

## Supporting Information

for

Copper-Decorated Covalent Organic Framework as a Heterogeneous  
Photocatalyst for Phosphorylation of Terminal Alkynes

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## Evaluation of green metrics of the process:

$$\text{Atom economy (AE) (\%)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

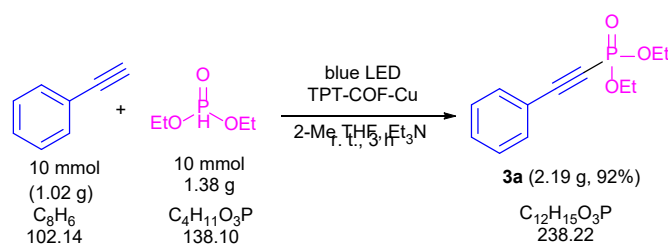
$$\text{Reaction mass efficiency (RME) (\%)} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$

$$\text{Carbon efficiency (\%)} = \frac{\text{amount of carbon in desired product total}}{\text{producttotal amount of carbon presented in all reactants}} \times 100$$

$$\text{Atom efficiency (\%)} = (\% \text{ yield of product} \times \% \text{ atom economy}) \times 100$$

$$\text{E-Factor} = \frac{\text{Amount of waste}}{\text{Amount of product}}$$

## Evaluation of green chemistry metrics for the synthesis of alkynylphosphonate



Yield of product **3a** = 92%

$$\text{Atom economy (AE) (\%)} = \frac{238.22}{102.14 + 138.10} \times 100 = 99\%$$

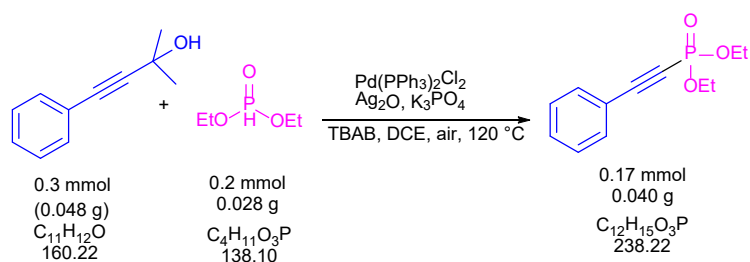
$$\text{Reaction mass efficiency (RME) (\%)} = \frac{2.19}{1.02 + 1.38} \times 100 = 91\%$$

$$\text{Carbon efficiency (\%)} = \frac{12}{8 + 4} \times 100 = 100\%$$

$$\text{Atom efficiency (\%)} = (92 \times 99.16) \times 100 = 91\%$$

Reactant <b>1</b>	ethynylbenzene	1.02 g	10.0 mmol	FW 102.14
Reactant <b>2</b>	diethyl phosphonate	1.38 g	10.0 mmol	FW 138.10
Solvent	2-Me THF (20.0 mL)	17.10 g	19.85 mmol	FW 86.13
Base	Et <sub>3</sub> N	1.01 g	10.0 mmol	FW 101.12
Product <b>3a</b>	diethyl (phenylethynyl)phosphonate	2.19 g	9.20 mmol	FW 238.08

$$\text{E-Factor} = \frac{(1.02 + 1.38 + 17.10 + 1.01) - 2.19}{2.19} = 8.36 \text{ kg waste per kg product}$$



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Yield of product = 84%

$$\text{Atom economy (AE) (\%)} = \frac{238.08}{160.09 + 138.04} \times 100 = 80\%$$

$$\text{Reaction mass efficiency (RME) (\%)} = \frac{0.040}{0.048 + 0.028} \times 100 = 53\%$$

$$\text{Carbon efficiency (\%)} = \frac{12}{11+4} \times 100 = 80\%$$

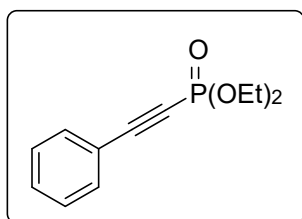
$$\text{Atom efficiency (\%)} = (84 \times 80.0) \times 100 = 67\%$$

Reactant 1	ethynylbenzene	0.048 g	0.3 mmol	FW 160.09
Reactant 2	diethyl phosphonate	0.028 g	0.2 mmol	FW 138.10
Solvent	dichloroethane (2 mL)	2.504 g	25.5 mmol	FW 97.97
Base	$\text{K}_3\text{PO}_4$	0.127 g	0.6 mmol	FW 212.26
Phase	tetrabutylammonium bromide	0.064 g	0.2 mmol	FW 322.38
transfer catalyst	(TBAB)			
Oxidant	$\text{Ag}_2\text{O}$	0.070	0.3 mmol	FW 231.74
Product	diethyl (phenylethynyl)phosphonate	0.040g	9.20 mmol	FW 238.22

$$\text{E-Factor} = \frac{(0.048 + 0.028 + 2.504 + 0.127 + 0.064 + 0.070) - 0.040}{0.040} = 70.03 \text{ kg waste per kg product}$$

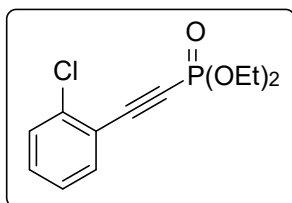
Spectra data of products **3a-3af**:

**Diethyl (phenylethynyl)phosphonate (3a)**<sup>[1]</sup>



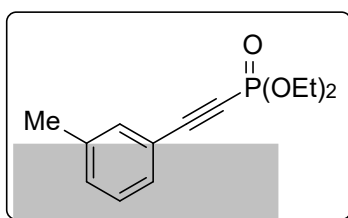
Yellow oil; IR (KBr): 3481, 2984, 2184, 1446, 1265, 1023, 975, 863, 785, 609  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.2$  Hz, 2H), 7.43 (t,  $J = 7.6$  Hz, 1H), 7.35 (t,  $J = 7.6$  Hz, 2H), 5.18 – 3.32 (m, 4H), 1.39 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.7 (d,  $J_{\text{C-P}} = 2.3$  Hz), 130.8, 128.6, 119.5 (d,  $J_{\text{C-P}} = 5.5$  Hz), 99.3 (d,  $J_{\text{C-P}} = 52.8$  Hz), 79.8, 63.3 (d,  $J_{\text{C-P}} = 5.4$  Hz), 16.2 (d,  $J_{\text{C-P}} = 6.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.684. ESI-MS:  $m/z = 239$  ( $M + 1$ )<sup>+</sup>.

**Diethyl ((2-chlorophenyl)ethynyl)phosphonate (3b)**<sup>[2]</sup>



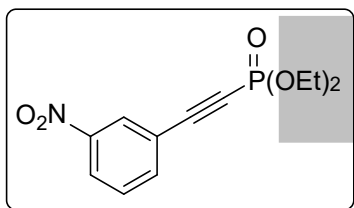
Yellow oil; IR (KBr): 3446, 2985, 2930, 2192, 1646, 1472, 1263, 1024, 977, 863, 759, 701  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.6$  Hz, 1H), 7.48 – 7.35 (m, 2H), 7.29 – 7.27 (m, 1H), 4.58 – 3.97 (m, 4H), 1.42 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 134.4 (d,  $J_{\text{C-P}} = 2.2$  Hz), 131.7, 129.6, 126.8, 119.9 (d,  $J_{\text{C-P}} = 5.7$  Hz), 95.2 (d,  $J_{\text{C-P}} = 52.1$  Hz), 83.2 (d,  $J_{\text{C-P}} = 293.6$  Hz), 63.5 (d,  $J_{\text{C-P}} = 5.5$  Hz), 16.2 (d,  $J_{\text{C-P}} = 6.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -6.715. ESI-MS:  $m/z = 273$  ( $M + 1$ )<sup>+</sup>.

**Diethyl (*m*-tolylethynyl)phosphonate (3c)**<sup>[3]</sup>



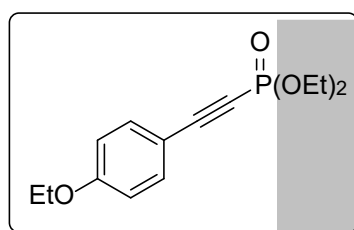
Yellow oil; IR (KBr): 3447, 2984, 2928, 2176, 1601, 1481, 1272, 1024, 875, 787, 690  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.34 (m, 2H), 7.30 – 7.24 (m, 2H), 4.82 – 3.45 (m, 4H), 2.35 (s, 3H), 1.41 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 133.1 (d,  $J_{\text{C-P}} = 2.2$  Hz), 131.7, 129.8 (d,  $J_{\text{C-P}} = 2.2$  Hz), 128.5, 119.4 (d,  $J_{\text{C-P}} = 5.6$  Hz), 99.5 (d,  $J_{\text{C-P}} = 52.7$  Hz), 78.0 (d,  $J_{\text{C-P}} = 298.3$  Hz), 63.2 (d,  $J_{\text{C-P}} = 5.4$  Hz), 21.2, 16.2 (d,  $J_{\text{C-P}} = 7.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.854. ESI-MS:  $m/z = 253$  ( $M + 1$ )<sup>+</sup>.

**Diethyl ((3-nitrophenyl)ethynyl)phosphonate (3d)**<sup>[4]</sup>



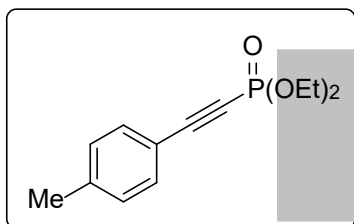
Yellow oil; IR (KBr): 3446, 2986, 2195, 1534, 1355, 1266, 1023, 978, 830, 736  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (s, 1H), 8.28 – 8.26 (m, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.58 (t,  $J = 8.0$  Hz, 1H), 4.78 – 3.67 (m, 4H), 1.38 (t,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.0, 138.1 (d,  $J_{\text{C-P}} = 2.1$  Hz), 130.0, 127.4 (d,  $J_{\text{C-P}} = 2.3$  Hz), 125.31, 121.4 (d,  $J_{\text{C-P}} = 5.6$  Hz), 121.41, 95.3 (d,  $J_{\text{C-P}} = 51.6$  Hz), 81.0 (d,  $J_{\text{C-P}} = 293.3$  Hz), 63.6 (d,  $J_{\text{C-P}} = 5.6$  Hz), 16.2 (d,  $J_{\text{C-P}} = 6.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -7.373. ESI-MS:  $m/z = 284$  ( $M + 1$ ) $^+$ .

### Diethyl ((4-ethoxyphenyl)ethynyl)phosphonate (3e)



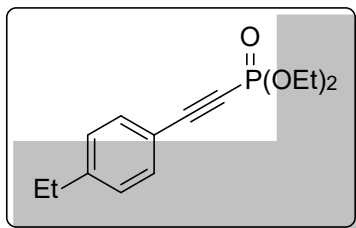
Red oil; IR (KBr) 3481, 2982, 2181, 1603, 1508, 1477, 1254, 1025, 973, 865, 793, 545, 507  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.46 (m, 2H), 7.04 – 6.55 (m, 2H), 4.44 – 3.89 (m, 6H), 1.73 – 1.10 (m, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 134.4 (d,  $J_{\text{C-P}} = 2.0$  Hz), 132.1, 114.7, 114.0, 111.1 (d,  $J_{\text{C-P}} = 5.7$  Hz), 100.0 (d,  $J_{\text{C-P}} = 53.7$  Hz), 77.0 (d,  $J_{\text{C-P}} = 301.1$  Hz), 63.7, 63.2 (d,  $J_{\text{C-P}} = 5.4$  Hz), 58.3, 18.4, 16.1 (d,  $J_{\text{C-P}} = 7.0$  Hz), 14.7.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.348. ESI-MS:  $m/z = 283$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_{19}\text{O}_4\text{NaP}$  ( $M + \text{Na}$ ): 305.0919, found: 305.0915.

### Diethyl (*p*-tolylethynyl)phosphonate (3f)<sup>[2]</sup>



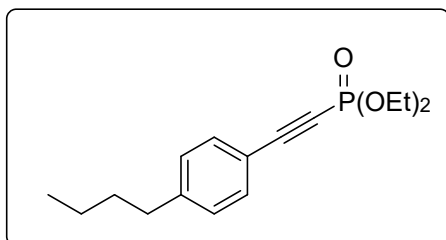
Yellow oil; IR (KBr) 3466, 2984, 2184, 1478, 1264, 1024, 975, 863, 817, 785, 609  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.6$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 4.54 – 4.11 (m, 4H), 2.36 (s, 3H), 1.39 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.4, 132.6 (d,  $J_{\text{C-P}} = 2.0$  Hz), 130.1, 129.4, 129.0, 116.4 (d,  $J_{\text{C-P}} = 5.6$  Hz), 99.4 (d,  $J_{\text{C-P}} = 53.1$  Hz), 77.7 (d,  $J_{\text{C-P}} = 299.5$  Hz), 63.2 (d,  $J_{\text{C-P}} = 5.4$  Hz), 21.7, 16.2 (d,  $J_{\text{C-P}} = 7.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.667. ESI-MS:  $m/z = 253$  ( $M + 1$ ) $^+$ .

### Diethyl ((4-ethylphenyl)ethynyl)phosphonate (3g)<sup>[5]</sup>



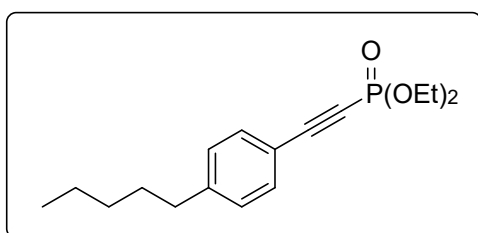
Yellow oil; IR (KBr) 3482, 2968, 2184, 1412, 1263, 1024, 972, 862, 834, 774, 609  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.0$  Hz, 2H), 7.31 – 7.12 (d,  $J = 8.0$  Hz, 2H), 4.43 – 4.02 (m, 4H), 2.65 – 2.62 (m, 2H), 1.39 (t,  $J = 7.2$  Hz, 6H), 1.22 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.6, 132.7 (d,  $J_{\text{C-P}} = 2.2$  Hz), 130.2, 128.2, 127.8, 116.6 (d,  $J_{\text{C-P}} = 5.6$  Hz), 99.7 (d,  $J_{\text{C-P}} = 53.0$  Hz), 77.7 (d,  $J_{\text{C-P}} = 299.4$  Hz), 63.2 (d,  $J_{\text{C-P}} = 5.3$  Hz), 28.9, 16.16 (d,  $J_{\text{C-P}} = 7.0$  Hz), 15.2.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.662. ESI-MS:  $m/z = 267$  ( $\text{M} + 1$ ) $^+$ .

### Diethyl ((4-pentylphenyl)ethynyl)phosphonate (3h)



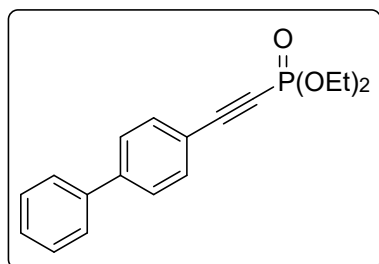
Yellow oil; IR (KBr) 3459, 2958, 2931, 2860, 2185, 1606, 1413, 1264, 1025, 974, 863, 752, 616  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 8.4$  Hz, 2H), 7.19 (t,  $J = 8.0$  Hz, 2H), 4.33 – 4.07 (m, 4H), 2.82 – 2.46 (m, 2H), 1.56 (m, 3H), 1.44 – 1.25 (m, 9H), 0.90 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.3, 132.6 (d,  $J_{\text{C-P}} = 2.2$  Hz), 130.0, 128.7, 128.4, 116.6 (d,  $J_{\text{C-P}} = 5.6$  Hz), 99.7 (d,  $J_{\text{C-P}} = 53.1$  Hz), 77.3 (d,  $J_{\text{C-P}} = 299.5$  Hz), 63.2 (d,  $J_{\text{C-P}} = 5.3$  Hz), 35.7, 33.4, 33.2, 22.3, 16.2 (d,  $J_{\text{C-P}} = 6.9$  Hz), 13.9.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.666. ESI-MS:  $m/z = 295$  ( $\text{M} + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{16}\text{H}_{23}\text{O}_3\text{NaP}$  ( $\text{M} + \text{Na}$ ): 317.1283, found: 317.1279.

### Diethyl ((4-pentylphenyl)ethynyl)phosphonate (3i)



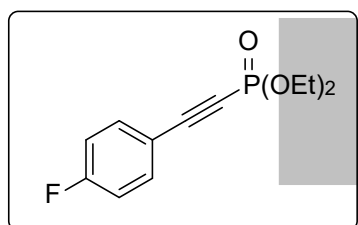
Yellow oil; IR (KBr) 3446, 2930, 2857, 2184, 1607, 1456, 1264, 1025, 974, 863, 797, 616  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.0$  Hz, 2H), 7.17 (d,  $J = 8.0$  Hz, 2H), 4.42 – 4.00 (m, 4H), 2.70 – 2.47 (m, 2H), 1.66 – 1.53 (m, 2H), 1.39 (t,  $J = 7.2$  Hz, 6H), 1.35 – 1.26 (m, 4H), 0.87 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 132.7 (d,  $J_{\text{C-P}} = 2.1$  Hz), 132.6, 130.1, 128.7, 128.4, 116.6 (d,  $J_{\text{C-P}} = 5.7$  Hz), 100.0 (d,  $J_{\text{C-P}} = 53.1$  Hz), 77.7 (d,  $J_{\text{C-P}} = 299.5$  Hz), 63.2 (d,  $J_{\text{C-P}} = 5.8$  Hz), 36.0, 31.4, 30.8, 22.5, 16.2 (d,  $J_{\text{C-P}} = 6.9$  Hz), 14.0.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.641. ESI-MS:  $m/z = 309$  ( $\text{M} + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{17}\text{H}_{25}\text{O}_3\text{NaP}$  ( $\text{M} + \text{Na}$ ): 331.1439, found: 331.1435.

### Diethyl ((1,1'-biphenyl)-4-ylethynyl)phosphonate (3j)<sup>[6]</sup>



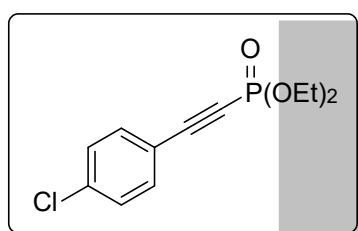
Yellow oil; IR (KBr) 3446, 2984, 2929, 2184, 1602, 1486, 1263, 1026, 976, 862, 798, 764, 638  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.55 (m, 6H), 7.47 – 7.44 (m, 2H), 7.41 – 7.32 (m, 1H), 4.64 – 3.80 (m, 4H), 1.42 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 139.7, 133.1 (d,  $J_{\text{C-P}} = 2.1$  Hz), 129.0, 128.2, 127.2 (d,  $J_{\text{C-P}} = 10.3$  Hz), 118.3 (d,  $J_{\text{C-P}} = 5.7$  Hz), 99.1 (d,  $J_{\text{C-P}} = 52.7$  Hz), 80.4, 63.3 (d,  $J_{\text{C-P}} = 5.4$  Hz), 16.2 (d,  $J_{\text{C-P}} = 7.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.910. ESI-MS:  $m/z = 315$  ( $M + 1$ )<sup>+</sup>.

### Diethyl ((4-fluorophenyl)ethynyl)phosphonate (3k)<sup>[2]</sup>



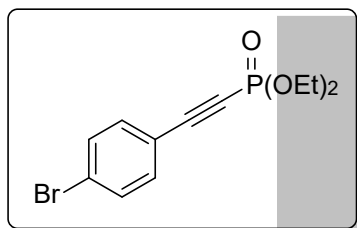
Yellow oil; IR (KBr) 3479, 2986, 2931, 2188, 1507, 1266, 1024, 799  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (dd,  $J = 7.6, 5.2$  Hz, 1H), 7.07 – 7.03 (m, 2H), 4.37 – 3.92 (m, 4H), 1.39 – 1.36 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9 (d,  $J_{\text{C-F}} = 252.3$  Hz), 134.95 (d,  $J_{\text{C-P}} = 2.1$  Hz), 134.86 (d,  $J_{\text{C-P}} = 2.1$  Hz), 116.1 (d,  $J_{\text{C-F}} = 22.3$  Hz), 115.7 (d,  $J_{\text{C-P}} = 3.7$  Hz), 115.7 (d,  $J_{\text{C-P}} = 3.8$  Hz), 98.0 (d,  $J_{\text{C-P}} = 52.9$  Hz), 78.3 (d,  $J_{\text{C-P}} = 298.5$  Hz), 63.3 (d,  $J_{\text{C-P}} = 5.4$  Hz), 16.17 (d,  $J_{\text{C-P}} = 7.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -6.167. ESI-MS:  $m/z = 257$  ( $M + 1$ )<sup>+</sup>.

### Diethyl ((4-chlorophenyl)ethynyl)phosphonate (3l)<sup>[2]</sup>



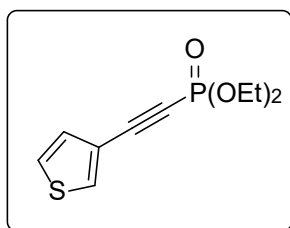
Yellow oil; IR (KBr) 3480, 2983, 2189, 1488, 1265, 1024, 976, 857, 701, 537  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 8.4$  Hz, 2H), 4.63 – 3.93 (m, 4H), 1.39 (t,  $J = 7.1$  Hz, 6.8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 133.9 (d,  $J_{\text{C-P}} = 2.1$  Hz), 129.1, 118.0 (d,  $J_{\text{C-P}} = 5.7$  Hz), 97.6 (d,  $J_{\text{C-P}} = 52.6$  Hz), 79.4 (d,  $J_{\text{C-P}} = 297.3$  Hz), 63.4 (d,  $J_{\text{C-P}} = 5.4$  Hz), 16.2 (d,  $J_{\text{C-P}} = 6.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -6.347. ESI-MS:  $m/z = 273$  ( $M + 1$ )<sup>+</sup>.

### Diethyl ((4-bromophenyl)ethynyl)phosphonate (3m)<sup>[2]</sup>



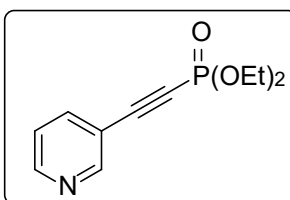
Yellow oil; IR (KBr) 3445, 2983, 2187, 1584, 1481, 1394, 1264, 1023, 974, 857, 824, 758, 682, 536  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 8.4$  Hz, 2H), 7.41 (d,  $J = 8.4$  Hz, 2H), 4.76 – 3.84 (m, 4H), 1.39 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9 (d,  $J_{\text{C-P}} = 2.2$  Hz), 132.0, 125.5, 118.5 (d,  $J_{\text{C-P}} = 5.6$  Hz), 97.7 (d,  $J_{\text{C-P}} = 52.5$  Hz), 71.6 (d,  $J_{\text{C-P}} = 297.1$  Hz), 63.4 (d,  $J_{\text{C-P}} = 5.4$  Hz), 16.2 (d,  $J_{\text{C-P}} = 6.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -6.359. ESI-MS:  $m/z = 317$  ( $M + 1$ ) $^+$ .

### Diethyl (thiophen-3-ylethynyl)phosphonate (3n)<sup>[2]</sup>



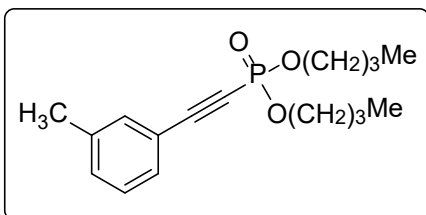
Red oil; IR (KBr) 3479, 3081, 2984, 2907, 2189, 1443, 1392, 1360, 1262, 1022, 954, 874, 778, 627  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (s, 1H), 7.30 – 7.29 (m, 1H), 7.19 – 7.18 (m, 1H), 4.47 – 4.02 (m, 4H), 1.38 (t,  $J = 7.0$  Hz, 6.8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.4 (d,  $J_{\text{C-P}} = 2.5$  Hz), 129.9 (d,  $J_{\text{C-P}} = 1.0$  Hz), 126.2, 118.8 (d,  $J_{\text{C-P}} = 5.9$  Hz), 94.4 (d,  $J_{\text{C-P}} = 33.7$  Hz), 79.8, 63.2 (d,  $J_{\text{C-P}} = 5.4$  Hz), 16.1 (d,  $J_{\text{C-P}} = 7.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.891. ESI-MS:  $m/z = 245$  ( $M + 1$ ) $^+$ .

### Diethyl (pyridin-3-ylethynyl)phosphonate (3o)<sup>[3]</sup>



Yellow oil; IR (KBr) 3446, 2984, 2191, 1682, 1475, 1262, 1163, 1023, 973, 859, 704  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 – 8.87 (m, 1H), 8.67 – 8.64 (m, 1H), 8.00 – 7.84 (m, 1H), 7.35 – 7.32 (m, 1H), 4.25 – 4.17 (m, 4H), 1.40 – 1.34 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9 (d,  $J_{\text{C-P}} = 2.4$  Hz), 150.6, 140.0 (d,  $J_{\text{C-P}} = 2.1$  Hz), 123.5 (d,  $J_{\text{C-P}} = 23.9$  Hz), 117.2 (d,  $J_{\text{C-P}} = 5.4$  Hz), 95.0 (d,  $J_{\text{C-P}} = 52.0$  Hz), 82.2 (d,  $J_{\text{C-P}} = 294.4$  Hz), 63.5 (d,  $J_{\text{C-P}} = 5.5$  Hz), 16.2 (d,  $J_{\text{C-P}} = 6.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -11.731, -7.142. ESI-MS:  $m/z = 240$  ( $M + 1$ ) $^+$ .

### Dibutyl (*m*-tolylethynyl)phosphonate (3p)<sup>[7]</sup>

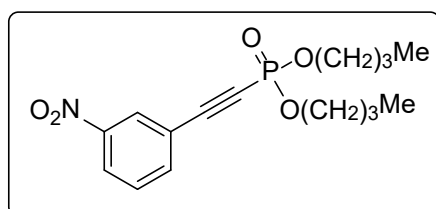


Yellow oil; IR (KBr) 3446, 2960, 2933, 2874, 2177, 1601, 1465, 1275, 1062, 1023, 933, 792, 689, 657  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.32 (m, 2H), 7.30 – 7.21 (m, 2H), 4.16 (dd,  $J = 14.0, 6.4$  Hz, 4H), 2.35 (s, 3H),



1.87 – 1.64 (m, 4H), 1.59 – 1.32 (m, 4H), 0.96 (t,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 133.1 (d,  $J_{\text{C-P}} = 2.2$  Hz), 131.6, 129.8 (d,  $J_{\text{C-P}} = 2.1$  Hz), 128.5, 119.4 (d,  $J_{\text{C-P}} = 5.5$  Hz), 99.4 (d,  $J_{\text{C-P}} = 52.4$  Hz), 78.0 (d,  $J_{\text{C-P}} = 298.2$  Hz), 66.9 (d,  $J_{\text{C-P}} = 5.8$  Hz), 32.2 (d,  $J_{\text{C-P}} = 7.0$  Hz), 21.2, 18.7, 13.6.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.465. ESI-MS:  $m/z = 308$  ( $M + 1$ ) $^+$ .

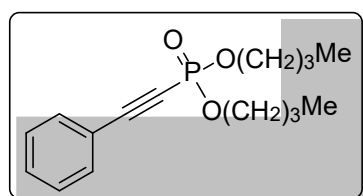
#### Dibutyl ((3-nitrophenyl)ethynyl)phosphonate (3q)



Yellow oil; IR (KBr) 3446, 3086, 2961, 2934, 1534, 1466, 1353, 1272, 1023, 932, 827, 735, 673, 644  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (s, 1H), 8.26 (d,  $J = 8.4$  Hz, 1H), 7.83 (d,  $J = 7.6$  Hz, 1H), 7.57 (t,  $J = 8.0$  Hz, 1H),

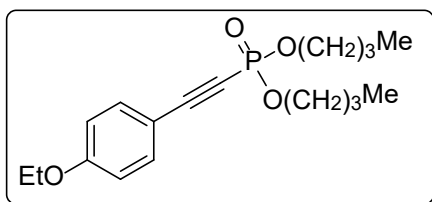
4.13 (dd,  $J = 14.0, 6.8$  Hz, 4H), 1.89 – 1.63 (m, 4H), 1.52 – 1.31 (m, 4H), 0.90 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.0, 138.1 (d,  $J_{\text{C-P}} = 2.0$  Hz), 130.0, 127.3 (d,  $J_{\text{C-P}} = 2.2$  Hz), 125.3, 121.5 (d,  $J_{\text{C-P}} = 5.6$  Hz), 95.3 (d,  $J_{\text{C-P}} = 51.5$  Hz), 81.0 (d,  $J_{\text{C-P}} = 293.1$  Hz), 77.4, 67.2 (d,  $J_{\text{C-P}} = 5.6$  Hz), 32.2 (d,  $J_{\text{C-P}} = 7.0$  Hz), 18.6 (d,  $J_{\text{C-P}} = 8.0$  Hz), 13.5.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -6.956. ESI-MS:  $m/z = 340$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{16}\text{H}_{22}\text{NO}_5\text{NaP}$  ( $M + \text{Na}$ ): 362.1133, found: 362.1129.

#### Dibutyl (phenylethynyl)phosphonate (3r)



Yellow oil; IR (KBr) 3446, 2962, 2934, 2874, 2244, 2187, 1658, 1490, 1259, 1025, 908, 860, 733, 646  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 7.2$  Hz, 2H), 7.41 (d,  $J = 7.6$  Hz, 1H), 7.34 (t,  $J = 7.6$  Hz, 2H), 4.13 (dd,  $J = 14.4, 6.8$  Hz, 4H), 1.69 (dd,  $J = 14.4, 6.8$  Hz, 4H), 1.43 (dd,  $J = 15.2, 7.6$  Hz, 4H), 0.92 (t,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.8 (d,  $J_{\text{C-P}} = 2.1$  Hz), 130.9, 128.8, 119.8 (d,  $J_{\text{C-P}} = 5.5$  Hz), 99.3 (d,  $J_{\text{C-P}} = 52.4$  Hz), 80.0, 67.2 (d,  $J_{\text{C-P}} = 5.8$  Hz), 32.4 (d,  $J_{\text{C-P}} = 7.1$  Hz), 18.9, 13.8.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.590. ESI-MS:  $m/z = 295$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{16}\text{H}_{23}\text{O}_3\text{NaP}$  ( $M + \text{Na}$ ): 317.1283, found: 317.1279.

#### Dibutyl ((4-ethoxyphenyl)ethynyl)phosphonate (3s)



Yellow oil; IR (KBr) 3447, 2960, 2934, 2874, 2182, 1604, 1508, 1477, 1392, 1254, 1174, 1024, 866, 796, 732  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 8.4$  Hz, 2H), 6.82 (d,  $J = 8.8$  Hz, 2H), 4.10 (dd,  $J = 14.0, 6.8$  Hz, 4H),

4.01 (dd,  $J = 13.6, 6.8$  Hz, 2H), 1.76 – 1.58 (m, 4H), 1.45 – 1.36 (m, 7H), 0.91 (t,  $J = 7.2$  Hz, 6H).

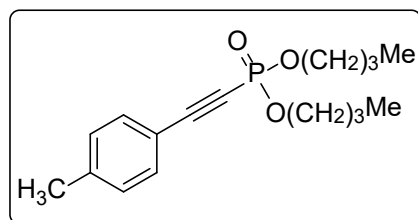
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 134.4 (d,  $J_{\text{C-P}} = 2.0$  Hz), 114.7, 111.1 (d,  $J_{\text{C-P}} = 5.8$  Hz), 100.0

(d,  $J_{\text{C-P}} = 53.4$  Hz), 77.0 (d,  $J_{\text{C-P}} = 300.7$  Hz), 66.8 (d,  $J_{\text{C-P}} = 5.7$  Hz), 63.7, 32.2 (d,  $J_{\text{C-P}} = 7.0$  Hz),

18.7, 14.7, 13.6.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -4.791. ESI-MS:  $m/z = 339$  ( $M + 1$ ) $^+$ . HRMS-ESI

( $m/z$ ) calcd. for  $\text{C}_{18}\text{H}_{27}\text{O}_4\text{NaP}$  ( $M + \text{Na}$ ): 361.1545, found: 361.1541.

### Dibutyl (*p*-tolylethynyl)phosphonate (3t)



Yellow oil; IR (KBr) 3480, 2960, 2934, 2874, 2185, 1606,

1509, 1271, 1022, 864, 817, 732, 612  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400

MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.0$  Hz, 2H), 7.19 (d,  $J = 8.0$

Hz, 2H), 4.12 (dd,  $J = 14.4, 6.8$  Hz, 4H), 2.35 (s, 3H), 1.81

– 1.62 (m, 4H), 1.56 – 1.35 (m, 4H), 0.92 (t,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3,

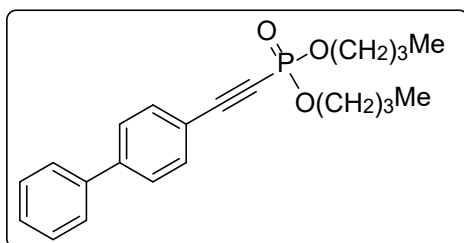
132.6 (d,  $J_{\text{C-P}} = 2.0$  Hz), 129.3, 116.5 (d,  $J_{\text{C-P}} = 5.5$  Hz), 99.6 (d,  $J_{\text{C-P}} = 52.8$  Hz), 77.7 (d,  $J_{\text{C-P}} =$

298.8 Hz), 66.8 (d,  $J_{\text{C-P}} = 5.7$  Hz), 32.2 (d,  $J_{\text{C-P}} = 7.1$  Hz), 21.7, 18.7, 13.6.  $^{31}\text{P}$  NMR (162 MHz,

$\text{CDCl}_3$ )  $\delta$  -5.294. ESI-MS:  $m/z = 308$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{17}\text{H}_{25}\text{O}_3\text{NaP}$  ( $M + \text{Na}$ ):

331.14391, found: 331.1435.

### Dibutyl ([1,1'-biphenyl]-4-ylethynyl)phosphonate (3u)



Yellow oil; IR (KBr) 3446, 2960, 2932, 2873, 2184,

1602, 1486, 1673, 1062, 1023, 863, 764, 697  $\text{cm}^{-1}$ .  $^1\text{H}$

NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.55 (m, 6H), 7.45

(t,  $J = 7.6$  Hz, 2H), 7.38 (t,  $J = 7.2$  Hz, 1H), 4.17 (dd,

$J = 13.6, 6.4$  Hz, 4H), 1.95 – 1.65 (m, 4H), 1.62 – 1.33

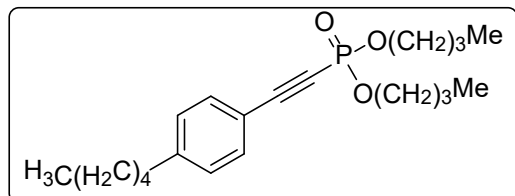
(m, 4H), 0.96 (t,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 139.8, 133.1 (d,  $J_{\text{C-P}} = 1.9$

Hz), 129.0, 128.2, 127.2 (d,  $J_{\text{C-P}} = 10.9$  Hz), 118.3 (d,  $J_{\text{C-P}} = 5.6$  Hz), 99.1 (d,  $J_{\text{C-P}} = 52.5$  Hz), 78.9

(d,  $J_{\text{C-P}} = 314.3$  Hz), 67.0 (d,  $J_{\text{C-P}} = 5.8$  Hz), 32.2 (d,  $J_{\text{C-P}} = 7.0$  Hz), 18.8, 13.6.  $^{31}\text{P}$  NMR (162 MHz,

CDCl<sub>3</sub>)  $\delta$  -5.506. ESI-MS:  $m/z = 371$  (M + 1)<sup>+</sup>. HRMS-ESI ( $m/z$ ) calcd. for C<sub>22</sub>H<sub>27</sub>O<sub>3</sub>NaP (M + Na): 393.1596, found: 393.1592.

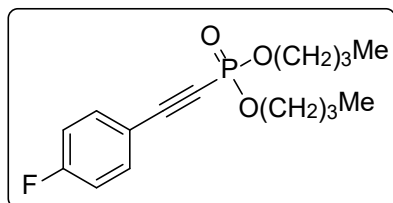
### Dibutyl ((4-pentylphenyl)ethynyl)phosphonate (3v)



Yellow oil; IR (KBr) 3459, 2959, 2931, 2872, 2185, 1606, 1508, 1466, 1274, 1023, 978, 865, 731, 556 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d,  $J = 8.4$  Hz, 2H), 7.15 (d,  $J = 8.0$  Hz, 2H), 4.12

(dd,  $J = 14.0, 6.8$  Hz, 4H), 2.93 – 2.39 (m, 2H), 1.75 – 1.65 (m, 4H), 1.61 – 1.54 (m, 2H), 1.48–1.39 (m, 4H), 1.35 – 1.19 (m, 4H), 0.92 (t,  $J = 7.6$  Hz, 6H), 0.86 (t,  $J = 6.8$  Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.3, 132.6 (d,  $J_{C-P} = 2.1$  Hz), 128.7, 116.7 (d,  $J_{C-P} = 5.6$  Hz), 99.6 (d,  $J_{C-P} = 52.7$  Hz), 77.7 (d,  $J_{C-P} = 299.0$  Hz), 66.9 (d,  $J_{C-P} = 5.8$  Hz), 36.0, 32.2 (d,  $J_{C-P} = 7.1$  Hz), 31.4, 30.8, 22.5, 18.7, 14.0, 13.6. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -5.275. ESI-MS:  $m/z = 365$  (M + 1)<sup>+</sup>. HRMS-ESI ( $m/z$ ) calcd. for C<sub>21</sub>H<sub>33</sub>O<sub>3</sub>NaP (M + Na): 387.2065, found: 387.2061.

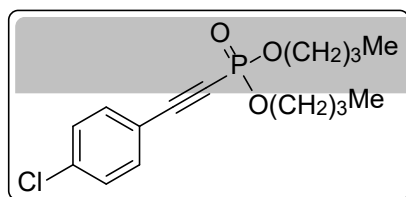
### Dibutyl ((4-fluorophenyl)ethynyl)phosphonate (3w)



Yellow oil; IR (KBr) 3446, 2962, 2935, 2875, 2189, 1600, 1507, 1274, 1236, 1158, 1095, 1024, 840, 801 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 – 7.51 (m, 2H), 7.06 – 7.02 (m, 2H), 4.14 – 4.09 (m, 2H), 1.80 – 1.62 (m, 4H), 1.46 –

1.38 (m, 2H), 0.92 (t,  $J = 7.6$  Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.9 (d,  $J_{C-F} = 252.1$  Hz), 134.9 (dd,  $J_{C-F} = 2.2$  Hz,  $J_{C-P} = 2.2$  Hz, ), 116.2 (d,  $J_{C-P} = 22.2$  Hz), 98.1 (d,  $J_{C-P} = 52.6$  Hz), 78.4 (d,  $J_{C-P} = 298.6$  Hz), 66.9 (d,  $J_{C-P} = 5.8$  Hz), 32.2 (d,  $J_{C-P} = 7.0$  Hz), 18.7, 13.6. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -5.777. ESI-MS:  $m/z = 313$  (M + 1)<sup>+</sup>. HRMS-ESI ( $m/z$ ) calcd. for C<sub>16</sub>H<sub>22</sub>FO<sub>3</sub>NaP (M + Na): 335.1188, found: 335.1184.

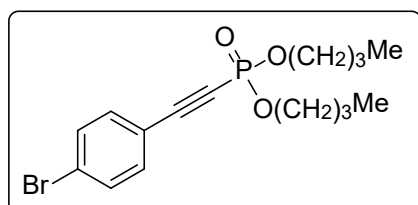
### Dibutyl ((4-chlorophenyl)ethynyl)phosphonate (3x)



Yellow oil; IR (KBr) 3446, 2961, 2933, 2874, 2189, 1591, 1489, 1274, 1062, 1023, 860, 701 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (d,  $J = 7.6$  Hz, 2H), 7.34 (d,  $J = 7.2$  Hz, 2H), 4.14 (dd,  $J = 13.6, 6.8$  Hz, 4H), 1.98 – 1.64 (m, 4H), 1.44 –

1.39 (m, 4H), 0.93 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 133.8 (d,  $J_{\text{C-P}} = 2.1$  Hz), 129.1, 118.1 (d,  $J_{\text{C-P}} = 5.7$  Hz), 97.6 (d,  $J_{\text{C-P}} = 52.4$  Hz), 79.5 (d,  $J_{\text{C-P}} = 297.1$  Hz), 67.0 (d,  $J_{\text{C-P}} = 5.8$  Hz), 32.2 (d,  $J_{\text{C-P}} = 7.0$  Hz), 18.7, 13.6.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.949. ESI-MS:  $m/z = 328$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{16}\text{H}_{22}\text{ClO}_3\text{NaP}$  ( $M + \text{Na}$ ): 351.0893 found: 351.0889.

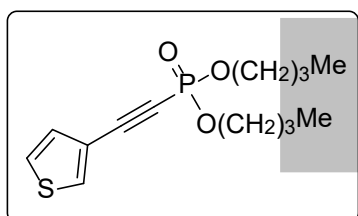
### Dibutyl ((4-bromophenyl)ethynyl)phosphonate (3y)



Yellow oil; IR (KBr) 3446, 2960, 2933, 2873, 2188, 1585, 1486, 1262, 1023, 1010, 824, 730, 680  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.8$  Hz, 2H), 7.37 (d,  $J = 8.4$  Hz, 2H), 4.12 – 4.07 (m, 4H), 1.76 – 1.62 (m, 4H), 1.46 –

1.36 (m, 4H), 0.90 (t,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9 (d,  $J_{\text{C-P}} = 2.1$  Hz), 132.0, 131.8, 128.5, 125.4, 118.5 (d,  $J_{\text{C-P}} = 3.7$  Hz), 97.7 (d,  $J_{\text{C-P}} = 52.3$  Hz), 79.6 (d,  $J_{\text{C-P}} = 296.9$  Hz), 67.0 (d,  $J_{\text{C-P}} = 5.8$  Hz), 66.97, 32.2 (d,  $J_{\text{C-P}} = 7.0$  Hz), 18.7, 13.6.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -6.405. ESI-MS:  $m/z = 373$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{16}\text{H}_{22}\text{BrO}_3\text{PNa}$  ( $M + \text{Na}$ ): 395.0388 found: 395.0384.

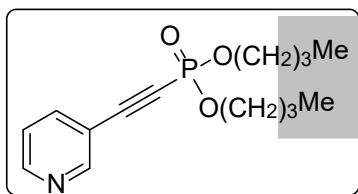
### Dibutyl (thiophen-3-ylethynyl)phosphonate (3z)



Yellow oil; IR (KBr) 3446, 3081, 2960, 2933, 2874, 2189, 1680, 1507, 1465, 1262, 1134, 1060, 1023, 953, 875, 788, 742, 626  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 2.8$  Hz, 1H), 7.30 (dd,  $J = 4.8, 2.8$  Hz, 1H), 7.18 (dd,  $J = 4.8, 0.8$  Hz, 1H),

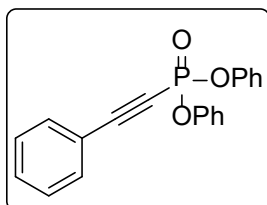
4.12 (dd,  $J = 14.0, 6.8$  Hz, 4H), 1.87 – 1.62 (m, 4H), 1.43 (m, 4H), 0.92 (t,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.3 (d,  $J_{\text{C-P}} = 2.6$  Hz), 129.9 (d,  $J_{\text{C-P}} = 1.4$  Hz), 126.2, 118.9 (d,  $J_{\text{C-P}} = 5.9$  Hz), 94.4 (d,  $J_{\text{C-P}} = 53.5$  Hz), 78.5 (d,  $J_{\text{C-P}} = 247.7$  Hz), 66.9 (d,  $J_{\text{C-P}} = 5.8$  Hz), 32.2 (d,  $J_{\text{C-P}} = 7.1$  Hz), 18.7, 13.6.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.501. ESI-MS:  $m/z = 301$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_{21}\text{O}_3\text{NaPS}$  ( $M + \text{Na}$ ): 323.0847 found: 323.0843.

