# Silver-Mediated Selective Oxidative Cross-Coupling between C-H/P-H: A Strategy to Construct Alkynyl(diaryl)phosphine Oxide†

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## Supporting Information

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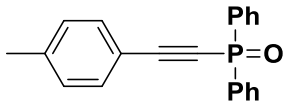
# General Information

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 60-90 $^{o}$C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios. NMR spectra were recorded on a Varian Mercury spectrometer at 300 MHz ($^{1}$H NMR), 75 MHz ($^{13}$C NMR) or on a Bruker spectrometer at 400 MHz ($^{1}$H NMR), 101 MHz ($^{13}$C NMR). Tetramethylsilane was used as an internal standard. All $^{1}$H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument, accurate masses are reported for the molecular ion ($[M+H]^{+}$). Selective ratios were recorded with a Varian GC 2000 gas chromatography instrument with a FID detector. GC-Ms spectra were recorded on a Varian GC-Ms 3900-2100T.

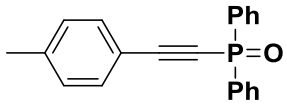
# General Procedures for Preparation of phosphine oxide




**Diphenyl(p-tolylethynyl)phosphine oxide (3a)[1]**

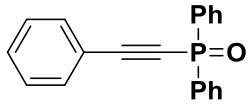
A mixture of diphenylphosphine oxide 2a (0.2 mmol) and Silver carbonate (0.4 mmol, 110 mg), alkyny 1a (0.3 mmol) in DMSO (3 mL) was stirred in $N_2$ at 120 $^oC$ for 15 h. After completion of the reaction, as indicated by TLC and GC-Ms, the solvent then diluted with 3% $Na_2CO_3$ and extracted with EtOAc. The combined extracts were washed with brine, dried over anhydrous $Na_2SO_4$; the residue was then purified by flash chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. After concentrating the fractions containing the product, the residue was dried under reduced pressure. The spectroscopic data of all the products are presented below. All the known compounds gave satisfactory spectroscopic values and are analogue to spectroscopic data reported in the literature.

## Detail descriptions for products



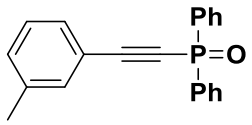
**Diphenyl(p-tolylethynyl)phosphine oxide (3a)[1]**

white solid (44.3 mg, 70% yield). PE/EA = 1:1, $R_f$ = 0.30. Mp = 164-165 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.92 -7.86 (m, 4H), 7.55 - 7.44 (m, 8H), 7.16 (d, *J* = 8 Hz, 2H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.4, 133.1 (d, $^1J_{C\text{-}P}$ = 121.0 Hz, *C*), 132.5 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.2 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, *C*H), 1301.0 (d, $^3J_{C\text{-}P}$ = 13.1 Hz, *C*H), 129.4, 128.7 (d, $^2J_{C\text{-}P}$ = 14.1 Hz, *C*H), 116.8 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, *C*H), 106.1 (d, $^2J_{C\text{-}P}$ = 30.3 Hz, *C*), 82.2 (d, $^1J_{C\text{-}P}$ = 172.7 Hz, *C*), 21.8. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.38. HRMS (ESI) calcd for $C_{21}H_{17}OP$ $[M+H]^+$: 317.1090; found: 317.1094.



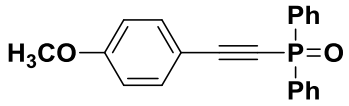
**Diphenyl(phenylethynyl)phosphine oxide (3b)[1]**

white solid (39.8 mg, 66% yield). PE/EA = 1:1, $R_f$ = 0.30. Mp = 101-102 °C. $^1$H NMR (400 MHz, CDCl3): δ 7.91 - 7.85 (m, 4H), 7.56 - 7.38 (m, 9H), 7.32 (t, *J* = 14.8 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.0 (d, $^1J_{C\text{-}P}$ = 121.0 Hz, *C*), 132.6 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.3 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.0 (d, $^3J_{C\text{-}P}$ = 11.1 Hz, *C*H), 130.8, 128.7 (d, $^2J_{C\text{-}P}$ = 13.0 Hz, *C*H), 119.9 (d, $^3J_{C\text{-}P}$ = 4.0 Hz,*C*H), 128.6, 105.5 (d, $^2J_{C\text{-}P}$ = 30.3 Hz, *C*), 82.8 (d, $^1J_{C\text{-}P}$ = 170.7 Hz, *C*). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.38. HRMS (ESI) calcd for $C_{20}H_{15}OP$ $[M+H]^+$: 303.0933; found: 303.0935.



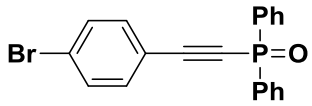
**Diphenyl(m-tolylethynyl)phosphine oxide (3c)[1]**

white solid (39.2 mg, 62% yield). PE/EA = 1:1, $R_f$ = 0.30. Mp = 155-156 $^oC$.$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.93 - 7.87 (m, 4H), 7.55- 7.46 (m, 6H), 7.41 - 7.39 (m, 2H), 7.26 - 7.25 (m, 2H), 2.34 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 138.5, 133.3 (d, $^1J_{C\text{-}P}$ = 121.0 Hz, *C*H), 133.0 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.2, 131.7, 131.0 (d, $^3J_{C\text{-}P}$ = 11.1 Hz, *C*H), 129.7 (d, $^4J_{C\text{-}P}$ = 1.0 Hz, *C*H), 128.7, 128.6 (d, $^2J_{C\text{-}P}$ = 10.1 Hz, *C*H), 119.7 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, *C*H), 105.8 (d, $^2J_{C\text{-}P}$ = 30.3 Hz, *C*), 82.4 (d, $^1J_{C\text{-}P}$ = 171.7 Hz, *C*), 21.2. $^{31}P$ NMR (162 MHz, $CDCl_3$): δ 8.26. HRMS (ESI) calcd for $C_{21}H_{17}OP$ $[M+H]^+$: 317.1090; found: 317.1094.



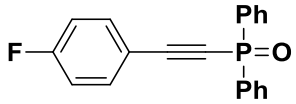
**((4-Methoxyphenyl)ethynyl)diphenylphosphine oxide (3d)[1]**

yellow oil (41.2 mg, 62% yield). PE/EA = 1:1, $R_f$ = 0.25. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 13.7, 7.1 Hz, 4H), 7.53 - 7.46 (m, 8H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 161.5, 134.3 (d, $^4J_{C\text{-}P}$ = 1.0 Hz, *C*H), 134.0 (d, $^1J_{C\text{-}P}$ = 122.0 Hz, *C*), 132.7, 132.1 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.0 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, *C*H), 128.6 (d, $^2J_{C\text{-}P}$ = 13.1 Hz, *C*H), 114.3, 111.8 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, *C*H), 106.2 (d, $^2J_{C\text{-}P}$ = 30.3 Hz, *C*), 81.7 (d, $^1J_{C\text{-}P}$ = 173.7 Hz, *C*), 55.4. $^{31}P$ NMR (162 MHz, $CDCl_3$): δ 8.19. HRMS (ESI) calcd for $C_{21}H_{17}O_2P$ $[M+H]^+$: 333.1036; found: 333.1040.



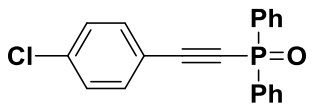

**((4-Bromophenyl)ethynyl)diphenylphosphine oxide (3e):**

white solid (34.2 mg, 45% yield). PE/EA = 1:1, $R_f$ = 0.31. Mp = 143-144 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.91 - 7.85 (m, 4H), 7.59 - 7.48 (m, 8H), 7.36 (d, *J* = 8.5 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.9 (d, $^{4}J_{C-P}$ = 2.0 Hz, *C*H), 132.5 (d, $^{1}J_{C-P}$ = 121.0 Hz, *C*), 132.4 (d, $^{4}J_{C-P}$ = 3.0 Hz, *C*H), 132.0, 131.0 (d, $^{3}J_{C-P}$ = 11.1 Hz, *C*H), 128.8 (d, $^{2}J_{C-P}$ = 13.1 Hz, *C*H), 125.5, 118.9 (d, $^{3}J_{C-P}$ = 4.0 Hz, *C*H), 104.1 (d, $^{2}J_{C-P}$ = 30.3 Hz, *C*), 84.1 (d, $^{1}J_{C-P}$ = 167.7 Hz, *C*). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.47. HRMS (ESI) calcd for $C_{20}H_{14}BrOP$ $[M+H]^+$: 381.0038; found: 381.0046.



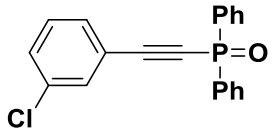

**((4-Fluorophenyl)ethynyl)diphenylphosphine oxide (3f)**

yellow solid (44.8 mg, 71% yield). PE/EA = 1:1, $R_f$ = 0.35. Mp = 117-119 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.91 - 7.86 (m, 4H), 7.57 - 7.48 (m, 8H), 7.09 - 7.05 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.9 (d, $^{1}J_{C-F}$ = 254.5 Hz), 134.8 (d, $^{4}J_{C-P}$ = 2.0,d $^{2}J_{C-F}$ = 11.1 Hz), 132.8 (d, $^{1}J_{C-P}$ = 122.0 Hz, *C*), 132.4 (d, $^{3}J_{C-P}$ = 3.0 Hz, *C*H), 131.0 (d, $^{3}J_{C-P}$ = 11.1 Hz, *C*H), 128.8, 128.7, 116.2 (d, $^{2}J_{C-P}$ = 22.2 Hz, *C*H), 104.4 (d, $^{2}J_{C-P}$ = 30.0 Hz, *C*), 82.8 (d, $^{1}J_{C-P}$ = 168.0 Hz, *C*). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.43. HRMS (ESI) calcd for $C_{20}H_{14}FOP$ $[M+H]^+$: 321.0845; found: 321.0840.



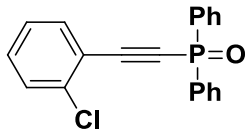

**((4-Chlorophenyl)ethynyl)diphenylphosphine oxide (3g)**

white solid (47.0 mg, 70% yield). PE/EA = 1:1, $R_f$ = 0.30. Mp = 131-132 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.91 - 7.85 (m, 4H), 7.55 - 7.47 (m, 8H), 7.36 - 7.33 (m, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 137.1, 133.8 (d, $^4J_{C-P}$ = 1.0 Hz, *C*H), 132.6 (d, $^1J_{C-P}$ = 121.0 Hz, *C*H), 132.4 (d, $^4J_{C-P}$ = 3.0 Hz, *C*H), 131.0 (d, $^3J_{C-P}$ = 11.1 Hz, *C*H), 129.1, 128.8 (d, $^2J_{C-P}$ = 13.1 Hz, *C*H), 118.4 (d, $^3J_{C-P}$ = 4.0 Hz, *C*H), 104.2 (d, $^2J_{C-P}$ = 30.3 Hz, *C*), 83.8 (d, $^1J_{C-P}$ = 168.7 Hz, *C*), $^{31}P$ NMR (162 MHz, $CDCl_3$): δ 8.45. HRMS (ESI) calcd for $C_{20}H_{14}ClOP$ $[M+H]^+$: 337.0549; found: 337.0544.




**((3-Chlorophenyl)ethynyl)diphenylphosphine oxide (3h)**

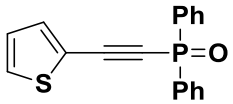
yellow oil (42.3 mg, 63% yield). PE/EA = 1:1, $R_f$ = 0.30 $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 13.8, 7.2 Hz, 4H), 7.57 - 7.43 (m, 10H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 134.5, 132.6 (d, $^1J_{C-P}$ = 121.0 Hz, *C*), 132.5 (d, $^4J_{C-P}$ = 3.0 Hz, *C*H), 132.2, 131.0 (d, $^3J_{C-P}$ = 11.1 Hz, *C*H), 130.7 (d, $^4J_{C-P}$ = 2.0 Hz, *C*H), 129.9, 128.8 (d, $^2J_{C-P}$ = 14.1 Hz,*C*H), 121.6 (d, $^3J_{C-P}$ = 4.0 Hz, *C*H), 103.4 (d, $^2J_{C-P}$ = 30.3 Hz, *C*), 84.1 (d, $^1J_{C-P}$ = 166.7 Hz, *C*). $^{31}P$ NMR (162 MHz, $CDCl_3$): δ 8.37. HRMS (ESI) calcd for $C_{20}H_{14}ClOP$ $[M+H]^+$: 337.0549; found: 337.0541.




**((2-Chlorophenyl)ethynyl)diphenylphosphine oxide (3i)**

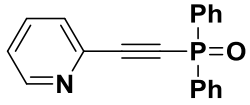
yellow oil (33.6 mg, 50% yield). PE/EA = 1:1, $R_f$ = 0.30. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.91 (m, 4H), 7.61 - 7.43 (m, 8H), 7.39 - 7.34 (m 1H), 7.28 - 7.24 (m,

1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.1, 134.3 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.8 (d, $^1J_{C\text{-}P}$ = 122.0 Hz, *C*), 132.3 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.7, 131.0 (d, $^3J_{C\text{-}P}$ = 12.1 Hz, *C*H), 129.6, 128.7 (d, $^2J_{C\text{-}P}$ = 13.1 Hz, *C*H), 126.8, 120.3 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, *C*H), 101.4 (d, $^2J_{C\text{-}P}$ = 29.3 Hz, *C*), 87.8 (d, $^1J_{C\text{-}P}$ = 167.7 Hz, *C*). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 8.61. HRMS (ESI) calcd for $C_{20}H_{14}ClOP$ $[M+H]^+$: 337.0549; found: 337.0544.




**Diphenyl(thiophen-2-ylethynyl)phosphine oxide (3j)**

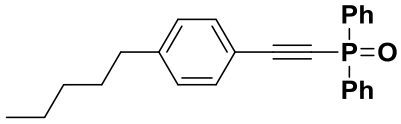
yellow oil (33.3 mg, 62% yield). PE/EA = 1:1, $R_f$ = 0.35. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.91 - 7.85 (m, 4H), 7.56 - 7.42 (m, 8H), 7.03 (dd, *J* = 5.1, 3.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 135.9 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.8 (d, $^1J_{C\text{-}P}$ = 122.0 Hz, *C*), 132.4 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.0 (d, $^3J_{C\text{-}P}$ = 11.1 Hz, *C*H), 130.7, 128.7 (d, $^2J_{C\text{-}P}$ = 13.1 Hz, *C*H), 127.5, 119.6 (d, $^3J_{C\text{-}P}$ = 5.1 Hz, *C*H), 98.8 (d, $^2J_{C\text{-}P}$ = 31.3 Hz, *C*), 86.9 (d, $^1J_{C\text{-}P}$ = 169.7 Hz, *C*). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.53. HRMS (ESI) calcd for $C_{18}H_{13}OPS$ $[M+H]^+$: 309.0503; found: 309.0497.




**Diphenyl(pyridin-2-ylethynyl)phosphine oxide (3k)**

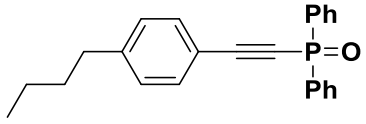
Brown solid (31.5 mg, 52% yield). PE/EA = 1:2, $R_f$ = 0.20. Mp = 168-169 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.63 - 8.62 (m, 1H), 7.92 - 7.87 (m, 4H), 7.72 - 7.68(m, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.54 - 7.46 (m, 6H), 7.35 - 7.31 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.5, 140.7 (d, $^4J_{C\text{-}P}$ = 4.0 Hz, *C*H), 136.5, 132.3 (d, $^1J_{C\text{-}P}$ = 122.0 Hz,

*C*H), 132.5 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.7, 131.1 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 128.8 (d, $^{2}J_{C\text{-}P}$ = 13.1 Hz, *C*H), 124.9, 103.0 (d, $^{2}J_{C\text{-}P}$ = 28.3 Hz, *C*), 82.2 (d, $^{1}J_{C\text{-}P}$ = 163.6 Hz, *C*). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.84. HRMS (ESI) calcd for $C_{19}H_{14}NOP$ $[M+H]^+$: 304.0891; found: 304.0887.




**((4-Pentylphenyl)ethynyl)diphenylphosphine oxide (3l)**

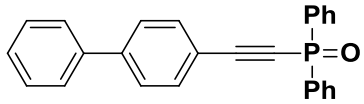
yellow oil (27.1 mg, 45% yield). PE/EA = 1:1, $R_f$ = 0.35. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.93 - 7.87 (m, 4H), 7.57 - 7.46 (m, 8H), 7.19 (d, *J* = 8.4Hz, 2H), 2.78 - 2.49 (m, 2H), 1.64 - 1.56 (m, 2H), 1.33 - 1.27 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 146.4, 133.8, 132.5 (d, $^{4}J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.2 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.0 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 128.7 (d, $^{2}J_{C\text{-}P}$ = 14.1 Hz, *C*H), 117.0 (d, $^{3}J_{C\text{-}P}$ = 4.0 Hz, *C*H), 106.1 (d, $^{2}J_{C\text{-}P}$ = 30.3 Hz, *C*), 82.1 (d, $^{1}J_{C\text{-}P}$ = 172.7 Hz, *C*), 36.0, 31.4, 30.8, 22.5, 14.0. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.44. HRMS (ESI) calcd for $C_{25}H_{25}OP$ $[M+H]^+$: 373.1721; found: 373.1714.




**((4-Butylphenyl)ethynyl)diphenylphosphine oxide (3m)**

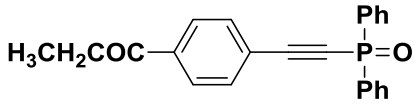
yellow oil (43.0 mg, 60% yield). PE/EA = 1:1, $R_f$ = 0.35. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 13.8, 8.0 Hz, 4H), 7.56 - 7.46 (m, 8H), 7.18 (d, *J* = 3.6 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.69 - 1.54 (m, 2H), 1.38 - 1.29 (m, 2H), 0.93 - 0.90 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 146.4, 133.1 (d, $^{1}J_{C\text{-}P}$ = 121.0 Hz, *C*), 132.5 (d,

$^{4}J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.2 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.0 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 130.1, 128.7 (d, $^{2}J_{C\text{-}P}$ = 13.1 Hz, *C*H), 128.4, 117.0 (d, $^{3}J_{C\text{-}P}$ = 4.0 Hz, *C*H), 106.2 (d, $^{2}J_{C\text{-}P}$ = 30.3 Hz, *C*), 82.1 (d, $^{1}J_{C\text{-}P}$ = 173.7 Hz, *C*), 35.8, 33.3, 22.3, 13.9. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.41. HRMS (ESI) calcd for $C_{24}H_{23}OP$ $[M+H]^+$: 359.1565; found: 359.1558.




**([1,1'-Biphenyl]-4-ylethynyl)diphenylphosphine oxide (3n)**

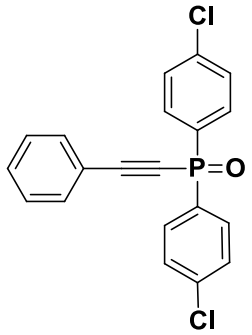
yellow oil (28.1 mg, 40% yield). PE/EA = 1:1, $R_f$ = 0.30. $^{1}$H NMR (400 MHz, $CDCl_3$) δ7.93 - 7.89 (m, 4H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.62 - 7.44 (m, 12H), 7.41 - 7.37 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.7, 133.0 (d, $^{1}J_{C\text{-}P}$ = 122.0 Hz, *C*), 133.0 (d, $^{4}J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.3 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.0 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 129.0, 128.7 (d,$^{2}J_{C\text{-}P}$ = 13.1 Hz, *C*H), 128.2, 127.2 (d, $^{3}J_{C\text{-}P}$ = 10.1Hz, *C*H), 118.6 (d, $^{3}J_{C\text{-}P}$ = 4.0 Hz, *C*H), 105.5 (d, $^{2}J_{C\text{-}P}$ = 30.3 Hz, *C*), 83.4 (d, $^{1}J_{C\text{-}P}$ = 170.7 Hz, *C*). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.47. HRMS (ESI) calcd for $C_{26}H_{19}OP$ $[M+H]^+$: 379.1252; found: 379.1246.




**1-(4-((Diphenylphosphoryl)ethynyl)phenyl)propan-1-one (3o)**

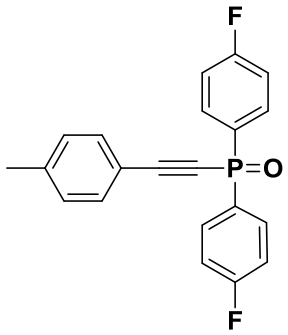
yellow oil (50.8 mg, 71% yield). PE/EA = 1:1, $R_f$ = 0.35. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.92 - 7.86 (m, 4H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.59 - 7.48 (m, 6H), 4.41 - 4.35 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.6 ,131.6 (d, $^{1}J_{C\text{-}P}$ = 121.0 Hz, *C*), 132.5 (d, $^{4}J_{C\text{-}P}$ = 2.0 Hz, *C*H), 132.0 (d,

$^{2}J_{C\text{-}P}$ = 14.1 Hz, *C*H), 131.0 (d, $^{2}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 129.6, 128.8 (d, $^{3}J_{C\text{-}P}$ = 13.1 Hz, *C*H), 124.2 (d, $^{3}J_{C\text{-}P}$ = 4.0 Hz, *C*H), 104.0 (d, $^{2}J_{C\text{-}P}$ = 29.3 Hz, *C*), 85.4 (d, $^{1}J_{C\text{-}P}$ = 170.7 Hz, *C*), 61.5, 14.3. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.50. HRMS (ESI) calcd for $C_{23}H_{19}O_2P$ $[M+H]^+$: 359.1195; found: 359.1196.




**Bis(4-chlorophenyl)(p-tolylethynyl)phosphine oxide (3p)**

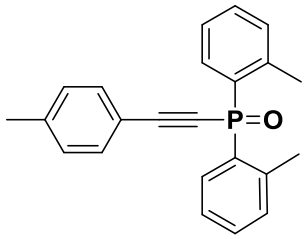
yellow oil (31.1 mg, 42% yield). PE/EA = 1:1, $R_f$ = 0.35. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.84 - 7.77 (m, 4H), 7.59 - 7.57 (m, 2H), 7.49 – 7.45 (m, 5H), 7.39 (t, *J* = 7.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.2, 132.6 (d, $^{4}J_{C\text{-}P}$ = 1.0 Hz, *C*H), 132.3 (d, $^{2}J_{C\text{-}P}$ = 13.1 Hz, *C*H), 131.2 (d, $^{1}J_{C\text{-}P}$ = 125.1 Hz, *C*), 131.1, 129.2 (d, $^{2}J_{C\text{-}P}$ = 14.1 Hz, *C*H), 128.7, 119.5 (d, $^{3}J_{C\text{-}P}$ = 4.0 Hz, *C*H), 106.4 (d, $^{2}J_{C\text{-}P}$ = 31.3 Hz, *C*), 81.9 (d, $^{1}J_{C\text{-}P}$ = 175.7 Hz, *C*). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 6.32. HRMS (ESI) calcd for $C_{20}H_{13}Cl_2OP$ $[M+H]^+$: 371.0159; found: 371.0157.




**Bis(4-fluorophenyl)(p-tolylethynyl)phosphine oxide (3q)**

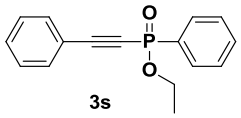
yellow oil (38.7 mg, 55% yield). PE/EA = 1:1, $R_f$ = 0.35. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.92 - 7.85 (m, 4H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.21 - 7.16 (m, 6H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, $^{4}J_{C\text{-}P}$ = 4.0 Hz, d, $^{1}J_{C\text{-}F}$ = 254.5Hz, C),

141.7, 133.5 (d, $^{3}J_{C\text{-}F}$ = 9.1,d, $^{2}J_{C\text{-}P}$ = 13.1 Hz, C), 132.5 (d, $^{4}J_{C\text{-}P}$ = 2.0Hz, *C*H), 129.6 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, *C*H), 129.4, 128.4 (d, $^{3}J_{C\text{-}P}$ = 3.0 Hz, *C*H), 116.5 (d $^{3}J_{C\text{-}P}$ = 3.0 Hz , *C*H), 116.2 (d, $^{2}J_{C\text{-}P}$ = 21.2,d, $^{2}J_{C\text{-}P}$ = 14.1 Hz, C), 106.6 (d, $^{2}J_{C\text{-}P}$ = 31.3 Hz, *C*), 81.8 (d, $^{1}J_{C\text{-}P}$ = 176.8 Hz, *C*), 21.8. $^{31}$P NMR (162 MHz, $CDCl_3$) δ 6.24. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.50. HRMS (ESI) calcd for $C_{21}H_{15}F_2OP$ $[M+H]^+$: 353.0907; found: 353.0901.




**Di-o-tolyl(p-tolylethynyl)phosphine oxide (3r)**

yellow oil (41.3 mg, 60% yield). PE/EA = 1:1, $R_f$ = 0.30. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m , 2H), 7.47- 7.41 (m, 4H), 7.34 - 7.30 (m, 2H), 7.23 - 7.20 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 6H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.6 (d, $^{4}J_{C\text{-}P}$ = 10.6 Hz, *C*), 141.2, 132.8 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 132.6 - 132.1 (m), 131.7 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 130.5 (d, $^{1}J_{C\text{-}P}$ = 122.0 Hz, *C*), 129.4, 125.8 (d, $^{2}J_{C\text{-}P}$ = 13.1 Hz, *C*H), 117.1 (d, $^{4}J_{C\text{-}P}$ = 4.0 Hz, *C*H), 105.5 (d, $^{2}J_{C\text{-}P}$ = 29.3Hz, *C*), 82.5 (d, $^{1}J_{C\text{-}P}$ = 169.7 Hz, *C*), 21.8, 21.2 (d, $J_{C\text{-}P}$ = 5.1 Hz, *C*H). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 8.50. HRMS (ESI) calcd for $C_{23}H_{21}OP$ $[M+H]^+$: 345.1408; found: 345.1403.

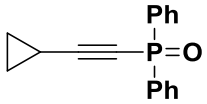



3s

**Ethyl phenyl(phenylethynyl)phosphinate (3s)**

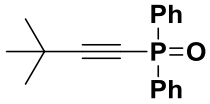
yellow oil (29.2 mg, 54% yield). PE/EA = 1:1, $R_f$ = 0.35. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.98 - 7.92 (m, 2H), 7.59 - 7.48 (m, 5H), 7.45-7.41 (m,1H), 7.37- 7.33 (m, 2H), 4.34 – 4.25 (m, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 132.8 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, *C*H), 132.6 (d, $^{4}J_{C\text{-}P}$ = 2.0 Hz, *C*H), 131.1 (d, $^{1}J_{C\text{-}P}$ = 166.7 Hz, *C*), 131.1 (d, $^{2}J_{C\text{-}P}$ = 12.1 Hz, *C*H), 130.7, 128.7, 128.5 (d, $^{3}J_{C\text{-}P}$ = 4.0 Hz, *C*H),

119.8 (d, $^{3}J_{C\text{-}P}$ = 5.0 Hz, *C*H), 101.6 (d, $^{2}J_{C\text{-}P}$ = 39.4 Hz, *C*), 81.7 (d, $^{1}J_{C\text{-}P}$ = 217.2 Hz, *C*), 62.4 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, *C*H), 16.4 (d, $^{3}J_{C\text{-}P}$ = 7.0 Hz, *C*H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 9.78. $C_{16}H_{15}O_2P$ $[M+H]^+$: 271.0888; found: 271.0892.



