

Electronic Supplementary Information

for

Photoredox/copper-catalyzed coupling of terminal alkynes with P(O)SH compounds leading to alkynyl phosphorothioates

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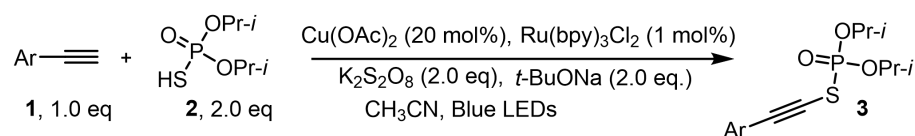
General information	ESI-2
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¹ H, ¹³ C, ³¹ P and ¹⁹ F NMR spectra for all compounds	ESI-16-91

General Information:

^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Av600 spectrometer using tetramethylsilane (TMS) in CDCl_3 as the internal standard for ^1H , and ^{13}C NMR (^1H NMR: TMS at 0.00 ppm, CHCl_3 at 7.26 ppm; ^{13}C NMR: CDCl_3 at 77.16 ppm) and 85% H_3PO_4 as external standard for ^{31}P NMR. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. The products were purified by Column chromatography on silica gel 300 – 400 mesh. All products were firstly examined by Bruker AmaZon SL ESI-IT-MS (Bruker Daltonics Inc., Germany) in positive ion mode, then further characterized by HRMS (ESI-qTOF MS, Bruker micrOTOF-Q II) in positive ion mode too.

1. Synthesis of substrates.

Experimental procedure for synthesis of *O,O*-diisopropyl *S*-(phenylethynyl) phosphorothioate



To an oven-dried vial were added $\text{Ru(bpy)}_3\text{Cl}_2$ (1 mol%), Cu(OAc)_2 (3.9 mg, 0.02 mmol, 0.2 equiv), $\text{K}_2\text{S}_2\text{O}_8$ (54mg, 0.2 mmol 2.0 equiv) and $t\text{-BuONa}$ (19.2mg, 0.2 mmol, 0.2equiv). Freshly distilled CH_3CN (2.0 mL), **1** (10.2 mg, 0.1 mmol, 1.0 equiv) and **2** (39.6 mg, 0.2 mmol, 2.0 equiv) were sequentially added to the system at room temperature. The resulting mixture was irradiated with 30 W blue LEDs strip for 24 h. After the removal of solvents under reduced pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether [1:3 (v/v)] as the eluent to give the pure product *O,O*-diisopropyl *S*-(phenylethynyl) phosphorothioate (**3**) (20.9 mg, 70%).

EPR experiments

(T=300 K)

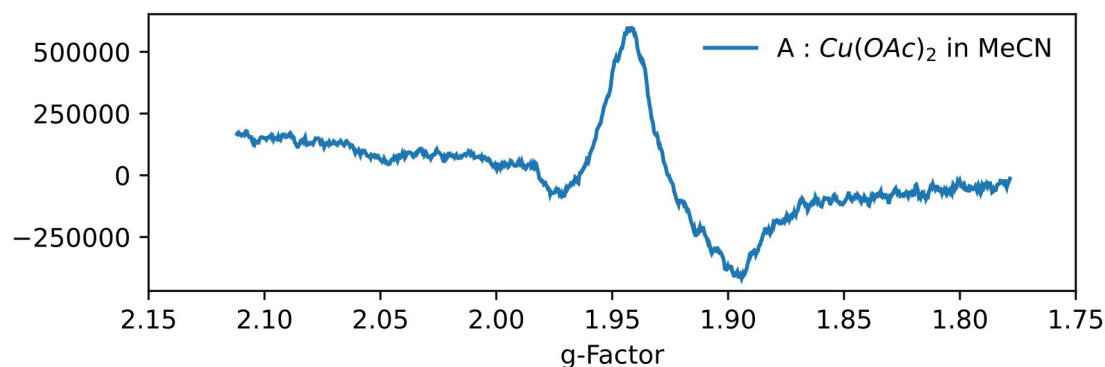


Fig 1 A: Cu(OAc)_2 (20 mol%) in MeCN (2 mL) ($g=1.926$)

(T=300 K)

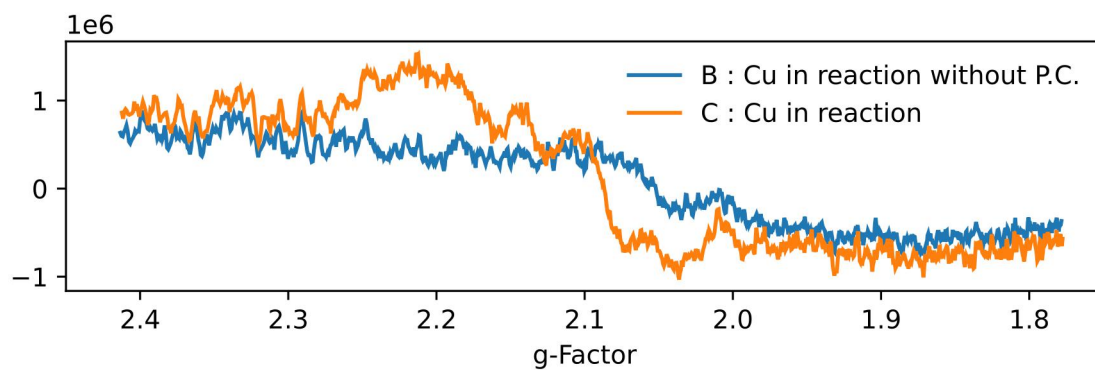
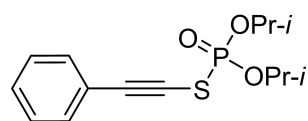


Fig 2 B: **1** (0.1 mmol), **2** (0.2 mmol), Cu(OAc)₂ (20 mol%), K₂S₂O₈ (0.2 mmol) and *t*-BuONa (0.2 mmol) in MeCN (2 mL) at room temperature for 16 h. C: **1** (0.1 mmol), **2** (0.2 mmol), Ru(bpy)₃Cl₂ (1 mol%), Cu(OAc)₂ (20 mol%), K₂S₂O₈ (0.2 mmol) and *t*-BuONa (0.2 mmol) in MeCN (2 mL) at room temperature under irradiation by blue LEDs (30 W) for 16 h ($g = 2.087$).

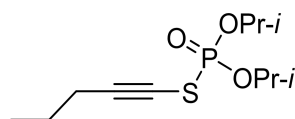
Spectral data

O,O-diisopropyl *S*-(phenylethynyl) phosphorothioate (3)



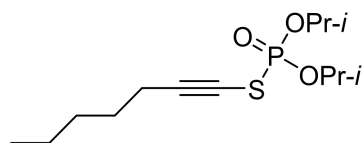
Yield: 20.9 mg, 70%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.42-7.41 (m, 2H), 7.35-7.29 (m, 3H), 4.97-4.91 (m, 2H), 1.45 (t, $J = 5.64$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 131.9 (d, $J = 3.1$ Hz), 128.9 (s), 128.5 (s), 122.7 (d, $J = 4.0$ Hz), 92.2 (d, $J = 8.7$ Hz), 74.7 (d, $J = 6.2$ Hz), 70.6 (d, $J = 11.8$ Hz), 24.0 (d, $J = 4.2$ Hz), 23.7 (d, $J = 6.3$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.4 (s). HRMS calcd for $\text{C}_{14}\text{H}_{19}\text{NaO}_3\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 321.0685; found, 321.0681.

O,O-diisopropyl *S*-(pent-1-yn-1-yl) phosphorothioate (4)



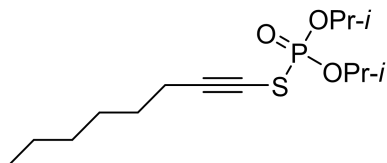
Yield: 15.8 mg, 60%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 4.90-4.84 (m, 2H), 2.27-2.24 (m, 2H), 1.55-1.52 (m, 2H), 1.41 (dd, $J_1 = 2.16$ Hz, $J_2 = 6.18$ Hz, 12H), 0.98 (t, $J = 7.38$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 94.0 (d, $J = 8.7$ Hz), 74.3 (d, $J = 5.8$ Hz), 59.6 (d, $J = 11.3$ Hz), 24.0 (d, $J = 4.3$ Hz), 23.6 (d, $J = 5.7$ Hz), 22.04 (s), 22.01 (d, $J = 2.4$ Hz), 13.6 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 17.2 (s). HRMS calcd for $\text{C}_{11}\text{H}_{22}\text{O}_3\text{PS}^+$ $[\text{M}+\text{H}]^+$, 265.1022; found, 265.1028.

S-(hept-1-yn-1-yl) *O,O*-diisopropyl phosphorothioate (5)



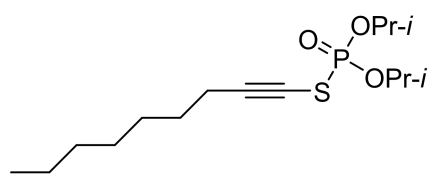
Yield: 18.7 mg, 64%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 4.88-4.85 (m, 2H), 2.29-2.25 (m, 2H), 1.52-1.48 (m, 2H), 1.41 (dd, $J_1 = 2.13$ Hz, $J_2 = 6.15$ Hz, 12H), 1.39-1.33 (m, 2H), 1.32-1.28 (m, 2H), 0.89 (t, $J = 7.17$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 94.2 (d, $J = 8.7$ Hz), 74.3 (d, $J = 6.1$ Hz), 59.4 (d, $J = 11.5$ Hz), 31.1 (s), 28.2 (d, $J = 2.1$ Hz), 24.0 (d, $J = 4.3$ Hz), 23.6 (d, $J = 6.3$ Hz), 22.3 (s), 20.0 (d, $J = 3.1$ Hz), 14.1 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 17.2 (s). HRMS calcd for $\text{C}_{13}\text{H}_{26}\text{O}_3\text{PS}^+$ $[\text{M}+\text{H}]^+$, 293.1335; found, 293.1333.

O,O-diisopropyl *S*-(oct-1-yn-1-yl) phosphorothioate (6)



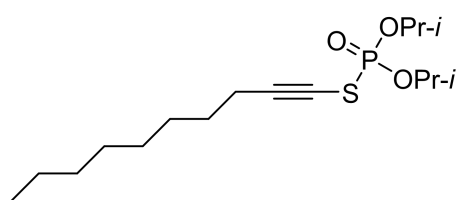
Yield: 19.6 mg, 64%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 4.88-4.84 (m, 2H), 2.28-2.25 (m, 2H), 1.50-1.47 (m, 2H), 1.41 (dd, $J_1 = 2.37$ Hz, $J_2 = 6.21$ Hz, 12H), 1.39-1.34 (m, 2H), 1.31-1.23 (m, 4H), 0.88 (t, $J = 7.08$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 94.2 (d, $J = 8.0$ Hz), 74.2 (d, $J = 5.9$ Hz), 59.4 (d, $J = 11.3$ Hz), 31.4 (s), 28.6 (s), 28.5 (d, $J = 2.3$ Hz), 24.0 (d, $J = 3.6$ Hz), 23.6 (d, $J = 5.8$ Hz), 22.7 (s), 20.1 (d, $J = 2.4$ Hz), 14.2 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 17.2 (s). HRMS calcd for $\text{C}_{14}\text{H}_{27}\text{NaO}_3\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 329.1311; found, 329.1304.

***O,O*-diisopropyl *S*-(non-1-yn-1-yl) phosphorothioate (7)**



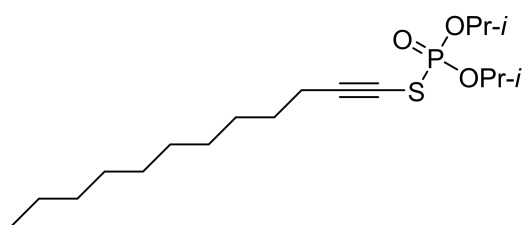
Yield: 18.9 mg, 59%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 4.89-4.84 (m, 2H), 2.28-2.25 (m, 2H), 1.51-1.47 (m, 2H), 1.41 (dd, $J_1 = 2.59$ Hz, $J_2 = 6.18$ Hz, 12H), 1.37-1.34 (m, 2H), 1.30-1.24 (m, 6H), 0.87 (t, $J = 6.99$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 94.2 (d, $J = 8.0$ Hz), 74.2 (d, $J = 6.2$ Hz), 59.4 (d, $J = 11.3$ Hz), 31.8 (s), 28.9 (s), 28.8 (s), 28.5 (d, $J = 2.5$ Hz), 24.0 (d, $J = 4.3$ Hz), 23.6 (d, $J = 5.9$ Hz), 22.7 (s), 20.1 (d, $J = 3.0$ Hz), 14.2 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 17.2 (s). HRMS calcd for $\text{C}_{15}\text{H}_{29}\text{NaO}_3\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 343.1467; found, 343.1459.

***S*-(dec-1-yn-1-yl) *O,O*-diisopropyl phosphorothioate (8)**



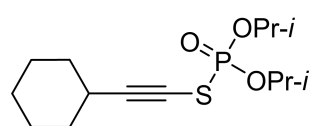
Yield: 21.1 mg, 63%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 4.88-4.83 (m, 2H), 2.27-2.24 (m, 2H), 1.51-1.46 (m, 2H), 1.40 (dd, $J_1 = 2.40$ Hz, $J_2 = 6.18$ Hz, 12H), 1.38-1.33 (m, 2H), 1.30-1.25 (m, 8H), 0.86 (t, $J = 6.99$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 94.1 (d, $J = 8.0$ Hz), 74.2 (d, $J = 6.1$ Hz), 59.4 (d, $J = 11.5$ Hz), 31.9 (s), 29.3 (s), 29.2 (s), 28.9 (s), 28.5 (d, $J = 2.0$ Hz), 24.0 (d, $J = 4.2$ Hz), 23.6 (d, $J = 6.2$ Hz), 22.7 (s), 20.0 (d, $J = 3.1$ Hz), 14.2 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 17.0 (s). HRMS calcd for $\text{C}_{16}\text{H}_{32}\text{O}_3\text{PS}^+$ $[\text{M}+\text{H}]^+$, 335.1804; found, 335.1809.

***S*-(dodec-1-yn-1-yl) *O,O*-diisopropyl phosphorothioate (9)**



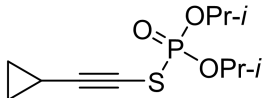
Yield: 24.2 mg, 67%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 4.89-4.83 (m, 2H), 2.28-2.24 (m, 2H), 1.50-1.46 (m, 2H), 1.41 (dd, $J_1 = 2.58$ Hz, $J_2 = 6.18$ Hz, 12H), 1.38-1.33 (m, 2H), 1.30-1.25 (m, 12H), 0.87 (t, $J = 7.05$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 94.2 (d, $J = 8.2$ Hz), 74.2 (d, $J = 5.6$ Hz), 59.4 (d, $J = 11.8$ Hz), 32.0 (s), 29.7 (s), 29.6 (s), 29.4 (s), 29.2 (s), 28.9 (s), 28.5 (d, $J = 2.0$ Hz), 24.0 (d, $J = 3.8$ Hz), 23.6 (d, $J = 6.2$ Hz), 22.8 (s), 20.0 (d, $J = 3.1$ Hz), 14.2 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 17.2 (s). HRMS calcd for $\text{C}_{18}\text{H}_{35}\text{O}_3\text{PS}^+$ $[\text{M}+\text{H}]^+$, 363.2117; found, 363.2114.

***S*-(cyclohexylethynyl) *O,O*-diisopropyl phosphorothioate (10)**

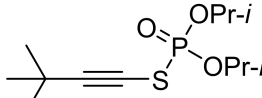


Yield: 19.5 mg, 64%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 4.90-4.84 (m, 2H), 2.48-2.45 (m, 1H), 1.77-1.75 (m, 2H), 1.71-1.66 (m, 2H), 1.52-1.46 (m, 1H), 1.42 (d, $J = 6.18$ Hz, 12H), 1.39-1.34 (m, 1H), 1.33-1.28 (m, 4H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 97.8 (d, $J = 8.3$ Hz), 74.2 (d, $J = 5.8$ Hz), 59.6 (d, $J = 11.8$ Hz), 32.4 (s), 30.3 (s), 25.9 (s), 24.8 (s), 24.0 (d, $J = 4.0$ Hz), 23.7 (d, $J = 5.7$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 17.1 (s). HRMS calcd for $\text{C}_{14}\text{H}_{25}\text{NaO}_3\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 327.1154; found, 327.1153.

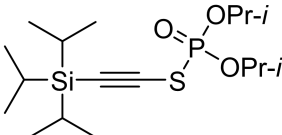
***S*-(cyclopropylethynyl) *O,O*-diisopropyl phosphorothioate (11)**

 Yield: 15.7 mg, 60%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 4.89-4.82 (m, 2H), 1.42 (dd, *J*₁ = 4.80 Hz, *J*₂ = 5.88 Hz, 12H), 1.33-1.29 (m, 1H), 0.81-0.78 (m, 2H), 0.72-0.69 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 97.5 (d, *J* = 8.5 Hz), 74.3 (d, *J* = 6.0 Hz), 55.0 (d, *J* = 11.6 Hz), 24.0 (d, *J* = 4.1 Hz), 23.6 (d, *J* = 5.8 Hz), 8.7 (d, *J* = 2.9 Hz), 0.8 (d, *J* = 3.3 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 17.3 (s). HRMS calcd for C₁₁H₁₉NaO₃PS⁺ [M+Na]⁺, 285.0685; found, 285.0683.

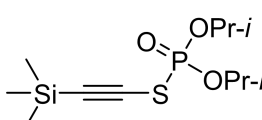
***S*-(3,3-dimethylbut-1-yn-1-yl) *O,O*-diisopropyl phosphorothioate (12)**

 Yield: 21.1 mg, 76%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 4.88-4.82 (m, 2H), 1.40 (d, *J* = 6.24 Hz, 12H), 1.20 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 101.5 (d, *J* = 8.5 Hz), 74.1 (d, *J* = 5.7 Hz), 58.6 (d, *J* = 11.4 Hz), 30.6 (d, *J* = 2.1 Hz), 28.8 (d, *J* = 2.2 Hz), 23.9 (d, *J* = 4.1 Hz), 23.6 (d, *J* = 5.8 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 16.8 (s). HRMS calcd for C₁₂H₂₄O₃PS⁺ [M+H]⁺, 279.1178; found, 279.1171.

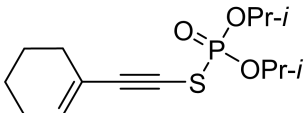
***O,O*-diisopropyl *S*-((triisopropylsilyl)ethynyl) phosphorothioate (13)**

 Yield: 27.6 mg, 73%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 4.92-4.87 (m, 2H), 1.44 (dd, *J*₁ = 3.42 Hz, *J*₂ = 6.18 Hz, 12H), 1.08-1.06 (m, 21H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 97.4 (d, *J* = 7.5 Hz), 86.0 (d, *J* = 11.1 Hz), 74.4 (d, *J* = 6.0 Hz), 24.0 (d, *J* = 4.3 Hz), 23.6 (d, *J* = 5.7 Hz), 18.7 (s), 11.5 (s). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.9 (s). HRMS calcd for C₁₇H₃₆O₃PSSi⁺ [M+H]⁺, 379.1887; found, 379.1881.

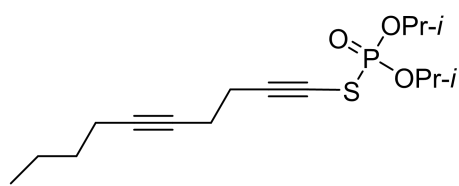
***O,O*-diisopropyl *S*-((trimethylsilyl)ethynyl) phosphorothioate (14)**

 Yield: 21.8 mg, 74%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 4.91-4.85 (m, 2H), 1.42 (dd, *J*₁ = 5.94 Hz, *J*₂ = 12.1 Hz, 12H), 0.16 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 100.6 (d, *J* = 7.3 Hz), 85.0 (d, *J* = 11.1 Hz), 74.7 (d, *J* = 6.0 Hz), 23.9 (d, *J* = 4.1 Hz), 23.6 (d, *J* = 6.4 Hz), 0.27 (s). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.1 (s). HRMS calcd for C₁₁H₂₄O₃PSSi⁺ [M+H]⁺, 295.0948; found, 295.0943.

***S*-(cyclohex-1-en-1-ylethynyl) *O,O*-diisopropyl phosphorothioate (15)**

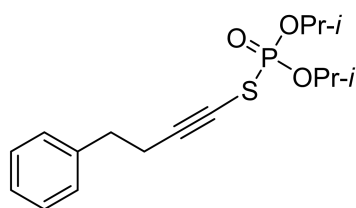
 Yield: 21.8 mg, 72%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 6.14-6.12 (m, 1H), 4.91-4.85 (m, 2H), 2.69-2.08 (m, 4H), 1.62-1.55 (m, 4H), 1.42 (d, *J* = 5.94 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 137.0 (d, *J* = 4.3 Hz), 120.6 (d, *J* = 4.3 Hz), 94.2 (d, *J* = 8.7 Hz), 74.5 (d, *J* = 6.2 Hz), 66.9 (d, *J* = 12.1 Hz), 28.9 (s), 25.8 (s), 24.0 (d, *J* = 4.1 Hz), 23.6 (d, *J* = 6.3 Hz), 22.3 (s), 21.5 (s). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.9 (s). HRMS calcd for C₁₄H₂₃NaO₃PS⁺ [M+Na]⁺, 325.0998; found, 325.0995.

***S*-(deca-1,5-diyn-1-yl) *O,O*-diisopropyl phosphorothioate (16)**



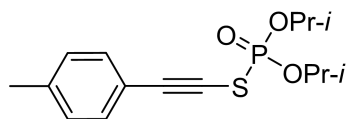
Yield: 20.1 mg, 61%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 4.89-4.85 (m, 2H), 2.48-2.45 (m, 2H), 2.37-2.34 (m, 2H), 2.15-2.12 (m, 2H), 1.46-1.37 (m, 3H), 0.90 (t, $J = 7.26$ Hz, 16H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 92.3 (d, $J = 8.6$ Hz), 81.7 (s), 77.9 (s), 74.3 (d, $J = 5.7$ Hz), 60.8 (d, $J = 11.9$ Hz), 31.0 (s), 23.8 (d, $J = 3.7$ Hz), 23.5 (d, $J = 5.6$ Hz), 21.9 (s), 20.7 (d, $J = 3.0$ Hz), 18.8 (d, $J = 2.3$ Hz), 18.4 (s), 13.6 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 17.0 (s). HRMS calcd for $\text{C}_{16}\text{H}_{27}\text{NaO}_3\text{PS}^+ [\text{M}+\text{Na}]^+$, 353.1311; found, 353.1317

***O,O*-diisopropyl *S*-(4-phenylbut-1-yn-1-yl) phosphorothioate (17)**



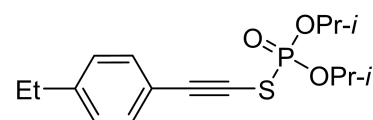
Yield: 18.6 mg, 57%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.28 (t, $J = 7.44$ Hz, 2H), 7.19 (t, $J = 7.94$ Hz, 3H), 4.85-4.76 (m, 2H), 2.81 (t, $J = 7.50$ Hz, 2H), 2.59-2.55 (m, 2H), 1.36 (d, $J = 6.81$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 140.2 (s), 128.5 (s), 128.4 (s), 126.7 (s), 93.1 (d, $J = 8.1$ Hz), 74.3 (d, $J = 5.6$ Hz), 60.5 (d, $J = 11.3$ Hz), 34.8 (d, $J = 2.1$ Hz), 23.9 (d, $J = 4.1$ Hz), 23.5 (d, $J = 5.5$ Hz), 22.1 (d, $J = 3.1$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 16.9 (s). HRMS calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{PS}^+ [\text{M}+\text{H}]^+$, 327.1178; found, 327.1171.

***O,O*-diisopropyl *S*-(*p*-tolylethynyl) phosphorothioate (18)**



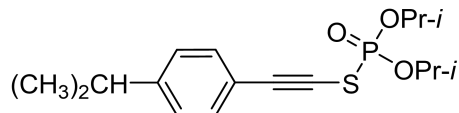
Yield: 22.1 mg, 71%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.30 (d, $J = 8.03$ Hz, 2H), 7.10 (d, $J = 7.92$ Hz, 2H), 4.94-4.91 (m, 2H), 2.34 (s, 3H), 1.44 (t, $J = 5.44$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 139.2 (s), 131.9 (d, $J = 2.5$ Hz), 129.2 (s), 119.6 (d, $J = 4.1$ Hz), 92.3 (d, $J = 8.7$ Hz), 74.6 (d, $J = 5.8$ Hz), 69.5 (d, $J = 11.7$ Hz), 24.0 (d, $J = 4.1$ Hz), 23.6 (d, $J = 5.8$ Hz), 21.6 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.5 (s). HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{NaO}_3\text{PS}^+ [\text{M}+\text{Na}]^+$, 335.0841; found, 335.0848.

***S*-((4-ethylphenyl)ethynyl) *O,O*-diisopropyl phosphorothioate (19)**



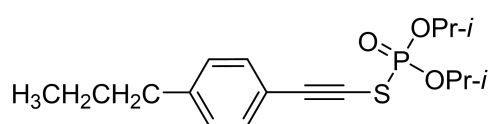
Yield: 23.8 mg, 73%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.33 (d, $J = 7.98$ Hz, 2H), 7.14 (d, $J = 8.06$ Hz, 2H), 4.96-4.90 (m, 2H), 2.66-2.62 (m, 2H), 1.44 (t, $J = 5.61$ Hz, 12H), 1.22 (t, $J = 7.56$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 145.5 (s), 132.0 (d, $J = 2.9$ Hz), 128.1 (s), 119.9 (d, $J = 4.0$ Hz), 94.4 (d, $J = 8.8$ Hz), 74.7 (d, $J = 6.1$ Hz), 69.5 (d, $J = 12.0$ Hz), 29.0 (s), 24.0 (d, $J = 3.6$ Hz), 23.7 (d, $J = 5.7$ Hz), 15.4 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.5 (s). HRMS calcd for $\text{C}_{16}\text{H}_{23}\text{NaO}_3\text{PS}^+ [\text{M}+\text{Na}]^+$, 349.0998; found, 349.0993.

***O,O*-diisopropyl *S*-((4-isopropylphenyl)ethynyl) phosphorothioate (20)**



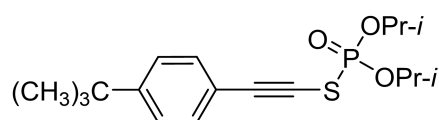
Yield: 25.5 mg, 75%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.34 (d, $J = 8.04$ Hz, 2H), 7.16 (d, $J = 8.10$ Hz, 2H), 4.95-4.91 (m, 2H), 2.91-2.87 (m, 1H), 1.45 (t, $J = 5.70$ Hz, 12H), 1.23 (d, $J = 6.96$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 150.1 (s), 132.0 (d, $J = 2.6$ Hz), 126.7 (s), 120.0 (d, $J = 3.8$ Hz), 92.4 (d, $J = 8.4$ Hz), 74.6 (d, $J = 6.3$ Hz), 69.5 (d, $J = 12.0$ Hz), 34.2 (s), 24.0 (d, $J = 3.8$ Hz), 23.8 (s), 23.7 (d, $J = 5.9$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.5 (s). HRMS calcd for $\text{C}_{17}\text{H}_{25}\text{O}_3\text{PS}^+ [\text{M}+\text{H}]^+$, 341.1335; found, 341.1333.

***O,O*-diisopropyl *S*-((4-propylphenyl)ethynyl) phosphorothioate (21)**



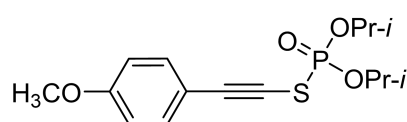
Yield: 23.5 mg, 69%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.33 (d, *J* = 8.03 Hz, 2H), 7.11 (d, *J* = 8.11 Hz, 2H), 4.95-4.91 (m, 2H), 2.57 (t, *J* = 7.56 Hz, 2H), 1.64-1.60 (m, 2H), 1.44 (t, *J* = 5.90 Hz, 12H), 0.92 (t, *J* = 7.35, 3H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 144.0 (s), 131.9 (d, *J* = 3.0 Hz), 128.7 (s), 119.9 (d, *J* = 3.7 Hz), 92.4 (d, *J* = 8.6 Hz), 74.7 (d, *J* = 6.1 Hz), 69.6 (d, *J* = 12.0 Hz), 30.1 (s), 24.4 (s), 24.0 (d, *J* = 3.7 Hz), 23.7 (d, *J* = 5.9 Hz), 13.9 (s). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.5 (s). HRMS calcd for C₁₇H₂₅NaO₃PS⁺ [M+Na]⁺, 363.1154; found, 363.1159.

***S*-((4-(tert-butyl)phenyl)ethynyl) *O,O*-diisopropyl phosphorothioate (22)**



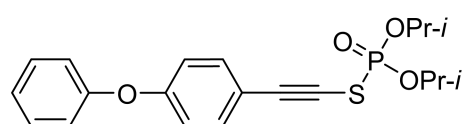
Yield: 27.2 mg, 77%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.36-7.32 (m, 4H), 4.95-4.92 (m, 2H), 1.45 (t, *J* = 5.60 Hz, 12H), 1.30 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 152.4 (s), 131.7 (d, *J* = 2.5 Hz), 125.5 (s), 119.7 (d, *J* = 4.0 Hz), 92.4 (d, *J* = 8.2 Hz), 74.7 (d, *J* = 5.9 Hz), 69.6 (d, *J* = 12.0 Hz), 35.0 (s), 31.2 (s), 24.0 (d, *J* = 3.7 Hz), 23.7 (d, *J* = 6.2 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.3 (s). HRMS calcd for C₁₈H₂₇NaO₃PS⁺ [M+Na]⁺, 377.1311; found, 377.1313.

***O,O*-diisopropyl *S*-((4-methoxyphenyl)ethynyl) phosphorothioate (23)**



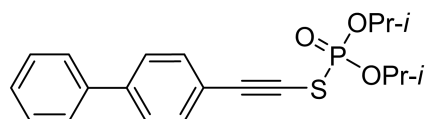
Yield: 22.9 mg, 68%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.36 (d, *J* = 8.59 Hz, 2H), 6.83 (d, *J* = 8.70 Hz, 2H), 4.94-4.91 (m, 2H), 3.81 (s, 3H), 1.44 (t, *J* = 6.15 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 160.2 (s), 133.7 (d, *J* = 2.3 Hz), 114.8 (d, *J* = 3.6 Hz), 114.2 (s), 92.2 (d, *J* = 8.2 Hz), 74.6 (d, *J* = 5.9 Hz), 68.6 (d, *J* = 11.6 Hz), 55.5 (s), 24.0 (d, *J* = 4.1 Hz), 23.7 (d, *J* = 6.2 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.7 (s). HRMS calcd for C₁₂H₂₁NaO₄PS⁺ [M+Na]⁺, 351.0790; found, 351.0785.

***O,O*-diisopropyl *S*-((4-phenoxyphenyl)ethynyl) phosphorothioate (24)**



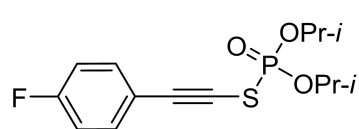
Yield: 24.2 mg, 62%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.37-7.33 (m, 4H), 7.13 (t, *J* = 7.32 Hz, 1H), 7.00 (d, *J* = 8.34 Hz, 2H), 6.89 (d, *J* = 8.64 Hz, 2H), 4.94-4.90 (m, 2H), 1.43 (t, *J* = 6.00 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 158.3 (s), 156.1 (s), 133.7 (d, *J* = 3.0 Hz), 130.0 (s), 124.2 (s), 119.7 (s), 118.2 (s), 117.0 (s), 91.8 (d, *J* = 8.3 Hz), 74.6 (d, *J* = 6.2 Hz), 69.6 (d, *J* = 12.2 Hz), 23.9 (d, *J* = 4.2 Hz), 23.6 (d, *J* = 5.8 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.5 (s). HRMS calcd for C₂₀H₂₃NaO₄PS⁺ [M+Na]⁺, 413.0947; found, 413.0955.

***S*-([1,1'-biphenyl]-4-ylethynyl) *O,O*-diisopropyl phosphorothioate (25)**

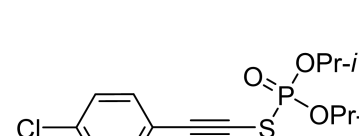


Yield: 18.7 mg, 50%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.59-7.54 (m, 4H), 7.50-7.43 (m, 4H), 7.38-7.34 (m, 1H), 5.00-4.92 (m, 2H), 1.47 (t, *J* = 5.28 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 141.7 (s), 140.2 (s), 132.3 (d, *J* = 2.3 Hz), 129.0 (s), 127.9 (s), 127.2 (s), 127.1 (s), 121.5 (d, *J* = 3.7 Hz), 92.1 (d, *J* = 8.7 Hz), 74.7 (d, *J* = 6.2 Hz), 71.2 (d, *J* = 11.6 Hz), 24.0 (d, *J* = 4.1 Hz), 23.7 (d, *J* = 6.1 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.5 (s). HRMS calcd for C₂₀H₂₃NaO₃PS⁺ [M+Na]⁺, 397.0998; found, 397.0992.

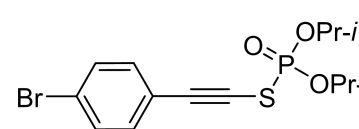
***S*-((4-fluorophenyl)ethynyl) *O,O*-diisopropyl phosphorothioate (26)**


Yield: 21.2 mg, 67%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.40-7.38 (m, 2H), 6.99 (d, *J* = 8.58 Hz, 2H), 4.94-4.89 (m, 2H), 1.43 (dd, *J*₁ = 3.87 Hz, *J*₂ = 5.85 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 162.9 (d, *J* = 250.6 Hz), 134.0 (dd, *J*₁ = 2.8 Hz, *J*₂ = 8.7 Hz), 118.8 (t, *J* = 3.7 Hz), 115.9 (d, *J* = 22.2 Hz), 91.1 (d, *J* = 8.4 Hz), 74.7 (d, *J* = 5.8 Hz), 70.4 (d, *J* = 12.1 Hz), 23.9 (d, *J* = 4.2 Hz), 23.6 (d, *J* = 5.8 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 14.7 (s). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -109.5 (s). HRMS calcd for C₁₄H₁₈FNaO₃PS⁺ [M+Na]⁺, 339.0591; found, 339.0590.

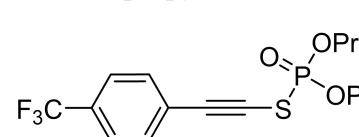
***S*-((4-chlorophenyl)ethynyl) *O,O*-diisopropyl phosphorothioate (27)**


Yield: 25.6 mg, 77%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.33 (d, *J* = 8.43 Hz, 2H), 7.28 (d, *J* = 8.60 Hz, 2H), 4.94-4.90 (m, 2H), 1.44 (t, *J* = 6.18 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 135.1 (s), 133.1 (d, *J* = 3.2 Hz), 128.9 (s), 121.2 (d, *J* = 4.1 Hz), 91.0 (d, *J* = 8.8 Hz), 74.8 (d, *J* = 6.4 Hz), 72.0 (d, *J* = 11.5 Hz), 24.0 (d, *J* = 4.3 Hz), 23.6 (d, *J* = 5.7 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.2 (s). HRMS calcd for C₁₄H₁₈ClNaO₃PS⁺ [M+Na]⁺, 355.0295; found, 355.0294.

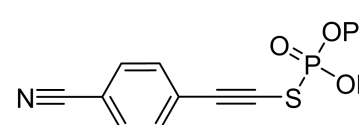
***S*-((4-bromophenyl)ethynyl) *O,O*-diisopropyl phosphorothioate (28)**


Yield: 28.2 mg, 75%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.45 (d, *J* = 8.40 Hz, 2H), 7.28 (d, *J* = 8.28 Hz, 2H), 4.95-4.91 (m, 2H), 1.45 (d, *J* = 6.24 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 133.2 (d, *J* = 2.4 Hz), 131.8 (s), 123.2 (s), 121.6 (d, *J* = 3.9 Hz), 91.1 (d, *J* = 8.4 Hz), 74.7 (d, *J* = 5.9 Hz), 72.2 (d, *J* = 11.6 Hz), 23.9 (d, *J* = 3.6 Hz), 23.6 (d, *J* = 6.0 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.0 (s). HRMS calcd for C₁₄H₁₈BrNaO₃PS⁺ [M+Na]⁺, 398.9790; found, 398.9798.

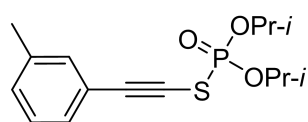
***O,O*-diisopropyl *S*-((4-(trifluoromethyl)phenyl)ethynyl) phosphorothioate (29)**


Yield: 19.4 mg, 53%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.56 (d, *J* = 8.27 Hz, 2H), 7.50 (d, *J* = 8.12 Hz, 2H), 4.96-4.90 (m, 2H), 1.45 (d, *J* = 6.18 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 131.9 (d, *J* = 3.0 Hz), 130.5 (q, *J* = 32.8 Hz), 126.5 (s), 125.5 (q, *J* = 4.0 Hz), 123.9 (q, *J* = 272.2 Hz), 90.8 (d, *J* = 8.5 Hz), 74.9 (d, *J* = 5.9 Hz), 74.2 (d, *J* = 11.9 Hz), 24.0 (d, *J* = 4.0 Hz), 23.6 (d, *J* = 6.2 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 14.3 (s). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -62.9 (s). HRMS calcd for C₁₅H₂₈F₃NaO₃PS⁺ [M+Na]⁺, 389.0559; found, 389.0553.

***S*-((4-cyanophenyl)ethynyl) *O,O*-diisopropyl phosphorothioate (30)**

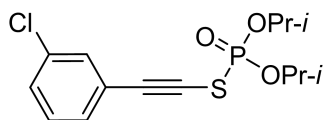

Yield: 14.9 mg, 46%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.58 (d, *J* = 8.16 Hz, 2H), 7.47 (d, *J* = 8.16 Hz, 2H), 4.94-4.88 (m, 2H), 1.43 (dd, *J*₁ = 2.25 Hz, *J*₂ = 6.09 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 132.2 (s), 132.1 (d, *J* = 3.2 Hz), 127.5 (d, *J* = 3.8 Hz), 118.4 (s), 112.0 (s), 90.5 (d, *J* = 8.1 Hz), 76.7 (d, *J* = 11.5 Hz), 75.0 (d, *J* = 6.3 Hz), 23.9 (d, *J* = 4.1 Hz), 23.6 (d, *J* = 5.9 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 14.5 (s). HRMS calcd for C₁₅H₁₈NNaO₃PS⁺ [M+Na]⁺, 346.0637; found, 346.0634.

***O,O*-diisopropyl *S*-(*m*-tolylethynyl) phosphorothioate (32)**



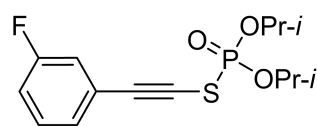
Yield: 20.6 mg, 66%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.23-7.18 (m, 3H), 7.14 (d, $J = 7.36$ Hz, 1H), 4.96-4.91 (m, 2H), 2.32 (s, 3H), 1.45 (t, $J = 5.31$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 138.2 (s), 132.4 (d, $J = 2.3$ Hz), 129.9 (s), 129.0 (d, $J = 3.1$ Hz), 128.4 (s), 122.5 (d, $J = 4.1$ Hz), 92.4 (d, $J = 8.4$ Hz), 74.7 (d, $J = 6.1$ Hz), 70.1 (d, $J = 12.0$ Hz), 24.0 (d, $J = 3.9$ Hz), 23.7 (d, $J = 5.6$ Hz), 21.3 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.5 (s). HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{NaO}_3\text{PS}^+ [\text{M}+\text{Na}]^+$, 335.0841; found, 335.0845.

***S*-(3-chlorophenyl)ethynyl *O,O*-diisopropyl phosphorothioate (33)**



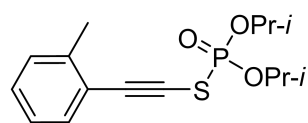
Yield: 23.6 mg, 71%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.38 (s, 1H), 7.31-7.28 (m, 2H), 7.24 (t, $J = 7.86$ Hz, 1H), 4.95-4.80 (m, 2H), 1.45 (dd, $J_1 = 0.99$ Hz, $J_2 = 6.15$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 134.4 (s), 131.6 (d, $J = 3.1$ Hz), 130.0 (d, $J = 3.1$ Hz), 129.8 (s), 129.2 (s), 124.4 (d, $J = 4.0$ Hz), 90.7 (d, $J = 8.7$ Hz), 74.8 (d, $J = 5.8$ Hz), 72.6 (d, $J = 11.9$ Hz), 24.0 (d, $J = 4.2$ Hz), 23.6 (d, $J = 5.7$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.9 (s). HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{ClNaO}_3\text{PS}^+ [\text{M}+\text{Na}]^+$, 355.0295; found, 355.0296.

***S*-(3-fluorophenyl)ethynyl *O,O*-diisopropyl phosphorothioate (34)**



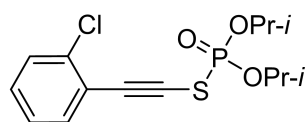
Yield: 19.0 mg, 60%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.29-7.25 (m, 1H), 7.19 (d, $J = 7.68$ Hz, 1H), 7.09 (d, $J = 9.30$ Hz, 1H), 7.05-7.02 (m, 1H), 4.95-4.91 (m, 2H), 1.45 (dd, $J_1 = 2.10$ Hz, $J_2 = 6.18$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 162.4 (d, $J = 246.9$ Hz), 130.2 (d, $J = 8.8$ Hz), 127.8 (t, $J = 2.6$ Hz), 124.5 (dd, $J_1 = 9.3$ Hz, $J_2 = 4.0$ Hz), 118.6 (dd, $J_1 = 2.8$ Hz, $J_2 = 22.7$ Hz), 116.3 (d, $J = 21.1$ Hz), 90.9 (d, $J = 8.2$ Hz), 74.8 (d, $J = 5.8$ Hz), 72.3 (d, $J = 11.9$ Hz), 24.0 (d, $J = 4.3$ Hz), 23.6 (d, $J = 5.9$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.0 (s). ^{19}F NMR (376 MHz, CDCl_3) δ (ppm) -112.6 (s). HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{FNaO}_3\text{PS}^+ [\text{M}+\text{Na}]^+$, 339.0591; found, 339.0594.

***O,O*-diisopropyl *S*-(*o*-tolylethynyl) phosphorothioate (35)**



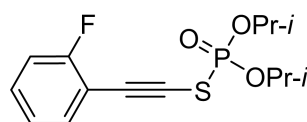
Yield: 19.0 mg, 61%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.36 (d, $J = 7.62$ Hz, 1H), 7.21 (t, $J = 7.32$ Hz, 1H), 7.17 (d, $J = 7.31$ Hz, 1H), 7.11 (d, $J = 7.44$ Hz, 1H), 4.96-4.90 (m, 2H), 2.42 (s, 3H), 1.43 (dd, $J_1 = 3.15$ Hz, $J_2 = 6.21$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 140.8 (d, $J = 2.1$ Hz), 132.1 (d, $J = 3.1$ Hz), 129.6 (s), 128.8 (s), 125.6 (s), 122.4 (d, $J = 3.5$ Hz), 91.2 (d, $J = 8.6$ Hz), 74.5 (d, $J = 5.7$ Hz), 73.9 (d, $J = 11.9$ Hz), 23.9 (d, $J = 4.2$ Hz), 23.6 (d, $J = 5.9$ Hz), 20.6 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.7 (s). HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{NaO}_3\text{PS}^+ [\text{M}+\text{Na}]^+$, 335.0841; found, 335.0838.

***S*-(2-chlorophenyl)ethynyl *O,O*-diisopropyl phosphorothioate (36)**



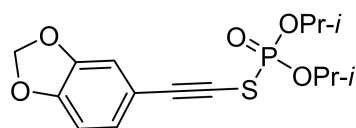
Yield: 21.6 mg, 65%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.45-7.43 (m, 1H), 7.38 (d, $J = 8.04$ Hz, 1H), 7.27-7.24 (m, 1H), 7.20 (t, $J = 7.54$ Hz, 1H), 4.98-4.93 (m, 2H), 1.45 (t, $J = 6.72$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 136.3 (d, $J = 2.9$ Hz), 133.7 (d, $J = 2.5$ Hz), 129.9 (s), 129.5 (s), 126.6 (s), 122.7 (d, $J = 4.0$ Hz), 88.9 (d, $J = 8.7$ Hz), 76.4 (d, $J = 12.0$ Hz), 74.9 (d, $J = 6.0$ Hz), 24.0 (d, $J = 4.3$ Hz), 23.7 (d, $J = 5.8$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.6 (s). HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{ClNaO}_3\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 355.0295; found, 355.0297.

***S*-(2-fluorophenyl)ethynyl *O,O*-diisopropyl phosphorothioate (37)**



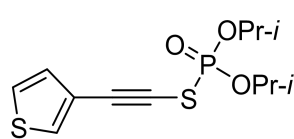
Yield: 16.8 mg, 53%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.37 (t, $J = 7.32$ Hz, 1H), 7.31-7.37 (m, 1H), 7.07-7.02 (m, 2H), 4.94-4.91 (m, 2H), 1.42 (t, $J = 6.30$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 163.3 (dd, $J_1 = 252.8$ Hz, $J_2 = 2.2$ Hz), 133.7 (d, $J = 2.6$ Hz), 130.7 (d, $J = 7.9$ Hz), 124.1 (d, $J = 3.5$ Hz), 115.7 (d, $J = 20.8$ Hz), 111.3 (dd, $J_1 = 3.7$ Hz, $J_2 = 15.6$ Hz), 85.5 (d, $J = 8.5$ Hz), 76.2 (dd, $J_1 = 11.9$ Hz, $J_2 = 3.2$ Hz), 74.9 (d, $J = 6.4$ Hz), 23.9 (d, $J = 3.7$ Hz), 23.5 (d, $J = 6.0$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.5 (s). ^{19}F NMR (376 MHz, CDCl_3) δ (ppm) -109.5 (s). HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{FNaO}_3\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 339.0591; found, 339.0585.

***S*-(benzo[d][1,3]dioxol-5-ylethynyl) *O,O*-diisopropyl phosphorothioate (38)**



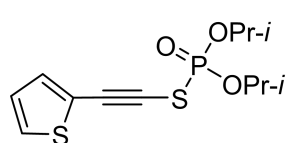
Yield: 20.9 mg, 61%. Bright yellow oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 6.94 (d, $J = 7.98$ Hz, 1H), 6.84 (s, 1H), 6.73 (d, $J = 8.04$ Hz, 1H), 5.96 (s, 2H), 4.94-4.88 (m, 2H), 1.43 (d, $J = 5.56$ Hz, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 148.6 (s), 147.5 (s), 127.1 (d, $J = 2.6$ Hz), 115.9 (d, $J = 3.7$ Hz), 111.9 (d, $J = 2.7$ Hz), 108.6 (s), 101.6 (s), 92.1 (d, $J = 8.7$ Hz), 74.6 (d, $J = 6.4$ Hz), 68.7 (d, $J = 12.0$ Hz), 23.9 (d, $J = 4.1$ Hz), 23.6 (d, $J = 5.7$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.5 (s). HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{NaO}_5\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 365.0583; found, 365.0580.

***O,O*-diisopropyl *S*-(thiophen-3-ylethynyl) phosphorothioate (39)**



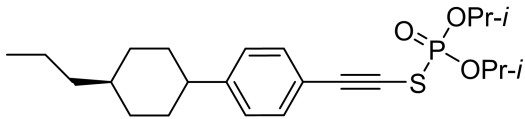
Yield: 13.4 mg, 44%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.46-7.45 (m, 1H), 7.25-7.34 (m, 1H), 7.08-7.07 (m, 1H), 4.93-4.89 (m, 2H), 1.43 (t, $J = 5.85$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 130.2 (d, $J = 3.6$ Hz), 130.0 (s), 125.6 (s), 121.7 (d, $J = 4.2$ Hz), 87.3 (d, $J = 8.7$ Hz), 74.7 (d, $J = 6.4$ Hz), 70.1 (d, $J = 11.7$ Hz), 23.9 (d, $J = 3.6$ Hz), 23.6 (d, $J = 6.3$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.4 (s). HRMS calcd for $\text{C}_{12}\text{H}_{17}\text{NaO}_3\text{PS}_2^+$ $[\text{M}+\text{Na}]^+$, 327.0249; found, 327.0246.

