Electronic Supporting Information (ESI)

Aerobic Oxidative Alkynylation of H-Phosphonates and Amides: An Efficient Route for the Synthesis of Alkynylphosphonates and Ynamides by Recyclable Cu-MnO Catalyst

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1. General Methods and materials

All reactions were carried out in oven-dried glassware under standard reaction conditions. All substrates of acetylene, amide and phosphate were purchased from commercial source like S. D. Fine chemicals Ltd India and TCI Chemicals (India) Pvt. Ltd and used without further purification. All the solvents were purchased from S. D. Fine chemicals Ltd India and TCI Chemicals (India) Pvt. Ltd. and dried through standard procedure and stored under nitrogen. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by UV light (254 nm). Flash column chromatography purification of compounds was carried out by gradient elution using ethyl acetate (EA) in light petroleum ether (PE) or Hexane unless otherwise stated. ^{1}H, ^{13}C & ^{31}P NMR was recorded on 600/150/243MHz. NMR spectrometer, in $CDCl_3$ unless otherwise stated, using either TMS or the undeuterated solvent residual signal as the reference The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, td = triplet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). Mass spectral data were obtained from ADCIF division of our Institution by using electro spray ionization time-of-flight (ESI-TOF) mode on mass spectrometer.

List of Abbreviation

Calcd	Calculated
MnO	Manganous oxide
$Cu(OAc)_2$	Copper acetate
DMSO	Dimethyl sulfoxide
DMF	Dimethylformamide
CH_3CN	Acetonitrile
THF	Tetrahydrofuran
equiv	Equivalent
HRMS	High resolution mass spectrometry
Hz	Hertz
J	Coupling constant
TMS-Cl	Trimethylsilyl chloride

2. Synthesis of spherical Cu-MnO catalysts

Synthesis of spherical MnO_2:

Spherical MnO_2 synthesized according to our previews reported method. [1, 2]

Typical synthetic procedure: In a typical synthetic procedure, manganese acetate (2g, $1.01x10^{-2}$mol) and oxalic acid (2g, 1.04 $x10^{-2}$ mol) was dissolved in deionised water to make the clear solution in stirring condition. Then an aqueous solution of ammonium carbonate (4g, 0.025mol) was added dropwise to a pre-mixed solution to make the total volume 40mL. After stirring, the resulting clear solution was transferred to 60 ml Teflon-lined stainless steel autoclave, sealed tightly, and heated at 150°C for 15h. After that, the autoclave was allowed to cool down and the resultant precipitates washed with deionised water and ethanol by centrifugation and dried at 70°C for an hours. Finally, the dried powder was calcined at 350°C for 6h under air atmosphere.

Synthesis of Cu-MnO catalysts:

Impregnation method has been used for the preparation of Cu impregnated MnO (Cu-MnO) by using $Cu(OAc)_2$ H_2O and MnO_2 followed by calcination under 5% H_2 and 95% N_2 condition.

Synthetic procedure: In stirring condition, 500 mg of MnO_2 and 67.5 mg (5 wt% with respect to MnO_2) Copper Acetate [$Cu(OAc)_2$ H_2O] were added in methanol solution followed by sonication. The resultant slurry was evaporated to dryness with continuous stirring (500 rpm) at 70°C under atmospheric pressure. The resultant dried powder was calcined at 350°C for 6 h under 5% H_2 and 95% N_2.

3. Typical procedure for preparation of alkynylphosphonates (I)

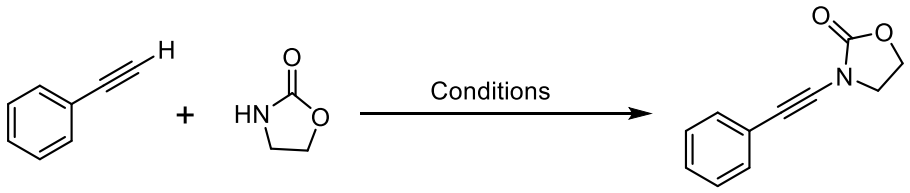
In a carousel reaction tube Cu-MnO catalyst (12 mg) was taken, terminal alkyne (0.25 mmol), dialkyl phosphate (0.5 mmol) and 1 mL DMSO were added over it. The reaction mixture was stirred at 100 °C for 1.5h under air atmosphere. After completion of the reaction, the crude reaction mixture was filtered and washed with ethyl acetate (25 mL). The organic layer was washed with water, and then water layer was re-extracted with ethyl acetate (2x 25 mL). The combined organic layer was washed with brine solution, dried over Na_2SO_4, and then concentrated under reduced pressure. The resulting residue was

purified by flash chromatography (ethyl acetate: hexane) to afford the desired alkynylphosphonates.

4. Typical procedure for preparation of ynamides (II)

In a carousel reaction tube Cu-MnO catalyst (12 mg) and Na_2CO_3 (53 mg, 0.5 mmol) were taken, the tube was then evacuated and refill with oxygen for three times. Next, the terminal alkyne (0.25 mmol), oxazolidin-2-one (0.5 mmol) and 1 mL Toluene were added over it via syringe. The reaction mixture was stirred at 100 °C for 2h under oxygen atmosphere. After completion of the reaction, the crude reaction mixture was filtered and washed with ethyl acetate (25 mL). The organic layer was washed with water and brine solution, dried over Na_2SO_4, and then concentrated under reduced pressure. The resulting residue was purified by flash chromatography (ethyl acetate: hexane) to afford the desired ynamides.

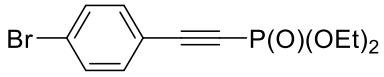
Table S1: Solvent screening for ynamide synthesis



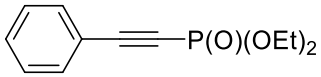
Entry	Catalyst	Solvent	Base	T (°C)	Yield (%)
1	5 wt% Cu-MnO	toluene	Na_2CO_3	100	98
2	5 wt% Cu-MnO	THF	Na_2CO_3	100	trace
3	5 wt% Cu-MnO	DMSO	$NaHCO_3$	100	trace
4	5 wt% Cu-MnO	Ph-Cl	Na_2CO_3	100	92
5	5 wt% Cu-MnO	O-xylene	Na_2CO_3	100	97
6	5 wt% Cu-MnO	H_2O	Na_2CO_3	100	NR
7	5 wt% Cu-MnO	MeOH	Na_2CO_3	100	NR

Standard reaction conditions: 0.25 mmol phenyl acetylene, 2-Oxazolidone (2 equiv., 0.5 mmol), solvent 1 ml, catalyst 12 mg, 100°C, under O_2 atm., for 2h

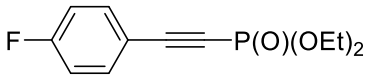
5. Spectral characterization:



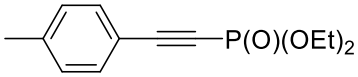
Diethyl (4-bromophenyl)ethynyl]phosphonate (3a):[3] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3a product as a yellow oil, (74 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 4.27 – 4.18 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 134.08 (d, *J* = 1.8 Hz), 132.1, 125.6, 118.6 (d, *J* = 6.2 Hz), 97.8 (d, *J* = 52.6 Hz), 79.8 (d, *J* = 298.6 Hz), 63.49 (d, *J* = 5.5 Hz), 16.3 (d, *J* = 7.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.77; **IR** (neat): 3437, 2931, 2194, 1483, 1262, 1021, 977, 862, 684; **HRMS** (ESI+) calcd for $C_{12}H_{14}BrO_3P$ $[M+H]^+$: 316.9942, found: 316.9951.



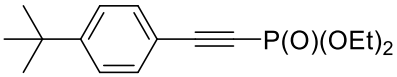
Diethyl (phenylethynyl)phosphonate (3b):[4] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3b product as a yellow oil, (56 mg, 93%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 4.24-4.19 (m, 4H), 1.39 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR (151 MHz, $CDCl_3$) δ** 132.7, 130.8, 128.6, 119.6 (d, *J* = 5.5 Hz), 99.1 (d, *J* = 53.0 Hz), 78.5 (d, *J* = 300.3 Hz), 63.3 (d, *J* = 5.2 Hz), 16.2 (d, *J* = 7.1 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.48; **IR** (neat): 3482, 2985, 2194, 1439 1270, 1021, 977, 862, 764, 692; **HRMS** (ESI+) calcd for $C_{12}H_{15}O_3P$ $[M+H]^+$: 239.0837, found: 239.0835.



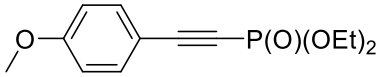
Diethyl [(4-fluorophenyl)ethynyl]phosphonate (3c):[3] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3c product as a yellow oil, (65 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.11 – 7.05 (m, 2H), 4.28 – 4.19 (m, 4H), 1.41 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.9 (d, $J_{C\text{-}F}$ = 253.8 Hz), 136.1 (m, $J_{C\text{-}F}$= 8.5 Hz), 116.2 (d, $J_{C\text{-}F}$ = 22.1 Hz), 115.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 98.0 (d, $J_{C\text{-}P}$ = 53.3 Hz), 78.4 (d, $J_{C\text{-}P}$ = 300.5 Hz), 63.4 (d, $J_{C\text{-}P}$ = 5.5 Hz), 16.2 (d, $J_{C\text{-}P}$ = 7.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.52; **IR** (neat): 3435, 2929, 2190, 1506, 1264, 1025, 801; **HRMS** (ESI+) calcd for $C_{12}H_{14}FO_3P$ $[M+Na]^+$: 279.0562, found: 279.0569.



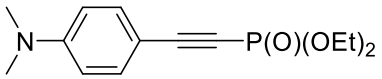
Diethyl (4-tolylethynyl)phosphonate (3d):[4] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3d product as a pale yellow oil, (61 mg, 97%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.20 (m, 4H), 2.36 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.4, 132.7 (d, *J* = 2.0 Hz), 129.4, 116.5 (d, *J* = 5.7 Hz), 99.7 (d, *J* = 53.4 Hz), 77.8 (d, *J* = 300.5 Hz), 63.3 (d, *J* = 5.6 Hz), 21.8, 16.2 (d, *J* = 7.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.06; **IR** (neat): 3481, 2994, 2189, 1514, 1262, 1028, 981, 866, 817,786, 610; **HRMS** (ESI+) calcd for $C_{13}H_{17}O_3P$ $[M+Na]^+$: 275.0813, found: 275.0809.



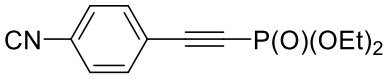
Diethyl [(4-*tert*-butylphenyl)ethynyl]phosphonate (3e):[3] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3e product as a yellow oil, (70 mg, 95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 4.27 – 4.19 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 6H), 1.32 (s, 9H) ; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.5, 132.6, 125.7, 116.6 (d, *J* = 5.5 Hz), 99.7 (d, *J* = 53.4 Hz), 77.8 (d, *J* = 300.88 Hz), 63.3 (d, *J* = 5.0 Hz), 35.2, 31.2, 16.26 (d, *J* = 7.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.03; **IR** (neat): 3476, 2962, 2186, 1265, 1023, 976, 867, 836, 763, 569; **HRMS** (ESI+) calcd for $C_{16}H_{23}O_3P$ $[M+H]+$: 295.1483, found: 295.1489.



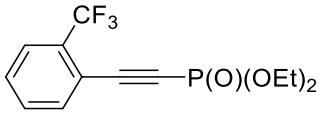
Diethyl [(4-methoxyphenyl)ethynyl]phosphonate (3f):[4] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3f product as a yellow oil, (52 mg, 78%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.24 – 4.17 (m, 4H), 3.82 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.5, 134.5, 114.3, 111.5 (d, *J* = 5.8 Hz), 99.8 (d, *J* = 53.7 Hz), 77.3 (d, *J* =303.01 Hz), 63.2 (d, *J* = 5.6 Hz), 55.5, 16.21 (d, *J* = 7.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.47; **IR** (neat): 3471, 2985, 2189, 1604, 1511, 1262, 1028, 981, 859, 793, 616.



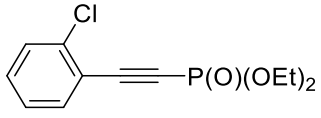
Diethyl [(4-N, N dimethylaminophenyl)ethynyl]phosphonate (3g):[4] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3g product as a maroon oil, (58 mg, 83%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 4.24 – 4.14 (m, 4H), 2.99 (s, 6H), 1.37 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.6, 134.2, 111.5, 105.3 (d, *J* = 6.0 Hz), 102.3 (d, *J* = 54.5 Hz), 76.4 (d, *J* = 310.6 Hz), 63.1 (d, *J* = 5.2 Hz), 40.1, 16.3 (d, *J* = 7.1 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -3.86; **IR** (neat): 3478, 2984, 2930, 2171, 1605, 1529, 1368, 1266, 1021, 974, 864, 766, 599; **HRMS** (ESI+) calcd for $C_{12}H_{20}NO_3P$ $[M+H]^+$: 282.1268, found: 282.1263.



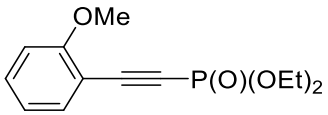
Diethyl [(4-Cyanophenyl)ethynyl]phosphonate (3h):[5] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3h product as a yellow oil, (58 mg, 88%). **^{1}H NMR** (600 MHz, $CDCl_3$)) δ 7.69-7.66 (m, 4H), 4.27-4.22 (m, 4H), 1.42 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$)) δ 133.16 (d, *J* = 1.8 Hz), 132.31, 124.40 (d, *J* = 5.5 Hz), 117.84, 114.20, 95.98 (d, *J* = 51.4 Hz),, 82.56 (d, *J* = 295.3 Hz), 63.64 (d, *J* = 5.2 Hz), 16.22 (d, *J* = 6.9 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -6.63; **IR** (neat): 3435, 2929, 2191, 1261, 1026, 860, 561; **HRMS** (ESI+) calcd for $C_{13}H_{14}NO_3P$ $[M+H]^+$: 264.0789, found: 264.0783.



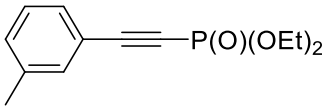
Diethyl [(2-trifluoromethylbenzene)ethynyl]phosphonate (3i):[6] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3i product as a yellow oil, (66 mg, 87%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 14.4, 7.1 Hz, 2H), 7.61 – 7.53 (m, 2H), 4.29 – 4.19 (m, 4H), 1.41 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.2, 131.9, 130.6, 126.3 (q, $J_{C\text{-}F}$ = 4.7 Hz), 125.0 (q, $J_{C\text{-}F}$ = 274.5 Hz), 117.9, 94.2 (d, $J_{C\text{-}P}$ = 51.8 Hz), 84.0 (d, $J_{C\text{-}P}$ = 292.5 Hz), 63.7 (d, $J_{C\text{-}P}$ = 5.4 Hz), 16.2 (d, $J_{C\text{-}P}$ = 7.1 Hz); **^{31}P NMR** (243 $CDCl_3$)MHz,) δ -6.46; **IR** (neat): 3432, 2928, 2193, 1321, 1267, 1135, 1026, 865, 775, 665.



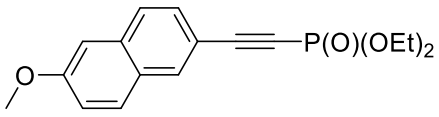
Diethyl [(2-chlorophenyl)ethynyl]phosphonate (3j): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3j product as a yellow oil, (64 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.40-7.37 (m, 1H), 7.30 – 7.27 (m, 1H), 4.26 (m, 4H), 1.42 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.1, 134.5, 131.7, 129.7, 126.8, 120.1 (d, *J* = 5.9 Hz), 95.2 (d, *J* = 52.2 Hz), 83.4 (d, *J* = 295.0 Hz), 63.6 (d, *J* = 5.4 Hz), 16.2 (d, *J* = 7.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -6.10; **IR** (neat): 3435, 2985, 2192, 1264, 1026, 978, 862, 760; **HRMS** (ESI+) calcd for $C_{12}H_{14}ClO_3P$ [M+Na]+ : 295.0267, found: 295.0259.



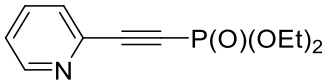
Diethyl [(2-methoxyphenyl)ethynyl]phosphonate (3k):[7] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3k product as a yellow oil, (54 mg, 81%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 1H), 7.40-7.37 (m, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.22 (m, 4H), 3.86 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.7, 134.6 (d, *J* = 2.2 Hz), 132.4, 120.6, 110.9, 109.1 (d, *J* = 5.1 Hz), 96.5 (d, *J* = 53.4 Hz), 82.2 (d, *J* = 300.4 Hz), 63.3 (d, *J* = 5.4 Hz), 55.9 (s), 16.2 (d, *J* = 6.9 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.03; **IR** (neat): 3466, 2930, 2184, 1260, 1025, 976, 868, 784, 755.



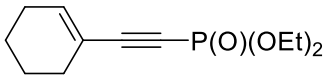
Diethyl [(3-methylphenyl)ethynyl]phosphonate (3l):[4] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3l product as a yellow oil, (59 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.35 (m, 1H), 7.24 (m, 2H), 4.27 – 4.14 (m, 4H), 2.33 (s, 3H), 1.39 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.5, 133.2, 131.7, 129.8, 128.5, 119.4 (d, *J* = 5.4 Hz), 99.5 (d, *J* = 52.9 Hz), 78.05 (d, *J* = 299.03 Hz) 63.3 (d, *J* = 5.6 Hz), 21.2, 16.2 (d, *J* = 7.1 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.26; **IR** (neat): 3483, 2983, 2178, 1260, 1025, 976, 793, 654; **HRMS** (ESI+) calcd for $C_{13}H_{17}O_3P$ [M+H]+ : 253.1003, found: 253.0989.



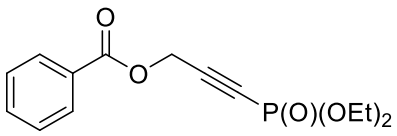
Diethyl [(6-methoxynaphthalen-2-yl)ethynyl]phosphonate (3m):[8] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3m product as a colorless oil, (49 mg, 62%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.73 – 7.66 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.11 (m, 1H), 4.24 (m, 4H), 3.92 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.4, 135.5, 133.7, 129.8, 128.7, 128.1, 127.2, 120.10, 114.2 (d, *J* = 5.6 Hz), 105.9, 100.1 (d, *J* = 52.7 Hz), 77.9 (d, *J* = 300.9 Hz), 63.3 (d, *J* = 5.2 Hz), 55.5, 16.3 (d, *J* = 7.1 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.00; **IR** (neat): 3469, 2930, 2181, 1625, 1482, 1390, 1260, 1167, 1024, 973, 782; **HRMS** (ESI+) calcd for $C_{17}H_{19}O_4P$ $[M+Na]^+$: 341.0919, found: 341.0917.



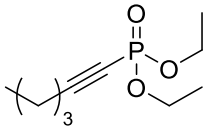
Diethyl (pyridine-2-ylethynyl)phosphonate (3n): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:1.5) to afford 3n product as a Yellow oil, (22 mg, 38%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.66 (m, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 7.0, 5.5 Hz, 1H), 4.26 (m, 4H), 1.41 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.5, 136.5, 128.7, 124.9, 96.8 (d, J = 50.7 Hz), 77.8 (d, J = 291.6 Hz), 63.7 (d, J = 5.6 Hz), 16.2 (d, J = 7.1 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ -6.58; **IR** (neat): 3436, 2929, 2197, 1462, 1262, 1023, 870, 781; **HRMS** (ESI+) calcd for $C_{11}H_{14}NO_3P$ $[M+Na]^+$: 262.0609, found: 262.0618.



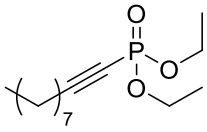
Diethyl (cyclohexen-1-ylethynyl)phosphonate (3o):[4] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3o product as a pale yellow oil, (54 mg, 89%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.44 (s, 1H), 4.19 – 4.12 (m, 4H), 2.16-2.14 (m, 4H), 1.66 – 1.59 (m, 4H), 1.37 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.0, 118.5 (d, *J* = 5.7 Hz), 101.5 (d, *J* = 52.4 Hz), 75.6 (d, *J* = 302.4 Hz), 63.1 (d, *J* = 5.5 Hz), 28.0, 25.9, 21.9, 21.1, 16.2 (d, *J* = 6.9 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -4.58; **IR** (neat): 3433, 2928, 2176, 1262, 1025, 971, 807.



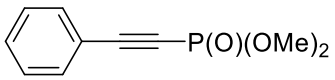
3-(diethoxyphosphoryl)prop-2-yn-1-yl benzoate (3p): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3p product as a colorless oil, (67 mg, 91%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.00 (d, *J* = 4.1 Hz, 2H), 4.24 – 4.09 (m, 4H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 133.7, 129.9, 128.9, 128.6, 93.9 (d, *J* = 50.9 Hz), 76.8 (d, *J* = 293.4 Hz), 63.6 (d, *J* = 5.6 Hz), 52.0 (d, *J* = 4.3 Hz), 16.1 (d, *J* = 7.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.30; **IR** (neat): 3436, 2984, 2930, 2218, 1730, 1602, 1453, 1265, 1166, 1102, 1030, 806, 715, 648; **HRMS** (ESI+) calcd for $C_{14}H_{17}O_5P$ $[M+H]^+$: 297.0892, found: 297.0884.



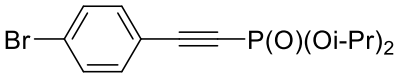
Diethyl hex-1-yn-1-ylphosphonate (3r): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:1) to afford 3r product as a colorless oil, (52 mg, 95%). **^{1}H NMR** (600 MHz,) δ 4.17 – 4.10 (m, 4H), 2.35-2.32 (m, 2H), 1.57 – 1.54 (m, 2H), 1.44-1.40 (m, 2H), 1.35 (t, *J* = 7.0 Hz, 6H), 0.91 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz,) δ 103.4 (d, *J* = 53.1 Hz), 70.3 (d, *J* = 303.9 Hz), 63.1 (d, *J* = 5.1 Hz), 29.5, 21.9 (d, *J* = 10.1 Hz), 19.0 (d, *J* = 4.2 Hz), 16.1 (d, *J* = 7.1 Hz), 13.5; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -5.45; **IR** (neat): 2934, 2205, 1727, 1459, 1393, 1256, 1027, 981; **HRMS** (ESI+) calcd for $C_{10}H_{19}O_3P$ $[M+H]^+$: 219.1150, found: 219.1149.



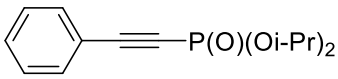
Diethyl dec-1-yn-1-ylphosphonate (3s): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:1) to afford 3s product as a yellow oil, (64 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.16 – 4.09 (m, 4H), 2.33-2.30 (m, 2H), 1.58 – 1.54 (m, 2H), 1.38-1.37 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 6H), 1.29-1.25 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 103.5 (d, *J* = 53.2 Hz), 70.3 (d, *J* = 303.7 Hz), 63.0 (d, *J* = 5.5 Hz), 31.8, 29.1, 29.0, 28.8, 27.5, 22.7, 19.3 (d, *J* = 4.4 Hz), 16.1 (d, *J* = 6.8 Hz), 14.1; **^{31}P NMR** (243 MHz,) δ -5.48; **IR** (neat): 2928, 2206, 1463, 1258, 1030, 976, 733; **HRMS** (ESI+) calcd for $C_{14}H_{28}O_3P$ $[M+H]^+$: 275.1776, found: 275.1788.



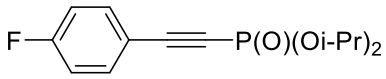
Dimethyl (phenylethynyl)phosphonate (3t):[9] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 3t product as a colorless oil, (47 mg, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, J = 7.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 132.8, 130.9, 128.7, 119.4 (d, *J* = 5.6 Hz), 100.0 (d, *J* = 53.3 Hz), 77.0 (d, *J* = 302.3 Hz), 53.5 (d, *J* = 5.1 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -2.09; **IR** (neat): 3480, 2955, 2188, 1448, 1269, 1036, 862, 762, 690, 653.



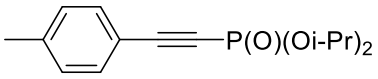
Diisopropyl [(4-bromophenyl)ethynyl]phosphonate (4a):[9] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4a product as a colorless oil, (80 mg, 93%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 4.84 – 4.75 (m, 2H), 1.39 (d, *J* = 3.1 Hz, 6H), 1.38 (d, *J* = 2.4 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 133.9, 132.1, 125.4, 118.9, 96.9 (d, *J* = 52.4 Hz), 81.3 (d, *J* = 297.7 Hz), 72.6 (d, *J* = 5.6 Hz), 24.1 (d, *J* = 4.6 Hz), 23.8 (d, *J* = 4.5 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.26; **IR** (neat): 3436, 2925, 2189, 1466, 1380, 1262, 1005, 889, 682, 535; **HRMS** (ESI+) calcd for $C_{14}H_{18}BrO_3P$ $[M+H]^+$: 345.0255, found: 345.0266.



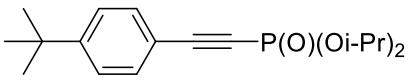
Diisopropyl (phenylethynyl)phosphonate (4b):[9] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4b product as a colorless oil, (61 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 4.88 – 4.77 (m, 2H), 1.41 (dd, *J* = 5.8, 3.5 Hz, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 132.6, 130.6, 128.5 (d, *J* = 24.2 Hz), 119.9 (d, *J* = 5.0 Hz), 98.2 (d, *J* = 53.0 Hz), 78.4 (d, *J* = 295.8 Hz), 72.5 (d, *J* = 5.5 Hz), 24.0 (d, *J* = 4.3 Hz), 23.7 (d, *J* = 4.9 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.92; **IR** (neat): 3462, 2981, 2188, 1382, 1262, 1005, 889, 852, 760, 690, 656, 513; **HRMS** (ESI+) calcd for $C_{14}H_{19}O_3P$ $[M+H]^+$: 267.1152, found: 267.1151.



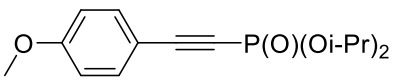
Diisopropyl [(4-fluorophenyl)ethynyl]phosphonate (4c):[9] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4c product as a colorless oil**,** (64 mg, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.05 (t, *J* = 8.5 Hz, 2H), 4.83 – 4.76 (m, 2H), 1.40-1.38 (m, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.86 (d, $J_{C\text{-}F}$ = 253.2 Hz), 134.81 (d, $J_{C\text{-}F}$ = 8.0 Hz), 116.16 (d, $J_{C\text{-}F}$ = 22.7 Hz), 97.02 (d, $J_{C\text{-}P}$ = 53.0 Hz), 79.96 (d, $J_{C\text{-}P}$ = 298.3 Hz), 72.47 (d, $J_{C\text{-}P}$ = 5.6 Hz), 24.00 (d, $J_{C\text{-}P}$ = 4.3 Hz), 23.73 (d, $J_{C\text{-}P}$= 4.6 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.06; **IR** (neat): 3435, 2924, 2189, 1628, 1462, 1005, 798.



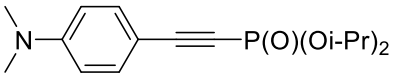
Diisopropyl (4-tolylethynyl)phosphonate (4d):[9] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4d product as a colorless oil, (61 mg, 95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.83 – 4.75 (m, 2H), 2.36 (s, 3H), 1.38 (dd, *J* = 6.3, 2.9 Hz, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.2, 132.5, 129.4, 116.8 (d, *J* = 5.7 Hz), 98.7 (d, *J* = 53.0 Hz), 79.3 (d, *J* = 300.0 Hz), 72.3 (d, *J* = 5.6 Hz), 24.0 (d, *J* = 4.3 Hz), 23.7 (d, *J* = 5.2 Hz), 21.75; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.64; **IR** (neat) : 3433, 2926, 2338, 2186, 1648, 1463, 1263, 1165, 1018, 817 647; **HRMS** (ESI+) calcd for $C_{15}H_{21}O_3P$ $[M+Na]^+$: 281.1314, found: 281.1304.



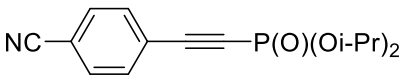
Diisopropyl [(4-*tert*-butylphenyl)ethynyl]phosphonate (4e):[3] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4e product as a colorless oil, (76 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.86 – 4.76 (m, 2H), 1.43 – 1.38 (m, 12H), 1.31 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.2, 132.4, 125.7, 116.9 (d, *J* = 5.7 Hz), 98.7 (d, *J* = 53.1 Hz), 79.3 (d, *J* = 300.1 Hz), 72.3 (d, *J* = 5.6 Hz), 35.1, 31.1, 24.0 (d, *J* = 4.2 Hz), 23.7 (d, *J* = 4.5 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.65; **IR** (neat): 3435, 2962, 2187, 1467, 1382, 1264, 1105, 1002, 889, 834, 773; **HRMS** (ESI+) calcd for $C_{18}H_{27}O_3P$ [M+Na]+ : 345.1596, found: 345.1607.



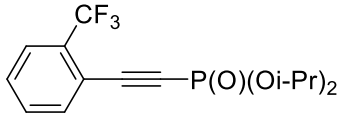
Diisopropyl [(4-methoxyphenyl)ethynyl]phosphonate (4f):[9] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4f product as a colorless oil, (60 mg, 81%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 4.83 – 4.74 (m, 2H), 3.81 (s, 3H), 1.38 (dd, *J* = 6.0, 2.9 Hz, 12H) ; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.4, 134.4, 114.3, 111.8 (d, J = 5.6 Hz), 98.9 (d, J = 53.6 Hz), 78.8 (d, J = 301.1 Hz), 72.2 (d, J = 5.5 Hz), 55.5, 24.0 (d, J = 4.4 Hz), 23.7 (d, J = 5.1 Hz).**^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.33; ; **IR** (neat): 3432, 2928, 2182, 1605, 1258, 1021, 784.



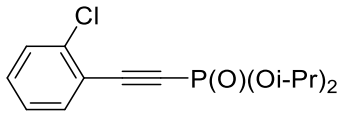
Diisopropyl [(4-N,N dimethylaminophenyl)ethynyl]phosphonate (4g): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4g product as a colorless oil**,** (61 mg, 79%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 2H), 4.79 (m, 2H), 3.01 (s, 6H), 1.41 – 1.38 (m, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.5, 134.1, 111.5, 105.8 (d, *J* = 5.5 Hz), 101.2 (d, *J* = 54.2 Hz), 77.9 (d, *J* = 313.8 Hz), 72.0 (d, *J* = 5.5 Hz), 40.1, 24.1 (d, *J* = 4.3 Hz), 23.8 (d, *J* = 4.8 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -6.43; **IR** (neat): 3433, 2979, 2929, 2172, 1606, 1527, 1373, 1263, 1008, 889, 858, 820, 773; **HRMS** (ESI+) calcd for $C_{16}H_{24}NO_3P$ $[M+H]^+$: 310.1580, found: 310.1580.



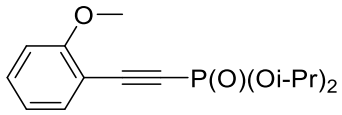
Diisopropyl [(4-Cyanophenyl)ethynyl]phosphonate (4h):[10] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4h product as a colorless oil, (52 mg, 72%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69-7.64 (m, 4H), 4.86-4.80 (m, 2H), 1.42-1.41 (m, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 133.09 (d, *J* = 1.9 Hz), 132.34, 124.74 (d, *J* = 5.6 Hz), 117.93, 114.08, 95.15 (d, *J* = 51.4 Hz), 84.43 (d, *J* = 378.2 Hz), 72.94 (d, *J* = 5.3 Hz), 23.95 (d, *J* = 4.4 Hz), 23.79 (d, *J* = 4.6 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -9.18; **IR** (neat): 3433, 2981, 2929, 2184, 1264, 1026, 888, 863. 755; **HRMS** (ESI+) calcd for $C_{15}H_{18}FO_3P$ [M+Na]+ : 314.0922, found: 314.0912.



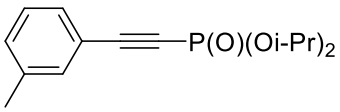
Diisopropyl [(2-trifluoromethylbenzene)ethynyl]phosphonate (4i): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4i product as a colorless oil, (72 mg, 86%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73-7.70 (m, 2H), 7.61 – 7.52 (m, 2H), 4.90 – 4.74 (m, 2H), 1.41 (d, *J* = 6.0 Hz, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.2 (d, $J_{C\text{-}F}$ = 2.3 Hz), 131.8, 130.3, 126.2 (q, $J_{C\text{-}F}$ = 4.4 Hz), 123.1 (q, $J_{C\text{-}F}$ = 275.4 Hz), 117.8, 93.1 (d, $J_{C\text{-}P}$ = 51.8 Hz), 85.3 (d, $J_{C\text{-}P}$ = 291.4 Hz), 72.8 (d, $J_{C\text{-}P}$ = 5.8 Hz), 23.9 (d, $J_{C\text{-}P}$ = 4.3 Hz), 24.0 (d, $J_{C\text{-}P}$ = 5.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -9.32; **IR** (neat): 3432, 2984, 2928, 2194, 1318, 1265, 1137, 1002, 890, 861, 772, 666; **HRMS** (ESI+) calcd for $C_{15}H_{18}F_3O_3P$ $[M+H]^+$: 335.0954, found: 335.0965.



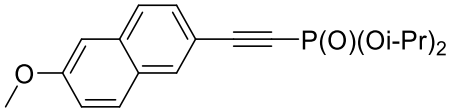
Diisopropyl [(2-chlorophenyl)ethynyl]phosphonate (4j):[9] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4j product as a colorless oil, (64 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 4.84 (m, 2H), 1.42 (dd, *J* = 6.2, 4.3 Hz, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.1, 134.5 (d, *J* = 2.0 Hz), 131.6, 129.7, 126.8, 120.3 (d, *J* = 5.6 Hz), 94.4 (d, *J* = 52.5 Hz), 84.9 (d, *J* = 293.6 Hz), 72.8 (d, *J* = 5.6 Hz), 24.1 (d, *J* = 4.3 Hz), 23.8 (d, *J* = 4.6 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -8.76; **IR** (neat): 3433, 2980, 2930, 2192, 1468, 1264, 1005, 760.



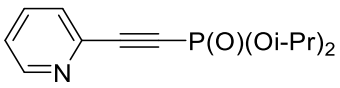
Diisopropyl [(2-methoxyphenyl)ethynyl]phosphonate (4k):[11] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4k product as a yellow solid, (59 mg, 79%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 1H), 7.40 – 7.35 (m, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.85 – 4.77 (m, 2H), 3.85 (s, 3H), 1.41 – 1.38 (m, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.7, 134.4, 132.2, 120.6, 110.9, 109.4 (d, *J* = 5.8 Hz), 95.6 (d, *J* = 53.9 Hz), 84.6 (d, *J* = 295.0 Hz), 72.4 (d, *J* = 5.4 Hz), 55.8, 24.1 (d, *J* = 4.4 Hz), 23.7 (d, *J* = 5.2 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.67; **IR** (neat): 3440, 2928, 2186, 1597, 1464, 1262, 1016, 890, 716, 650; **HRMS** (ESI+) calcd for $C_{15}H_{21}O_4P$ $[M+H]^+$: 297.1263, found: 297.1250.



Diisopropyl [(3-methylphenyl)ethynyl]phosphonate (4l):[6] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4l product as a colorless oil**,** (64 mg, 91%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.22 (d, *J* = 4.3 Hz, 2H), 4.83 – 4.74 (m, 2H), 2.32 (s, 3H), 1.38 (dd, *J* = 5.9, 3.4 Hz, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.5, 133.0 (d, *J* = 1.8 Hz), 131.5, 129.7, 128.5, 119.7 (d, *J* = 5.4 Hz), 98.5 (d, *J* = 52.9 Hz), 79.6 (d, *J* = 298.4 Hz), 72.4 (d, *J* = 5.5 Hz), 24.0 (d, J = 4.3 Hz), 23.7 (d, *J* = 4.6 Hz), 21.2; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.84; **IR** (neat): 3433, 2982, 2929, 2178, 1384, 1265, 1004, 786, 656.

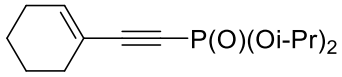


Diisopropyl [(6-methoxynaphthalen-2-yl)ethynyl]phosphonate (4m): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4m product as a colorless oil, (54 mg, 63%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.72-7.68 (m, 2H), 7.50 – 7.48 (m, 1H), 7.17 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.10 (s, 1H), 4.88 – 4.78 (m, 2H), 3.91 (s, 3H), 1.42 (t, *J* = 6.2 Hz, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.3, 135.4, 133.5 (d, *J* = 2.0 Hz), 129.8, 128.7, 128.1, 127.2, 120.1, 114.5 (d, *J* = 5.2 Hz), 106.0, 99.3 (d, *J* = 52.9 Hz), 79.5 (d, *J* = 299.7 Hz), 72.4 (d, *J* = 5.6 Hz), 55.5, 24.1 (d, *J* = 4.5 Hz), 23.8 (d, *J* = 5.1 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.61; **IR** (neat): 3465, 2980, 2932, 2184, 1628, 1465, 1388, 1260, 999, 780, 640; **HRMS** (ESI+) calcd for $C_{19}H_{23}O_4P$ $[M+H]^+$: 347.1412, found: 347.1392.

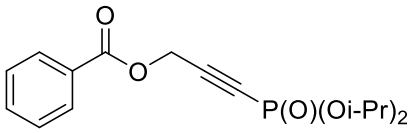


Diisopropyl (pyridine-2-ylethynyl)phosphonate (4n): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4n product as a colorless oil, (25 mg, 37%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.7 Hz, 1H), 7.72-7.69 (m, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.34 (dd, *J* = 7.5, 5.0 Hz, 1H), 4.82 (m, 2H), 1.40 (t, *J* = 5.7 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 136.4, 128.6, 124.7, 95.9 (d, J = 50.6 Hz), 79.3 (d, J = 291.8 Hz), 72.9 (d, J = 5.6 Hz), 24.0 (d, J = 4.6 Hz), 23.7 (d,

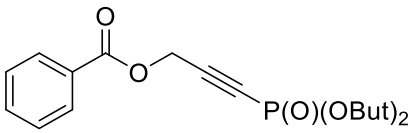
J = 4.7 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ -9.13; **IR** (neat) : 3432, 2929, 2345, 2195, 1460, 1262, 1014, 785; **HRMS** (ESI+) calcd for $C_{13}H_{18}NO_3P$ $[M+H]^+$: 268.1110, found: 268.1097.



Diisopropyl (cyclohexen-1-ylethynyl)phosphonate (4o):[12] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4o product as a colorless oil, (61 mg, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.40 (s, 1H), 4.79 – 4.69 (m, 2H), 2.14 (d, *J* = 5.0 Hz, 4H), 1.66 – 1.62 (m, 2H), 1.60 (m, 2H), 1.37 (d, *J* = 6.1 Hz, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.4 (d, *J* = 3.1 Hz), 118.7 (d, *J* = 5.6 Hz), 100.6 (d, J = 52.8 Hz), 77.2 (d, *J* = 301.5 Hz), 72.1 (d, *J* = 5.3 Hz), 28.0, 25.9, 24.0 (d, *J* = 4.5 Hz), 23.7 (d, *J* = 5.1 Hz), 21.9, 21.1; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.10; **IR** (neat): 3434, 2929, 2341, 1651, 1265, 1166, 1026, 864, 815, 656.

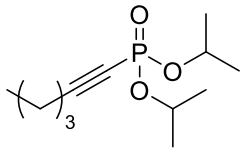


3-(diisopropylphosphoryl)prop-2-yn-1-yl benzoate (4p): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4p product as a colorless oil, (75 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 6.9 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 2H), 4.98 (s, 2H), 4.74 (m, 2H), 1.34 (d, *J* = 5.7 Hz, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 133.7, 129.9, 129.0, 128.6, 93.0 (d, *J* = 51.2 Hz), 78.3 (d, J = 292.9 Hz), 72.8 (d, *J* = 5.6 Hz), 52.1 (d, *J* = 4.3 Hz), 23.9 (d, *J* = 4.3 Hz), 23.6 (d, *J* = 4.5 Hz); **IR** (neat) : 3448, 2983, 2218, 1730, 1452, 1376, 1262, 1101, 1003, 774, 715, 648; **HRMS** (ESI+) calcd for $C_{16}H_{21}O_5P$ $[M+K]^+$: 363.0764, found: 363.0766.

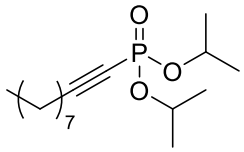


3-(dibutylphosphoryl)prop-2-yn-1-yl benzoate (4q): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4q product as a colorless oil, (78 mg, 88%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.99 (s, 2H), 4.09 (m, 4H), 1.68 – 1.65 (m, 4H), 1.41-1.37 (m, 4H), 0.91-0.88 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.4,

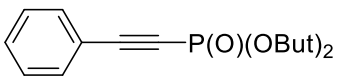
133.7, 129.9, 128.6, 93.9 (d, *J* = 50.8 Hz), 76.7 (d, *J* = 293.8 Hz), 67.3 (d, *J* = 5.8 Hz), 52.0 (d, *J* = 4.3 Hz), 32.2 (d, *J* = 7.1 Hz), 18.7, 13.6; **IR** (neat): 3446, 2962, 2220, 1730, 1554, 1263, 1021, 715; **HRMS** (ESI+) calcd for $C_{18}H_{25}O_5P$ $[M+H]^+$: 353.1518, found: 353.1512.



Diisopropyl hex-1-yn-1-ylphosphonate (4r): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:1) to afford 4r product as a colorless oil, (58 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.75-4.70 (m, 2H), 2.35-2.32 (m, 2H), 1.59 – 1.53 (m, 2H), 1.45-1.41 (m, 2H), 1.39 – 1.33 (m, 12H), 0.92 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 102.3 (d, *J* = 53.2 Hz), 72.0 (d, *J* = 5.4 Hz), 71.8 (d, *J* = 302.8 Hz), 29.5, 23.9 (d, *J* = 4.6 Hz), 23.6 (d, *J* = 4.5 Hz), 21.9 (s), 18.9 (d, *J* = 4.5 Hz), 13.5; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -7.98; **IR** (neat): 2982, 2937, 2206, 1466, 1382, 1256, 1108, 1001, 889, 775; **HRMS** (ESI+) calcd for $C_{12}H_{23}O_3P$ $[M+Na]^+$: 269.1283, found: 269.1301.

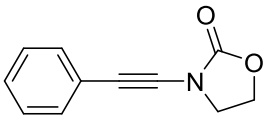


Diisopropyl dec-1-yn-1-ylphosphonate (4s): Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:1) to afford 4s product as a yellow oil, (69 mg, 91%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.75 – 4.62 (m, 2H), 2.30-2.27 (m, 2H), 1.56-1.52 (m, 2H), 1.39 – 1.34 (m, 2H), 1.32 (d, *J* = 6.2 Hz, 12H), 1.26 – 1.21 (m, 8H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 102.3 (d, *J* = 53.3 Hz), 72.0 (d, *J* = 5.2 Hz), 71.8 (d, *J* = 302.8 Hz), 31.8, 29.1, 29.0, 28.8, 27.5, 23.9 (d, *J* = 4.3 Hz), 23.6 (d, *J* = 4.5 Hz), 22.7, 19.2 (d, *J* = 4.3 Hz), 14.1; **^{31}P NMR** (243 MHz,) δ -8.00; **IR** (neat): 2929, 2206, 1729, 1466, 1382, 1257, 1106, 996, 732; **HRMS** (ESI+) calcd for $C_{16}H_{31}O_3P$ $[M+K]^+$: 341.1648, found: 341.1655.

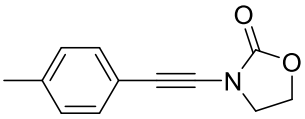


Dibutyl (phenylethynyl)phosphonate (4t):[9] Prepared according to typical procedure I. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 4t product as a colorless oil, (68 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.46

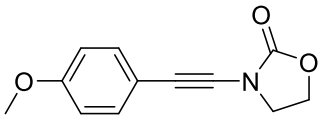
(t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 4.16 (m, 4H), 1.76 – 1.71 (m, 4H), 1.46 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 132.7 (d, *J* = 2.0 Hz), 130.7, 128.6, 119.7 (d, *J* = 5.4 Hz), 99.1 (d, *J* = 52.5 Hz), 78.4 (d, *J* = 299.6 Hz), 67.0 (d, *J* = 5.8 Hz), 32.3 (d, *J* = 7.1 Hz), 18.8, 13.6; **^{31}P NMR** (243 MHz, $CDCl_3$) δ -4.97; **IR** (neat): 3433, 2933, 2188, 1466, 1269, 1023, 857, 760, 689.



3-(phenylethynyl)oxazolidin-2-one (5a):[13] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5a product as a white solid, (44 mg, 95%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.30 (m, 3H), 4.51 – 4.44 (m, 2H), 4.00 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.0, 131.7, 128.4, 128.3, 122.3, 79.1, 71.3, 63.2, 47.1; **IR** (KBr): 2934, 2264, 1757, 1423, 1218, 1091, 748, 690; **HRMS** (ESI+) calcd for $C_{11}H_9NO_2$ $[M+H]^+$: 188.0711, found: 188.0701.

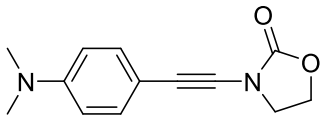


3-(p-tolylethynyl)oxazolidin-2-one (5b):[13] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5b product as a white solid, solid (46 mg, 91%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 4.48 (t, *J* = 7.9 Hz, 2H), 4.04 – 3.97 (m, 2H), 2.34 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.2, 138.5, 131.8, 129.2, 119.1, 78.4, 71.4, 63.1, 47.2, 21.6; **IR** (KBr): 2954, 2922, 1706, 1601, 1428, 1316, 1274, 1118, 1054, 972, 763.

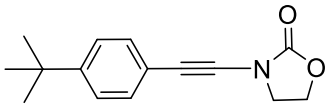


3-(4-methoxyphenylethynyl)oxazolidin-2-one (5c):[13] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5c product as a white solid, (50 mg, 93%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 6.86 – 6.79 (m, 2H), 4.46 (m, 2H), 4.01 – 3.94 (m, 2H), 3.80 (s, 3H); **^{13}C NMR** (126 MHz, CDCl3) δ 159.8, 156.2, 133.6, 114.0, 77.7, 71.0, 63.1, 55.4, 47.2; **IR** (KBr)f: 2959, 2920,

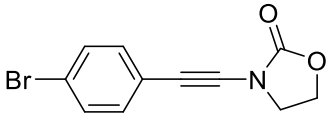
2266, 1746, 1606, 1423, 1253, 1217, 1089, 1025, 838; **HRMS** (ESI+) calcd for $C_{12}H_{11}NO_3$ $[M+H]^+$: 218.0817, found: 218.0817.



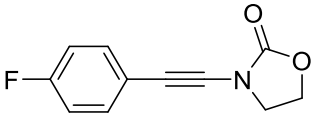
3-(4-N,N-dimethylaminophenylethynyl)oxazolidin-2-one (5d): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5d product as a white solid, (47 mg, 82%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.49 – 4.42 (m, 2H), 4.01 – 3.94 (m, 2H), 2.97 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.4, 150.4, 133.5, 111.8, 108.6, 72.02, 63.0, 47.4, 40.3; **IR** (KBr) : 2919, 2257, 1745, 1612, 1424, 1224, 1085, 1028, 816; **HRMS** (ESI+) calcd for $C_{13}H_{14}N_2O_2$ $[M+H]^+$: 231.1134, found: 231.1138.



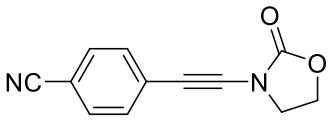
3-(4-*tert*-butylphenylethynyl)oxazolidin-2-one (5e):[14] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5e product as a white solid, (55 mg, 90%)**, ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.48 (t, *J* = 7.8 Hz, 2H), 4.03 – 3.97 (m, 2H), 1.30 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.1, 151.6, 131.5, 125.4, 119.1, 78.4, 71.3, 63.1, 60.5, 47.2, 34.9, 31.3; **IR** (KBr) : 2959, 2925, 2260, 1766, 1428, 1218, 1168, 1086, 1031, 837, 749.



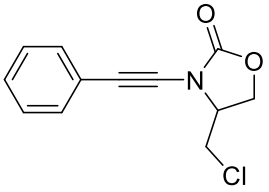
3-(4-bromophenylethynyl)oxazolidin-2-one (5f):[15] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5f product as a white solid, (58 mg, 88%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.32 – 7.28 (m, 2H), 4.54 – 4.46 (m, 2H), 4.04 – 3.99 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.9, 133.1, 131.7, 122.5, 121.3, 80.1, 70.5, 63.2, 47.1, 29.8; **IR** (KBr) : 2925, 2266, 1753, 1639, 1423, 1216, 1163, 1030, 826, 745; **HRMS** (ESI+) calcd for $C_{11}H_8BrNO_2$ $[M+H]^+$: 265.9817, found: 265.9816.



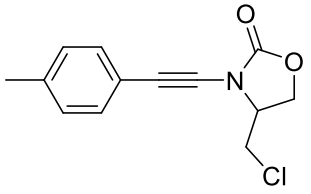
3-(4-fluorophenylethynyl)oxazolidin-2-one (5g):[15] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5g product as a white solid, (46 mg, 90%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 6.93 (t, *J* = 8.7 Hz, 2H), 4.43-4.39 (m, 2H), 3.94-3.91 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.5 (d, *J* = 249.5 Hz), 156.0, 133.7 (d, *J* = 8.2 Hz), 118.2, 115.6 (d, *J* = 22.1 Hz), 78.7, 70.2, 63.2, 47.0; **IR** (KBr): 2922, 2257, 1748, 1639, 1425, 1213, 1168, 1032, 829, 744.



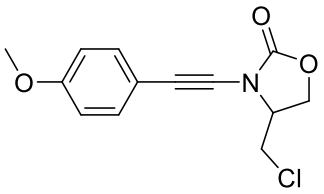
3-(4-cyanophenylethynyl)oxazolidin-2-one (5h):[16] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5h product as a colourless oil, (43 mg, 81%) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 4.55 – 4.50 (m, 2H), 4.06 – 4.02 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.9, 132.1, 131.5, 127.5, 118.6, 111.3, 84.5, 70.6, 63.3, 46.9, 31.0; **IR** (neat) : 2954, 2928, 2187, 1776, 1445, 1268, 1038, 862, 762.



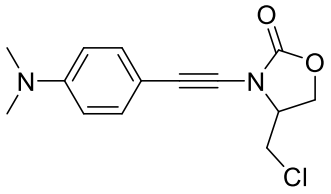
4-(chloromethyl)-3-(phenylethynyl)oxazolidin-2-one (5i): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5i product as a white solid, (57 mg, 96%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.36 – 7.28 (m, 3H), 4.91-4.86 (m, 1H), 4.10 (t, *J* = 9.0 Hz, 1H), 3.92-3.89 (m, 1H), 3.75 (d, *J* = 5.0 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.6, 131.5, 128.2, 121.8, 78.2, 72.6, 71.3, 49.6, 44.0, 30.8, 29.5; **IR** (KBr) : 2921, 2263, 1760, 1418, 1213, 1167, 1045, 757; **HRMS** (ESI+) calcd for $C_{12}H_{10}ClNO_2$ [M+H]+ : 236.0478, found: 236.0483.



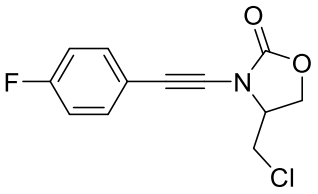
4-(chloromethyl)-3-(p-tolylethynyl)oxazolidin-2-one (5j): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5j product as a solid (57 mg, 92%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.89-4.84 (m, 1H), 4.08 (t, *J* = 9.0 Hz, 1H), 3.89 (q, *J* = 9.2, 5.8 Hz, 1H), 3.74 (d, *J* = 5.0 Hz, 2H), 2.34 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.9, 138.7, 131.7, 129.2, 118.8, 77.8, 72.8, 71.4, 49.7, 44.3, 21.5; **IR** (KBr): 2916, 2247, 1771, 1424, 1212, 1044, 821, 744; **HRMS** (ESI+) calcd for $C_{13}H_{12}ClNO_2$ $[M+H]^+$: 250.0635, found: 250.0638.



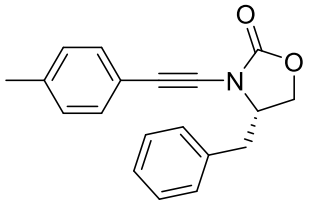
4-(chloromethyl)-3-(4-methoxyphenylethynyl)oxazolidin-2-one (5k): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5k product as a solid (56 mg, 85%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.84 – 4.76 (m, 1H), 3.99 (t, *J* = 9.0 Hz, 1H), 3.79 (q, *J* = 9.2, 5.8 Hz, 1H), 3.72 (s, 3H), 3.66 (t, *J* = 4.9 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 155.0, 133.6, 114.0, 72.7, 71.1, 55.3, 49.7, 44.4; **IR** (KBr): 2933, 2257, 1763, 1604, 1422, 1246, 1097, 1044, 832, 743; **HRMS** (ESI+) calcd for $C_{13}H_{12}ClNO_3$ [M+H]+ : 266.0584, found: 266.0564.



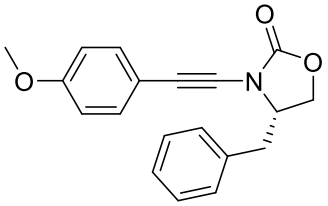
4-(chloromethyl)-3-(4-N,N-dimethylaminophenylethynyl)oxazolidin-2-one (5l): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5l product as a white solid (57 mg, 82%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 4.77 (m, 1H), 3.99 (t, *J* = 9.0 Hz, 1H), 3.79 (q, *J* = 9.2, 5.9 Hz, 1H), 3.65 (d, *J* = 5.2 Hz, 2H), 2.90 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.0, 150.4, 140.5, 124.5, 115.2, 112.2, 107.6, 70.5, 47.4, 46.4, 40.4; **IR** (KBr) : 2929, 2251, 1730, 1607, 1400, 1197, 1086, 947, 812, 747; **HRMS** (ESI+) calcd for $C_{14}H_{15}ClN_2O_2$ $[M+H]^+$: 279.0900, found: 279.0898.



4-(chloromethyl)-3-(4-fluorophenylethynyl)oxazolidin-2-one (5m): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5m product as a solid (57 mg, 90%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 2H), 7.04 – 6.94 (m, 2H), 4.95 – 4.85 (m, 1H), 4.09 (t, *J* = 9.0 Hz, 1H), 3.89 (q, *J* = 9.2, 5.8 Hz, 1H), 3.81 – 3.69 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.6 (d, *J* = 249.6 Hz), 154.9, 133.8 (d, *J* = 7.9 Hz), 118.0, 115.7 (d, *J* = 22.1 Hz), 78.1, 72.8, 70.4, 49.6, 44.3; **IR** (KBr): 2922, 2259, 1758, 1421, 1207, 1168, 1040, 837; **HRMS** (ESI+) calcd for $C_{12}H_9FClNO_2$ [M+H]+ : 276.0204, found: 276.0215.

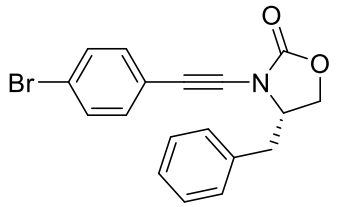


(*S*)4-Benzyl-3-(4-methylphenylethynyl)oxazolidin-2-one (5n):[17] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5n product as a white solid (55 mg, 75%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 8.0 Hz, 4H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.40 – 4.32 (m, 2H), 4.17 (dd, *J* = 7.0, 4.2 Hz, 1H), 3.30 (dd, *J* = 13.9, 3.3 Hz, 1H), 3.05 – 2.97 (m, 1H), 2.36 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.7, 138.6, 134.4, 131.8, 129.7, 129.5, 129.2, 127.7, 119.2, 73.5, 67.6, 58.7, 38.1, 29.8, 21.6; **IR** (KBr) : 2922, 2258, 1757, 1419, 1262, 1092, 1025, 815.

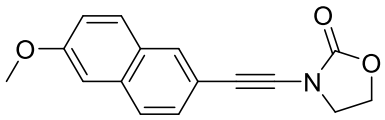


(*S*)4-Benzyl-3-(4-methoxyphenylethynyl)oxazolidin-2-one (5o):[17] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5o product as a white solid (63 mg, 82%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 –

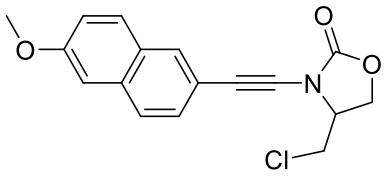
7.33 (m, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.33 – 4.25 (m, 2H), 4.12 – 4.07 (m, 1H), 3.75 (s, 3H), 3.22 (dd, *J* = 13.8, 3.7 Hz, 1H), 2.95-2.91 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 155.8, 134.4, 133.7, 129.5, 129.2, 127.7, 114.2, 114.1, 73.2, 67.6, 58.7, 55.4, 38.1, 29.8; **IR** (KBr): 2924, 2256, 1766, 1638, 1419, 1214, 1086, 831, 746.



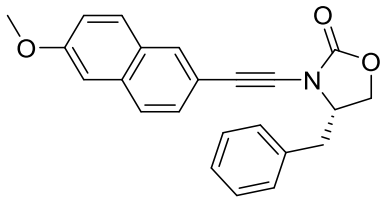
(*S*)4-Benzyl-3-(4-bromophenylethynyl)oxazolidin-2-one (5p): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5p product as a white solid (60 mg, 68%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 7.6, 3.2 Hz, 3H), 7.24 (d, *J* = 7.2 Hz, 2H), 4.42 – 4.34 (m, 2H), 4.18 (dd, *J* = 7.6, 4.5 Hz, 1H), 3.28 (dd, *J* = 13.9, 3.9 Hz, 1H), 3.03-2.98 (m, 1H); ^{13}C NMR (151 MHz,) δ 155.5, 134.3, 133.1, 131.7, 129.5, 129.2, 128.1, 127.8, 122.6, 121.3, 79.1, 72.6, 67.7, 58.6, 38.3, 31.1; **IR** (KBr): 2920, 2253, 1759, 1414, 1210, 1187, 1093, 1066, 994, 820, 752, 704; **HRMS** (ESI+) calcd for $C_{18}H_{14}BrNO_3$ $[M+H]^+$: 356.0286 found: 356.0283.



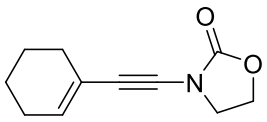
3[(6-methoxynaphthalen-2yl)ethynyl]oxazolidin-2-one (5q): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5q product as a solid, (52 mg, 78%), **^{1}H NMR** (500 MHz, DMSO+$CDCl_3$) δ 7.88 (s, 1H), 7.73 (s, 2H), 7.41 (s, 1H), 7.18 (m, 2H), 4.52 (s, 2H), 4.06 (s, 2H), 3.91 (d, *J* = 2.6 Hz, 3H); **^{13}C NMR** (126 MHz, DMSO+$CDCl_3$) δ 156.6, 154.4, 132.3, 129.2, 127.6, 127.1, 126.6, 125.5, 117.9, 115.4, 104.3, 78.2, 69.2, 62.0, 53.7, 45.4; **IR** (KBr): 2923, 2253, 1756, 1647, 1486, 1220, 1026, 1002, 826, 765; **HRMS** (ESI+) calcd for $C_{16}H_{13}NO_3$ $[M+H]^+$: 268.0974, found: 268.0982.



4-(chloromethyl)-3-[(6-methoxynaphthalen-2yl)ethynyl]oxazolidin-2-one (5r): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5r product as a solid, (63 mg, 80%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.4 Hz, 1H), 7.74 (s, 2H), 7.42 (s, 1H), 7.27 – 7.11 (m, 2H), 5.07 (s, 1H), 4.18-4.16 (m, 1H), 3.97-3.94 (m, 2H), 3.87-3.85 (m, 1H), 3.39 – 3.33 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.4, 153.2, 132.2, 129.1, 127.5, 127.4, 127.0, 126.9, 126.5, 125.4, 125.3, 117.7, 115.0, 104.2, 77.6, 71.7, 69.2, 53.6, 47.4, 43.9; **IR** (KBr): 2924, 2253, 1759, 1640, 1487, 1218, 1027, 1002, 825, 764; **HRMS** (ESI+) calcd for $C_{17}H_{14}ClNO_3$ $[M+H]^+$: 316.0740, found: 316.0725.

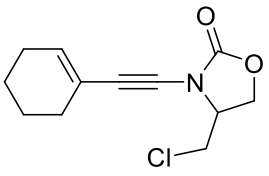


(*S*)4-Benzyl-3-[(6-methoxynaphthalen-2yl)ethynyl]oxazolidin-2-one (5s): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5s product as a solid, (67 mg, 75%), **^{1}H NMR** (500 MHz, DMSO) δ 7.93 (s, 1H), 7.84-7.80 (m, 2H), 7.41 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.38-7.34 (m, 5H), 7.30 – 7.26 (m, 1H), 7.20 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.62 – 4.54 (m, 1H), 4.50 (t, *J* = 8.5 Hz, 1H), 4.23 (dd, *J* = 8.6, 5.4 Hz, 1H), 3.88 (s, 3H), 3.19 – 3.08 (m, 2H); **^{13}C NMR** (126 MHz, DMSO) δ 159.7, 157.2, 137.1, 135.6, 132.5, 131.5, 131.1, 130.5, 129.9, 129.0, 128.9, 121.3, 118.5, 107.9, 74.5, 69.4, 59.5, 57.2, 38.9, 30.9; **IR** (KBr): 2924, 2254, 1653, 1486, 1221, 1027, 1002, 826, 764; **HRMS** (ESI+) calcd for $C_{23}H_{19}NO_3$ $[M+H]^+$: 380.1263 found: 380.1249.

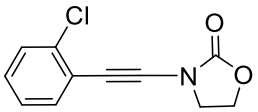


3-(cyclohex-1-en-1-ylethynyl)oxazolidin-2-one (5t):[15] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5t product as a colorless oil, (46 mg, 96%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.14-6.11

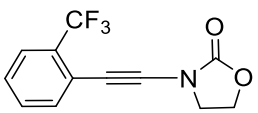
(m, 1H), 4.45-4.42 (m, 2H), 3.91 (dd, *J* = 8.7, 7.3 Hz, 2H), 2.18 – 2.06 (m, 4H), 1.65 – 1.62 (m, 2H), 1.60 – 1.56 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.2, 135.6, 119.6, 76.6, 72.9, 63.0, 47.3, 29.8, 29.5, 25.8, 22.4, 21.6; **IR** (neat): 2923, 2311, 1636, 1464 1384, 1270, 1118, 708.



4-(chloromethyl)-3-(cyclohex-1-en-1-ylethynyl)oxazolidin-2-one (5u):[18] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5u product as a colorless oil, (54 mg, 90%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.17 – 6.10 (m, 1H), 4.88 – 4.78 (m, 1H), 4.01 (t, *J* = 9.0 Hz, 1H), 3.81 (dd, *J* = 9.3, 5.8 Hz, 1H), 3.75 – 3.68 (m, 2H), 2.20 – 1.99 (m, 4H), 1.66 – 1.61 (m, 2H), 1.61 – 1.55 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.0, 135.8, 119.4, 76.0, 73.0, 72.6, 49.9, 44.2, 29.8, 29.4, 25.8, 22.4, 21.5; **IR** (neat):2923, 2262, 1757, 1633, 1422, 1384, 1218, 1025, 746.

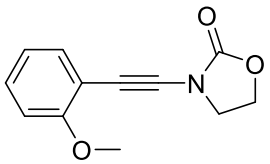


3-(2-chlorophenylethynyl)oxazolidin-2-one (5v): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5v product as a solid, (49 mg, 89%) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.23 – 7.16 (m, 2H), 4.49 (t, *J* = 7.9 Hz, 2H), 4.05 – 4.01 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.7, 135.5, 133.1, 129.3, 129.2, 126.6, 122.4, 84.0, 68.6, 63.3, 47.1; **IR** (neat): 2922, 2261, 1748, 1632, 1613, 1419, 1087, 1027, 747; **HRMS** (ESI+) calcd for $C_{11}H_8ClNO_2$ $[M+H]^+$: 222.0322 found: 222.0326.

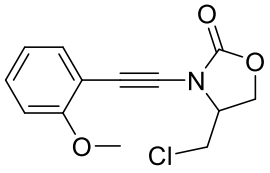


3-(2-trifluoromethylphenylethynyl)oxazolidin-2-one (5w): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5w product as a yellow oil (52 mg, 81%) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 4.52 – 4.48

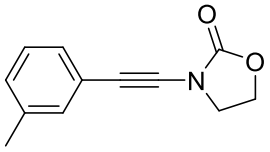
(m, 2H), 4.05 – 4.00 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.5, 133.3, 131.6, 130.9 (q, *J* = 30.4 Hz), 127.7, 125.9 (q, *J* = 4.5 Hz), 123.7 (q, *J* = 273.2 Hz), 120.8, 84.5, 68.3, 63.3, 46.9; **IR** (neat): 2925, 2262, 1768, 1481, 1415, 1317, 1260, 1168, 1112, 1033, 768, 746; **HRMS** (ESI+) calcd for $C_{12}H_8F_3NO_2$ $[M+Na]^+$: 278.0405 found: 278.0411.



3-(2-methoxyphenylethynyl)oxazolidin-2-one (5x):[15] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5x product as a white solid, (46 mg, 84%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.29 (m, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.52 – 4.44 (m, 2H), 4.07 – 4.00 (m, 2H), 3.88 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0, 155.9, 133.9, 129.8, 120.4, 111.3, 110.6, 82.5, 77.3, 77.0, 76.8, 67.4, 63.0, 55.8, 47.1; **IR** (KBr): 2923, 2329, 1637, 1464, 1384, 1250, 1025, 617.

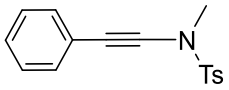


4-(chloromethyl)-3-(2-methoxyphenylethynyl)oxazolidin-2-one (5y): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5y product as a white solid, (56 mg, 85%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.32 – 7.27 (m, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.89-4.84 (m, 1H), 4.13 (t, *J* = 9.0 Hz, 1H), 3.93 (dd, *J* = 9.3, 5.9 Hz, 1H), 3.88 (s, 3H), 3.78 – 3.70 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.1, 154.8, 134.0, 130.1, 120.6, 111.2, 110.7, 82.0, 72.8, 67.8, 55.9, 50.0, 44.1; **IR** (KBr): 2921, 2332, 2250, 1772, 1574, 1424, 1214, 1044, 986, 775; **HRMS** (ESI+) calcd for $C_{13}H_{12}ClNO_3$ $[M+Na]^+$: 288.0403 found: 288.0411.

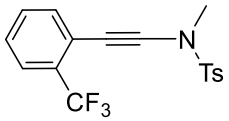


3-(3-methylphenylethynyl)oxazolidin-2-one (5z):[13] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5z

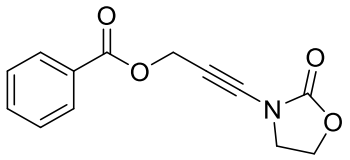
product as a solid, (47 mg, 94%) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 4.49-4.46 (m, 2H), 4.01-3.98 (m, 2H), 2.32 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.0, 138.1, 132.3, 129.2, 128.7, 128.3, 122.0, 78.7, 71.5, 63.1, 47.2, 21.3; **IR** (KBr): 2917, 2254, 1756, 1423, 1226, 1147, 1030, 792, 746.



N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide (5aa):[13] Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5aa product as a solid, (57 mg, 80%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.33 (m, 4H), 7.30 – 7.26 (m, 3H), 3.14 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.9, 133.4, 131.5, 129.9, 128.4, 128.0, 122.8, 84.1, 69.2, 39.5, 21.8; **IR** (KBr): 2922, 2306, 2253, 1716, 1409, 1323, 1161, 1093, 816, 701.

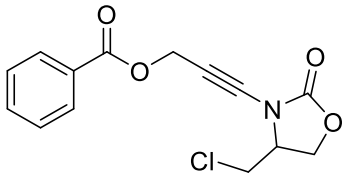


N,4-dimethyl-N-(2-trifluoromethylphenylethynyl)benzenesulfonamide (5ab): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5ab product as a solid, (63 mg, 71%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.30 (m, 3H), 3.16 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.1, 133.6, 133.1, 131.5, 130.5 (d, J = 30.3 Hz), 130.0, 127.9, 127.3, 125.9 (q, J = 4.9 Hz), 123.7 (d, J = 273.5 Hz), 121.5, 89.6, 66.0, 60.5, 39.3, 21.8; **IR** (KBr): 2923, 2241, 1606, 1362, 1318, 1165, 1029, 813, 746; **HRMS** (ESI+) calcd for $C_{17}H_{14}F_3NO_2S$ $[M+Na]^+$: 376.0595 found: 376.0592.



3-(2-oxooxazolidin-3-yl)prop-2-yn-1-yl benzoate (5ac): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5ac product as a colorless oil, (52 mg, 85%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.0 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.54 – 7.40 (m, 2H), 5.10 (s, 2H), 4.58 – 4.36 (m, 2H),

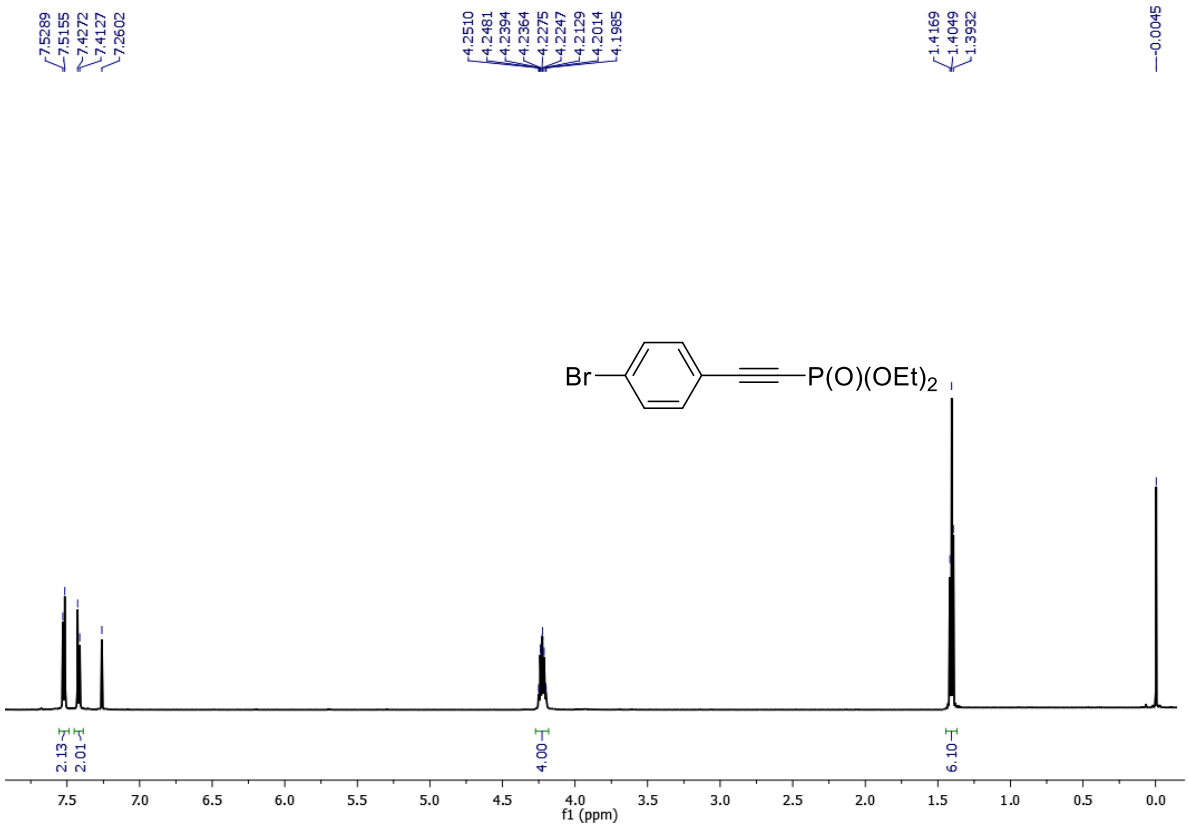
4.06 – 3.88 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.1, 156.1, 133.4, 129.9, 129.7, 128.6, 76.8, 66.8, 63.2, 53.1, 46.7; **IR** (neat): 2923, 2266, 1770, 1719, 1420, 1263, 1200, 1093, 1026, 748, 710; **HRMS** (ESI+) calcd for $C_{13}H_{11}NO_4$ $[M+Na]^+$: 268.0586 found: 268.0602.

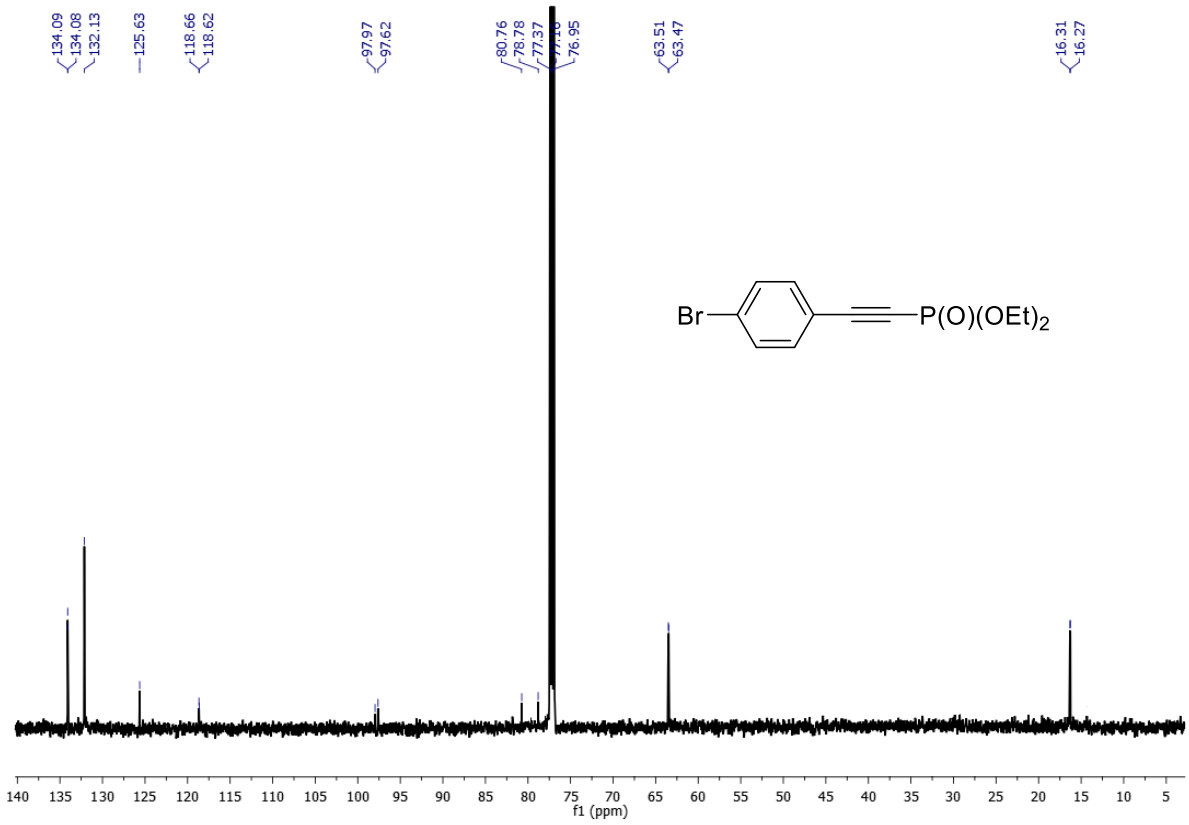


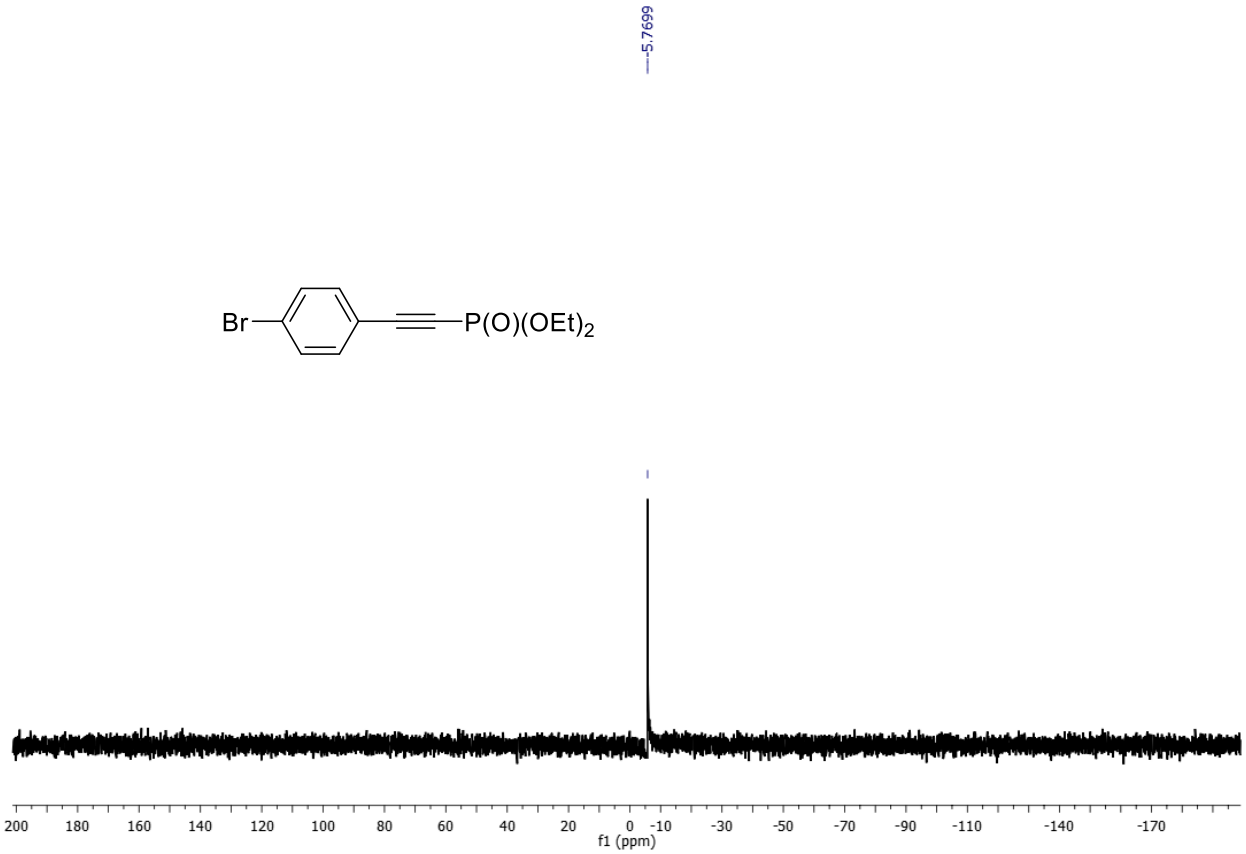
3-(4-(3-chloromethyl)-2-oxooxazolidin-3-yl)prop-2-yn-1-yl benzoate (5ad): Prepared according to typical procedure II. The crude product was purified by flash chromatography (EtOAc/hexanes 1:2) to afford 5ad product as a colorless oil, (59 mg, 82%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.09 (s, 2H), 4.86 (m, 1H), 4.05 (t, *J* = 9.1 Hz, 1H), 3.85 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.72 (d, *J* = 5.3 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.1, 154.9, 133.4, 129.9, 129.6, 128.6, 76.2, 72.9, 67.0, 52.9, 49.4, 44.1; **IR** (neat) : 2927, 2267, 1718, 1600, 1425, 1266, 1025, 712; **HRMS** (ESI+) calcd for $C_{14}H_{12}ClNO_4$ $[M+Na]^+$: 316.0353 found: 316.0395.