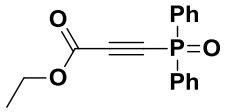

**(Cyclopropylethynyl)diphenylphosphine oxide (3t)**

yellow oil (23.9 mg, 45% yield). PE/EA = 1:1, $R_f$ = 0.35. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.82 - 7.76 (m, 4H), 7.50 - 7.43 (m, 6H), 1.49 - 1.42 (m, 1H), 0.95 - 0.93 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.5 (d, $^{1}J_{C\text{-}P}$ = 121.0 Hz, *C*), 132.0 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, *C*H), 130.9 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 128.5 (d, $^{2}J_{C\text{-}P}$ = 13.1 Hz, *C*H), 112.4 (d, $^{2}J_{C\text{-}P}$ = 31.3 Hz, *C*), 69.7 (d, $^{1}J_{C\text{-}P}$ = 177.8 Hz, *C*), 9.4 (d, $^{3}J_{C\text{-}P}$ = 10.0 Hz, *C*H), 0.4 (d, $^{4}J_{C\text{-}P}$ = 40.0 Hz, *C*H),. $^{31}$P NMR (162 MHz, $CDCl_3$) δ 7.57. HRMS (ESI) calcd for $C_{17}H_{15}OP$ $[M+H]^+$: 266.0861; found: 266.0865.




**(3,3-dimethylbut-1-yn-1-yl)diphenylphosphine oxide (3u)**

white solid (25.3 mg, 45% yield). PE/EA = 1:1, $R_f$ = 0.35. Mp = 121-123 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 13.8, 7.7 Hz, 4H), 7.54 - 7.43 (m, 6H), 1.33 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.6 (d, $^{1}J_{C\text{-}P}$ = 121.0 Hz, *C*), 133.0, 132.0 (d, $^{4}J_{C\text{-}P}$ = 2.0 Hz, *C*), 130.8 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, *C*H), 128.5 (d, $^{2}J_{C\text{-}P}$ = 13.1 Hz, *C*H), 116.8 (d, $^{2}J_{C\text{-}P}$ = 30.3 Hz, *C*), 73.1 (d, $^{1}J_{C\text{-}P}$ = 175.7 Hz, *C*), 30.0 (d, $^{4}J_{C\text{-}P}$= 2.0 Hz, *C*H), 28.5 (d, $^{3}J_{C\text{-}P}$= 3.0 Hz, *C*H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 7.68. $C_{18}H_{19}OP$ $[M+H]^+$: 283.1252; found: 283.1256.



**Ethyl 3-(diphenylphosphoryl)propiolate (3v)**

yellow oil (35.8 mg, 60% yield). PE/EA = 1:1, $R_f$ = 0.35 $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 14.1, 8.0 Hz, 4H), 7.61 – 7.49 (m, 6H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.8 (d, $^4J_{C\text{-}P}$ = 4.0 Hz, *C*H), 133.0 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, *C*H), 131.0 (d, $^1J_{C\text{-}P}$ = 123.2 Hz, *C*), 131.1 (d, $^3J_{C\text{-}P}$ = 12.1 Hz, *C*H), 128.9 (d, $^2J_{C\text{-}P}$ = 13.1 Hz, *C*H), 92.8 (d, $^2J_{C\text{-}P}$ = 23.2 Hz, *C*H),79.3 (d, $^1J_{C\text{-}P}$ = 146.5 Hz, *C*), 63.2, 13.9.$^{31}$P NMR (162 MHz, $CDCl_3$) δ 9.02. $C_{17}H_{15}O_3P$ $[M+H]^+$: 299.0837; found: 299.0842.

## Procedure for the Synthesis of Phenylacetylene Silver[2]

To a solution of 1-trimethylsilyl-2-phenylacetylene (5 mmol ) in 20 mL methanol ( $H_2O$:MeOH = 1:3), was added silver nitrate (5 mmol) at room temperature. The starting materials rapidly disappeared and a white precipitate formed within 5 - 15 min. This solid was recovered by filtration and washed with cold methanol (stored at 0 $^oC$). Subsequent drying led to the phenylacetylene silver as a white powder.

## Procedure for the Synthesis of (diphenylphosphoryl)silver[3]

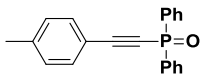
To a stirred solution (The solution pH = 2.90) of $HP(O)Ph_2$ (404 mg, 2.0 mmol) in $H_2O$ (20 mL) were added $AgNO_3$(340 mg, 2.0 mmol). The mixture was allowed to stir at room temperature for 2 hours. The reaction mixture pH = 1.45. The silver salt was filtered off. The acidity was increased, which indicates that $HNO_3$ was generated. (pH were mearsured using METTLE TOLEDOFE20-FiveEasyTM pH)

## General Procedures for the $Ag_2CO_3$ Recovery Experiment:

A mixture of diphenylphosphine oxide **2a** (0.2 mmol) and Silver carbonate (0.4 mmol, 110 mg), 1-ethynyl-4-methylbenzene **1a** (0.3 mmol) in DMSO (3 mL) was stirred in $N_2$ at 120 $^oC$ for 15 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. Then the residue was washed with $CH_2Cl_2$ (3 × 5 mL) and the solid was dissolved in 25 mL $HNO_3$ (10%, v/v in $H_2O$). After stirring for 1 h, the reaction mixture was filtered. To the filtrate was added $Na_2CO_3$ (10%, v/v in $H_2O$, 25 mL). The suspension was filtered and the solid residue washed with water (3 × 5 mL) to afford 82.5 mg $Ag_2CO_3$ (yield 75%) as a green powder.

## Reference:


1. J. Hu, N. Zhao, B. Yang, G. Wang, L.-N. Guo, Y.-M. Liang and S.-D. Yang, *Chem-Eur. J.*, 2011, **17**, 5516-5521.
2. A. Viterisi, A. Orsini, J. M. Weibel and P. Pale, *Tetrahedron Lett.*, 2006, **47**, 2779-2781.
3. Y.-M. Li, M. Sun, H. L. Wang, Q. P. Tian and S.-D. Yang, *Angew. Chem. Int. Ed.*, 2013, **52**, 3972-3976.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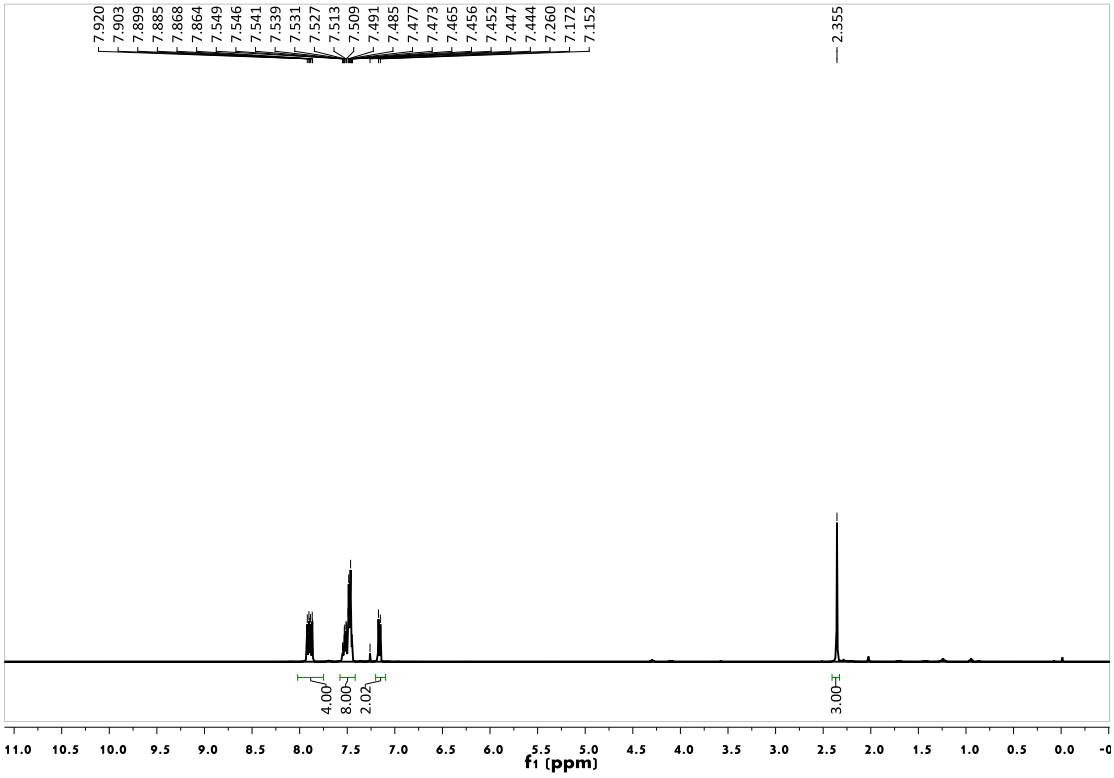
Ph

3a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7.513
7.509
7.491
7.485
7.477
7.473
7.465
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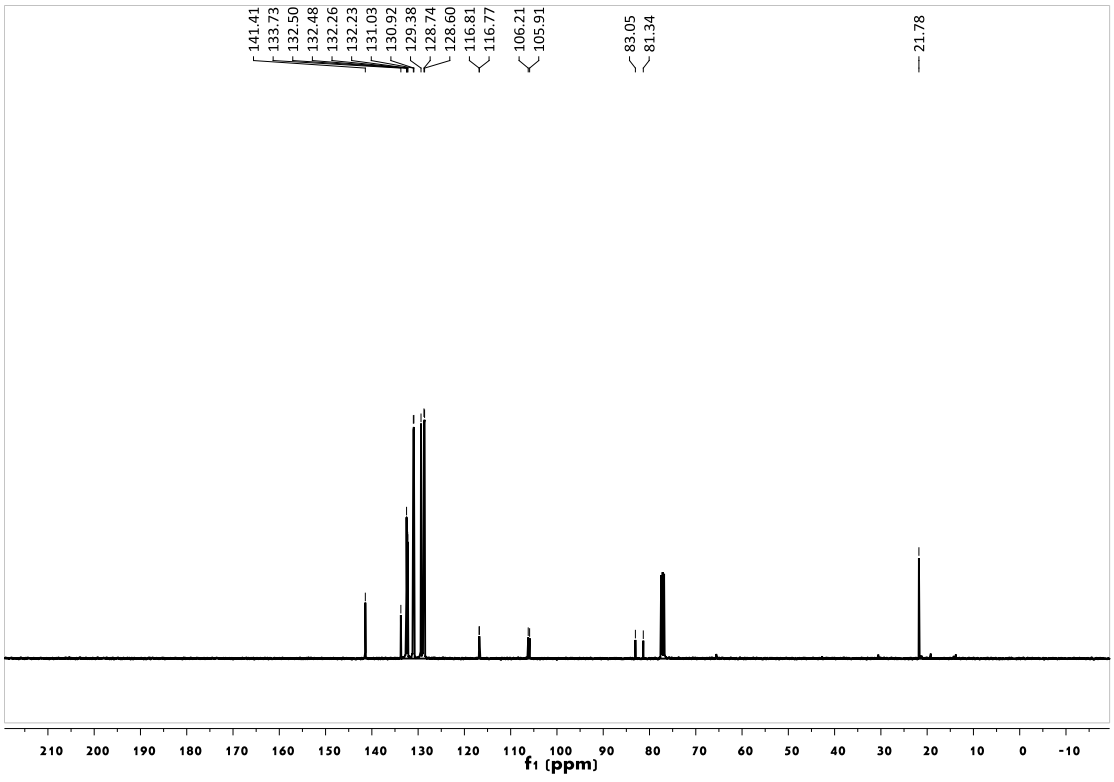
8.00
2.02
3.00
f1 (ppm)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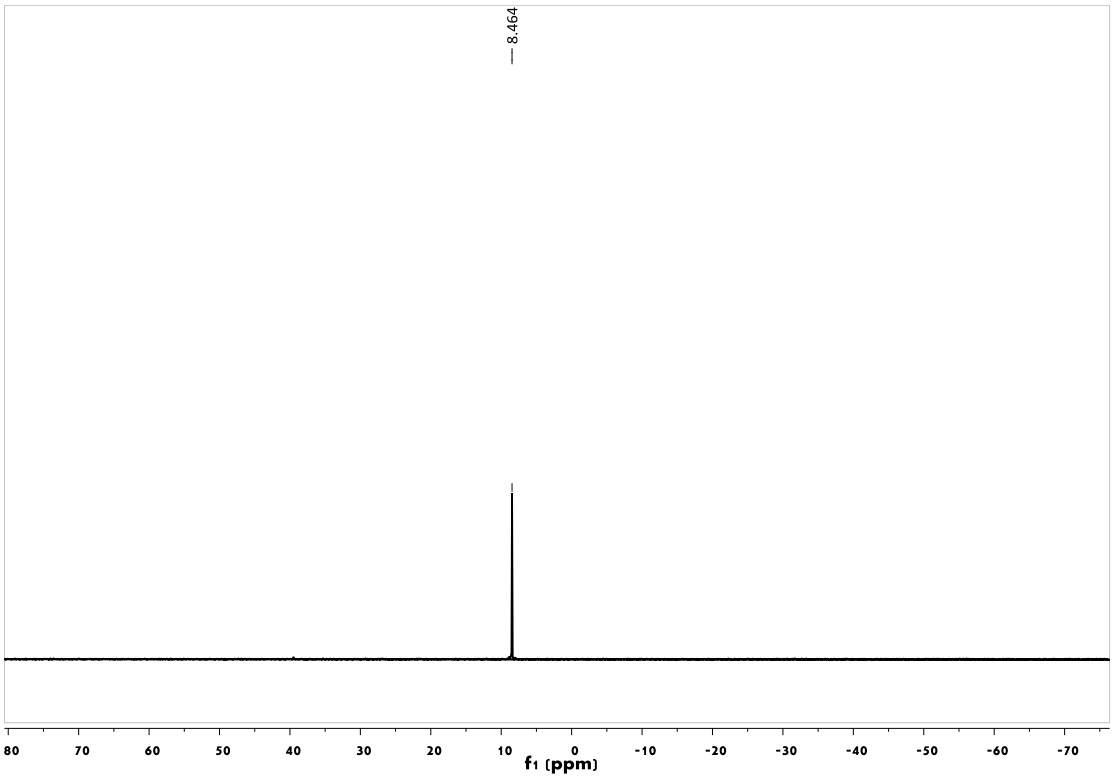
f1 (ppm)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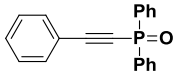
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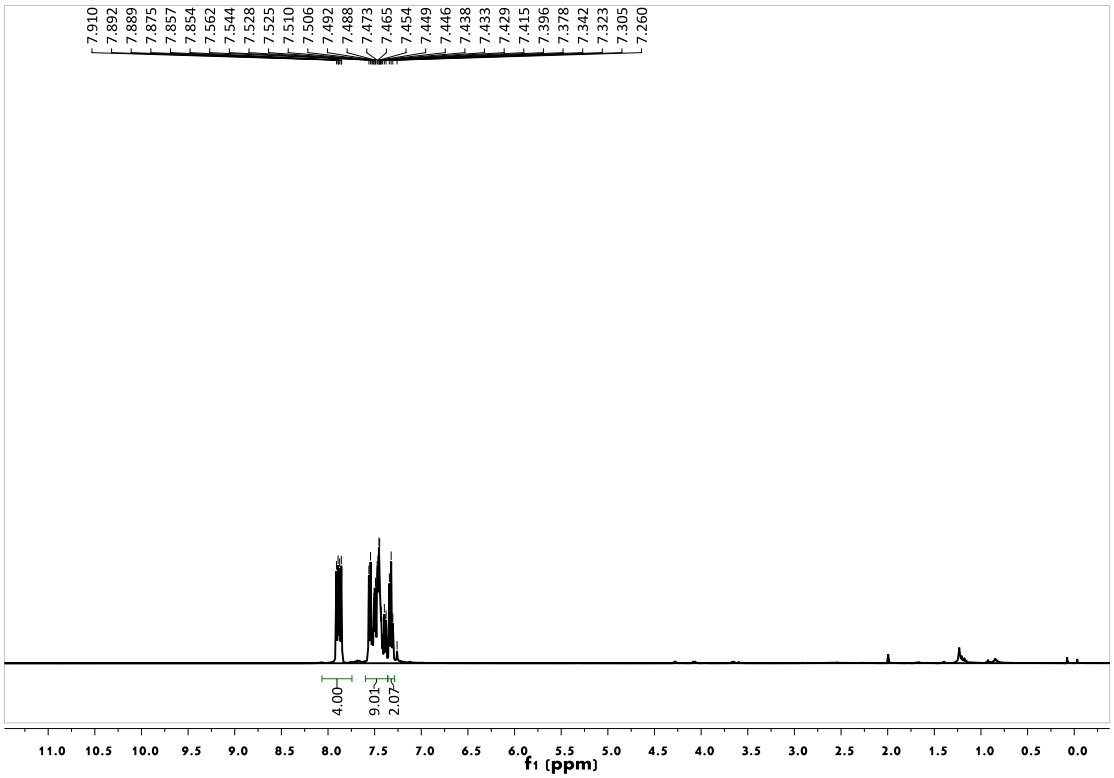
P=O
Ph

3b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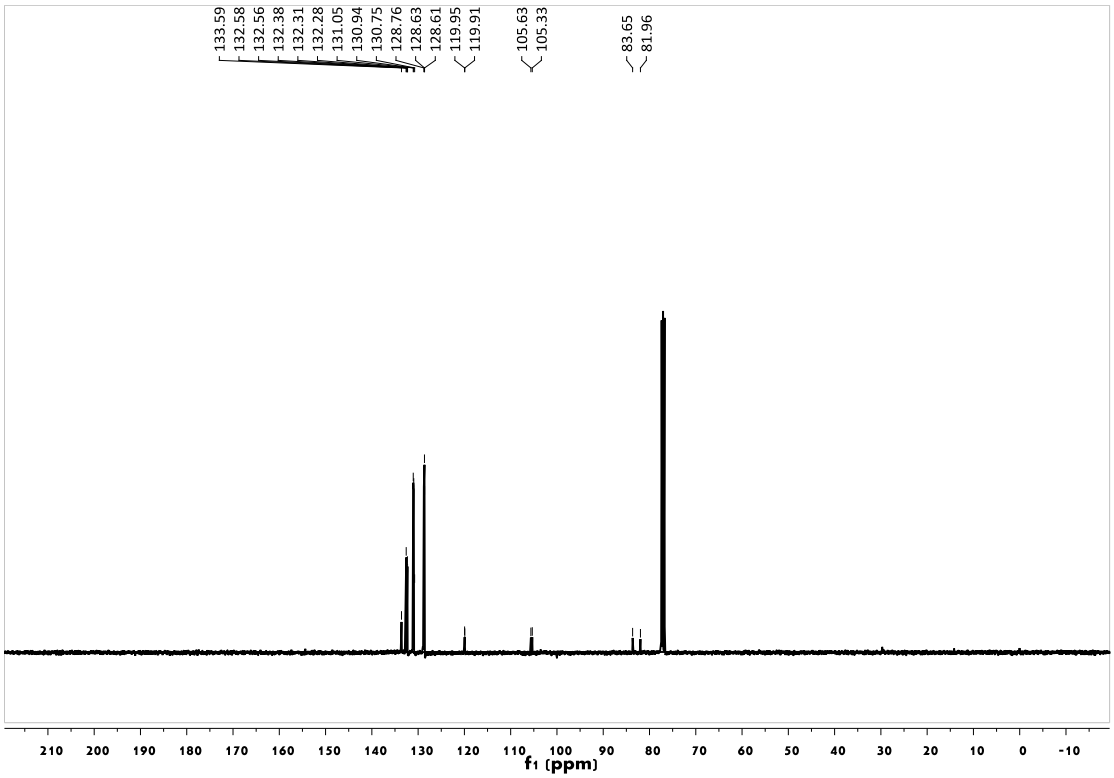
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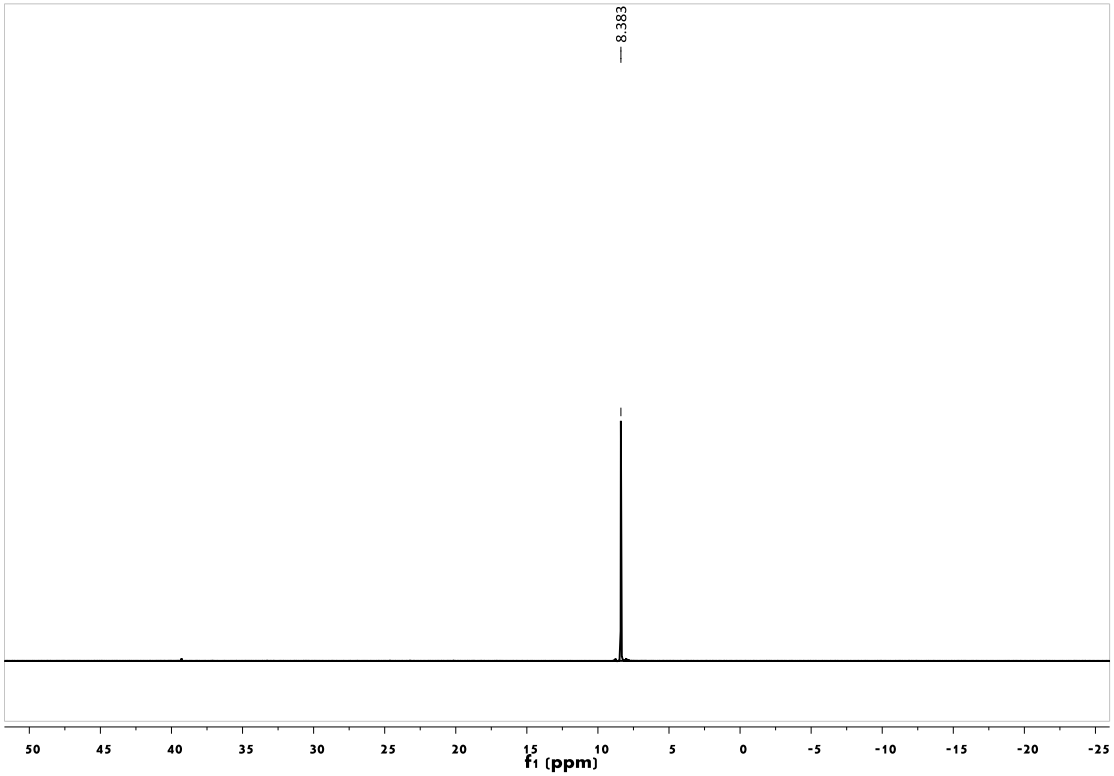
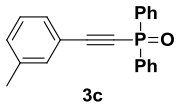
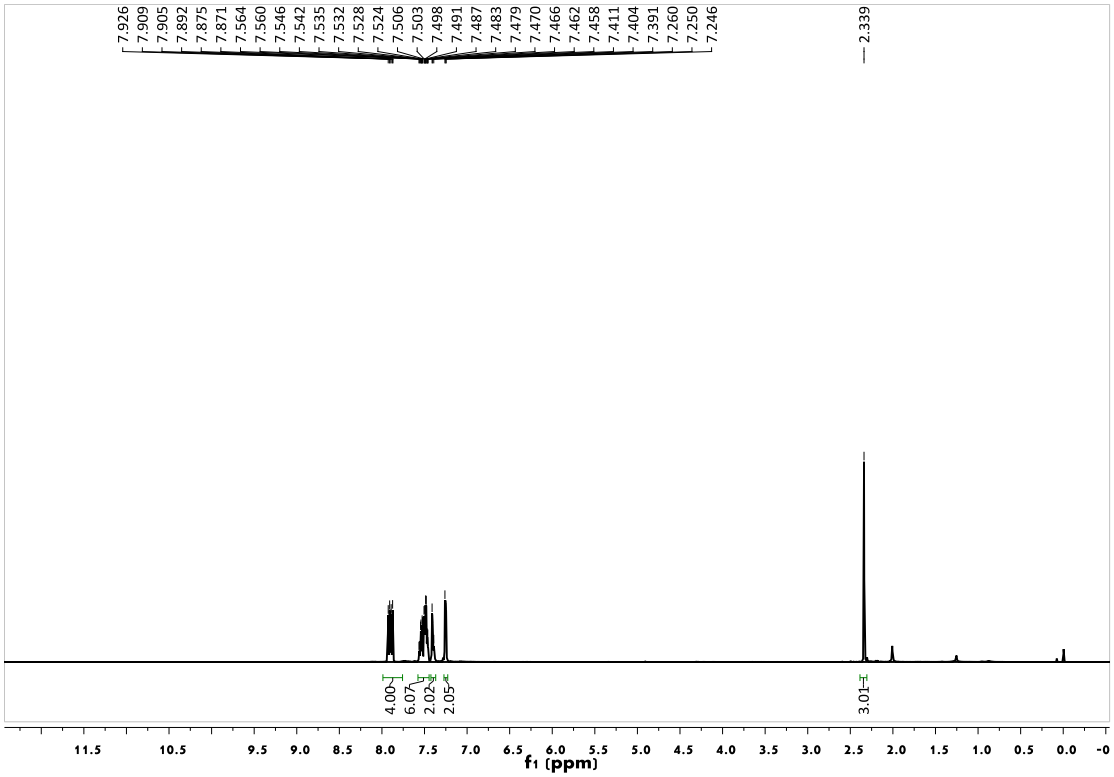
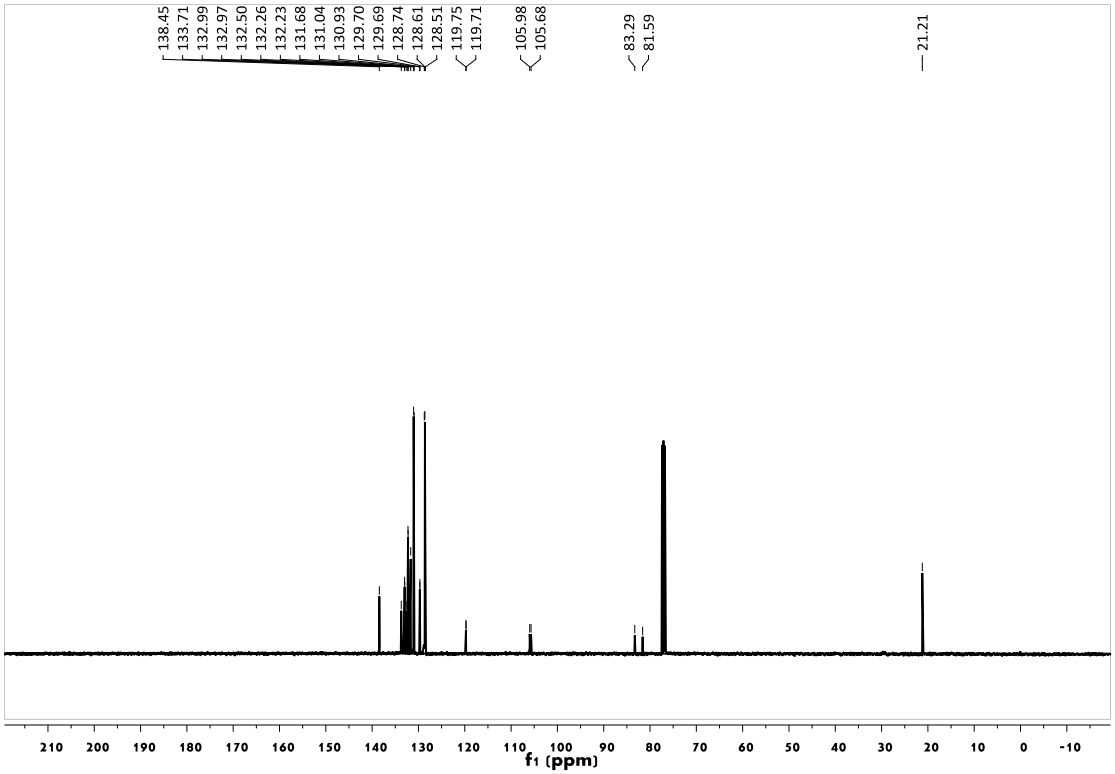
81.96
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

