Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-catalyzed oxidative dehydrogenative coupling of carboxylic acids with H-phosphonates: an efficient and practical approach to acyl phosphate esters

Hong Fu,[a] Tao Yang,[a] Jia-Qi Shang,[a] Jia-Li Zhou,[a] Meng Sun,[b] Ya-Min Li*[a]

[a] Faculty of Life Science and Technology, Kunming University of Science and Technology, Kunming 650500, P. R. China. E-mail: liym@kmust.edu.cn.

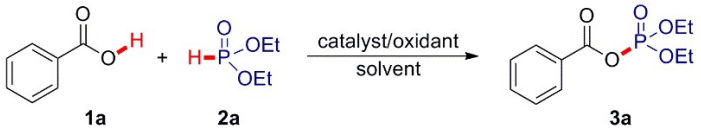
[b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry & Materials Science, Northwest University, Xi'an 710127, P. R. China.

1. General Information

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker AVANCE DRX 500 (500 MHz for ^{1}H; 126 MHz for ^{13}C; 202 MHz for ^{31}P) and Bruker AVANCE III HD 600 (600 MHz for ^{1}H; 151 MHz for ^{13}C; 243 MHz for ^{31}P) instruments internally referenced to tetramethylsilane (TMS) signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. $CDCl_3$ was used as the NMR solvent in all cases. Mass spectra were mearsured using Thermo LTQ Orbitrap XL spectrometer. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer and only major peaks are reported in cm^{-1}. The starting materials were purchased from Aldrich, Acros Organics, TCI or J&K Chemicals and used without further purification. Column chromatography was carried out on silica gel (particle size 200-300 mesh ASTM).

2. Screening of the reaction conditions

Table S1. Reaction conditions screening[a]



1a 2a 3a

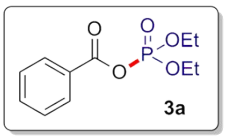
Entry	Catalyst	Oxidant (equiv)	Solvent	Yield[b] (%)
1	$CuBr_2$	TBHP (3.0)	CH_3CN	47
2	$CuCl_2$	TBHP (3.0)	CH_3CN	47
3	$Cu(OAc)_2$	TBHP (3.0)	CH_3CN	19
4	Cu_2O	TBHP (3.0)	CH_3CN	56
5	CuCl	TBHP (3.0)	CH_3CN	40
6	CuBr	TBHP (3.0)	CH_3CN	43
7	CuI	TBHP (3.0)	CH_3CN	50
8	Cu_2O	$K_2S_2O_8$ (3.0)	CH_3CN	trace
9	Cu_2O	BQ (3.0)	CH_3CN	39
10	Cu_2O	DTBP (3.0)	CH_3CN	16
11	Cu_2O	DCP (3.0)	CH_3CN	67
12	Cu_2O	DCP (4.0)	CH_3CN	82
13	Cu_2O	DCP (5.0)	CH_3CN	71
14	Cu_2O	DCP (3.0)	THF	0
15	Cu_2O	DCP (3.0)	toluene	trace
16	Cu_2O	DCP (3.0)	DMF	19
17	Cu_2O	DCP (3.0)	dioxane	0
18	$AgNO_3$	DCP (4.0)	CH_3CN	0
19	Ag_2CO_3	DCP (4.0)	CH_3CN	0
20	Ag_2O	DCP (4.0)	CH_3CN	0
21	$FeCl_2$	DCP (4.0)	CH_3CN	0
22	$FeBr_2$	DCP (4.0)	CH_3CN	0
23	$Fe(OAc)_2$	DCP (4.0)	CH_3CN	0
24	$FeCl_3$	DCP (4.0)	CH_3CN	0
25	$CoCl_2$	DCP (4.0)	CH_3CN	0
26	$Co(acac)_2$	DCP (4.0)	CH_3CN	0
27	$Co(acac)_3$	DCP (4.0)	CH_3CN	0
28	$NiCl_2$	DCP (4.0)	CH_3CN	0
29	NiI_2	DCP (4.0)	CH_3CN	0
30	$NiCl_2(PPh_3)_2$	DCP (4.0)	CH_3CN	0
31[c]	Cu_2O	DCP (4.0)	CH_3CN	50
32[d]	Cu_2O	DCP (4.0)	CH_3CN	54
33[e]	Cu_2O	DCP (4.0)	CH_3CN	81
34[f]	Cu_2O	DCP (4.0)	CH_3CN	72
35	Cu_2O		CH_3CN	0
36		DCP (4.0)	CH_3CN	0

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), 10 mol% catalyst, and oxidant in solvent (5.0 mL) at 70 °C for 12 h under air atmosphere. [b] Isolated yield. [c] 60 °C. [d] 80 °C. [e] Under Ar atmosphere. [f] Under O_2 atmosphere.

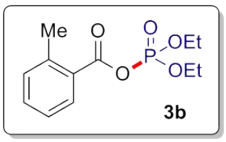
3. General procedure for oxidative dehydrogenative coupling

In a Schlenk tube, carboxylic acid **1** (0.5 mmol), H-phosphonate **2** (1.5 mmol), Cu_2O (0.05 mmol), DCP (2.0 mmol) and CH_3CN (5.0 mL) were added. The mixture was allowed to stir at 70 °C for 12 h under air atmosphere. Upon completion as shown by TLC, the reaction mixture was cooled to room temperature and diluted with CH_3CN (5.0 mL), then filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/EtOAc as the eluent to give the product **3**.

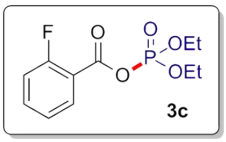
4. Characterization of products



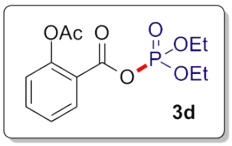
Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 4.49–4.27 (m, 4H), 1.43 (td, *J* = 7.1, 0.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8 (d, *J* = 8.3 Hz), 134.4, 130.4, 128.6, 128.0 (d, *J* = 8.2 Hz), 65.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 6.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -7.84. IR (film) *υ* 2306, 1747, 1641, 1425, 1265, 1030, 746 cm^{-1}. HRMS (ESI) calcd. for $C_{11}H_{15}O_5P$ $(M + Na)^+$, 281.0549; found 281.0552.



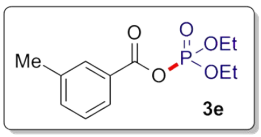
Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 1H), 7.30 (d, *J* = 7.0 Hz, 2H), 4.51–4.25 (m, 4H), 2.65 (s, 3H), 1.42 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8 (d, *J* = 8.2 Hz), 142.6, 133.7, 132.1, 131.7, 126.61 (d, *J* = 7.8 Hz), 125.9, 65.1 (d, *J* = 5.8 Hz), 21.9, 16.01 (d, *J* = 6.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -7.77. IR (film) *υ* 2686, 2306, 1747, 1642, 1428, 1266, 1031, 741 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{17}O_5P$ $(M + Na)^+$, 295.0706; found 295.0711.



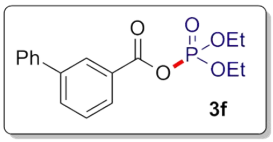
Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (td, *J* = 7.7, 1.7 Hz, 1H), 7.70–7.57 (m, 1H), 7.30–7.22 (m, 1H), 7.20–7.17 (m, 1H), 4.46–4.28 (m, 4H), 1.42 (td, *J* = 7.0, 0.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6 (d, *J* = 263.2 Hz), 158.3 (dd, *J* = 8.1, 3.8 Hz), 136.3 (d, *J* = 9.3 Hz), 133.0, 124.3 (d, *J* = 3.9 Hz), 117.3 (d, *J* = 22.1 Hz), 116.7 (t, *J* = 8.5 Hz), 65.5 (d, *J* = 5.9 Hz), 16.0 (d, *J* = 6.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -8.50. IR (film) *υ* 1752, 1615, 1456, 1286, 1241, 1030, 876, 820, 747 cm^{-1}. HRMS (ESI) calcd. for $C_{11}H_{14}FO_5P$ $(M + Na)^+$, 299.0455; found 299.0456.



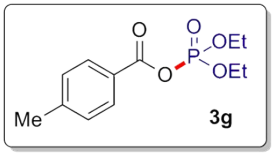
Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 7.9 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.16 (d, J = 8.1 Hz, 1H), 4.44–4.26 (m, 4H), 2.37 (s, 3H), 1.40 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 158.2 (d, J = 8.1 Hz), 151.7, 135.5, 132.5, 126.2, 124.3, 121.2 (d, J = 8.6 Hz), 65.3 (d, J = 5.8 Hz), 20.9, 16.0 (d, J = 6.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -8.27. IR (film) υ 1668, 1612, 1483, 1298, 1205, 1038, 758, 530 cm^{-1}. HRMS (ESI) calcd. for $C_{13}H_{17}O_7P$ $(M + Na)^+$, 317.0785; found 317.0784.



Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87–7.85 (m, 2H), 7.45 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 4.46–4.31 (m, 4H), 2.42 (s, 3H), 1.42 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1 (d, J = 8.4 Hz), 138.6, 135.3, 131.1, 128.6, 128.0 (d, J = 8.4 Hz), 127.8, 65.2 (d, J = 5.6 Hz), 21.1, 16.1 (d, J = 6.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -7.71. IR (film) υ 2351, 2027, 1640, 1462, 1400, 1268, 1186, 1035, 751 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{17}O_5P$ $(M + Na)^+$, 295.0706; found 295.0710.

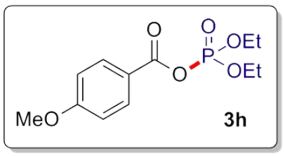


Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.8 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 4.47–4.32 (m, 4H), 1.43 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0 (d, J = 8.3 Hz), 142.0 (s), 139.5 (s), 133.1 (s), 129.3 (s), 129.2 (s), 129.2 (s), 129.0 (s), 128.7 (d, J = 8.1 Hz), 128.0 (s), 127.1 (s), 65.3 (d, J = 5.7 Hz), 16.1 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -7.70. IR (film): υ 1673, 1462, 1310, 1245, 1033, 814, 742, 694 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{19}O_5P$ $(M + Na)^+$, 335.1043; found 335.1038.

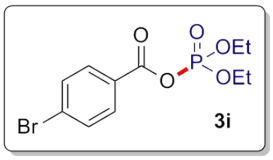


Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 4.45–4.27 (m, 4H), 2.44 (s, 3H), 1.42 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0 (d, J = 8.3 Hz), 145.6, 130.6, 129.4, 125.3 (d, J = 8.3 Hz), 65.2 (d, J =

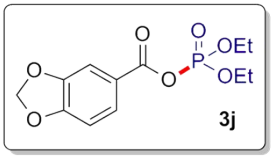
5.8 Hz), 21.7, 16.0 (d, J = 6.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -7.67. IR (film) υ 1746, 1645, 1616, 1456, 1397, 1259, 1171, 1035, 868, 748 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{17}O_5P$ (M + Na)$^+$, 295.0706; found 295.0710.



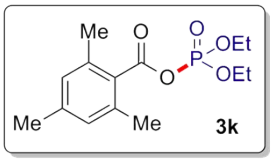
Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 4.44–4.29 (m, 4H), 3.89 (s, 3H), 1.42 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6, 160.6 (d, J = 7.4 Hz), 132.9, 120.2 (d, J = 8.9 Hz), 114.0, 65.1 (d, J = 5.7 Hz), 55.5, 16.0 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -7.62. IR (film) υ 2306, 2642, 1514, 1459, 1423, 1265, 1167, 1030, 741 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{17}O_6P$ (M + Na)$^+$, 311.0655; found 311.0658.



Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94–7.88 (m, 2H), 7.67–7.60 (m, 2H), 4.46–4.27 (m, 4H), 1.42 (td, J = 7.1, 1.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3 (d, J = 8.2 Hz), 132.1, 131.9, 129.8, 127.0 (d, J = 8.5 Hz), 65.3 (d, J = 5.8 Hz), 16.0 (d, J = 6.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -7.82. IR (film) υ 1747, 1653, 1589, 1400, 1258,1031, 1006, 752 cm^{-1}. HRMS (ESI) calcd. for $C_{11}H_{14}BrO_5P$ (M + Na)$^+$, 358.9654; found 358.9652.

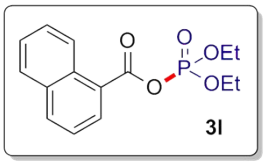


Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 1H), 7.44 (s, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.09 (s, 2H), 4.38–4.33 (m, 4H), 1.42 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2 (d, J = 8.2 Hz), 153.0, 148.0, 127.1, 121.8 (d, J = 8.4 Hz), 110.0, 108.2, 102.1, 65.2 (d, J = 5.8 Hz), 16.0 (d, J = 6.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -7.75. IR (film) υ 2306, 1740, 1445, 1265, 1154, 1030, 918, 741 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{15}O_5P$ (M + Na)$^+$, 325.0448; found 325.0450.

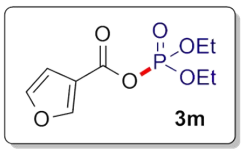


Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (s, 2H), 4.41–4.25 (m, 4H), 2.39 (s, 6H), 2.29 (s, 3H), 1.39 (td, J = 7.1, 0.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8 (d, J = 9.1 Hz), 140.8, 136.3, 128.8, 128.3, 65.2 (d, J = 5.8 Hz), 21.1, 20.2, 16.0 (d, J = 6.9

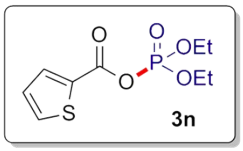
Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -8.30. IR (film) υ 2026, 1639, 1458, 1394, 1234, 1163, 1036 cm^{-1}. HRMS (ESI) calcd. for $C_{14}H_{21}O_5P$ $(M + Na)^+$, 323.1019; found 321.1018.



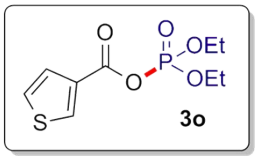
Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (d, J = 8.7 Hz, 1H), 8.33 (d, J = 7.3 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 4.5–4.27 (m, 4H), 1.44 (t, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9 (d, J = 8.1 Hz), 135.6, 133.8, 132.5, 131.7, 128.7, 128.7, 126.6, 125.4, 124.3, 123.9 (d, J = 8.1 Hz), 65.2 (d, J = 5.7 Hz), 16.1 (d, J = 6.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -7.73. IR (film) υ 1740, 1669, 1513, 1264, 1235, 1036, 963, 775, 739 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{17}O_5P$ $(M + Na)^+$, 331.0706; found 331.0707.



Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 0.6 Hz, 1H), 7.49 (s, 1H), 6.83–6.73 (m, 1H), 4.47–4.23 (m, 4H), 1.41 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6 (d, J = 7.6 Hz), 149.7, 144.5, 117.9 (d, J = 9.8 Hz), 109.9, 65.2 (d, J = 5.8 Hz), 16.0 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -8.34. IR (film) υ 2306, 1425, 1265, 1163, 1038, 949, 741 cm^{-1}. HRMS (ESI) calcd. for $C_9H_{13}O_6P$ $(M + Na)^+$, 271.0342; found 271.0349.

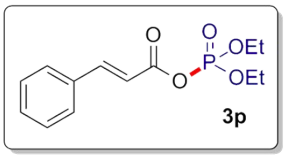


Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 3.4 Hz, 1H), 7.72 (d, J = 4.8 Hz, 1H), 7.17 (t, J = 4.3 Hz, 1H), 4.49–4.28 (m, 4H), 1.42 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0 (d, J = 7.5 Hz), 136.1, 135.2, 131.5 (d, J = 9.9 Hz), 128.3, 65.4 (d, J = 5.9 Hz), 16.0 (d, J = 6.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -8.52. IR (film) υ 2026, 1740, 1642, 1408, 1164, 1039, 731 cm^{-1}. HRMS (ESI) calcd. for $C_9H_{13}O_5PS$ $(M + Na)^+$, 287.0114; found 287.0116.

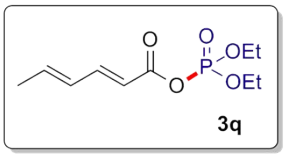


Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (dd, J = 3.0, 1.2 Hz, 1H), 7.55 (dd, J = 5.1, 1.1 Hz, 1H), 7.37 (dd, J = 5.1, 3.0 Hz, 1H), 4.41–4.30 (m, 1H), 1.41 (td, J = 7.1, 1.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3 (d, J = 8.0 Hz), 135.8, 131.5 (d, J = 9.1

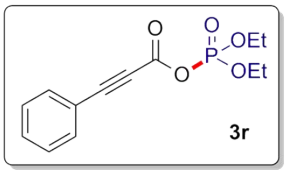
Hz), 128.2, 126.9, 65.2 (d, J = 5.7 Hz), 16.0 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -8.06. IR (film) υ 1746, 1641, 1520, 1398, 1242, 1034, 924, 747 cm^{-1}. HRMS (ESI) calcd. for $C_9H_{13}O_5PS$ (M + Na)$^+$, 287.0114; found 287.0118.



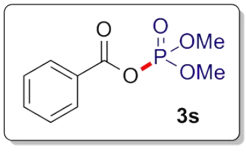
Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 15.9 Hz, 1H), 7.55 (d, J = 7.7 Hz, 2H), 7.47–7.39 (m, 3H), 6.42 (dd, J = 15.9, 1.9 Hz, 1H), 4.45–4.23 (m, 4H), 1.41 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7 (d, J = 8.2 Hz), 149.0, 133.5, 131.3, 129.0, 128.5, 116.0 (d, J = 9.1 Hz), 65.1 (d, J = 5.8 Hz), 16.0 (d, J = 6.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -8.00. IR (film) υ 1737, 1635, 1266, 1139, 1035, 946, 874, 741, 535 cm^{-1}. HRMS (ESI) calcd. for c $C_{13}H_{17}O_5P$ (M + Na)$^+$, 307.0706; found 307.0708.



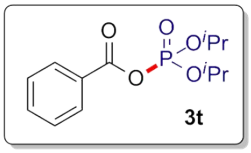
Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dd, J = 15.2, 10.2 Hz, 1H), 6.34–6.17 (m, 2H), 5.80–5.70 (m, 1H), 4.39–4.19 (m, 4H), 1.90 (d, J = 5.8 Hz, 3H), 1.38 (td, J = 7.1, 0.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0 (d, J = 8.2 Hz), 149.4, 142.7, 129.4, 116.7 (d, J = 9.0 Hz), 65.0 (d, J = 5.7 Hz), 18.8, 16.0 (d, J = 6.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -7.97. IR (film) υ 1739, 1640, 1282, 1234, 1036, 945, 820 cm^{-1}. HRMS (ESI) calcd. for $C_{10}H_{17}O_5P$ (M + Na)$^+$, 271.0706; found 271.0710.



Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 4.40–4.12 (m, 4H), 1.41 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.5 (d, J = 2.4 Hz), 130.6, 128.4, 119.3 (d, J = 5.6 Hz), 99.1, 98.7, 79.4, 63.1 (d, J = 5.5 Hz), 16.0 (d, J = 7.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.01. IR (film) υ 2187, 1643, 1265, 1163, 1024, 857, 759 cm^{-1}. HRMS (ESI) calcd. for $C_{13}H_{15}O_5P$ (M + Na)$^+$, 305.0549; found 305.0552.

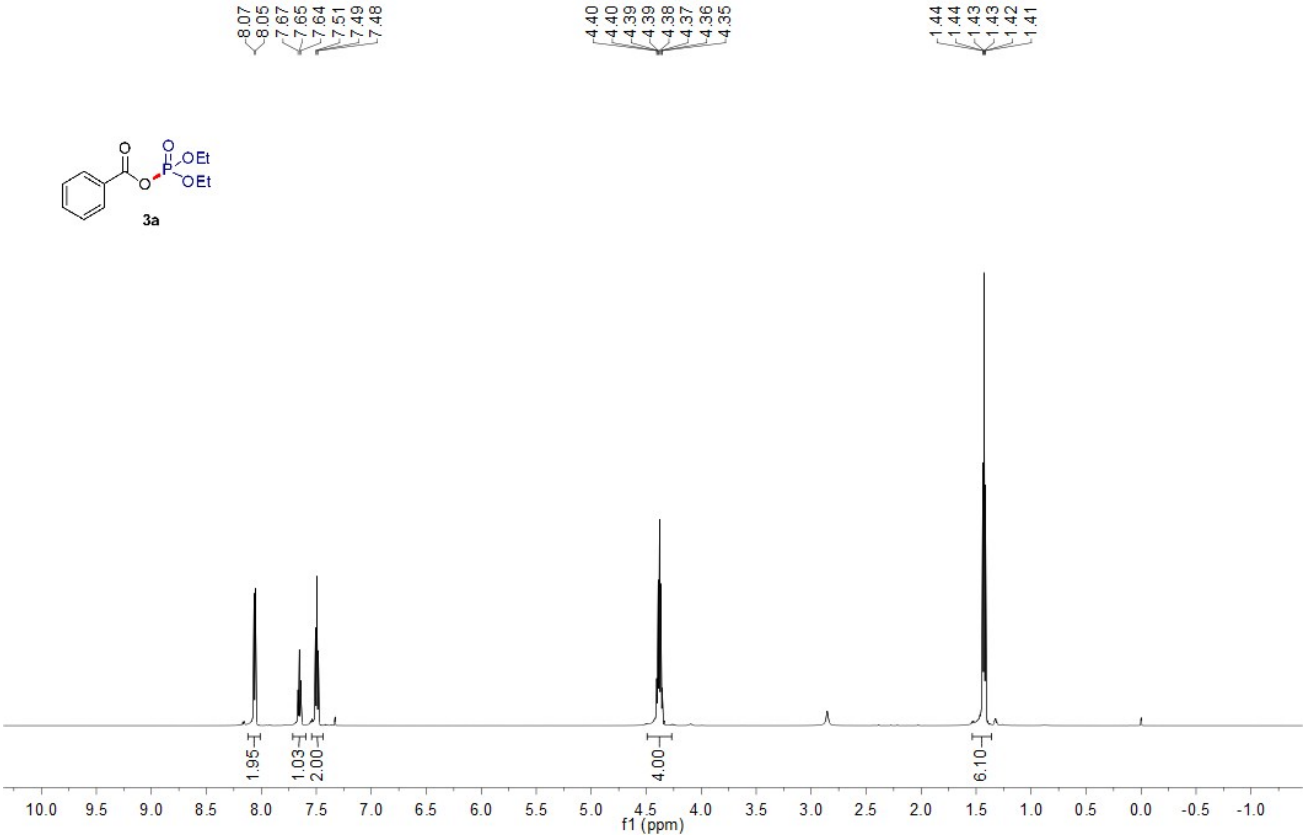


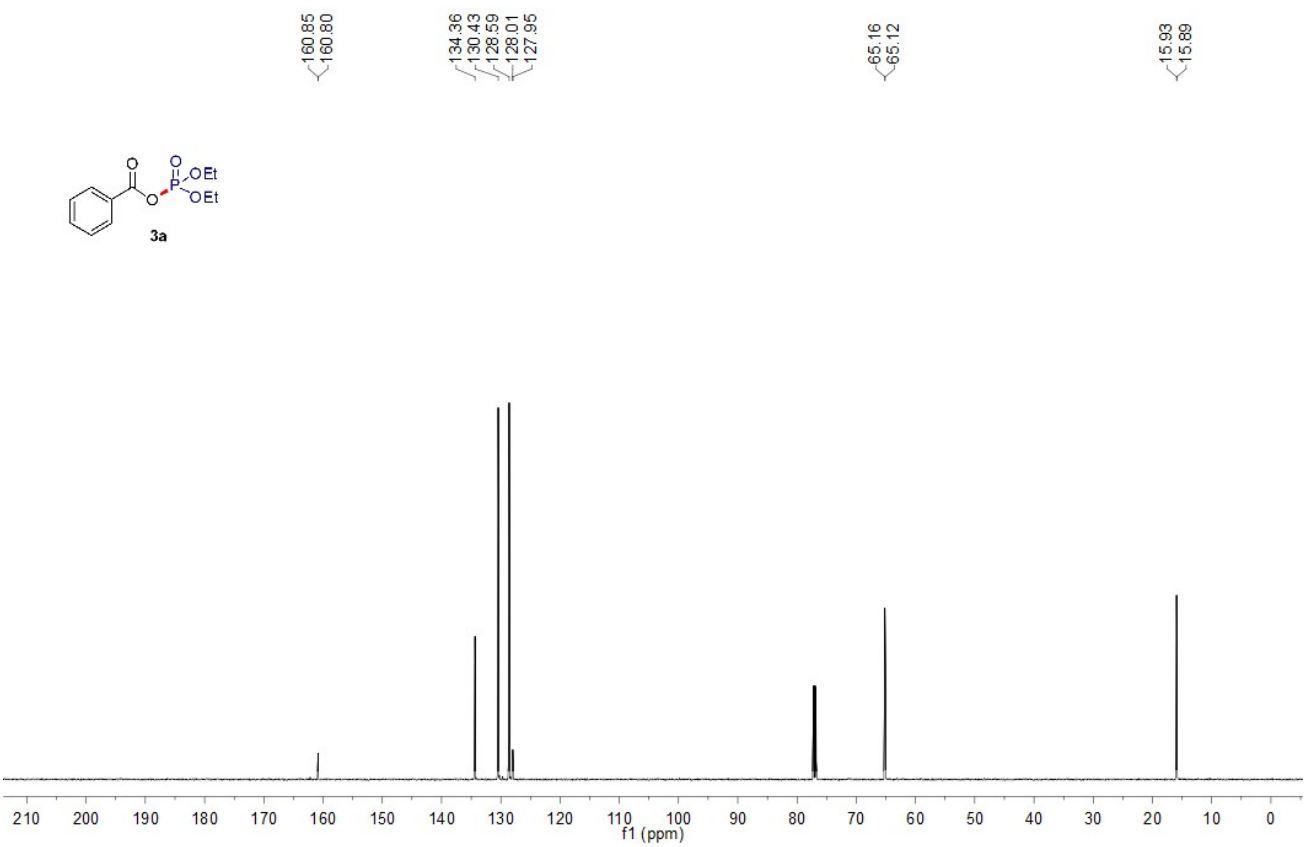
Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.69–7.63 (m, 1H), 7.53–7.46 (m, 2H), 4.00 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5 (d, *J* = 8.1 Hz), 134.3, 130.2, 128.4, 127.4 (d, *J* = 8.3 Hz), 55.0 (d, *J* = 5.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -5.10. IR (film) *υ* 1750, 1454, 1261, 1044, 866, 707, 536 cm^{-1}. HRMS (ESI) calcd. for $C_9H_{11}O_5P$ $(M + Na)^+$, 253.0236; found 253.0237.