***O,O*-diisopropyl *S*-(thiophen-3-ylethynyl) phosphorothioate (40)**

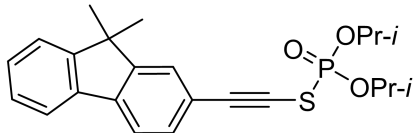


Yield: 12.5 mg, 41%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.29 (d, $J = 5.16$ Hz, 1H), 7.23 (dd, $J_1 = 1.11$ Hz, $J_2 = 2.49$ Hz, 1H), 6.97 (dd, $J_1 = 3.72$ Hz, $J_2 = 5.04$ Hz, 1H), 4.95-4.89 (m, 2H), 1.44 (t, $J = 6.24$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 133.6 (d, $J = 2.6$ Hz), 128.5 (s), 127.2 (s), 122.8 (d, $J = 4.6$ Hz), 85.4 (d, $J = 8.7$ Hz), 75.2 (d, $J = 12.1$ Hz), 74.9 (d, $J = 12.1$ Hz), 23.9 (d, $J = 3.7$ Hz), 23.7 (d, $J = 5.8$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.7 (s). HRMS calcd for $\text{C}_{12}\text{H}_{17}\text{NaO}_3\text{PS}_2^+$ $[\text{M}+\text{Na}]^+$, 327.0249; found, 327.0255.

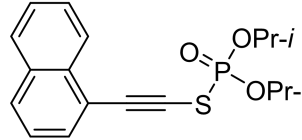
***O,O*-diisopropyl *S*-((4-(4-propylcyclohexyl)phenyl)ethynyl) phosphorothioate (42)**


Yield: 30.4 mg, 72%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.33 (d, *J* = 8.10 Hz, 2H), 7.15 (d, *J* = 8.16 Hz, 2H), 4.96-4.90 (m, 2H), 2.45 (t, *J* = 12.27 Hz, 1H), 1.86 (d, *J* = 12.24 Hz, 4H), 1.45 (t, *J* = 5.37 Hz, 12H), 1.40-1.30 (m, 5H), 1.22-1.19 (m, 2H), 1.06-1.00 (m, 2H), 0.90 (t, *J* = 7.29 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 149.2 (s), 132.0 (d, *J* = 2.3 Hz), 127.1 (s), 120.0 (d, *J* = 4.0 Hz), 92.4 (d, *J* = 8.6 Hz), 74.6 (d, *J* = 6.2 Hz), 69.5 (d, *J* = 11.9 Hz), 44.7 (s), 39.8 (s), 37.1 (s), 34.2 (s), 33.6 (s), 24.0 (d, *J* = 3.6 Hz), 23.7 (d, *J* = 6.2 Hz), 20.1 (s), 14.5 (s). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.5 (s). HRMS calcd for C₂₃H₃₅NaO₃PS⁺ [M+Na]⁺, 445.1937; found, 445.1942.

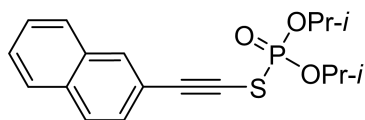
***S*-((9,9-dimethyl-9*H*-fluoren-2-yl)ethynyl) *O,O*-diisopropyl phosphorothioate (43)**

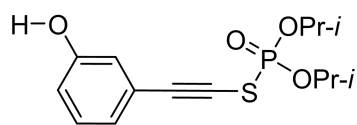

Yield: 26.9 mg, 65%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.71-7.0 (m, 1H), 7.65 (d, *J* = 7.80 Hz, 1H), 7.48 (s, 1H), 7.44-7.40 (m, 2H), 7.36-7.33 (m, 2H), 4.99-4.94 (m, 2H), 1.49-1.46 (m, 18H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 154.1 (s), 153.7 (s), 140.2 (s), 138.4 (s), 131.2 (d, *J* = 3.1 Hz), 128.0 (s), 127.3 (s), 126.3 (d, *J* = 3.0 Hz), 122.8 (s), 121.1 (d, *J* = 3.7 Hz), 120.5 (s), 120.1 (s), 93.1 (d, *J* = 8.8 Hz), 74.7 (d, *J* = 6.3 Hz), 70.3 (d, *J* = 12.1 Hz), 47.0 (s), 24.0 (d, *J* = 3.8 Hz), 23.7 (d, *J* = 5.6 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 15.6 (s). HRMS calcd for C₂₃H₂₇FN₃O₃PS⁺ [M+Na]⁺, 437.1311; found, 437.1308.

***O,O*-diisopropyl *S*-(naphthalen-1-ylethynyl) phosphorothioate (44)**


Yield: 20.9 mg, 60%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.32 (d, *J* = 8.34 Hz, 1H), 7.84 (t, *J* = 7.92 Hz, 2H), 7.65 (d, *J* = 7.08 Hz, 1H), 7.59-7.56 (m, 1H), 7.54-7.51 (m, 1H), 7.41 (dd, *J*₁ = 7.38 Hz, *J*₂ = 7.98 Hz, 1H), 5.02-4.97 (m, 2H), 1.47 (dd, *J*₁ = 2.58 Hz, *J*₂ = 6.18 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 133.6 (d, *J* = 2.0 Hz), 133.2 (s), 130.7 (d, *J* = 3.5 Hz), 129.3 (s), 128.4 (s), 127.1 (s), 126.7 (s), 126.2 (s), 125.3 (s), 120.4 (d, *J* = 4.1 Hz), 90.7 (d, *J* = 8.1 Hz), 75.3 (d, *J* = 12.0 Hz), 74.8 (d, *J* = 6.1 Hz), 24.0 (d, *J* = 4.3 Hz), 23.7 (d, *J* = 6.3 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 14.9 (s). HRMS calcd for C₁₈H₂₁NaO₃PS⁺ [M+Na]⁺, 371.0841; found, 371.0836.

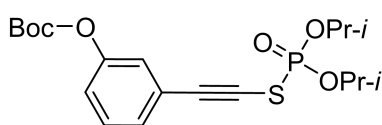
***O,O*-diisopropyl *S*-(naphthalen-2-ylethynyl) phosphorothioate (45)**


Yield: 22.6 mg, 65%. Bright yellow oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.94 (s, 1H), 7.81-7.75 (m, 3H), 7.51-7.43 (m, 3H), 5.01-4.93 (m, 2H), 1.47 (t, *J* = 6.24 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 133.0 (s), 132.9 (s), 132.0 (d, *J* = 3.3 Hz), 128.3 (d, *J* = 2.2 Hz), 128.2 (s), 127.9 (s) (two carbon), 127.1 (s), 126.8 (s), 119.9 (d, *J* = 4.0 Hz), 92.6 (d, *J* = 8.2 Hz), 74.8 (d, *J* = 6.4 Hz), 70.9 (d, *J* = 11.7 Hz), 24.0 (d, *J* = 4.1 Hz), 23.7 (d, *J* = 5.7 Hz). ³¹P NMR (242 MHz, CDCl₃) δ (ppm) 14.7 (s). HRMS calcd for C₁₈H₂₁NaO₃PS⁺ [M+Na]⁺, 371.0841; found, 371.0837.

***S*-((3-hydroxyphenyl)ethynyl) *O,O*-diisopropyl phosphorothioate (46)**

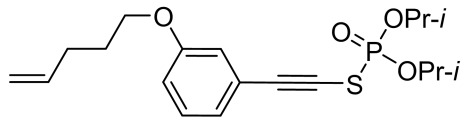
Yield: 10.7 mg, 34%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.31 (t, $J = 7.92$ Hz, 1H), 6.94 (d, $J = 7.56$ Hz, 1H), 6.89 (s, 1H), 6.83 (dd, $J_1 = 2.40$ Hz, $J_2 = 8.16$ Hz, 1H), 4.96-4.90 (m, 2H), 1.45 (dd, $J_1 = 3.87$ Hz, $J_2 = 6.15$ Hz, 12H).

^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 156.1 (s), 129.7 (s), 124.2 (d, $J = 3.0$ Hz), 123.6 (d, $J = 4.0$ Hz), 118.7 (d, $J = 3.0$ Hz), 116.7 (s), 92.4 (d, $J = 8.7$ Hz), 75.2 (d, $J = 6.1$ Hz), 69.9 (d, $J = 12.0$ Hz), 24.0 (d, $J = 4.1$ Hz), 23.7 (d, $J = 5.6$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.0 (s). HRMS calcd for $\text{C}_{14}\text{H}_{19}\text{NaO}_4\text{PS}^+ [\text{M}+\text{Na}]^+$, 337.0634; found, 337.0632.

***tert*-butyl 3-(((diisopropoxyphosphoryl)thio)ethynyl)phenyl carbonate (47)**

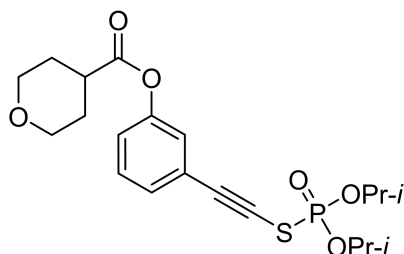
Yield: 31.9 mg, 77%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.29 (t, $J = 7.94$ Hz, 1H), 7.25 (d, $J = 7.70$ Hz, 1H), 7.20 (s, 1H), 7.14 (d, $J = 8.01$ Hz, 1H), 4.94-4.88 (m, 2H), 1.54 (s, 9H), 1.43 (dd, $J_1 = 2.03$ Hz, $J_2 = 6.16$ Hz, 12H).

^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 151.6 (s), 150.9 (s), 129.5 (s), 129.2 (d, $J = 3.0$ Hz), 124.5 (d, $J = 2.8$ Hz), 123.9 (d, $J = 3.9$ Hz), 122.2 (s), 91.1 (d, $J = 8.5$ Hz), 84.0 (s), 74.8 (d, $J = 6.1$ Hz), 71.9 (d, $J = 11.5$ Hz), 27.7 (s), 23.9 (d, $J = 4.2$ Hz), 23.6 (d, $J = 5.9$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.0 (s). HRMS calcd for $\text{C}_{19}\text{H}_{27}\text{NaO}_6\text{PS}^+ [\text{M}+\text{Na}]^+$, 437.1158; found, 437.1152.

***O,O*-diisopropyl *S*-((3-(pent-4-en-1-yloxy)phenyl)ethynyl) phosphorothioate (48)**

Yield: 28.7 mg, 75%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.20 (t, $J = 7.98$ Hz, 1H), 6.99 (d, $J = 7.52$ Hz, 1H), 6.92 (s, 1H), 6.89-6.86 (m, 1H), 5.89-5.79 (m, 1H), 5.08-4.89 (m, 4H), 3.94 (t, $J = 6.44$ Hz, 2H), 2.25-2.20 (m, 2H), 1.90-1.84 (m, 2H), 1.45 (dd, $J_1 = 2.56$ Hz, $J_2 = 6.16$ Hz, 12H).

^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 158.9 (s), 137.8 (s), 129.6 (s), 124.3 (d, $J = 2.9$ Hz), 123.6 (d, $J = 3.7$ Hz), 117.5 (d, $J = 2.9$ Hz), 115.9 (s), 115.4 (s), 92.2 (d, $J = 8.4$ Hz), 74.7 (d, $J = 6.1$ Hz), 70.4 (d, $J = 11.9$ Hz), 67.4 (s), 30.2 (s), 28.4 (s), 24.0 (d, $J = 3.9$ Hz), 23.7 (d, $J = 5.9$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.8 (s). HRMS calcd for $\text{C}_{19}\text{H}_{27}\text{NaO}_3\text{PS}^+ [\text{M}+\text{Na}]^+$, 405.1260; found, 405.1256.

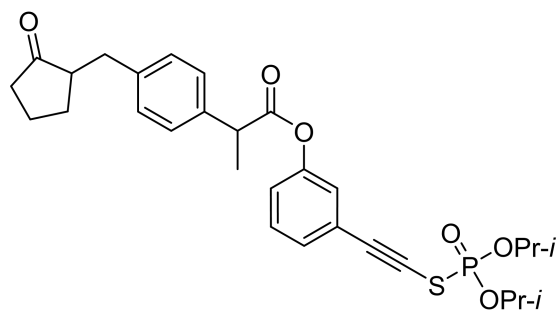
3-(((diisopropoxyphosphoryl)thio)ethynyl)phenyl (tetrahydro-2H-pyran-4-yl) carbonate (49)

Yield: 34.1 mg, 80%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.35-7.28 (m, 2H), 7.14 (s, 1H), 7.07 (d, $J = 8.04$ Hz, 1H), 4.97-4.91 (m, 2H), 4.06-4.01 (m, 2H), 3.54-3.50 (m, 2H), 2.84-2.79 (m, 1H), 2.01-1.99 (m, 2H), 1.96-1.89 (m, 2H), 1.46 (dd, $J_1 = 6.24$ Hz, $J_2 = 0.48$ Hz, 12H).

^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 172.9 (s), 150.5 (s), 129.6 (s), 129.4 (d, $J = 2.4$ Hz), 124.7 (d, $J = 3.1$ Hz), 124.0 (d, $J = 3.5$ Hz), 122.4 (s), 91.1 (d, $J = 8.7$ Hz), 74.8 (d, $J = 5.7$ Hz), 72.1 (d, $J = 11.6$ Hz), 67.1 (s), 40.3 (s), 28.6 (s), 23.9 (d, $J = 4.0$ Hz), 23.6 (d, $J = 5.7$ Hz). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 15.1 (s). HRMS calcd for $\text{C}_{20}\text{H}_{27}\text{NaO}_6\text{PS}^+ [\text{M}+\text{Na}]^+$, 449.1158; found, 449.1153.

**3-(((diisopropoxyphosphoryl)thio)ethynyl)phenyl
oxocyclopentyl)methyl)phenyl)propanoate (50)**

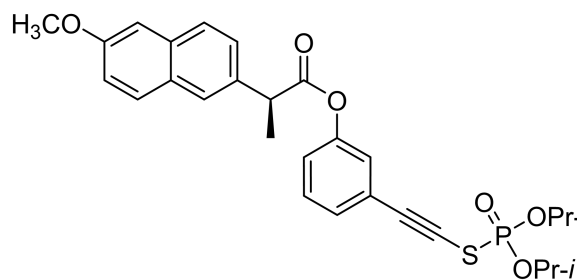
2-(4-((2-



Yield: 35.8 mg, 66%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.29-7.23 (m, 4H), 7.17 (d, $J = 8.10$ Hz, 2H), 7.04 (s, 1H), 6.99-6.97 (m, 1H), 4.98-4.88 (m, 2H), 3.92 (q, $J = 7.14$ Hz, 1H), 3.14 (dd, $J_1 = 4.14$ Hz, $J_2 = 13.98$ Hz, 1H), 2.53 (dd, $J_1 = 9.54$ Hz, $J_2 = 13.92$ Hz, 1H), 2.37-2.32 (m, 2H), 2.14-2.08 (m, 2H), 1.99-1.93 (m, 1H), 1.77-1.70 (m, 1H), 1.59 (d, $J = 7.20$ Hz, 3H), 1.57-1.52 (m, 1H), 1.49 (dd, $J_1 = 1.41$ Hz, $J_2 = 6.21$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 220.2 (s), 172.9 (s), 150.7 (s), 139.4 (s), 137.7 (s), 129.47 (s), 129.45 (s), 129.3 (d, $J = 3.0$ Hz), 127.6 (s), 124.7 (s), 123.9 (d, $J = 3.5$ Hz), 122.3 (s), 91.1 (d, $J = 8.3$ Hz), 74.8 (d, $J = 6.6$ Hz), 71.9 (d, $J = 11.1$ Hz), 51.1 (s), 45.3 (s), 38.3 (s), 35.3 (s), 29.4 (s), 23.9 (d, $J = 3.5$ Hz), 23.6 (d, $J = 5.8$ Hz), 20.6 (s), 18.6 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.8 (s). HRMS calcd for $\text{C}_{29}\text{H}_{35}\text{NaO}_6\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 565.1784; found, 565.1778.

**3-(((diisopropoxyphosphoryl)thio)ethynyl)phenyl
yl)propanoate (51)**

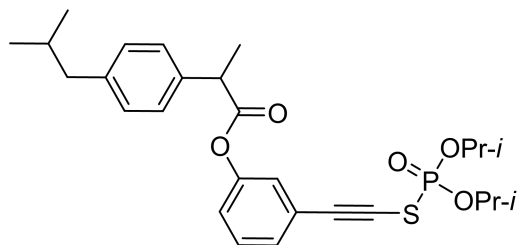
(S)-2-(6-methoxynaphthalen-2-



Yield: 36.8 mg, 70%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.76-7.24 (m, 3H), 7.48-7.47 (m, 1H), 7.26-7.22 (m, 2H), 7.17-7.14 (m, 2H), 7.02 (s, 1H), 6.98-6.96 (m, 1H), 4.94-4.87 (m, 2H), 4.08 (q, $J = 7.10$ Hz, 1H), 3.92 (s, 3H), 1.68 (d, $J = 7.14$ Hz, 3H), 1.41 (t, $J = 6.30$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 173.0

(s), 157.9 (s), 150.7 (s), 135.0 (s), 134.0 (s), 129.5 (s), 129.4 (s), 129.3 (d, $J = 2.5$ Hz), 129.1 (s), 127.6 (s), 126.3 (s), 126.1 (s), 124.7 (d, $J = 3.1$ Hz), 123.9 (d, $J = 4.0$ Hz), 122.4 (s), 119.3 (s), 105.7 (s), 91.1 (d, $J = 8.7$ Hz), 74.8 (d, $J = 6.4$ Hz), 72.0 (d, $J = 11.9$ Hz), 55.5 (s), 45.6 (s), 23.9 (d, $J = 4.2$ Hz), 23.6 (d, $J = 6.0$ Hz), 18.5 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.3 (s). HRMS calcd for $\text{C}_{28}\text{H}_{31}\text{NaO}_6\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 549.1471; found, 549.1470.

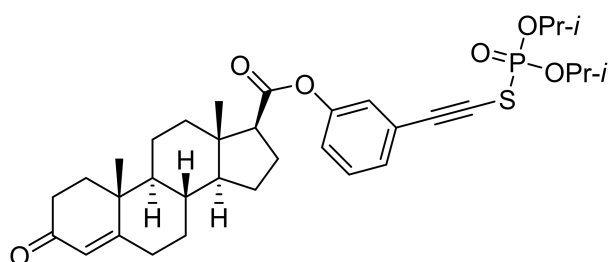
3-(((diisopropoxyphosphoryl)thio)ethynyl)phenyl 2-(4-isobutylphenyl)propanoate (52)



Yield: 34.7 mg, 69%. Bright yellow oil. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.31-7.26 (m, 4H), 7.17-7.15 (m, 2H), 7.07 (s, 1H), 7.01-6.99 (m, 1H), 4.97-4.91 (m, 2H), 3.95 (q, $J = 7.12$ Hz, 1H), 2.49 (d, $J = 7.20$ Hz, 2H), 1.91-1.87 (m, 1H), 1.62 (d, $J = 7.14$ Hz, 3H), 1.45 (dd, $J_1 = 1.92$ Hz, $J_2 = 6.18$ Hz, 12H), 0.93 (d, $J = 6.60$ Hz, 6H). ^{13}C NMR

(150 MHz, CDCl_3) δ (ppm) 173.1 (s), 150.8 (s), 141.1 (s), 137.1 (s), 129.7 (s), 129.5 (s), 129.3 (d, $J = 2.8$ Hz), 127.3 (s), 124.7 (d, $J = 3.1$ Hz), 123.9 (s), 122.4 (s), 91.2 (d, $J = 8.6$ Hz), 74.9 (d, $J = 6.3$ Hz), 71.8 (d, $J = 12.1$ Hz), 45.3 (s), 45.2 (s), 30.3 (s), 23.7 (d, $J = 3.9$ Hz), 23.6 (d, $J = 5.7$ Hz), 22.5 (s), 18.6 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.9 (s). HRMS calcd for $\text{C}_{27}\text{H}_{35}\text{NaO}_5\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 525.1835; found, 525.1838.

3-(((diisopropoxyphosphoryl)thio)ethynyl)phenyl (8S,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-17-carboxylate (53)

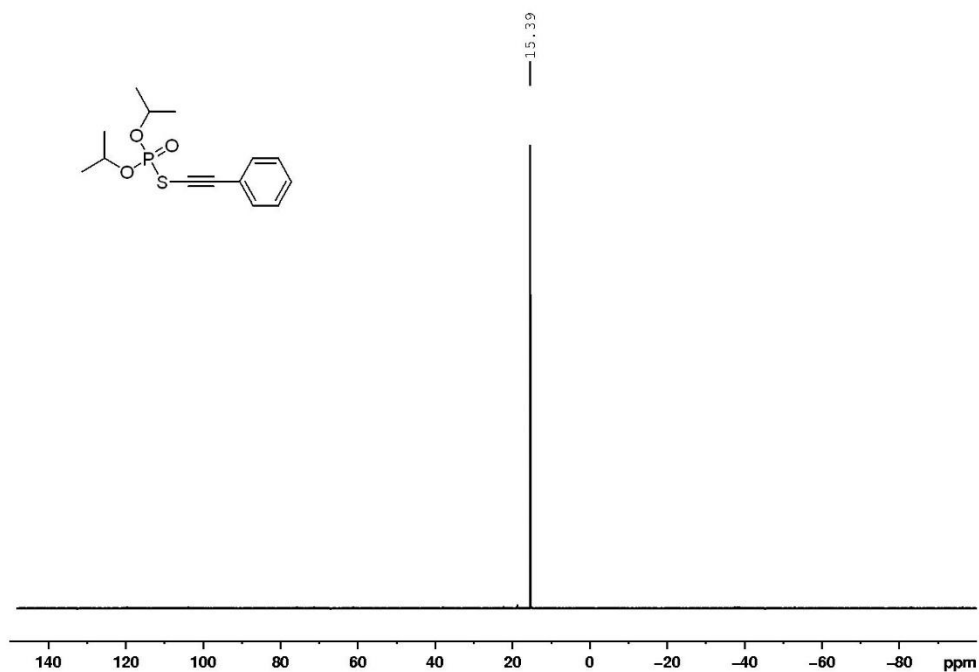


Yield: 32.5 mg, 52%. Bright yellow oil.

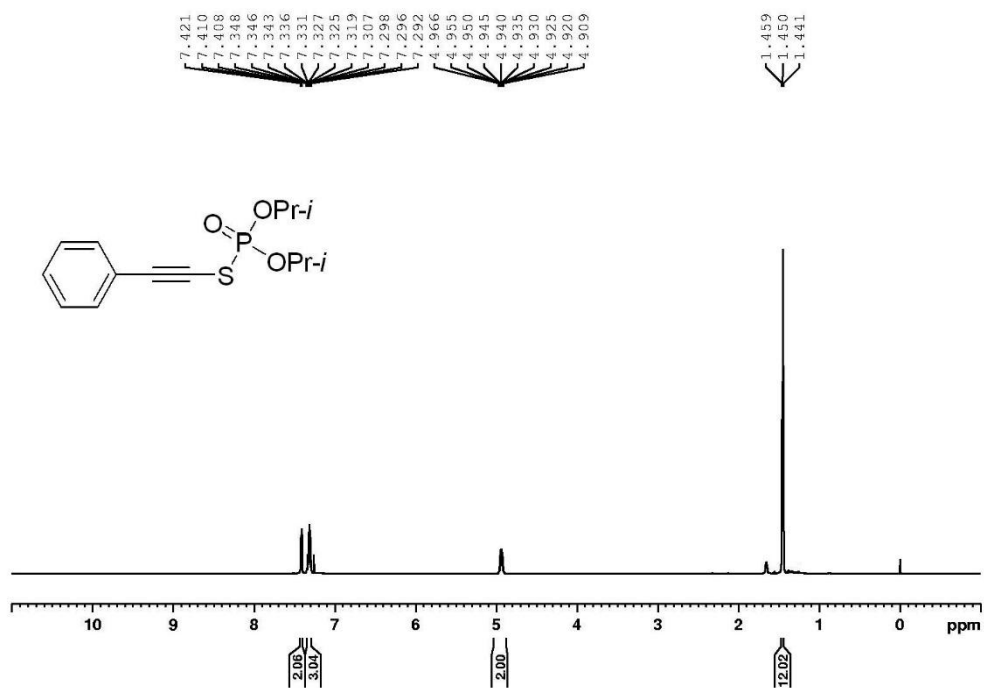
^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.32-7.27 (m, 2H), 7.11 (s, 1H), 7.06 (d, J = 8.04 Hz, 1H), 5.74 (s, 1H), 4.95-4.90 (m, 2H), 2.60 (t, J = 9.42 Hz, 1H), 2.49-2.39 (m, 2H), 2.37-2.33 (m, 1H), 2.31-2.28 (m, 1H), 2.23-2.17 (m, 2H), 2.06-2.03 (m, 1H), 1.95-1.88 (m, 2H), 1.81-1.76 (m, 1H), 1.75-1.70 (m, 2H), 1.67-1.57 (m, 2H), 1.44 (d, J = 6.18 Hz, 12H), 1.39-1.34 (m, 2H), 1.25-1.22 (m, 1H), 1.20 (s, 3H), 1.13-1.06 (m, 1H), 1.03-0.98 (m, 1H), 0.85 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 199.6 (s), 172.3 (s), 171.0 (s), 150.7 (s), 129.5 (s), 129.2 (d, J = 2.5 Hz), 124.9 (d, J = 2.7 Hz), 124.1 (s), 124.0 (d, J = 3.6 Hz), 122.6 (s), 91.2 (d, J = 8.3 Hz), 74.8 (d, J = 6.2 Hz), 71.9 (d, J = 11.5 Hz), 51.6 (s), 55.2 (s), 53.8 (s), 44.6 (s), 38.7 (s), 38.4 (s), 35.9 (s), 34.1 (s), 32.9 (s), 32.0 (s), 29.8 (s), 24.6 (s), 24.0 (d, J = 3.7 Hz), 23.74 (s), 23.70 (d, J = 5.6 Hz), 21.1 (s), 17.5 (s), 13.9 (s). ^{31}P NMR (242 MHz, CDCl_3) δ (ppm) 14.4 (s). HRMS calcd for $\text{C}_{34}\text{H}_{45}\text{NaO}_6\text{PS}^+$ $[\text{M}+\text{Na}]^+$, 635.2567; found, 635.2571.

³¹P NMR, ¹H NMR and ¹³C NMR Spectra for All Compounds

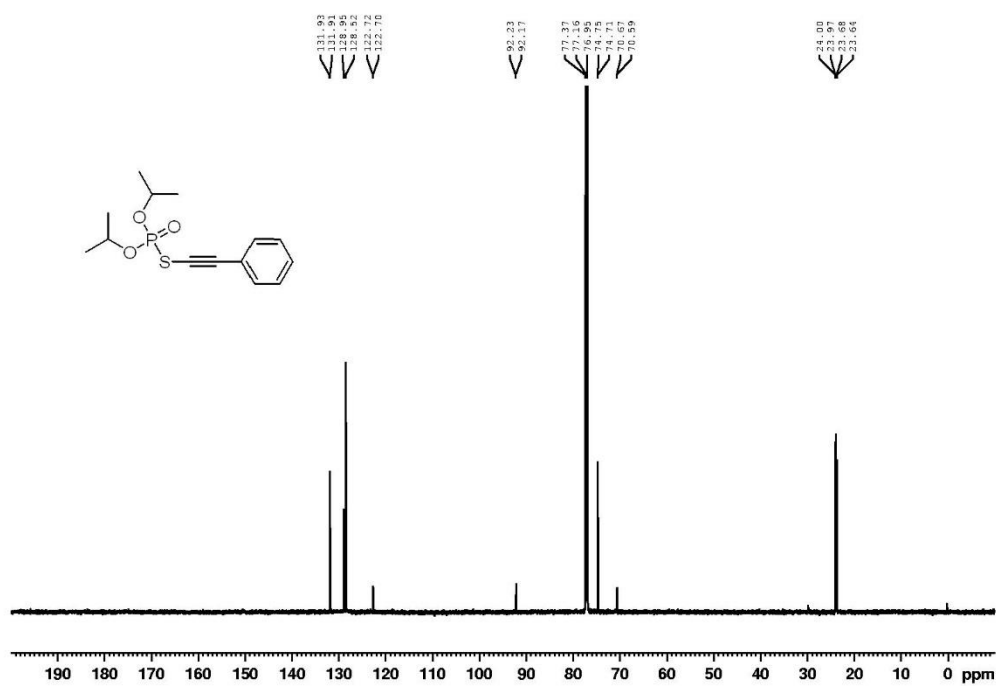
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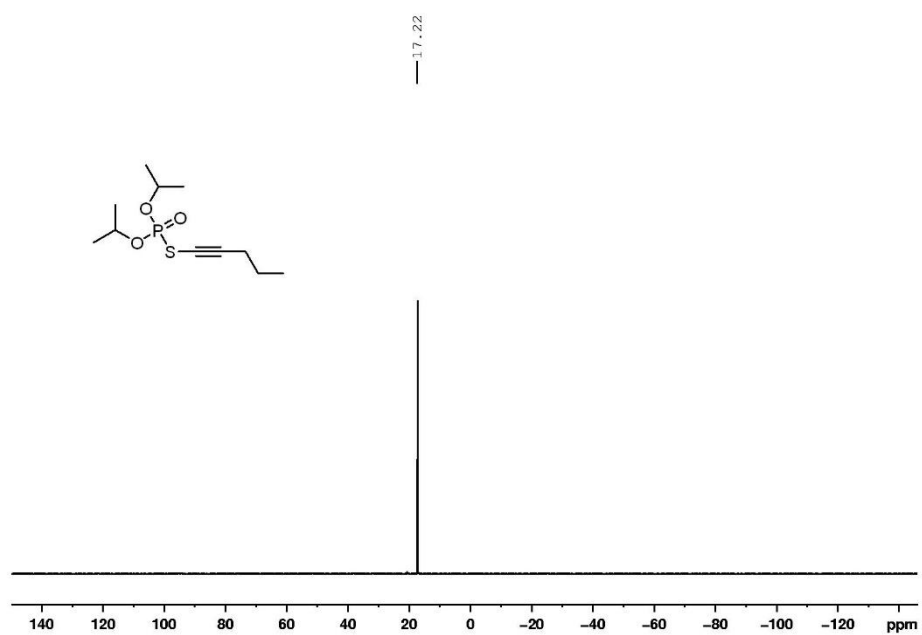
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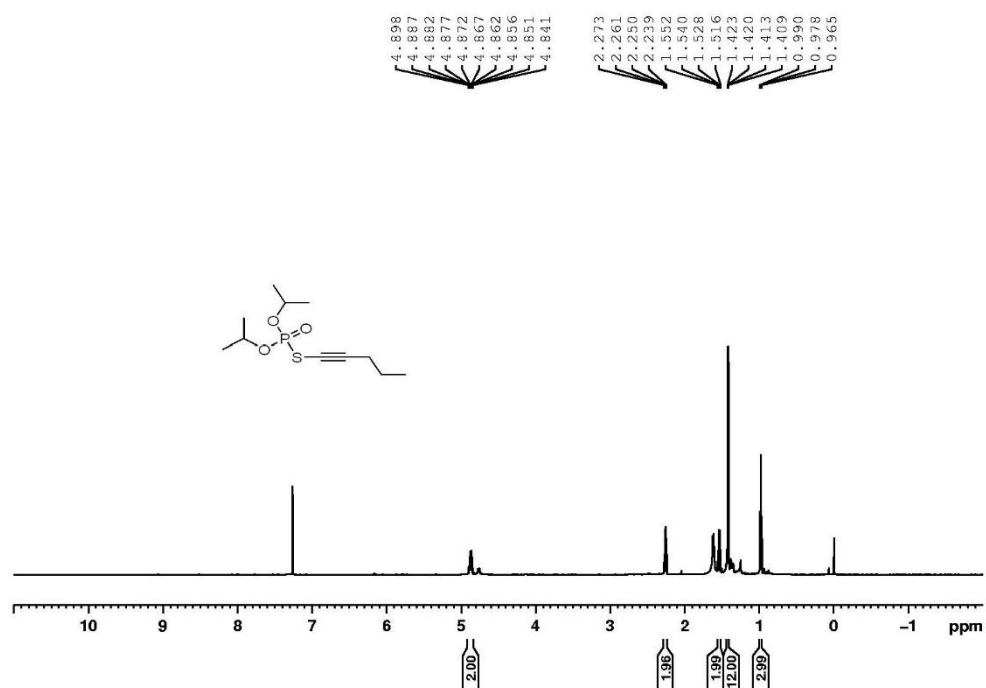
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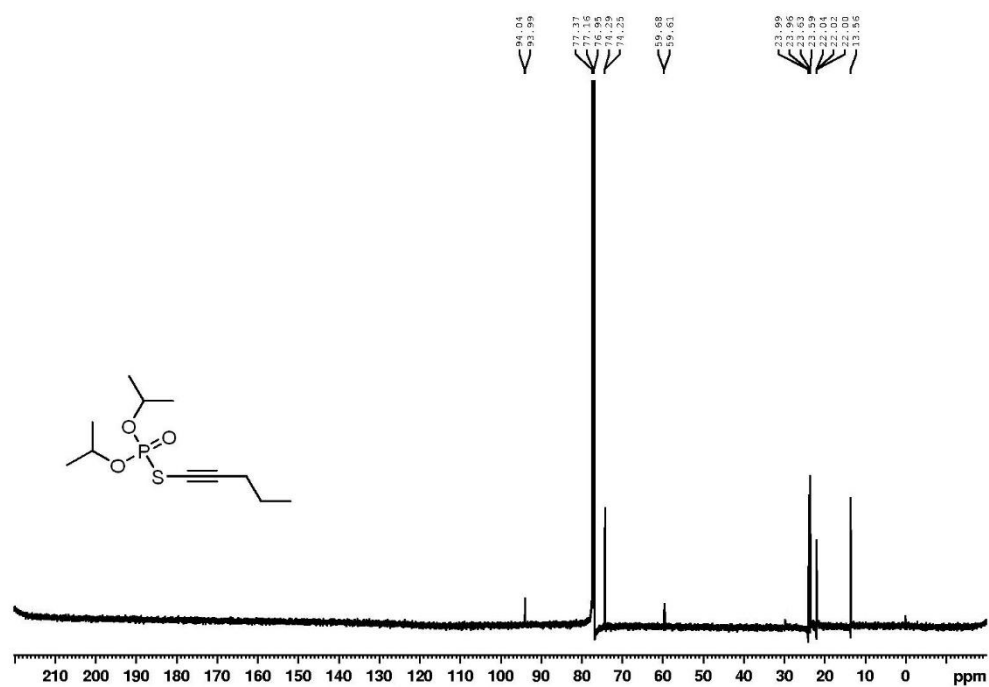
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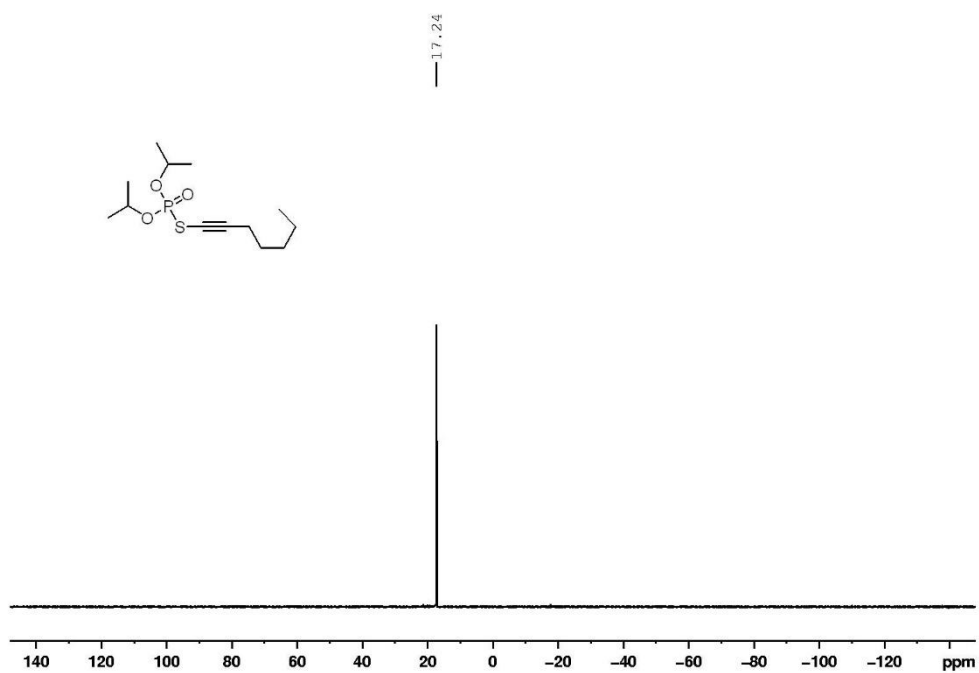
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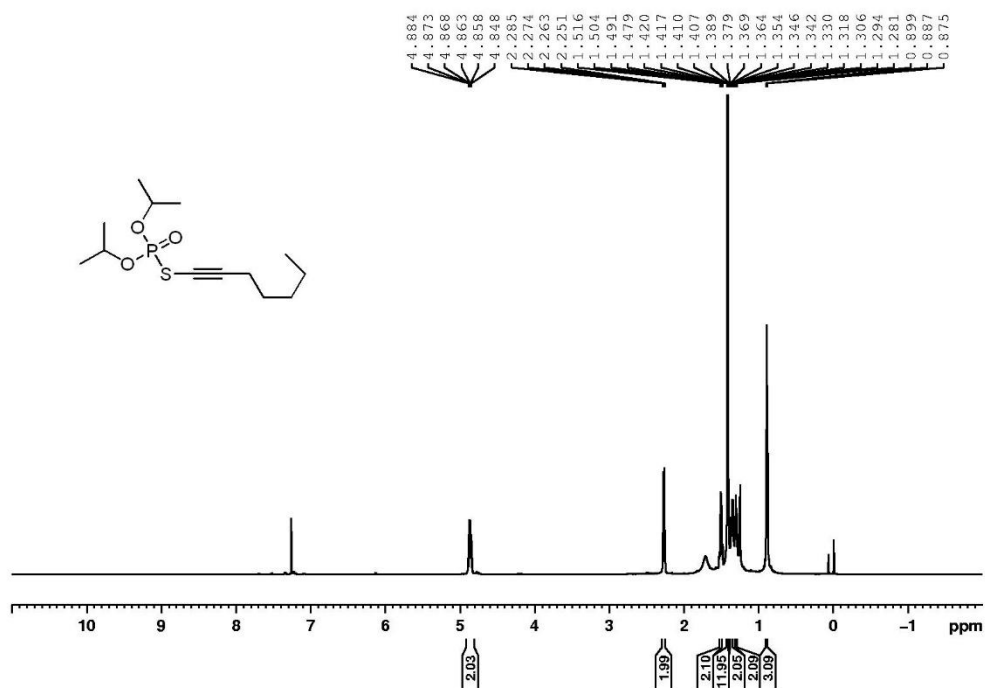
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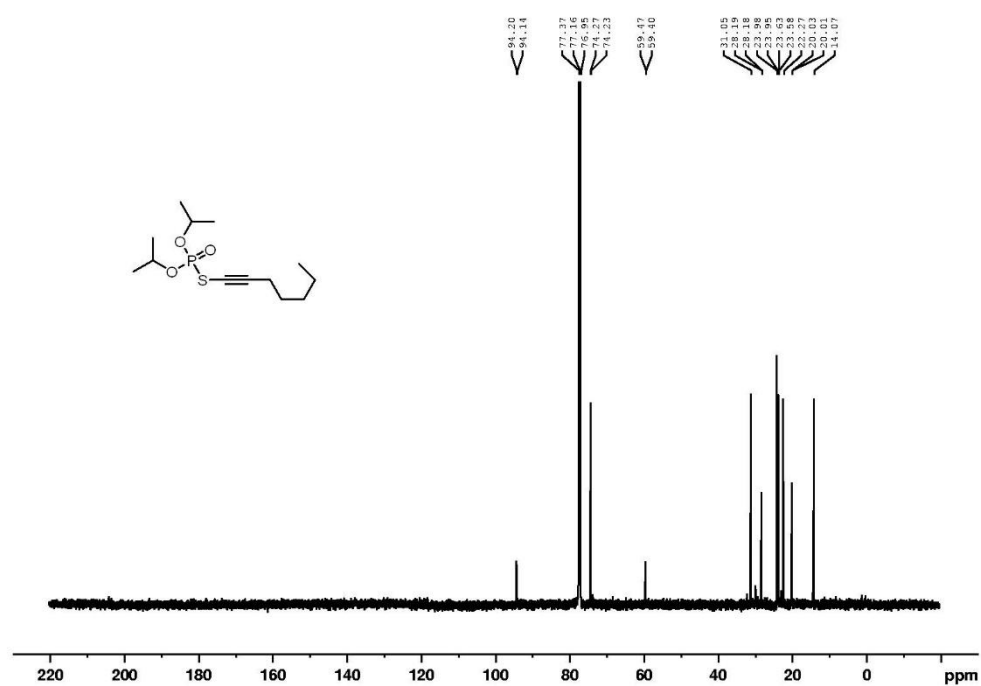
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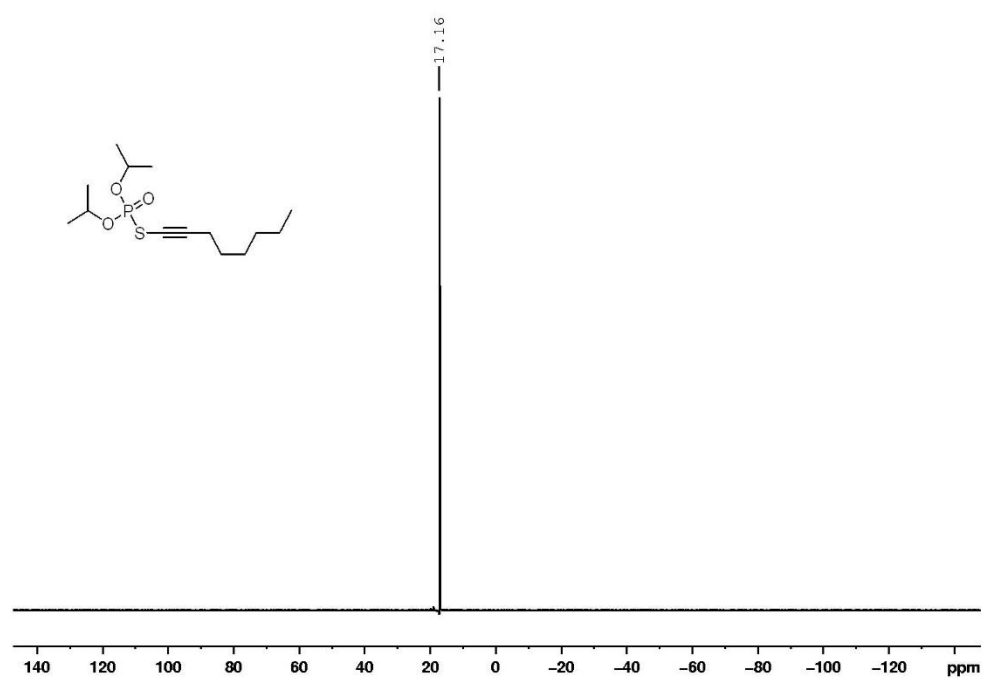
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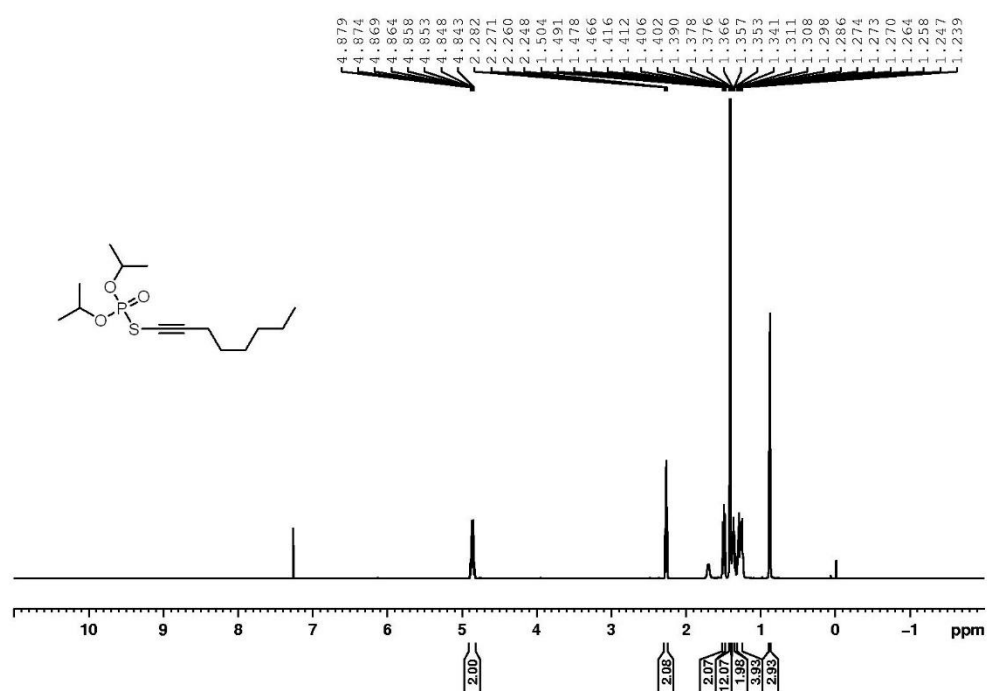


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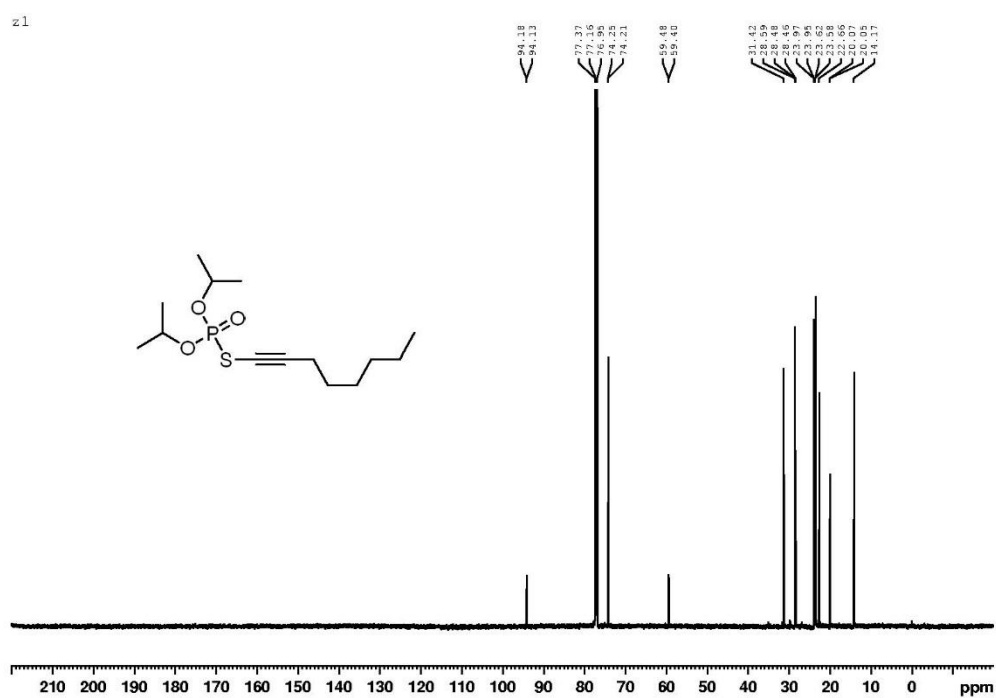


