Electronic Supplementary Information

for

Direct synthesis of phosphorotrithioites and phosphorotrithioates from white phosphorus and thiols

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General Information:

Spectroscopy data of the known compounds matches with the data reported in the corresponding references. ^{1}H, ^{13}C,^{31}P and ^{19}F NMR spectra were recorded on a Bruker Av400 spectrometer using tetramethylsilane (TMS) in $CDCl_3$ as the internal standard for ^{1}H, and ^{13}C NMR (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.23 ppm) and 85% H_3PO_4 as external standard for ^{31}P NMR. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, quint = quintet, m = multiplet), coupling constants in Hertz (Hz), integration. The products were purified by Column chromatography on silica gel 300 ─ 400 mesh. All products were further characterized by HRMS (FT-ICR-MS) and an electrospray ionization source in positive-ion mode.

Experimental Section

Safety note for P_4: White phosphorus is spontaneously flammable; it should be stored in water or glove box. On the other hand, white phosphorus is soluble in toluene.

Preparation of P_4-toluene solution: A piece of white phosphorus was taken out of water and then put in ethanol under argon. One minute later, white phosphorus was taken out and the surface ethanol was blowed off with argon. Then, the dry white phosphorus was put in a round bottomed flask containing toluene. White phosphorus-toluene solution prepared with 0.1 mol/L (12.4 g/L) should be sealed in argon and stored away from light.

Synthesis of (n-$C_{10}H_{21}S)_3P(O)$ (4w) from 1-decanethiol and P_4:

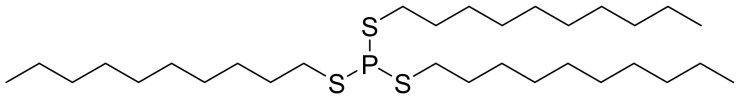
KOH (0.26 mmol, 16 mg), n-$C_{10}H_{21}SH$ (210 mg, 1.2 mmol), and DMSO (0.5 mL) were put into a Schlenk tube with a stirer under air conditions. Then white phosphorus-toluene solution (6.2 mg total P_4, 0.5 mL, 0.1 mol/L) was added under air conditions. The tube was sealed and the reaction mixture was stirred for 4 hours at room temperature. After completion, H_2O_2 (0.5 mL) was added, and the mixture was stirred at room temperature for another 30 min. The mixture was extracted by EtOAc (3×10.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash chromatography using petroleum−AcOEt [from 50:1 to 10:1 (v/v)] as the eluent to give the product **4w** (95 mg, 84%)**.**

Gram-scale synthesis of (n-$C_4H_9S)_3P(O)$ (4u) from n-C_4H_9SH and P_4:

KOH (0.74 g), n-C_4H_9SH (5.41 g), and DMSO (25 mL) were put into a 100 mL-round bottomed flask with a stirer under air conditions. Then white phosphorus-toluene solution (25 mL, 310 mg total P_4, 0.1 mol/L) was added under air conditions. The flask was stoppered with a glass stopper and the reaction mixture was stirred for 7 hours at room temperature. After completion, H_2O_2 (15 mL) was added slowly within 10 min, and the mixture was stirred at room temperature for another 2 hours. Saturated brine (30 mL) was added into the above reaction mixture. The mixture was extracted by EtOAc (3×20.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash chromatography using petroleum−AcOEt [from 50:1 to 10:1 (v/v)] as the eluent to give the product **4u** (2.61 g, 87%).

Spectral data

Tris(decyl) Phosphorotrithioite (**3a**) (*CAS Registry No.* 5116-92-7)



Colorless Wax. Yield: 75%.

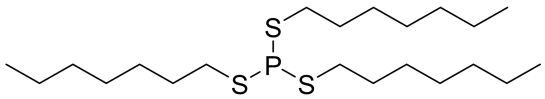
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.80 – 2.76 (m, 6H), 1.69 (quint, *J* = 7.7 Hz, 6H), 1.40 (quint, *J* = 7.6 Hz, 6H), 1.33 – 1.26 (m, 36H), 0.88 (t, *J* = 6.9 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 33.1 (d, *J* = 16.6 Hz), 32.1, 31.2 (d, *J* = 3.4 Hz), 29.8, 29.7, 29.5, 29.4, 29.0, 22.9, 14.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 116.70.

HRMS Calcd for $C_{30}H_{64}PS_3$ $[M+H]^+$ 551.3902, found 551.3907.

Triheptyl Phosphorotrithioite (**3b**) (*CAS Registry No.* 1217597-46-0)



Colorless Wax. Yield: 76%.

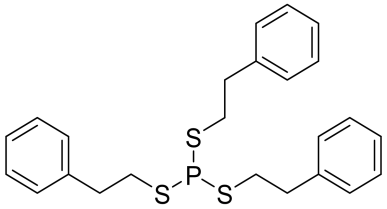
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78 (dd, *J* = 8.6 Hz, *J* = 17.9 Hz, 6H), 1.69 (quint, *J* = 7.6 Hz, 6H), 1.40 (quint, *J* = 7.1 Hz, 6H), 1.32 – 1.25 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 33.1 (d, *J* = 16.6 Hz), 31.9, 31.2 (d, *J* = 3.3 Hz), 29.0, 28.9, 22.8, 14.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 116.67.

HRMS Calcd for $C_{21}H_{45}NaPS_3$ $[M+Na]^+$ 447.2313, found 447.2317.

Triphenethyl Phosphorotrithioite (**3c**) (*CAS Registry No.* 63671-73-8)



Colorless Wax. Yield: 63%.

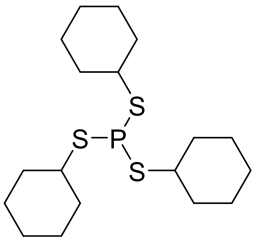
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.6 Hz, 6H), 7.22 – 7.19 (m, 9H), 3.02 – 2.96 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 128.9, 128.7, 126.7, 37.6 (d, *J* = 3.4 Hz), 34.2 (d, *J* = 16.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 117.30.

HRMS Calcd for $C_{24}H_{27}NaPS_3$ $[M+Na]^+$ 465.0905, found 465.0903.

Tricyclohexyl Phosphorotrithioite (**3d**) (*CAS Registry No.* 13676-85-2)



Colorless Wax. Yield: 69%.

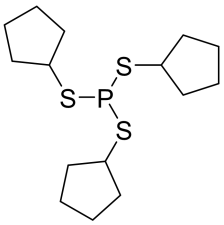
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.07 – 3.02 (m, 3H), 2.06 – 2.04 (m, 6H), 1.77 – 1.74 (m, 6H), 1.58 – 1.55 (m, 3H), 1.53 – 1.47 (m, 6H), 1.38 – 1.31 (m, 6H), 1.28 – 1.24 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 47.1 (d, *J* = 15.4 Hz), 35.6 (d, *J* = 3.3 Hz), 26.3, 25.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ 104.44.

HRMS Calcd for $C_{18}H_{33}NaPS_3$ $[M+Na]^+$ 399.1374, found 399.1379.

Tricyclopentyl Phosphorotrithioite (**3e**)



Colorless Wax. Yield: 62%.

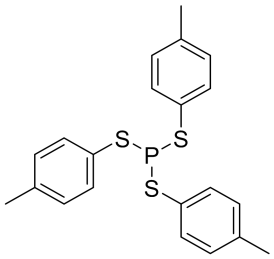
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.40 (dt, *J* = 7.0 Hz, 3H), 2.10 – 2.06 (m, 6H), 1.79 – 1.73 (m, 6H), 1.72 – 1.67 (m, 6H), 1.62 – 1.56 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 47.1 (d, *J* = 15.4 Hz), 35.6 (d, *J* = 3.3 Hz), 26.3, 25.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ 106.20.

HRMS Calcd for $C_{15}H_{27}NaPS_3$ $[M+Na]^+$ 357.0905, found 357.0913.

Tri-p-tolyl Phosphorotrithioite (**3f**) (*CAS Registry No.* 3948-84-3)



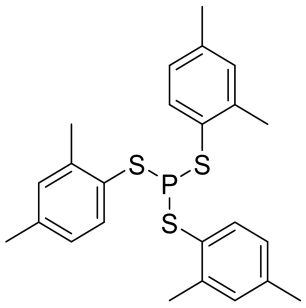
White solid. Yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.0 Hz, 6H), 7.08 (d, *J* = 8.0 Hz, 6H), 2.31 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.8, 134.5 (d, *J* = 4.4 Hz), 130.1, 128.7 (d, *J* = 13.2 Hz), 21.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ 132.74.

HRMS Calcd for $C_{21}H_{21}NaPS_3$ $[M+Na]^+$ 423.0435, found 423.0433.

Tris(2,4-dimethylphenyl) Phosphorotrithioite (**3g**)



White solid. Yield: 80%.

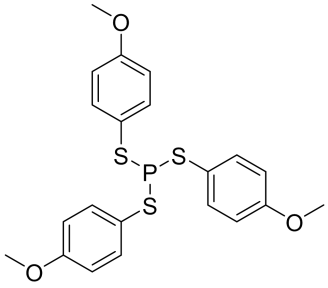
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.0 Hz, 3H), 7.02(s, 3H), 6.92 (d, *J* = 8.0 Hz, 3H), 2.34 (s, 9H), 2.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9 (d, *J* = 2.2 Hz), 139.0 (d, *J* = 2.2 Hz), 135.9 (d, *J* = 5.6 Hz), 131.6, 128.5 (d, *J* = 11.0 Hz), 127.6, 21.6, 21.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 136.71

HRMS Calcd for $C_{24}H_{27}NaPS_3$ $[M+Na]^+$ 465.0905, found 465.0906.

Tris(4-methoxyphenyl) Phosphorotrithioite (**3h**)



Colorless Wax. Yield: 95%.

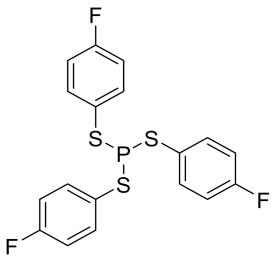
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.5 Hz, 6H), 6.82 (d, *J* = 8.2 Hz, 6H), 3.78 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 136.4 (d, *J* = 3.4 Hz), 122.7 (d, *J* = 13.2 Hz), 114.9, 55.5.

^{31}P NMR (162 MHz, $CDCl_3$): δ 134.91.

HRMS Calcd for $C_{21}H_{21}NaO_3PS_3$ $[M+Na]^+$ 471.0283, found 471.0283.

Tris(4-fluorophenyl) Phosphorotrithioite (**3i**)



Colorless Wax. Yield: 71%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 - 7.42 (m, 6H), 7.00 (t, *J* = 8.6 Hz, 6H).

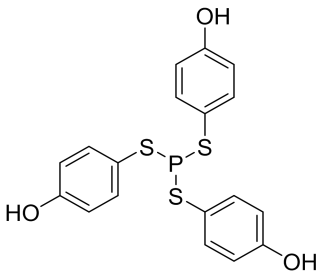
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3 (dd, *J* = 250.0 Hz, *J* = 2.2 Hz), 136.6 (dd, *J* = 8.8 Hz, *J* = 4.4 Hz), 126.9 (dd, *J* = 13.2 Hz, *J* = 3.3 Hz), 116.6 (d, *J* = 22.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 134.43 (d, *J* = 7.5 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -111.46 (d, *J* = 5.2 Hz).

HRMS Calcd for $C_{18}H_{13}F_3PS_3$$[M+H]^+$ 412.9864, found 412.9872.

Tris(4-hydroxyphenyl) Phosphorotrithioite (**3j**)



White solid. Yield: 95%.

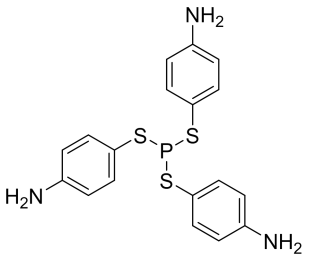
^{1}H NMR (400 MHz, CD_3OD): δ 7.26 (d, *J* = 8.5 Hz, 6H), 6.74 – 6.73 (m, 6H), 4.87 (s, OH).

^{13}C NMR (100 MHz, CD_3OD): δ 159.2, 137.3 (d, *J* = 3.3 Hz), 121.9 (d, *J* = 13.2 Hz),116.9.

^{31}P NMR (162 MHz, CD_3OD): δ 137.42.

HRMS Calcd for $C_{18}H_{15}NaO_3PS_3$ $[M+Na]^+$ 428.9813, found 428.9818.

Tris(4-aminophenyl) Phosphorotrithioite (**3k**)



White solid. Yield: 95%.

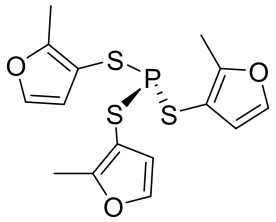
^{1}H NMR (400 MHz, DMSO-d6): δ 7.08 (d, *J* = 8.2 Hz, 6H), 6.52 (d, *J* = 8.2 Hz, 6H), 5.43 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d6): δ 149.8, 135.9 (d, *J* = 2.5 Hz), 114.6 (d, *J* = 12.2 Hz),114.5.

^{31}P NMR (162 MHz, DMSO-d6): δ 135.05.

HRMS Calcd for $C_{18}H_{19}N_3PS_3$ $[M+H]^+$ 404.0473, found 404.0473.

Tris(2-methylfuran-3-yl) Phosphorotrithioite (**3l**)



Brown Wax. Yield: 48%.

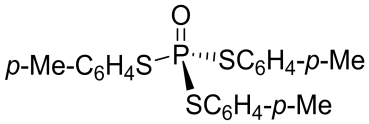
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 1.5 Hz, 3H), 6.33 (d, *J* = 1.8 Hz, 3H), 2.31 (d, *J* = 1.8 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8 (d, *J* = 5.5Hz), 140.82, 115.7 (d, *J* = 2.2 Hz), 107.5 (d, *J* = 13.3 Hz), 12.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 136.80.

HRMS Calcd for $C_{15}H_{16}O_3PS_3$ $[M+H]^+$ 370.9994, found 370.9994.

S,S,S-Triphenyl Phosphorotrithioate (**4a**) (*CAS Registry No.* 13799-87-6)



White solid. Yield: 96%.

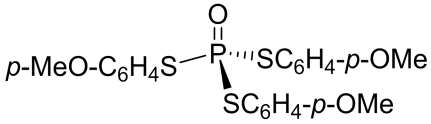
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 - 7.40 (m, 6H), 7.15 (d, *J* = 8.14 Hz, 6H), 2.35(d, *J* = 2.3 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2 (d, *J* = 3.6 Hz), 135.8 (d, *J* = 4.5 Hz), 130.3, 123.4 (d, *J* = 6.4 Hz), 21.5 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 56.70.

HRMS Calcd for $C_{21}H_{21}NaOPS_3$ $[M+Na]^+$ 439.0384, found 439.0392.

S,S,S-Tris(4-methoxyphenyl) Phosphorotrithioate (**4b**)



White solid. Yield: 99%.

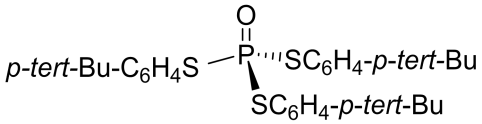
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.44 (m, 6H), 6.90 – 6.87 (m, 6H), 3.81 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (d, *J* = 3.6 Hz), 137.7 (d, *J* = 4.5 Hz), 117.3 (d, *J* = 7.1 Hz), 115.1 (d, *J* = 2.7 Hz), 55.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 57.78.

HRMS Calcd for $C_{21}H_{21}NaO_4PS_3$ $[M+Na]^+$ 487.0232, found 487.0232.

S,S,S-Tris(4-(tert-butyl)phenyl) Phosphorotrithioate (**4c**)



White solid. Yield: 99%.

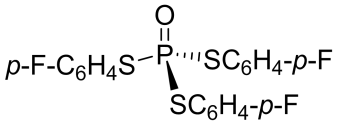
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 - 7.45 (m, 6H), 7.38 - 7.37 (m, 6H), 1.33 (s, 27H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2 (d, *J* = 3.6 Hz), 135.6 (d, *J* = 4.5 Hz), 126.7, 123.6 (d, *J* = 7.2 Hz), 35.0, 31.4 (d, *J* = 3.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 56.48.

HRMS Calcd for $C_{30}H_{40}OPS_3$ $[M+H]^+$ 543.1973, found 543.1980.

S,S,S-Tris(4-fluorophenyl) Phosphorotrithioate (**4d**)



White solid. Yield: 80%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 - 7.48 (m, 6H), 7.06 (t, *J* = 8.6 Hz, 6H).

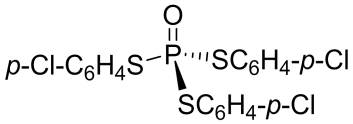
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2 (dd, *J* = 251.7 Hz, *J* = 3.7 Hz), 138.0 (dd, *J* = 9.0 Hz, *J* = 4.5 Hz), 121.7 (dd, *J* = 7.1 Hz, *J* = 3.7 Hz), 116.9 (dd, *J* = 22.7 Hz, *J* = 2.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 54.32 (d, *J* = 7.5 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -109.86 (d, *J* = 5.2 Hz).

HRMS Calcd for $C_{18}H_{13}F_3OPS_3[M+H]^+$ 428.9813, found 428.9813.

S,S,S-Tris(4-chlorophenyl) Phosphorotrithioate (**4e**) (*CAS Registry No.* 35075-27-5)



White solid. Yield: 72%.

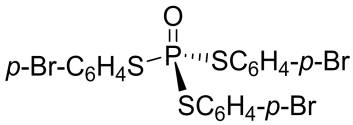
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 6H), 7.33 (d, *J* = 8.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1 (d, *J* = 4.6 Hz), 136.9 (d, *J* = 4.6 Hz), 129.9 (d, *J* = 2.8 Hz), 124.8 (d, *J* = 7.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 53.32.

HRMS Calcd for $C_{18}H_{13}Cl_3OPS_3[M+H]^+$ 476.8926, found 476.8928.

S,S,S-Tris(3-bromophenyl) Phosphorotrithioate (**4f**) (*CAS Registry No.* 154963-11-8)



White solid. Yield: 64%.

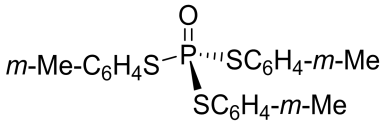
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.5 Hz, 6H), 7.36 (dd, *J* = 8.7 Hz, *J* = 2.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3 (d, *J* = 4.3 Hz), 132.8, 125.4 (d, *J* = 7.1 Hz), 125.2 (d, *J* = 4.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 52.42.

HRMS Calcd for $C_{18}H_{13}Br_3OPS_3$ $[M+H]^+$ 608.7411, found 608.7415.

S,S,S-Tri-*m*-tolyl Phosphorotrithioate (**4g**)



White solid. Yield: 87%.

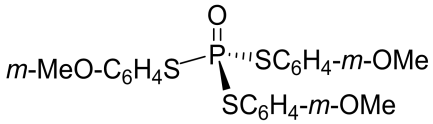
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 - 7.31 (m, 6H), 7.23 - 7.17 (m, 6H), 2.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3 (d, *J* = 2.7 Hz), 136.3 (d, *J* = 1.8 Hz), 132.8 (d, *J* = 4.6 Hz), 130.7 (d, *J* = 3.3 Hz), 129.2, 126.6 (d, *J* = 7.2 Hz), 21.4(d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 55.60.

HRMS Calcd for $C_{21}H_{22}OPS_3$ $[M+H]^+$ 417.0565, found 417.0565.

S,S,S-Tris(3-methoxyphenyl) Phosphorotrithioate (**4h**)



White solid. Yield: 86%.

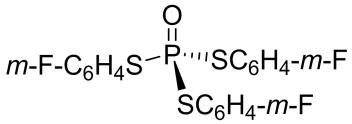
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 8.1 Hz, 3H), 7.13 – 7.12 (m, 3H), 7.09 – 7.08 (m, 3H), 6.94 – 6.92 (m, 3H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (d, *J* = 2.4 Hz), 130.2, 127.9 (d, *J* = 5.3 Hz), 127.7 (d, *J* = 7.3 Hz), 120.5 (dd, *J* = 9.4 Hz, *J* = 4.1 Hz), 116.3 (d, *J* = 6.6 Hz), 55.6 (d, *J* = 11.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 55.83.

HRMS Calcd for $C_{21}H_{21}NaO_4PS_3$ $[M+Na]^+$ 487.0232, found 487.0231.

S,S,S-Tris(3-fluorophenyl) Phosphorotrithioate (**4i**)



White solid. Yield: 56%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 - 7.34 (m, 6H), 7.29 - 7.27 (m, 3H), 7.15 - 7.13 (m, 3H).

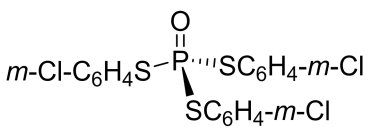
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6 (dd, *J* = 251.2 Hz, *J* = 2.8 Hz), 131.6, 130.8 (d, *J* = 8.2 Hz), 128.1 (t, *J* = 7.5 Hz), 122.6 (d, *J* = 22.8 Hz), 117.5 (d, *J* = 21.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 52.90.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -110.48.

HRMS Calcd for $C_{18}H_{12}F_3NaOPS_3$ $[M+Na]^+$ 450.9632, found 450.9637.

S,S,S-Tris(3-chlorophenyl) Phosphorotrithioate (**4j**)



White solid. Yield: 62%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 1.9 Hz, 3H), 7.44 – 7.39 (m, 6H), 7.30 (t, *J* = 7.9 ,3H),

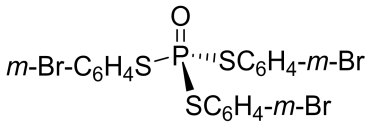
7.31 (t, *J* = 8.0 ,3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 135.2 (d, *J* = 3.3 Hz), 133.9 (d, *J* = 4.6 Hz), 130.6 (d, *J* = 2.2 Hz), 130.5 (d, *J* = 3.6 Hz), 128.0 (d, *J* = 7.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 53.11.

HRMS Calcd for $C_{18}H_{13}Cl_3OPS_3[M+H]^+$ 476.8926, found 476.8934.

S,S,S-Tris(3-bromophenyl) Phosphorotrithioate (**4k**)



White solid. Yield: 61%.

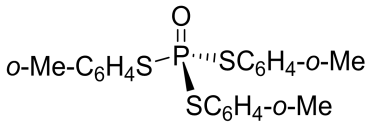
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 4.6 Hz, *J* = 1.9 Hz, 3H), 7.55 (d, *J* = 8.2 Hz, 3H), 7.47 (d, *J* = 7.6 Hz, 3H), 7.24 (t, *J* = 7.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0 (d, *J* = 5.4 Hz), 134.4 (d, *J* = 4.5 Hz), 133.4 (d, *J* = 2.8 Hz), 130.9 (d, *J* = 2.6 Hz), 128.2 (d, *J* = 7.2 Hz), 123.1 (d, *J* = 2.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 53.33.

HRMS Calcd for $C_{18}H_{13}Br_3OPS_3$ $[M+H]^+$ 608.7411, found 608.7415.

S,S,S-Tri-*o*-tolyl Phosphorotrithioate (**4l**) (*CAS Registry No.* 35029-38-0)



White solid. Yield: 80%.

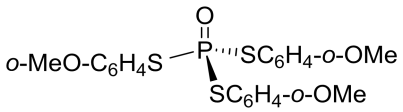
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.7 Hz, 3H), 7.25 (t, *J* = 7.2 Hz, 3H), 7.20 (d, *J* = 7.5 Hz, 3H), 7.12 (t, *J* = 7.4 Hz, 3H), 2.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4 (d, *J* = 5.3 Hz), 137.5 (d, *J* = 4.4 Hz), 131.0 (d, *J* = 3.3 Hz), 130.2 (d, *J* = 3.3 Hz), 126.7 (d, *J* = 2.2 Hz), 126.5 (d, *J* = 6.7 Hz), 21.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 52.52.

HRMS Calcd for $C_{21}H_{21}NaOPS_3$ $[M+Na]^+$ 439.0384, found 439.0385.

S,S,S-Tris(2-methoxyphenyl) Phosphorotrithioate (**4m**)



White solid. Yield: 62%.

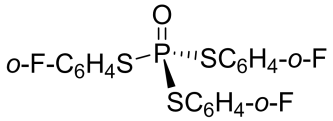
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.59 (m, 3H), 7.35 – 7.31 (m, 3H), 6.91 – 6.87 (m, 6H), 3.79 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (d, *J* = 4.5 Hz), 137.6 (d, *J* = 1.8 Hz), 131.4, 121.1 (d, *J* = 8.4 Hz), 115.8 (d, *J* = 7.2 Hz), 111.8 (d, *J* = 8.9 Hz), 56.0 (d, *J* = 11.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 54.86.

HRMS Calcd for $C_{21}H_{21}NaO_4PS_3$ $[M+Na]^+$ 487.0232, found 487.0237.

S,S,S-Tris(2-fluorophenyl) Phosphorotrithioate (**4n**)



White solid. Yield: 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.58 (m, 3H), 7.41 - 7.40 (m, 3H), 7.14 (t, *J* = 7.9 ,6H).

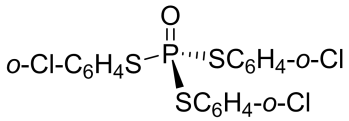
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (dd, *J* = 251.2 Hz, *J* = 5.4 Hz), 138.2 (d, *J* = 3.7 Hz), 132.7 (d, *J* = 6.9 Hz), 125.0, 116.6 (d, *J* = 22.6 Hz), 113.8 (dd, *J* = 18.8 Hz, *J* = 7.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 54.26.

^{19}F NMR (377 MHz, CDCl3) δ (ppm) -104.61.

HRMS Calcd for $C_{18}H_{12}F_3NaOPS_3[M+Na]^+$ 450.9632, found 450.9634.

S,S,S-Tris(2-chlorophenyl) Phosphorotrithioate (**4o**)



White solid. Yield: 53%.

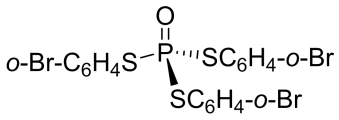
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.7 Hz, 3H), 7.45 (d, *J* = 7.9 Hz, 3H), 7.32 (t, *J* = 7.3 Hz ,6H), 7.23 (t, *J* = 7.6 Hz ,6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2 (d, *J* = 5.6 Hz), 138.1 (d, *J* = 4.4 Hz), 131.4 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 2.2 Hz), 127.5 (d, *J* = 2.2 Hz), 126.2 (d, *J* = 6.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 52.13.

HRMS Calcd for $C_{18}H_{13}Cl_3OPS_3$ $[M+H]^+$ 476.8926, found 476.8931.

S,S,S-Tris(2-bromophenyl) Phosphorotrithioate (**4p**)



White solid. Yield: 50%.

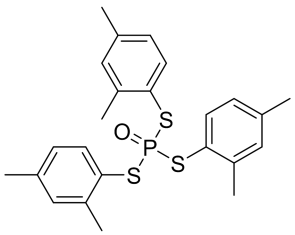
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.72 (m, 3H), 7.62 (d, *J* = 7.7, 3H), 7.29 – 7.19 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0 (d, *J* = 4.5 Hz), 133.9 (d, *J* = 2.6 Hz), 133.4 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 2.7 Hz), 130.1 (d, *J* = 6.3 Hz), 128.4 (d, *J* = 6.6 Hz), 128.2 (d, *J* = 2.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 51.64.

HRMS Calcd for $C_{18}H_{13}Br_3OPS_3$ $[M+H]^+$ 608.7411, found 608.7416.

S,S,S-Tris(2,4-dimethylphenyl) Phosphorotrithioate (**4q**)



White solid. Yield: 82%.

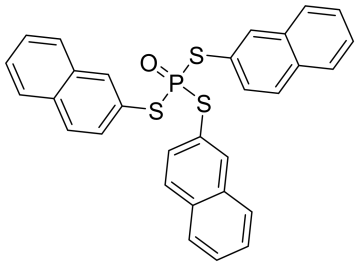
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.42 (m, 3H), 7.05 (s, 3H), 6.96 (d, *J* = 7.8 Hz, 3H), 2.29 (d, *J* = 13.3 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2 (d, *J* = 4.5 Hz), 140.4 (d, *J* = 3.6 Hz), 137.4, 131.9 (d, *J* = 8.3 Hz), 127.6, 123.2 (d, *J* = 6.8 Hz), 21.5 (dd, *J* = 23.4 Hz, *J* = 7.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 53.45.

HRMS Calcd for $C_{24}H_{27}NaOPS_3$ $[M+Na]^+$ 481.0854, found 481.0859.

S,S,S-Tri(naphthalen-2-yl) Phosphorotrithioate (**4r**) (*CAS Registry No.* 14974-75-5.)



White solid. Yield: 95%.

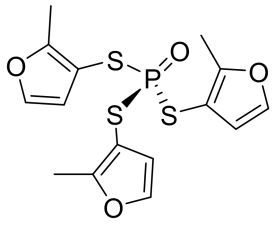
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0 (s, 3H), 7.84 - 7.79 (m, 6H), 7.75 (d, *J* = 8.3 Hz, 3H), 7.60 – 7.59 (m, 3H), 7.55 – 7.49 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2 (d, *J* = 6.7 Hz), 133.7 (d, *J* = 2.8 Hz), 133.6 (d, *J* = 1.9 Hz), 132.0 (d, *J* = 2.8 Hz), 129.1, 128.2, 127.9, 127.6, 126.9, 124.1 (d, *J* = 7.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 55.45.

HRMS Calcd for $C_{30}H_{22}OPS_3$ $[M+H]^+$ 525.0565, found 525.0565.

S,S,S-Tris(2-methylfuran-3-yl) Phosphorotrithioate (**4s**)



Brown Wax. Yield: 50%.

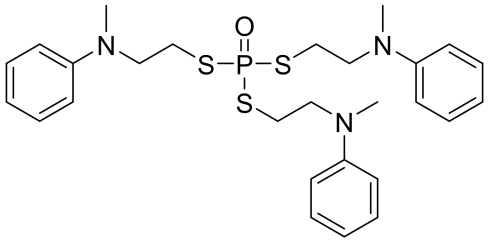
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 1.9 Hz, 3H), 6.42 (d, *J* = 1.9 Hz, 3H), 2.31 (d, *J* = 4.4 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6 (d, *J* = 8.8 Hz), 141.1, 115.9, 102.8 (d, *J* = 6.6 Hz), 12.37 (d, *J* = 3.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 57.30.

HRMS Calcd for $C_{15}H_{15}NaO_4PS_3$ $[M+Na]^+$ 408.9762, found 408.9766.

S,S,S-Tris(2-(methyl(phenyl)amino)ethyl) Phosphorotrithioate (**4t**)



Colorless Wax. Yield: 78%.

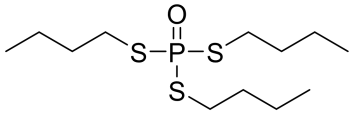
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, *J* = 6.9 Hz, 6H), 6.76 – 6.71 (m, 9H), 3.70 (d, *J* = 7.4 Hz, 6H), 3.16 – 3.11 (m, 6H), 2.97 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 129.6, 117.2, 112.52, 53.4 (d, *J* = 3.3 Hz), 38.7, 29.8 (d, *J* = 4.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 64.72.

HRMS Calcd for $C_{27}H_{36}N_3NaOPS_3$ $[M+H]^+$ 525.0565, found 568.1660.

S,S,S-Tributyl Phosphorotrithioate (**4u**)(*CAS Registry No.* 78-48-8)



Colorless liquid. Yield: 80%.

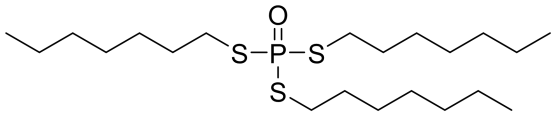
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 (quint, *J* = 7.2 Hz, 6H), 1.73 (quint, *J* = 7.5 Hz, 6H), 1.45 (dt, *J* = 7.4 Hz, 6H), 0.94 (t, *J* = 7.5 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 32.8 (d, *J* = 4.5 Hz), 32.6 (d, *J* = 5.4 Hz), 21.9, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 64.78.

HRMS Calcd for $C_{12}H_{27}NaOPS_3$ $[M+Na]^+$ 337.0854, found 337.0855.

S,S,S-Triheptyl Phosphorotrithioate (**4v**)



Colorless Wax. Yield: 82%.

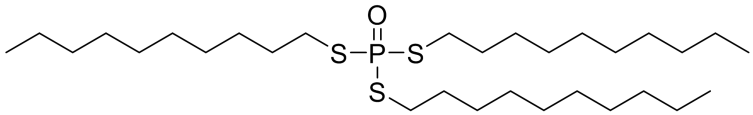
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (quint, *J* = 7.3 Hz, 6H), 1.74 (quint, *J* = 7.7 Hz, 6H), 1.41 – 1.38 (m, 6H), 1.32 – 1.25 (m, 18H), 0.89 – 0.87 (t, *J* = 6.9 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 33.2 (d, *J* = 3.3 Hz), 31.9, 30.7 (d, *J* = 5.6 Hz), 28.9, 28.8, 22.8, 14.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 64.85.

HRMS Calcd for $C_{21}H_{45}NaOPS_3$ $[M+Na]^+$ 463.2262, found 463.2261.

S,S,S-Tris(decyl) Phosphorotrithioate (**4w**)



Colorless Wax. Yield: 84%.

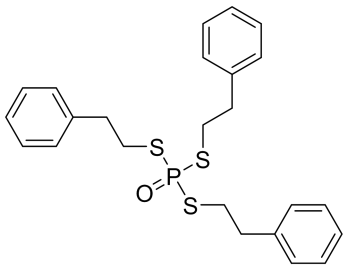
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.93 (quint, *J* = 7.3 Hz, 6H), 1.70 (quint, *J* = 7.4 Hz, 6H),1.38 – 1.35 (m, 6H), 1.27 – 1.22 (m, 36H) , 0.86 – 0.83 (t, *J* = 6.9 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 33.0 (d, *J* = 3.8 Hz), 32.0, 30.6 (d, *J* = 5.5 Hz), 29.7, 29.6, 29.4, 29.2, 28.8, 22.8, 14.2.

^{31}P NMR (162 MHz, $CDCl_3$): δ 64.63.

HRMS Calcd for $C_{30}H_{64}OPS_3$ $[M+H]^+$ 567.3851, found 567.3847.

S,S,S-Triphenethyl Phosphorotrithioate (**4x**) (*CAS Registry No.* 14974-77-7)



Colorless Wax. Yield: 73%.