6. ^{1}H, ^{13}C, & ^{31}P Spectra:

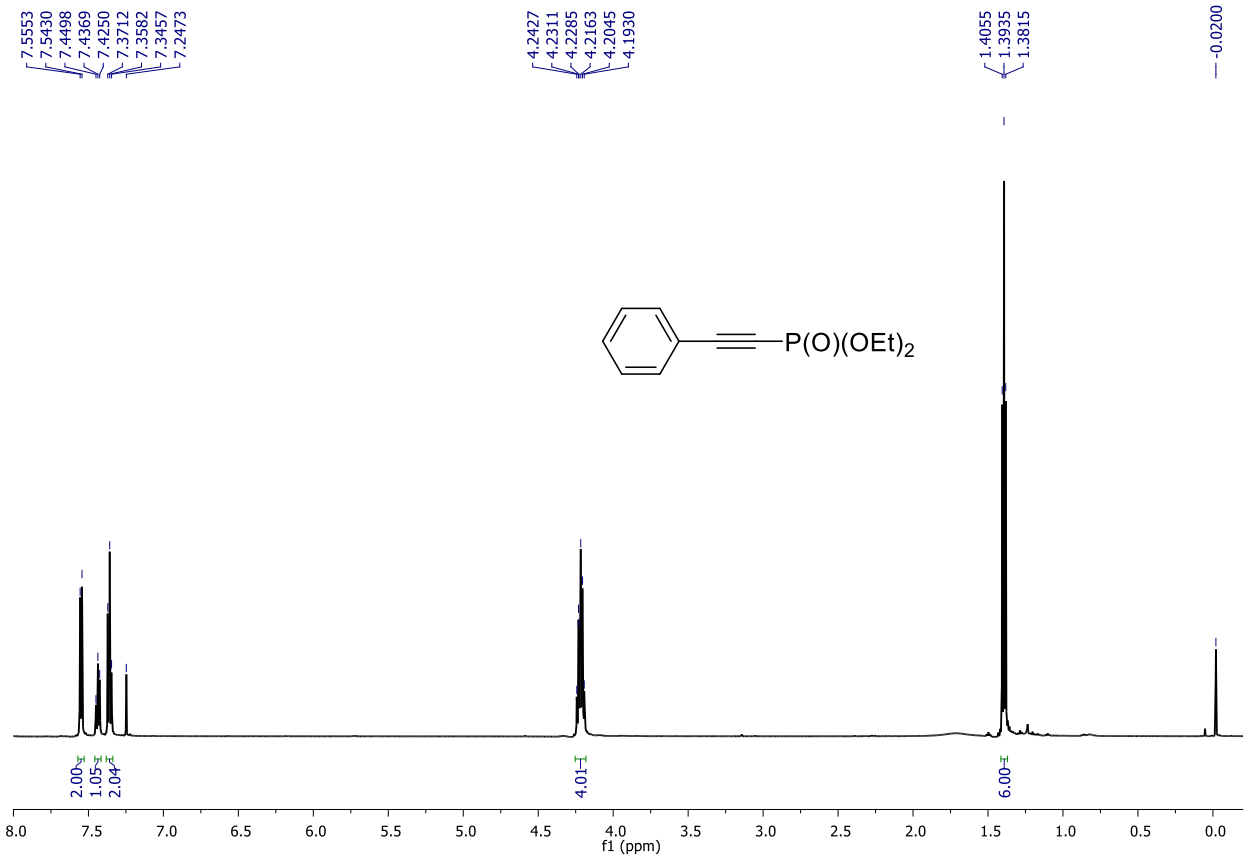
Diethyl [(4-bromophenyl)ethynyl]phosphonate (3a):

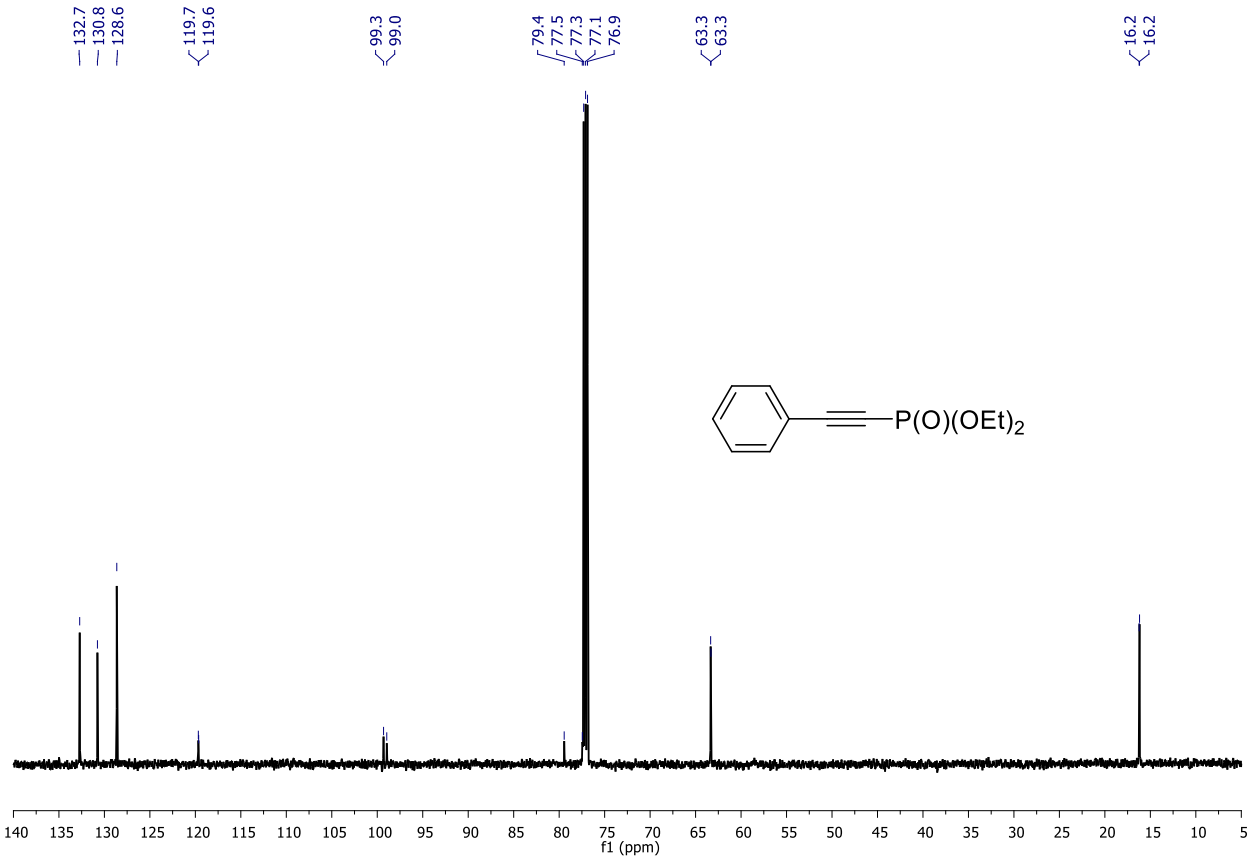

7.5289
7.5155
7.4272
7.4127
7.2602
4.2510
4.2481
4.2394
4.2364
4.2275
4.2247
4.2129
4.2014
4.1985
1.4169
1.4049
1.3932
-0.0045
Br
P(O)(OEt)2
2.13
2.01
4.00
6.10
f1 (ppm)

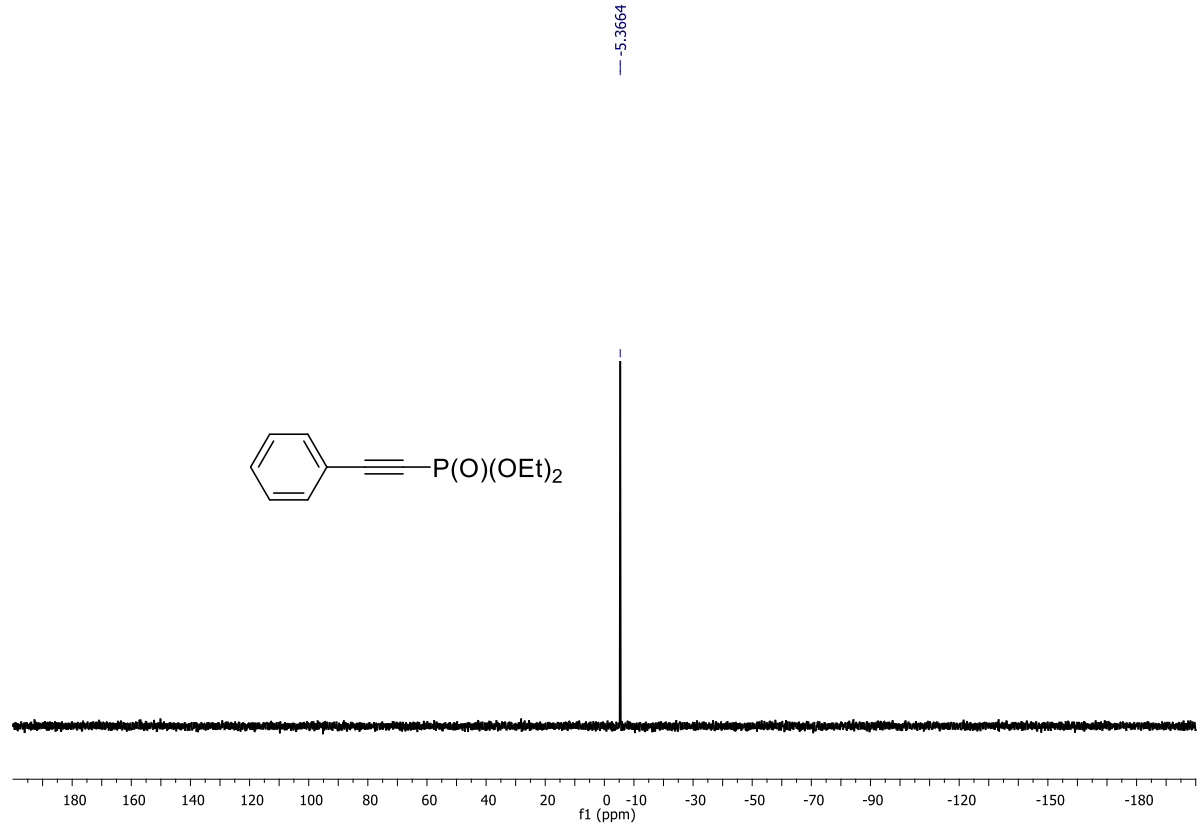

134.09
134.08
132.13
125.63
118.66
118.62
97.97
97.62
80.76
78.78
77.37
76.95
63.51
63.47
16.31
16.27
Br
P(O)(OEt)2
f1 (ppm)



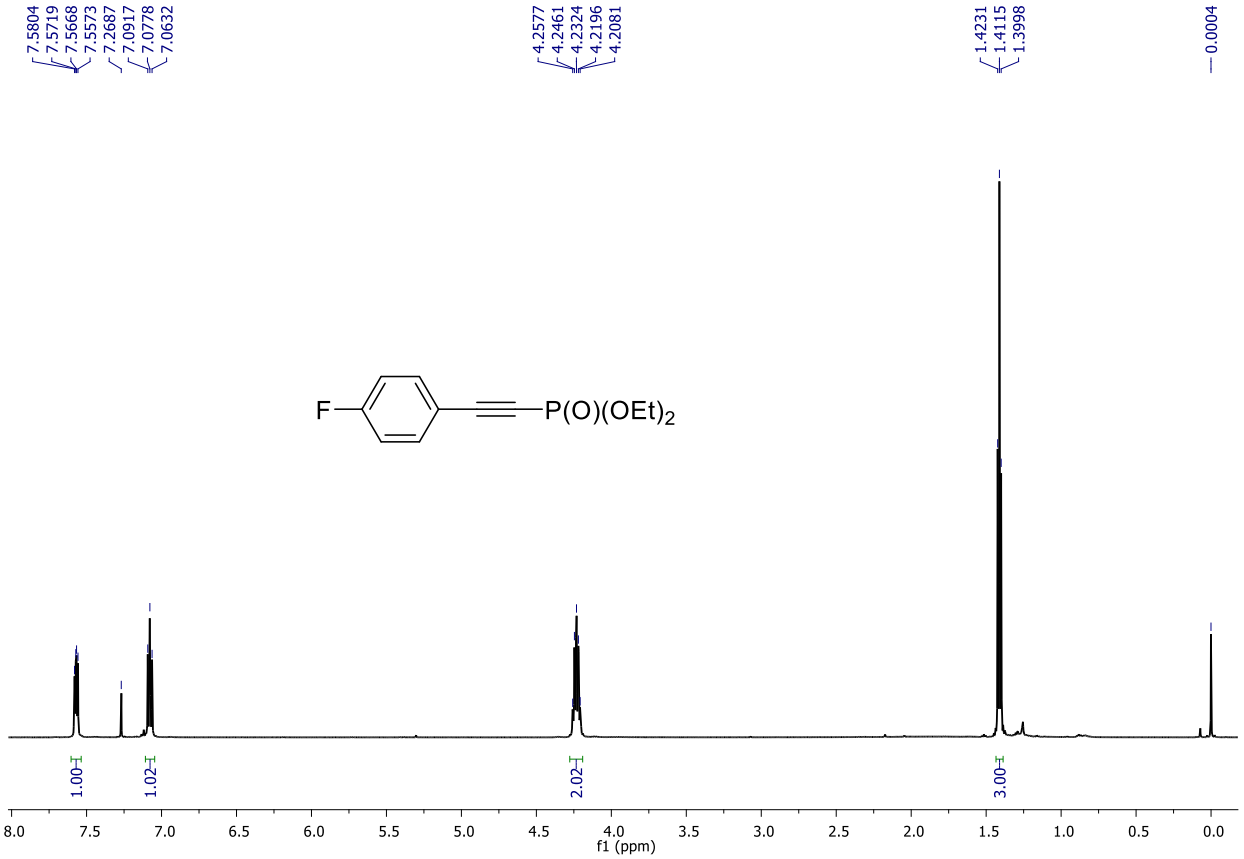
Diethyl (phenylethynyl)phosphonate (3b):

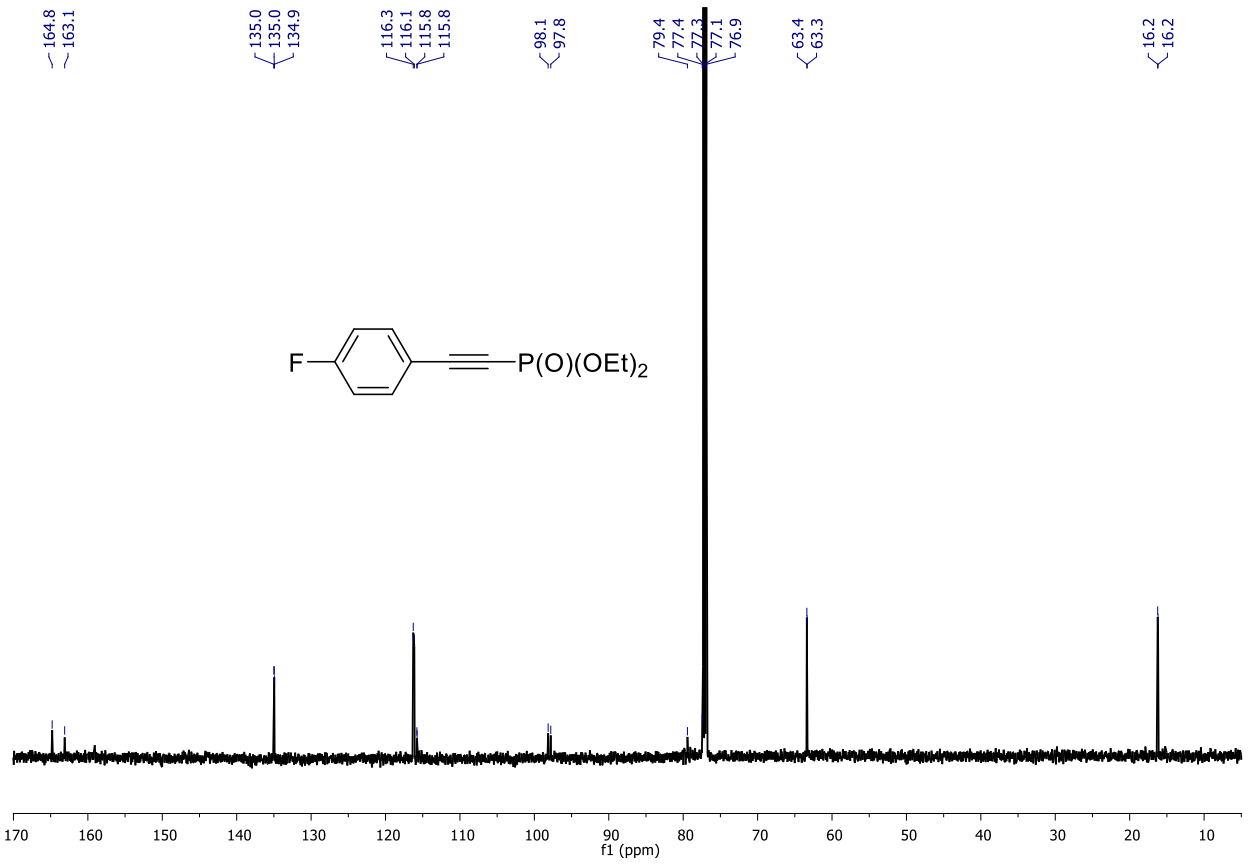


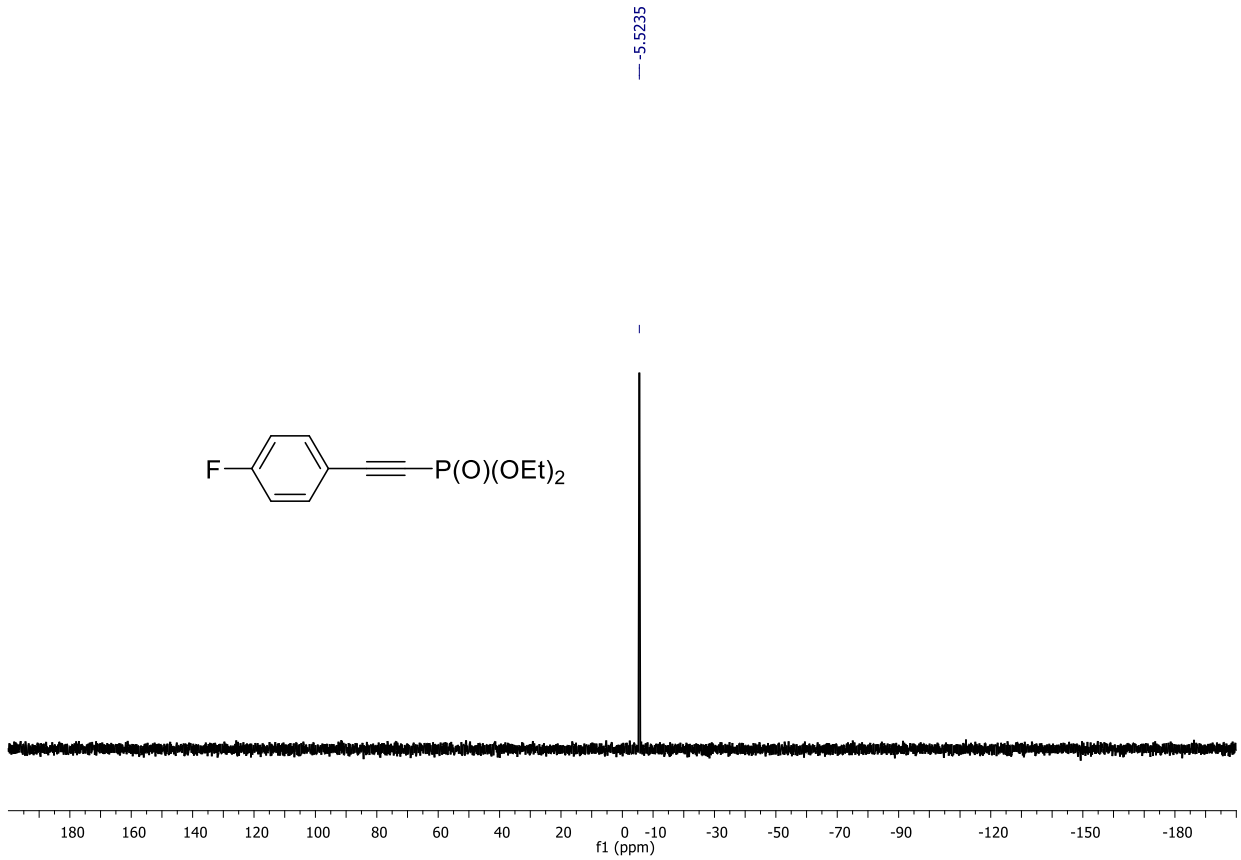

132.7
130.8
128.6
119.7
119.6
99.3
99.0
79.4
77.5
77.3
77.1
76.9
63.3
63.3
16.2
16.2
P(O)(OEt)2
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


-5.3664
P(O)(OEt)2
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

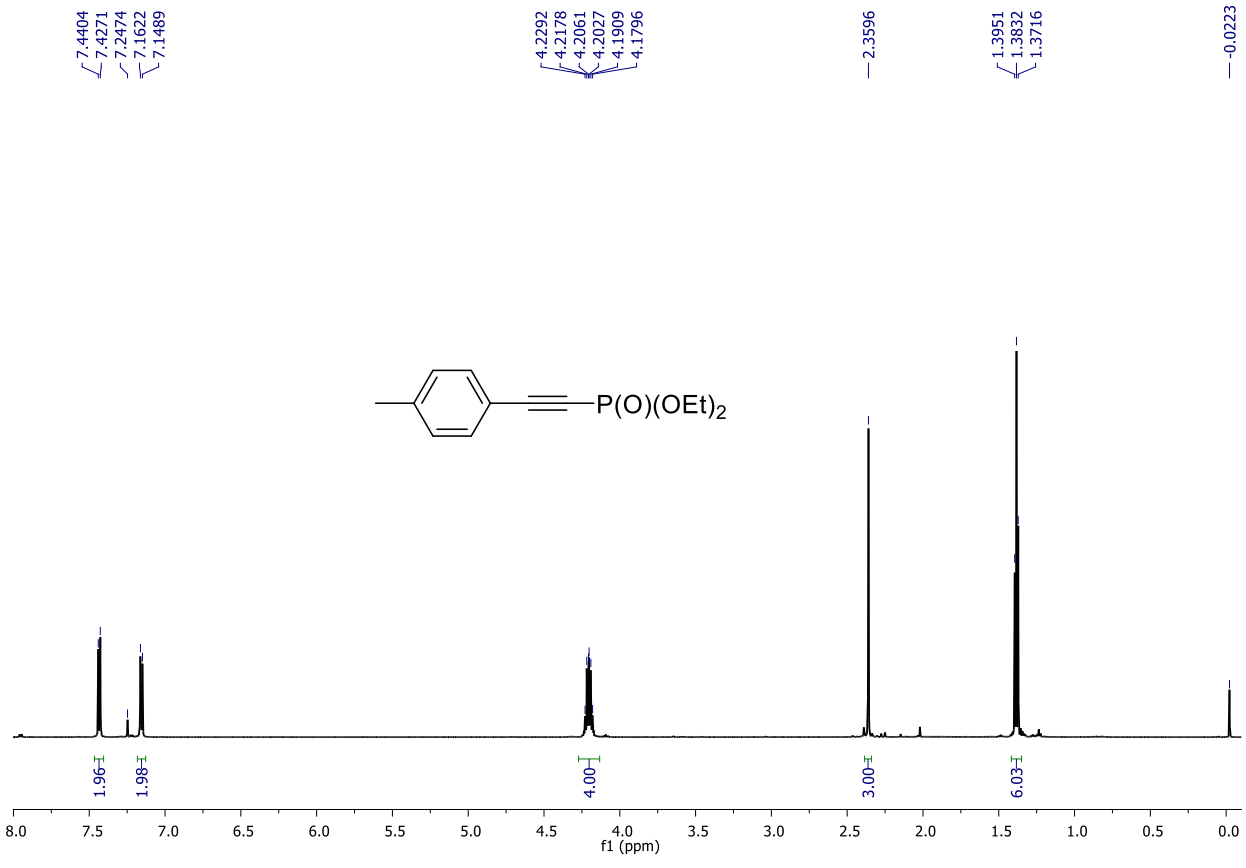
Diethyl [(4-fluorophenyl)ethynyl]phosphonate (3c):

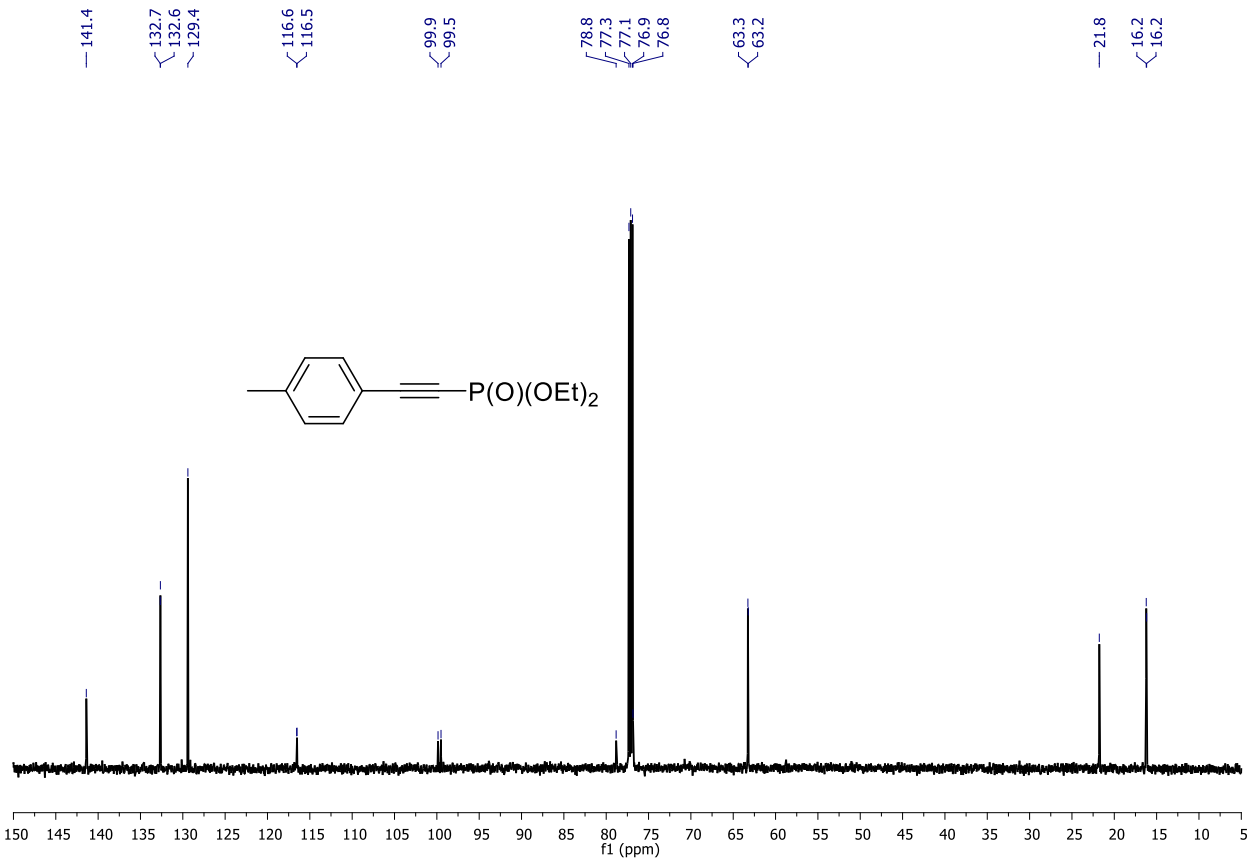


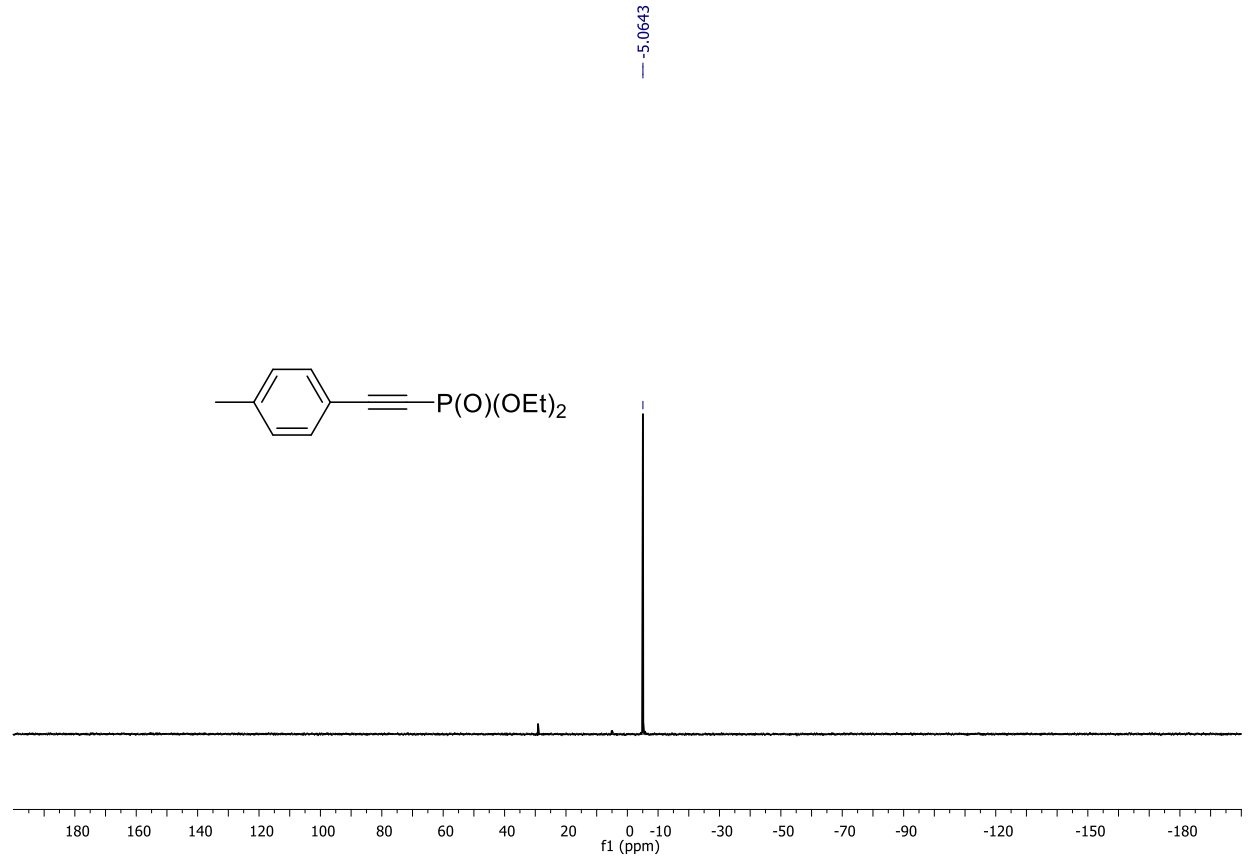




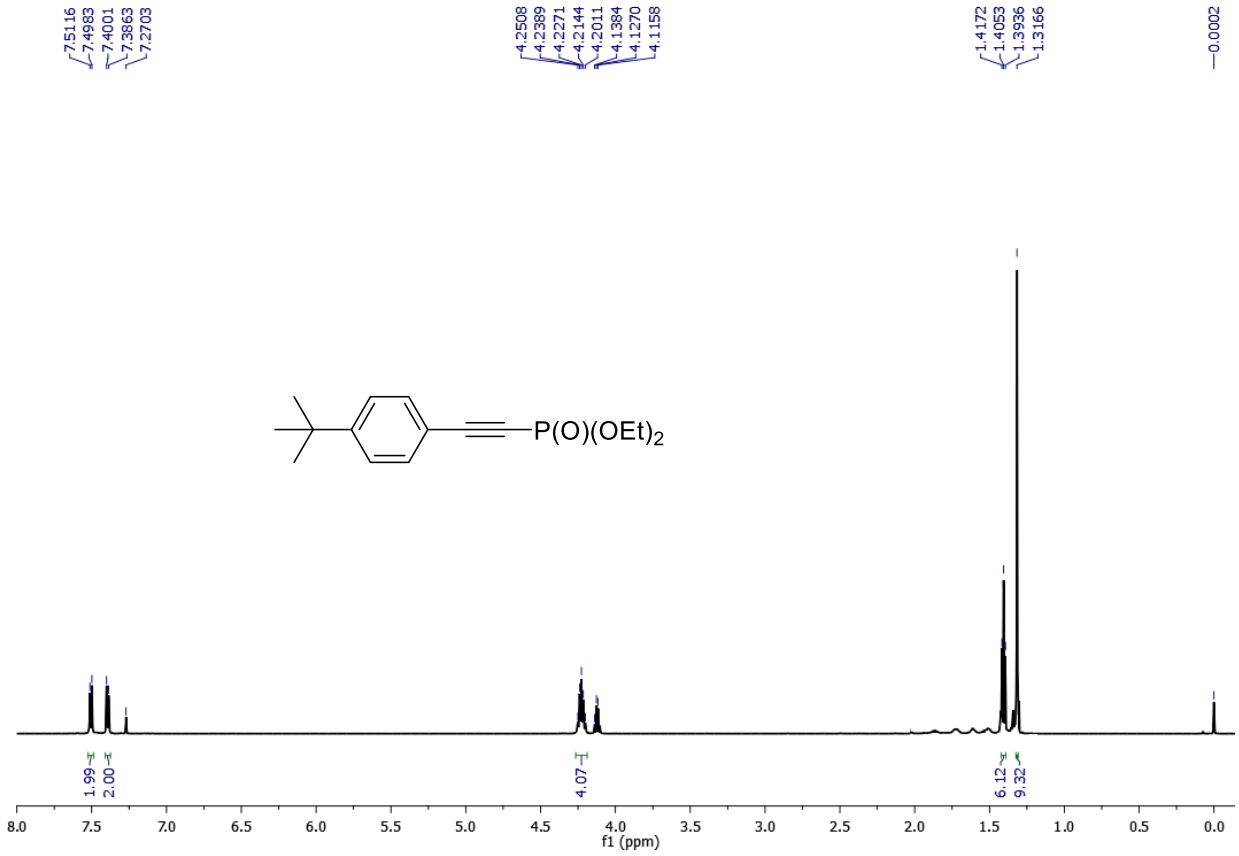
Diethyl (4-tolylethynyl)phosphonate (3d):

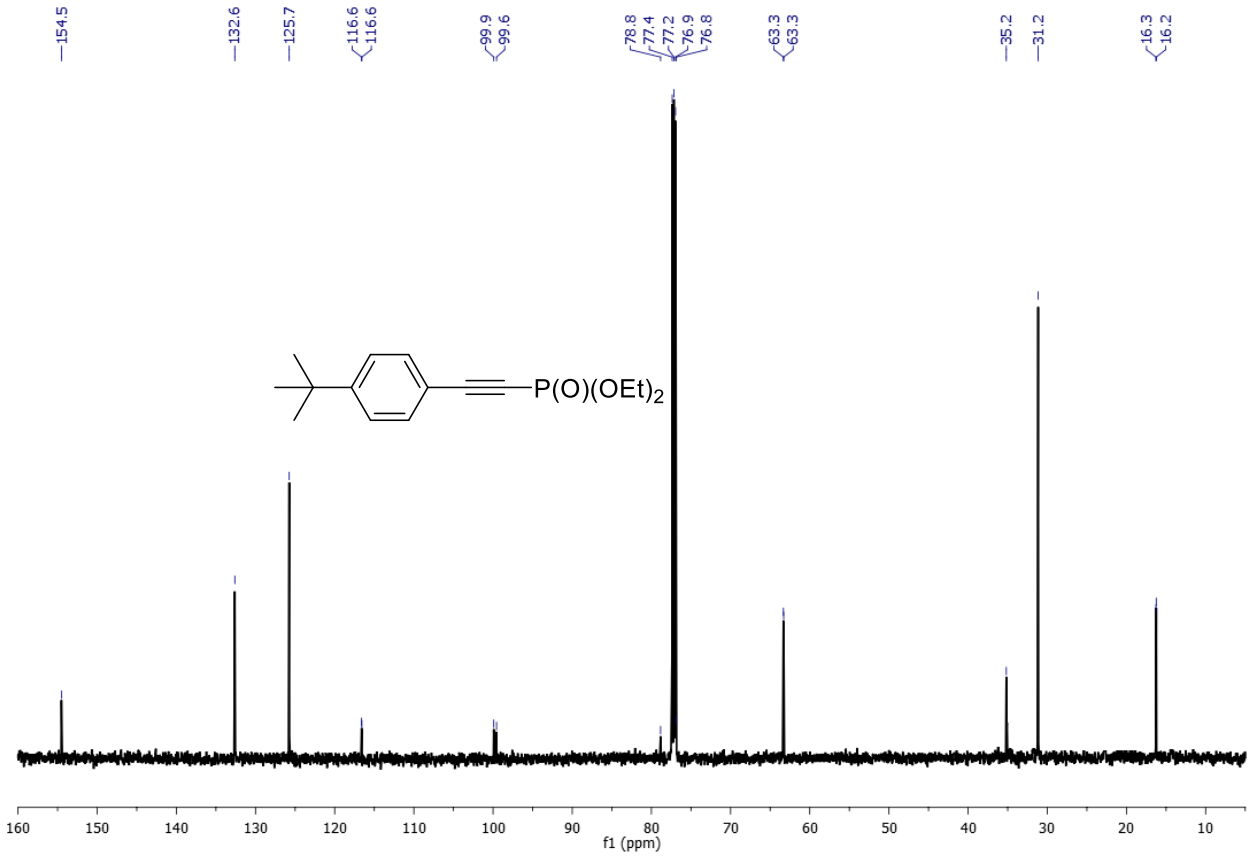


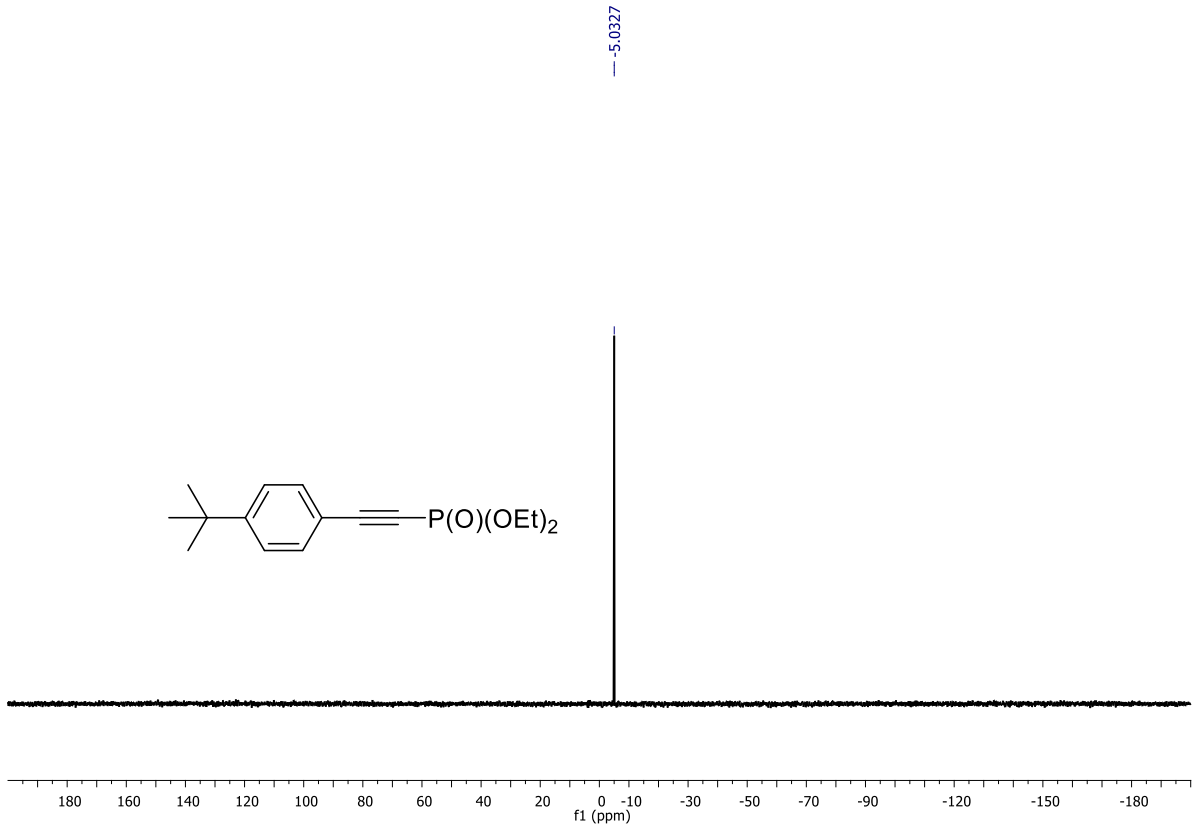

141.4
132.7
132.6
129.4
116.6
116.5
99.9
99.5
78.8
77.3
77.1
76.9
76.8
63.3
63.2
21.8
16.2
16.2
P(O)(OEt)2
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


-5.0643
P(O)(OEt)2
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

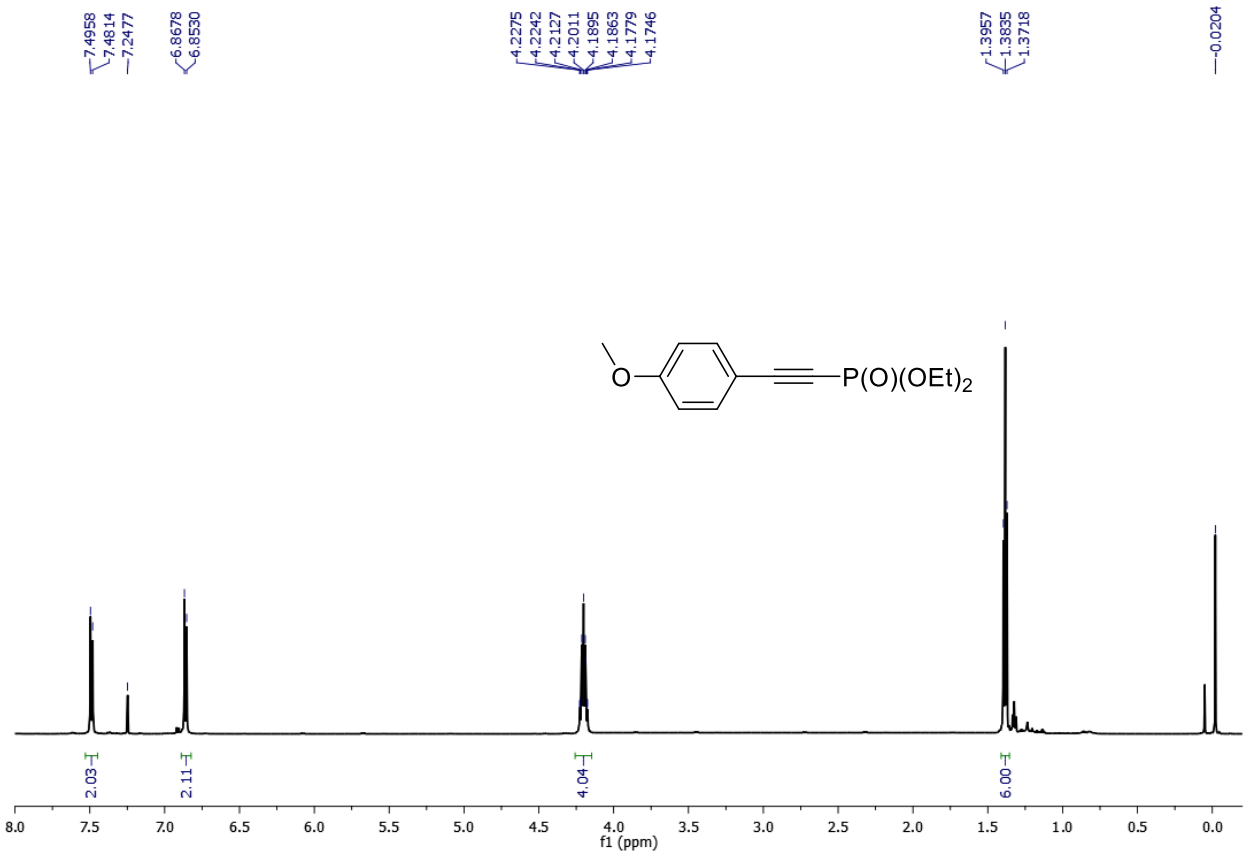
Diethyl [(4-*tert*-butylphenyl)ethynyl]phosphonate (3e):

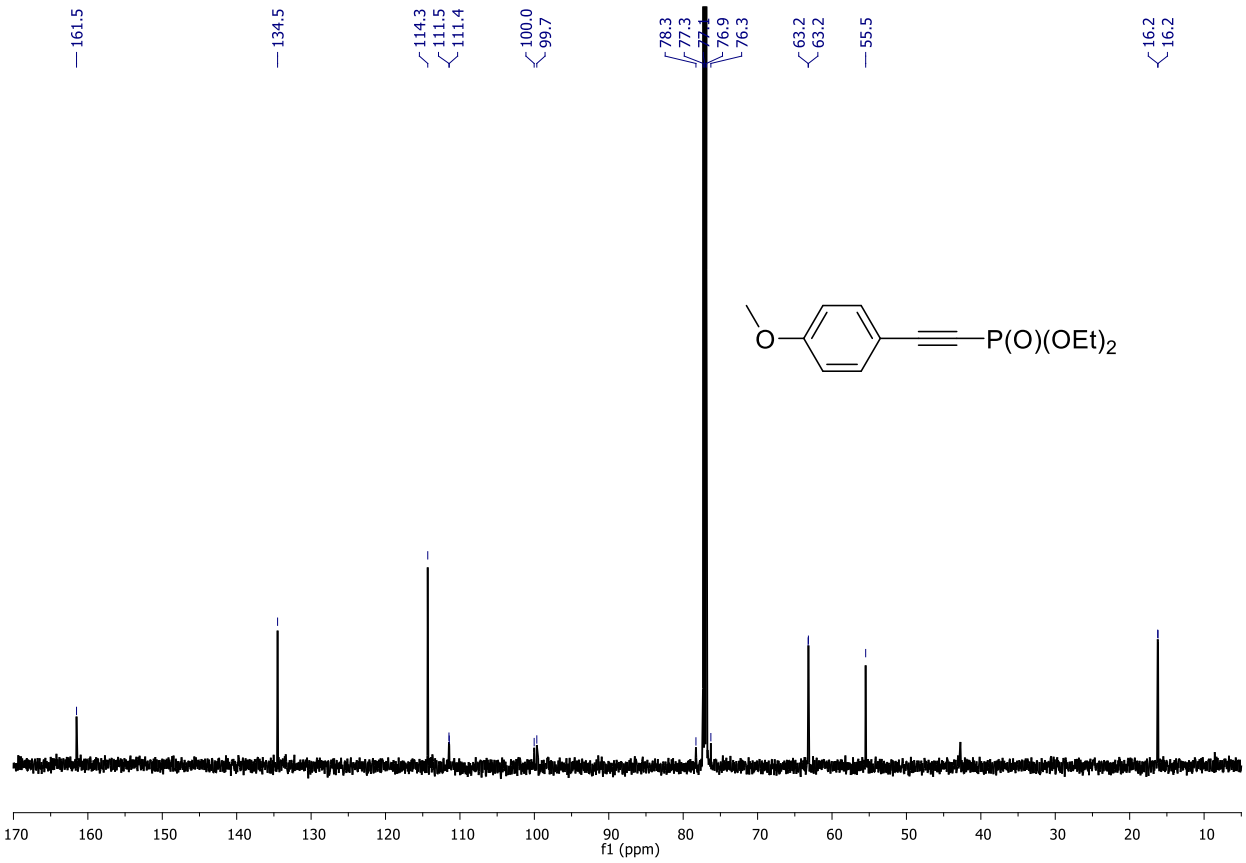


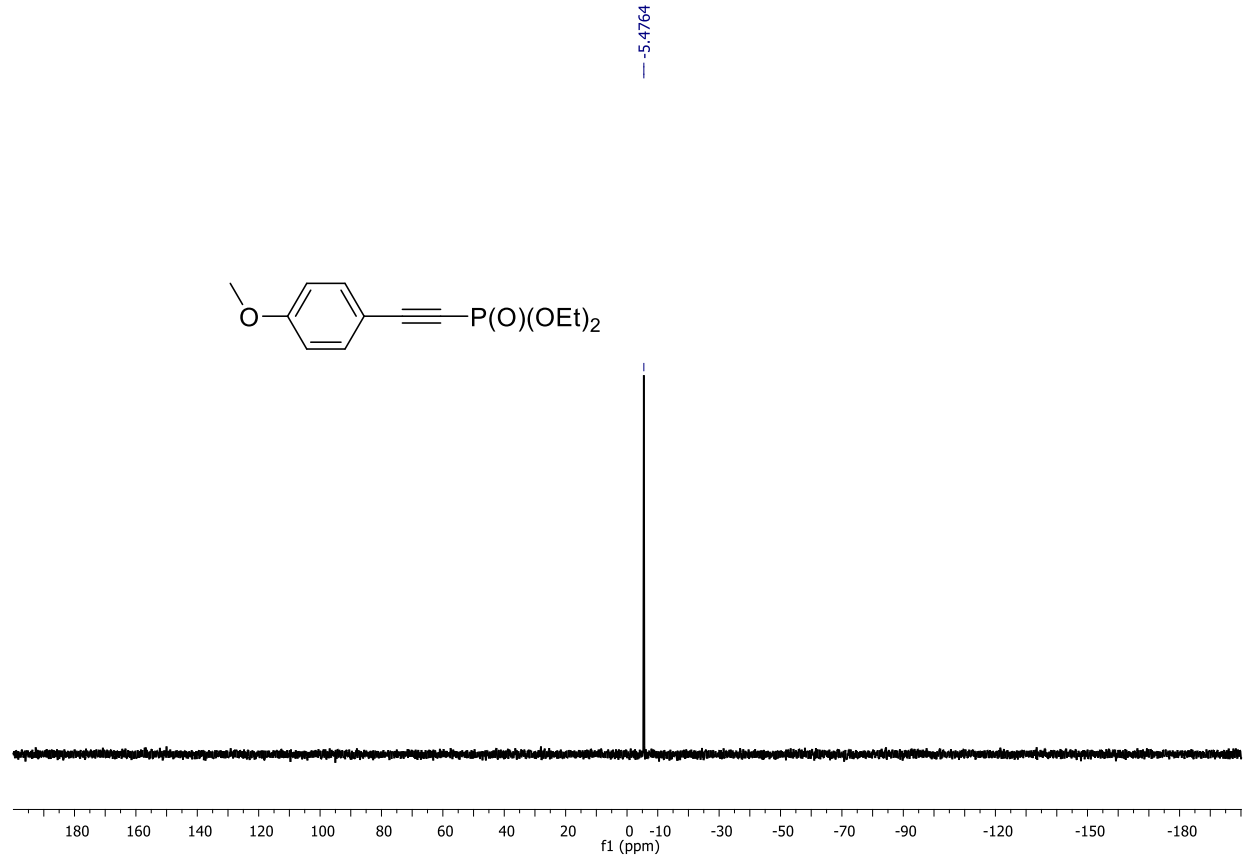




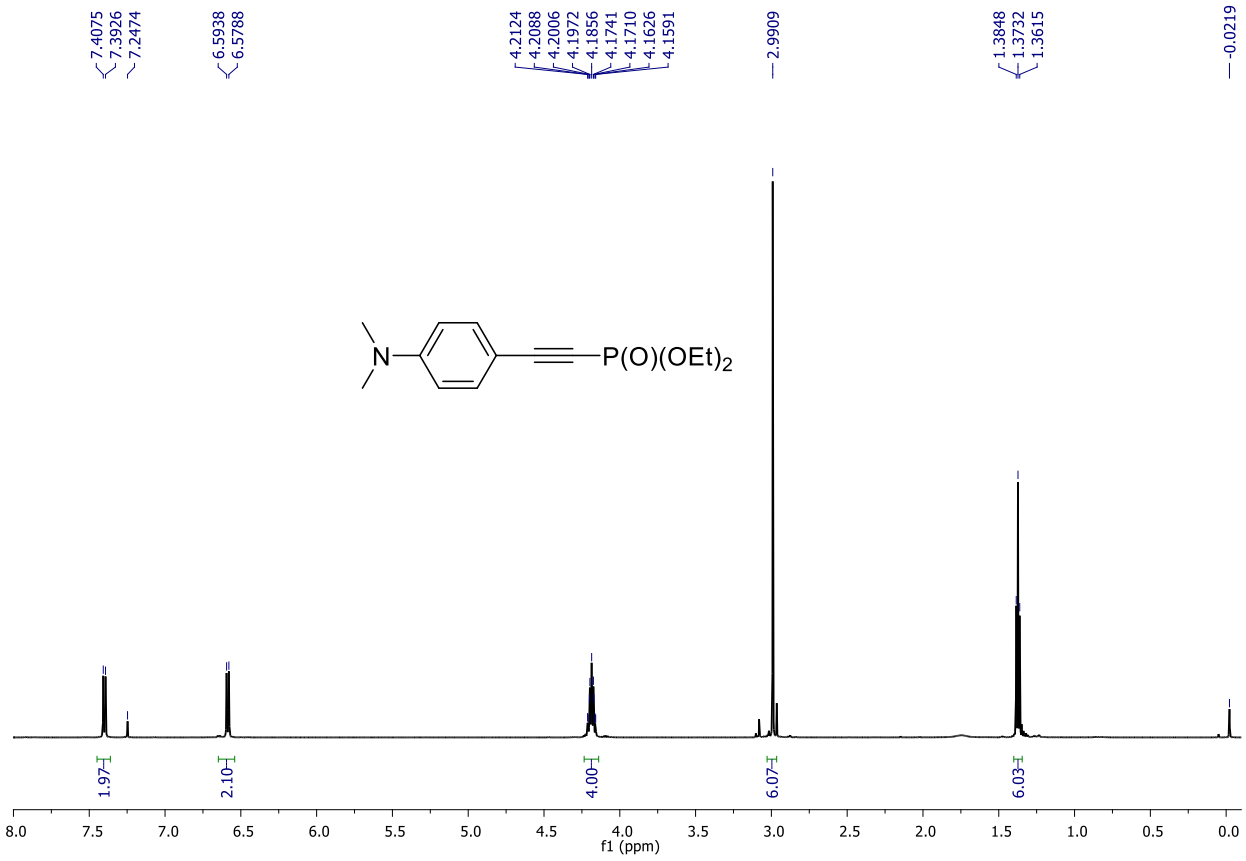
Diethyl [(4-methoxyphenyl)ethynyl]phosphonate (3f):

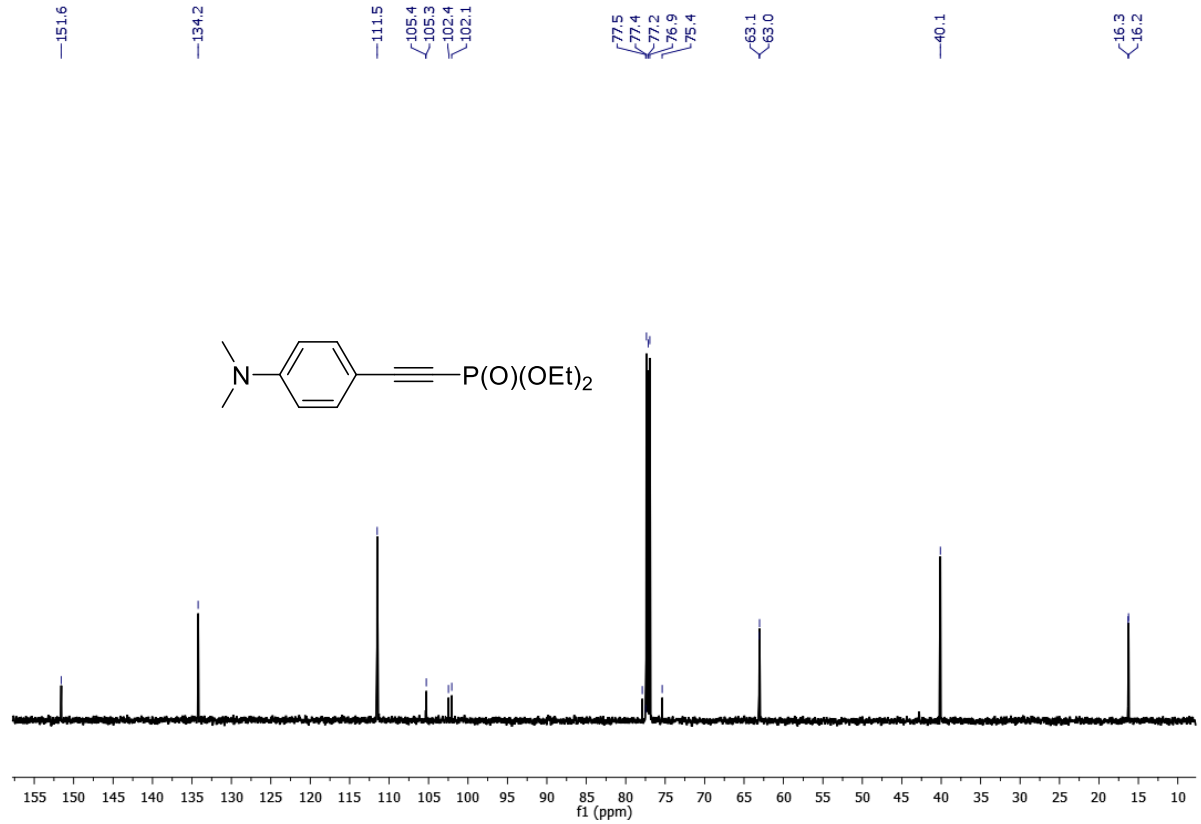


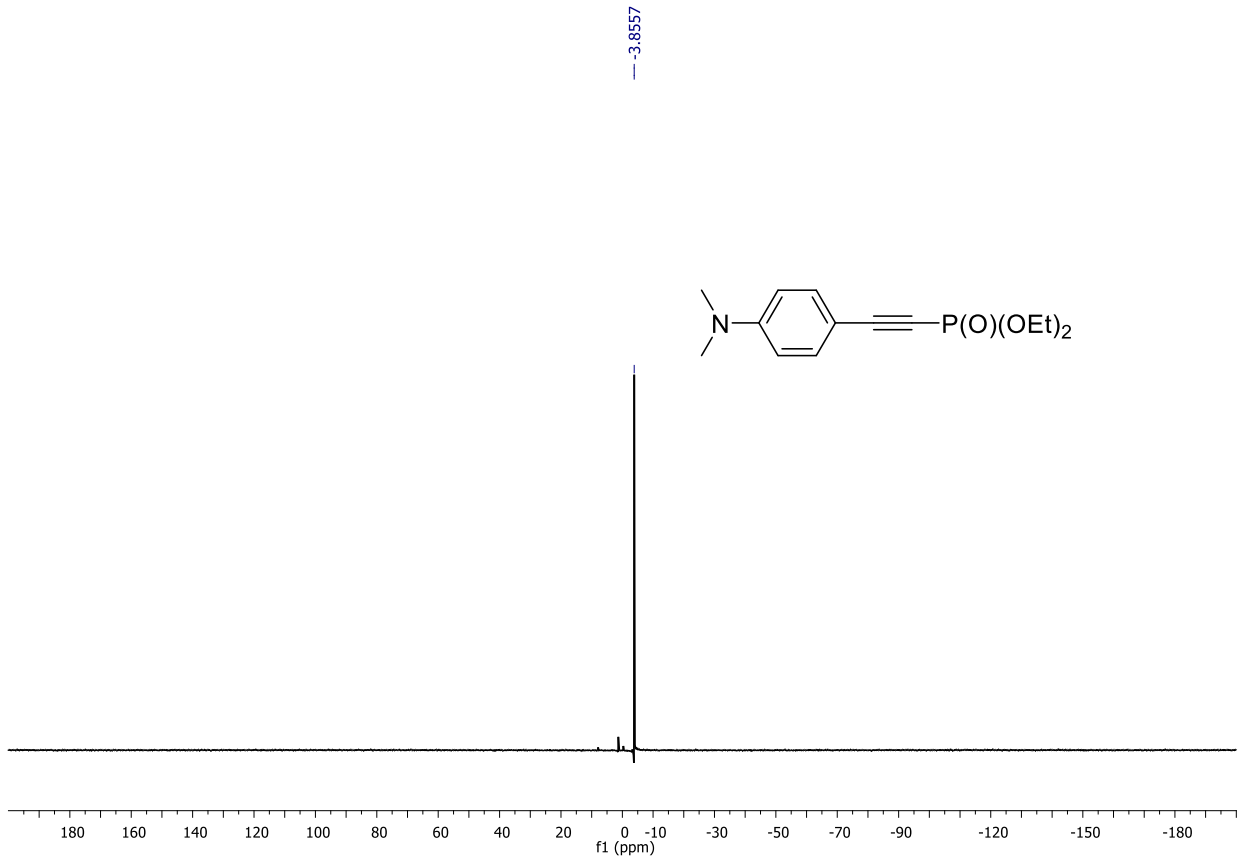

161.5
134.5
114.3
111.5
111.4
100.0
99.7
78.3
77.3
77.1
76.9
76.3
63.2
63.2
55.5
16.2
16.2
O
P(O)(OEt)2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-5.4764
O
P(O)(OEt)2
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

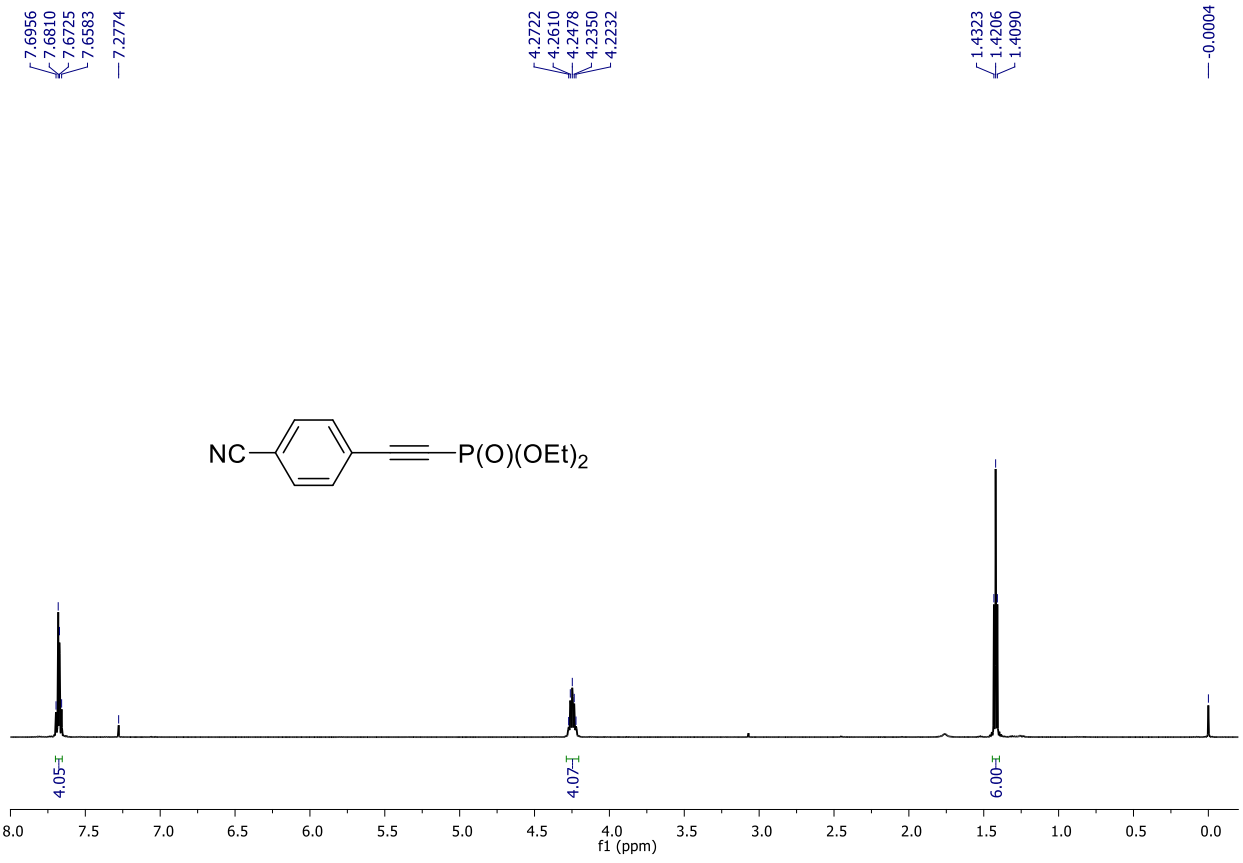
Diethyl [(4-N,N dimethylaminophenyl)ethynyl]phosphonate (3g):

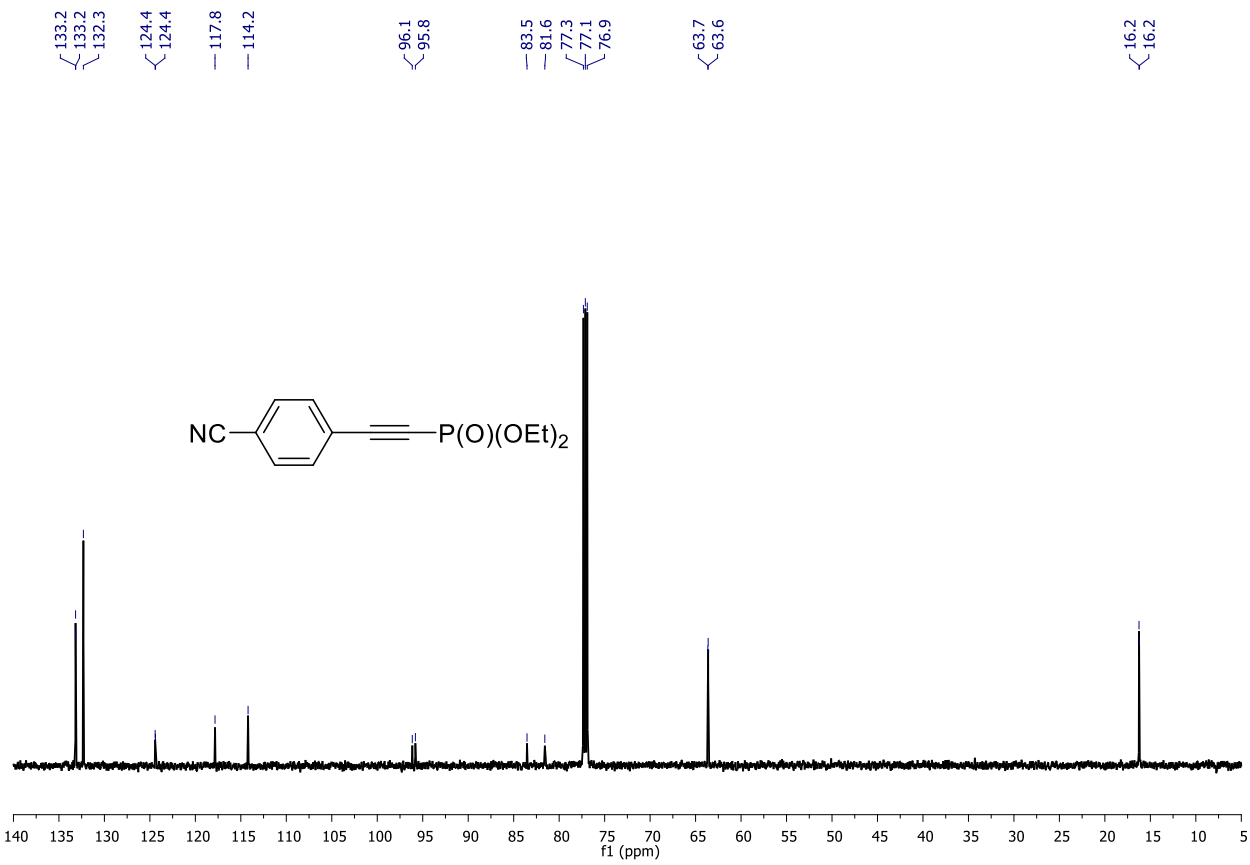


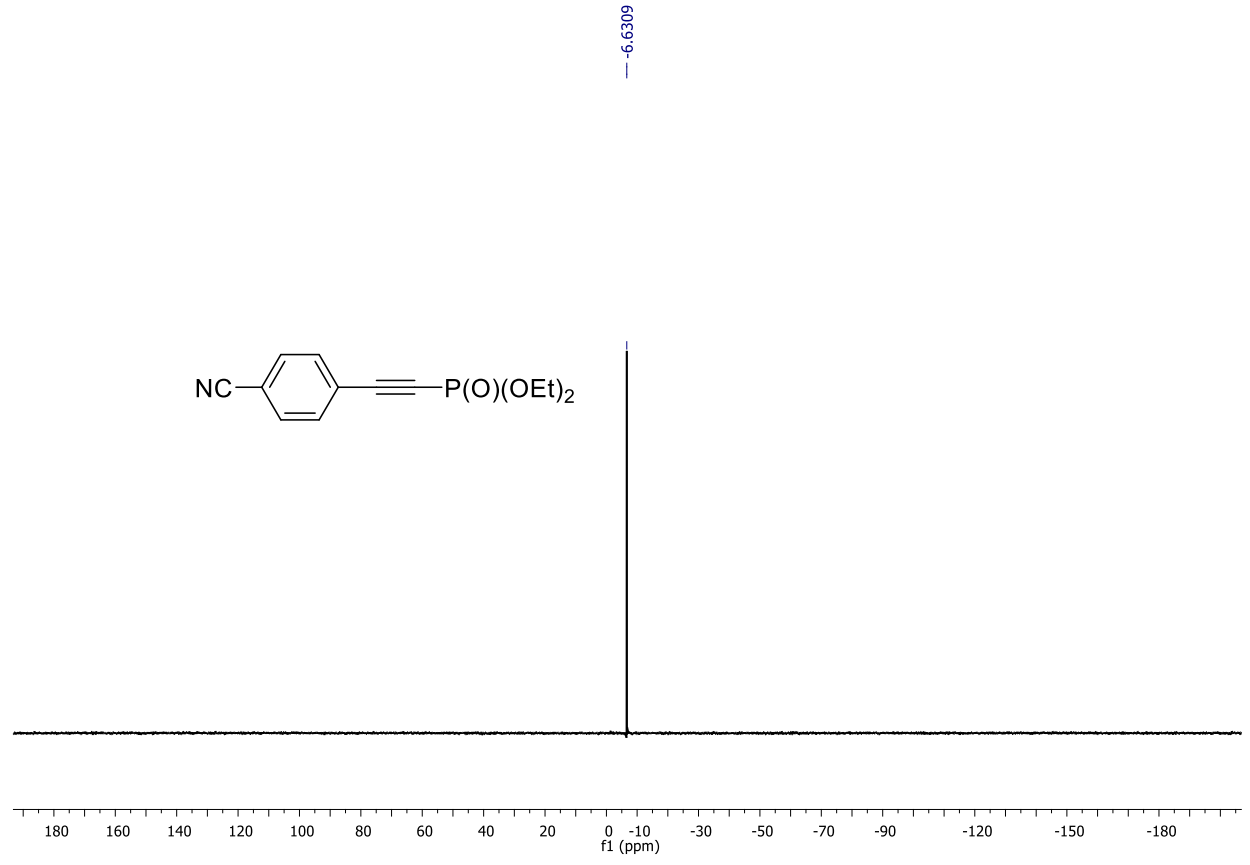




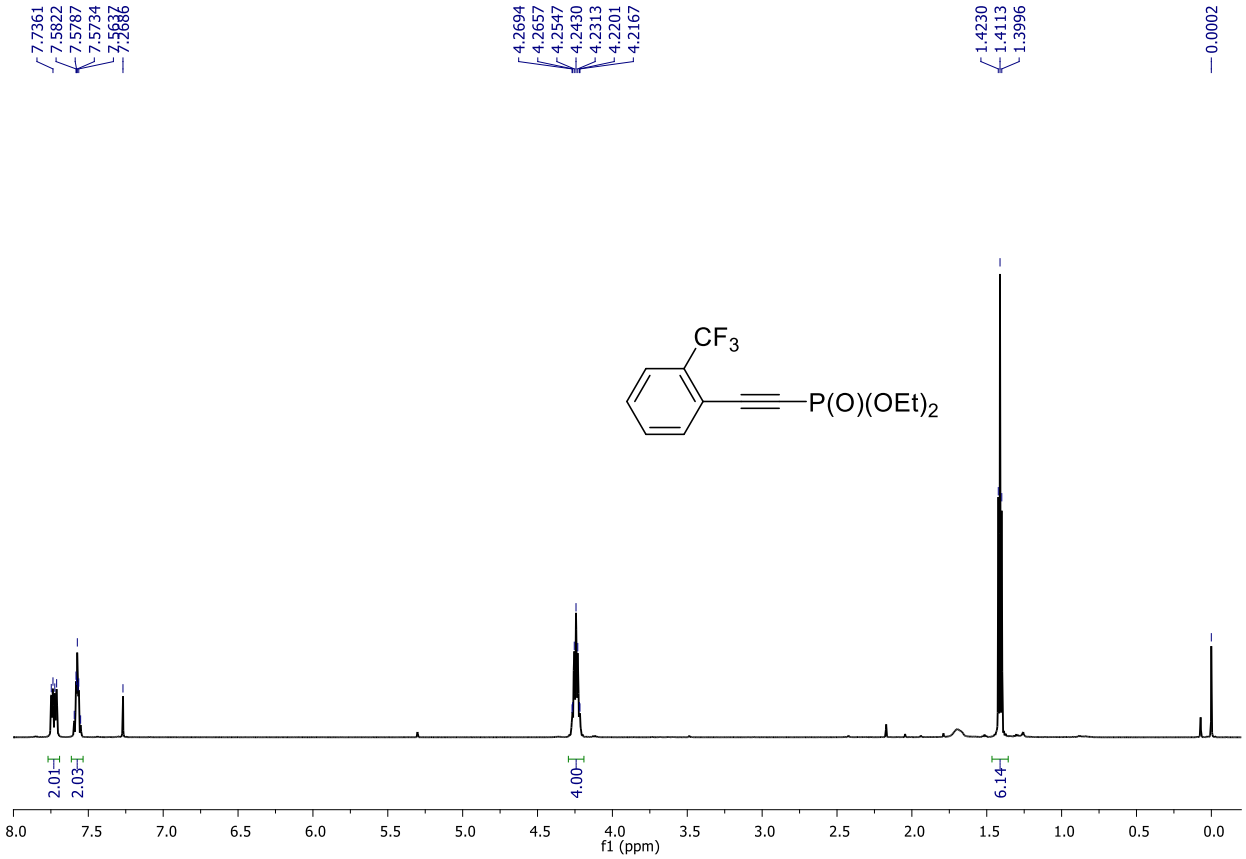
Diethyl [(4-cyanophenyl)ethynyl]phosphonate (3h):

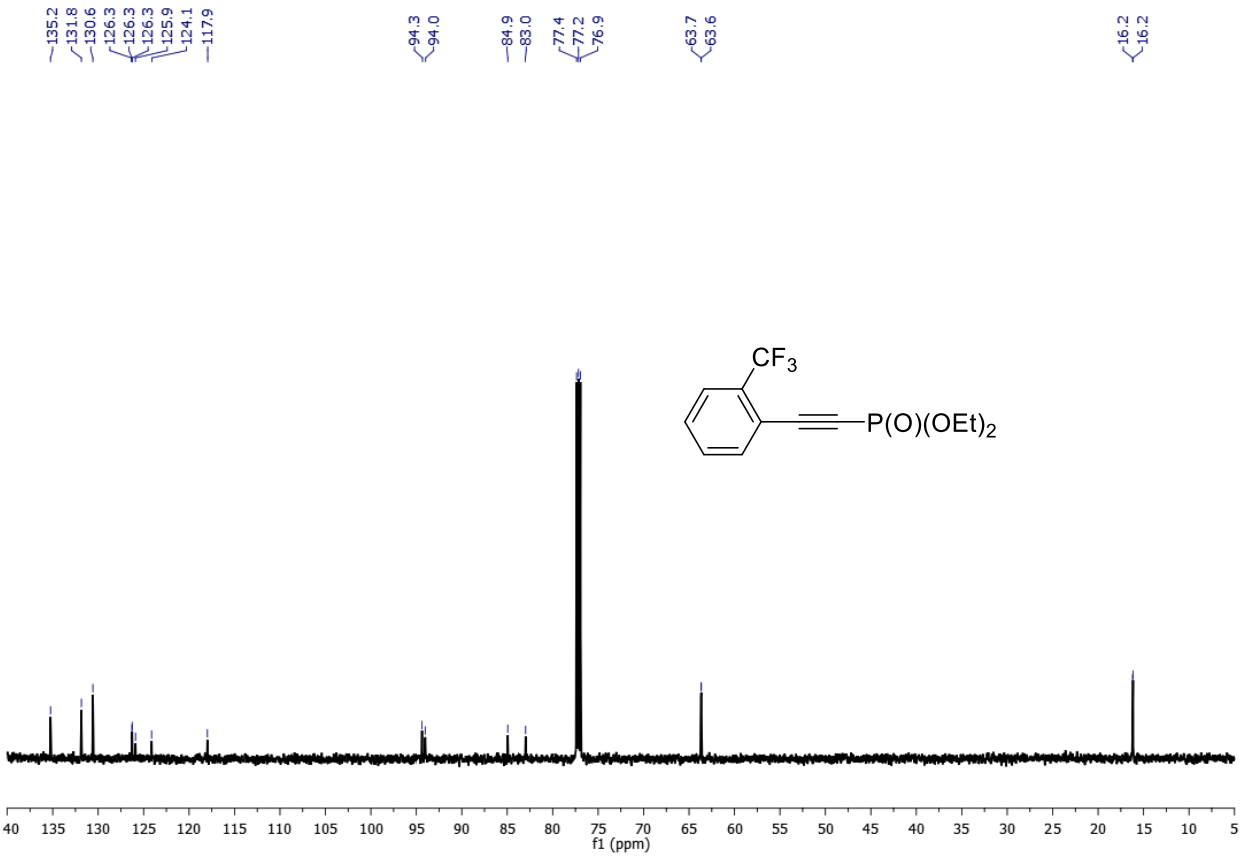


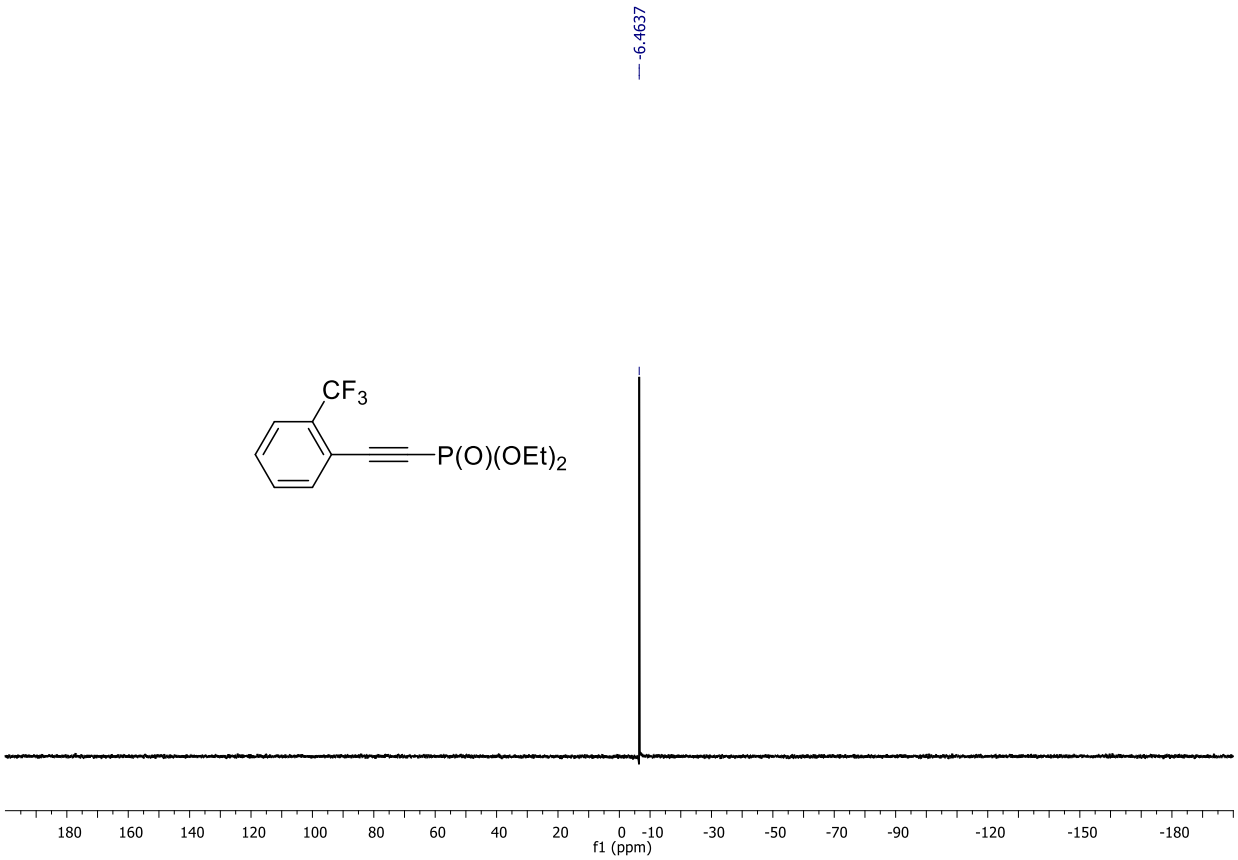

133.2
133.2
132.3
124.4
124.4
117.8
114.2
96.1
95.8
83.5
81.6
77.3
77.1
76.9
63.7
63.6
16.2
16.2
NC
P(O)(OEt)2
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


