

Electronic Supplementary Information

Brønsted Base-Catalyzed 1,2-Addition/[1,2]-Phospha-Brook Rearrangement Sequence Providing Functionalized Phosphonates

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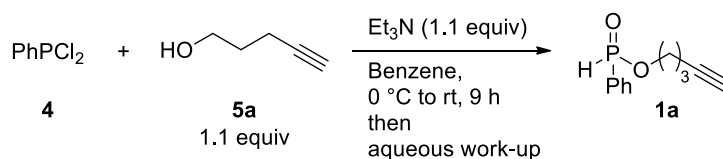
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General Information

All reactions were carried out with dried glassware under argon atmosphere. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), and toluene were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents and reagents were purchased from commercial suppliers and used without further purification. ^1H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard (CDCl_3 : 7.26 ppm, TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl_3 : 77.0 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECA600 (243 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with 85% H_3PO_4 solution as an external standard (0.0 ppm in CDCl_3). ^{19}F NMR spectra were recorded on a JEOL JNM-ECA600 (565 MHz) spectrometer. Chemical shifts are reported in ppm from the $\text{C}_6\text{F}_5\text{CF}_3$ (-67.2 ppm) resonance as the external standard. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm). Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40-50 μm ; Kanto Chemical Co., Inc.). High resolution mass spectra analysis was performed on a JEOL JMS-T100GCV Time-of-Flight Mass Spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Experimental Procedure

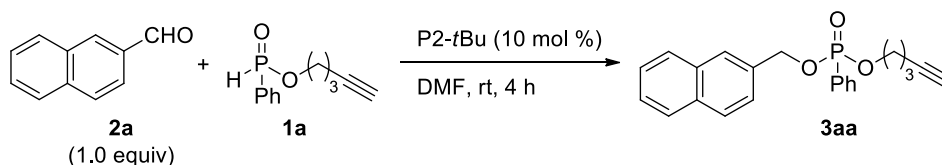
Procedure for Preparation of Phosphinate **1**.



Synthesis of **1a** is representative (eq. 1).

To a solution of 4-pentyn-1-ol (0.31 mL, 3.3 mmol) and triethylamine (0.46 mL, 3.3 mmol) in benzene (6.0 mL) was added dichlorophenylphosphine (0.41 mL, 3.0 mmol) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 9 h. The reaction was quenched with H₂O, and the product was extracted with AcOEt. The combined organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hexane/AcOEt = 1:1 to 1:2) to afford **1a** (0.53 g, 2.6 mmol, 86%) as a colorless oil.

General Procedure for Brønsted Base-Catalyzed 1,2-Addition/[1,2]-Phospha-Brook Rearrangement Sequence.

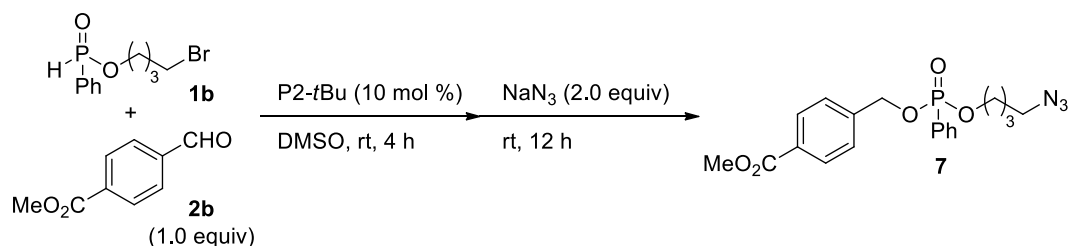


The reaction of **1a** with **2a** is representative (Table 1, entry 1). To a solution of **1a** (21 mg, 0.10 mmol) and **2a** (16 mg, 0.10 mmol) in DMF (1.0 mL) was added a solution of P2-*t*Bu in THF (2.0 M, 5.0 μL, 0.010 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with sat. aq. NH₄Cl, and the product was extracted with AcOEt. The combined organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hexane/AcOEt = 1:1) to provide **3aa** (35 mg, 0.095 mmol, 95%) as a colorless oil.

Procedure for 1 mmol Scale Reaction (Table 1, entry 13)

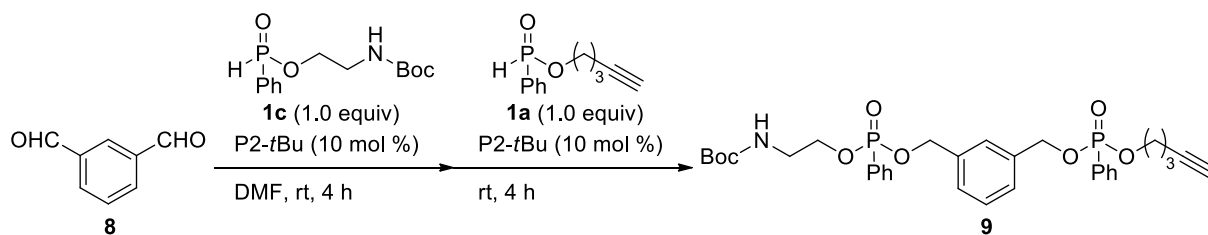
To a solution of **1a** (0.21 g, 1.0 mmol) and **2a** (0.16 g, 1.0 mmol) in DMF (4.0 mL) was added a solution of P2-*t*Bu in THF (2.0 M, 50 μL, 0.10 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with sat. aq. NH₄Cl, and the product was extracted with AcOEt. The combined organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hexane/AcOEt = 1:1) to provide **3aa** (0.32 g, 0.87 mmol, 87%) as a colorless oil.

Procedure for Preparation of 7 (Scheme 4a).



To a solution of **1b** (28 mg, 0.10 mmol) and **2b** (16 mg, 0.10 mmol) in DMSO (1.0 mL) was added a solution of P2-*t*Bu in THF (2.0 M, 5.0 μ L, 0.010 mmol) at room temperature. After stirring at room temperature for 4 h, sodium azide (13 mg, 0.20 mmol) was added. The resulting mixture was further stirred at room temperature for 12 h. The reaction was quenched with sat. aq. NH₄Cl, and the product was extracted with a 1:2 mixture of hexane and AcOEt. The combined organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hexane/AcOEt = 1:1) to provide **7** (33 mg, 0.081 mmol, 81%) as a colorless oil.

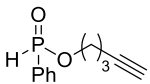
Procedure for Preparation of 9 (Scheme 4b).



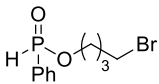
To a solution of **1c** (29 mg, 0.10 mmol) and **8** (13 mg, 0.10 mmol) in DMF (1.0 mL) was added a solution of P2-*t*Bu in THF (2.0 M, 5.0 μ L, 0.010 mmol) at room temperature. After stirring at room temperature for 4 h, **1a** (21 mg, 0.10 mmol) and a solution of P2-*t*Bu in THF (2.0 M, 5.0 μ L, 0.010 mmol) were sequentially added. The resulting mixture was further stirred at room temperature for 4 h. The reaction was quenched with sat. aq. NH₄Cl, and the product was extracted with AcOEt. The combined organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hexane/AcOEt = 1:2) to provide **9** (39 mg, 0.063 mmol, 63%) as a colorless oil.

Analytical Data

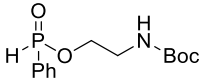
Pent-4-yn-1-yl phenylphosphinate (1a):

 Purification with silica gel column chromatography (Hexane/AcOEt = 1:1 to 1:2); 0.53 g, 86% yield, Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.82-7.77 (m, 2H), 7.64-7.60 (m, 1H), 7.61 (d, *J* = 141.2 Hz, 1H), 7.55-7.50 (m, 2H), 4.26-4.16 (m, 2H), 2.36 (td, *J* = 6.6, 2.4 Hz, 2H), 1.96 (t, *J* = 2.4 Hz, 1H), 1.94 (tt, *J* = 6.6, 6.0 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 133.2 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 11.5 Hz), 129.6 (d, *J* = 132.2 Hz), 128.8 (d, *J* = 12.9 Hz), 82.6, 69.3, 64.2 (d, *J* = 5.7 Hz), 29.1 (d, *J* = 7.2 Hz), 14.7; ³¹P NMR (243 MHz, CDCl₃) δ 26.1; IR (ATR): 3295, 3059, 2951, 2892, 2372, 1715, 1620, 1439, 1200, 1123, 964, 749 cm⁻¹; HRMS (FD+) *m/z*: [M] Calcd for C₁₁H₁₃O₂P 208.0653, Found 208.0652.

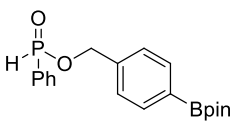
4-Bromobutyl phenylphosphinate (1b):

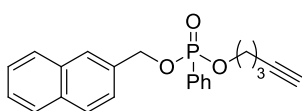
 Purification with silica gel column chromatography (Hexane/AcOEt = 1:1 to 1:2); 0.56 g, 67% yield, Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.82-7.76 (m, 2H), 7.64-7.60 (m, 1H), 7.60 (d, *J* = 141.0 Hz, 1H), 7.55-7.50 (m, 2H), 4.17-4.07 (m, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.03-1.98 (m, 2H), 1.92-1.87 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 133.2 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 12.9 Hz), 129.6 (d, *J* = 130.7 Hz), 128.8 (d, *J* = 12.9 Hz), 64.8 (d, *J* = 7.2 Hz), 32.9, 29.0 (d, *J* = 5.8 Hz), 28.8; ³¹P NMR (243 MHz, CDCl₃) δ 25.8; IR (ATR): 3316, 3060, 2943, 2365, 1688, 1439, 1126, 964, 749 cm⁻¹; HRMS (FD+) *m/z*: [M+H] Calcd for C₁₀H₁₅BrO₂P 276.9993, Found 276.9992.

2-(tert-Butoxycarbonylamino)ethyl phenylphosphinate (1c):

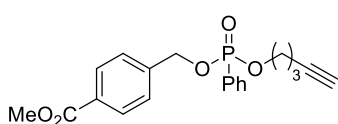
 Purification with silica gel column chromatography (Hexane/AcOEt = 1:2); 0.38 g, 45% yield, White solid; ¹H NMR (600 MHz, CDCl₃) δ 7.81-7.76 (m, 2H), 7.65-7.60 (m, 1H), 7.60 (d, *J* = 142.2 Hz, 1H), 7.55-7.50 (m, 2H), 5.19 (brs, 1H), 4.20-4.05 (m, 2H), 3.50-3.35 (m, 2H), 1.43 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 155.8, 133.3 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 11.6 Hz), 129.2 (d, *J* = 130.6 Hz), 128.9 (d, *J* = 12.9 Hz), 79.6, 65.5 (d, *J* = 4.4 Hz), 41.1 (d, *J* = 3.0 Hz), 28.3; ³¹P NMR (243 MHz, CDCl₃) δ 27.2; IR (ATR): 3317, 3059, 2977, 2934, 2374, 1704, 1527, 1440, 1365, 1220, 1171, 1126, 961 cm⁻¹; HRMS (FD+) *m/z*: [M] Calcd for C₁₃H₂₀NO₄P 285.1130, Found 285.1129; M.p. 86.0-87.6 °C.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl phenylphosphinate (1d):

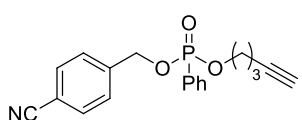
 Purification with silica gel column chromatography (Hexane/AcOEt = 3:2 to 1:1); 0.23 g, 43% yield (1.5 mmol scale), Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.81-7.76 (m, 2H), 7.65 (d, *J* = 141.6 Hz, 1H), 7.62-7.59 (m, 1H), 7.53-7.49 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 5.18 (dd, *J* = 12.0, 8.4 Hz, 1H), 5.09 (dd, *J* = 12.0, 9.6 Hz, 1H), 1.34 (s, 12H); ¹³C NMR (150 MHz, CDCl₃) δ 138.5 (d, *J* = 7.2 Hz), 135.1, 133.2 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 11.6 Hz), 129.6 (d, *J* = 130.8 Hz), 128.8 (d, *J* = 14.4 Hz), 127.1, 83.9, 67.0 (d, *J* = 6.9 Hz), 24.8; ³¹P NMR (243 MHz, CDCl₃) δ 25.7; IR (ATR): 3419, 3056, 2979, 2933, 2361, 1614, 1399, 1359, 1221, 1143, 1088, 957, 858 cm⁻¹; HRMS (FD+) *m/z*: [M] Calcd for C₁₉H₂₄BO₄P 358.1505, Found 358.1504.

2-Naphthylmethyl pent-4-yn-1-yl phenylphosphonate (3aa):

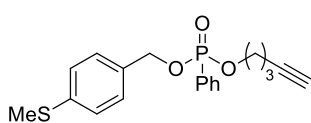
Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 35 mg, 95% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.86-7.79 (m, 6H), 7.57-7.53 (m, 1H), 7.51-7.43 (m, 5H), 5.31 (dd, $J = 12.0$, 7.8 Hz, 1H), 5.20 (dd, $J = 12.0$, 8.4 Hz, 1H), 4.21-4.11 (m, 2H), 2.27 (td, $J = 7.2$, 3.0 Hz, 2H), 1.90 (t, $J = 3.0$ Hz, 1H), 1.86 (tt, $J = 7.2$, 7.2 Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 133.6 (d, $J = 5.7$ Hz), 133.1 (d, $J = 7.0$ Hz), 132.6 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.1$ Hz), 128.5 (d, $J = 14.4$ Hz), 128.4, 128.0, 127.8 (d, $J = 187.2$ Hz), 127.7, 127.0, 126.31, 126.29 (2C), 125.5, 82.8, 69.1, 67.7 (d, $J = 4.4$ Hz), 64.6 (d, $J = 4.2$ Hz), 29.2 (d, $J = 7.2$ Hz), 14.8; ^{31}P NMR (243 MHz, CDCl_3) δ 20.2; IR (ATR): 3454, 3297, 3227, 3057, 2959, 2896, 2117, 1439, 1244, 1131, 1014, 976, 814 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{22}\text{H}_{21}\text{O}_3\text{P}$ 364.1228, Found 364.1227.

(4-Methoxycarbonyl)benzyl pent-4-yn-1-yl phenylphosphonate (3ab):

Purification with silica gel column chromatography (Hexane/AcOEt = 3:2 to 1:1); 33 mg, 89% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.85-7.79 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 5.20 (dd, $J = 12.6$, 7.8 Hz, 1H), 5.09 (dd, $J = 12.6$, 7.8 Hz, 1H), 4.22-4.12 (m, 2H), 3.92 (s, 3H), 2.29 (td, $J = 7.2$, 2.4 Hz, 2H), 1.92 (t, $J = 2.4$ Hz, 1H), 1.87 (tt, $J = 7.2$, 7.2 Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.6, 141.2 (d, $J = 7.2$ Hz), 132.7 (d, $J = 2.9$ Hz), 131.8 (d, $J = 8.5$ Hz), 130.0, 129.8, 128.6 (d, $J = 15.8$ Hz), 127.5 (d, $J = 188.1$ Hz), 127.2, 82.7, 69.1, 66.7 (d, $J = 4.2$ Hz), 64.6 (d, $J = 5.7$ Hz), 52.1, 29.1 (d, $J = 7.2$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.3; IR (ATR): 3438, 3303, 2996, 2953, 1720, 1438, 1280, 1244, 1109, 1010, 748 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{20}\text{H}_{21}\text{O}_5\text{P}$ 372.1127, Found 372.1126.

4-Cyanobenzyl pent-4-yn-1-yl phenylphosphonate (3ac):

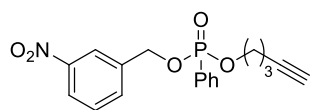
Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 30 mg, 88% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.84-7.78 (m, 2H), 7.64 (d, $J = 9.0$ Hz, 2H), 7.61-7.57 (m, 1H), 7.51-7.45 (m, 4H), 5.19 (dd, $J = 12.6$, 7.8 Hz, 1H), 5.10 (dd, $J = 12.6$, 7.8 Hz, 1H), 4.24-4.12 (m, 2H), 2.29 (td, $J = 7.2$, 3.0 Hz, 2H), 1.94 (t, $J = 3.0$ Hz, 1H), 1.88 (tt, $J = 7.2$, 6.6 Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 141.5 (d, $J = 7.2$ Hz), 132.9 (d, $J = 2.9$ Hz), 132.3, 131.8 (d, $J = 10.1$ Hz), 128.6 (d, $J = 15.9$ Hz), 127.8, 127.2 (d, $J = 186.6$ Hz), 118.5, 112.1, 82.6, 69.2, 66.2 (d, $J = 5.9$ Hz), 64.7 (d, $J = 5.9$ Hz), 29.1 (d, $J = 5.8$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.5; IR (ATR): 3463, 3296, 3060, 2961, 2898, 2229, 2117, 1440, 1245, 1131, 1011, 819 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_3\text{P}$ 339.1024, Found 339.1023.

(4-Methylthio)benzyl pent-4-yn-1-yl phenylphosphonate (3ad):

Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 32 mg, 88% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.82-7.77 (m, 2H), 7.57-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 5.10 (dd, $J = 12.0$, 7.8 Hz, 1H), 4.99 (dd, $J = 12.0$, 7.8 Hz, 1H), 4.18-4.09 (m, 2H), 2.48 (s, 3H), 2.28 (td, $J = 7.2$, 2.4 Hz, 2H), 1.92 (t, $J = 2.4$ Hz, 1H), 1.86 (tt, $J = 7.2$, 6.6 Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.9, 132.9 (d, $J = 5.7$ Hz), 132.5 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.1$ Hz), 128.6, 128.5 (d, $J = 14.2$ Hz), 127.8 (d, $J = 188.6$ Hz), 126.4, 82.8,

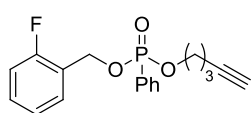
69.1, 67.2 (d, $J = 5.9$ Hz), 64.5 (d, $J = 5.7$ Hz), 29.2 (d, $J = 7.2$ Hz), 15.7, 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.1; IR (ATR): 3463, 3294, 3227, 3058, 2959, 2922, 2896, 1602, 1496, 1439, 1246, 1131, 994 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{19}\text{H}_{21}\text{O}_3\text{PS}$ 360.0949, Found 360.0948.

3-Nitrobenzyl pent-4-yn-1-yl phenylphosphonate (3ae):



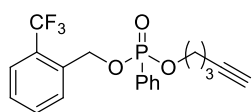
Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 17 mg, 48% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 8.21 (s, 1H), 8.17 (d, $J = 7.8$ Hz, 1H), 7.86-7.79 (m, 2H), 7.69 (d, $J = 7.8$ Hz, 1H), 7.60-7.56 (m, 1H), 7.53 (dd, $J = 7.8, 7.8$ Hz, 1H), 7.50-7.45 (m, 2H), 5.23 (dd, $J = 12.6, 7.8$ Hz, 1H), 5.14 (dd, $J = 12.6, 7.8$ Hz, 1H), 4.26-4.14 (m, 2H), 2.30 (td, $J = 7.2, 2.4$ Hz, 2H), 1.94 (t, $J = 2.4$ Hz, 1H), 1.89 (tt, $J = 7.2, 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.3, 138.3 (d, $J = 7.2$ Hz), 133.4, 132.9 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.1$ Hz), 129.6, 128.7 (d, $J = 14.4$ Hz), 127.2 (d, $J = 188.1$ Hz), 123.2, 122.4, 82.6, 69.2, 66.0 (d, $J = 4.3$ Hz), 64.8 (d, $J = 5.7$ Hz), 29.1 (d, $J = 7.2$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.6; IR (ATR): 3465, 3297, 3231, 3067, 2961, 2924, 1530, 1351, 1244, 1131, 1015, 979 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_5\text{P}$ 359.0923, Found 359.0922.

2-Fluorobenzyl pent-4-yn-1-yl phenylphosphonate (3af):

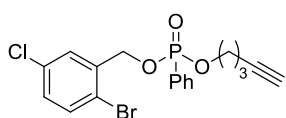


Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 33 mg, 92% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.84-7.79 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.41 (m, 3H), 7.33-7.28 (m, 1H), 7.13 (ddd, $J = 7.2, 7.2, 1.2$ Hz, 1H), 7.04 (ddd, $J = 9.6, 8.4, 1.2$ Hz, 1H), 5.21 (dd, $J = 12.0, 7.8$ Hz, 1H), 5.11 (dd, $J = 12.0, 7.8$ Hz, 1H), 4.21-4.12 (m, 2H), 2.28 (td, $J = 7.2, 2.4$ Hz, 2H), 1.92 (t, $J = 3.0$ Hz, 1H), 1.87 (tt, $J = 7.2, 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 160.6 (d, $J = 247.0$ Hz), 132.6 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.0$ Hz), 130.3 (d, $J = 6.5$ Hz), 130.2, 128.5 (d, $J = 15.7$ Hz), 127.6 (d, $J = 186.7$ Hz), 124.2 (d, $J = 2.9$ Hz), 123.4 (dd, $J = 14.4, 7.2$ Hz), 115.3 (d, $J = 20.1$ Hz), 82.8, 69.0, 64.5 (d, $J = 5.7$ Hz), 61.5 (dd, $J = 4.3, 4.2$ Hz), 29.2 (d, $J = 7.2$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.2; ^{19}F NMR (565 MHz, CDCl_3) δ -118.0 (m); IR (ATR): 3306, 3236, 3060, 2998, 2899, 2119, 1591, 1494, 1240, 1132, 996, 747 cm^{-1} ; HRMS (FD+) m/z : [M+H] Calcd for $\text{C}_{18}\text{H}_{19}\text{FO}_3\text{P}$ 333.1056, Found 333.1055.

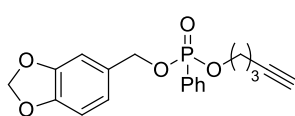
Pent-4-yn-1-yl (2-trifluoromethyl)benzyl phenylphosphonate (3ag):



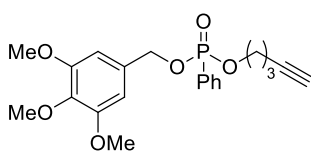
Purification with silica gel column chromatography (Hexane/AcOEt = 3:2); 31 mg, 82% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.86-7.81 (m, 2H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.59-7.54 (m, 2H), 7.50-7.45 (m, 2H), 7.42 (dd, $J = 7.8, 7.2$ Hz, 1H), 5.34 (dd, $J = 13.2, 7.2$ Hz, 1H), 5.25 (dd, $J = 12.6, 7.2$ Hz, 1H), 4.24-4.13 (m, 2H), 2.29 (td, $J = 7.2, 2.4$ Hz, 2H), 1.92 (t, $J = 2.4$ Hz, 1H), 1.88 (tt, $J = 7.2, 7.2$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.6 (d, $J = 7.2$ Hz), 132.7 (d, $J = 2.8$ Hz), 132.1, 131.8 (d, $J = 10.1$ Hz), 129.4, 128.6 (d, $J = 15.8$ Hz), 128.2, 127.7 (q, $J = 30.3$ Hz), 127.4 (d, $J = 188.1$ Hz), 125.9 (q, $J = 5.7$ Hz), 124.1 (q, $J = 272.8$ Hz), 82.7, 69.1, 64.7 (d, $J = 5.7$ Hz), 63.6, 29.2 (d, $J = 7.2$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.1; ^{19}F NMR (565 MHz, CDCl_3) δ -59.8; IR (ATR): 3473, 3306, 3232, 3062, 2963, 1599, 1440, 1314, 1250, 1169, 1119, 1010, 863 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_3\text{O}_3\text{P}$ 382.0946, Found 382.0944.

(2-Bromo-5-chloro)benzyl pent-4-yn-1-yl phenylphosphonate (3ah):

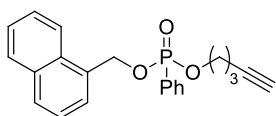
Purification with silica gel column chromatography (Hexane/AcOEt = 3:2); 39 mg, 90% yield, Colorless oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.88-7.82 (m, 2H), 7.61-7.56 (m, 1H), 7.52-7.42 (m, 4H), 7.16-7.13 (m, 1H), 5.18 (dd, $J = 13.2, 7.2$ Hz, 1H), 5.06 (dd, $J = 13.2, 7.2$ Hz, 1H), 4.28-4.17 (m, 2H), 2.32 (td, $J = 7.2, 2.4$ Hz, 2H), 1.95 (t, $J = 2.4$ Hz, 1H), 1.91 (tt, $J = 7.2, 6.6$ Hz, 2H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 137.4 (d, $J = 7.2$ Hz), 133.7, 133.6, 132.8 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.0$ Hz), 129.5, 128.8, 128.6 (d, $J = 15.8$ Hz), 127.2 (d, $J = 188.1$ Hz), 119.8, 82.6, 69.2, 66.2 (d, $J = 4.3$ Hz), 64.7 (d, $J = 4.2$ Hz), 29.1 (d, $J = 7.2$ Hz), 14.8; $^{31}\text{P NMR}$ (243 MHz, CDCl_3) δ 20.3; IR (ATR): 3462, 3303, 3233, 3061, 2961, 2118, 1440, 1249, 1131, 1016, 876 cm^{-1} ; HRMS (FD+) m/z : $[\text{M}+\text{H}]$ Calcd for $\text{C}_{18}\text{H}_{18}\text{BrClO}_3\text{P}$ 426.9866, Found 426.9862.

Benzo[d][1,3]dioxol-5-ylmethyl pent-4-yn-1-yl phenylphosphonate (3ai):

Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 27 mg, 75% yield, Colorless oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.80 (dd, $J = 13.8, 7.8$ Hz, 2H), 7.58-7.53 (m, 1H), 7.48-7.43 (m, 2H), 6.86 (d, $J = 0.60$ Hz, 1H), 6.81 (d, $J = 7.8$ Hz, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 5.95 (s, 2H), 5.04 (dd, $J = 12.0, 8.4$ Hz, 1H), 4.93 (dd, $J = 12.0, 8.4$ Hz, 1H), 4.18-4.08 (m, 2H), 2.28 (td, $J = 7.2, 2.4$ Hz, 2H), 1.93 (t, $J = 2.4$ Hz, 1H), 1.86 (tt, $J = 7.2, 7.2$ Hz, 2H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 147.8, 147.7, 132.5 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.0$ Hz), 129.9 (d, $J = 7.2$ Hz), 128.5 (d, $J = 14.4$ Hz), 127.9 (d, $J = 188.1$ Hz), 122.0, 108.8, 108.1, 101.1, 82.8, 69.1, 67.6 (d, $J = 4.3$ Hz), 64.5 (d, $J = 5.9$ Hz), 29.2 (d, $J = 7.2$ Hz), 14.8; $^{31}\text{P NMR}$ (243 MHz, CDCl_3) δ 20.0; IR (ATR): 3442, 3298, 2994, 2960, 2896, 1492, 1445, 1240, 1131, 1038, 970 cm^{-1} ; HRMS (FD+) m/z : $[\text{M}]$ Calcd for $\text{C}_{19}\text{H}_{19}\text{O}_5\text{P}$ 358.0970, Found 358.0969.

Pent-4-yn-1-yl (3,4,5-trimethoxy)benzyl phenylphosphonate (3aj):

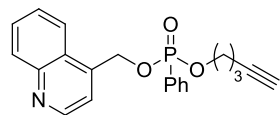
Purification with silica gel column chromatography (Hexane/AcOEt = 1:1 to 1:2); 36 mg, 90% yield, Colorless oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.83-7.78 (m, 2H), 7.58-7.53 (m, 1H), 7.48-7.43 (m, 2H), 6.56 (s, 2H), 5.06 (dd, $J = 12.0, 8.4$ Hz, 1H), 5.00 (dd, $J = 12.0, 8.4$ Hz, 1H), 4.21-4.11 (m, 2H), 3.824 (s, 3H), 3.816 (s, 6H), 2.30 (td, $J = 7.2, 2.4$ Hz, 2H), 1.93 (t, $J = 3.0$ Hz, 1H), 1.88 (tt, $J = 7.2, 6.0$ Hz, 2H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 153.2, 137.9, 132.5 (d, $J = 2.9$ Hz), 131.7 (d, $J = 10.1$ Hz), 131.6 (d, $J = 5.7$ Hz), 128.4 (d, $J = 15.7$ Hz), 127.9 (d, $J = 188.1$ Hz), 105.1, 82.7, 69.1, 67.9 (d, $J = 5.7$ Hz), 64.5 (d, $J = 5.7$ Hz), 60.7, 56.0, 29.2 (d, $J = 7.2$ Hz), 14.7; $^{31}\text{P NMR}$ (243 MHz, CDCl_3) δ 20.1; IR (ATR): 3462, 3294, 2942, 2841, 1593, 1508, 1462, 1423, 1334, 1008, 962 cm^{-1} ; HRMS (FD+) m/z : $[\text{M}]$ Calcd for $\text{C}_{21}\text{H}_{25}\text{O}_6\text{P}$ 404.1389, Found 404.1386.

