Supplementary Information

Oxidant-free oxidation of C−H bond by cathodic hydrogen evolution: a phosphonic Kolbe oxidation/cyclization process

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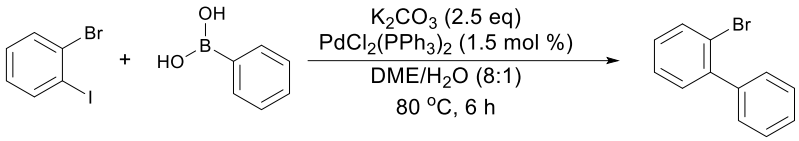
Contents

1. General Information

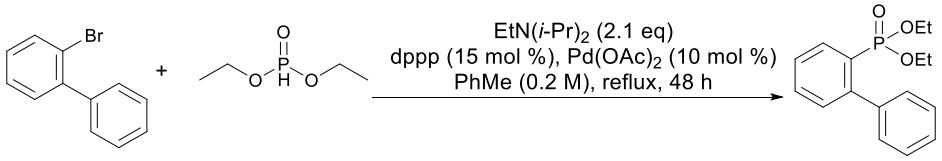
Unless otherwise noted, chemicals and solvents were purchased with the highest purity grade available and were used without further purification. Purification of products was conducted by column chromatography on silica gel (200-300 mesh, from Qingdao, China) if not mentioned. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz respectively with Brucker ARX 400 spectrometer. ^{31}P NMR was recorded at 202 MHz and ^{19}F NMR was recorded at 471 MHz both with Brucker ARX 500 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (J) were reported in hertz (Hz). For ^{1}H NMR spectra, tetramethylsilane was used as internal standard with chemical shift at 0 ppm when $CDCl_3$ was solvent. For ^{13}C NMR spectra, $CDCl_3$ was used as the internal standard with chemical shift at 77 ppm. For ^{31}P NMR spectra, 85% H_3PO_4 were used as the reference with chemical shift at 0 ppm. For ^{19}F NMR spectra, $CFCl_3$ was used as the reference with chemical shift at 0 ppm. The following abbreviations were used to symbolize the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet. HRMS data were obtained on a VG ZAB-HS mass spectrometer and Bruker Apex IV FTMS spectrometer.

2. Preparation of Substrates

2.1 General methods for preparation of ethyl hydrogen [1,1'-biphenyl]-2-ylphosphonate (1a)[1]

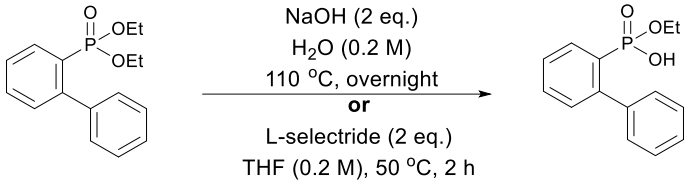


To a solution of $PdCl_2(PPh_3)_2$ (52.6 mg, 0.075 mmol) and potassium carbonate (1.728 g, 12.5 mmol) in water (2.5 mL) and DME (20.0 mL) were added 2-bromoiodobenzene (1.414 g, 5.0 mmol) and phenylboronic acid (0.914 g, 7.5 mmol). The reaction mixture was stirred at 80 °C under N_2 atmosphere for 6 h in oil bath until substrate disappeared on TLC. When the reaction was complete, water (20 mL) and ether (20 mL) were added. The aqueous layer was separated and extracted with ether (20 mL × 3). The combined organic layer was washed with brine and the organic fraction was dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (petroleum ether) on silica gel, producing the title compound as a colorless oil (874 mg, 75%).



An oven dried 100 mL Schlenk tube, 2-bromobiphenyl (1.166 g, 5.0 mmol), diisopropylethylamine

(1.357 g, 10.5 mmol), diethylphosphonate (2.762 g, 20.0 mmol), palladium(II) acetate (112 mg, 0.5 mmol), and 1,3-bis(diphenylphosphino)propane (309 mg, 0.75 mmol) were dissolved in dry toluene (25 mL, dried over Na), heated at 120 °C with seal for 48 hours. The reaction was cooled to room temperature and diluted with 100 mL EtOAc. The organic layer was washed three times with saturated $NaHCO_3$ solution, then once with brine. The organic layer was dried over Na_2SO_4, filtered, and the solvent was removed via vacuum yielding a crude yellow oil. The crude product was purified by flash column chromatography (PE/EA = 2:1), yielding a viscous colorless oil (1.002 g, 69% yield).

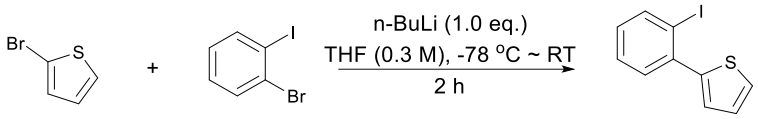


Ethyl hydrogen [1,1'-biphenyl]-2-ylphosphonate (**1a**) can be synthesized through two methods as shown above.

1,1'-biphenylphosphonic acid diethyl ester (580 mg, 2.0 mmol), NaOH (4.0 mmol), and H_2O (10.0 mL) were stirred under reflux overnight. The reaction solution was diluted with water (10 mL). The solution was neutralized with cooled concentrated hydrochloric acid and extracted with EtOAc. The extracts were evaporated under reduced pressure to give 1,1'-biphenylphosphonic acid monoethyl ester (472 mg, 90%) as a white crystalline solid.

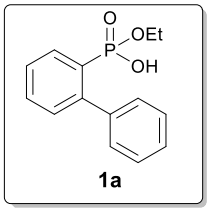
A solution of 1,1'-biphenylphosphonic acid diethyl ester (580 mg, 2.0 mmol) in THF (6.0 mL) was treated with *L*-selectride (1.0 M solution in THF, 4.0 mL, 4.0 mmol) at 50 °C for 2 h. When the reaction was complete, the solution was quenched by addition of water. The aqueous layer was extracted with ethyl acetate (20 mL × 3) to remove impurities, then acidified to pH = 1 with 1 N HCl (10 mL) and extracted with ethyl acetate (20 mL × 5). The combined organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. Then, the crude product was dried in vacuum to afford 1,1'-biphenylphosphonic acid monoethyl ester (383 mg, 73%) as a white crystalline solid.

2.2 Preparation of 2-(2-iodophenyl)thiophene[2]

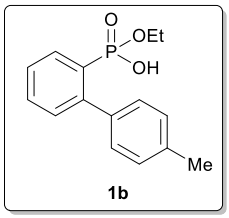


To a solution of 2-bromothiophene (9.0 mmol) in dry THF (30 mL) was added n-BuLi (2.5 M solution in n-hexane, 3.8 mL, 9.45 mmol) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 30 min and then, 1-bromo-2-iodobenzene (9.0 mmol) was dropwise at -78 °C. The mixture was warmed to room temperature and stirred for 1 h. When the reaction was complete, the solution was quenched with ammonium chloride. The aqueous layer was extracted with ethyl ether (3 × 20 mL) and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure.The crude product was then purified by flash column chromatography (petroleum ether) on silica gel, producing the title compound as a yellow oil (1.95 g, 76%).

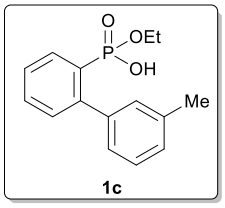
2.3 Data of substrates



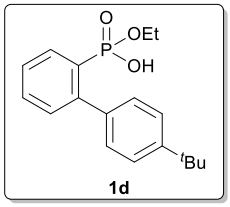
Ethyl hydrogen [1,1'-biphenyl]-2-ylphosphonate (**1a**): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.64 (br, 1H), 8.04 (ddd, *J* = 14.8, 7.7, 1.4 Hz, 1H), 7.55 (tt, *J* = 7.6, 1.5 Hz, 1H), 7.48 – 7.29 (m, 7H), 3.70 (p, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.1 (d, *J* = 10.1 Hz), 141.4 (d, *J* = 4.1 Hz), 133.6 (d, *J* = 10.0 Hz), 132.0 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 14.3 Hz), 129.4, 127.5, 127.4, 127.3 (d, *J* = 192.7 Hz), 126.8 (d, *J* = 14.9 Hz), 61.5 (d, *J* = 6.4 Hz), 15.8 (d, *J* = 7.4 Hz).



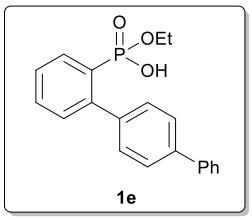
Ethyl hydrogen (4'-methyl-[1,1'-biphenyl]-2-yl)phosphonate (1b): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.88 (br, 1H), 8.03 (ddd, *J* = 14.8, 7.7, 1.4 Hz, 1H), 7.53 (tt, *J* = 7.6, 1.5 Hz, 1H), 7.40 (dd, *J* = 7.6, 3.5 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.16 (d, *J* = 7.8 Hz, 2H), 3.71 (p, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.2 (d, *J* = 10.1 Hz), 138.5 (d, *J* = 4.4 Hz), 137.0, 133.6 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 14.4 Hz), 129.3, 128.2, 126.6 (d, *J* = 14.7 Hz), 126.4, 61.5 (d, *J* = 6.1 Hz), 21.3, 15.8 (d, *J* = 7.4 Hz).



Ethyl hydrogen (3'-methyl-[1,1'-biphenyl]-2-yl)phosphonate (1c): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.10 (br, 1H), 8.02 (ddd, *J* = 14.8, 7.7, 1.4 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.39 (tdd, *J* = 7.6, 3.6, 1.3 Hz, 1H), 7.31 (ddd, *J* = 7.3, 5.6, 1.2 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.14 (dt, *J* = 6.2, 2.3 Hz, 1H), 3.72 (p, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.3 (d, *J* = 10.2 Hz), 141.3 (d, *J* = 4.4 Hz), 137.0, 133.5 (d, *J* = 10.2 Hz), 131.9 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 14.5 Hz), 130.1, 128.1, 127.4, 127.2 (d, *J* = 192.6 Hz), 126.7 (d, *J* = 14.7 Hz), 126.5, 61.4 (d, *J* = 6.4 Hz), 21.4, 15.8 (d, *J* = 7.4 Hz).

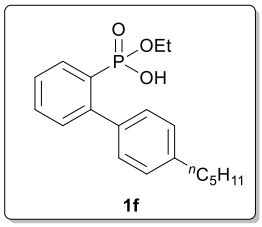


Ethyl hydrogen (4'-(*tert*-butyl)-[1,1'-biphenyl]-2-yl)phosphonate (1d): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.23 (br, 1H), 8.07 (ddd, *J* = 14.9, 7.7, 1.4 Hz, 1H), 7.60 – 7.49 (m, 1H), 7.43 – 7.37 (m, 5H), 7.34 (ddd, *J* = 7.3, 5.6, 1.2 Hz, 1H), 3.66 (p, *J* = 7.1 Hz, 2H), 1.34 (s, 9H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 146.1 (d, *J* = 9.8 Hz), 138.6 (d, *J* = 4.3 Hz), 133.6 (d, *J* = 10.3 Hz), 131.9 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 14.5 Hz), 129.1, 127.4 (d, *J* = 192.4 Hz), 126.6 (d, *J* = 15.2 Hz), 124.4, 61.4 (d, *J* = 6.2 Hz), 34.6, 31.4, 15.6 (d, *J* = 7.6 Hz).



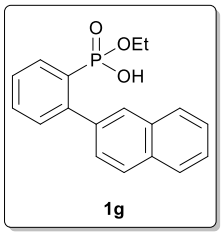
Ethyl hydrogen [1,1':4',1''-terphenyl]-2-ylphosphonate (1e): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.01 (m, 1H), 7.66 – 7.49 (m, 7H), 7.48 – 7.31 (m, 5H), 3.74 (p, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d6) *δ* 144.5 (d, *J* = 9.4 Hz), 140.7 (d, *J* = 3.9 Hz), 139.8, 138.8, 133.0 (d, *J* = 9.2 Hz), 131.5, 131.2 (d, *J* =

13.2 Hz), 129.8, 129.4 (d, *J* = 181.6 Hz), 128.5, 127.4, 126.9 (d, *J* = 13.9 Hz), 126.6, 125.6, 60.2 (d, *J* = 5.6 Hz), 15.8 (d, *J* = 7.0 Hz).



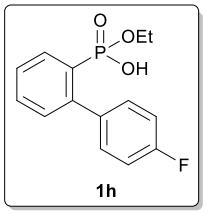
1f

Ethyl hydrogen (4'-pentyl-[1,1'-biphenyl]-2-yl)phosphonate (1f): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.00 (br, 1H), 8.05 (ddd, *J* = 14.8, 7.7, 1.4 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.45 – 7.29 (m, 4H), 7.17 (d, *J* = 8.1 Hz, 2H), 3.68 (p, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.63 (p, *J* = 7.6 Hz, 2H), 1.42 – 1.28 (m, 4H), 1.01 – 0.80 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.2 (d, *J* = 9.9 Hz), 142.0, 138.7 (d, *J* = 4.3 Hz), 133.6 (d, *J* = 10.2 Hz), 131.9 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 14.2 Hz), 129.3, 127.6, 127.3 (d, *J* = 192.3 Hz), 126.6 (d, *J* = 14.8 Hz), 61.4 (d, *J* = 6.2 Hz), 35.7, 31.6, 31.2, 22.6, 15.7 (d, *J* = 7.4 Hz), 14.1.



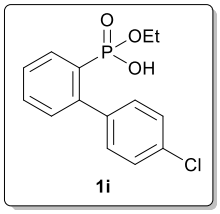
1g

Ethyl hydrogen (2-(naphthalen-2-yl)phenyl)phosphonate (1g): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 14.8, 7.7 Hz, 1H), 7.86 (s, 1H), 7.84 – 7.75 (m, 3H), 7.63 – 7.50 (m, 2H), 7.49 – 7.32 (m, 4H), 3.58 (p, *J* = 7.1 Hz, 2H), 0.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) *δ* 146.0 (d, *J* = 9.9 Hz), 138.8 (d, *J* = 4.3 Hz), 133.5 (d, *J* = 10.1 Hz), 132.8, 132.6, 131.9 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 14.4 Hz), 128.0 (d, *J* = 53.2 Hz), 127.9 (d, *J* = 64.9 Hz), 127.5 (d, *J* = 192.9 Hz), 126.9, 126.9 (d, *J* = 14.7 Hz), 126.0, 61.4 (d, *J* = 6.4 Hz), 15.7 (d, *J* = 7.2 Hz).



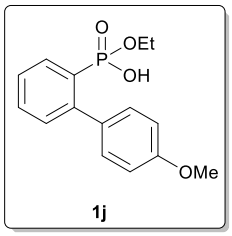
1h

Ethyl hydrogen (4'-fluoro-[1,1'-biphenyl]-2-yl)phosphonate (1h): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (ddd, *J* = 14.7, 7.8, 1.4 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.47 – 7.37 (m, 3H), 7.33 – 7.27 (m, 1H), 7.04 (t, *J* = 8.7 Hz, 2H), 3.76 (p, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 246.3 Hz), 145.0 (d, *J* = 10.1 Hz), 137.4 – 137.2 (m), 133.5 (d, *J* = 9.8 Hz), 132.1 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 14.2 Hz), 131.1 (d, *J* = 8.1 Hz), 127.4 (d, *J* = 192.4 Hz), 127.0 (d, *J* = 14.8 Hz), 114.4 (d, *J* = 21.3 Hz), 61.5 (d, *J* = 6.3 Hz), 15.8 (d, *J* = 7.0 Hz).

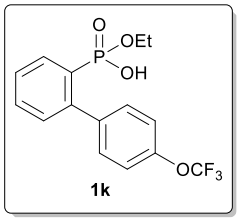


1i

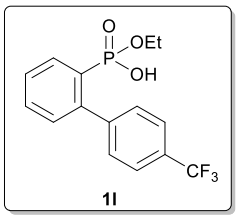
Ethyl hydrogen (4'-chloro-[1,1'-biphenyl]-2-yl)phosphonate (1i): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (ddd, *J* = 14.8, 7.8, 1.4 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.48 – 7.41 (m, 1H), 7.40 – 7.27 (m, 5H), 5.91 (br, 1H), 3.76 (p, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.8 (d, *J* = 10.1 Hz), 139.8 (d, *J* = 4.3 Hz), 133.5, 133.5 (d, *J* = 9.6 Hz), 132.1 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 14.0 Hz), 130.8, 127.7, 127.3 (d, *J* = 192.4 Hz), 127.2 (d, *J* = 14.7 Hz), 61.6, 15.9.



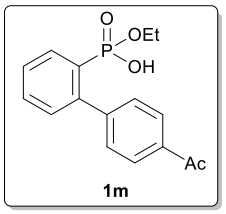
Ethyl hydrogen (4'-methoxy-[1,1'-biphenyl]-2-yl)phosphonate (1j): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (ddd, *J* = 14.8, 8.4, 1.9 Hz, 1H), 7.53 (tt, *J* = 7.6, 1.5 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.30 (ddd, *J* = 7.2, 5.6, 1.2 Hz, 1H), 6.94 – 6.86 (m, 2H), 3.82 (s, 3H), 3.73 (p, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.1, 145.8 (d, *J* = 10.2 Hz), 133.8 (d, *J* = 4.4 Hz), 133.6 (d, *J* = 10.2 Hz), 131.9 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 14.5 Hz), 130.6, 127.3 (d, *J* = 191.9 Hz), 126.5 (d, *J* = 15.2 Hz), 113.0, 61.5 (d, *J* = 6.3 Hz), 55.2, 15.8 (d, *J* = 7.3 Hz).



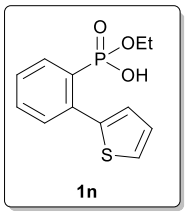
Ethyl hydrogen (4'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl)phosphonate (1k): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.10 (br, 1H), 8.03 (ddd, *J* = 14.8, 7.7, 1.4 Hz, 1H), 7.57 (tt, *J* = 7.6, 1.5 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.30 (ddd, *J* = 7.2, 5.6, 1.2 Hz, 1H), 7.24 – 7.17 (m, 2H), 3.73 (p, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 144.6 (d, *J* = 9.6 Hz), 140.1 (d, *J* = 4.5 Hz), 133.5 (d, *J* = 10.1 Hz), 132.1 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 14.3 Hz), 130.9, 127.4 (d, *J* = 192.9 Hz), 127.2 (d, *J* = 14.9 Hz), 120.6 (q, *J* = 257.3 Hz), 120.0, 61.5 (d, *J* = 6.2 Hz), 15.6 (d, *J* = 7.4 Hz).



Ethyl hydrogen (4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)phosphonate (1l): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (ddd, *J* = 14.8, 7.7, 1.4 Hz, 1H), 7.67 – 7.53 (m, 5H), 7.51 – 7.42 (m, 1H), 7.33 – 7.28 (m, 1H), 5.20 (br, 1H), 3.74 (p, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.0 (d, *J* = 4.6 Hz), 144.5 (d, *J* = 9.7 Hz), 133.5 (d, *J* = 10.1 Hz), 132.2 (d, *J* = 2.9 Hz), 131.0 (d, *J* = 14.1 Hz), 129.8, 129.6 (q, *J* = 32.4 Hz), 127.5 (d, *J* = 14.7 Hz), 127.3 (d, *J* = 193.0 Hz), 124.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.9 Hz), 61.5 (d, *J* = 6.5 Hz), 15.7 (d, *J* = 7.3 Hz).

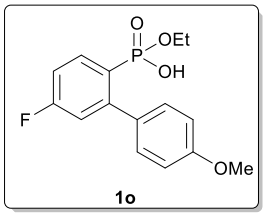


Ethyl hydrogen (4'-acetyl-[1,1'-biphenyl]-2-yl)phosphonate (1m): white solid and it was synthesized by using NaOH in water; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.00 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.59 (tt, *J* = 7.6, 1.5 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.46 (tdd, *J* = 7.6, 3.6, 1.3 Hz, 1H), 7.34 – 7.28 (m, 1H), 3.73 (p, *J* = 7.2 Hz, 2H), 2.62 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 146.2 (d, *J* = 4.3 Hz), 144.8 (d, *J* = 10.0 Hz), 136.0, 133.6 (d, *J* = 10.0 Hz), 132.2 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 14.2 Hz), 129.7, 127.6, 127.4 (d, *J* = 14.7 Hz), 127.1 (d, *J* = 192.3 Hz), 61.6 (d, *J* = 6.1 Hz), 26.7, 15.8 (d, *J* = 7.3 Hz).

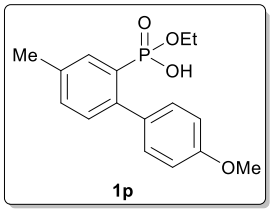


Ethyl hydrogen (2-(thiophen-2-yl)phenyl)phosphonate (1n): yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (ddd, *J* = 14.9, 7.7, 1.4 Hz, 1H), 7.86 (br, 1H), 7.56 – 7.44 (m, 2H), 7.44 – 7.37 (m, 2H), 7.32 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.02 (dd, *J* = 5.1, 3.5 Hz, 1H), 3.83 (p, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.5 (d, *J* = 5.0 Hz), 138.2 (d, *J* = 8.8

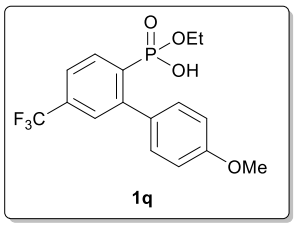
Hz), 134.1 (d, *J* = 9.6 Hz), 132.3 (d, *J* = 13.3 Hz), 131.9 (d, *J* = 2.9 Hz), 128.7, 128.2 (d, *J* = 192.2 Hz), 127.4 (d, *J* = 14.7 Hz), 127.1, 125.8.



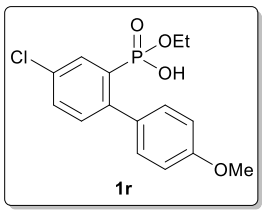
6-Ethoxy-9-fluoro-3-methoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (1o): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.70 (br, 1H), 8.01 (ddd, *J* = 14.5, 8.6, 6.1 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.12 – 6.97 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 3.72 (p, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.6 (dd, *J* = 253.9, 3.7 Hz), 159.4, 149.0 (dd, *J* = 11.8, 8.5 Hz), 136.3 (dd, *J* = 11.4, 9.4 Hz), 132.6 (dd, *J* = 4.0, 1.5 Hz), 130.4, 123.4 (dd, *J* = 196.8, 3.1 Hz), 118.6 (dd, *J* = 21.3, 15.7 Hz), 113.6 (dd, *J* = 20.6, 16.2 Hz), 113.1, 61.6 (d, *J* = 6.4 Hz), 55.3, 15.8 (d, *J* = 7.3 Hz).



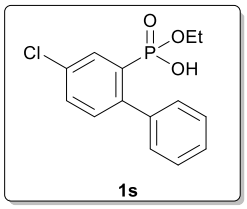
Ethyl hydrogen (4'-methoxy-4-methyl-[1,1'-biphenyl]-2-yl)phosphonate (1p): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.99 (br, 1H), 7.85 (d, *J* = 15.2 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 6.8 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 2H), 3.81 (s, 3H), 3.72 (p, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 0.98 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.9, 142.9 (d, *J* = 9.7 Hz), 136.3 (d, *J* = 14.9 Hz), 134.1 (d, *J* = 10.2 Hz), 133.8 (d, *J* = 4.4 Hz), 132.7 (d, *J* = 3.2 Hz), 131.5 (d, *J* = 15.3 Hz), 130.6, 127.0 (d, *J* = 190.7 Hz), 112.9, 61.4 (d, *J* = 6.0 Hz), 55.2, 21.0, 15.8 (d, *J* = 7.4 Hz).



Ethyl hydrogen (4'-methoxy-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)phosphonate (1q): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.97 (br, 1H), 8.13 (dd, *J* = 14.5, 8.0 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 4.8 Hz, 1H), 7.41 – 7.33 (m, 2H), 6.98 – 6.87 (m, 2H), 3.83 (s, 3H), 3.75 (p, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.6, 146.8 (d, *J* = 10.3 Hz), 134.2 (d, *J* = 10.5 Hz), 133.7 (dd, *J* = 32.7, 3.2 Hz), 132.4 (d, *J* = 4.3 Hz), 131.4 (d, *J* = 191.3 Hz), 130.5, 128.2 (dq, *J* = 14.3, 3.6 Hz), 123.5 (q, *J* = 272.8 Hz), 123.1 (dq, *J* = 15.4, 3.8 Hz), 113.2, 62.0 (d, *J* = 6.1 Hz), 55.3, 15.8 (d, *J* = 7.2 Hz).



Ethyl hydrogen (4-chloro-4'-methoxy-[1,1'-biphenyl]-2-yl)phosphonate (1r): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 15.3, 2.3 Hz, 1H), 7.49 (ddd, *J* = 8.2, 2.4, 1.0 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.26 – 7.20 (m, 1H), 6.93 – 6.88 (m, 2H), 3.82 (s, 3H), 3.75 (p, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3, 144.2 (d, *J* = 9.5 Hz), 133.3 (d, *J* = 11.1 Hz), 133.0 (d, *J* = 15.8 Hz), 132.9 (d, *J* = 20.3 Hz), 132.6 (d, *J* = 4.3 Hz), 132.0 (d, *J* = 3.0 Hz), 130.5, 129.3 (d, *J* = 192.0 Hz), 113.1, 61.9 (d, *J* = 6.1 Hz), 55.3, 15.8 (d, *J* = 7.3 Hz).



Ethyl hydrogen (4-chloro-[1,1'-biphenyl]-2-yl)phosphonate (1s): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.59 (br, 1H), 7.99 (dd, *J* = 15.2, 2.3 Hz, 1H), 7.51 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.29 – 7.23 (m, 1H), 3.72 (p, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.4 (d, *J* = 9.5 Hz), 140.2 (d, *J* = 4.2 Hz), 133.3, 133.1 (d, *J* = 9.4 Hz), 132.8 (d, *J* = 15.5 Hz), 132.0 (d, *J* = 3.0 Hz), 129.4, 129.3 (d, *J* = 192.4 Hz), 127.7, 127.7, 61.9 (d, *J* = 6.1 Hz), 15.8 (d, *J* = 7.3 Hz).

3. Electrochemical Reactions and Cyclized Products

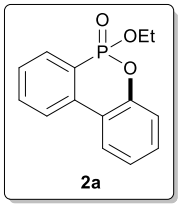
3.1 Equipment and experiments setup pictures

Figure S1 Electrodes, power supply and reaction tube

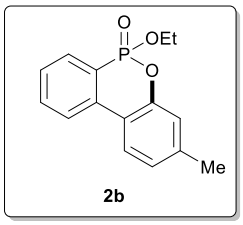
3.2 General Procedure for the Electrochemical Experiments

A 15 mL test tube with a stir bar was charged with 0.5 mmol of 2-(aryl)aryl phosphonic acid monoester **1**, followed by 2,7 mL of MeOH, 0.3 mL DMF and 0.3 mL of an aqueous NaOH solution (0.167 M, 0.05 mmol). Two platinum net electrodes (1.0 cm × 1.0 cm) were set up in the tube, and the electrodes were totally immersed. The resulting mixture was electrolyzed at a constant current mode with a current of 23 mA under ambient temperature. The reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with PE/EA to give the desired product **2**.

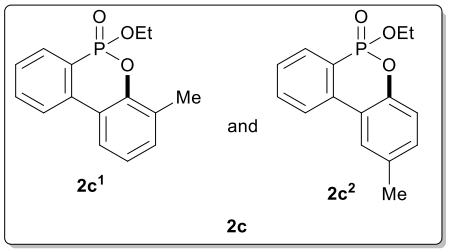
3.3 Characterization data of cyclized products



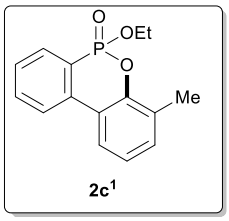
6-Ethoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2a): reaction time 3 h; R_f = 0.4 (PE: EA = 1:1); yellow oil (71%, 91.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.89 (m, 3H), 7.75 – 7.67 (m, 1H), 7.55 – 7.47 (m, 1H), 7.42 – 7.35 (m, 1H), 7.30 – 7.20 (m, 2H), 4.22 (dq, *J* = 9.0, 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.9 (d, *J* = 8.0 Hz), 137.0 (d, *J* = 6.7 Hz), 133.4, 130.4, 130.1 (d, *J* = 9.4 Hz), 128.3 (d, *J* = 15.4 Hz), 125.2, 124.7, 124.0 (d, *J* = 11.9 Hz), 122.6 (d, *J* = 12.3 Hz), 122.4 (d, *J* = 181.8 Hz), 120.2 (d, *J* = 6.6 Hz), 62.9 (d, *J* = 6.6 Hz), 16.3 (d, *J* = 6.0 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.09.



6-Ethoxy-3-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2b): reaction time 3.0 h; R_f = 0.4 (PE: EA = 1:1); yellow oil (71%, 97.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.87 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.52 – 7.43 (m, 1H), 7.10 – 7.01 (m, 2H), 4.27 – 4.14 (m, 2H), 2.39 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8 (d, *J* = 7.9 Hz), 141.2, 137.2 (d, *J* = 7.3 Hz), 133.3 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 8.9 Hz), 127.8 (d, *J* = 15.4 Hz), 125.6, 125.0, 123.7 (d, *J* = 12.0 Hz), 122.0 (d, *J* = 181.3 Hz), 120.4 (d, *J* = 6.7 Hz), 119.8 (d, *J* = 11.8 Hz), 62.9 (d, *J* = 6.6 Hz), 21.2, 16.3 (d, *J* = 5.9 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.42.

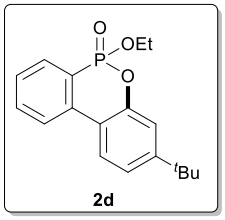


6-Ethoxy-4-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide and 6-ethoxy-2-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2c): reaction time 3.0 h; R_f = 0.4 (PE: EA = 1:1); yellow oil (68%, 93.6 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.93 (m, 2H), 7.81 – 7.68 (m, 2H), 7.55 – 7.48 (m, 1H), 7.29 – 7.10 (m, 3H), 4.30 – 4.12 (m, 2H), 2.42 (s, 1.4 H, **2c²**), 2.41 (s, 1.6 H, **2c¹**) 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4 (d, *J* = 8.1 Hz, **2c¹**), 147.9 (d, *J* = 7.9 Hz, **2c²**), 137.4 (d, *J* = 7.0 Hz, **2c¹**), 137.1 (d, *J* = 6.7 Hz, **2c²**), 134.1 (**2c²**), 133.4 (d, *J* = 2.4 Hz, **2c¹**), 133.3 (d, *J* = 2.9 Hz, **2c²**), 131.9 (**2c¹**), 131.2 (**2c²**), 130.1 (t, *J* = 9.8 Hz, **2c¹** and **2c²**), 129.0 (d, *J* = 6.0 Hz, **2c¹**), 128.11 (d, *J* = 15.4 Hz, **2c²**), 128.08 (d, *J* = 15.4 Hz, **2c¹**), 125.5 (**2c²**), 124.3 (d, *J* = 12.0 Hz, **2c¹**), 124.1 (**2c¹**), 124.0 (d, *J* = 11.9 Hz, **2c²**), 123.0 (**2c¹**), 122.5 (d, *J* = 181.3 Hz, **2c²**), 122.4 (d, *J* = 11.8 Hz, **2c¹**), 122.3 (d, *J* = 181.9 Hz, **2c¹**), 122.2 (d, *J* = 12.2 Hz, **2c²**), 119.9 (d, *J* = 6.6 Hz, **2c²**), 62.84 (d, *J* = 6.6 Hz, **2c²**), 62.81 (d, *J* = 6.6 Hz, **2c¹**), 21.0 (**2c²**), 16.3 (d, *J* = 5.8 Hz, **2c¹** and **2c²**), 16.2 (**2c¹**); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.37 (**2c²**), 10.32 (**2c¹**).



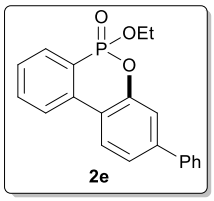
6-Ethoxy-4-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2c¹): R_f = 0.3 (Chloroform; column chromatography on silica gel, 300-400 mesh, from Qingdao, China); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.92 (m, 2H), 7.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.54 – 7.48 (m, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 4.30 – 4.10 (m, 2H), 2.41 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-

d) δ 148.4 (d, *J* = 8.1 Hz), 137.5 (d, *J* = 7.2 Hz), 133.4 (d, *J* = 2.7 Hz), 131.9, 130.1 (d, *J* = 9.4 Hz), 129.1 (d, *J* = 6.5 Hz), 128.1 (d, *J* = 15.4 Hz), 124.3 (d, *J* = 12.0 Hz), 124.1, 123.0, 122.4 (d, *J* = 12.1 Hz), 122.4 (d, *J* = 182.1 Hz), 62.8 (d, *J* = 6.7 Hz), 16.3 (d, *J* = 5.9 Hz), 16.2; ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.32. HRMS (ESI): calcd for $C_{15}H_{16}O_3P^+$ [M + H]$^+$, 275.0832; found, 275.0831.



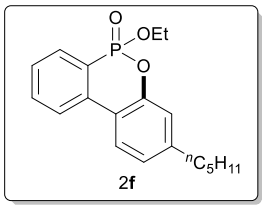
2d

3-(*tert*-Butyl)-6-ethoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2d): reaction time 2.5 h; R_f = 0.3 (PE: EA = 2:1); yellow oil (78%, 124.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.90 (m, 2H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 4.28 – 4.16 (m, 2H), 1.35 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 149.8 (d, *J* = 7.5 Hz), 137.0 (d, *J* = 7.1 Hz), 133.3 (d, *J* = 2.5 Hz), 130.0 (d, *J* = 9.0 Hz), 127.8 (d, *J* = 15.4 Hz), 124.7, 123.7 (d, *J* = 12.3 Hz), 122.1 (d, *J* = 181.0 Hz), 121.9, 119.6 (d, *J* = 11.8 Hz), 117.0 (d, *J* = 6.7 Hz), 63.0 (d, *J* = 6.6 Hz), 34.9, 31.1, 16.3 (d, *J* = 5.8 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.45.