ESI-20

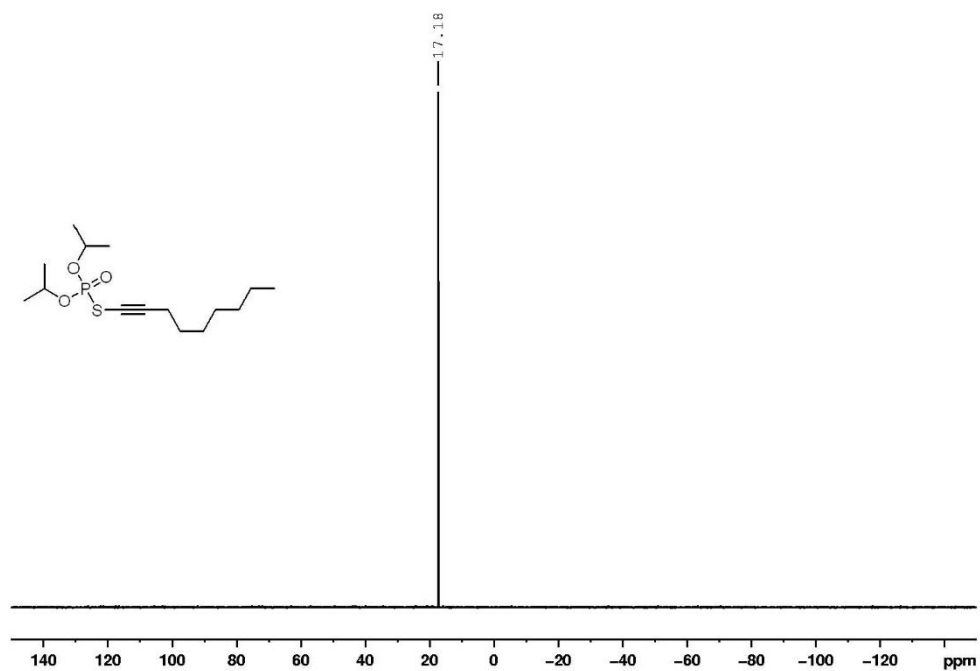
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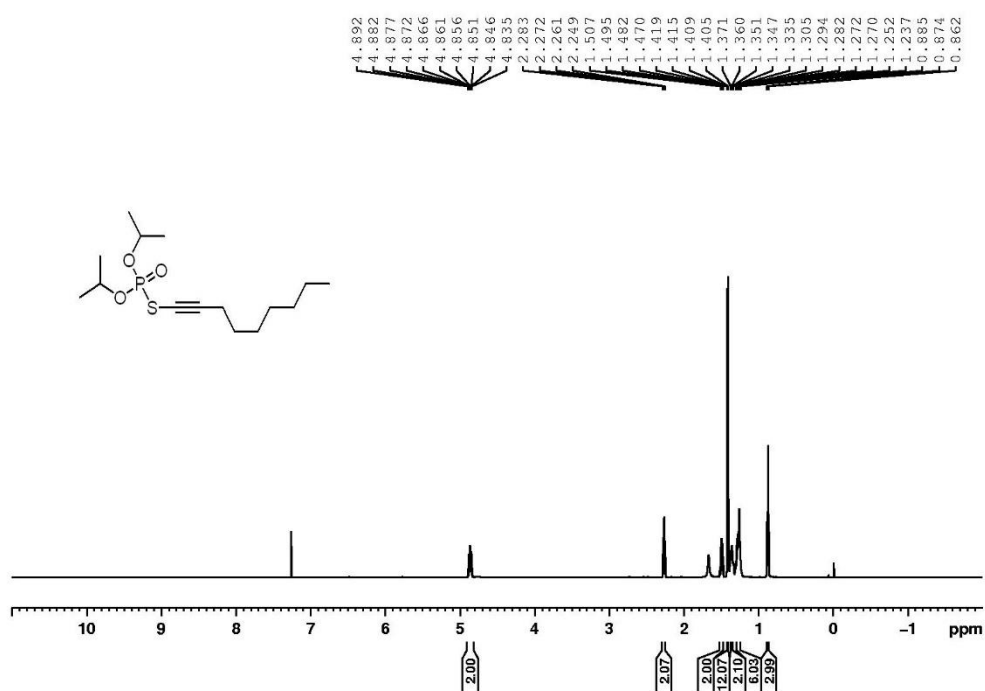
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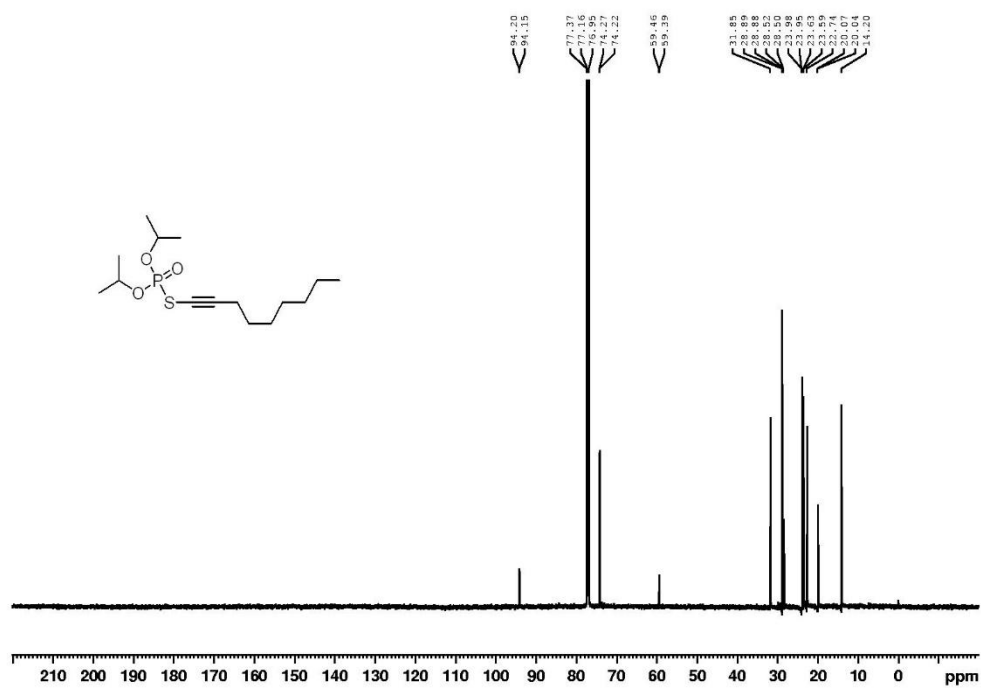


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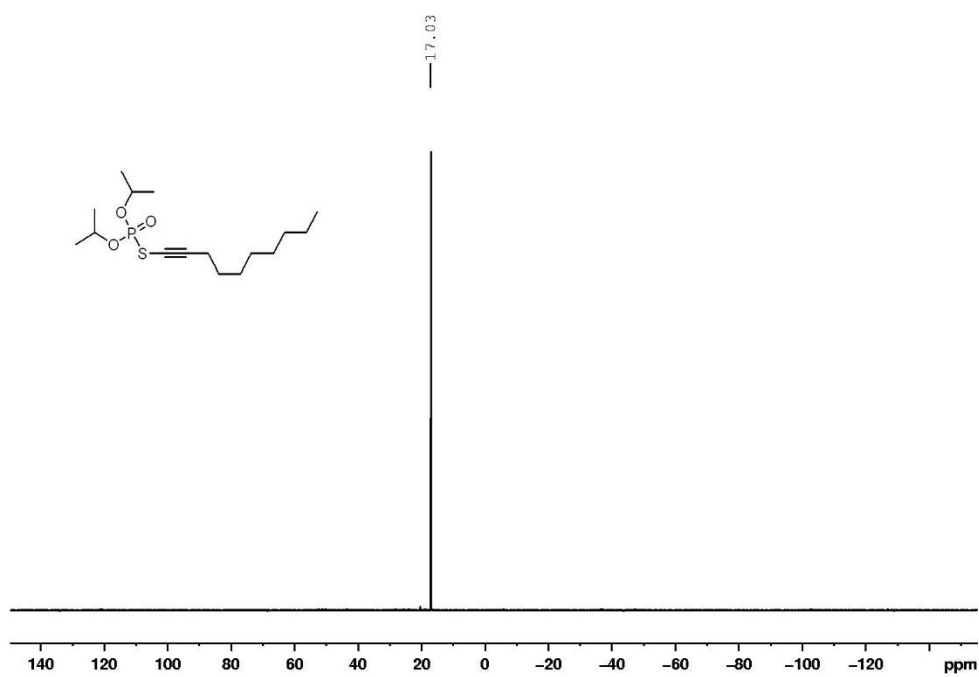


ESI-22

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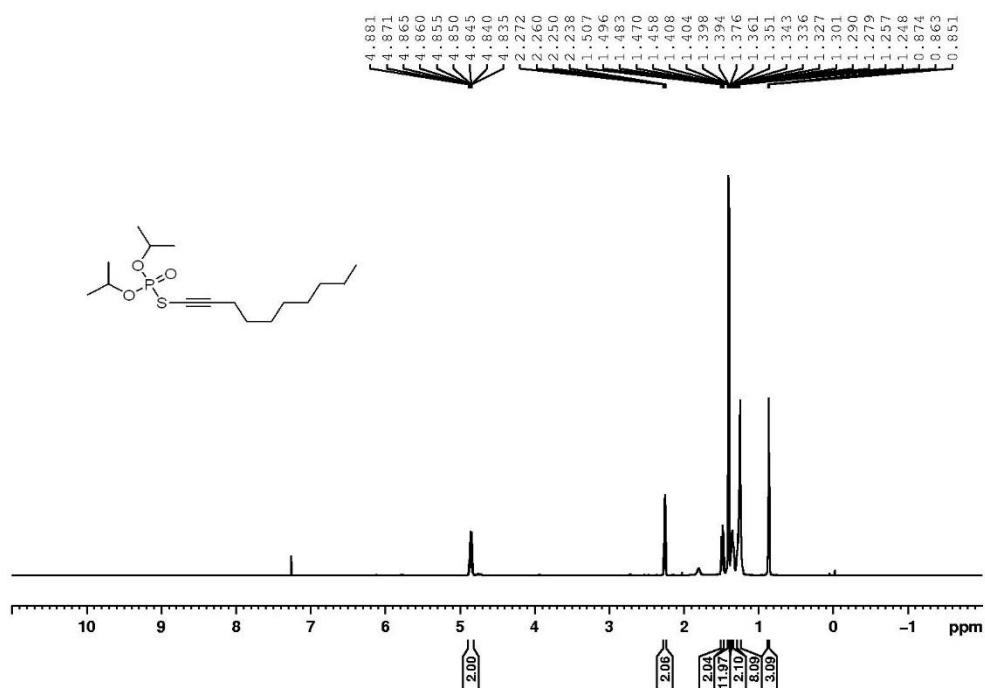


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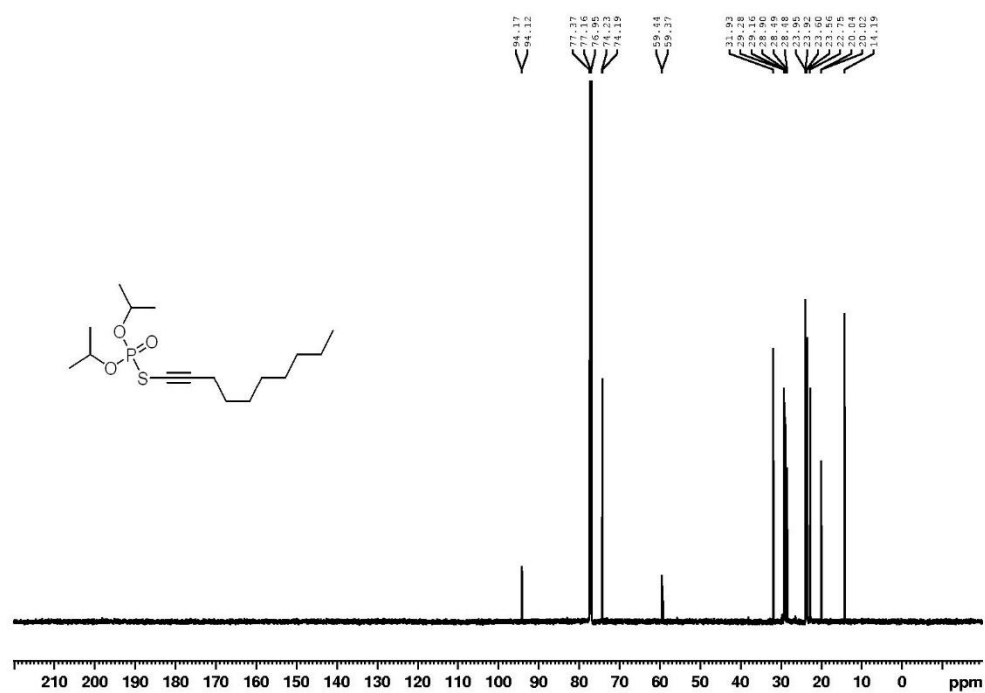


ESI-23

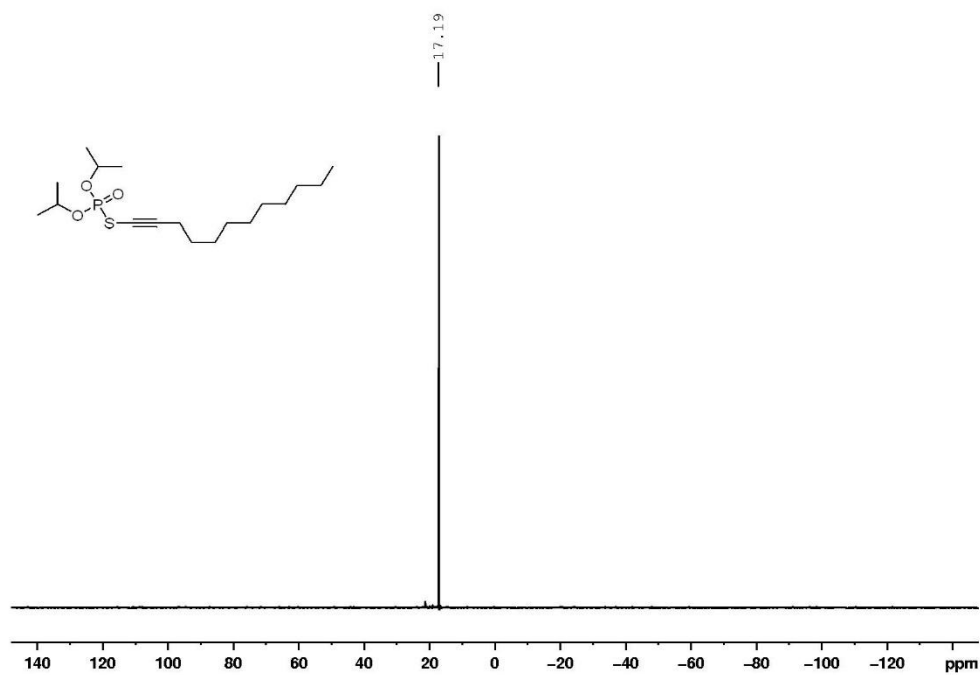
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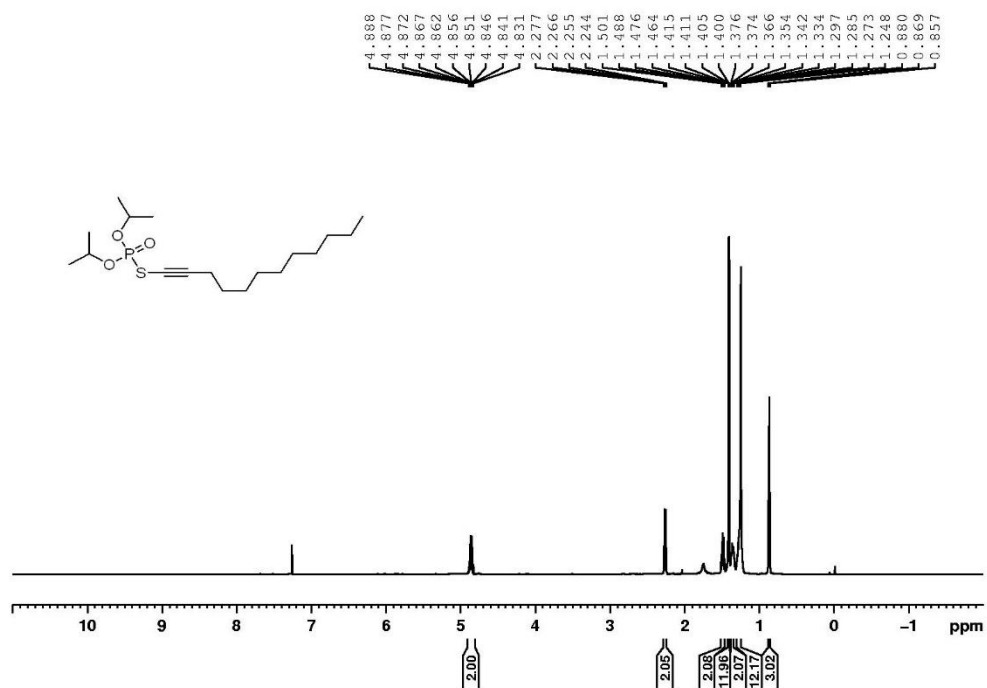
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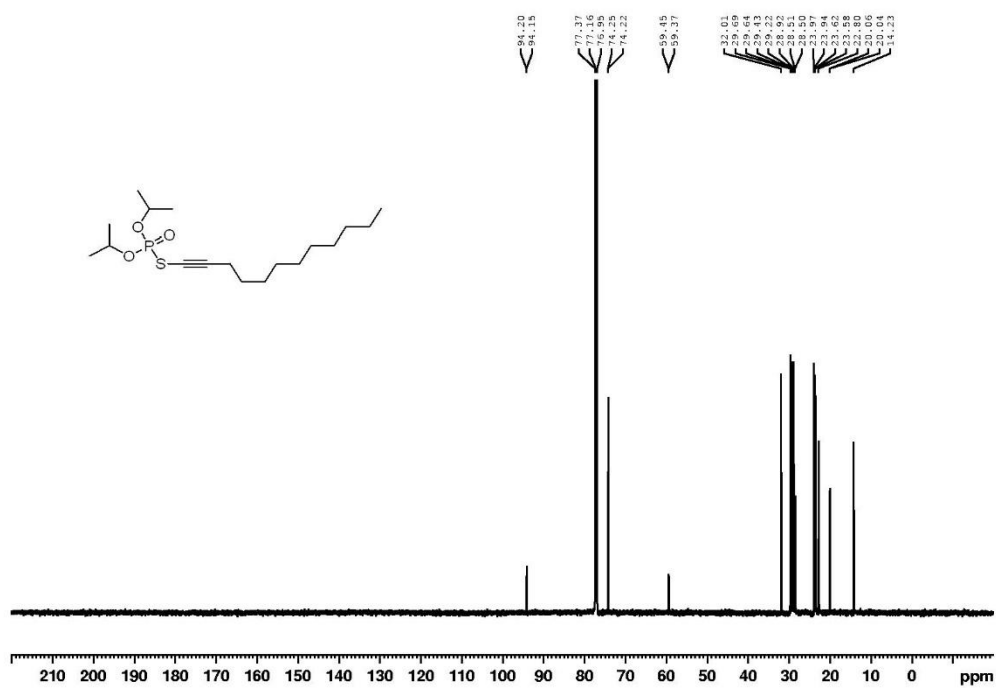


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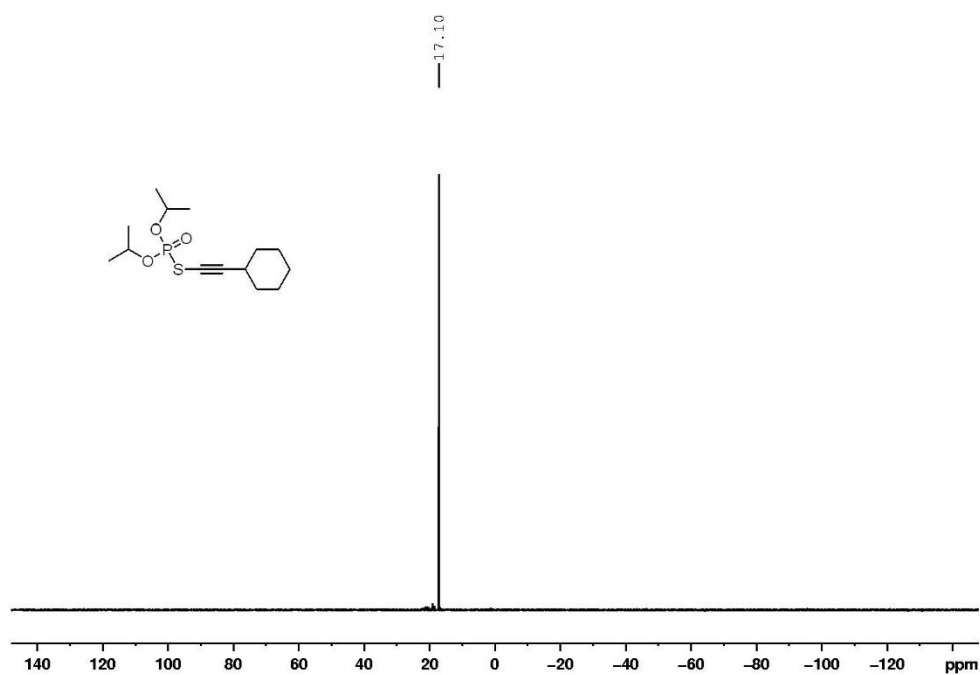


ESI-25

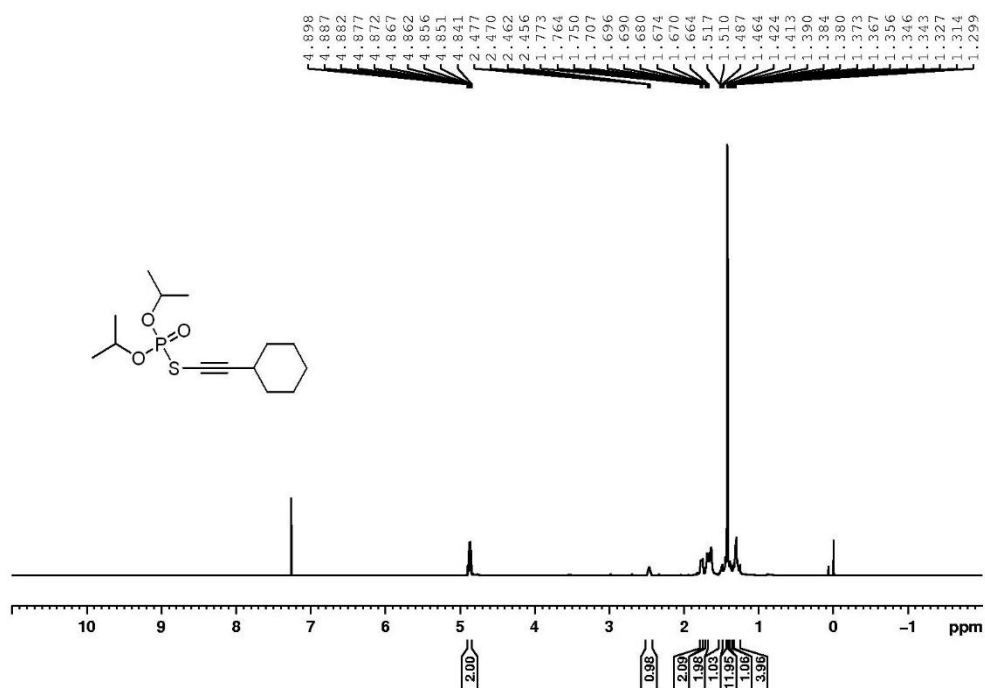
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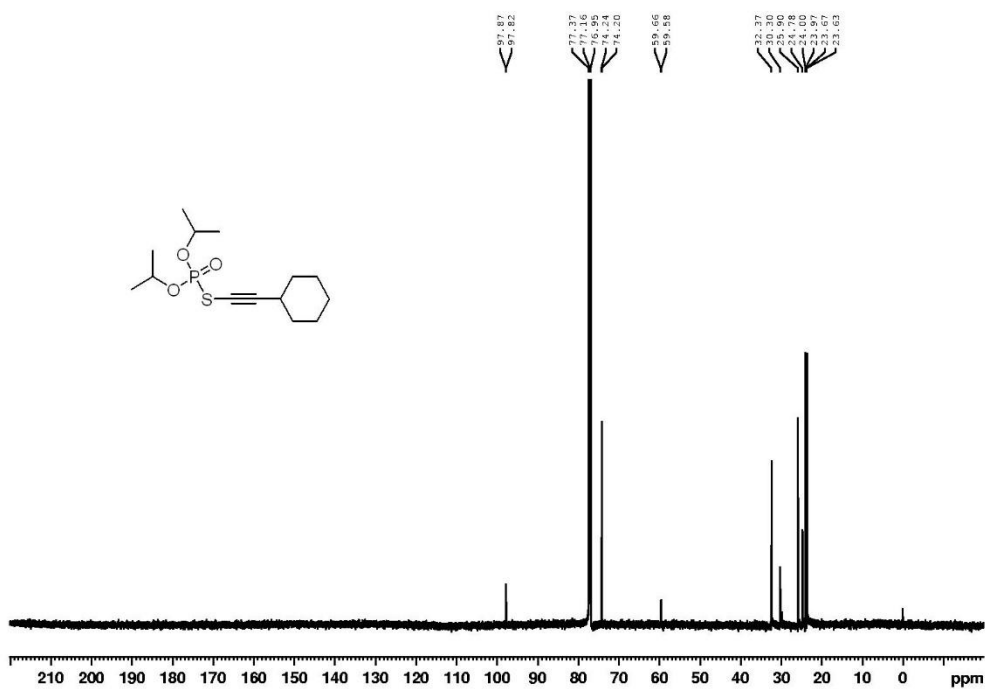
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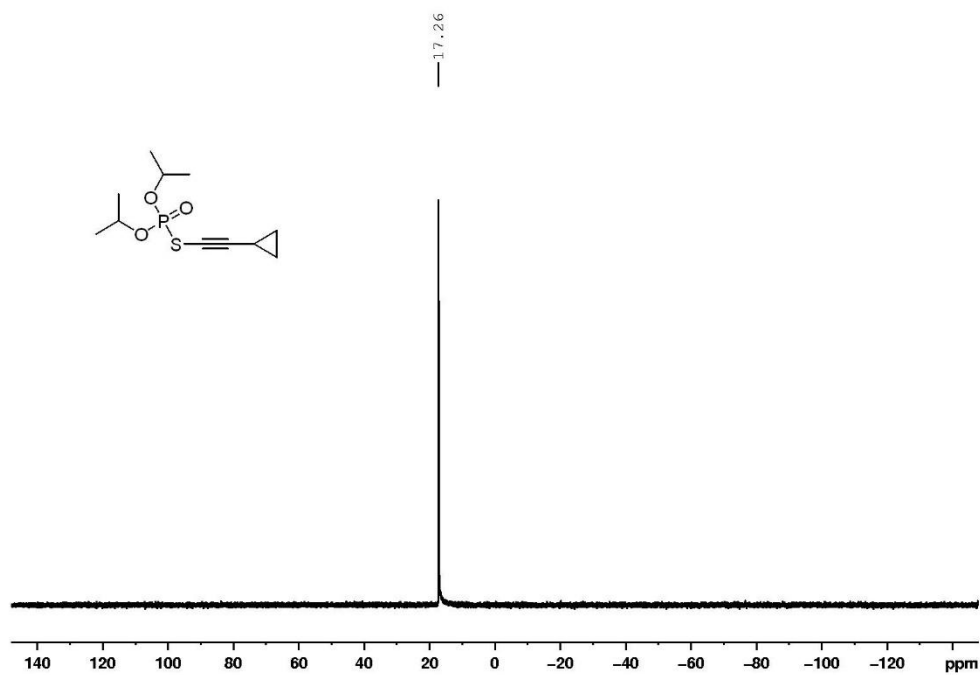


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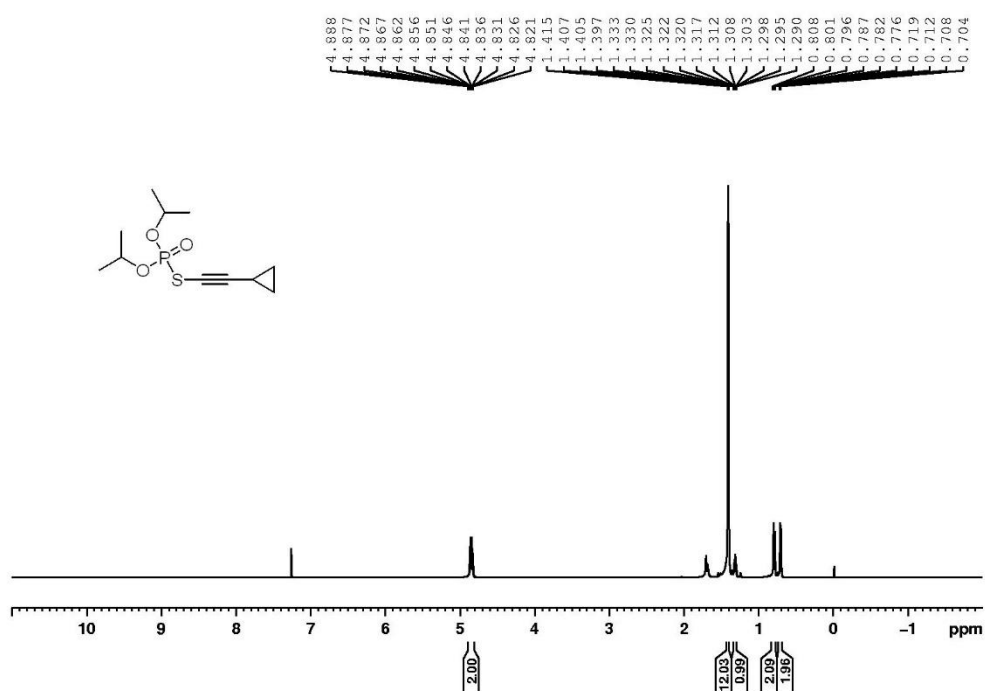


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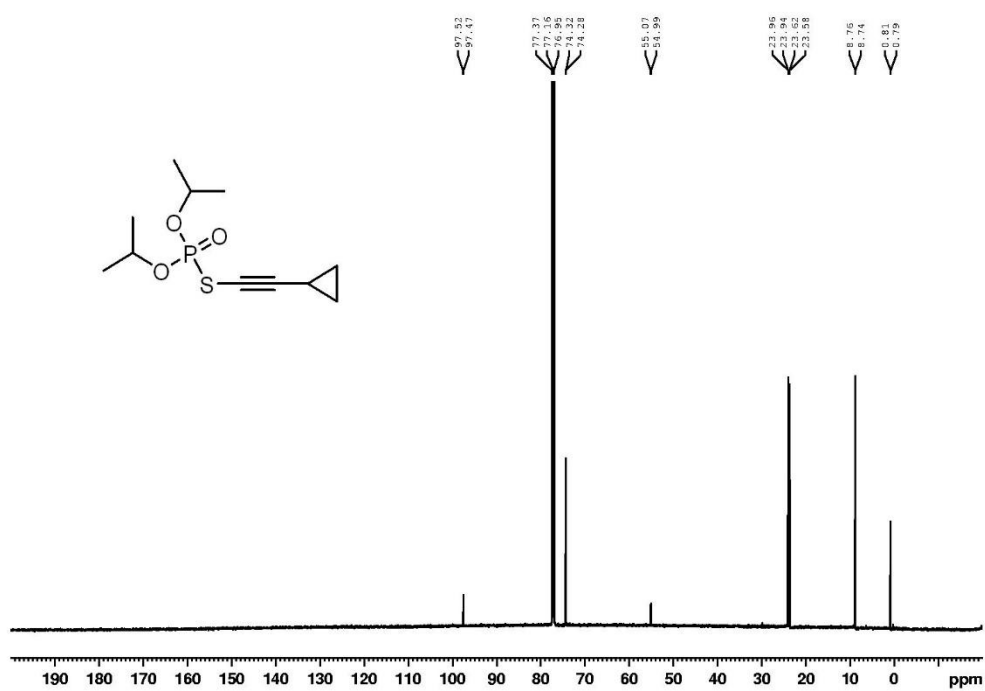


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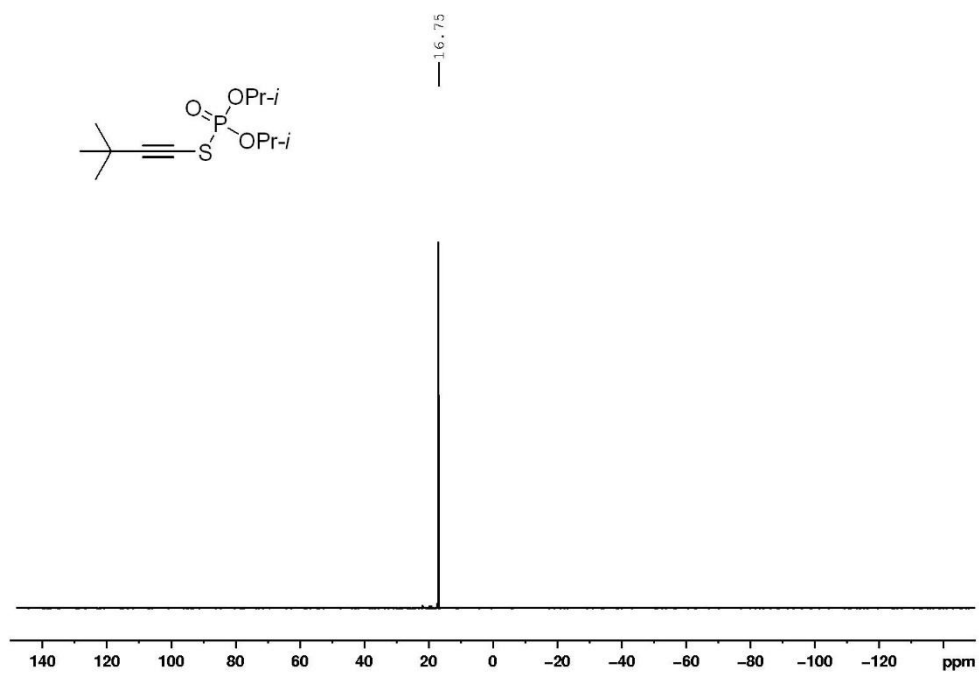


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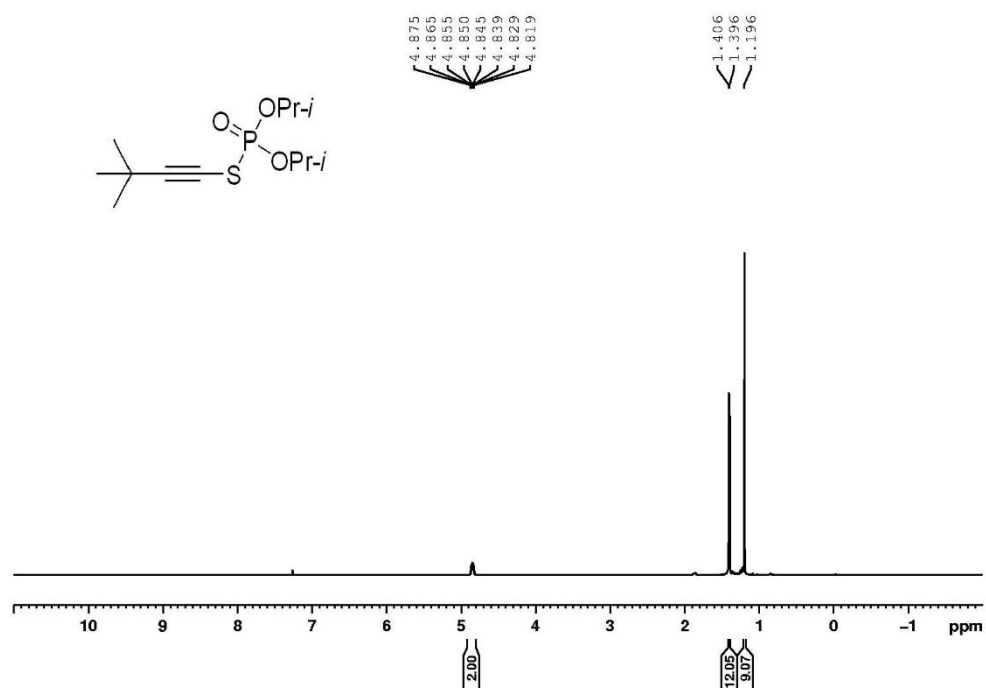
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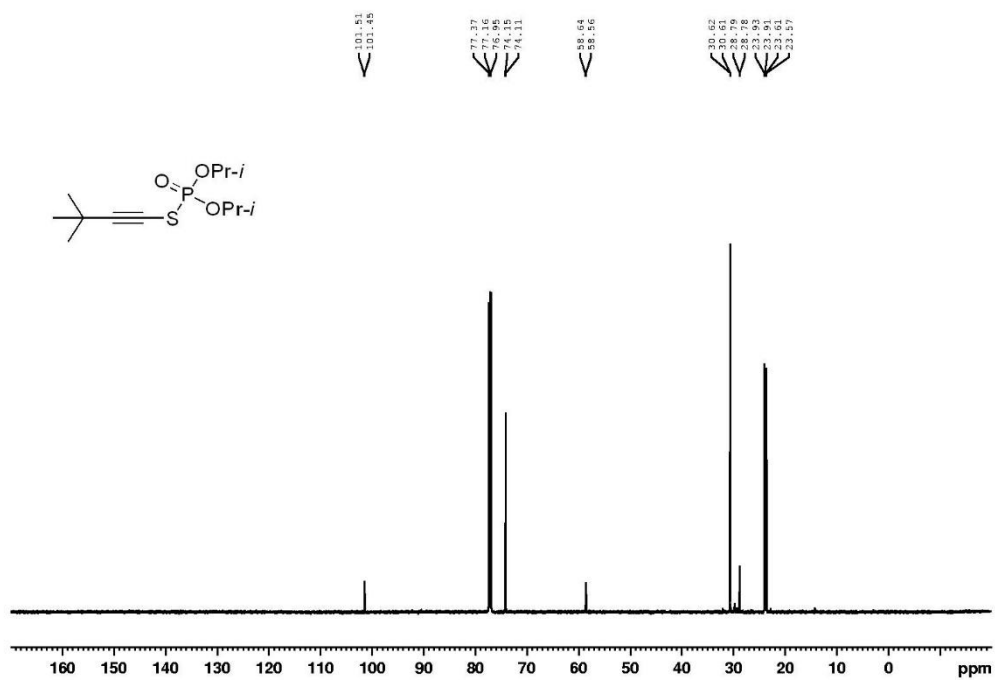
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12

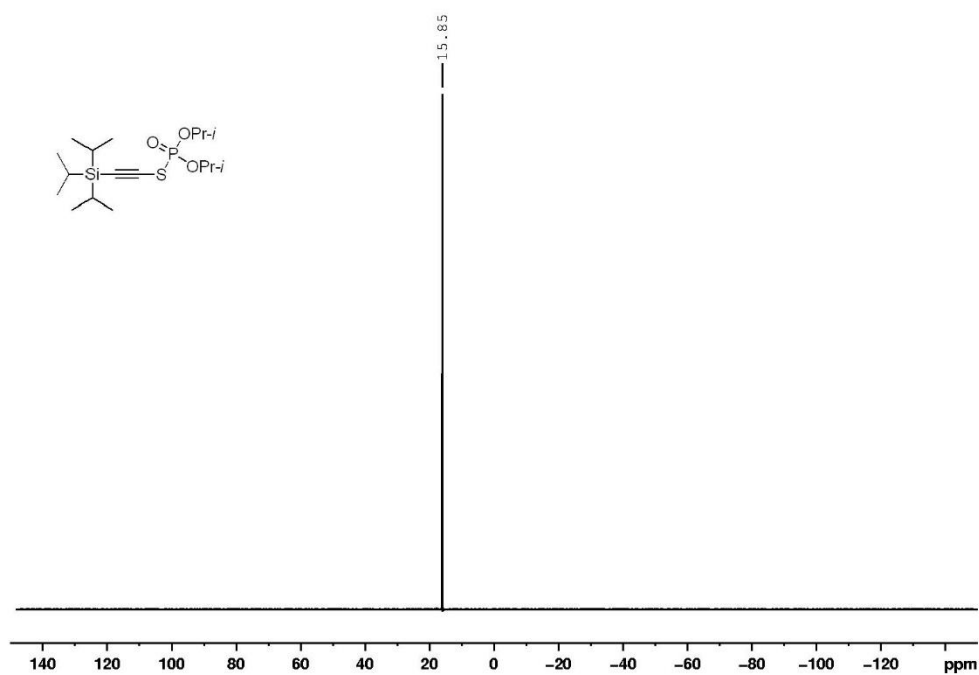


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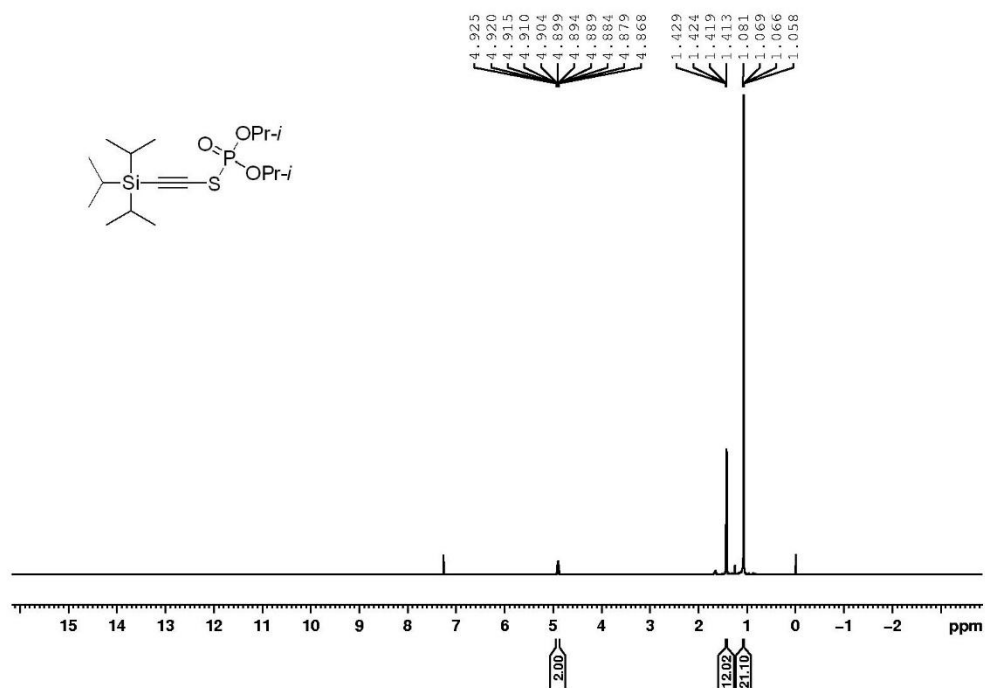


ESI-30

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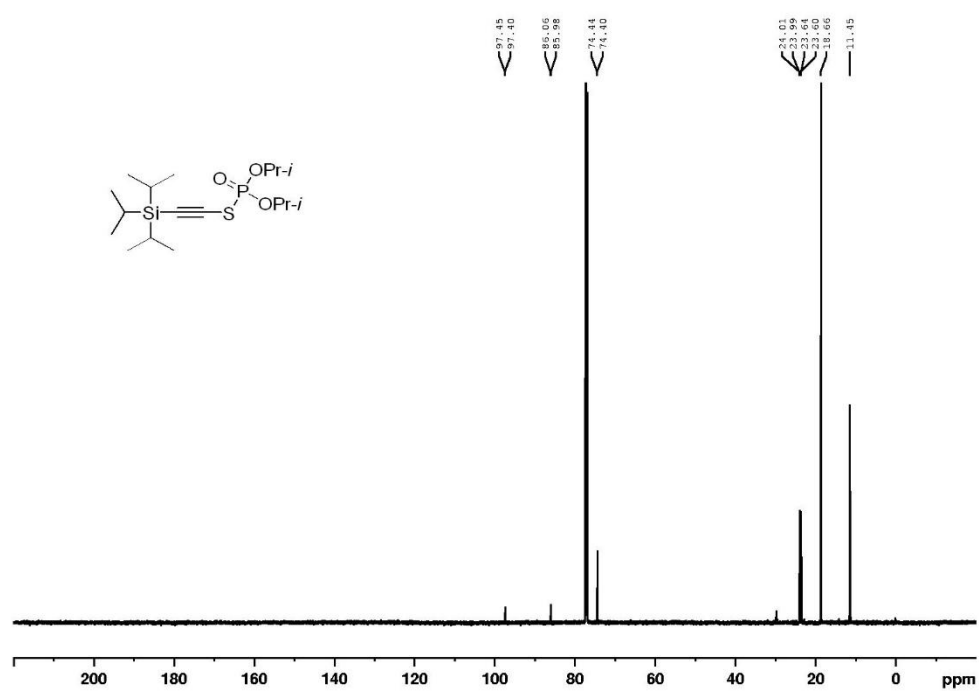


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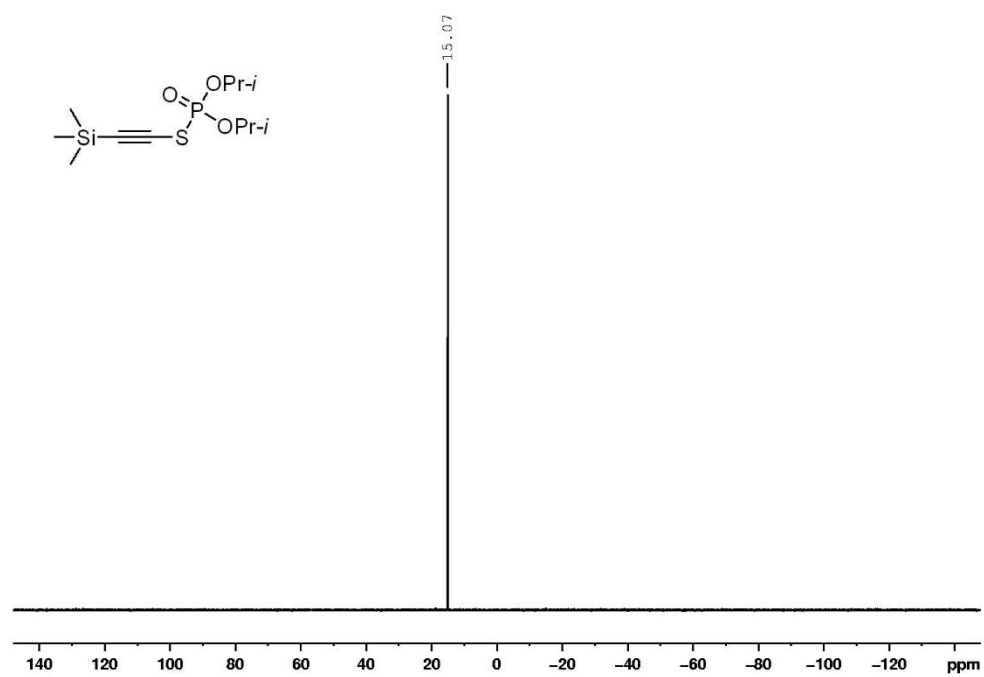


ESI-31

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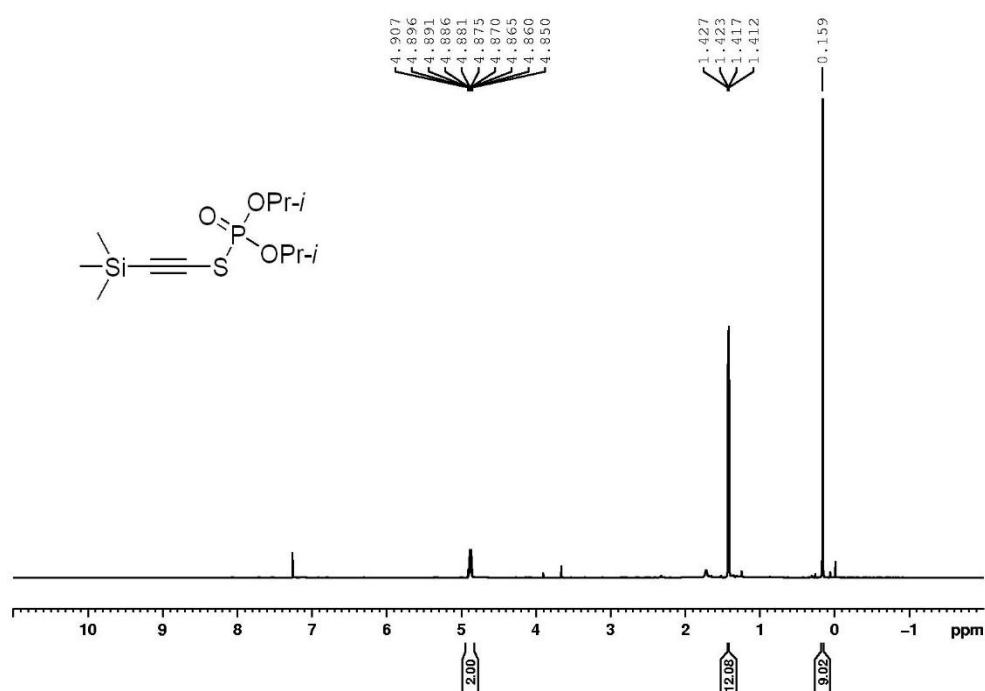


