Versatile Synthesis of Phospholides from Open-Chain Precursors. Application to Annelated Pyrrole and Silole-Phosphole Rings

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Experimental section

All reactions were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Dry THF was obtained by distillation from Na/benzophenone. *n*-butyl lithium (1.6 M or 2.4 M in hexane) and lithium wire were purchased from Alfa Aesar. Silica gel (200-300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker 300 and 400 MHz spectrometer. Chemical shifts are expressed in ppm from internal TMS (^{1}H and ^{13}C). All coupling constants (*J* values) are reported in Hertz (Hz). HRMS were obtained on an Agilent 1290-6540 Q-Tof spectrometer by electrospray ionization (ESI). Element analytic data were obtained on a Thermo Electron Corporation flash EA 1112 element spectrometer.

General procedure for the synthesis of phosphines ***2a-i***

The starting *ortho*-bromophenylalkynes were synthesized by Sonogashira coupling.[11] To a solution of alkyne (10 mmol) in THF (40 mL) was added dropwise *n*-butyllithium in *n*-hexane (6.8 mL, 1.6 mol/L, 11.0 mmol) at –78ºC over 5 min. under N_2 atmosphere. The reaction mixture was stirred for 50 min, then Ph_2PCl (2.1 g, 12 mmol) was added at -78 °C, then the temperature was slowly raised to room temperature to give a pale yellow solution. After removal of the solvent under reduced pressure, the residue was chromatographed over silica gel (hexane/ethyl acetate = 20/1) to give pure products.

2a: pale yellow solid (83% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.00 (dd, *J* = 7.8 Hz, *J* = 3.6 Hz, 1H), 7.28-7.56 (m, 17H), 7.72 (dd, *J* = 7.4 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 88.9 (d, J_{PC} = 7.3 Hz), 96.6 (d, J_{PC} = 2.7 Hz), 123.2, 127.9 (d, J_{PC} = 28.4 Hz), 128.3(2CH), 128.4(CH), 128.7 (d, J_{PC} = 7.1 Hz, CH), 129.0(CH), 131.6 (2CH), 132.4 (d, J_{PC} = 3.4 Hz, CH), 132.5(CH), 134.3 (d, J_{PC} = 20.1 Hz, CH), 136.5 (d,

J_{PC} = 10.6 Hz), 140.9 (d, J_{PC} = 12.6 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= -8.5; HRMS Calcd. for $C_{26}H_{20}P$ [M + H^+] 363.1297, Found: 363.1298.

2b: pale yellow solid (75% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 2.29 (s, 3H), 6.81 (br, 1H), 7.02-7.20 (m, 5H), 7.25-7.36 (m, 11H), 7.55 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.6 (CH_3), 88.1, 96.7, 120.0, 128.0 (d, J_{PC} = 28.3 Hz), 128.1 (CH), 128.3 (CH), 128.6 (d, J_{PC} = 7.2 Hz, CH), 128.9 (d, J_{PC} = 5.9 Hz, CH), 131.4 (CH), 132.2 (CH), 132.4 (CH), 134.2 (d, J_{PC} = 20.2 Hz, CH), 136.5 (d, J_{PC} = 10.5 Hz), 138.4, 140.6 (d, J_{PC} = 12.3 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= -8.6; HRMS Calcd. for $C_{27}H_{22}P$ [M + H^+] 377.1453. Found: 377.1455.

2c: pale yellow oil (80% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 0.13(s, 9H), 6.82 (dd, *J* = 7.5 Hz, *J* = 3.6 Hz, 1H), 7.20-7.40 (m, 12H), 7.56-7.60 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = -0.3 (CH_3), 101.8 (d, J_{PC} = 3.0 Hz), 103.5 (d, J_{PC} = 6.8 Hz), 127.4 (d, J_{PC} = 28.1 Hz), 128.0 (CH), 128.3 (CH), 128.4 (d, J_{PC} = 7.1 Hz, CH), 128.7 (CH), 132.0 (CH), 132.5 (d, J_{PC} = 3.3 Hz, CH), 134.1 (d, J_{PC} = 20.1 Hz, CH), 136.3 (d, J_{PC} = 10.6Hz), 141.0 (d, J_{PC} = 13.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= -8.1; HRMS Calcd. for $C_{23}H_{24}PSi$ [M + H^+] 359.1379, Found: 359.1385.

2d: pale yellow solid (80% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 3.75(s, 3H), 6.73-6.84 (m, 3H), 7.10-7.37 (m, 14H), 7.53 (dd, *J* = 3.0 Hz, *J* = 7.2 Hz, 1H); 13C NMR (75 MHz, $CDCl_3$) δ = 55.2 (OCH_3), 87.4 (d, J_{PC} = 7.4 Hz), 96.5, 113.7 (CH), 115.1, 127.9 (CH), 128.0 (d, J_{PC} = 28.5 Hz), 128.3 (CH), 128.5 (d, J_{PC} = 7.2 Hz, CH), 128.8 (CH), 132.0 (d, J_{PC} = 3.5 Hz, CH), 132.3 (CH), 132.9 (CH), 134.1 (d, J_{PC} = 20.0 Hz, CH), 136.5 (d, J_{PC} = 10.4 Hz), 140.4 (d, J_{PC} = 12.0 Hz), 159.6; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= -8.7; HRMS Calcd. for $C_{27}H_{22}OP$ [M + H+] 393.1402, Found: 393.1406.

2e *P*-oxide**:** white soil (68% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 0.74(t, J_{HH} = 5.7 Hz, 3H), 1.12-1.15 (m, 4H), 1.91 (t, J_{HH} = 6.6 Hz, 2H), 7.24-7.29 (m, 1H), 7.35-7.48 (m, 8H), 7.62-7.74 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.6 (CH_3), 19.1 (CH_2), 21.9 (CH_2), 29.8 (CH_2), 79.6 (d, J_{PC} =6.0 Hz), 99.3, 127.2 (d, J_{PC} = 11.3 Hz, CH), 127.3 (d, J_{PC} = 6.8 Hz), 128.2 (d, J_{PC} = 12.8 Hz, CH), 131.6 (d, J_{PC} = 3.0 Hz, CH), 131.7 (d, J_{PC} = 2.3 Hz, CH), 132.0 (d, J_{PC} = 10.5 Hz, CH), 132.5 (d, J_{PC} =105.8 Hz), 133.5 (d, J_{PC} = 102.0 Hz), 133.7 (d, J_{PC} = 9.0 Hz, CH), 133.9 (d, J_{PC} = 9.0 Hz, CH); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 28.3; HRMS Calcd. for $C_{24}H_{24}OP$ [M + H+] 359.1559, Found: 359.1601.

2f *P*-oxide**:** white solid (72% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 0.86 (t, J_{HH} = 7.2 Hz, 3H), 1.24-1.31 (m, 2H), 1.46-1.54 (m, 2H), 2.51(t, J_{HH} = 7.6 Hz, 2H), 6.88-7.00 (m, 4H),7.30-7.37 (m, 5H), 7.39-7.45 (m, 3H), 7.54-7.58 (m, 1H), 7.74-7.85 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.9 (CH_3), 22.3 (CH_2), 33.3 (CH_2), 35.5 (CH_2), 87.9 (d, J_{PC} =5.7 Hz), 97.7, 119.6 (CH), 126.6 (d, J_{PC} = 7.1 Hz, CH), 127.8 (d, J_{PC} = 11.5 Hz, CH), 128.2 (CH), 128.3 (d, J_{PC} = 12.4 Hz, CH), 131.3 (CH), 131.7 (d, J_{PC} = 2.7 Hz, CH), 131.8 (d, J_{PC} = 2.3 Hz), 132.1 (d, J_{PC} = 9.9 Hz, CH), 132.3 (d, J_{PC} = 105.4 Hz), 133.6 (d, J_{PC} = 101.3 Hz), 133.8 (d, J_{PC} = 4.7 Hz) , 133.9 (d, J_{PC} = 4.9 Hz), 143.7 (CH); HRMS Calcd. for $C_{30}H_{28}OP$ [M + H+] 435.1872, Found: 435.1883.

2g: pale yellow solid (75% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.86 (dd, J = 3.6 Hz, J = 7.5 Hz,1H), 7.19 (t, J_{HH} = 7.5 Hz,1H), 7.28-7.51 (m, 15H), 7.66-7.74 (m, 3H), 8.14-8.17 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 93.4 (d, J_{PC} = 7.0 Hz), 94.3 (d, J_{PC} = 3.0 Hz), 120.9, 125.2 (CH), 126.4 (CH), 126.81 (CH), 126.82 (d, J_{PC} = 2.6 Hz, CH), 128.2 (CH), 128.5 (CH), 128.6 (CH), 128.75 (d, J_{PC} = 7.0 Hz, CH), 128.9 (CH), 129.0 (CH), 130.7 (CH), 132.8 (CH), 132.9 (d, J_{PC} = 3.9 Hz, CH), 133.2, 133.4, 134.2 (d, J_{PC} = 19.8 Hz, CH), 136.6 (d, J_{PC} = 10.9 Hz),140.4 (d, J_{PC} = 12.5 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = -9.2; HRMS Calcd. for $C_{30}H_{22}P$ [M + H^+] 413.1453, Found: 413.1453.

2h: pale yellow solid (78% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.66 (s, 3H), 6.78 (s, 1H), 6.95 (dd, J = 7.5Hz, J = 3.6 Hz, 1H), 7.14-7.43 (m, 15H), 7.64 (d, J_{HH}= 7.8 Hz, 1H), 7.73 (dd, J= 7.2 Hz, J = 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 30.6(d, J_{PC} = 3.2 Hz), 87.6, 94.2 (d, J_{PC} = 6.9 Hz), 107.7 (CH), 109.4 (CH), 120.0 (CH), 121.0 (CH), 122.0, 123.0 (CH), 127.3, 127.7(d, J_{PC} = 29.7 Hz), 128.5 (CH), 128.6 (CH),128.7 (d, J_{PC} = 7.1 Hz, CH), 128.9 (CH), 132.6 (d, J_{PC} = 3.9 Hz, CH), 132.7 (CH), 134.1 (d, J_{PC} = 19.8 Hz, CH), 136.3 (d, J_{PC} = 10.8 Hz), 137.4, 140.1 (d, J_{PC} = 12.8 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = -8.9; HRMS Calcd. for $C_{29}H_{23}NP$ [M + H^+] 416.1562, Found: 416.1564.

2i: colorless oil (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.70 (s, 9H), 7.19(dd, J = 3.6 Hz, J = 7.4 Hz,1H), 7.41 (t, J_{HH}= 7.4 Hz,1H), 7.45-7.48 (m, 3H), 7.51-7.56 (m, 7H), 7.65-7.69 (m, 4H), 7.73-7.75 (m, 1H), 7.90 (dd, J = 3.6 Hz, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = -0.4, 91.7 (d, J_{PC} = 7.3 Hz), 98.1 (d, J_{PC} = 2.4 Hz), 127.8 (CH) , 128.5 (d, J_{PC} = 17.3 Hz), 128.6 (CH), 128.7 (d, J_{PC} = 4.4 Hz), 128.74 (CH), 128.9 (d, J_{PC} = 7.0 Hz, CH), 129.0 (CH), 129.1 (CH), 132.1 (d, J_{PC} = 3.5 Hz, CH), 133.0 (CH), 133.1 (CH), 134.0 (CH), 134.4 (d, J_{PC} = 20.1 Hz, CH), 136.9 (d, J_{PC} = 11.4 Hz), 141.0 (d, J_{PC} = 13.2 Hz), 142.1; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = -9.0; HRMS Calcd. for $C_{29}H_{28}PSi$ [M + H^+] 435.1692, Found: 435.1699.

General procedure for the synthesis of phosphines ***4a,b***

The synthesis of the starting enynes has been reported in the literature.[5] To a solution of enyne (10 mmol) in THF (40 mL) was added dropwise *n*-butyllithium in *n*-hexane (6.8 mL, 1.6 mol/L, 11.0 mmol) at –78ºC over 5 min under N_2 atmosphere. The reaction mixture was stirred for 50 min, then Ph_2PCl (2.1g, 12mmol) was added at -78 °C, then the temperature was slowly increased back to room temperature to give a pale yellow solution. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (hexane/ethyl acetate = 20/1) to give pure products.

4a *P*-oxide**:** pale yellow solid (80% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.08 (t, J_{HH} = 7.4 Hz, 3H), 1.23 (t, J_{HH} = 7.4Hz, 3H), 2.25 (s, 3H), 2.47-2.63 (m, 4H), 6.74- 6.76 (m, 2H), 6.93-6.96 (m, 2H), 7.29-7.38 (m, 6H), 7.76-7.83 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.2 (CH_3), 14.8 (CH_3), 21.4 (CH_3), 23.0 (d, J_{PC} = 9.7 Hz, CH_2), 27.9 (d, J_{PC} = 11.4 Hz, CH_2), 88.9 (d, J_{PC} = 11.7 Hz), 100.7, 119.3, 128.1 (d, J_{PC} = 12.1 Hz, CH), 128.6 (CH), 131.1 (CH), 131.3 (d, J_{PC} = 2.5 Hz, CH), 131.7 (d, J_{PC} = 9.9 Hz, CH), 133.5 (d, J_{PC} = 102.4 Hz), 137.9 (d, J_{PC} = 4.9 Hz), 138.5, 139.6 (d, J_{PC} = 93.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 29.4; HRMS Calcd. for $C_{27}H_{28}OP$ [M + H^+] 399.1872, Found: 399.1872.

4b *P*-oxide**:** colorless oil (83% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.81 (t, J_{HH} = 7.5 Hz, 3H), 0.94 (t, J_{HH} = 7.5 Hz, 3H), 1.38-1.50 (m, 2H), 1.60-1.72 (m, 2H), 2.38-2.54 (m, 4H), 6.79-6.82 (m, 2H), 7.03-7.37 (m, 9H), 7.71-7.78 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.8 (CH_3), 14.2 (CH_3), 21.7 (CH_2), 23.6 (CH_2), 32.1 (d, J_{PC} = 9.3 Hz, CH_2), 36.5(d, J_{PC} = 11.0 Hz, CH_2), 89.6 (d, J_{PC} = 11.9 Hz), 100.3, 122.5, 127.9 (CH), 128.1 (d, J_{PC} = 12.0 Hz, CH), 128.3 (CH), 131.1 (CH), 131.2 (d, J_{PC} = 2.7 Hz, CH), 131.7 (d, J_{PC} = 9.9 Hz, CH), 133.6 (d, J_{PC} = 102.5 Hz), 136.5(d, J_{PC} = 4.9 Hz), 139.8 (d, J_{PC} = 92.8 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ= 29.6; HRMS Calcd. for $C_{28}H_{30}OP$ [M + H^+] 413.2028, Found: 413.2031.

General procedure for the synthesis of phosphindoles ***7***

To a solution of **2a-h** (2 mmol) in THF (8 mL) was added 80 mg of lithium wire under N_2 atmosphere. The reaction mixture was stirred for 2h, the excess of lithium wire was removed, then 2 eq. of CH_3I or benzyl bromide was added at 0 °C. Then S_8 or H_2O_2 was added 10 min later, the reaction mixture was stirred for another 2h. After removal of the solvent under reduced pressure, the residue was treated with water (10 mL), and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue of oxide was chromatographed on silica gel (dichloromethane/ethyl acetate = 8/1). The sulfide was chromatographed on silica gel (*n*-hexane/dichloromethane = 2/1).

7a: pale yellow oil (67% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.7 (d, J_{PH} = 12.9 Hz, 3H), 7.27-7.39 (m, 7H), 7.67-7.80 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.7 (d, J_{PC} = 67.2 Hz, PCH_3), 124.6 (d, J_{PC} = 9.4 Hz, CH), 126.4 (d, J_{PC} = 6.1 Hz, CH), 128.2 (d, J_{PC} = 10.3 Hz, CH), 128.8 (d, J_{PC} = 10.4 Hz, CH), 129.0(CH), 129.1(CH), 132.0 (d, J_{PC} = 91.2 Hz), 132.8 (d, J_{PC} = 3.2 Hz), 133.0 (d, J_{PC} = 1.8 Hz, CH), 134.6 (d, J_{PC} = 20.1 Hz, CH), 138.6 (d, J_{PC} = 92.5 Hz) , 140.6 (d, J_{PC} = 28.4 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 45.2; HRMS Calcd. for $C_{15}H_{14}OP$ [M + H^+] 241.0776, Found: 241.0780.

7b: white solid (53% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.98 (d, J_{PH} = 13.5Hz, 3H), 2.37 (s, 3H), 7.22-7.51 (m, 6H), 7.78 (t, J_{HH} = 8.5 Hz, 1H), 7.87-7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.4 (d, J_{PC} = 51.6 Hz, PCH_3), 21.4 (CH_3), 124.5 (d, J_{PC} = 8.7 Hz, CH), 126.6 (d, J_{PC} = 6.5Hz, CH), 127.8 (d, J_{PC} = 11.5 Hz, CH), 128.7 (d, J_{PC} = 11.1 Hz, CH), 129.73 (d, J_{PC} = 11.6 Hz), 129.7, (CH), 132.5 (d, J_{PC} = 2.0 Hz, CH), 133.1 (d, J_{PC} = 17.5 Hz, CH), 135.6 (d, J_{PC} = 89.5 Hz), 139.02, 139.7 (d, J_{PC} = 75.1 Hz) , 141.1 (d, J_{PC} = 24.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 45.0; HRMS Calcd. for $C_{16}H_{16}PS$ [M + H^+] 271.0704, Found: 271.0708. Anal. Calcd. for $C_{16}H_{15}PS$: C, 71.09; H, 5.59. Found: C, 71.08; H, 5.73.

7c. colorless oil (46% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0. 25 (s, 9H), 1.62 (d, J_{PH} = 12.9 Hz, 3H), 7.21-7.39 (m, 4H), 7.65 (t, J_{HH} = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = -0.9 (d, J_{PC} = 1.3 Hz, CH_3), 15.9 (d, J_{PC} = 66.5 Hz, PCH_3), 124.3 (d, J_{PC} = 10.7 Hz, CH), 127.8 (d, J_{PC} = 9.9 Hz, CH), 129.1 (d, J_{PC} = 9.4 Hz, CH), 132.5 (d, J_{PC} = 1.9 Hz, CH), 134.8 (d, J_{PC} = 99.0 Hz), 141.1 (d, J_{PC} = 117.3 Hz), 141.3 (d, J_{PC} = 22.8 Hz), 150.5 (d, J_{PC} = 8.0 Hz, CH); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 53.9; HRMS Calcd. for $C_{12}H_{18}POSi$ [M + H^+] 237.0859. Found: 237.0867.

7d: white solid (65% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.93 (d, J_{PH} = 13.5 Hz, 3H), 3.75 (s, 3H), 6.89 (d, J_{PH} = 8.7 Hz, 2H), 7.29-7.43 (m, 4H), 7.69-7.75 (m, 1H) , 7.91 (d, J_{PH} = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.4 (d, J_{PC} = 51.6 Hz, PCH_3), 55.4 (OCH_3), 114.4 (CH), 124.5 (d, J_{PC} = 8.7 Hz, CH), 125.1 (d, J_{PC} = 11.3 Hz), 127.7 (d, J_{PC} = 11.5 Hz, CH), 128.1 (d, J_{PC} = 6.7 Hz, CH), 128.5 (d, J_{PC} = 11.2 Hz, CH), 132.0 (d, J_{PC} = 17.5 Hz, CH), 132.6 (d, J_{PC} = 1.9 Hz, CH), 135.2 (d, J_{PC} = 89.8 Hz), 139.0 (d,

J_{PC} = 75.2 Hz) , 141.3 (d, J_{PC} = 24.6 Hz), 160.2; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= 44.7; HRMS Calcd. for $C_{16}H_{16}OPS$ [M + H^+] 287.0654, Found: 287.0659. Anal. Calcd. for $C_{16}H_{15}OPS$: C, 67.12; H, 5.28. Found: C, 67.26; H, 5.37.

7e: white solid (60% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 0.98 (t, J_{HH} = 7.5 Hz, 3H), 1.40-1.52 (m, 2H), 1.64-1.75(m, 2H),1.88(d, J_{PH} = 13.5 Hz, 3H), 2.43-2.71(m, 2H), 6.87 (d, J_{PH} = 37.2 Hz, 1H),7.30-7.47(m, 3H),7.73(t, J_{HH} = 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.9 (CH_3), 20.4 (d, J_{PC} = 50.9 Hz, PCH_3), 22.5 (CH_2), 26.7 (d, J_{PC} = 11.7 Hz, CH_2), 30.1 (d, J_{PC} = 5.7 Hz, CH_2), 123.8 (d, J_{PC} = 9.1 Hz, CH), 127.7 (d, J_{PC} = 11.1 Hz, CH), 128.1 (d, J_{PC} = 10.7 Hz, CH), 132.3 (d, J_{PC} = 2.2 Hz, CH), 134.9 (d, J_{PC} = 18.0 Hz, CH), 135.1 (d, J_{PC} = 87.7 Hz), 141.6 (d, J_{PC} = 26.7 Hz) , 143.7 (d, J_{PC} = 71.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= 46.2; HRMS Calcd. for $C_{13}H_{18}PS$ [M + H^+] 237.0861, Found: 237.0867. Anal. Calcd. for $C_{13}H_{17}PS$: C, 66.07; H, 7.25. Found: C, 66.06; H, 7.37.

7f: white solid (60% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 0.93 (t, J_{HH} = 7.3 Hz, 3H), 1.32-1.43 (m, 2H), 1.55-1.66 (m, 2H), 1.76 (d, J_{PH} = 12.9 Hz, 3H), 2.62 (t, J_{HH} = 7.6 Hz, 2H), 7.22-7.47 (m, 6H), 7.73-7.78 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.7 (CH_3), 15.5 (d, J_{PC} = 67.1 Hz, PCH_3), 22.1 (CH_2), 33.2 (CH_2), 35.2 (CH_2), 124.3 (d, J_{PC} = 9.3 Hz, CH), 126.1 (d, J_{PC} = 6.2 Hz, CH), 127.8 (d, J_{PC} = 10.3 Hz, CH), 128.3 (d, J_{PC} = 10.5 Hz, CH), 128.9 (CH), 129.8 (d, J_{PC} = 10.8 Hz), 131.8 (d, J_{PC} = 105.4 Hz), 132.7 (d, J_{PC} = 1.9 Hz, CH), 133.3 (d, J_{PC} = 20.2 Hz, CH), 138.2(d, J_{PC} = 92.0 Hz) , 140.5(d, J_{PC} = 28.2 Hz), 143.9; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 45.2; HRMS Calcd. for $C_{19}H_{22}OP$ [M + H^+] 297.1402, Found: 297.1406.

7g: white solid (40% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 3.14-3.55 (m, 2H), 6.83-6.85 (m, 2H), 7.00-7.52 (m, 11H), 7.83-7.90 (m, 2H), 7.99-8.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 36.6 (d, J_{PC} = 61.1 Hz, PCH2), 124.6 (d, J_{PC} = 9.3 Hz, CH), 125.5(CH), 125.6(CH), 126.0(CH), 126.5(CH), 126.7 (d, J_{PC} = 4.3 Hz, CH), 126.8 (d, J_{PC} = 3.4 Hz, CH), 128.2 (d, J_{PC} = 2.9 Hz, CH), 128.6 (CH), 128.7 (d, J_{PC} = 9.8 Hz, CH), 129.0 (CH), 129.4 (d, J_{PC} = 9.3 Hz, CH), 129.8 (d, J_{PC} = 102.7 Hz), 129.8 (d, J_{PC} = 5.3 Hz, CH), 130.6 (d, J_{PC} = 7.3 Hz), 131.0 (d, J_{PC} = 6.0 Hz), 131.2 (d, J_{PC} = 9.3 Hz), 133.1 (d, J_{PC} = 1.8 Hz, CH), 134.1, 136.6 (d, J_{PC} = 87.6 Hz), 141.2 (d, J_{PC} = 27.8 Hz), 141.3 (d, J_{PC} = 19.7 Hz, CH); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 47.3; HRMS Calcd. for $C_{25}H_{20}OP$ [M + H^+] 367.1246, Found: 367.1250.

7h: white solid (57% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 1.77 (d, J_{PH} = 13.2 Hz, 3H), 3.87 (s, 3H), 7.09-7.65 (m, 9H), 7.78 (t, J_{HH}= 8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ = 15.9 (d, J_{PC} = 68.3 Hz, PCH_3), 32.1 (NCH_3), 105.6 (d, J_{PC} =3.3Hz, CH), 109.4 (CH), 120.2 (CH), 121.4 (CH), 123.4 (CH), 124.7 (d, J_{PC} = 8.9 Hz, CH), 127.7, 128.3 (d, J_{PC} = 10.4 Hz, CH), 128.7 (d, J_{PC} = 10.4 Hz, CH), 131.0 (d, J_{PC} = 105.9 Hz), 131.8 (d, J_{PC} = 92.9 Hz), 132.5 (d, J_{PC} = 16.3 Hz), 133.1 (d, J_{PC} = 1.8Hz, CH), 133.6 (d, J_{PC} = 18.6 Hz, CH) , 139.4, 141.0 (d, J_{PC} = 28.5Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 46.2; HRMS Calcd. for $C_{18}H_{17}NOP$ [M + H^+] 294.1042, Found: 294.1043.

*General procedure for the synthesis of phosphole sulfides **9***

To a solution of **4a,b** (2 mmol) in THF (8 mL) was added 80 mg of lithium wire under N_2 atmosphere. The reaction mixture was stirred for 2h, the excess lithium wire was removed, then 2 eq. of CH_3I was added at 0 °C. Then, 10 min later, 1.5 eq. of S_8 was added and the reaction mixture was stirred for 2h. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (*n*-hexane/dichloromethane = 2/1).

9a: colorless oil (48% yield); ^1H NMR (300 MHz, $CDCl_3$) δ = 1.12-1.26 (m, 6H), 1.83 (d, J_{PH} = 12.9 Hz, 3H), 2.34-2.73 (m, 7H), 6.95 (d, J_{PH} = 38.1 Hz, 1H), 7.18(d, J_{HH} = 7.8 Hz, 2H), 7.78 (d, J_{HH} = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.8 (CH_3), 14.9 (CH_3), 18.1 (d, J_{PC} = 14.0 Hz, CH_2), 20.2 (d, J_{PC} = 47.6 Hz, PCH_3), 21.4 (CH_3), 22.7 (d, J_{PC} = 12.8 Hz, CH_2), 126.2 (d, J_{PC} = 6.2 Hz, CH), 129.61 (d, J_{PC} = 12.0 Hz), 129.62(CH), 133.5 (d, J_{PC} = 25.6 Hz, CH), 135.5 (d, J_{PC} = 77.7 Hz), 138.4 (d, J_{PC} = 73.9 Hz), 138.6, 148.1 (d, J_{PC} = 22.9 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 52.9; HRMS Calcd. for $C_{16}H_{22}PS$ [M + H^+] 277.1174, Found: 277.1177. Anal. Calcd. for $C_{16}H_{21}PS$: C, 69.53; H, 7.66. Found: C, 69.71; H, 8.09.

9b: pale yellow oil (46% yield); ^1H NMR (300 MHz, $CDCl_3$) δ= 0.97-1.03 (q, J_{HH} = 11.7 Hz, 6H), 1.52-1.70 (m, 4H), 1.83 (d, J_{PH} = 12.6 Hz, 3H), 2.31-2.46 (m, 3H), 2.54-2.64 (m, 1H), 6.99 (d, J_{PH} = 38.1 Hz, 1H), 7.27-7.40 (m, 3H), 7.87-7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.0 (CH_3), 14.4 (CH_3), 20.2 (d, J_{PC} = 47.7 Hz, PCH_3), 21.5 (CH_2), 23.2 (CH_2), 27.2 (d, J_{PC} = 13.7 Hz, CH_2), 31.5 (d, J_{PC} = 12.7 Hz, CH_2), 126.3 (d, J_{PC} = 6.0 Hz, CH), 128.6 (CH), 128.8 (CH), 132.3 (d, J_{PC} = 12.1 Hz), 134.8 (d, J_{PC} = 25.7 Hz, CH), 135.5 (d, J_{PC} = 76.8 Hz), 138.3 (d, J_{PC} = 73.8 Hz), 147.0 (d, J_{PC} = 22.6 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 53.0; HRMS Calcd. for $C_{17}H_{24}PS$ [M + H^+] 291.1330, Found: 291.1335.

