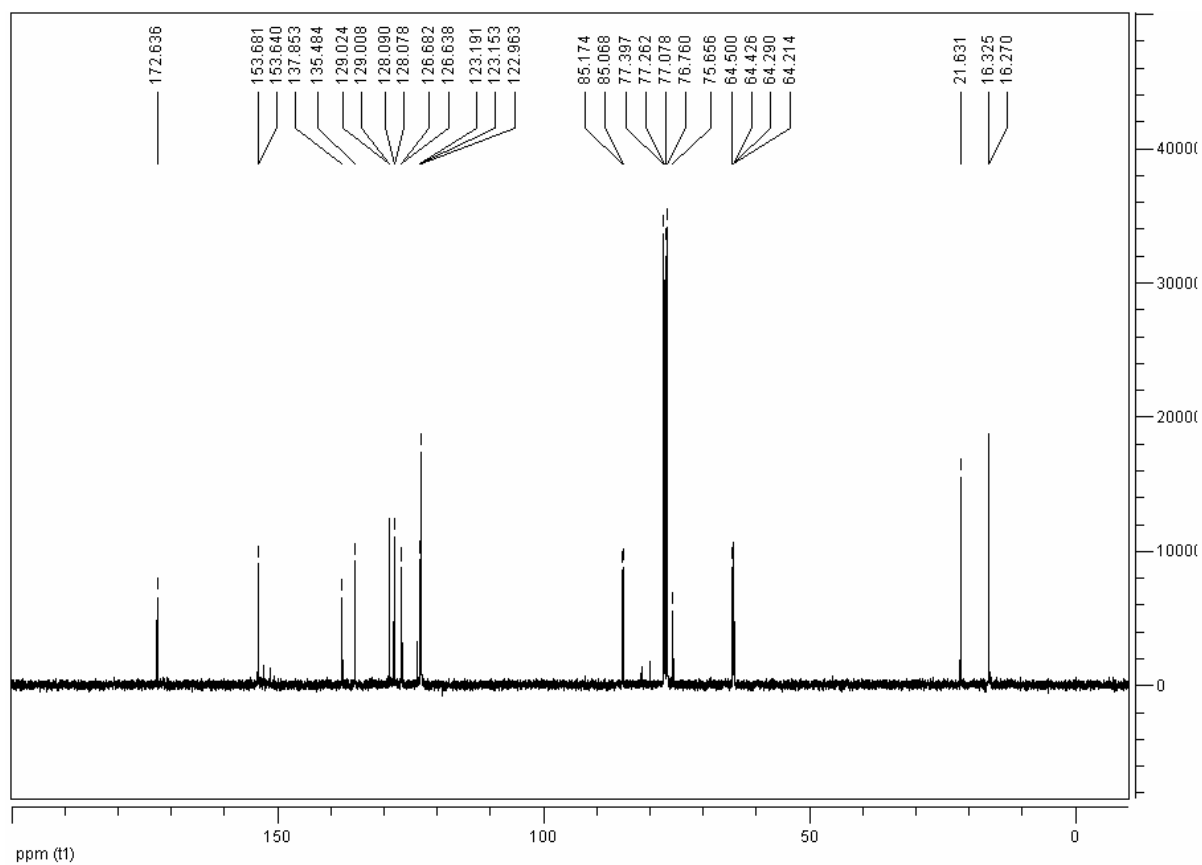


Diethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*m*-tolyl)methylphosphonate (3f):

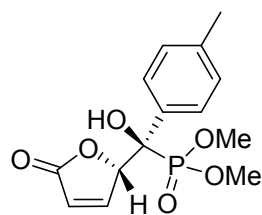


White solid; mp 48-51 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 18.67; ^1H -NMR (400 MHz, CDCl_3): δ 1.22 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 1.28 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 2.37 (s, 3H, CH_3), 3.84-4.16 (m, 4H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 5.62 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.12 (dd, $^3J_{\text{H-H}} = 5.6$ Hz, $^3J_{\text{H-H}} = 1.8$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.13 (d, $^3J_{\text{H-H}} = 7.4$ Hz, 1H, Ph), 7.26 (d, $^3J_{\text{H-H}} = 15.2$ Hz, 1H, Ph), 7.42 (d, $^3J_{\text{H-H}} = 11.1$ Hz, 2H, Ph), 7.69 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 16.30 (d, $^3J_{\text{C,P}} = 5.5$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 21.63, 64.25 (d, $^2J_{\text{C,P}} = 7.7$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.46 (d, $^2J_{\text{C,P}} = 7.3$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 76.46 (d, $^1J_{\text{C,P}} = 161.5$ Hz, $\text{CP}(\text{OCH}_2\text{CH}_3)_2$), 85.12 (d, $^2J_{\text{C,P}} = 10.6$ Hz, $\text{HC}=\text{CHCH}$), 122.96, 123.17 (d, $^3J_{\text{C,P}} = 3.9$ Hz), 126.66 (d, $^3J_{\text{C,P}} = 4.4$ Hz), 128.08 (d, $^4J_{\text{C,P}} = 1.2$ Hz), 129.02 (d, $^4J_{\text{C,P}} = 1.6$ Hz), 135.48, 137.85, 153.66 (d, $^3J_{\text{C,P}} = 4.1$ Hz), 172.63; ESI-MS: 340.7 ($[\text{M}+\text{H}]^+$); HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{O}_6\text{P}$: 363.0968 ($\text{M}+\text{Na}$) $^+$, found: 363.0962.