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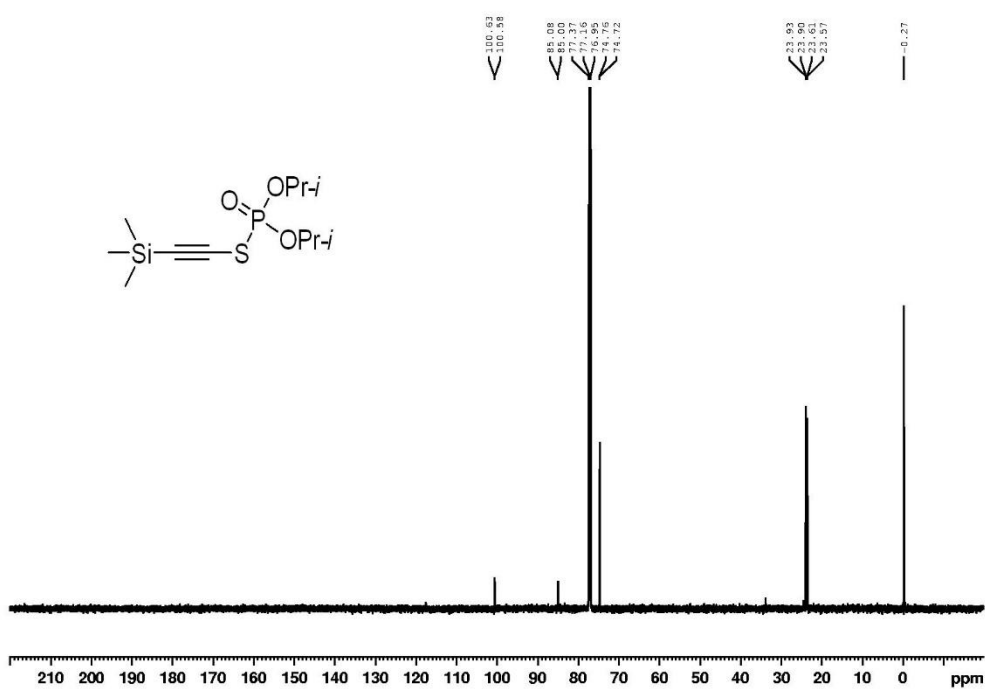


ESI-32

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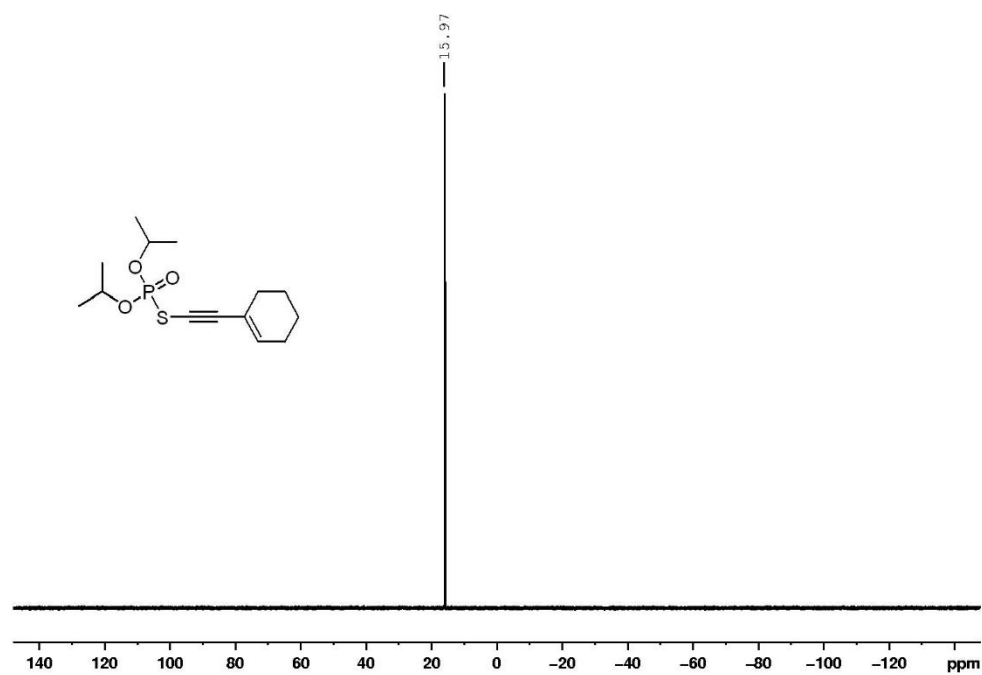


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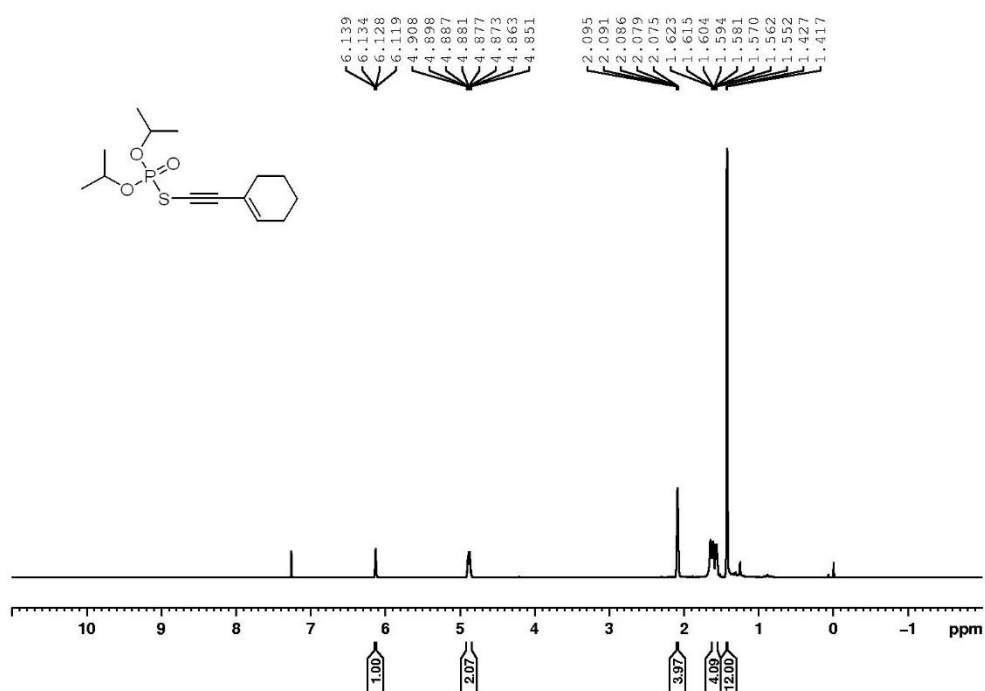


ESI-33

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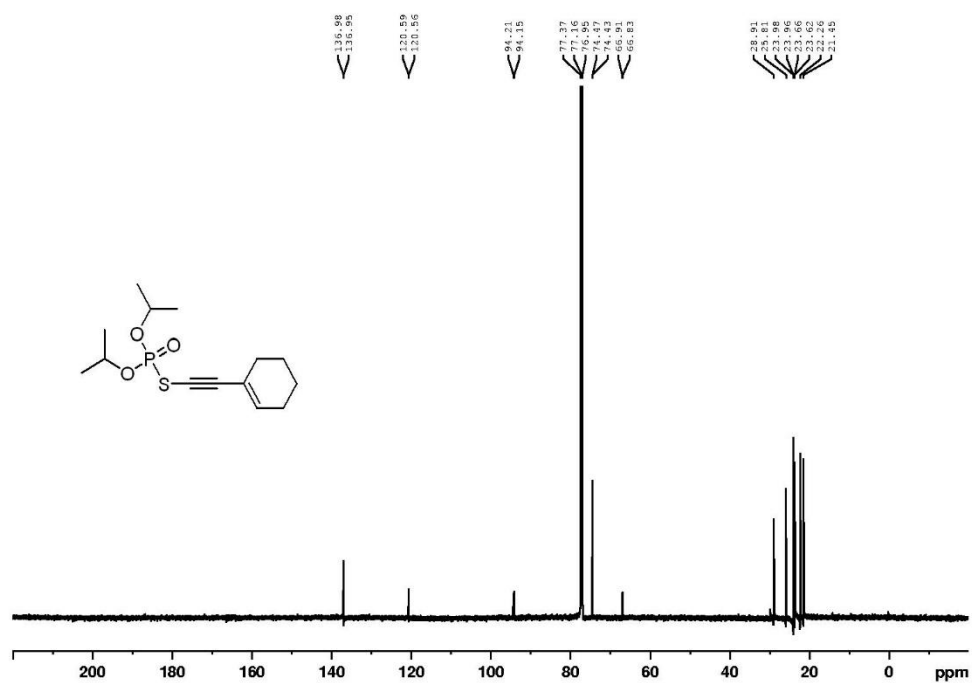


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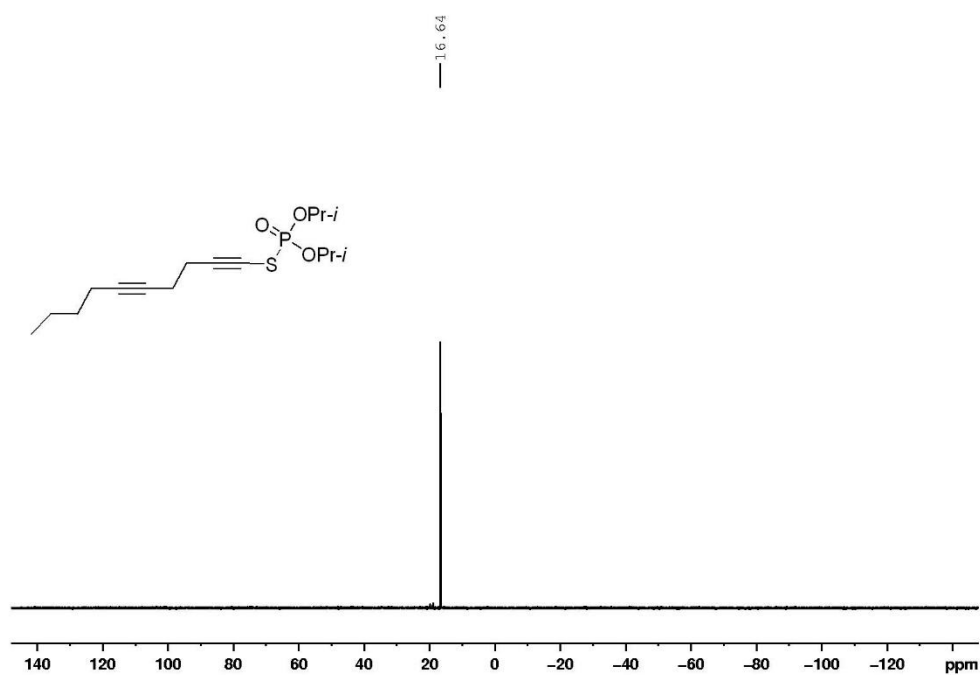


ESI-34

15



16



ESI-35

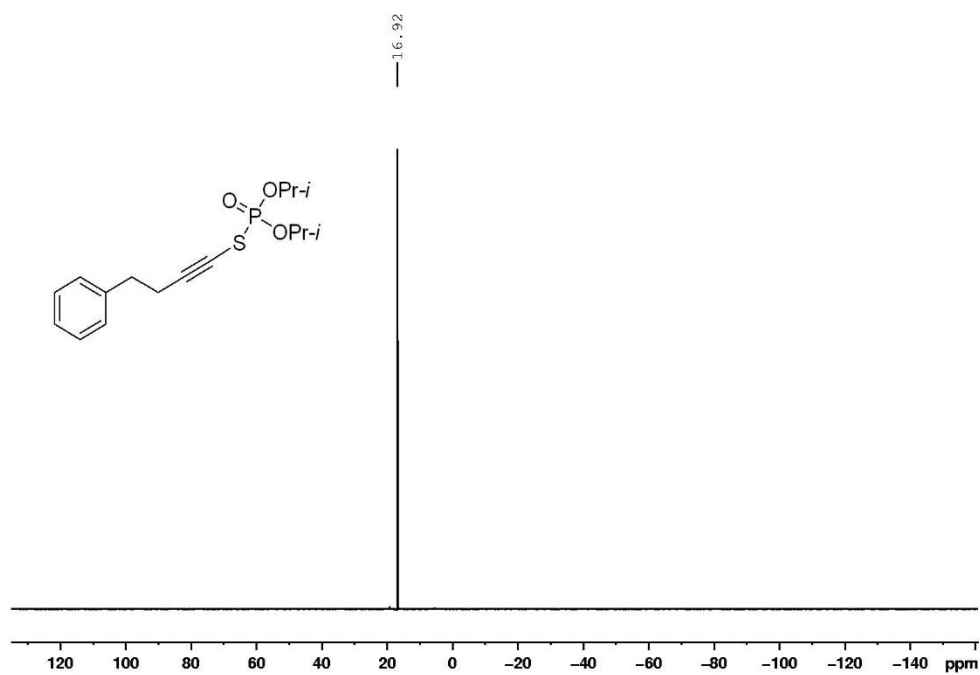
Chemical structure of compound 10: CCCCC#CC#CCOP(=O)(OC)OC

¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from 0 to 10. The spectrum shows several peaks, with integration values indicated below the baseline: 2.00, 2.09, 1.97, 2.17, 16.00, and 3.01. A list of chemical shifts (δ) in ppm is provided at the top of the spectrum.

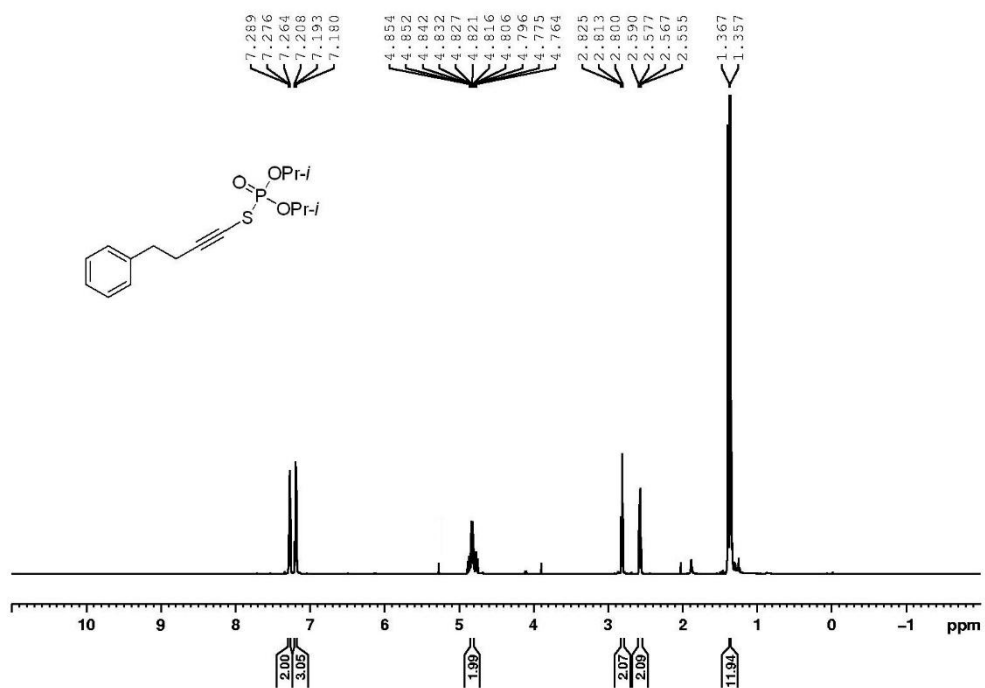
Chemical shifts (ppm): 4.889, 4.879, 4.874, 4.869, 4.864, 4.853, 2.485, 2.473, 2.463, 2.460, 2.450, 2.371, 2.368, 2.364, 2.358, 2.355, 2.351, 2.343, 2.147, 2.143, 2.139, 2.136, 2.132, 2.128, 2.124, 2.120, 2.116, 1.464, 1.451, 1.447, 1.439, 1.424, 1.414, 1.398, 1.394, 1.382, 1.369.

ESI-36

17

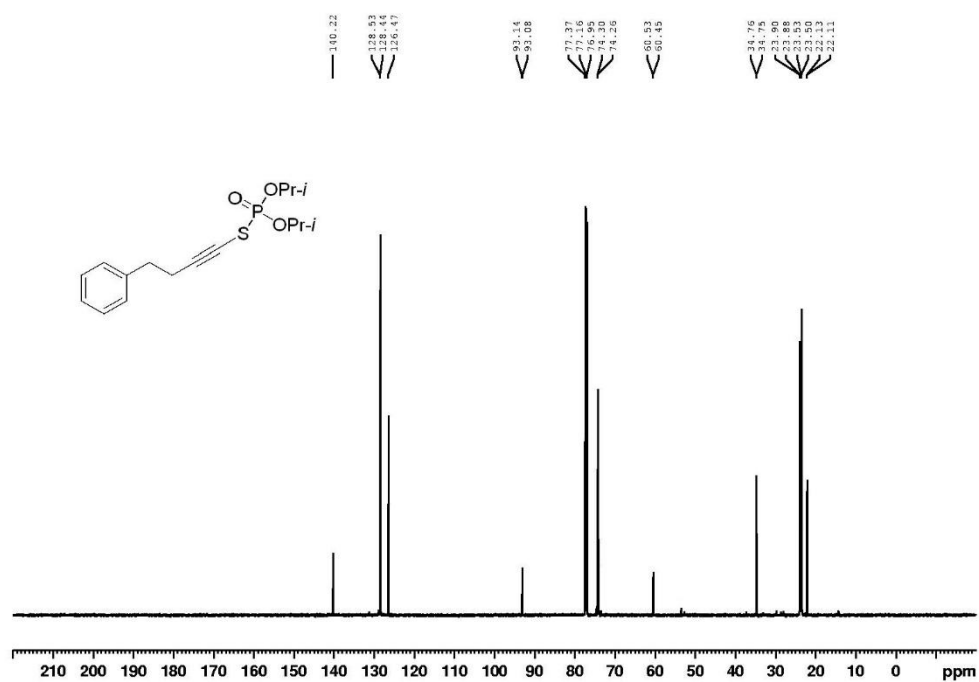


17

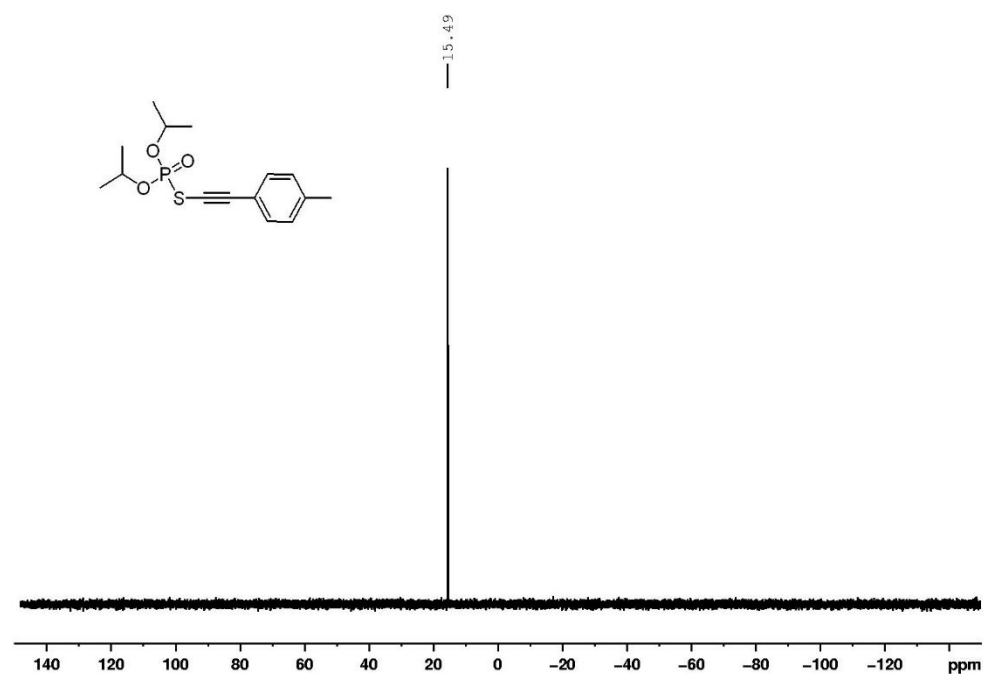


ESI-37

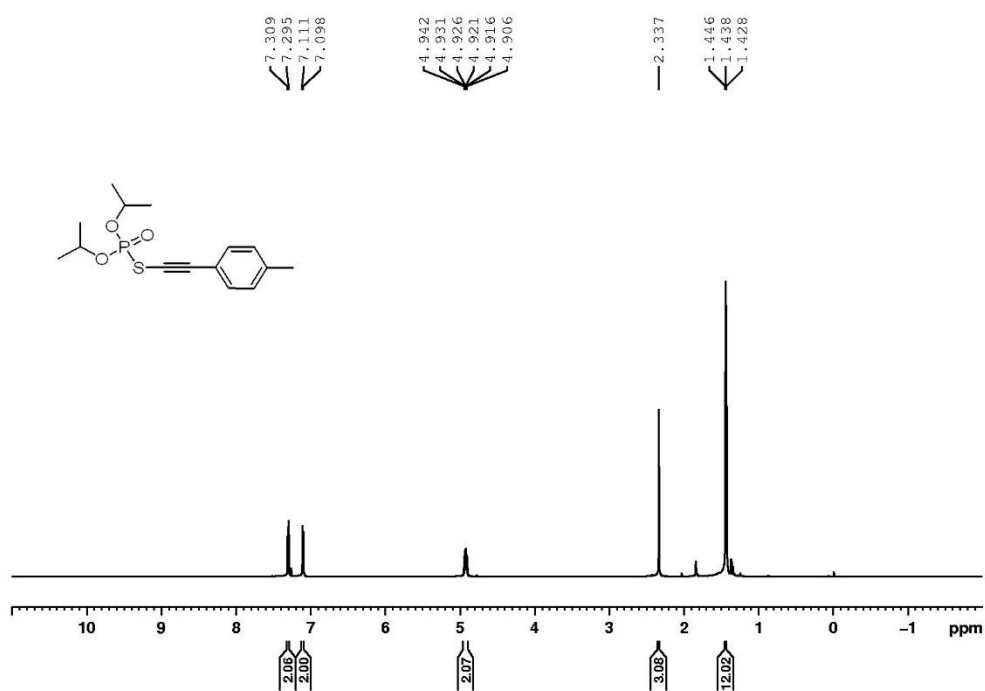
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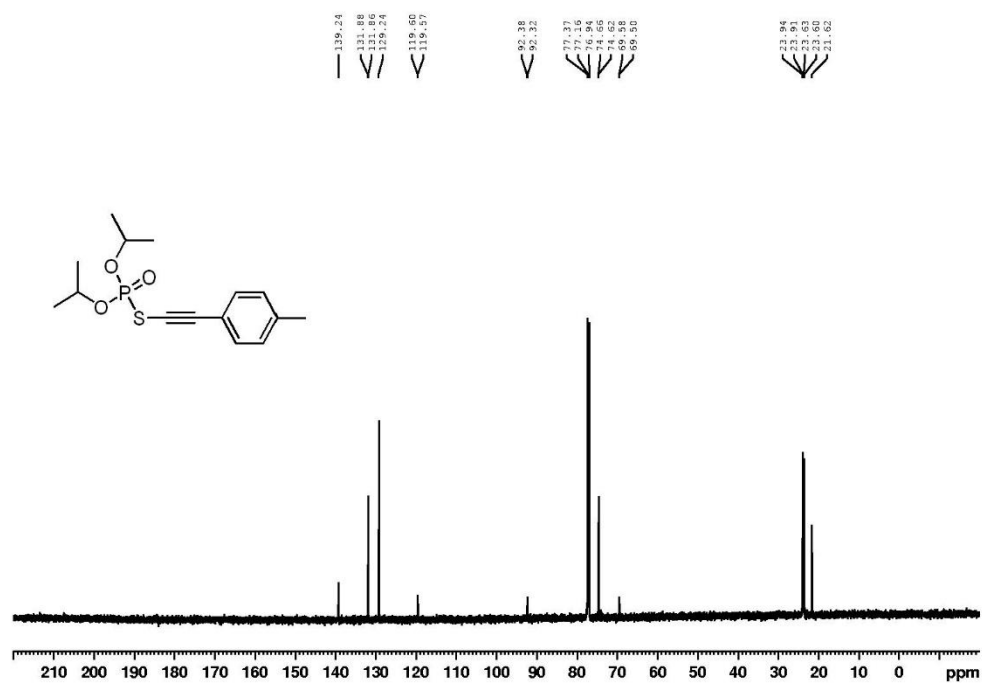
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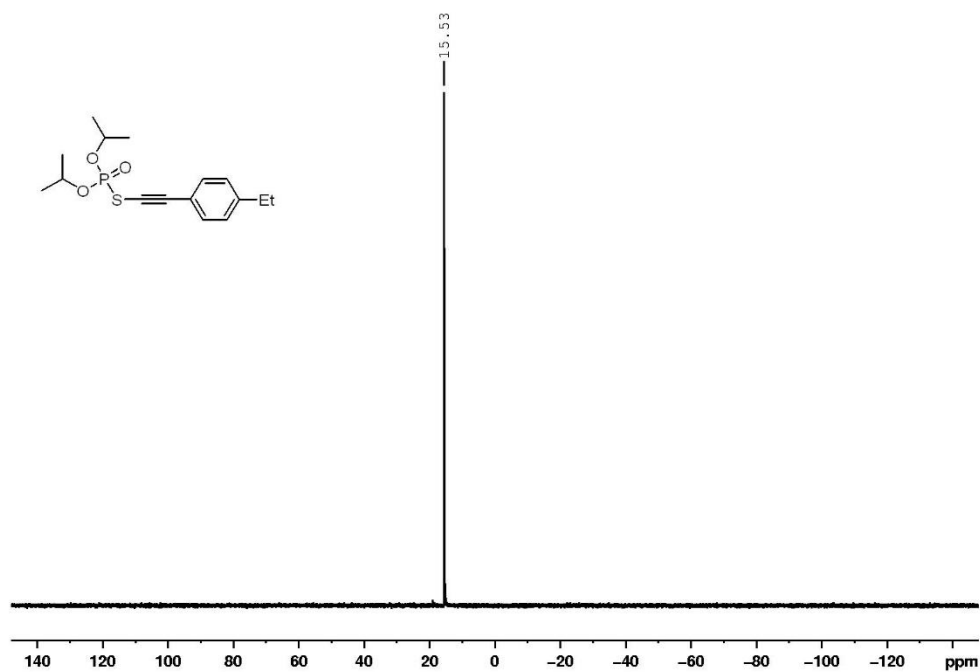
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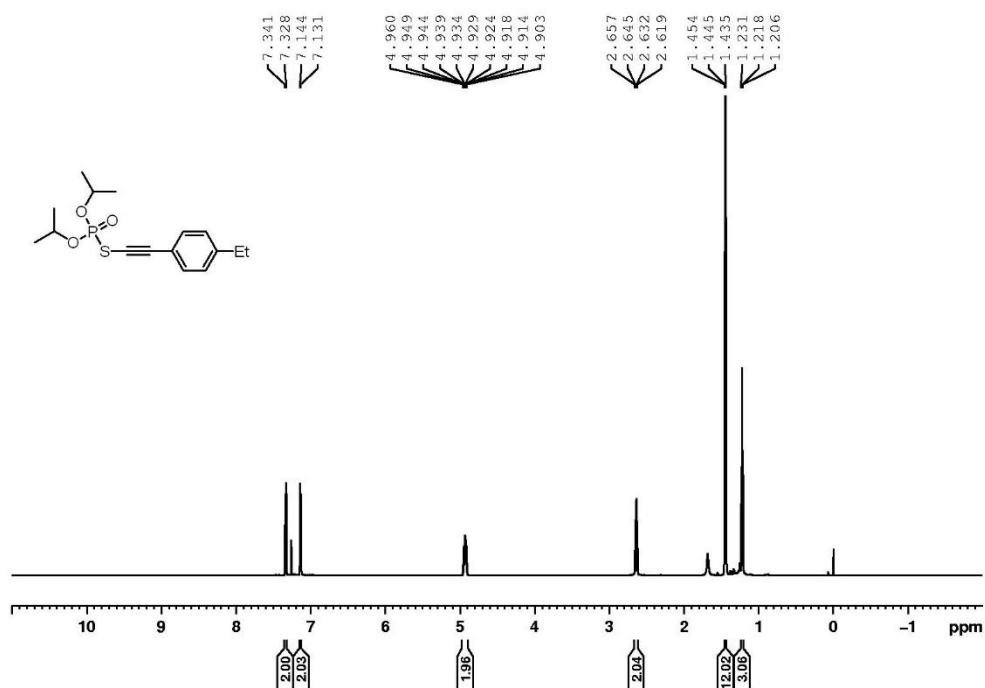
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19

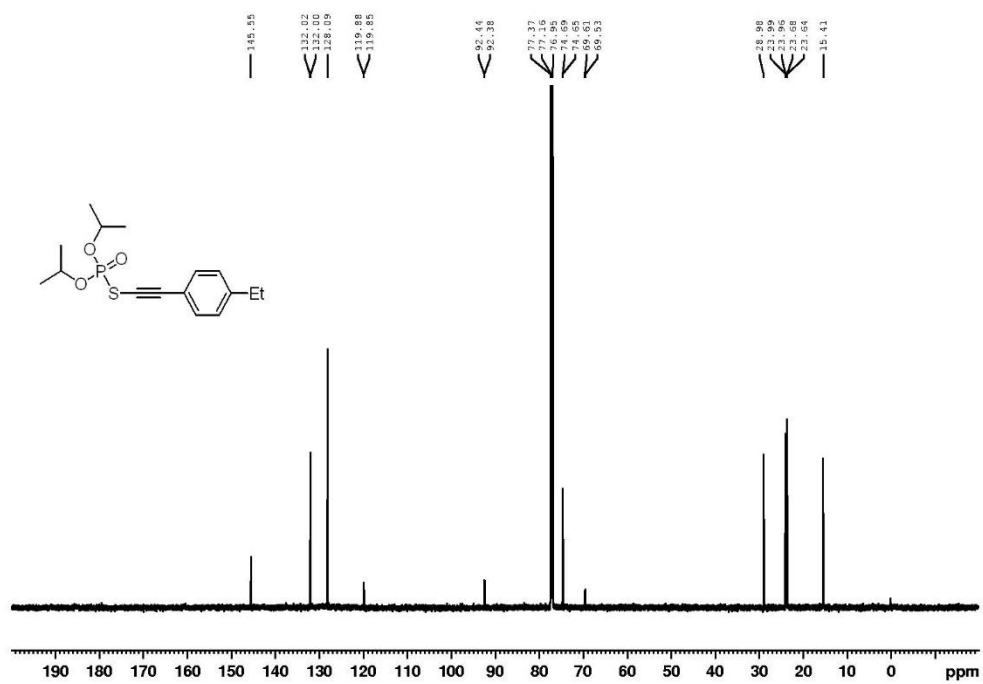


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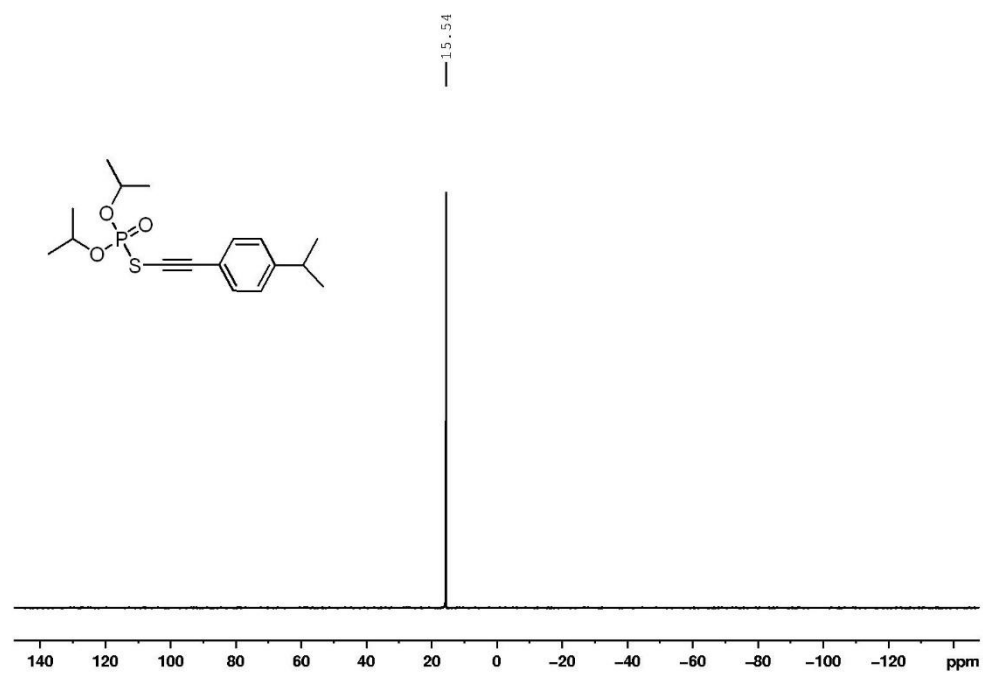


ESI-40

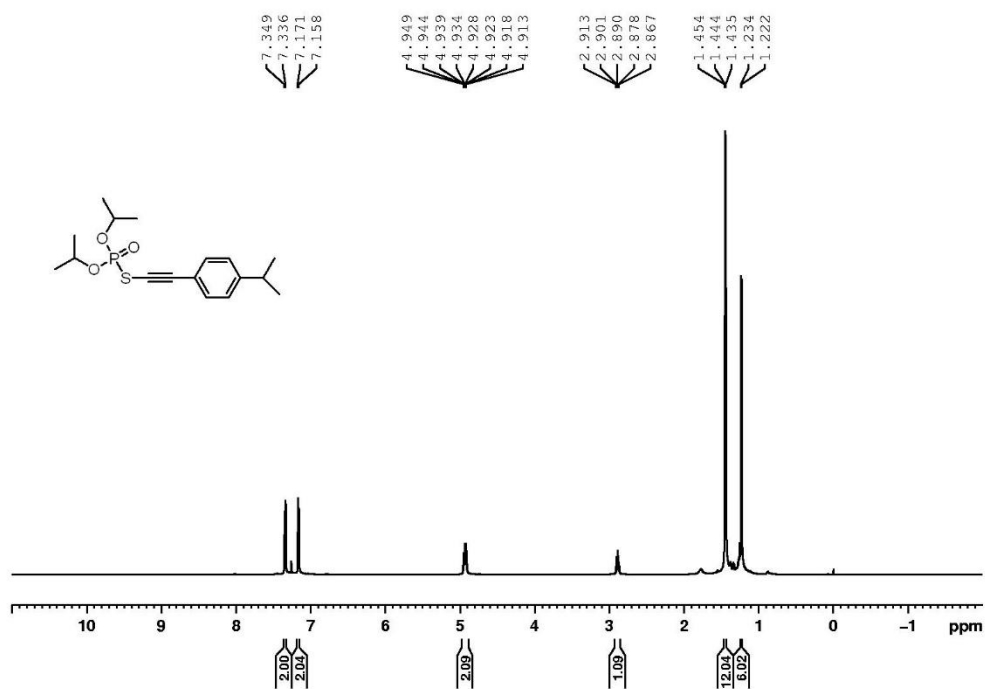
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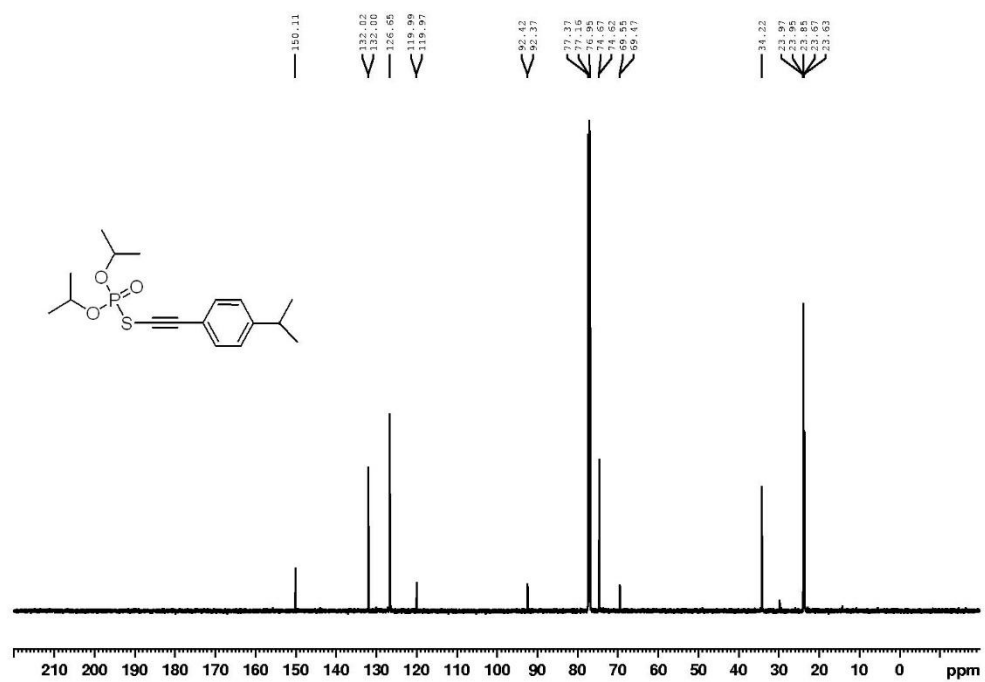
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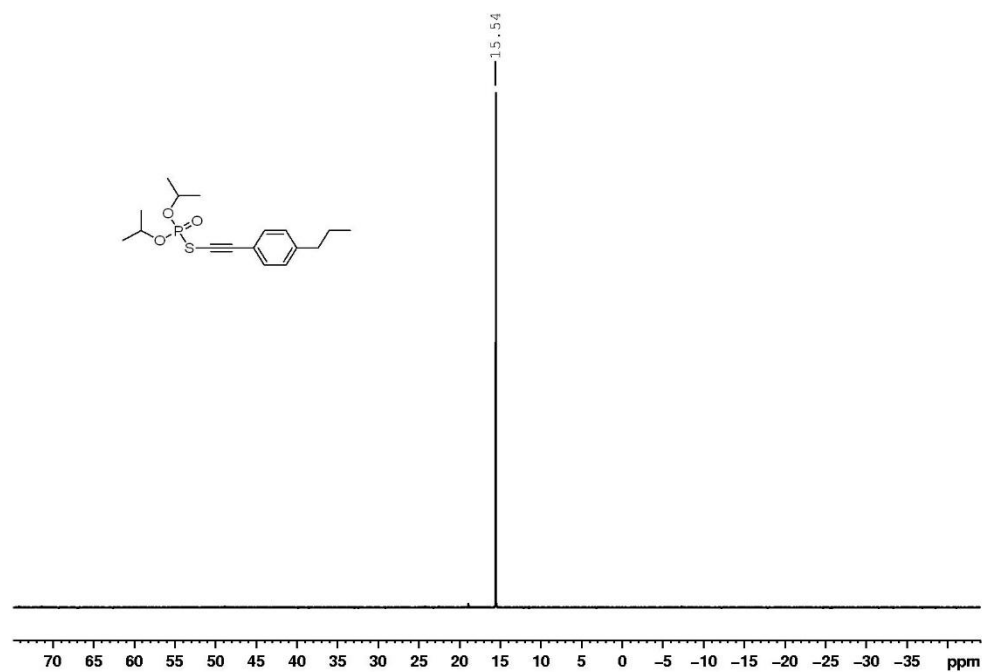
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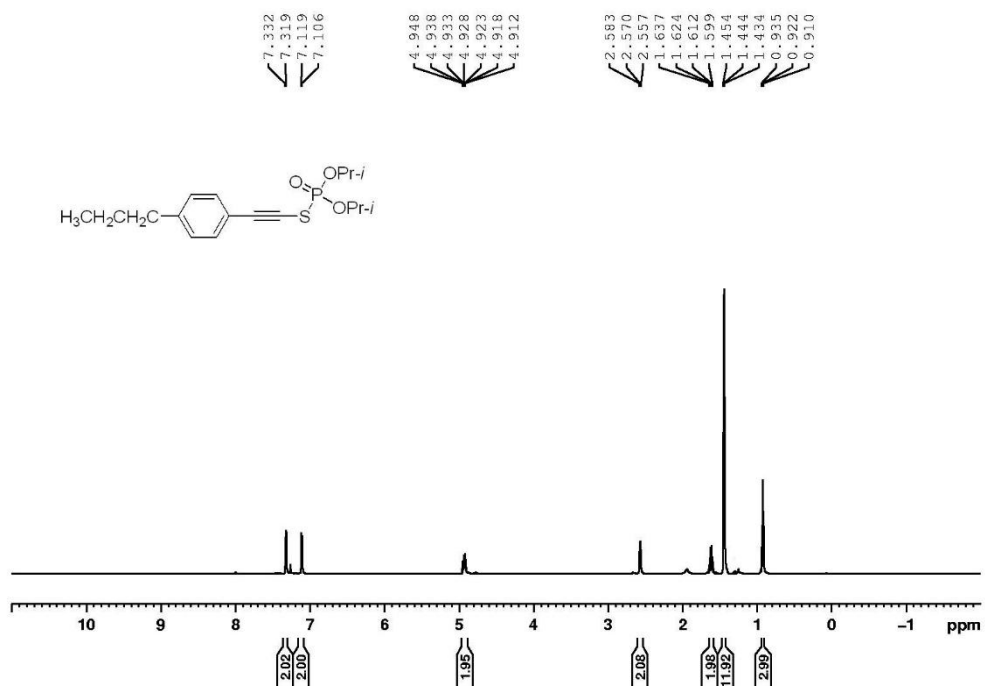
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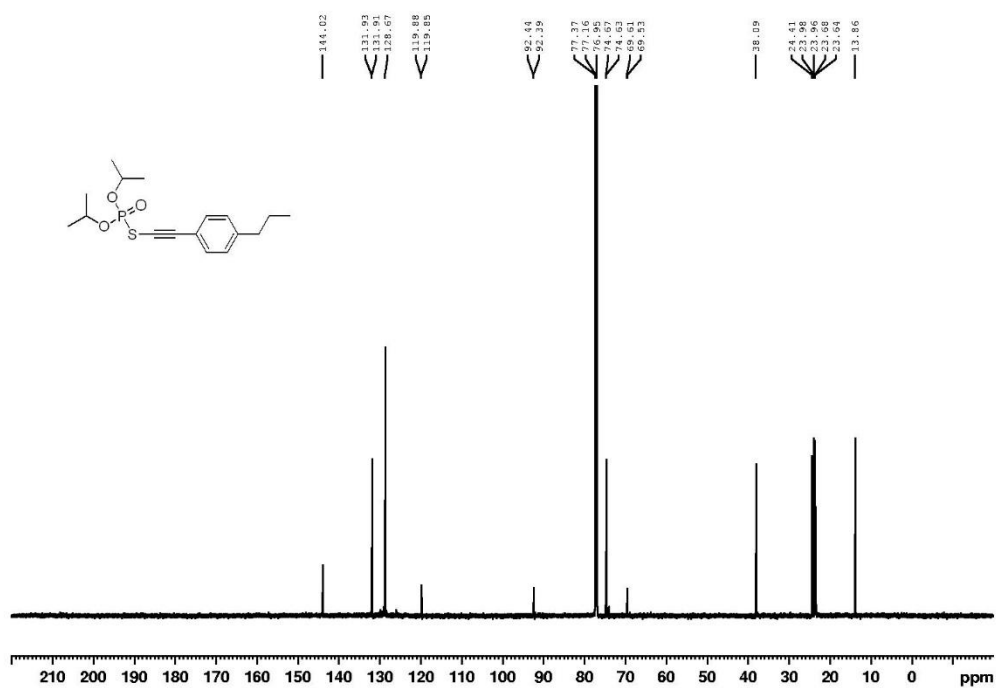
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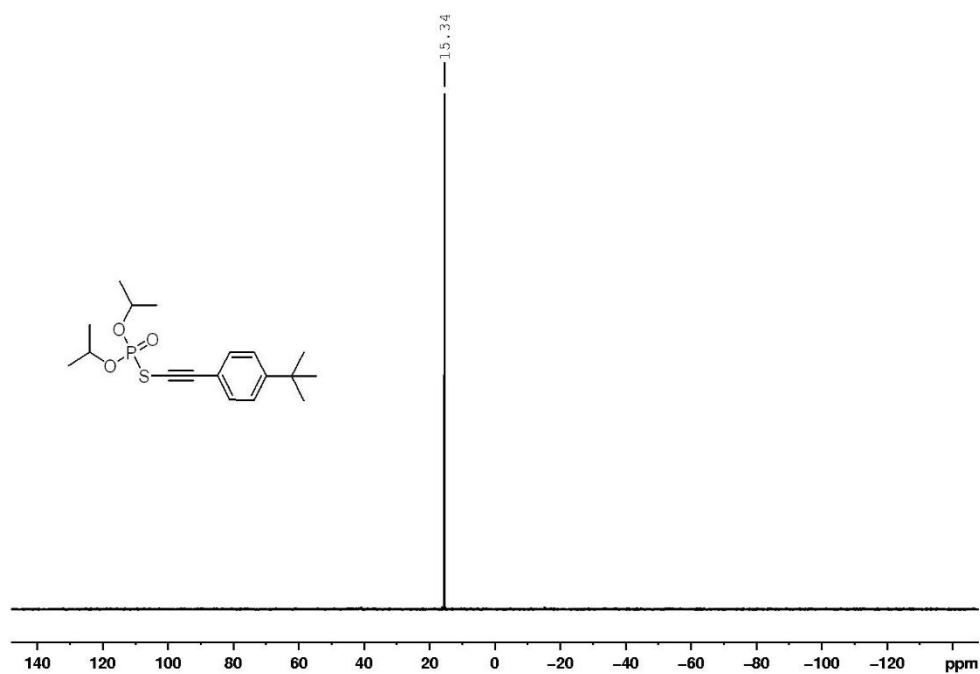
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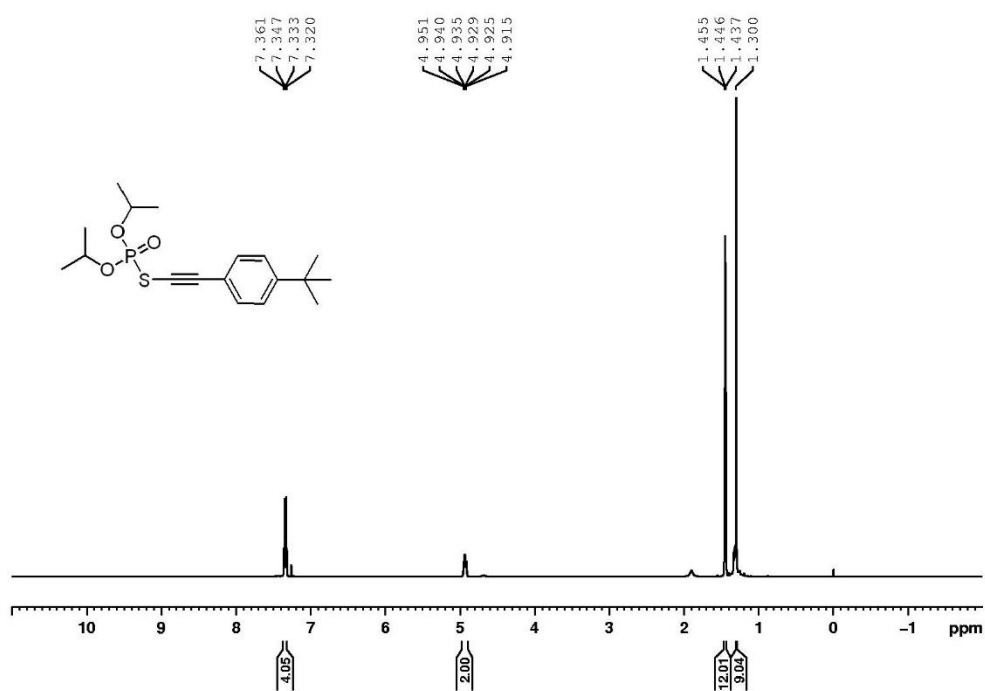
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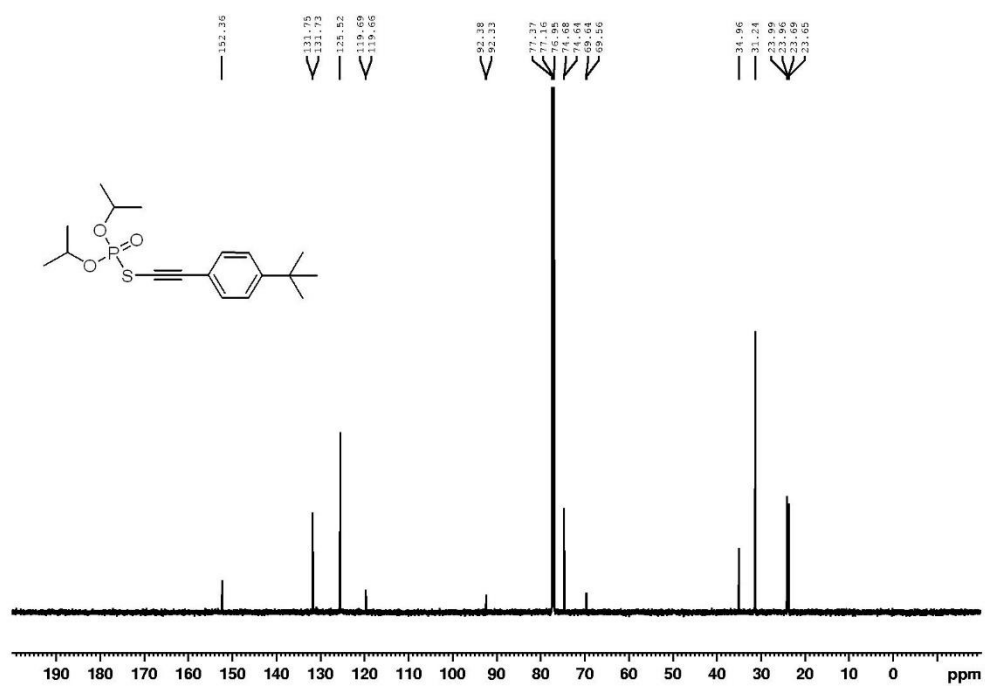
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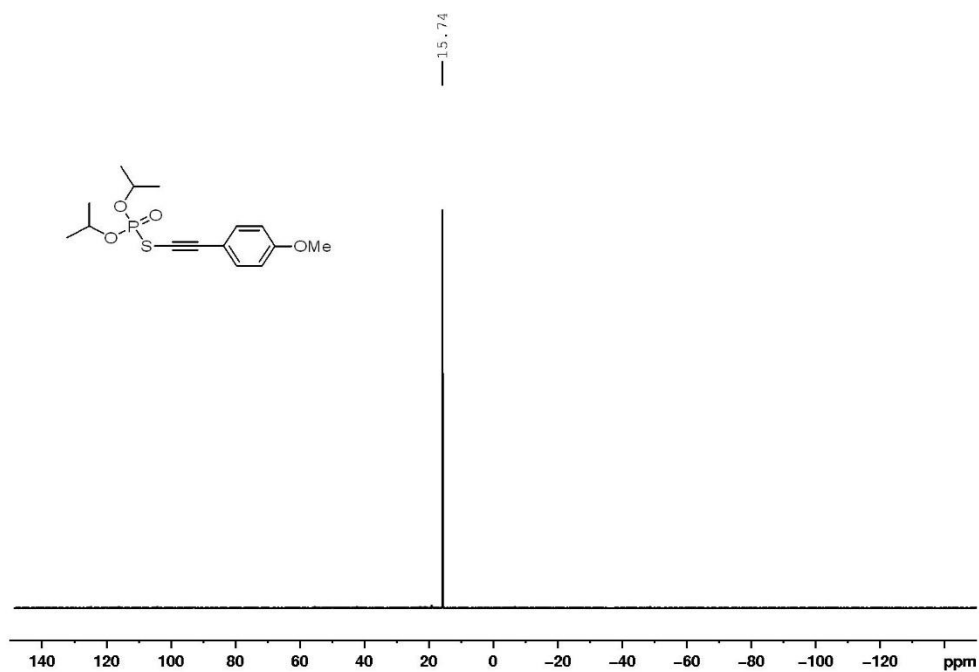
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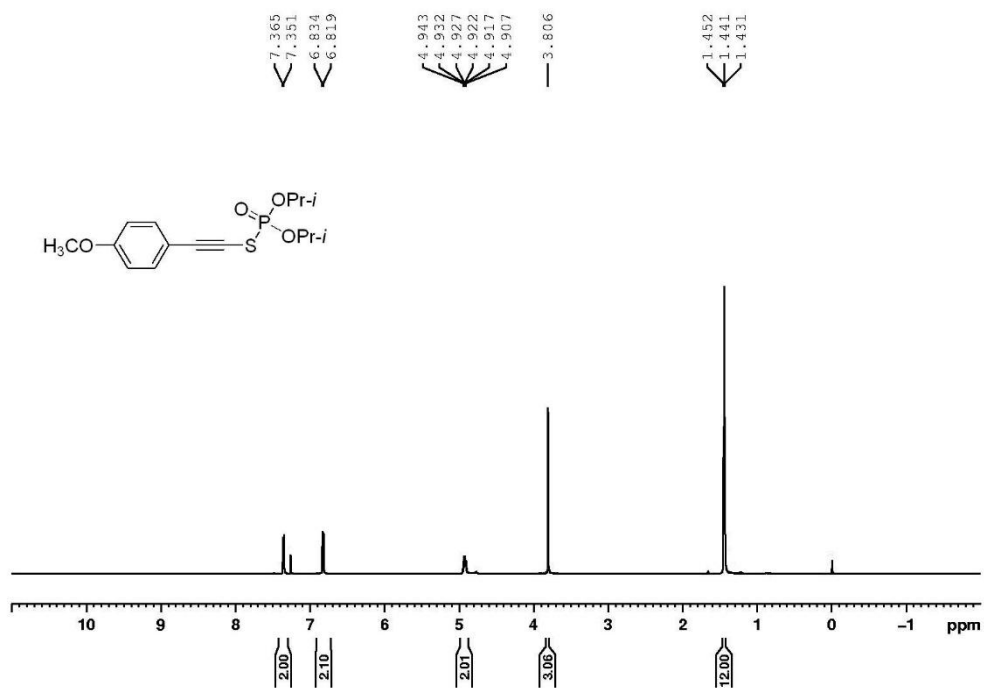
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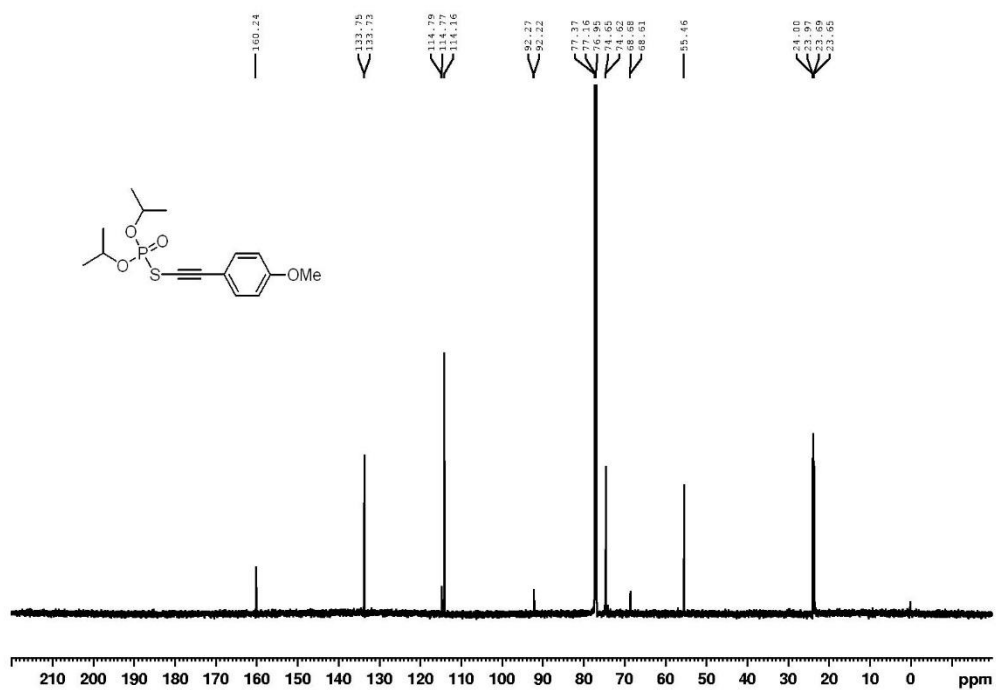
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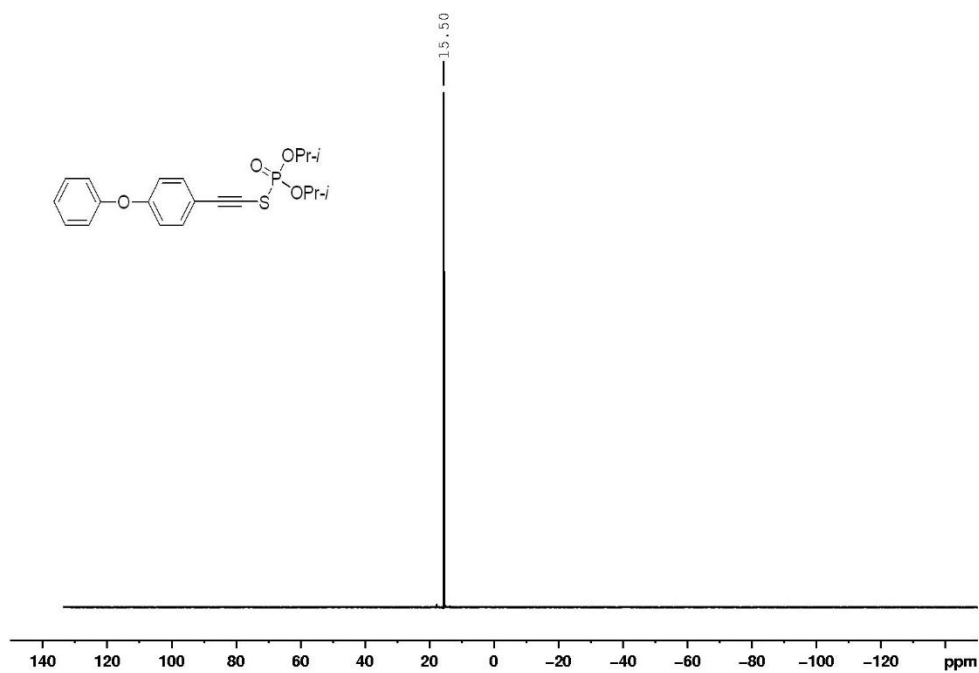
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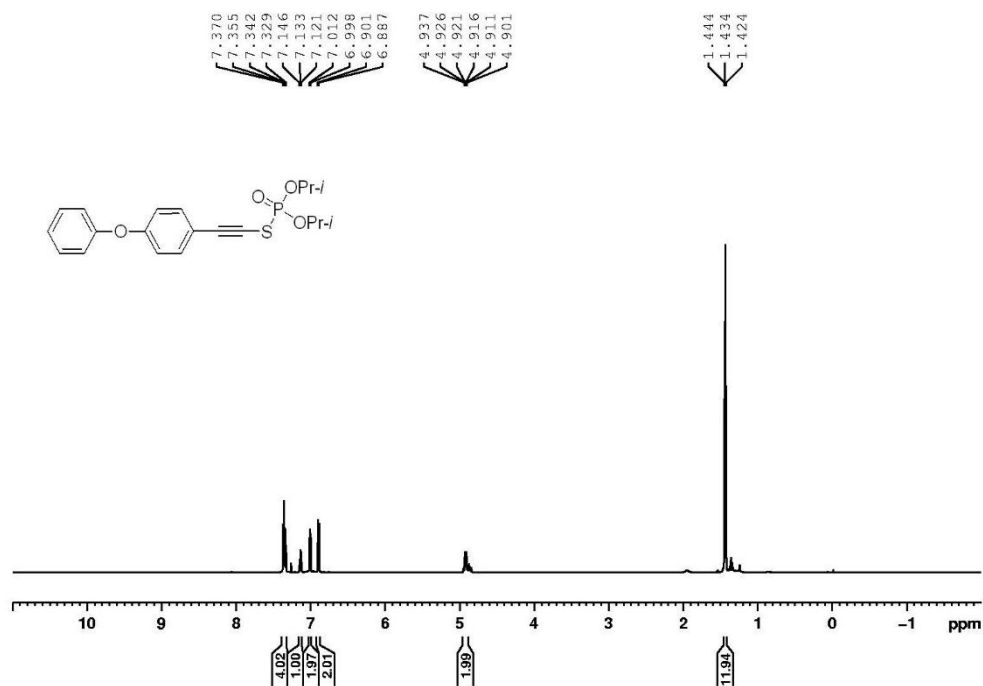
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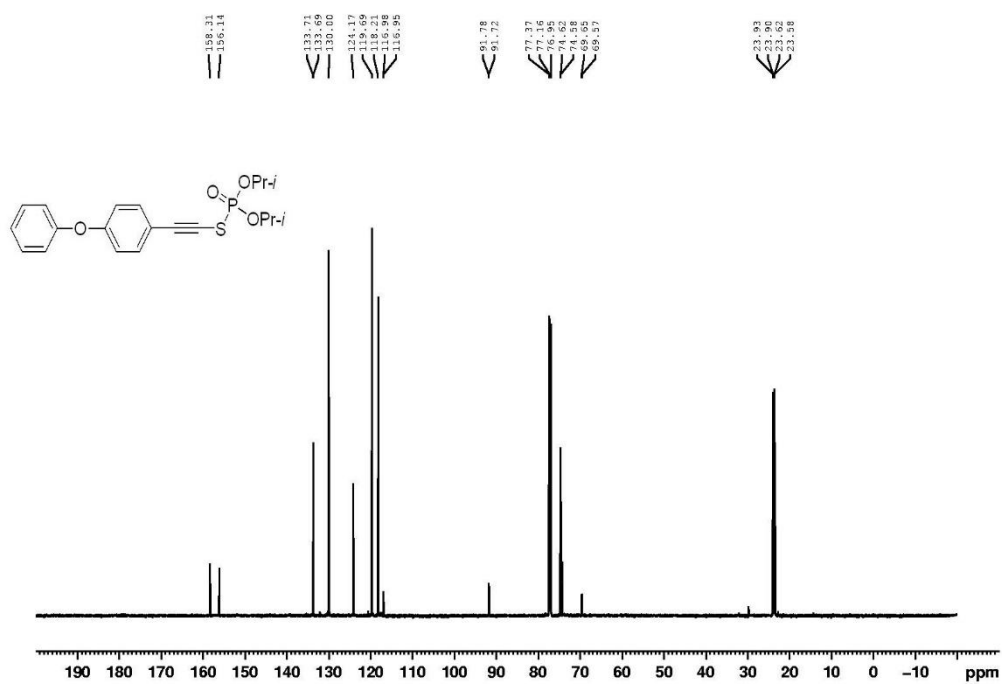
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24

