Supporting Information

Electrochemical Selenium-π-Acid Promoted Hydration of Alkynyl Phosphonates

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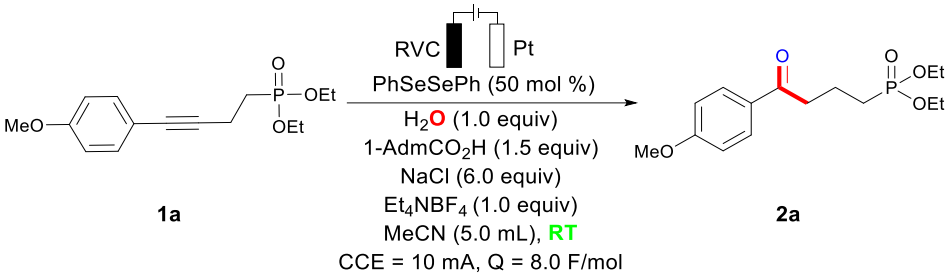
General Remarks

Catalytic reactions were carried out in undivided electrochemical cells under an air atmosphere using pre–dried glassware. If not noted otherwise. Alkynes **1** were synthesized according to a previously described method.[1] Other chemicals were obtained from commercial sources and were used without further purification. Platinum electrodes (10 mm × 15 mm × 0.20 mm) and RVC electrodes (10 mm × 15 mm × 6 mm) are commercially available from Tianjin Aida. Electrolysis was conducted using an AXIOMET AX3003P potentiostat in constant current mode. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR. Chromatography separations were carried out on silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China). High-resolution mass spectrometry (HR-MS) was measured on Thermo-DFS mass spectrometer. NMR spectra were recorded on JEOL 600 NMR (^{1}H 600 MHz, ^{13}C 150 MHz, ^{31}P 243 MHz) in $CDCl_3$. If not otherwise specified, chemical shifts (δ) are given in ppm. The cyclic voltammetry was carried out with a CHI650E workstation from Shanghai Chenhua.

Optimization of the Reaction Conditions

Table S-1 Optimization of the Electrochemical Selenium-π-Acid Promoted Hydration of Alkynyl Phosphonate **1a**



Entry	T [°C]	Solvent	Additive	electrolyte	$(PhSe)_2$	NaCl	Yield (%)
1	**r.t**	**CH_3CN**	**$AdmCO_2H$**	**Et_4NBF_4**	**0.5**	**6**	**89**[a]
2	r.t	CH_3CN	$AdmCO_2H$	Et_4NBF_4	0.2	6	42
3	r.t	CH_3CN	$AdmCO_2H$	Et_4NBF_4	1	6	88
4	r.t	CH_3CN	$AdmCO_2H$	Et_4NBF_4	1.5	6	95
5	r.t	CH_3CN	$AdmCO_2H$	Et_4NBF_4	-	6	trace
6	r.t	CH_3CN	$AdmCO_2H$	Bu_4NPF_6	0.5	6	81
7	r.t	CH_3CN	$AdmCO_2H$	Bu_4NClO_4	0.5	6	48
8	r.t	CH_3CN	$AdmCO_2H$	Bu_4NBr	0.5	6	26
9	r.t	CH_3CN	$AdmCO_2H$	Bu_4NCl	0.5	6	trace
10	r.t	CH_3CN	$AdmCO_2H$	Et_4NPF_6	0.5	6	86
11	r.t	CH_3CN	$AdmCO_2H$	Bu_4NBF_4	0.5	6	84
13	r.t	CH_3CN	$AdmCO_2H$	---	0.5	6	trace
14	50°C	CH_3CN	$AdmCO_2H$	Et_4NBF_4	0.5	6	trace
15	0°C	CH_3CN	$AdmCO_2H$	Et_4NBF_4	0.5	6	20
16	r.t	THF	$AdmCO_2H$	Et_4NBF_4	0.5	6	21
17	r.t	DCM	$AdmCO_2H$	Et_4NBF_4	0.5	6	48
18	r.t	DMF	$AdmCO_2H$	Et_4NBF_4	0.5	6	0
19	r.t	CH_3CN	CH_3COOH	Et_4NBF_4	0.5	6	78
20	r.t	CH_3CN	PivOH	Et_4NBF_4	0.5	6	trace

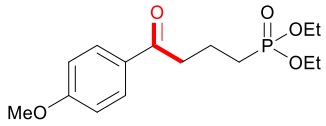
21	r.t	CH_3CN	TFA	Et_4NBF_4	0.5	6	0
22	r.t	CH_3CN	$AdmCO_2H$	Et_4NBF_4	0.5	---	39
23	r.t	CH_3CN	$AdmCO_2H$	Bu_4NPF_6	1	6	19[b]
24	r.t	CH_3CN	$AdmCO_2H$	Bu_4NPF_6	1	6	15[c]
25	r.t	CH_3CN	$AdmCO_2H$	Bu_4NPF_6	1	6	0[d]
26	r.t	CH_3CN	$AdmCO_2H$	Et_4NBF_4	---	6	25%[e]
27	r.t	CH_3CN	$AdmCO_2H$	Et_4NBF_4	---	6	27%[f]
28	r.t	CH_3CN	$AdmCO_2H$	Et_4NBF_4	---	6	0[g]

[a] Standard condition: undivided cell, RVC as the anode, platinum plate as the cathode, **1a** (0.20 mmol), PhSeSePh (0.50 equiv), MeCN (5.0 mL), Et_4NBF_4 (1 .0 equiv), CCE = 10 mA for 4.3 h, under air, 23 ℃, isolated yield. [b] CCE = 10 mA for 2.2 h，4.0 F/mol，[c] CCE = 10 mA for 8.0 h，15.0 F/mol. [d] no electrolyte. [e] PhSeCl (0.5 equiv). [f] PhSeH (0.5 equiv). [g] PhSeCl (1.0 equiv), no electricity.

General Procedure for the Electrochemical Selenium-π-Acid Promoted Hydration of Alkynyl Phosphonates

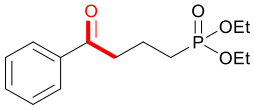
The electrolysis was carried out in an undivided cell, with an RVC anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.20 mm). PhSeSePh (31.2 mg, 0.1 mmol, 0.50 equiv), alkyne **1** (0.20 mmol, 1.0 equiv), NaCl (70.1 mg, 1.2 mmol, 6.0 equiv), 1-AdmCO_2H (54.1 mg, 0.30 mmol, 1.5 equiv), H_2O (18 mg, 0.20 mmol, 1.0 equiv) and Et_4NBF_4 (0.50 mmol, 1.0 equiv) were dissolved in CH_3CN (5.0 mL) under an air atmosphere. At ambient temperature, electrolysis was started with a constant current of 10.0 mA which was then maintained for 4.3 h. The mixture was transferred into a flask and the electrodes were rinsed with EtOAc (3 × 5.0 mL). Then, silica gel (0.8 g) was added and the mixture was removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum/EtOAc) to yield the desired products **2**.

Characterization Data of Products 2



Diethyl[4-(4-methoxyphenyl)-4-oxobutyl]phosphonate (2a)

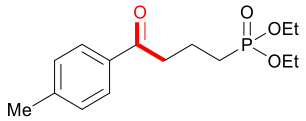
The general procedure was followed using alkyne **1a** (59.3 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2a** (56.2 mg, 89%) as a pale-yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.9 Hz, 2H, 2CH), 6.93 (d, J = 8.9 Hz, 2H, 2CH), 4.20–4.02 (m, 4H, $2CH_2$), 3.87 (s, 3H, OCH_3), 3.08 (t, J = 7.0 Hz, 2H, CH_2), 2.13–1.97 (m, 2H, CH_2), 1.91–1.78 (m, 2H, CH_2), 1.32 (t, J = 7.1 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.6, 163.4, 130.1 (2C), 129.8, 113.6 (2C), 61.4 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, 2C), 55.3, 37.9 (d, $^2J_{C\text{-}P}$ = 13.8 Hz), 24.7 (d, $^1J_{C\text{-}P}$ = 140.8 Hz), 17.2 (d, $^3J_{C\text{-}P}$ = 4.8 Hz), 16.3 (d, $^3J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{24}O_5P$ [M+H$^+$] 315.1356, found 315.1348.



Diethyl(4-oxo-4-phenylbutyl)phosphonate (2b)

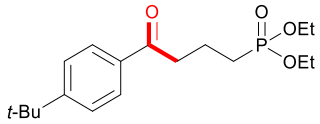
The general procedure was followed using alkyne **1b** (53.2 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2b** (33.5 mg, 59%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.95 (d, J = 7.6 Hz, 2H, 2CH), 7.56 (t, J = 7.1 Hz, 1H, CH), 7.45 (d, J = 7.6 Hz, 2H, 2CH), 4.15–4.06 (m, 4H, $2OCH_2$), 3.13 (t, J = 6.9, 2H, CH_2), 2.09–2.01 (m, 2H, CH_2), 1.92–1.79 (m, 2H, CH_2), 1.31 (t, J = 6.5, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 199.2, 136.7, 133.1, 128.6 (2C), 127.9 (2C), 61.6 (d, $^2J_{C\text{-}P}$ = 6.4 Hz, 2C), 38.4 (d, $^2J_{C\text{-}P}$ = 13.8 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 140.8 Hz), 17.1 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, 2C). **^{31}P**

{^{1}H}-NMR (243 MHz, $CDCl_3$) δ = 32.2. **HR-MS** (ESI) *m/z* calcd for $C_{14}H_{22}O_4P$ [M+H$^+$] 285.1250, found 285.1252.



Diethyl[4-oxo-4-(p-tolyl) butyl]phosphonate (2c)

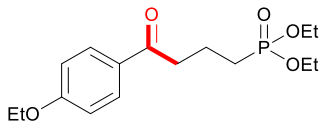
The general procedure was followed using alkyne **1c** (56.0 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.26) yielded **2c** (40.2 mg, 67%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.2 Hz, 2H, 2CH), 7.24 (d, *J* = 8.2 Hz, 2H, 2CH), 4.14–4.04 (m, 4H, 2OCH_2), 3.09 (t, *J* = 7.0 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.07–1.98 (m, 2H, CH_2), 1.90–1.79 (m,2H, CH_2), 1.30 (t, *J* = 7.0 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 198.9, 143.9, 134.3, 129.3 (2C), 128.1 (2C), 61.5 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, 2C), 38.2 (d, $^2J_{C\text{-}P}$ = 14.0 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 140.3 Hz), 21.6, 17.2 (d, $^3J_{C\text{-}P}$ = 4.8 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 5.8 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{24}O_4P$ [M+H$^+$] 299.1407, found 299.1406.



Diethyl{4-[4-(tert-butyl) phenyl]-4-oxobutyl}phosphonate (2d)

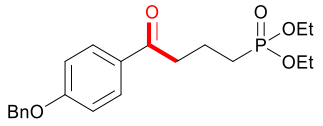
The general procedure was followed using alkyne **1d** (64.4 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2d** (34.7 mg, 51%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.5 Hz, 2H, 2CH), 7.46 (d, *J* = 8.5 Hz, 2H, 2CH), 4.17–4.02 (m, 4H, 2OCH_2), 3.09 (t, *J* = 7.0 Hz, 2H, CH_2), 2.09–1.99 (m, 2H, CH_2), 1.88–1.78 (m, 2H, CH_2), 1.33 (s, 9H, 3CH_3), 1.31 (t, *J* = 7.1 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 198.9, 156.8, 134.2, 127.9 (2C), 125.5 (2C), 61.5 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, 2C), 38.3 (d, $^2J_{C\text{-}P}$ = 14.0 Hz), 35.1, 31.0 (3C), 24.8 (d, $^1J_{C\text{-}P}$ = 140.7 Hz), 17.2 (d, $^3J_{C\text{-}P}$ = 4.8 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.0

Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{30}O_4P$ [M+H$^+$] 341.1876, found 341.1881.



Diethyl[4-(4-ethoxyphenyl)-4-oxobutyl]phosphonate (2e)

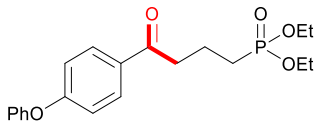
The general procedure was followed using alkyne **1e** (62.0 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.24) yielded **2e** (50.1 mg, 76%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.91 (d, J = 7.4 Hz, 2H, 2CH), 6.90 (d, J = 7.4 Hz, 2H, 2CH), 4.11–4.06 (m, 6H, 3OCH_2), 3.05 (t, J = 6.1 Hz, 2H, CH_2), 2.07–1.97 (m, 2H, CH_2), 1.88–1.80 (m, 2H, CH_2), 1.42 (t, J = 6.1 Hz, 3H, CH_3), 1.30 (t, J = 6.3 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.8, 162.9, 130.2 (2C), 129.7, 114.1 (2C), 63.7, 61.5 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, 2C), 38.0 (d, $^{2}J_{C\text{-}P}$ = 13.8 Hz), 24.8 (d, $^{1}J_{C\text{-}P}$ = 140.7 Hz), 17.3 (d, $^{3}J_{C\text{-}P}$ = 4.7 Hz), 16.4 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, 2C), 14.6. **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{26}O_5P$ [M+H$^+$] 329.1512, found 329.1512.



Diethyl{4-[4-(benzyloxy) phenyl]-4-oxobutyl}phosphonate (2f)

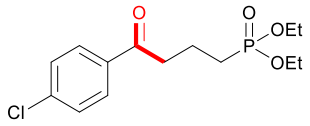
The general procedure was followed using alkyne **1f** (74.4 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.23) yielded **2f** (29.2 mg, 37%) as a pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.93 (d, J = 8.8 Hz, 2H, 2CH), 7.42–7.40 (m, 2H, 2CH), 7.39–7.36 (m, 2H, 2CH), 7.34–7.31 (m, 1H, CH), 6.99 (d, J = 8.8 Hz, 2H, 2CH), 5.11 (s, 2H, CH_2), 4.21–4.03 (m, 4H, 2OCH_2), 3.05 (t, J = 6.9 Hz, 2H, CH_2), 2.09–1.99 (m, 2H, CH_2), 1.89–1.80 (m, 2H, CH_2), 1.30 (t, J = 7.0 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.7, 162.6, 136.1, 130.2 (2C), 130.0, 128.6 (2C), 128.2, 127.4 (2C), 114.5 (2C), 70.0, 61.5 (d, $^{2}J_{C\text{-}P}$ = 6.3 Hz, 2C),

38.0 (d, $^{2}J_{C\text{-}P}$ = 13.6 Hz), 24.8 (d, $^{1}J_{C\text{-}P}$ = 140.6 Hz), 17.3 (d, $^{3}J_{C\text{-}P}$ = 4.3 Hz), 16.4 (d, $^{3}J_{C\text{-}P}$ = 5.6 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.4. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{28}O_5P$ [M+H$^+$] 391.1669, found 391.1671.



Diethyl[4-oxo-4-(4-phenoxyphenyl) butyl]phosphonate (2g)

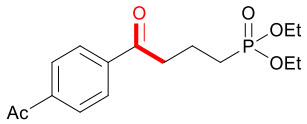
The general procedure was followed using alkyne **1g** (71.6 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2g** (48.1 mg, 64%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.8 Hz, 2H, 2CH), 7.40–7.37 (m, 2H, 2CH), 7.21–7.17 (m, 1H, CH), 7.07–7.04 (m, 2H, 2CH), 6.98 (d, *J* = 8.8 Hz, 2H, 2CH), 4.19–4.02 (m, 4H, 2OCH_2), 3.07 (t, *J* = 7.0 Hz, 2H, CH_2), 2.08–2.00 (m, 2H, CH_2), 1.87–1.81 (m, 2H, CH_2), 1.31 (t, *J* = 7.1 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.8, 162.0, 155.4, 131.4, 130.2 (2C), 130.0 (2C), 124.6, 120.1 (2C), 117.3 (2C), 61.5 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, 2C), 38.1 (d, $^{2}J_{C\text{-}P}$ = 13.6 Hz), 24.8 (d, $^{1}J_{C\text{-}P}$ = 140.9 Hz), 17.2 (d, $^{3}J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{26}O_5P$ [M+H$^+$] 377.1512, found 377.1516.



Diethyl[4-(4-chlorophenyl)-4-oxobutyl]phosphonate (2h)

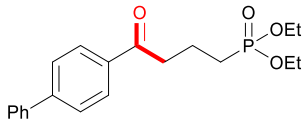
The general procedure was followed using alkyne **1h** (60.0 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.24) yielded **2h** (33.7 mg, 53%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.6 Hz, 2H, 2CH), 7.42 (d, *J* = 8.6 Hz, 2H, 2CH), 4.20–3.98 (m, 4H, 2OCH_2), 3.10 (t, *J* = 7.0 Hz, 2H, CH_2), 2.11–1.98 (m, 2H, CH_2), 1.88–1.75 (m, 2H, CH_2), 1.30 (t, *J* = 7.1 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 198.0, 139.6, 135.0, 129.4 (2C),

128.9 (2C), 61.6 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, 2C), 38.3 (d, $^{2}J_{C\text{-}P}$ = 13.3 Hz), 24.7 (d, $^{1}J_{C\text{-}P}$ = 141.0 Hz), 17.1 (d, $^{3}J_{C\text{-}P}$ = 5.0 Hz), 16.4 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.0. **HR-MS** (ESI) *m/z* calcd for $C_{14}H_{21}ClO_4P$ [M+H$^+$] 319.0860, found 3159.0862.



Diethyl (4-[4-acetylphenyl]-4-oxobutyl) phosphonate (2i)

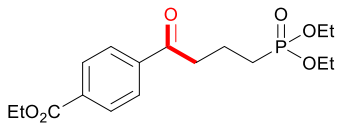
The general procedure was followed using alkyne **1i** (61.6 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.26) yielded **2i** (49.1 mg, 75%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 2.9 Hz, 4H, 4CH), 4.17 – 3.99 (m, 4H, 2OCH_2), 3.15 (t, *J* = 4.4 Hz, 2H, CH_2), 2.62 (d, *J* = 2.9 Hz, 3H, CH_3), 2.10 – 2.02 (m, 2H, CH_2), 1.89 – 1.81 (m, 2H, CH_2), 1.30 (t, *J* = 7.6, 3.7 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 198.6, 197.4, 140.1, 139.8, 128.5 (2C), 128.1 (2C), 61.5 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, 2C), 38.7 (d, $^{2}J_{C\text{-}P}$ = 13.0 Hz), 26.8, 24.6 (d, $^{1}J_{C\text{-}P}$ = 141.1 Hz), 17.0 (d, $^{3}J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.0. **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{23}O_5PNa$ [M+Na$^+$] 349.1175. found 349.1176.



Diethyl{4-([1,1'-biphenyl]-4-yl)-4-oxobutyl}phosphonate (2j)

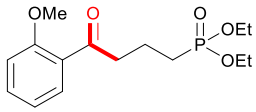
The general procedure was followed using alkyne **1j** (68.4 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2j** (64.3 mg, 89%) as a pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 8.5 Hz, 2H, 2CH), 7.67 (d, *J* = 8.4 Hz, 2H, 2CH), 7.62 (dd, *J* = 8.2, 1.3 Hz, 2H, 2CH), 7.46 (dd, *J* = 8.4, 7.0 Hz, 2H, 2CH), 7.42–7.37 (m, 1H, CH), 4.17–4.04 (m, 4H, 2OCH_2), 3.16 (t, *J* = 7.0 Hz, 2H, CH_2), 2.13–2.03 (m, 2H, CH_2), 1.94–1.82 (m, 2H, CH_2), 1.32

(t, J = 7.1 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 198.8, 145.8, 139.8, 135.4, 128.9 (2C), 128.6 (2C), 128.2, 127.2 (4C), 61.5 (d, $^2J_{C\text{-}P}$ = 6.4 Hz, 2C), 38.4 (d, $^2J_{C\text{-}P}$ = 13.6 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 140.9 Hz), 17.2 (d, $^3J_{C\text{-}P}$ = 4.8 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.1 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.2. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{26}O_4P$ [M+H$^+$] 361.1563, found 361.1562.



Ethyl 4-[4-(diethoxyphosphoryl)butanoyl]benzoate (2k)

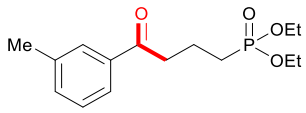
The general procedure was followed using alkyne **1k** (67.6 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.24) yielded **2k** (44.9 mg, 63%) as a pale orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.11 (d, J = 8.6 Hz, 2H, 2CH), 8.00 (d, J = 8.6 Hz, 2H, 2CH), 4.44–4.36 (m, 2H, OCH_2), 4.19–4.05 (m, 4H, 2OCH_2), 3.16 (t, J = 7.0 Hz, 2H, CH_2), 2.12–2.02 (m, 2H, CH_2), 1.90–1.81 (m, 2H, CH_2), 1.41 (t, J = 7.1 Hz, 3H, CH_3), 1.31 (t, J = 7.1 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 198.7, 165.7, 139.8, 134.3, 129.8 (2C), 127.8 (2C), 61.6 (d, $^2J_{C\text{-}P}$ = 6.4 Hz, 2C), 61.4, 38.7 (d, $^2J_{C\text{-}P}$ = 13.5 Hz), 24.7 (d, $^1J_{C\text{-}P}$ = 141.3 Hz), 17.0 (d, $^3J_{C\text{-}P}$ = 4.7 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, 2C), 14.2. **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.1. **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{26}O_6P$ [M+H$^+$] 357.1462, found 357.1463.



Diethyl[4-(2-methoxyphenyl)-4-oxobutyl]phosphonate (2l)

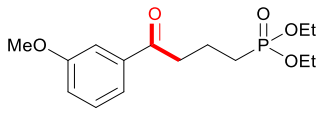
The general procedure was followed using alkyne **1l** (59.2 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2l** (36.4 mg, 58%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.68 (dd, J = 7.7, 1.8 Hz, 1H, CH), 7.45 (ddd, J = 8.3, 7.3, 1.8 Hz, 1H, CH), 6.99 (ddd, J = 7.5, 7.5, 1.0 Hz,

1H, CH), 6.96 (dd, J = 8.4, 1.0 Hz, 1H, CH), 4.15–4.03 (m, 4H, 2OCH_2), 3.90 (s, 3H, OCH_3), 3.09 (t, J = 7.0 Hz, 2H, CH_2), 2.04–1.95 (m, 2H, CH_2), 1.86–1.79 (m, 2H, CH_2), 1.31 (t, J = 7.1 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 201.5, 158.6, 133.5, 130.2, 128.1, 120.7, 111.5, 61.5 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, 2C), 55.5, 43.8 (d, $^2J_{C\text{-}P}$ = 15.3 Hz), 25.0 (d, $^1J_{C\text{-}P}$ = 140.8 Hz), 17.4 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.5. **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{24}O_5P$ [M+H$^+$] 315.1356, found 315.1356.



Diethyl[4-oxo-4-(m-tolyl) butyl]phosphonate (2m)

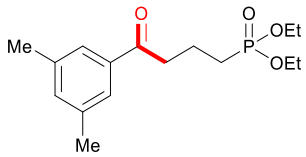
The general procedure was followed using alkyne **1m** (56.0 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.24) yielded **2m** (29.8 mg, 50%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.75 (s, 1H, CH), 7.73 (s, 1H, CH), 7.38–7.31 (m, 2H, 2CH), 4.28–3.95 (m, 4H, 2OCH_2), 3.11 (t, J = 6.3 Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.09–2.00 (m, 2H, CH_2), 1.92–1.81 (m,2H, CH_2), 1.31 (t, J = 6.6 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 199.4, 138.4, 136.8, 133.9, 128.5, 128.5, 125.2, 61.5 (d, $^2J_{C\text{-}P}$ = 6.4 Hz, 2C), 38.4 (d, $^2J_{C\text{-}P}$ = 13.9 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 141.1 Hz), 21.3, 17.2 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{24}O_4P$ [M+H$^+$] 299.1407, found 299.1406.



Diethyl[4-(3-methoxyphenyl)-4-oxobutyl]phosphonate (2n)

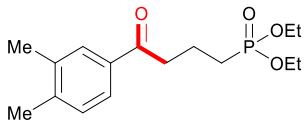
The general procedure was followed using alkyne **1n** (59.3 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2n** (49 mg, 78%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.53 (ddd, J = 7.7, 1.4, 1.0 Hz,1H, CH), 7.48 (dd, J = 2.6, 1.5 Hz, 1H, CH), 7.36 (dd, J = 7.9, 7.9

Hz, 1H, CH), 7.10 (ddd, J = 8.2, 2.7, 0.9 Hz, 1H, CH), 4.15–4.04 (m, 4H, $2OCH_2$), 3.85 (s, 3H, OCH_3), 3.11 (t, J = 7.0 Hz, 2H, CH_2), 2.10–2.00 (m, 2H, CH_2), 1.90–1.81 (m, 2H, CH_2), 1.31 (t, J = 7.1 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 199.1, 159.8, 138.1, 129.6, 120.6, 119.6, 112.2, 61.6 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, 2C), 55.4, 38.5 (d, $^2J_{C\text{-}P}$ = 14.1 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 141.0 Hz), 17.2 (d, $^3J_{C\text{-}P}$ = 4.8 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{24}O_5P$ [M+H$^+$] 315.1356, found 315.1356.



Diethyl[4-(3,5-dimethylphenyl)-4-oxobutyl]phosphonate (2o)

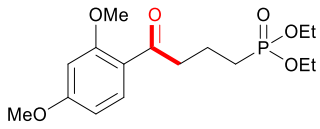
The general procedure was followed using alkyne **1o** (58.8 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2o** (31.2 mg, 50%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.55 (d, J = 0.9 Hz, 2H, 2CH), 7.19–7.18 (m, 1H, CH), 4.14–4.05 (m, 4H, $2OCH_2$), 3.09 (t, J = 7.0 Hz, 2H, CH_2), 2.35 (s, 6H, $2CH_3$), 2.09–1.99 (m, 2H, CH_2), 1.88–1.79 (m, 2H, CH_2), 1.31 (t, J = 7.0 Hz, 6H, $2CH_3$). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 199.6, 138.2 (2C), 136.9, 134.7, 125.8 (2C), 61.5 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, 2C), 38.5 (d, $^2J_{C\text{-}P}$ = 14.1 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 140.8 Hz), 21.2 (2C), 17.2 (d, $^3J_{C\text{-}P}$ = 4.7 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.2. **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{26}O_4P$ [M+H$^+$] 313.1563, found 313.1567.



Diethyl[4-(3,4-dimethylphenyl)-4-oxobutyl]phosphonate (2p)

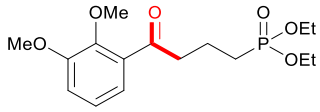
The general procedure was followed using alkyne **1p** (58.8 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.24) yielded **2p** (29.3 mg, 47%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.06 (d,

J = 1.9 Hz, 1H, CH), 8.02 (dd, *J* = 7.8, 1.9 Hz, 1H, CH), 7.54 (d, *J* = 7.9 Hz, 1H, CH), 4.49–4.38 (m, 4H, $2OCH_2$), 3.42 (t, *J* = 7.0 Hz, 2H, CH_2), 2.64 (s, 6H, $2CH_3$), 2.41–2.33 (m, 2H, CH_2), 2.24–2.06 (m, 2H, CH_2), 1.65 (t, *J* = 7.1 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 199.2, 142.7, 136.9, 134.6, 129.8, 129.1, 125.7, 61.5 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, 2C), 38.3 (d, $^2J_{C\text{-}P}$ = 14.1 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 140.7 Hz), 20.0, 19.8, 17.2 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.4. **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{26}O_4P$ [M+H$^+$] 313.1563, found 313.1566.



Diethyl[4-(2,4-dimethoxyphenyl)-4-oxobutyl]phosphonate (2q)

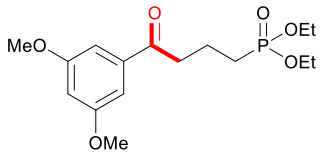
The general procedure was followed using alkyne **1q** (65.2 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2q** (31.1 mg, 45%) as a pale orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.7 Hz, 1H, CH), 6.51 (dd, *J* = 8.7, 2.3 Hz, 1H, CH), 6.44 (d, *J* = 2.3 Hz, 1H, CH), 4.12–4.05 (m, 4H, $2OCH_2$), 3.88 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.05 (t, *J* = 6.9 Hz, 2H, CH_2), 2.02–1.94 (m, 2H, CH_2), 1.85–1.77 (m, 2H, CH_2), 1.30 (t, *J* = 7.1 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 199.1, 164.4, 160.8, 132.6, 120.8, 105.1, 98.3, 61.4 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, 2C), 55.5, 55.4, 43.7 (d, $^2J_{C\text{-}P}$ = 15.6 Hz), 25.0 (d, $^1J_{C\text{-}P}$ = 140.3 Hz), 17.5 (d, $^3J_{C\text{-}P}$ = 4.8 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 5.8 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.6. **HR-MS (ESI)** *m/z* calcd for $C_{16}H_{26}O_6P$ [M+H$^+$] 345.1462, found 345.1466.



Diethyl[4-(2,3-dimethoxyphenyl)-4-oxobutyl]phosphonate (2r)

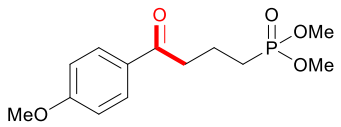
The general procedure was followed using alkyne **1r** (65.2 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.26) yielded **2r** (38.5 mg, 56%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.58 (dd, *J* = 8.4,

2.0 Hz, 1H, CH), 7.51 (d, J = 2.0 Hz, 1H, CH), 6.87 (d, J = 8.4 Hz, 1H, CH), 4.15–4.03 (m, 4H, 2OCH_2), 3.94 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.08 (t, J = 7.0 Hz, 2H, CH_2), 2.09–2.00 (m, 2H, CH_2), 1.91–1.81 (m, 2H, CH_2), 1.31 (t, J = 7.0 Hz, 6H, 2CH_3).**^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.7, 153.3, 149.0, 130.1, 122.7, 110.0, 109.9, 61.5 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, 2C), 56.0, 55.9, 37.9, (d, $^2J_{C\text{-}P}$ = 13.7 Hz), 24.9 (d, $^1J_{C\text{-}P}$ = 140.7 Hz), 17.5 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.2. **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{26}O_6P$ [M+H$^+$] 345.1462, found 345.1462.



Diethyl[4-(3,5-dimethoxyphenyl)-4-oxobutyl]phosphonate (2s)

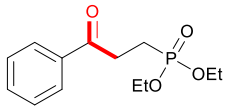
The general procedure was followed using alkyne **1s** (65.2mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2s** (38.1 mg, 55%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.07 (d, J = 2.3 Hz, 2H, 2CH), 6.63 (s, 1H, CH), 4.17–4.02 (m, 4H, 2OCH_2), 3.82 (s, 6H, 2OCH_3), 3.07 (t, J = 7.0 Hz, 2H, CH_2), 2.06–1.97 (m, 2H, CH_2), 1.89–1.77 (m, 2H, CH_2), 1.31 (t, J = 7.1 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.9, 160.9 (2C), 138.7, 105.8 (2C), 105.3, 61.6 (d, $^2J_{C\text{-}P}$ = 6.9 Hz, 2C), 55.6 (2C), 38.5 (d, $^2J_{C\text{-}P}$ = 13.8 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 140.9 Hz), 17.2 (d, $^3J_{C\text{-}P}$ = 5.1 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 5.9 Hz, 2C).**^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{26}O_6P$ [M+H$^+$] 345.1462, found 345.1460.