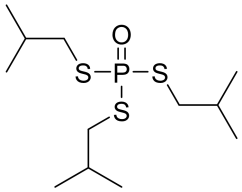
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48 – 3.41 (m, 3H), 1.77 – 1.68 (m, 6H), 1.45 (d, *J* = 6.9 Hz, 9H), 1.00 (t, *J* = 7.4 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 46.8 (q, *J* = 6.3 Hz), 31.5 (d, *J* = 5.6 Hz), 23.1 (q, *J* = 2.3 Hz), 11.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ 59.94.

HRMS Calcd for $C_{24}H_{28}OPS_3$ $[M+H]^+$ 459.1034, found 459.1033.

S,S,S-Triisobutyl Phosphorotrithioate (**4y**) (*CAS Registry No.* 108751-77-5)



Colorless Wax. Yield: 75%.

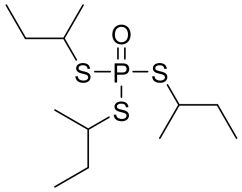
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 – 2.81 (dd, *J* = 14.2 Hz, *J* = 6.8 Hz, 6H), 1.99 – 1.92 (m, 3H), 0.98 (d, *J* = 6.8 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 41.3 (d, *J* = 4.4 Hz), 29.5 (d, *J* = 4.6 Hz), 21.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ 65.39.

HRMS Calcd for $C_{12}H_{27}NaOPS_3$ $[M+Na]^+$ 337.0854, found 337.0878.

S,S,S-Tri-*sec*-butyl Phosphorotrithioate (**4z**) (*CAS Registry No.* 78788-15-5)



Colorless Wax. Yield: 67%.

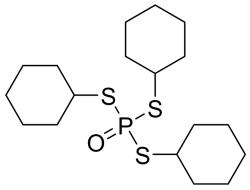
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48 – 3.41 (m, 3H), 1.77 – 1.68 (m, 6H), 1.45 (d, *J* = 6.9 Hz, 9H), 1.00 (t, *J* = 7.4 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 46.8 (q, *J* = 6.3 Hz), 31.5 (d, *J* = 5.6 Hz), 23.1 (q, *J* = 2.3 Hz), 11.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ 59.94.

HRMS Calcd for $C_{12}H_{27}NaOPS_3$ $[M+Na]^+$ 337.0854, found 337.0863.

S,S,S-Tricyclohexyl Phosphorotrithioate (**4aa**) (*CAS Registry No.* 78788-17-7)



White solid. Yield: 72%.

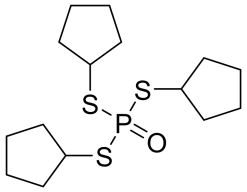
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.47 – 3.41 (m, 3H), 2.14 – 2.11 (m, 6H),1.74 – 1.72 (m, 6H), 1.58 – 1.55 (m, 9H), 1.45 – 1.38 (m, 6H), 1.30 – 1.24 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 48.0 (d, *J* = 4.3 Hz), 35.5 (d, *J* = 4.5 Hz), 26.1, 25.5.

^{31}P NMR (162 MHz, $CDCl_3$): δ 60.17.

HRMS Calcd for $C_{18}H_{33}NaOPS_3$ $[M+Na]^+$ 415.1323, found 415.1324.

S,S,S-Tricyclopentyl Phosphorotrithioate (**4ab**)



White solid. Yield: 65%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69 – 3.61 (m, 3H), 2.17 – 2.16 (m, 6H), 1.73 – 1.72 (m, 12H), 1.59 – 1.58 (m, 6H).

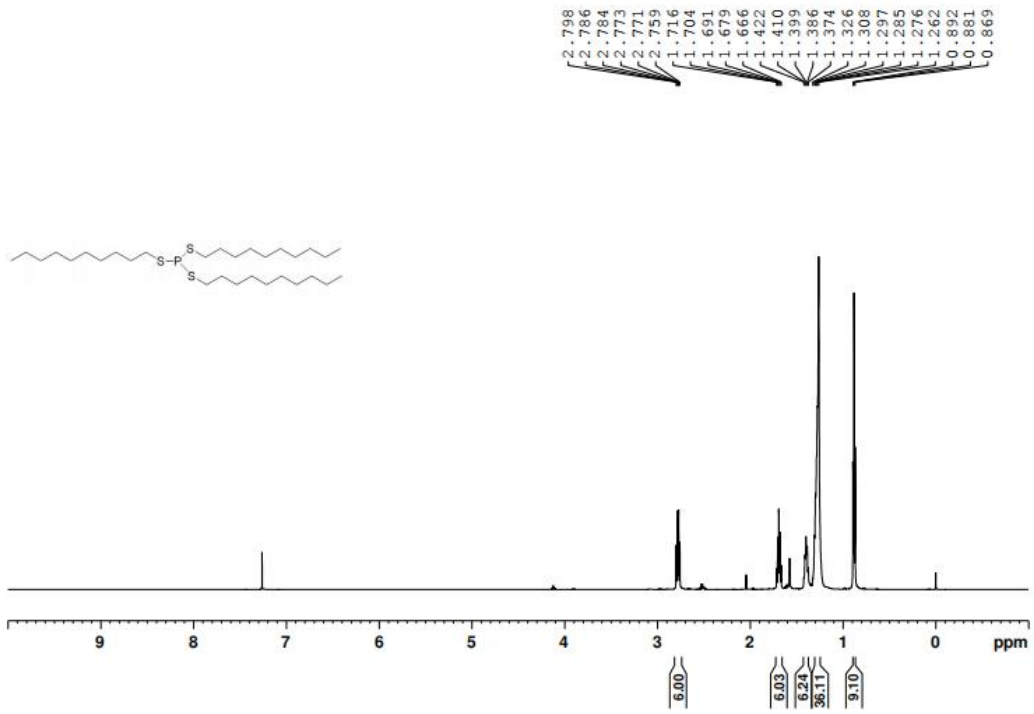
^{13}C NMR (100 MHz, $CDCl_3$): δ 47.0 (d, *J* = 3.7 Hz), 35.4 (d, *J* = 5.4 Hz), 24.5.

^{31}P NMR (162 MHz, $CDCl_3$): δ 60.13.

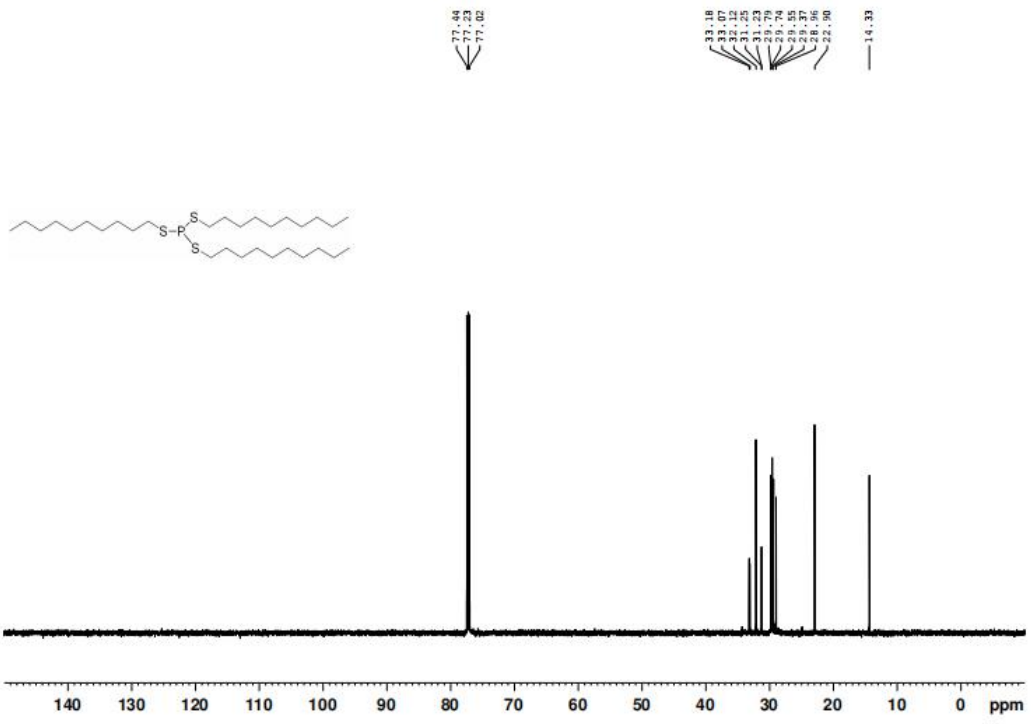
HRMS Calcd for $C_{15}H_{27}NaOPS_3$ $[M+Na]^+$ 373.0854, found 373.0859.

^{1}H、^{13}C、^{31}P and ^{19}F NMR spectra

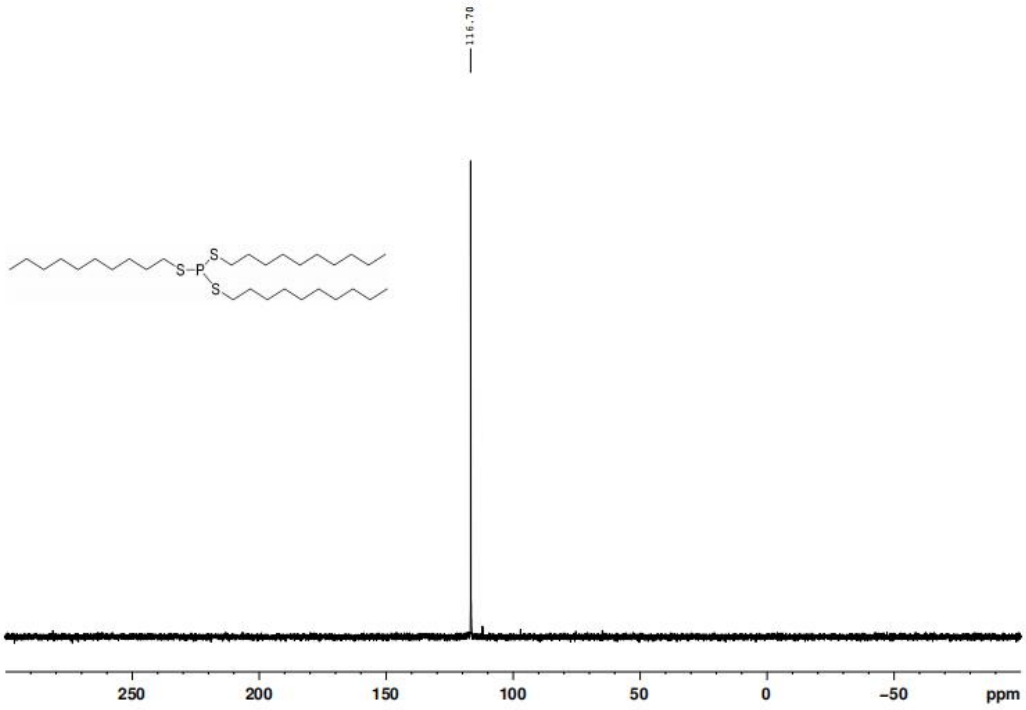
3a



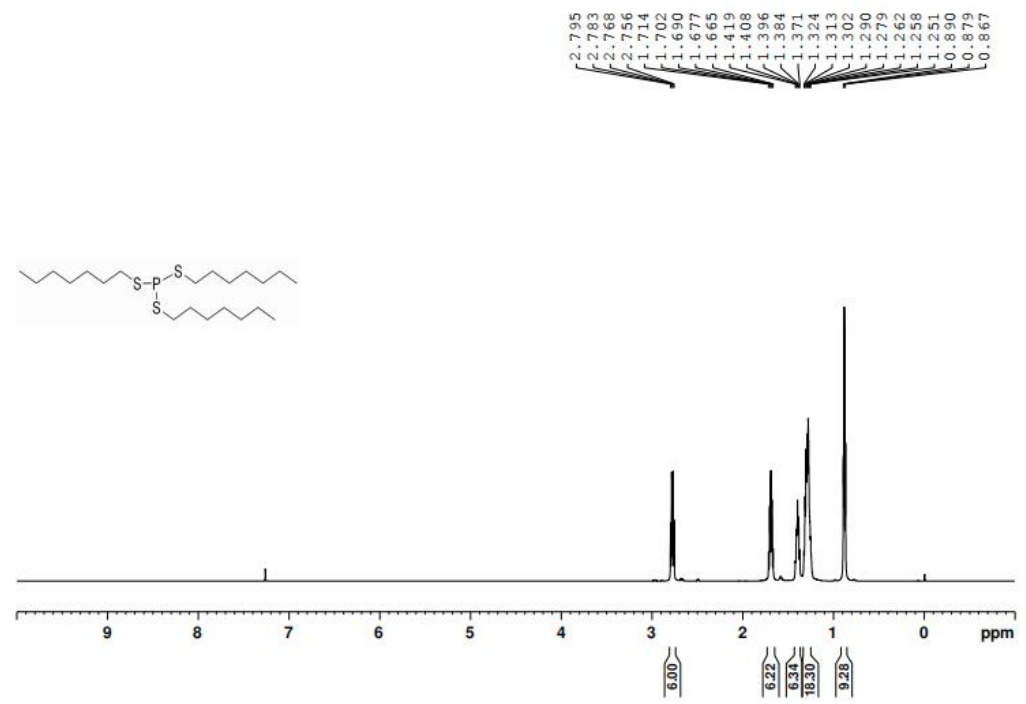
3a



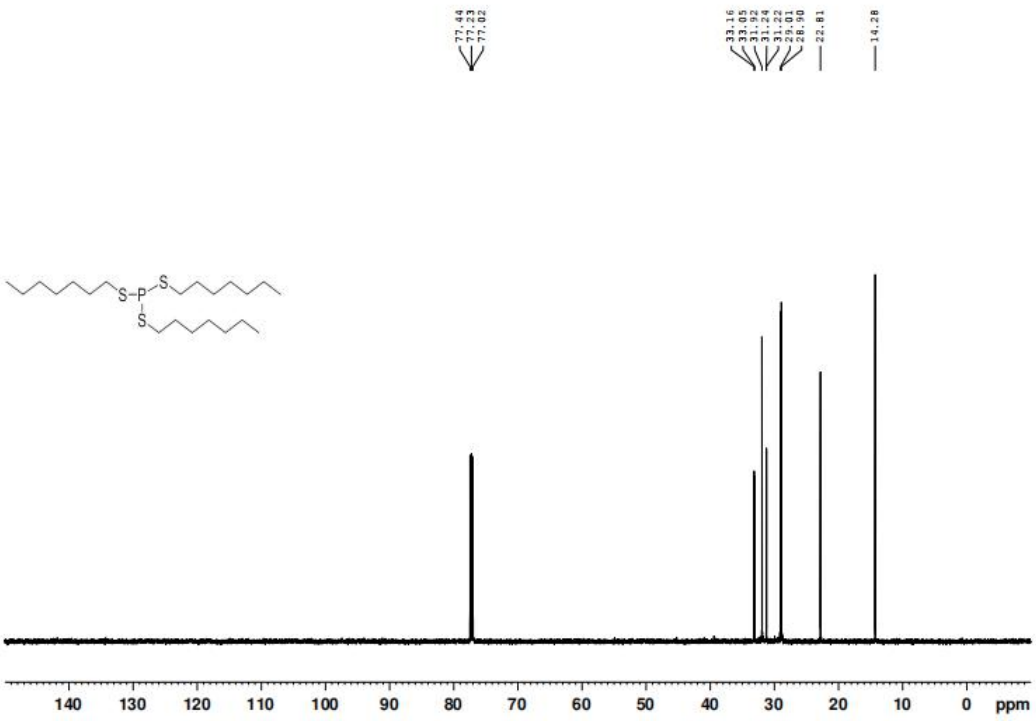
3a


116.70
250
200
150
100
50
0
-50
ppm

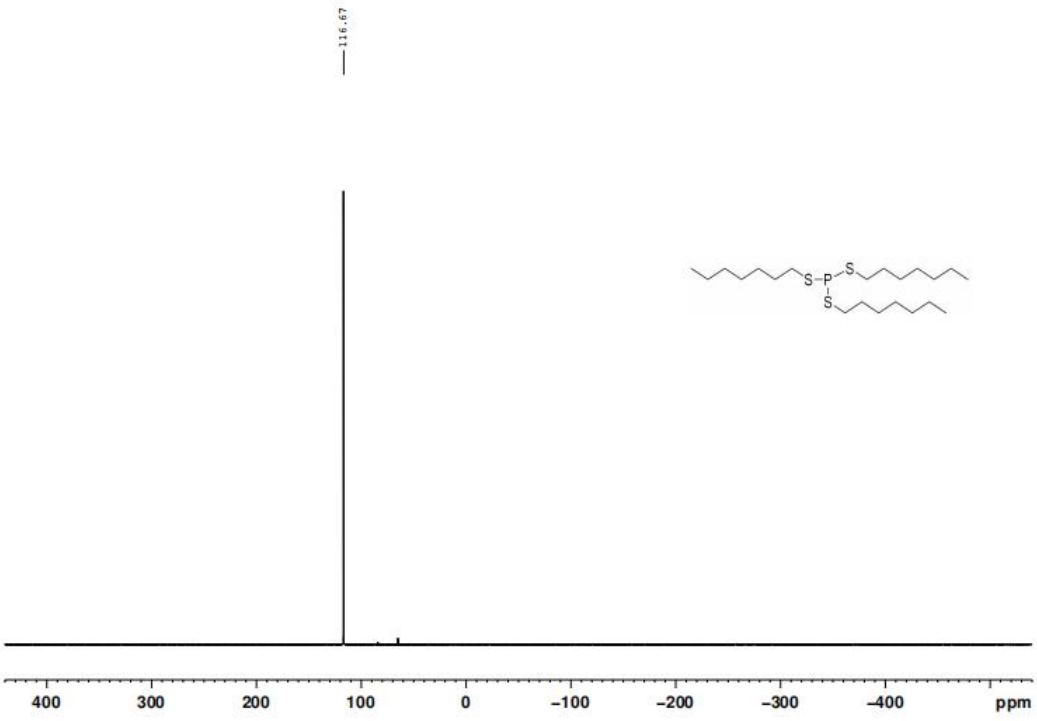
3b


2.795
2.783
2.768
2.756
1.714
1.702
1.690
1.677
1.665
1.419
1.408
1.396
1.384
1.371
1.324
1.313
1.302
1.290
1.279
1.262
1.258
1.251
0.890
0.879
0.867
9
8
7
6
5
4
3
2
1
0
ppm
6.00
6.22
6.34
18.30
9.28

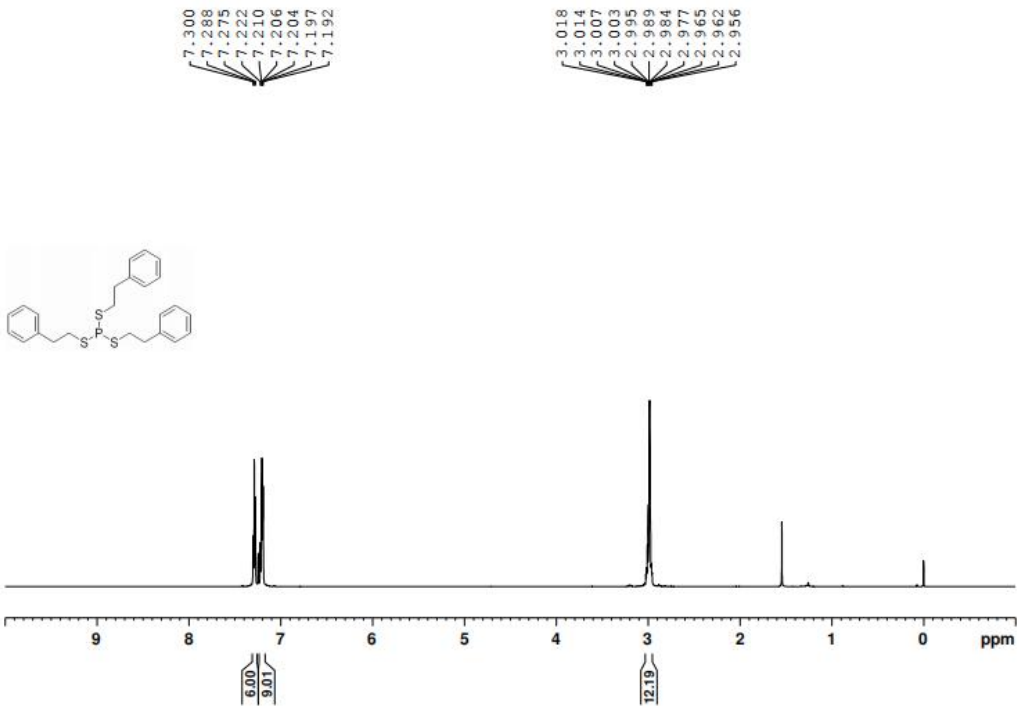
3b


77.44
77.23
77.02
33.16
33.05
31.92
31.24
31.22
29.01
28.90
22.81
14.28
S
P
S
S
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

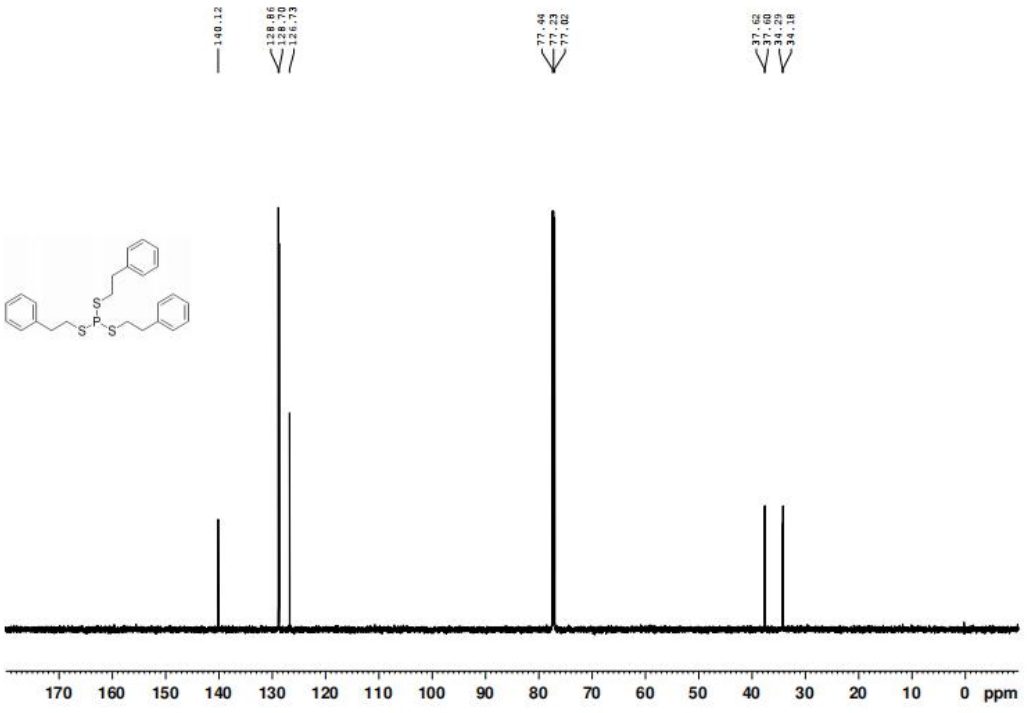
3b


116.67
S
P
S
S
400
300
200
100
0
−100
−200
−300
−400
ppm

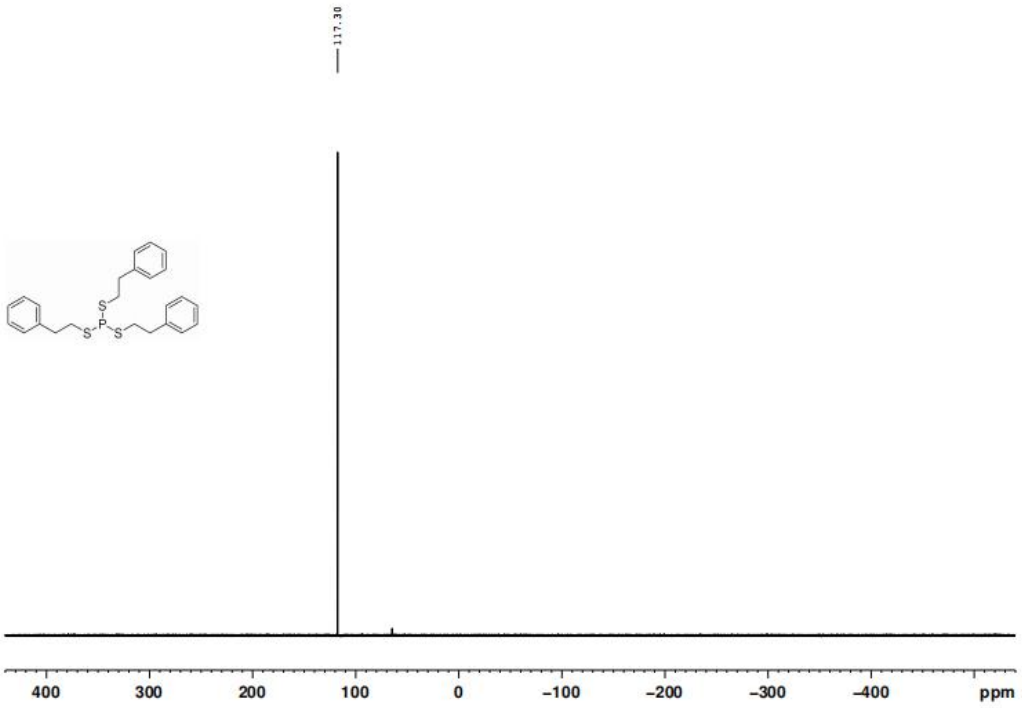
3c


7.300
7.288
7.275
7.222
7.210
7.206
7.204
7.197
7.192
3.018
3.014
3.007
3.003
2.995
2.989
2.984
2.977
2.965
2.962
2.956
9
8
7
6
5
4
3
2
1
0
ppm
6.00
9.01
12.19

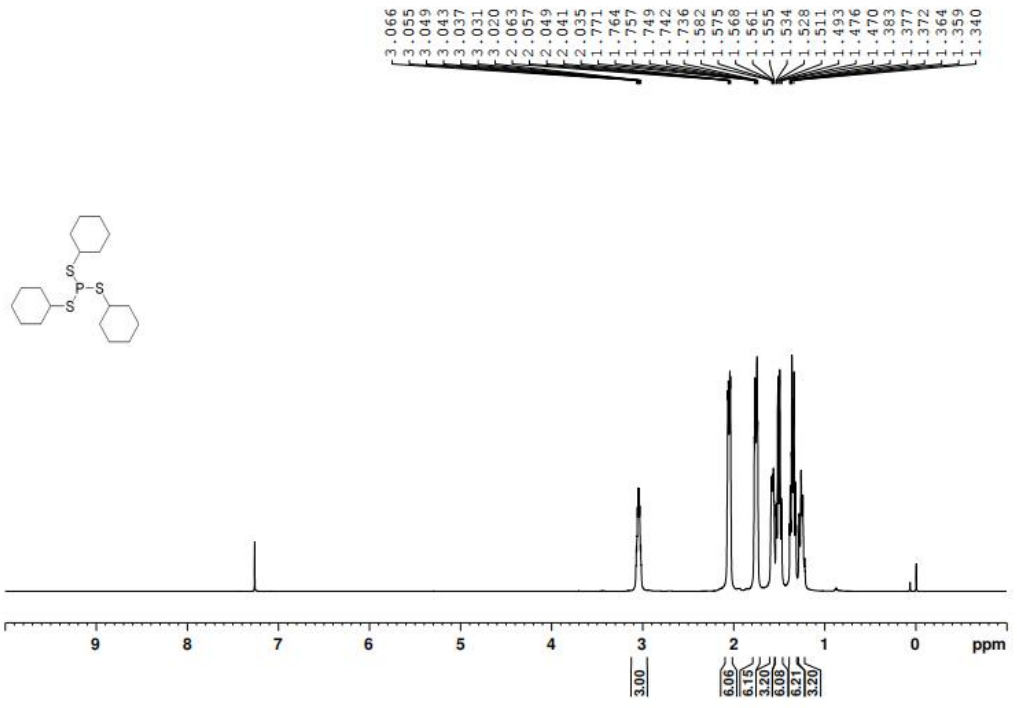
3c


140.12
128.86
128.70
126.73
77.44
77.23
77.02
37.62
37.40
34.29
34.18
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

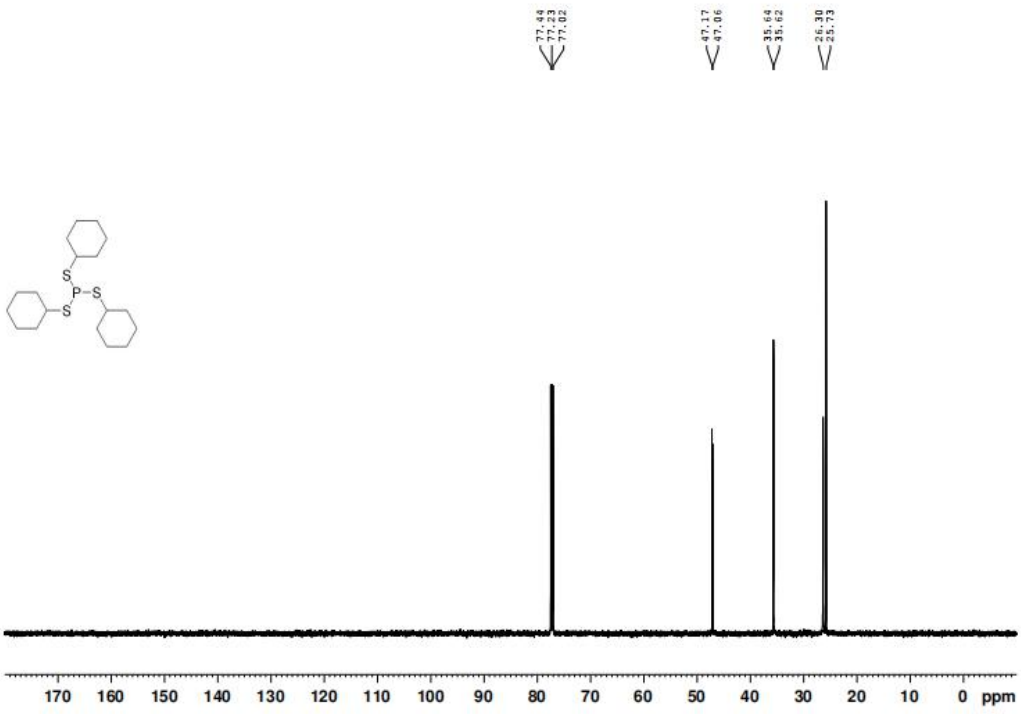
3c


117.30
400
300
200
100
0
−100
−200
−300
−400
ppm

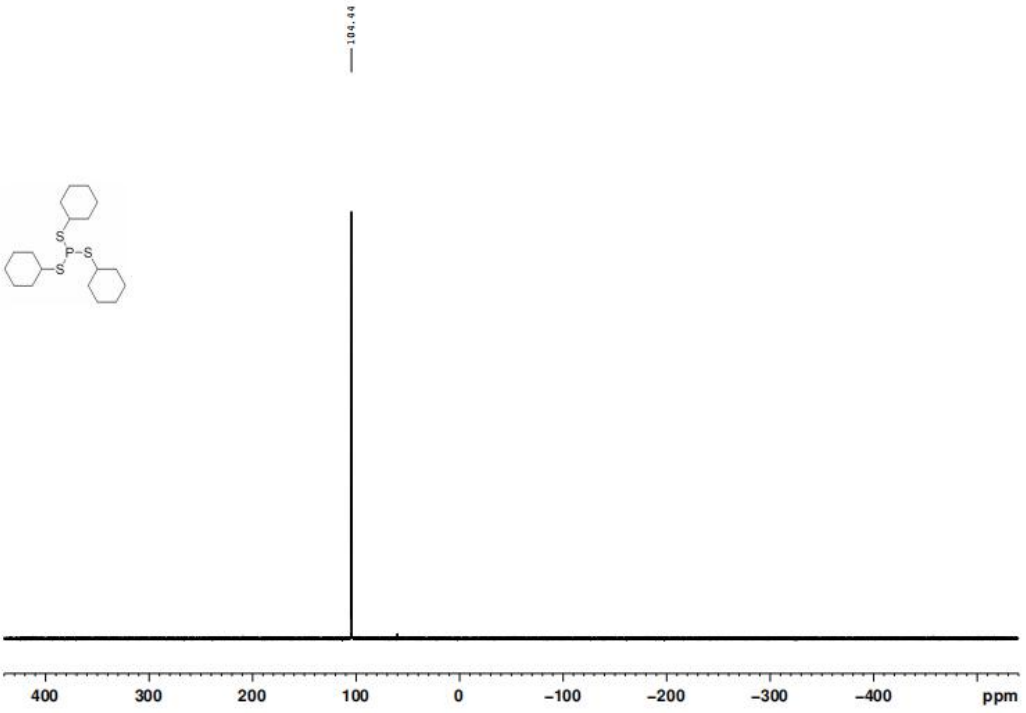
3d


3.066
3.055
3.049
3.043
3.037
3.031
3.020
2.063
2.057
2.049
2.041
2.035
1.771
1.764
1.757
1.749
1.742
1.736
1.582
1.575
1.568
1.561
1.555
1.534
1.528
1.511
1.493
1.476
1.470
1.383
1.377
1.372
1.364
1.359
1.340
9
8
7
6
5
4
3
2
1
0
ppm
3.00
6.06
6.15
3.20
6.08
6.21
3.20