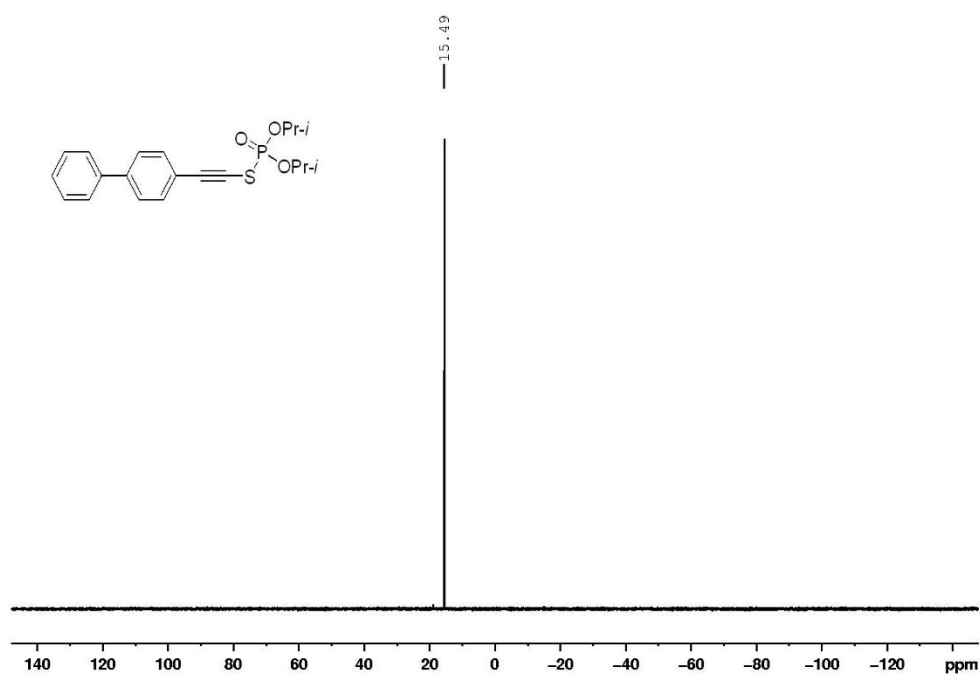


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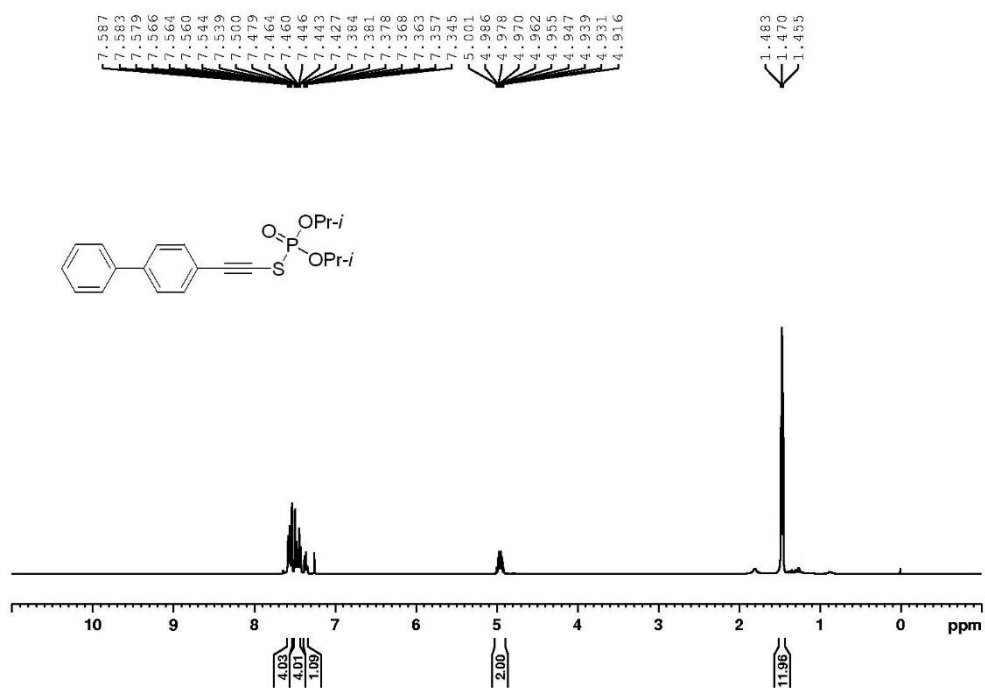


ESI-48

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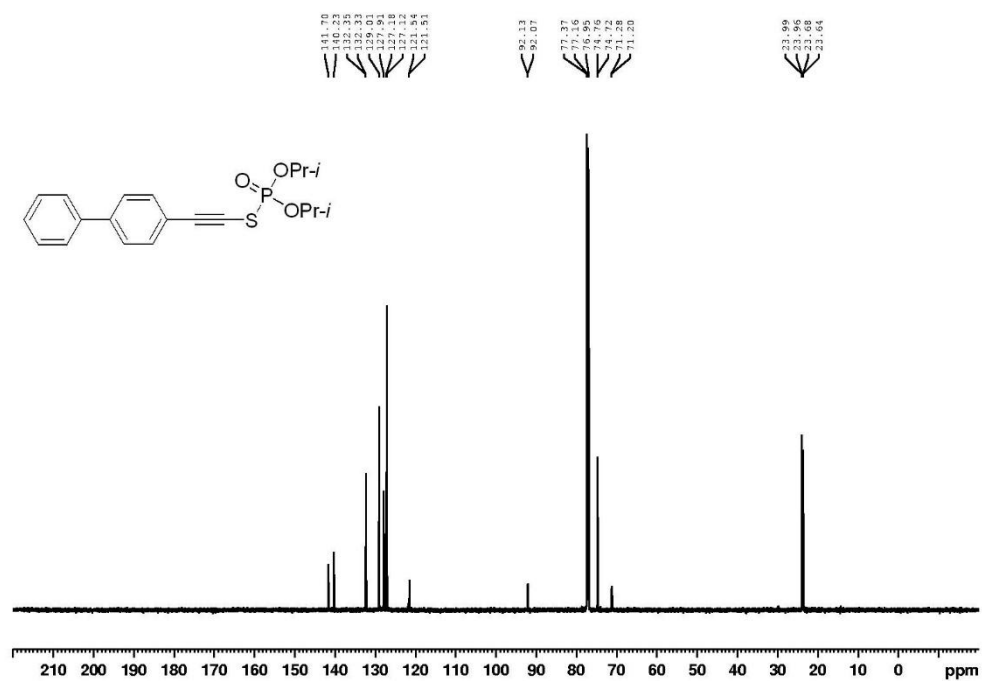


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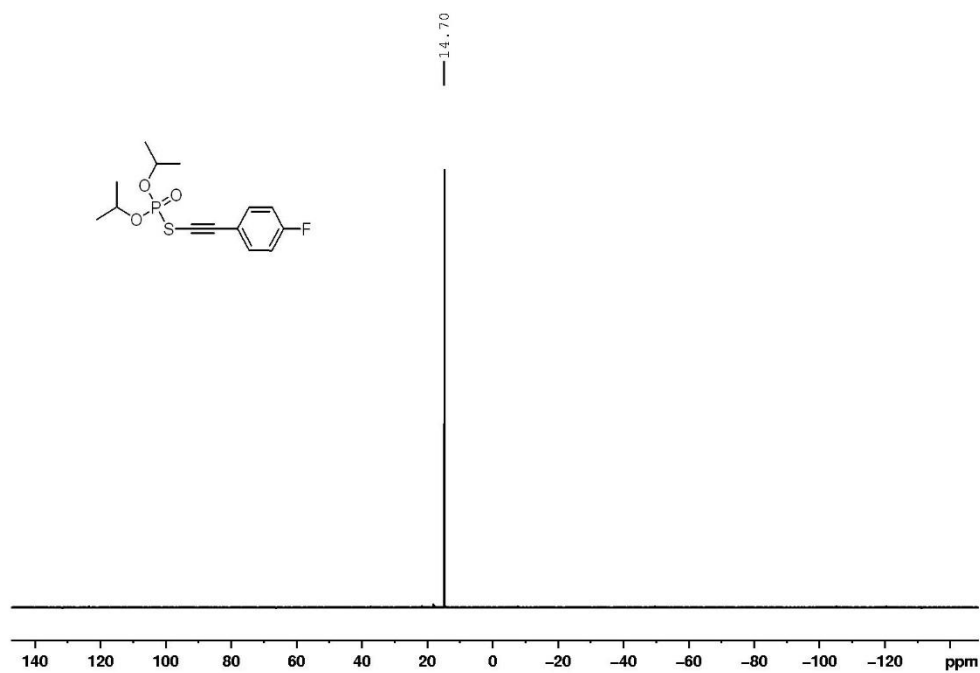


ESI-49

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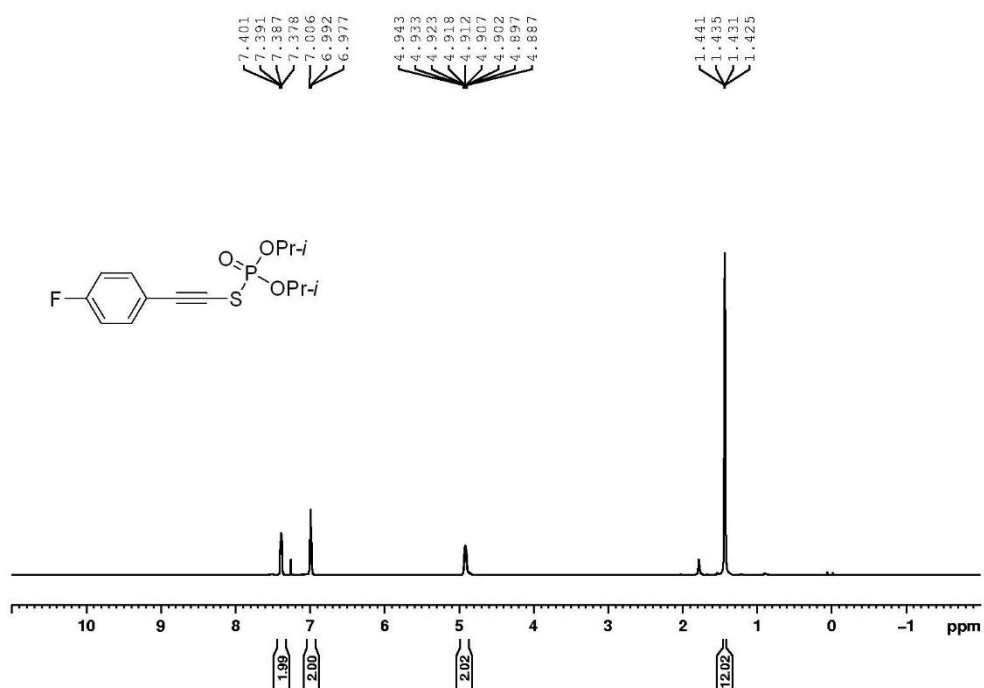


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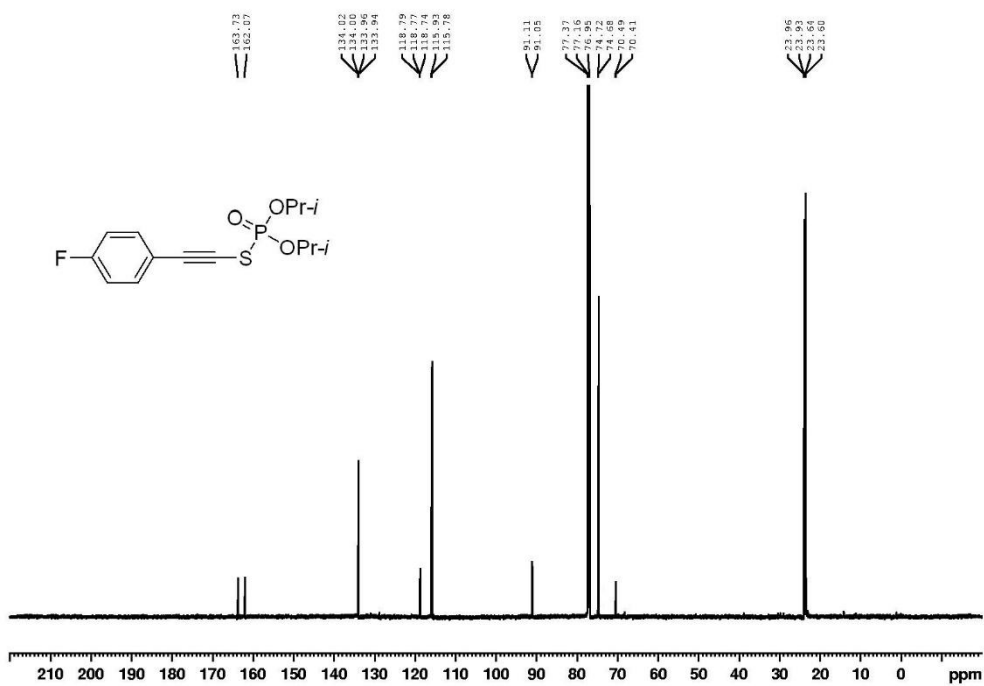


ESI-50

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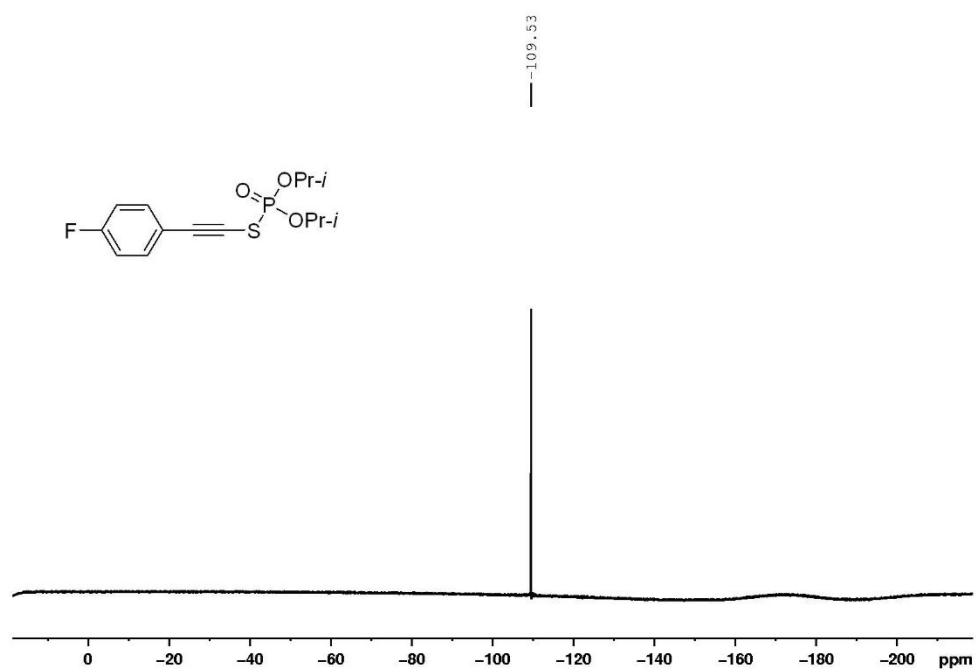


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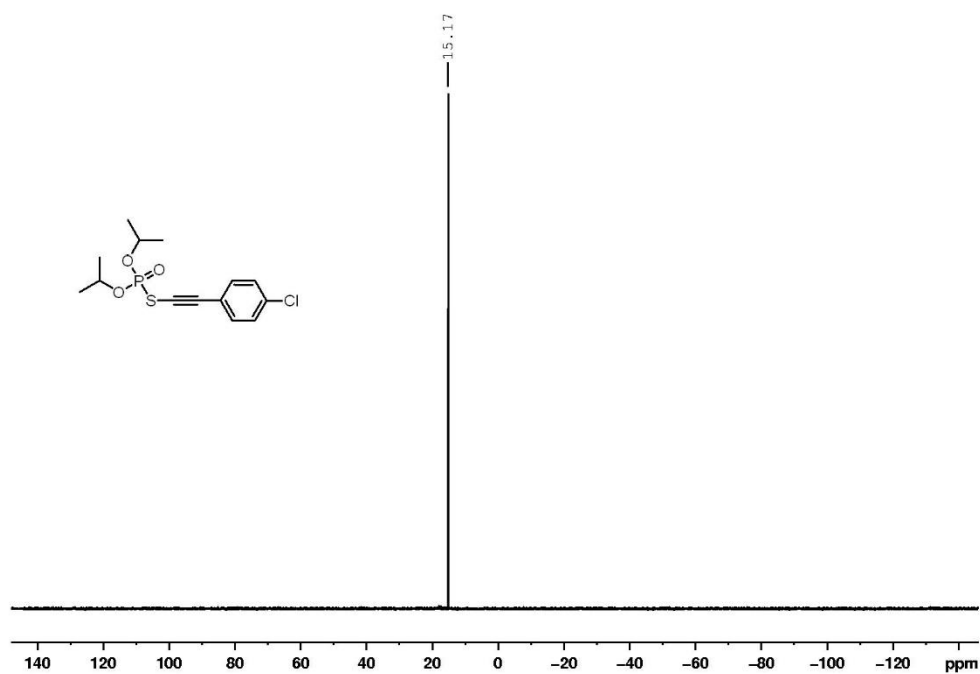


ESI-51

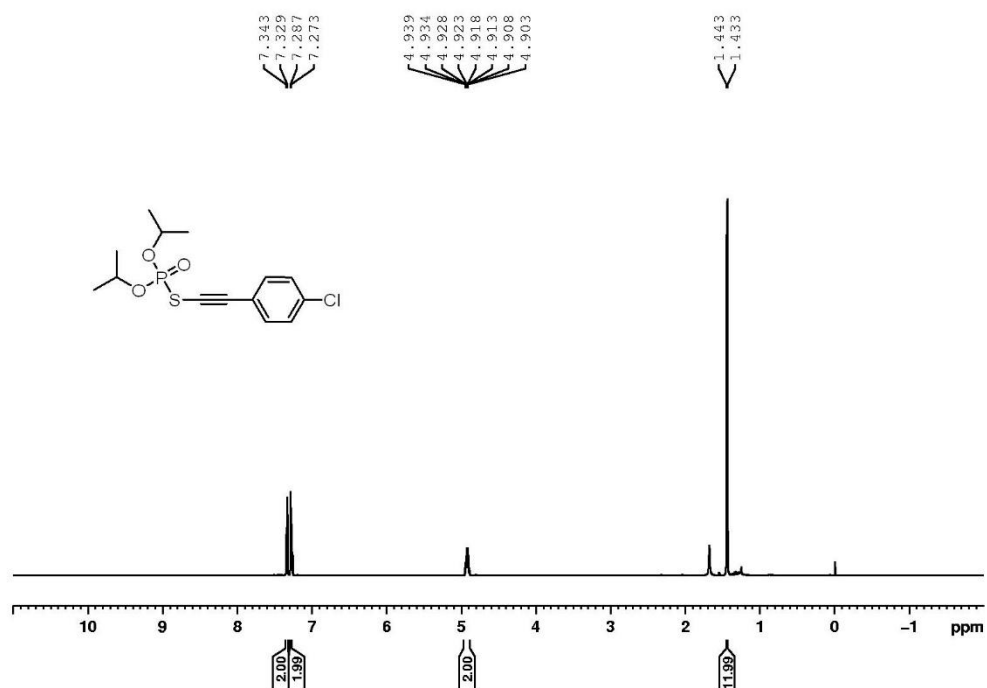
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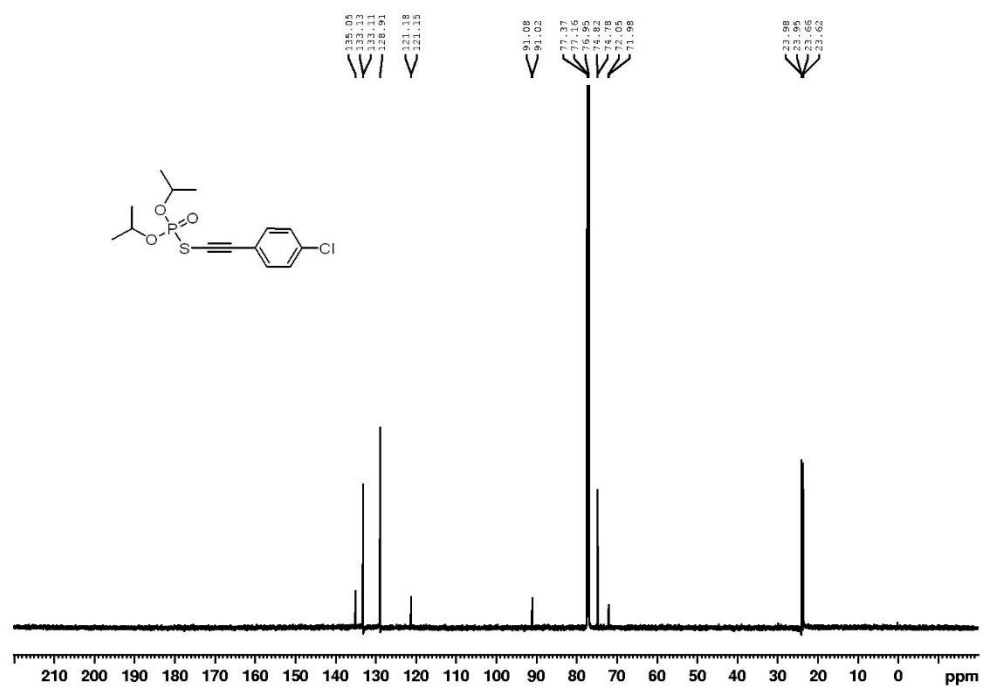
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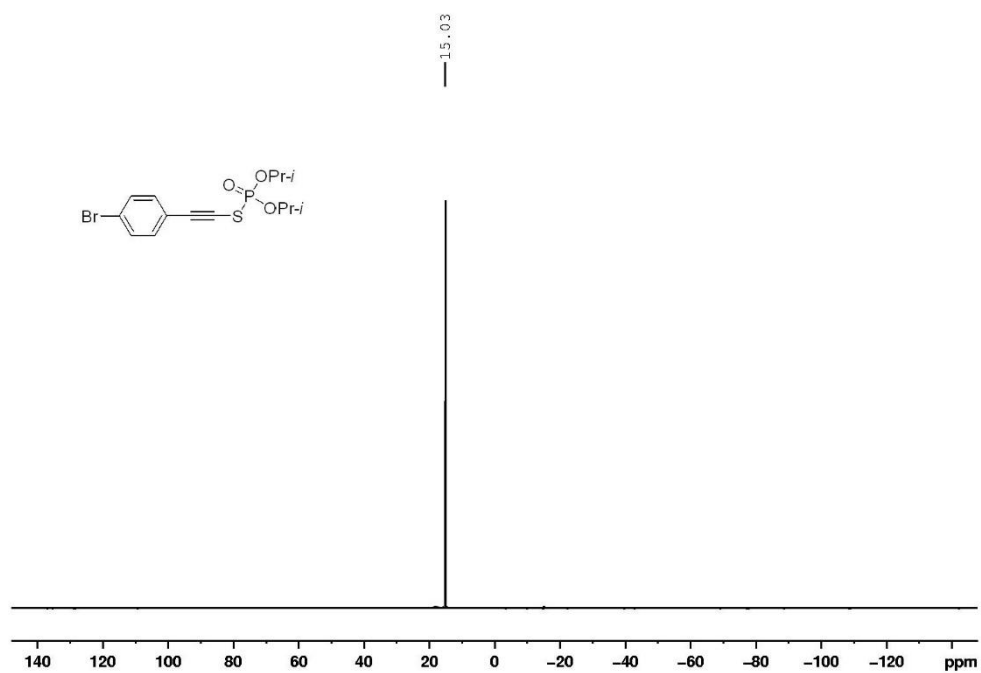
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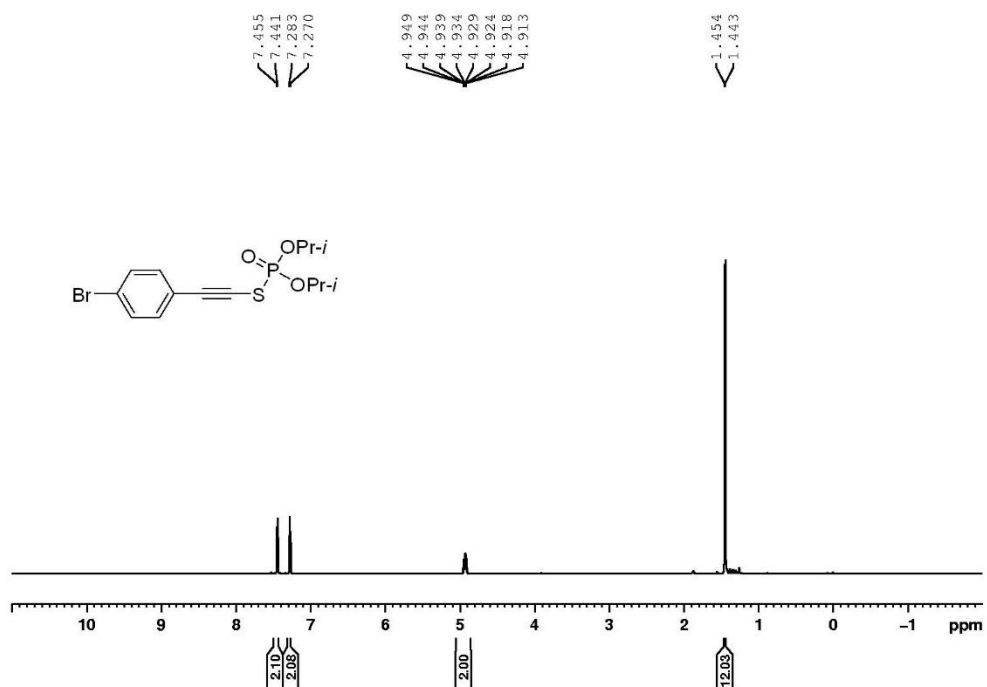
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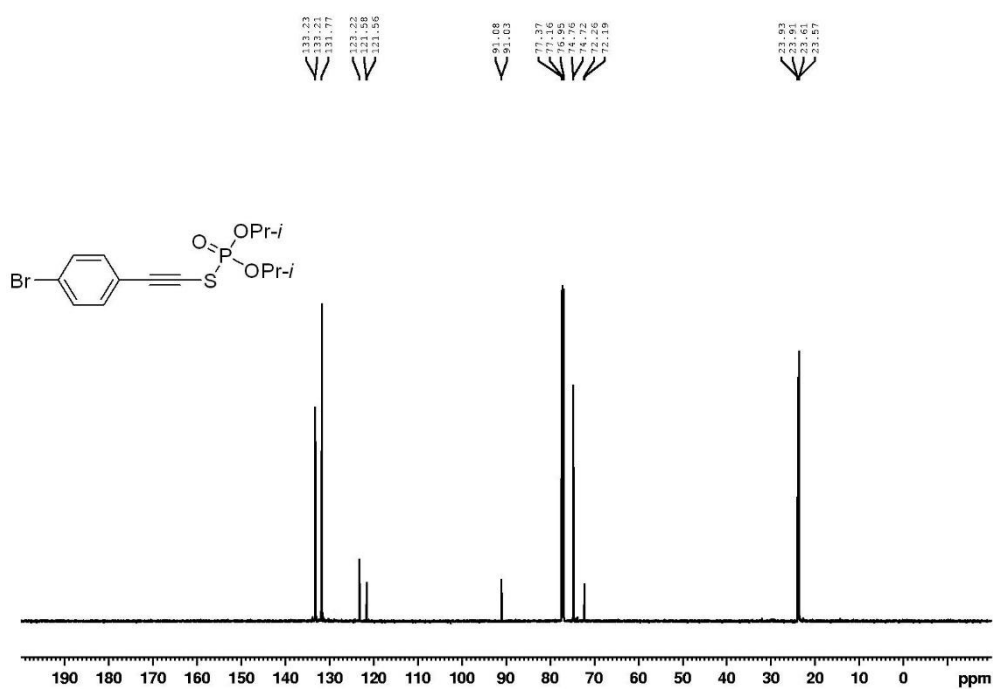


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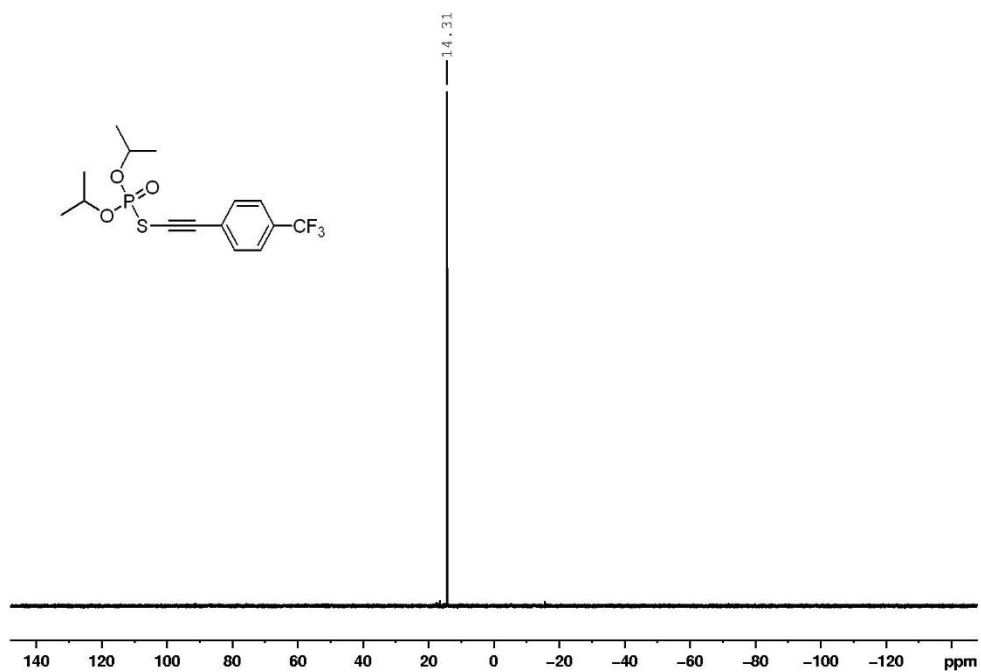