Dimethyl[4-(4-methoxyphenyl)-4-oxobutyl]phosphonate (2t)

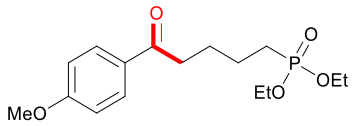
The general procedure was followed using alkyne **1t** (53.6 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.24) yielded **2t**

(31.2 mg, 54%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.93 (d, J = 8.9 Hz, 2H, 2CH), 6.92 (d, J = 8.9 Hz, 2H, 2CH), 3.86 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.06 (t, J = 7.0 Hz, 2H, CH_2), 2.07–1.98 (m, 2H, CH_2), 1.92–1.83 (m, 2H, CH_2). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.7, 163.5, 130.3 (2C), 129.9, 113.7 (2C), 55.4, 52.3 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, 2C), 37.9 (d, $^{2}J_{C\text{-}P}$ = 13.8 Hz), 23.8 (d, $^{1}J_{C\text{-}P}$ = 140.7 Hz), 17.2 (d, $^{3}J_{C\text{-}P}$ = 5.0 Hz). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 35.1. **HR-MS** (ESI) *m/z* calcd for $C_{13}H_{20}O_5P$ [M+H$^+$] 287.1043, found 287.1044.



Diethyl[3-oxo-3-phenylpropyl] phosphonate (2u)

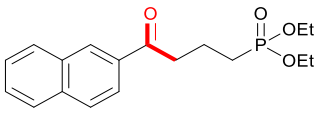
The general procedure was followed using alkyne **1u** (50.4 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2u** (21.1 mg, 39%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.99–7.96 (m, 2H, 2CH), 7.60–7.56 (m, 1H, CH), 7.47–7.46 (m, 2H, 2CH), 4.17–4.07 (m, 4H, $2OCH_2$), 3.37–3.24 (m, 2H, CH_2), 2.24–2.16 (m, 2H, CH_2), 1.33 (t, J = 7.0 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.5 (d, $^{3}J_{C\text{-}P}$ = 15.8 Hz), 136.3 133.4, 128.7 (2C), 128.1 (2C), 61.8 (d, $^{2}J_{C\text{-}P}$ = 6.3 Hz, 2C), 31.7 (d, $^{2}J_{C\text{-}P}$ = 2.8 Hz), 19.8 (d, $^{1}J_{C\text{-}P}$ = 145.0 Hz), 16.4 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.5. **HR-MS** (ESI) *m/z* calcd for $C_{13}H_{20}O_4P$ [M+H$^+$] 271.1091, found 271.1094.



Diethyl[5-(4-methoxyphenyl)-5-oxopentyl]phosphonate (2v)

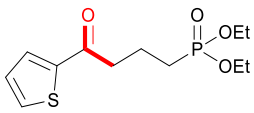
The general procedure was followed using alkyne **1v** (62.0 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.24) yielded **2v** (39.4 mg, 60%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.92 (d, J = 8.9 Hz, 2H, 2CH), 6.92 (d, J = 8.9 Hz, 2H, 2CH), 4.14–4.00 (m, 4H, $2OCH_2$), 3.86

(s, 3H, OCH_3), 2.93 (t, J = 7.3 Hz, 2H, CH_2), 1.83–1.77 (m, 2H, CH_2), 1.77–1.73 (m, 2H, CH_2), 1.72–1.65 (m, 2H, CH_2), 1.30 (t, J = 7.1 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 198.3, 163.4, 130.2 (2C), 129.9, 113.7 (2C), 61.5 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, 2C), 55.4, 37.6, 25.6 (d, $^1J_{C\text{-}P}$ = 140.9 Hz), 25.2 (d, $^2J_{C\text{-}P}$ = 17.9 Hz), 22.3 (d, $^3J_{C\text{-}P}$ = 5.0 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.6. **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{26}O_5P$ [M+H$^+$] 329.1512, found 329.1514.



Diethyl[4-(naphthalen-2-yl)-4-oxobutyl]phosphonate (2w)

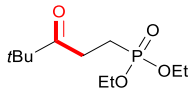
The general procedure was followed using alkyne **1w** (63.2 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2w** (44.1 mg, 66%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.50–8.46 (m, 1H, CH), 8.02 (dd, J = 8.6, 1.7 Hz, 1H, CH), 7.96 (dd, J = 8.2, 1.2 Hz, 1H, CH), 7.91–7.86 (m, 2H, 2CH), 7.62–7.58 (m, 1H, CH), 7.57–7.53 (m, 1H, CH), 4.16–4.08 (m, 4H, $2OCH_2$), 3.27 (t, J = 7.0 Hz, 2H, CH_2), 2.17–2.07 (m, 2H, CH_2), 1.95–1.89 (m, 2H, CH_2), 1.32 (t, J = 7.0 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 199.2, 135.6, 134.1, 132.5, 129.7, 129.6, 128.6, 128.6, 127.8, 126.8, 123.7, 61.6 (d, $^2J_{C\text{-}P}$ = 5.7 Hz, 2C), 38.4 (d, $^2J_{C\text{-}P}$ = 13.4 Hz), 28.8 (d, $^1J_{C\text{-}P}$ = 143.8 Hz), 17.4 (d, $^3J_{C\text{-}P}$ = 4.1 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 5.5 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.3. **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{24}O_4P$ [M+H$^+$] 335.1407, found 335.1407.



Diethyl [4-oxo-4-(thiophen-2-yl) butyl] phosphonate (2x)

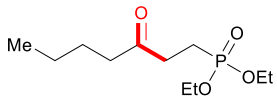
The general procedure was followed using alkyne **1x** (54.4 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, Rf: 0.25) yielded **2x** (29.6 mg, 51%) as a colorless oil.**^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.71 (dd, J = 3.8, 1.1 Hz, 1H, CH), 7.61 (dd, J = 4.9, 1.1 Hz, 1H, CH), 7.11 (dd, J = 4.9, 3.8 Hz,

1H, CH), 4.12–4.04 (m, 4H, 2OCH_2), 3.04 (t, J = 7.1 Hz, 2H, CH_2), 2.07–2.01 (m, 2H, CH_2), 1.87–1.80 (m, 2H, CH_2), 1.30 (t, J = 7.1 Hz, 6H, 2CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 192.2, 144.1, 133.6, 131.9, 128.1, 61.6 (d, $^2J_{C\text{-}P}$ = 6.4 Hz, 2C), 39.0 (d, $^2J_{C\text{-}P}$ = 14.0 Hz), 24.7 (d, $^1J_{C\text{-}P}$ = 141.0 Hz), 17.5 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 6.2 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.0. **HR-MS** (ESI) *m/z* calcd for $C_{12}H_{20}O_4PS$ [M+H^+] 291.0814, found 291.0815.



Diethyl (4,4-dimethyl-3-oxopentyl) phosphonate (2y)

The general procedure was followed using alkyne **1y** (46.4 mg, 0.20 mmol). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.25) yielded **2y** (21.5 mg, 43%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 4.17–4.00 (m, 4H, 2OCH_2), 2.86–2.70 (m, 2H, CH_2), 2.04–1.93 (m, 2H, CH_2), 1.31 (t, J = 7.1, 0.9 Hz, 6H, 2CH_3), 1.15 (s, 9H, 3CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 213.5 (d, $^3J_{C\text{-}P}$ = 14.2 Hz), 61.8 (d, $^2J_{C\text{-}P}$ = 6.4 Hz, 2C), 44.1, 29.8 (d, $^2J_{C\text{-}P}$ = 3.3 Hz), 26.6 (3C), 19.7 (d, $^1J_{C\text{-}P}$ = 144.1 Hz), 16.5 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.9. **HR-MS** (ESI) *m/z* calcd for $C_{11}H_{24}O_4P$ [M+H^+] 251.1407, found 251.1407.

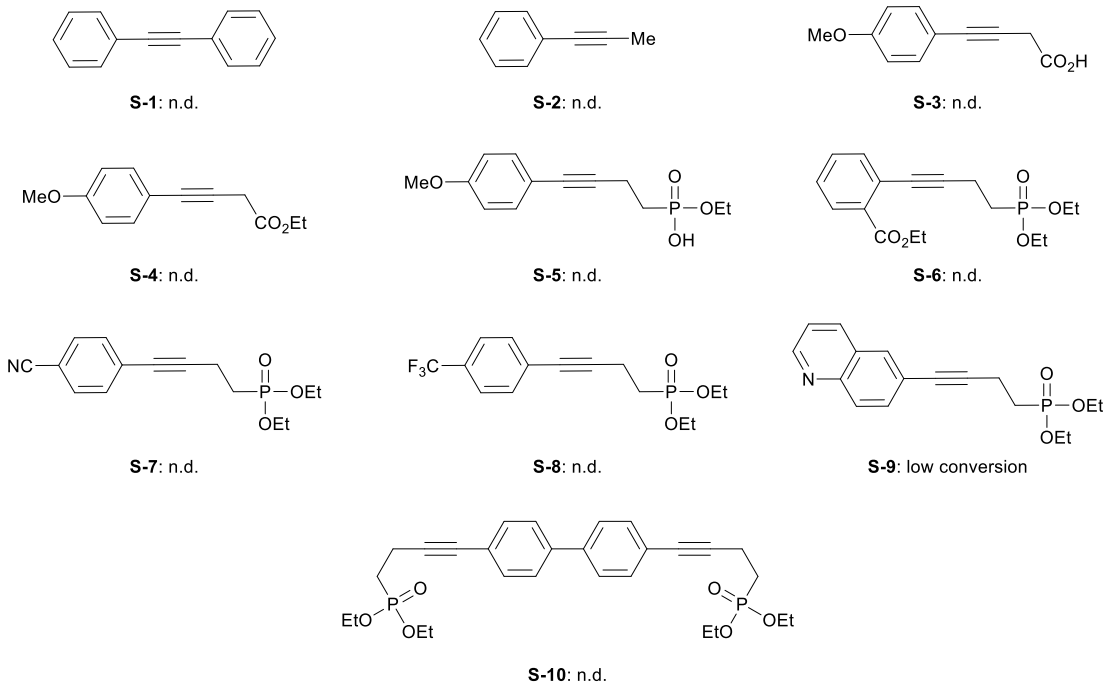


Diethyl (3-oxoheptyl) phosphonate (2z)

The general procedure was followed using alkyne **1z** (46.5 mg, 0.20 mmol) and PhSeSePh (93.6 mg, 1.50 equiv). Purification by column chromatography on silica gel (petroleum/EtOAc 1/3, R_f = 0.24) yielded **2z** (19.2 mg, 38%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 4.13–4.04 (m, 4H, 2OCH_2), 2.73–2.67 (m, 2H, CH_2), 2.43 (t, J = 7.5 Hz, 2H, CH_2), 2.06–1.97 (m, 2H, CH_2), 1.71 (q, J = 12.8 Hz, 2H, CH_2), 1.60 – 1.53 (m, 2H, CH_2), 1.31 (t, J = 7.1 Hz, 6H, 2CH_3), 0.90 (t, J = 7.4 Hz, 3H, CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 208.5, 61.9 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, 2C), 42.6, 35.6 (d, $^2J_{C\text{-}P}$ =

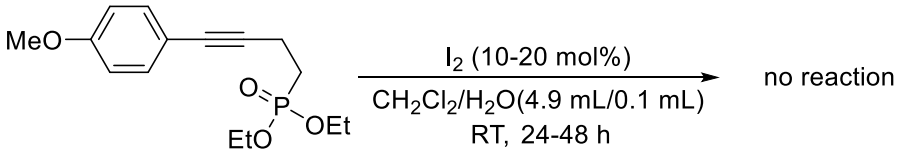
3.6 Hz), 26.1, 22.5, 19.6 (d, $^{1}J_{C\text{-}P}$ = 144.2 Hz), 16.6 (d, J = 5.9 Hz, 2C), 14.0. **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.4. **HR-MS** (ESI) *m/z* calcd for $C_{11}H_{24}O_4P$ [$M+H^+$] 251.1407, found 251.1412.

List of Unsuccessful Examples



Scheme S-1. Unsuccessful examples for selenium acid promoted hydration of internal alkynes

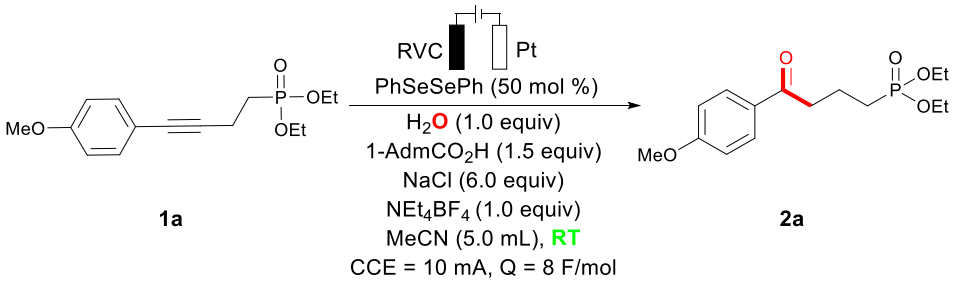
Test of Our Substrates with Previous Method



Scheme S-2. Iodine catalyzed hydration with alkyne **1a**

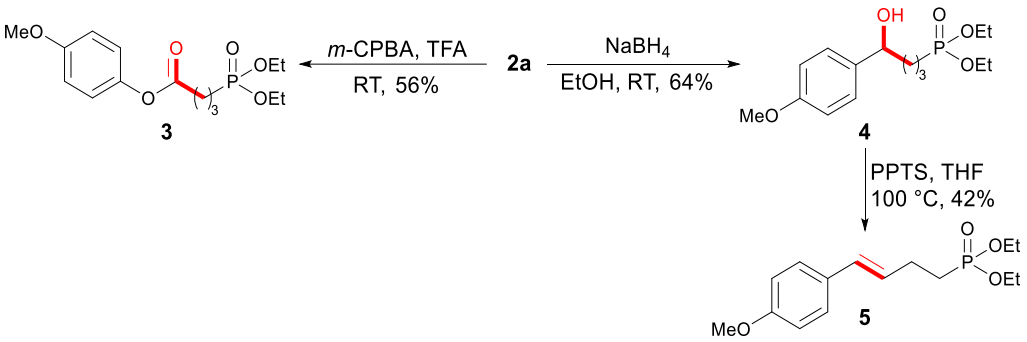
Although the protocol described by Pal (B. Dulla, S. K. Kolli, U. R. Chamakura, G. S. Deora, R. R. Raju and M. Pal, *Synth. Commun.*, 2014, **44**, 1466.) is much simpler than the current condition in our manuscript, we tried their conditions with our substrates, unfortunately, it did not work for our substrates.

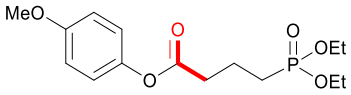
Gram-Scale Preparation of 2a



To a 50 mL three-neck round bottom flask was added PhSeSePh (692.4 mg, 2.20 mmol，0.50 equiv), NaCl (1.56 g, 26.6 mmol, 6.0 equiv), 1-AdmCO$_2$H (1.20 g, 0.3 mmol, 1.5 equiv), H$_2$O (79.9 mg, 4.4 mmol, 1.0 equiv), NEt$_4$BF$_4$ (965.4 mg, 4.4 mmol, 1.0 equiv) alkyne **1a** (1.32 g, 4.4 mmol, 1.0 equiv) and CH$_3$CN (40.0 mL) under an air atmosphere. Then, the flask was equipped with rubber stoppers, two pieces of platinum plates (15 × 10 mm) as cathode and one piece of reticulated vitreous carbon (30 × 10 mm) as the anode. At ambient temperature, electrolysis was started with a constant current of 20 mA which was then maintained for 35.4 h (5.95 F/mol). The mixture was transferred to a flask and the electrodes were rinsed with EtOAc (3 × 15 mL). Then, silica gel (3.0 g) was added and the combined solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum/EtOAc = 1/1 to 1/3) to yield the desired product **2a** (1.07 g, 77%) as a pale-yellow oil.

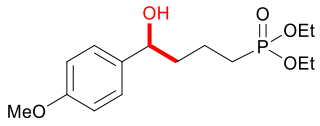
Product Diversification of 2a





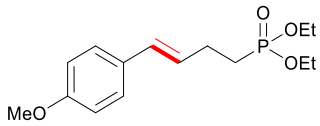
4-Methoxyphenyl 4-(diethoxyphosphoryl)butanoate (3)

According to a modified procedure,[2] TFA (1.4 mmol, 100 µl) was added to a stirred solution of *m*-chloroperbenzoic acid (85%, 2.0 mmol, 413.0 mg) in CH_2Cl_2 (2.0 mL) at ambient temperature and the stirring was continued for 6 h. A solution of **1a** (0.25 mmol, 78.5 mg) in CH_2Cl_2 (1.0 ml) was added to the reaction mixture and the stirring was continued for another 14 h at ambient temperature. The mixture was diluted with Et_2O (15 ml), washed with aqueous NaOH solution (1.0 M, 10 mL×1), brine (10 ml×1) and dried over anhydrous sodium sulfate. The organic layer was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (petroleum/EtOAc: 2/1) to afford ester **3** (46.2 mg, 56%) as a light yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.93 (d, J = 8.8 Hz, 2H, 2CH), 6.91 (d, J = 8.8 Hz, 2H, 2CH), 4.16–4.03 (m, 4H, $2OCH_2$), 3.85 (s, 3H, OCH_3), 3.06 (t, J = 7.0 Hz, 2H, CH_2), 2.08–1.99 (m, 2H, CH_2), 1.90–1.77 (m, 2H, CH_2), 1.30 (t, J = 7.0 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.8, 163.4, 130.2 (2C), 129.8, 113.7 (2C), 61.5 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, 2C), 55.4, 38.0 (d, $^2J_{C\text{-}P}$ = 14.1 Hz), 24.8 (d, $^1J_{C\text{-}P}$ = 140.8 Hz), 17.3 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 16.4 (d, $^3J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.4. **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{24}O_6P$ [$M+H^+$] 331.1305, found 331.1302.



Diethyl [4-hydroxy-4-(4-methoxyphenyl) butyl] phosphonate (4)

According to a modified procedure,[3] $NaBH_4$ (8.3 mg, 0.22 mmol) was added to a stirred solution of ketone (62.8 mg, 0.20 mmol) in absolute EtOH (3.0 ml). After stirring for 5 h, the mixture was concentrated in *vacuo* and the residue was dissolved in CH_2Cl_2 (50 ml). The organic layer was subsequently washed with distilled H_2O (50 ml ×3). The organic phase was dried over $MgSO_4$ and concentrated in *vacuo* to afford alcohol **4** (40.5 mg, 64%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.23 (d, J = 8.6 Hz, 2H, 2CH), 6.84 (d, J = 8.6 Hz, 2H, 2CH), 4.58 (d, J = 6.7 Hz, 1H, CH), 4.05–3.97 (m, 4H, $2OCH_2$), 3.77 (s, 3H, OCH_3), 1.87–1.77 (m, 1H, CH), 1.75–1.65 (m, 4H, $2CH_2$), 1.64–1.52 (m, 1H, CH), 1.26 (m, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 158.9, 136.8, 127.0 (2C), 113.7 (2C), 73.2, 61.4 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, 2C), 55.2, 39.5 (d, $^2J_{C\text{-}P}$ = 15.5 Hz), 25.3 (d, $^1J_{C\text{-}P}$ = 140.8 Hz), 18.7 (d, $^3J_{C\text{-}P}$ = 4.7 Hz), 16.3 (d, $^3J_{C\text{-}P}$ = 6.1 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.9. **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{25}O_5PNa$ [M+Na^+] 339.1332, found 339.1334.



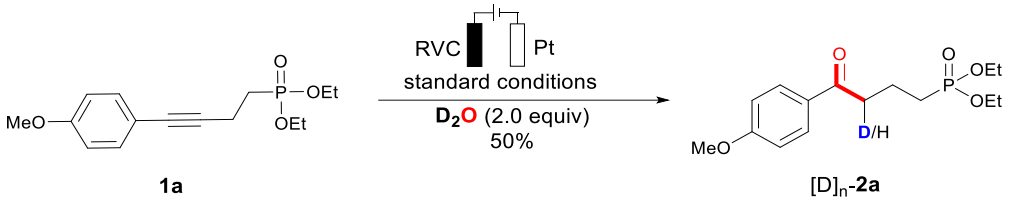
Diethyl (E)-[4-(4-methoxyphenyl)but-3-en-1-yl]phosphonate (5)

According to a modified procedure,[4] To a solution of **4** (122.9 mg, 0.39 mmol) in toluene (3.0 mL), was added PPTS (195.4 mg, 0.78 mmol) and the mixture stirred at 100 ℃ under nitrogen for 29 h. The solution is then poured into water and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Then, silica gel (0.8 g) was added and the combined solvents were removed under reduced pressure. The residue was purified by column chromatography on silica

gel (petroleum/EtOAc = 1/1) to yield the desired product **5** as a light yellow oli (47.7 mg, 42%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.25 (d, J = 5.3 Hz, 2H, 2CH), 6.82 (d, J = 8.7 Hz, 2H, 2CH), 6.36 (d, J = 15.7 Hz, 1H, CH), 6.11–6.02 (m, 1H, CH), 4.16–4.05 (m, 4H, $2OCH_2$), 3.78 (s, 3H, OCH_3), 2.54–2.38 (m, 2H, CH_2), 1.94–1.82 (m, 2H, CH_2), 1.32 (d, J = 7.1 Hz, 6H, $2CH_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 158.9, 130.0, 129.9, 127.1 (2C), 126.8 (d, $^{3}J_{C\text{-}P}$ = 17.1 Hz), 113.9 (2C), 61.5 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, 2C), 55.3, 25.9 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz), 25.7 (d, $^{1}J_{C\text{-}P}$ = 140.9 Hz), 16.46 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, 2C). **^{31}P {^{1}H}-NMR** (243 MHz, $CDCl_3$) δ = 32.1. **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{24}O_4P$ $[M+H^+]$ 299.1407, found 299.1406.

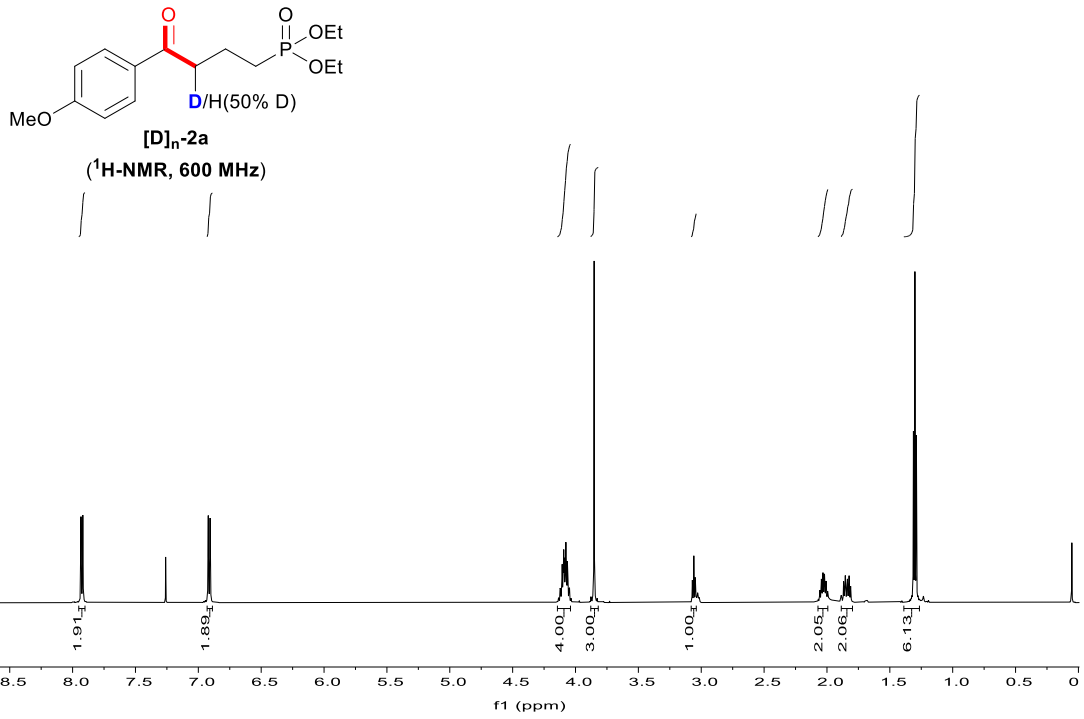
Mechanistic Studies

(a) H/D Exchange Experiments

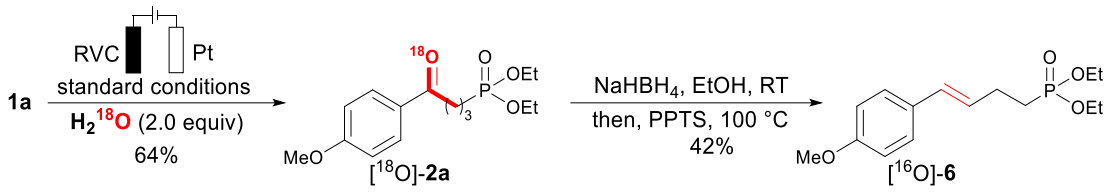


1a $[D]_n$-**2a**

Alkyne **1a** (0.20 mmol, 1.0 equiv), PhSeSePh (31.2 mg, 0.10 mmol, 0.5 equiv), NaCl (70.1 mg, 1.20 mmol, 6.0 equiv), 1-AdmCO_2H (54.1 mg, 0.30 mmol, 1.5 equiv), D_2O (8.0 mg, 0.20 mmol, 2.0 equiv), NEt_4BF_4(0.50 mmol, 1.0 equiv) and CH_3CN (5.0 mL) were added into a schlenk tube under an air atmosphere. At ambient temperature, electrolysis was started with a constant current of 10.0 mA which was then maintained for 4.3 h. The mixture was transferred to a flask and the electrodes were rinsed with EtOAc (5.0 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents in *vacuo*, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 1/1→1/3) to afford the desired product $[D]_n$-**1a** (38.3 mg, 60%) as a pale orange oil. The D-incorporation in $[D]_n$-**2a** was estimated by **^{1}H-NMR** spectroscopy.



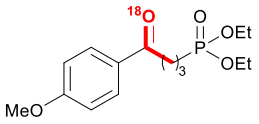
(b) **O^{18} isotope label experiment**

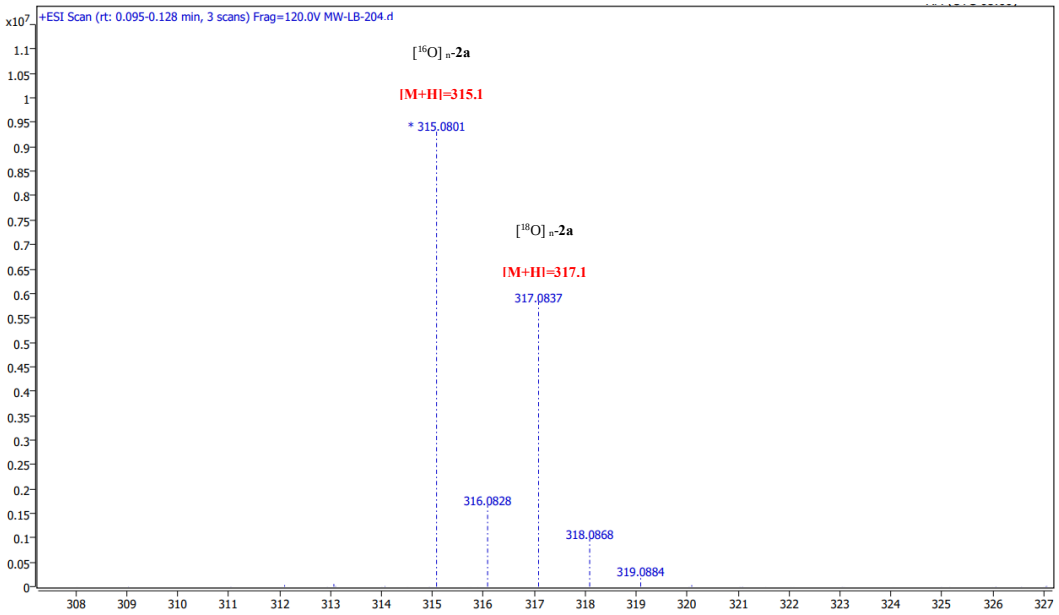


Alkyne **1a** (0.20 mmol, 1.0 equiv), PhSeSePh (31.2 mg, 0.10 mmol, 0.5 equiv), NaCl (70.1 mg, 1.2 mmol, 6.0 equiv), 1-AdmCO$_2$H (54.1 mg, 0.30 mmol, 1.5 equiv), $H_2{}^{18}O$ (8.0 mg, 0.20 mmol, 2.0 equiv), NEt_4BF_4(0.50 mmol, 1.0 equiv) and CH_3CN (5 mL) were added into a schlenk tube under an air atmosphere. At ambient temperature, electrolysis was started with a constant current of 10.0 mA which was then maintained for 4.3 h. The mixture was transferred into a flask and the electrodes were rinsed with EtOAc (3 × 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents in *vacuo*, the resedue was purified by column chromatography on silica gel (petroleum ether /EtOAc: 1/1→1/3) to afford the desired product [^{18}O]$_n$-**2a** (38.3 mg, 64%) as a pale orange oil.

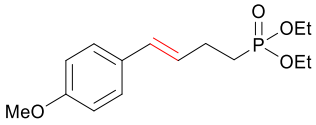
$NaBH_4$ (4.2 mg, 0.11 mmol) was added to a stirred solution of [^{18}O]$_n$-**2a** (34.6 mg, 0.11 mmol) in absolute EtOH (2.0 ml). After stirred for 5 h, the mixture was concentrated in *vacuo* and the residue was re-dissolved in CH_2Cl_2 (50 mL). The organic layer was subsequently washed with distilled water (3 × 50 mL), dried over $MgSO_4$ and concentrated in *vacuo* to deliver the crude alcohol. Then, PPTS (50.3 mg, 0.20 mmol) and the crude alcohol in PhMe (2.0 mL) was stirred at 100 ℃ under a nitrogen atmosphere for 29 h. At ambient temperature, the solution was then poured into ice water and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Then, silica gel (0.8 g) was added and the combined solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum/EtOAc = 1/1) to yield the desired product [^{18}O] $_n$-**6** (13.7 mg, 42%) as a light-yellow oil. No ^{18}O-incorporation was detected in the elimination product of [^{18}O]$_n$-**2a**.

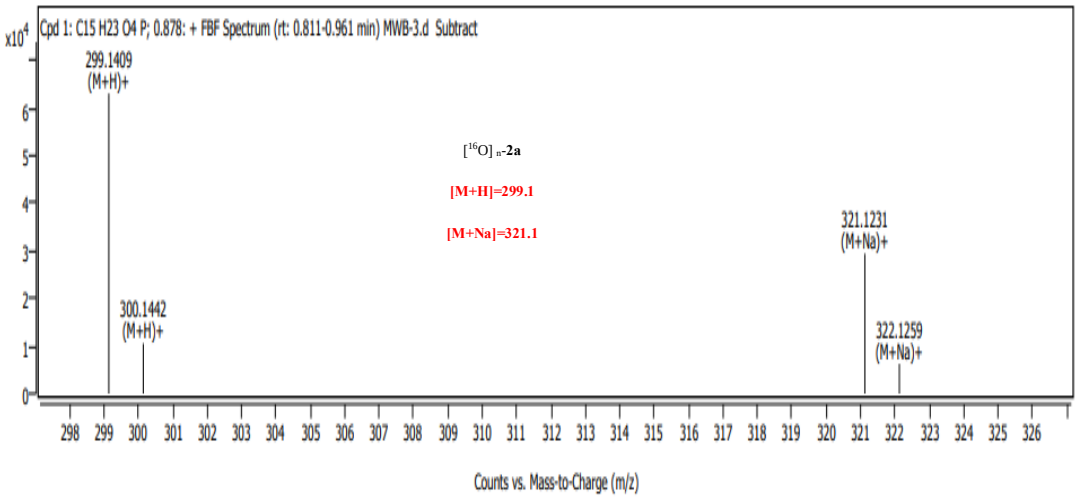
The ^{18}O-incorporation in $[^{18}O]_n$-**2a**



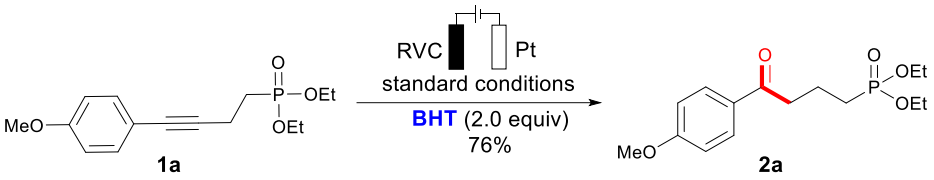


The **HR-MS** spectrum for $[^{16}O]$-**6**





(c) **radical scavenger experiment**



Alkyne **1a** (0.20 mmol, 1.0 equiv), PhSeSePh (31.2 mg, 0.10 mmol, 0.50 equiv), NaCl (70.1 mg, 1.20 mmol, 6.0 equiv), 1-AdmCO_2H (54.1 mg, 0.30 mmol, 1.5 equiv), H_2O (8.0 mg, 0.20 mmol, 2.0 equiv), BHT (88.1 mg, 0.4 mmol, 2.0 equiv), NEt_4BF_4(0.50 mmol, 1.0 equiv) and CH_3CN (5.0 mL) were added into a schlenk tube under an air atmosphere. At ambient temperature, electrolysis was started with a constant current of 10.0 mA which was then maintained for 4.3 h. The mixture was transferred into a flask and the electrodes were rinsed with EtOAc (3 × 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc: 1/1→1/3) to afford the desired product **2a** (47.8 mg, 76%) as a pale orange oil.