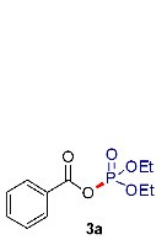


Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 5.04–4.87 (m, 2H), 1.42 (dd, *J* = 12.9, 6.2 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0 (d, *J* = 8.5 Hz), 134.3, 130.5, 128.7, 128.4 (d, *J* = 8.4 Hz), 74.3 (d, *J* = 5.9 Hz), 23.7 (d, *J* = 4.6 Hz), 23.4 (d, *J* = 5.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ -9.78. IR (film) *υ* 1748, 1748, 1643, 1458, 1385, 1256, 1013, 710 cm^{-1}. HRMS (ESI) calcd. for $C_{13}H_{19}O_5P$ $(M + Na)^+$, 309.0862; found 309.0869.

5. Charts of products



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OEt
3a

7.84
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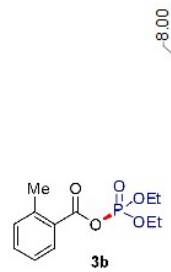
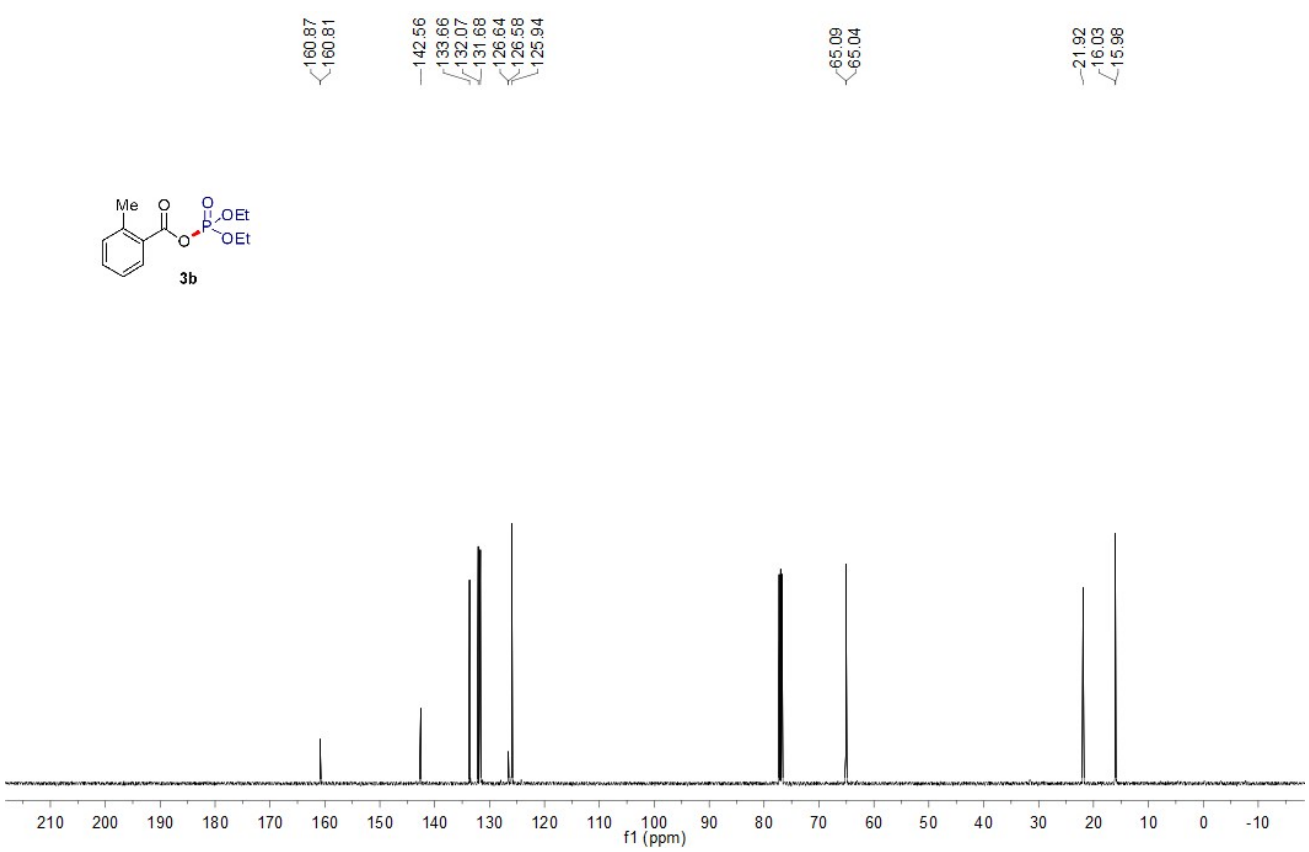