### Dibutyl (pyridin-2-ylethynyl)phosphonate (3aa)



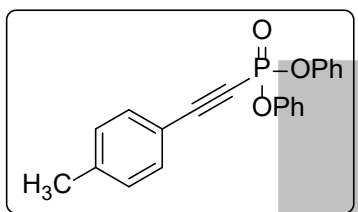
Yellow oil; IR (KBr) 3432, 2960, 2874, 1636, 1466, 1415, 1251, 1024, 802, 732  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (s, 1H), 8.73 (d,  $J = 4.8$  Hz, 1H), 7.93 (d,  $J = 7.6$  Hz, 1H), 7.43 – 7.40 (m, 1H), 4.19 – 4.14 (m, 4H), 2.02 – 1.60 (m, 4H), 1.48 – 1.42 (m, 4H), 0.95 (t,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 150.2, 140.7, 123.8, 117.8, 94.4 (d,  $J_{\text{C-P}} = 51.6$  Hz), 82.7 (d,  $J_{\text{C-P}} = 293.4$  Hz), 67.3 (d,  $J_{\text{C-P}} = 5.9$  Hz), 32.2 (d,  $J_{\text{C-P}} = 6.9$  Hz), 18.7, 13.6.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.673. ESI-MS:  $m/z = 296$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{15}\text{H}_{22}\text{NO}_3\text{NaP}$  ( $M + \text{Na}$ ): 318.1235, found: 318.1227.

### Diphenyl (phenylethynyl)phosphonate (3ab)<sup>[8]</sup>



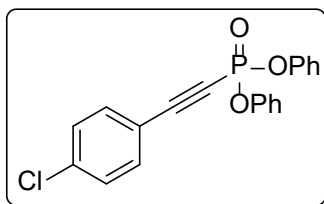
Light pink oil; IR (KBr) 3446, 2925, 2187, 1646, 1589, 1489, 1284, 1208, 1185, 950, 860, 758  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (t,  $J = 7.6$  Hz, 3H), 7.36 (dt,  $J = 15.6, 8.4$  Hz, 10H), 7.24 – 7.21 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.00 (d,  $J_{\text{C-P}} = 7.3$  Hz), 132.8 (d,  $J_{\text{C-P}} = 2.3$  Hz), 131.3, 129.9, 128.7, 125.8, 120.8 (d,  $J_{\text{C-P}} = 4.8$  Hz), 118.7 (d,  $J_{\text{C-P}} = 5.9$  Hz), 102.6 (d,  $J_{\text{C-P}} = 56.1$  Hz), 76.9 (d,  $J_{\text{C-P}} = 320.7$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -14.092. ESI-MS:  $m/z = 335$  ( $M + 1$ ) $^+$ .

### Diphenyl (p-tolyethynyl)phosphonate (3ac)



Light pink oil; IR (KBr) 3421, 2925, 2184, 1633, 1590, 1488, 1284, 1185, 951, 866, 767, 689  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.29 (m, 10H), 7.24 – 7.20 (m, 2H), 7.15 (d,  $J = 7.6$  Hz, 2H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.0 (d,  $J_{\text{C-P}} = 7.4$  Hz), 142.0, 132.7 (d,  $J_{\text{C-P}} = 2.3$  Hz), 129.9, 129.4, 125.7, 120.8 (d,  $J_{\text{C-P}} = 4.7$  Hz), 120.2 (d,  $J_{\text{C-P}} = 4.8$  Hz), 103.0 (d,  $J_{\text{C-P}} = 56.0$  Hz), 76.6 (d,  $J_{\text{C-P}} = 321.7$  Hz), 21.8.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -13.846. ESI-MS:  $m/z = 349$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{21}\text{H}_{17}\text{O}_3\text{NaP}$  ( $M + \text{Na}$ ): 371.0813 found: 371.0810.

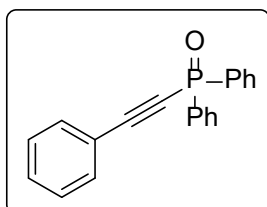
### Diphenyl ((4-chlorophenyl)ethynyl)phosphonate (3ad)



Light pink oil; IR (KBr) 3427, 2924, 2189, 1640, 1591, 1488, 1285, 1184, 953, 861, 772, 703, 688, 537  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.31 (m, 10H), 7.27 – 7.11 (m, 3H), 6.88 – 6.82 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 149.8 (d,  $J_{\text{C-P}} = 7.4$

Hz), 137.8, 134.0 (d,  $J_{\text{C-P}} = 2.4$  Hz), 130.0, 129.7, 129.5, 129.2, 126.0, 125.8, 120.8 (d,  $J_{\text{C-P}} = 4.7$  Hz), 120.2 (d,  $J_{\text{C-P}} = 4.8$  Hz), 120.1, 117.1 (d,  $J_{\text{C-P}} = 6.0$  Hz), 115.5, 101.6 (d,  $J_{\text{C-P}} = 55.8$  Hz), 77.8 (d,  $J_{\text{C-P}} = 320.6$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -14.377. ESI-MS:  $m/z = 369$  ( $M + 1$ ) $^+$ . HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{20}\text{H}_{14}\text{ClO}_3\text{NaP}$  ( $M + \text{Na}$ ): 391.0267 found: 391.0263.

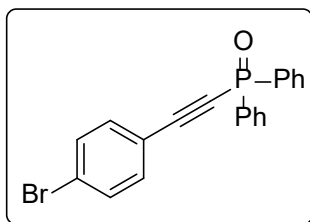
### Diphenyl(phenylethynyl)phosphine oxide (3ae)<sup>[9]</sup>



Yellow solid; m.p.: 102-103  $^\circ\text{C}$ ; IR (KBr) 3441, 2940, 2850, 2174, 1633, 1438, 1203, 1120, 1026, 846, 756, 691  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.86 (m, 4H), 7.63 – 7.43 (m, 9H), 7.40 – 7.36 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.1 (d,  $J_{\text{C-P}} = 23.9$  Hz), 132.6 (d,  $J_{\text{C-P}} =$

1.5 Hz), 132.3 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.1 (d,  $J_{\text{C-P}} = 11.2$  Hz), 130.8, 128.7 (d,  $J_{\text{C-P}} = 13.7$  Hz), 128.6, 120.0 (d,  $J_{\text{C-P}} = 3.9$  Hz), 105.5 (d,  $J_{\text{C-P}} = 29.9$  Hz), 82.9 (d,  $J_{\text{C-P}} = 169.1$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  8.054. ESI-MS:  $m/z = 303$  ( $M + 1$ ) $^+$ .

### ((4-Bromophenyl)ethynyl)diphenylphosphine oxide (3af)<sup>[10]</sup>



Yellow solid; m.p.: 109-110  $^\circ\text{C}$ ; IR (KBr) 3448, 2922, 2851, 2175, 1637, 1483, 1437, 1202, 1120, 1069, 1010, 845, 724, 708, 693, 670, 544  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (dd,  $J = 14.0, 7.6$  Hz, 1H), 7.57 – 7.44 (m, 10H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9 (d,

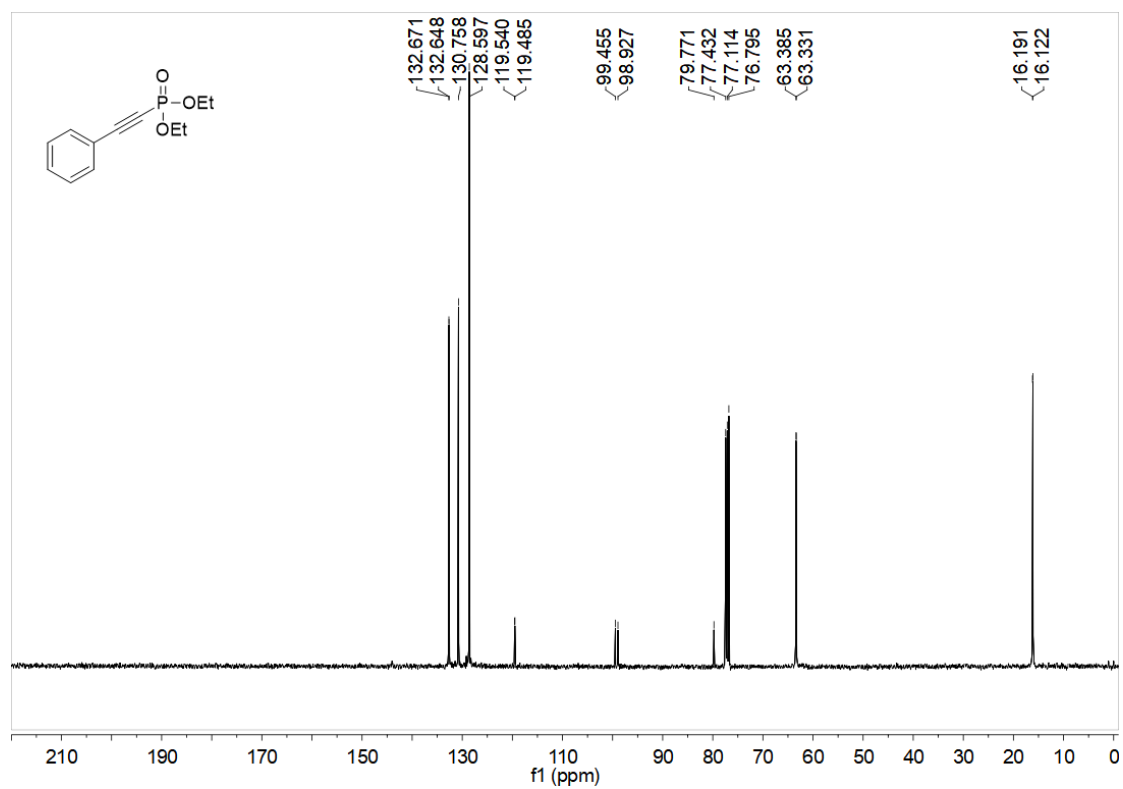
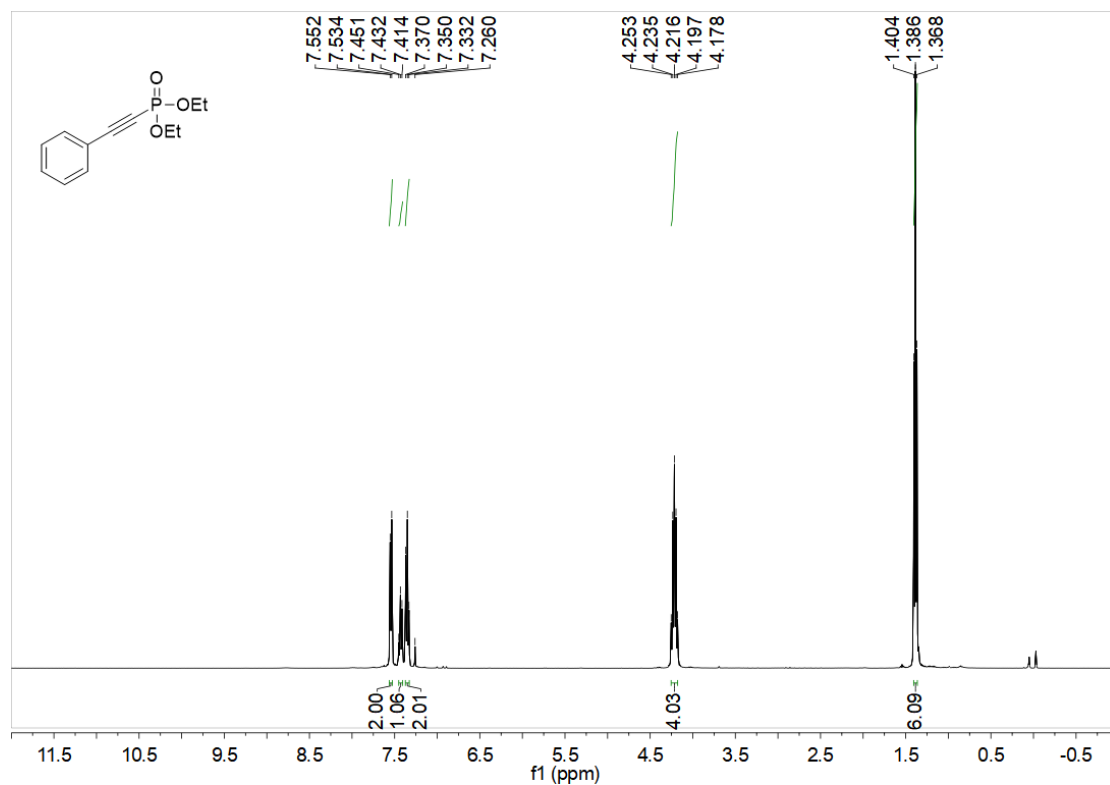
$J_{\text{C-P}} = 1.2$  Hz), 133.4, 132.4 (d,  $J_{\text{C-P}} = 2.7$  Hz), 132.1, 132.0, 131.0 (d,  $J_{\text{C-P}} = 11.2$  Hz), 128.7 (d,  $J_{\text{C-P}} = 13.4$  Hz), 125.5, 118.9 (d,  $J_{\text{C-P}} = 4.0$  Hz), 104.1 (d,  $J_{\text{C-P}} = 29.4$  Hz), 84.1 (d,  $J_{\text{C-P}} = 164.4$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  8.092. ESI-MS:  $m/z = 381$  ( $M + 1$ ) $^+$ .

## References

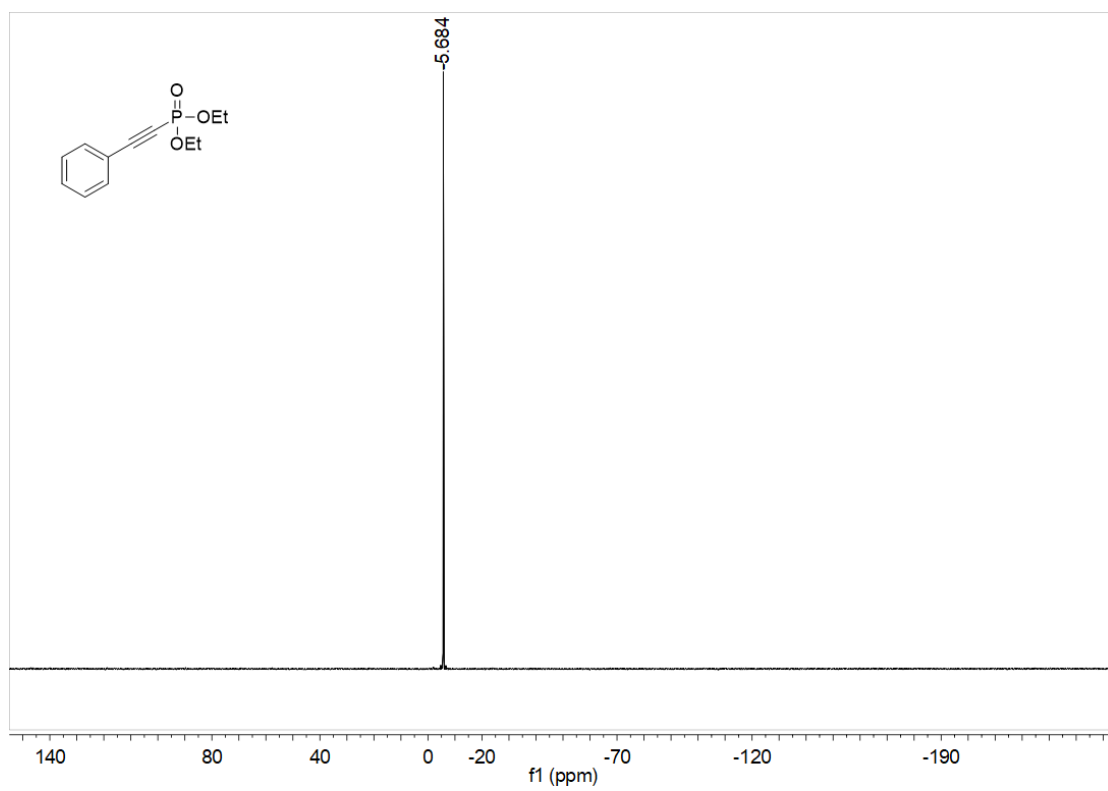
- 1 Y. X. Gao, G. Wang, L. Chen, P. X. Xu, Y. F. Zhao, Y. B. Zhou and L. B. Han, *J. Am. Chem. Soc.*, 2009, **131**, 7956-7957.
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Copies of NMR spectra for products **3a-3af**:

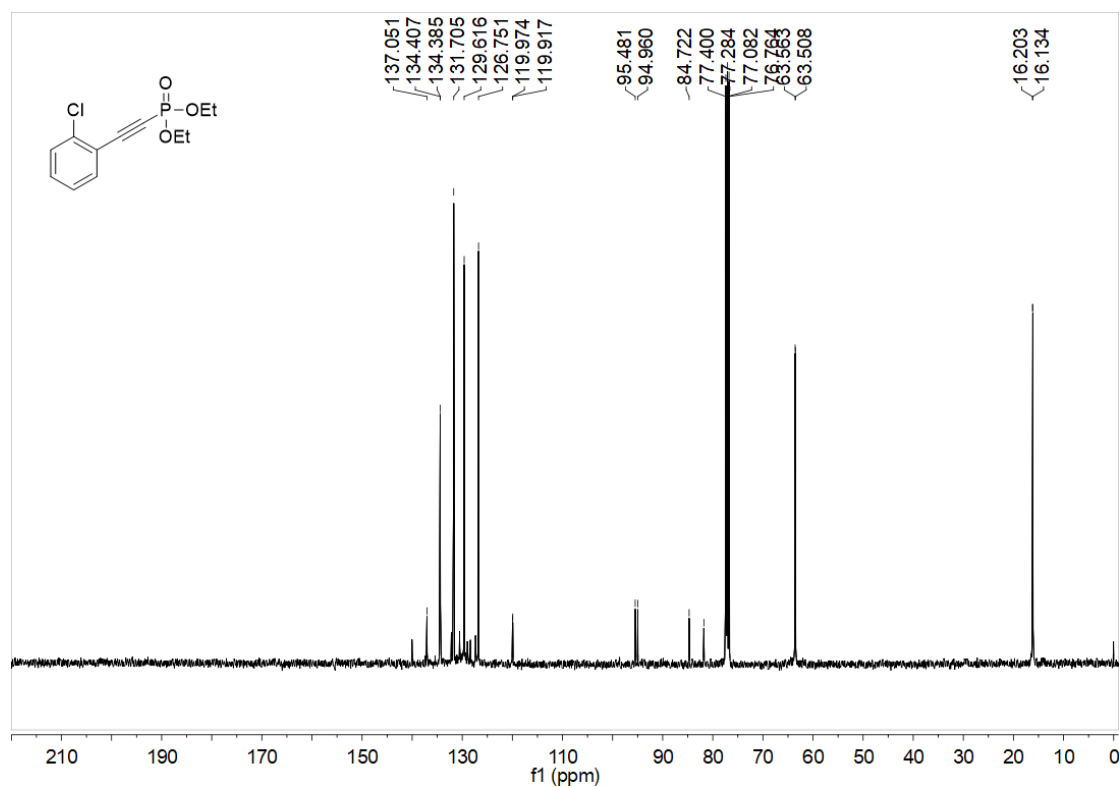
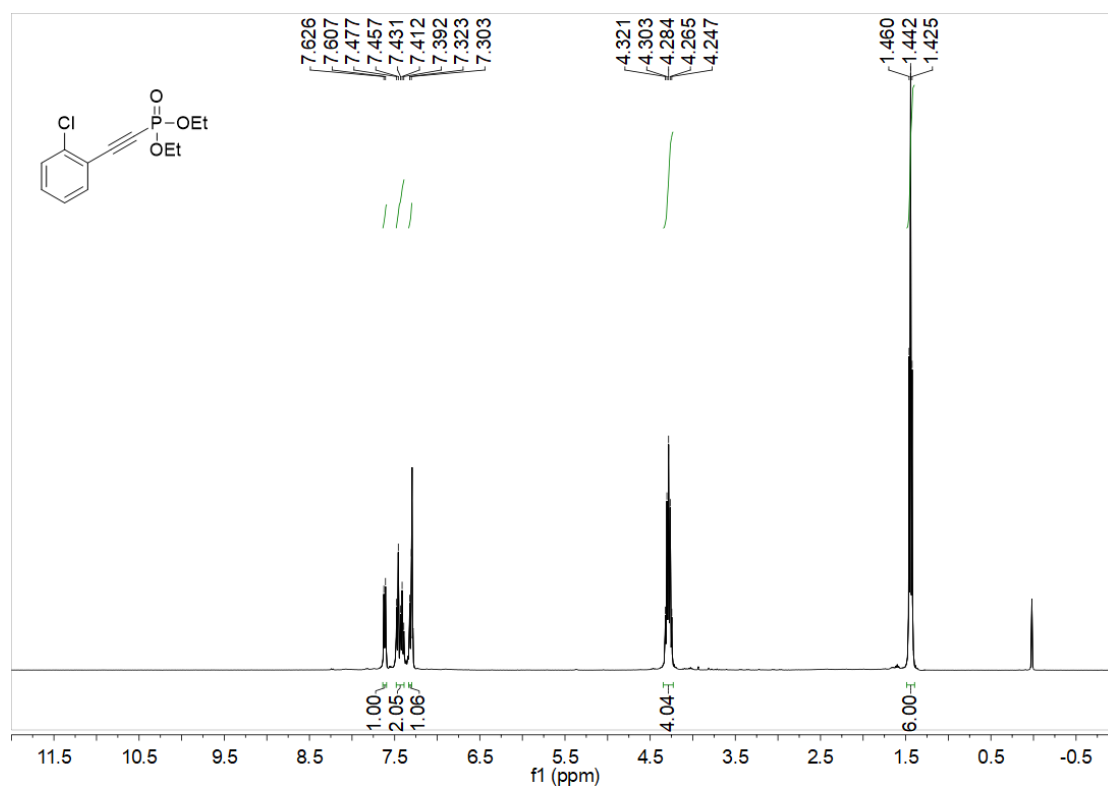
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3a**

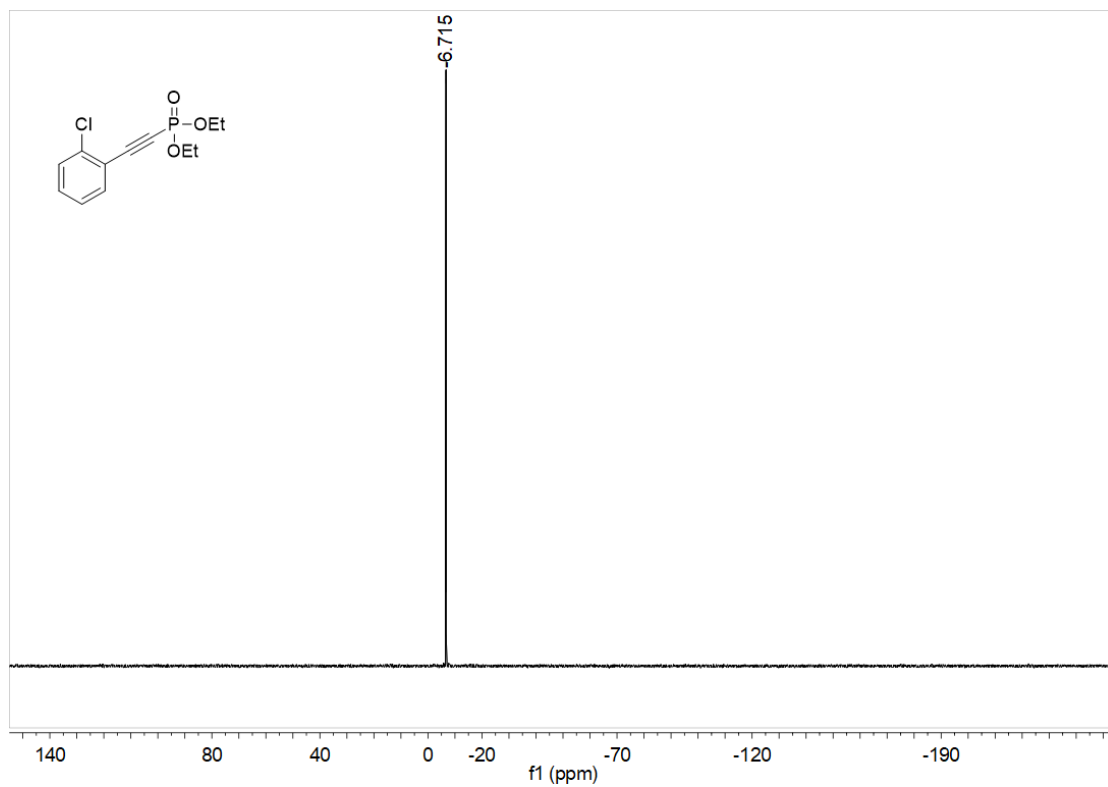




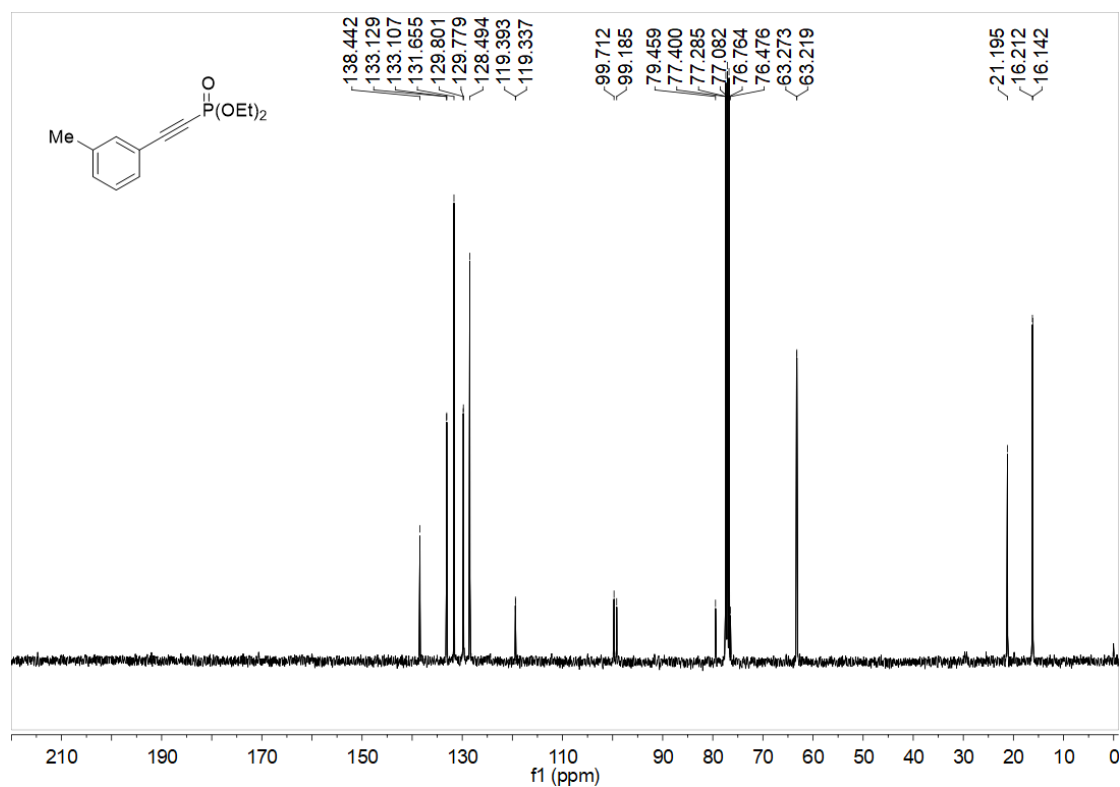
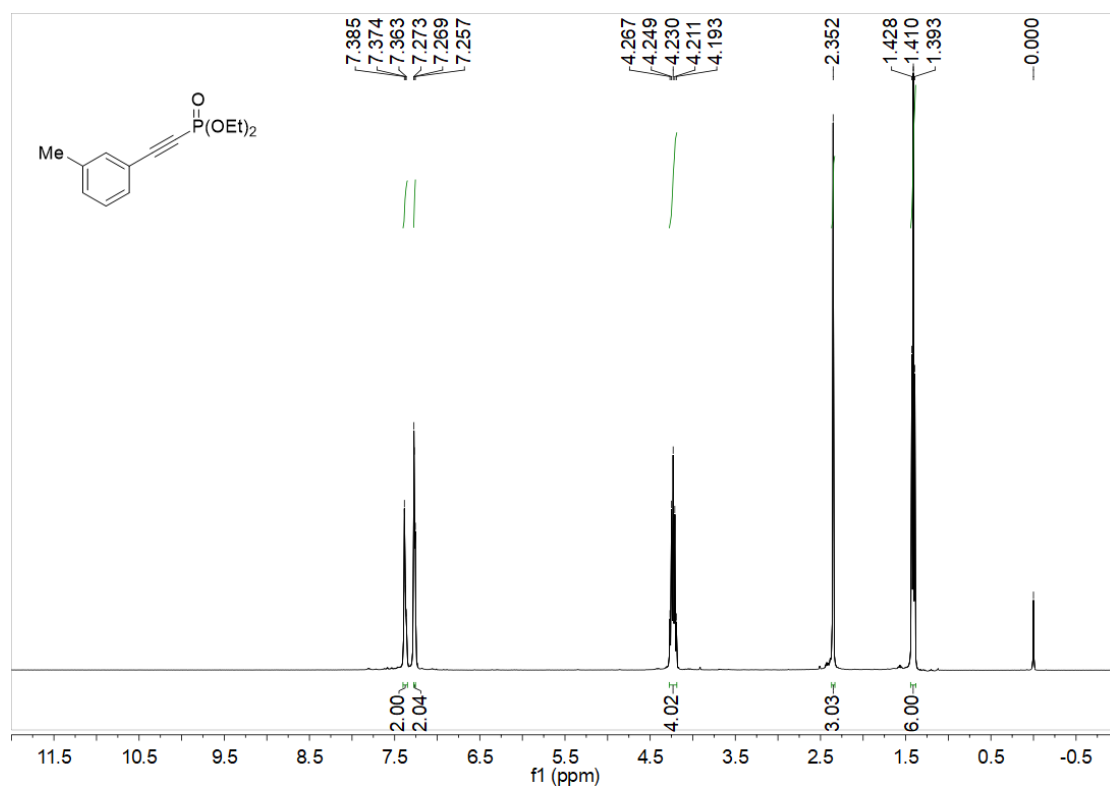


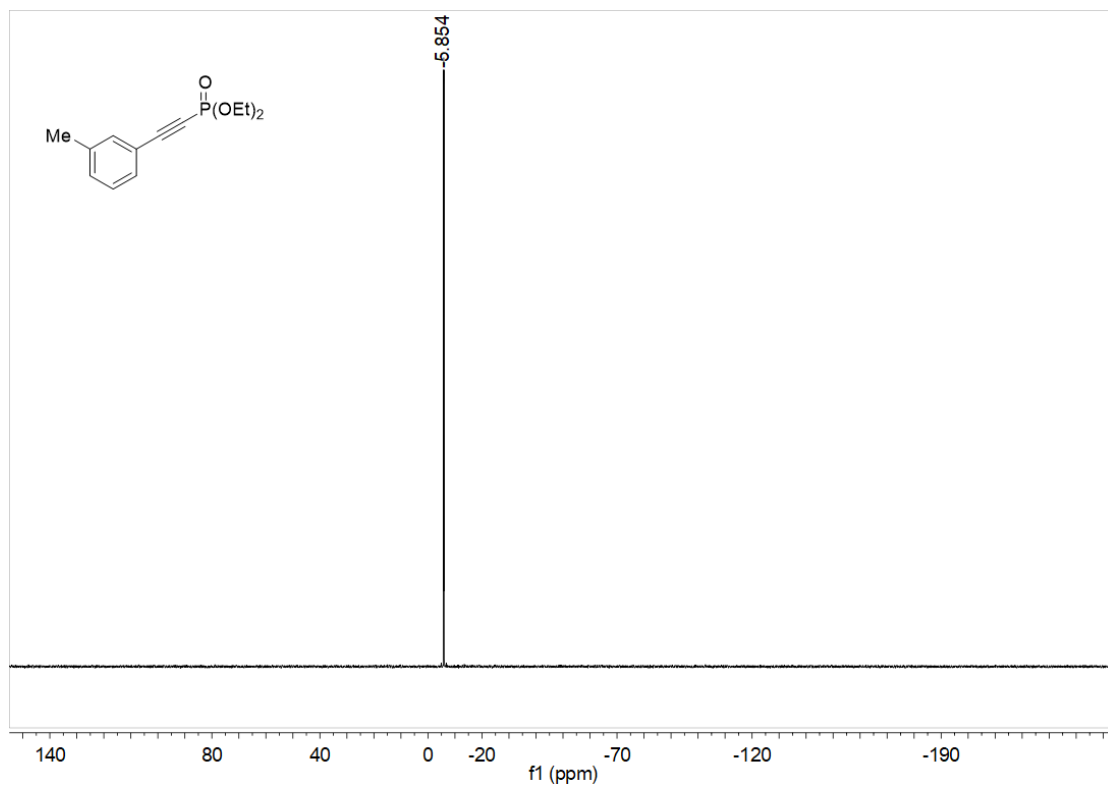
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3b**



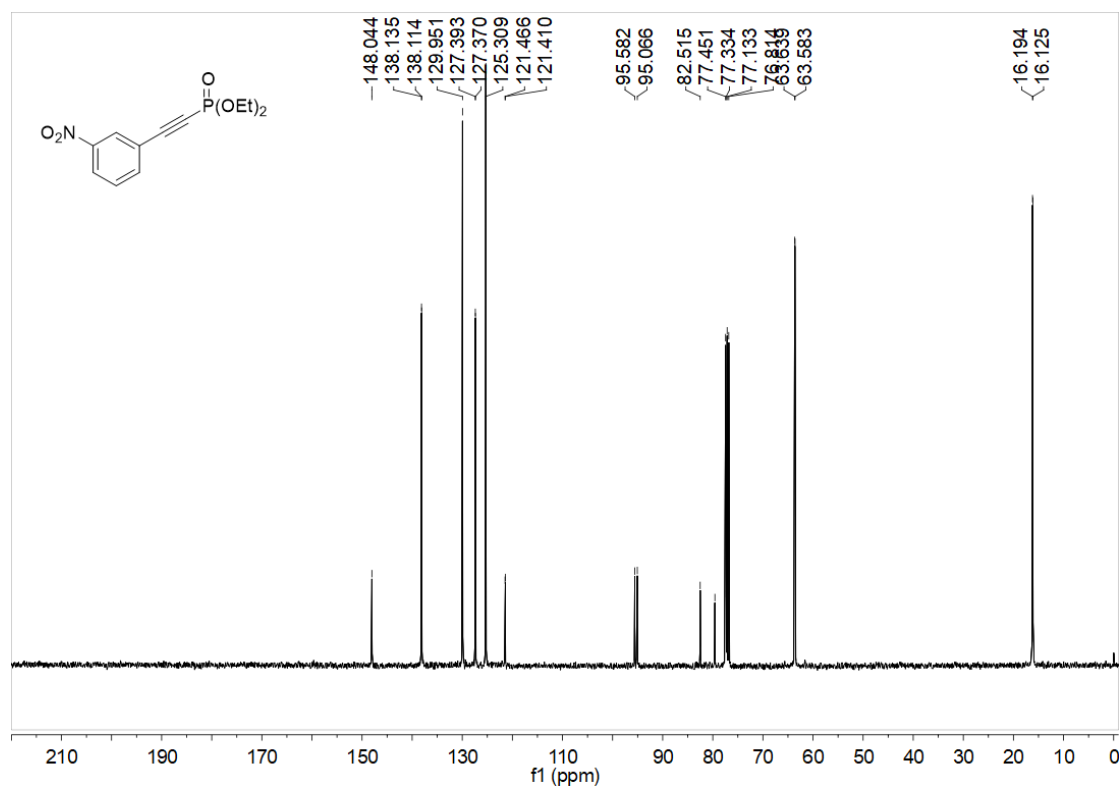
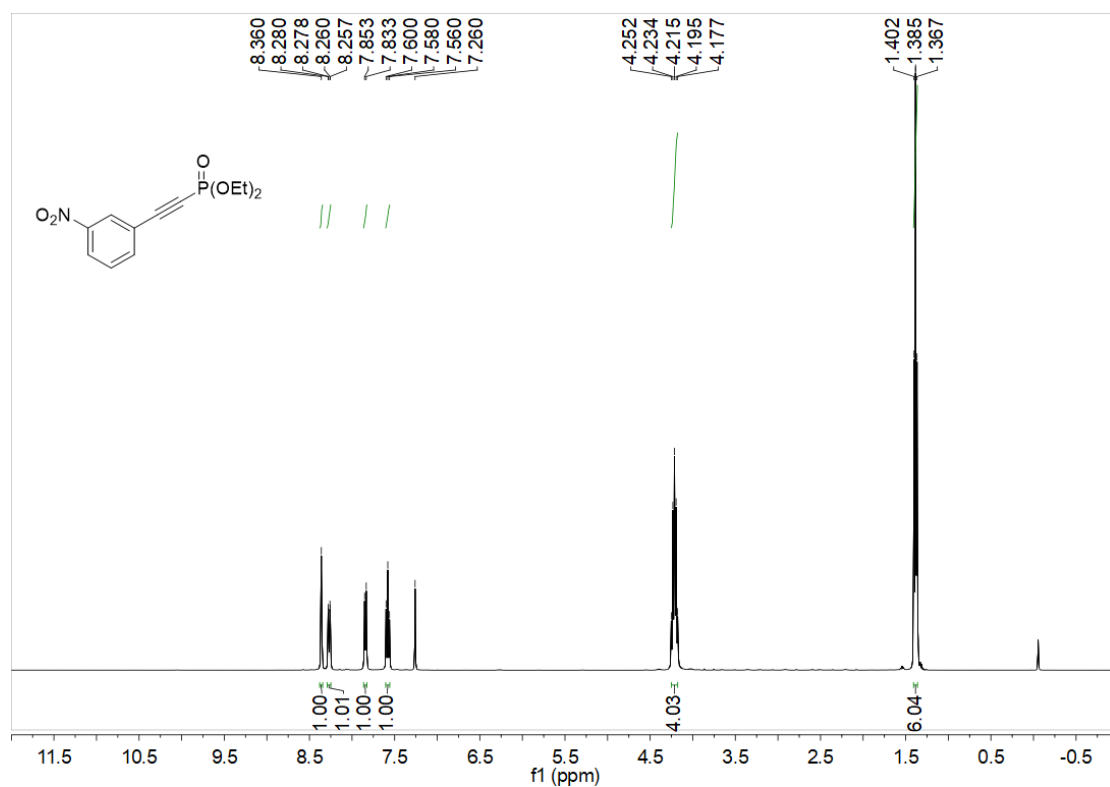


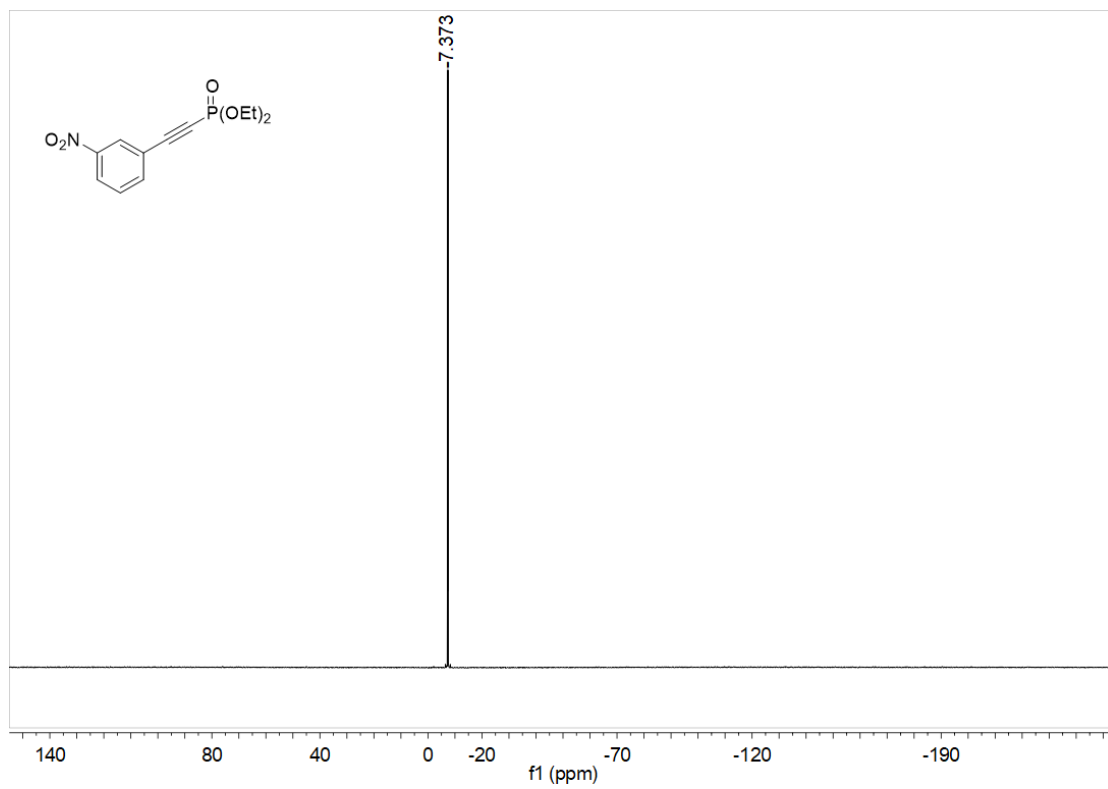
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3c**