1-Naphthylmethyl pent-4-yn-1-yl phenylphosphonate (3ak):

Purification with silica gel column chromatography (Hexane/AcOEt = 3:2); 35 mg, 95% yield, Colorless oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.87-7.76 (m, 4H), 7.56-7.48 (m, 4H), 7.43-7.38 (m, 3H), 5.64 (dd, $J = 12.0, 7.8$ Hz, 1H), 5.48 (dd, $J = 12.0, 7.8$ Hz, 1H), 4.16-4.08 (m, 2H), 2.23 (td, $J = 6.6, 3.0$ Hz, 2H), 1.89 (t, $J = 3.0$ Hz, 1H), 1.81 (tt, $J = 6.6, 6.6$ Hz, 2H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 133.6, 132.5 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.0$ Hz), 131.7 (d, $J = 7.2$ Hz), 131.4, 129.5, 128.6, 128.4 (d, $J = 15.9$ Hz), 127.8 (d, $J = 188.1$ Hz), 127.1, 126.6, 125.9, 125.2, 123.6, 82.8, 69.0, 66.0 (d, $J = 4.2$ Hz), 64.5 (d, $J = 5.7$ Hz), 29.2 (d, $J = 7.2$ Hz), 14.7; $^{31}\text{P NMR}$ (243 MHz, CDCl_3) δ 20.1; IR (ATR): 3464,

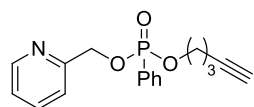
3296, 3226, 3057, 2960, 2897, 2117, 1825, 1439, 1244, 1131, 982 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{22}\text{H}_{21}\text{O}_3\text{P}$ 364.1228, Found 364.1227.

Pent-4-yn-1-yl (quinolin-4-yl)methyl phenylphosphonate (3al):



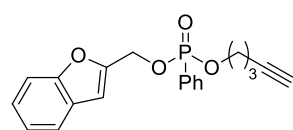
Purification with silica gel column chromatography (Hexane/AcOEt = 1:2 to 1:3); 27 mg, 73% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 8.90 (d, $J = 4.8$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.86-7.80 (m, 2H), 7.76-7.71 (m, 1H), 7.60-7.55 (m, 2H), 7.50-7.44 (m, 3H), 5.66 (dd, $J = 13.2, 7.2$ Hz, 1H), 5.53 (dd, $J = 13.2, 7.2$ Hz, 1H), 4.26-4.16 (m, 2H), 2.29 (td, $J = 6.6, 2.4$ Hz, 2H), 1.92 (t, $J = 2.4$ Hz, 1H), 1.88 (tt, $J = 6.6, 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 150.2, 148.0, 141.2 (d, $J = 7.2$ Hz), 132.8 (d, $J = 2.9$ Hz), 131.7 (d, $J = 10.1$ Hz), 130.2, 129.4, 128.6 (d, $J = 15.9$ Hz), 127.1 (d, $J = 188.1$ Hz), 127.0, 125.5, 122.8, 119.2, 82.6, 69.2, 64.7 (d, $J = 5.7$ Hz), 63.9 (d, $J = 4.3$ Hz), 29.1 (d, $J = 5.7$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.7; IR (ATR): 3467, 3298, 3235, 3060, 2960, 2899, 1599, 1511, 1439, 1244, 1131, 944, 848 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_3\text{P}$ 365.1181, Found 365.1180.

Pent-4-yn-1-yl (2-pyridyl)methyl phenylphosphonate (3am):



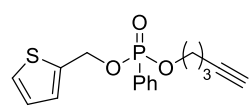
Purification with silica gel column chromatography (Hexane/AcOEt = 1:2); 26 mg, 81% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 8.55 (ddd, $J = 4.8, 1.8, 1.2$ Hz, 1H), 7.88-7.83 (m, 2H), 7.70 (dd, $J = 7.2, 1.8$ Hz, 1H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 3H), 7.21 (ddd, $J = 7.2, 4.8, 1.2$ Hz, 1H), 5.22 (dd, $J = 13.2, 7.8$ Hz, 1H), 5.16 (dd, $J = 13.2, 7.8$ Hz, 1H), 4.26-4.16 (m, 2H), 2.30 (dd, $J = 6.6, 2.4$ Hz, 2H), 1.92 (t, $J = 2.4$ Hz, 1H), 1.90 (tt, $J = 6.6, 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 156.2 (d, $J = 8.7$ Hz), 149.1, 136.8, 132.6 (d, $J = 3.0$ Hz), 131.8 (d, $J = 10.1$ Hz), 128.5 (d, $J = 15.8$ Hz), 127.4 (d, $J = 188.1$ Hz), 122.8, 121.3, 82.7, 69.1, 67.8 (d, $J = 5.8$ Hz), 64.7 (d, $J = 5.7$ Hz), 29.2 (d, $J = 5.9$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.2; IR (ATR): 3464, 3299, 3234, 3060, 2961, 2925, 1725, 1593, 1439, 1239, 1131, 1016, 870 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3\text{P}$ 315.1024, Found 315.1024.

(Benzofuran-2-yl)methyl pent-4-yn-1-yl phenylphosphonate (3an):



Purification with silica gel column chromatography (Hexane/AcOEt = 3:2 to 1:1); 28 mg, 79% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.83-7.78 (m, 2H), 7.55-7.50 (m, 2H), 7.45-7.40 (m, 3H), 7.29 (ddd, $J = 8.4, 7.2, 1.2$ Hz, 1H), 7.22 (ddd, $J = 7.8, 7.2, 0.6$ Hz, 1H), 6.75 (s, 1H), 5.25 (dd, $J = 12.6, 8.4$ Hz, 1H), 5.14 (dd, $J = 12.6, 8.4$ Hz, 1H), 4.22-4.13 (m, 2H), 2.28 (td, $J = 7.2, 3.0$ Hz, 2H), 1.90 (t, $J = 3.0$ Hz, 1H), 1.87 (tt, $J = 7.2, 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.2, 151.9 (d, $J = 7.2$ Hz), 132.6 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.0$ Hz), 128.4 (d, $J = 15.7$ Hz), 127.7, 127.5 (d, $J = 189.6$ Hz), 124.9, 122.9, 121.4, 111.4, 107.0, 82.8, 69.1, 64.6 (d, $J = 5.7$ Hz), 60.1 (d, $J = 4.2$ Hz), 29.2 (d, $J = 7.2$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.5; IR (ATR): 3466, 3298, 3233, 3058, 2961, 1594, 1440, 1246, 1131, 972 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_4\text{P}$ 354.1021, Found 354.1020.

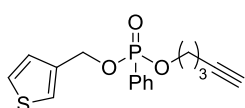
Pent-4-yn-1-yl (2-thienyl)methyl phenylphosphonate (3ao):



Purification with silica gel column chromatography (Hexane/AcOEt = 3:2); 16 mg, 49% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.82-7.77 (m, 2H), 7.57-7.53 (m, 1H), 7.48-7.43 (m, 2H), 7.31 (dd, $J = 5.4, 1.2$ Hz, 1H), 7.06 (dd, $J = 3.6, 1.2$ Hz, 1H), 6.95 (dd, $J = 3.6, 1.2$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.2, 151.9 (d, $J = 7.2$ Hz), 132.6 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.0$ Hz), 128.4 (d, $J = 15.7$ Hz), 127.7, 127.5 (d, $J = 189.6$ Hz), 124.9, 122.9, 121.4, 111.4, 107.0, 82.8, 69.1, 64.6 (d, $J = 5.7$ Hz), 60.1 (d, $J = 4.2$ Hz), 29.2 (d, $J = 7.2$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.5; IR (ATR): 3466, 3298, 3233, 3058, 2961, 1594, 1440, 1246, 1131, 972 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_4\text{P}$ 354.1021, Found 354.1020.

= 5.4, 3.6 Hz, 1H), 5.32 (dd, $J = 12.0, 8.4$ Hz, 1H), 5.20 (dd, $J = 12.0, 8.4$ Hz, 1H), 4.18-4.09 (m, 2H), 2.28 (td, $J = 6.6, 3.0$ Hz, 2H), 1.93 (t, $J = 3.0$ Hz, 1H), 1.86 (tt, $J = 6.6, 6.0$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.4 (d, $J = 7.2$ Hz), 132.6 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.1$ Hz), 128.5 (d, $J = 15.7$ Hz), 128.0, 127.7 (d, $J = 188.1$ Hz), 127.0, 126.8, 82.8, 69.1, 64.5 (d, $J = 5.7$ Hz), 62.0 (d, $J = 4.4$ Hz), 29.2 (d, $J = 7.2$ Hz), 14.8; ^{31}P NMR (243 MHz, CDCl_3) δ 20.0; IR (ATR): 3455, 3297, 3229, 3061, 2959, 2898, 1594, 1439, 1243, 1131, 980, 851 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{16}\text{H}_{17}\text{O}_3\text{PS}$ 320.0636, Found 320.0635.

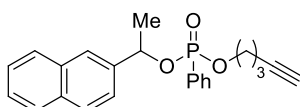
Pent-4-yn-1-yl (3-thienyl)methyl phenylphosphonate (3ap):



Purification with silica gel column chromatography (Hexane/AcOEt = 3:2 to 1:1); 23 mg,

71% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.82-7.76 (m, 2H), 7.58-7.53 (m, 1H), 7.48-7.43 (m, 2H), 7.30-7.27 (m, 2H), 7.09-7.06 (m, 1H), 5.16 (dd, $J = 12.0, 8.4$ Hz, 1H), 5.06 (dd, $J = 12.0, 8.4$ Hz, 1H), 4.18-4.09 (m, 2H), 2.28 (td, $J = 7.2, 2.4$ Hz, 2H), 1.93 (t, $J = 2.4$ Hz, 1H), 1.86 (tt, $J = 7.2, 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.2 (d, $J = 5.7$ Hz), 132.5 (d, $J = 2.8$ Hz), 131.7 (d, $J = 10.0$ Hz), 128.5 (d, $J = 15.7$ Hz), 127.8 (d, $J = 188.1$ Hz), 127.3, 126.3, 124.2, 82.8, 69.1, 64.5 (d, $J = 5.9$ Hz), 62.8 (d, $J = 5.7$ Hz), 29.2 (d, $J = 7.2$ Hz), 14.8; ^{31}P NMR (243 MHz, CDCl_3) δ 20.1; IR (ATR): 3454, 3297, 3228, 3099, 2896, 2117, 1439, 1243, 1131, 1008, 973 cm^{-1} ; HRMS (FD+) m/z : [M+H] Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3\text{PS}$ 321.0714, Found 321.0712.

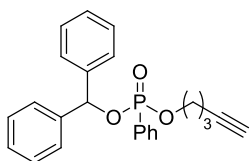
1-(2-Naphthyl)ethyl pent-4-yn-1-yl phenylphosphonate (3aq):



Purification with silica gel column chromatography (Hexane/AcOEt = 3:2); 29 mg,

77% yield, 51:49 diastereomeric mixture, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.88-7.82 (m, 3H), 7.80-7.72 (m, 1.5H), 7.68-7.63 (m, 1.5H), 7.58-7.39 (m, 5H), 7.31-7.27 (m, 1H), 5.84 (dq, $J = 7.8, 6.6$ Hz, 0.5H), 5.67 (dq, $J = 7.8, 6.6$ Hz, 0.5H), 4.17 (dt, $J = 6.6, 6.6$ Hz, 1H), 3.92 (dt, $J = 6.6, 6.6$ Hz, 1H), 2.30 (td, $J = 7.2, 2.4$ Hz, 1H), 2.06 (td, $J = 7.2, 2.4$ Hz, 1H), 1.93 (t, $J = 2.4$ Hz, 0.5H), 1.89 (tt, $J = 7.2, 6.6$ Hz, 1H), 1.79 (t, $J = 2.4$ Hz, 0.5H), 1.76 (d, $J = 6.6$ Hz, 1.5 H), 1.70-1.60 (m, 2.5H); ^{13}C NMR (150 MHz, CDCl_3) δ 139.4 (d, $J = 2.9$ Hz), 138.8 (d, $J = 4.2$ Hz), 133.1 (2C), 133.01, 132.97, 132.4 (d, $J = 3.0$ Hz), 132.2 (d, $J = 2.8$ Hz), 131.7 (d, $J = 8.7$ Hz), 131.6 (d, $J = 10.1$ Hz), 128.7 (d, $J = 194.0$ Hz), 128.44 (d, $J = 15.7$ Hz), 128.43, 128.3, 128.20 (d, $J = 186.8$ Hz), 128.18 (d, $J = 14.4$ Hz), 128.1, 128.0, 127.7, 127.6, 126.3, 126.2, 126.15, 126.08, 125.0, 14.9, 123.85, 123.78, 82.9, 82.8, 75.7 (d, $J = 4.3$ Hz), 75.4 (d, $J = 5.9$ Hz), 69.0, 68.9, 64.32 (d, $J = 5.7$ Hz), 64.29 (d, $J = 4.3$ Hz), 29.3 (d, $J = 7.2$ Hz), 29.1 (d, $J = 5.8$ Hz), 24.5 (d, $J = 4.3$ Hz), 24.4 (d, $J = 5.7$ Hz), 14.8, 14.6; ^{31}P NMR (243 MHz, CDCl_3) δ 19.3, 18.8; IR (ATR): 3437, 3304, 3058, 2983, 1595, 1440, 1242, 1130, 970, 945, 745 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{23}\text{H}_{23}\text{O}_3\text{P}$ 378.1385, Found 378.1384.

Diphenylmethyl pent-4-yn-1-yl phenylphosphonate (3ar):

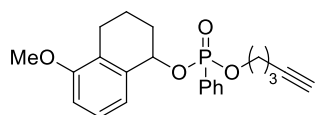


Purification with silica gel column chromatography (Hexane/AcOEt = 2:1); 36 mg, 91%

yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73-7.68 (m, 2H), 7.51-7.47 (m, 1H), 7.43-7.33 (m, 6H), 7.31-7.19 (m, 6H), 6.55 (d, $J = 9.0$ Hz, 1H), 4.04-3.92 (m, 2H), 2.14 (td, $J = 7.2, 3.0$ Hz, 2H), 1.90 (t, $J = 3.0$ Hz, 1H), 1.73 (tt, $J = 7.2, 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 140.8 (d, $J = 4.3$ Hz), 140.4, (d, $J = 5.7$ Hz), 132.3 (d, $J = 2.9$ Hz), 131.6 (d, $J = 10.1$ Hz), 128.5, 128.31, 128.29 (d, $J = 15.7$ Hz), 128.28 (d, $J = 189.4$ Hz), 128.0, 127.9, 127.1, 127.0, 82.9, 79.6 (d, $J = 5.8$ Hz), 68.9,

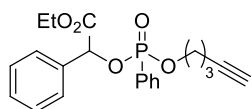
64.4 (d, $J = 5.9$ Hz), 29.1 (d, $J = 5.7$ Hz), 14.7; ^{31}P NMR (243 MHz, CDCl_3) δ 19.5; IR (ATR): 3437, 3303, 3232, 3063, 2997, 1595, 1496, 1440, 1246, 1131, 975 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{24}\text{H}_{23}\text{O}_3\text{P}$ 390.1385, Found 390.1384.

5-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl pent-4-yn-1-yl phenylphosphonate (3as):



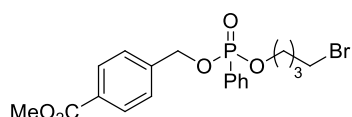
Purification with silica gel column chromatography (Hexane/AcOEt = 2:1); 29 mg, 75% yield, 55:45 diastereomeric mixture, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.86-7.77 (m, 2H), 7.57-7.52 (m, 1H), 7.48-7.41 (m, 2H), 7.24-7.19 (m, 1H), 7.04 (dd, $J = 7.8, 7.8$ Hz, 0.45H), 6.81-6.70 (m, 1.55H), 5.69-5.65 (m, 0.55H), 5.60-5.56 (m, 0.45H), 4.21-4.04 (m, 2H), 3.82 (s, 1.65H), 3.80 (s, 1.35H), 2.84-2.75 (m, 1H), 2.50-2.47 (m, 1H), 2.33-2.23 (m, 2.45H), 2.08-1.70 (m, 6.55H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.0, 156.9, 135.9 (d, $J = 5.7$ Hz), 135.5 (d, $J = 5.9$ Hz), 132.3 (d, $J = 2.9$ Hz, 2C), 131.9 (d, $J = 10.1$ Hz), 131.7 (d, $J = 10.1$ Hz), 129.0 (d, $J = 185.3$ Hz), 128.6 (d, $J = 188.1$ Hz), 128.4 (d, $J = 14.4$ Hz), 128.3 (d, $J = 14.4$ Hz), 126.8, 126.7, 126.4, 126.2, 121.82, 121.77, 109.3, 109.2, 82.92, 82.89, 73.4 (d, $J = 5.9$ Hz), 73.2 (d, $J = 5.7$ Hz), 69.0, 68.9, 64.4 (d, $J = 5.7$ Hz), 64.3 (d, $J = 5.9$ Hz), 55.31, 55.28, 30.5, 30.1, 29.3 (d, $J = 7.2$ Hz), 29.2 (d, $J = 7.2$ Hz), 22.63, 22.60, 17.6, 17.5, 14.81, 14.79; ^{31}P NMR (243 MHz, CDCl_3) δ 19.5 (minor), 18.6 (major); IR (ATR): 3443, 3303, 3228, 2994, 2944, 2838, 1588, 1472, 1439, 1250, 1131, 1038, 975, 747 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{22}\text{H}_{25}\text{O}_4\text{P}$ 384.1490, Found 384.1489.

(Ethoxycarbonyl)(Phenyl)methyl pent-4-yn-1-yl phenylphosphonate (3at):



Purification with silica gel column chromatography (Hexane/AcOEt = 2:1 to 1:1); 34 mg, 88% yield, 50:50 diastereomeric mixture, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.93-7.88 (m, 1H), 7.73-7.68 (m, 1H), 7.60-7.56 (m, 0.5H), 7.53-7.46 (m, 2.5H), 7.42-7.34 (m, 3.5H), 7.31-7.28 (m, 1.5H), 5.92 (d, $J = 9.0$ Hz, 0.5H), 5.81 (d, $J = 8.4$ Hz, 0.5H), 4.38-3.91 (m, 4H), 2.35 (td, $J = 7.8, 2.4$ Hz, 1H), 2.16 (td, $J = 7.2, 3.0$ Hz, 1H), 1.99-1.92 (m, 1.5H), 1.87 (t, $J = 3.0$ Hz, 0.5H), 1.73 (tt, $J = 7.2, 7.2$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.1 (d, $J = 4.2$ Hz), 168.8 (d, $J = 5.8$ Hz), 135.5 (d, $J = 4.4$ Hz), 134.9 (d, $J = 5.9$ Hz), 132.6 (d, $J = 2.9$ Hz), 132.5 (d, $J = 2.9$ Hz), 131.7 (d, $J = 10.0$ Hz), 131.6 (d, $J = 10.1$ Hz), 129.1, 129.0, 128.7, 128.5, 128.4 (d, $J = 15.7$ Hz), 128.3 (d, $J = 14.4$ Hz), 127.6 (d, $J = 189.6$ Hz, 2C), 127.3, 127.1, 82.9, 82.7, 75.5 (d, $J = 4.4$ Hz, 2C), 69.0 (2C), 64.9 (d, $J = 5.7$ Hz), 64.5 (d, $J = 5.7$ Hz), 61.8, 61.7, 29.3 (d, $J = 7.2$ Hz), 29.0 (d, $J = 7.2$ Hz), 14.8, 14.6, 14.0, 13.8; ^{31}P NMR (243 MHz, CDCl_3) δ 20.2, 19.9; IR (ATR): 3489, 3300, 3063, 2982, 1754, 1440, 1251, 1212, 1058, 1020, 982 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{21}\text{H}_{23}\text{O}_5\text{P}$ 386.1283, Found 383.1283.

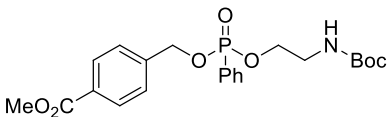
4-Bromobut-1-yl (4-methoxycarbonyl)benzyl phenylphosphonate (3bb):



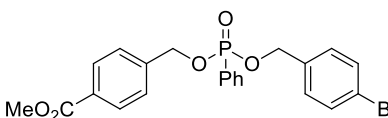
Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 39 mg, 88% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 8.02 (d, $J = 9.0$ Hz, 2H), 7.84-7.78 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.45 (m, 2H), 7.42 (d, $J = 9.0$ Hz, 2H), 5.19 (dd, $J = 12.6, 7.8$ Hz, 1H), 5.07 (dd, $J = 12.6, 7.8$ Hz, 1H), 4.13-4.04 (m, 2H), 3.92 (s, 3H), 3.38 (t, $J = 7.2$ Hz, 2H), 1.96-1.90 (m, 2H), 1.84-1.79 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.6, 141.1 (d, $J = 7.2$ Hz), 132.7, 131.7 (d, $J = 10.1$ Hz), 130.0, 129.8, 128.6 (d, $J = 15.9$ Hz), 127.4 (d, $J = 186.6$ Hz), 127.3, 66.7 (d, $J = 4.3$ Hz), 65.2 (d, $J = 5.9$ Hz), 52.1, 32.9, 28.9 (d, $J = 7.2$ Hz), 28.7; ^{31}P NMR (243 MHz, CDCl_3) δ 20.4; IR (ATR): 3454, 3060, 2953,

2845, 1720, 1615, 1438, 1280, 1246, 1131, 998 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{19}\text{H}_{22}\text{BrO}_5\text{P}$ 440.0388, Found 440.0387.

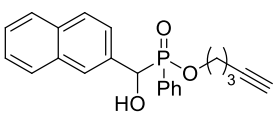
2-(*tert*-Butoxycarbonylamino)ethyl (4-methoxycarbonyl)benzyl phenylphosphonate (3cb):

 Purification with silica gel column chromatography (Hexane/AcOEt = 1:2); 35 mg, 78% yield, White solid; ^1H NMR (600 MHz, CDCl_3) δ 8.02 (d, $J = 7.8$ Hz, 2H), 7.84-7.78 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.45 (m, 2H), 7.42 (d, $J = 7.8$ Hz, 2H), 5.19 (dd, $J = 12.6, 7.8$ Hz, 1H), 5.10 (dd, $J = 12.6, 7.8$ Hz, 1H), 5.05 (brs, 1H), 4.13-4.07 (m, 2H), 3.92 (s, 3H), 3.47-3.37 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.6, 155.8, 141.0 (d, $J = 7.2$ Hz), 132.9 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.1$ Hz), 130.1, 129.9, 128.7 (d, $J = 15.7$ Hz), 127.4, 127.1 (d, $J = 188.1$ Hz), 79.5, 66.9 (d, $J = 4.3$ Hz), 65.6 (d, $J = 5.7$ Hz), 52.2, 41.0 (d, $J = 2.8$ Hz), 28.3; ^{31}P NMR (243 MHz, CDCl_3) δ 20.9; IR (ATR): 3347, 2978, 1713, 1515, 1439, 1279, 1247, 1173, 1008, 750 cm^{-1} ; HRMS (FD+) m/z : [M+H] Calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_7\text{P}$ 450.1682, Found 450.1681; M.p. 110.0-112.0 $^\circ\text{C}$.

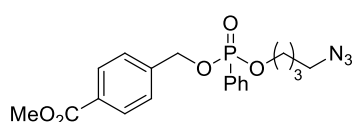
(4-Methoxycarbonyl)benzyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl phenylphosphonate (3db):

 Purification with silica gel column chromatography (Hexane/AcOEt = 3:2); 28 mg, 54% yield, Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.84-7.79 (m, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 5.17-5.03 (m, 4H), 3.91 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.7, 141.1 (d, $J = 7.2$ Hz), 138.9 (d, $J = 7.2$ Hz), 135.0, 132.7 (d, $J = 2.9$ Hz), 131.8 (d, $J = 10.1$ Hz), 129.9, 129.8, 128.6 (d, $J = 15.8$ Hz), 127.4 (d, $J = 188.2$ Hz), 127.3, 126.9, 83.9, 67.6 (d, $J = 5.7$ Hz), 66.7 (d, $J = 4.3$ Hz), 52.1, 24.8; ^{31}P NMR (243 MHz, CDCl_3) δ 20.6; IR (ATR): 3446, 3056, 2978, 2952, 1930, 1720, 1614, 1359, 1277, 995, 858 cm^{-1} ; HRMS (FD+) m/z : [M+H] Calcd for $\text{C}_{28}\text{H}_{33}\text{BO}_7\text{P}$ 523.2057, Found 523.2053.

Pent-4-yn-1-yl (hydroxy(2-naphthyl)methyl)(phenyl)phosphinate (6aa):

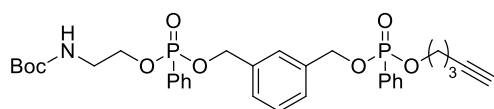
 Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 69:31 diastereomeric mixture, Colorless oil; ^1H NMR (600 MHz, CDCl_3) major diastereomer δ 7.82-7.78 (m, 1H), 7.75-7.62 (m, 4H), 7.49-7.37 (m, 5H), 7.34 (d, $J = 8.4$ Hz, 1H), 7.30-7.26 (m, 1H), 5.38-5.33 (m, 1H), 4.27 (brs, 1H), 4.24-4.17 (m, 1H), 4.05-3.98 (m, 1H), 2.31 (td, $J = 7.2, 2.4$ Hz, 2H), 1.94 (t, $J = 2.4$ Hz, 1H), 1.87-1.80 (m, 2H); minor diastereomer δ 7.82-7.78 (m, 1H), 7.75-7.62 (m, 3H), 7.56-7.52 (m, 1H), 7.49-7.37 (m, 5H), 7.30-7.26 (m, 2H), 5.31-5.28 (m, 1H), 4.17-4.12 (m, 1H), 4.09-4.05 (m, 1H), 3.88 (brs, 1H), 2.25 (td, $J = 7.2, 2.4$ Hz, 2H), 1.92 (t, $J = 2.4$ Hz, 1H), 1.92-1.86 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) For major diastereomer δ 82.9, 73.3 (d, $J = 112.1$ Hz), 69.2, 64.0 (d, $J = 7.2$ Hz), 29.3 (d, $J = 5.7$ Hz), 14.8; For minor diastereomer δ 83.0, 73.6 (d, $J = 110.5$ Hz), 69.1, 64.1 (d, $J = 7.2$ Hz), 29.3 (d, $J = 5.7$ Hz), 14.8; Other peaks δ 133.9, 133.6, 133.1, 133.0, 132.9, 132.7, 132.6, 132.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.4, 127.3, 126.9, 126.5, 126.4, 126.2, 126.1, 126.06, 126.02, 125.99, 125.96, 125.0, 124.9; ^{31}P NMR (243 MHz, CDCl_3) δ 39.6 (major), 38.3 (minor); IR (ATR): 3297, 3059, 3011, 2963, 2896, 1592, 1508, 1438, 1217, 1120, 1024, 977, 744 cm^{-1} ; HRMS (FD+) m/z : [M] Calcd for $\text{C}_{22}\text{H}_{21}\text{O}_3\text{P}$ 364.1228, Found 364.1226.