Me
OEt
OEt
3b

8.00
7.98
7.50
7.49
7.48
7.30
7.29
4.38
4.37
4.36
2.65
1.43
1.42
1.41
1.00
1.08
2.09
4.00
3.10
6.00
10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)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131.68
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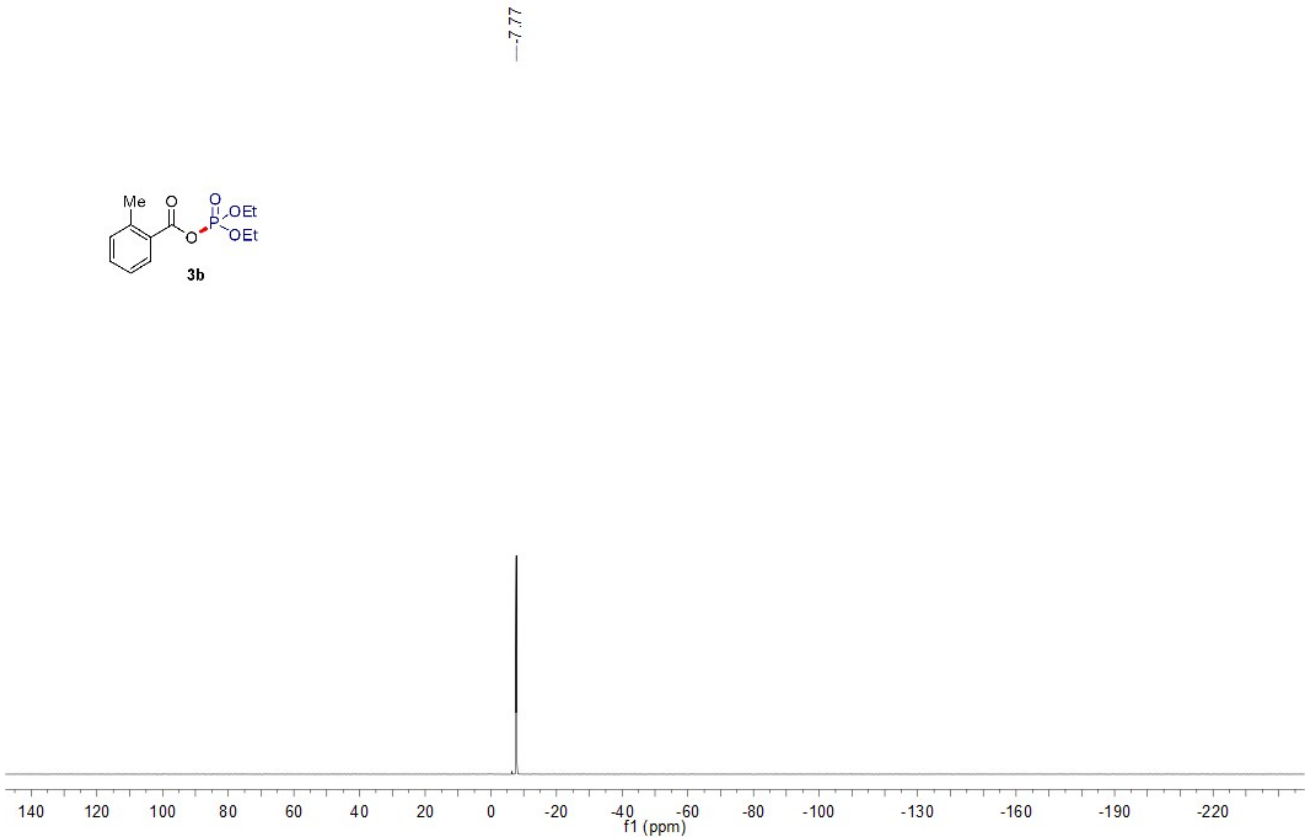
65.04
21.92
16.03
15.98
Me
O
O
OEt
P
OEt
O
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
3b
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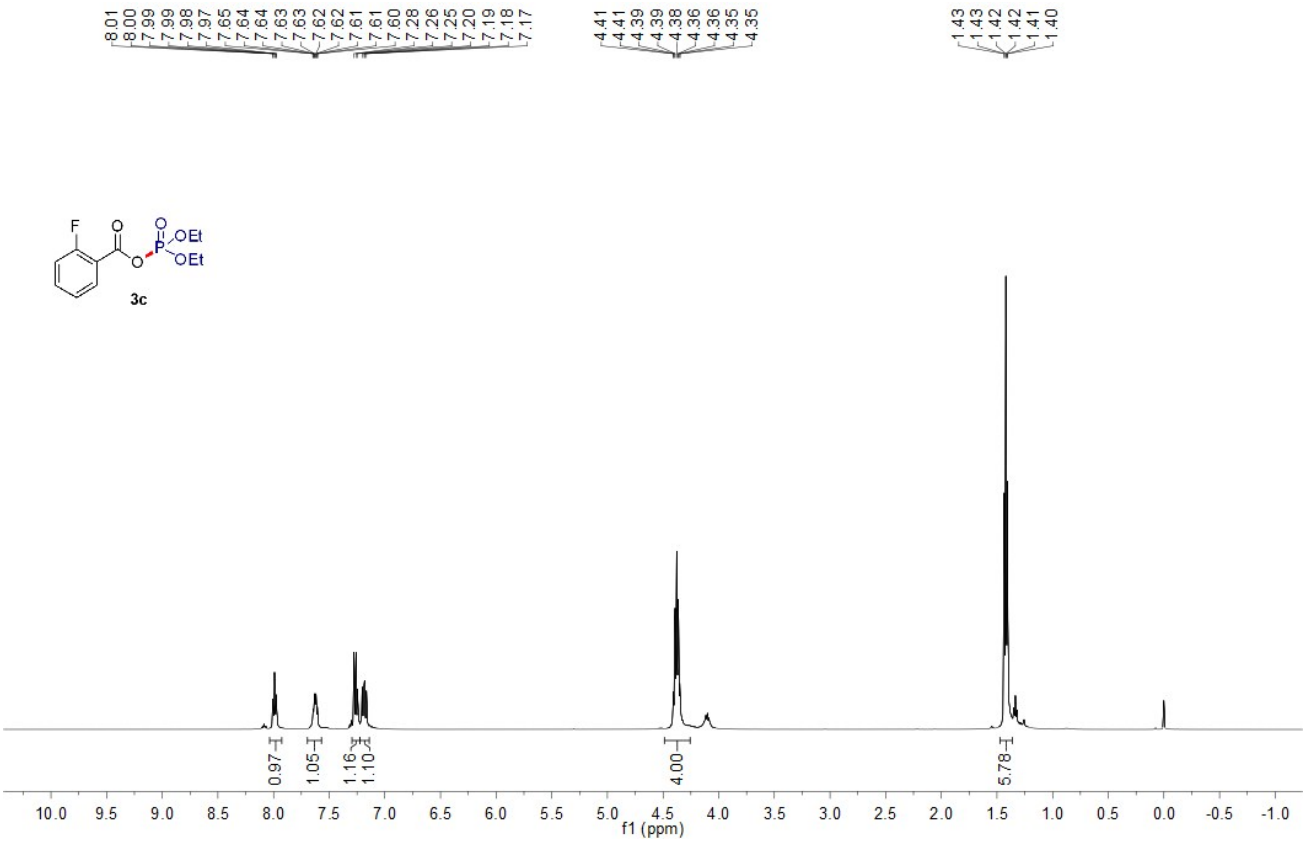
f1 (ppm)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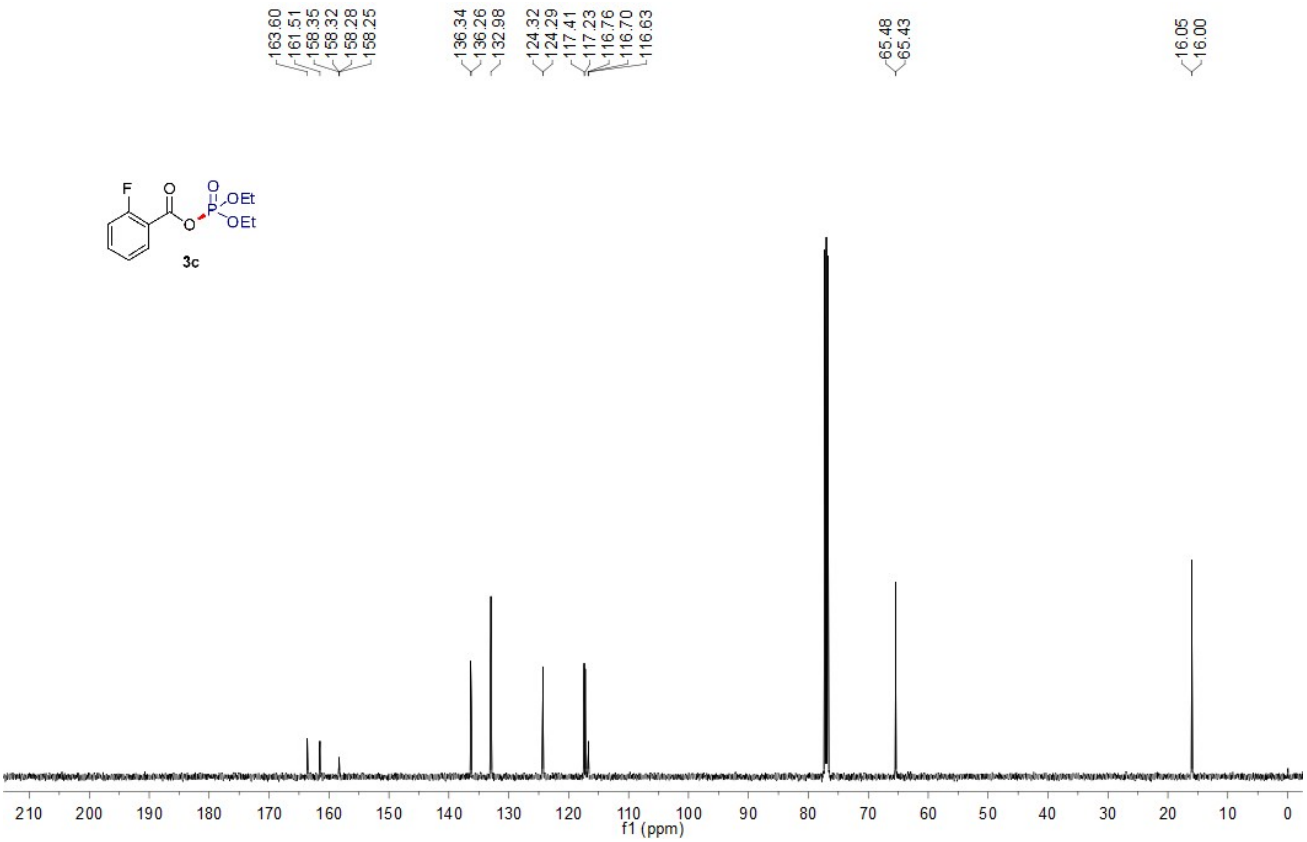
7.25
7.20
7.19
7.18
7.17
4.41
4.41
4.39
4.39
4.38
4.36
4.36
4.35
4.35
1.43
1.43
1.42
1.42
1.41
1.40
F
O
O
P
OEt
OEt
3c
0.97
1.05
1.16
1.10
4.00
5.78
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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124.29
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117.23
116.76
116.70
116.63
65.48
65.43
16.05
16.00
F
O
O
P
OEt
OEt
3c
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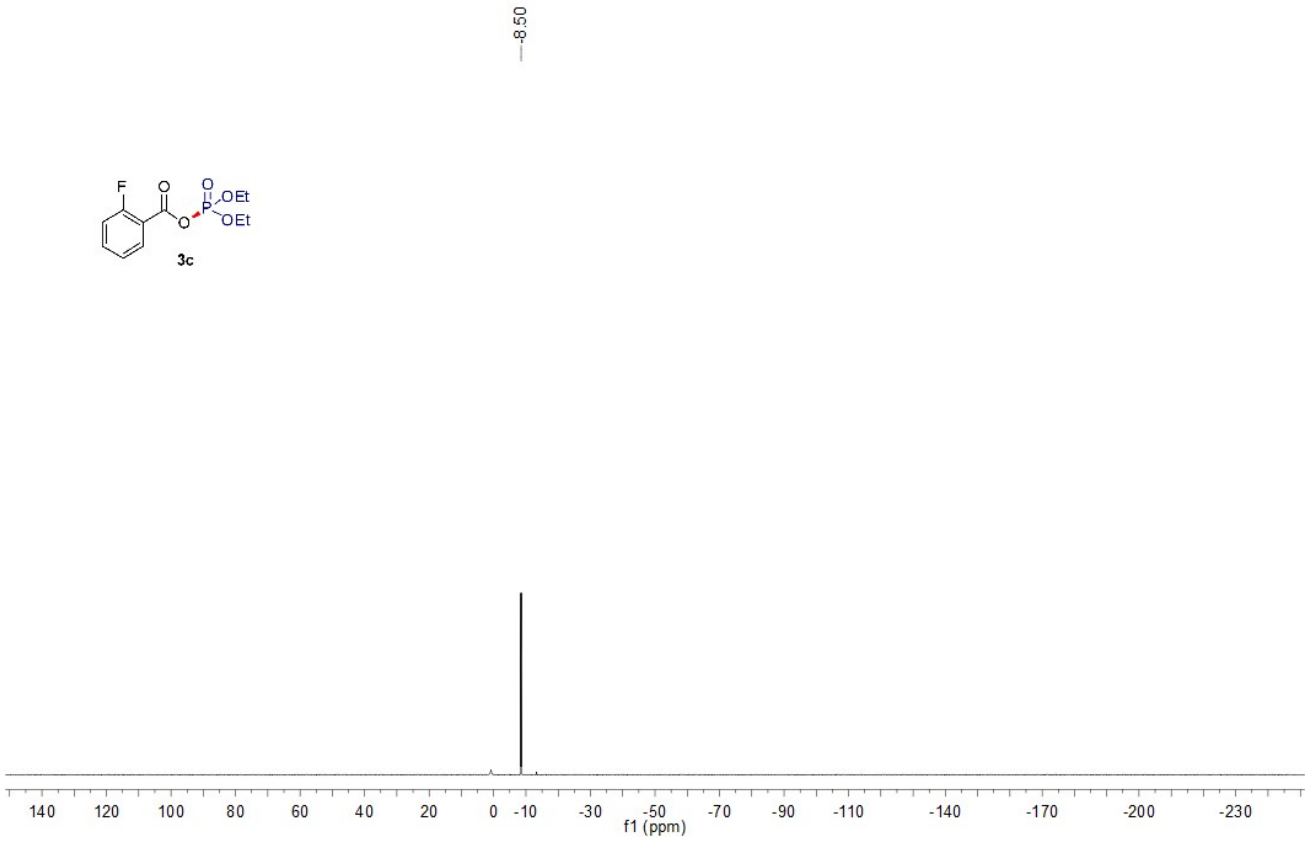
f1 (ppm)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O
O
P
OEt
OEt
3c
140
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100
80
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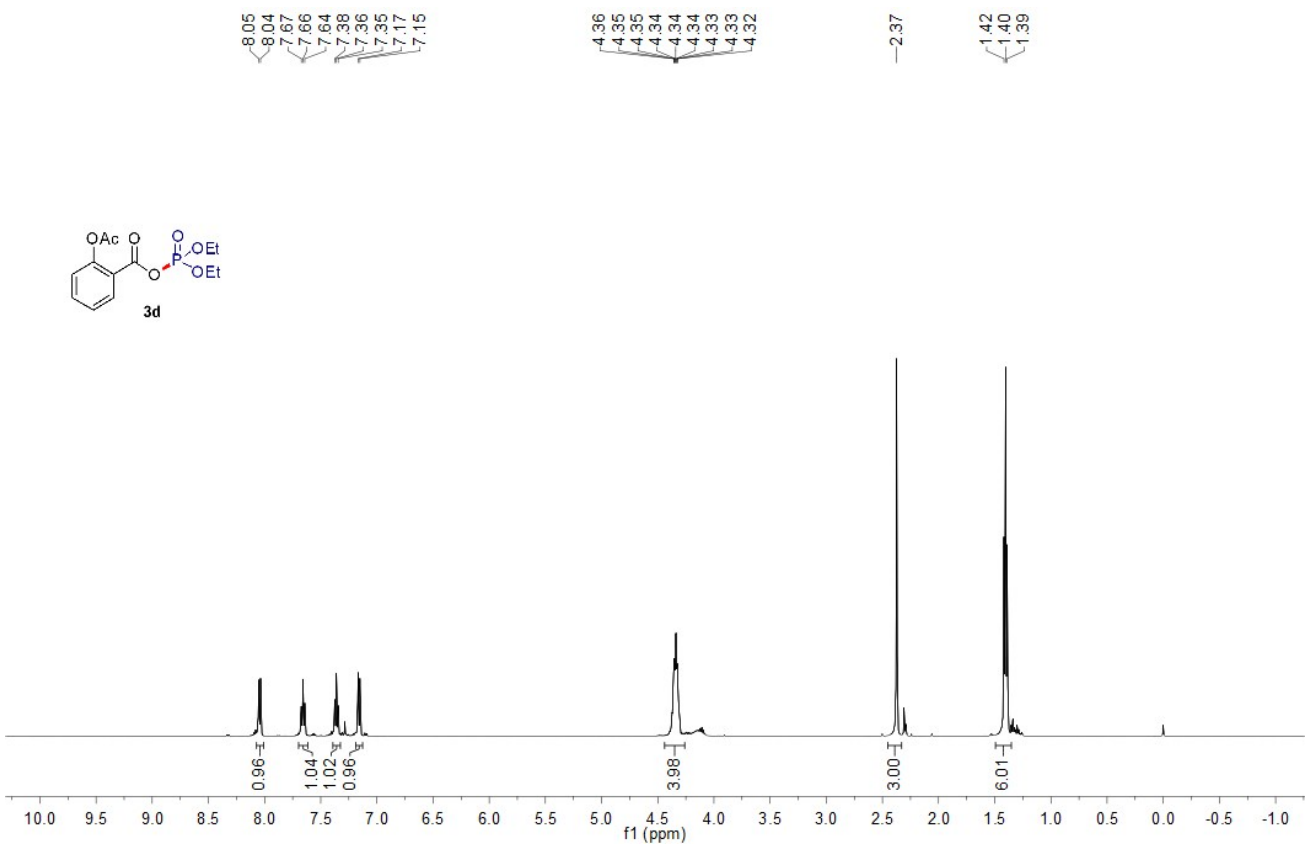
40
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
-230
f1 (ppm)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4.33
4.33
4.32
2.37
1.42
1.40
1.39
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O
O
P
OEt
OEt
3d
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1.04
1.02
0.96
3.98
3.00
6.01
10.0
9.5
9.0
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8.0
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7.0
6.5
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4.0
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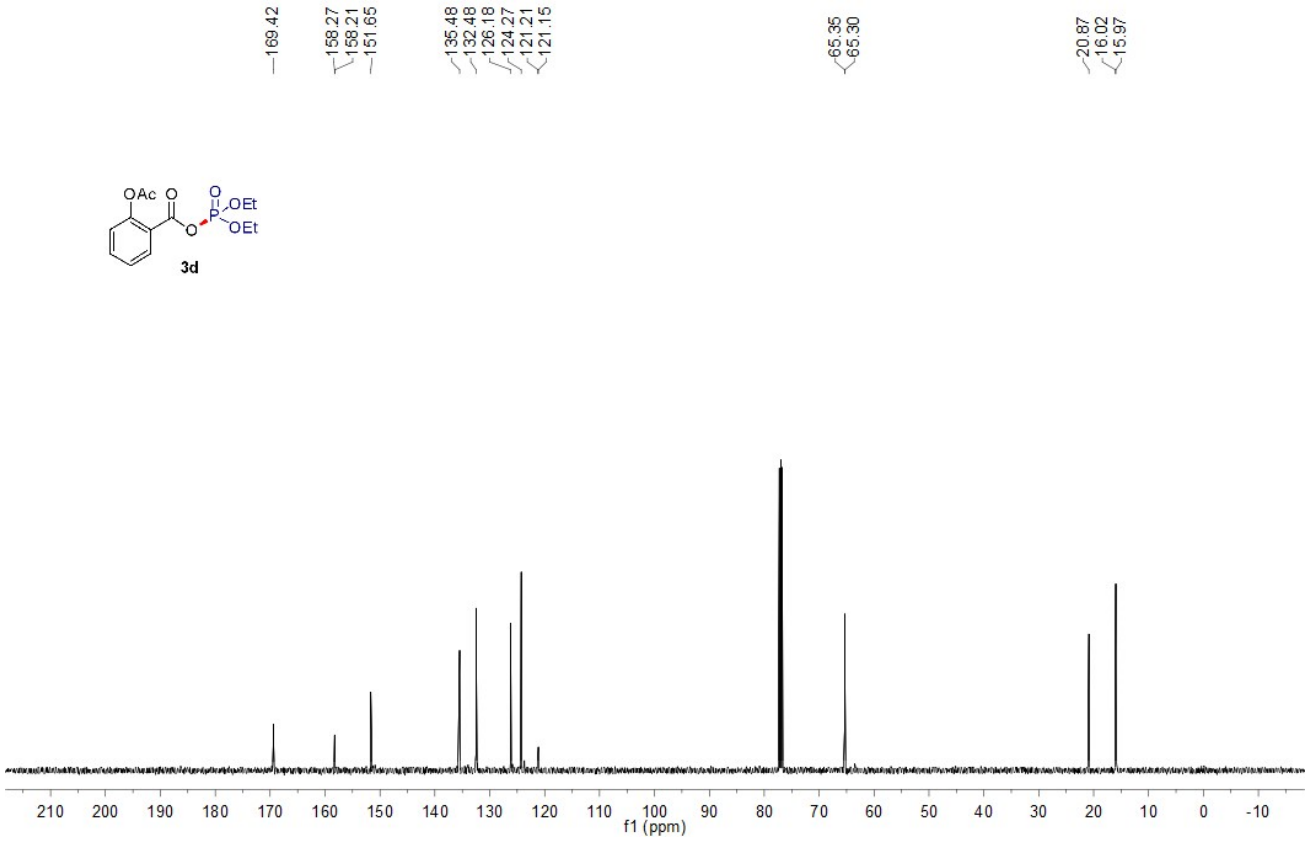
f1 (ppm)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16.02
15.97
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P
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OEt
O
3d
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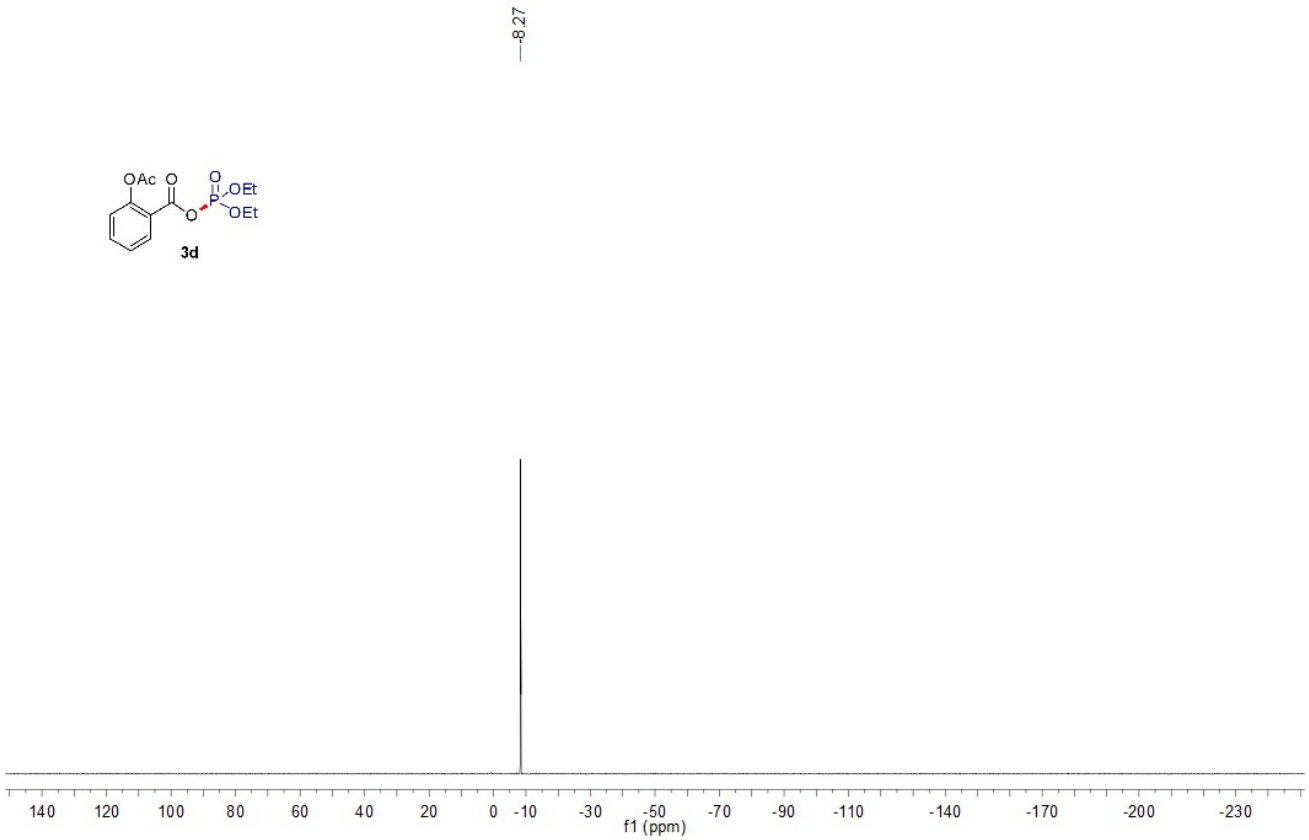
f1 (ppm)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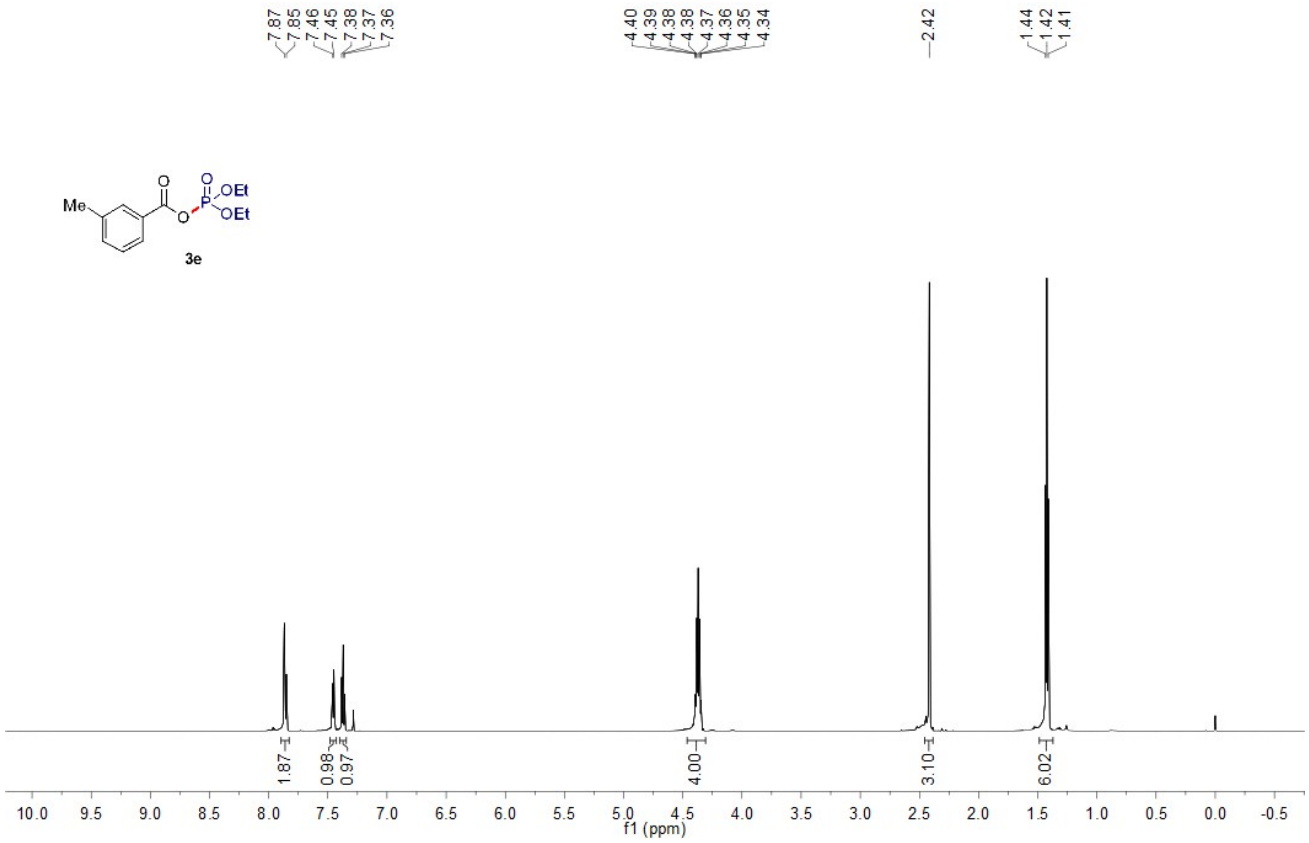
f1 (ppm)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4.34
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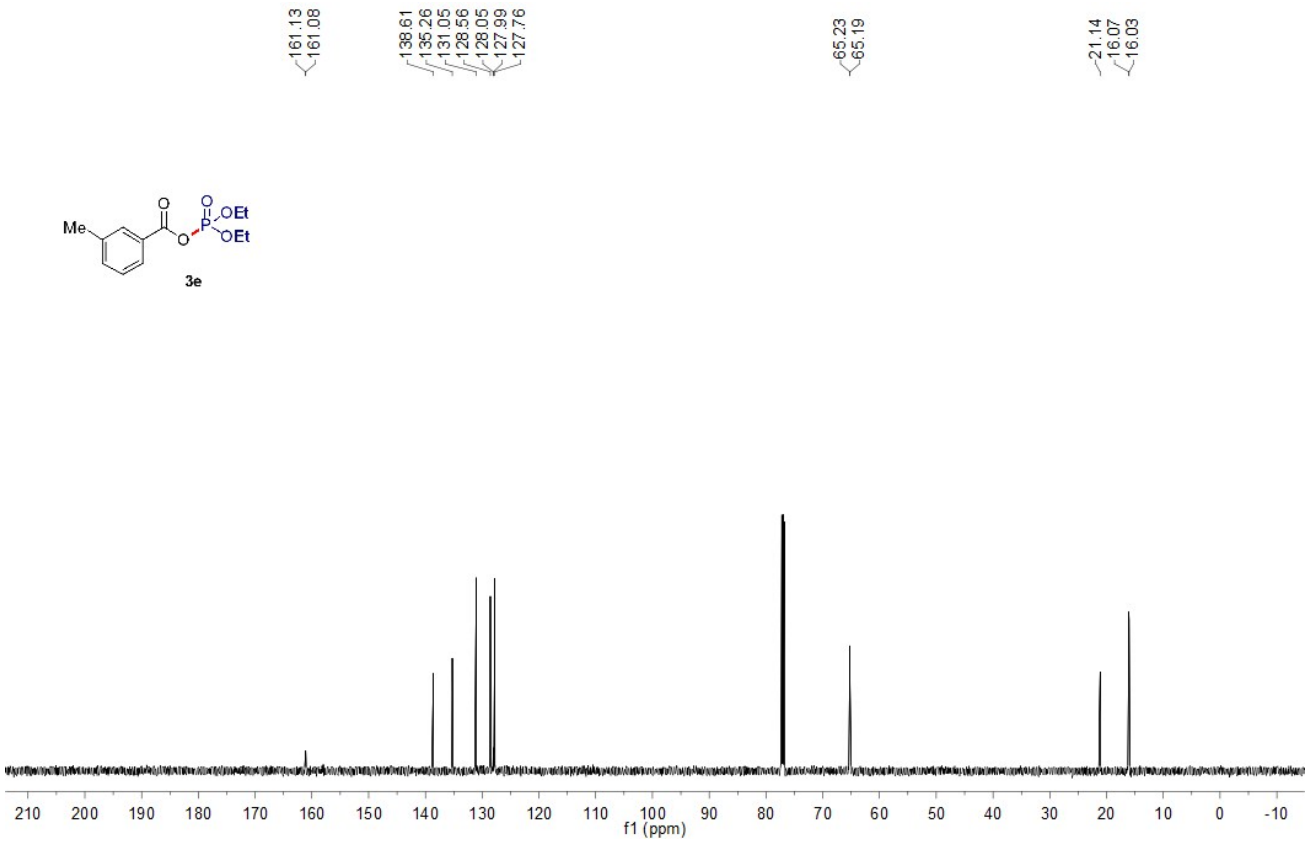
f1 (ppm)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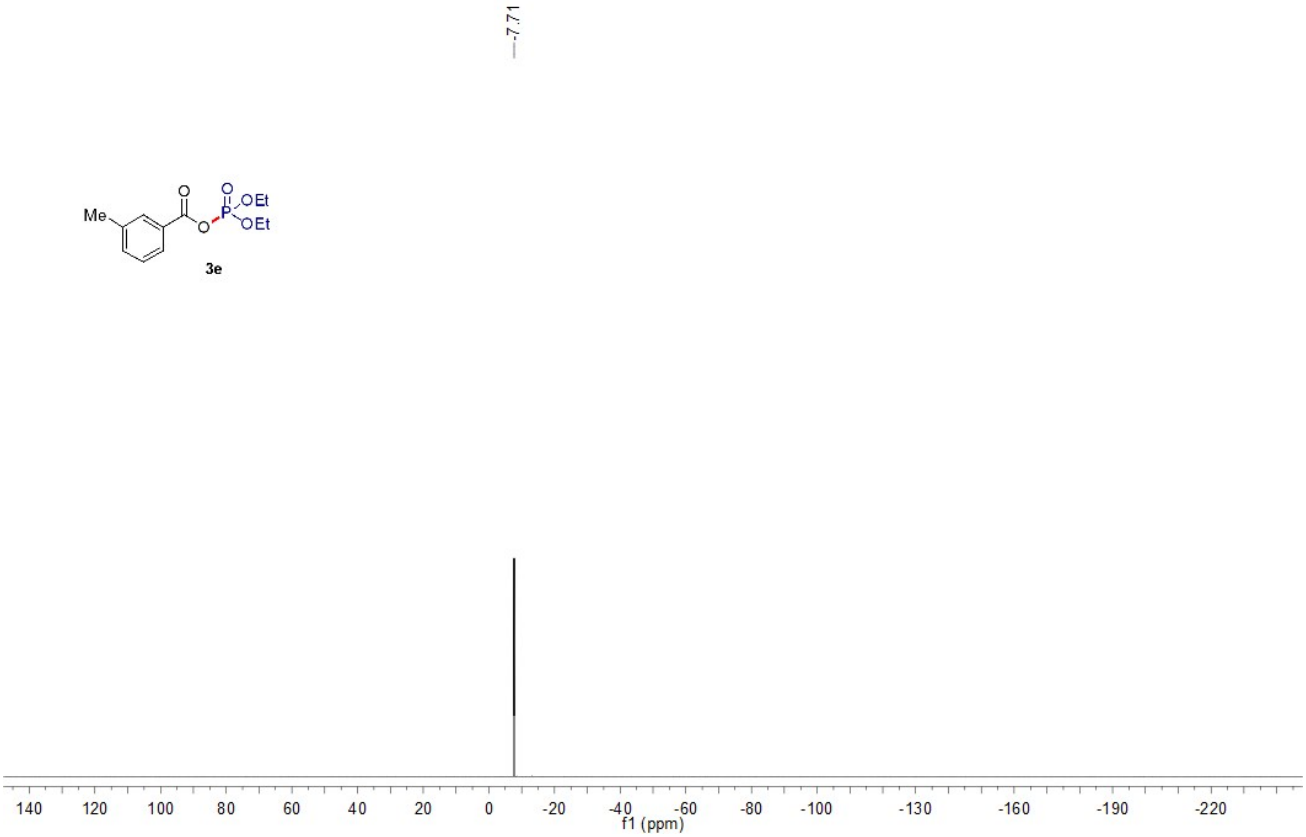
OEt
3e
f1 (ppm)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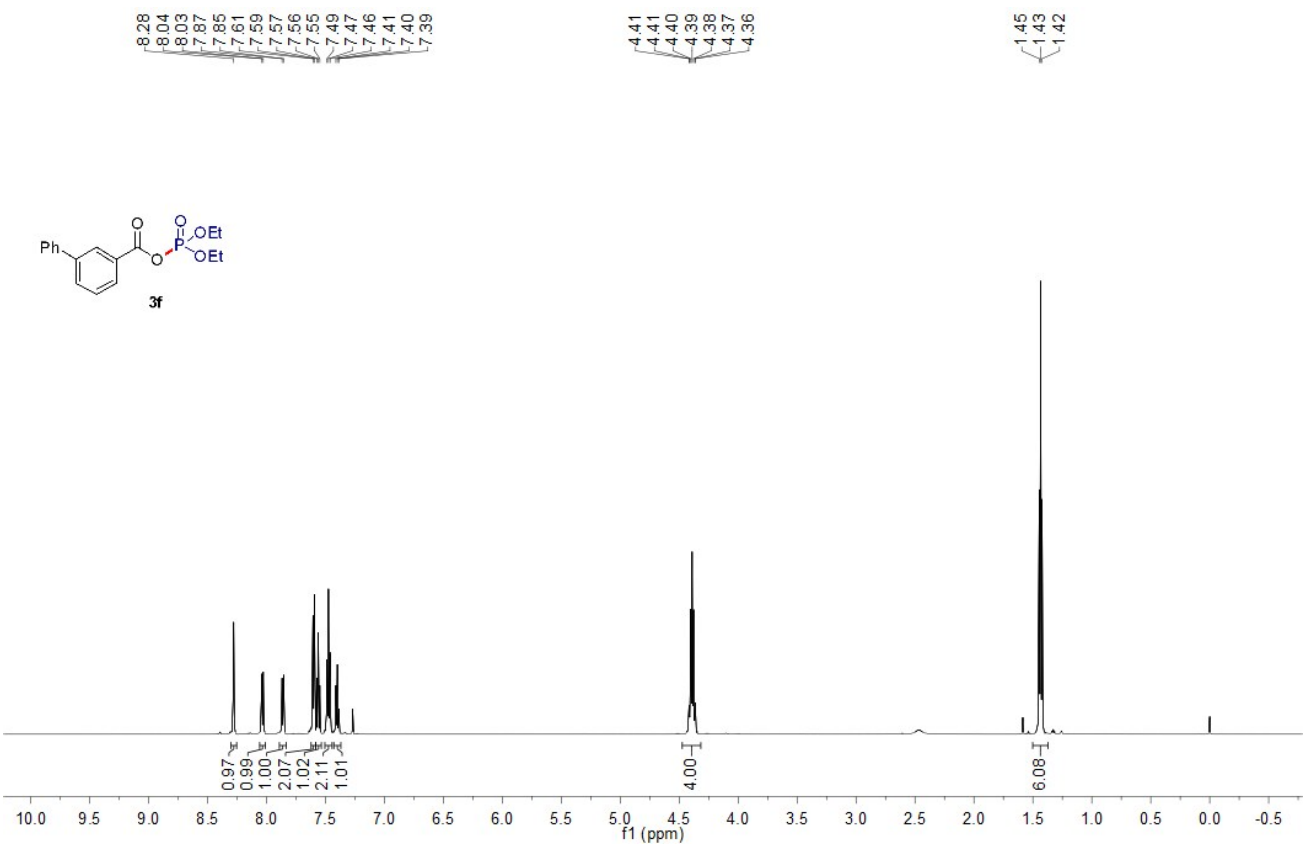
f1 (ppm)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4.39
4.38
4.37
4.36
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1.43
1.42
Ph
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O
P
OEt
OEt
3f
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0.99
1.00
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1.02
2.11
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4.00
6.08
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6.0
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5.0
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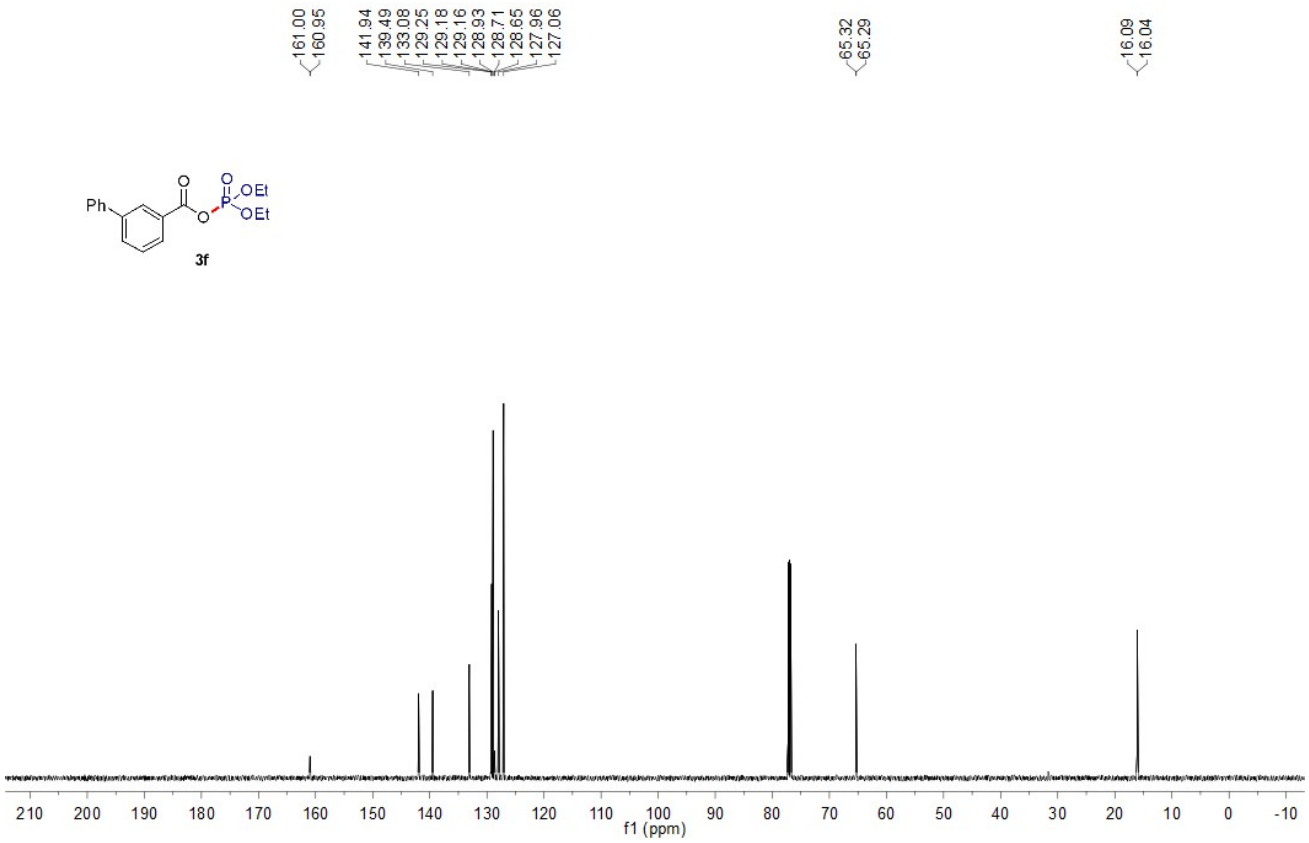
f1 (ppm)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127.06
65.32
65.29
16.09
16.04
Ph
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O
P
OEt
OEt
3f
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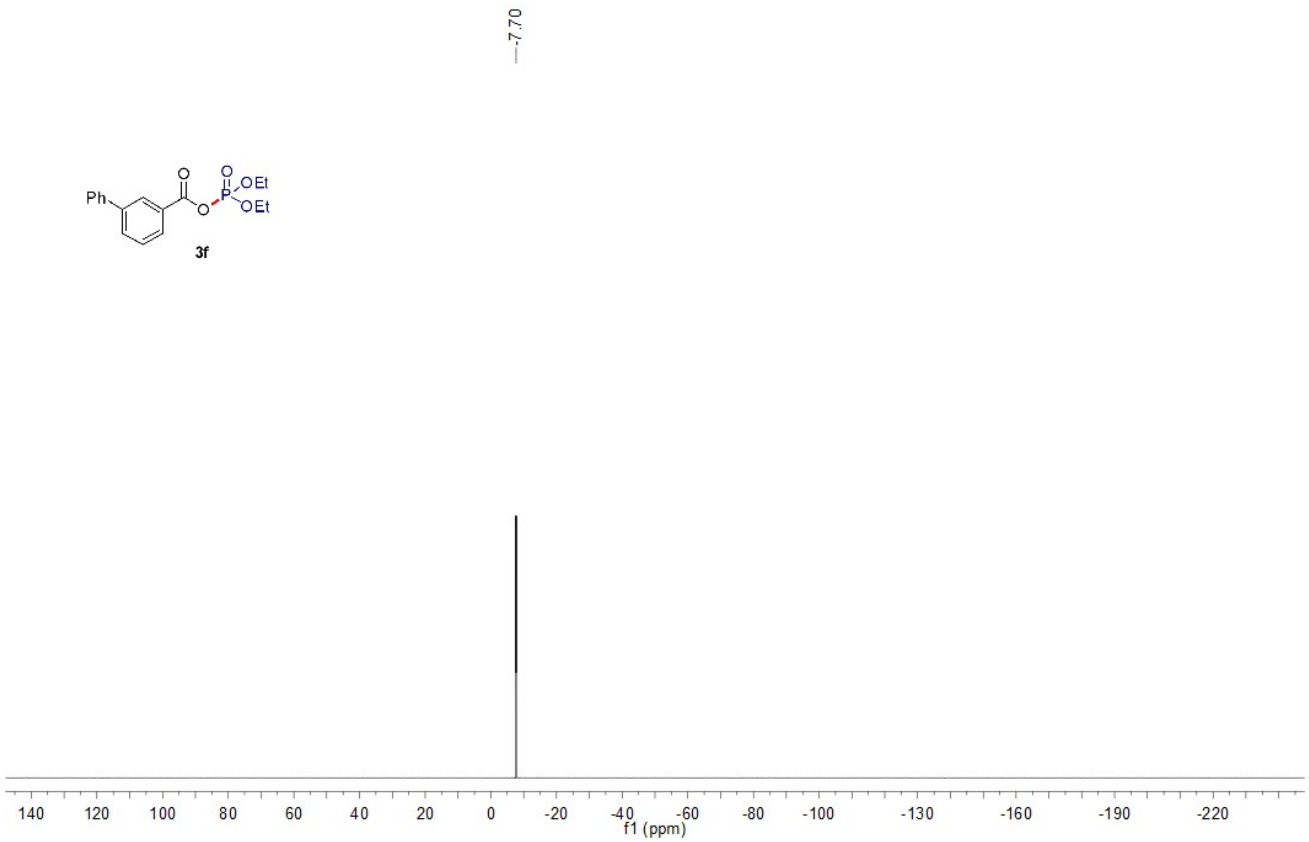
f1 (ppm)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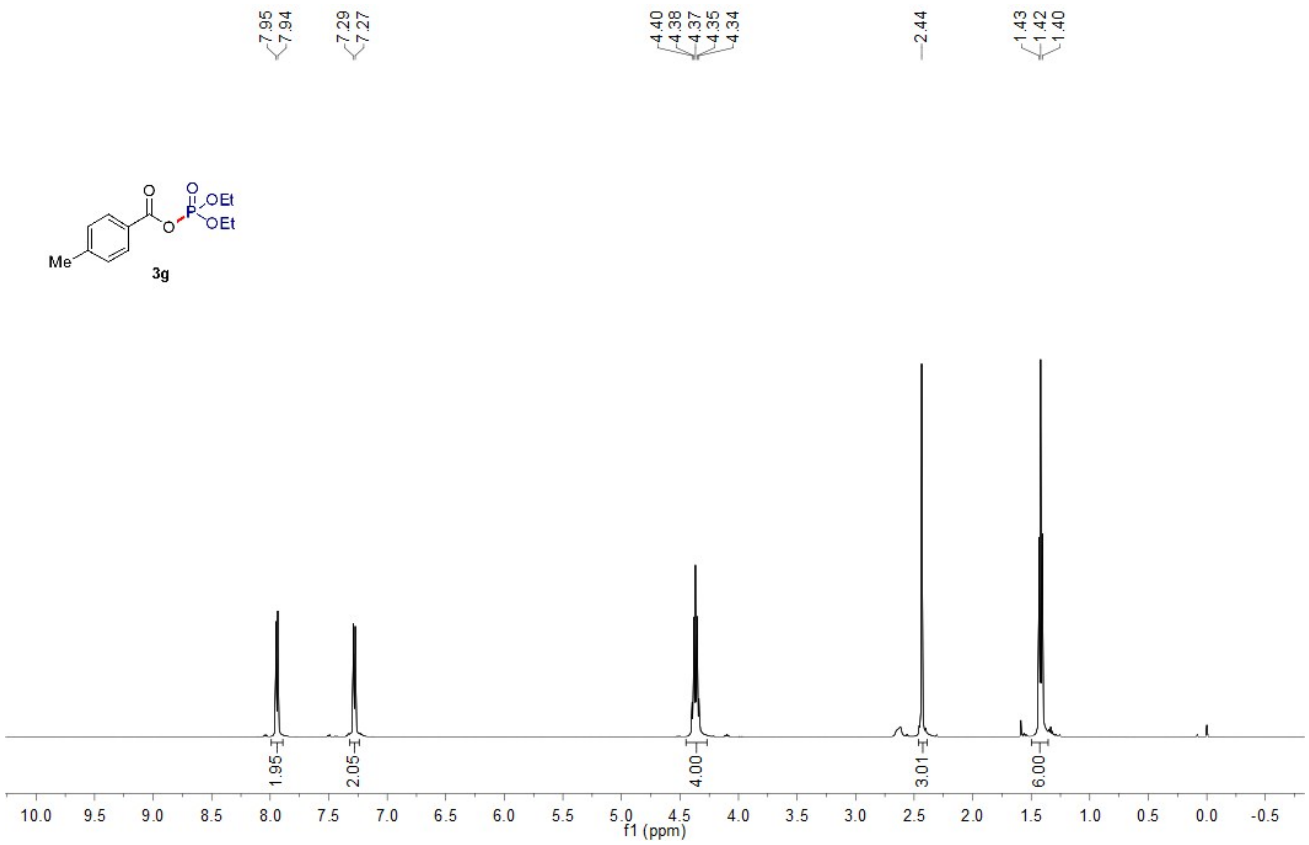
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2.05
4.00
3.01
6.00
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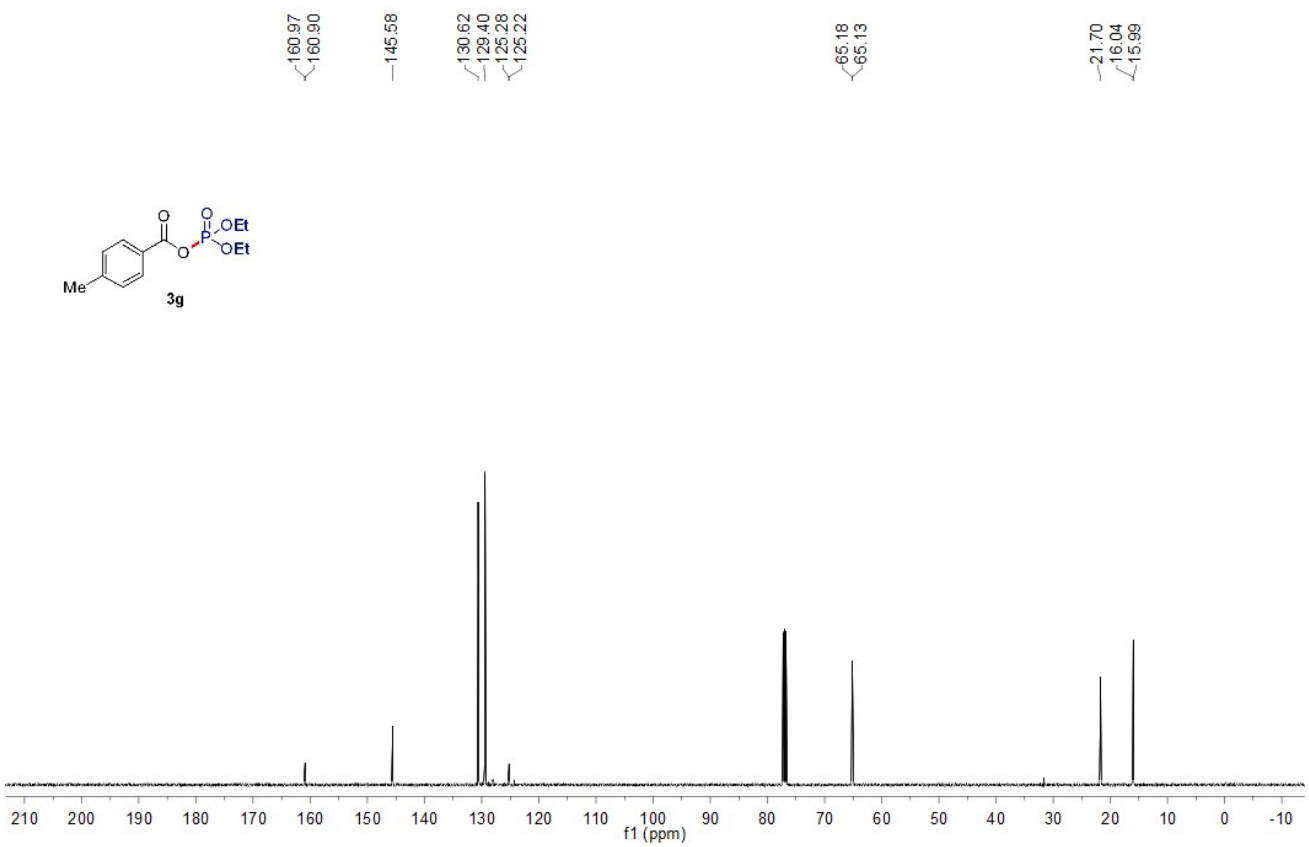
f1 (ppm)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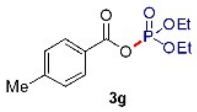
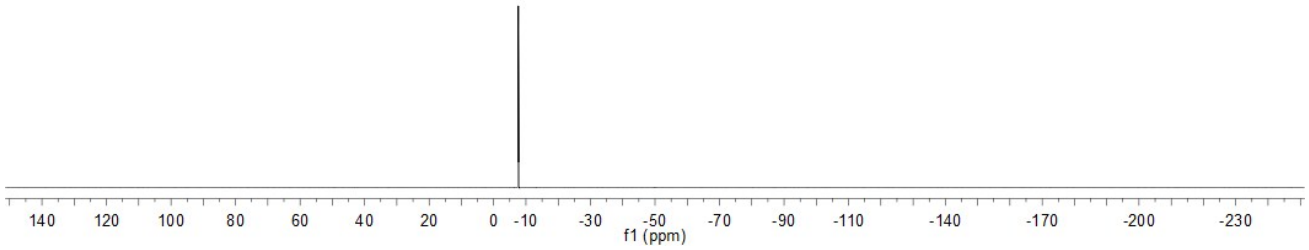
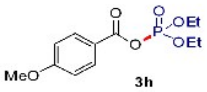
125.28
125.22
65.18
65.13
21.70
16.04
15.99
O
O
P
OEt
OEt
O
Me
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
OEt
OEt

