Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Direct synthesis of alkynylphosphonates from alkynes and phosphite esters catalyzed by Cu/Cu_2O nanoparticles supported on Nb_2O_5

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1 XRD spectra

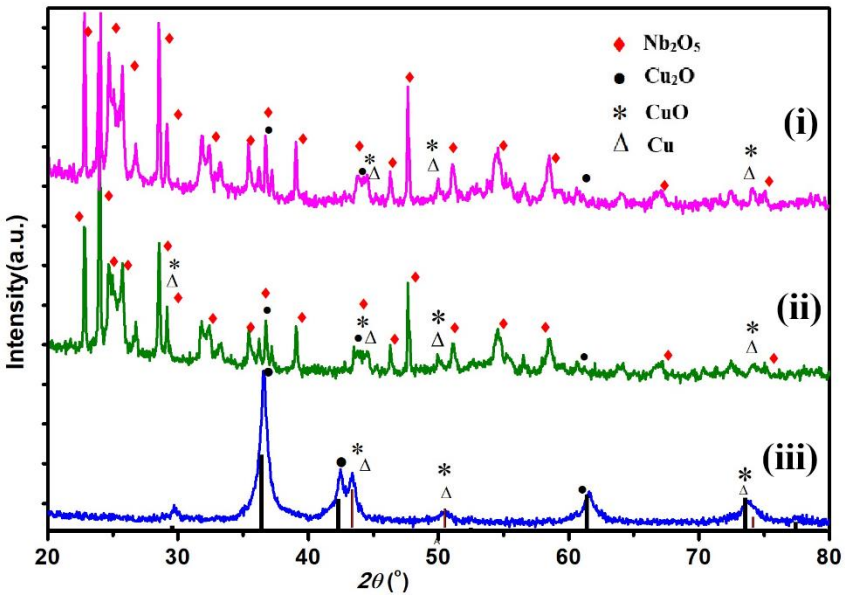


Fig. S1 XRD images. (i) Recycled Cu/Cu_2O@Nb_2O_5; (ii) fresh Cu_2O@Nb_2O_5; (iii) Cu/Cu_2O NPs

2 XPS spectra

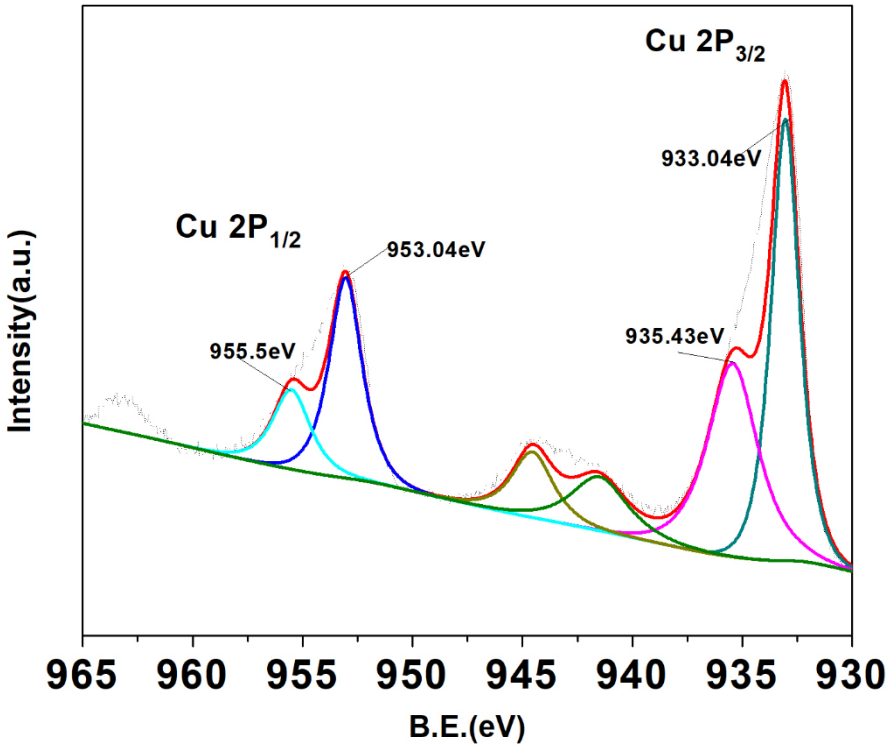


Fig. S2 XPS image of Cu/Cu_2O@SiO_2

3 ICP results

Table S1 ICP results of $Cu/Cu_2O@Nb_2O_5$

Sampling quality (g)	Constant volume/mL	Dilution multiple	The amount of Cu (mg/L)	Content of Cu in the catalyst (wt.%)
0.0837	25	100	0.8986	2.68

4 Raman and TEM images

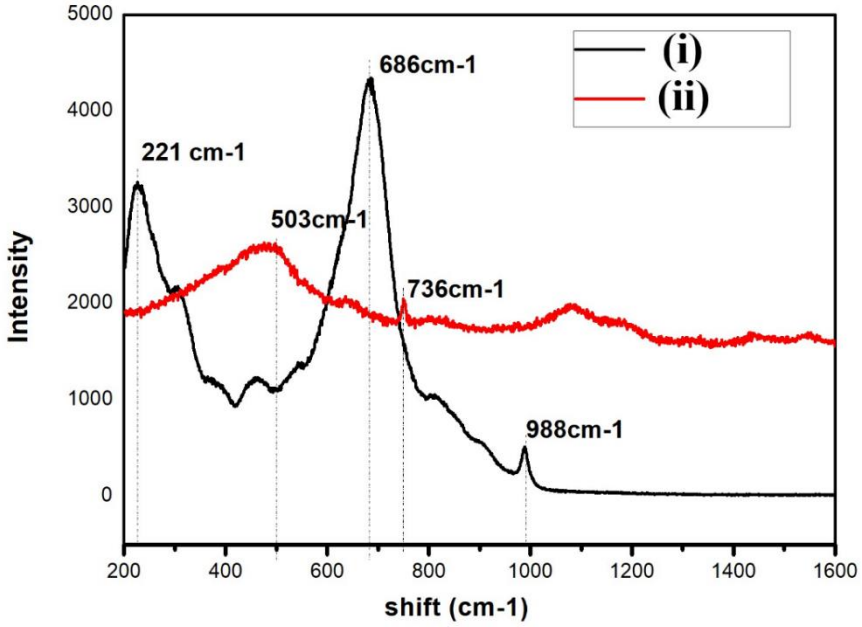


Fig. S3 Raman images. (i) Nb_2O_5; (ii) $Cu/Cu_2O@Nb_2O_5$.

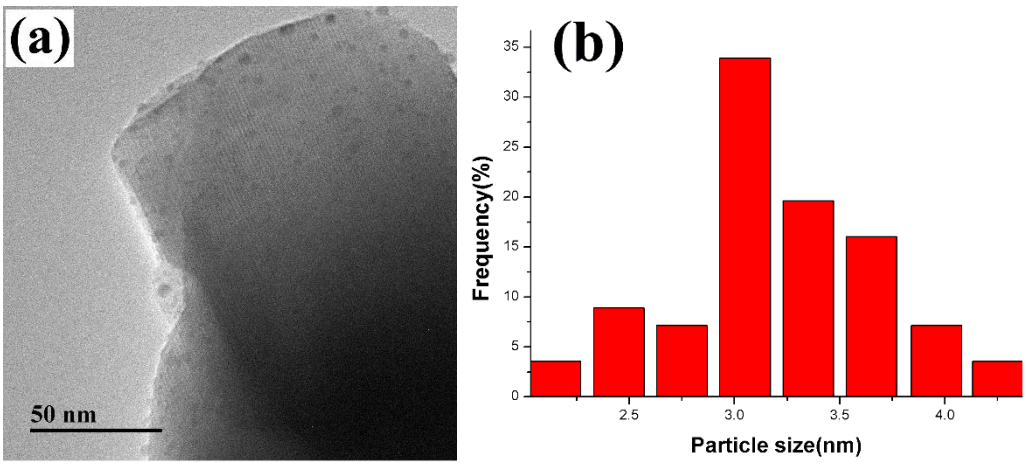
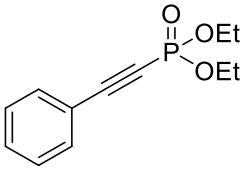


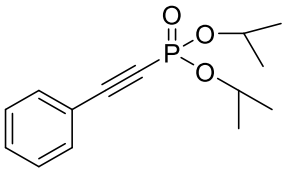
Fig. S4 TEM and size distribution images. (a) $Cu/Cu_2O@Nb_2O_5$; (b) size distribution of Cu/Cu_2O NPs in the catalyst

5 Characterization Data



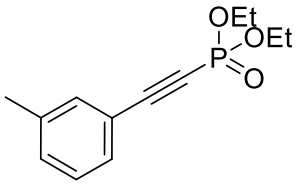
Chemical Formula: $C_{12}H_{15}O_3P$
Mass: 238

Diethyl (phenylethynyl)phosphonate[1] **3a**, brown oil, (91%, 43 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60–7.56 (m, 2H), 7.50–7.44 (m, 1H), 7.42–7.37 (m, 2H), 4.25 (dqd, *J* = 8.5, 7.0, 1.3 Hz, 4H), 1.42 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 131.68, 129.73, 127.60, 118.61, 98.33, 97.91, 78.58, 62.31, 15.20, 15.15. GC-MS (EI) *m/z*: 238.



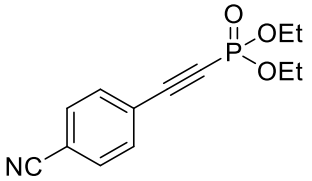
Chemical Formula: $C_{14}H_{19}O_3P$
Mass: 266

Diisopropyl (phenylethynyl)phosphonate[1] **3b**, yellow oil, (93%, 49 mg). ^{1}H N MR (500 MHz, Chloroform-*d*) δ 7.63–7.57 (m, 2H), 7.52–7.47 (m, 1H), 7.45–7.39 (m, 2H), 4.87 (dp, *J* = 8.8, 6.2 Hz, 2H), 1.46 (dd, *J* = 6.2, 2.9 Hz, 12 H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 131.55, 129.53, 127.57, 118.93, 97.1 5 (d, *J* = 52.7 Hz), 78.97 (d, *J* = 297.9 Hz), 71.38, 22.97, 22.69. GC-MS (EI) *m/z*: 266.



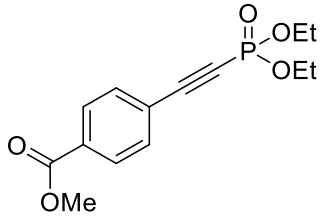
Chemical Formula: $C_{13}H_{17}O_3P$
Mass: 252

Diethyl (m-tolylethynyl)phosphonate[1] **3c**, colorless oil, m.p. (76%, 38 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 8.3, 3.2 Hz, 2H), 7.25 (d, *J* = 4.6 Hz, 2H), 4.26–4.17 (m, 4H), 2.34 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.45, 132.13, 130.65, 128.80, 127.49, 118.39, 98.66, 98.24, 78.20, 62.25, 20.19, 15.21, 15.16. GC-MS (EI) *m/z*: 252.



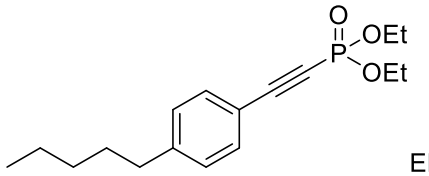
Chemical Formula: $C_{13}H_{14}NO_3P$
Mass: 263

Diethyl ((4-cyanophenyl)ethynyl)phosphonate[1] **3d**, light yellow oil, (79%, 42 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72–7.62 (m, 4H), 4.24 (h, *J* = 6.6, 5.6 Hz, 4H), 1.41 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 132.11, 131.25, 123.39, 116.77, 113.19, 95.14, 94.73, 82.73, 80.37, 62.60, 15.20, GC-MS (EI) *m/z*: 263.



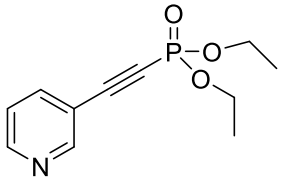
Chemical Formula: $C_{14}H_{17}O_5P$
Mass: 296

Methyl 4-((diethoxyphosphoryl)ethynyl)benzoate[1] **3e**, light yellow oil, (92% 54 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07–8.01 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 4.31–4.18 (m, 4H), 3.96–3.87 (m, 3H), 1.41 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.03, 131.60, 130.82, 128.65, 127.72, 123.02, 96.70, 96.29, 81.19, 78.83, 62.47, 51.50, 15.21, 15.15. GC-MS (EI) *m/z*: 296.



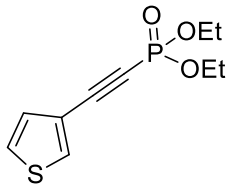
Chemical Formula: $C_{17}H_{25}O_3P$
Exact Mass: 308.1541
Elemental Analysis: C, 66.22; H, 8.17; O, 15.57; P, 10.04

Diethyl ((4-pentylphenyl)ethynyl)phosphonate **3f**, light yellow oil (76%, 47 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.25 (tt, *J* = 8.5, 6.4 Hz, 4H), 2.69–2.61 (m, 2H), 1.63 (p, *J* = 7.5 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 6H), 1.37–1.30 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.36, 131.67, 131.65, 127.72, 115.63, 98.93, 98.51, 77.96, 62.24, 62.20, 35.04, 30.41, 29.79, 21.50, 15.21, 15.15, 13.01. GC-MS (EI) *m/z*: 308. Anal. Calcd for $C_{17}H_{25}O_3P$: C, 66.22%; H, 8.17%. Found: C, 66.35%; H, 8.23%.