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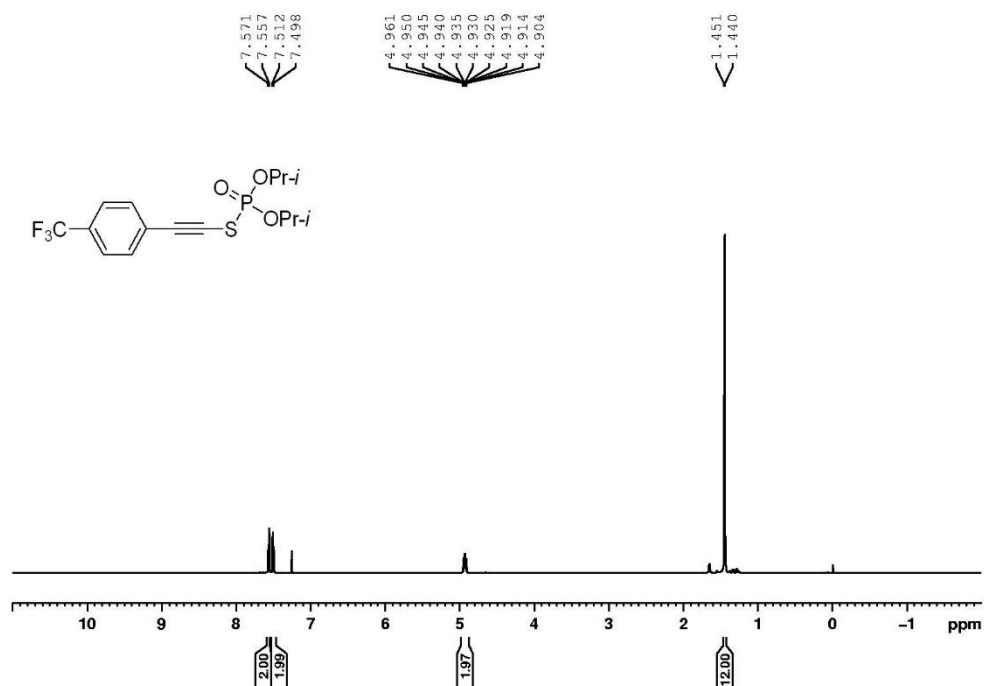
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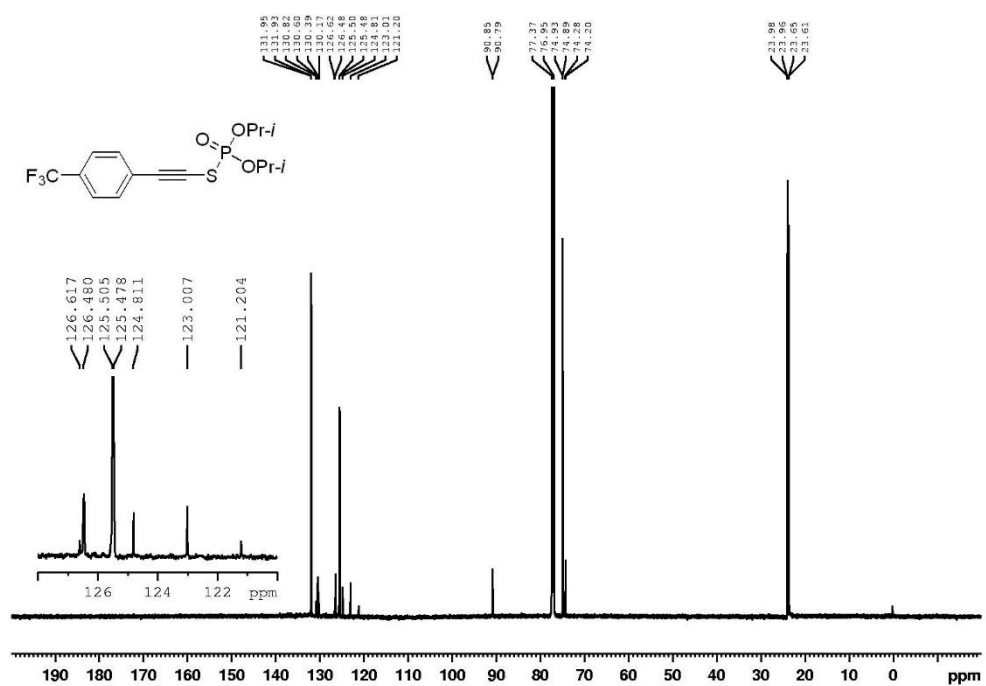
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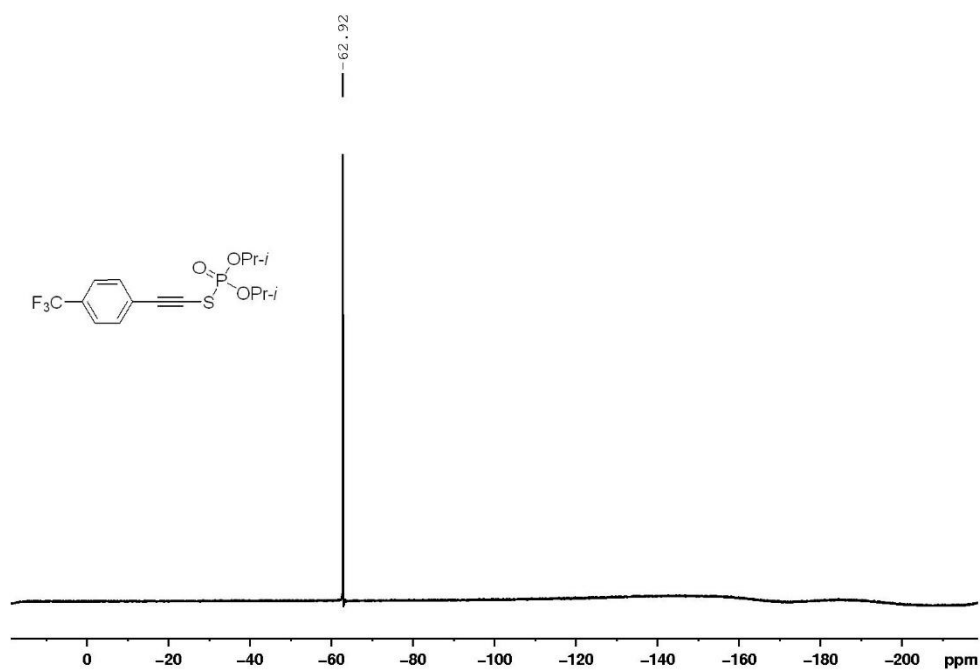
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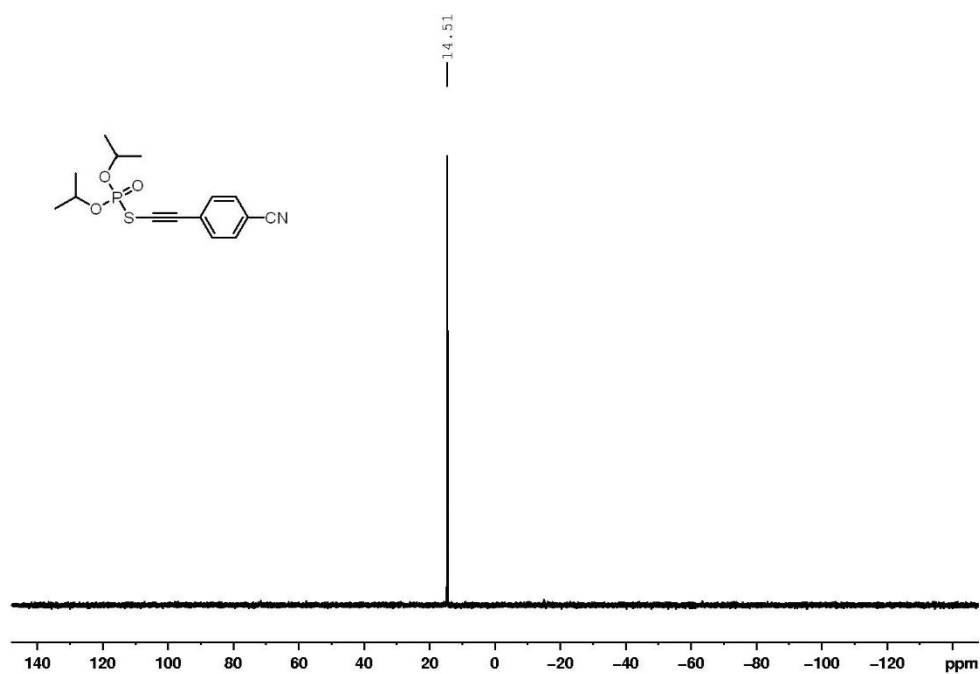
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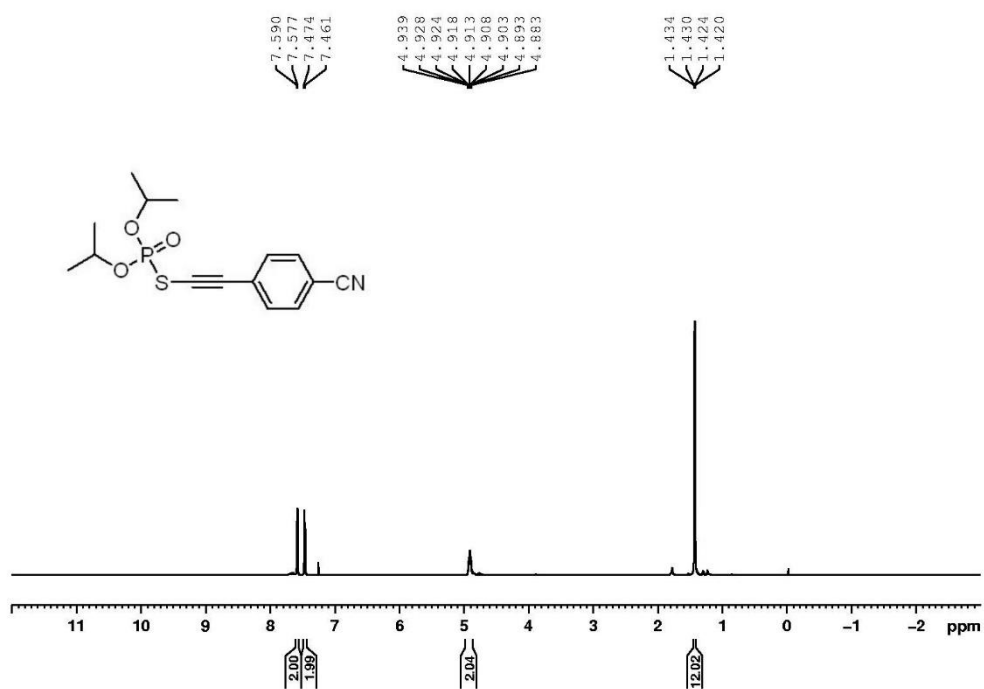
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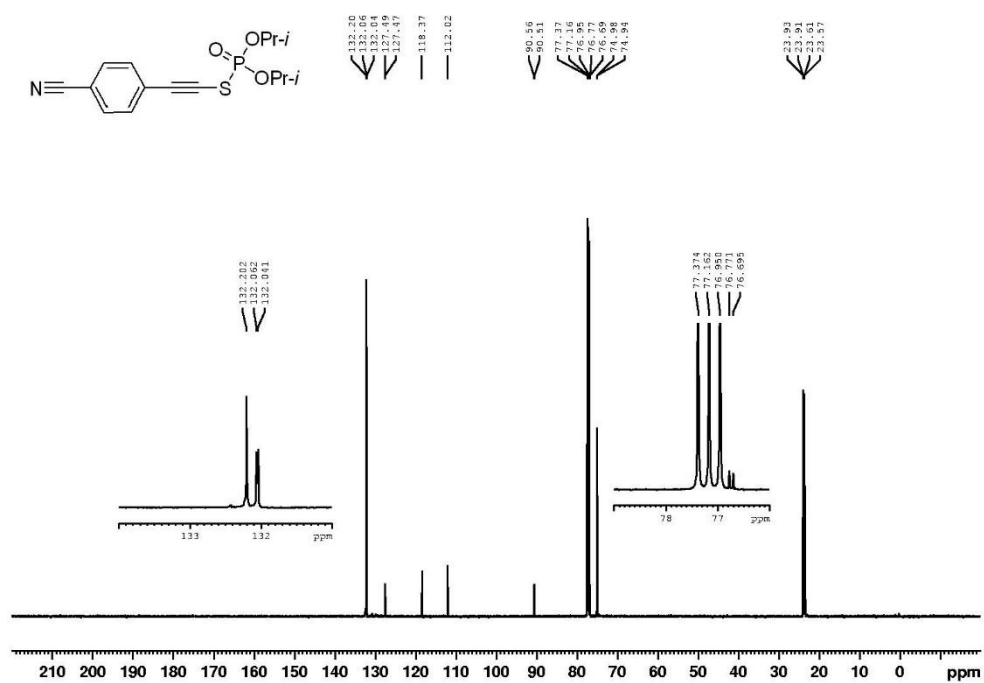
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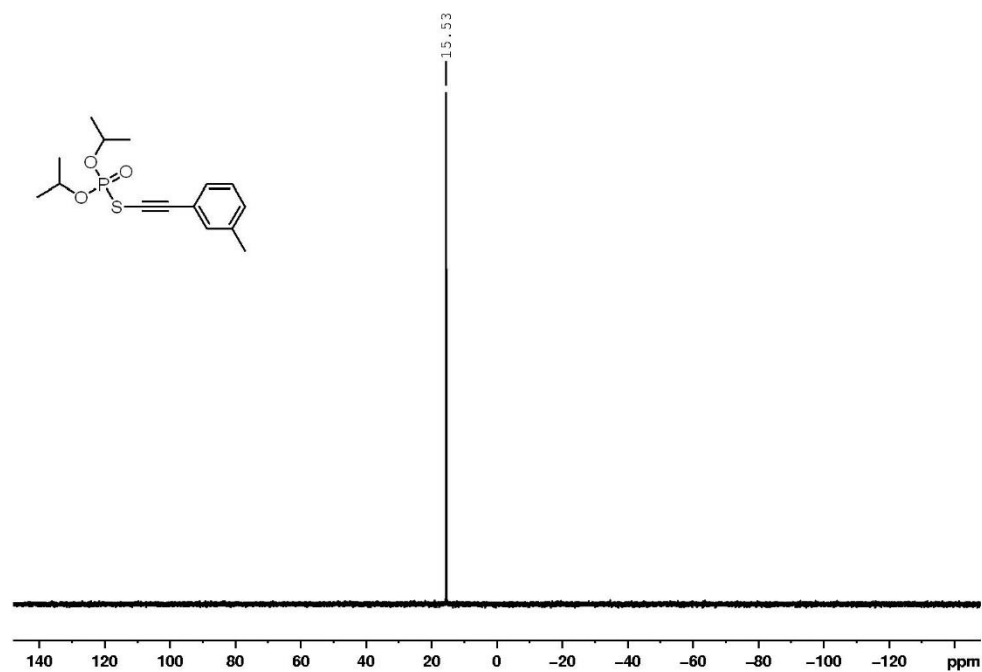
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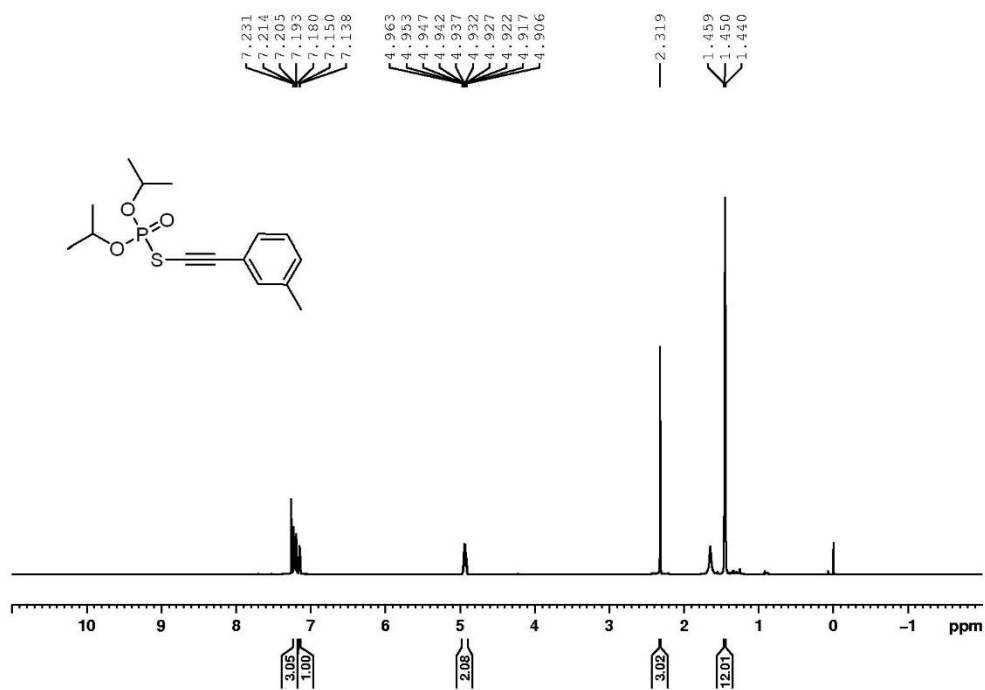
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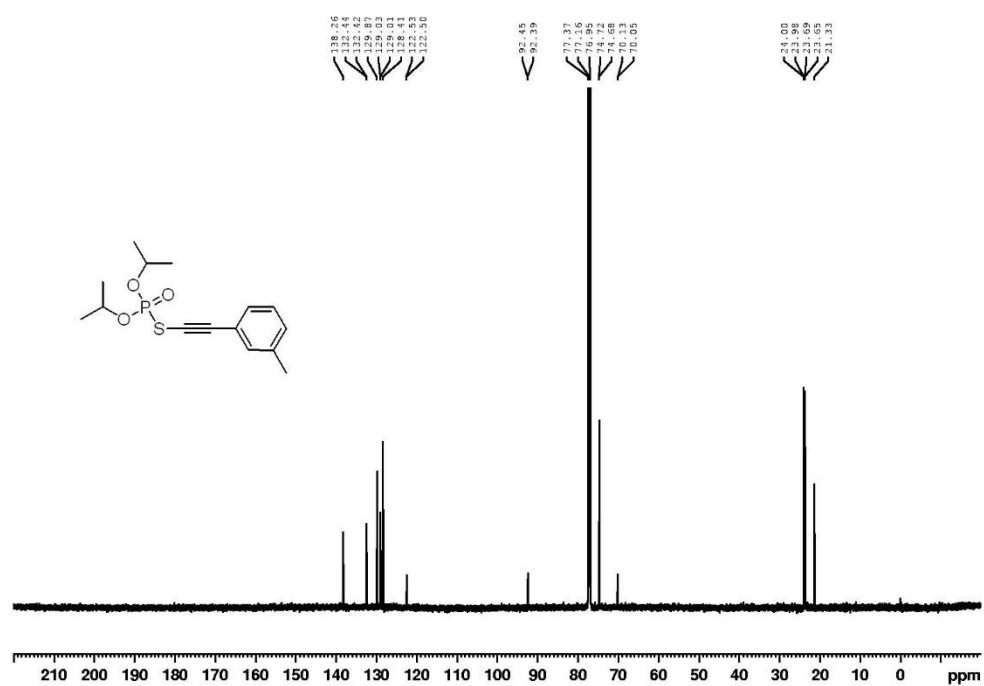


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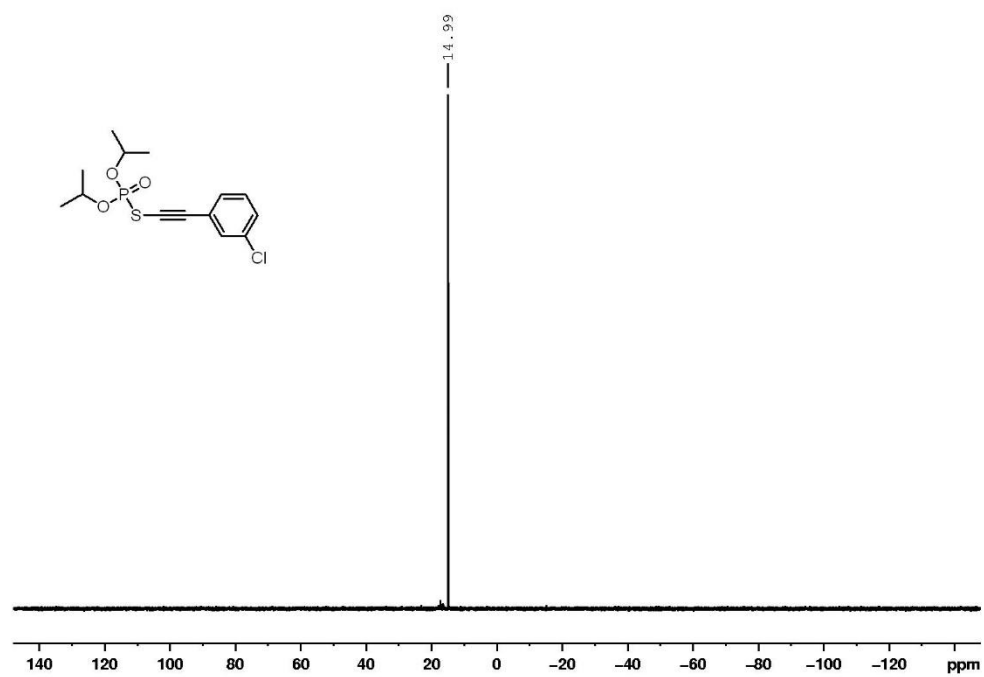


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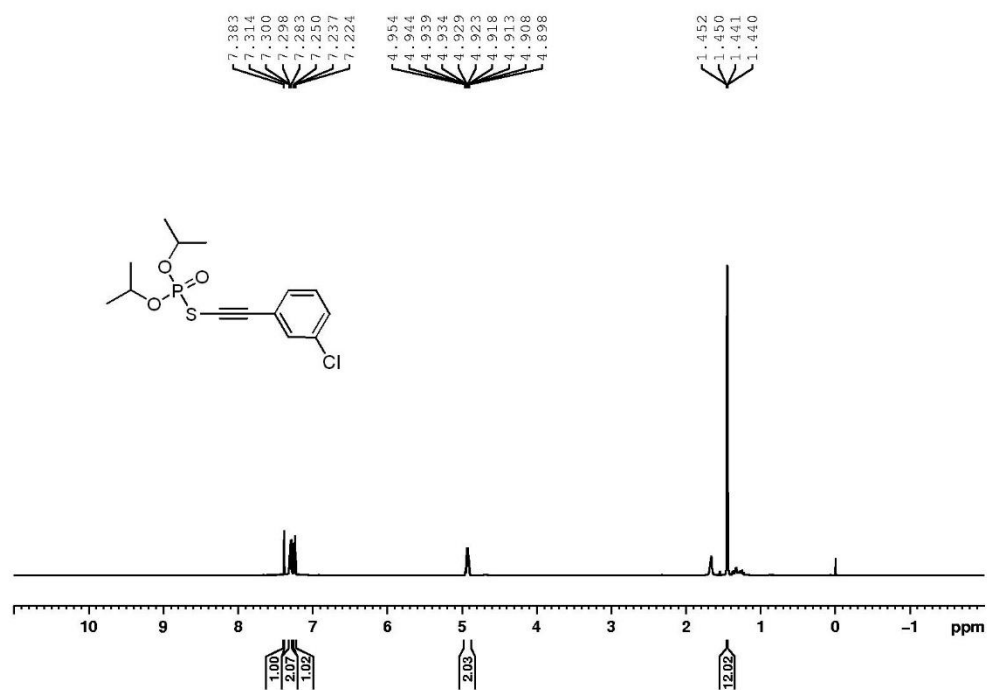


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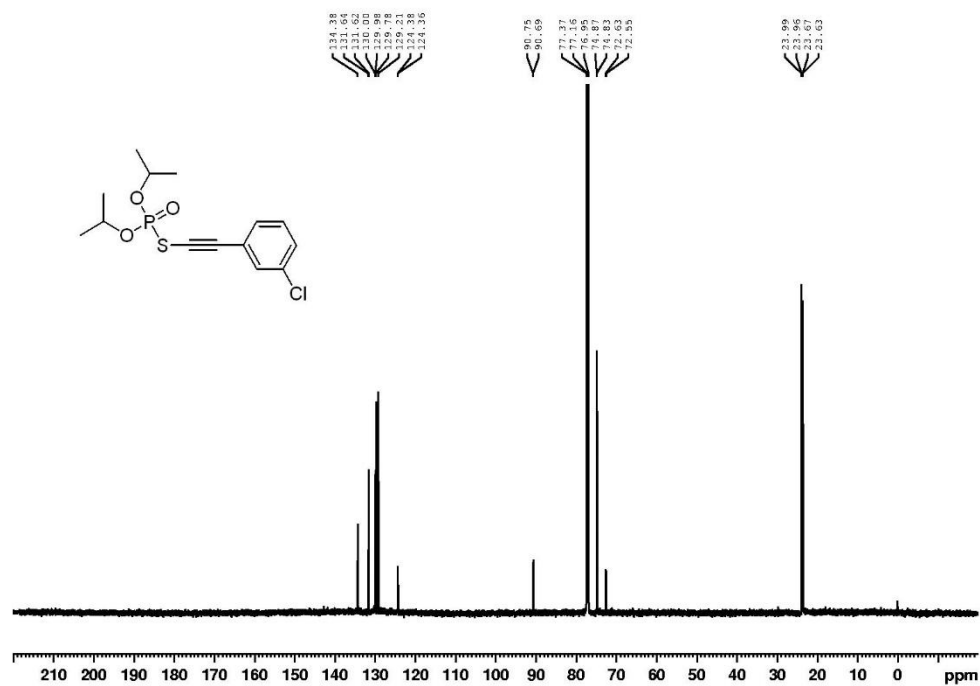


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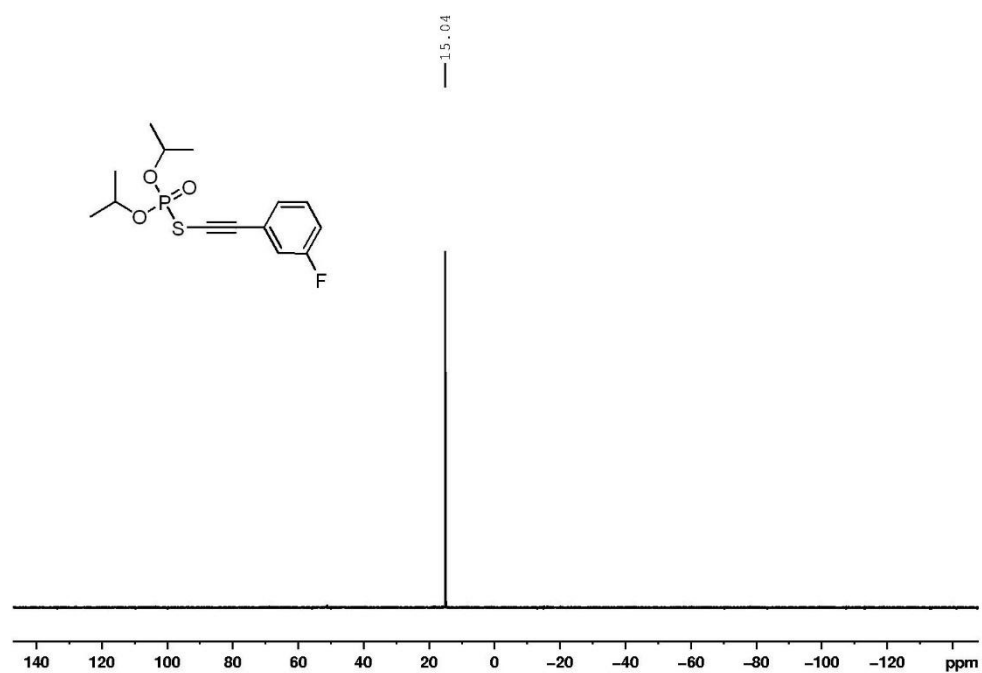


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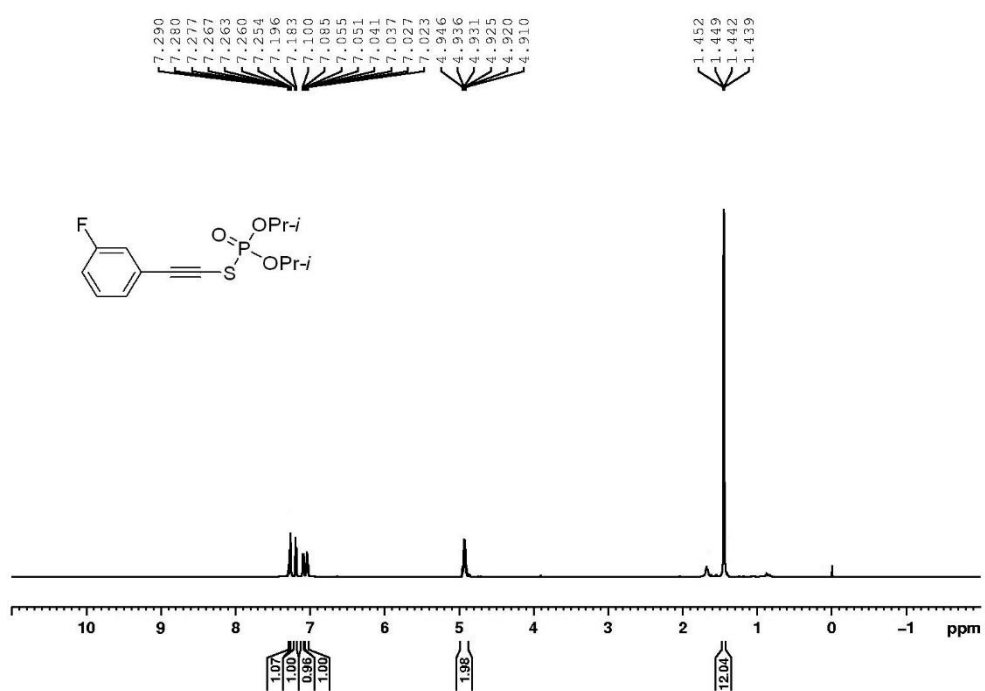


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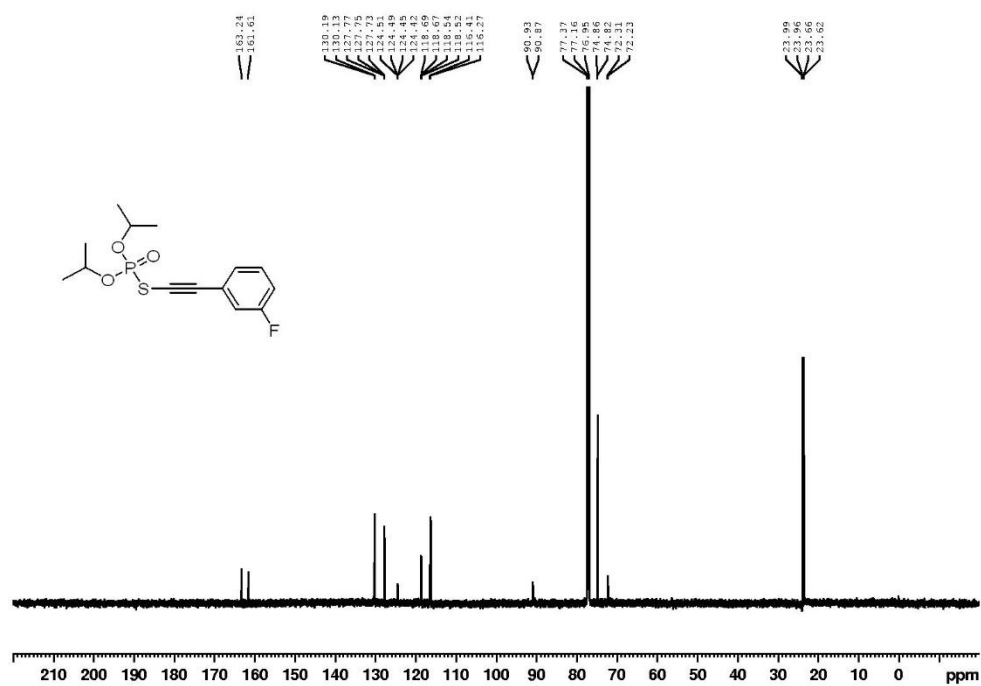


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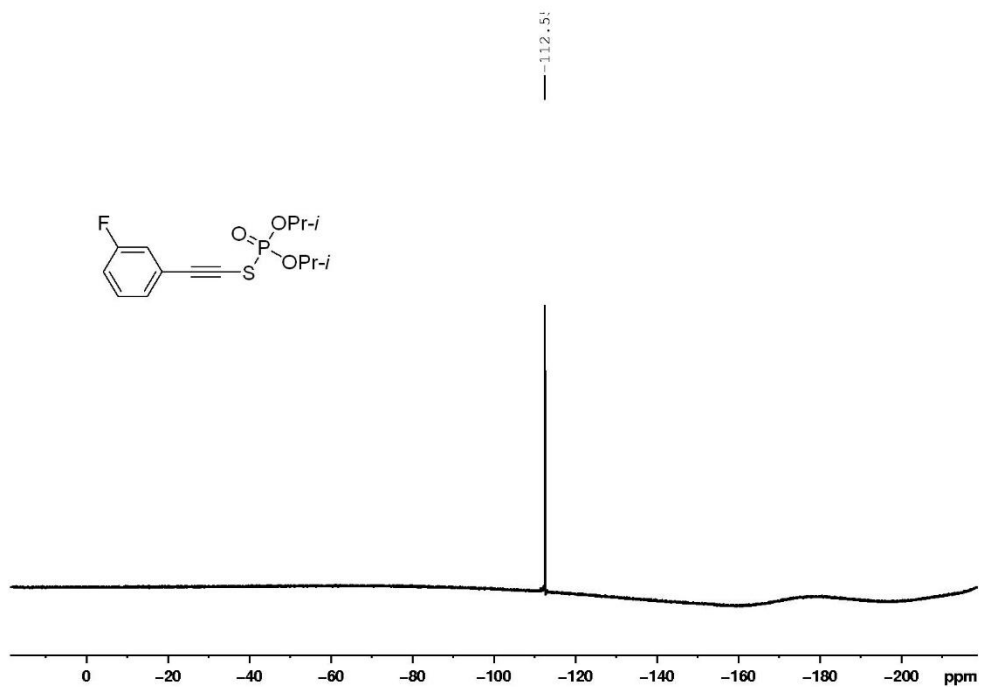


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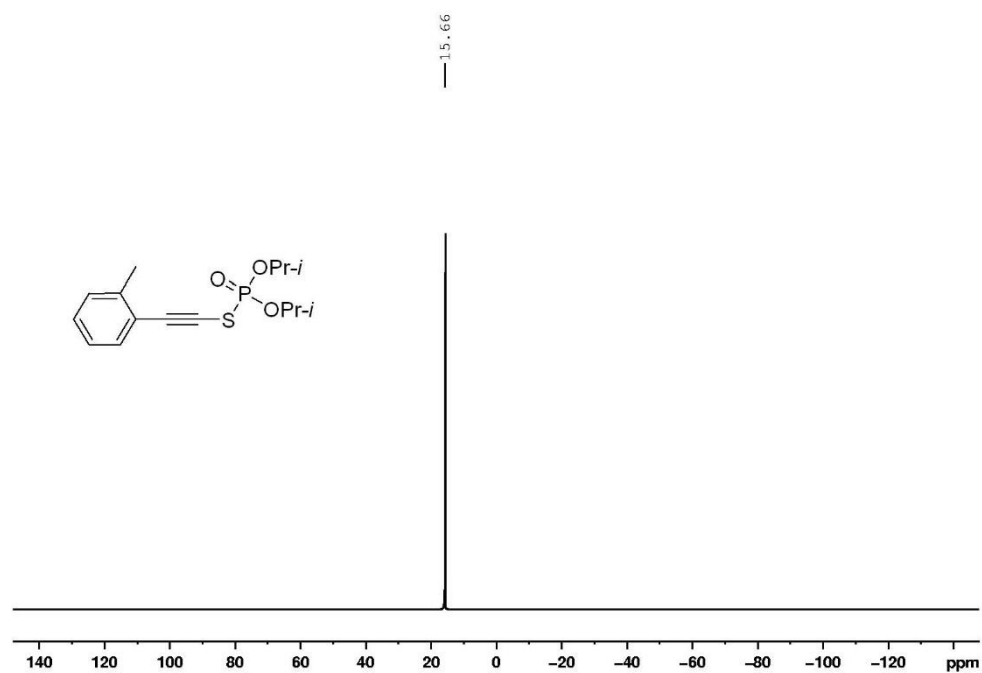
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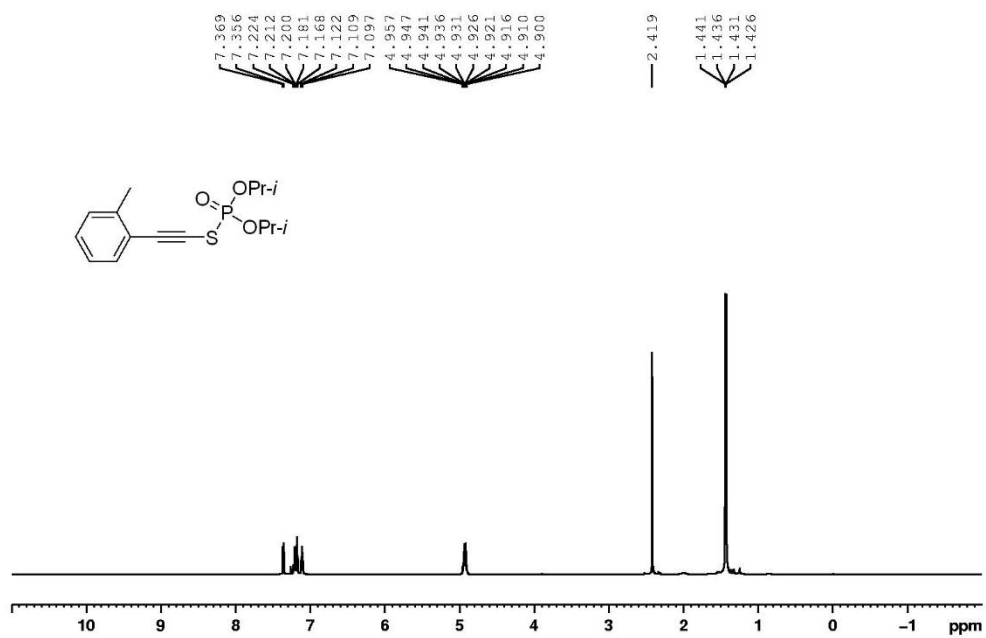
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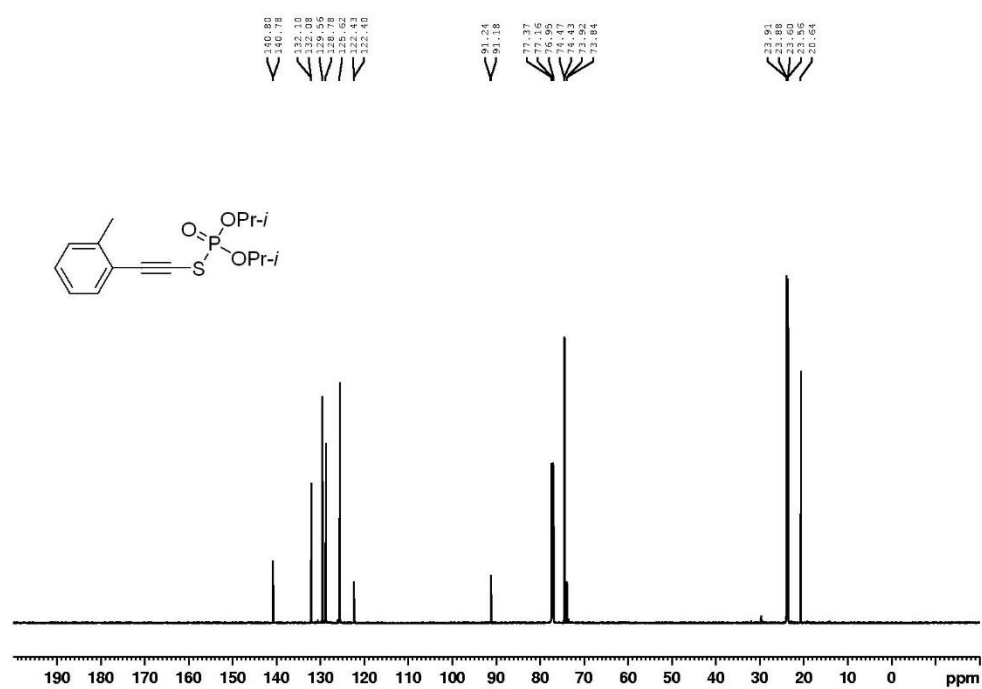


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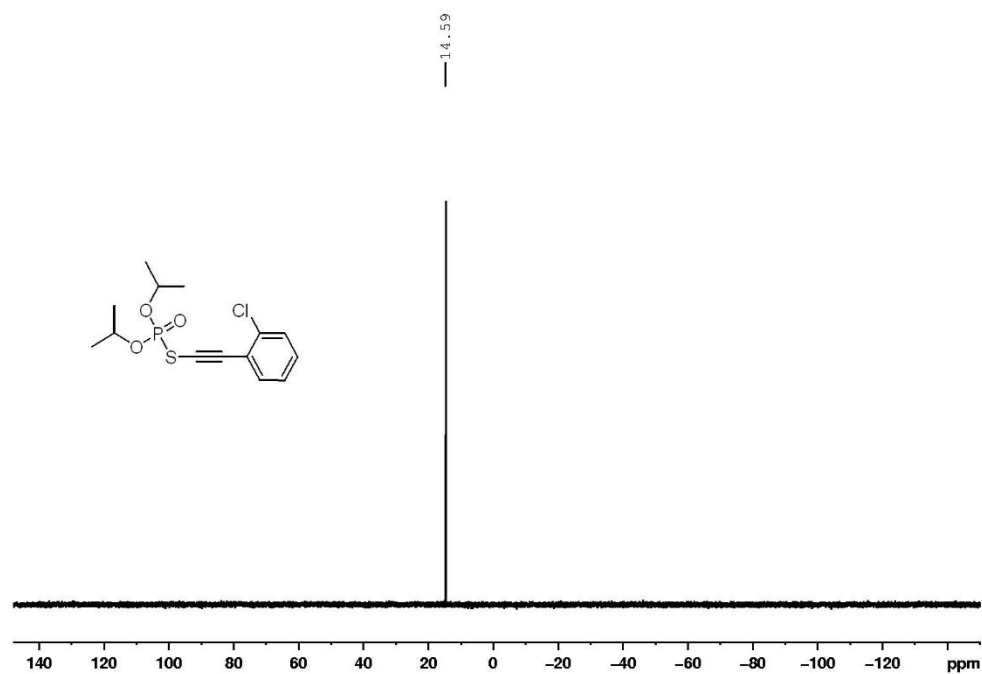


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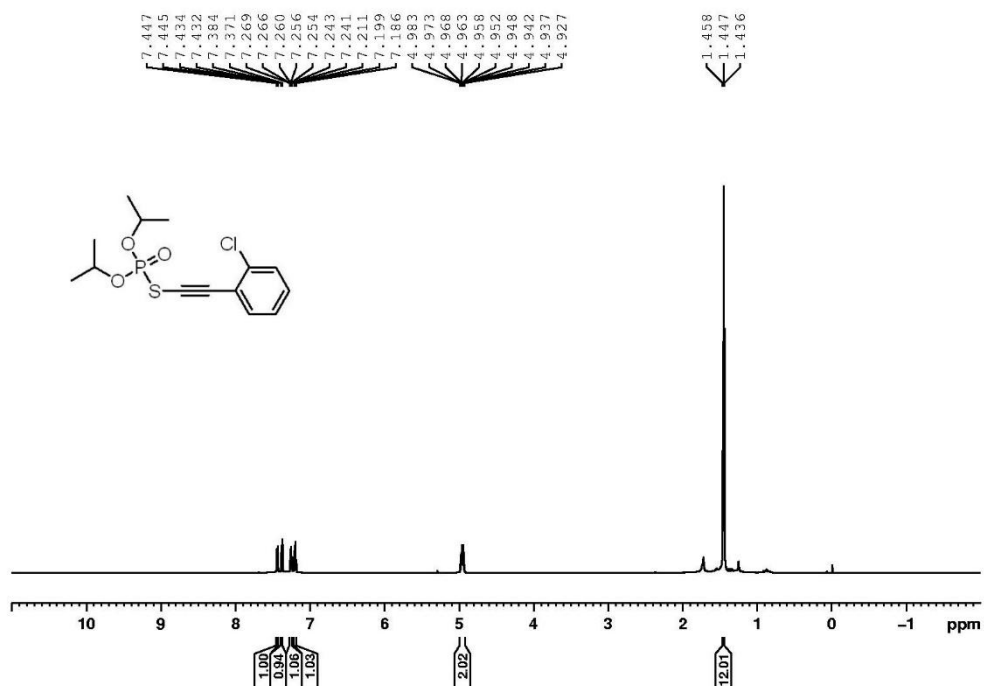


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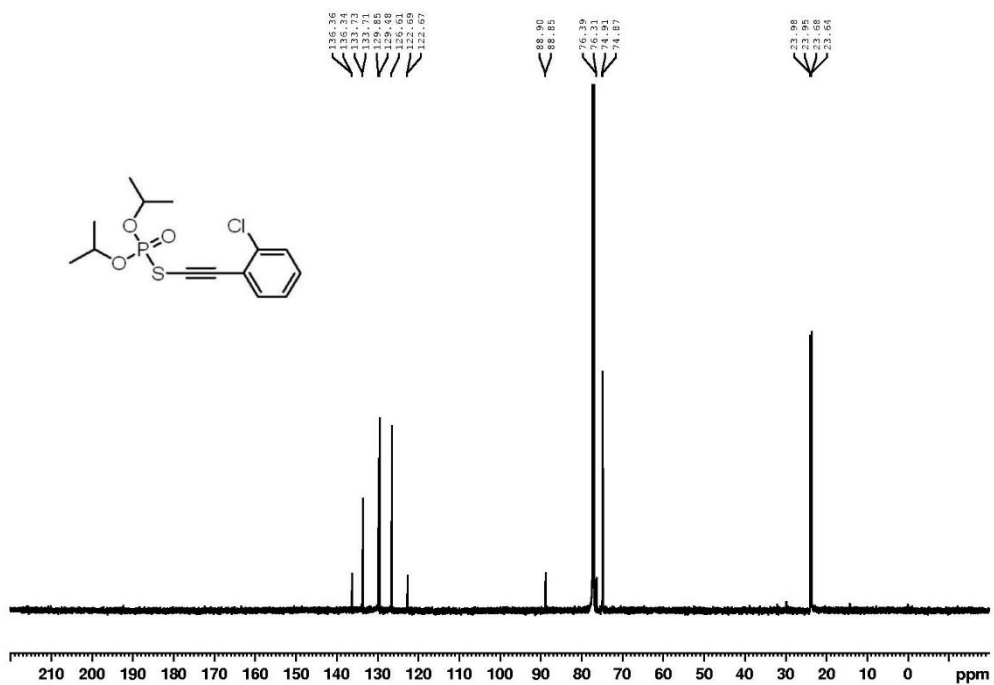


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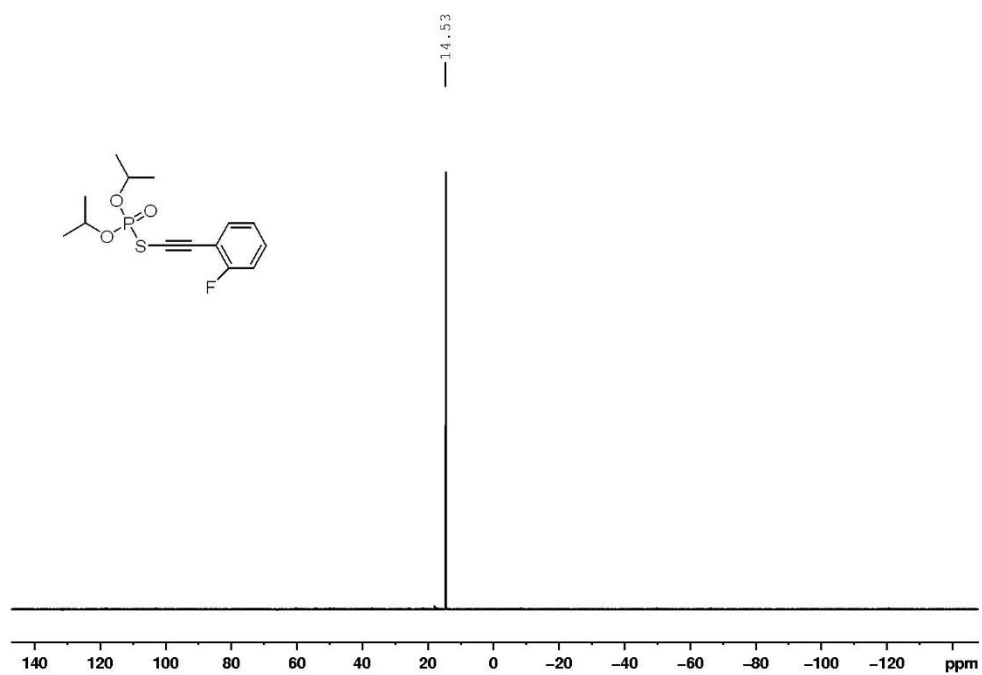
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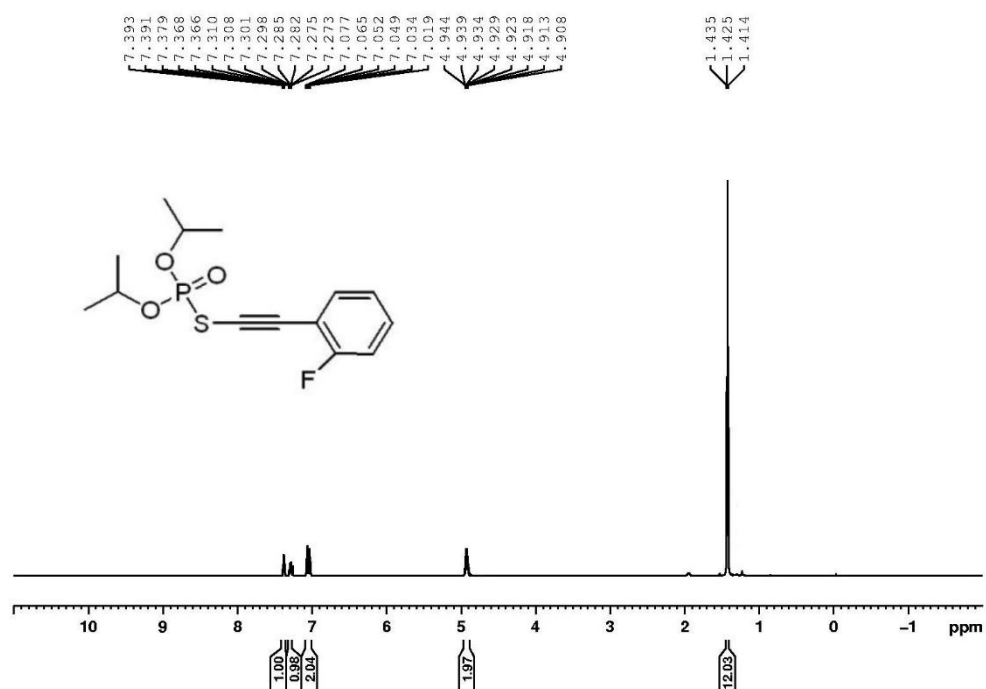
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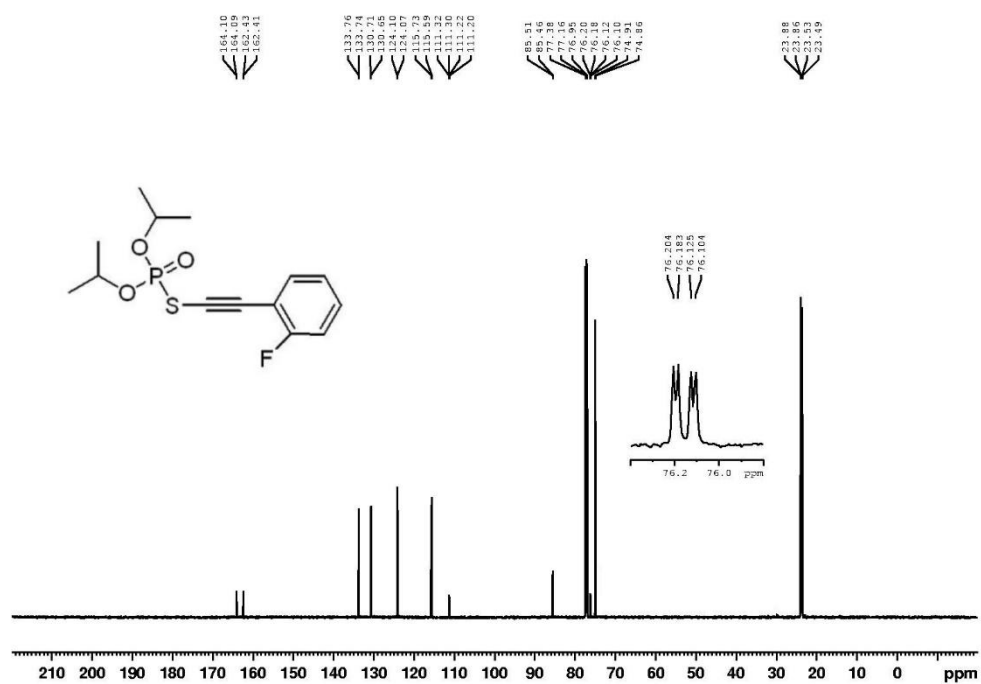