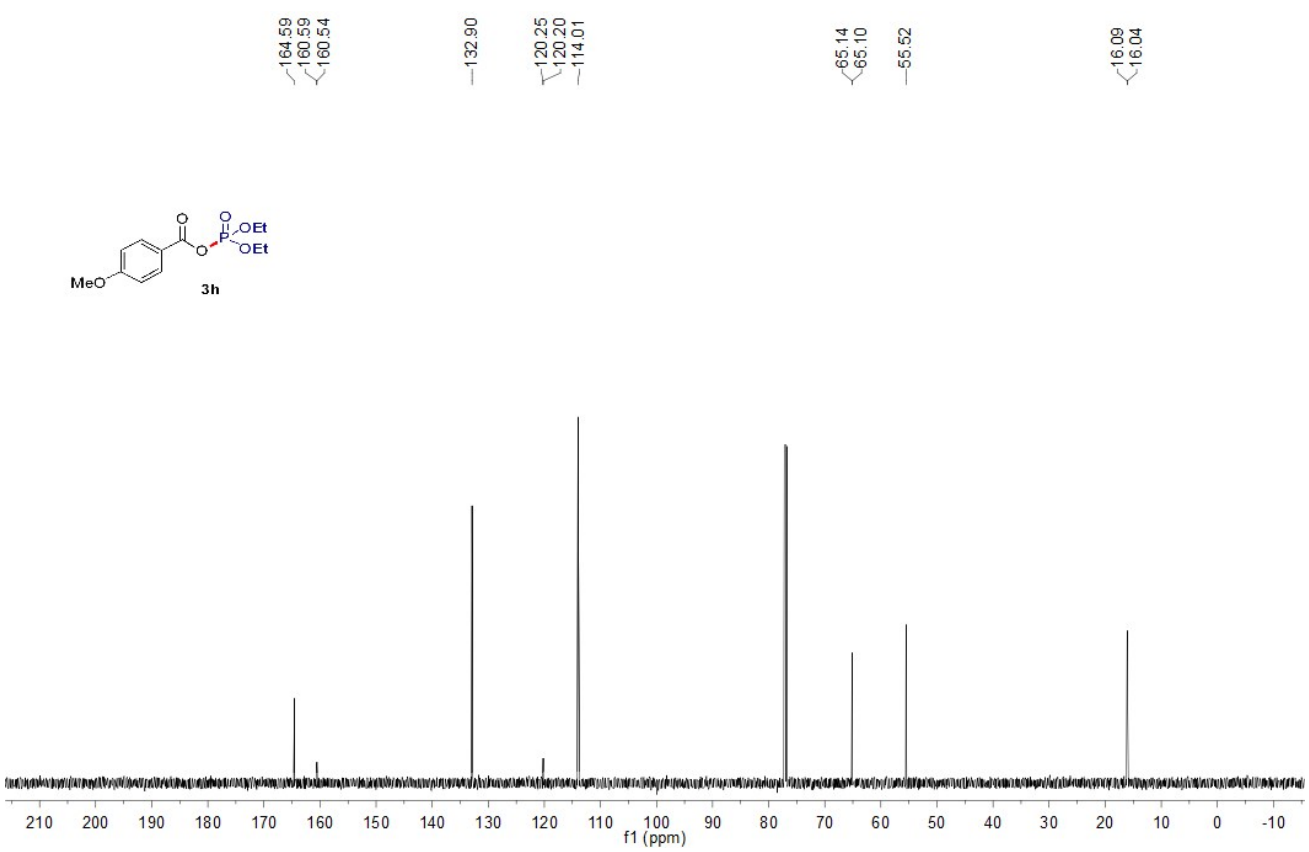
3g

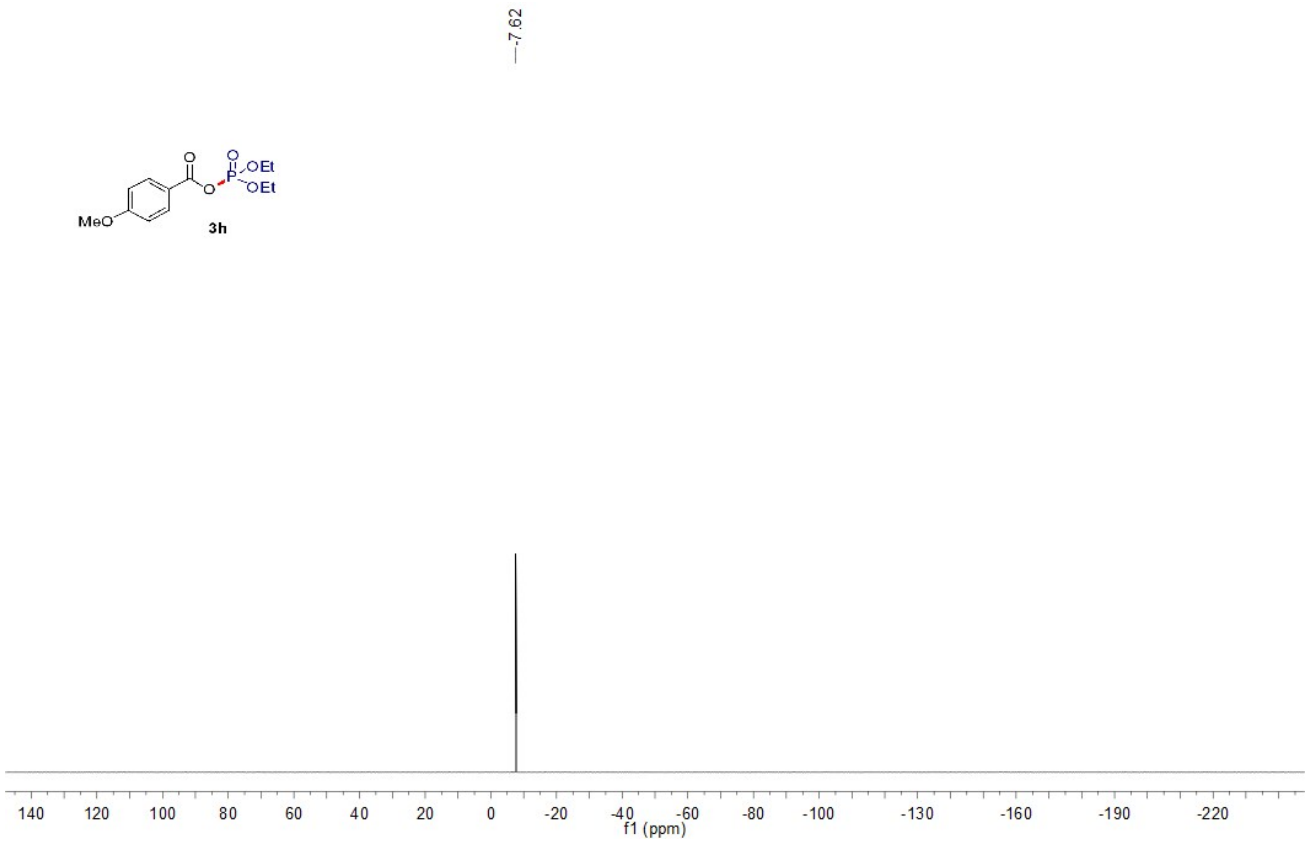

7.67
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
f1 (ppm)

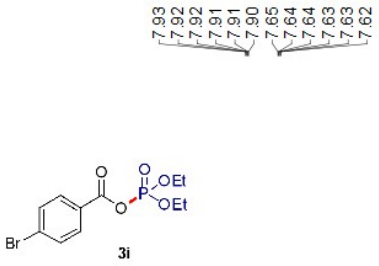

MeO
OEt
OEt

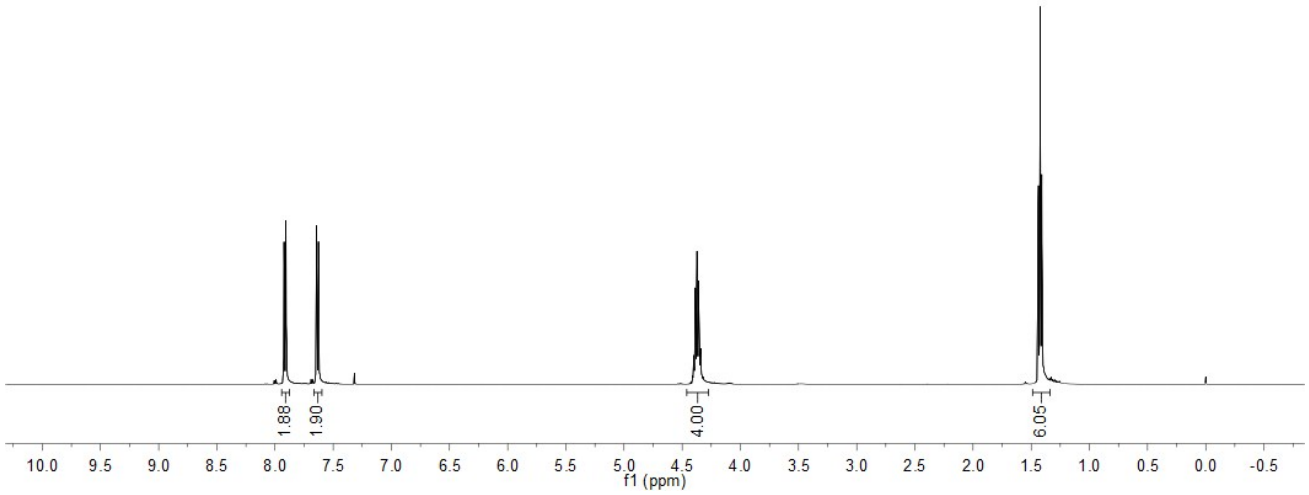
3h

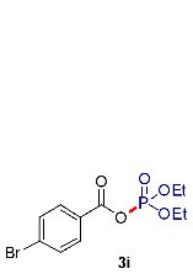
8.02
8.00
6.96
6.94
4.38
4.37
4.36
4.35
4.34
4.33
3.89
1.43
1.42
1.40
0.00
2.03
2.09
4.00
3.10
6.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

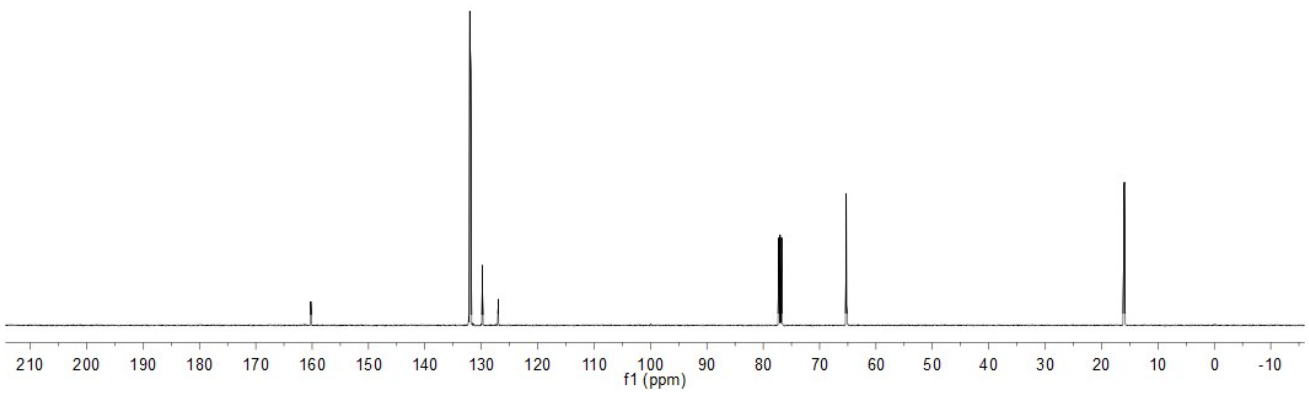

164.59
160.59
160.54
132.90
120.25
120.20
114.01
65.14
65.10
55.52
16.09
16.04
MeO
OEt
OEt
3h
f1 (ppm)

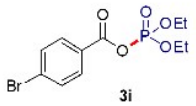

-7.62
MeO
OEt
OEt
3h
f1 (ppm)


7.93
7.92
7.92
7.91
7.91
7.90
7.65
7.64
7.64
7.63
7.63
7.62
4.40
4.40
4.39
4.39
4.38
4.38
4.38
4.37
4.37
4.36
4.36
4.35
4.35
4.34
1.44
1.44
1.43
1.42
1.41
1.41
O
O
P
OEt
OEt
Br
3i


1.88
1.90
4.00
6.05
10.0
9.5
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
0.0
-0.5
f1 (ppm)

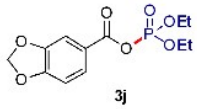

160.29
160.22
132.06
131.87
129.83
127.06
126.99
65.30
65.25
16.00
15.94
O
O
P
OEt
OEt
Br
3i