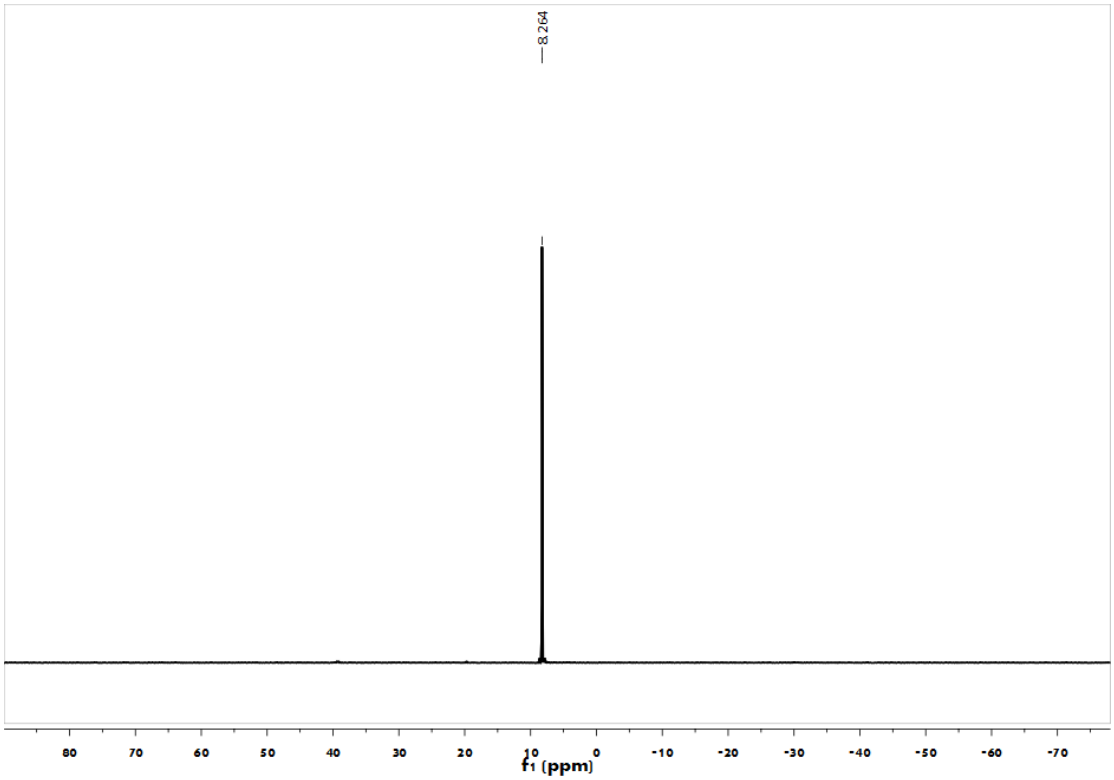

8.383
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

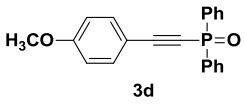

Ph
P=O
Ph

3c

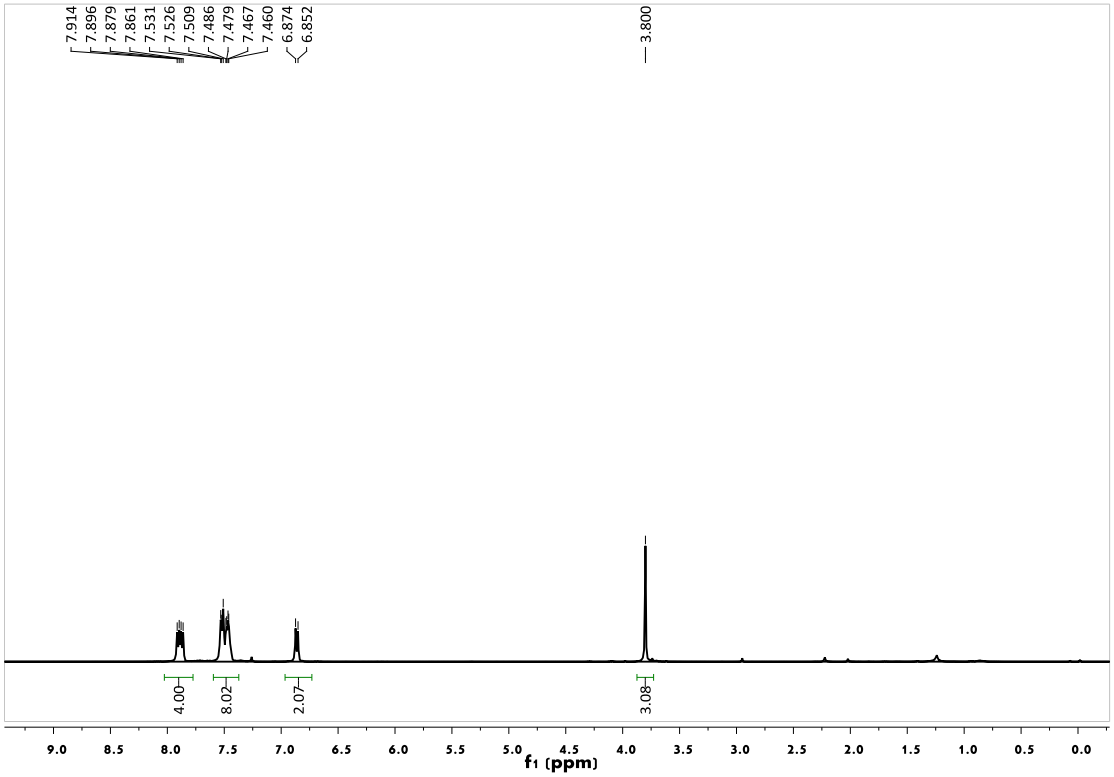

7.926
7.909
7.905
7.892
7.875
7.871
7.564
7.560
7.546
7.542
7.535
7.532
7.528
7.524
7.506
7.503
7.498
7.491
7.487
7.483
7.479
7.470
7.466
7.462
7.458
7.411
7.404
7.391
7.260
7.250
7.246
2.339
4.00
6.07
2.02
2.05
3.01
f1 (ppm)

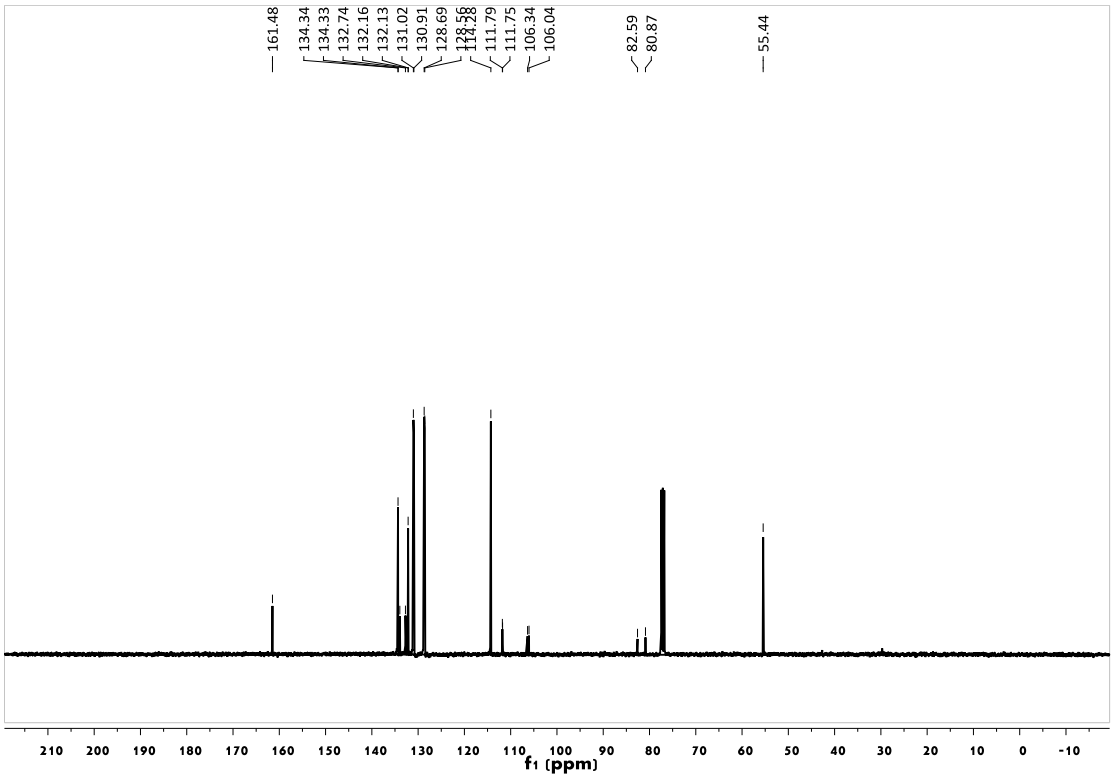

138.45
133.71
132.99
132.97
132.50
132.26
132.23
131.68
131.04
130.93
129.70
129.69
128.74
128.61
128.51
119.75
119.71
105.98
105.68
83.29
81.59
21.21
f1 (ppm)

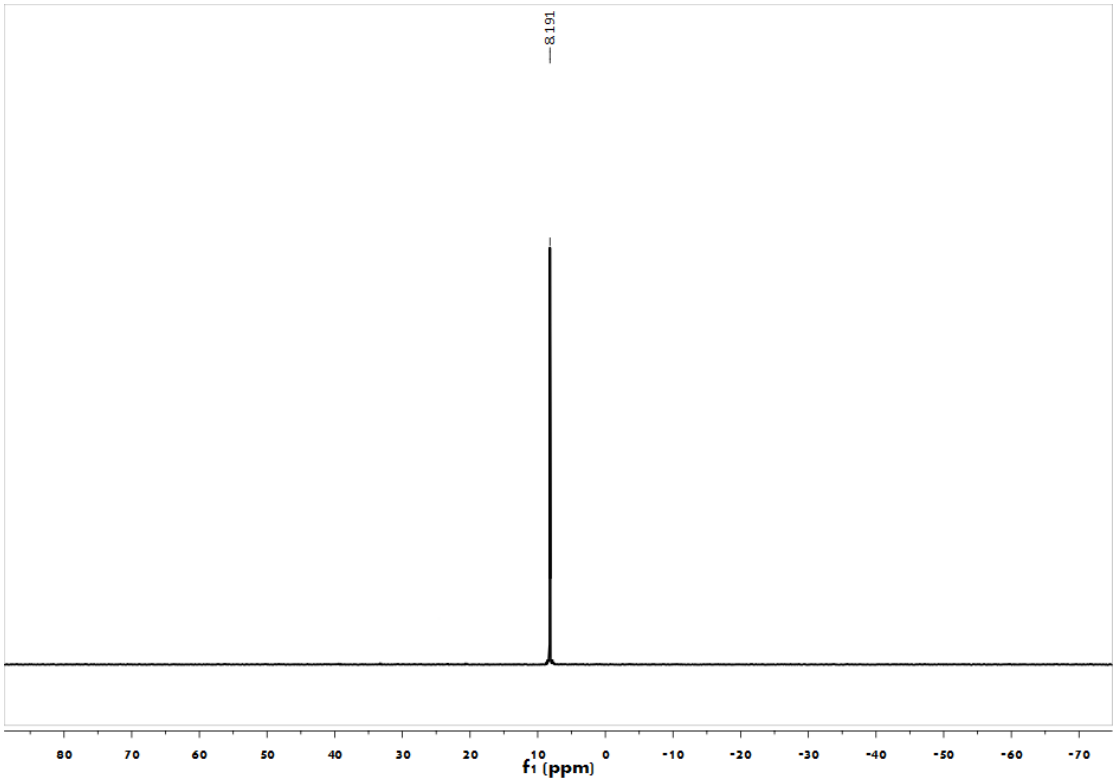

8.264
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

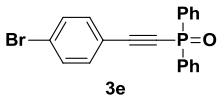

Ph
H3CO
P=O
Ph

3d

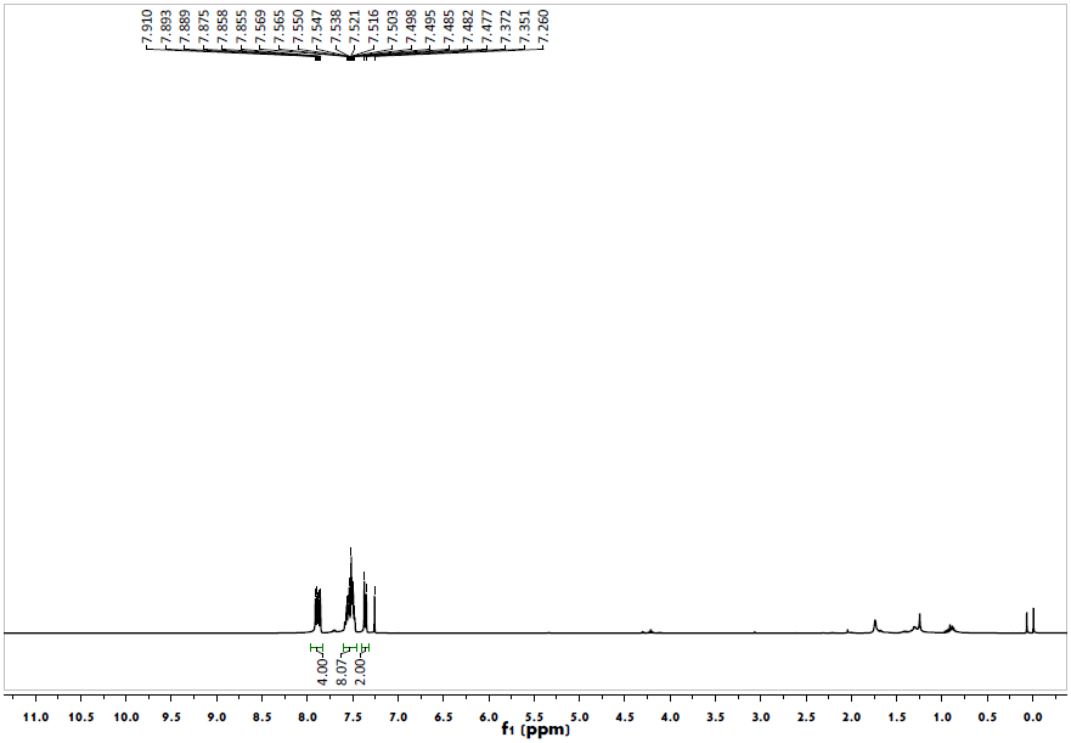

7.914
7.896
7.879
7.861
7.531
7.526
7.509
7.486
7.479
7.467
7.460
6.874
6.852
3.800
4.00
8.02
2.07
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


161.48
134.34
134.33
132.74
132.16
132.13
131.02
130.91
128.69
128.56
114.28
111.79
111.75
106.34
106.04
82.59
80.87
55.44
f1 (ppm)


8.191
f1 (ppm)


Br
Ph
P=O
Ph

3e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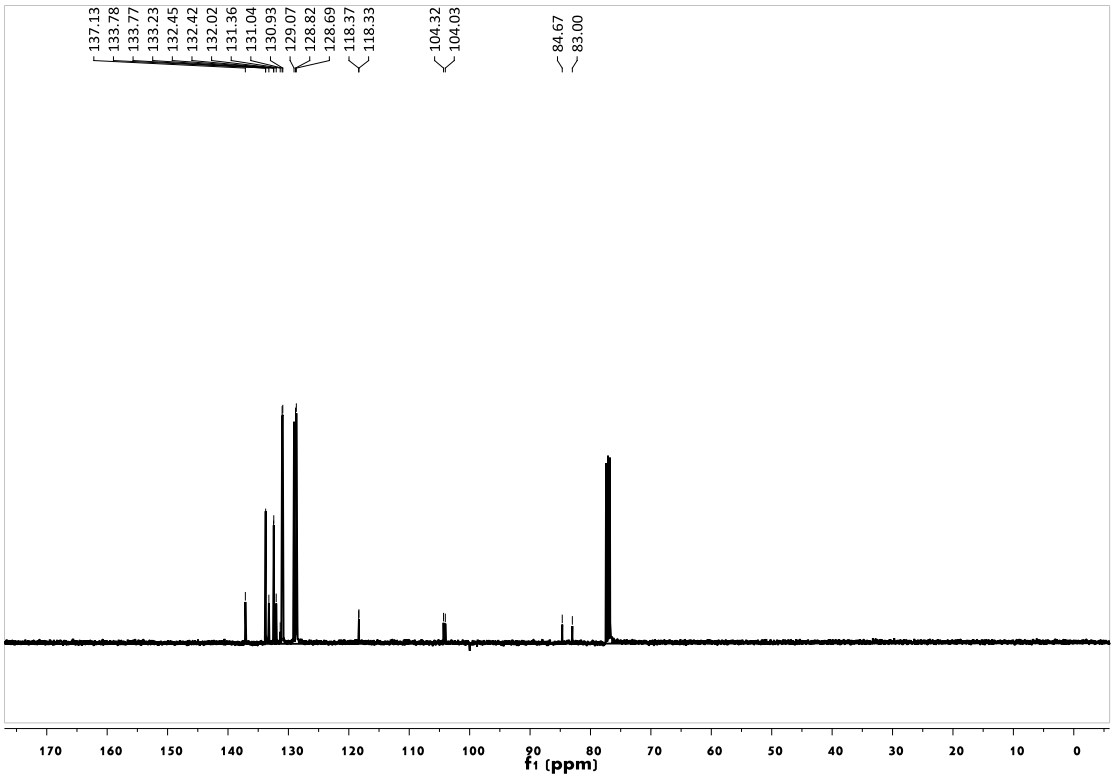
7.893
7.889
7.875
7.858
7.855
7.569
7.565
7.550
7.547
7.538
7.521
7.516
7.503
7.498
7.495
7.485
7.482
7.477
7.372
7.351
7.260
4.00
8.07
2.00
f1 (ppm)


137.13
133.78
133.77
133.23
132.45
132.42
132.02
131.36
131.04
130.93
129.07
128.82
128.69
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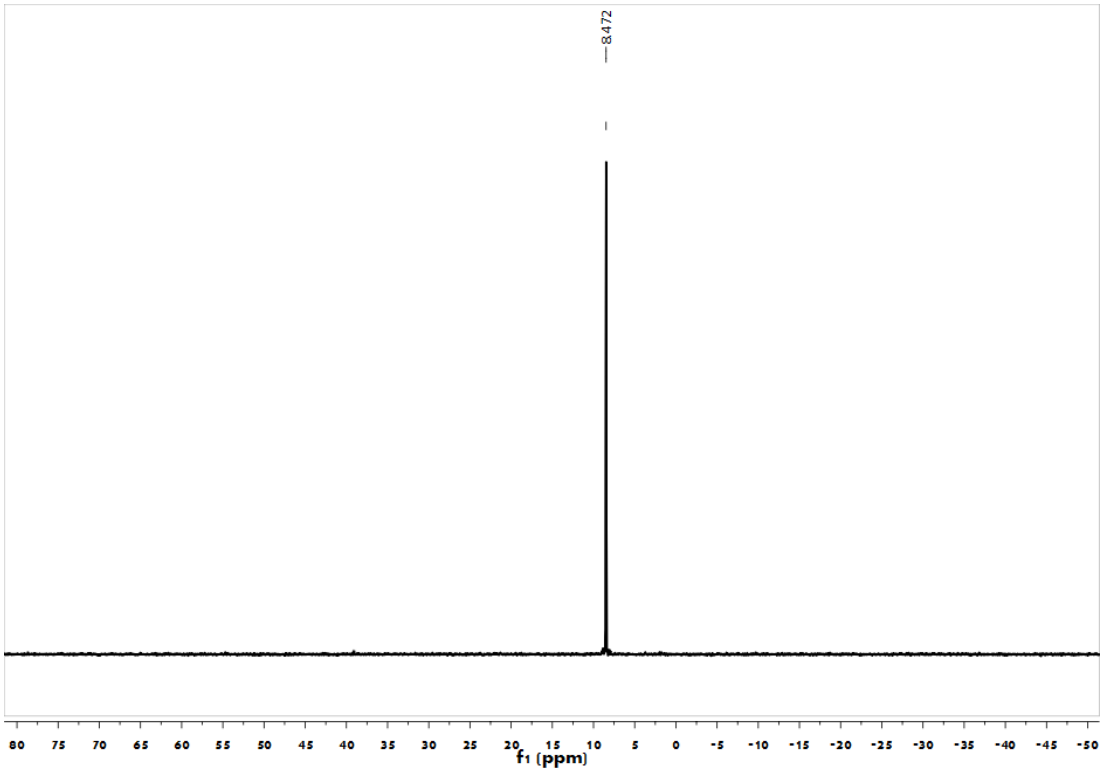
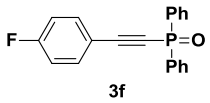
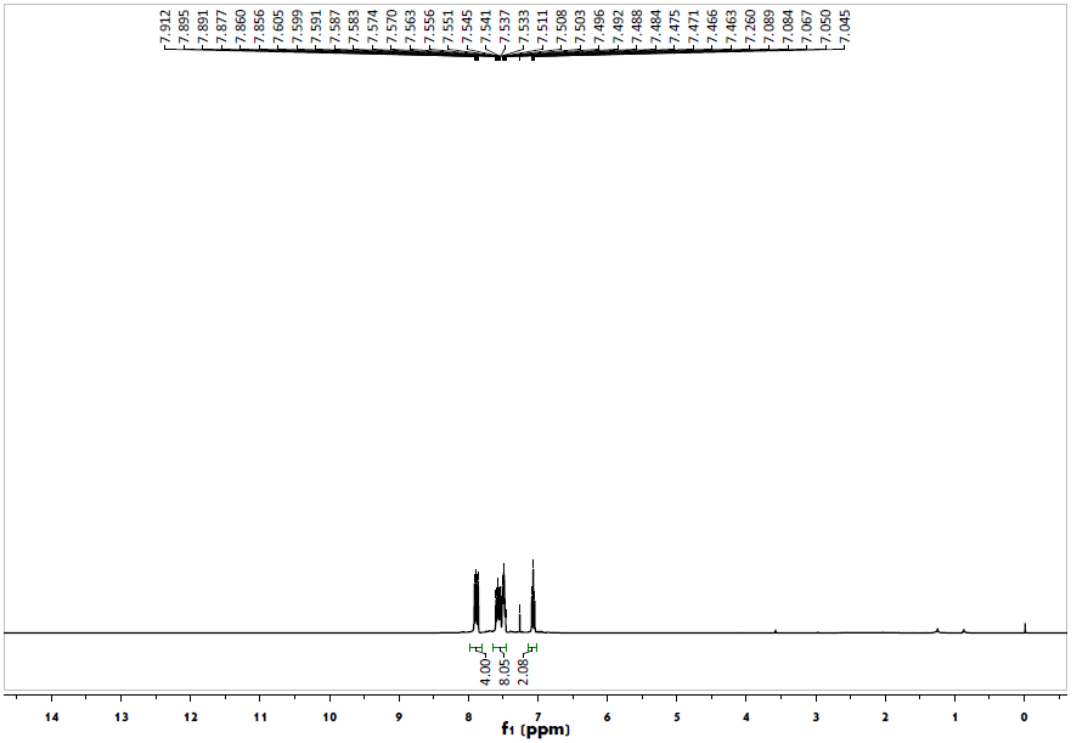
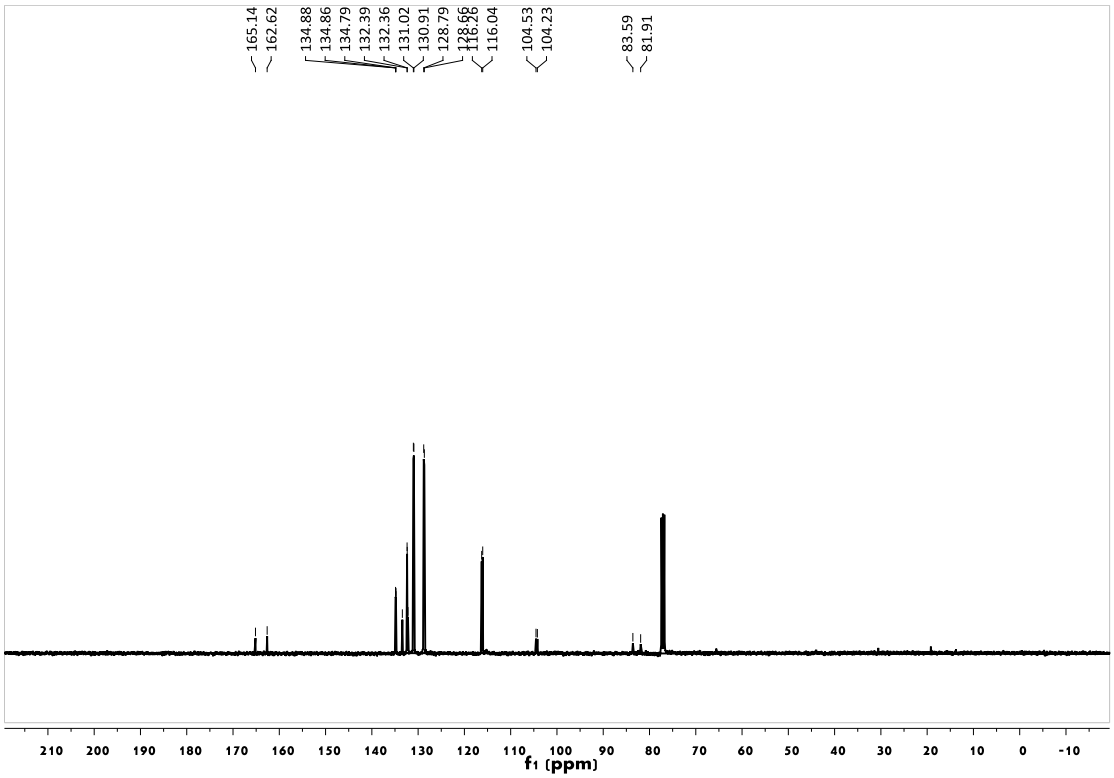
118.33
104.32
104.03
84.67
83.00
f1 (ppm)