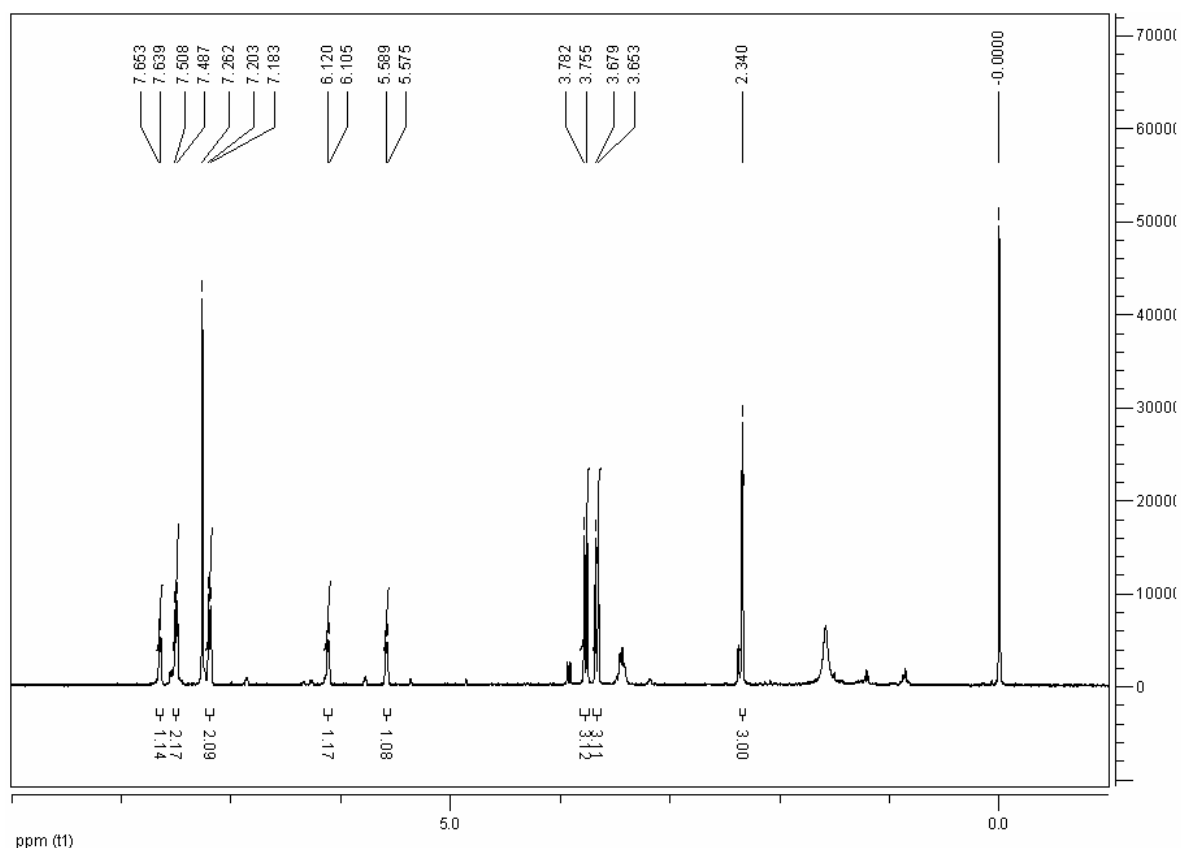


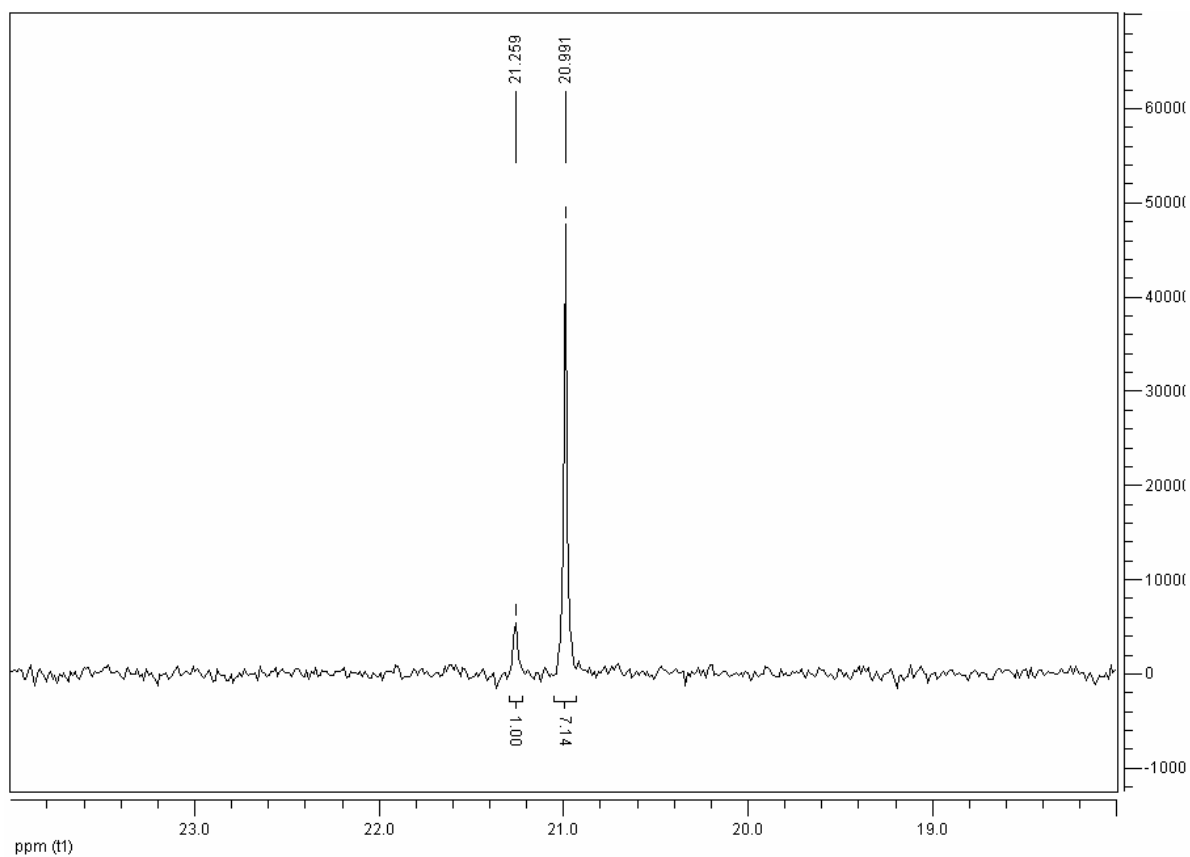
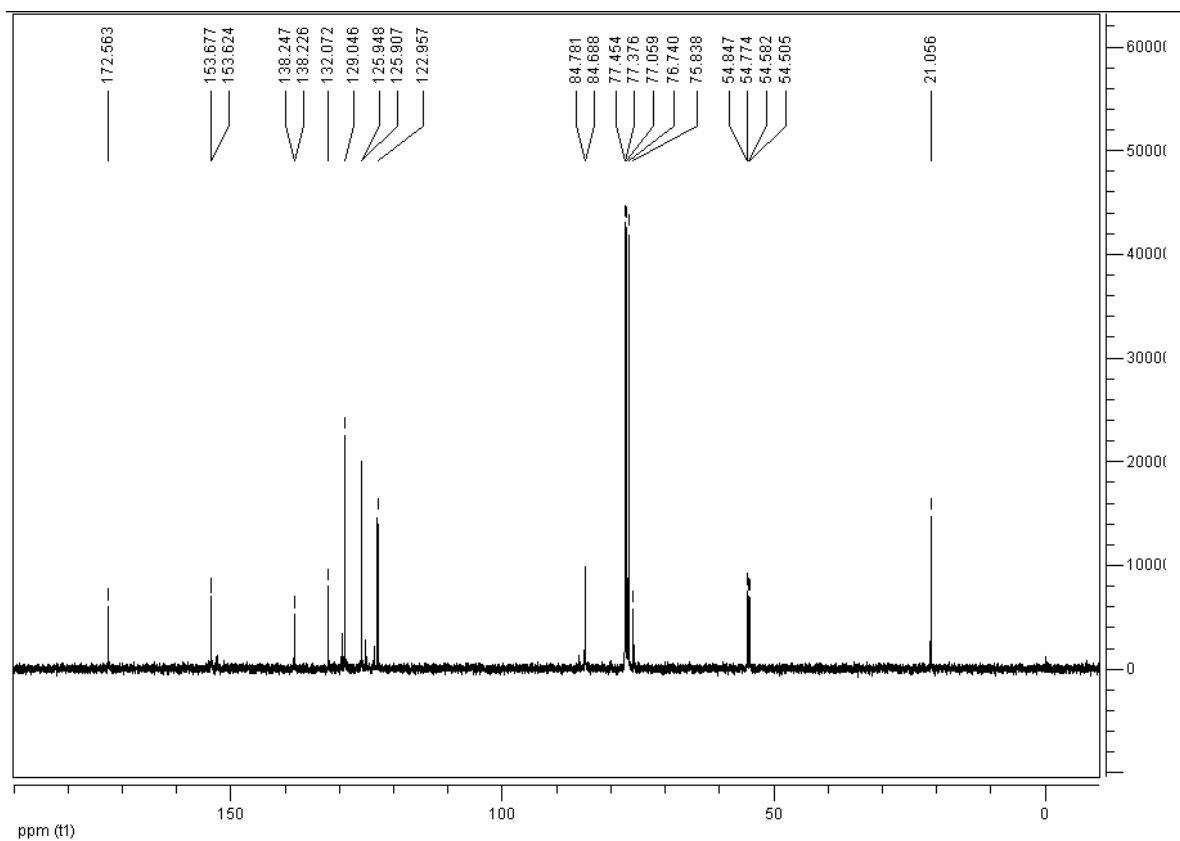


Dimethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*p*-tolyl)methylphosphonate (3g):

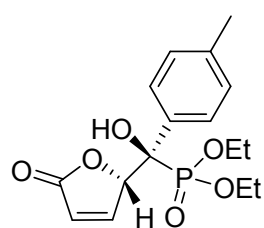


White solid; mp 127-130 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 20.99, 21.26; ^1H -NMR (400 MHz, CDCl_3): δ 2.34 (s, 3H, CH_3), 3.67 (d, $^3J_{\text{P-H}} = 10.4$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 3.77 (d, 3H, $^3J_{\text{P-H}} = 10.5$ Hz, $\text{P}(\text{OCH}_3)_2$), 5.58 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.11 (dd, $^3J_{\text{H-H}} = 5.7$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.19 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Ph), 7.50 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 2H, Ph), 7.65 (d, $^3J_{\text{H-H}} = 5.7$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 21.06, 54.54 (d, $^2J_{\text{C,P}} = 7.7$ Hz, $\text{P}(\text{OCH}_3)_2$), 54.81 (d, $^2J_{\text{C,P}} = 7.4$ Hz, $\text{P}(\text{OCH}_3)_2$), 76.65 (d, $^1J_{\text{C,P}} = 162.5$ Hz, $\text{CP}(\text{OCH}_3)_2$), 84.73 (d, $^2J_{\text{C,P}} = 9.4$ Hz, $\text{HC}=\text{CHCH}$), 122.96, 125.93 (d, $^3J_{\text{C,P}} = 4.1$ Hz), 129.05, 132.07, 138.24 (d, $^4J_{\text{C,P}} = 2.1$ Hz), 153.65 (d, $^3J_{\text{C,P}} = 5.4$ Hz), 172.56; ESI-MS: 312.7 ($[\text{M}+\text{H}]^+$); HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{O}_6\text{P}$: 335.0655 ($\text{M}+\text{Na}$) $^+$, found: 335.0662.