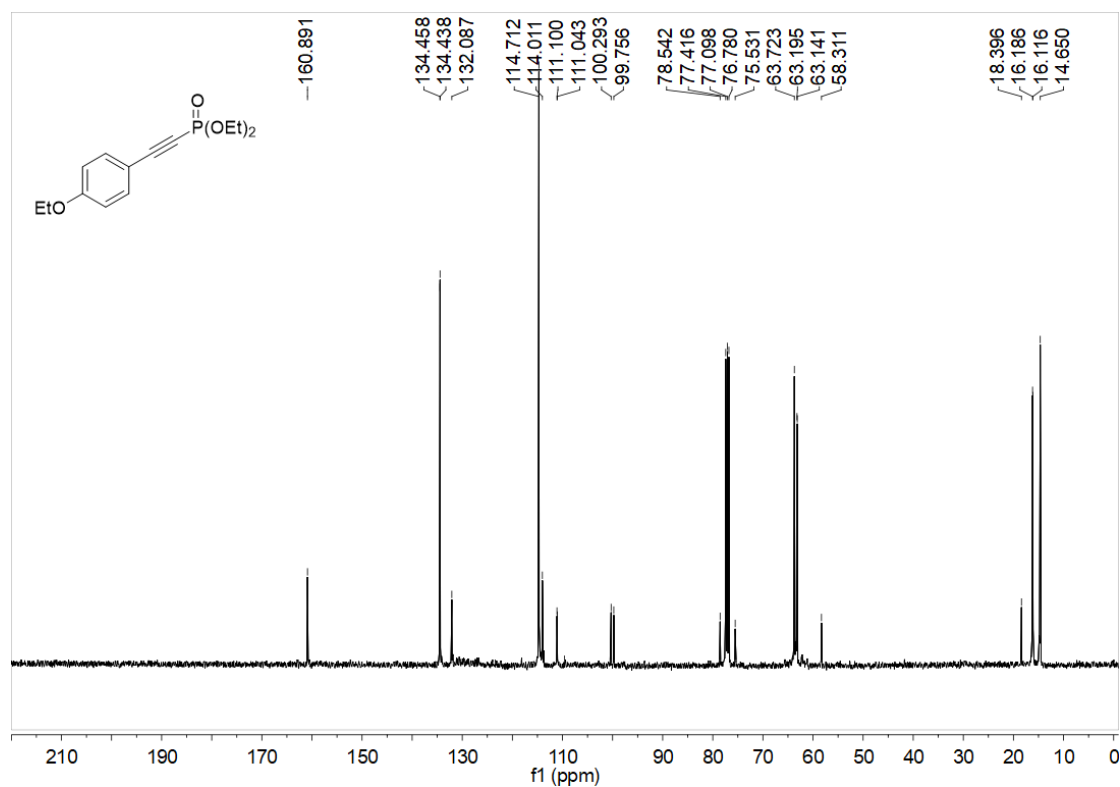
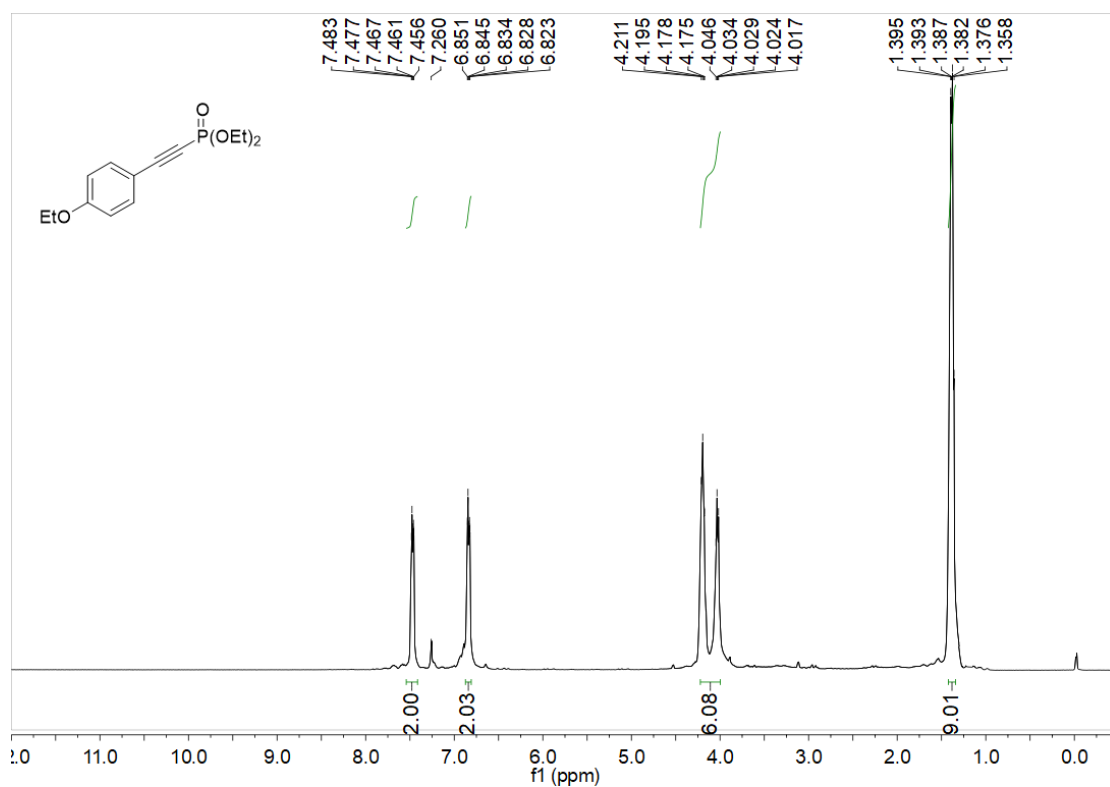


$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3d**

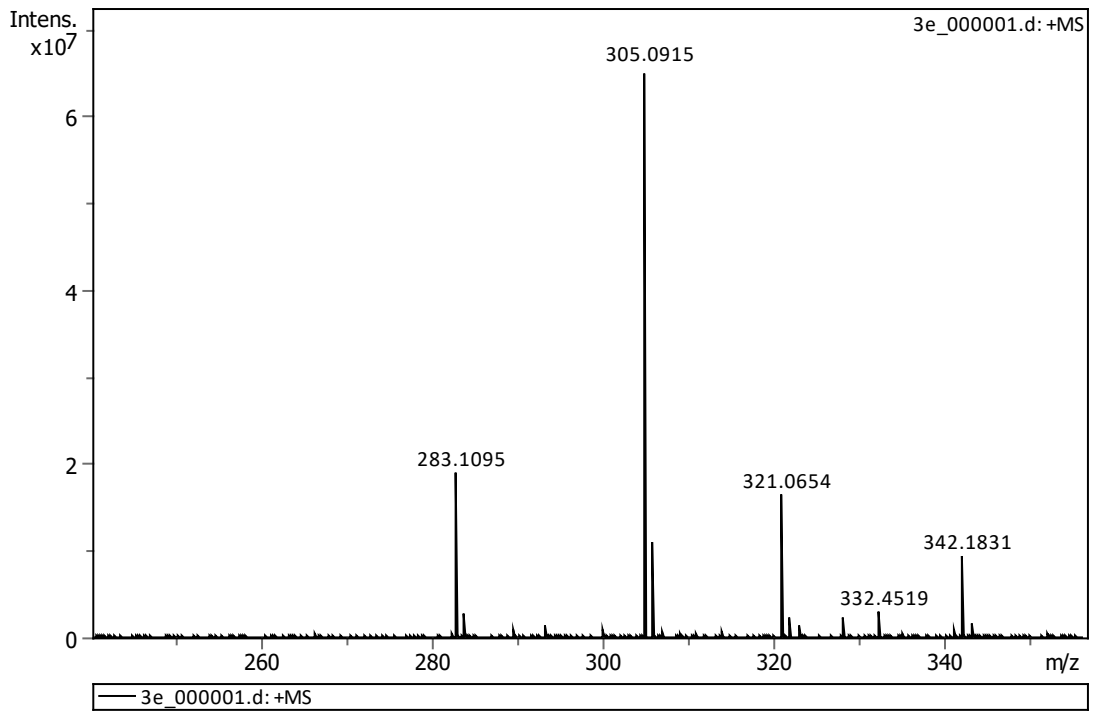
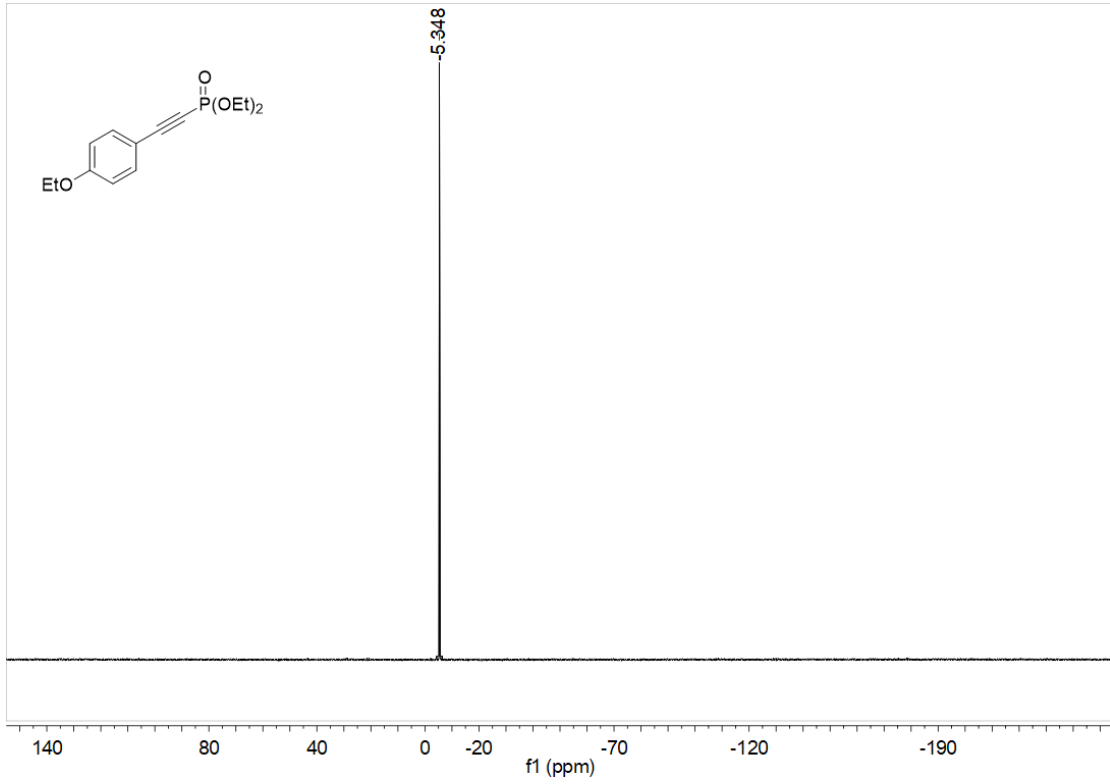




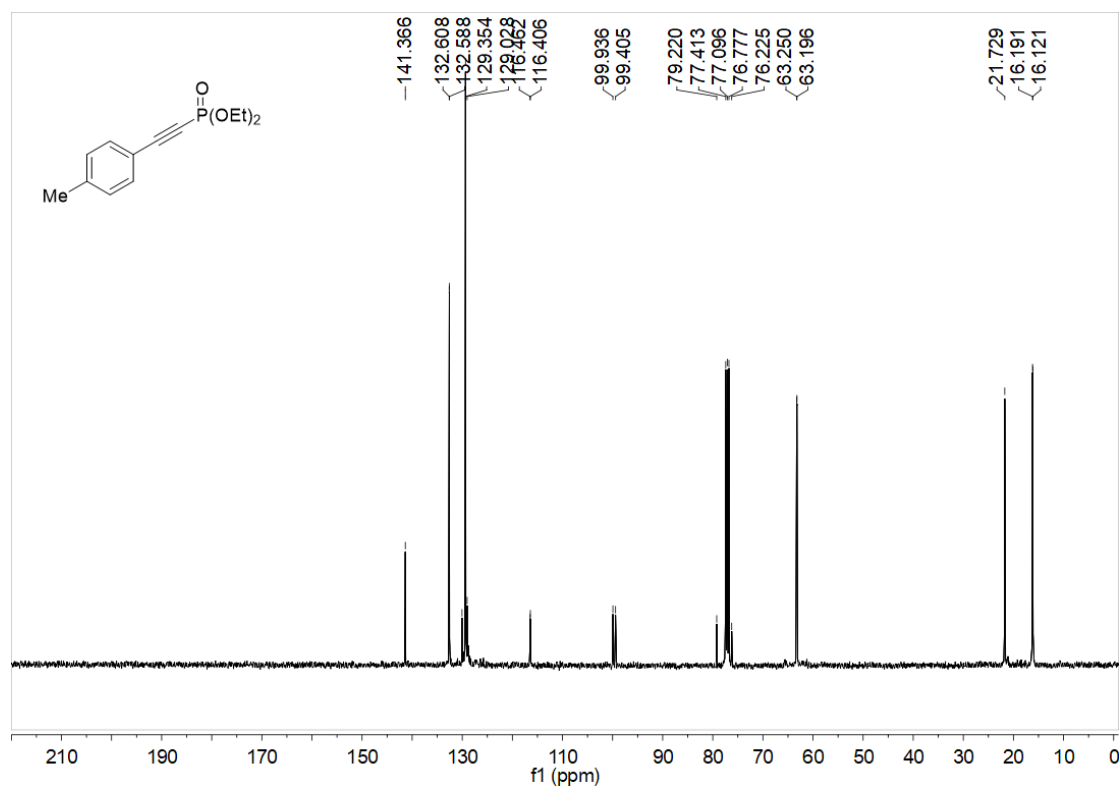
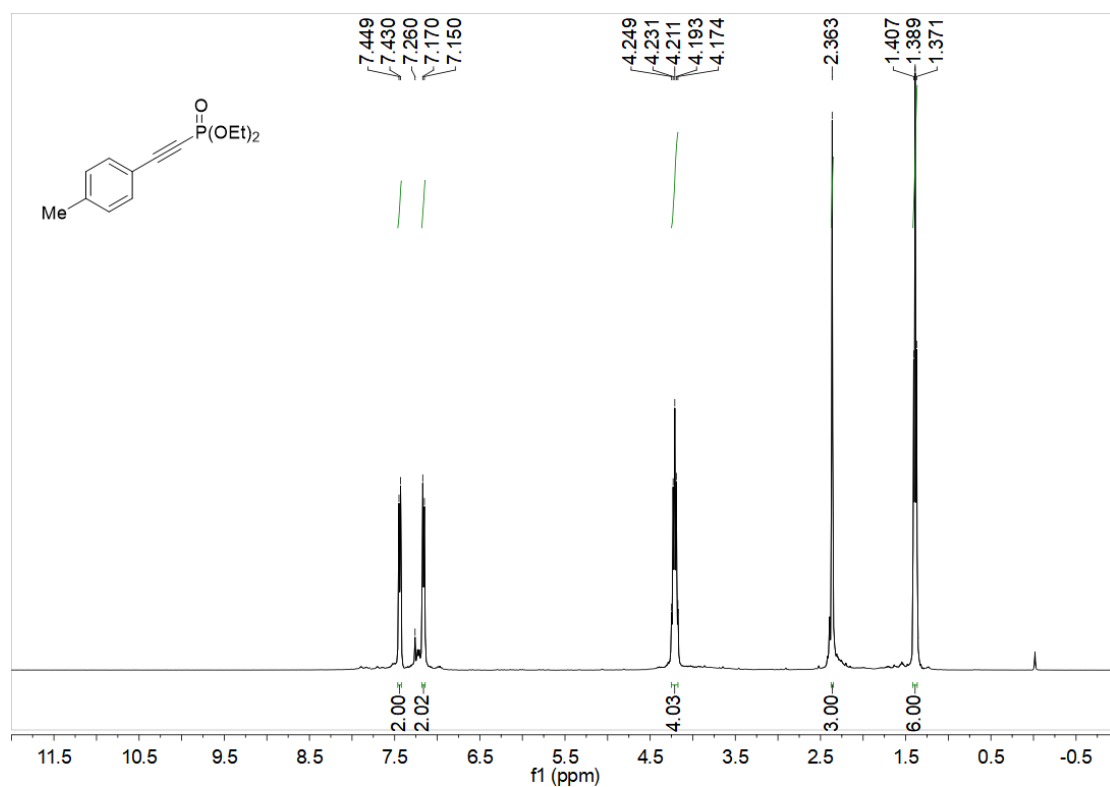
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3e**

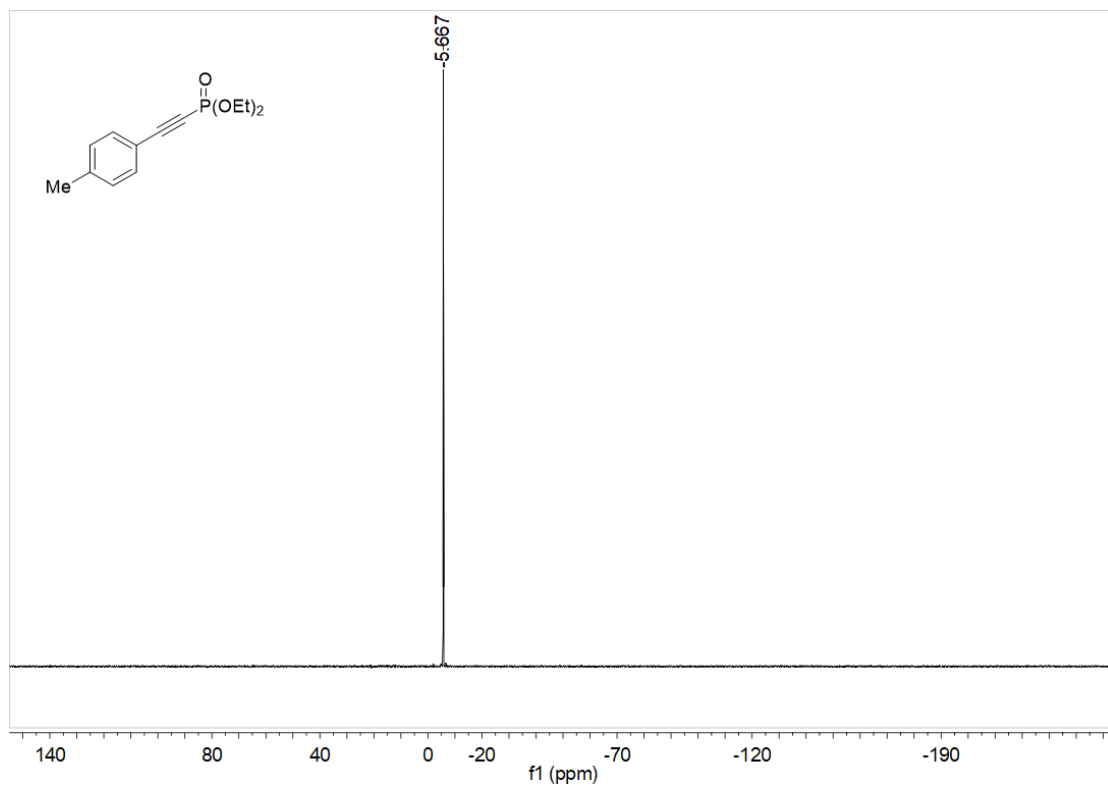




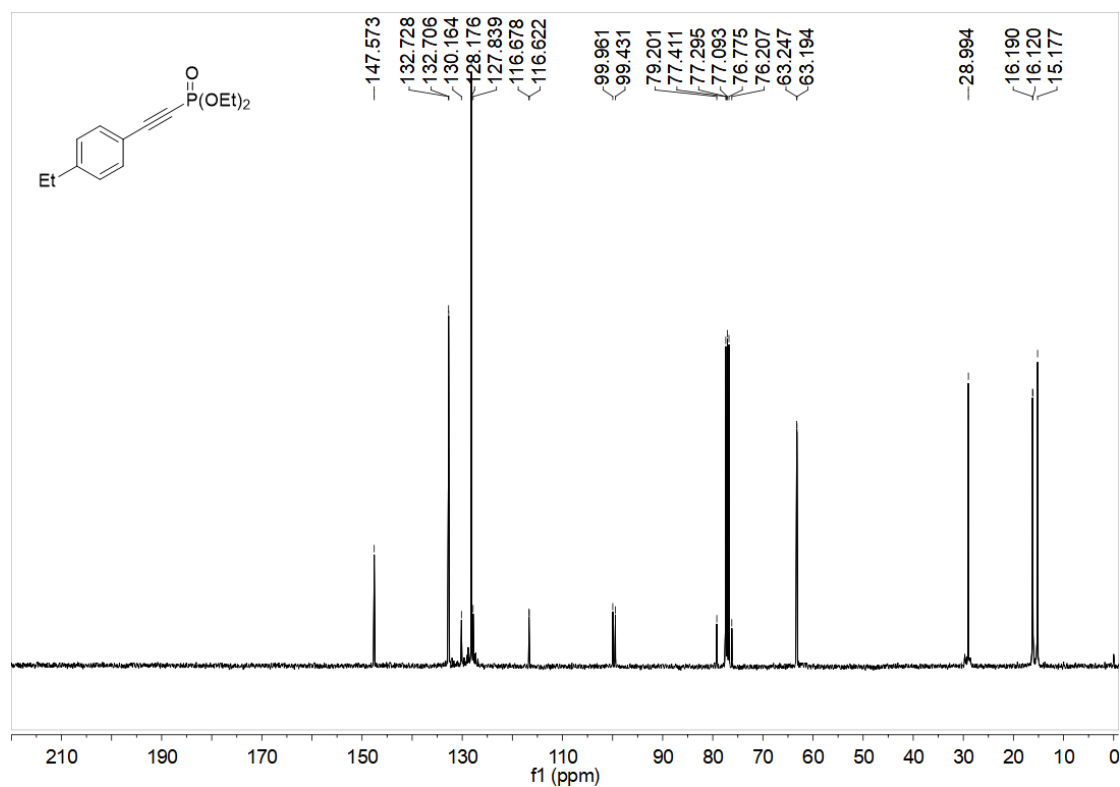
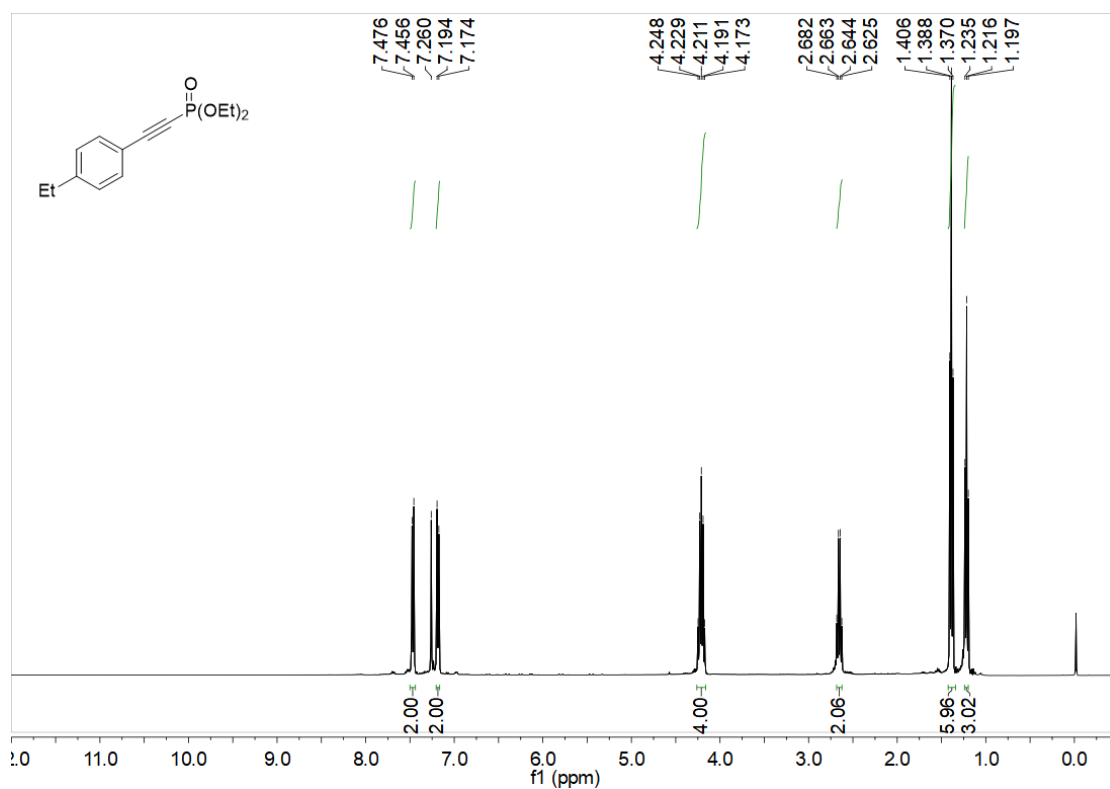


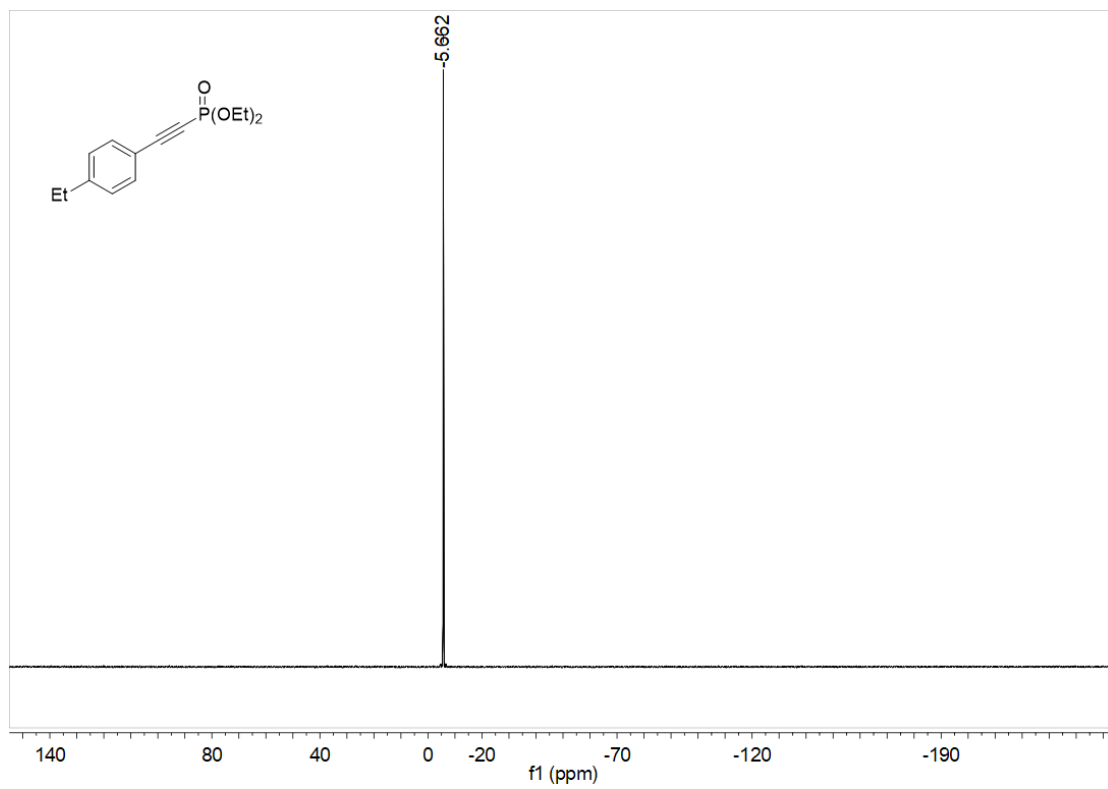
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3f**



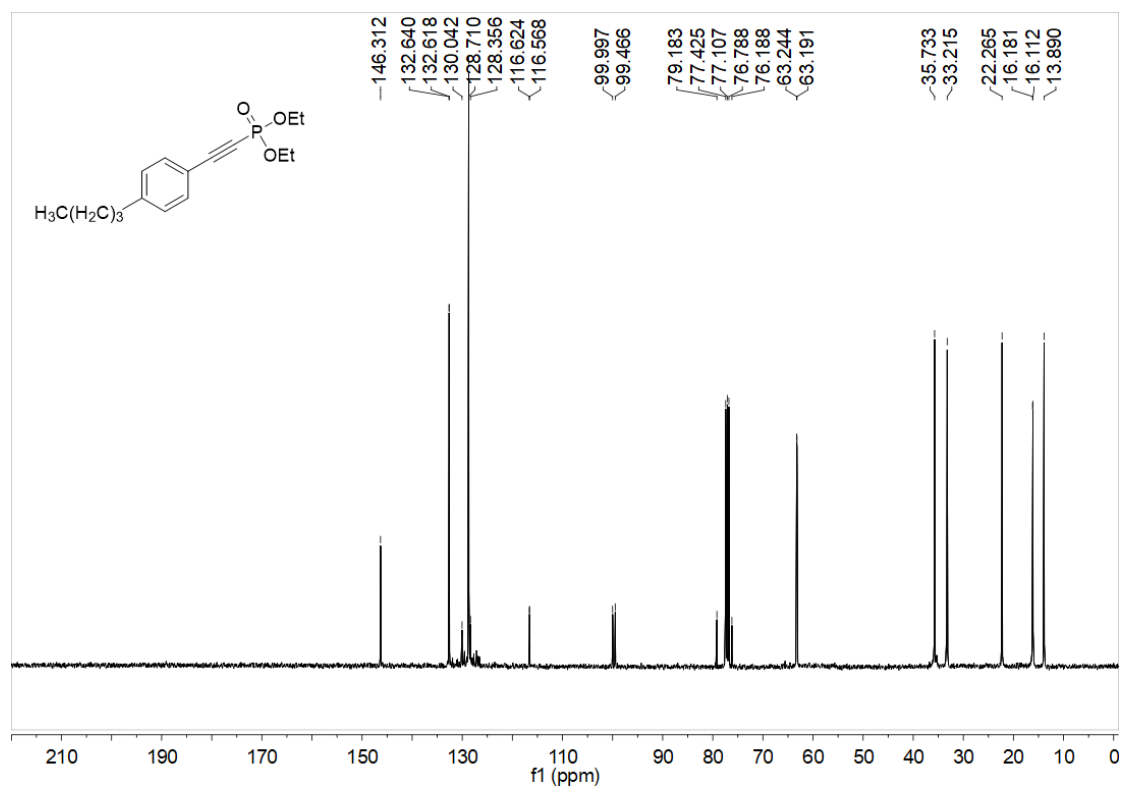
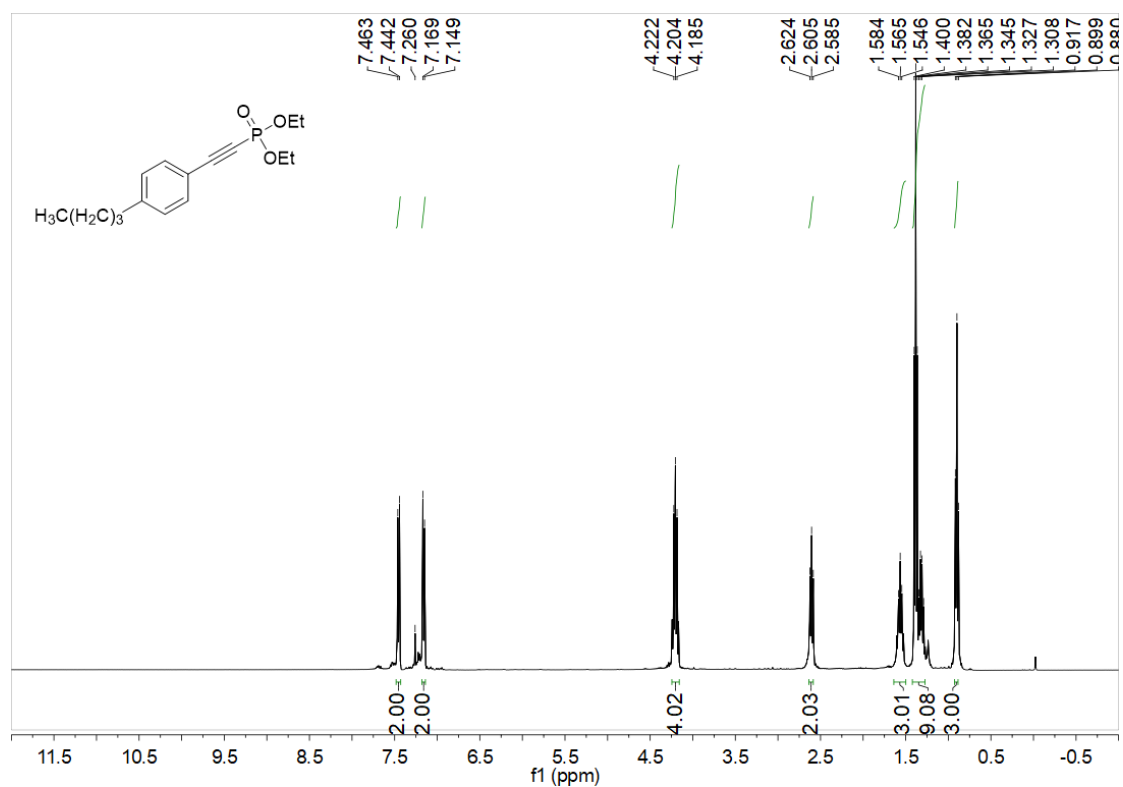


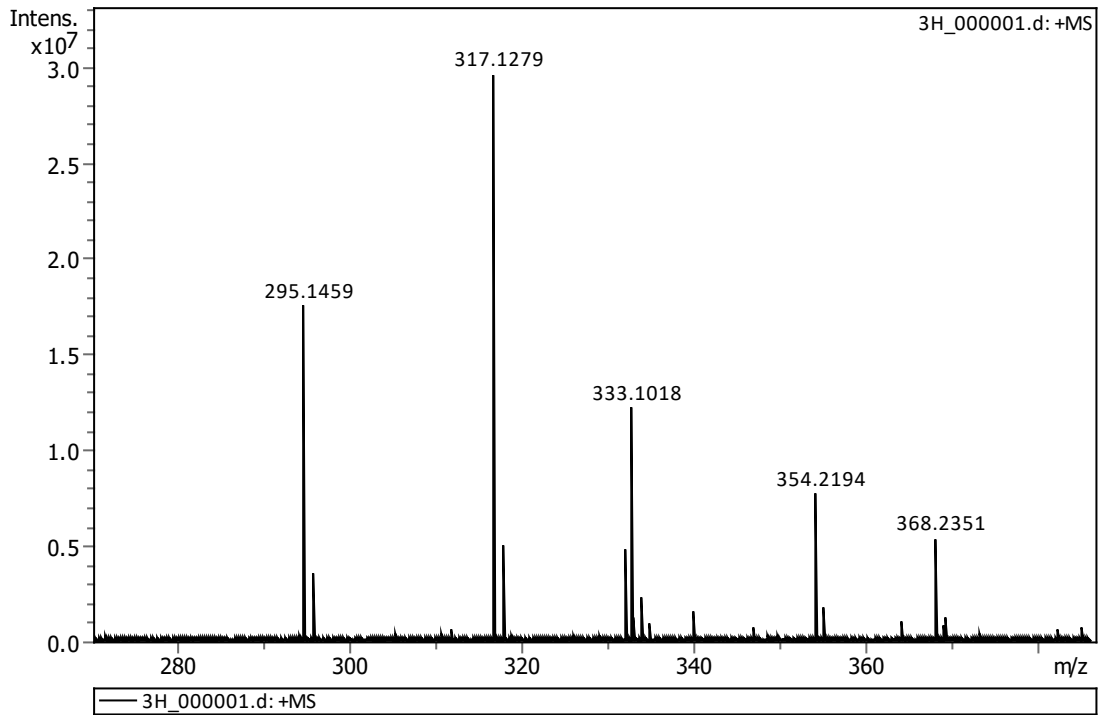
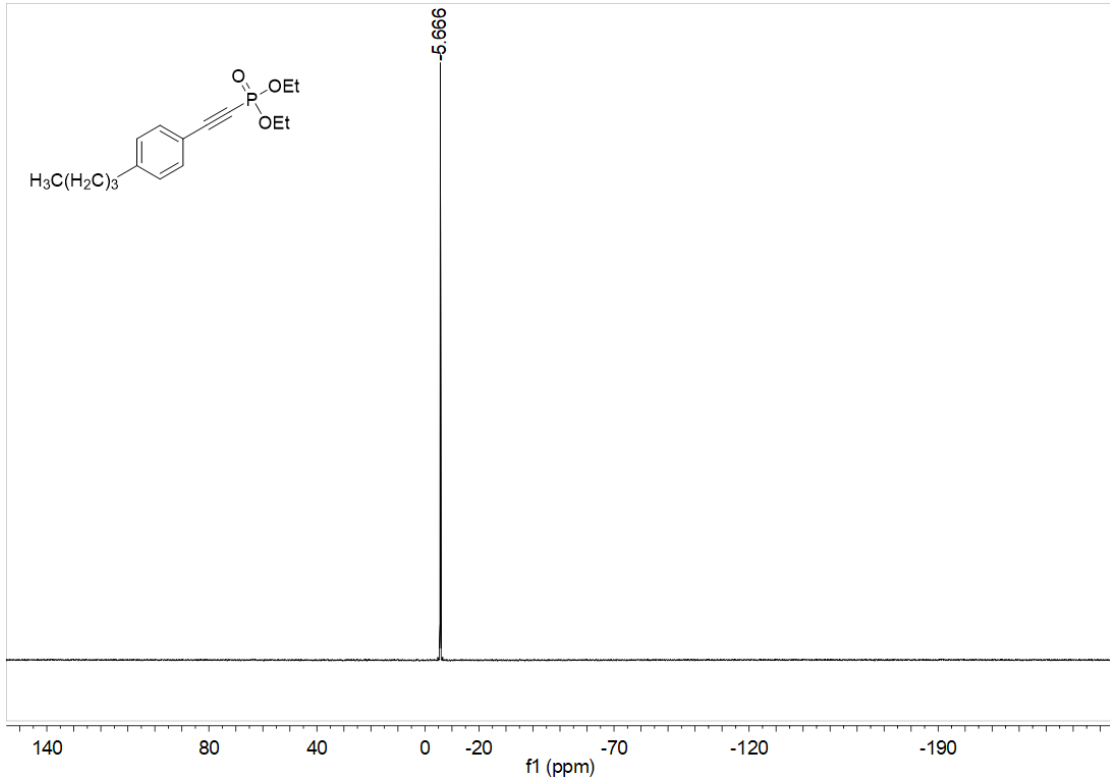
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3g**



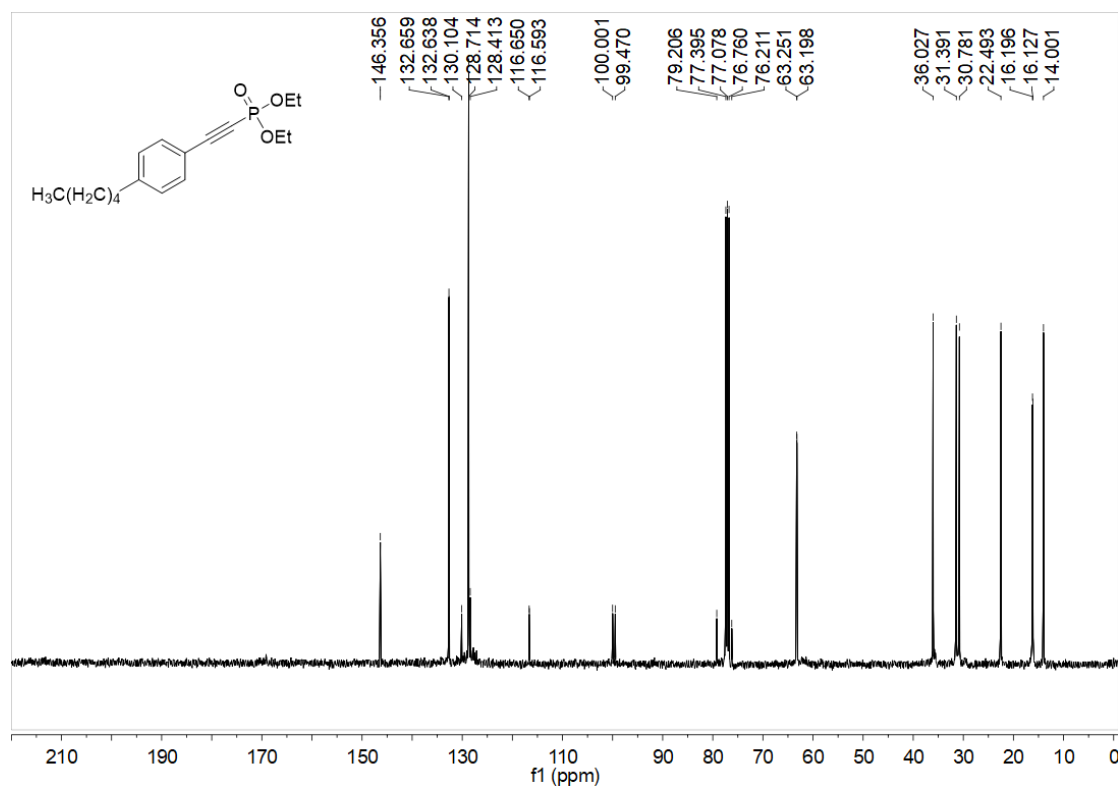
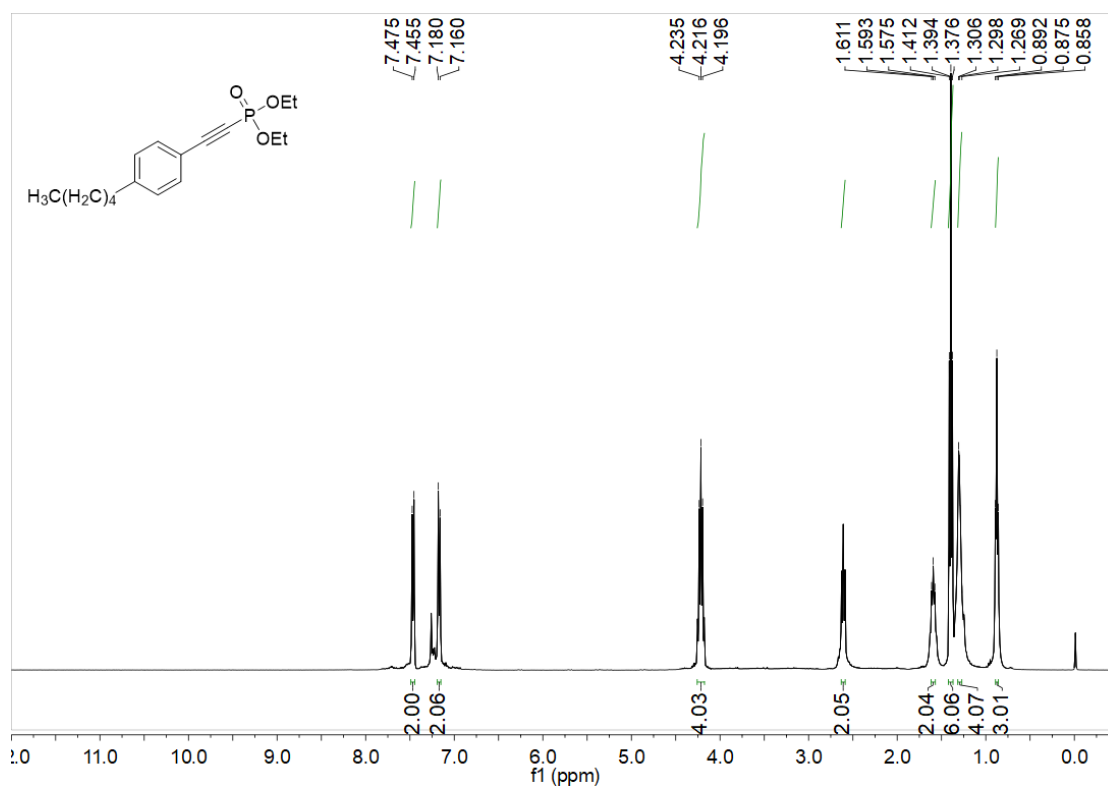