4-Azidobut-1-yl (4-methoxycarbonyl)benzyl phenylphosphonate (7):

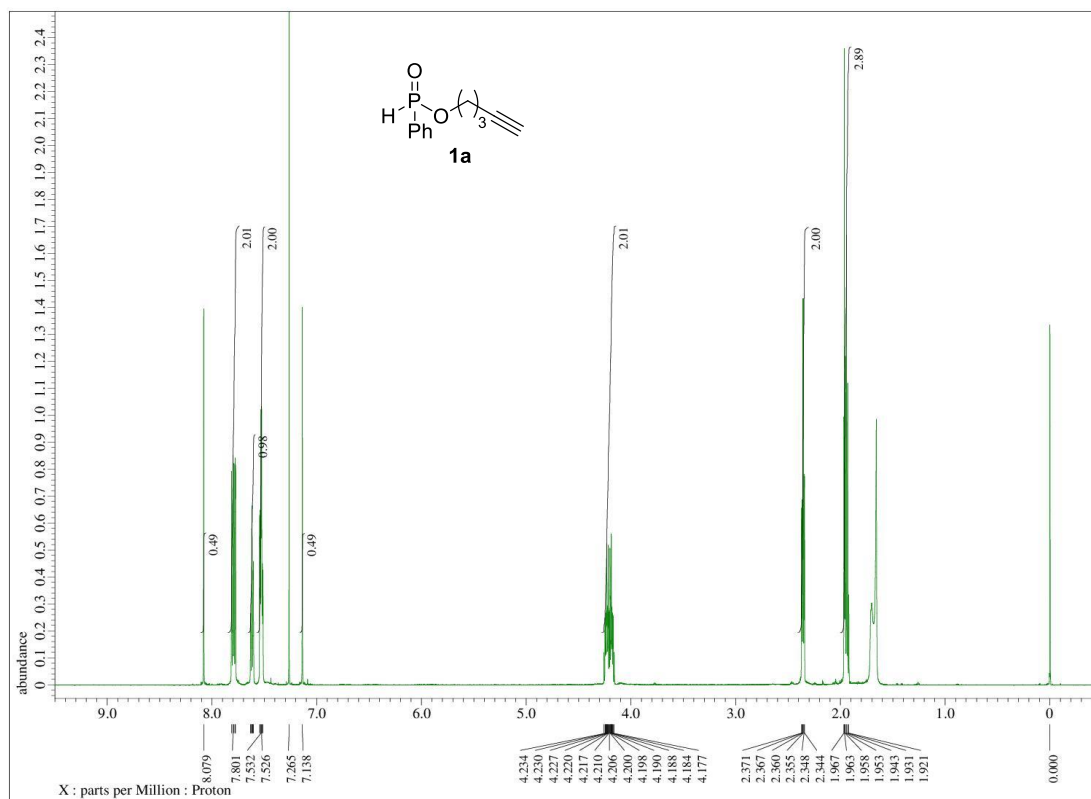


Purification with silica gel column chromatography (Hexane/AcOEt = 1:1); 33 mg, 81% yield, Colorless oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.84-7.79 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 5.19 (dd, $J = 12.0, 7.2$ Hz, 1H), 5.08 (dd, $J = 12.0, 7.2$ Hz, 1H), 4.13-4.03 (m, 2H), 3.91 (s, 3H), 3.27 (t, $J = 6.6$ Hz, 2H), 1.77-1.71 (m, 2H), 1.68-1.62 (m, 2H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 166.6, 141.1 (d, $J = 5.7$ Hz), 132.7 (d, $J = 2.9$ Hz), 131.7 (d, $J = 10.2$ Hz), 130.0, 129.8, 128.6 (d, $J = 15.8$ Hz), 127.5 (d, $J = 188.1$ Hz), 127.3, 66.7 (d, $J = 4.3$ Hz), 65.4 (d, $J = 5.7$ Hz), 52.1, 50.8, 27.5 (d, $J = 7.2$ Hz), 25.1; $^{31}\text{P NMR}$ (243 MHz, CDCl_3) δ 20.4; IR (ATR): 3429, 2999, 2953, 2897, 2098, 1720, 1438, 1281, 1247, 997, 745 cm^{-1} ; HRMS (FD+) m/z : [M+H] Calcd for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_5\text{P}$ 404.1375, Found 404.1373.

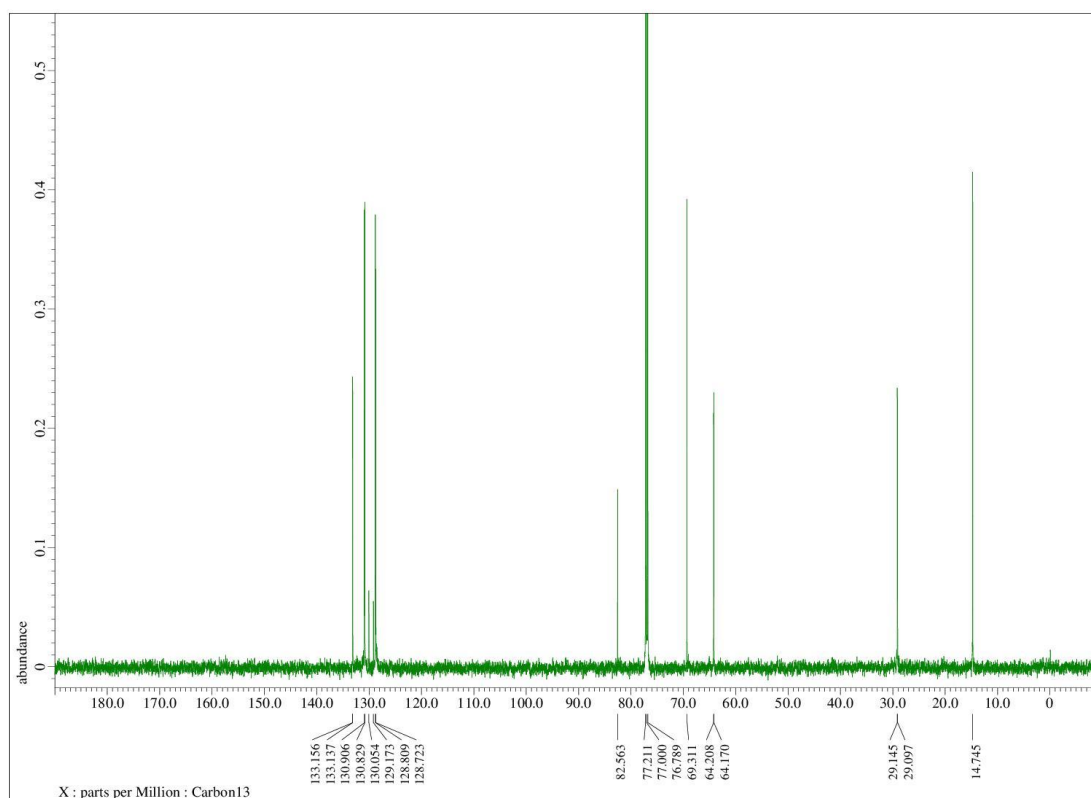
Adduct 9:



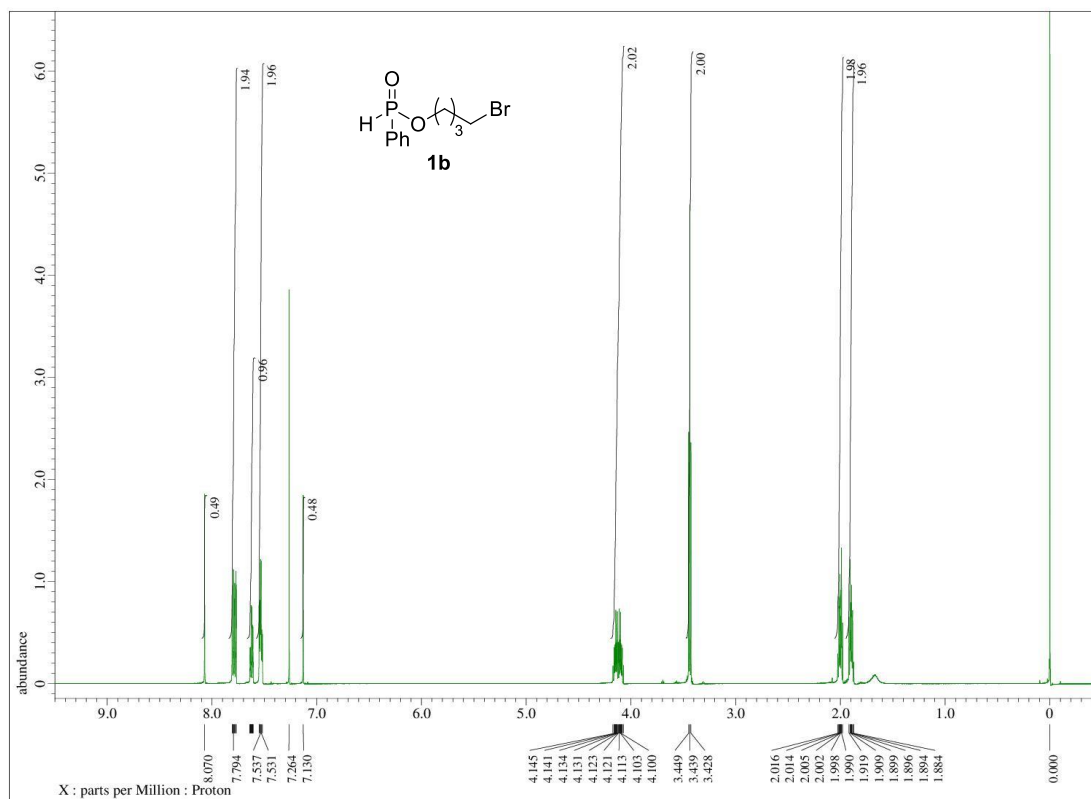
Purification with silica gel column chromatography (Hexane/AcOEt = 1:2); 39 mg, 63% yield, 50:50 diastereomeric mixture, Colorless oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.83-7.77 (m, 4H), 7.58-7.53 (m, 2H), 7.48-7.43 (m, 4H), 7.34-7.29 (m, 4H), 5.15-5.08 (m, 3H), 5.05-4.98 (m, 2H), 4.20-4.04 (m, 4H), 3.43-3.28 (m, 2H), 2.30-2.25 (m, 2H), 1.94-1.91 (m, 1H), 1.89-1.82 (m, 2H), 1.41 (s, 9H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 155.7, 136.6 (d, $J = 5.7$ Hz), 136.3 (d, $J = 5.9$ Hz), 132.7, 132.6, 131.78 (d, $J = 10.1$ Hz), 131.73 (d, $J = 10.1$ Hz), 128.8, 128.6 (d, $J = 14.3$ Hz), 128.5 (d, $J = 15.8$ Hz), 127.82, 127.77, 127.6 (d, $J = 188.1$ Hz), 127.21 (d, $J = 185.3$ Hz), 127.17, 82.7, 79.4, 69.1, 67.3 (d, $J = 4.3$ Hz), 67.1 (d, $J = 5.7$ Hz), 65.5 (d, $J = 4.3$ Hz), 64.5 (d, $J = 5.9$ Hz), 41.0 (d, $J = 4.2$ Hz), 29.1 (d, $J = 7.2$ Hz), 28.3, 14.7; $^{31}\text{P NMR}$ (243 MHz, CDCl_3) δ 20.7, 20.1; IR (ATR): 3442, 3307, 2980, 1704, 1510, 1440, 1366, 1238, 1131, 1018, 746 cm^{-1} ; HRMS (FD+) m/z : [M+H] Calcd for $\text{C}_{32}\text{H}_{40}\text{NO}_8\text{P}_2$ 628.2229, Found 628.2227.