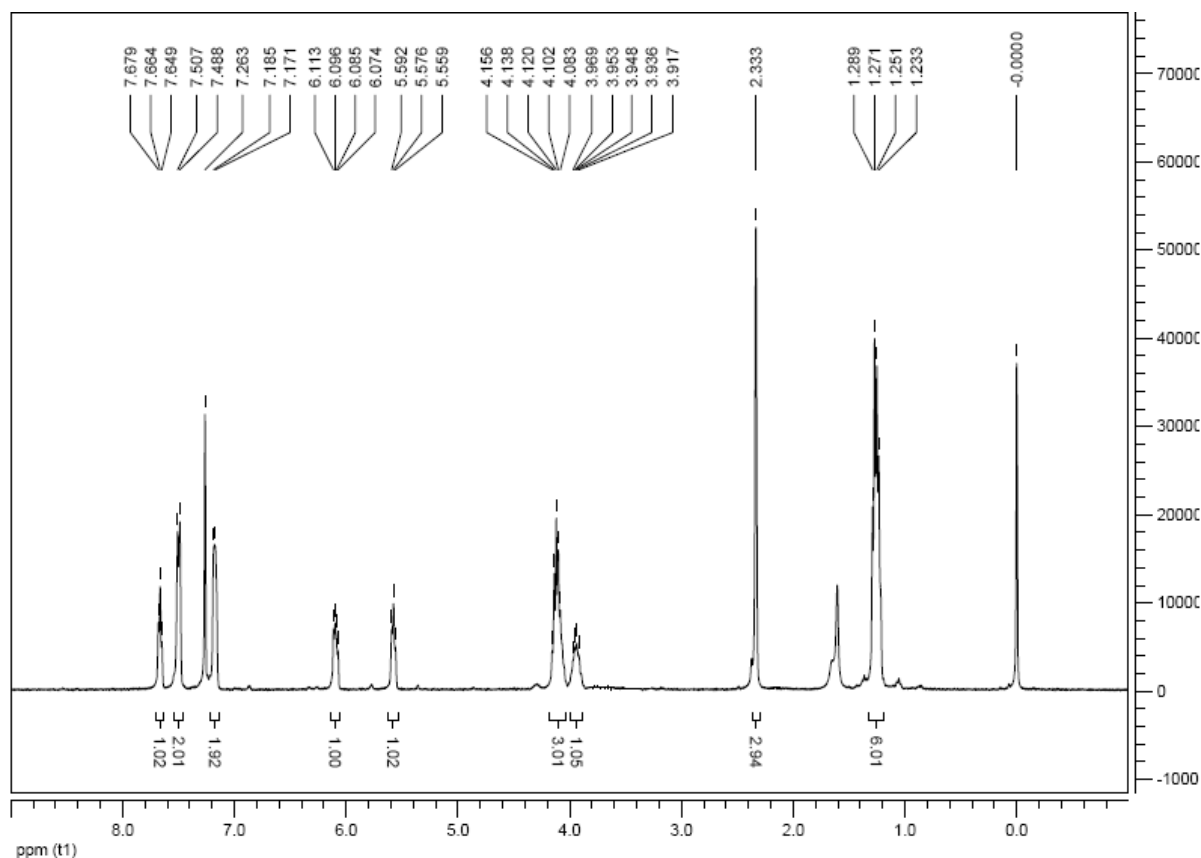


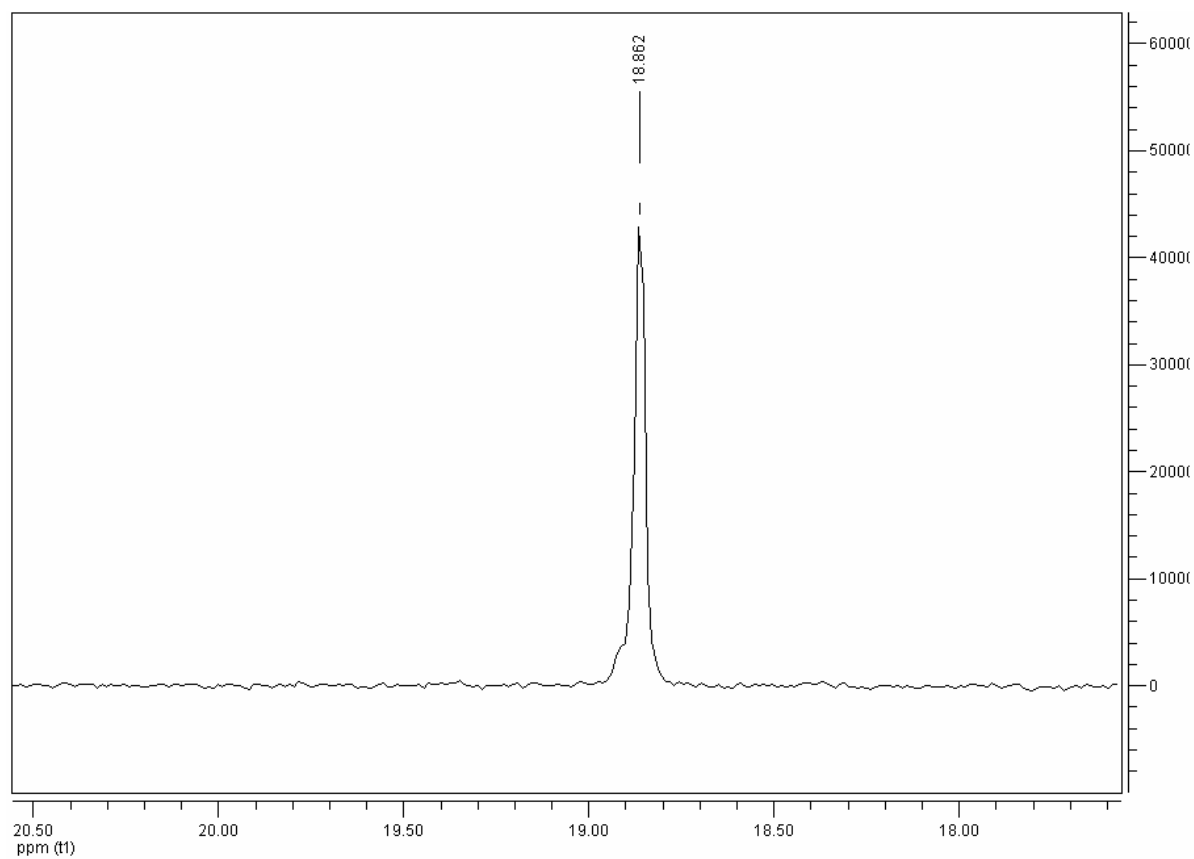
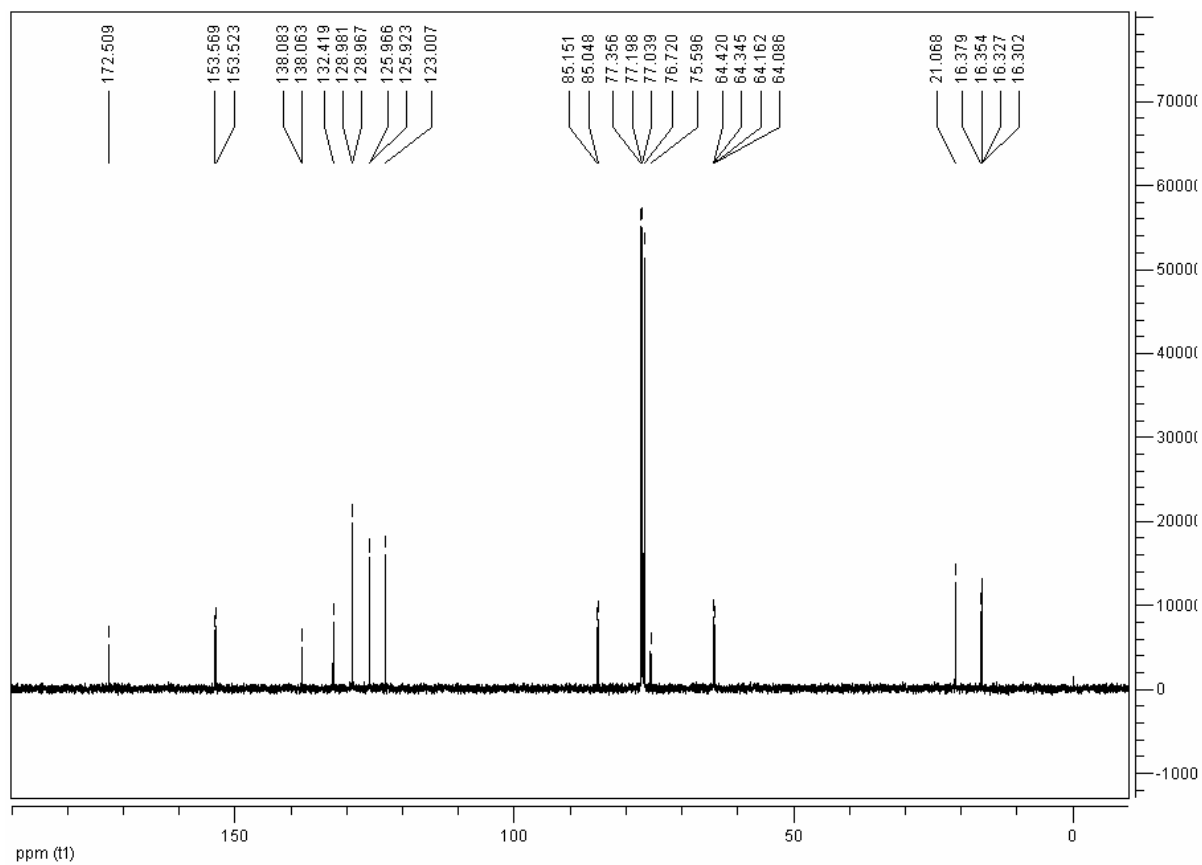


Diethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*p*-tolyl)methylphosphonate (3h):

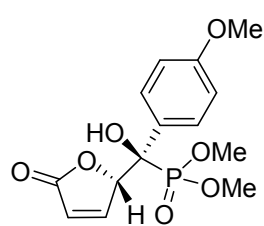


White solid; mp 87-89 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 18.86; ^1H -NMR (400 MHz, CDCl_3): δ 1.26 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 6H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 2.33 (s, 3H, CH_3), 3.92-4.16 (m, 4H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 5.58 (t, $^3J_{\text{H-H}} = 6.2$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.12 (dd, $^3J_{\text{H-H}} = 9.9$ Hz, $^3J_{\text{H-H}} = 4.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.18 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Ph), 7.50 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Ph), 7.66 (t, $^3J_{\text{H-H}} = 6.2$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 16.31 (d, $^3J_{\text{C,P}} = 2.5$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 16.37 (d, $^3J_{\text{C,P}} = 2.5$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 21.07, 64.12 (d, $^2J_{\text{C,P}} = 7.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.38 (d, $^2J_{\text{C,P}} = 7.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 76.40 (d, $^1J_{\text{C,P}} = 161.2$ Hz, $\text{CP}(\text{OCH}_2\text{CH}_3)_2$), 85.10 (d, $^2J_{\text{C,P}} = 10.4$ Hz, $\text{HC}=\text{CHCH}$), 123.01, 125.94 (d, $^4J_{\text{C,P}} = 4.3$ Hz), 128.97 (d, $^3J_{\text{C,P}} = 5.6$ Hz), 132.42, 138.07 (d, $^4J_{\text{C,P}} = 2.0$ Hz), 153.55 (d, $^3J_{\text{C,P}} = 4.6$ Hz), 172.51; ESI-MS: 340.7 ($[\text{M}+\text{H}]^+$); HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{O}_6\text{P}$: 363.0968 ($\text{M}+\text{Na}$) $^+$, found: 363.0962.