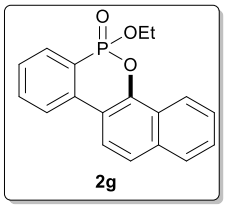
2e

6-Ethoxy-3-phenyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2e): reaction time 14.0 h; R_f = 0.35 (PE: EA = 1:1); white solid (40%, 67.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.93 (m, 3H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.43 (m, 5H), 7.42 – 7.36 (m, 1H), 4.24 (dq, *J* = 9.1, 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.3 (d, *J* = 8.0 Hz), 143.5, 139.1, 136.8 (d, *J* = 7.2 Hz), 133.4 (d, *J* = 2.4 Hz), 130.2 (d, *J* = 8.9 Hz), 129.0, 128.2, 128.2 (d, *J* = 15.4 Hz), 126.9, 125.6, 123.9 (d, *J* = 11.9 Hz), 123.2, 122.2 (d, *J* = 193.0 Hz), 121.4, 118.3 (d, *J* = 6.7 Hz), 63.0 (d, *J* = 6.6 Hz), 16.3 (d, *J* = 5.8 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.29.



2f

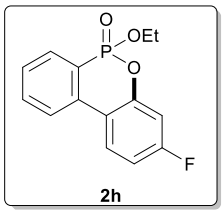
6-Ethoxy-3-pentyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2f): reaction time 7.3 h; R_f = 0.3 (PE: EA = 2:1); colorless oil (36%, 60.0 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.88 (m, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.47 (td, *J* = 7.4, 3.6 Hz, 1H), 7.12 – 7.02 (m, 2H), 4.21 (dq, *J* = 9.0, 7.1 Hz, 2H), 2.69 – 2.58 (m, 2H), 1.72 – 1.58 (m, 2H), 1.35 (dp, *J* = 8.9, 5.0 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.9 (d, *J* = 7.5 Hz), 146.3, 137.2 (d, *J* = 6.7 Hz), 133.3 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 9.0 Hz), 127.8 (d, *J* = 15.4 Hz), 124.9 (d, *J* = 5.0 Hz), 123.7 (d, *J* = 12.4 Hz), 122.0 (d, *J* = 181.2 Hz), 120.0 (d, *J* = 12.3 Hz), 119.8 (d, *J* = 6.6 Hz), 62.9 (d, *J* = 6.6 Hz), 35.5, 31.4, 30.7, 22.5, 16.3 (d, *J* = 5.8 Hz), 14.0; ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.45. HRMS (ESI): calcd for $C_{19}H_{24}O_3P^+$ [M + H]$^+$, 331.1458; found, 331.1464.



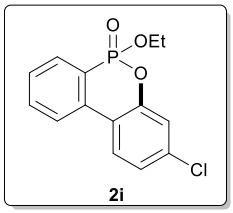
2g

6-Ethoxybenzo[c]naphtho[2,1-e][1,2]oxaphosphinine 6-oxide (2g): reaction time 4.0 h; R_f = 0.35 (PE: EA = 1:1); white solid (39%, 60.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 – 8.40 (m, 1H), 8.09 – 8.00 (m, 2H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.79 – 7.69 (m, 2H), 7.63 – 7.50 (m, 3H), 4.77 – 3.86 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.8 (d, *J* = 8.6 Hz), 137.5 (d, *J* = 7.0 Hz), 134.5, 133.5 (d, *J* = 2.3 Hz), 130.3 (d, *J* = 9.0 Hz), 128.1 (d, *J* = 15.6 Hz), 127.7, 127.6, 127.1, 126.0 (d, *J* = 5.8 Hz), 124.4 (d, *J*

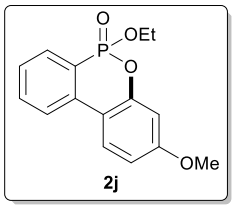
= 11.9 Hz), 124.3, 122.3 (d, *J* = 182.7 Hz), 122.3, 121.7, 117.4 (d, *J* = 12.4 Hz), 62.9 (d, *J* = 6.7 Hz), 16.4 (d, *J* = 5.9 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.80. HRMS (ESI): calcd for $C_{18}H_{16}O_3P^+$ [M + H]$^+$, 311.0832; found, 311.0830.



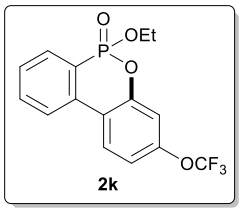
6-Ethoxy-3-fluorodibenzo[c,e][1,2]oxaphosphinine 6-oxide (2h): reaction time 3.7 h; R_f = 0.4 (PE: EA = 1:1); white solid (62%, 86.7 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.81 (m, 3H), 7.74 – 7.65 (m, 1H), 7.56 – 7.44 (m, 1H), 7.04 – 6.89 (m, 2H), 4.30 – 4.17 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2 (d, *J* = 251.4 Hz), 150.8 (dd, *J* = 12.1, 7.6 Hz), 136.3 (d, *J* = 7.1 Hz), 133.6 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 9.4 Hz), 128.2 (d, *J* = 15.5 Hz), 126.7 (d, *J* = 9.7 Hz), 123.9 (d, *J* = 12.2 Hz), 121.6 (d, *J* = 182.1 Hz), 119.1 (dd, *J* = 11.9, 3.6 Hz), 112.2 (d, *J* = 21.5 Hz), 107.6 (dd, *J* = 24.8, 7.1 Hz), 63.2 (d, *J* = 6.6 Hz), 16.3 (d, *J* = 5.8 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.20; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -108.98 – -109.08 (m). HRMS (ESI): calcd for $C_{14}H_{13}FO_3P^+$ [M + H]$^+$, 279.0581; found, 279.0587.



3-Chloro-6-ethoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2i): reaction time 3.8 h; R_f = 0.4 (PE: EA = 1:1); white solid (60%, 87.6 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 14.7, 7.6 Hz, 1H), 7.90 (t, *J* = 7.3 Hz, 1H), 7.85 (dd, *J* = 9.1, 1.7 Hz, 1H), 7.72 (t, *J* = 8.1 Hz, 1H), 7.58 – 7.48 (m, 1H), 7.28 – 7.21 (m, 2H), 4.30 – 4.17 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.22 (d, *J* = 7.5 Hz), 136.08 (d, *J* = 7.0 Hz), 135.58, 133.59 (d, *J* = 2.7 Hz), 130.23 (d, *J* = 9.3 Hz), 128.57 (d, *J* = 15.4 Hz), 126.18, 125.07, 123.99 (d, *J* = 11.9 Hz), 122.21 (d, *J* = 167.3 Hz), 121.24 (d, *J* = 2.8 Hz), 120.41 (d, *J* = 6.9 Hz), 63.22 (d, *J* = 6.6 Hz), 16.35 (d, *J* = 5.9 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 9.93.

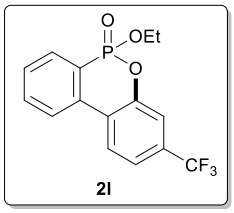


6-Ethoxy-3-methoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2j): reaction time 1.7 h; R_f = 0.3 (PE: EA = 1:1); white solid (80%, 116.1 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (ddd, *J* = 14.6, 7.6, 1.5 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.69 – 7.59 (m, 1H), 7.47 – 7.38 (m, 1H), 6.80 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.74 (d, *J* = 2.6 Hz, 1H), 4.20 (dq, *J* = 9.0, 7.1 Hz, 2H), 3.83 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.3, 151.1 (d, *J* = 7.3 Hz), 137.1 (d, *J* = 7.3 Hz), 133.4 (d, *J* = 2.7 Hz), 130.0 (d, *J* = 9.3 Hz), 127.2 (d, *J* = 15.4 Hz), 126.1, 123.3 (d, *J* = 12.1 Hz), 121.1 (d, *J* = 181.4 Hz), 115.3 (d, *J* = 12.3 Hz), 111.4, 104.8 (d, *J* = 7.0 Hz), 62.9 (d, *J* = 6.6 Hz), 55.6, 16.3 (d, *J* = 5.9 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.76.



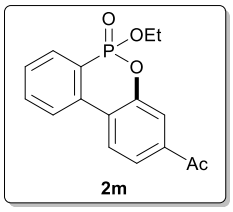
6-Ethoxy-3-(trifluoromethoxy)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (2k): reaction time 3.2 h; R_f = 0.3 (PE: EA = 1:1); yellow oil (68%, 116.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.87 (m, 3H), 7.78 – 7.69 (m, 1H), 7.59 – 7.49 (m, 1H), 7.19 – 7.08 (m, 2H), 4.33 – 4.19 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5 (d, *J* = 7.3 Hz), 149.9, 135.8 (d, *J* = 7.3 Hz), 133.6 (d, *J* = 2.6 Hz), 130.2 (d, *J* = 9.0 Hz), 128.7 (d, *J* = 15.4 Hz), 126.5, 124.1 (d, *J* = 12.3 Hz), 122.2 (d, *J* = 162.8 Hz), 121.2 (d, *J* = 7.3 Hz), 120.3 (q, *J* = 258.6 Hz), 116.8, 112.6 (d, *J* = 7.1 Hz), 63.3 (d, *J* = 6.6 Hz), 16.3 (d, *J* = 5.8 Hz); ^{31}P NMR (202

MHz, Chloroform-*d*) δ 9.90; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -57.86. HRMS (ESI): calcd for $C_{15}H_{13}F_3O_4P^+$ [M + H]$^+$, 345.0498; found, 345.0497..



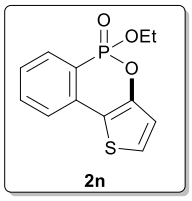
2l

6-Ethoxy-3-(trifluoromethyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (2l): reaction time 18.0 h; R_f = 0.4 (PE: EA = 1:1); yellow oil (61%, 100.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.95 (m, 3H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.56 – 7.47 (m, 2H), 4.32 – 4.21 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8 (d, *J* = 7.5 Hz), 135.5 (d, *J* = 7.0 Hz), 133.7 (d, *J* = 2.6 Hz), 132.2 (q, *J* = 33.6 Hz), 130.3 (d, *J* = 8.9 Hz), 129.4 (d, *J* = 14.9 Hz), 126.0, 125.9 (d, *J* = 12.3 Hz), 123.2 (q, *J* = 273.6 Hz), 124.6 (d, *J* = 12.1 Hz), 122.9 (d, *J* = 182.0 Hz), 121.3 (d, *J* = 3.7 Hz), 117.5 (dq, *J* = 7.9, 4.0 Hz), 63.4 (d, *J* = 6.6 Hz), 16.3 (d, *J* = 5.9 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 9.45; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.91. HRMS (ESI): calcd for $C_{15}H_{13}F_3O_3P^+$ [M + H]$^+$, 329.0549; found, 329.0544.



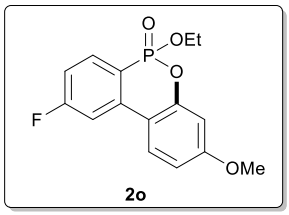
2m

1-(6-Ethoxy-6-oxidodibenzo[c,e][1,2]oxaphosphinin-3-yl)ethan-1-one (2m): reaction time 9.0 h; R_f = 0.25 (PE: EA = 1:1); white solid (40%, 59.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.95 (m, 3H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.63 – 7.55 (m, 1H), 4.31 – 4.19 (m, 2H), 2.64 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.4, 150.0 (d, *J* = 7.5 Hz), 138.5, 135.8 (d, *J* = 7.3 Hz), 133.6 (d, *J* = 2.5 Hz), 130.3 (d, *J* = 9.3 Hz), 129.4 (d, *J* = 15.4 Hz), 126.8 (d, *J* = 11.8 Hz), 125.6, 124.7 (d, *J* = 11.9 Hz), 124.2, 123.1 (d, *J* = 181.5 Hz), 120.1 (d, *J* = 7.0 Hz), 63.3 (d, *J* = 6.6 Hz), 26.7, 16.3 (d, *J* = 5.8 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 9.56. HRMS (ESI): calcd for $C_{16}H_{16}O_4P^+$ [M + H]$^+$, 303.0781; found, 303.0778.



2n

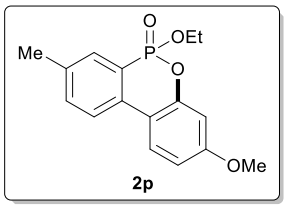
5-Ethoxybenzo[c]thieno[2,3-e][1,2]oxaphosphinine 5-oxide (2n): reaction time 2.0 h; R_f = 0.4 (PE: EA = 1:1); yellow solid (29%, 38.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (ddd, *J* = 14.2, 7.6, 1.3 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.41 (tdd, *J* = 7.6, 3.7, 1.1 Hz, 1H), 7.26 (dd, *J* = 5.4, 1.8 Hz, 1H), 6.92 (d, *J* = 5.4 Hz, 1H), 4.23 (dq, *J* = 9.0, 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5 (d, *J* = 7.8 Hz), 134.5 (d, *J* = 7.3 Hz), 133.6 (d, *J* = 2.8 Hz), 130.4 (d, *J* = 9.4 Hz), 127.4 (d, *J* = 15.5 Hz), 124.1, 123.1 (d, *J* = 11.0 Hz), 120.3 (d, *J* = 6.6 Hz), 118.5 (d, *J* = 183.4 Hz), 118.5 (d, *J* = 13.4 Hz), 63.1 (d, *J* = 6.7 Hz), 16.3 (d, *J* = 6.0 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 13.2.



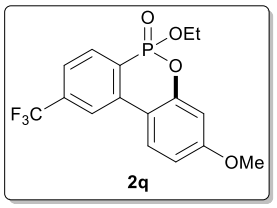
2o

6-Ethoxy-9-fluoro-3-methoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2o): reaction time 2.0 h; R_f = 0.3 (PE: EA = 1:1); white solid (81%, 124.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (ddd, *J* = 14.4, 8.5, 6.0 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.51 (ddd, *J* = 10.6, 5.2, 2.3 Hz, 1H), 7.14 (tt, *J* = 8.3, 2.6 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.75 (d, *J* = 2.6 Hz, 1H), 4.22 (dq, *J* = 9.0, 7.1 Hz, 2H), 3.86 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1 (dd, *J* = 252.6, 3.6 Hz), 161.9, 151.4 (d, *J* = 7.3 Hz), 140.4 (t, *J* = 8.8 Hz), 132.9 (t, *J* = 10.1 Hz), 126.3, 117.2 (dd, *J* = 186.3, 3.0

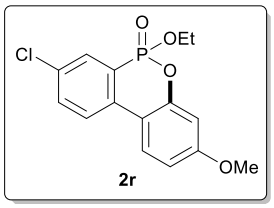
Hz), 114.8 (dd, *J* = 22.0, 16.6 Hz), 114.5 (d, *J* = 2.8 Hz), 111.6, 110.3 (dd, *J* = 23.4, 13.3 Hz), 104.9 (d, *J* = 7.3 Hz), 63.0 (d, *J* = 6.5 Hz), 55.7, 16.3 (d, *J* = 5.9 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 10.24; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -103.86 – -103.95 (m). HRMS (ESI): calcd for $C_{15}H_{15}FO_4P^+$ $[M + H]^+$, 309.0686; found,
309.0683.



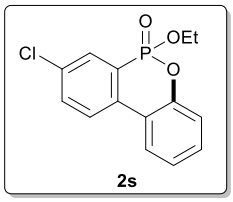
6-Ethoxy-3-methoxy-8-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2p): reaction time 2.0 h; R_f = 0.3 (PE: EA = 1:1); white solid (64%, 97.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.68 (m, 3H), 7.45 (d, *J* = 8.2 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 4.20 (dq, *J* = 8.9, 7.1 Hz, 2H), 3.83 (s, 3H), 2.41 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.9, 150.8 (d, *J* = 7.4 Hz), 137.4 (d, *J* = 15.3 Hz), 134.4, 134.4 (d, *J* = 2.9 Hz), 130.2 (d, *J* = 9.4 Hz), 125.8, 123.3 (d, *J* = 13.1 Hz), 120.8 (d, *J* = 180.5 Hz), 115.4 (d, *J* = 12.4 Hz), 111.3, 104.8 (d, *J* = 7.2 Hz), 62.8 (d, *J* = 6.6 Hz), 55.6, 21.0, 16.3 (d, *J* = 5.9 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 11.21. HRMS (ESI): calcd for $C_{16}H_{18}O_4P^+$ $[M + H]^+$, 305.0937; found, 305.0941..



6-Ethoxy-3-methoxy-9-(trifluoromethyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (2q): reaction time 3.0 h; R_f = 0.3 (PE: EA = 1:1); white solid (48%, 85.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.01 (m, 2H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.66 (m, 1H), 6.86 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 4.33 – 4.19 (m, 2H), 3.87 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 151.3 (d, *J* = 7.8 Hz), 138.1 (d, *J* = 7.4 Hz), 135.1 (qd, *J* = 32.3, 2.7 Hz), 130.9 (d, *J* = 9.6 Hz), 126.3, 124.7 (d, *J* = 181.3 Hz), 123.5 (dq, *J* = 15.9, 3.6 Hz), 123.5 (q, *J* = 273.1 Hz), 120.2 (dq, *J* = 11.8, 3.8 Hz), 114.4 (d, *J* = 11.8 Hz), 111.9, 105.0 (d, *J* = 6.9 Hz), 63.4 (d, *J* = 6.6 Hz), 55.7, 16.3 (d, *J* = 5.8 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 8.46; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.42. HRMS (ESI): calcd for $C_{16}H_{15}F_3O_4P^+$ $[M + H]^+$, 359.0655; found, 359.0657..



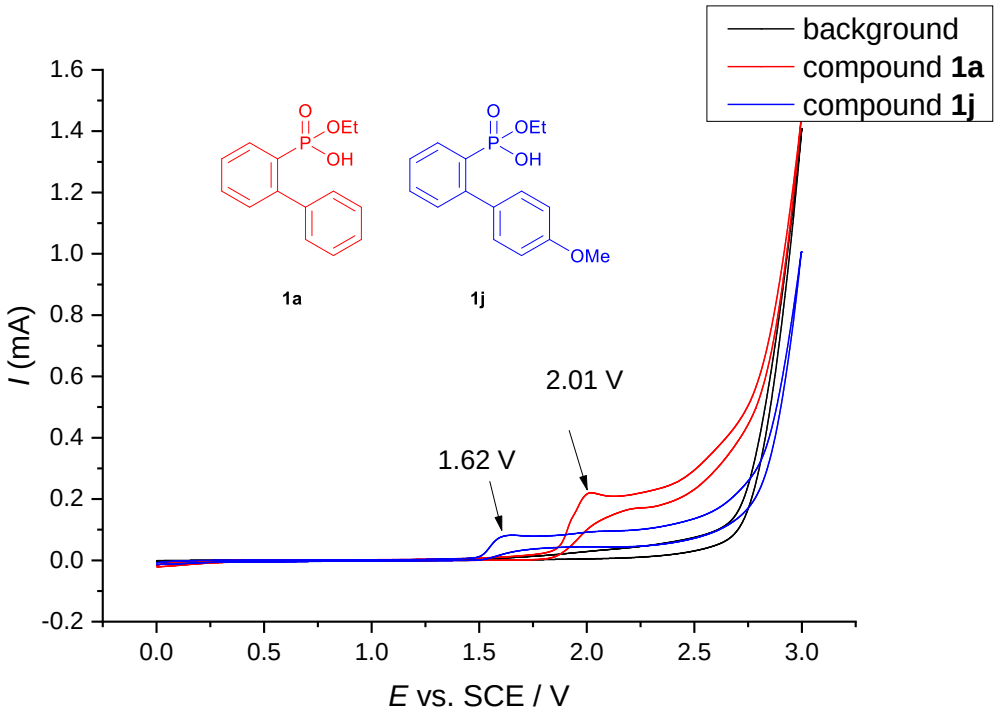
8-Chloro-6-ethoxy-3-methoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2r): reaction time 2.1 h; R_f = 0.3 (PE: EA = 1:1); white solid (52%, 84.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 15.1 Hz, 1H), 7.76 (ddd, *J* = 8.8, 6.6, 2.3 Hz, 2H), 7.60 (dt, *J* = 8.7, 2.4 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 1H), 6.74 (s, 1H), 4.31 – 4.16 (m, 2H), 3.85 (s, 1H), 1.30 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 150.9 (d, *J* = 7.5 Hz), 135.6 (d, *J* = 6.7 Hz), 133.5 (d, *J* = 2.8 Hz), 133.3 (d, *J* = 21.0 Hz), 129.8 (d, *J* = 10.2 Hz), 126.1, 125.0 (d, *J* = 13.7 Hz), 122.8 (d, *J* = 181.2 Hz), 114.6 (d, *J* = 11.7 Hz), 111.7, 104.9 (d, *J* = 6.9 Hz), 63.3 (d, *J* = 6.6 Hz), 55.7, 16.4 (d, *J* = 5.9 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 8.74. HRMS (ESI): calcd for $C_{15}H_{15}ClO_4P^+$ $[M + H]^+$, 325.0391; found, 325.0398.

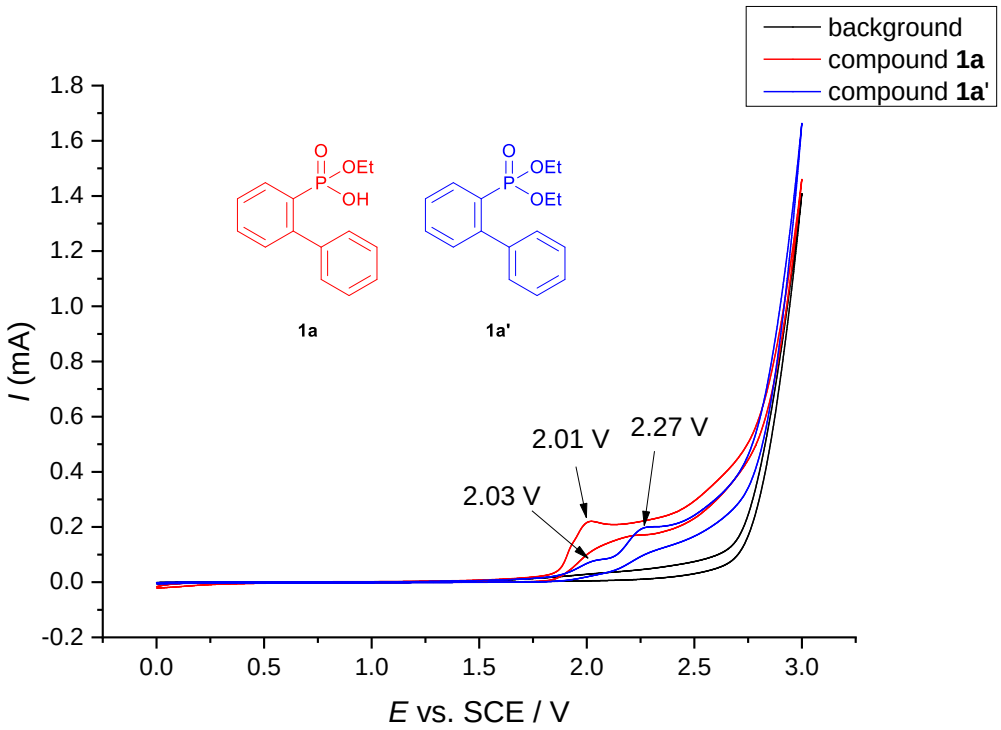


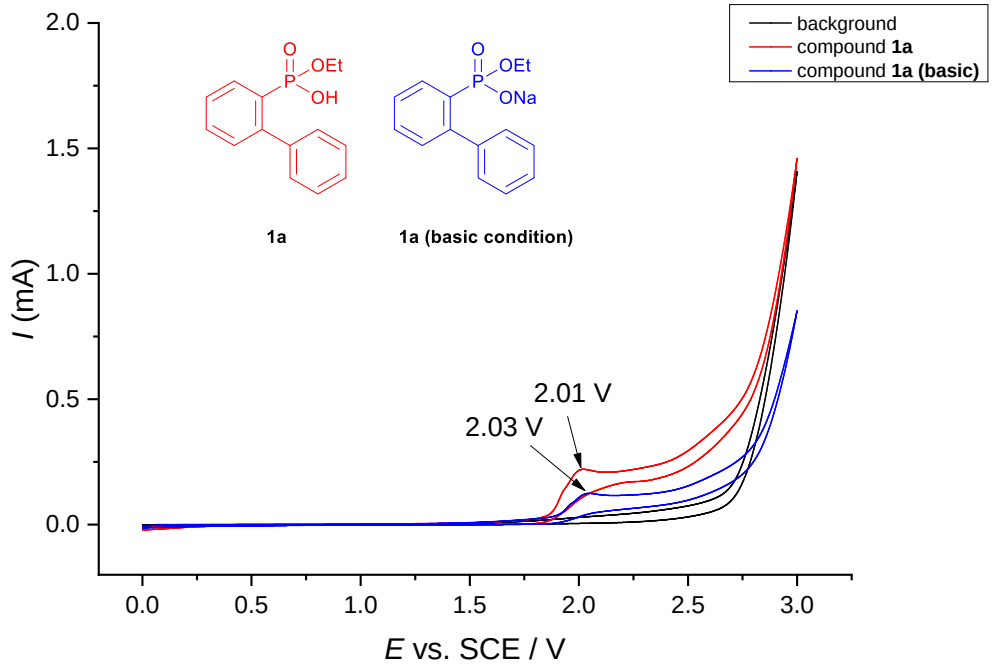
8-Chloro-6-ethoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2s): reaction time 3.2 h; R_f = 0.4 (PE: EA = 1:1); white solid (73%, 107.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 15.1, 2.3 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.64 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.30 – 7.20 (m, 2H), 4.29 – 4.18 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.7 (d, *J* = 8.0 Hz), 135.3 (d, *J* = 6.4 Hz), 134.5 (d, *J* = 20.7 Hz), 133.6 (d, *J* = 2.9 Hz), 130.8, 129.8 (d, *J* = 10.2 Hz), 125.8 (d, *J* = 13.4 Hz), 125.2, 124.9, 124.2 (d, *J* = 181.2 Hz), 121.8 (d, *J* = 11.7 Hz), 120.2 (d, *J* = 6.6 Hz), 63.3 (d, *J* = 6.6 Hz), 16.3 (d, *J* = 5.8 Hz); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 8.03. HRMS (ESI): calcd for $C_{14}H_{13}ClO_3P^+$ $[M + H]^+$, 295.0285; found, 295.0285.

4. CV measurements

Cyclic voltammetry of **1a** (0.001 M), **1j** (0.001 M), **1a** (0.001 M with ca. 5 equiv NaOH) and **1a'** (0.001 M) in CH_3CN with $LiClO_4$ (0.1 M) using platinum wires as working and counter electrodes and SCE as reference electrodes at a scan rate of 50 mV/s.






background
compound 1a
compound 1a (basic)
O
OEt
P
OH
1a
O
OEt
P
ONa
1a (basic condition)
2.01 V
2.03 V
I (mA)
E vs. SCE / V
0.0
0.5
1.0
1.5
2.0
2.5
3.0

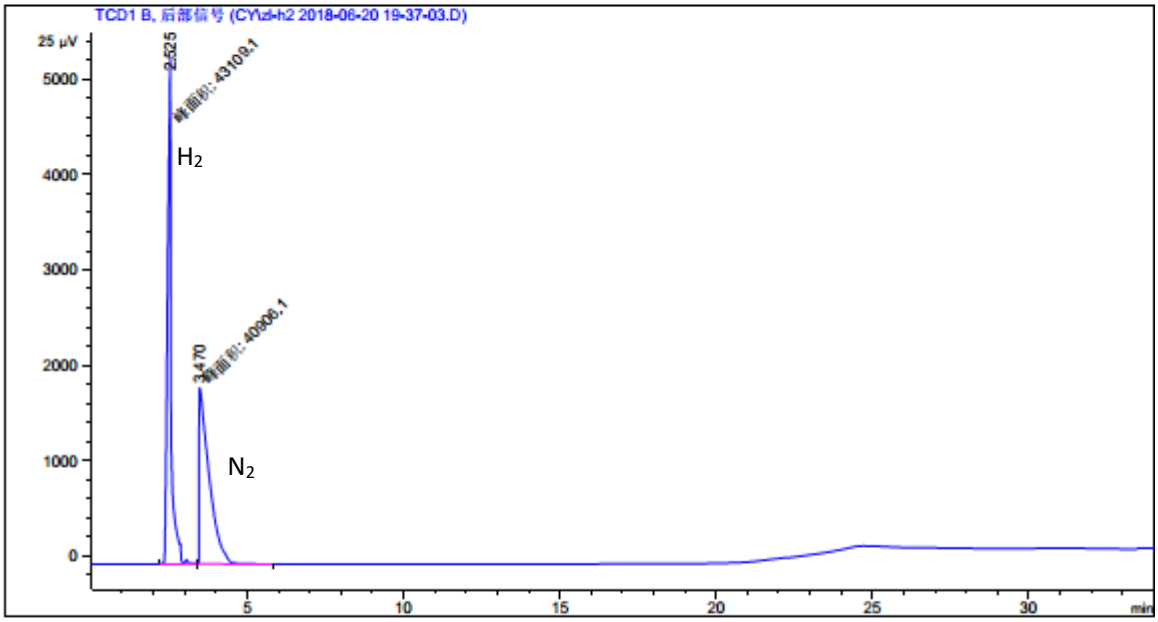
5. Detection of H_2 by GC Analysis

数据文件: C:\Chem32\1\Data\CY\z1-h2 2018-06-20 19-37-03.D
样品名称: z1-h2

==========

操作者 : 系统
样品操作者 : 系统
仪器 : 7890GC 位置 : - (B)
进样日期 : 2018/6/20 19:37:03
进样量 : 手动
采集方法 : C:\Chem32\1\Methods\tyh-H2.M
最后修改 : 2018/6/16 20:36:18 : 系统
分析方法 : C:\Chem32\1\Methods\Shutdown.M
最后修改 : 2018/6/20 17:20:15 : 系统
方法信息 : me

附加信息：峰被手动积分



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外标法报告

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排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
样品量: : 1.00000 [ml] (校正中没有使用)
内标中不使用乘积因子和稀释因子