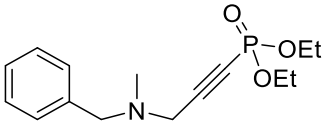
Chemical Formula: $C_{11}H_{14}NO_3P$
Mass: 239

Diethyl (pyridin-3-ylethynyl)phosphonate[2] **3g**, brown oil, (75%, 36 mg). ^{1}H N MR (500 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 2.1 Hz, 1H), 8.69 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.88 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.36 (dd, *J* = 7.9, 4.9 Hz, 1H), 4.30–4.24 (m, 4H), 1.44 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chlorofor m-*d*) δ 152.07, 152.05, 149.76, 138.61, 122.20, 116.10, 94.42, 94.00, 82.29, 79. 92, 63.01, 62.54, 62.50, 15.45, 15.21, 15.15. GC-MS (EI) *m/z*: 239.



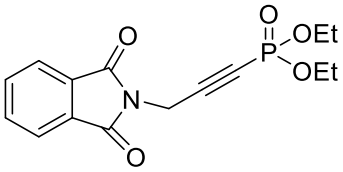
Chemical Formula: $C_{10}H_{13}O_3PS$
Exact Mass: 244
Elemental Analysis: C, 49.18; H, 5.37; O, 19.65; P, 12.68; S, 13.13

Diethyl ((2,5-dihydrothiophen-3-yl)ethynyl)phosphonate **3h**, brown oil, (88%, 43 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 3.0 Hz, 1H), 7.34 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.23 (dd, *J* = 5.0, 1.2 Hz, 1H), 4.30–4.17 (m, 4H), 1.42 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 132.42, 132.40, 128.95, 128.94, 125.18, 117.88, 93.60, 93.17, 78.53, 62.28, 62.24, 15.20, 15.14. GC-MS (EI) *m/z*: 246. Anal. Calcd for $C_{10}H_{15}O_3PS$: C, 49.18%; H, 5.37%. Found: C, 48.79%; H, 5.21%.



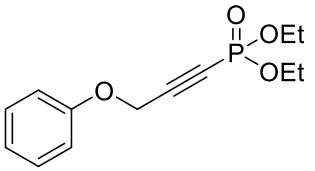
Chemical Formula: $C_{15}H_{22}NO_3P$
Exact Mass: 295.1337
Elemental Analysis: C, 61.01; H, 7.51; N, 4.74; O, 16.25; P, 10.49

Diethyl (3-(benzyl(methyl)amino)prop-1-yn-1-yl)phosphonate **3i**, light yellow oil, (83%, 49 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40–7.27 (m, 5H), 4.22 (p, *J* = 7.3 Hz, 4H), 3.61 (s, 2H), 3.47 (d, *J* = 3.7 Hz, 2H), 2.40 (s, 3H), 1. 43 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.78, 128.07, 127.48, 126.52, 95.79, 95.39, 73.70, 62.21, 62.16, 59.10, 44.21, 44.18, 41.01, 15.21, 15.15. GC-MS (EI) *m/z*: 295. Anal. Calcd for $C_{15}H_{22}NO_3P$: C, 61.01%; H, 7.51%; N, 4.74%. Found: C, 61.32%; H, 7.27%; N, 4.96%.



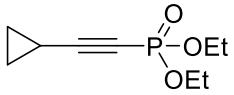
Chemical Formula: $C_{15}H_{16}NO_5P$
Mass: 321

Diethyl (3-(1,3-dioxoisoindolin-2-yl)prop-1-yn-1-yl)phosphonate[3] **3j**, light yellow solid, (89%, 57 mg), m.p. 84-86 °C (lit. 86-87 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.60 (d, *J* = 3.9 Hz, 2H), 4.27–4.08 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.55, 133.50, 130.83, 122.77, 92.66, 92.26, 73.71, 71.37, 62.48, 62.44, 26.34, 26.31, 15.11, 15.05. GC-MS (EI) *m/z*: 321.



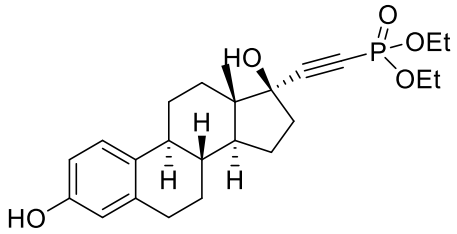
Chemical Formula: $C_{13}H_{17}O_4P$
Mass: 268

Diethyl (3-phenoxyprop-1-yn-1-yl)phosphonate[4] **3k**, colorless oil (85%, 46 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40–7.31 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 7.01–6.95 (m, 2H), 4.82 (d, *J* = 3.8 Hz, 2H), 4.20–4.07 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.17, 128.60, 12 1.14, 114.05, 94.12, 93.72, 77.48, 75.16, 62.48, 62.44, 54.78, 15.06, 15.00. GC -MS (EI) *m/z*: 268.



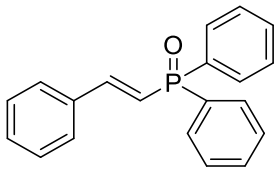
Chemical Formula: $C_9H_{15}O_3P$
Mass: 202

Diethyl (cyclopropylethynyl)phosphonate[5] **3l**, light yellow oil, (75%, 30 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.15 (tt, *J* = 8.6, 6.3 Hz, 4H), 1.76 (s, 1 H), 1.38 (t, *J* = 7.1 Hz, 6H), 1.03–0.85 (m, 4H). ^{13}C NMR (126 MHz, Chloro form-*d*) δ 105.13, 104.69, 65.51, 63.08, 61.91, 61.87, 15.15, 15.09, 8.15, 8.14, -1.18, -1.23. GC-MS (EI) *m/z*: 202.



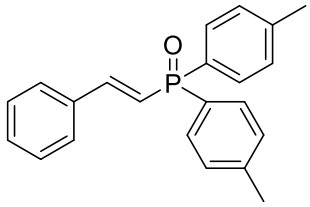
Chemical Formula: $C_{24}H_{33}O_5P$
Mass: 432

Diethyl (((8R,9S,13S,14S,17S)-3,17-dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,1 7-decahydro-6H-cyclopenta[a]phenanthren-17-yl)ethynyl)phosphonate[6] **3m**, yellow solid, (81%, 69 mg), m.p. 83-87 ºC (lit. 79.5-82 ºC). ^{1}H NMR (500 MHz, C hloroform-*d*) δ 7.05 (d, *J* = 8.5 Hz, 1H), 6.70 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.62 (d, *J* = 2.6 Hz, 1H), 4.27–4.18 (m, 4H), 2.87–2.74 (m, 2H), 2.38 (ddd, *J* = 14.6, 9.6, 5.6 Hz, 1H), 2.24–2.15 (m, 1H), 2.07 (ddd, *J* = 14.0, 11.7, 3.9 Hz, 2H), 1.96 (td, *J* = 11.3, 4.2 Hz, 1H), 1.86–1.72 (m, 4H), 1.59 (td, *J* = 11.4, 7. 3 Hz, 1H), 1.42 (td, *J* = 7.1, 4.0 Hz, 9H), 0.89 (s, 3H). MS (ESI) *m/z*: 432. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.42, 136.71, 130.38, 125.40, 114.23, 111.80, 104.46, 104.08, 79.10, 72.88, 63.15, 62.53, 49.11, 46.90, 42.26, 38.33, 37.65, 32.04, 28.57, 26.30, 25.27, 21.97, 15.44, 15.19, 11.68.



Chemical Formula: $C_{20}H_{17}OP$
Mass: 304

(*E*)-Diphenyl(styryl)phosphine oxide[7] **4a**, light yellow solid, (77%, 47 mg), m. p. 169-171 ºC (lit. 165-167 ºC), ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84–7. 76 (m, 4H), 7.60–7.48 (m, 9H), 7.40 (dt, *J* = 4.9, 2.6 Hz, 3H), 6.88 (dd, *J* = 22.4, 17.4 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.56, 146.64, 14 6.60, 130.93, 130.91, 130.47, 130.46, 130.39, 130.38, 129.15, 127.89, 127.71, 1 27.62, 126.81, 118.67. 117.84. GC-MS (EI) *m/z*: 304.



Chemical Formula: $C_{22}H_{21}OP$
Mass: 332

(*E*)-Styryldi-p-tolylphosphine oxide[8] **4b**, yellow solid, (73%, 48 mg). m.p. 176-179 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 11.9, 7.9 Hz, 4H), 7.59–7.44 (m, 3H), 7.39 (dt, *J* = 4.9, 2.9 Hz, 3H), 7.33–7.28 (m, 4H), 6.85 (dd, *J* = 21.9, 17.4 Hz, 1H), 2.43 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.09, 146.09, 141.30, 141.30, 134.39, 134.25, 134.25, 130.50, 130.42, 129.28, 128.99, 128.41, 128.31, 128.24, 128.14, 127.85, 126.77, 119.30, 119.30, 118.47, 118.47, 20.65. GC-MS (EI) *m/z*: 332.

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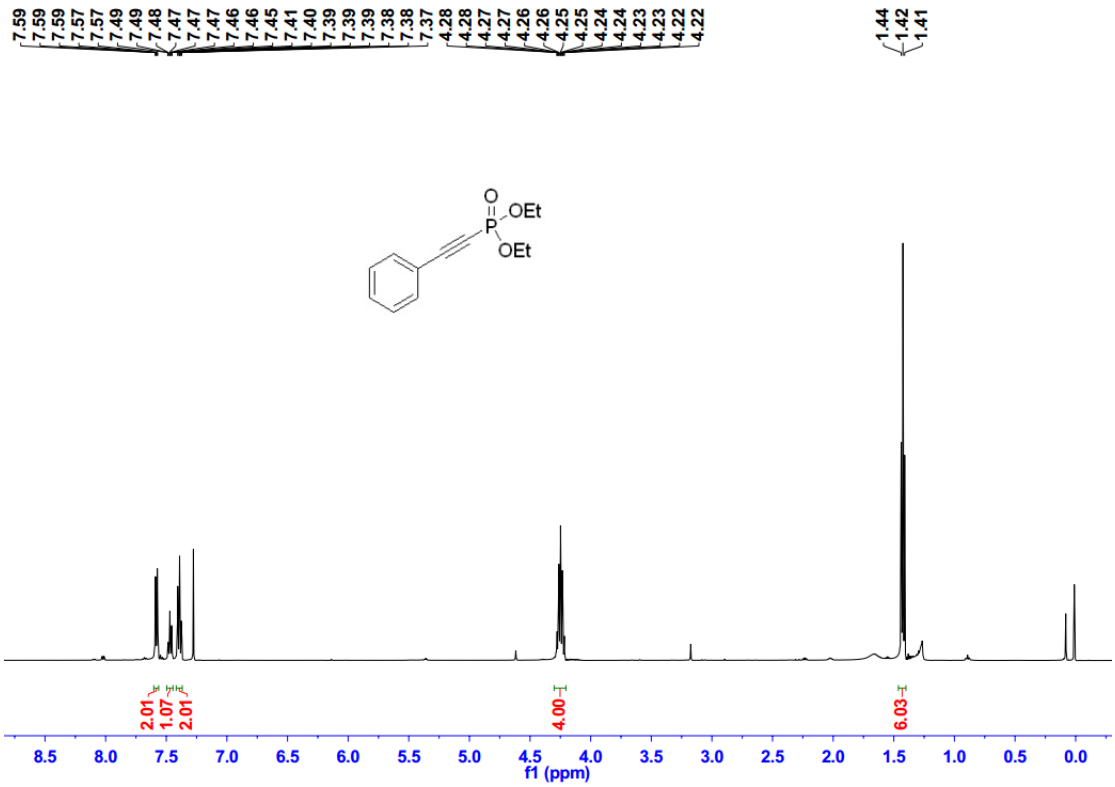
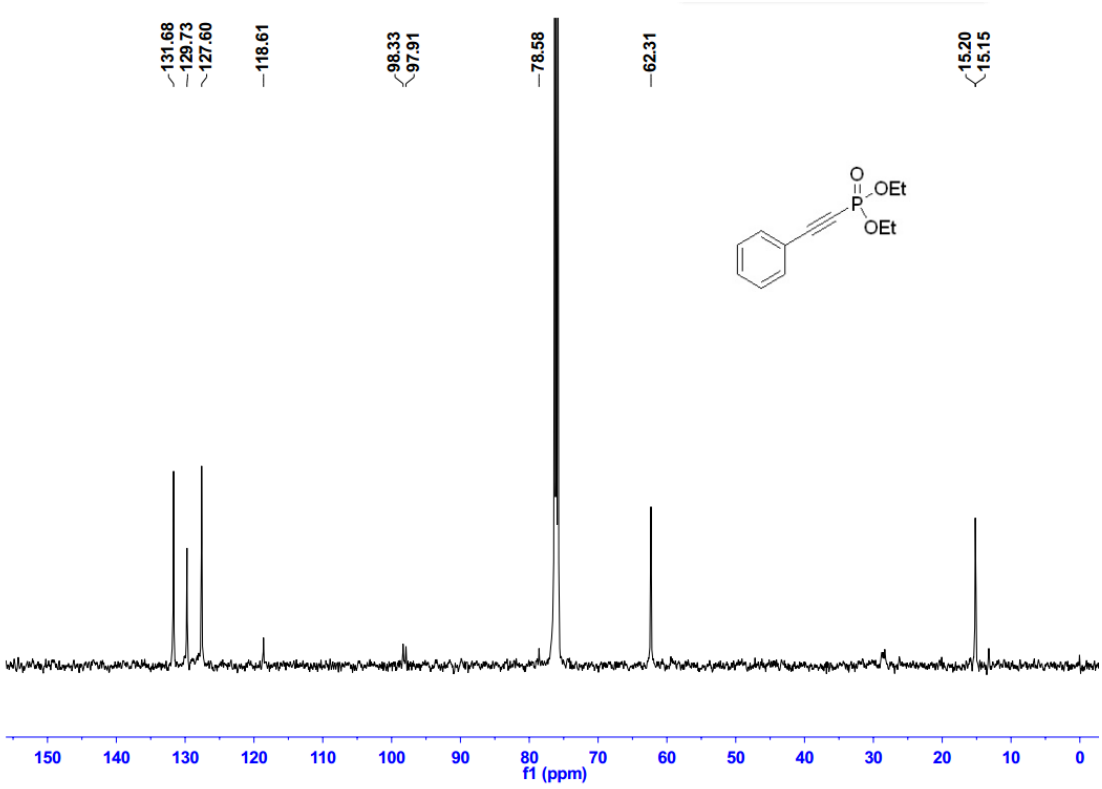
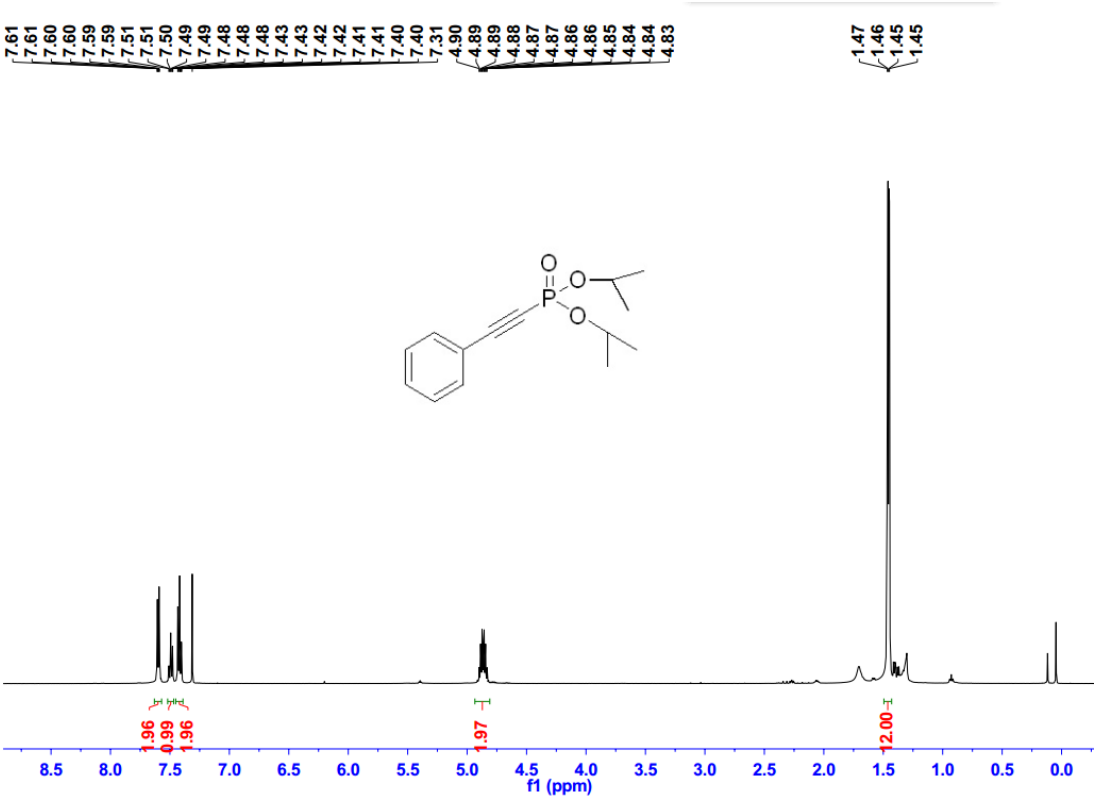
6 NMR Spectra of All Products