$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3h**

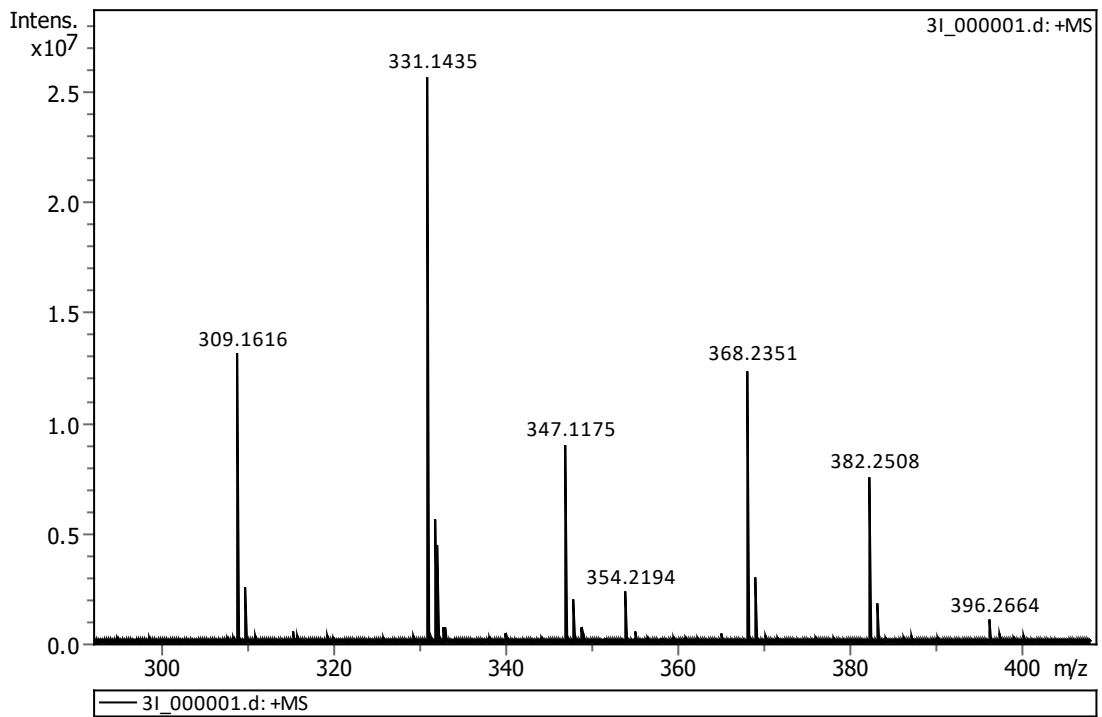
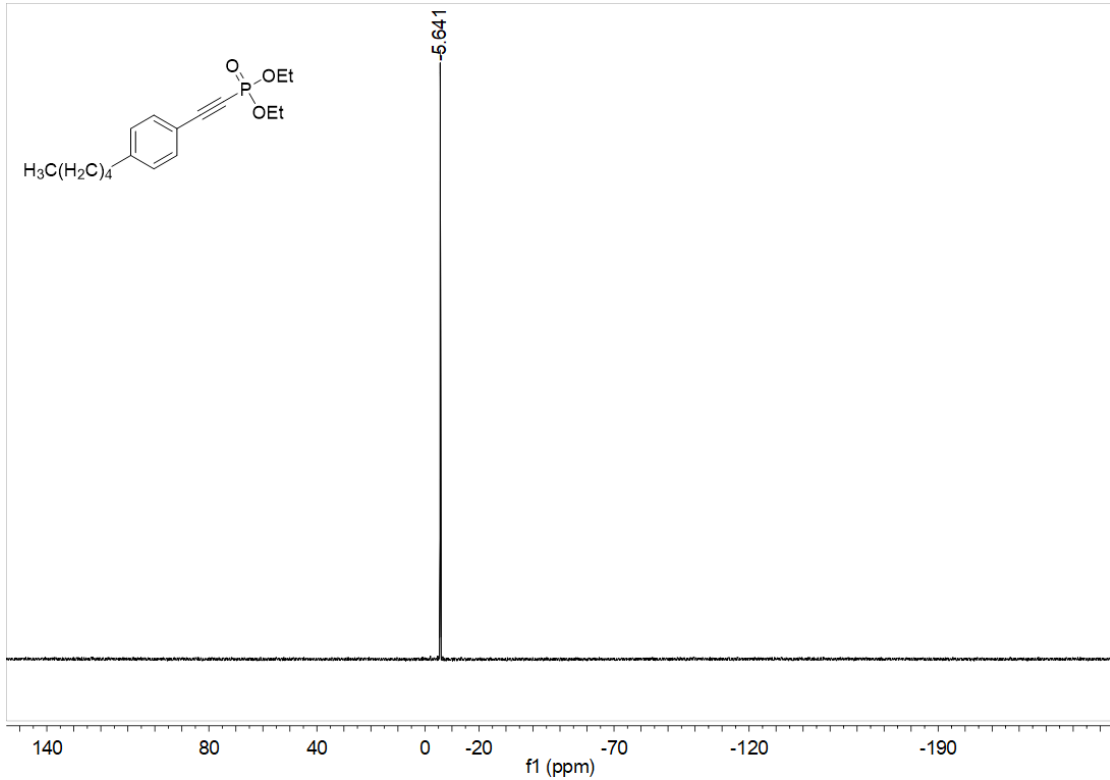




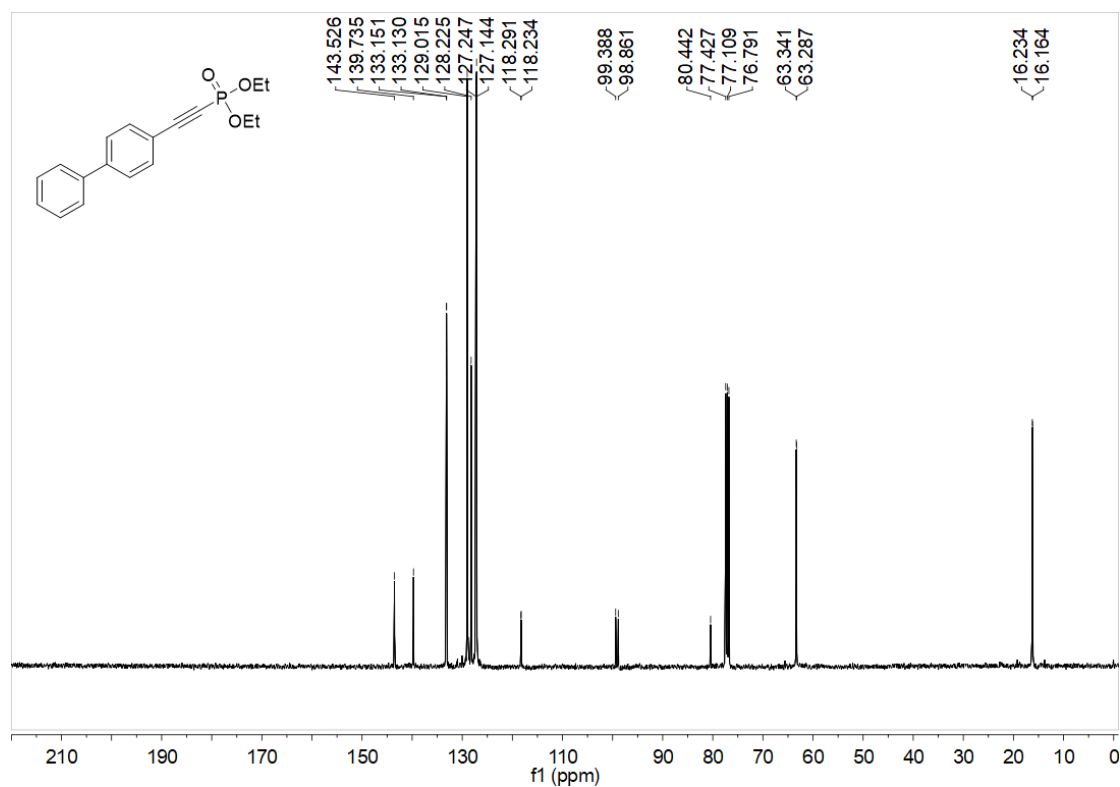
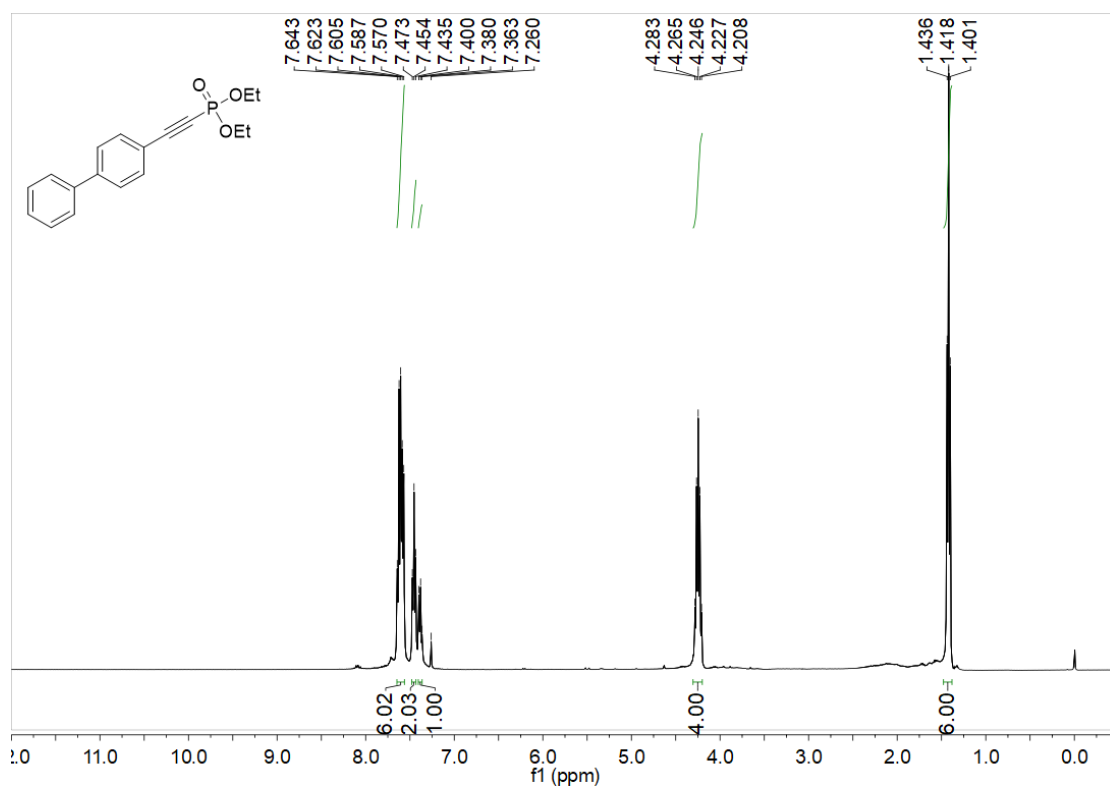
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3i**

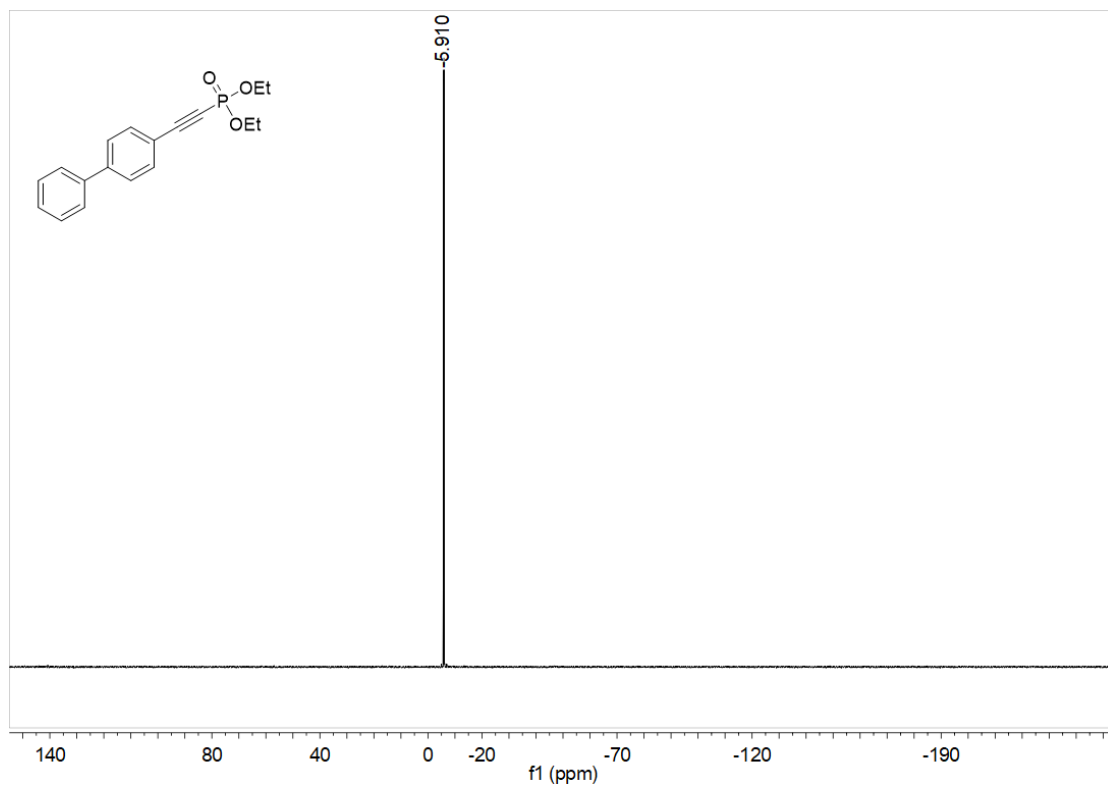




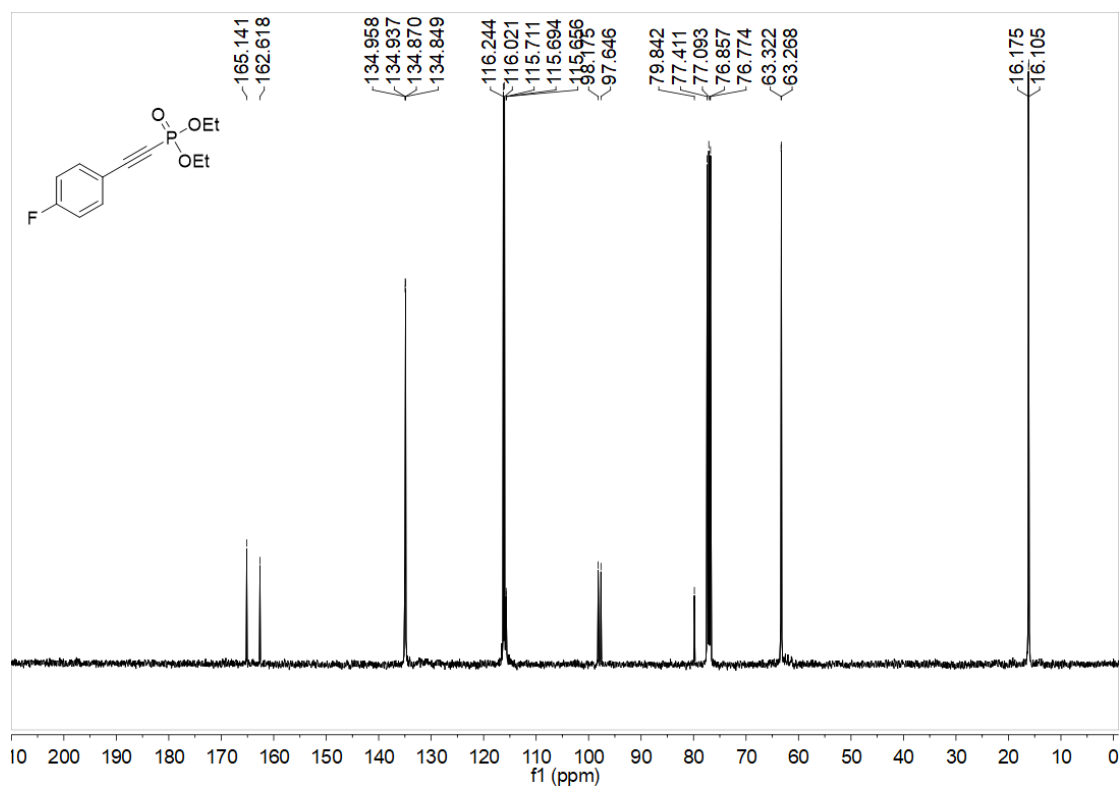
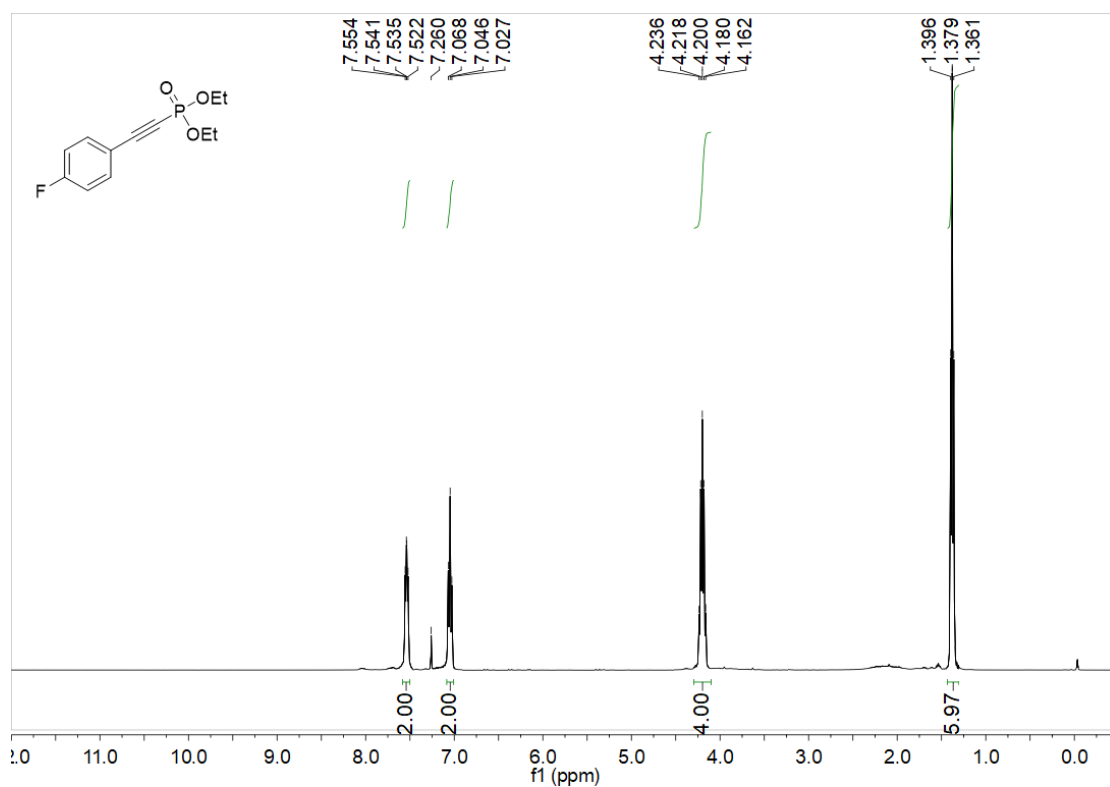


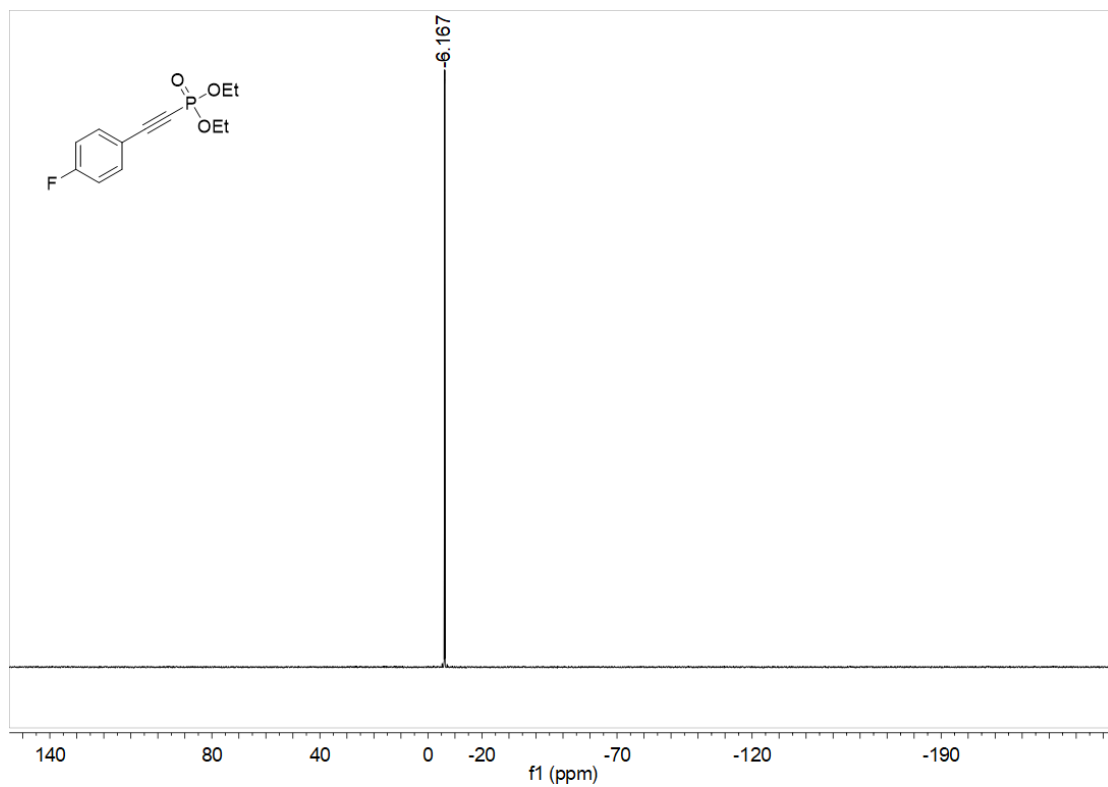
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3j**



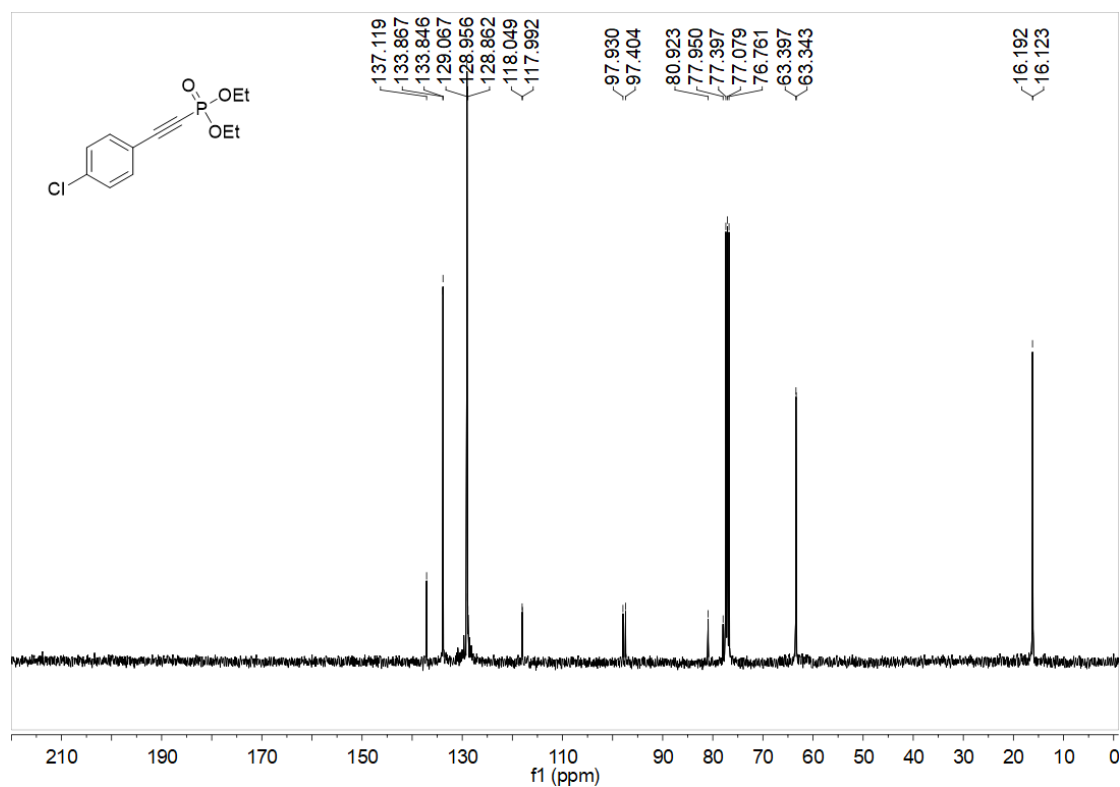
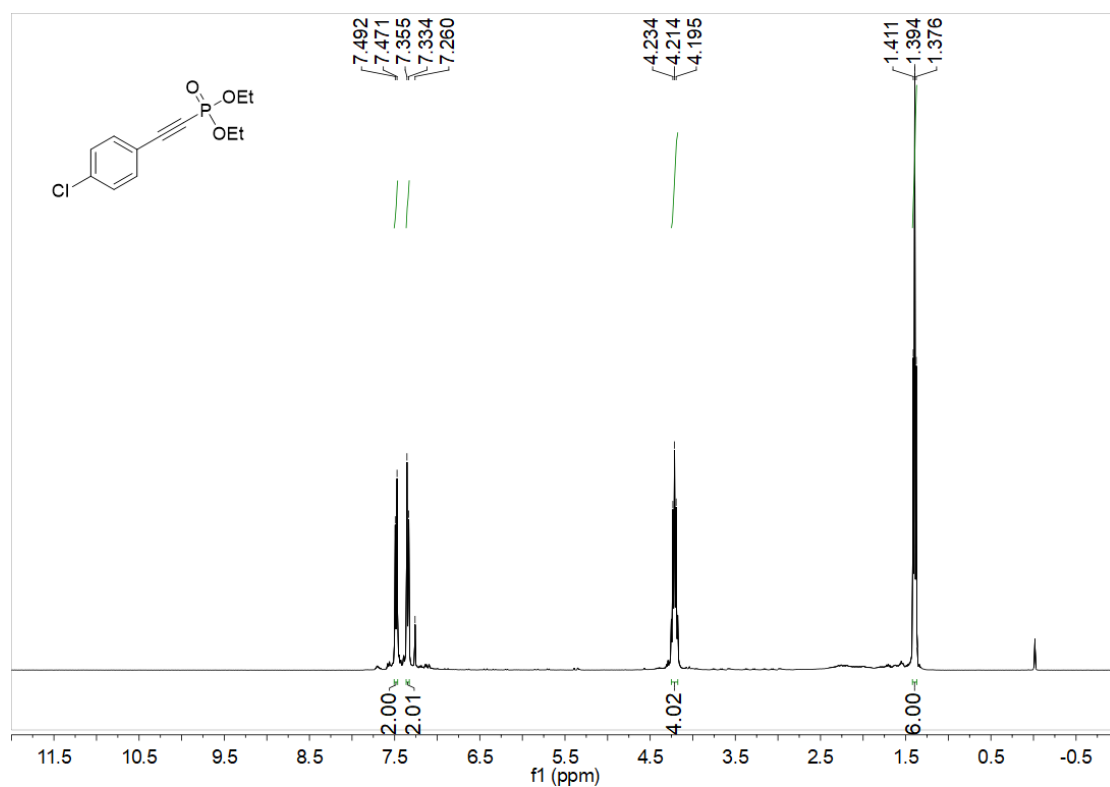


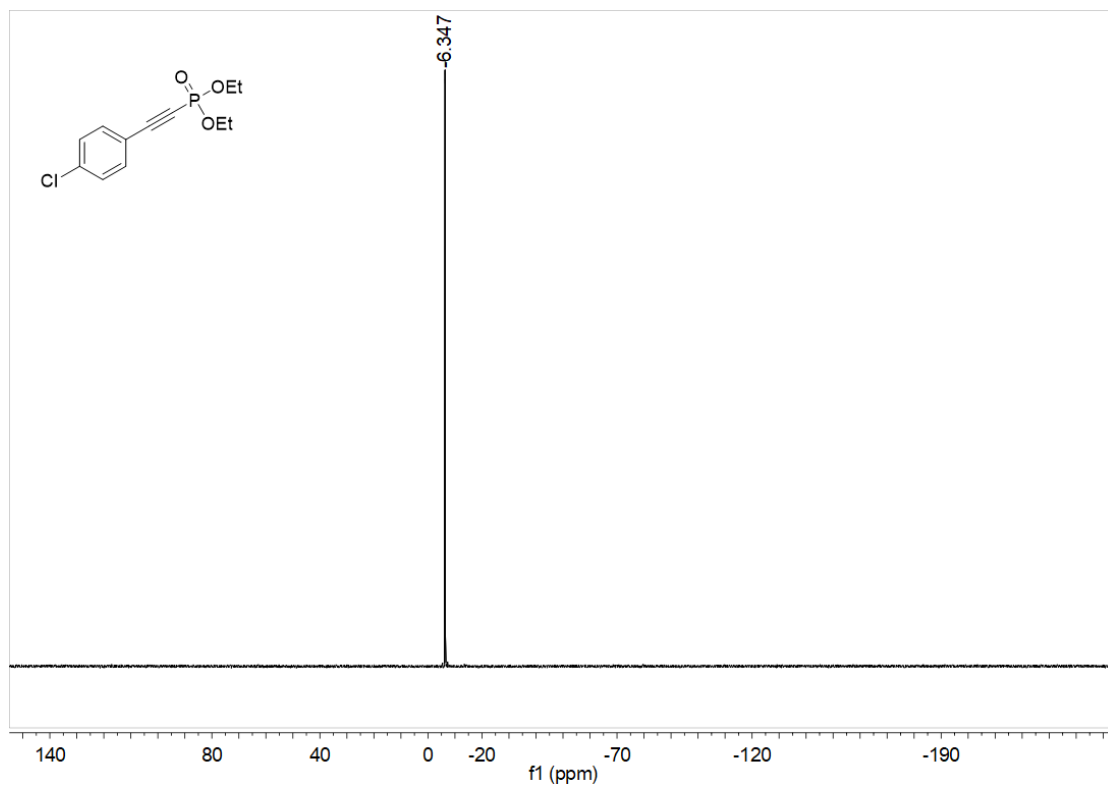
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3k**



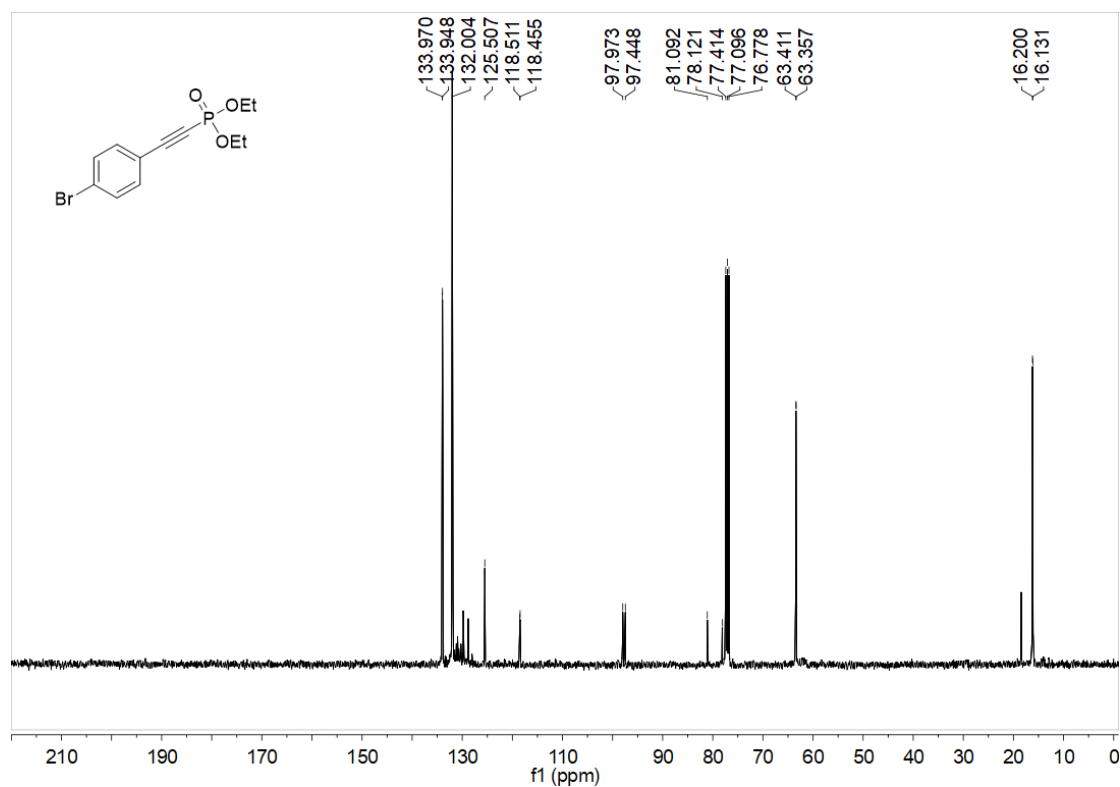
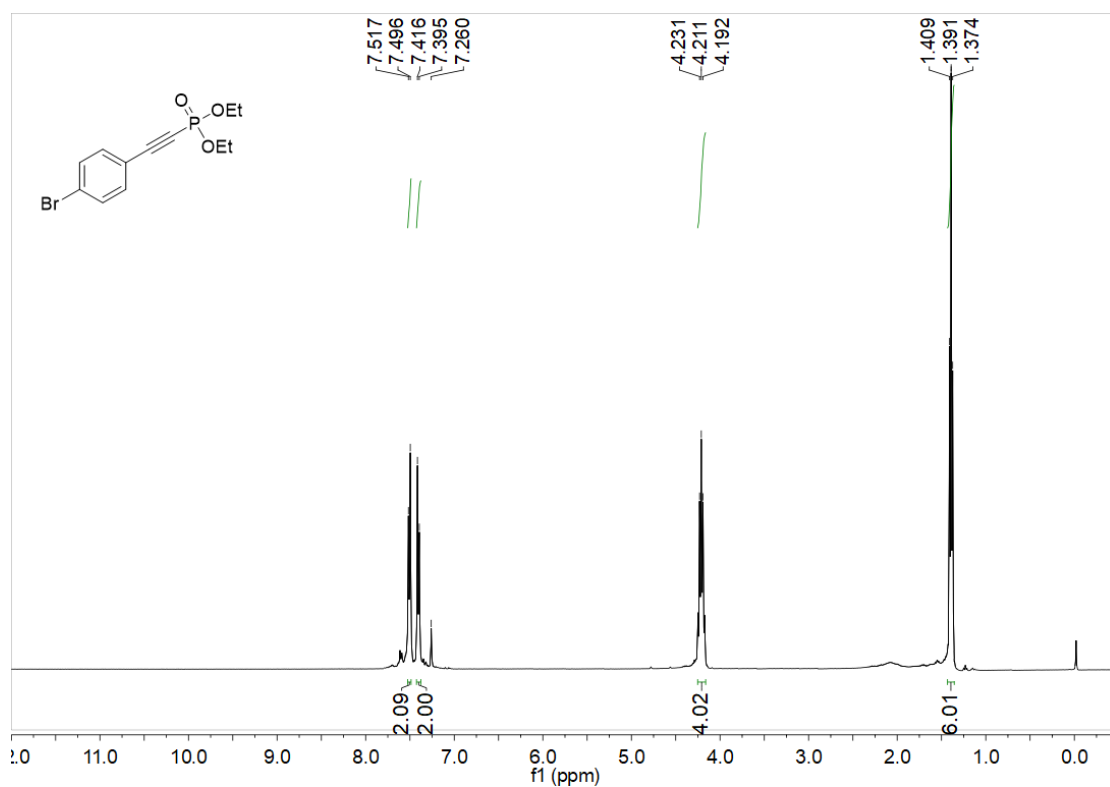


$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **31**

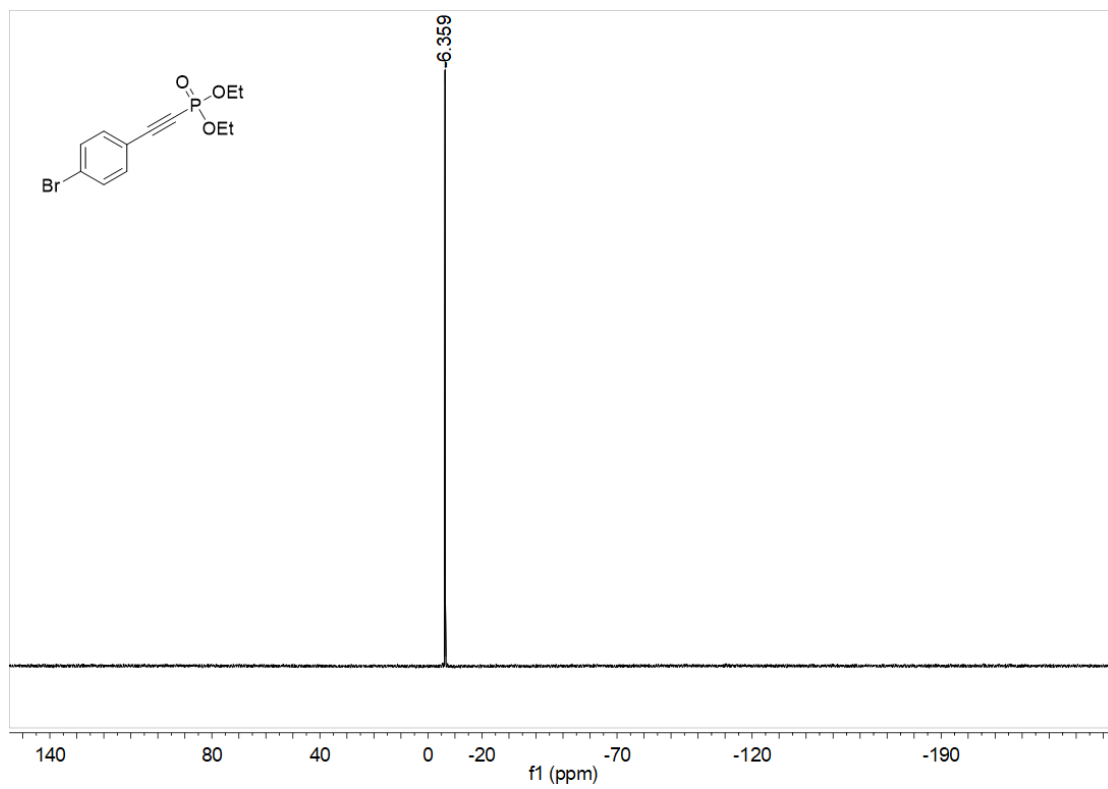




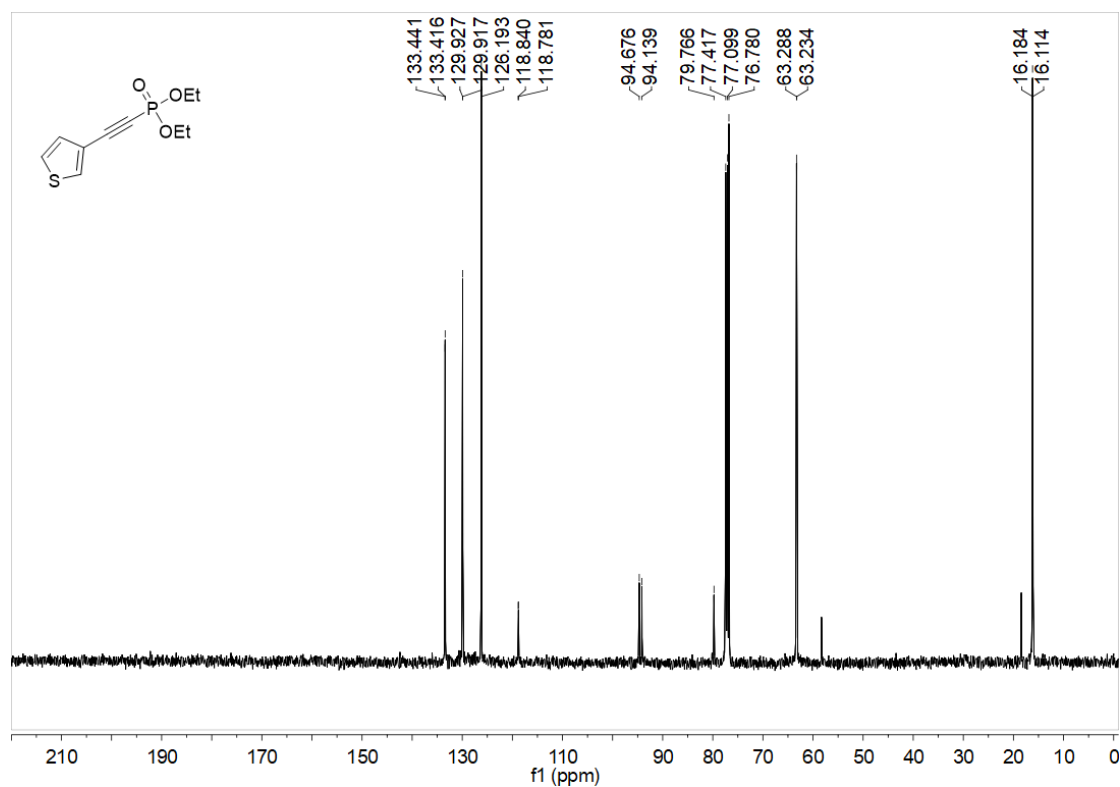
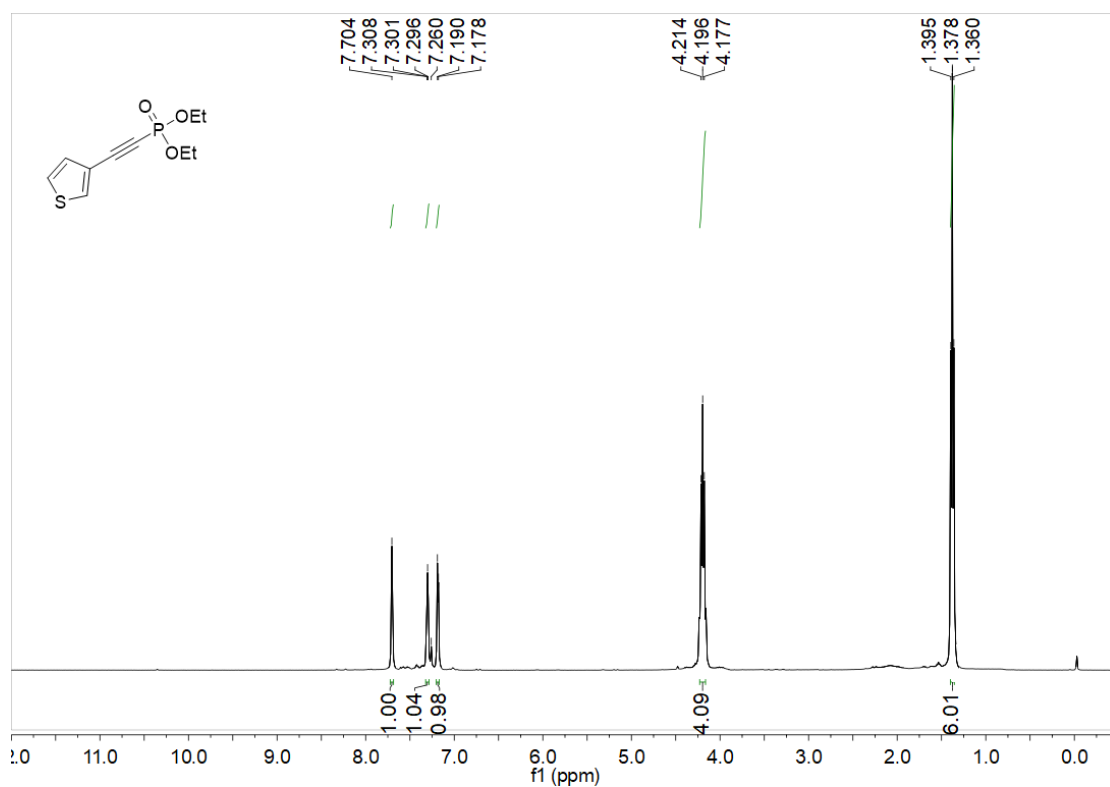
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3m**