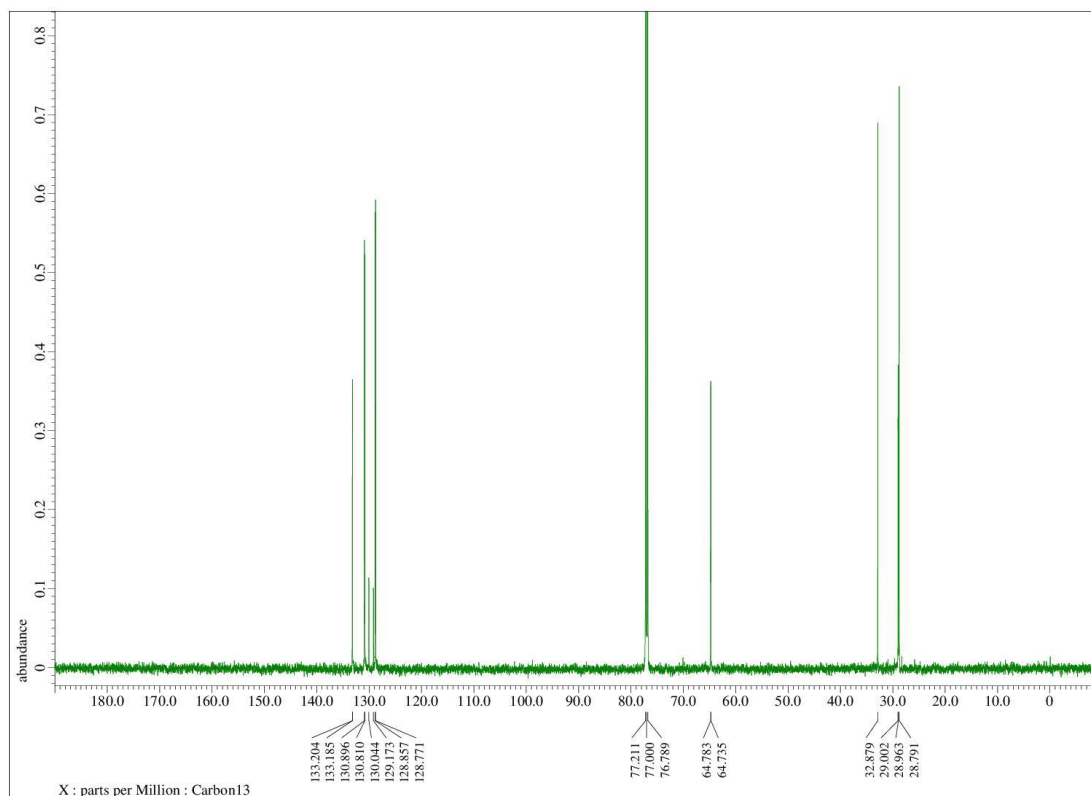
600 MHz, CDCl₃



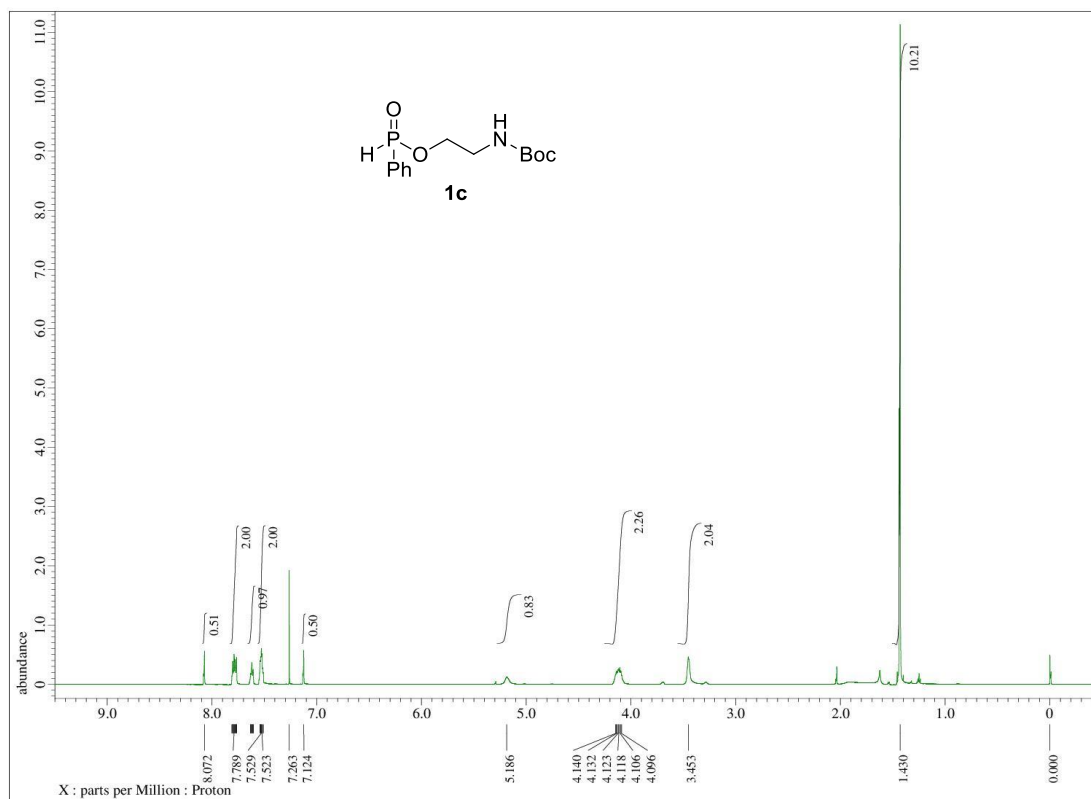
150 MHz, CDCl₃



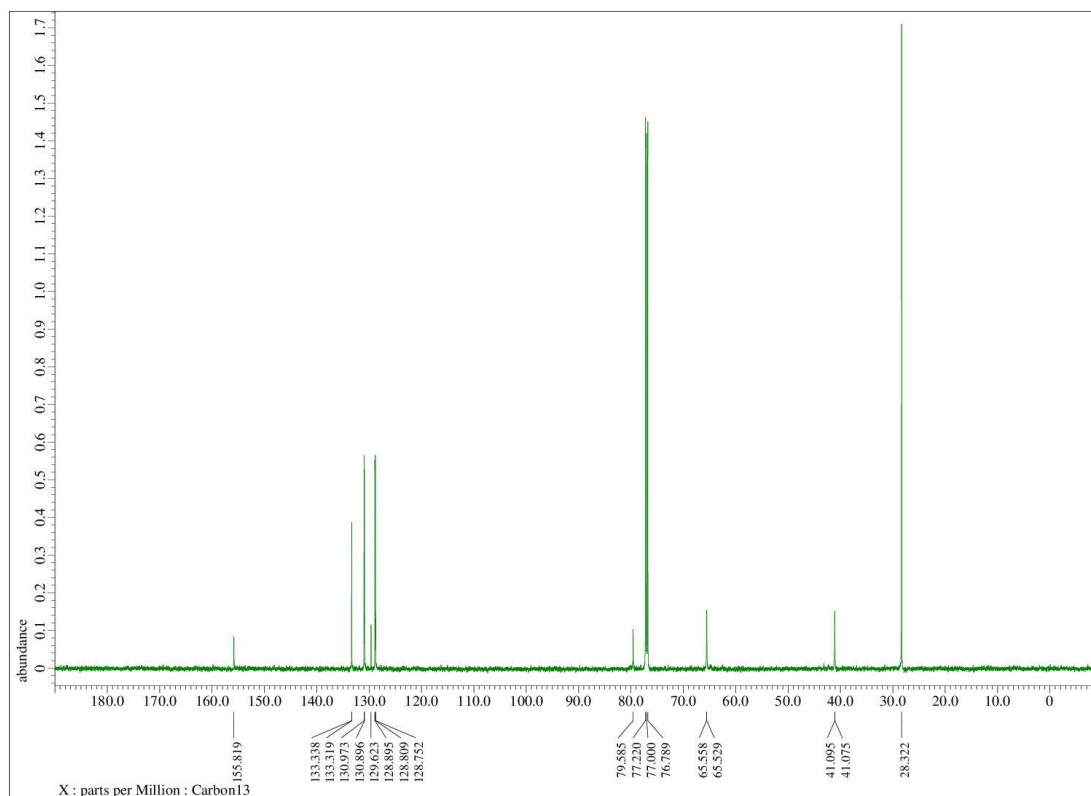
600 MHz, CDCl₃



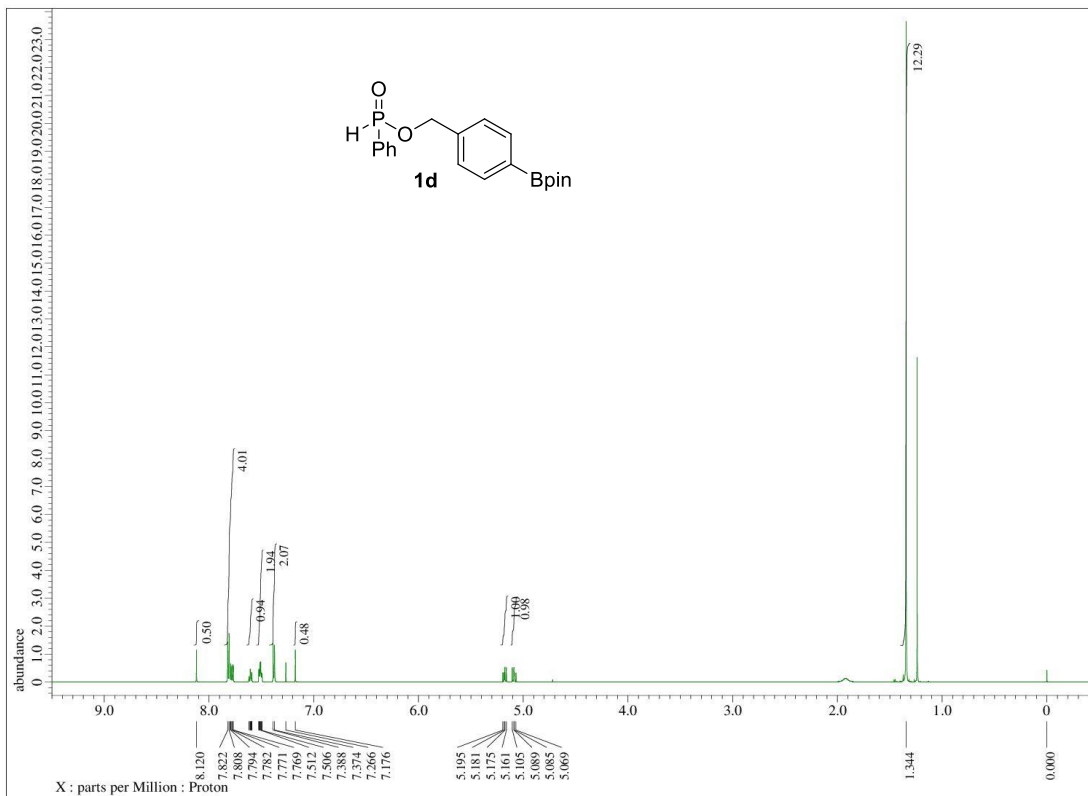
150 MHz, CDCl₃



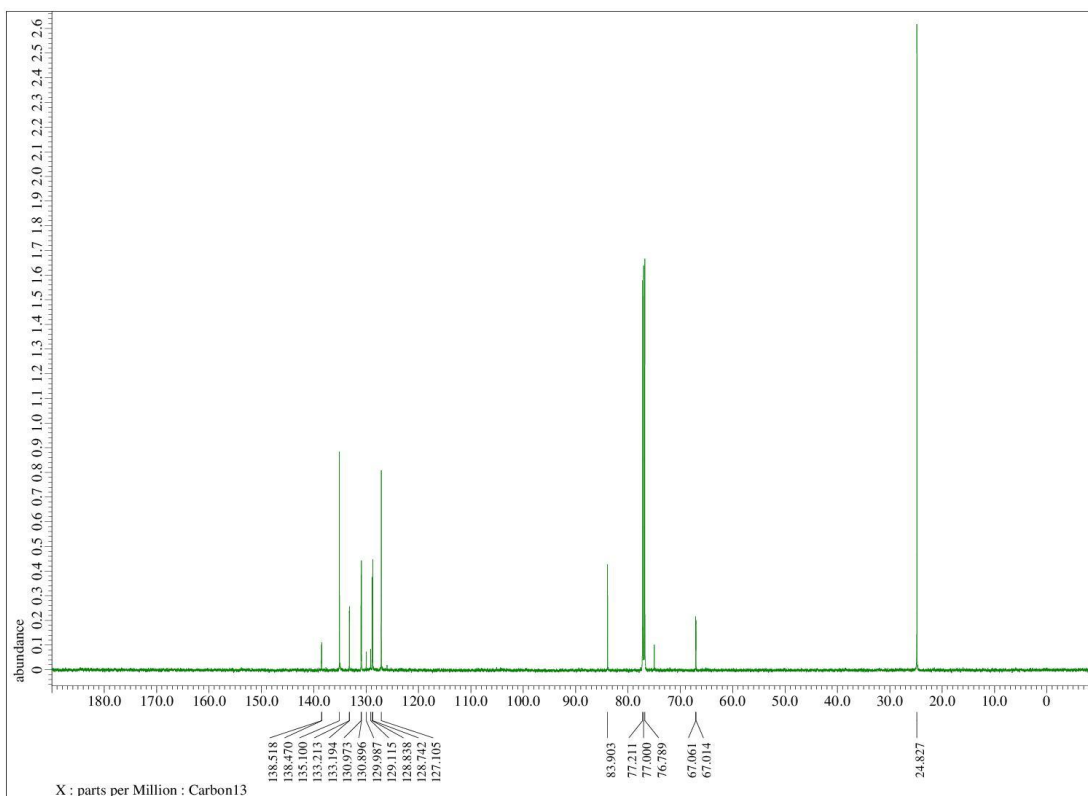
600 MHz, CDCl₃



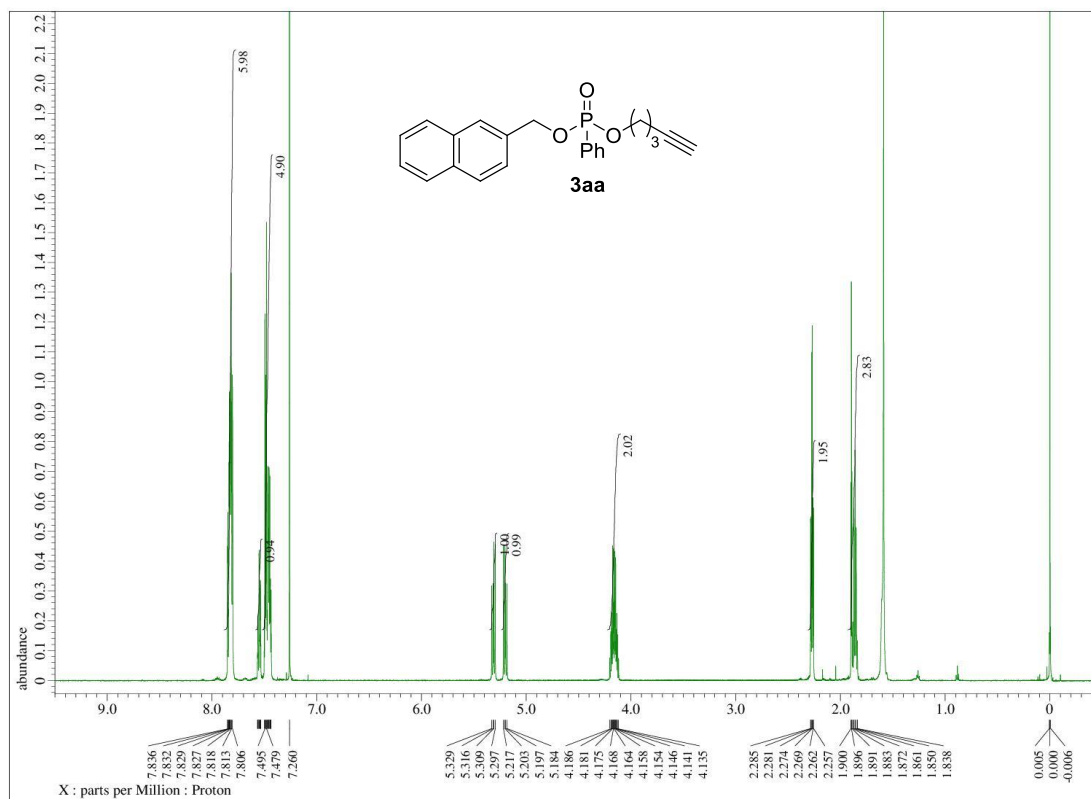
150 MHz, CDCl₃



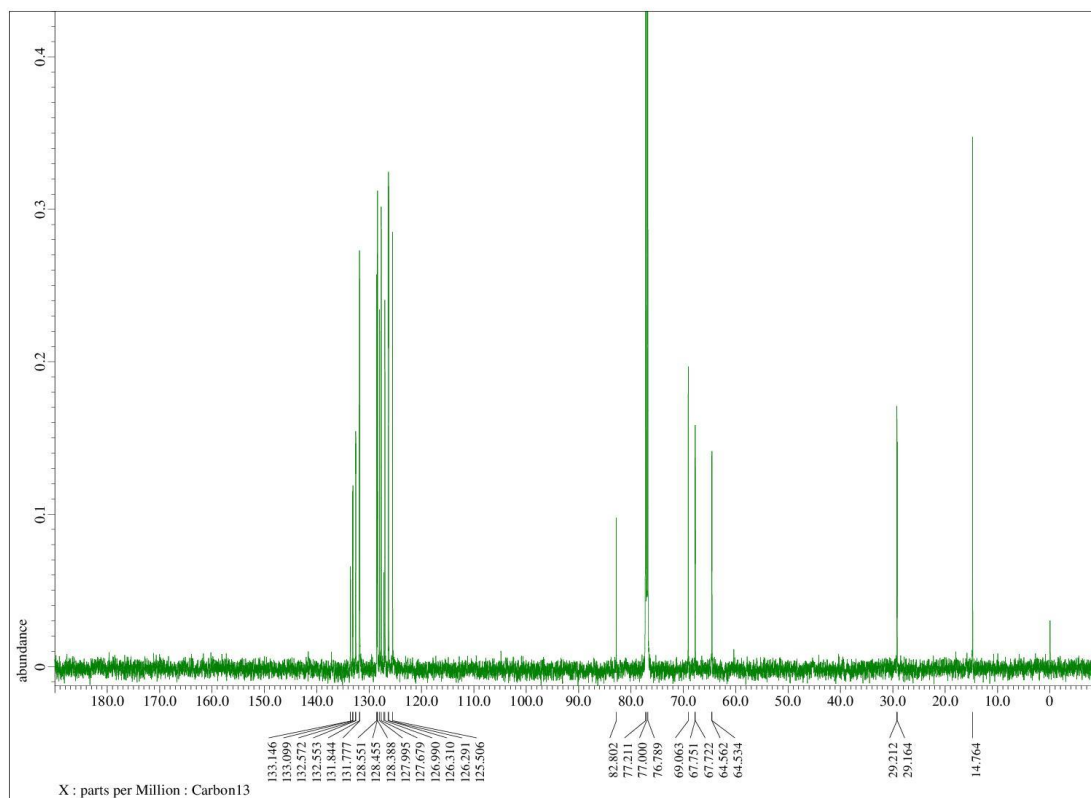
600 MHz, CDCl₃



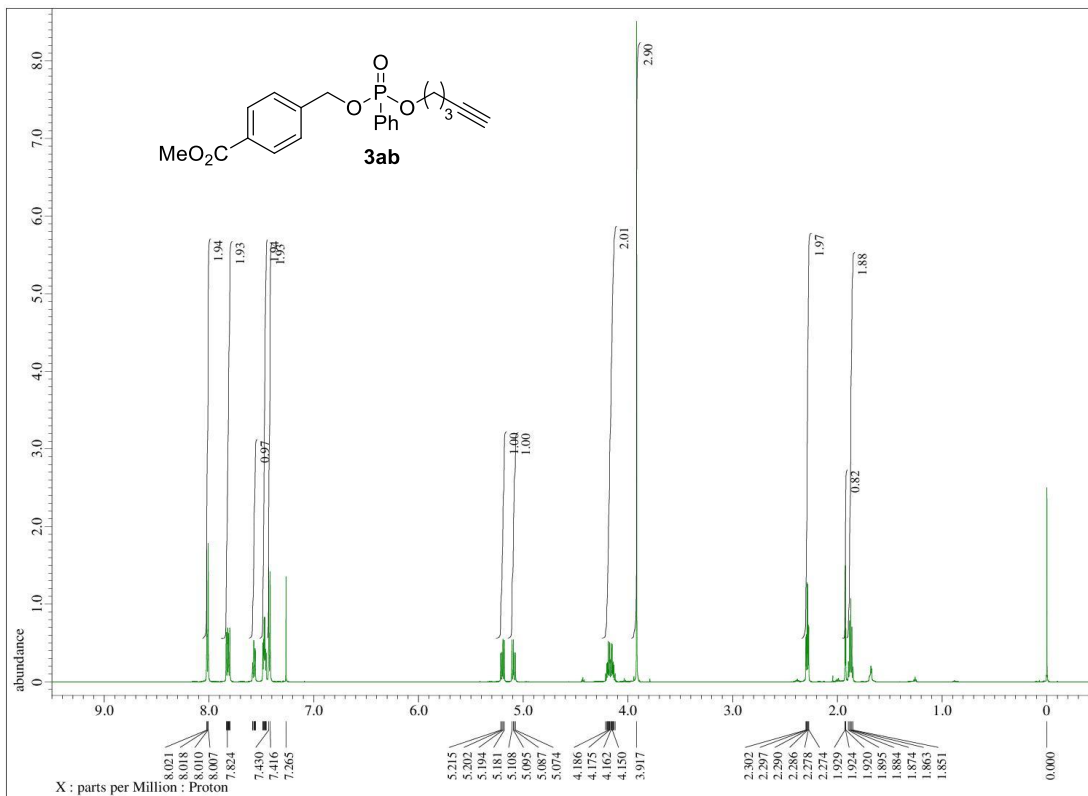
150 MHz, CDCl₃



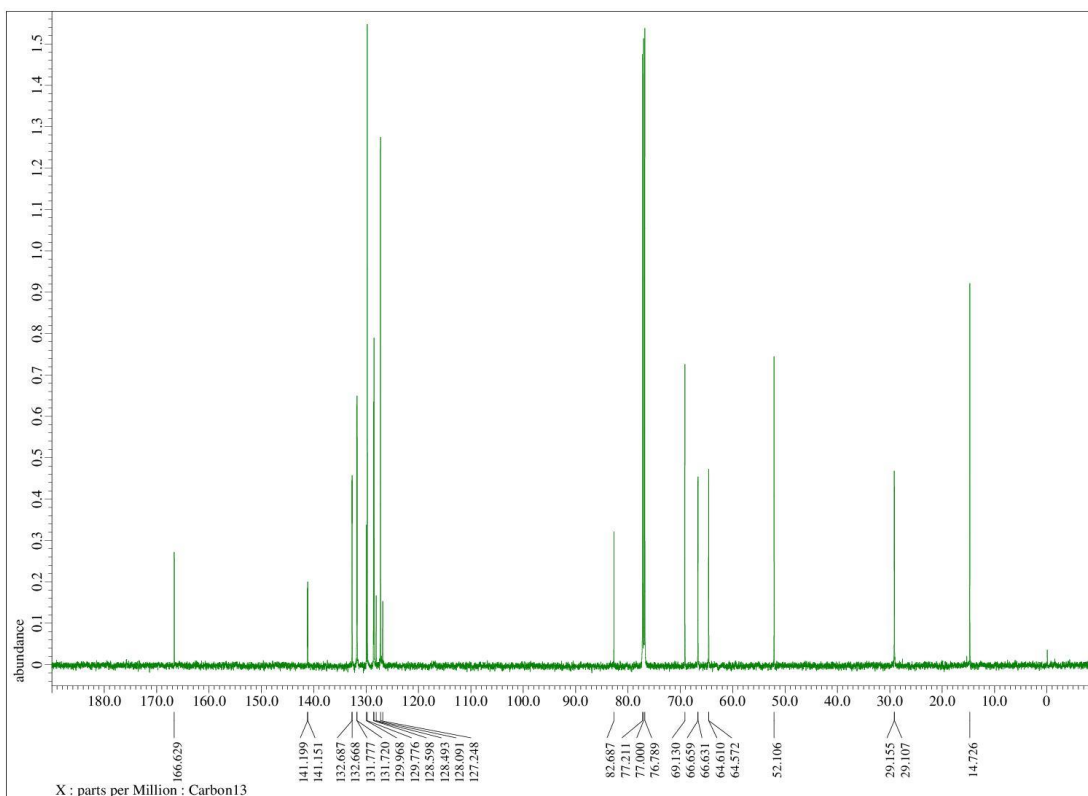
600 MHz, CDCl₃



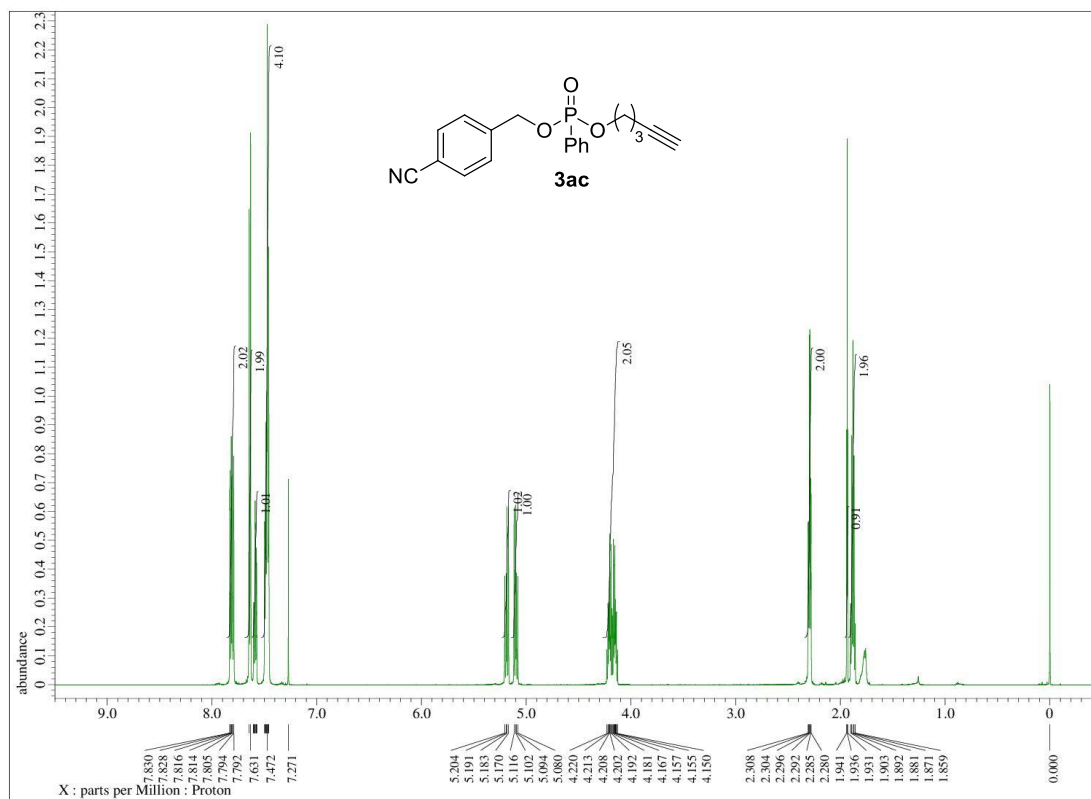
150 MHz, CDCl₃



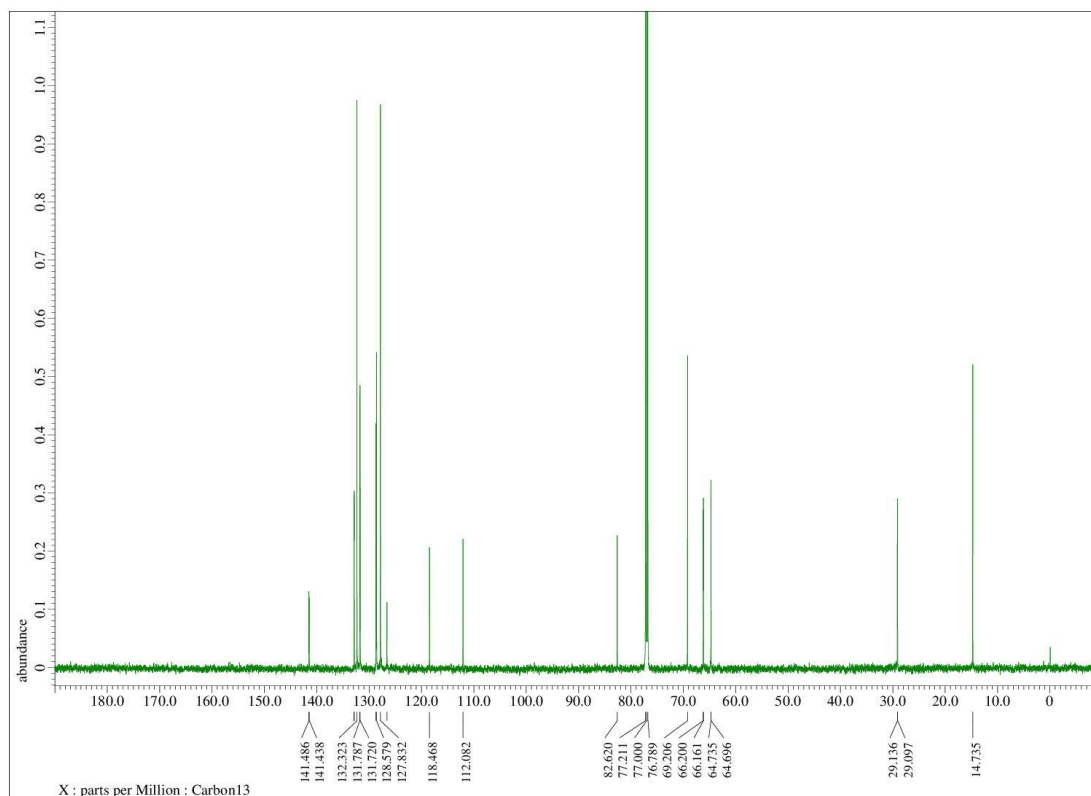
600 MHz, CDCl₃



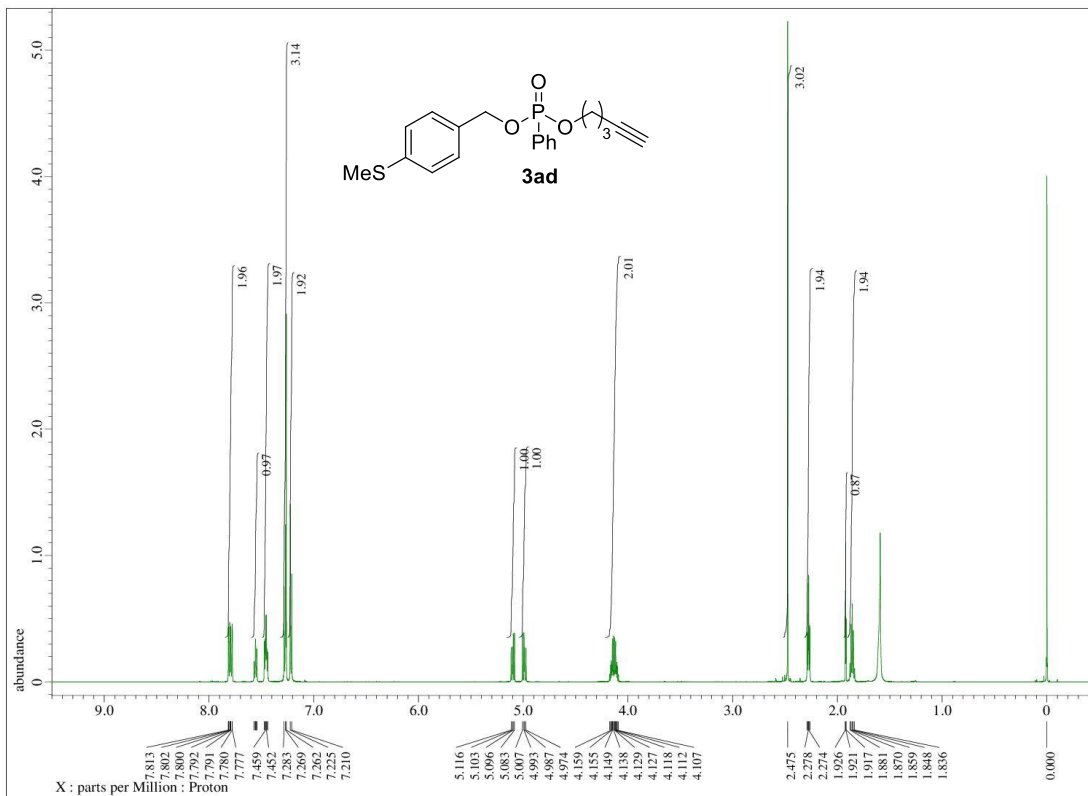
150 MHz, CDCl₃



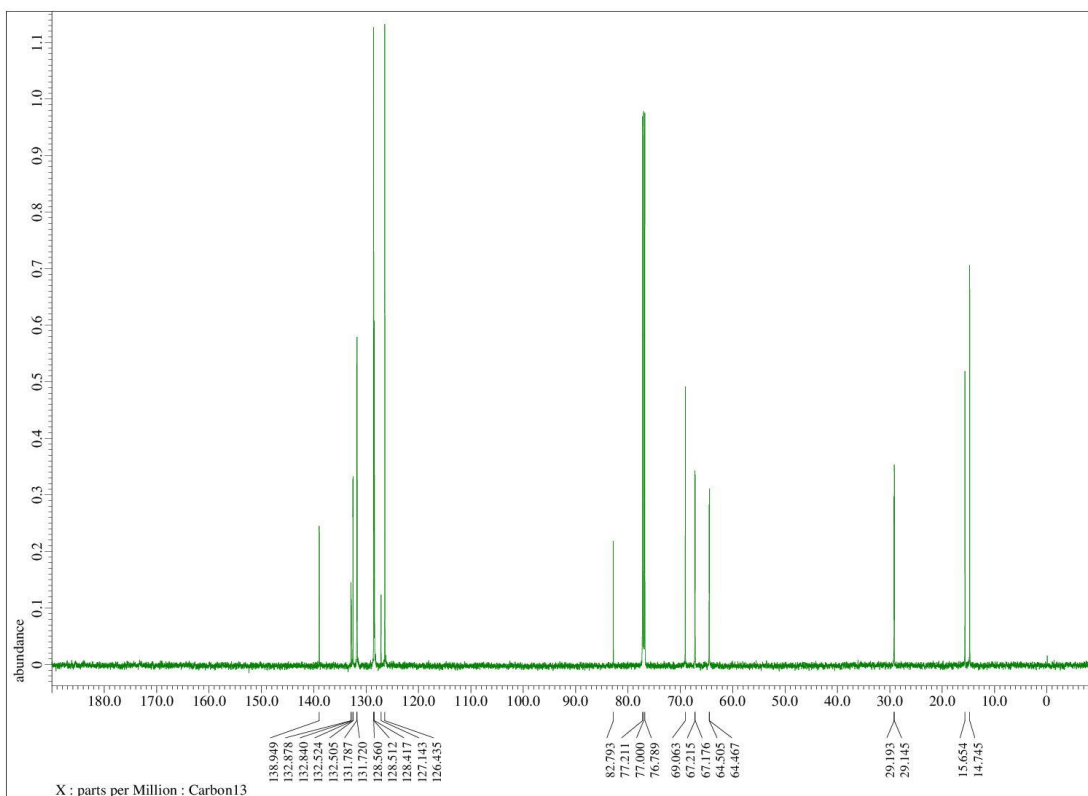
600 MHz, CDCl₃



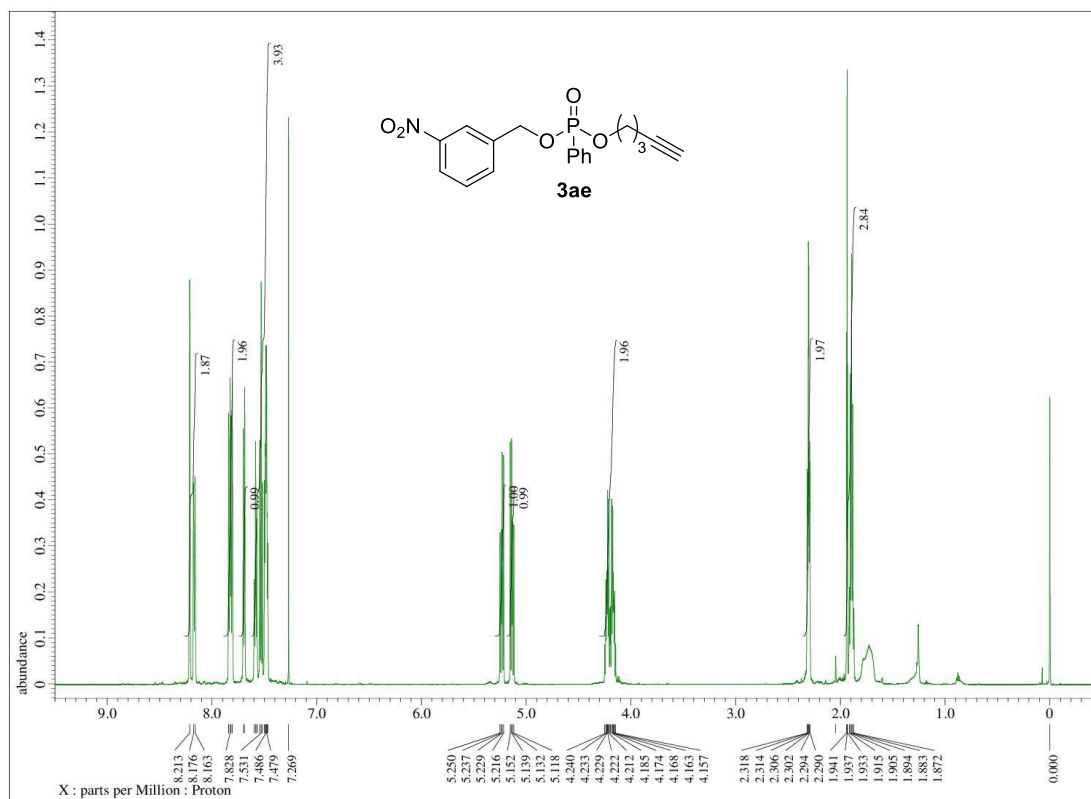
150 MHz, CDCl₃



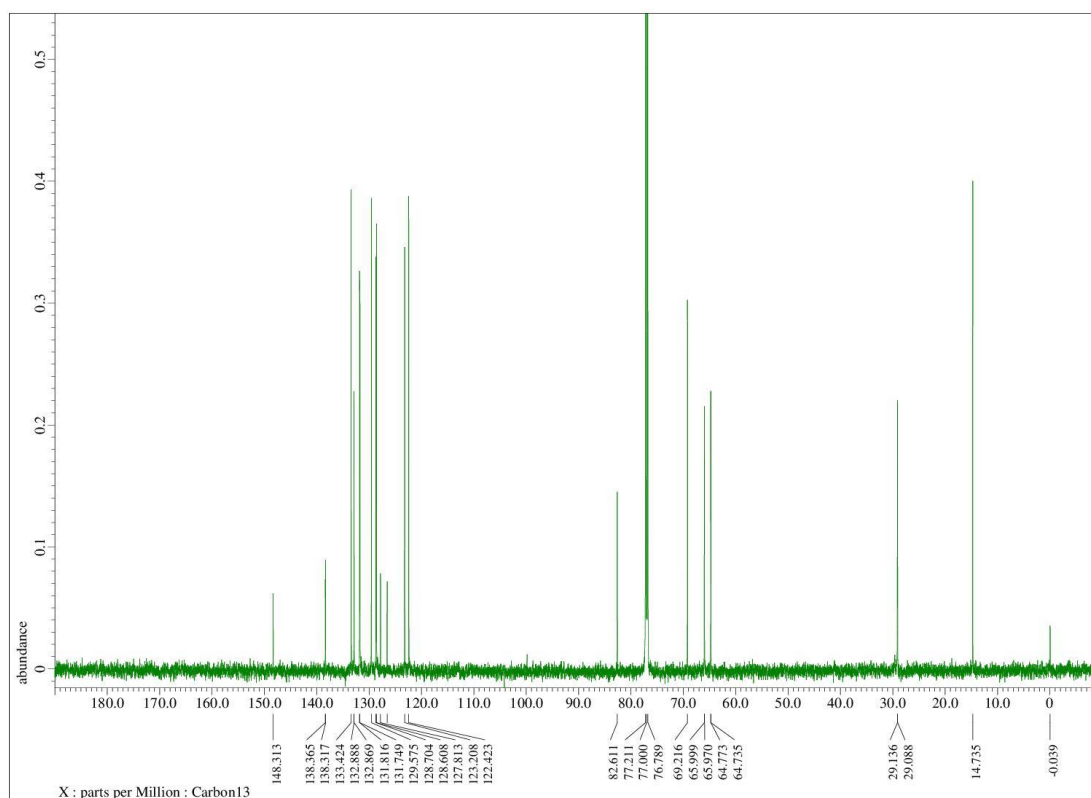
600 MHz, CDCl₃



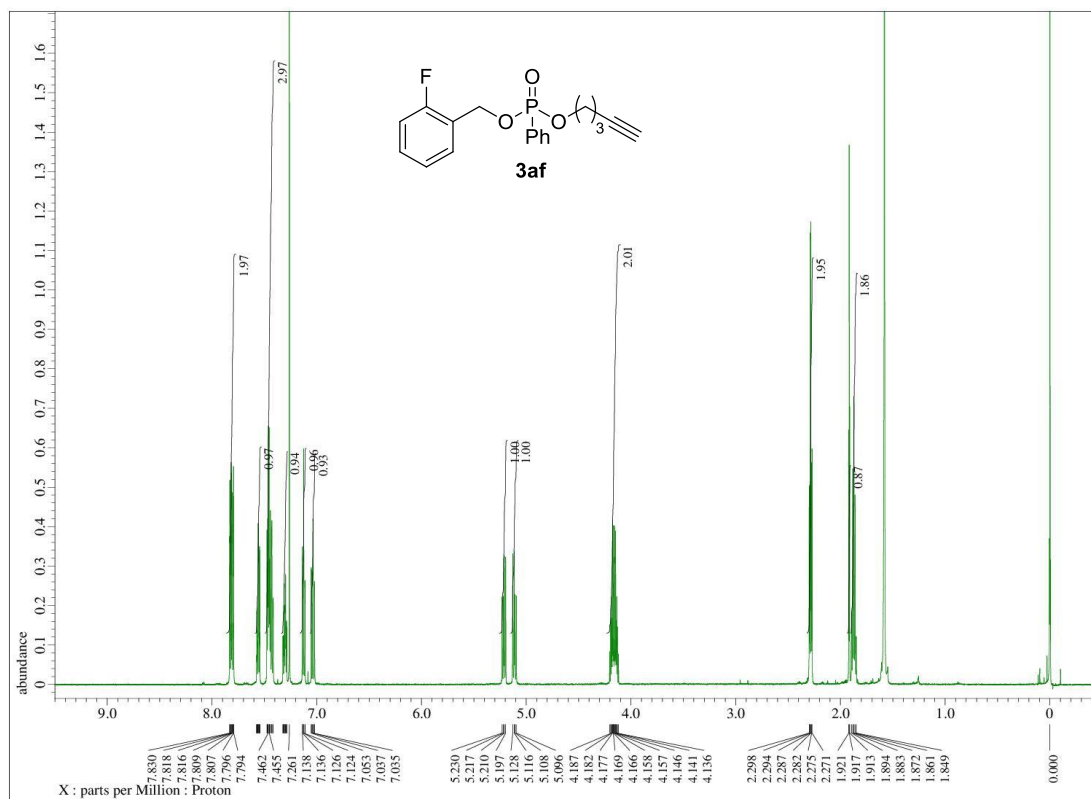
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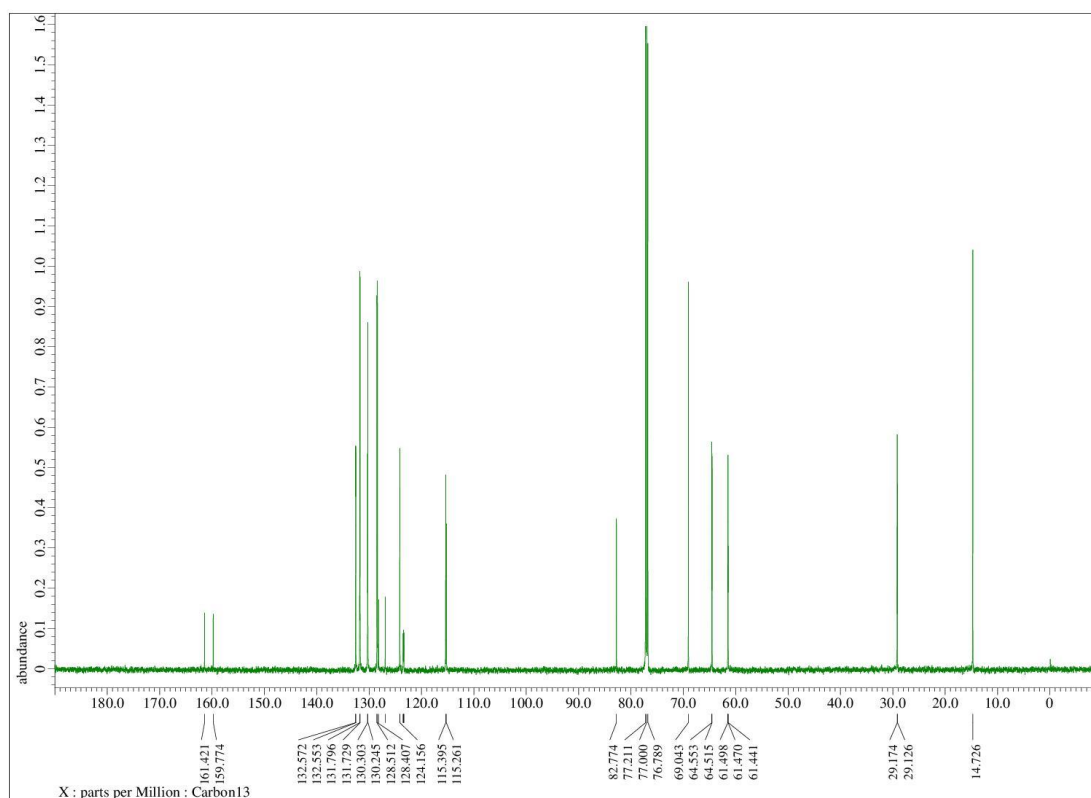
600 MHz, CDCl₃