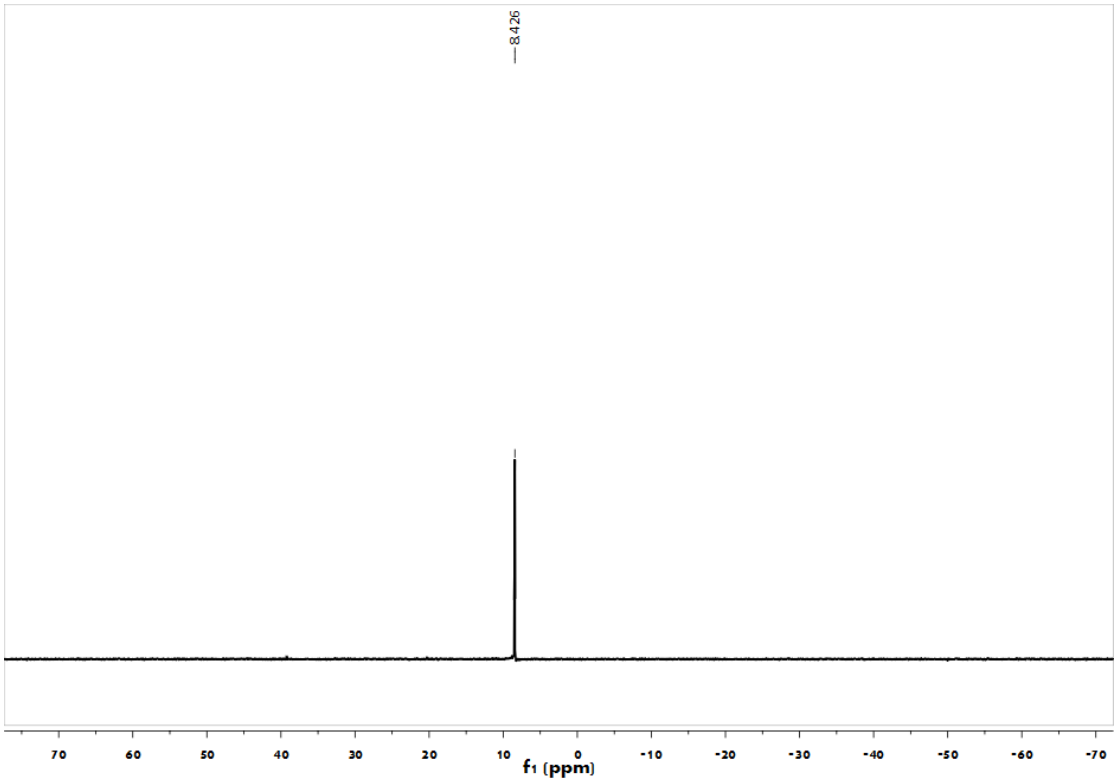

8.472
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

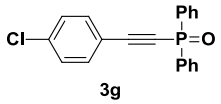

F
Ph
P=O
Ph

3f

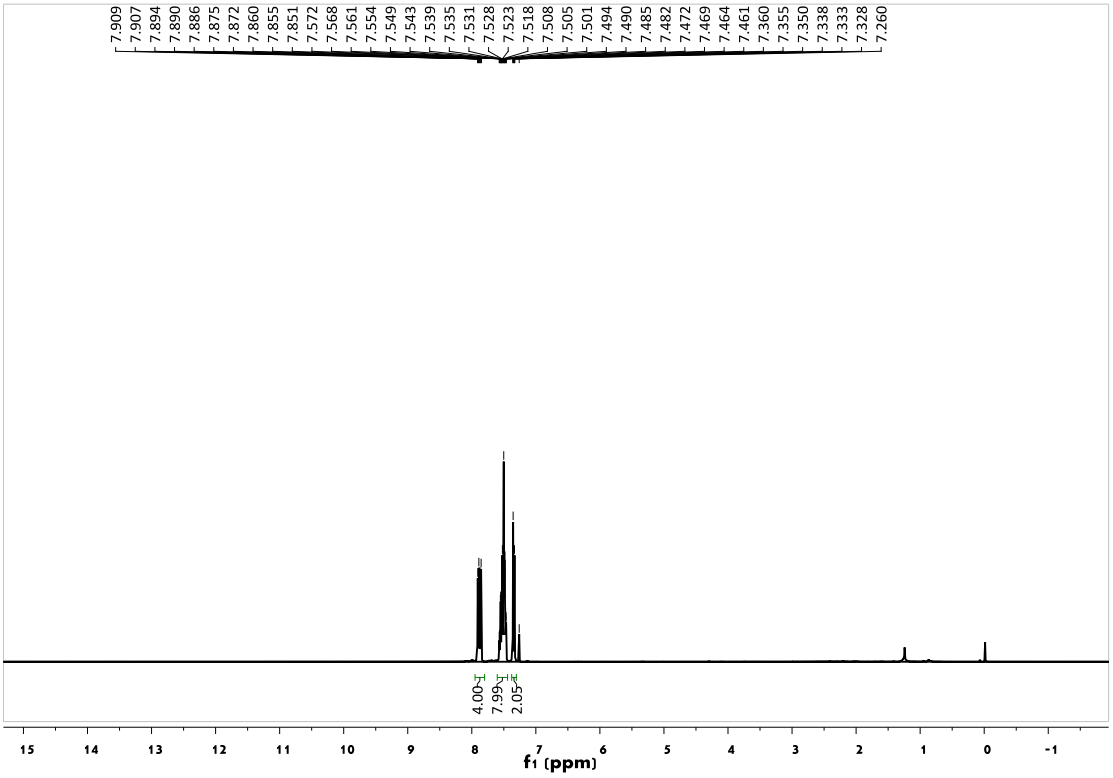

7.912
7.895
7.891
7.877
7.860
7.856
7.605
7.599
7.591
7.587
7.583
7.574
7.570
7.563
7.556
7.551
7.545
7.541
7.537
7.533
7.511
7.508
7.503
7.496
7.492
7.488
7.484
7.475
7.471
7.466
7.463
7.260
7.089
7.084
7.067
7.050
7.045
4.00
8.05
2.08
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

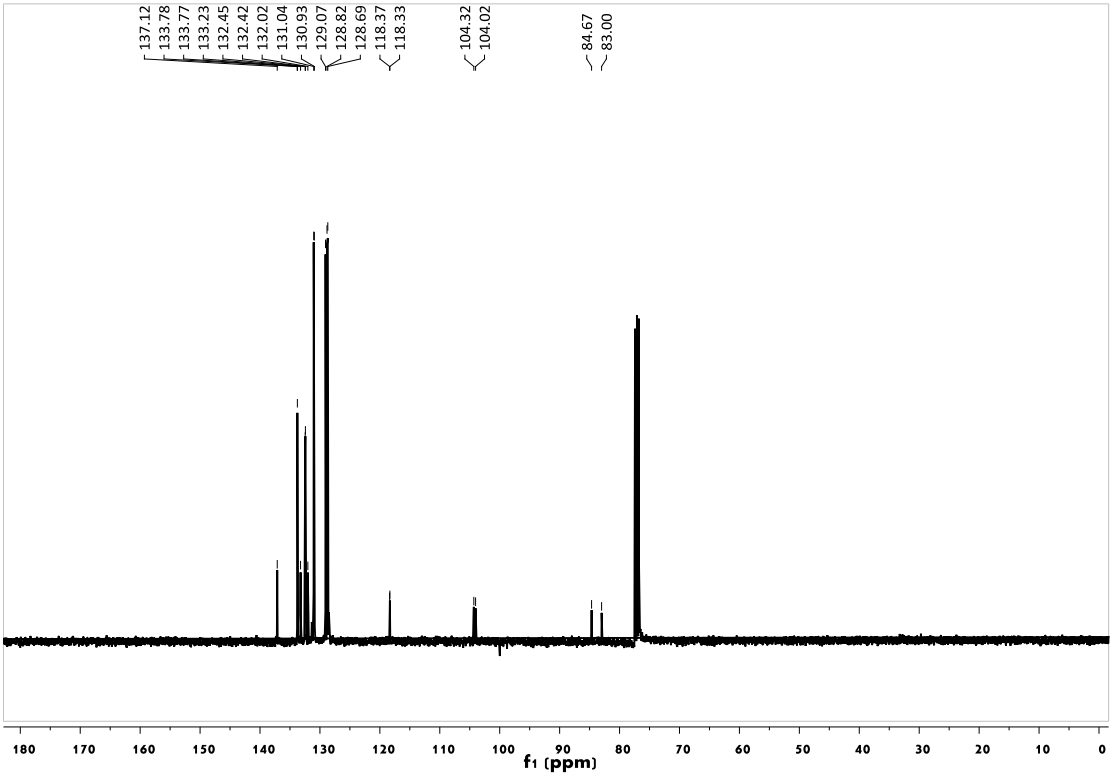

165.14
162.62
134.88
134.86
134.79
132.39
132.36
131.02
130.91
128.79
116.04
104.53
104.23
83.59
81.91
f1 (ppm)

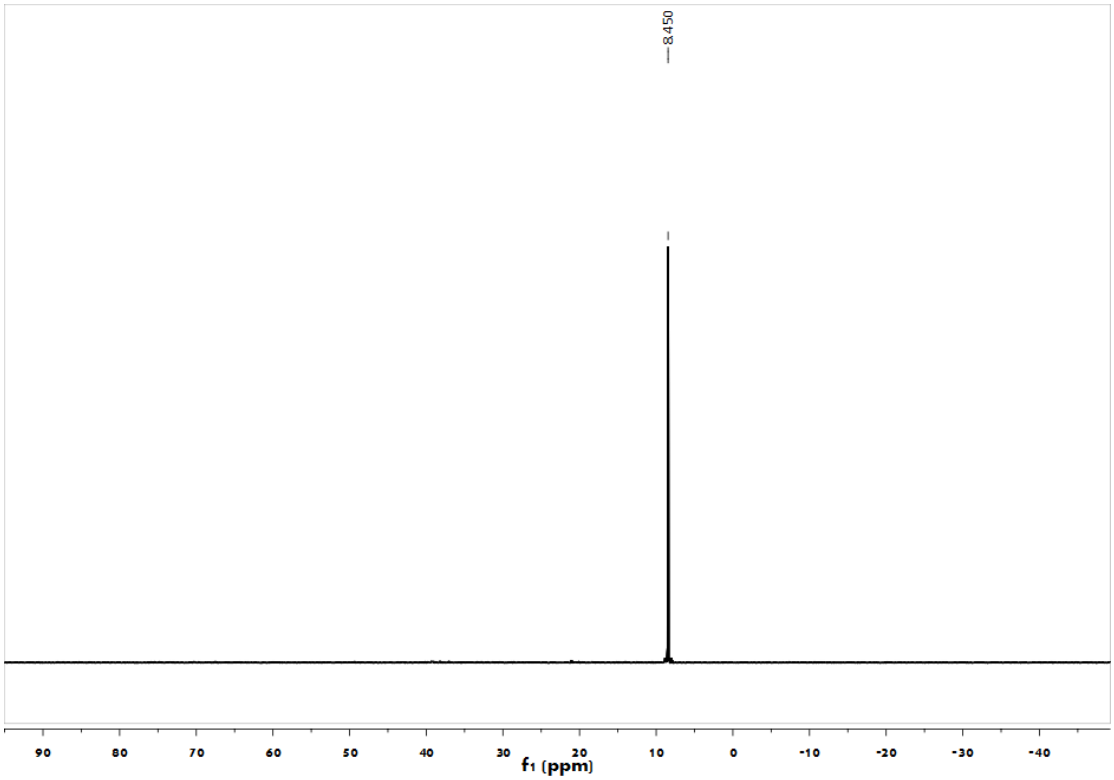

8.426
f1 (ppm)

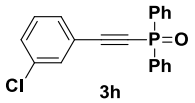

Ph
Cl
P=O
Ph

3g

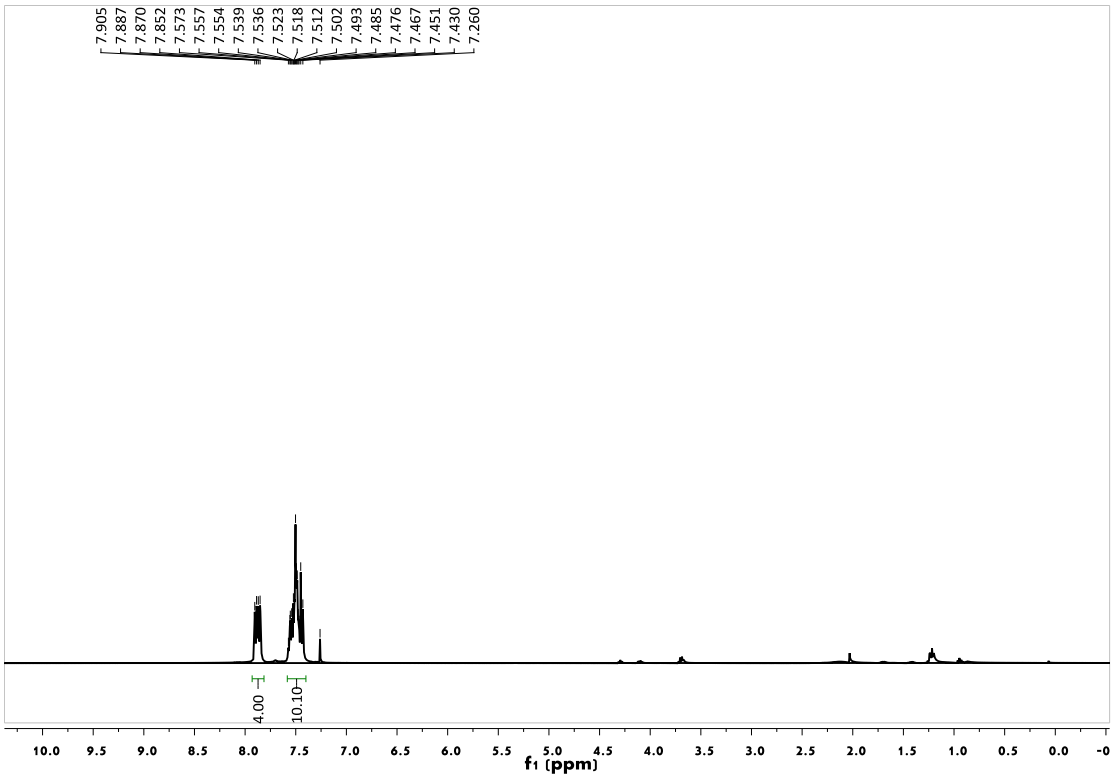

7.909
7.907
7.894
7.890
7.886
7.875
7.872
7.860
7.855
7.851
7.572
7.568
7.561
7.554
7.549
7.543
7.539
7.535
7.531
7.528
7.523
7.518
7.508
7.505
7.501
7.494
7.490
7.485
7.482
7.472
7.469
7.464
7.461
7.360
7.355
7.350
7.338
7.333
7.328
7.260
4.00
7.99
2.05
f1 (ppm)


137.12
133.78
133.77
133.23
132.45
132.42
132.02
131.04
130.93
129.07
128.82
128.69
118.37
118.33
104.32
104.02
84.67
83.00
f1 (ppm)


8.450
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


Ph
P=O
Ph
Cl

3h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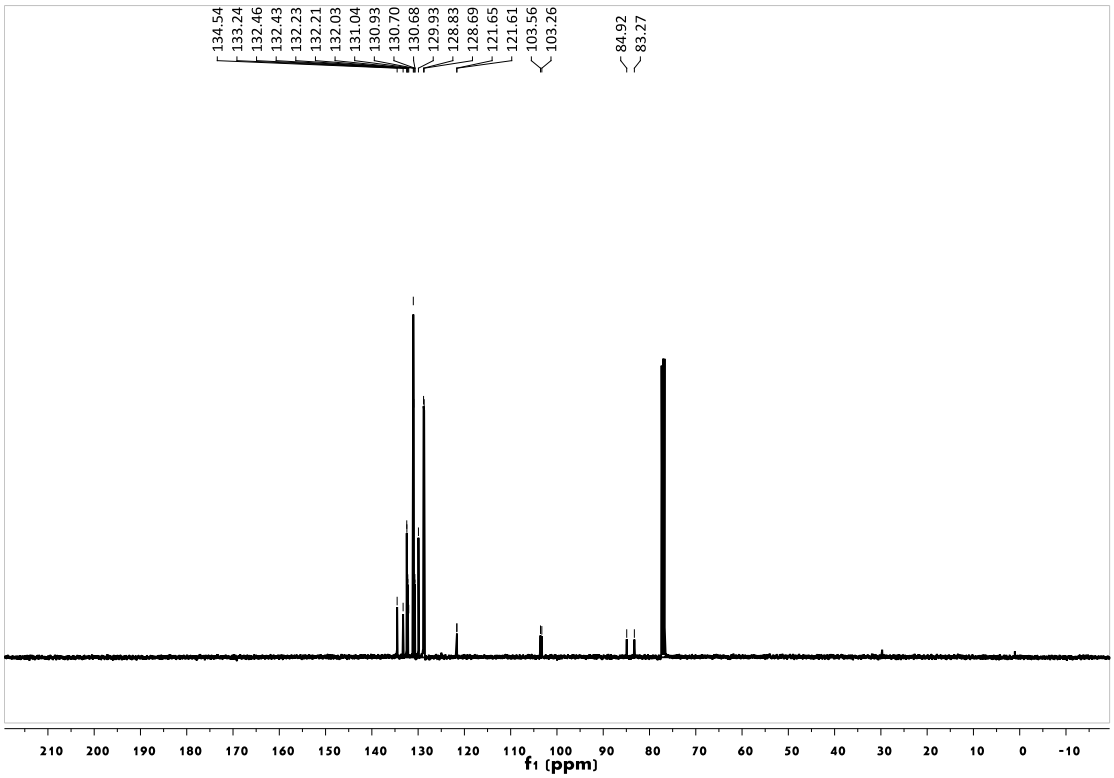
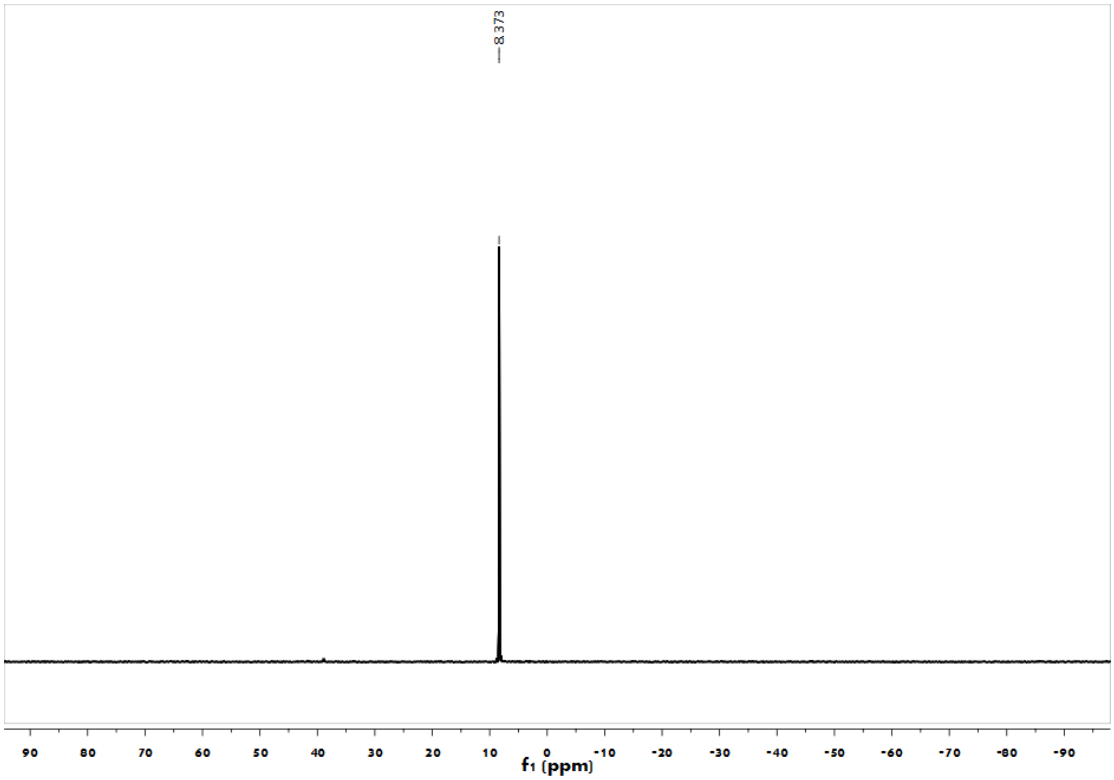
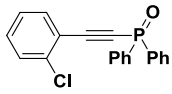
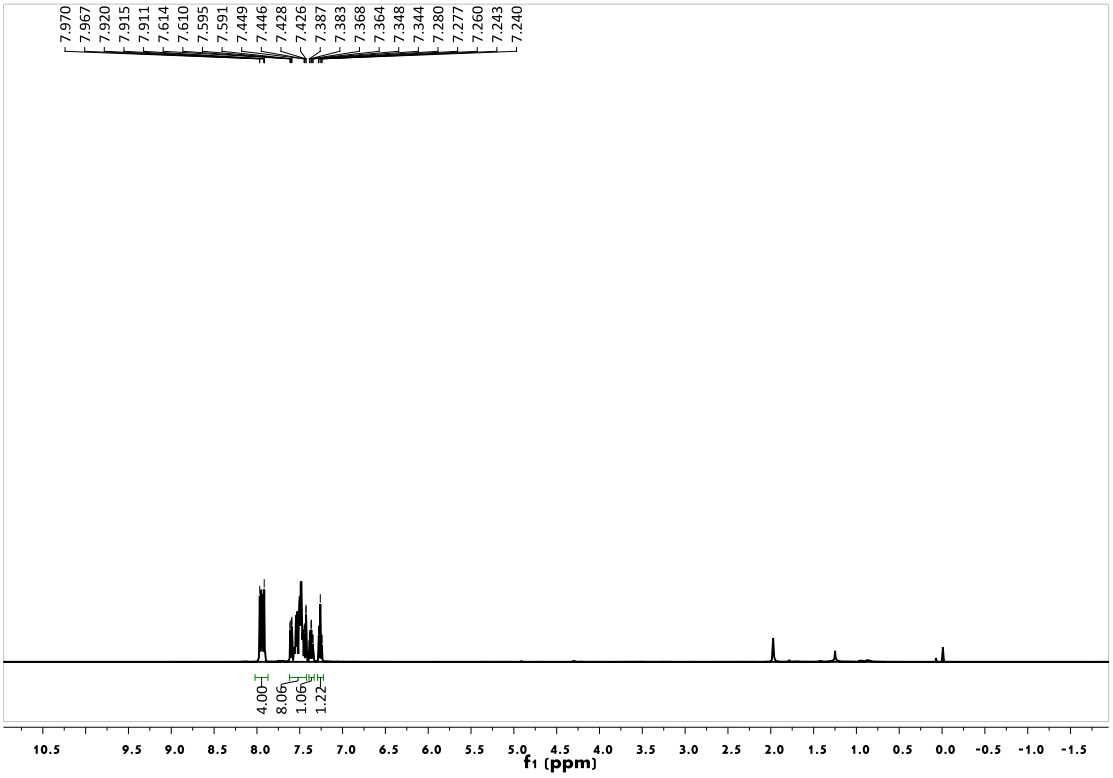
7.870
7.852
7.573
7.557
7.554
7.539
7.536
7.523
7.518
7.512
7.502
7.493
7.485
7.476
7.467
7.451
7.430
7.260
4.00
10.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


134.54
133.24
132.46
132.43
132.23
132.21
132.03
131.04
130.93
130.70
130.68
129.93
128.83
128.69
121.65
121.61
103.56
103.26
84.92
83.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.373
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


O
P
Ph
Ph
Cl

**3l**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7.967
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7.915
7.911
7.614
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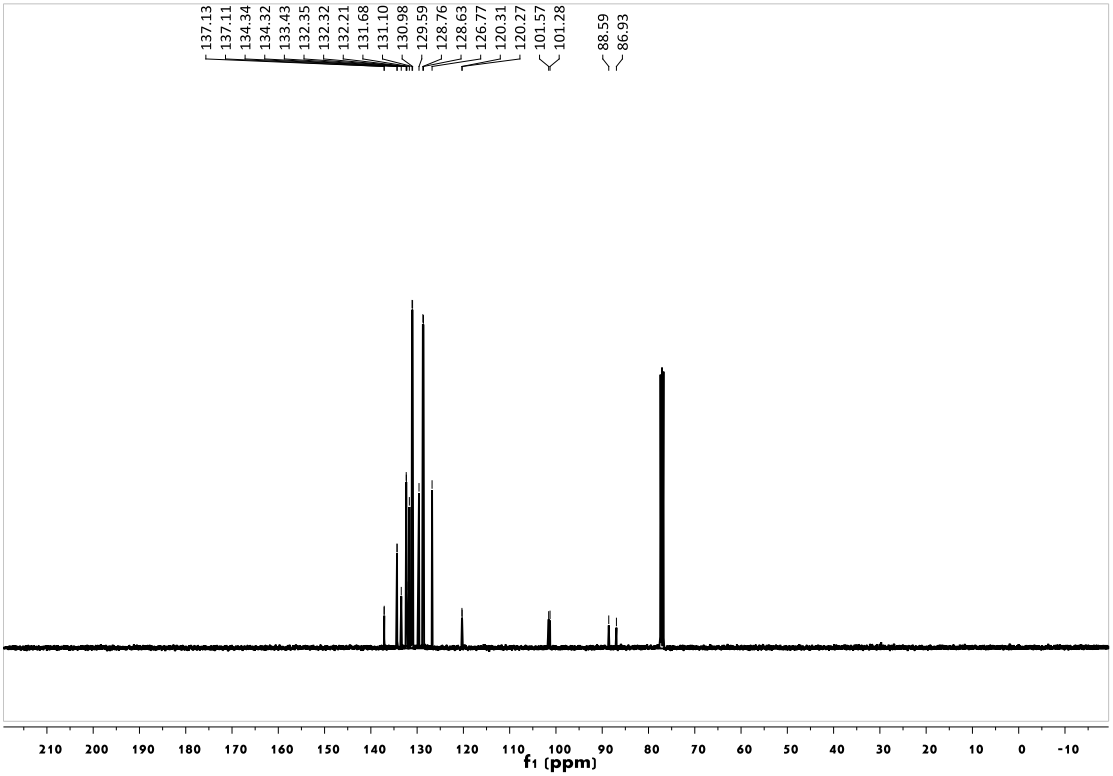
7.595
7.591
7.449
7.446
7.428
7.426
7.387
7.383
7.368
7.364
7.348
7.344
7.280
7.277
7.260
7.243
7.240
4.00
8.06
1.06
1.22
f1 (ppm)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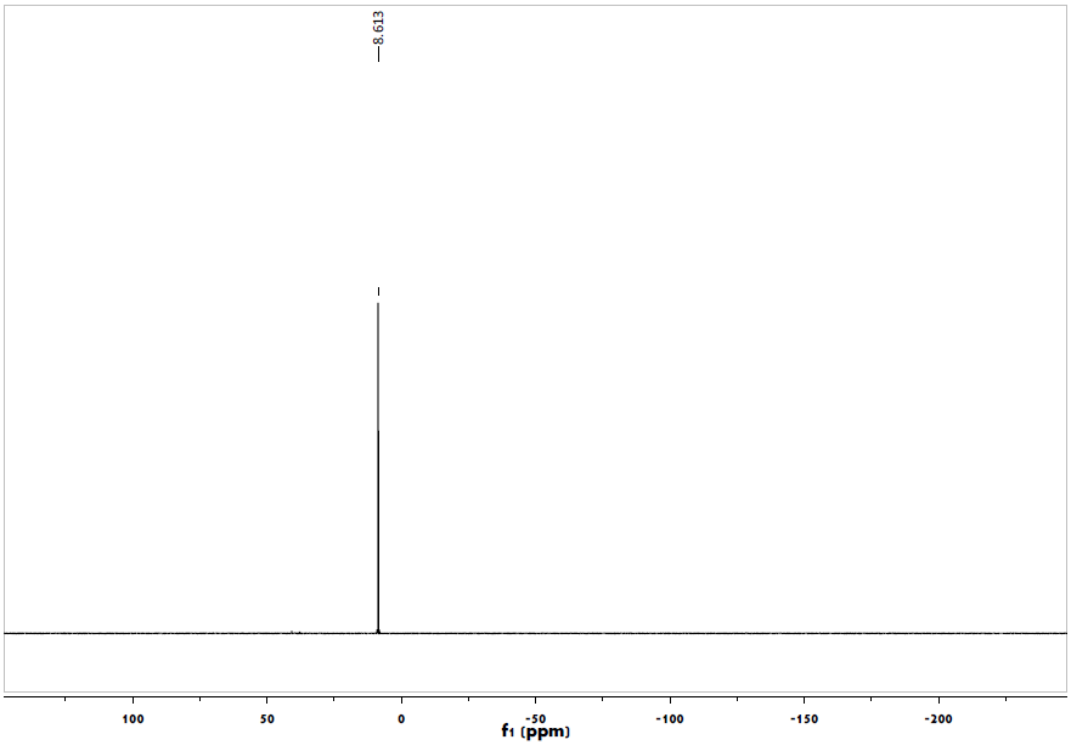
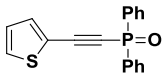
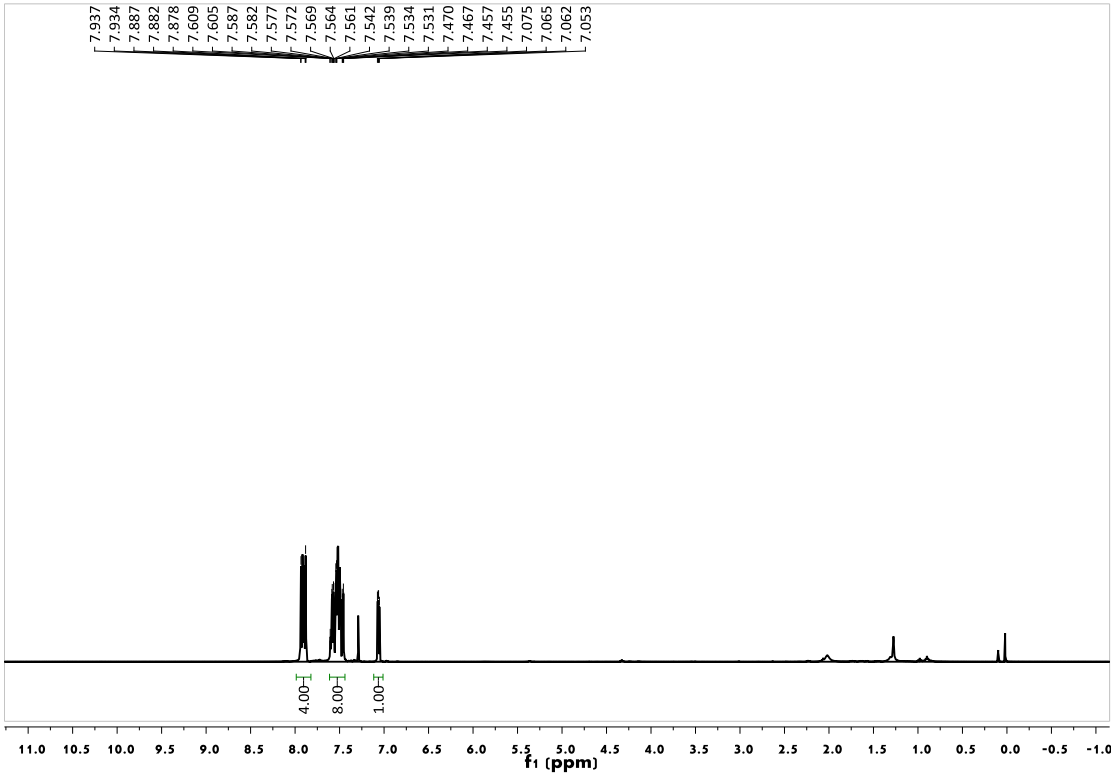
137.11
134.34
134.32
133.43
132.35
132.32
132.21
131.68
131.10
130.98
129.59
128.76
128.63
126.77
120.31
120.27
101.57
101.28
88.59
86.93
f1 (ppm)