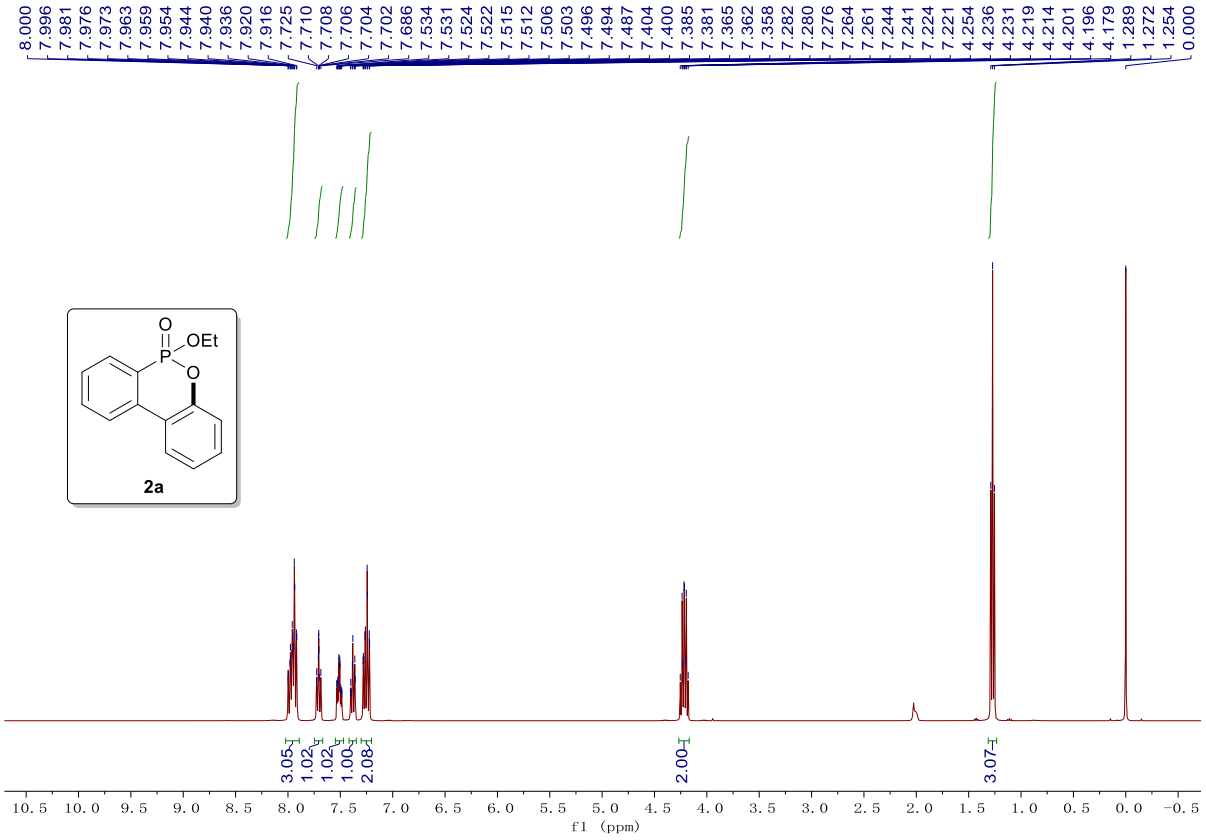
==========

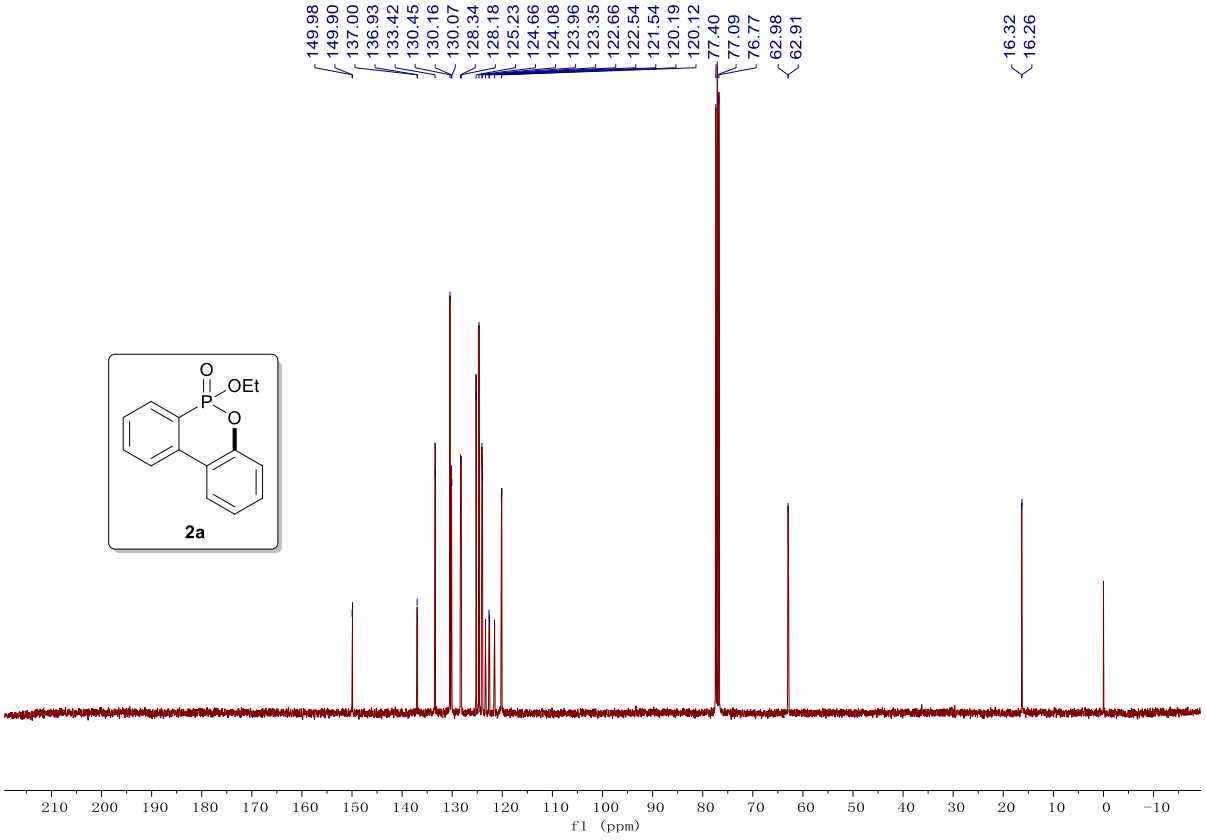
6. References

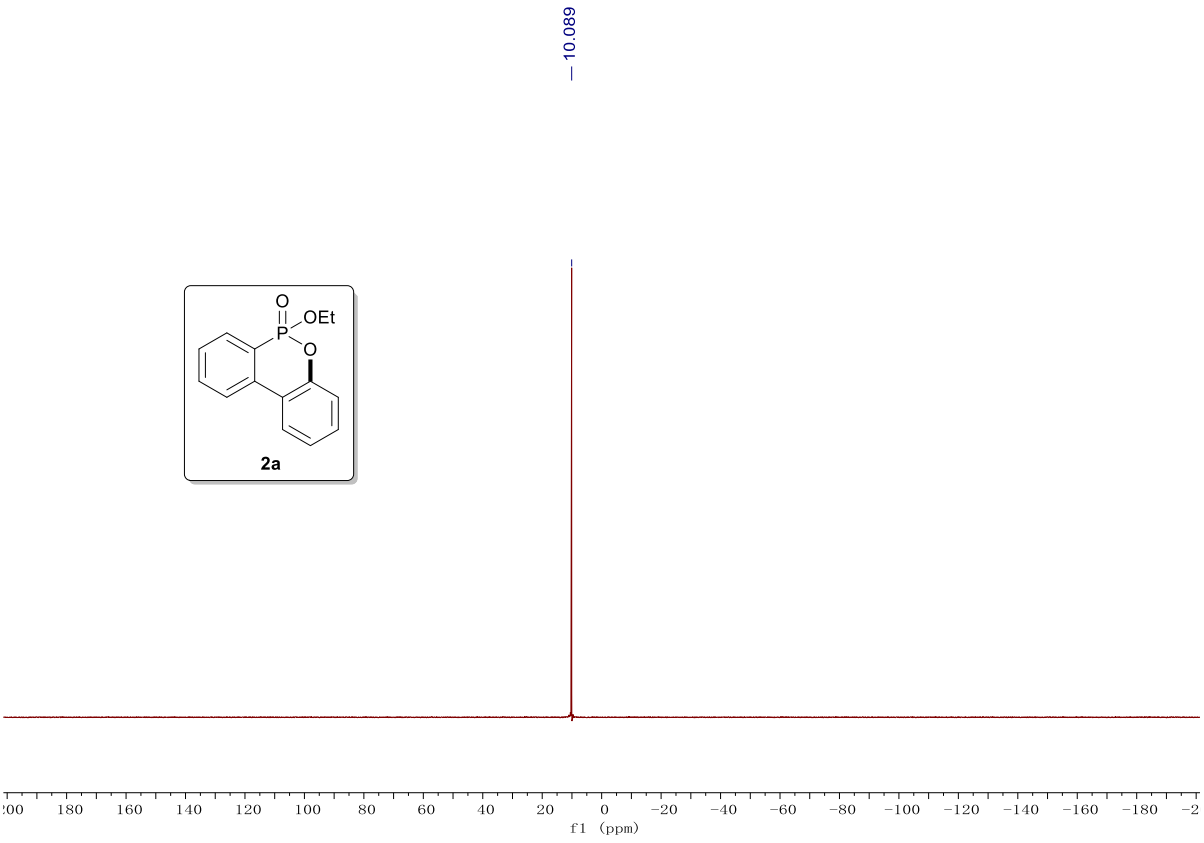
1. (a) Shin, S.; Kang, D.; Jeon, W. H.; Lee, P. H. *Beilstein Journal of Organic Chemistry* **2014,** *10*, 1220-1227; (b) Kendall, A. J.; Salazar, C. A.; Martino, P. F.; Tyler, D. R. *Organometallics* **2014,** *33*, 6171-6178; (c) Park, Y.; Jeon, I.; Shin, S.; Min, J.; Lee, P. H. *The Journal of Organic Chemistry* **2013,** *78*, 10209-10220.
2. Becht, J.-M.; Ngouela, S.; Wagner, A.; Mioskowski, C. *Tetrahedron* **2004,** *60*, 6853-6857.

7. NMR Spectra

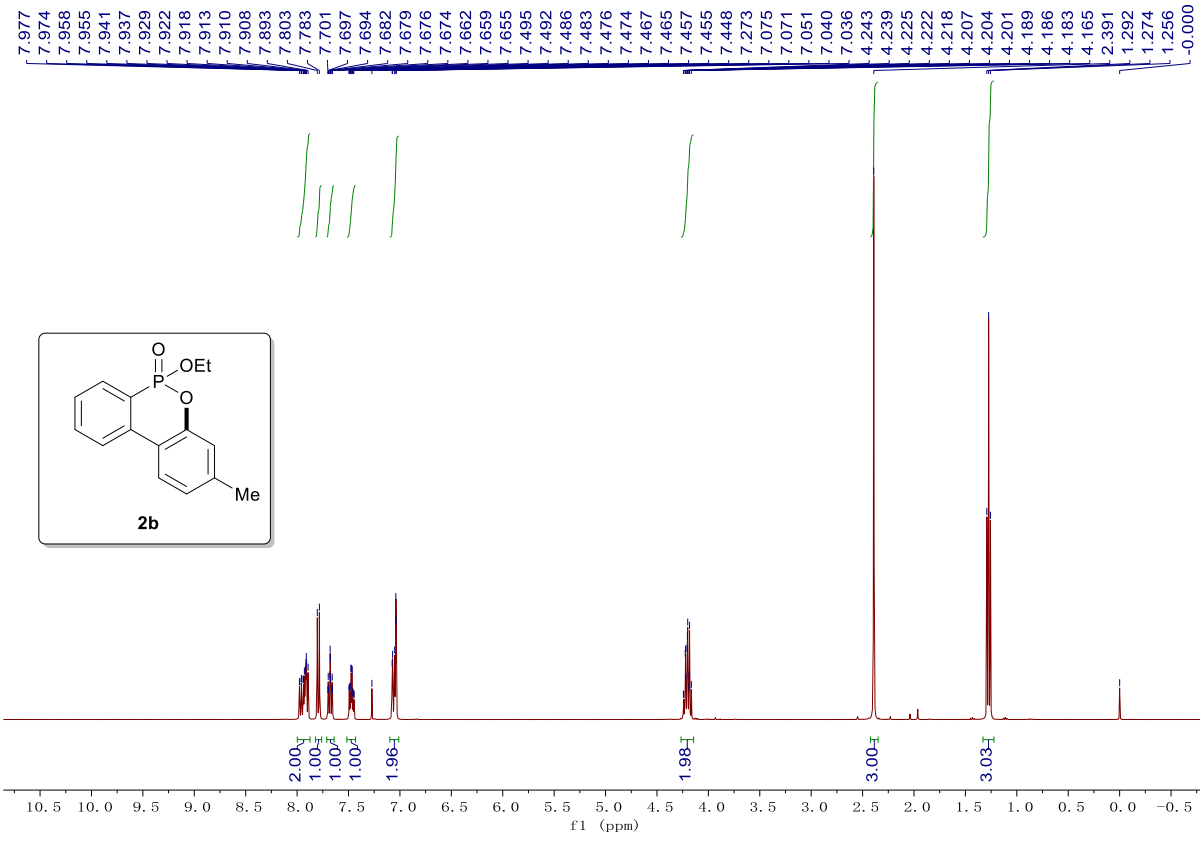
6-Ethoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2a)

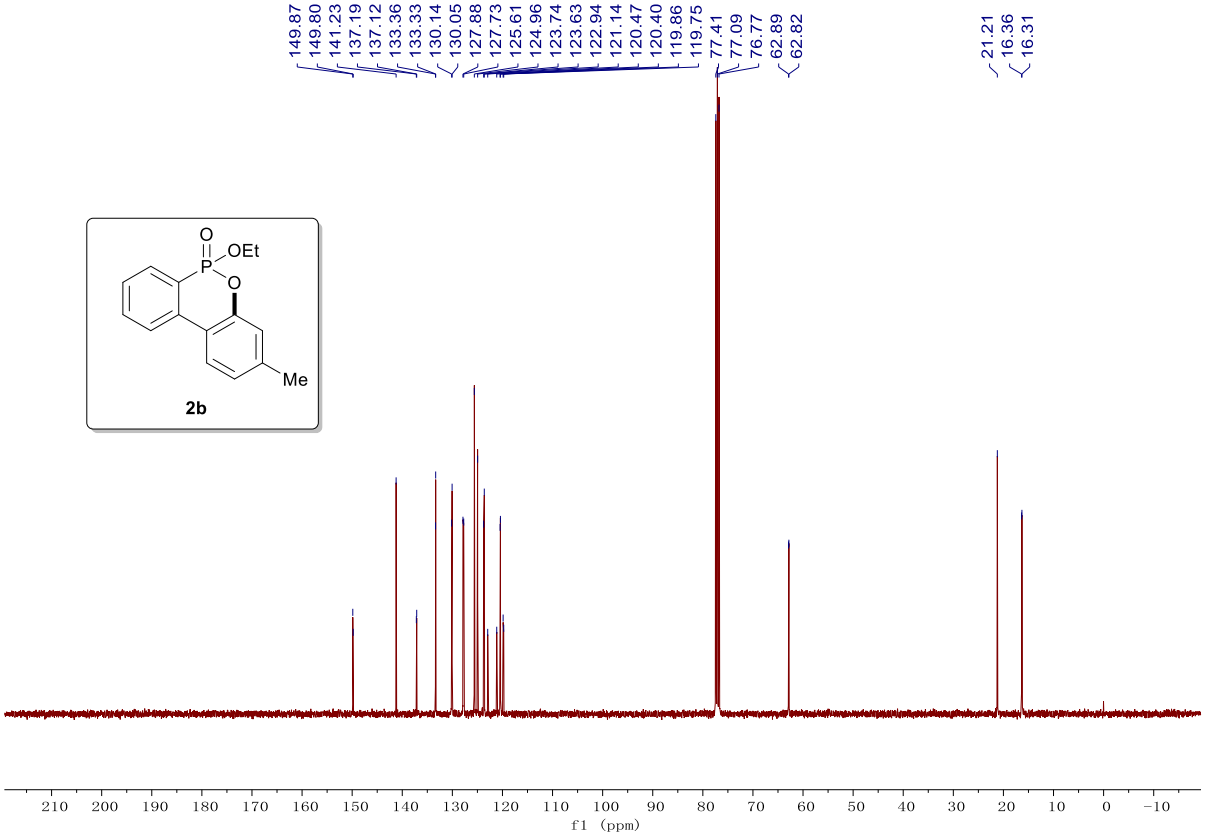






6-Ethoxy-3-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2b)

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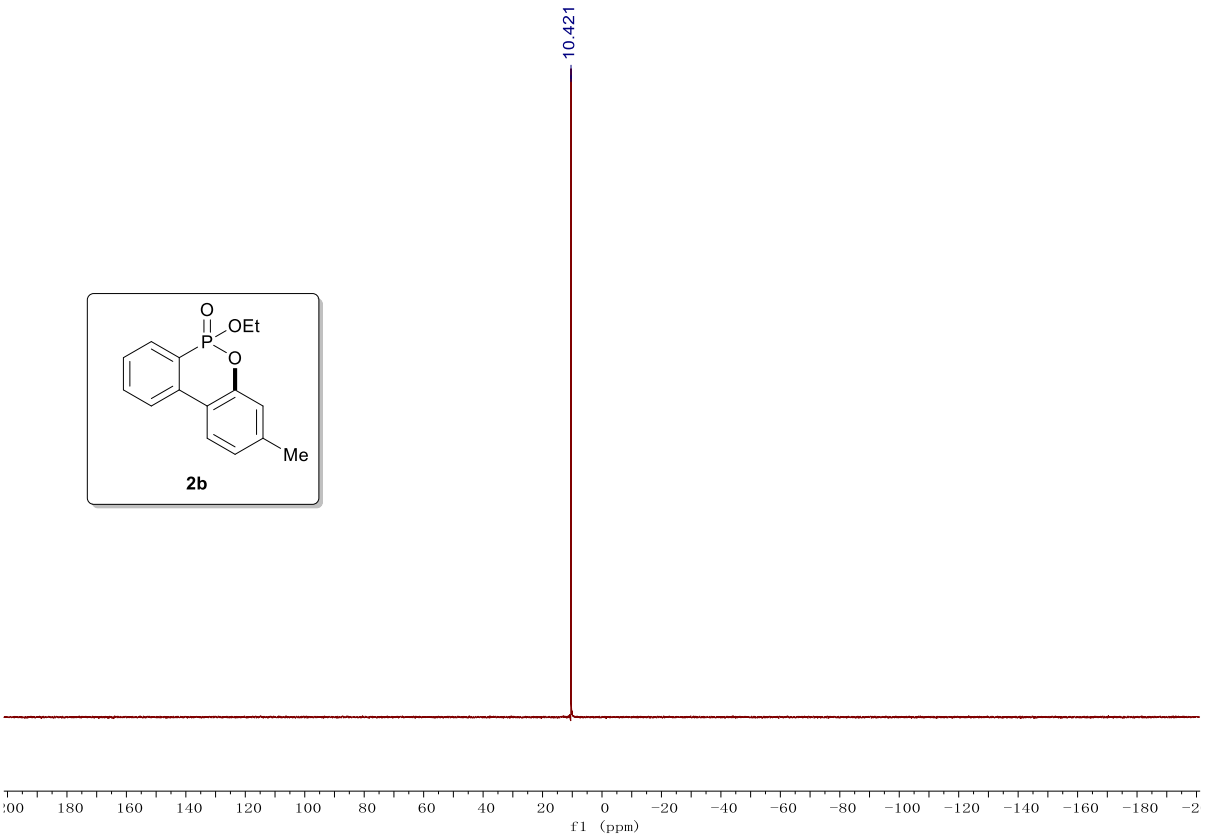
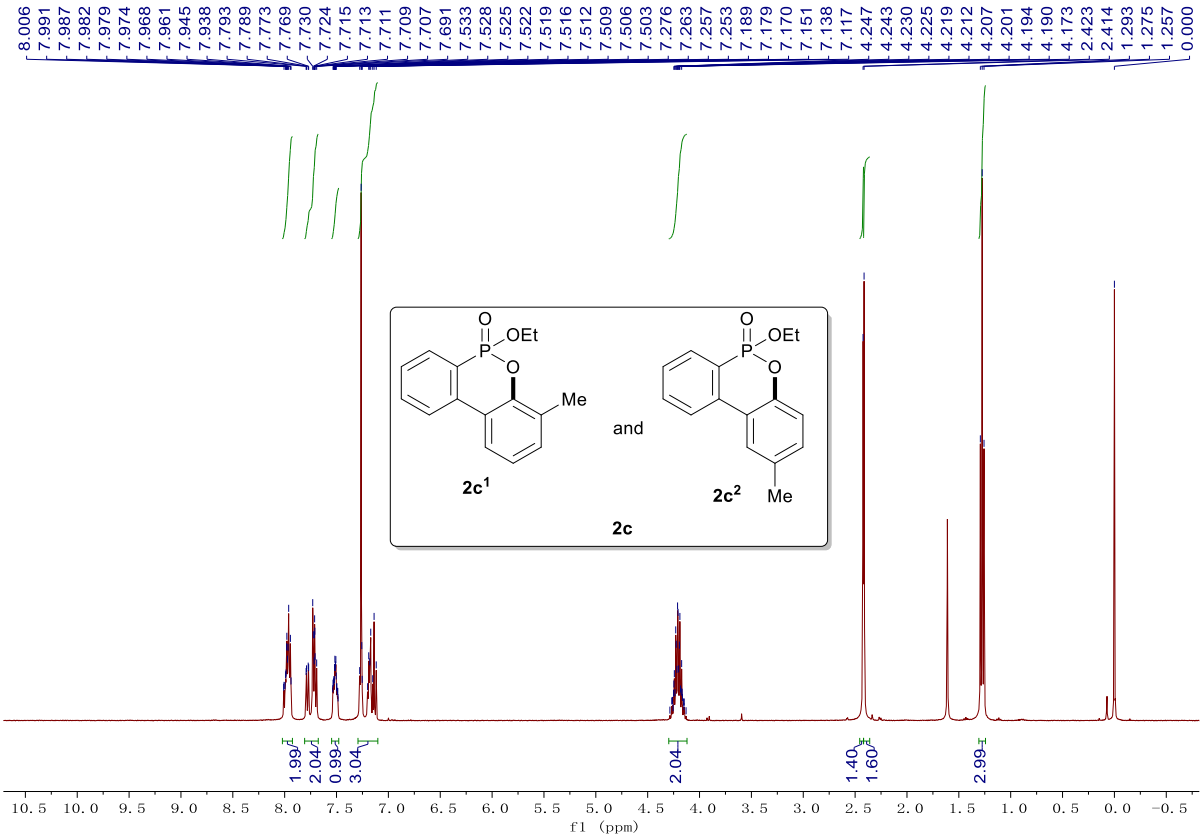
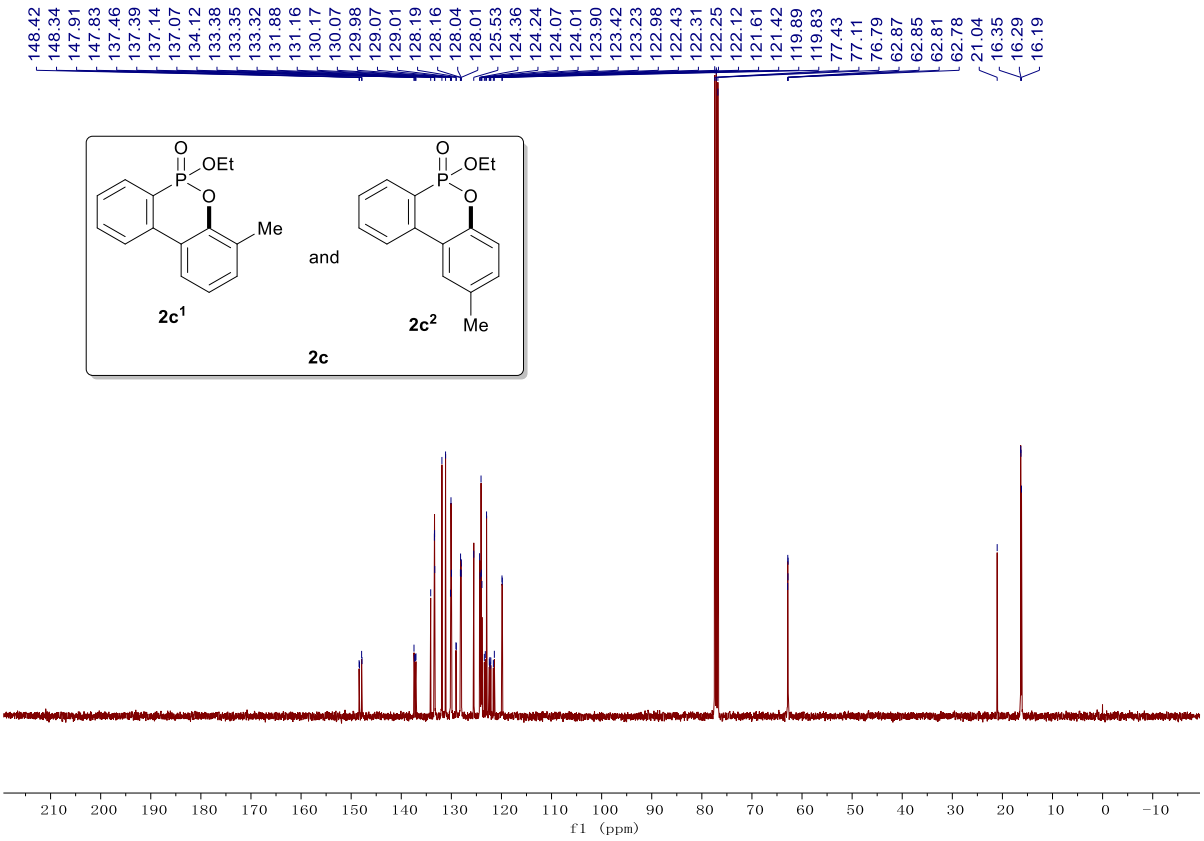
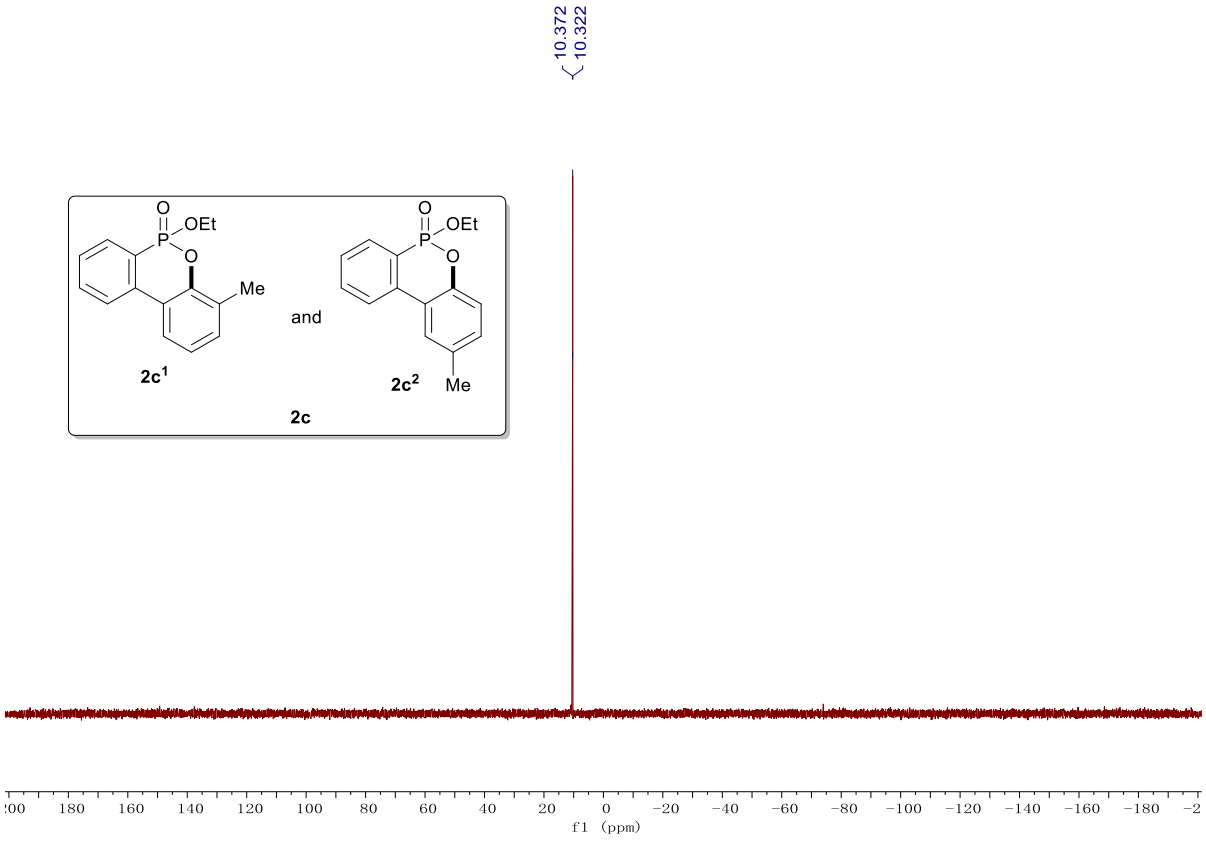
149.80
141.23
137.19
137.12
133.36
133.33
130.14
130.05
127.88
127.73
125.61
124.96
123.74
123.63
122.94
121.14
120.47
120.40
119.86
119.75
77.41
77.09
76.77
62.89
62.82
21.21
16.36
16.31
O
OEt
P
O
Me
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


10.421
O
OEt
P
O
Me
2b
200 180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −2
f1 (ppm)

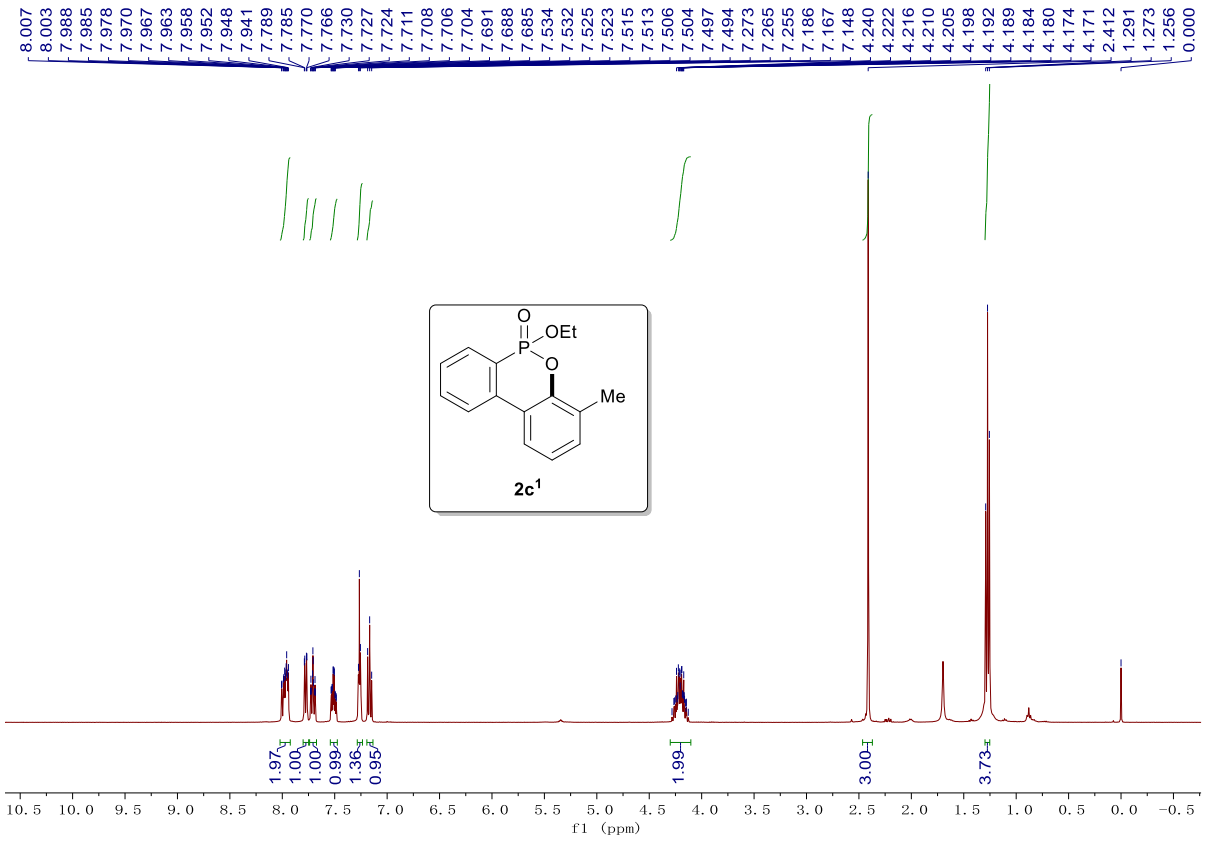
6-Ethoxy-4-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide and 6-ethoxy-2-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2c)

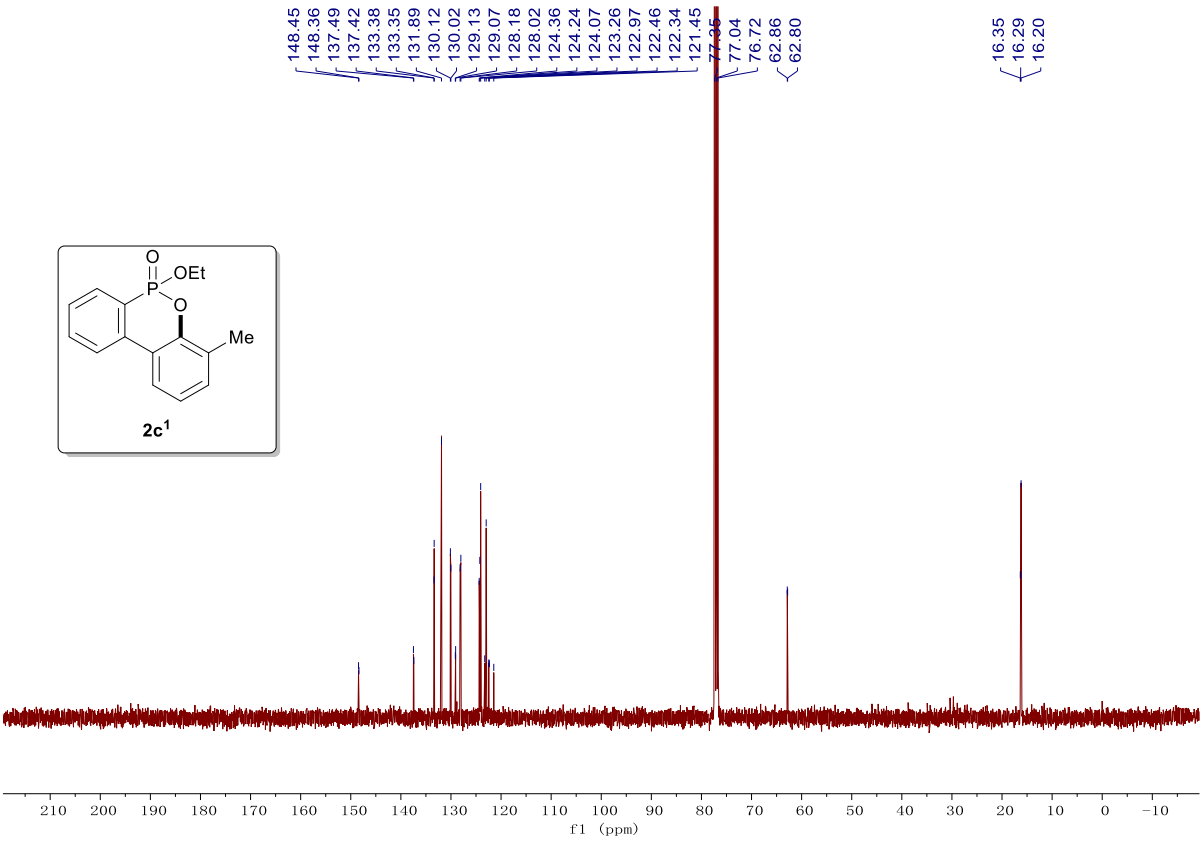


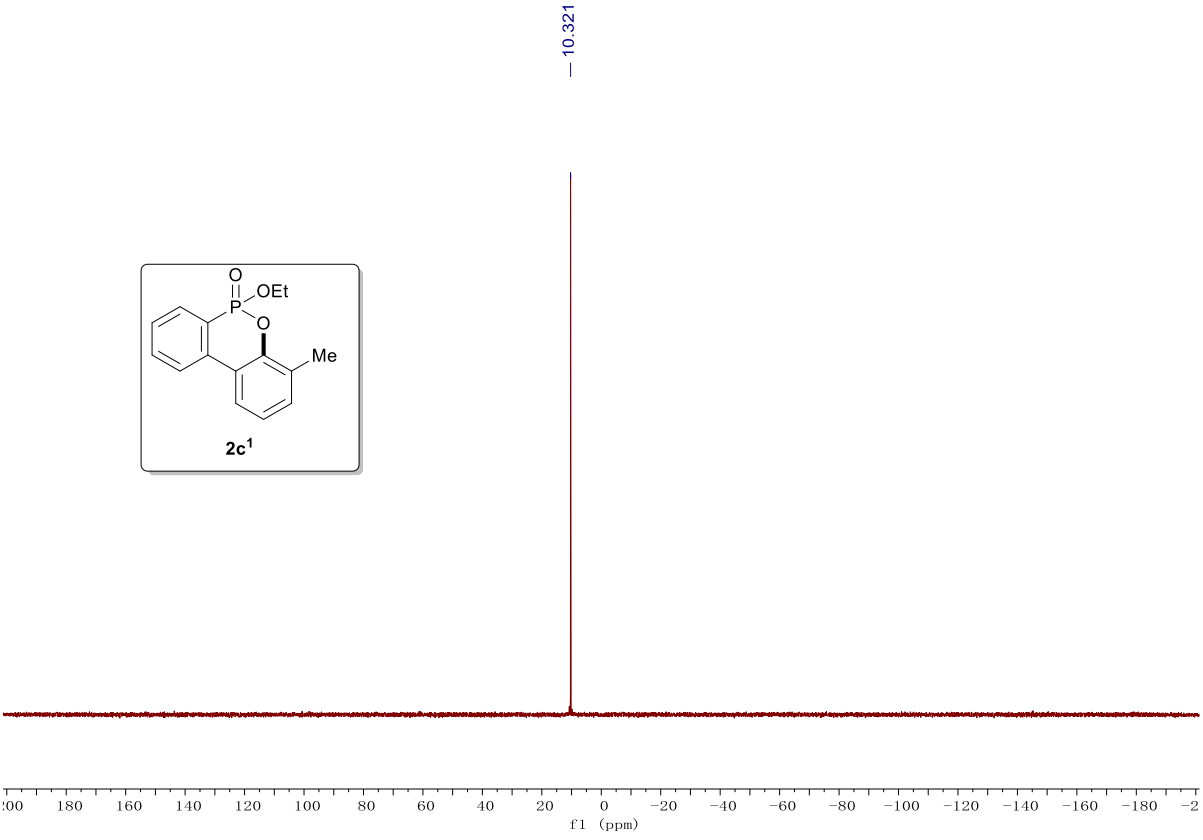




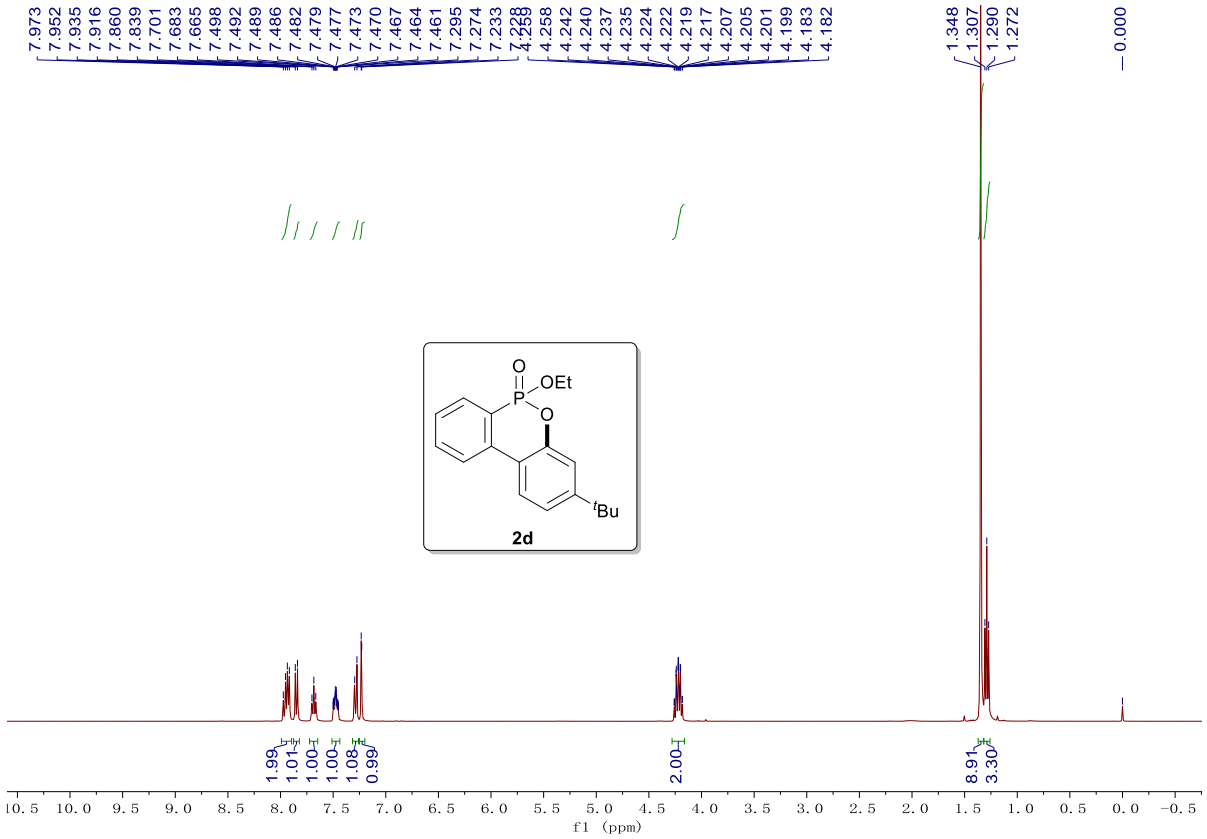
6-Ethoxy-4-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2c[1])