-6.6309
NC
P(O)(OEt)2
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

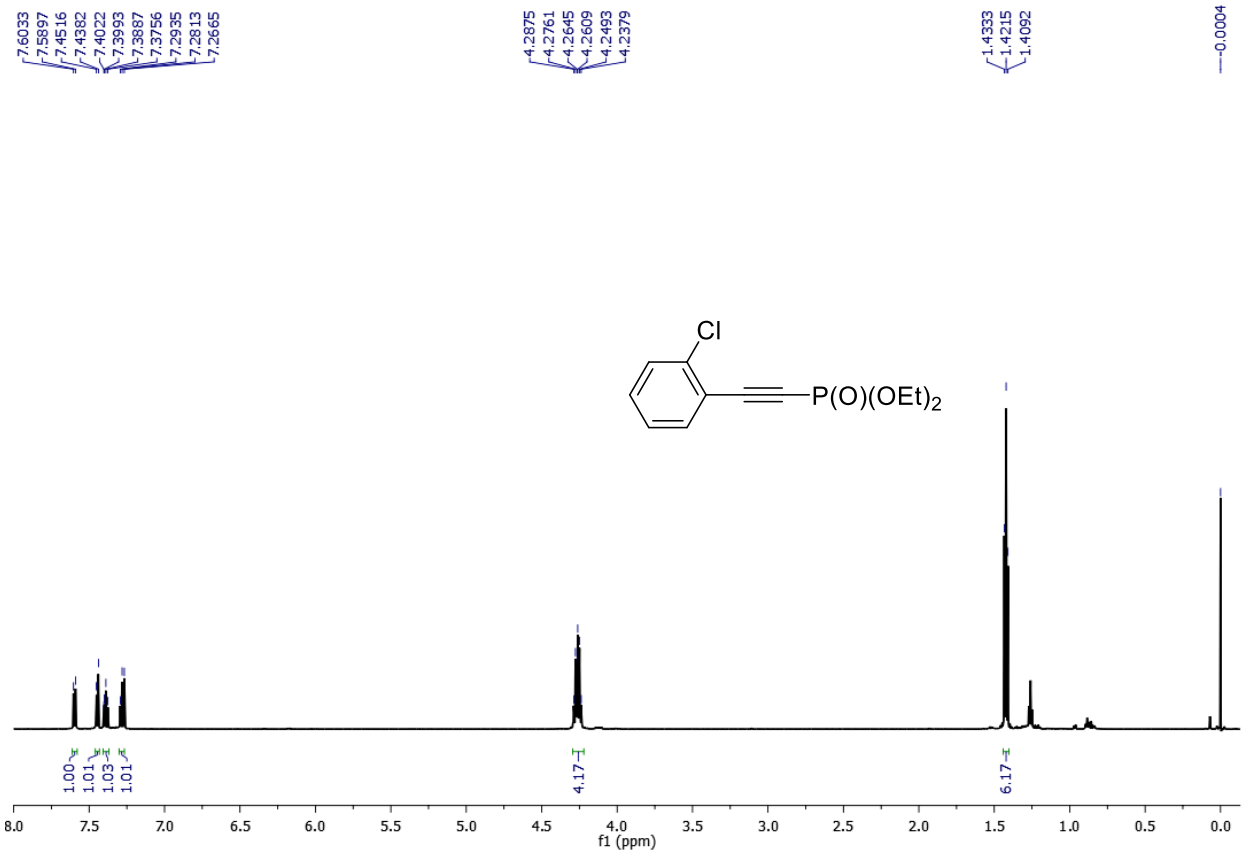
Diethyl [(2-trifluoromethylbenzene)ethynyl]phosphonate (3i):

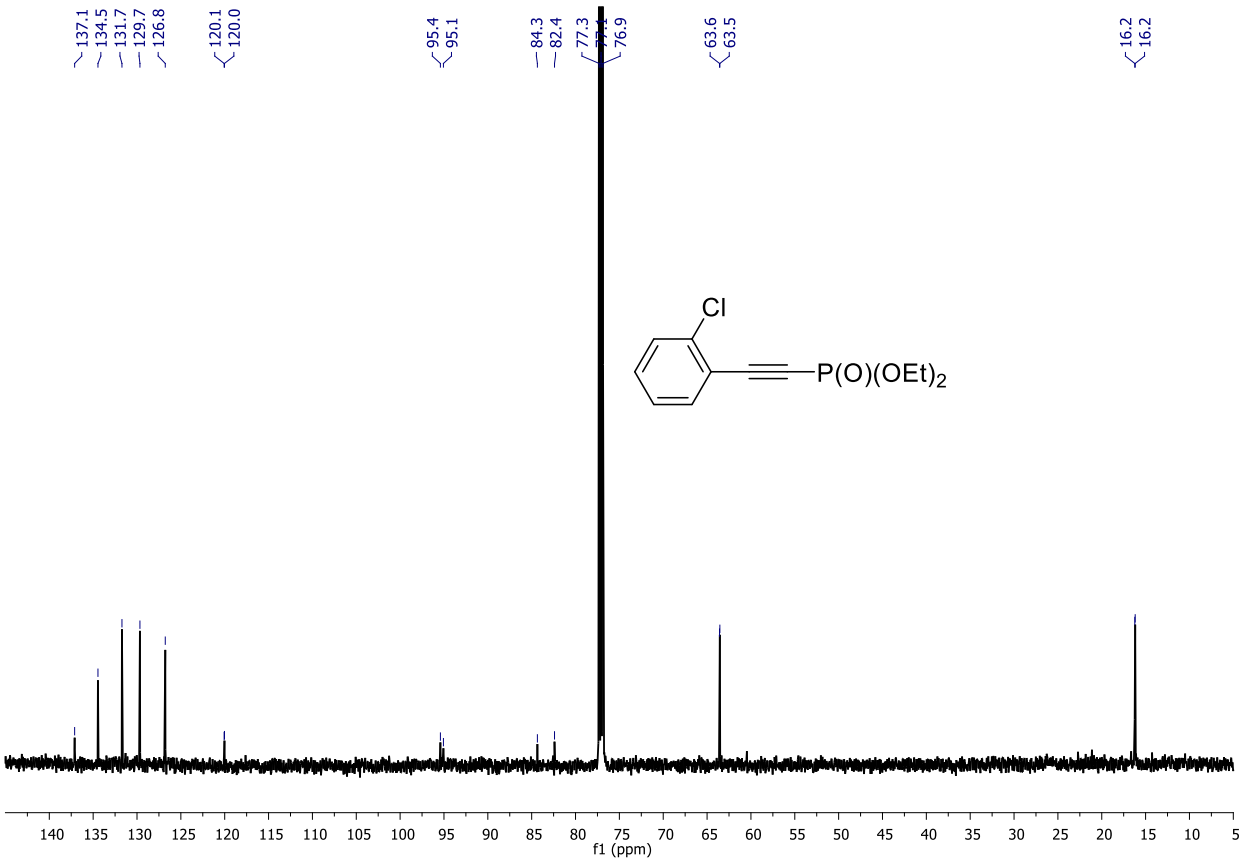


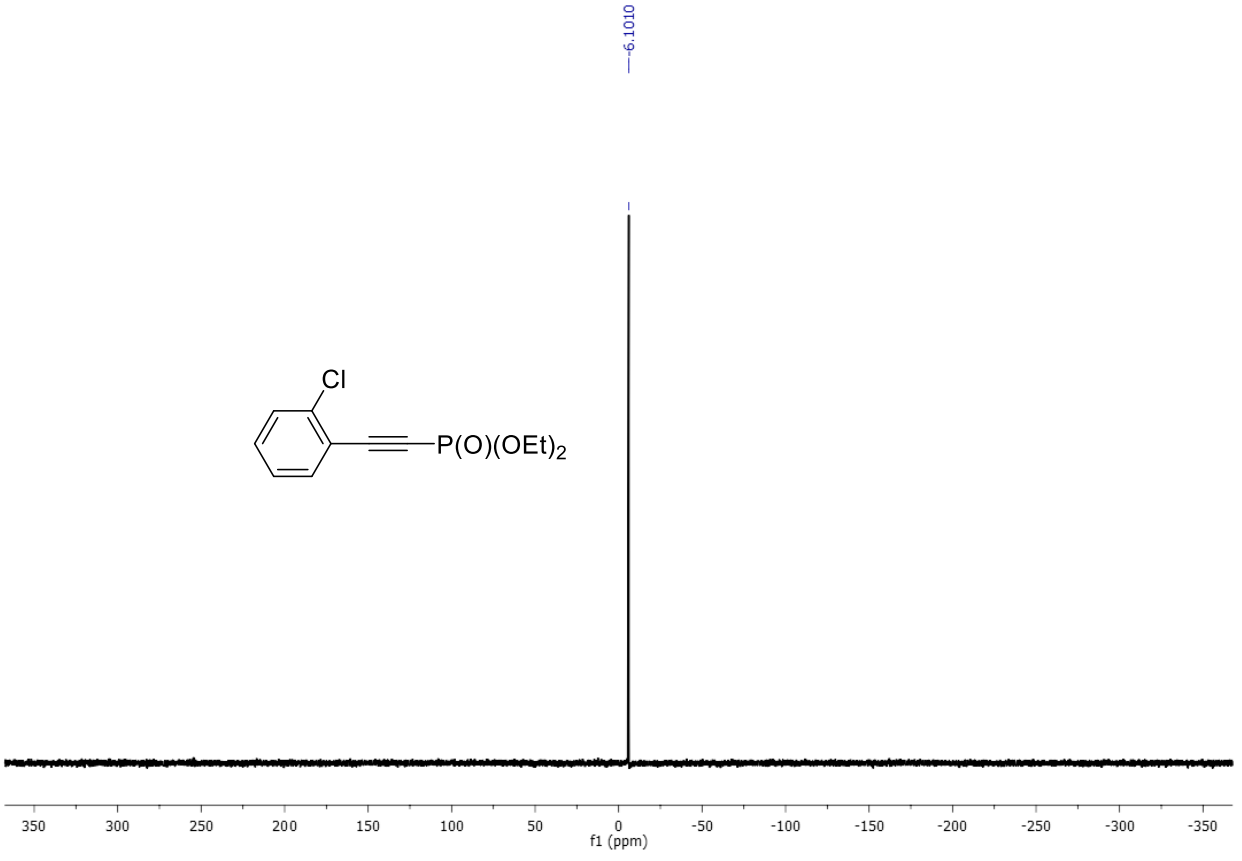




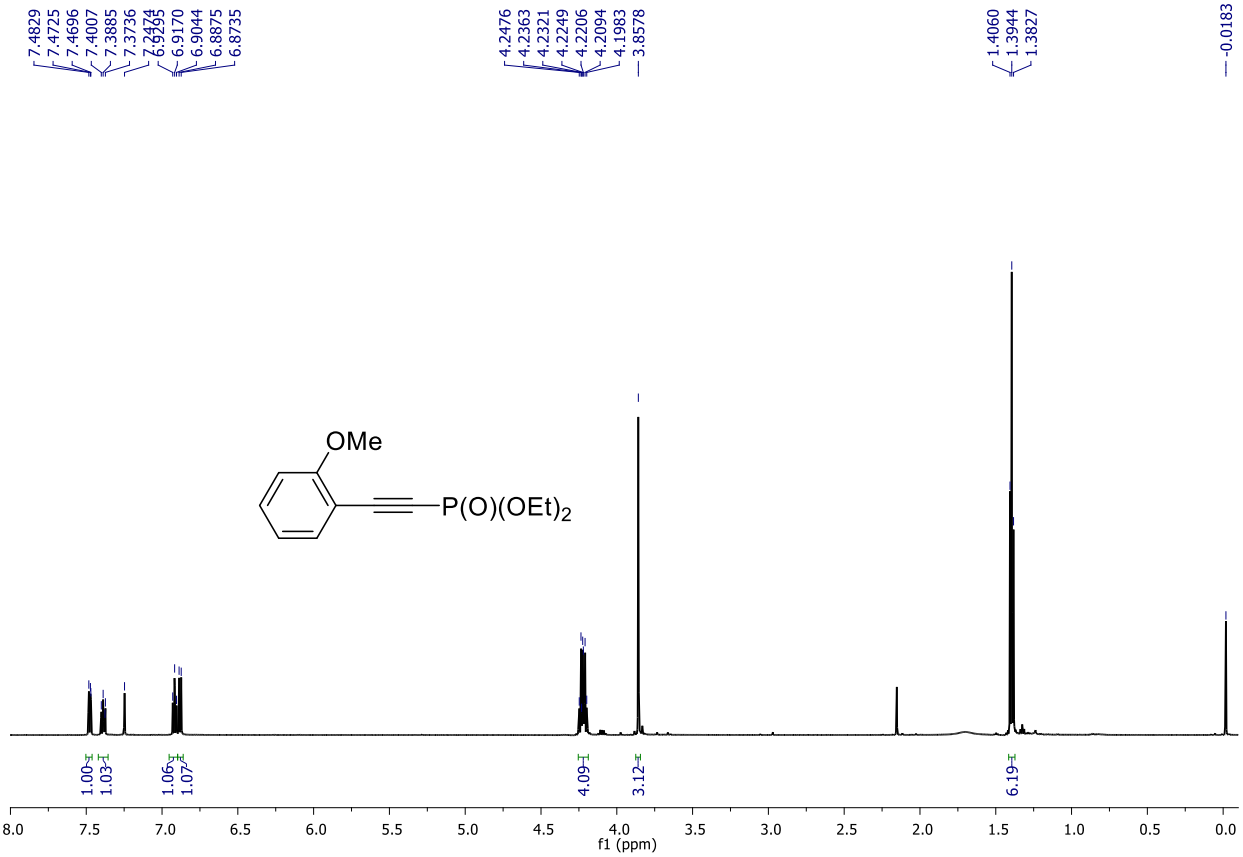
Diethyl [(2-chlorophenyl)ethynyl]phosphonate (3j):

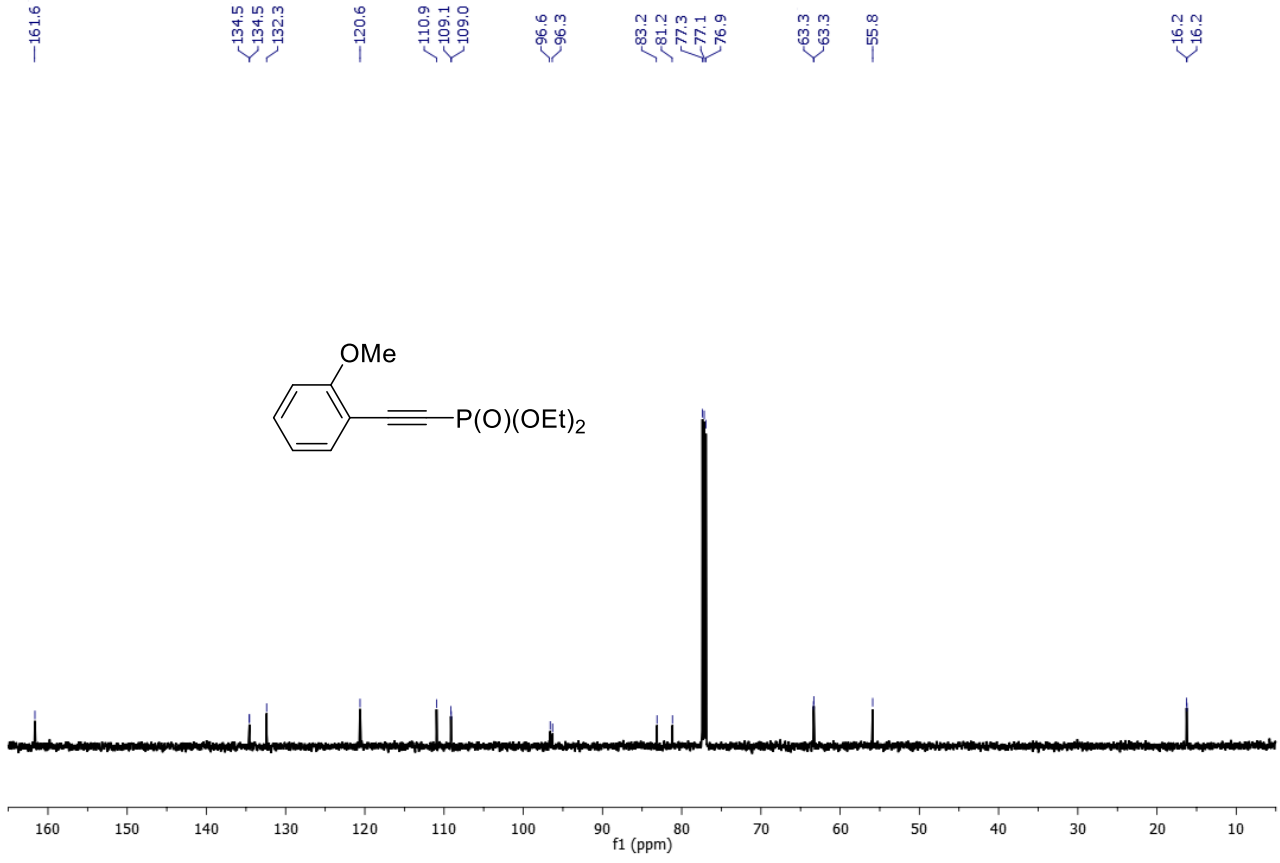


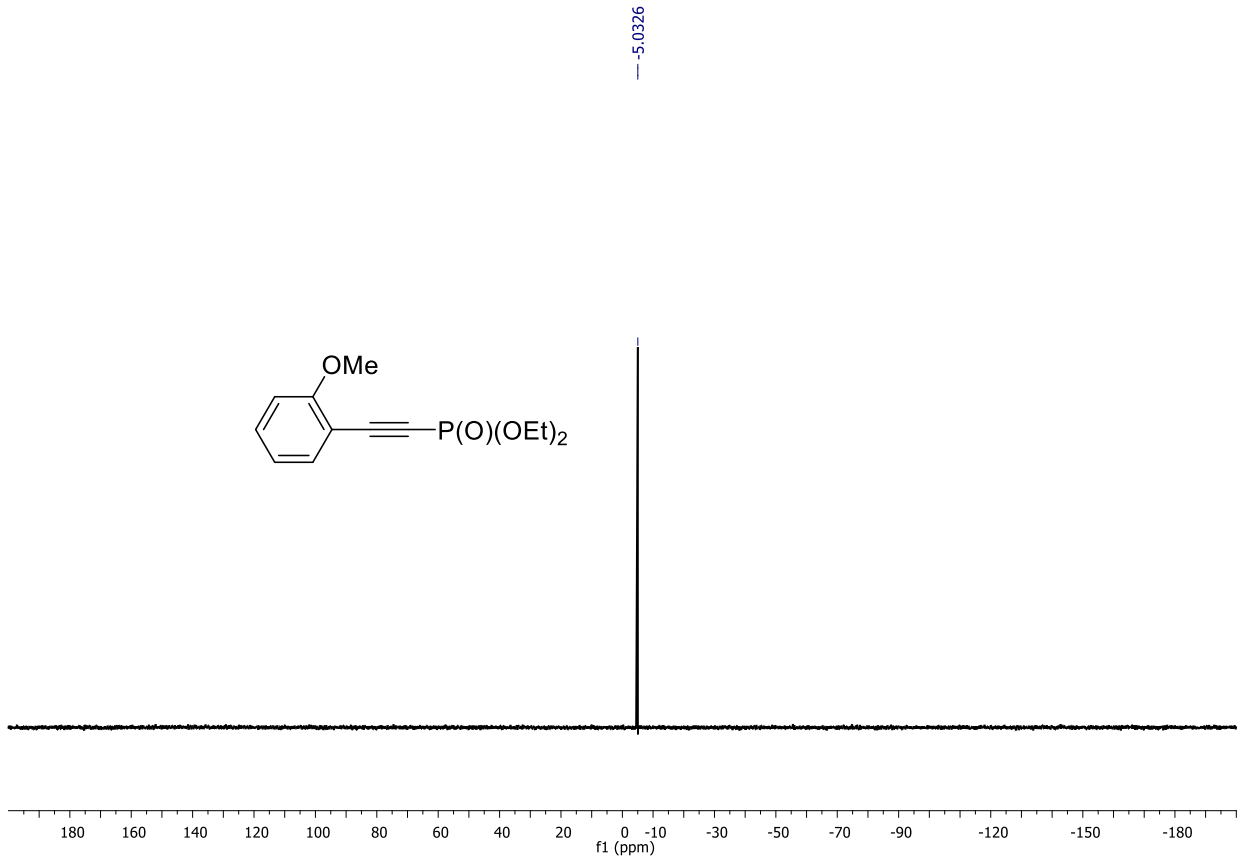

137.1
134.5
131.7
129.7
126.8
120.1
120.0
95.4
95.1
84.3
82.4
77.3
76.9
63.6
63.5
16.2
16.2
Cl
P(O)(OEt)2
f1 (ppm)


-6.1010
Cl
P(O)(OEt)2
f1 (ppm)

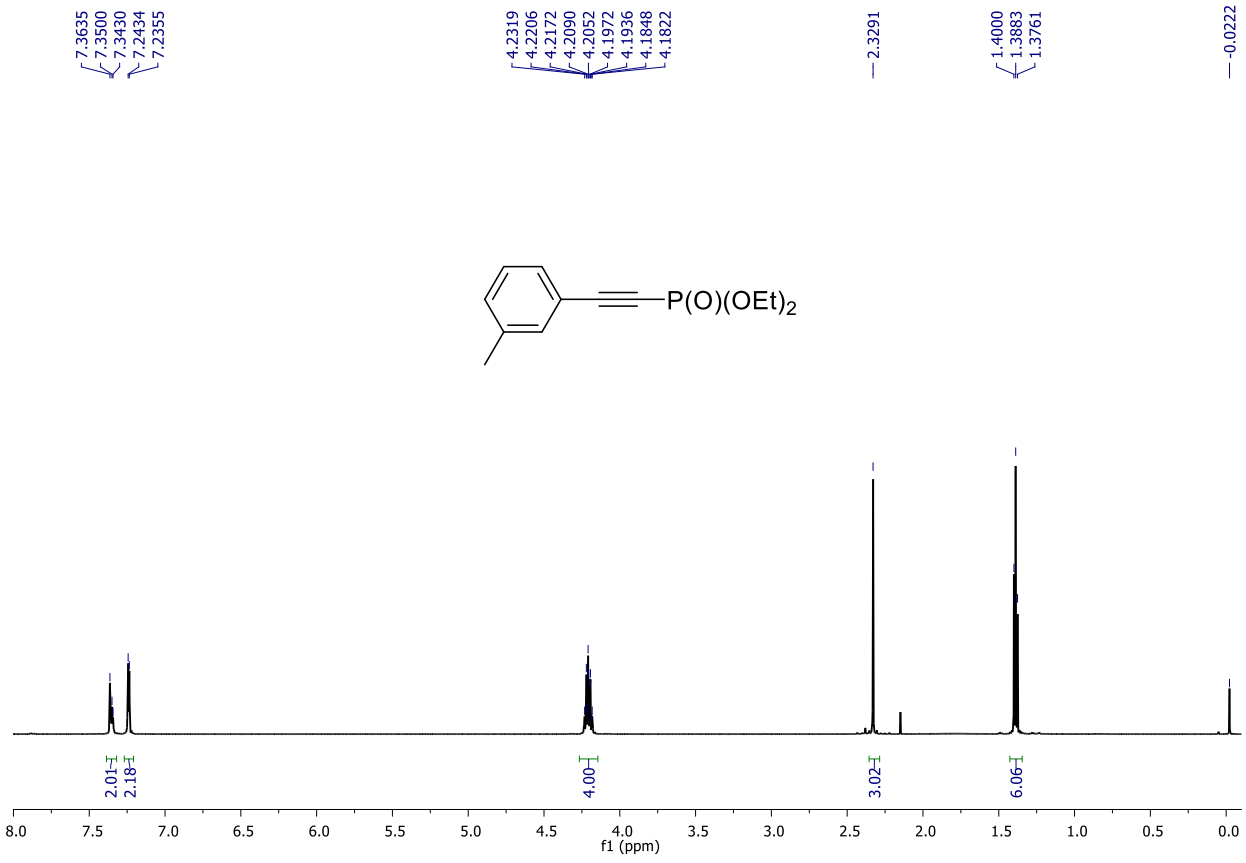
Diethyl [(2-methoxyphenyl)ethynyl]phosphonate (3k):

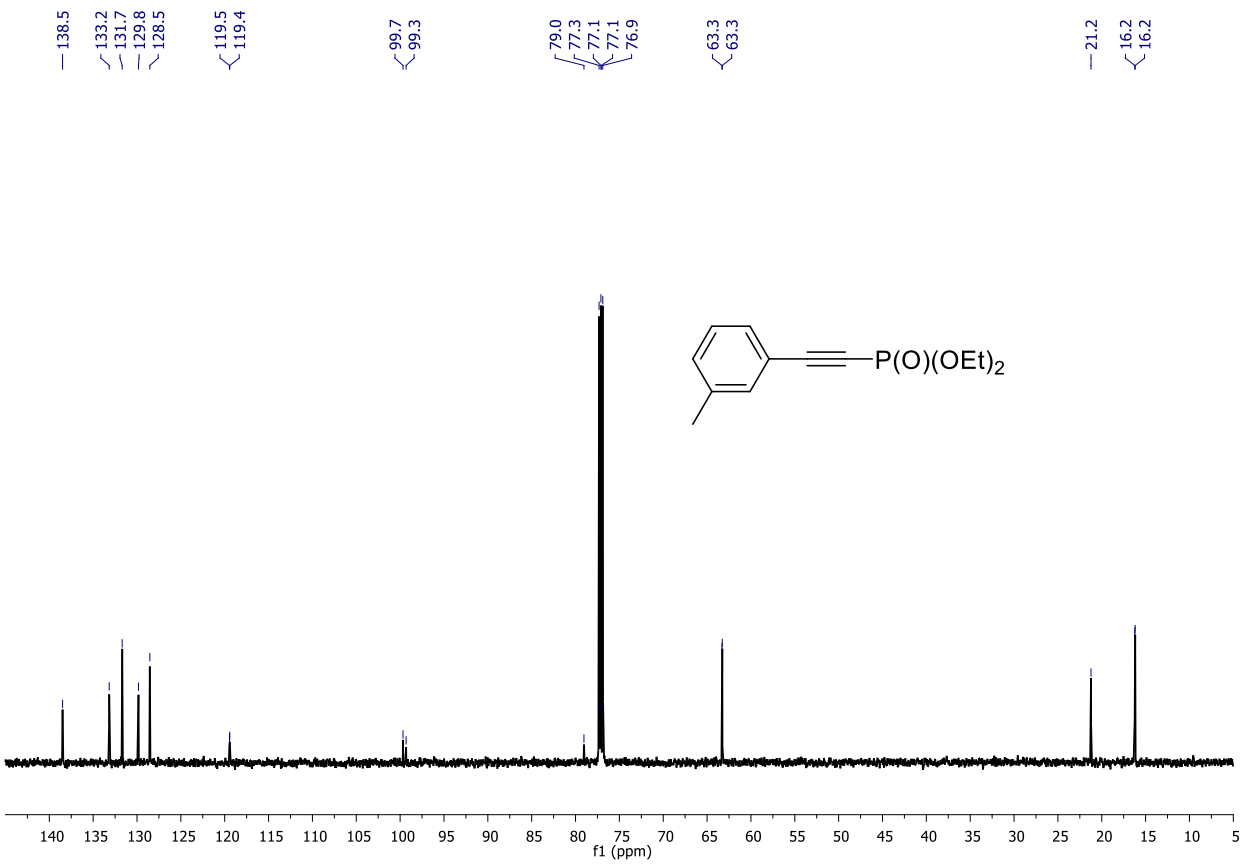


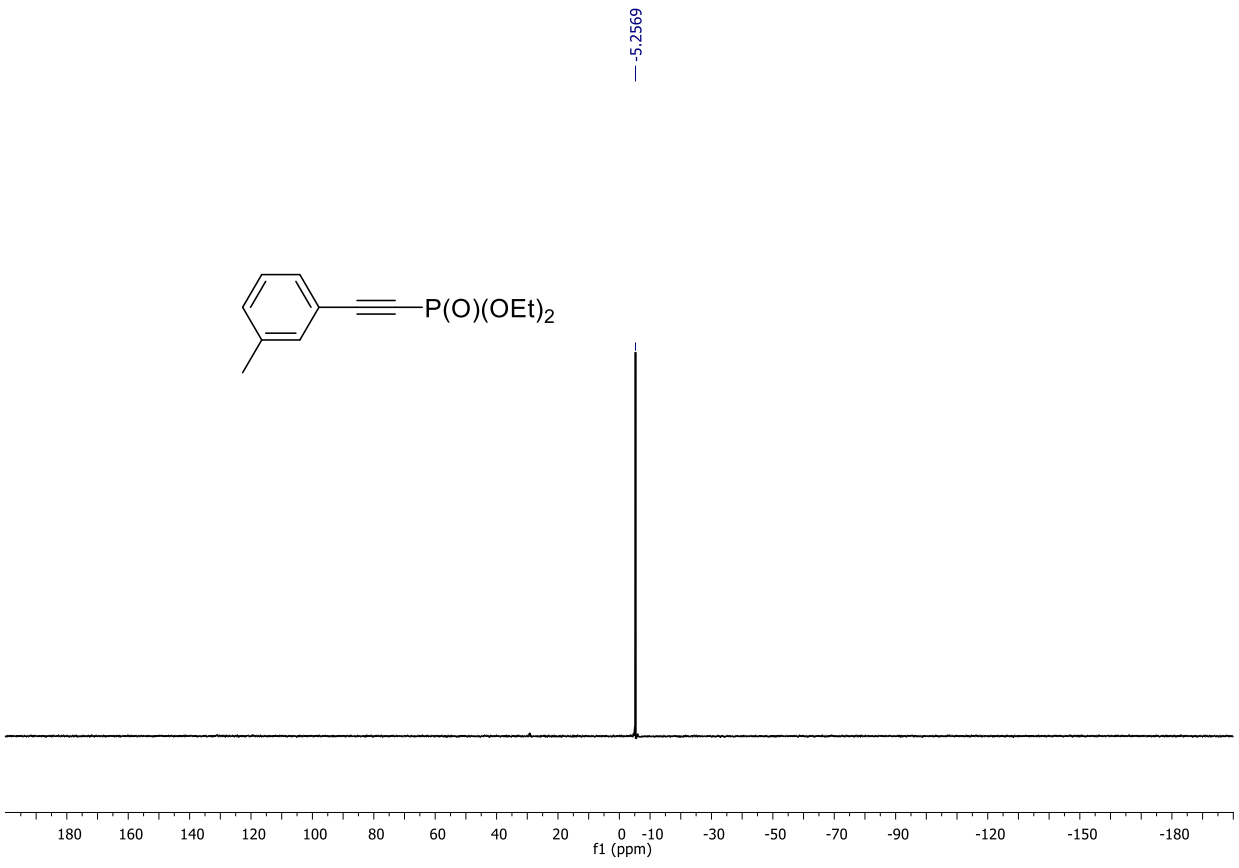




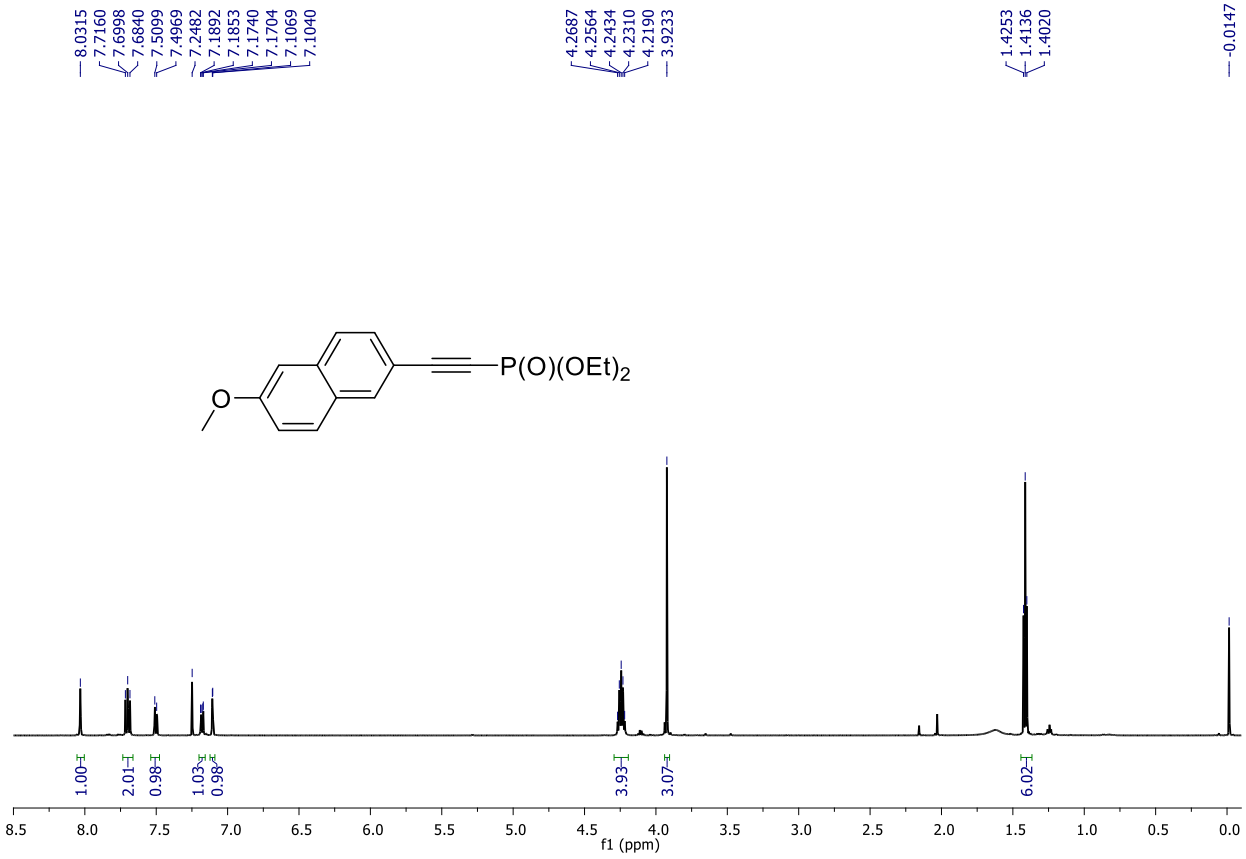
Diethyl [(3-methylphenyl)ethynyl]phosphonate (3l):

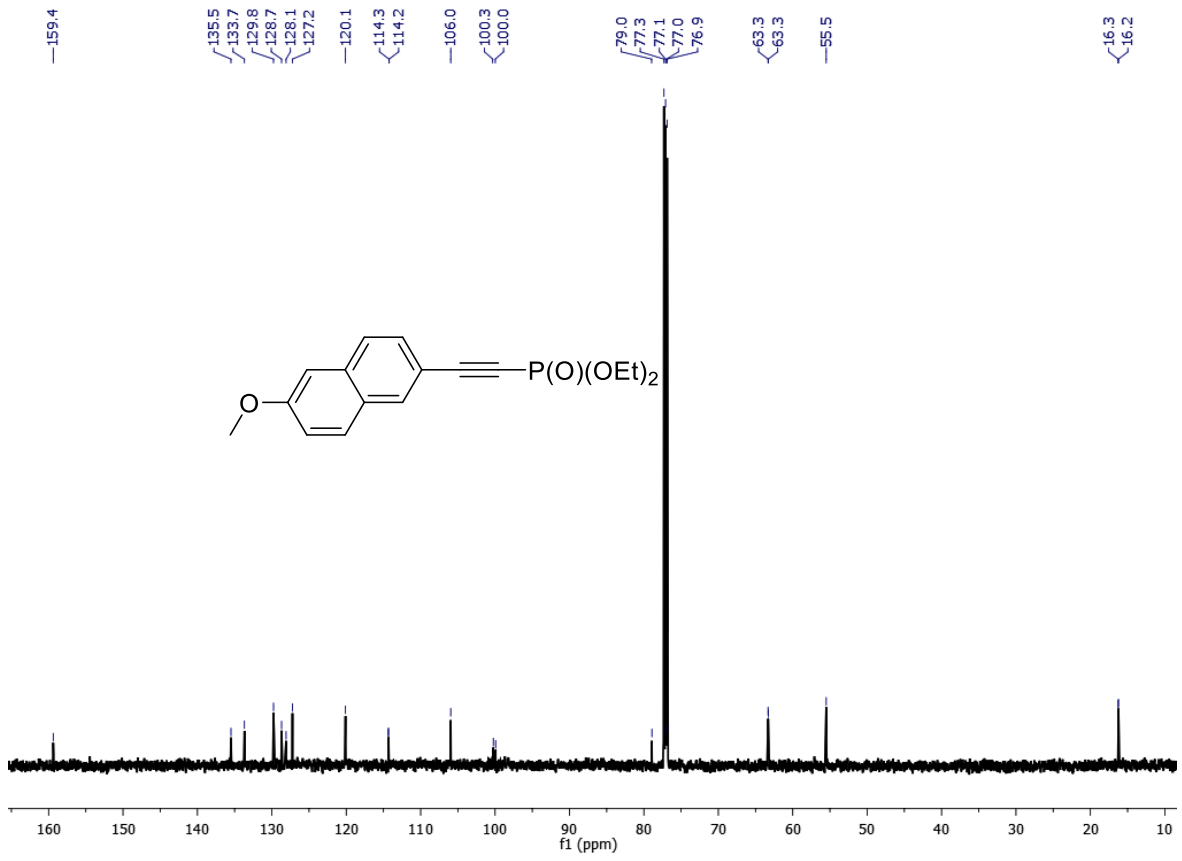


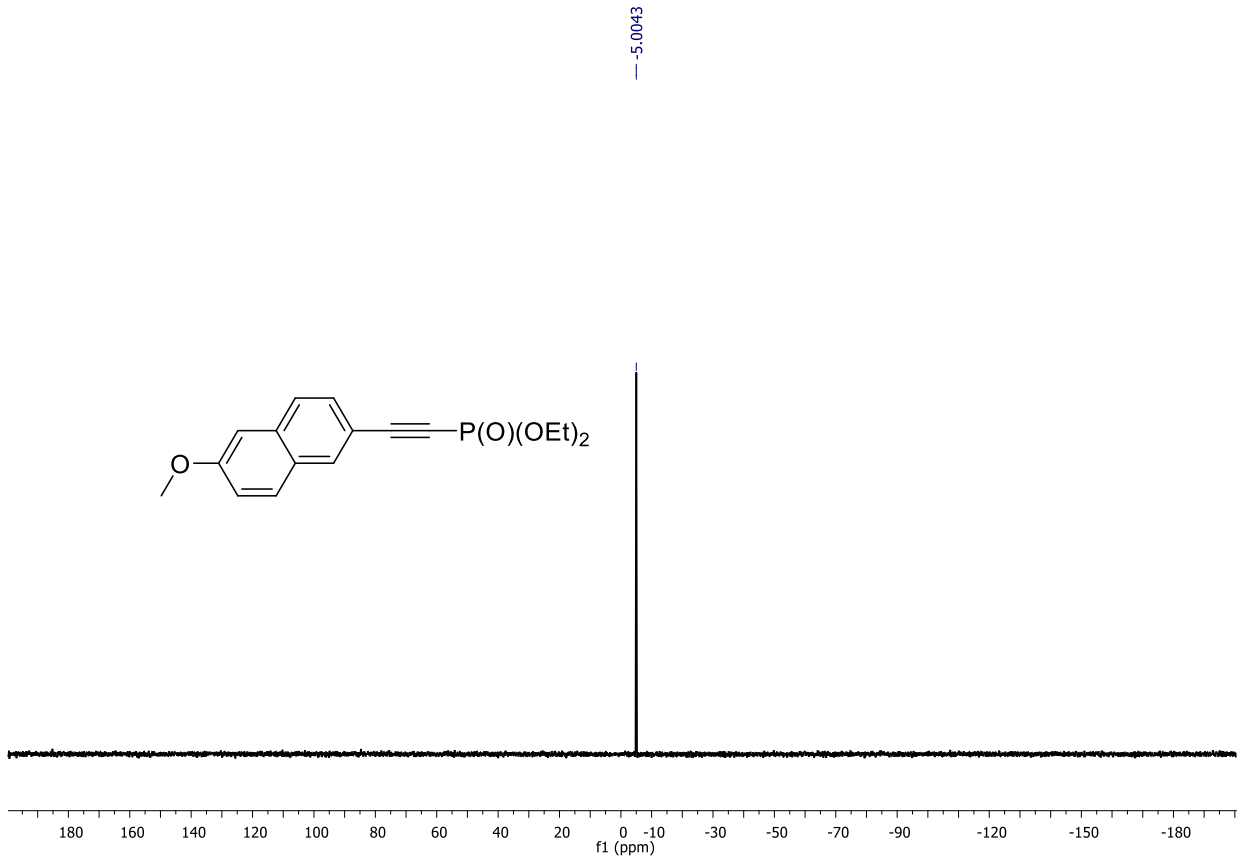

138.5
133.2
131.7
129.8
128.5
119.5
119.4
99.7
99.3
79.0
77.3
77.1
77.1
76.9
63.3
63.3
21.2
16.2
16.2
P(O)(OEt)2
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


-5.2569
P(O)(OEt)2
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

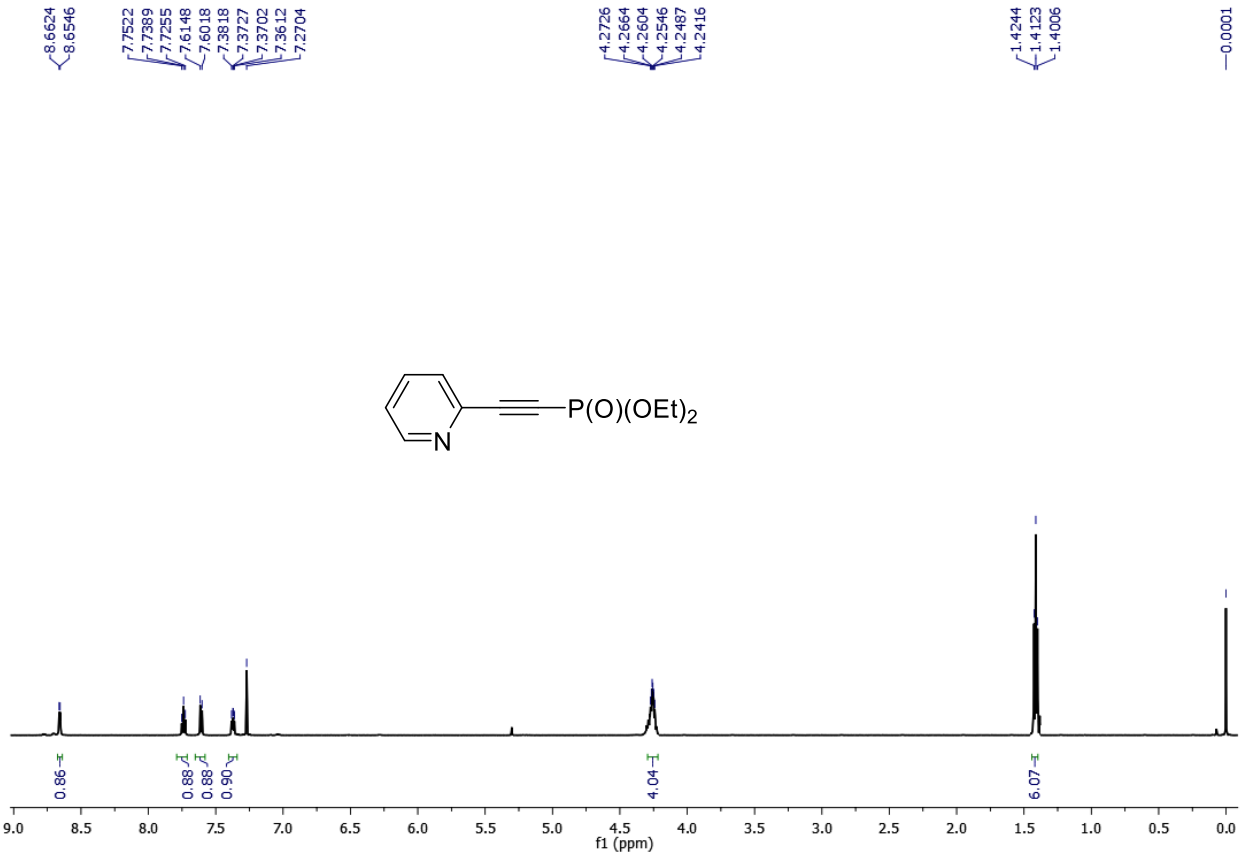
Diethyl [(6-methoxynaphthalen-2-yl)ethynyl]phosphonate (3m):

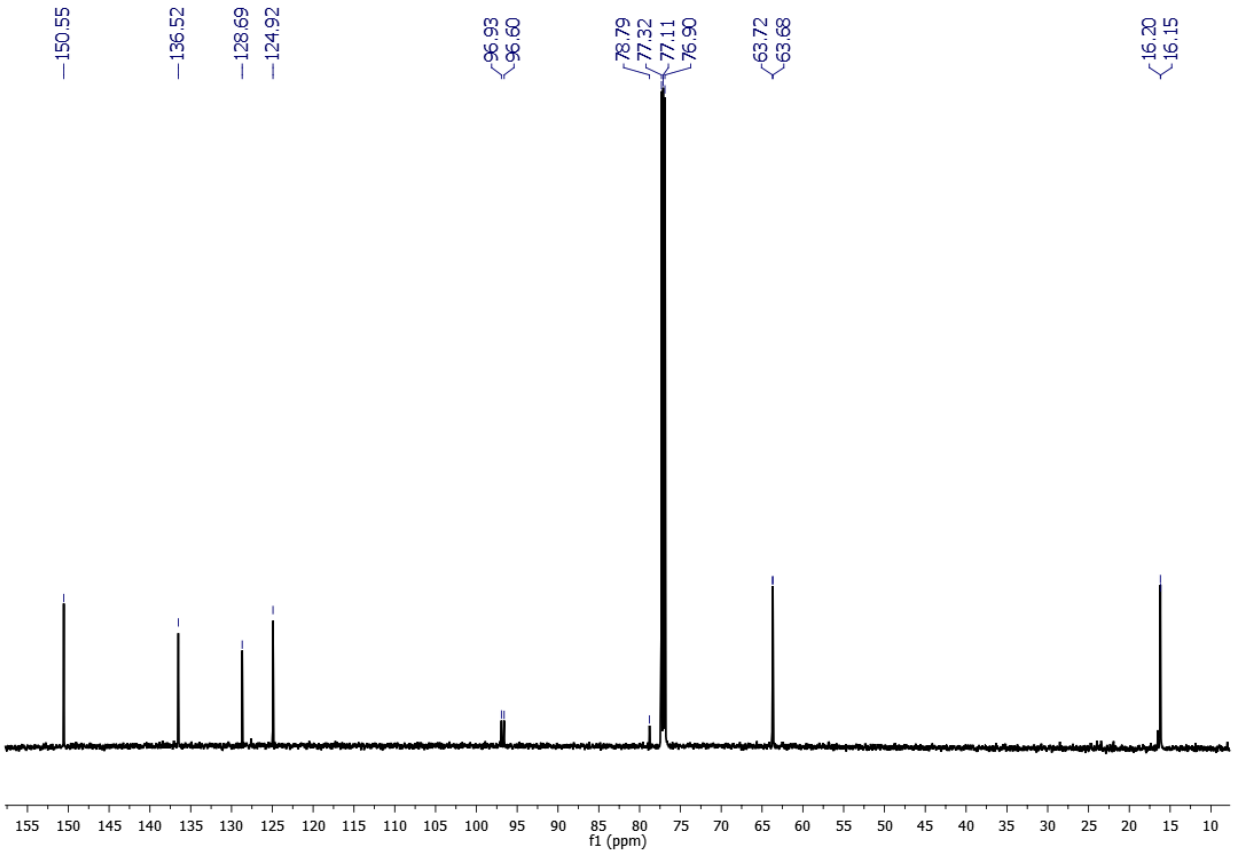


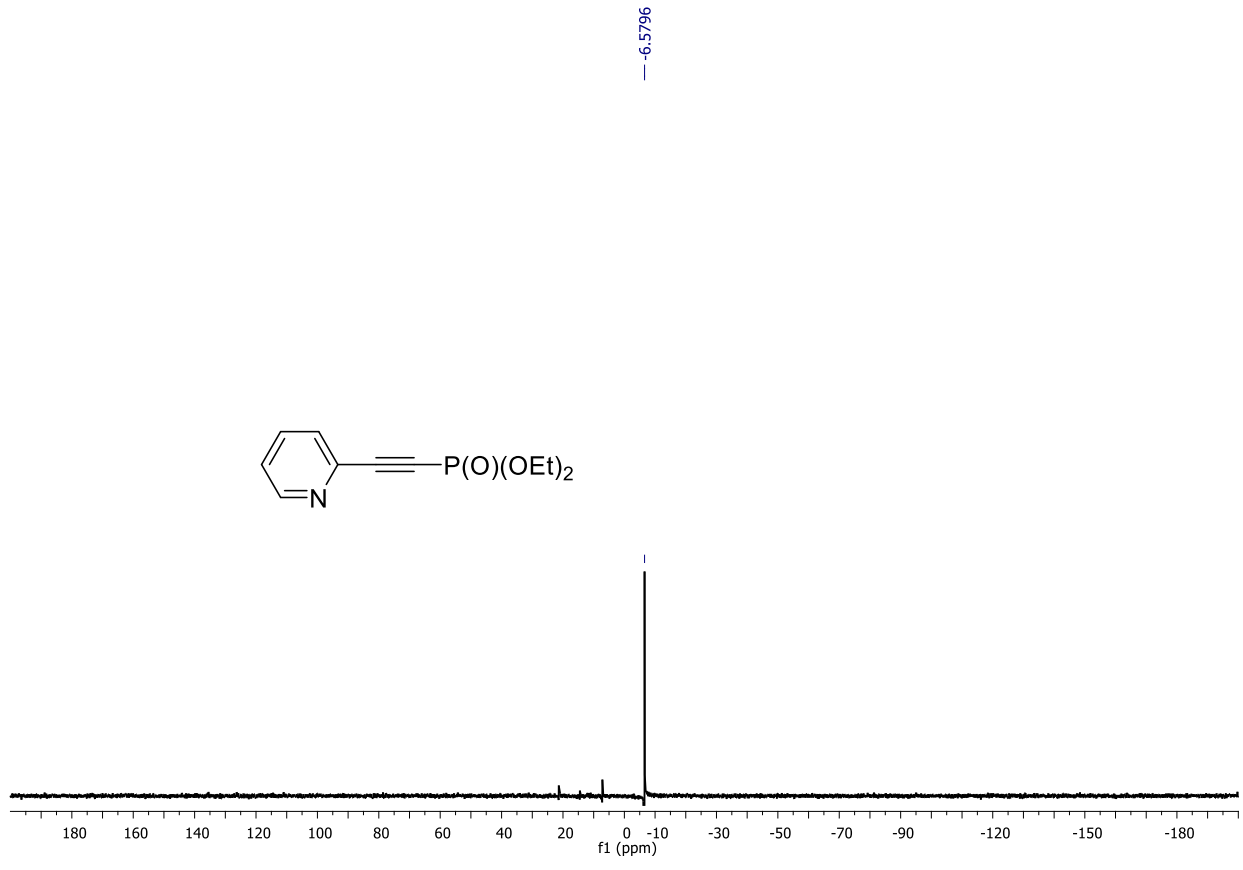




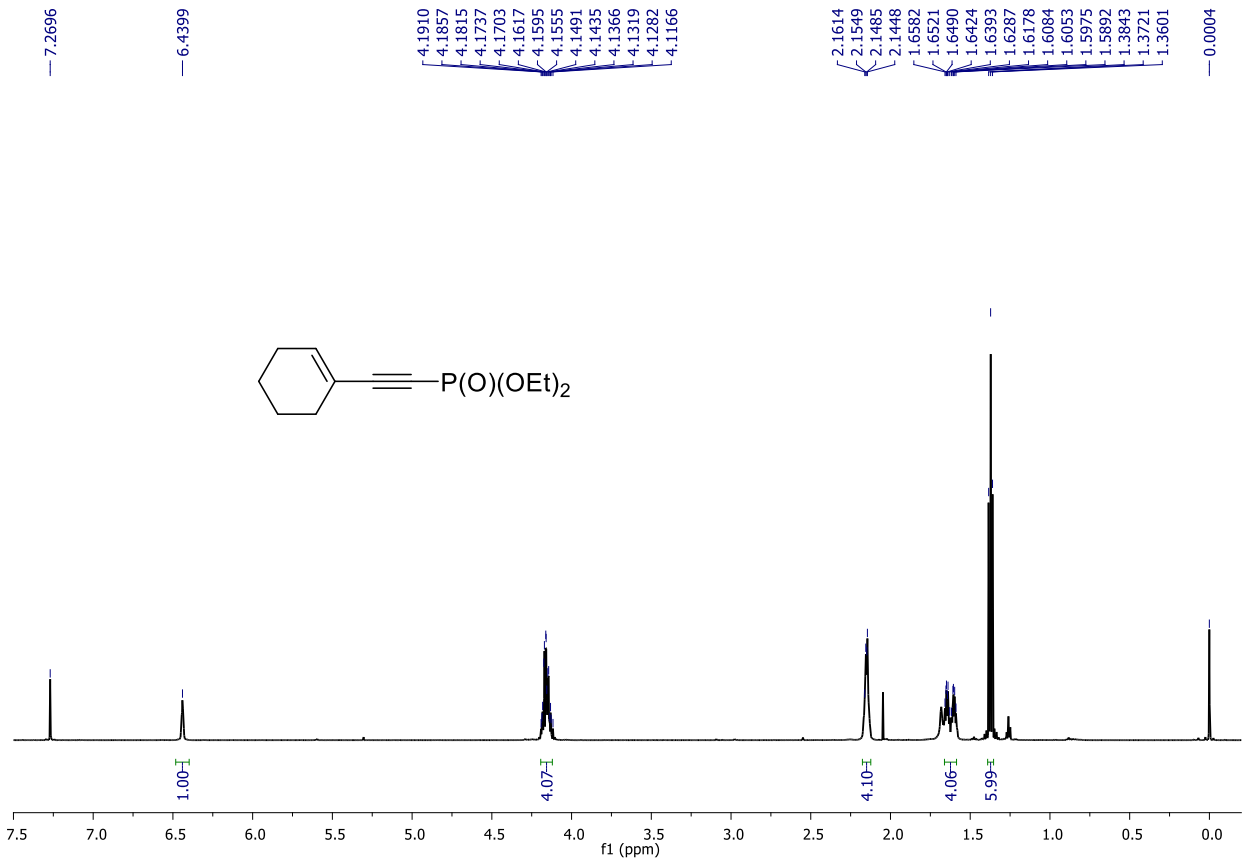
Diethyl (pyridine-2-ylethynyl)phosphonate (3n):

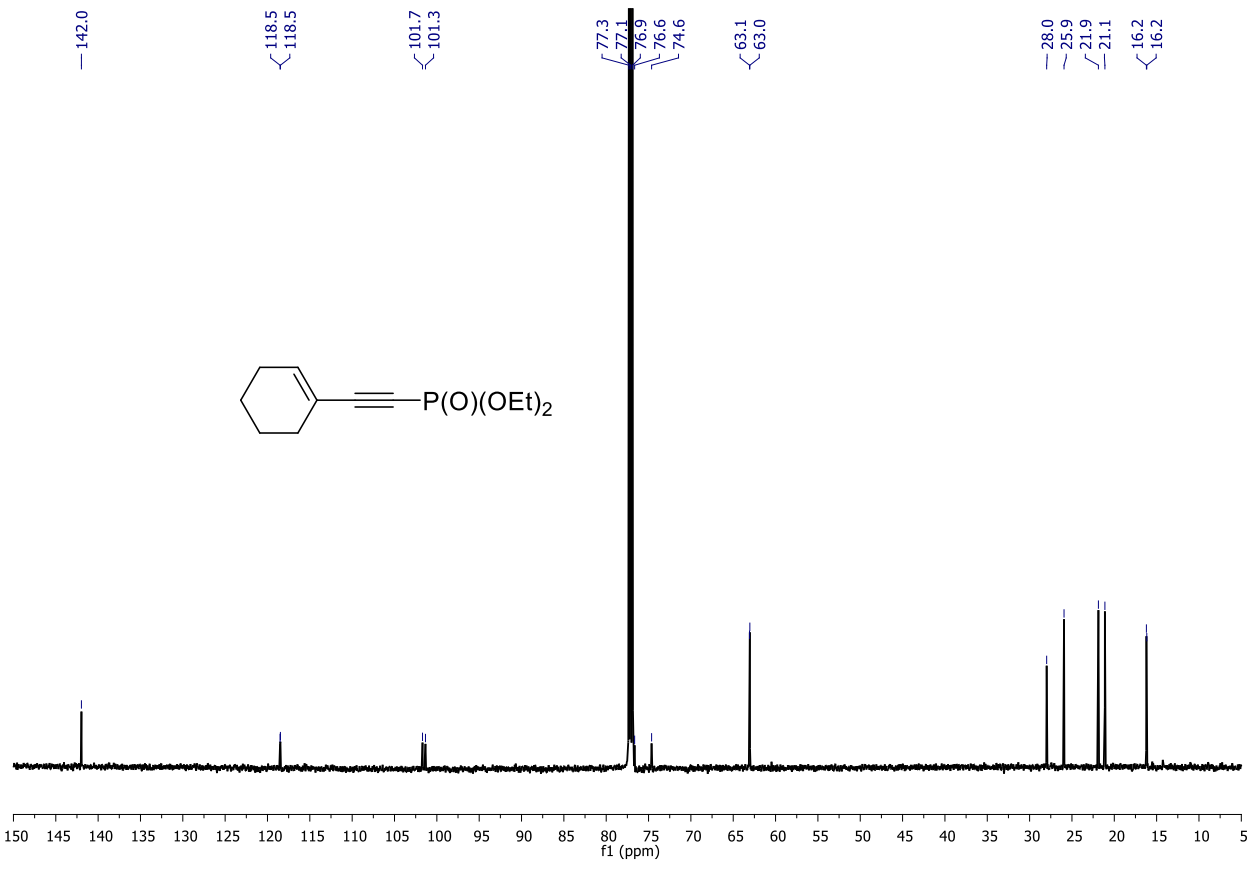


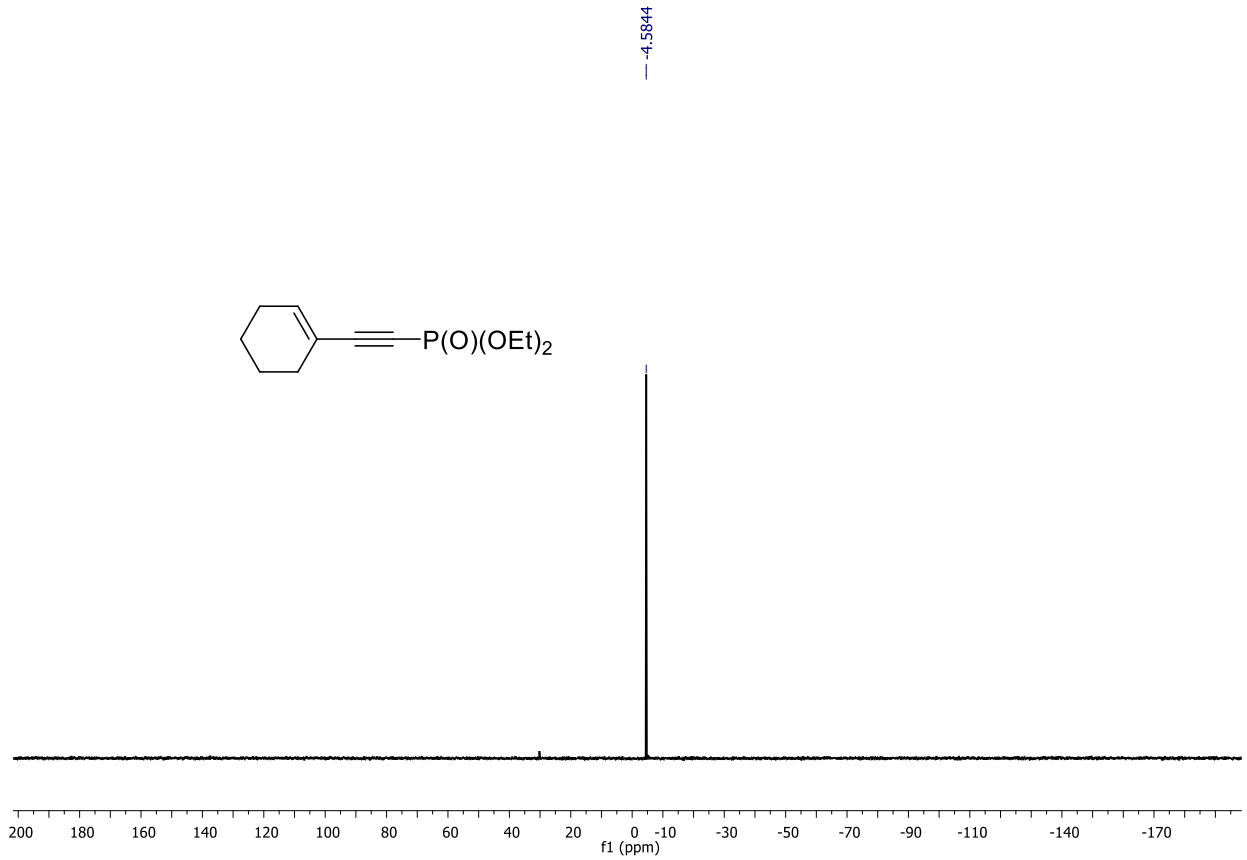




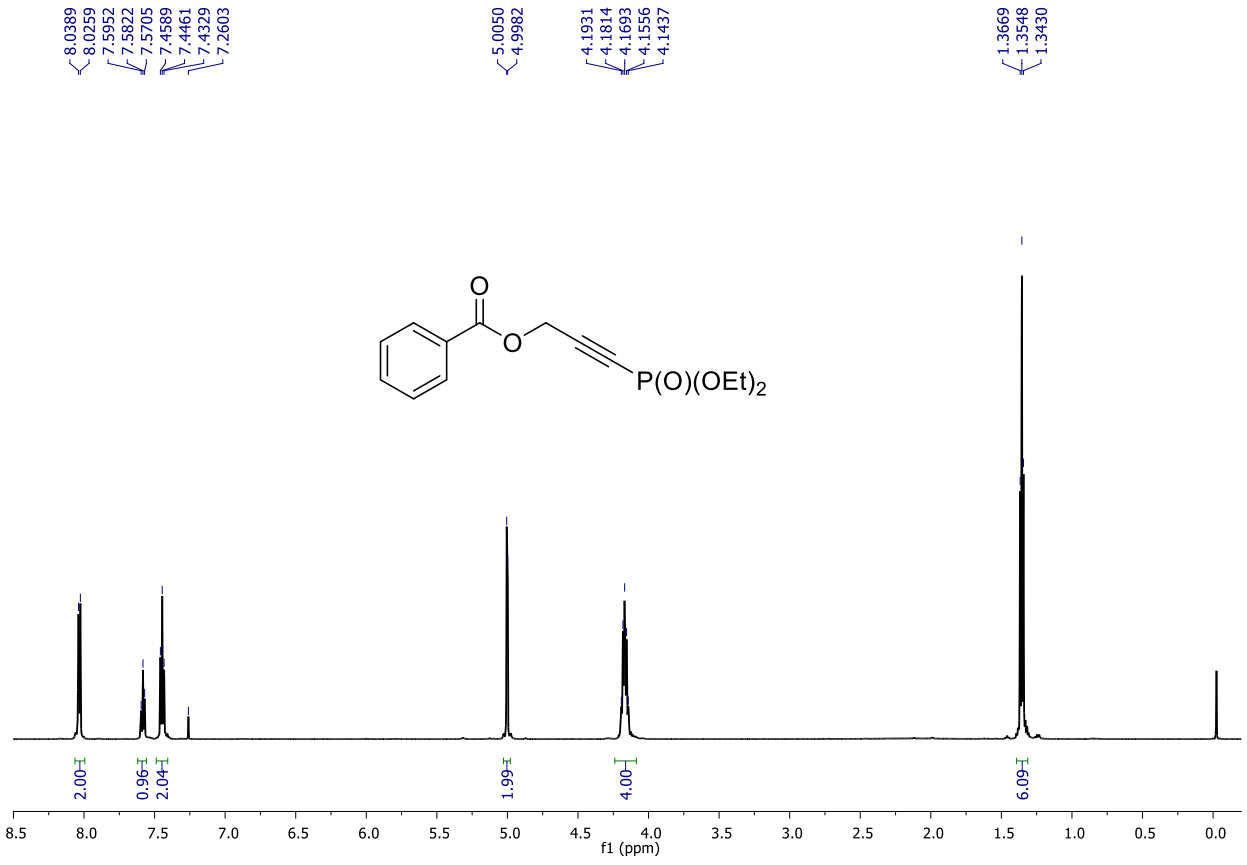
Diethyl (cyclohexen-1-ylethynyl)phosphonate (3o):

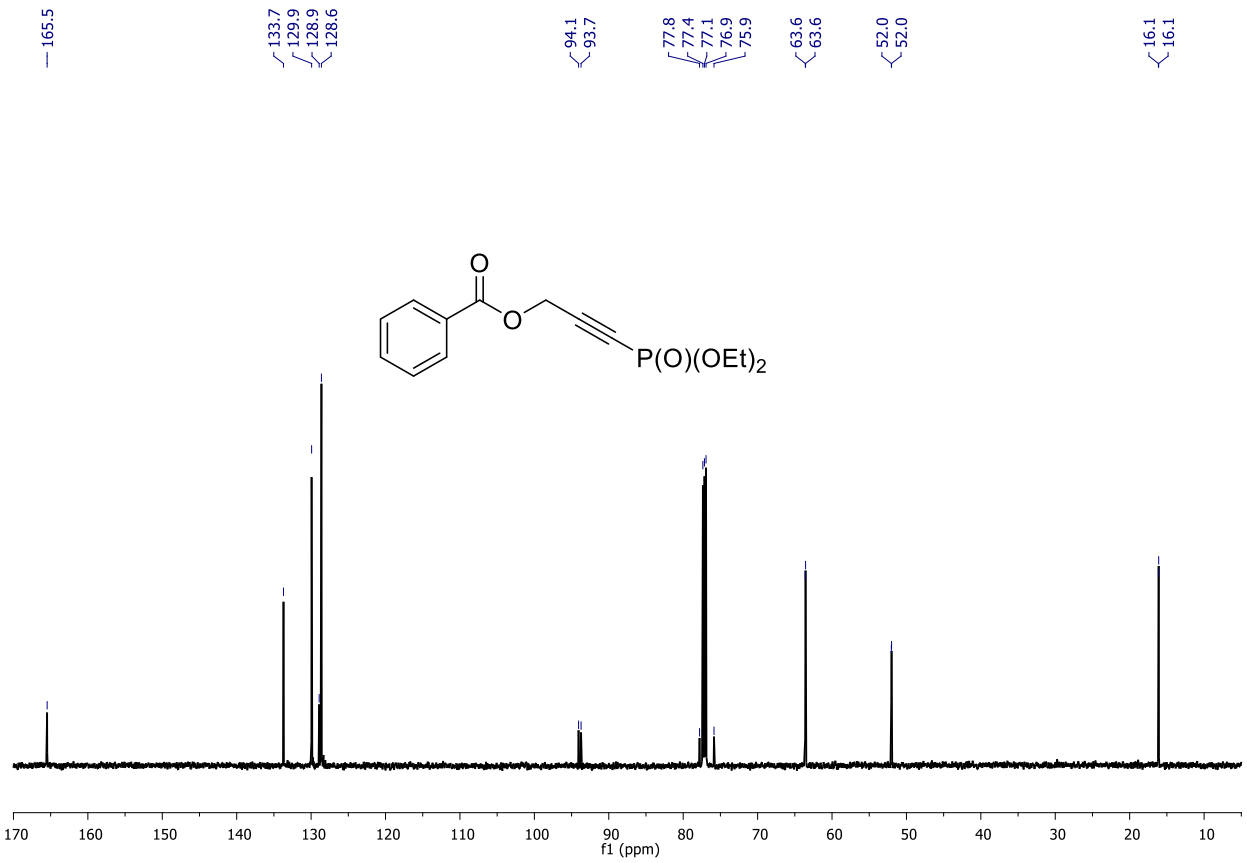

7.2696
6.4399
4.1910
4.1857
4.1815
4.1737
4.1703
4.1617
4.1595
4.1555
4.1491
4.1435
4.1366
4.1319
4.1282
4.1166
2.1614
2.1549
2.1485
2.1448
1.6582
1.6521
1.6490
1.6424
1.6393
1.6287
1.6178
1.6084
1.6053
1.5975
1.5892
1.3843
1.3721
1.3601
0.0004
P(O)(OEt)2
1.00
4.07
4.10
4.06
5.99
f1 (ppm)

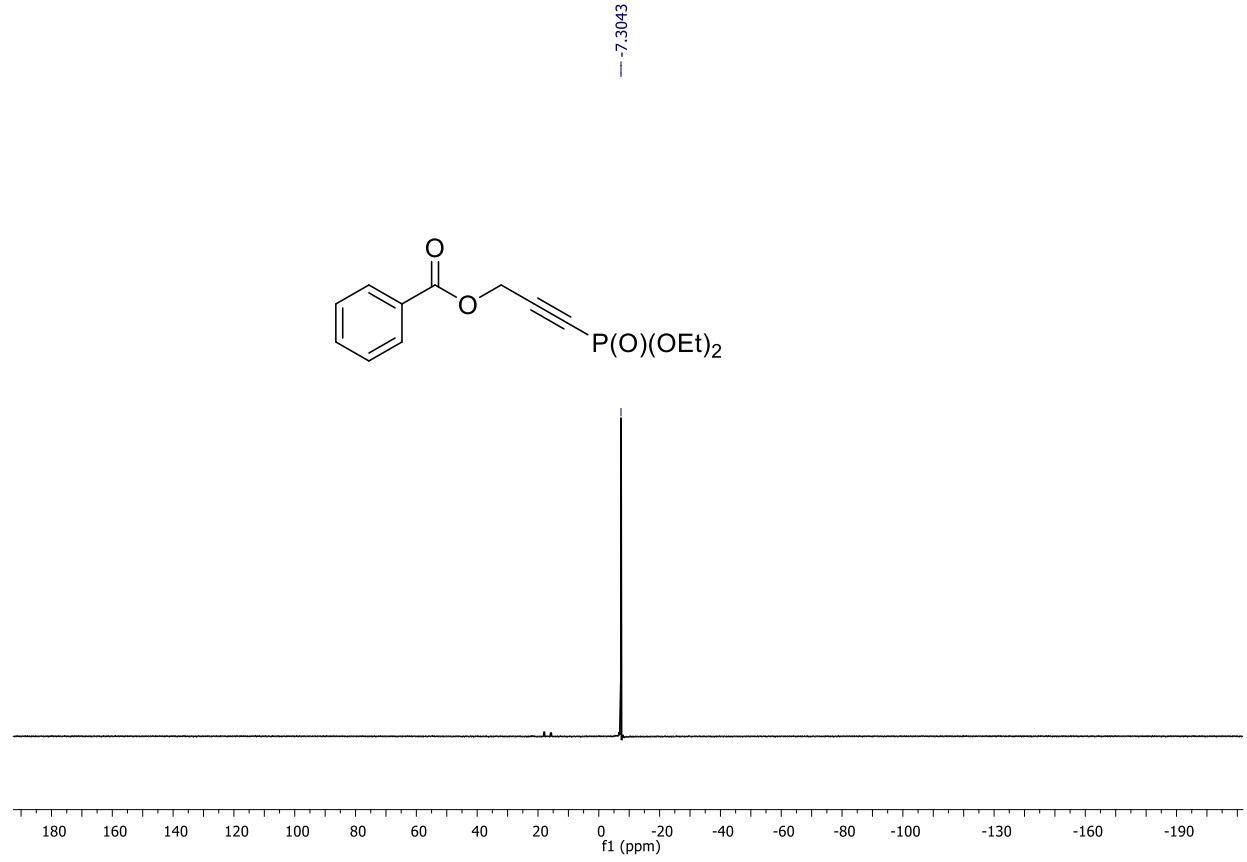

142.0
118.5
118.5
101.7
101.3
77.3
77.1
76.9
76.6
74.6
63.1
63.0
28.0
25.9
21.9
21.1
16.2
16.2
P(O)(OEt)2
f1 (ppm)



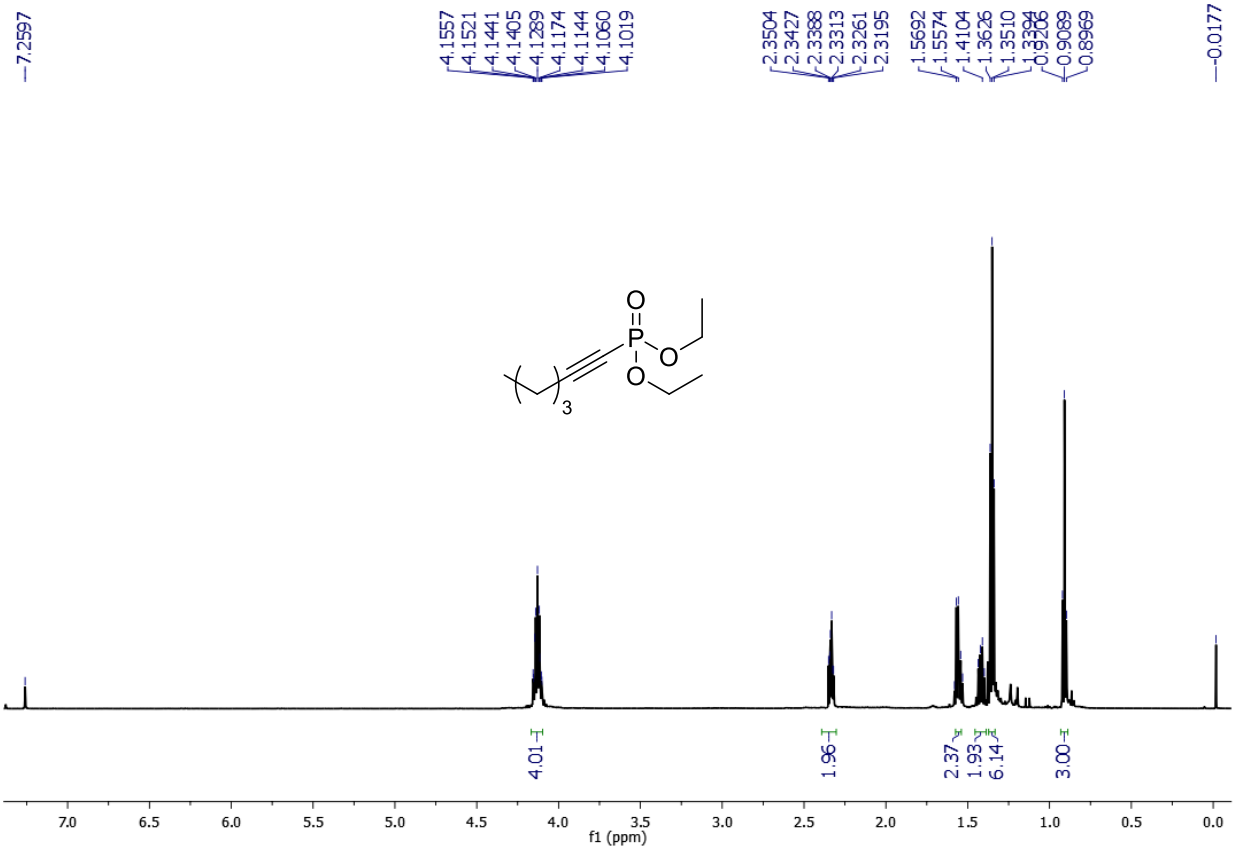
3-(diethoxyphosphoryl)prop-2-yn-1-yl benzoate (3p):

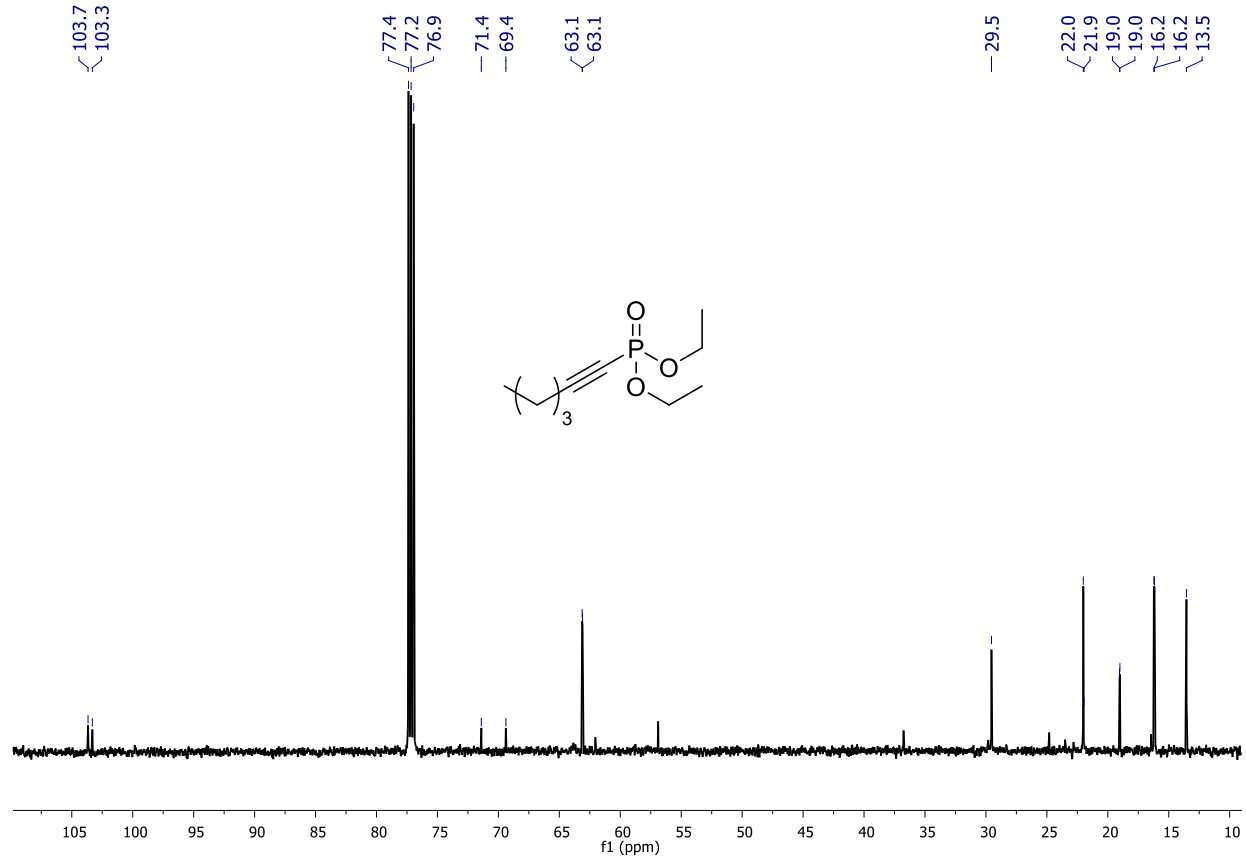


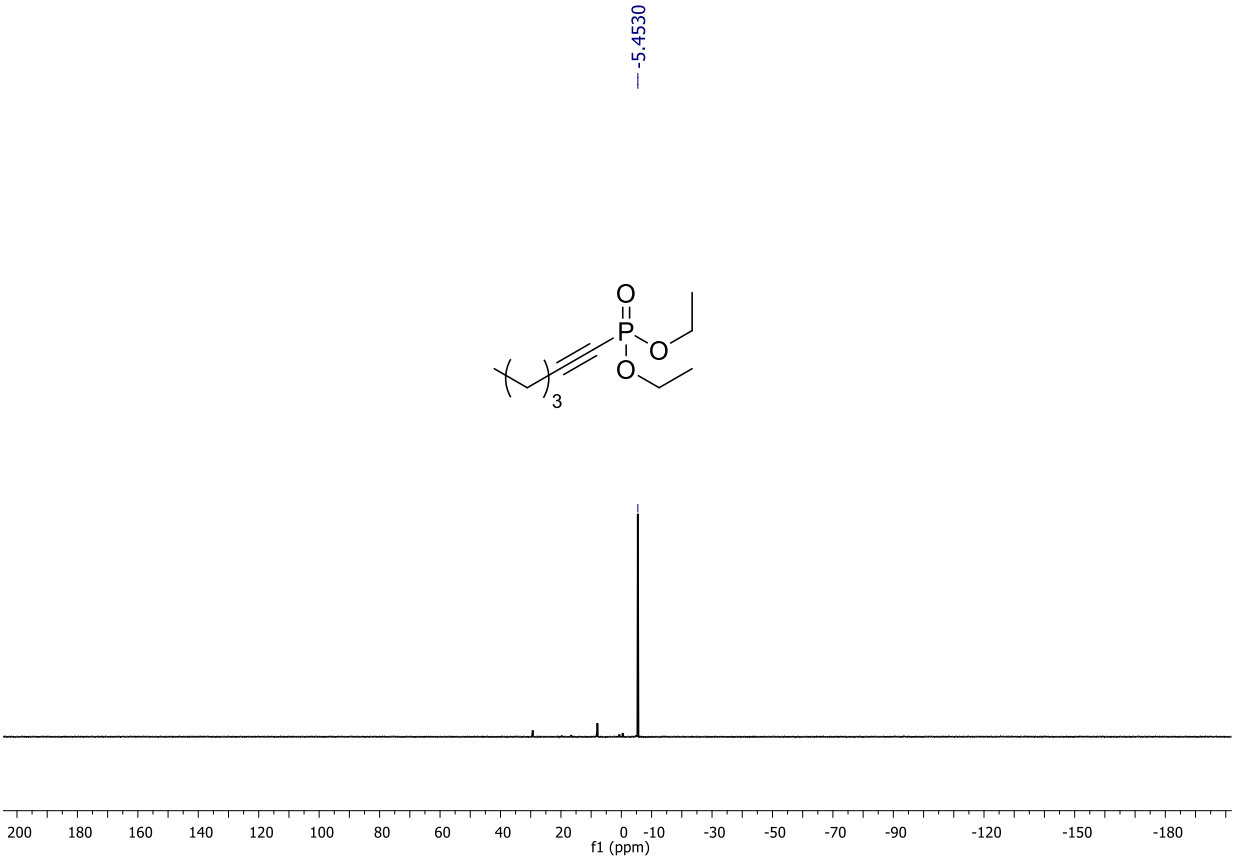

165.5
133.7
129.9
128.9
128.6
94.1
93.7
77.8
77.4
77.1
76.9
75.9
63.6
63.6
52.0
52.0
16.1
16.1
O
O
P(O)(OEt)2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-7.3043
O
O
P(O)(OEt)2
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