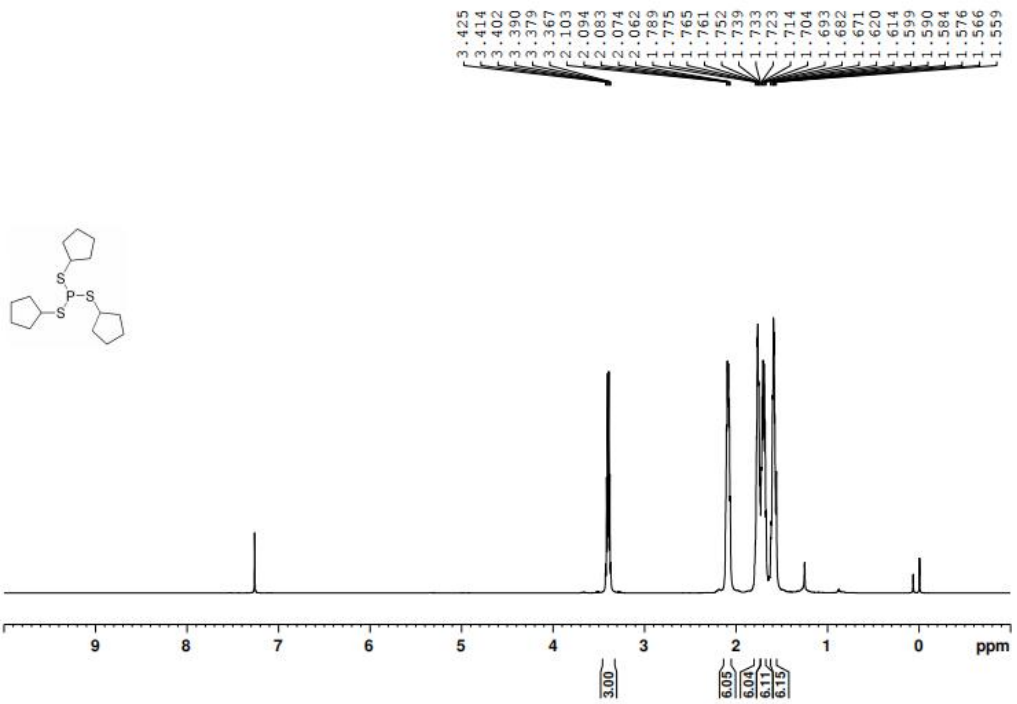
3d


77.44
77.23
77.02
47.17
47.06
35.64
35.62
26.30
25.73
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

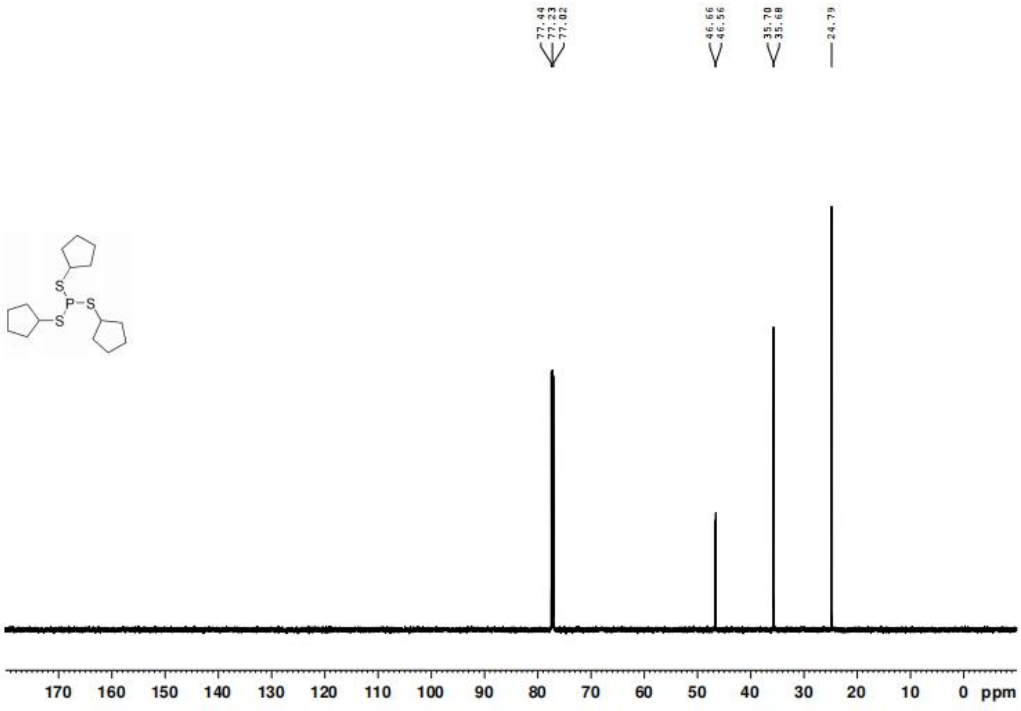
3d


104.44
400 300 200 100 0 −100 −200 −300 −400 ppm

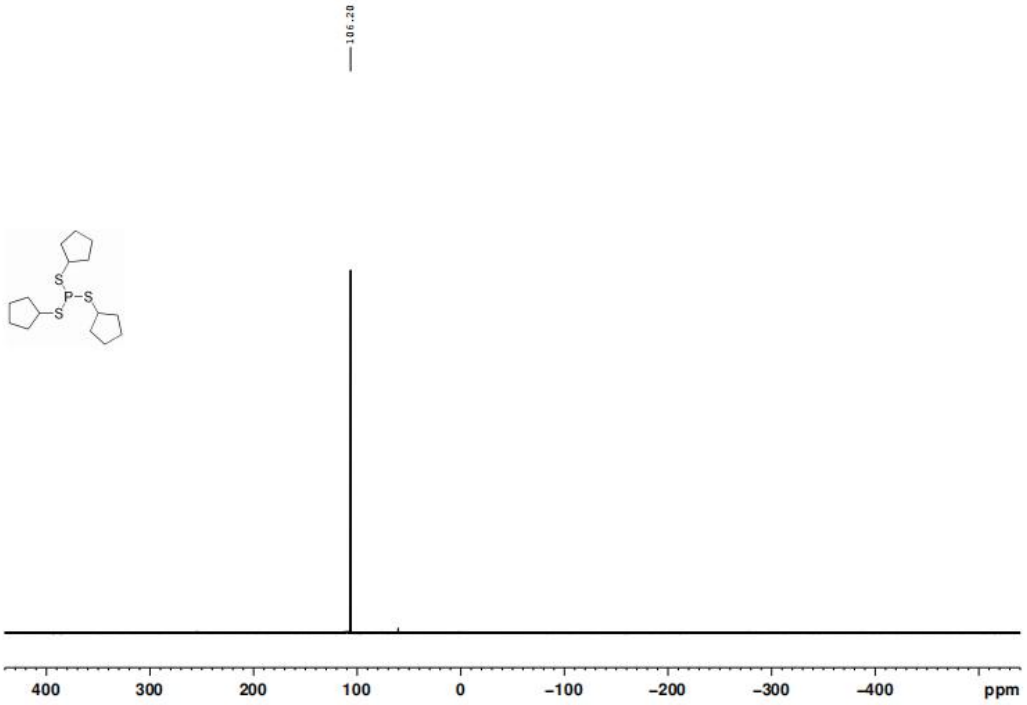
3e


3.425
3.414
3.402
3.390
3.379
3.367
2.103
2.094
2.083
2.074
2.062
1.789
1.775
1.765
1.761
1.752
1.739
1.733
1.723
1.714
1.704
1.693
1.682
1.671
1.620
1.614
1.599
1.590
1.584
1.576
1.566
1.559
S
P
S
S
9
8
7
6
5
4
3
2
1
0
ppm
3.00
6.05
6.04
6.11
6.15

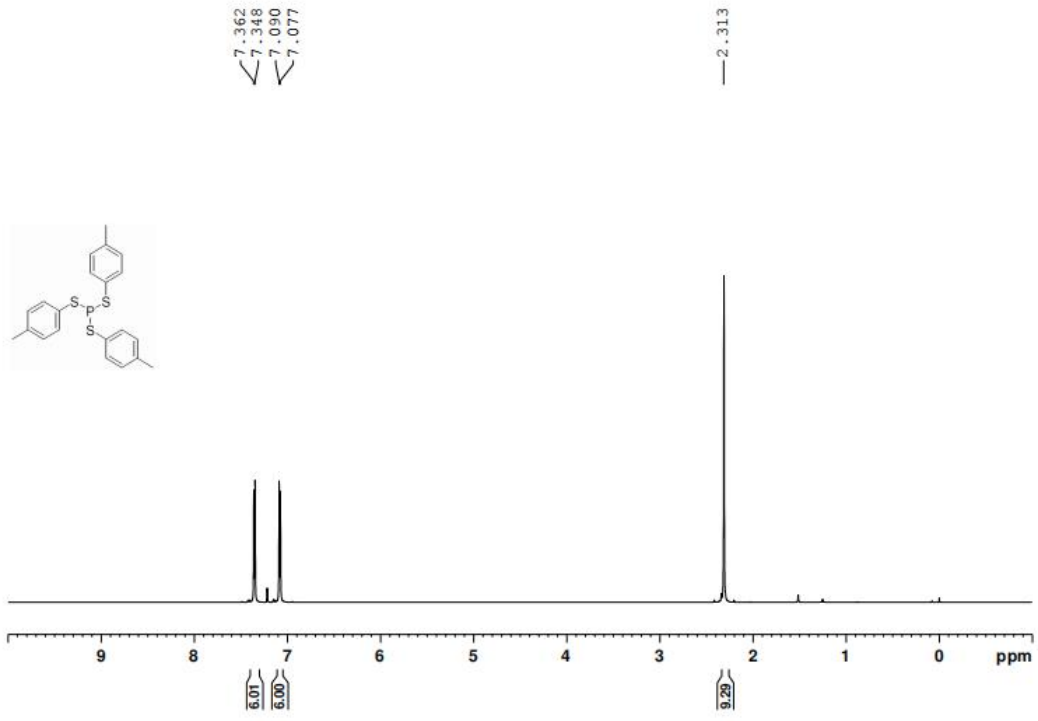
3e


77.44
77.23
77.02
46.66
46.56
35.70
35.68
24.79
S
P
S
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

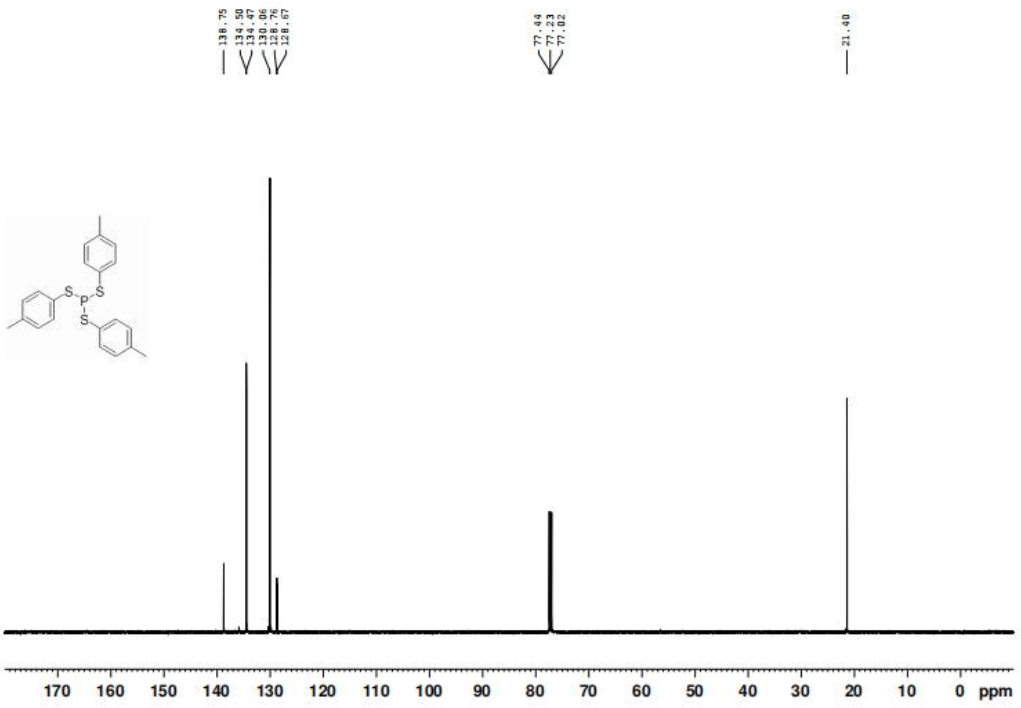
3e


106.20
400
300
200
100
0
−100
−200
−300
−400
ppm

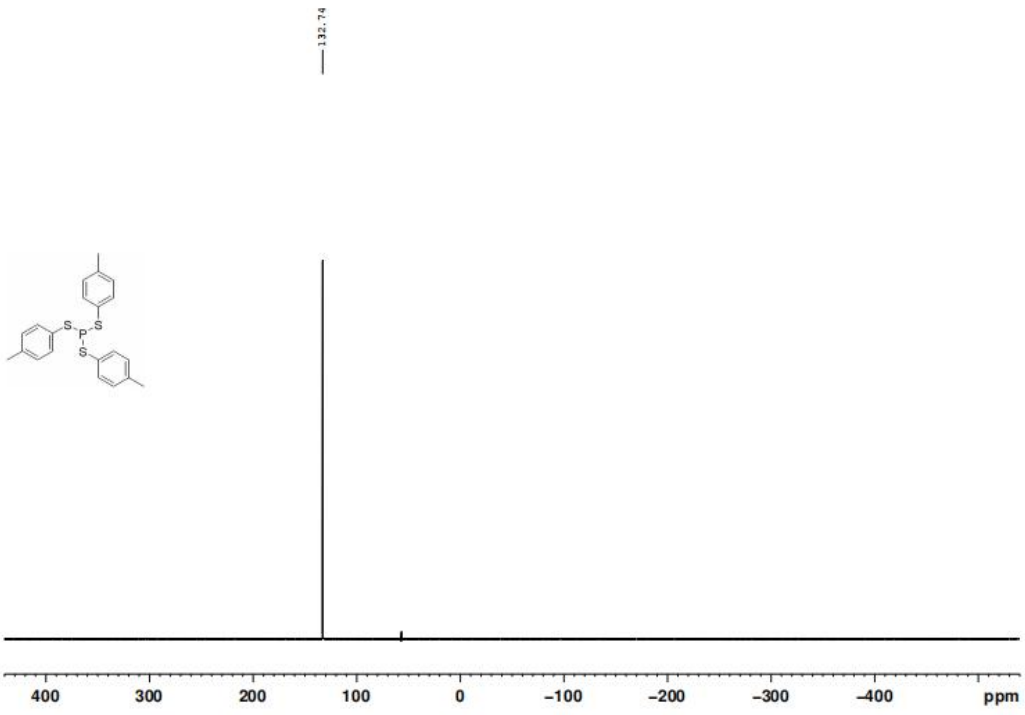
3f


7.362
7.348
7.090
7.077
2.313
9
8
7
6
5
4
3
2
1
0
ppm
6.01
6.00
9.29

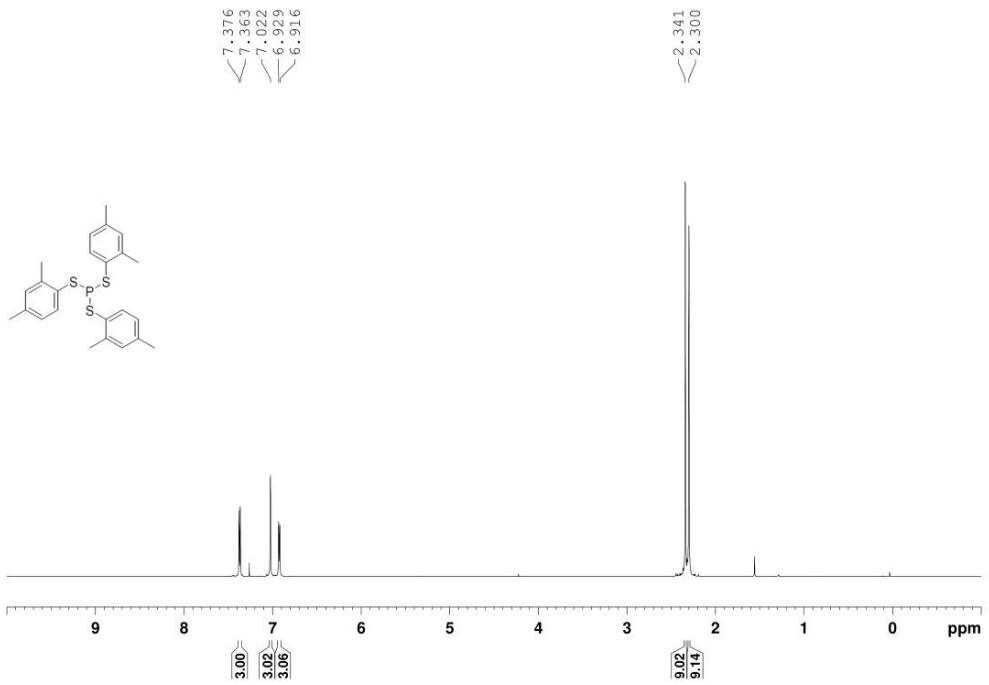
3f


138.75
134.50
134.47
130.06
128.76
128.67
77.44
77.23
77.02
21.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

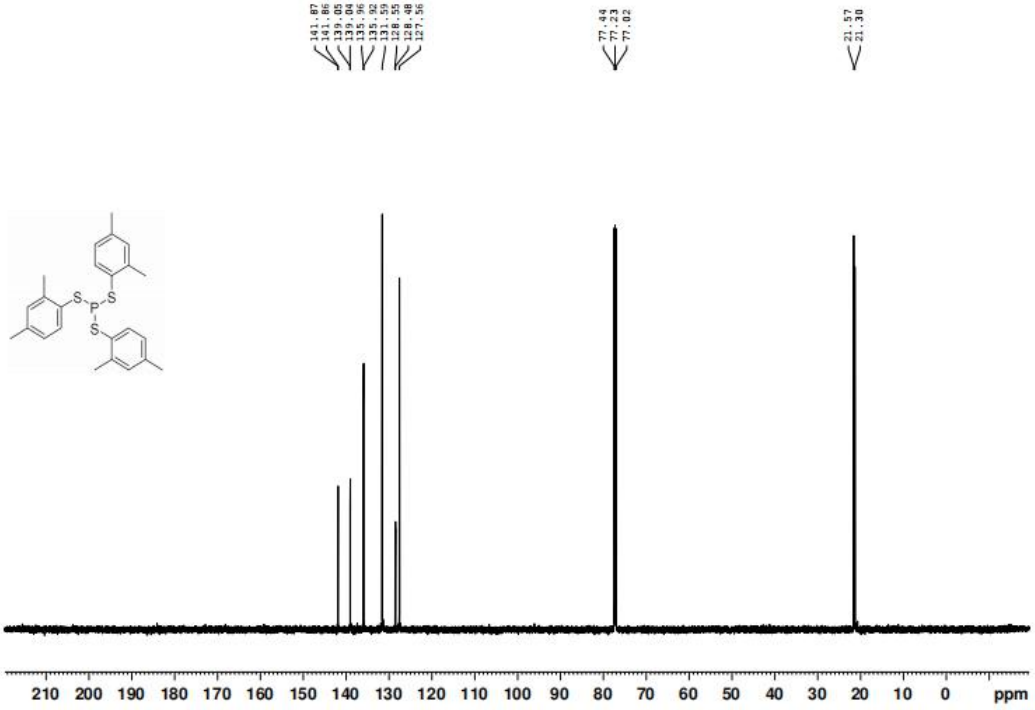
3f


132.74
400 300 200 100 0 -100 -200 -300 -400 ppm

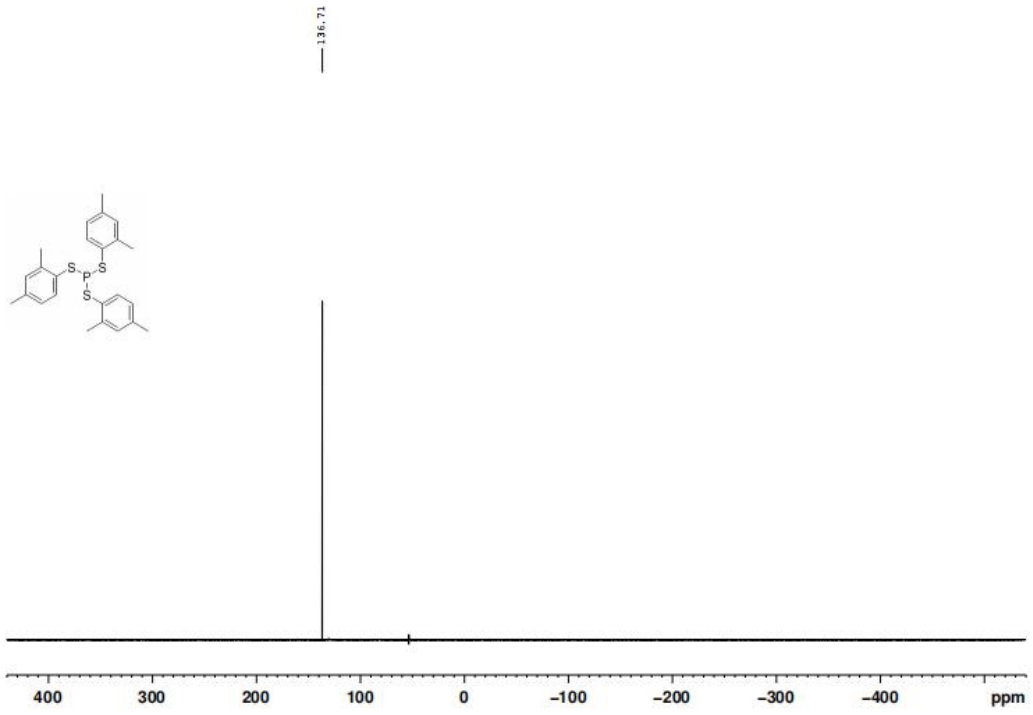
3g


7.376
7.363
7.022
6.929
6.916
2.341
2.300
9
8
7
6
5
4
3
2
1
0
ppm
3.00
3.02
3.06
9.02
9.14

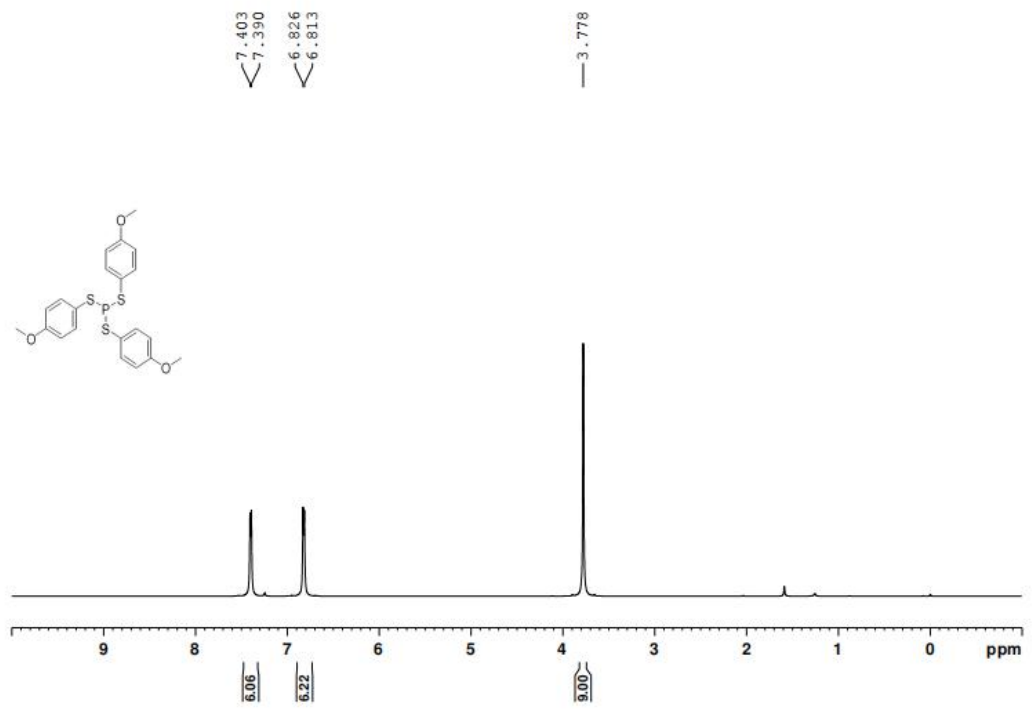
3g


141.87
141.86
139.05
139.04
135.96
135.92
131.59
128.55
128.48
127.56
77.44
77.23
77.02
21.57
21.30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

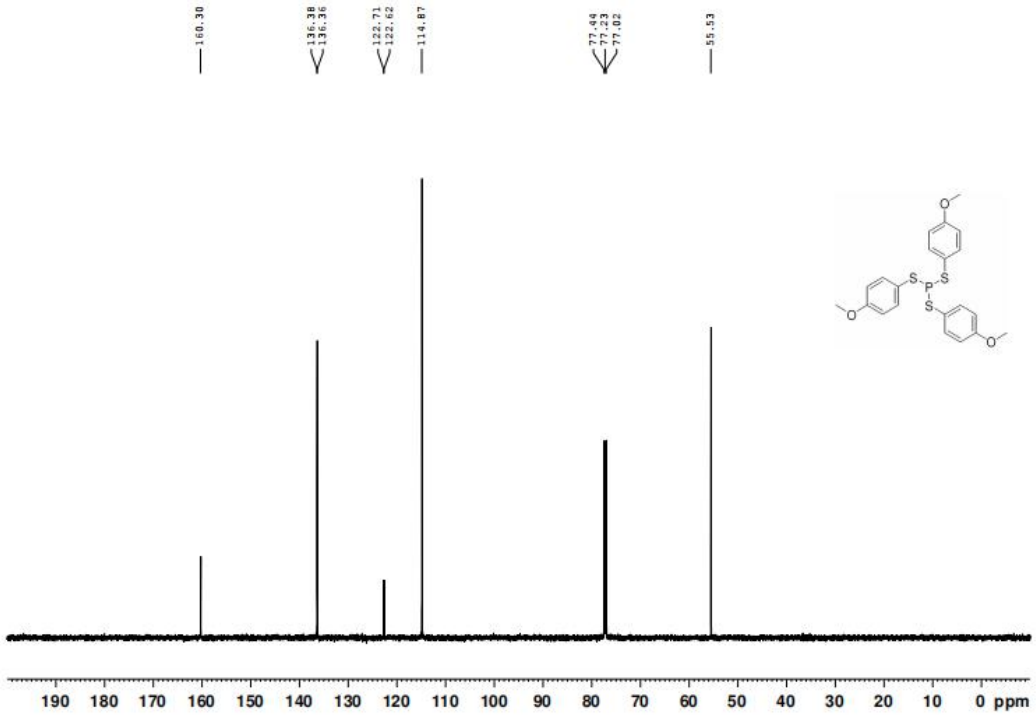
3g


136.71
400
300
200
100
0
−100
−200
−300
−400
ppm

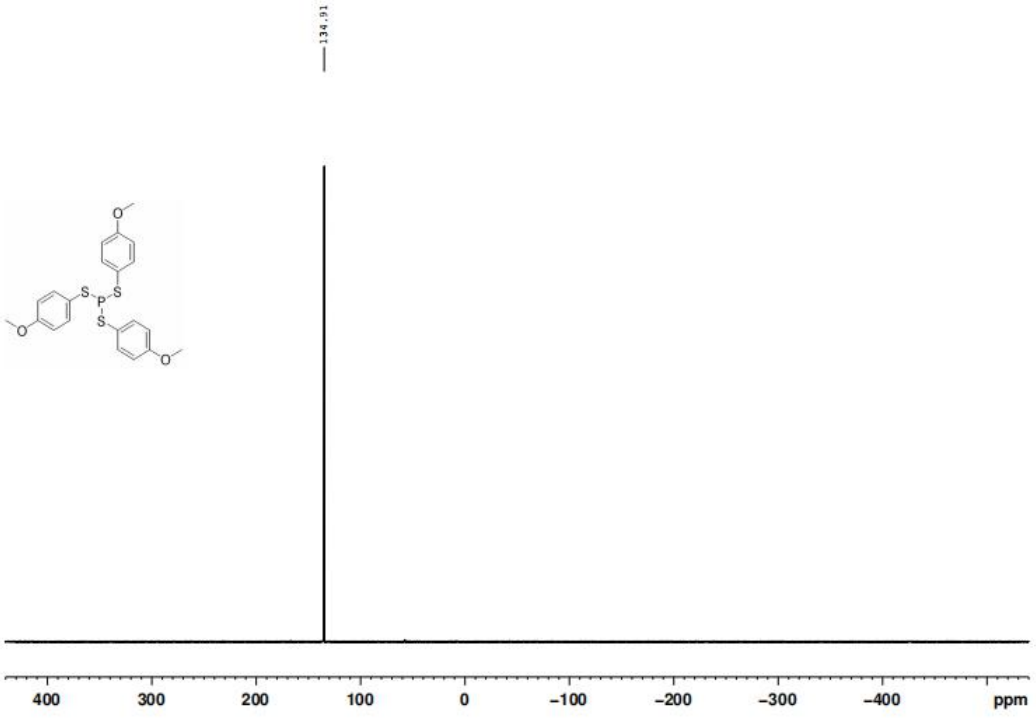
3h


7.403
7.390
6.826
6.813
3.778
9
8
7
6
5
4
3
2
1
0
ppm
6.06
6.22
9.00

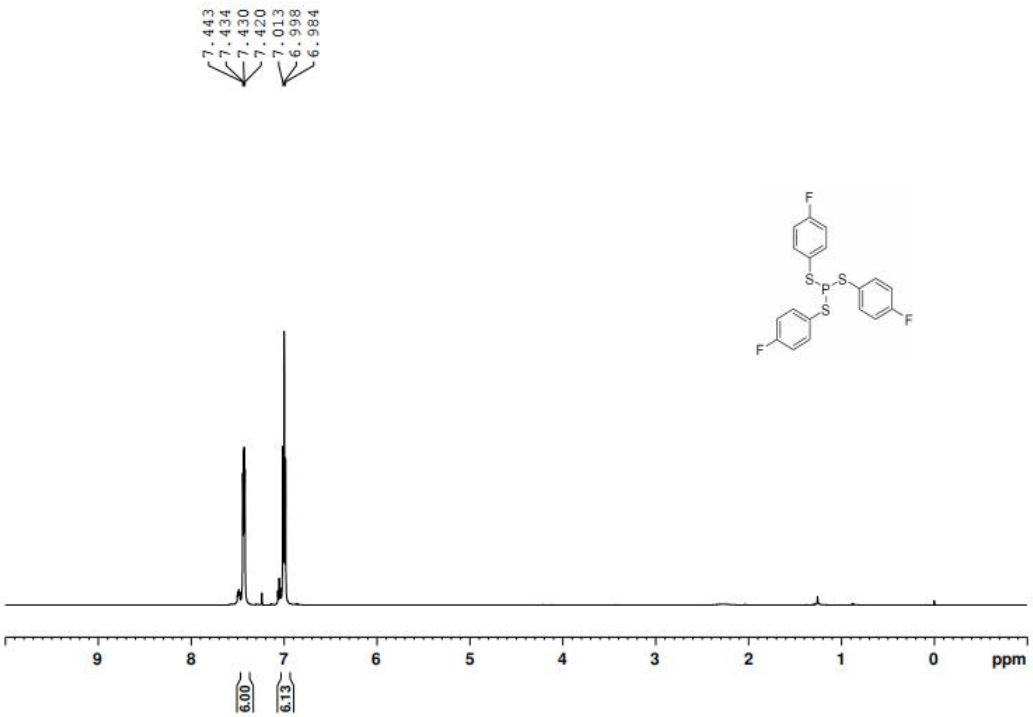
3h


160.30
136.38
136.36
122.71
122.62
114.87
77.44
77.23
77.02
55.53
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

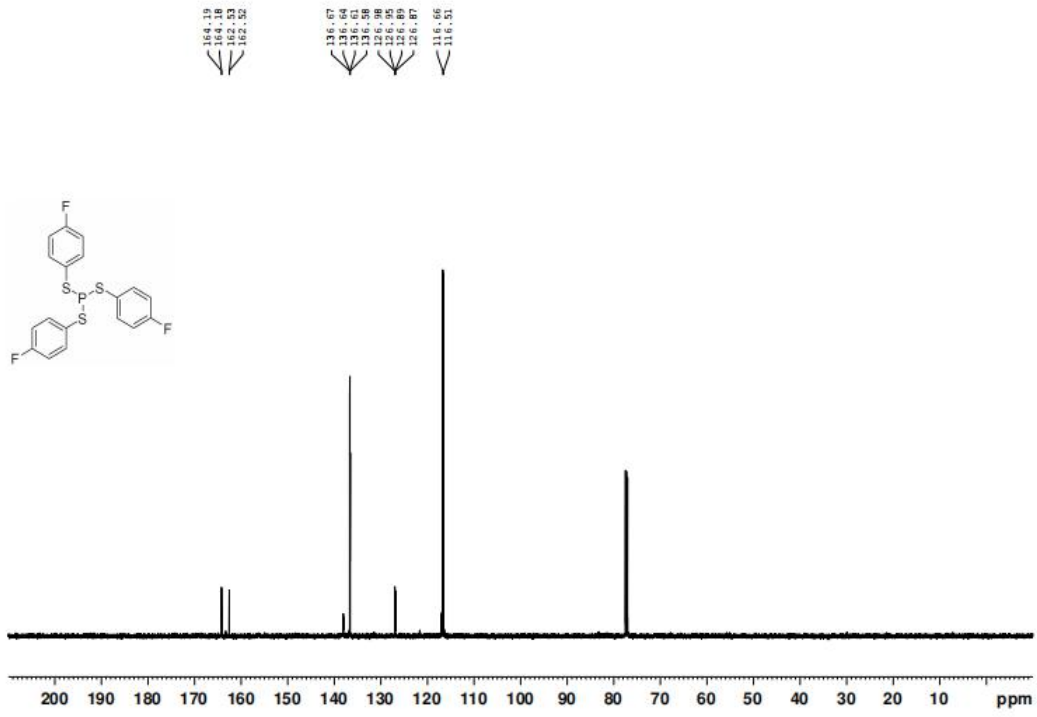
3h


134.91
400 300 200 100 0 -100 -200 -300 -400 ppm

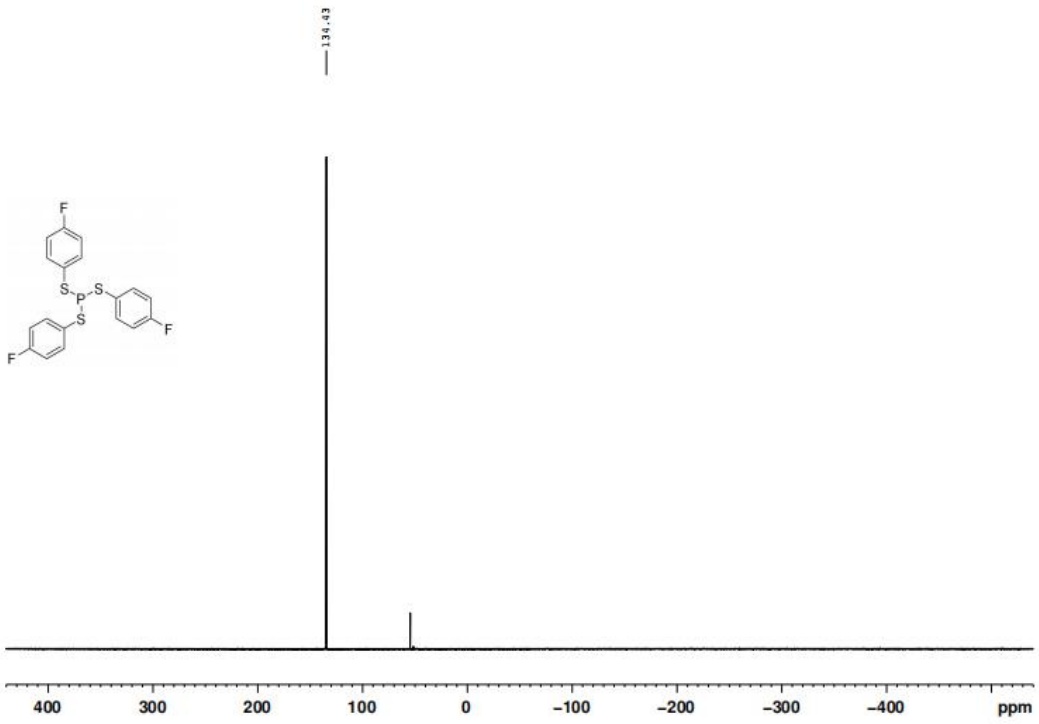
3i


7.443
7.434
7.430
7.420
7.013
6.998
6.984
F
S
P
S
S
F
F
9
8
7
6
5
4
3
2
1
0
ppm
6.00
6.13

