

## Supporting Information

### Palladium-Catalyzed Oxidative Deacetonative Coupling of 4-Aryl-2-methyl-3-butyn-2-ols with H-phosphonates

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**Diisopropyl (phenylethynyl)phosphonate (3a):**<sup>1</sup> colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.56-7.52 (m, 2H), 7.47-7.43 (m, 1H), 7.39-7.34 (m, 2H), 4.89-4.75 (m, 2H), 1.41 (d,  $J = 6.2$  Hz, 6H), 1.40 (d,  $J = 6.2$  Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  131.7 (d,  $J_{C-P} = 2.4$  Hz), 129.7, 127.7, 119.0 (d,  $J_{C-P} = 5.5$  Hz), 97.3 (d,  $J_{C-P} = 52.5$  Hz), 79.0 (d,  $J_{C-P} = 296.5$  Hz), 71.5 (d,  $J_{C-P} = 5.6$  Hz), 23.1 (d,  $J_{C-P} = 4.5$  Hz), 22.8 (d,  $J_{C-P} = 4.8$  Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -8.14.

**Diethyl (phenylethynyl)phosphonate (3b):**<sup>1</sup> colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.60-7.54 (m, 2H), 7.49-7.43 (m, 1H), 7.42-7.35 (m, 2H), 4.28-4.19 (m, 4H), 1.41 (t,  $J = 7.1$  Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  131.8 (d,  $J_{C-P} = 2.5$  Hz), 129.9, 127.7, 118.7 (d,  $J_{C-P} = 5.6$  Hz), 98.3 (d,  $J_{C-P} = 52.8$  Hz), 77.5 (d,  $J_{C-P} = 305.4$  Hz), 62.4 (d,  $J_{C-P} = 5.5$  Hz), 15.3 (d,  $J_{C-P} = 7.0$  Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -5.57.

**Dibutyl (phenylethynyl)phosphonate (3c):**<sup>1</sup> colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.57 (d,  $J = 7.2$  Hz, 2H), 7.50-7.44 (m, 1H), 7.42-7.35 (m, 2H), 4.20-4.10 (m, 4H), 1.79-1.69 (m, 4H), 1.53-1.41 (m, 4H), 0.96 (t,  $J = 7.4$  Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  131.8 (d,  $J_{C-P} = 2.4$  Hz), 129.8, 127.7, 118.8 (d,  $J_{C-P} = 5.7$  Hz), 98.2 (d,  $J_{C-P} = 52.4$  Hz), 77.5 (d,  $J_{C-P} = 297.6$  Hz), 66.1 (d,  $J_{C-P} = 5.8$  Hz), 31.4 (d,  $J_{C-P} = 7.1$  Hz), 17.9, 12.7; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -5.15.

**Diethyl ((3-methoxyphenyl)ethynyl)phosphonate (3d):** colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.26-7.20 (m, 1H), 7.14-7.08 (m, 1H), 7.01 (s, 1H), 6.99-6.90 (m, 1H), 4.25-4.12 (m, 4H), 3.75 (s, 3H), 1.35 (t,  $J = 7.0$  Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  158.3, 128.7, 124.1 (d,  $J_{C-P} = 2.4$  Hz), 119.4 (d,  $J_{C-P} = 5.6$  Hz), 116.5, 116.2 (d,  $J_{C-P} = 2.3$  Hz), 98.0 (d,  $J_{C-P} = 52.6$  Hz), 77.1 (d,  $J_{C-P} = 297.8$  Hz), 62.3 (d,  $J_{C-P} = 5.4$  Hz), 54.4, 15.1 (d,  $J_{C-P} = 6.9$  Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -5.63; HRMS (ESI<sup>+</sup>) calcd for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>P [M+H]<sup>+</sup>: 269.0937, found: 269.0937.

**Diethyl (naphthalen-1-ylethynyl)phosphonate (3e):** colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.23 (d,  $J = 8.3$  Hz, 1H), 7.91 (d,  $J = 8.3$  Hz, 1H), 7.84 (d,  $J = 8.1$  Hz, 1H), 7.79 (d,  $J = 7.1$  Hz, 1H), 7.61-7.49 (m, 2H), 7.42 (t,  $J = 7.9$  Hz, 1H), 4.34-4.18 (m, 4H), 1.40 (t,  $J = 7.1$  Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  132.3, 132.0, 131.7 (d,  $J_{C-P} = 2.7$  Hz), 130.4, 127.6, 126.7, 126.0, 124.6, 124.0, 116.1 (d,  $J_{C-P} = 5.6$  Hz), 96.5 (d,  $J_{C-P} = 52.3$  Hz), 82.1 (d,  $J_{C-P} = 296.9$  Hz), 62.3 (d,  $J_{C-P} = 5.4$  Hz), 15.2 (d,  $J_{C-P} = 6.9$  Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -5.57; HRMS (ESI<sup>+</sup>) calcd for C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>P [M+H]<sup>+</sup>: 289.0988, found: 289.0988.

**Dibutyl (naphthalen-1-ylethynyl)phosphonate (3f):** colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.25 (d,  $J = 8.2$  Hz, 1H), 7.91 (d,  $J = 8.2$  Hz, 1H), 7.85 (d,  $J = 8.0$  Hz, 1H), 7.79 (d,  $J = 7.1$  Hz, 1H), 7.61-7.50 (m, 2H), 7.43 (t,  $J = 7.7$  Hz, 1H), 4.25-4.14 (m, 4H), 1.78-1.69 (m, 4H), 1.52-1.40 (m, 4H), 0.93 (t,  $J = 7.3$  Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  132.4, 132.0, 131.7 (d,  $J_{C-P} = 2.7$  Hz), 130.3, 127.6, 126.7, 126.0, 124.6, 124.0, 116.2 (d,  $J_{C-P} = 5.5$  Hz), 96.5 (d,  $J_{C-P} = 52.1$  Hz), 82.1 (d,  $J_{C-P} = 296.5$  Hz), 66.0 (d,  $J_{C-P} = 5.8$  Hz), 31.3 (d,  $J_{C-P} = 7.0$  Hz), 17.8, 12.6; <sup>31</sup>P NMR

(CDCl<sub>3</sub>, 163 MHz):  $\delta$  -5.18; HRMS (ESI<sup>+</sup>) calcd for C<sub>20</sub>H<sub>25</sub>O<sub>3</sub>P [M+H]<sup>+</sup>: 345.1614, found: 345.1615.

**Diisopropyl (*p*-tolylethynyl)phosphonate (3g):**<sup>2</sup> colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.38 (d,  $J$  = 8.0 Hz, 2H), 7.11 (d,  $J$  = 8.0 Hz, 2H), 4.82-4.69 (m, 2H), 2.32 (s, 3H), 1.35 (d,  $J$  = 6.1 Hz, 6H), 1.34 (d,  $J$  = 6.1 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  140.3, 131.6 (d,  $J_{C-P}$  = 2.4 Hz), 128.5, 115.9 (d,  $J_{C-P}$  = 5.6 Hz), 97.8 (d,  $J_{C-P}$  = 52.8 Hz), 78.4 (d,  $J_{C-P}$  = 297.8 Hz), 71.4 (d,  $J_{C-P}$  = 5.5 Hz), 23.1 (d,  $J_{C-P}$  = 4.5 Hz), 22.8 (d,  $J_{C-P}$  = 4.8 Hz), 20.8. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -7.85.

**Diisopropyl (*m*-tolylethynyl)phosphonate (3h):** colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.37-7.30 (m, 2H), 7.25-7.19 (m, 2H), 4.85-4.71 (m, 2H), 2.33 (s, 3H), 1.39 (d,  $J$  = 6.0 Hz, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  137.4, 131.9 (d,  $J_{C-P}$  = 2.5 Hz), 130.5, 128.6 (d,  $J_{C-P}$  = 2.5 Hz), 127.5, 118.6 (d,  $J_{C-P}$  = 5.5 Hz), 97.5 (d,  $J_{C-P}$  = 52.6 Hz), 78.5 (d,  $J_{C-P}$  = 297.2 Hz), 71.3 (d,  $J_{C-P}$  = 5.5 Hz), 22.9 (d,  $J_{C-P}$  = 4.5 Hz), 22.7 (d,  $J_{C-P}$  = 4.8 Hz), 20.2; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -8.03; HRMS (ESI<sup>+</sup>) calcd for C<sub>15</sub>H<sub>21</sub>O<sub>3</sub>P [M+H]<sup>+</sup>: 281.1301, found: 281.1303.

**Diisopropyl ((3,4-dimethylphenyl)ethynyl)phosphonate (3i):** colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.34-7.24 (m, 2H), 7.14-1.07 (d,  $J$  = 7.6 Hz, 1H), 4.91-4.66 (m, 2H), 2.27 (s, 3H), 2.24 (s, 3H), 1.39 (d,  $J$  = 6.1 Hz, 6H), 1.38 (d,  $J$  = 6.1 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  139.1, 136.2, 132.6 (d,  $J_{C-P}$  = 2.4 Hz), 129.2 (d,  $J_{C-P}$  = 2.4 Hz), 129.0, 116.2 (d,  $J_{C-P}$  = 5.6 Hz), 98.1 (d,  $J_{C-P}$  = 52.9 Hz), 78.1 (d,  $J_{C-P}$  = 298.1 Hz), 71.4 (d,  $J_{C-P}$  = 5.5 Hz), 23.1 (d,  $J_{C-P}$  = 4.5 Hz), 22.8 (d,  $J_{C-P}$  = 4.8 Hz), 19.1, 18.7; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -7.71; HRMS (ESI<sup>+</sup>) calcd for C<sub>16</sub>H<sub>23</sub>O<sub>3</sub>P [M+H]<sup>+</sup>: 295.1458, found: 295.1458.

**Diisopropyl ((3,5-dimethylphenyl)ethynyl)phosphonate (3j):** colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.15 (s, 2H), 7.05 (s, 1H), 4.84-4.72 (m, 2H), 2.29 (s, 6H), 1.39 (d,  $J$  = 6.1 Hz, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  137.3, 131.5, 129.1 (d,  $J_{C-P}$  = 2.4 Hz), 118.5 (q,  $J_{C-P}$  = 5.5 Hz), 97.8 (d,  $J_{C-P}$  = 52.7 Hz), 78.1 (d,  $J_{C-P}$  = 297.1 Hz), 71.2 (d,  $J_{C-P}$  = 5.5 Hz), 22.9 (d,  $J_{C-P}$  = 4.5 Hz), 22.7 (d,  $J_{C-P}$  = 4.8 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -7.92; HRMS (ESI<sup>+</sup>) calcd for C<sub>16</sub>H<sub>23</sub>O<sub>3</sub>P [M+H]<sup>+</sup>: 295.1458, found: 295.1460.

**Diisopropyl ((4-butylphenyl)ethynyl)phosphonate (3k):** colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.44 (d,  $J$  = 8.0 Hz, 2H), 7.16 (d,  $J$  = 8.0 Hz, 1H), 4.85-4.72 (m, 2H), 2.61 (t,  $J$  = 7.6 Hz, 2H), 1.57 (q,  $J$  = 7.6 Hz, 2H), 1.39 (d,  $J$  = 6.0 Hz, 12H), 1.35-1.27 (m, 2H), 0.90 (t,  $J$  = 7.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  145.2, 131.7 (d,  $J_{C-P}$  = 2.3 Hz), 127.8, 116.1 (d,  $J_{C-P}$  = 5.6 Hz), 97.9 (d,  $J_{C-P}$  = 52.8 Hz), 78.4 (d,  $J_{C-P}$  = 297.6 Hz), 71.4 (d,  $J_{C-P}$  = 5.5 Hz), 34.9, 32.4, 23.1 (d,  $J_{C-P}$  = 4.5 Hz), 22.8 (d,  $J_{C-P}$  = 4.8 Hz), 21.4, 13.1; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 163 MHz):  $\delta$  -7.82; HRMS (ESI<sup>+</sup>) calcd for C<sub>18</sub>H<sub>27</sub>O<sub>3</sub>P [M+H]<sup>+</sup>: 323.1771, found: 323.1772.

**Diisopropyl ((3-methoxyphenyl)ethynyl)phosphonate (3l):** colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.21 (t,  $J$  = 8.0 Hz, 1H), 7.08 (d,  $J$  = 7.6 Hz, 1H), 6.99 (s, 1H),

6.96-6.90 (m, 1H), 4.82-4.68 (m, 2H), 3.74 (s, 3H), 1.35 (d,  $J = 6.0$  Hz, 6H), 1.34 (d,  $J = 6.0$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.5, 128.9, 124.1 (d,  $J_{\text{C-P}} = 2.4$  Hz), 119.9 (d,  $J_{\text{C-P}} = 5.6$  Hz), 116.4, 116.3 (d,  $J_{\text{C-P}} = 2.3$  Hz), 97.2 (d,  $J_{\text{C-P}} = 52.4$  Hz), 78.8 (d,  $J_{\text{C-P}} = 296.4$  Hz), 71.5 (d,  $J_{\text{C-P}} = 5.5$  Hz), 54.5, 23.1 (d,  $J_{\text{C-P}} = 4.5$  Hz), 22.8 (d,  $J_{\text{C-P}} = 4.8$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -8.21; HRMS (ESI<sup>+</sup>) calcd for  $\text{C}_{15}\text{H}_{21}\text{O}_4\text{P}$  [M+H]<sup>+</sup>: 297.1250, found: 297.1255.

**Diisopropyl (naphthalen-1-ylethynyl)phosphonate (3m):**<sup>2</sup> colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.28 (d,  $J = 8.3$  Hz, 1H), 7.94 (d,  $J = 8.3$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 1H), 7.81 (d,  $J = 7.1$  Hz, 1H), 7.65-7.51 (m, 2H), 7.45 (t,  $J = 7.8$  Hz, 1H), 4.95-4.82 (m, 2H), 1.47-1.42 (m, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  132.4 (d,  $J_{\text{C-P}} = 2.1$  Hz), 132.0, 131.5 (d,  $J_{\text{C-P}} = 2.7$  Hz), 130.2, 127.6, 126.7, 126.0, 124.6, 124.1, 116.4 (d,  $J_{\text{C-P}} = 5.6$  Hz), 95.6 (d,  $J_{\text{C-P}} = 52.2$  Hz), 83.6 (d,  $J_{\text{C-P}} = 295.2$  Hz), 71.5 (d,  $J_{\text{C-P}} = 5.6$  Hz), 23.0 (d,  $J_{\text{C-P}} = 4.5$  Hz), 22.8 (d,  $J_{\text{C-P}} = 4.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -8.18.

**Diisopropyl ((4-cyanophenyl)ethynyl)phosphonate (3n):** colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.68-7.58 (m, 4H), 4.88-4.70 (m, 2H), 1.39 (d,  $J = 6.1$  Hz, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  132.0 (d,  $J_{\text{C-P}} = 2.4$  Hz), 131.2, 127.5 (d,  $J_{\text{C-P}} = 12.1$  Hz), 116.8, 112.9, 94.1 (d,  $J_{\text{C-P}} = 51.4$  Hz), 83.0 (d,  $J_{\text{C-P}} = 292.7$  Hz), 71.8 (d,  $J_{\text{C-P}} = 5.6$  Hz), 22.9 (d,  $J_{\text{C-P}} = 4.5$  Hz), 22.6 (t,  $J_{\text{C-P}} = 4.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -9.41; HRMS (ESI<sup>+</sup>) calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_3\text{P}$  [M+H]<sup>+</sup>: 292.1097, found: 292.1096.

**Diisopropyl ((4-nitrophenyl)ethynyl)phosphonate (3o):** colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.21 (d,  $J = 8.5$  Hz, 2H), 7.69 (d,  $J = 8.5$  Hz, 2H), 4.88-4.74 (m, 2H), 1.39 (d,  $J = 6.0$  Hz, 6H), 1.38 (d,  $J = 6.0$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  147.4, 132.4 (d,  $J_{\text{C-P}} = 2.4$  Hz), 125.4 (d,  $J_{\text{C-P}} = 5.7$  Hz), 122.8, 93.7 (d,  $J_{\text{C-P}} = 51.3$  Hz), 83.6 (d,  $J_{\text{C-P}} = 291.1$  Hz), 71.9 (d,  $J_{\text{C-P}} = 5.6$  Hz), 22.9 (d,  $J_{\text{C-P}} = 4.6$  Hz), 22.6 (t,  $J_{\text{C-P}} = 5.3$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -9.55; HRMS (ESI<sup>+</sup>) calcd for  $\text{C}_{14}\text{H}_{18}\text{NO}_5\text{P}$  [M+H]<sup>+</sup>: 312.0995, found: 312.0994.

**Diisopropyl ((4-acetylphenyl)ethynyl)phosphonate (3p):**<sup>2</sup> colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.93 (d,  $J = 8.2$  Hz, 2H), 7.62 (d,  $J = 8.2$  Hz, 1H), 4.90-4.74 (m, 2H), 2.60 (s, 3H), 1.40 (d,  $J = 6.4$  Hz, 6H), 1.39 (d,  $J = 6.0$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  196.0, 137.0, 131.7 (d,  $J_{\text{C-P}} = 2.3$  Hz), 127.3, 123.4 (d,  $J_{\text{C-P}} = 5.5$  Hz), 95.5 (d,  $J_{\text{C-P}} = 51.9$  Hz), 81.6 (d,  $J_{\text{C-P}} = 294.0$  Hz), 71.6 (d,  $J_{\text{C-P}} = 5.6$  Hz), 25.7, 22.9 (d,  $J_{\text{C-P}} = 4.5$  Hz), 22.7 (d,  $J_{\text{C-P}} = 4.7$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -8.87.

**Diisopropyl ((4-fluorophenyl)ethynyl)phosphonate (3q):**<sup>2</sup> colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.55-7.49 (m, 2H), 7.10-7.02 (m, 2H), 4.87-4.71 (m, 2H), 1.39 (d,  $J = 6.1$  Hz, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  163.8 (d,  $J_{\text{C-F}} = 251.8$  Hz), 134.8 (dd,  $J_{\text{C-P}} = 2.4$  Hz,  $J_{\text{C-F}} = 8.8$  Hz), 116.1 (d,  $J_{\text{C-F}} = 22.3$  Hz), 115.9 (d,  $J_{\text{C-P}} = 3.7$  Hz), 97.0 (d,  $J_{\text{C-P}} = 52.8$  Hz), 79.8 (d,  $J_{\text{C-P}} = 297.2$  Hz), 72.4 (d,  $J_{\text{C-P}} = 5.5$  Hz), 23.9 (d,  $J_{\text{C-P}} = 4.6$  Hz), 23.7 (d,  $J_{\text{C-P}} = 4.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -8.28.

**Diisopropyl ((4-chlorophenyl)ethynyl)phosphonate (3r)**: colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.44 (d,  $J = 8.4$  Hz, 2H), 7.31 (d,  $J = 8.4$  Hz, 2H), 4.84-4.70 (m, 2H), 1.37 (d,  $J = 6.1$  Hz, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  135.9, 132.7 (d,  $J_{\text{C-P}} = 2.4$  Hz), 128.0, 117.3 (d,  $J_{\text{C-P}} = 5.7$  Hz), 95.7 (d,  $J_{\text{C-P}} = 52.4$  Hz), 80.0 (d,  $J_{\text{C-P}} = 296.8$  Hz), 71.5 (d,  $J_{\text{C-P}} = 5.6$  Hz), 22.9 (d,  $J_{\text{C-P}} = 4.5$  Hz), 22.6 (d,  $J_{\text{C-P}} = 4.8$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -8.53; HRMS (ESI $^+$ ) calcd for  $\text{C}_{14}\text{H}_{18}\text{ClO}_3\text{P}$  [ $\text{M}+\text{H}$ ] $^+$ : 301.0755, found: 301.0755.

**Diisopropyl ((4-(trifluoromethyl)phenyl)ethynyl)phosphonate (3s)**<sup>2</sup>: colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.68-7.60 (m, 4H), 4.87-4.74 (m, 2H), 1.40 (d,  $J = 6.0$  Hz, 6H), 1.39 (d,  $J = 6.4$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  132.8 (d,  $J_{\text{C-P}} = 2.3$  Hz), 132.2 (q,  $J_{\text{C-F}} = 33.0$  Hz), 125.6 (q,  $J_{\text{C-F}} = 3.7$  Hz), 123.7 (d,  $J_{\text{C-P}} = 5.3$  Hz), 123.5 (q,  $J_{\text{C-F}} = 270.9$  Hz), 95.8 (d,  $J_{\text{C-P}} = 51.7$  Hz), 82.4 (d,  $J_{\text{C-P}} = 293.6$  Hz), 72.7 (d,  $J_{\text{C-P}} = 5.6$  Hz), 23.9 (d,  $J_{\text{C-P}} = 4.5$  Hz), 23.7 (d,  $J_{\text{C-P}} = 4.8$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -9.03.