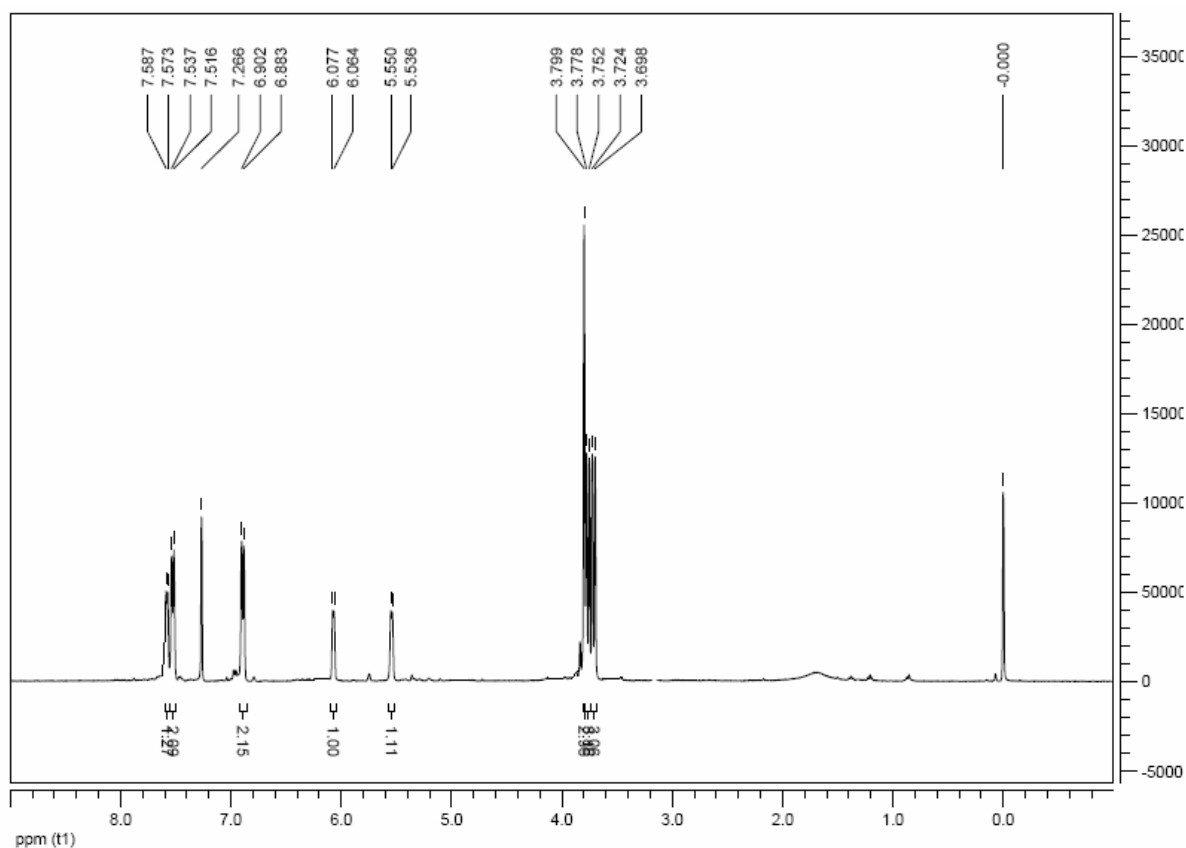


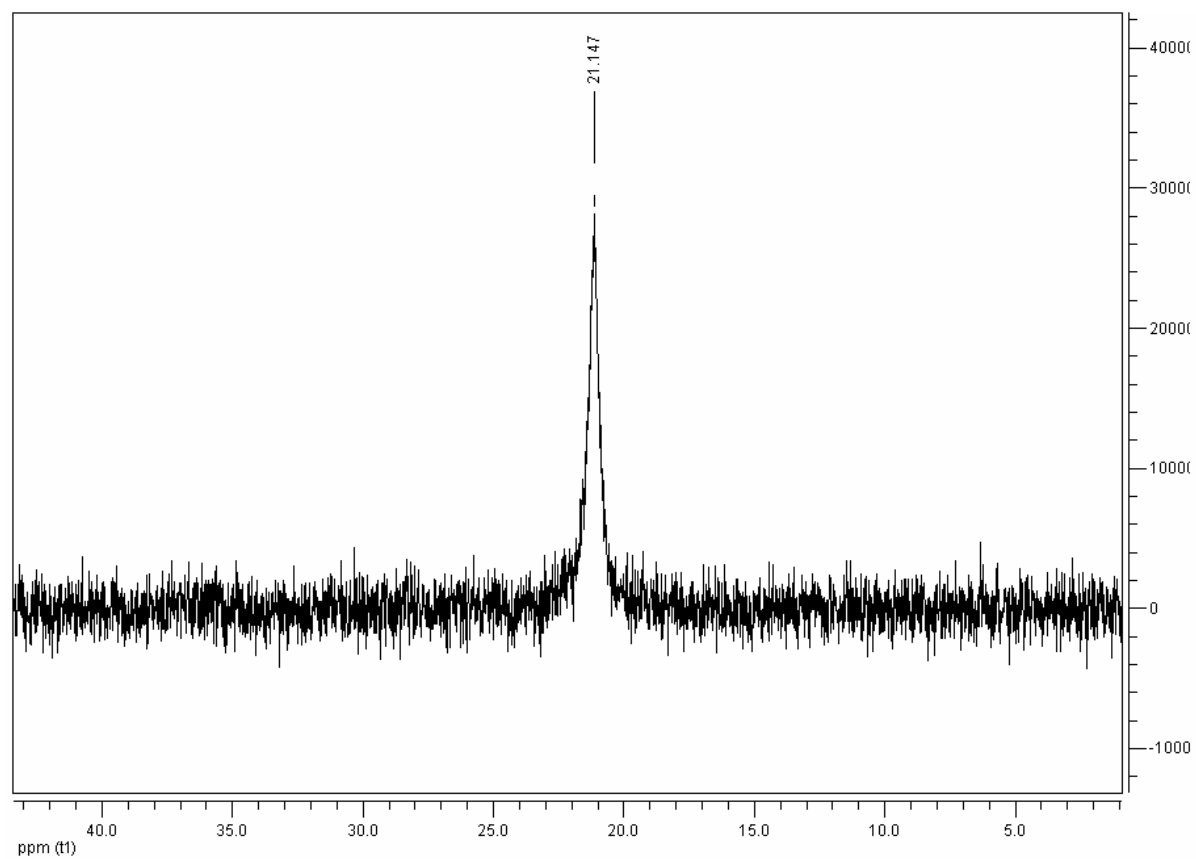
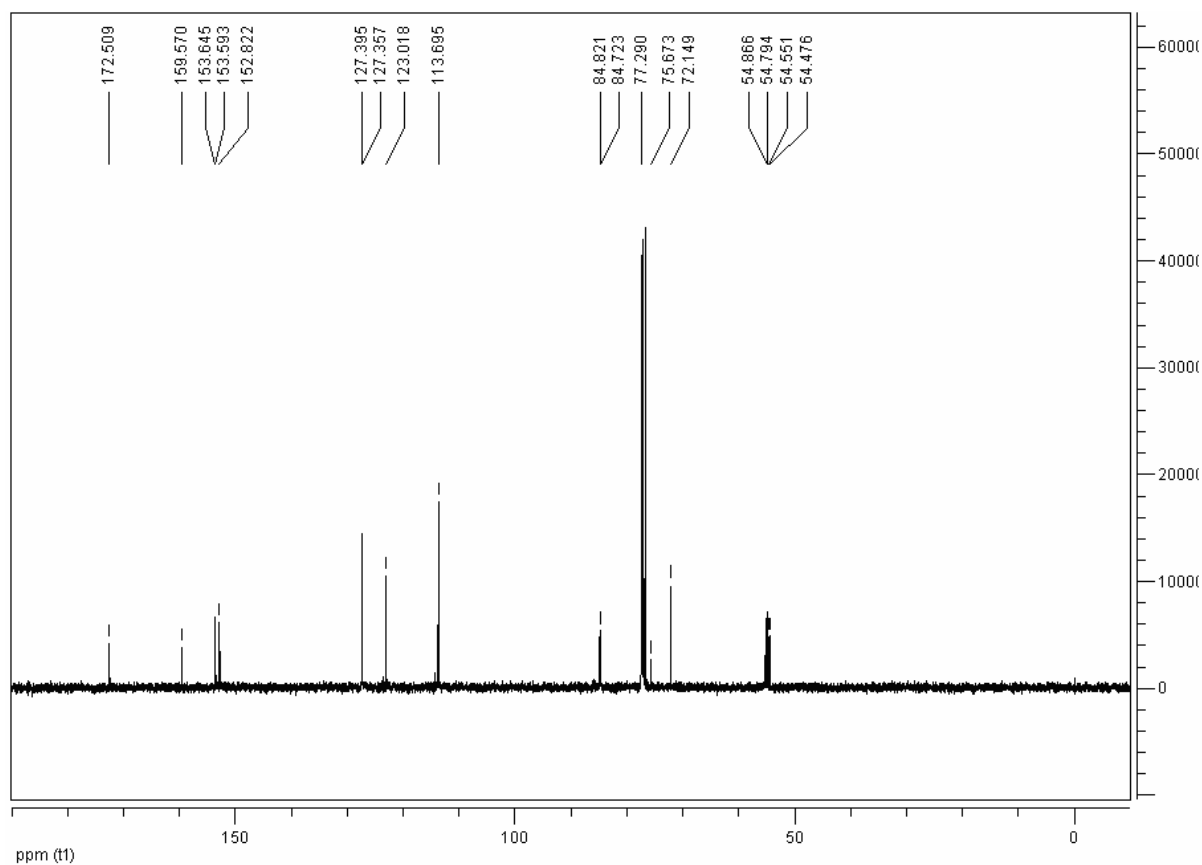


Dimethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*p*-methoxyphenyl)methylphosphonate (3i):

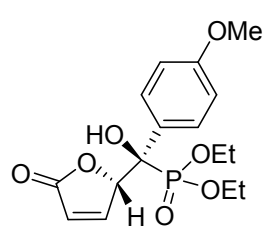


White solid; mp 82-84 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 21.15, 21.26; ^1H -NMR (400 MHz, CDCl_3): δ 3.71 (d, $^3J_{\text{P-H}} = 10.3$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 3.77 (d, $^3J_{\text{P-H}} = 10.4$ Hz, 3H, $\text{P}(\text{OCH}_3)_2$), 3.80 (s, 3H, CH_3), 5.54 (d, $^3J_{\text{H-H}} = 5.5$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.07 (dd, $^3J_{\text{H-H}} = 5.4$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.89 (d, $^3J_{\text{H-H}} = 7.9$ Hz, 2H, Ph), 7.53 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H, Ph), 7.61 (d, $^3J_{\text{H-H}} = 5.5$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 54.51 (d, $^2J_{\text{C,P}} = 7.5$ Hz, $\text{P}(\text{OCH}_3)_2$), 54.83 (d, $^2J_{\text{C,P}} = 7.3$ Hz, $\text{P}(\text{OCH}_3)_2$), 72.15, 76.48 (d, $^1J_{\text{C,P}} = 162.7$ Hz, $\text{CP}(\text{OCH}_3)_2$), 84.77 (d, $^2J_{\text{C,P}} = 9.9$ Hz, $\text{HC}=\text{CHCH}$), 113.70, 123.02, 127.38 (d, $^3J_{\text{C,P}} = 3.8$ Hz), 152.82, 153.62 (d, $^3J_{\text{C,P}} = 5.2$ Hz), 159.57, 172.51; ESI-MS: 328.6 ($[\text{M}+\text{H}]^+$); HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{P}$: 351.0600 ($\text{M}+\text{Na}^+$), found: 351.0604.