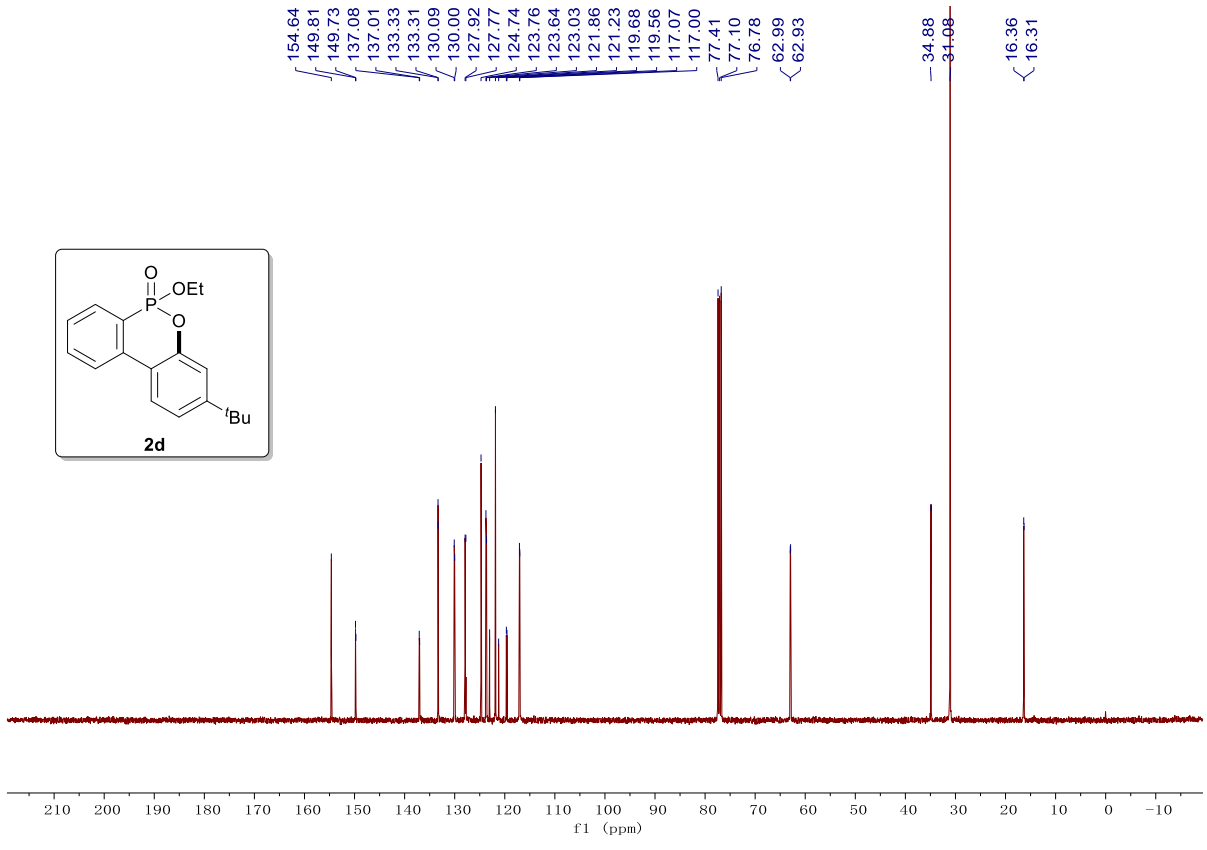


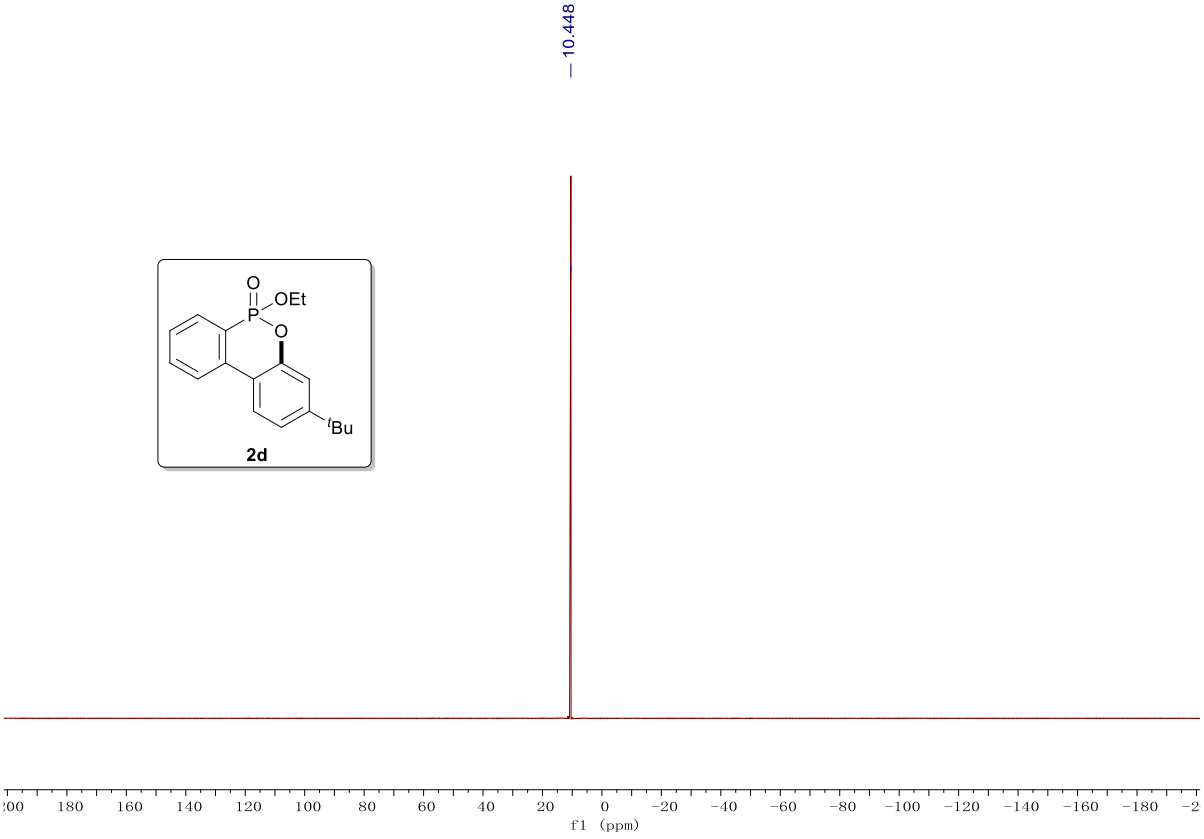

148.45
148.36
137.49
137.42
133.38
133.35
131.89
130.12
130.02
129.13
129.07
128.18
128.02
124.36
124.24
124.07
123.26
122.97
122.46
122.34
121.45
77.35
77.04
76.72
62.86
62.80
16.35
16.29
16.20
O
OEt
P
O
Me
2c1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


10.321
O
OEt
P
O
Me
2c1
:00 180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −2
f1 (ppm)

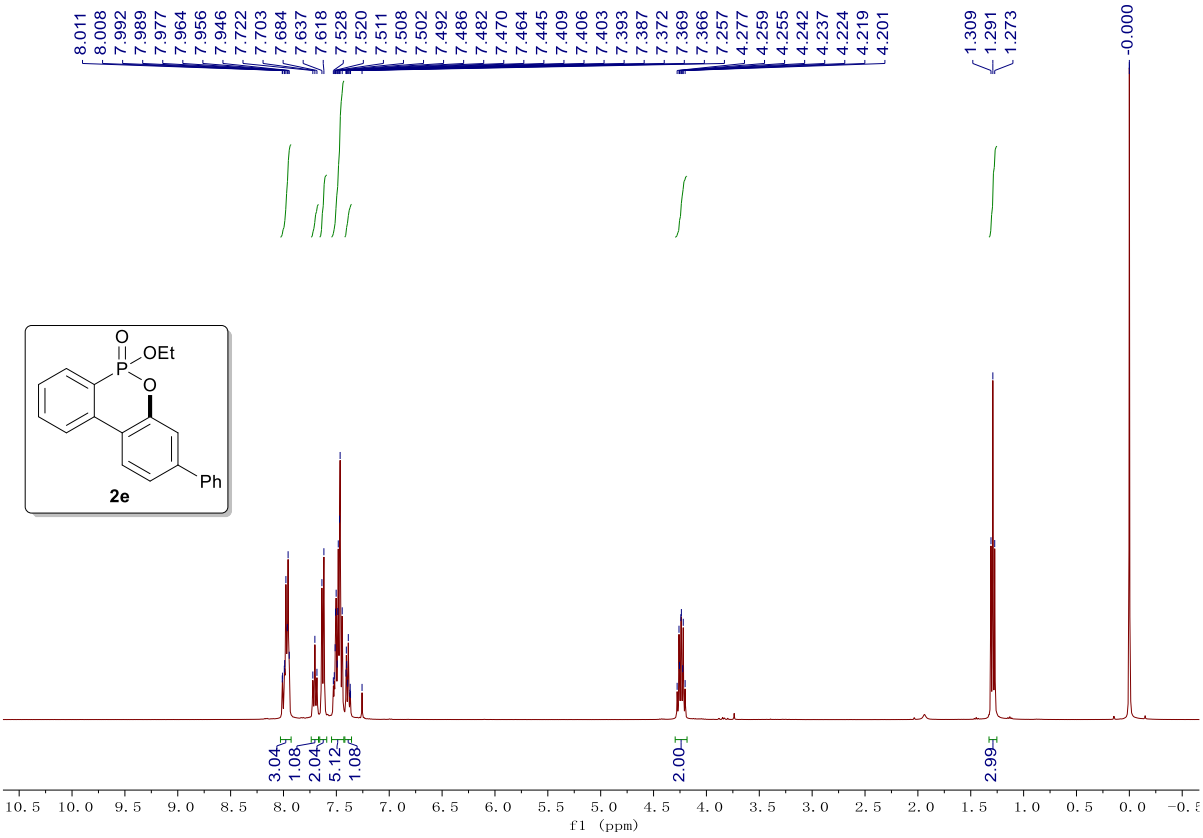
3-(*tert*-Butyl)-6-ethoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2d)

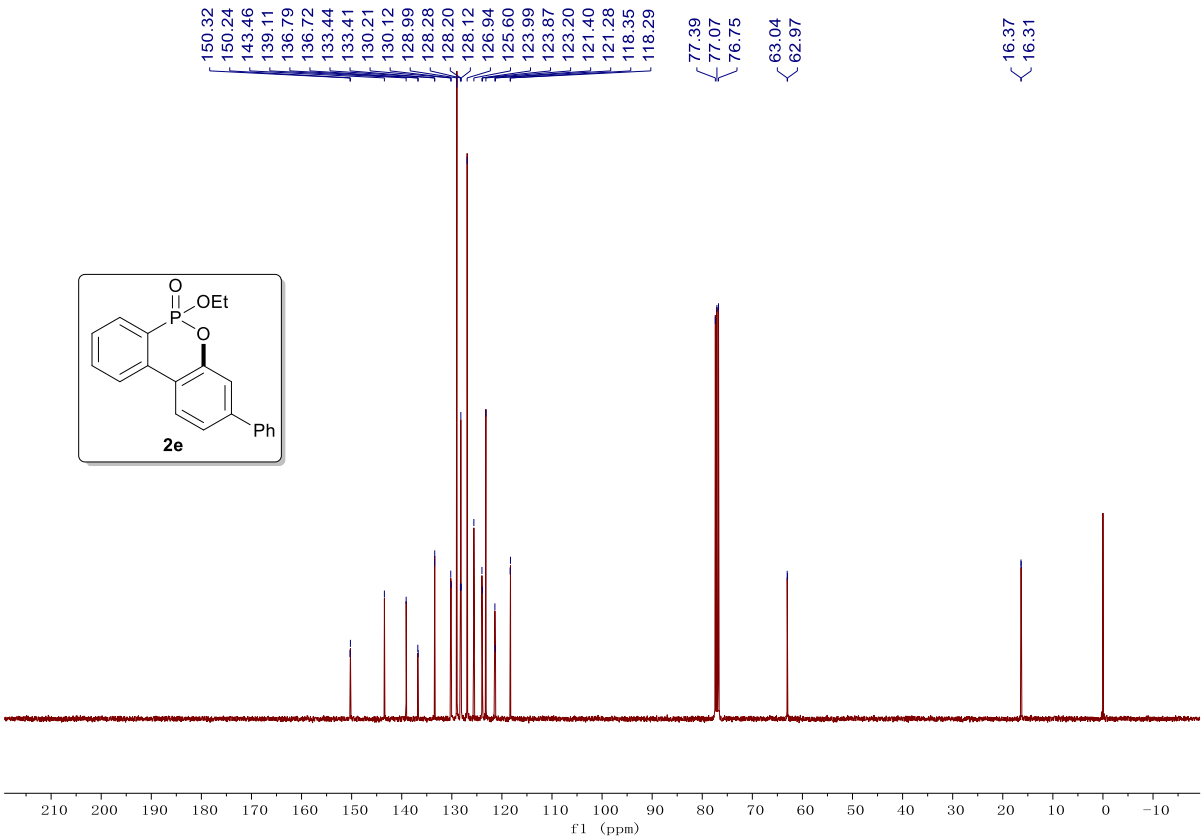






6-Ethoxy-3-phenyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2e)

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150.24
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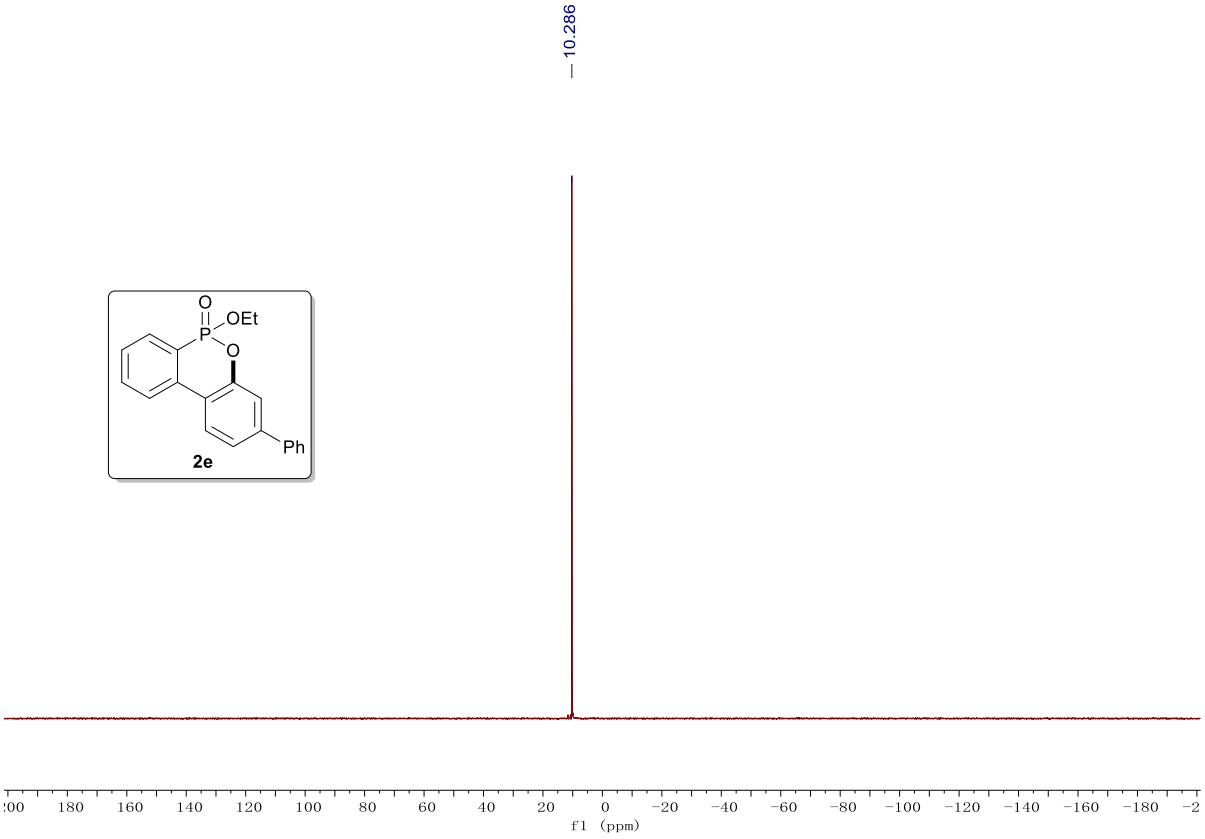
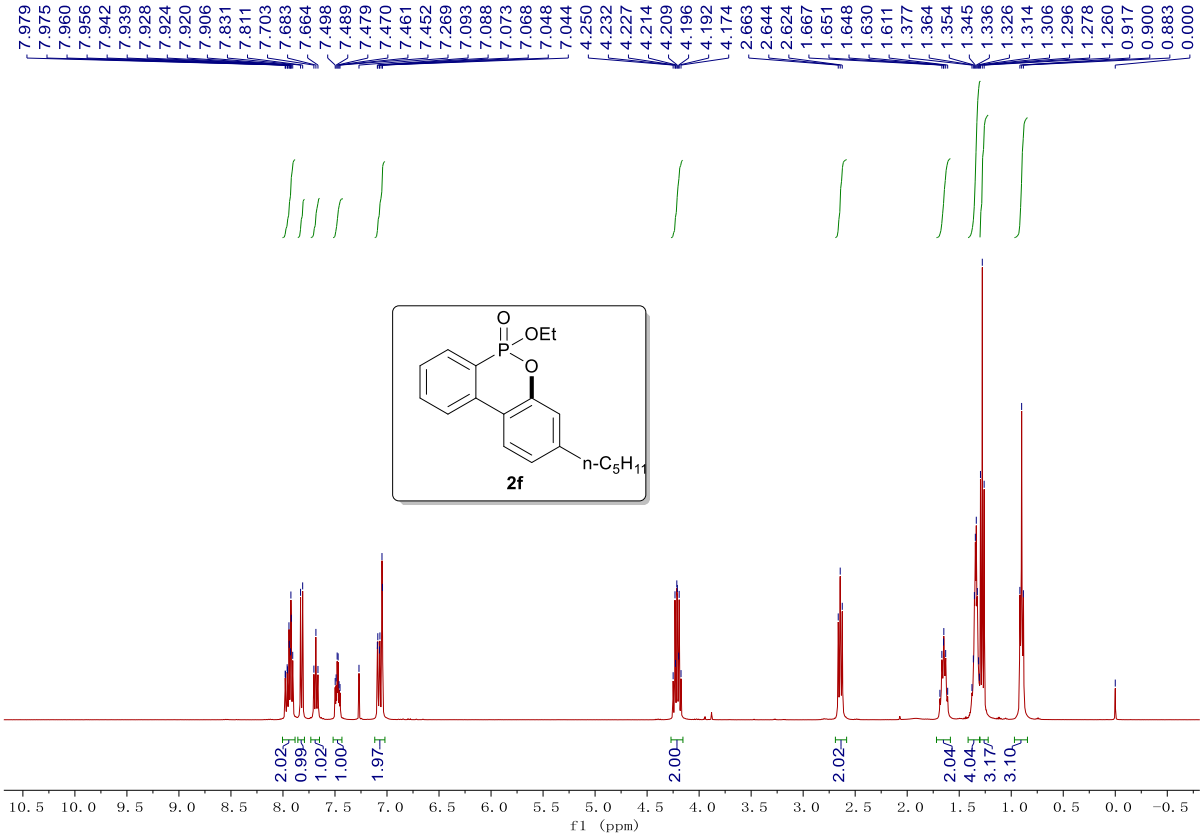
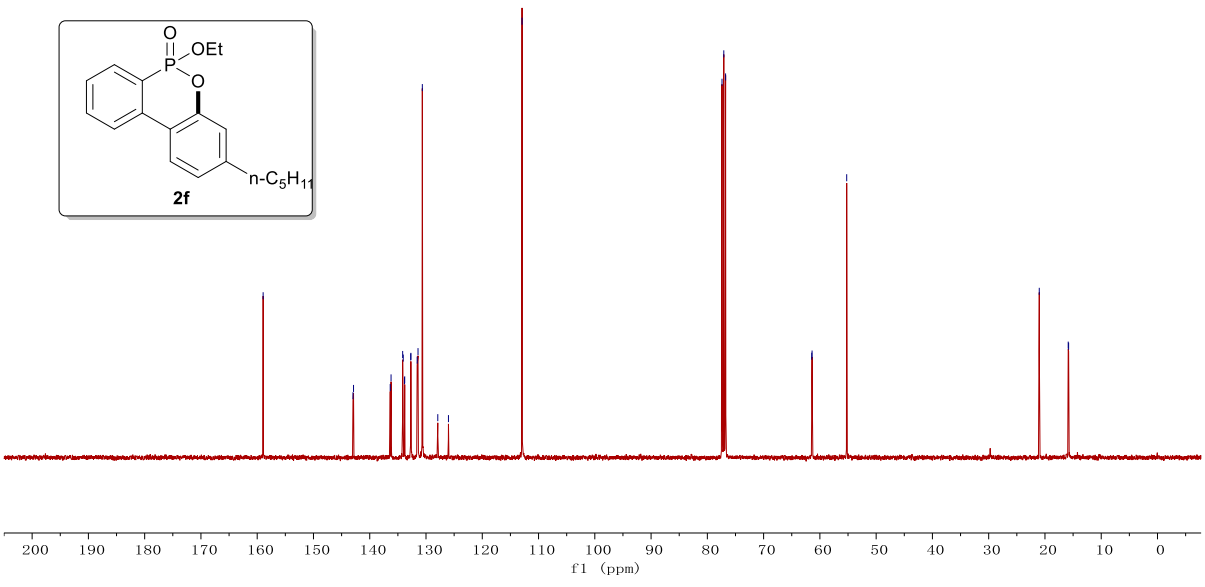
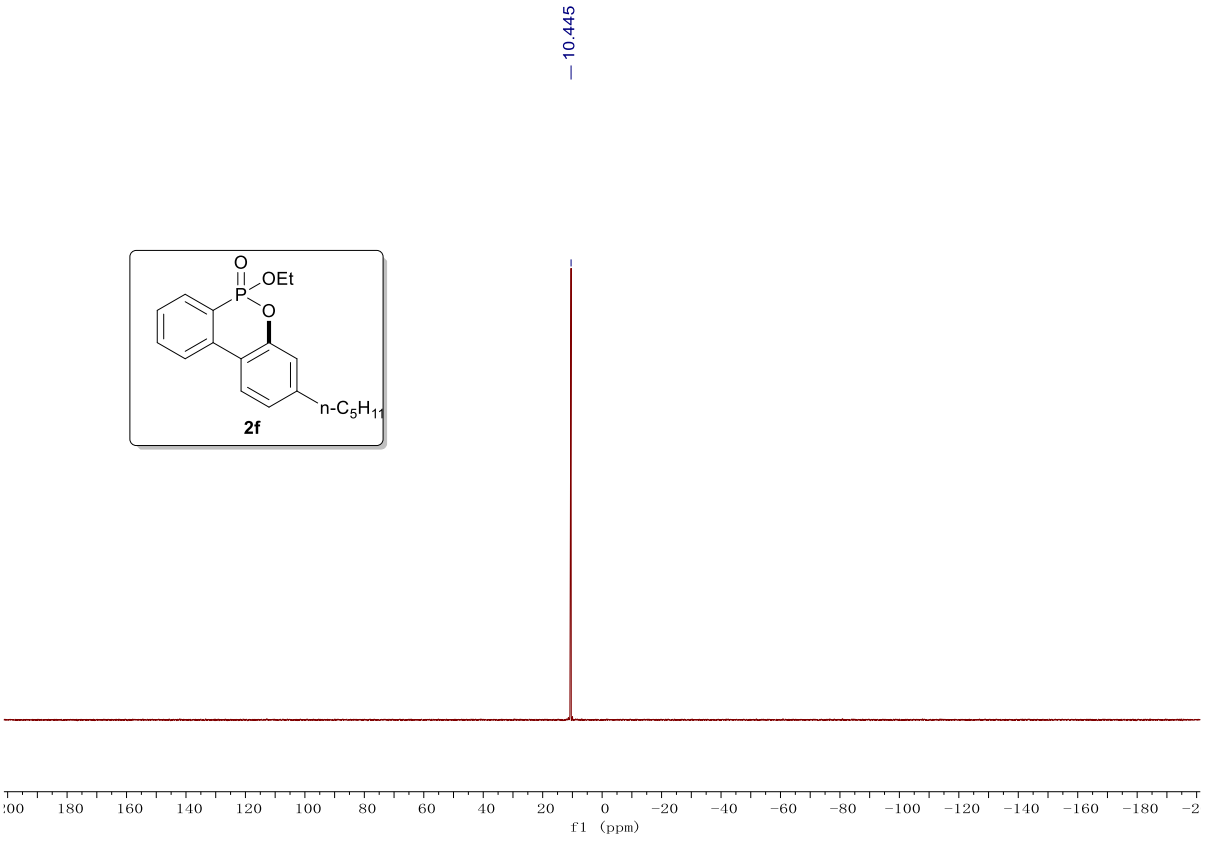
139.11
136.79
136.72
133.44
133.41
130.21
130.12
128.99
128.28
128.20
128.12
126.94
125.60
123.99
123.87
123.20
121.40
121.28
118.35
118.29
77.39
77.07
76.75
63.04
62.97
16.37
16.31
O
OEt
P
O
Ph
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


10.286
O
OEt
P
O
Ph
2e
180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −2
f1 (ppm)

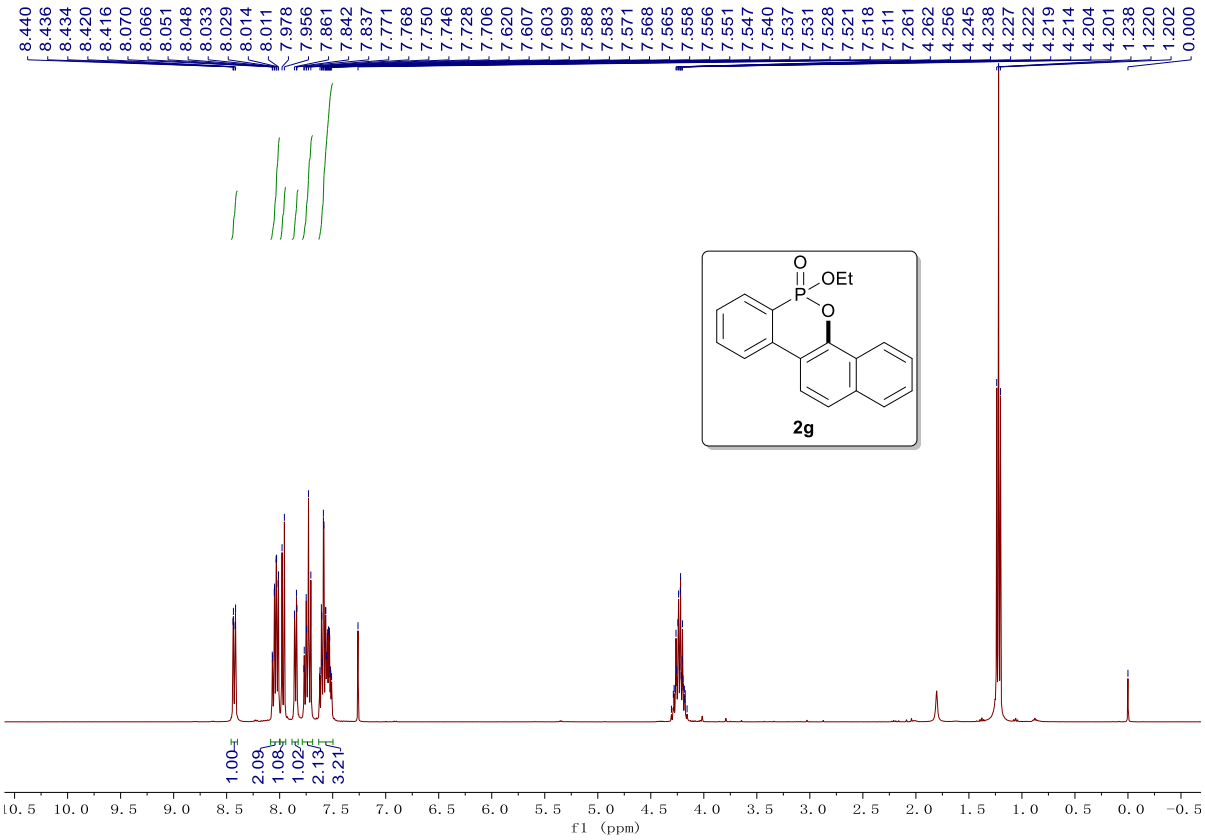
6-Ethoxy-3-pentyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2f)

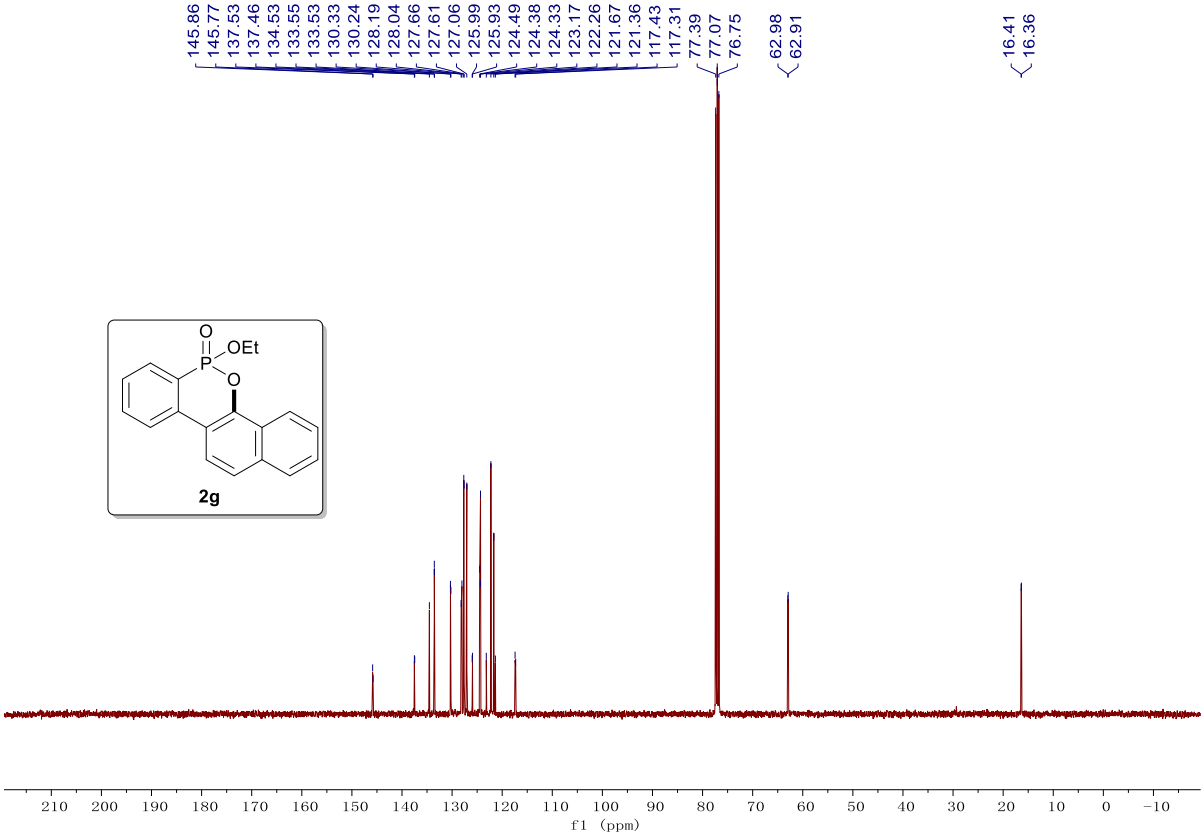






6-Ethoxybenzo[c]naphtho[2,1-e][1,2]oxaphosphinine 6-oxide (2g)