**Methyl 4-((diisopropoxyphosphoryl)ethynyl)benzoate (3t)**: colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.04 (d,  $J = 8.4$  Hz, 2H), 7.62 (d,  $J = 8.4$  Hz, 1H), 4.88-4.76 (m, 2H), 3.94 (s, 3H), 1.42 (d,  $J = 6.2$  Hz, 6H), 1.41 (d,  $J = 6.2$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  166.1, 132.5 (d,  $J_{\text{C-P}} = 2.3$  Hz), 131.7, 129.6, 124.3 (d,  $J_{\text{C-P}} = 5.4$  Hz), 96.7 (d,  $J_{\text{C-P}} = 52.0$  Hz), 82.5 (d,  $J_{\text{C-P}} = 294.6$  Hz), 72.7 (d,  $J_{\text{C-P}} = 5.5$  Hz), 52.5, 23.9 (d,  $J_{\text{C-P}} = 4.6$  Hz), 23.7 (t,  $J_{\text{C-P}} = 4.7$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -9.26; HRMS (ESI $^+$ ) calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_5\text{P}$  [ $\text{M}+\text{H}$ ] $^+$ : 325.1199, found: 325.1203.

**Diisopropyl ((2-aminophenyl)ethynyl)phosphonate (3u)**: colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.32 (d,  $J = 7.6$  Hz, 1H), 7.22-7.10 (m, 1H), 6.71-6.65 (m, 2H), 4.85-4.77 (m, 2H), 4.41 (s, 2H), 1.40 (d,  $J = 6.2$  Hz, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  150.0, 133.0 (d,  $J_{\text{C-P}} = 2.3$  Hz), 132.1, 117.7, 114.7, 103.5 (d,  $J_{\text{C-P}} = 5.5$  Hz), 96.3 (d,  $J_{\text{C-P}} = 52.5$  Hz), 85.0 (d,  $J_{\text{C-P}} = 296.7$  Hz), 72.4 (d,  $J_{\text{C-P}} = 5.5$  Hz), 24.0 (d,  $J_{\text{C-P}} = 4.5$  Hz), 23.7 (d,  $J_{\text{C-P}} = 4.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -8.29; HRMS (ESI $^+$ ) calcd for  $\text{C}_{14}\text{H}_{21}\text{NO}_3\text{P}$  [ $\text{M}+\text{H}$ ] $^+$ : 282.1254, found: 282.1256.

**Diisopropyl ((4-vinylphenyl)ethynyl)phosphonate (3v)**: colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.50 (d,  $J = 8.2$  Hz, 2H), 7.40 (d,  $J = 8.2$  Hz, 2H), 6.71 (dd,  $J = 17.6$  Hz, 10.9 Hz, 1H), 5.82 (d,  $J = 17.6$  Hz, 1H), 5.37 (d,  $J = 10.8$  Hz, 1H), 4.86-4.77 (m, 2H), 1.41 (d,  $J = 6.2$  Hz, 6H), 1.40 (d,  $J = 6.2$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  139.7, 135.9, 132.8 (d,  $J_{\text{C-P}} = 2.4$  Hz), 126.3, 118.9 (d,  $J_{\text{C-P}} = 5.7$  Hz), 116.3, 98.3 (d,  $J_{\text{C-P}} = 52.7$  Hz), 80.4 (d,  $J_{\text{C-P}} = 297.4$  Hz), 72.4 (d,  $J_{\text{C-P}} = 5.6$  Hz), 24.0 (d,  $J_{\text{C-P}} = 4.5$  Hz), 23.7 (d,  $J_{\text{C-P}} = 4.8$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -8.49; HRMS (ESI $^+$ ) calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{P}$  [ $\text{M}+\text{H}$ ] $^+$ : 293.1301, found: 293.1306.

**Diisopropyl (benzo[b]thiophen-6-ylethynyl)phosphonate (3x)**: colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.00 (s, 1H), 7.83 (d,  $J = 8.3$  Hz, 1H), 7.55-7.41 (m, 2H), 7.34-7.28 (m, 1H), 4.90-4.74 (m, 2H), 1.44-1.37 (m, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100

MHz):  $\delta$  140.8, 138.4, 127.2 (d,  $J_{C-P}$  = 2.5 Hz), 127.2, 126.3 (d,  $J_{C-P}$  = 2.2 Hz), 122.7, 121.8, 114.6 (d,  $J_{C-P}$  = 5.6 Hz), 97.8 (d,  $J_{C-P}$  = 52.8 Hz), 78.5 (d,  $J_{C-P}$  = 297.2 Hz), 71.3 (d,  $J_{C-P}$  = 5.5 Hz), 23.0 (d,  $J_{C-P}$  = 4.5 Hz), 22.7 (d,  $J_{C-P}$  = 4.9 Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -7.99; HRMS (ESI<sup>+</sup>) calcd for  $\text{C}_{16}\text{H}_{19}\text{O}_3\text{PS}$   $[\text{M}+\text{H}]^+$ : 323.0865, found: 323.0866.

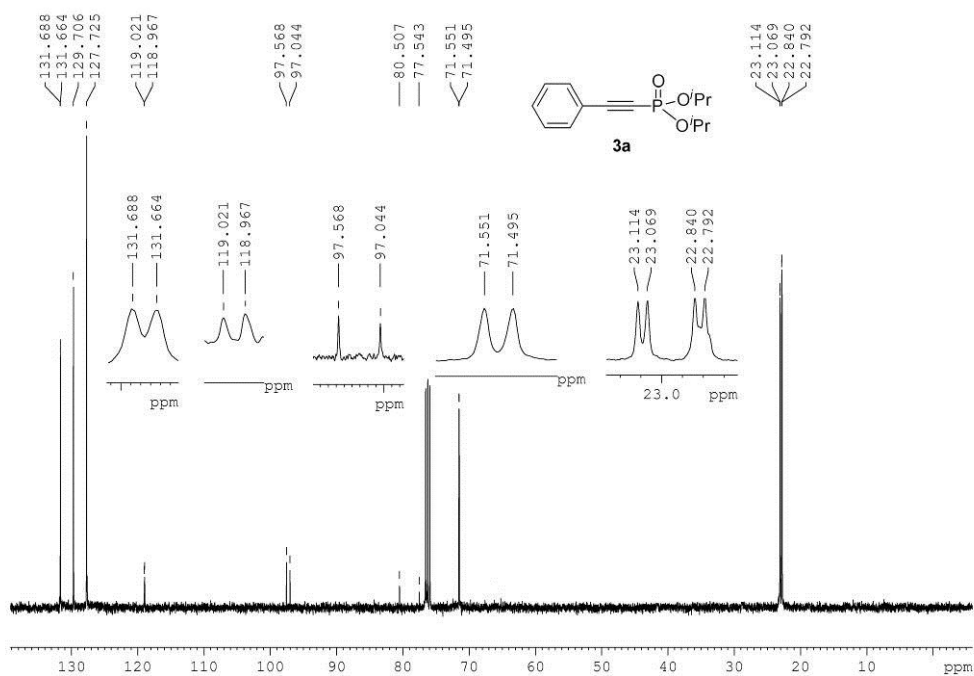
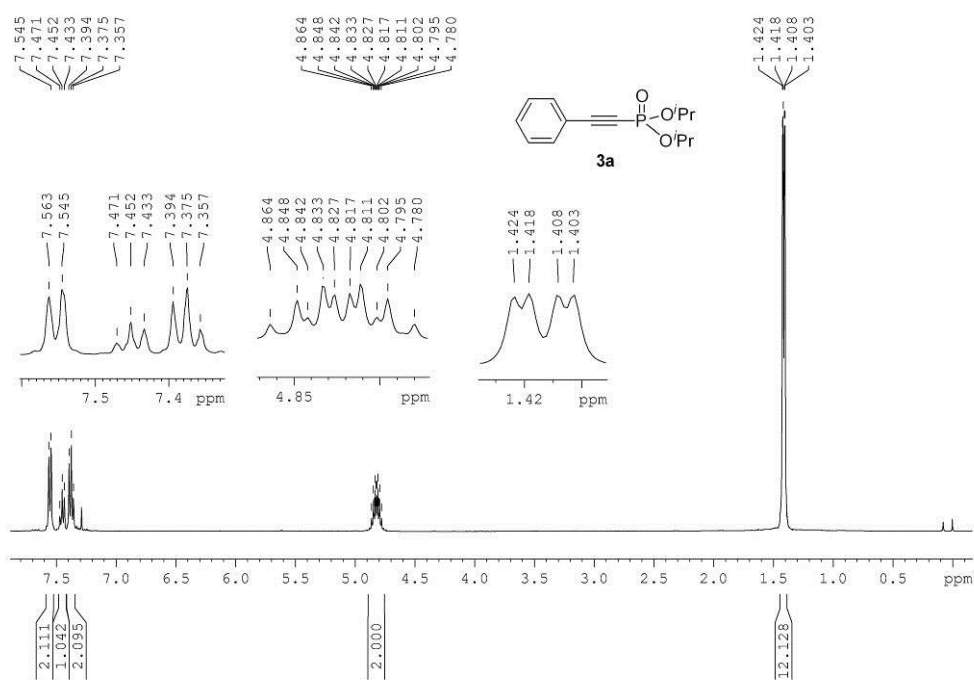
**Diisopropyl ((5-methylthiophen-2-yl)ethynyl)phosphonate (3y)**: colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.15 (d,  $J$  = 3.6 Hz, 1H), 6.61 (d,  $J$  = 3.6 Hz, 1H), 4.80-4.64 (m, 2H), 2.42 (s, 3H), 1.31 (d,  $J$  = 6.2 Hz, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  144.7, 135.1, 124.8, 116.1, 91.3 (d,  $J_{C-P}$  = 53.5 Hz), 82.1 (d,  $J_{C-P}$  = 298.0 Hz), 71.3 (d,  $J_{C-P}$  = 5.5 Hz), 22.9 (d,  $J_{C-P}$  = 4.5 Hz), 22.6 (d,  $J_{C-P}$  = 4.9 Hz), 14.5;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -8.04; HRMS (ESI<sup>+</sup>) calcd for  $\text{C}_{13}\text{H}_{19}\text{O}_3\text{PS}$   $[\text{M}+\text{H}]^+$ : 287.0865, found: 287.0865.

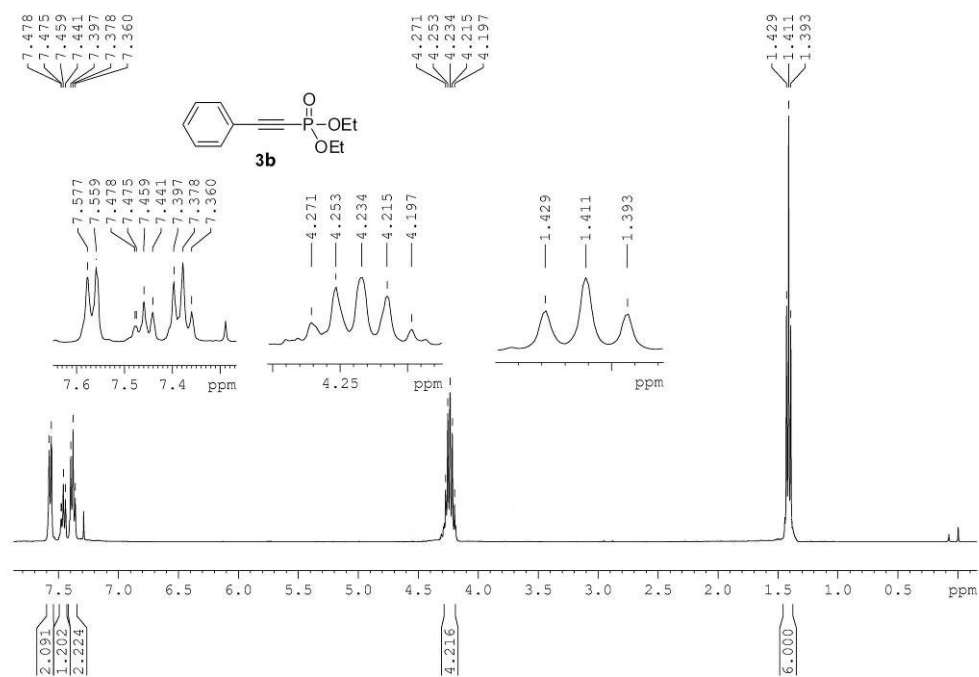
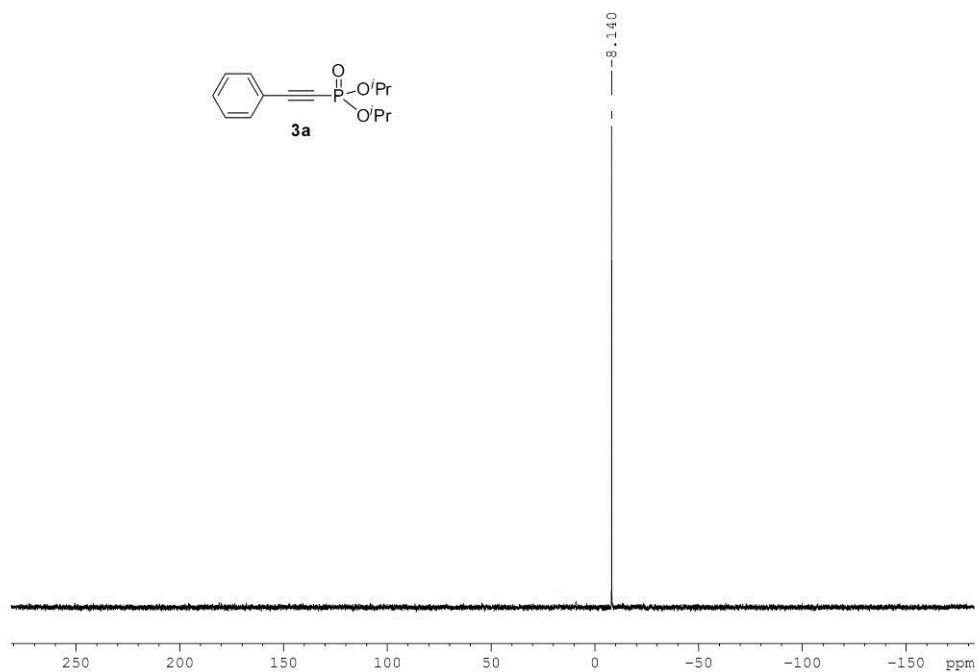
**Diisopropyl (isoquinolin-4-ylethynyl)phosphonate (3z)**: colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.22 (s, 1H), 8.72 (s, 1H), 8.13 (d,  $J$  = 8.2 Hz, 1H), 7.98 (d,  $J$  = 8.2 Hz, 1H), 7.78 (t,  $J$  = 7.6 Hz, 1H), 7.64 (t,  $J$  = 7.6 Hz, 1H), 4.87-4.78 (m, 2H), 1.38 (m, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  154.0, 148.1 (d,  $J_{C-P}$  = 2.7 Hz), 135.6, 128.6, 128.3, 124.6, 112.9, 93.4 (d,  $J_{C-P}$  = 52.1 Hz), 87.4 (d,  $J_{C-P}$  = 293.4 Hz), 72.8 (d,  $J_{C-P}$  = 5.5 Hz), 24.0 (d,  $J_{C-P}$  = 4.5 Hz), 23.8 (d,  $J_{C-P}$  = 4.8 Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 163 MHz):  $\delta$  -9.46; HRMS (ESI<sup>+</sup>) calcd for  $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{P}$   $[\text{M}+\text{H}]^+$ : 318.1254, found: 318.1258.

#### References:

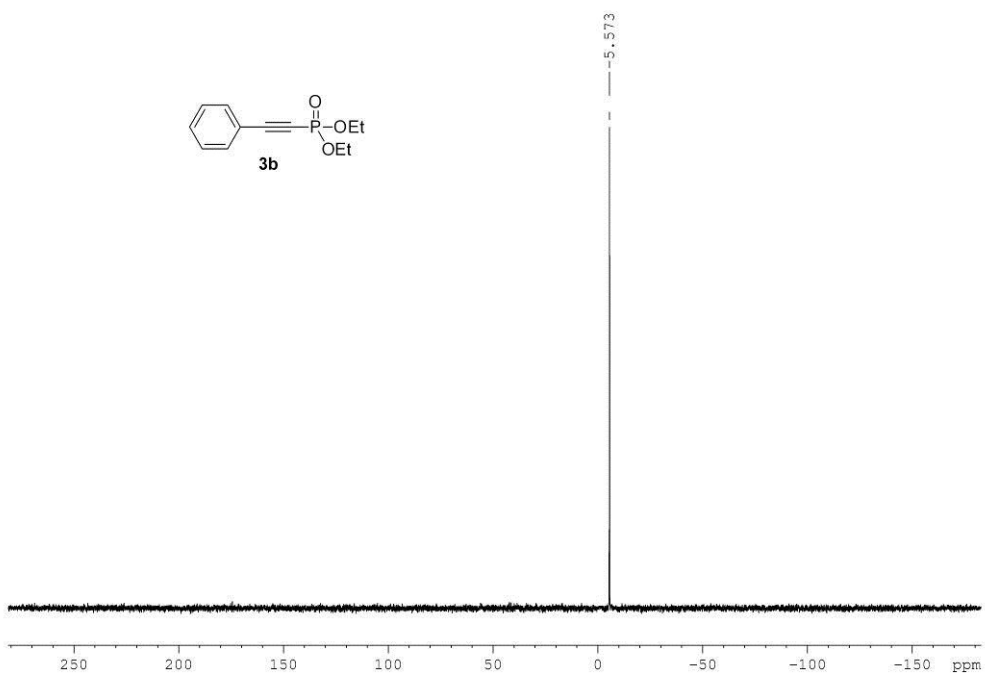
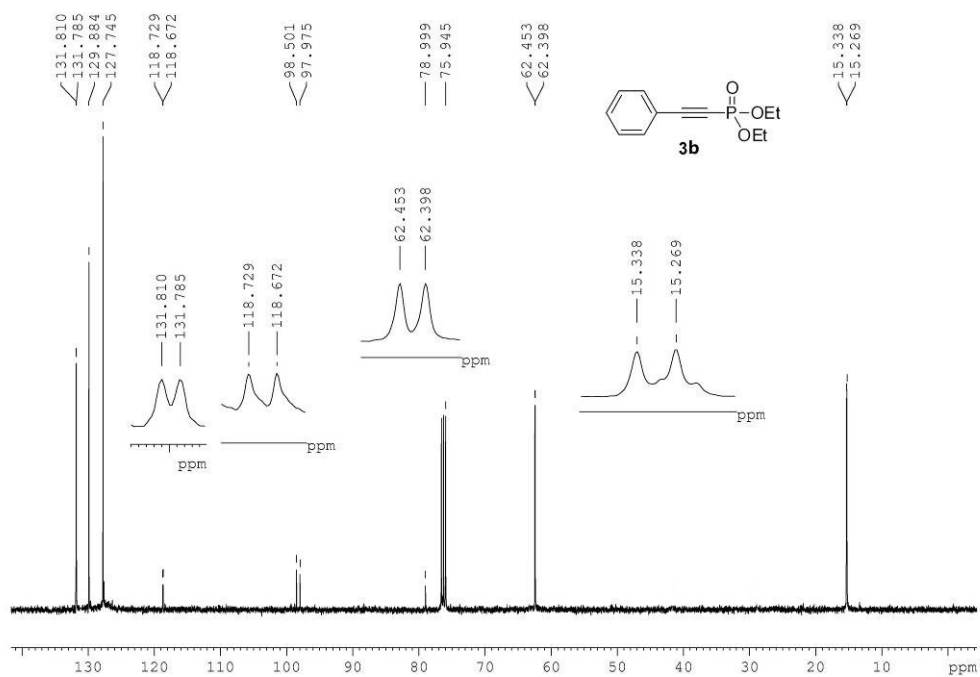
1. Gao, Y.; Wang, G.; Chen, L.; Xu, P.; Zhao, Y.; Zhou, Y.; Han, L.-B. *J. Am. Chem. Soc.* **2009**, *131*, 7956.
2. X. Li, F. Yang, Y.-J. Wu and Y.-S. Wu, *Org. Lett.*, 2014, **16**, 992.