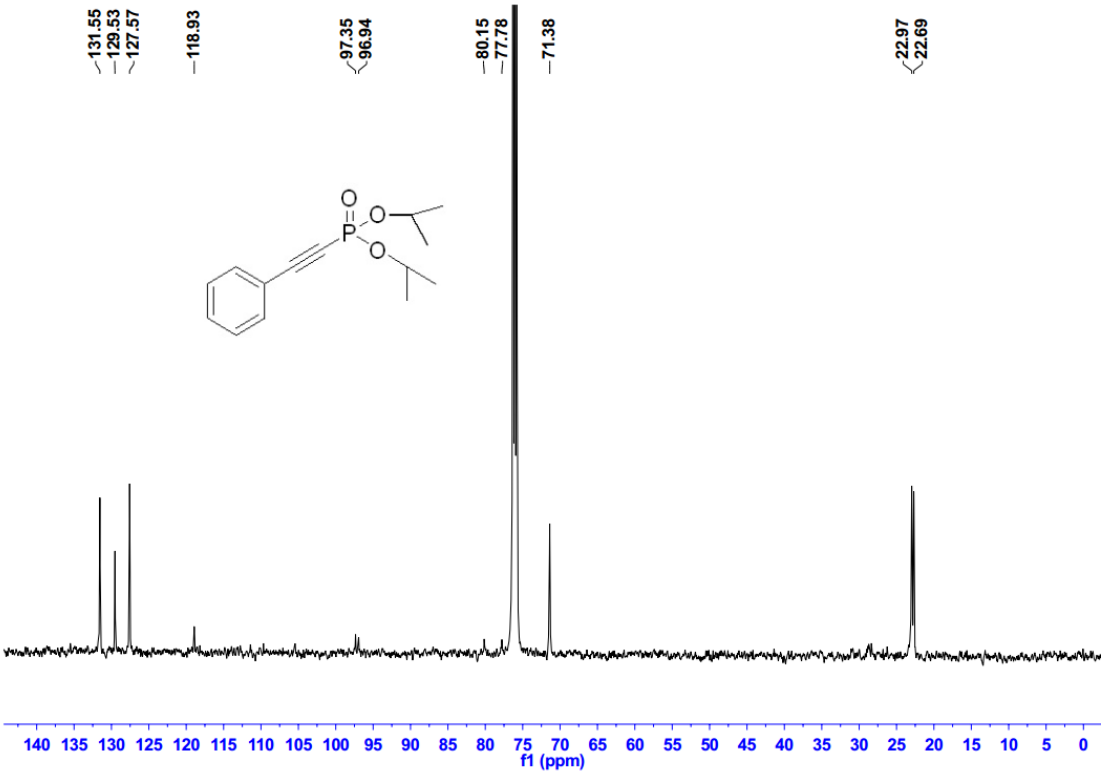
^{1}H NMR of **3a**



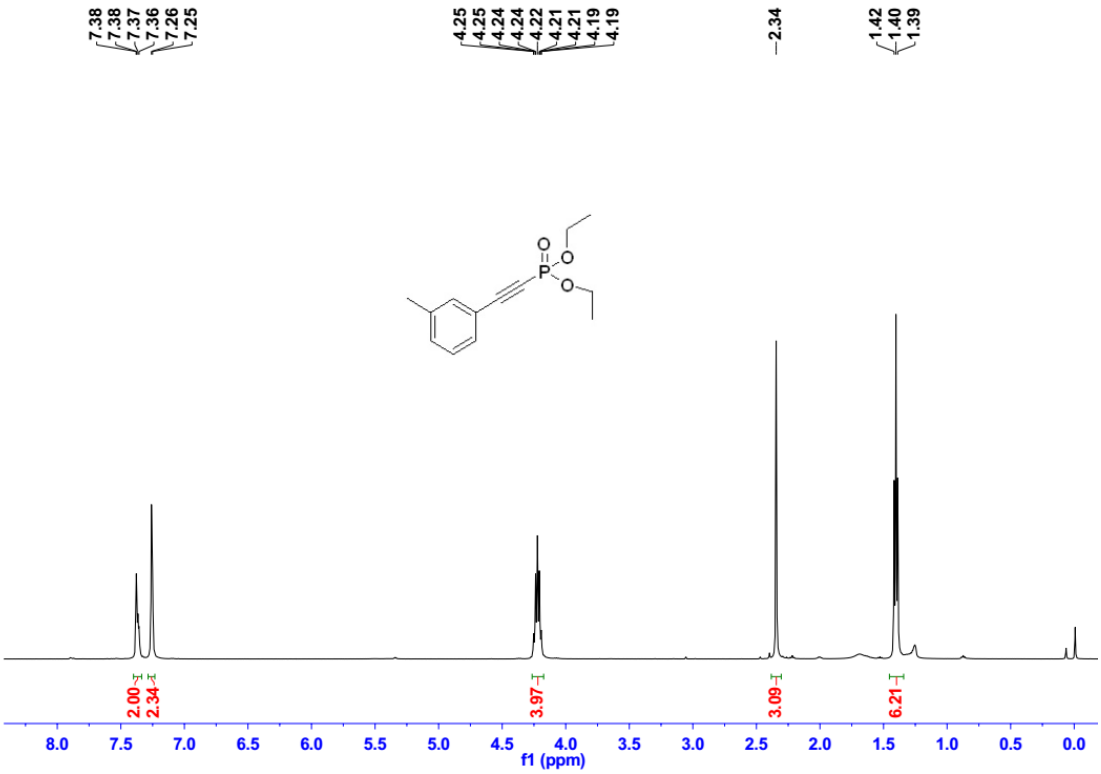
^{13}C NMR of **3a**



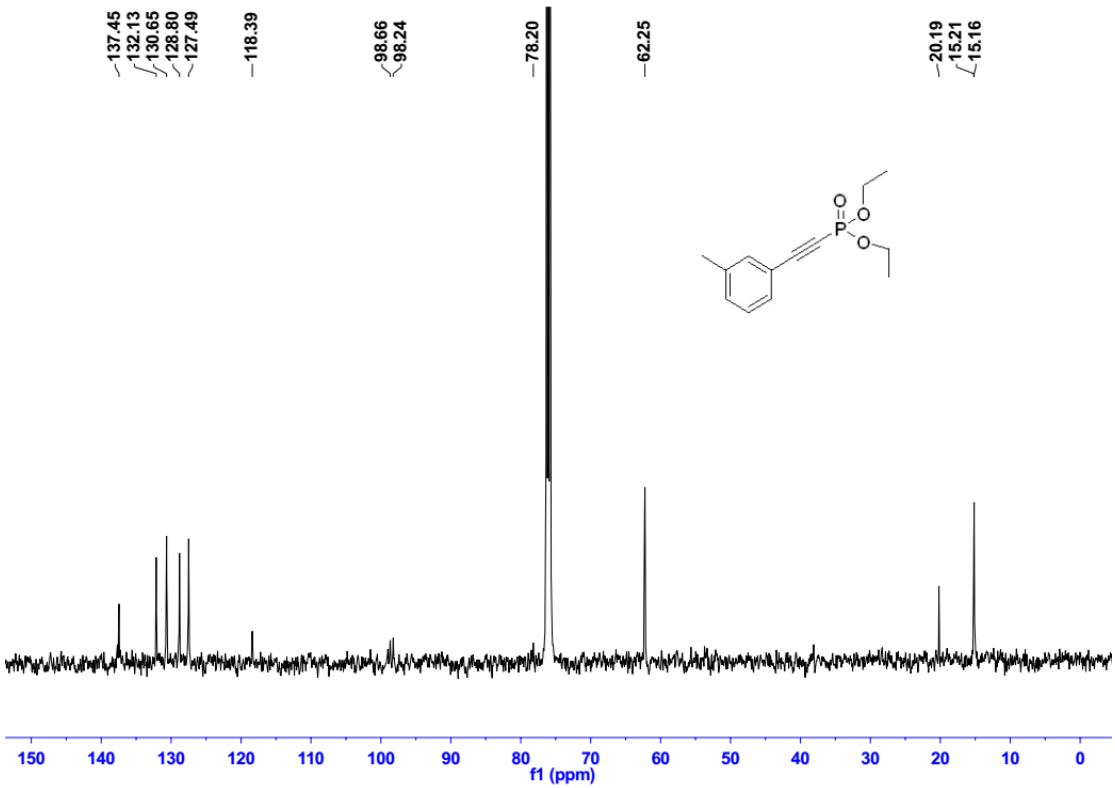
^{1}H NMR of **3b**



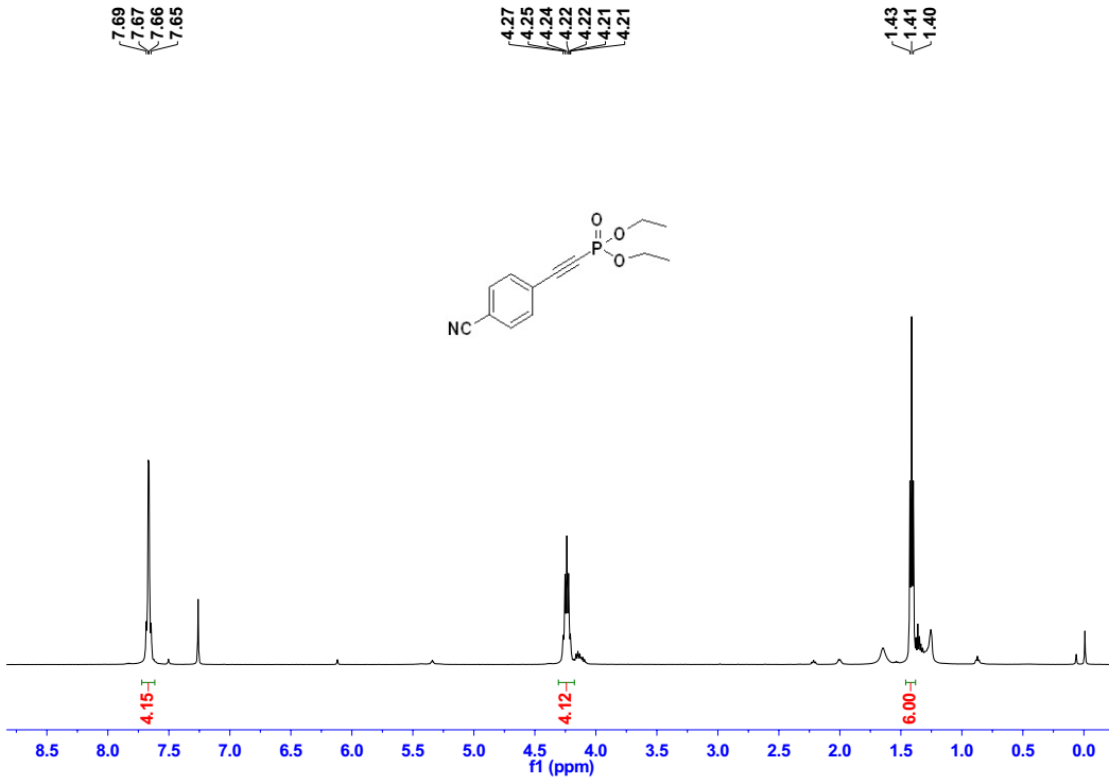
^{13}C NMR of **3b**



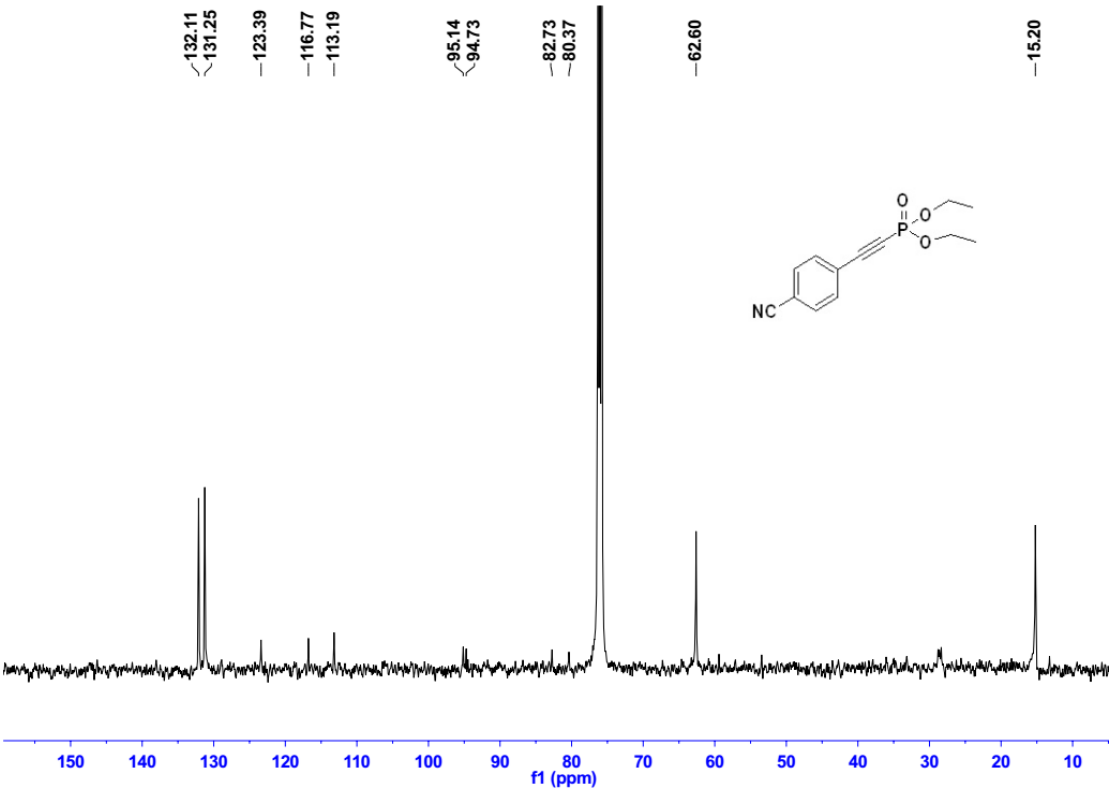