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


Br
O
O
P
OEt
OEt

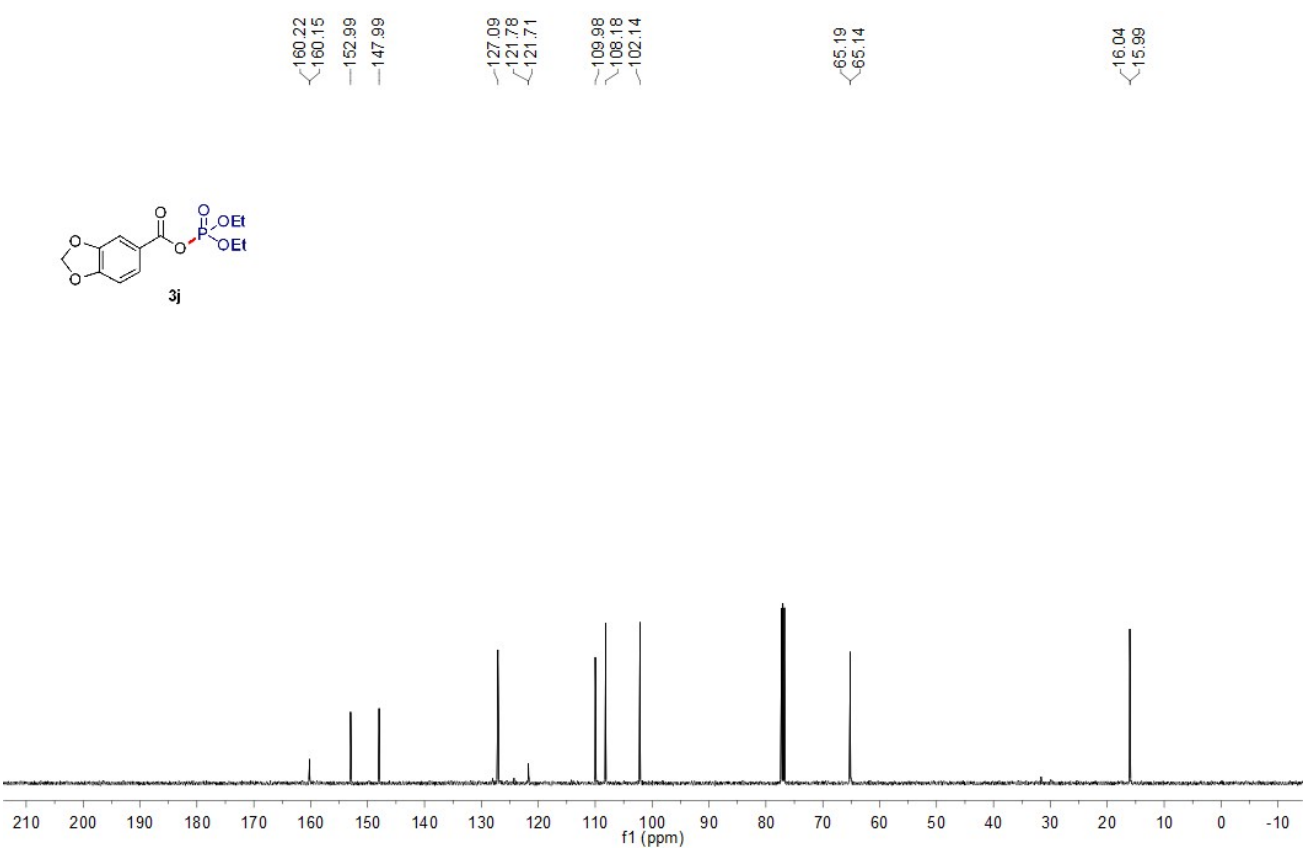
3i

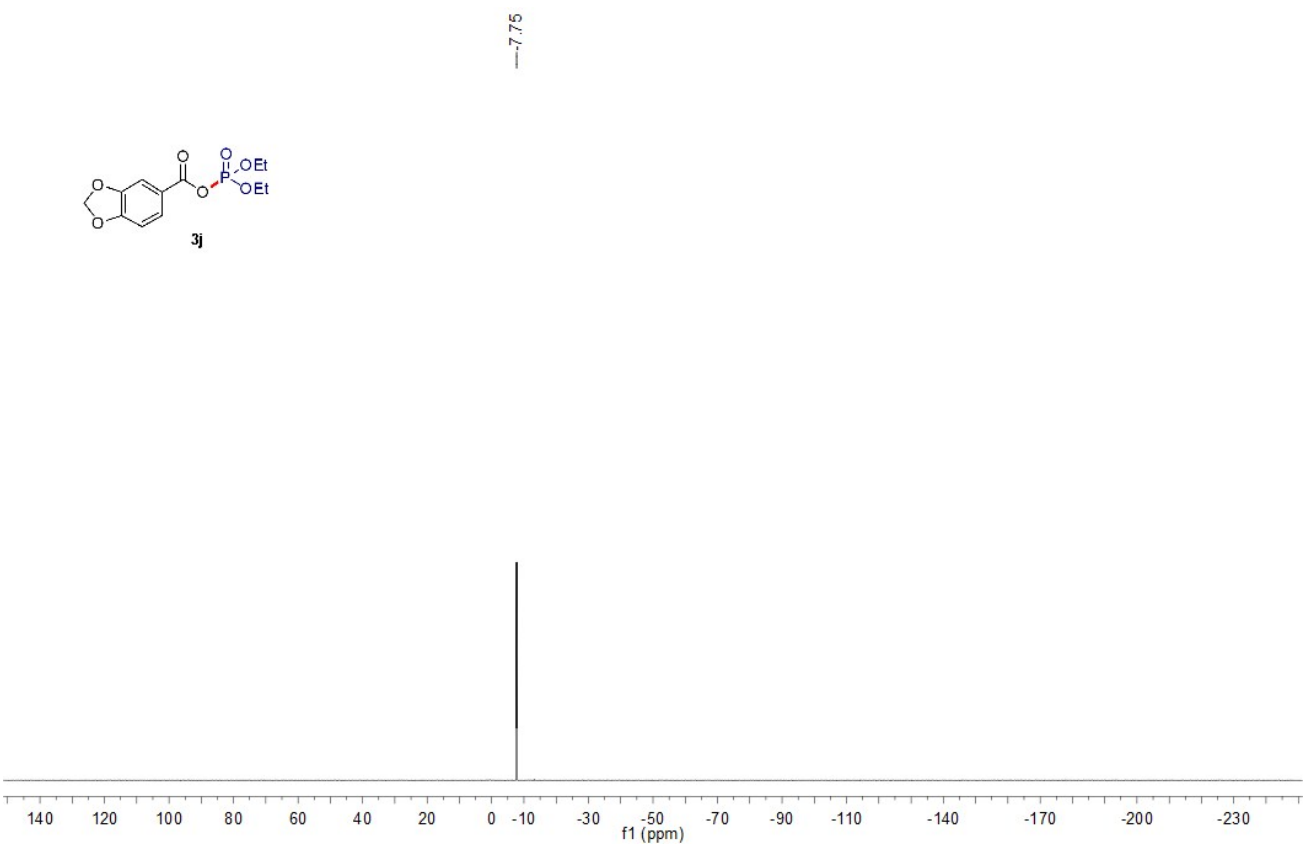
7.82
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
-230
f1 (ppm)

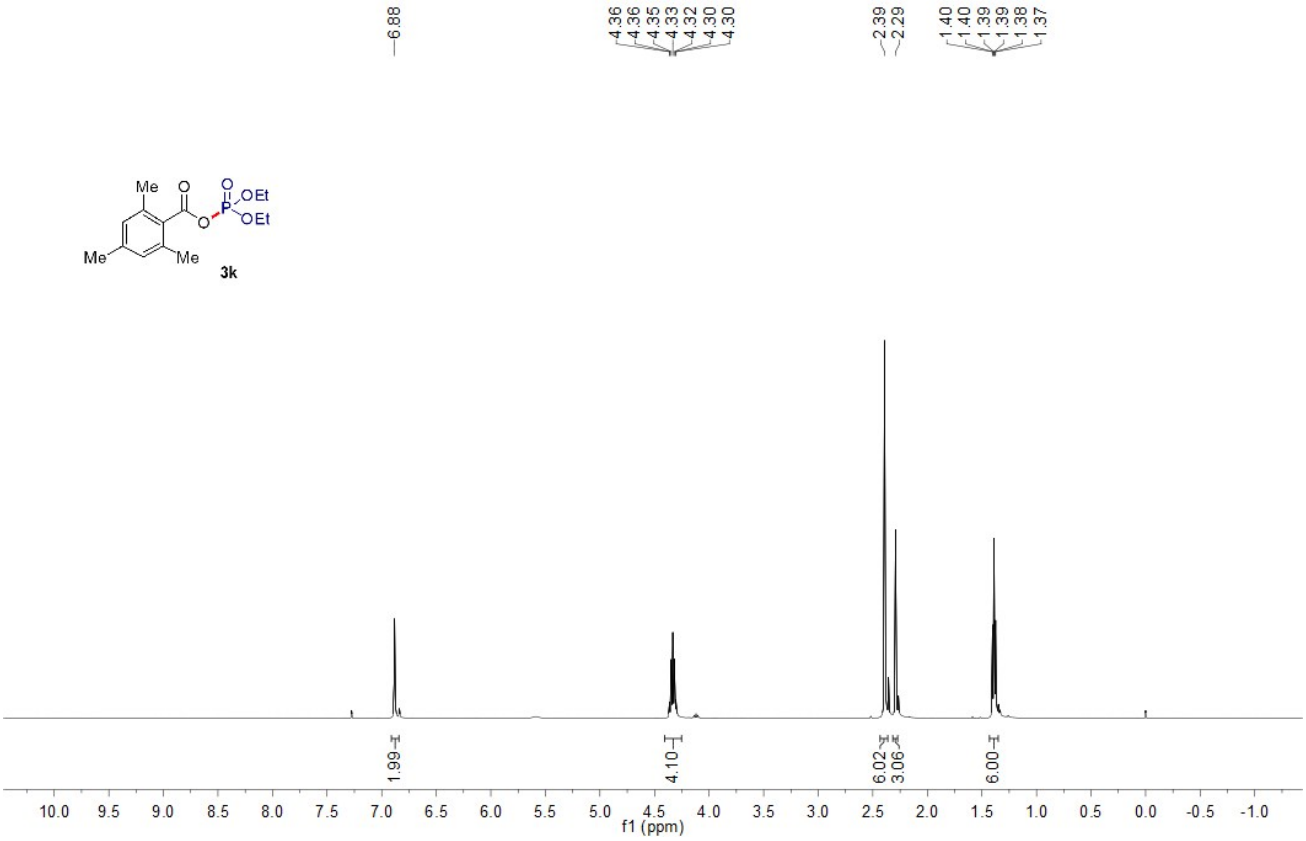

O
O
O
P
OEt
OEt

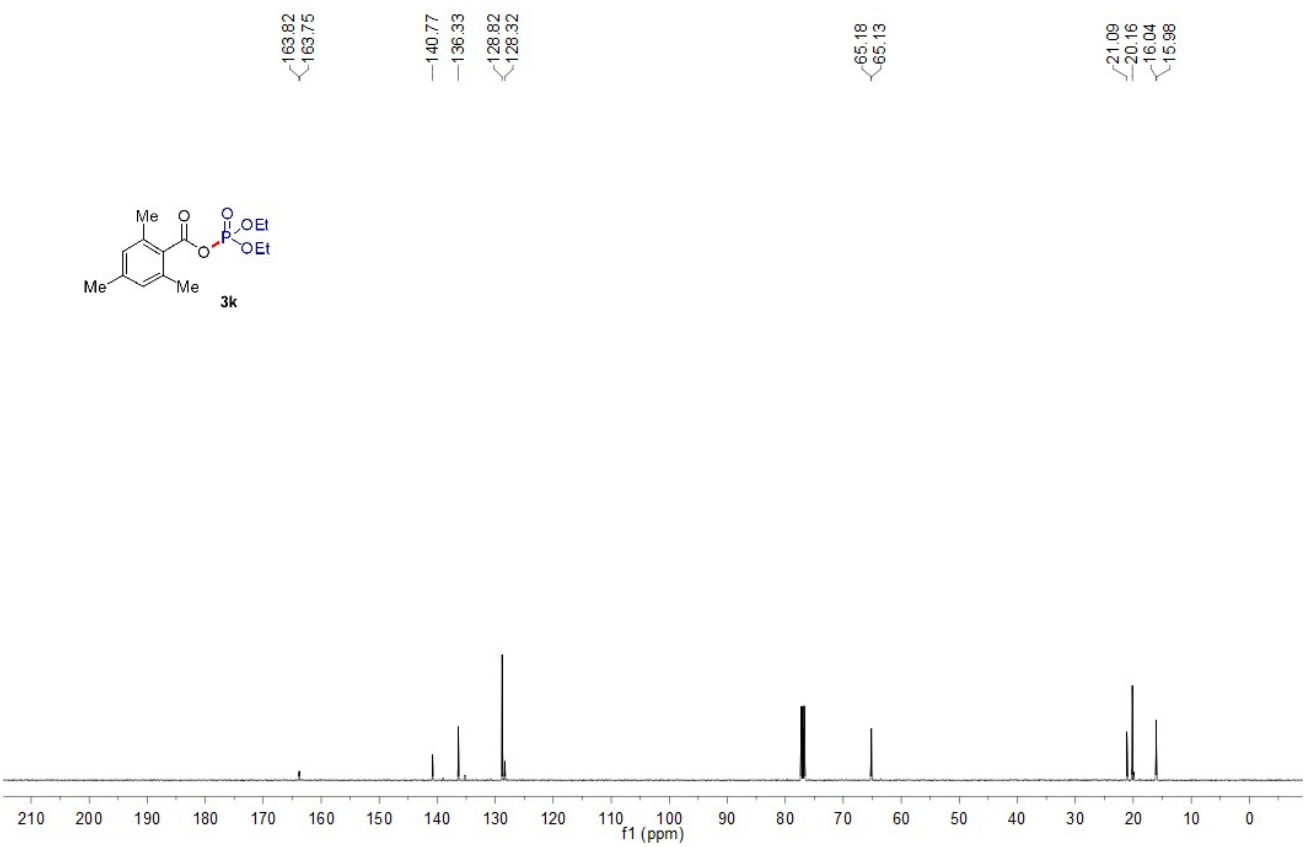
3j

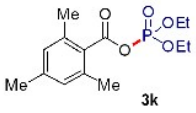
7.69
7.67
7.44
6.88
6.86
6.09
4.38
4.37
4.36
4.34
4.33
1.43
1.42
1.40
0.00
1.03
0.95
1.02
2.09
4.00
6.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


160.22
160.15
152.99
147.99
127.09
121.78
121.71
109.98
108.18
102.14
65.19
65.14
16.04
15.99
OEt
OEt
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-7.75
OEt
OEt
3j
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
f1 (ppm)

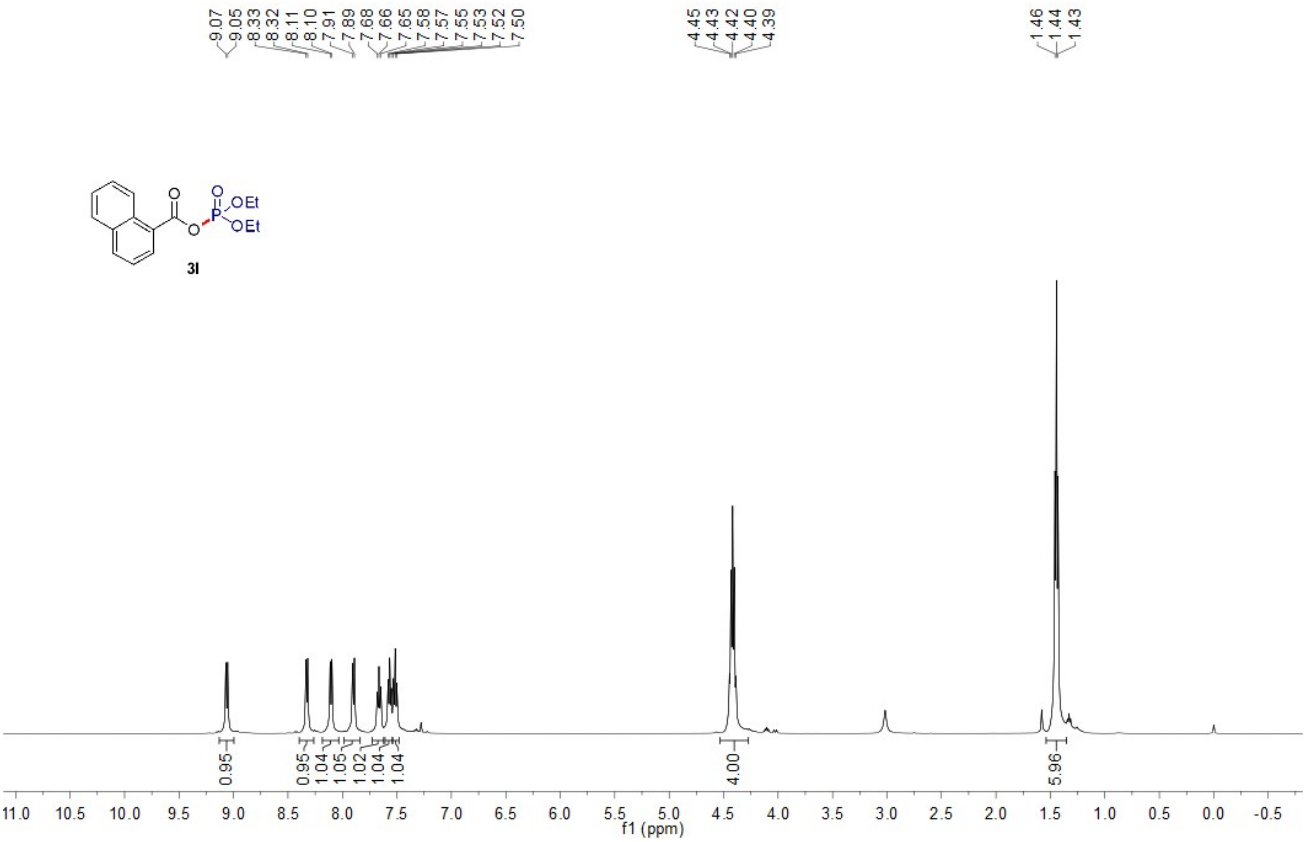

6.88
4.36
4.36
4.35
4.33
4.32
4.30
4.30
2.39
2.29
1.40
1.40
1.39
1.39
1.38
1.37
Me
O
O
OEt
OEt
Me
Me
3k
1.99
4.10
6.02
3.06
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


163.82
163.75
140.77
136.33
128.82
128.32
65.18
65.13
21.09
20.16
16.04
15.98
Me
O
O
OEt
OEt
Me
Me
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
O
O
OEt
P
OEt
O
Me
Me

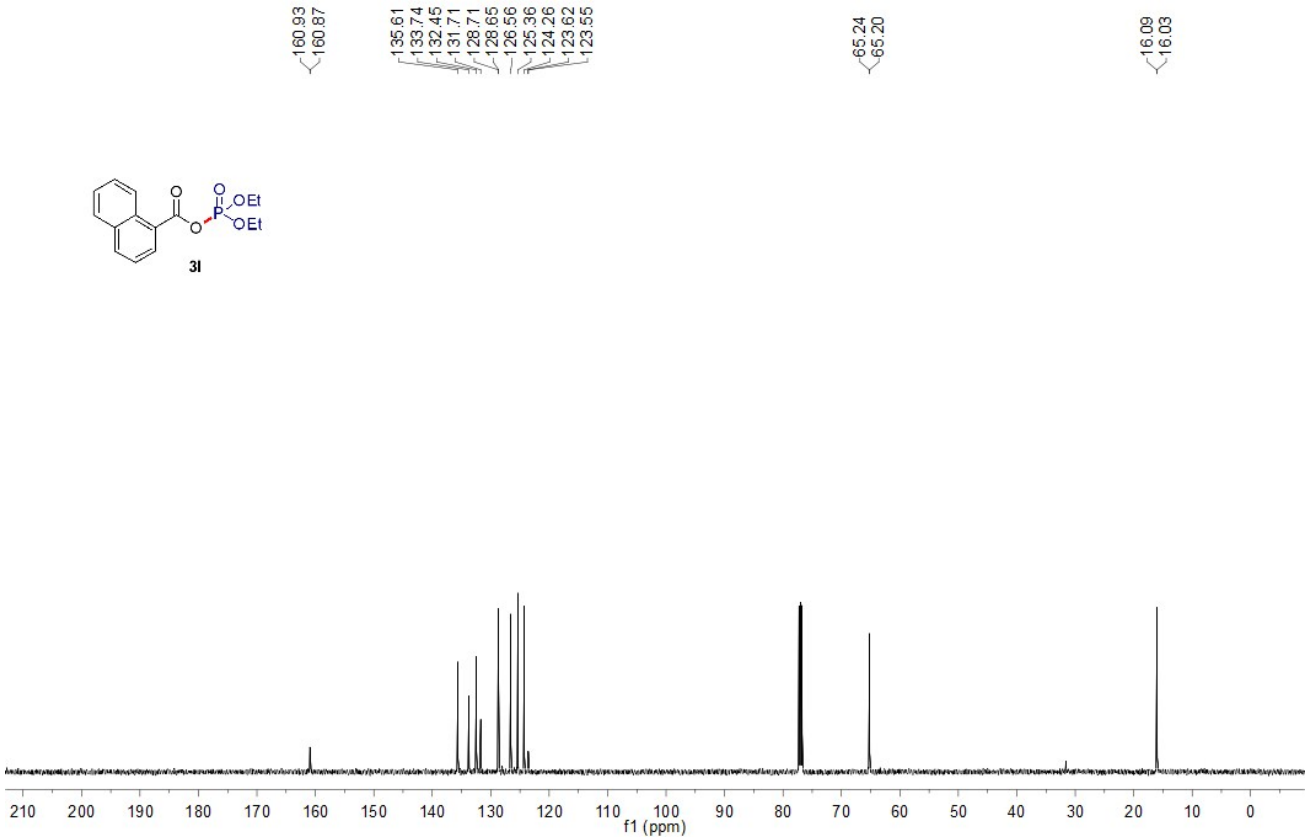
3k

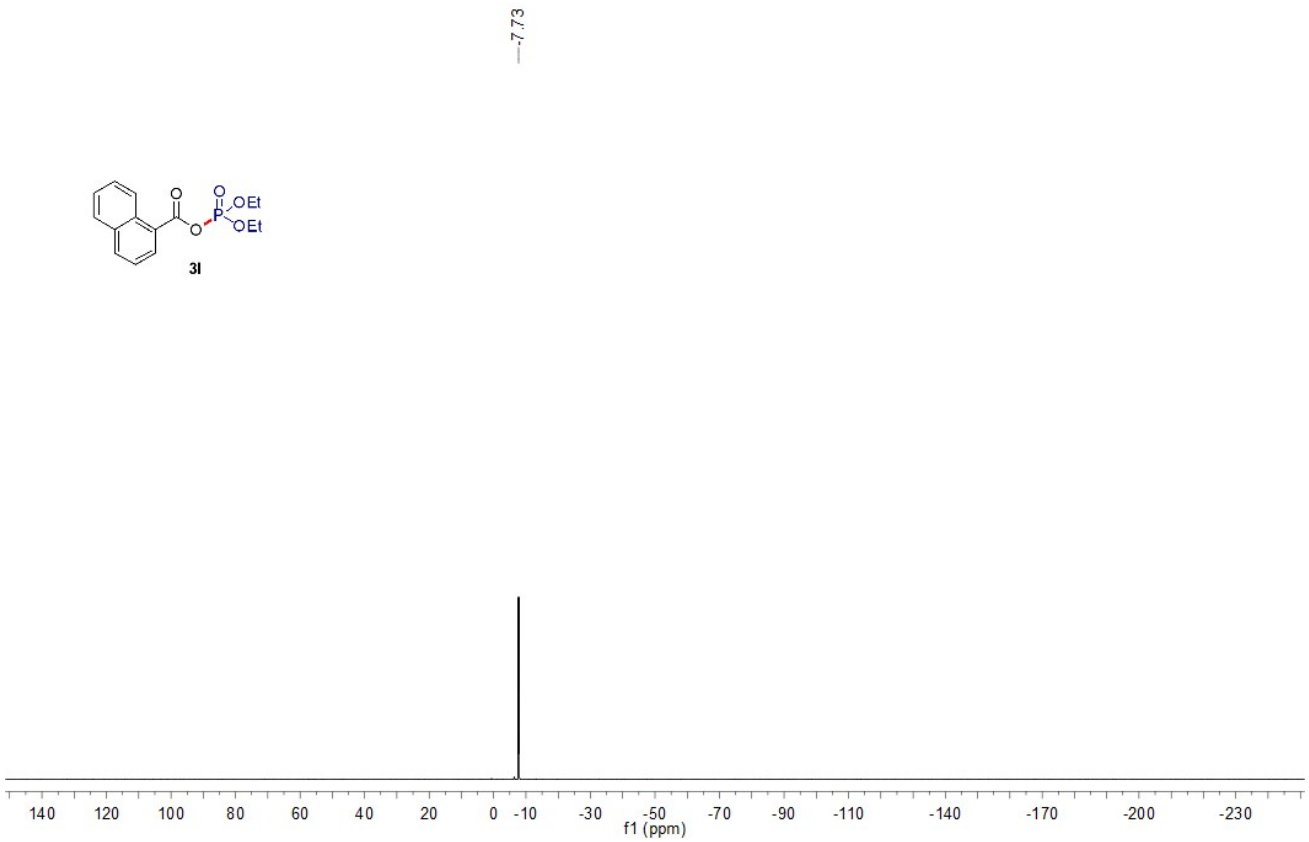
-8.30
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
-230
f1 (ppm)