8.613
100
50
0
-50
-100
-150
-200
f1 (ppm)


Ph
P=O
Ph
S

3j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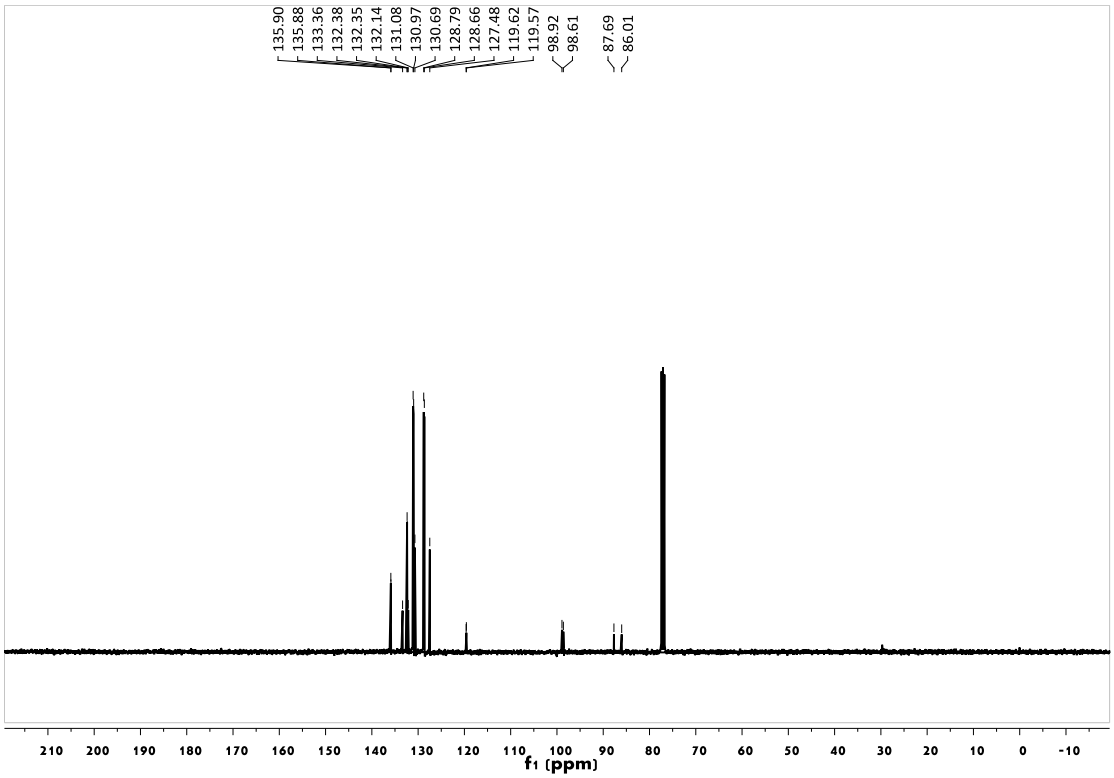
7.934
7.887
7.882
7.878
7.609
7.605
7.587
7.582
7.577
7.572
7.569
7.564
7.561
7.542
7.539
7.534
7.531
7.470
7.467
7.457
7.455
7.075
7.065
7.062
7.053
4.00
8.00
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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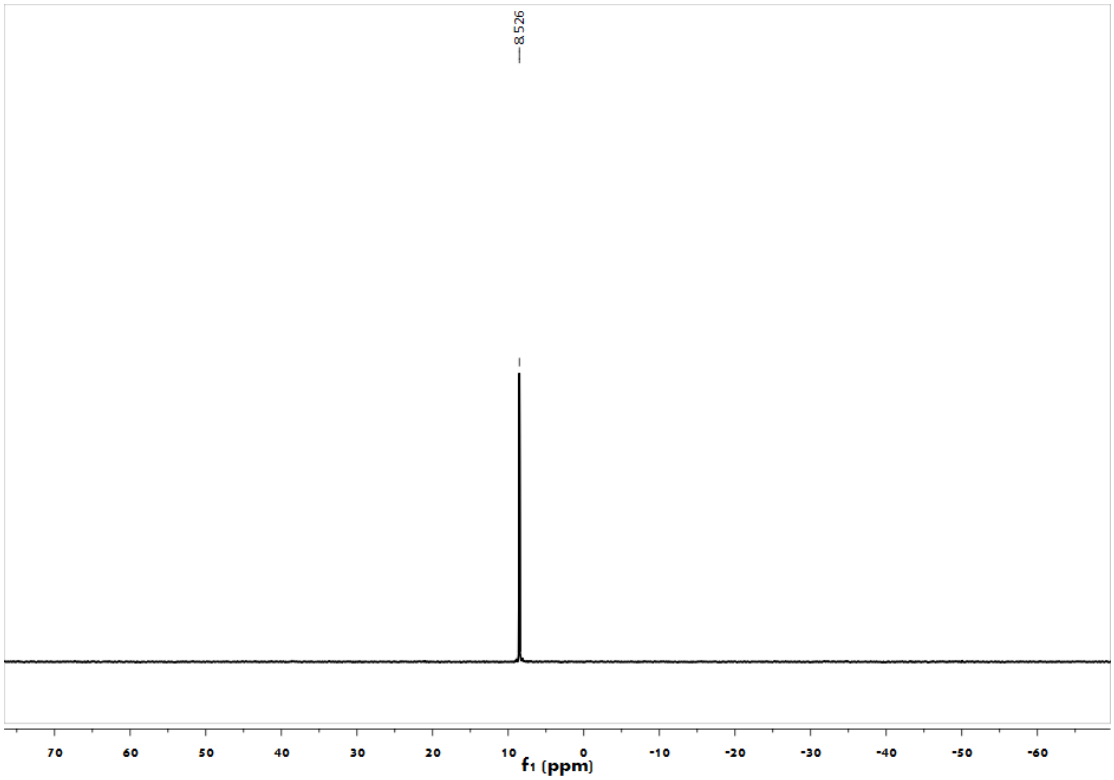
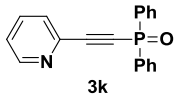
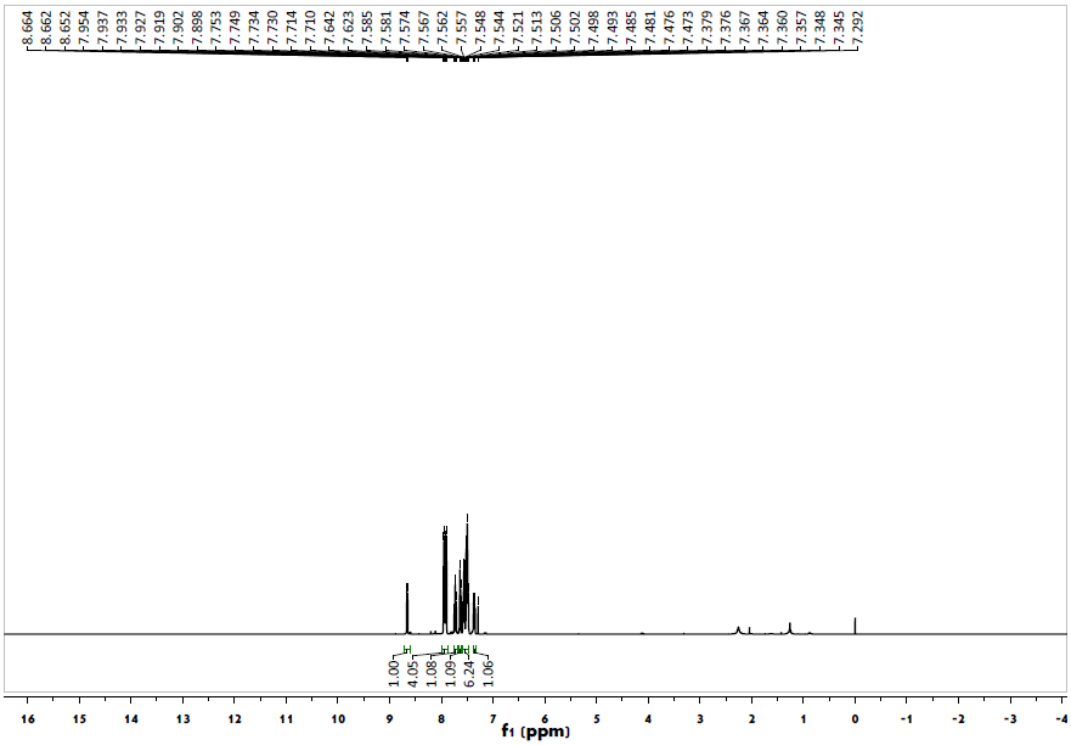
132.38
132.35
132.14
131.08
130.97
130.69
128.79
128.66
127.48
119.62
119.57
98.92
98.61
87.69
86.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.526
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)


Ph
P=O
Ph
N

3k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7.937
7.933
7.927
7.919
7.902
7.898
7.753
7.749
7.734
7.730
7.714
7.710
7.642
7.623
7.585
7.581
7.574
7.567
7.562
7.557
7.548
7.544
7.521
7.513
7.506
7.502
7.498
7.493
7.485
7.481
7.476
7.473
7.379
7.376
7.367
7.364
7.360
7.357
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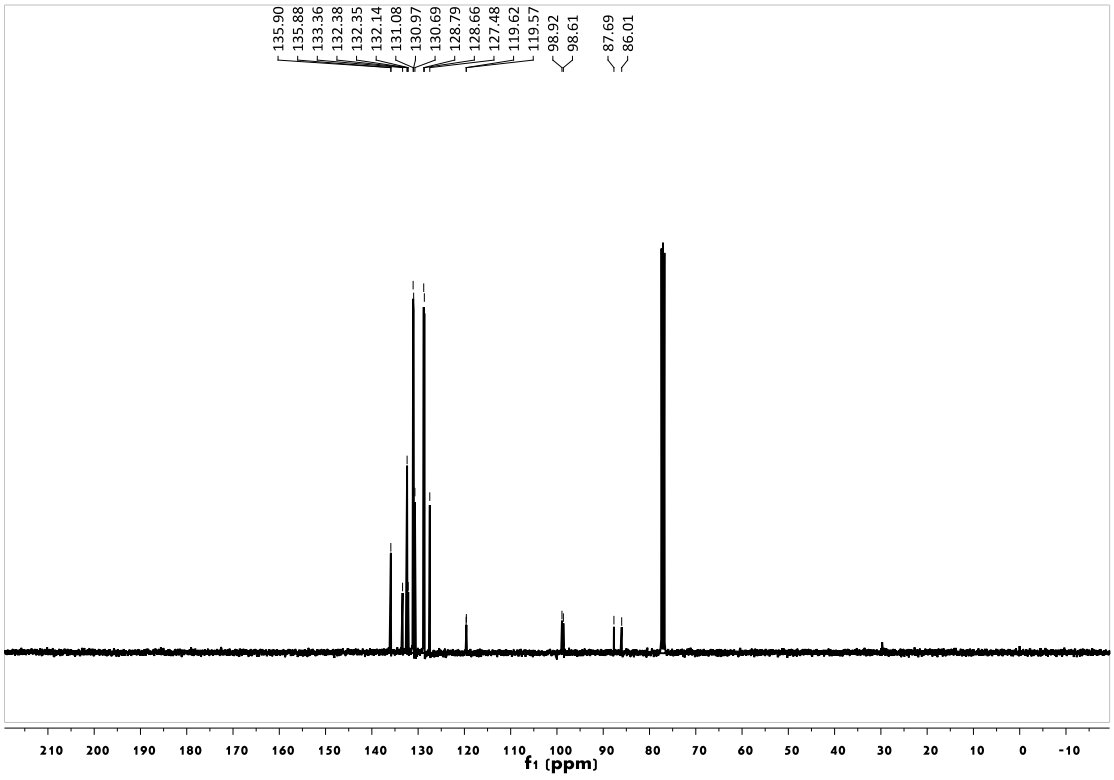
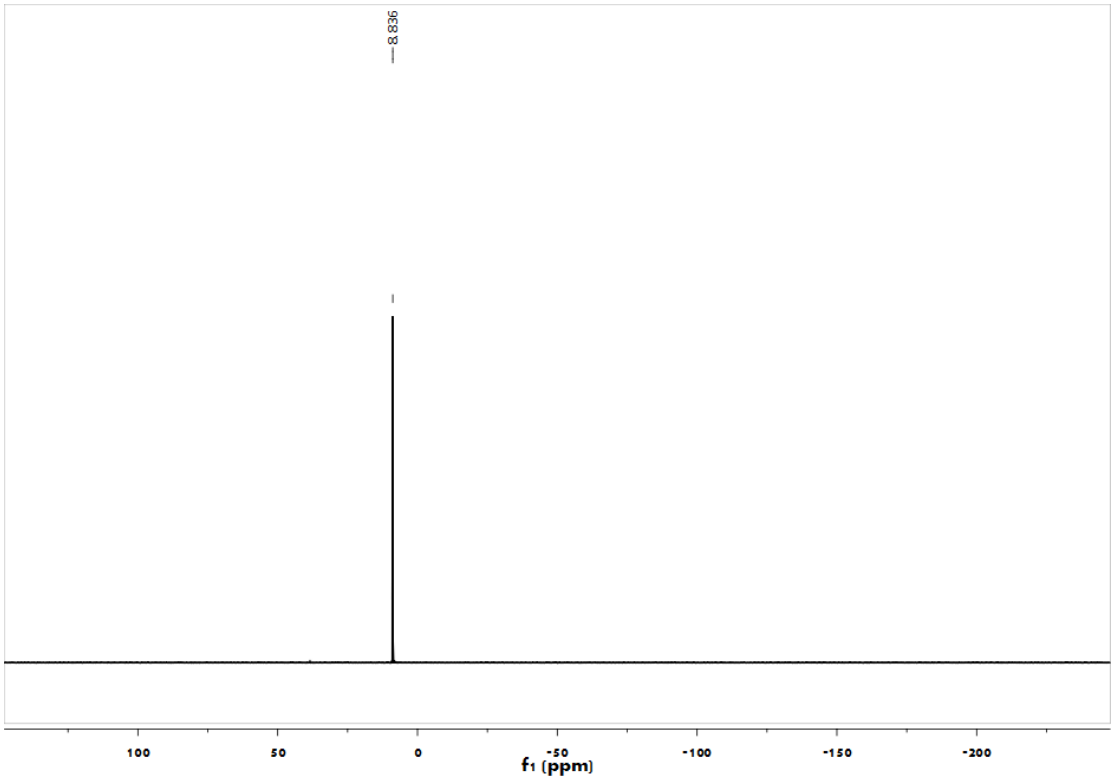
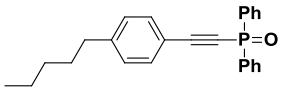
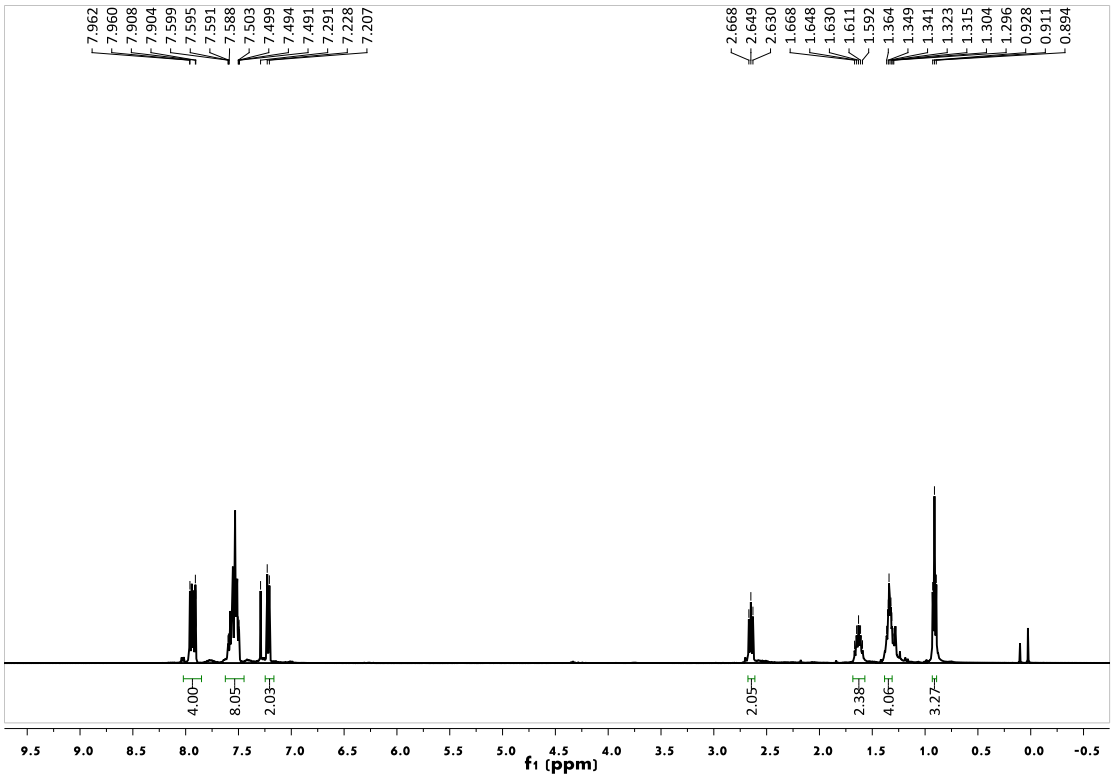
7.345
7.292
1.00
4.05
1.08
1.09
6.24
1.06
f1 (ppm)


135.90
135.88
133.36
132.38
132.35
132.14
131.08
130.97
130.69
128.79
128.66
127.48
119.62
119.57
98.92
98.61
87.69
86.01
f1 (ppm)


8.836
100
50
0
-50
-100
-150
-200
f1 (ppm)


Ph
P=O
Ph

3l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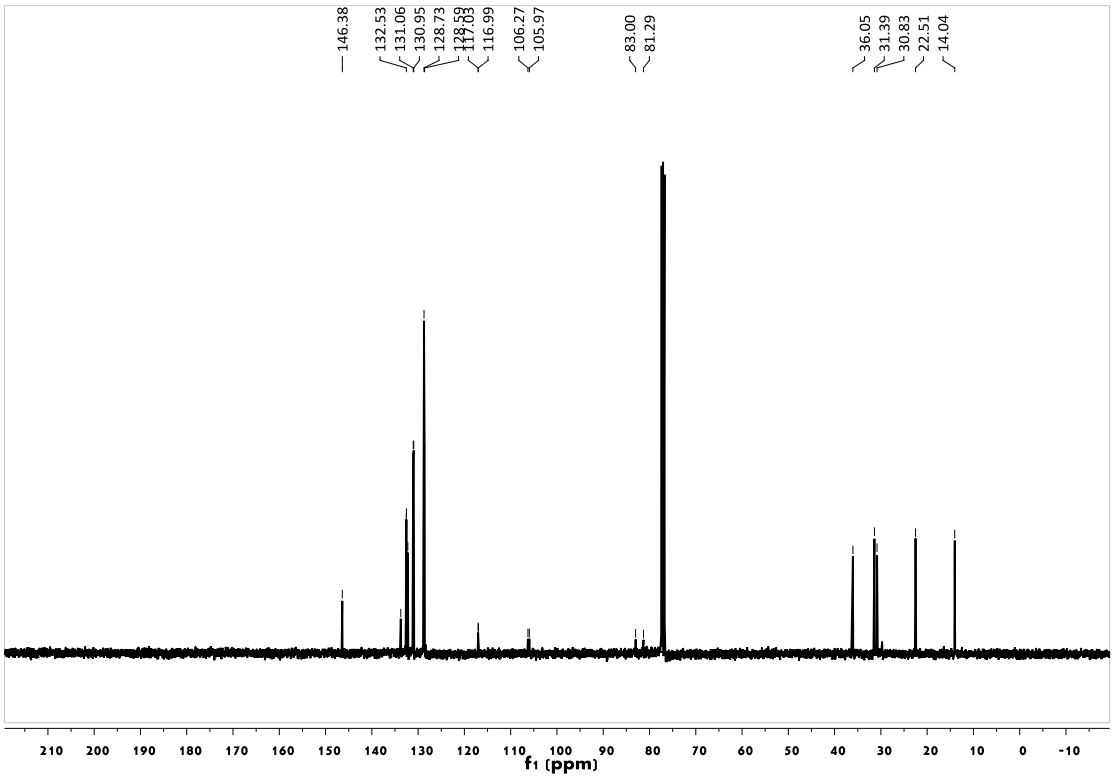
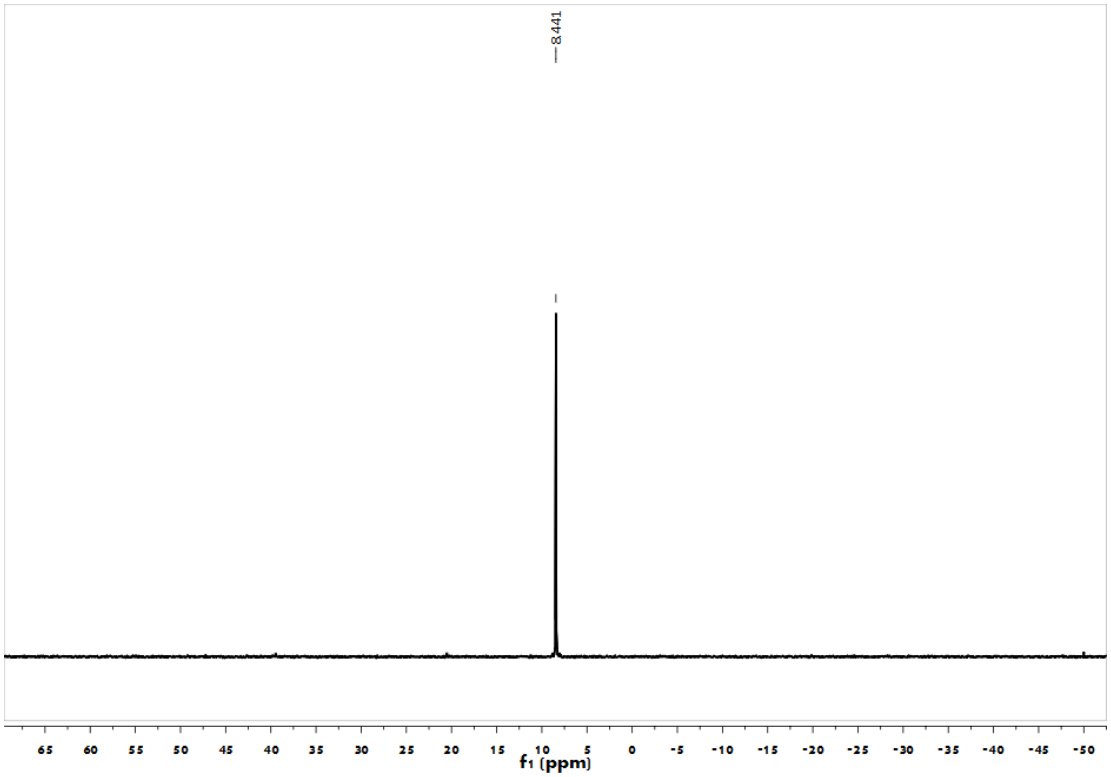
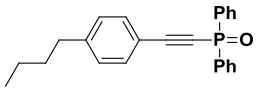
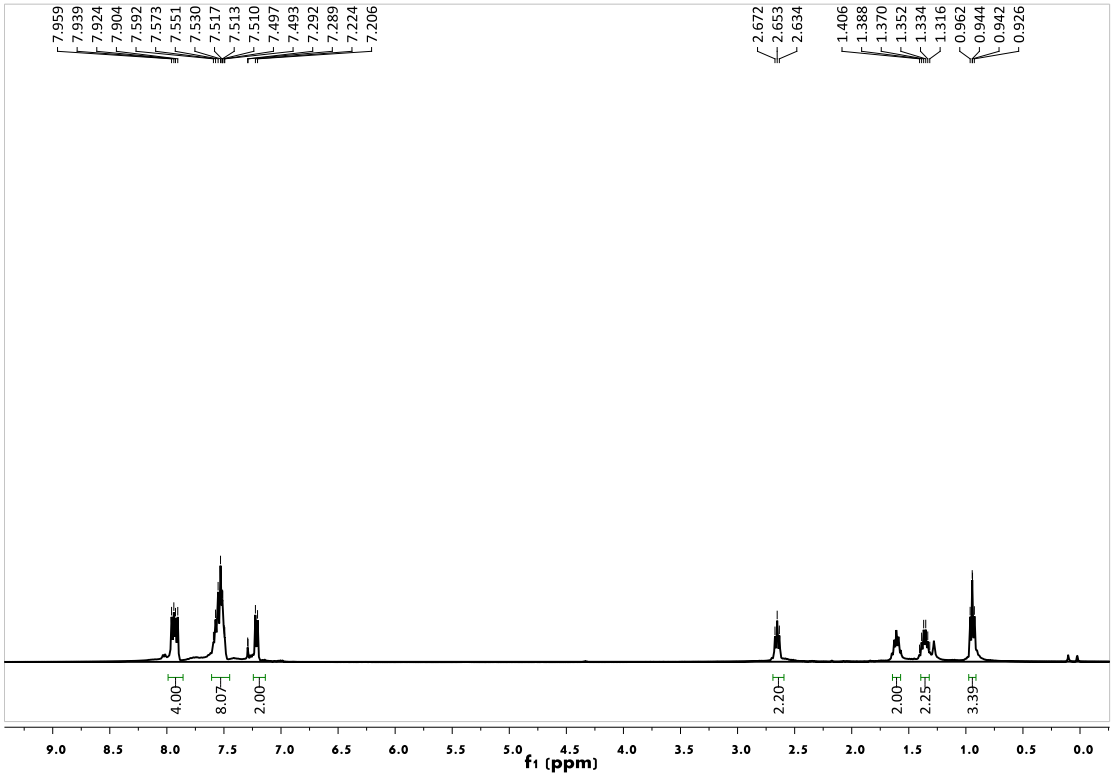
7.960
7.908
7.904
7.599
7.595
7.591
7.588
7.503
7.499
7.494
7.491
7.291
7.228
7.207
2.668
2.649
2.630
1.668
1.648
1.630
1.611
1.592
1.364
1.349
1.341
1.323
1.315
1.304
1.296
0.928
0.911
0.894
4.00
8.05
2.03
2.05
2.38
4.06
3.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