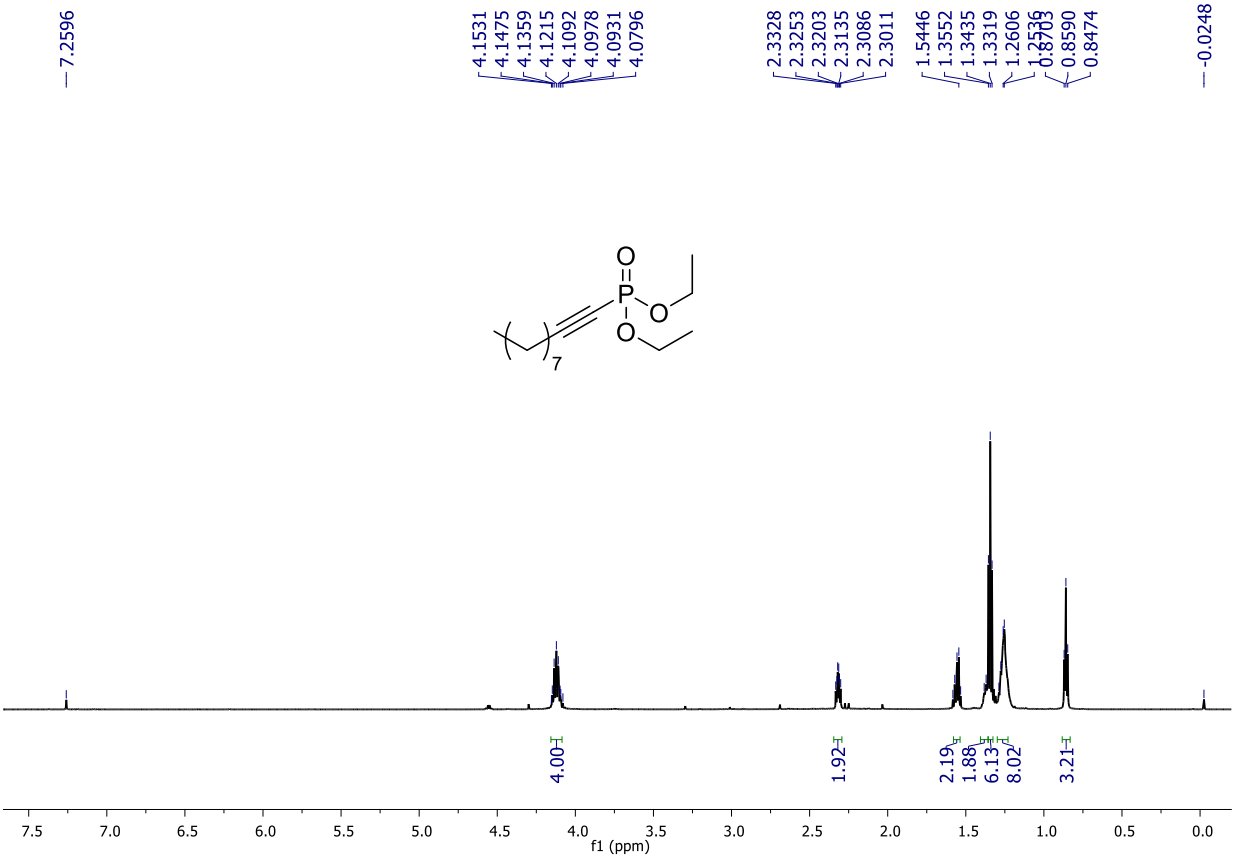
Diethyl hex-1-yn-1-ylphosphonate (3r):

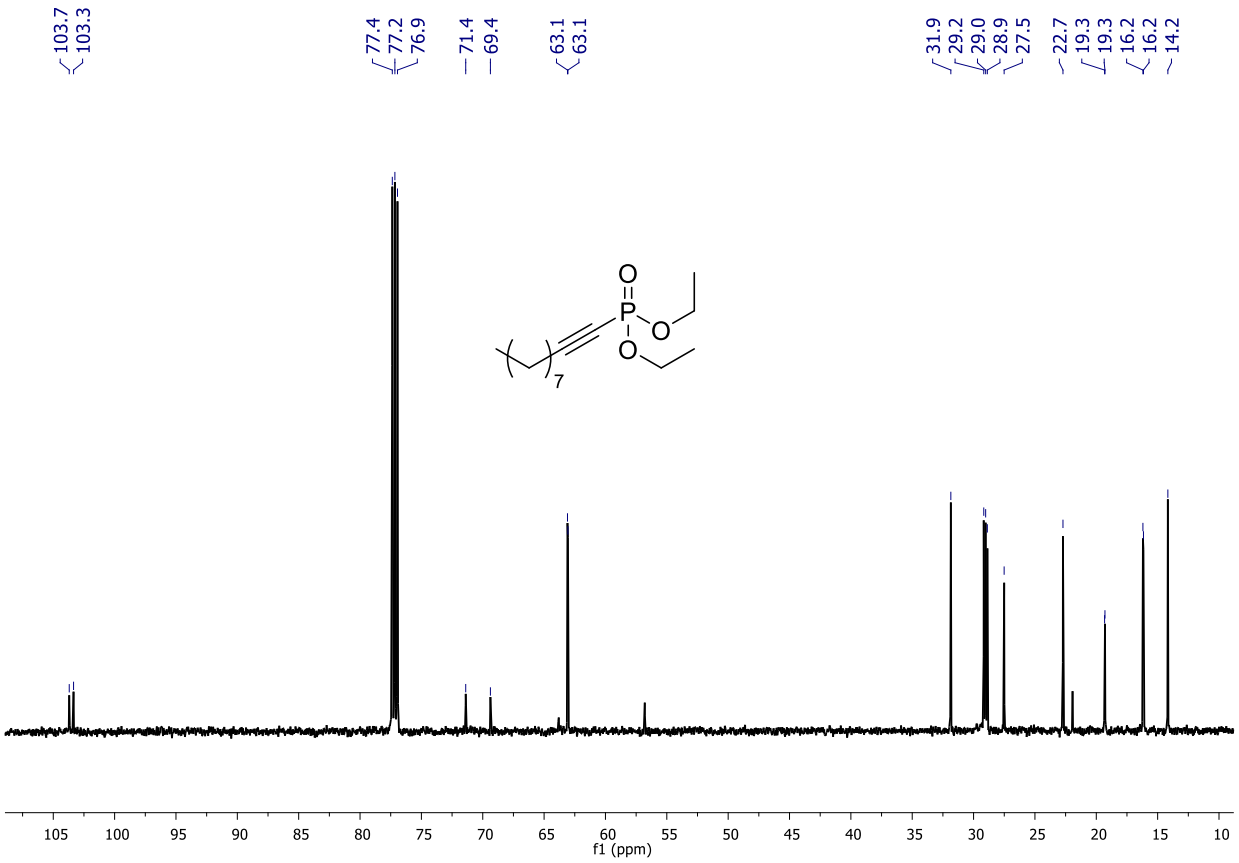


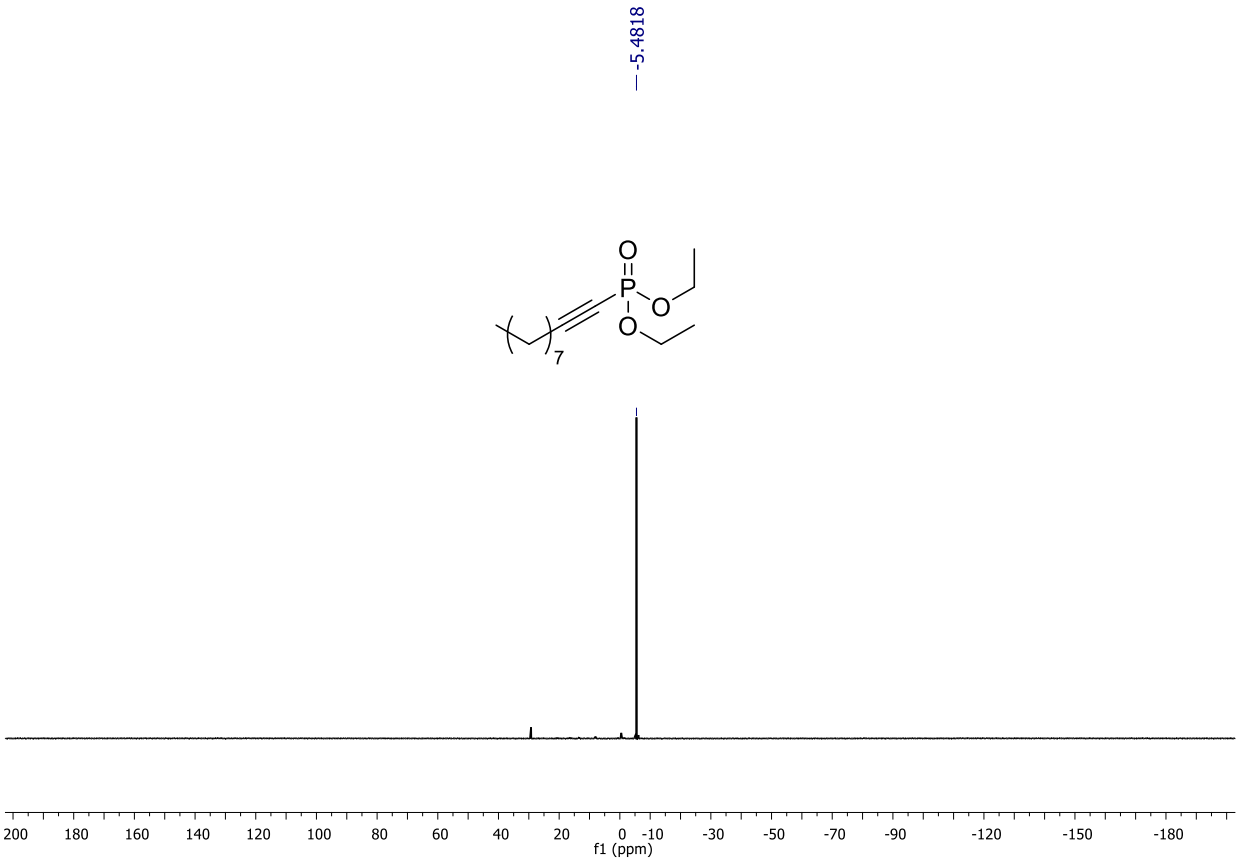




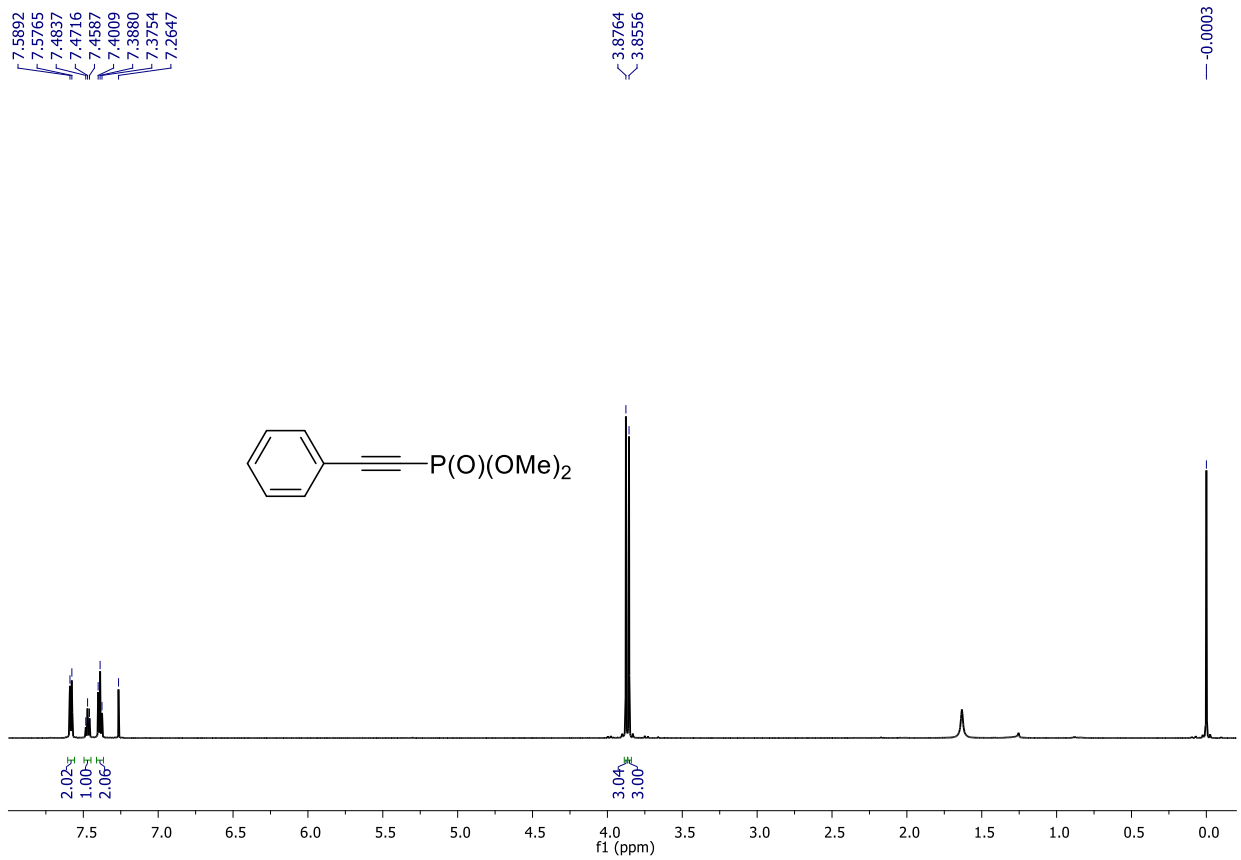
Diethyl dec-1-yn-1-ylphosphonate (3s):

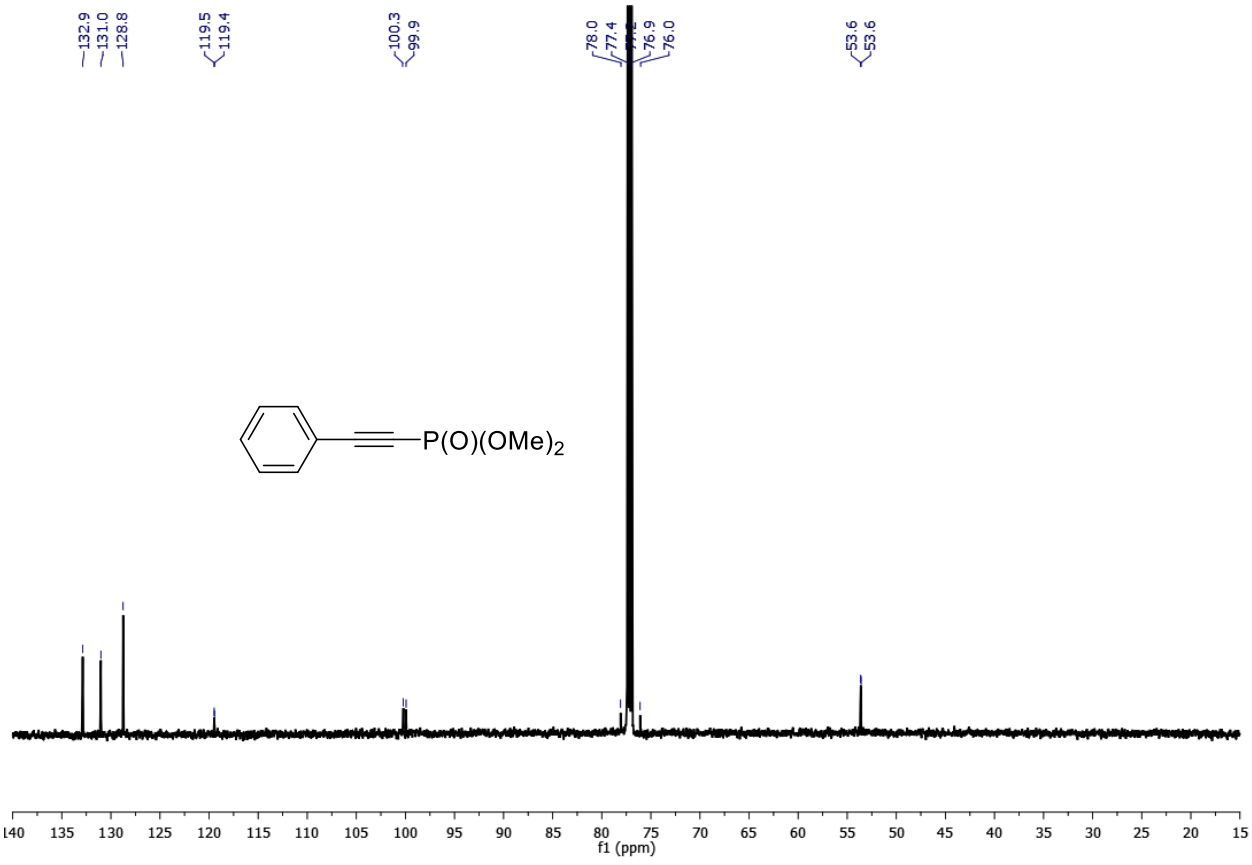


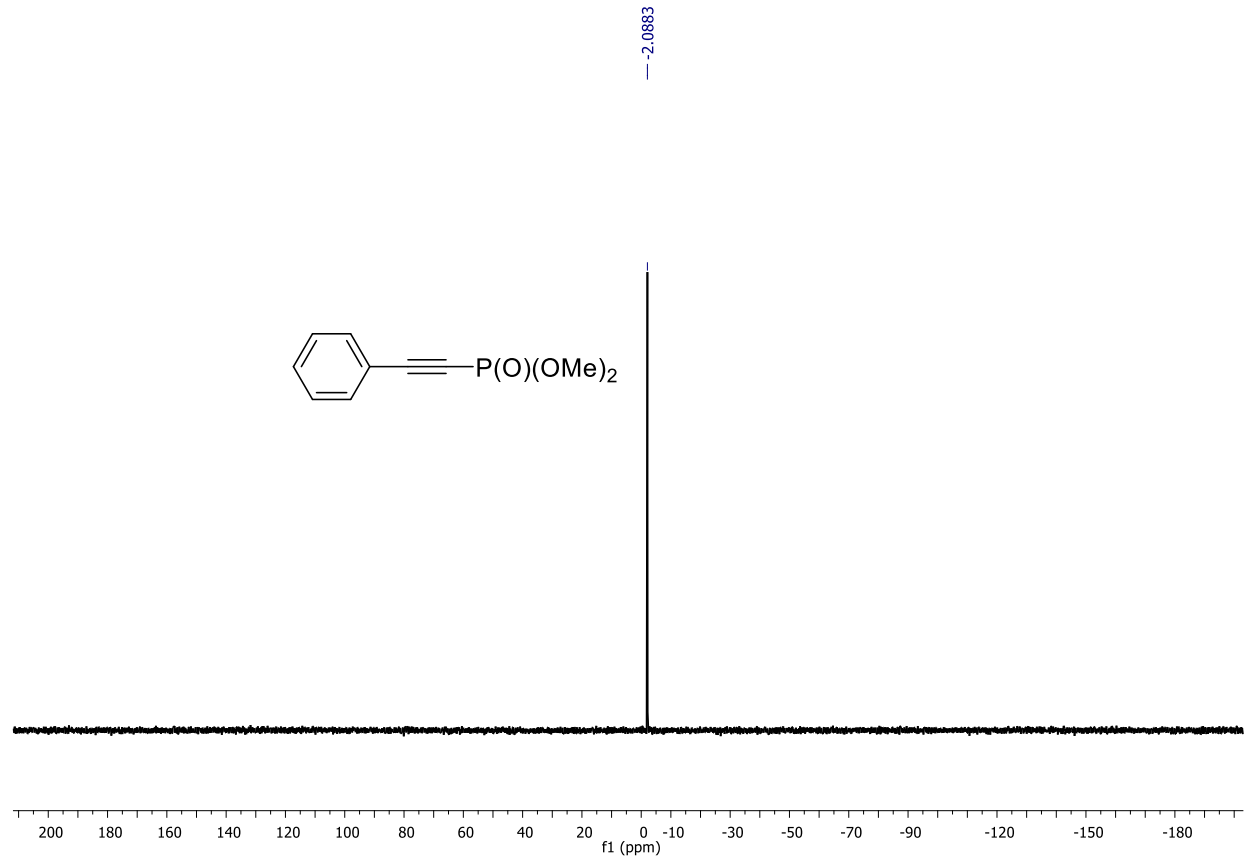




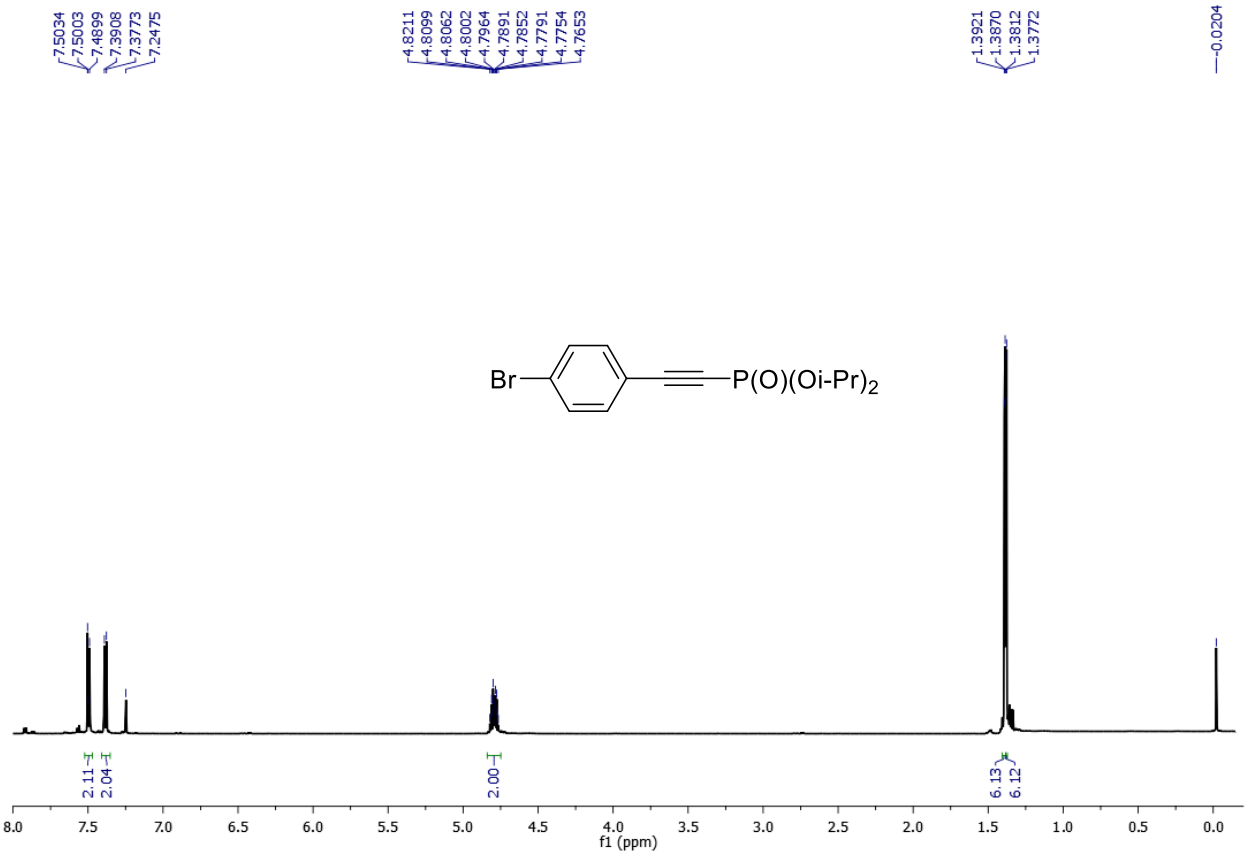
Dimethyl (phenylethynyl)phosphonate (3t):

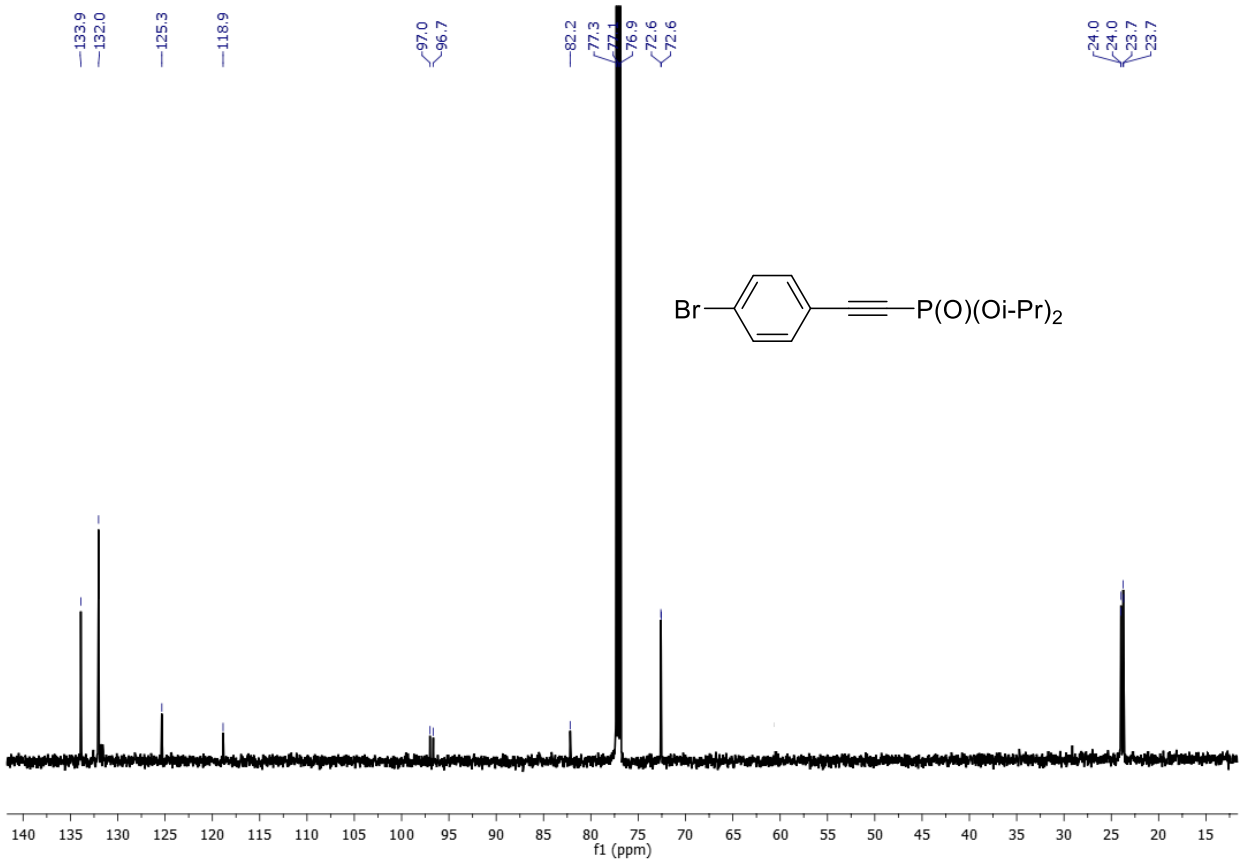

7.5892
7.5765
7.4837
7.4716
7.4587
7.4009
7.3880
7.3754
7.2647
3.8764
3.8556
-0.0003
P(O)(OMe)2
2.02
1.00
2.06
3.04
3.00
f1 (ppm)

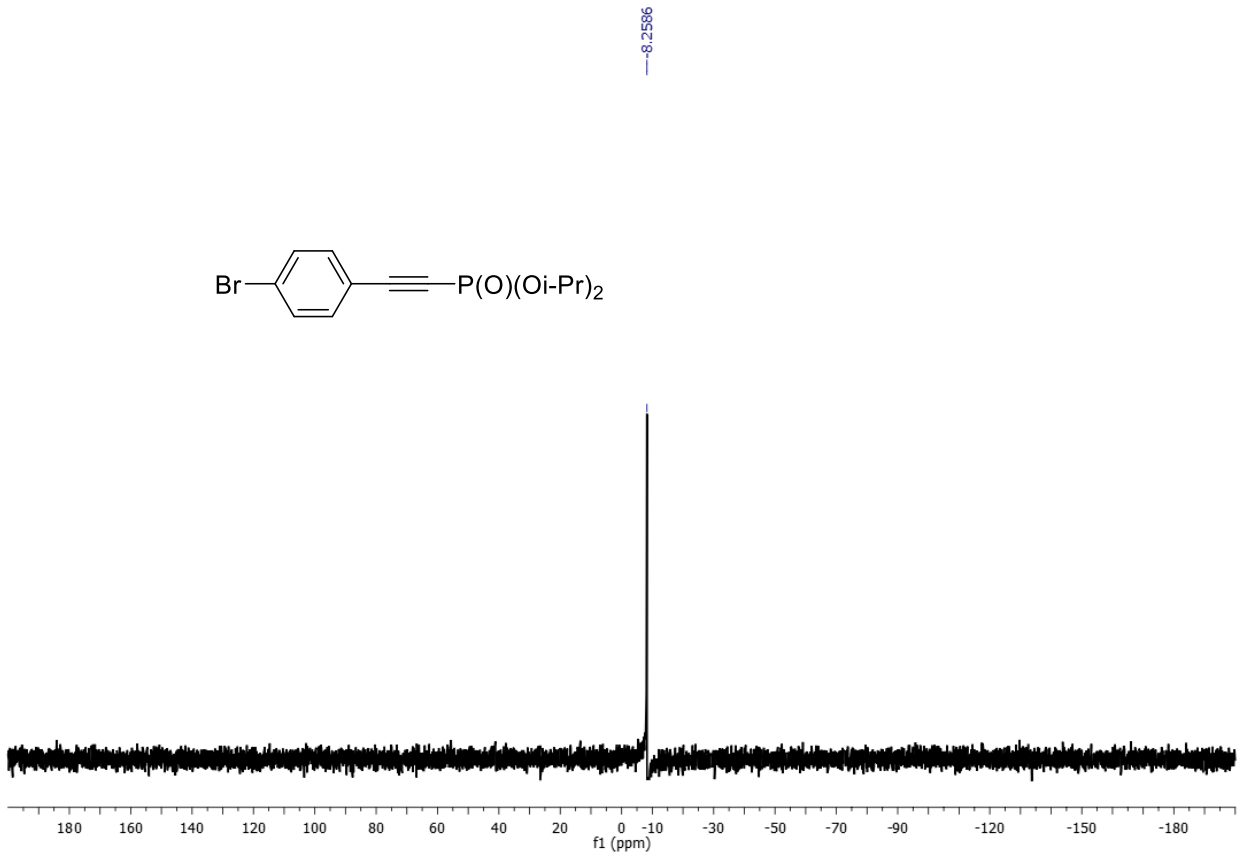

132.9
131.0
128.8
119.5
119.4
100.3
99.9
78.0
77.4
76.9
76.0
53.6
53.6
P(O)(OMe)2
f1 (ppm)



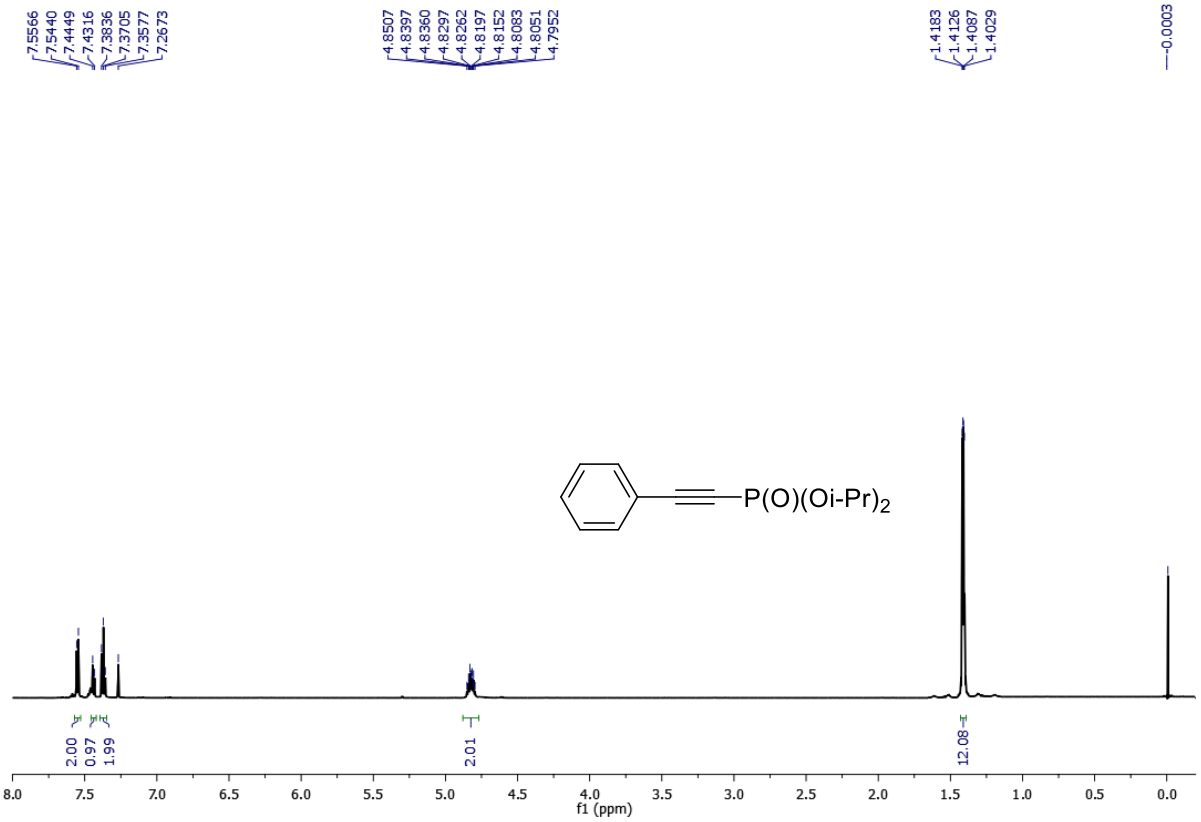
Diisopropyl [(4-bromophenyl)ethynyl]phosphonate (4a):

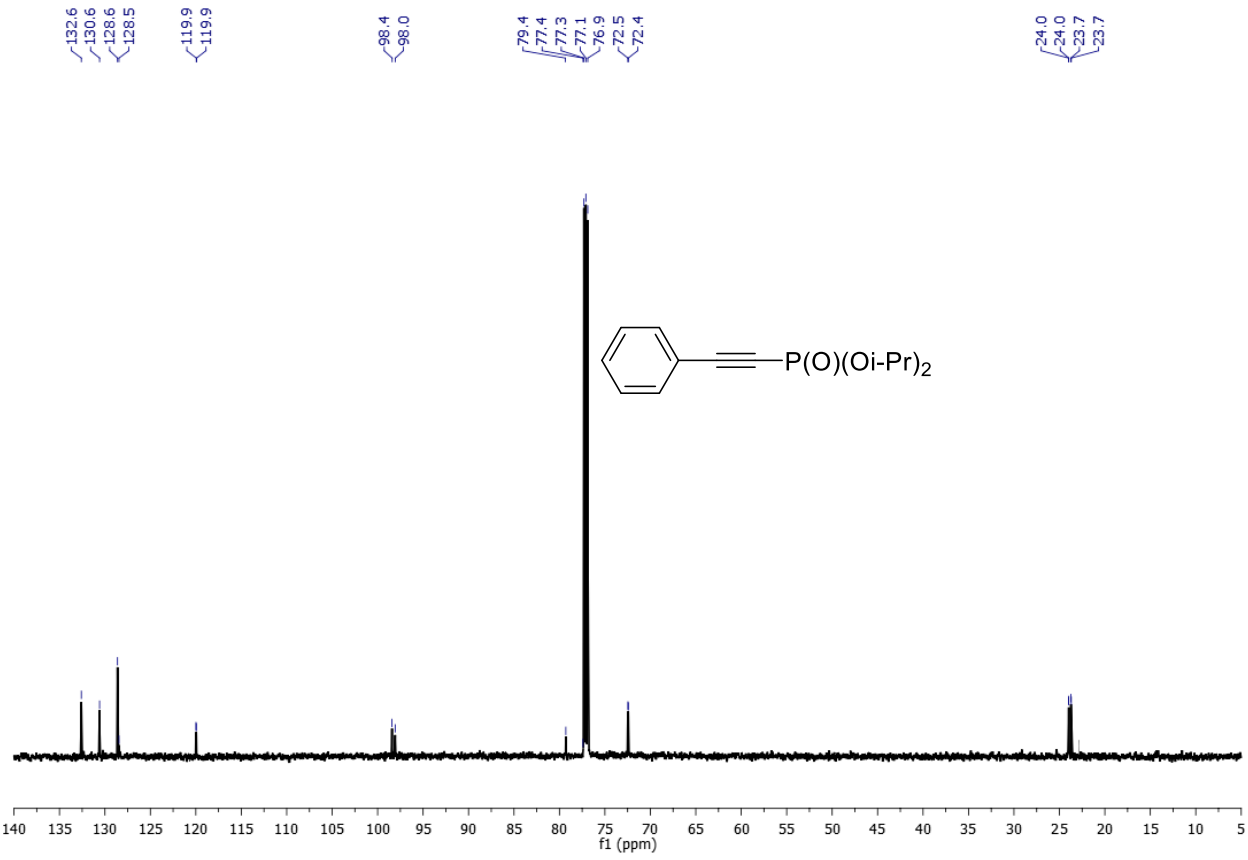


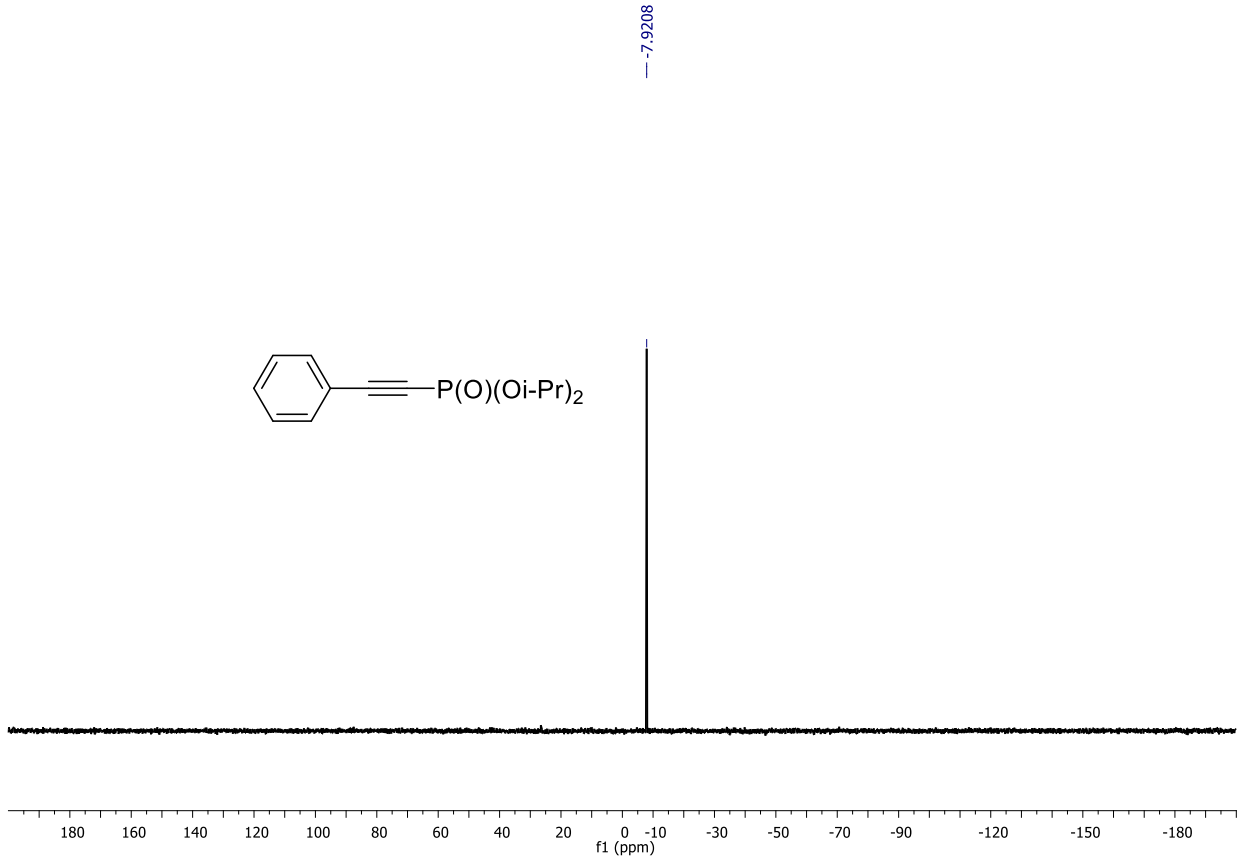

133.9
132.0
125.3
118.9
97.0
96.7
82.2
77.3
77.1
76.9
72.6
72.6
24.0
24.0
23.7
23.7
Br
P(O)(Oi-Pr)2
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)


8.2586
Br
P(O)(Oi-Pr)2
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

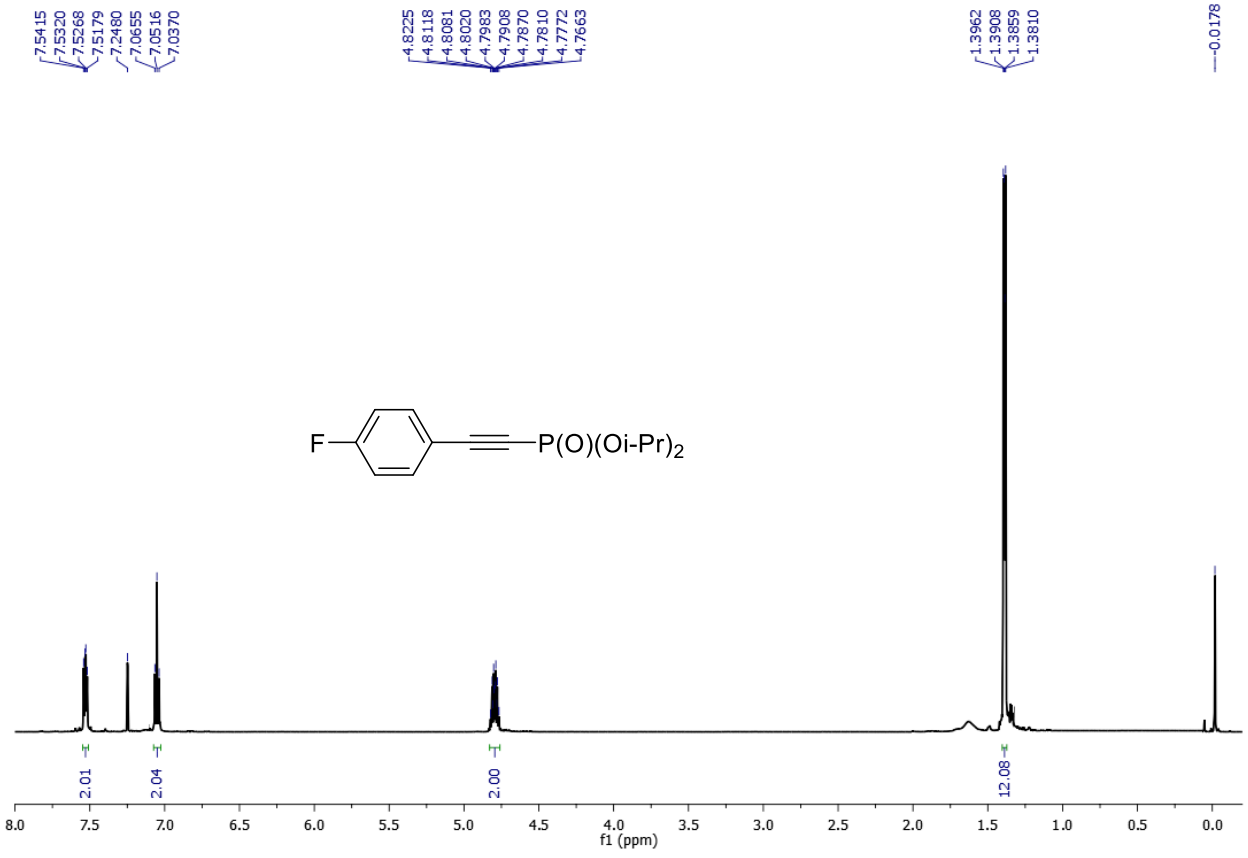
Diisopropyl (phenylethynyl)phosphonate (4b):

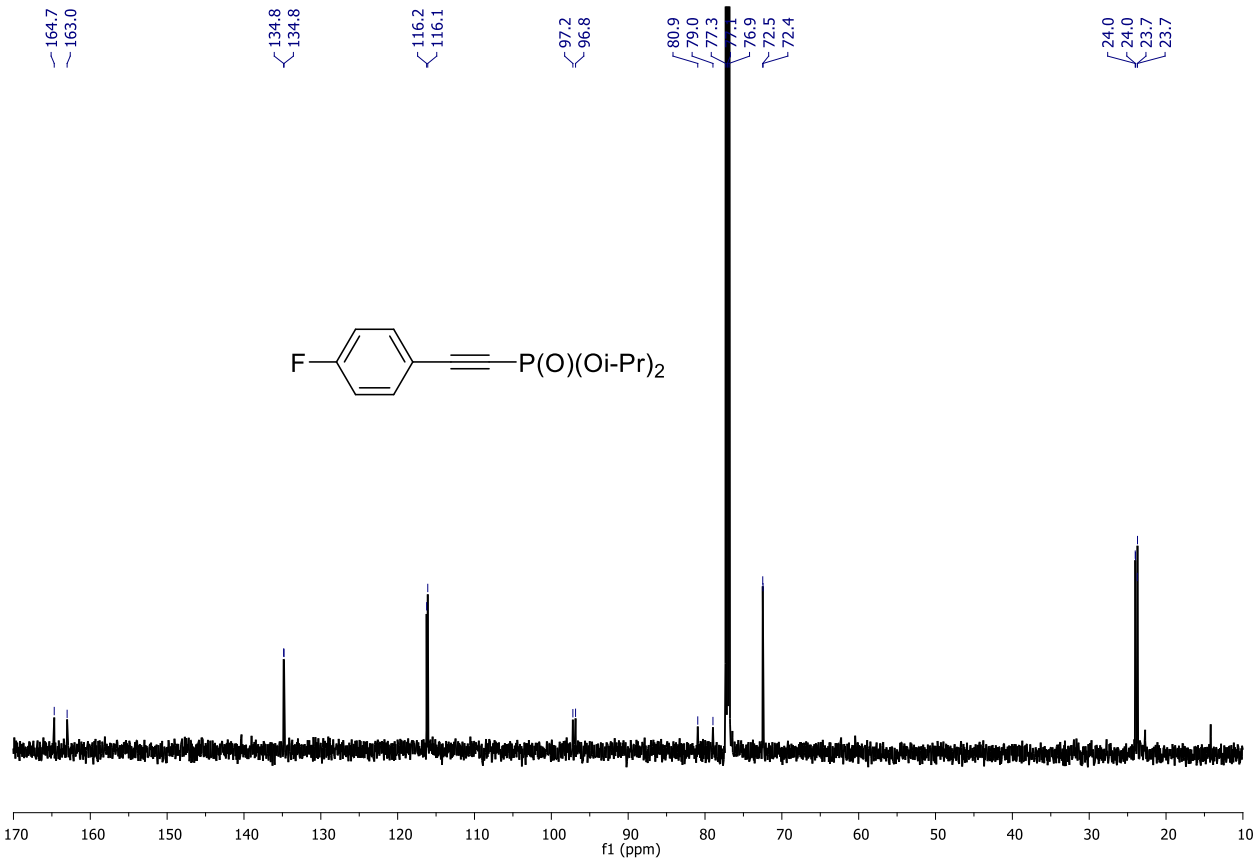


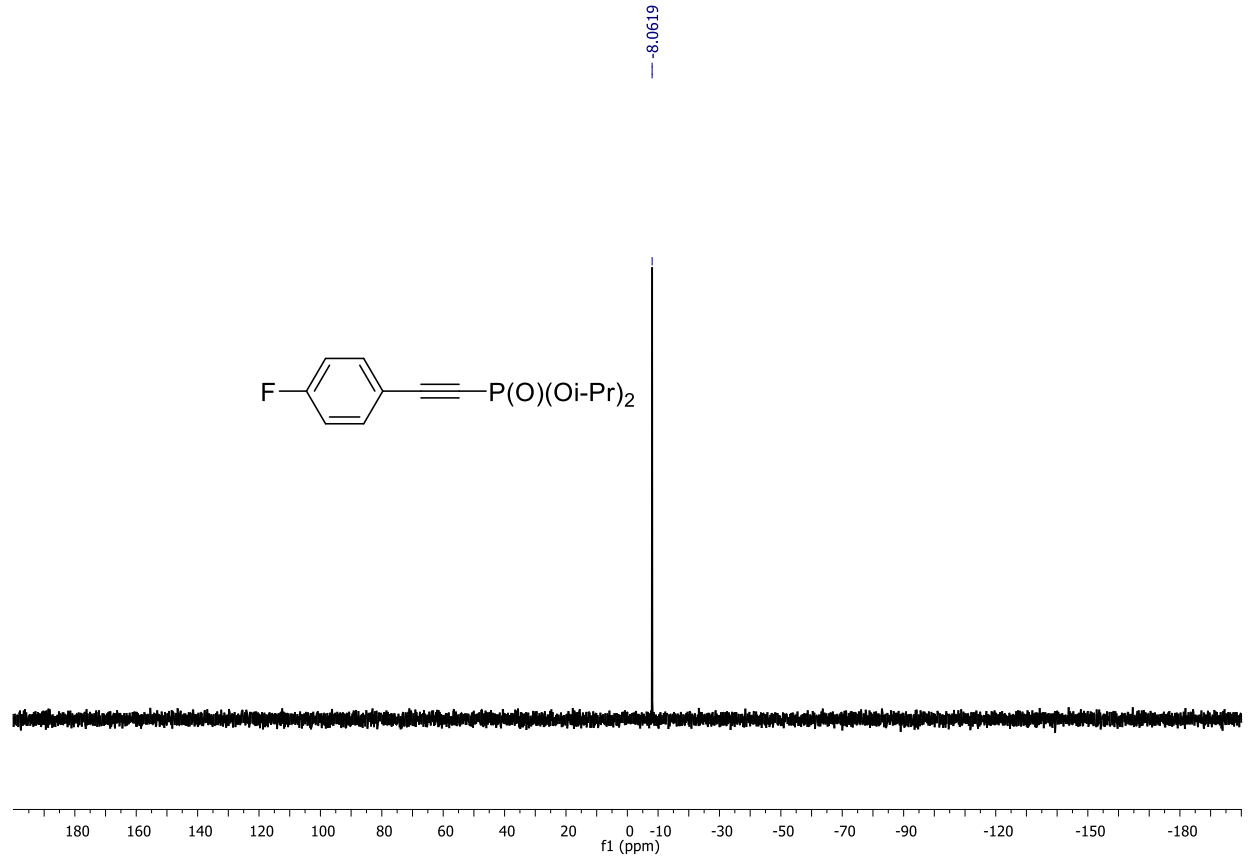




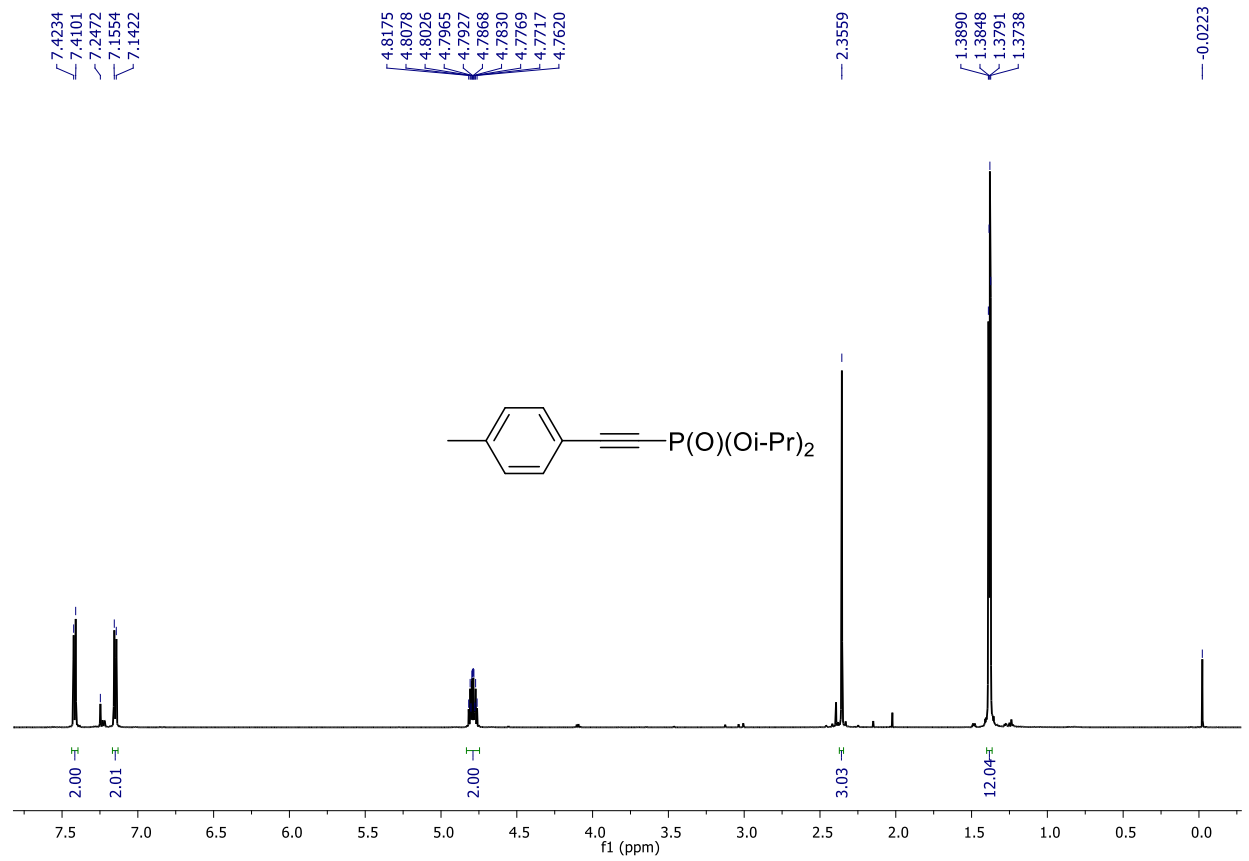
Diisopropyl [(4-fluorophenyl)ethynyl]phosphonate (4c):

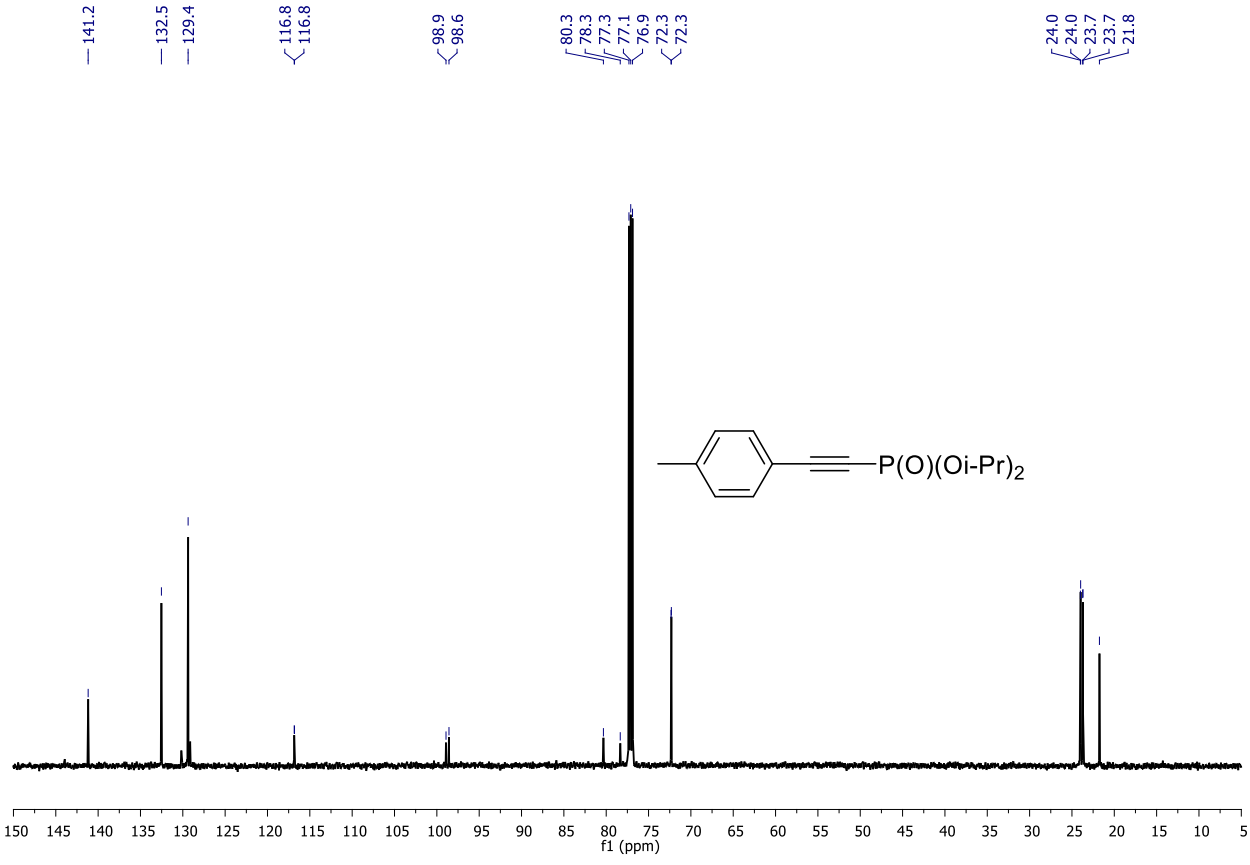


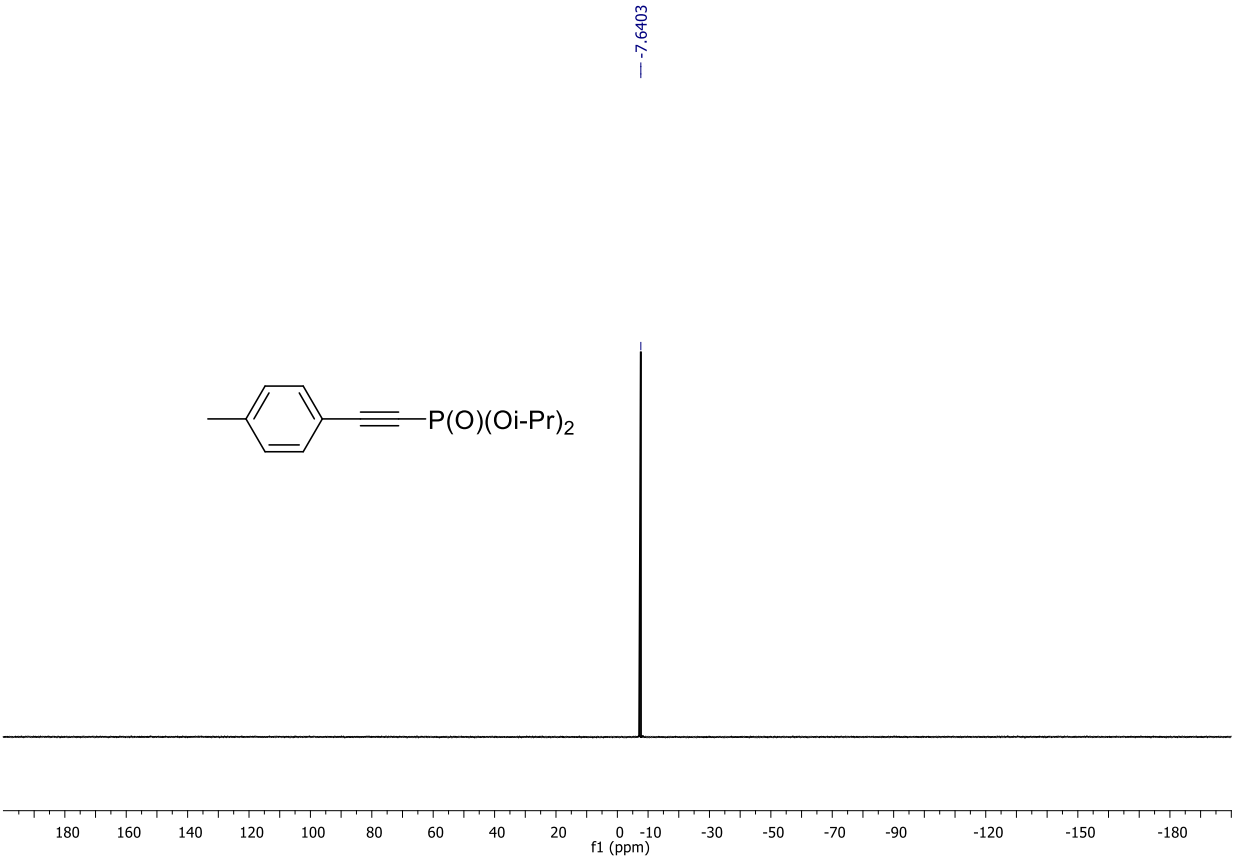




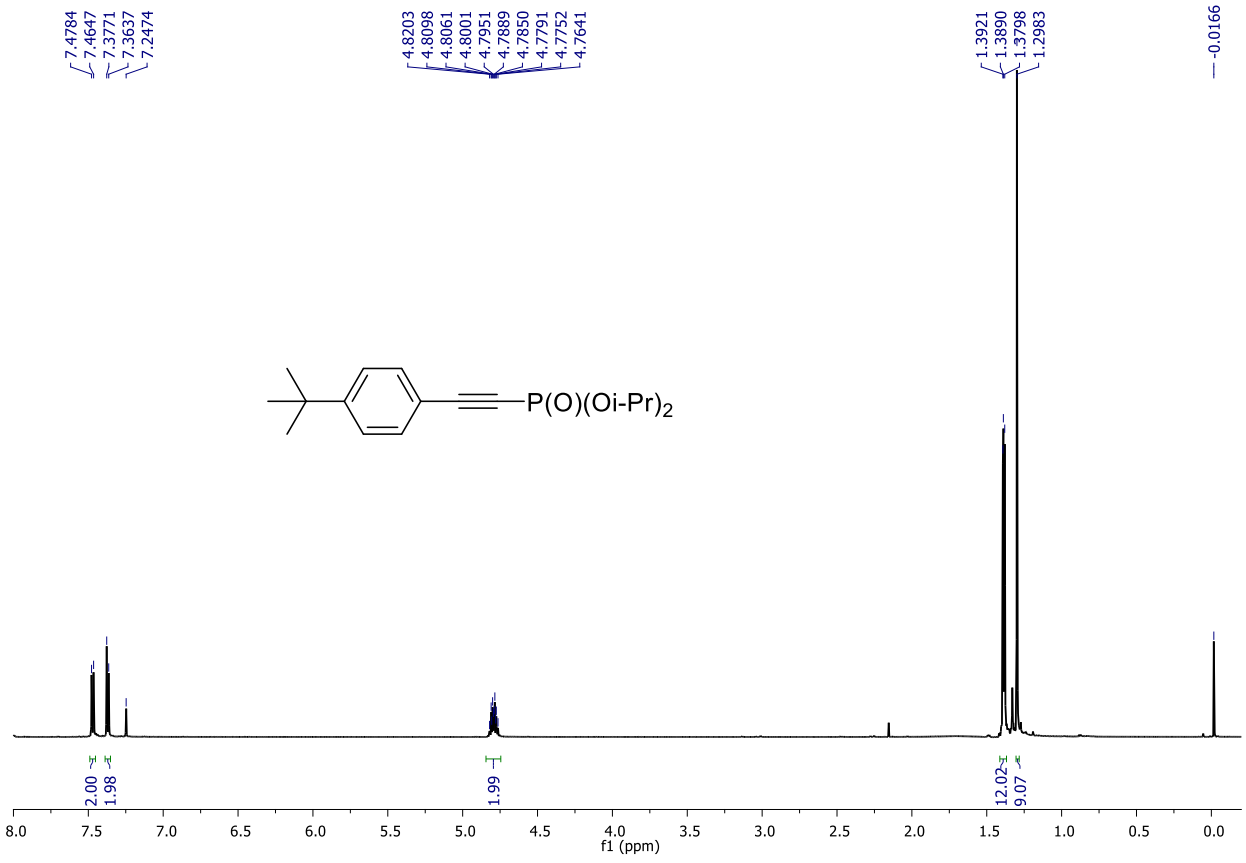
Diisopropyl (4-tolylethynyl)phosphonate (4d):

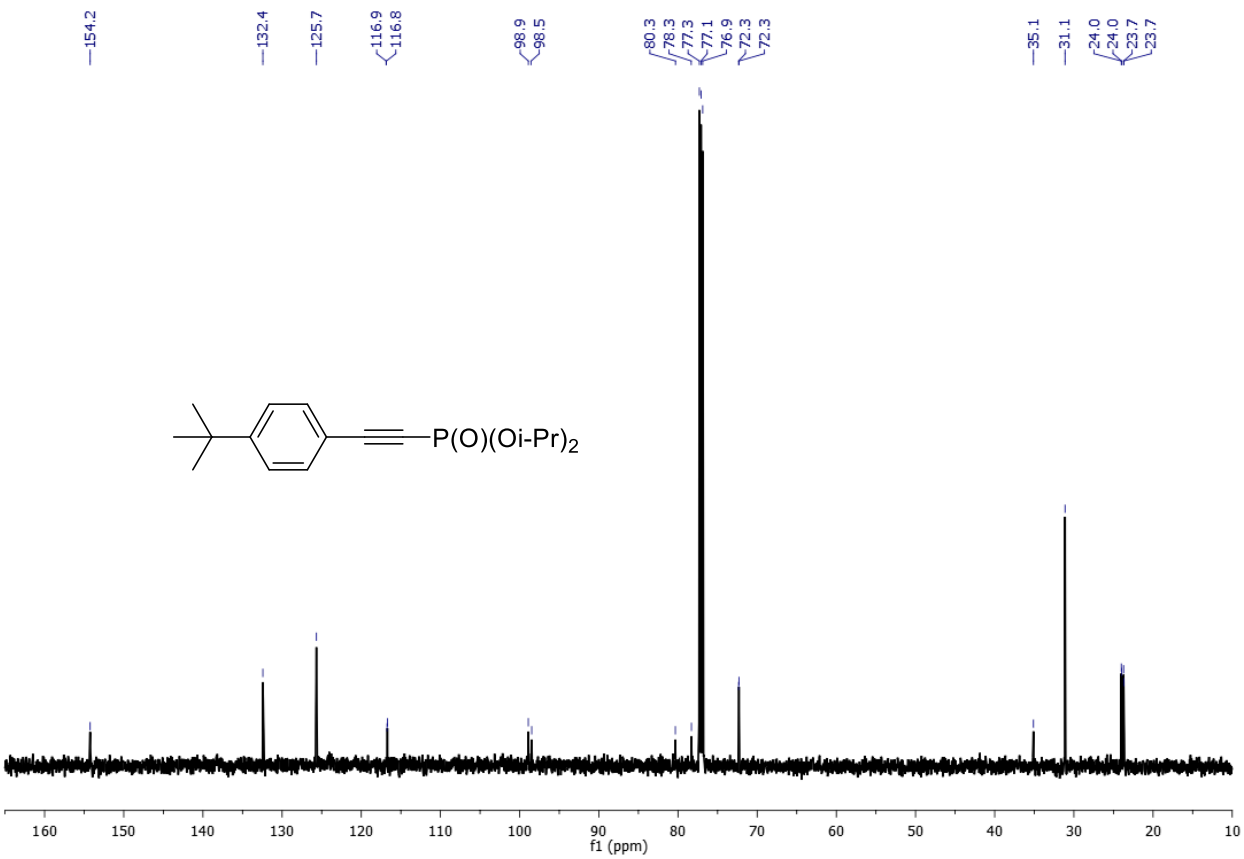

7.4234
7.4101
7.2472
7.1554
7.1422
4.8175
4.8078
4.8026
4.7965
4.7927
4.7868
4.7830
4.7769
4.7717
4.7620
2.3559
1.3890
1.3848
1.3791
1.3738
-0.0223
P(O)(Oi-Pr)2
2.00
2.01
2.00
3.03
12.04
f1 (ppm)

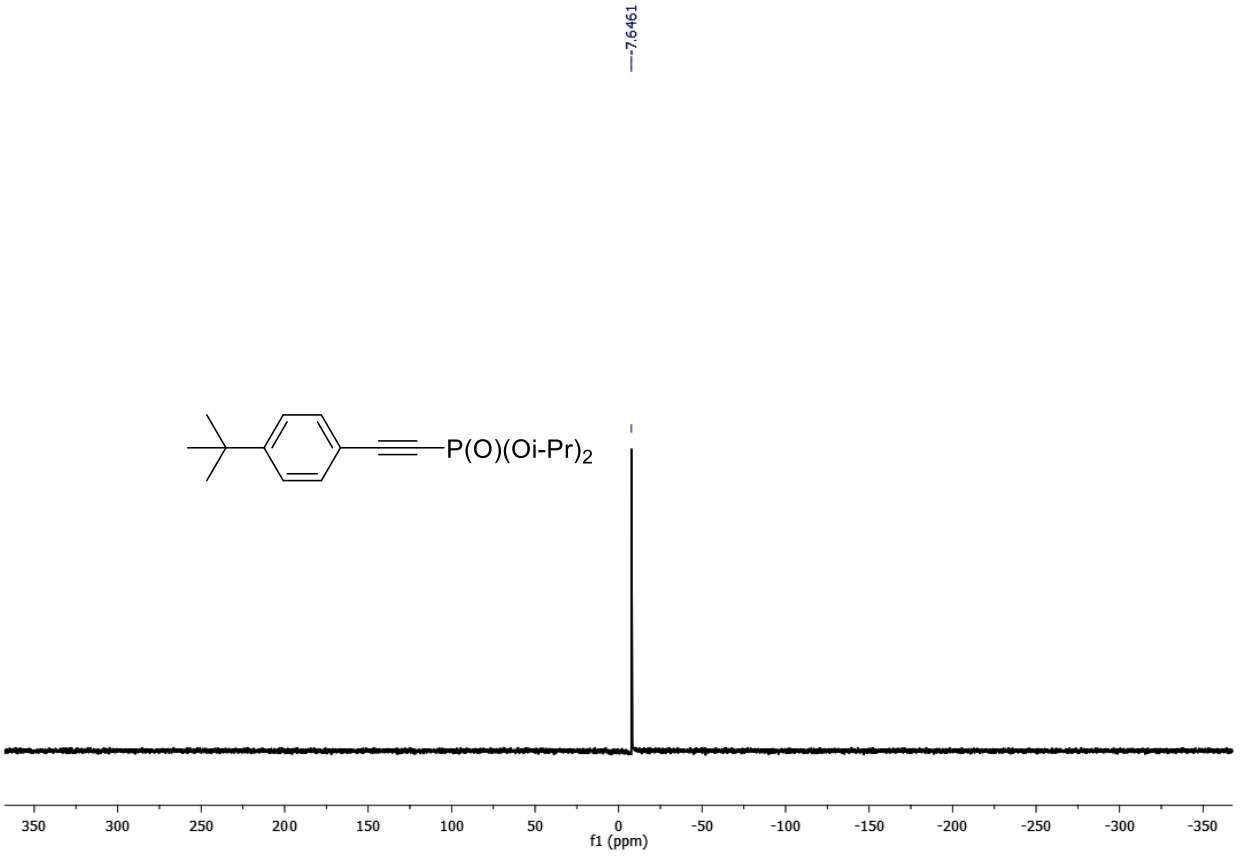

141.2
132.5
129.4
116.8
116.8
98.9
98.6
80.3
78.3
77.3
77.1
76.9
72.3
72.3
24.0
24.0
23.7
23.7
21.8
P(O)(Oi-Pr)2
f1 (ppm)



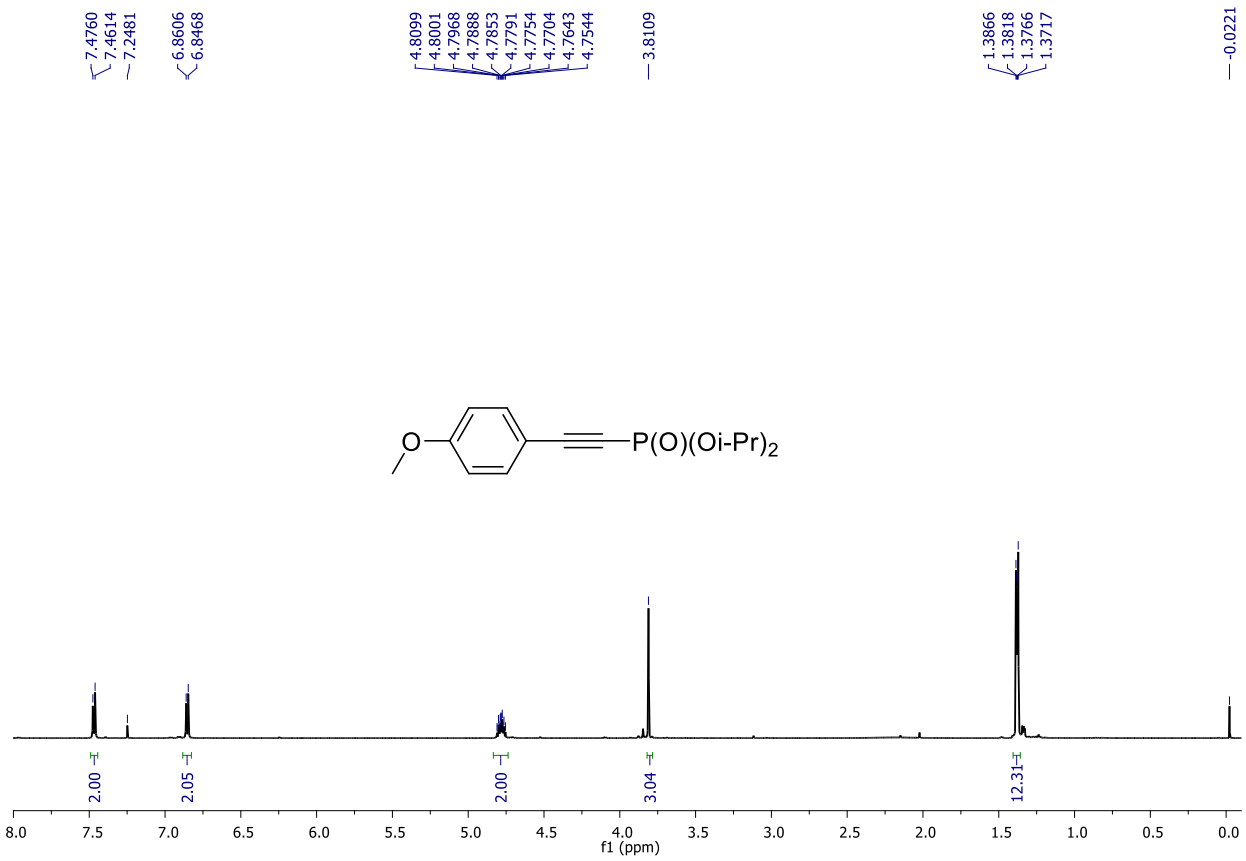
Diisopropyl [(4-*tert*-butylphenyl)ethynyl]phosphonate (4e):

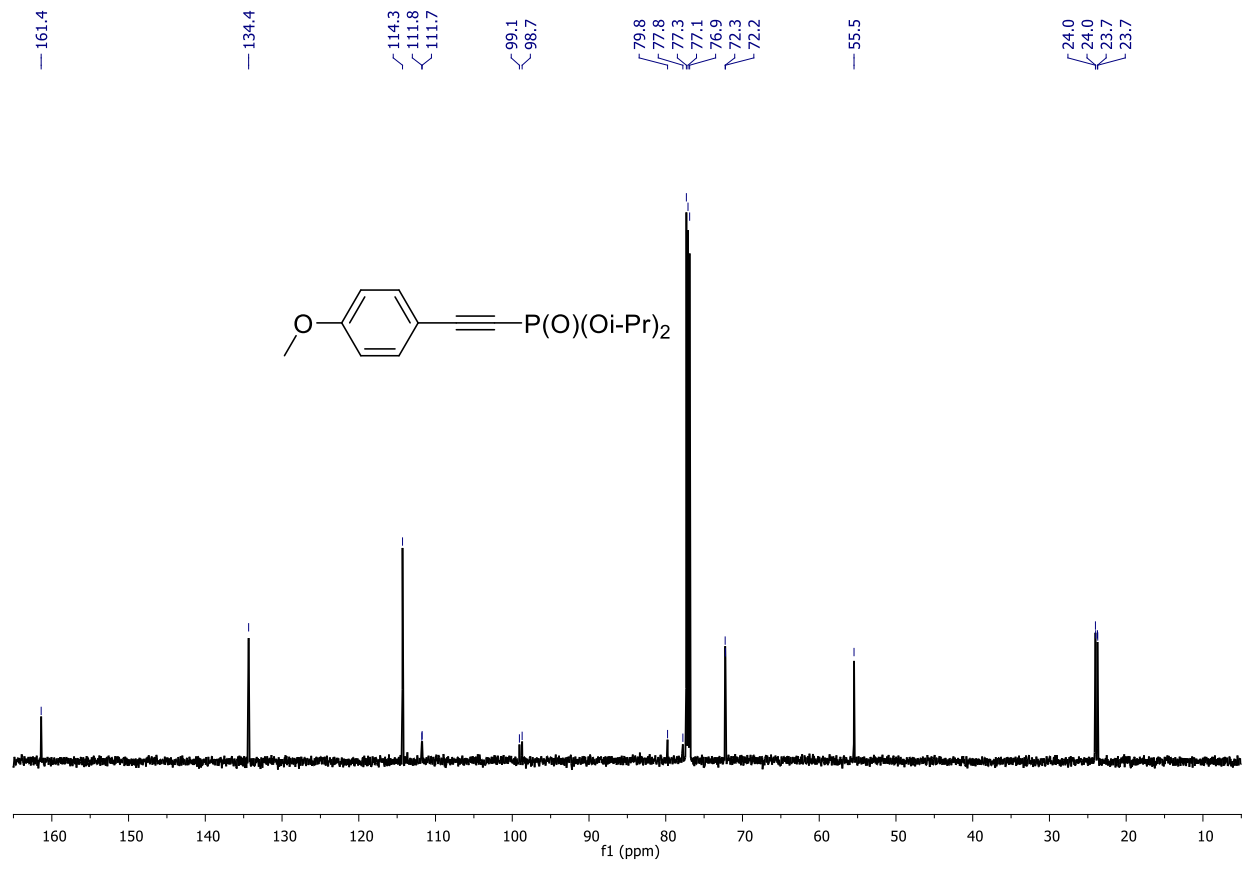


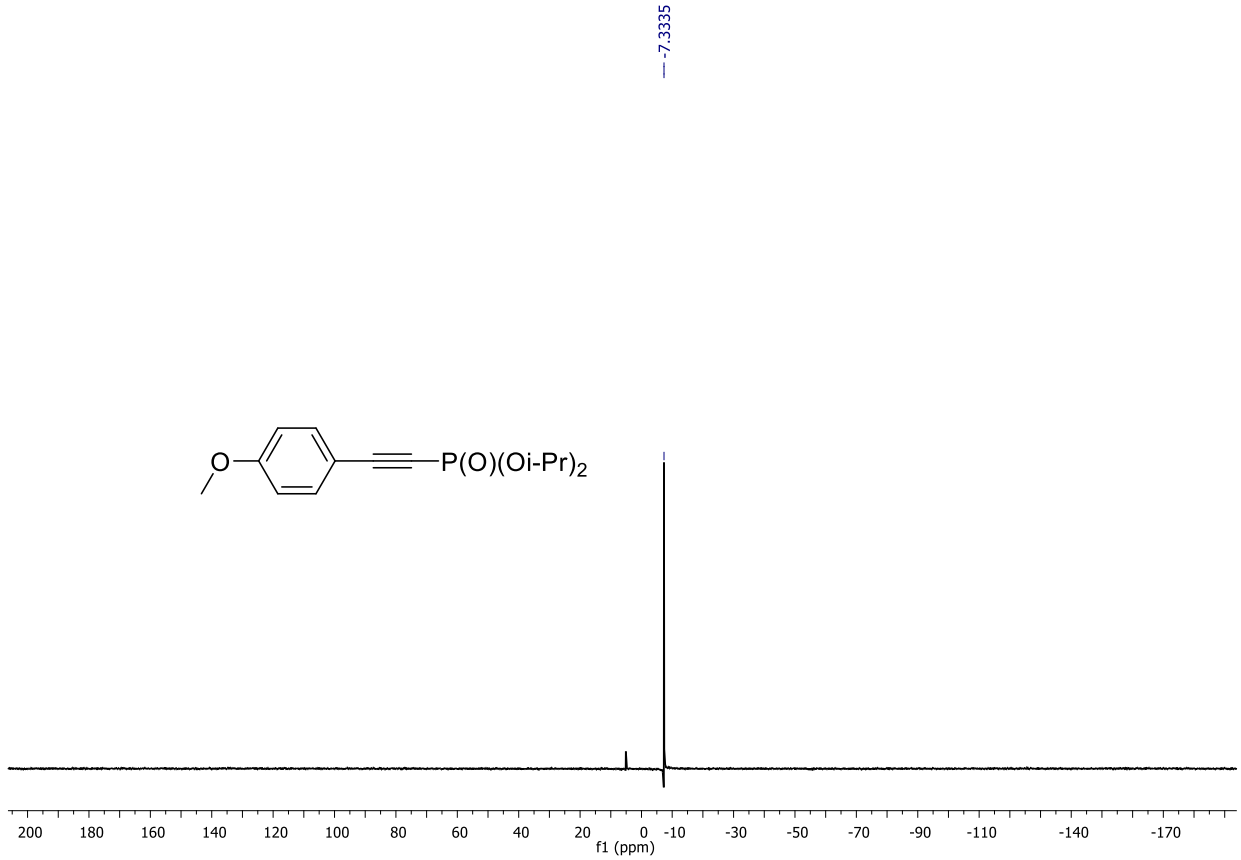




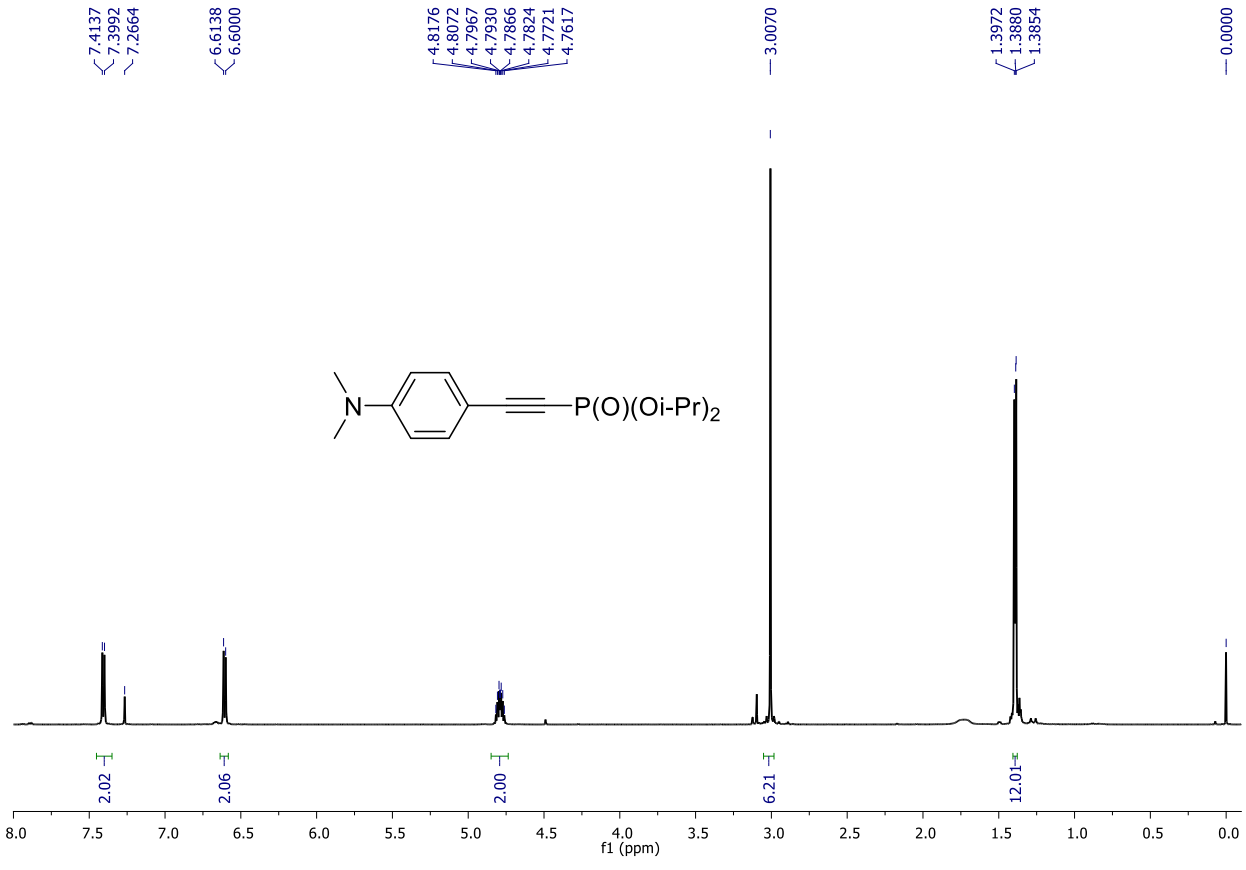
Diisopropyl [(4-methoxyphenyl)ethynyl]phosphonate (4f):