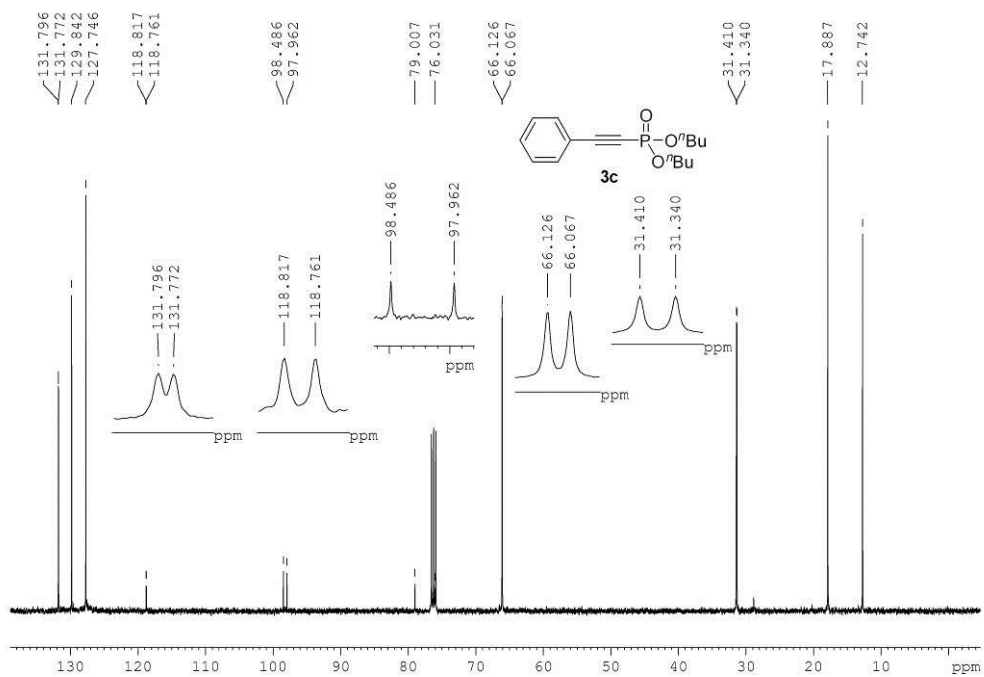
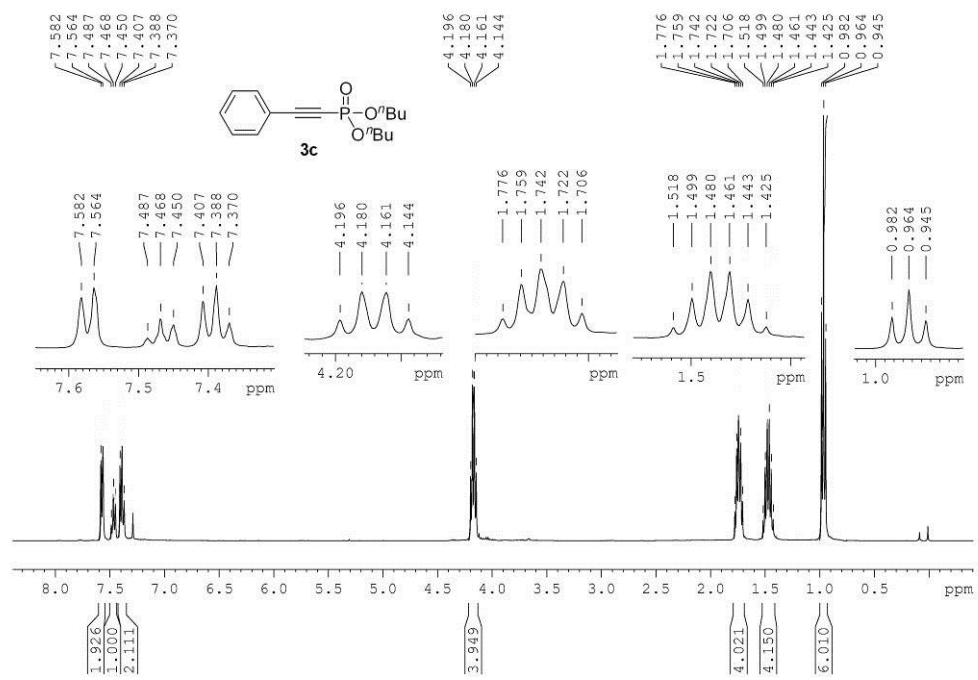
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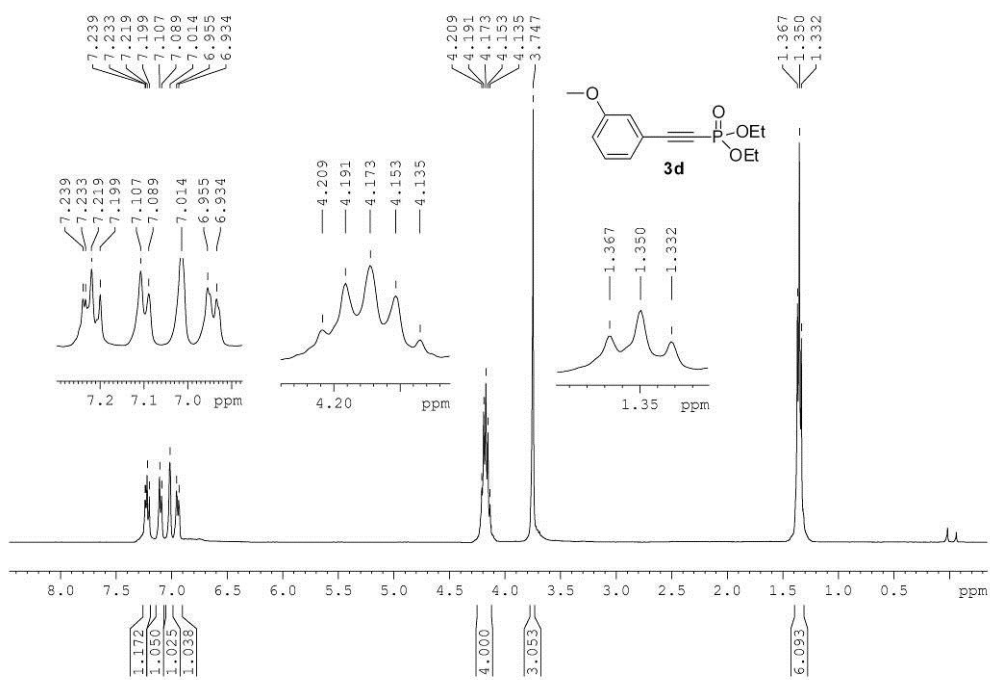
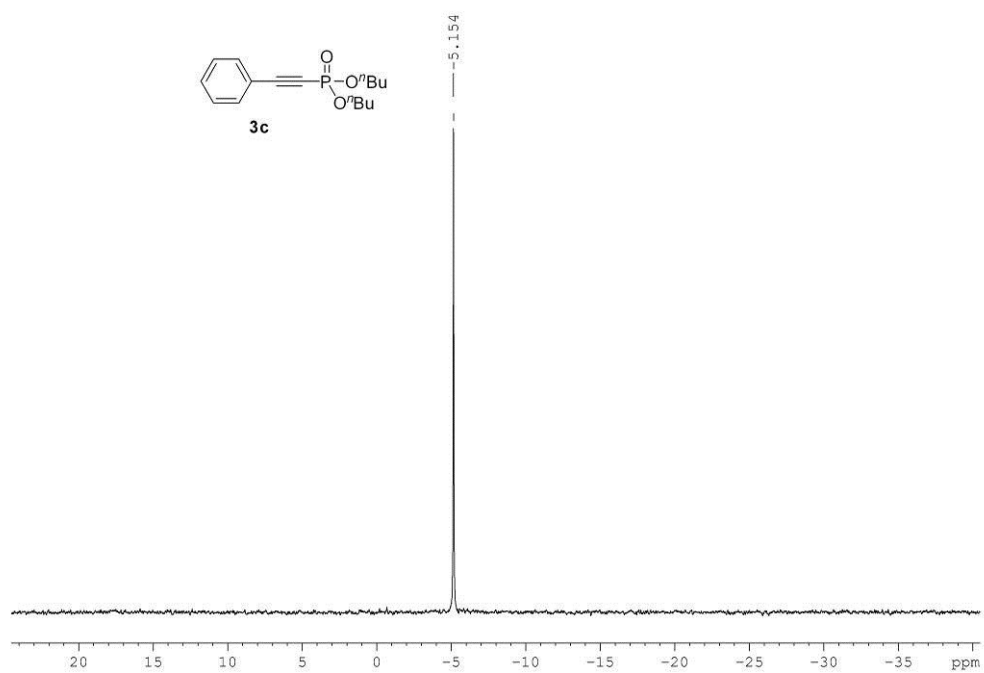


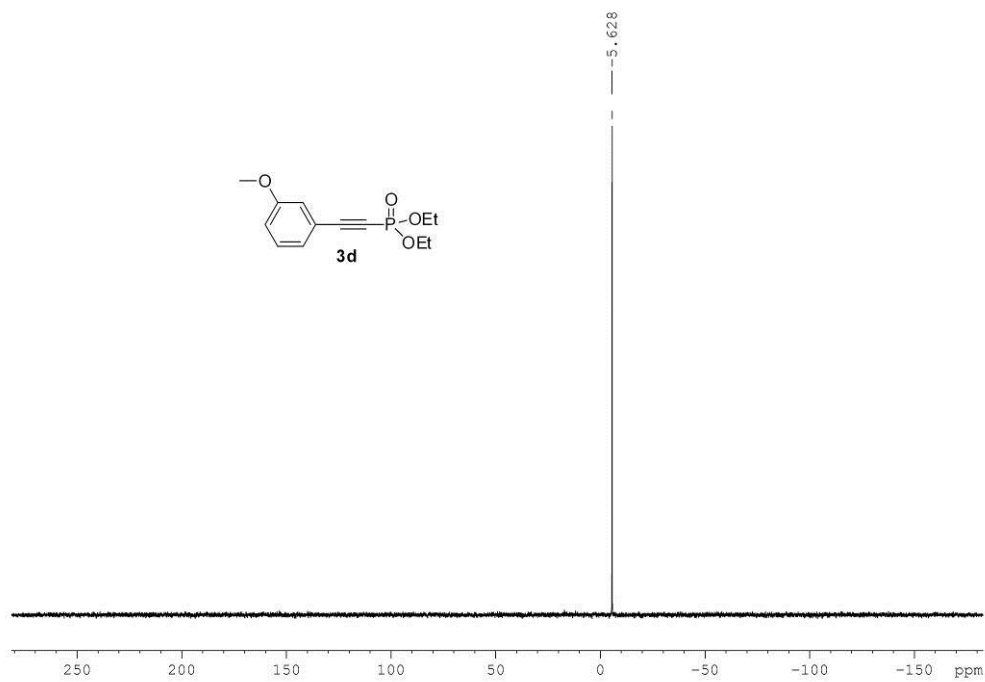
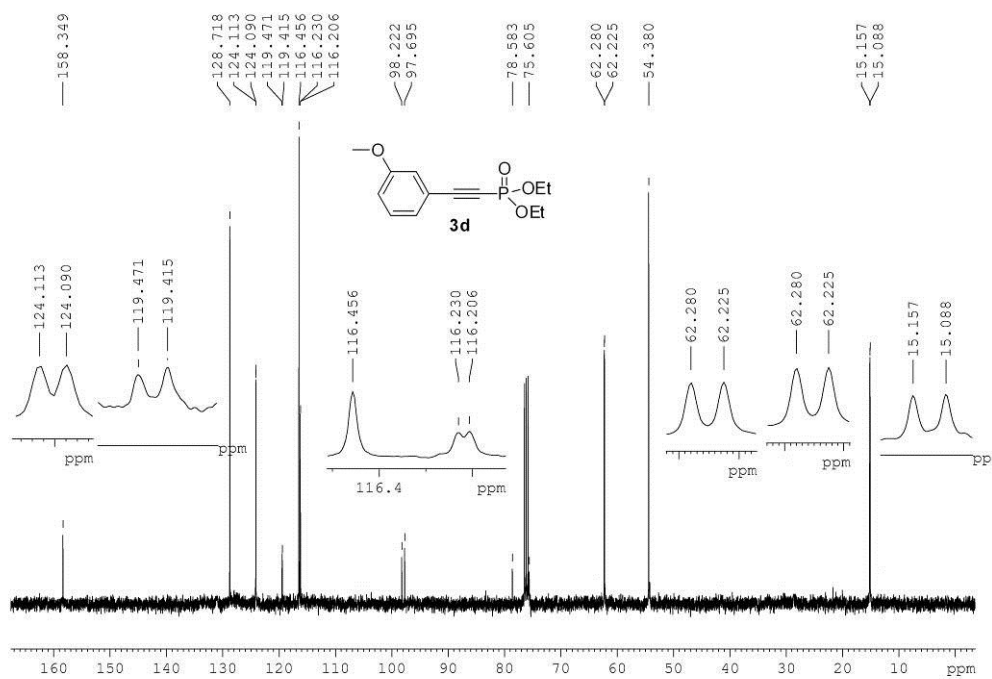


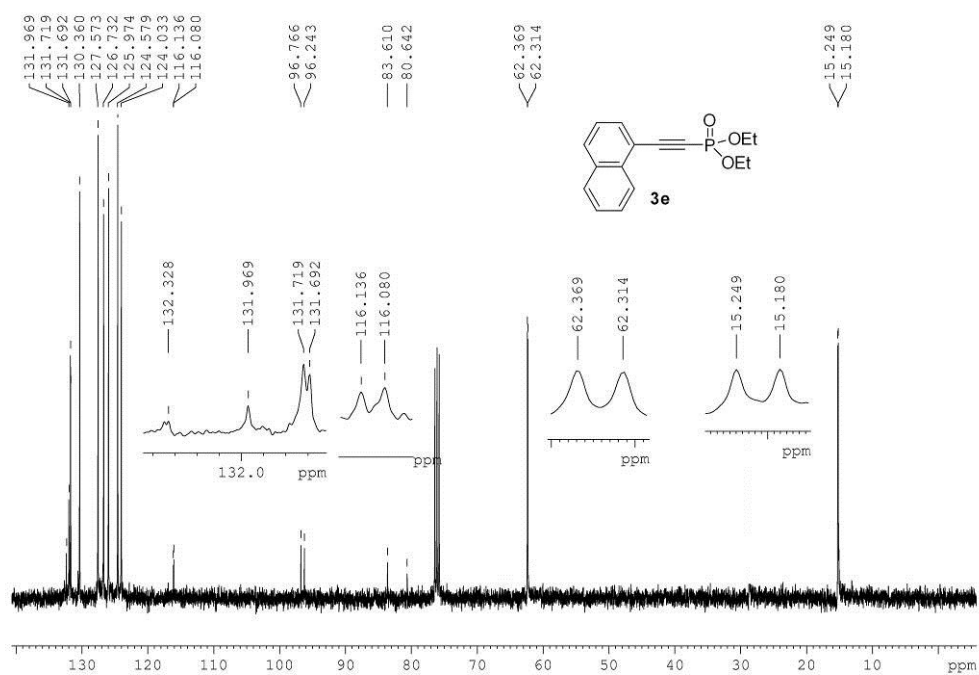
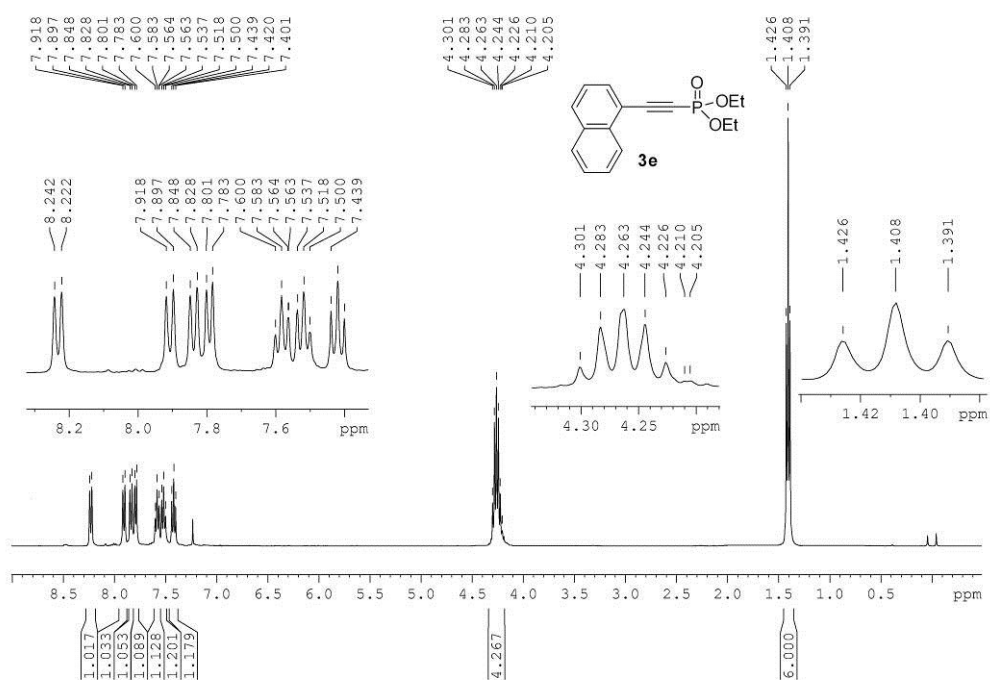


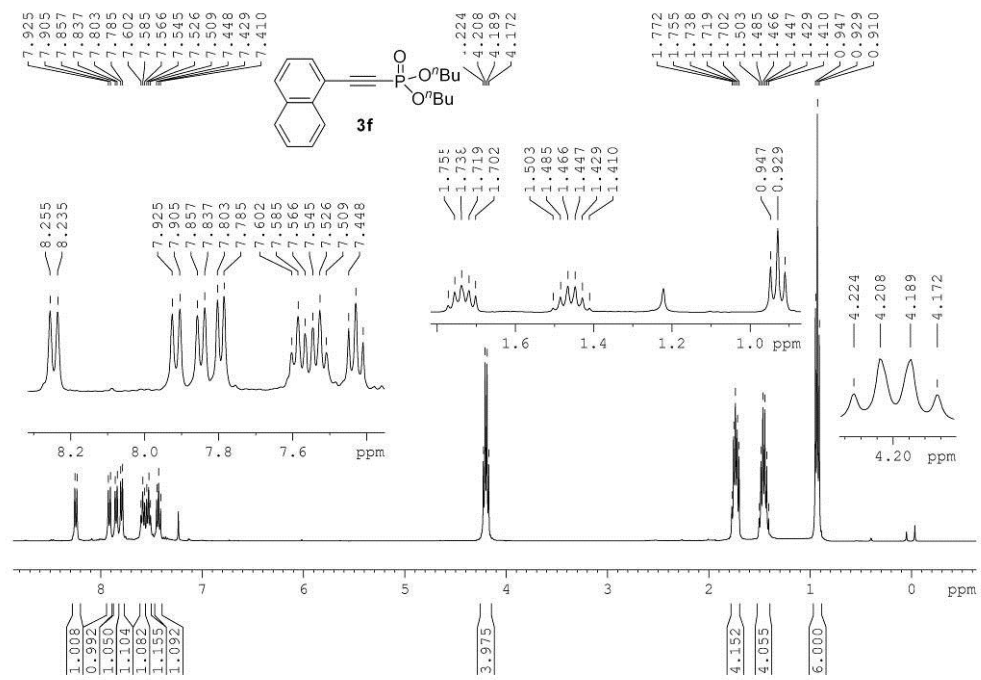
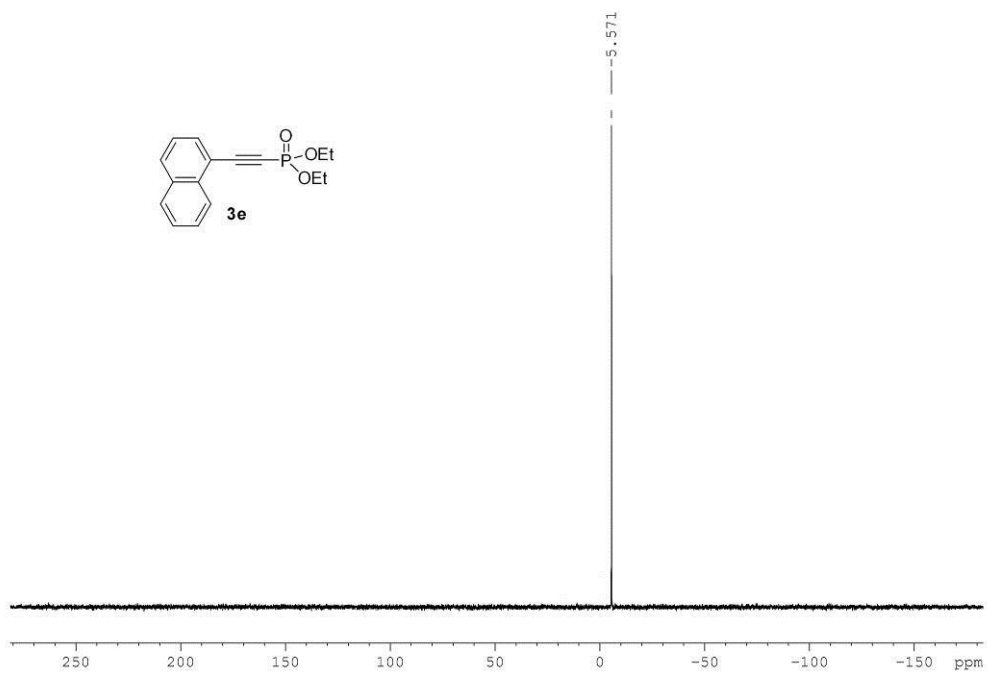