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137.46
134.53
133.55
133.53
130.33
130.24
128.19
128.04
127.66
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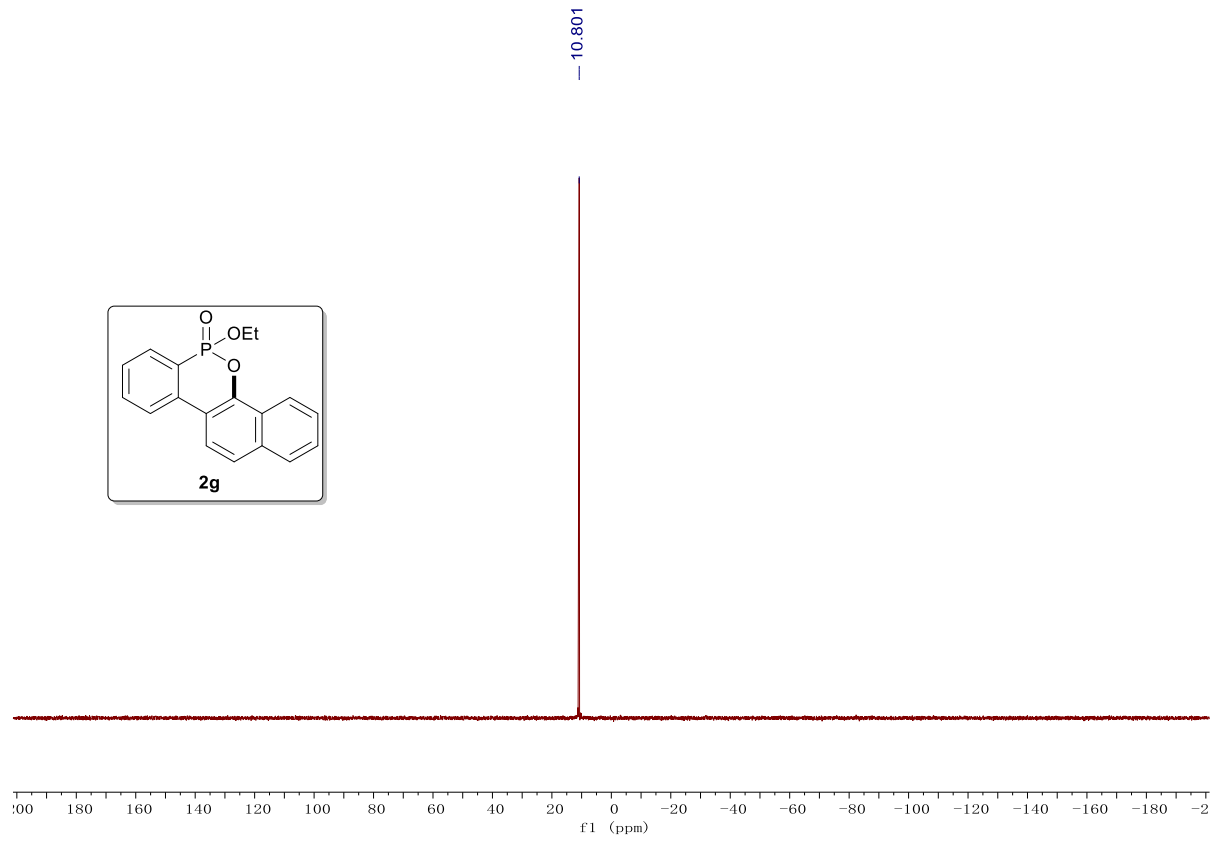
127.06
125.99
125.93
124.49
124.38
124.33
123.17
122.26
121.67
121.36
117.43
117.31
77.39
77.07
76.75
62.98
62.91
16.41
16.36
O
OEt
P
O
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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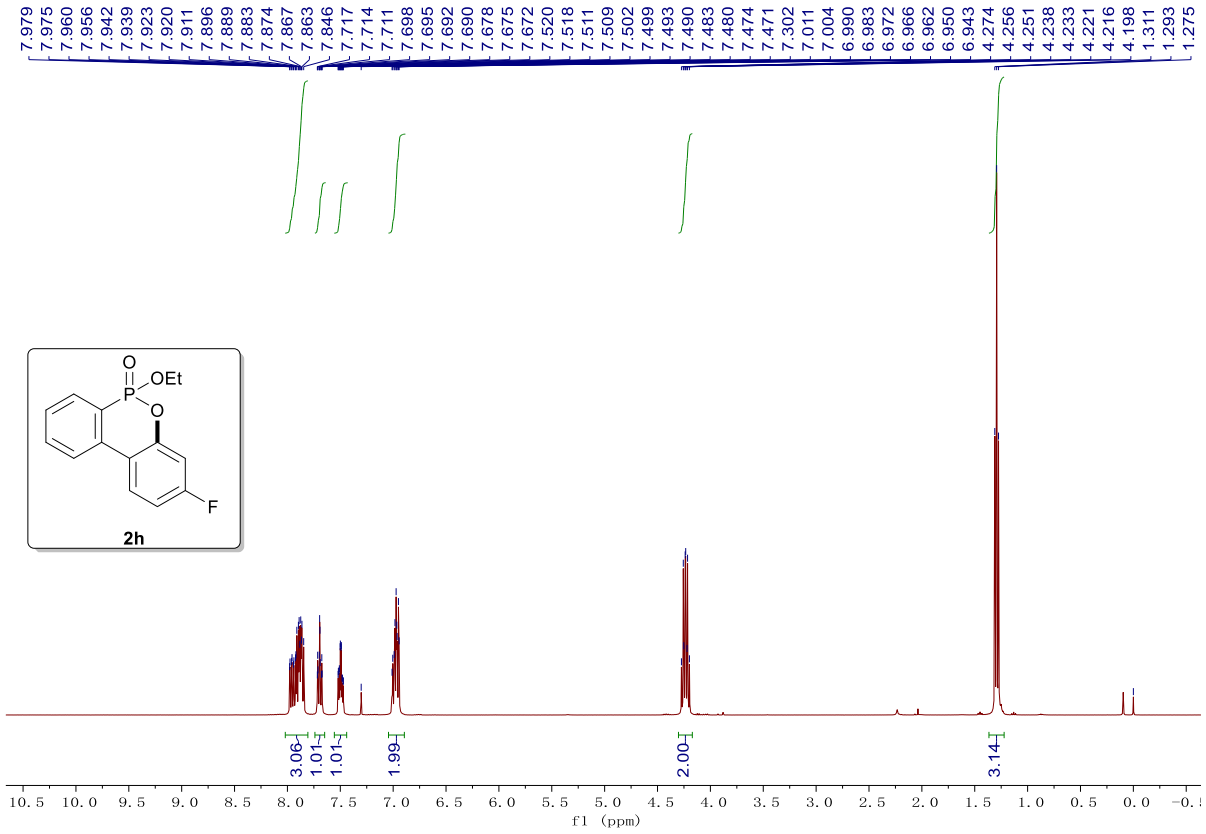
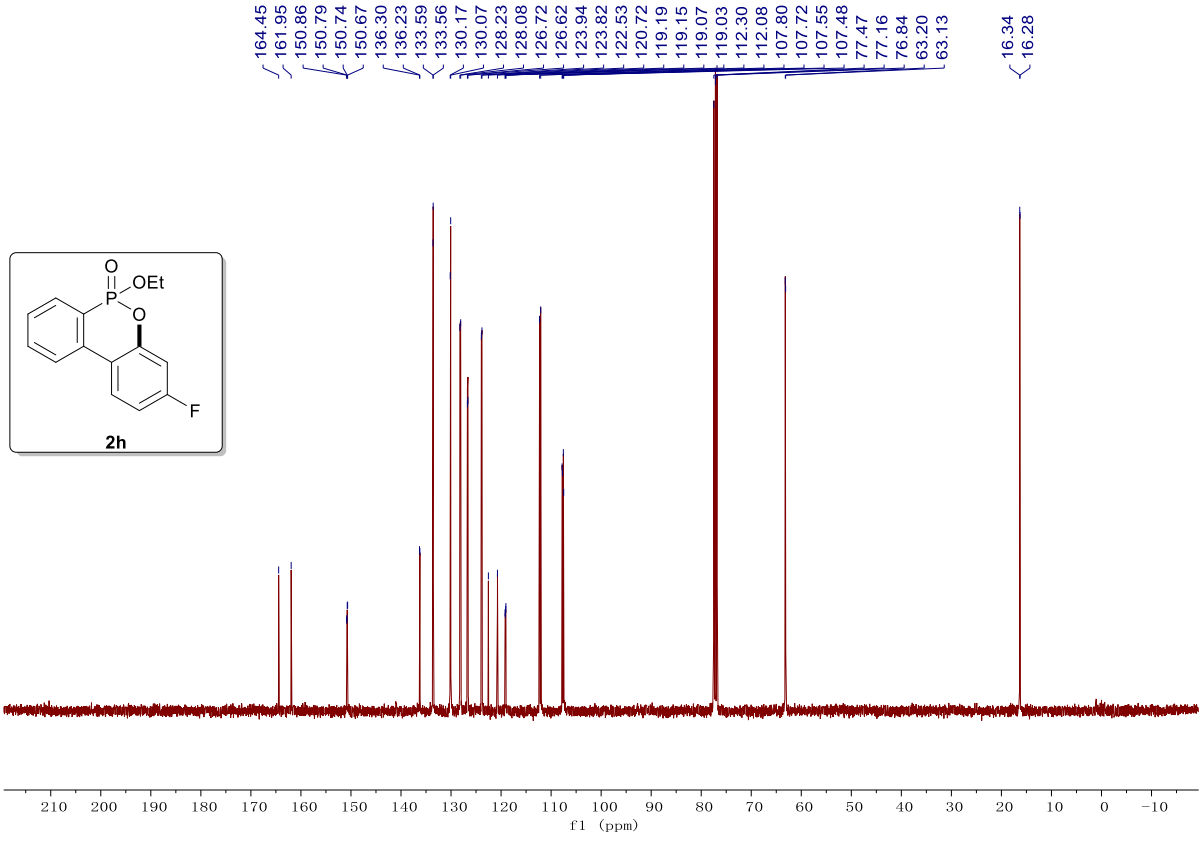
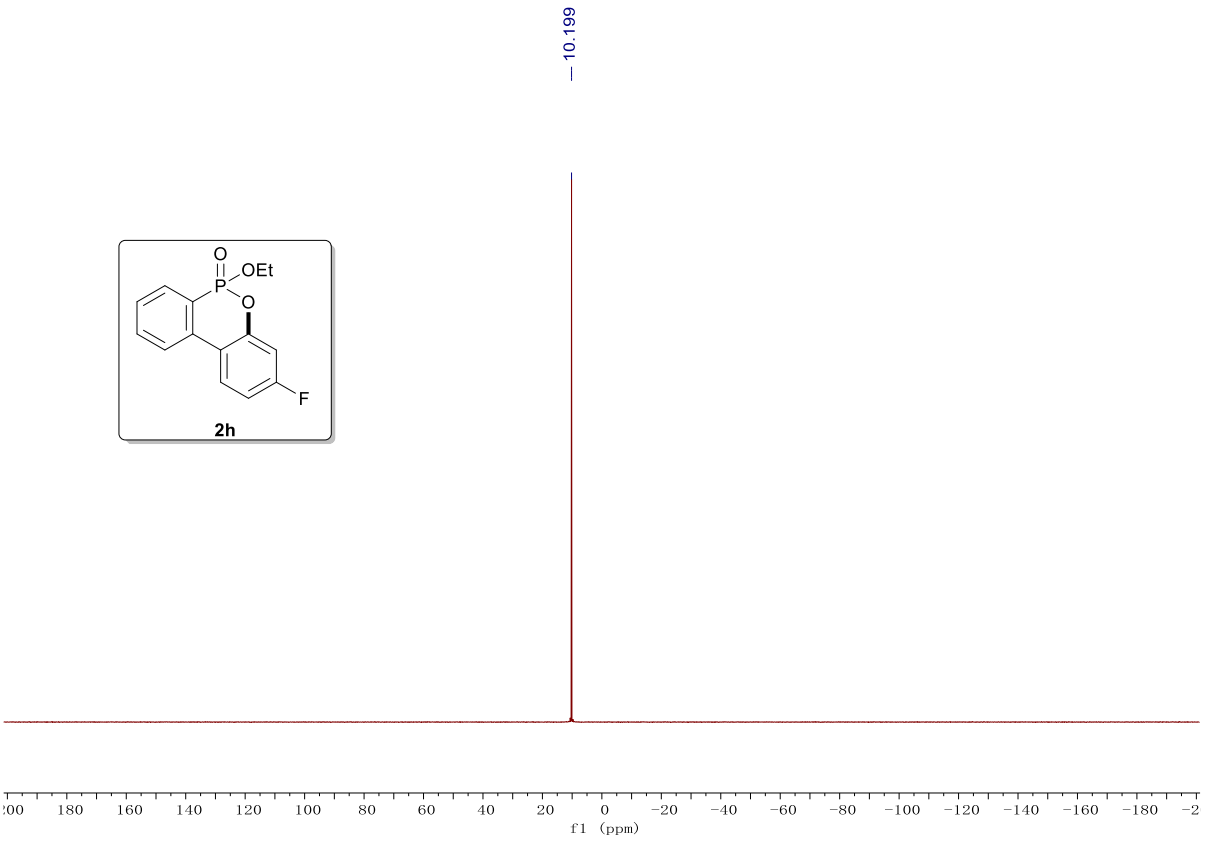
O
OEt
P
O
2g
00 180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −2
f1 (ppm)

6-Ethoxy-3-fluorodibenzo[c,e][1,2]oxaphosphinine 6-oxide (2h)



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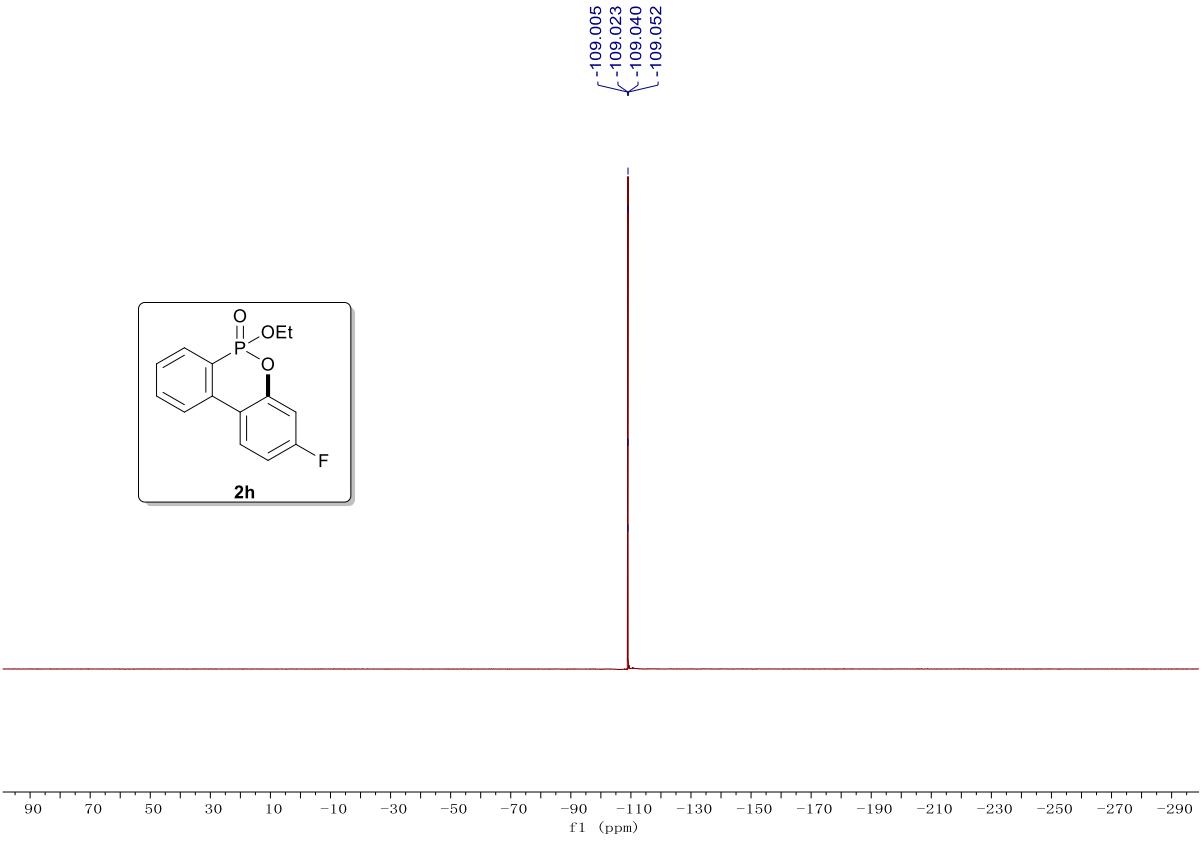
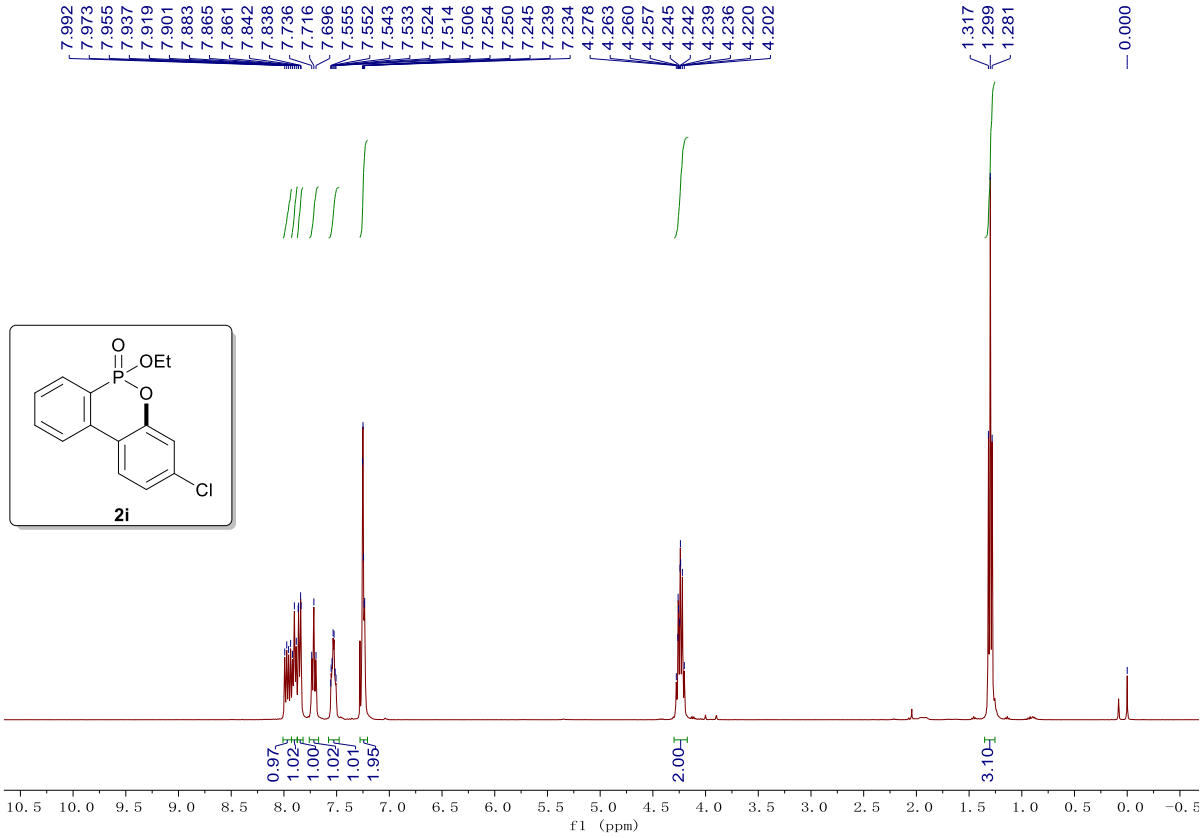
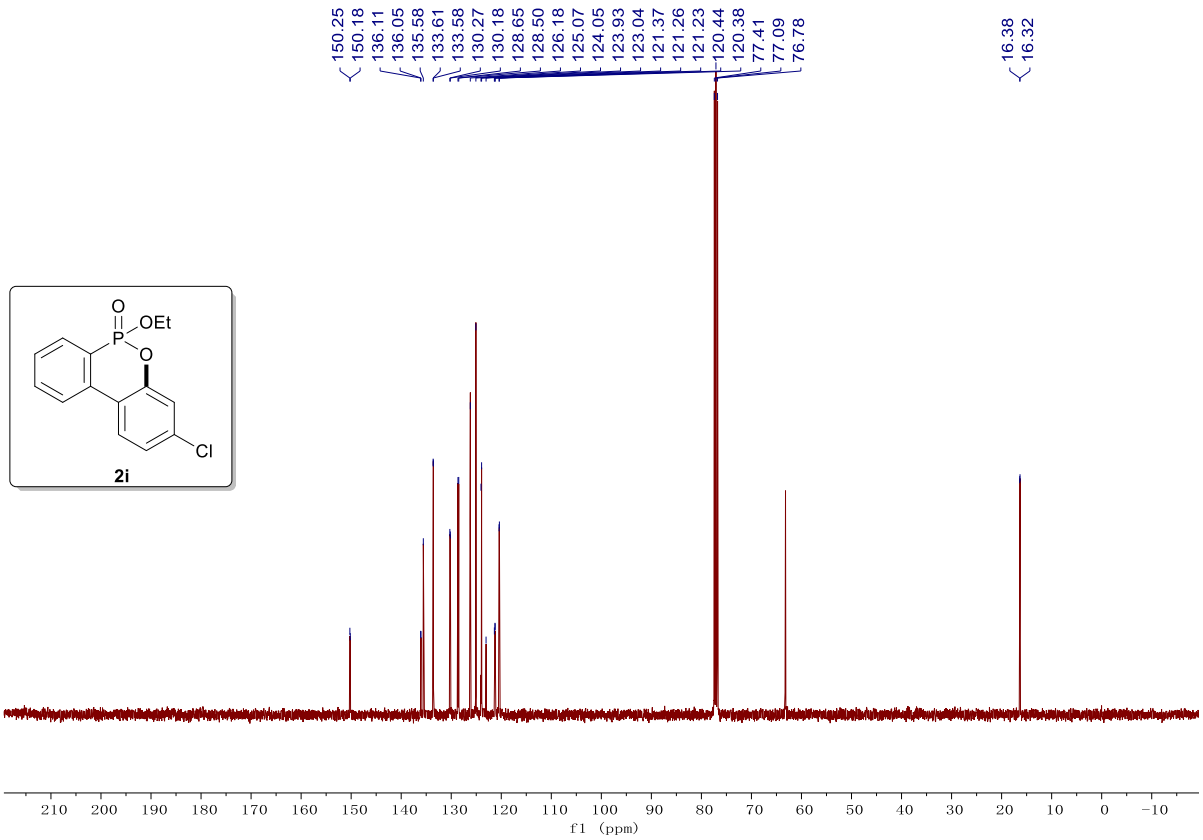
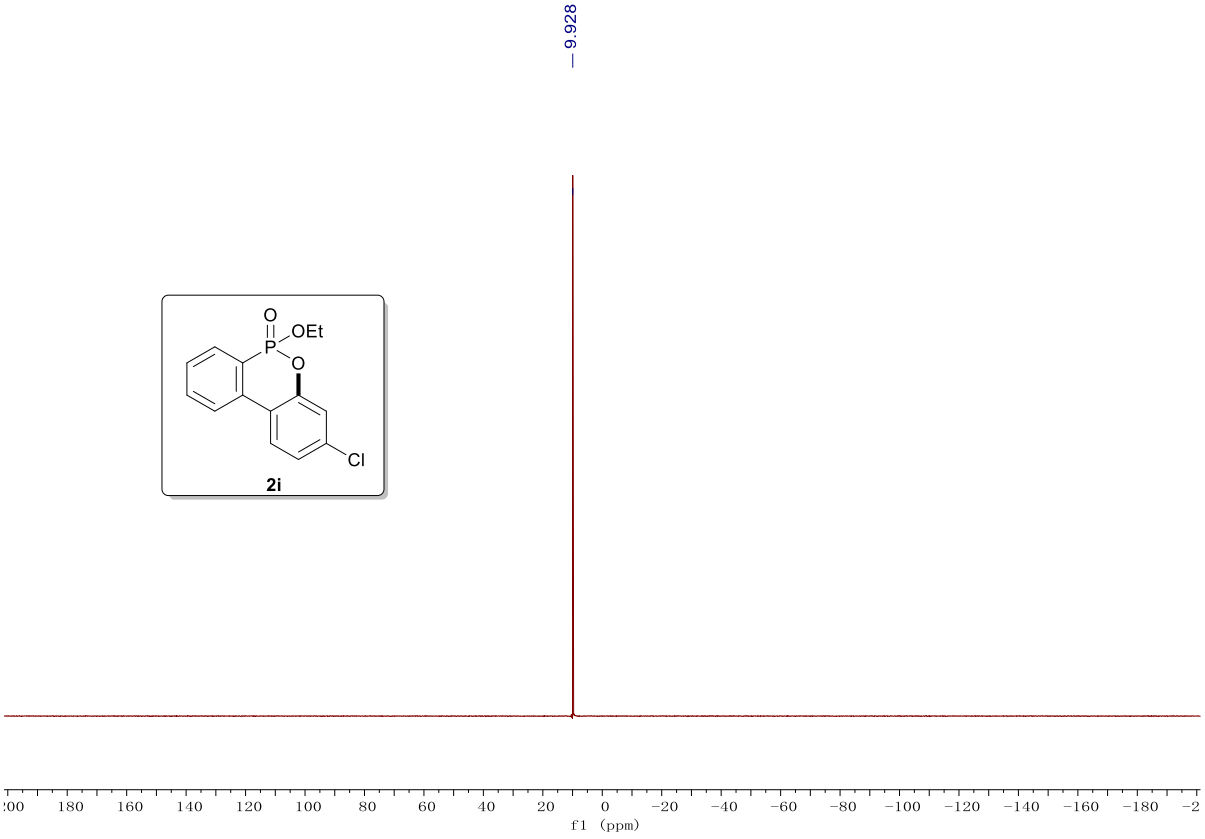
O
OEt
P
O
F
2h
f1 (ppm)


-109.005
-109.023
-109.040
-109.052
O
OEt
P
O
F
2h
f1 (ppm)

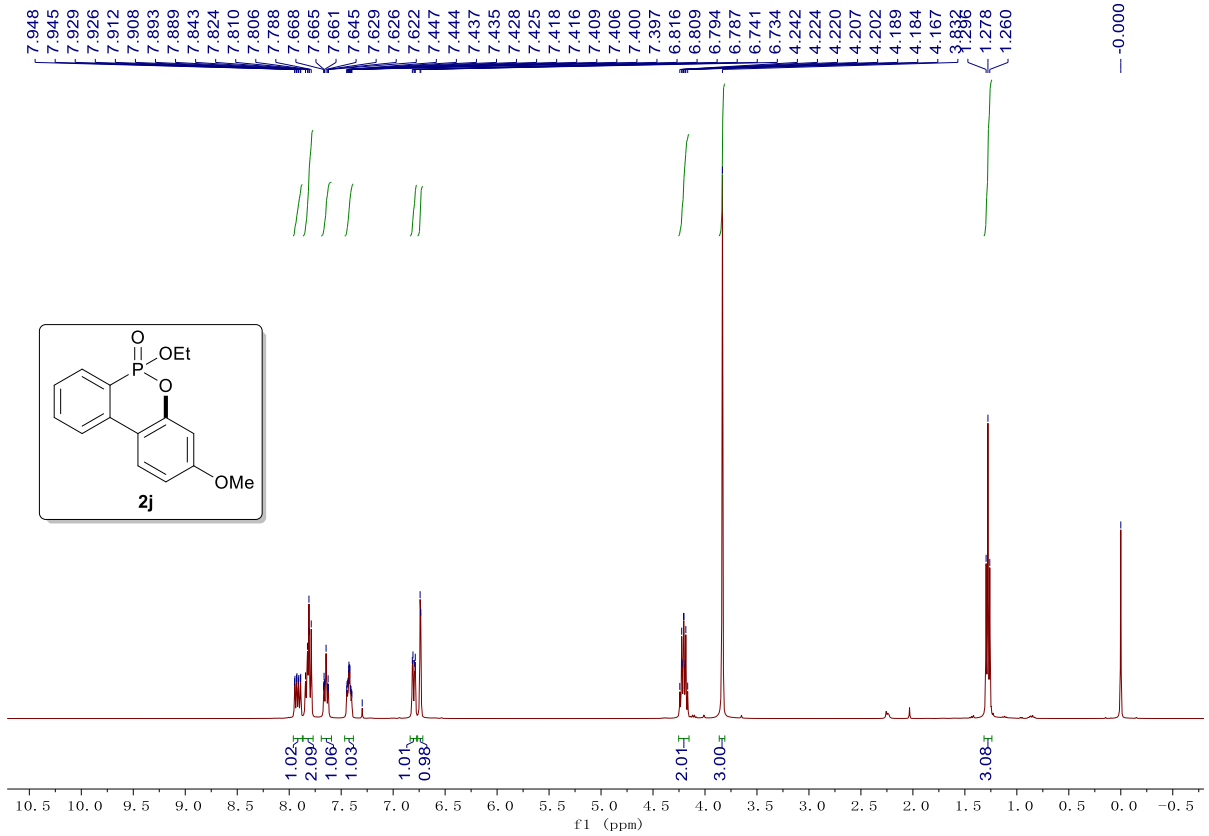
3-Chloro-6-ethoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2i)