*Synthesis of P-phenylphosphole sulfide **7i***

To a solution of **2a** (2 mmol) in THF (8 mL) was added 80 mg of lithium wire under N_2 atmosphere. The reaction mixture was stirred for 2h, the excess lithium wire was removed, then 2 eq. of I_2 was added at 0 °C. Then S_8 was added 10 min later, the reaction mixture was stirred for another 2h. After removal of the solvent under reduced pressure, the residue was treated with water (10 mL), and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, The sulfide was chromatographed on silica gel (*n*-hexane/dichloromethane = 2/1) to give **7i** as a white solid (55% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.20-7.43 (m, 9H), 7.53-7.70 (m, 4H), 7.81-7.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 124.8 (d, J_{PC} = 8.8 Hz, CH), 127.0 (d, J_{PC} = 6.7 Hz, CH), 128.4 (d, J_{PC} = 11.6 Hz, CH), 128.8 (CH), 128.9 (CH), 128.9 (d, J_{PC} = 13.5 Hz, CH), 129.2 (d, J_{PC} = 11.3 Hz, CH), 129.2 (d, J_{PC} = 76.5 Hz), 130.7 (d, J_{PC} = 11.7 Hz, CH), 132.1 (d, J_{PC} = 2.8 Hz, CH), 132.2 (d, J_{PC} = 11.2 Hz), 132.6 (d, J_{PC} = 2.1 Hz, CH), 135.9 (d, J_{PC} = 17.2 Hz, CH), 136.9 (d, J_{PC} = 93.0 Hz), 140.2 (d, J_{PC} = 78.4 Hz), 141.8 (d, J_{PC} = 24.4 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 43.4; HRMS Calcd. for $C_{20}H_{16}SP$ [M + H^+] 319.0704, Found: 319.0710.

*Heterotetracene **11***

Same procedure as before, starting from phosphine **2i.**

11c: white solid(47% yield) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.50 (d, J_{PH} = 2.0 Hz, 6H), 1.88 (d, J_{PH} = 13.2 Hz, 3H), 7.28-7.51 (m, 5H), 7.60 (d, J_{HH} = 7.2 Hz, 1H), 7.68 (d, J_{HH} = 7.2 Hz, 1H), 7.77(t, J_{HH} = 8.0 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = -4.0 (d, J_{PC} = 9.6 Hz, CH_3), 15.6 (d, J_{PC} = 66.1 Hz, PCH_3), 123.9 (CH) ,125.0 (d, J_{PC} = 8.3 Hz, CH), 127.8 (CH),128.4 (d, J_{PC} = 1.4 Hz, CH), 128.5 (d, J_{PC} = 24.0 Hz, CH), 130.5 (CH), 132.8 (CH), 133.0 (d, J_{PC} = 1.8 Hz, CH), 134.5 (d, J_{PC} = 110.1 Hz), 140.1 (d, J_{PC} = 8.1 Hz), 141.6 (d, J_{PC} = 29.0 Hz), 143.3 (d, J_{PC} = 14.6 Hz), 153.5 (d, J_{PC} = 86.0 Hz), 156.8 (d, J_{PC} = 9.5 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 39.5; HRMS Calcd. for $C_{17}H_{18}OPSi$ [M + H^+] 297.0859, Found: 297.0866**.**

11d: white solid (52% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.50 (s, 6H), 2.05 (d, J_{PH} = 13.2Hz, 3H), 7.29-7.61(m, 6H), 7.76-7.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = -3.9 (d, J_{PC} = 6.4 Hz, CH_3), 21.3 (d, J_{PC} = 51.1 Hz, PCH_3), 123.7 (CH), 125.1 (d, J_{PC} = 7.7 Hz, CH), 127.9 (CH), 128.1 (d, J_{PC} = 13.0 Hz, CH), 128.5 (d, J_{PC} = 11.3 Hz, CH), 130.5 (CH), 132.5 (d, J_{PC} = 2.1 Hz, CH), 132.8 (CH), 138.4 (d, J_{PC} = 93.2 Hz), 140.4

(d, J_{PC} = 8.3 Hz), 142.0 (d, J_{PC} = 26.1 Hz), 142.8 (d, J_{PC} = 15.4 Hz) , 153.9 (d, J_{PC} = 68.5 Hz), 155.4 (d, J_{PC} = 6.3 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 37.5; HRMS Calcd. for $C_{17}H_{18}PSSi$ [M + H^+] 313.0630, Found: 313.0630. Anal. Calcd. for $C_{17}H_{17}PSSi$: C, 65.35; H, 5.48. Found: C, 64.88; H, 5.50.

*Synthesis of **14b***

The alkyne **12** was synthesized in 86% yield using a Sonogashira coupling reaction as shown in scheme (7).

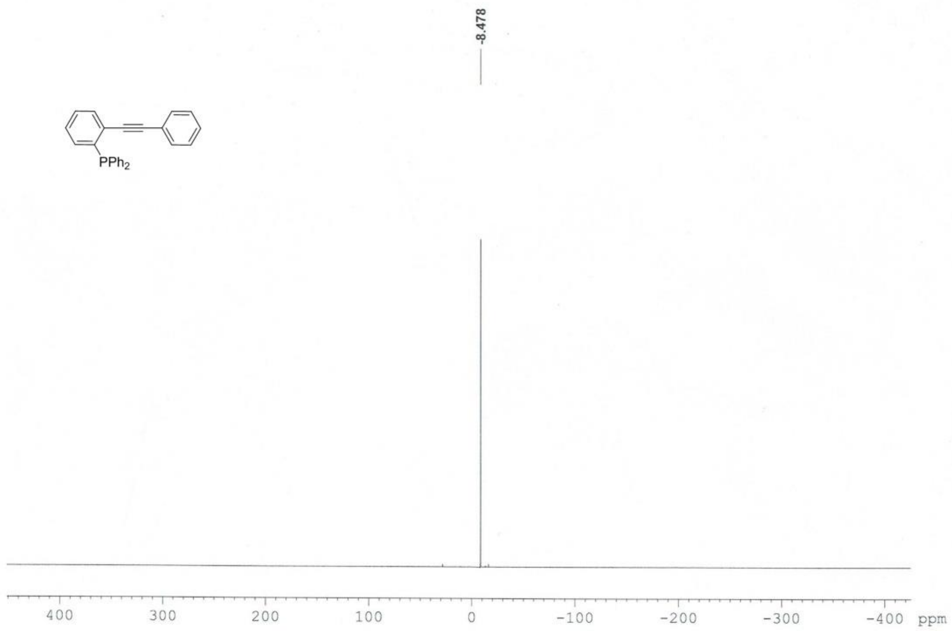
*Phosphine **13***

To a solution of **12** (2.6g, 8 mmol) in THF (30 mL) was added dropwise *n*-butyllithium in *n*-hexane (5.5 mL, 1.6 mol/L, 8.8 mmol) at –78ºC over 5 min under N_2 atmosphere. The reaction mixture was stirred for 50 min, then Ph_2PCl (2.1g, 9.6mmol) was added at -78 °C, then the temperature was slowly raised back to room temperature to give a pale yellow solution. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (hexane/ethyl acetate = 20/1) to give **13** as a pale yellow solid (2.57g, 75% yield). ^1H NMR (300 MHz, $CDCl_3$) δ = 2.41(s, 3H), 3.94 (s, 3H), 7.02 (t, J_{PH} = 7.3 Hz, 1H), 7.18-7.42 (m, 13H), 7.54-7.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.6 (CH_3), 31.1 (NCH_3), 80.2 (d, J_{PC} = 3.1Hz), 99.7, 109.7(CH), 110.7 (d, J_{PC} = 7.5 Hz), 119.4, 120.5 (CH), 121.7 (d, J_{PC} = 3.7 Hz, CH), 123.2 (CH), 128.0 (d, J_{PC} = 21.1 Hz, CH) , 128.2 (CH), 129.1 (CH), 130.0 (d, J_{PC} = 4.7 Hz), 130.1 (d, J_{PC} = 35.9 Hz), 131.6 (CH), 132.9 (d, J_{PC} = 18.7 Hz, CH),137.8 (d, J_{PC} = 8.4 Hz), 138.4 (d, J_{PC} = 3.5 Hz), 139.0; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = -34.4; HRMS Calcd. for $C_{30}H_{25}NP$ [M + H^+] 430.1719, Found: 430.1720.

*Compound **14b***

To a solution of **13** (858mg, 2 mmol) in THF (10 mL) was added 80 mg of lithium wire under N_2 atmosphere. The reaction mixture was stirred for 2h, remove the excess lithium wire, then 2eq.of CH_3I was added at 0 °C. Then, 10min later, S_8 (96mg,1.5 eq) was added and the reaction mixture was stirred for additional 2h. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (*n*-hexane/dichloromethane = 2/1) to get **14b** as an unstable yellow solid (355 mg, 55% yield). ^1H NMR (300 MHz, $CDCl_3$) δ = 2.06 (d, J_{PH} = 13.8 Hz, 3H), 2.32 (s, 3H), 3.66 (s, 3H), 7.10-7.13 (m, 2H), 7.21-7.24 (m, 3H), 7.36 (d, J_{PH} = 33 Hz, 1H), 7.74-7.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.4, 22.2 (d, J_{PC} = 55.4 Hz), 30.6, 110.6 (CH), 119.4 (CH), 120.2 (d, J_{PC} = 10.6 Hz, CH), 122.1 (CH), 122.5 (CH), 125.3 (d, J_{PC} = 9.8 Hz), 126.3(d, J_{PC} = 6.9 Hz, CH), 129.5 (CH), 130.1(d, J_{PC} = 11.2 Hz), 136.2 (d, J_{PC} = 89.2 Hz), 139.0, 141.2 (d, J_{PC} = 9.8Hz), 145.9(d, J_{PC} = 73.8 Hz), 148.5 (d, J_{PC} = 36.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= 31.9; HRMS Calcd. for $C_{19}H_{19}NPS$ [M + H^+] 324.0970, Found: 324.0973.

NMR DATA



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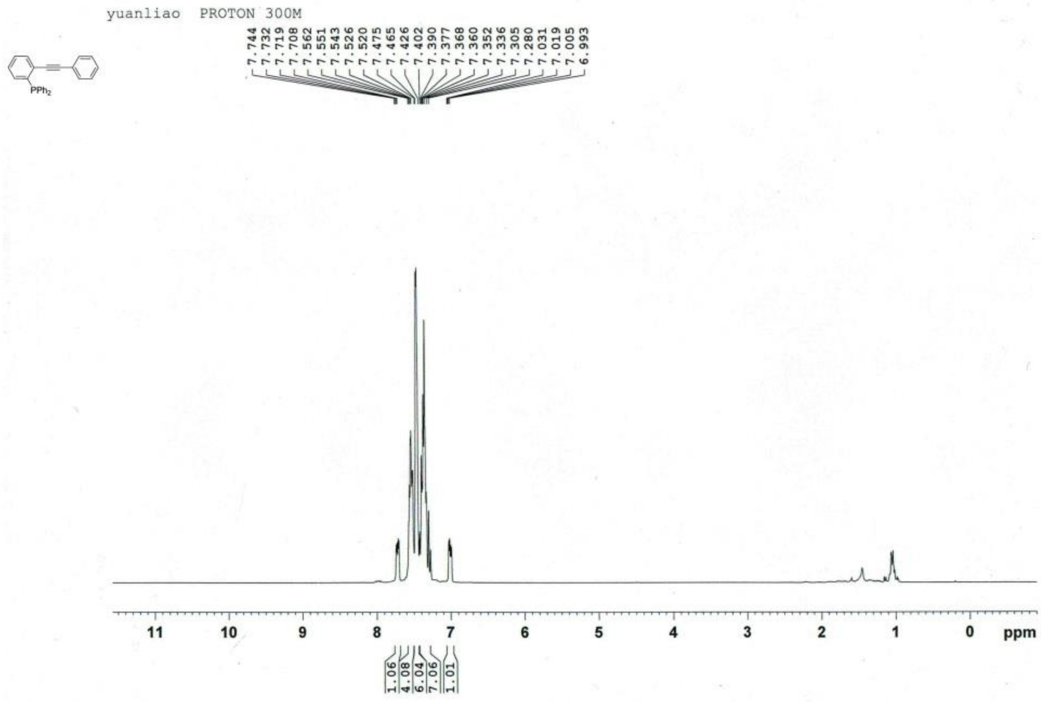

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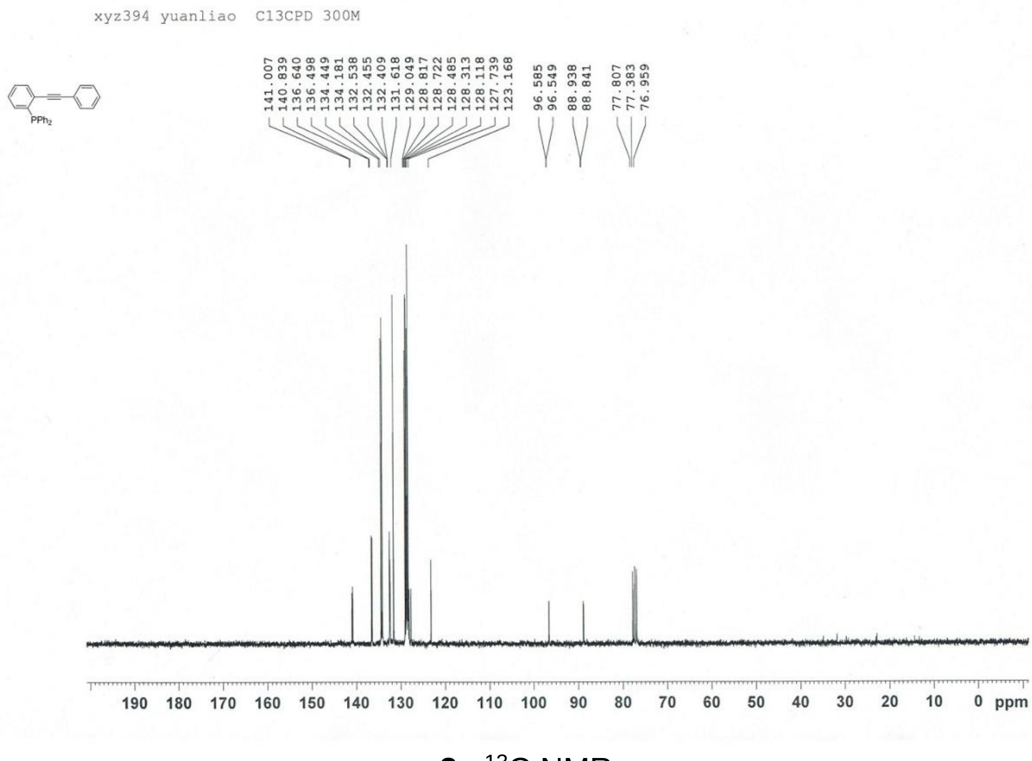

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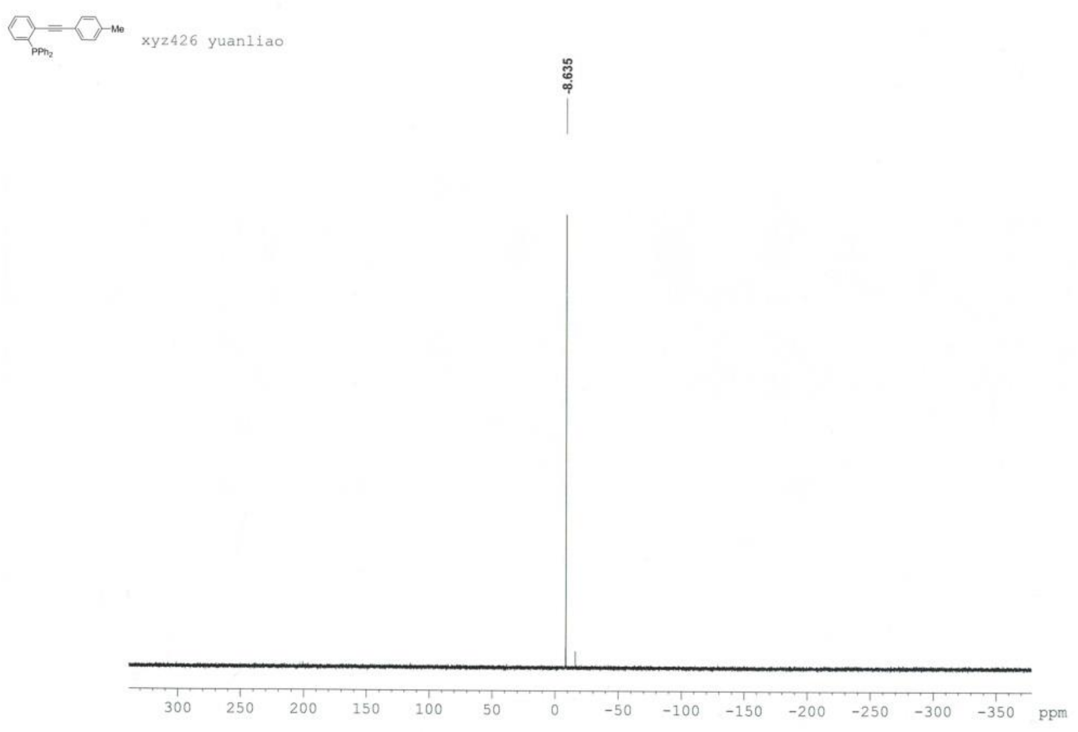

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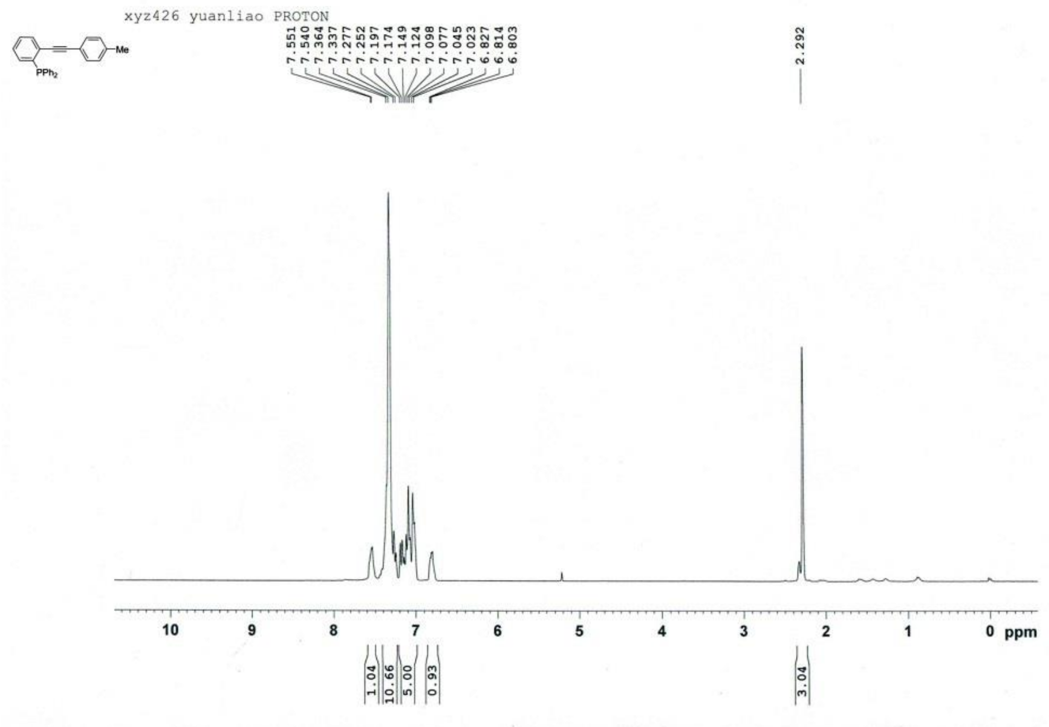

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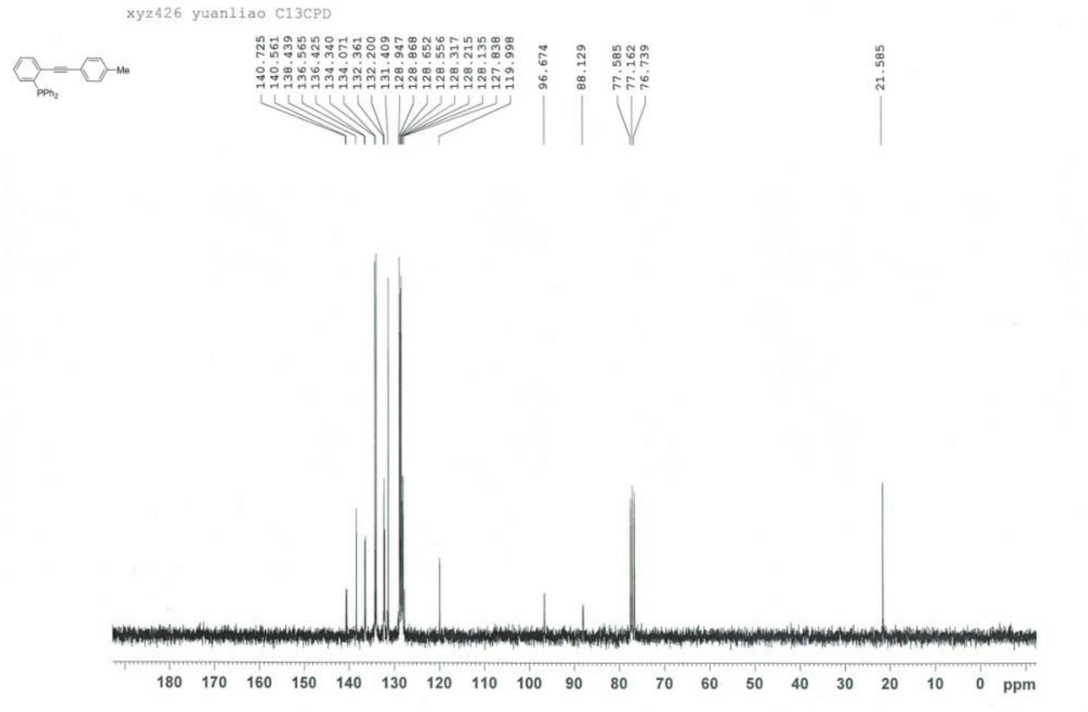

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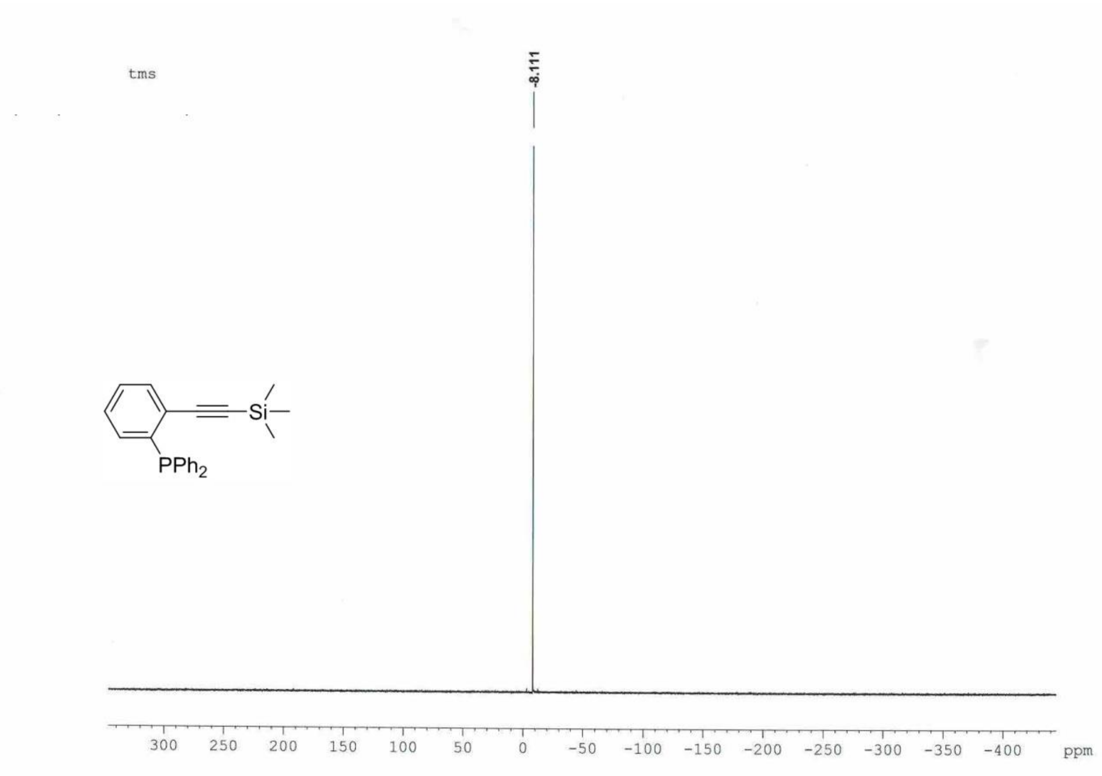

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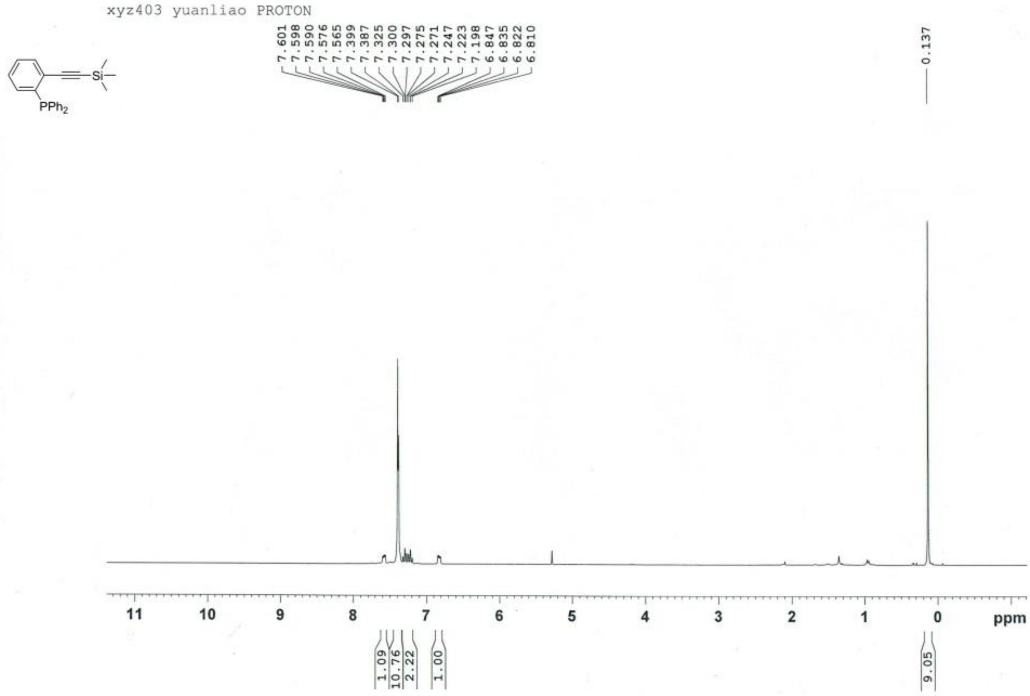

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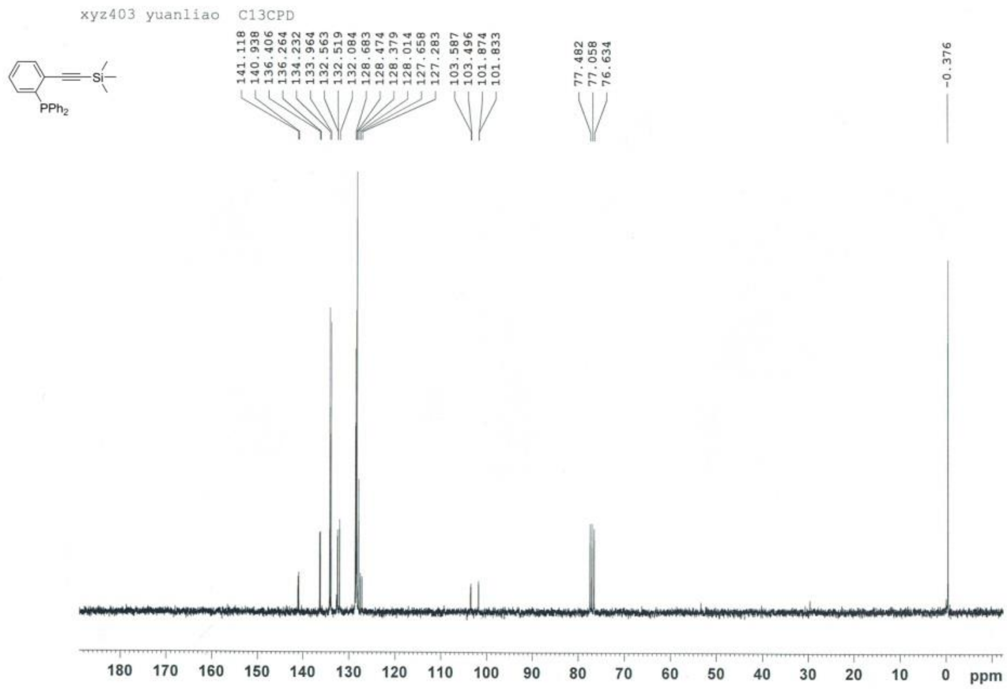