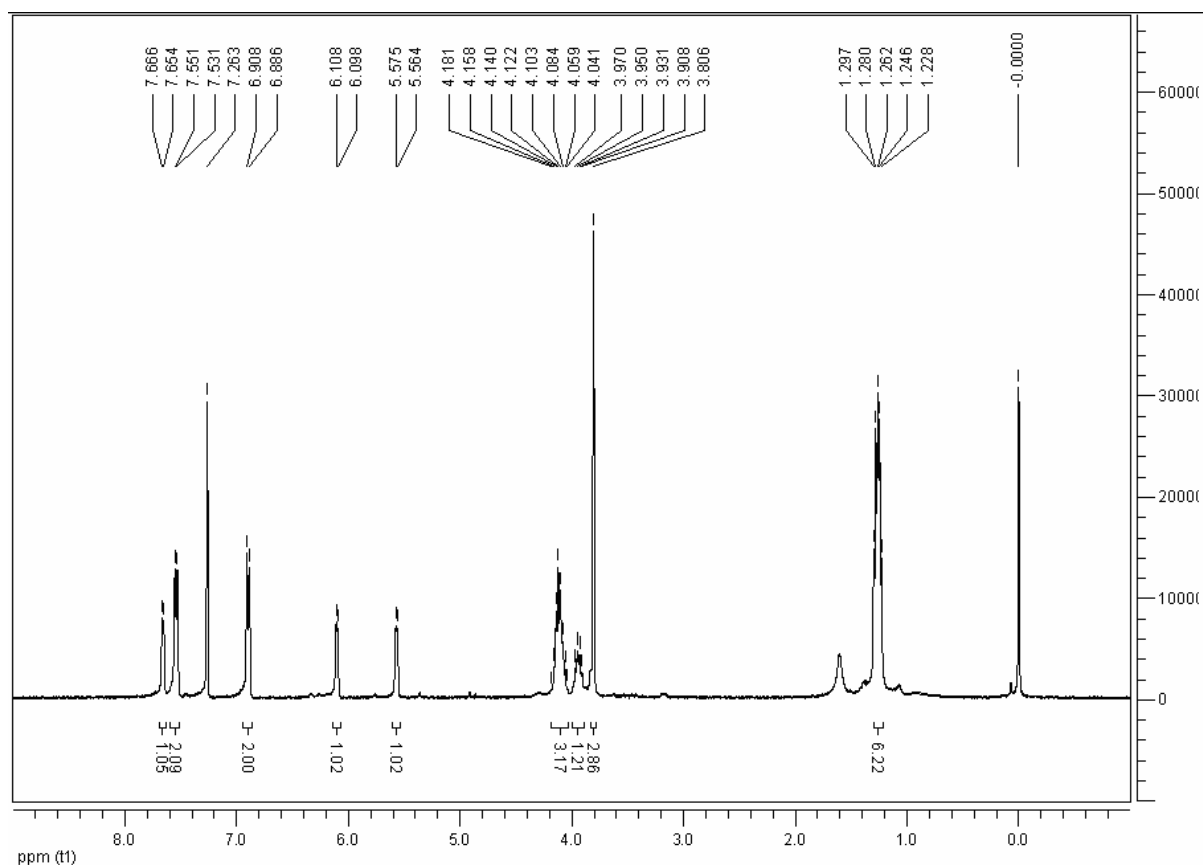


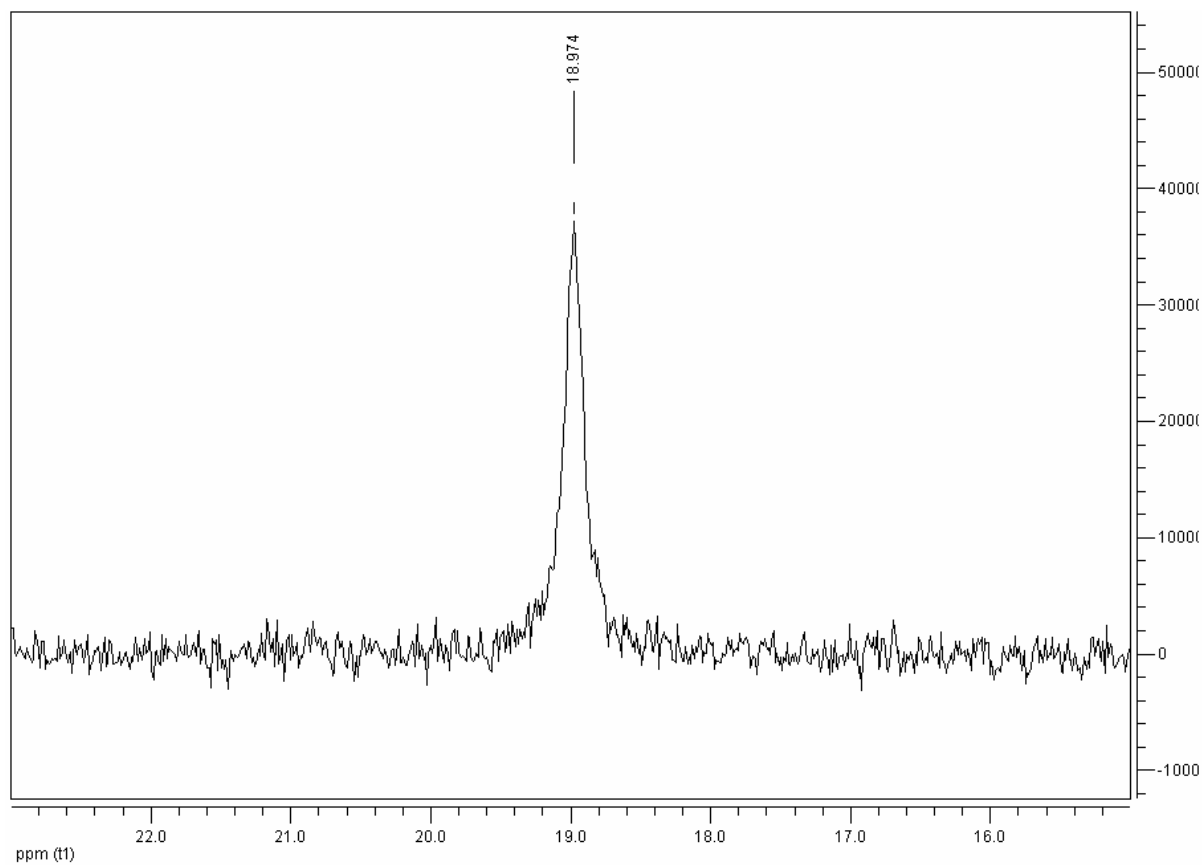
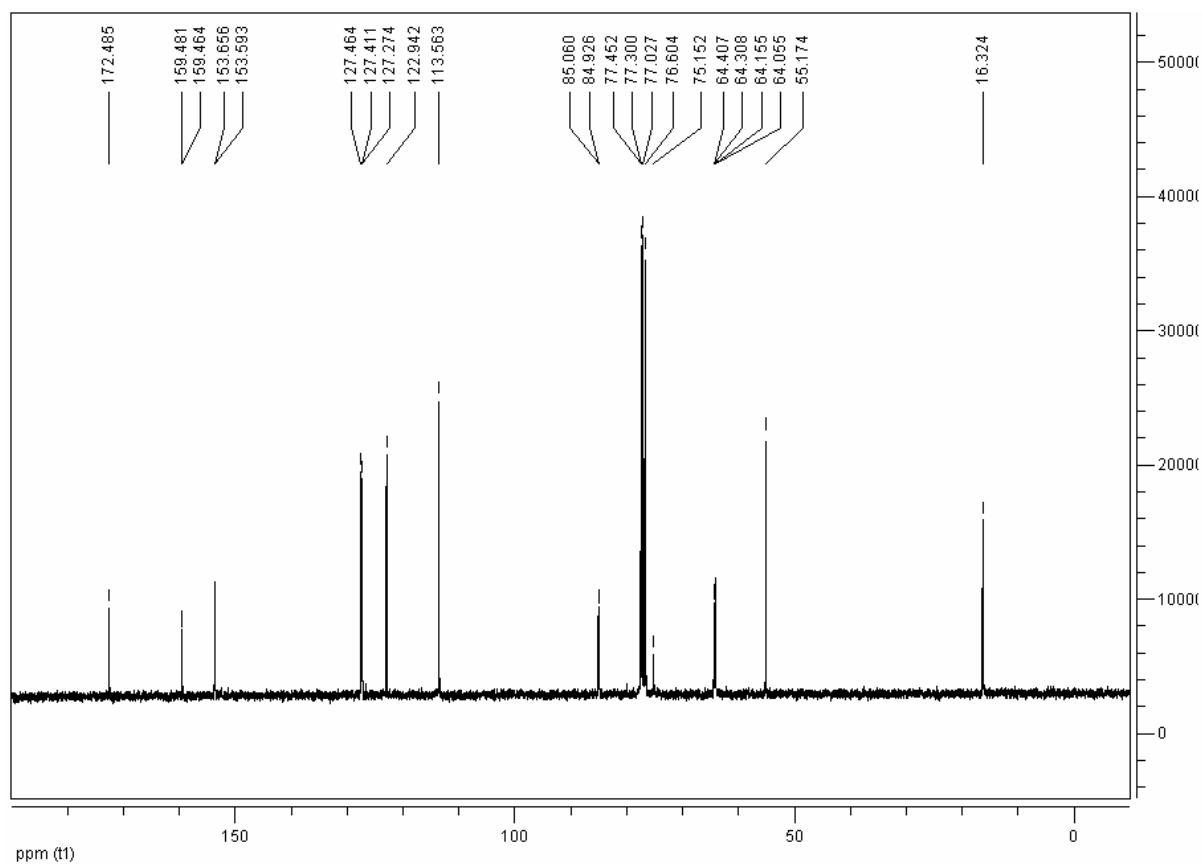


Diethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*p*-methoxyphenyl)methylphosphonate (3j):

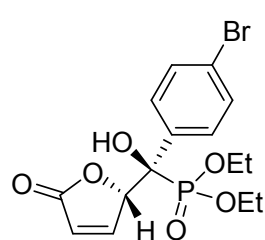


White solid; mp 72-75 °C; ^{31}P -NMR (121 MHz, CDCl_3): δ 18.97; ^1H -NMR (400 MHz, CDCl_3): δ 1.23-1.30 (m, 6H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 3.81 (s, 3H, CH_3), 3.91-4.18 (m, 4H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 5.57 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.10 (dd, $^3J_{\text{H-H}} = 4.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.18 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 2H, Ph), 7.50 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Ph), 7.66 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 16.32, 55.17, 64.10 (d, $^2J_{\text{C,P}} = 7.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.36 (d, $^2J_{\text{C,P}} = 7.4$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 76.23 (d, $^1J_{\text{C,P}} = 162.1$ Hz, $\text{CP}(\text{OCH}_2\text{CH}_3)_2$), 84.99 (d, $^2J_{\text{C,P}} = 10.1$ Hz, $\text{HC}=\text{CHCH}$), 113.56, 122.94, 127.27, 127.44 (d, $^3J_{\text{C,P}} = 4.0$ Hz), 153.62 (d, $^3J_{\text{C,P}} = 4.8$ Hz), 159.47 (d, $^4J_{\text{C,P}} = 1.2$ Hz), 172.49; ESI-MS: 356.7 ($[\text{M}+\text{H}]^+$); HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{O}_6\text{P}$: 379.0917 ($\text{M}+\text{Na}^+$), found: 379.0925.