(d) **GC-MS analysis of the crude reaction mixture of alkyne 1a**

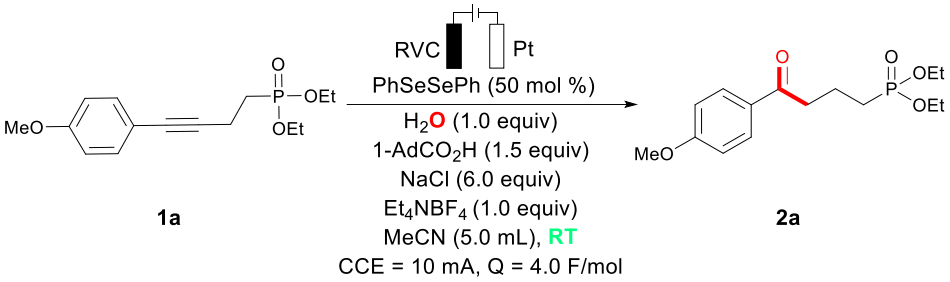
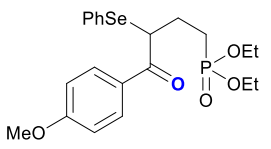
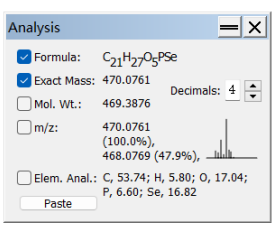
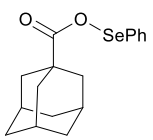
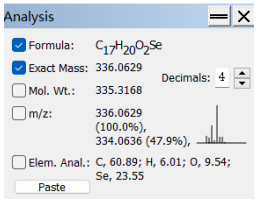


Table S-2. The detected species in crude reaction mixture of **1a** by GC-MS

		$[M+H]^+$	$[M+Na]^+$
		471.084	493.065

		[M+H]$^+$	[M+Na]$^+$
		337.07	359.05

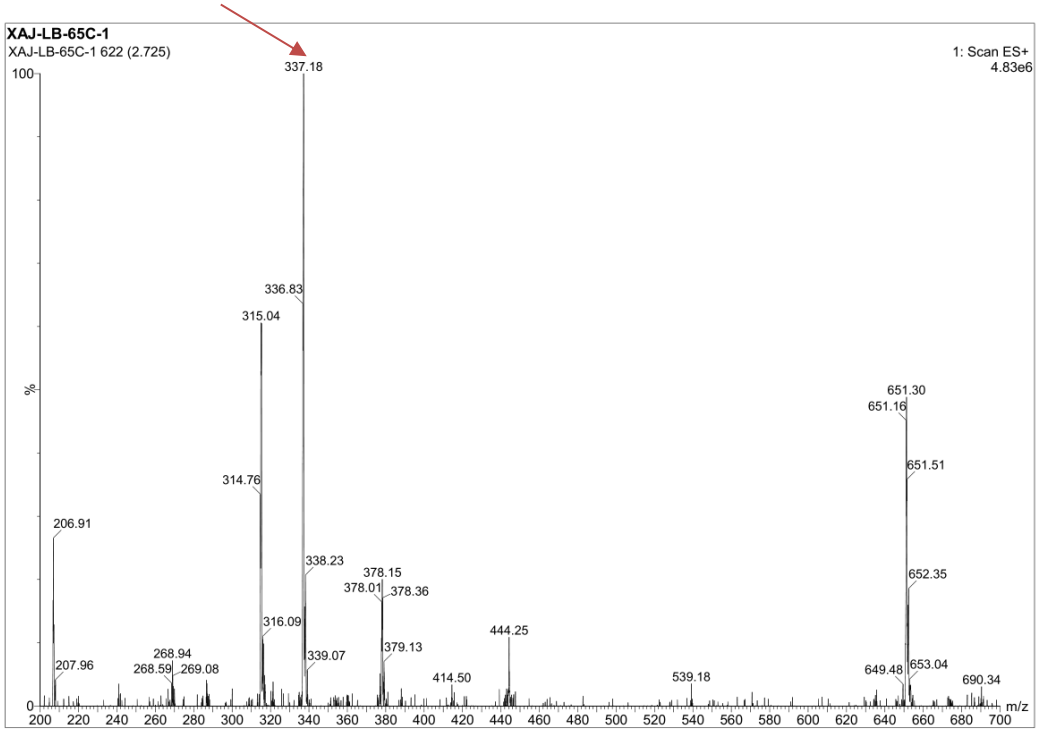


Figure S-1. GC-MS Spectrum for the crude reaction mixture **1a**

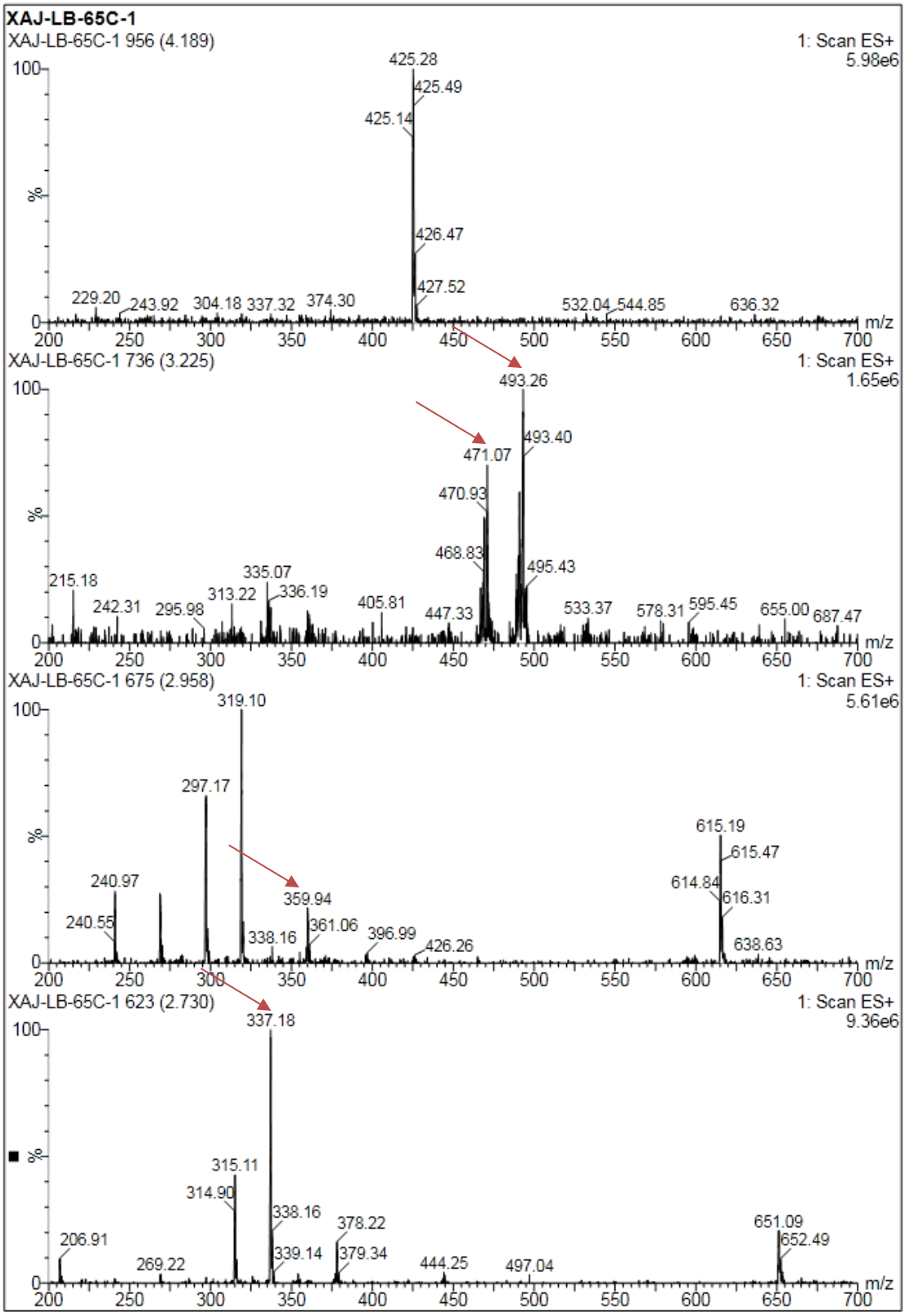


Figure S-2. GC-MS Spectrum for the crude reaction mixture **1a**

Cyclic Voltammetry

The cyclic voltammetry was carried out with a CHI650E workstation. A glassy-carbon electrode (5 mm-diameter, disc-electrode) was used as the working electrode, a Pt wire as auxiliary electrode and a SCE electrode was used as the reference. The measurements were carried out at a scan rate of 100 mVs^{-1}.

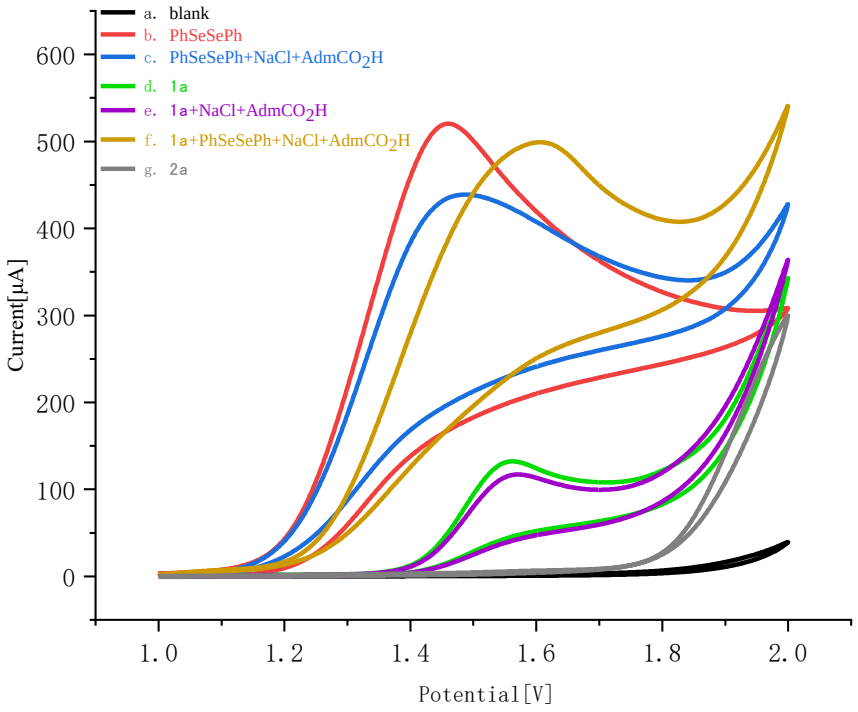


Figure S-1. Cyclic voltammograms at 100 mVs^{-1}: NEt_4BF_4 (0.1 M in MeCN), concentration of substrates 3 mM. (a) blank; (b) PhSeSePh; (c) PhSePhSe, NaCl and 1-$AdCO_2H$; (d) substrate **1a**; (e) **1a**, NaCl and 1-$AdCO_2H$; (f) **1a**, PhSeSePh, NaCl and 1-$AdCO_2H$; (g) **2a**.

Reference

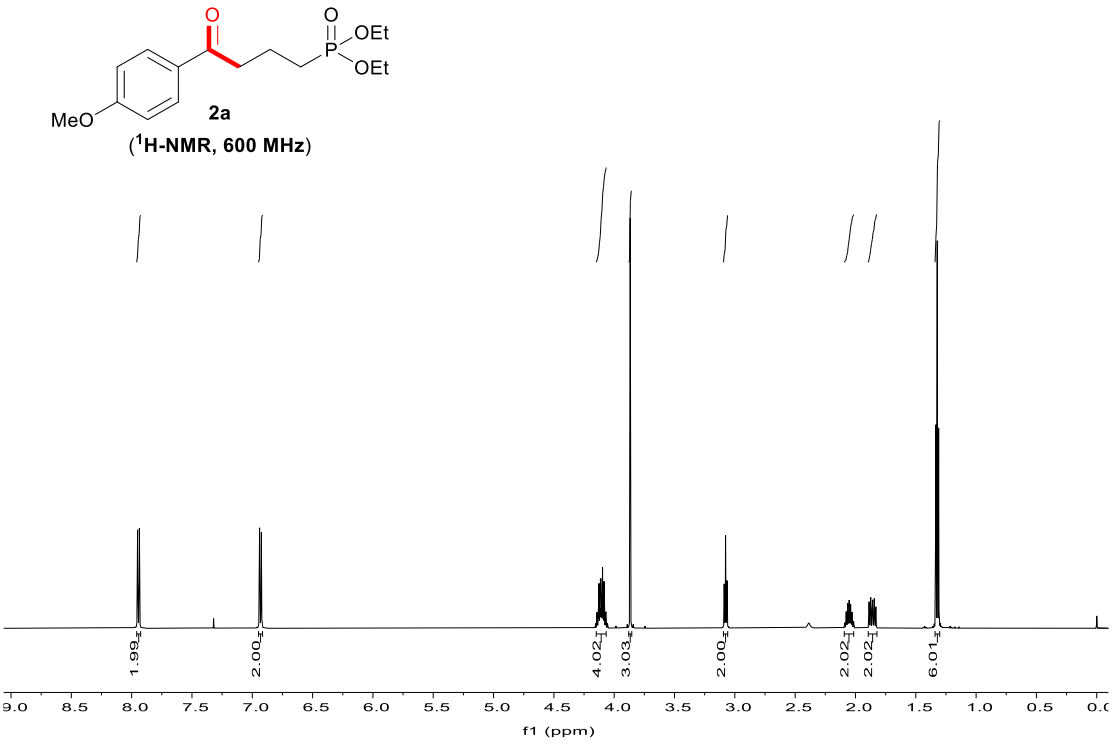
[1]. B. Pérez-Saavedra, N. Vázquez-Galiñanes, C. Saá and M. Fañanás-Mastral, *ACS Catalysis*, 2017, **7**, 6104.

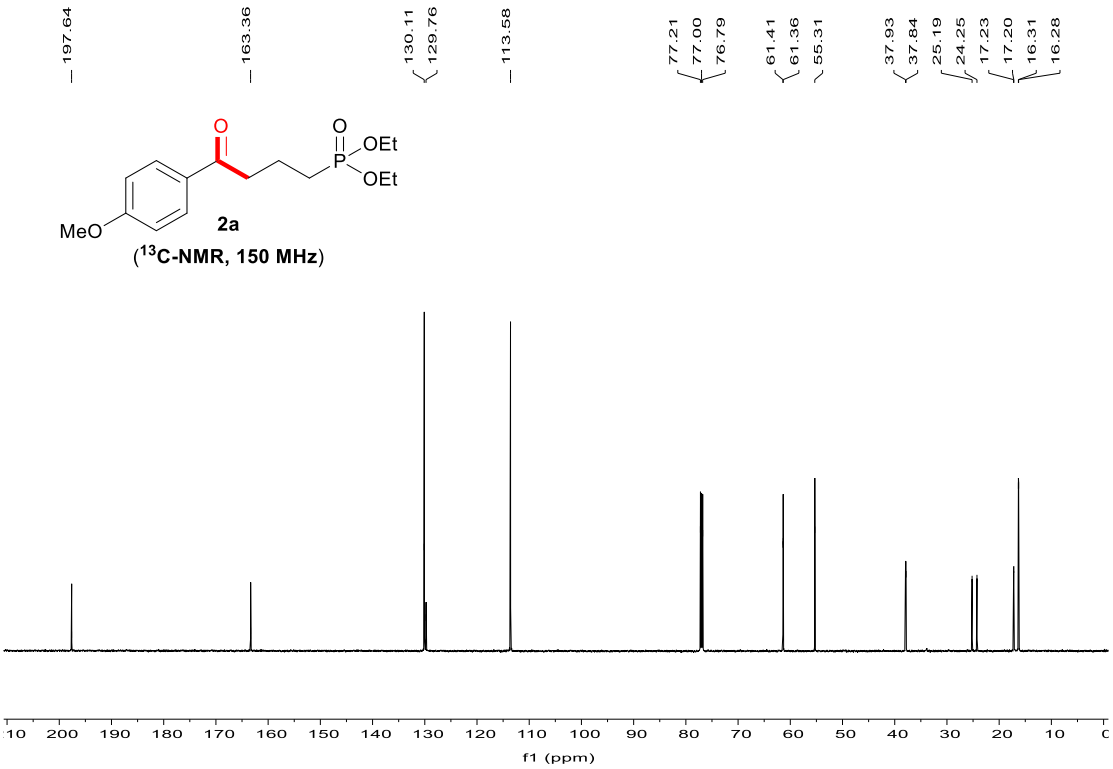
[2]. K. Bera and I. N. Namboothiri, *J Org Chem*, 2015, **80**, 1402.

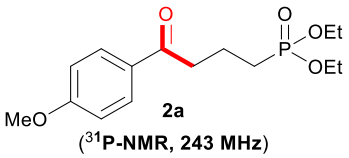
[3]. C. Wiles, P. Watts and S. J. Haswell, *Tetrahedron Letters*, 2006, **47**, 5261.

[4]. H. Lee and J. Yun, *Org Lett*, 2018, **20**, 7961.

NMR spectra

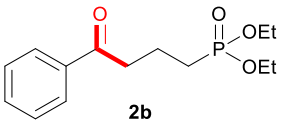

O
O
OEt
P
OEt
MeO
2a
(1H-NMR, 600 MHz)
1.99
2.00
4.02
3.03
2.00
2.02
2.02
6.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


197.64
163.36
130.11
129.76
113.58
77.21
77.00
76.79
61.41
61.36
55.31
37.93
37.84
25.19
24.25
17.23
17.20
16.31
16.28
O
O
OEt
P
OEt
MeO
2a
(13C-NMR, 150 MHz)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



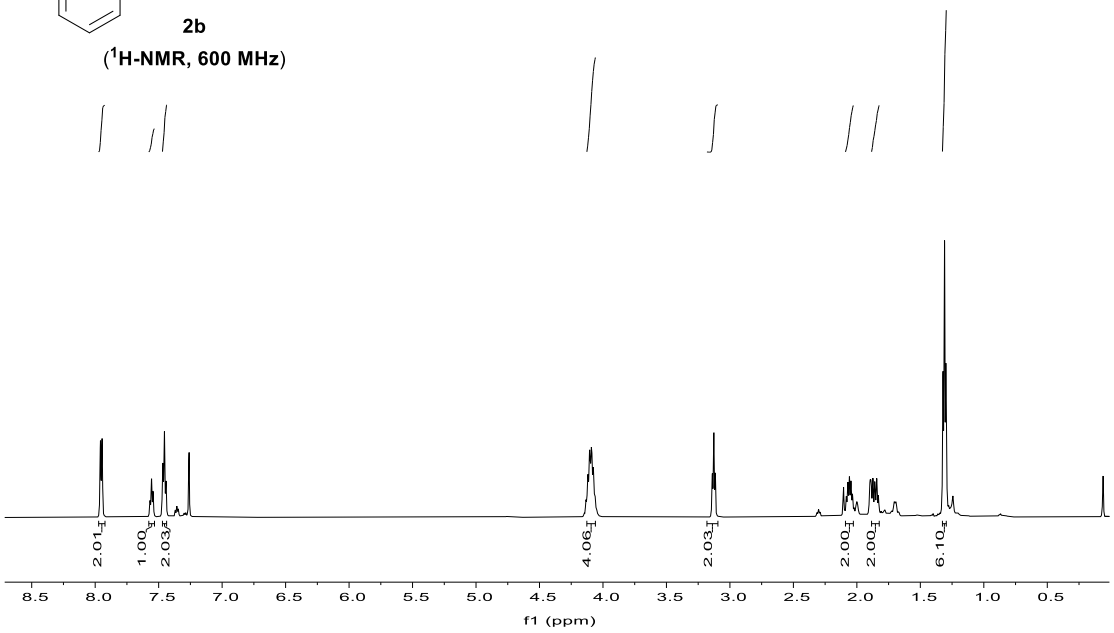
2a

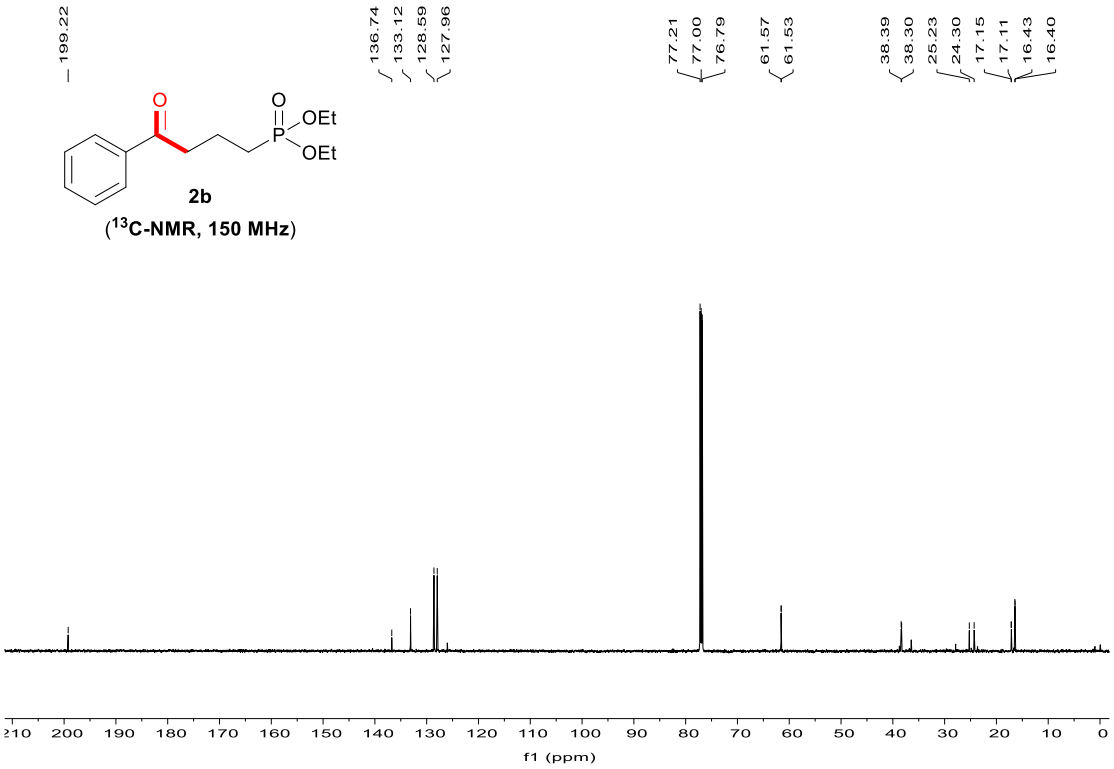
(**^{31}P-NMR, 243 MHz**)



2b

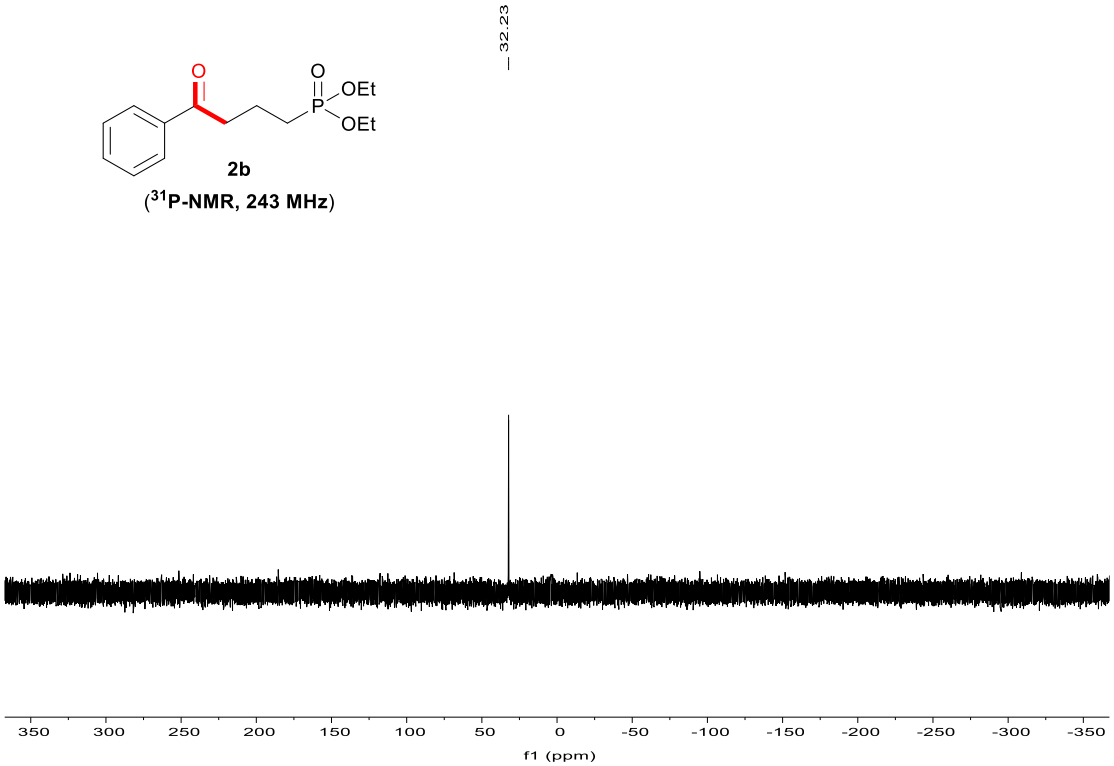
(**^{1}H-NMR, 600 MHz**)





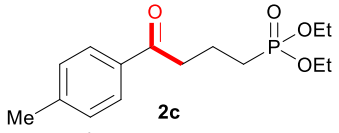
2b

(**^{13}C-NMR, 150 MHz**)



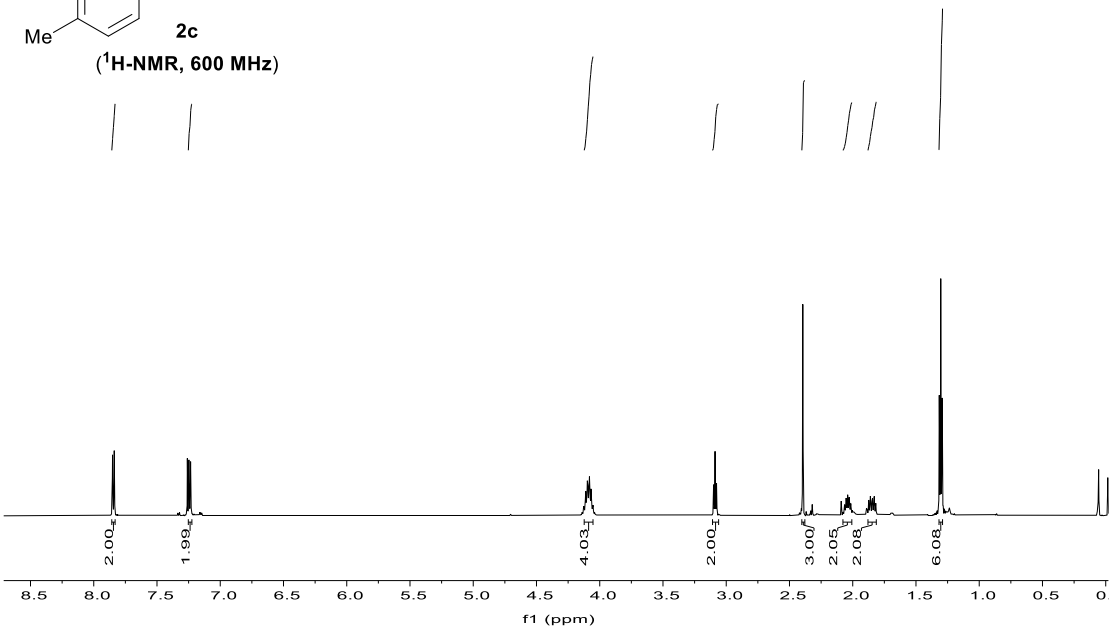
2b

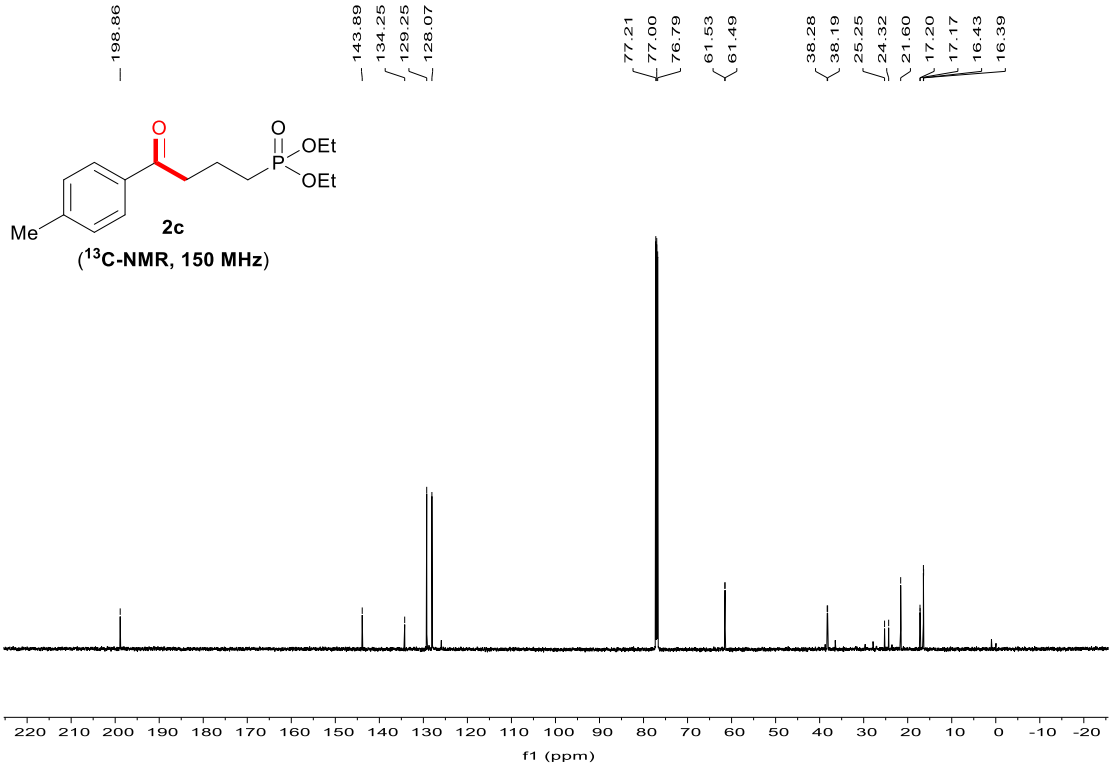
(**^{31}P-NMR, 243 MHz**)