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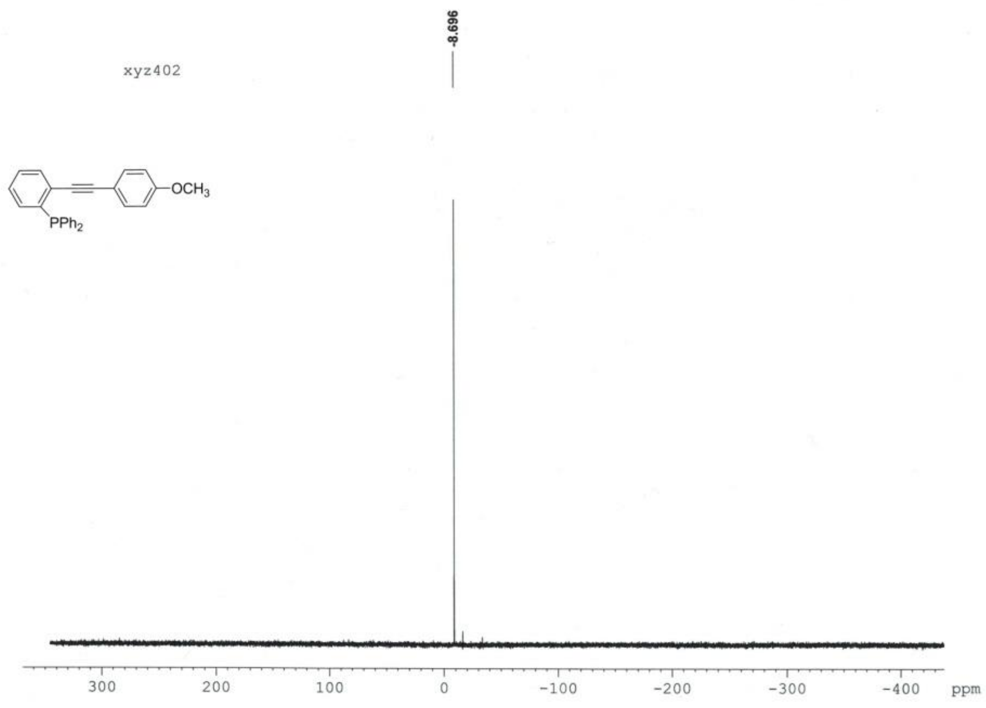

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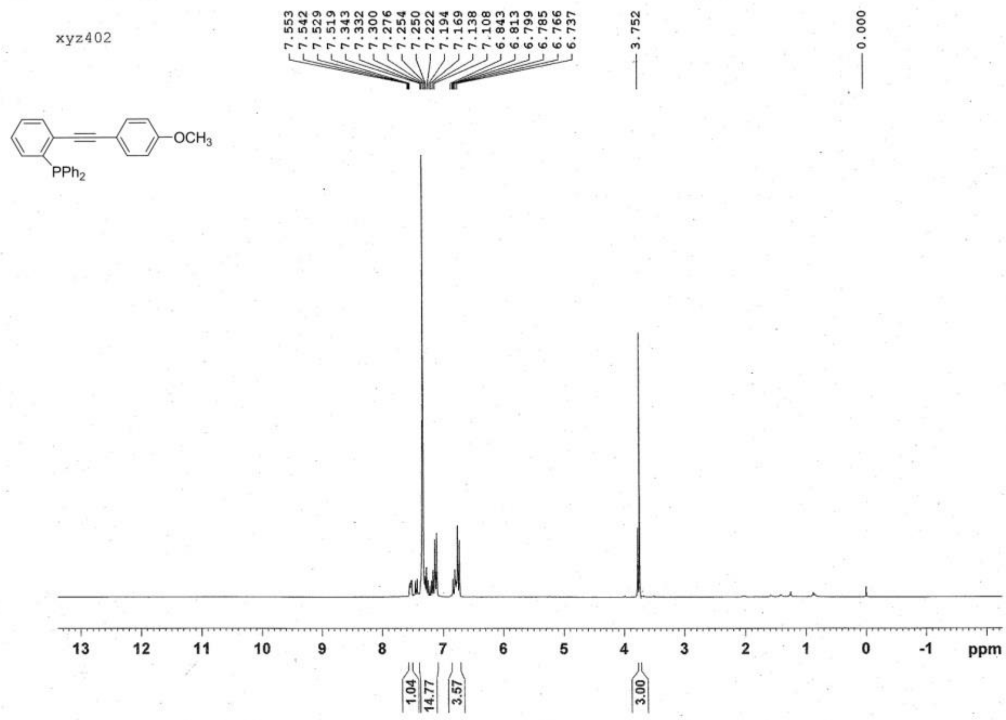

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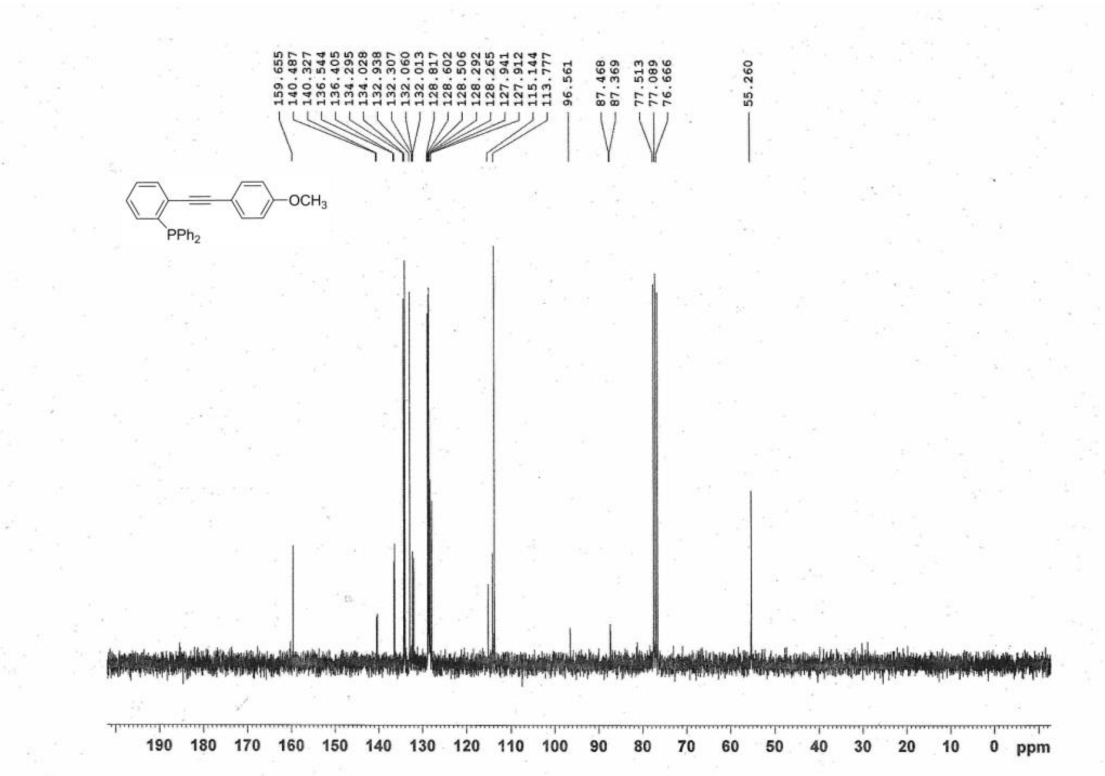

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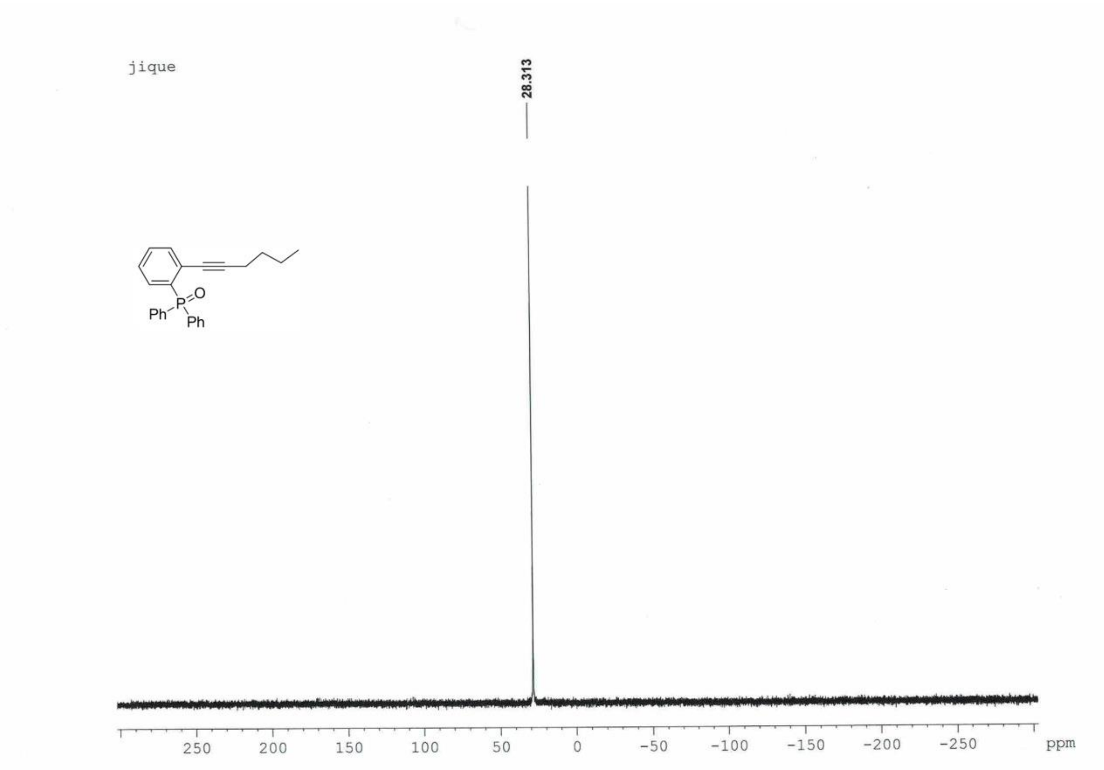

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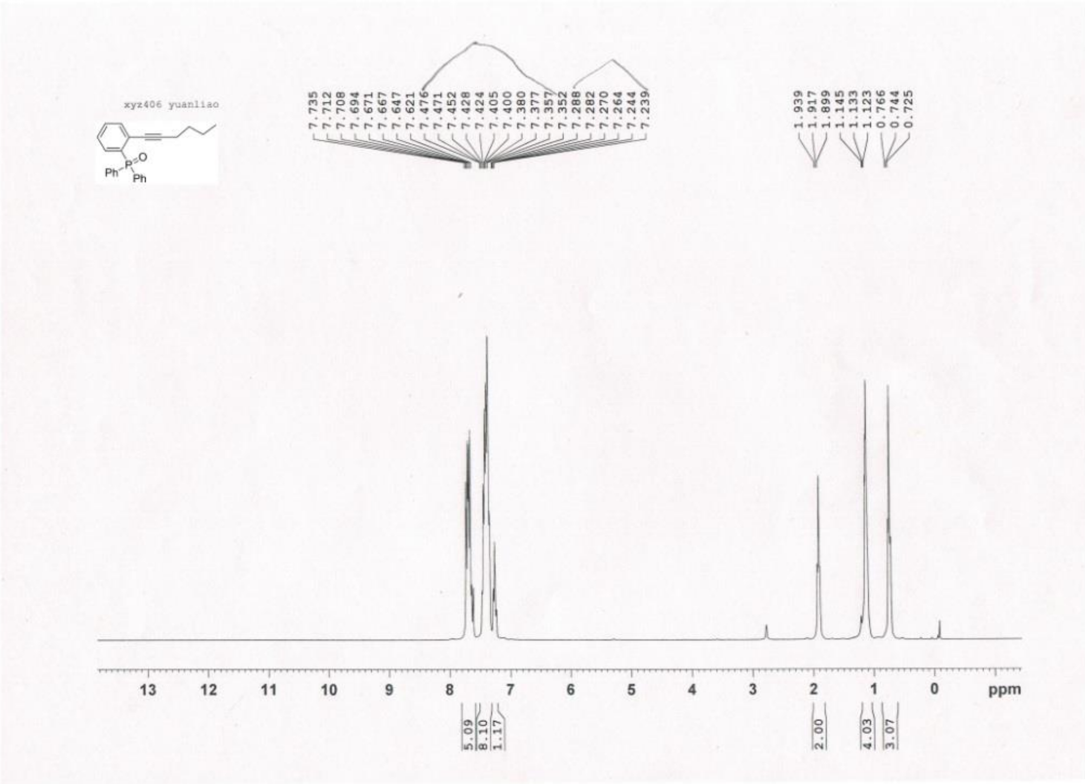

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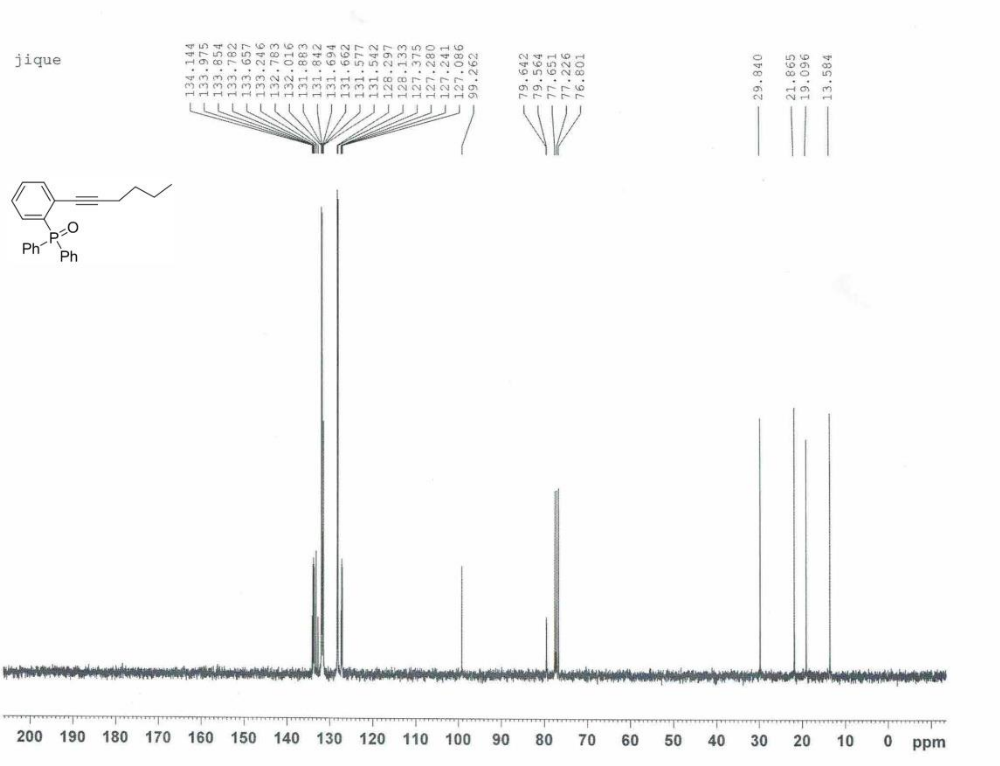

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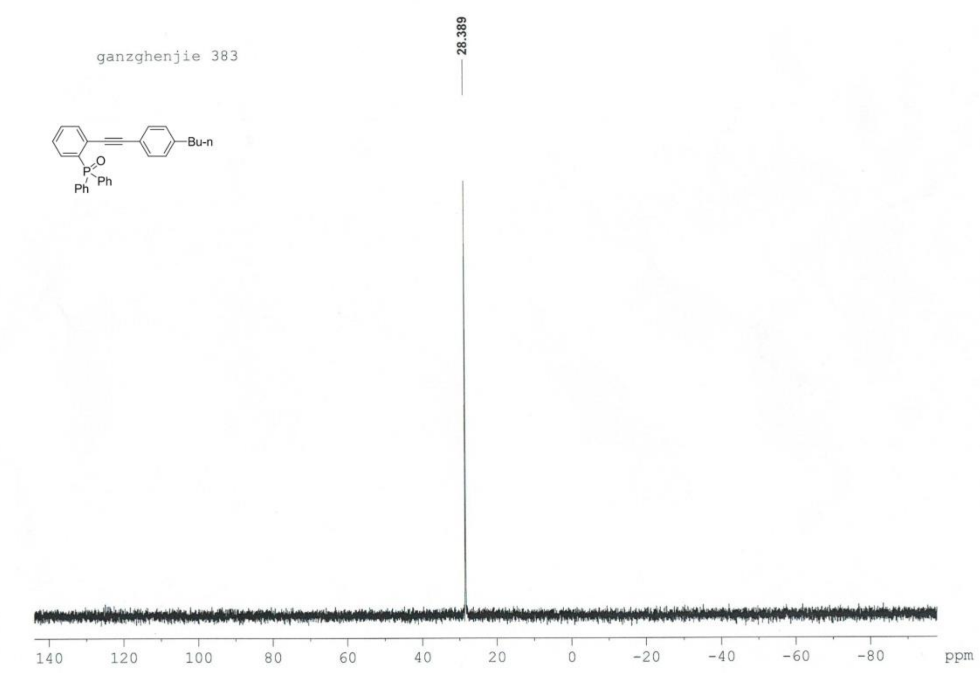

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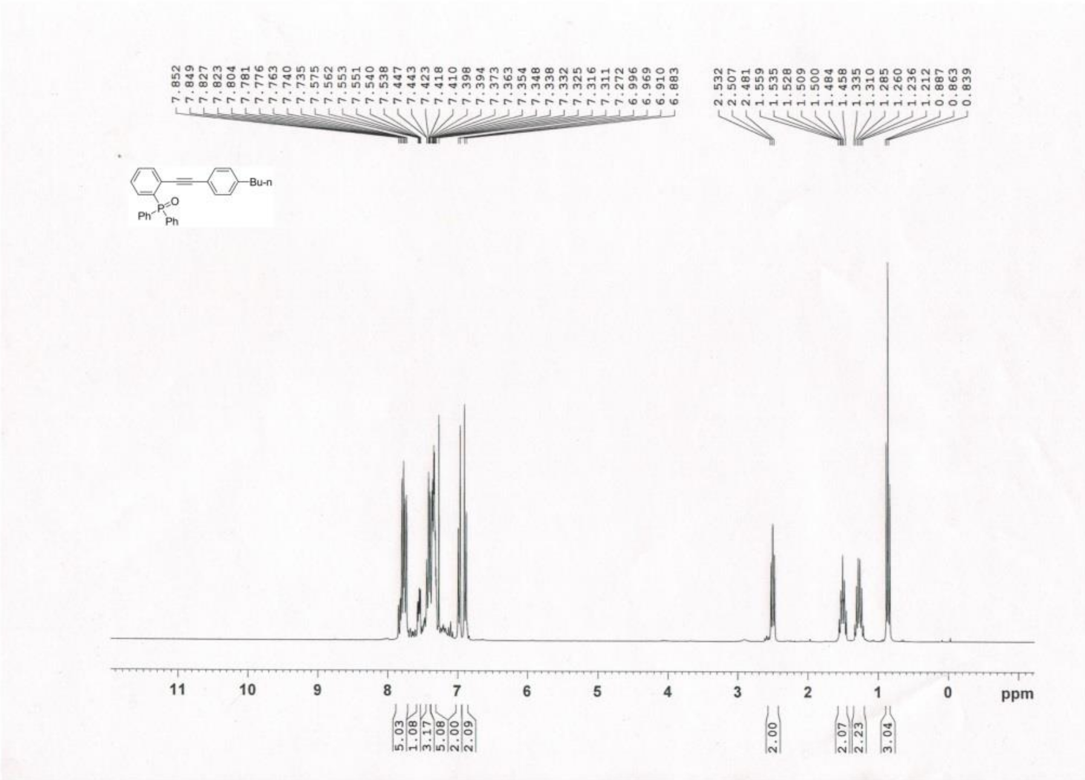

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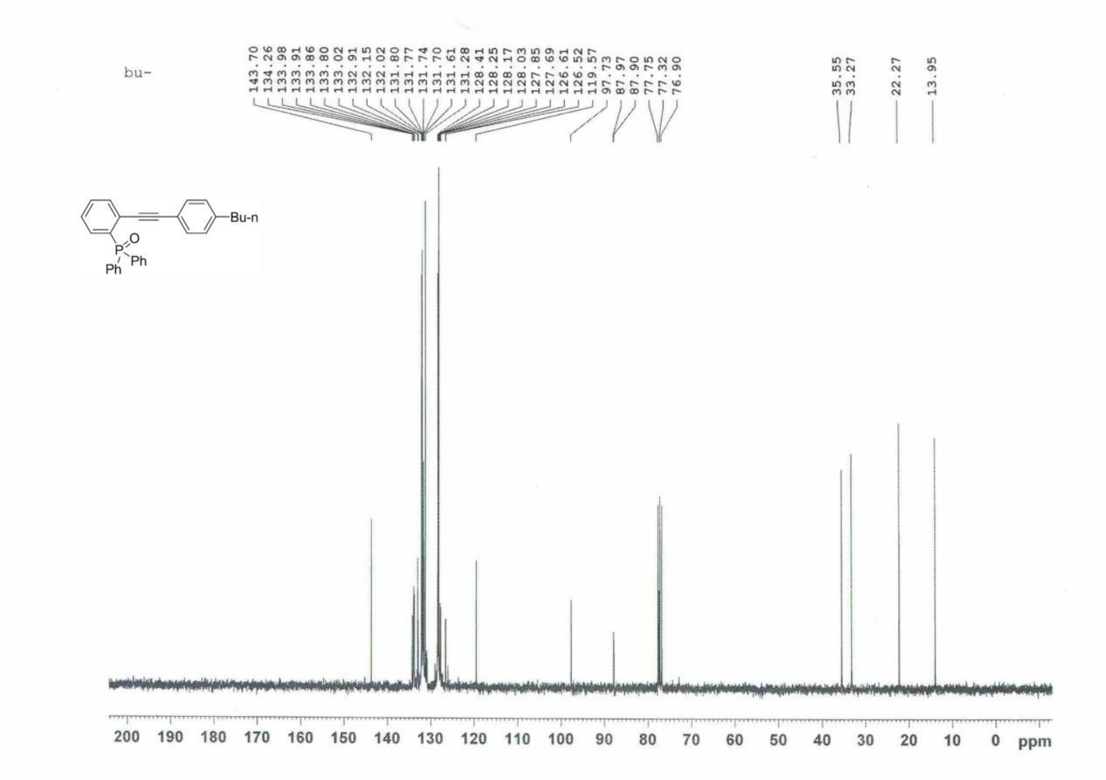

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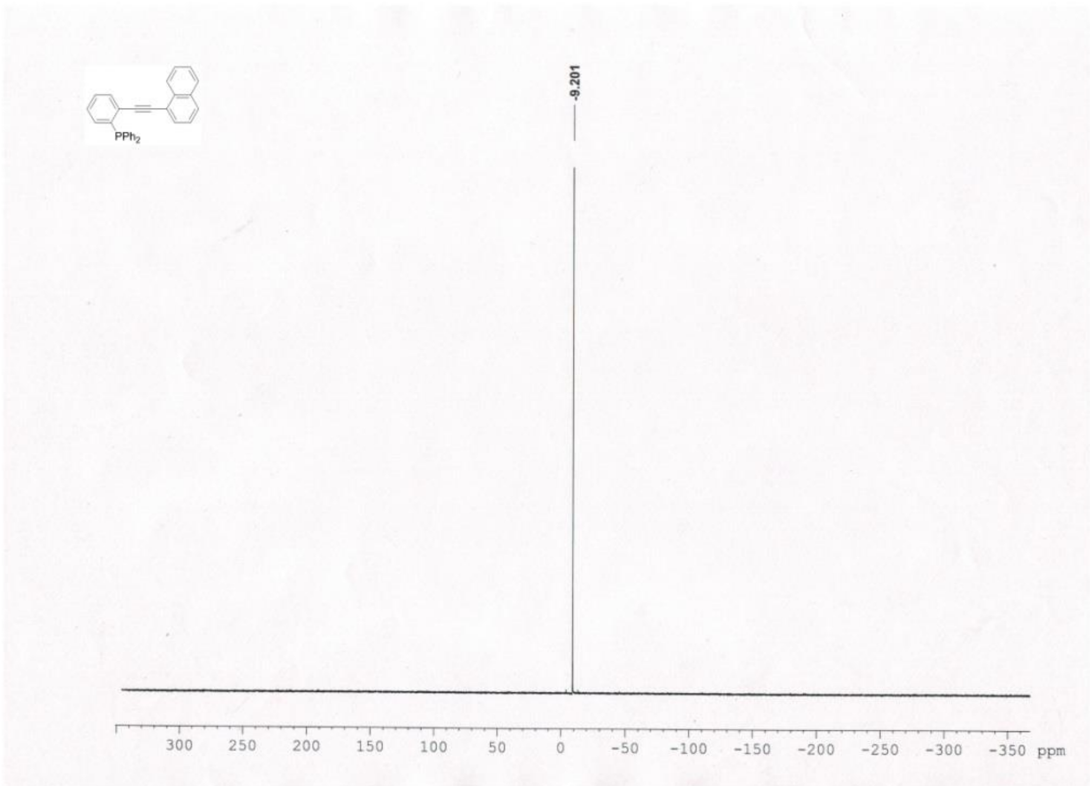

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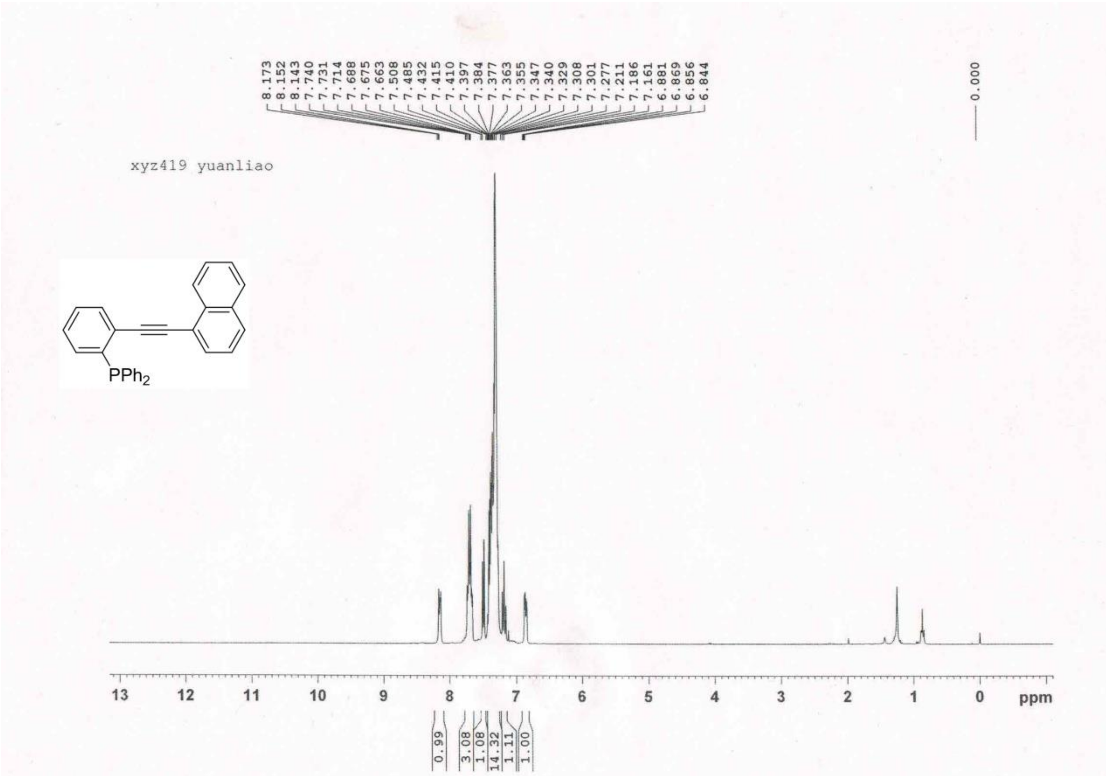

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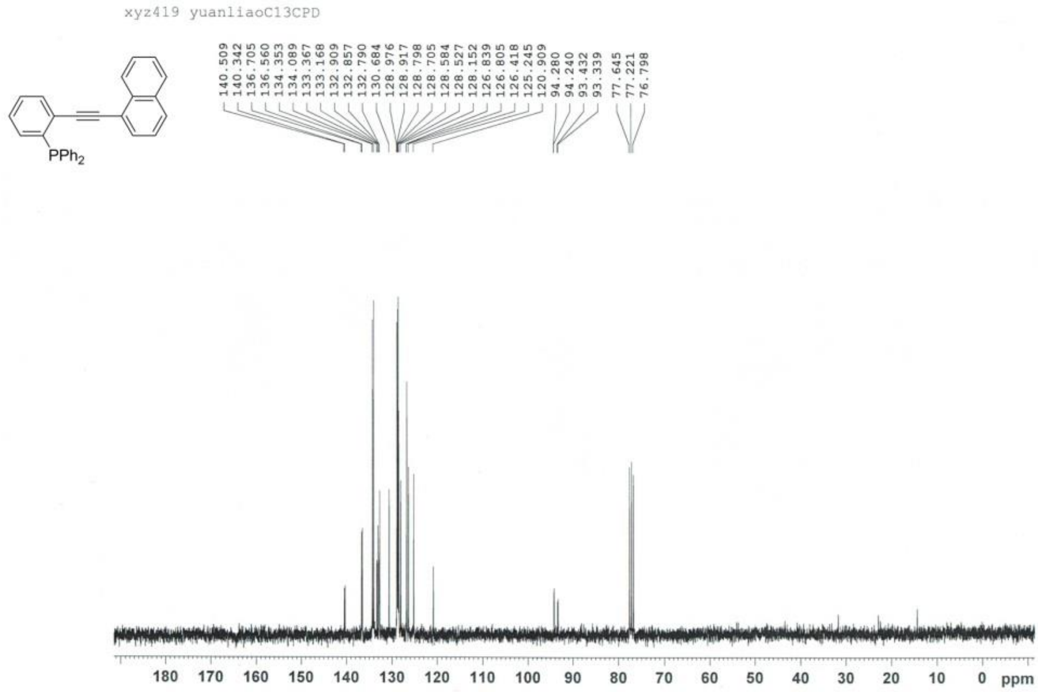