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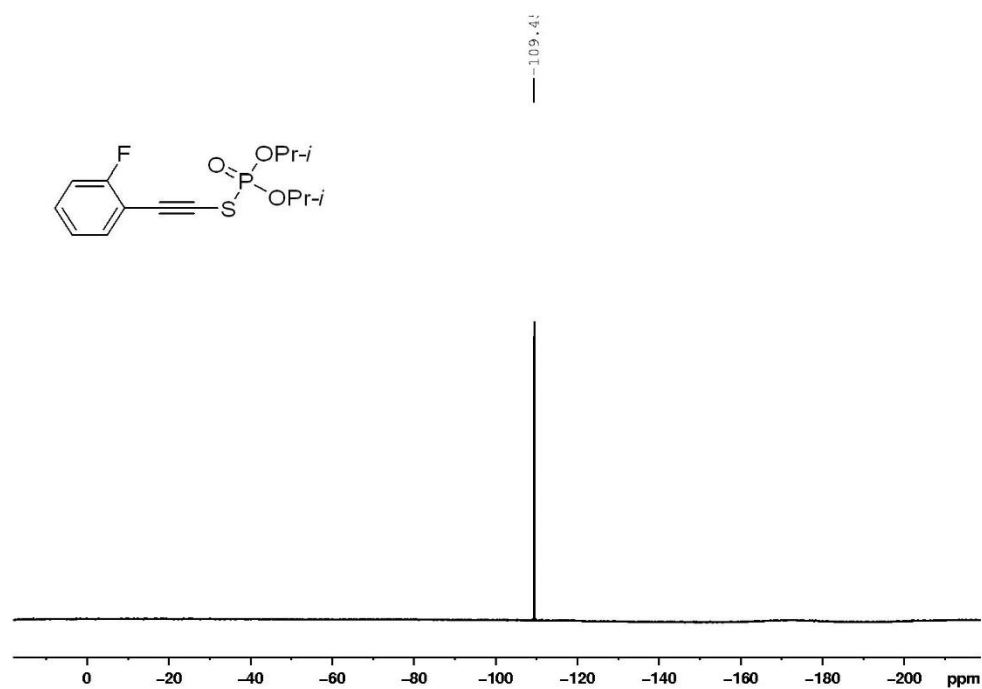


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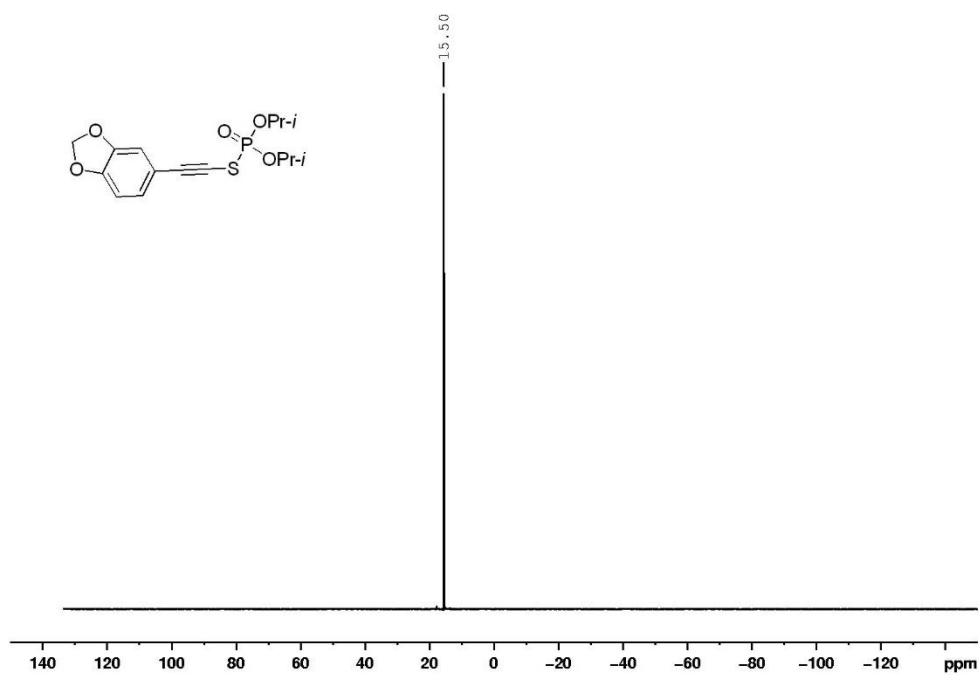


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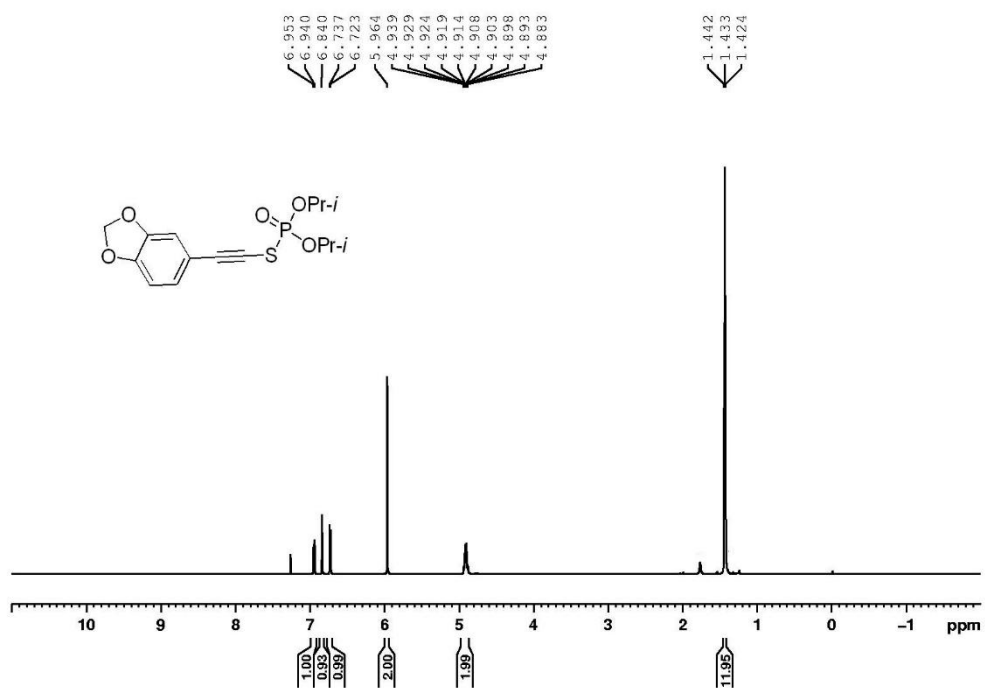


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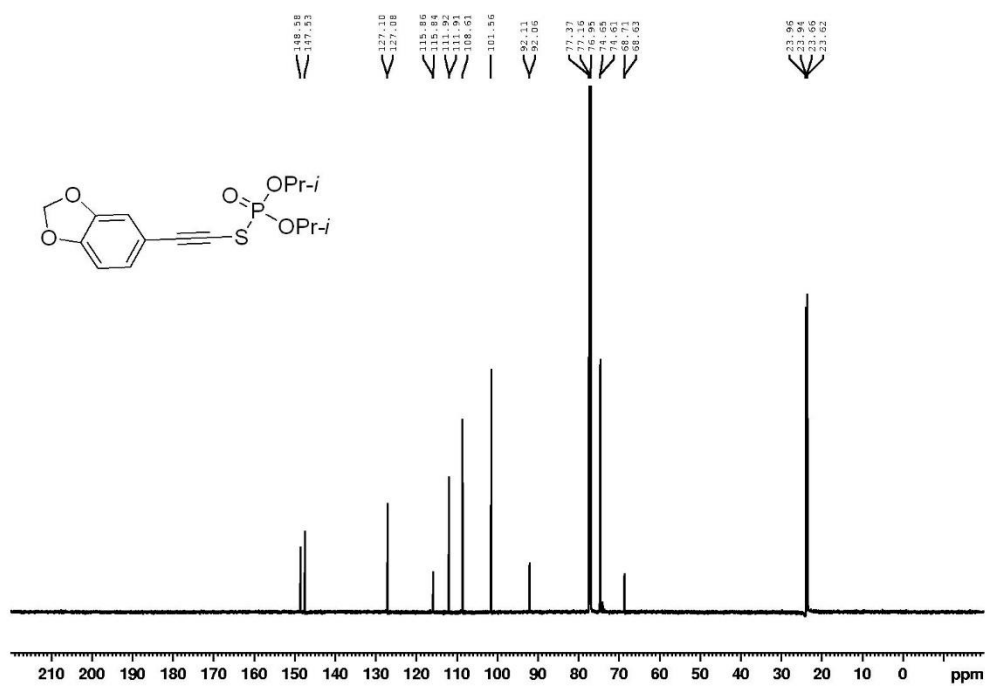


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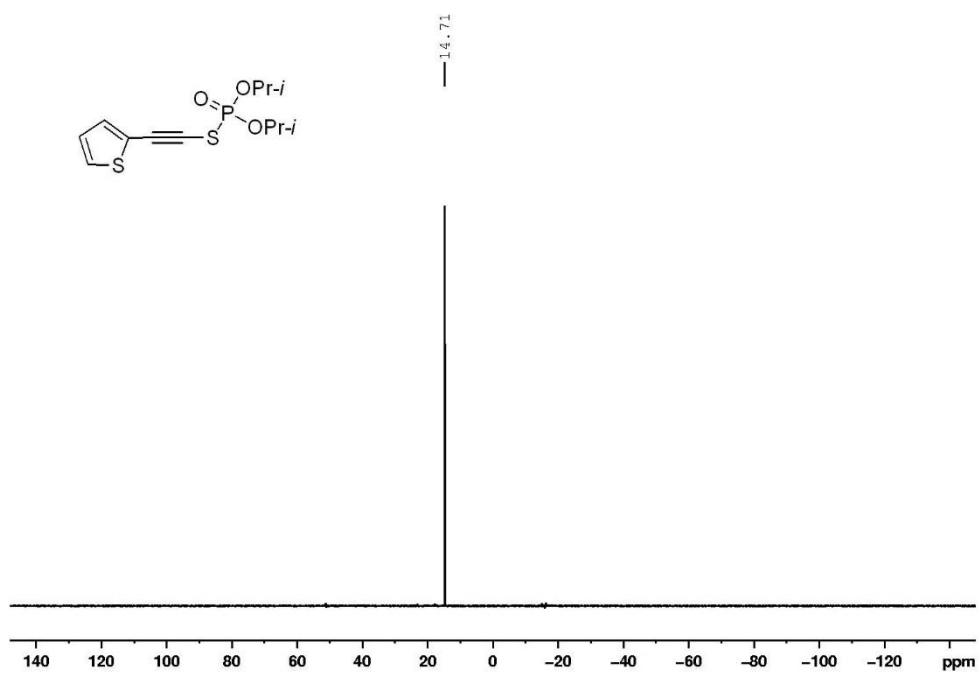


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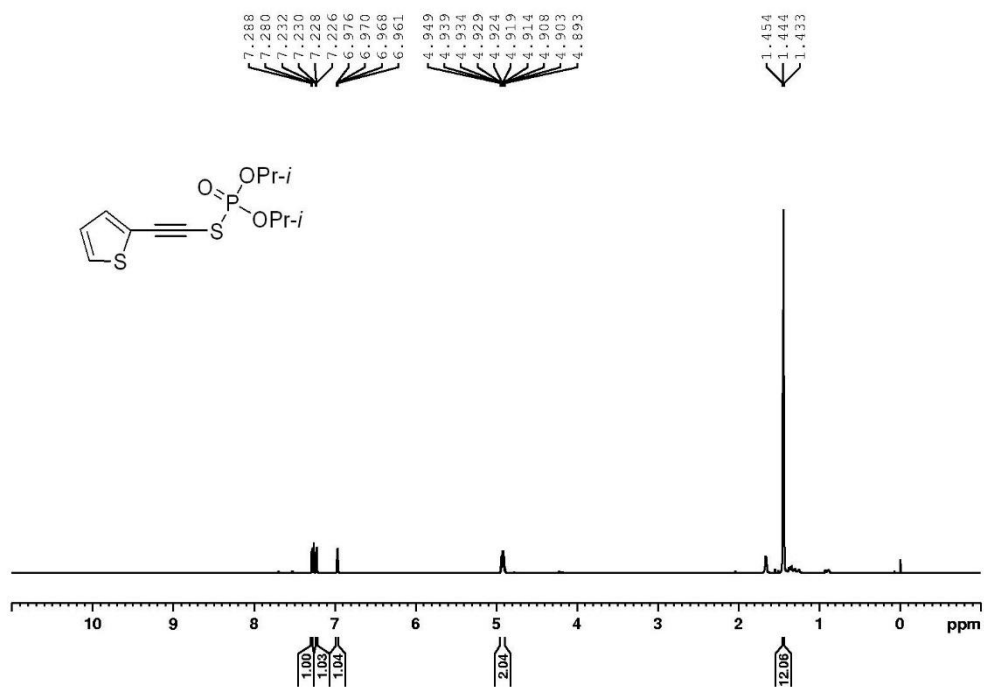


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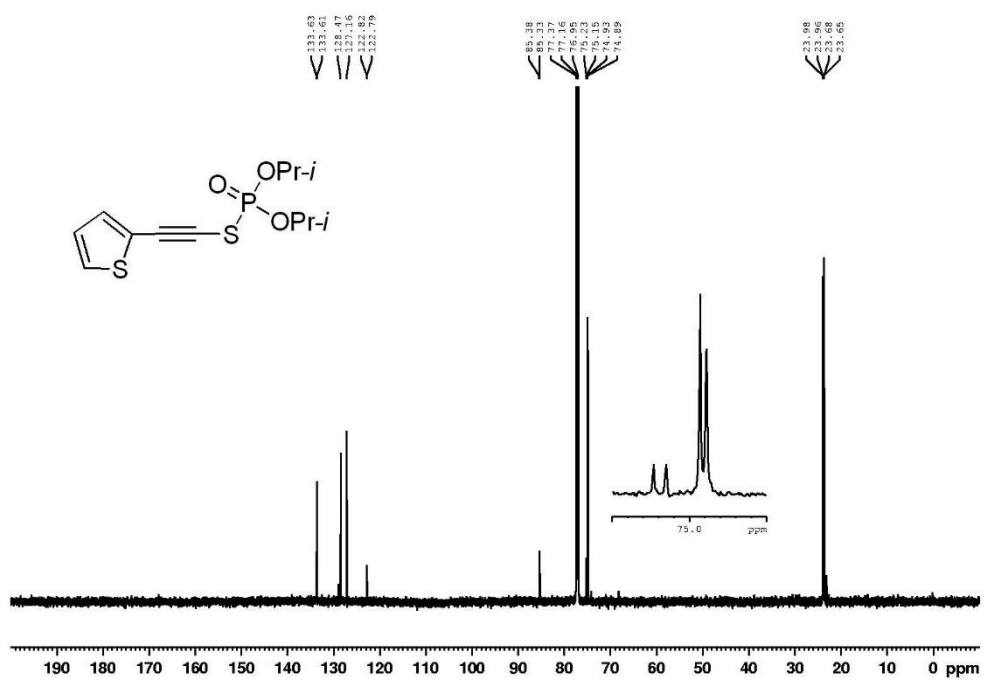


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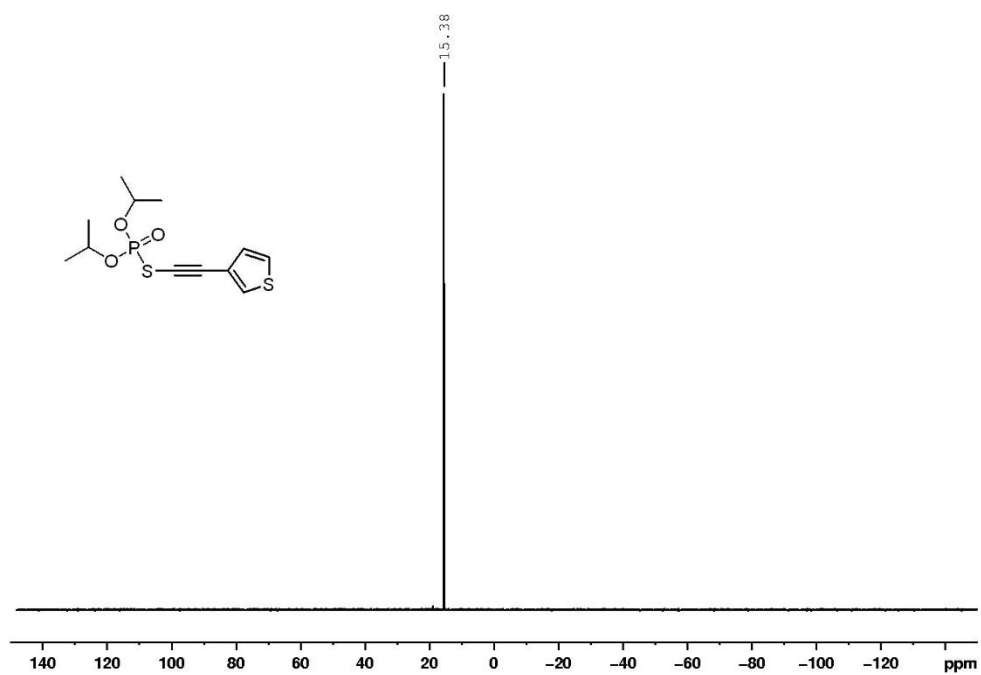


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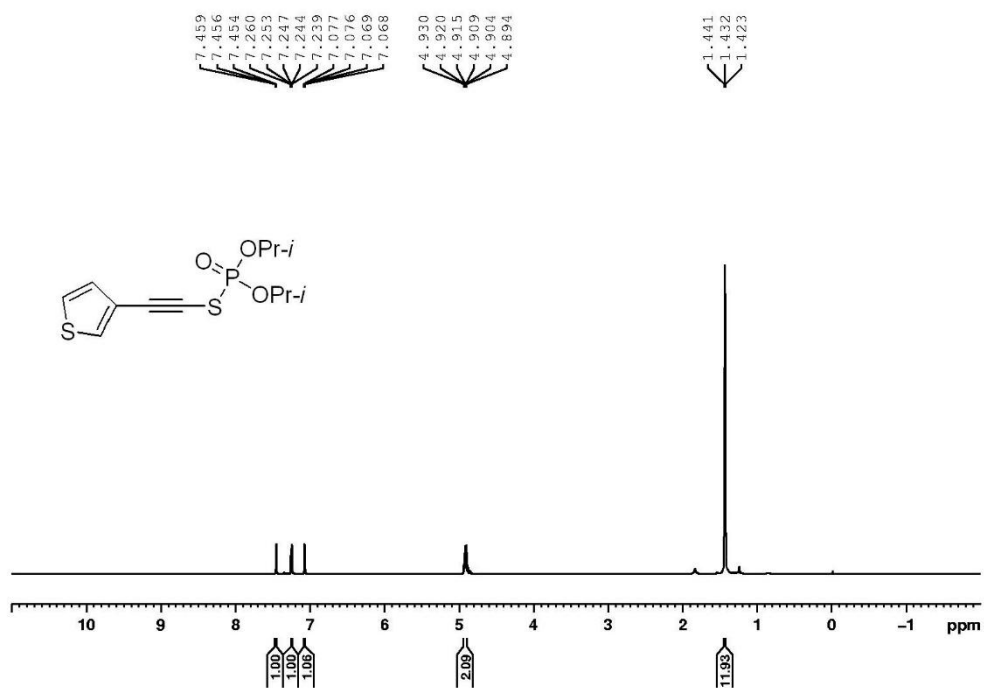


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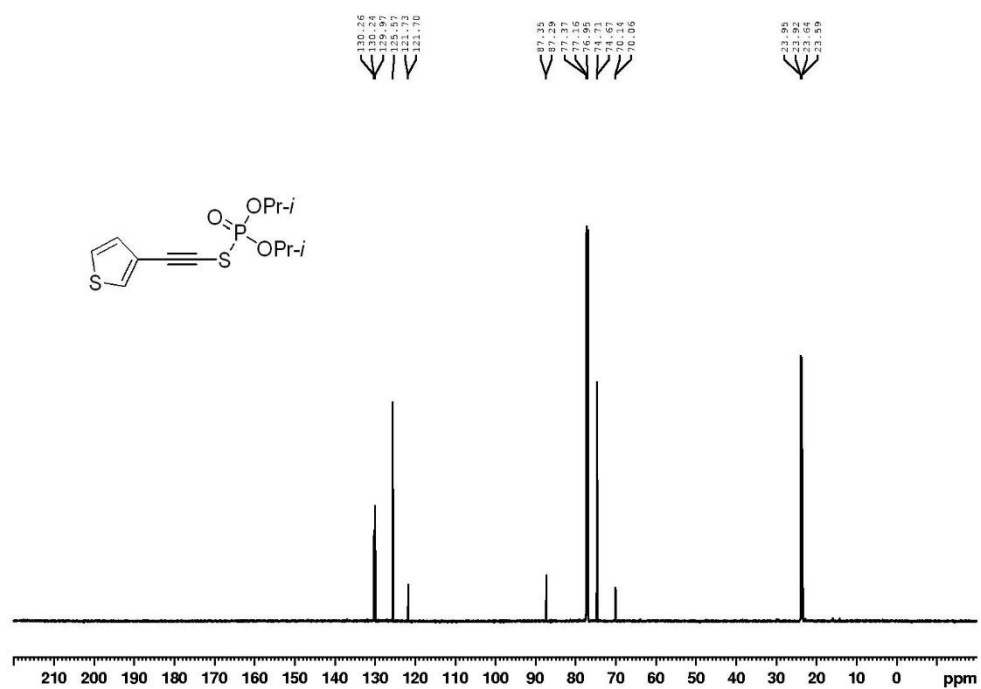


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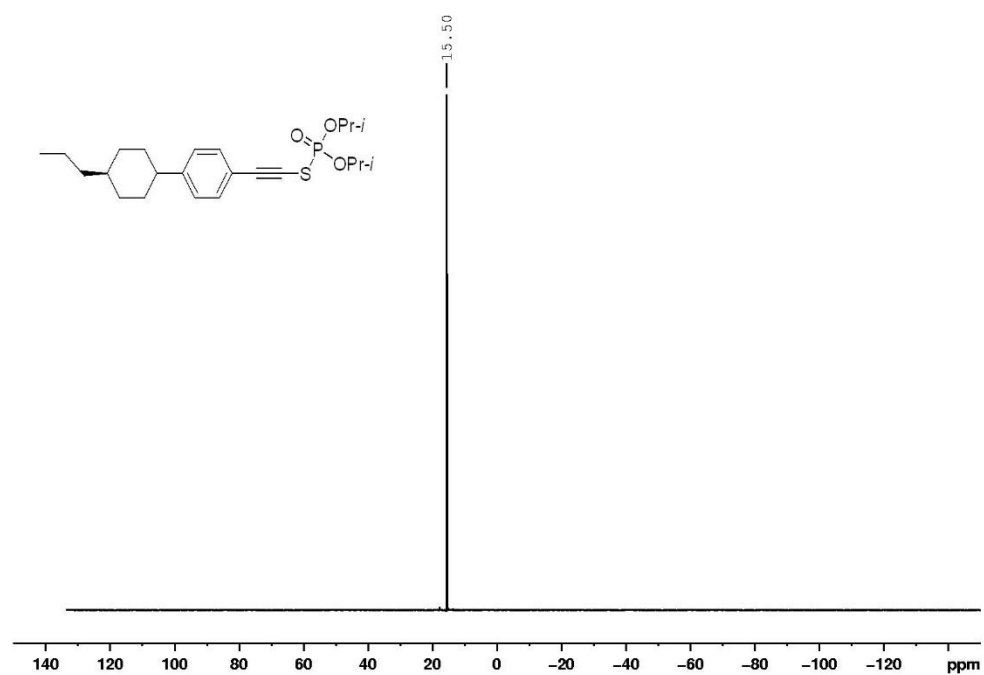


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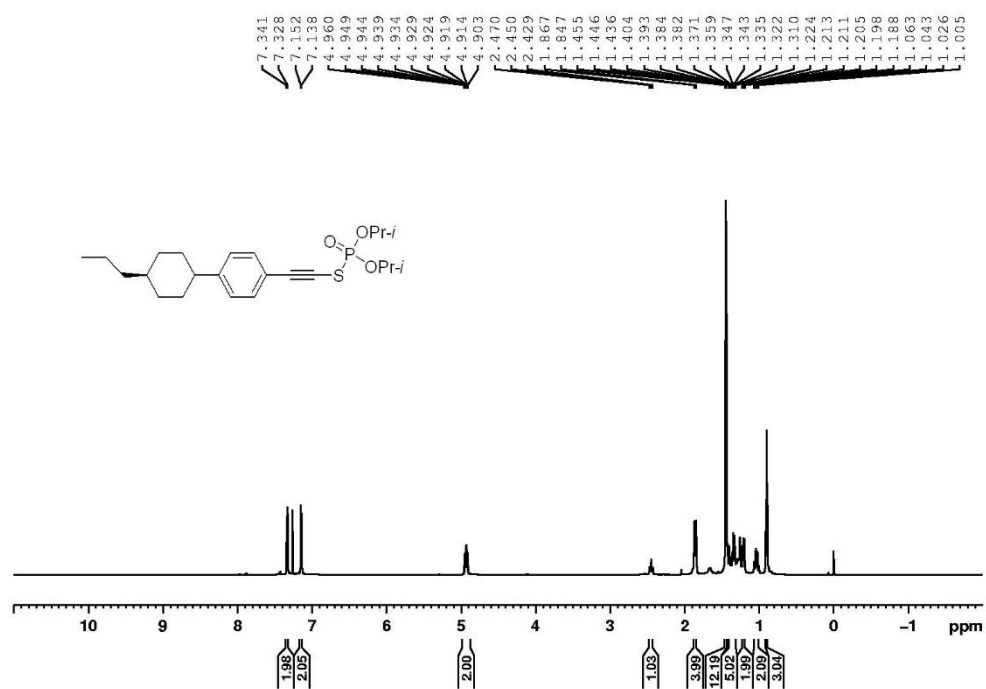


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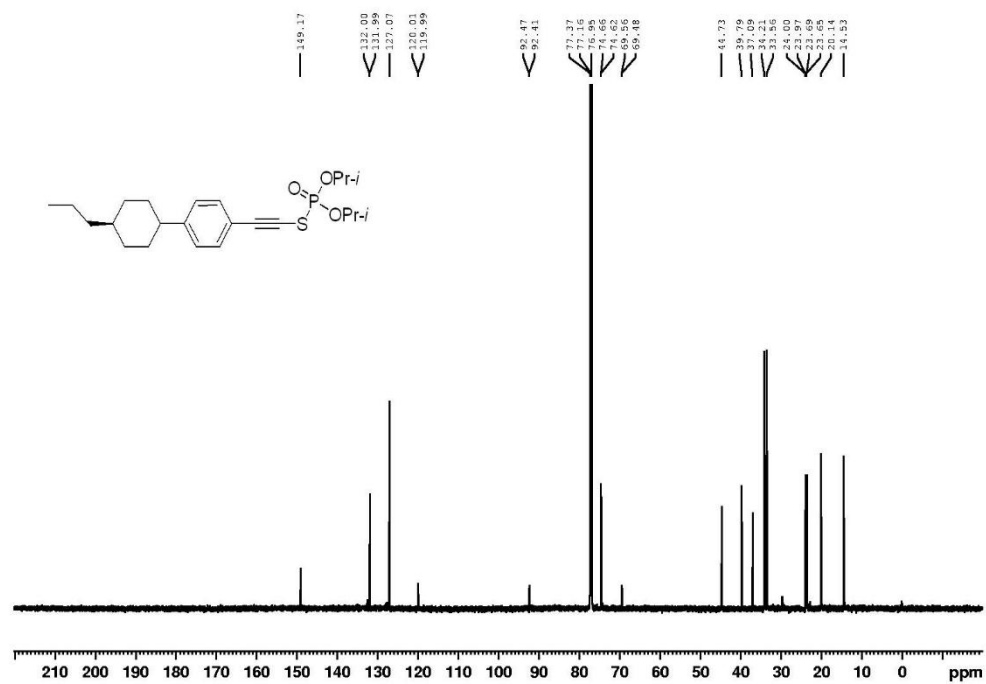


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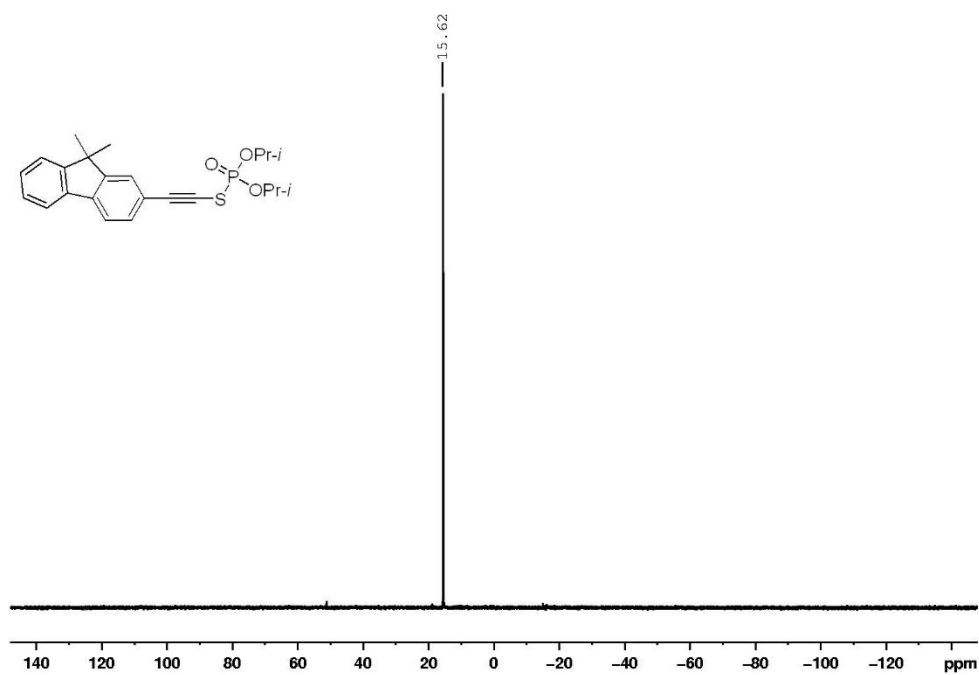


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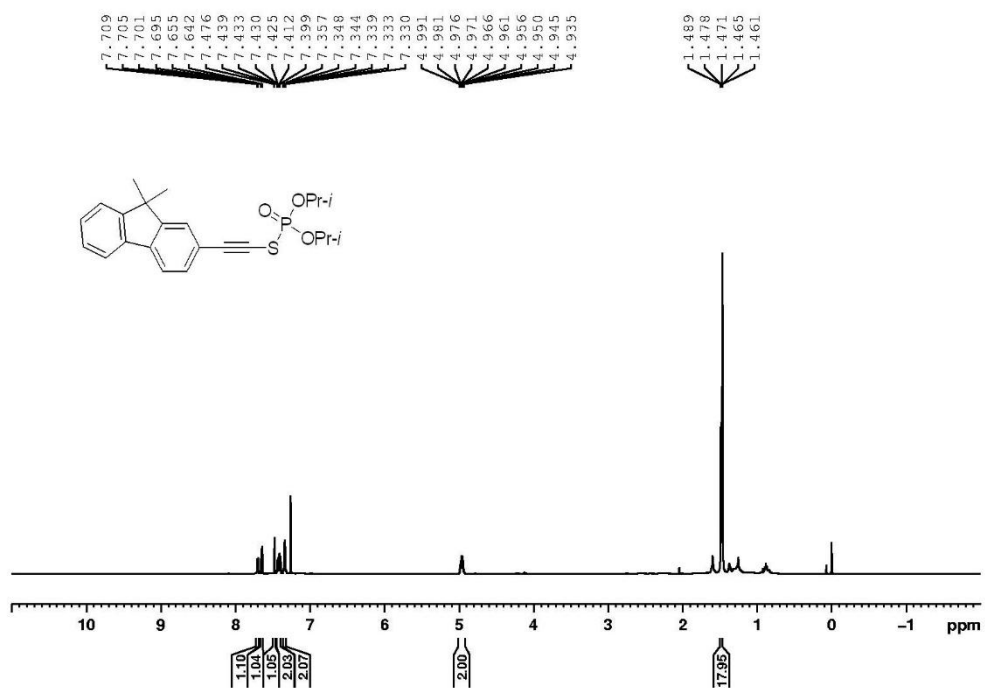


ESI-74

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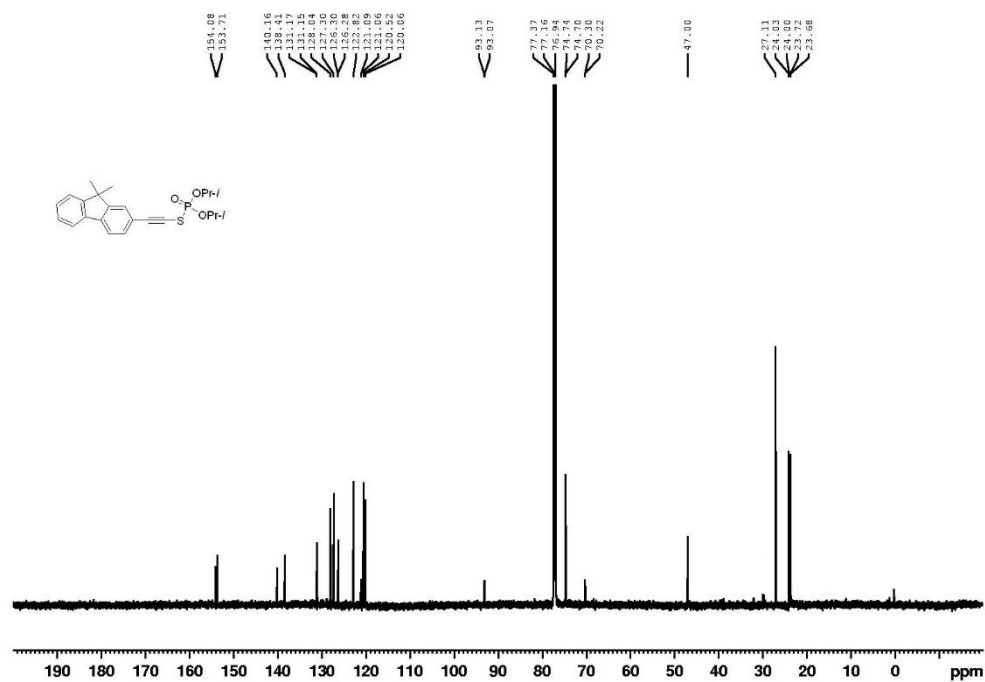


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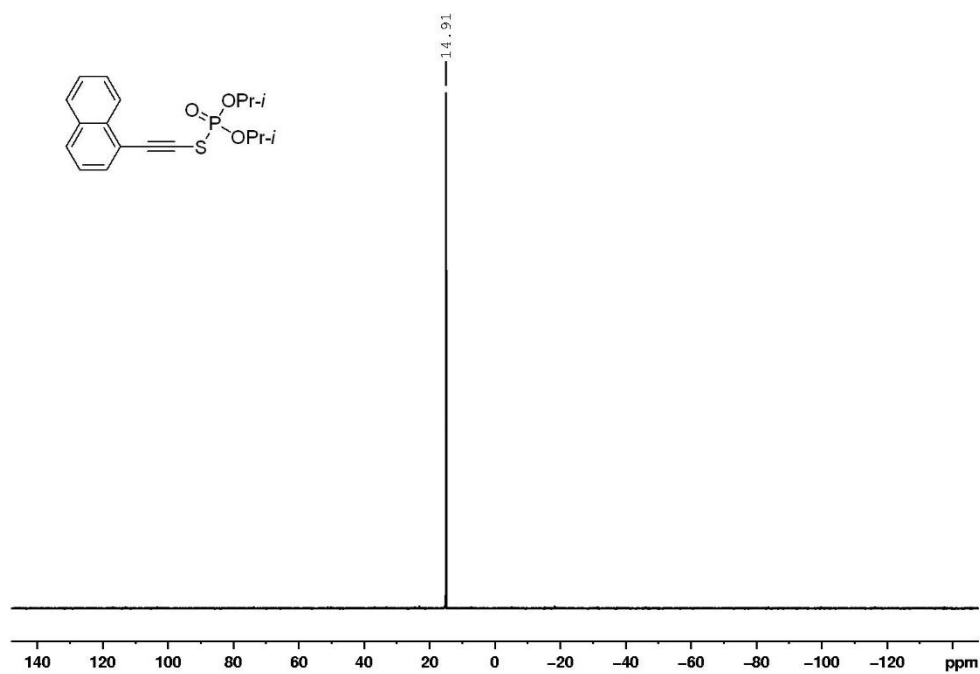


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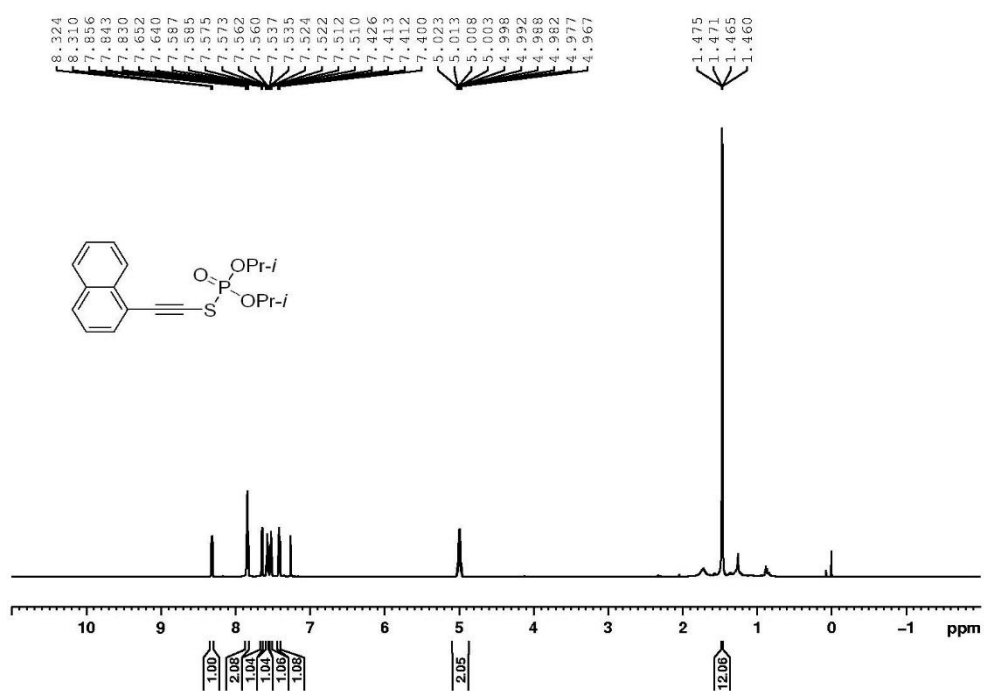
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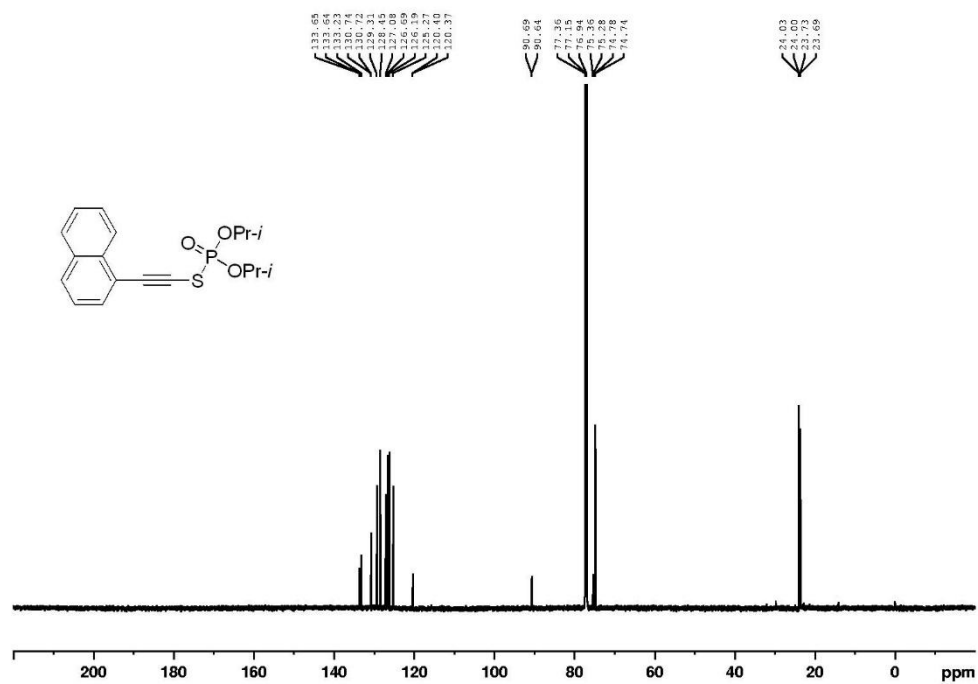
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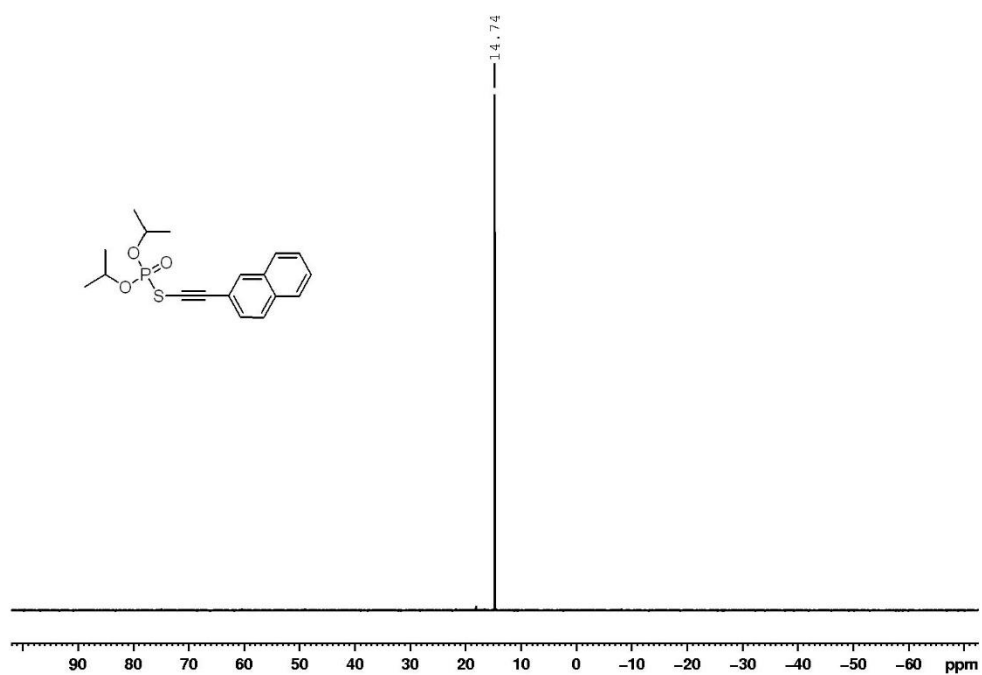
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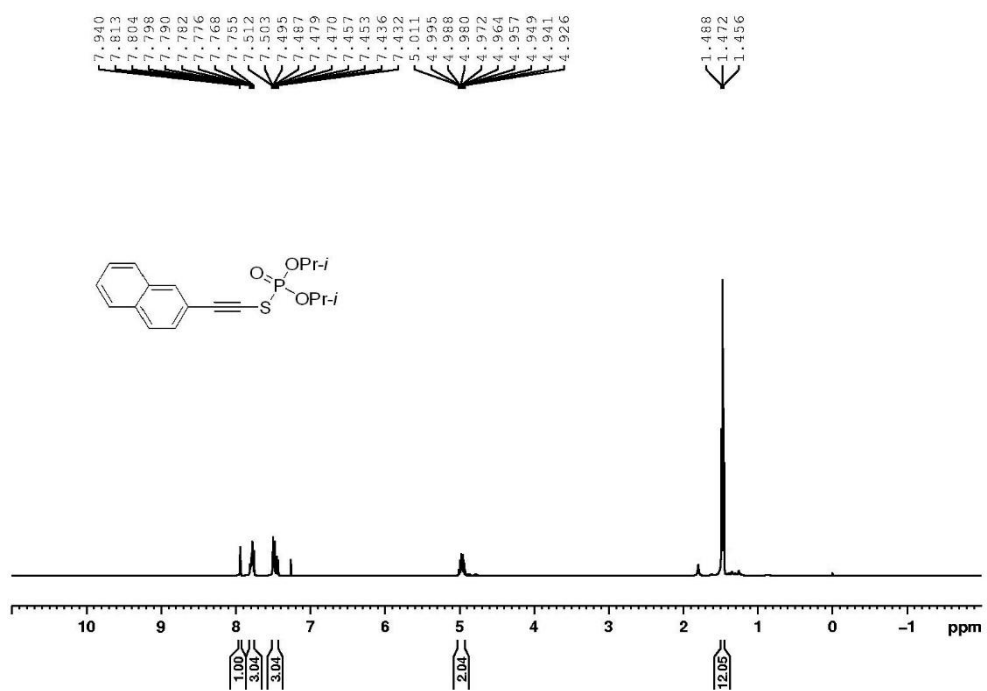
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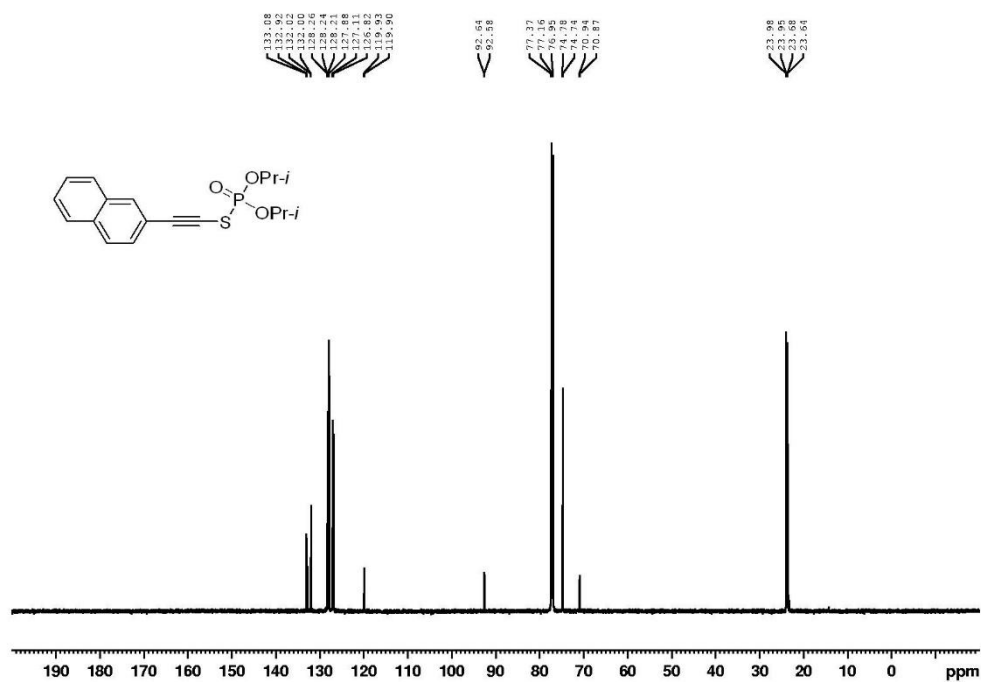