2c

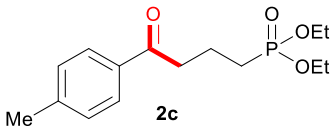
(**^{1}H-NMR, 600 MHz**)





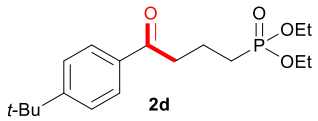
2c

(**^{13}C-NMR, 150 MHz**)



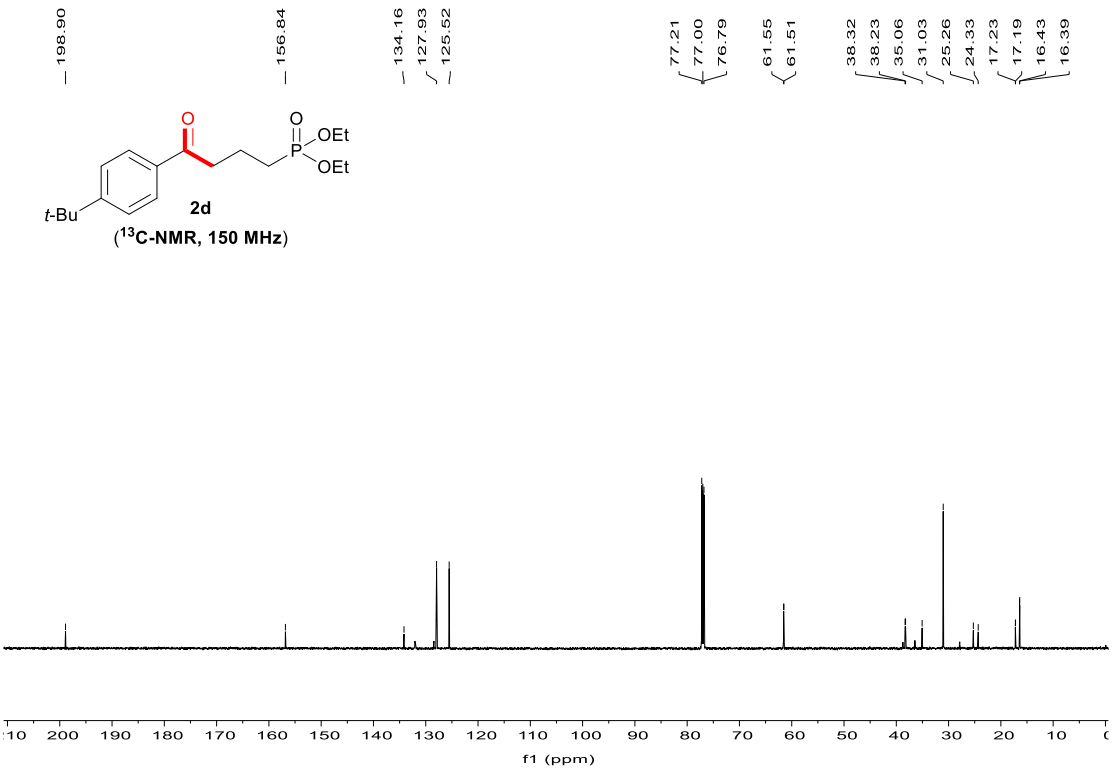
2c

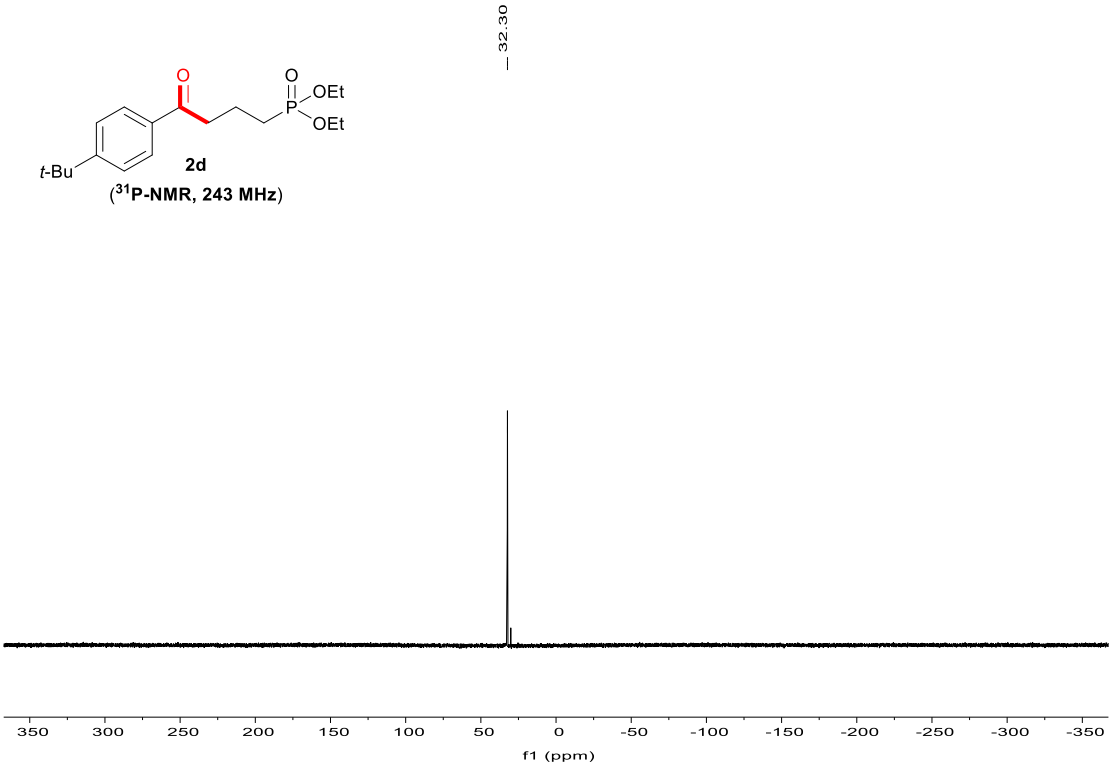
(**^{31}P-NMR, 243 MHz**)

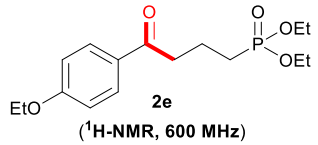


2d

(**^{1}H-NMR, 600 MHz**)

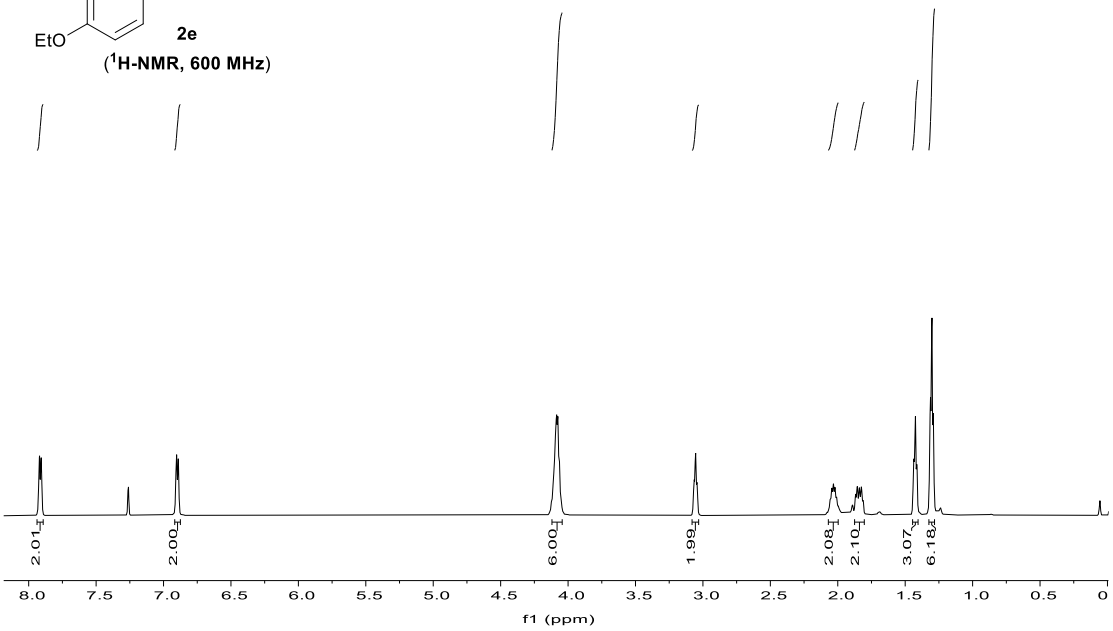

198.90
156.84
134.16
127.93
125.52
77.21
77.00
76.79
61.55
61.51
38.32
38.23
35.06
31.03
25.26
24.33
17.23
17.19
16.43
16.39
O
O
OEt
P
OEt
t-Bu
2d
(13C-NMR, 150 MHz)
f1 (ppm)

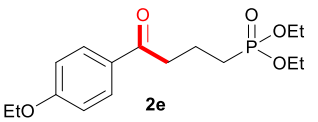

32.30
O
O
OEt
P
OEt
t-Bu
2d
(31P-NMR, 243 MHz)
f1 (ppm)



2e

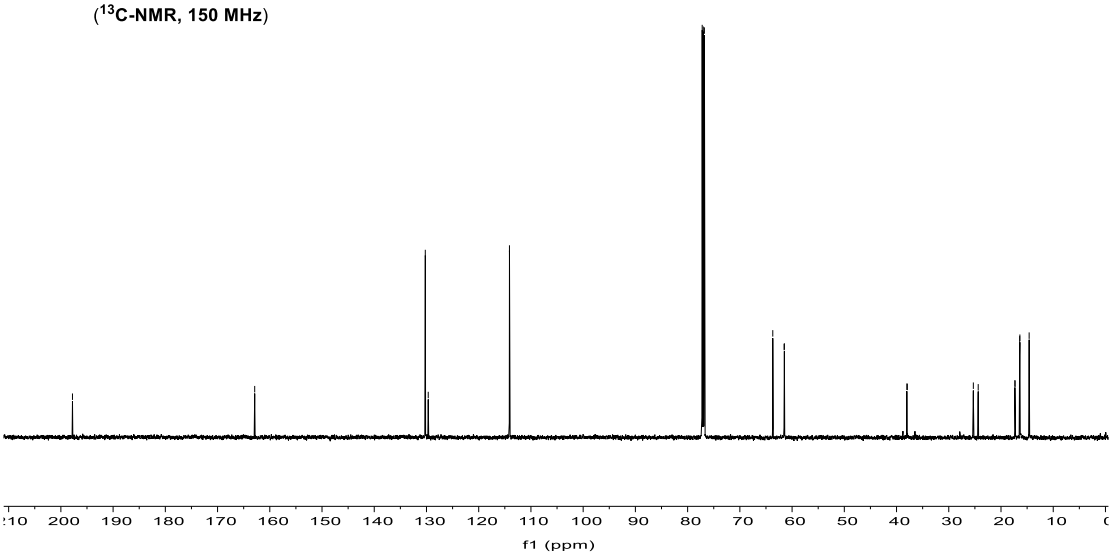
(**^{1}H-NMR, 600 MHz**)

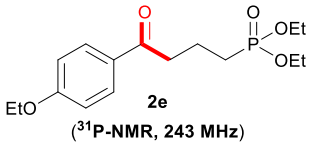




2e

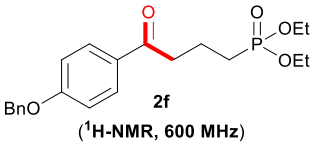
(**^{13}C-NMR, 150 MHz**)





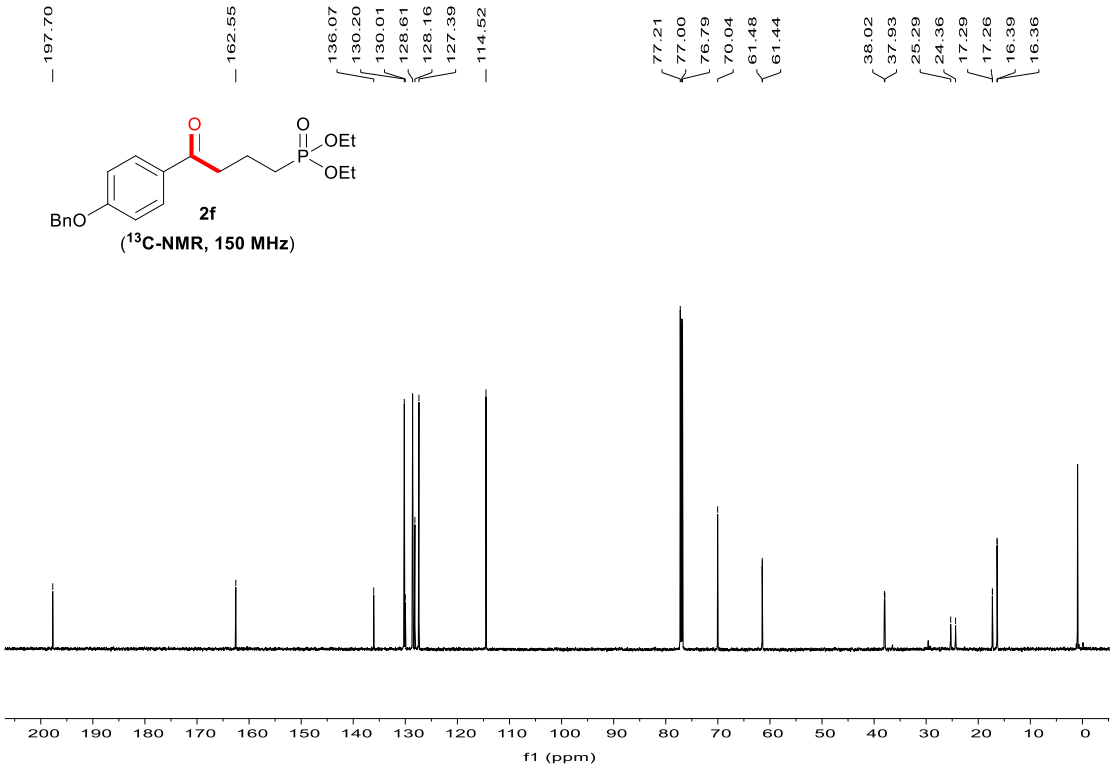
2e

(**^{31}P-NMR, 243 MHz**)



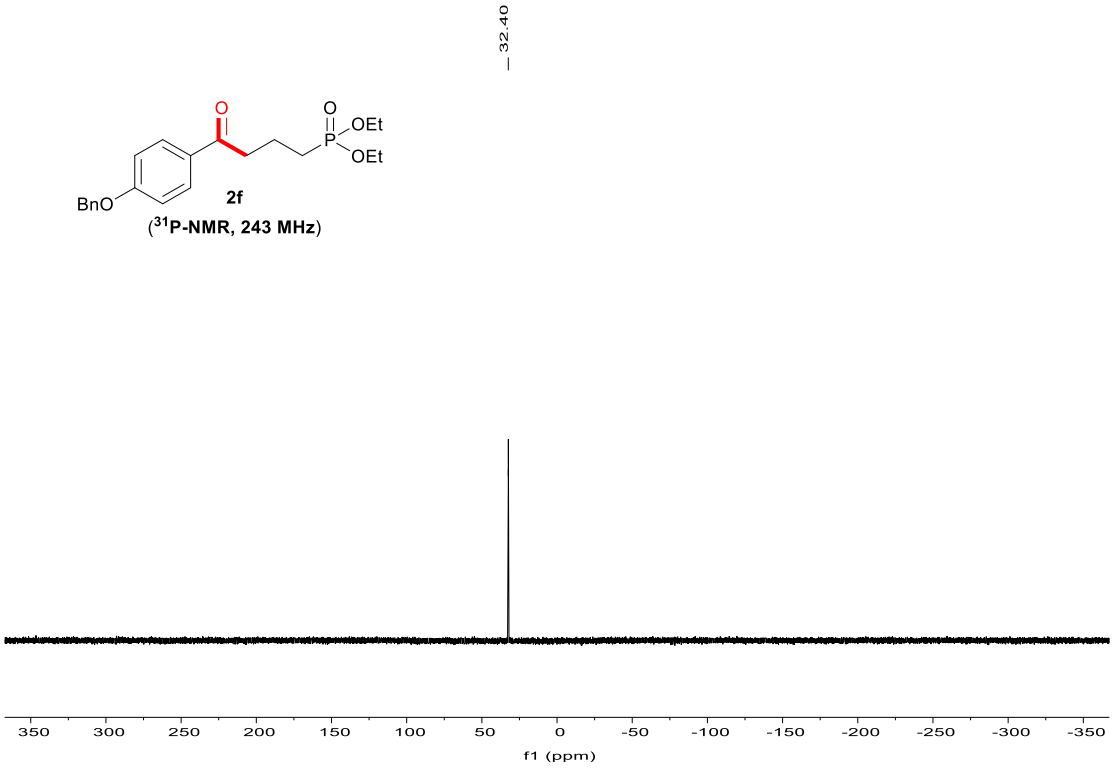
2f

(**^{1}H-NMR, 600 MHz**)



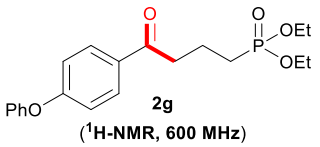
2f

(**^{13}C-NMR, 150 MHz**)



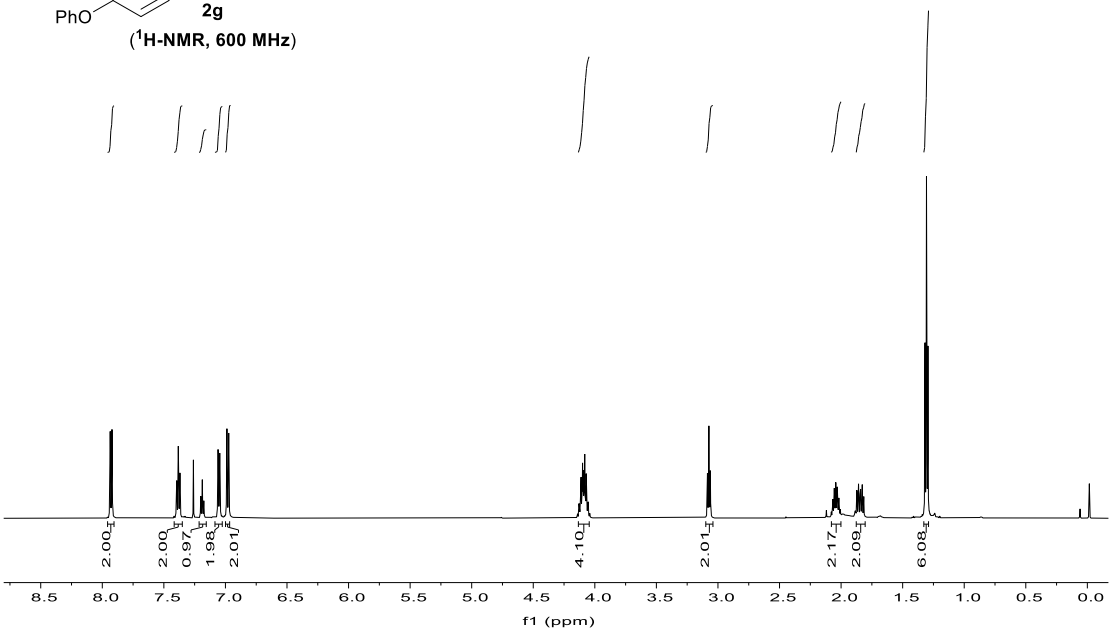
2f

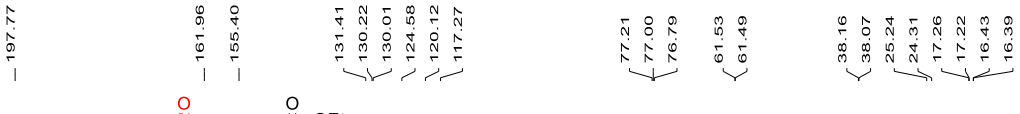
(**^{31}P-NMR, 243 MHz**)

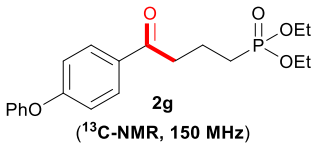


2g

(**^{1}H-NMR, 600 MHz**)

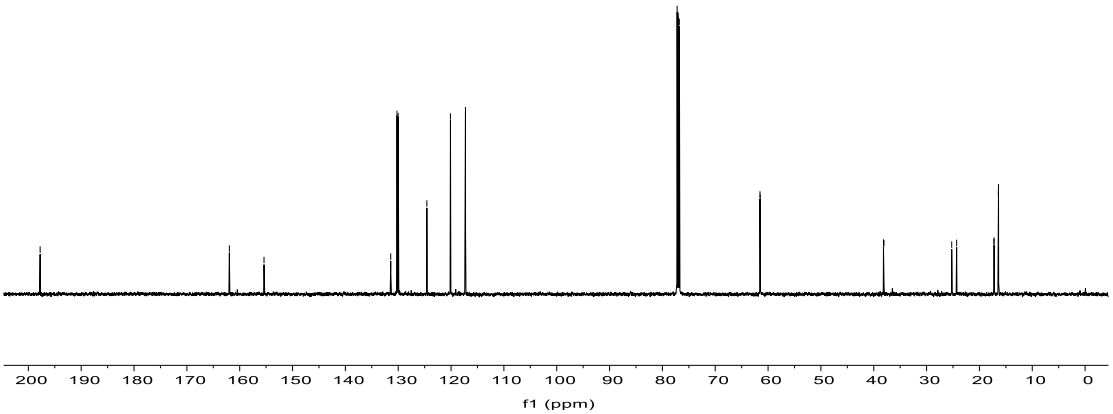


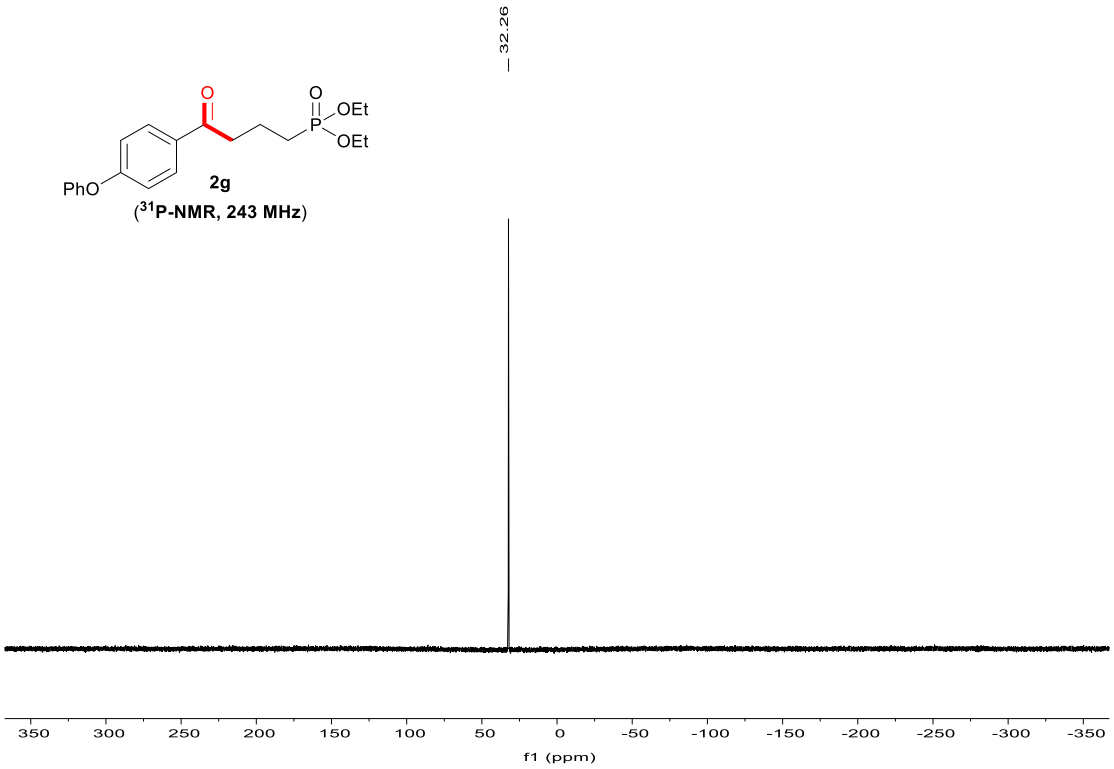


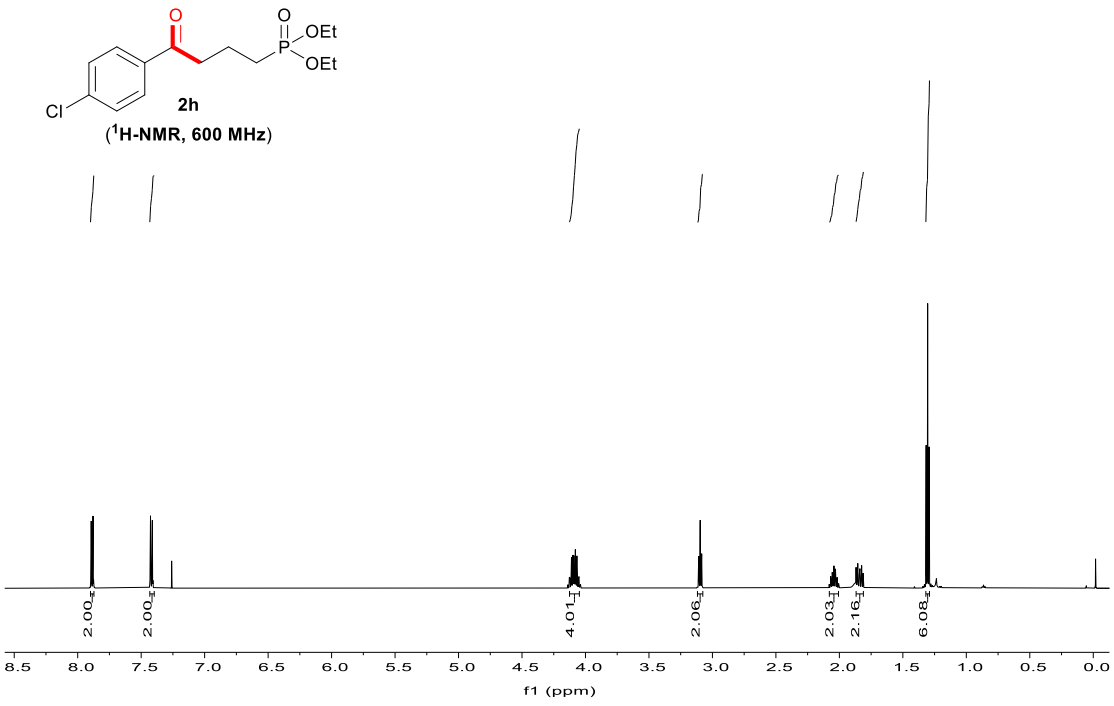


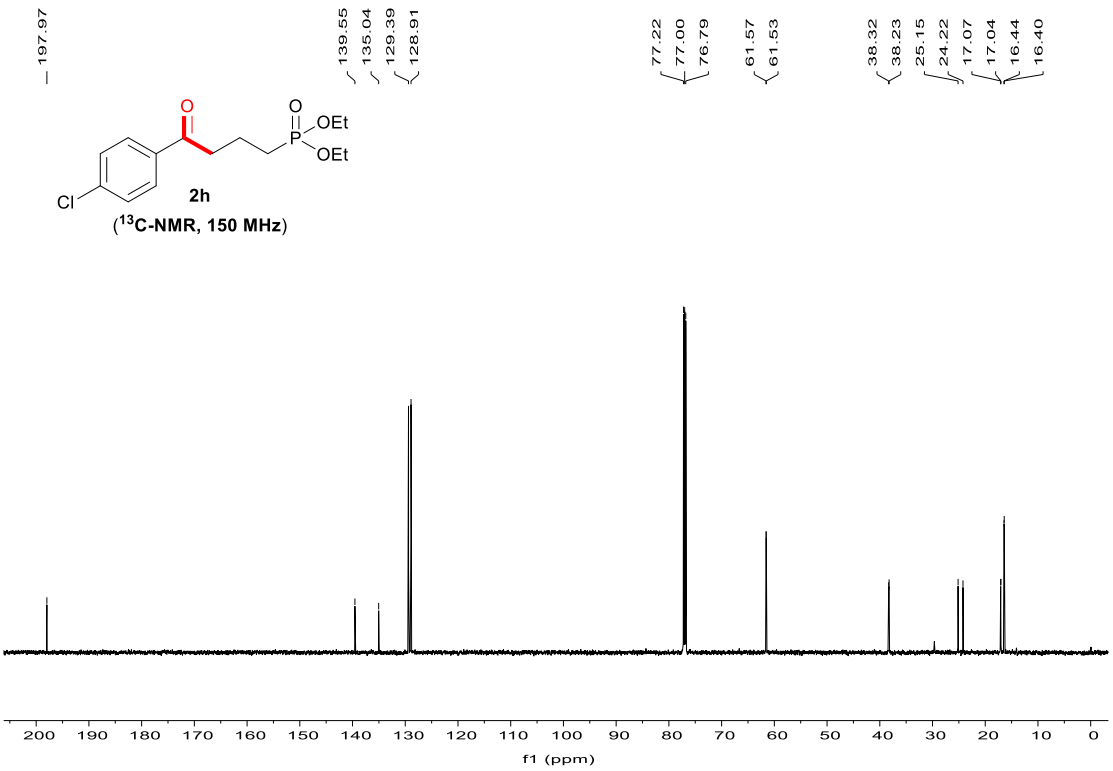
2g

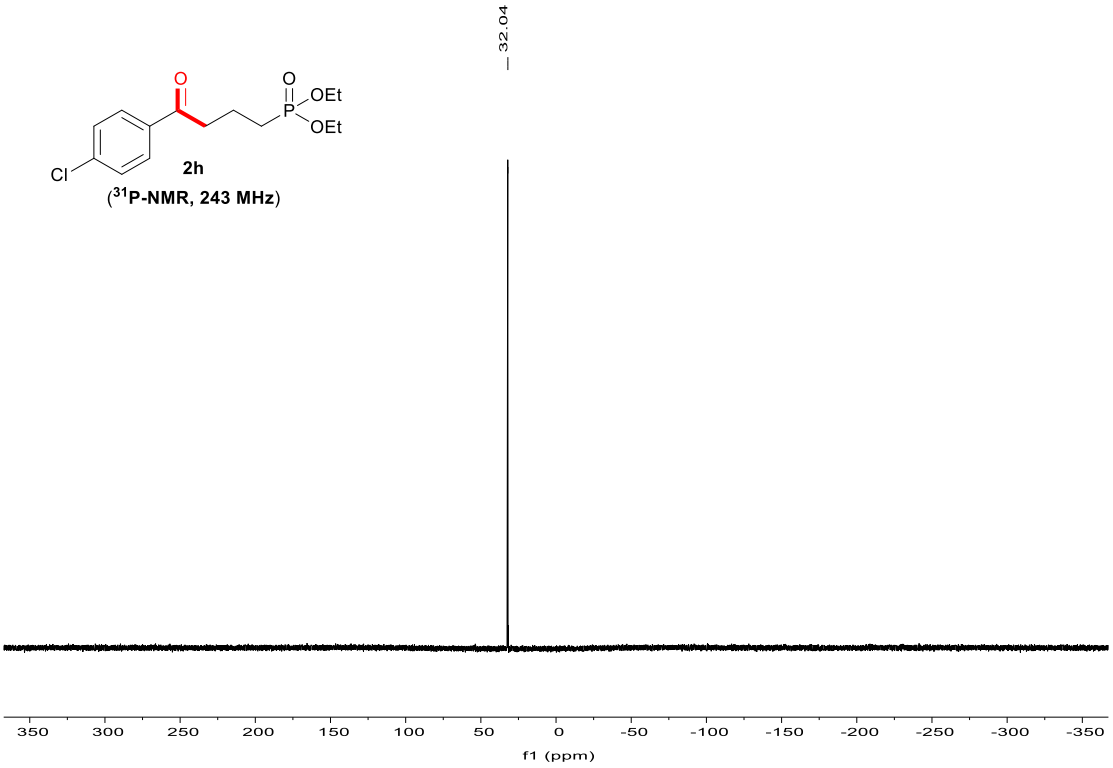
(**^{13}C-NMR, 150 MHz**)