^{1}H NMR of **3c**



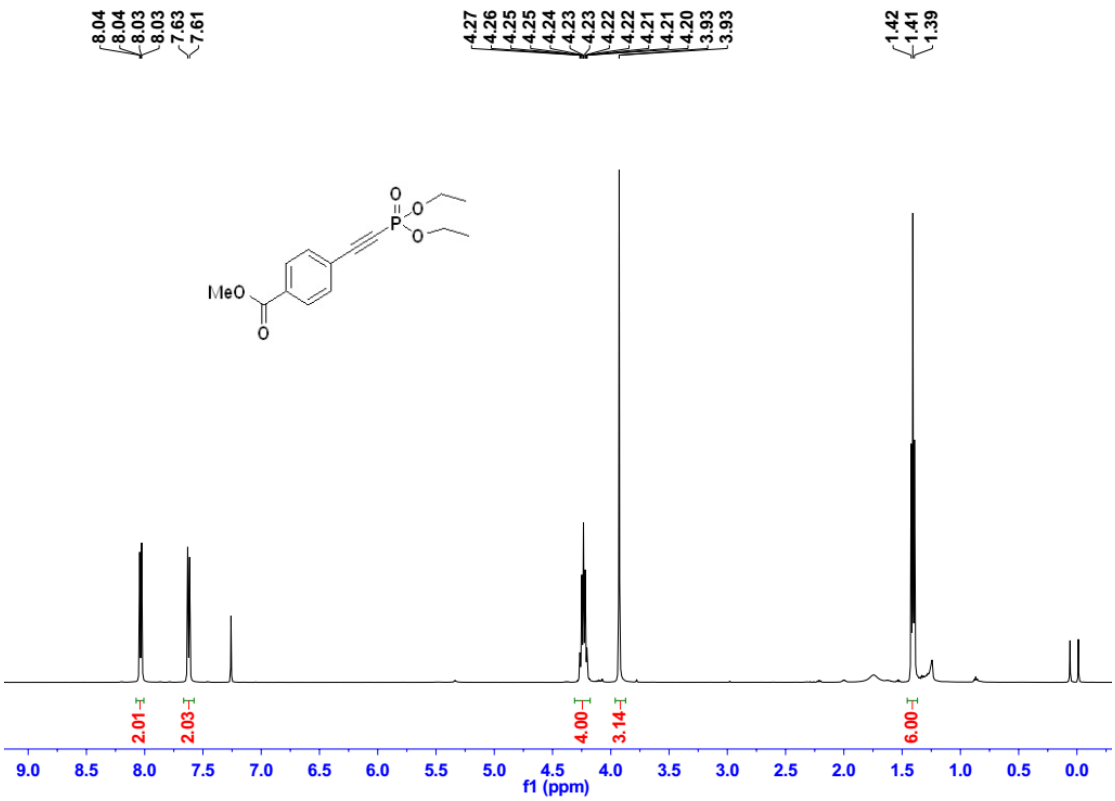
^{13}C NMR of **3c**



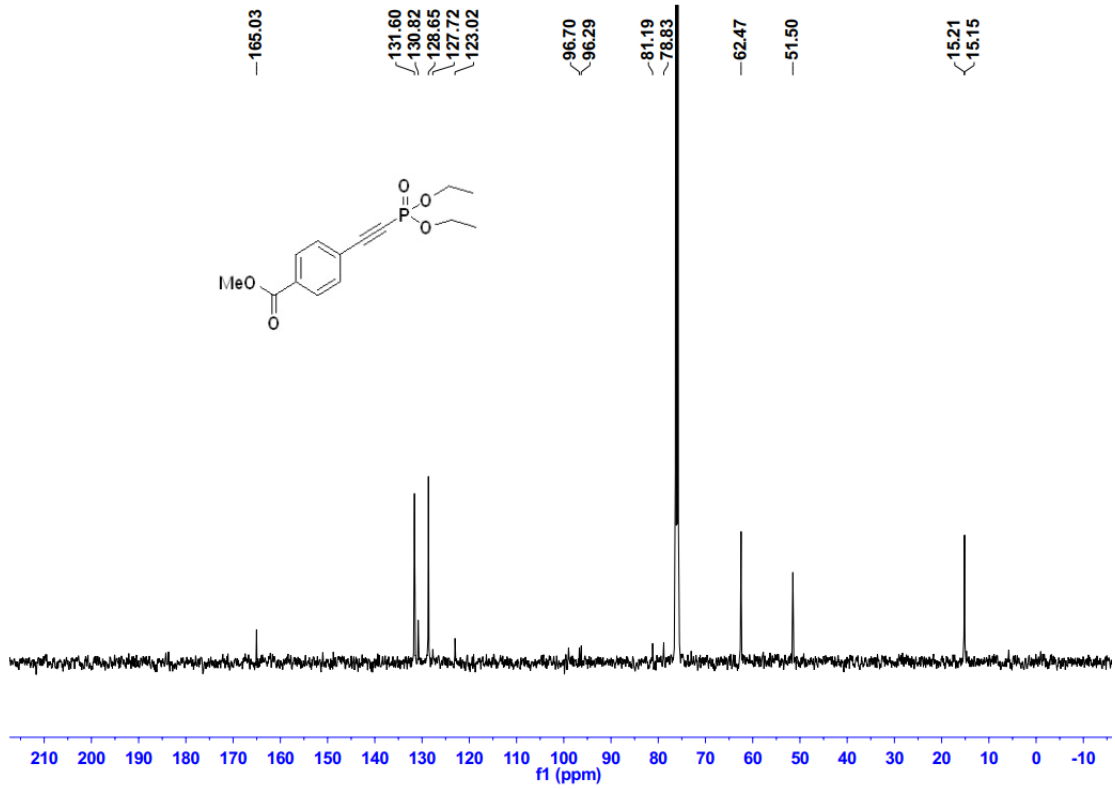
^{1}H NMR of **3d**



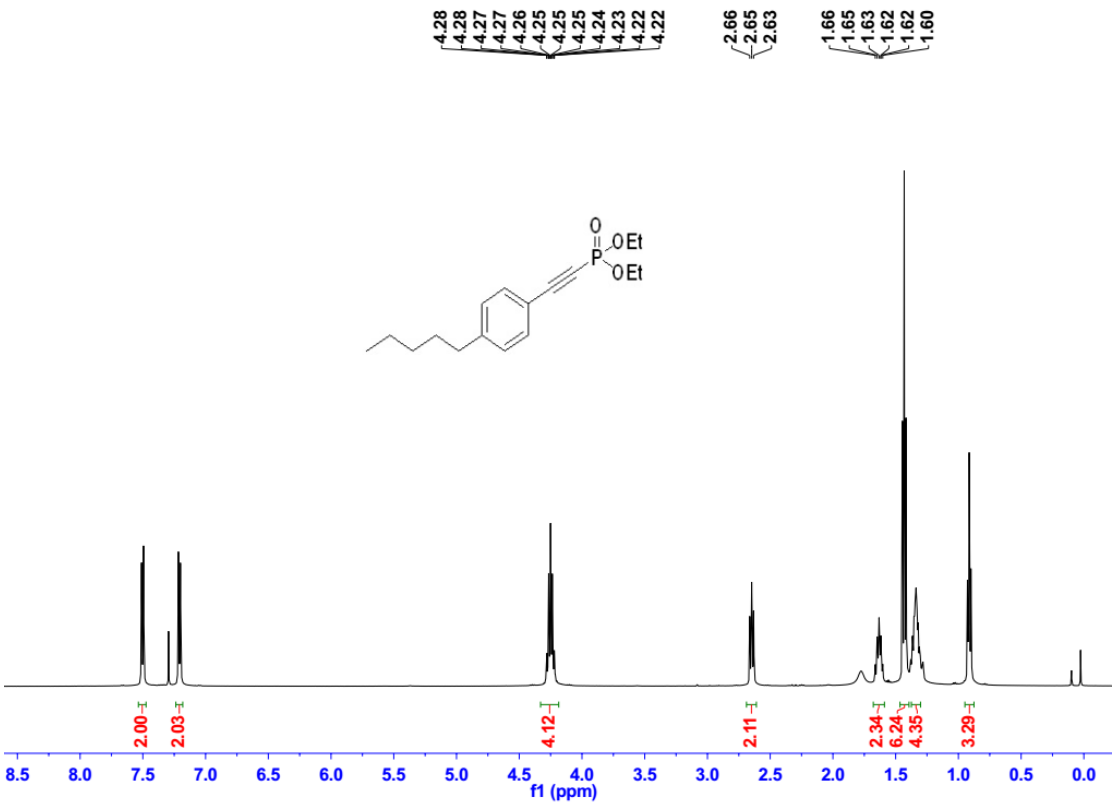
^{13}C NMR of **3d**



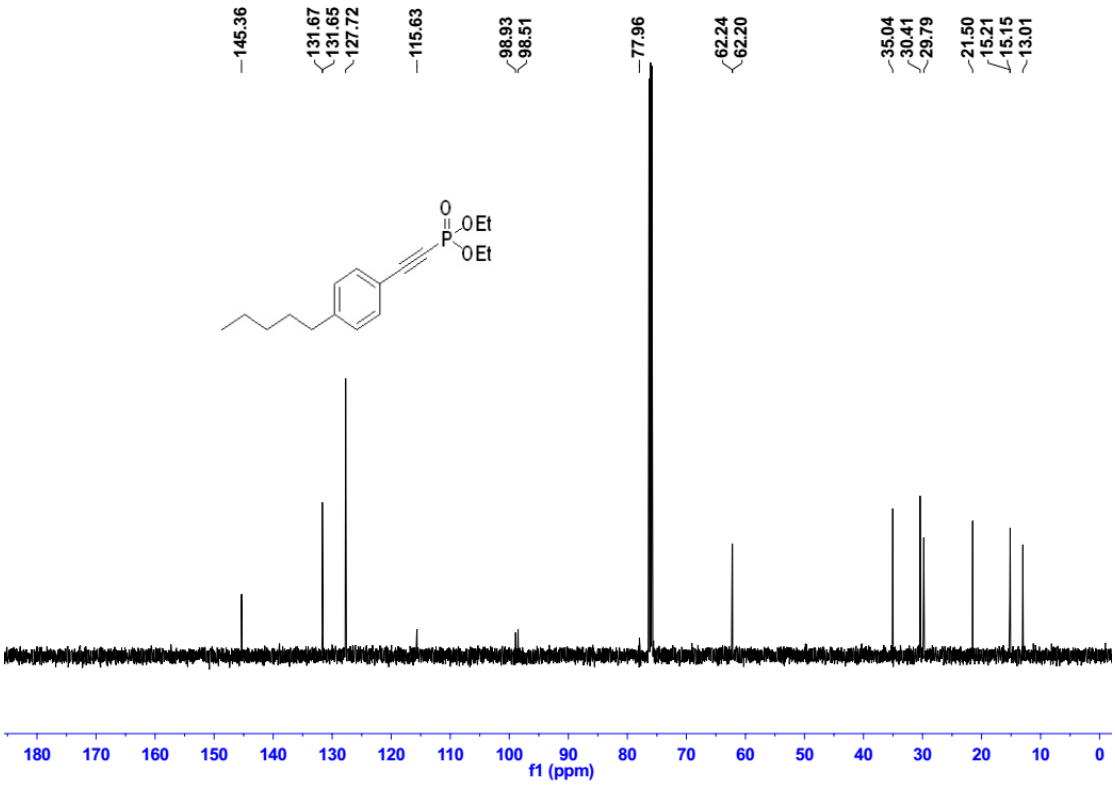
^{1}H NMR of **3e**



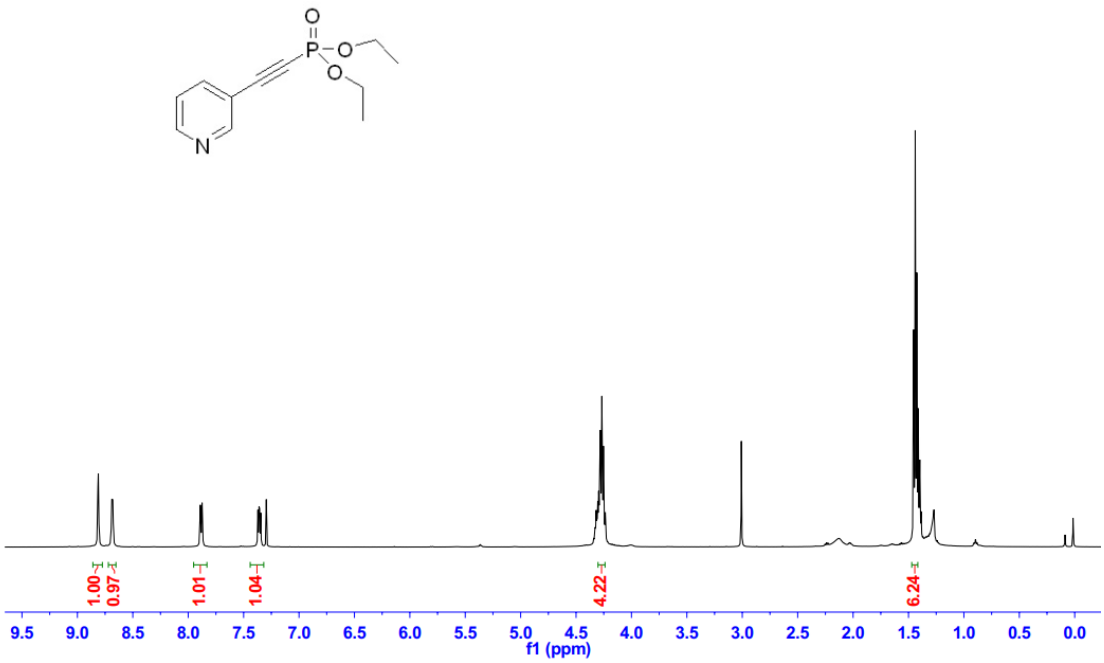