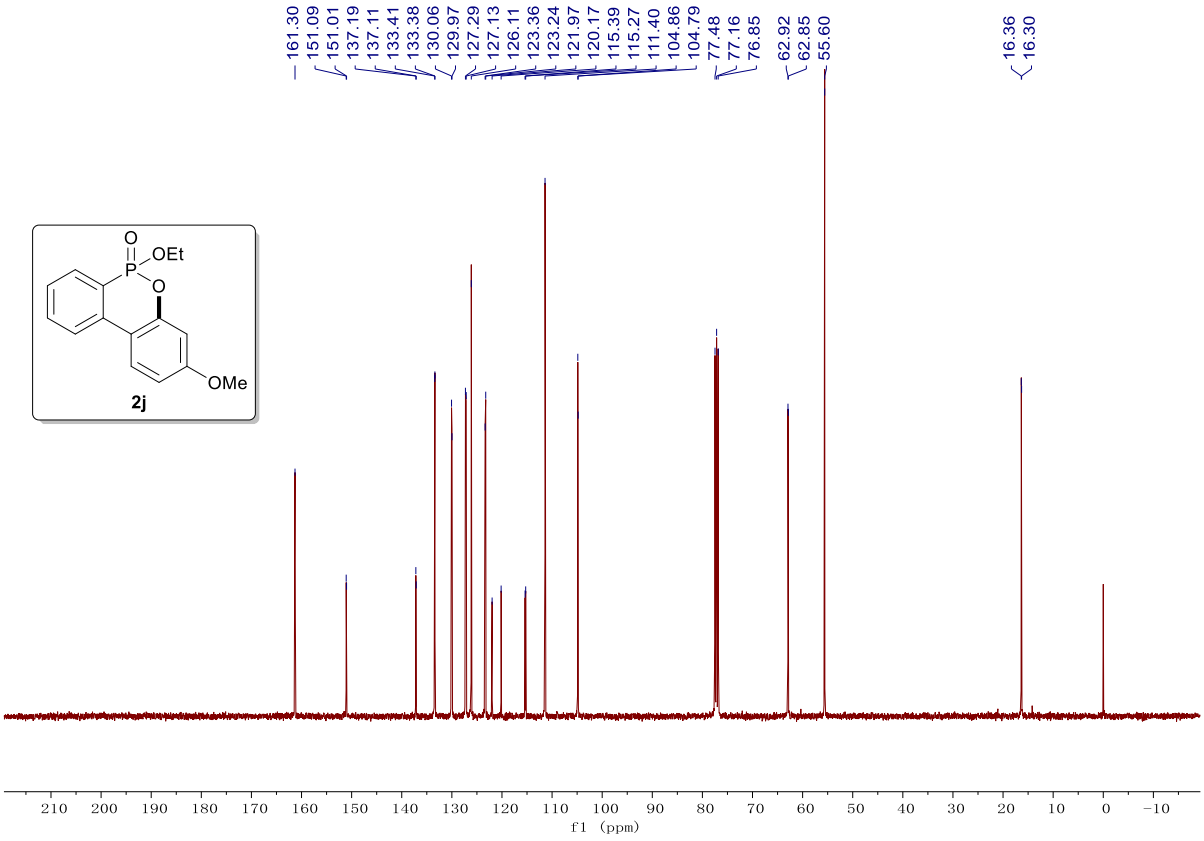


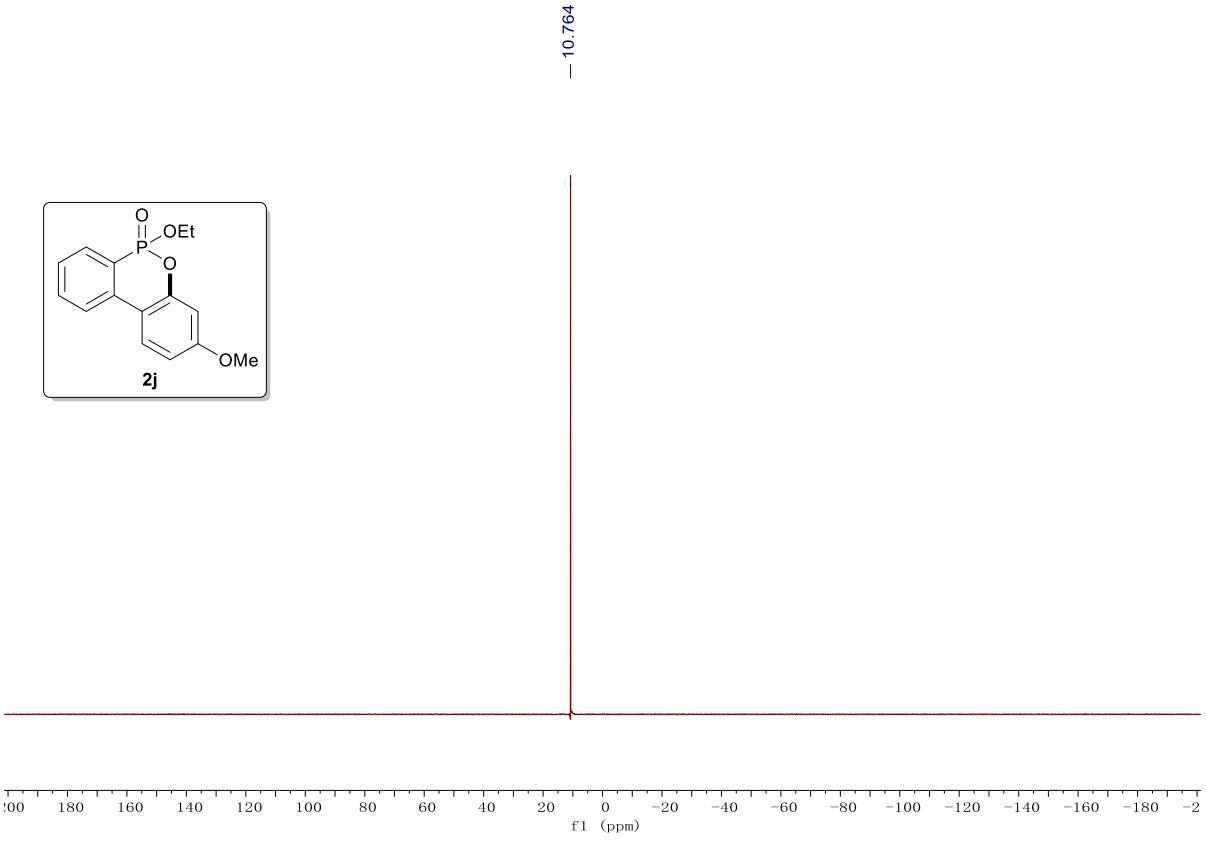




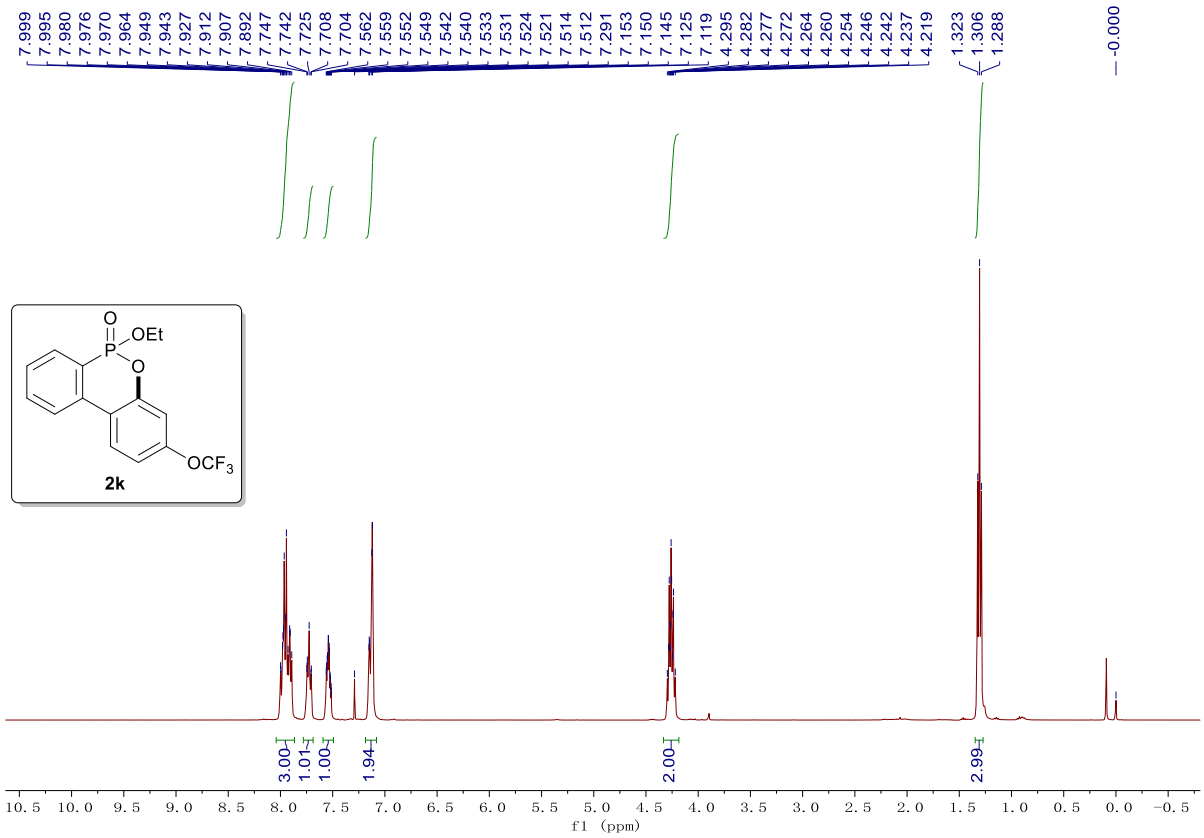
6-Ethoxy-3-methoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2j)

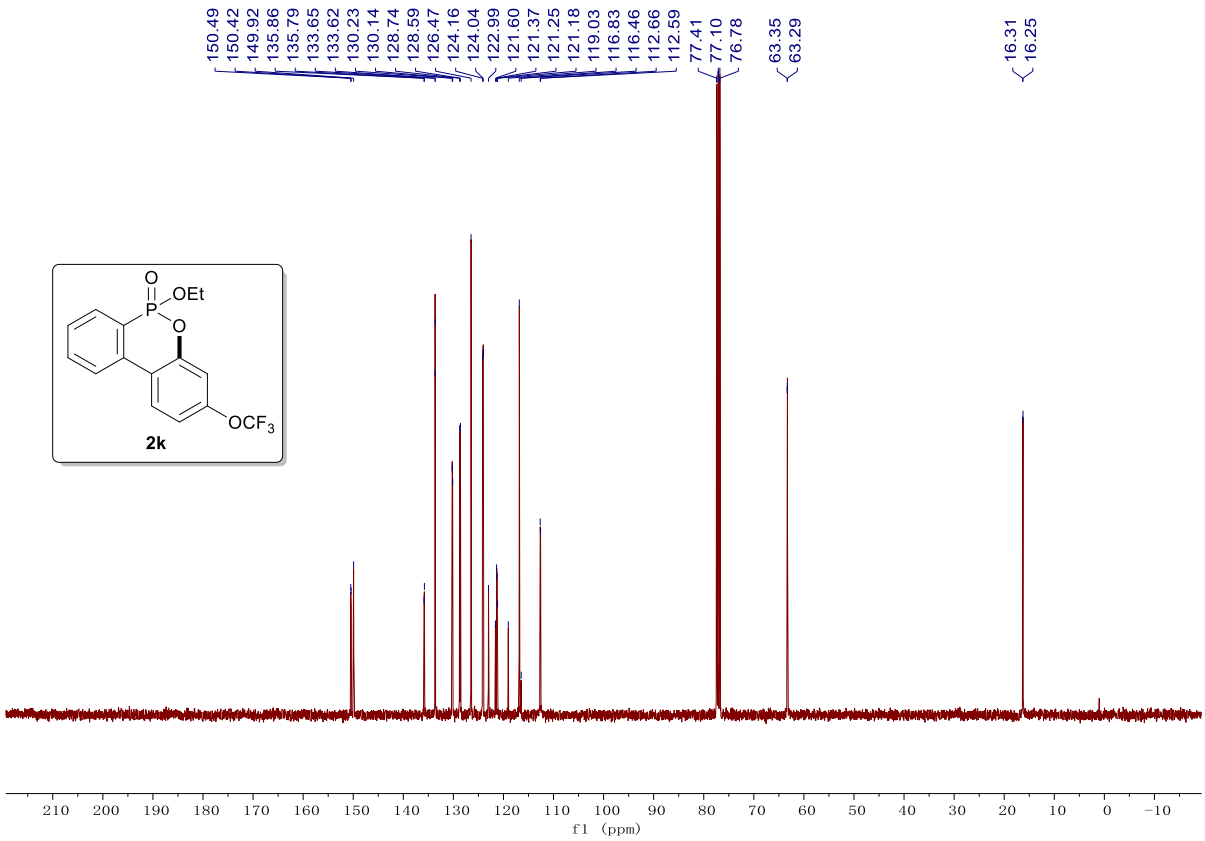


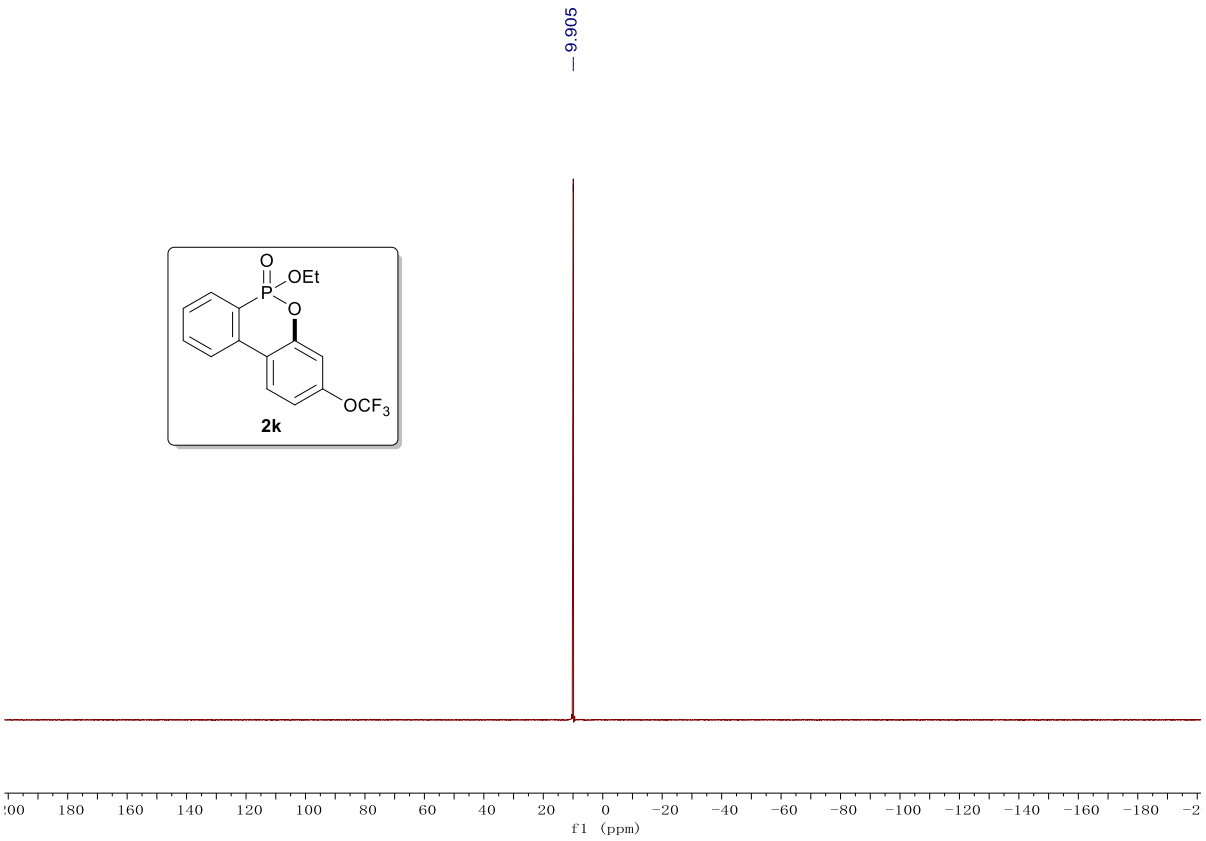

161.30
151.09
151.01
137.19
137.11
133.41
133.38
130.06
129.97
127.29
127.13
126.11
123.36
123.24
121.97
120.17
115.39
115.27
111.40
104.86
104.79
77.48
77.16
76.85
62.92
62.85
55.60
16.36
16.30
O
OEt
P
O
OMe
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

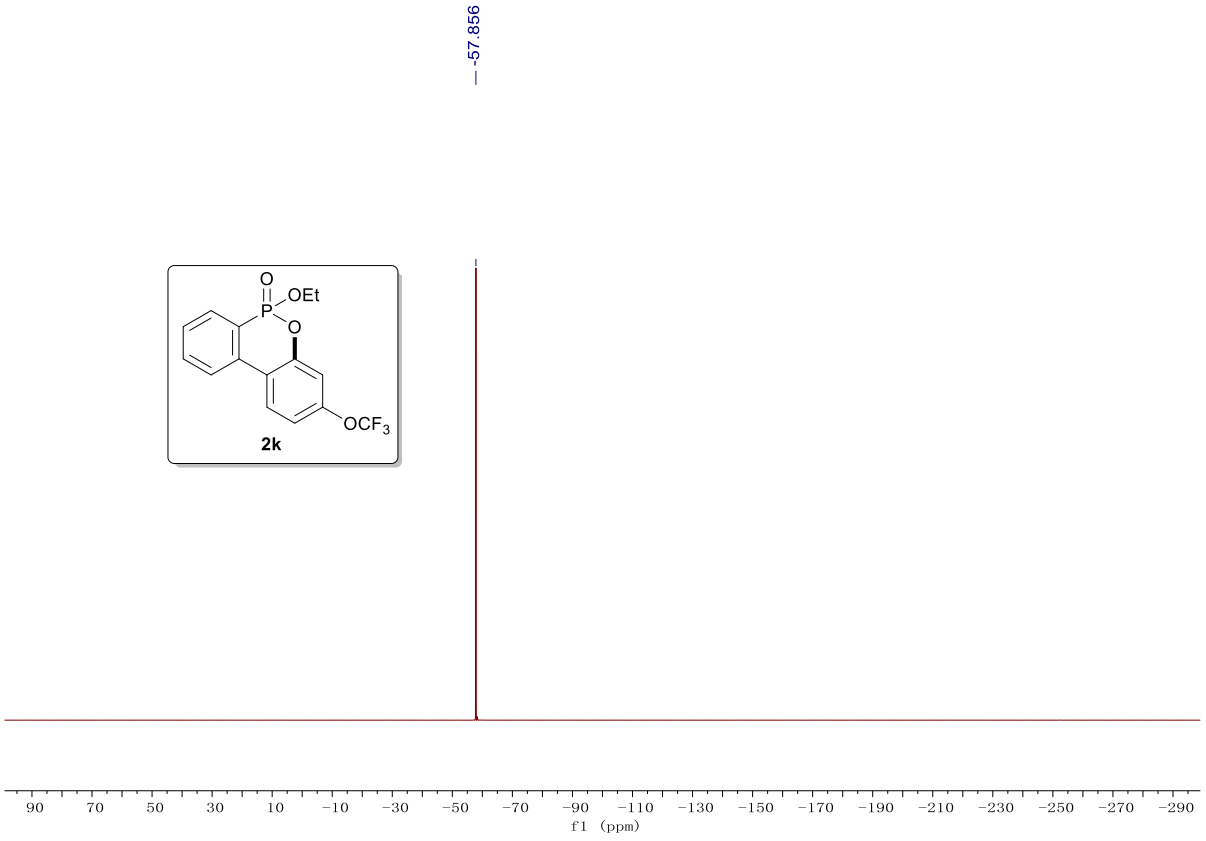

10.764
O
OEt
P
O
OMe
2j
200 180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −2
f1 (ppm)

6-Ethoxy-3-(trifluoromethoxy)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (2k)

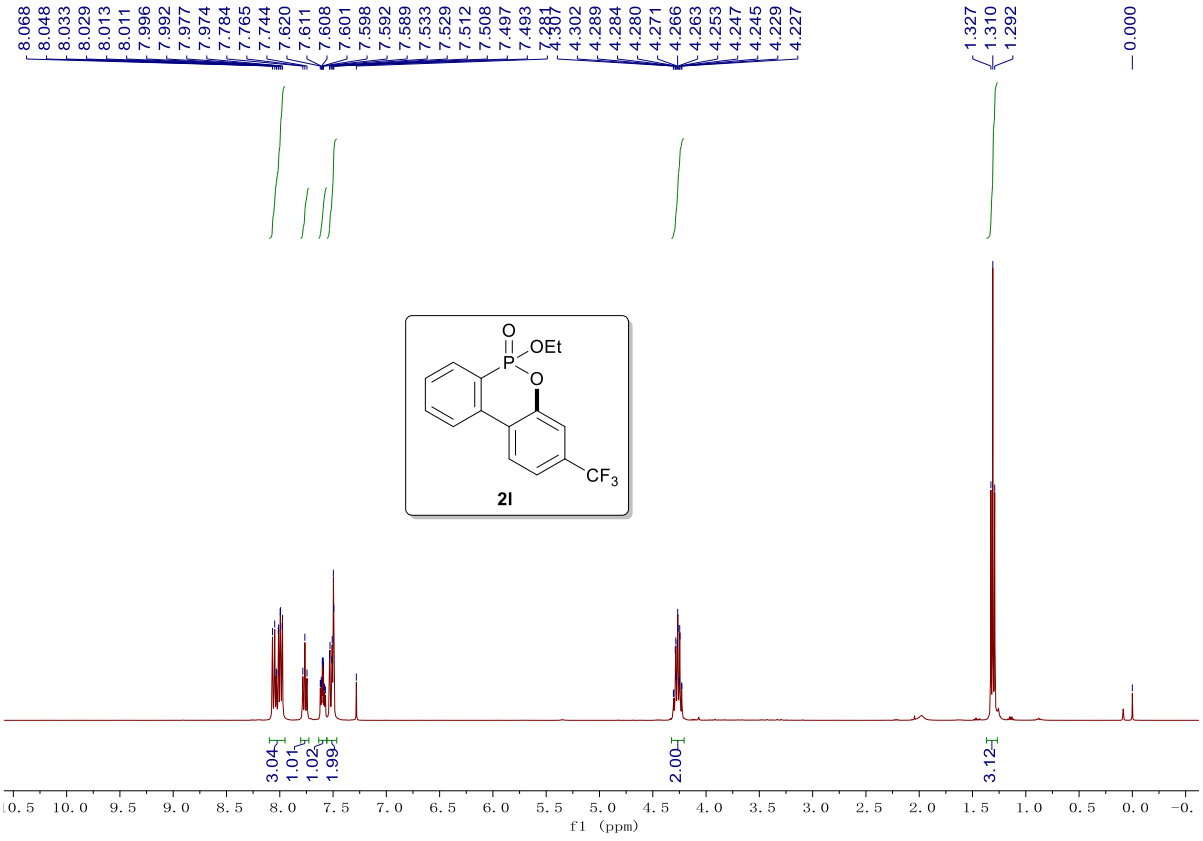


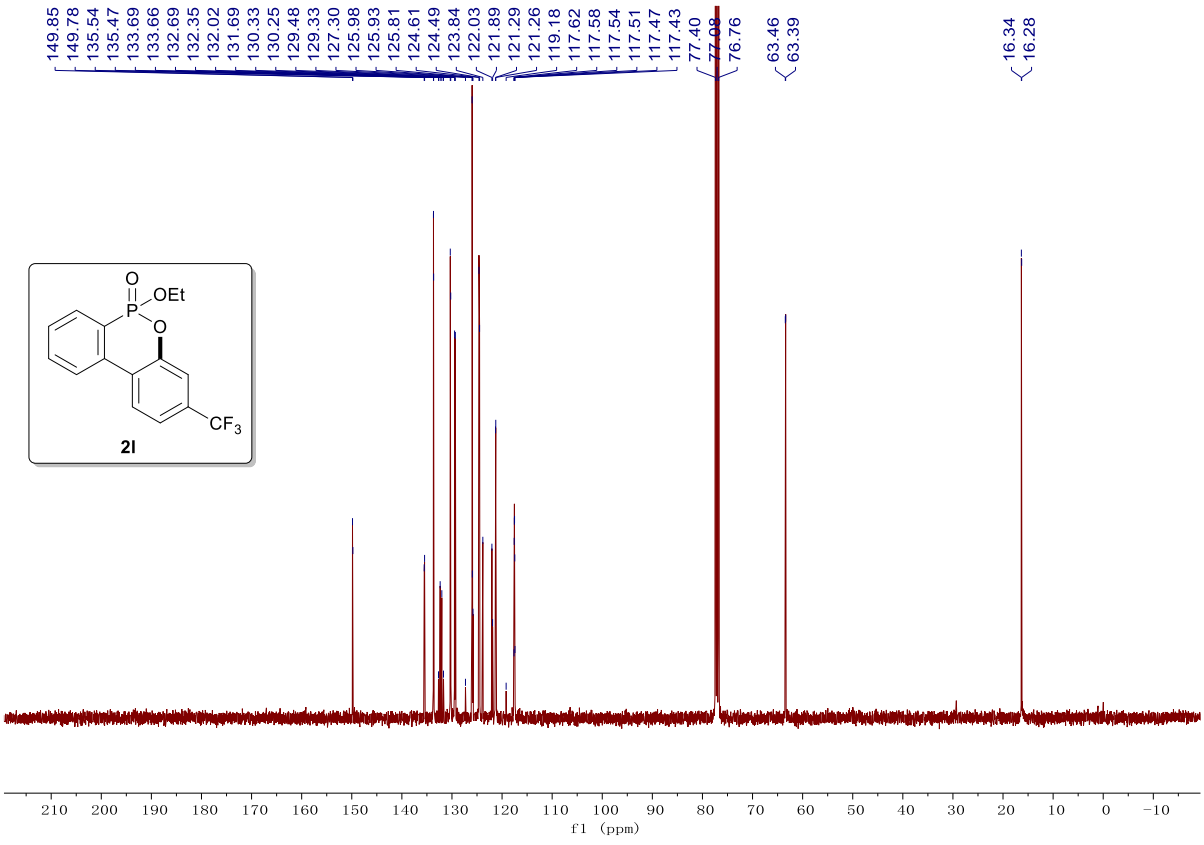


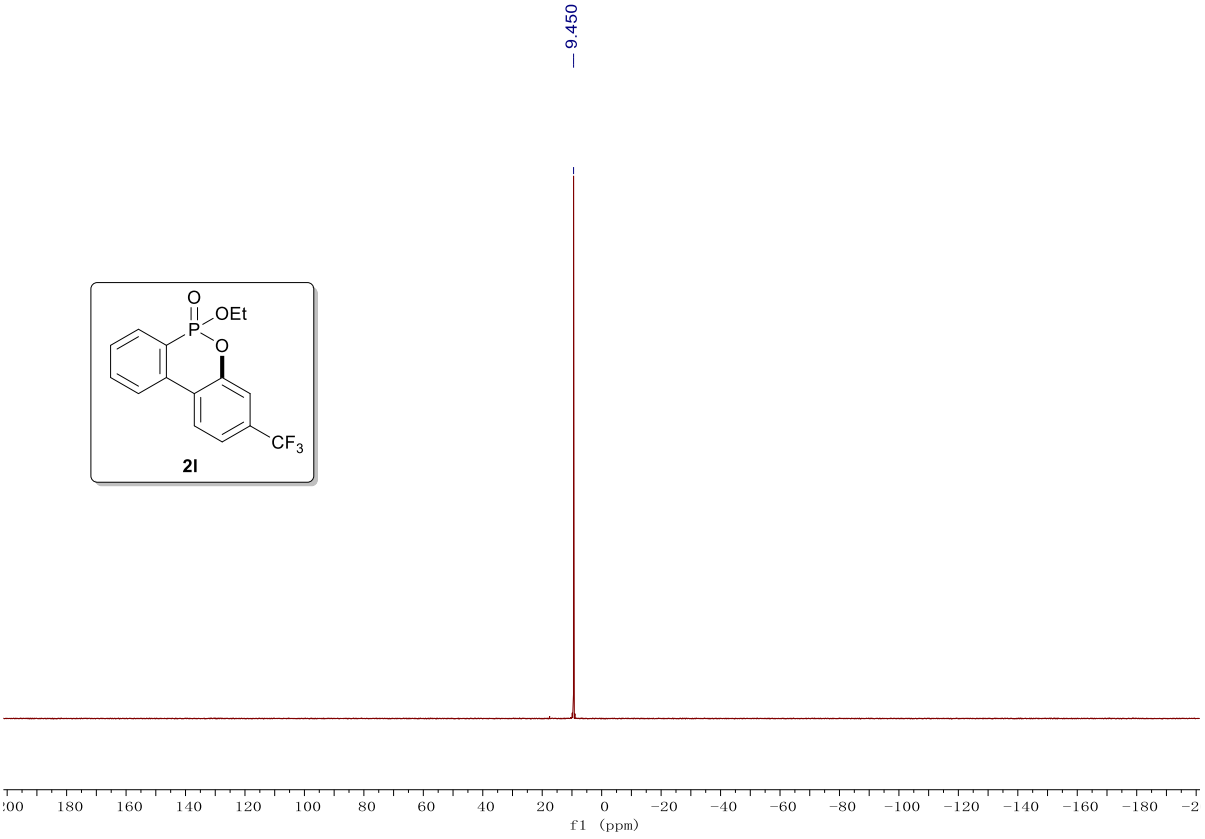

9.905
OEt
O
P
O
OCF3
2k
f1 (ppm)

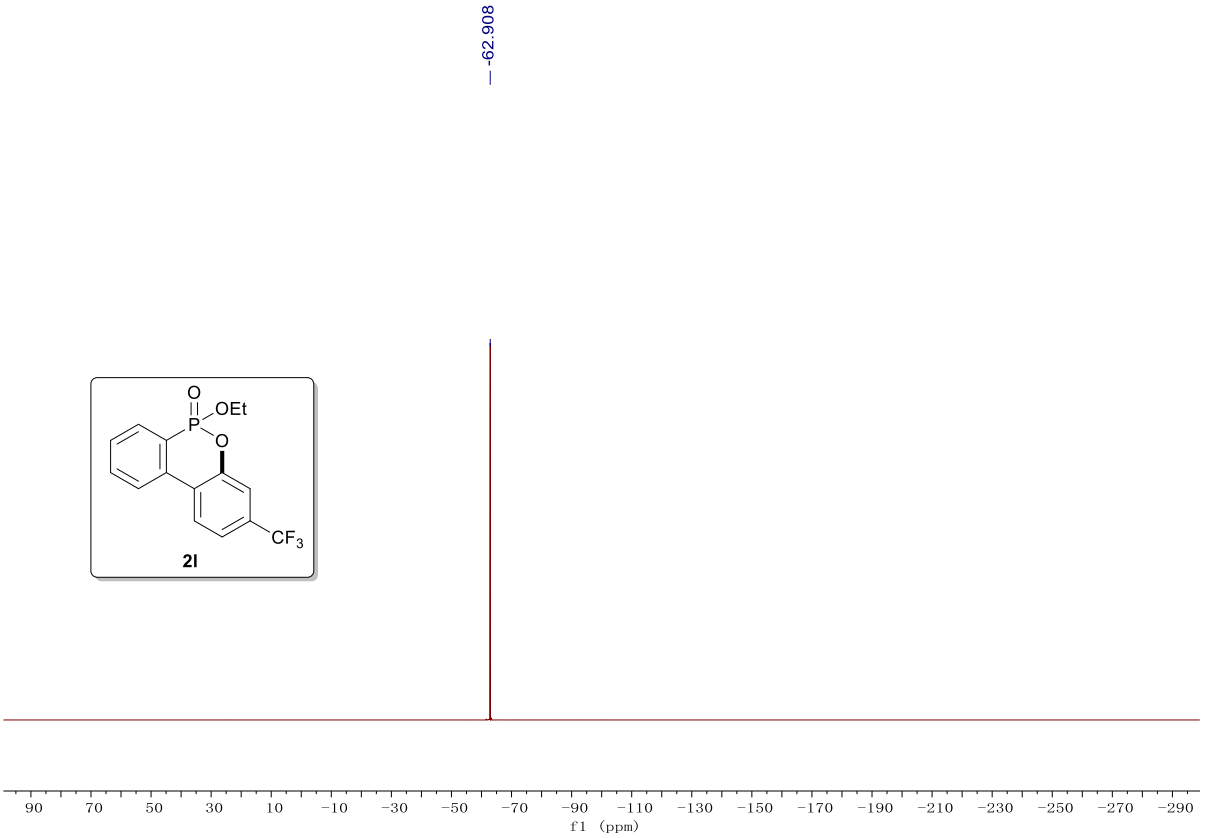

-57.856
OEt
O
P
O
OCF3
2k
f1 (ppm)

6-Ethoxy-3-(trifluoromethyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (2l)