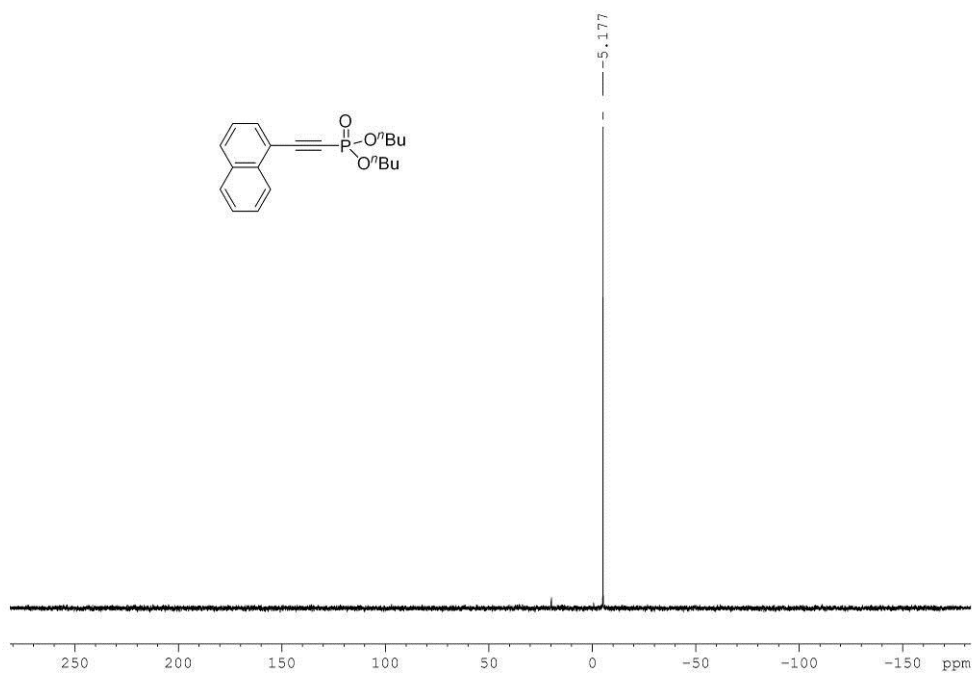
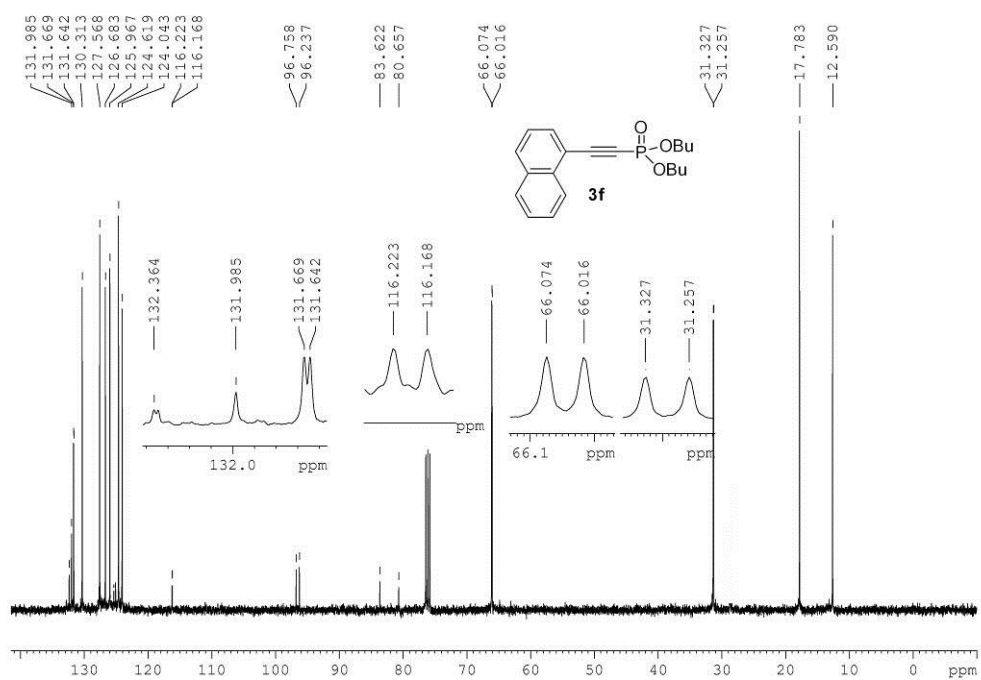


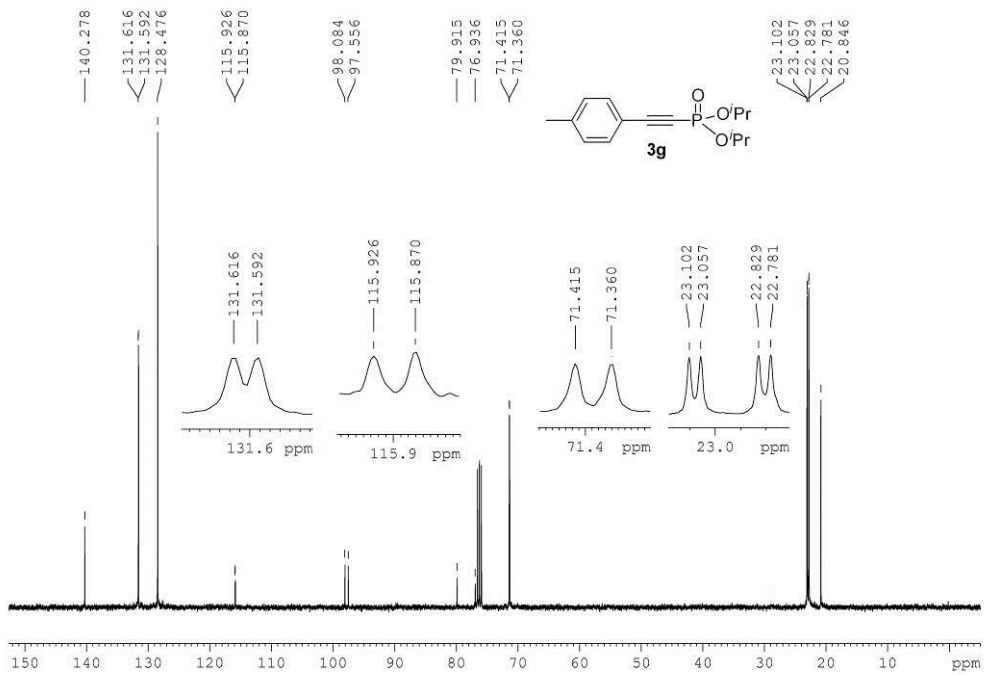
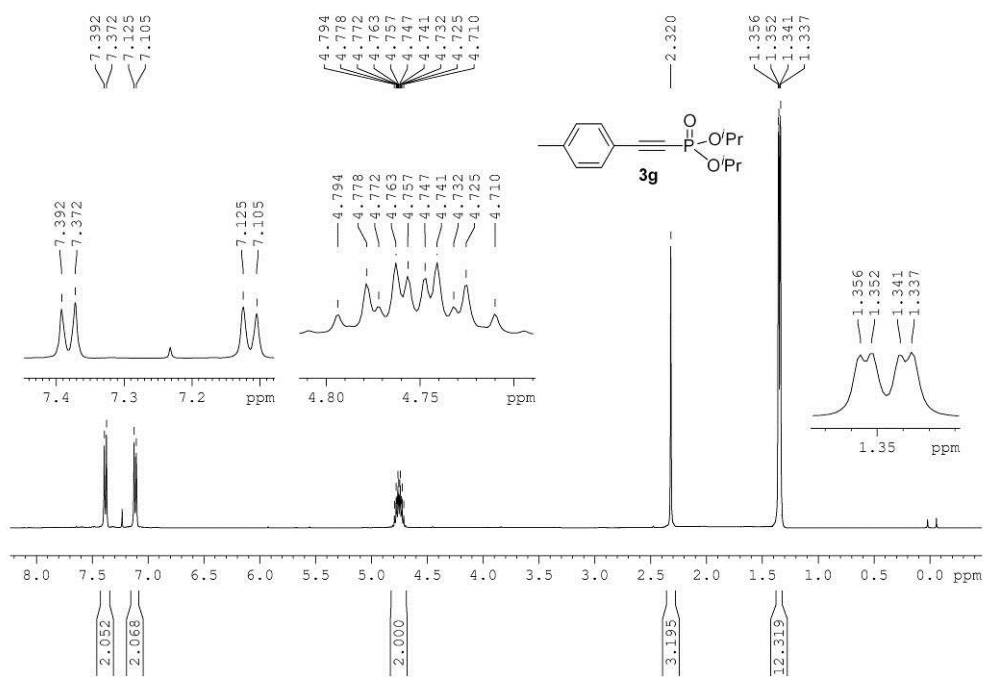




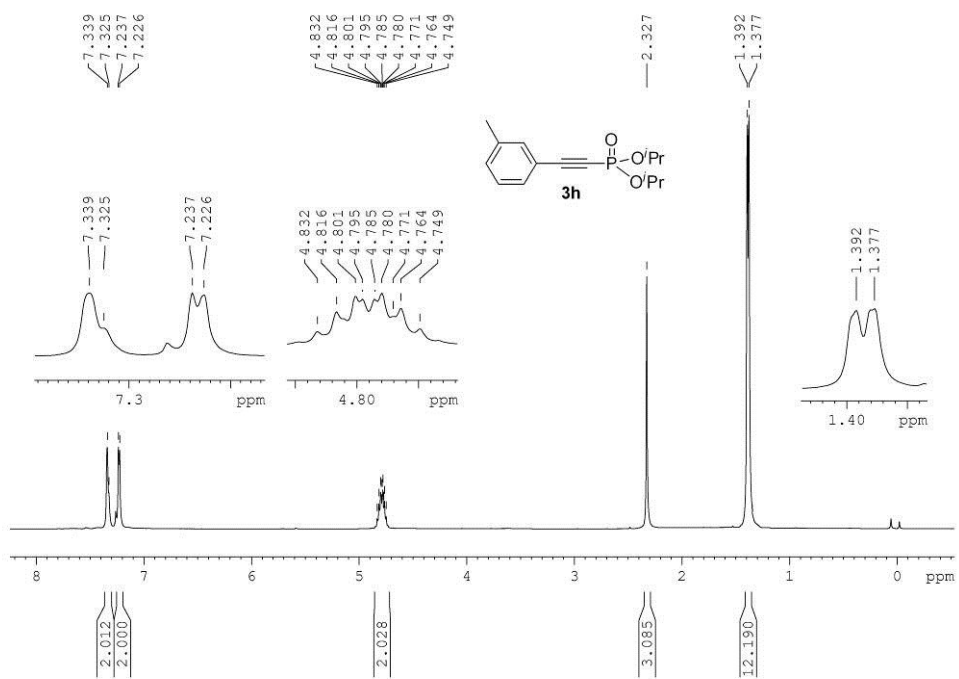
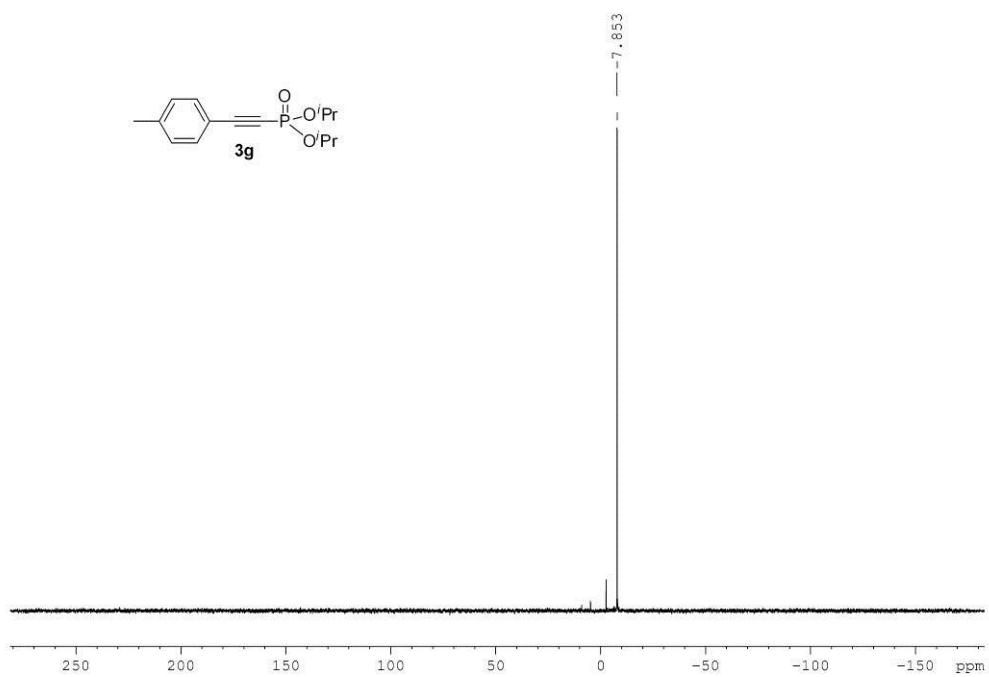


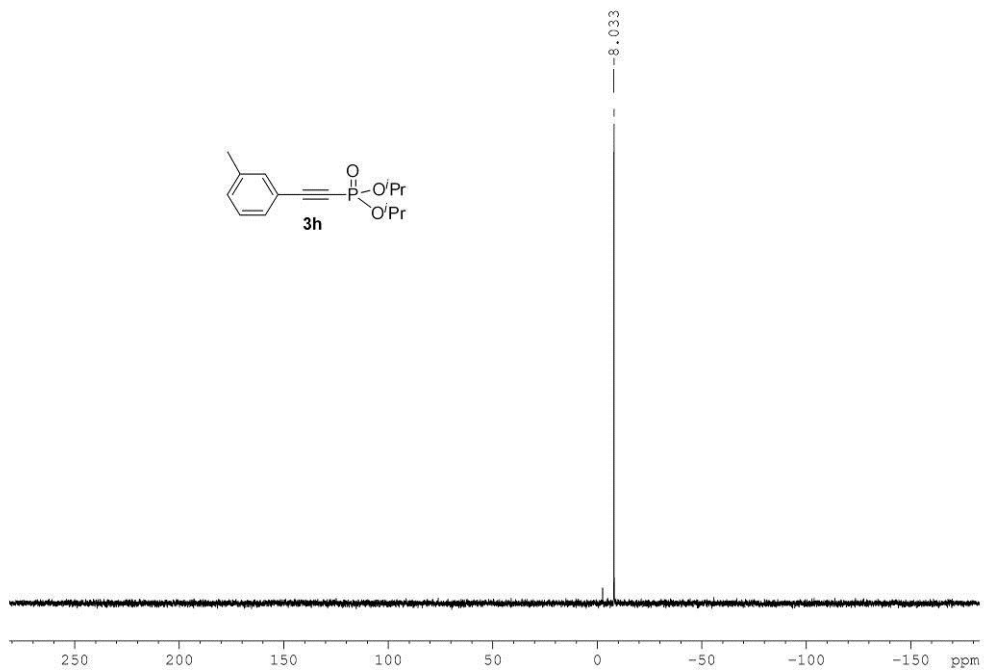
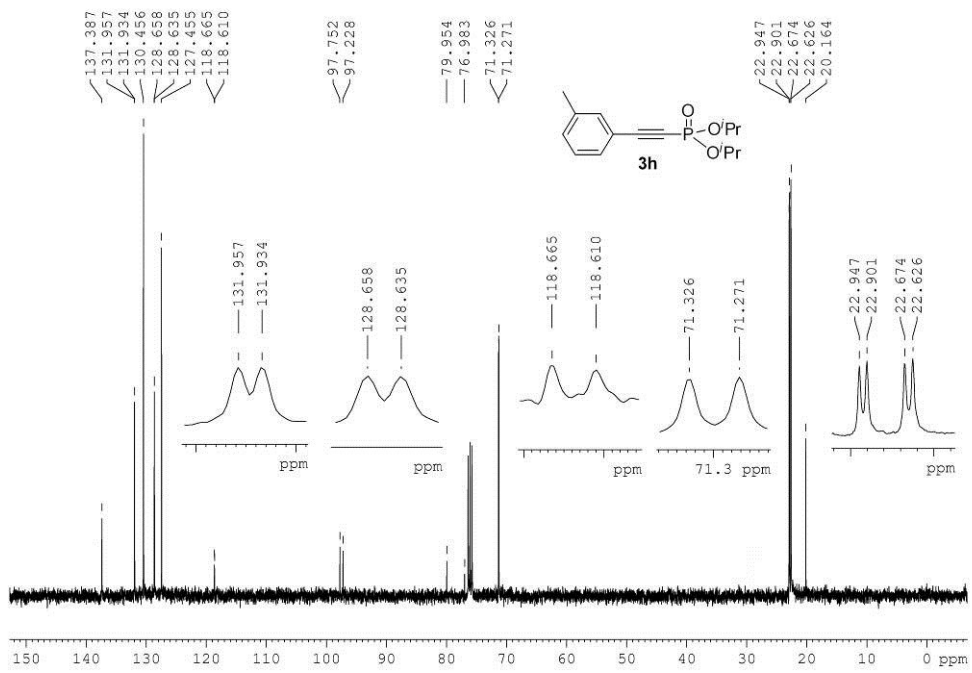


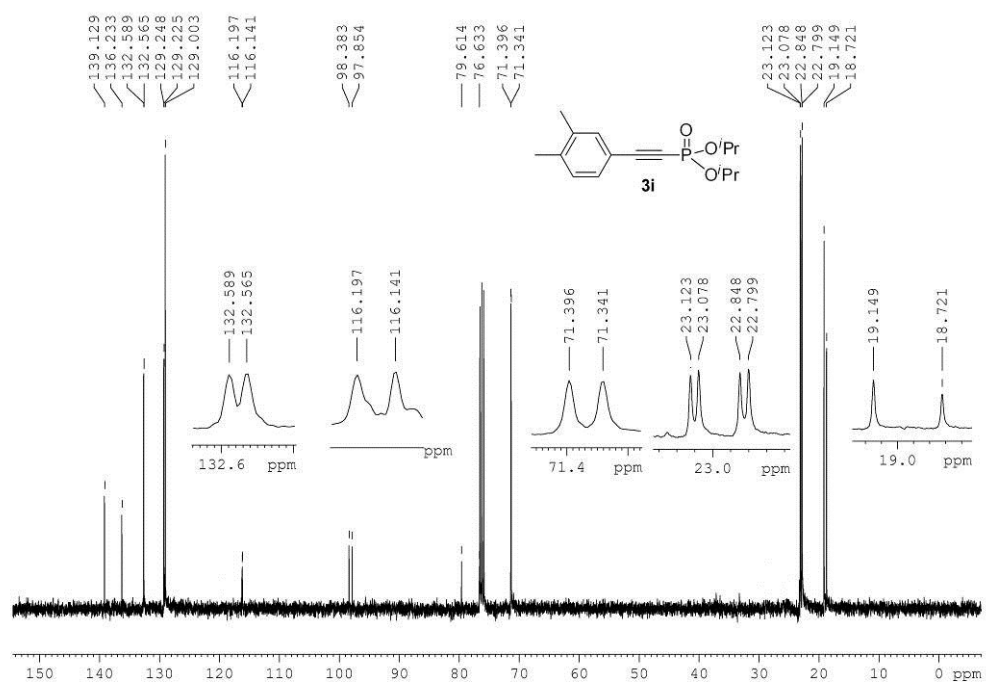
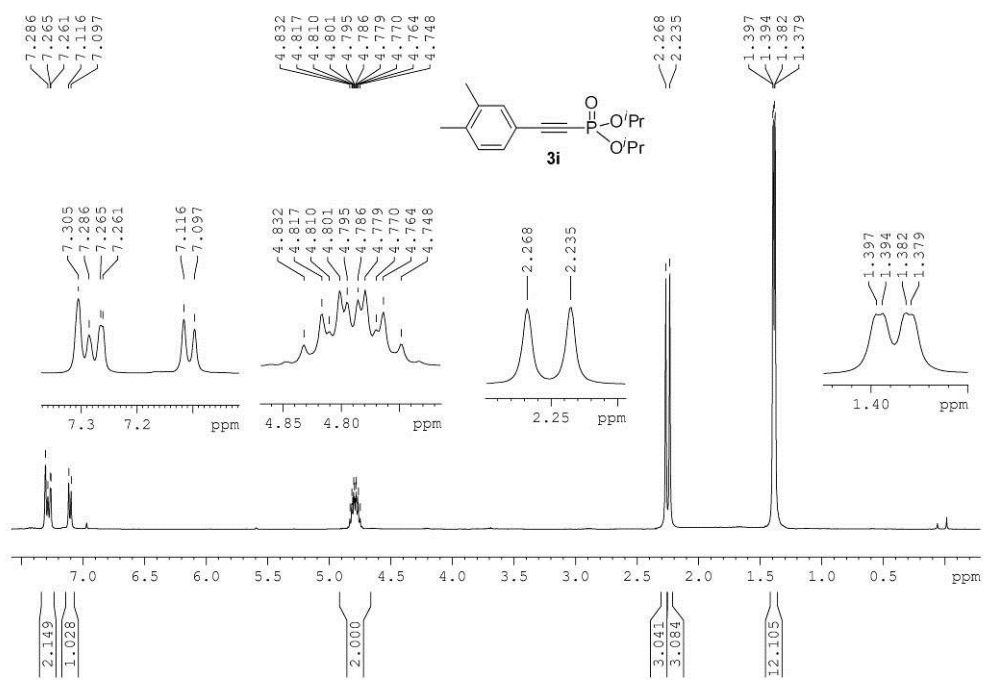