^{13}C NMR of **3e**



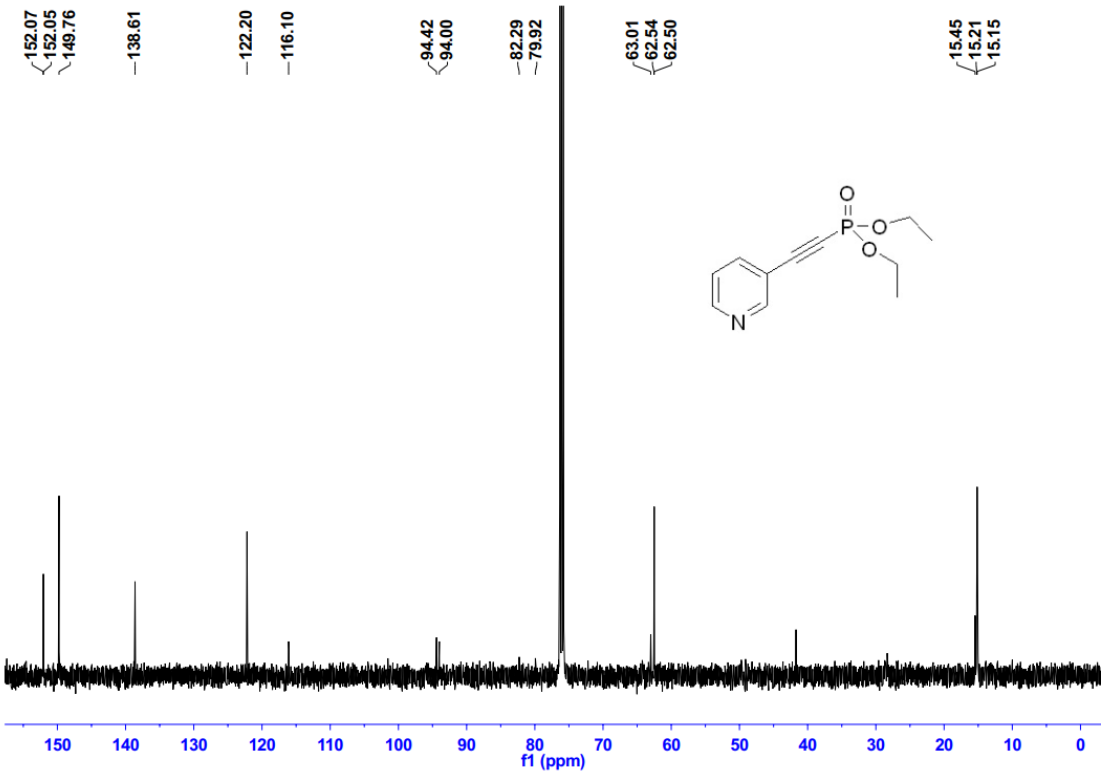
^{1}H NMR of **3f**



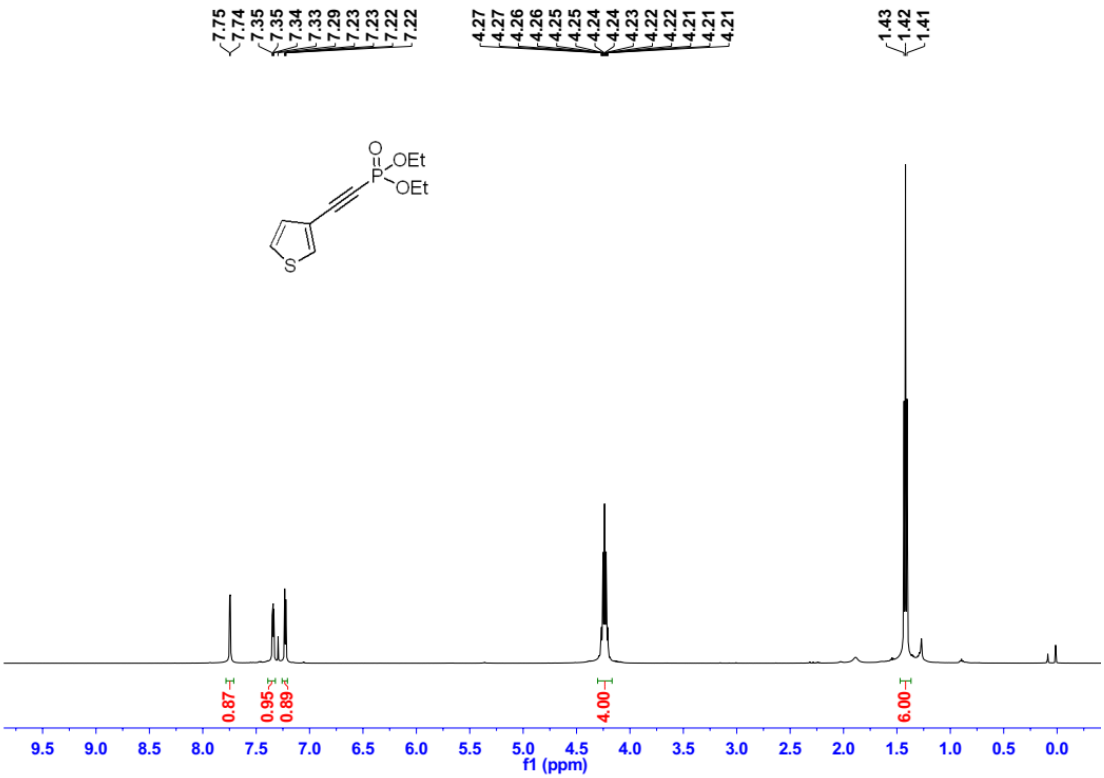
^{13}C NMR of **3f**



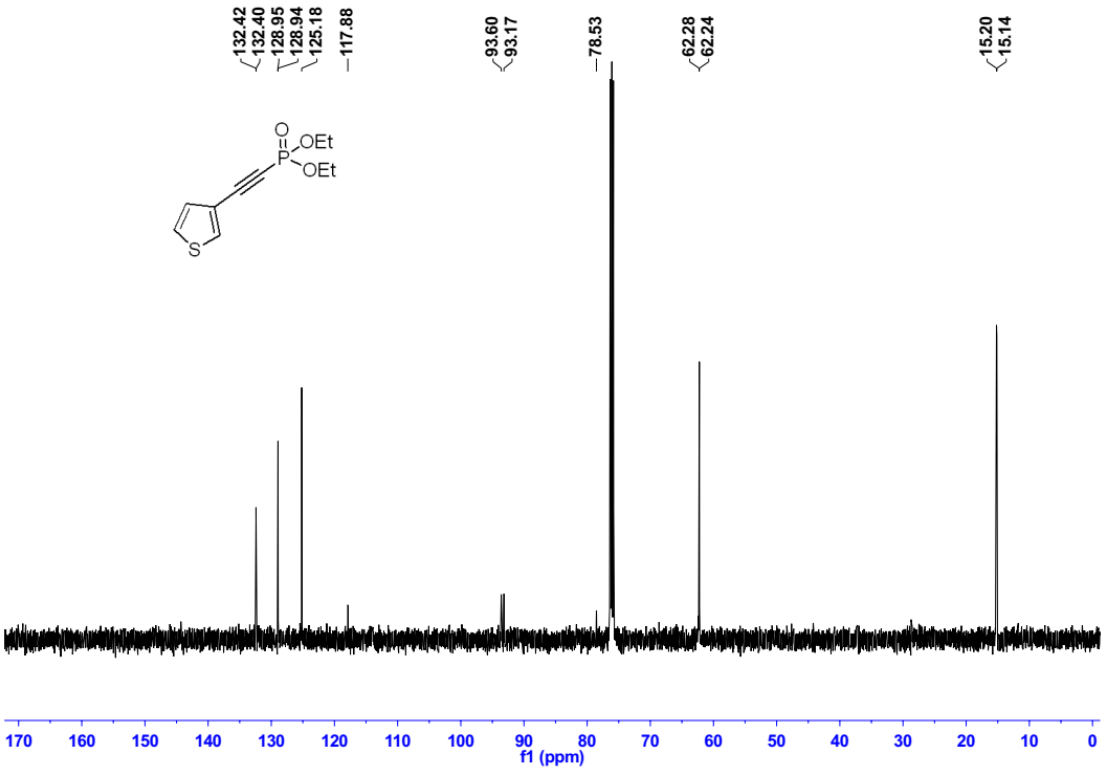
^{1}H NMR of **3g**



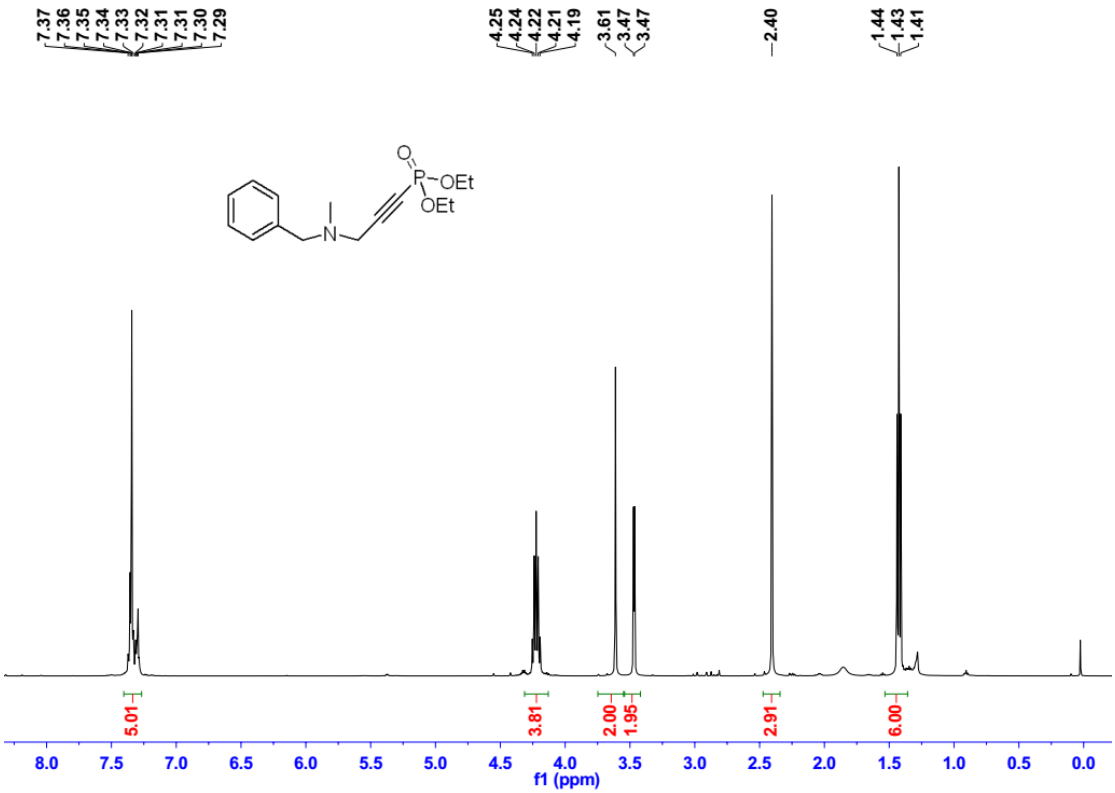
^{13}C NMR of **3g**