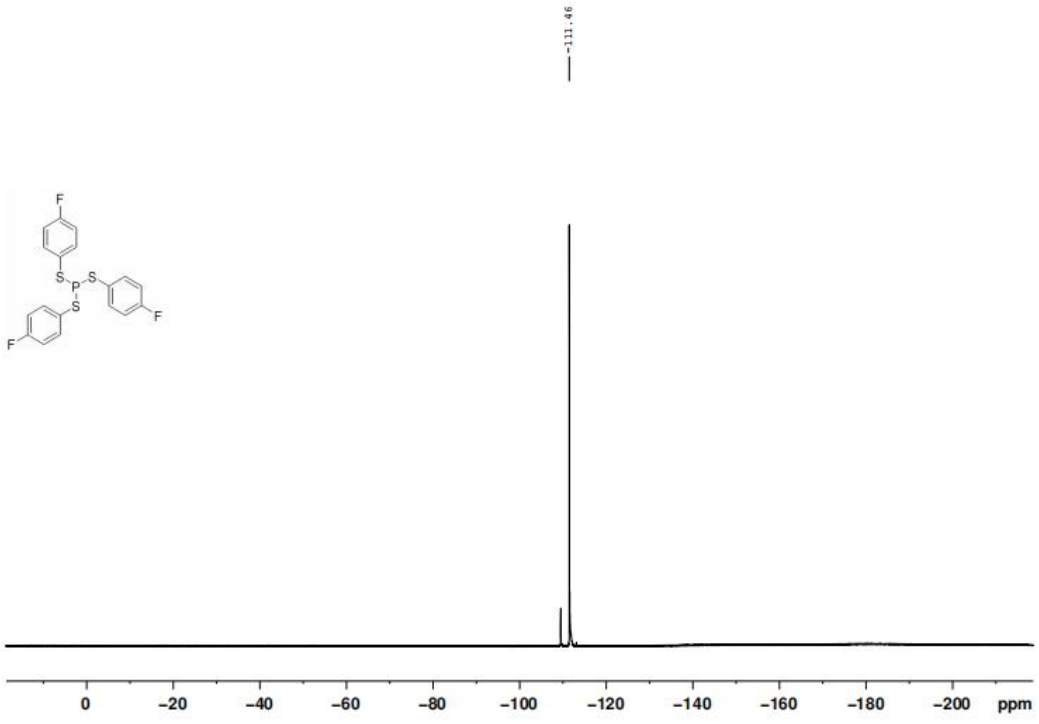
3i


164.19
164.18
162.53
162.52
136.67
136.64
136.61
136.58
126.98
126.95
126.89
126.87
116.66
116.51
F
S
P
S
S
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

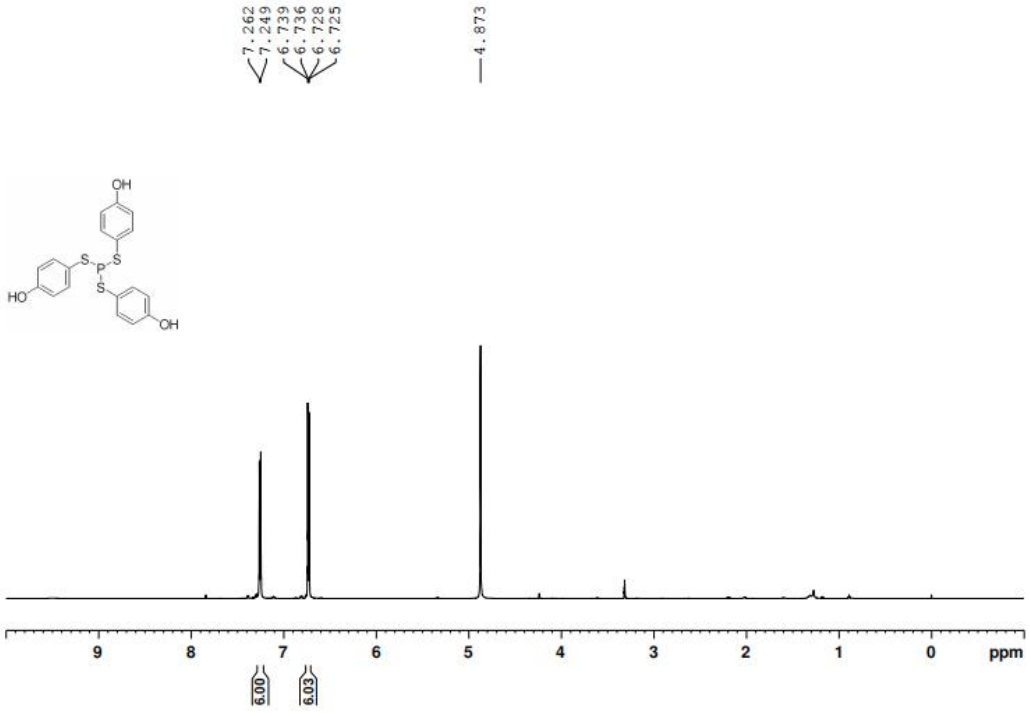
3i


134.43
F
S
P
S
S
F
F
400
300
200
100
0
−100
−200
−300
−400
ppm

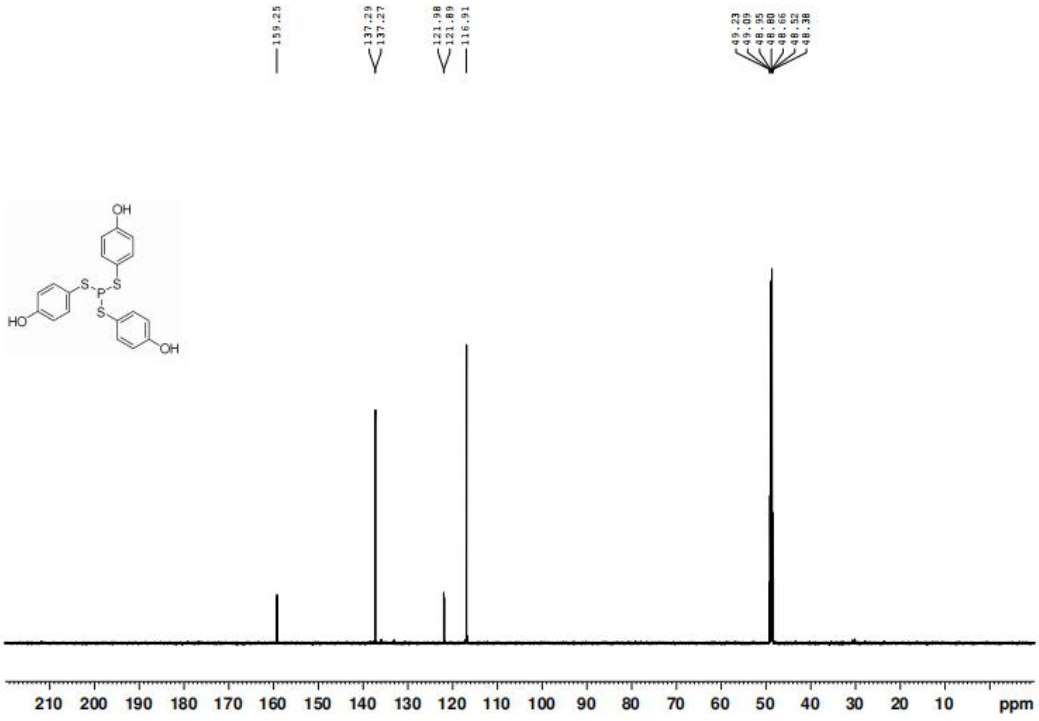
3i


−111.46
F
S
P
S
S
F
F
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm

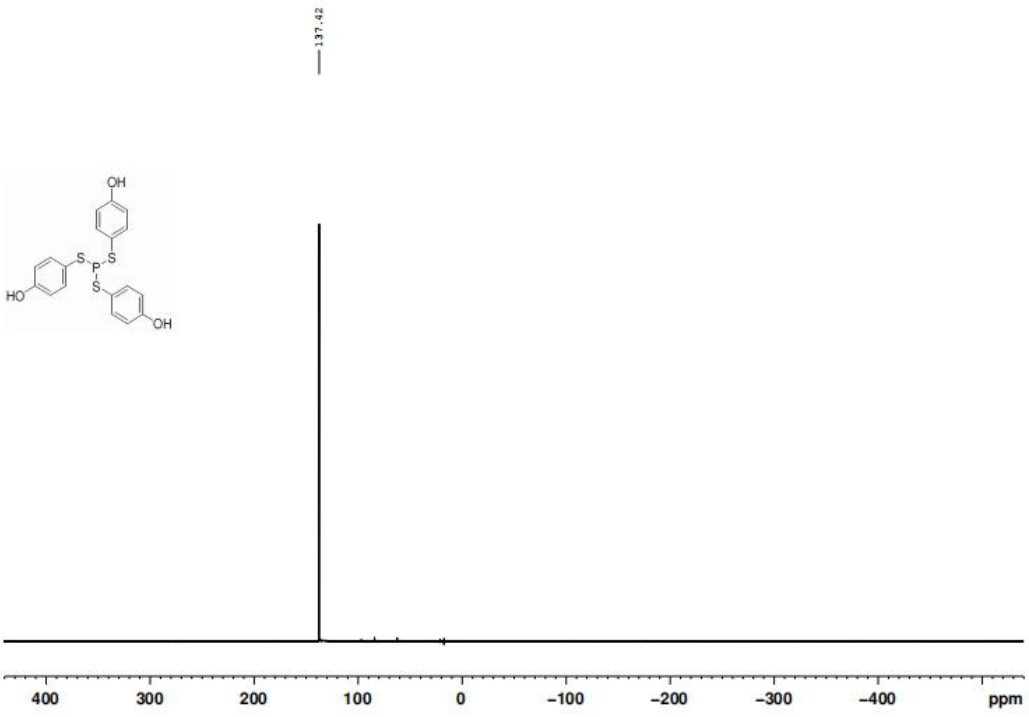
3j


7.262
7.249
6.739
6.736
6.728
6.725
4.873
OH
HO
OH
9
8
7
6
5
4
3
2
1
0
ppm
6.00
6.03

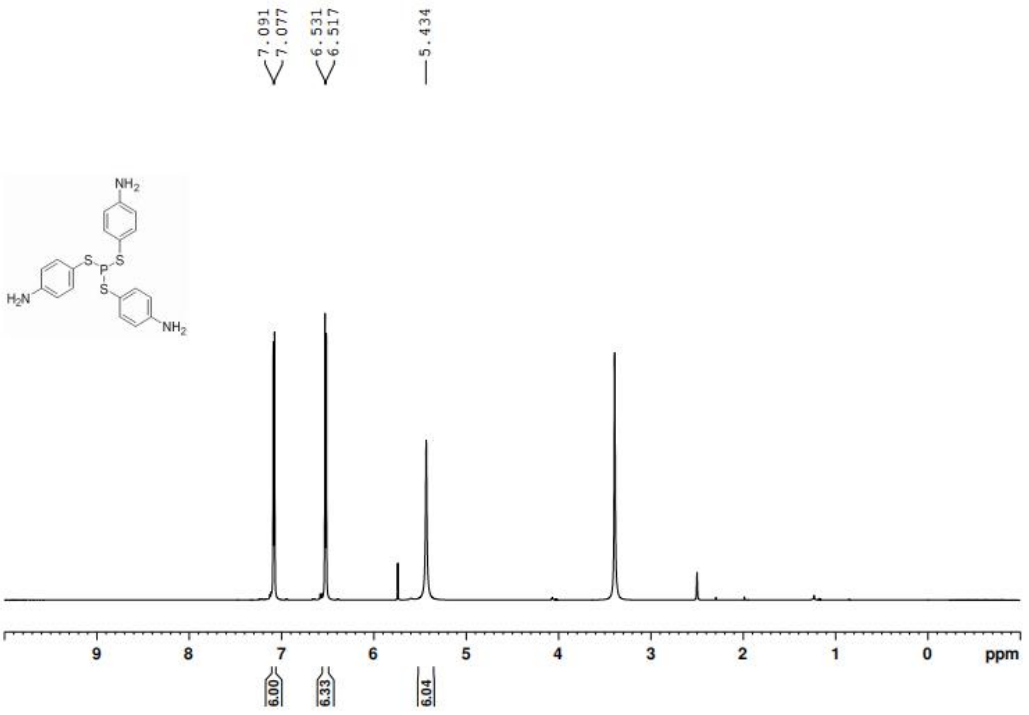
3j


159.25
137.29
137.27
121.98
121.89
116.91
49.23
49.09
48.95
48.80
48.66
48.52
48.38
OH
HO
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

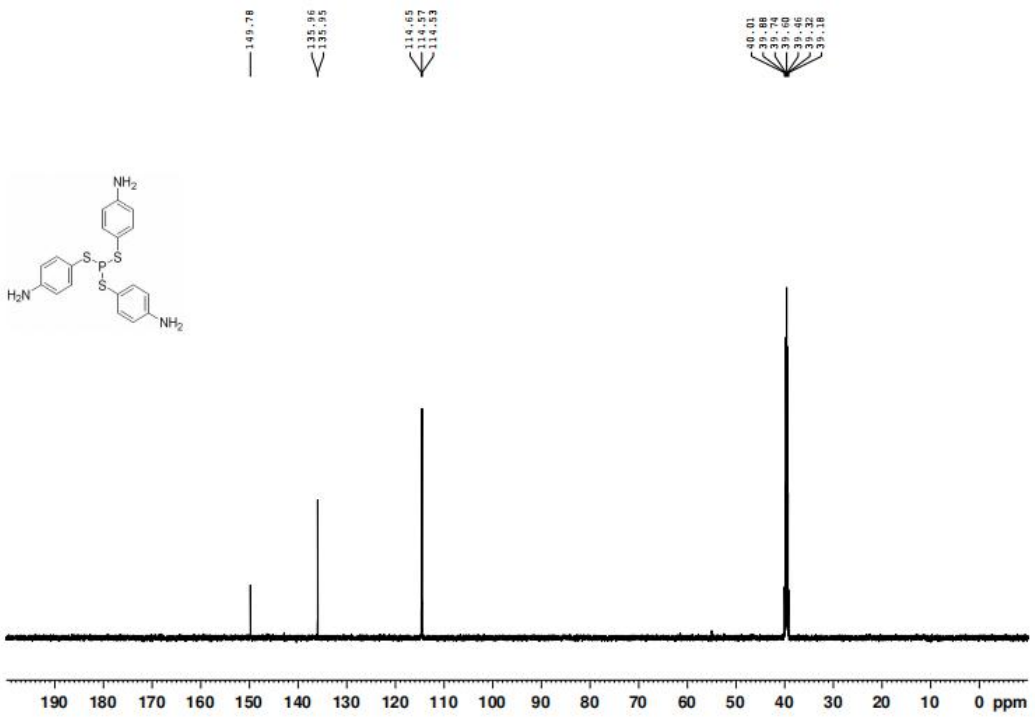
3j


137.42
OH
HO
OH
400
300
200
100
0
−100
−200
−300
−400
ppm

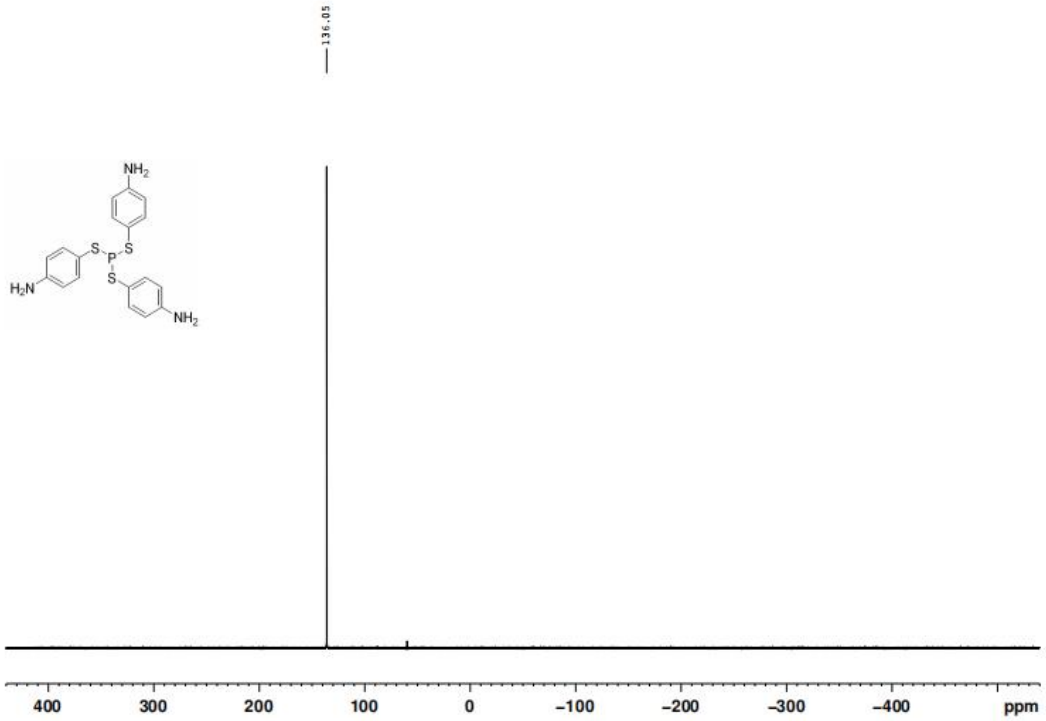
3k


7.091
7.077
6.531
6.517
5.434
NH2
H2N
NH2
9
8
7
6
5
4
3
2
1
0
ppm
6.00
6.33
6.04

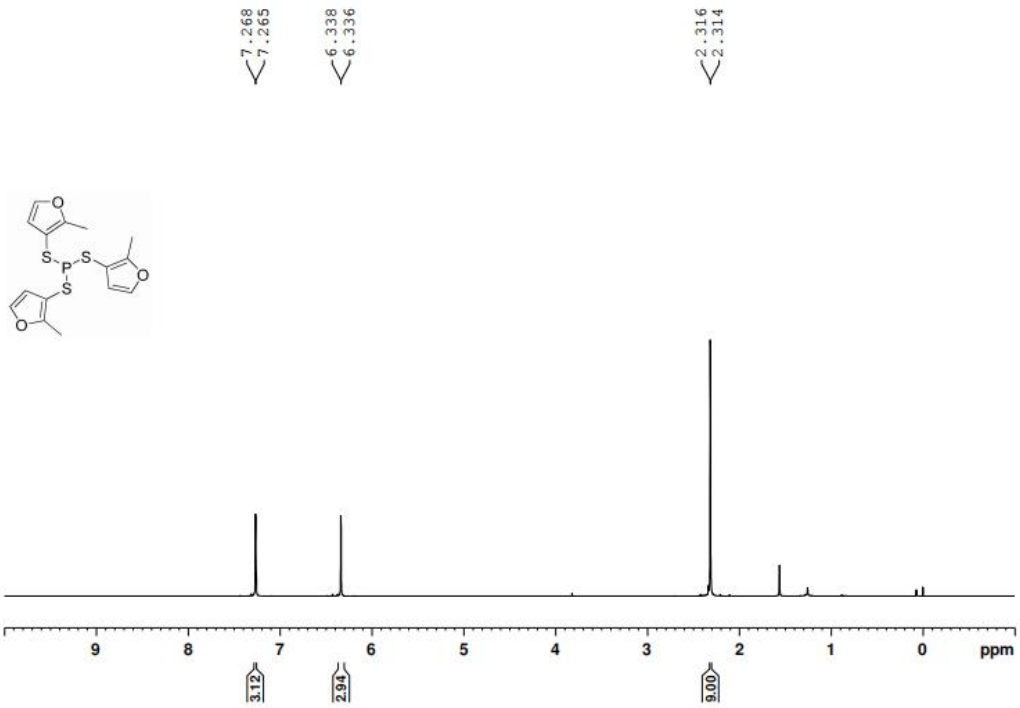
3k


149.78
135.96
135.95
114.65
114.57
114.53
40.01
39.88
39.74
39.60
39.46
39.32
39.18
NH2
S
P
S
S
H2N
NH2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

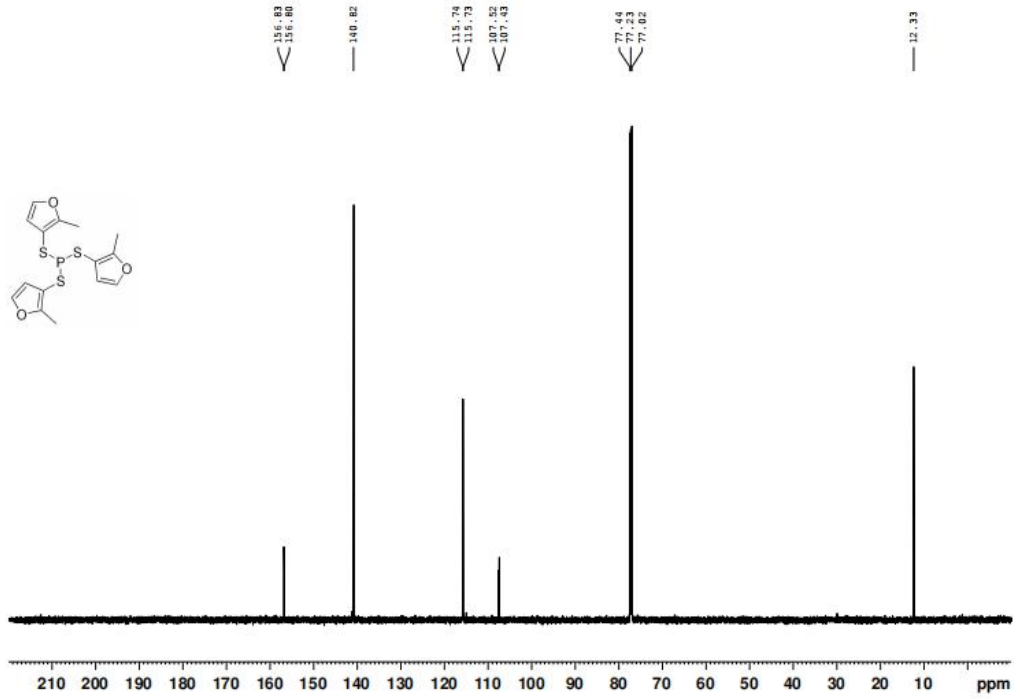
3k


136.05
NH2
S
P
S
S
H2N
NH2
400 300 200 100 0 −100 −200 −300 −400 ppm

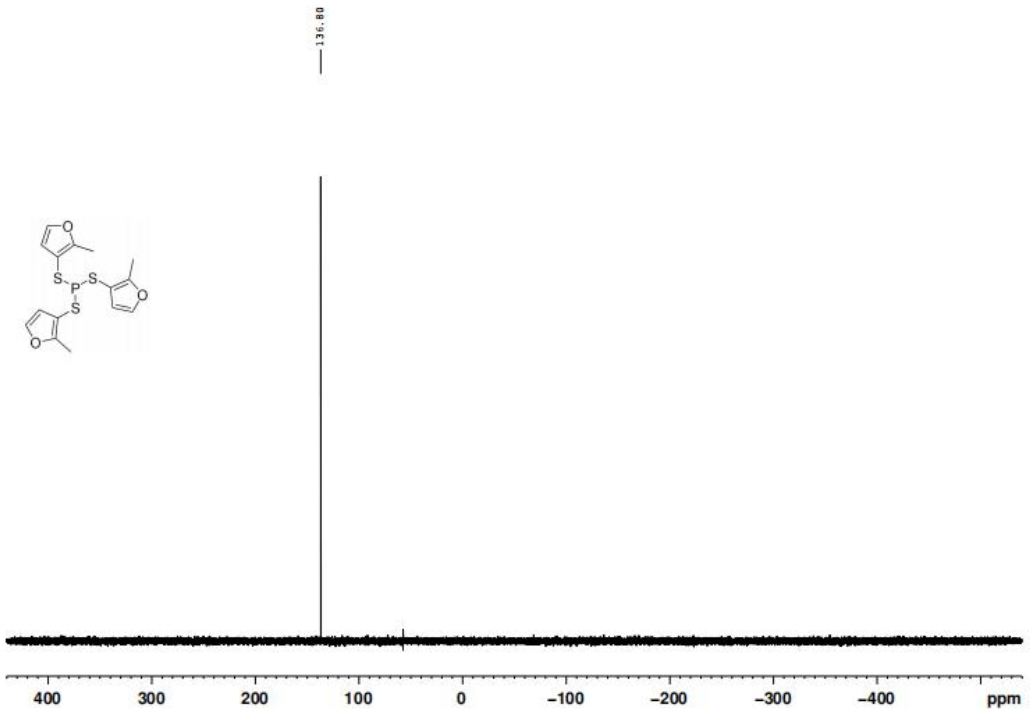
3l


7.268
7.265
6.338
6.336
2.316
2.314
9
8
7
6
5
4
3
2
1
0
ppm
3.12
2.94
9.00

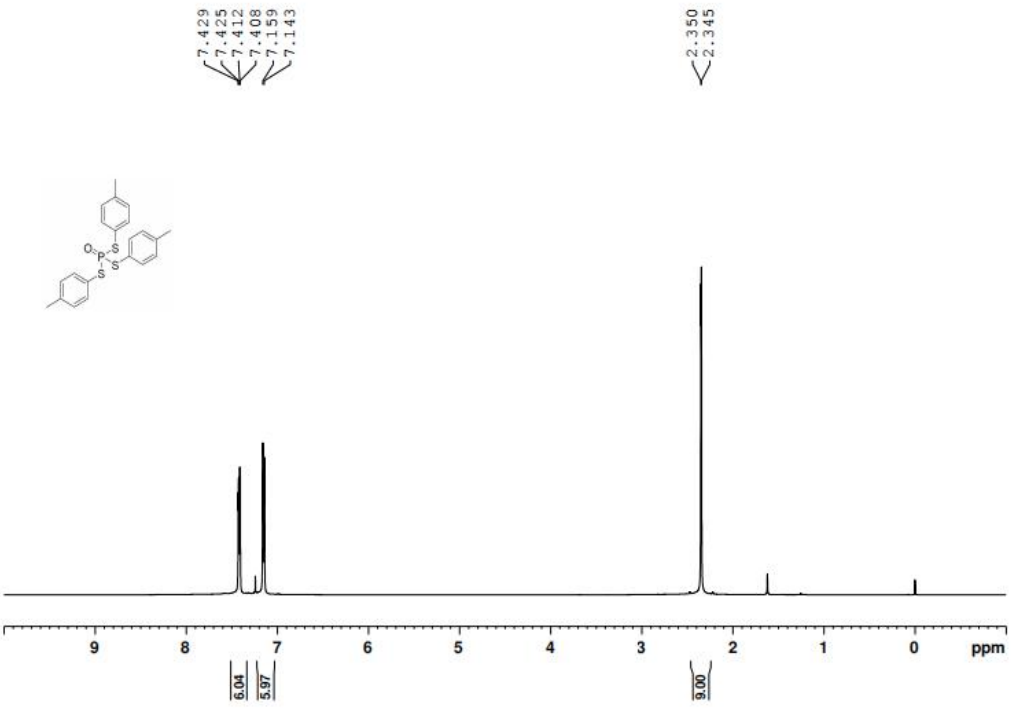
3l


156.83
156.80
140.82
115.74
115.73
107.52
107.43
77.44
77.23
77.02
12.33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

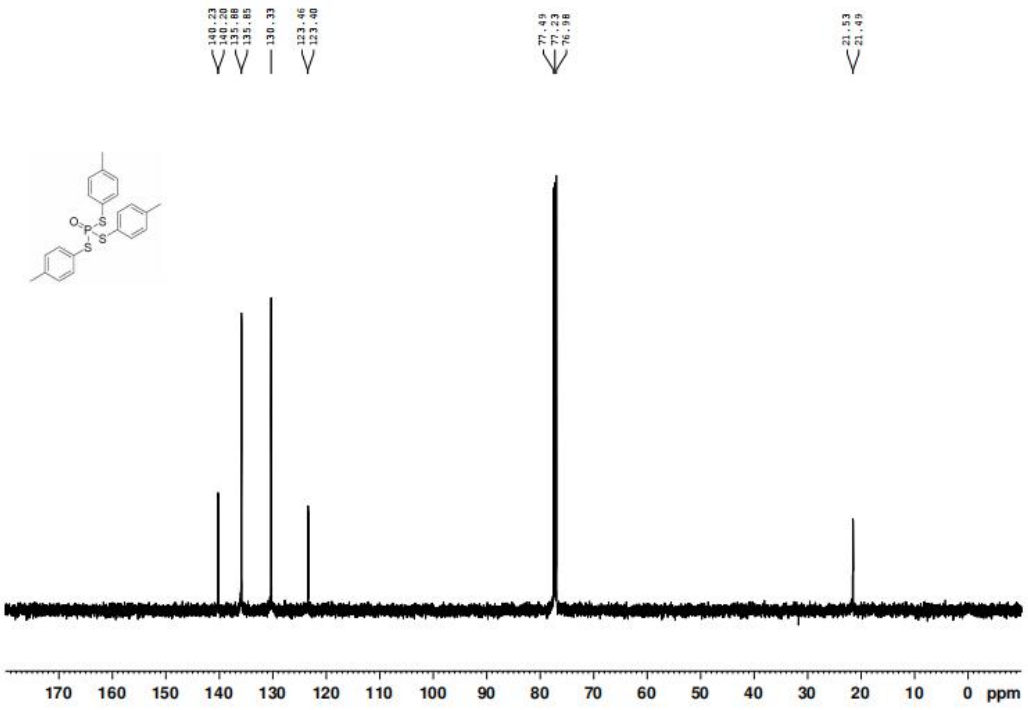
3l


136.80
400
300
200
100
0
-100
-200
-300
-400
ppm

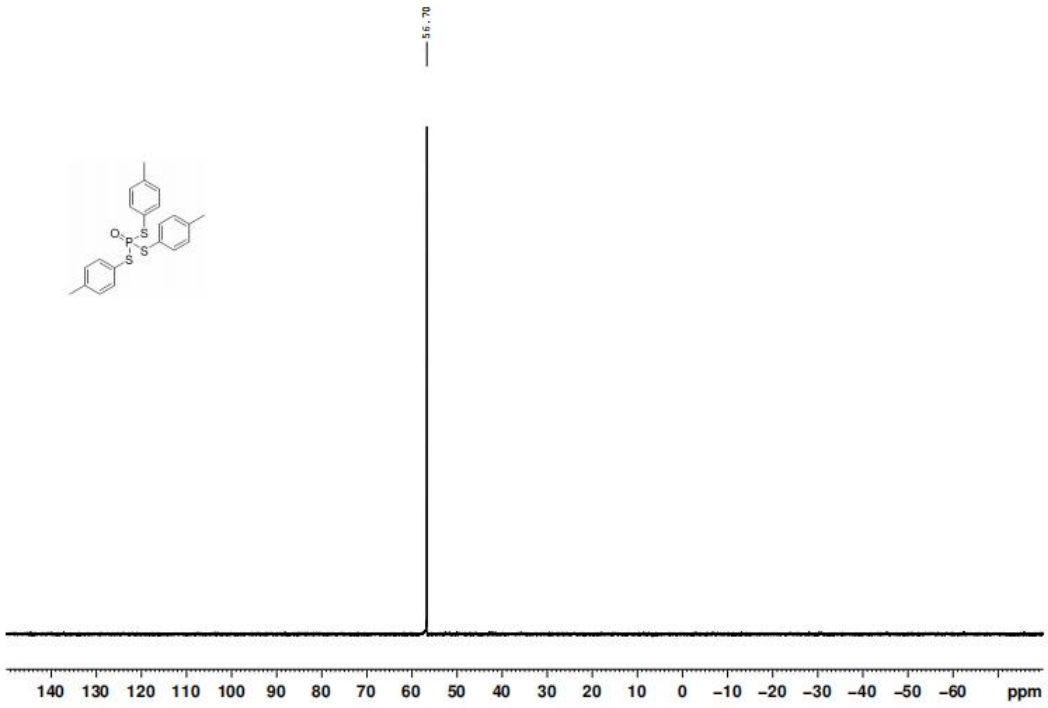
4a


7.429
7.425
7.412
7.408
7.159
7.143
2.350
2.345
9
8
7
6
5
4
3
2
1
0
ppm
6.04
5.97
9.00