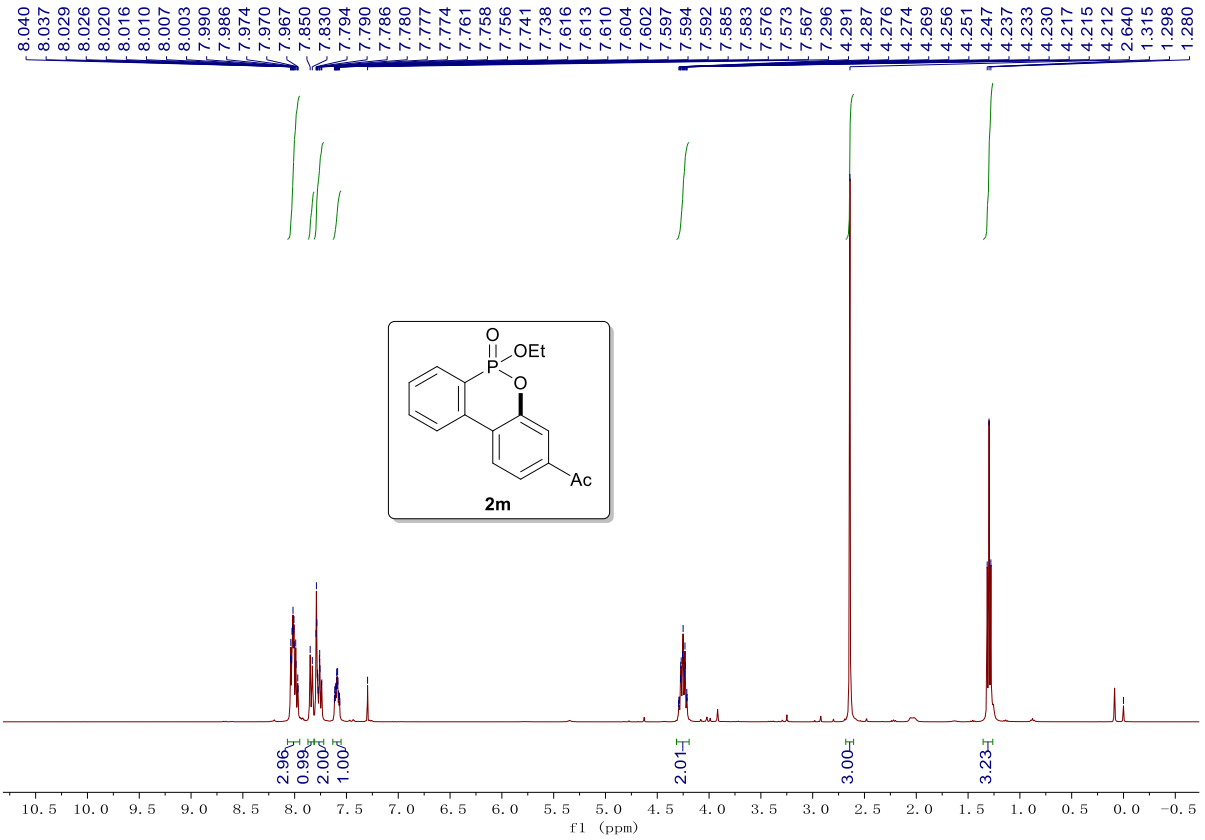


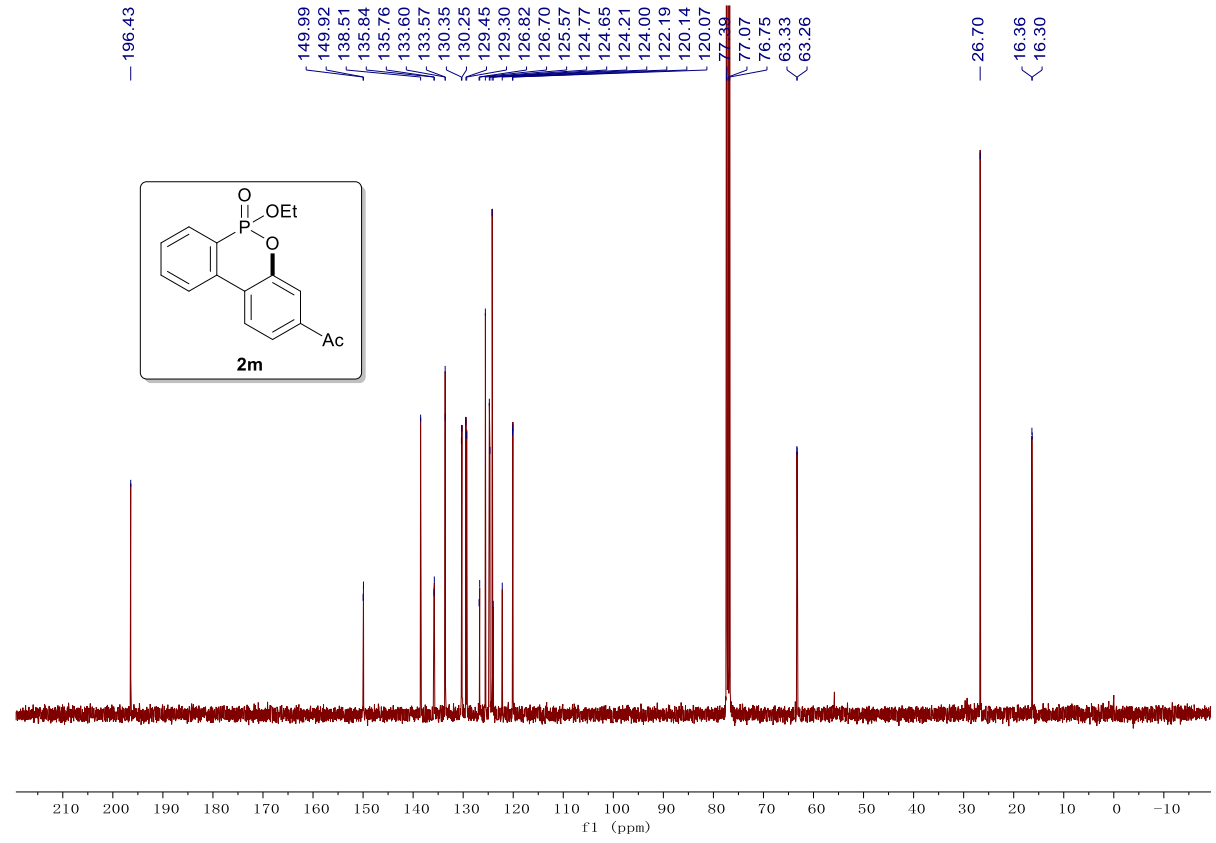


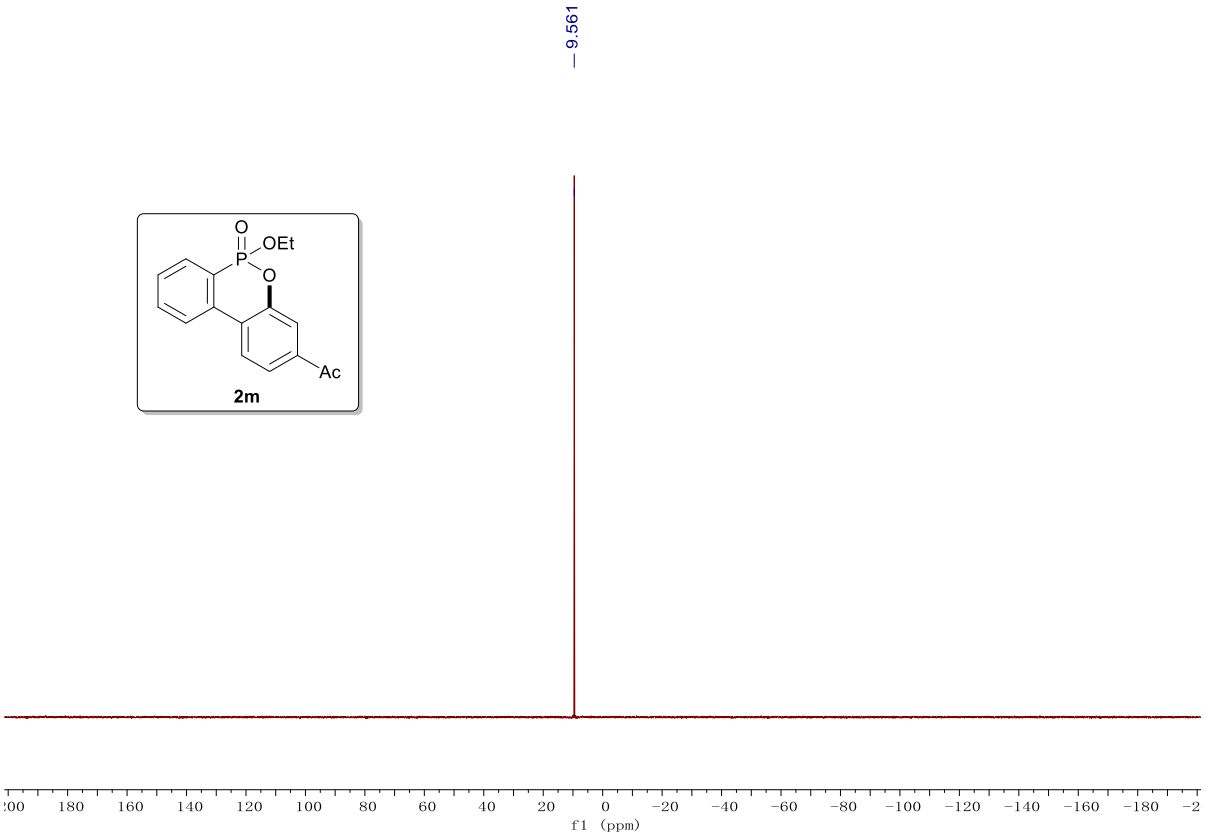

9.450
O
OEt
P
O
CF3
2l
f1 (ppm)


-62.908
O
OEt
P
O
CF3
2l
f1 (ppm)

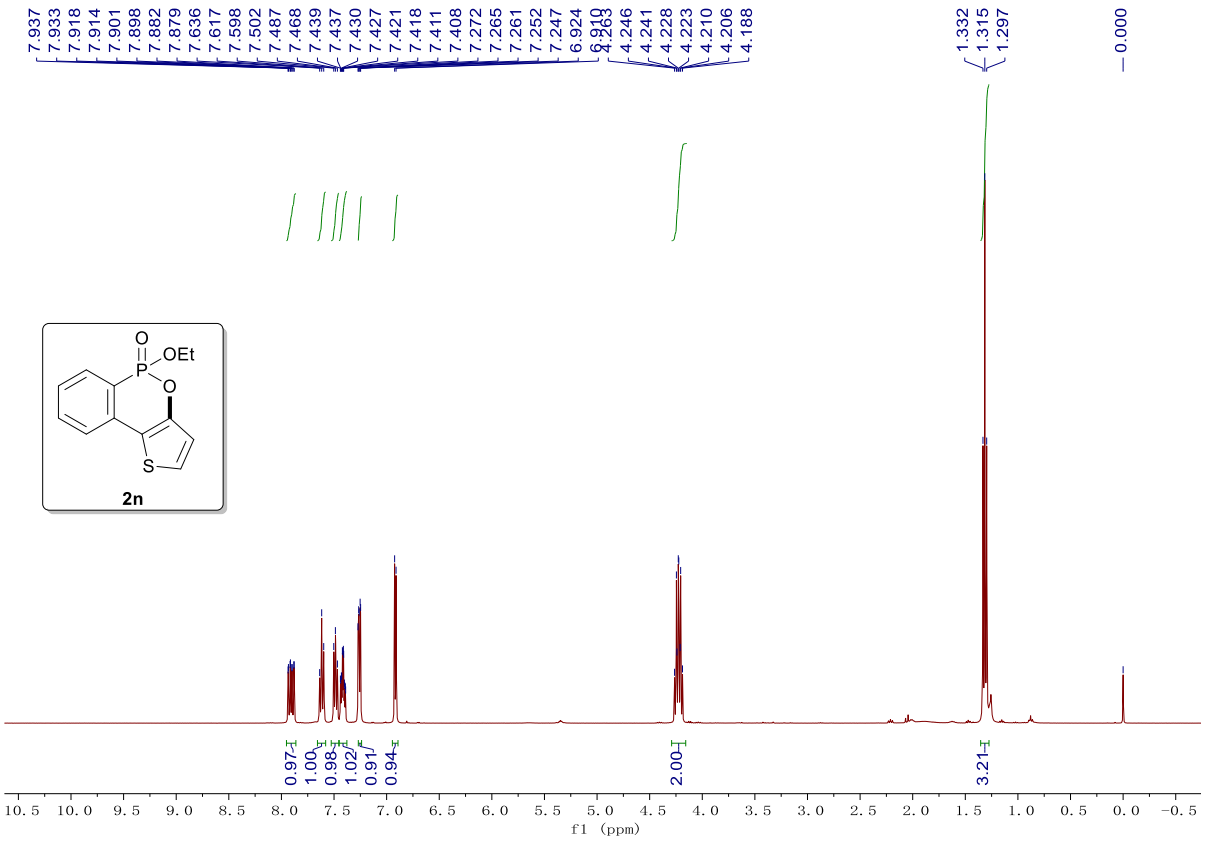
1-(6-Ethoxy-6-oxidodibenzo[c,e][1,2]oxaphosphinin-3-yl)ethan-1-one (2m)

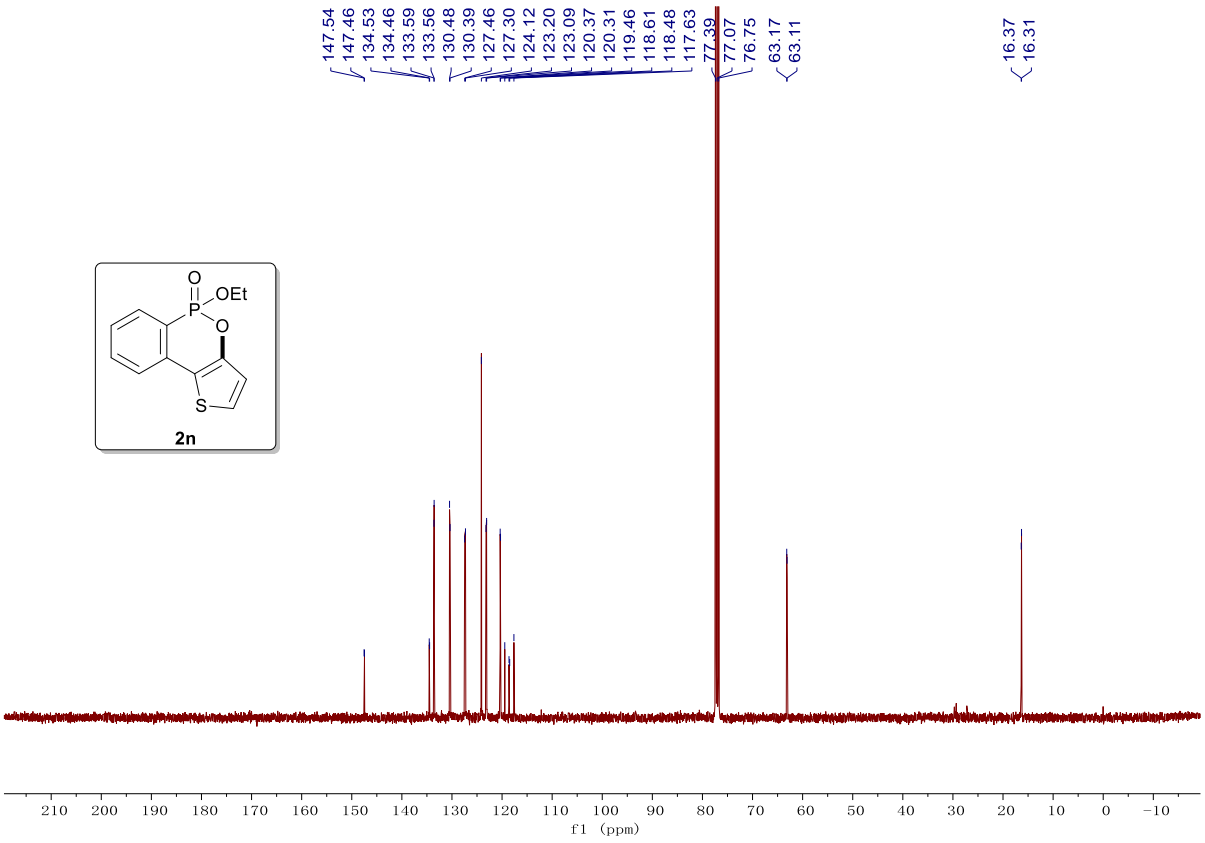


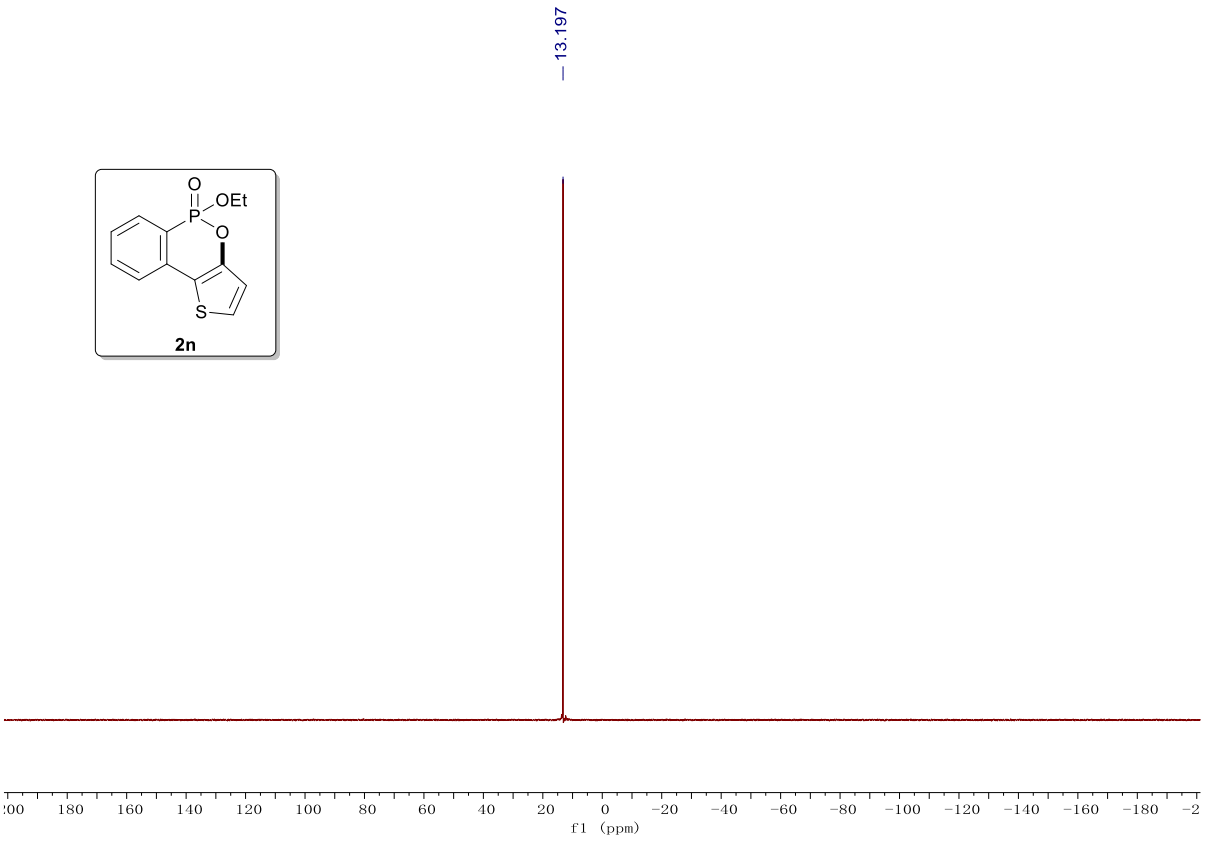




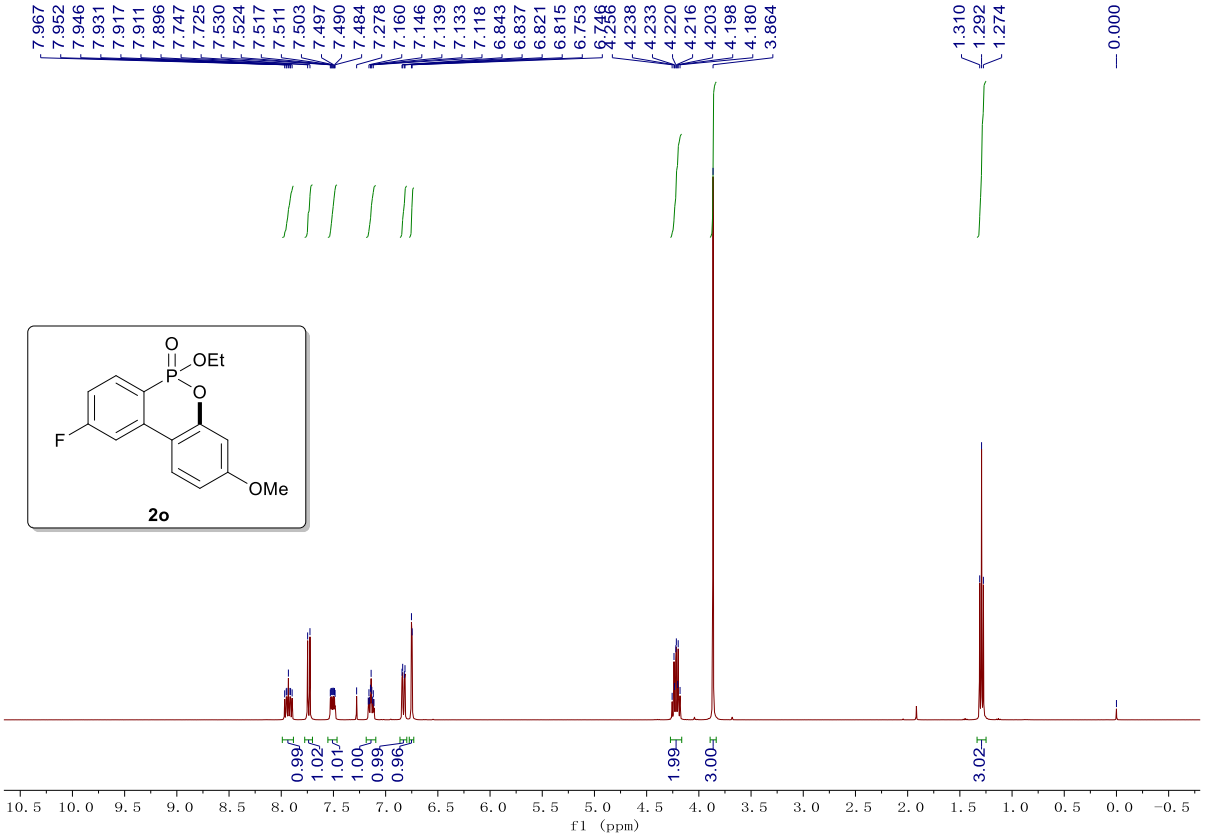
5-Ethoxybenzo[c]thieno[2,3-e][1,2]oxaphosphinine 5-oxide (2n)

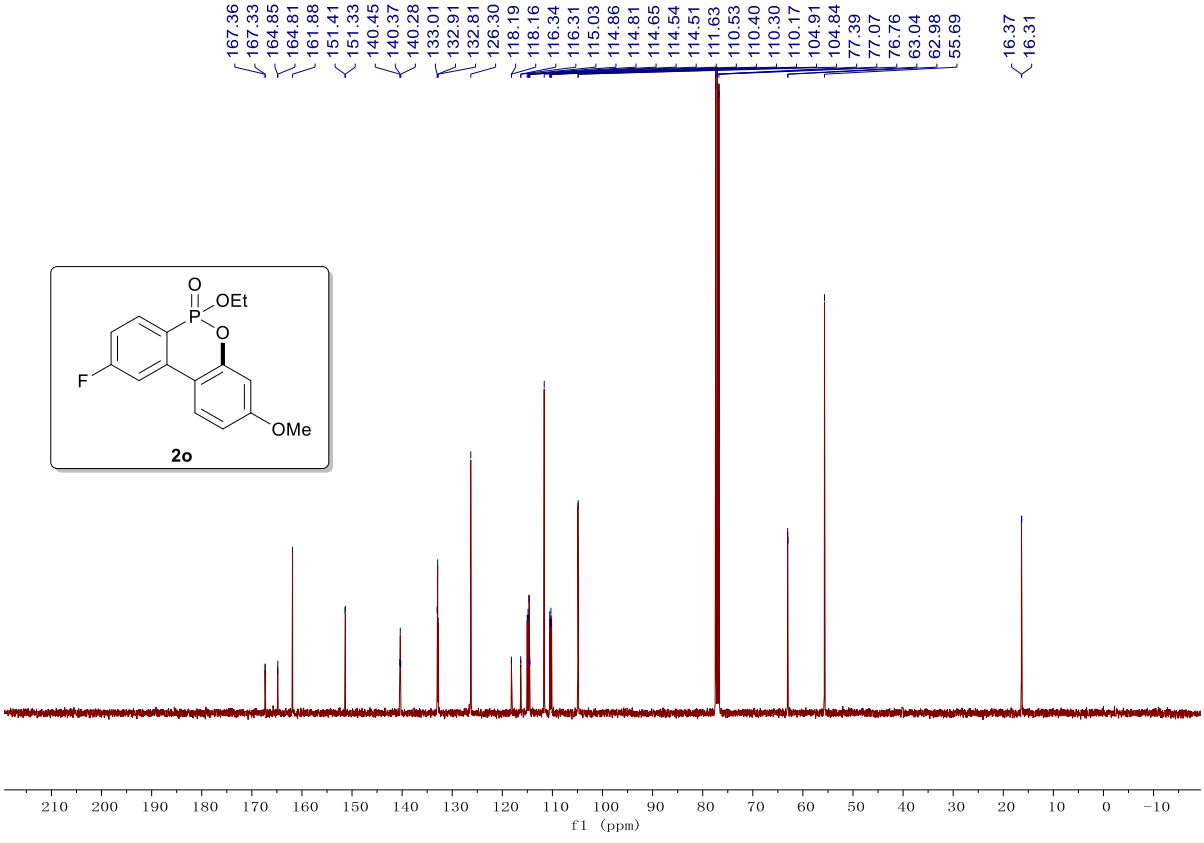


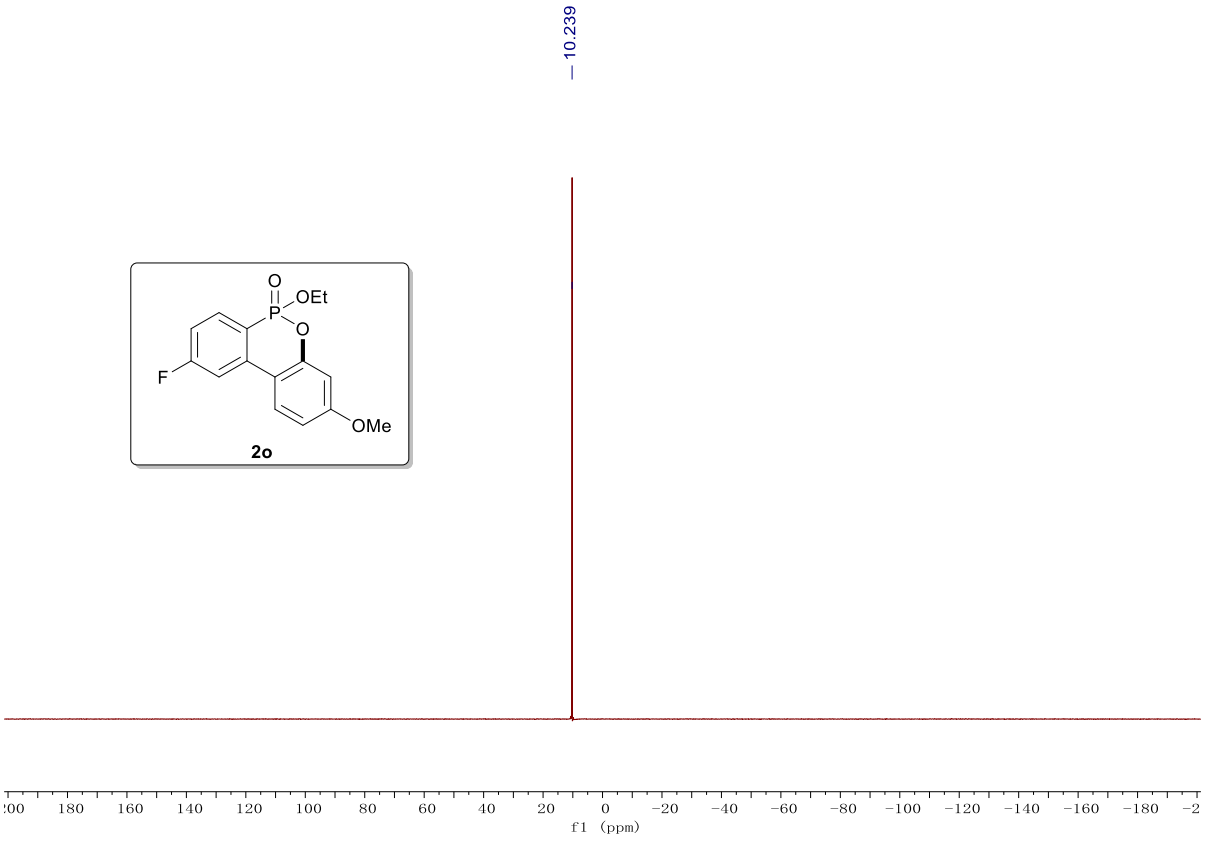

147.54
147.46
134.53
134.46
133.59
133.56
130.48
130.39
127.46
127.30
124.12
123.20
123.09
120.37
120.31
119.46
118.61
118.48
117.63
77.39
77.07
76.75
63.17
63.11
16.37
16.31
O
OEt
P
O
S
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


13.197
O
OEt
P
O
S
2n
:00 180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −2
f1 (ppm)

6-Ethoxy-9-fluoro-3-methoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2o)

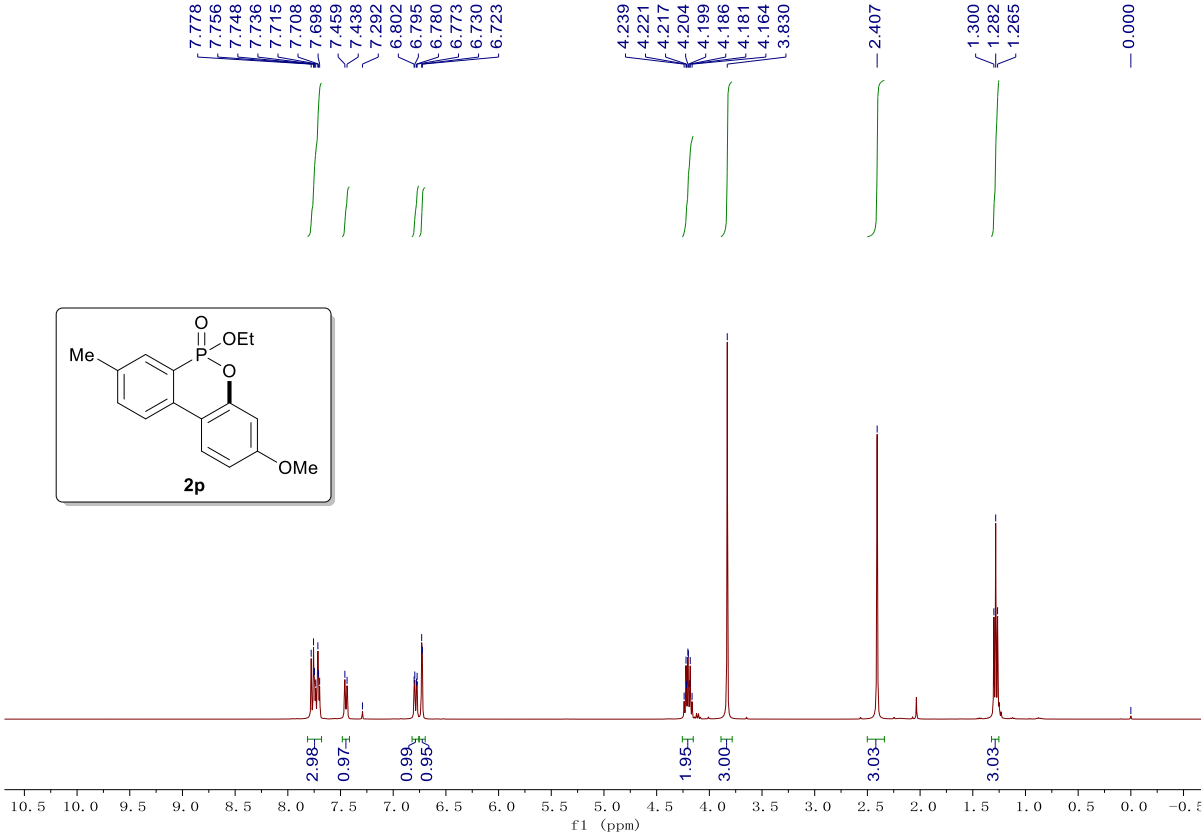


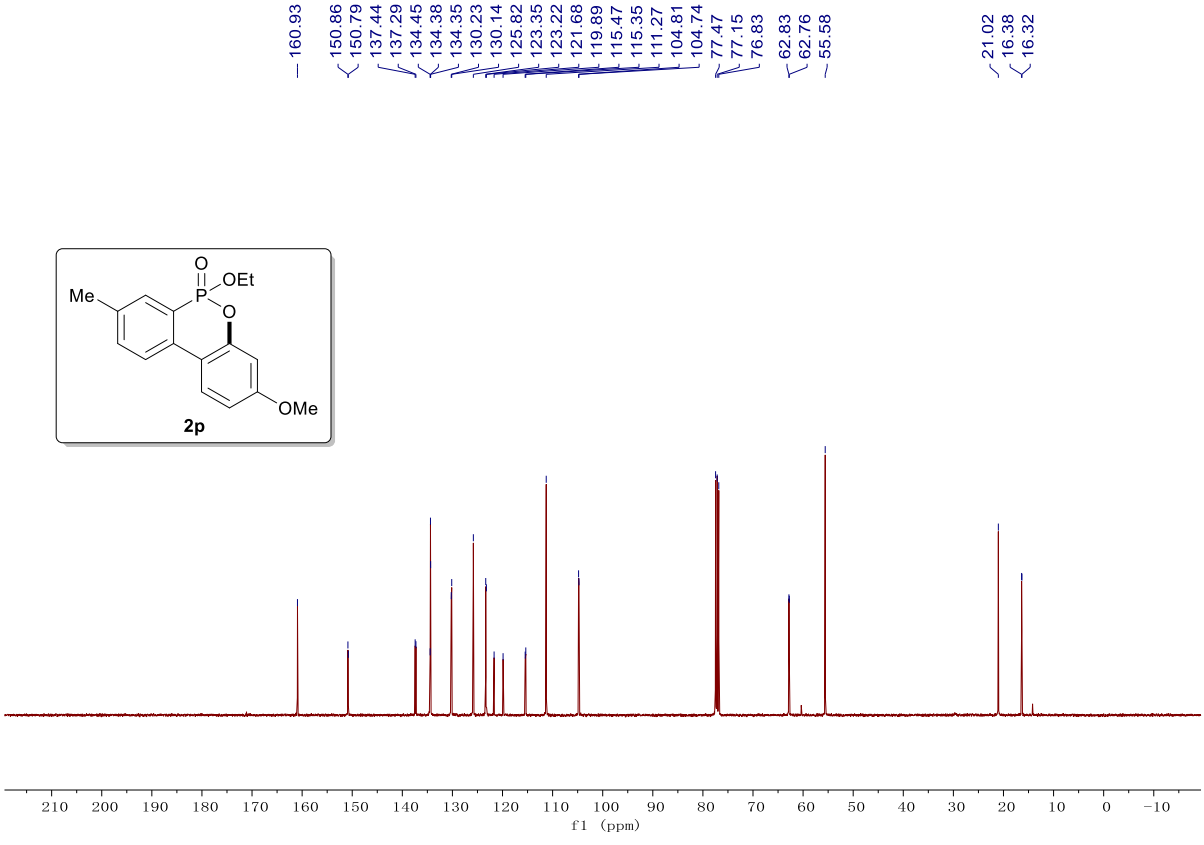


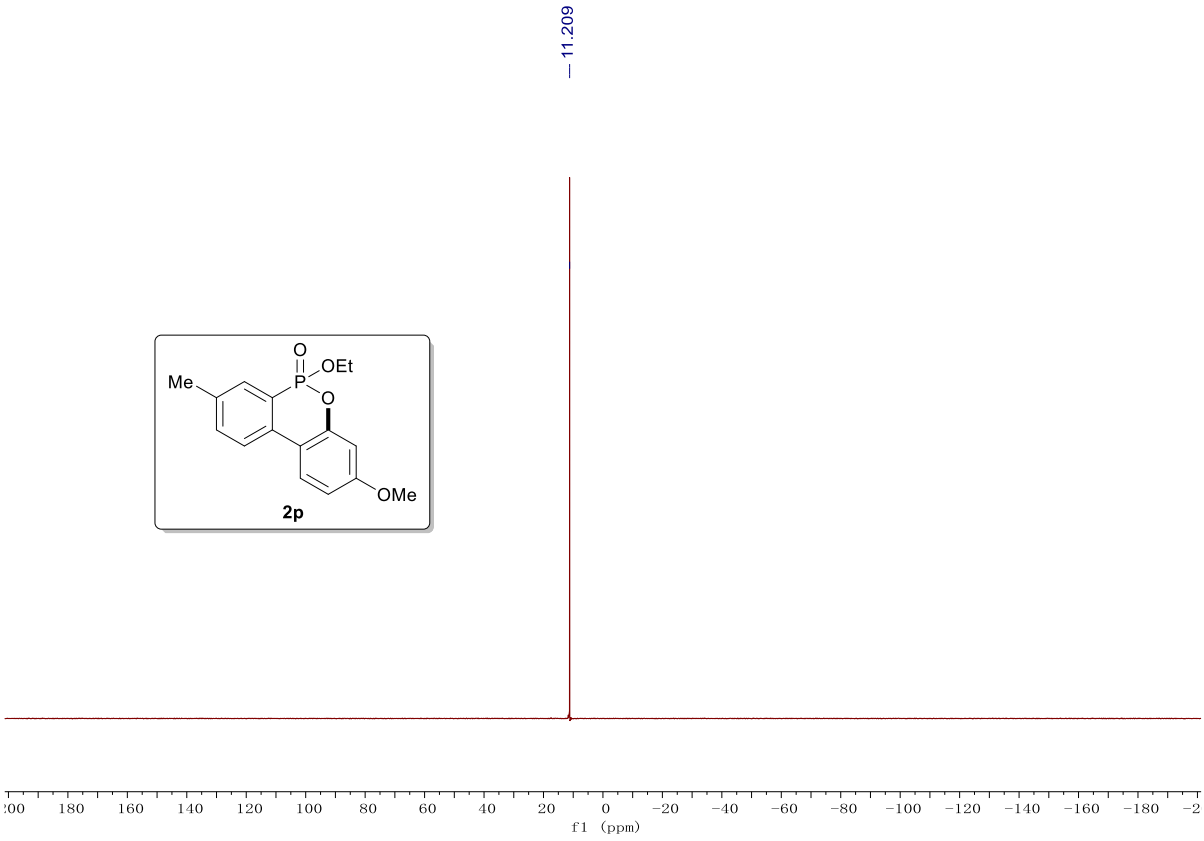

10.239
O
OEt
P
O
F
OMe
2o
f1 (ppm)


-103.879
-103.894
-103.913
-103.927
O
OEt
P
O
F
OMe
2o
f1 (ppm)