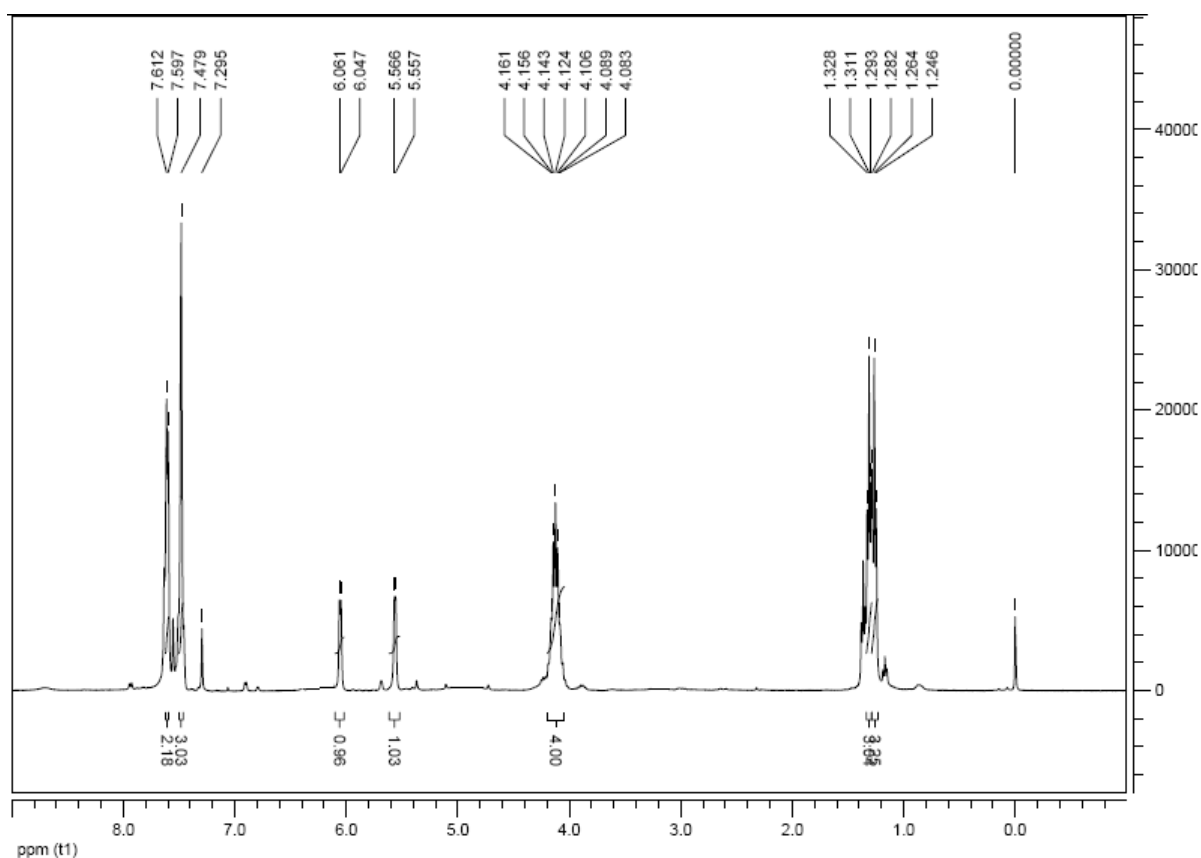


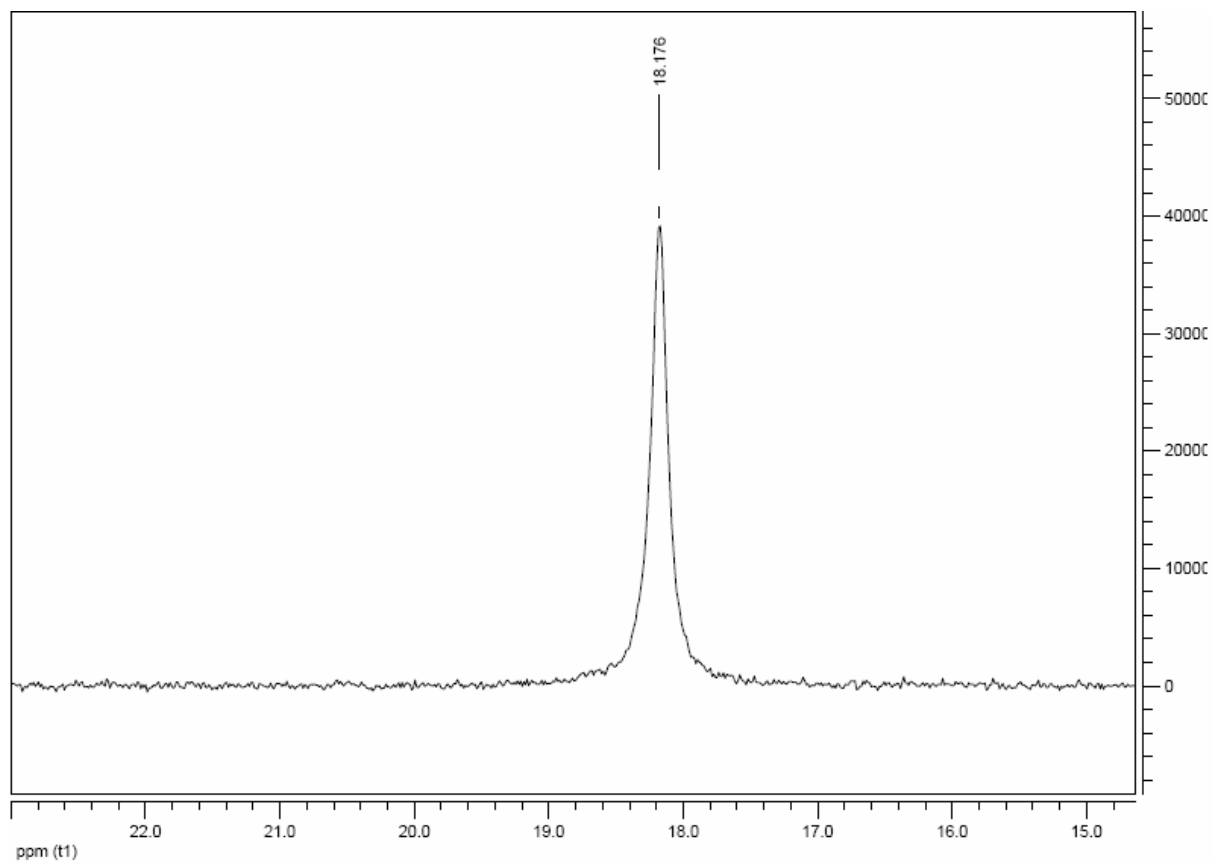
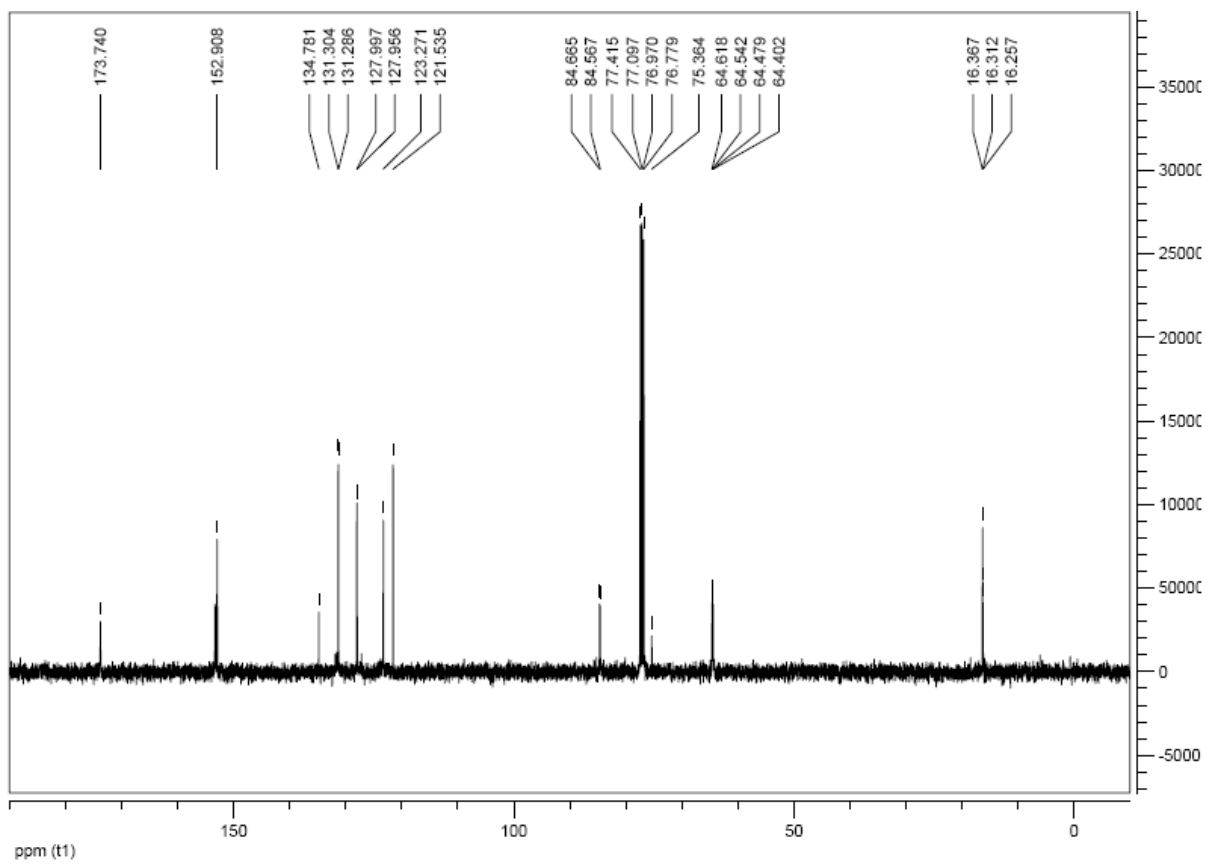


Diethyl hydroxy(5-oxo-2,5-dihydrofuran-2-yl)(*p*-bromophenyl)methylphosphonate (3k):

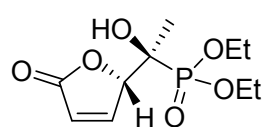


White oil; ^{31}P -NMR (121 MHz, CDCl_3): δ 18.18; ^1H -NMR (400 MHz, CDCl_3): δ 1.25-1.33 (m, 6H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 4.08-4.16 (m, 4H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 5.56 (d, $^3J_{\text{H-H}} = 3.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.05 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.48 (m, 3H, Ph, $\text{HC}=\text{CHCH}$), 7.60 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 2H, Ph); ^{13}C -NMR (100 MHz, CDCl_3): δ 16.32 (t, $^3J_{\text{C,P}} = 5.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.44 (d, $^2J_{\text{C,P}} = 7.7$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 64.58 (d, $^2J_{\text{C,P}} = 7.7$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 76.23 (d, $^1J_{\text{C,P}} = 161.7$ Hz, $\text{CP}(\text{OCH}_2\text{CH}_3)_2$), 84.61 (d, $^2J_{\text{C,P}} = 9.8$ Hz, $\text{HC}=\text{CHCH}$), 121.54, 123.27, 127.98 (d, $^3J_{\text{C,P}} = 4.1$ Hz), 131.30 (d, $^3J_{\text{C,P}} = 1.8$ Hz), 134.78, 152.91, 173.74; ESI-MS: 404.7 ($[\text{M}+\text{H}]^+$); HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{BrO}_6\text{P}$: 426.9916 ($\text{M}+\text{Na}^+$), found: 426.9919.