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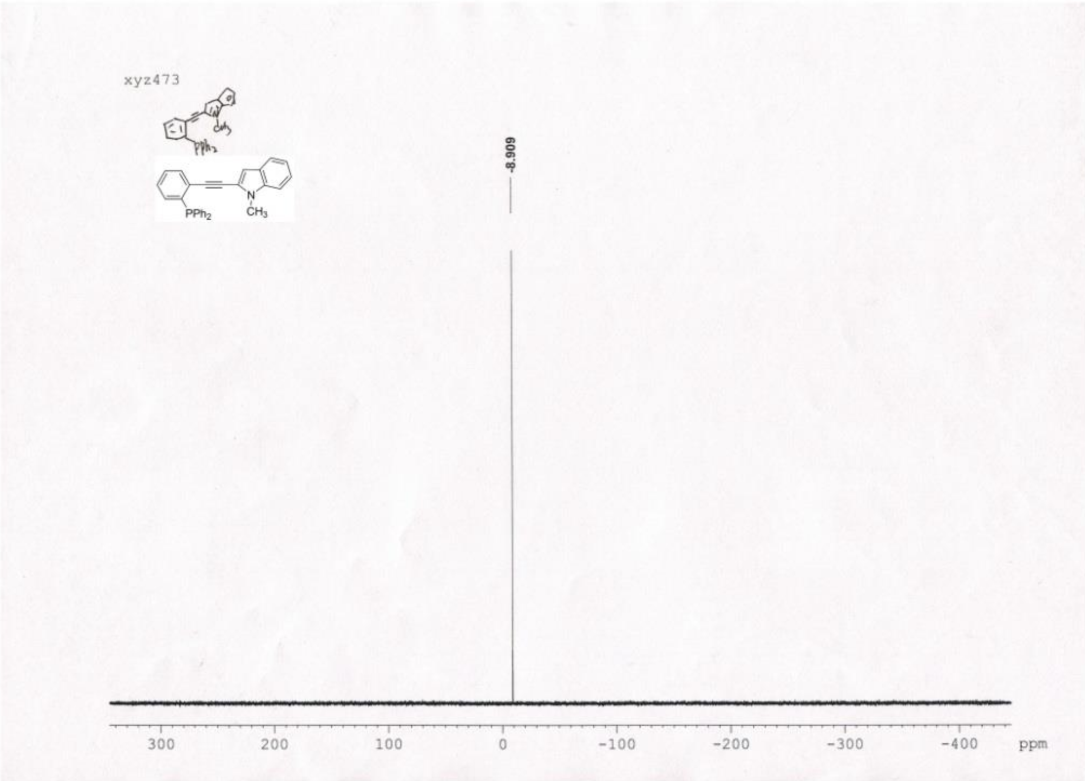

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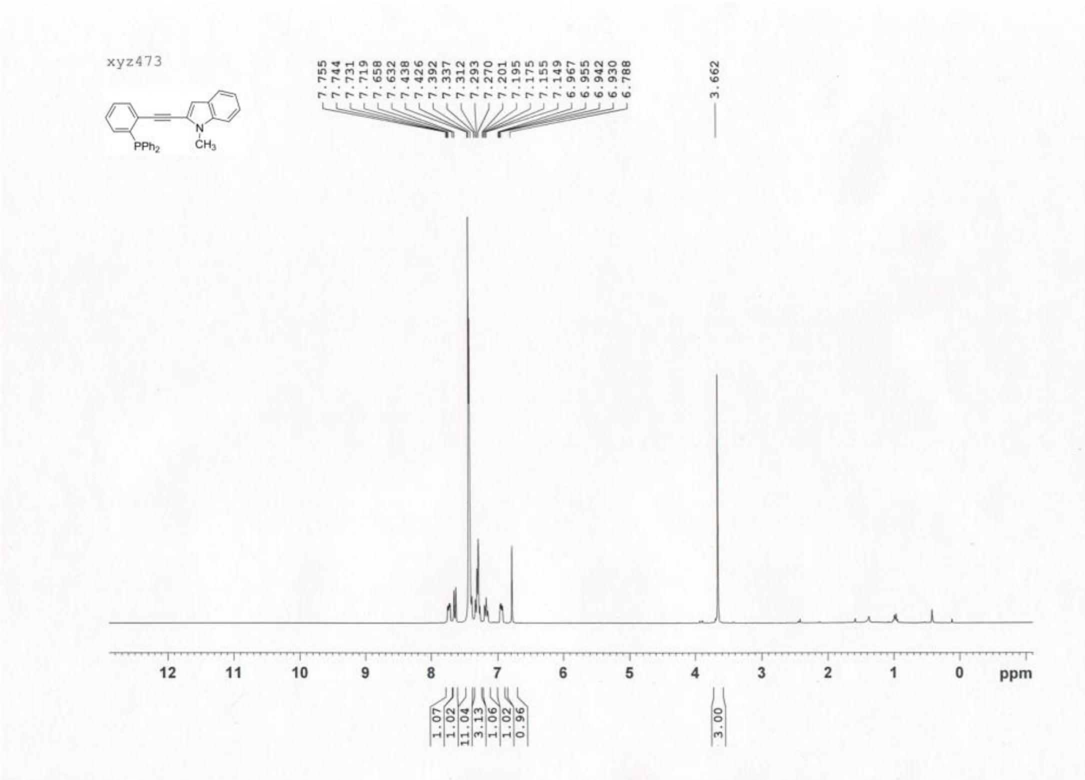

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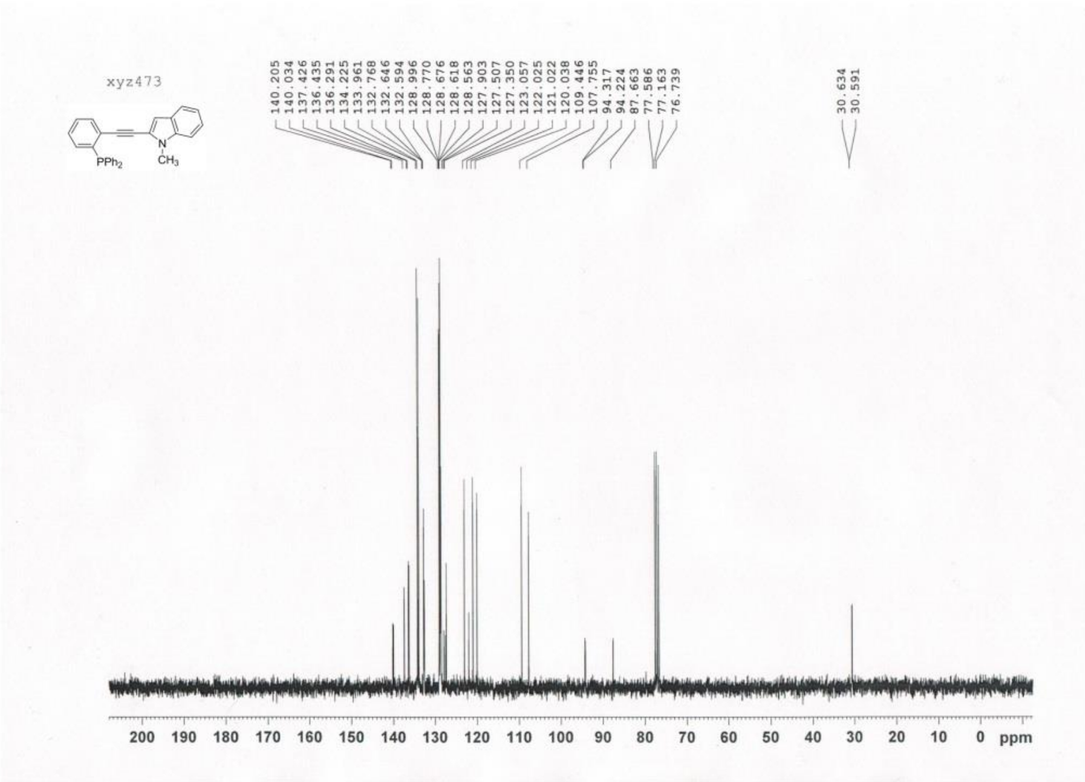

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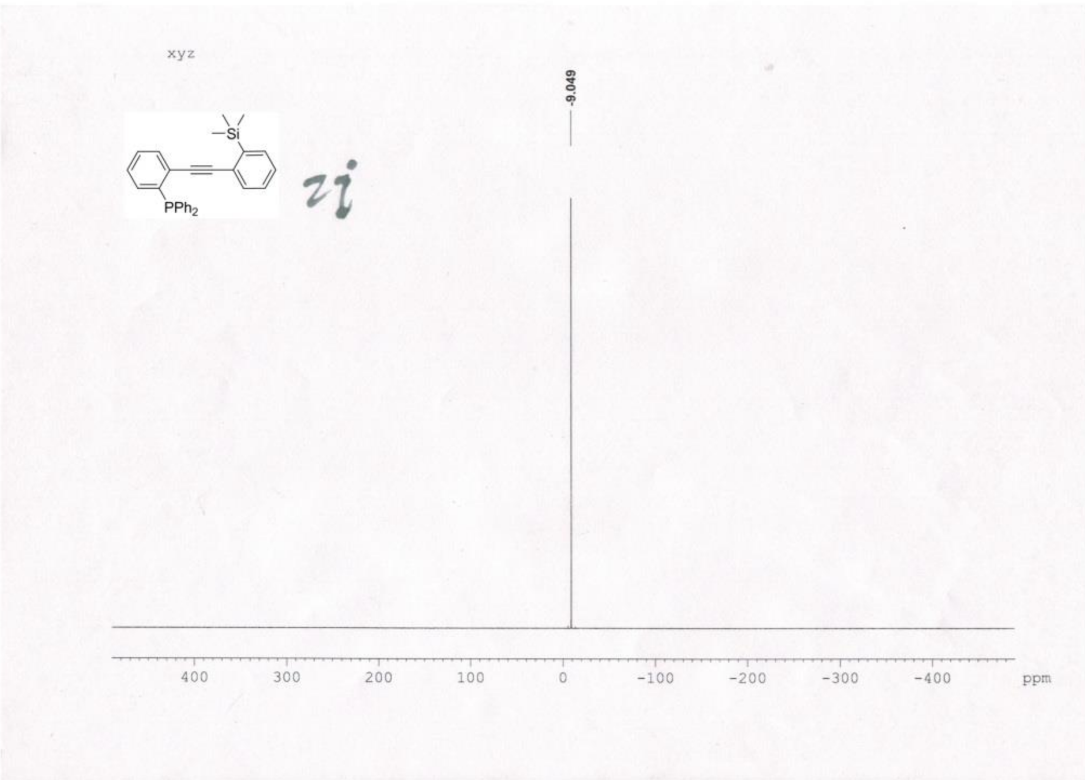

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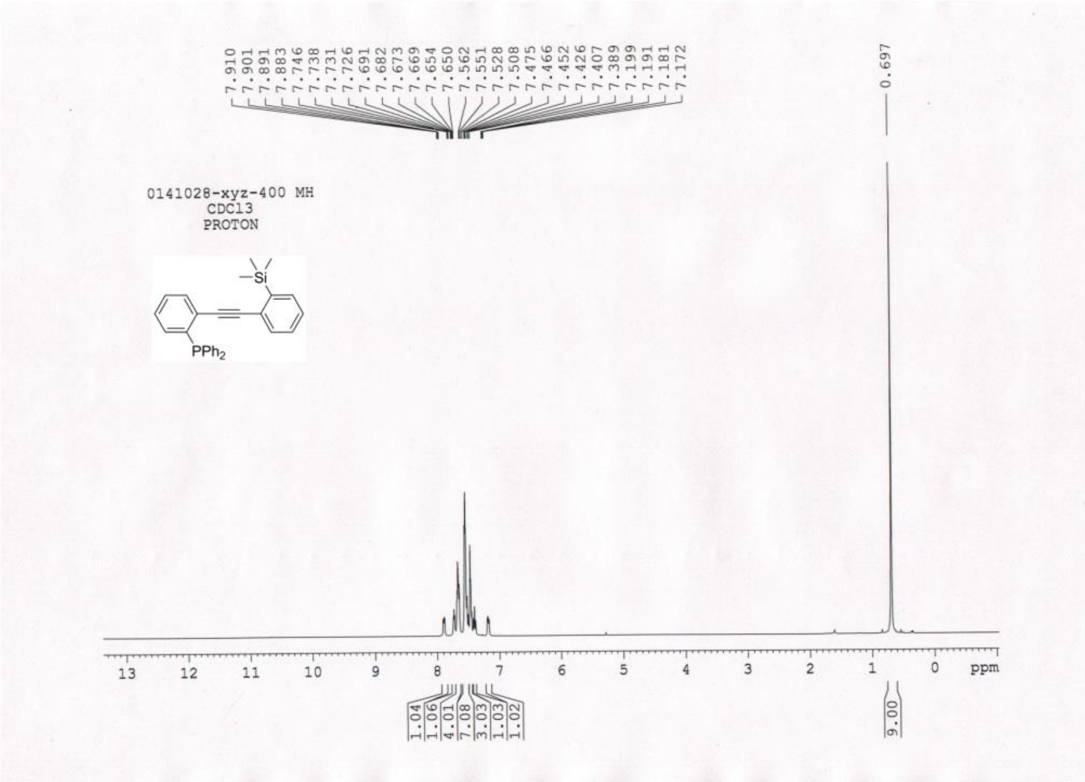

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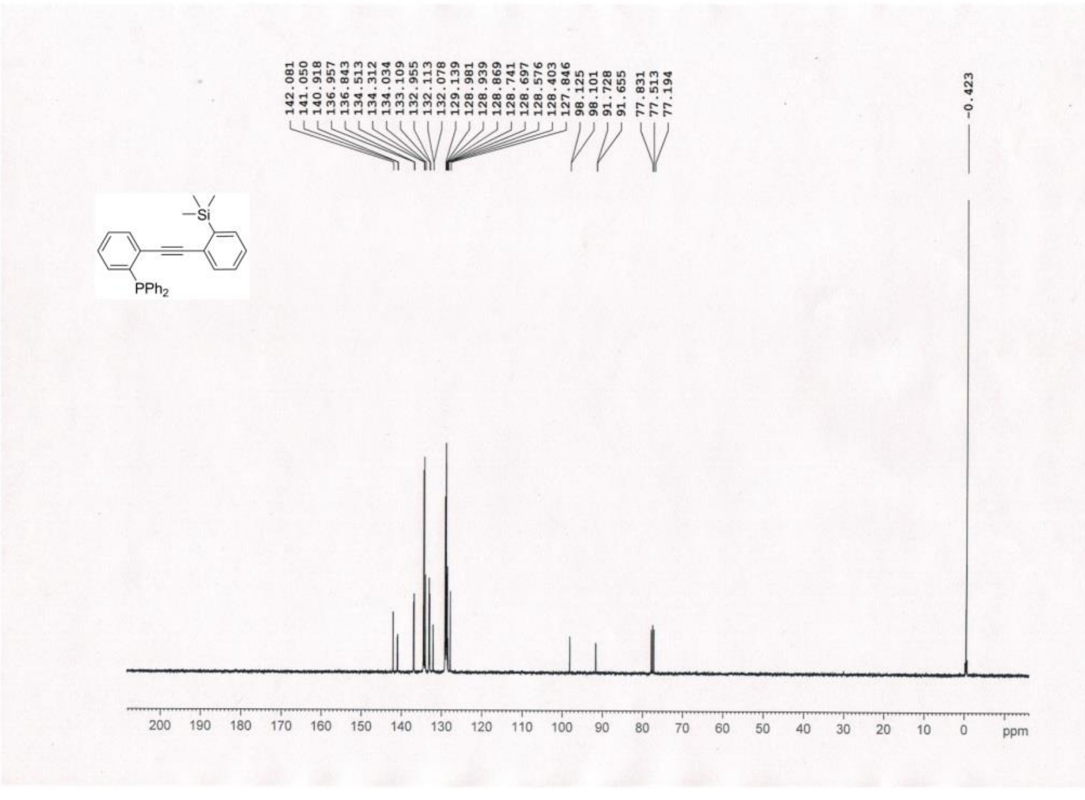

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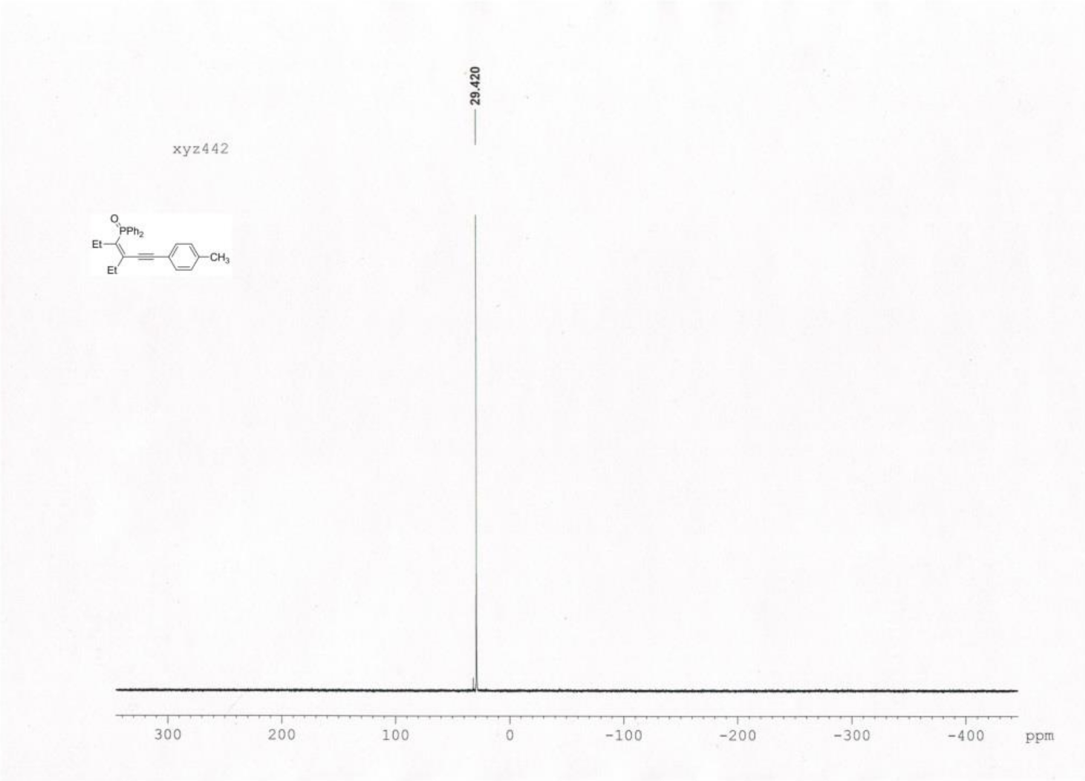

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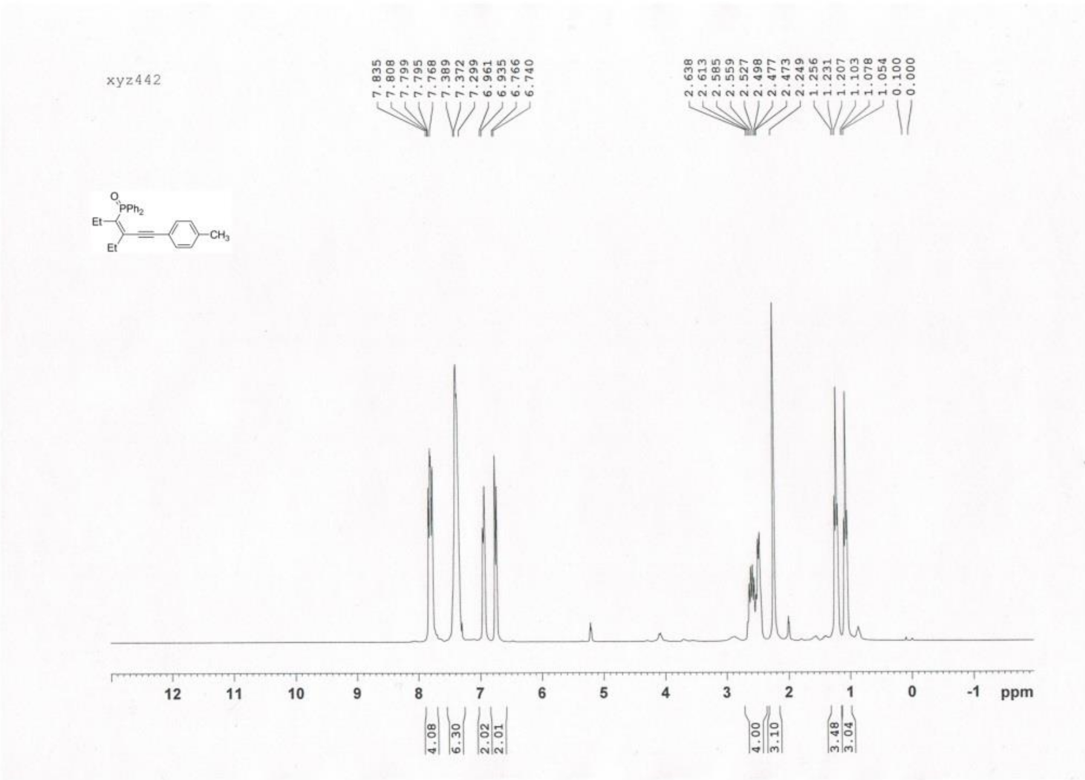

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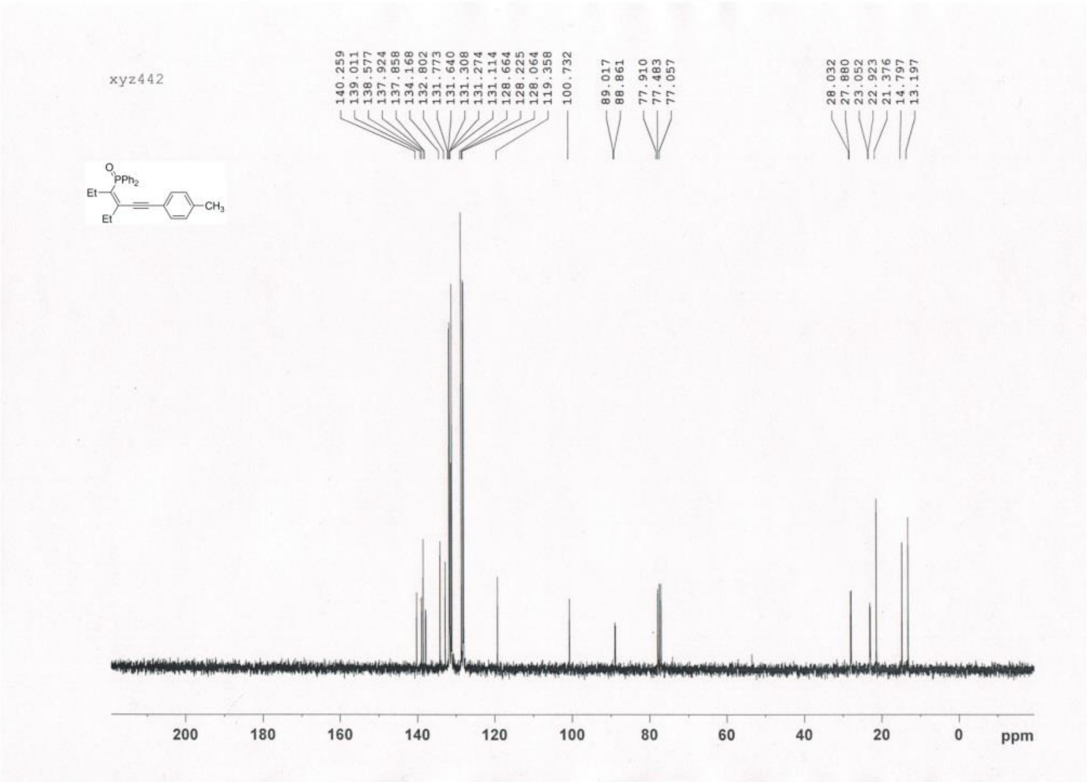
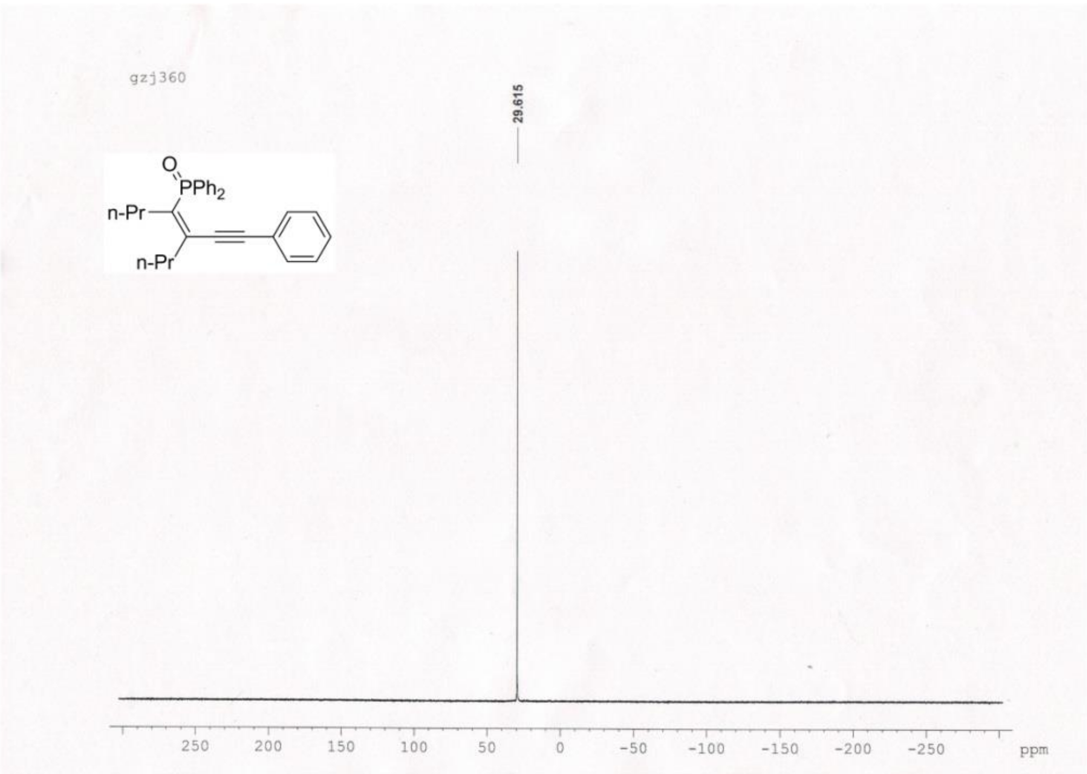


4a ^{13}C NMR



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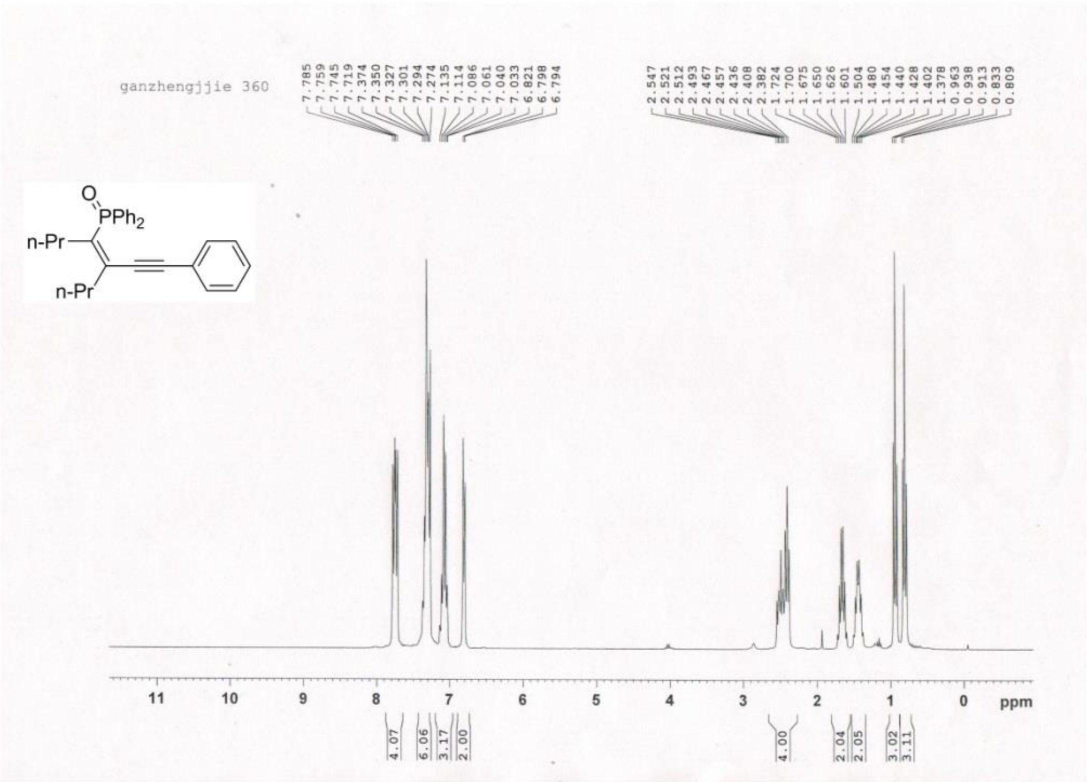