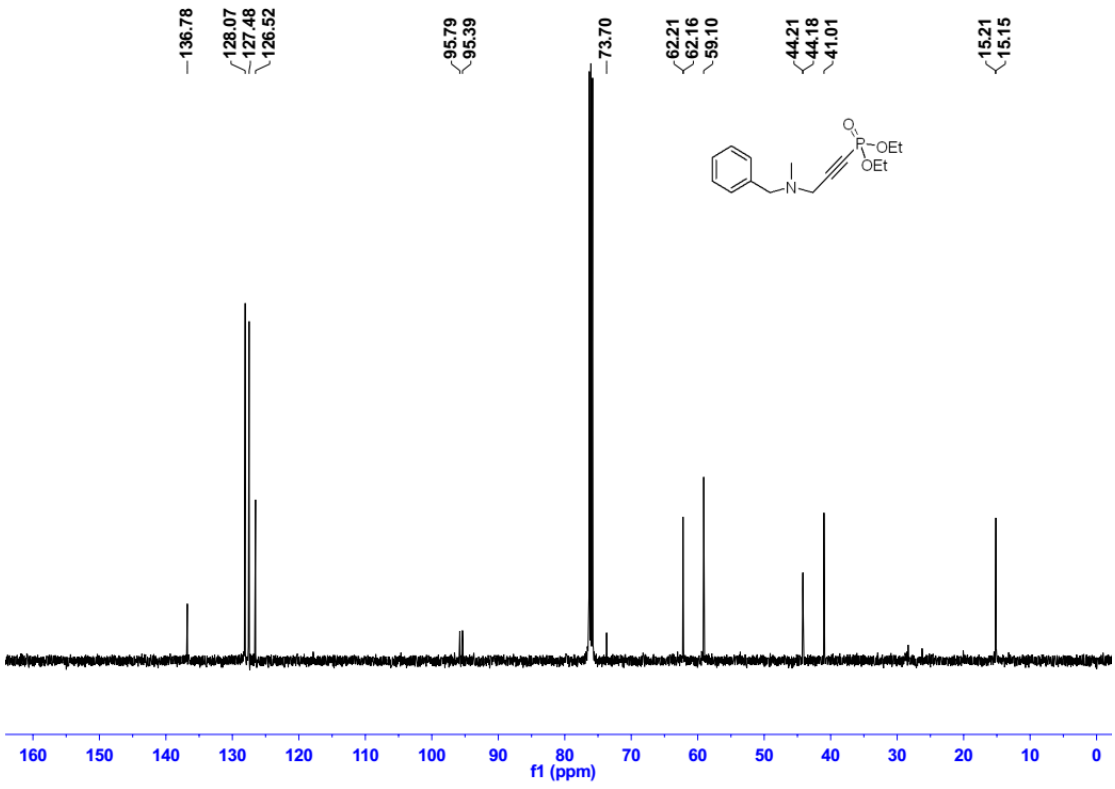
^{1}H NMR of **3h**



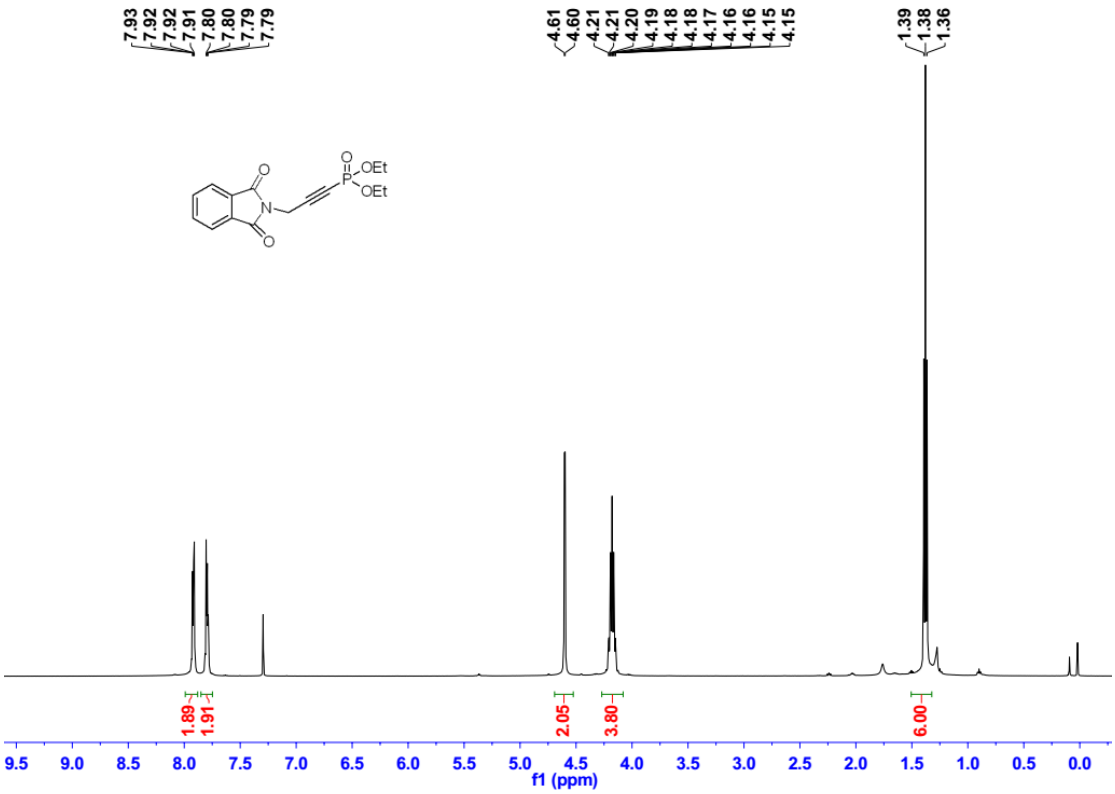
^{13}C NMR of **3h**



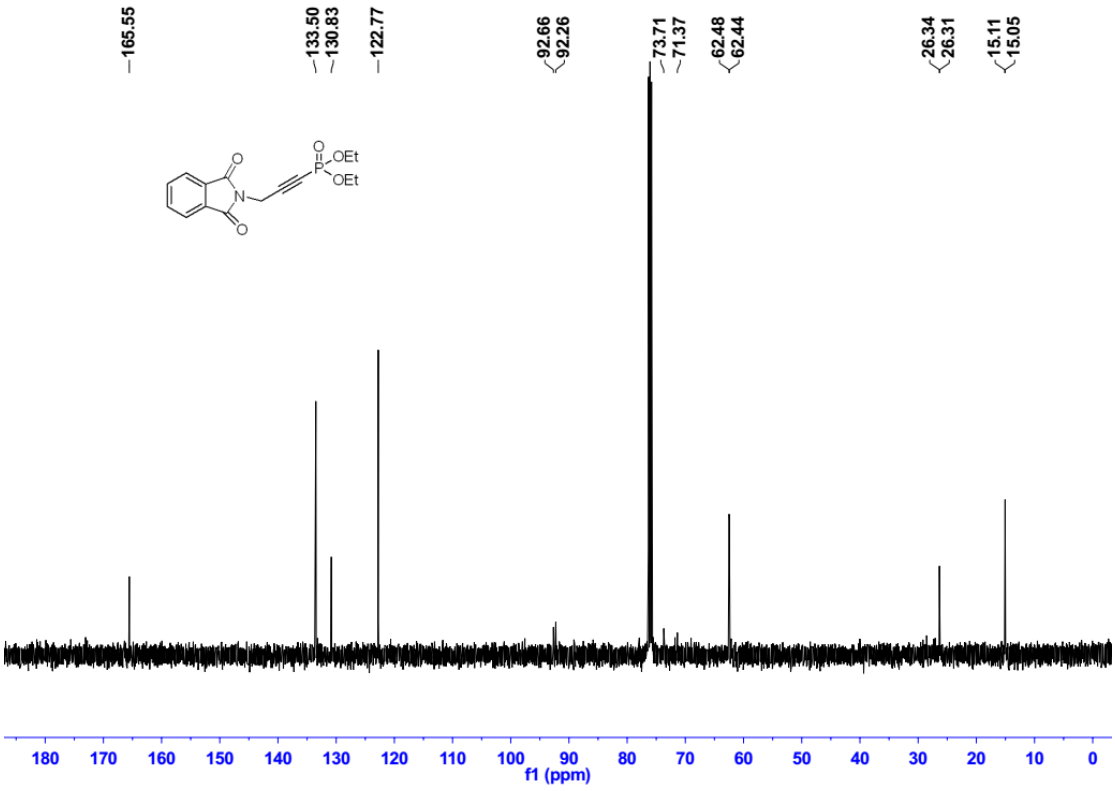
^{1}H NMR of **3i**



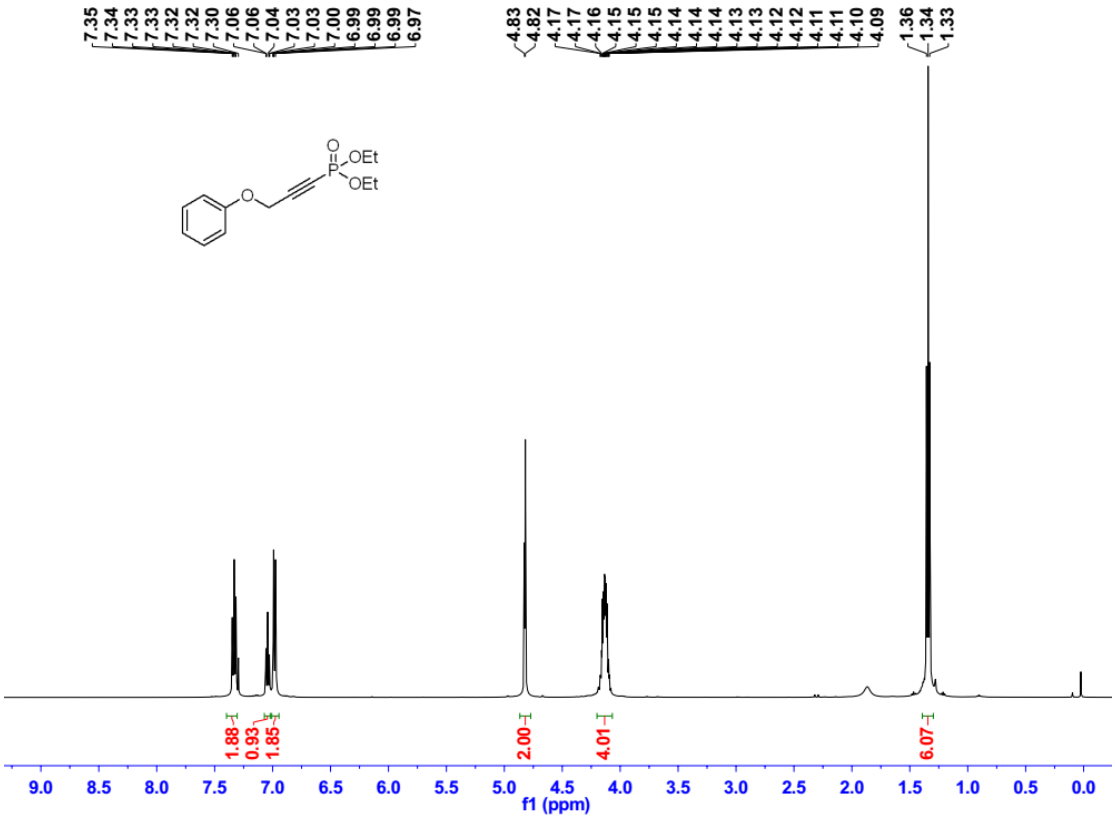
^{13}C NMR of **3i**



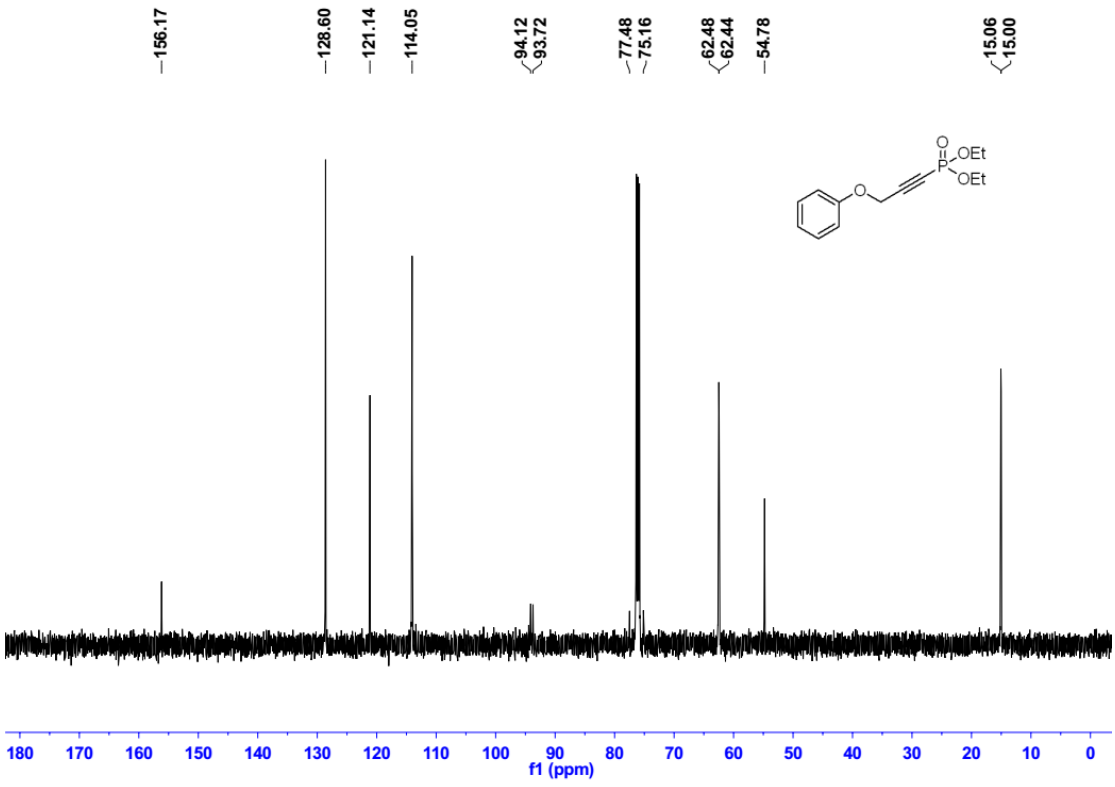