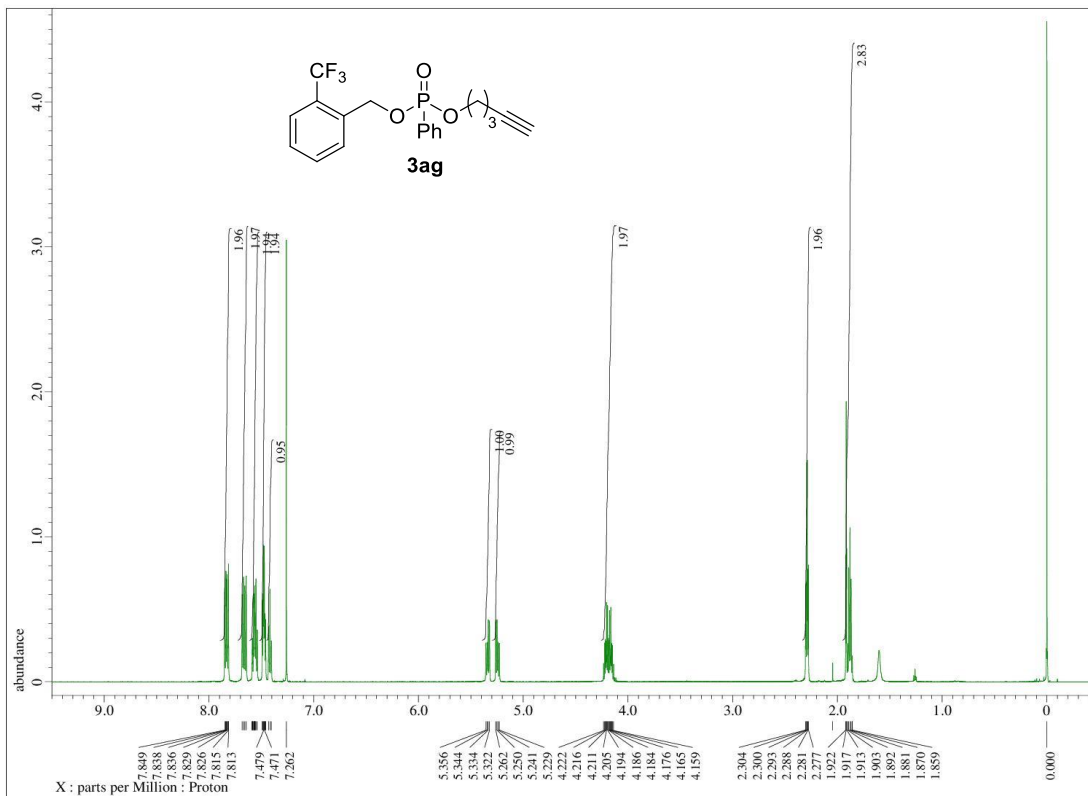
150 MHz, CDCl₃



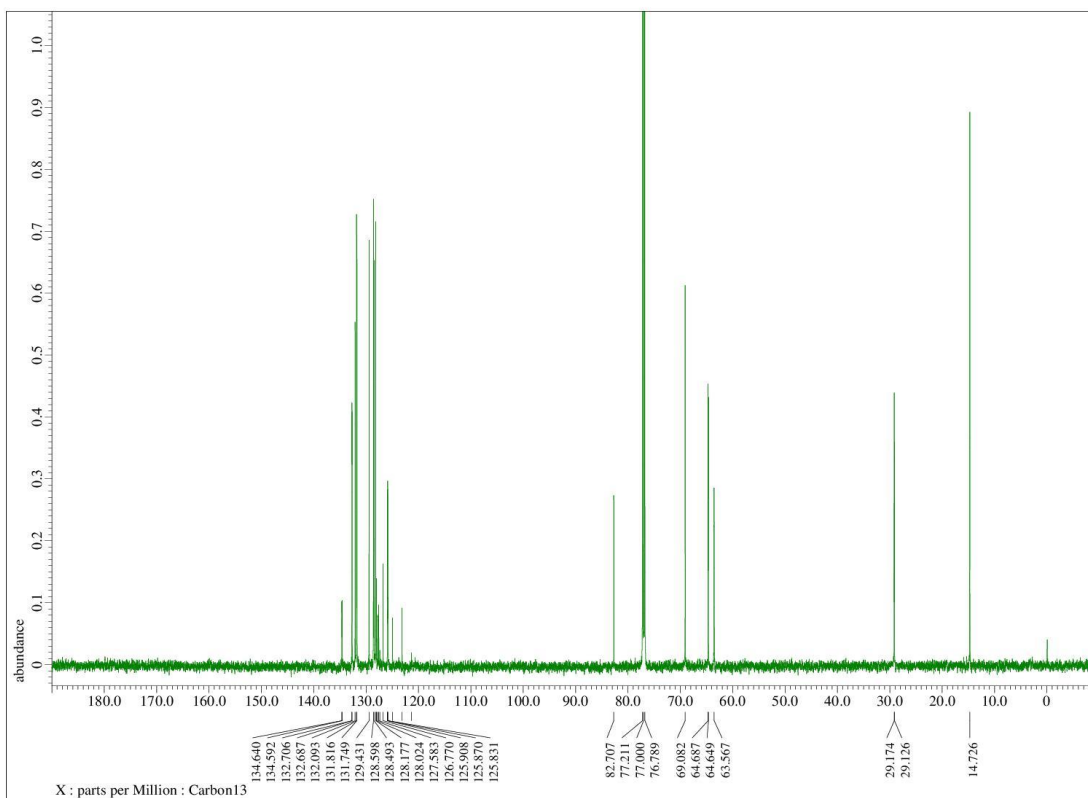
600 MHz, CDCl₃



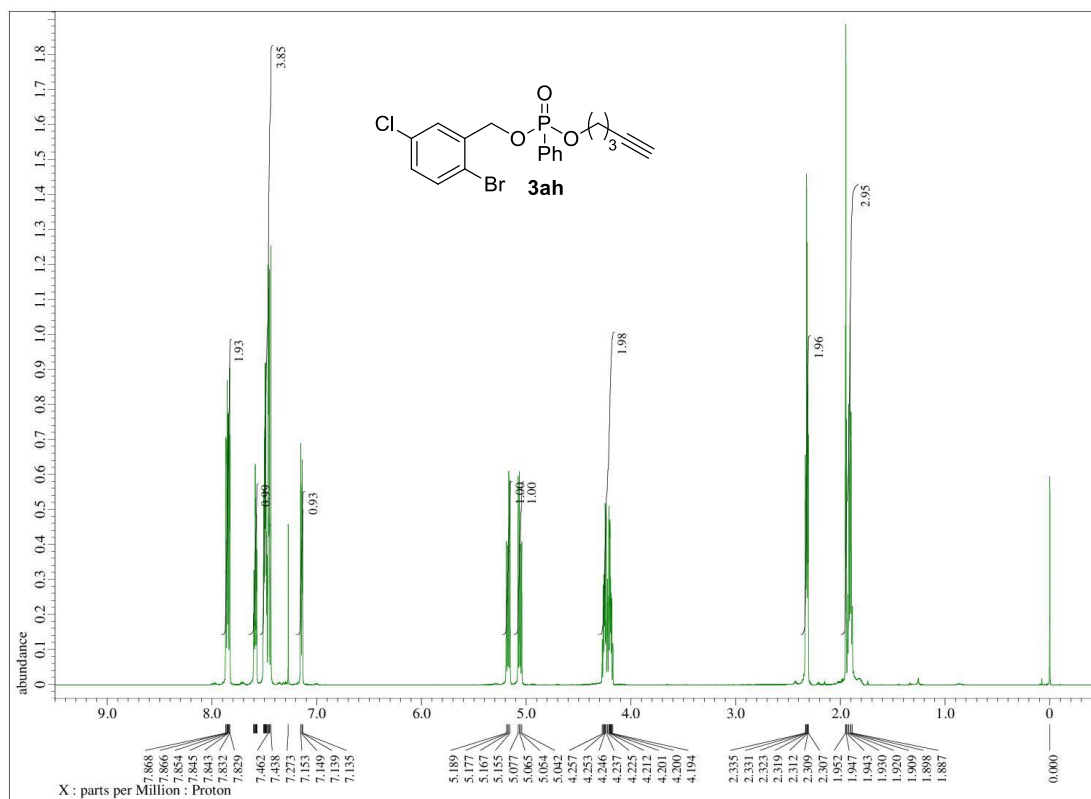
150 MHz, CDCl₃



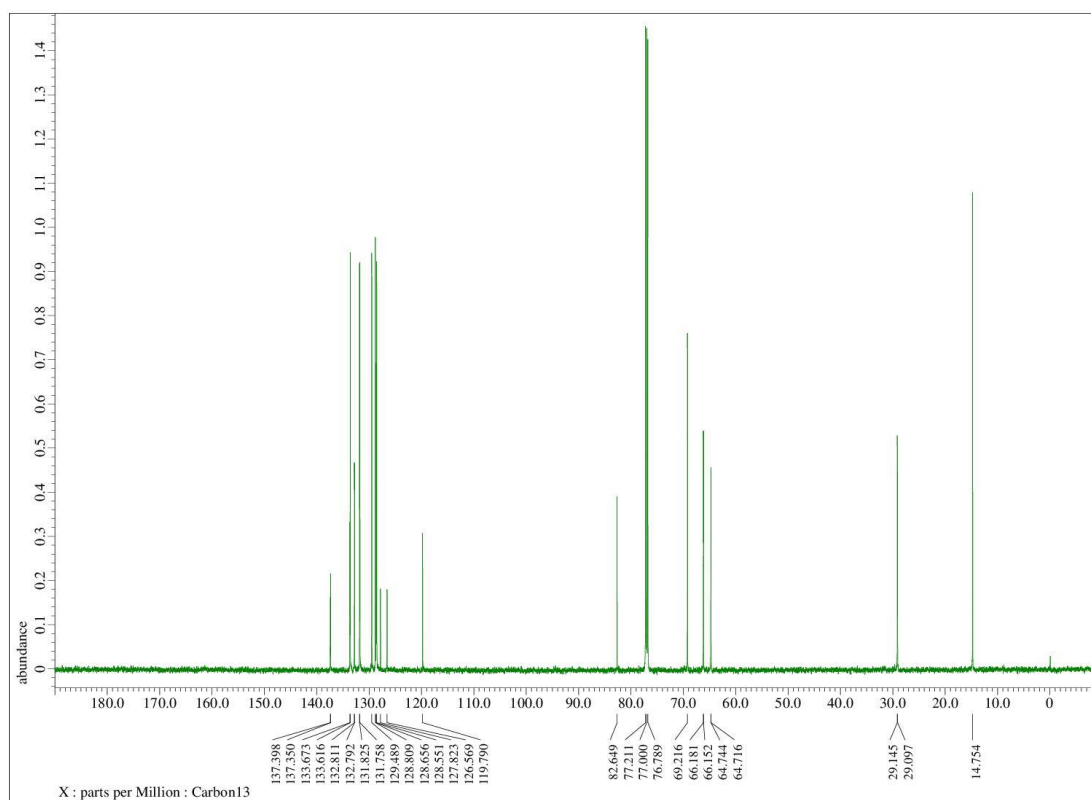
600 MHz, CDCl₃



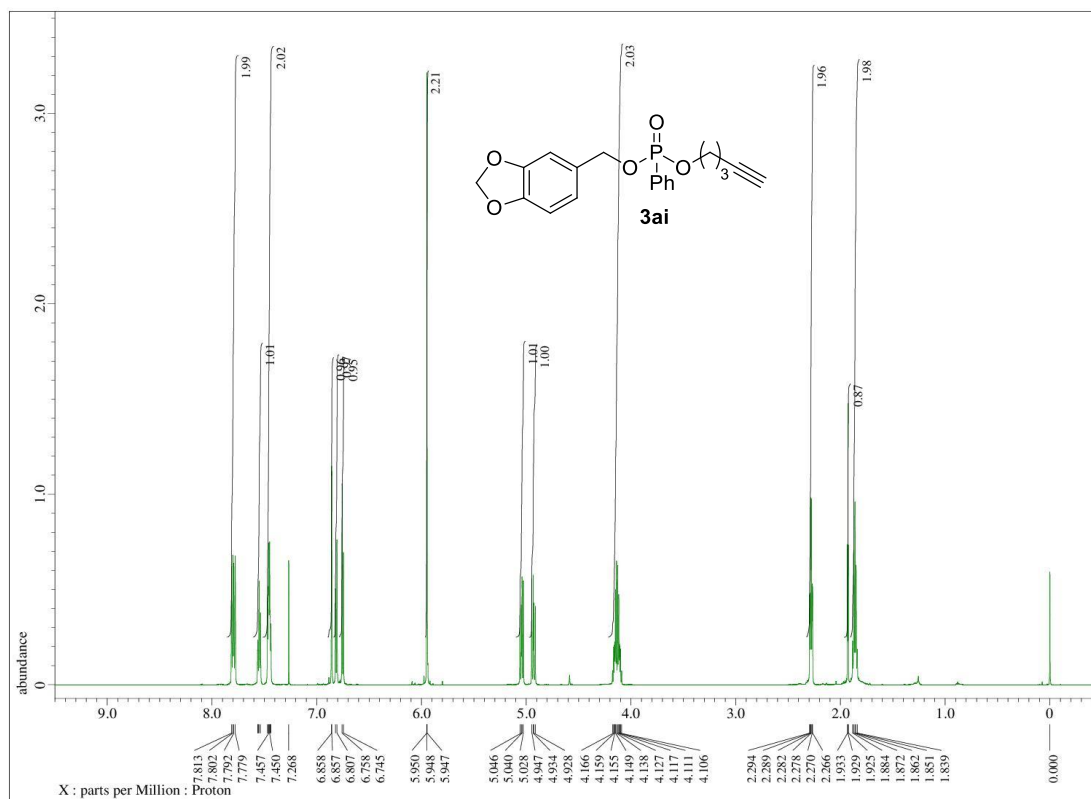
150 MHz, CDCl₃



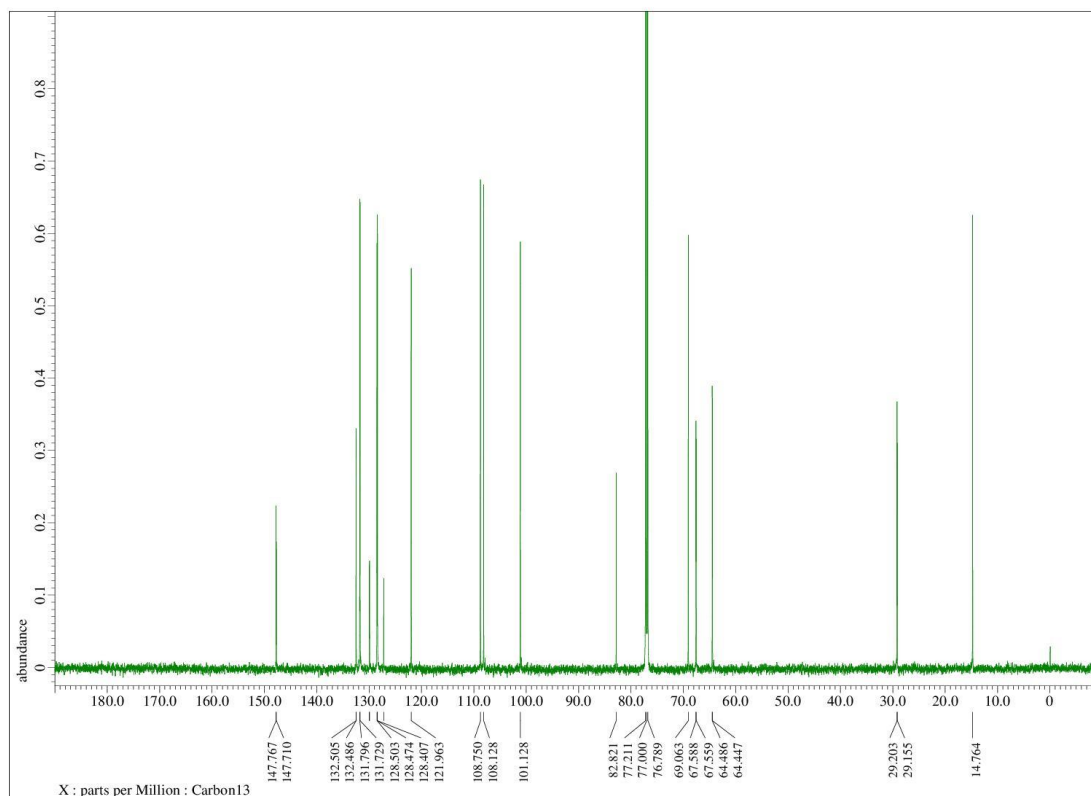
600 MHz, CDCl₃



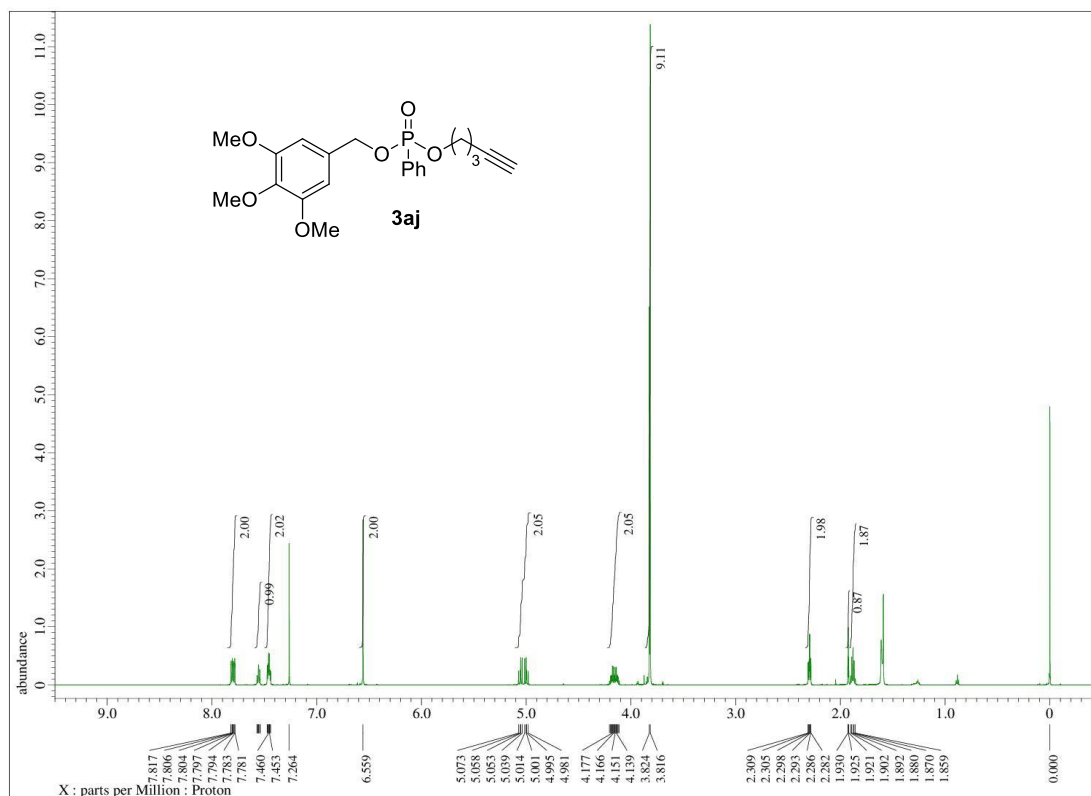
150 MHz, CDCl₃



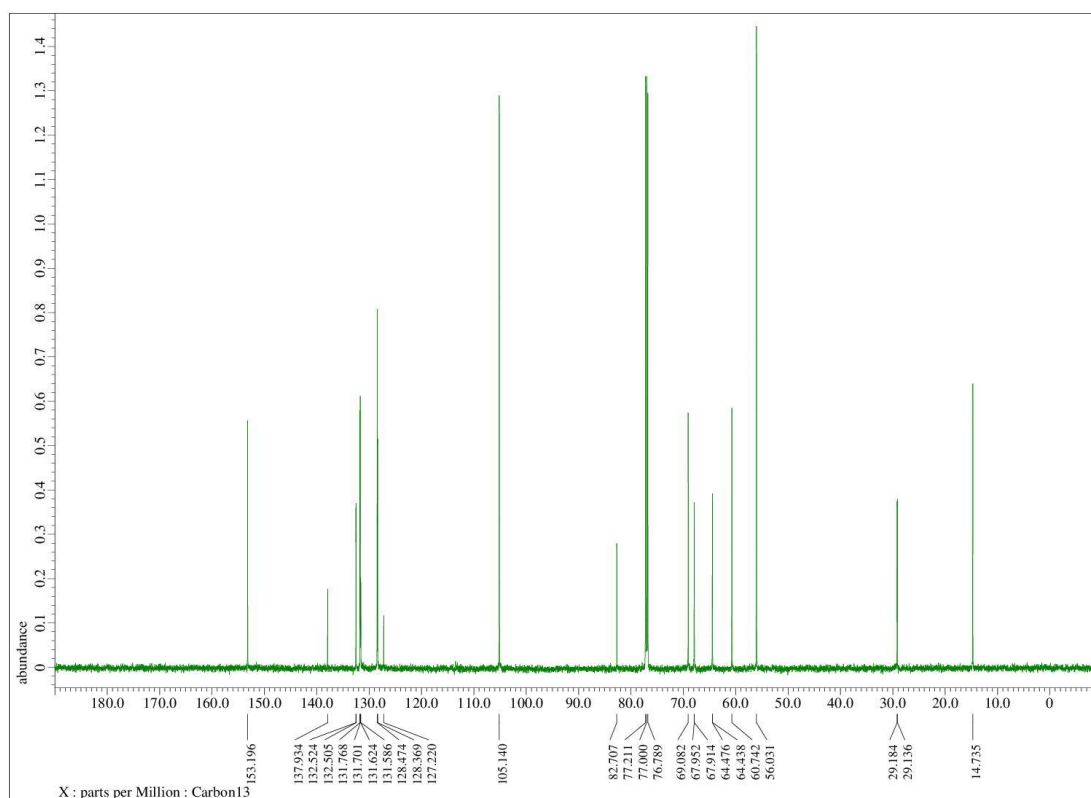
600 MHz, CDCl₃



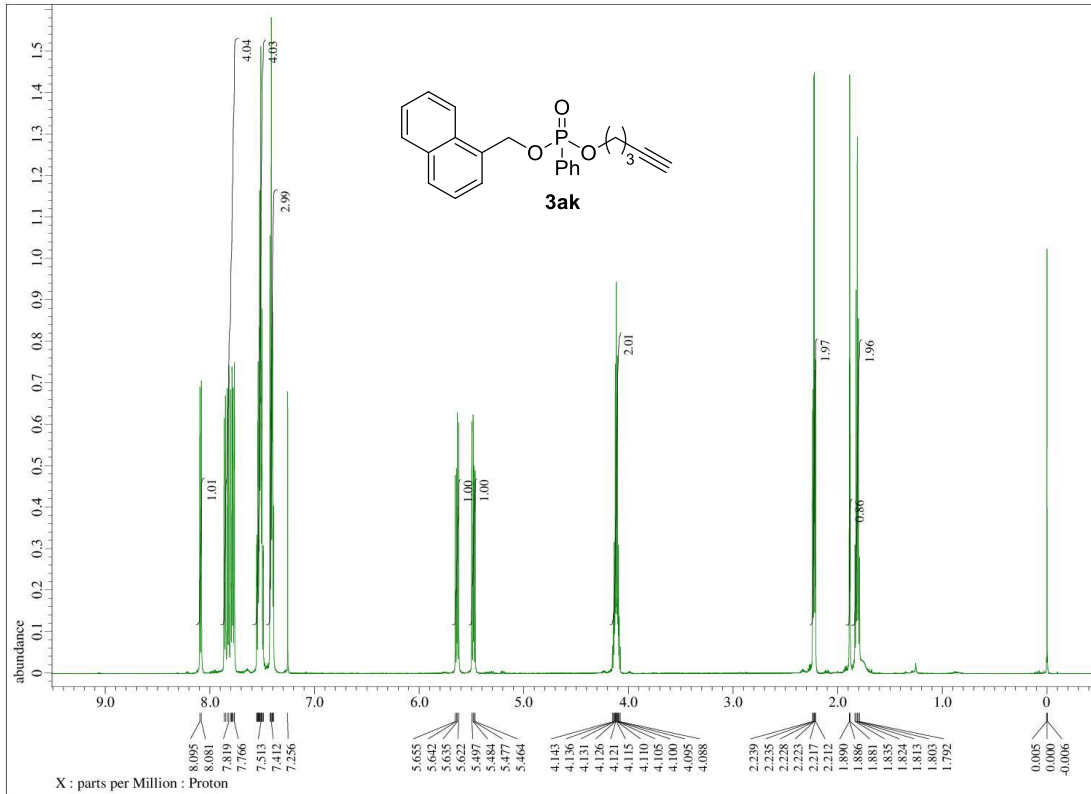
150 MHz, CDCl₃



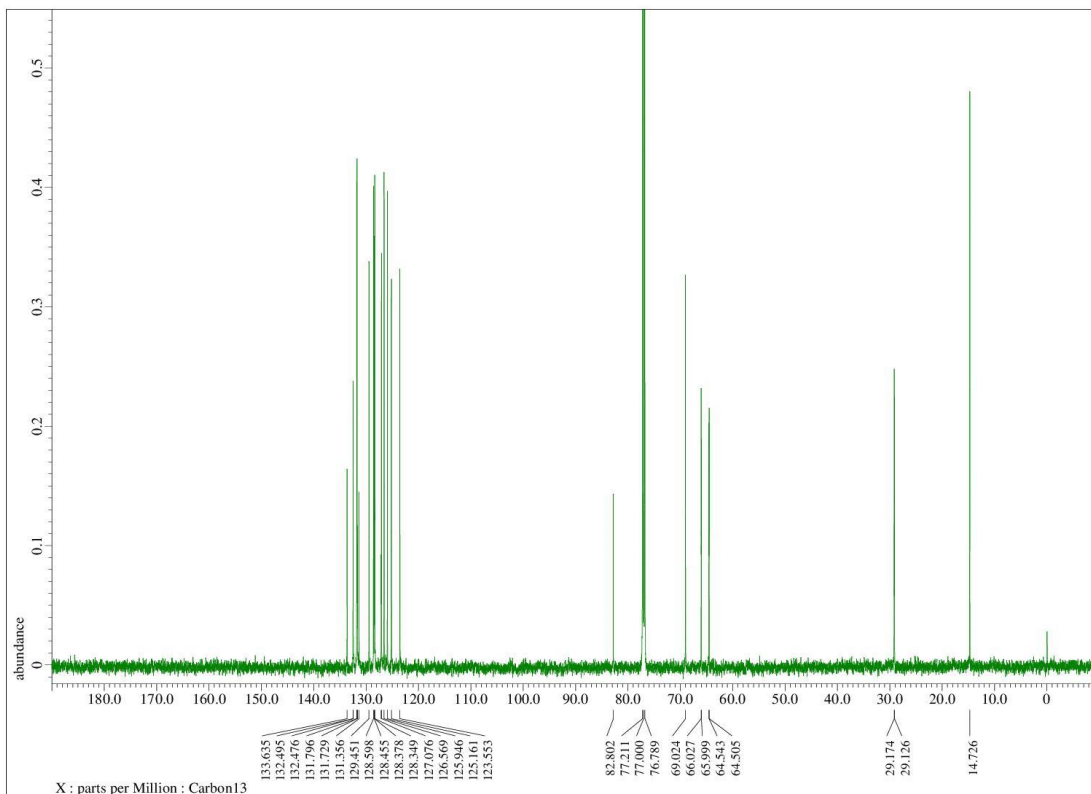
600 MHz, CDCl₃



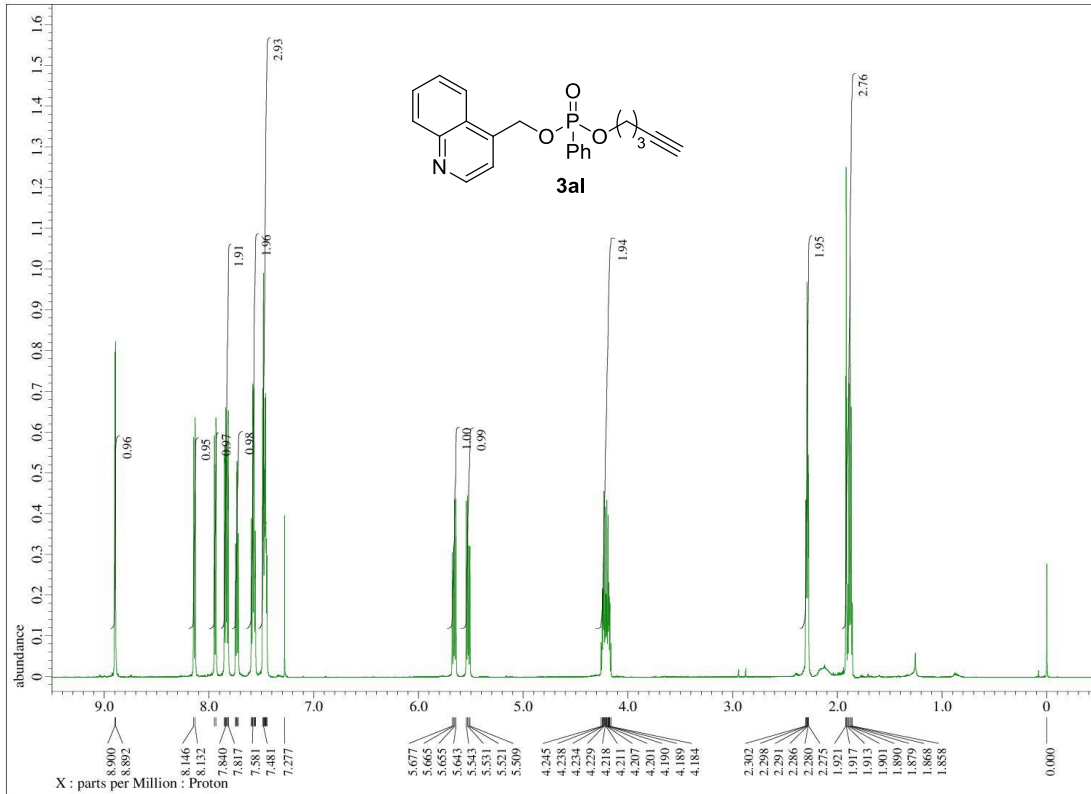
150 MHz, CDCl₃