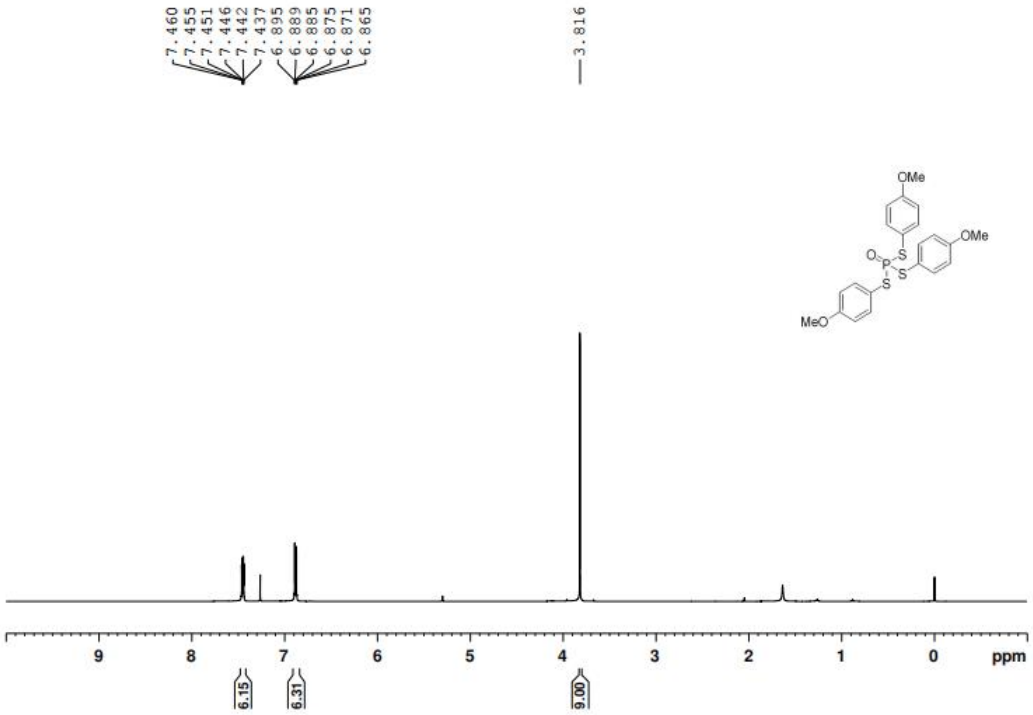
4a


140.23
140.20
135.88
135.65
130.33
123.46
123.40
77.49
77.23
76.98
21.53
21.49
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

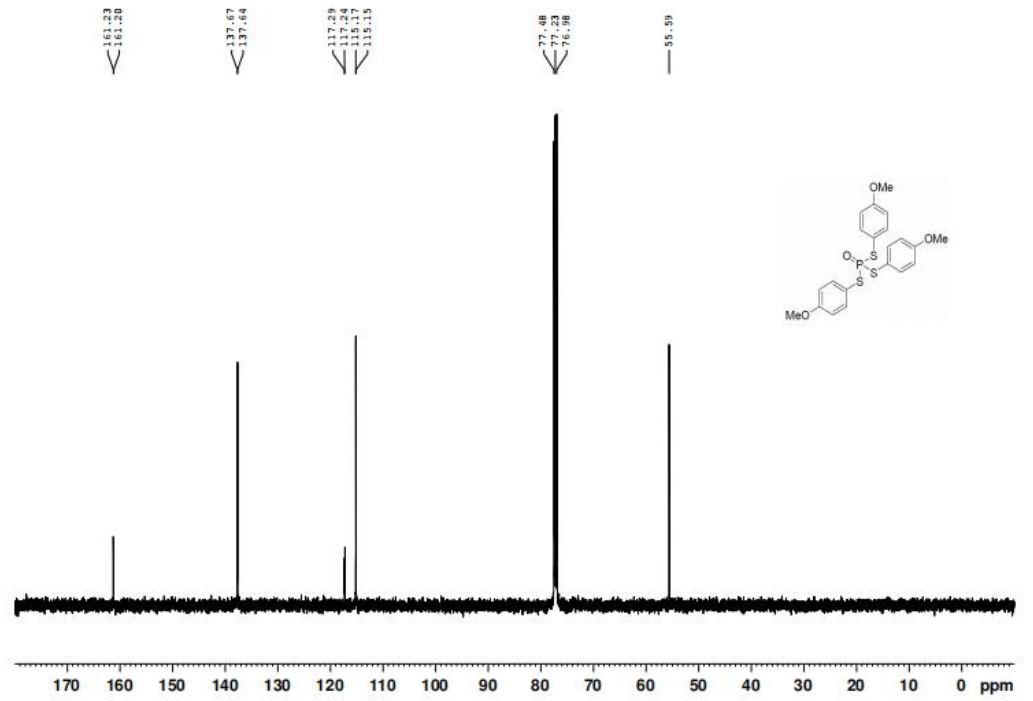
4a


56.70
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 ppm

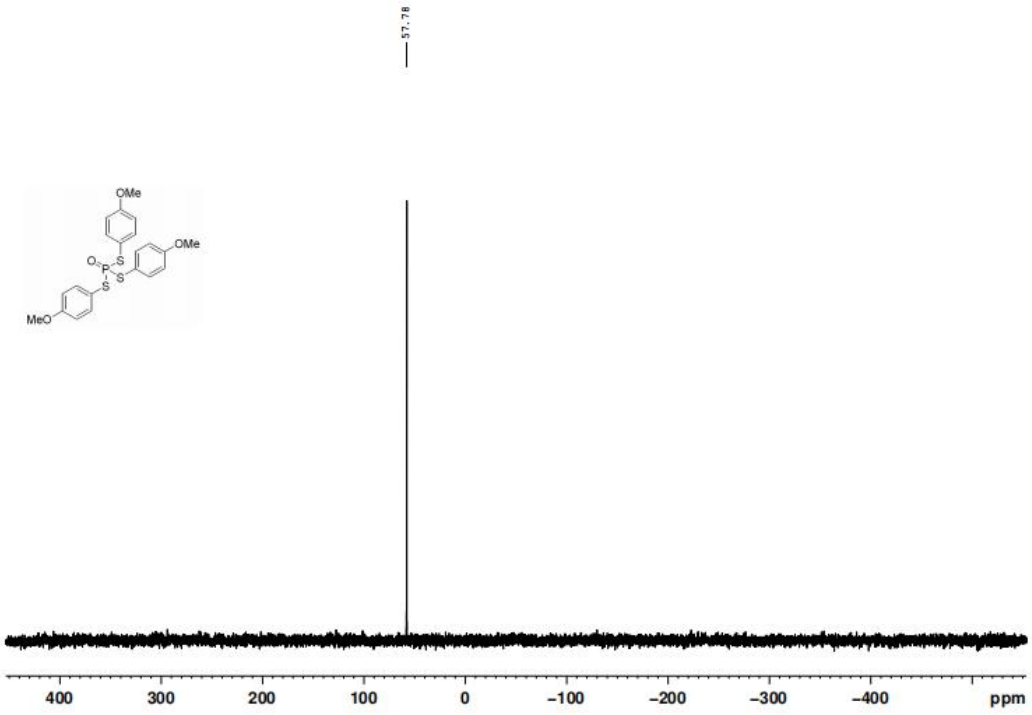
4b


7.460
7.455
7.451
7.446
7.442
7.437
6.895
6.889
6.885
6.875
6.871
6.865
3.816
OMe
OMe
MeO
9
8
7
6
5
4
3
2
1
0
ppm
6.15
6.31
9.00

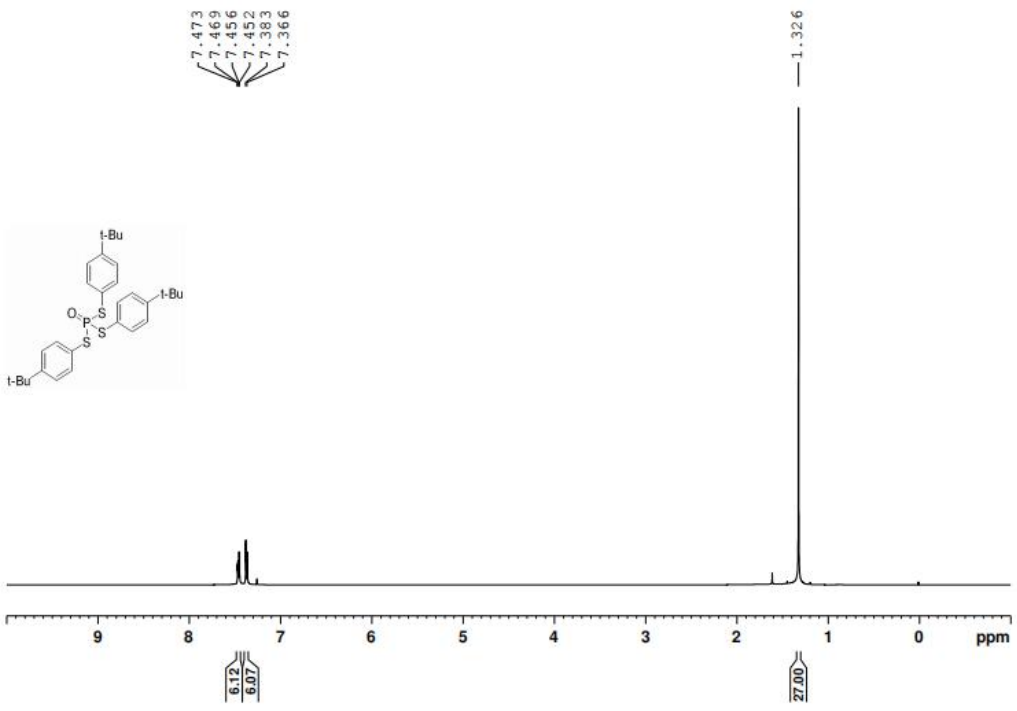
4b


161.23
161.20
137.67
137.64
117.29
117.24
115.17
115.15
77.48
77.23
76.98
55.59
OMe
OMe
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

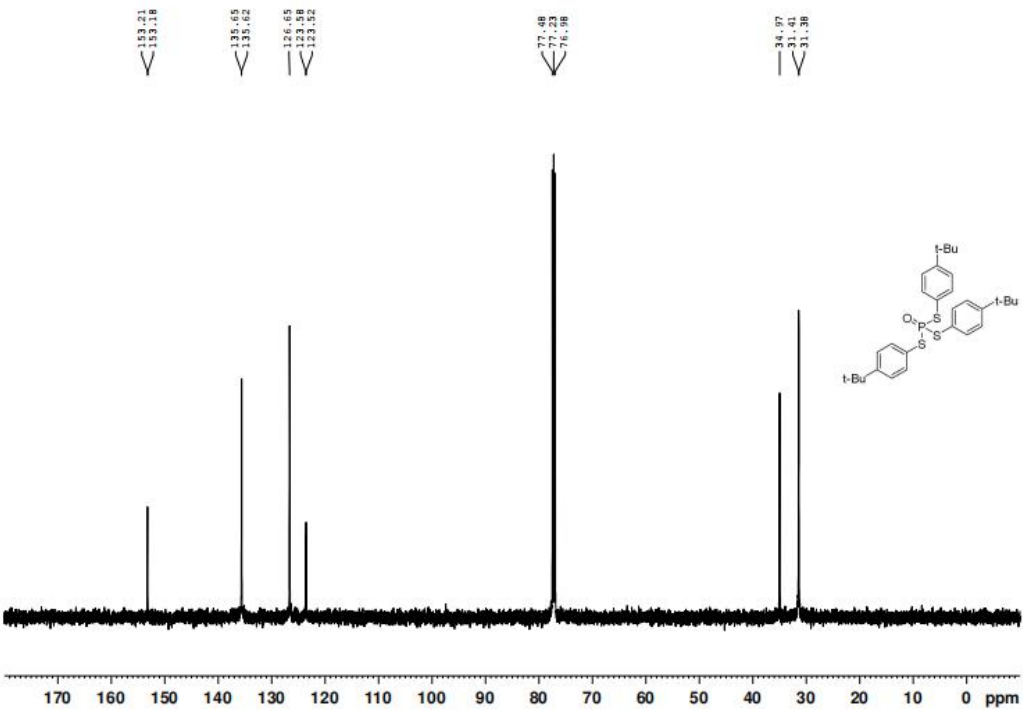
4b


57.78
OMe
OMe
MeO
400
300
200
100
0
−100
−200
−300
−400
ppm

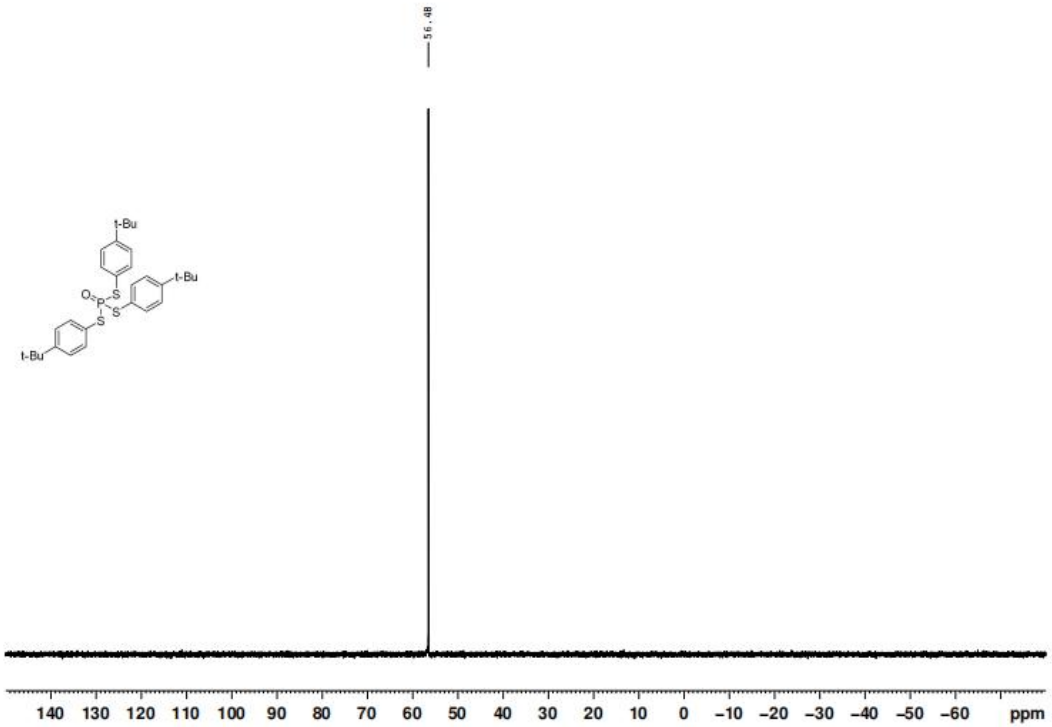
4c


7.473
7.469
7.456
7.452
7.383
7.366
1.326
t-Bu
t-Bu
t-Bu
9
8
7
6
5
4
3
2
1
0
ppm
6.12
6.07
27.00

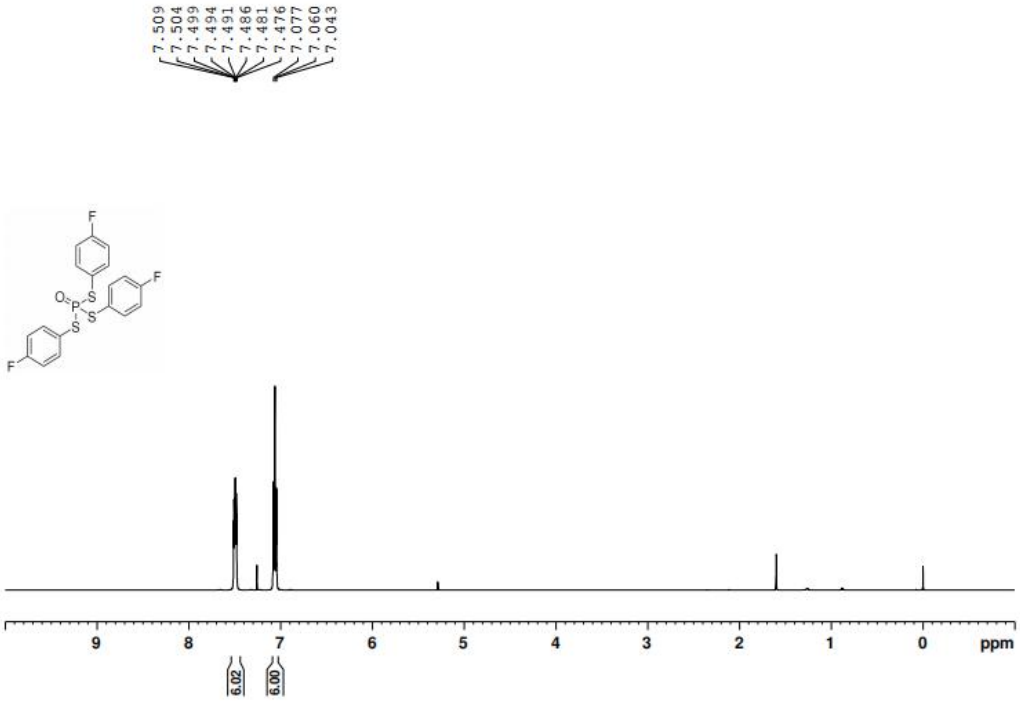
4c


153.21
153.18
135.65
135.62
126.65
123.58
123.52
77.48
77.23
76.98
34.97
31.41
31.38
t-Bu
t-Bu
t-Bu
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

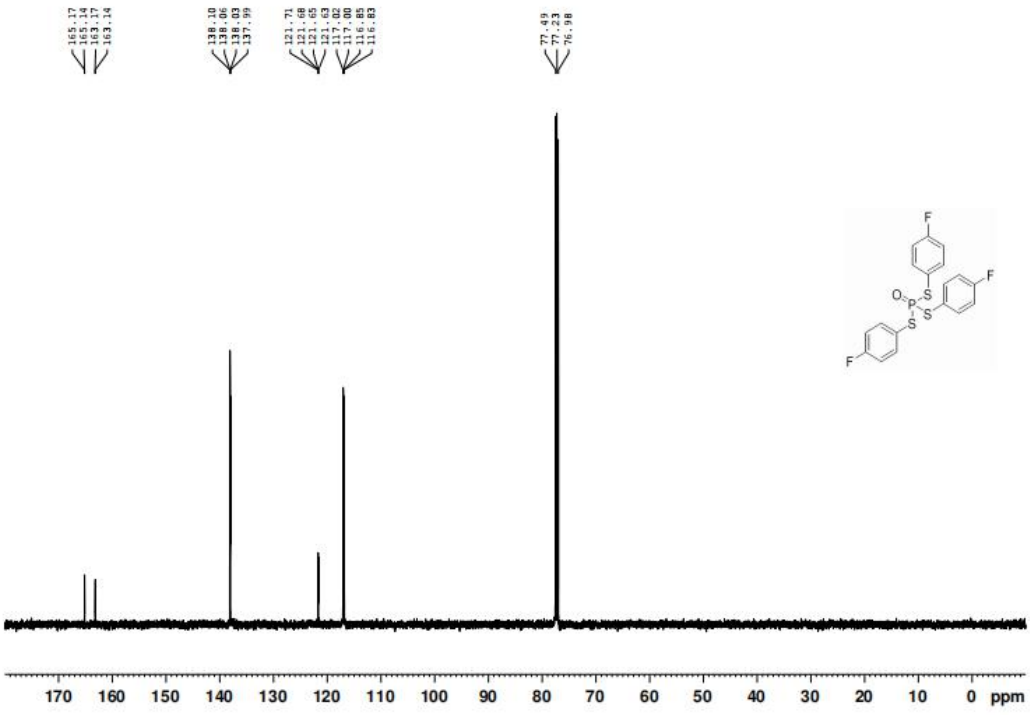
4c


56.48
t-Bu
t-Bu
t-Bu
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

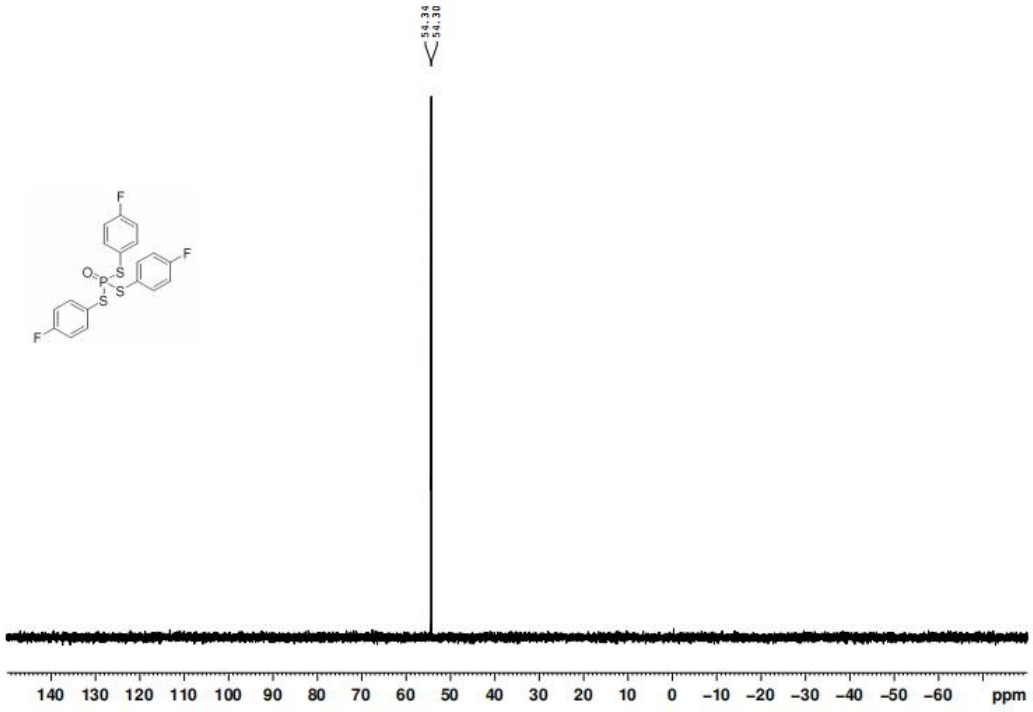
4d


7.509
7.504
7.499
7.494
7.491
7.486
7.481
7.476
7.077
7.060
7.043
F
F
O
P
S
S
S
F
9
8
7
6
5
4
3
2
1
0
ppm
6.02
6.00

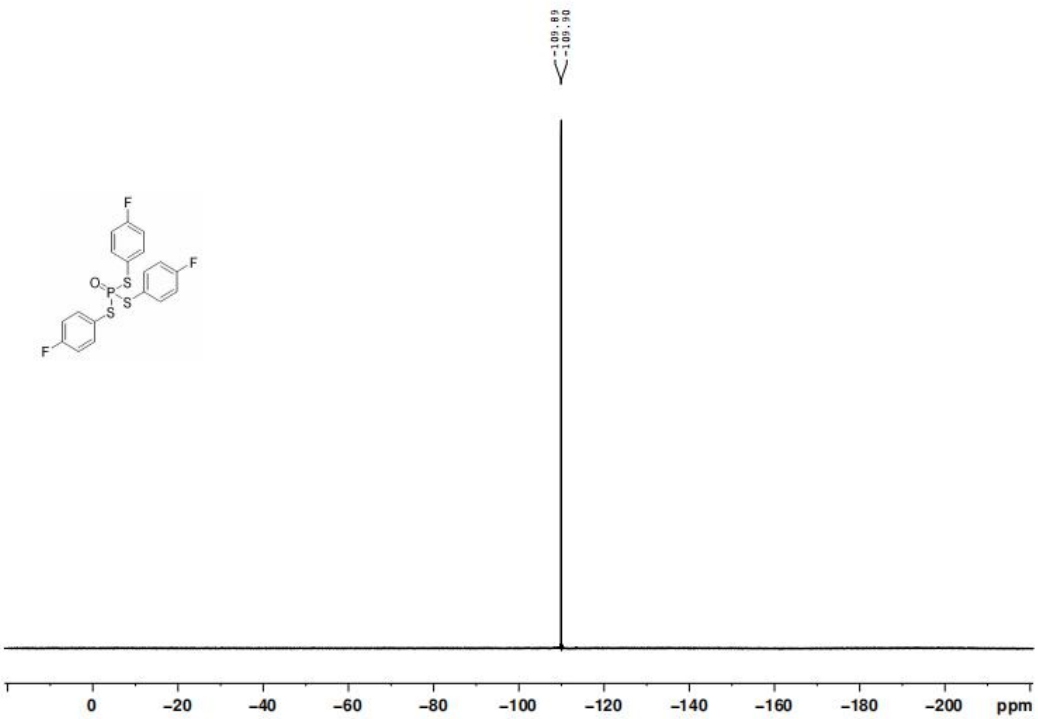
4d


165.17
165.14
163.17
163.14
138.10
138.06
138.03
137.99
121.71
121.68
121.65
121.63
117.02
117.00
116.85
116.83
77.49
77.23
76.98
F
F
O
P
S
S
S
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

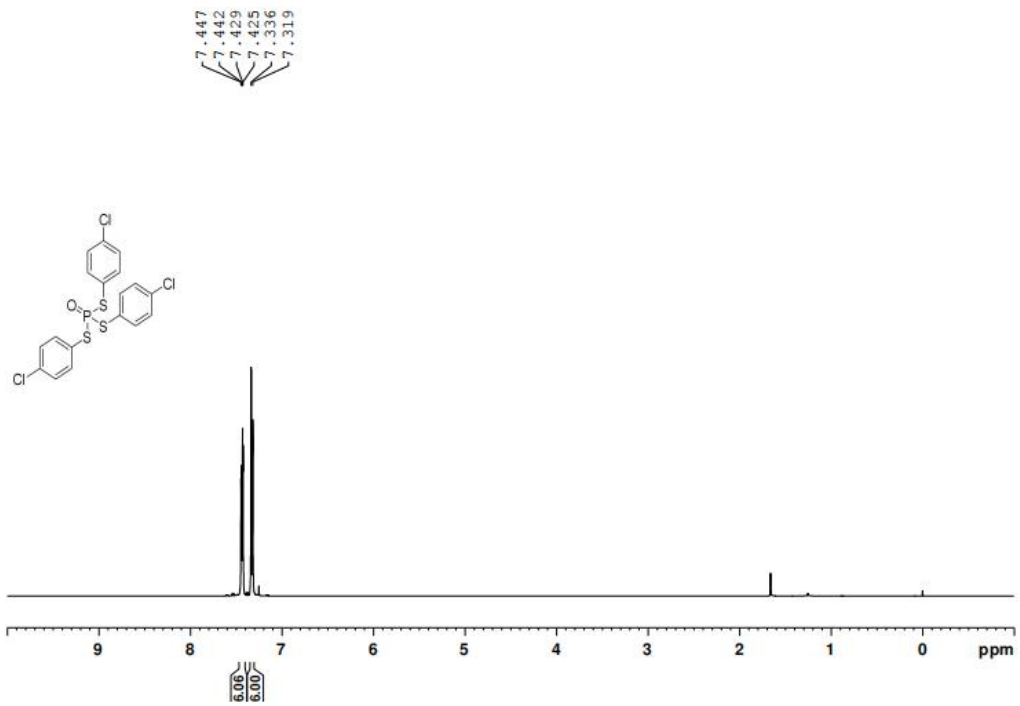
4d


54.34
54.30
F
F
F
O
P
S
S
S
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

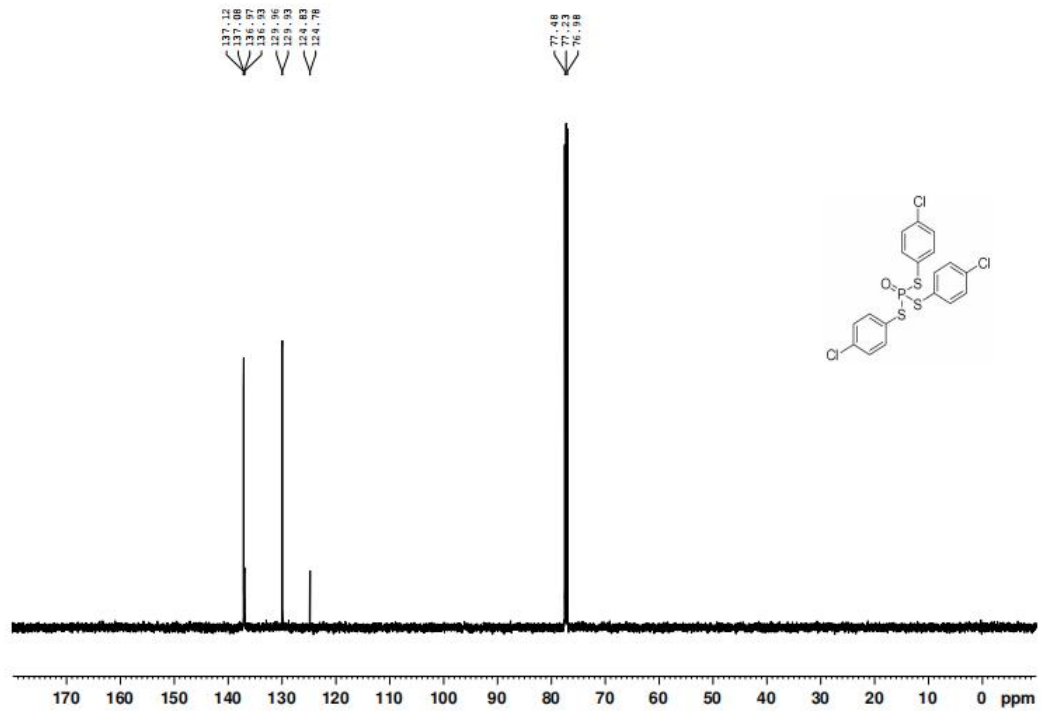
4d


−109.89
−109.90
F
F
F
O
P
S
S
S
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

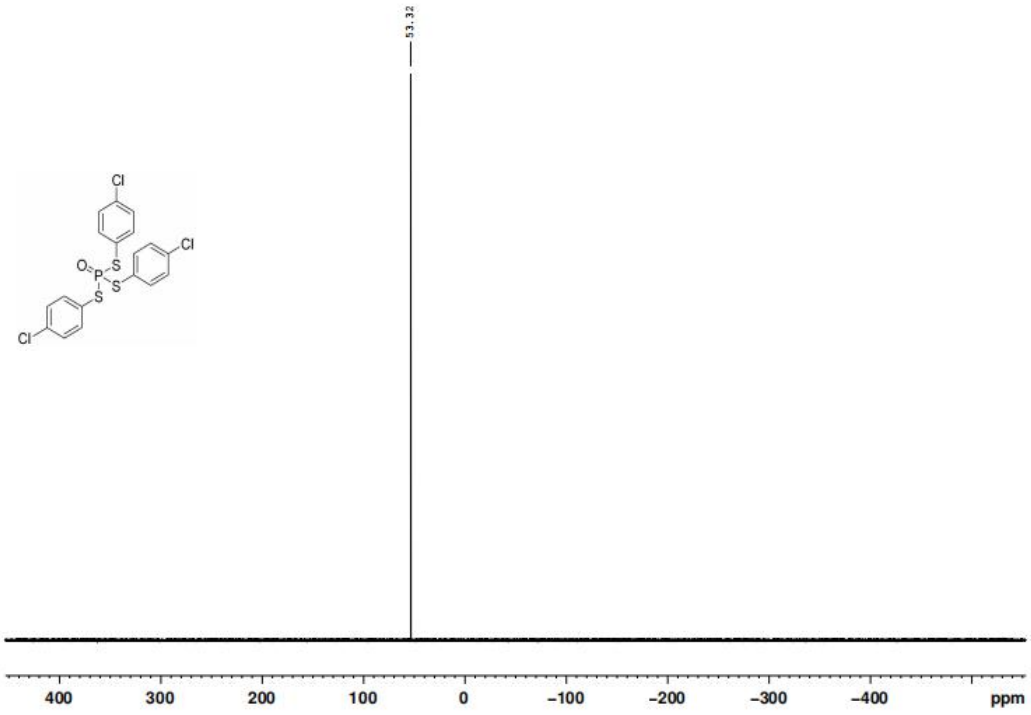
4e


7.447
7.442
7.429
7.425
7.336
7.319
Cl
Cl
Cl
O
P
S
S
S
9
8
7
6
5
4
3
2
1
0
ppm
6.06
6.00

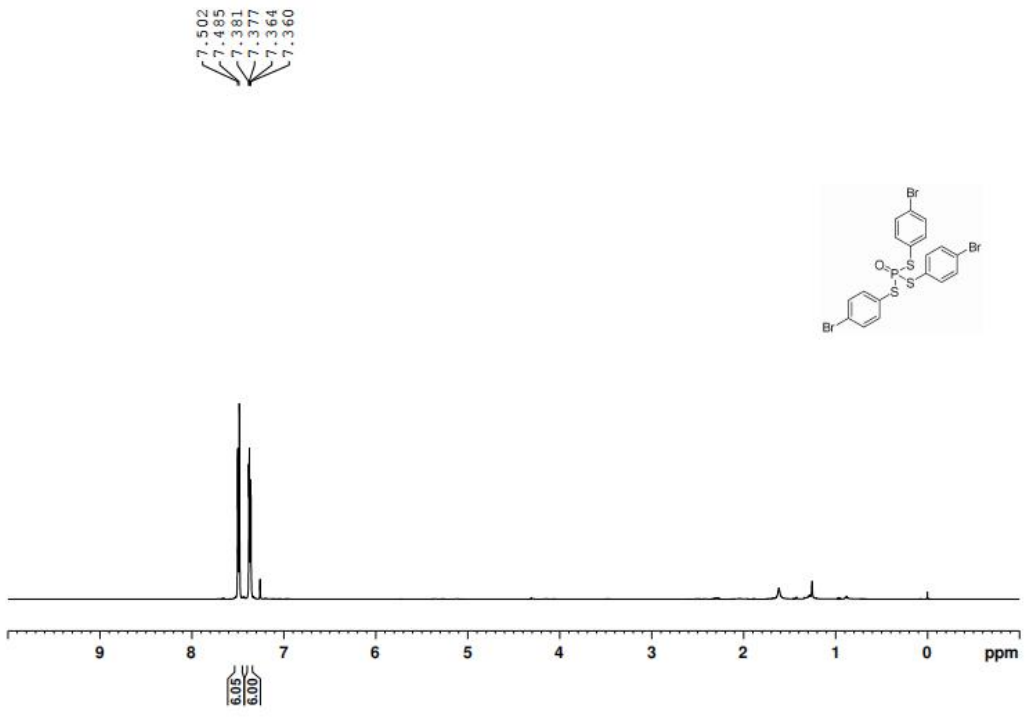
4e


137.12
137.08
136.97
136.93
129.96
129.93
124.83
124.78
77.48
77.23
76.98
Cl
Cl
Cl
O
P
S
S
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