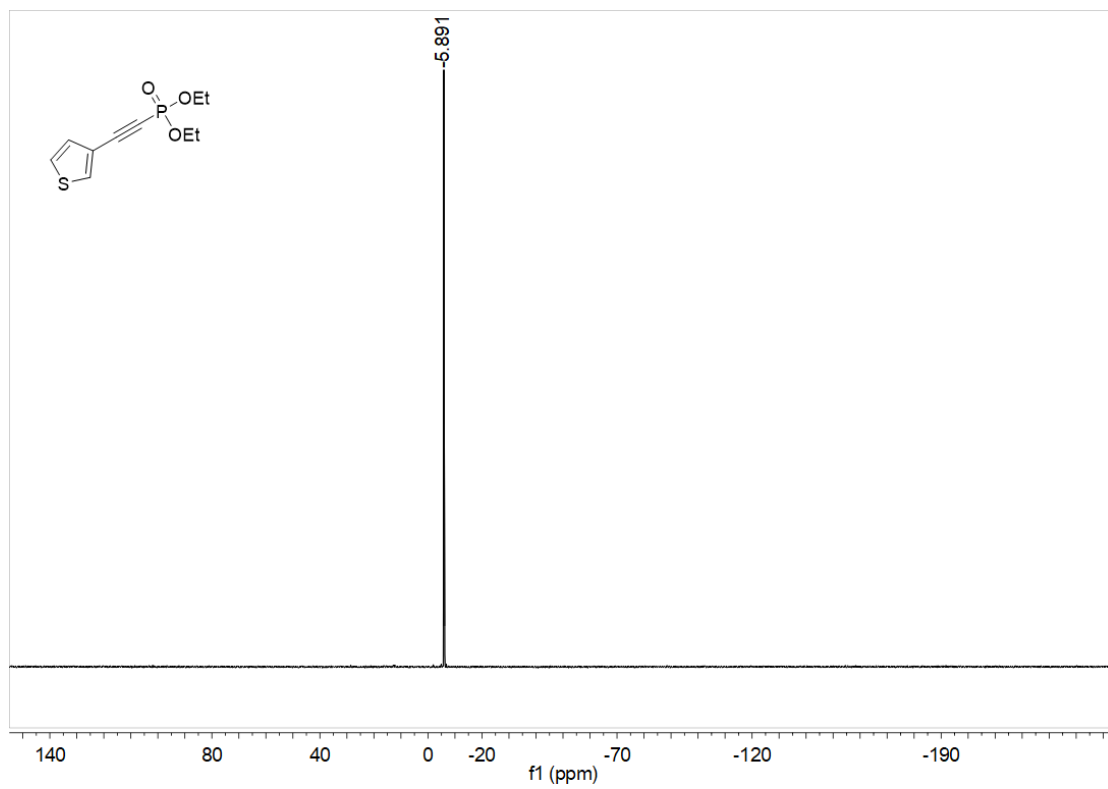




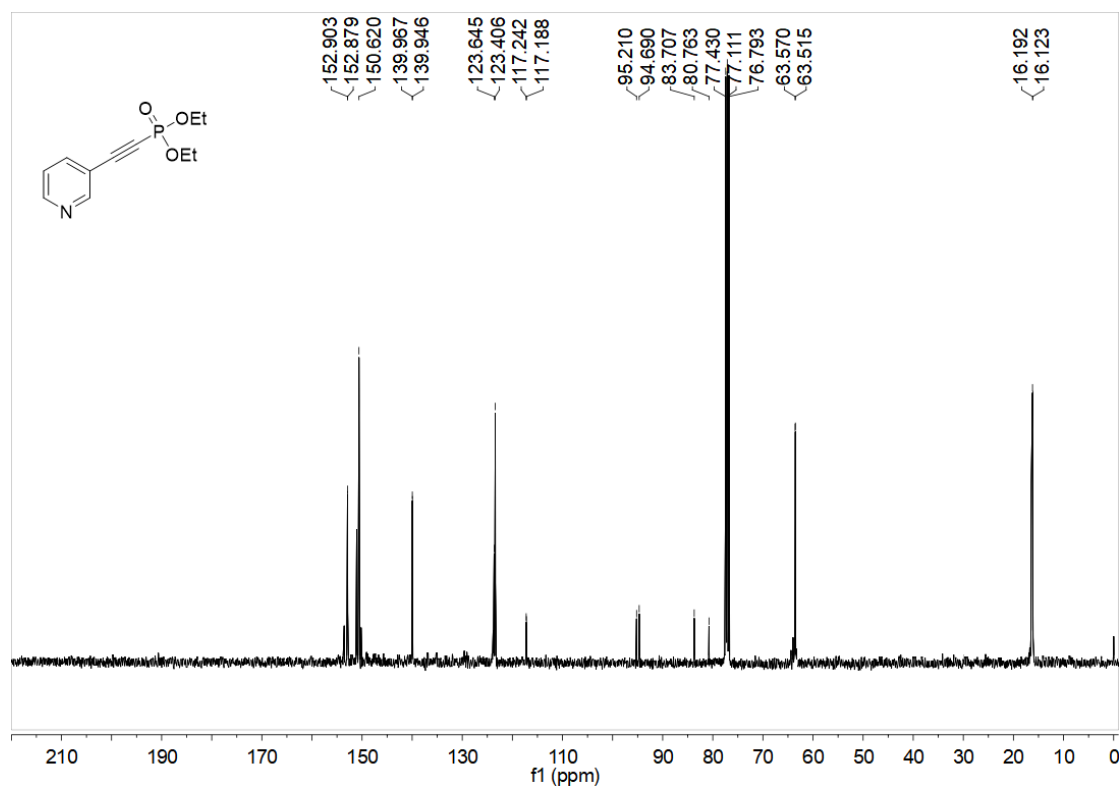
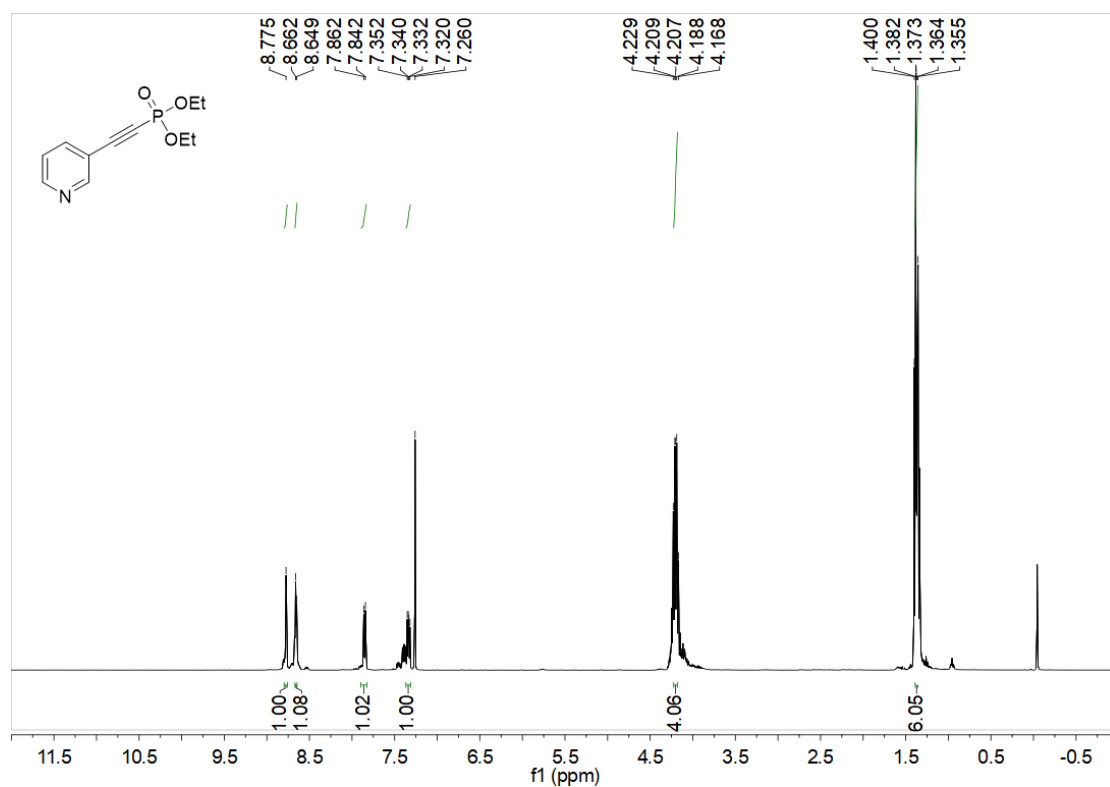


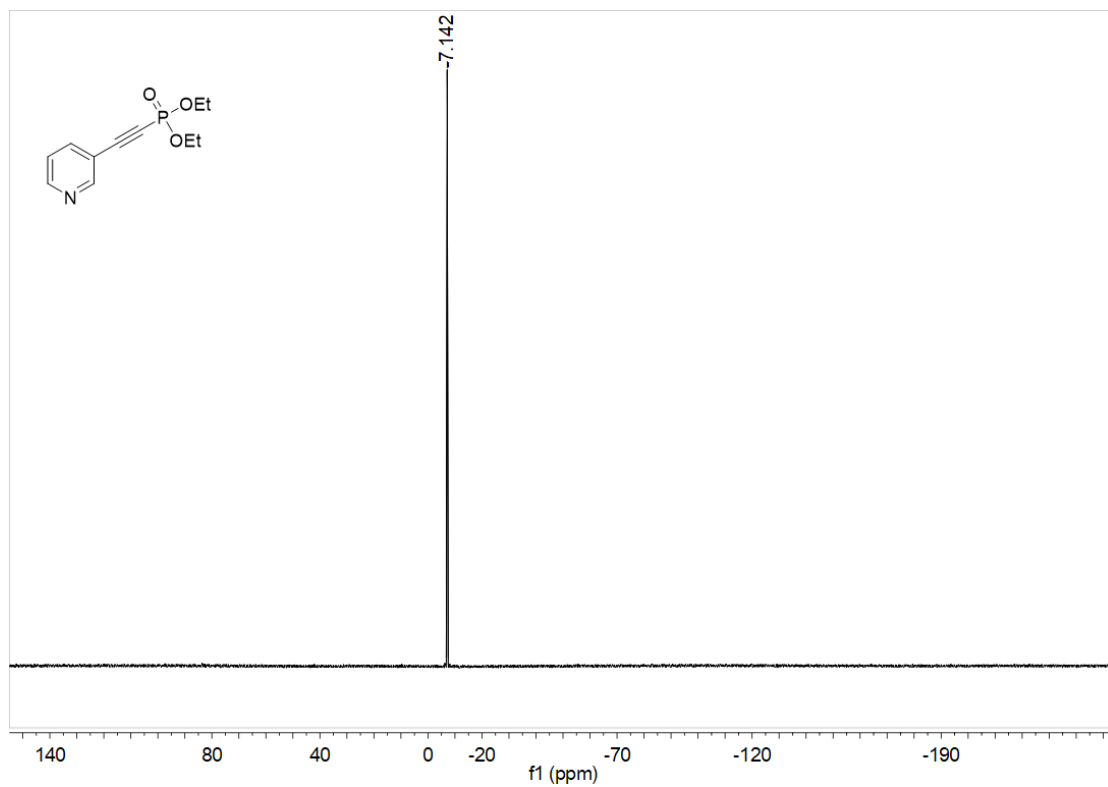
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3n**



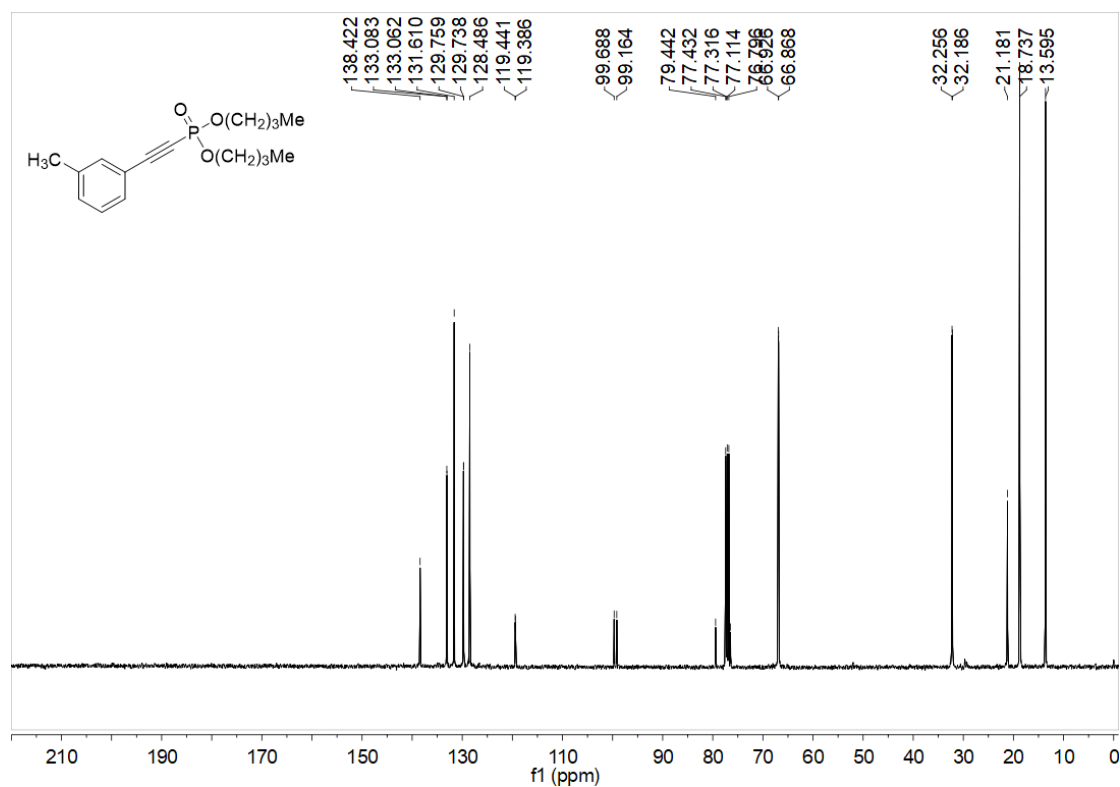
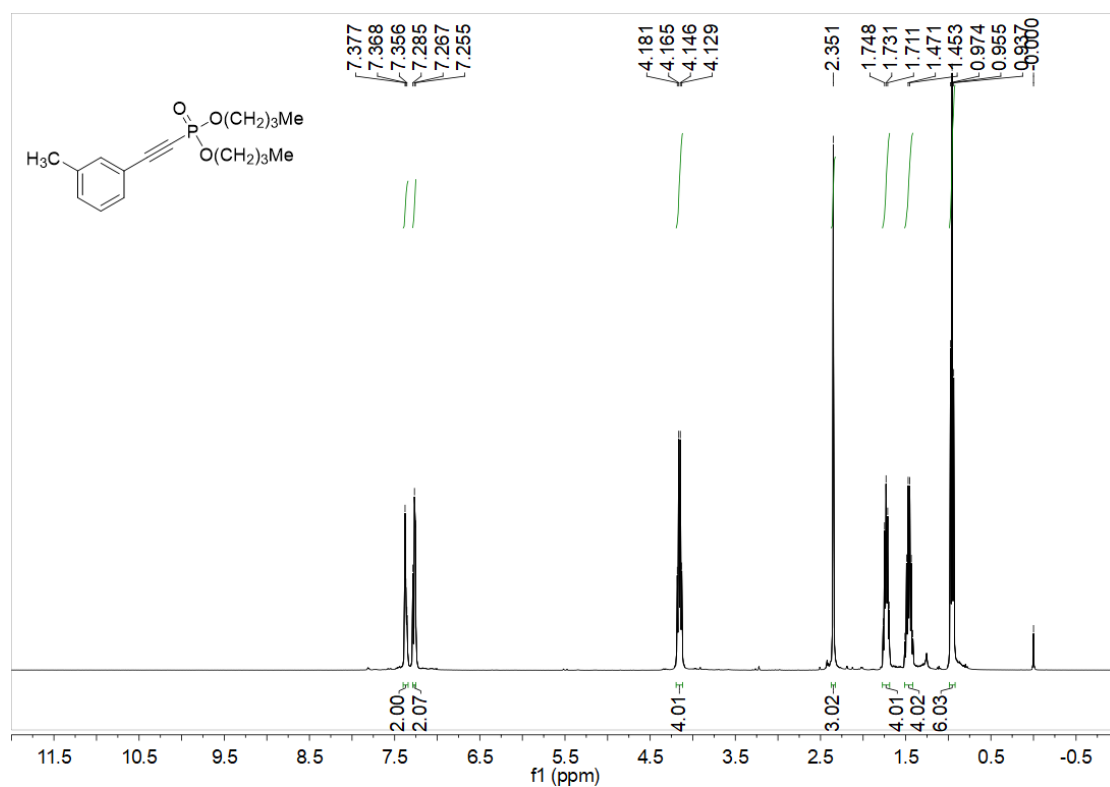


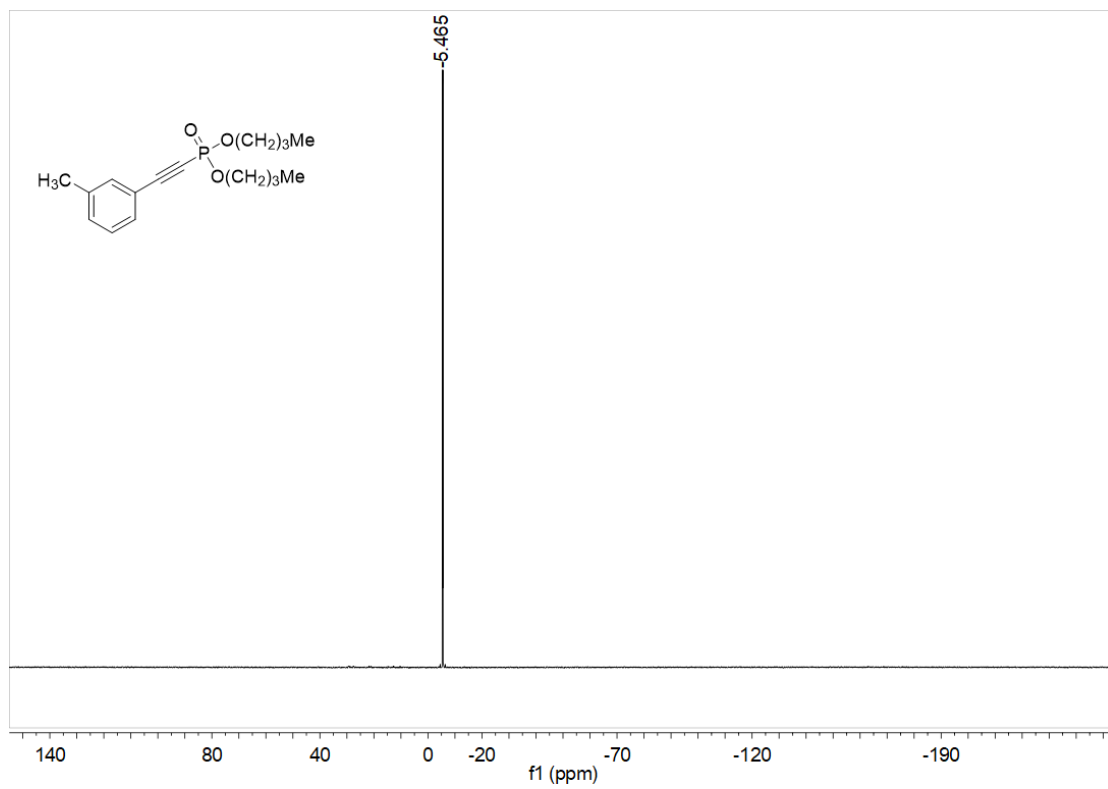
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3o**



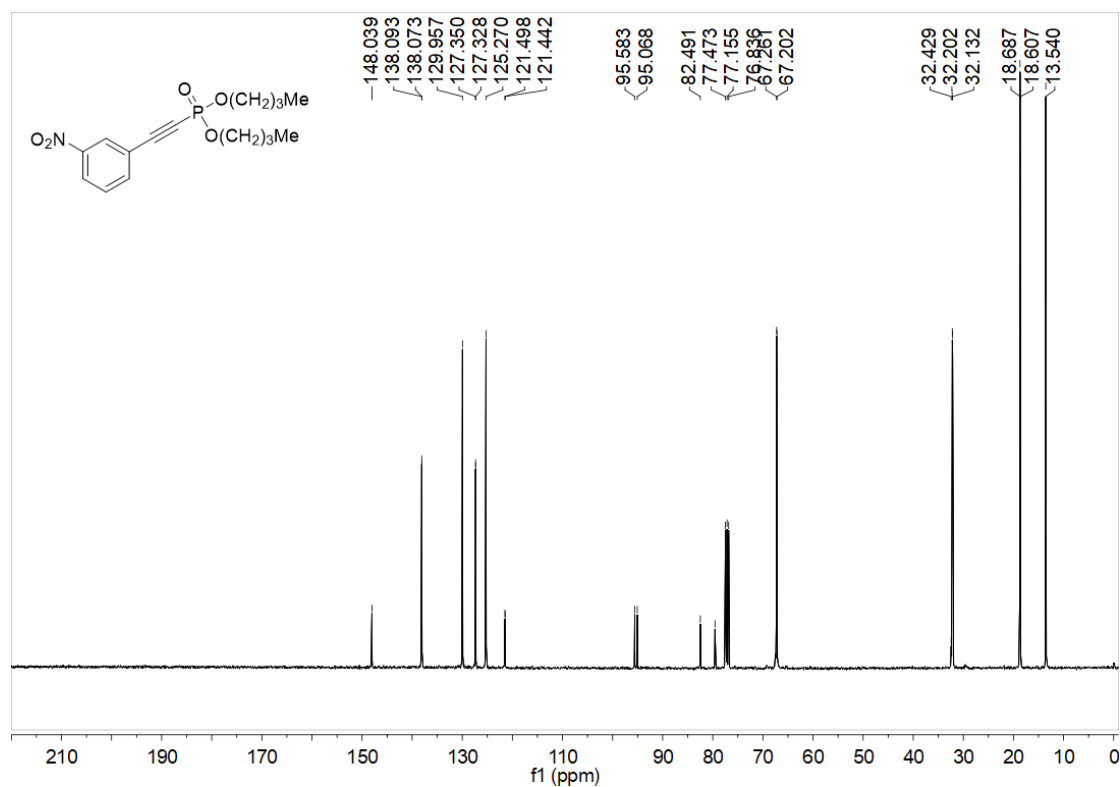
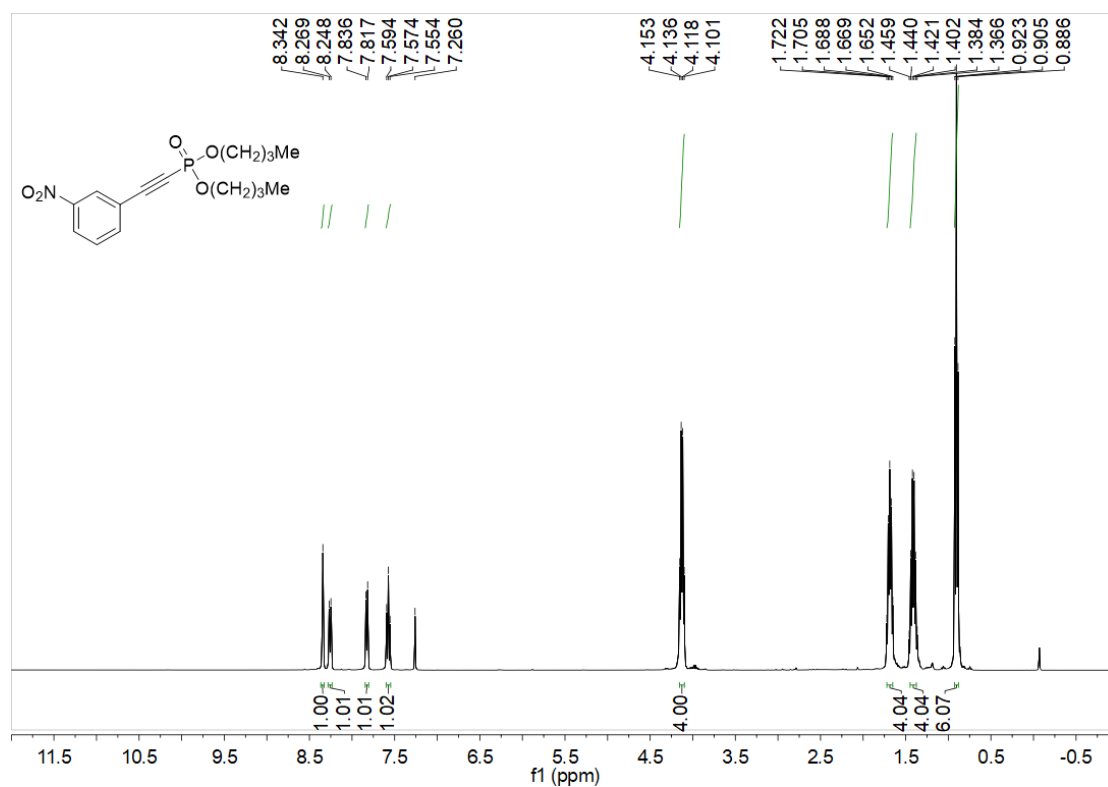


$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3p**

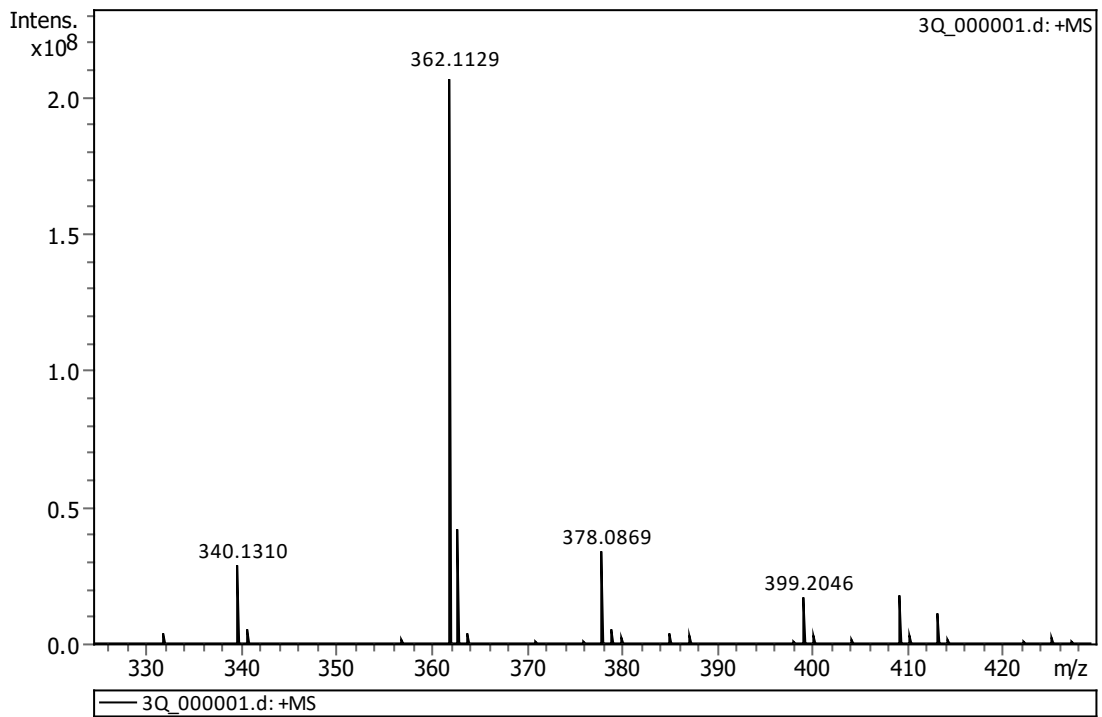
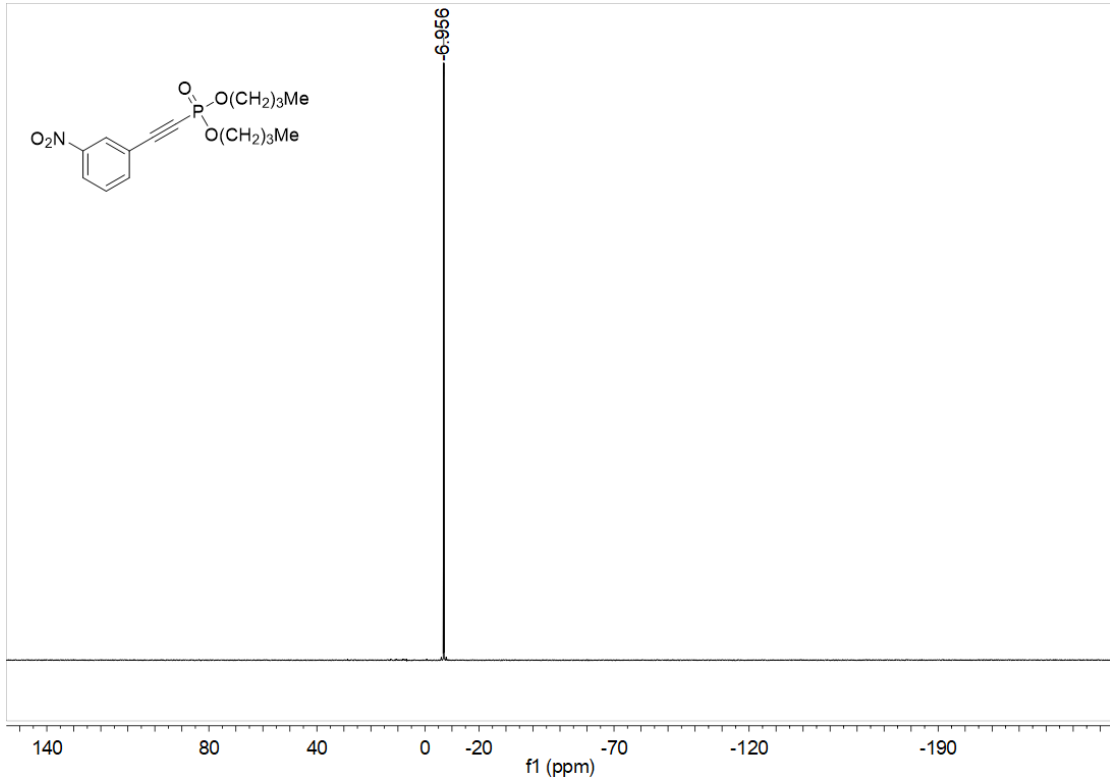




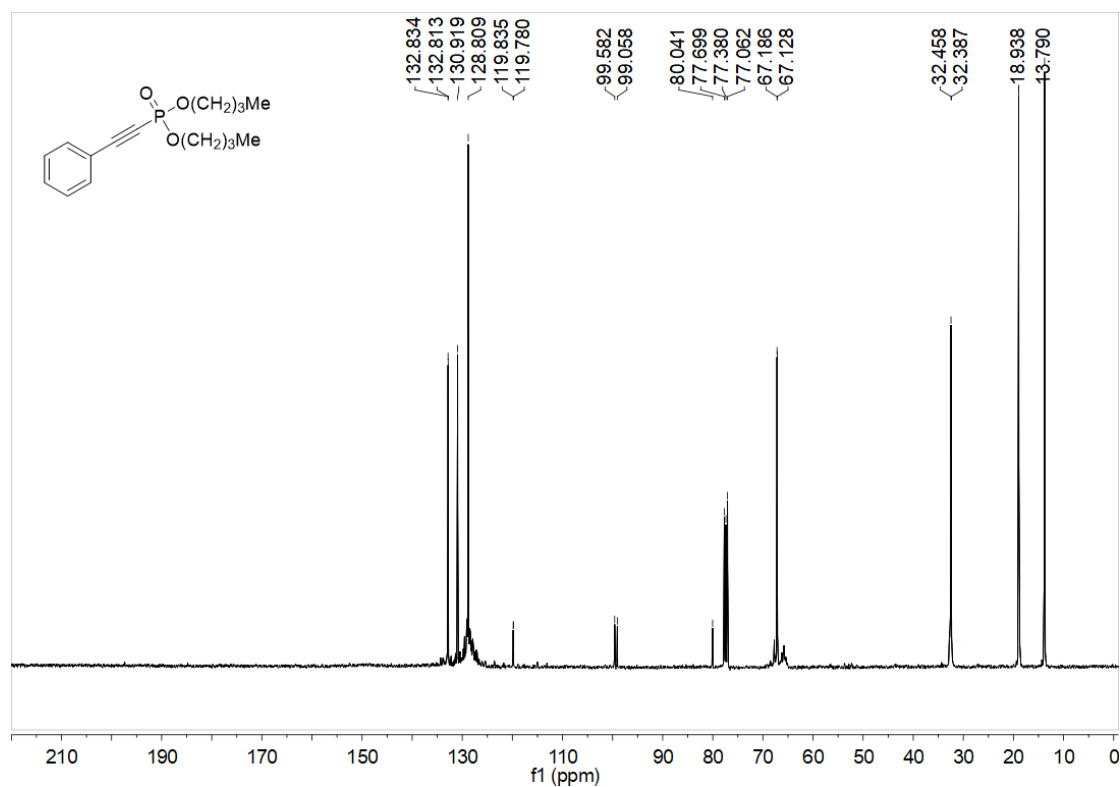
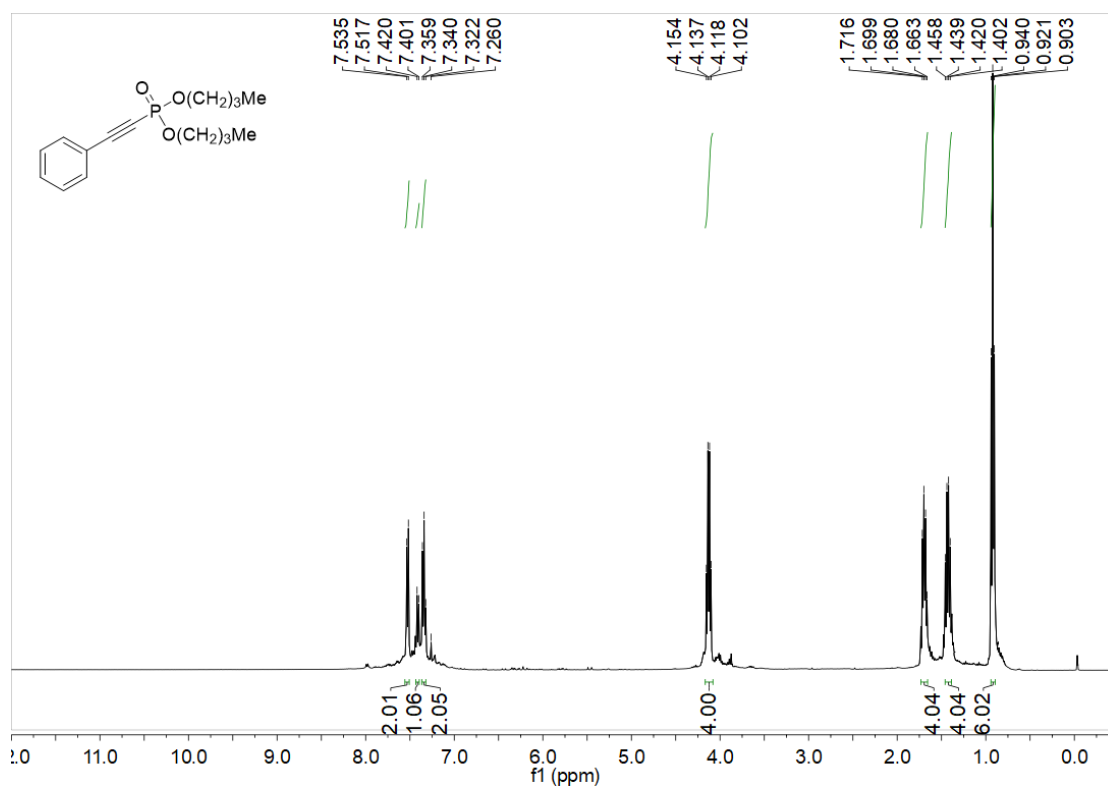
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3q**

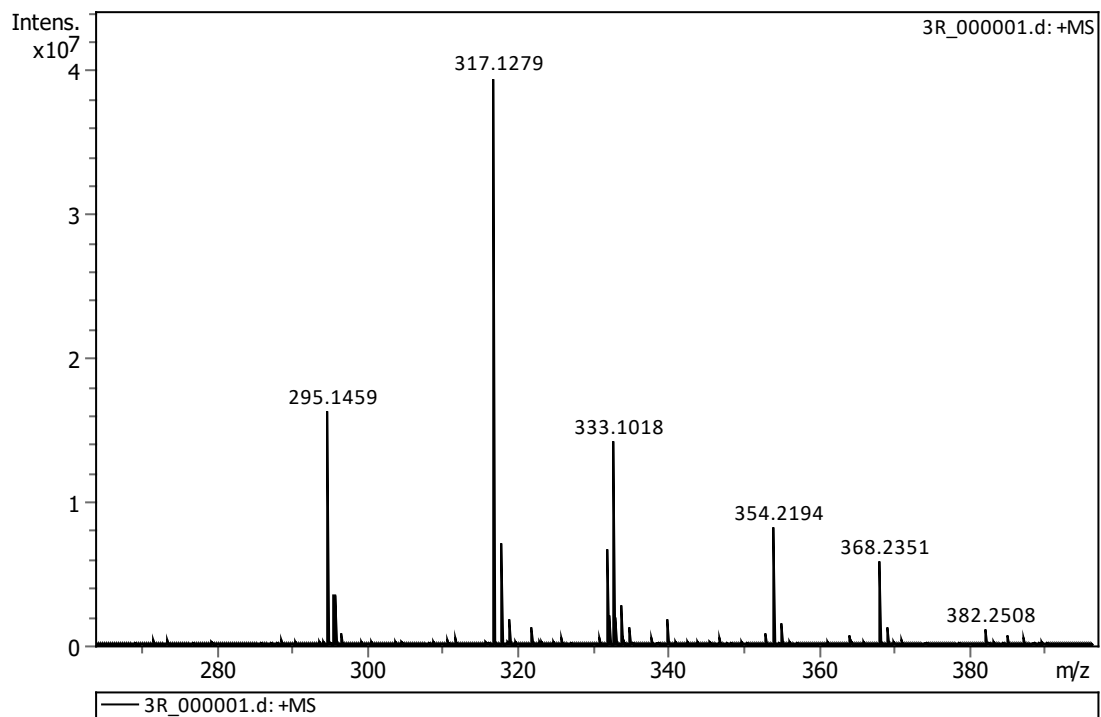
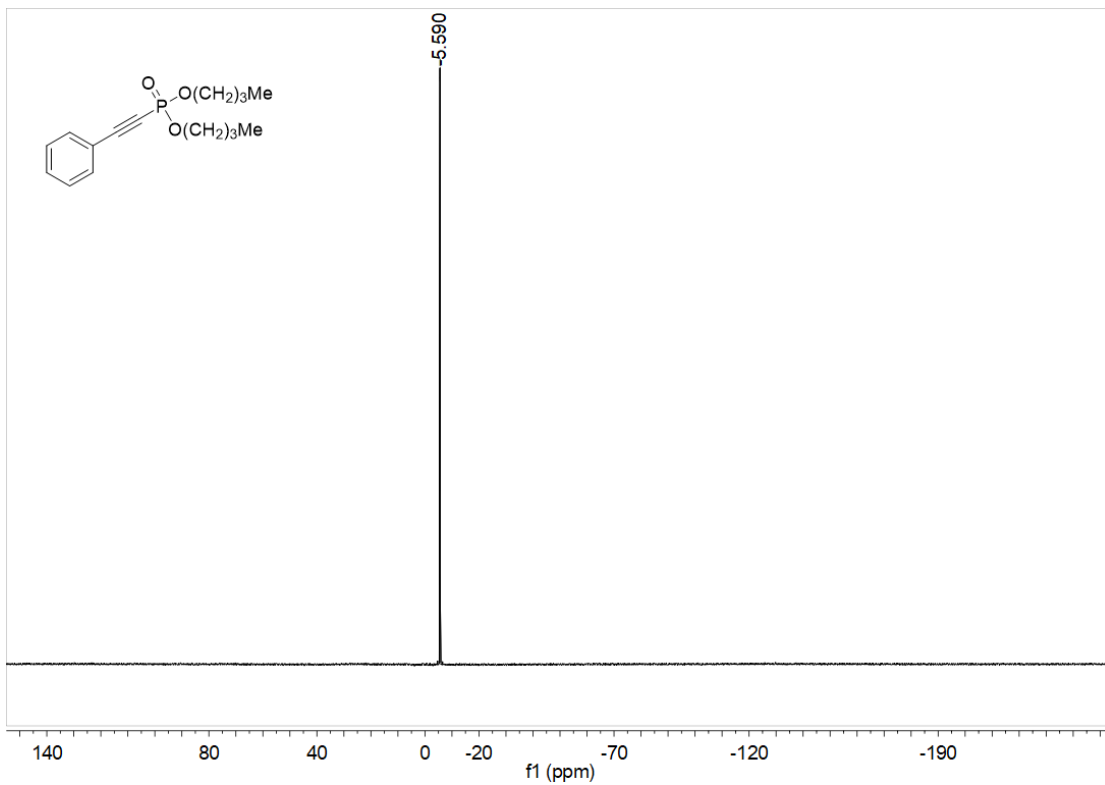




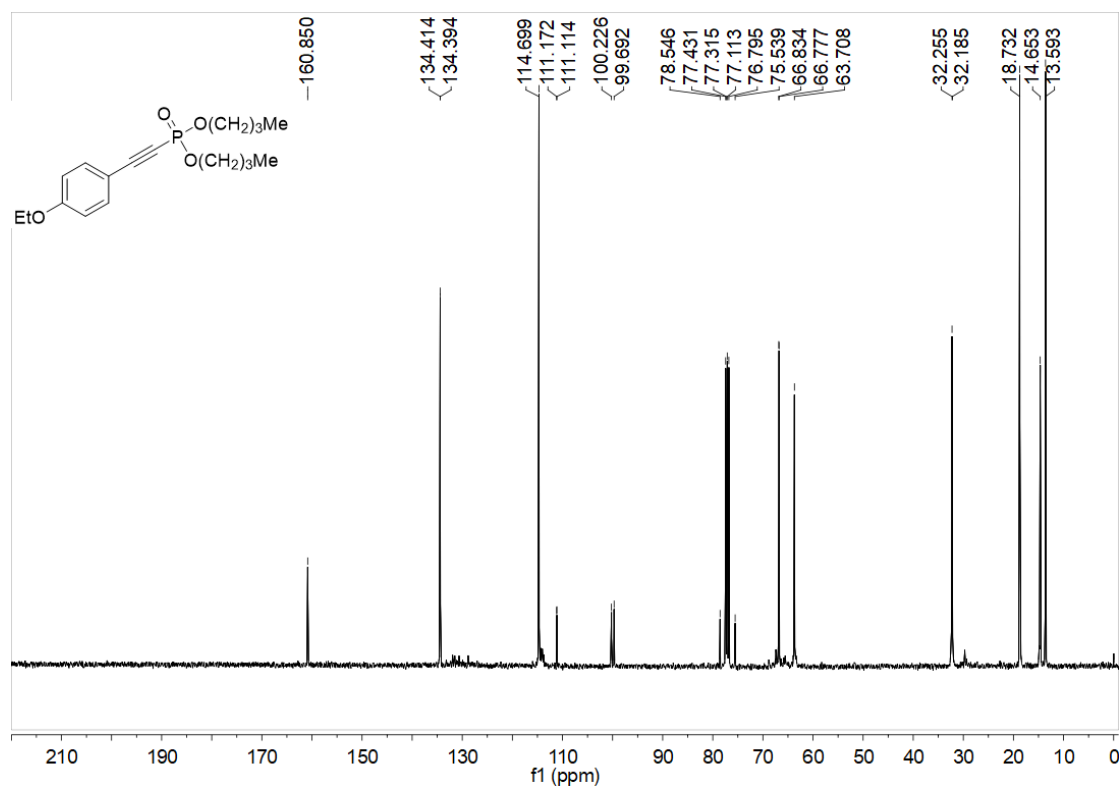
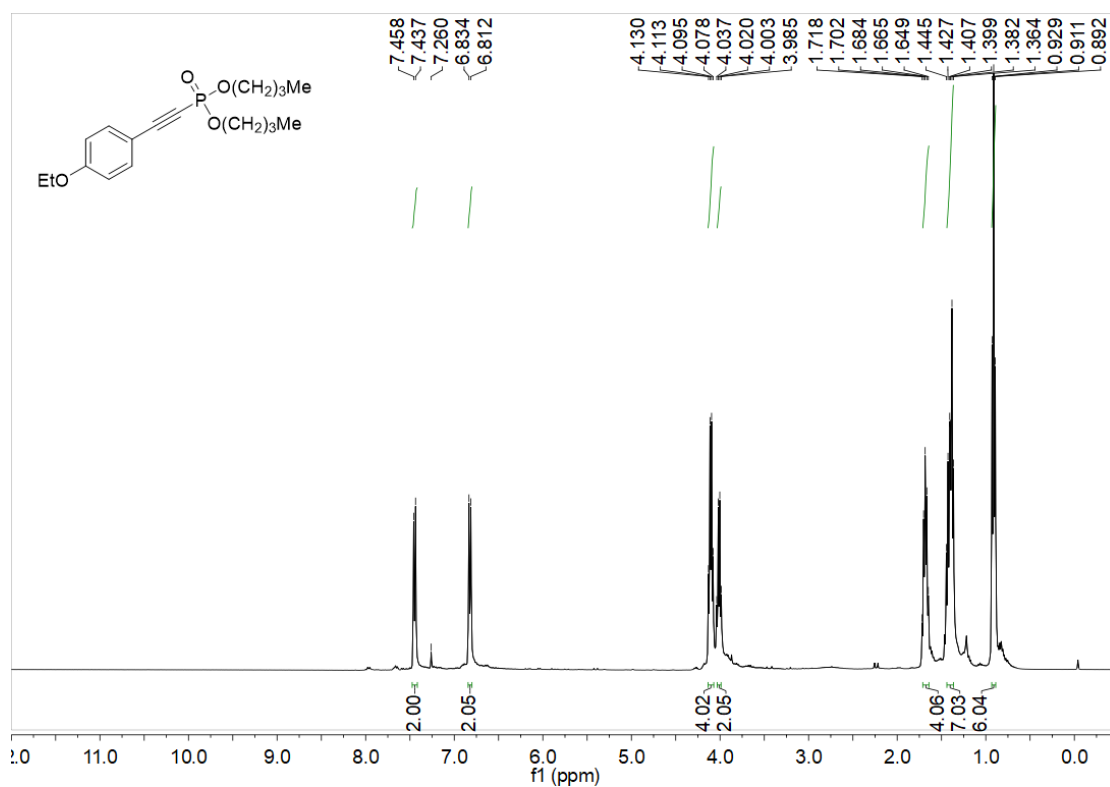