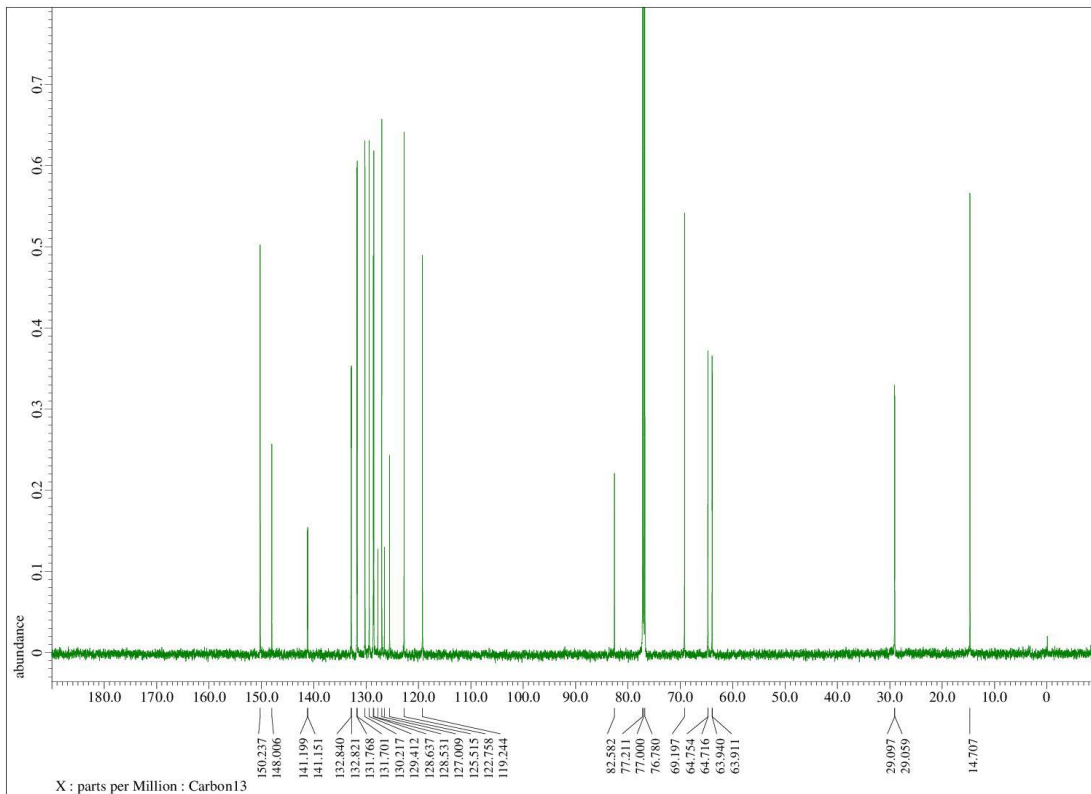
600 MHz, CDCl₃



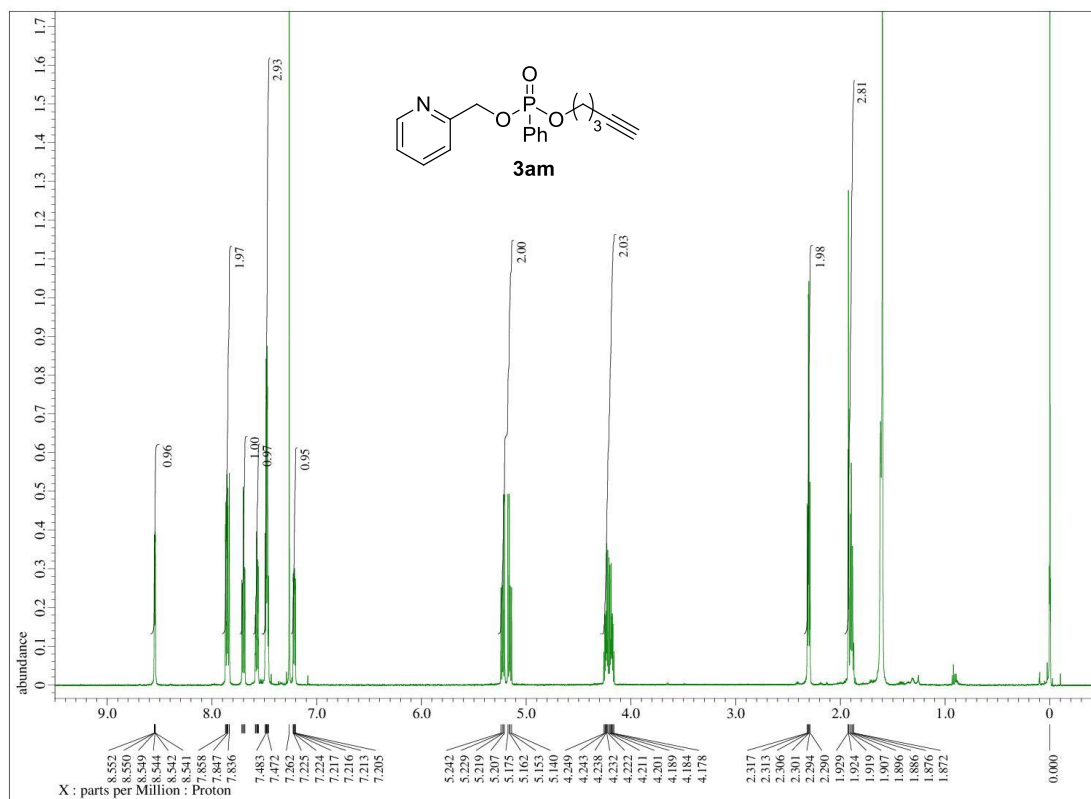
150 MHz, CDCl₃



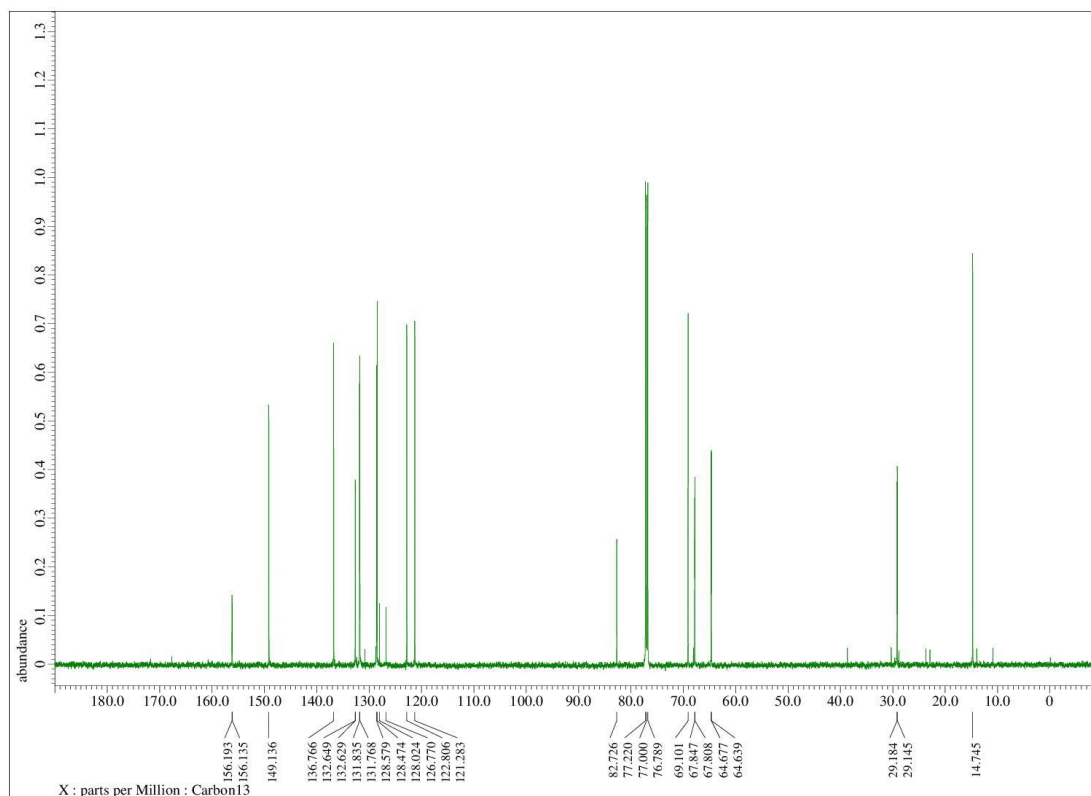
600 MHz, CDCl₃



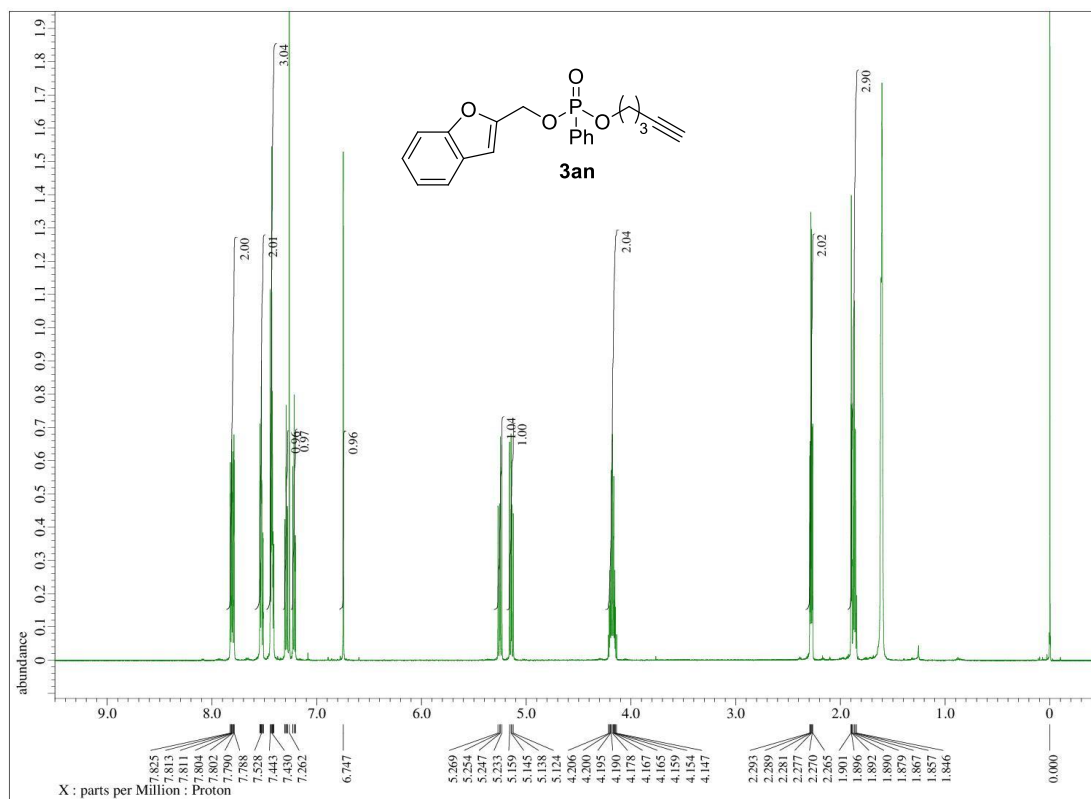
150 MHz, CDCl₃



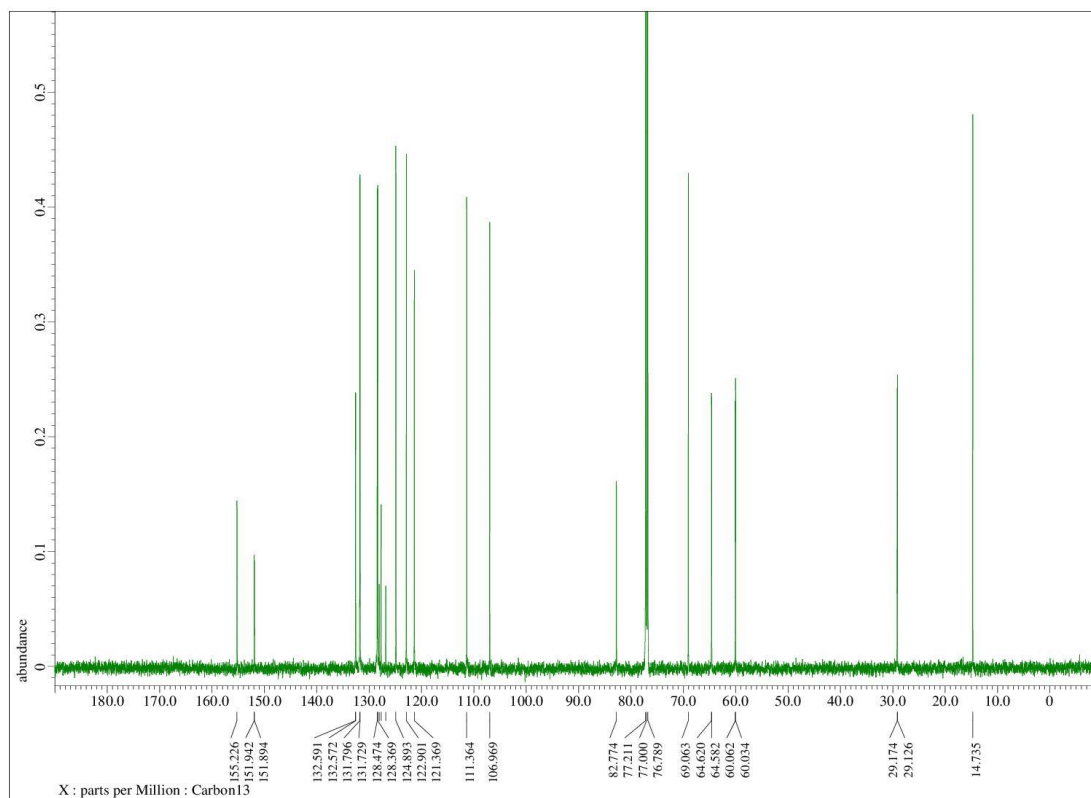
600 MHz, CDCl₃



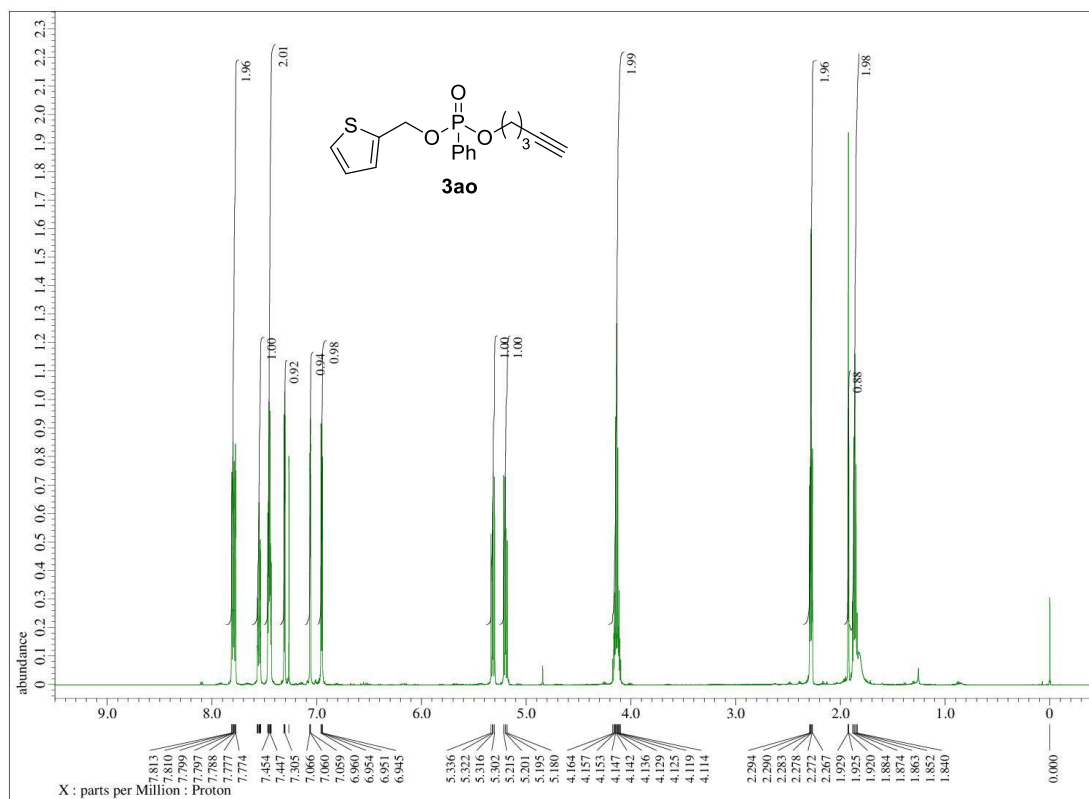
150 MHz, CDCl₃



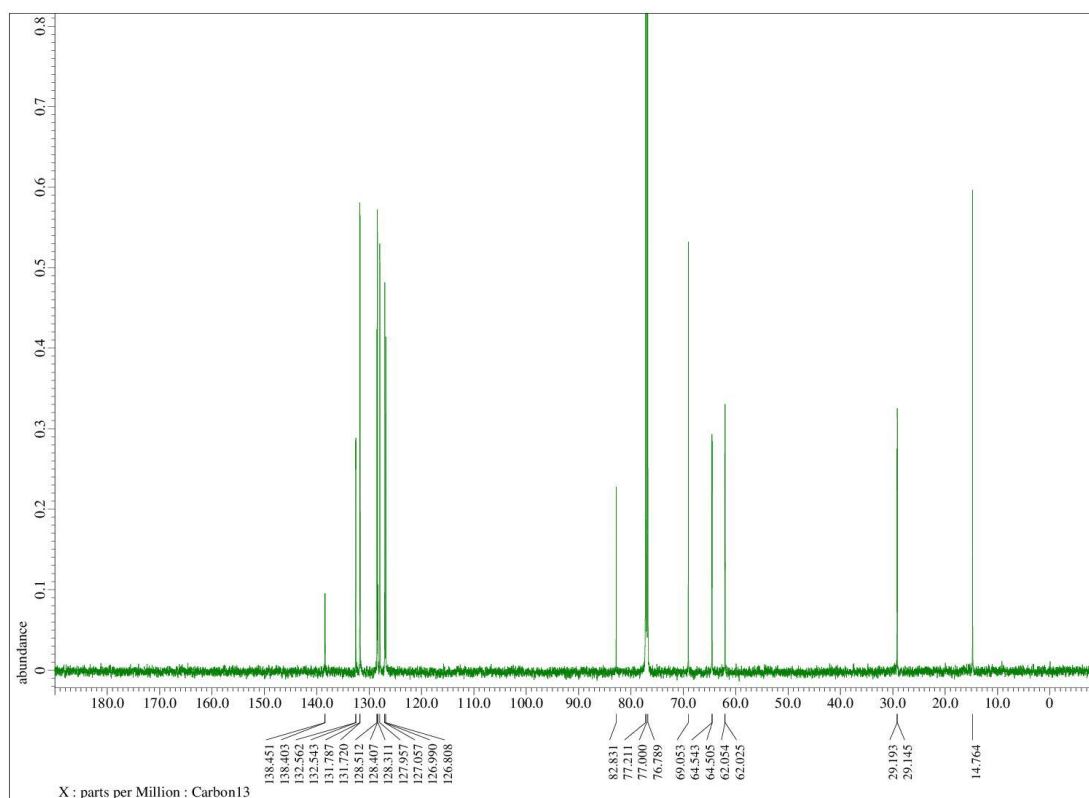
600 MHz, CDCl₃



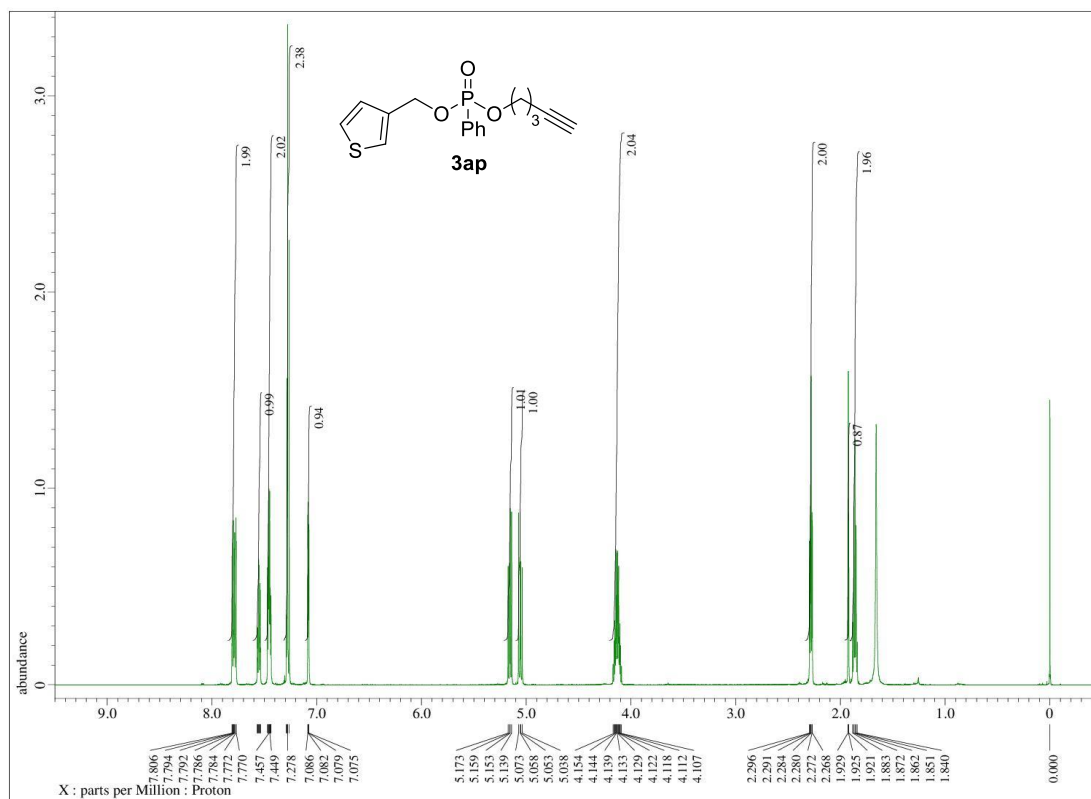
150 MHz, CDCl₃



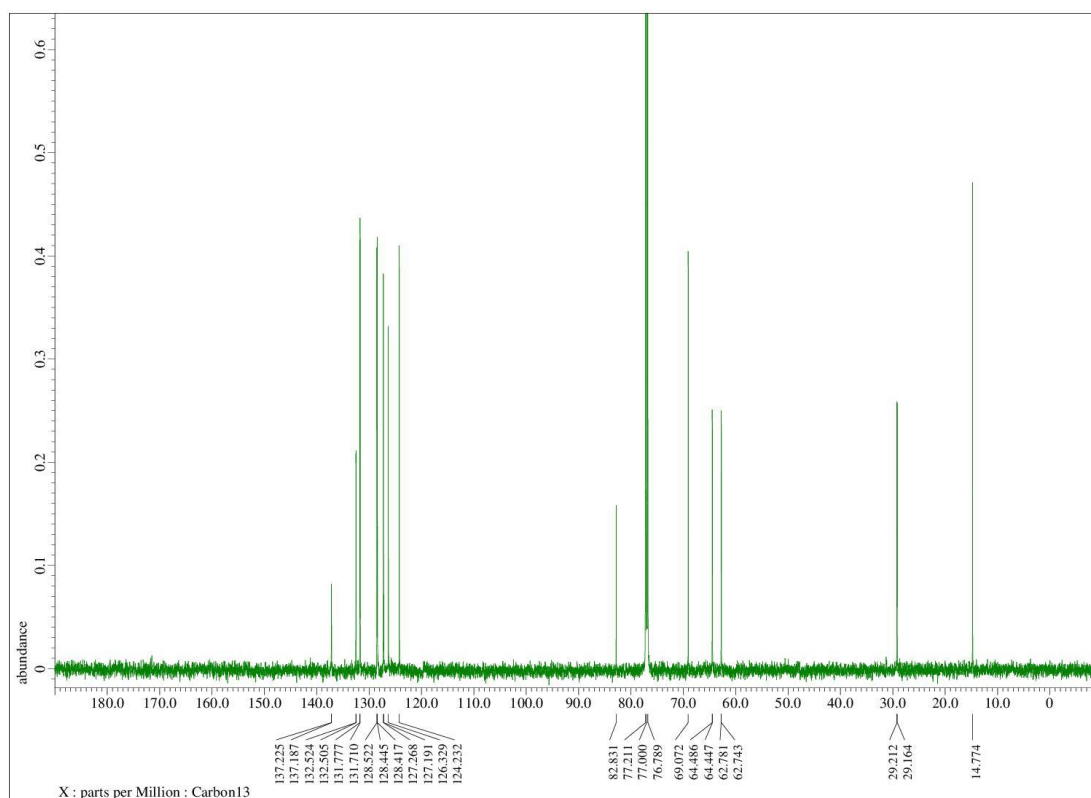
600 MHz, CDCl₃



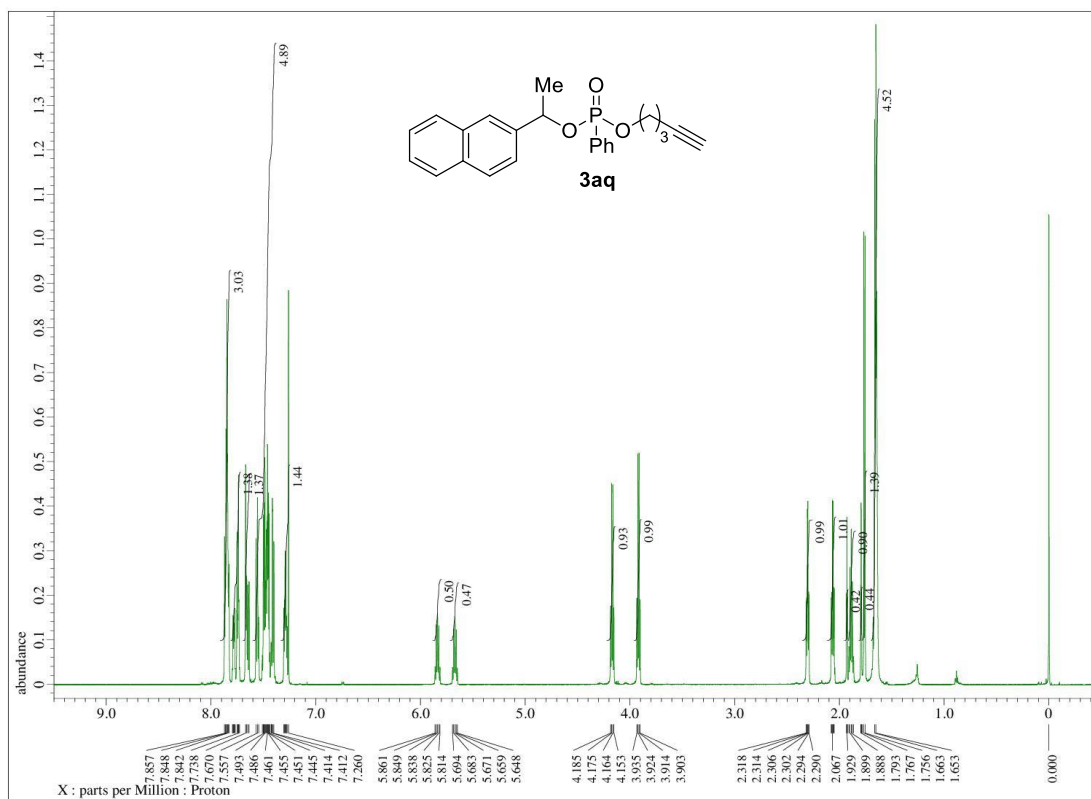
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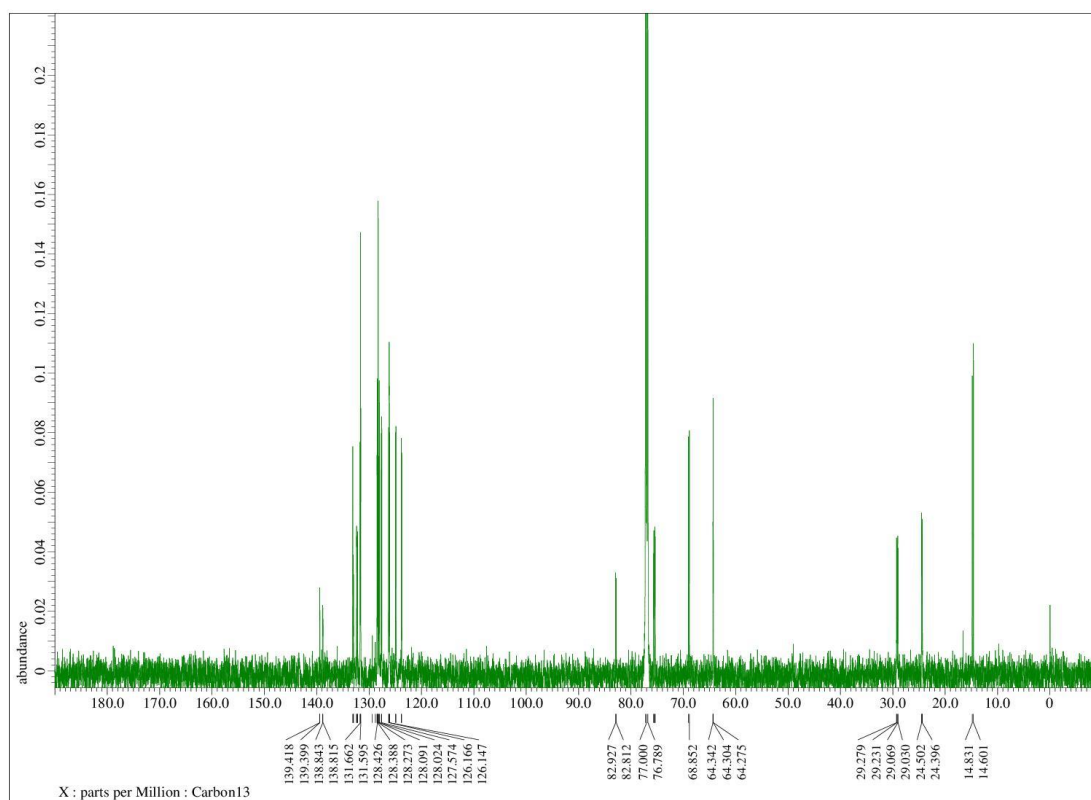
600 MHz, CDCl₃