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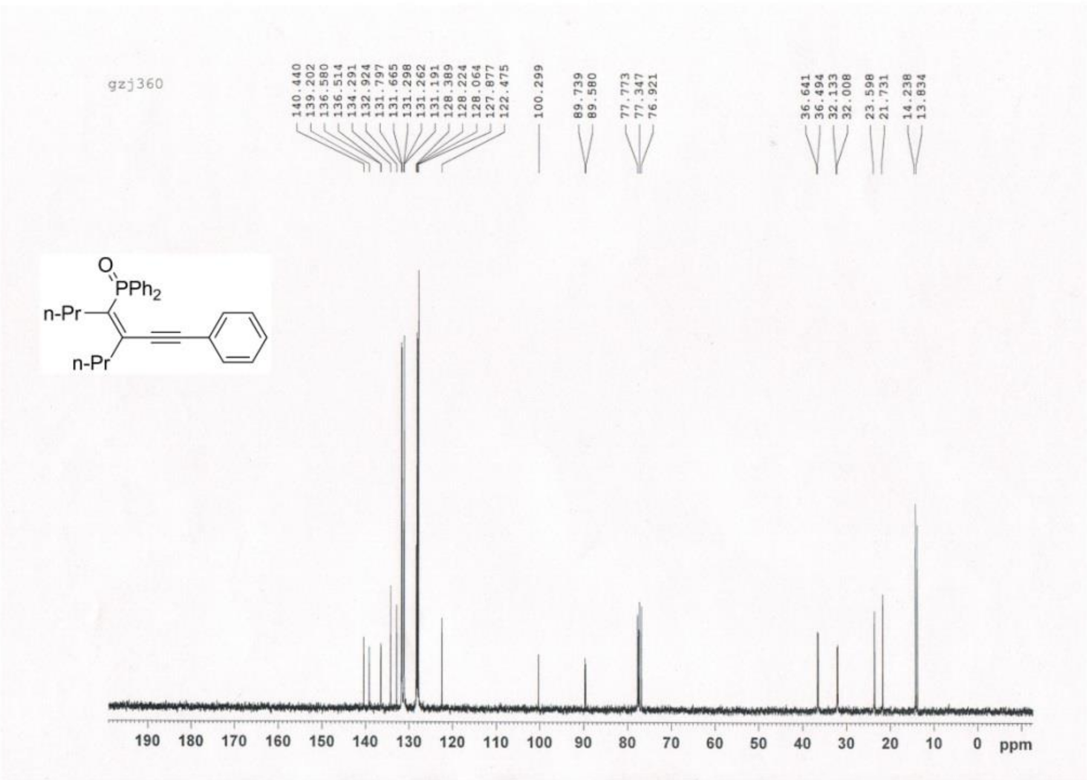

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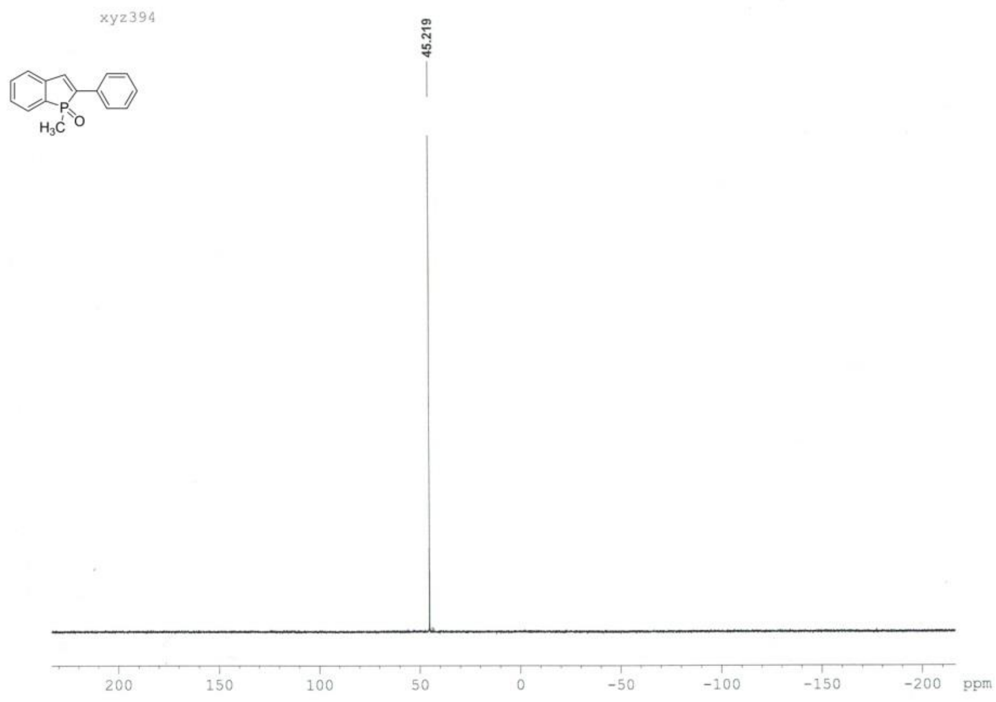

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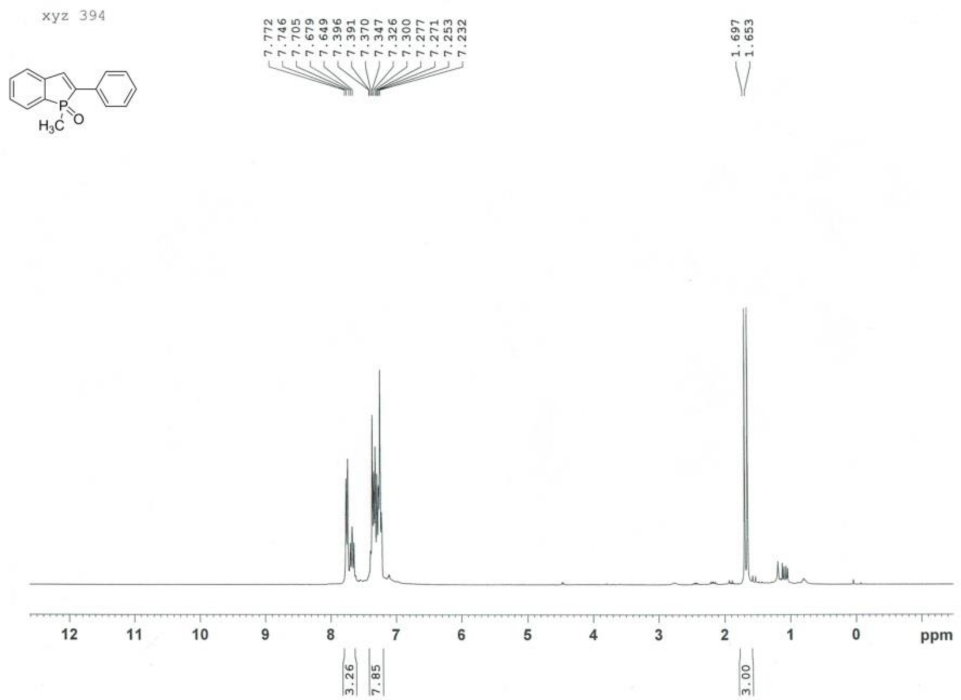

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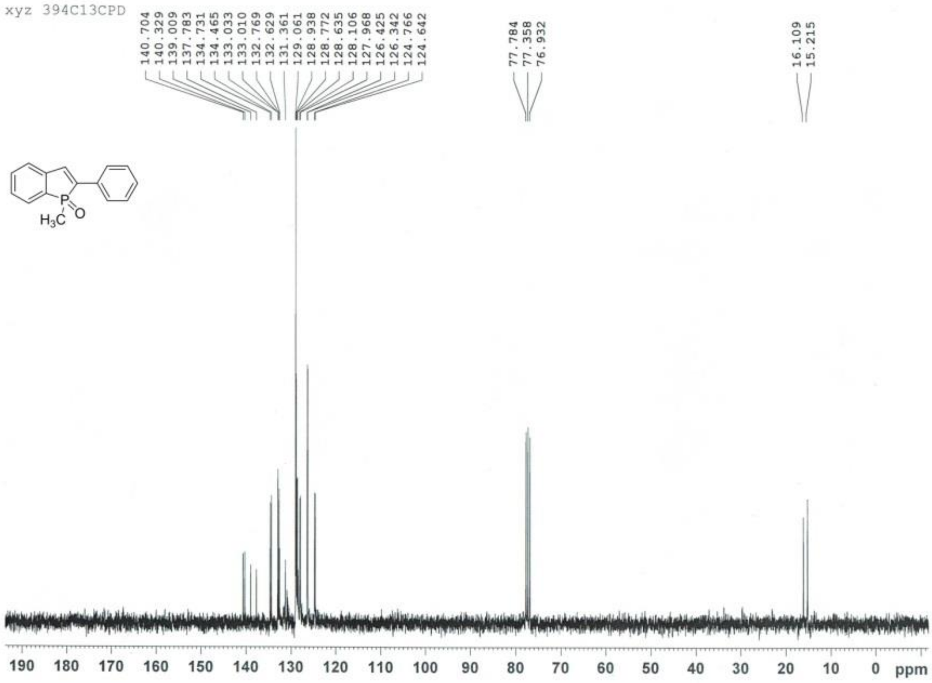

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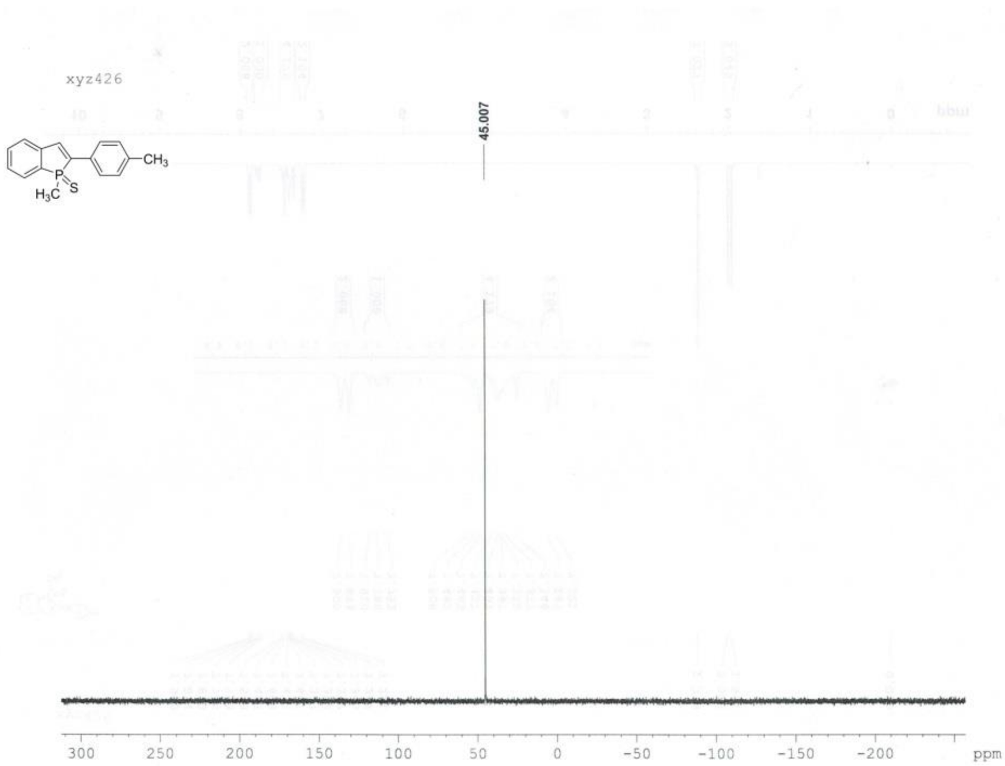

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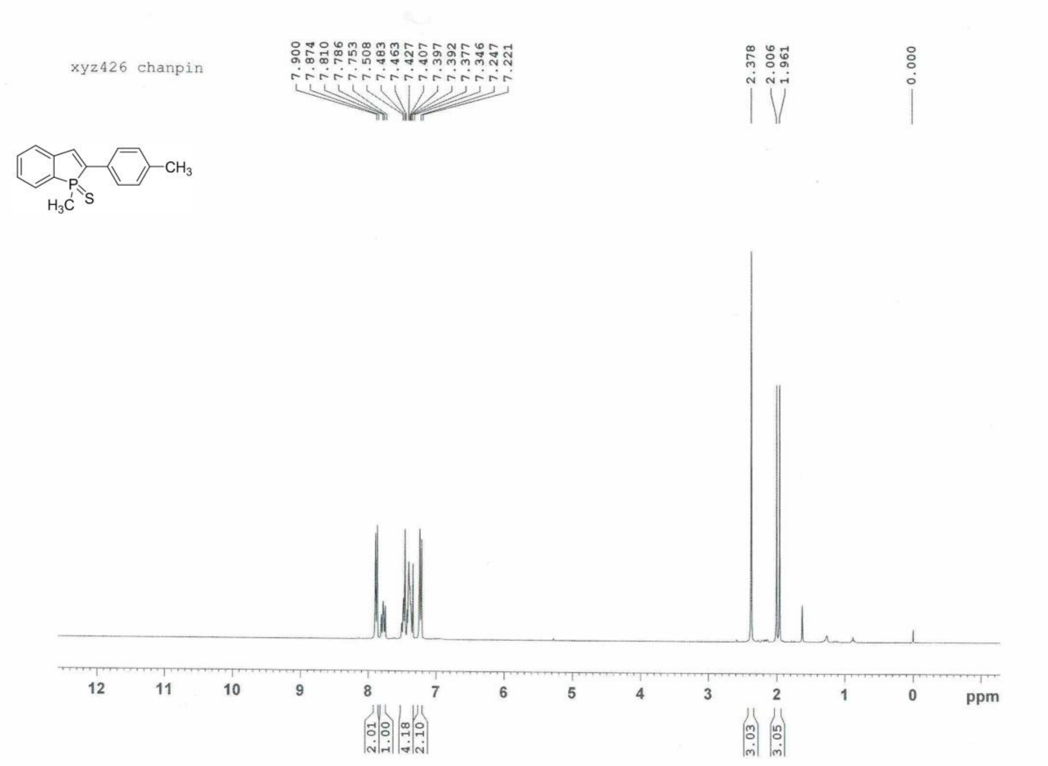

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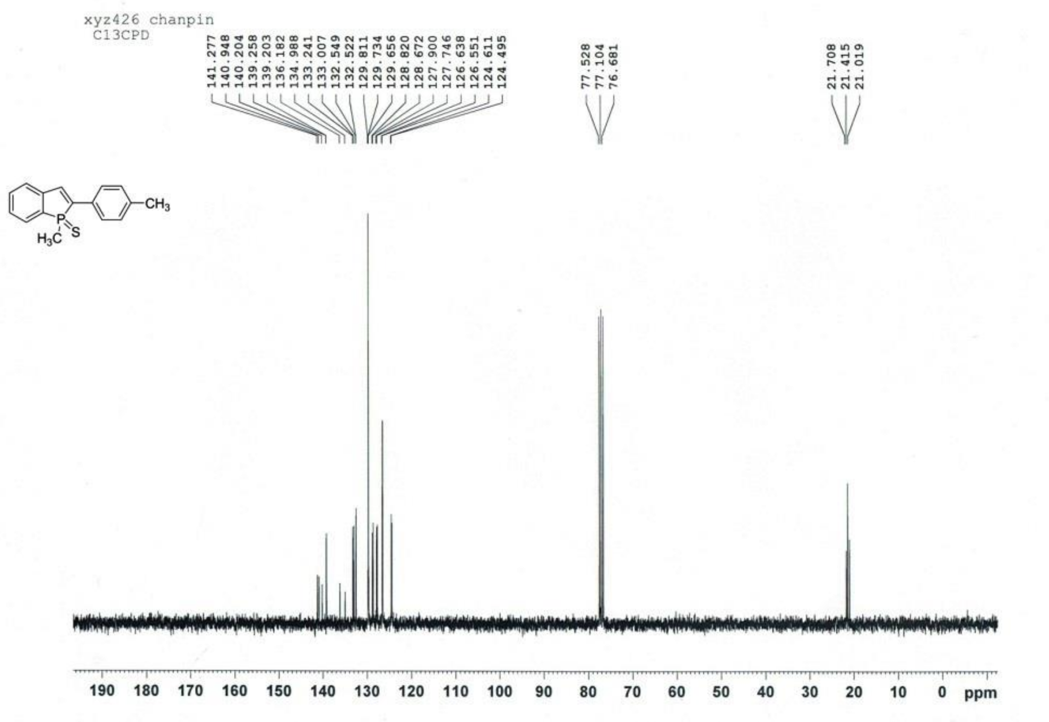

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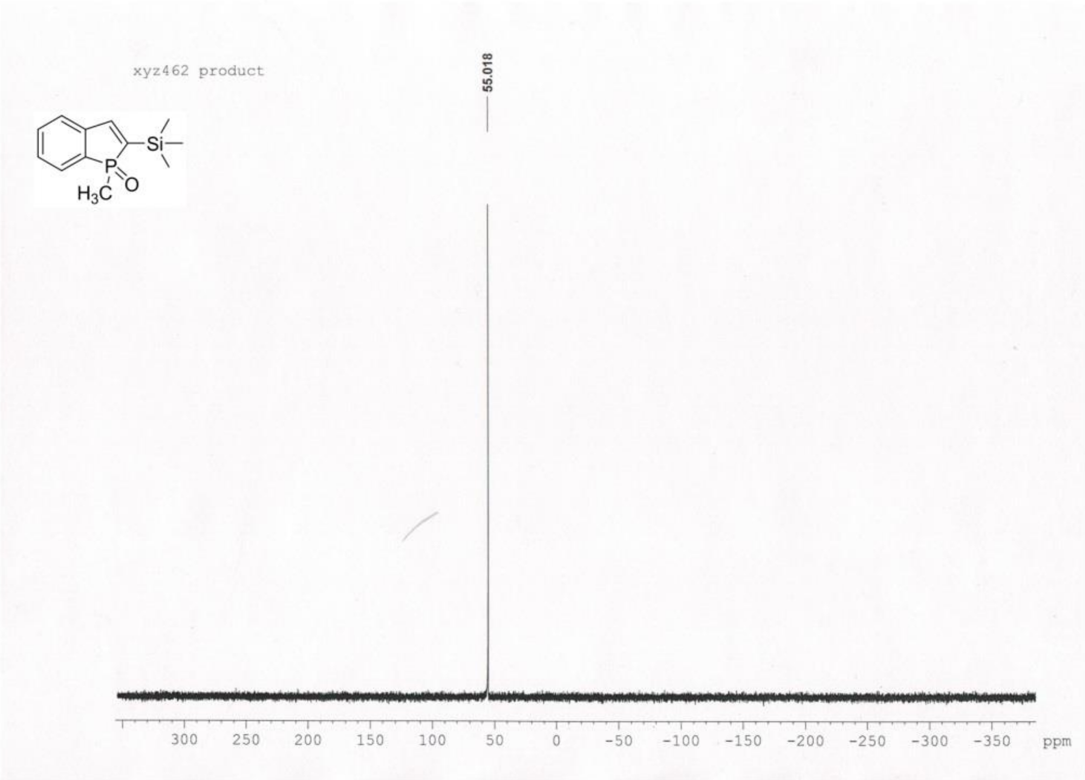

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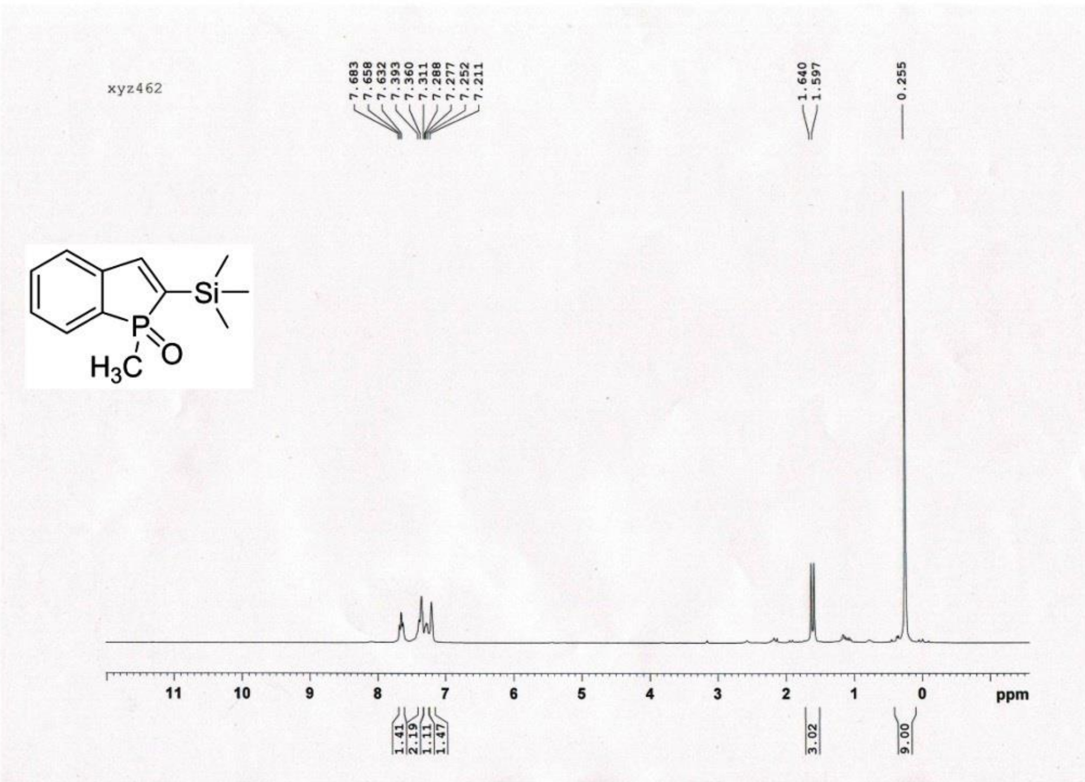

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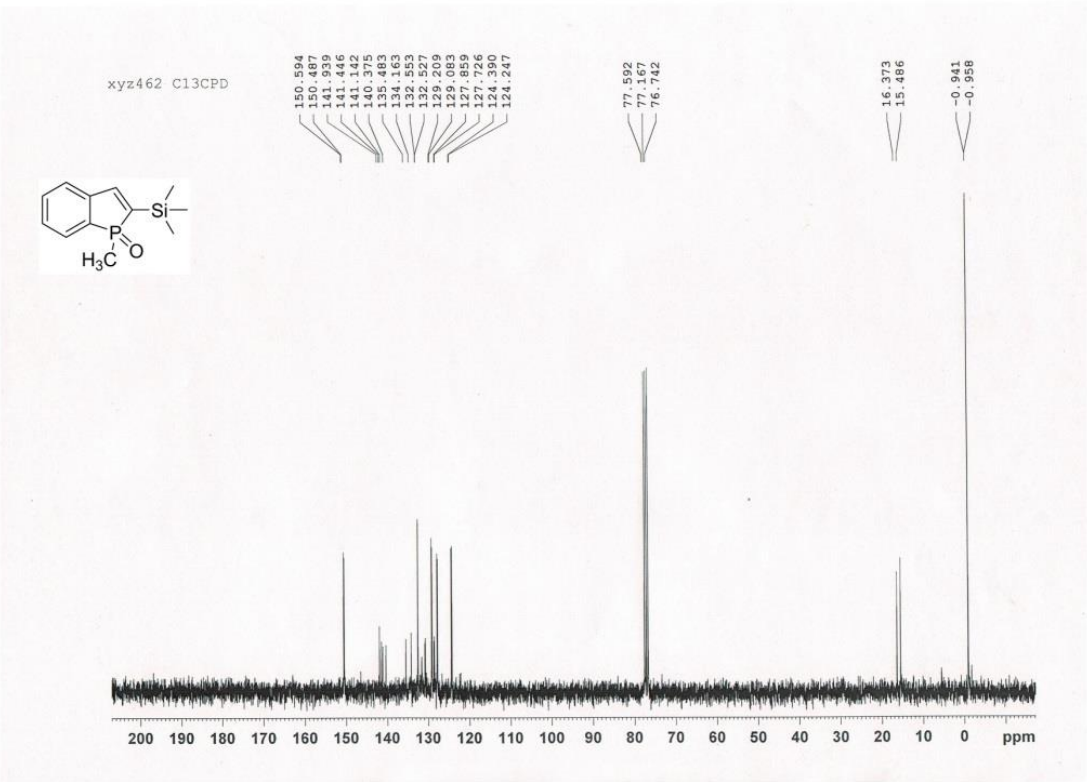

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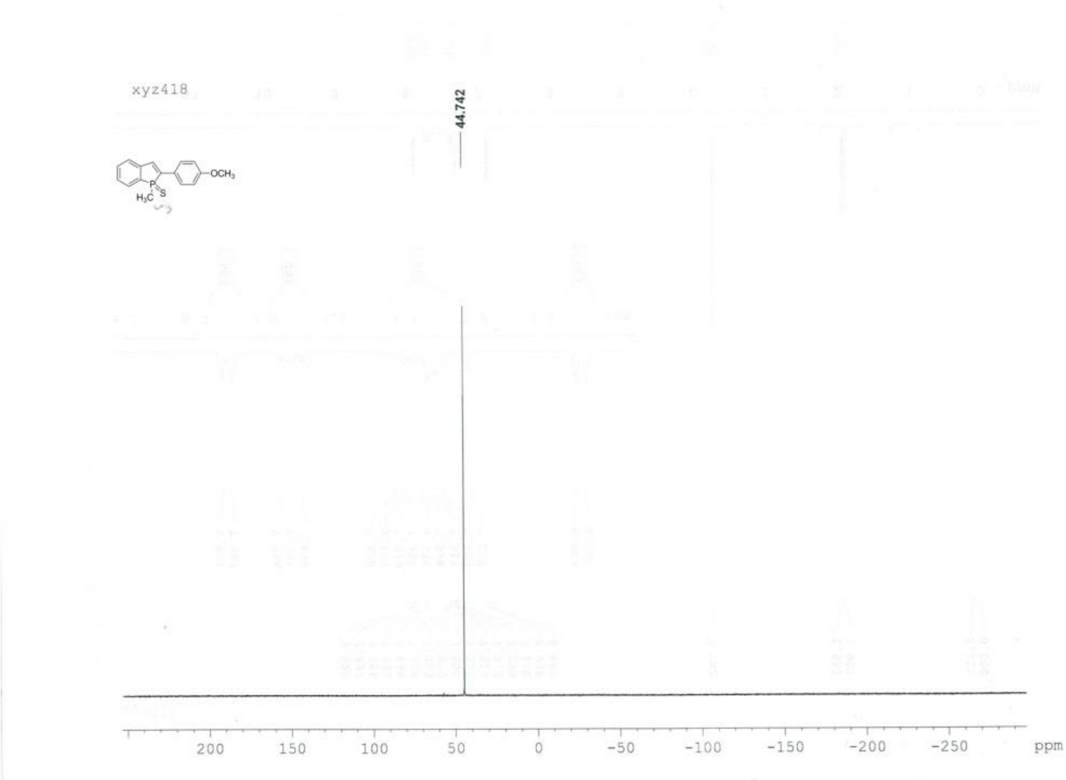