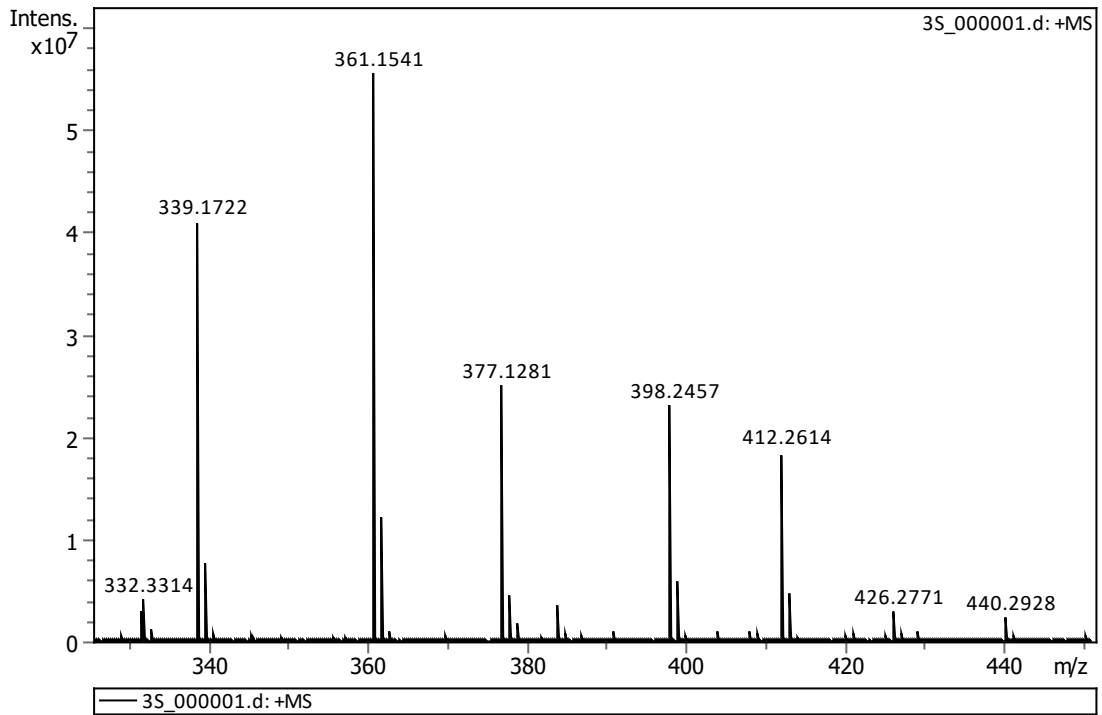
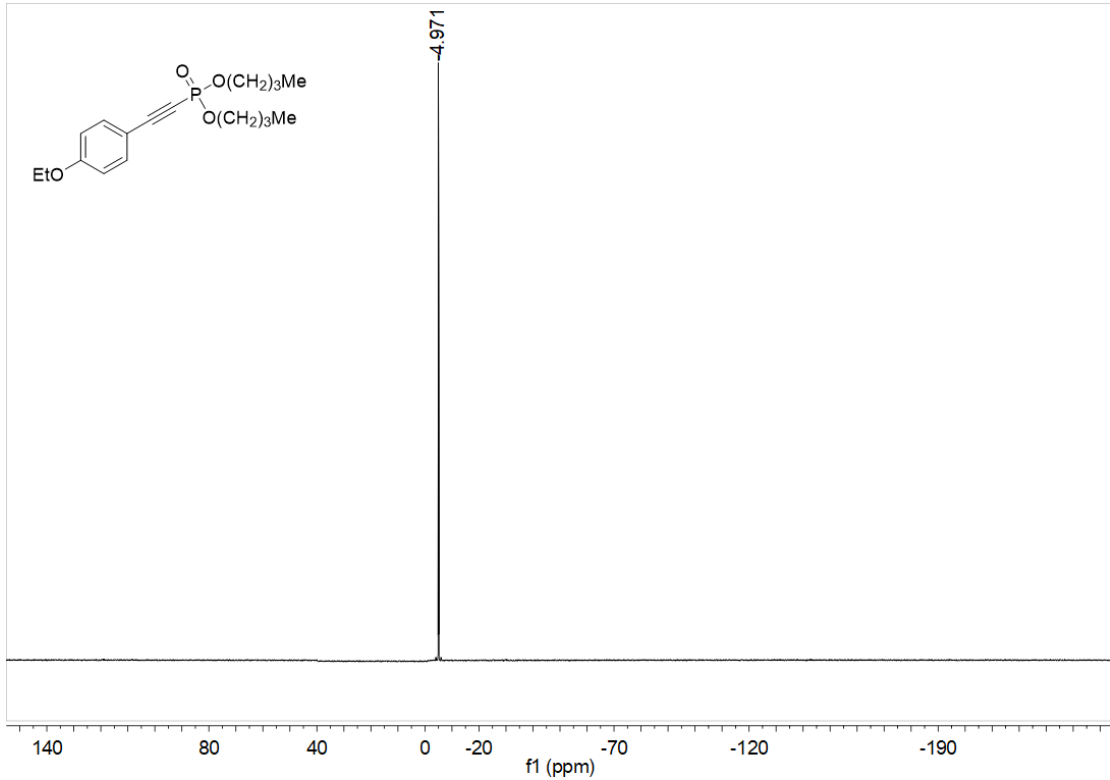
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3r**



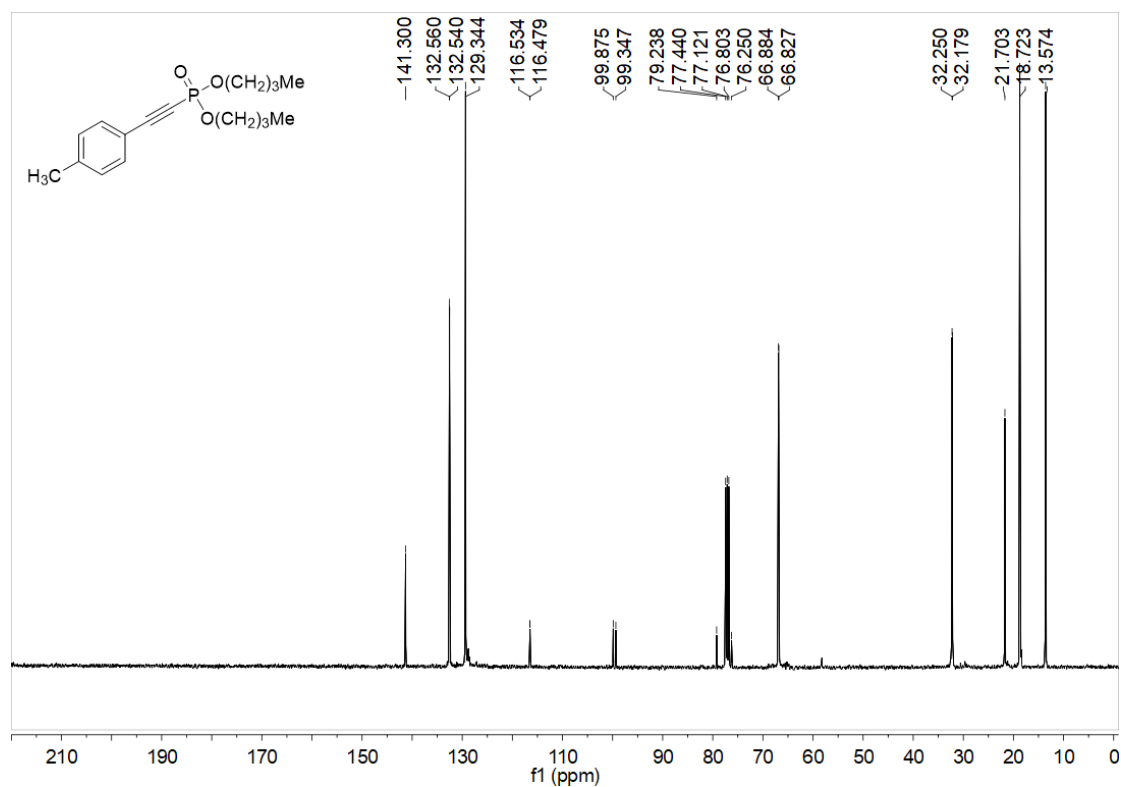
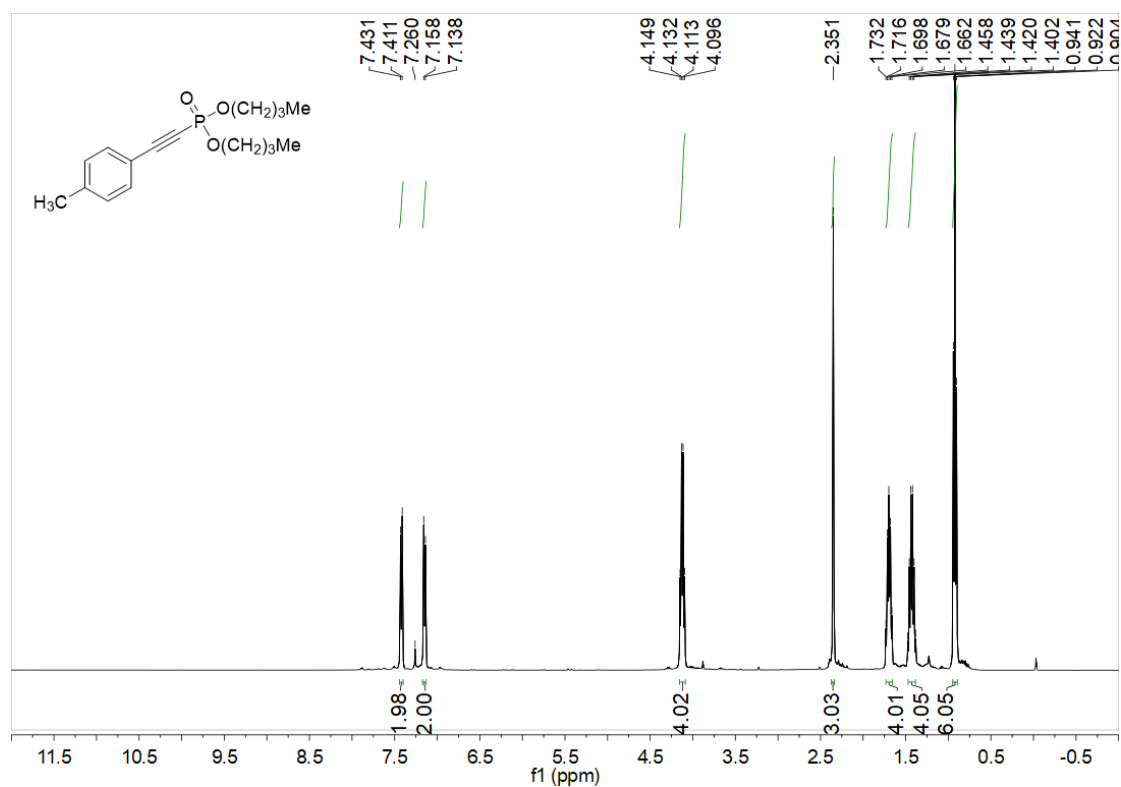


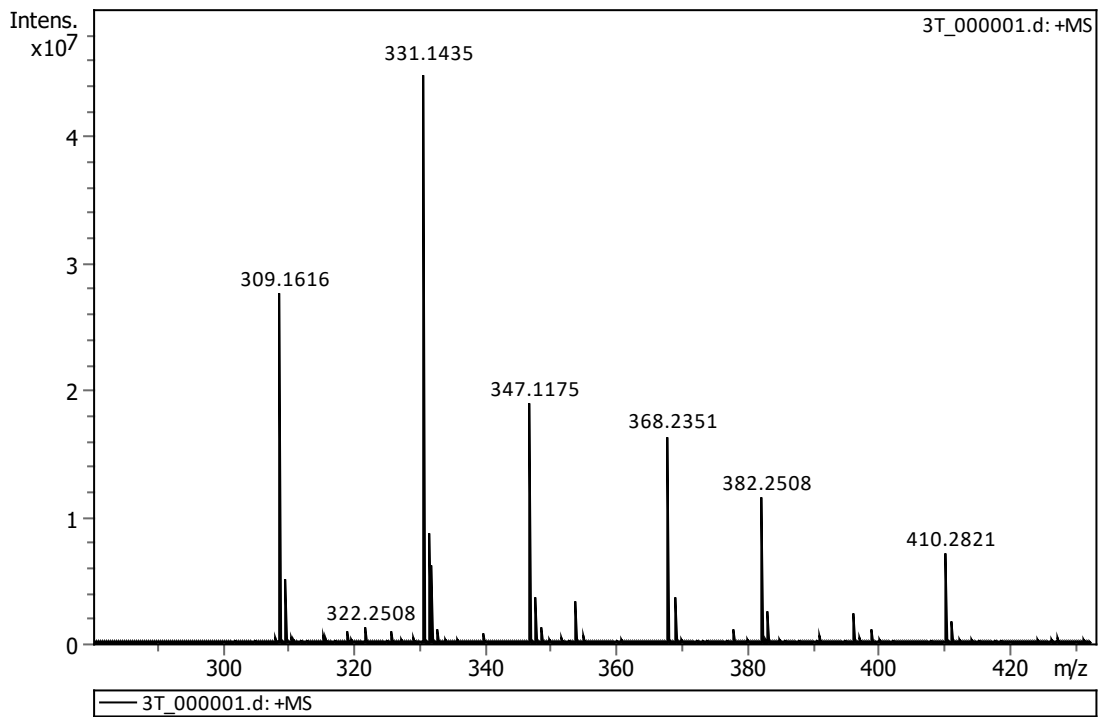
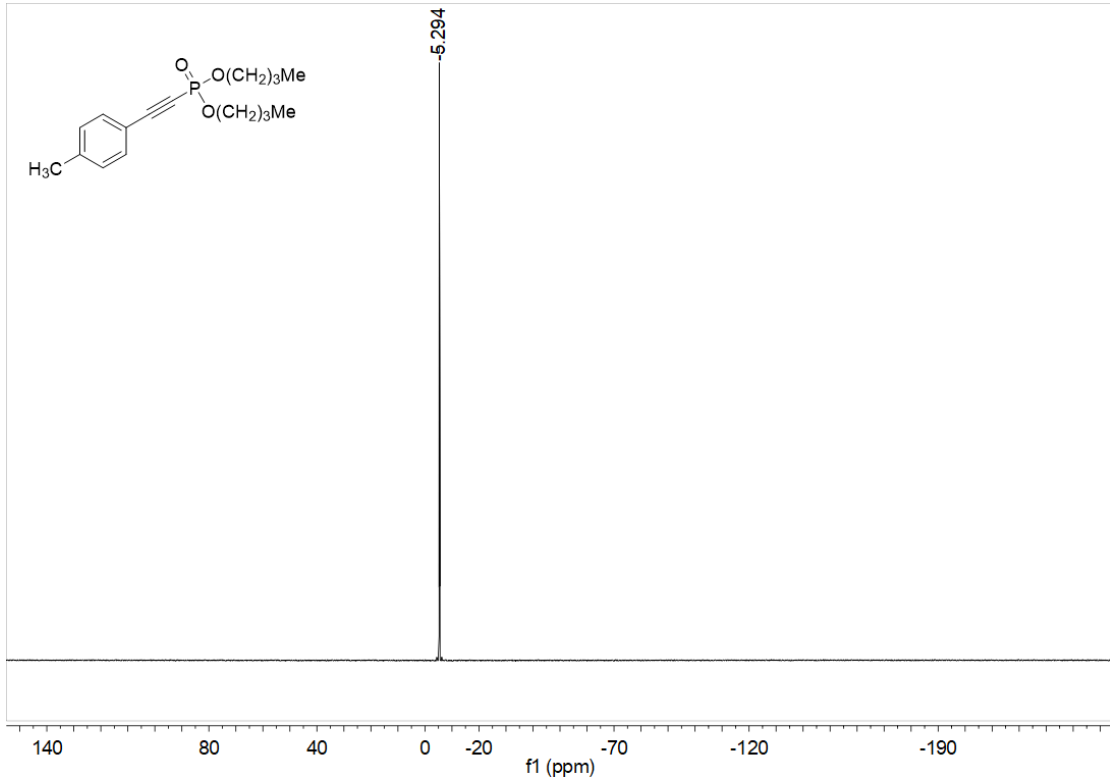
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3s**



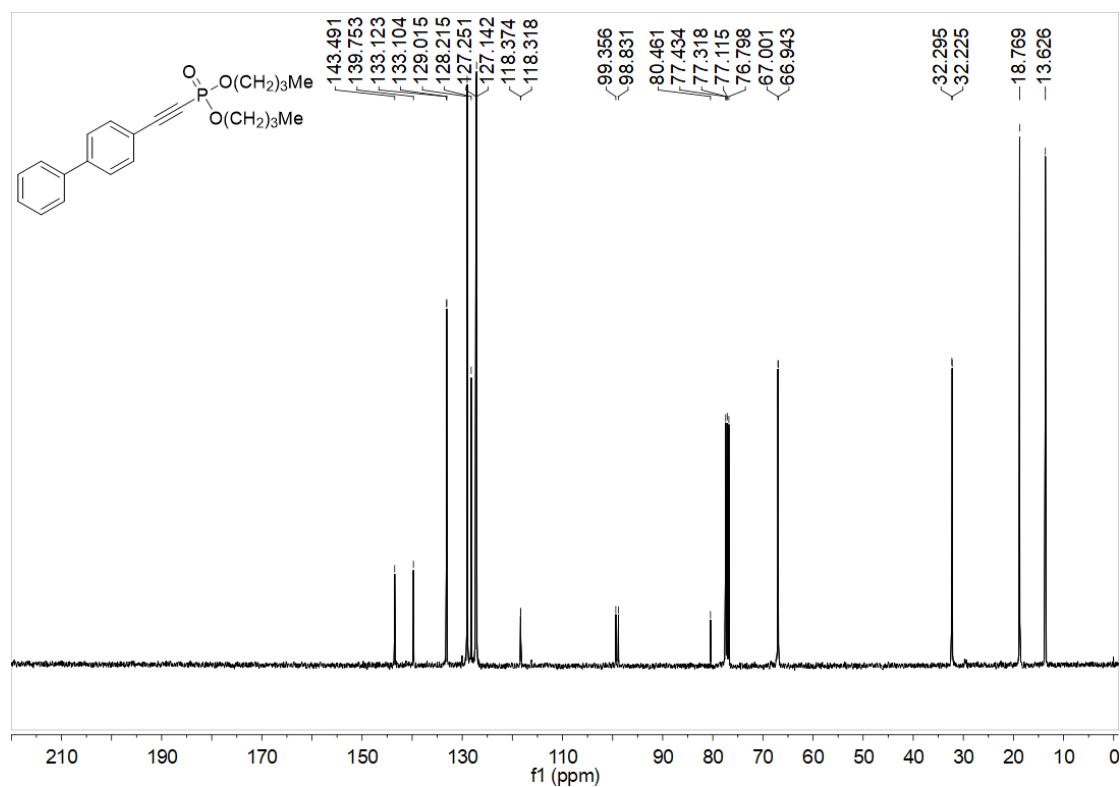
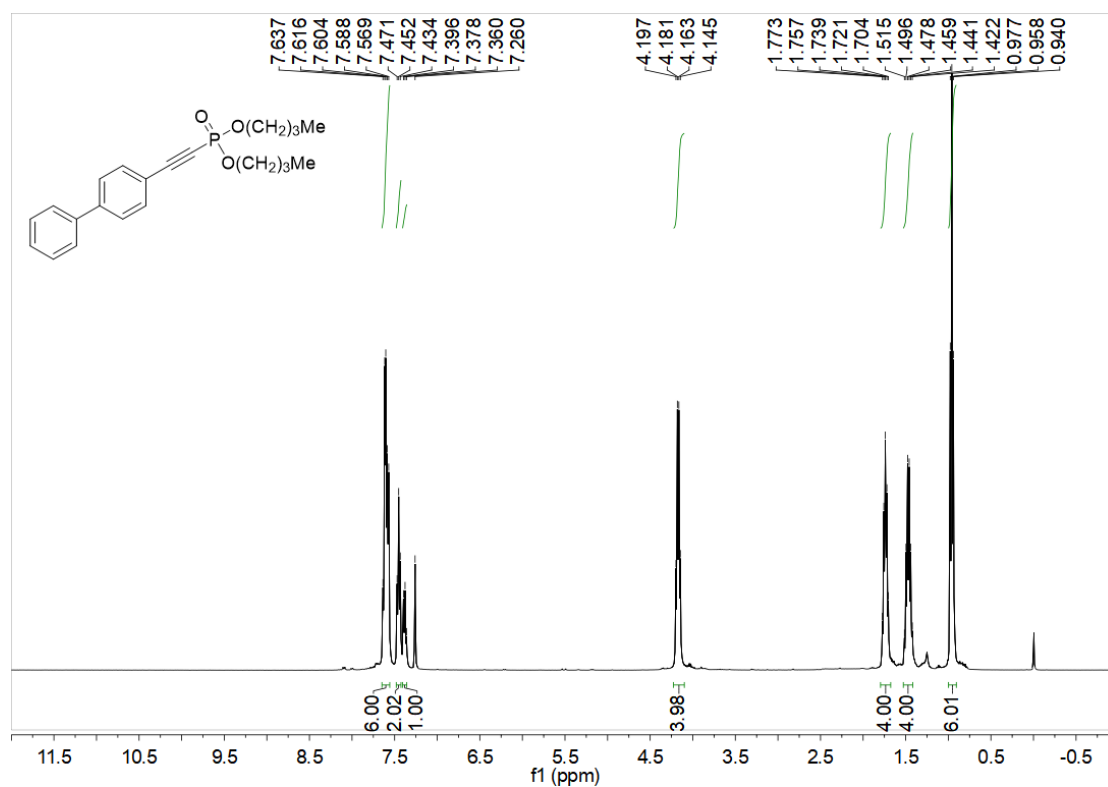


$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3t**

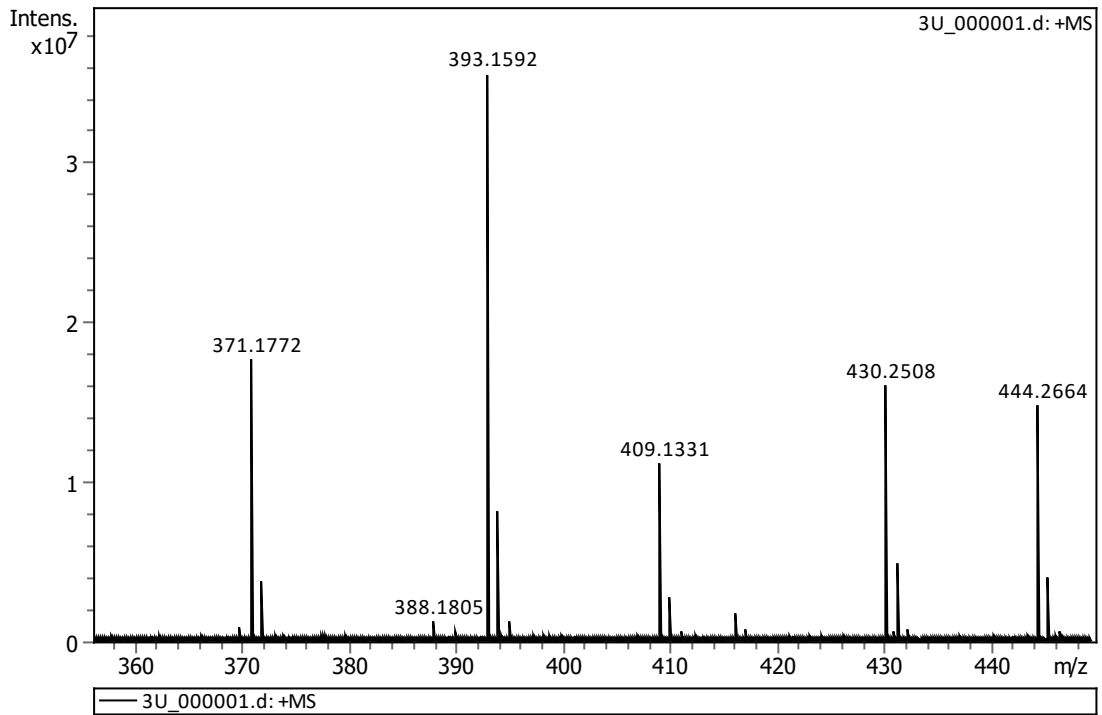
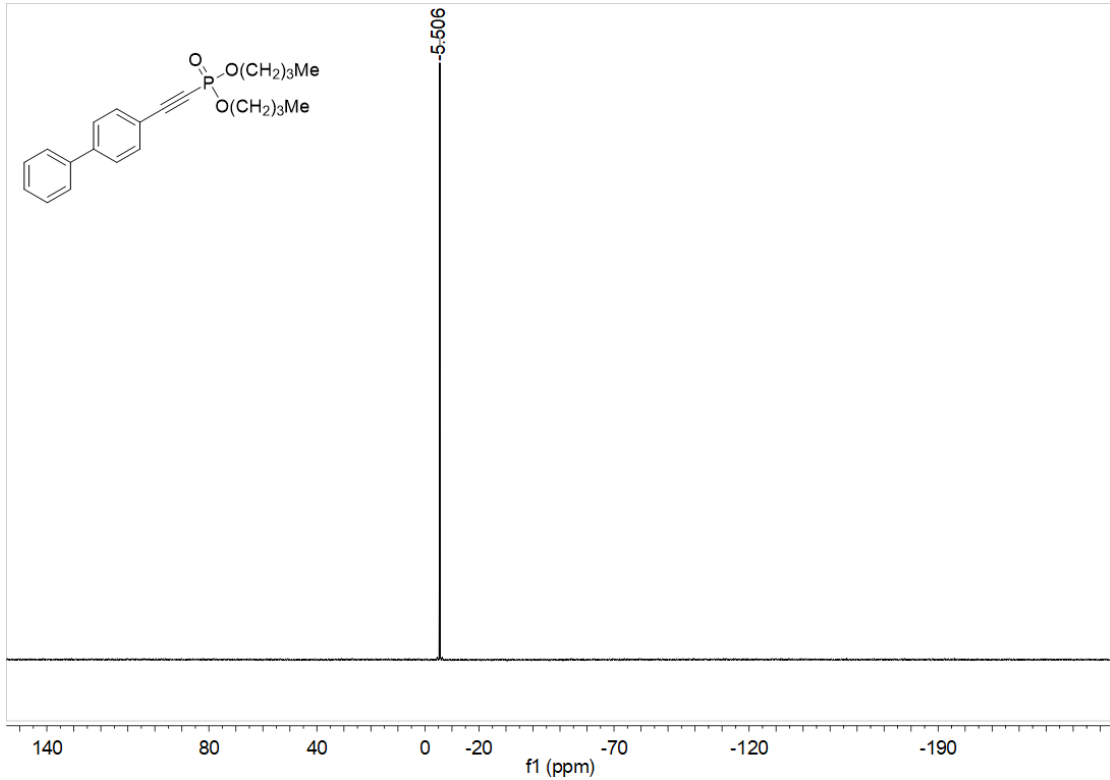




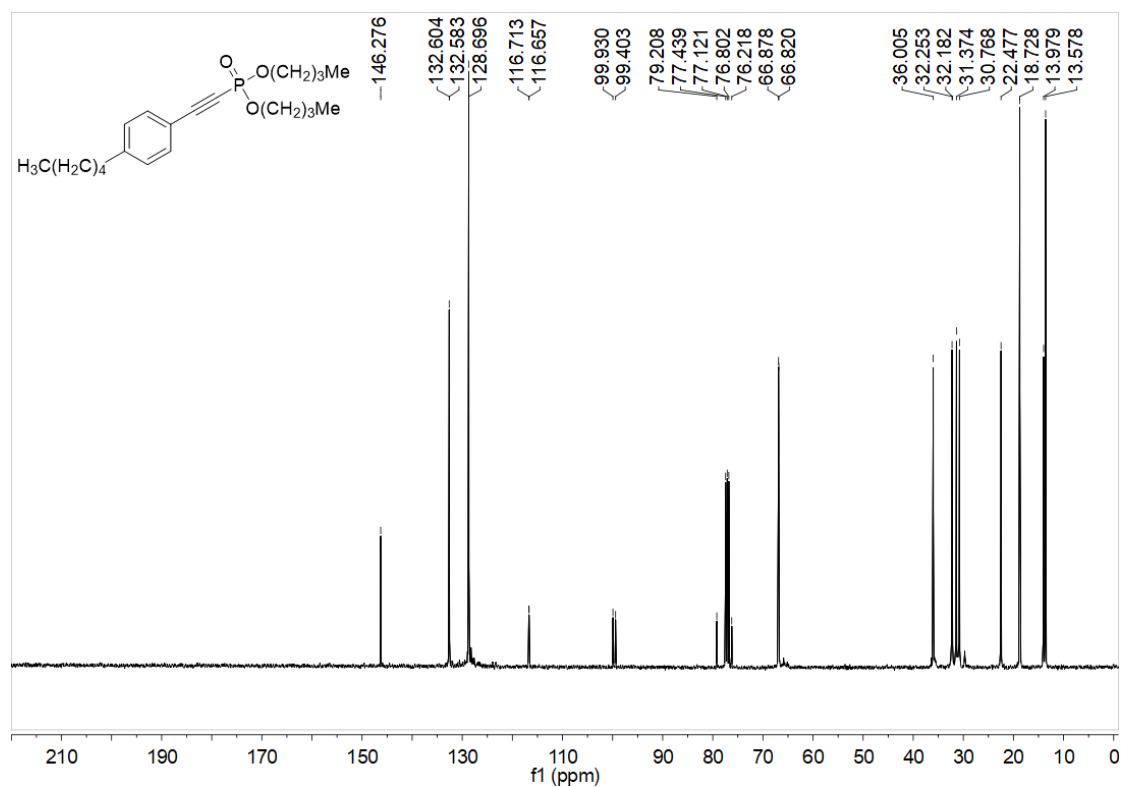
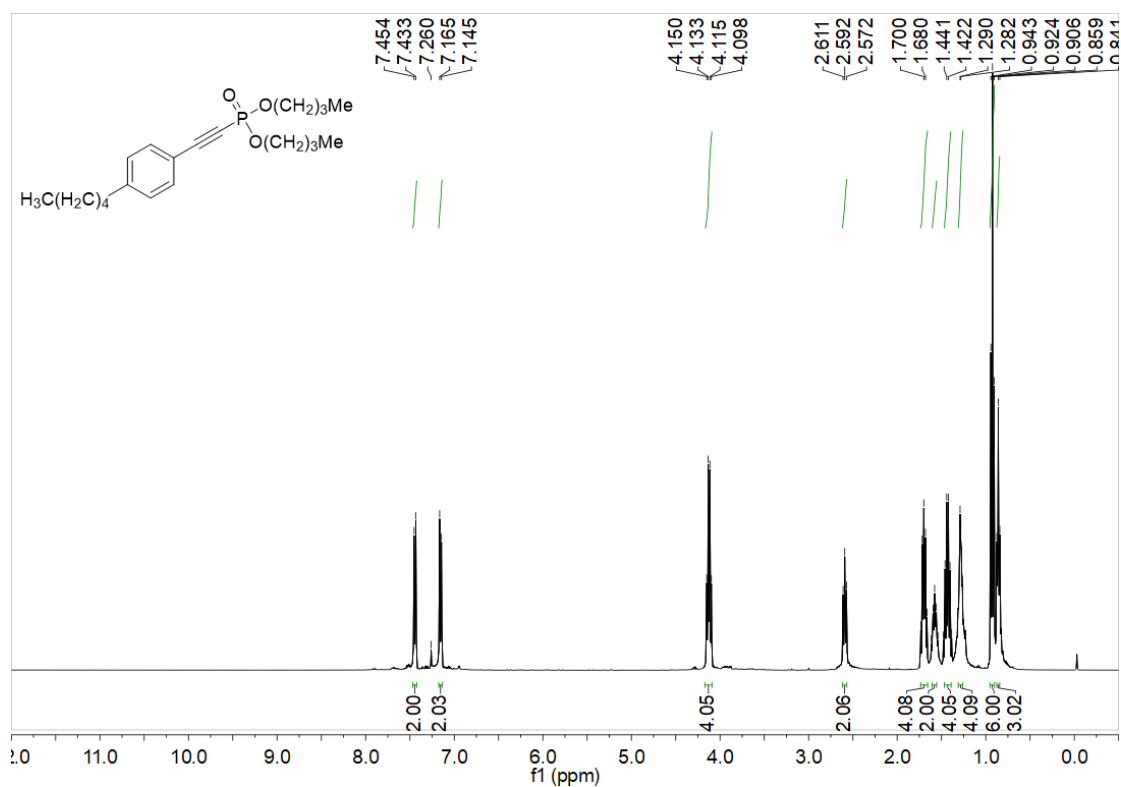
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3u**

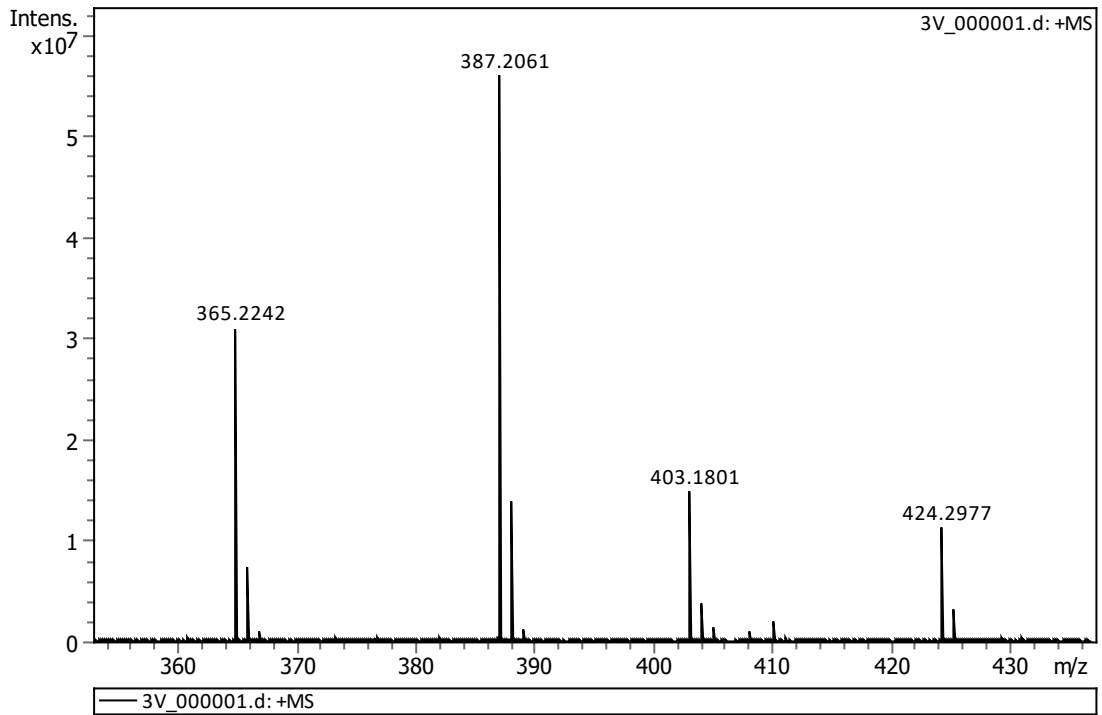
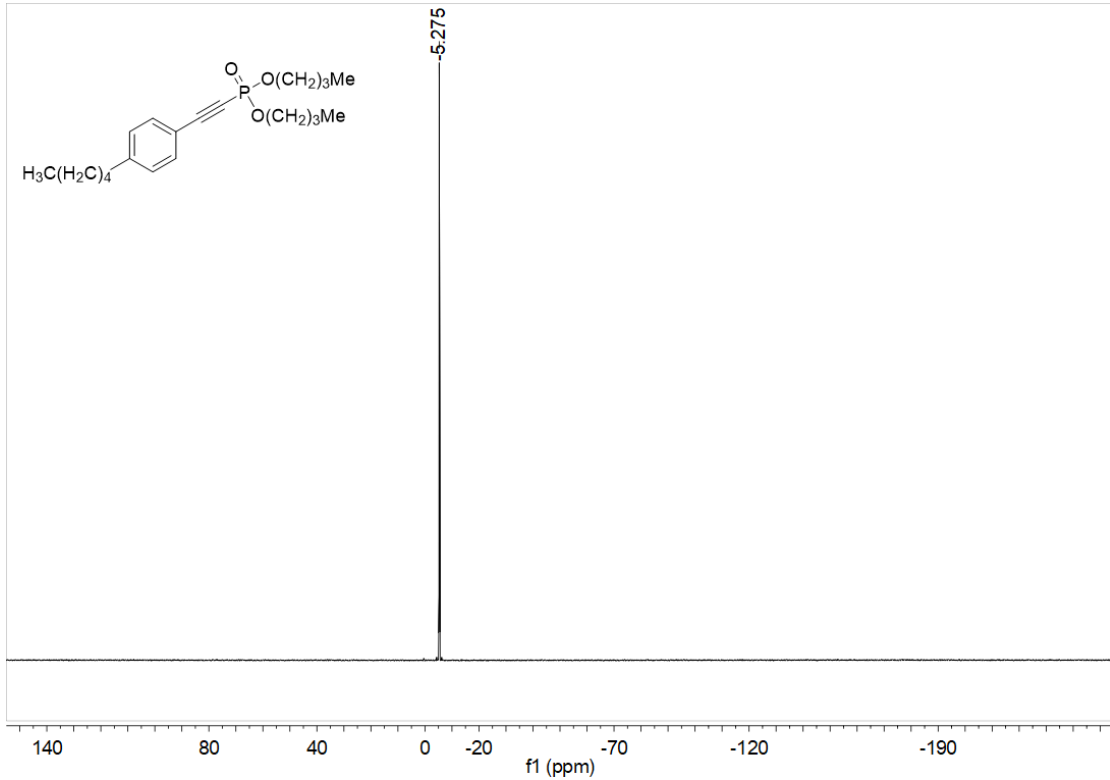




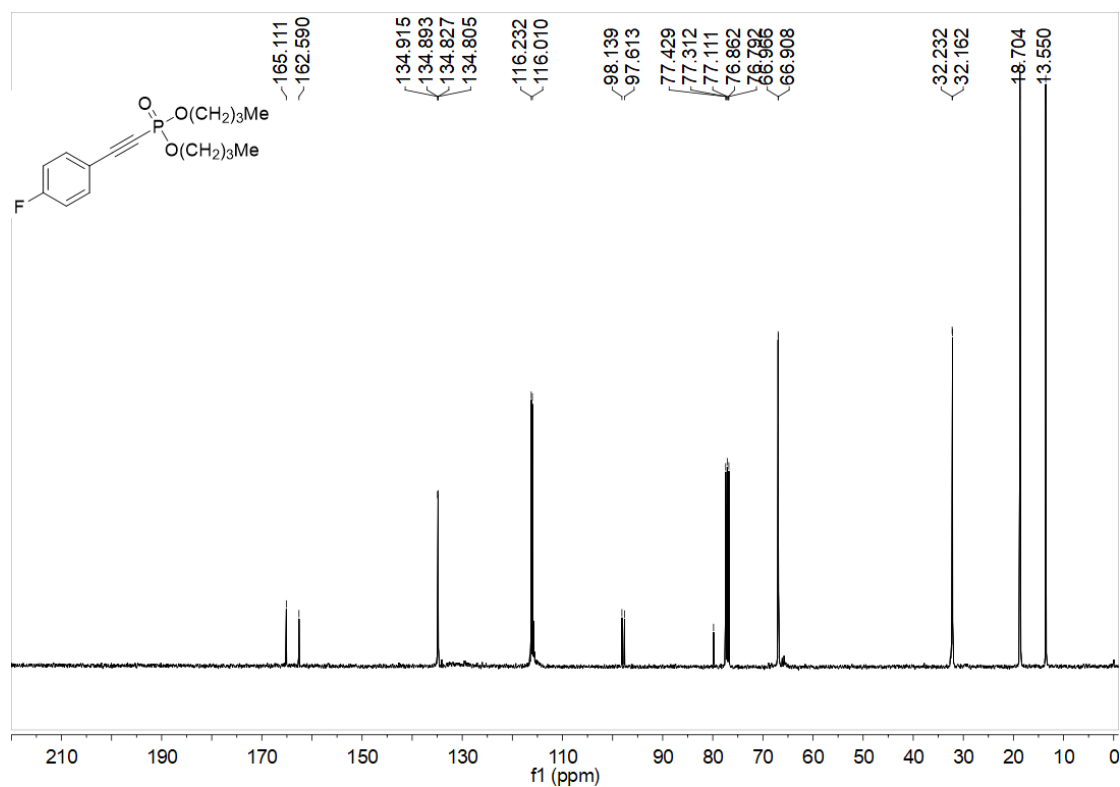
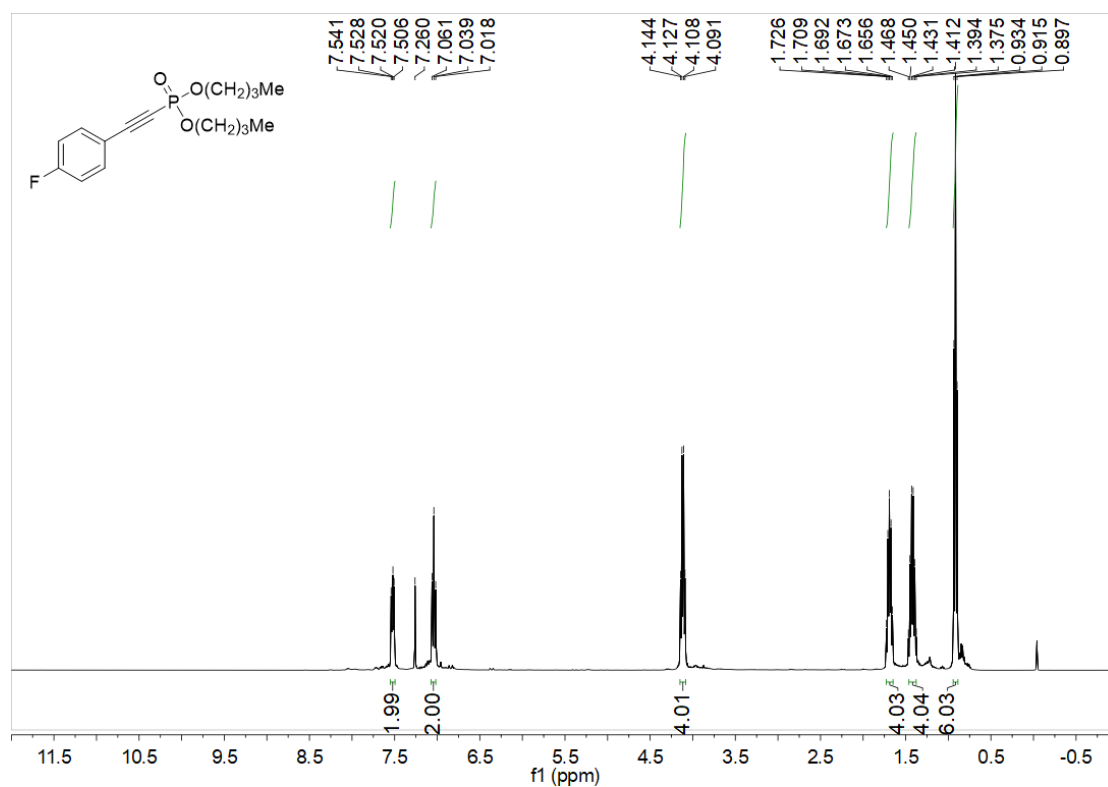