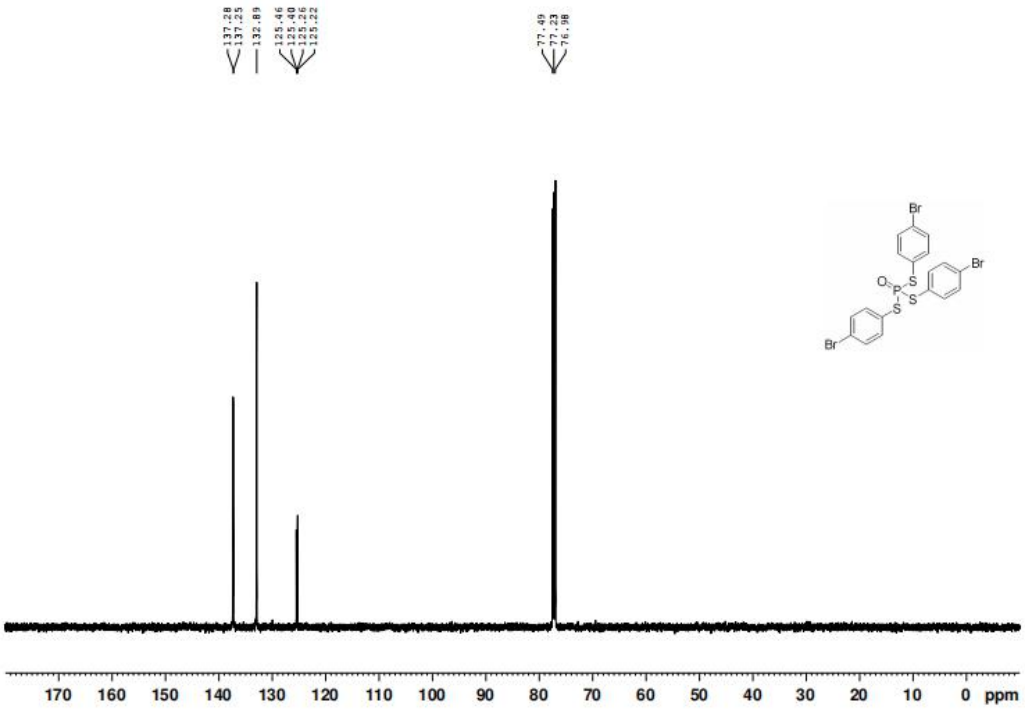
4e


53.32
Cl
Cl
Cl
O
P
S
S
S
400
300
200
100
0
−100
−200
−300
−400
ppm

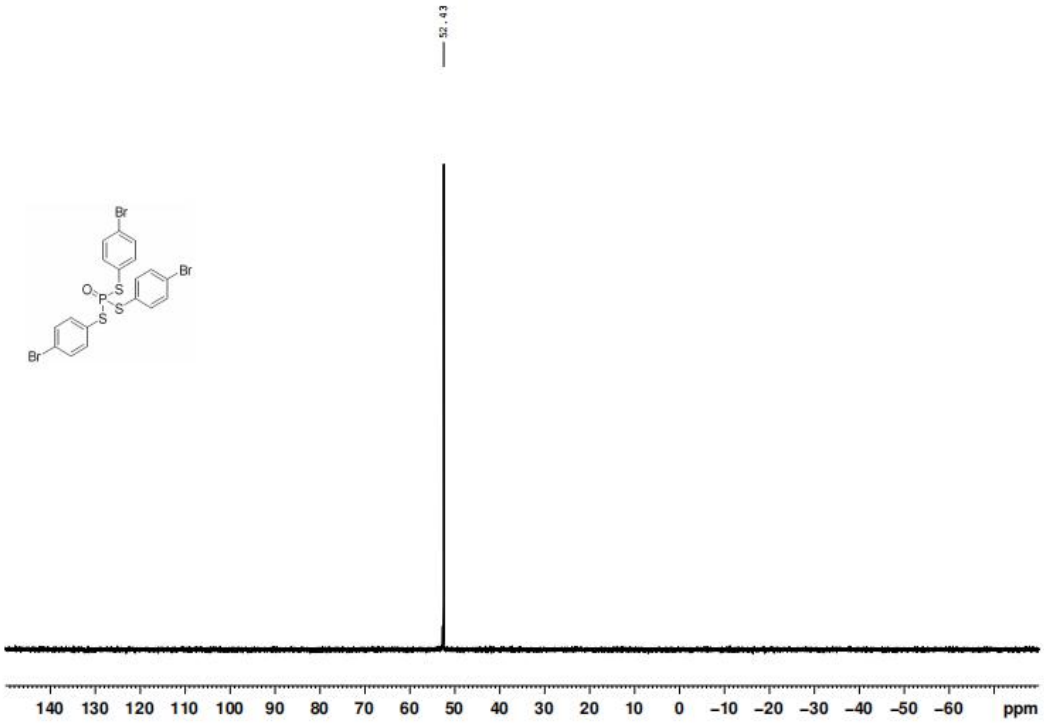
4f


7.502
7.485
7.381
7.377
7.364
7.360
Br
Br
Br
O
P
S
S
S
9
8
7
6
5
4
3
2
1
0
ppm
6.05
6.00

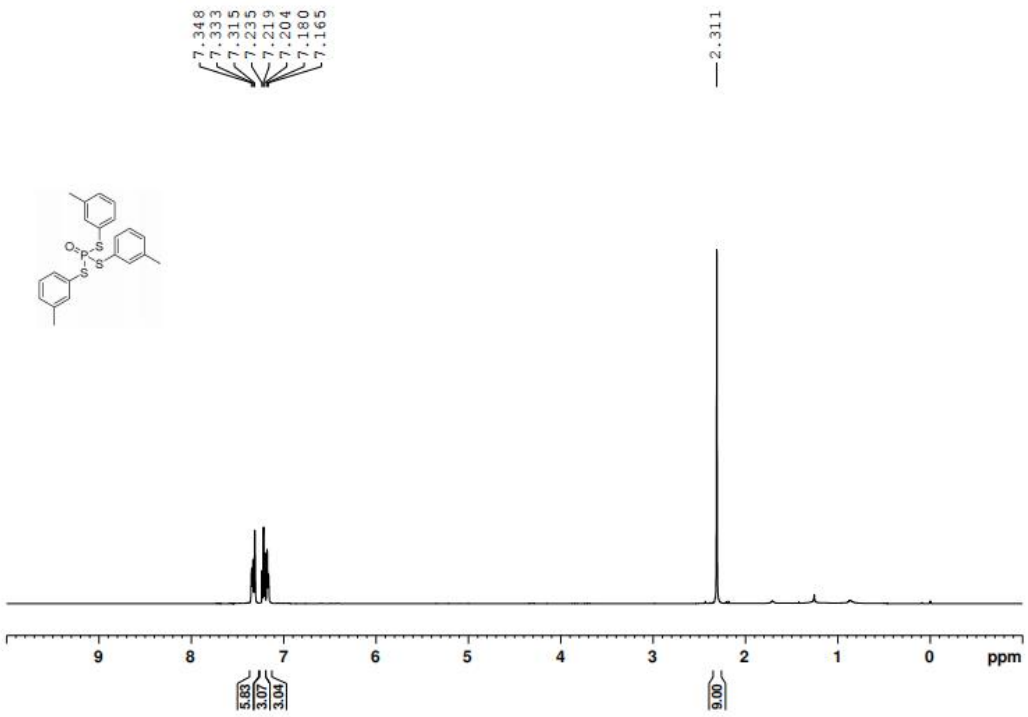
4f


137.28
137.25
132.89
125.46
125.40
125.26
125.22
77.49
77.23
76.98
Br
Br
Br
O
P
S
S
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

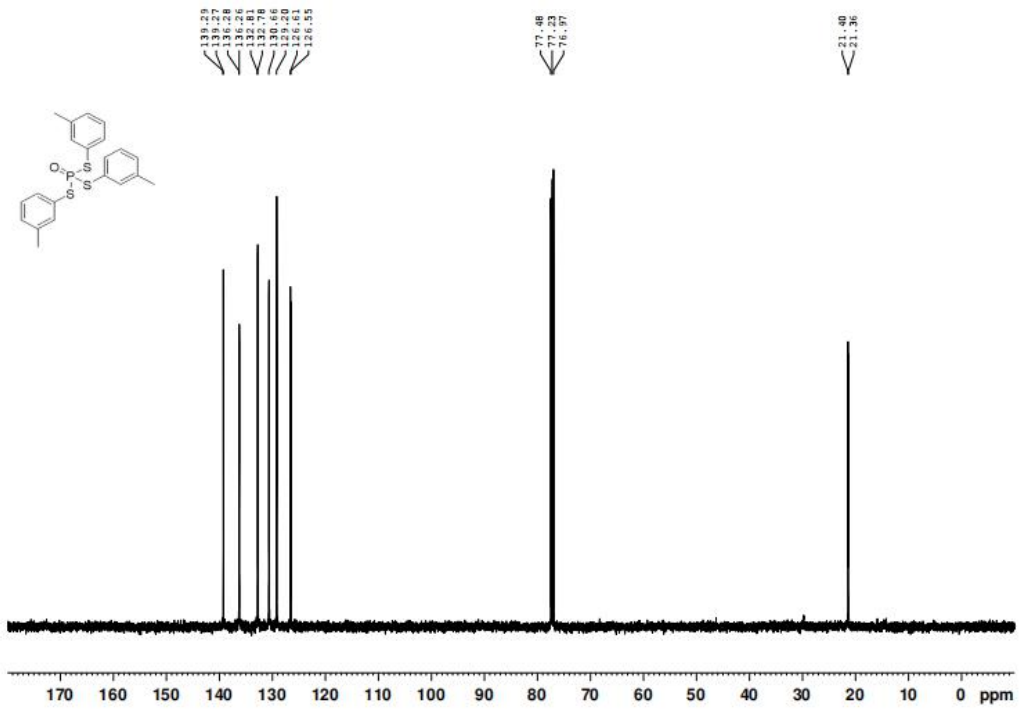
4f


52.43
Br
Br
Br
O
P
S
S
S
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

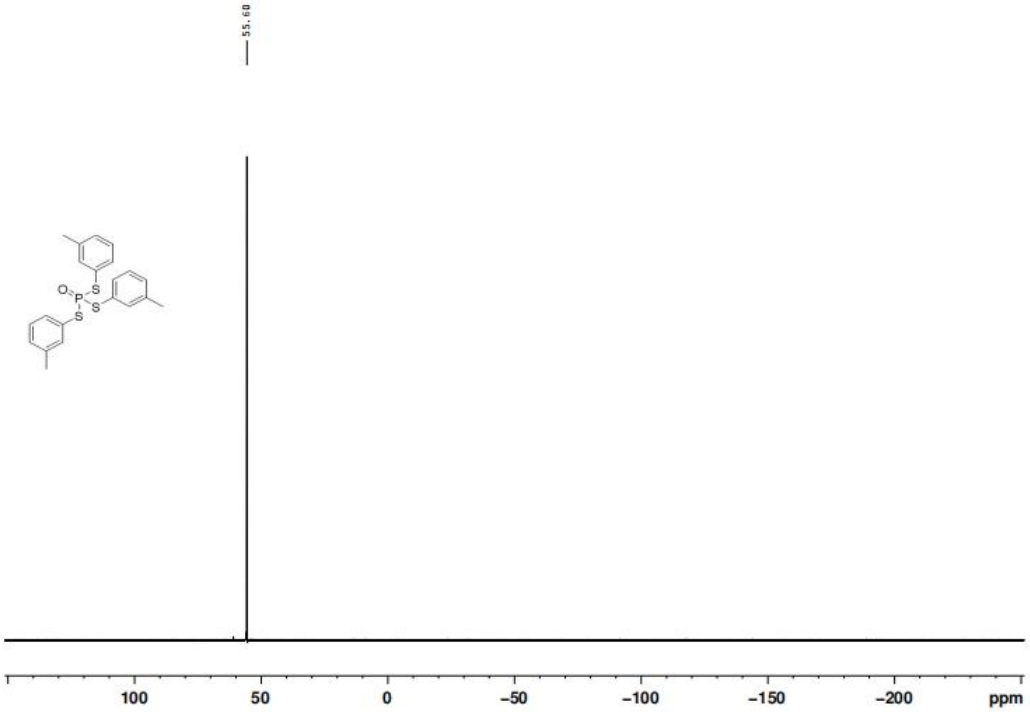
4g


7.348
7.333
7.315
7.235
7.219
7.204
7.180
7.165
2.311
9
8
7
6
5
4
3
2
1
0
ppm
5.83
3.07
3.04
9.00

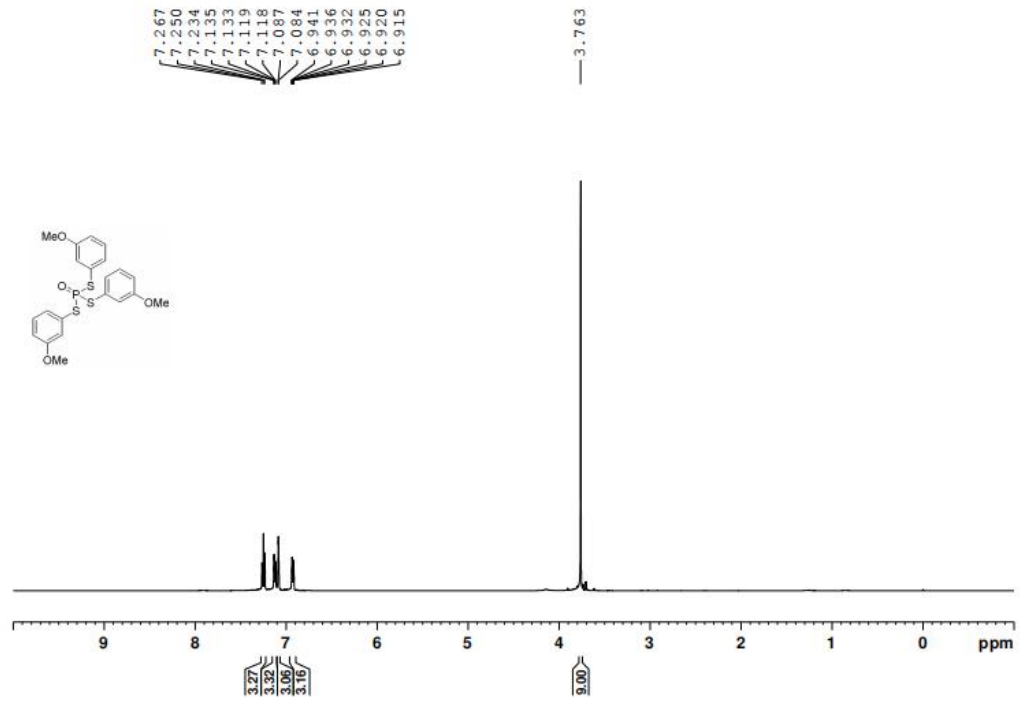
4g


139.29
139.27
136.28
136.26
132.81
132.78
130.66
129.20
126.61
126.55
77.48
77.23
76.97
21.40
21.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

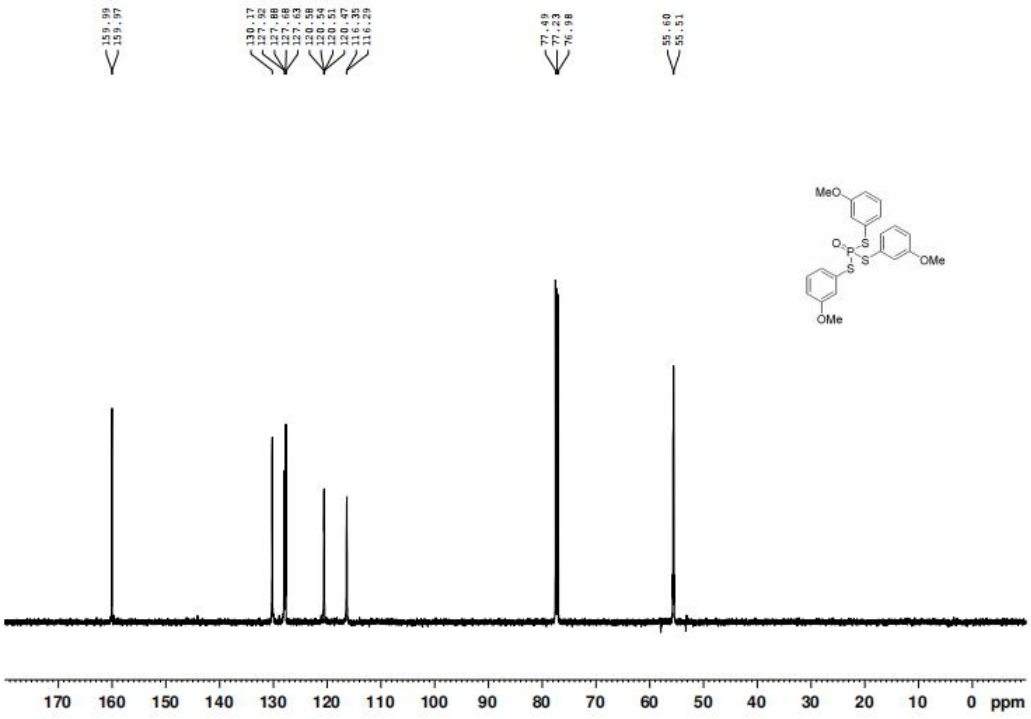
4g


55.60
100
50
0
−50
−100
−150
−200
ppm

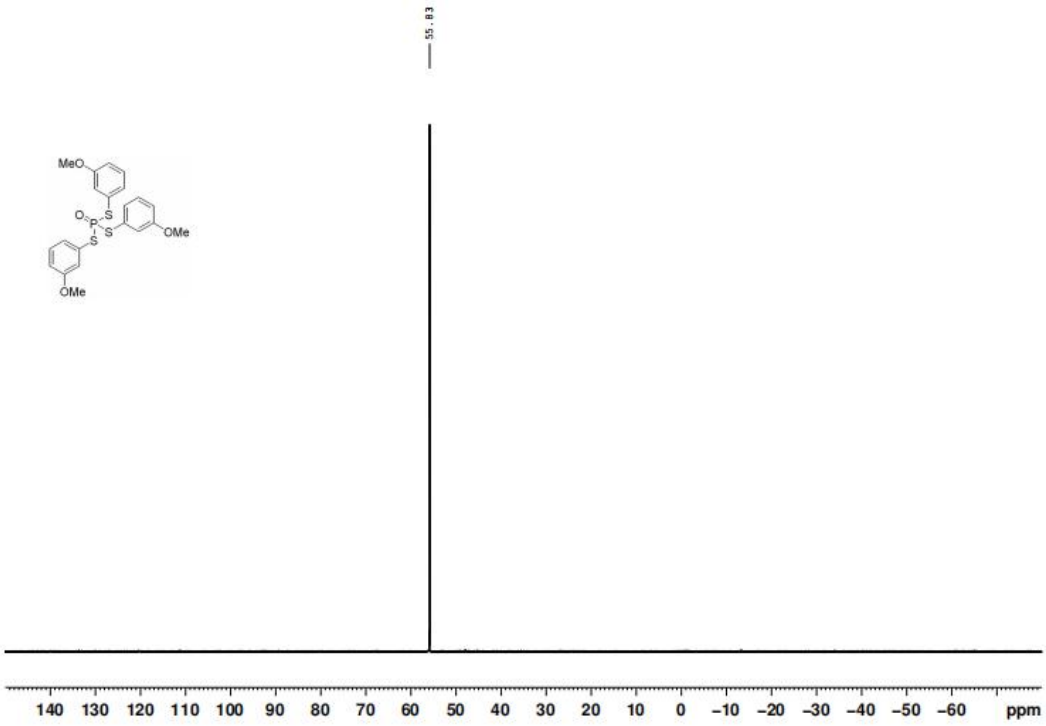
4h


7.267
7.250
7.234
7.135
7.133
7.119
7.118
7.087
7.084
6.941
6.936
6.932
6.925
6.920
6.915
3.763
MeO
OMe
OMe
9
8
7
6
5
4
3
2
1
0
ppm
3.27
3.32
3.06
3.16
9.00

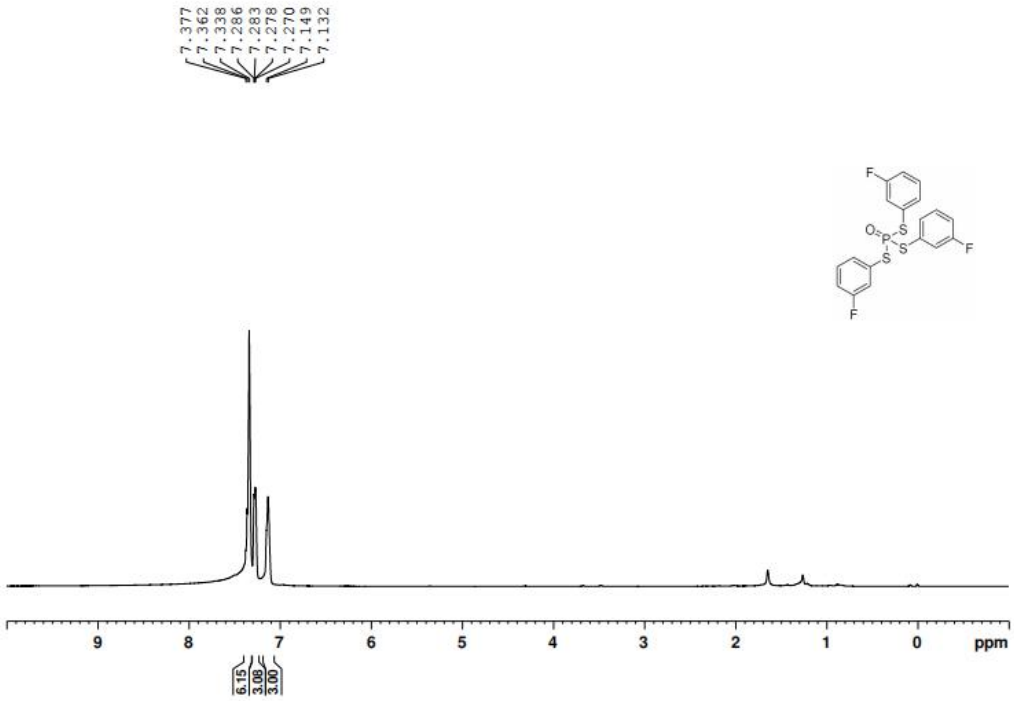
4h


159.99
159.97
130.17
127.92
127.88
127.68
127.63
120.58
120.54
120.51
120.47
116.35
116.29
77.49
77.23
76.98
55.60
55.51
MeO
OMe
OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

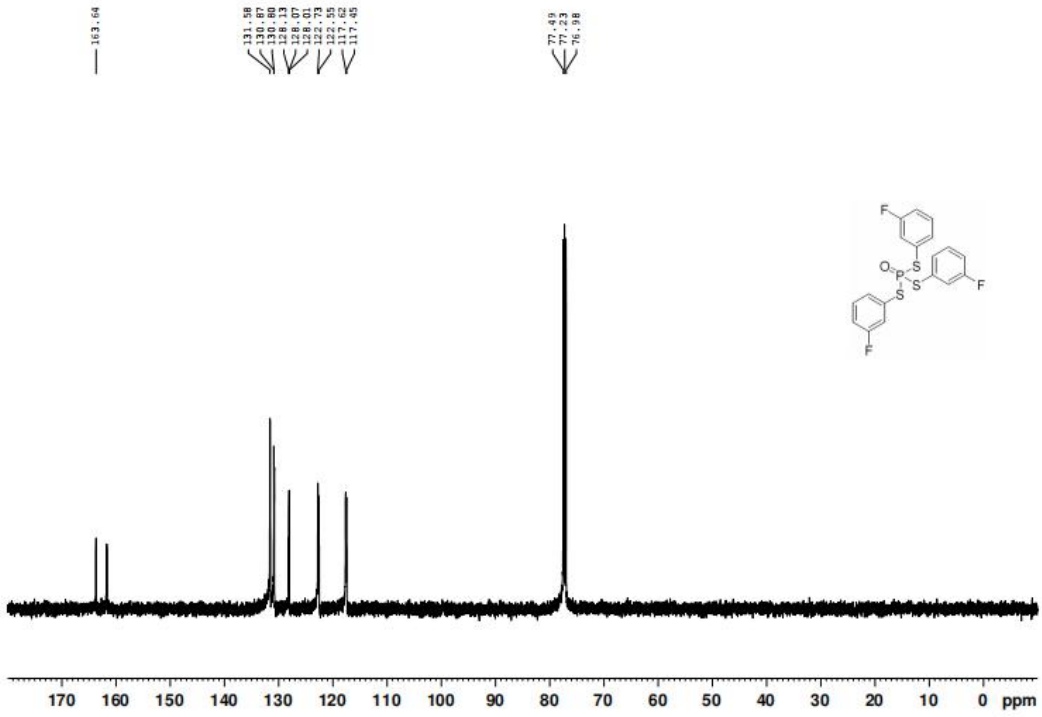
4h


55.83
MeO
OMe
OMe
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

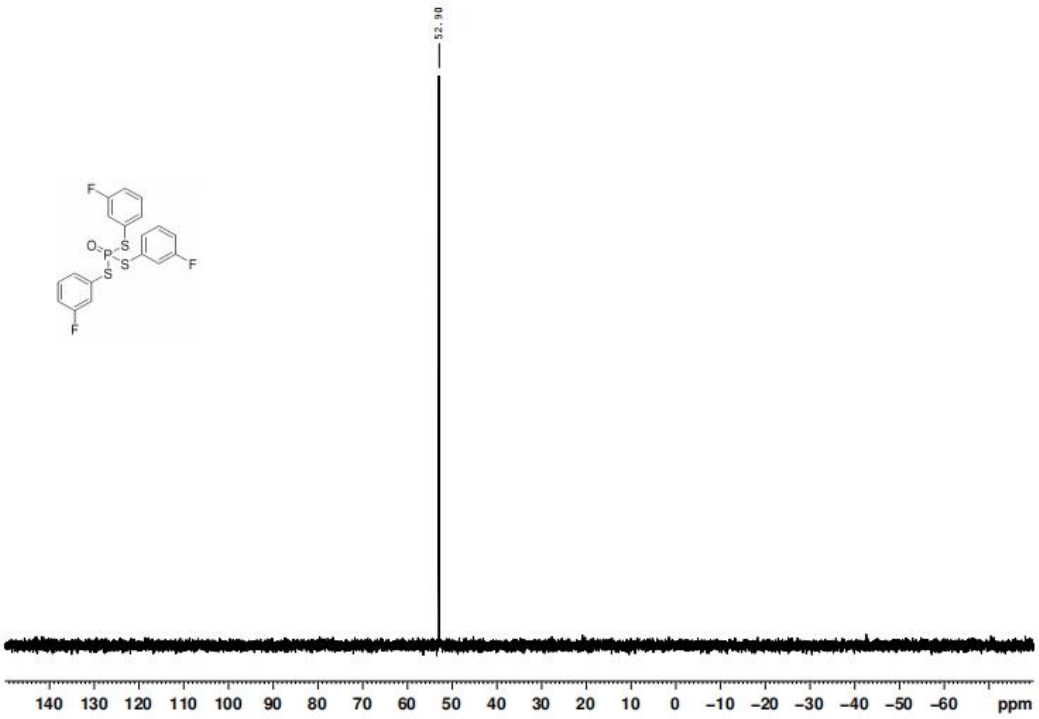
4i


7.377
7.362
7.338
7.286
7.283
7.278
7.270
7.149
7.132
F
O
P
S
S
S
F
F
9
8
7
6
5
4
3
2
1
0
ppm
6.15
3.08
3.00

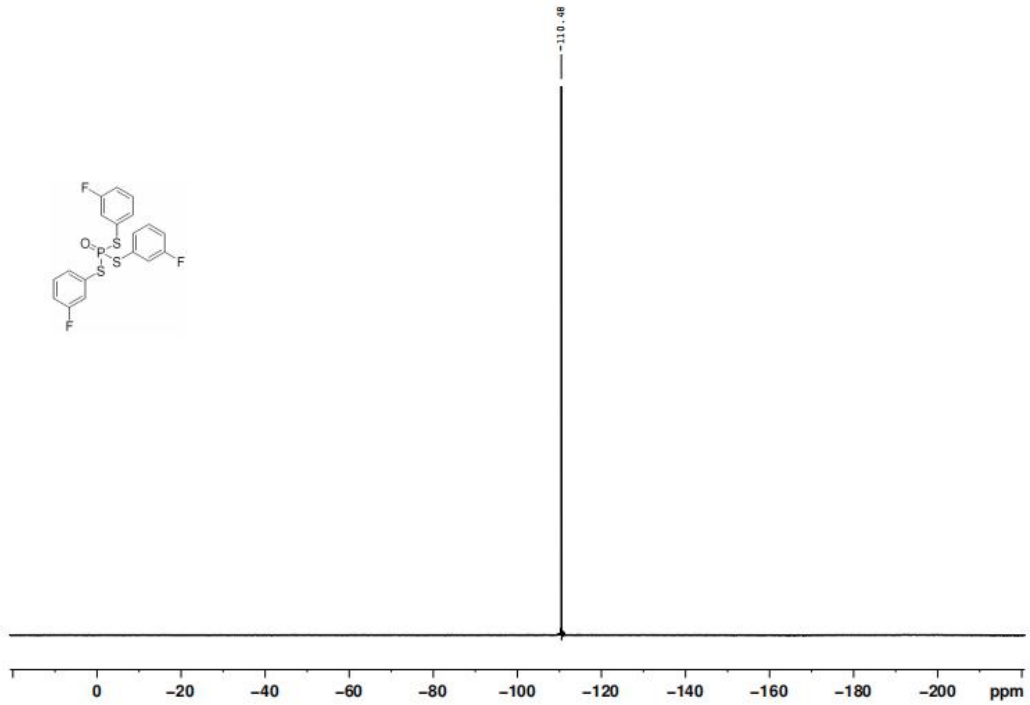
4i


163.64
131.58
130.87
130.80
128.13
128.07
128.01
122.73
122.55
117.62
117.45
77.49
77.23
76.98
F
O
P
S
S
S
F
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

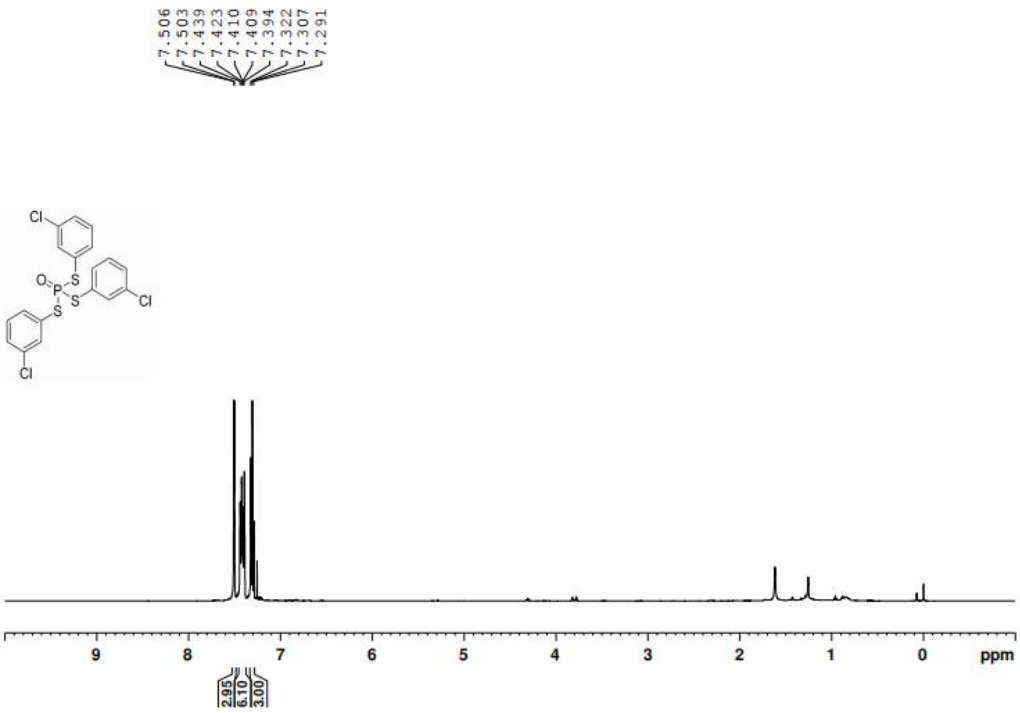
4i


52.90
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

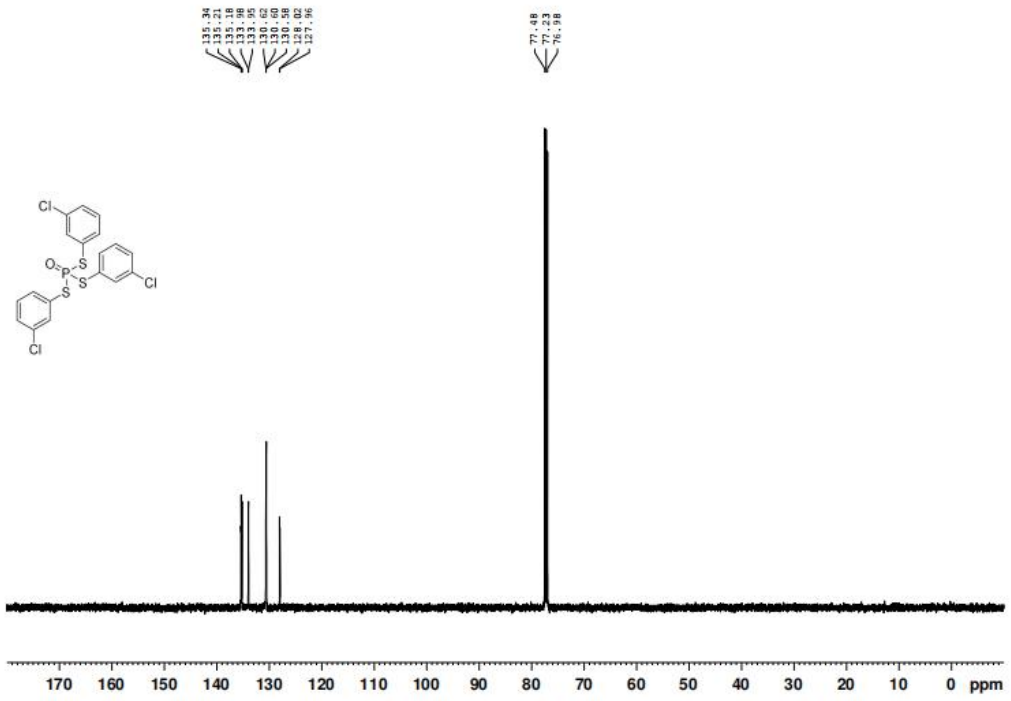
4i


−110.48
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

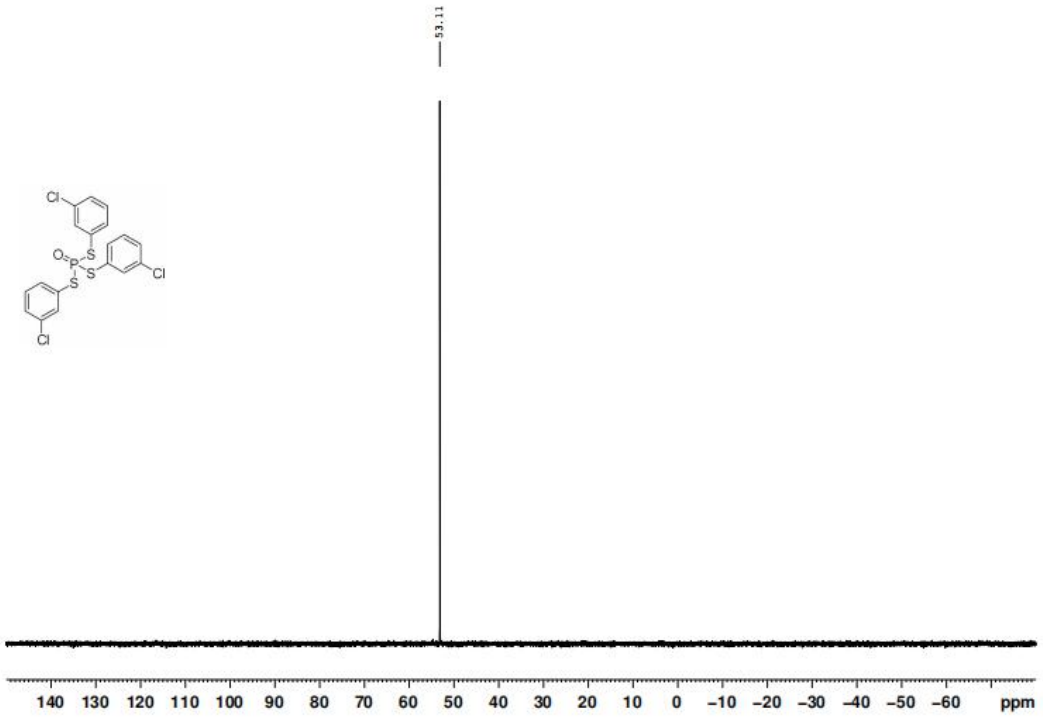
4j


7.506
7.503
7.439
7.423
7.410
7.409
7.394
7.322
7.307
7.291
Cl
O
P
S
S
S
Cl
Cl
9
8
7
6
5
4
3
2
1
0
ppm
2.95
6.10
3.00