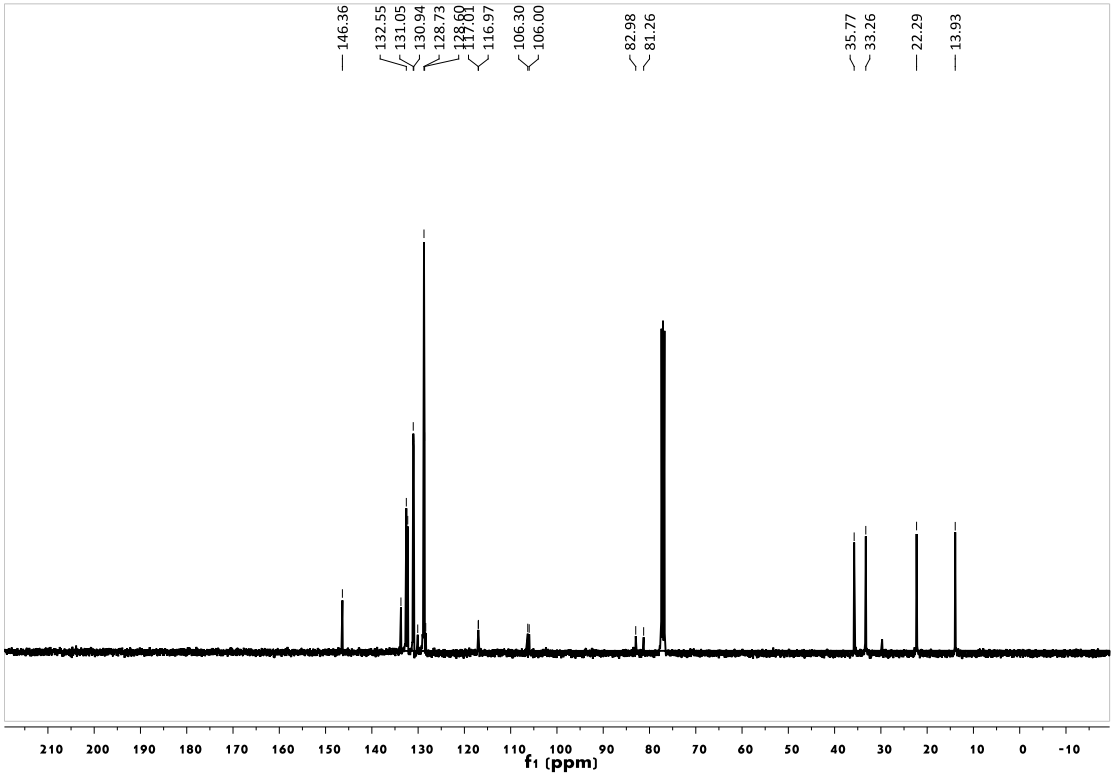

146.38
132.53
131.06
130.95
128.73
128.59
117.03
116.99
106.27
105.97
83.00
81.29
36.05
31.39
30.83
22.51
14.04
f1 (ppm)

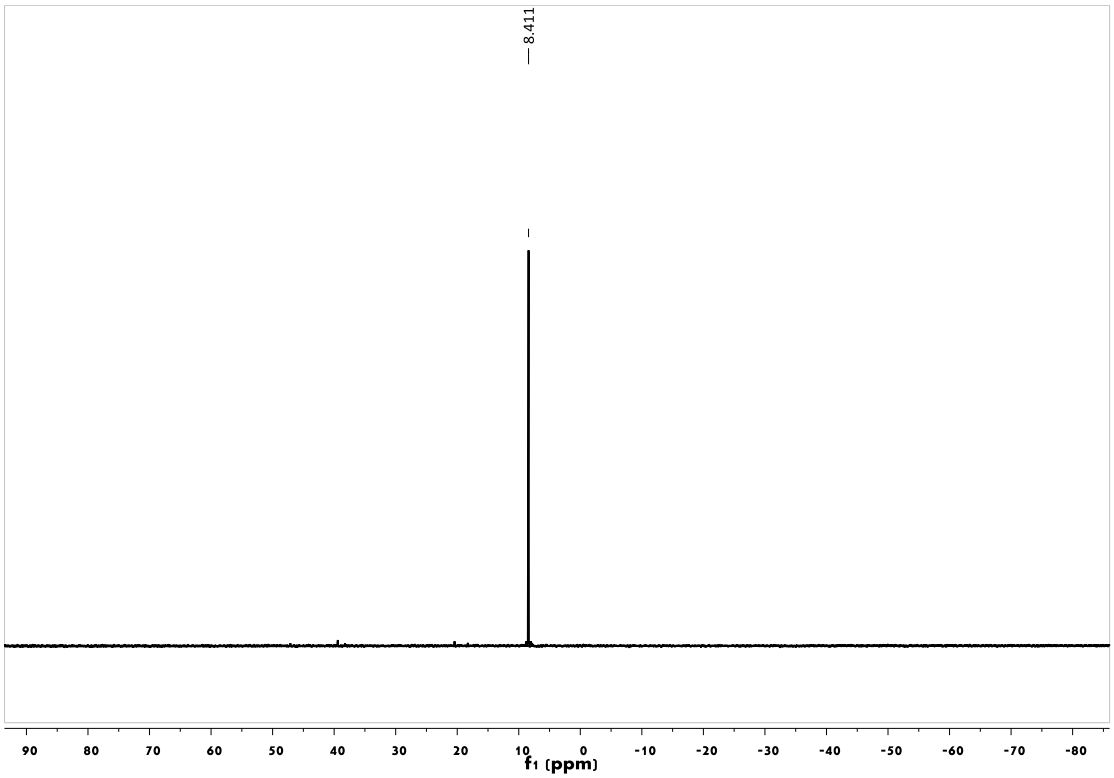

8.441
f1 (ppm)

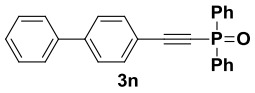

Ph
P=O
Ph

3m

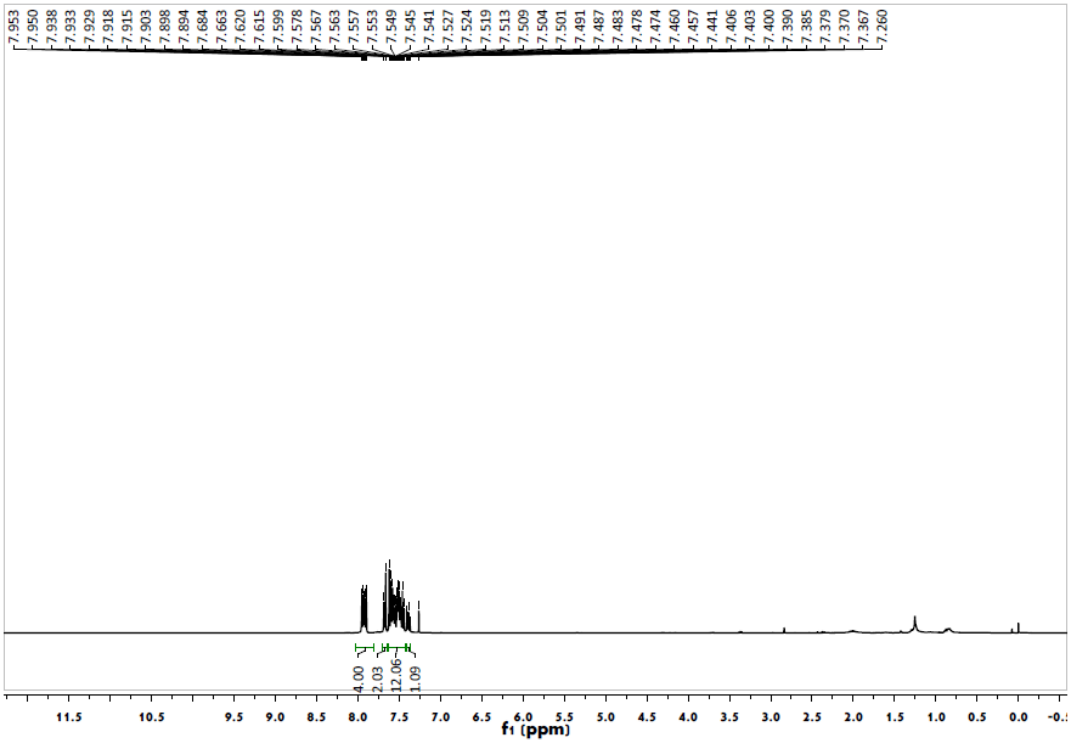

7.959
7.939
7.924
7.904
7.592
7.573
7.551
7.530
7.517
7.513
7.510
7.497
7.493
7.292
7.289
7.224
7.206
2.672
2.653
2.634
1.406
1.388
1.370
1.352
1.334
1.316
0.962
0.944
0.942
0.926
4.00
8.07
2.00
2.20
2.00
2.25
3.39
f1 (ppm)

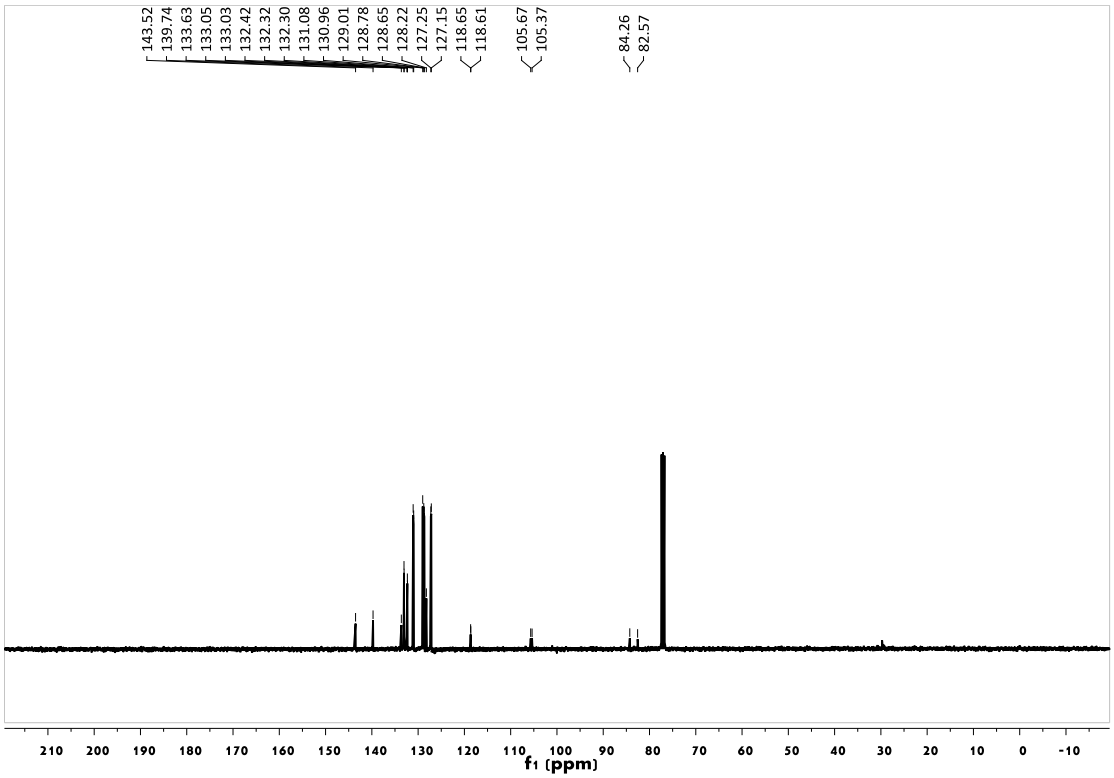

146.36
132.55
131.05
130.94
128.73
128.60
117.01
116.97
106.30
106.00
82.98
81.26
35.77
33.26
22.29
13.93
f1 (ppm)

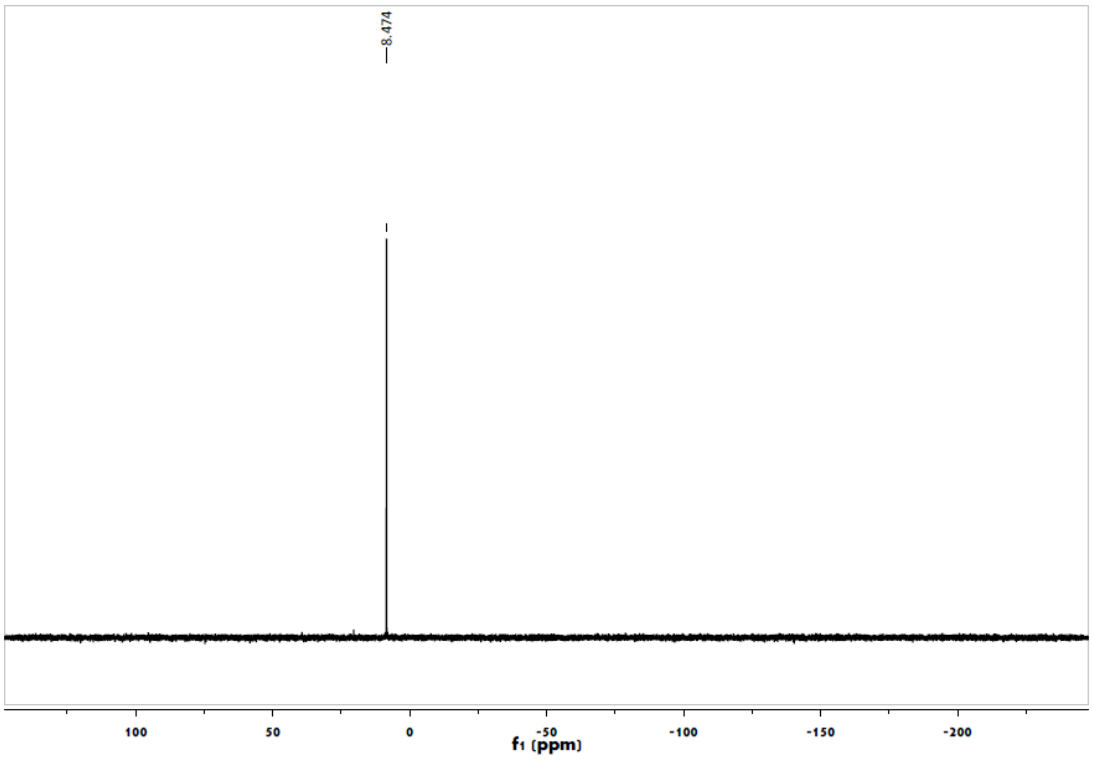

8.411
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

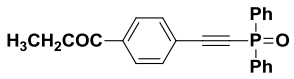

Ph
P=O
Ph

3n

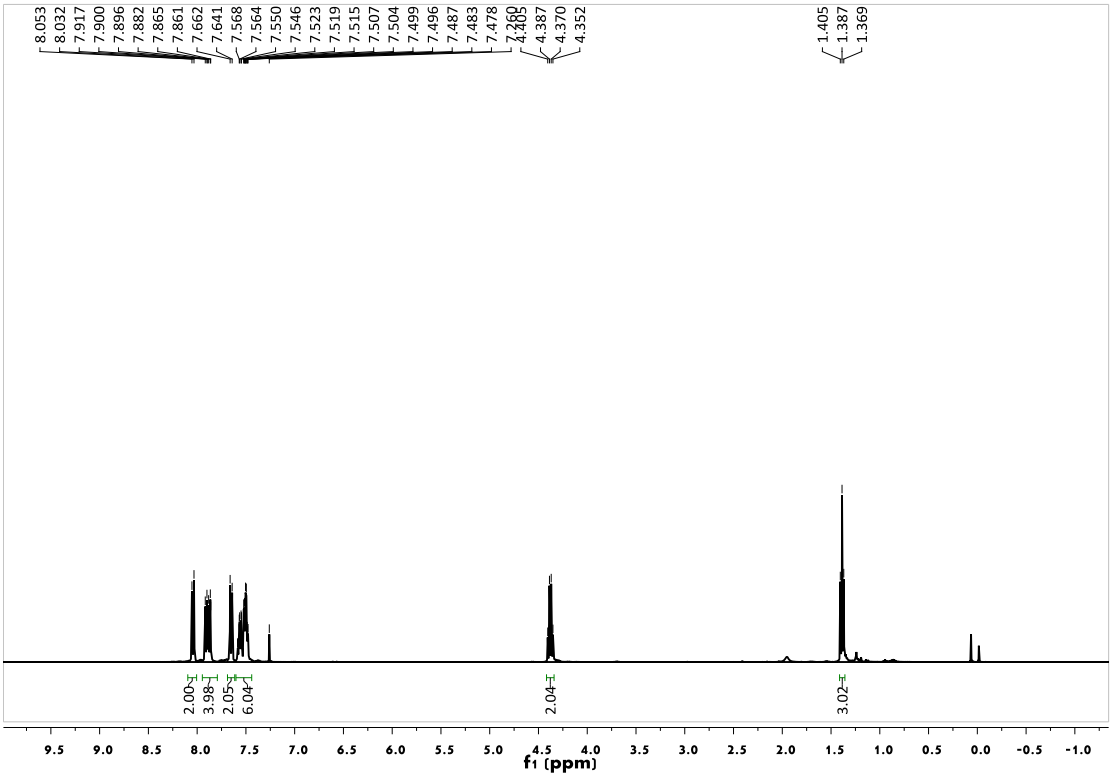

7.953 7.950 7.938 7.933 7.929 7.918 7.915 7.903 7.898 7.894 7.684 7.663 7.620 7.615 7.599 7.578 7.567 7.563 7.557 7.553 7.549 7.545 7.541 7.527 7.524 7.519 7.513 7.509 7.504 7.501 7.491 7.487 7.483 7.478 7.474 7.460 7.457 7.441 7.406 7.403 7.400 7.390 7.385 7.379 7.370 7.367 7.260
4.00 2.03 12.06 1.09
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

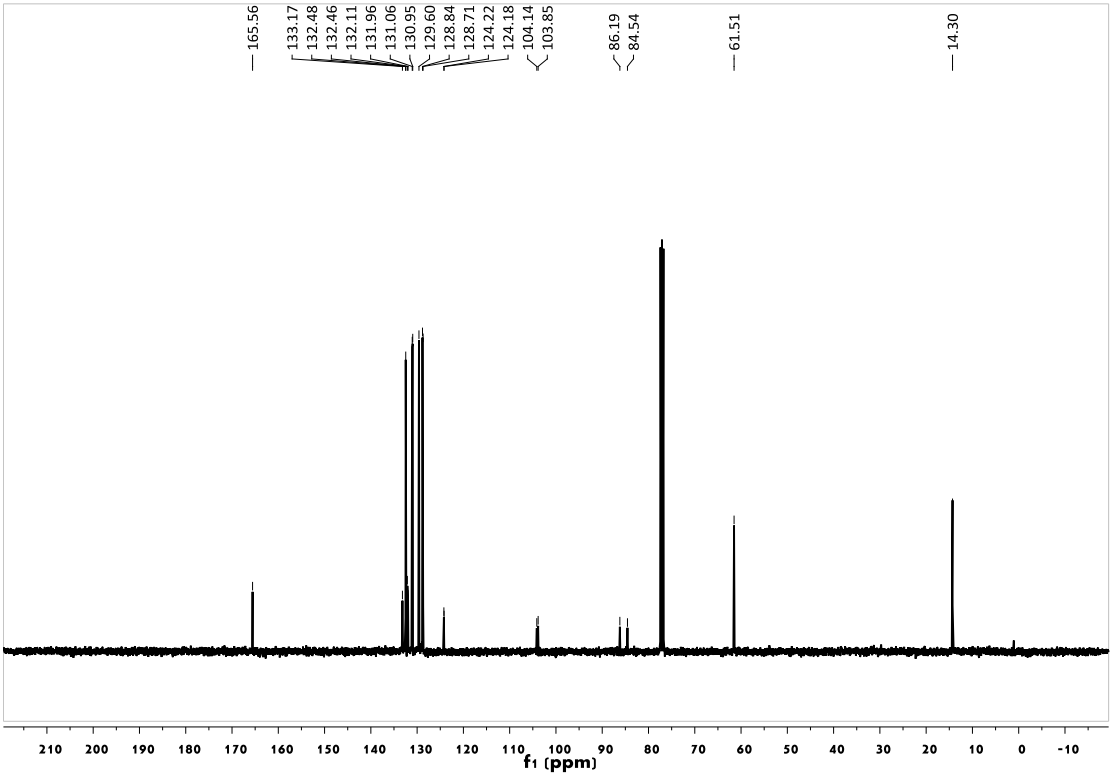

143.52
139.74
133.63
133.05
133.03
132.42
132.32
132.30
131.08
130.96
129.01
128.78
128.65
128.22
127.25
127.15
118.65
118.61
105.67
105.37
84.26
82.57
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

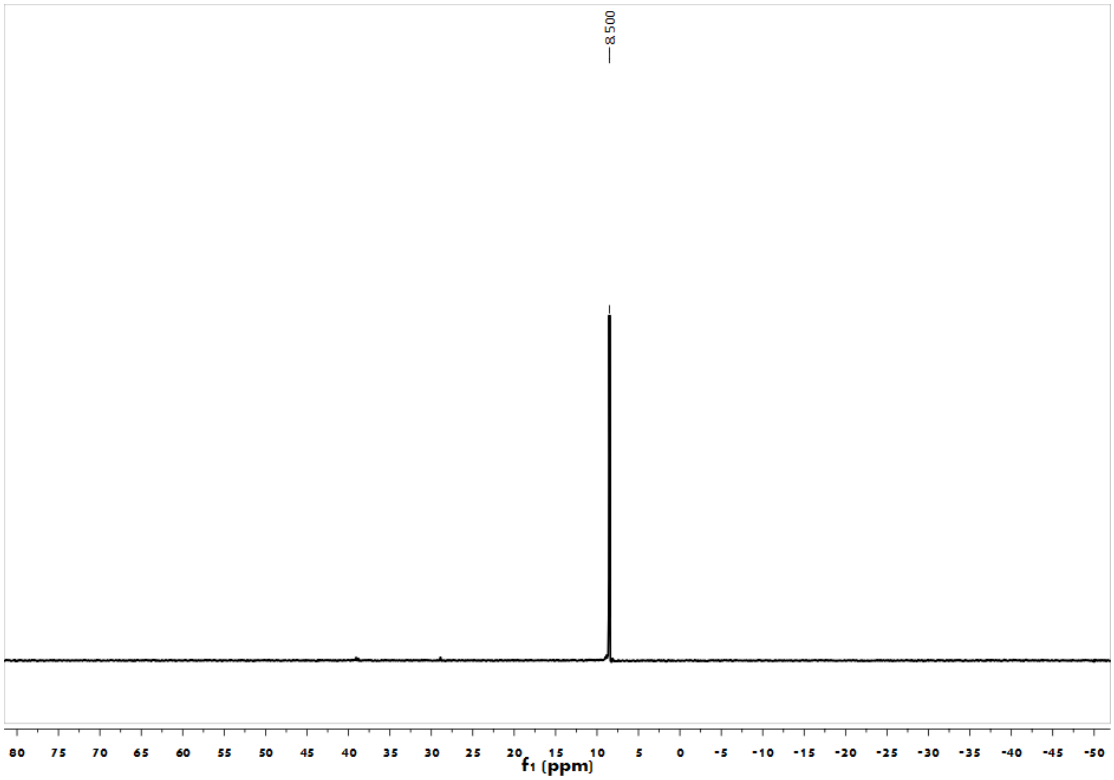

8.474
100 50 0 -50 -100 -150 -200
f1 (ppm)

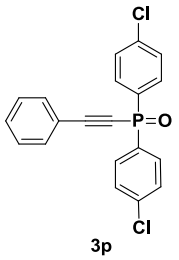

Ph
H3CH2COC
P=O
Ph

3o

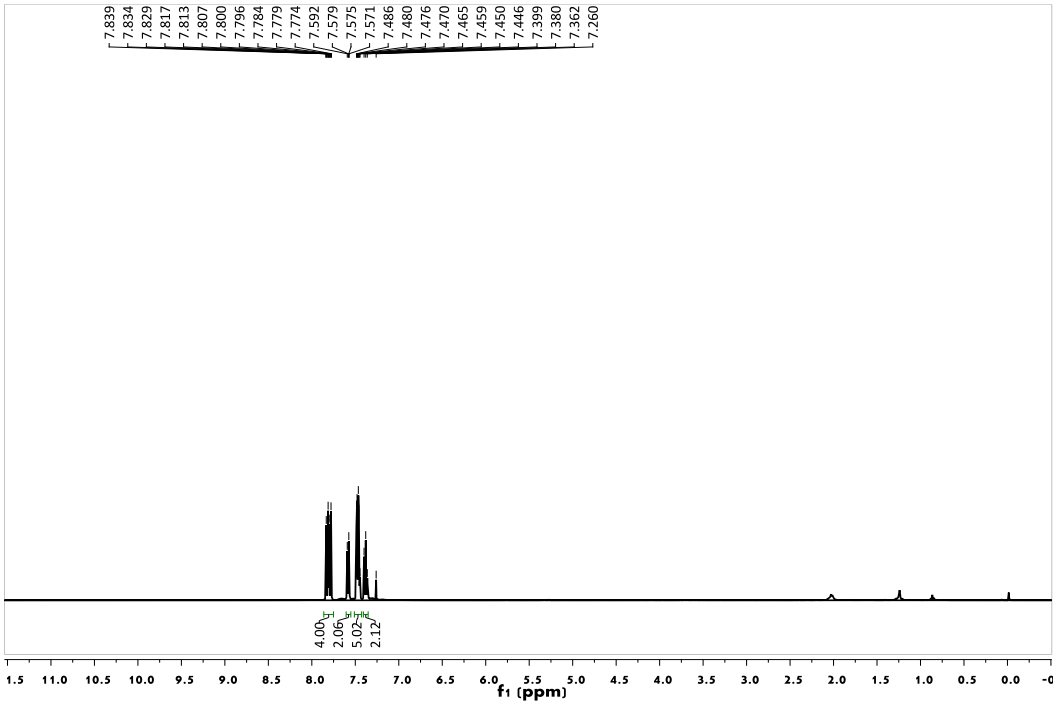

8.053
8.032
7.917
7.900
7.896
7.882
7.865
7.861
7.662
7.641
7.568
7.564
7.550
7.546
7.523
7.519
7.515
7.507
7.504
7.499
7.496
7.487
7.483
7.478
4.387
4.370
4.352
1.405
1.387
1.369
2.00
3.98
2.05
6.04
2.04
3.02
f1 (ppm)

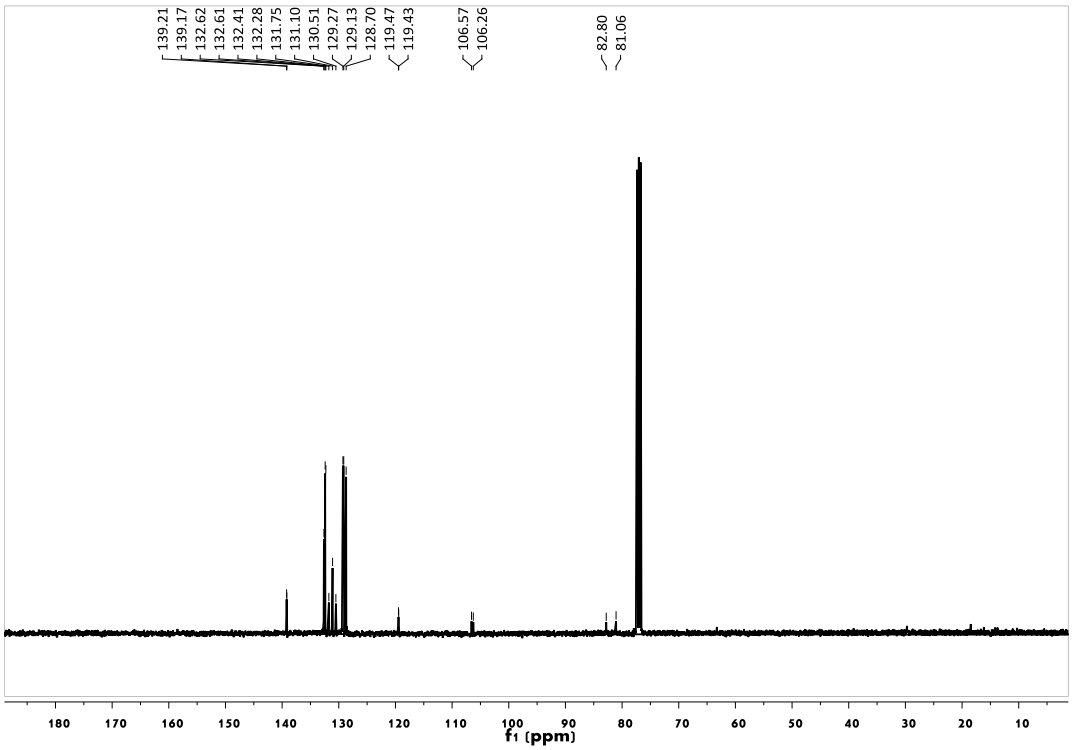

165.56
133.17
132.48
132.46
132.11
131.96
131.06
130.95
129.60
128.84
128.71
124.22
124.18
104.14
103.85
86.19
84.54
61.51
14.30
f1 (ppm)