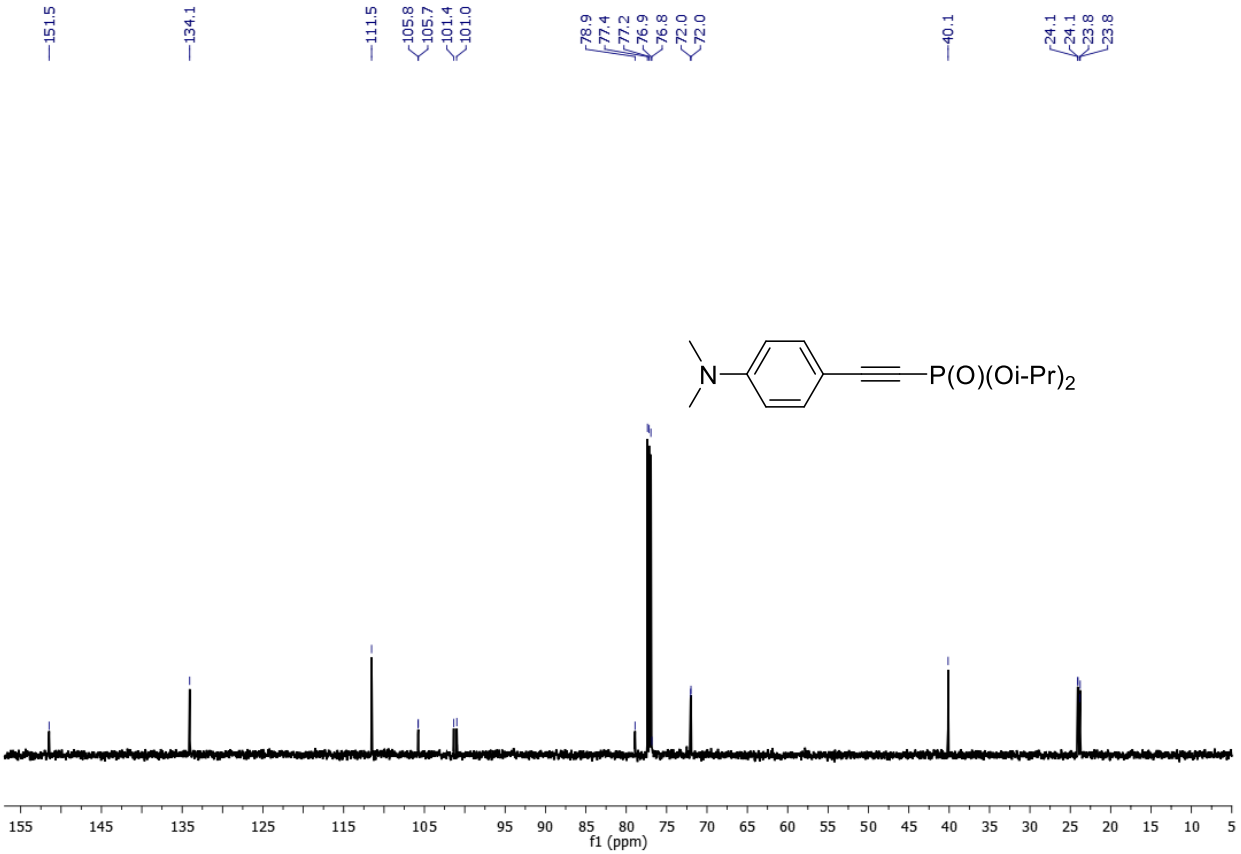

7.4760
7.4614
7.2481
6.8606
6.8468
4.8099
4.8001
4.7968
4.7888
4.7853
4.7791
4.7754
4.7704
4.7643
4.7544
3.8109
1.3866
1.3818
1.3766
1.3717
-0.0221
O
P(O)(Oi-Pr)2
2.00
2.05
2.00
3.04
12.31
f1 (ppm)

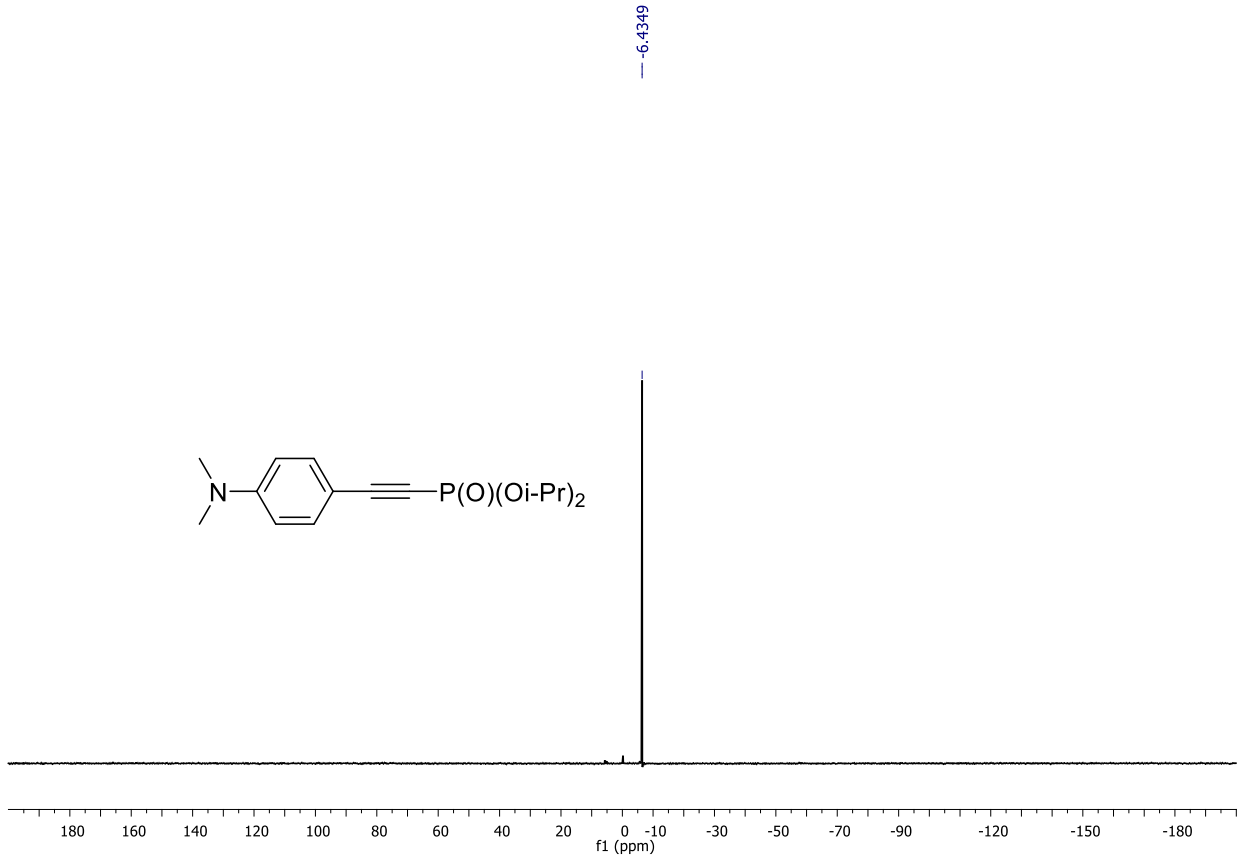

161.4
134.4
114.3
111.8
111.7
99.1
98.7
79.8
77.8
77.3
77.1
76.9
72.3
72.2
55.5
24.0
24.0
23.7
23.7
O
P(O)(Oi-Pr)2
f1 (ppm)



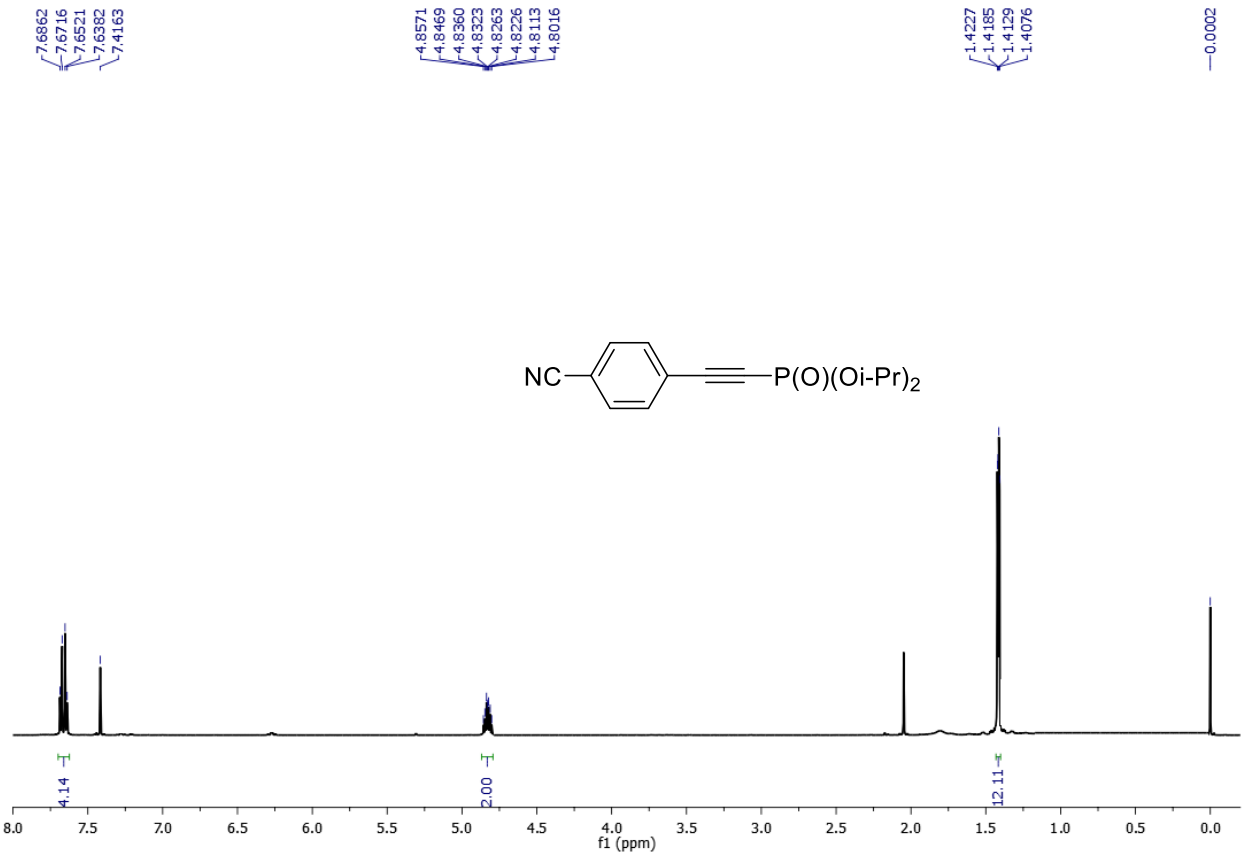
Diisopropyl [(4-N, N dimethylaminophenyl)ethynyl]phosphonate (4g):

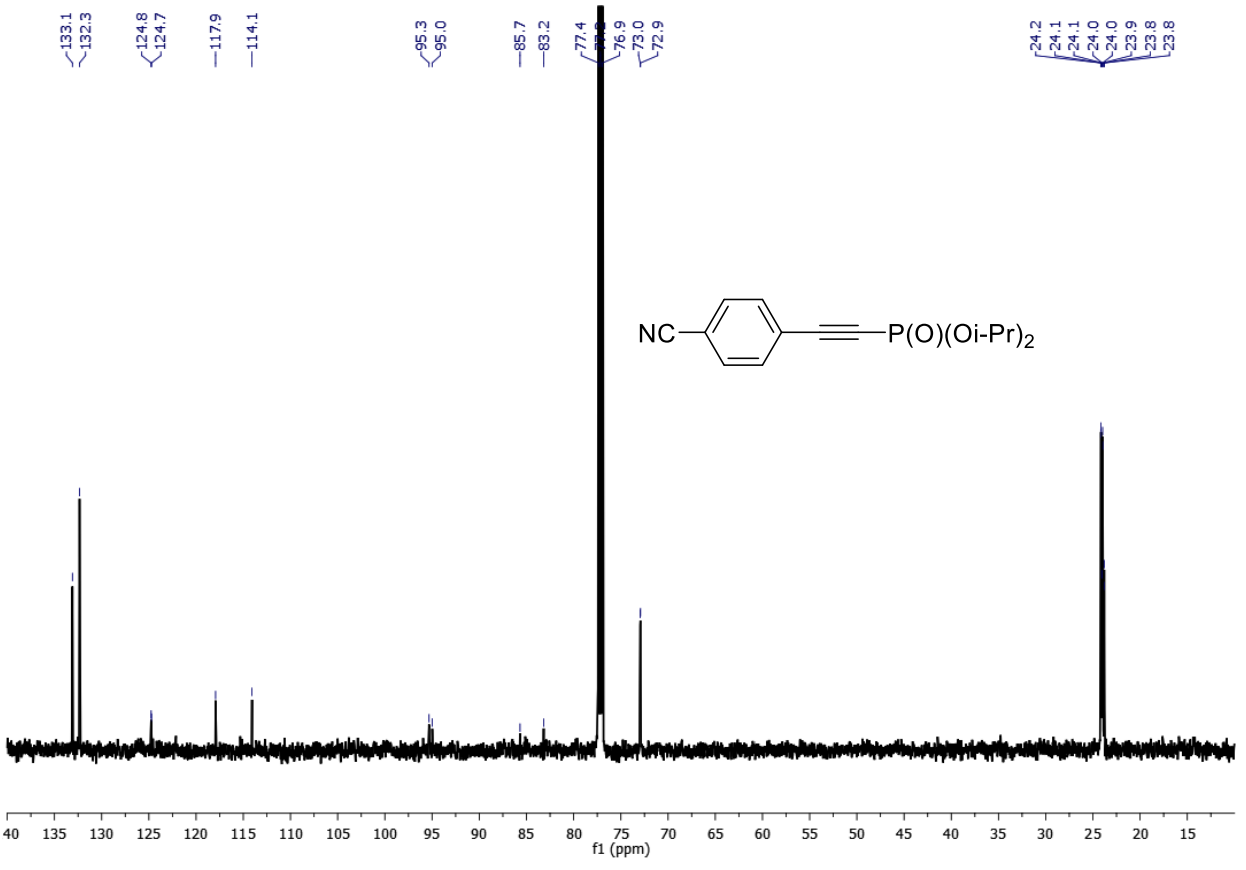


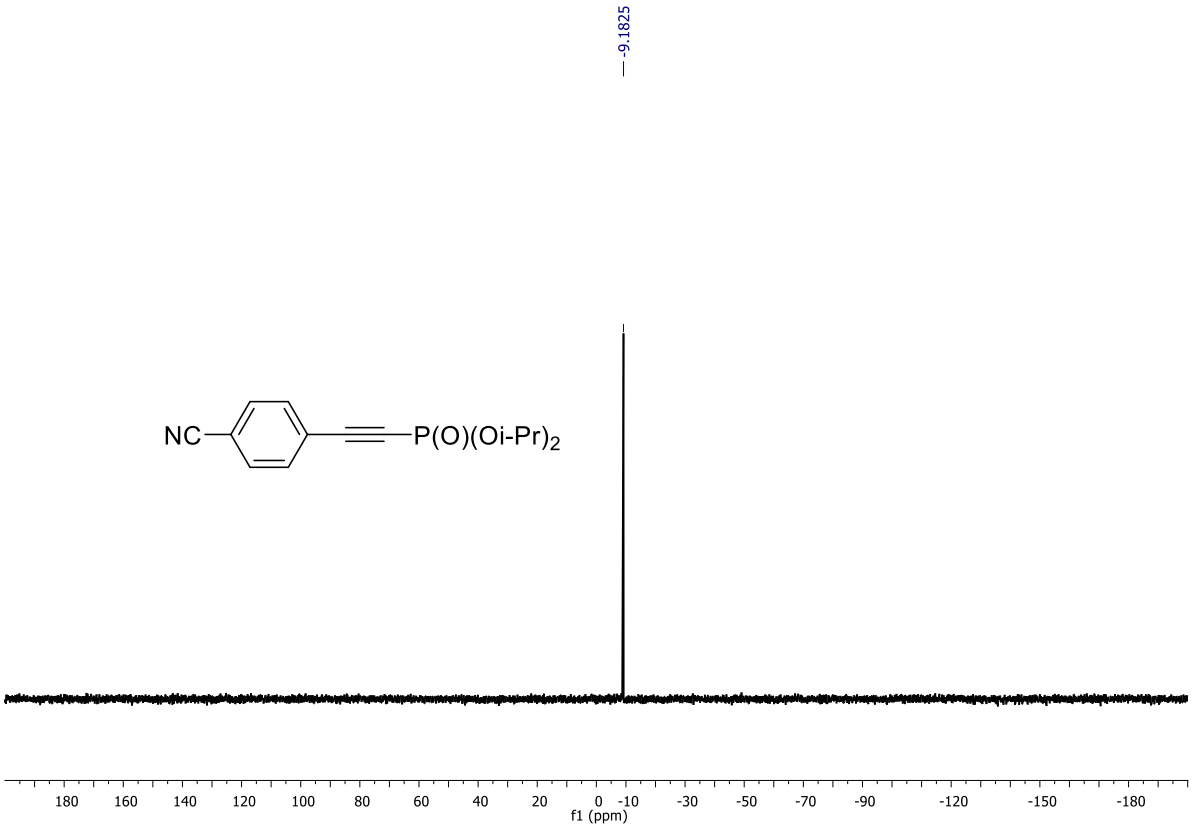




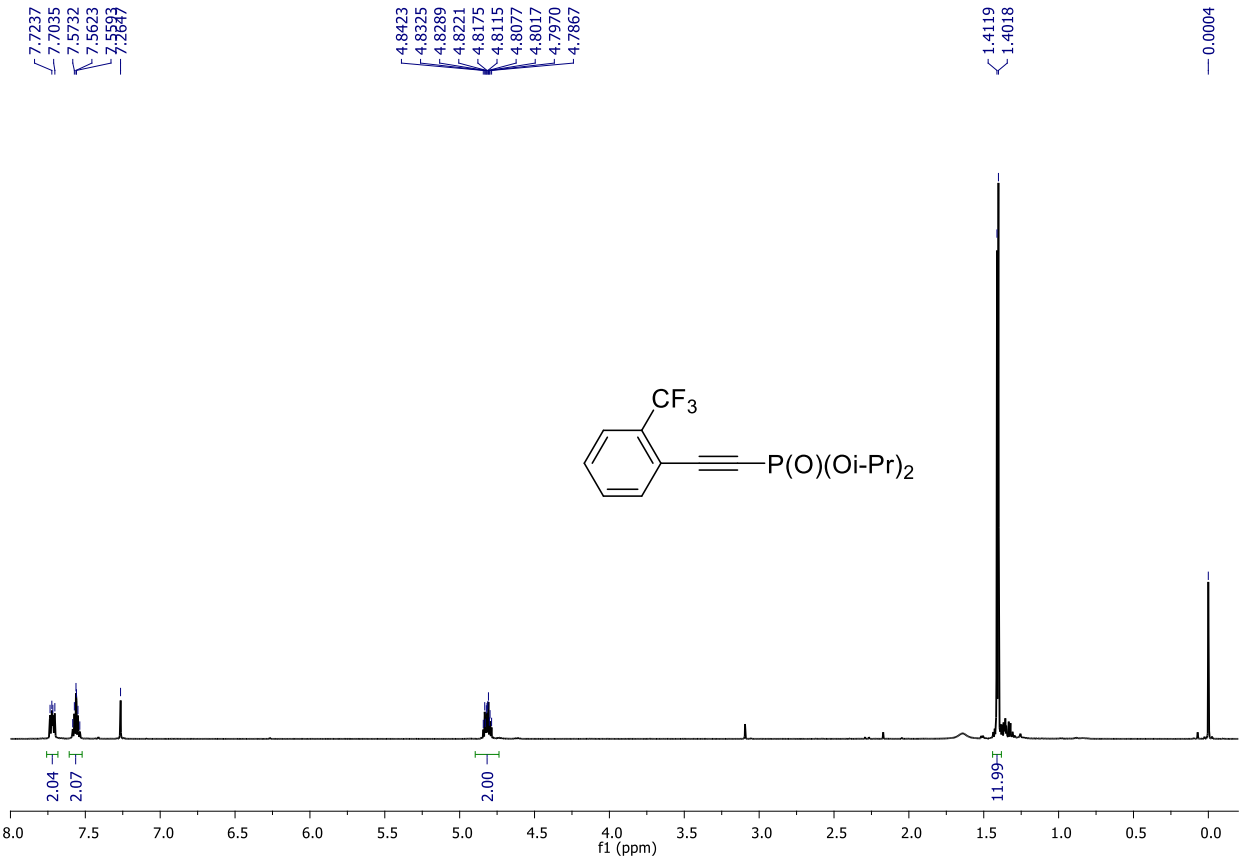
Diisopropyl [(4-cyanophenyl)ethynyl]phosphonate (4h):

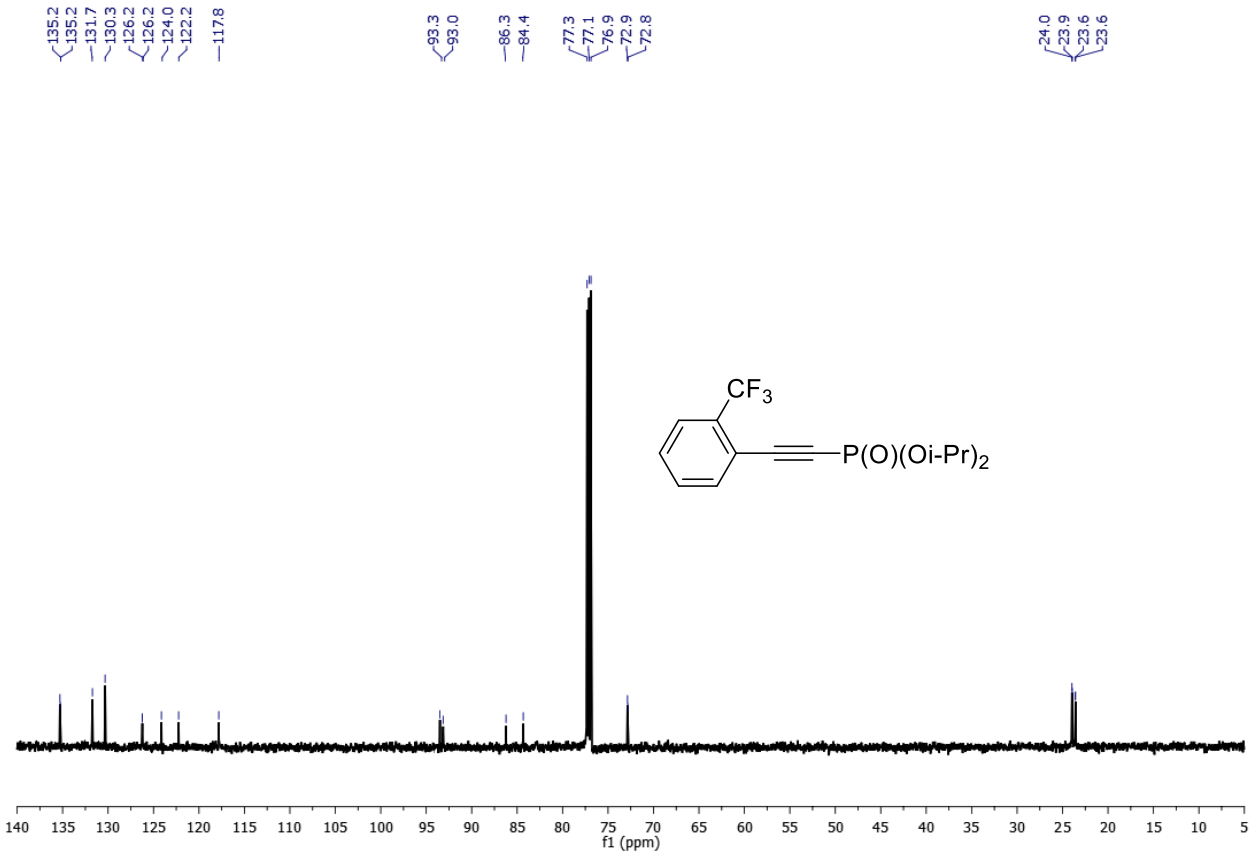

7.6862
7.6716
7.6521
7.6382
7.4163
4.8571
4.8469
4.8360
4.8323
4.8263
4.8226
4.8113
4.8016
1.4227
1.4185
1.4129
1.4076
0.0002
NC
P(O)(Oi-Pr)2
4.14
2.00
12.11
f1 (ppm)

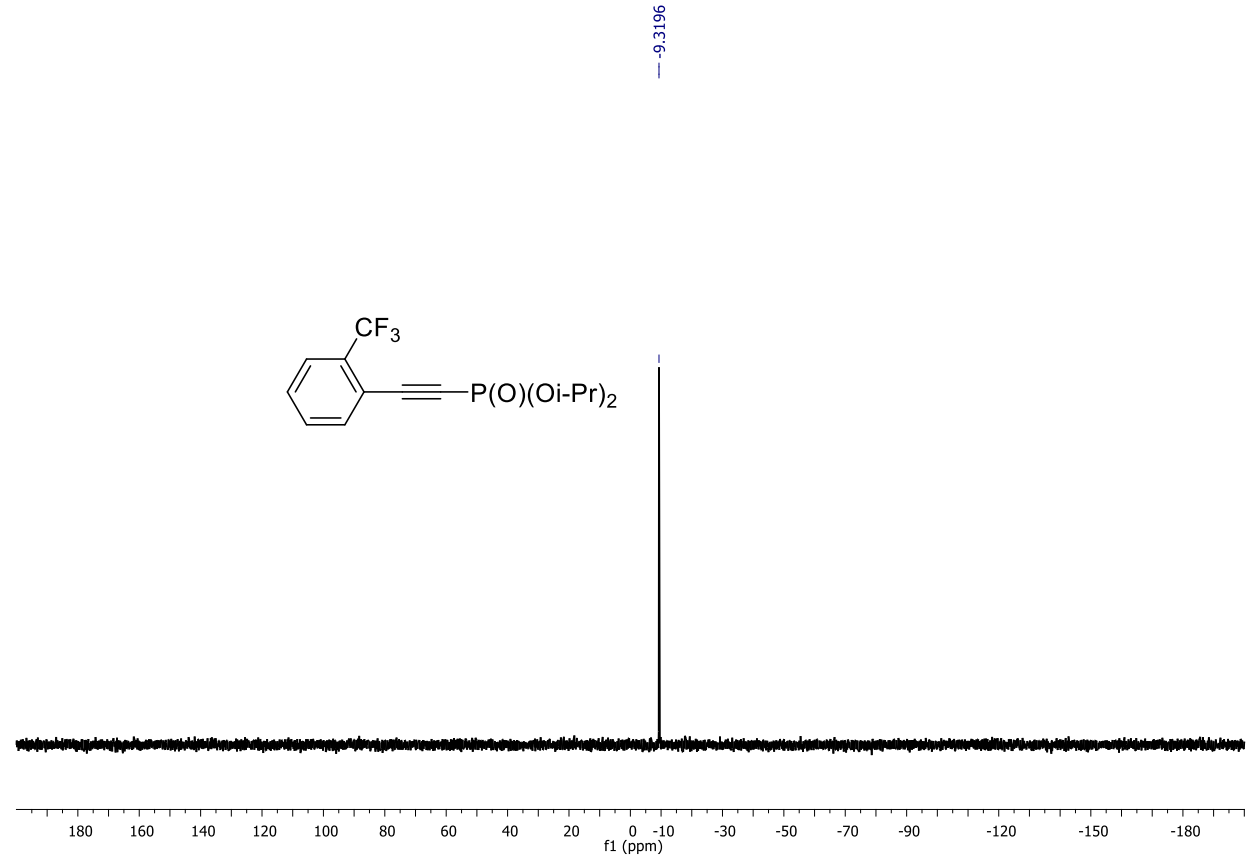

133.1
132.3
124.8
124.7
117.9
114.1
95.3
95.0
85.7
83.2
77.4
76.9
73.0
72.9
24.2
24.1
24.1
24.0
24.0
23.9
23.8
23.8
NC
P(O)(Oi-Pr)2
f1 (ppm)



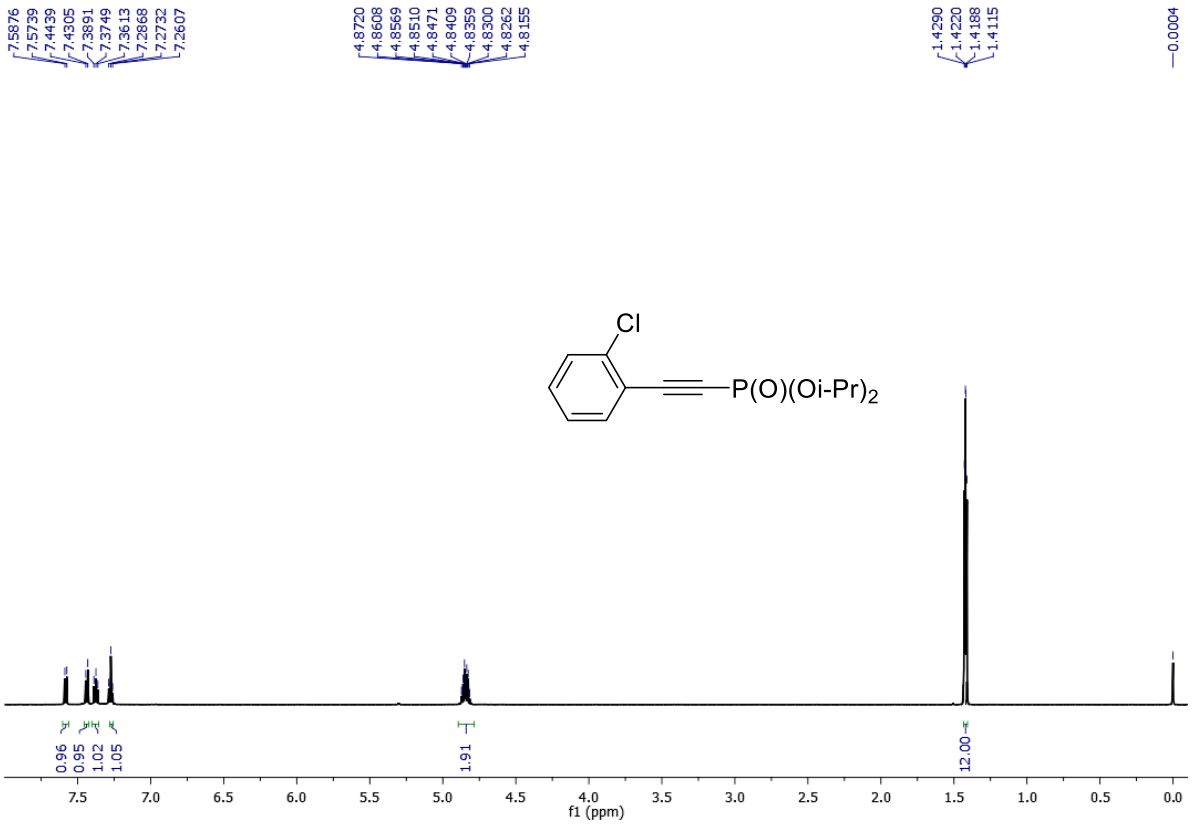
Diisopropyl [(2-trifluoromethylbenzene)ethynyl]phosphonate (4i):

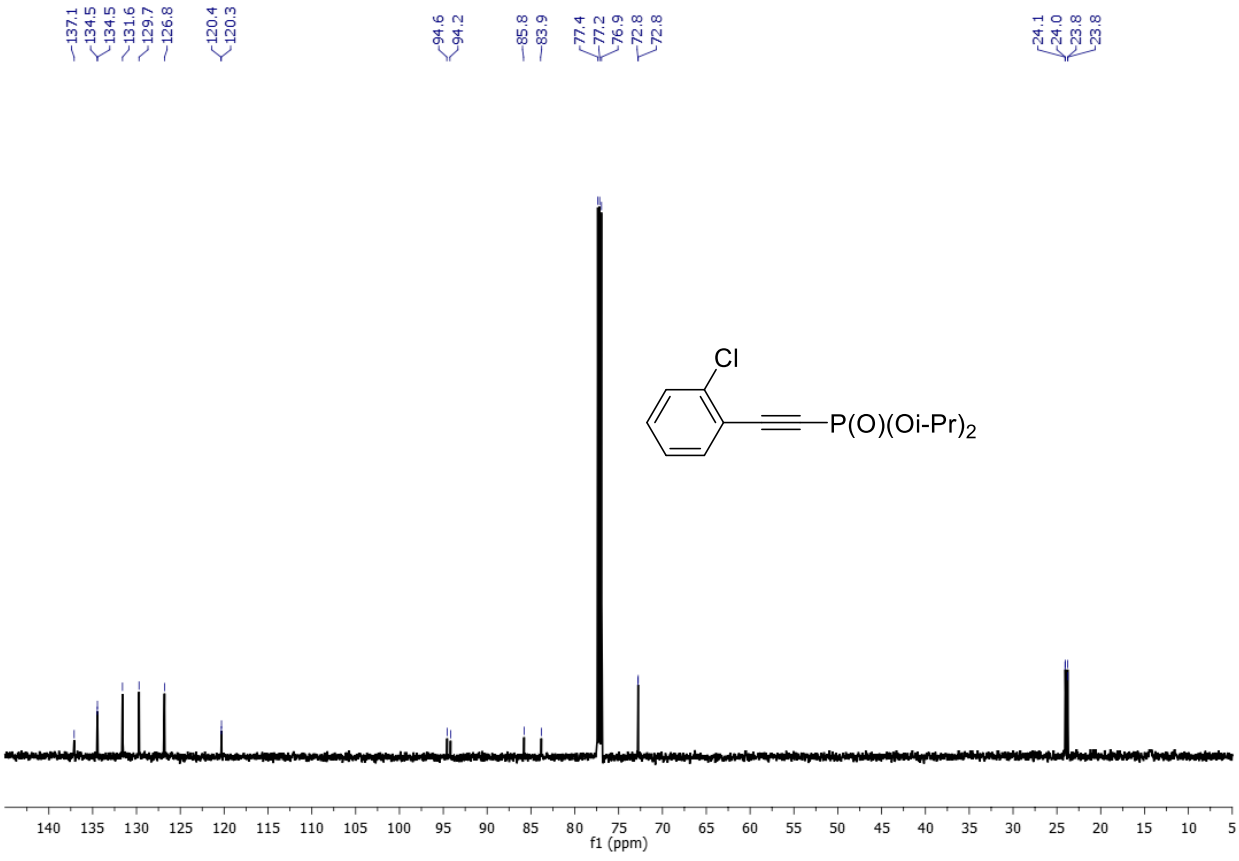


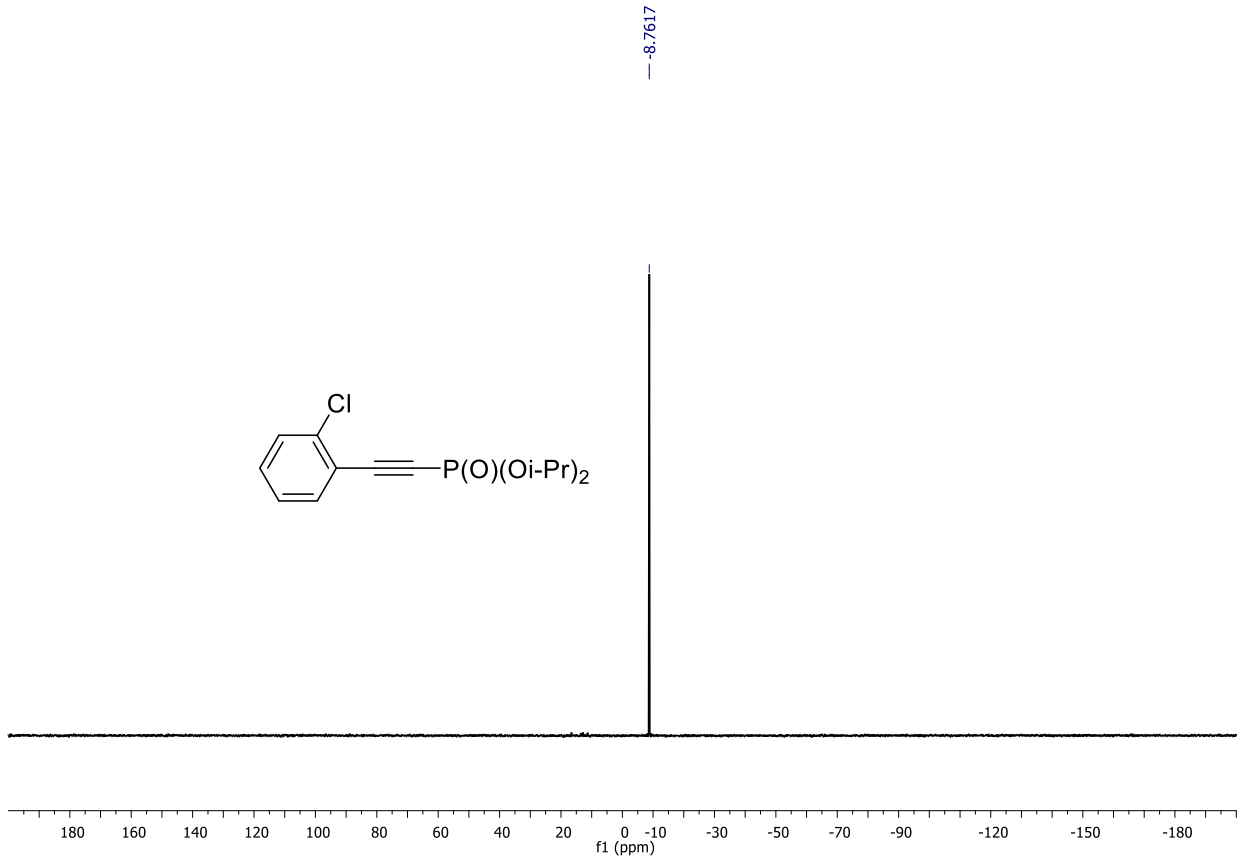




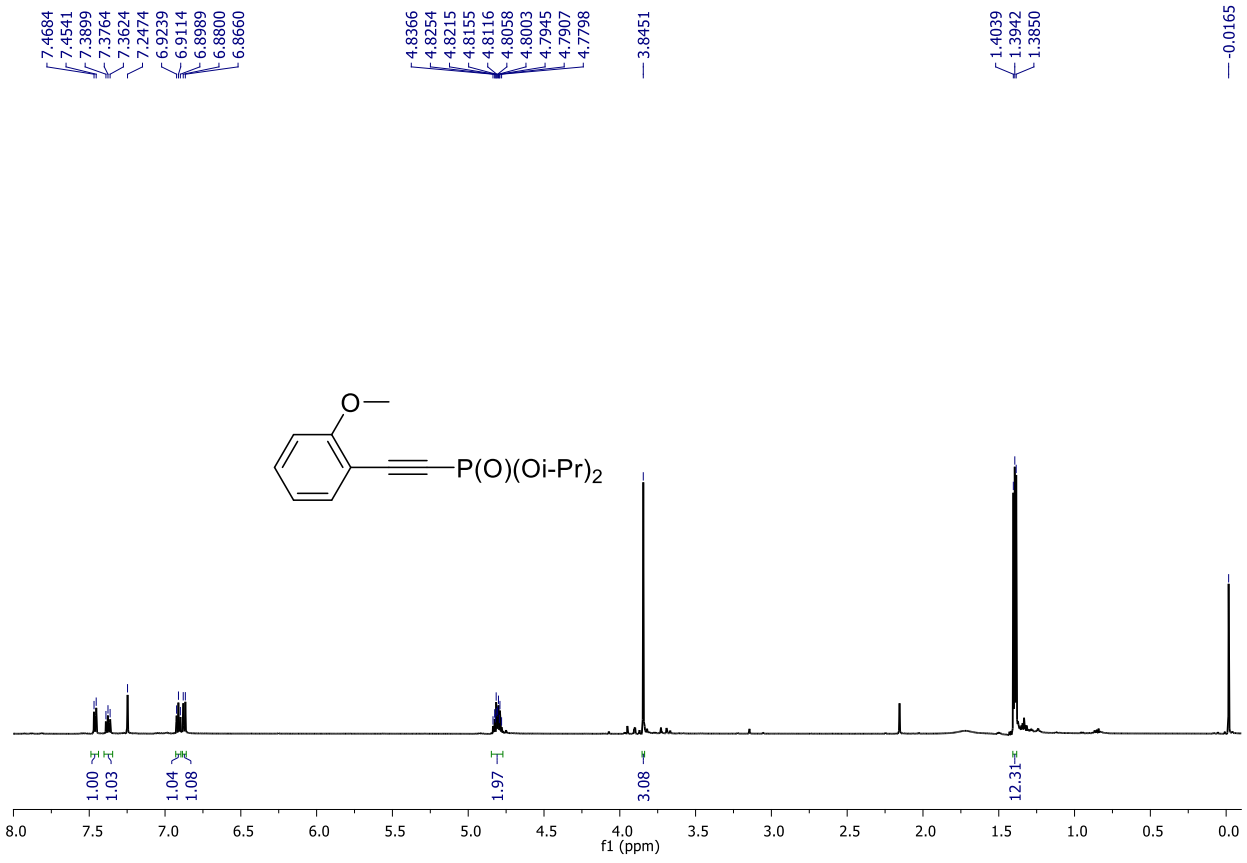
Diisopropyl [(2-chlorophenyl)ethynyl]phosphonate (4j):

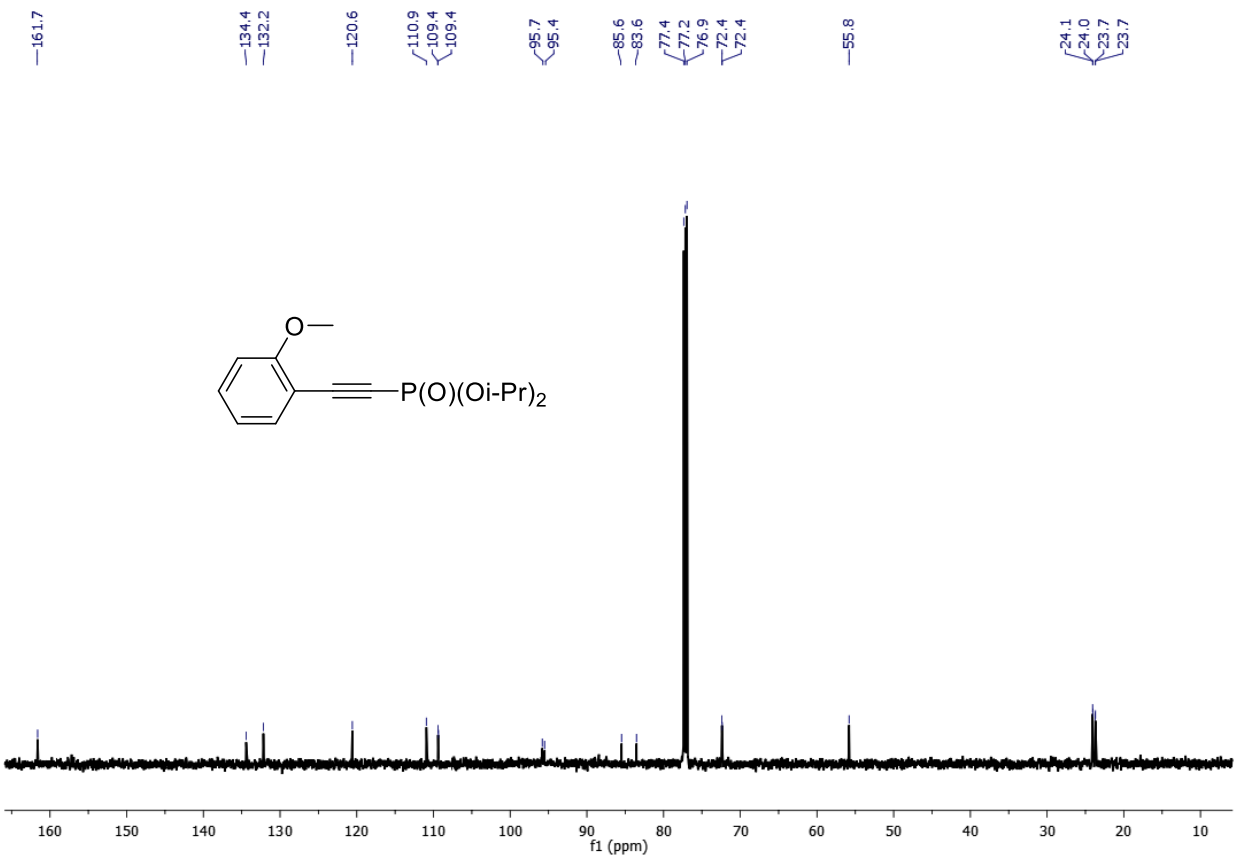

7.5876
7.5739
7.4439
7.4305
7.3891
7.3749
7.3613
7.2868
7.2732
7.2607
4.8720
4.8608
4.8569
4.8510
4.8471
4.8409
4.8359
4.8300
4.8262
4.8155
1.4290
1.4220
1.4188
1.4115
0.0004
Cl
P(O)(Oi-Pr)2
0.96
0.95
1.02
1.05
1.91
12.00
f1 (ppm)

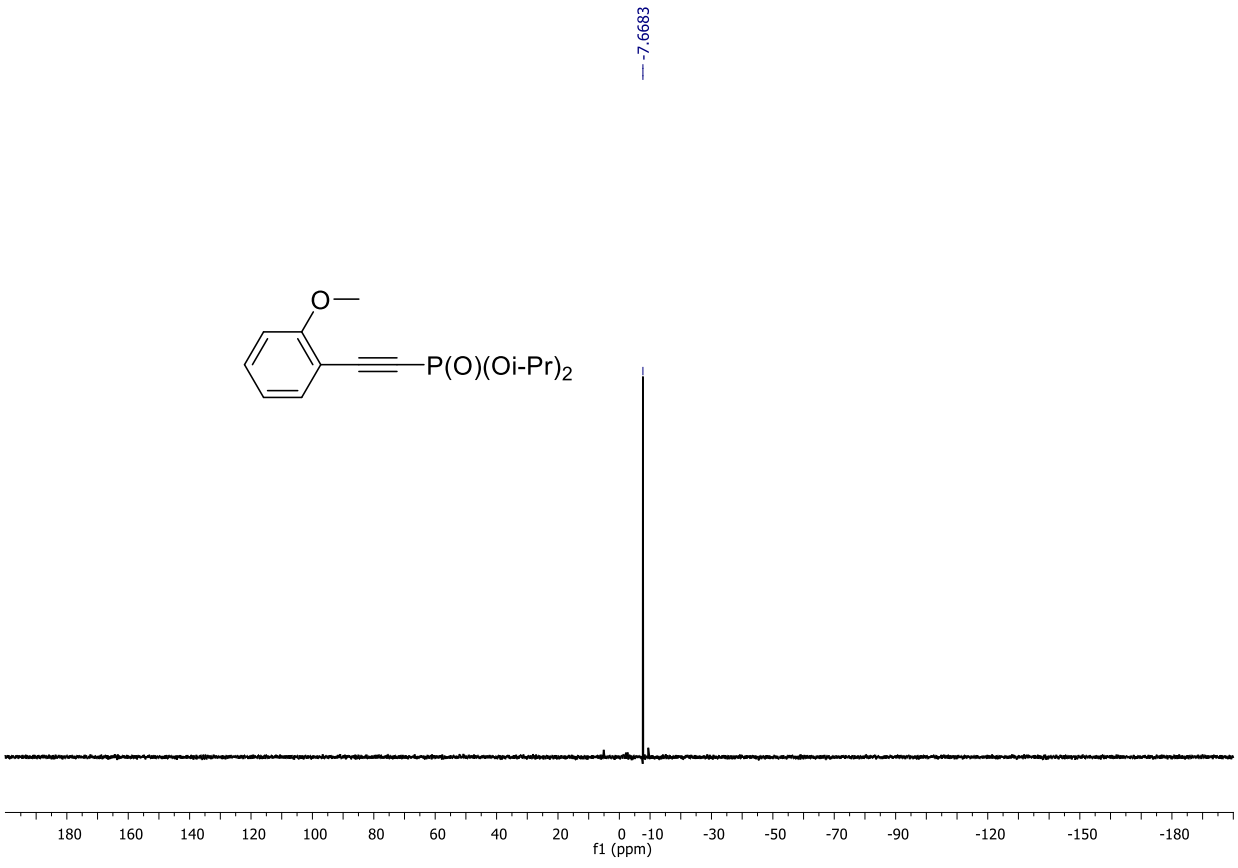

137.1
134.5
134.5
131.6
129.7
126.8
120.4
120.3
94.6
94.2
85.8
83.9
77.4
77.2
76.9
72.8
72.8
24.1
24.0
23.8
23.8
Cl
P(O)(Oi-Pr)2
f1 (ppm)



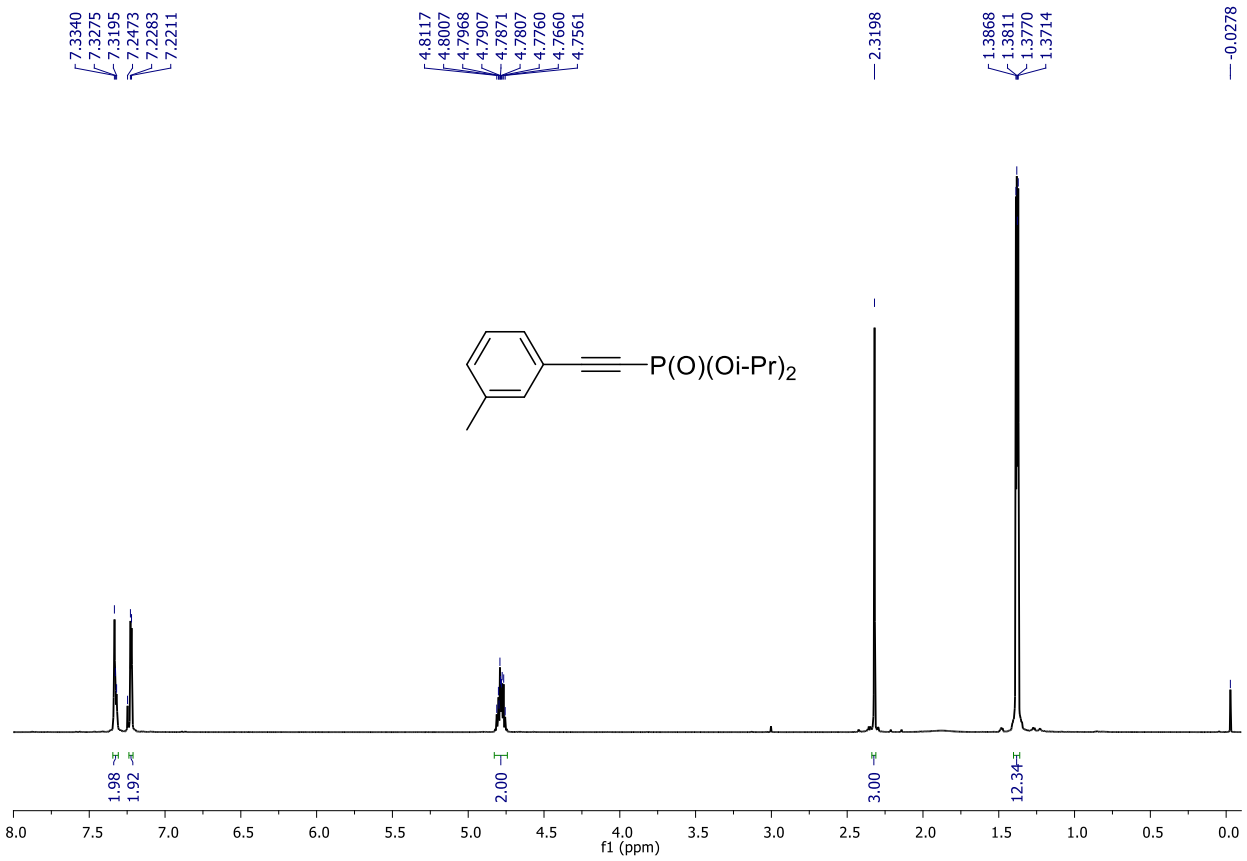
Diisopropyl [(2-methoxyphenyl)ethynyl]phosphonate (4k):

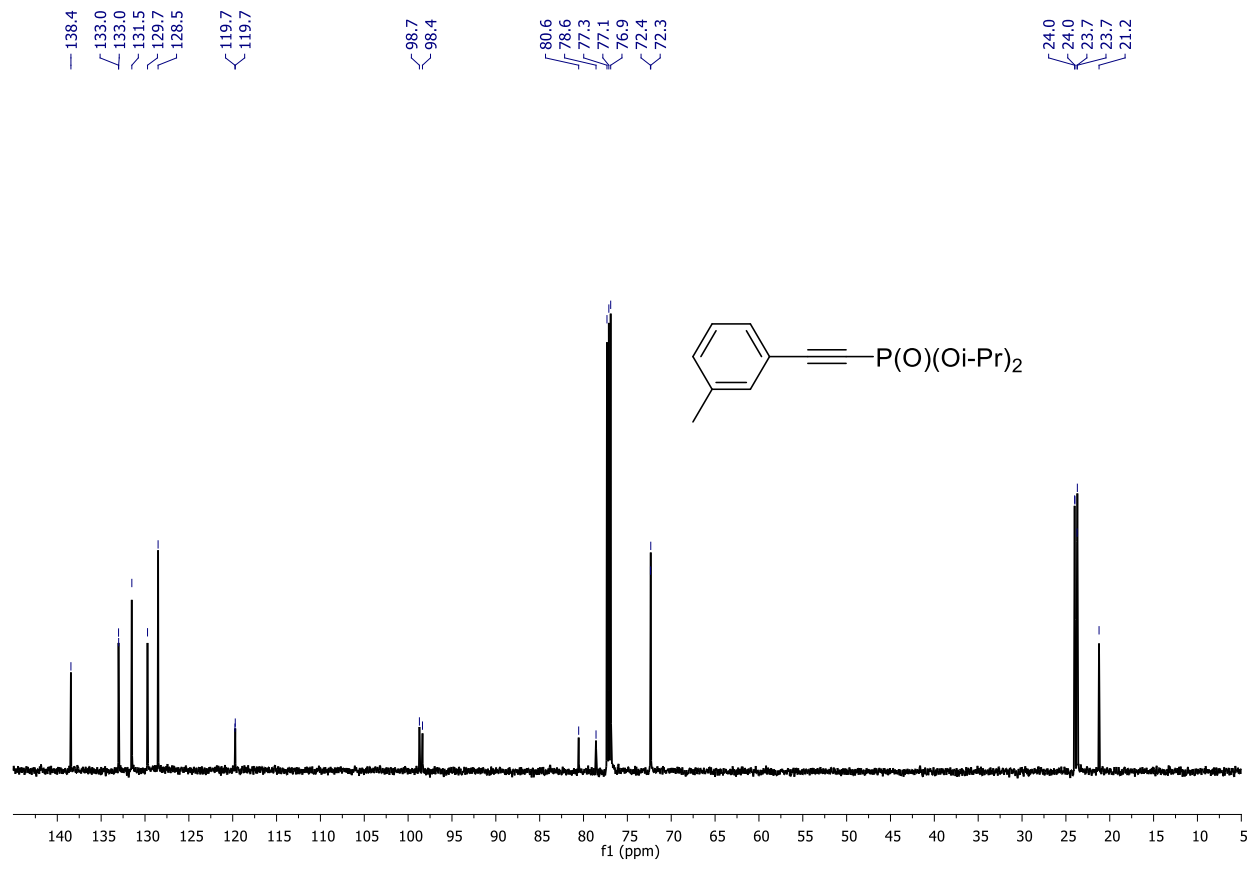


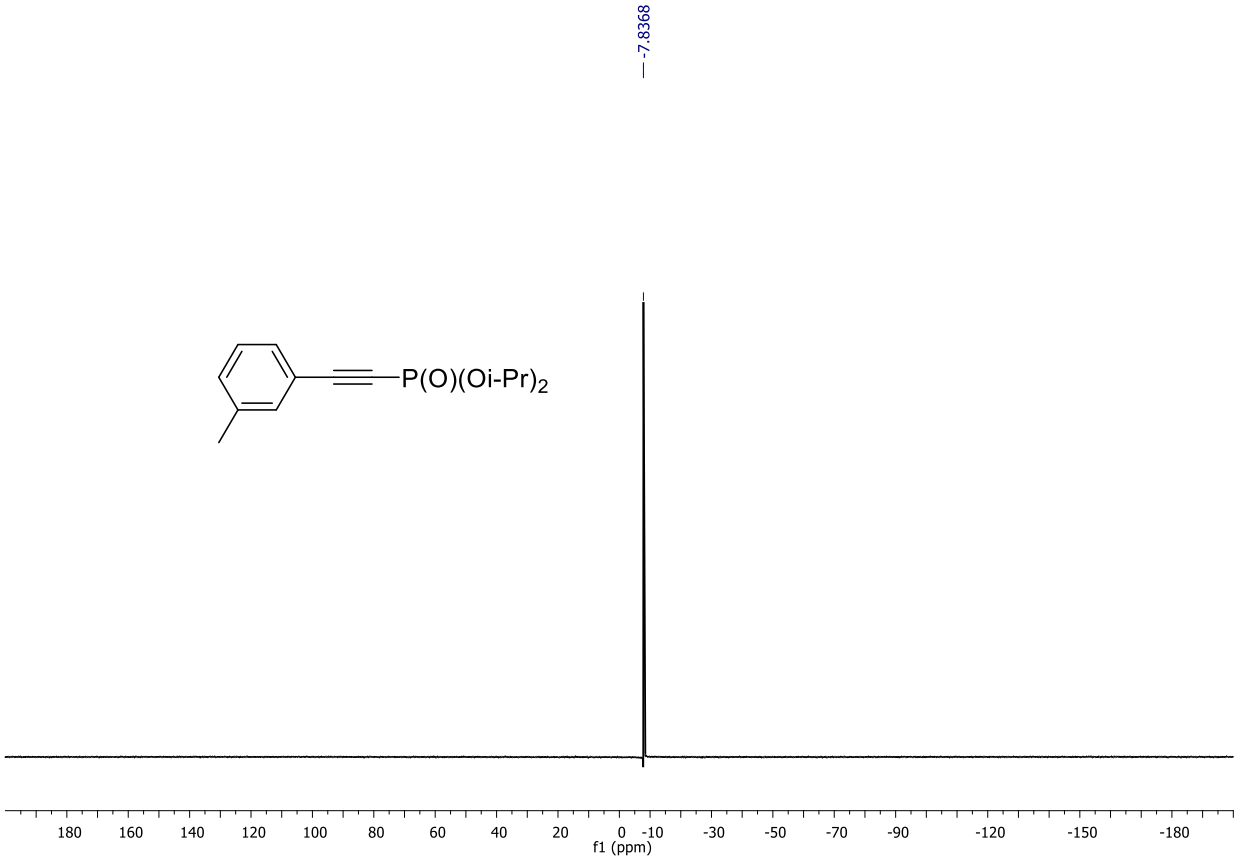




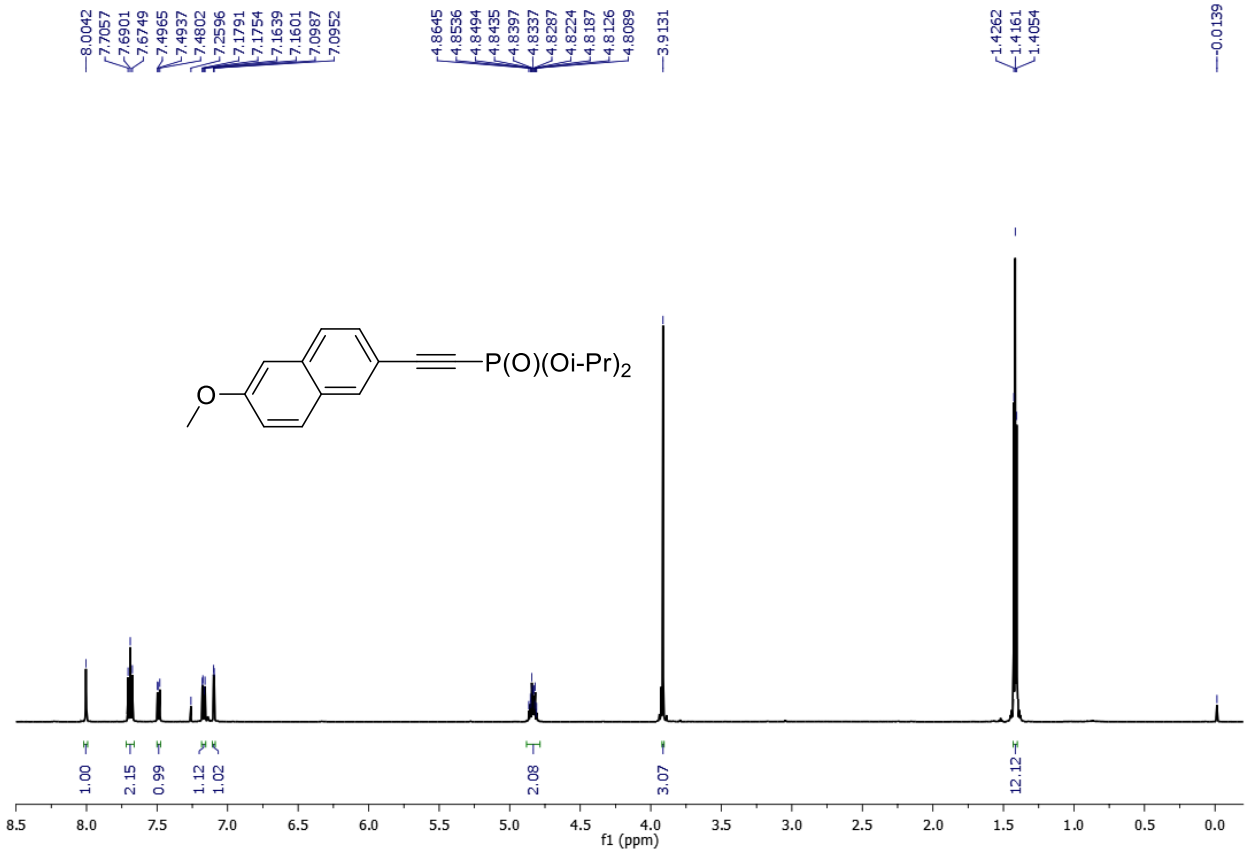
Diisopropyl [(3-methylphenyl)ethynyl]phosphonate (4l):

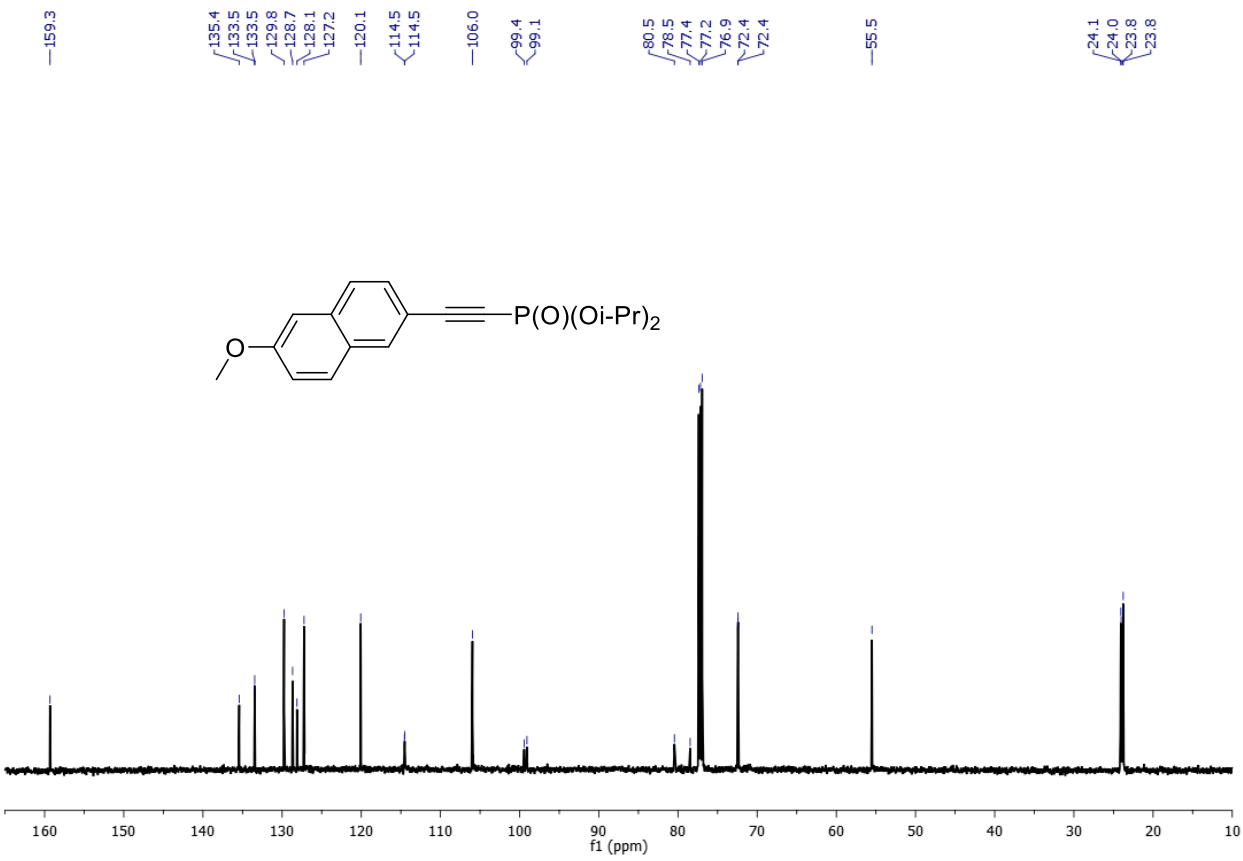

7.3340
7.3275
7.3195
7.2473
7.2283
7.2211
4.8117
4.8007
4.7968
4.7907
4.7871
4.7807
4.7760
4.7660
4.7561
2.3198
1.3868
1.3811
1.3770
1.3714
-0.0278
P(O)(Oi-Pr)2
1.98
1.92
2.00
3.00
12.34
f1 (ppm)

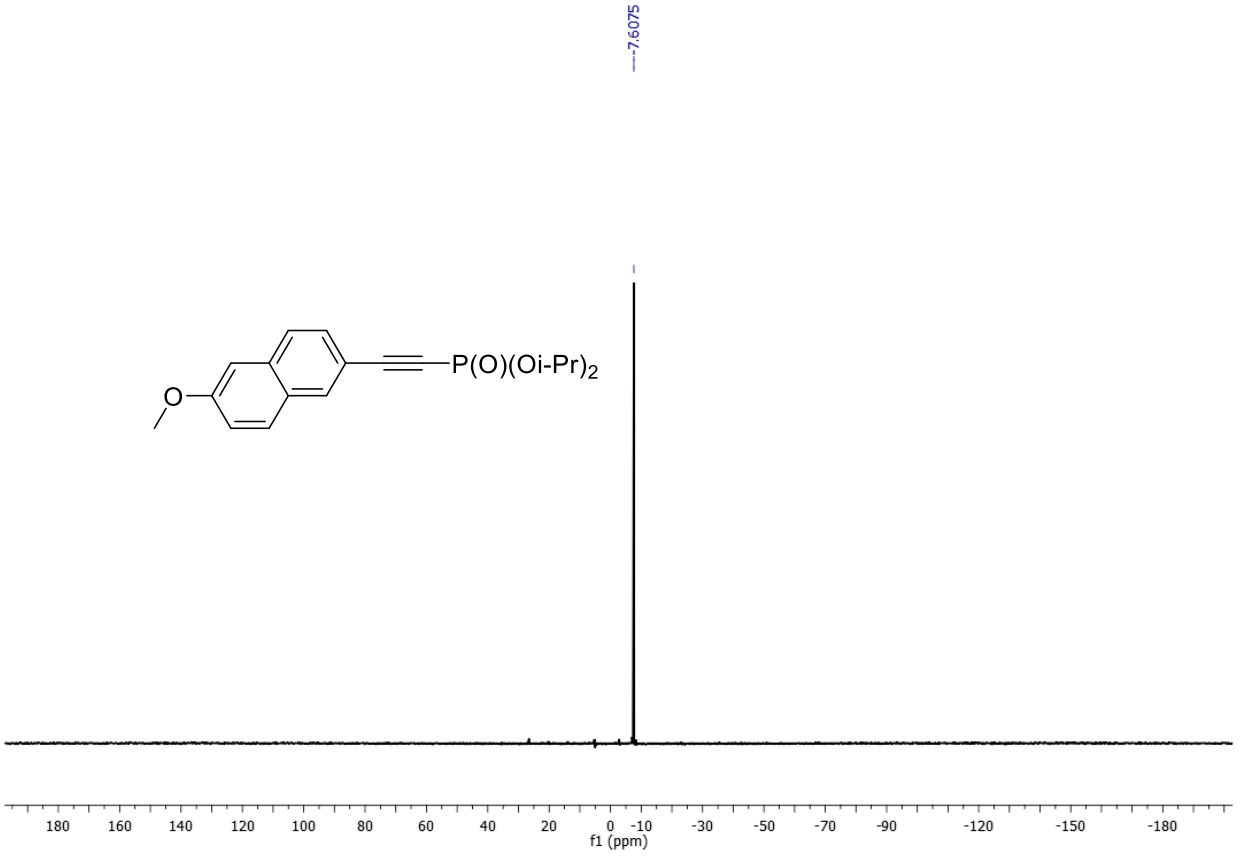

138.4
133.0
133.0
131.5
129.7
128.5
119.7
119.7
98.7
98.4
80.6
78.6
77.3
77.1
76.9
72.4
72.3
24.0
24.0
23.7
23.7
21.2
P(O)(Oi-Pr)2
f1 (ppm)



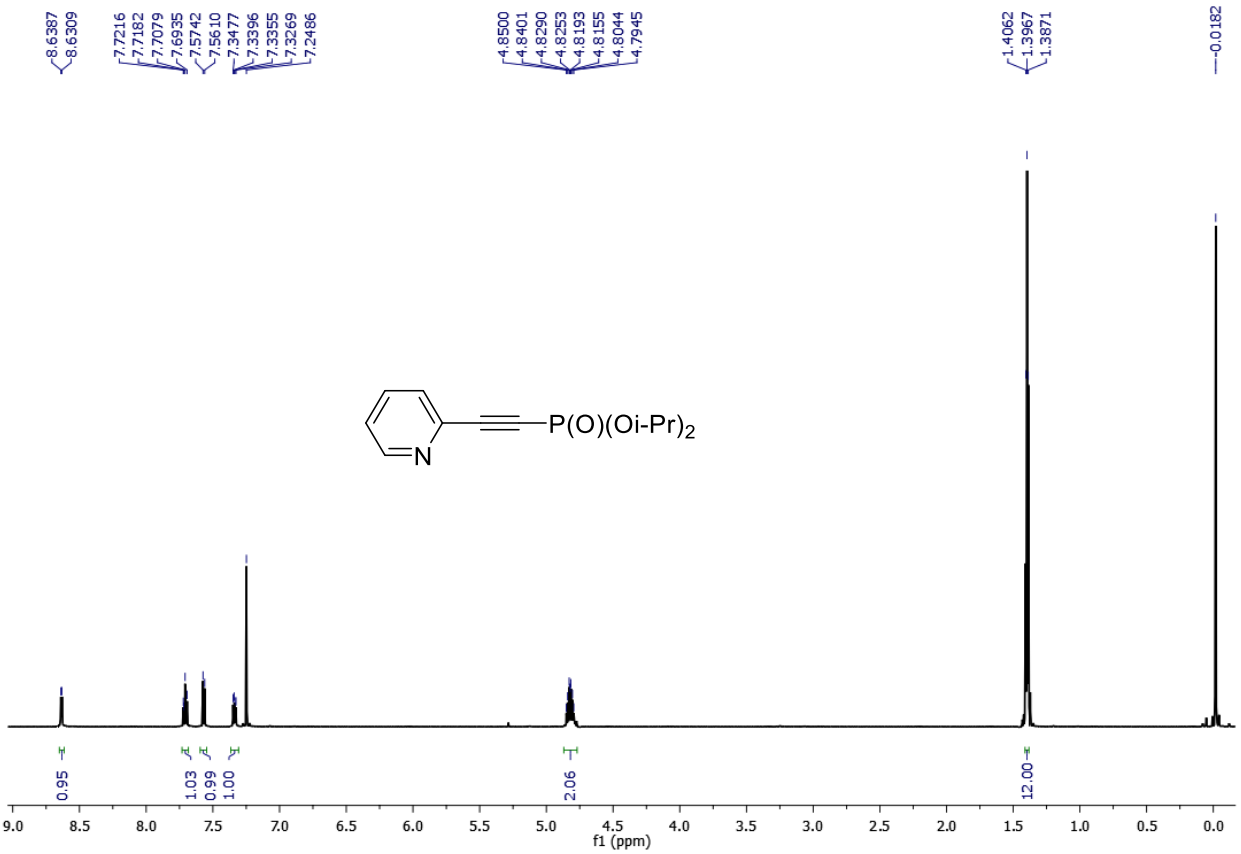
Diisopropyl [(6-methoxynaphthalen-2-yl)ethynyl]phosphonate (4m):