^{1}H NMR of **3j**



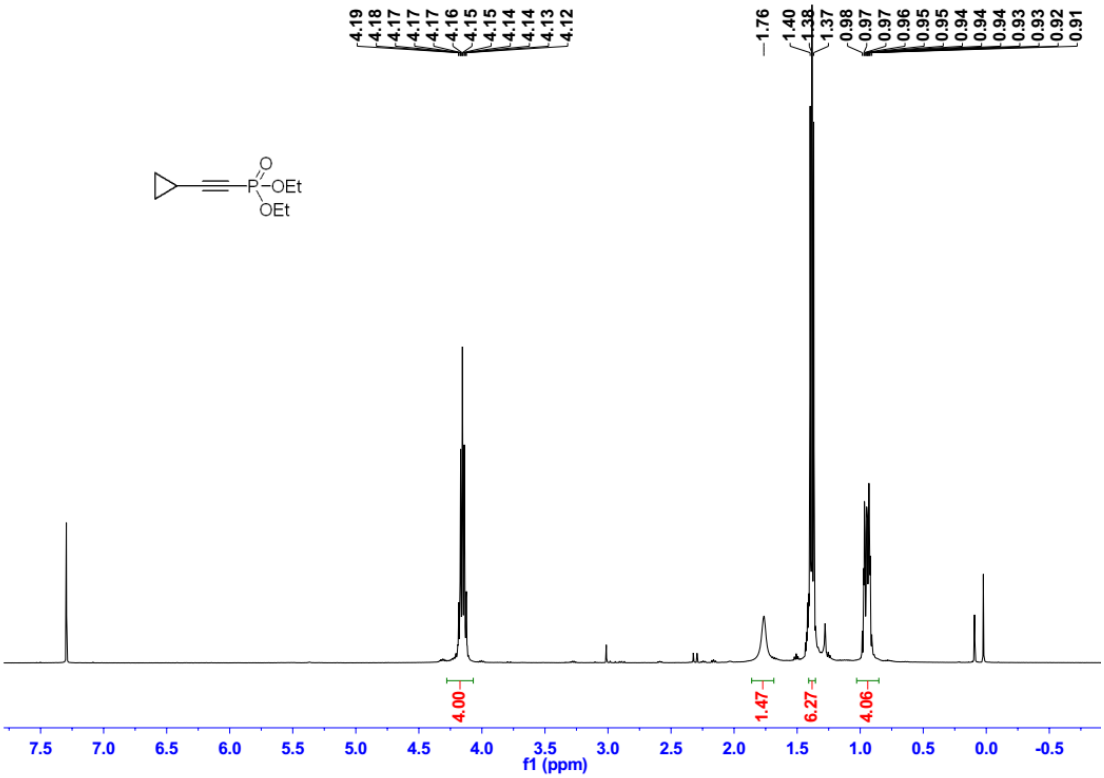
^{13}C NMR of **3j**



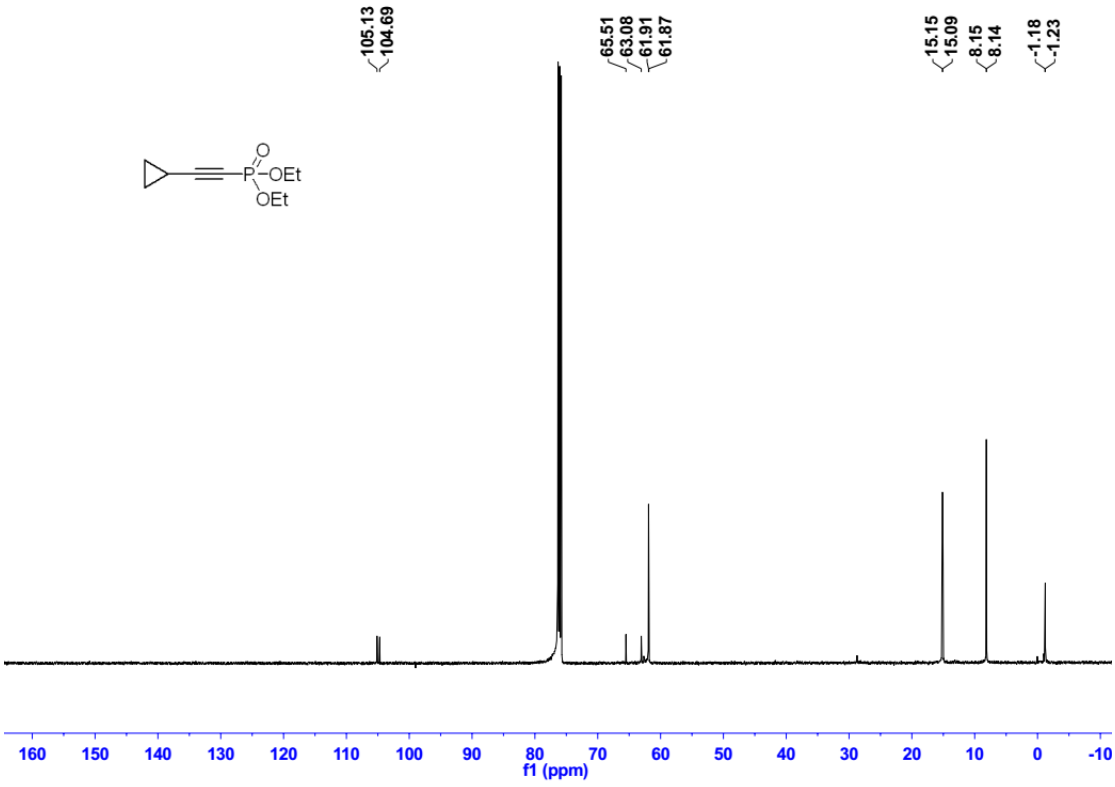
^{1}H NMR of **3k**



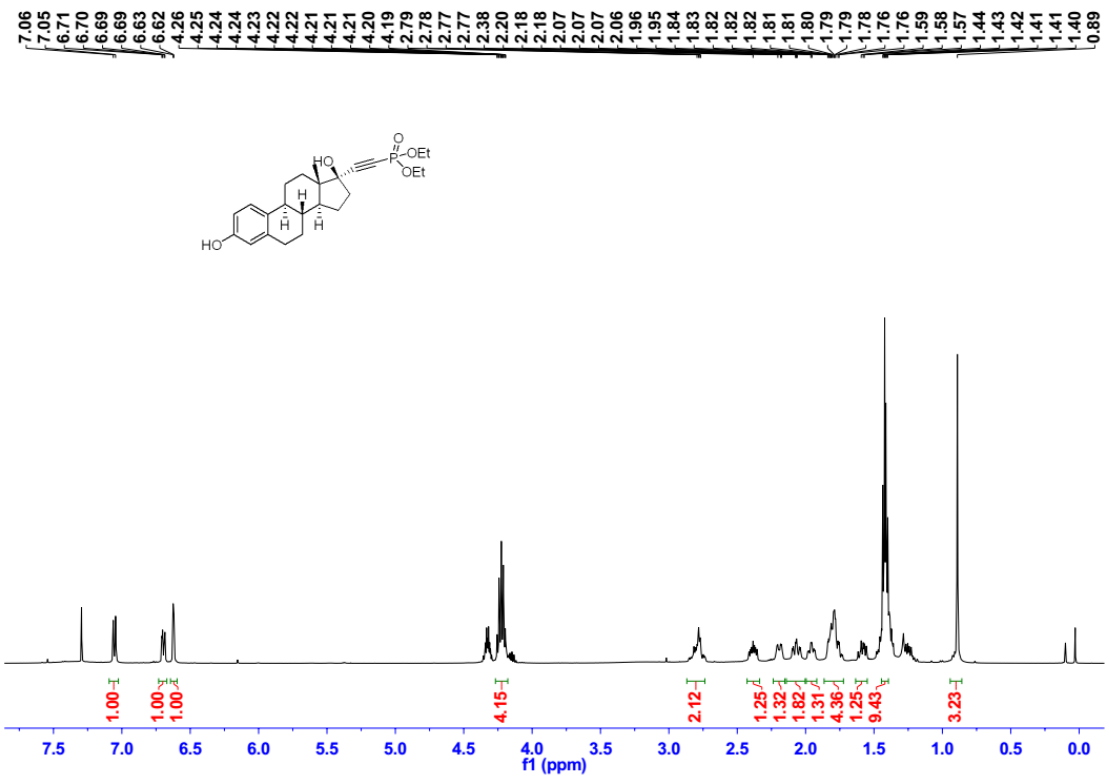
^{13}C NMR of **3k**



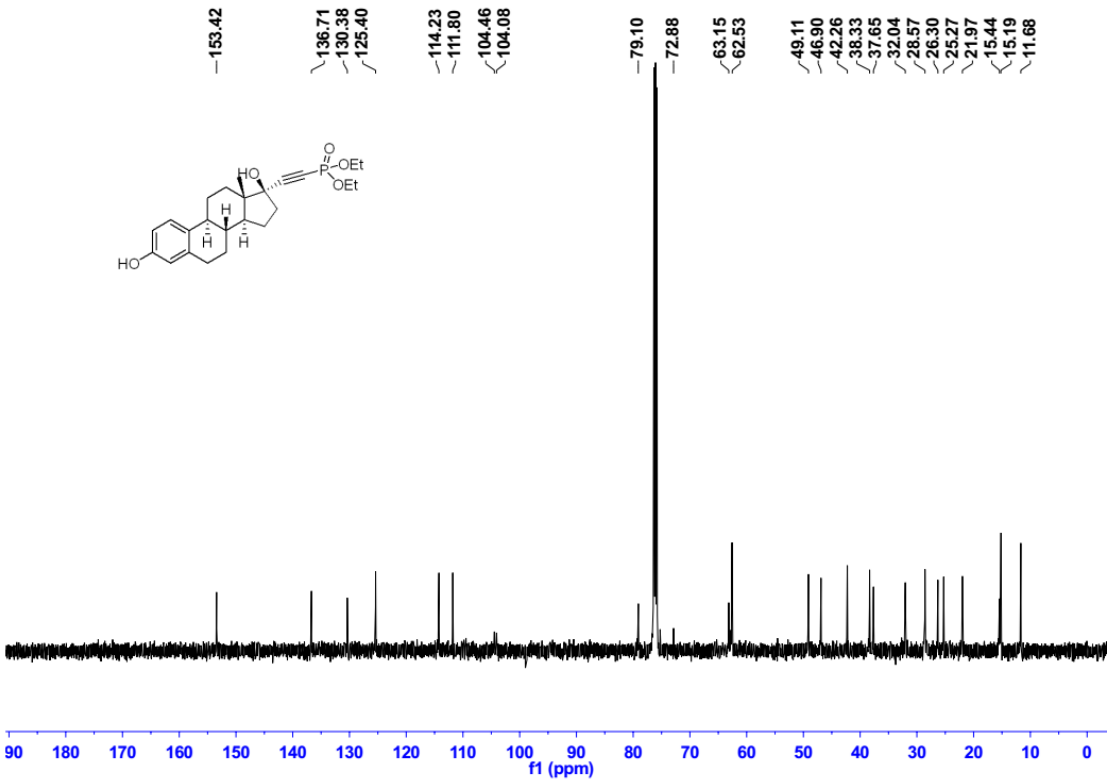
^{1}H NMR of **3l**



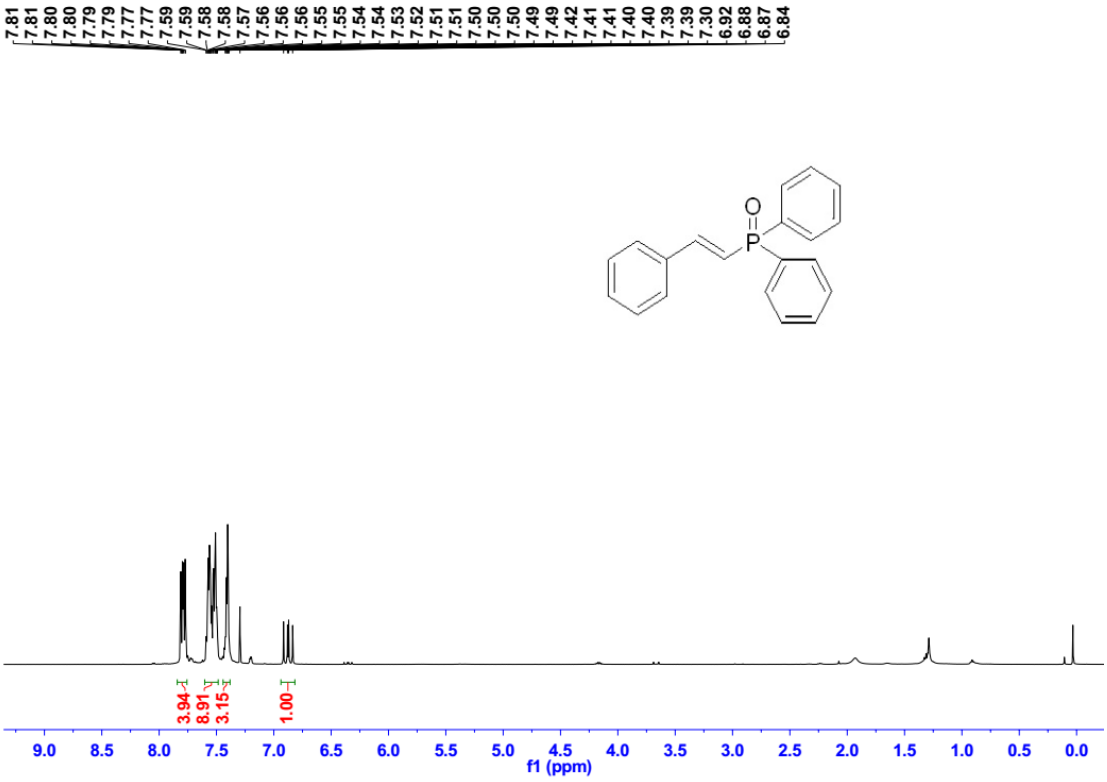