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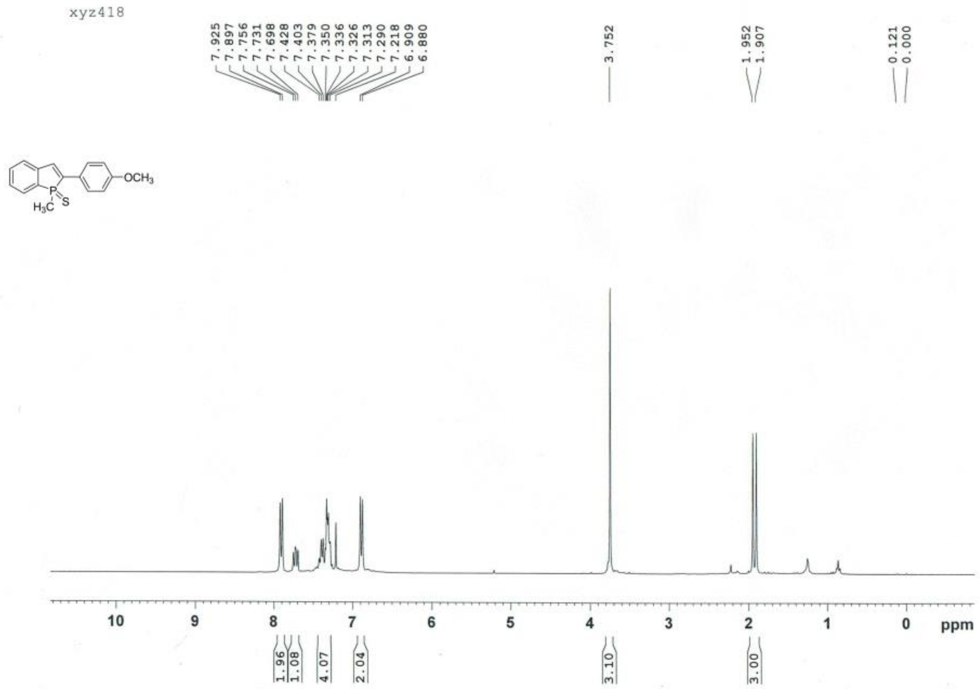

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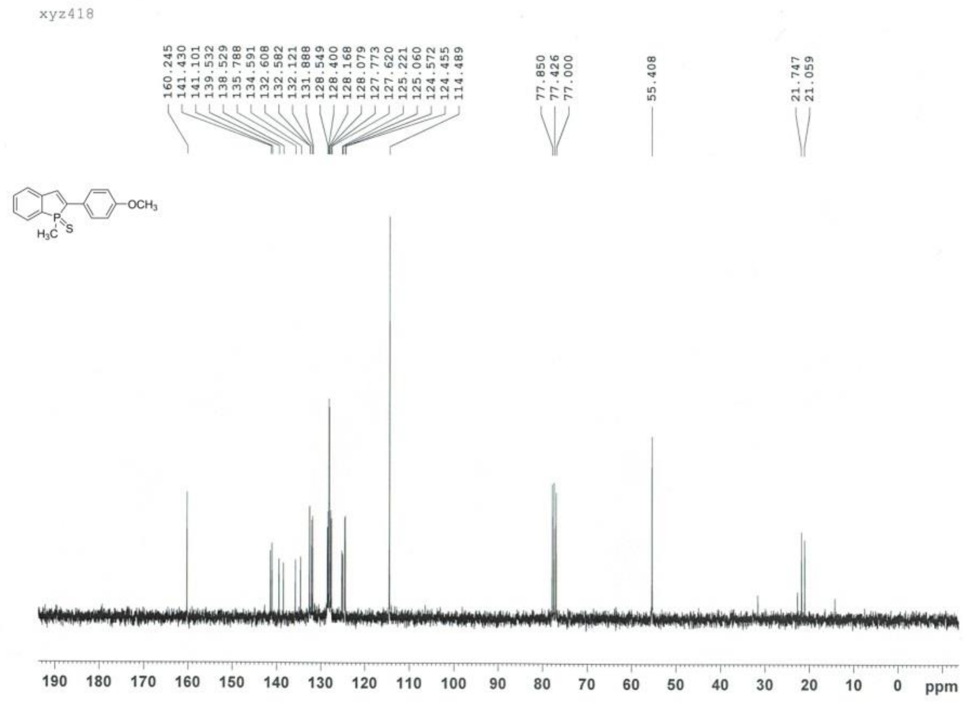

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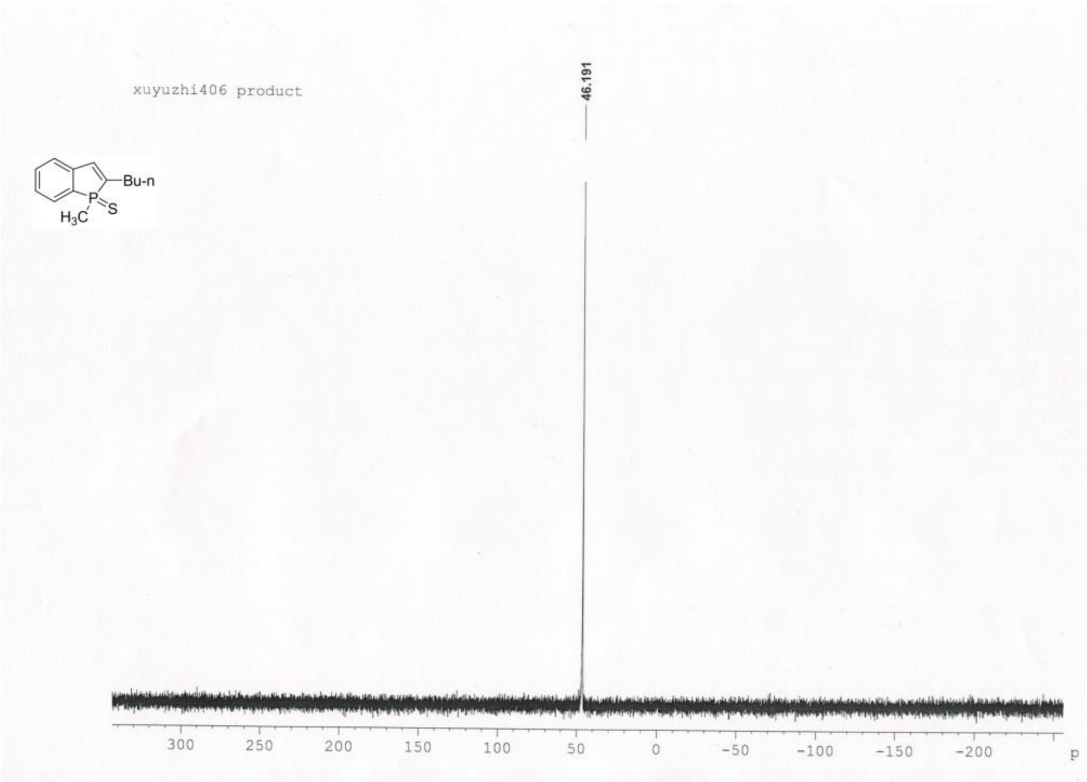

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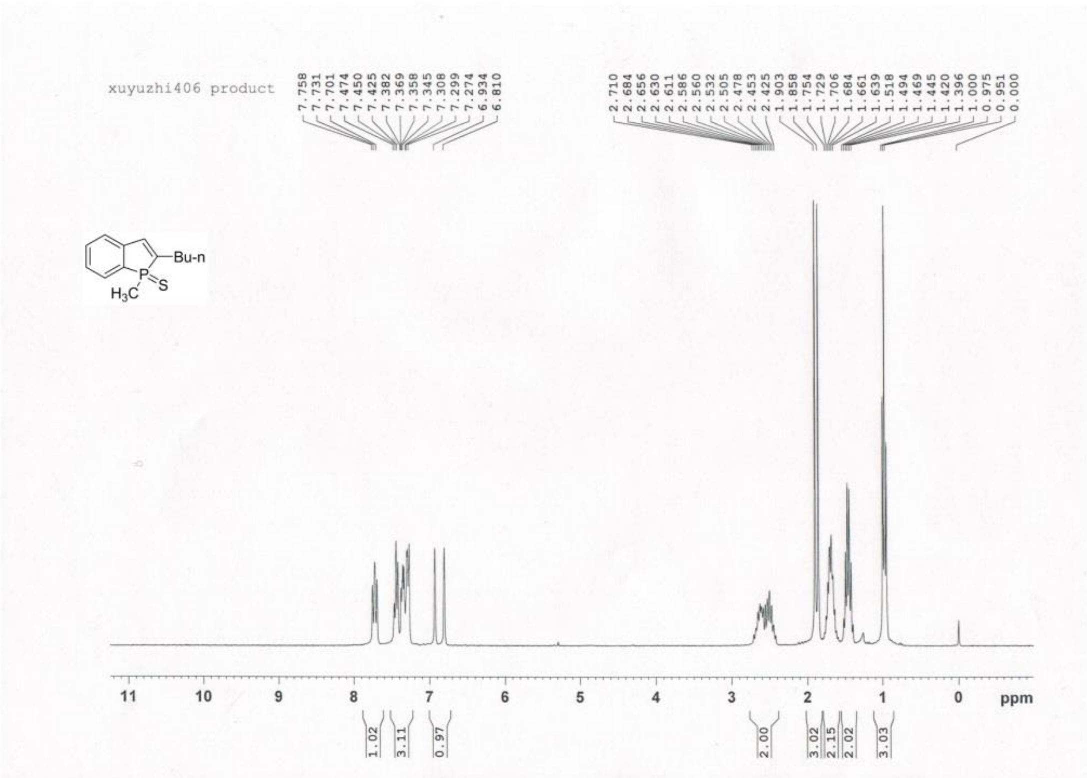

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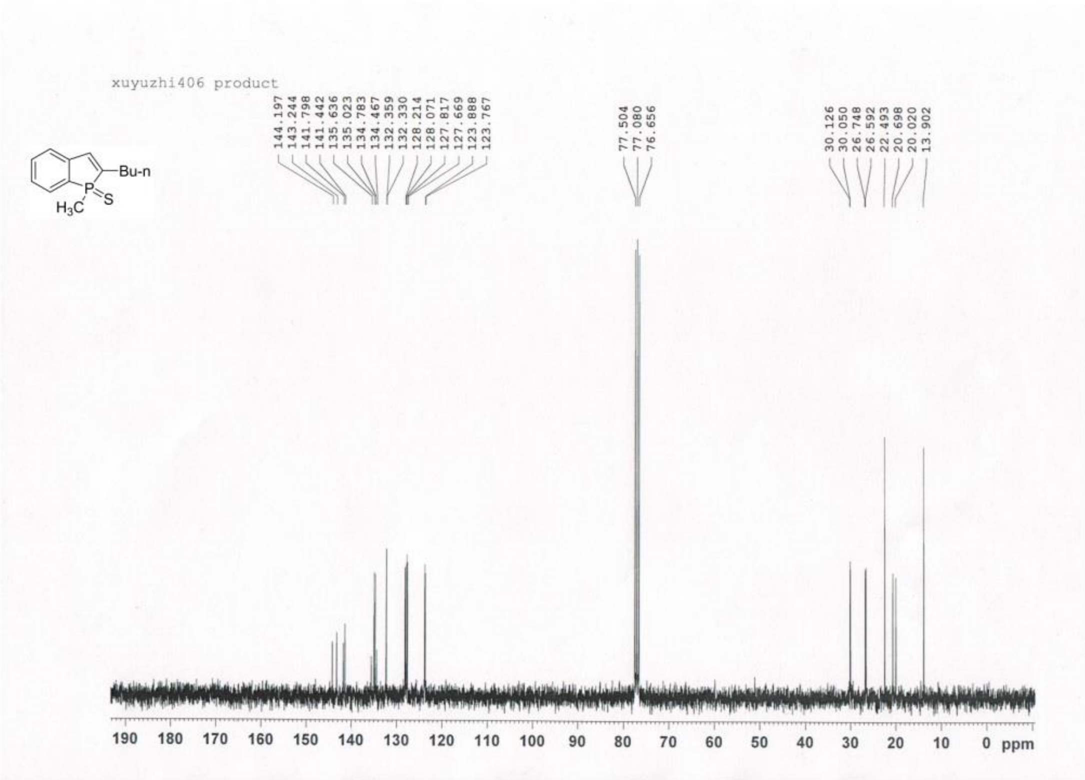

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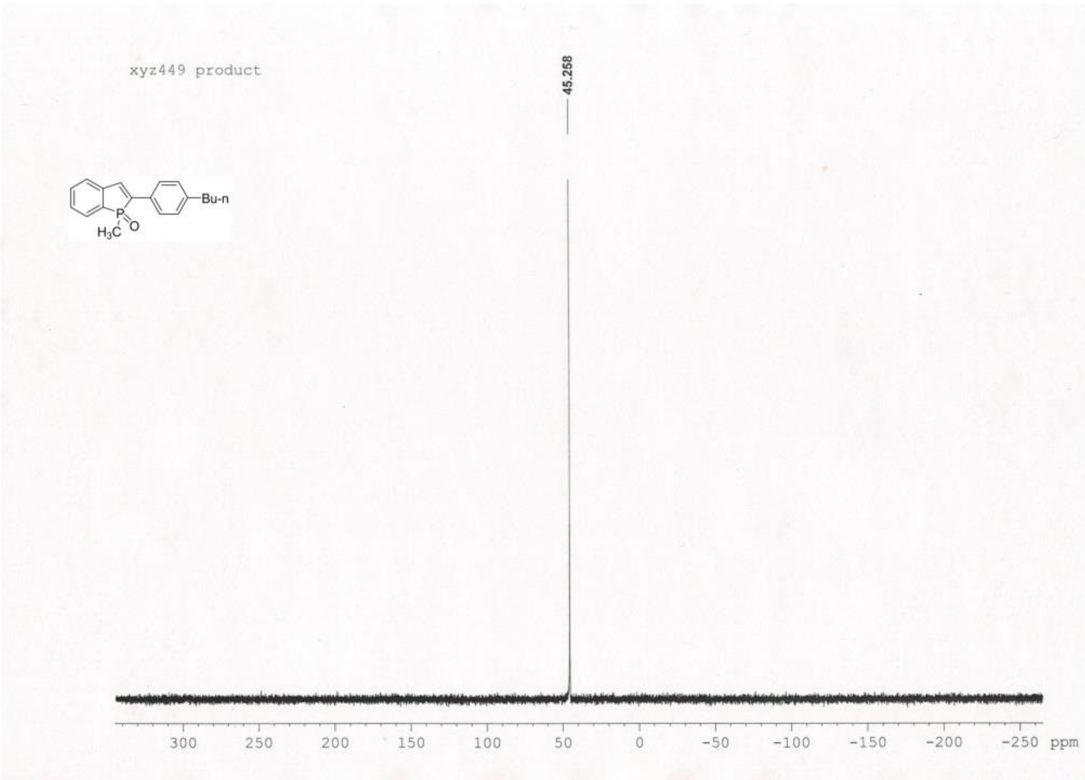

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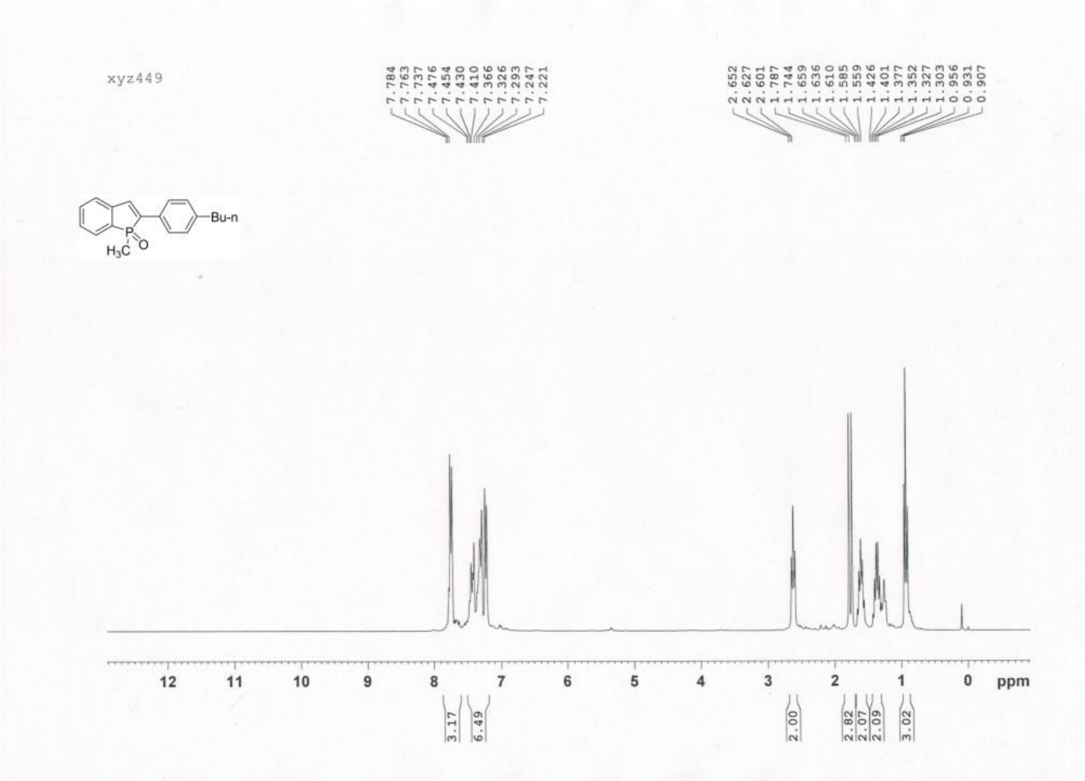

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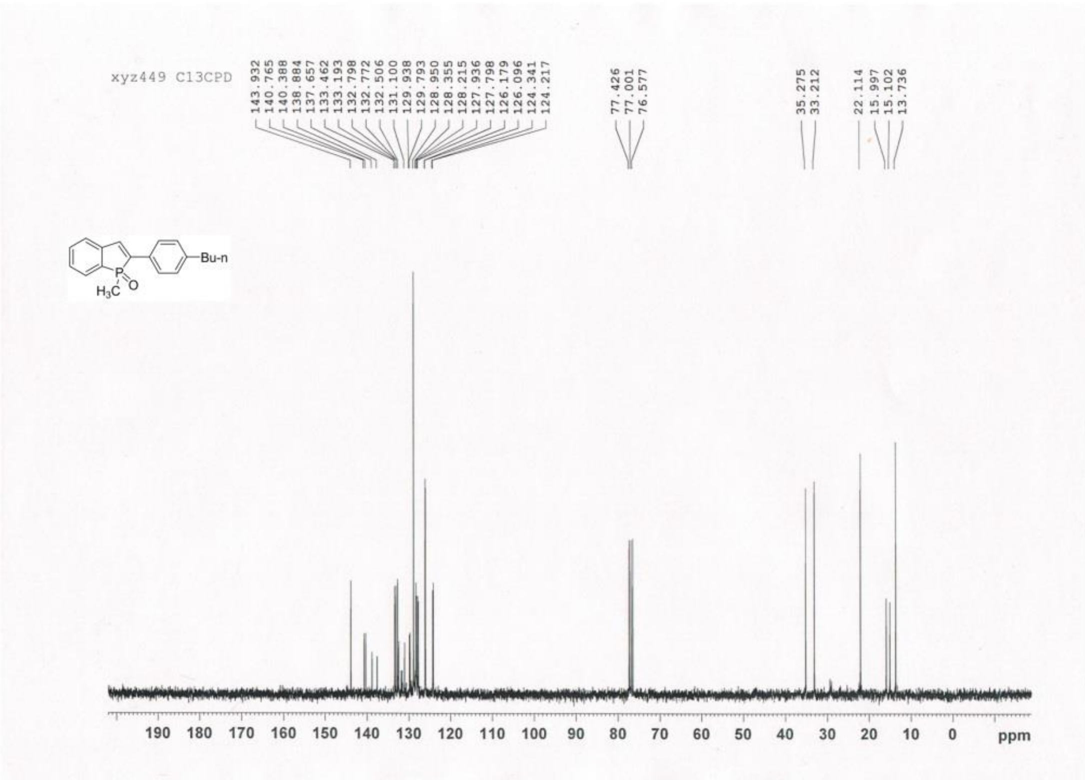

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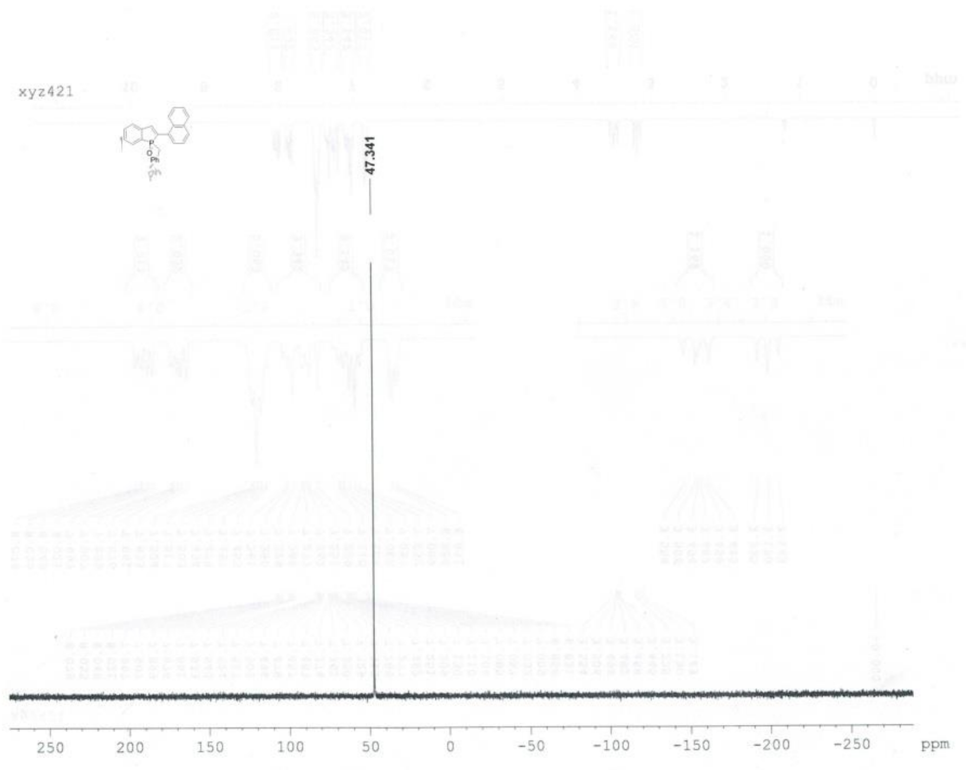

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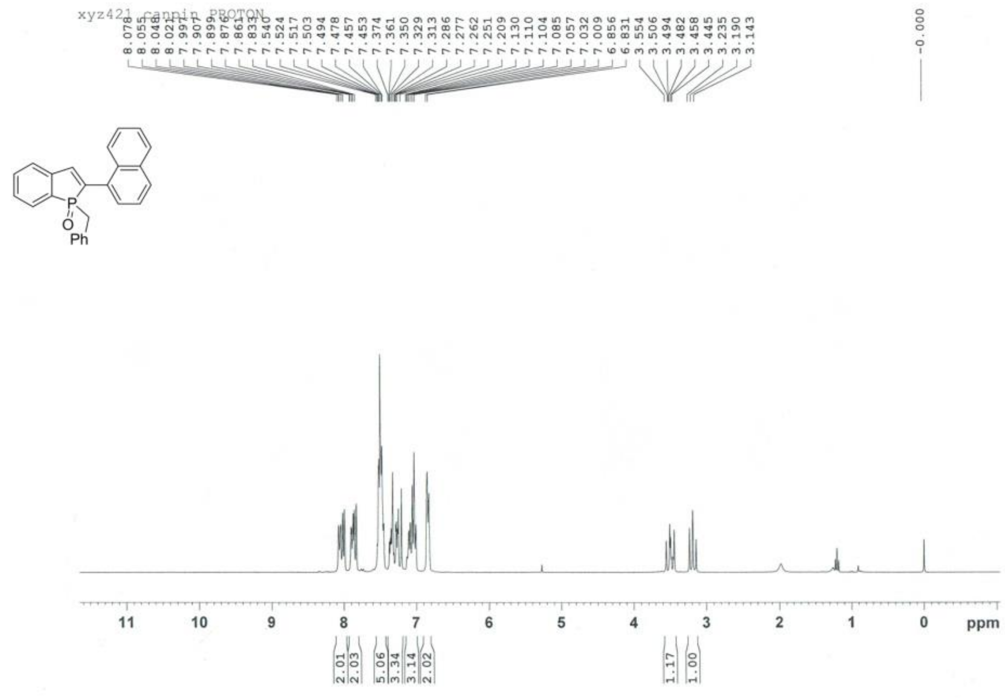

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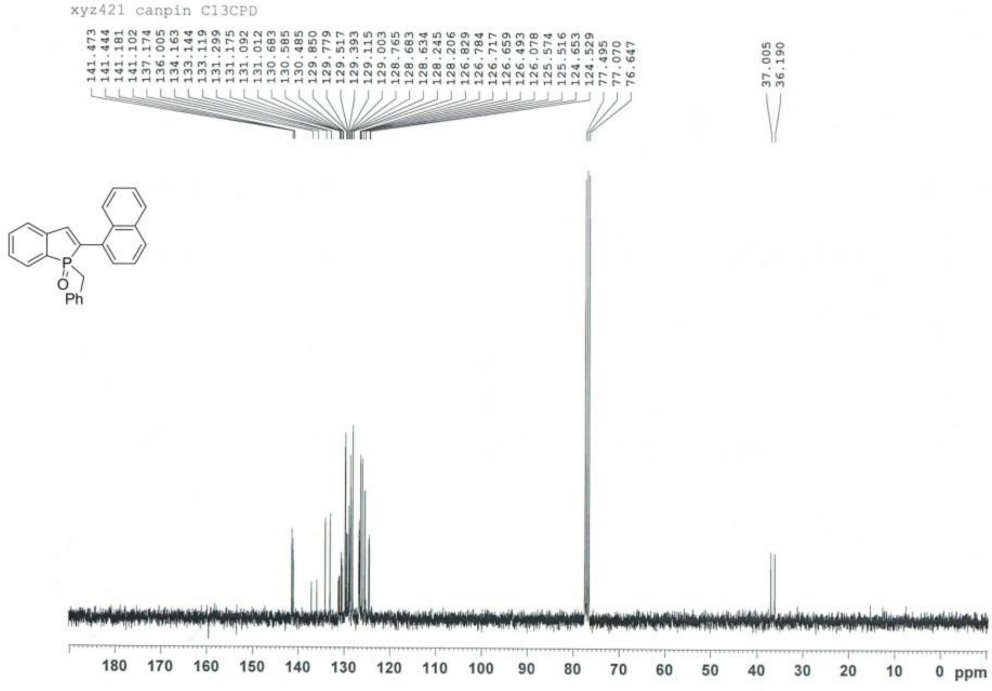

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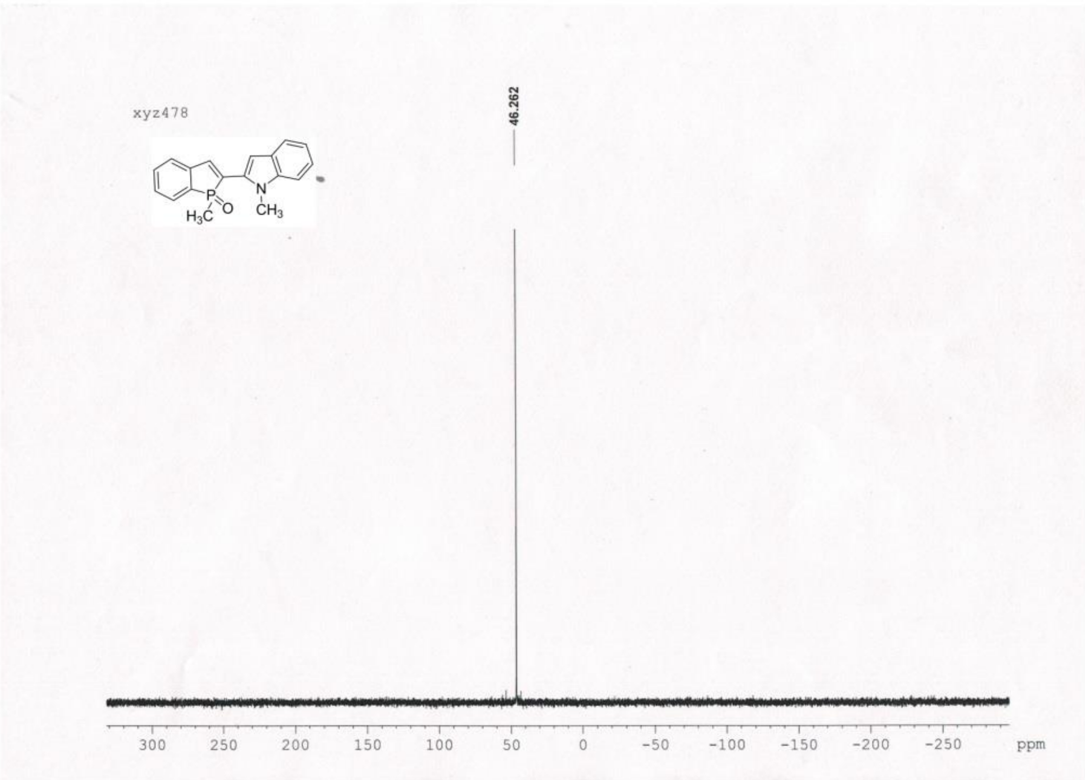