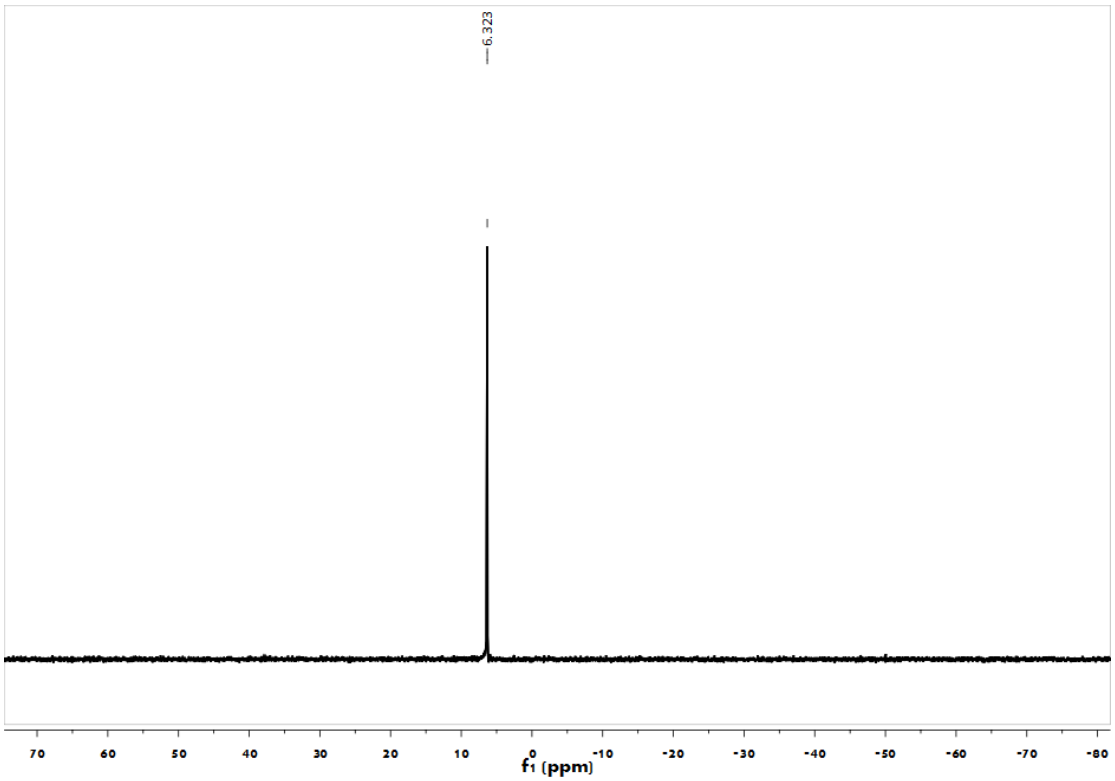

8.500
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

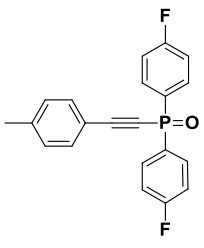

Cl
P=O
Cl

3p

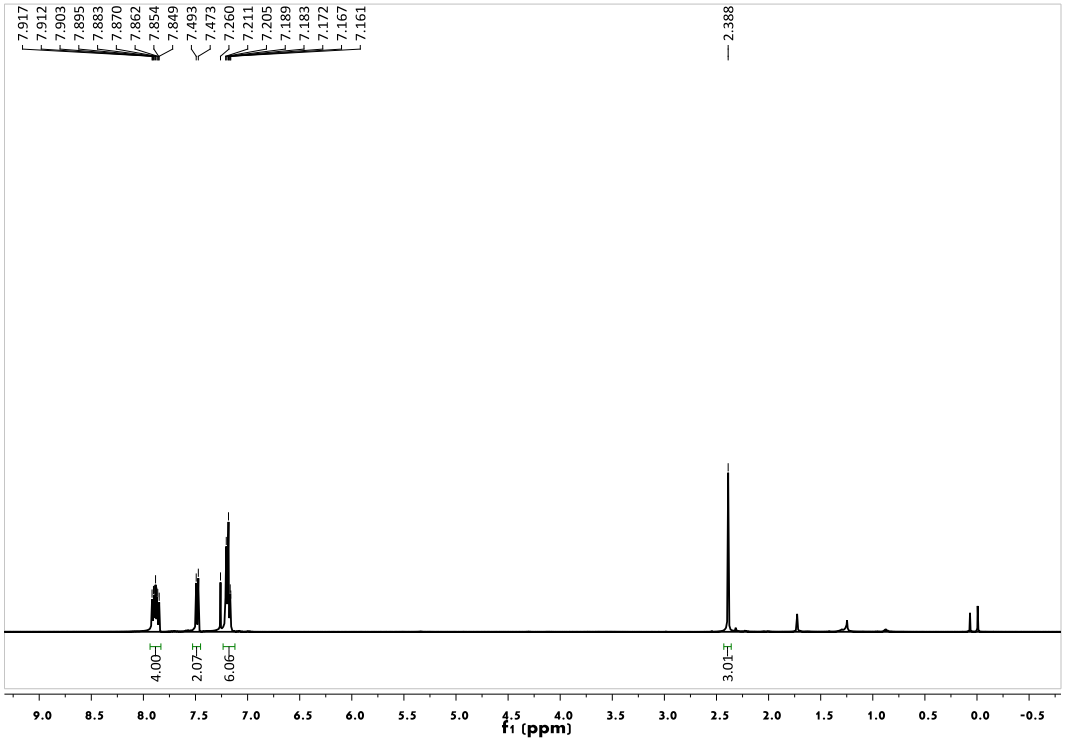

7.839
7.834
7.829
7.817
7.813
7.807
7.800
7.796
7.784
7.779
7.774
7.592
7.579
7.575
7.571
7.486
7.480
7.476
7.470
7.465
7.459
7.450
7.446
7.399
7.380
7.362
7.260
4.00
2.06
5.02
2.12
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


139.21
139.17
132.62
132.61
132.41
132.28
131.75
131.10
130.51
129.27
129.13
128.70
119.47
119.43
106.57
106.26
82.80
81.06
f1 (ppm)


6.323
f1 (ppm)


F
P=O
F

**3q**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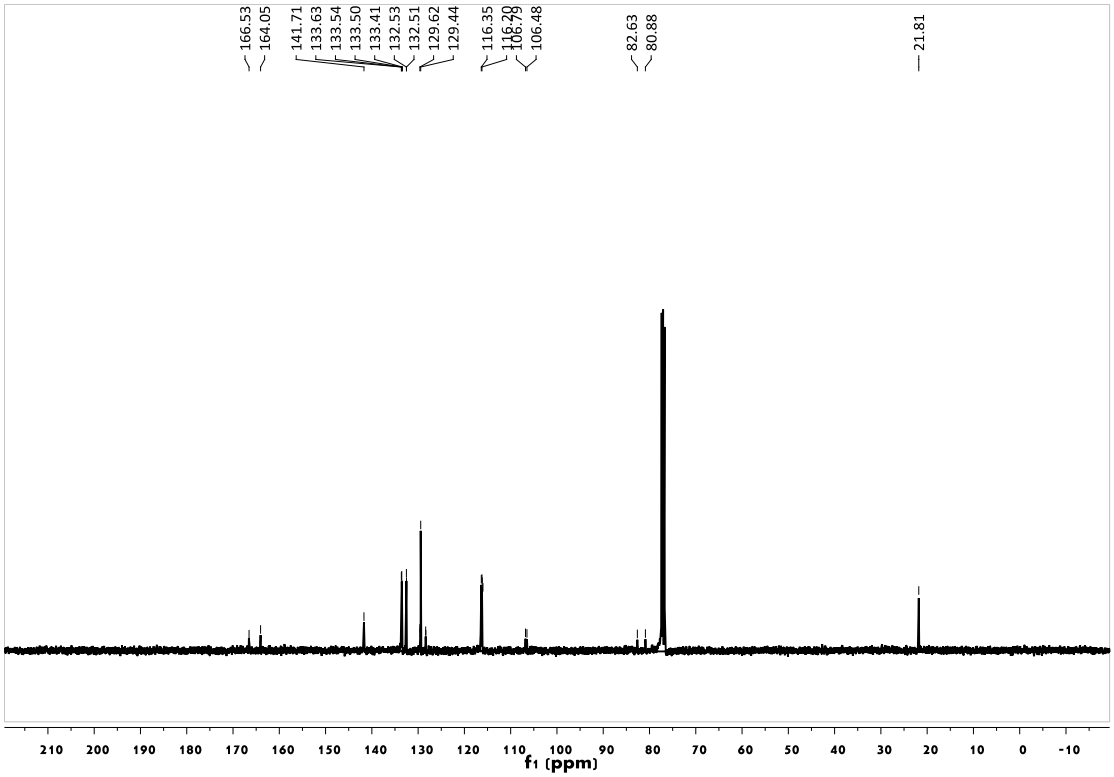
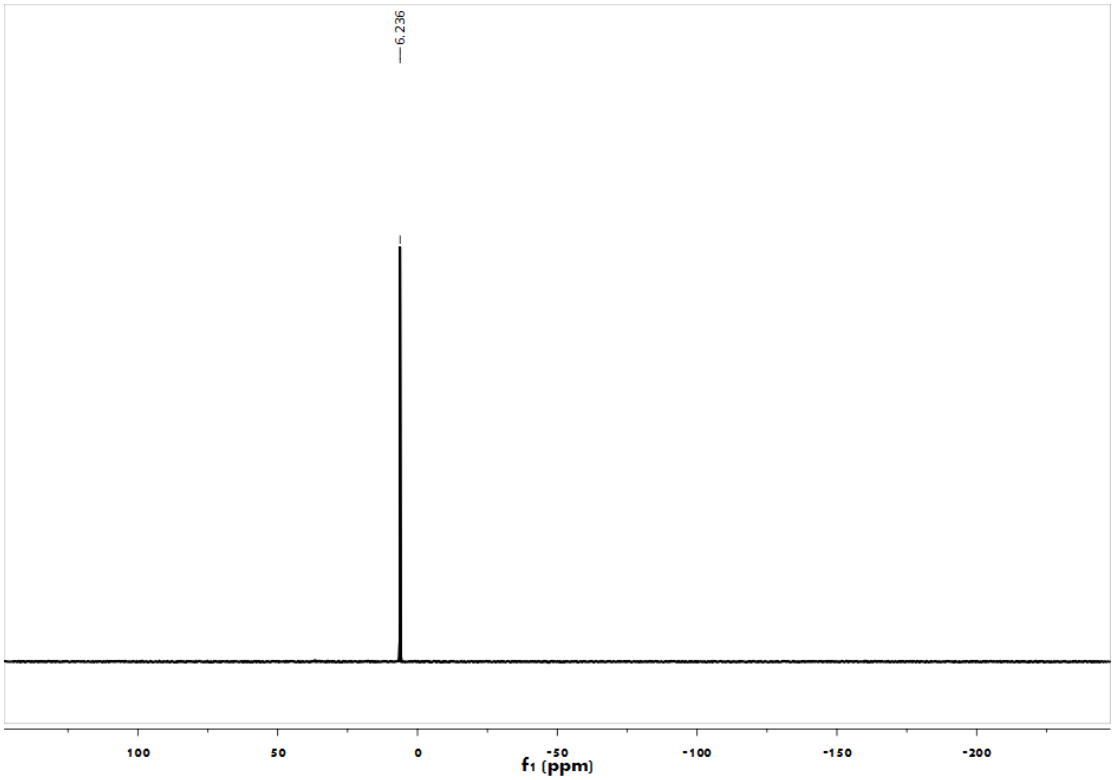
7.912
7.903
7.895
7.883
7.870
7.862
7.854
7.849
7.493
7.473
7.260
7.211
7.205
7.189
7.183
7.172
7.167
7.161
2.388
4.00
2.07
6.06
3.01
f1 (ppm)


166.53
164.05
141.71
133.63
133.54
133.50
133.41
132.53
132.51
129.62
129.44
116.35
116.20
106.78
106.48
82.63
80.88
21.81
f1 (ppm)


6.236
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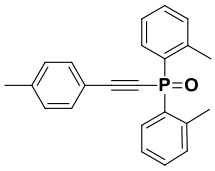
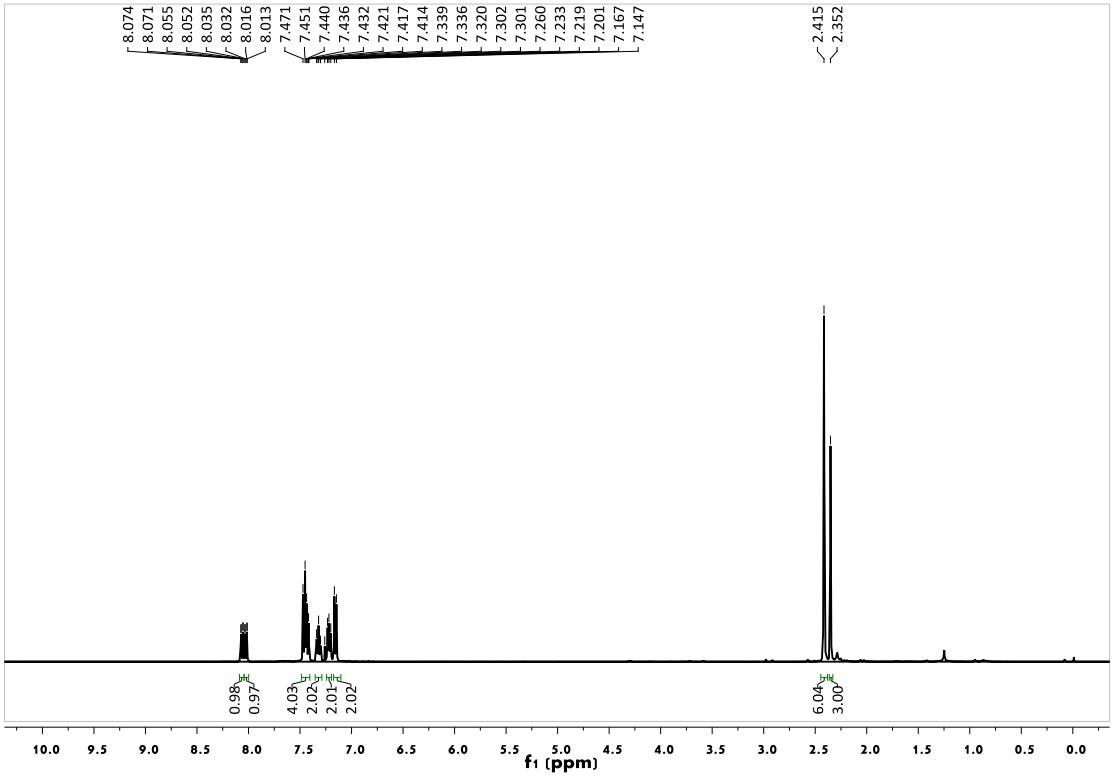
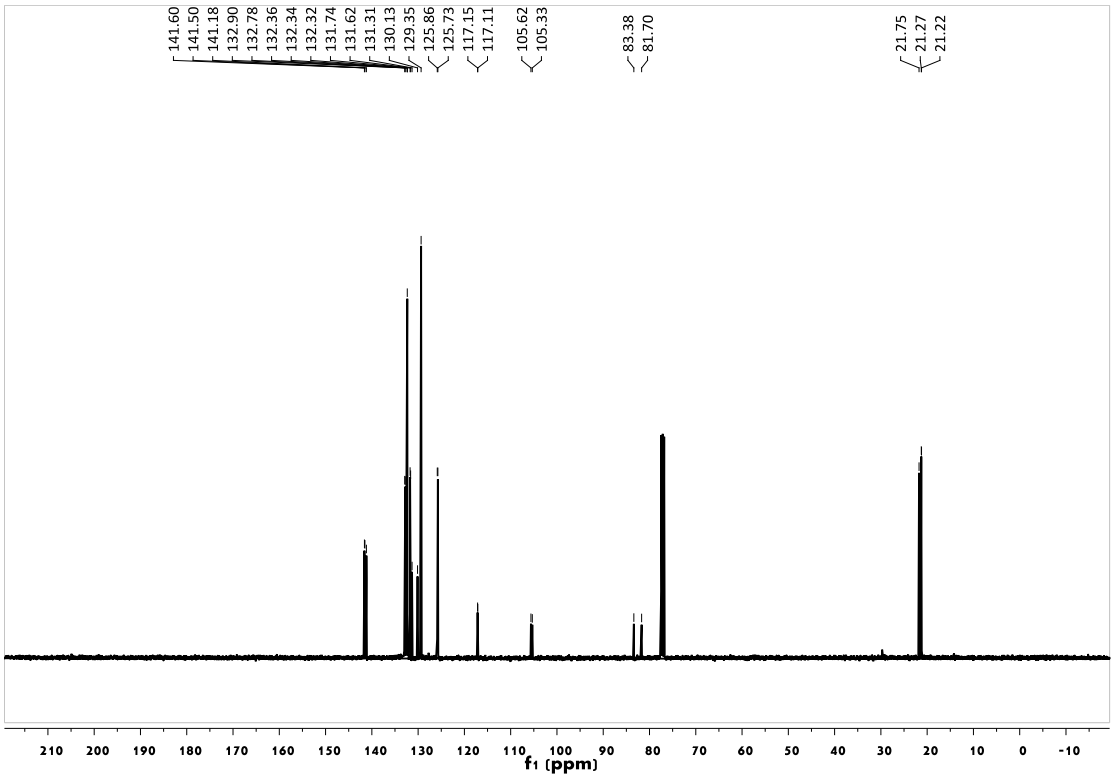
50
0
-50
-100
-150
-200
f1 (ppm)


P=O

3r


8.074
8.071
8.055
8.052
8.035
8.032
8.016
8.013
7.471
7.451
7.440
7.436
7.432
7.421
7.417
7.414
7.339
7.336
7.320
7.302
7.301
7.260
7.233
7.219
7.201
7.167
7.147
2.415
2.352
0.98
0.97
4.03
2.02
2.01
2.02
6.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.60
141.50
141.18
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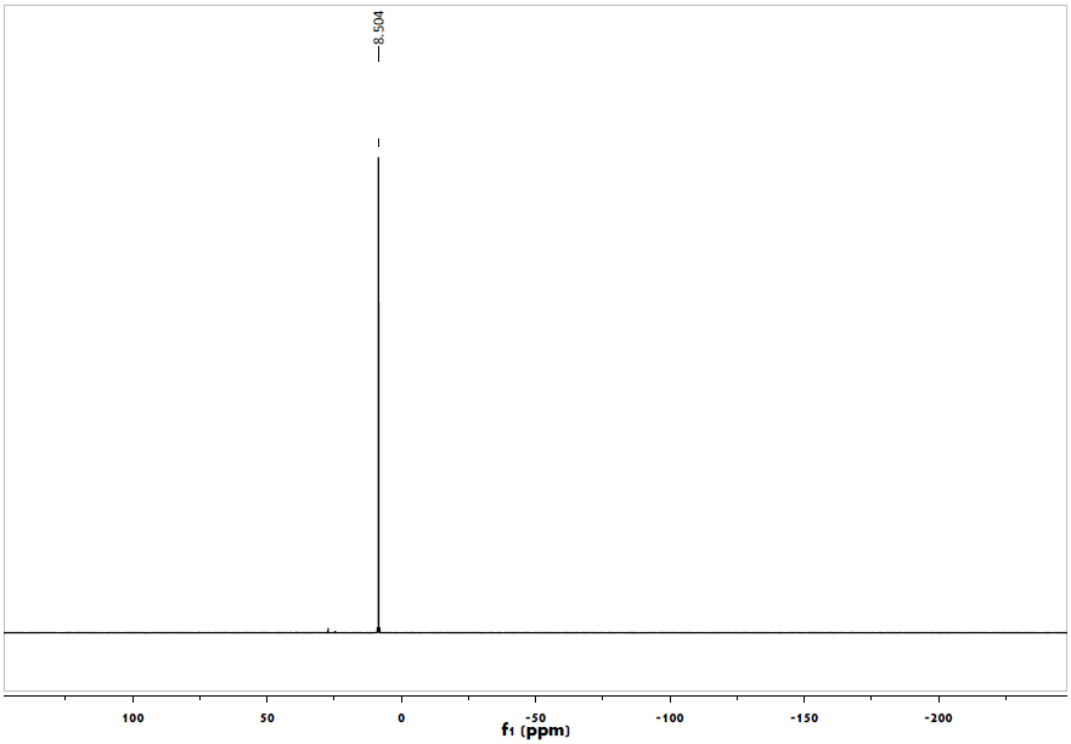
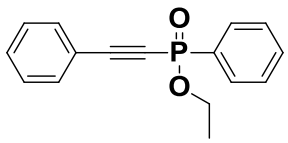
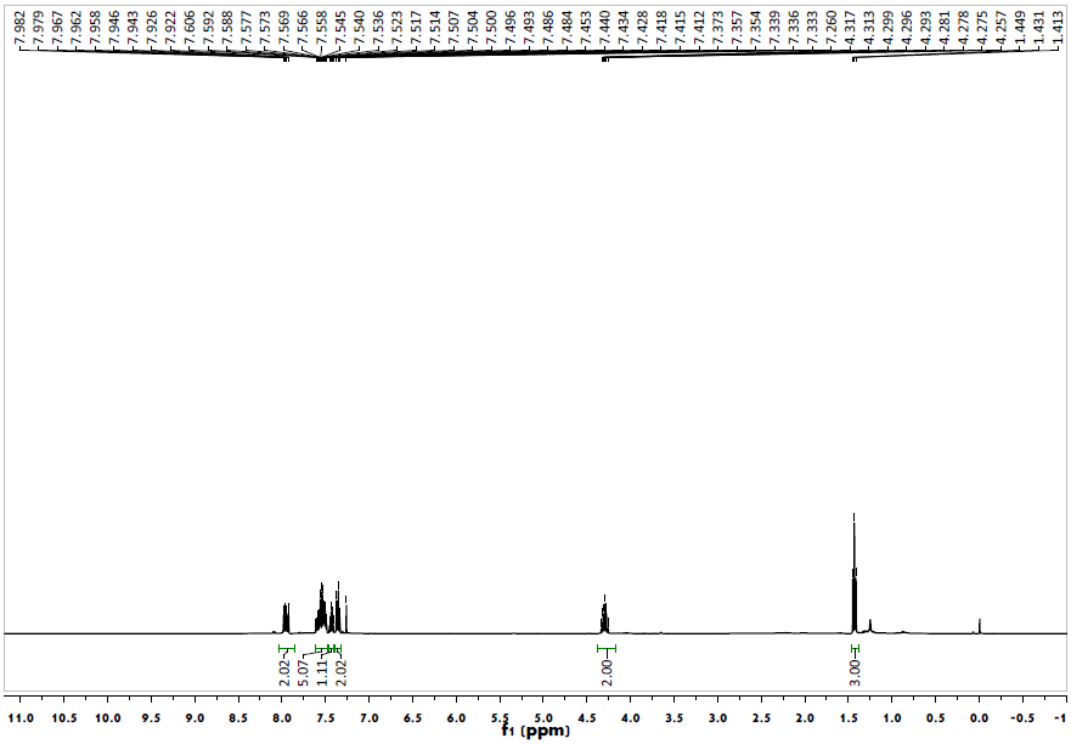
132.78
132.36
132.34
132.32
131.74
131.62
131.31
130.13
129.35
125.86
125.73
117.15
117.11
105.62
105.33
83.38
81.70
21.75
21.27
21.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.504
100 50 0 -50 -100 -150 -200
f1 (ppm)



3s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7.962
7.958
7.946
7.943
7.926
7.922
7.606
7.592
7.588
7.577
7.573
7.569
7.566
7.558
7.545
7.540
7.536
7.523
7.517
7.514
7.507
7.504
7.500
7.496
7.493
7.486
7.484
7.453
7.440
7.434
7.428
7.418
7.415
7.412
7.373
7.357
7.354
7.339
7.336
7.333
7.260
4.317
4.313
4.299
4.296
4.293
4.281
4.278
4.275
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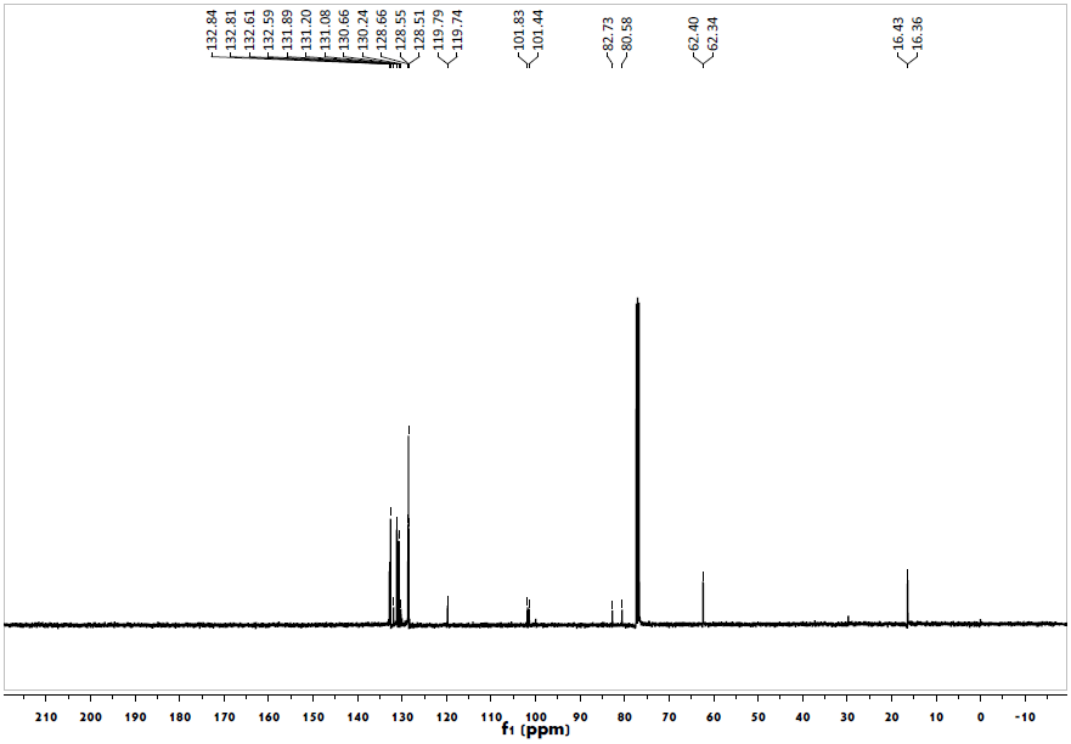
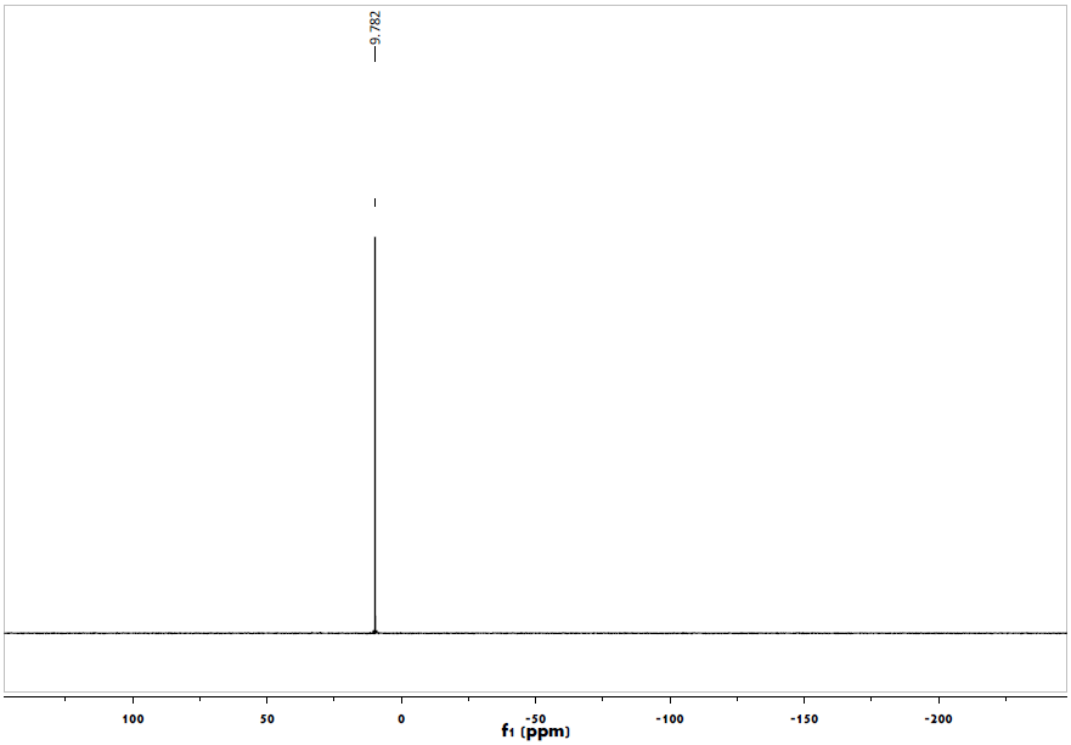
1.431
1.413
2.02
5.07
1.11
2.02
2.00
3.00
f1 (ppm)