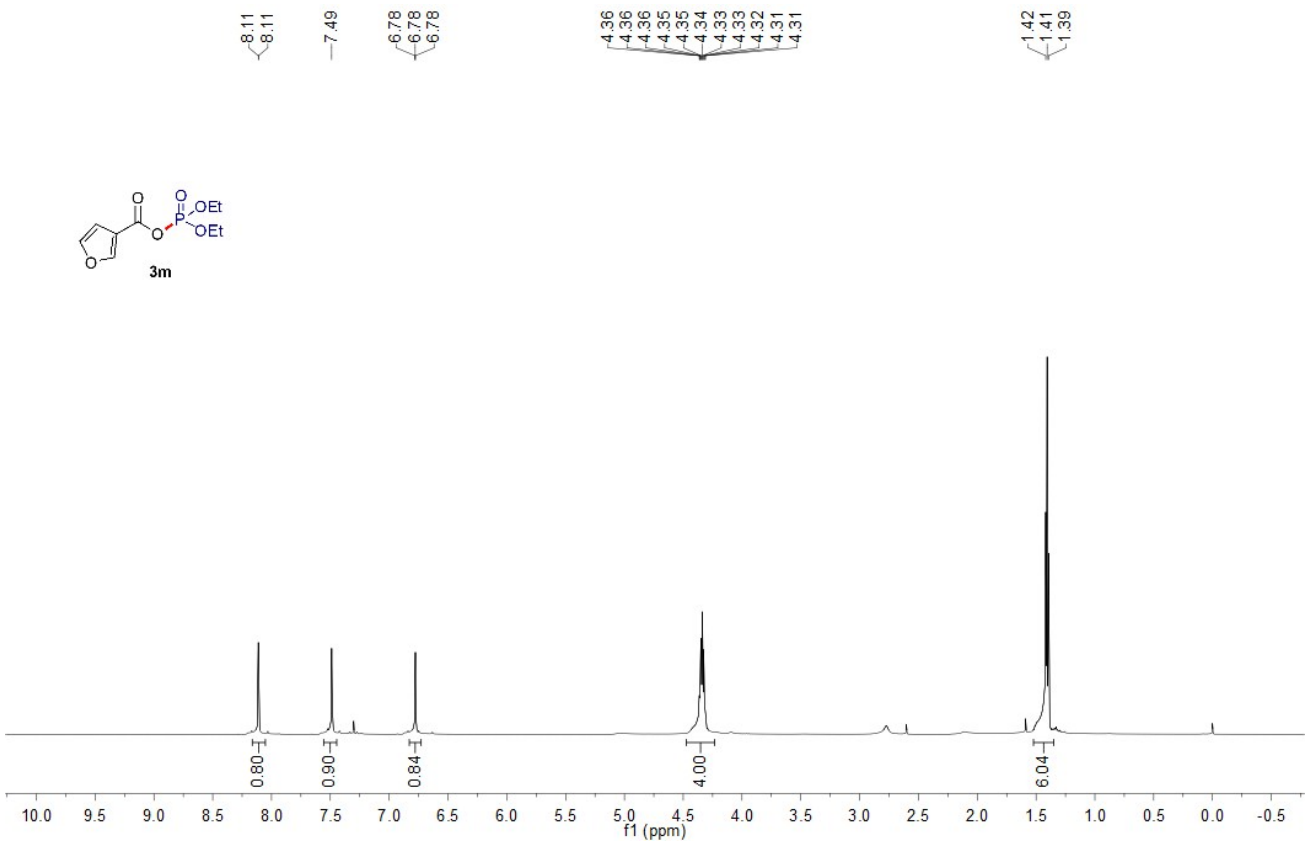

9.07
9.05
8.33
8.32
8.11
8.10
7.91
7.89
7.68
7.66
7.65
7.58
7.57
7.55
7.53
7.52
7.50
4.45
4.43
4.42
4.40
4.39
1.46
1.44
1.43
0.95
0.95
1.04
1.05
1.02
1.04
1.04
4.00
5.96
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

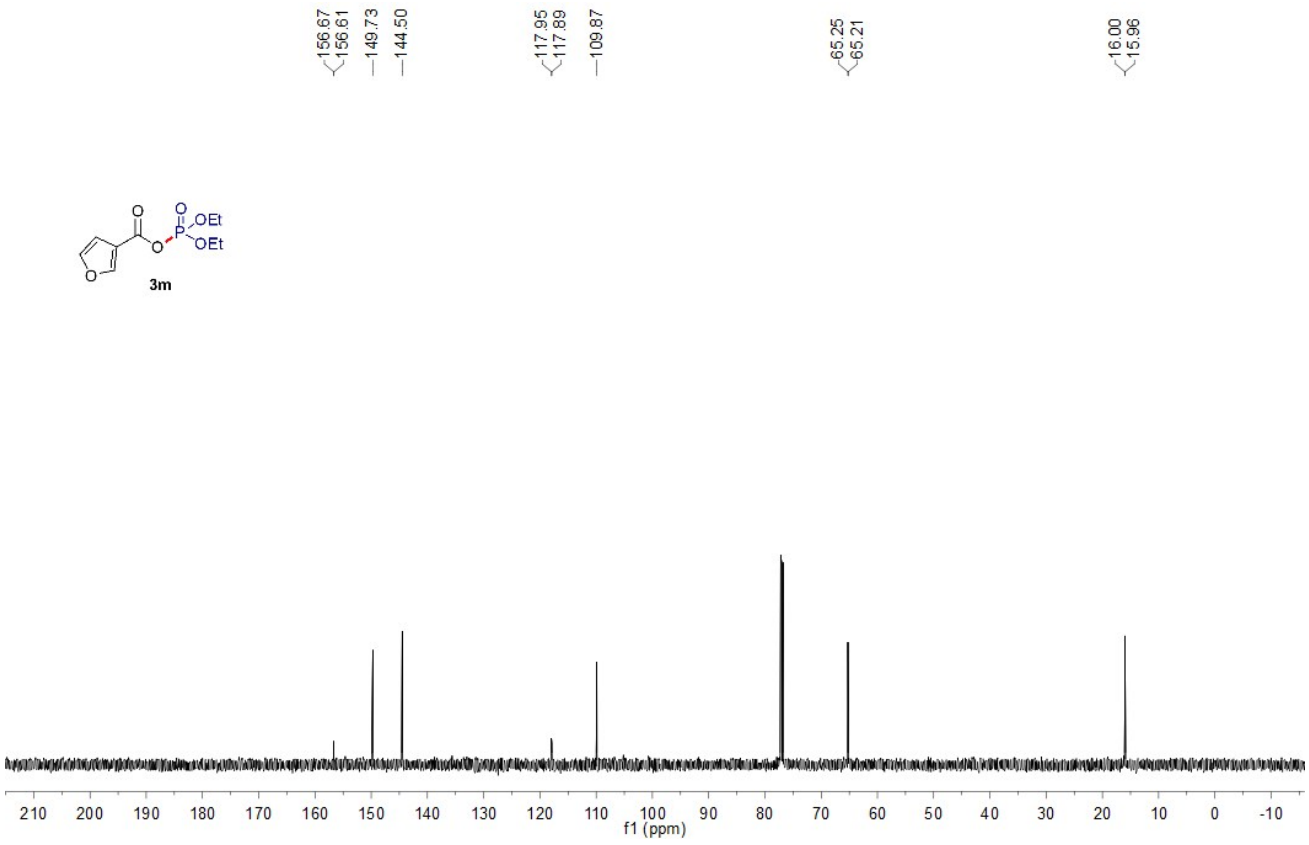
O
O
OEt
P
OEt
O

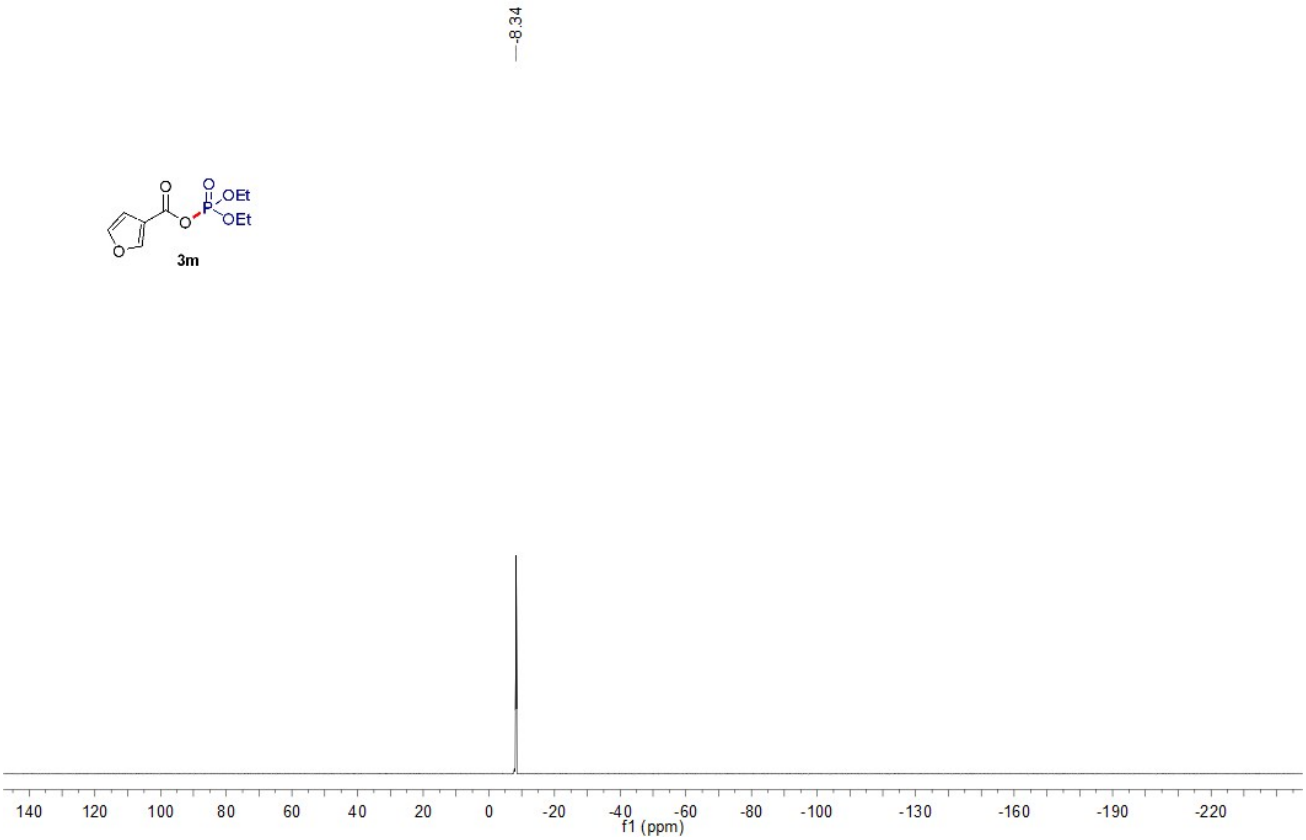
3l

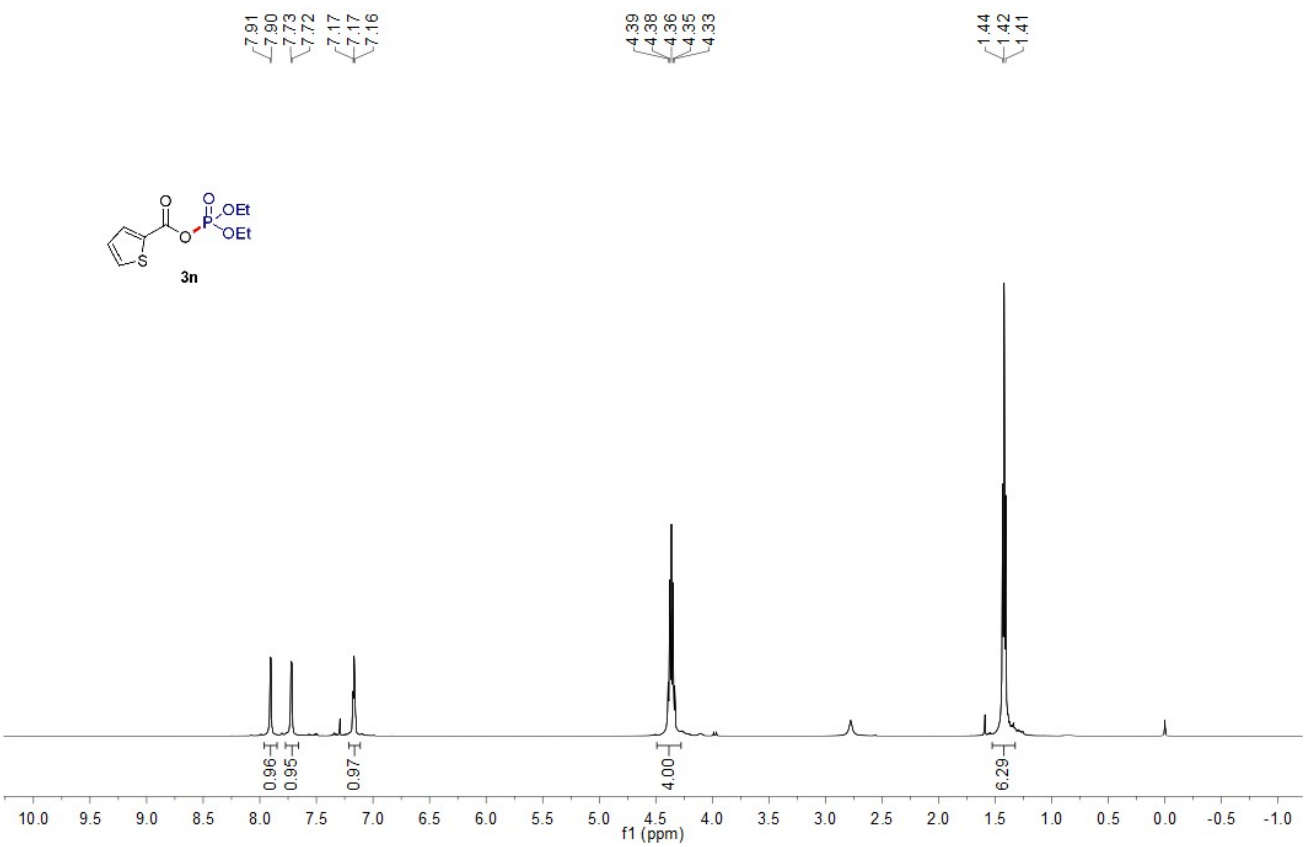

160.93
160.87
135.61
133.74
132.45
131.71
128.71
128.65
126.56
125.36
124.26
123.62
123.55
65.24
65.20
16.09
16.03
OEt
OEt
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

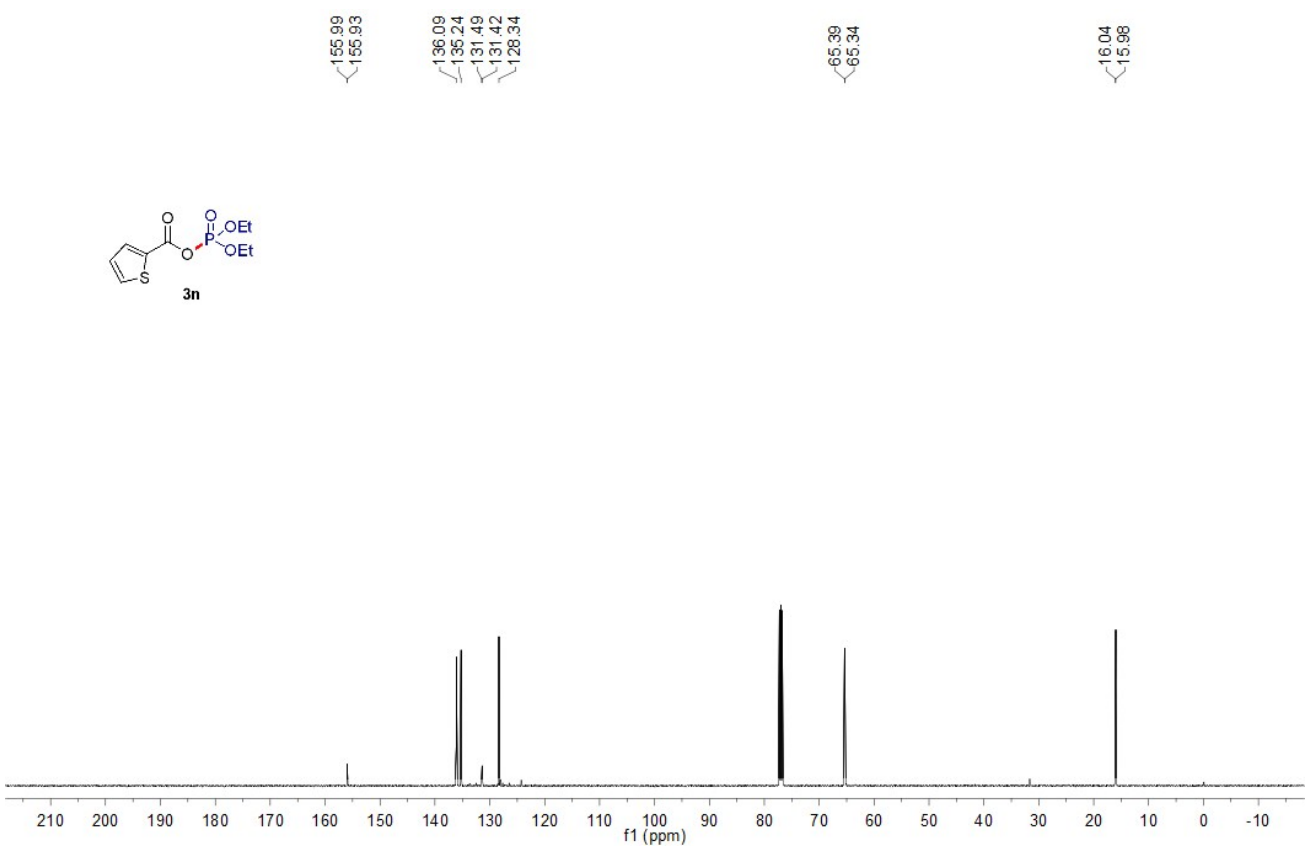

-7.73
OEt
OEt
3l
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
f1 (ppm)

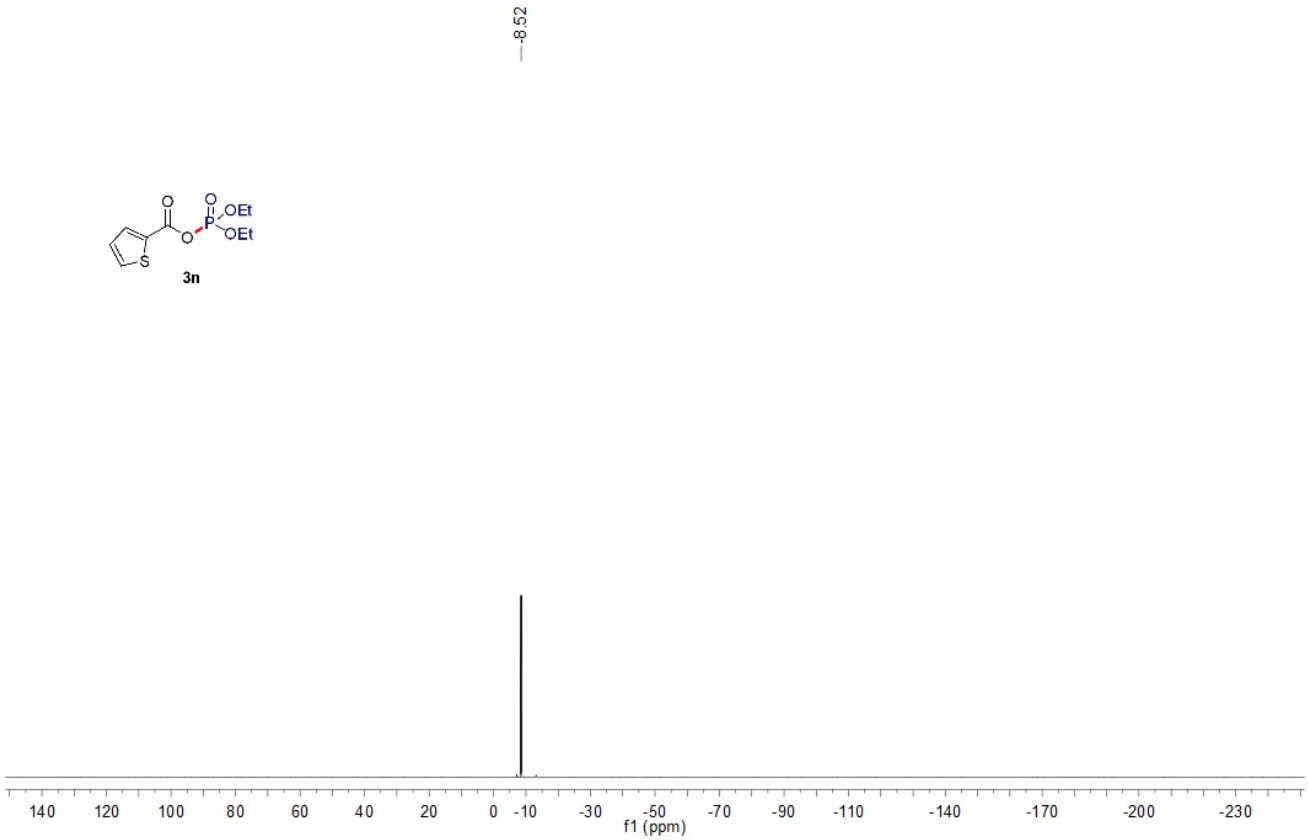

8.11
8.11
7.49
6.78
6.78
6.78
4.36
4.36
4.36
4.35
4.35
4.34
4.33
4.33
4.32
4.31
4.31
1.42
1.41
1.39
OEt
OEt
3m
0.80
0.90
0.84
4.00
6.04
f1 (ppm)

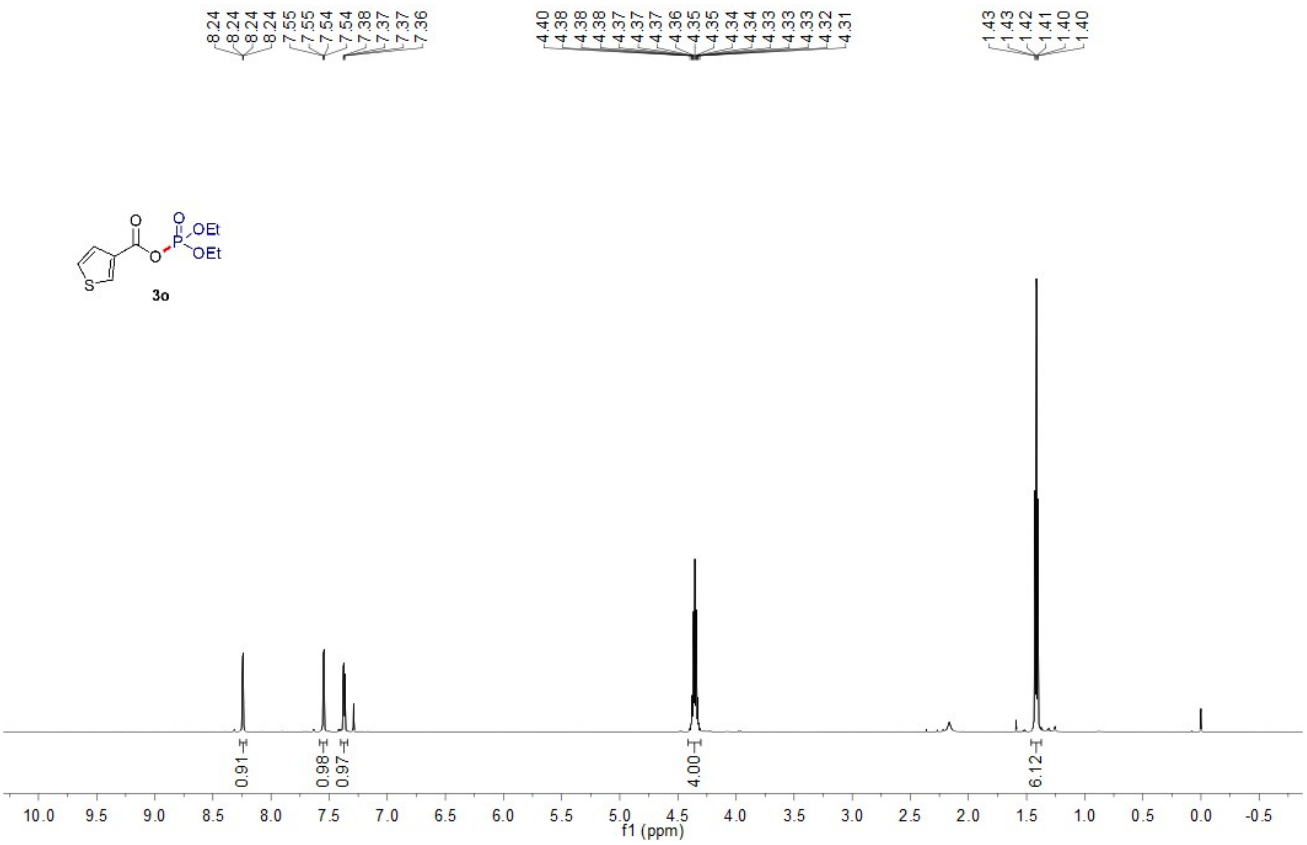

156.67
156.61
149.73
144.50
117.95
117.89
109.87
65.25
65.21
16.00
15.96
OEt
OEt
3m
f1 (ppm)