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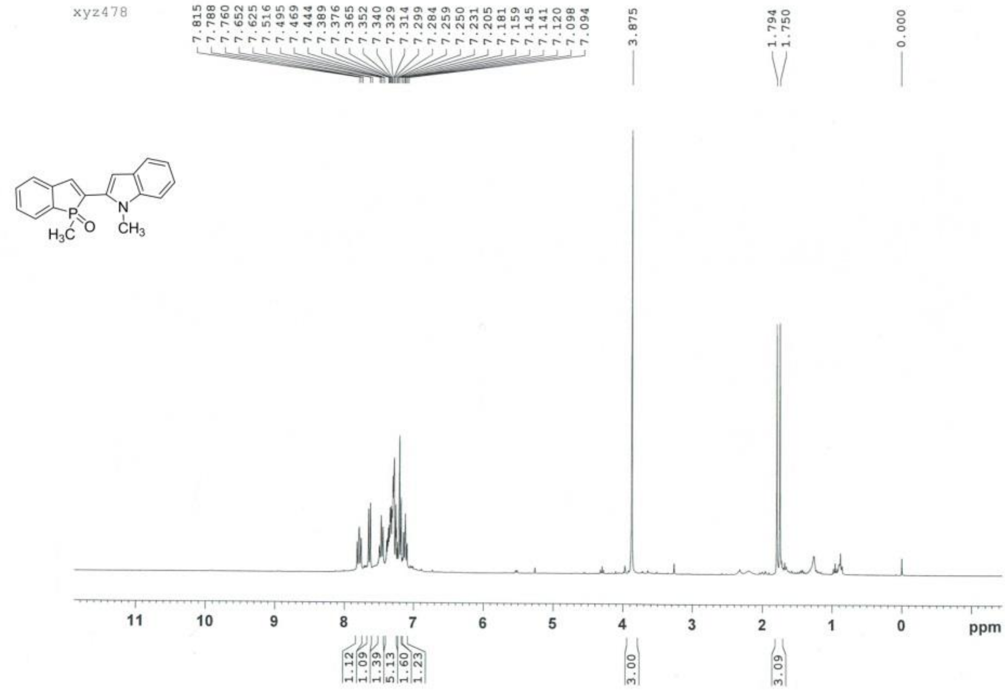

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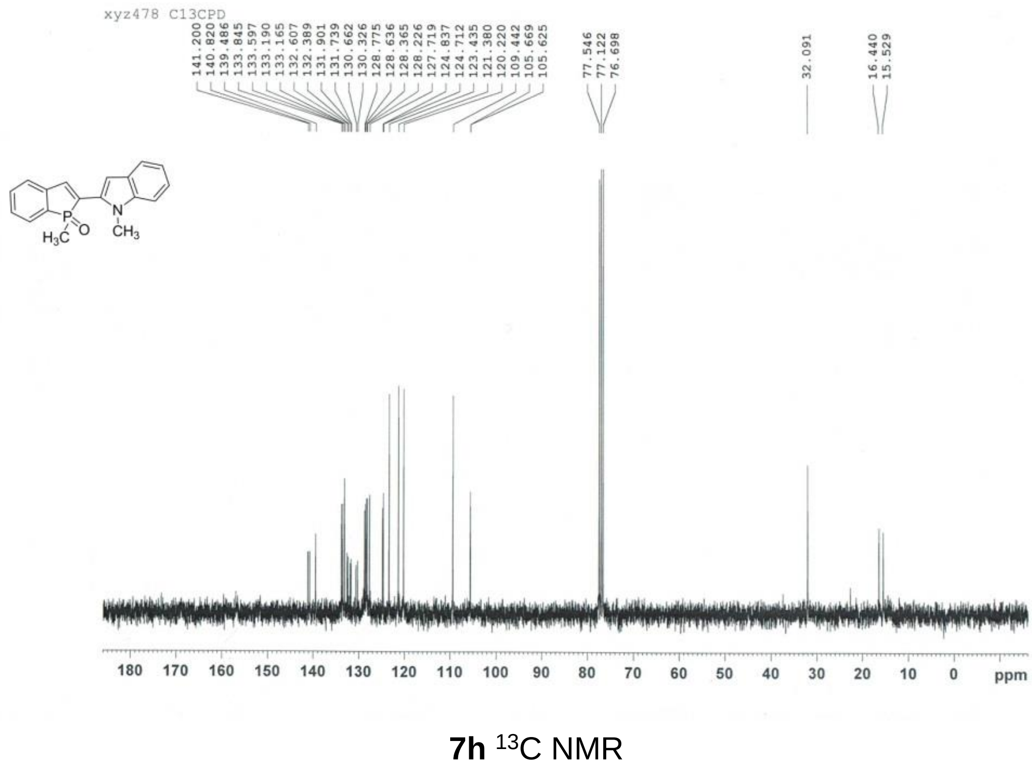

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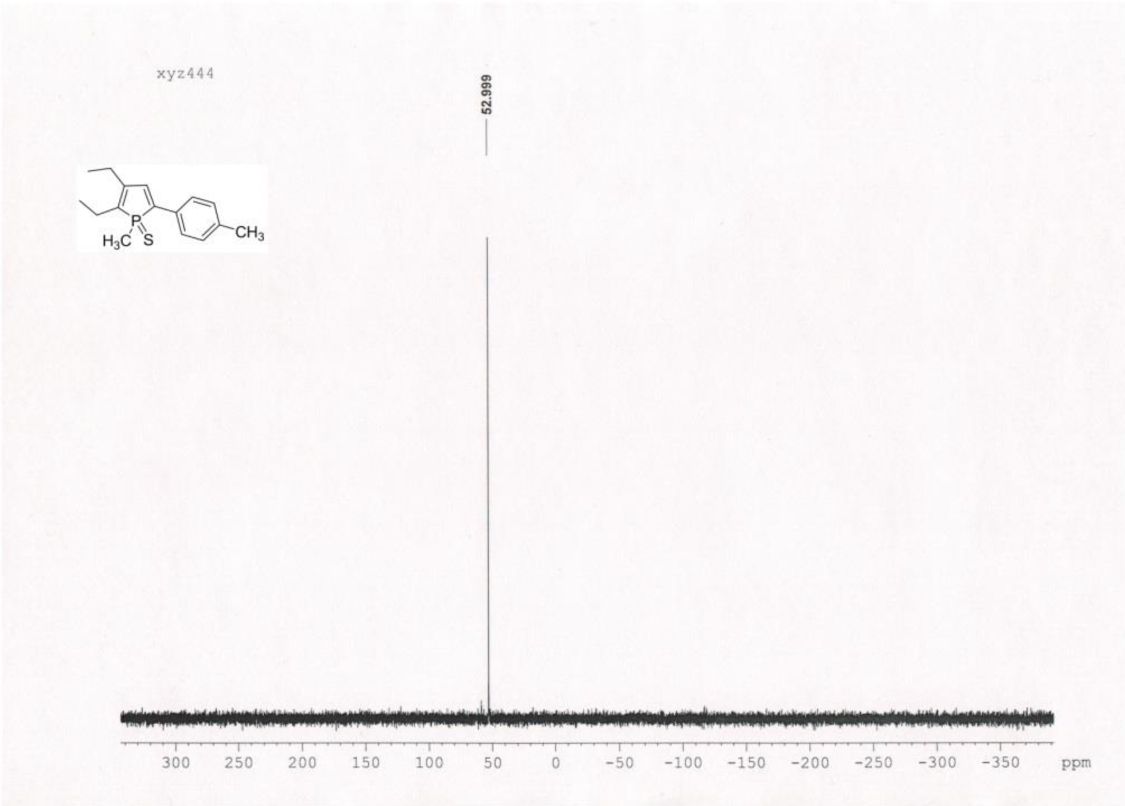

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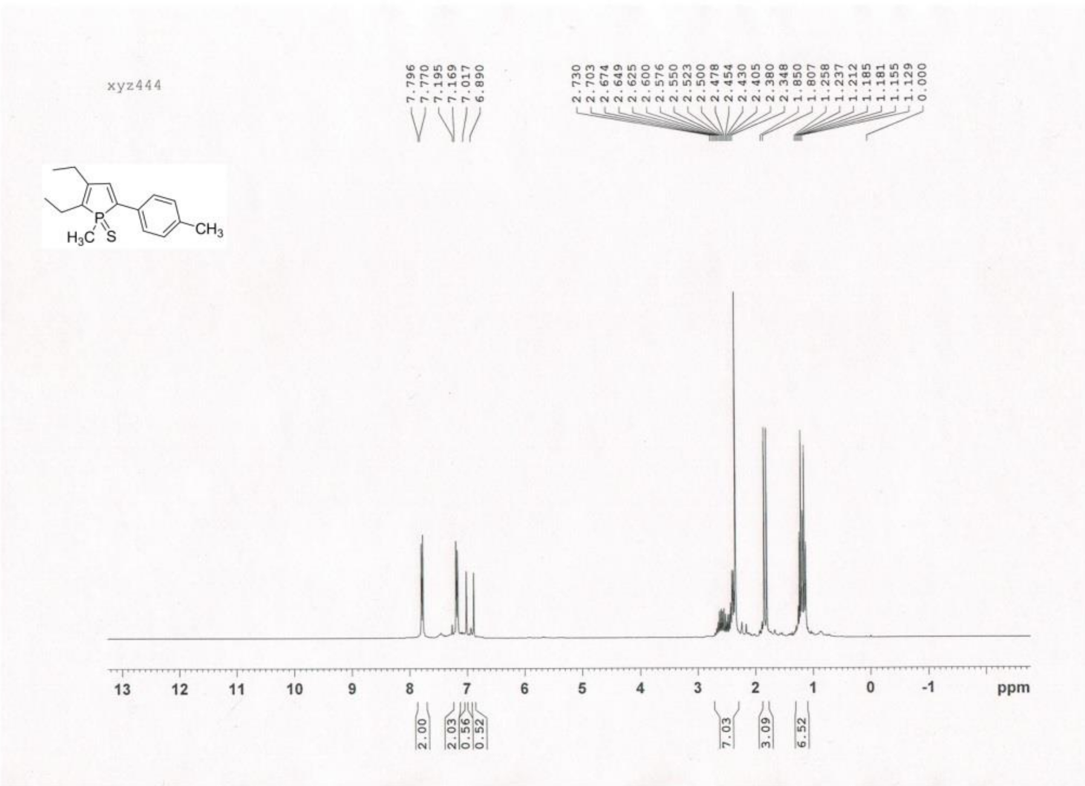

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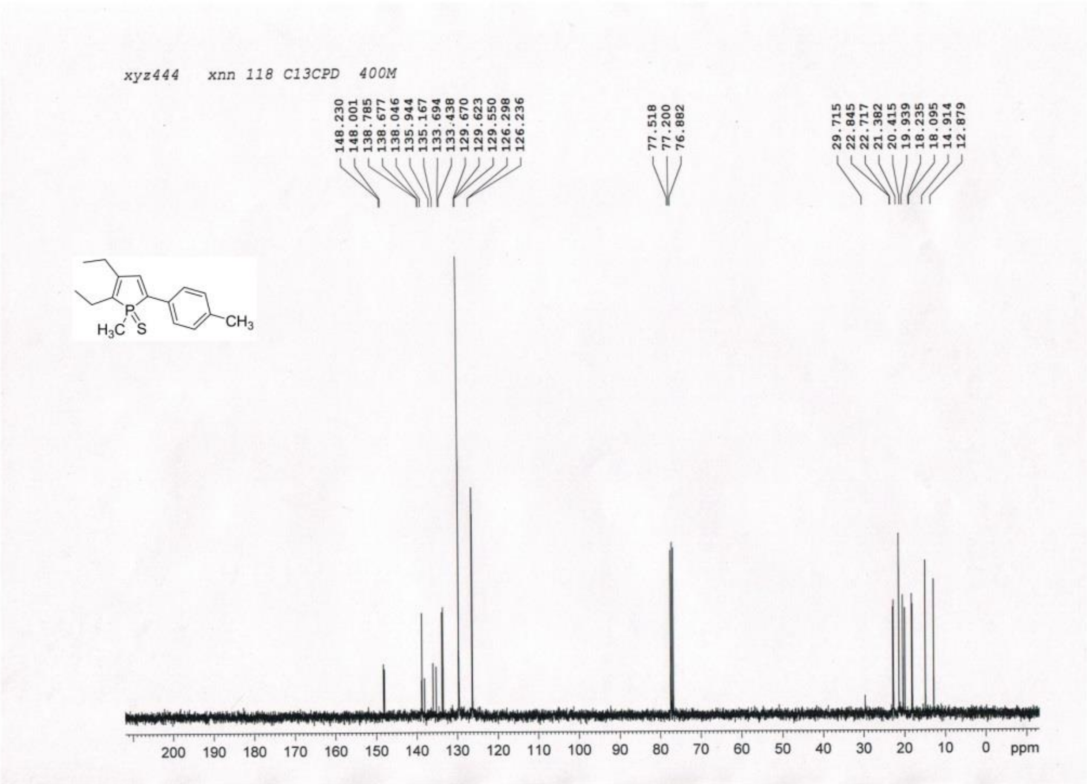

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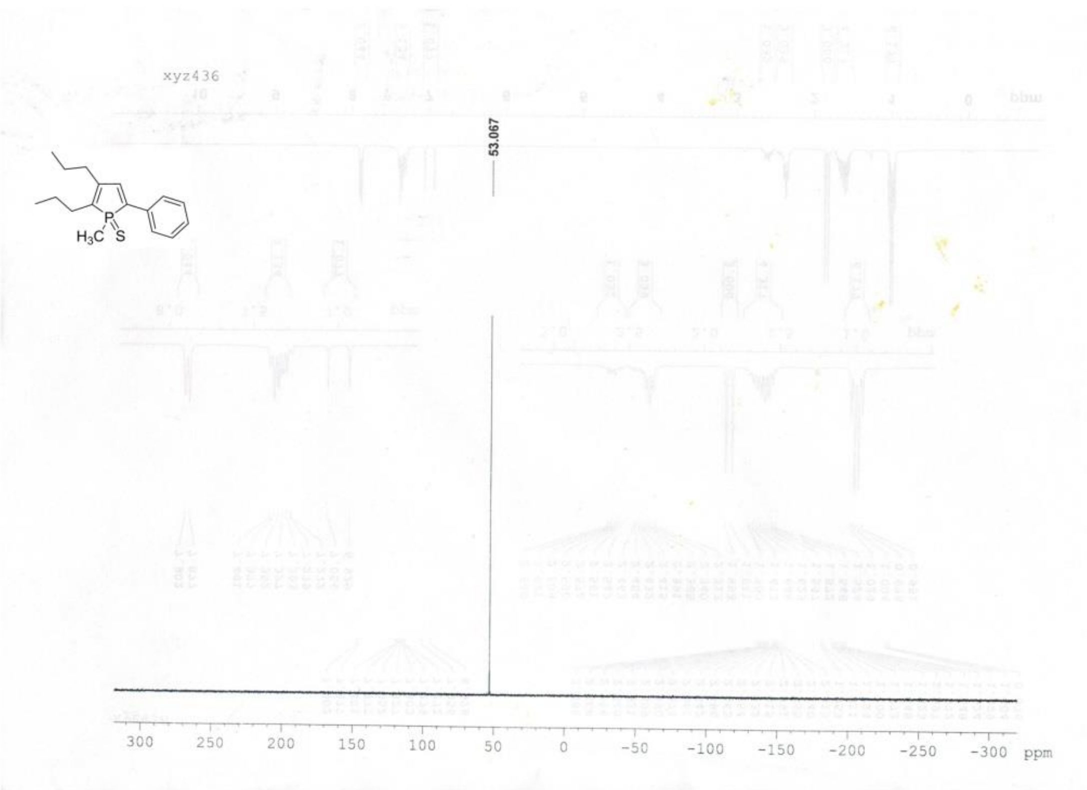

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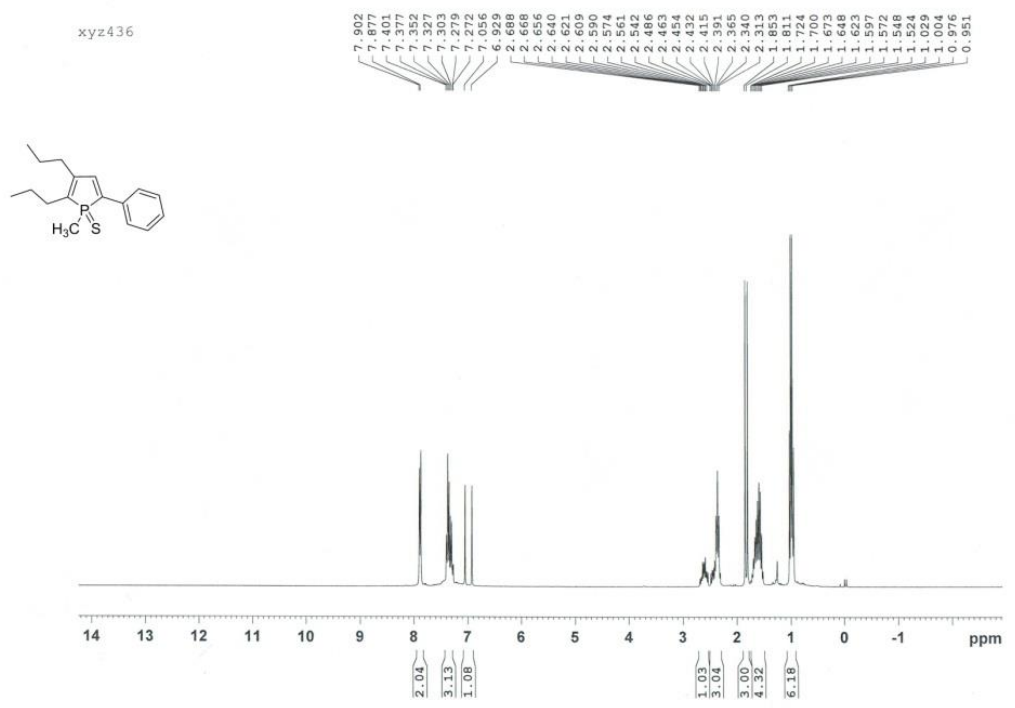

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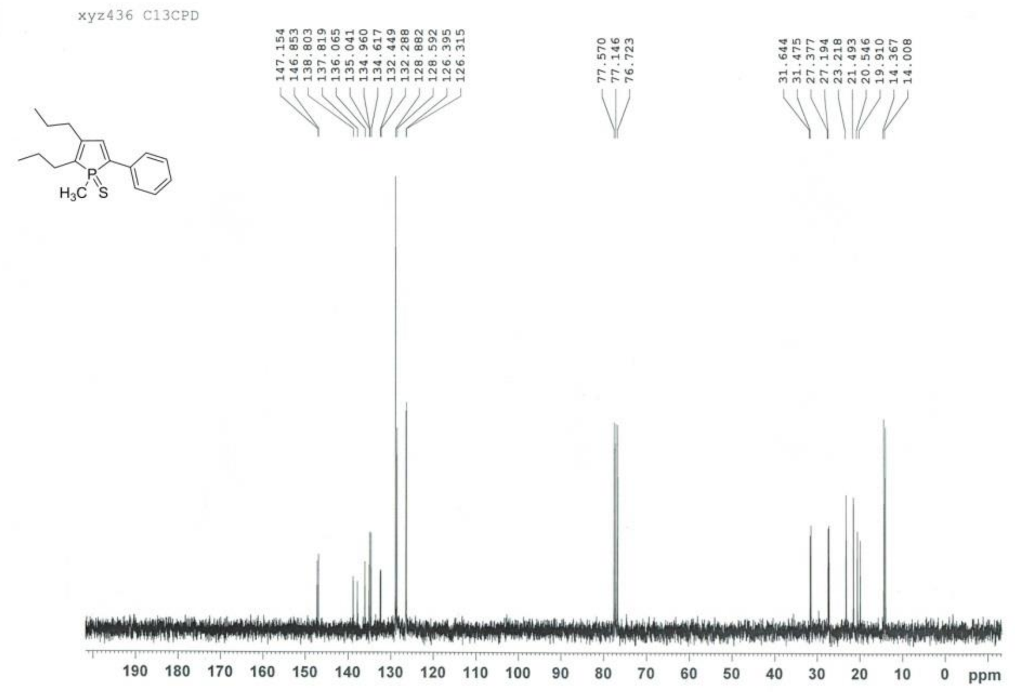

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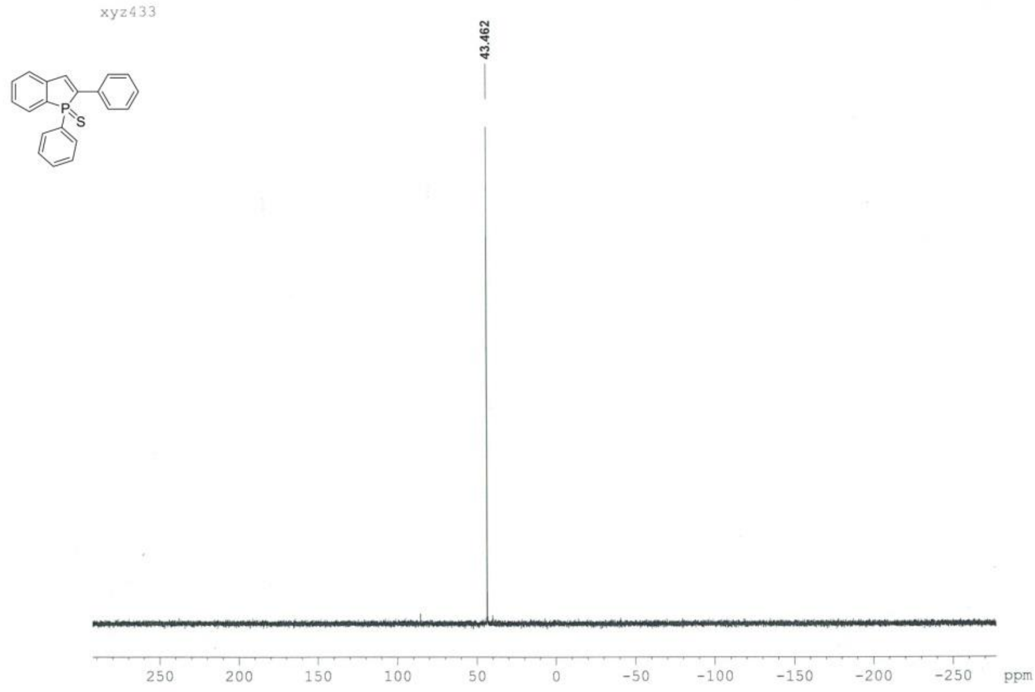

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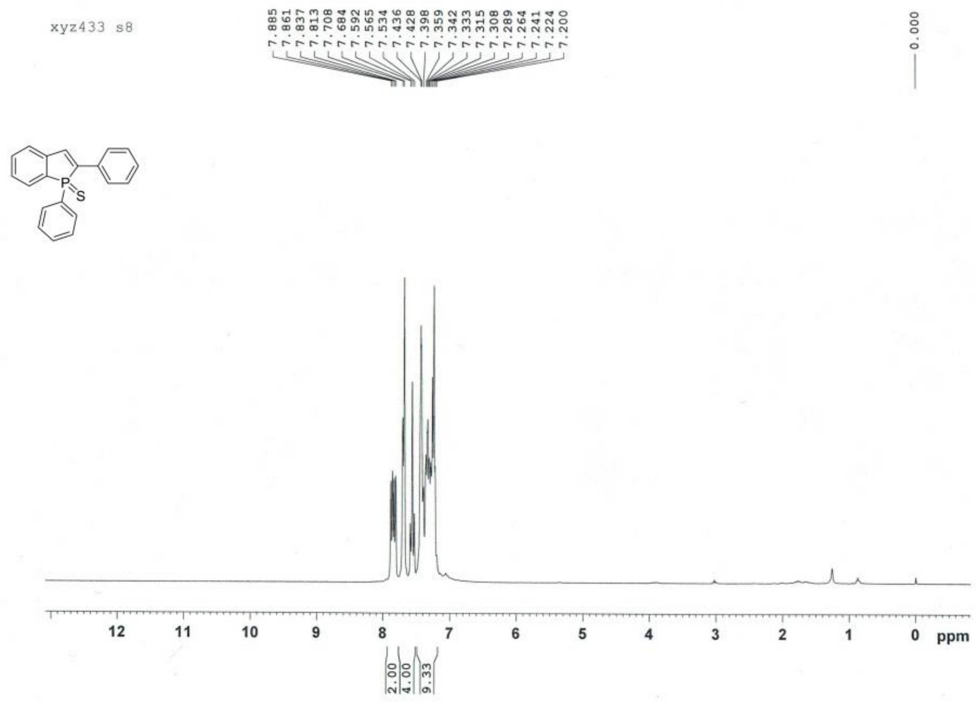

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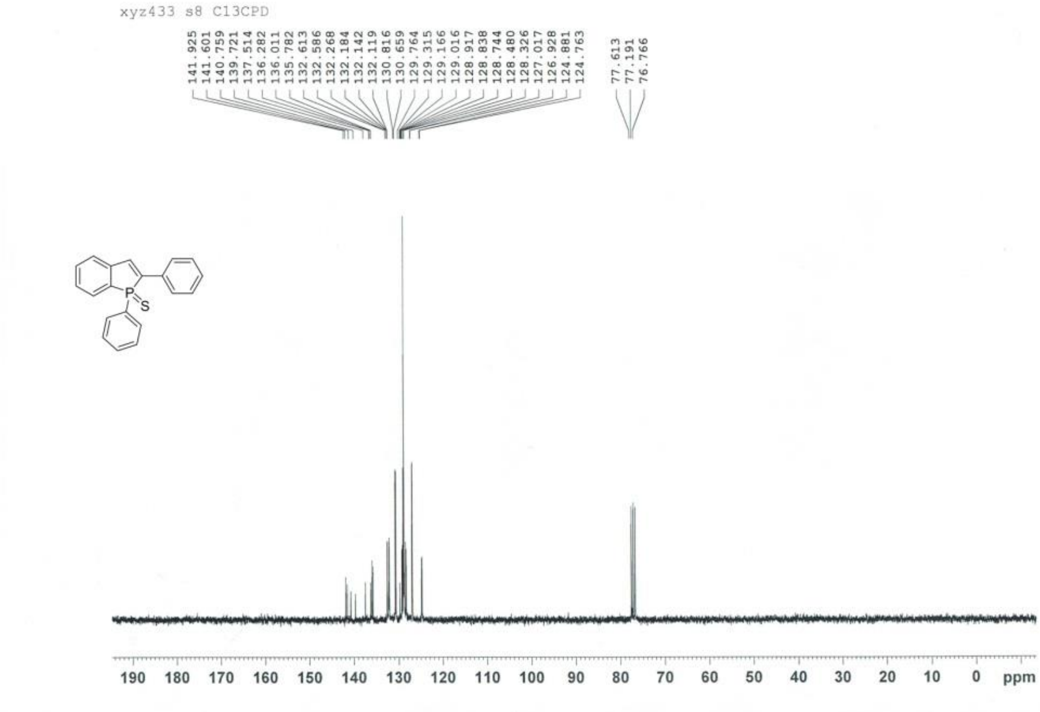

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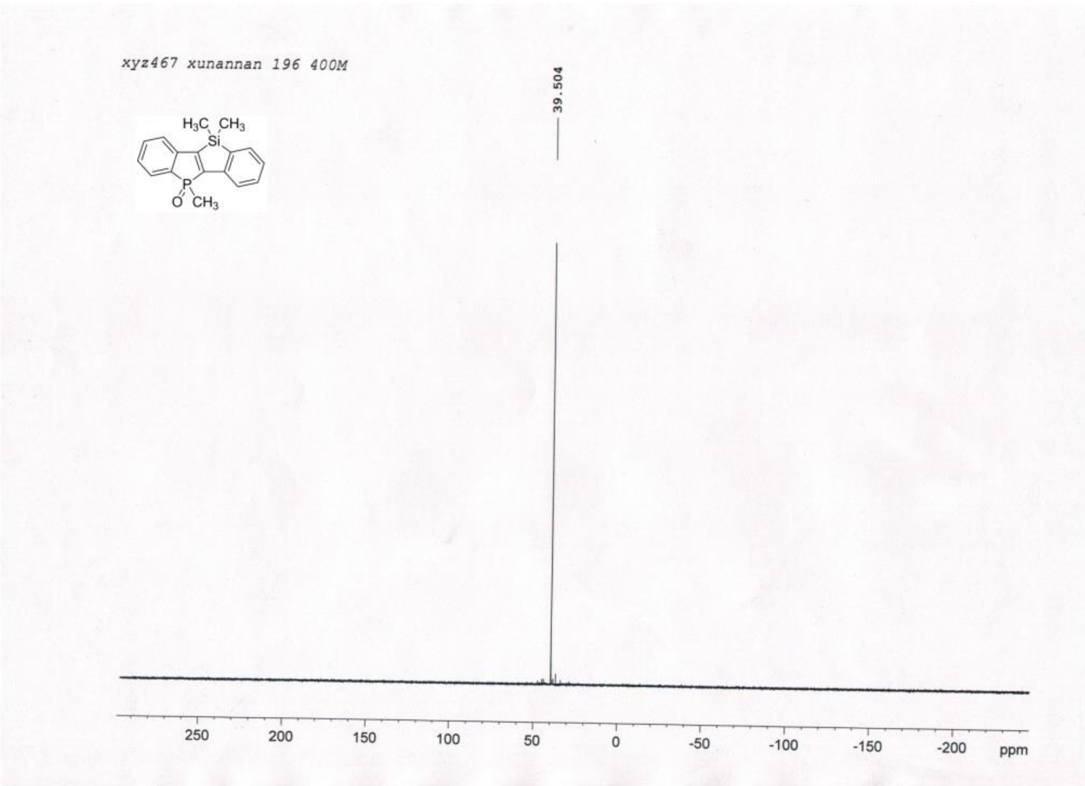