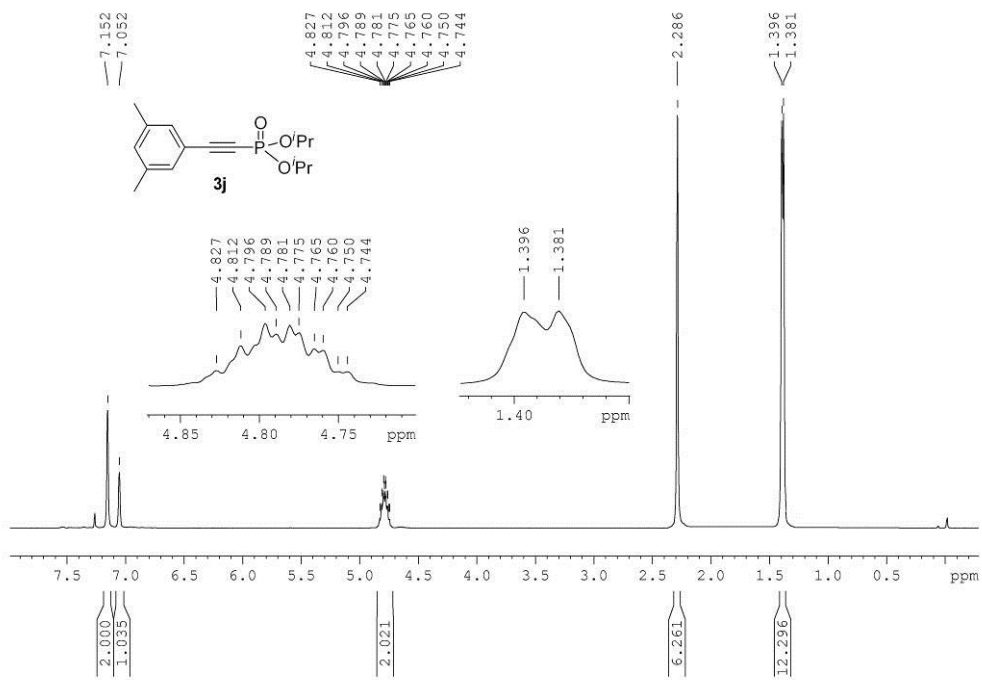
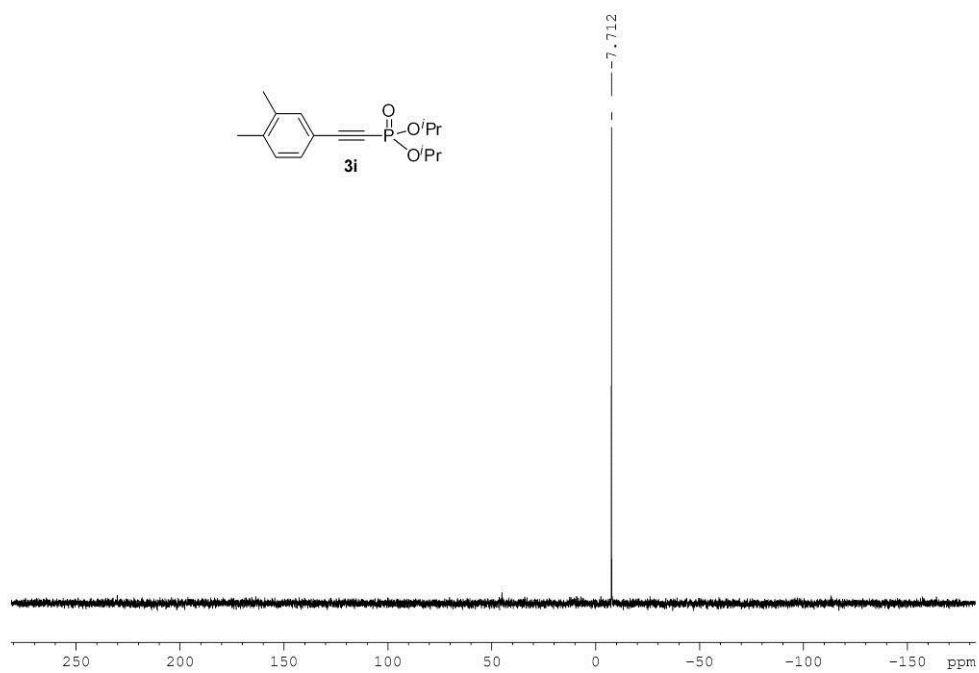


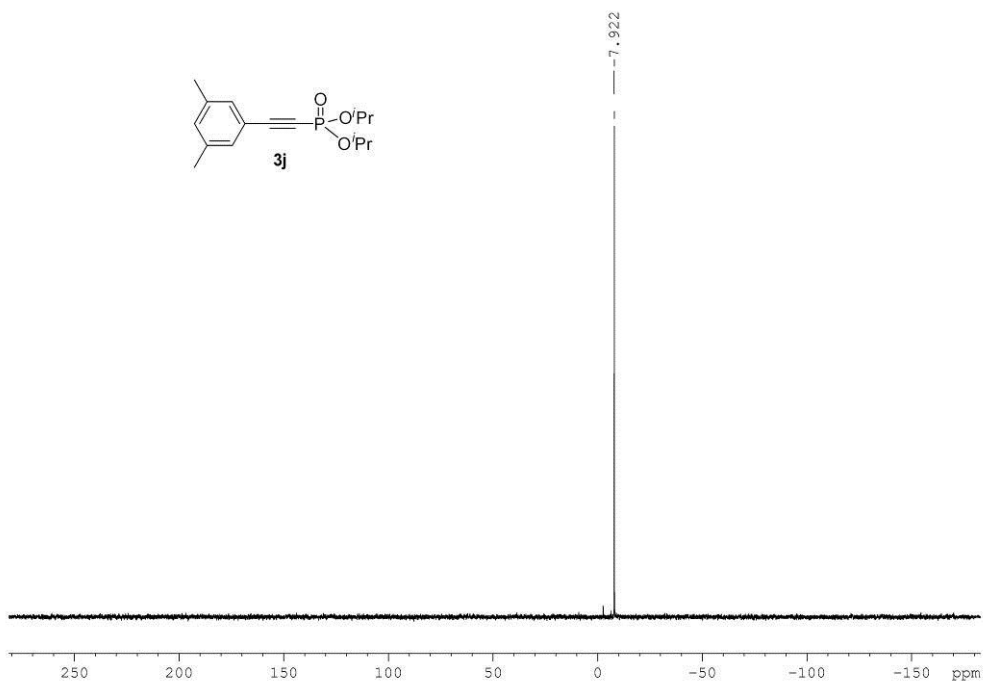
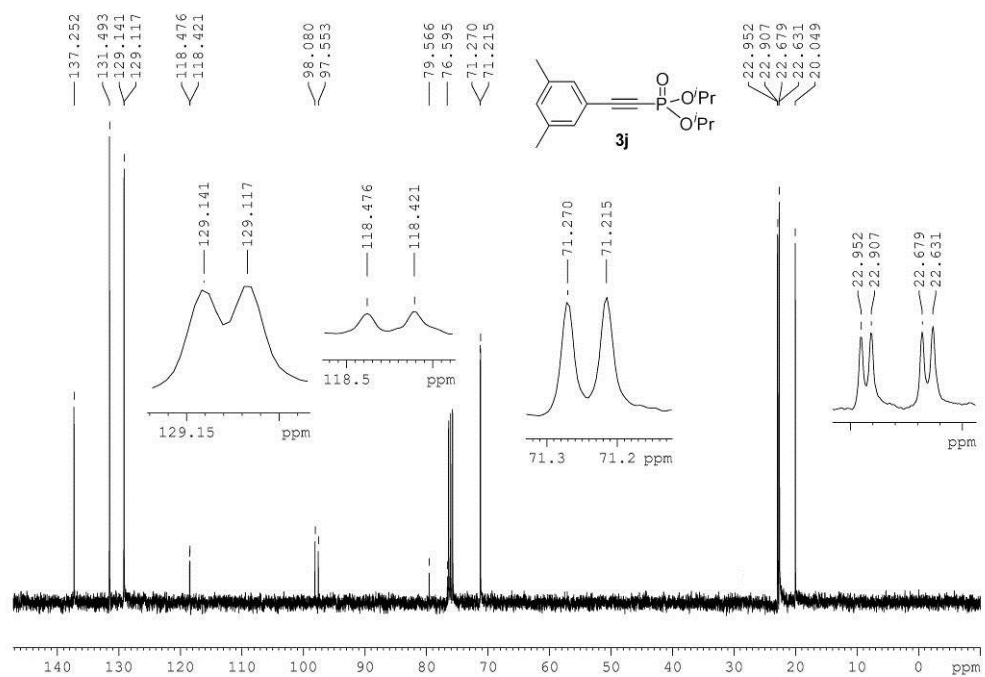


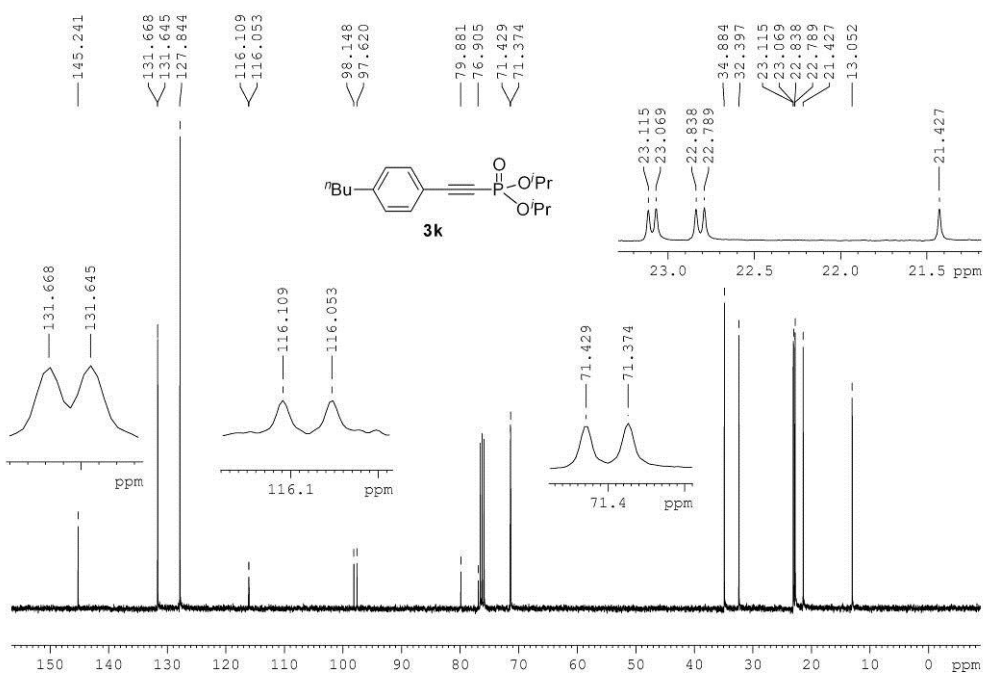
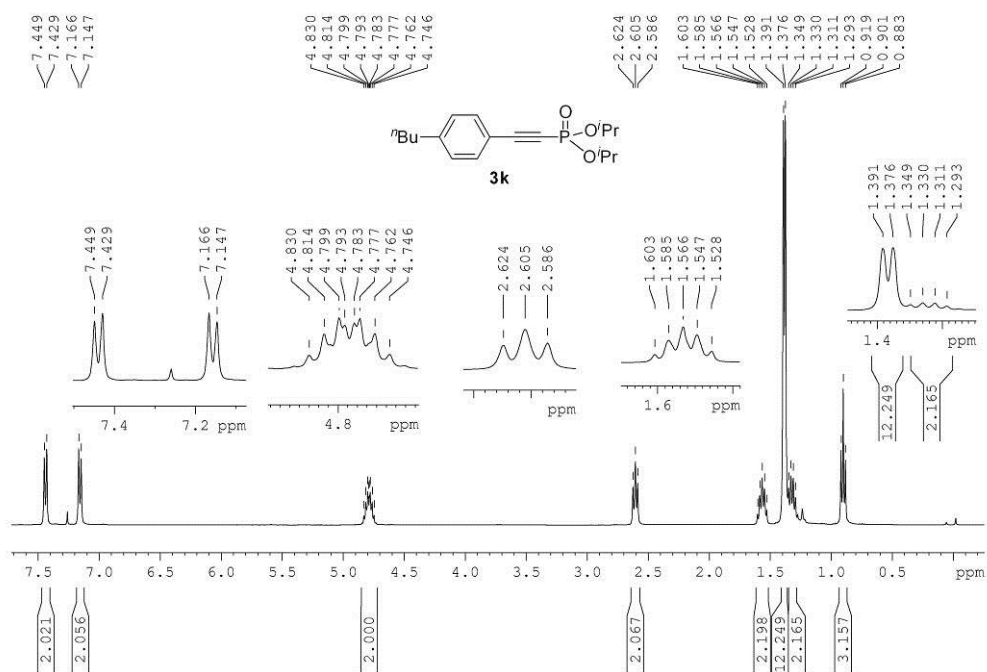


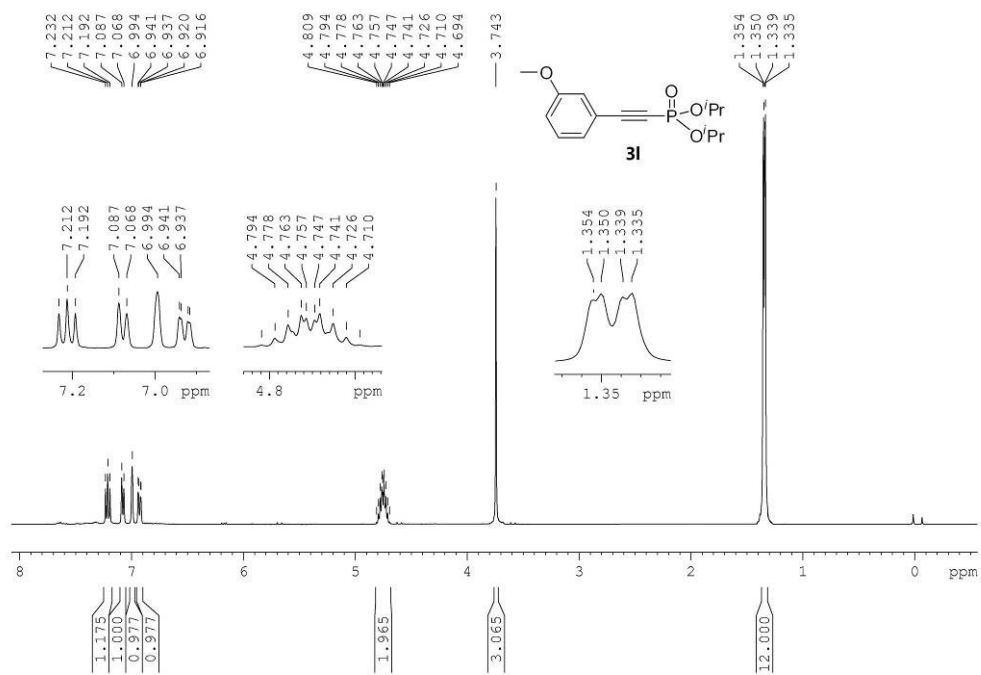
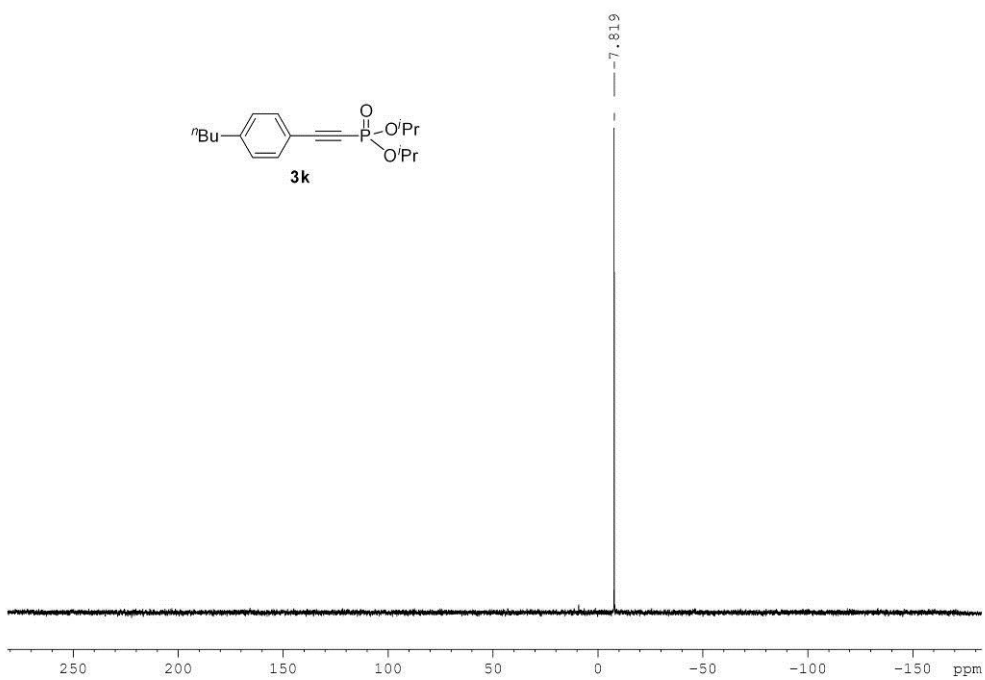


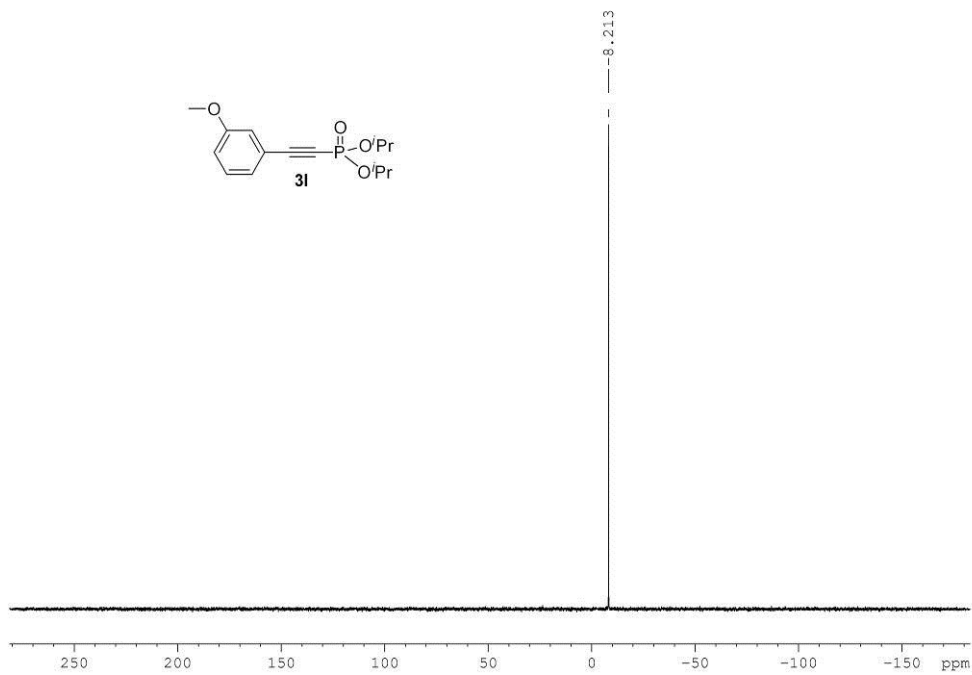
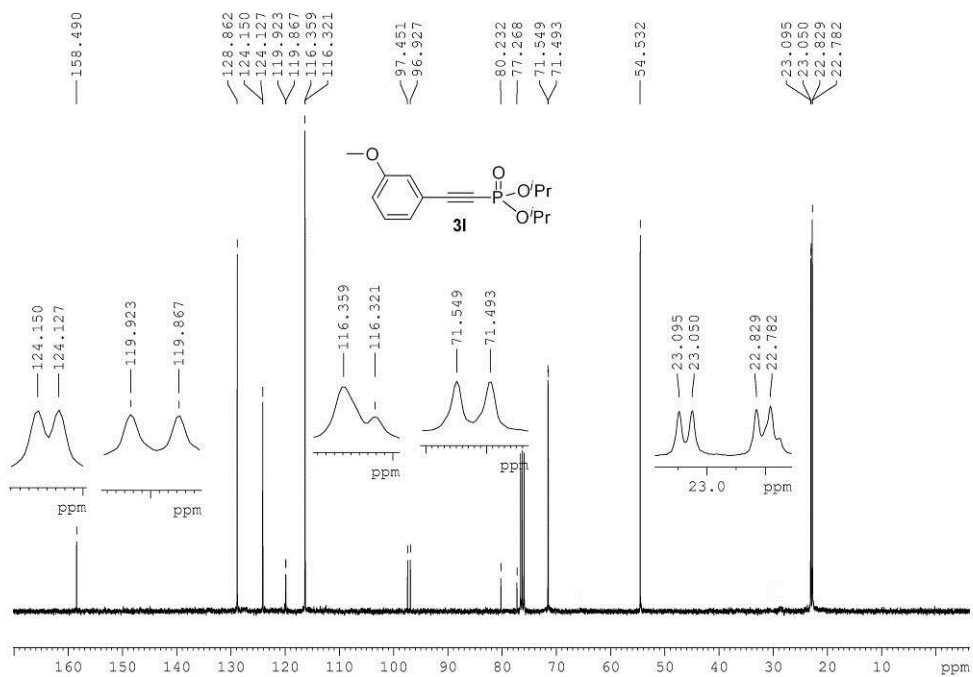