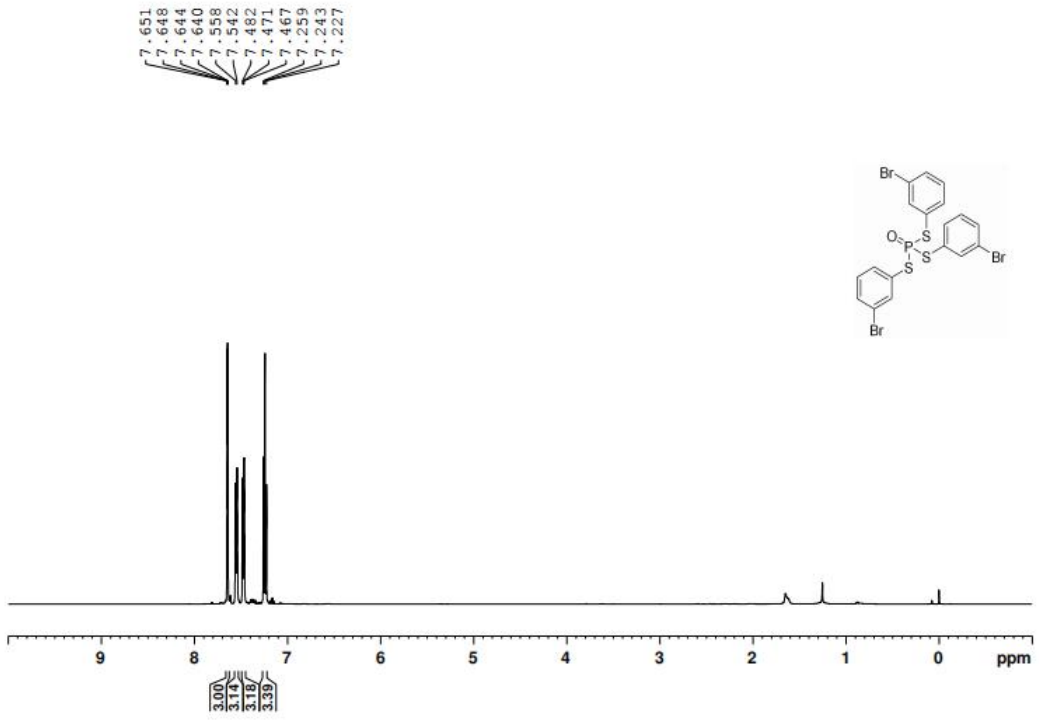
4j


135.34
135.21
135.18
133.98
133.95
130.62
130.60
130.58
128.02
127.98
77.48
77.23
76.98
Cl
O
P
S
S
S
Cl
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

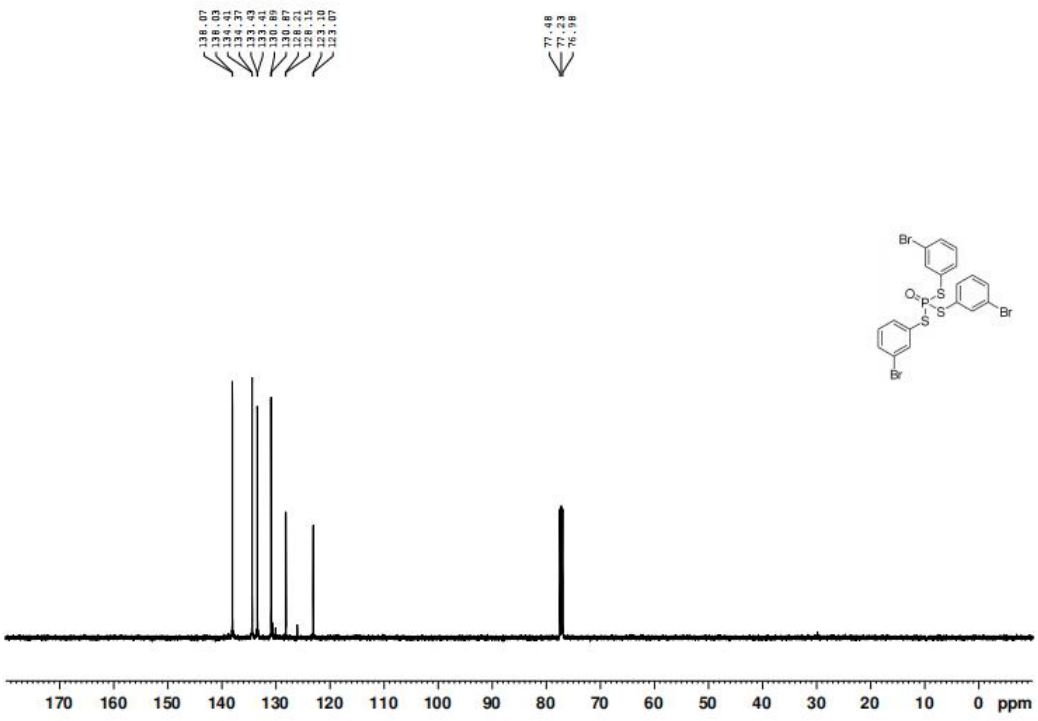
4j


53.11
Cl
Cl
Cl
O
P
S
S
S
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 ppm

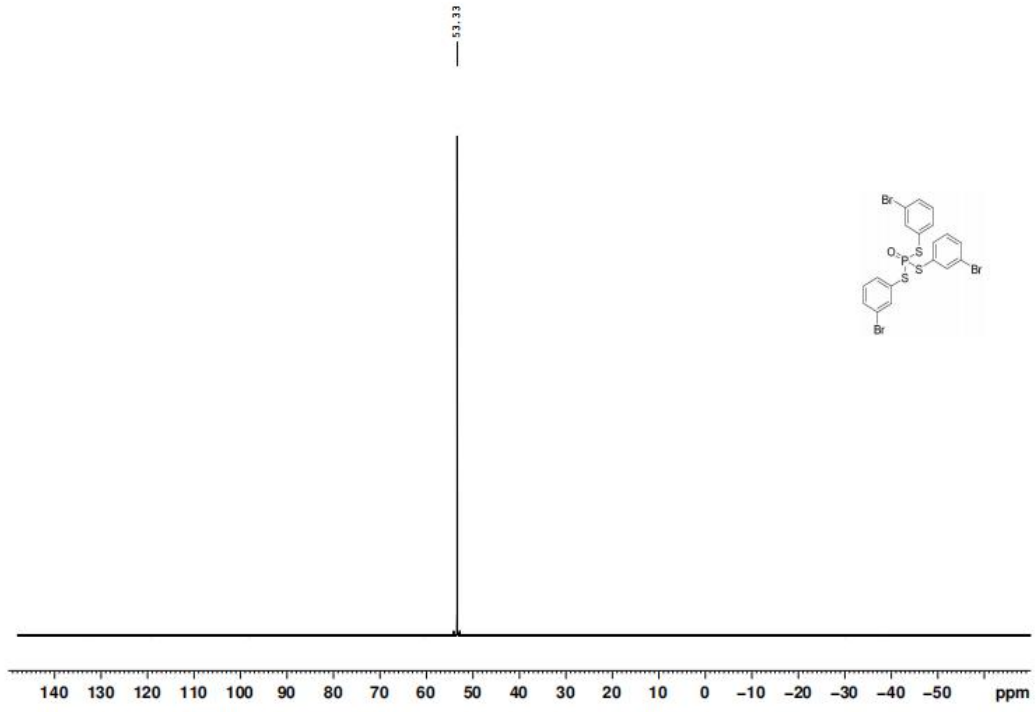
4k


7.651
7.648
7.644
7.640
7.558
7.542
7.482
7.471
7.467
7.259
7.243
7.227
Br
Br
Br
O
P
S
S
S
9 8 7 6 5 4 3 2 1 0 ppm
3.00
3.14
3.18
3.39

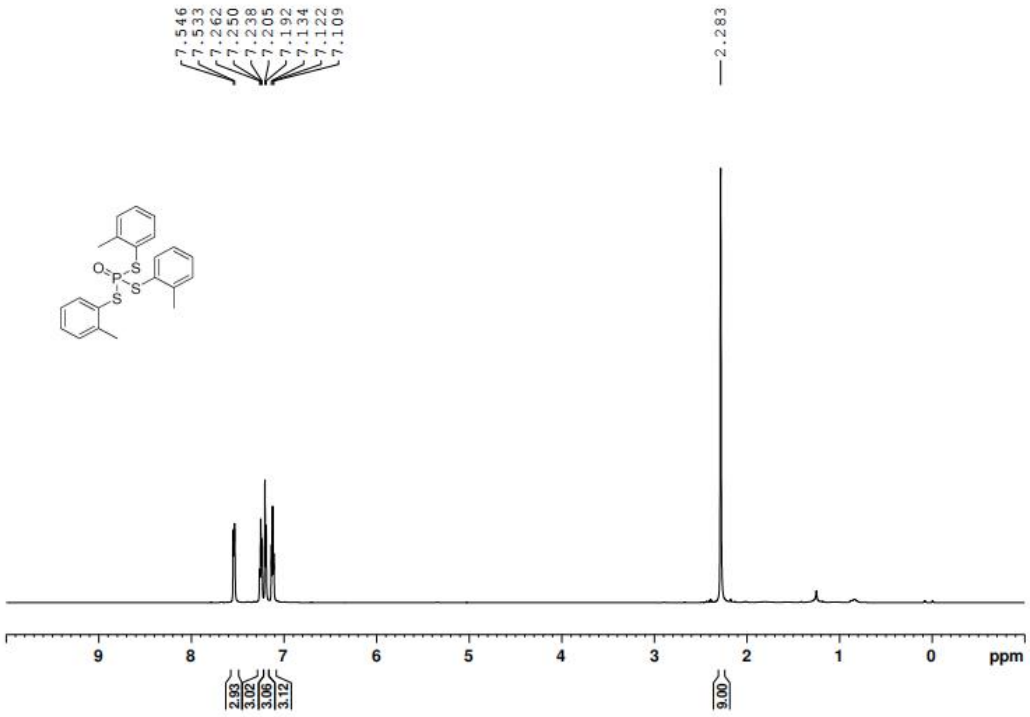
4k


138.07
138.03
134.41
134.37
133.43
133.41
130.89
130.87
128.21
128.15
123.10
123.07
77.48
77.23
76.98
Br
Br
Br
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

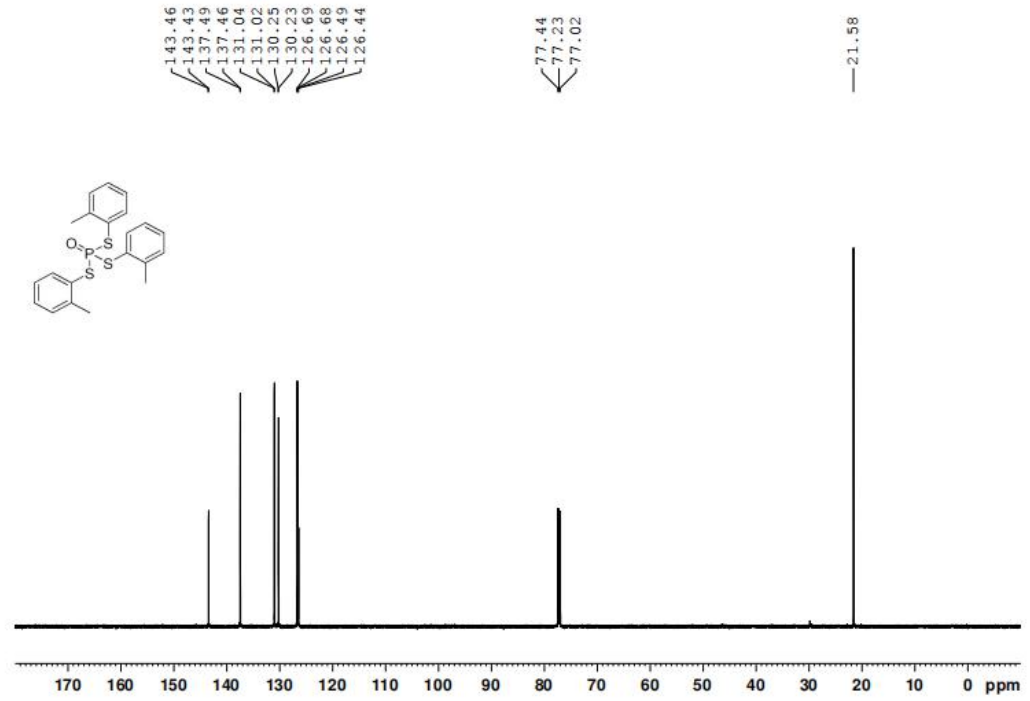
4k


53.33
Br
Br
Br
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 ppm

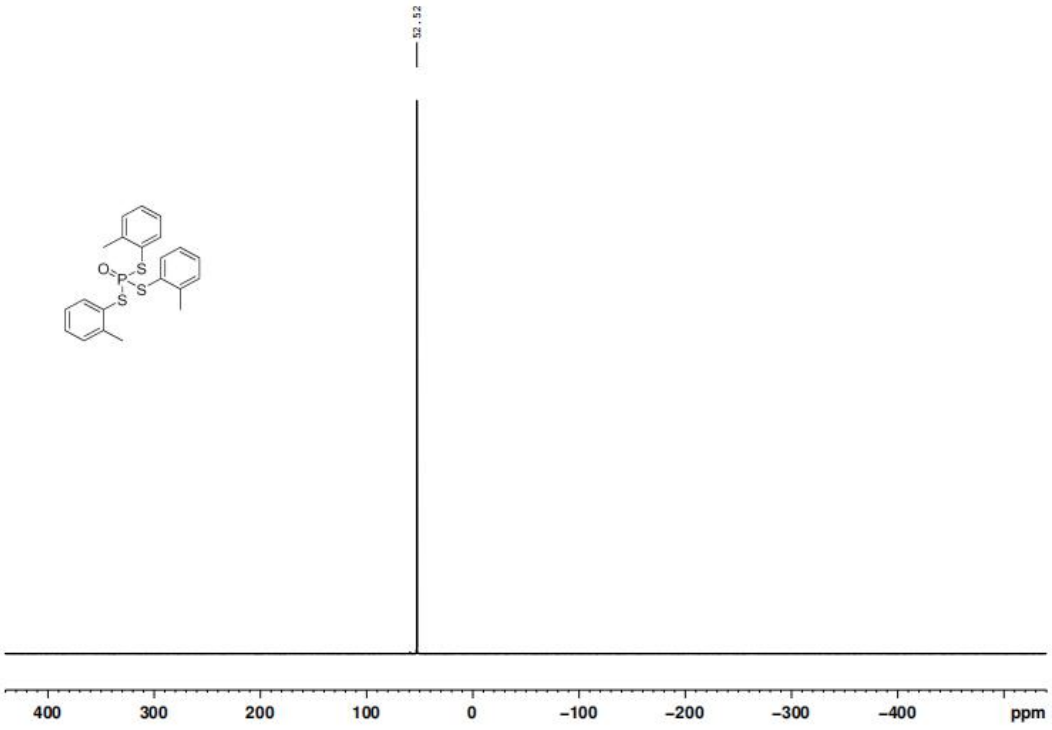
4l


7.546
7.533
7.262
7.250
7.238
7.205
7.192
7.134
7.122
7.109
2.283
9
8
7
6
5
4
3
2
1
0
ppm
2.93
3.02
3.06
3.12
9.00

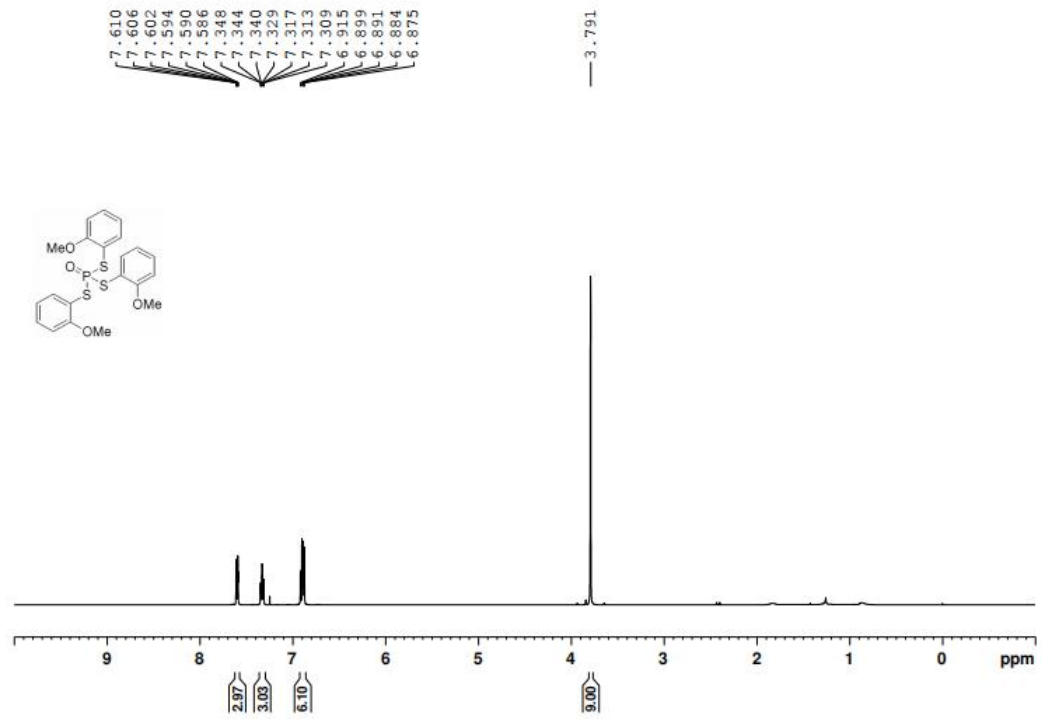
4l


143.46
143.43
137.49
137.46
131.04
131.02
130.25
130.23
126.69
126.68
126.49
126.44
77.44
77.23
77.02
21.58
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

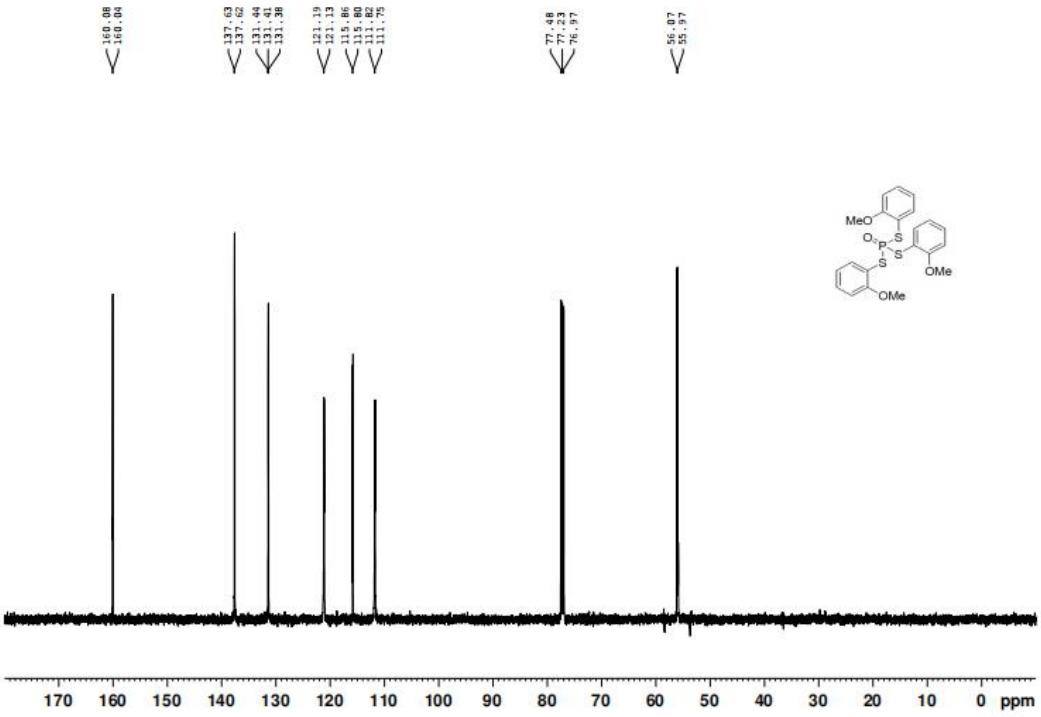
4l


52.52
400
300
200
100
0
−100
−200
−300
−400
ppm

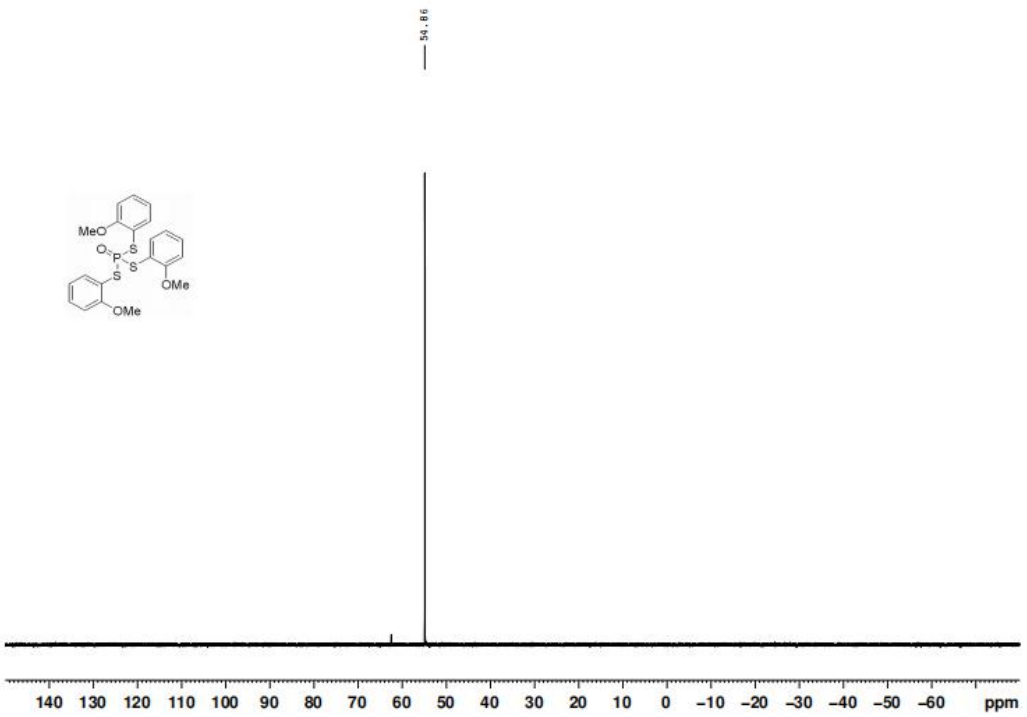
4m


7.610
7.606
7.602
7.594
7.590
7.586
7.348
7.344
7.340
7.329
7.317
7.313
7.309
6.915
6.899
6.891
6.884
6.875
3.791
MeO
OMe
OMe
9
8
7
6
5
4
3
2
1
0
ppm
2.97
3.03
6.10
9.00

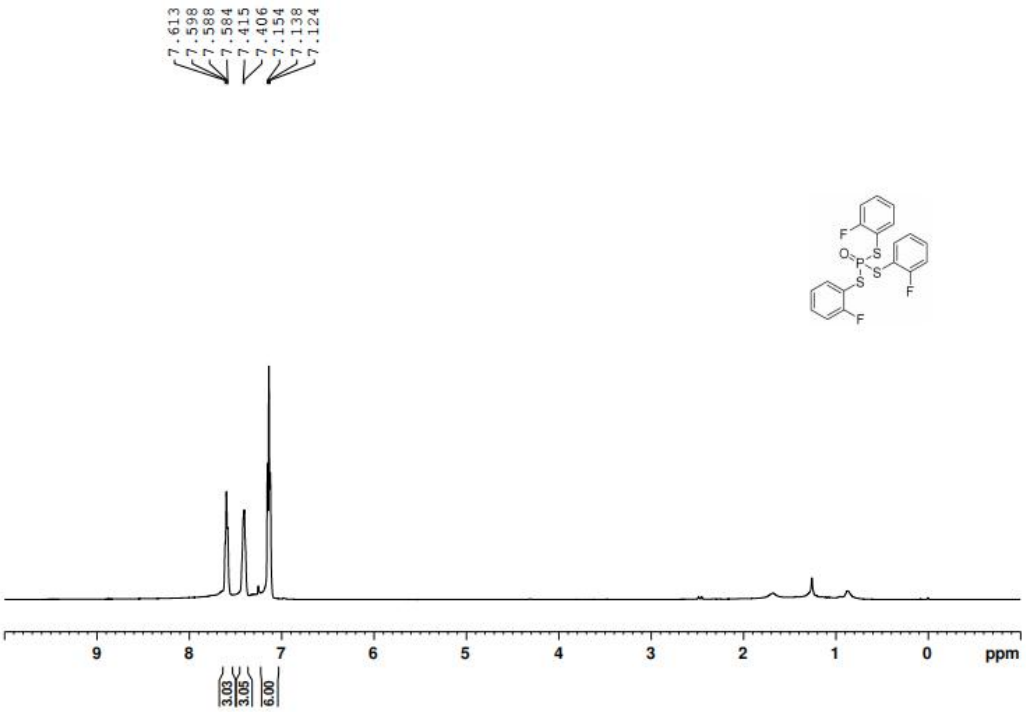
4m


160.08
160.04
137.63
137.62
131.44
131.41
131.38
121.19
121.13
115.86
115.80
111.82
111.75
77.48
77.23
76.97
56.07
55.97
MeO
OMe
OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

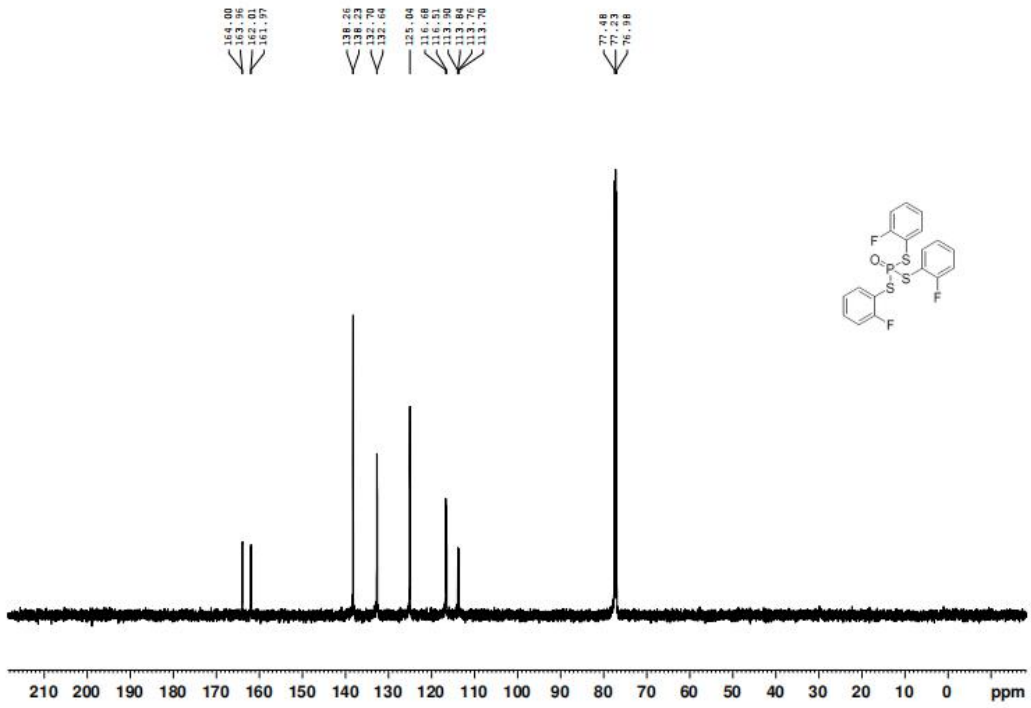
4m


54.86
MeO
OMe
OMe
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

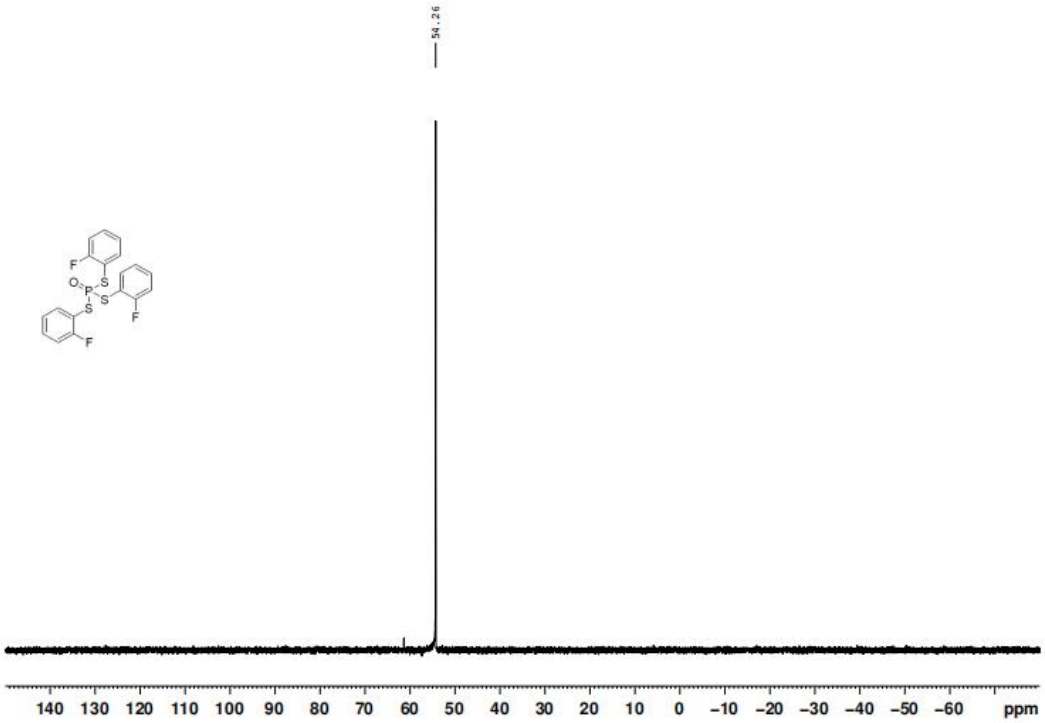
4n


7.613
7.598
7.588
7.584
7.415
7.406
7.154
7.138
7.124
9
8
7
6
5
4
3
2
1
0
ppm
3.03
3.05
6.00

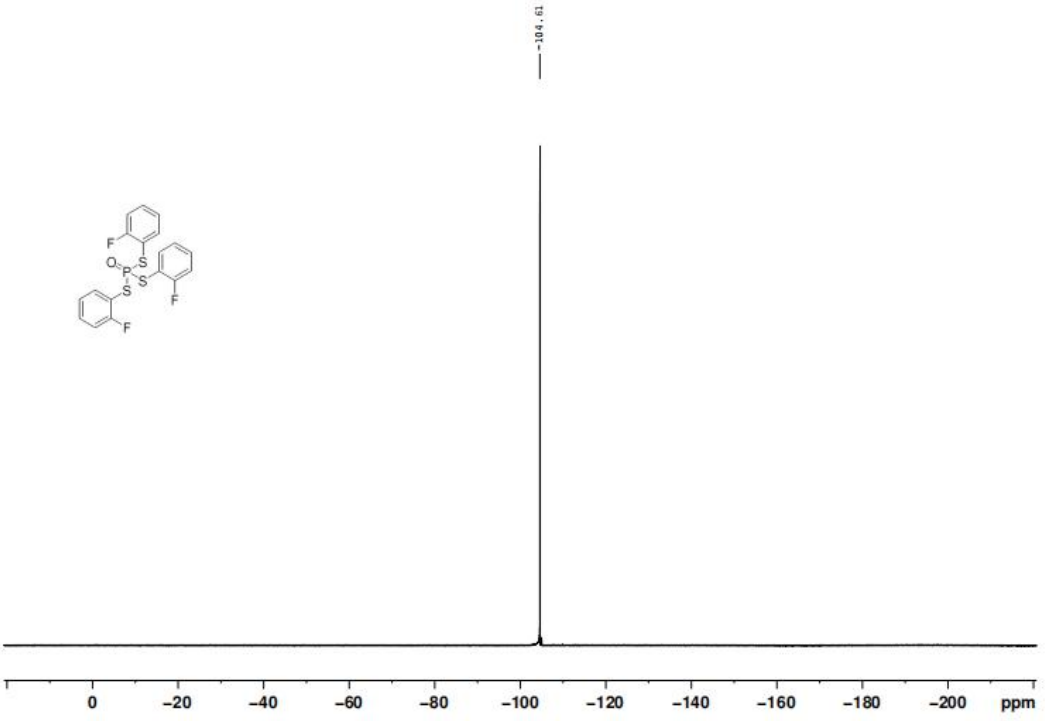
4n


164.00
163.86
162.01
161.97
138.26
138.23
132.70
132.64
125.04
116.68
116.51
113.90
113.84
113.76
113.70
77.48
77.23
76.98
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