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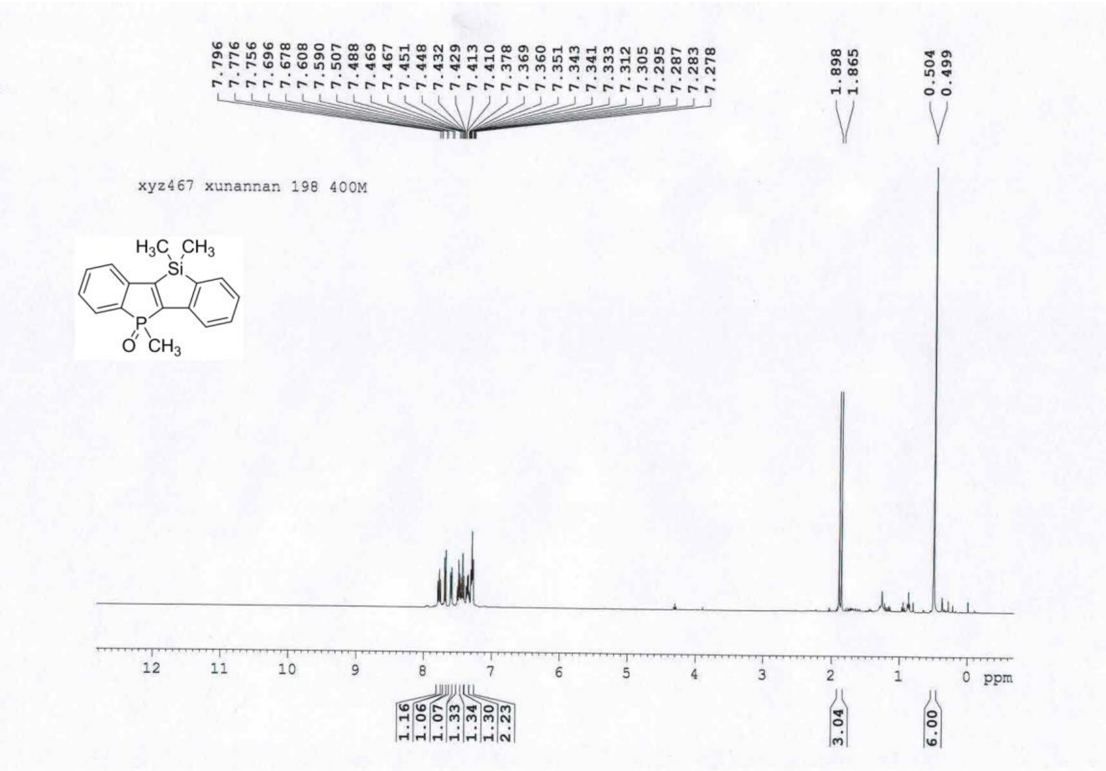

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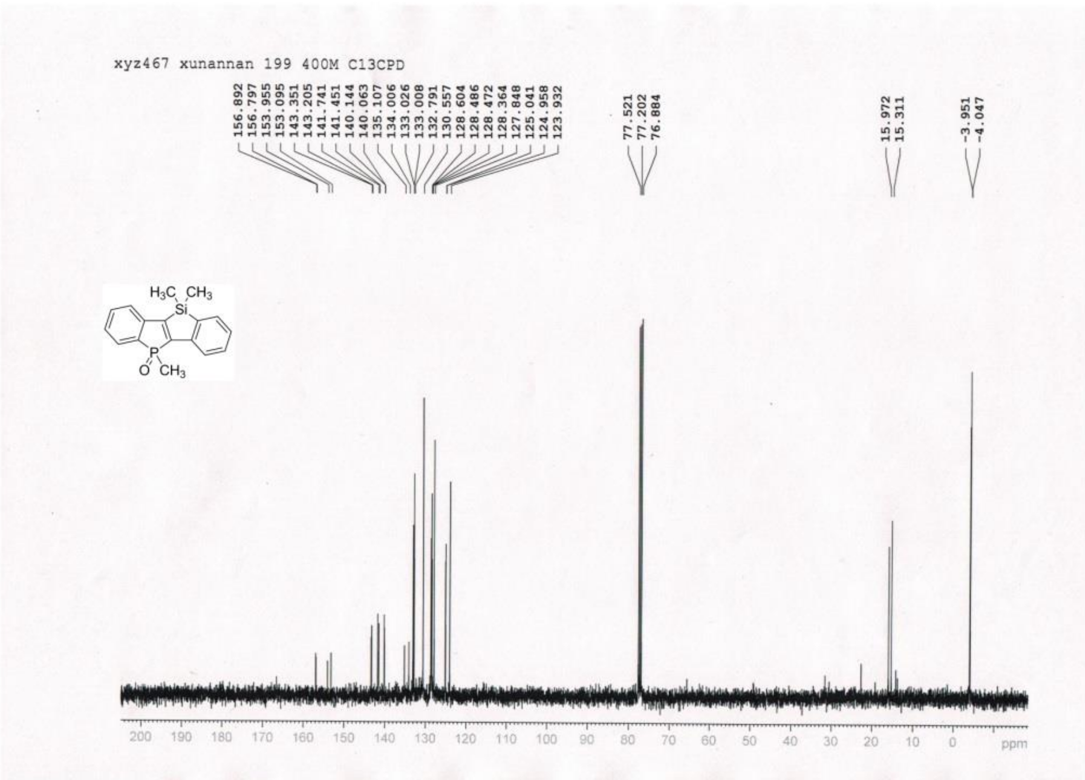

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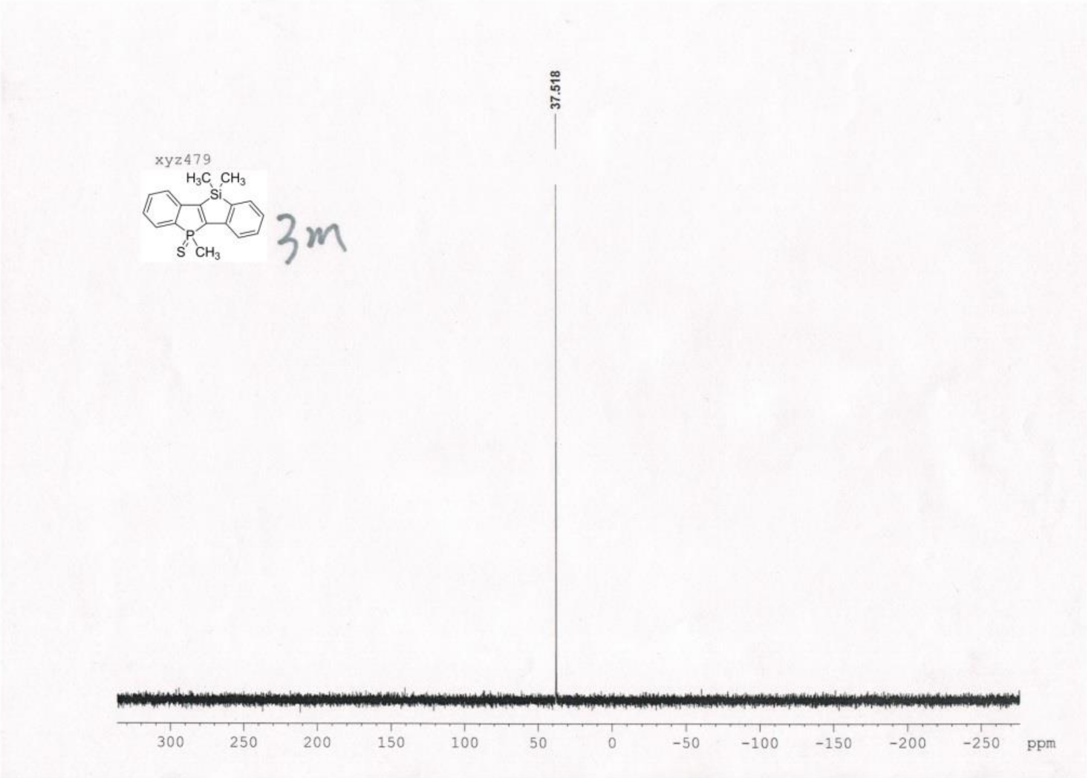

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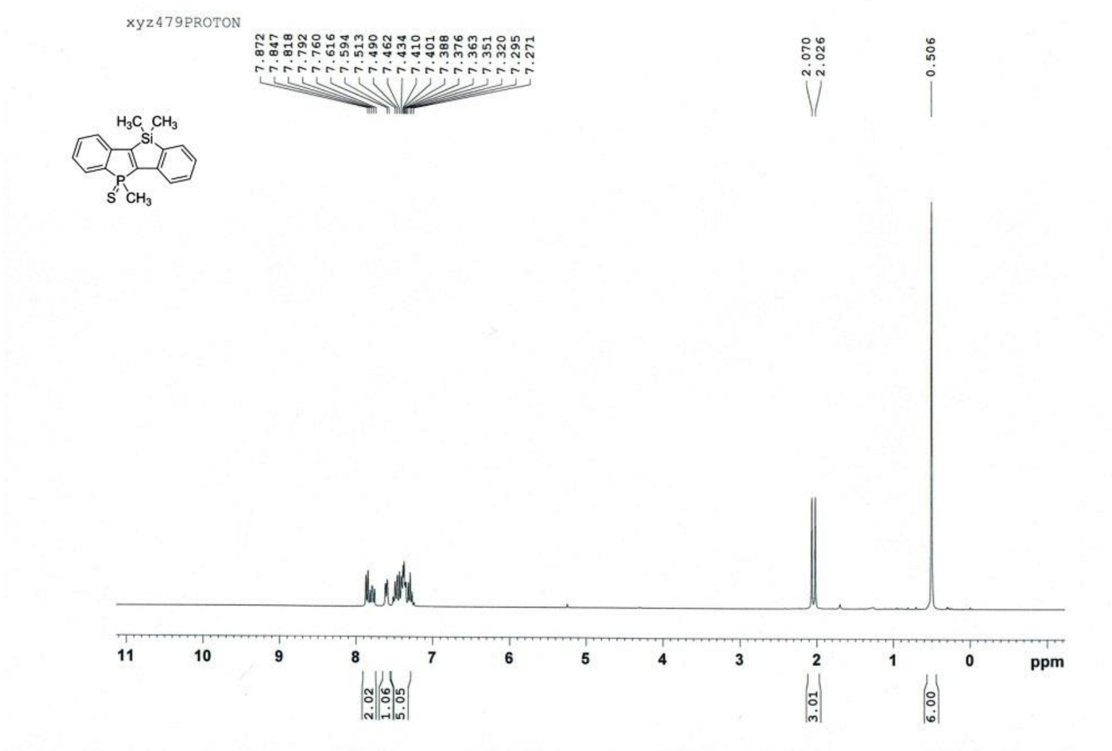

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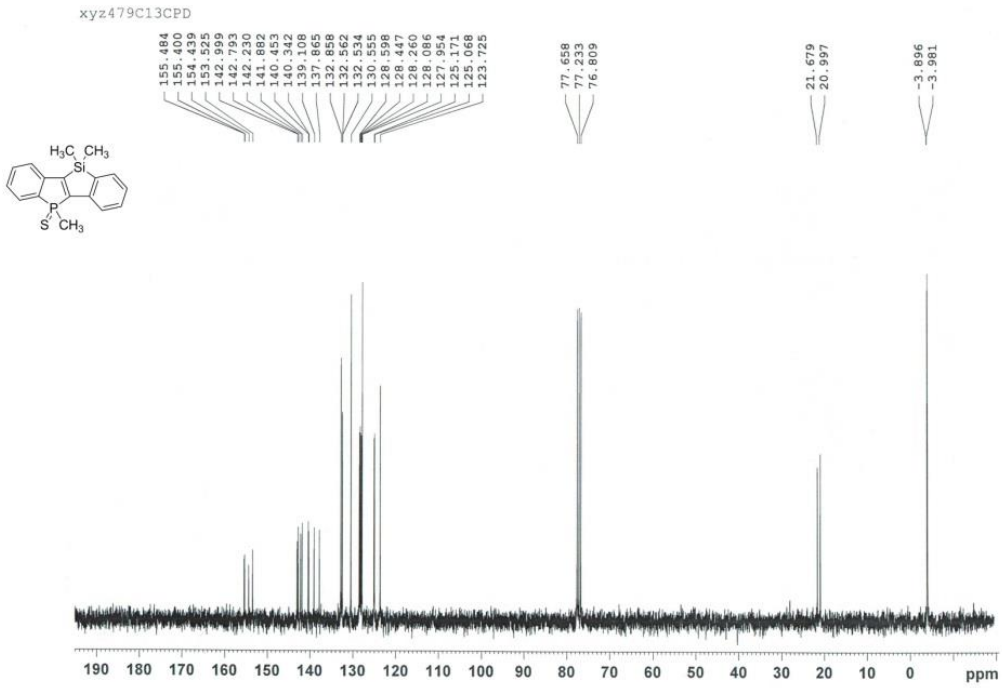

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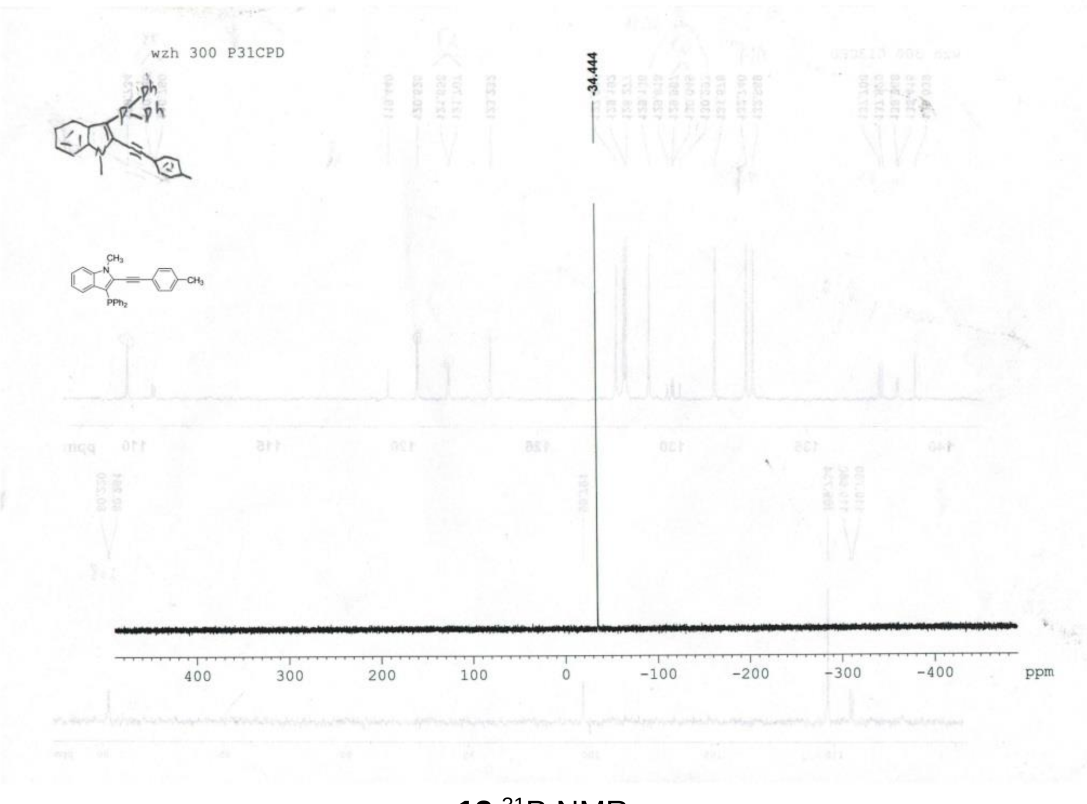

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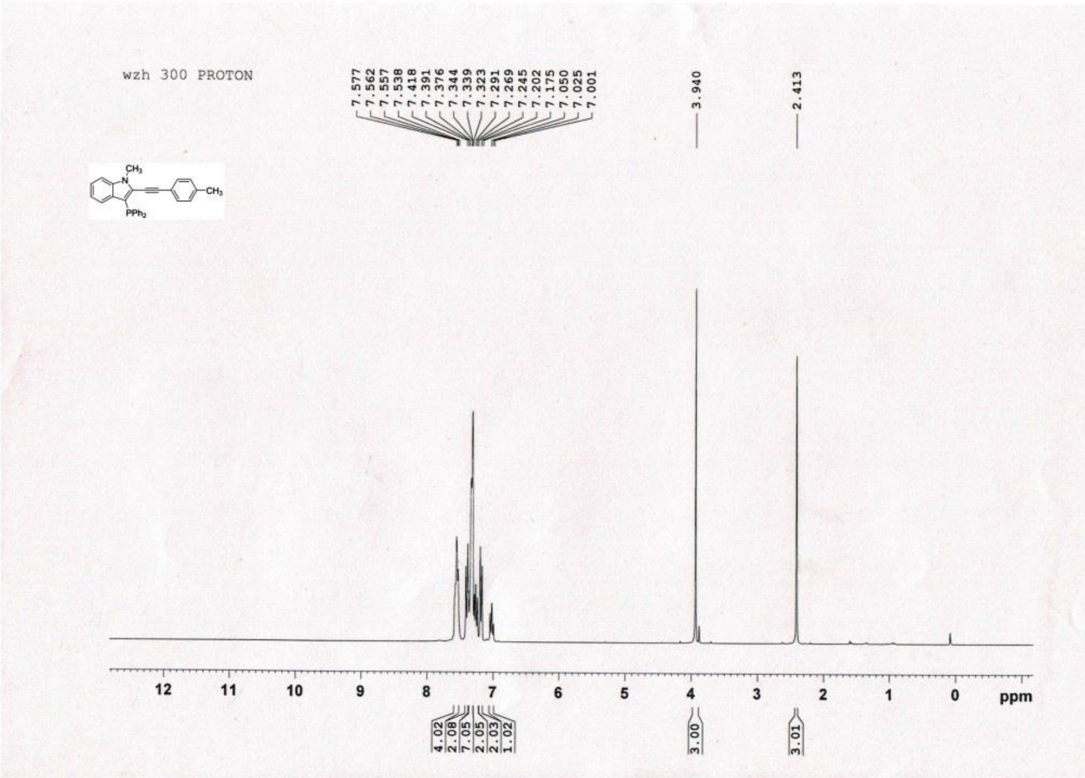

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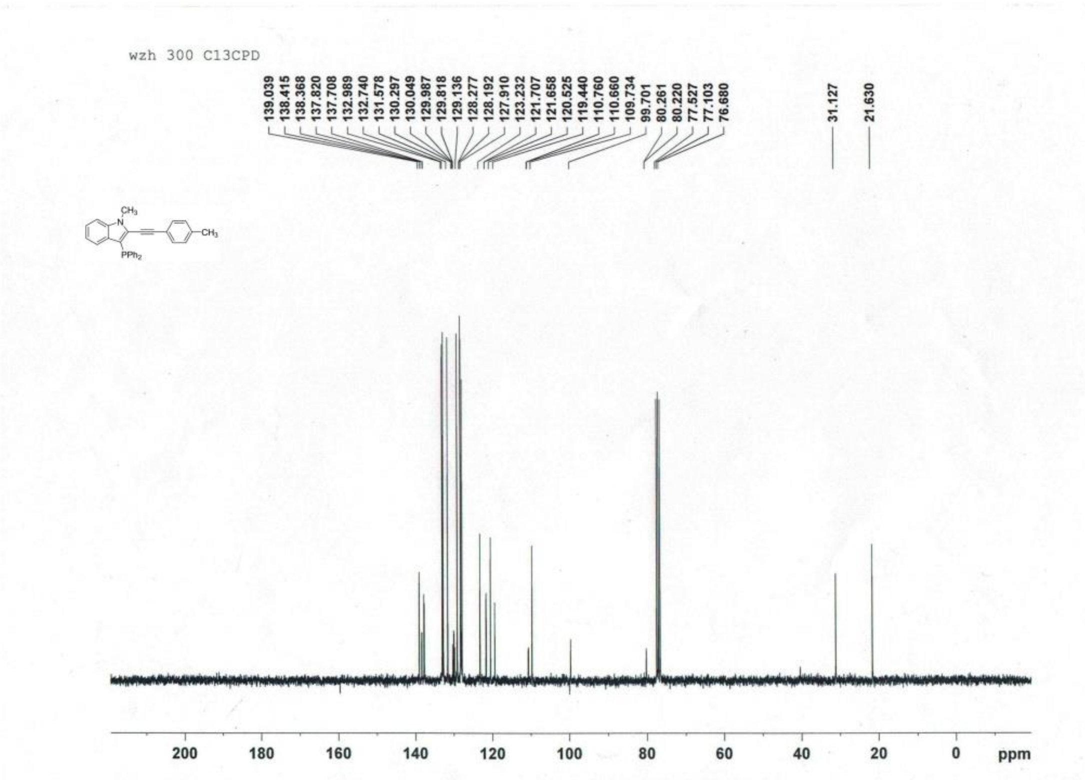

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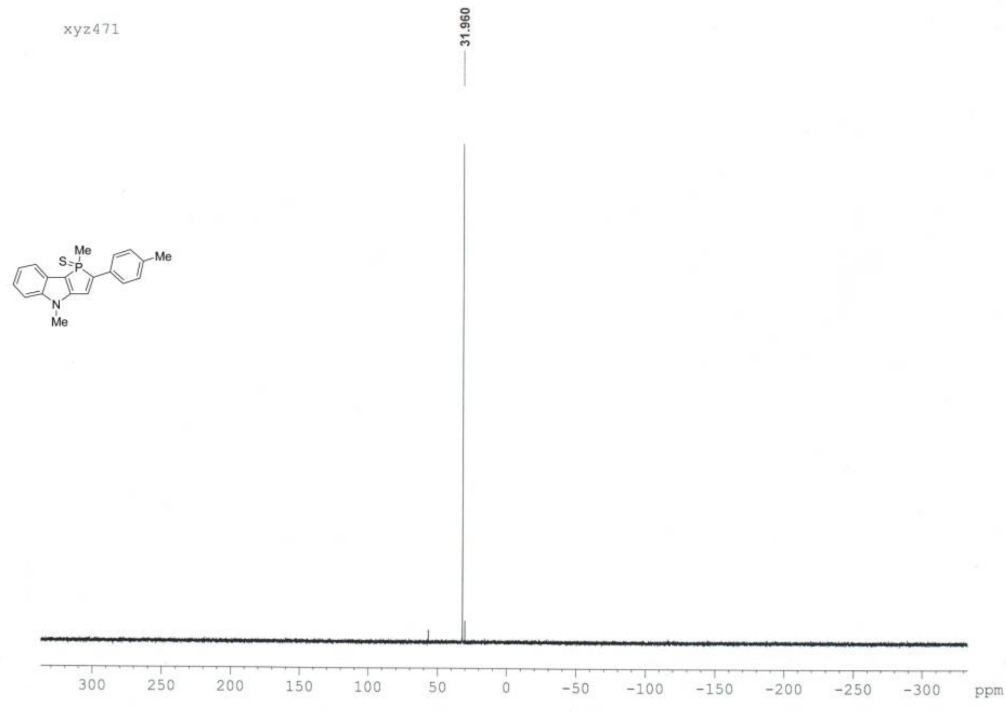

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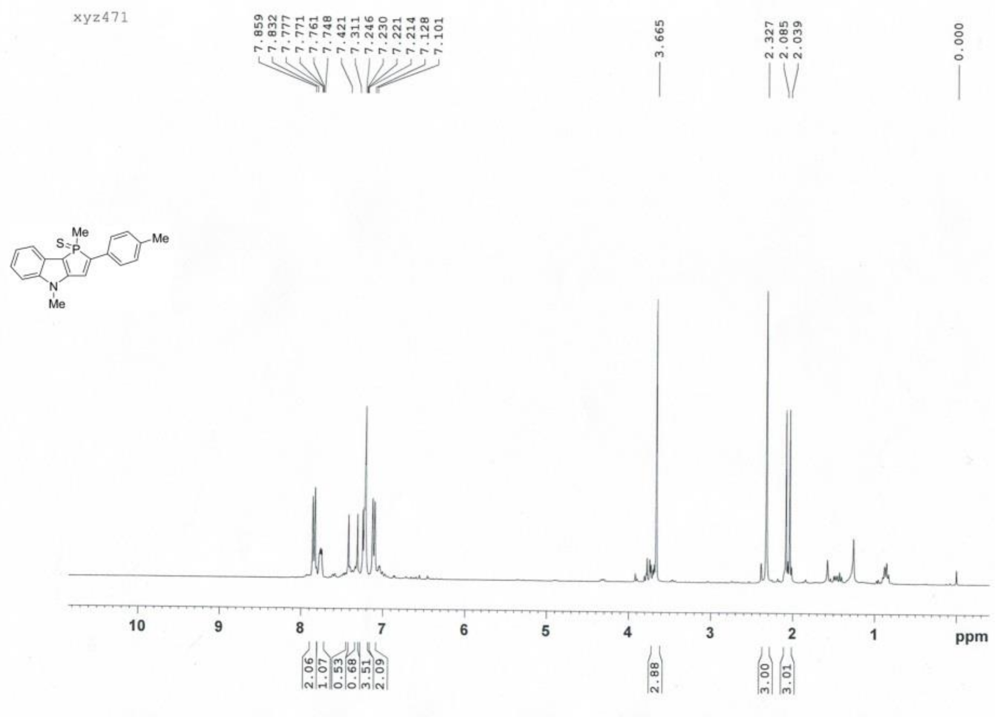

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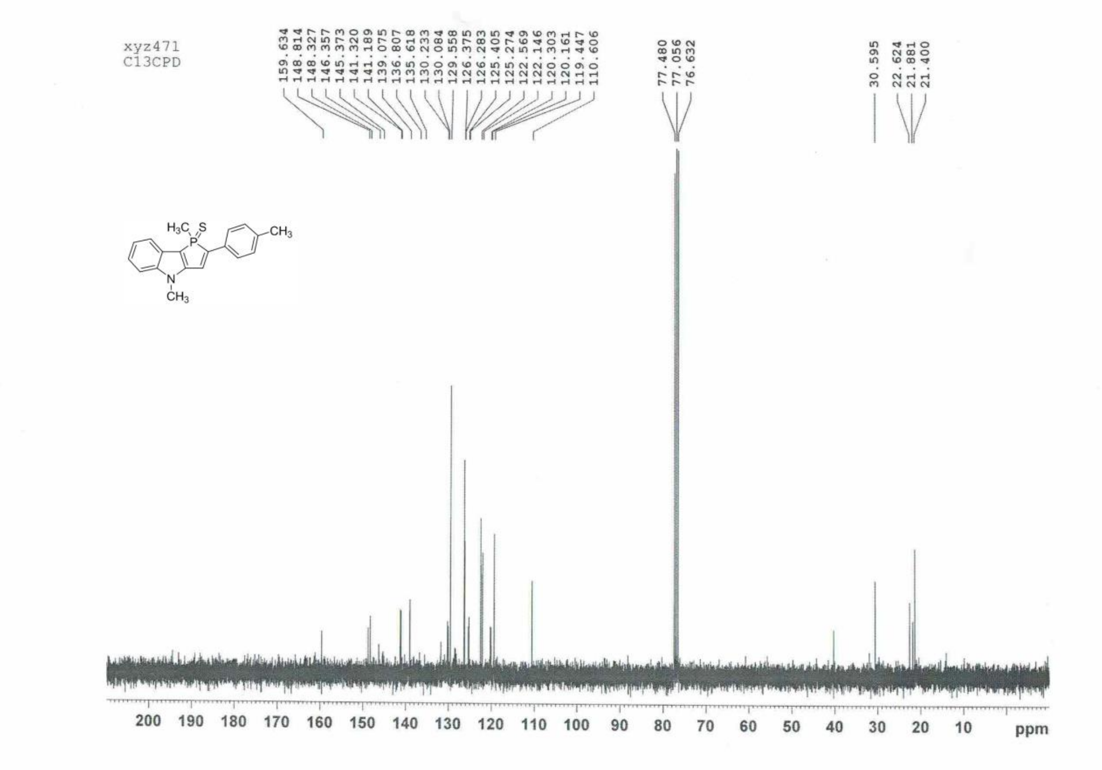
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22.624
21.881
21.400
ppm

14b ^{13}C NMR