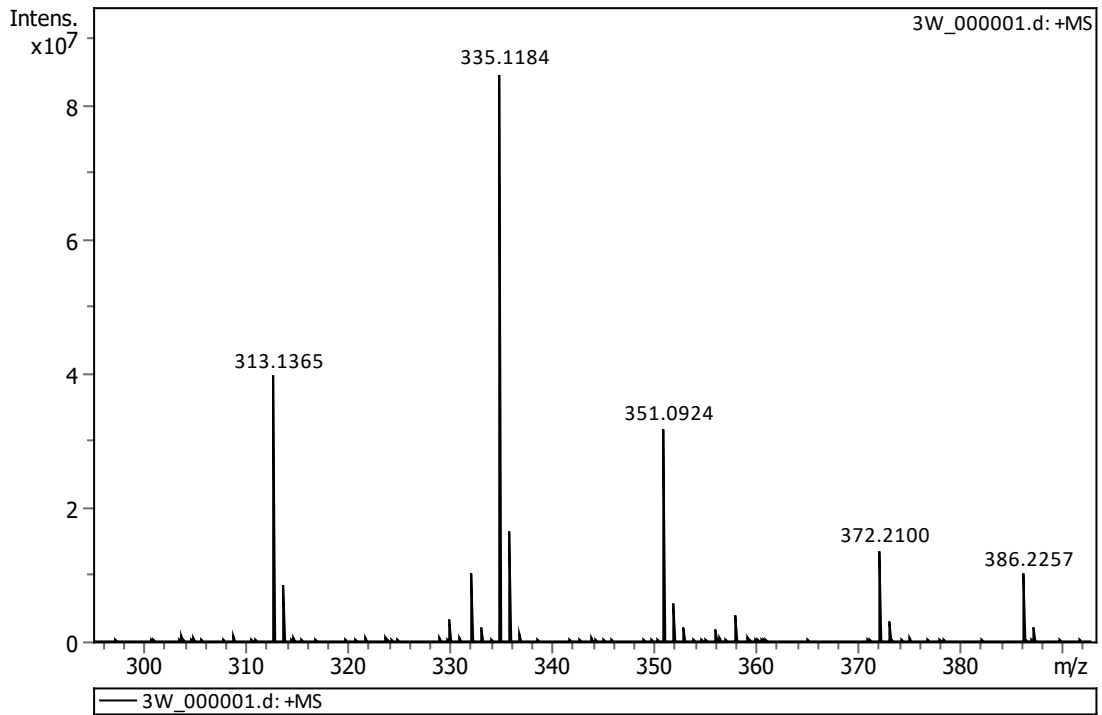
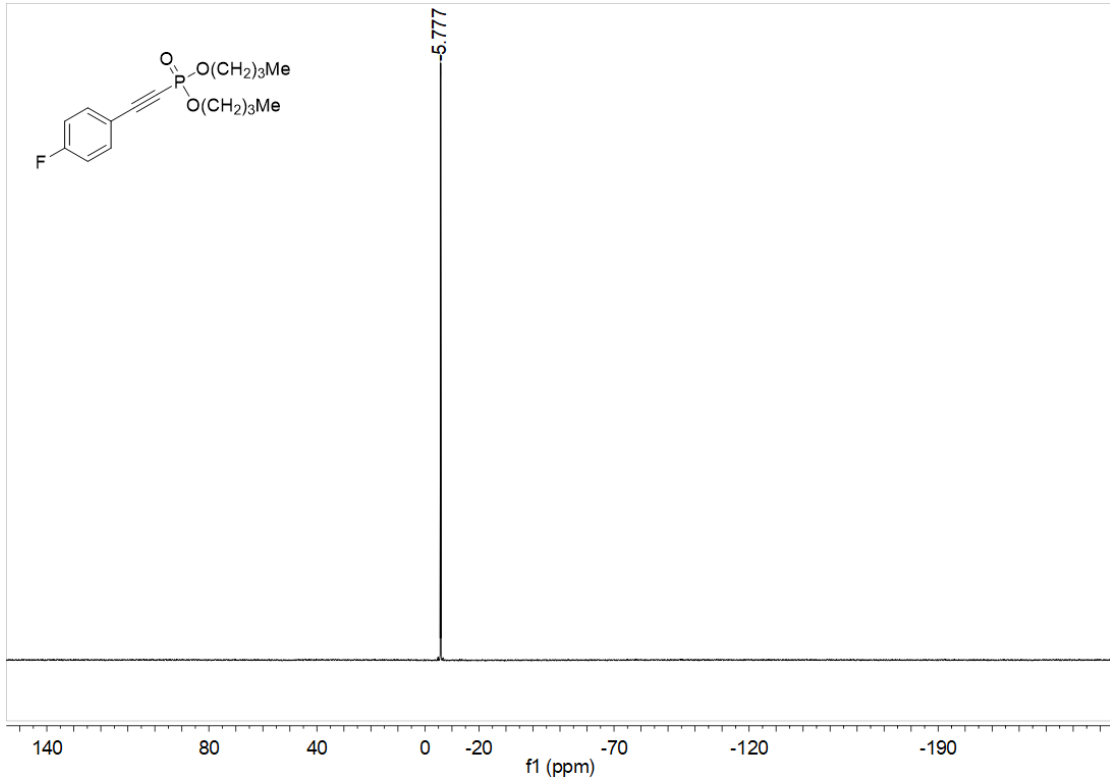
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3v**



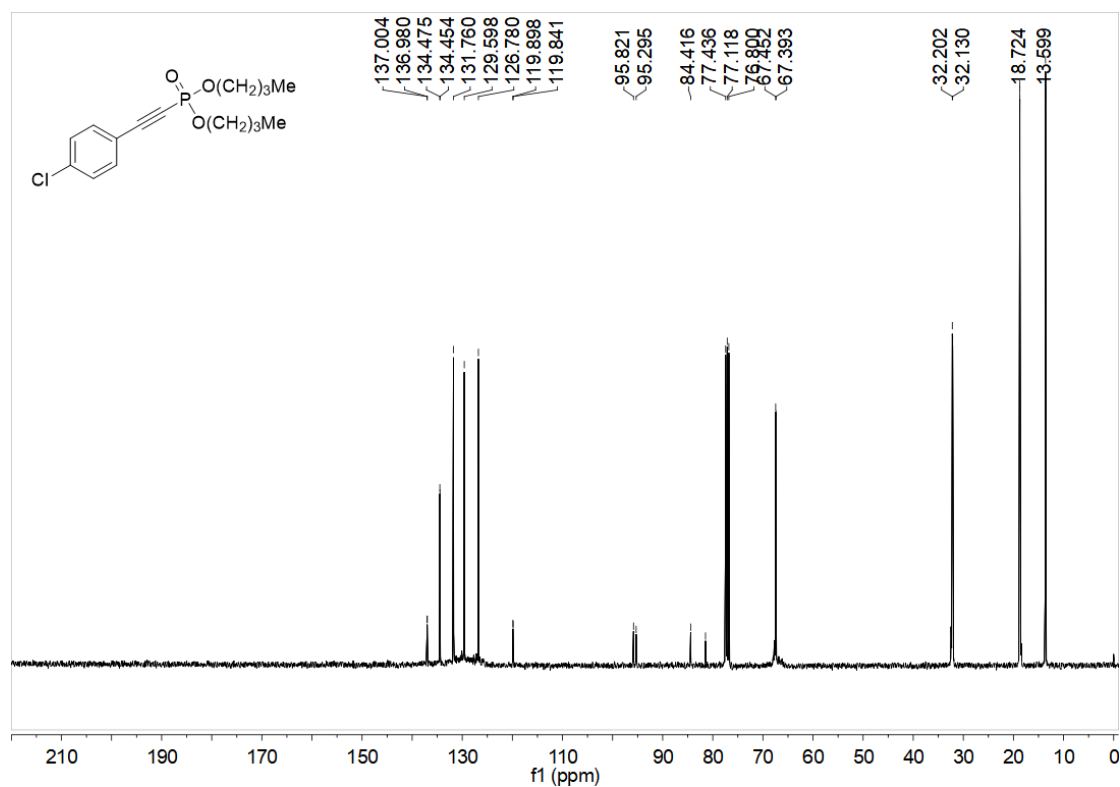
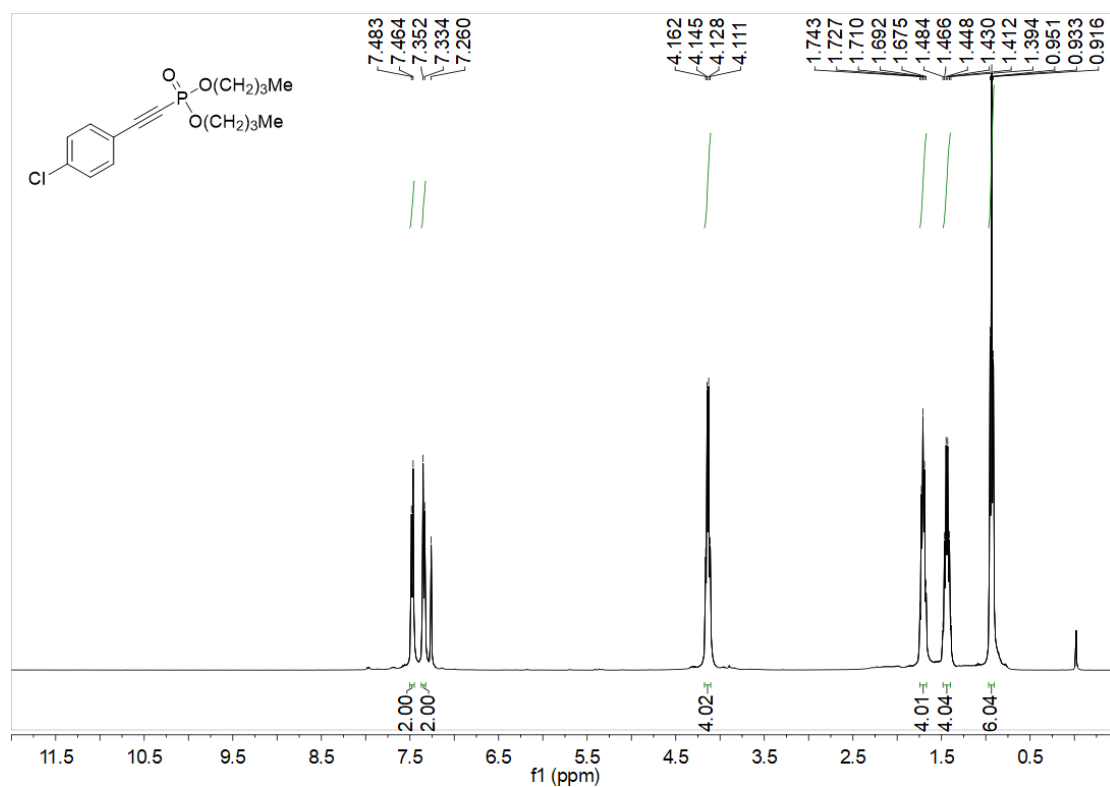


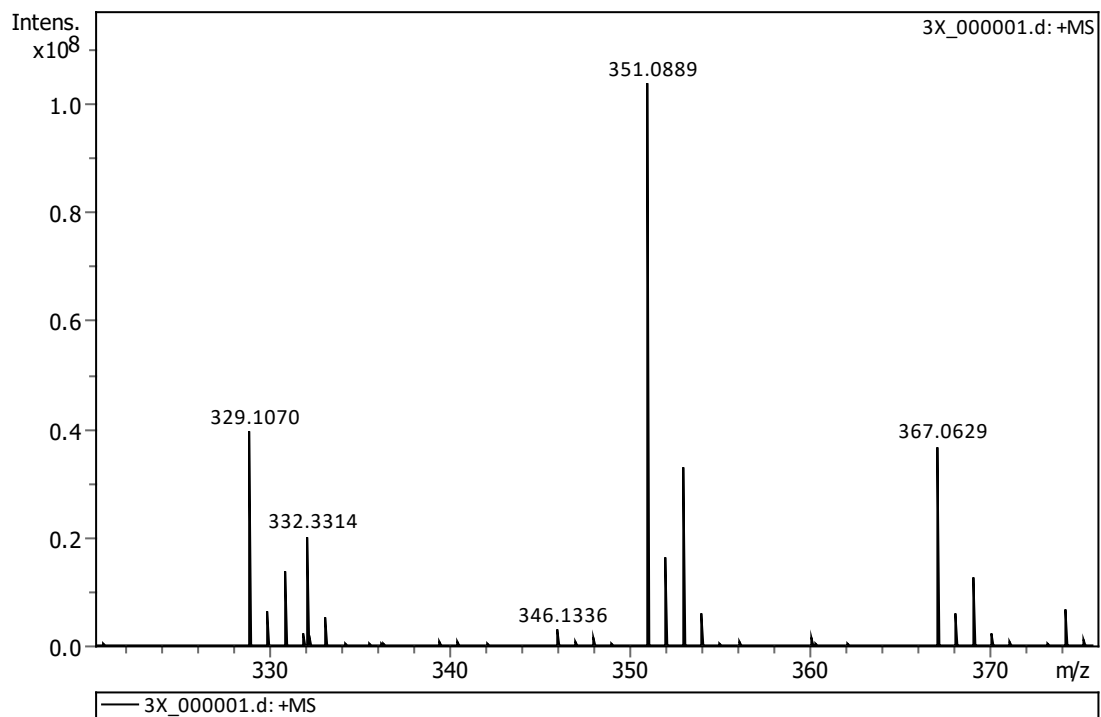
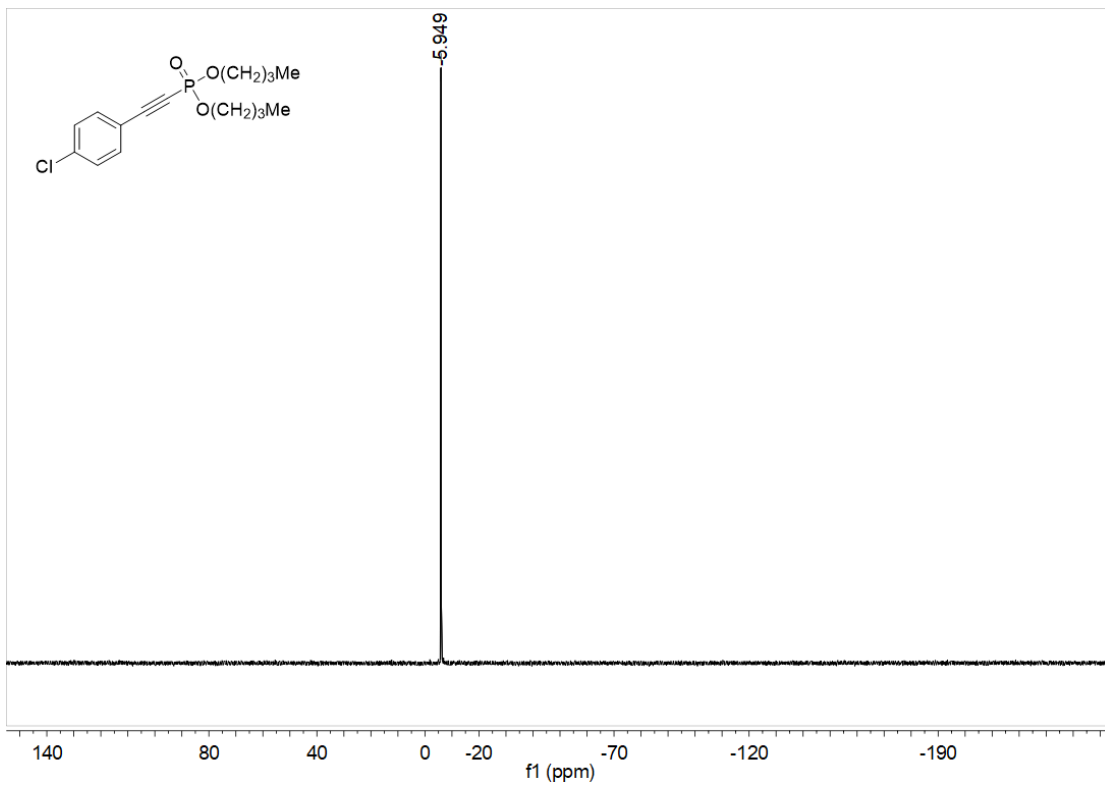
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3w**



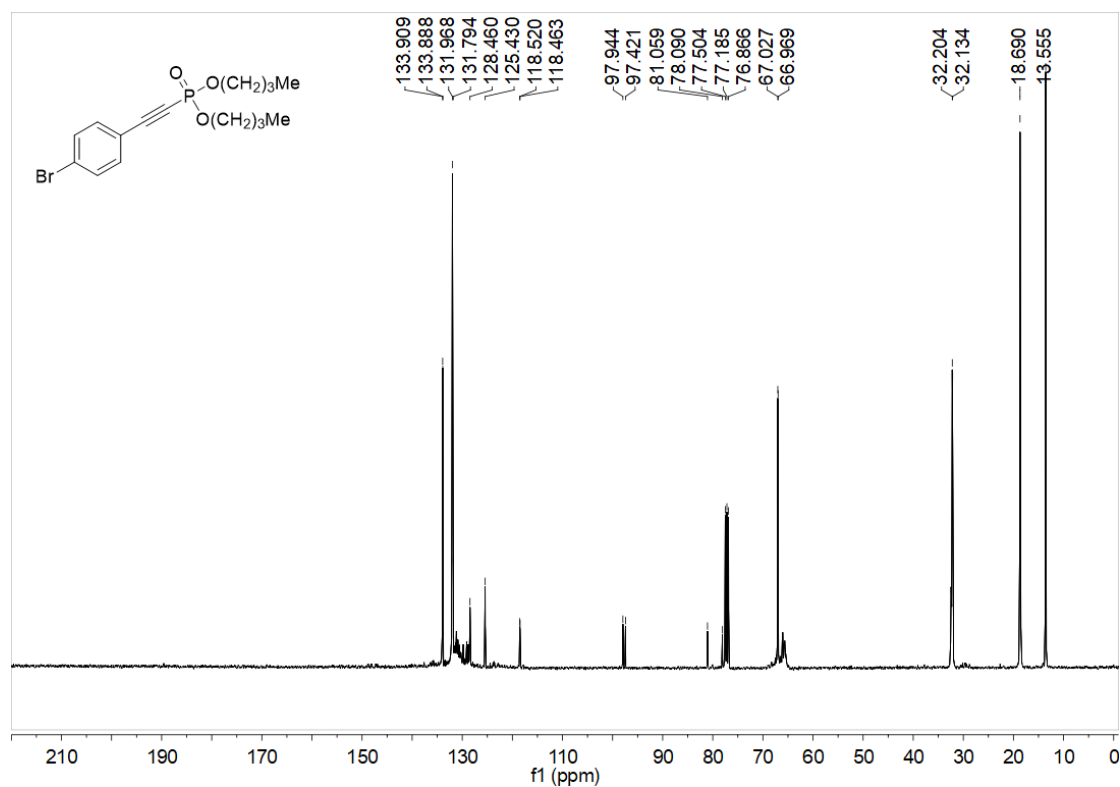
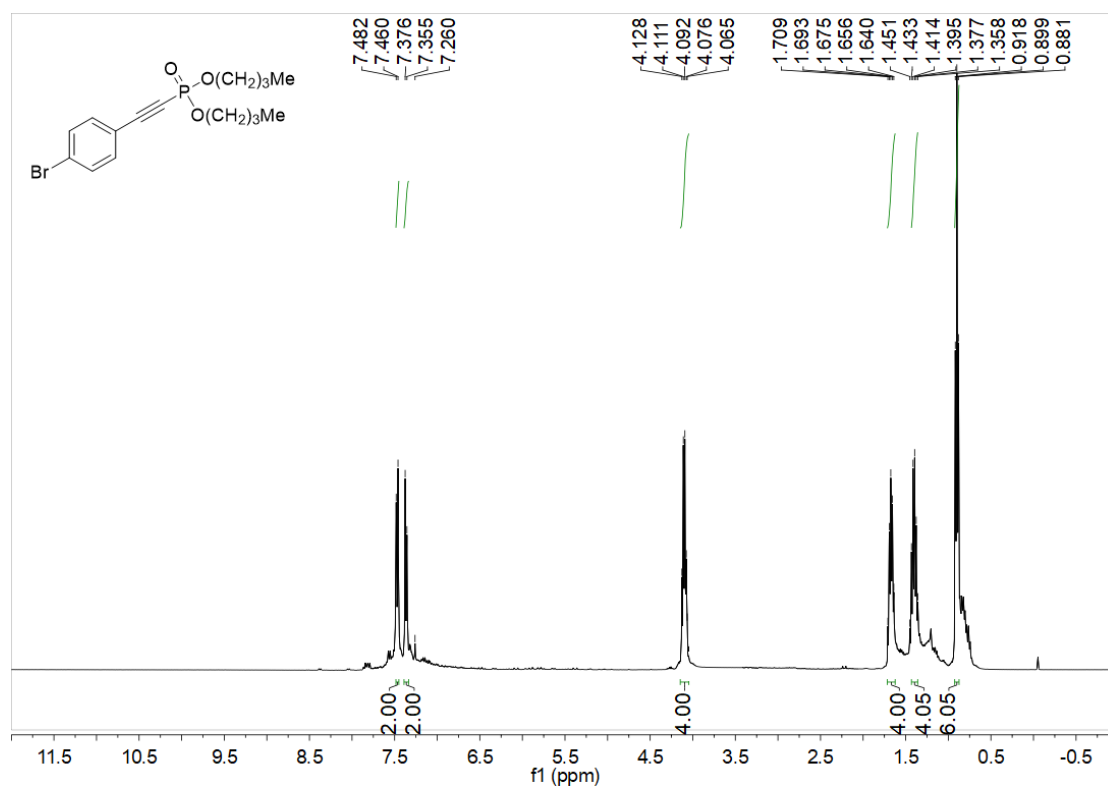


$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3x**

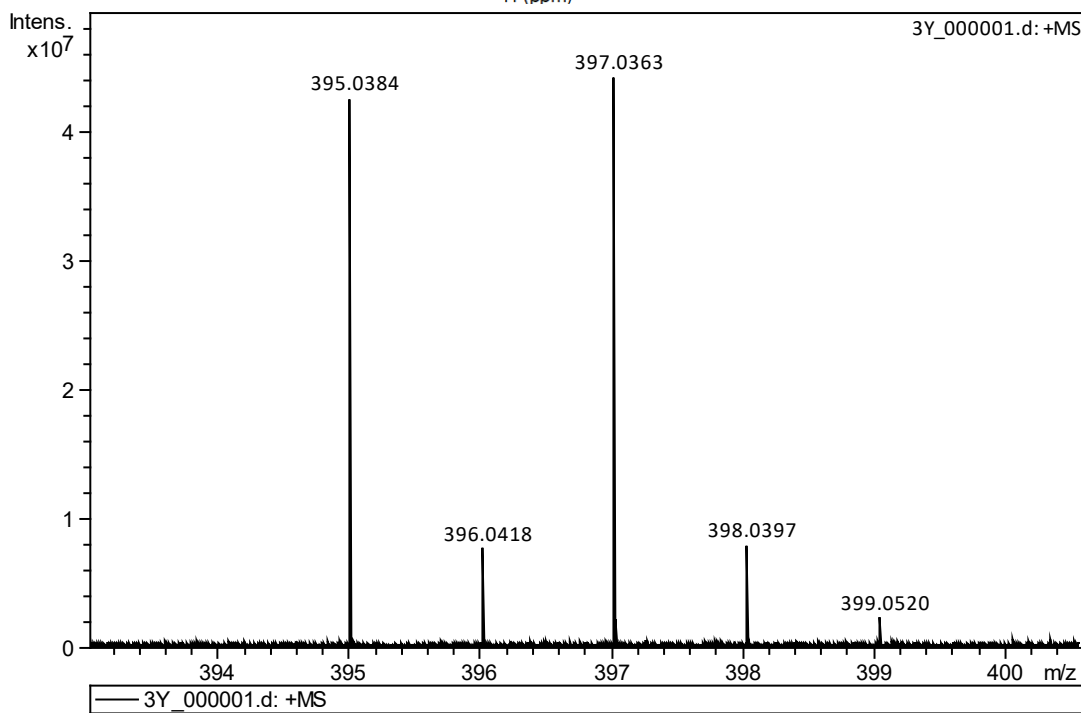
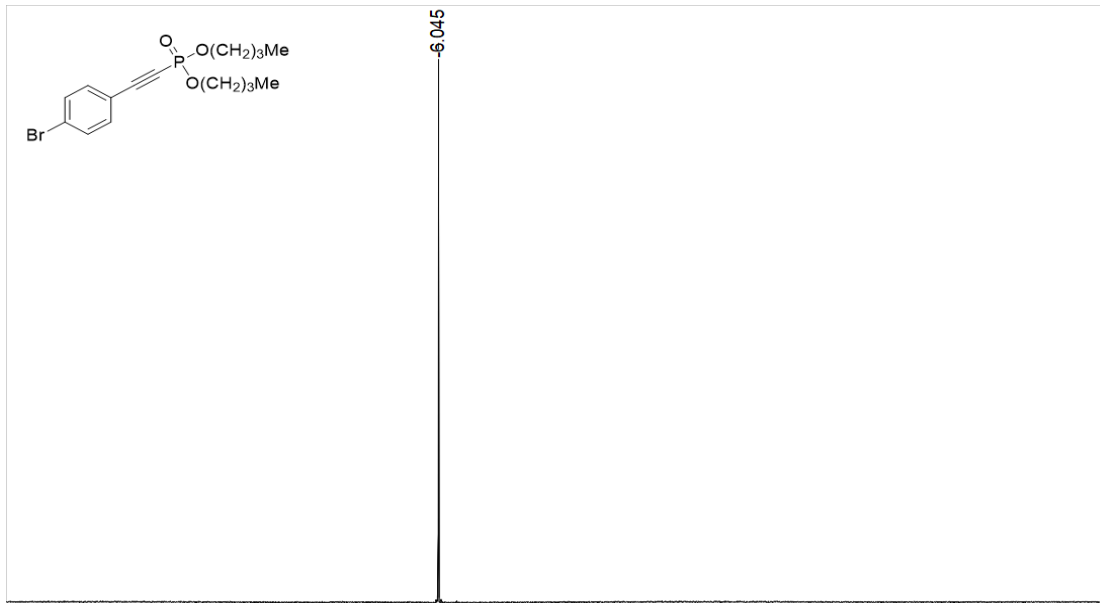




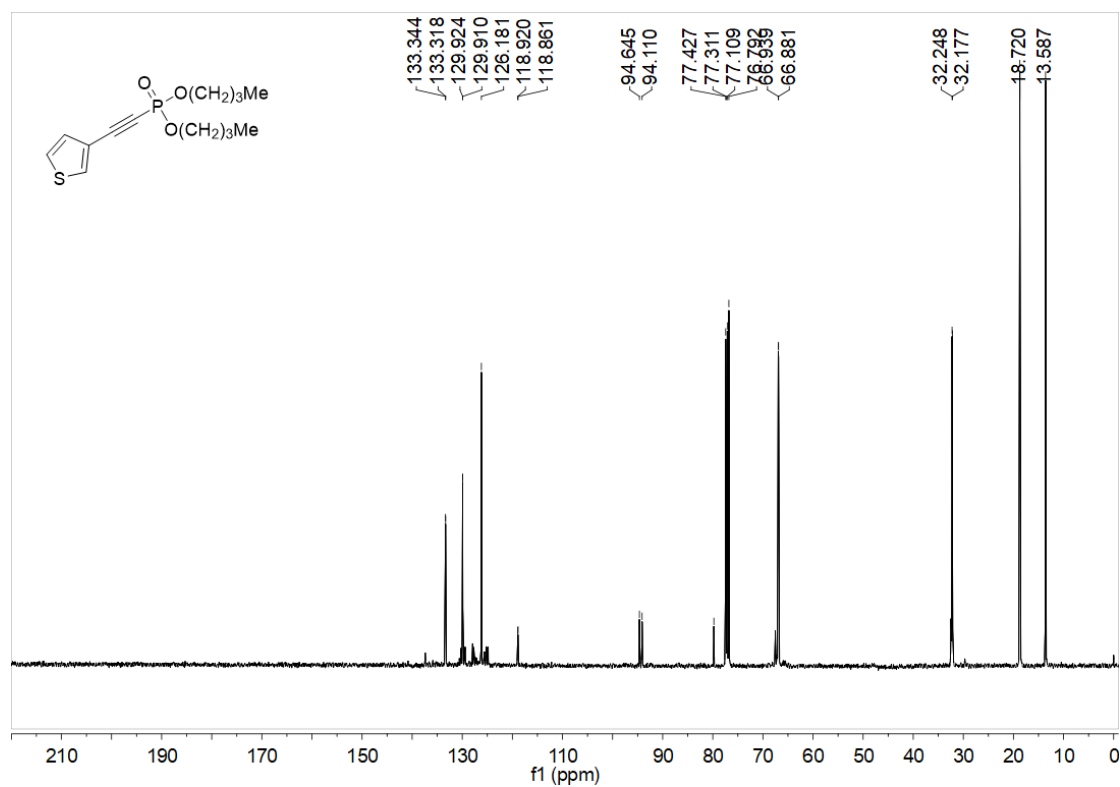
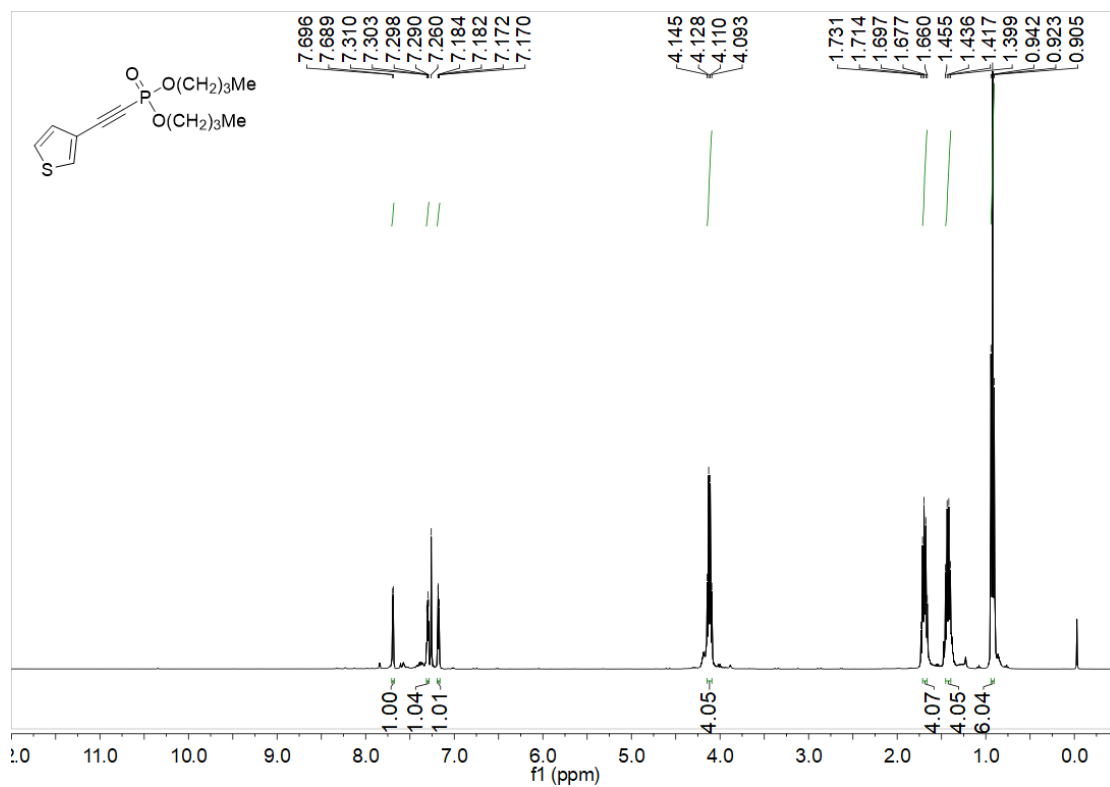
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3y**

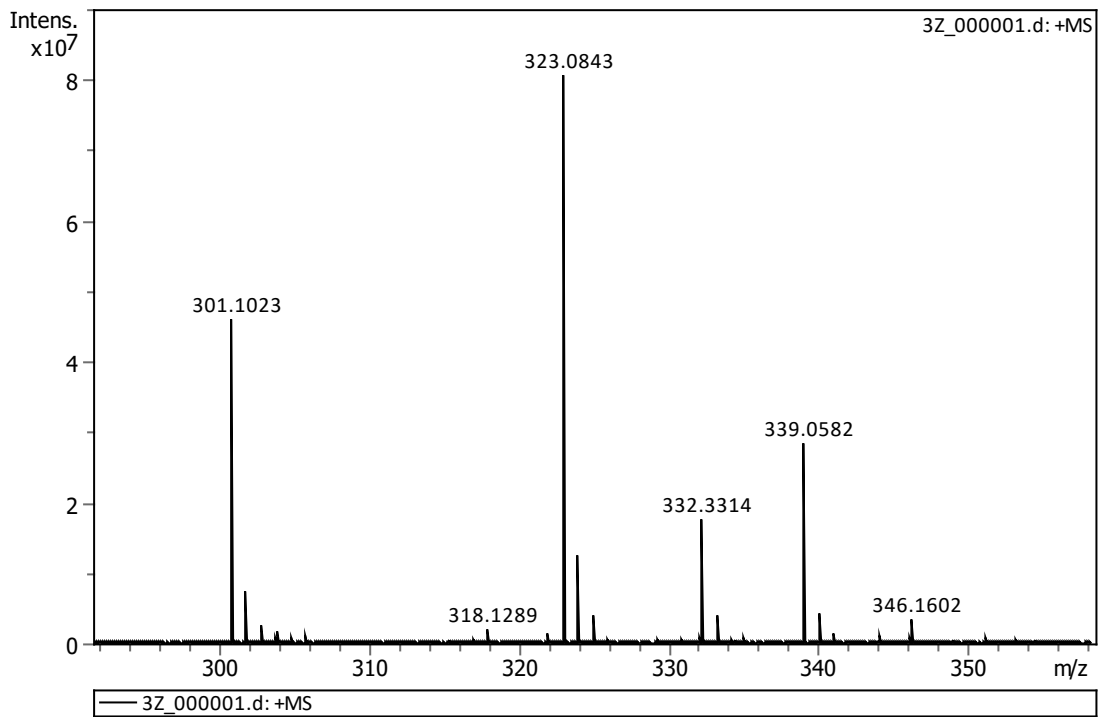
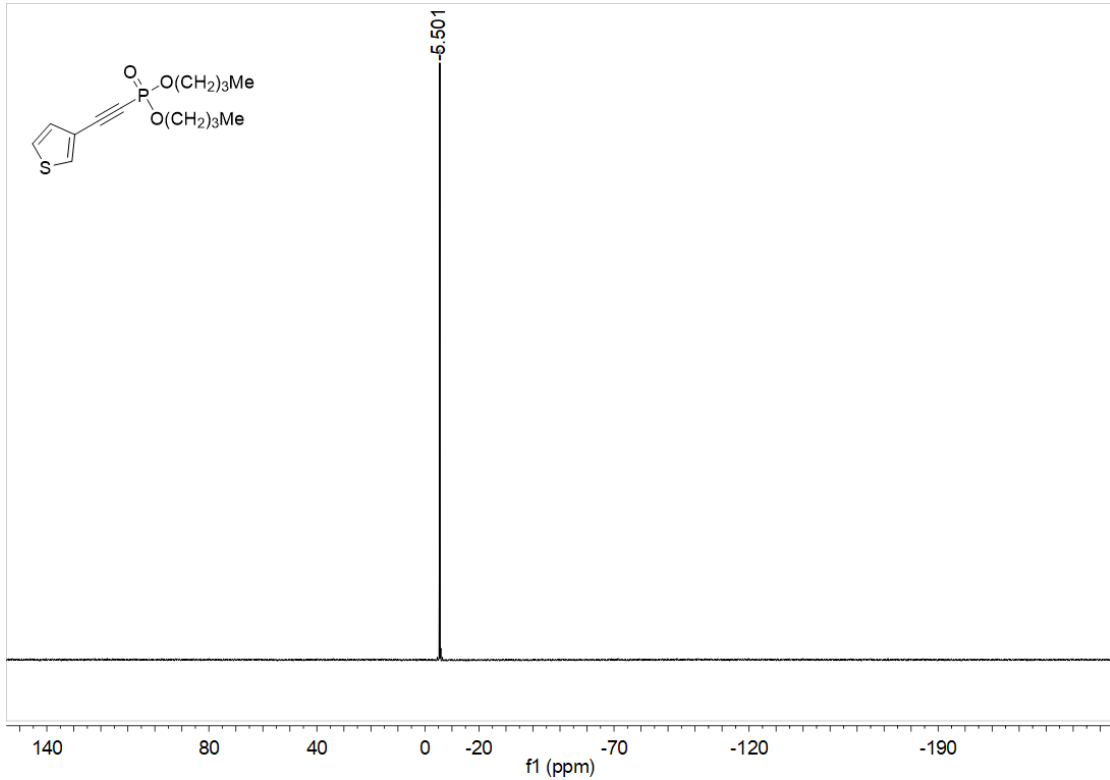




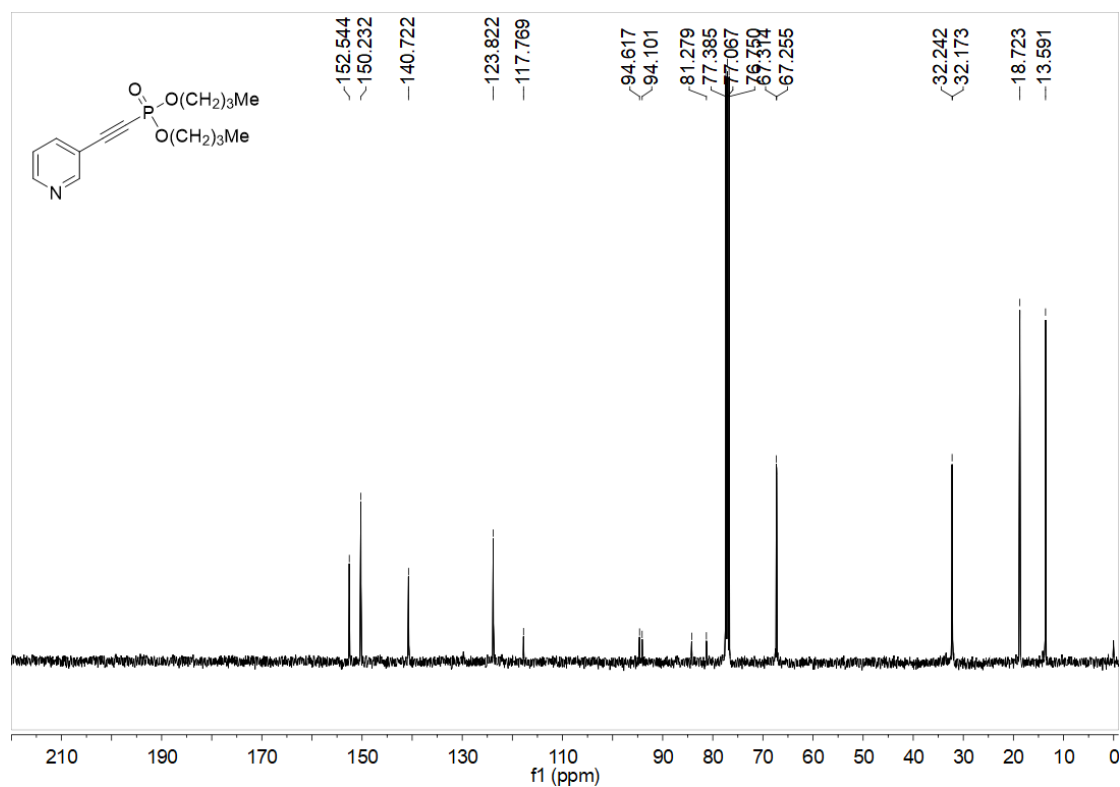
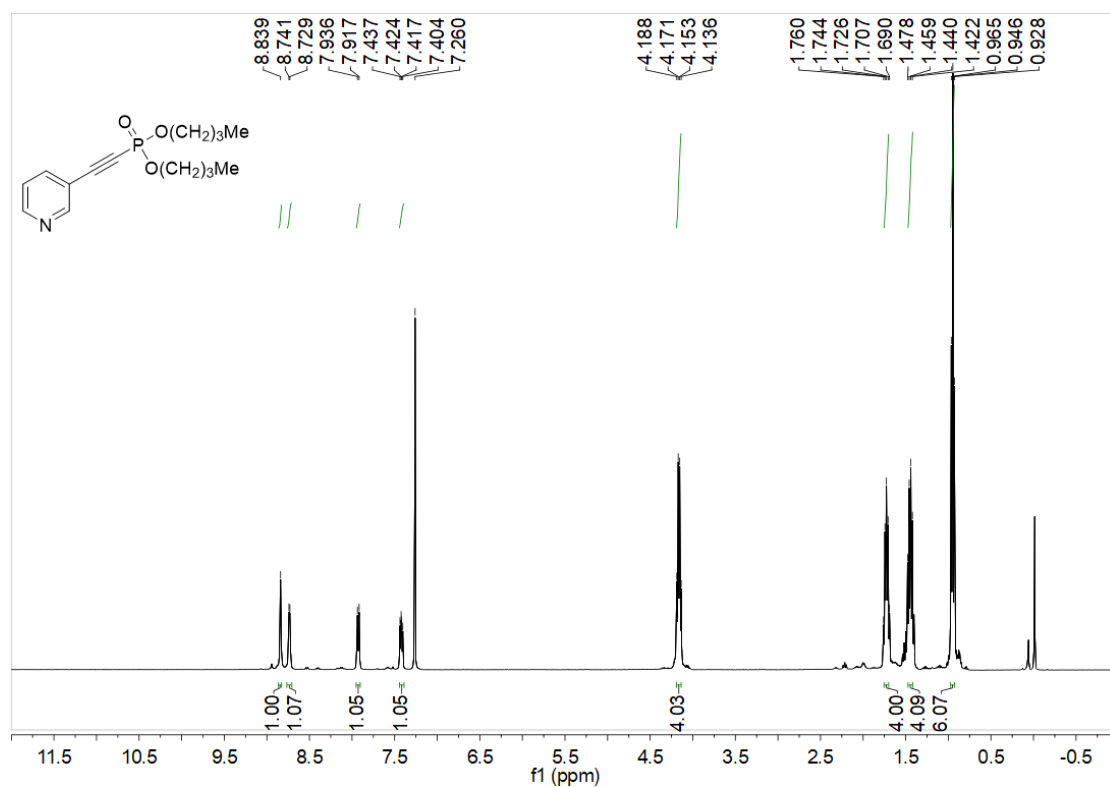