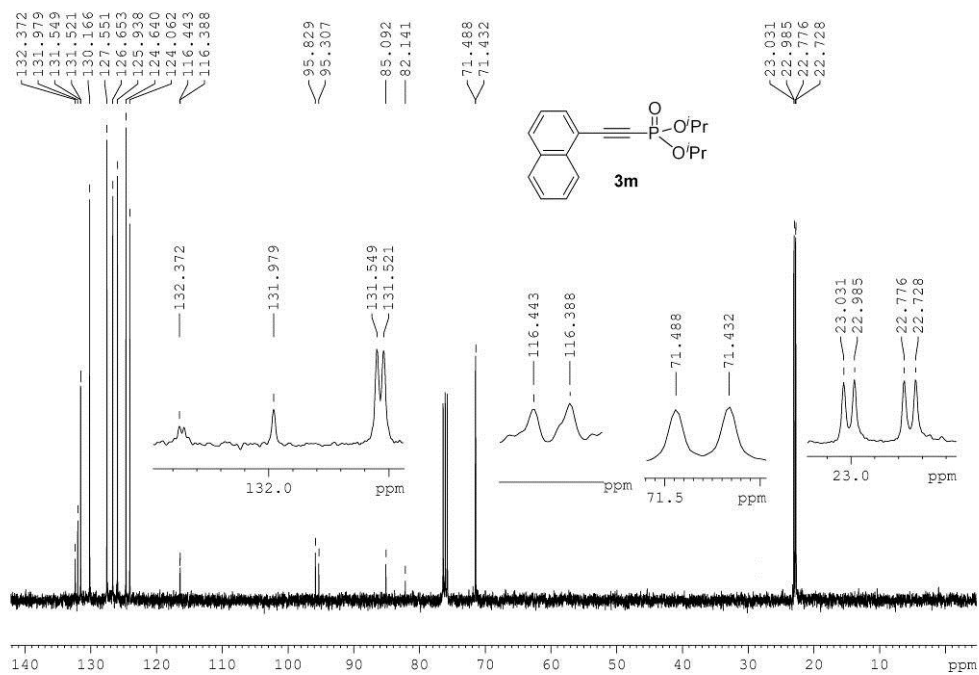
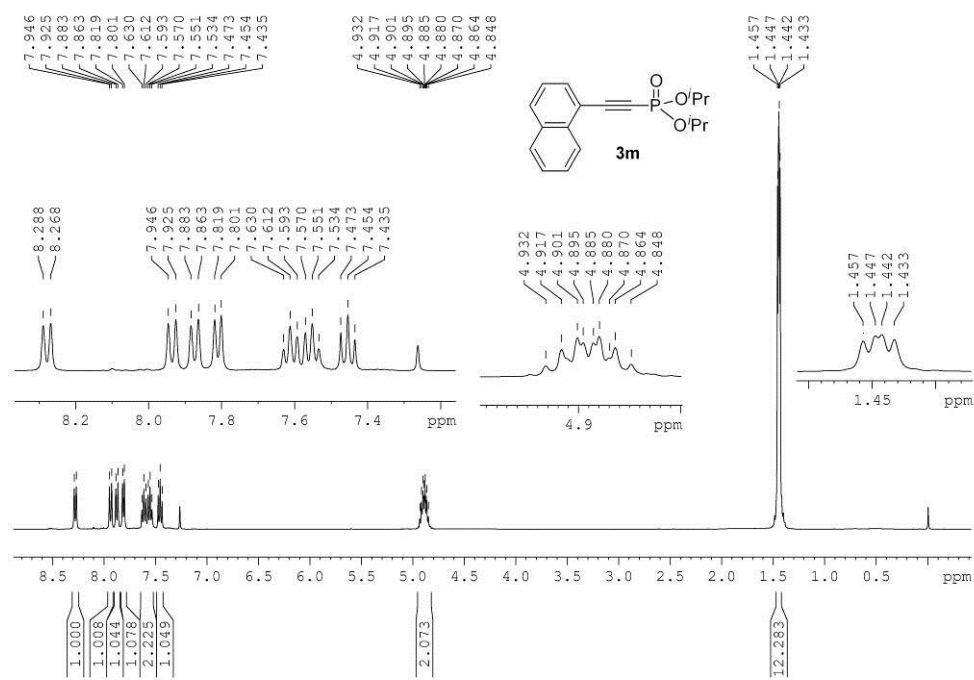


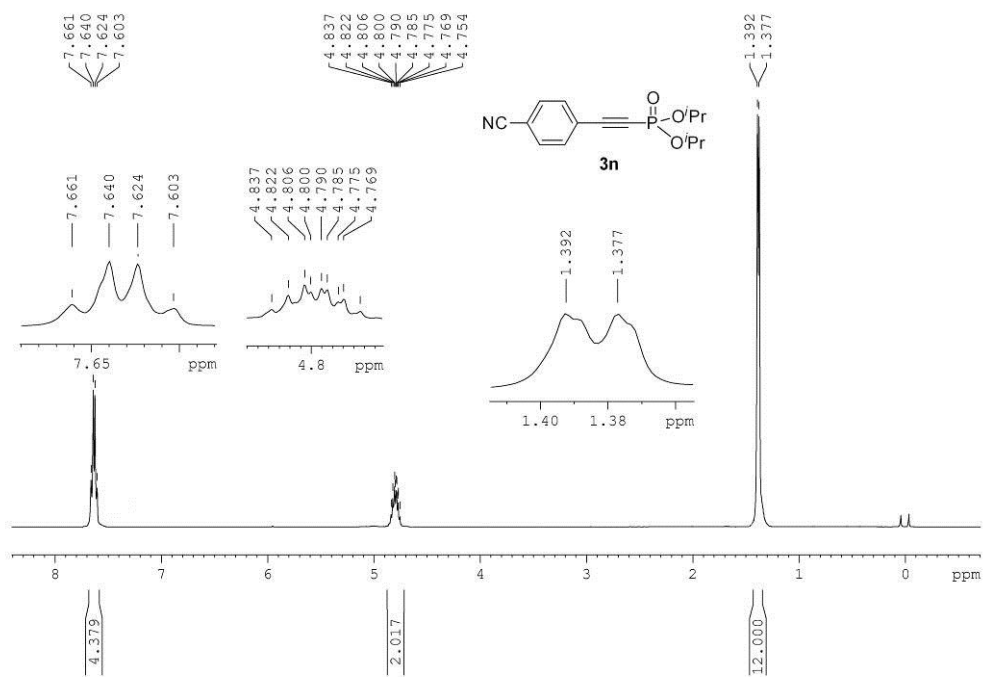
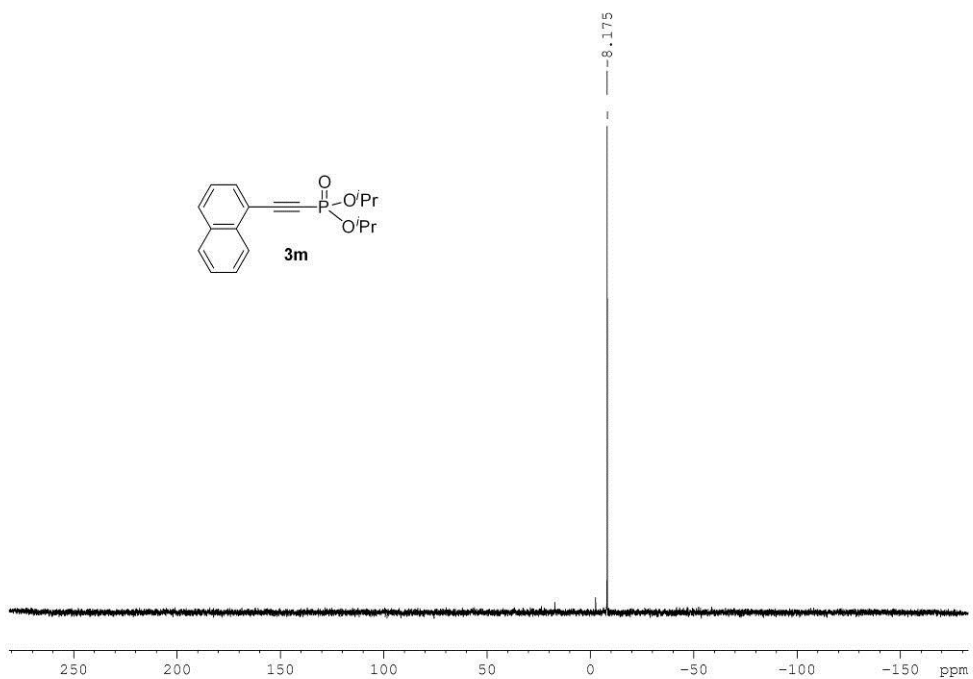


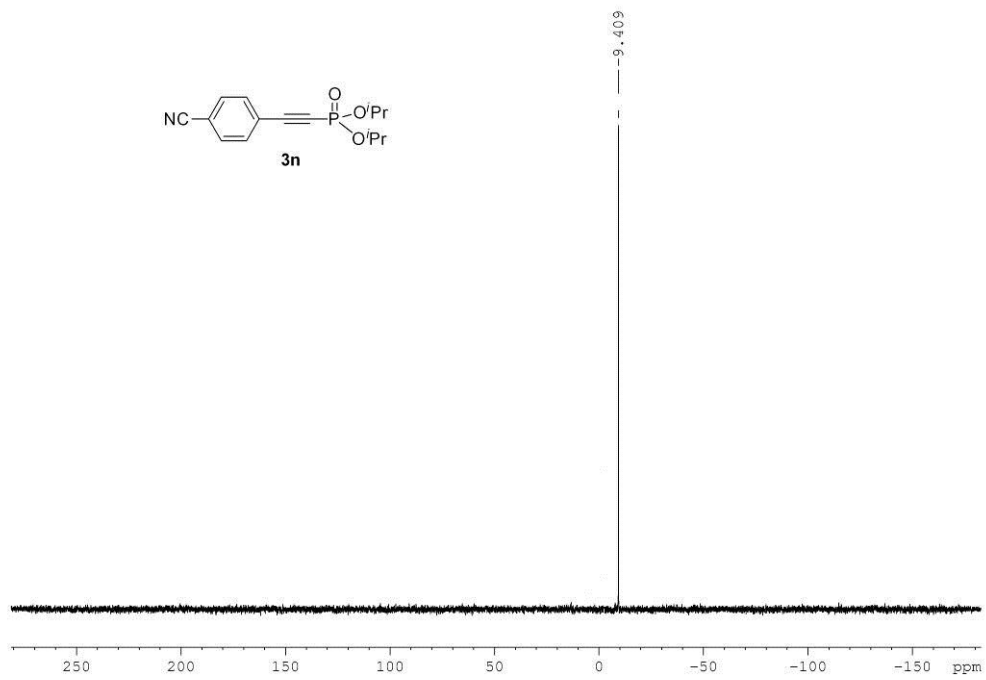
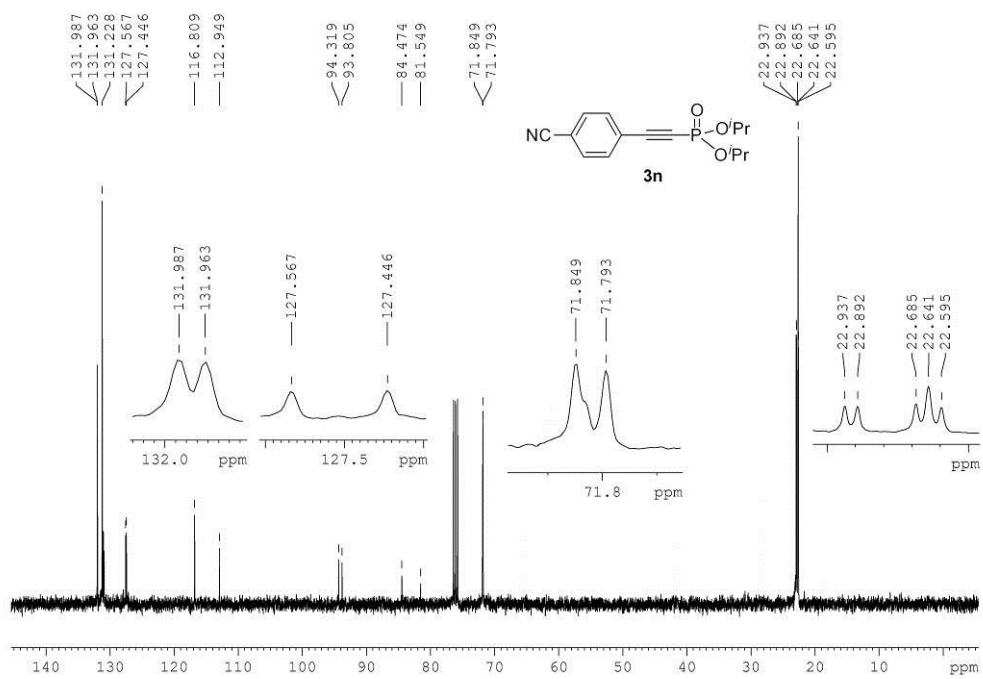


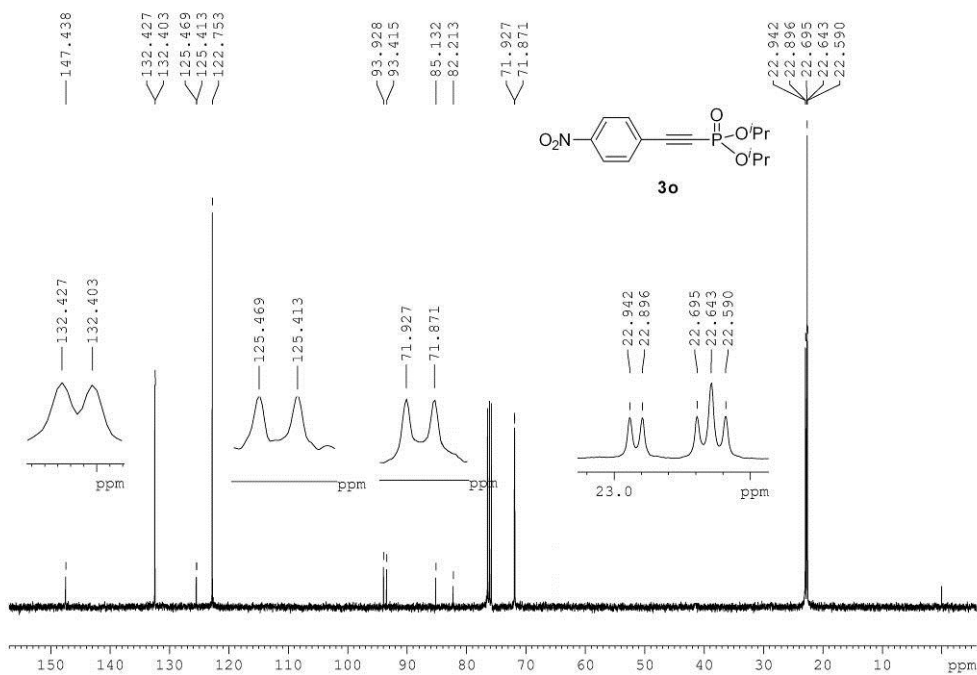
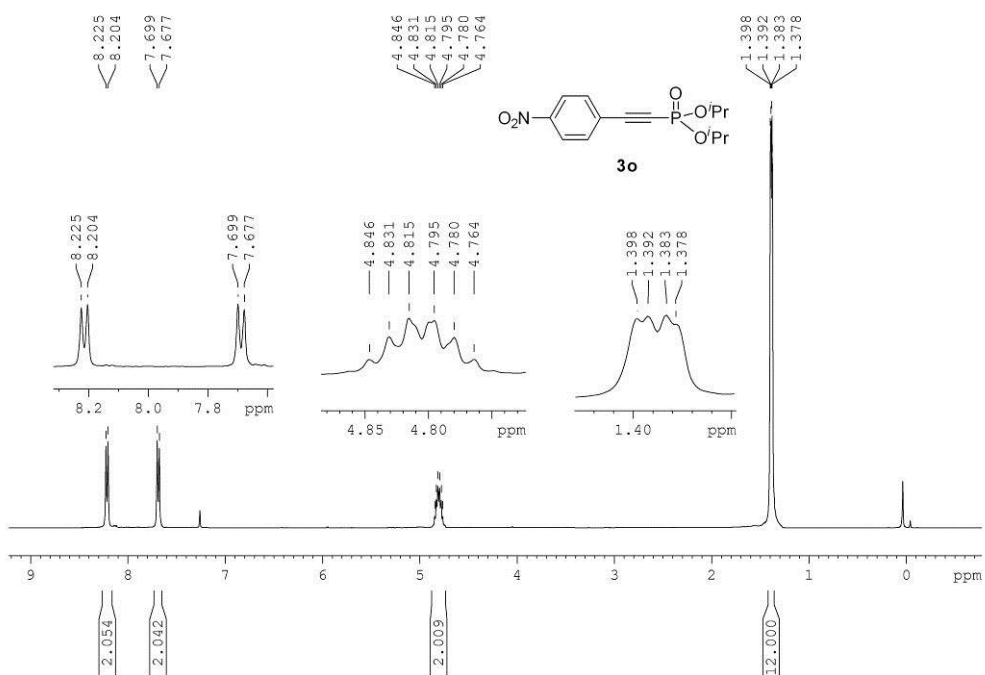


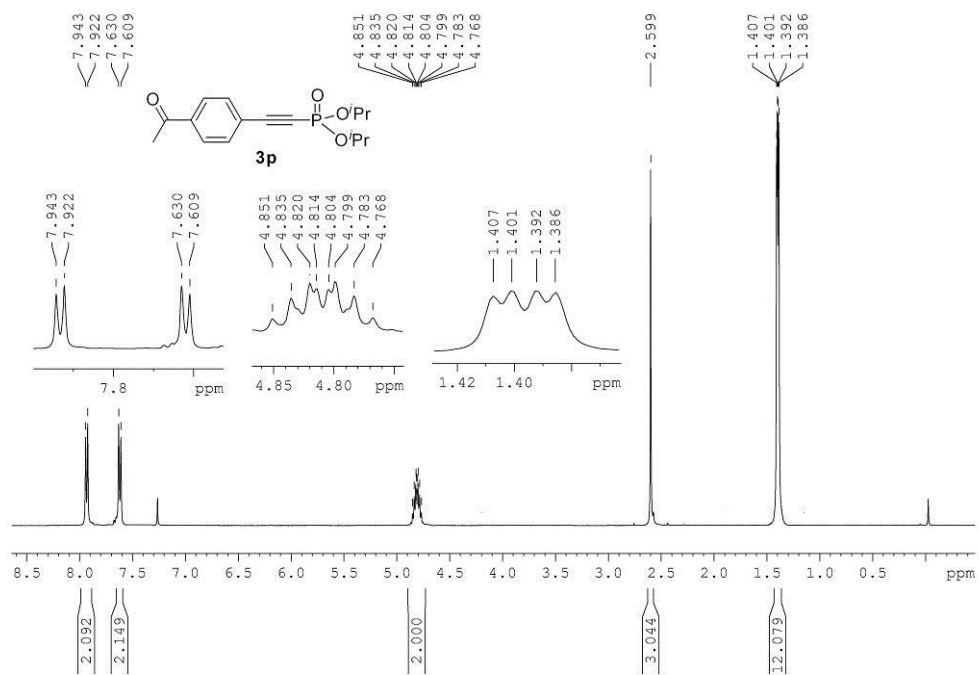
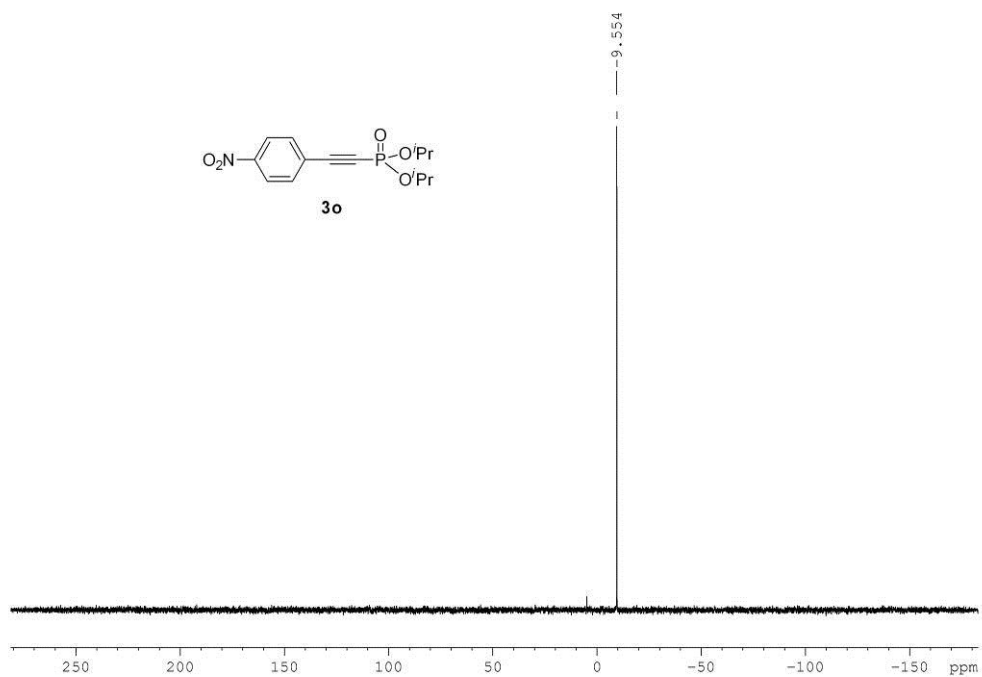