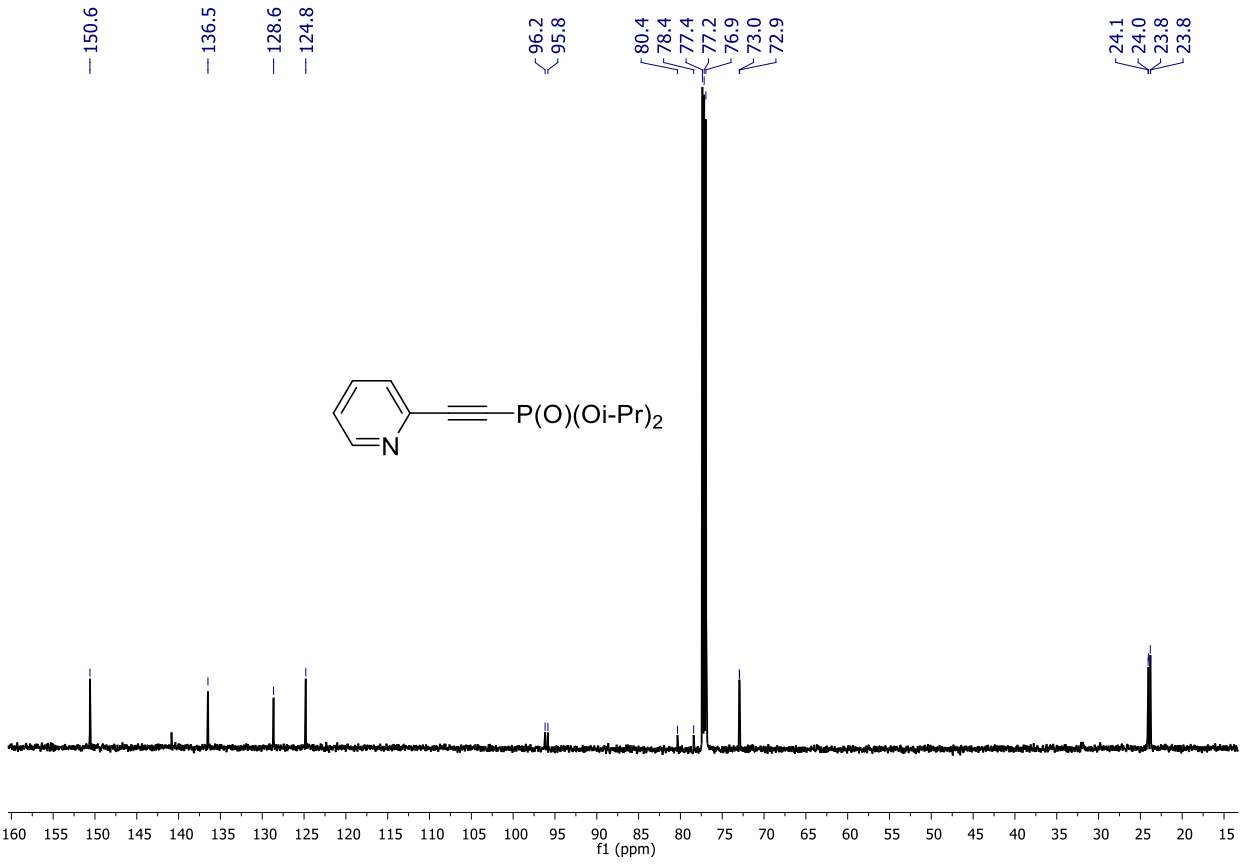


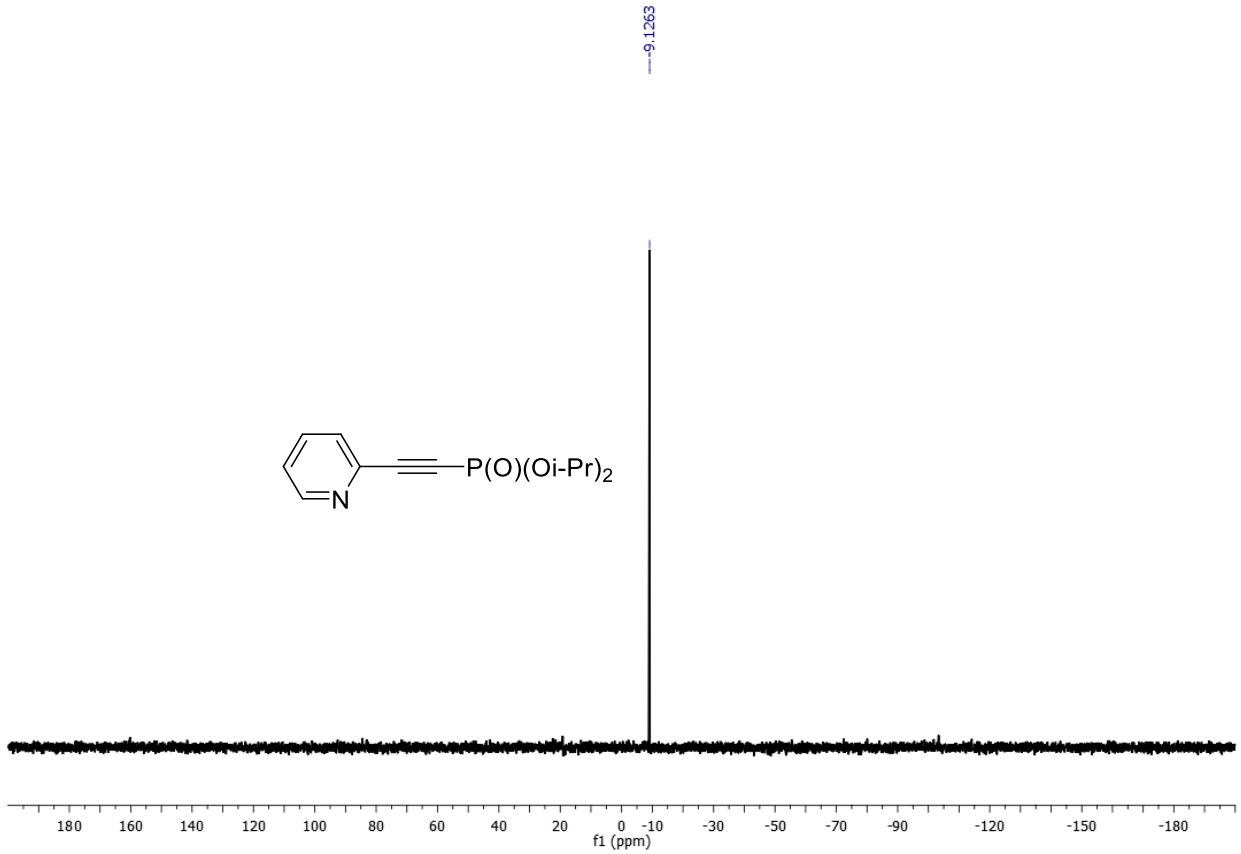




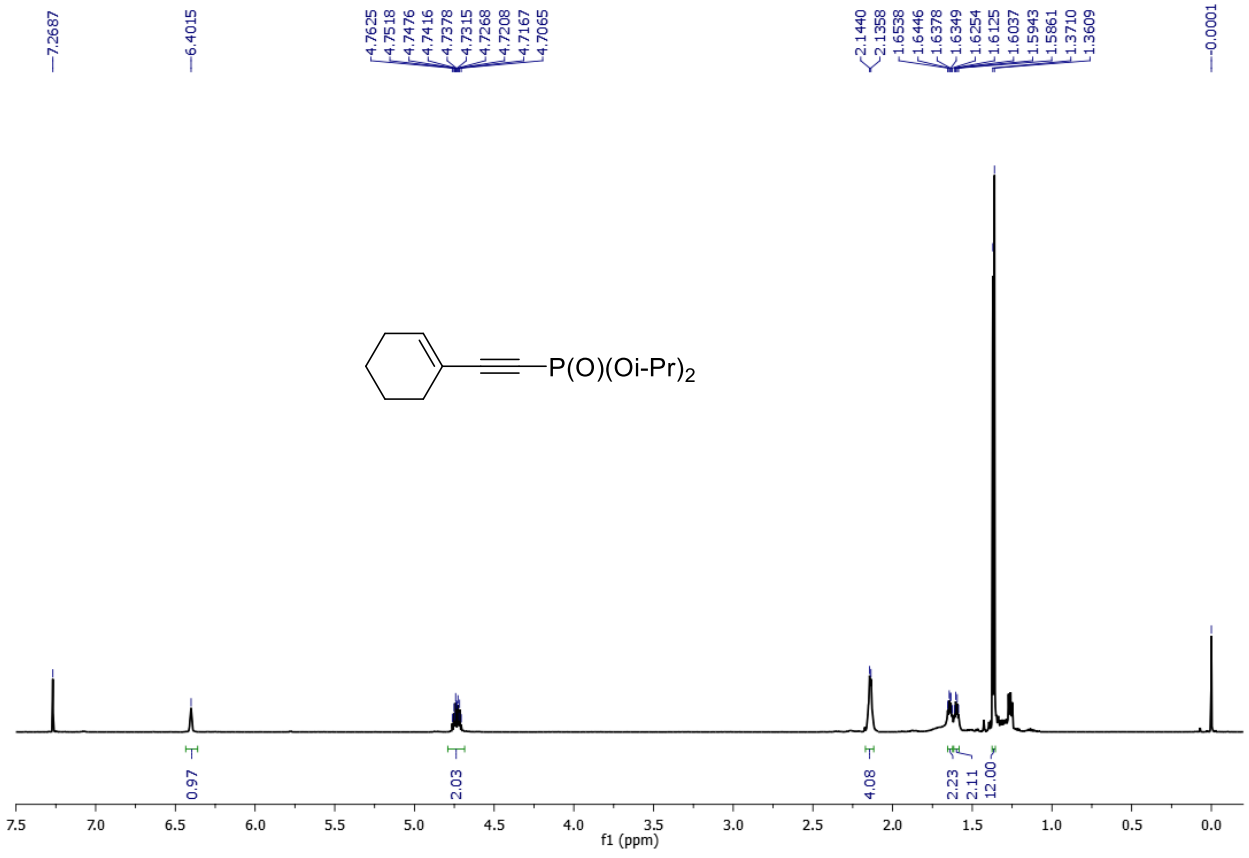
Diisopropyl (pyridine-2-ylethynyl)phosphonate (4n):

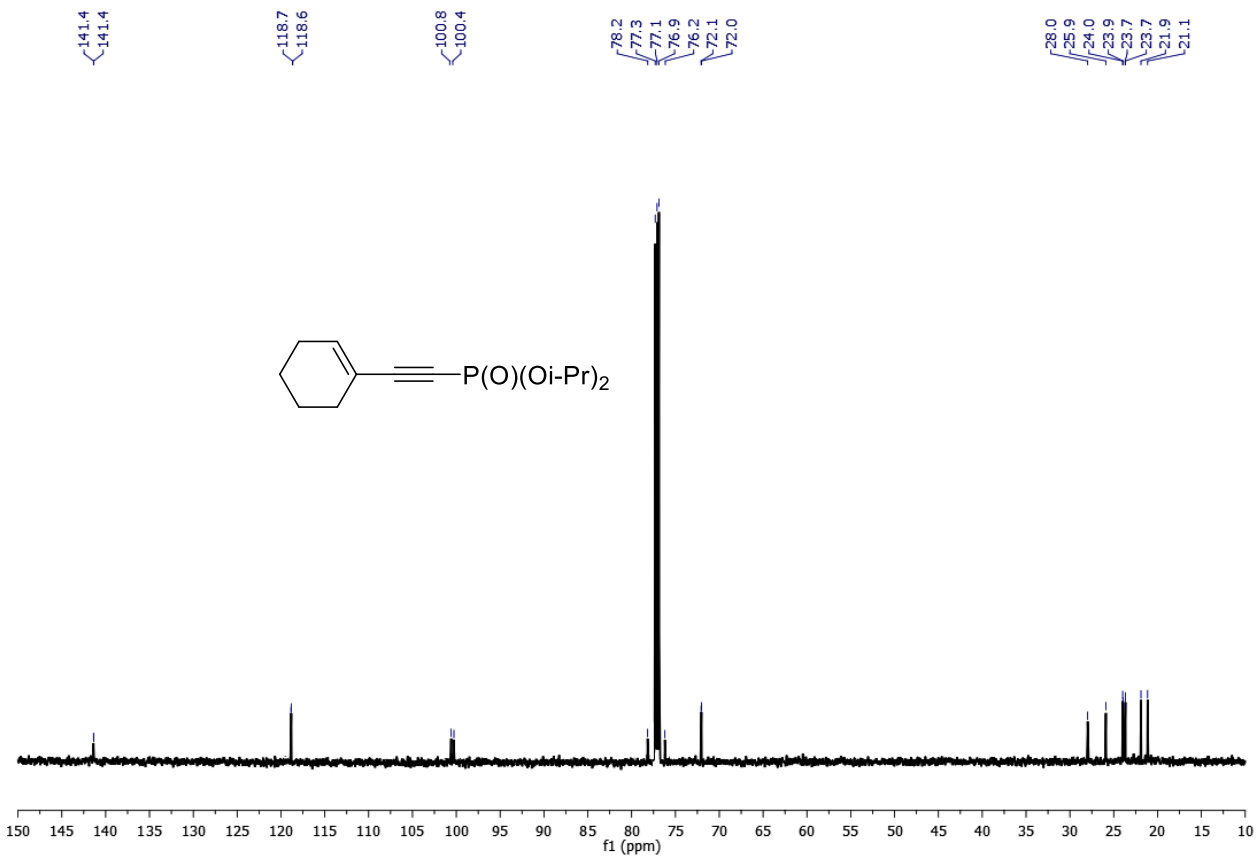

8.6387
8.6309
7.7216
7.7182
7.7079
7.6935
7.5742
7.5610
7.3477
7.3396
7.3355
7.3269
7.2486
4.8500
4.8401
4.8290
4.8253
4.8193
4.8155
4.8044
4.7945
1.4062
1.3967
1.3871
0.0182
P(O)(Oi-Pr)2
N
0.95
1.03
0.99
1.00
2.06
12.00
f1 (ppm)

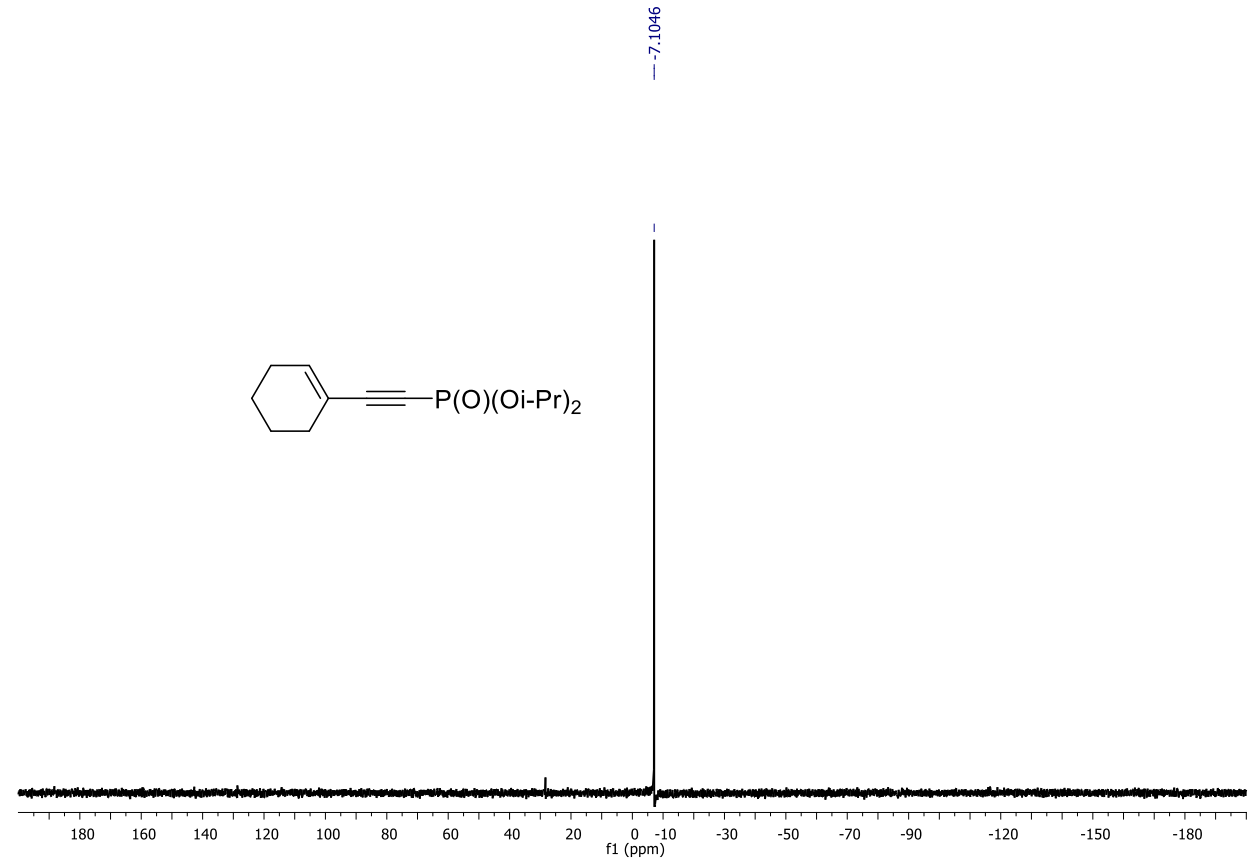

150.6
136.5
128.6
124.8
96.2
95.8
80.4
78.4
77.4
77.2
76.9
73.0
72.9
24.1
24.0
23.8
23.8
P(O)(Oi-Pr)2
N
f1 (ppm)



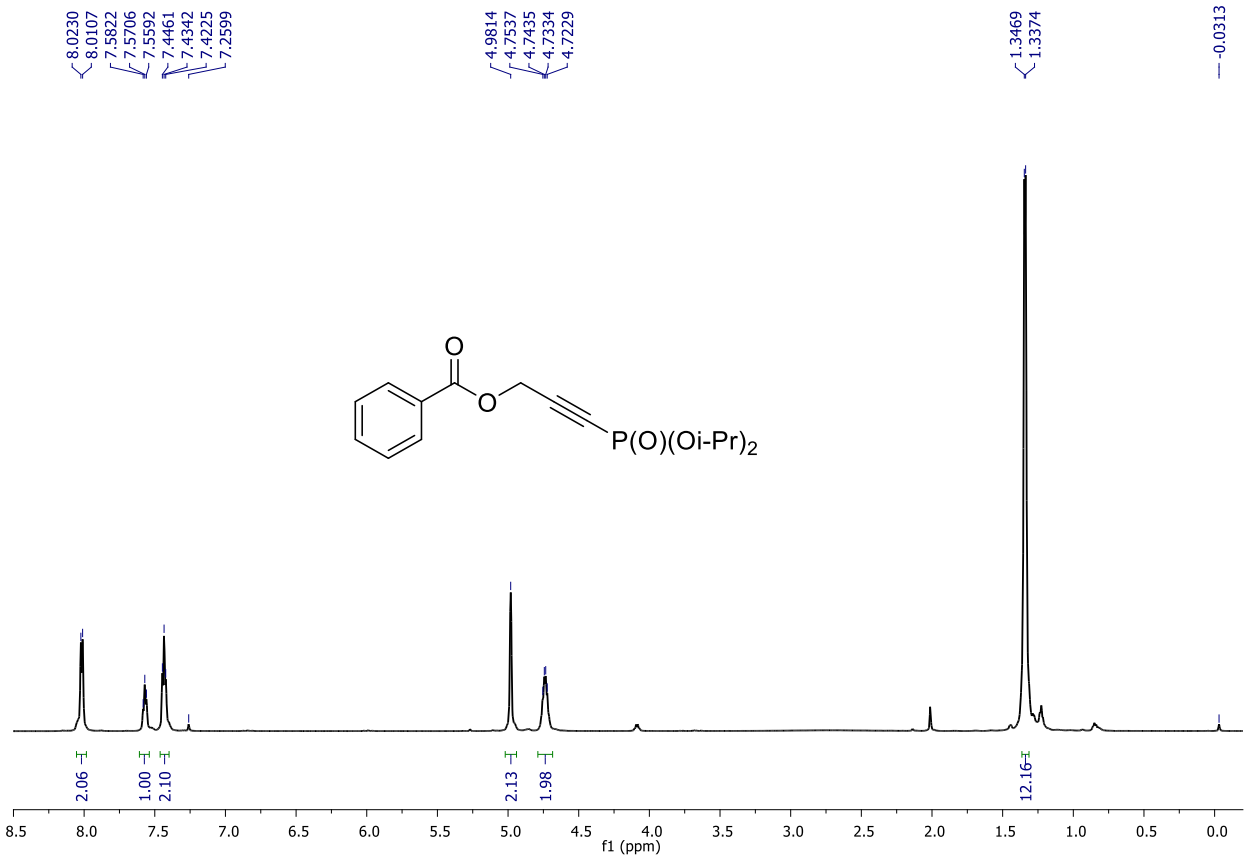
Diisopropyl (cyclohexen-1-ylethynyl)phosphonate (4o):

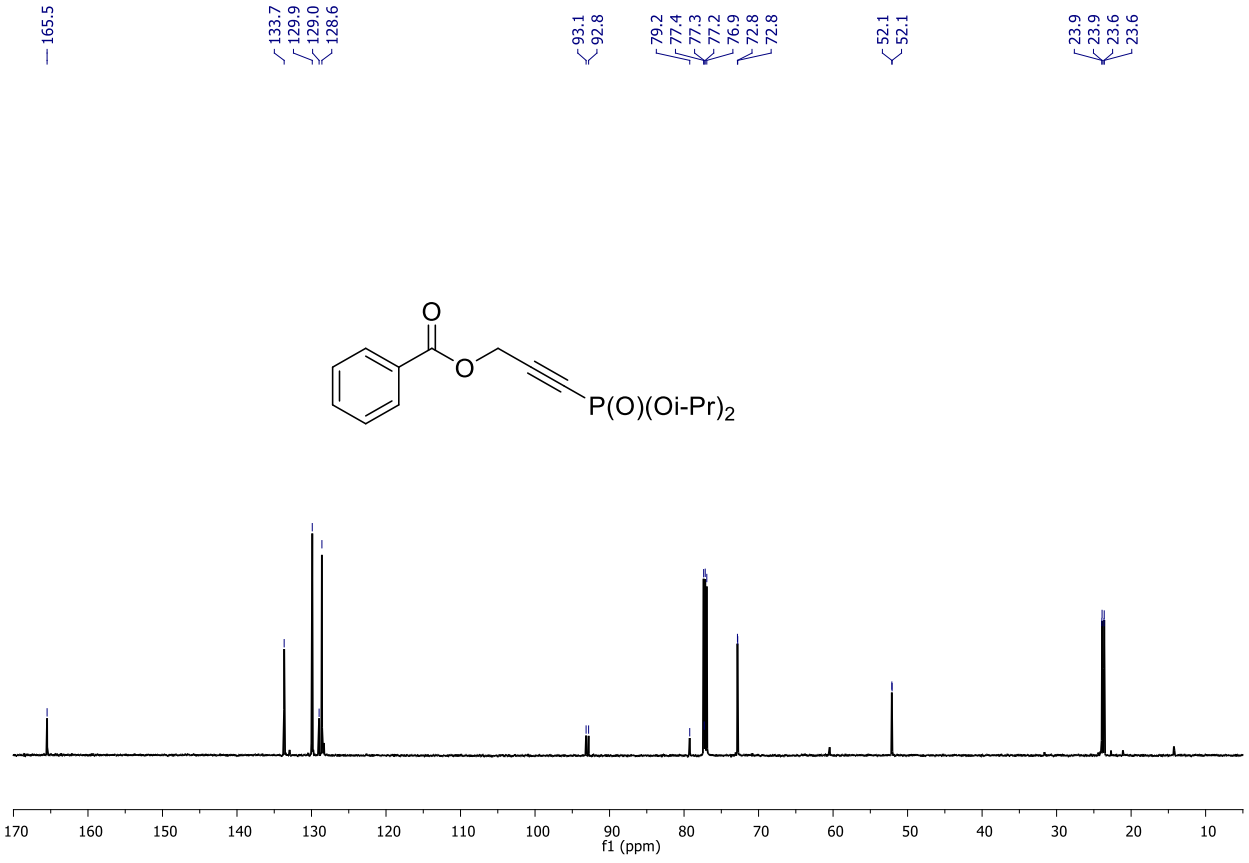



141.4
141.4
118.7
118.6
100.8
100.4
78.2
77.3
77.1
76.9
76.2
72.1
72.0
28.0
25.9
24.0
23.9
23.7
23.7
21.9
21.1
P(O)(Oi-Pr)2
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

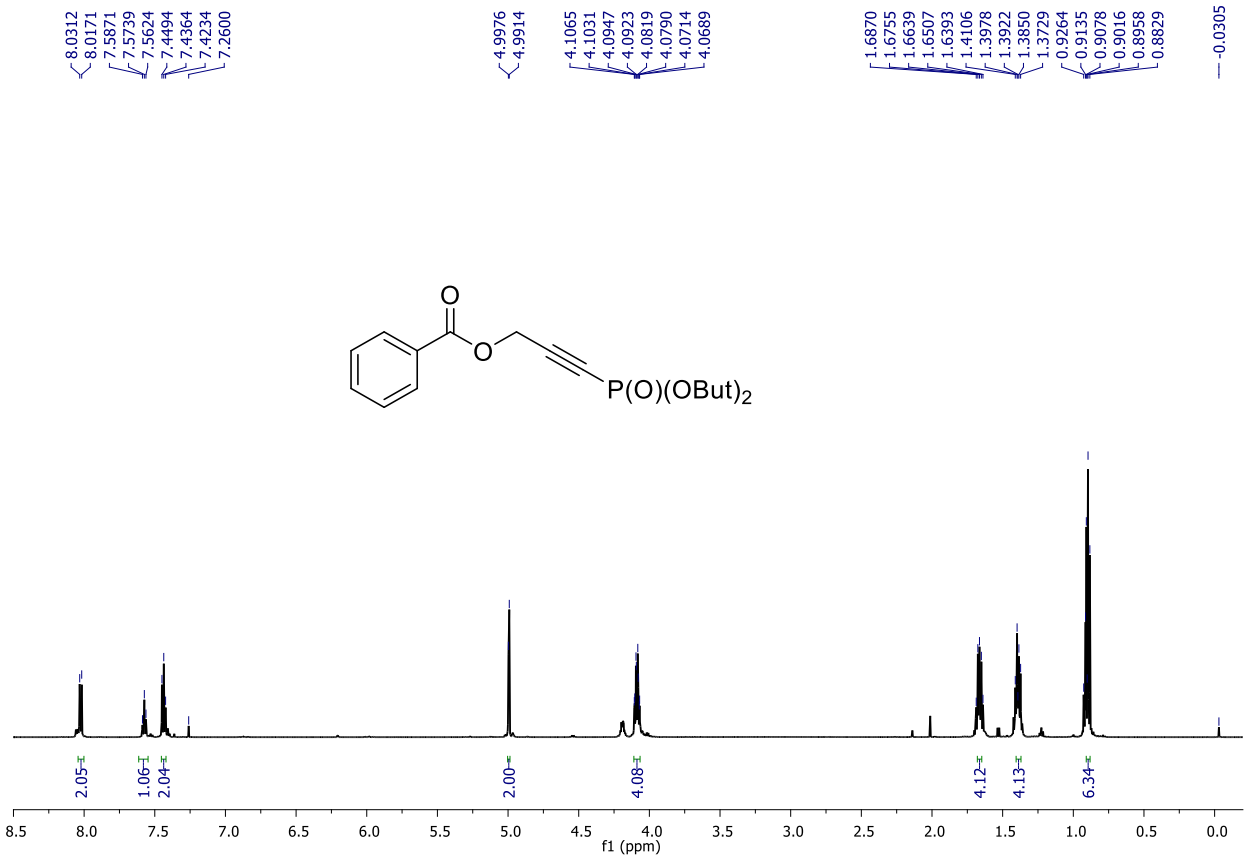

-7.1046
P(O)(Oi-Pr)2
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

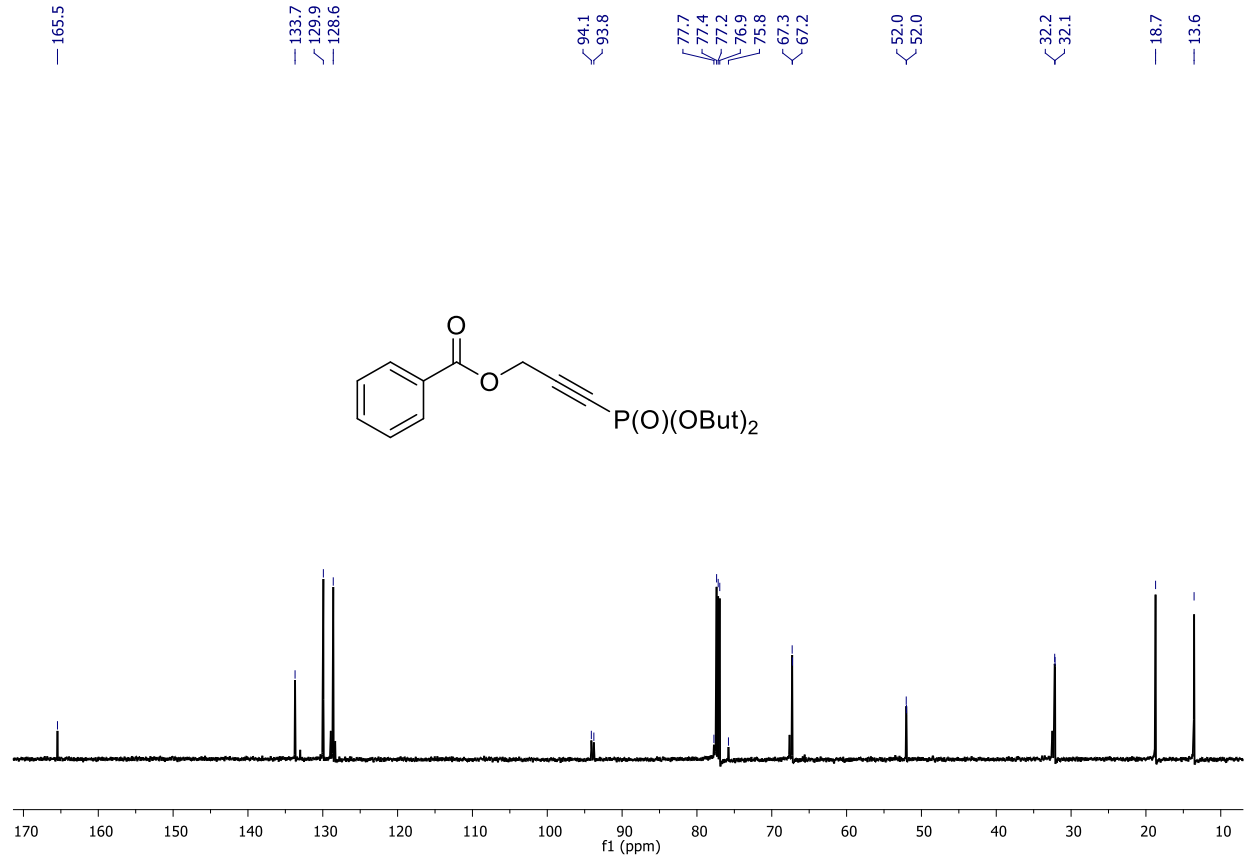
3-(diisopropylphosphoryl)prop-2-yn-1-yl benzoate (4p):



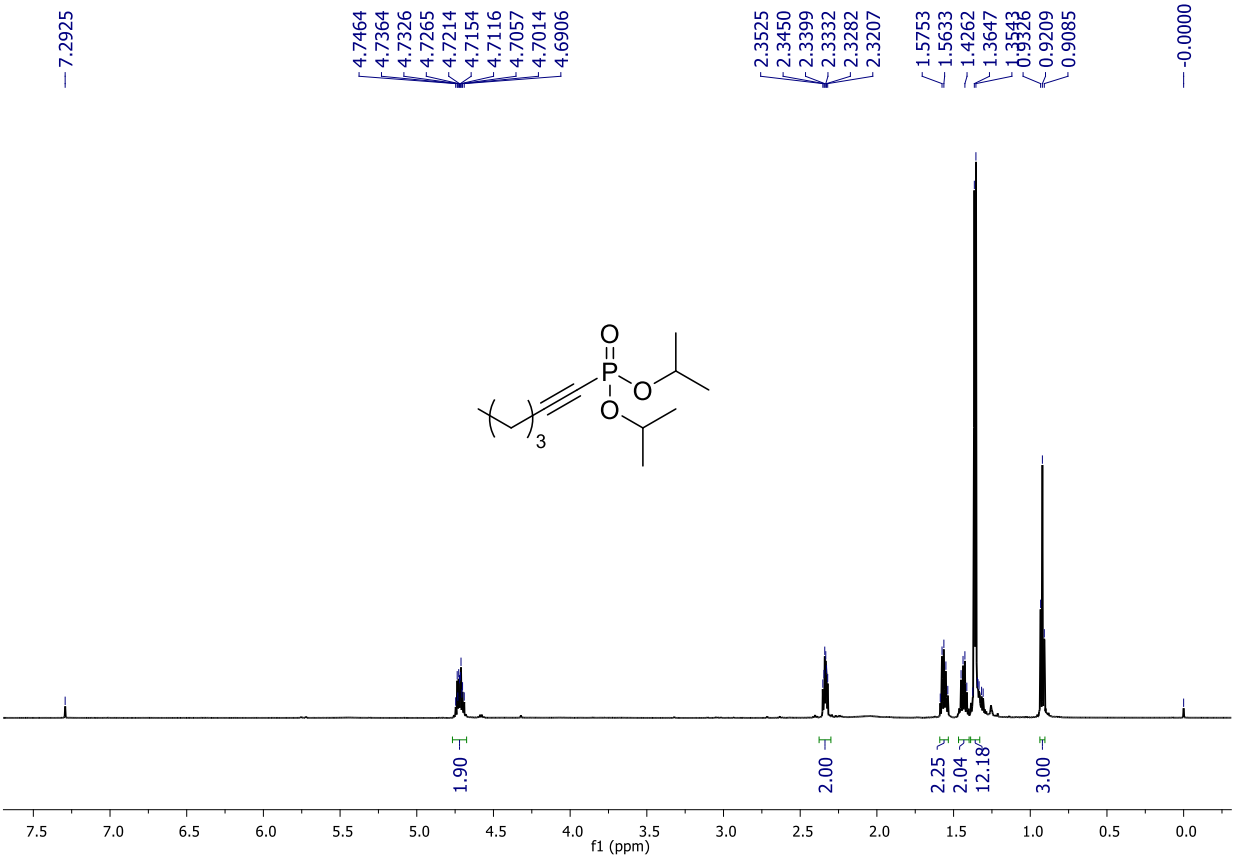


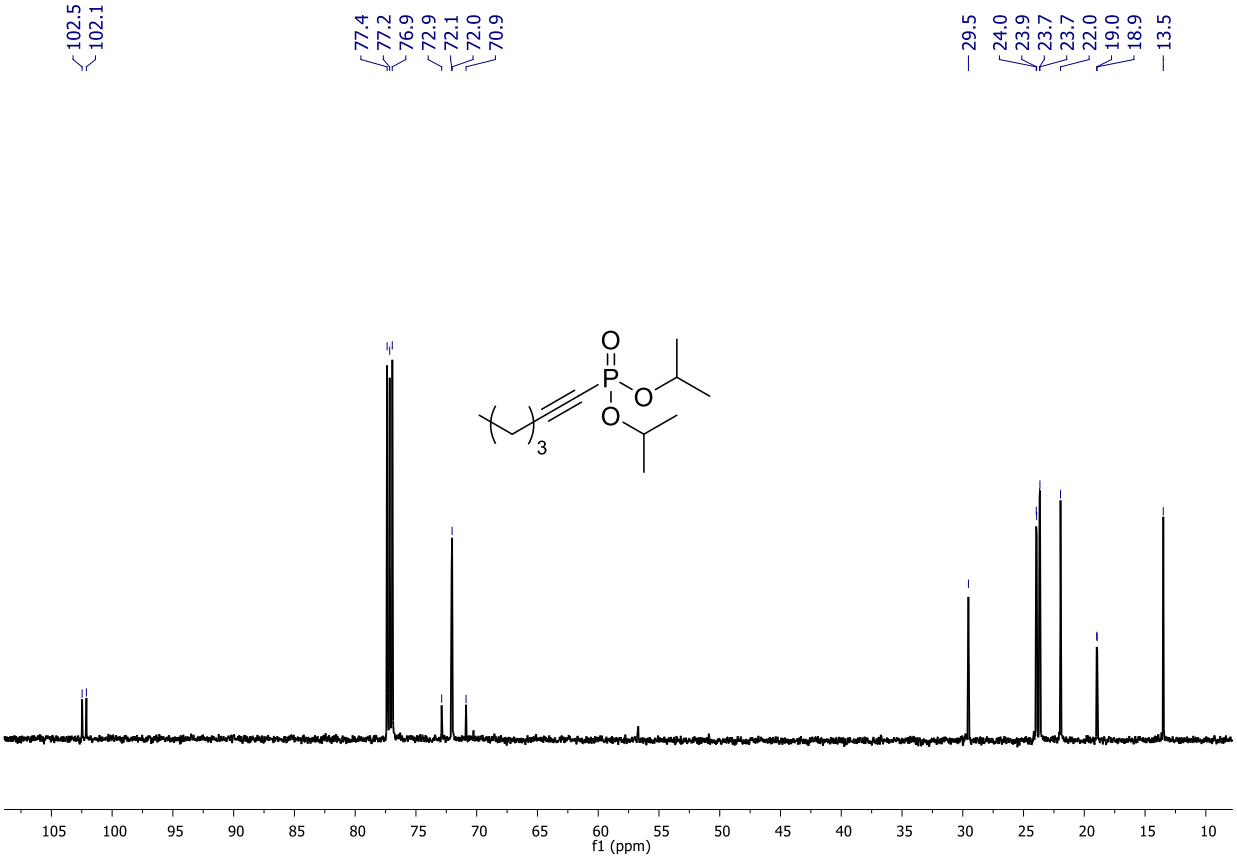
3-(dibutylphosphoryl)prop-2-yn-1-yl benzoate (4q):

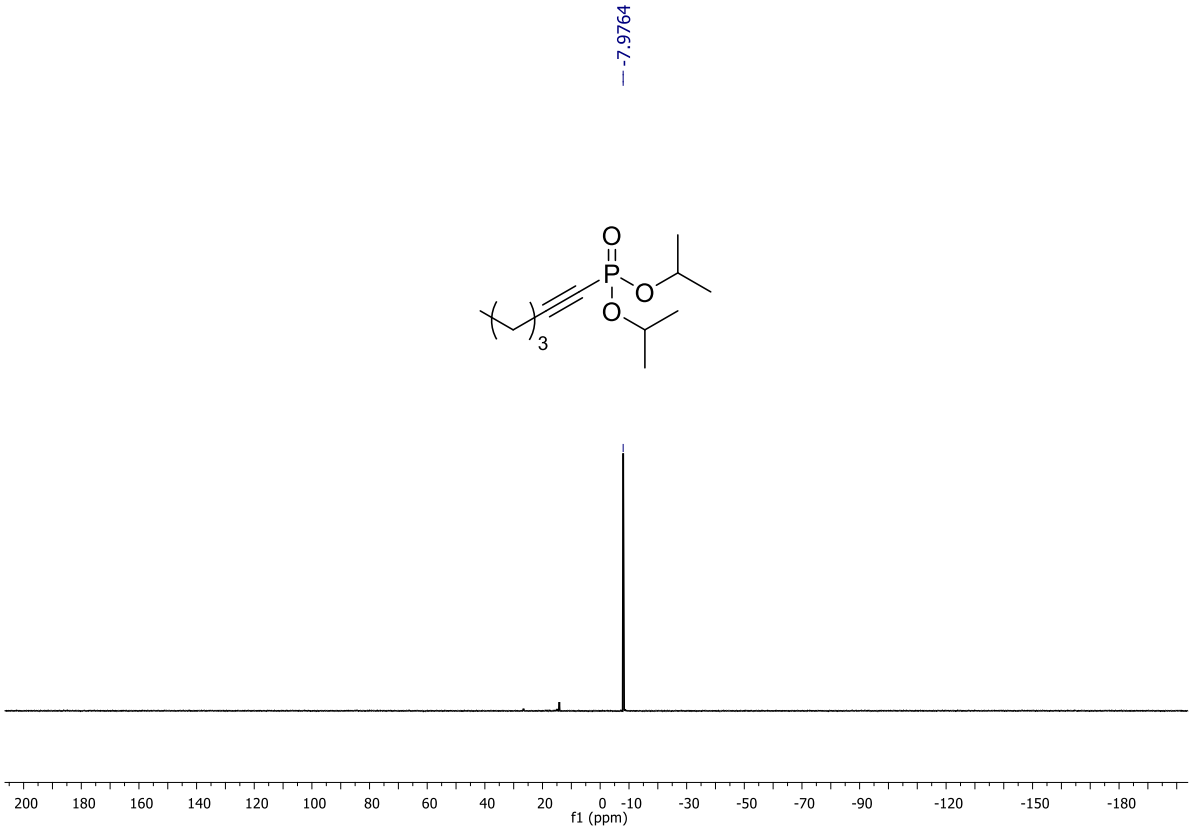




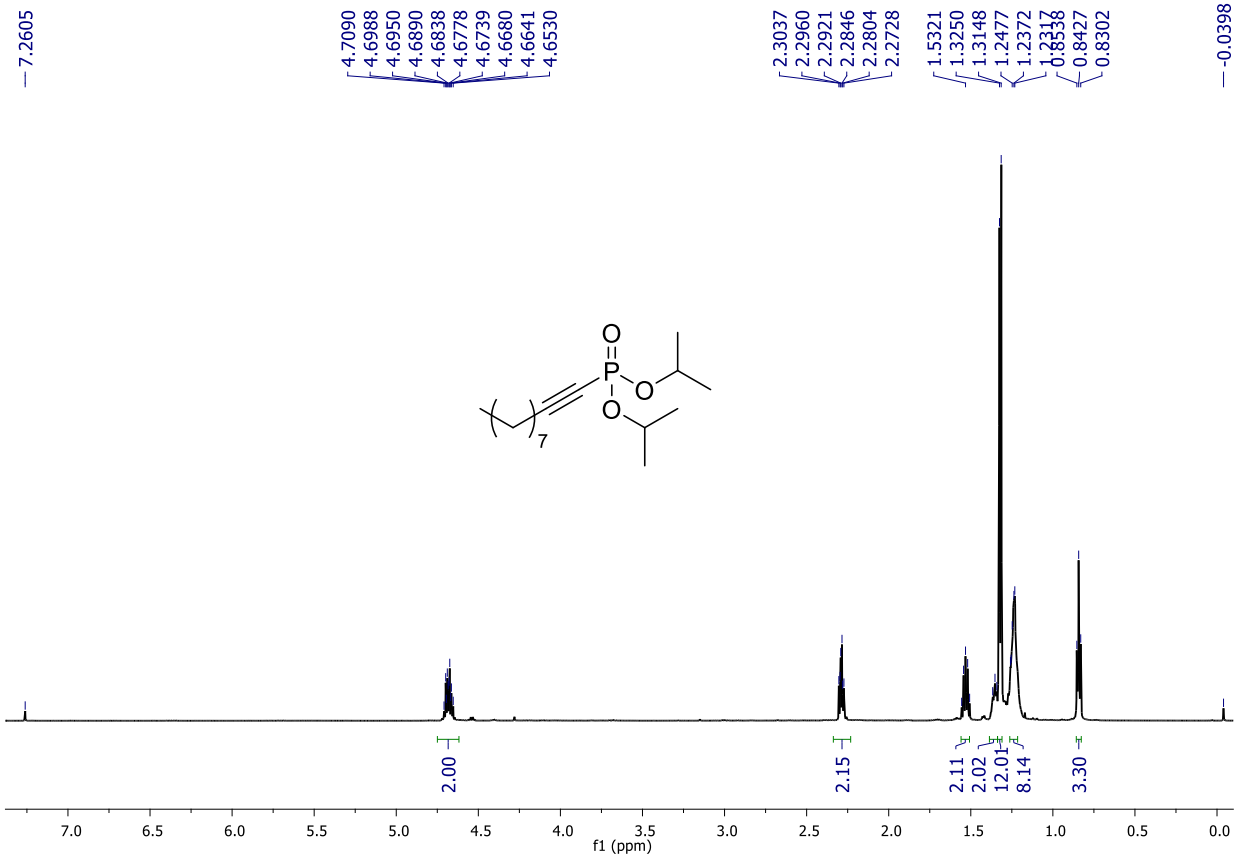
Diisopropyl hex-1-yn-1-ylphosphonate (4r):

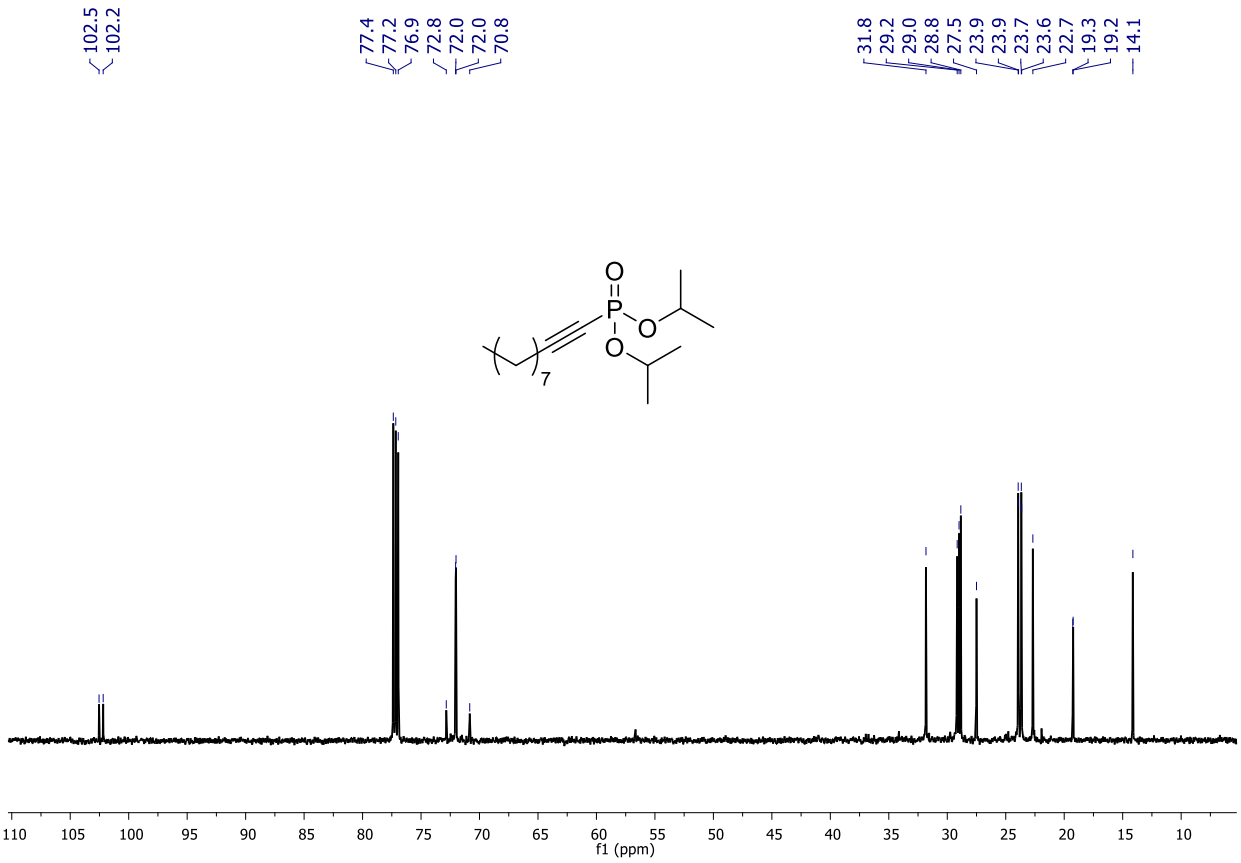


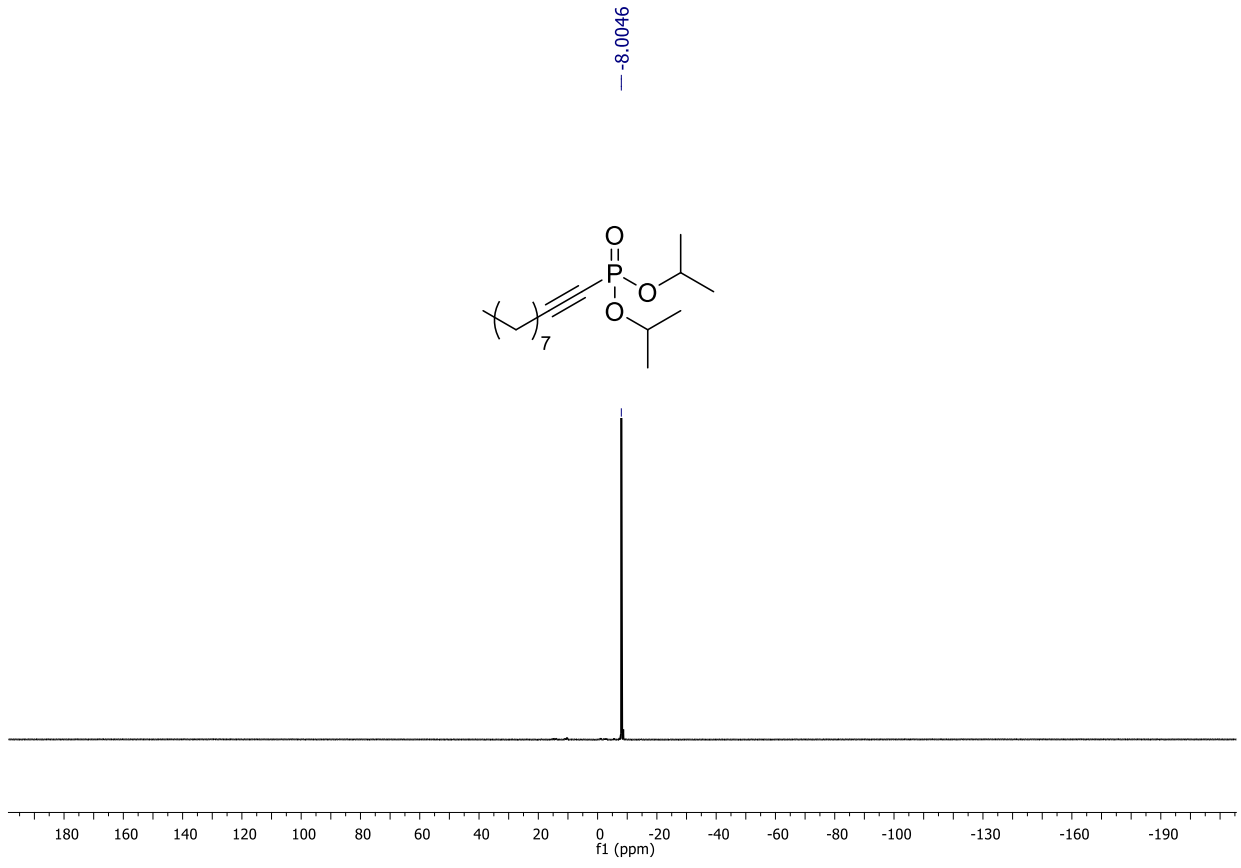




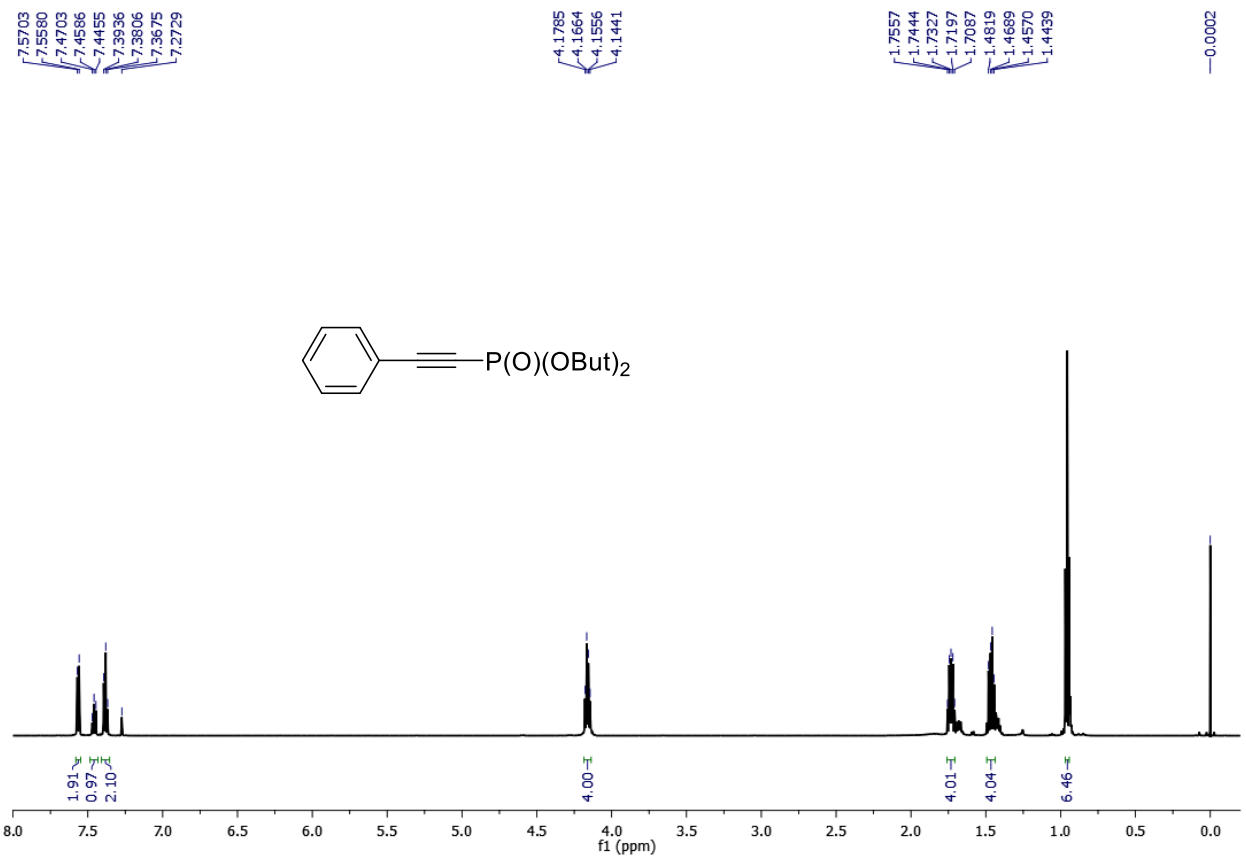
Diisopropyl dec-1-yn-1-ylphosphonate (4s):

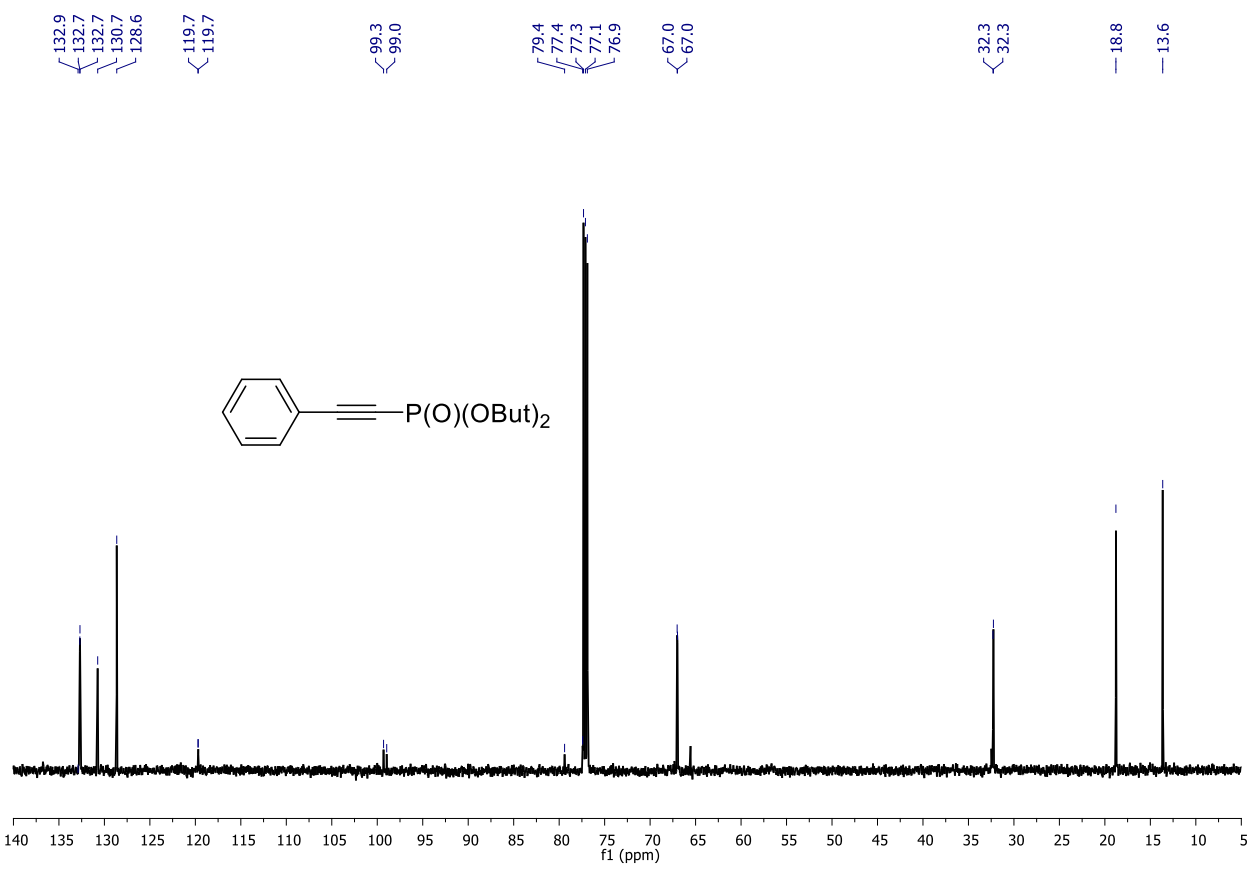


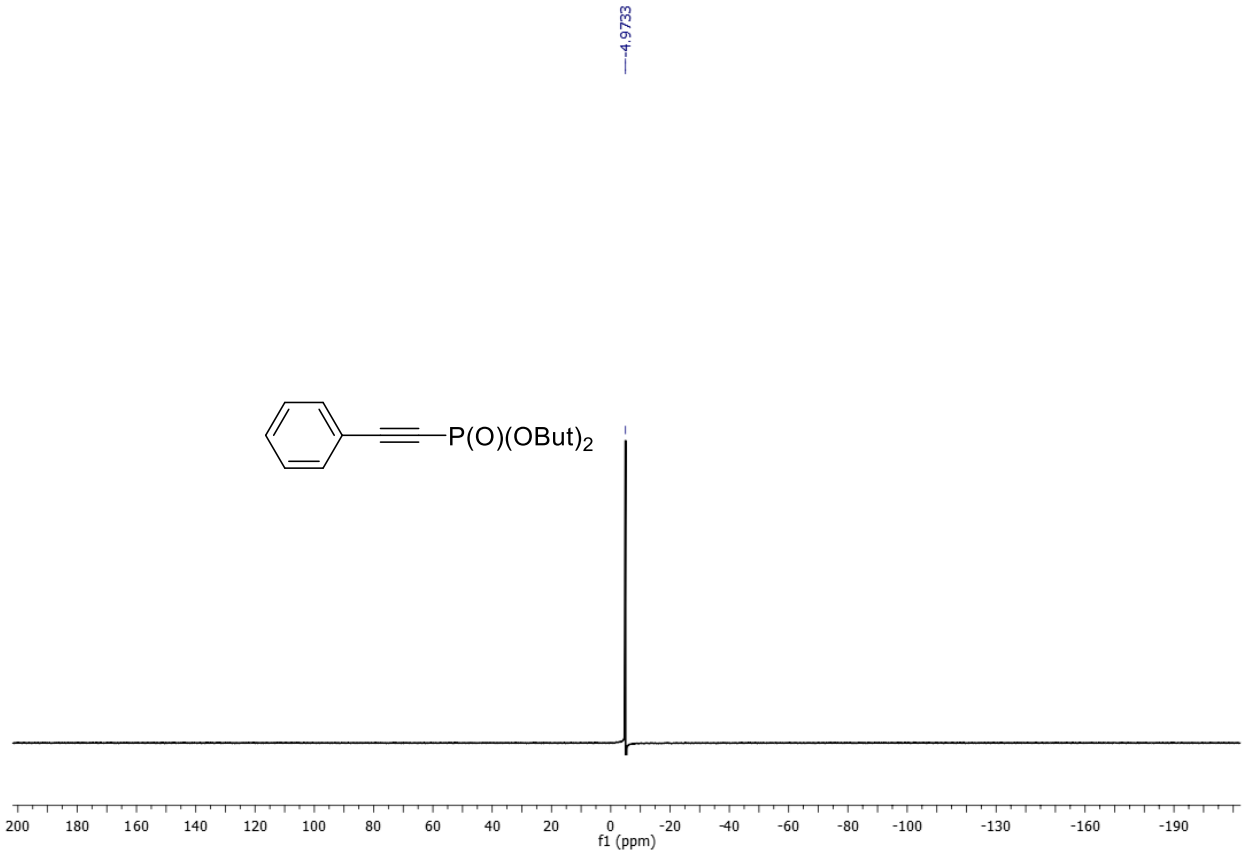




Dibutyl (phenylethynyl)phosphonate (4t):

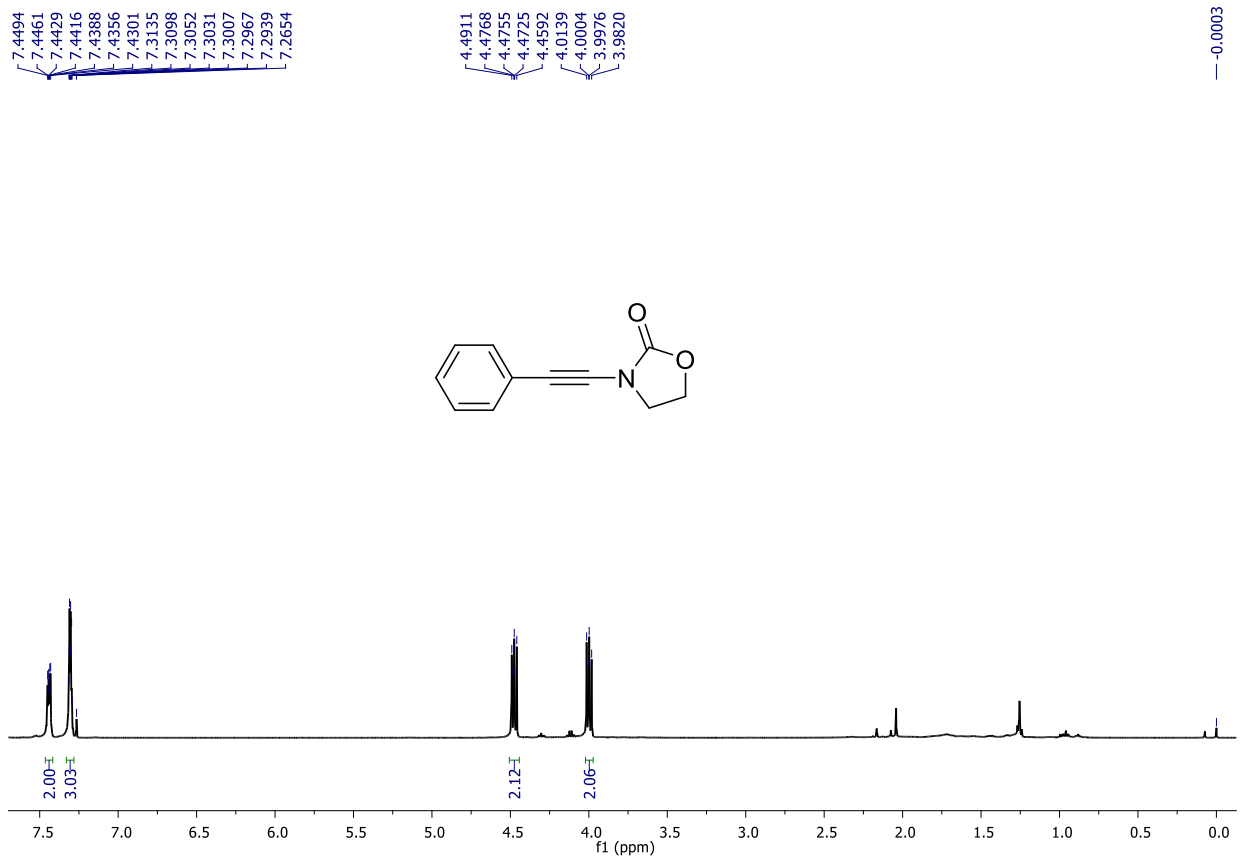

7.5703
7.5580
7.4703
7.4586
7.4455
7.3936
7.3806
7.3675
7.2729
4.1785
4.1664
4.1556
4.1441
1.7557
1.7444
1.7327
1.7197
1.7087
1.4819
1.4689
1.4570
1.4439
0.0002
P(O)(OBut)2
1.91
0.97
2.10
4.00
4.01
4.04
6.46
f1 (ppm)

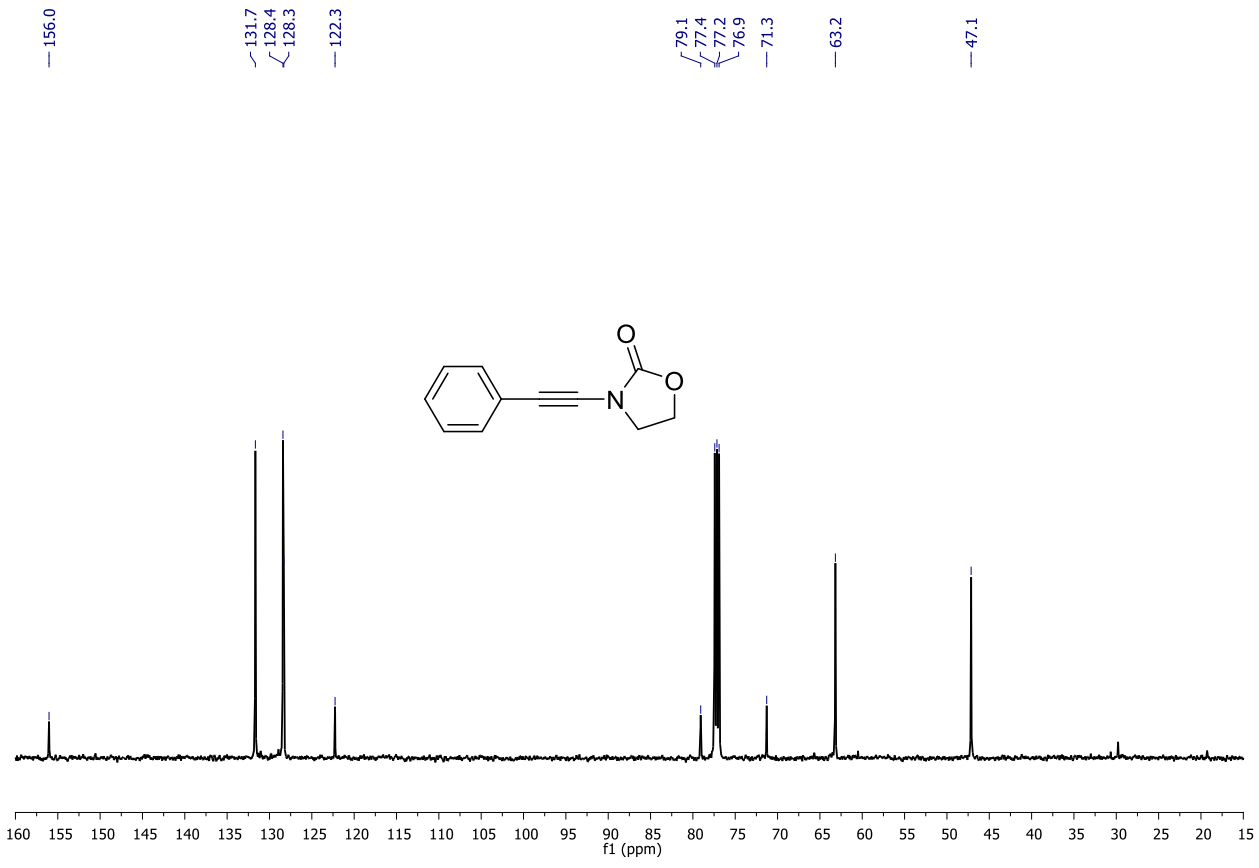

132.9
132.7
132.7
130.7
128.6
119.7
119.7
99.3
99.0
79.4
77.4
77.3
77.1
76.9
67.0
67.0
32.3
32.3
18.8
13.6
P(O)(OBut)2
f1 (ppm)



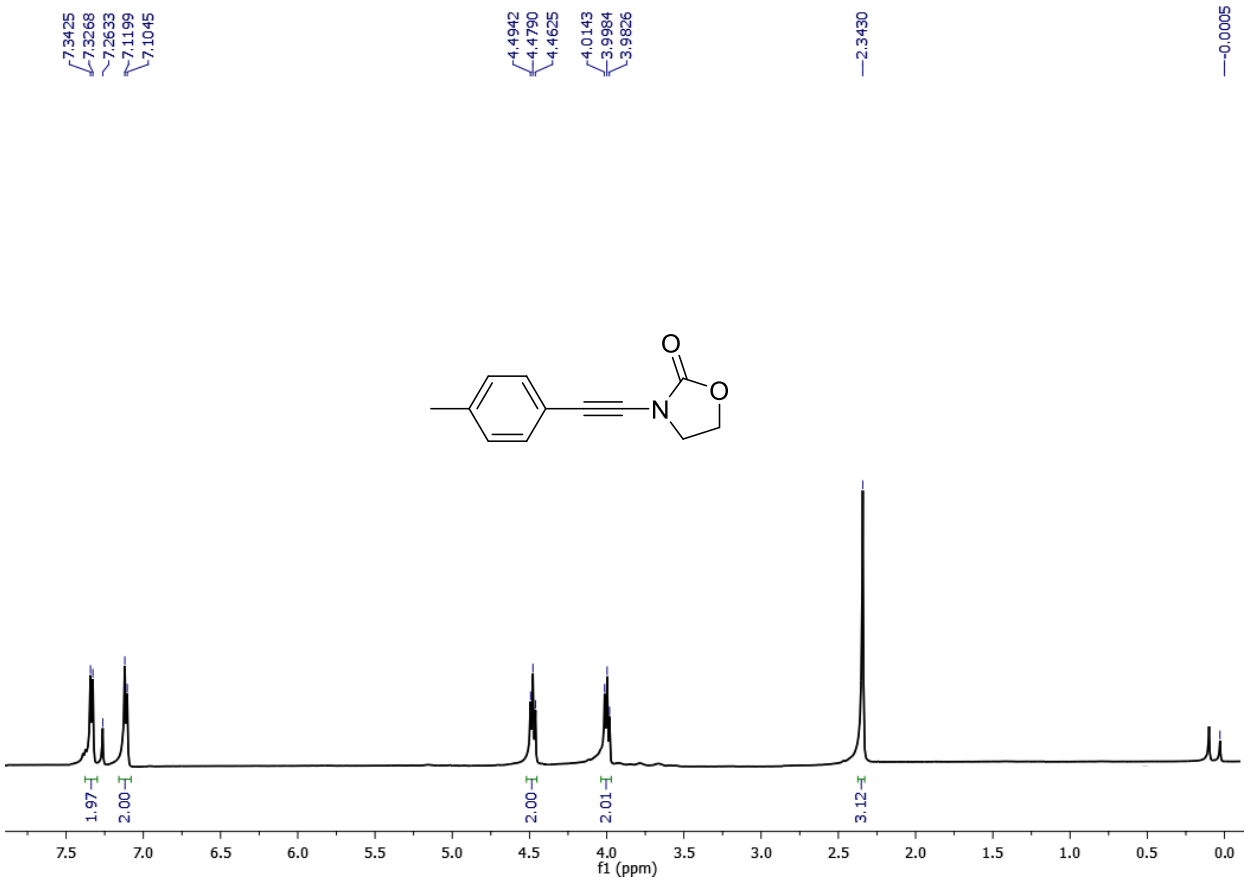
^{1}H & ^{13}C Spectra:

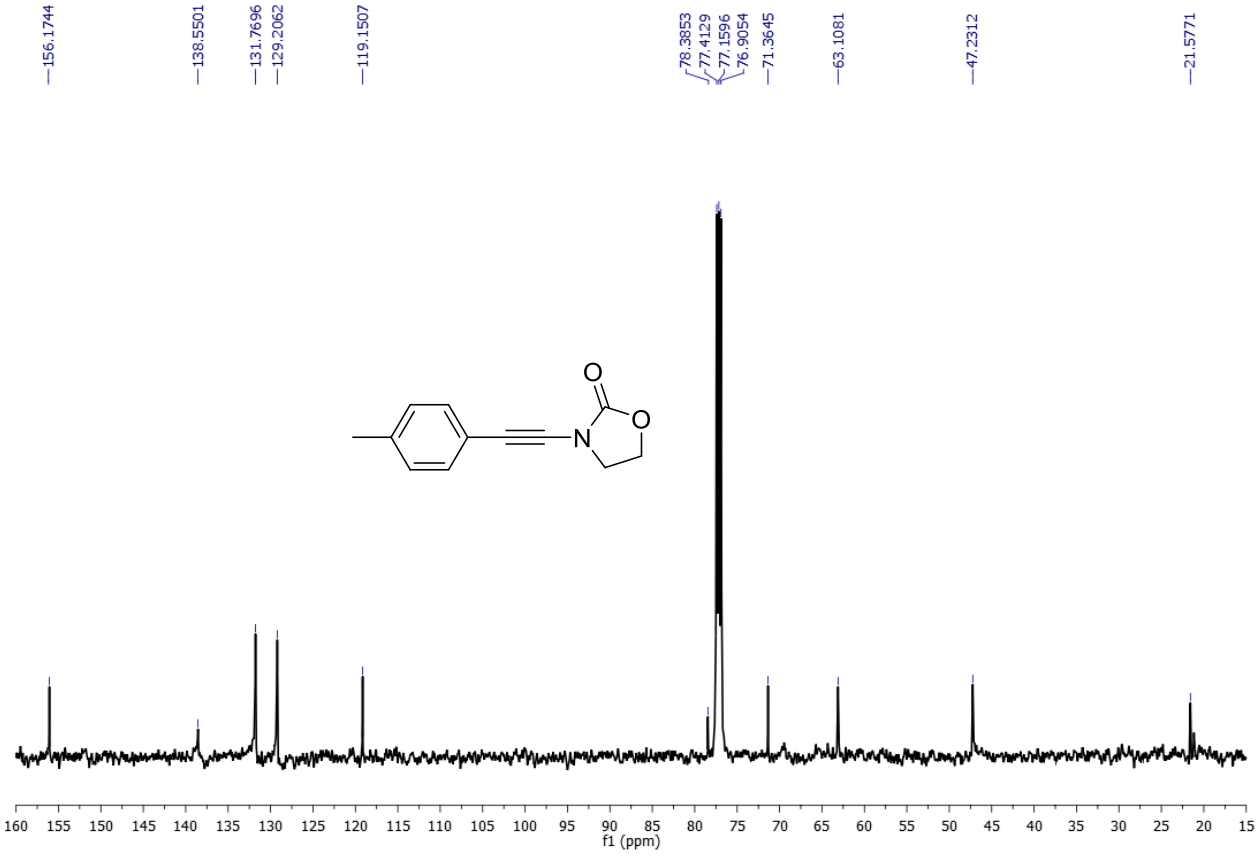
3-(phenylethynyl)oxazolidin-2-one (5a):



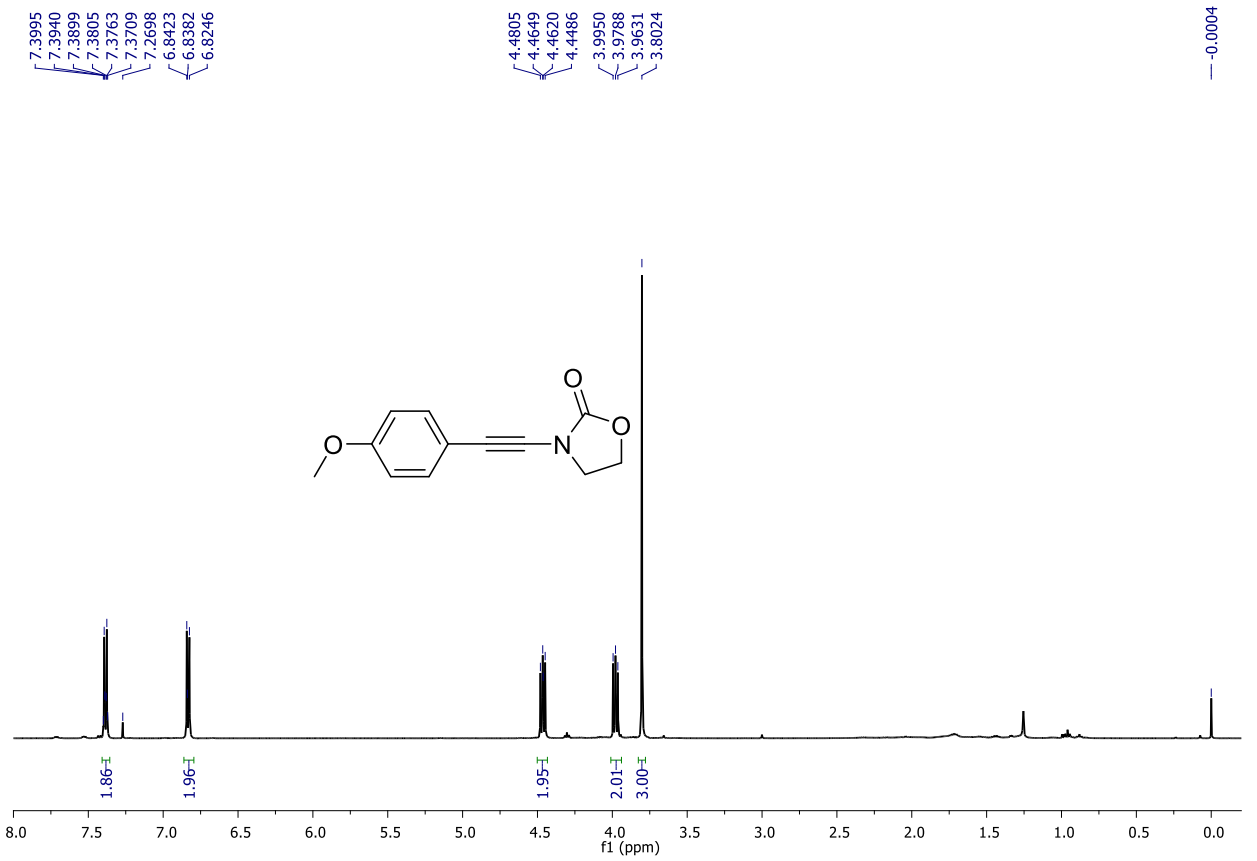


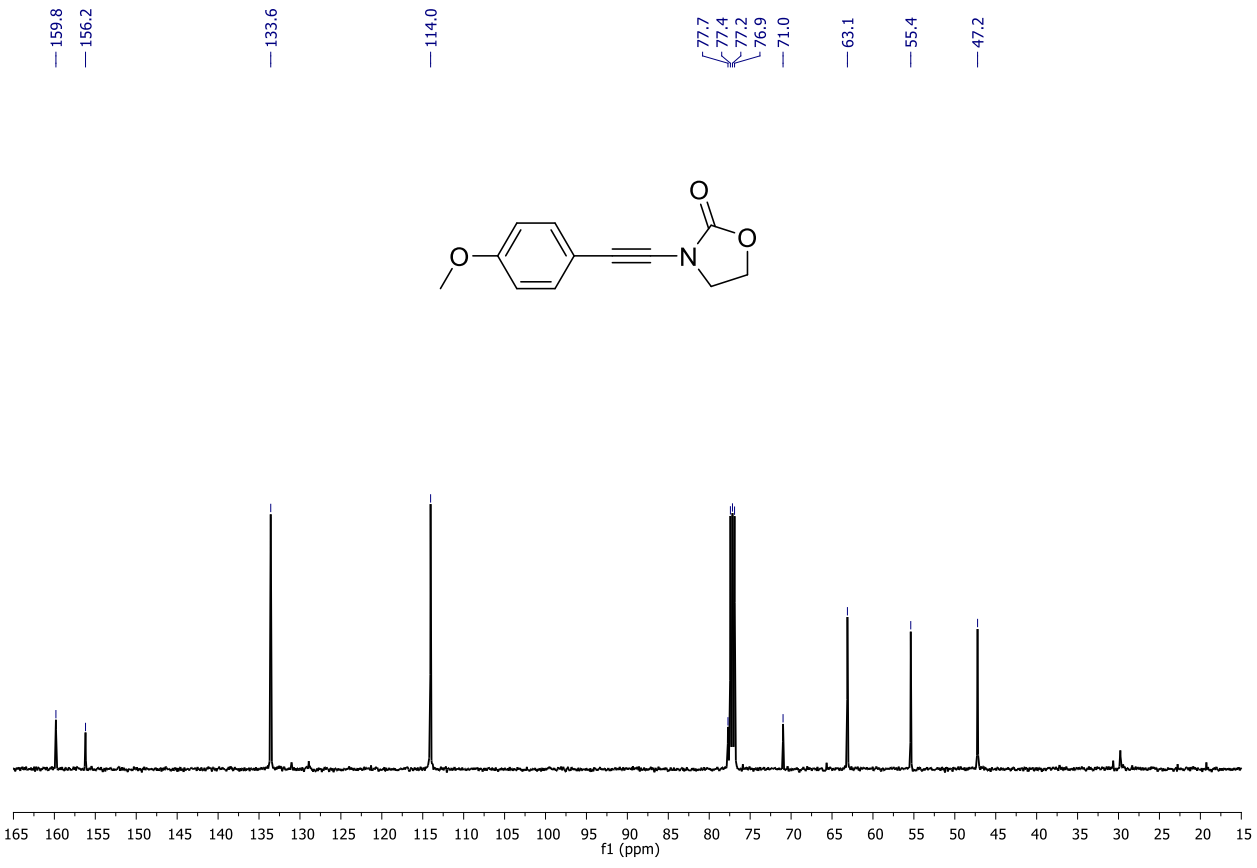
3-(p-tolylethynyl)oxazolidin-2-one (5b):