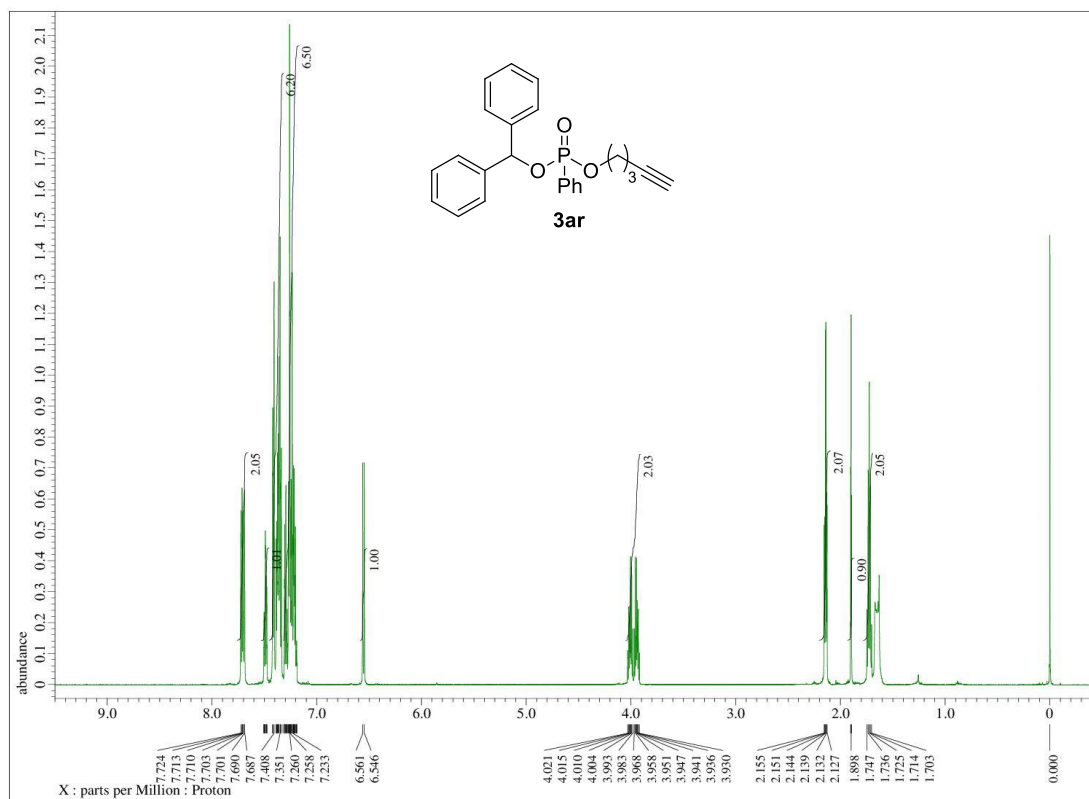
150 MHz, CDCl₃



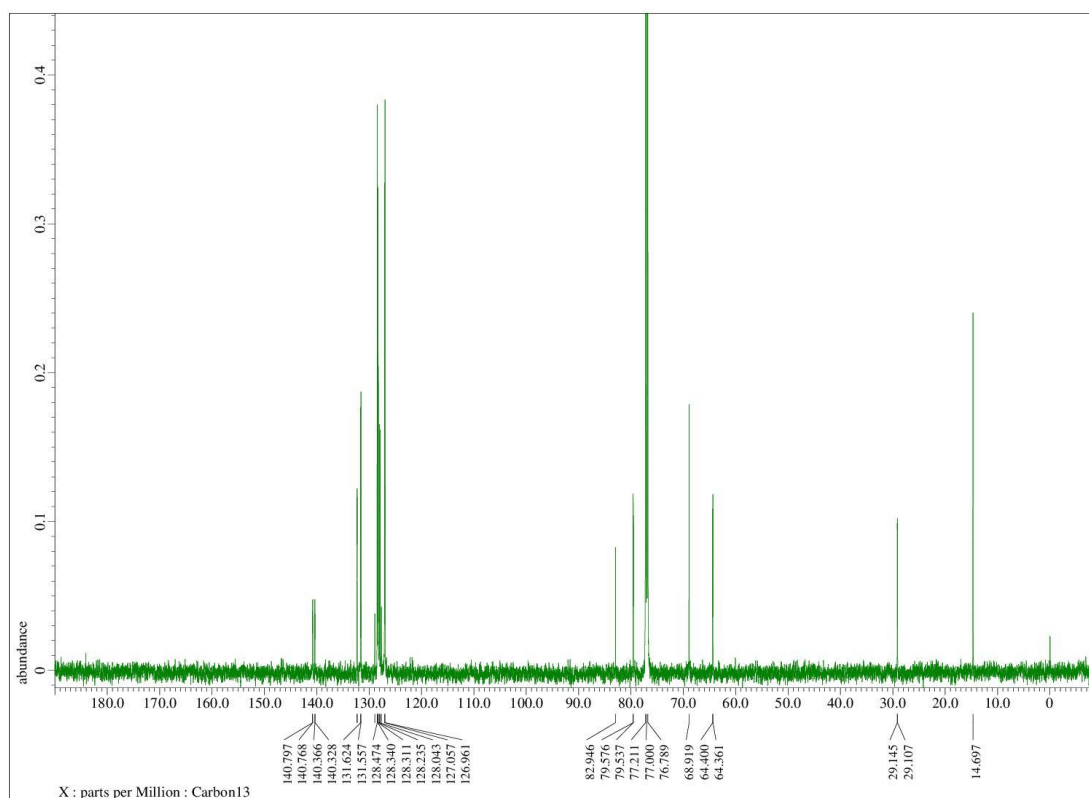
600 MHz, CDCl₃



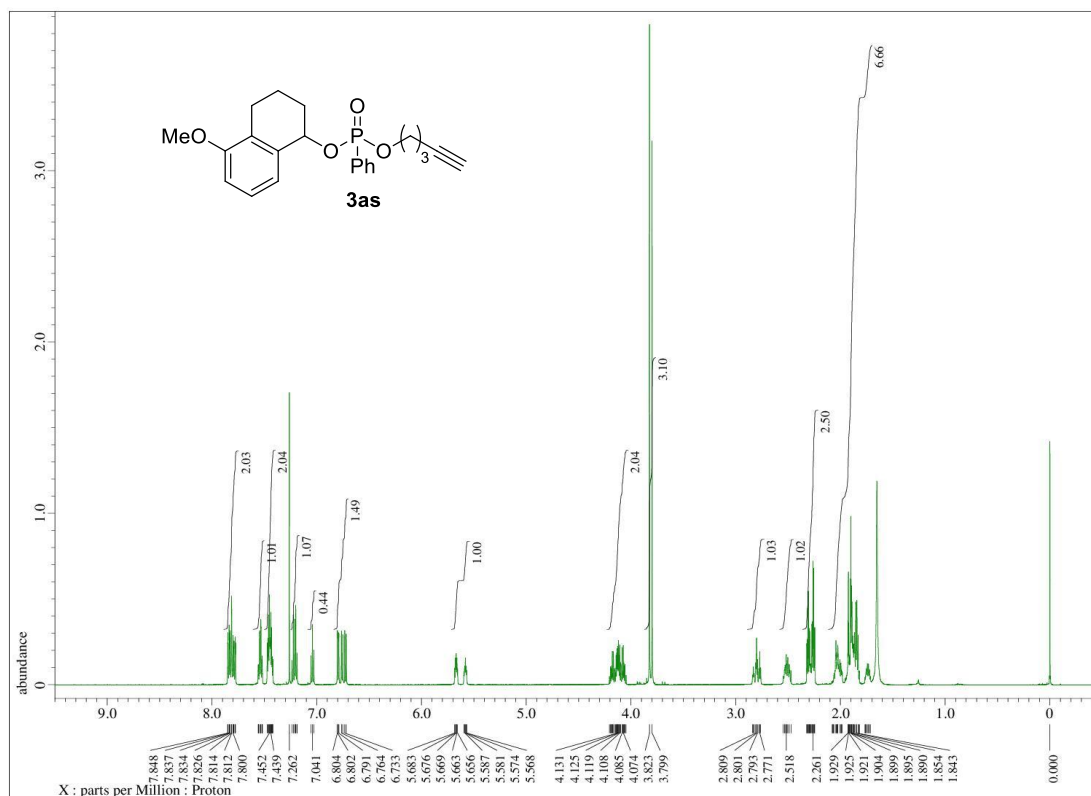
150 MHz, CDCl₃



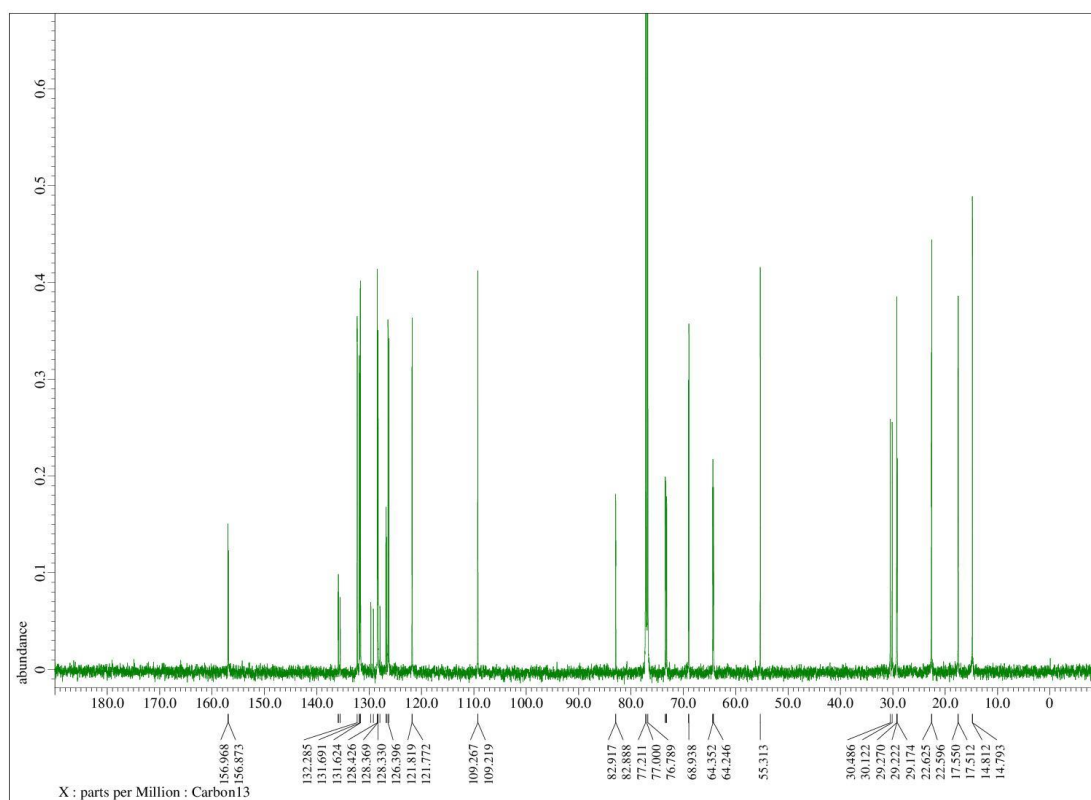
600 MHz, CDCl₃



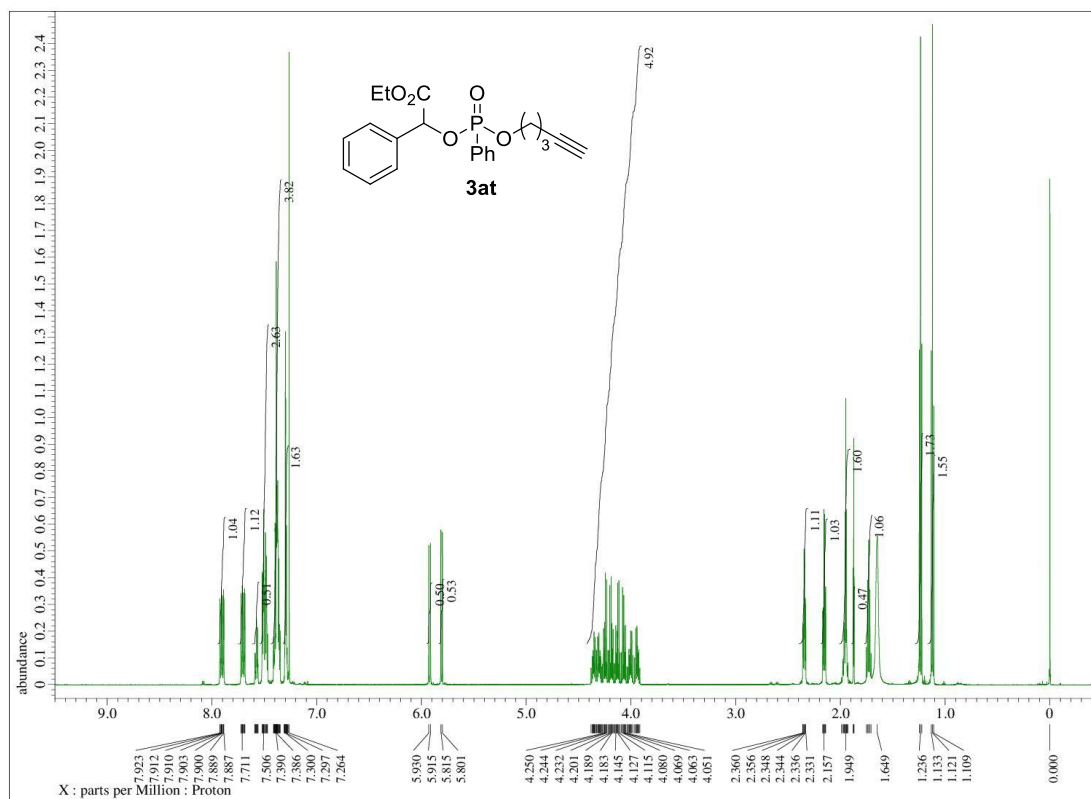
150 MHz, CDCl₃



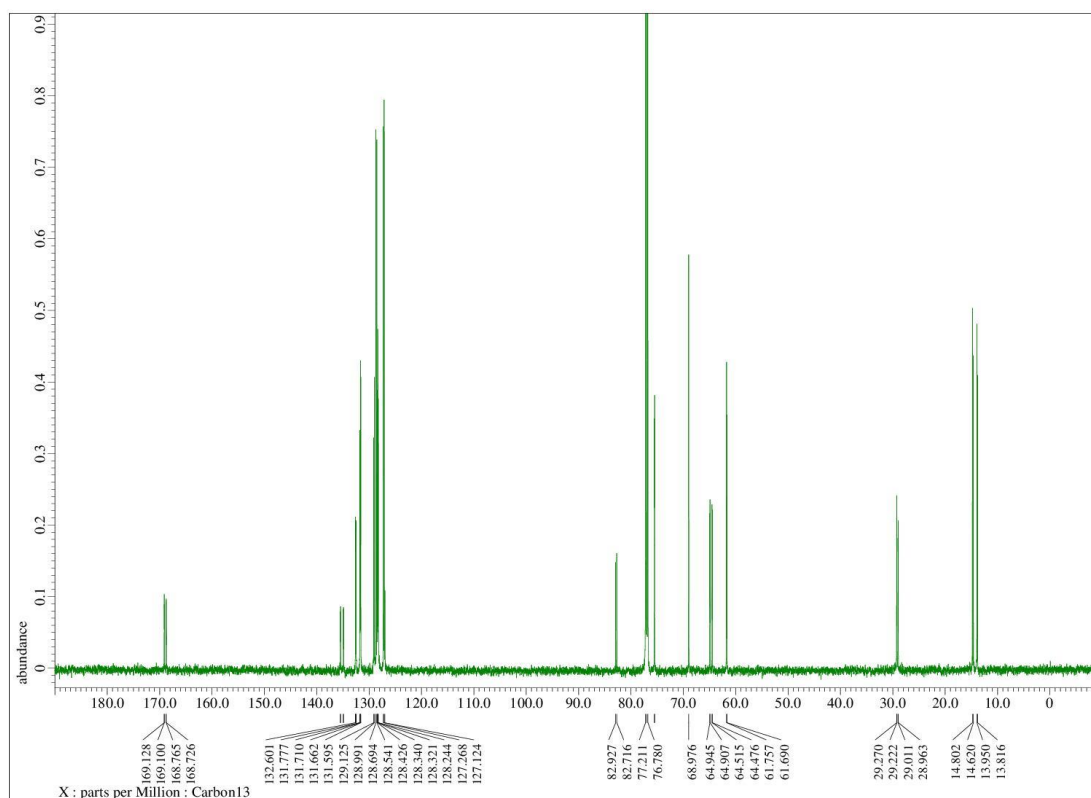
600 MHz, CDCl₃



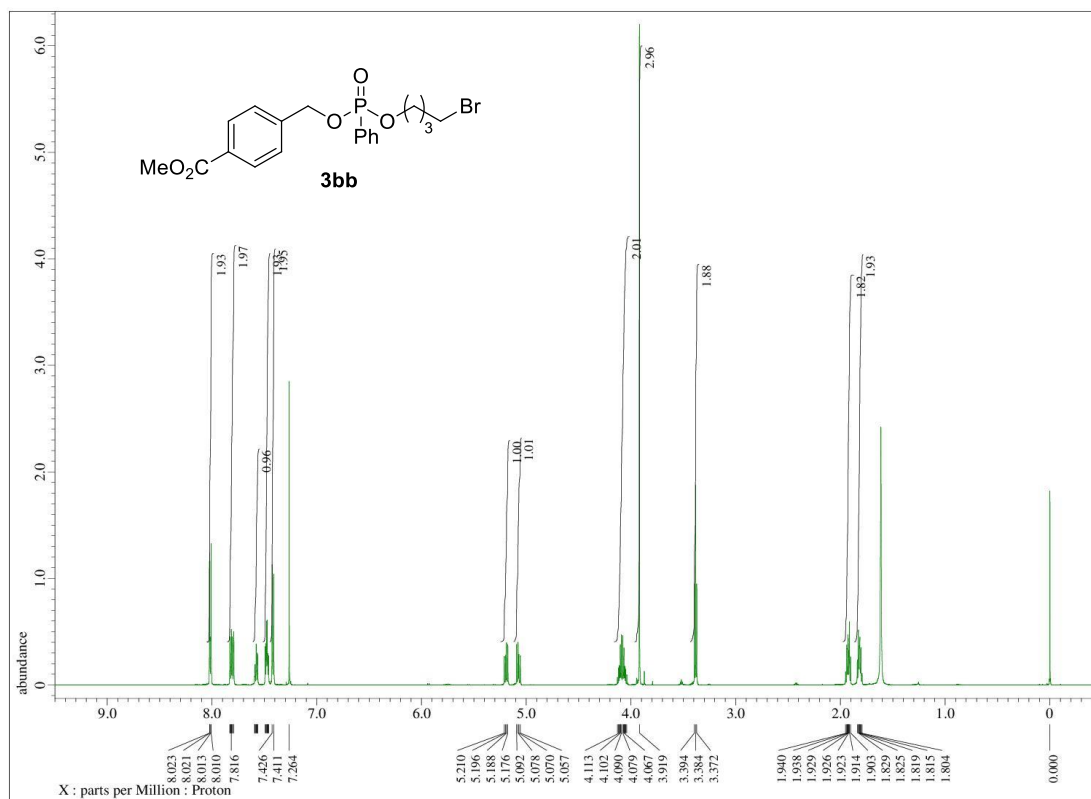
150 MHz, CDCl₃



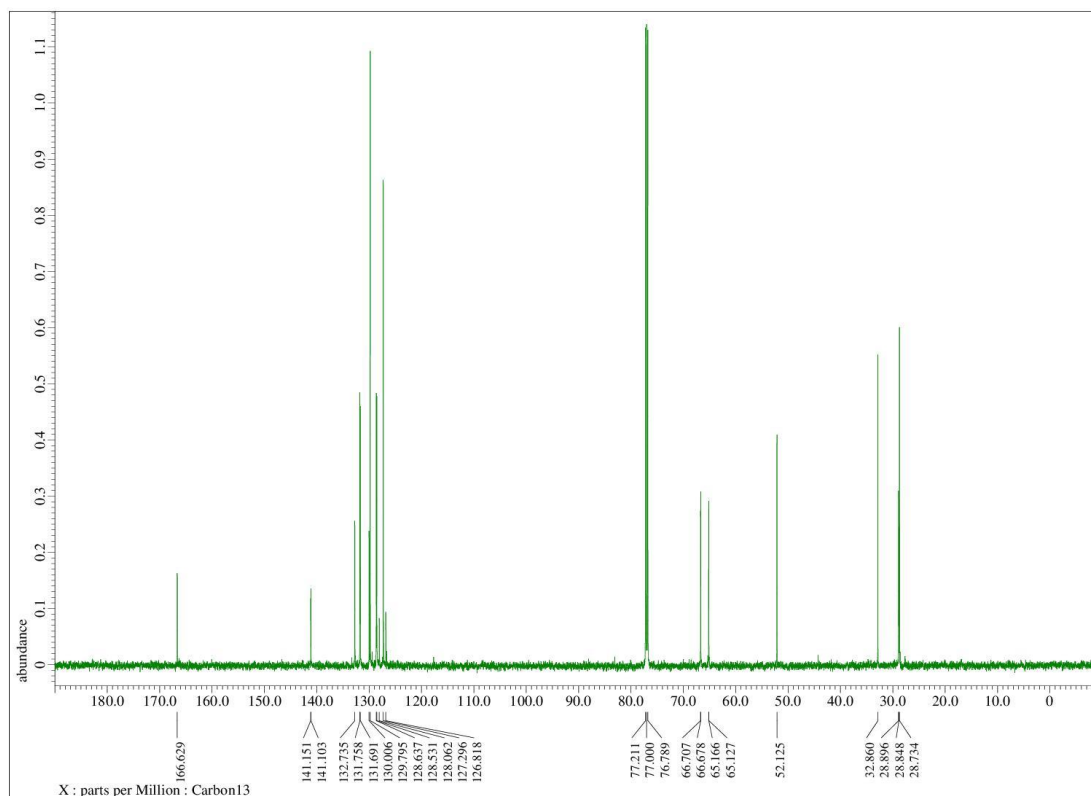
600 MHz, CDCl₃



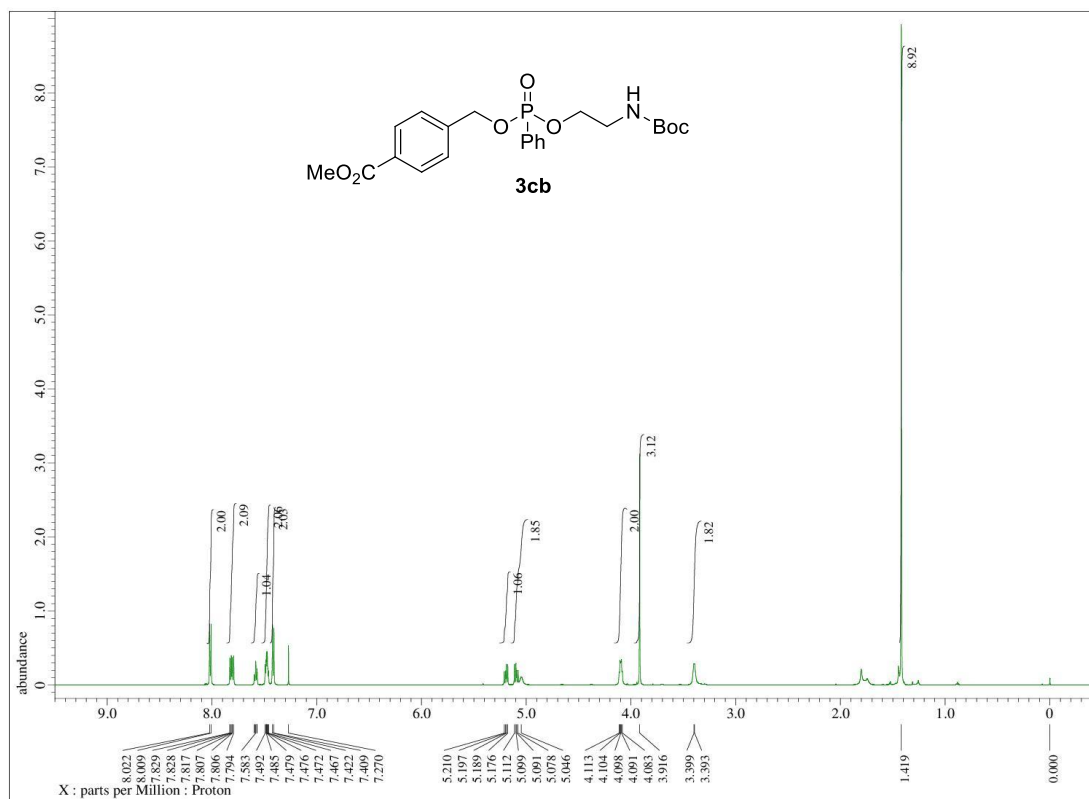
150 MHz, CDCl₃



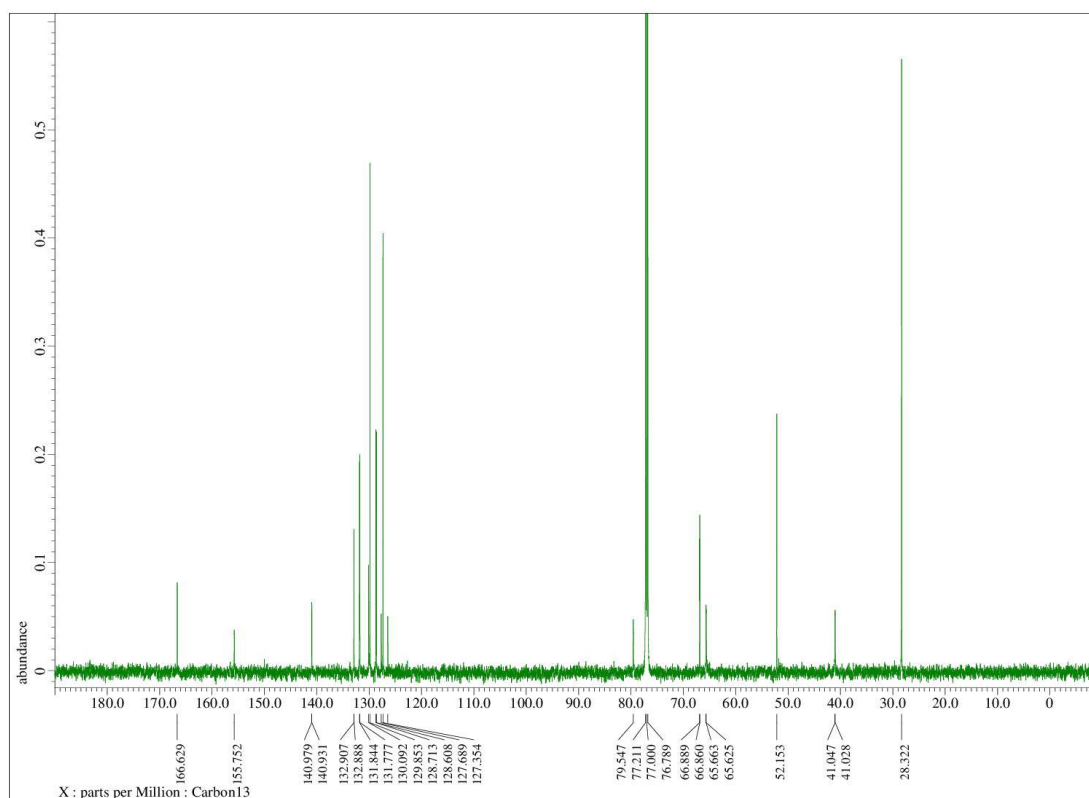
600 MHz, CDCl₃