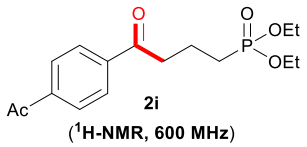



32.26
O
O
OEt
P
OEt
PhO
2g
(31P-NMR, 243 MHz)
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)


O
O
OEt
P
OEt
Cl
2h
(1H-NMR, 600 MHz)
2.00
2.00
4.01
2.06
2.03
2.16
6.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

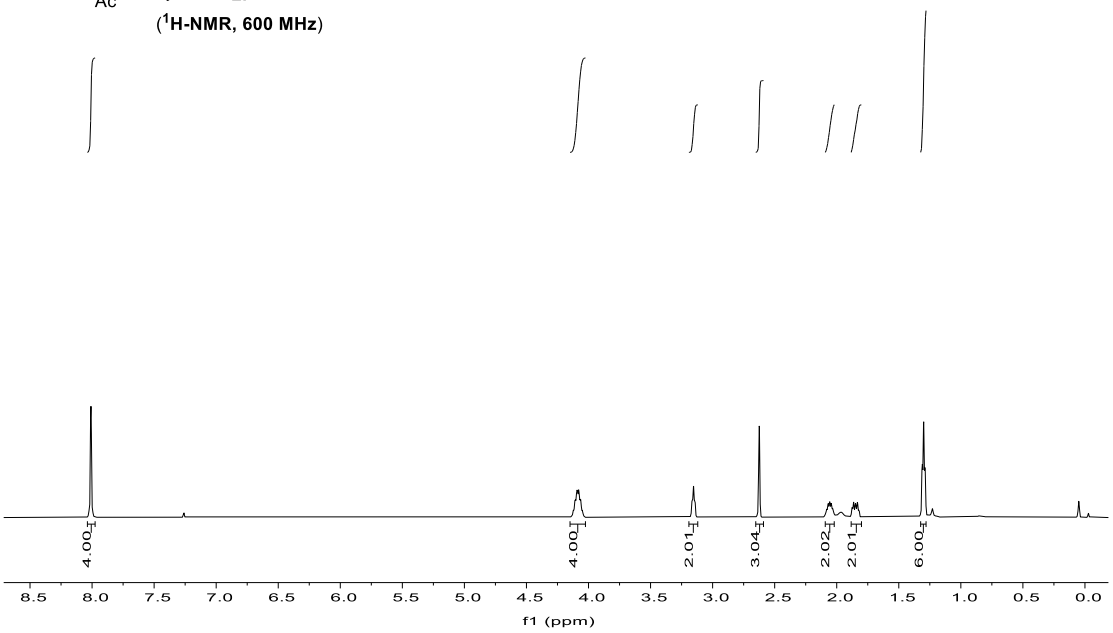

197.97
139.55
135.04
129.39
128.91
77.22
77.00
76.79
61.57
61.53
38.32
38.23
25.15
24.22
17.07
17.04
16.44
16.40
O
O
OEt
P
OEt
Cl
2h
(13C-NMR, 150 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


32.04
O
O
OEt
P
OEt
Cl
2h
(31P-NMR, 243 MHz)
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)

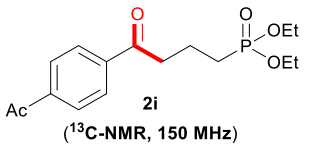


2i

(**^{1}H-NMR, 600 MHz**)

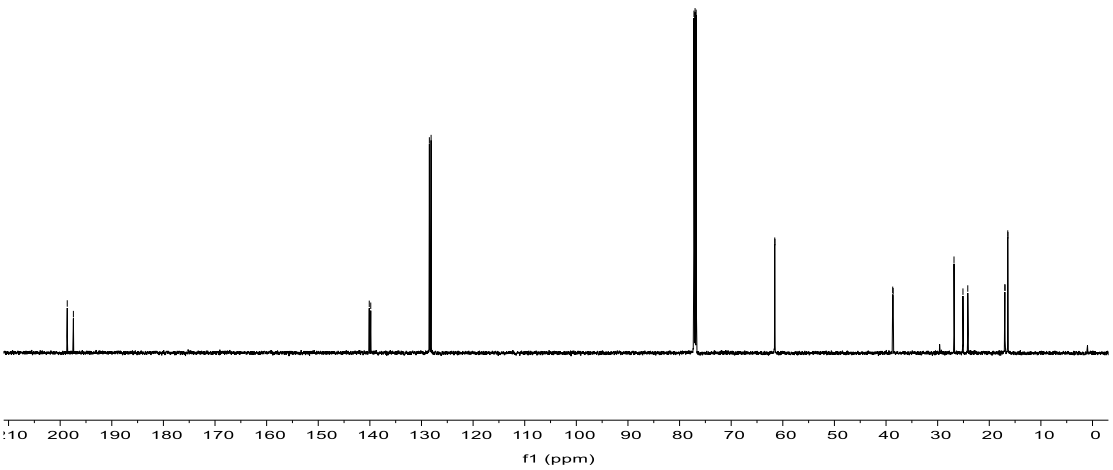


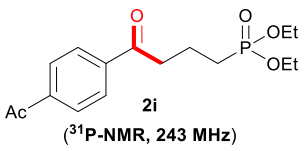
198.63
197.44
140.12
139.83
128.47
128.14
77.21
77.00
76.79
61.56
61.52
38.71
38.62
26.83
25.10
24.16
16.98
16.95
16.42
16.38



2i

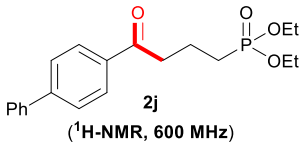
(**^{13}C-NMR, 150 MHz**)





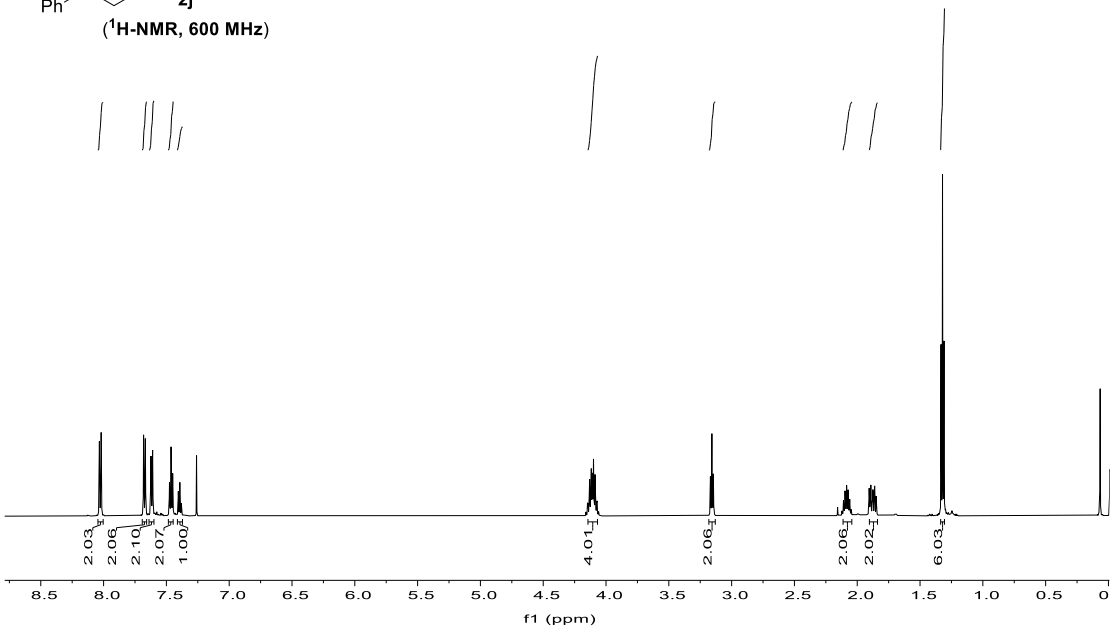
2i

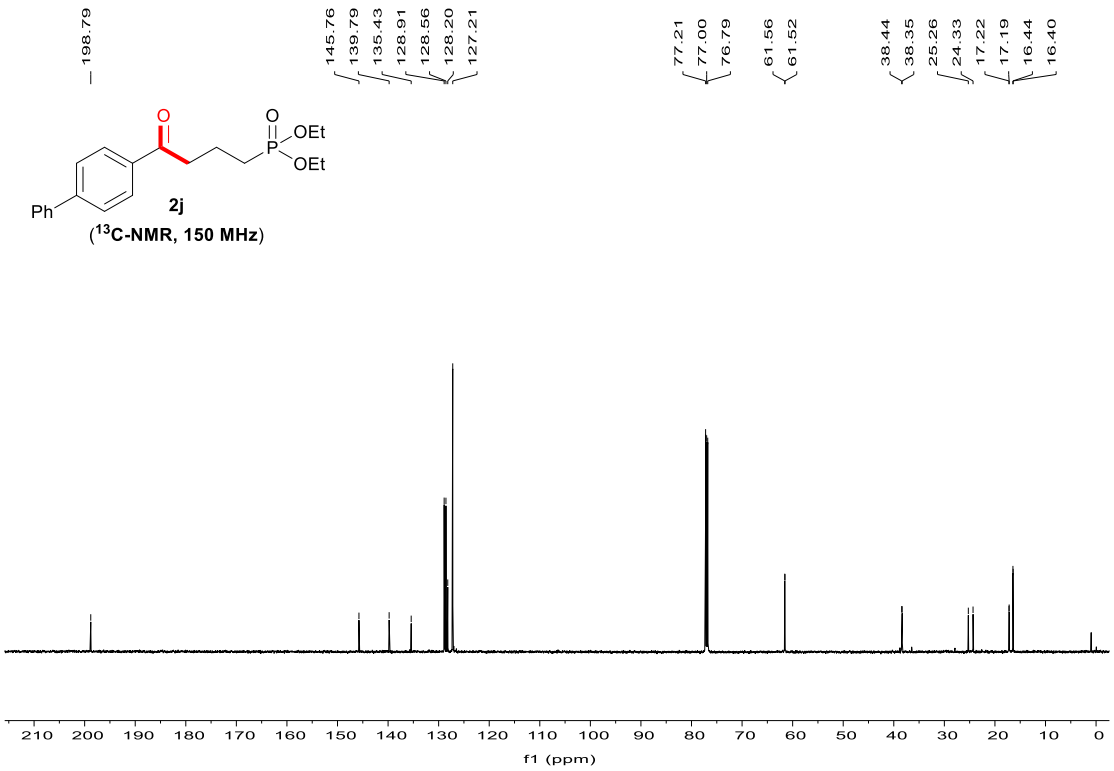
(**^{31}P-NMR, 243 MHz**)

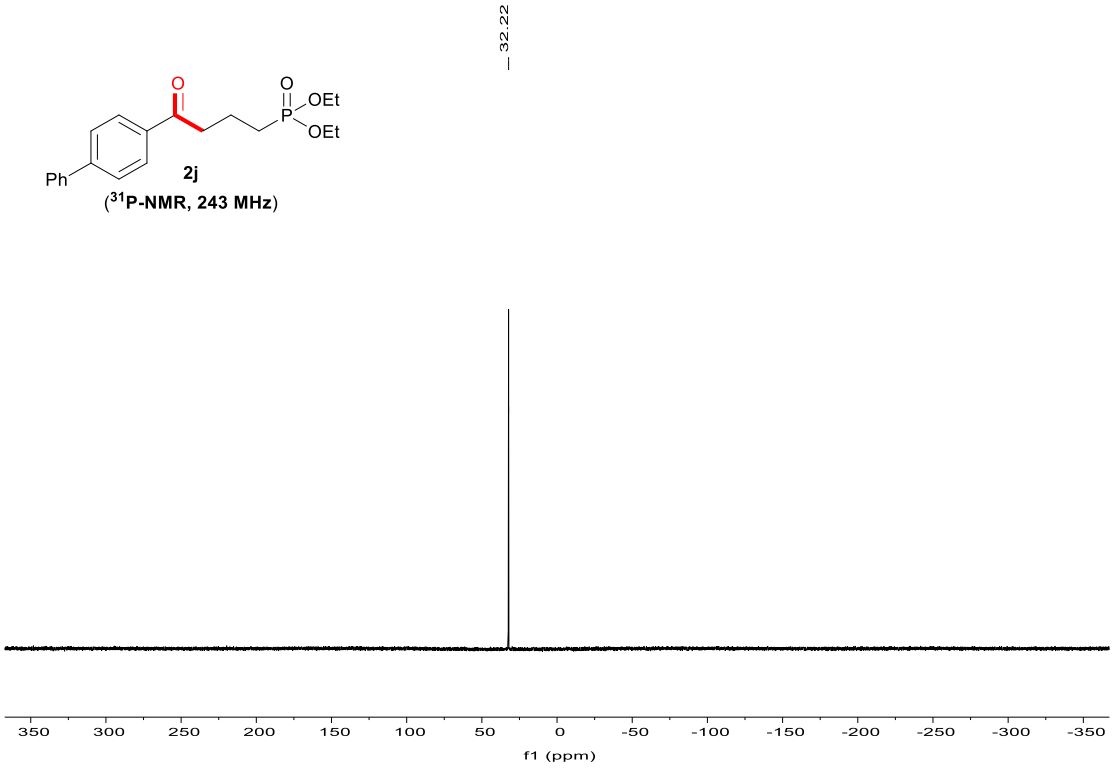


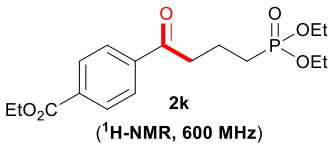
2j

(**^{1}H-NMR, 600 MHz**)



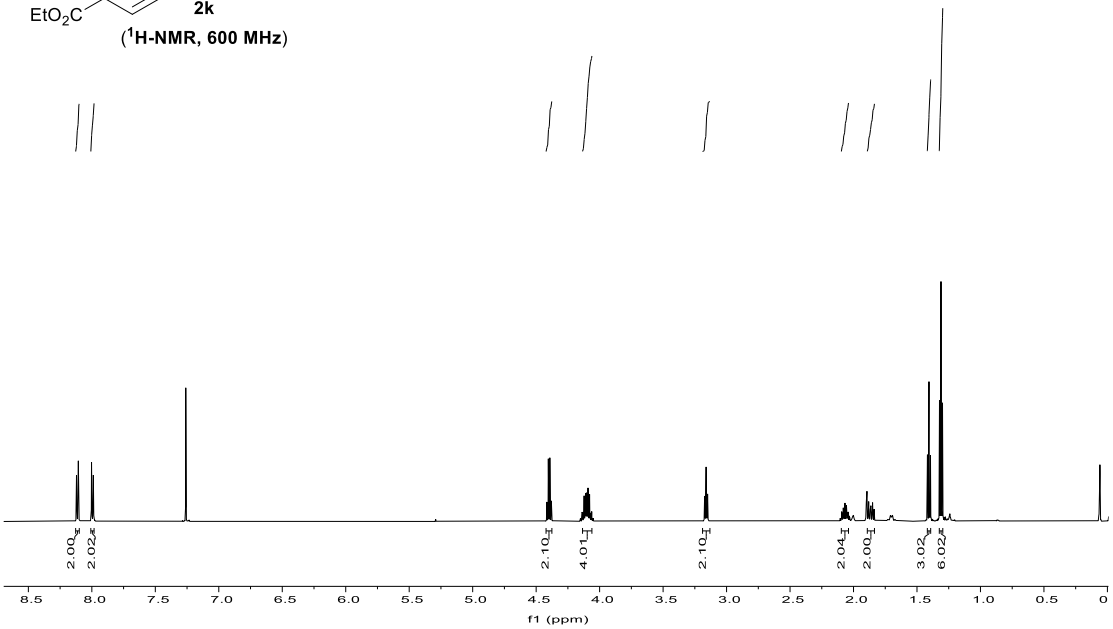

198.79
145.76
139.79
135.43
128.91
128.56
128.20
127.21
77.21
77.00
76.79
61.56
61.52
38.44
38.35
25.26
24.33
17.22
17.19
16.44
16.40
O
O
OEt
P
OEt
Ph
2j
(13C-NMR, 150 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

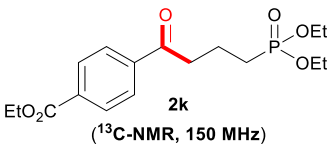

32.22
O
O
OEt
P
OEt
Ph
2j
(31P-NMR, 243 MHz)
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)



2k

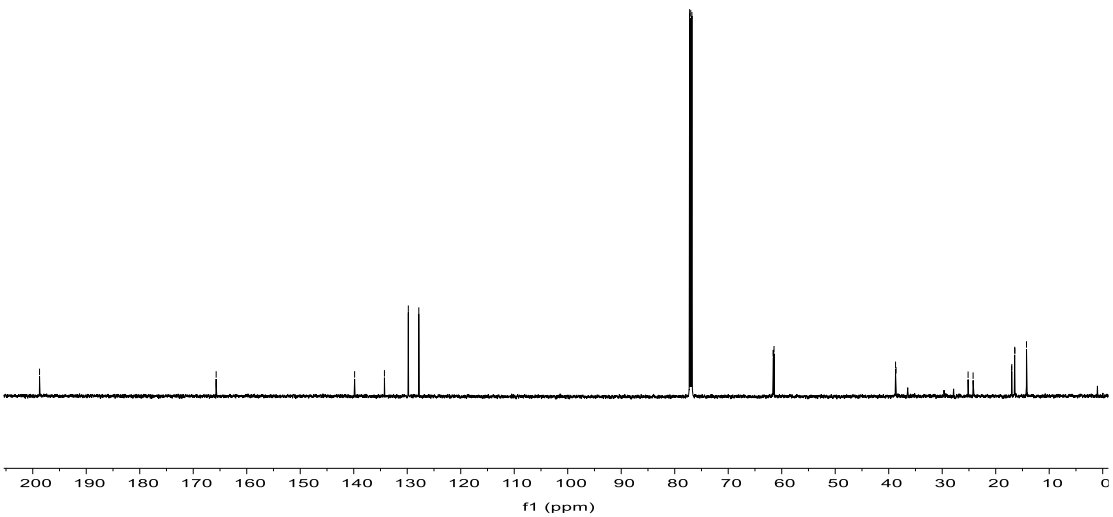
(**^{1}H-NMR, 600 MHz**)

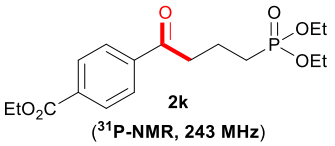




2k

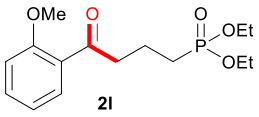
(**^{13}C-NMR, 150 MHz**)





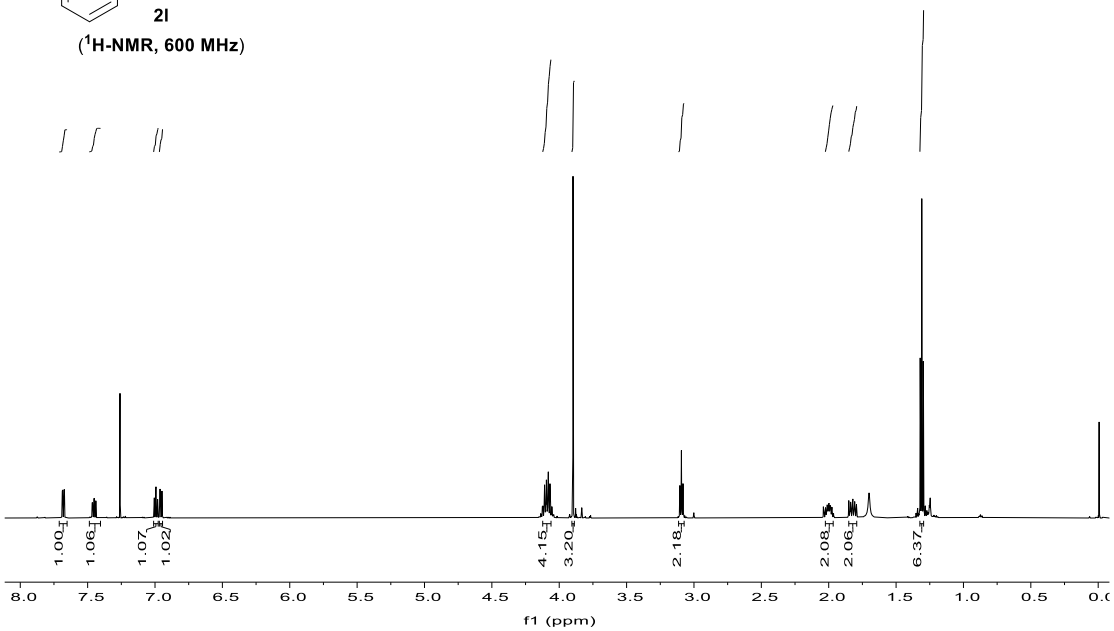
2k

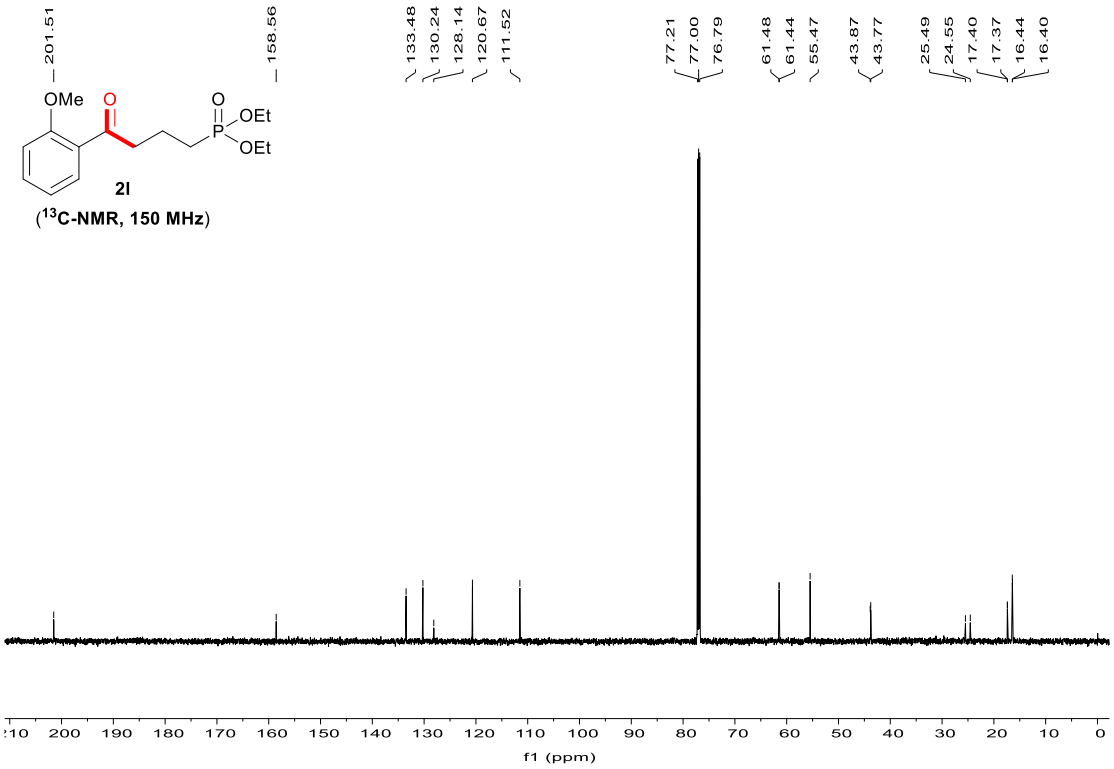
(**^{31}P-NMR, 243 MHz**)



2l

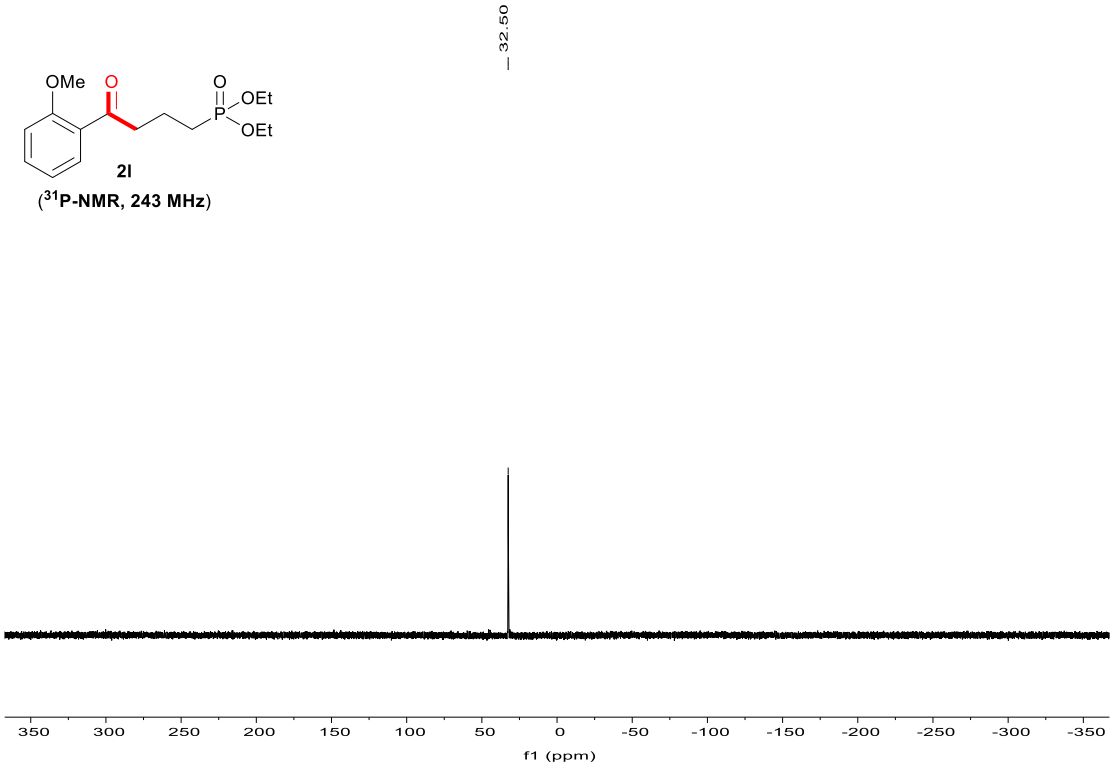
(**^{1}H-NMR, 600 MHz**)





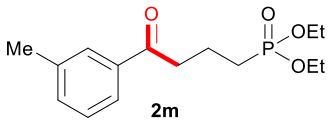
2l

(**^{13}C-NMR, 150 MHz**)



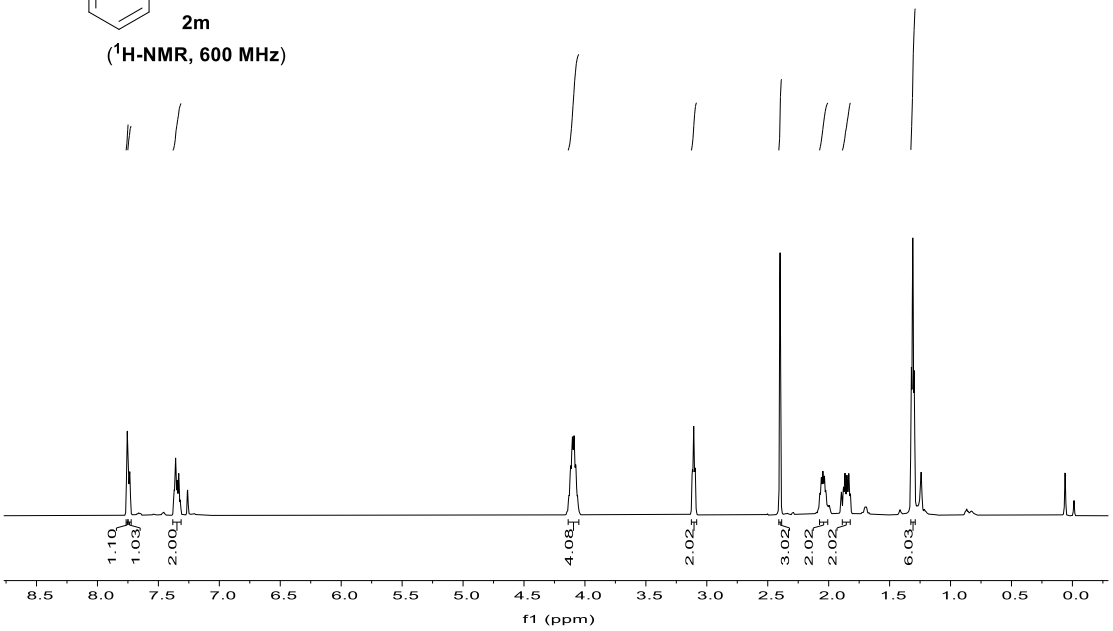
2l

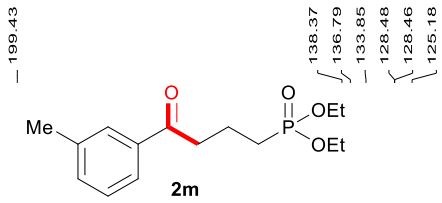
(**^{31}P-NMR, 243 MHz**)



2m

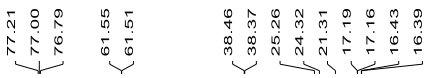
(**^{1}H-NMR, 600 MHz**)

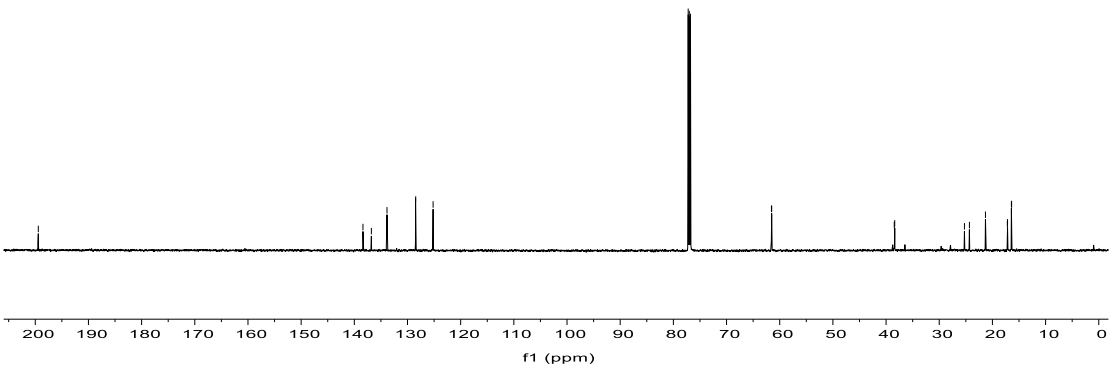


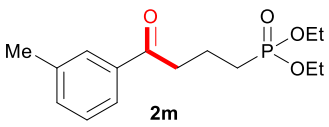


2m

(**^{13}C-NMR, 150 MHz**)