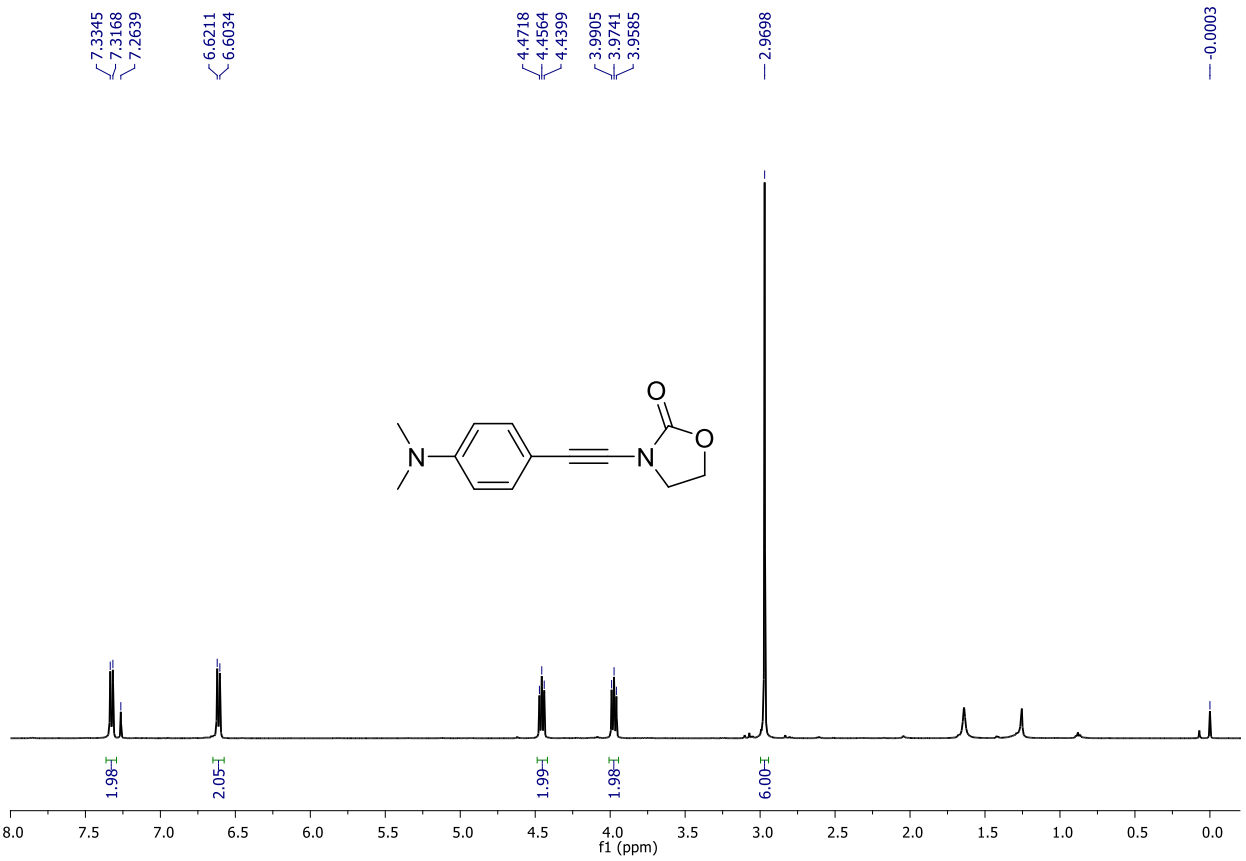


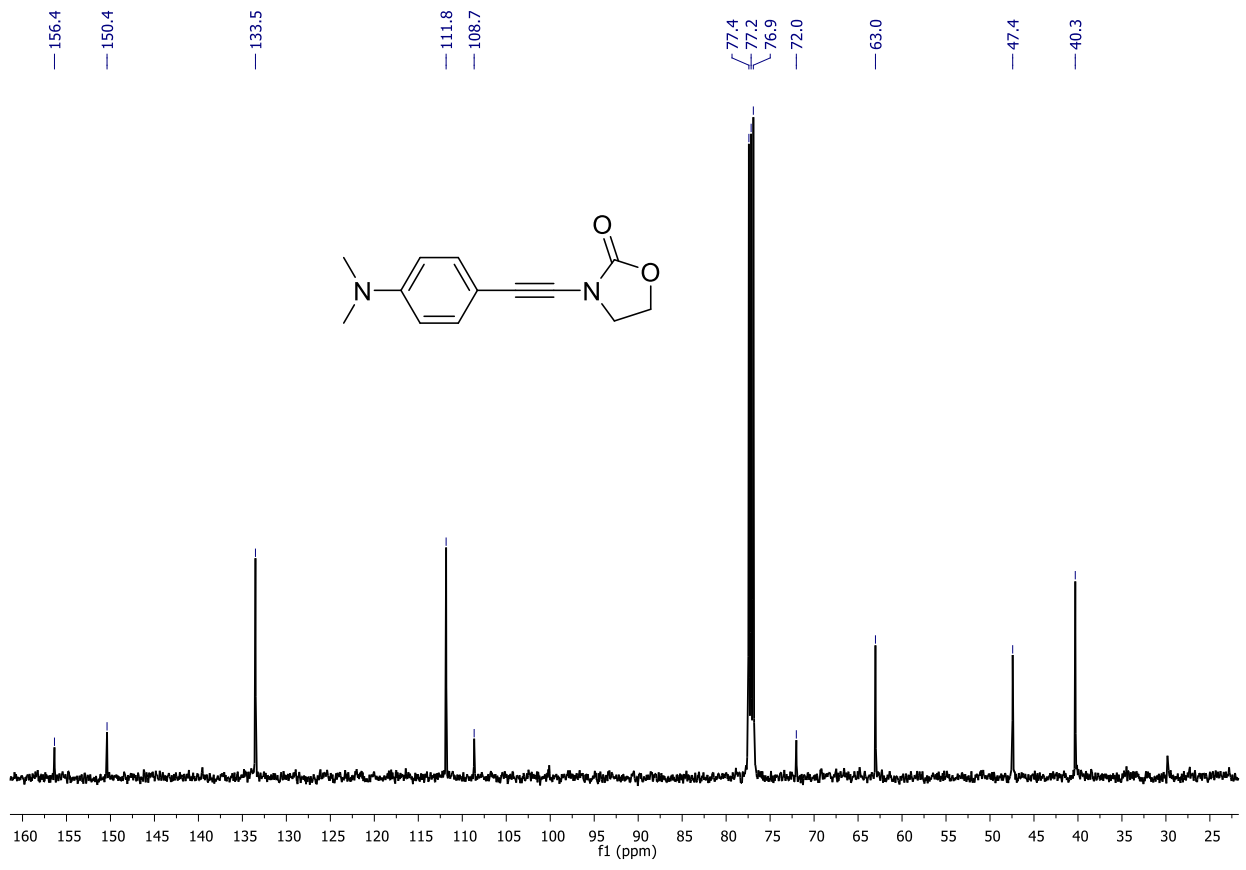
3-(4-methoxyphenylethynyl)oxazolidin-2-one (5c):



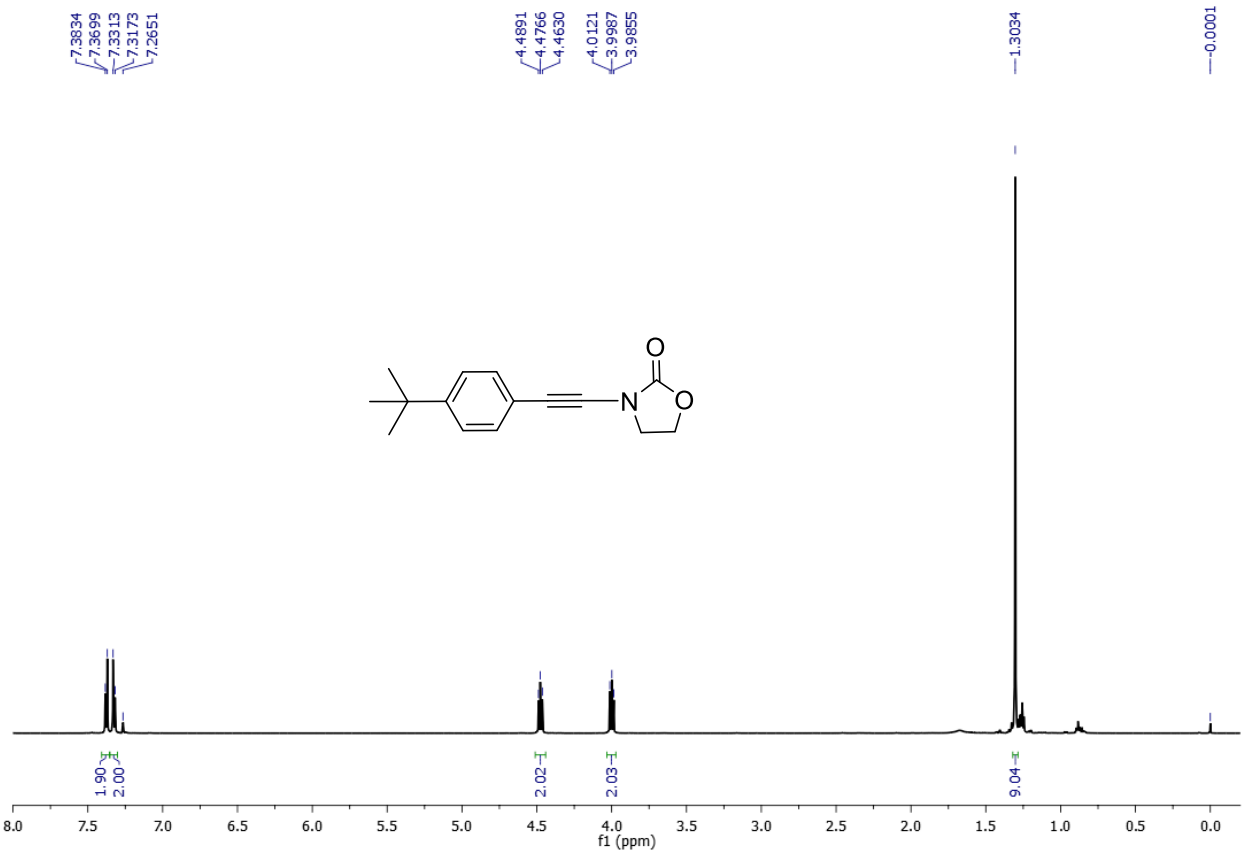


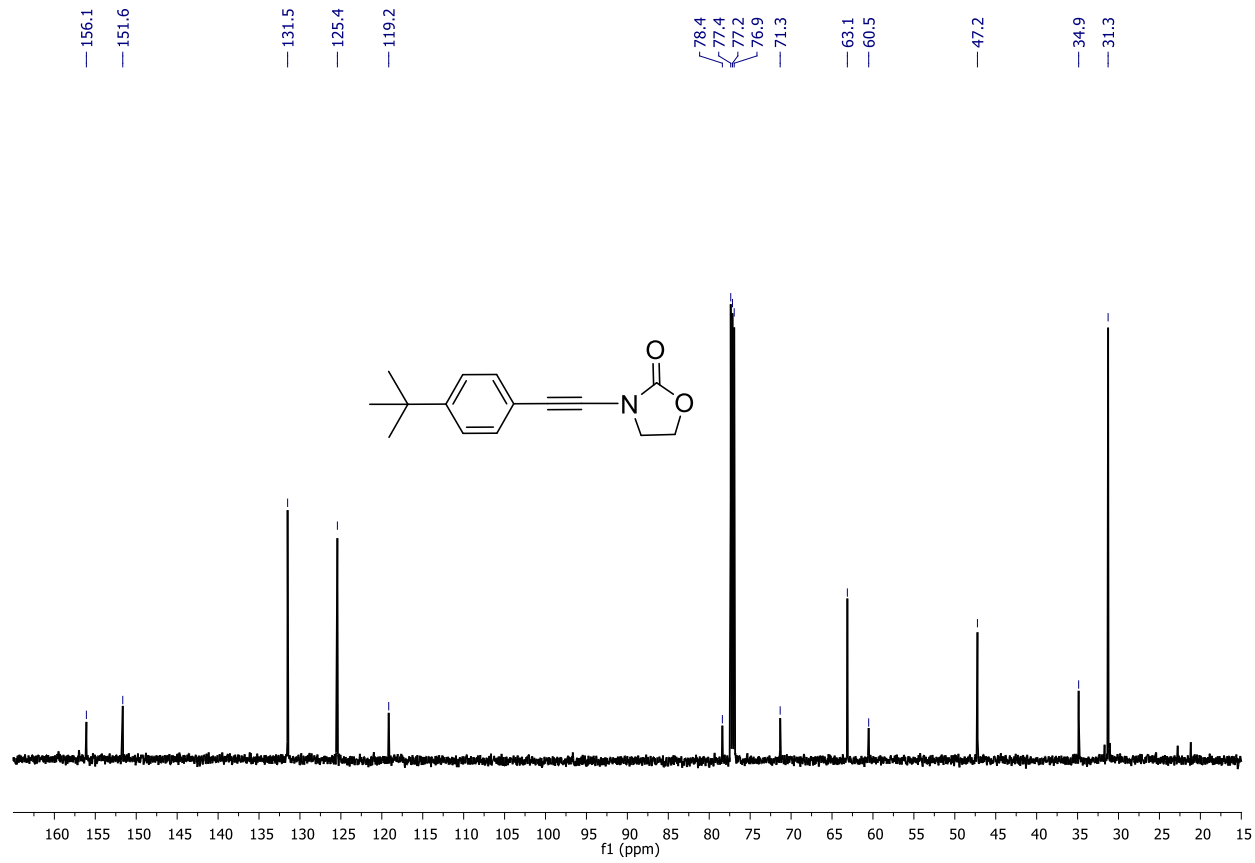
3-(4-N,N-dimethylaminophenylethynyl)oxazolidin-2-one (5d):



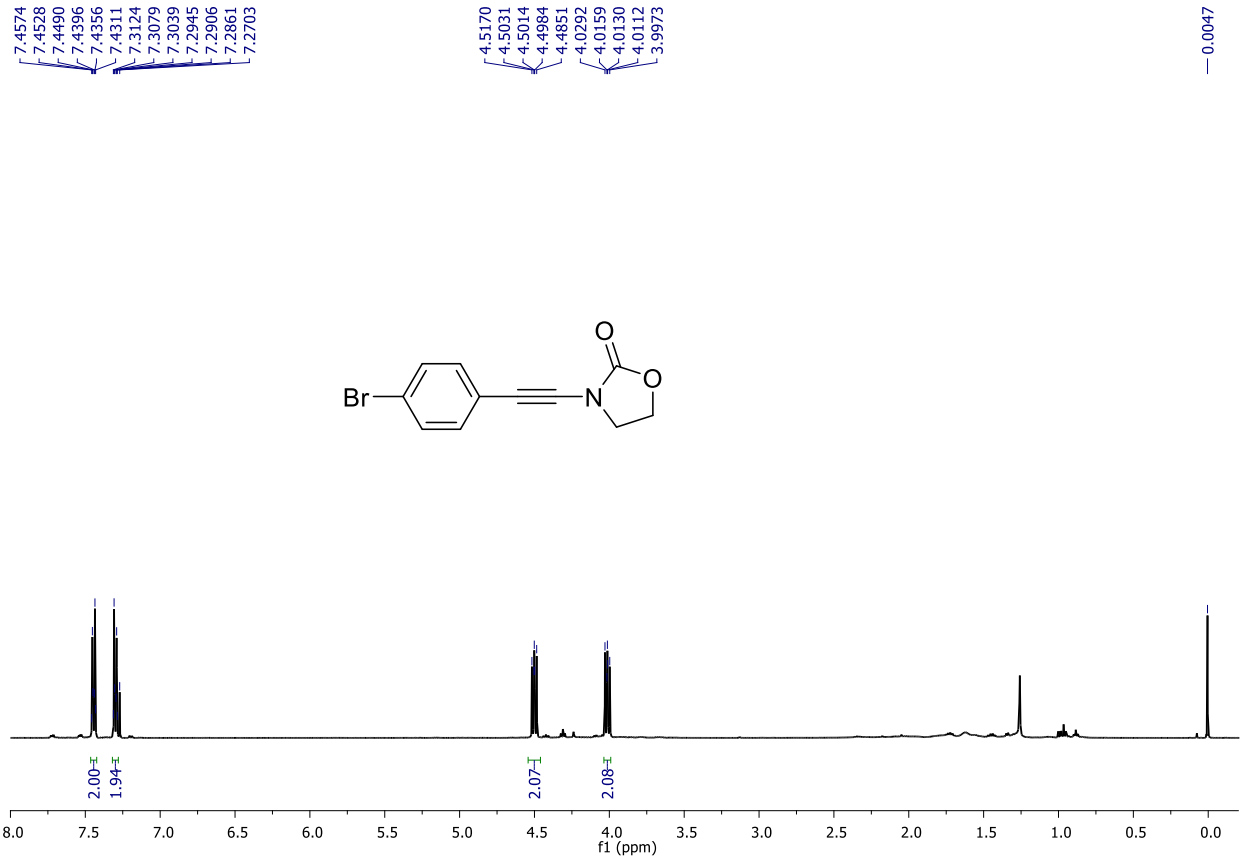


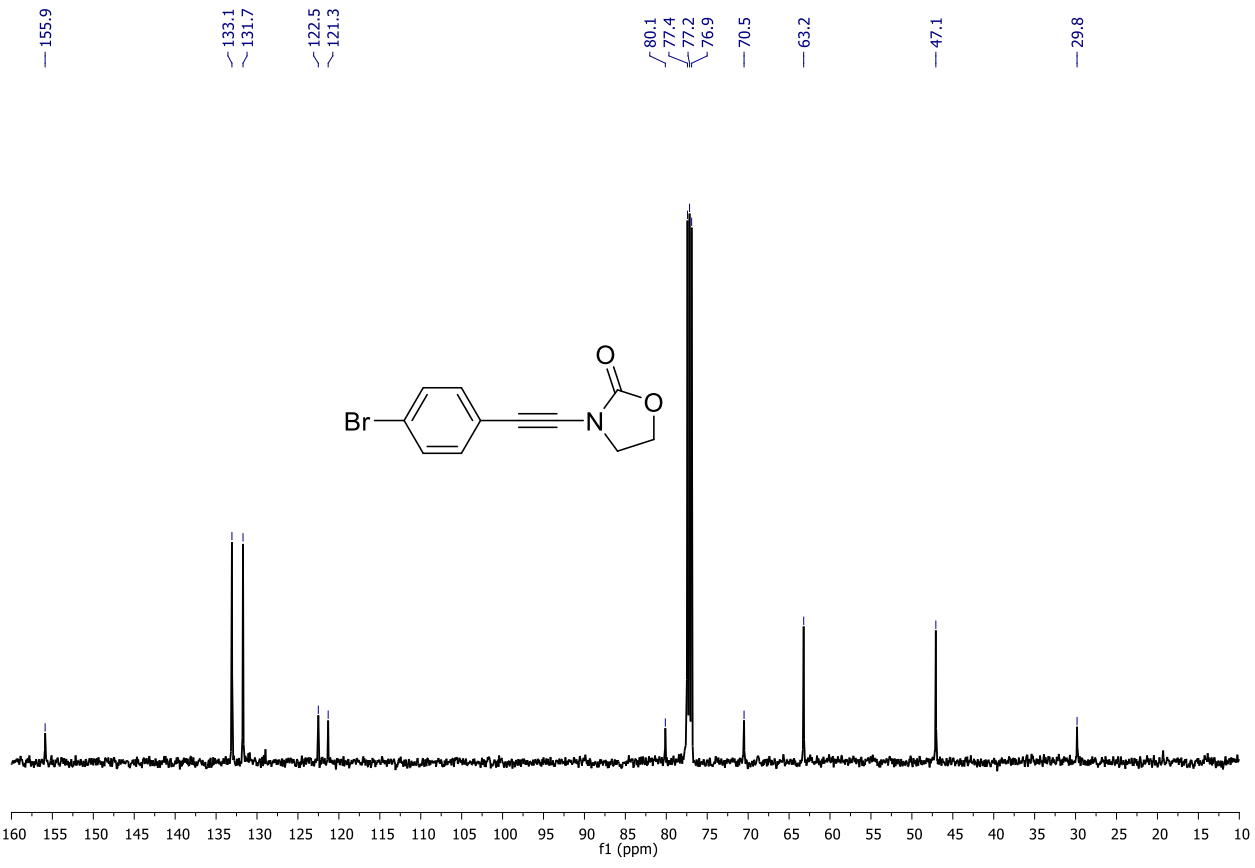
3-(4-*tert*-butylphenylethynyl)oxazolidin-2-one (5e):



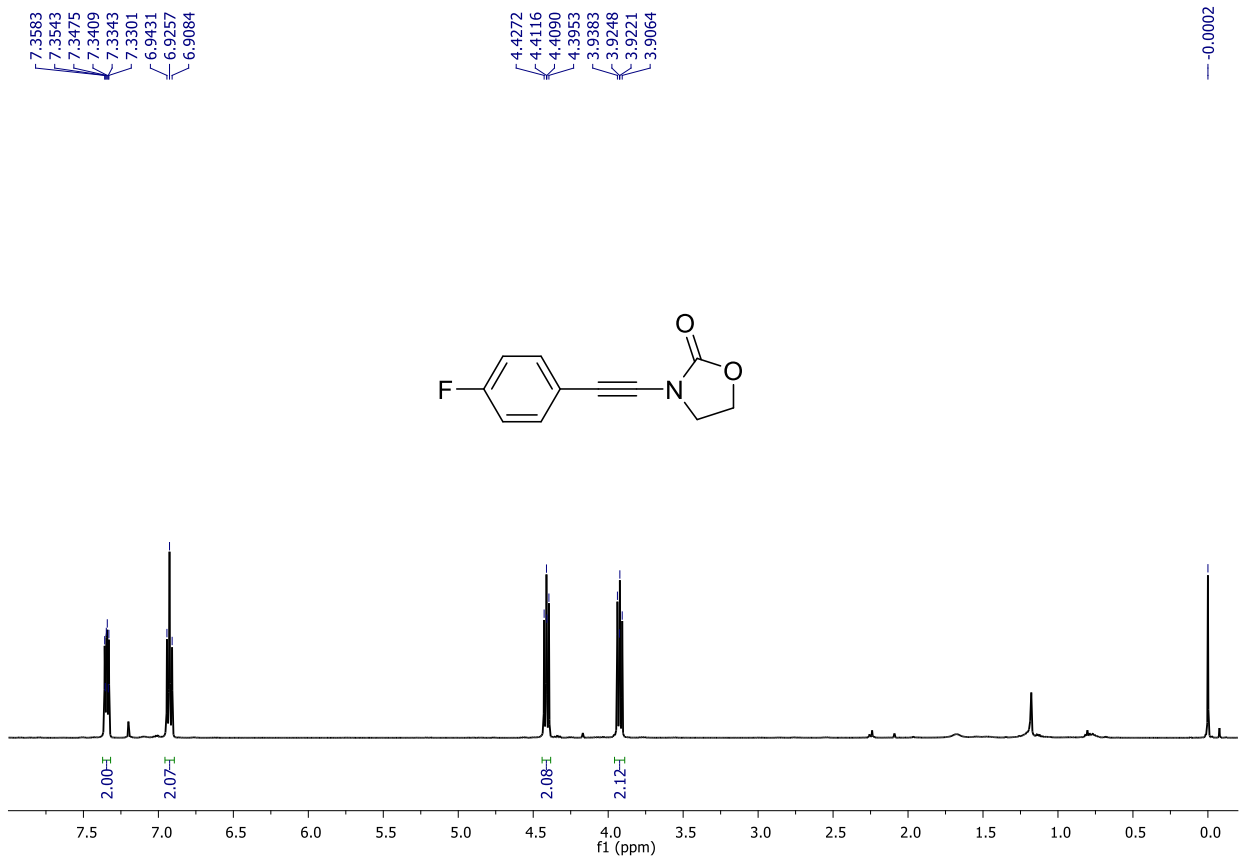


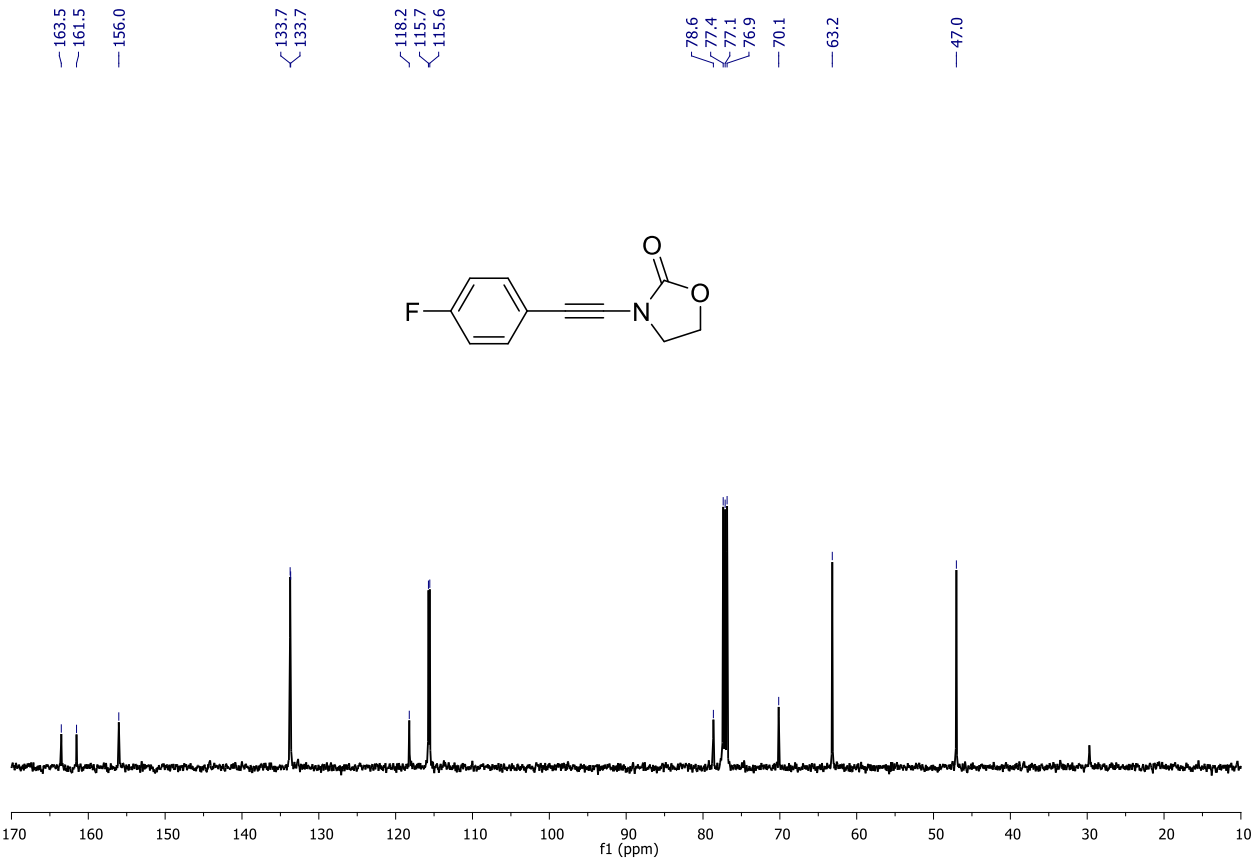
3-(4-bromophenylethynyl)oxazolidin-2-one (5f):



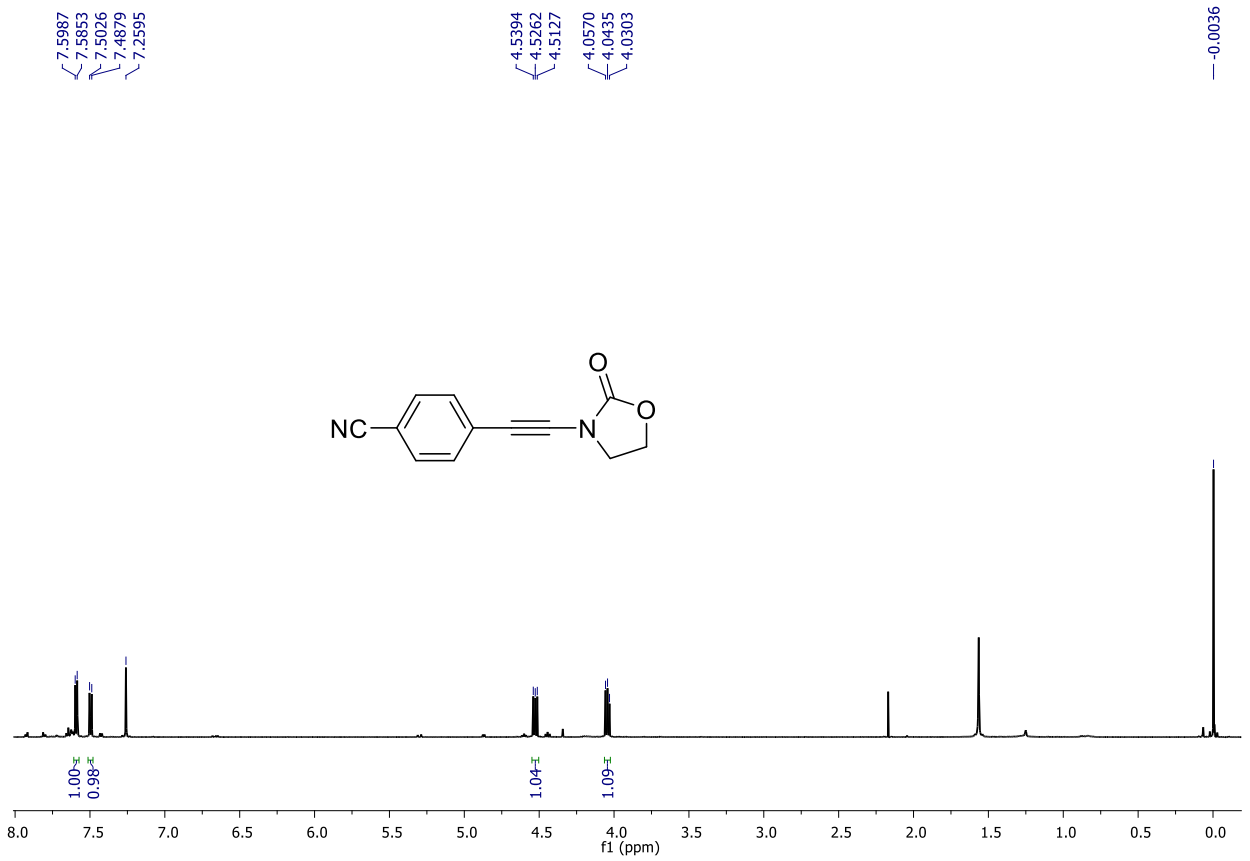


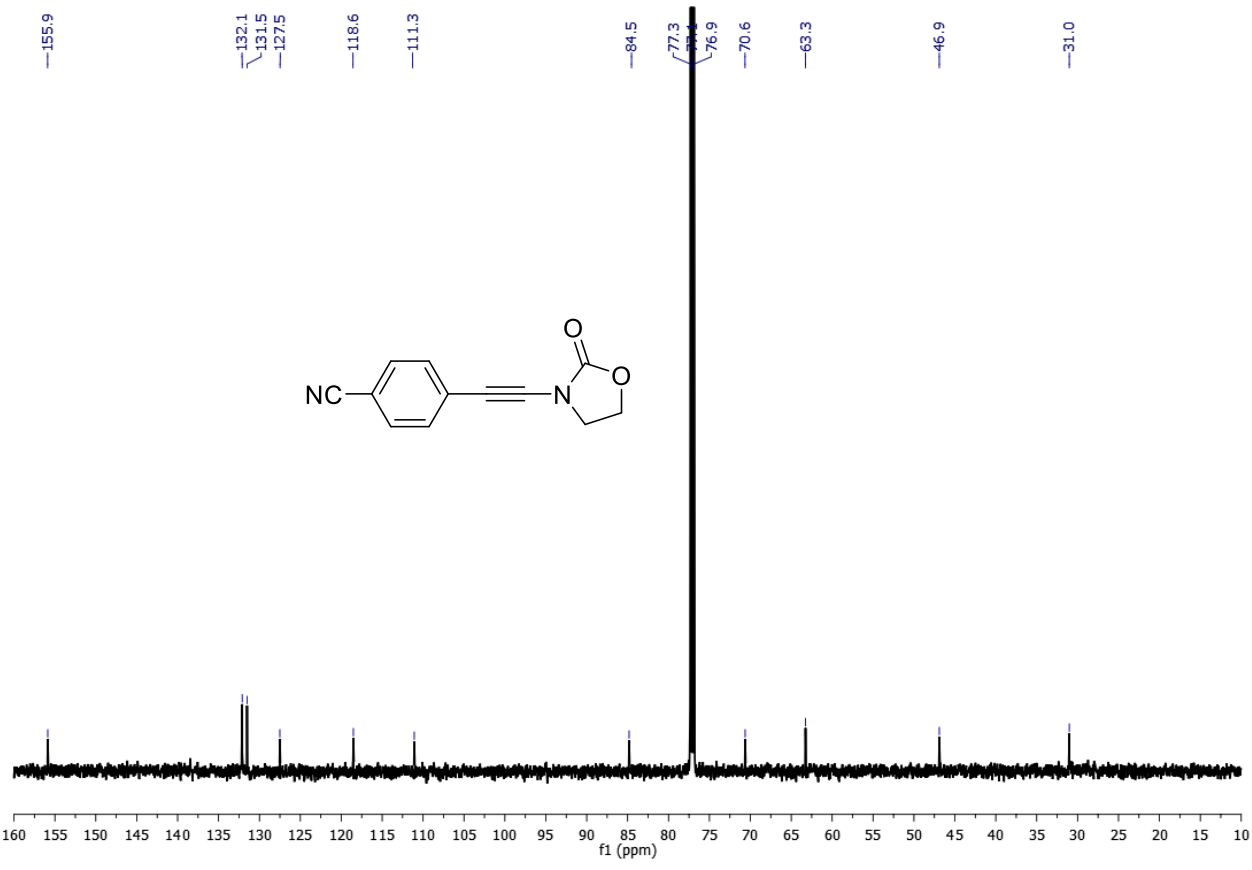
3-(4-fluorophenylethynyl)oxazolidin-2-one (5g):



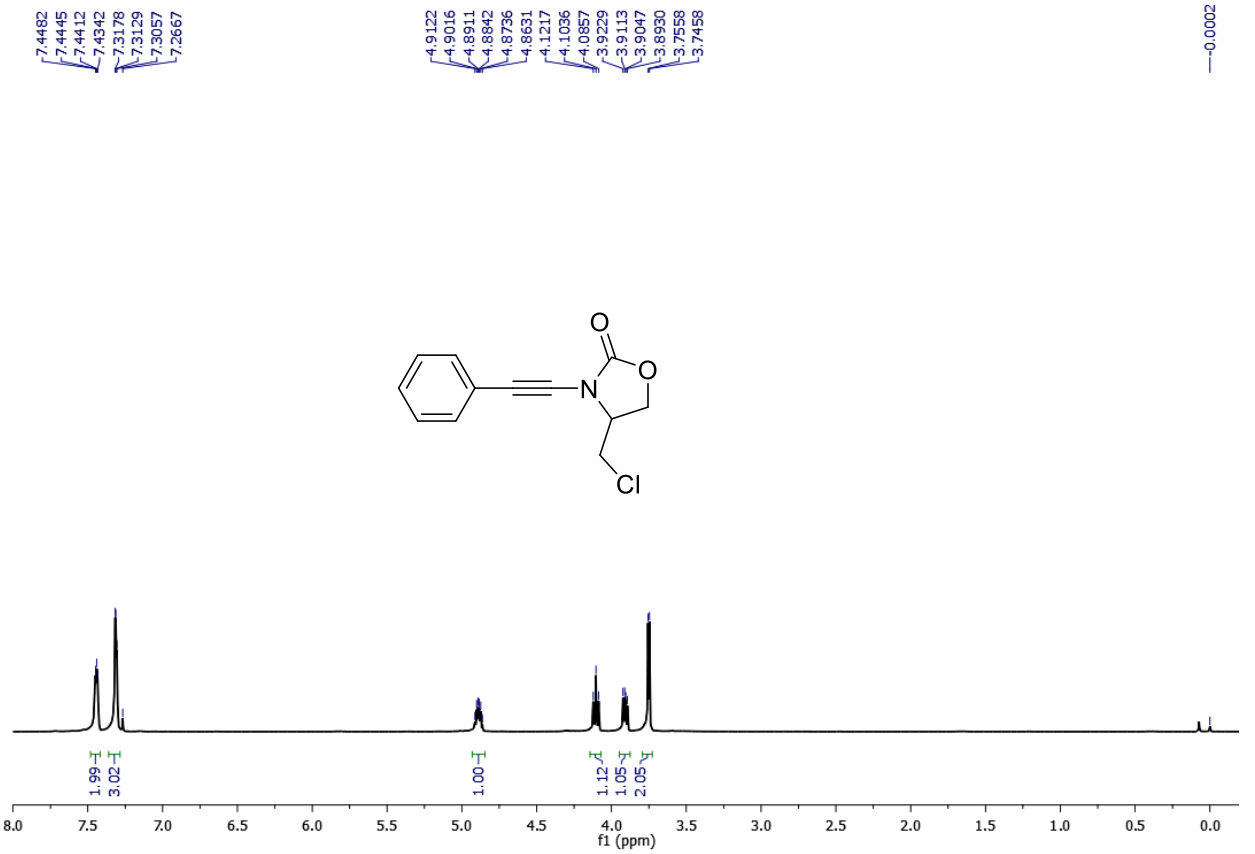


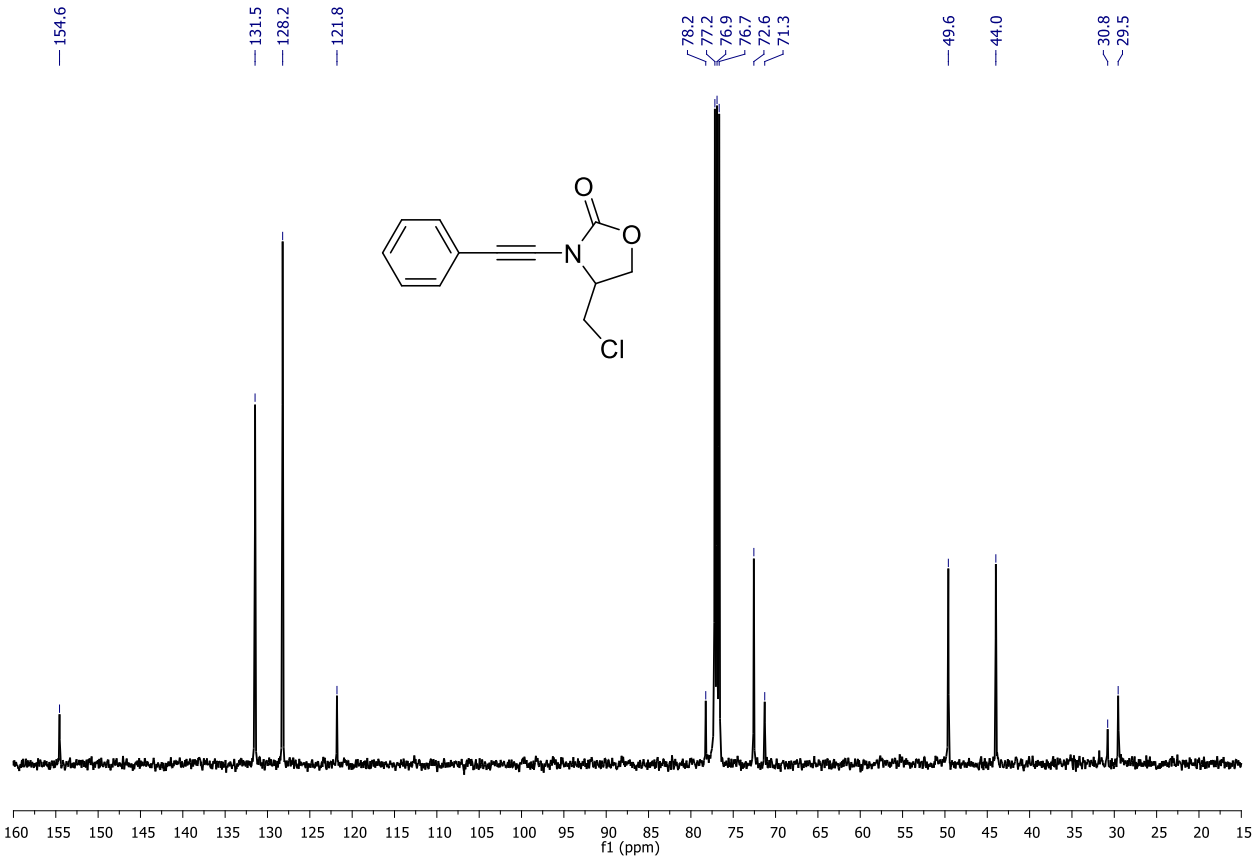
3-(4-cyanophenylethynyl)oxazolidin-2-one (5h):


7.5987
7.5853
7.5026
7.4879
7.2595
4.5394
4.5262
4.5127
4.0570
4.0435
4.0303
-0.0036
NC
O
O
N
1.00
0.98
1.04
1.09
f1 (ppm)

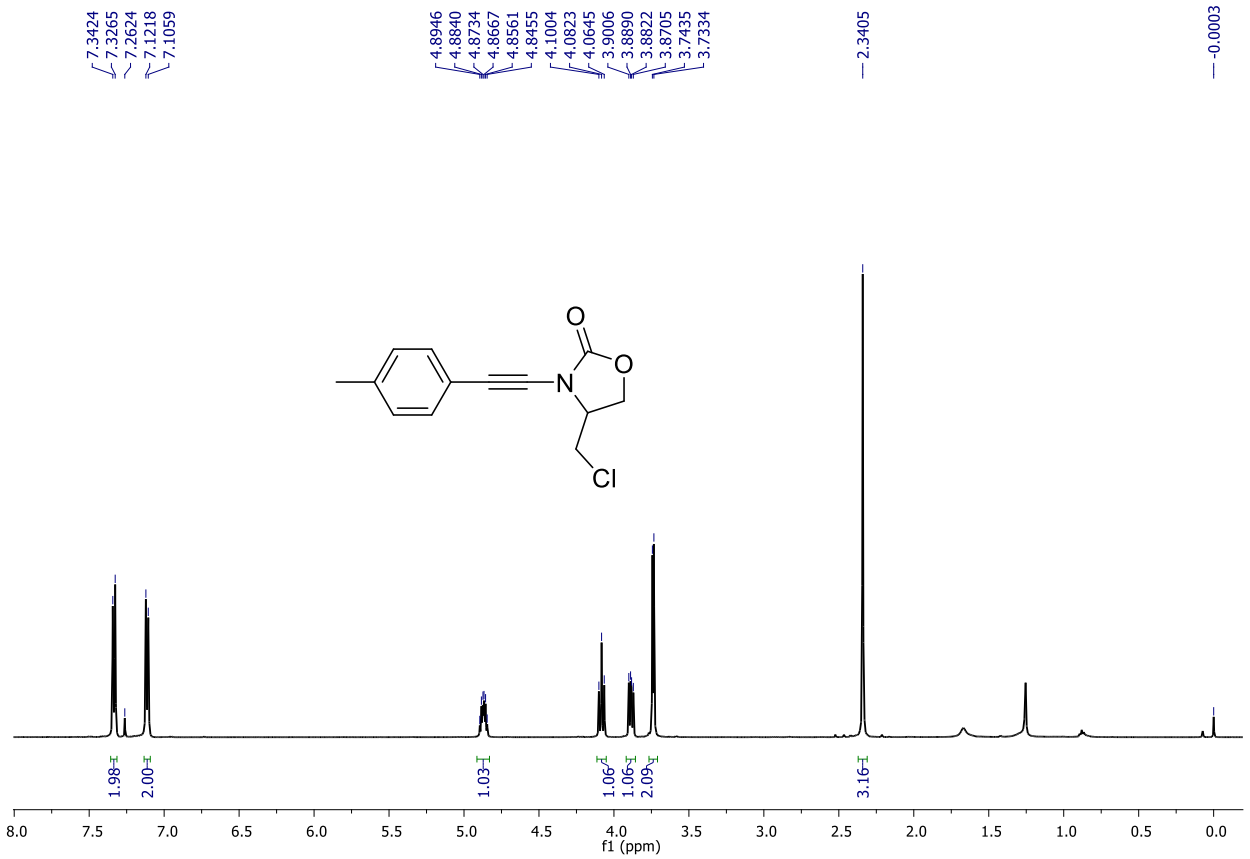

155.9
132.1
131.5
127.5
118.6
111.3
84.5
77.3
76.9
70.6
63.3
46.9
31.0
NC
O
O
N
f1 (ppm)

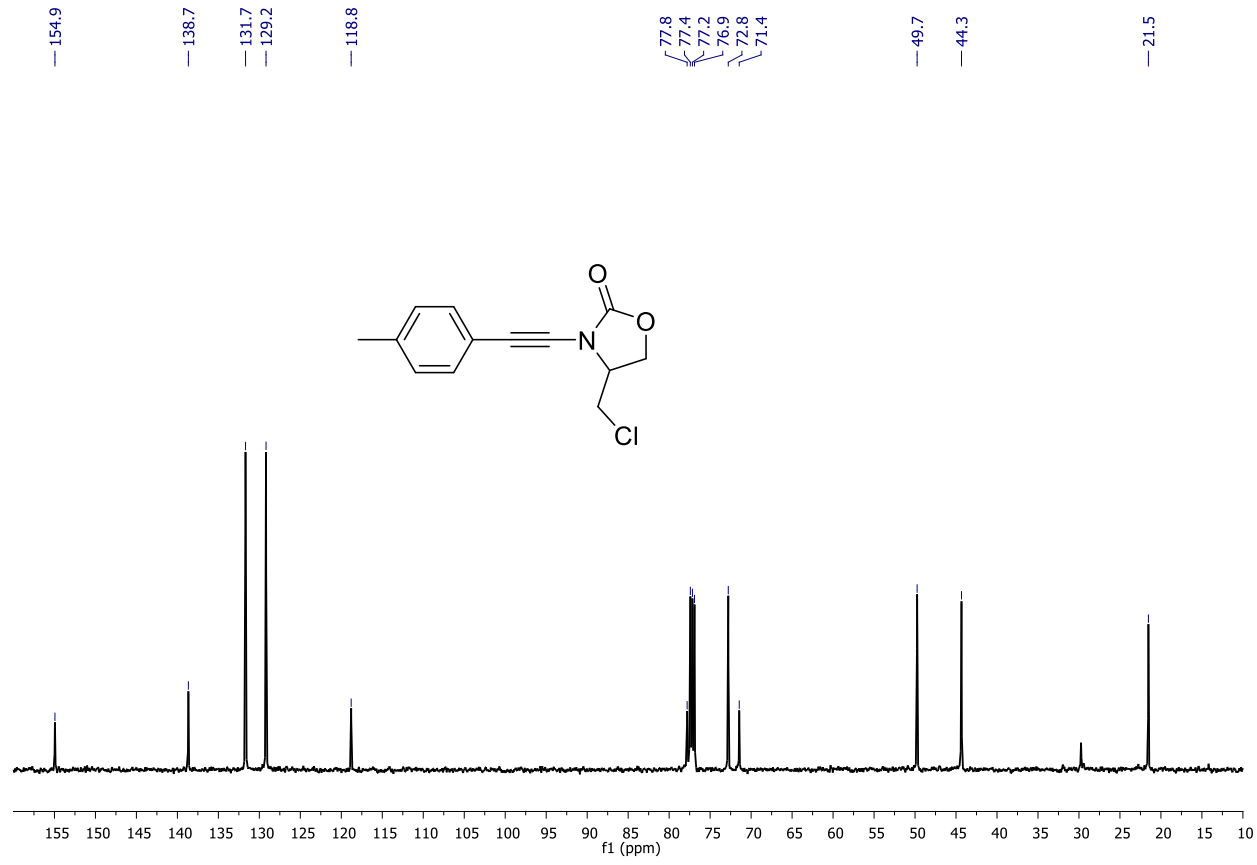
4-(chloromethyl)-3-(phenylethynyl)oxazolidin-2-one (5i):



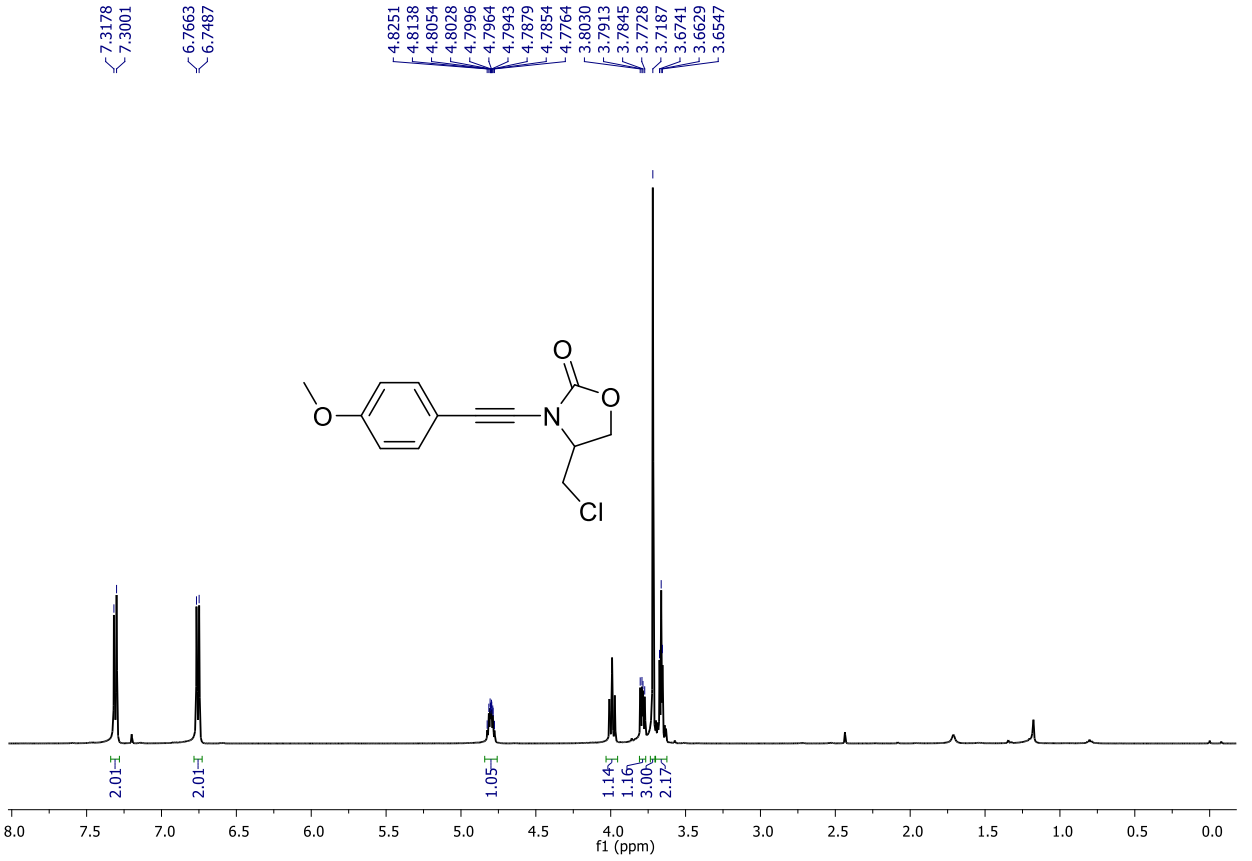


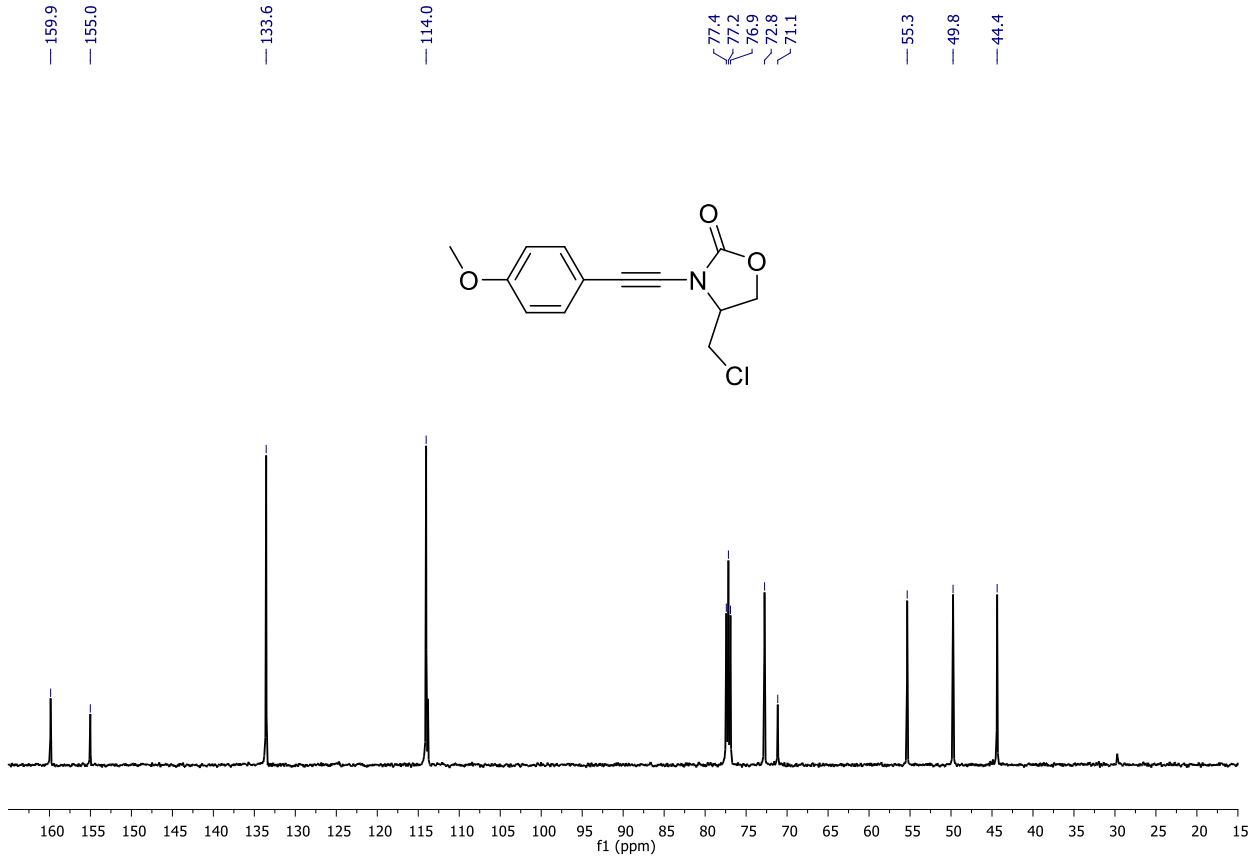
4-(chloromethyl)-3-(p-tolylethynyl)oxazolidin-2-one (5j):



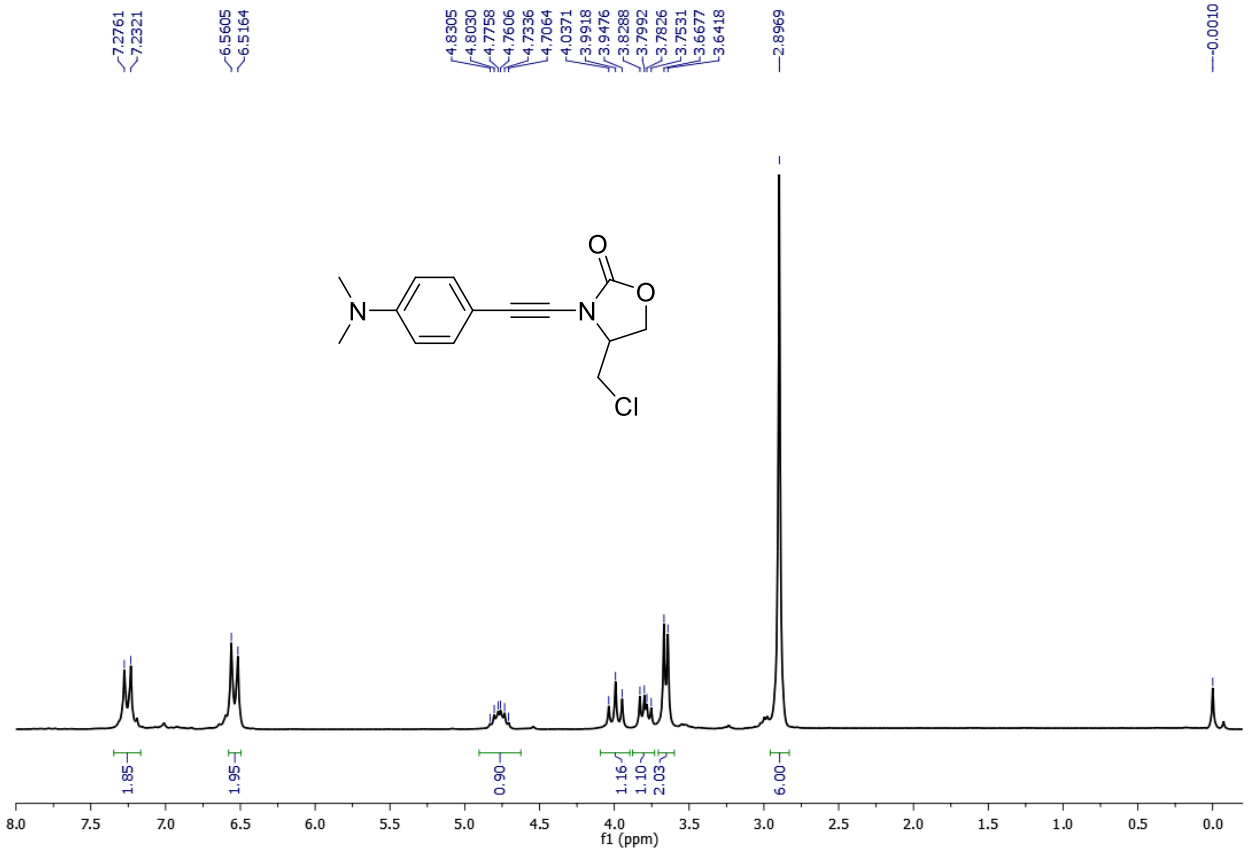


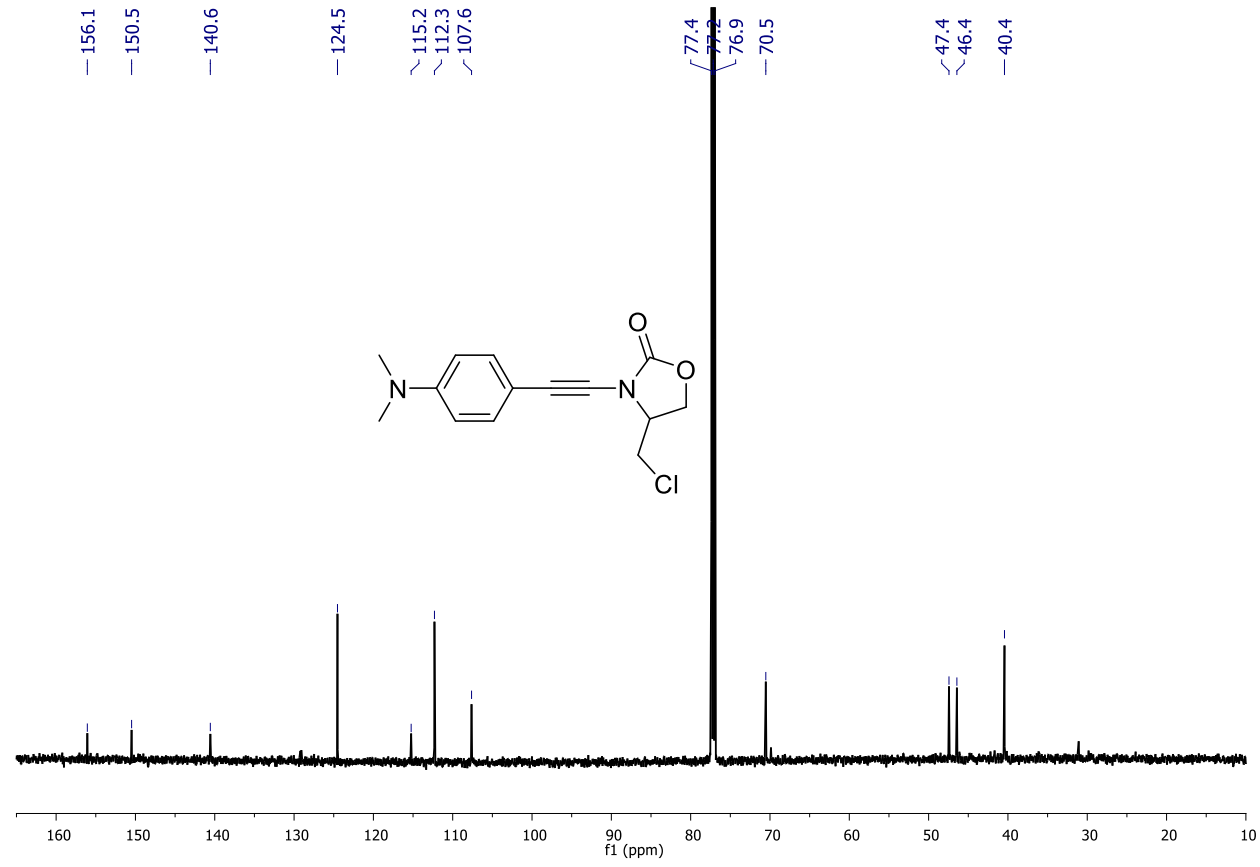
4-(chloromethyl)-3-(4-methoxyphenylethynyl)oxazolidin-2-one (5k):



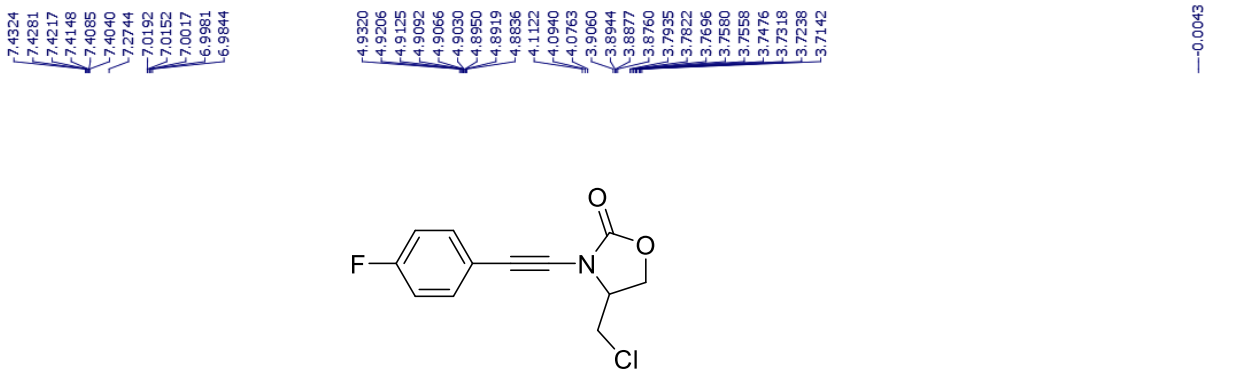


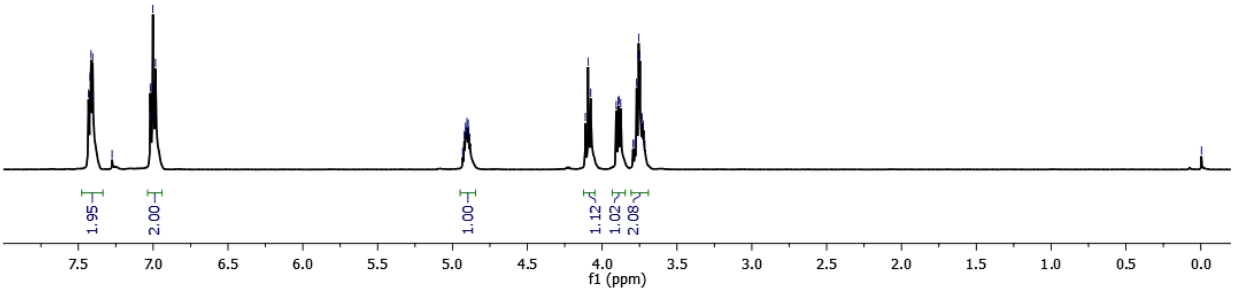
4-(chloromethyl)-3-(4-N,N-dimethylaminophenylethynyl)oxazolidin-2-one (5l):

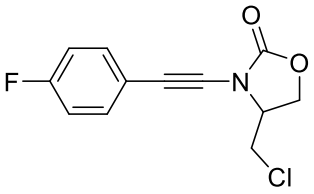


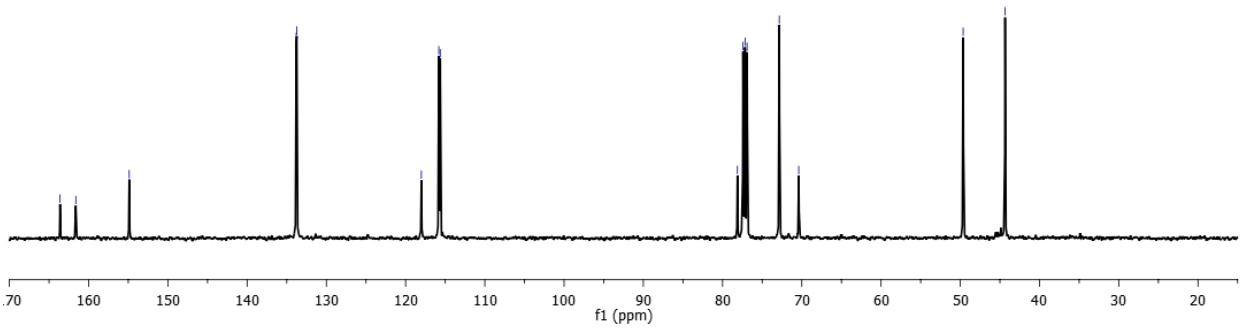


4-(chloromethyl)-3-(4-fluorophenylethynyl)oxazolidin-2-one (5m):

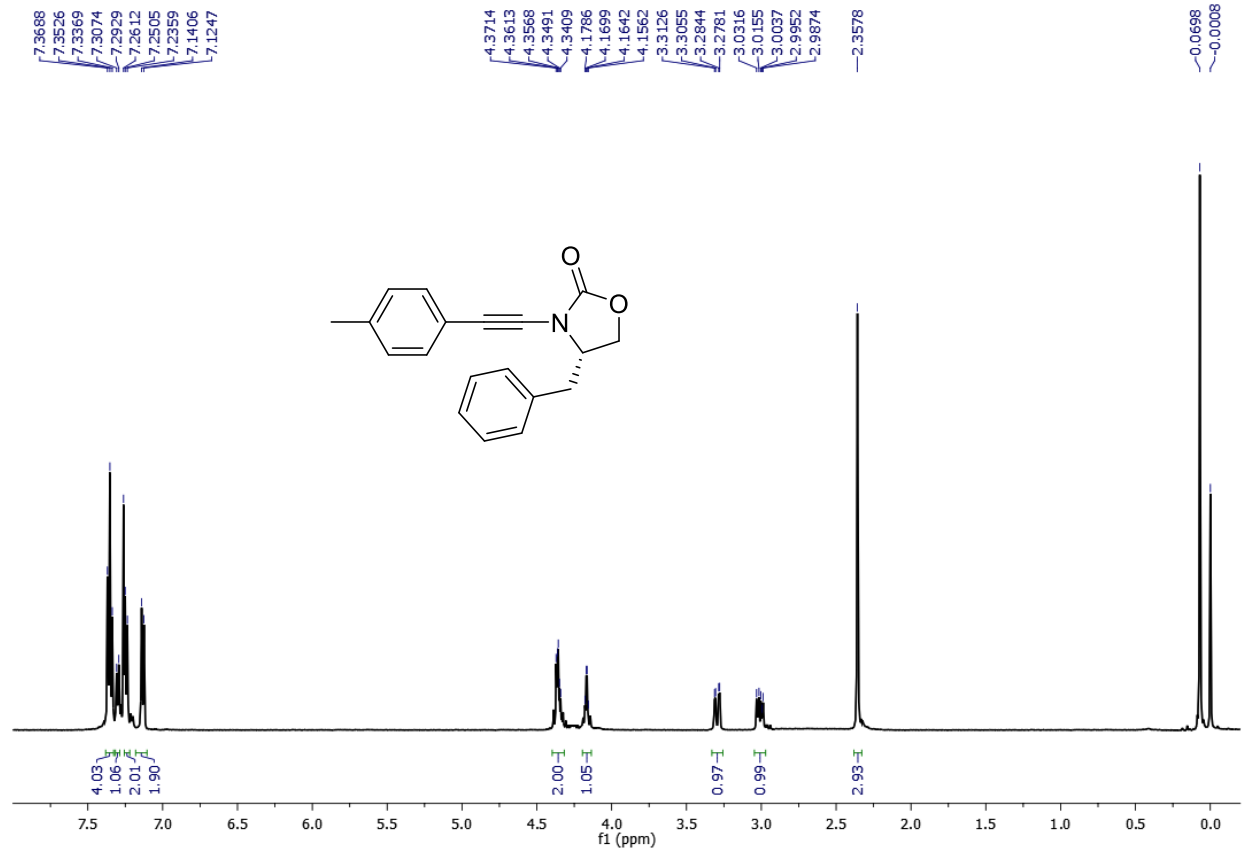


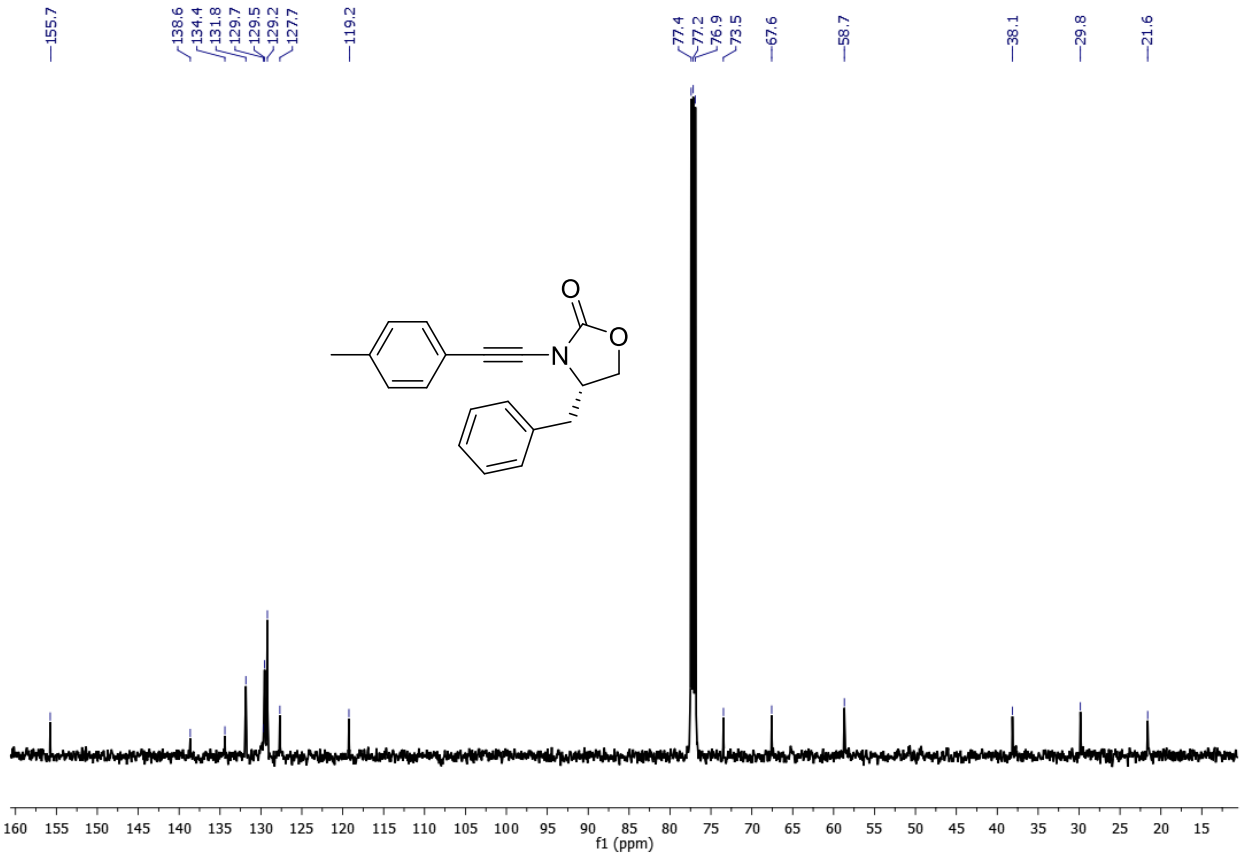




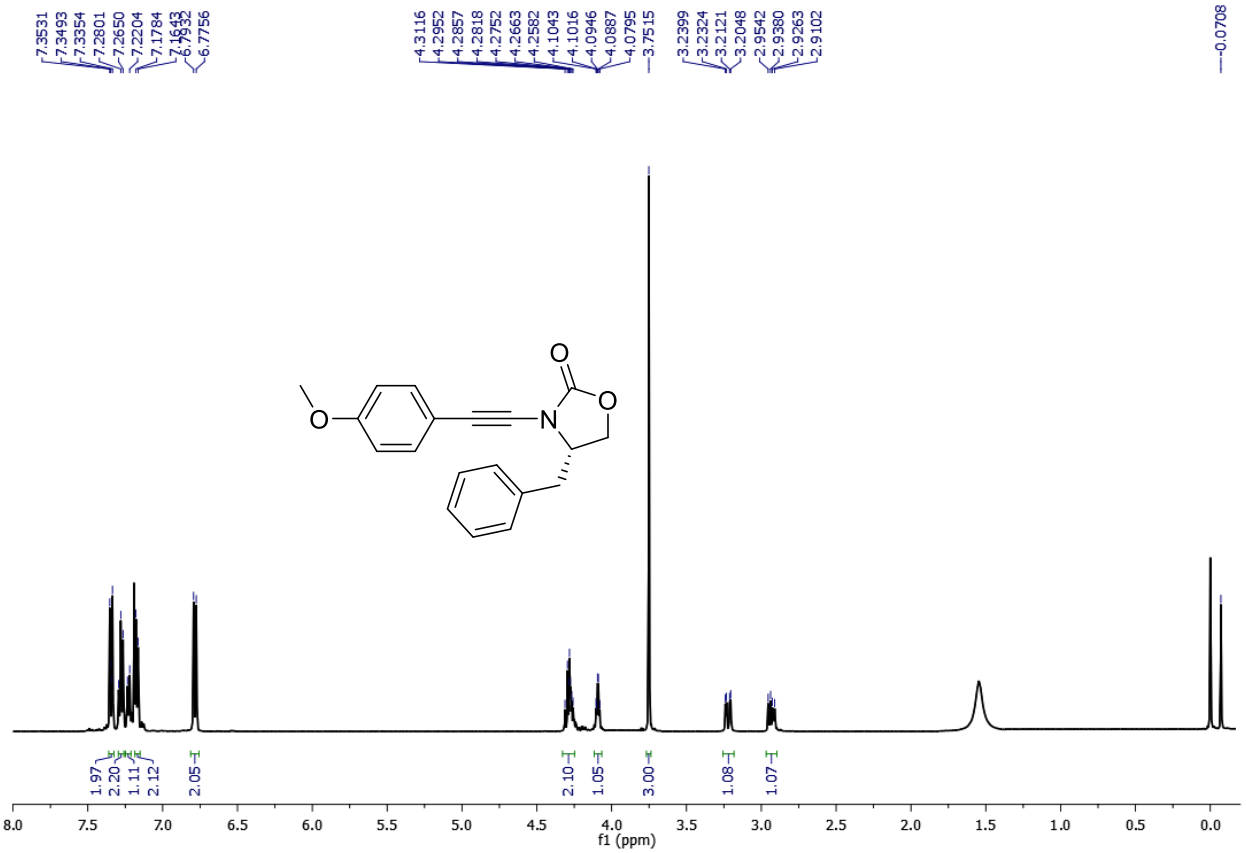


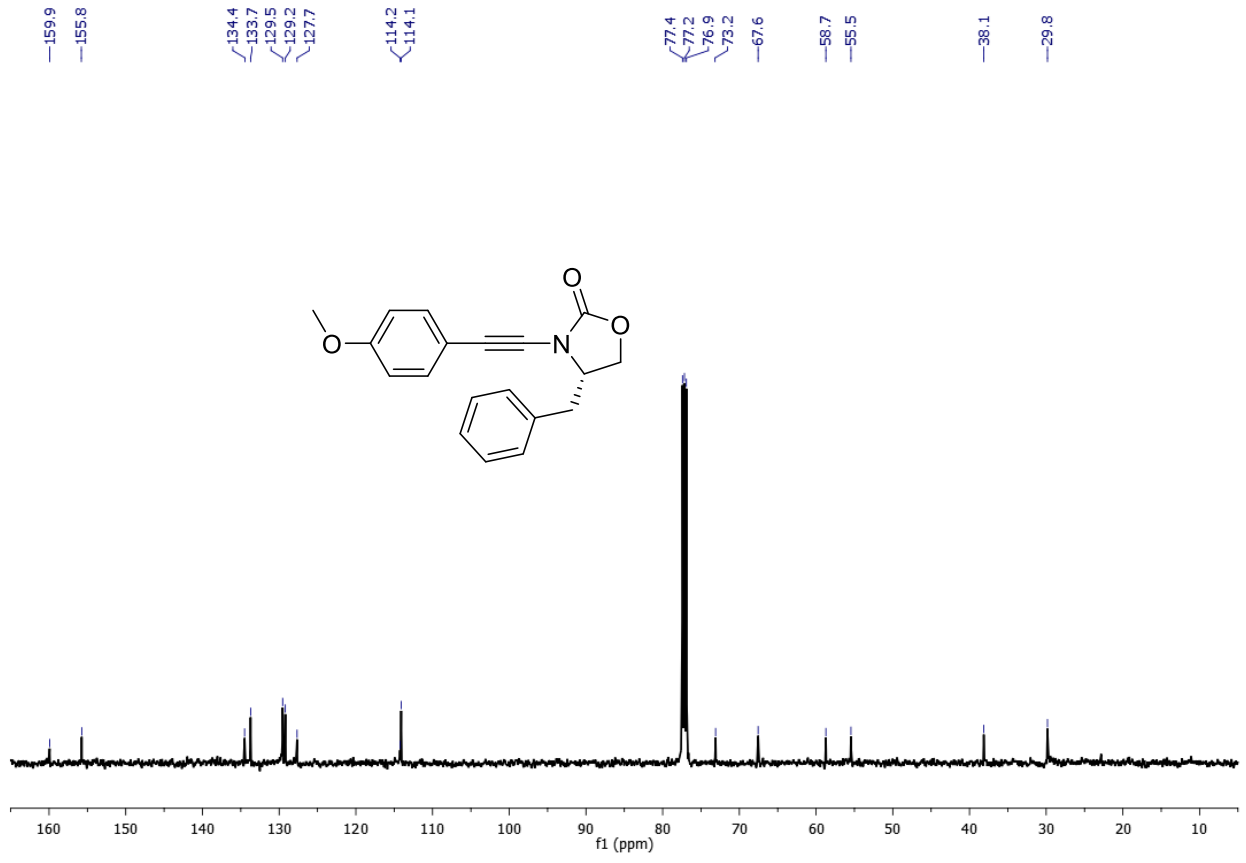
(*S*) 4-Benzyl-3-(4-methylphenylethynyl)oxazolidin-2-one (5n):



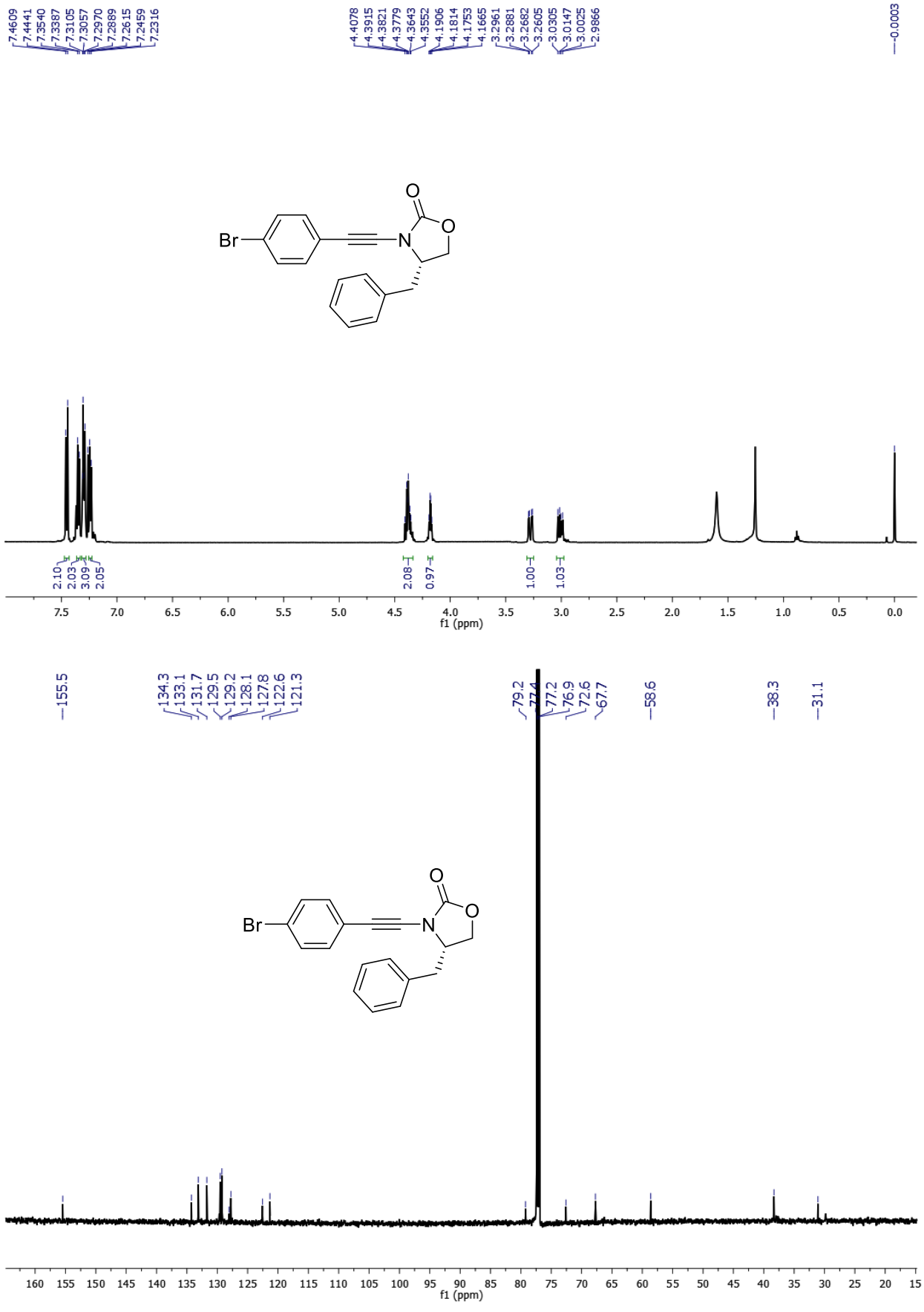


(*S*) 4-Benzyl-3-(4-methoxyphenylethynyl)oxazolidin-2-one (5o):