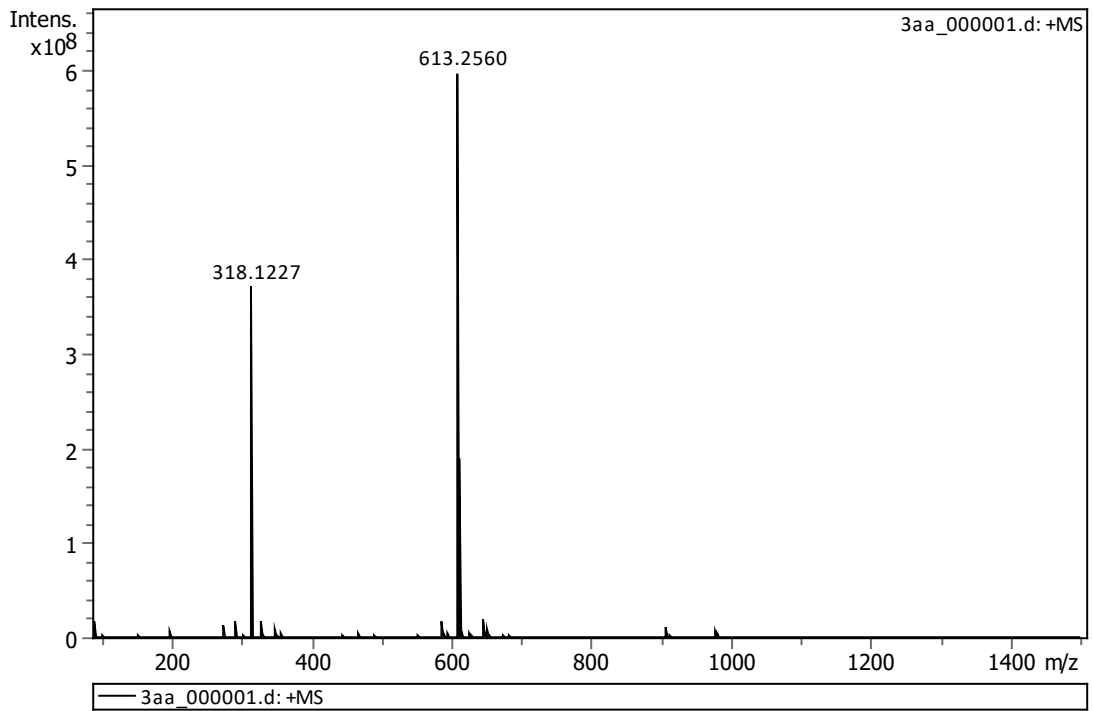
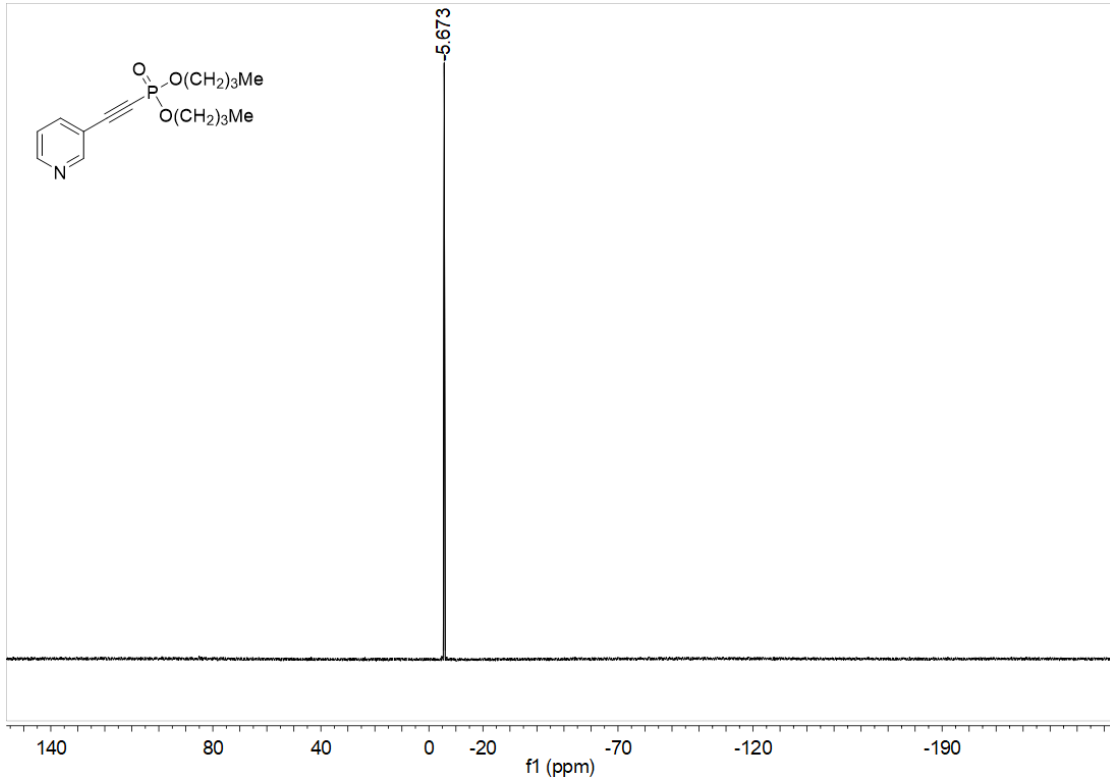
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3z**



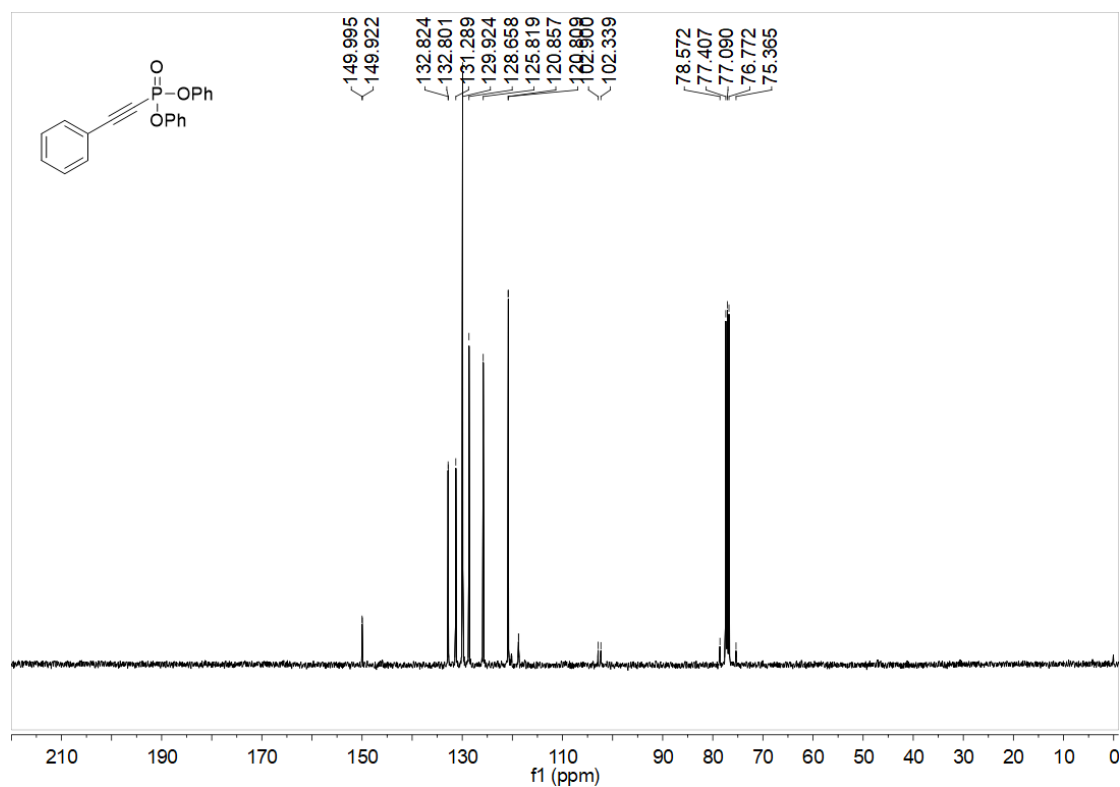
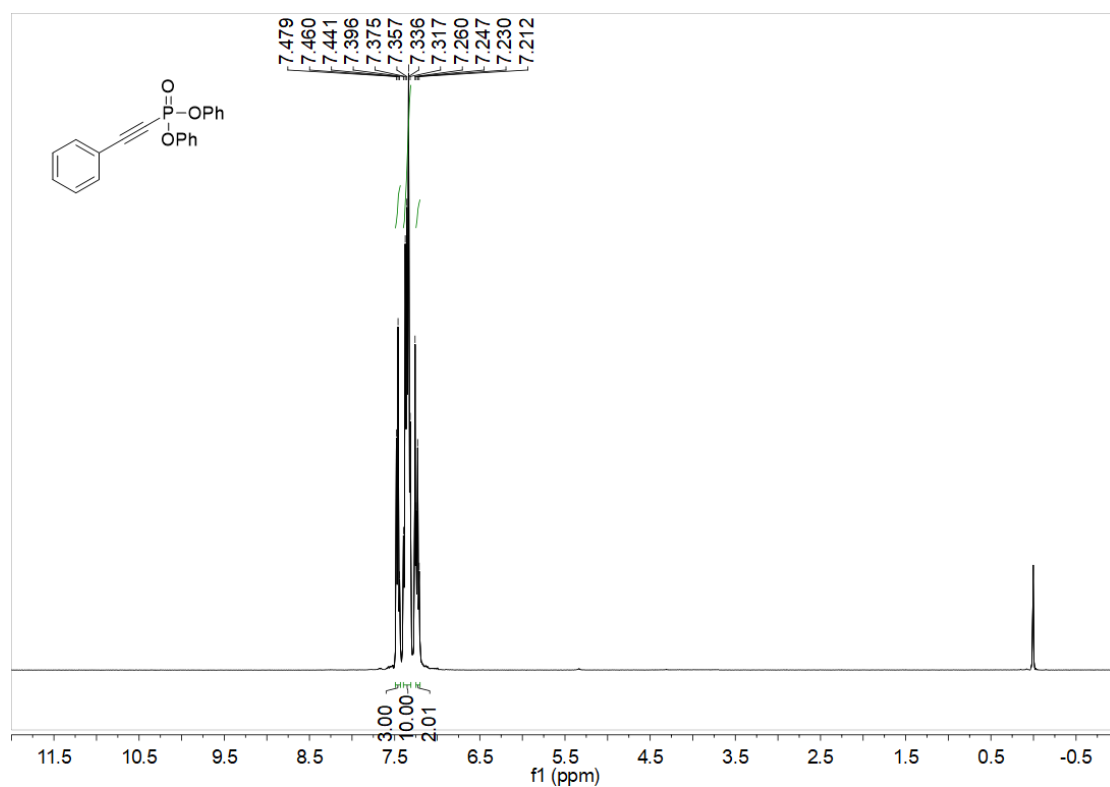


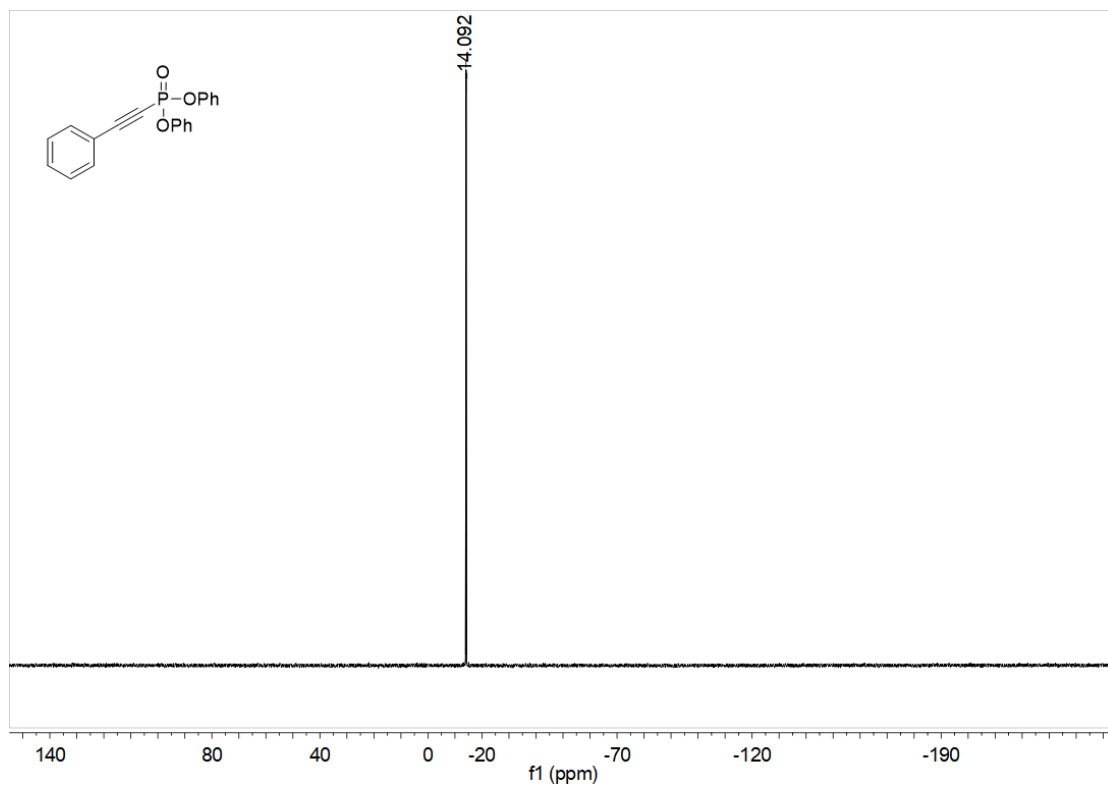
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3aa**



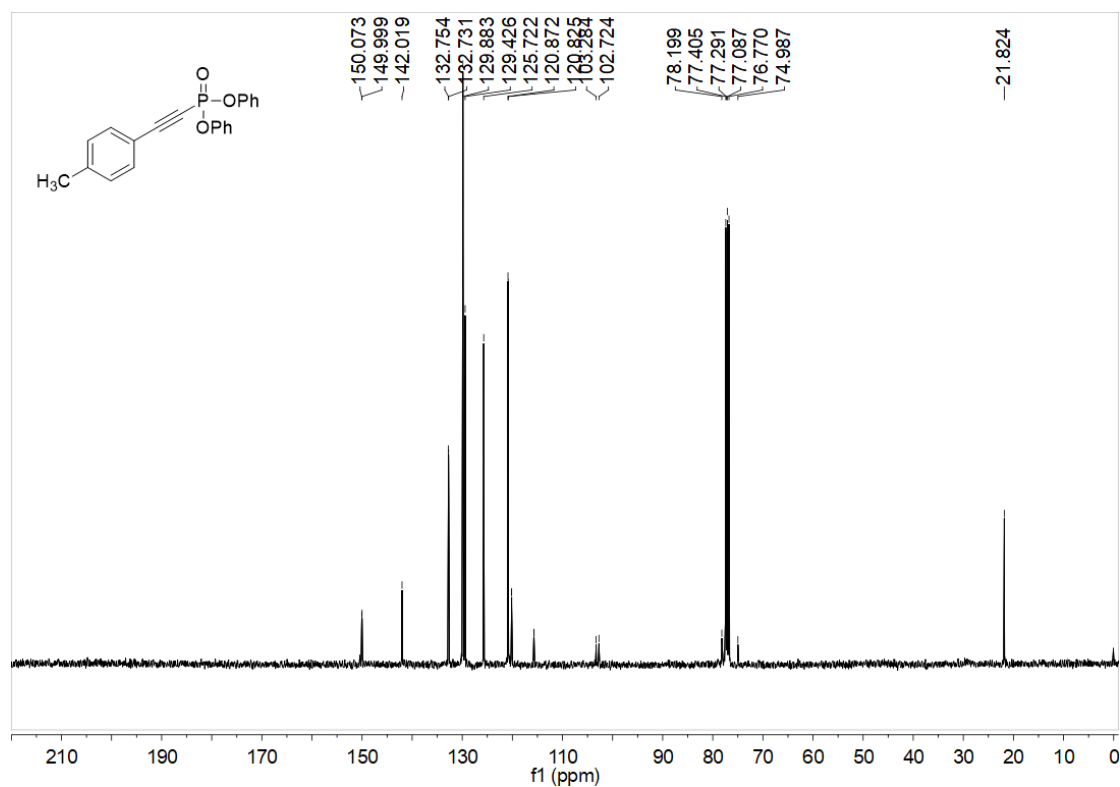
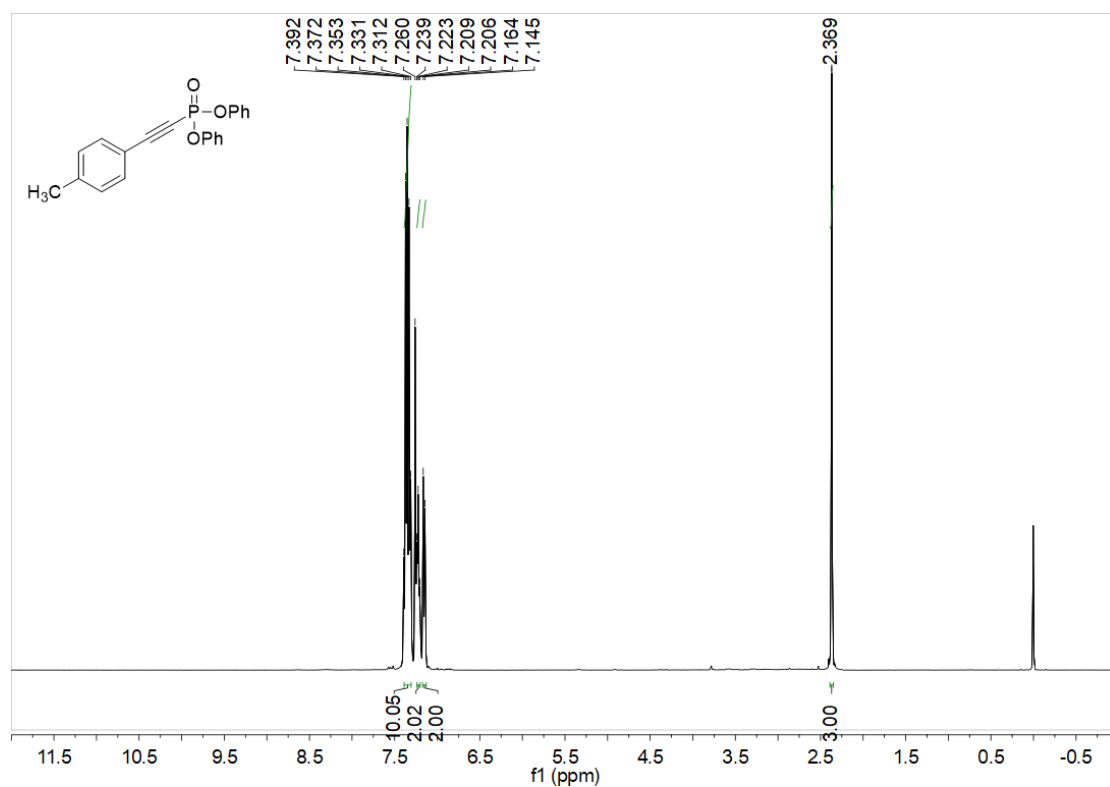


$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3ab**

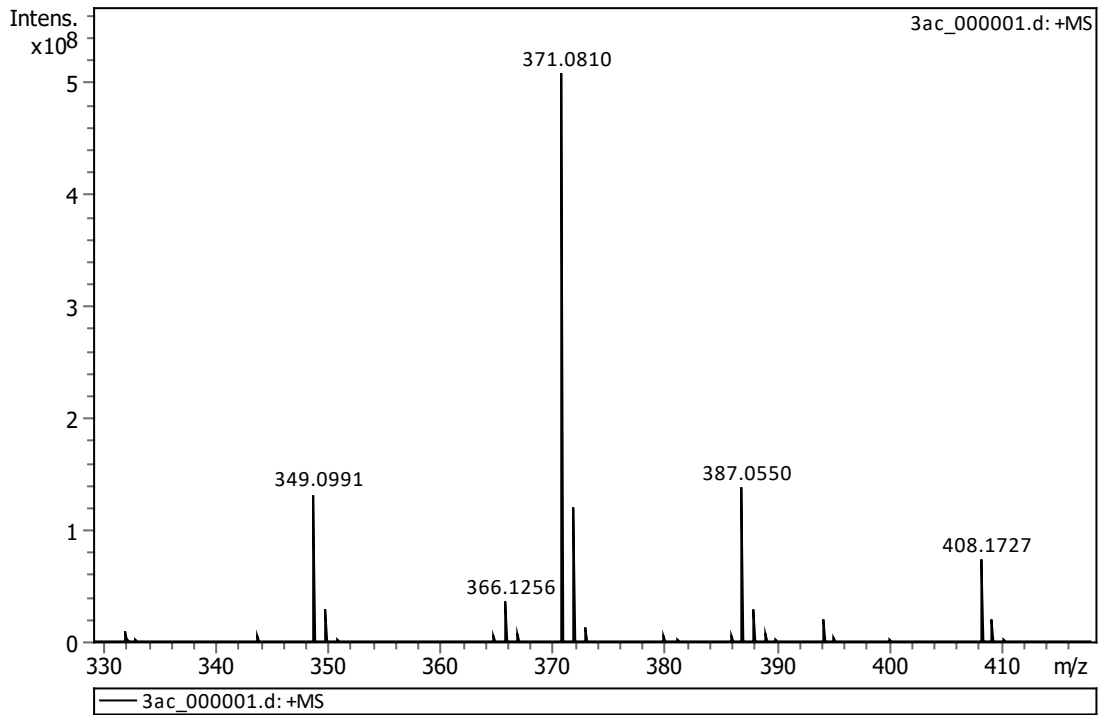
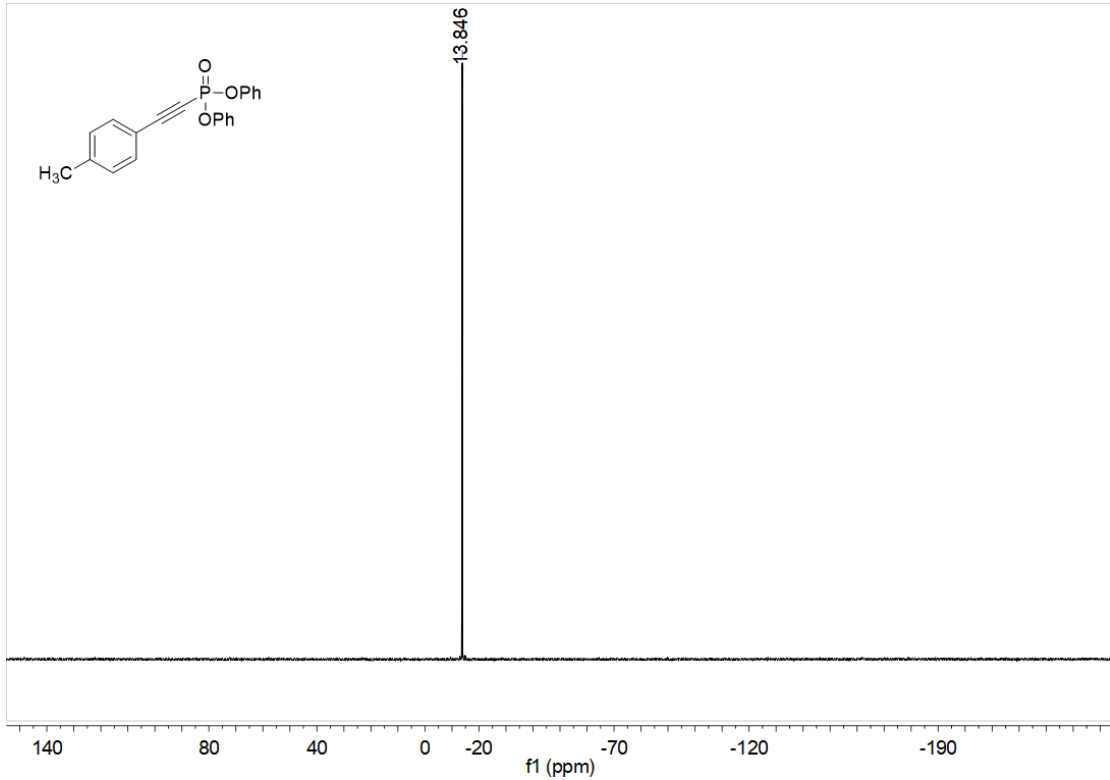




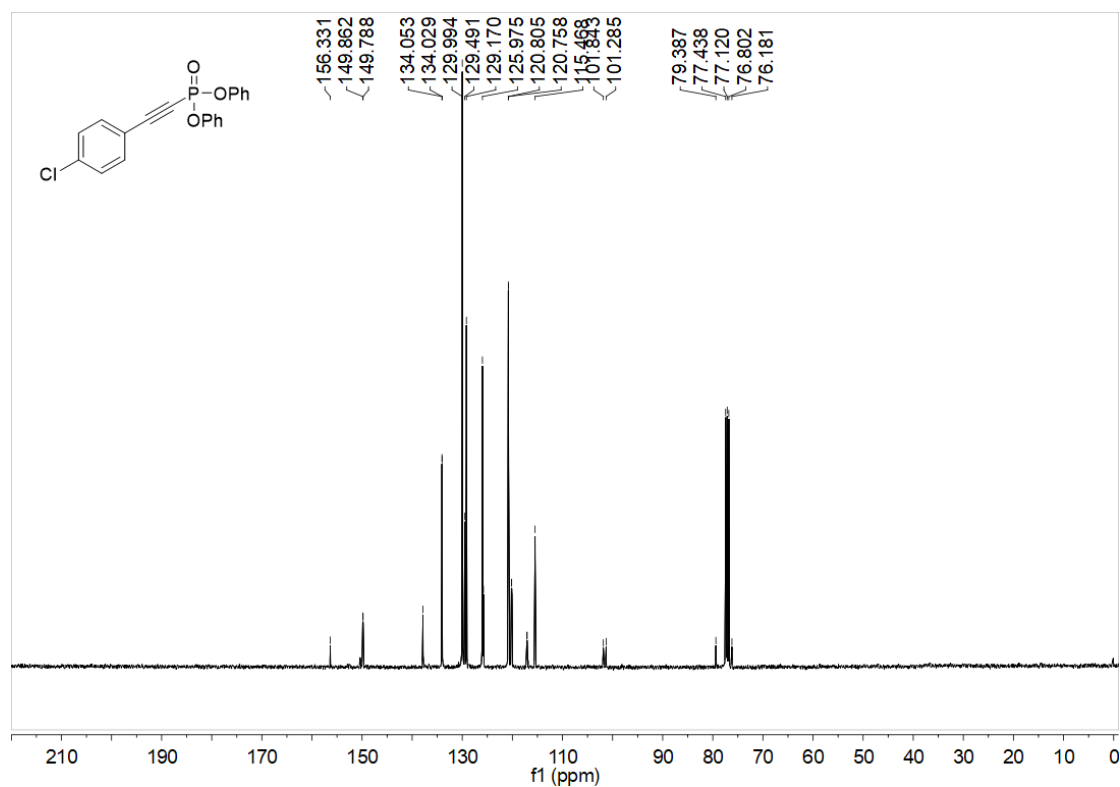
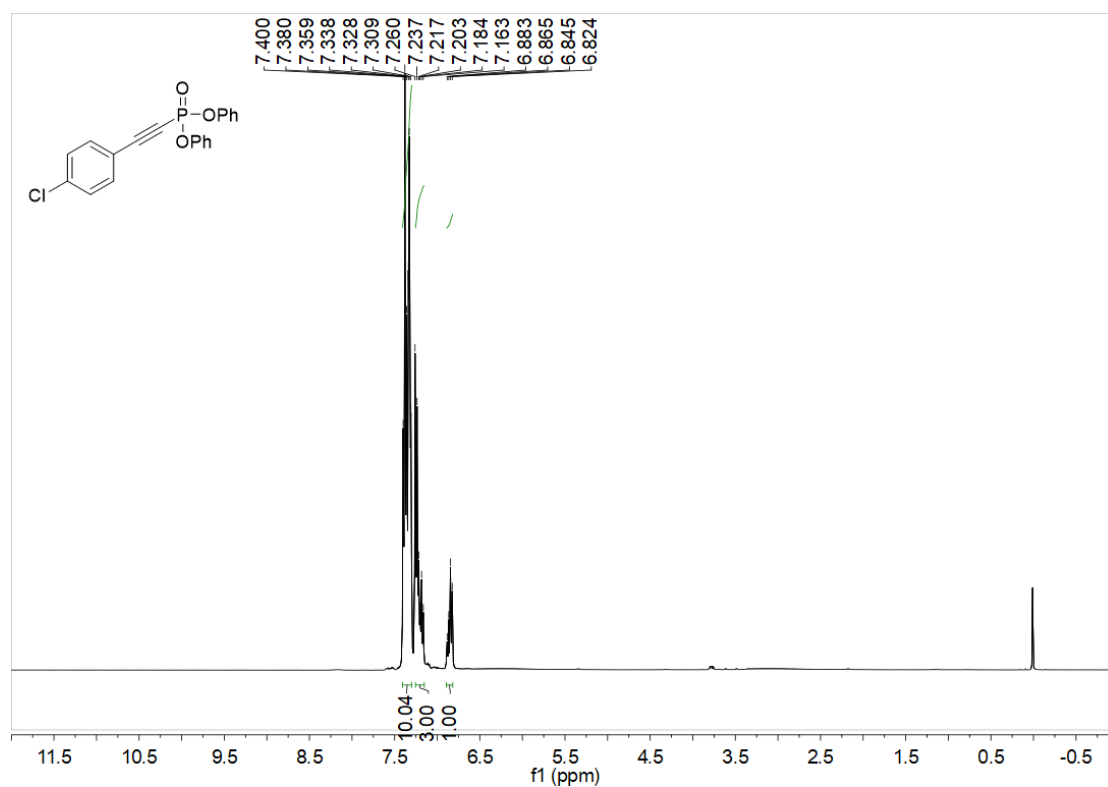
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3ac**

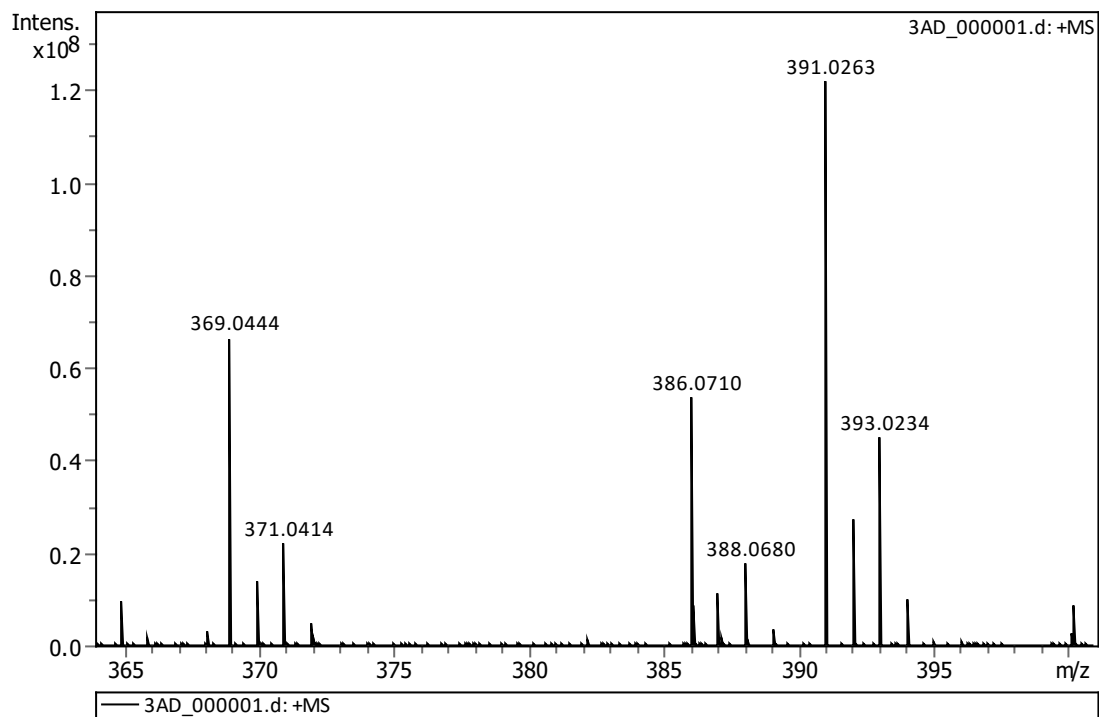
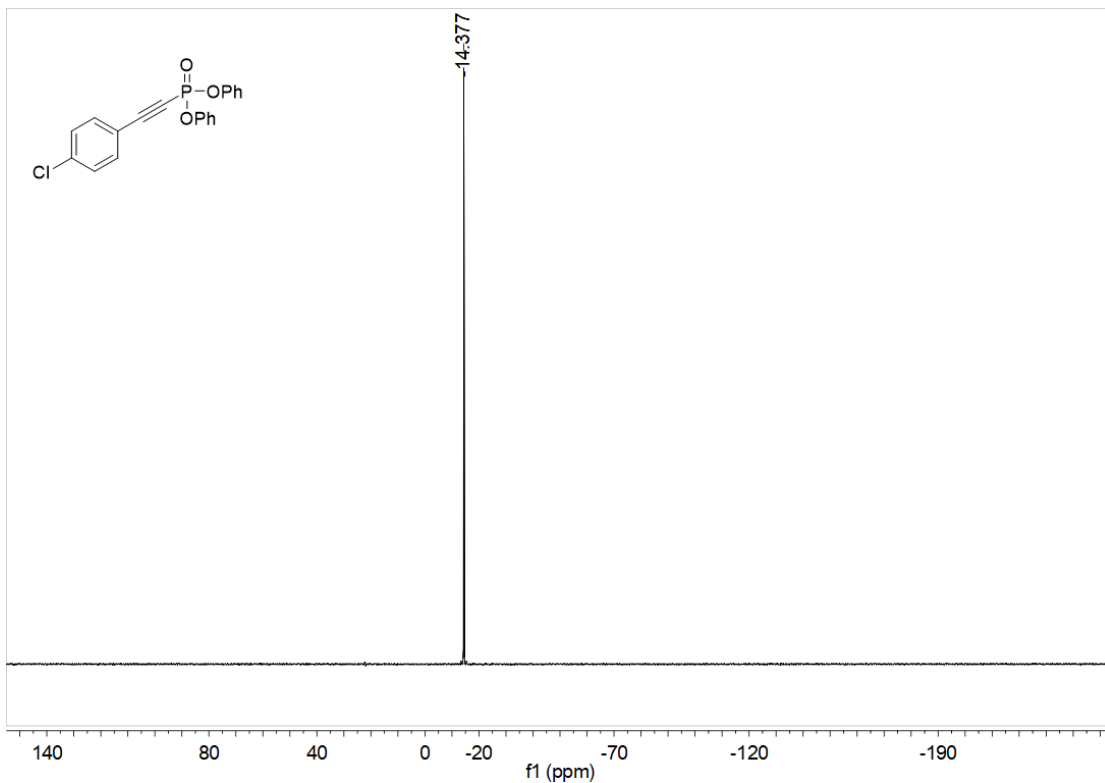




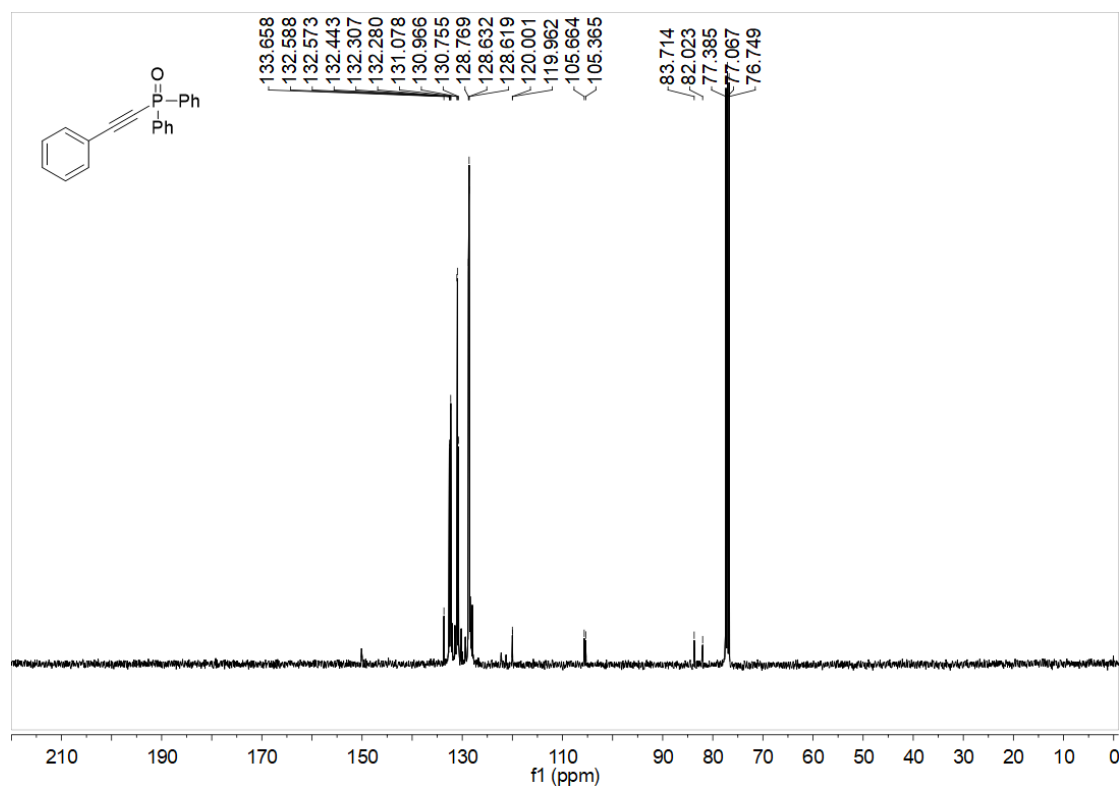
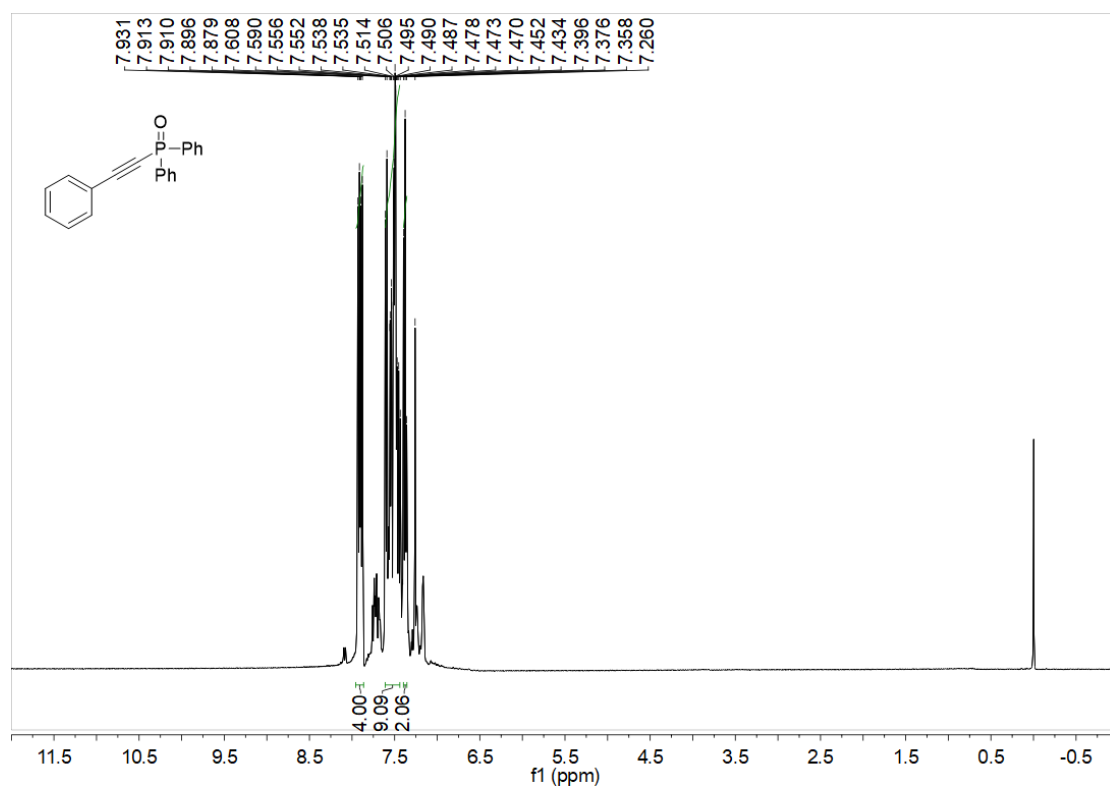


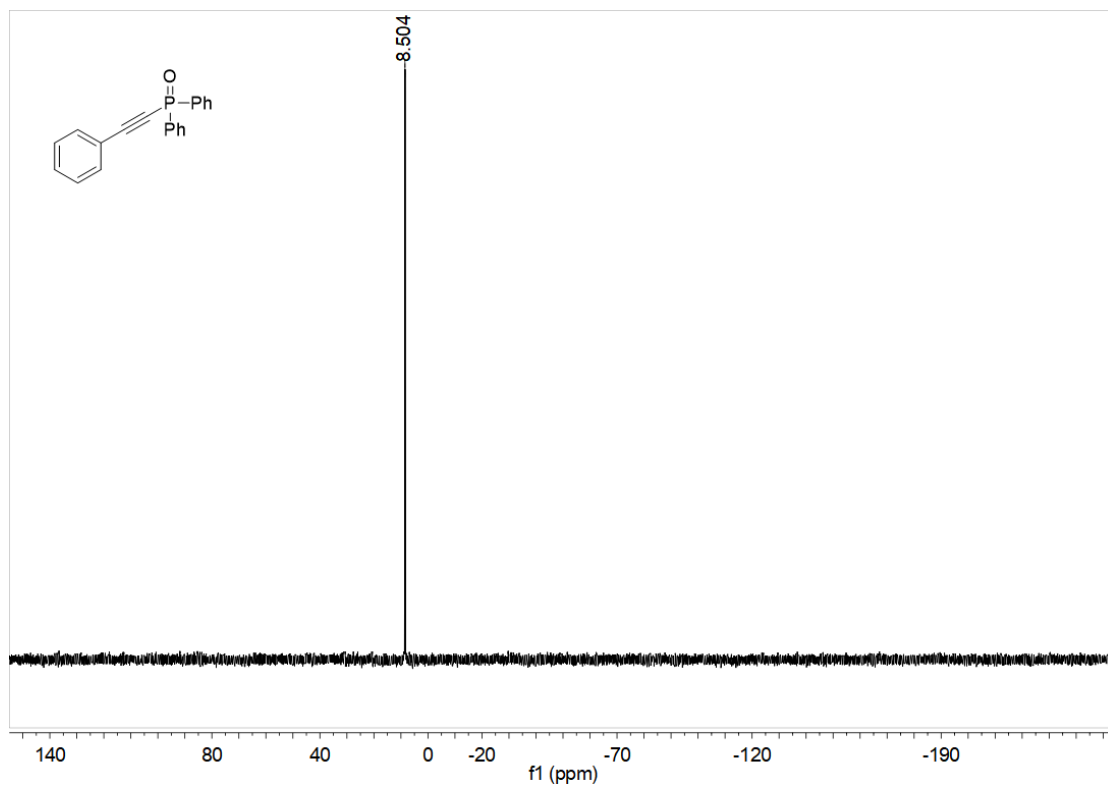
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS of compound **3ad**





$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3ae**





$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR of compound **3af**