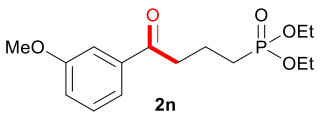






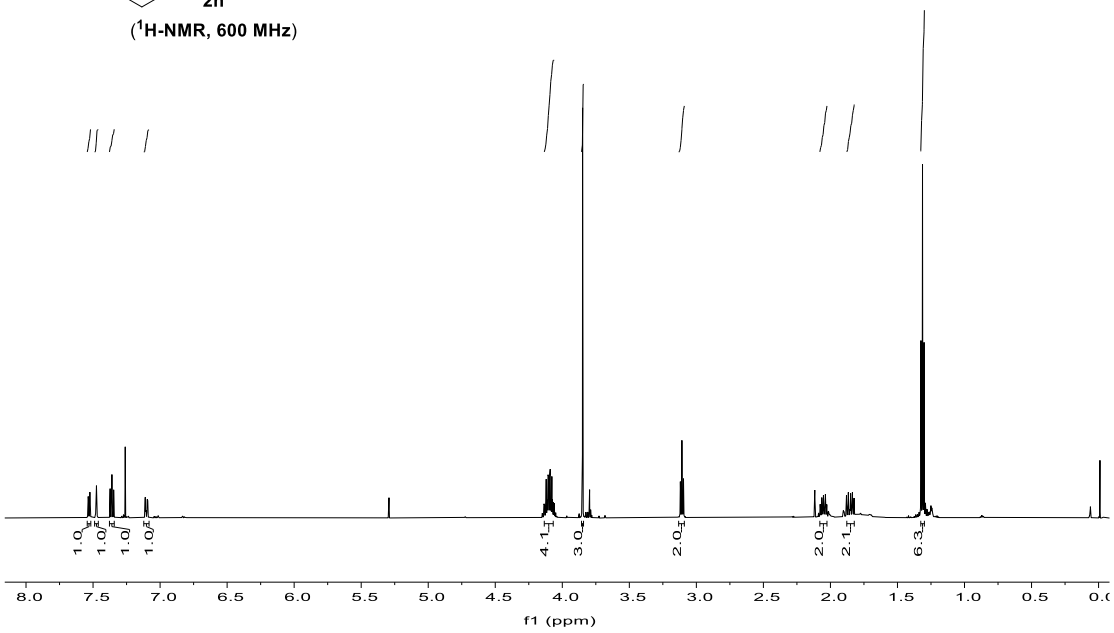
2m

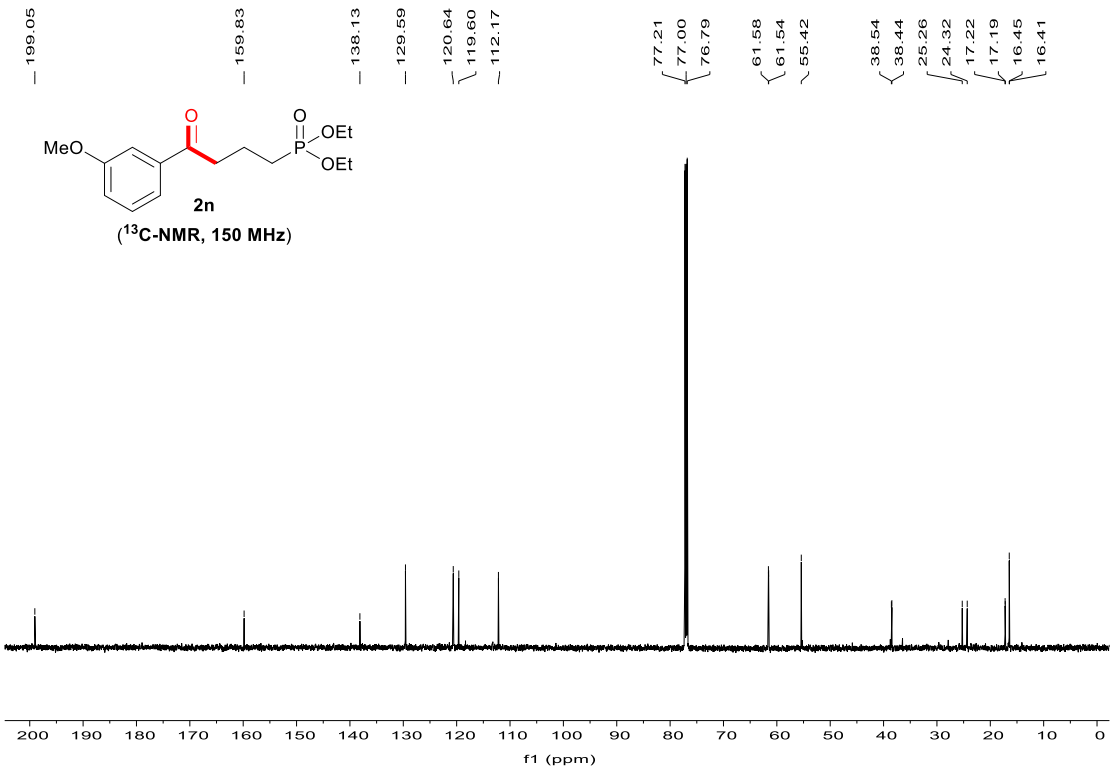
(**^{31}P-NMR, 243 MHz**)



2n

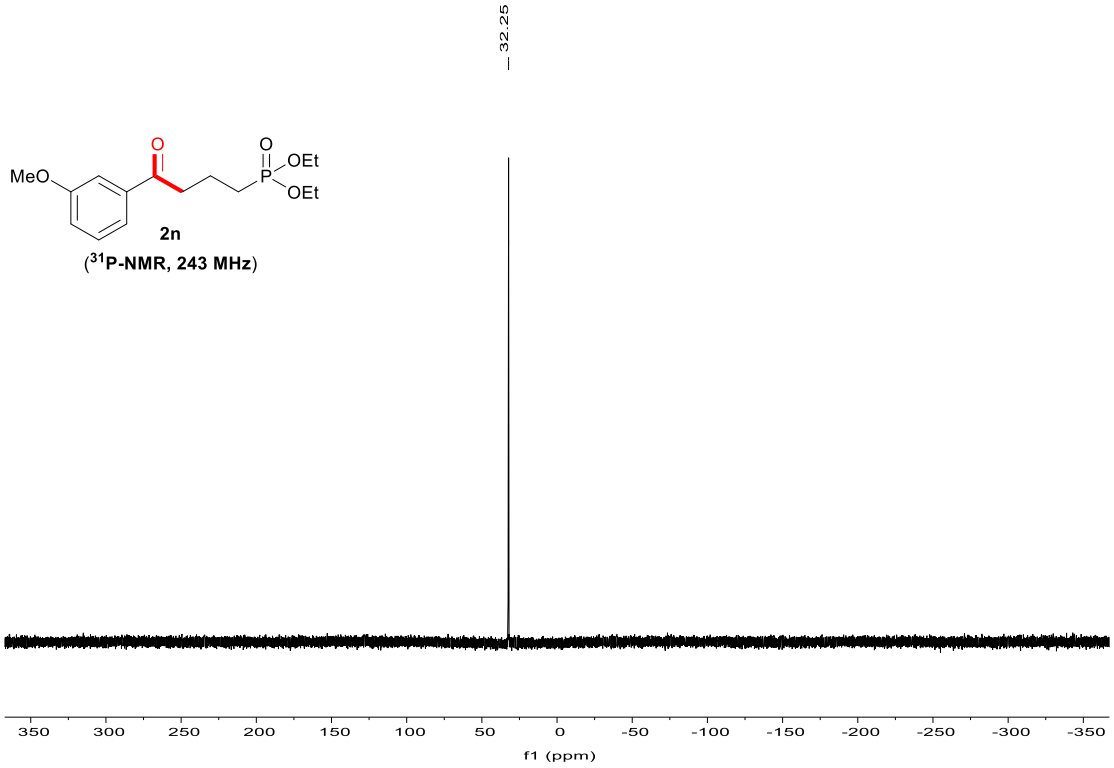
(**^{1}H-NMR, 600 MHz**)





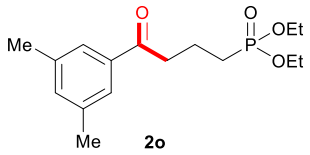
2n

(**^{13}C-NMR, 150 MHz**)



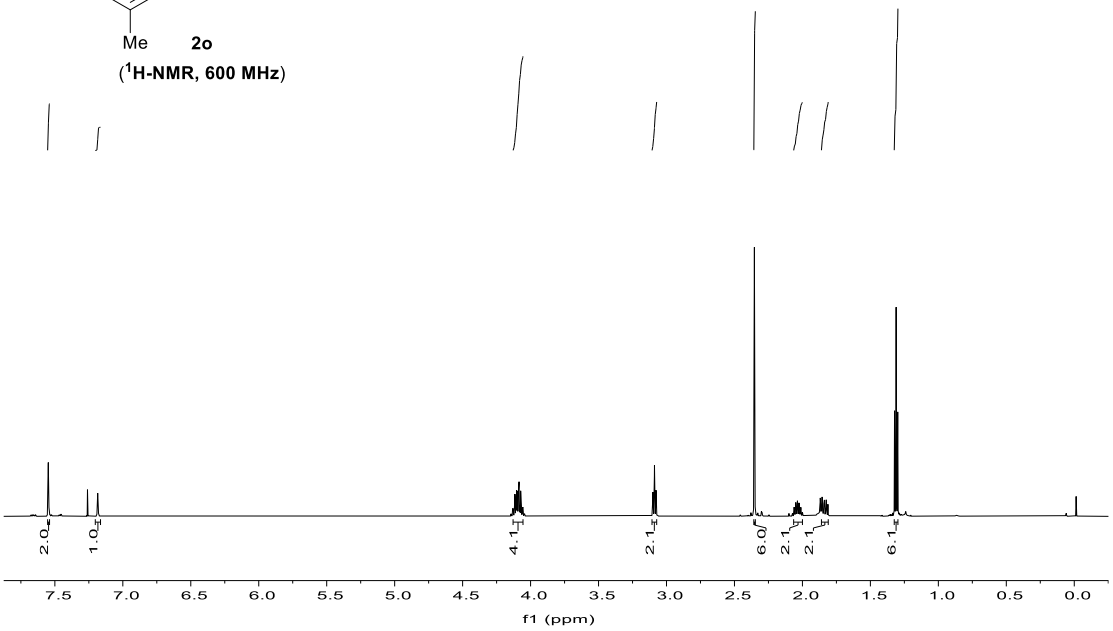
2n

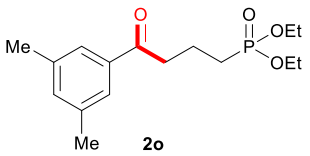
(**^{31}P-NMR, 243 MHz**)



2o

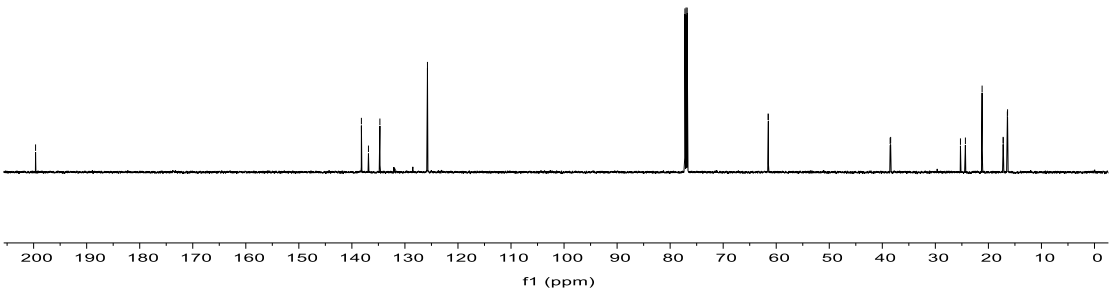
(**^{1}H-NMR, 600 MHz**)

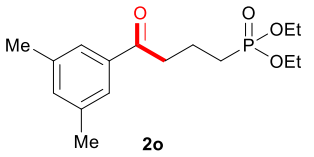




2o

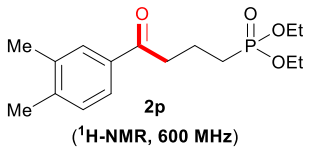
(**^{13}C-NMR, 150 MHz**)





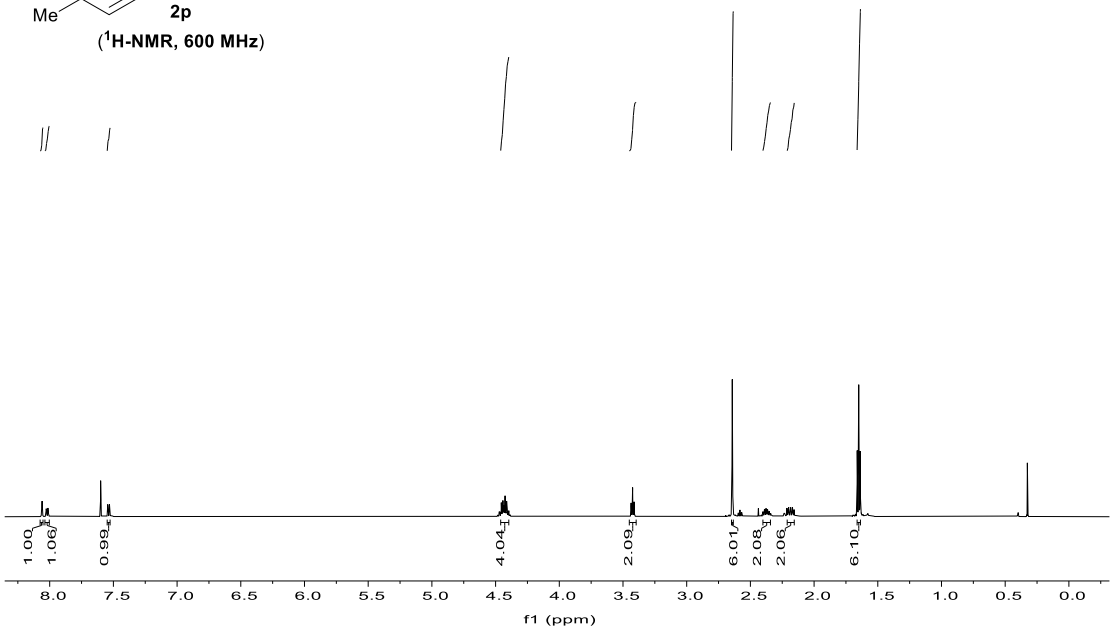
2o

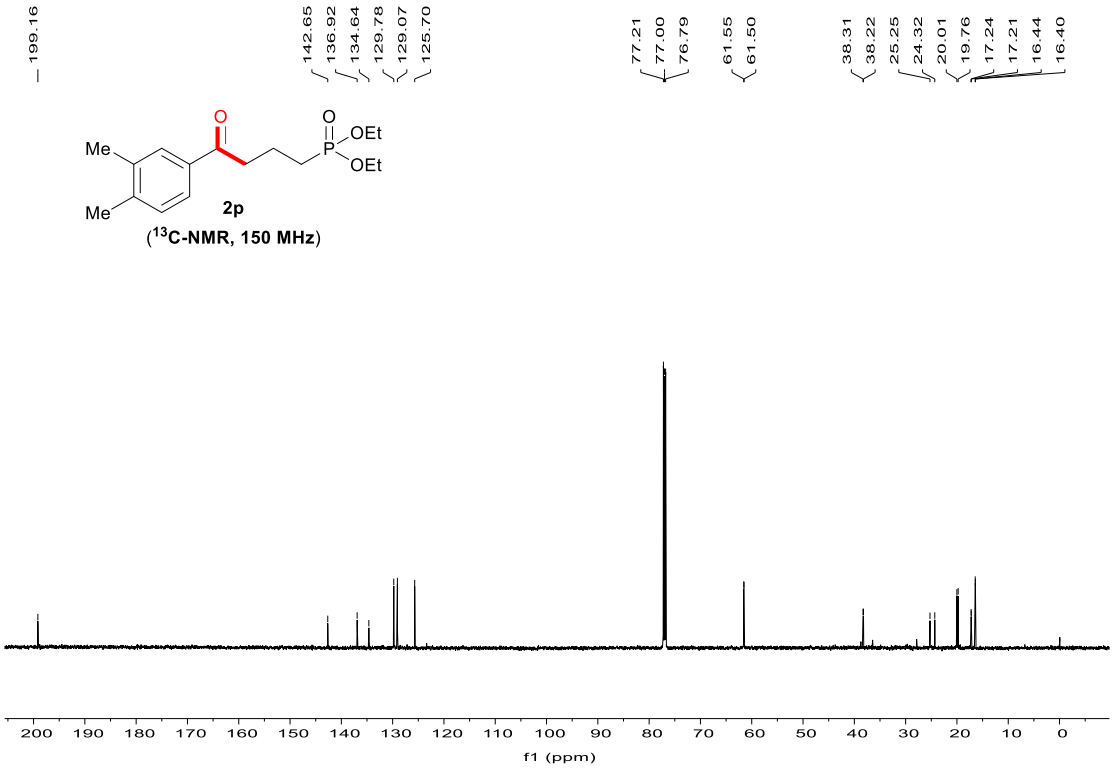
(**^{31}P-NMR, 243 MHz**)

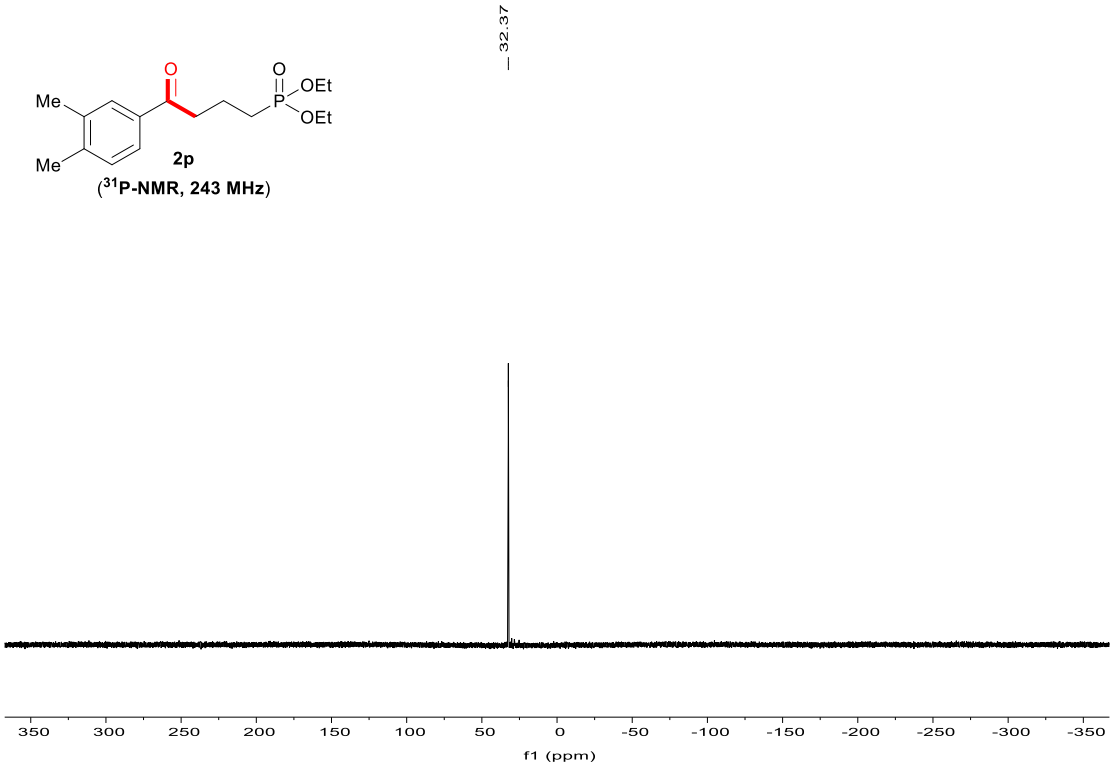


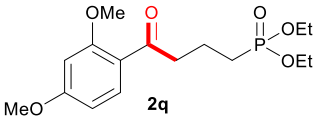
2p

(**^{1}H-NMR, 600 MHz**)



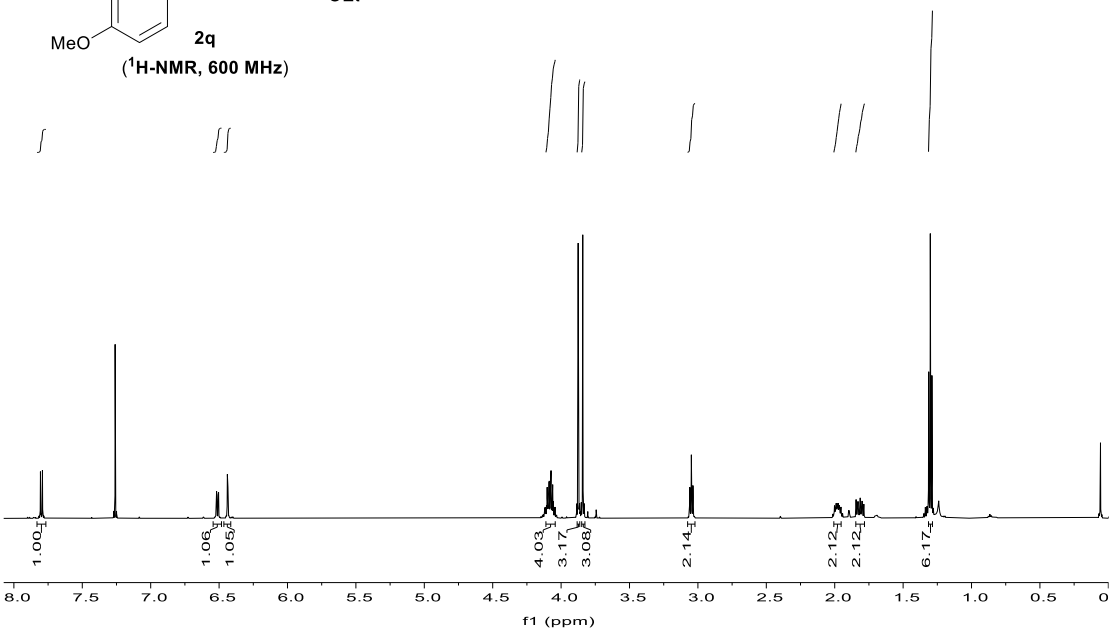

199.16
142.65
136.92
134.64
129.78
129.07
125.70
77.21
77.00
76.79
61.55
61.50
38.31
38.22
25.25
24.32
20.01
19.76
17.24
17.21
16.44
16.40
O
O
OEt
P
OEt
Me
Me
2p
(13C-NMR, 150 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

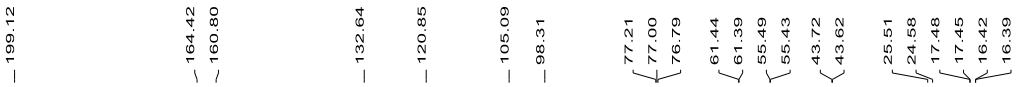

32.37
O
O
OEt
P
OEt
Me
Me
2p
(31P-NMR, 243 MHz)
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)

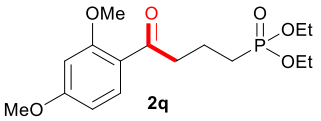


2q

(**^{1}H-NMR, 600 MHz**)

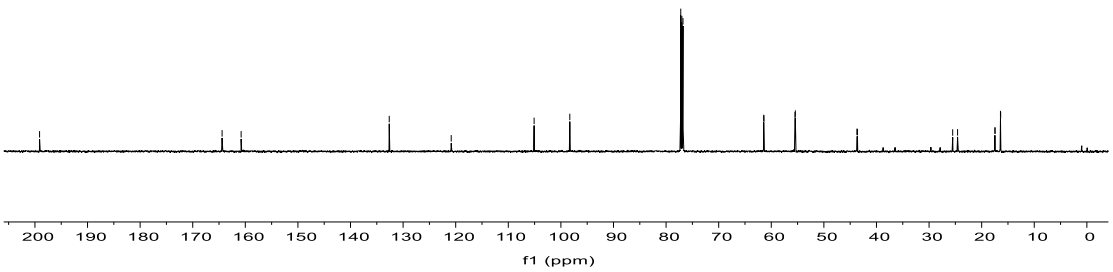


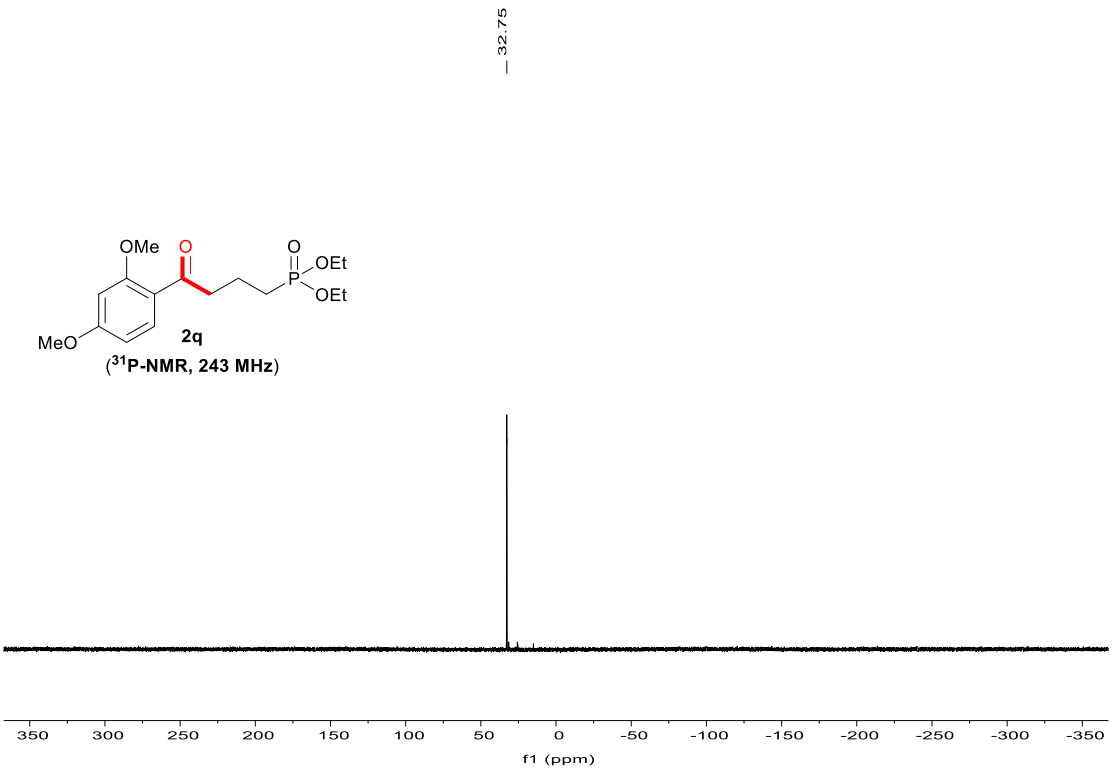


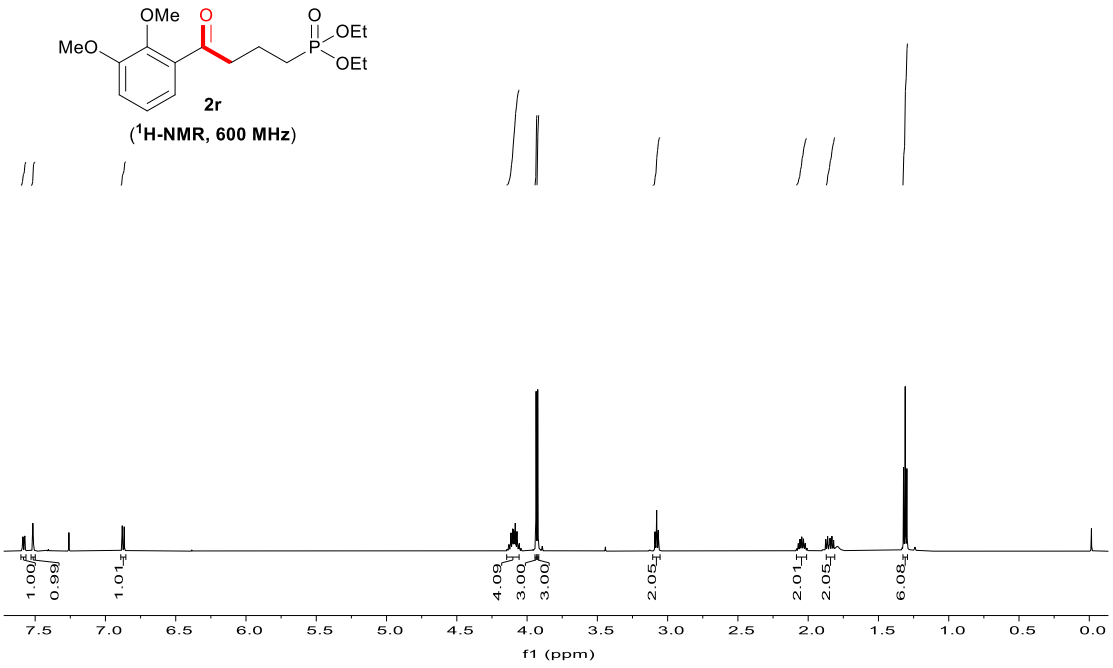


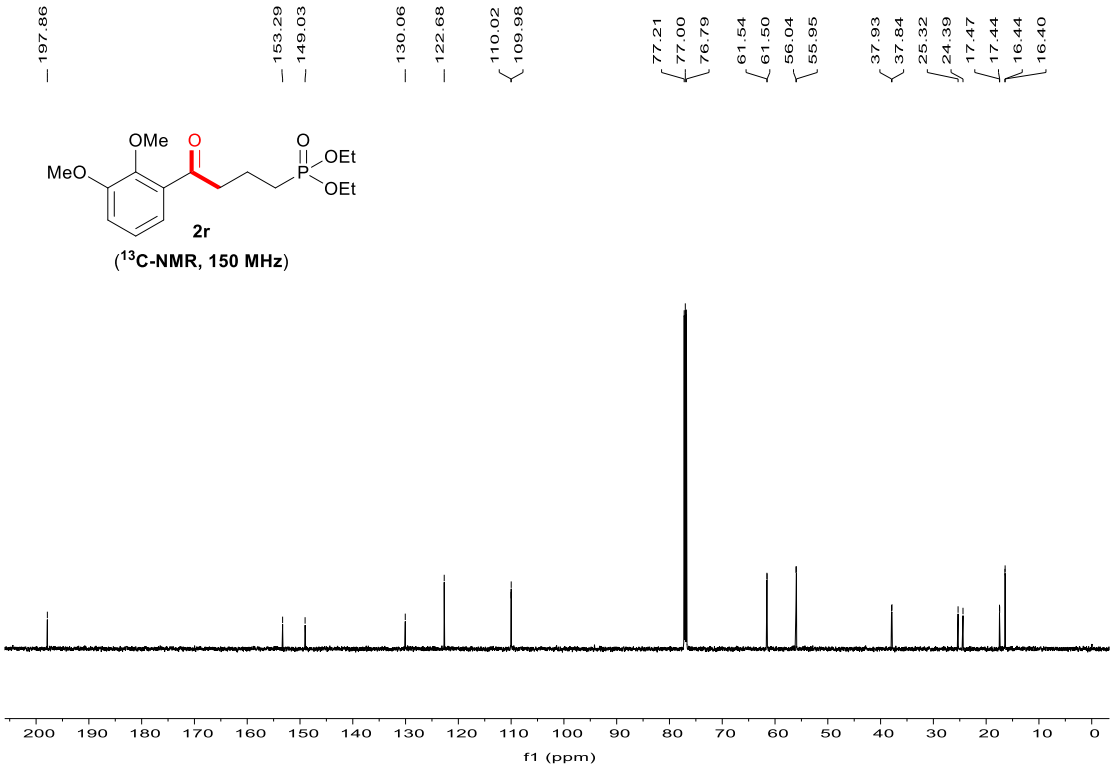
2q

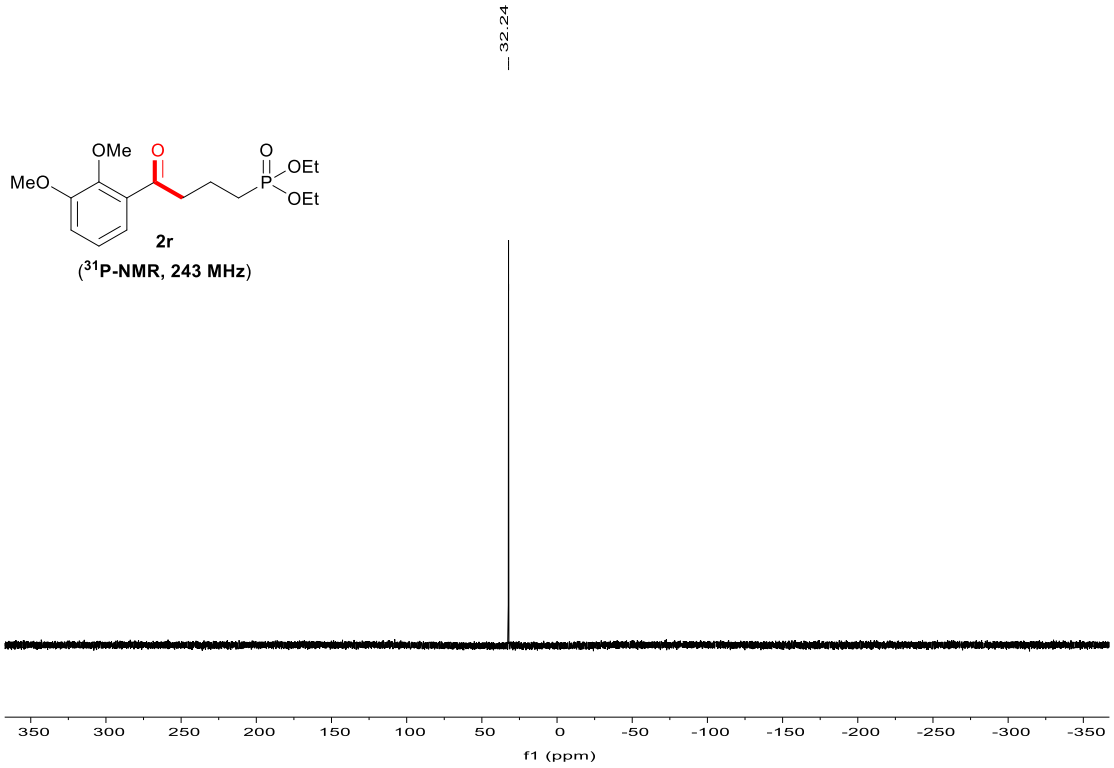
(**^{13}C-NMR, 150 MHz**)