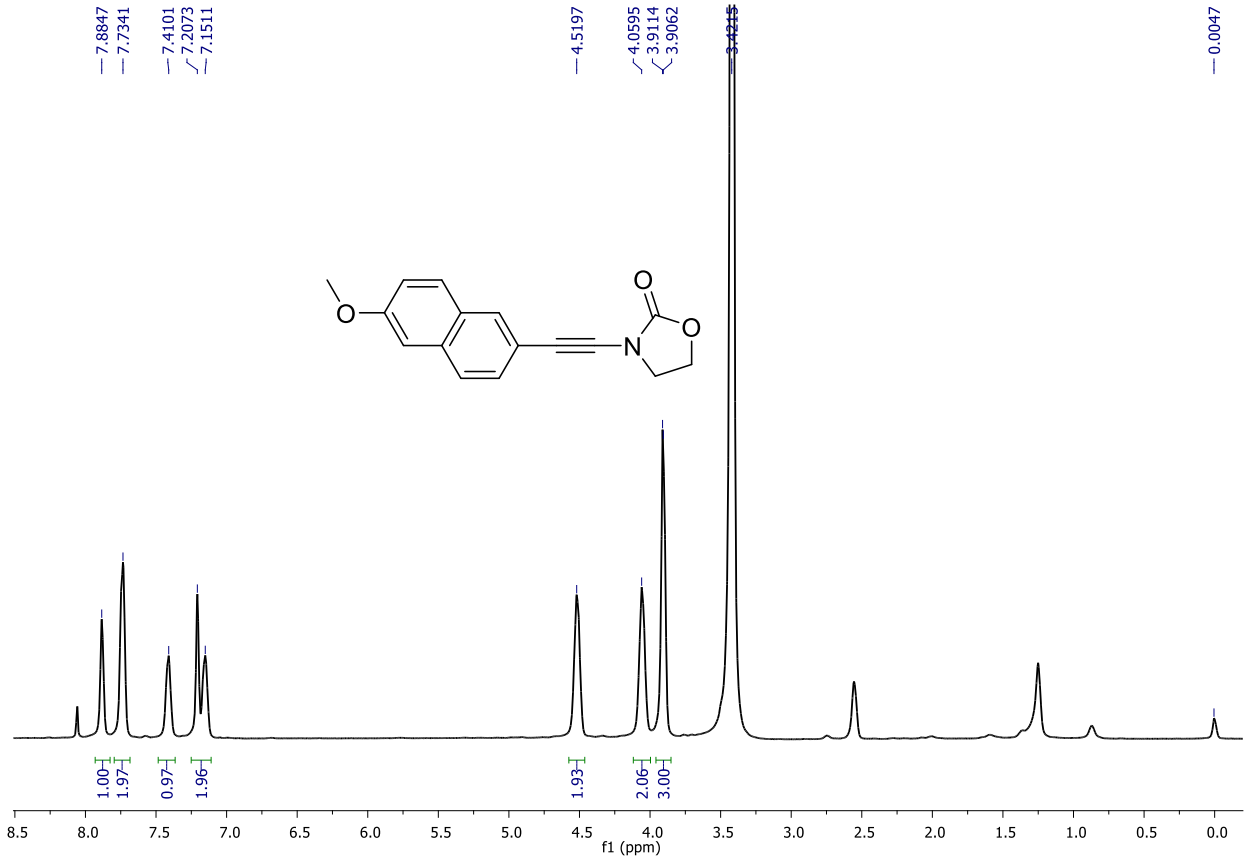


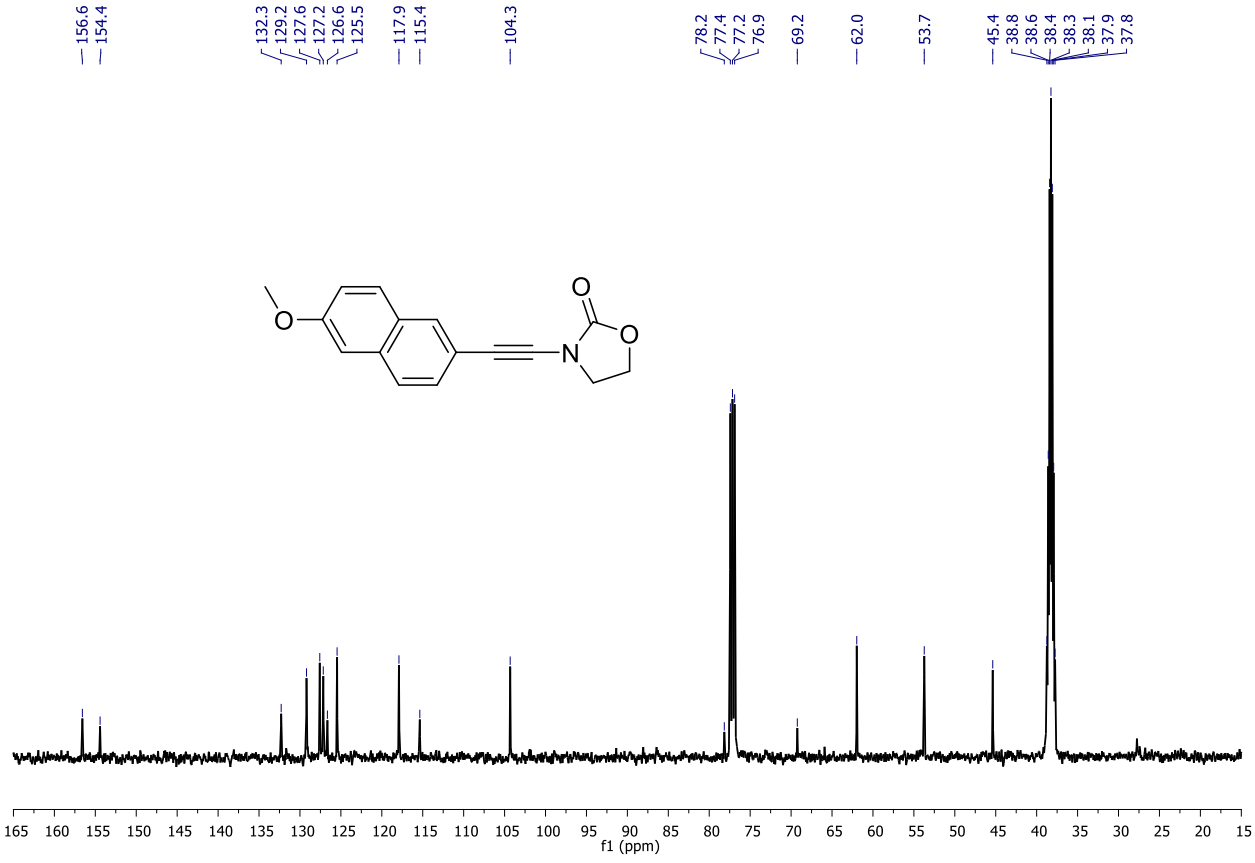


(*S*)4-Benzyl-3-(4-bromophenylethynyl)oxazolidin-2-one (5p):

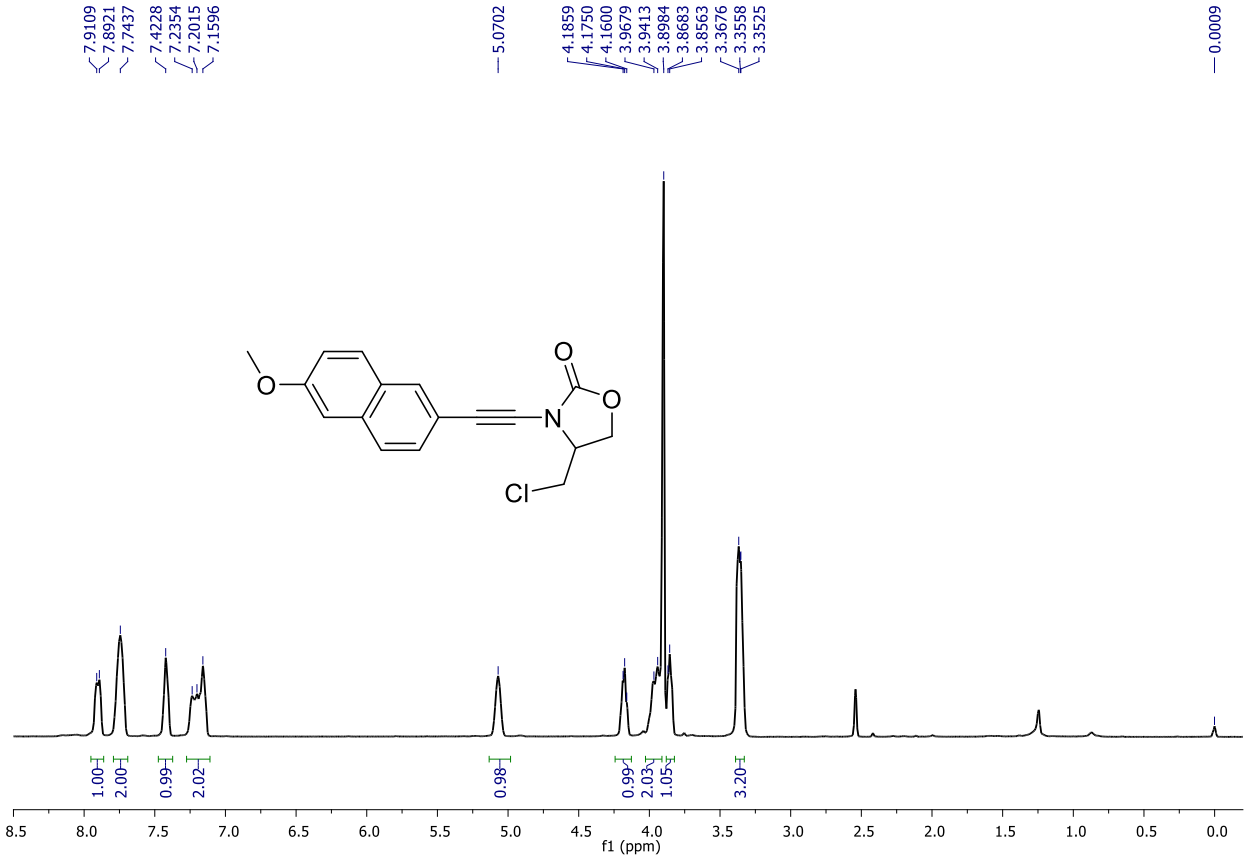


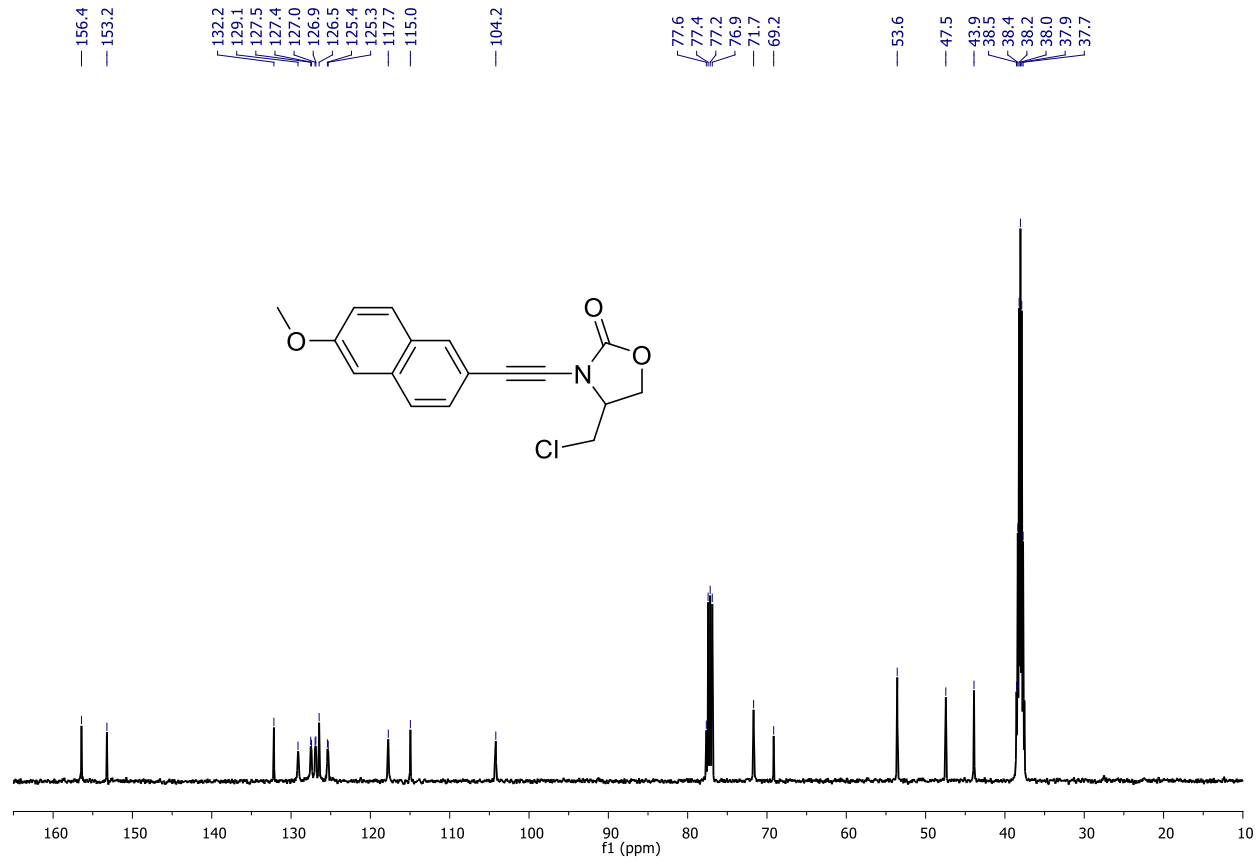
3[(6-methoxynaphthalen-2yl)ethynyl]oxazolidin-2-one (5q):



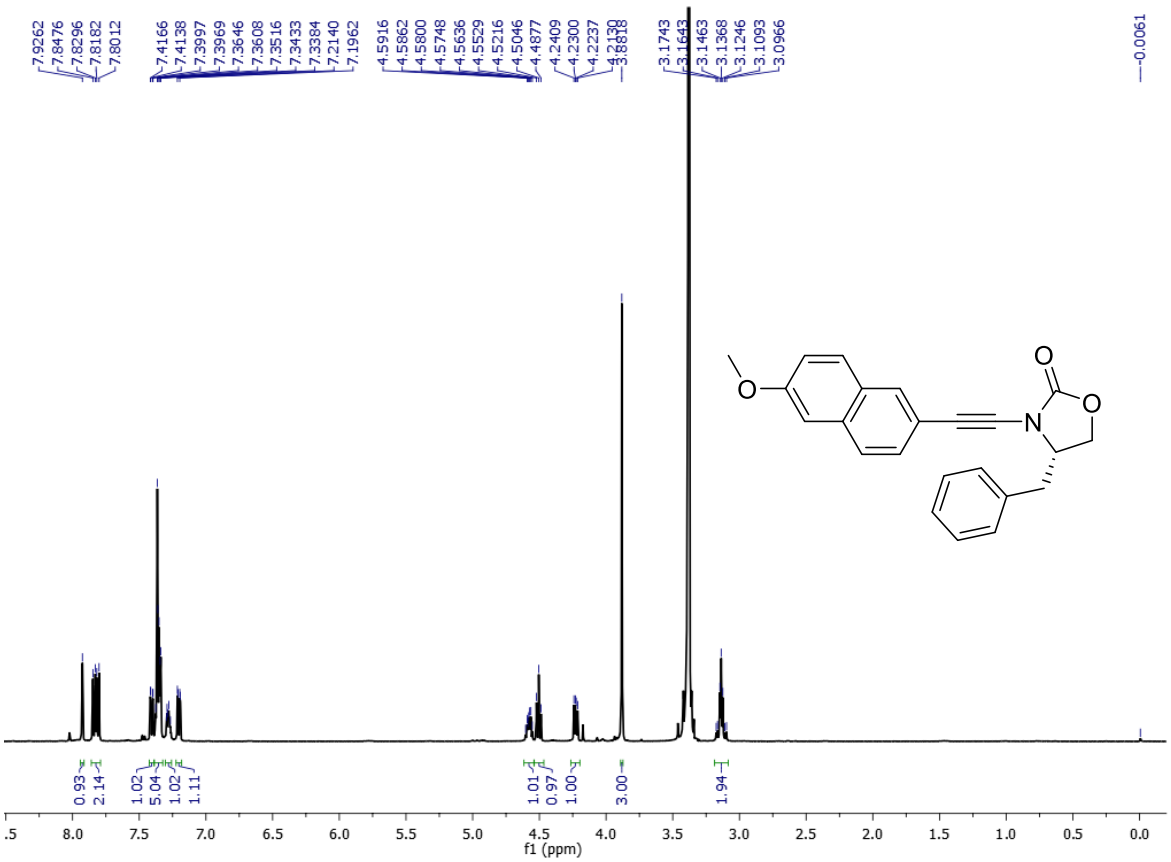


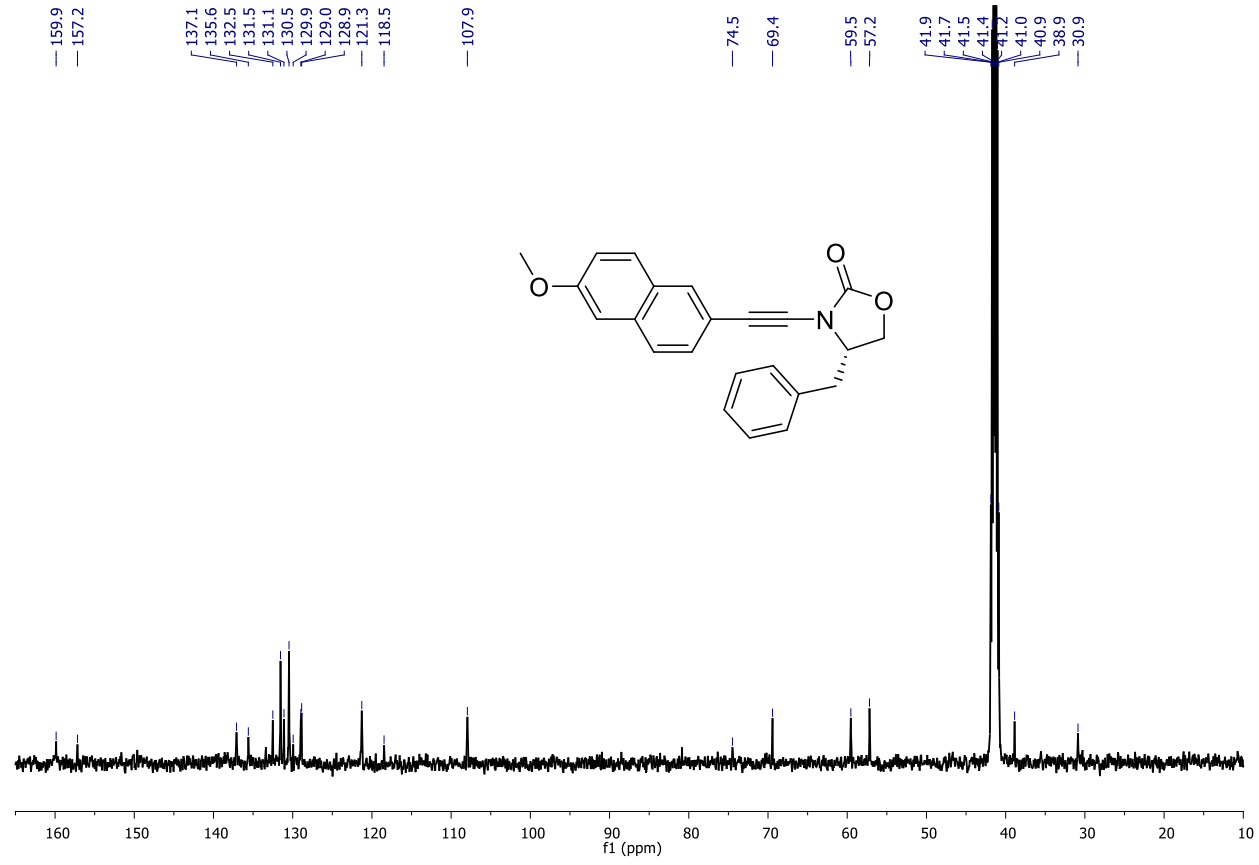
4-(chloromethyl)-3-[(6-methoxynaphthalen-2yl)ethynyl]oxazolidin-2-one (5r):



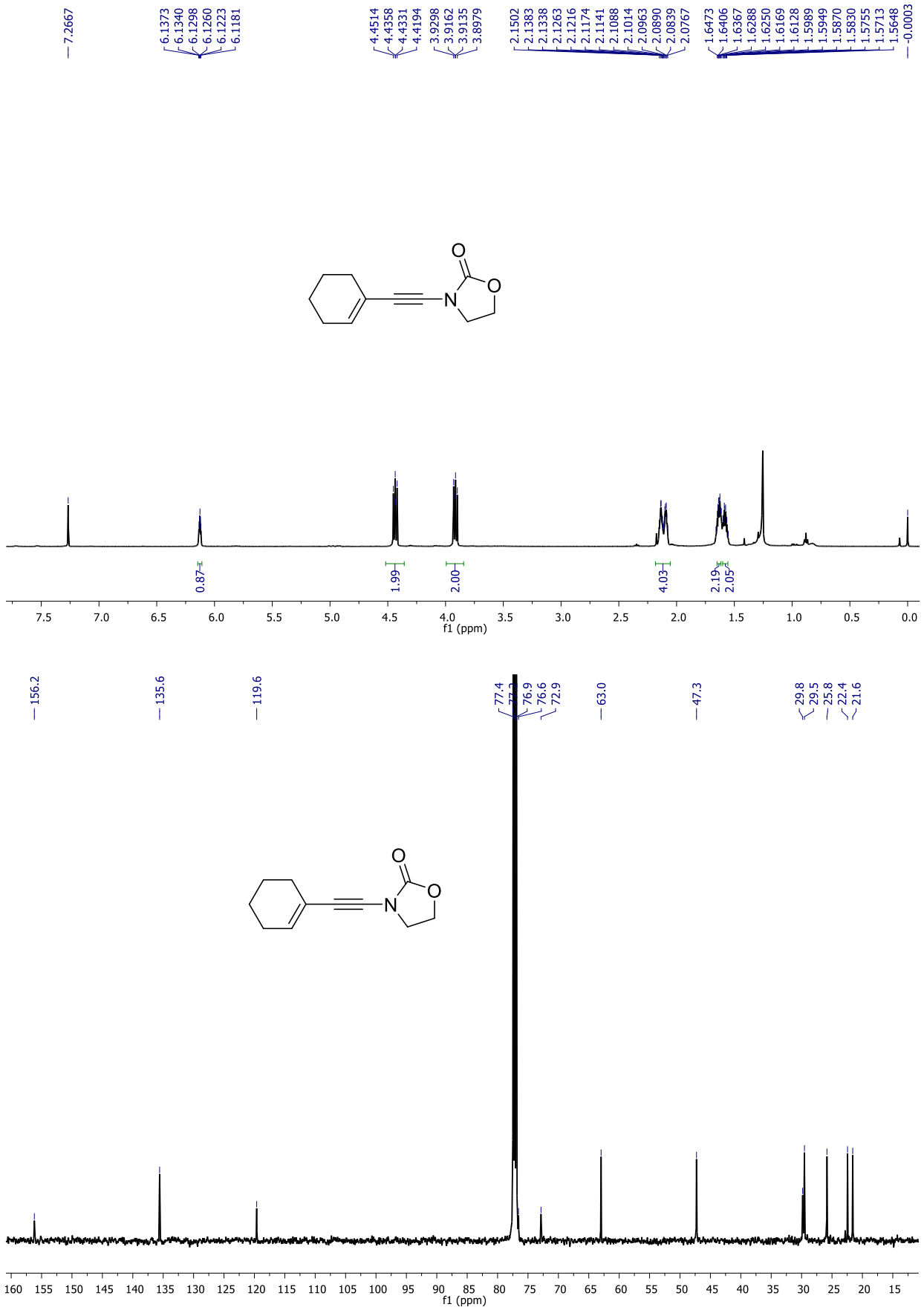


(*S*)4-Benzyl-3-[(6-methoxynaphthalen-2yl)ethynyl]oxazolidin-2-one (5s):

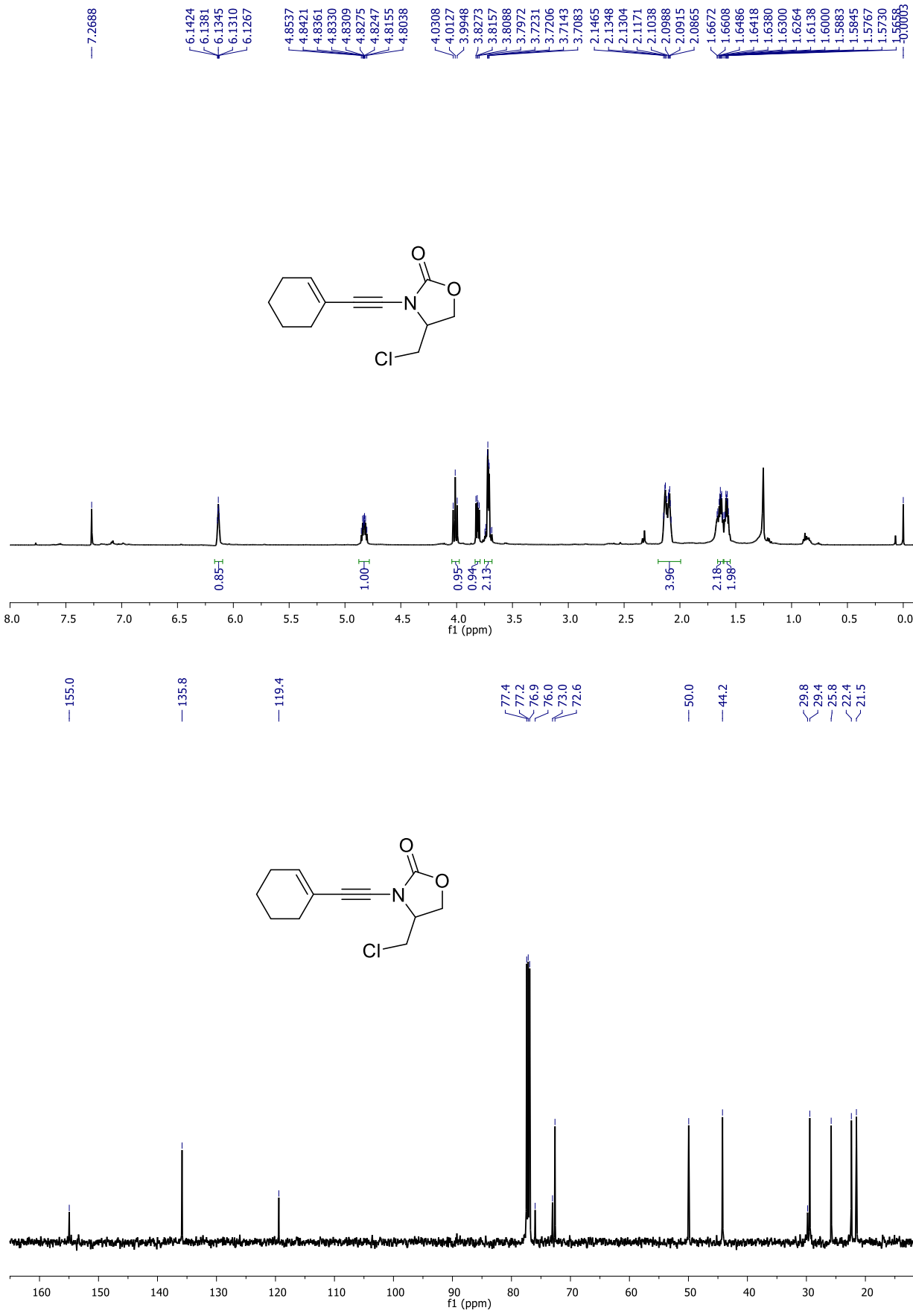




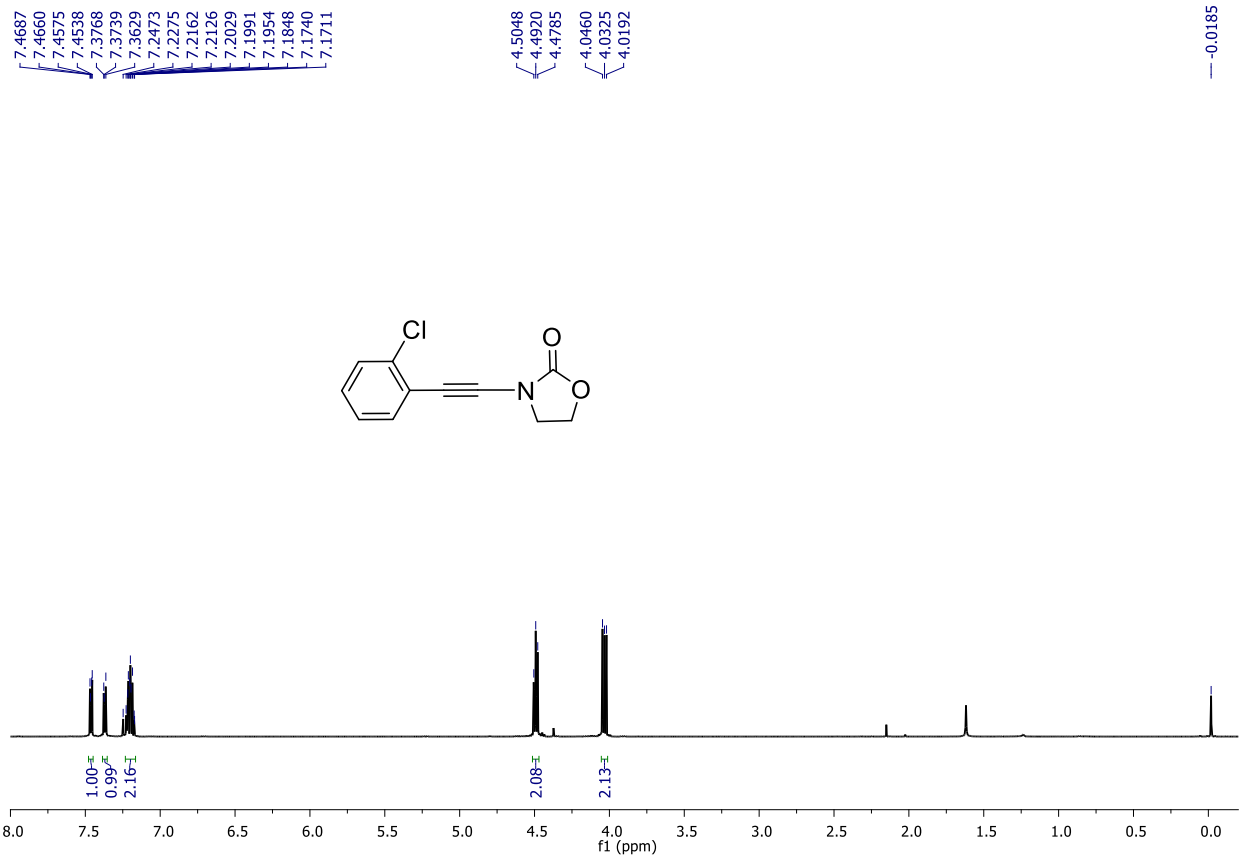
3-(cyclohex-1-en-1-ylethynyl)oxazolidin-2-one (5t):

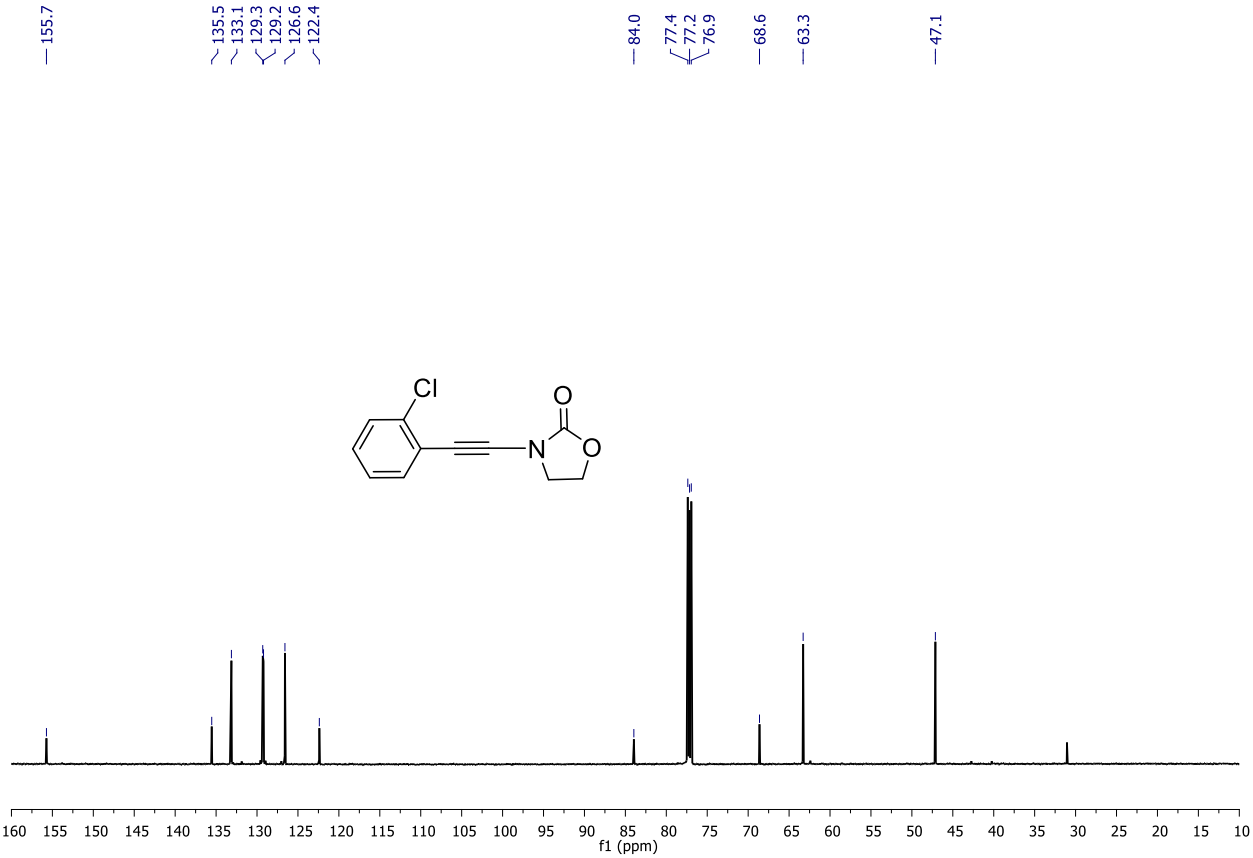


4-(chloromethyl)-3-(cyclohex-1-en-1-ylethynyl)oxazolidin-2-one (5u):

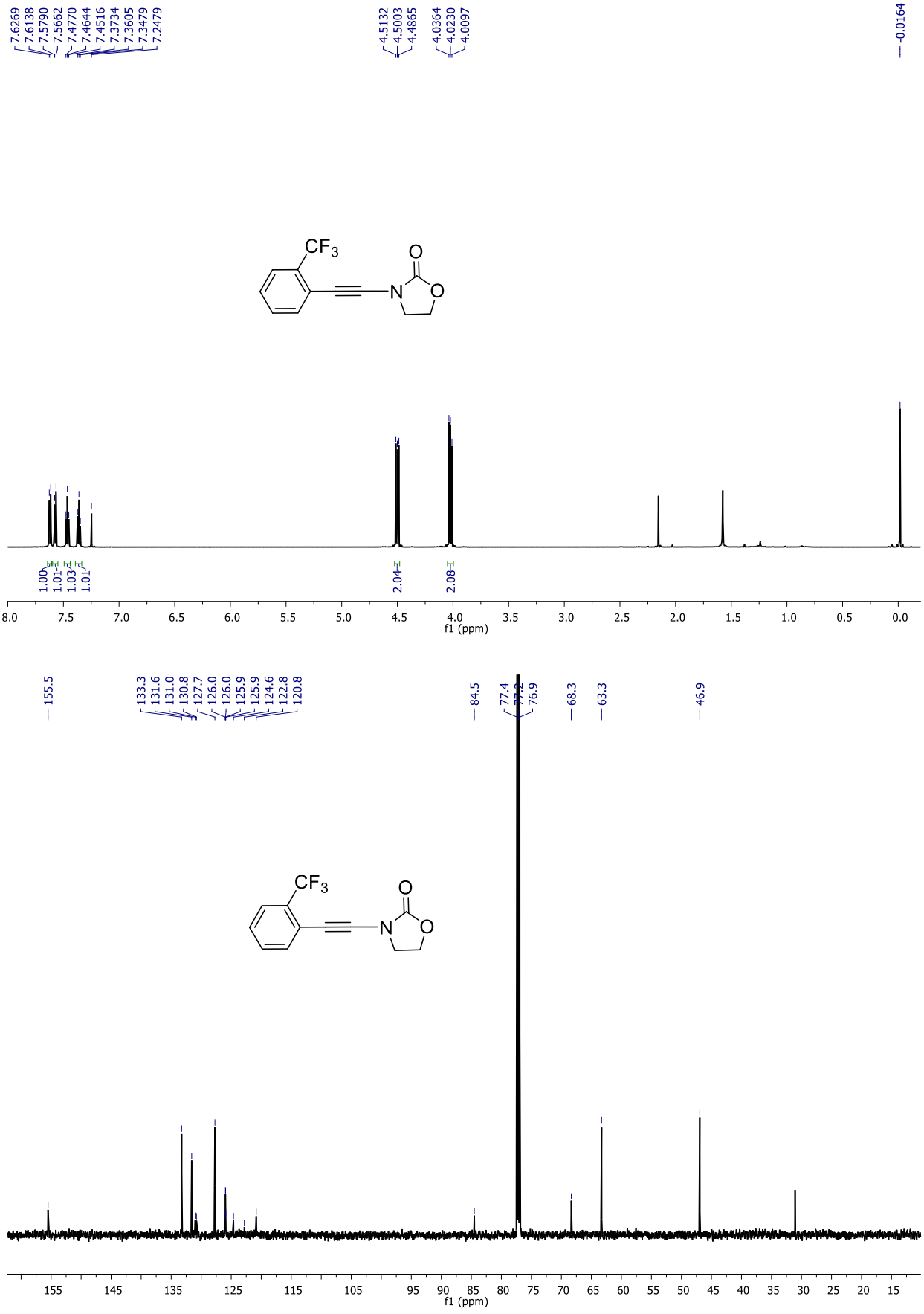


3-(2-chlorophenylethynyl)oxazolidin-2-one (5v):

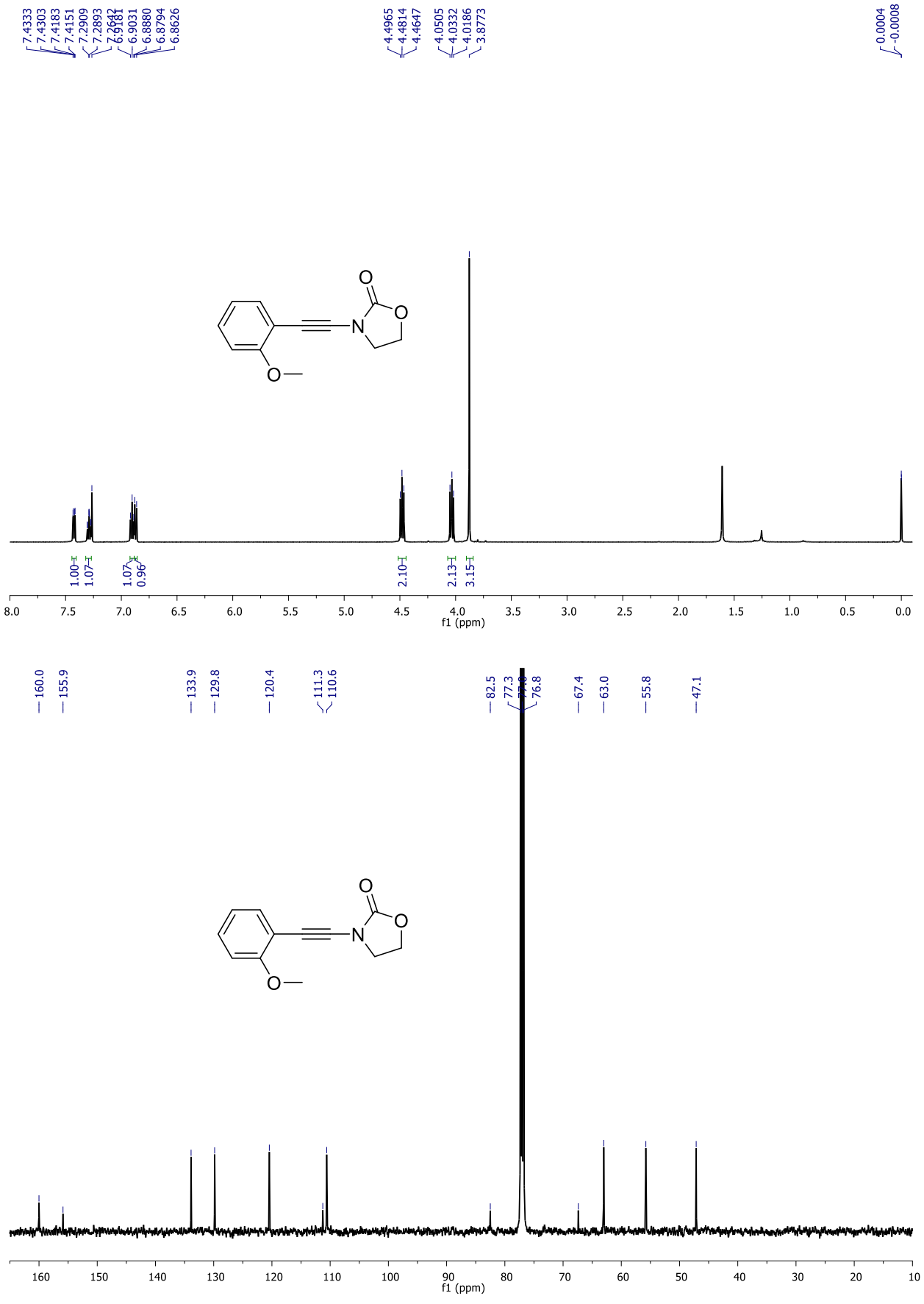




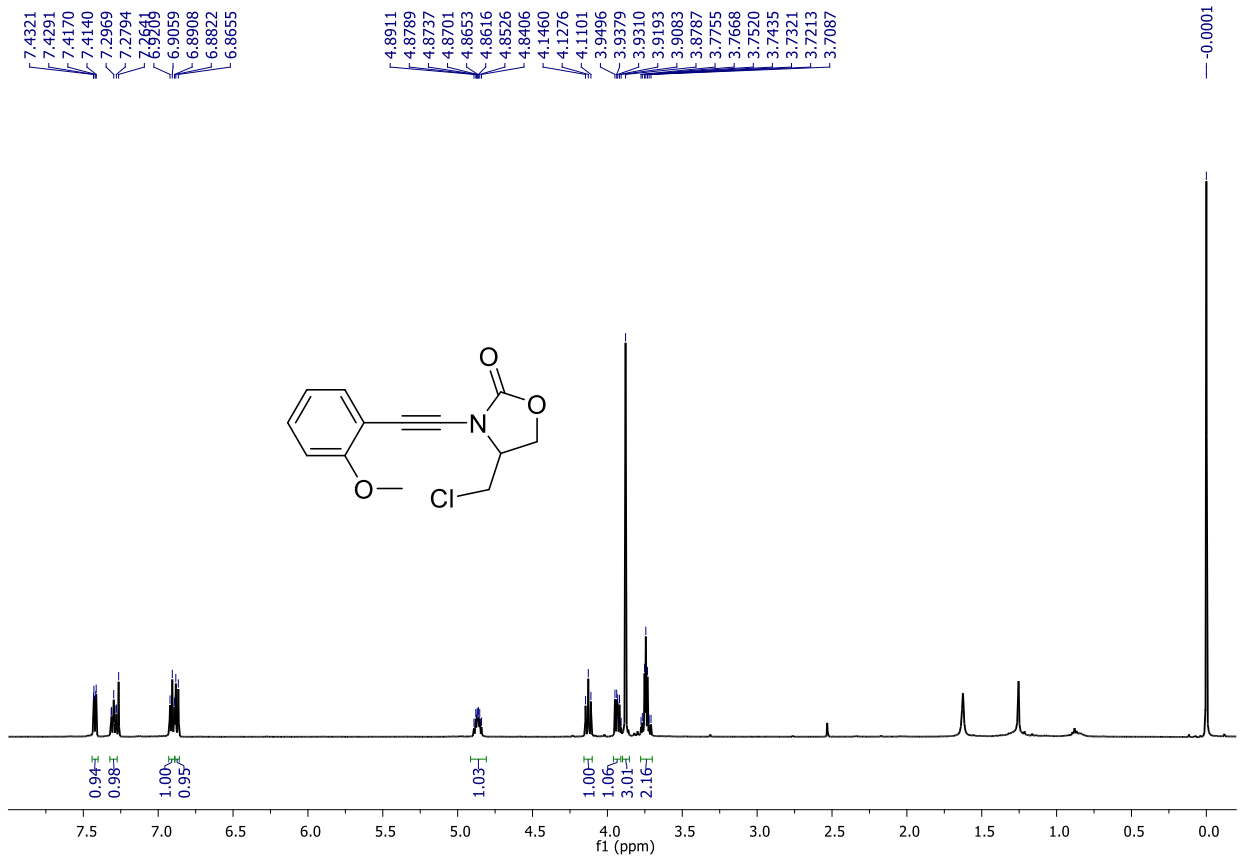
3-(2-trifluoromethylphenylethynyl)oxazolidin-2-one (5w):

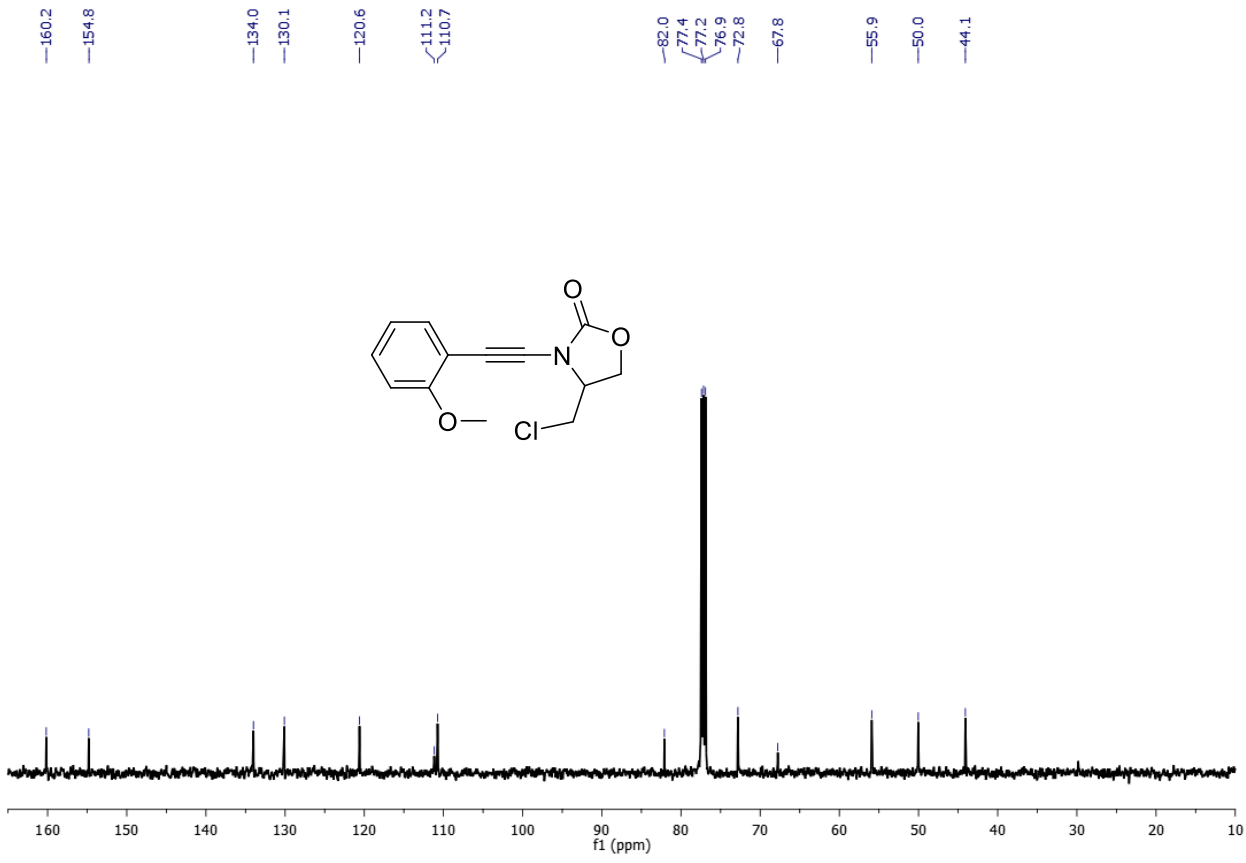


3-(2-methoxyphenylethynyl)oxazolidin-2-one (5x):

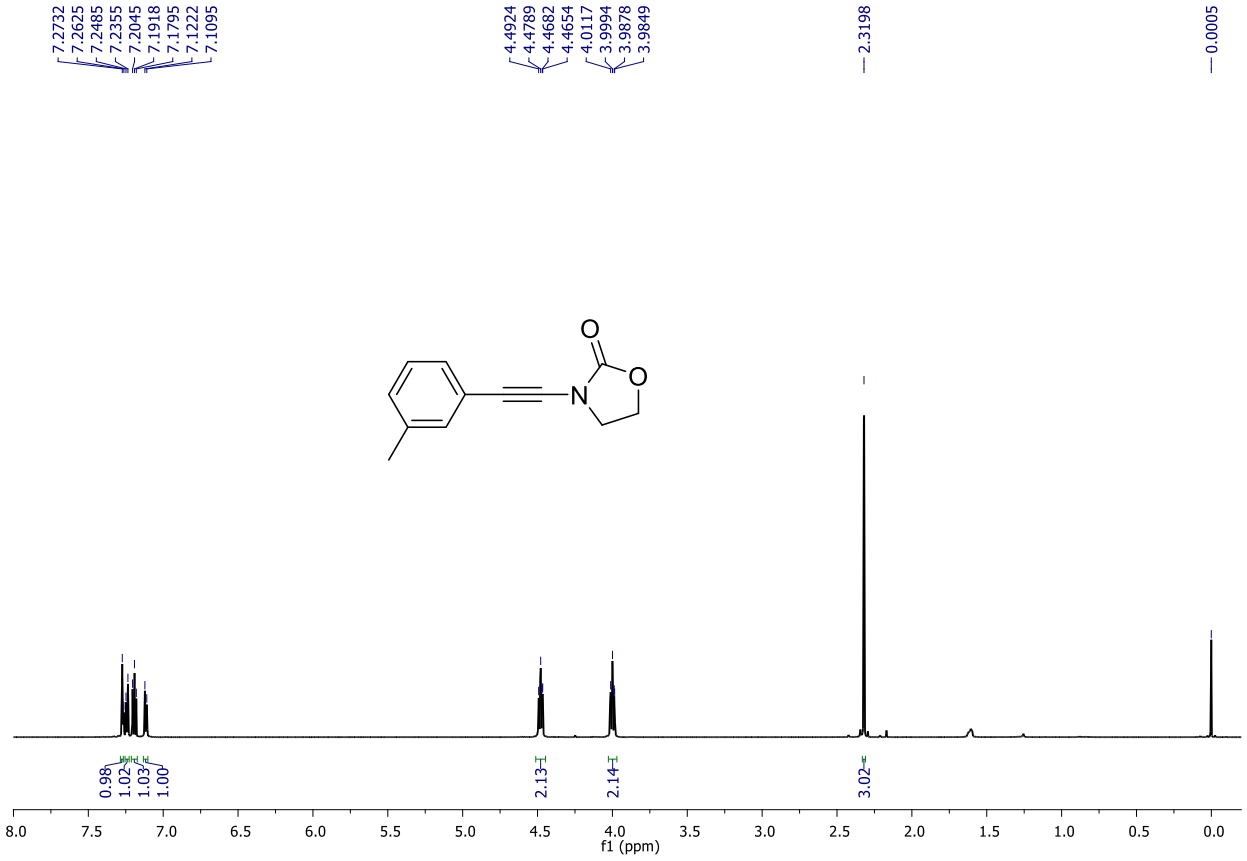


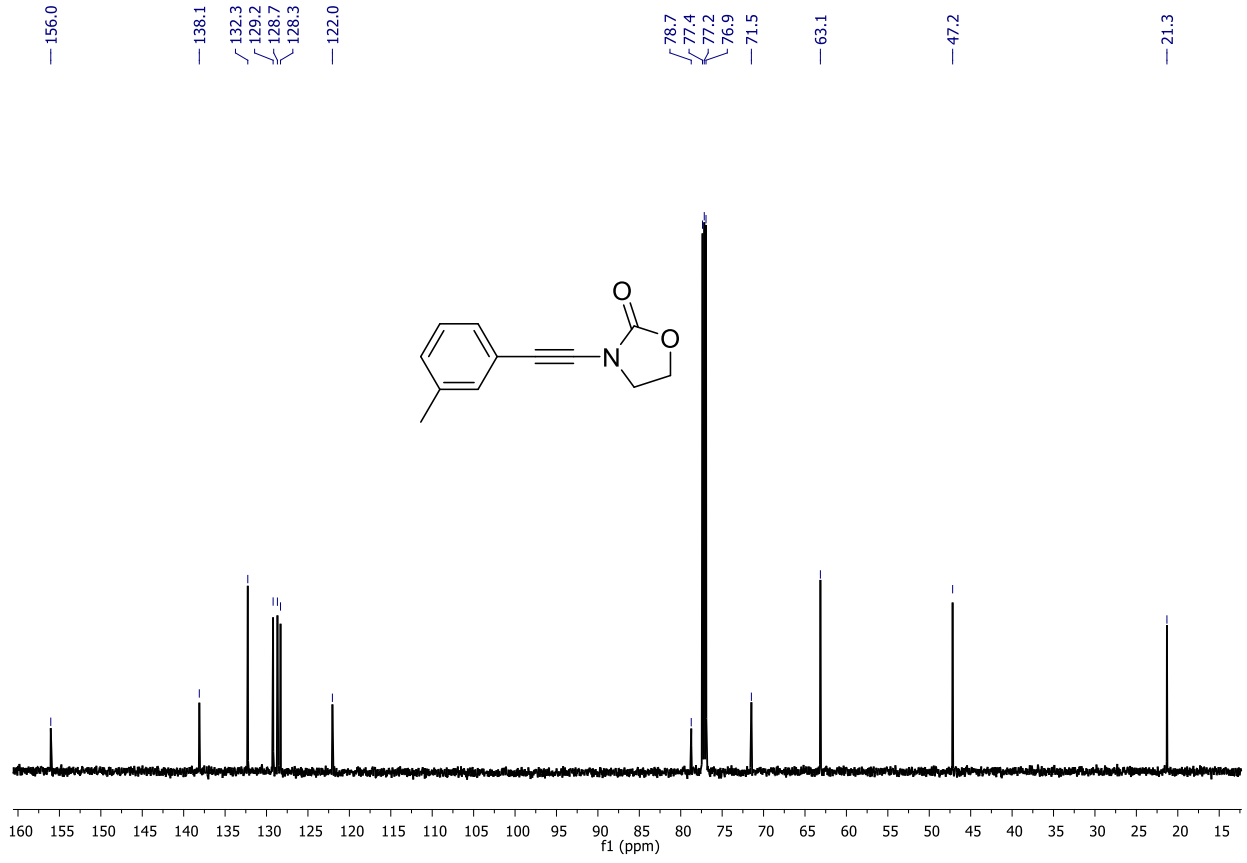
4-(chloromethyl)-3-(2-methoxyphenylethynyl)oxazolidin-2-one (5y):



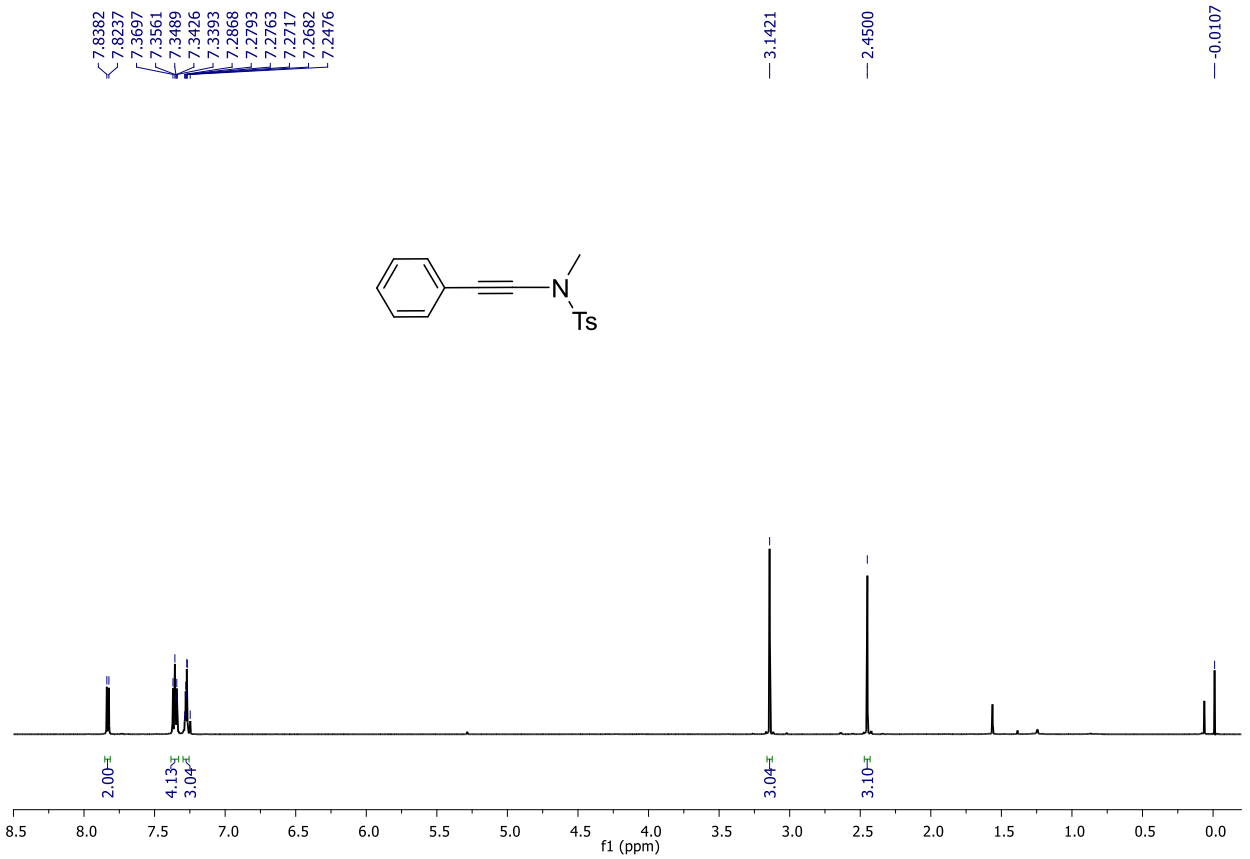


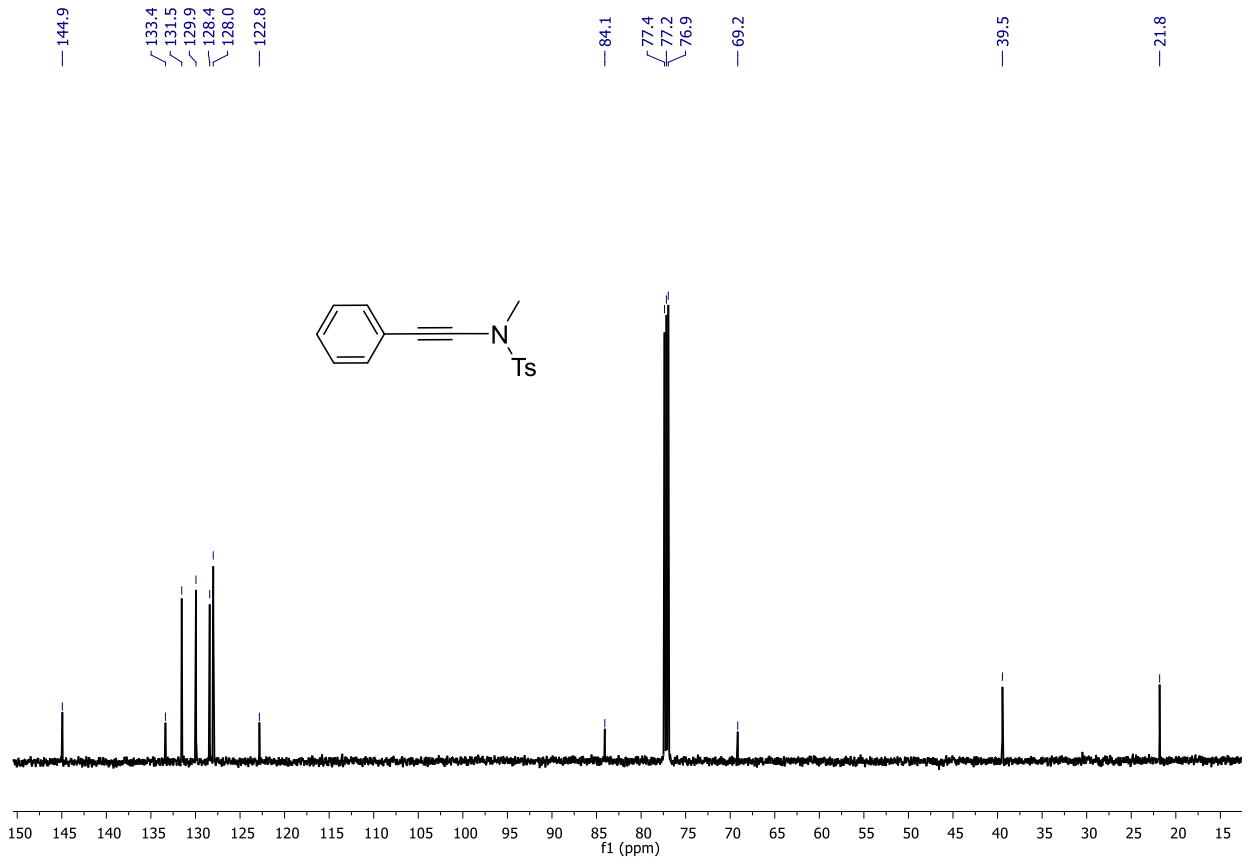
3-(3-methylphenylethynyl)oxazolidin-2-one (5z):



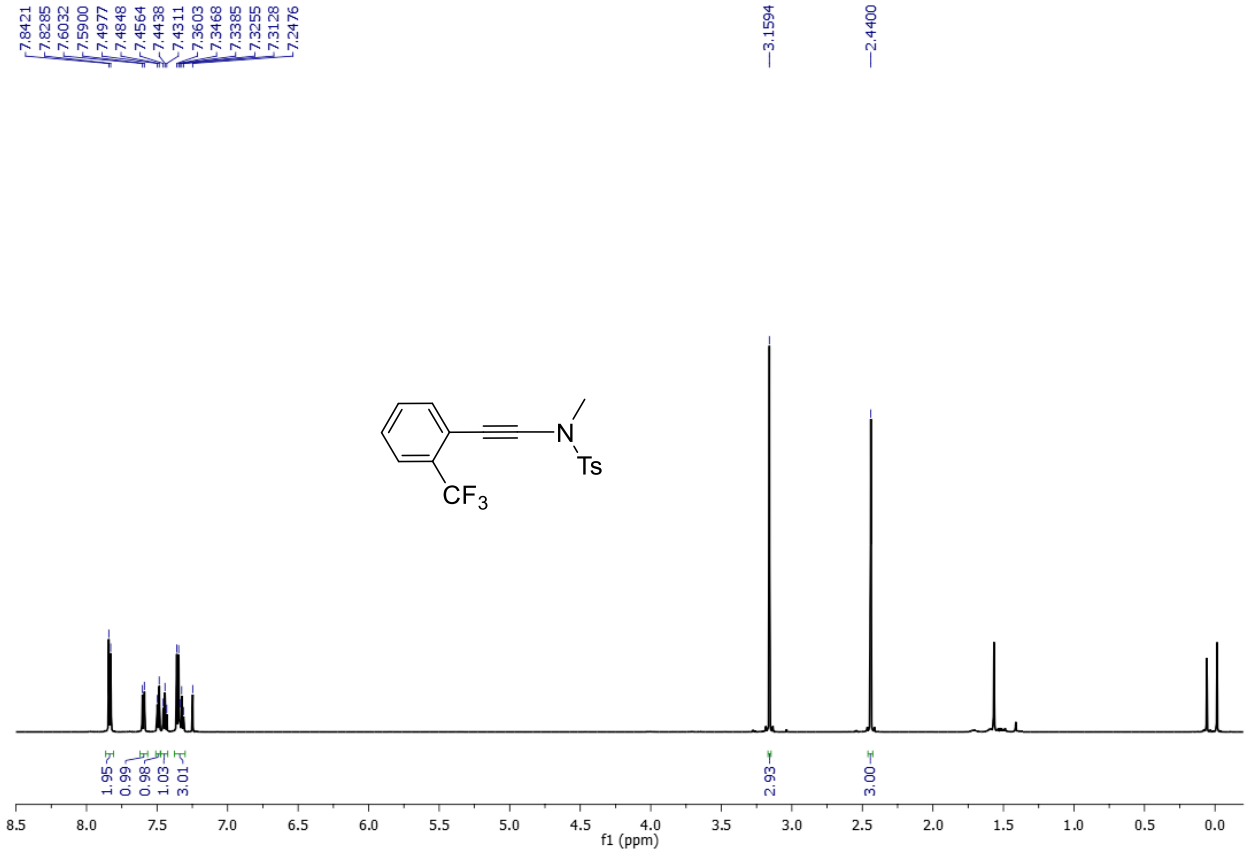


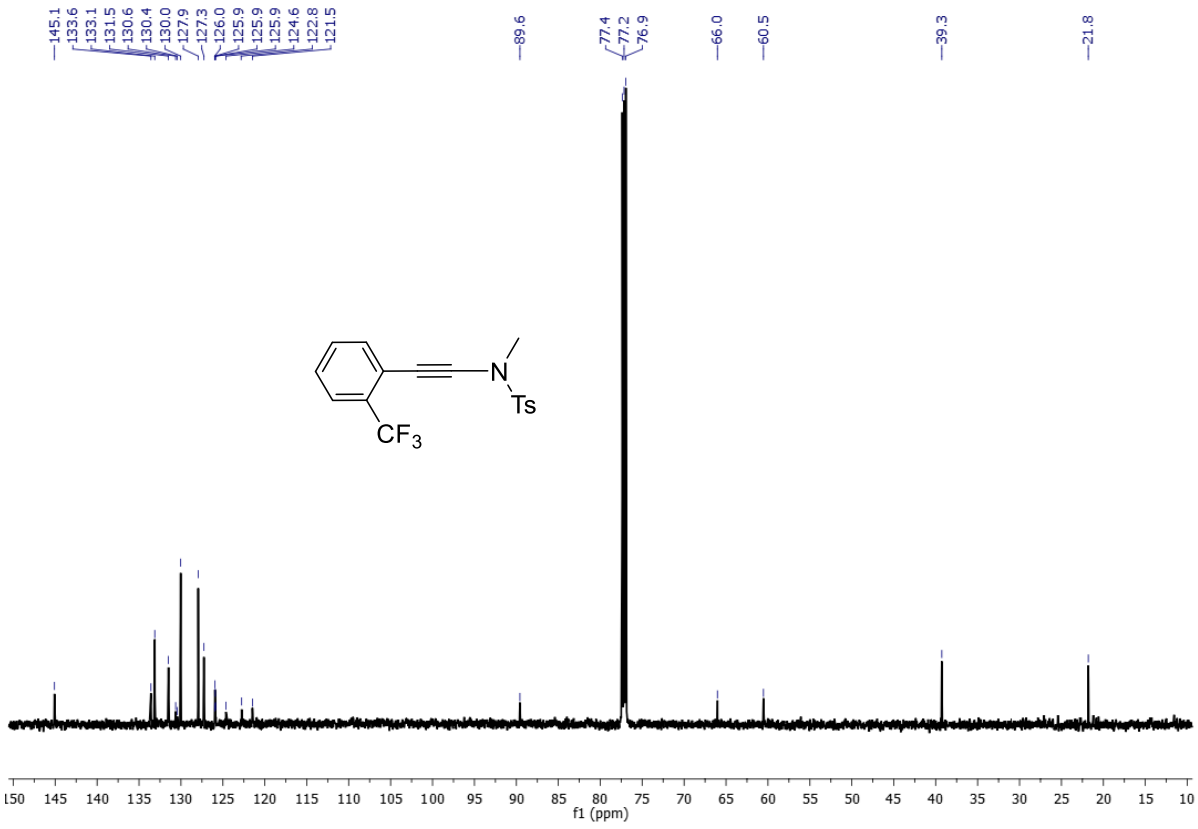
N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide (5aa):





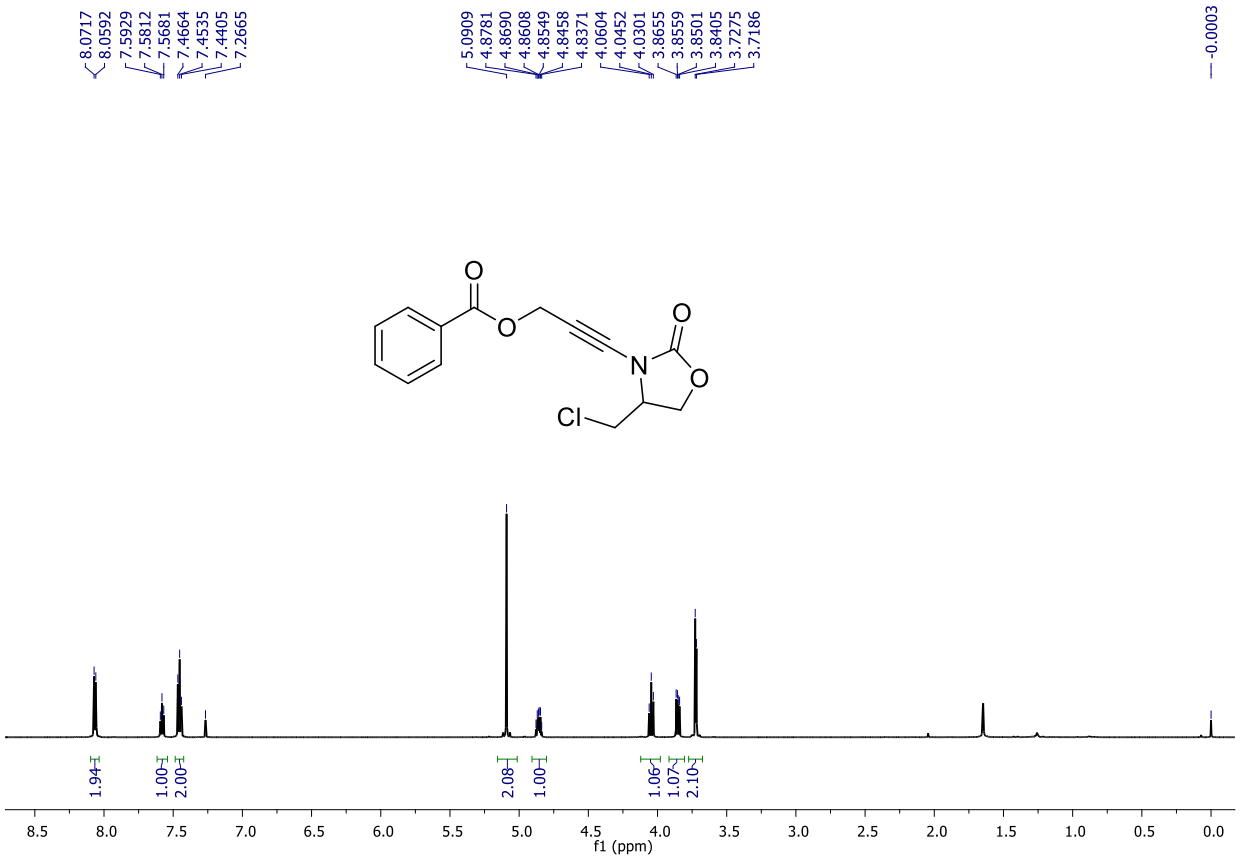
N, 4-dimethyl-N-(2-trifluoromethylphenylethynyl)benzenesulfonamide (5ab):

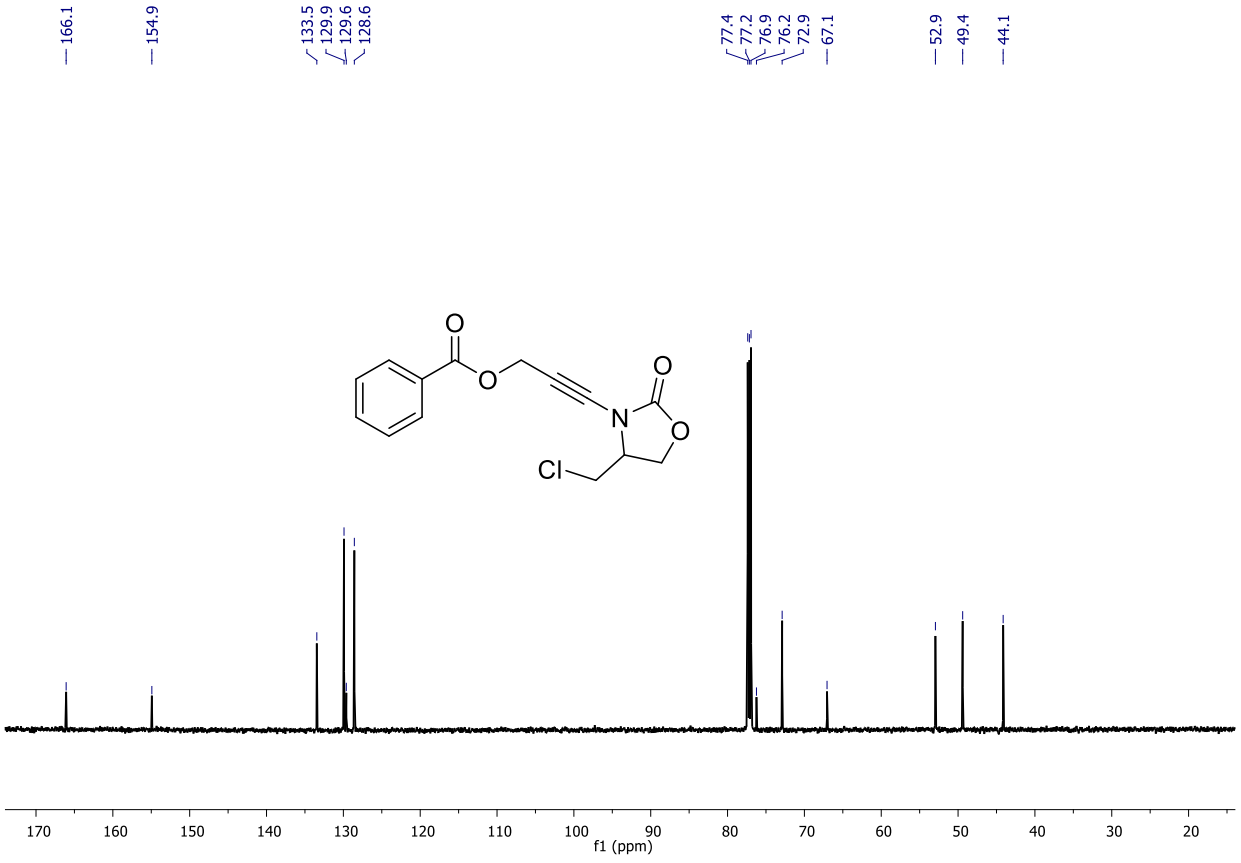




3-(2-oxooxazolidin-3-yl)prop-2-yn-1-yl benzoate (5ac):

3-(4-(3-chloromethyl)-2-oxooxazolidin-3-yl)prop-2-yn-1-yl benzoate (5ad):





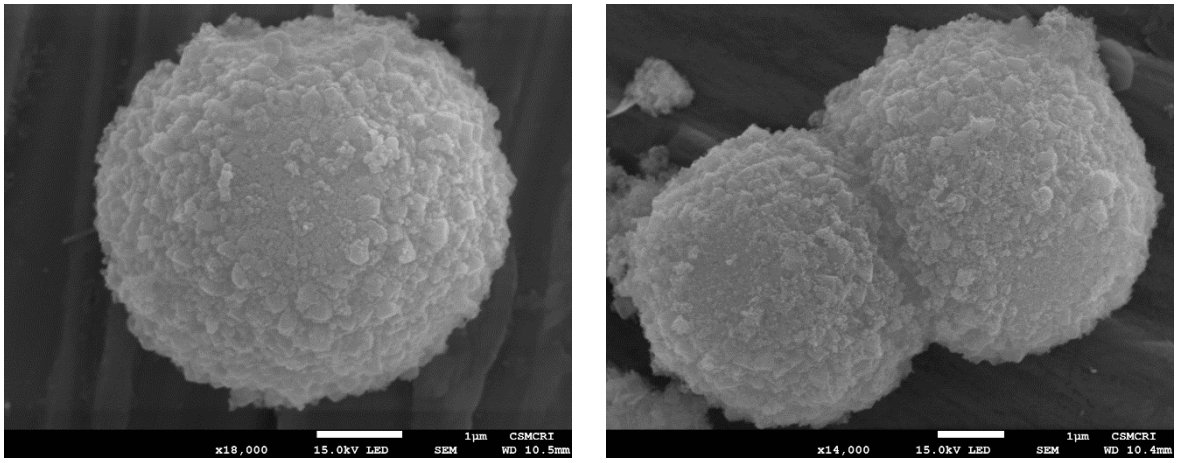


Figure S1: SEM images of the reused catalyst

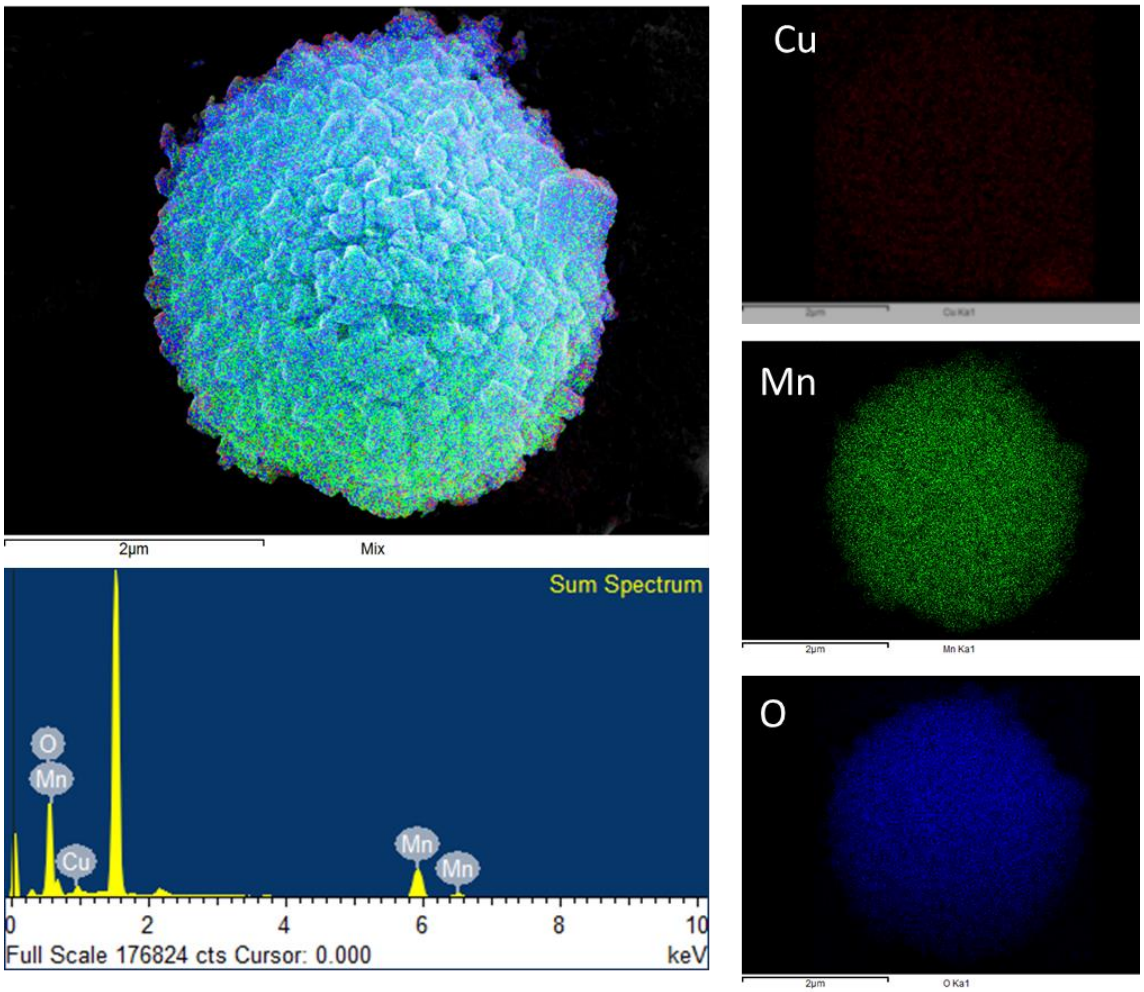


Figure S2: EDS-SEM images of the catalyst, to show the homogeneous distribution of Cu over manganese oxide sphere.

7. References

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