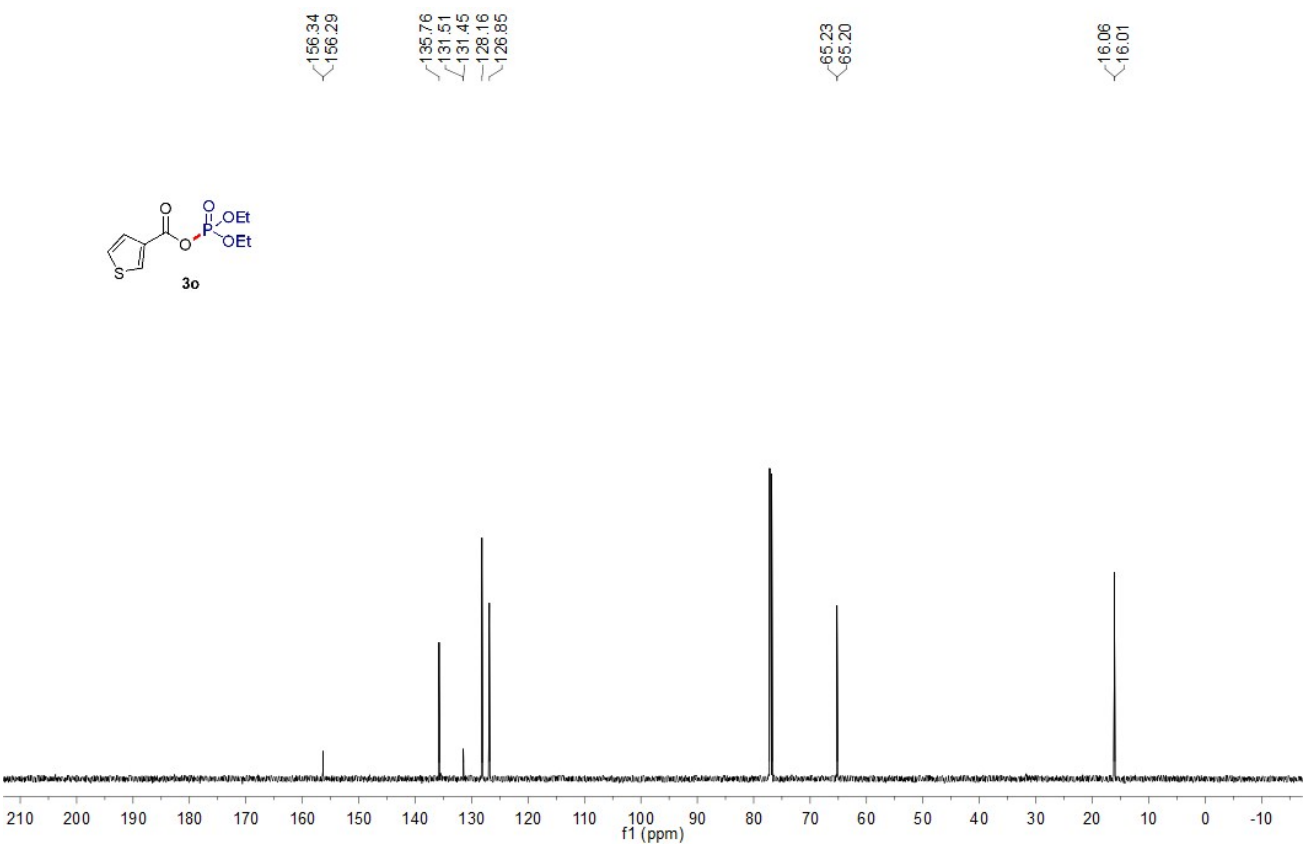

-8.34
OEt
OEt
3m
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

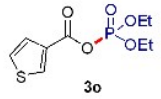

7.91
7.90
7.73
7.72
7.17
7.17
7.16
4.39
4.38
4.36
4.35
4.33
1.44
1.42
1.41
OEt
OEt
3n
0.96
0.95
0.97
4.00
6.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


155.99
155.93
136.09
135.24
131.49
131.42
128.34
65.39
65.34
16.04
15.98
OEt
OEt
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.52
OEt
OEt
3n
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
f1 (ppm)

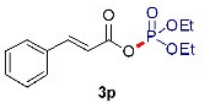

8.24
8.24
8.24
8.24
7.55
7.55
7.54
7.54
7.38
7.37
7.37
7.36
4.40
4.38
4.38
4.38
4.37
4.37
4.37
4.36
4.35
4.35
4.34
4.34
4.33
4.33
4.32
4.31
1.43
1.43
1.42
1.41
1.40
1.40
O
O
OEt
P
OEt
O
S
3o
0.91
0.98
0.97
4.00
6.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


156.34
156.29
135.76
131.51
131.45
128.16
126.85
65.23
65.20
16.06
16.01
O
O
OEt
P
OEt
O
S
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



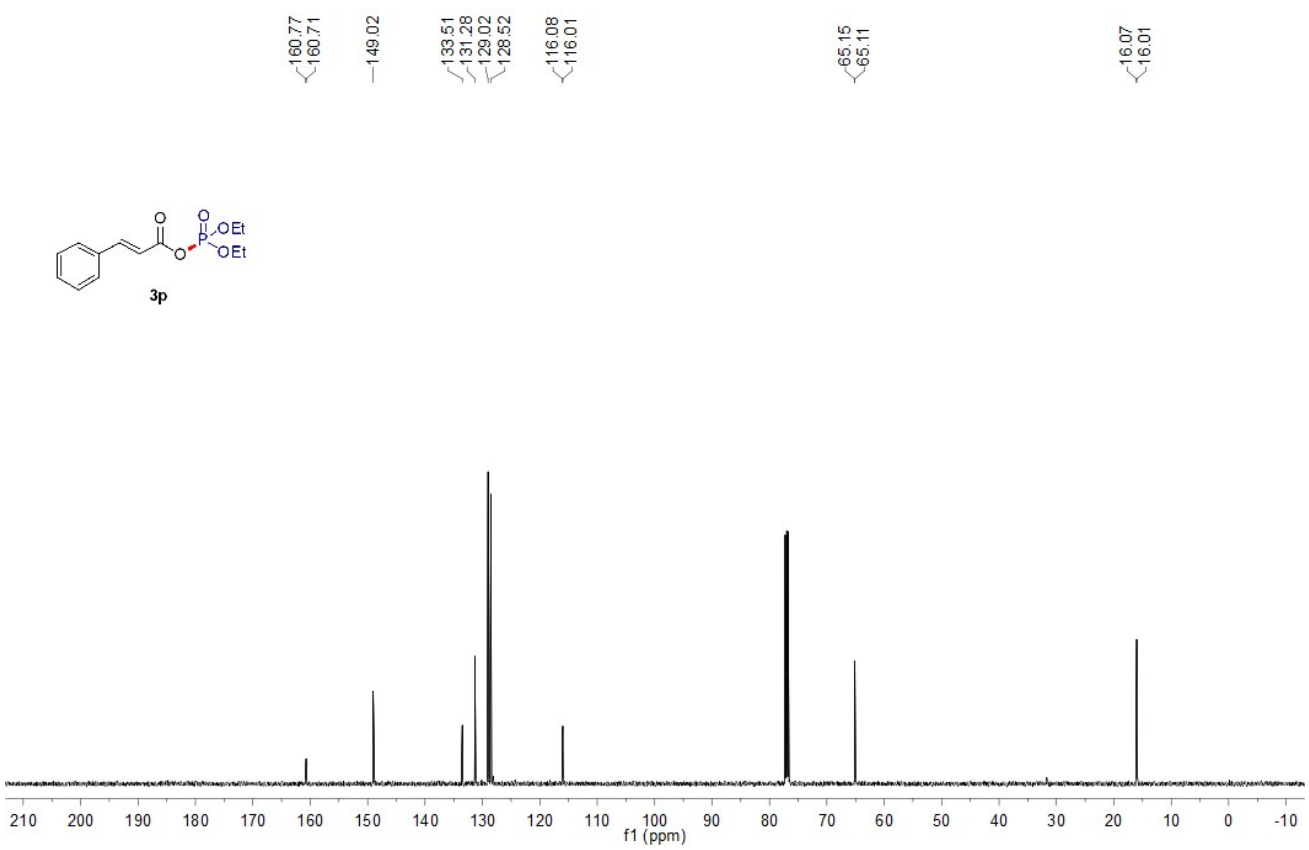
3o

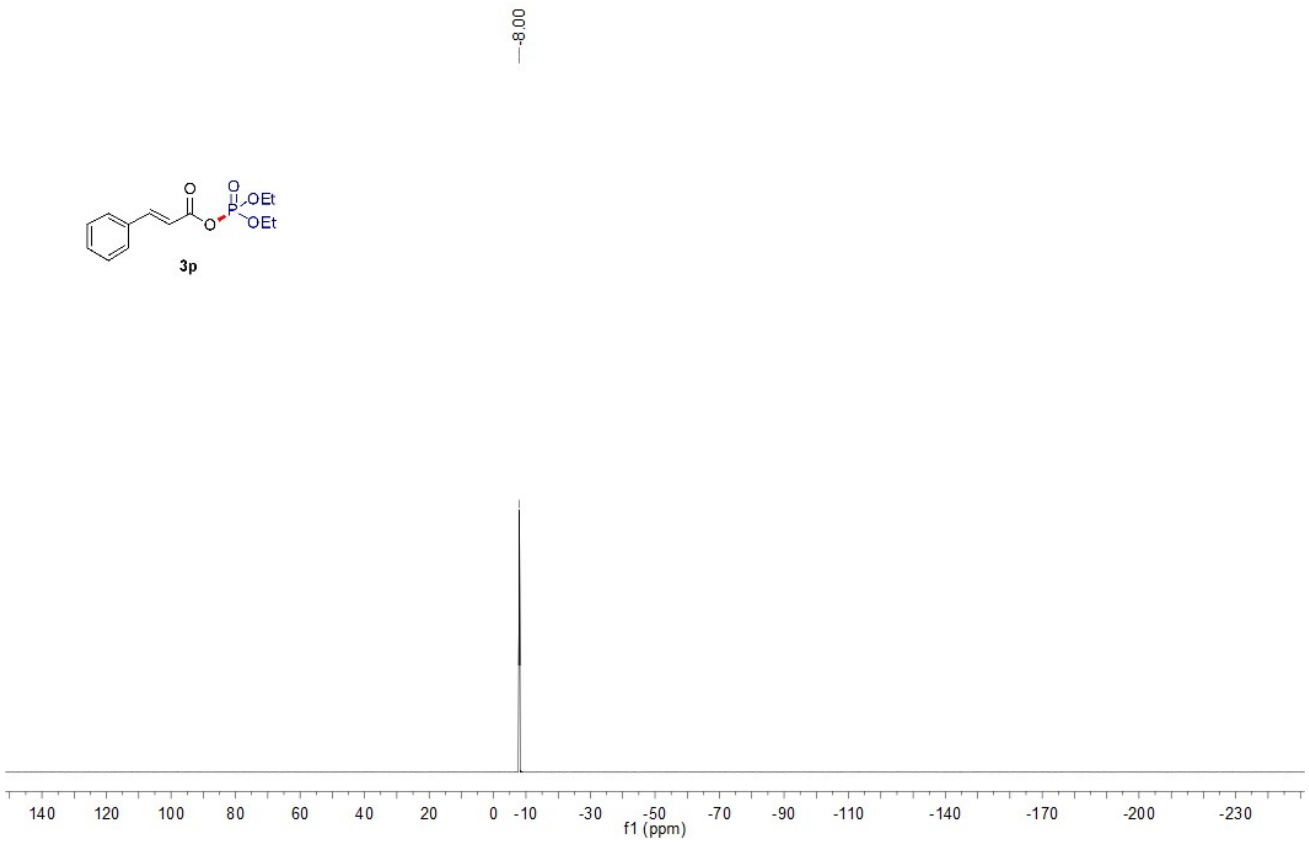
8.06
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

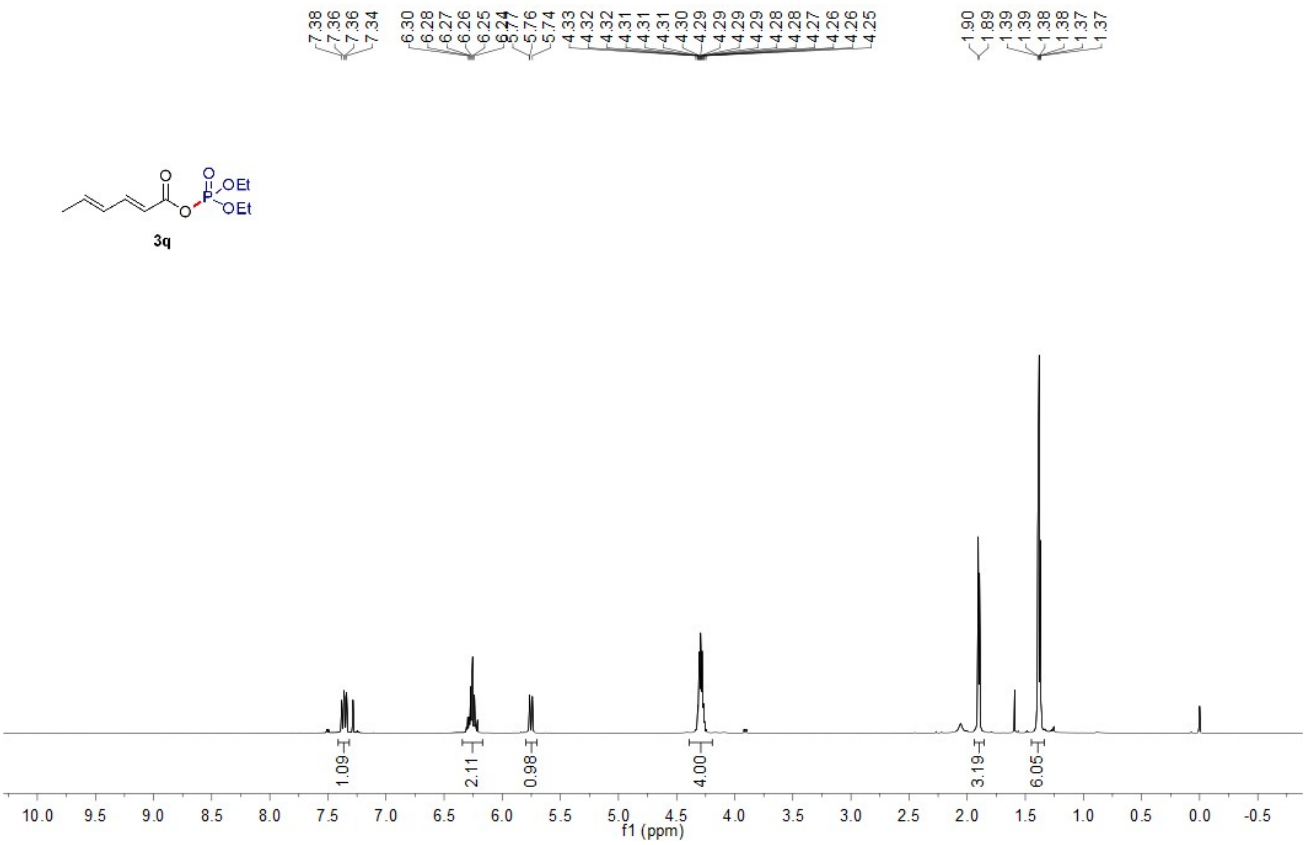


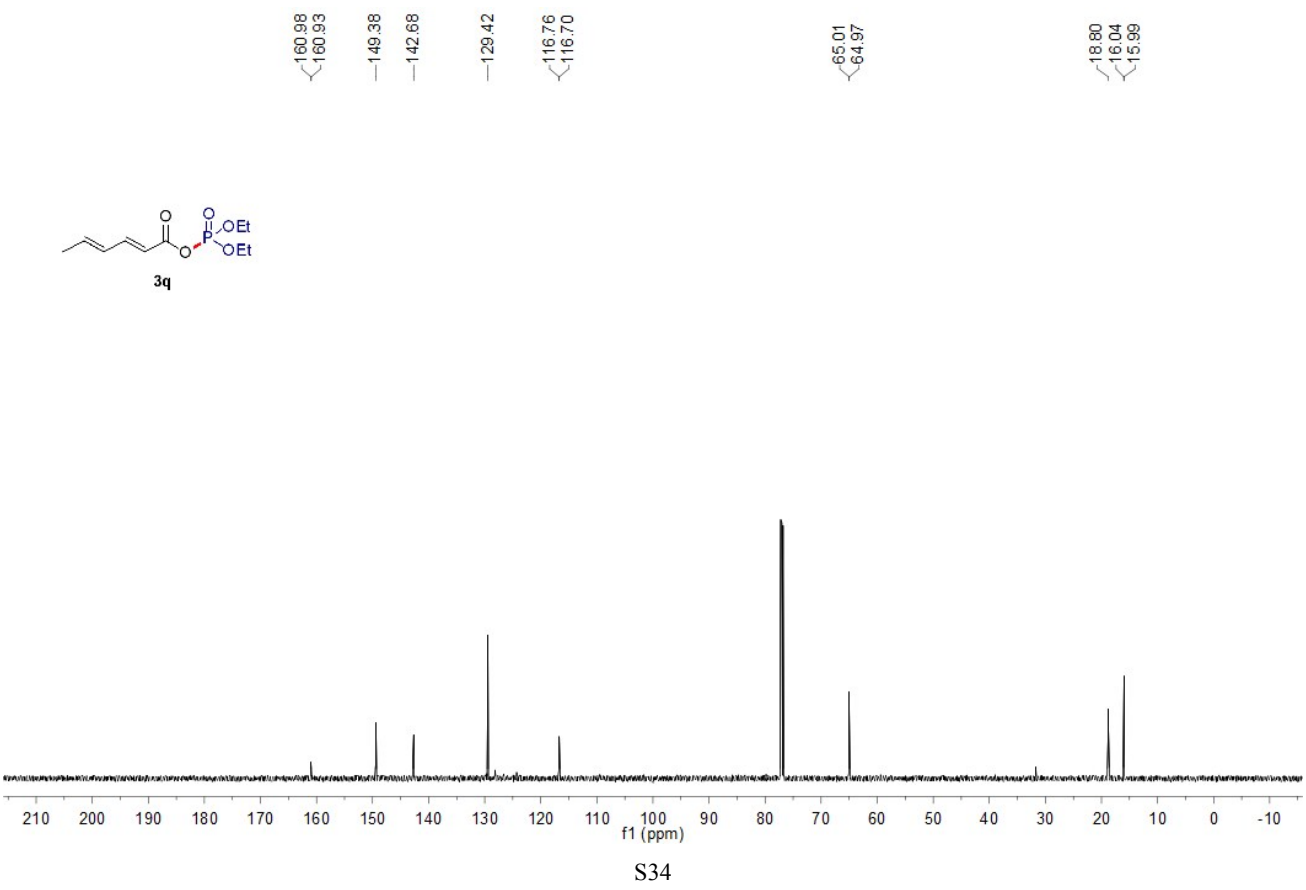
3p

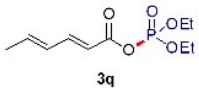
7.81
7.78
7.55
7.54
7.45
7.43
7.42
7.40
7.40
6.44
6.43
6.40
6.40
4.36
4.35
4.33
4.32
4.32
4.31
4.30
1.42
1.41
1.39
0.97
2.00
2.97
0.98
4.00
6.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


160.77
160.71
149.02
133.51
131.28
129.02
128.52
116.08
116.01
65.15
65.11
16.07
16.01
OEt
OEt
3p
f1 (ppm)

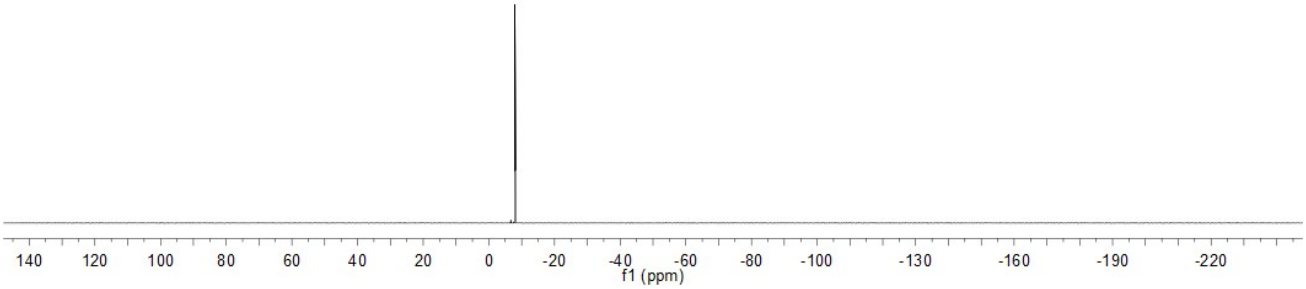

-8.00
OEt
OEt
3p
f1 (ppm)

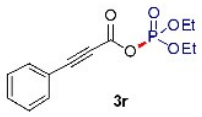

7.38
7.36
7.36
7.34
6.30
6.28
6.27
6.26
6.25
6.24
5.77
5.76
5.74
4.33
4.32
4.32
4.31
4.31
4.30
4.29
4.29
4.29
4.29
4.28
4.28
4.27
4.26
4.26
4.25
1.90
1.89
1.39
1.39
1.38
1.38
1.37
1.37
OEt
OEt
3q
1.09
2.11
0.98
4.00
3.19
6.05
f1 (ppm)


160.98
160.93
149.38
142.68
129.42
116.76
116.70
65.01
64.97
18.80
16.04
15.99
OEt
OEt
3q
f1 (ppm)