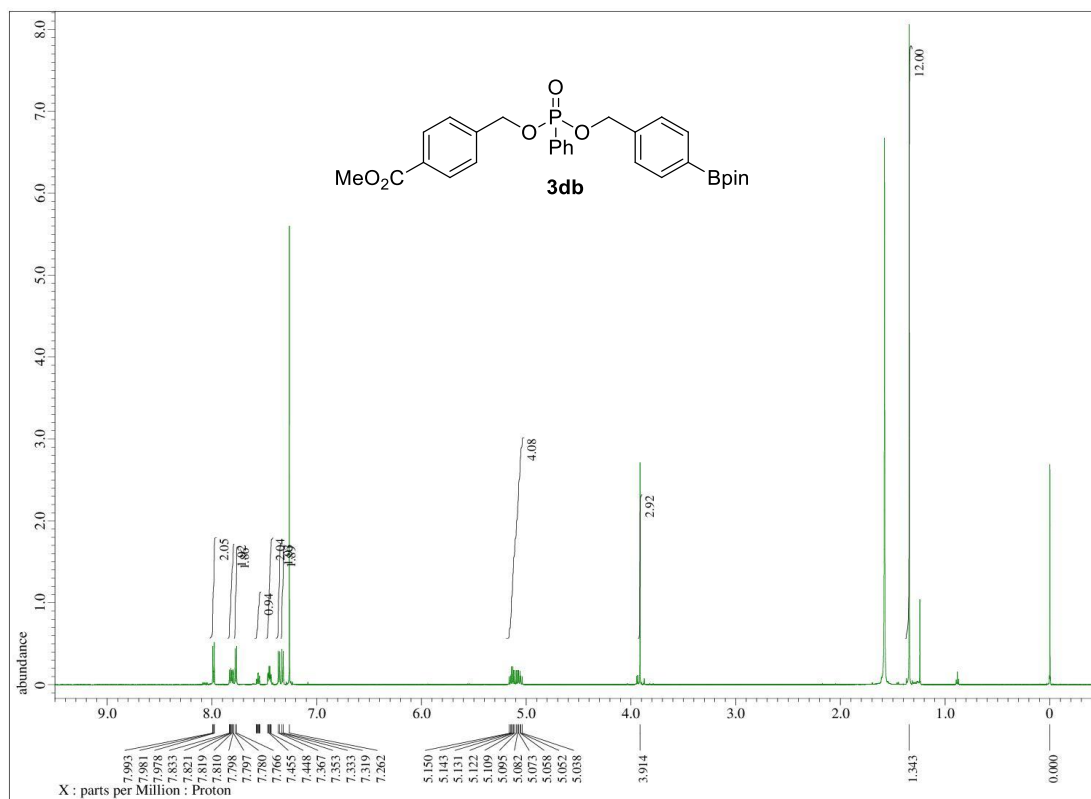
150 MHz, CDCl₃



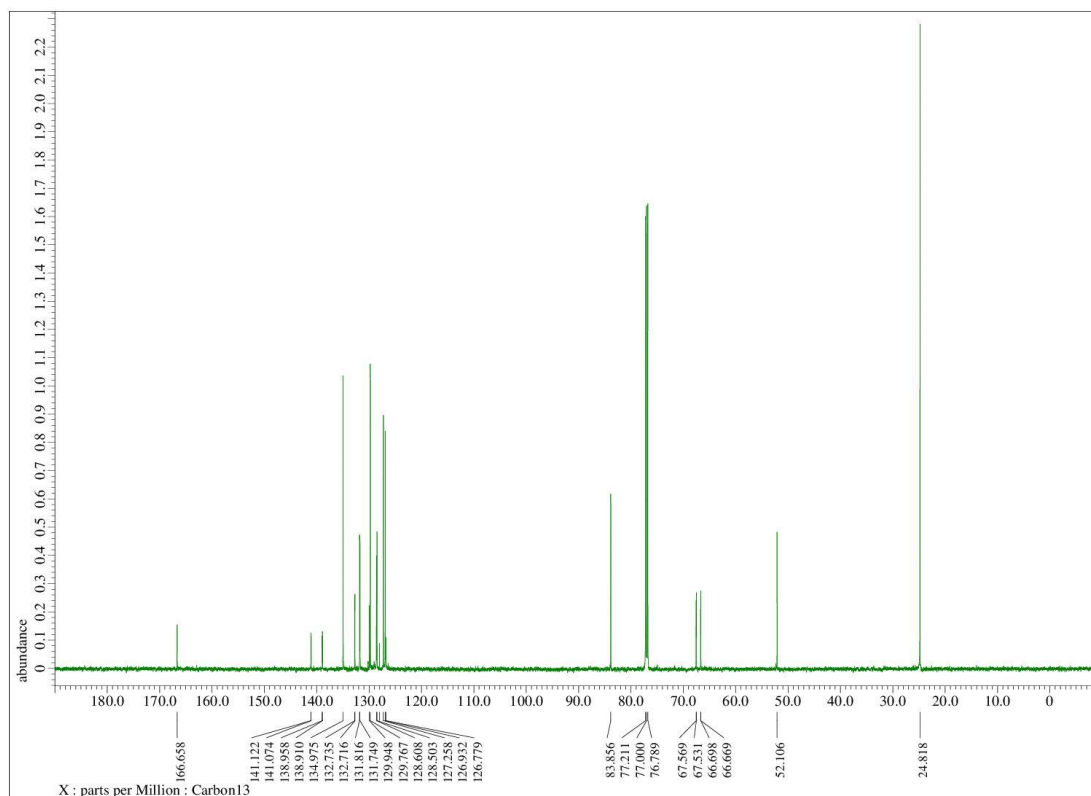
600 MHz, CDCl₃



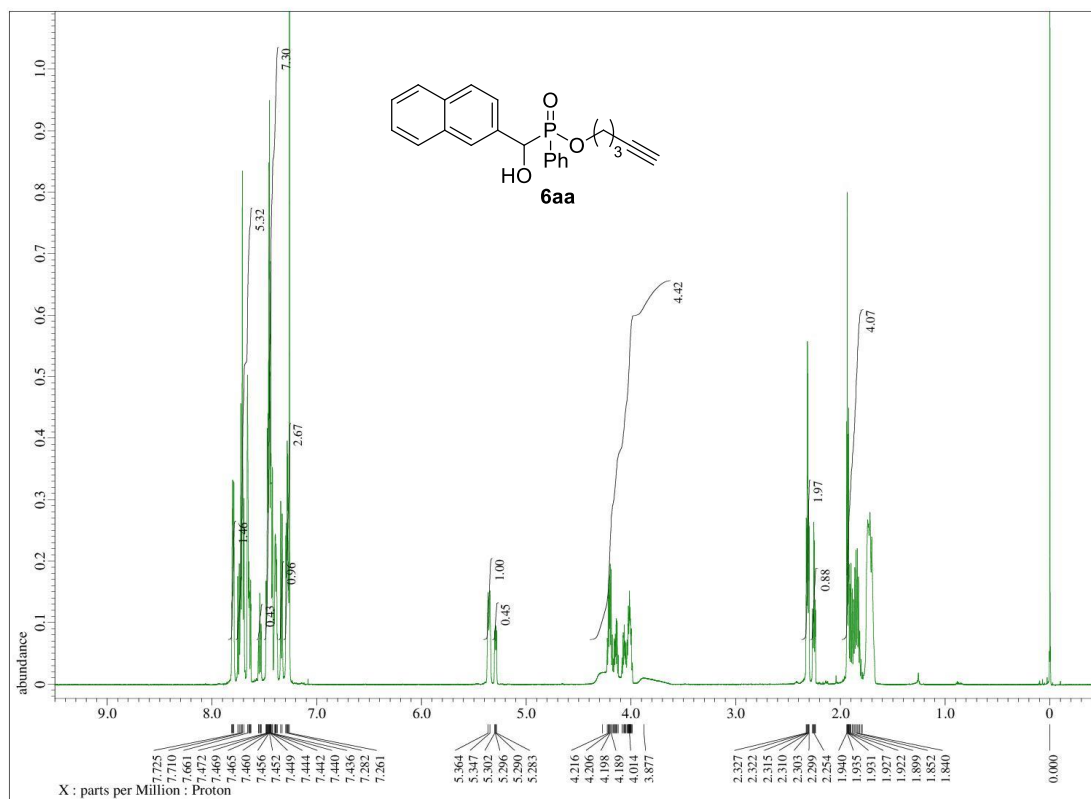
150 MHz, CDCl₃



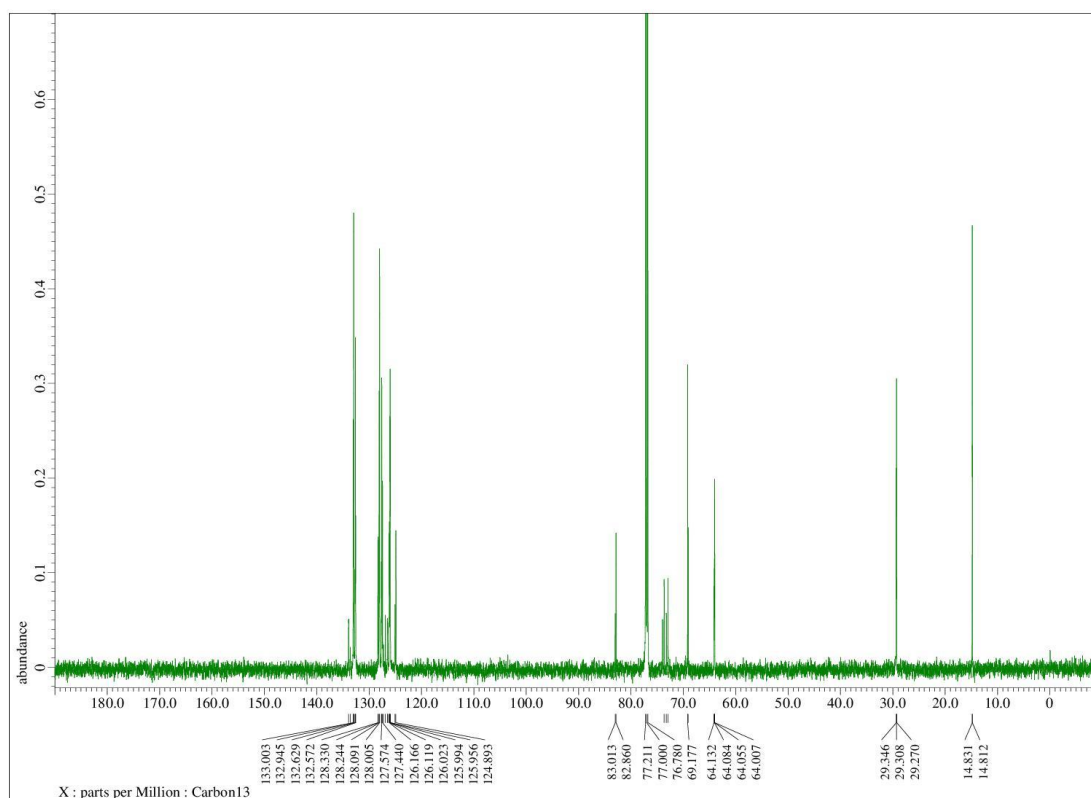
600 MHz, CDCl₃



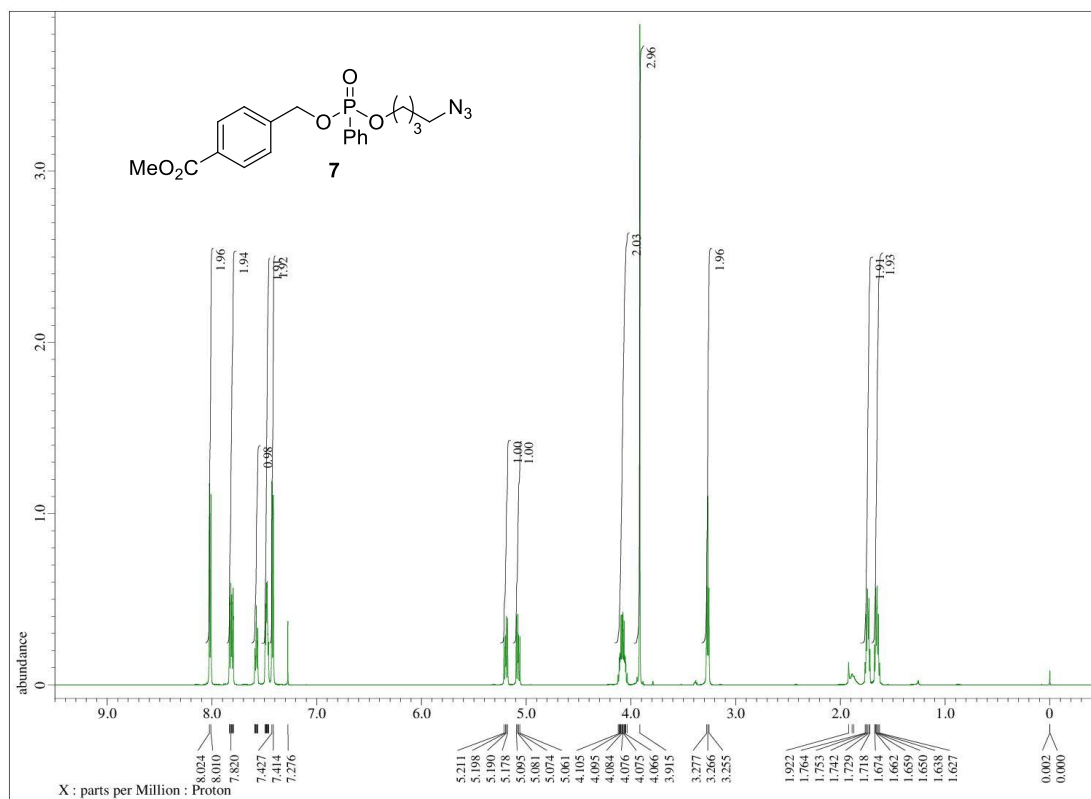
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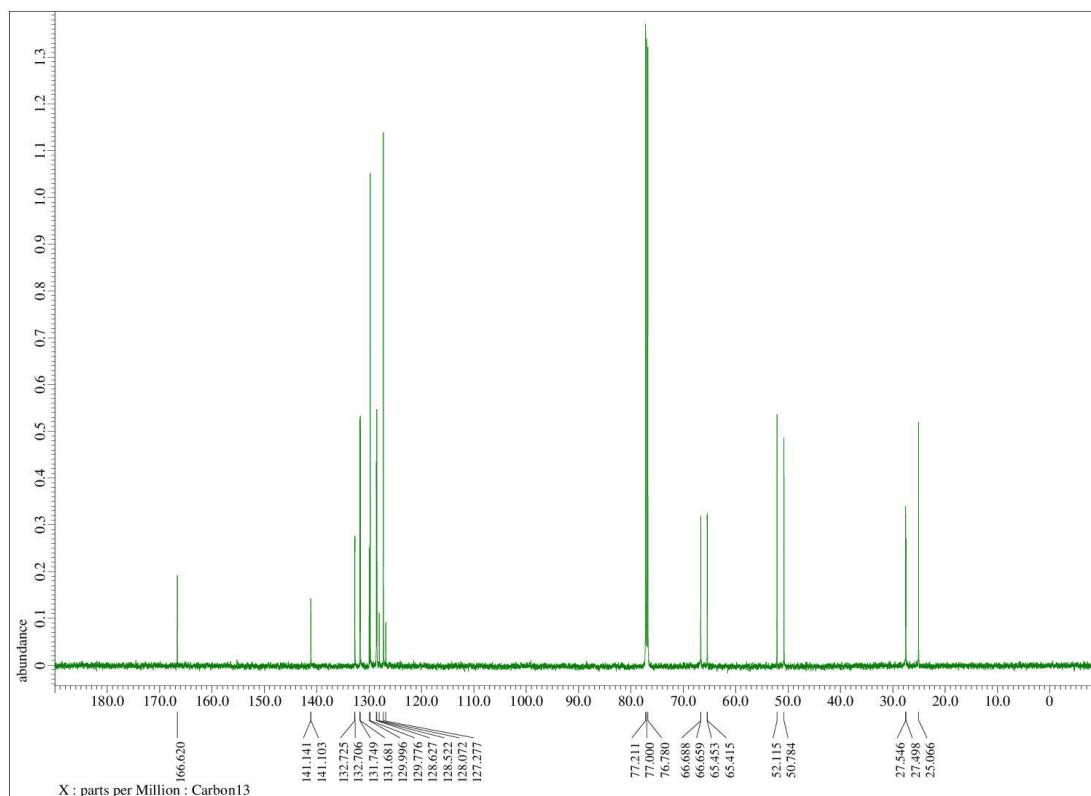
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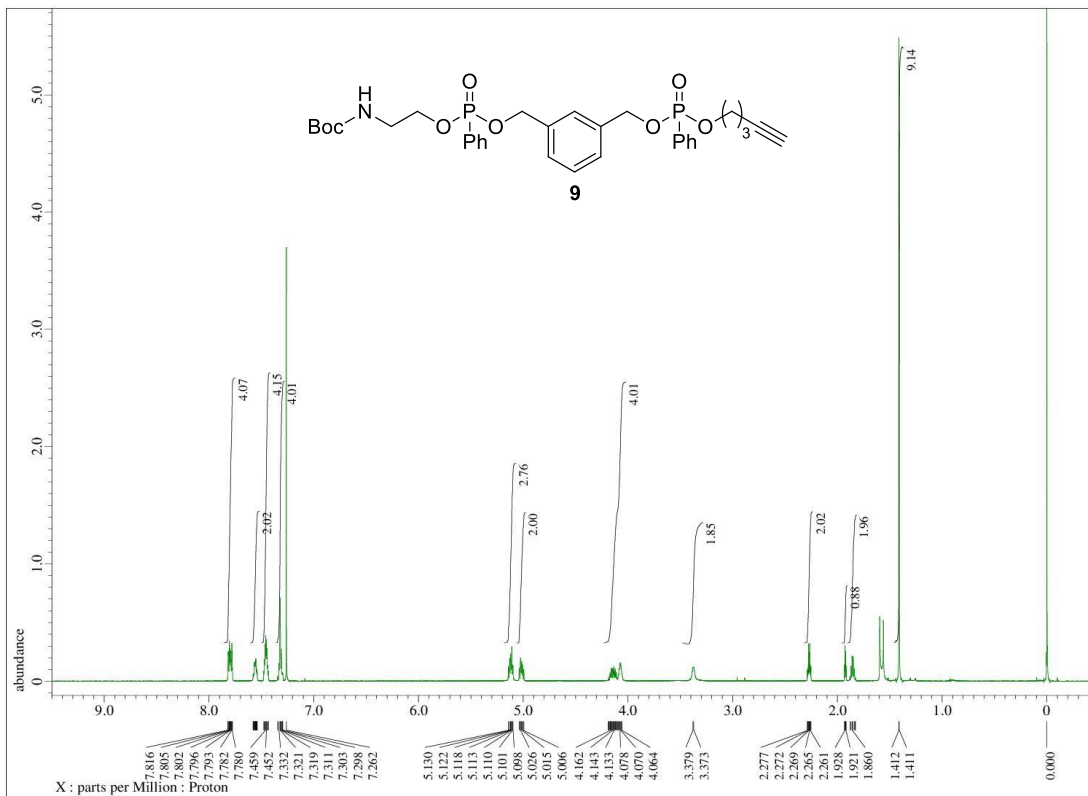
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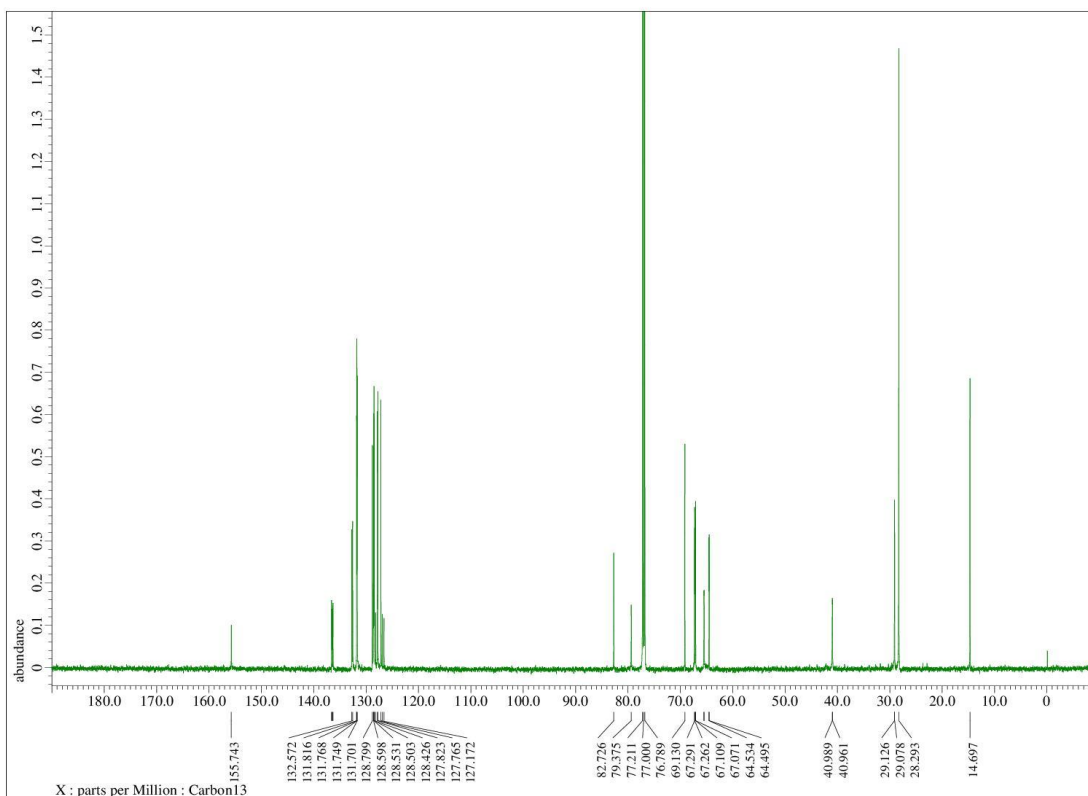
600 MHz, CDCl₃



150 MHz, CDCl₃



600 MHz, CDCl₃



150 MHz, CDCl₃