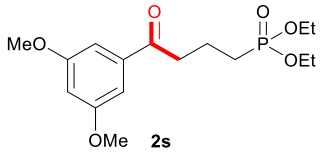



32.75
OMe
O
O
OEt
P
OEt
MeO
2q
(31P-NMR, 243 MHz)
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)


OMe
O
O
OEt
MeO
P
OEt
2r
(1H-NMR, 600 MHz)
1.00
0.99
1.01
4.09
3.00
3.00
2.05
2.01
2.05
6.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

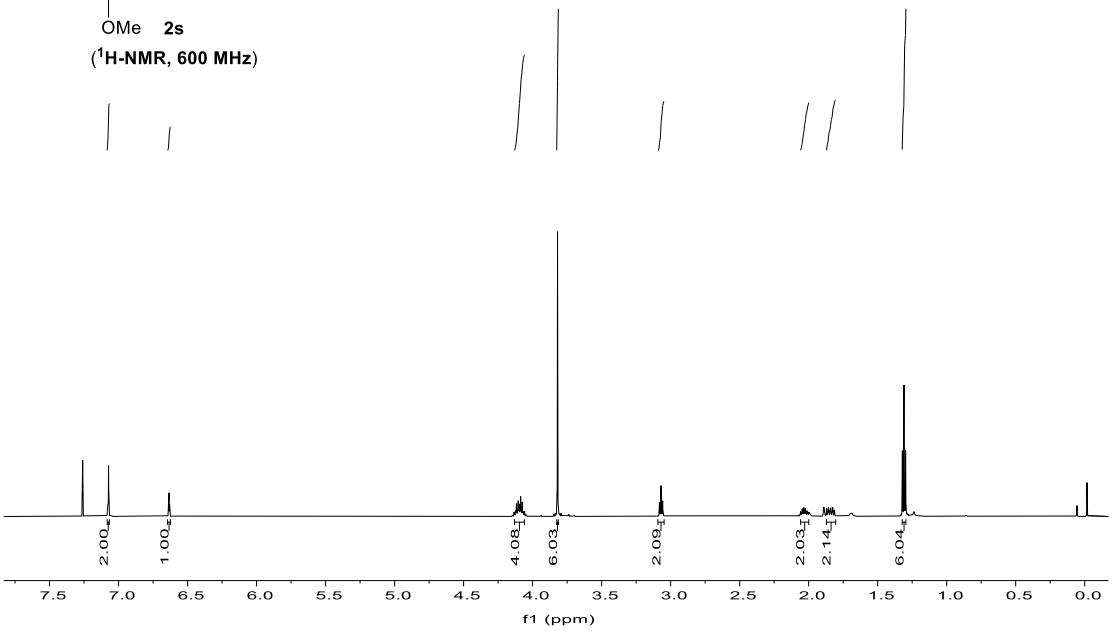

197.86
153.29
149.03
130.06
122.68
110.02
109.98
77.21
77.00
76.79
61.54
61.50
56.04
55.95
37.93
37.84
25.32
24.39
17.47
17.44
16.44
16.40
OMe
O
O
MeO
P
OEt
OEt
2r
(13C-NMR, 150 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

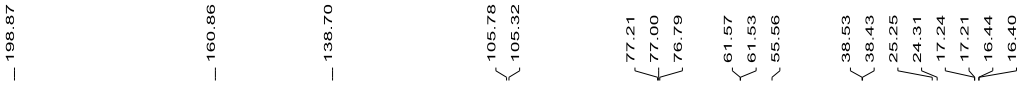

32.24
OMe
O
O
MeO
P
OEt
OEt
2r
(31P-NMR, 243 MHz)
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)

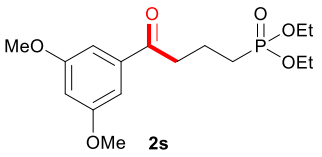


2s

(**^{1}H-NMR, 600 MHz**)

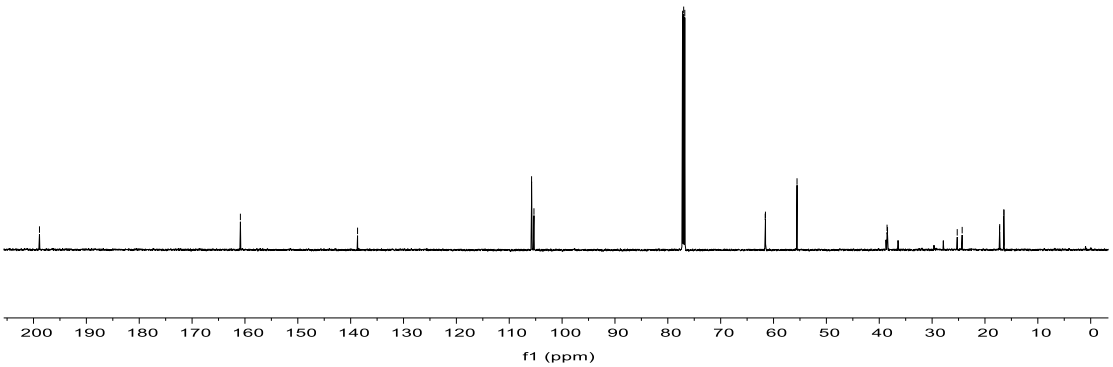


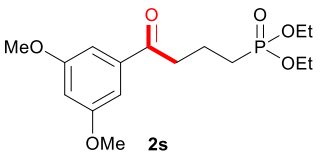




2s

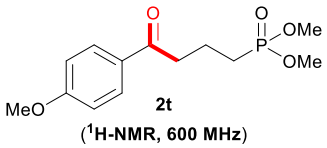
(**^{13}C-NMR, 150 MHz**)





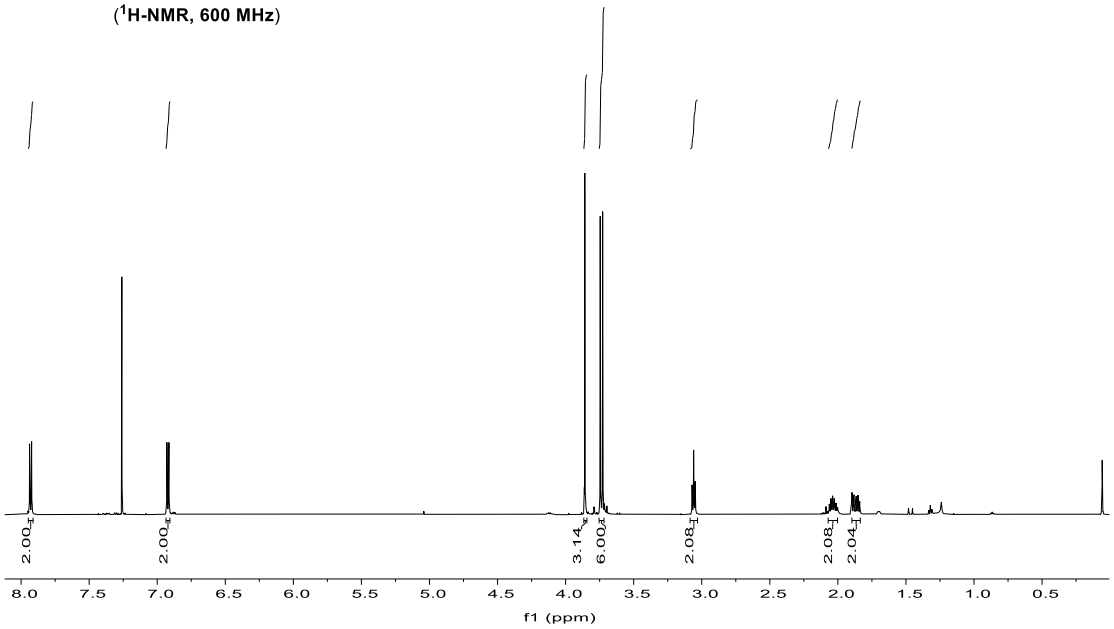
2s

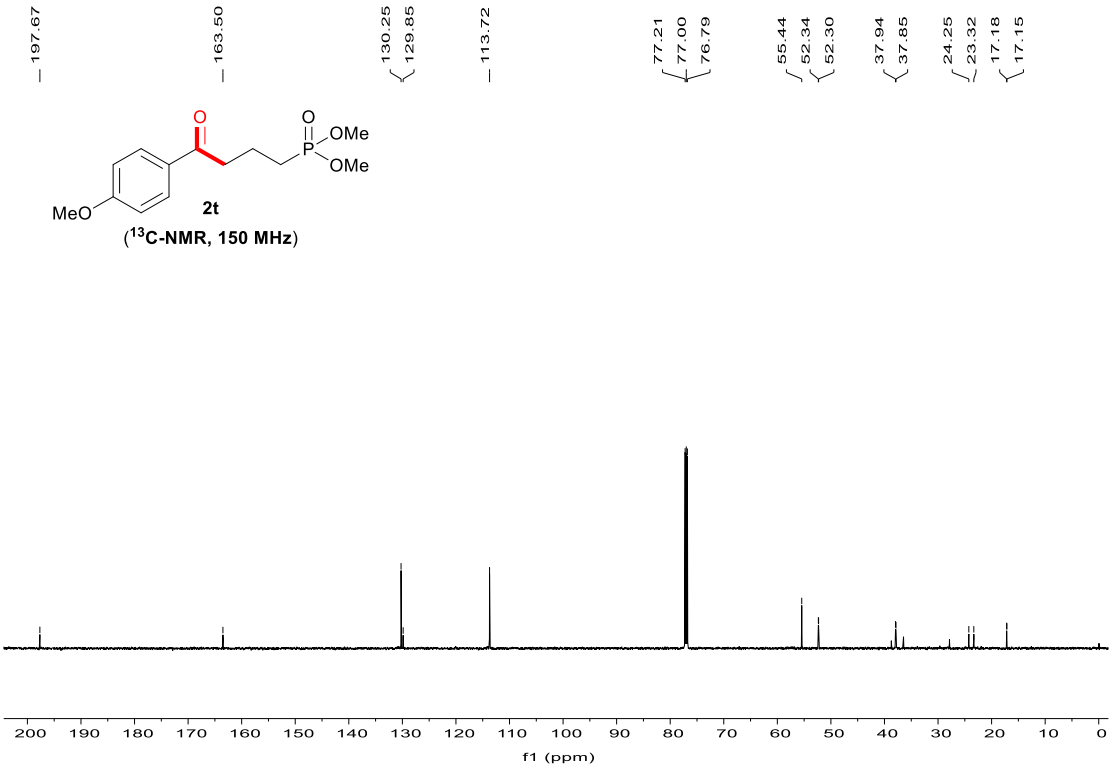
(**^{31}P-NMR, 243 MHz**)

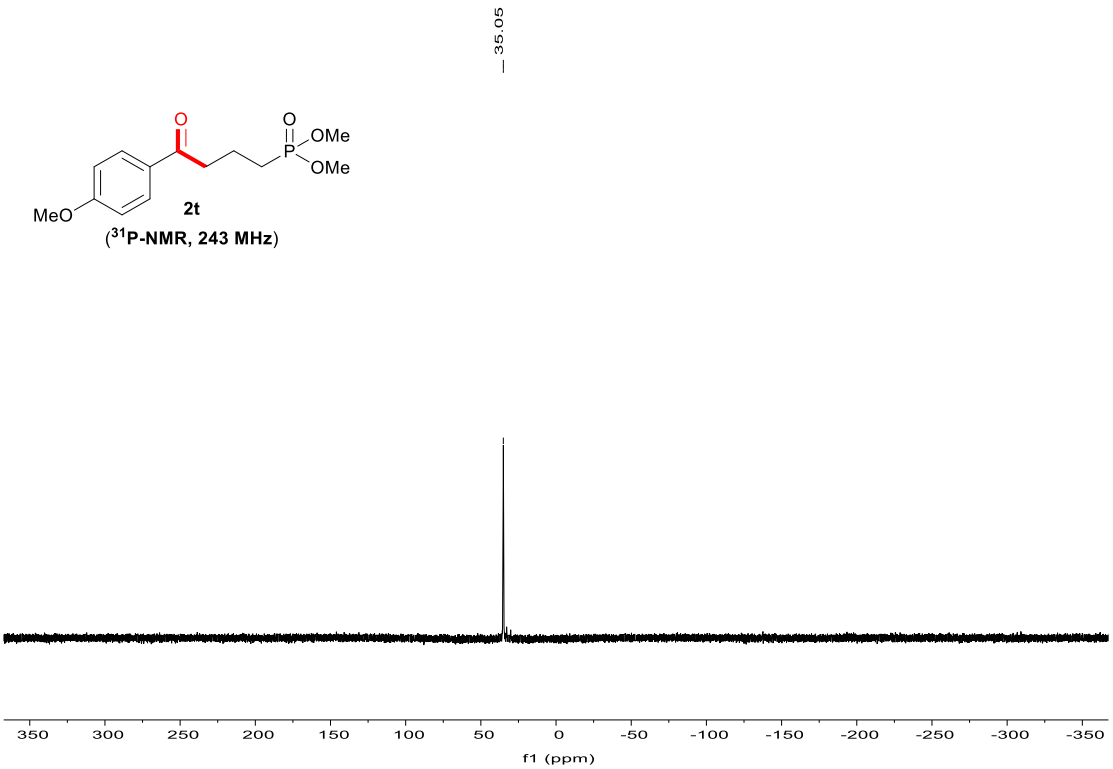


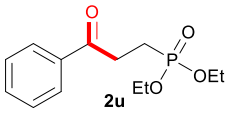
2t

(**^{1}H-NMR, 600 MHz**)



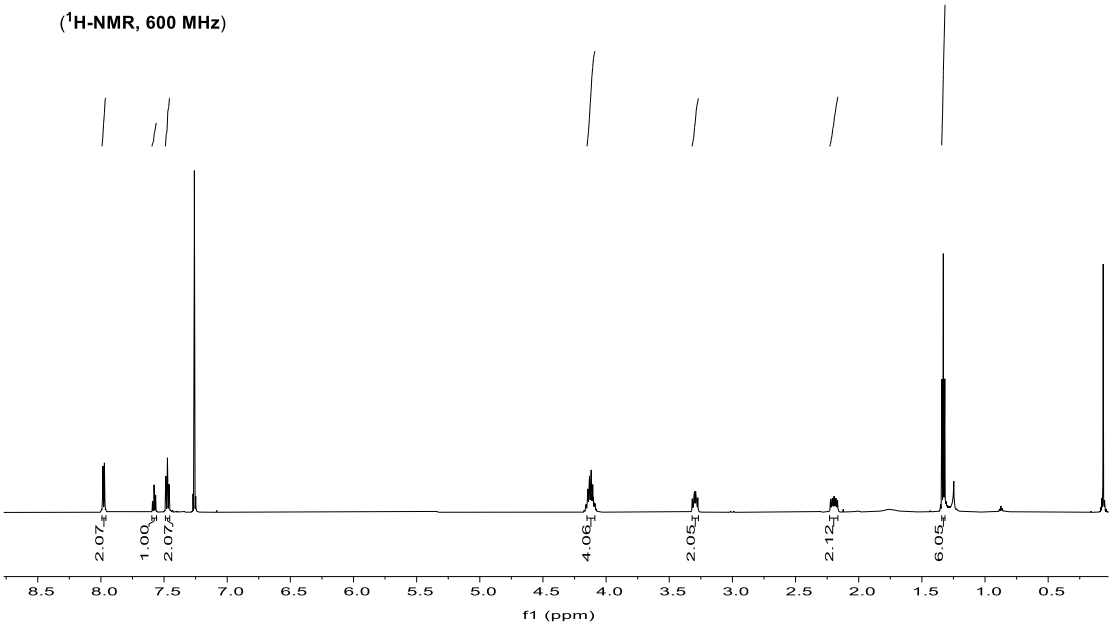

197.67
163.50
130.25
129.85
113.72
77.21
77.00
76.79
55.44
52.34
52.30
37.94
37.85
24.25
23.32
17.18
17.15
O
O
OMe
P
OMe
MeO
2t
(13C-NMR, 150 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

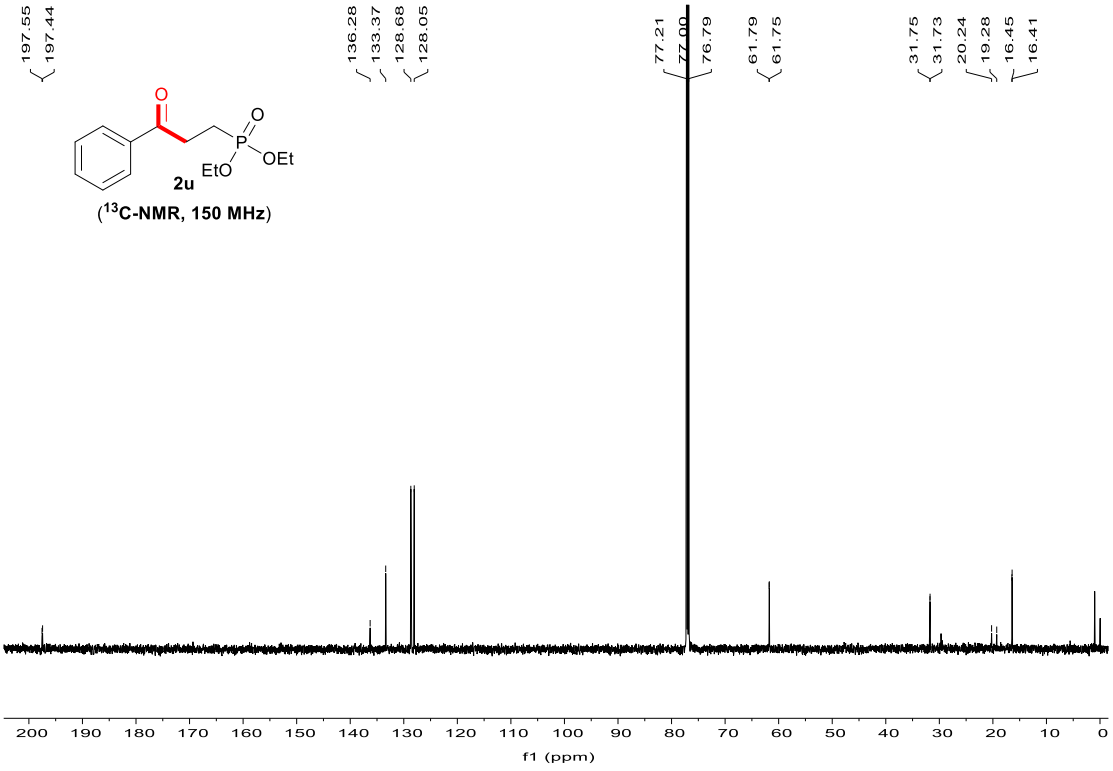

35.05
O
O
OMe
P
OMe
MeO
2t
(31P-NMR, 243 MHz)
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)



2u

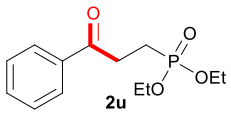
(**^{1}H-NMR, 600 MHz**)





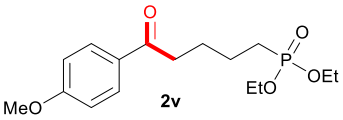
2u

(**^{13}C-NMR, 150 MHz**)



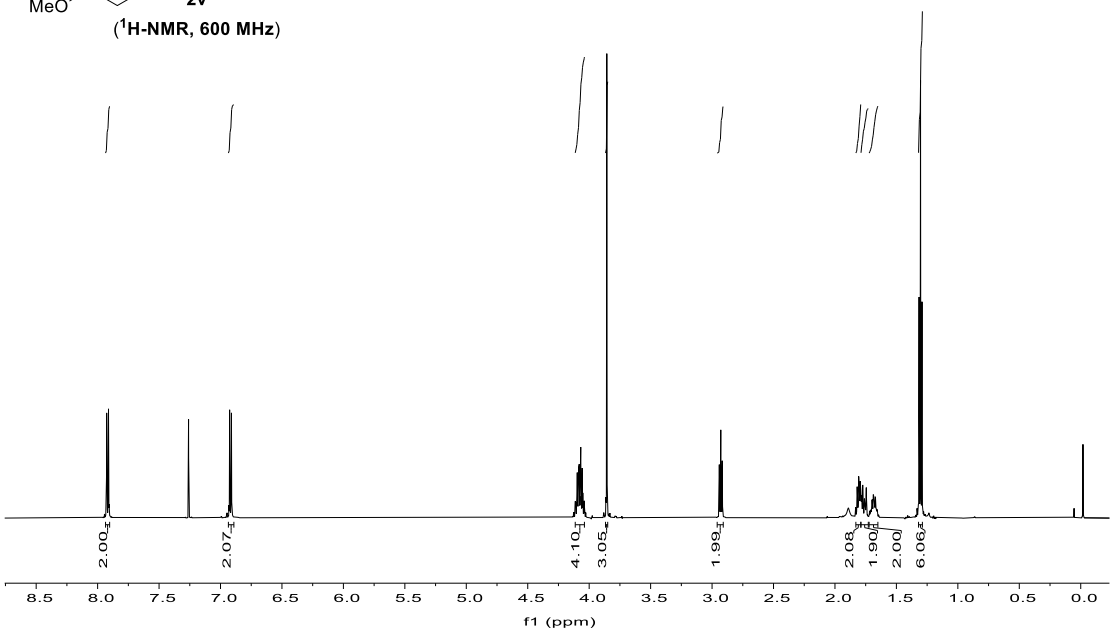
2u

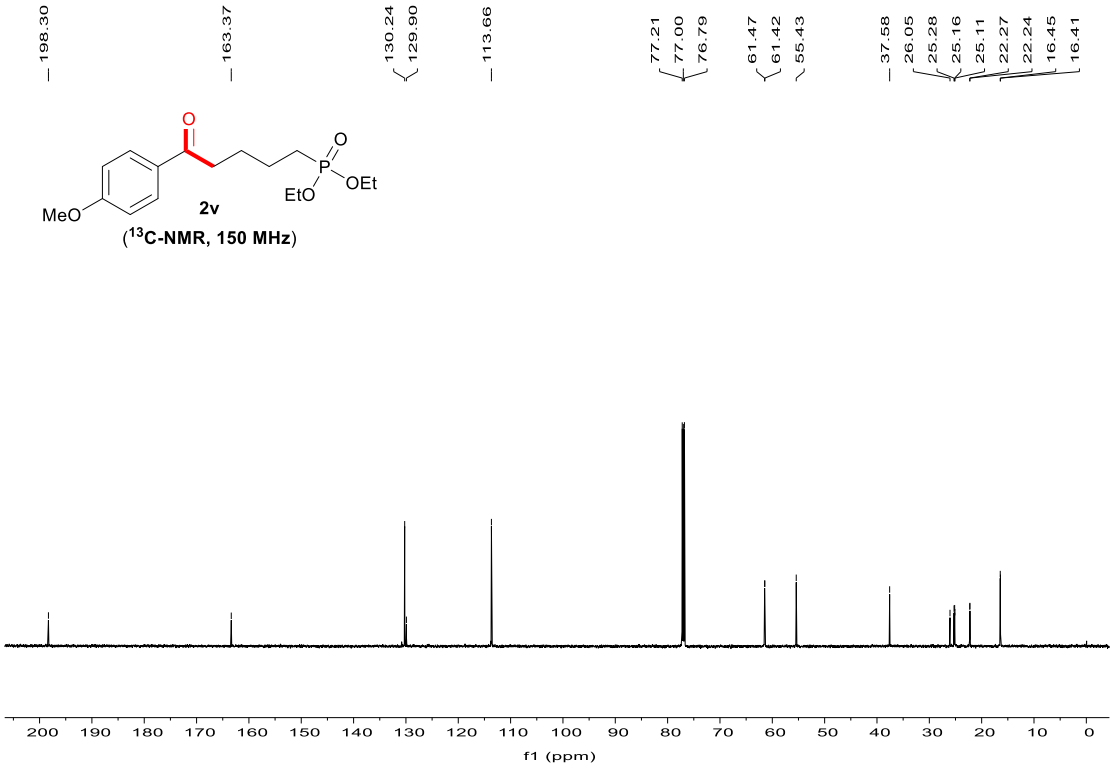
(**^{31}P-NMR, 243 MHz**)

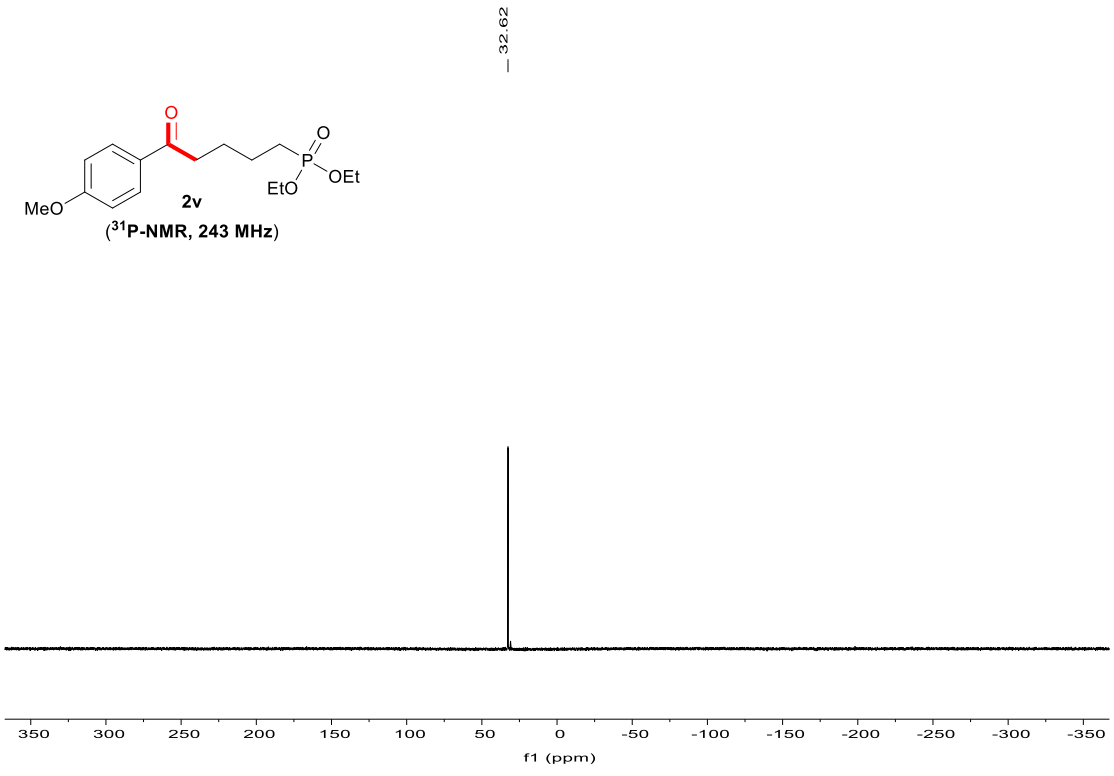


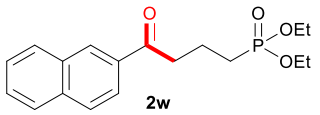
2v

(**^{1}H-NMR, 600 MHz**)



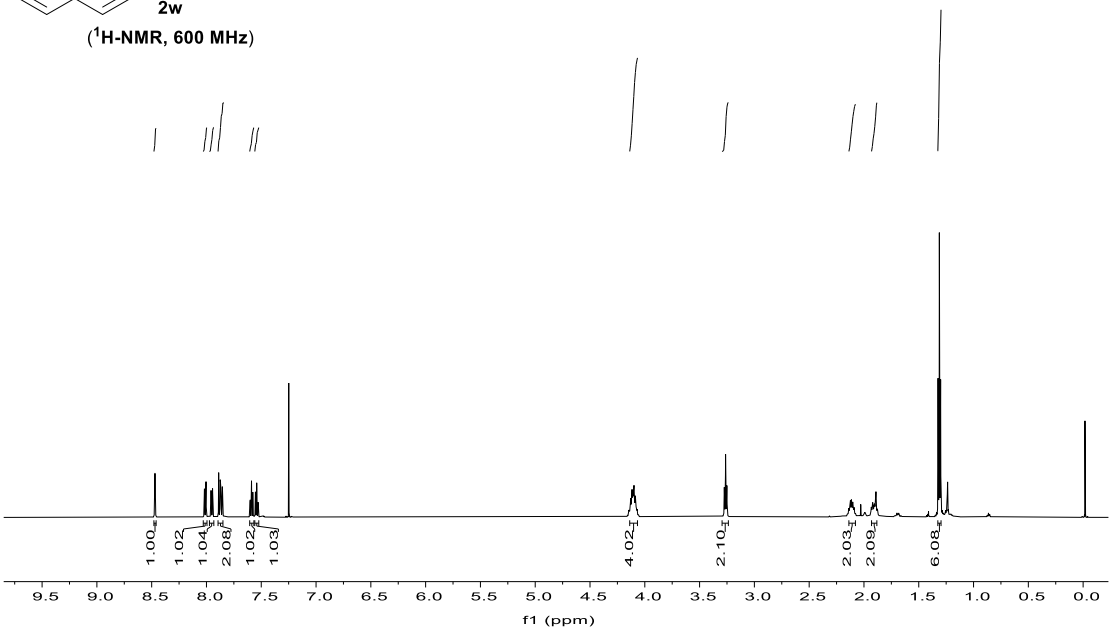

198.30
163.37
130.24
129.90
113.66
77.21
77.00
76.79
61.47
61.42
55.43
37.58
26.05
25.28
25.16
25.11
22.27
22.24
16.45
16.41
O
O
P
OEt
EtO
MeO
2v
(13C-NMR, 150 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