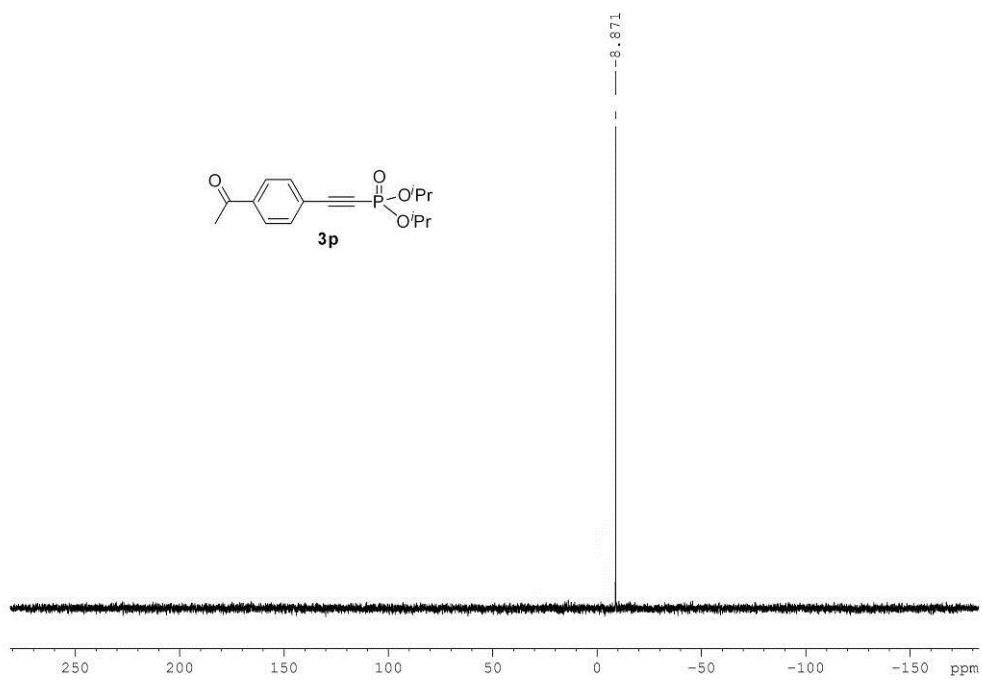
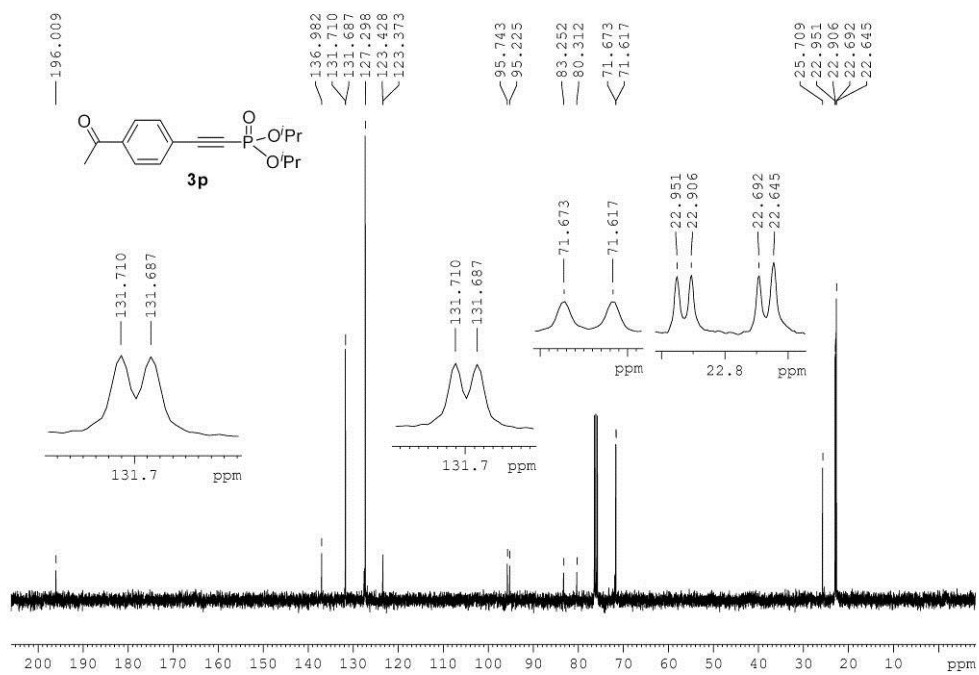


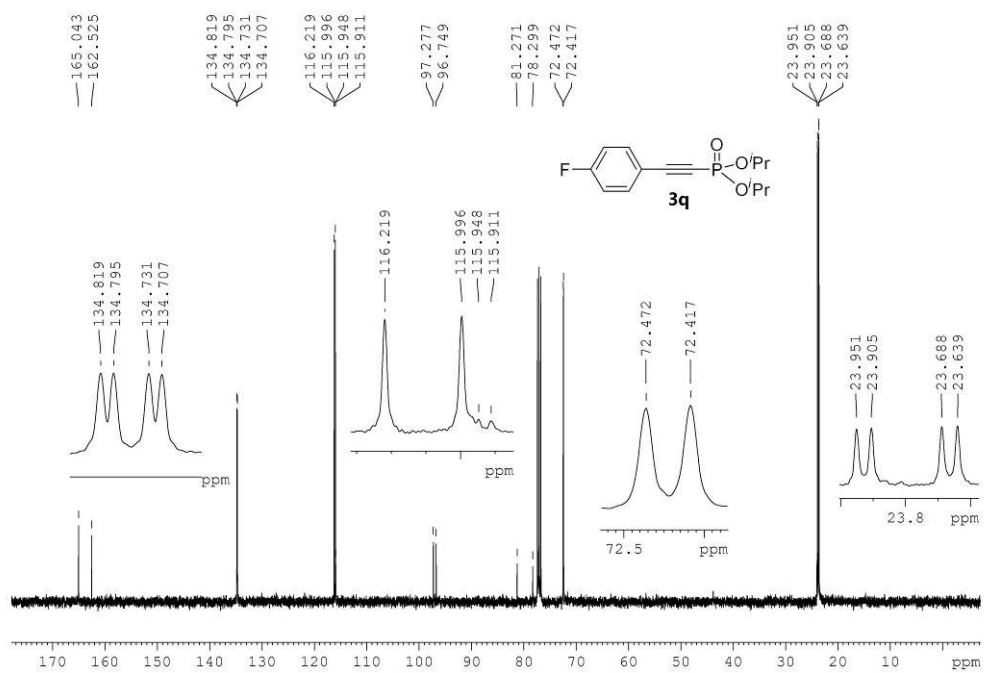
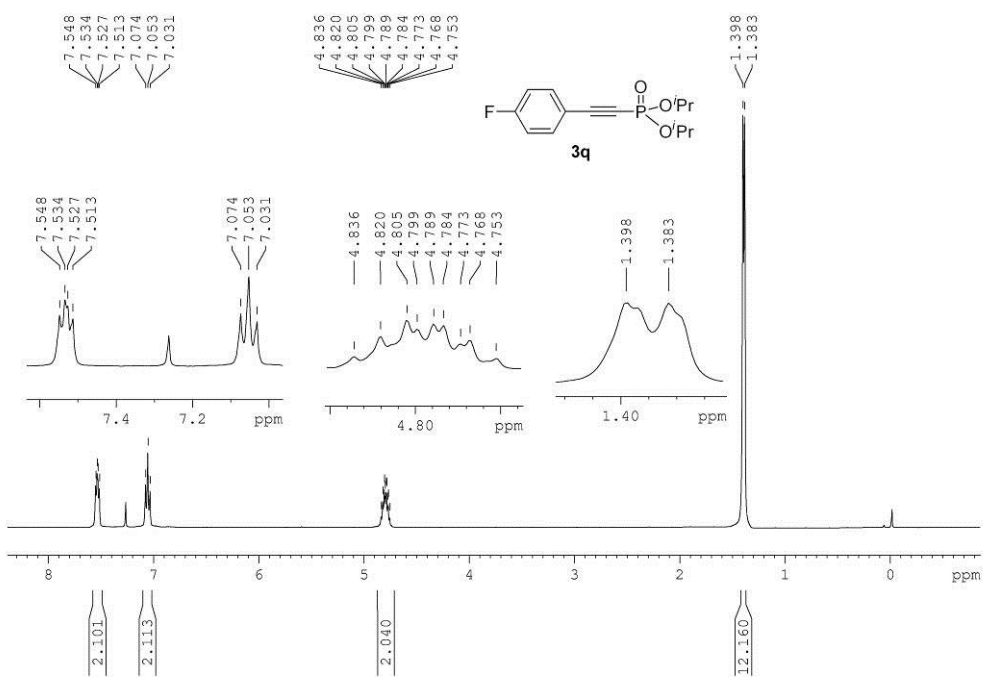


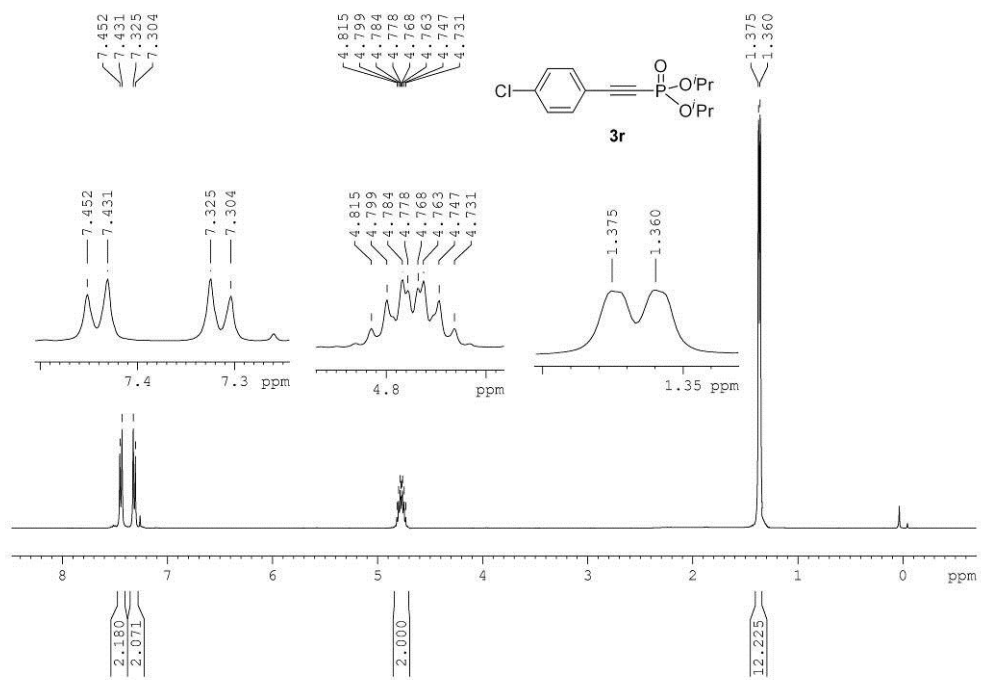
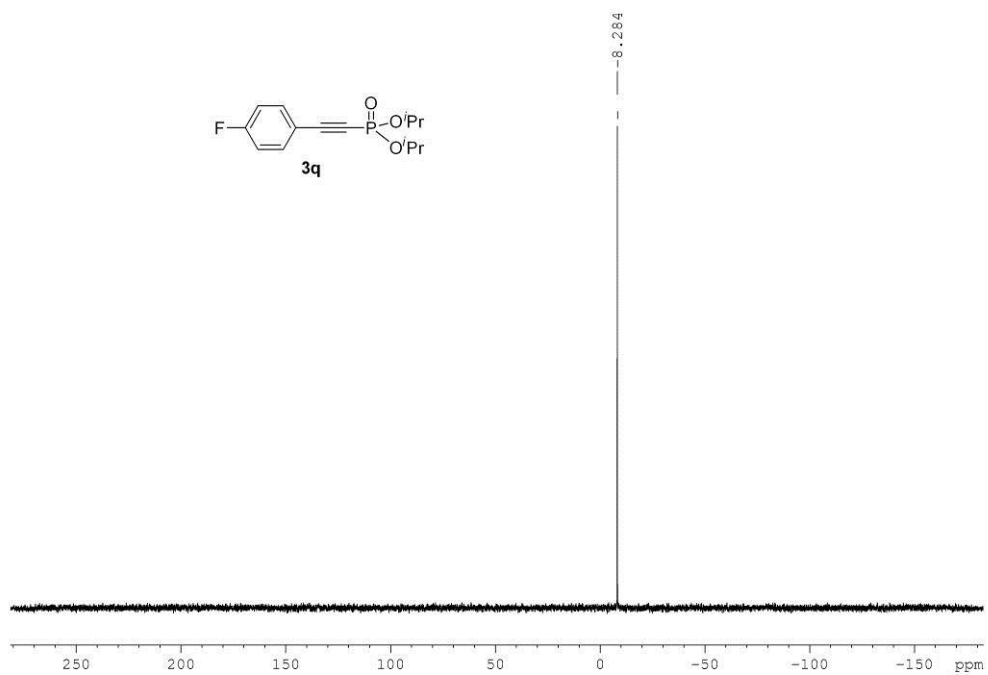




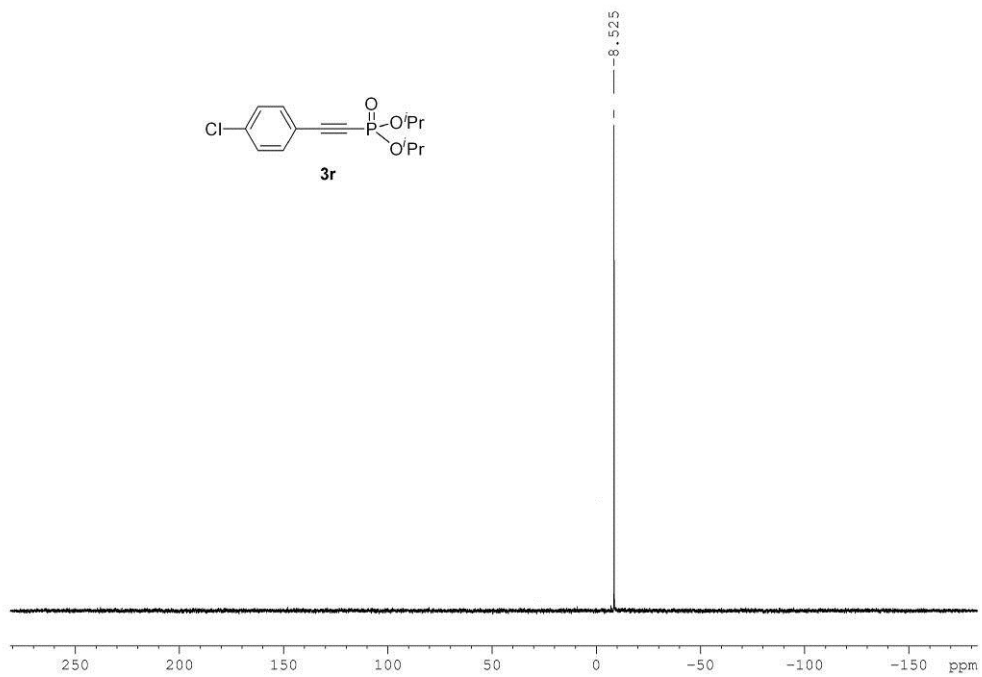
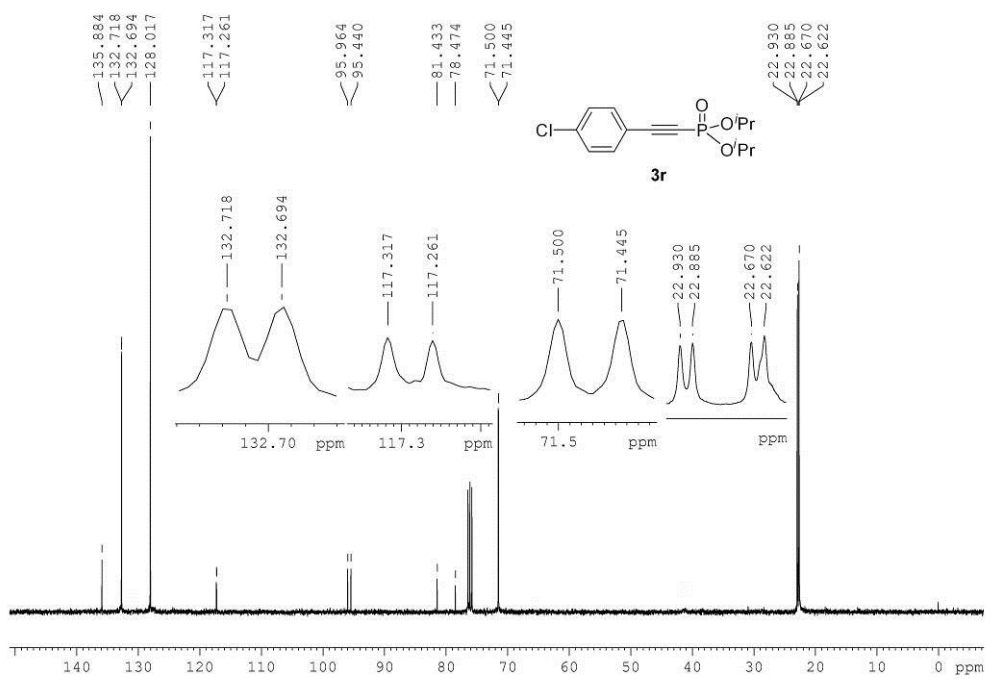


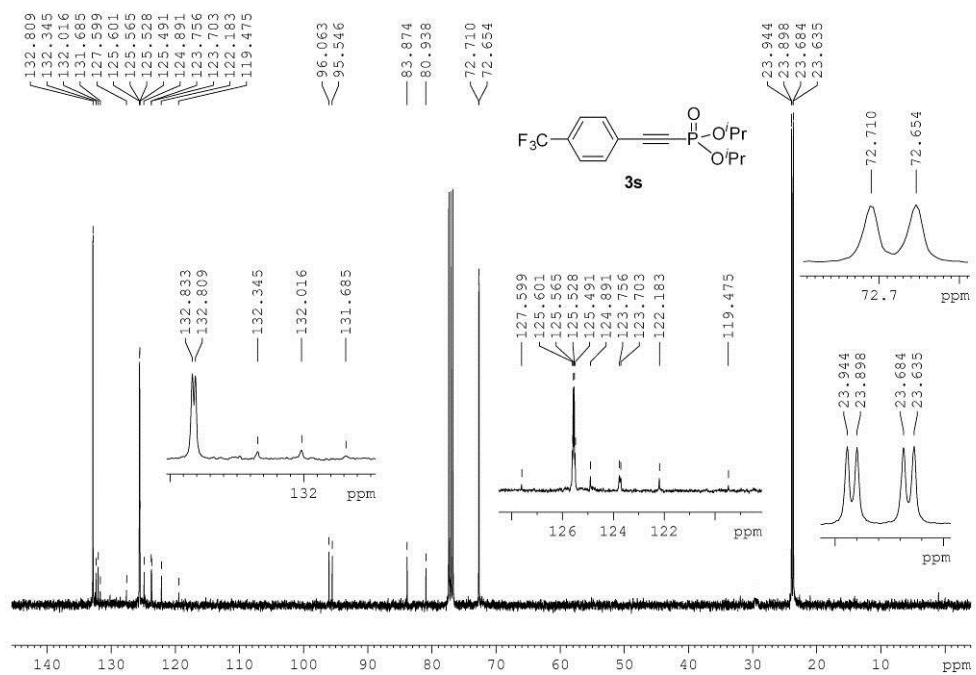
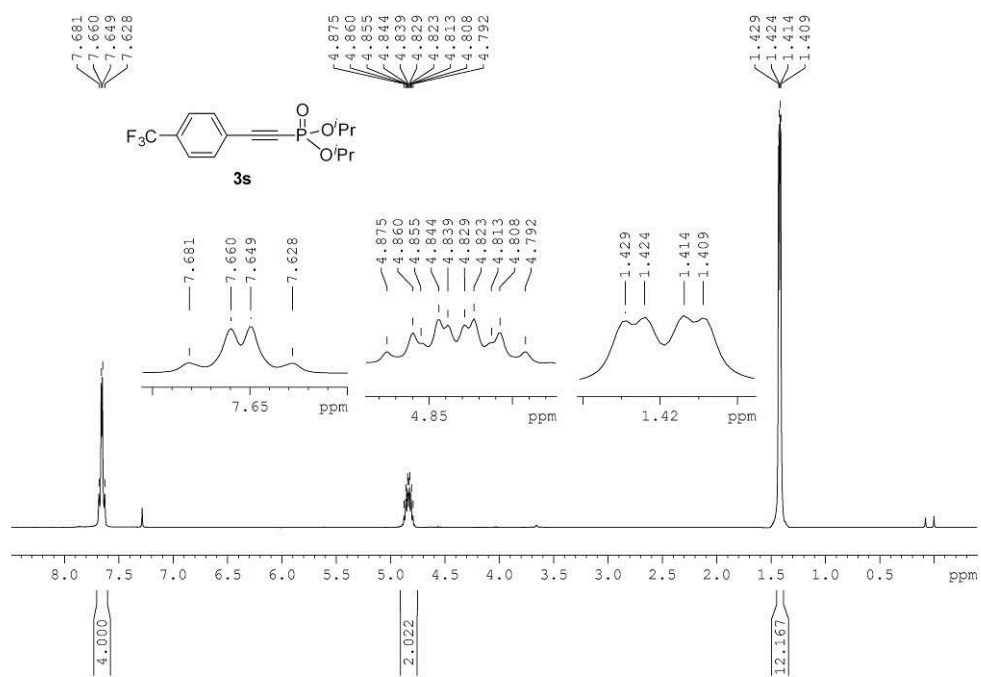