^{13}C NMR of **3l**



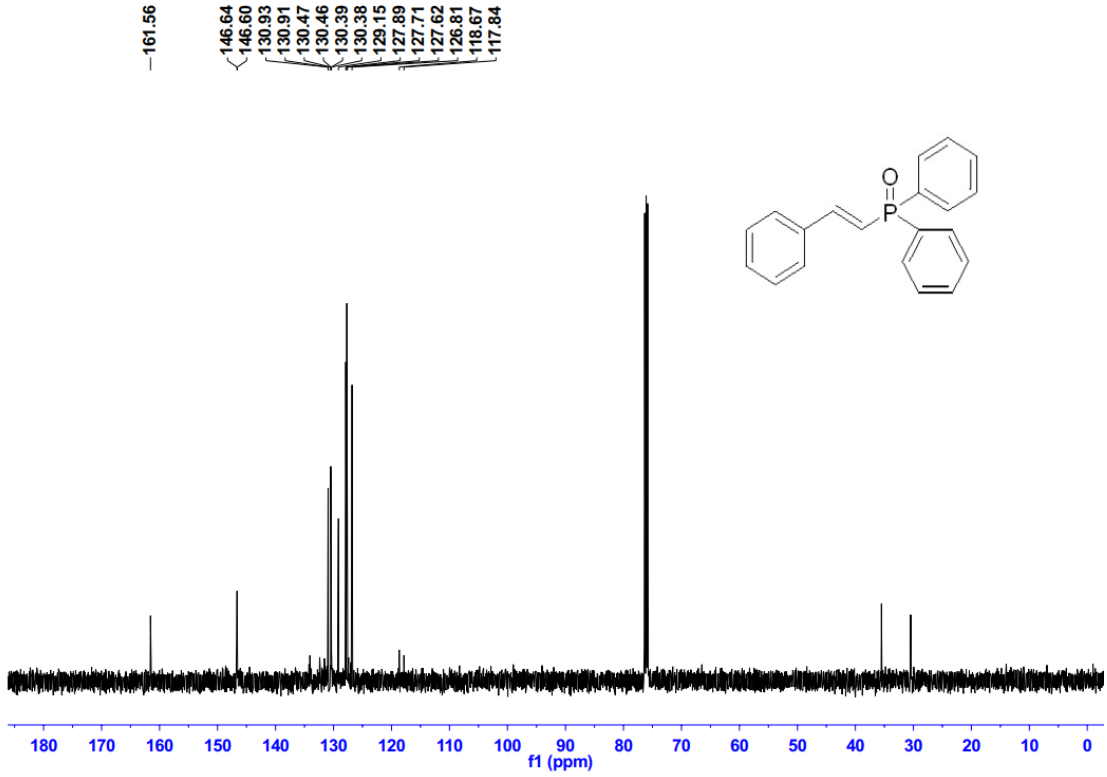
^{1}H NMR of **3m**



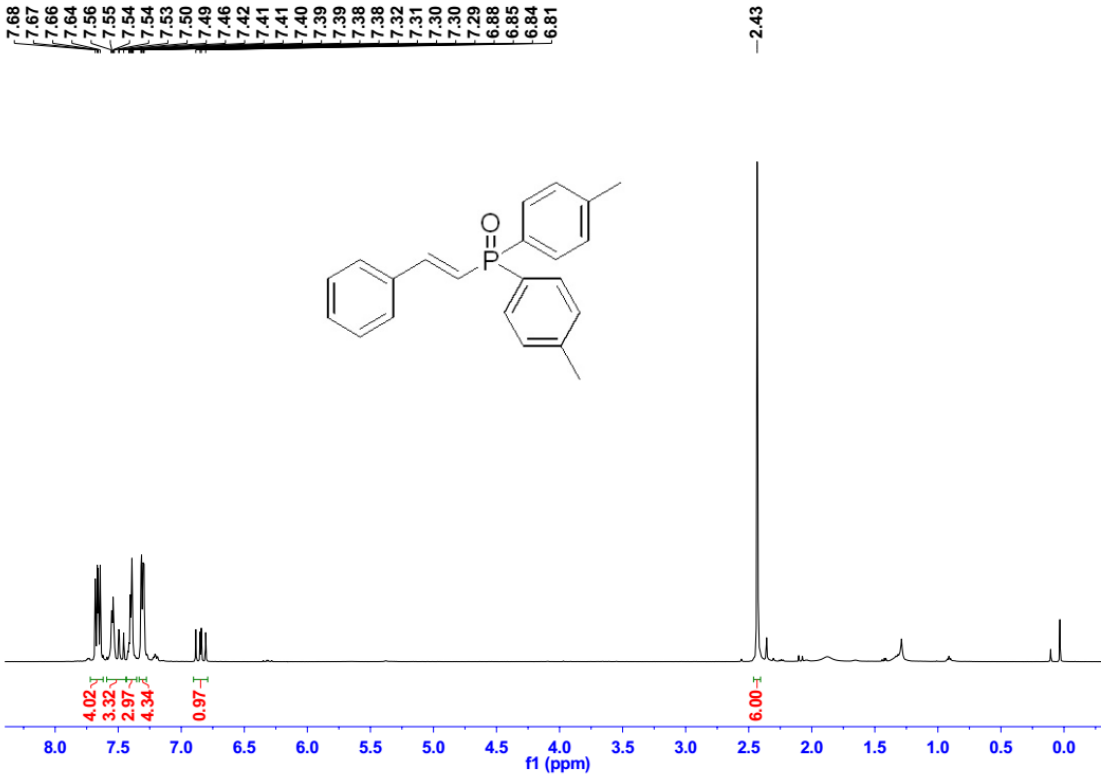
^{13}C NMR of **3m**



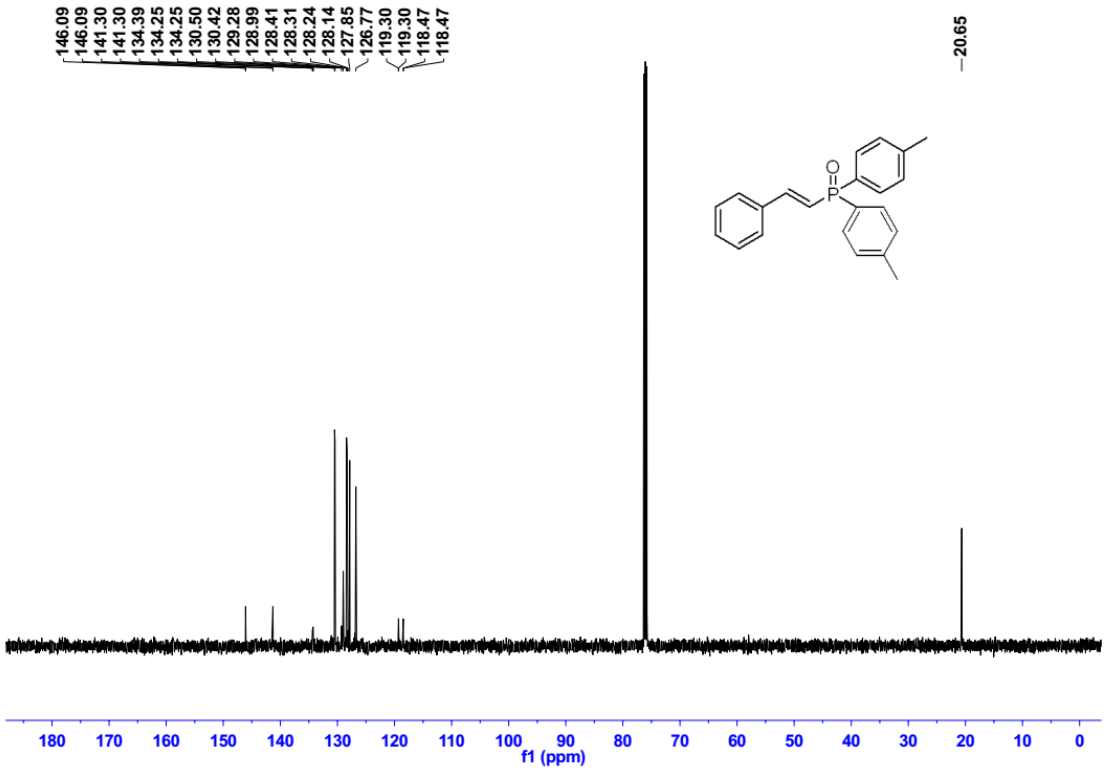
^{1}H NMR of **4a**



^{13}C NMR of **4a**



^{1}H NMR of **4b**



^{13}C NMR of **4b**