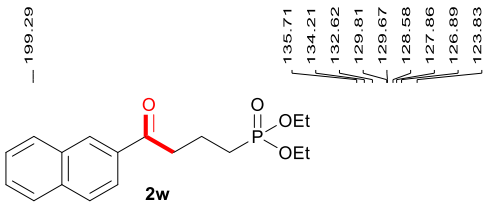

32.62
O
O
P
OEt
EtO
MeO
2v
(31P-NMR, 243 MHz)
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)



2w

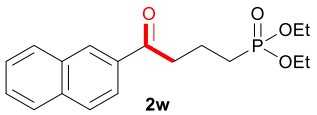
(**^{1}H-NMR, 600 MHz**)





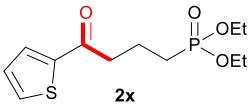
2w

(**^{13}C-NMR, 150 MHz**)



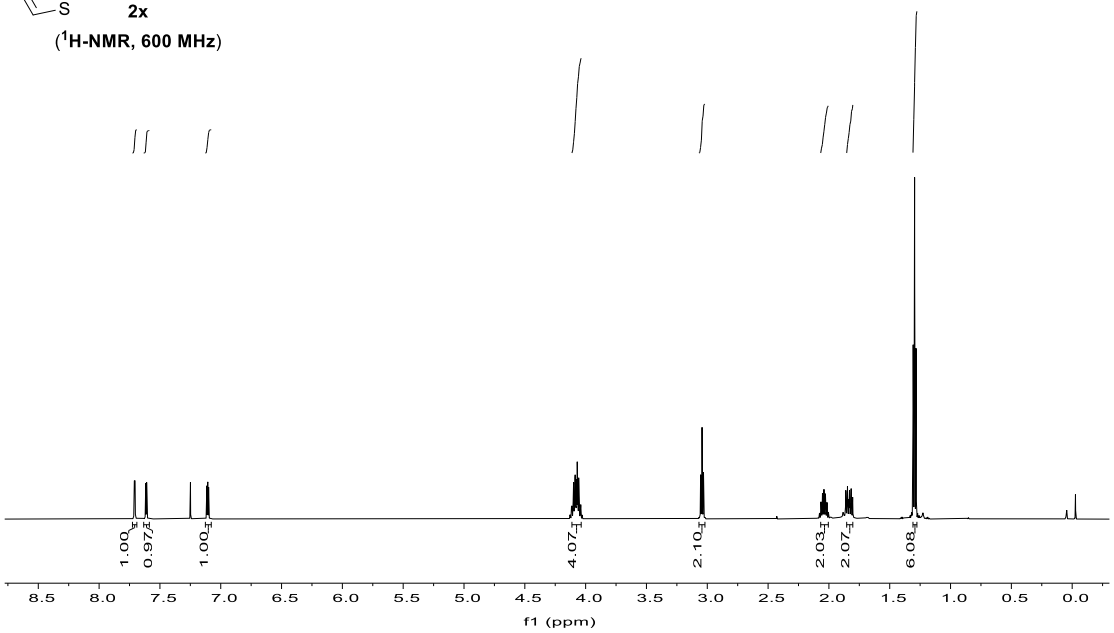
2w

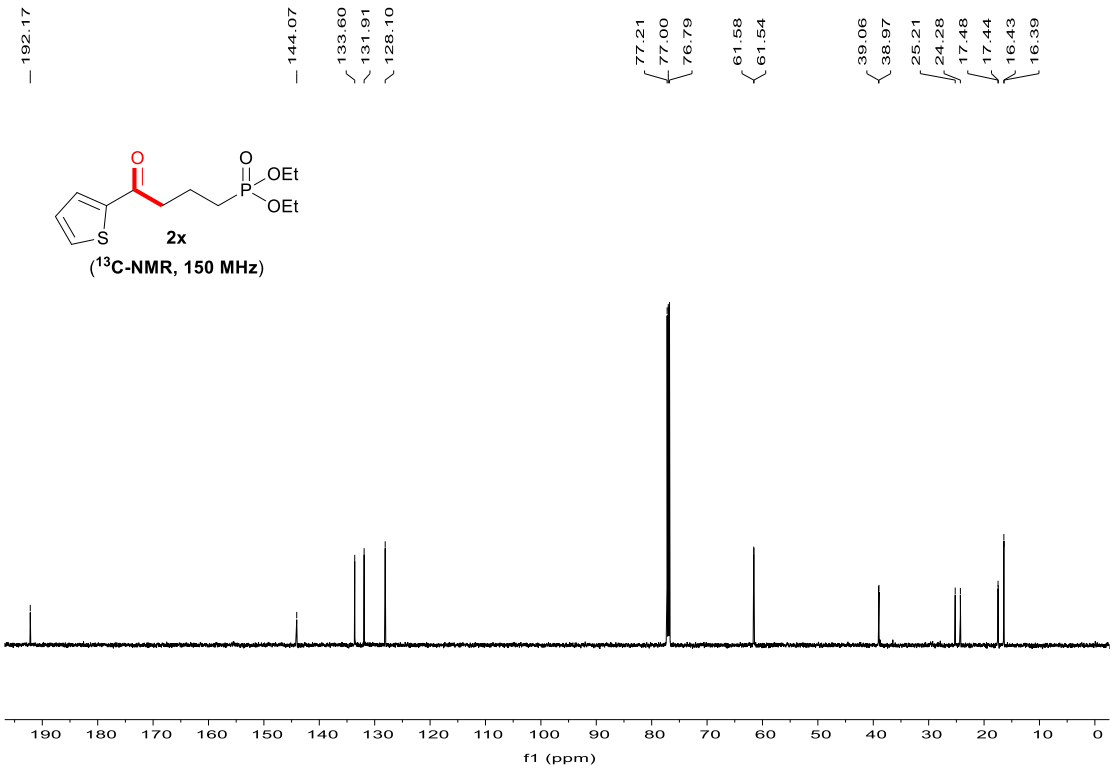
(**^{31}P-NMR, 243 MHz**)

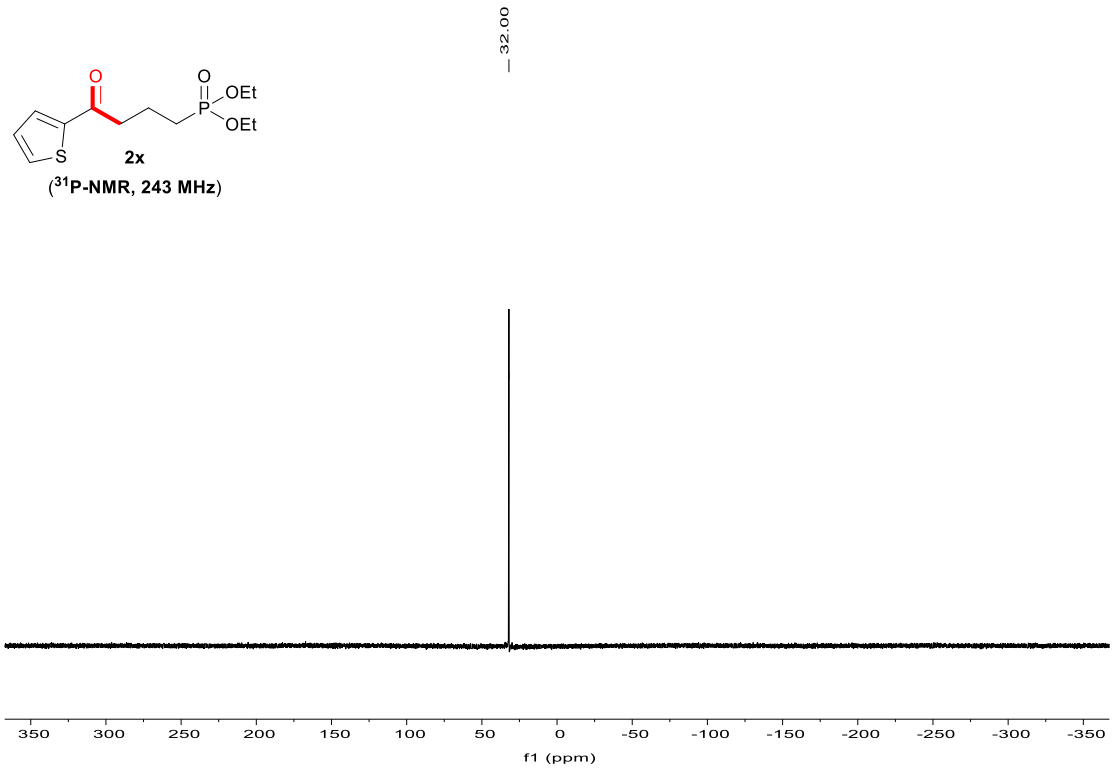


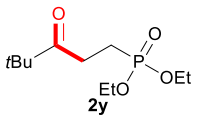
2x

(**^{1}H-NMR, 600 MHz**)




192.17
144.07
133.60
131.91
128.10
77.21
77.00
76.79
61.58
61.54
39.06
38.97
25.21
24.28
17.48
17.44
16.43
16.39
O
O
OEt
P
OEt
S
2x
(13C-NMR, 150 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


32.00
O
O
OEt
P
OEt
S
2x
(31P-NMR, 243 MHz)
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)

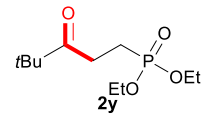


2y

(**^{1}H-NMR, 600 MHz**)

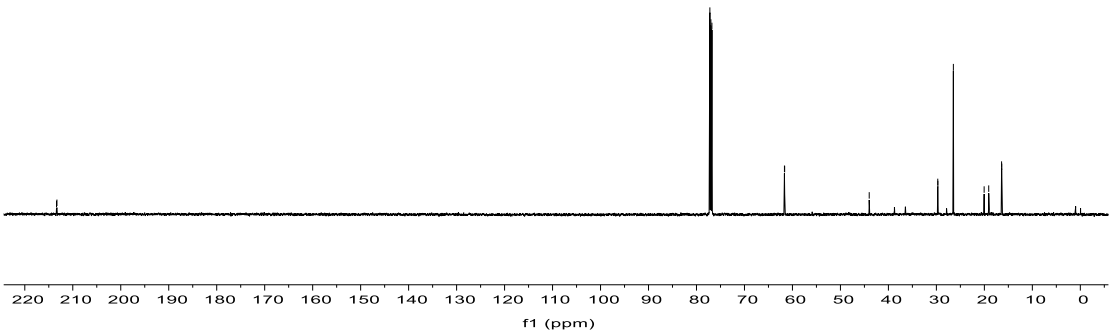
213.39
213.30

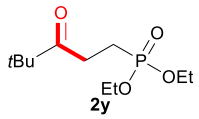
77.21
77.00
76.79
61.67
61.63
44.00
29.71
29.69
26.46
20.05
19.09
16.41
16.37



2y

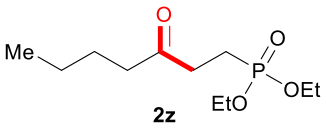
(**^{13}C-NMR, 150 MHz**)





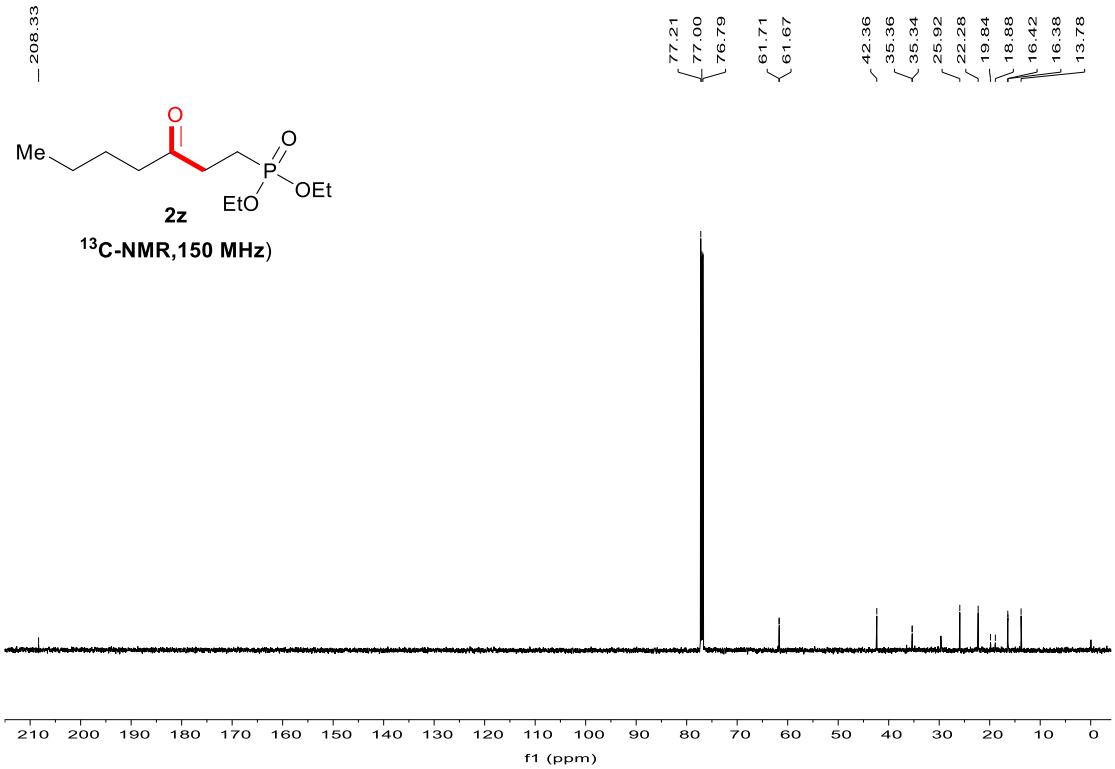
2y

(**^{31}P-NMR, 243 MHz**)



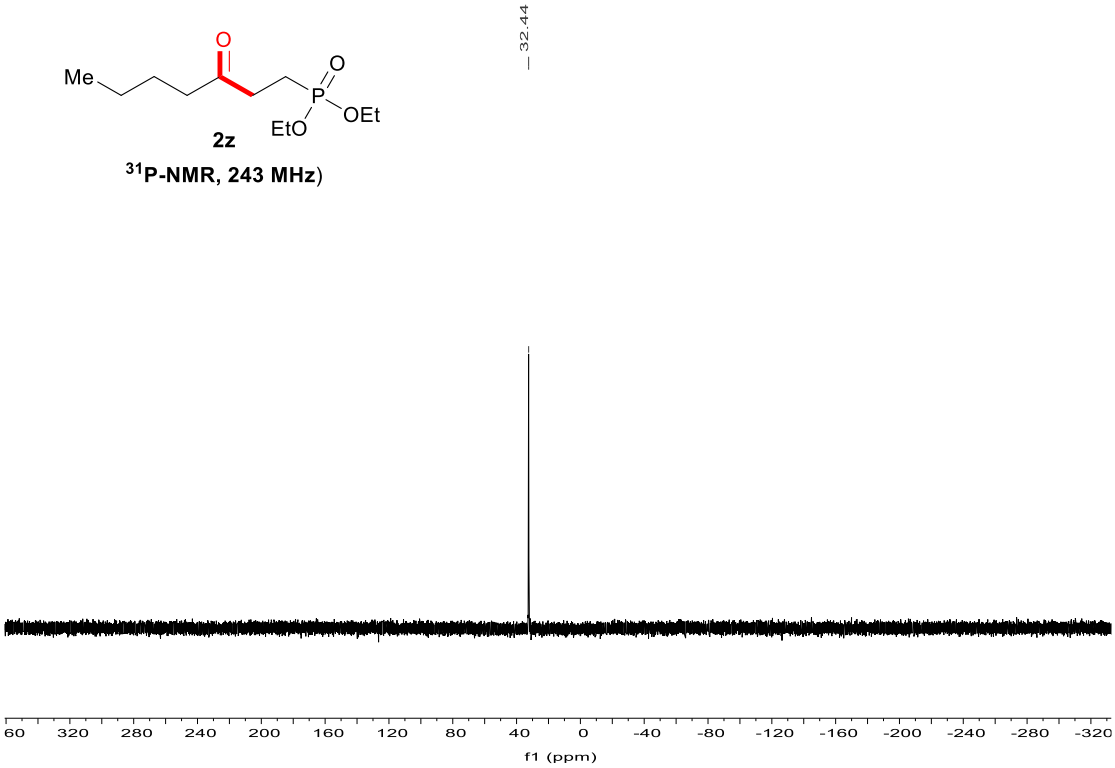
2z

(**^{1}H-NMR, 600 MHz**)



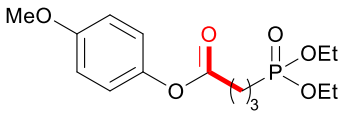
2z

^{13}C-NMR,150 MHz)



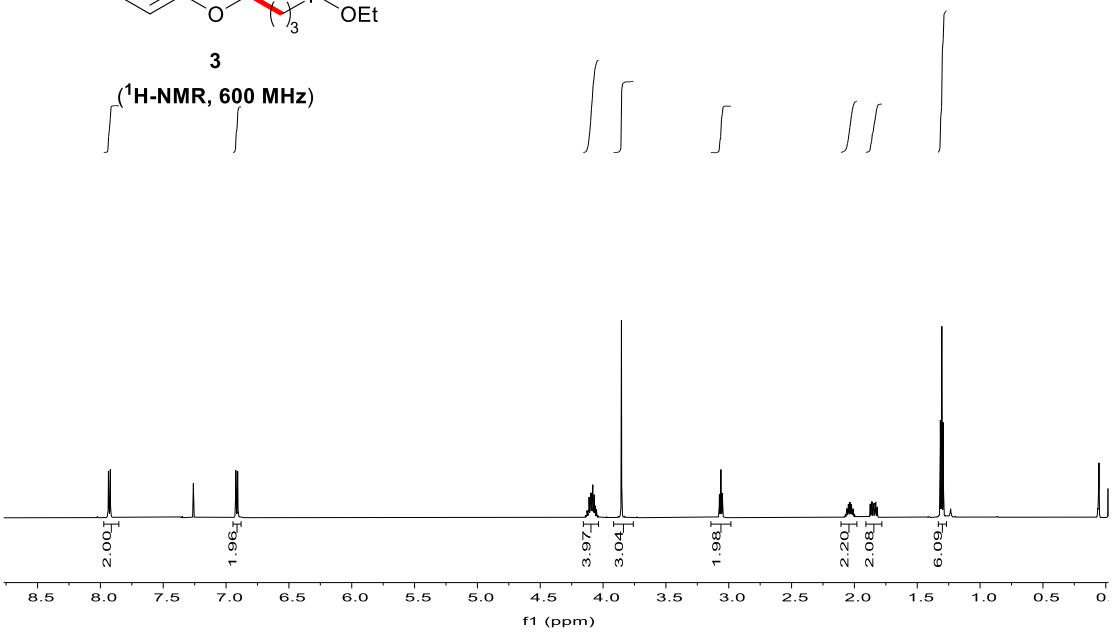
2z

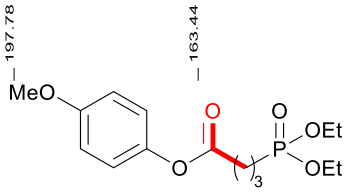
^{31}P-NMR, 243 MHz)



3

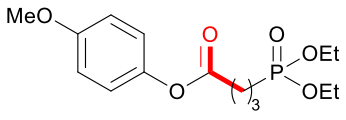
(**^{1}H-NMR, 600 MHz**)





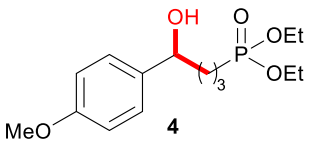
3

(**^{13}C-NMR, 150 MHz**)



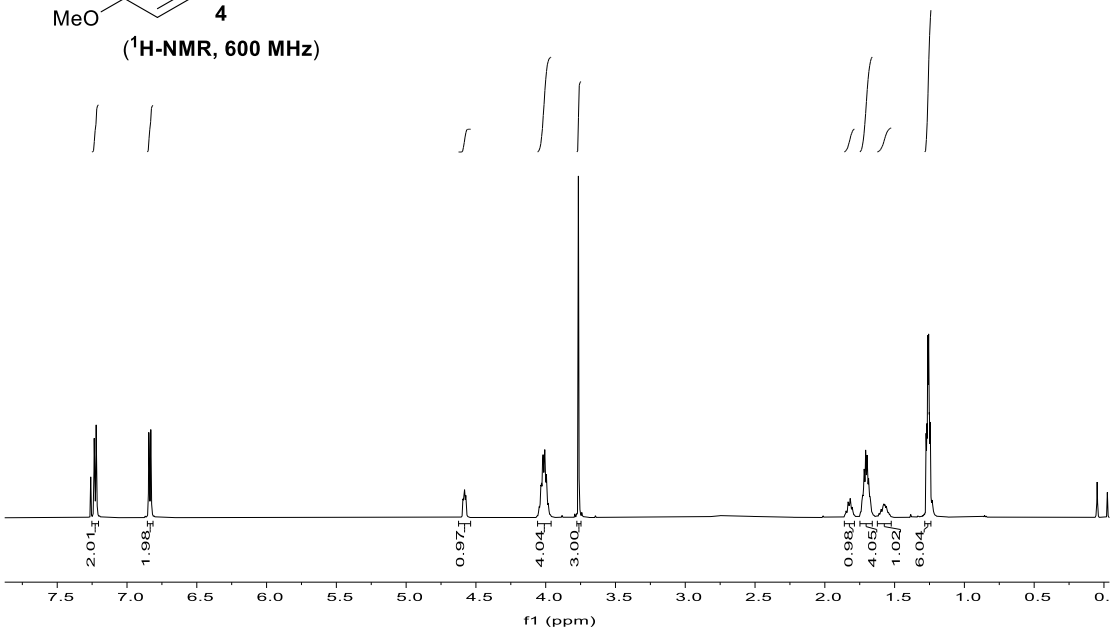
3

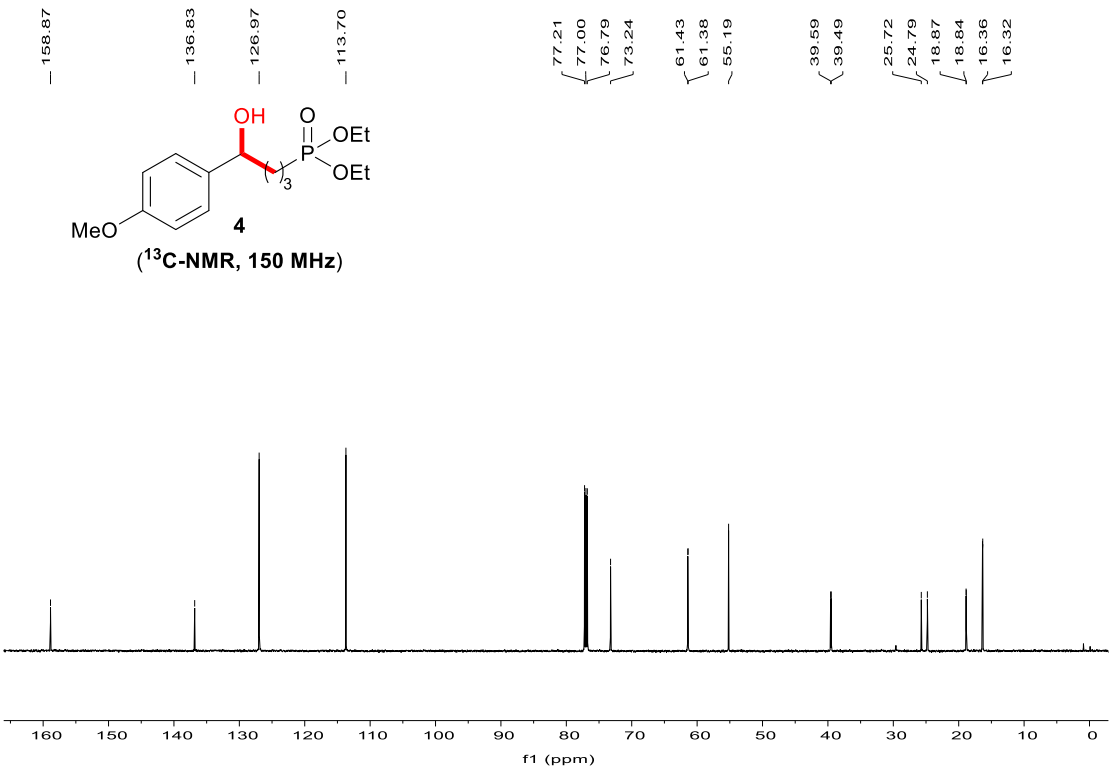
(**^{31}P-NMR, 243 MHz**)

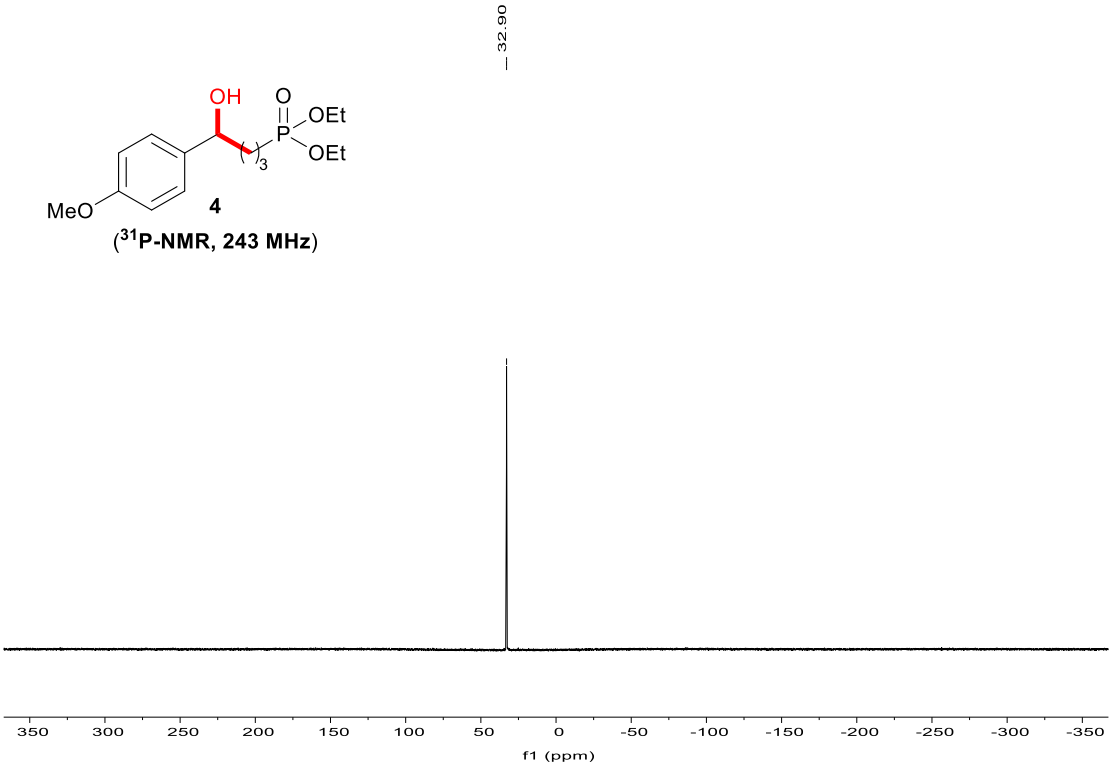


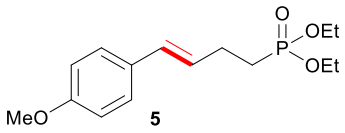
4

(**^{1}H-NMR, 600 MHz**)



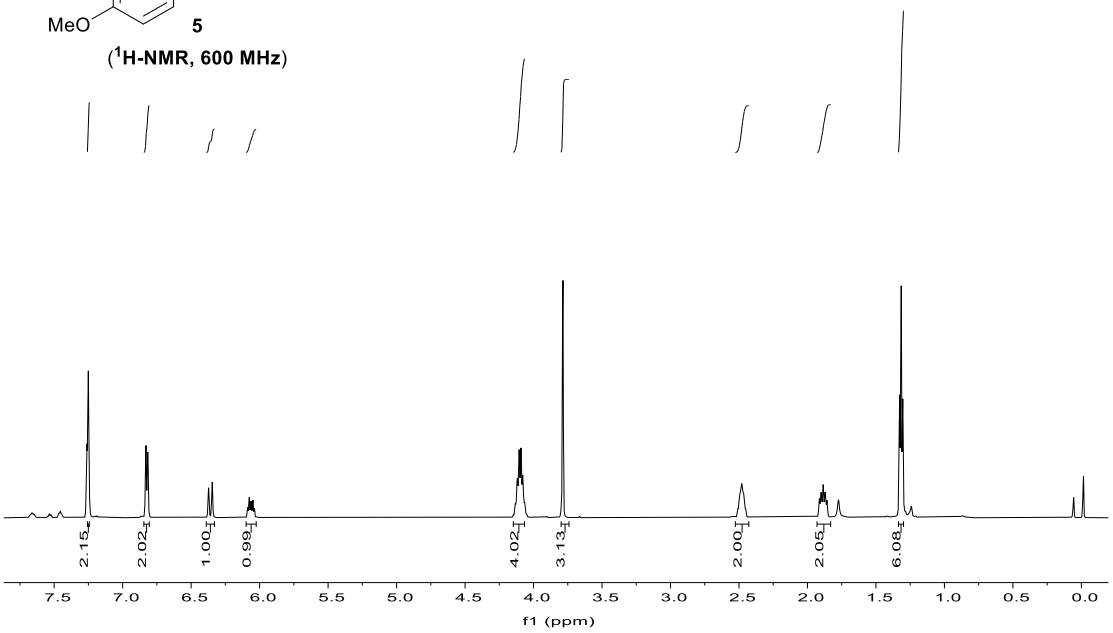

158.87
136.83
126.97
113.70
77.21
77.00
76.79
73.24
61.43
61.38
55.19
39.59
39.49
25.72
24.79
18.87
18.84
16.36
16.32
OH
O
OEt
P
OEt
3
MeO
4
(13C-NMR, 150 MHz)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

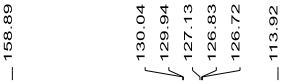

32.90
OH
O
OEt
P
OEt
3
MeO
4
(31P-NMR, 243 MHz)
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

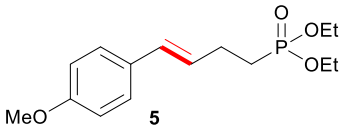


5

(**^{1}H-NMR, 600 MHz**)

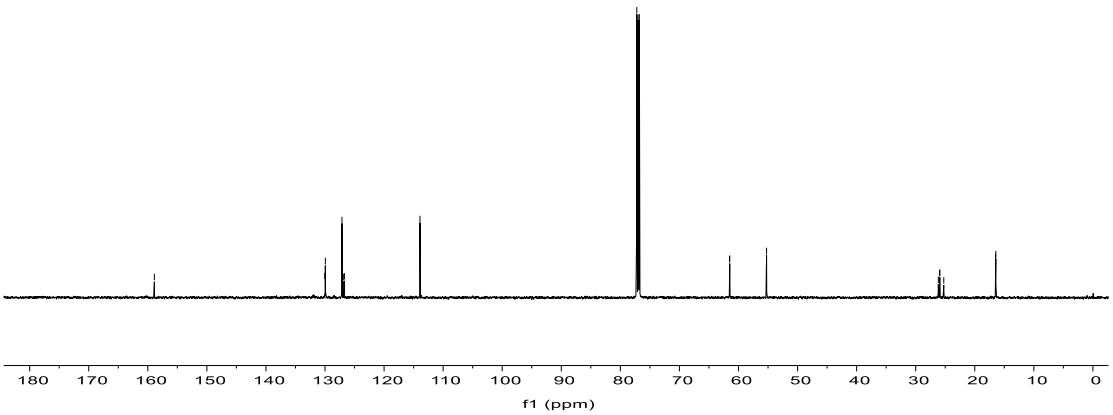


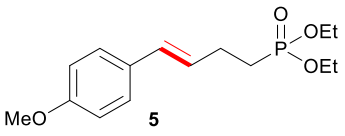




5

(**^{13}C-NMR, 150 MHz**)





5

(**^{31}P-NMR, 243 MHz**)