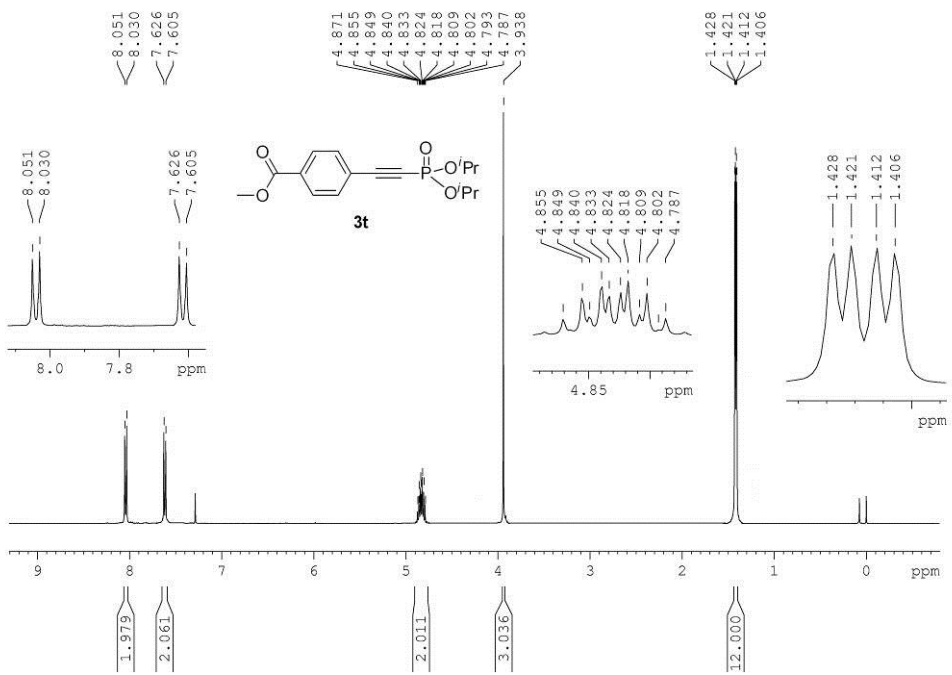
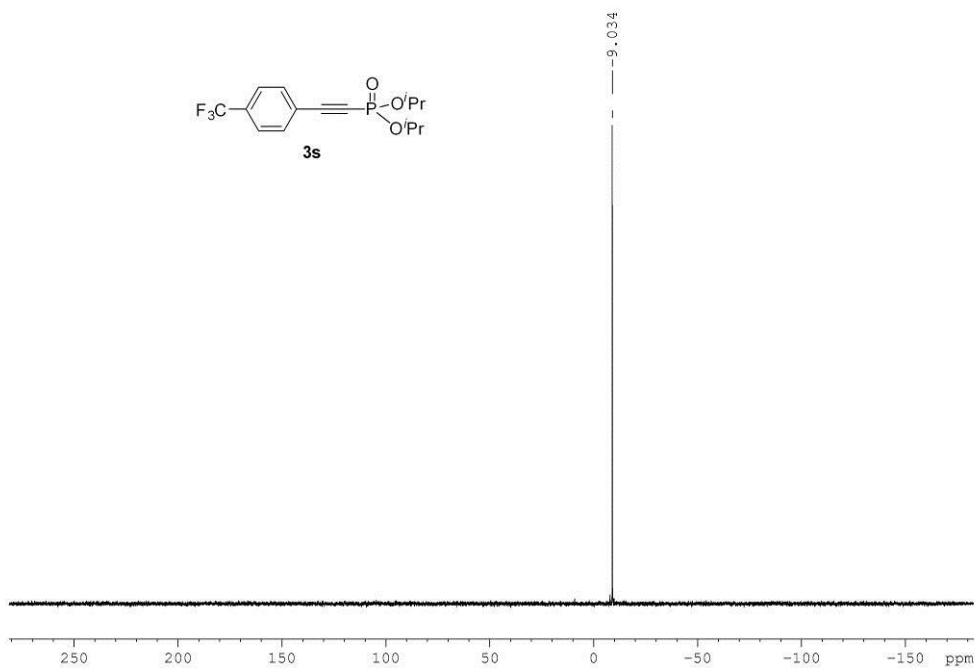


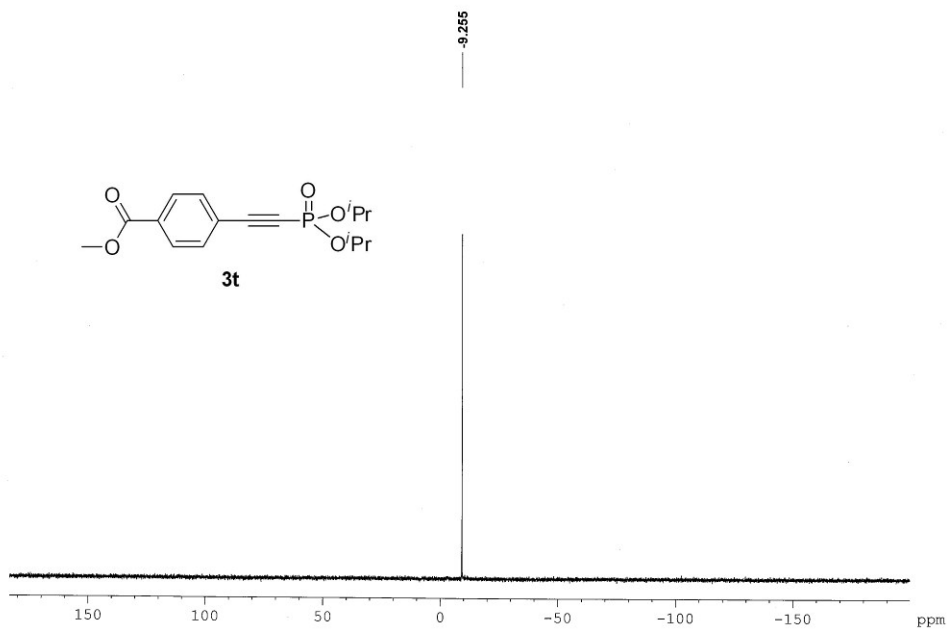
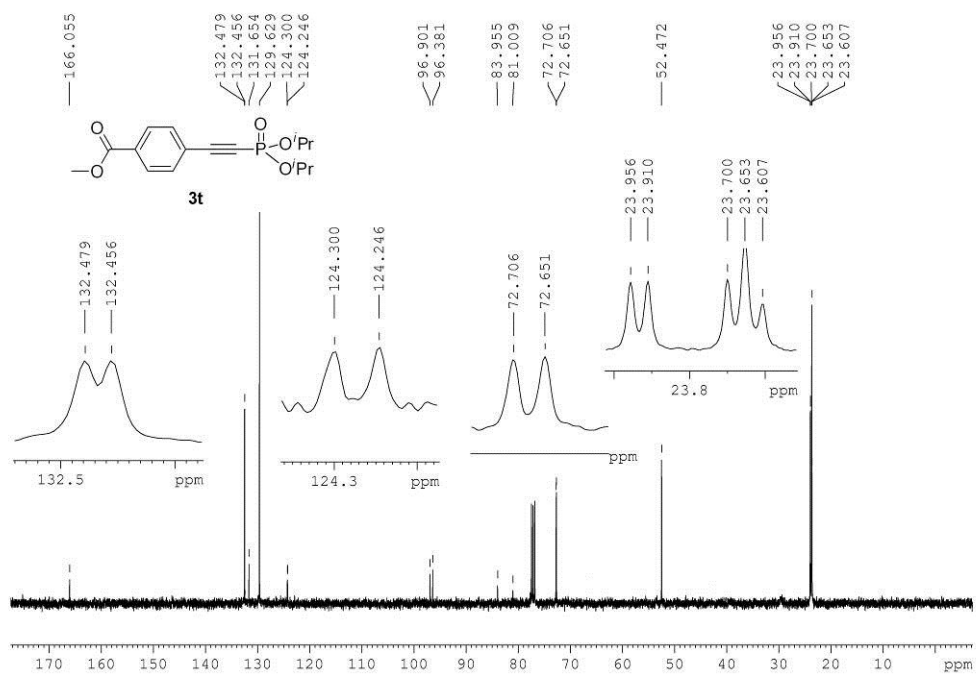


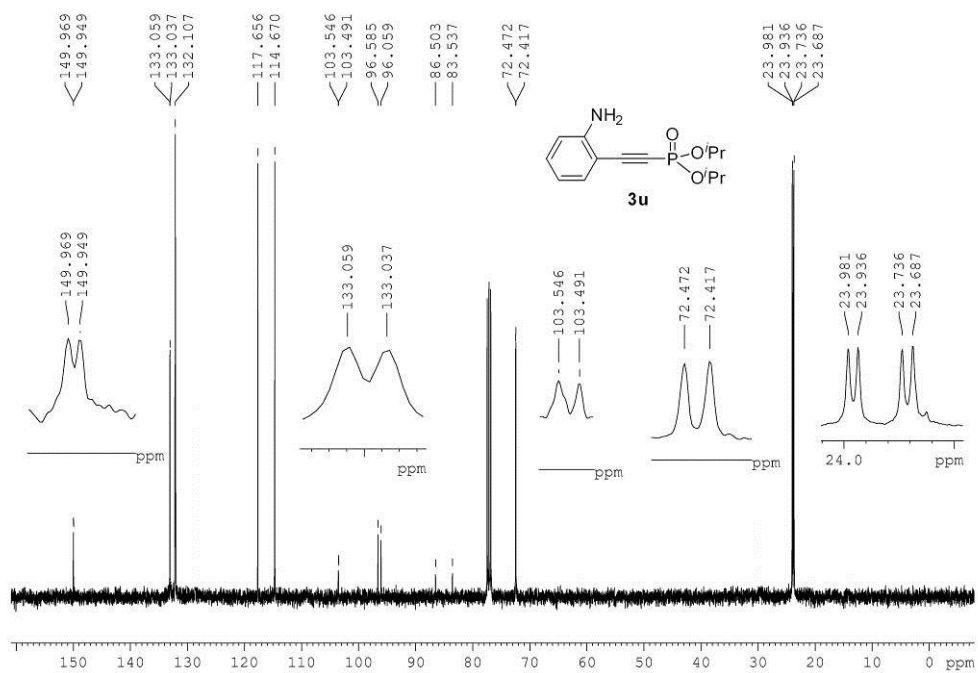
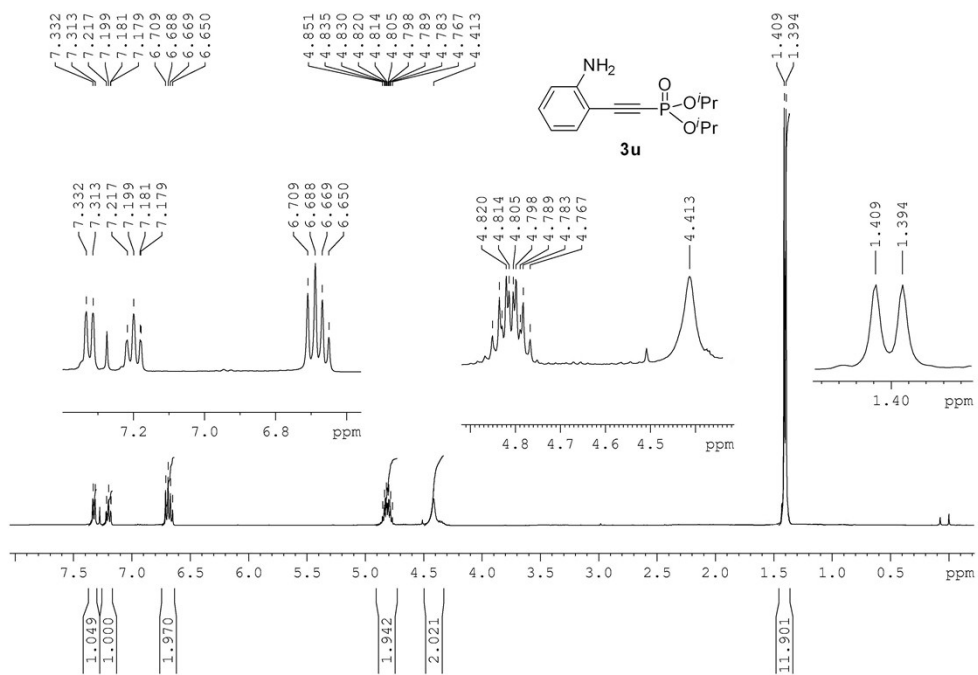


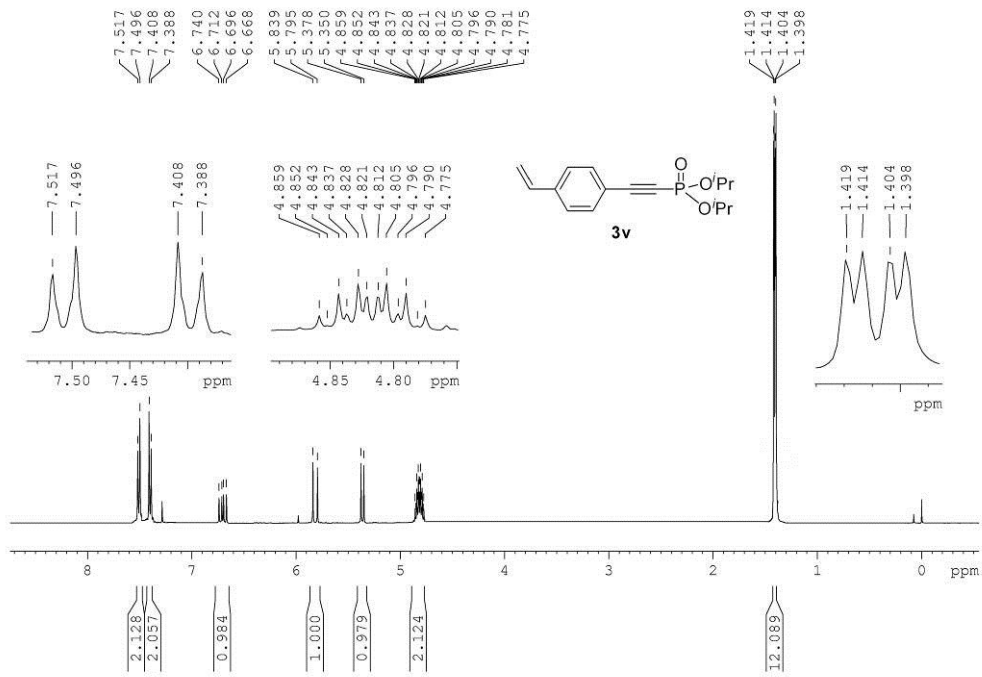
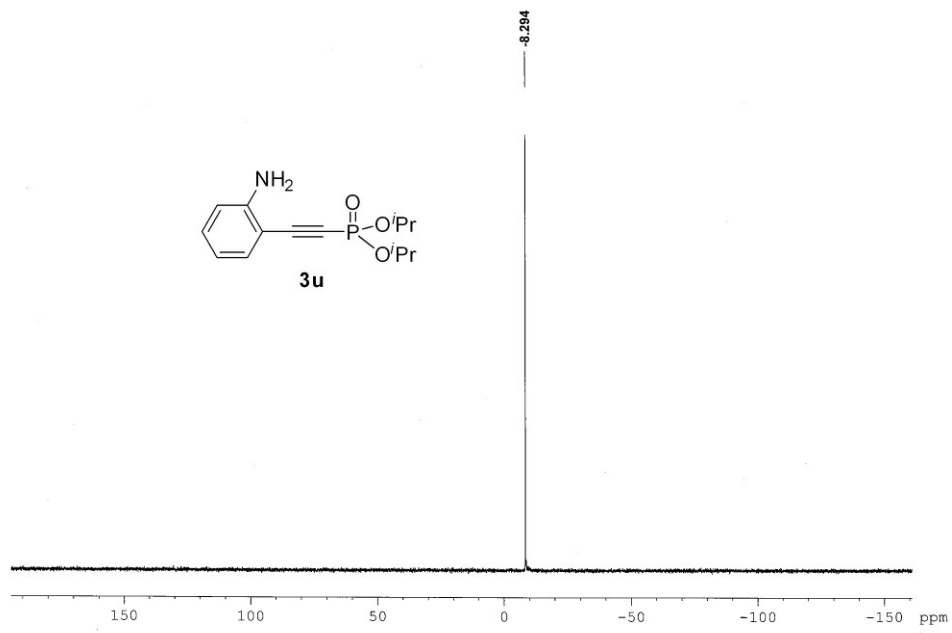


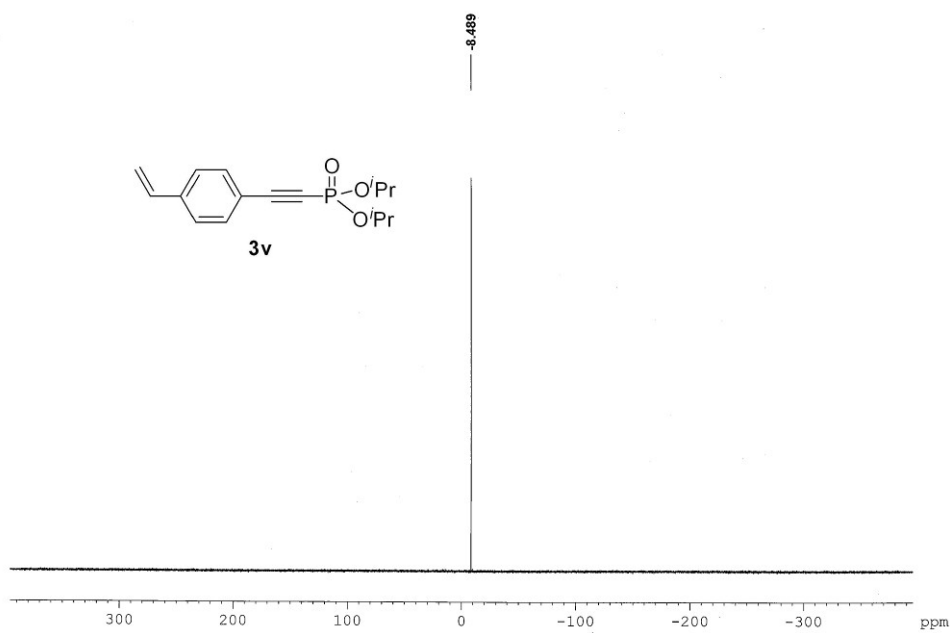
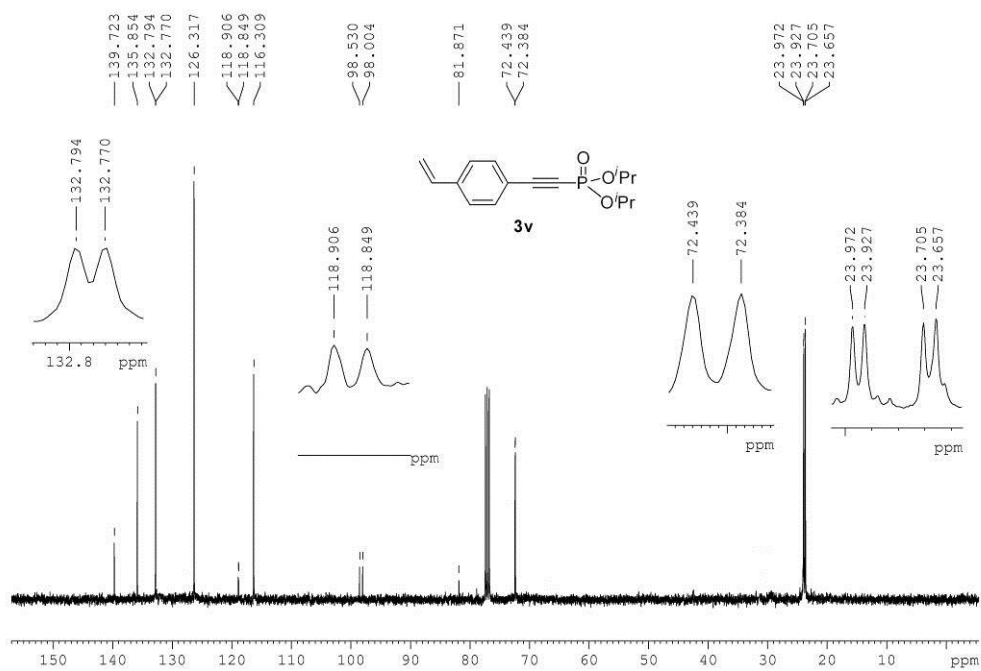












2024/05/28 10:00:00 AM 13C NMR (101 MHz, CDCl<sub>3</sub>) of 3v. 2024/05/28 10:00:00 AM 31P NMR (125 MHz, CDCl<sub>3</sub>) of 3v.