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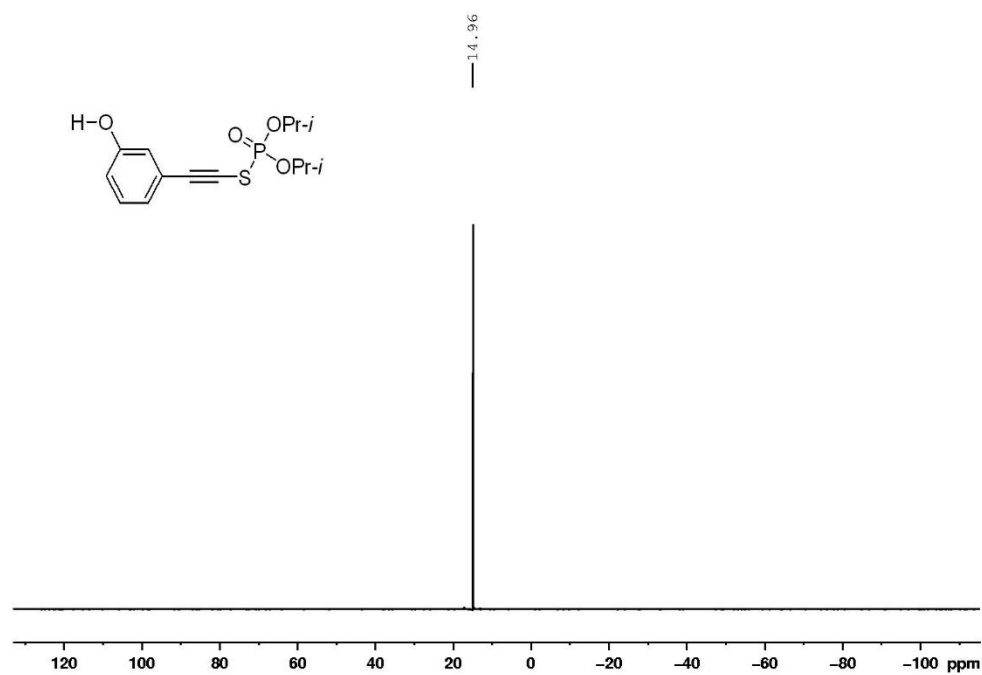


ESI-78

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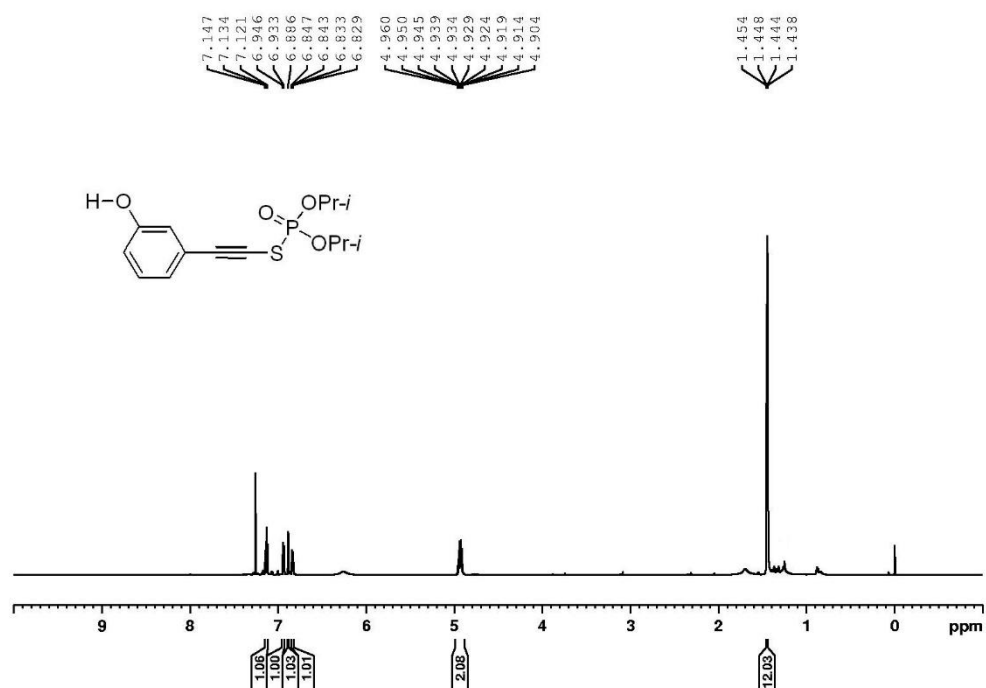


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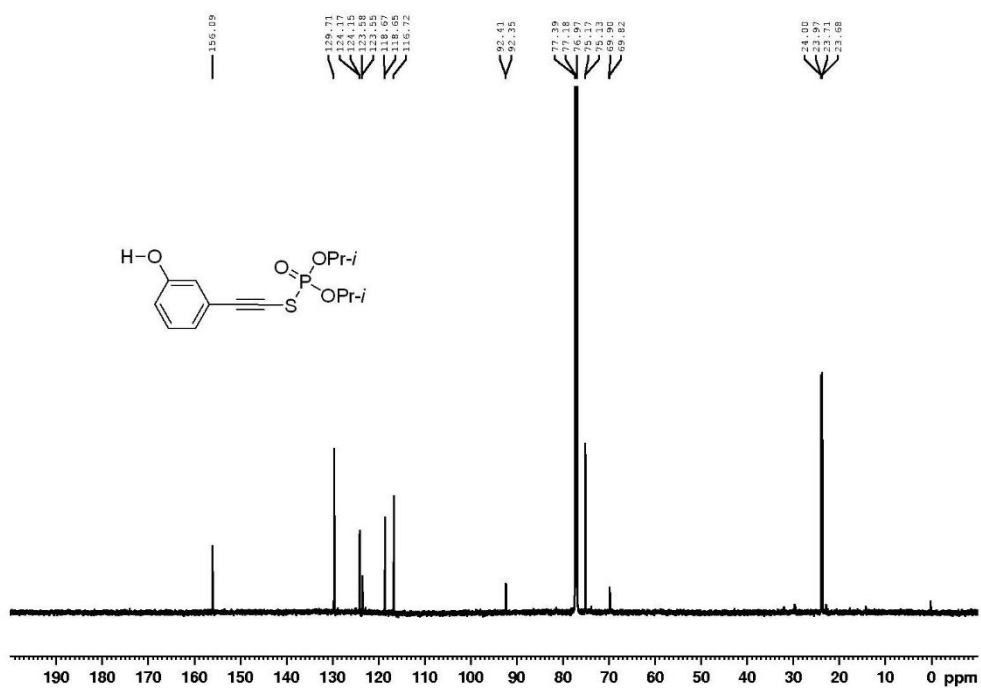


ESI-79

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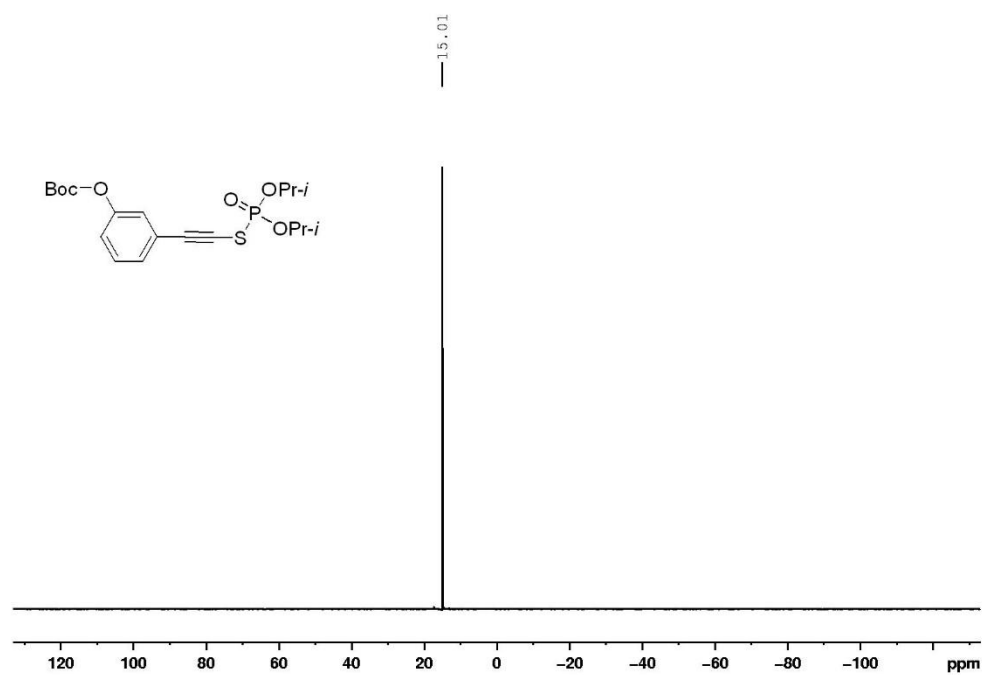


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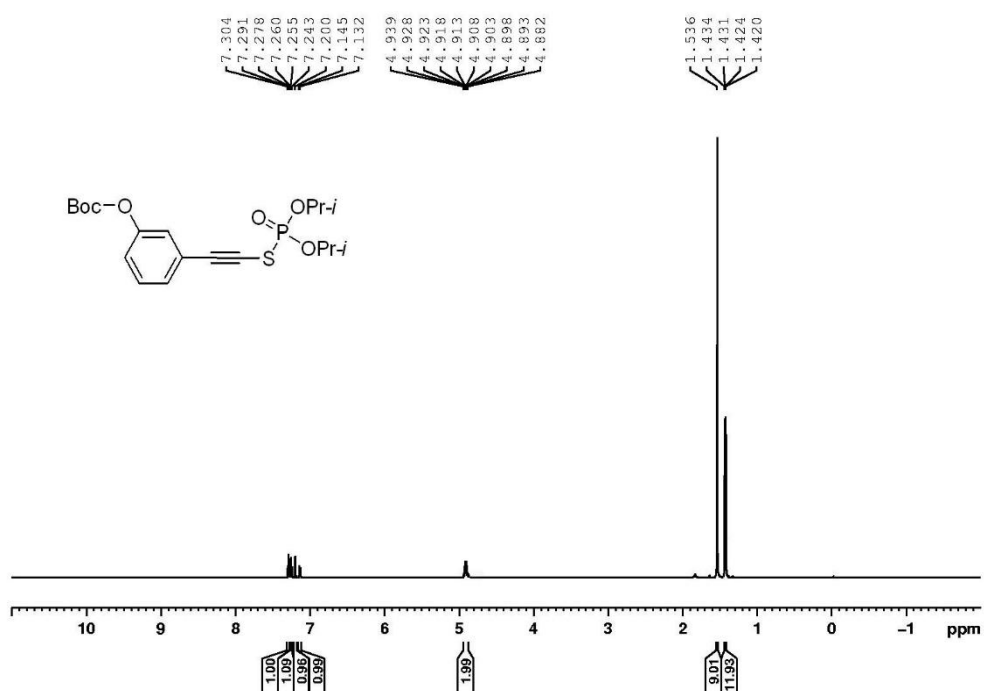


ESI-80

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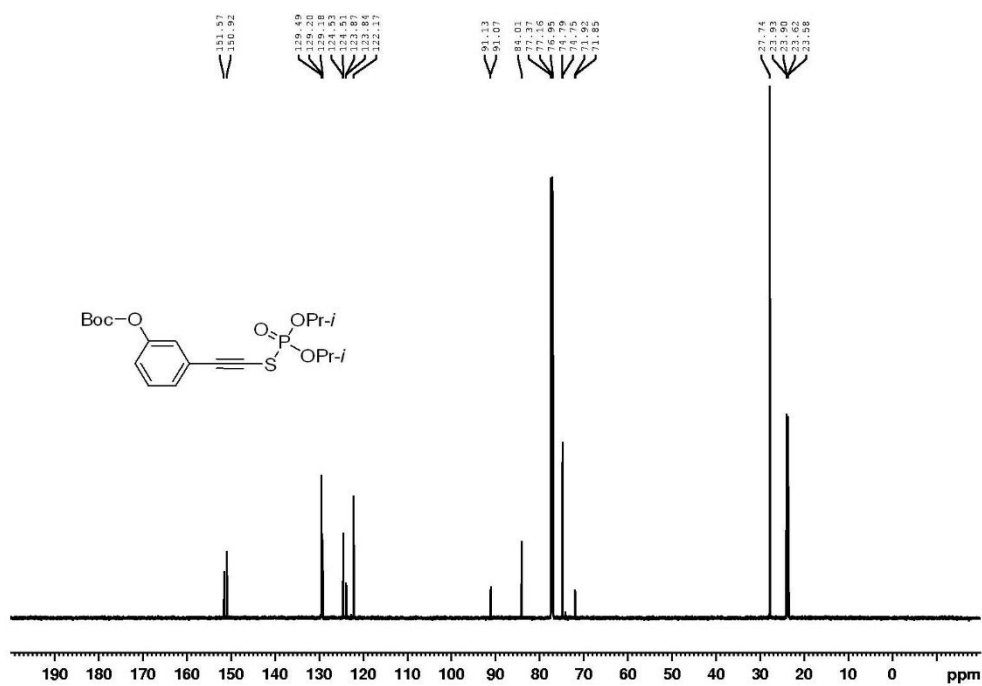


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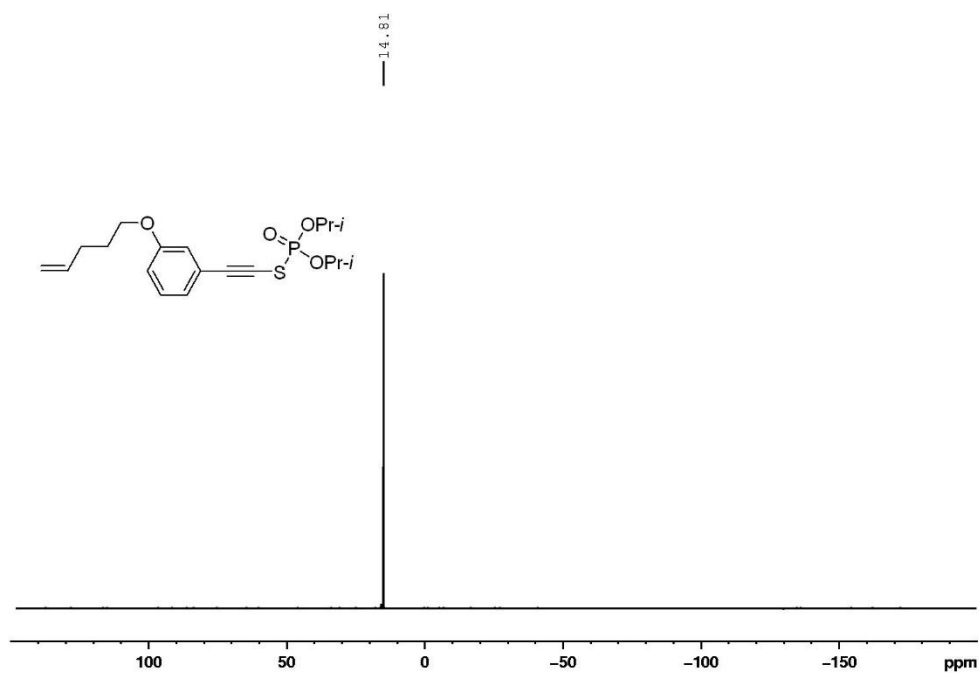


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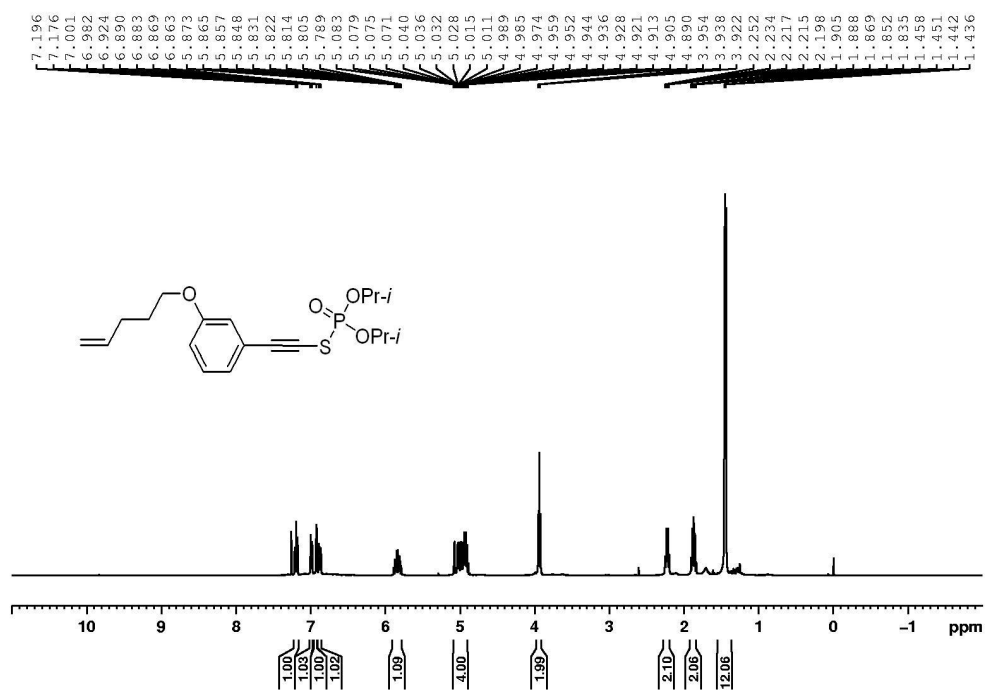


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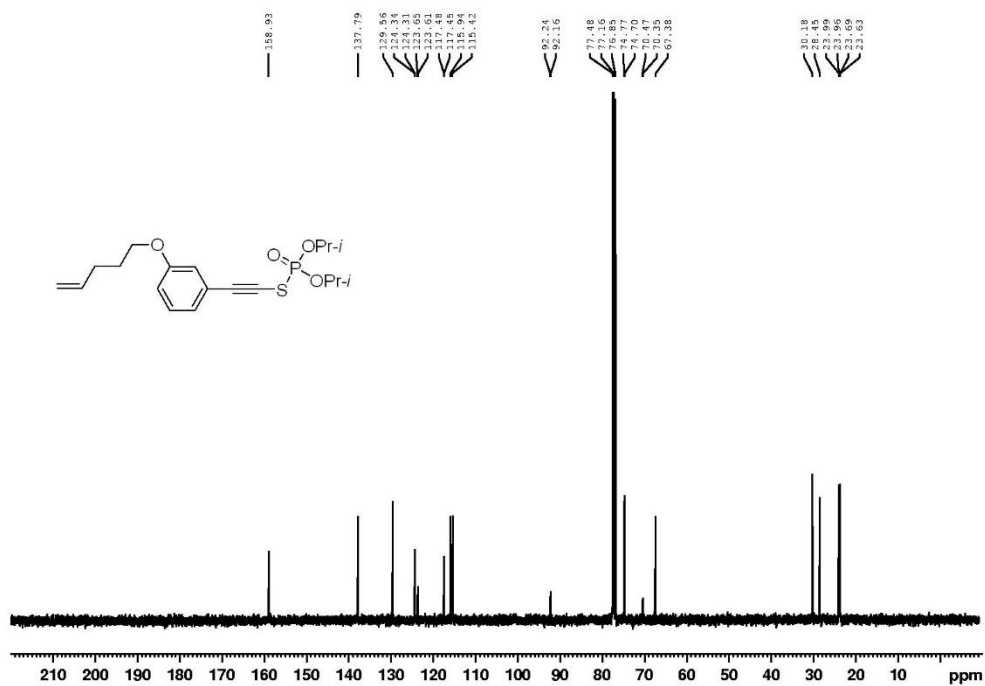


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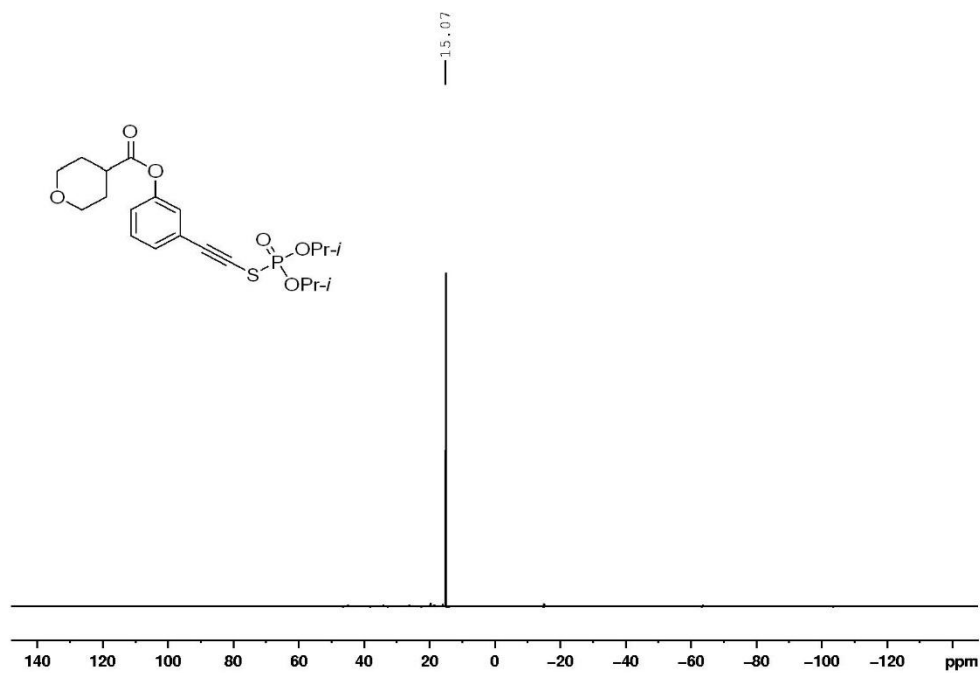


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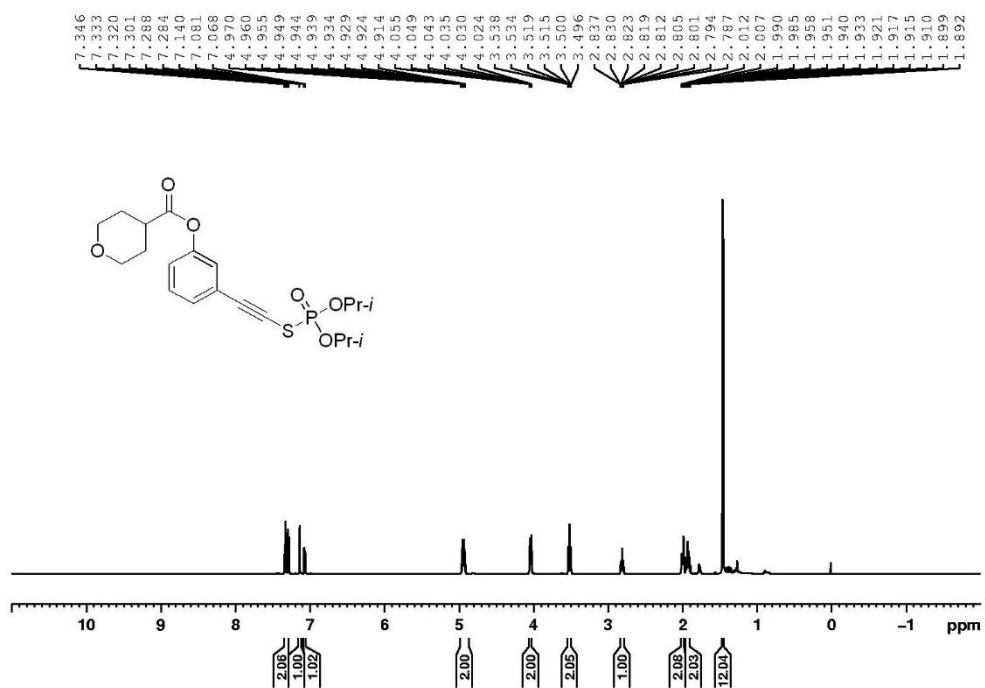


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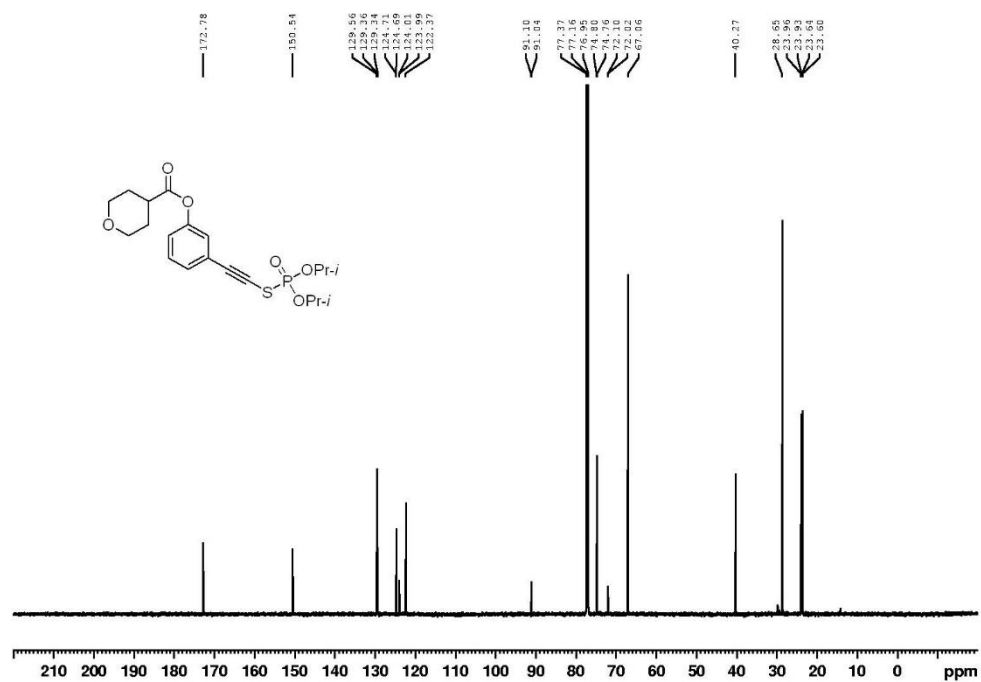


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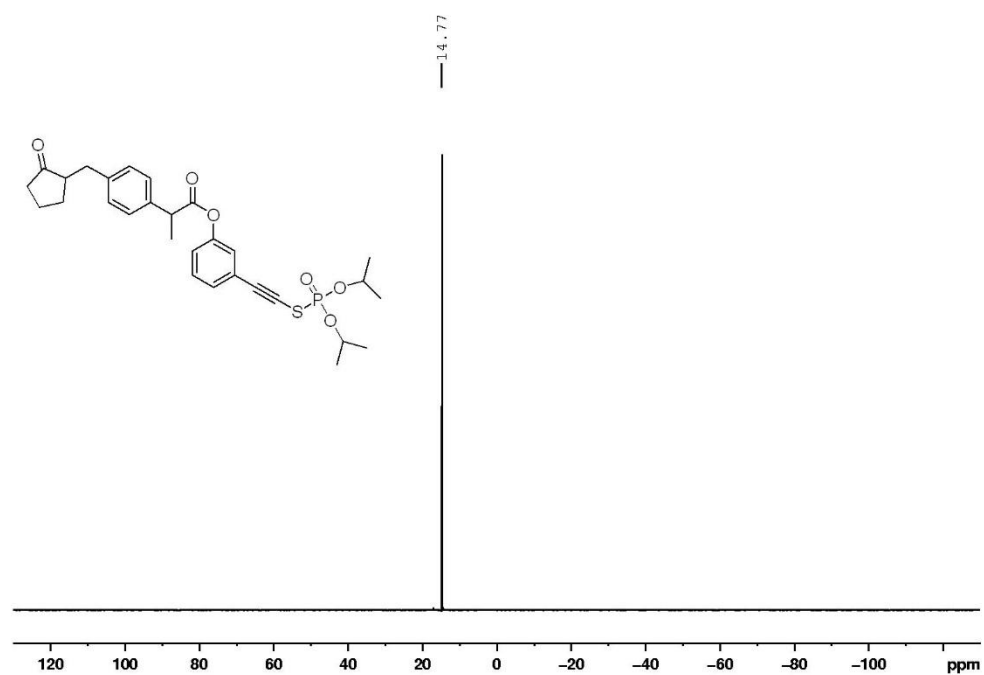


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Chemical structure of compound 10: CC(C)(C)OP(=O)(C(C)(C)C)C#Cc1ccc(OC(C)Cc2ccc(cc2)CC3CCCC3=O)cc1

¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from -1 to 10. The spectrum shows several peaks, with integrations provided below the baseline and a list of chemical shifts (δ) on the right side.

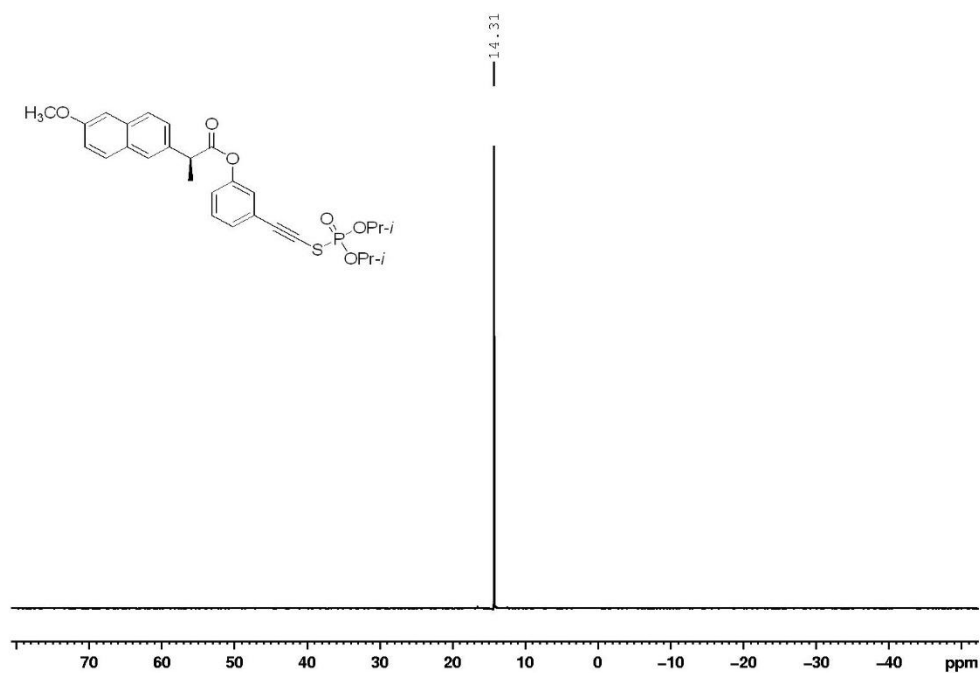
Integrations (from left to right): 4.01, 2.00, 1.00, 1.03, 2.00, 1.01, 0.95, 0.98, 2.00, 0.99, 1.00, 3.02, 0.96, 11.99.

Chemical shifts (δ, ppm) listed on the right (from top to bottom): 7.279, 7.267, 7.260, 7.254, 7.254, 7.245, 7.232, 7.173, 7.159, 7.043, 6.985, 6.983, 6.980, 6.973, 6.970, 6.967, 4.930, 4.919, 4.914, 4.909, 4.904, 4.894, 3.924, 3.912, 3.158, 3.151, 3.135, 3.128, 2.550, 2.534, 2.527, 2.511, 2.361, 2.353, 2.351, 2.335, 2.320, 2.126, 2.124, 2.110, 2.103, 2.100, 2.095, 2.093, 2.078, 1.954, 1.726, 1.718, 1.592, 1.580, 1.573, 1.562, 1.552, 1.541, 1.436, 1.433, 1.423, 1.423.

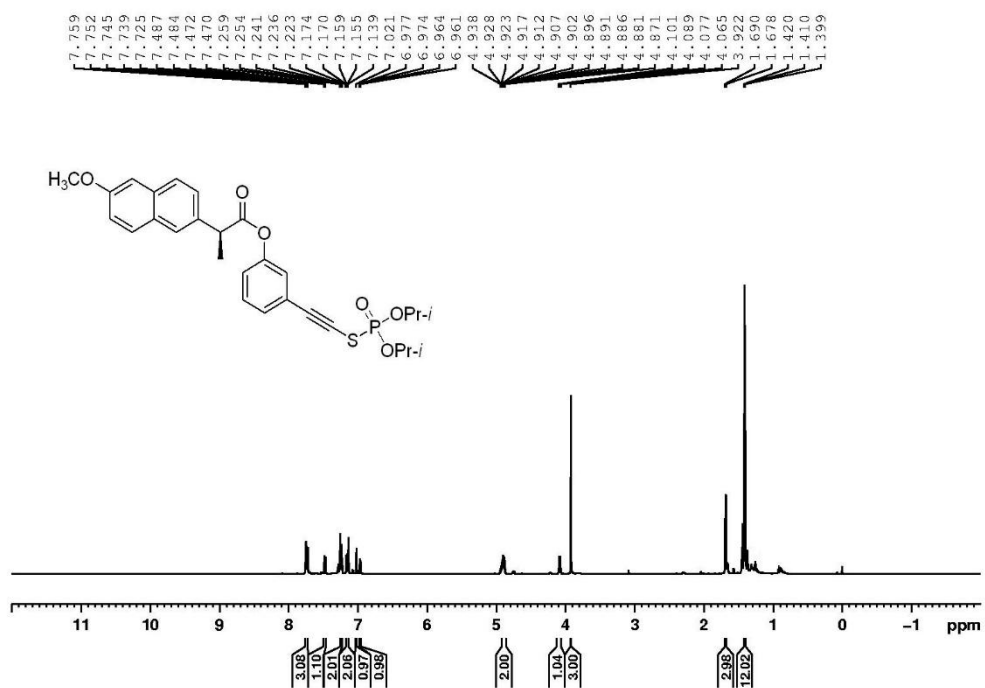
Chemical structure of compound 10 is shown above the ^{13}C NMR spectrum. The structure is a complex molecule featuring a cyclopentanone ring connected to a benzene ring, which is further connected to a carbonyl group, an ether linkage, another benzene ring, an alkyne group, and a phosphonate group.

The ^{13}C NMR spectrum displays peaks from 18 to 220 ppm. Key peaks are labeled with their chemical shifts: 220.24, 172.90, 150.69, 139.38, 137.72, 136.70, 136.45, 136.29, 136.25, 137.65, 124.65, 124.65, 123.87, 122.33, 81.14, 81.05, 74.81, 74.77, 74.72, 71.88, 51.07, 45.30, 38.28, 38.28, 32.42, 32.42, 23.93, 23.93, 23.64, 23.64, 20.65, 20.65, and 18.60.

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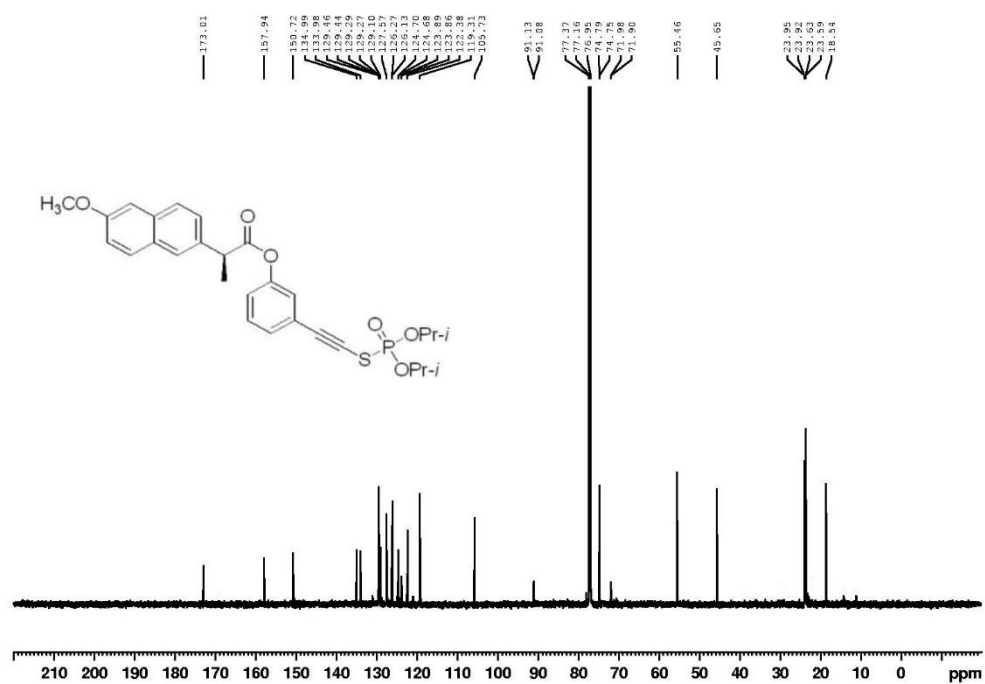


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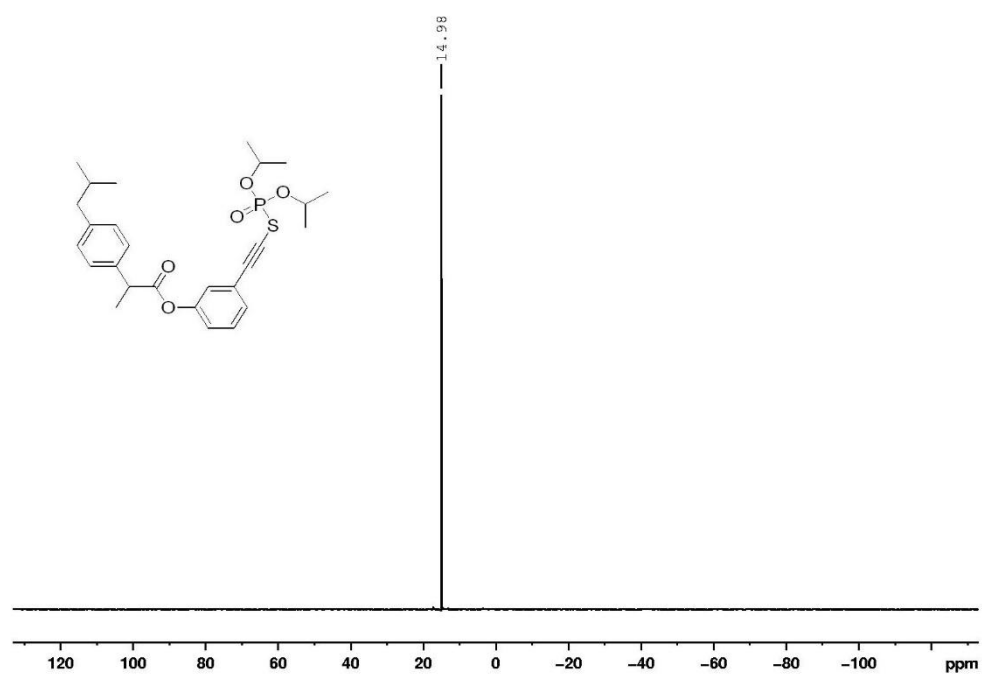


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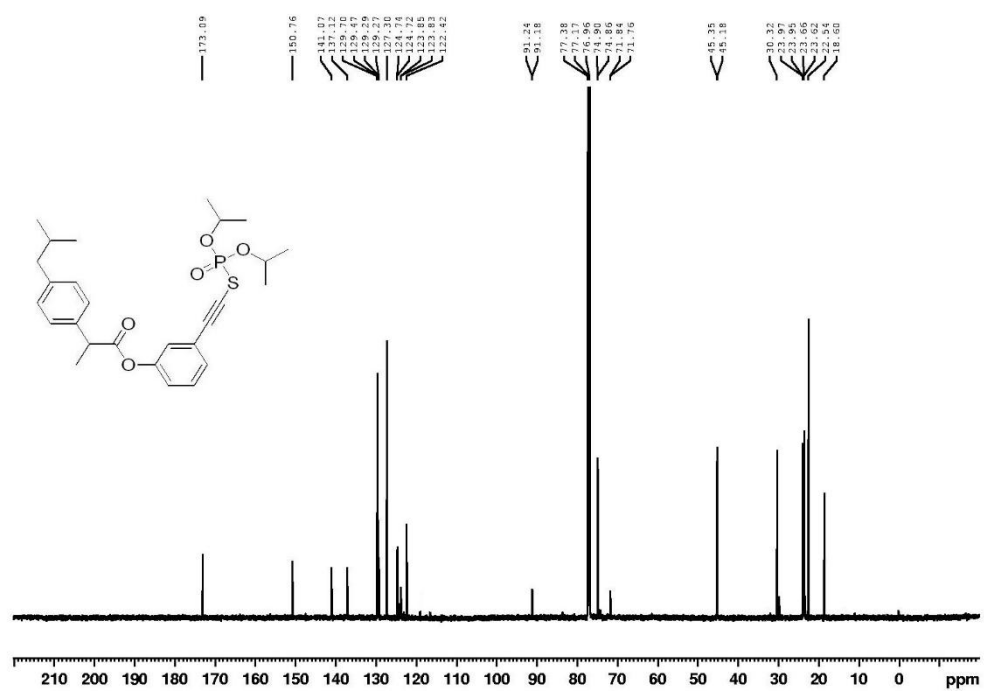
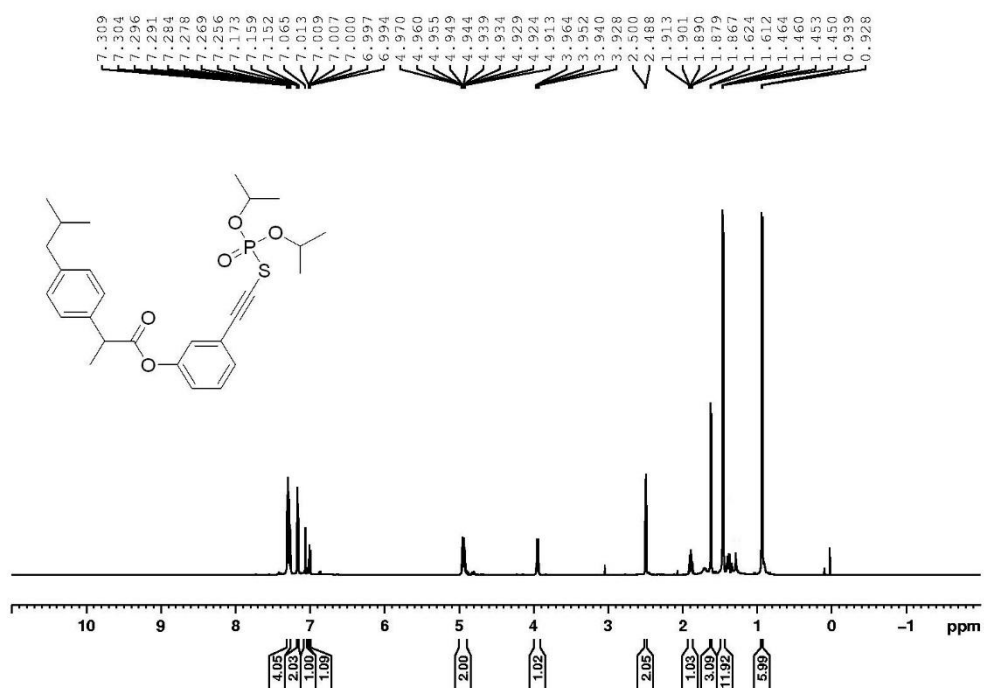
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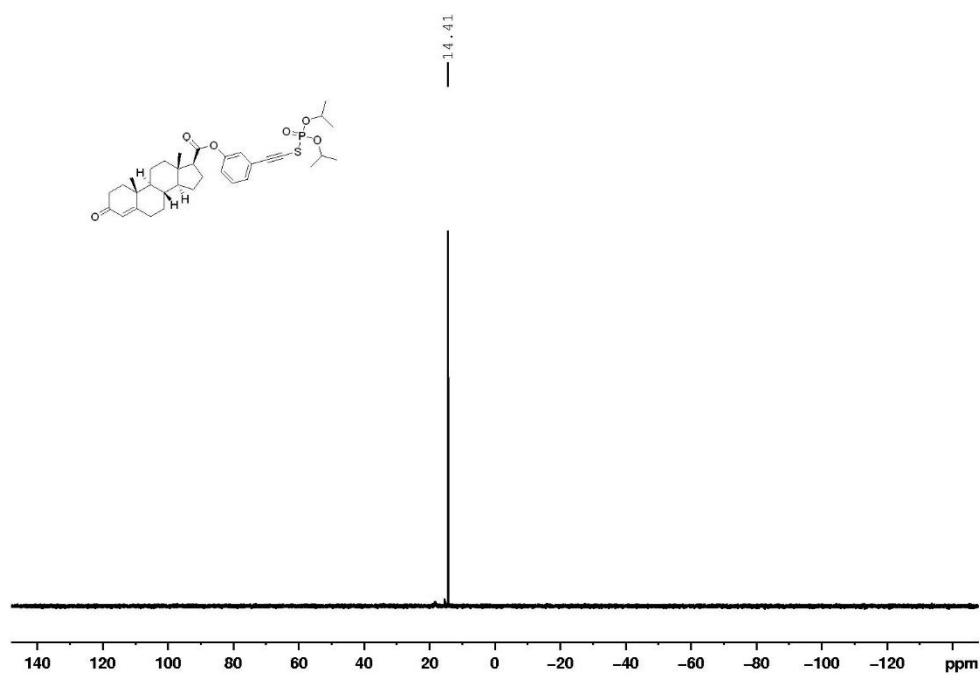
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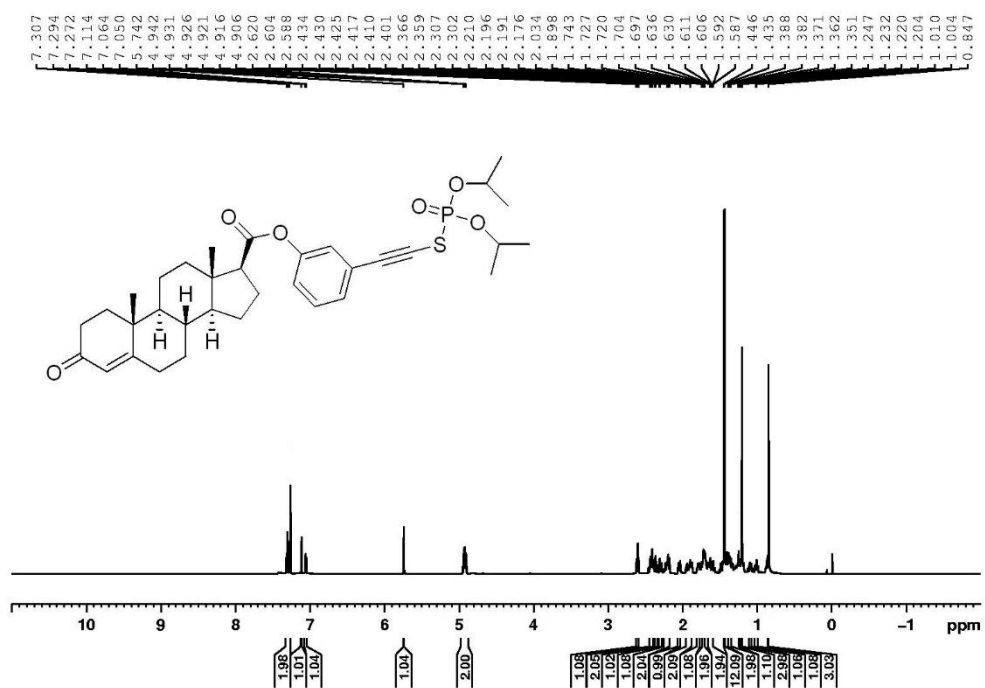
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ESI-90