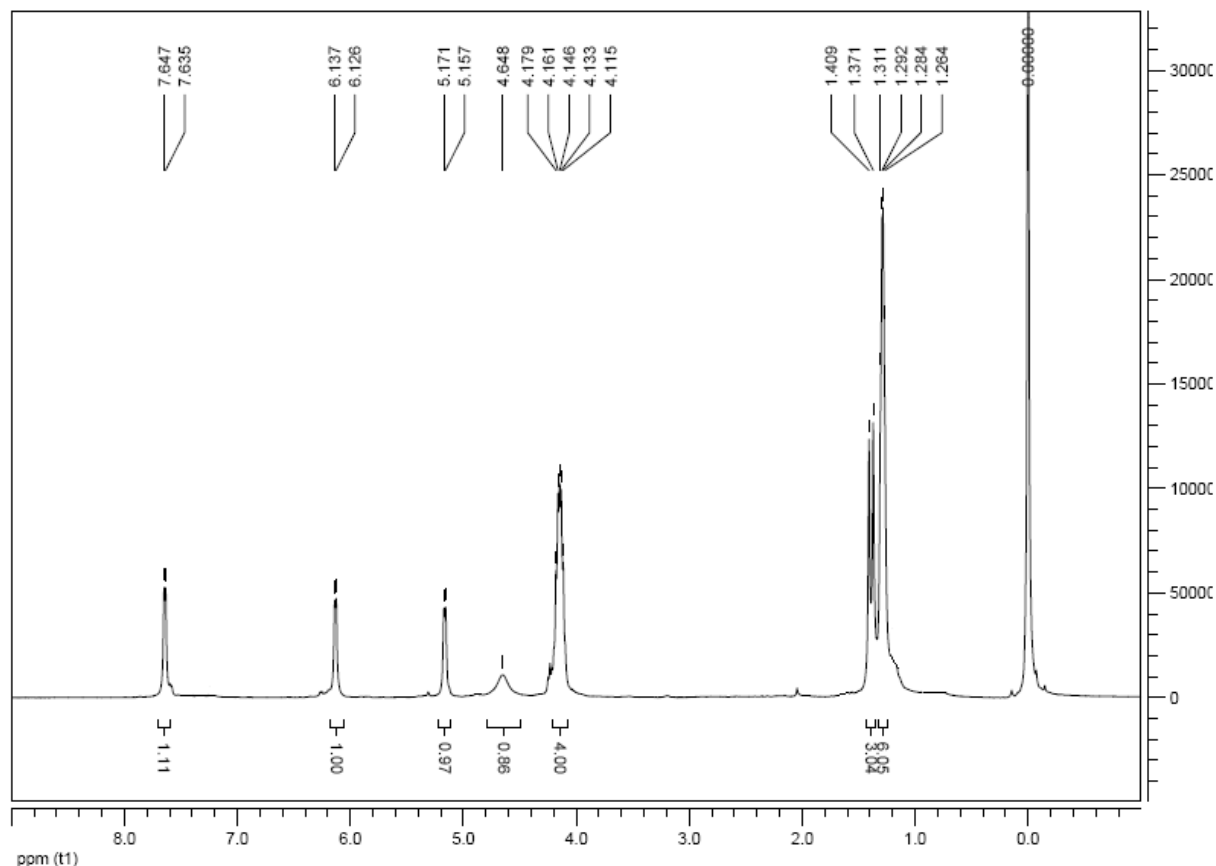


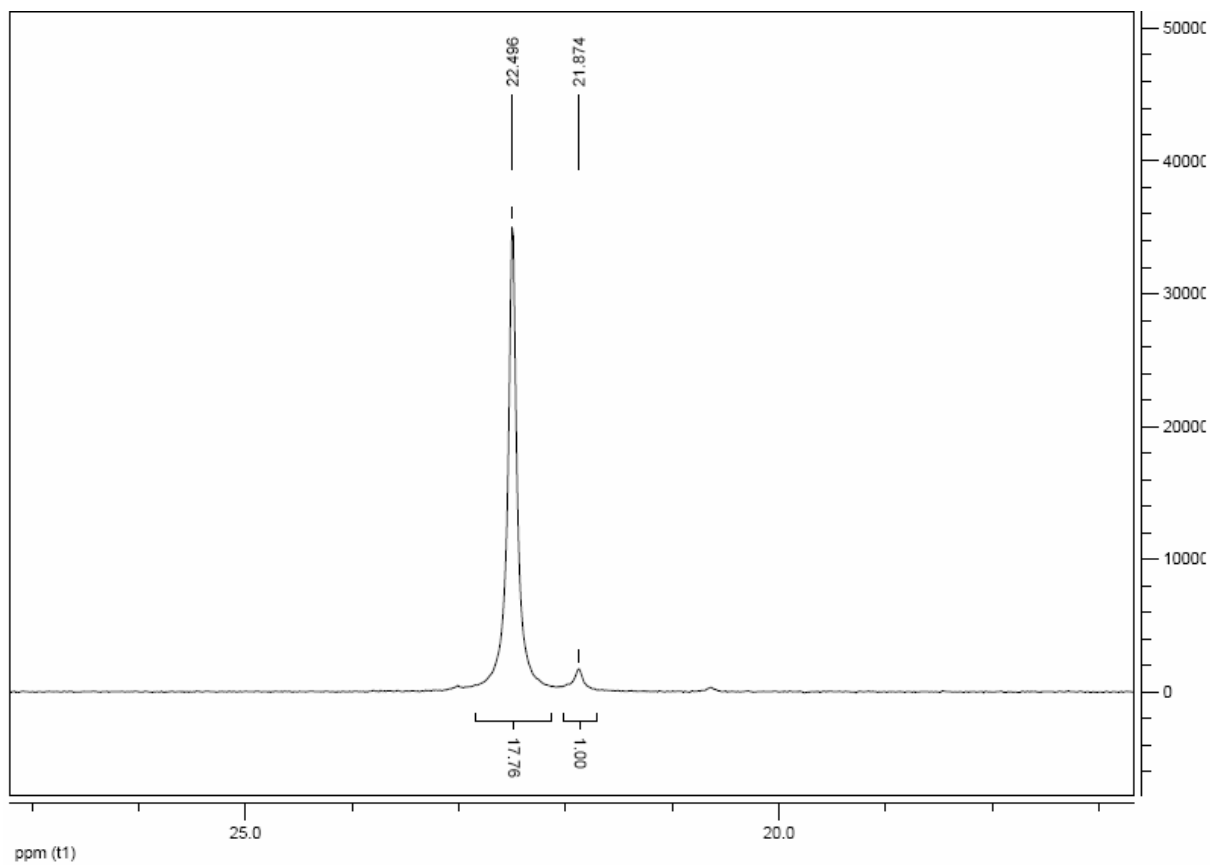
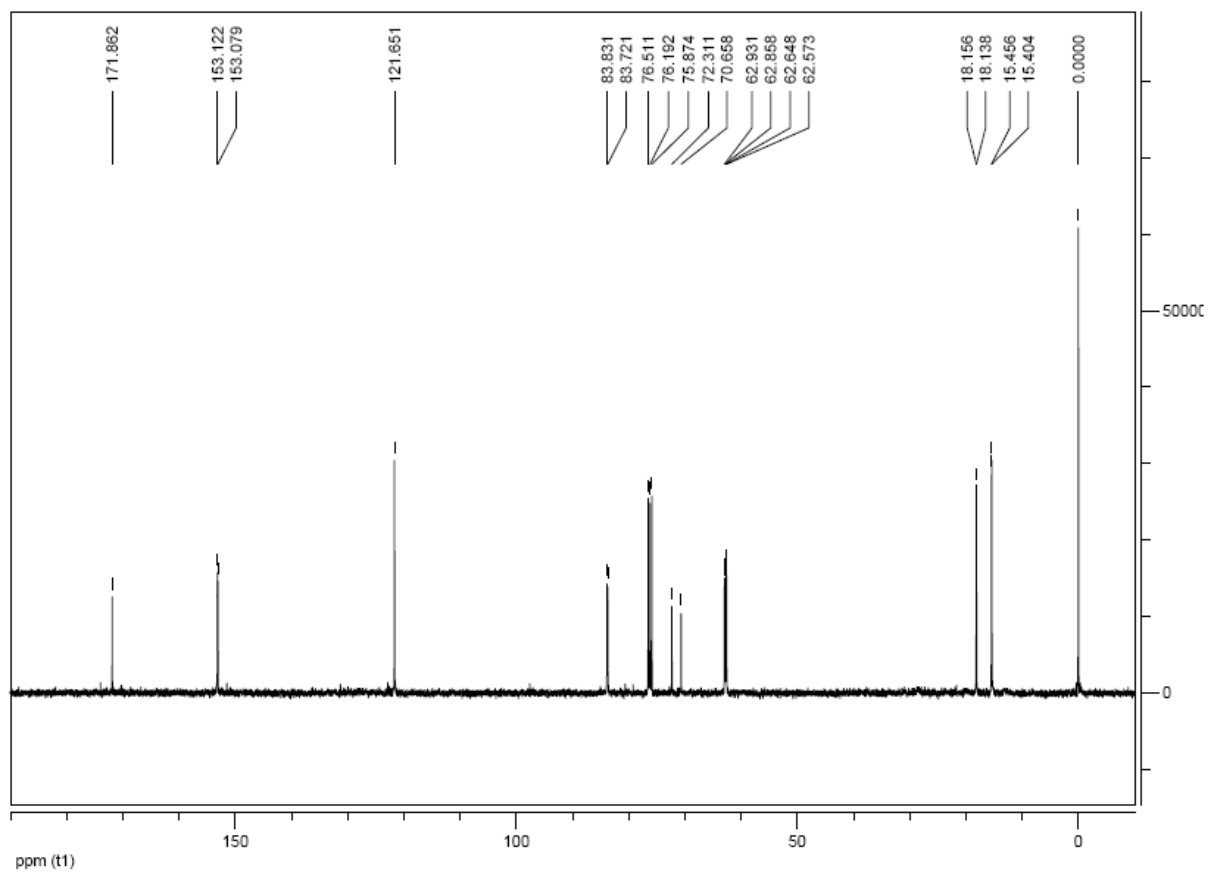


Diethyl 1-(2,5-dihydro-5-oxofuran-2-yl)-1-hydroxyethylphosphonate (3l):

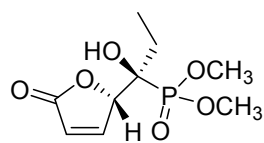


Colorless oil; ^{31}P -NMR (121 MHz, CDCl_3): δ 21.87, 22.50; ^1H -NMR (400 MHz, CDCl_3): δ 1.26-1.31 (m, 6H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 1.39 (d, $^3J_{\text{P-H}} = 15.1$ Hz, CCH_3), 4.12-4.18 (m, 4H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 4.65 (s, 1H, OH), 5.16 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.13 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.64 (d, $^3J_{\text{H-H}} = 5.0$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 15.43 (d, $^3J_{\text{C,P}} = 5.2$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 18.15 (d, $^2J_{\text{C,P}} = 1.8$ Hz, CCH_3), 62.61 (d, $^2J_{\text{C,P}} = 7.5$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 62.89 (d, $^2J_{\text{C,P}} = 7.3$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 71.48 (d, $^1J_{\text{C,P}} = 166.3$ Hz, $\text{CP}(\text{OCH}_2\text{CH}_3)_2$), 83.78 (d, $^2J_{\text{C,P}} = 11.0$ Hz, $\text{HC}=\text{CHCH}$), 121.65, 153.10 (d, $^3J_{\text{C,P}} = 4.3$ Hz), 171.86; ESI-MS: 286.8 ($[\text{M}+\text{Na}]^+$); HRMS calcd for $\text{C}_{10}\text{H}_{17}\text{O}_6\text{P}$: 287.0655 ($\text{M}+\text{Na}$) $^+$, found: 287.0649.