132.84
132.81
132.61
132.59
131.89
131.20
131.08
130.66
130.24
128.66
128.55
128.51
119.79
119.74
101.83
101.44
82.73
80.58
62.40
62.34
16.43
16.36
f1 (ppm)


9.782
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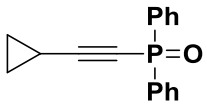
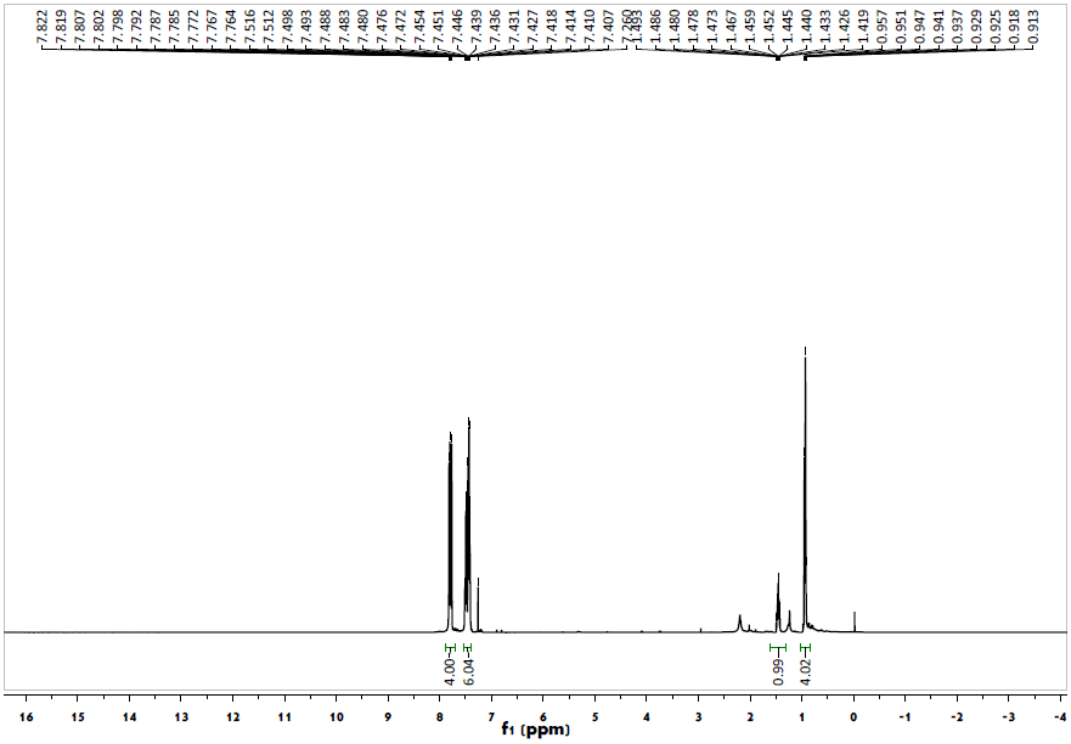
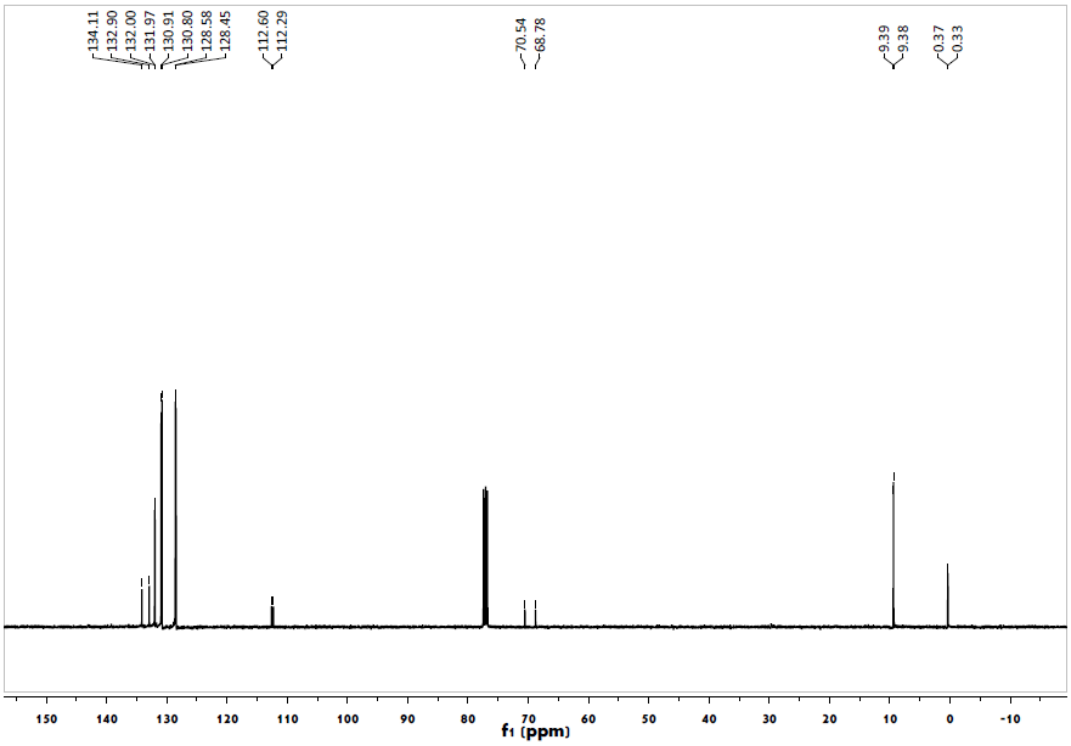
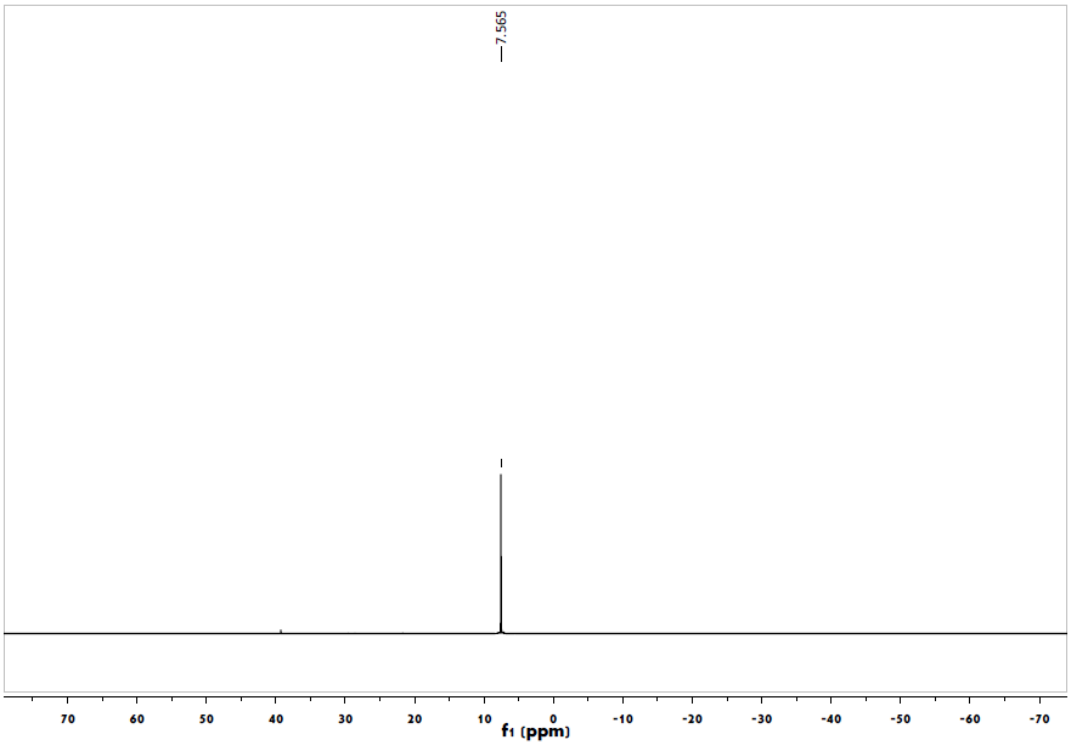
50
0
-50
-100
-150
-200
f1 (ppm)

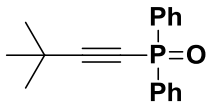

Ph
P=O
Ph

3t

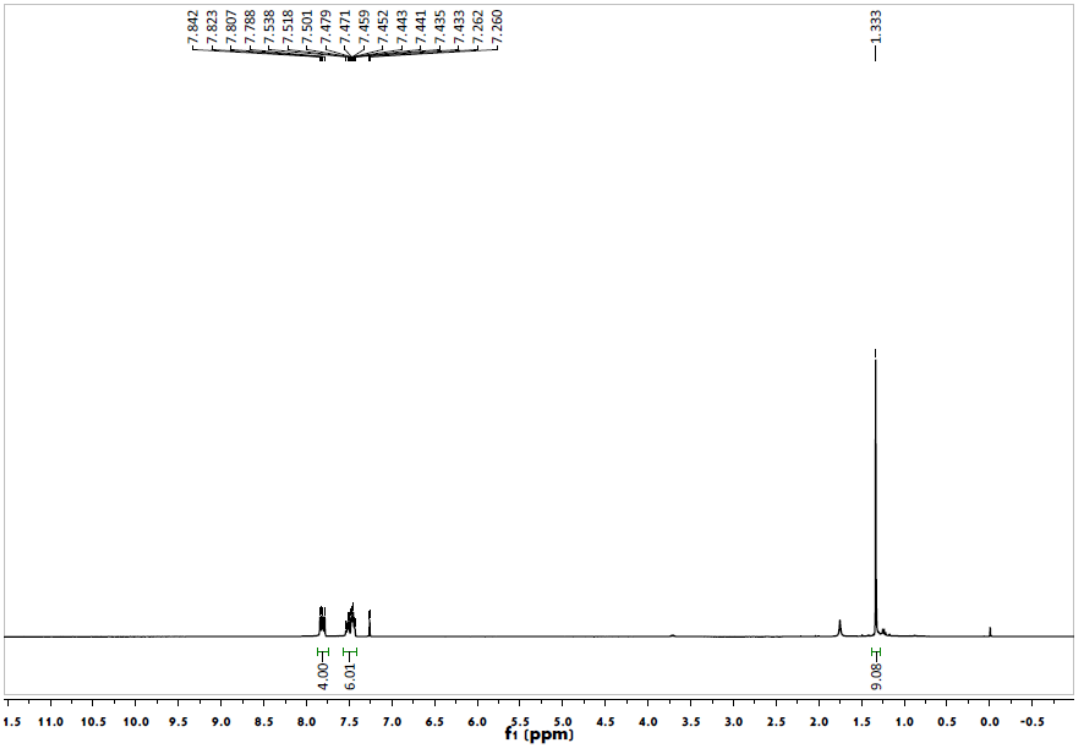

7.822
7.819
7.807
7.802
7.798
7.792
7.787
7.785
7.772
7.767
7.764
7.516
7.512
7.498
7.493
7.488
7.483
7.480
7.476
7.472
7.454
7.451
7.446
7.439
7.436
7.431
7.427
7.418
7.414
7.410
7.407
1.486
1.480
1.478
1.473
1.467
1.459
1.452
1.445
1.440
1.433
1.426
1.419
0.957
0.951
0.947
0.941
0.937
0.929
0.925
0.918
0.913
4.00
6.04
0.99
4.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

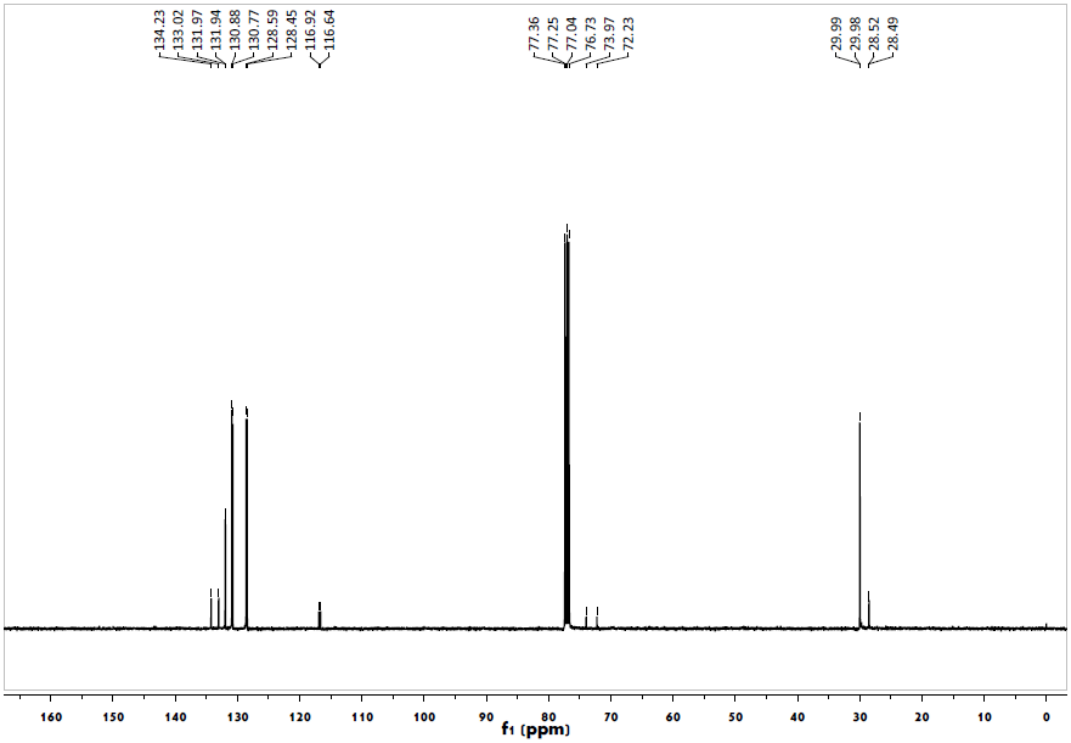

134.11
132.90
132.00
131.97
130.91
130.80
128.58
128.45
112.60
112.29
70.54
68.78
9.39
9.38
0.37
0.33
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

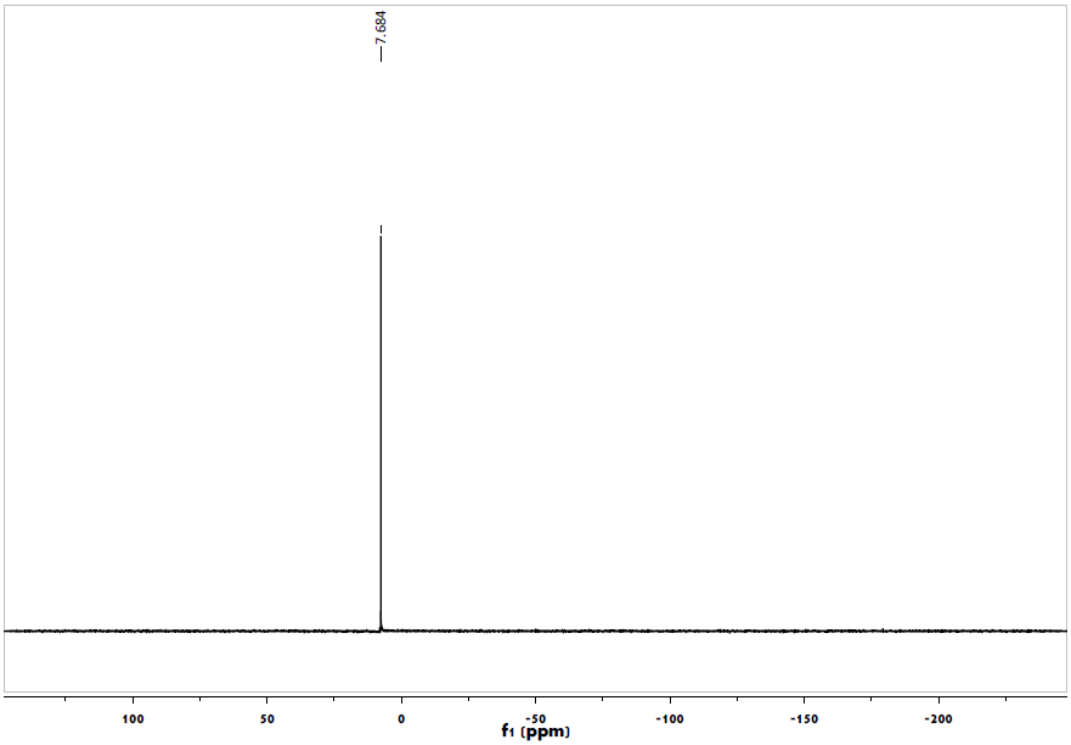

7.565
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

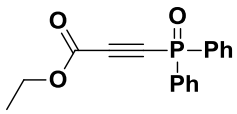

Ph
P=O
Ph

**3u**

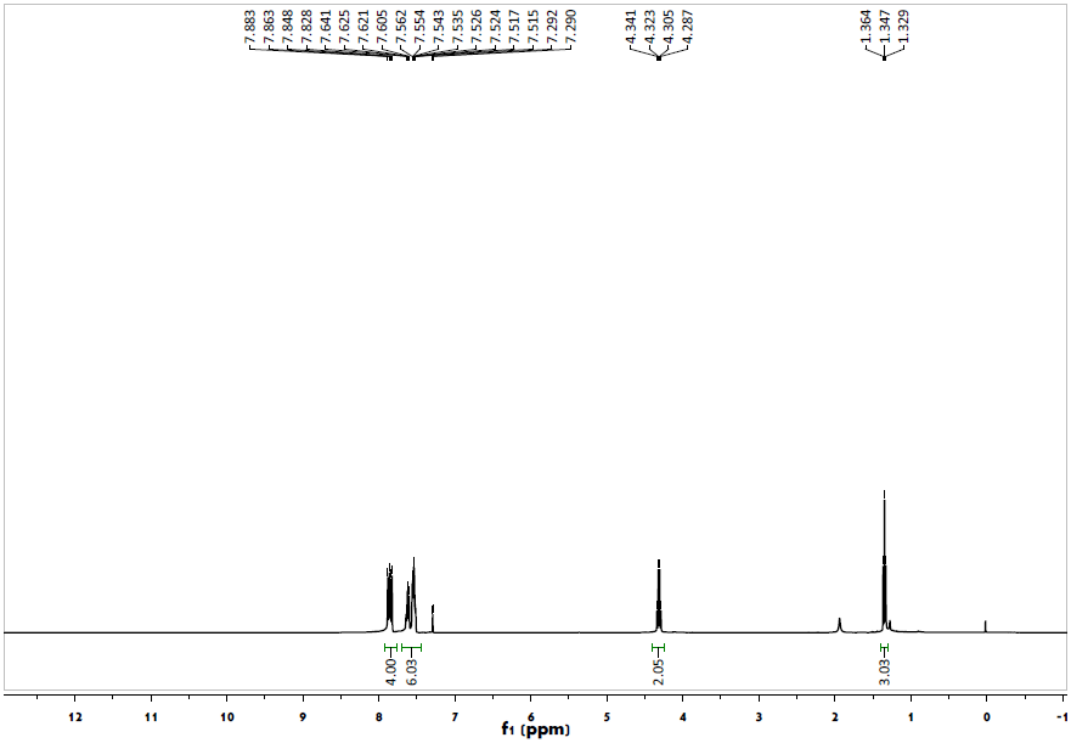

7.842
7.823
7.807
7.788
7.538
7.518
7.501
7.479
7.471
7.459
7.452
7.443
7.441
7.435
7.433
7.262
7.260
1.333
4.00
6.01
9.08
f1 (ppm)

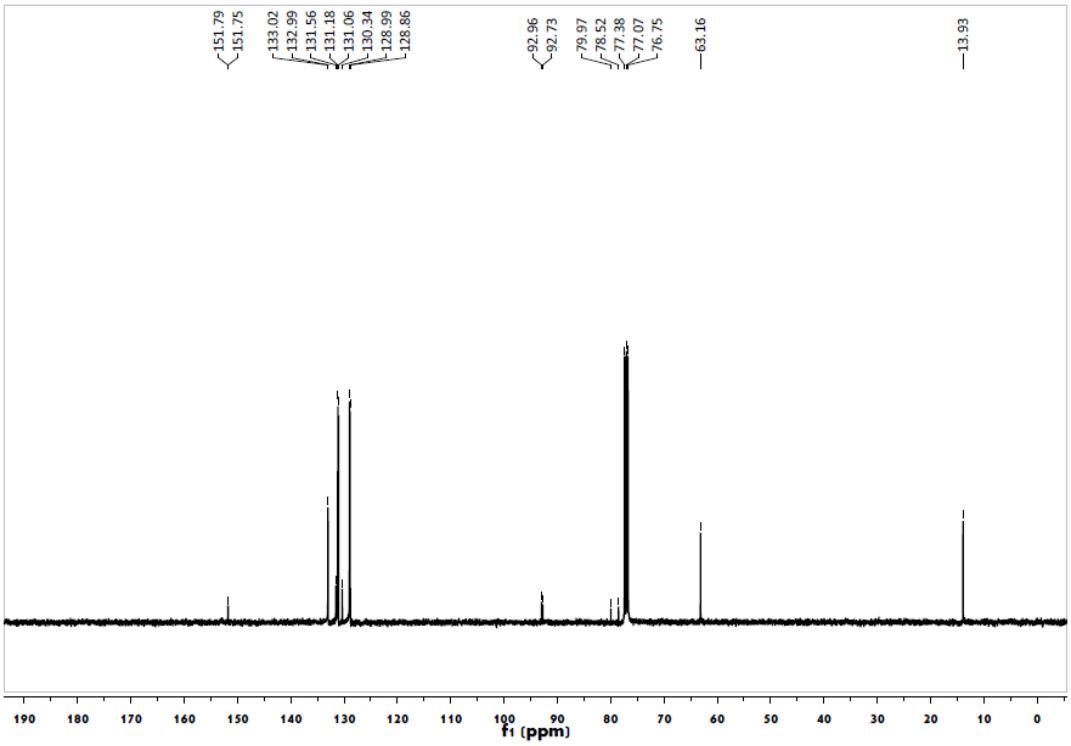

134.23
133.02
131.97
131.94
130.88
130.77
128.59
128.45
116.92
116.64
77.36
77.25
77.04
76.73
73.97
72.23
29.99
29.98
28.52
28.49
f1 (ppm)

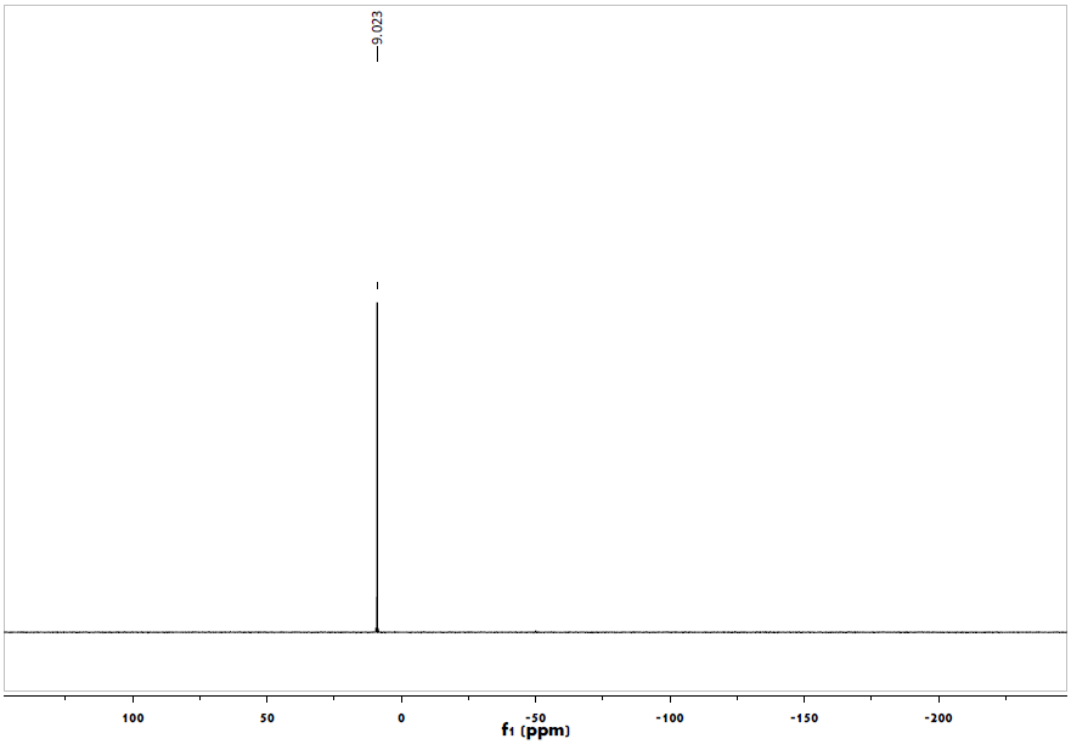

7.684
100
50
0
-50
-100
-150
-200
f1 (ppm)


O
O
P
Ph
O
Ph

**3v**


7.883
7.863
7.848
7.828
7.641
7.625
7.621
7.605
7.562
7.554
7.543
7.535
7.526
7.524
7.517
7.515
7.292
7.290
4.341
4.323
4.305
4.287
1.364
1.347
1.329
4.00
6.03
2.05
3.03
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


151.79
151.75
133.02
132.99
131.56
131.18
131.06
130.34
128.99
128.86
92.96
92.73
79.97
78.52
77.38
77.07
76.75
63.16
13.93
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.023
100 50 0 -50 -100 -150 -200
f1 (ppm)