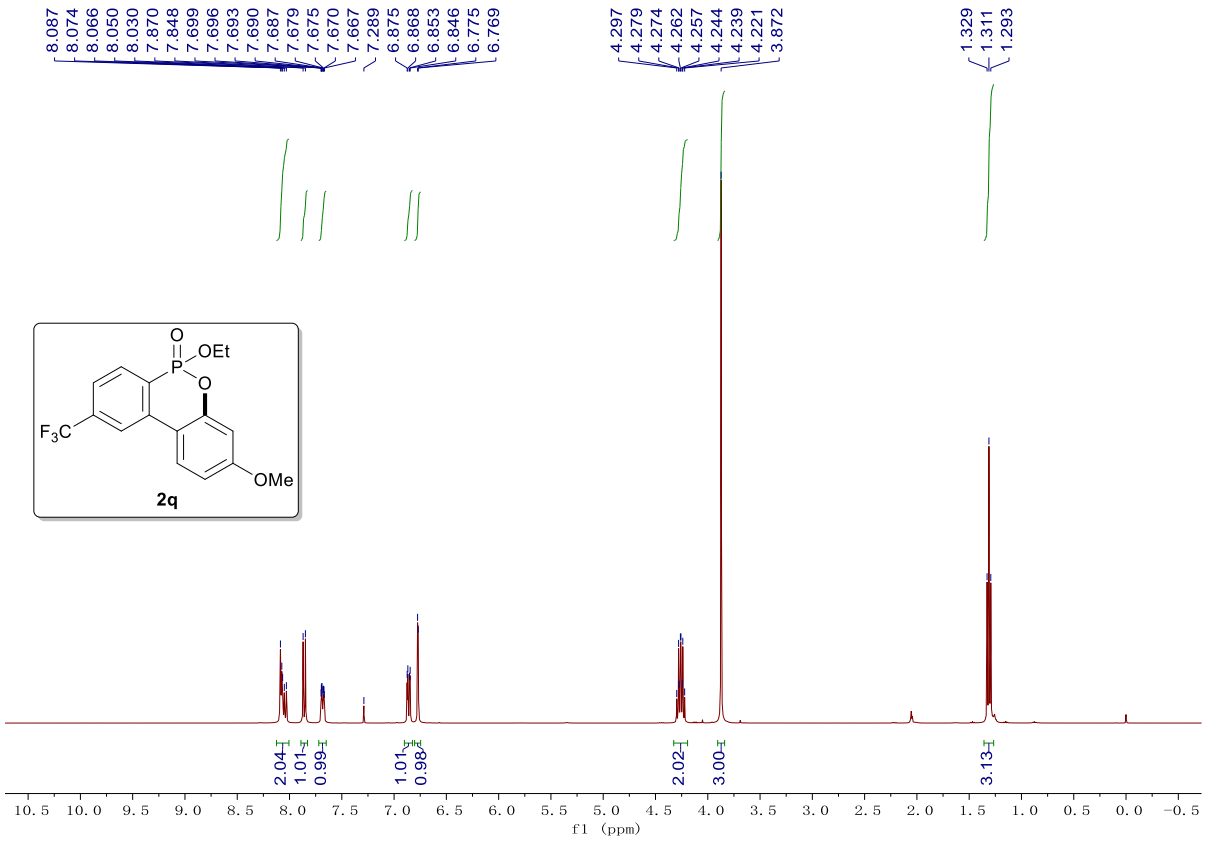
6-Ethoxy-3-methoxy-8-methyldibenzo[c,e][1,2]oxaphosphinine 6-oxide (2p)

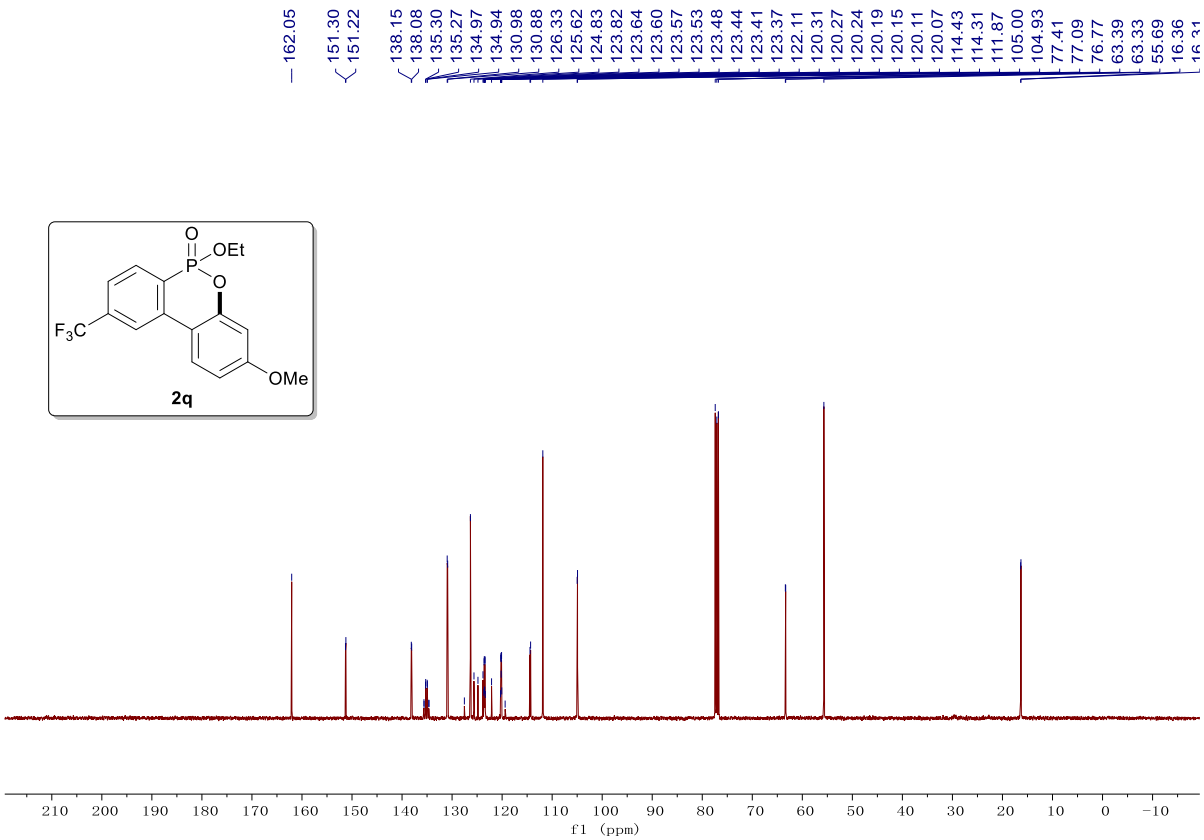


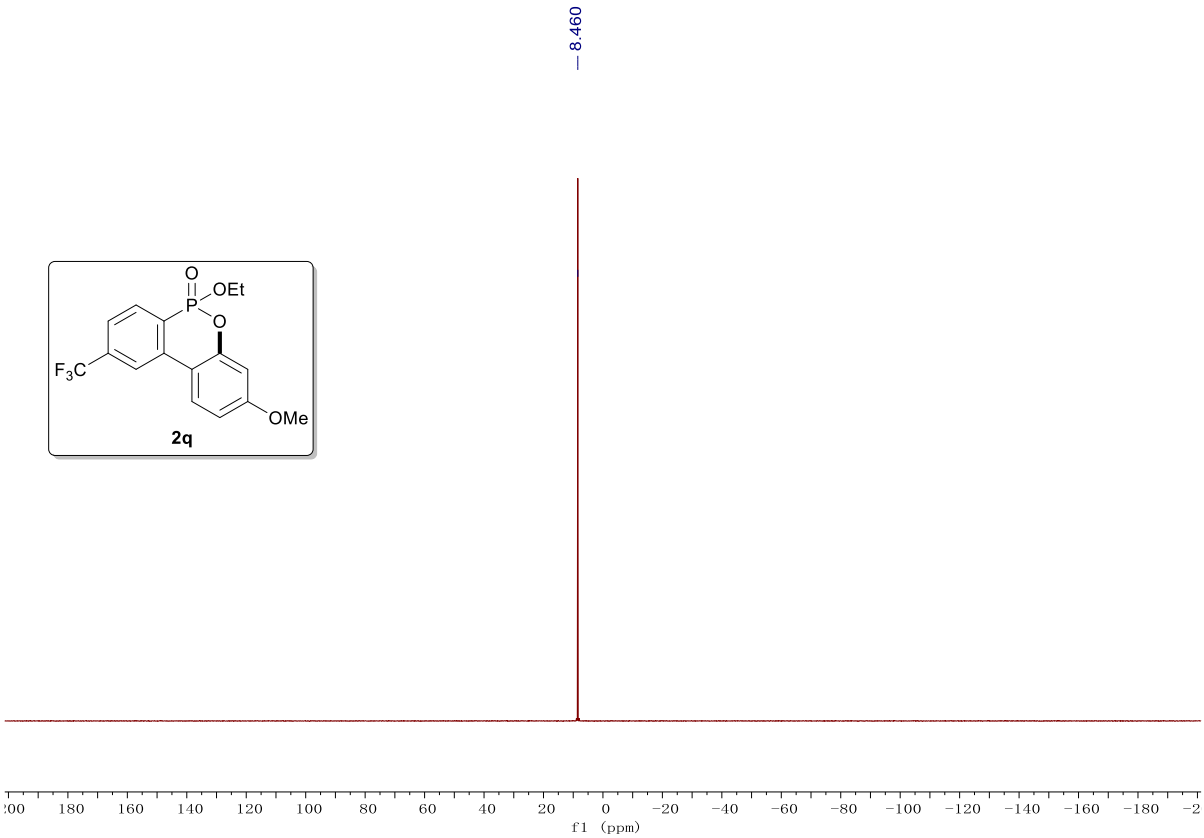


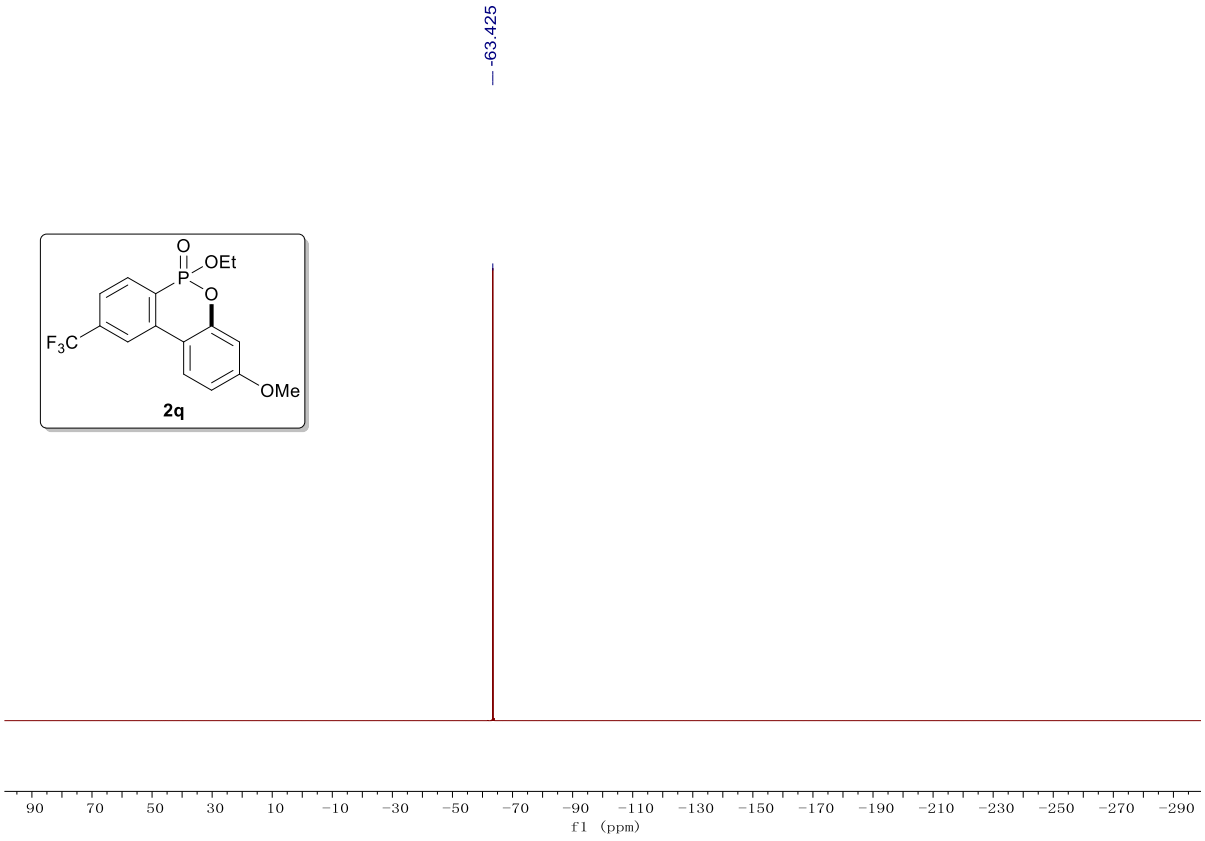


6-Ethoxy-3-methoxy-9-(trifluoromethyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (2q)

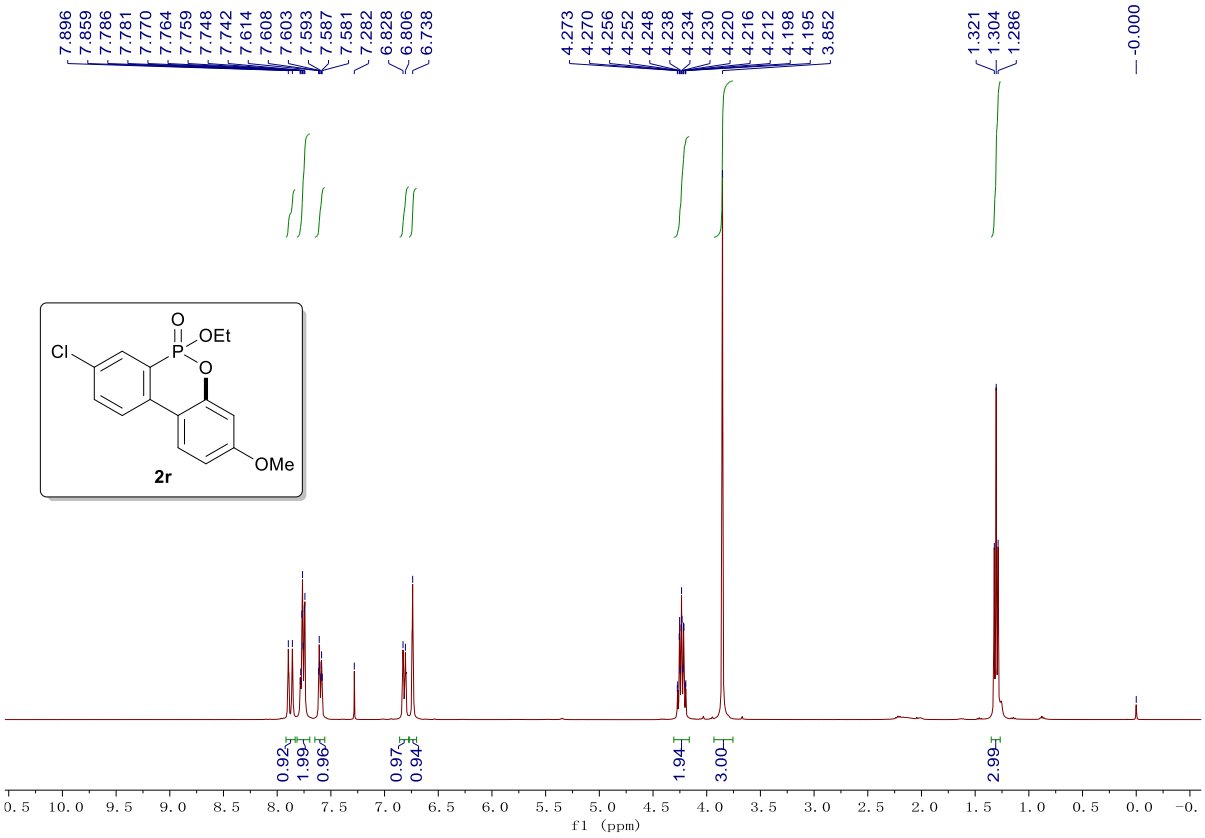


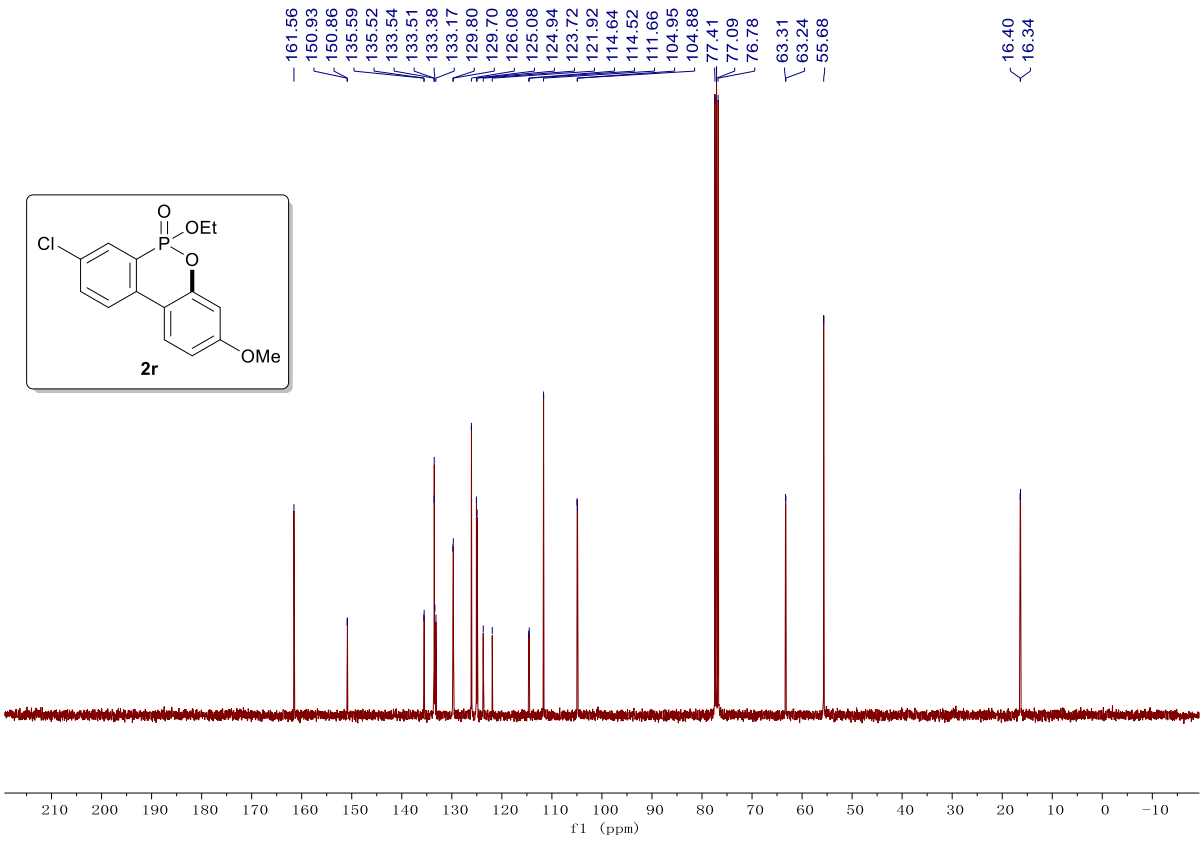

162.05
151.30
151.22
138.15
138.08
135.30
135.27
134.97
134.94
130.98
130.88
126.33
125.62
124.83
123.82
123.64
123.60
123.57
123.53
123.48
123.44
123.41
123.37
122.11
120.31
120.27
120.24
120.19
120.15
120.11
120.07
114.43
114.31
111.87
105.00
104.93
77.41
77.09
76.77
63.39
63.33
55.69
16.36
O
OEt
P
O
F3C
OMe
2q
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)

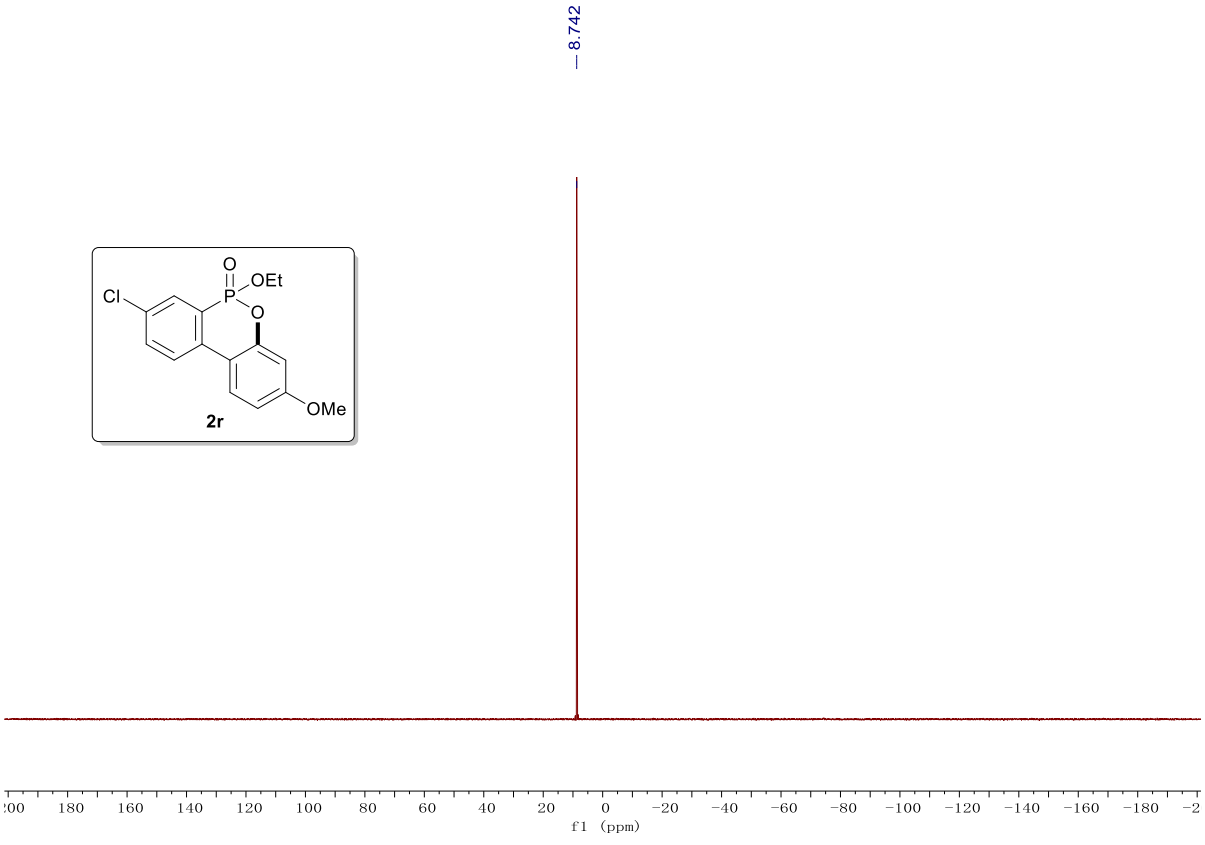

8.460
O
OEt
P
O
F3C
OMe
2q
200 180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −2
f1 (ppm)



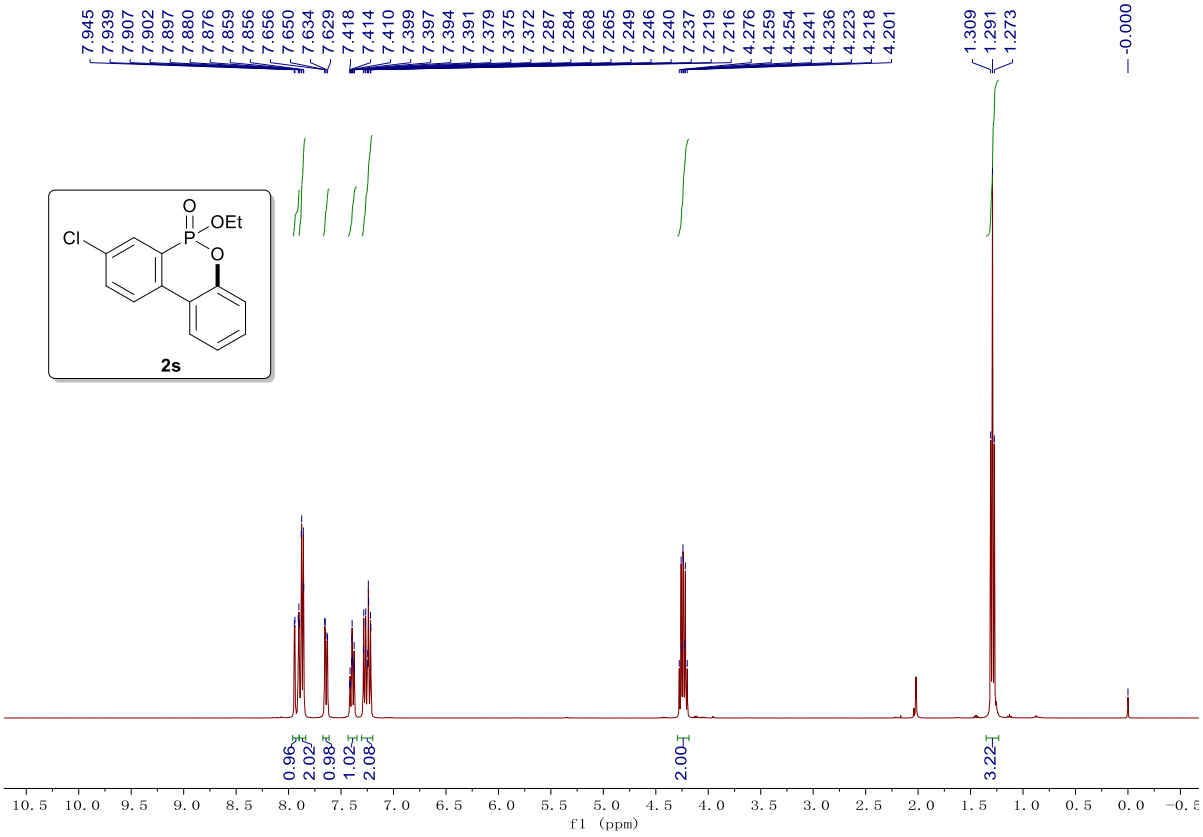
8-Chloro-6-ethoxy-3-methoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2r)

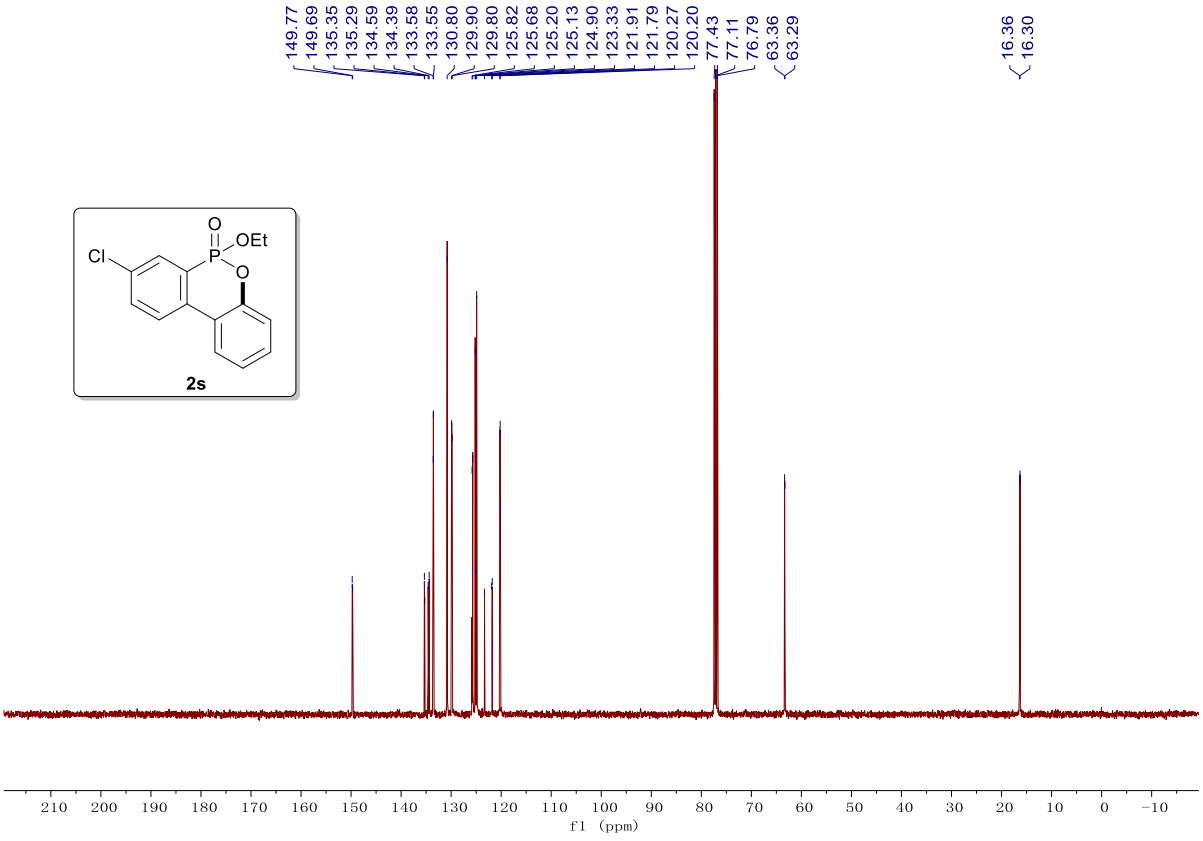


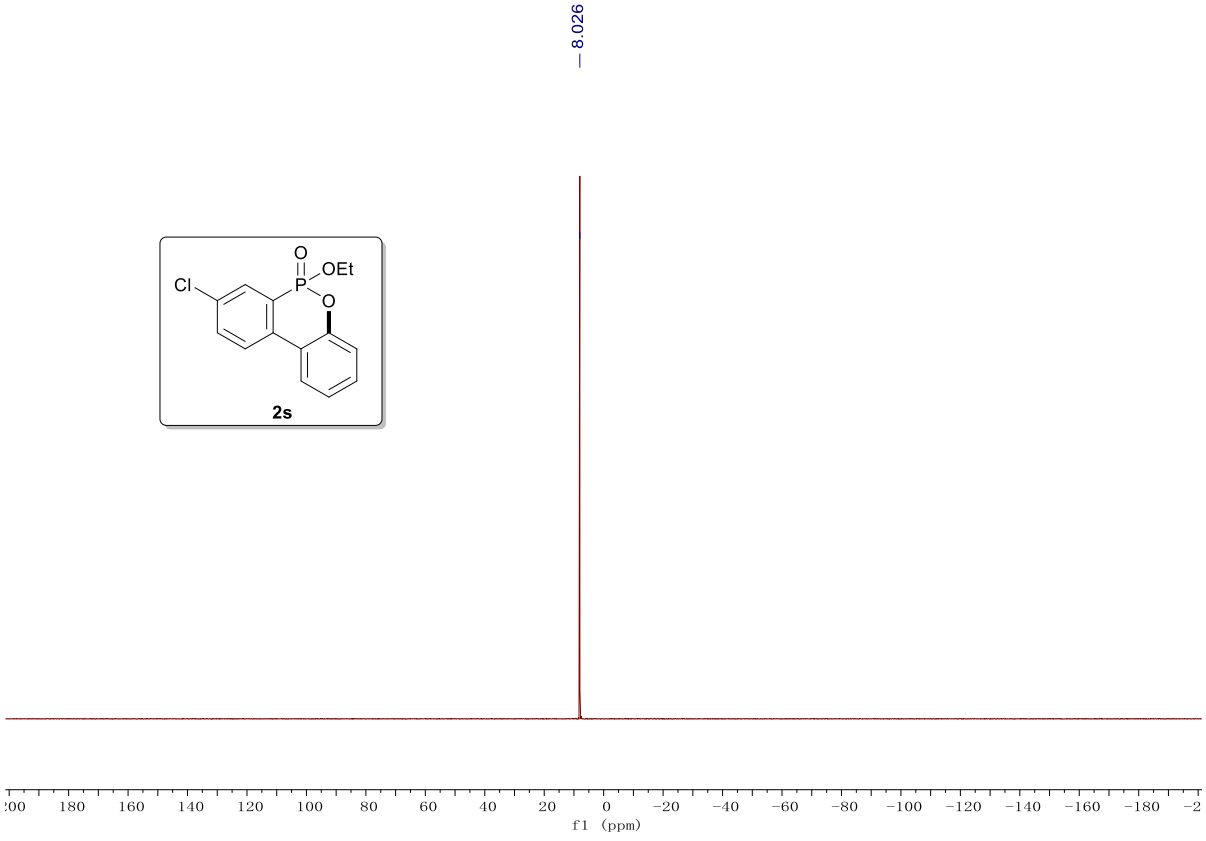

161.56
150.93
150.86
135.59
135.52
133.54
133.51
133.38
133.17
129.80
129.70
126.08
125.08
124.94
123.72
121.92
114.64
114.52
111.66
104.95
104.88
77.41
77.09
76.78
63.31
63.24
55.68
16.40
16.34
O
OEt
Cl
P
O
OMe
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


8.742
O
OEt
Cl
P
O
OMe
2r
:00 180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −2
f1 (ppm)

8-Chloro-6-ethoxydibenzo[c,e][1,2]oxaphosphinine 6-oxide (2s)






8.026
O
OEt
Cl
P
O
2s
f1 (ppm)