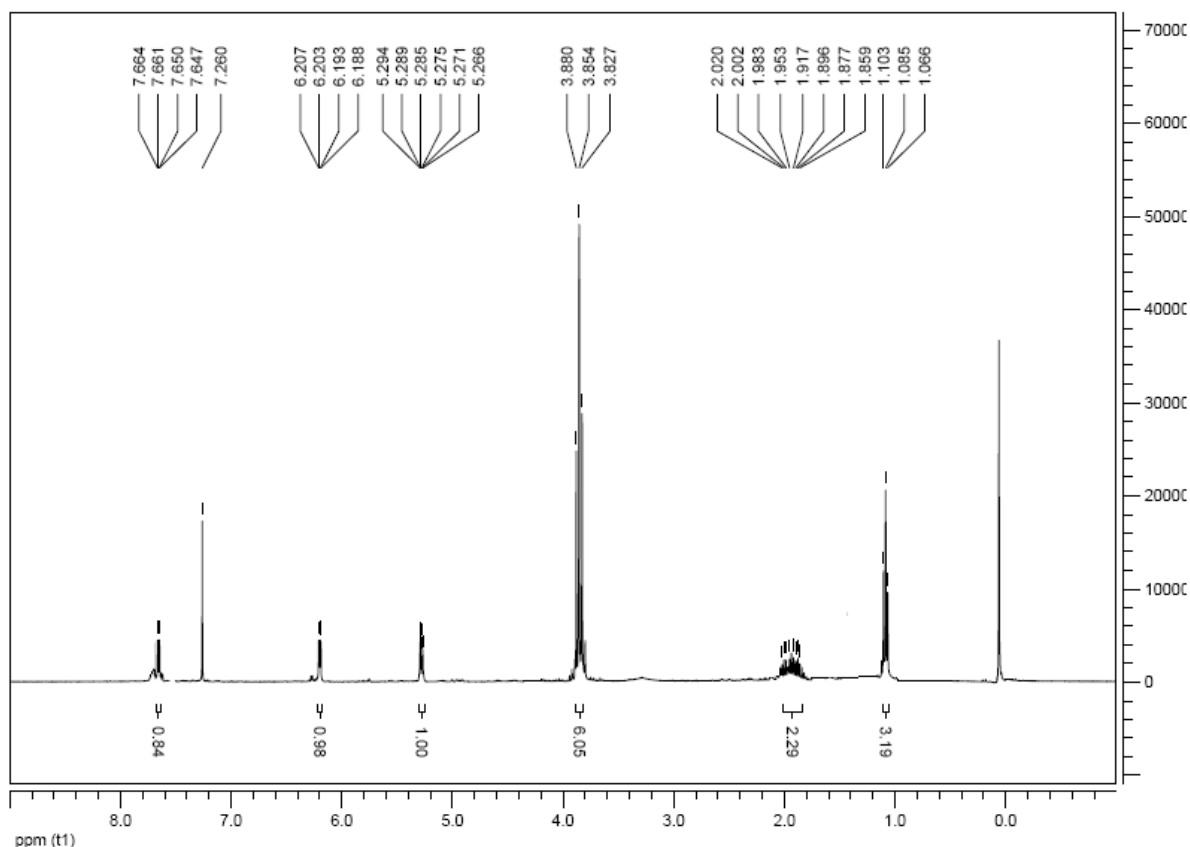


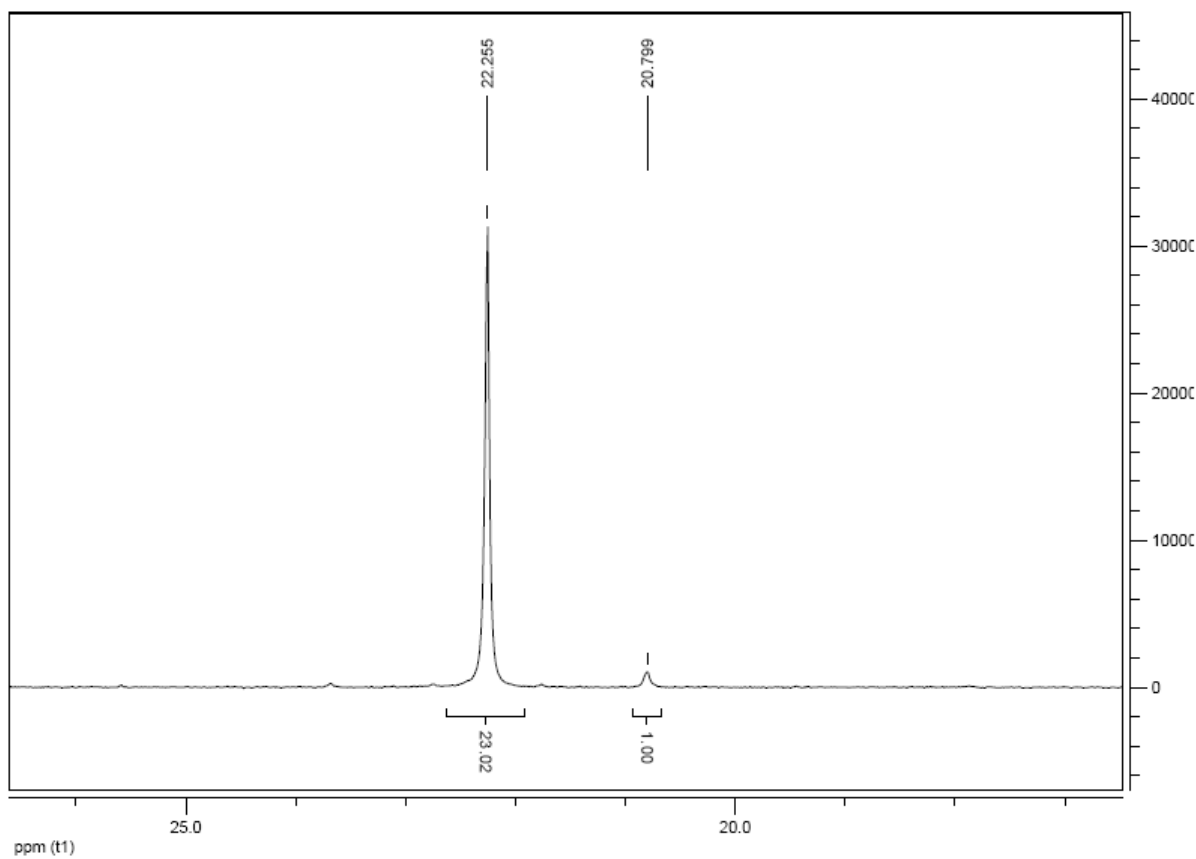
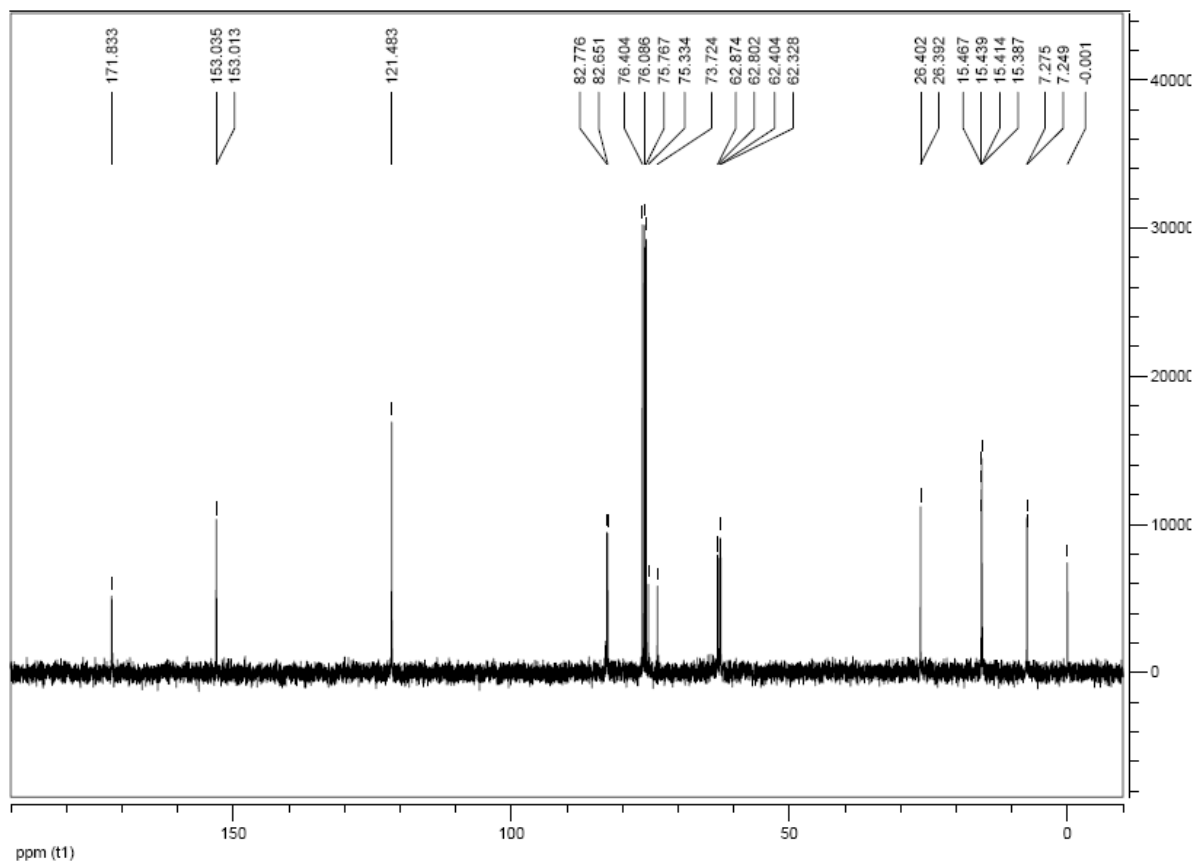


Dimethyl 1-(2,5-dihydro-5-oxofuran-2-yl)-1-hydroxypropylphosphonate (3m):

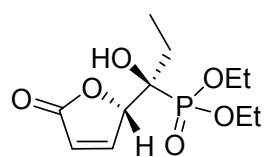


Colorless oil; ^{31}P -NMR (121 MHz, CDCl_3): δ 24.53, 24.59; ^1H -NMR (400 MHz, CDCl_3): δ 1.08 (t, 3H, $^3J_{\text{H-H}} = 7.4$ Hz, CH_2CH_3), 1.86-2.02 (m, 2H, CH_2CH_3), 3.85 (t, 6H, $^3J_{\text{P-H}} = 10.5$ Hz, $\text{P}(\text{OCH}_3)_2$), 5.28 (td, $^3J_{\text{H-H}} = 7.4$ Hz, $^3J_{\text{H-H}} = 1.8$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.20 (dd, $^3J_{\text{H-H}} = 5.8$ Hz, $^3J_{\text{H-H}} = 1.9$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.65 (dd, $^3J_{\text{H-H}} = 5.8$ Hz, $^3J_{\text{H-H}} = 1.2$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 7.14 (d, $^2J_{\text{C,P}} = 3.1$ Hz, CCH_2CH_3), 26.26 (d, $^2J_{\text{C,P}} = 2.0$ Hz, CCH_2CH_3), 52.70 (d, $^2J_{\text{C,P}} = 7.6$ Hz, $\text{P}(\text{OCH}_3)_2$), 53.35 (d, $^2J_{\text{C,P}} = 7.4$ Hz, $\text{P}(\text{OCH}_3)_2$), 75.00 (d, $^1J_{\text{C,P}} = 162.1$ Hz, $\text{CP}(\text{OCH}_2\text{CH}_3)_2$), 82.60 (d, $^2J_{\text{C,P}} = 11.8$ Hz, $\text{HC}=\text{CHCH}$), 121.62, 152.77 (d, $^3J_{\text{C,P}} = 3.2$ Hz), 171.70; ESI-MS: 272.6 ($[\text{M}+\text{Na}]^+$); HRMS calcd for $\text{C}_9\text{H}_{15}\text{O}_6\text{P}$: 273.0498 ($[\text{M}+\text{Na}]^+$), found: 274.0506.





Diethyl 1-(2,5-dihydro-5-oxofuran-2-yl)-1-hydroxypropylphosphonate (3n):



Colorless oil; ^{31}P -NMR (121 MHz, CDCl_3): δ 20.80, 22.26; ^1H -NMR (400 MHz, CDCl_3): δ 1.03 (t, 3H, $^3J_{\text{H-H}} = 7.5$ Hz, CH_2CH_3), 1.29 (t, 6H, $^3J_{\text{H-H}} = 7.0$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 1.81-1.95 (m, 2H, CH_2CH_3), 4.11-4.20 (m, 4H, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 5.23 (d, $^3J_{\text{H-H}} = 6.5$ Hz, 1H, $\text{HC}=\text{CHCH}$), 6.11 (d, $^3J_{\text{H-H}} = 5.0$ Hz, 1H, $\text{HC}=\text{CHCH}$), 7.63 (d, $^3J_{\text{H-H}} = 5.8$ Hz, 1H, $\text{HC}=\text{CHCH}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 7.26 (d, $^3J_{\text{C,P}} = 2.6$ Hz, CCH_2CH_3), 15.40 (d, $^3J_{\text{C,P}} = 2.7$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 15.45 (d, $^3J_{\text{C,P}} = 2.9$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 26.40 (d, $^2J_{\text{C,P}} = 1.1$ Hz, CCH_2CH_3), 62.37 (d, $^2J_{\text{C,P}} = 7.6$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 62.84 (d, $^2J_{\text{C,P}} = 7.3$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_2$), 74.53 (d, $^1J_{\text{C,P}} = 162.0$ Hz, $\text{CP}(\text{OCH}_2\text{CH}_3)_2$), 82.71 (d, $^2J_{\text{C,P}} = 12.6$ Hz, $\text{HC}=\text{CHCH}$), 121.48, 153.02 (d, $^3J_{\text{C,P}} = 2.2$ Hz), 171.83; ESI-MS: 300.6 ($[\text{M}+\text{Na}]^+$); HRMS calcd for $\text{C}_{11}\text{H}_{19}\text{O}_6\text{P}$: 301.0811 ($\text{M}+\text{Na}$) $^+$, found: 301.0818.