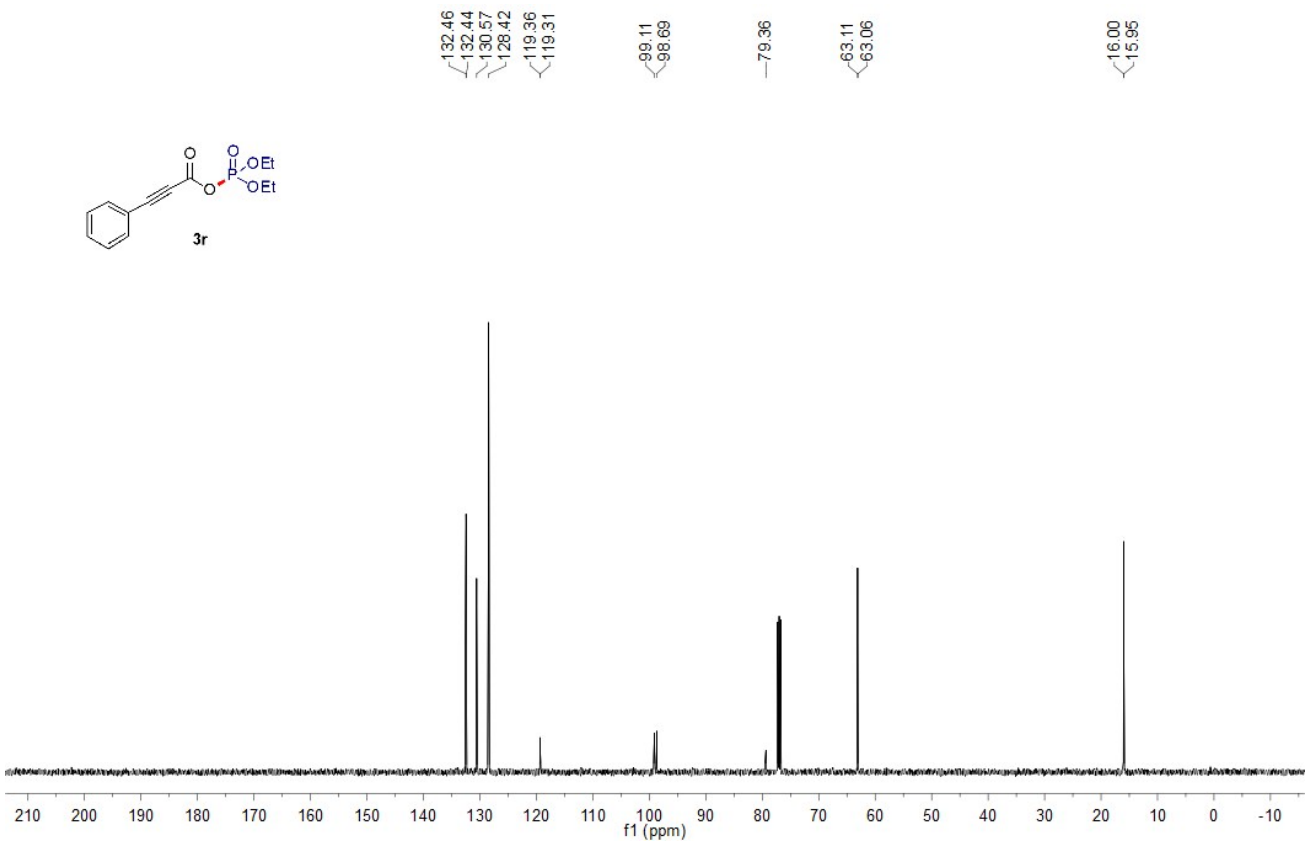
3q

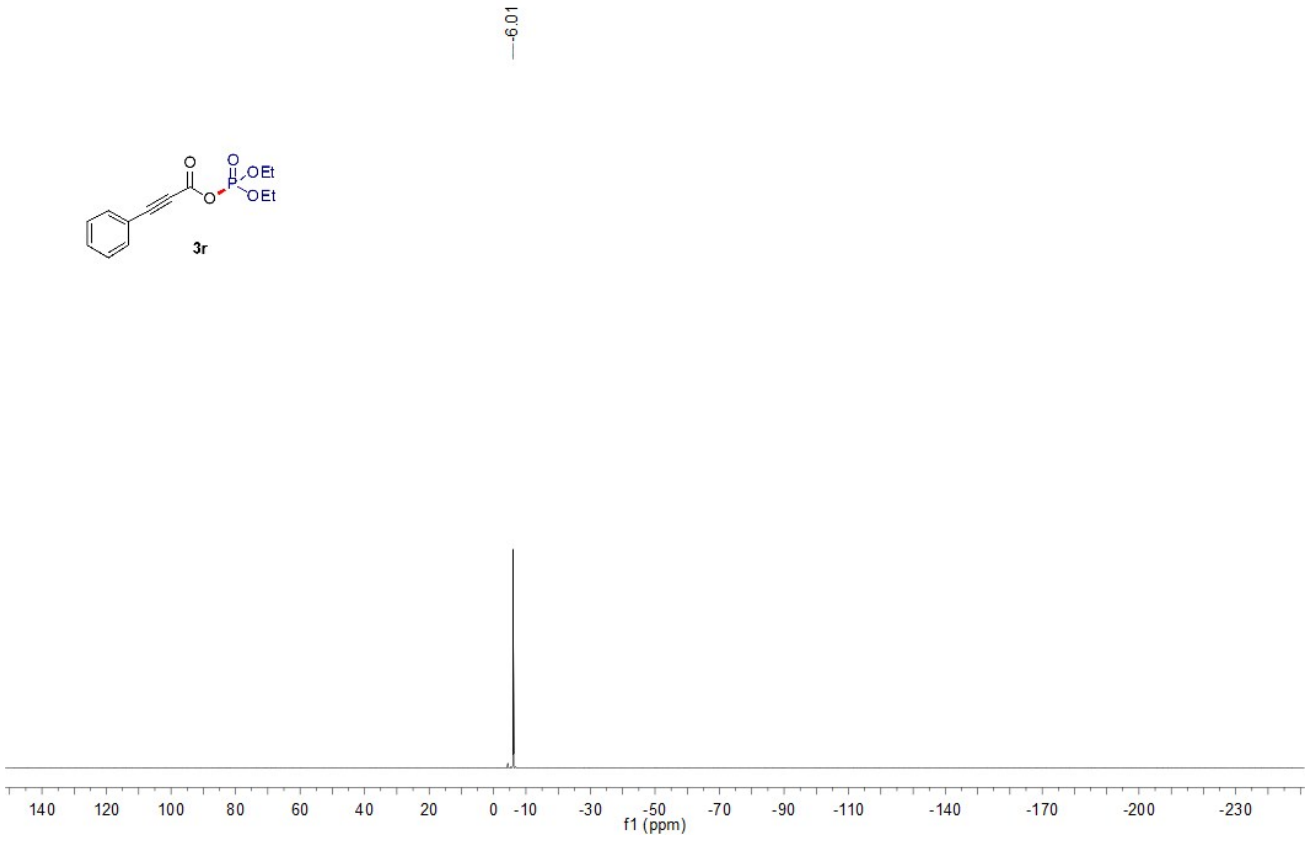

-7.97
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

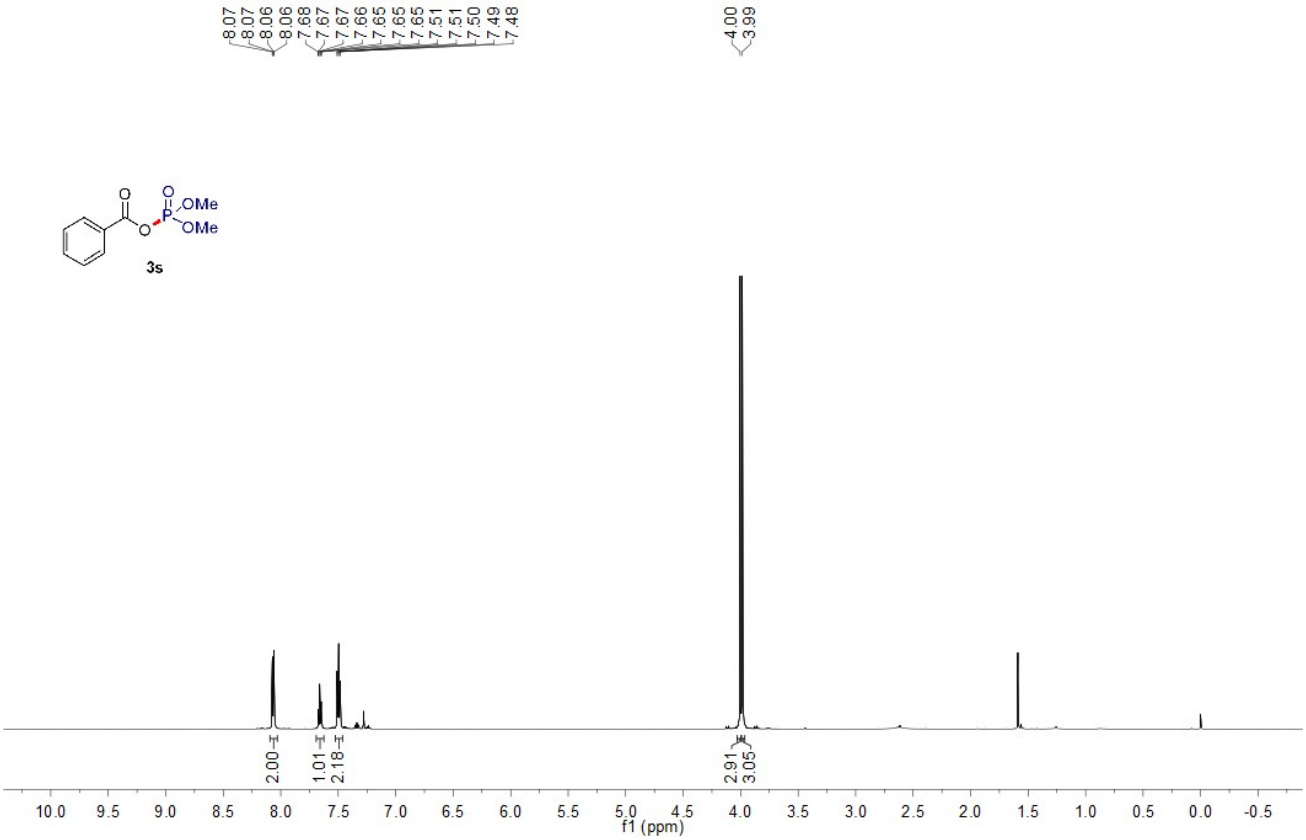


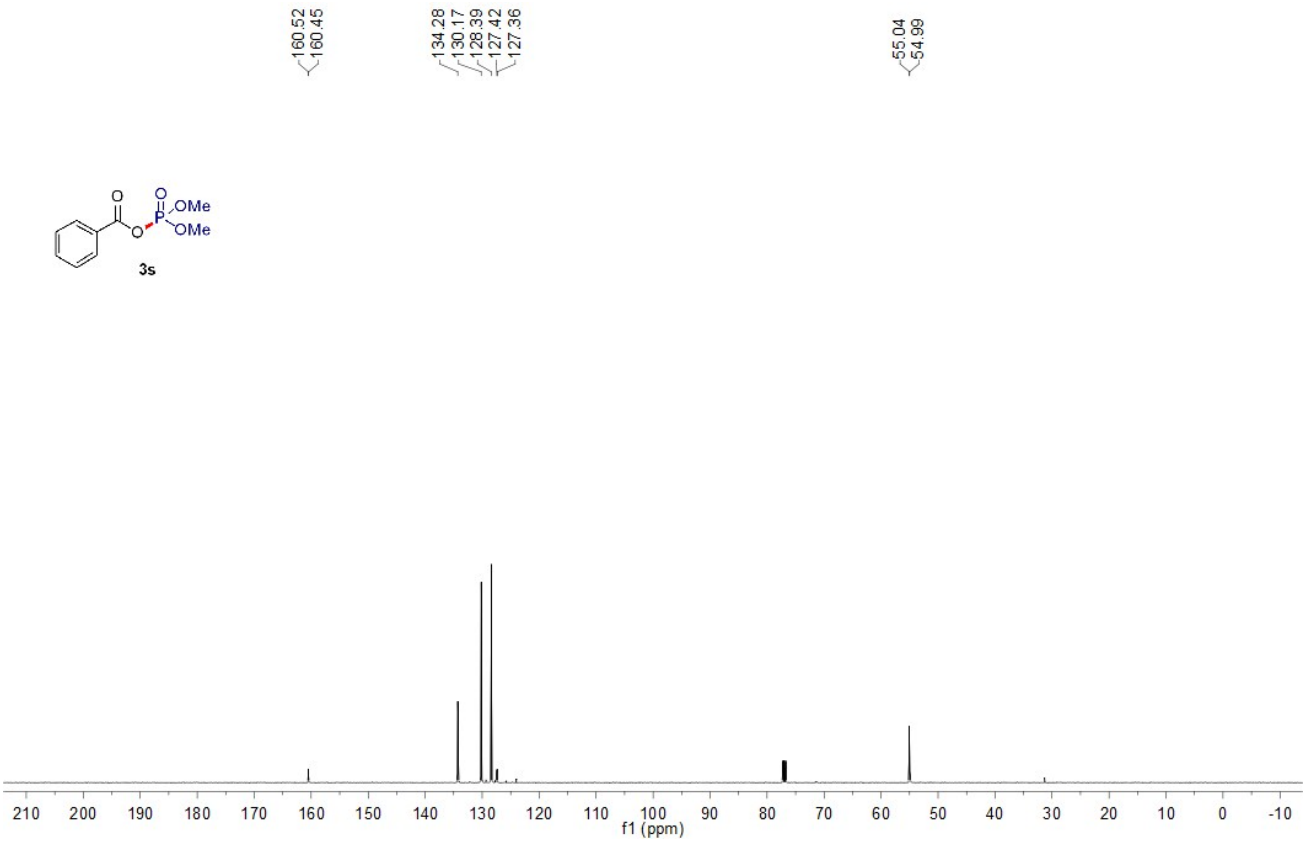
3r

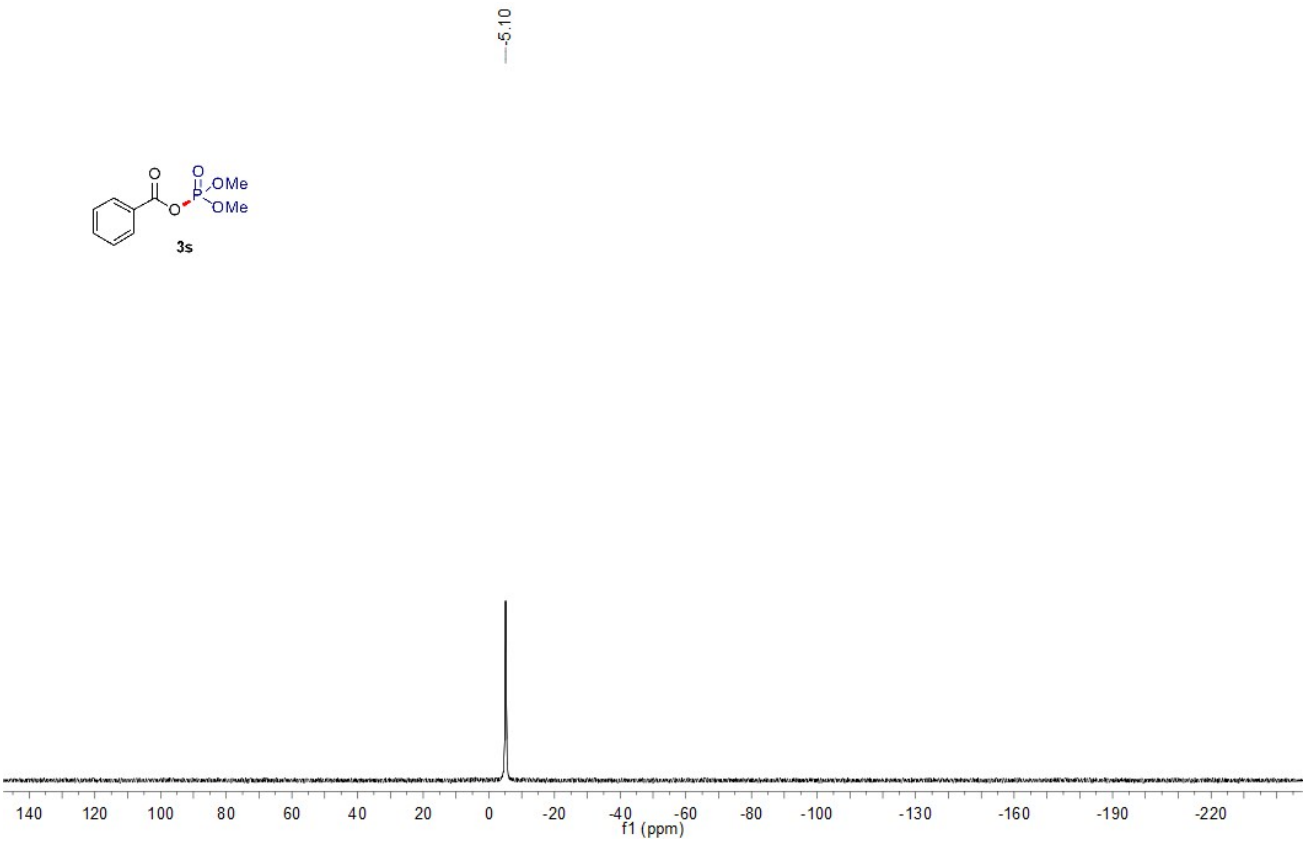
7.58
7.56
7.48
7.46
7.45
7.40
7.38
7.37
4.27
4.27
4.25
4.25
4.24
4.24
4.22
4.22
4.21
4.21
1.43
1.41
1.40
1.95
1.03
1.94
4.00
6.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

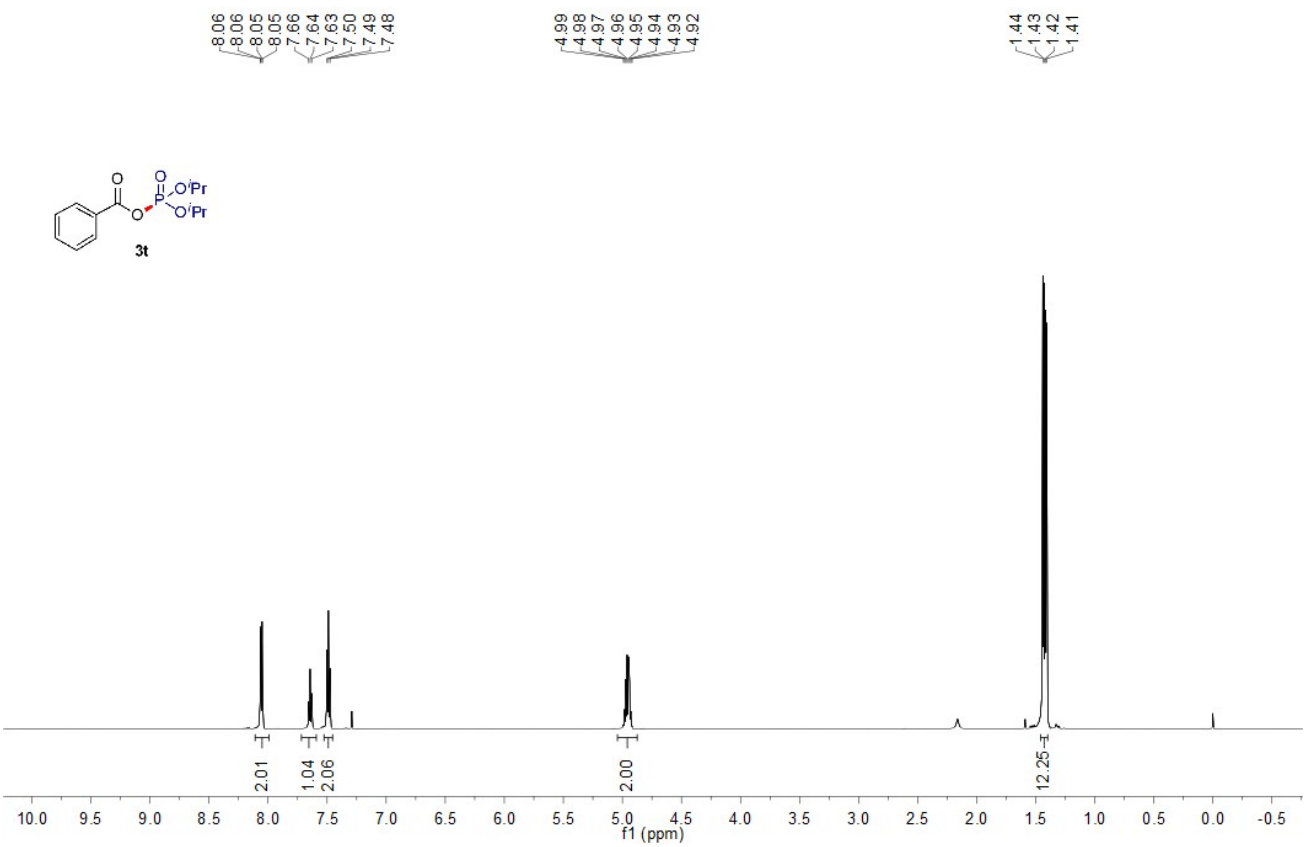

132.46
132.44
130.57
128.42
119.36
119.31
99.11
98.69
79.36
63.11
63.06
16.00
15.95
OEt
OEt
3r
f1 (ppm)

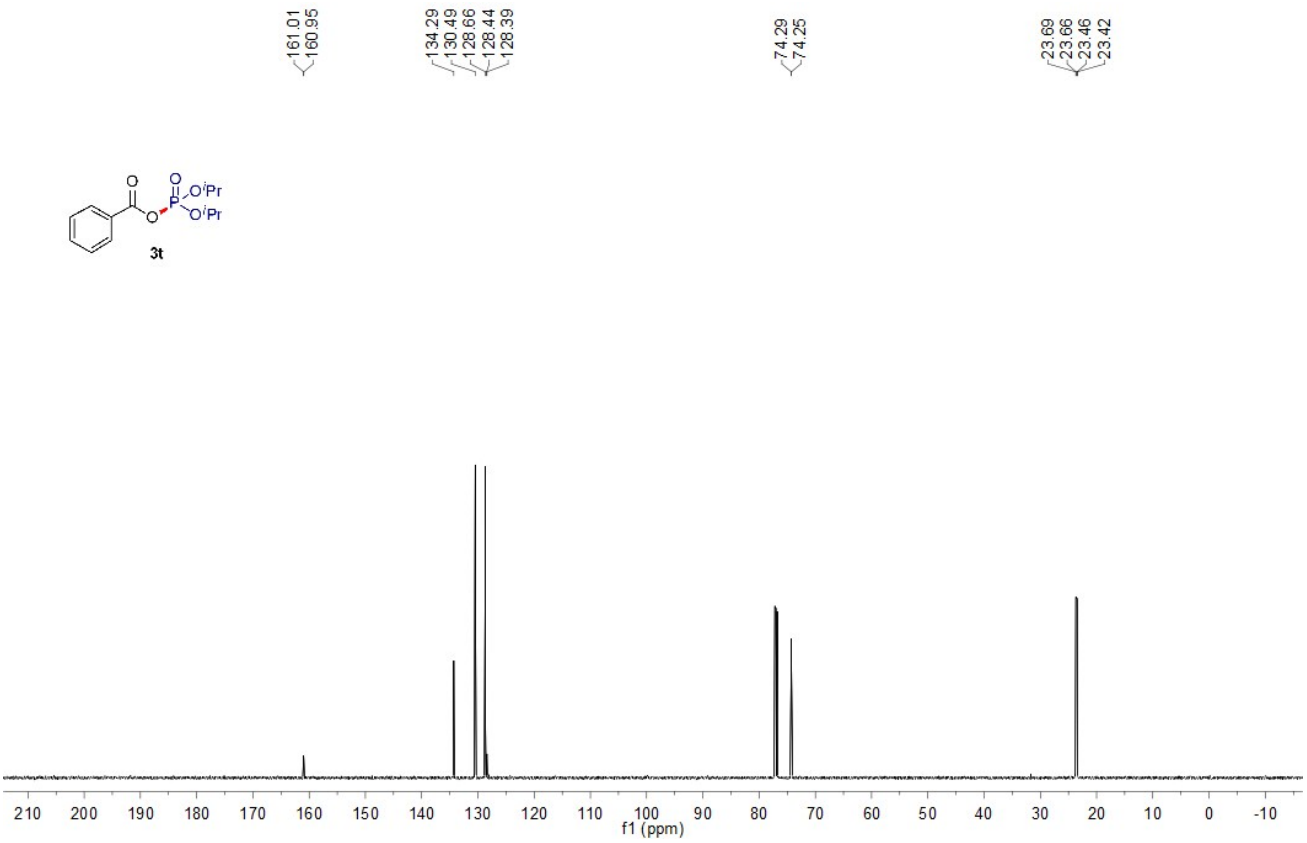

6.01
OEt
OEt
3r
f1 (ppm)

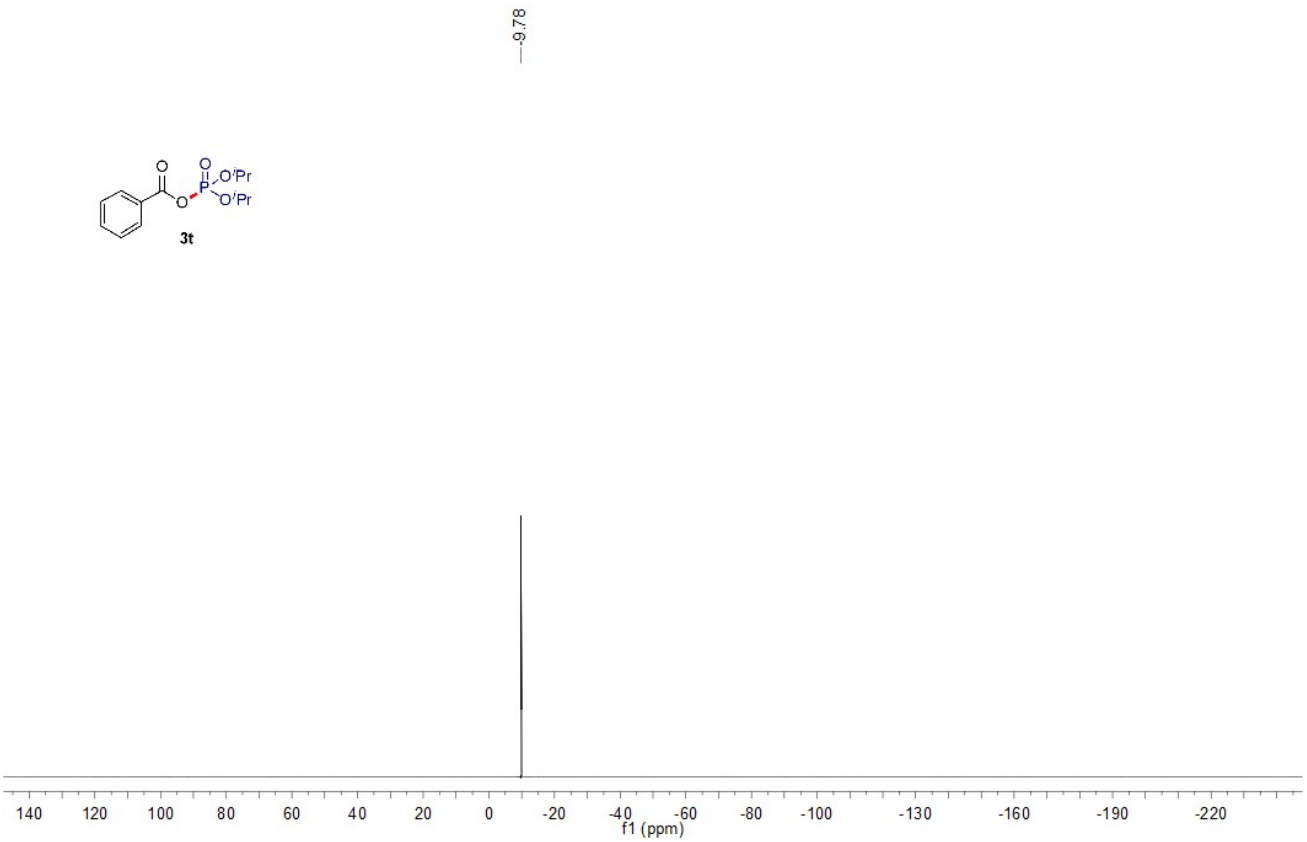

8.07
8.07
8.06
8.06
7.68
7.67
7.67
7.66
7.65
7.65
7.65
7.51
7.50
7.49
7.48
4.00
3.99
OMe
OMe
3s
2.00
1.01
2.18
2.91
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


160.52
160.45
134.28
130.17
128.39
127.42
127.36
55.04
54.99
OMe
OMe
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-5.10
OMe
OMe
3s
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220
f1 (ppm)


8.06
8.06
8.05
8.05
7.66
7.64
7.63
7.50
7.49
7.48
4.99
4.98
4.97
4.96
4.95
4.94
4.93
4.92
1.44
1.43
1.42
1.41
O
P
O
O
3t
2.01
1.04
2.06
2.00
12.25
10.0 9.5 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 0.0 -0.5
f1 (ppm)


161.01
160.95
134.29
130.49
128.66
128.44
128.39
74.29
74.25
23.69
23.66
23.46
23.42
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-9.78
3t
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220
f1 (ppm)