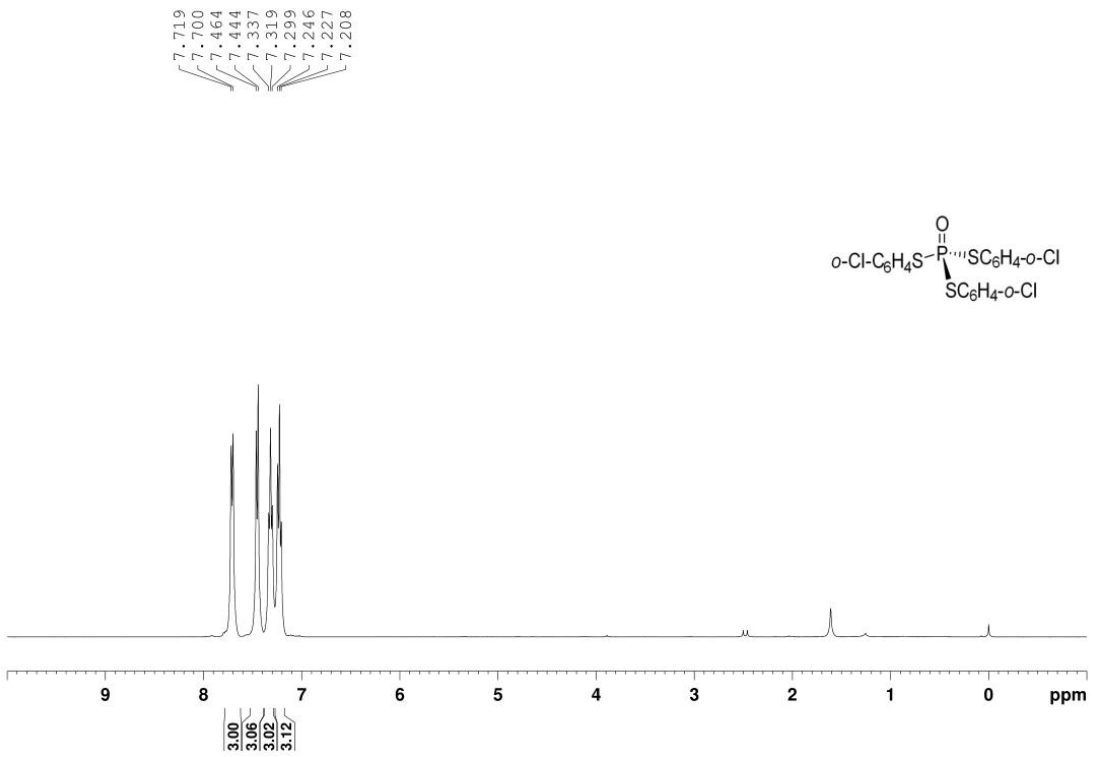
4n


54.26
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

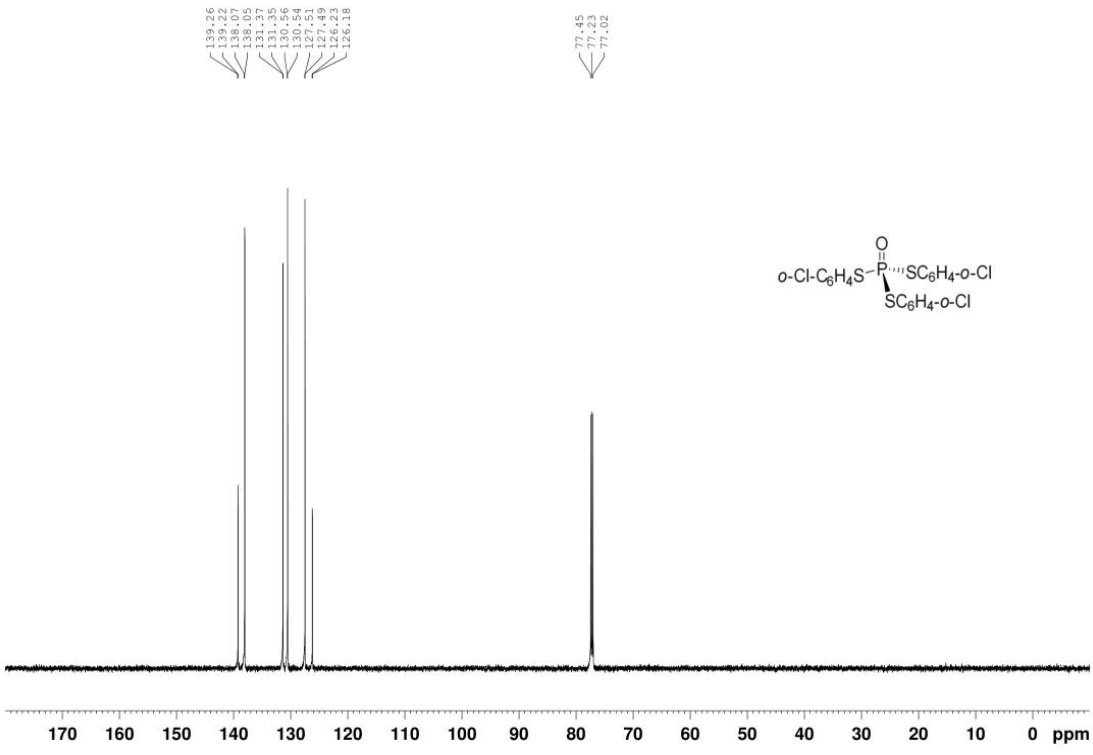
4n


−104.61
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

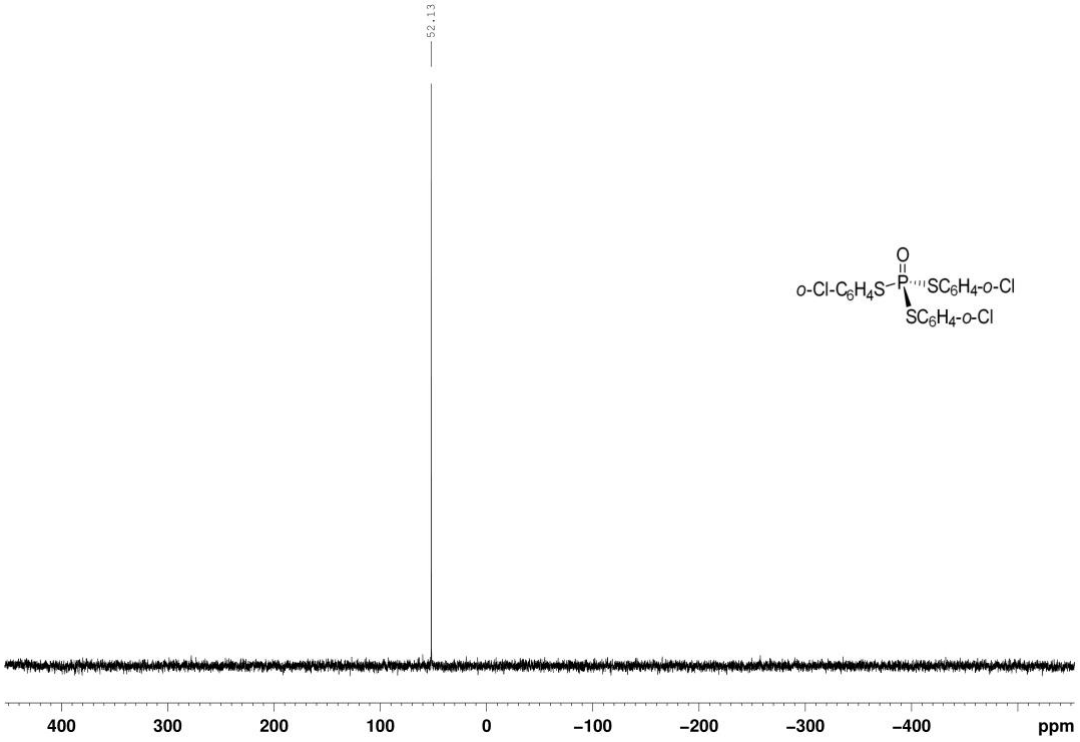
4o


7.719
7.700
7.464
7.444
7.337
7.319
7.299
7.246
7.227
7.208
o-Cl-C6H4S
P
O
SC6H4-o-Cl
SC6H4-o-Cl
9
8
7
6
5
4
3
2
1
0
ppm
3.00
3.06
3.02
3.12

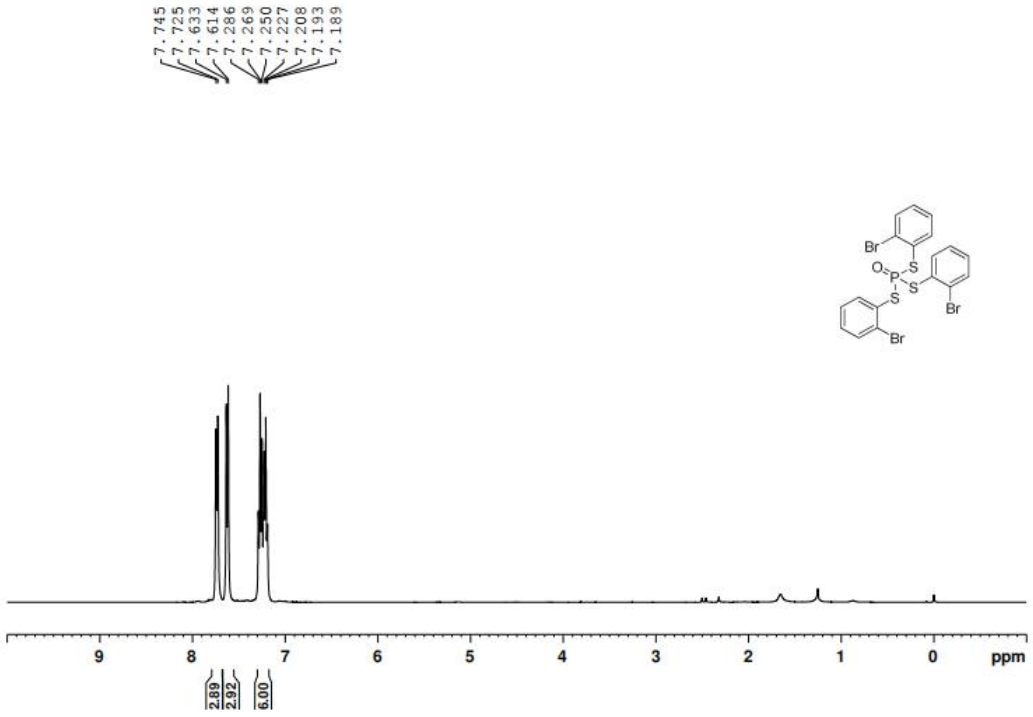
4o


139.26
139.22
138.07
138.05
131.37
131.35
130.56
130.54
127.51
127.49
126.23
126.18
77.45
77.23
77.02
o-Cl-C6H4S
P
O
SC6H4-o-Cl
SC6H4-o-Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

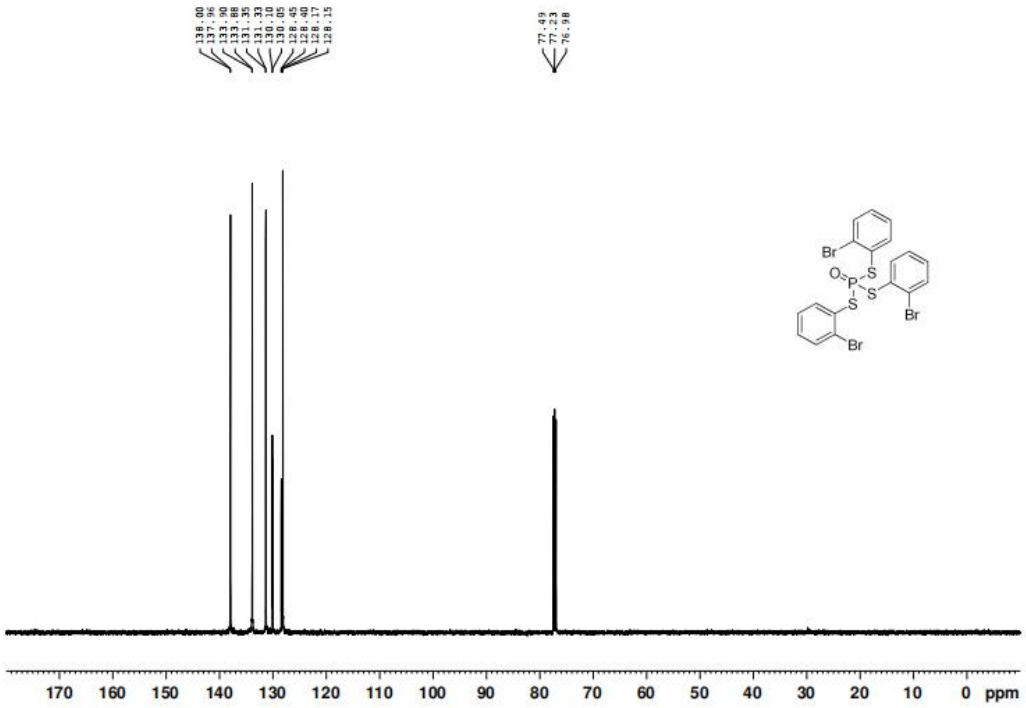
4o


52.13
o-Cl-C6H4S
P
O
SC6H4-o-Cl
SC6H4-o-Cl
400
300
200
100
0
−100
−200
−300
−400
ppm

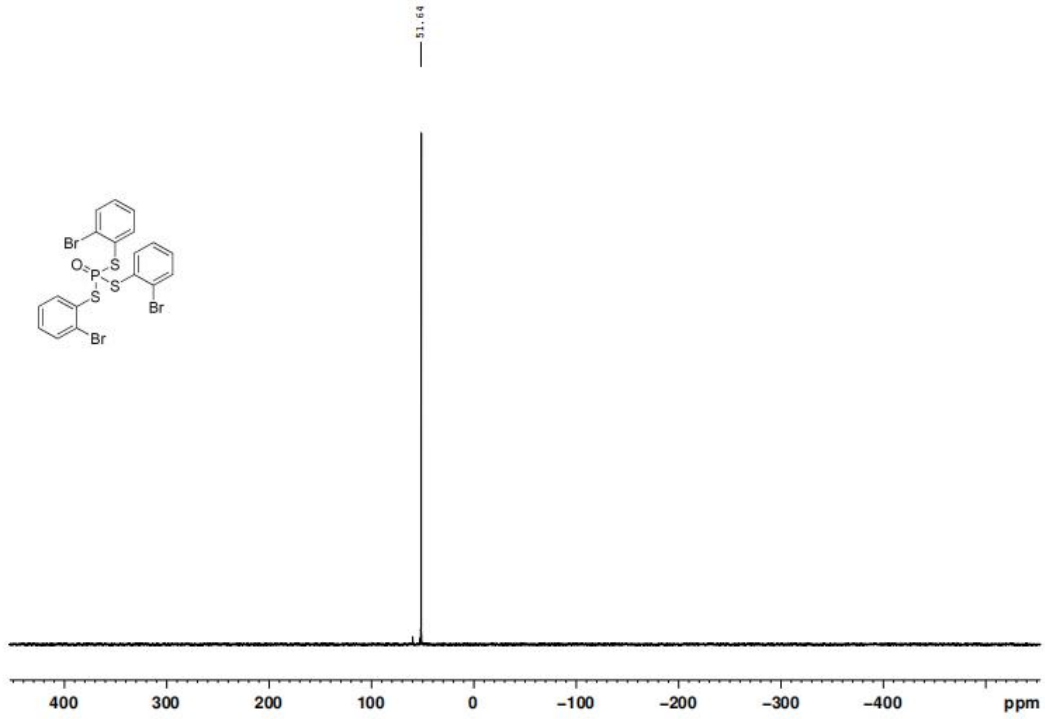
4p


7.745
7.725
7.633
7.614
7.286
7.269
7.250
7.227
7.208
7.193
7.189
Br
O
P
S
S
S
Br
Br
9
8
7
6
5
4
3
2
1
0
ppm
2.89
2.92
6.00

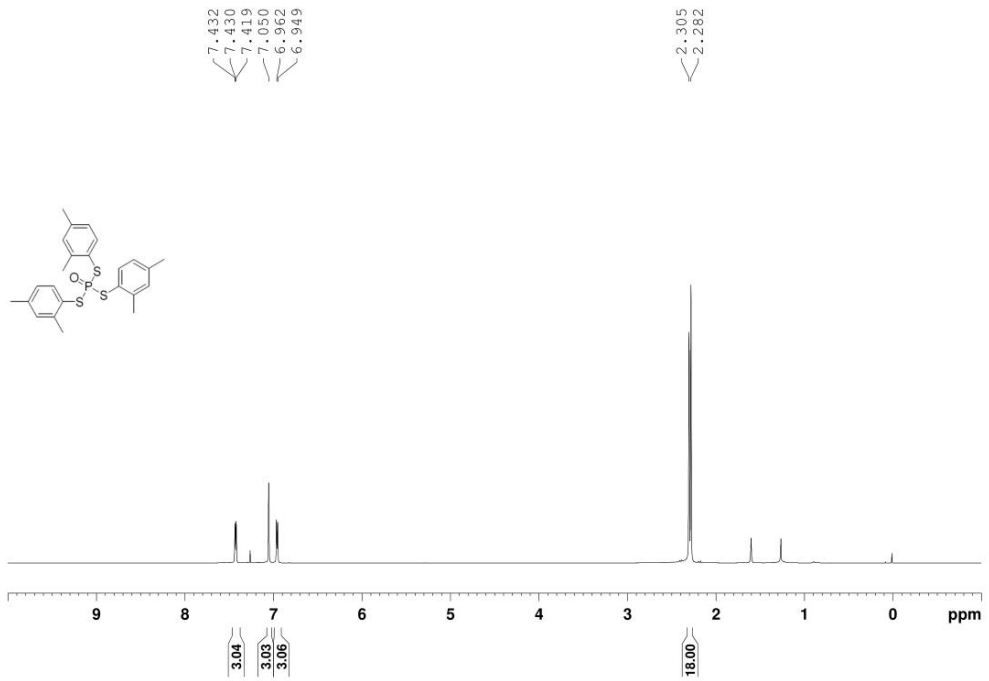
4p


138.00
137.96
133.90
133.88
131.35
131.33
130.10
130.05
128.45
128.40
128.17
128.15
77.49
77.23
76.98
Br
O
P
S
S
S
Br
Br
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

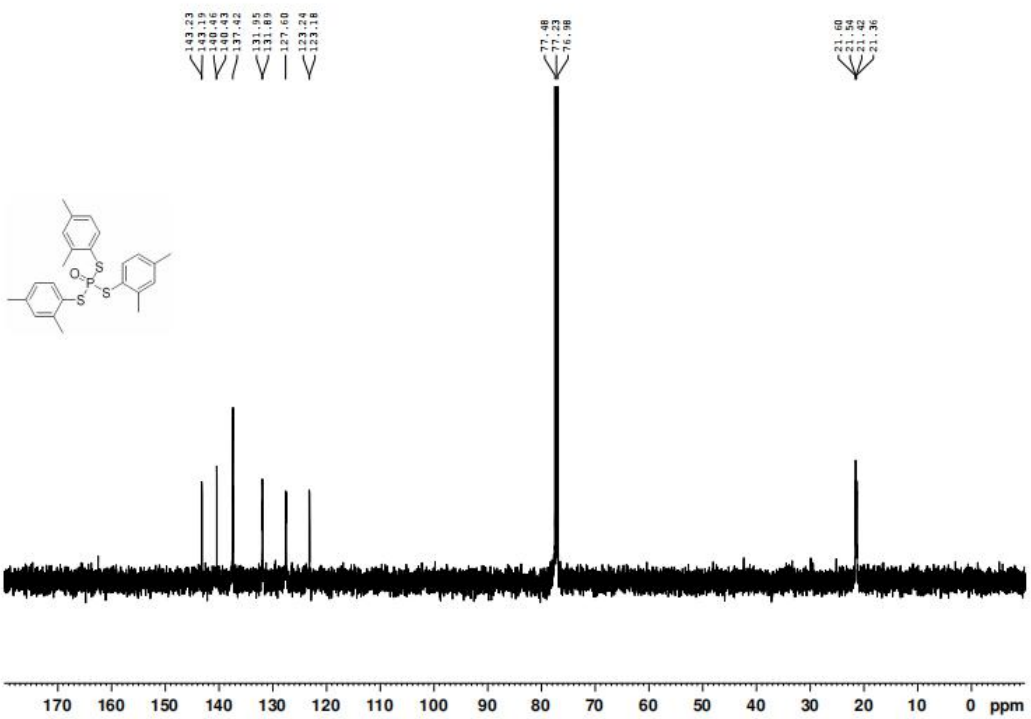
4p


51.64
Br
O
P
S
S
S
Br
Br
400 300 200 100 0 -100 -200 -300 -400 ppm

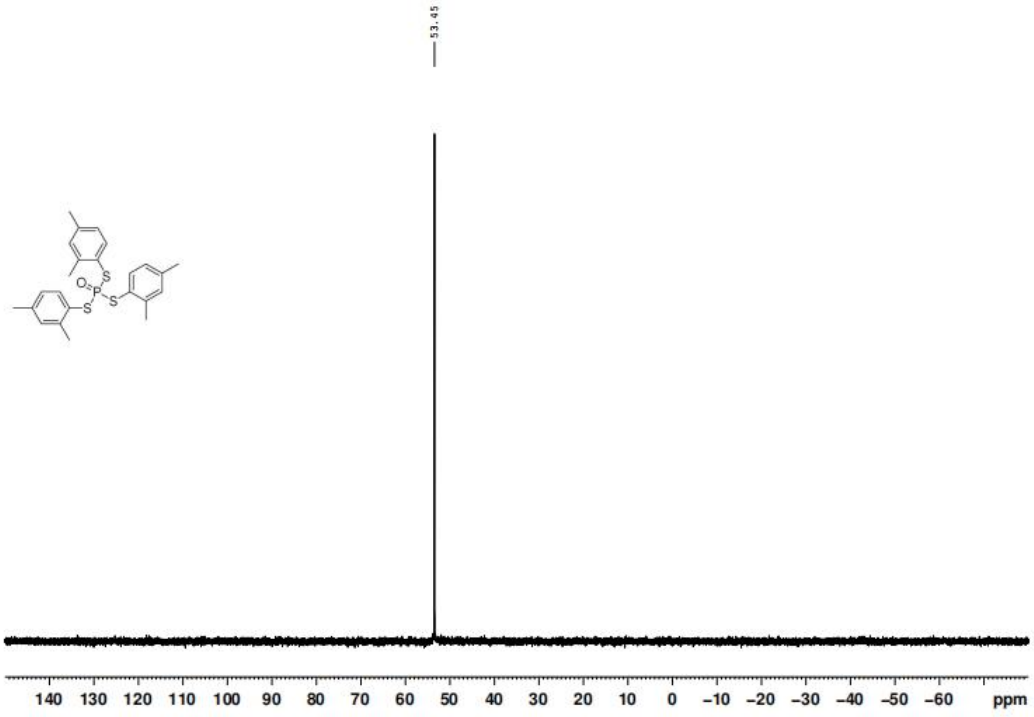
4q


7.432
7.430
7.419
7.050
6.962
6.949
2.305
2.282
9
8
7
6
5
4
3
2
1
0
ppm
3.04
3.03
3.06
18.00

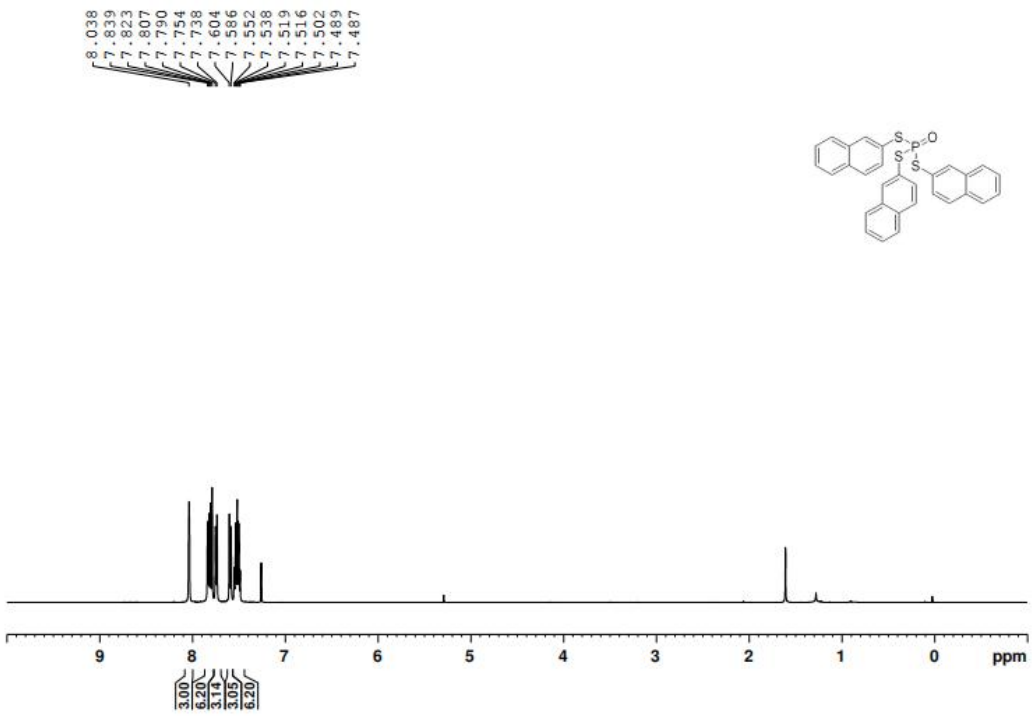
4q


143.23
143.19
140.46
140.43
137.42
131.95
131.89
127.60
123.24
123.18
77.48
77.23
76.98
21.60
21.54
21.42
21.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

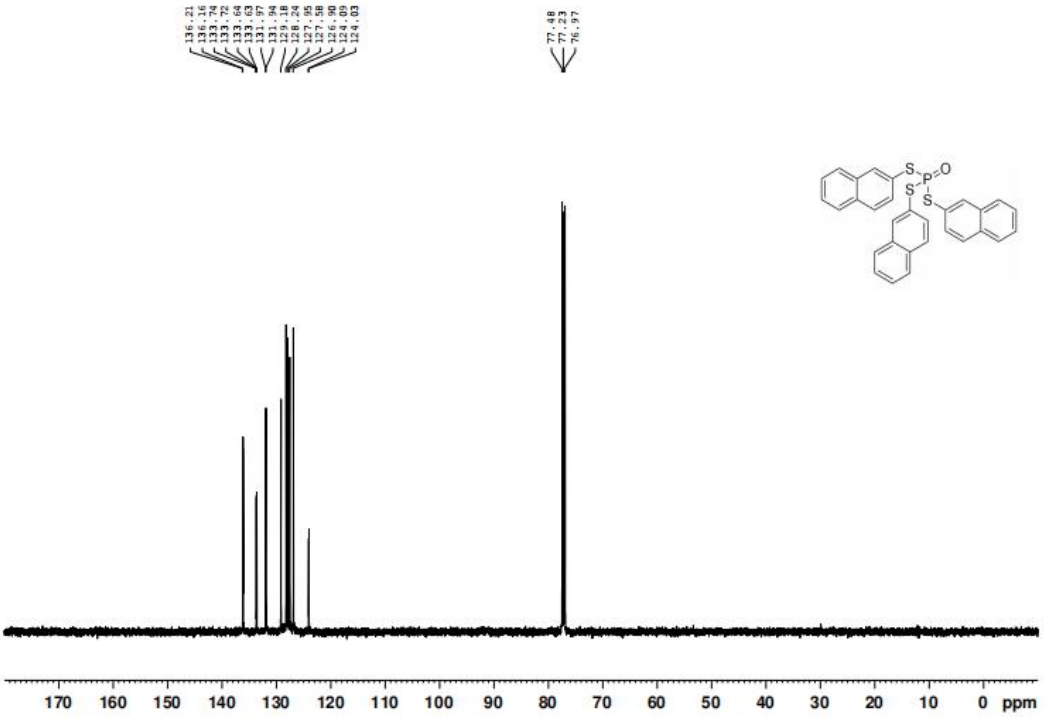
4q


53.45
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 ppm

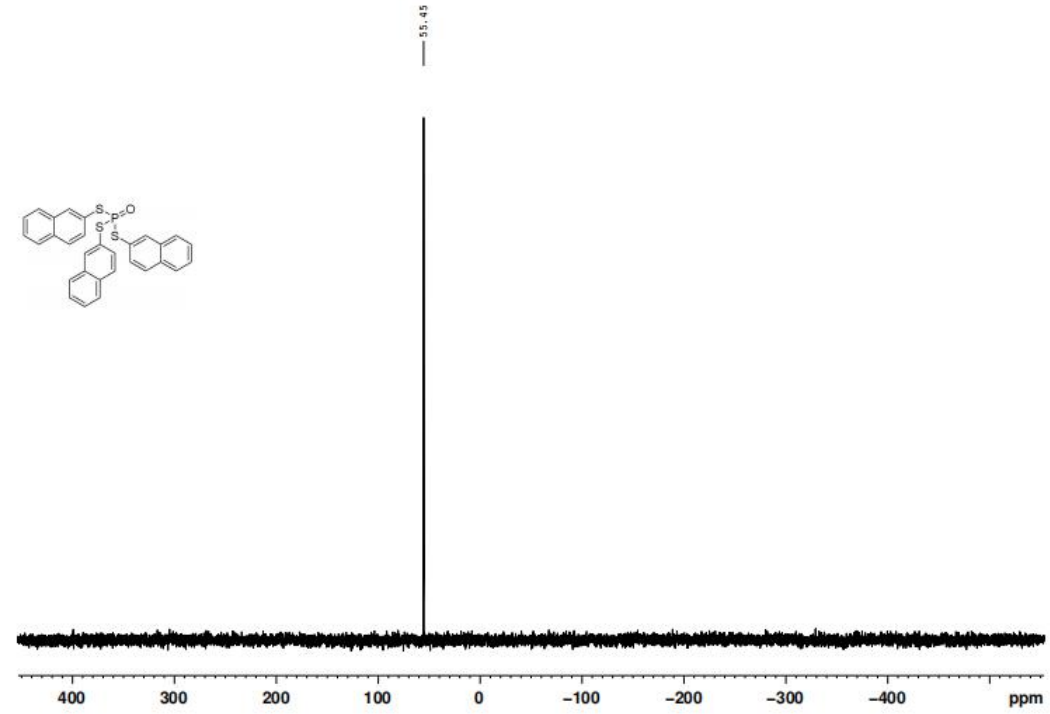
4r


8.038
7.839
7.823
7.807
7.790
7.754
7.738
7.604
7.586
7.552
7.538
7.519
7.516
7.502
7.489
7.487
9 8 7 6 5 4 3 2 1 0 ppm
3.00
6.20
3.14
3.05
6.20

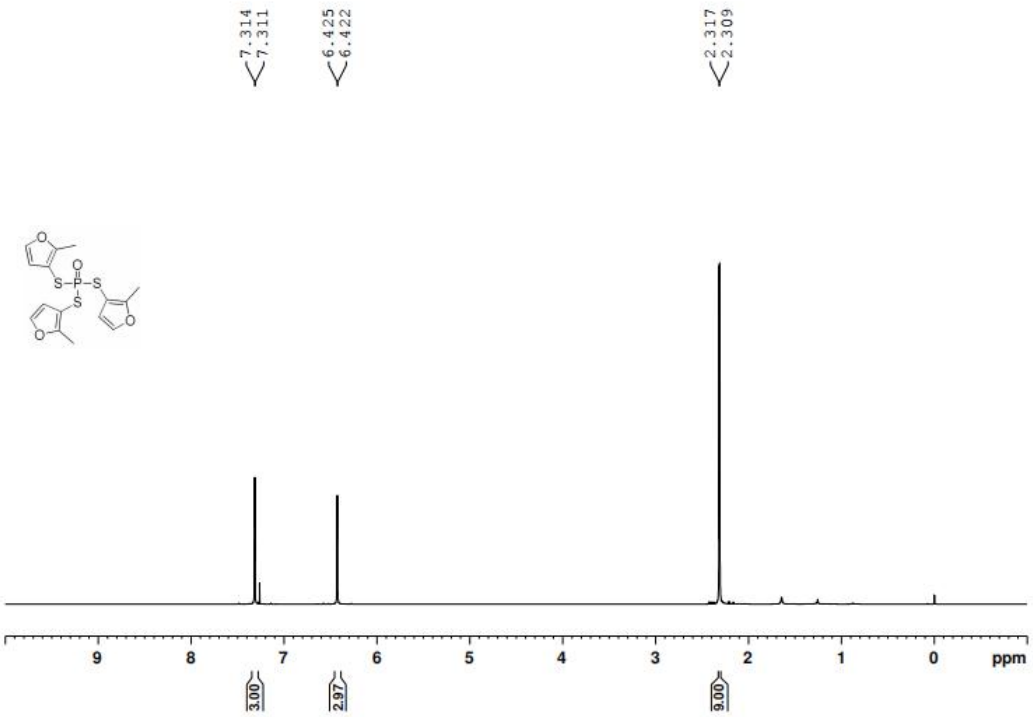
4r


136.21
136.16
133.74
133.72
133.64
133.45
131.97
131.94
129.18
128.24
127.95
127.88
126.90
124.09
124.03
77.48
77.23
76.97
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

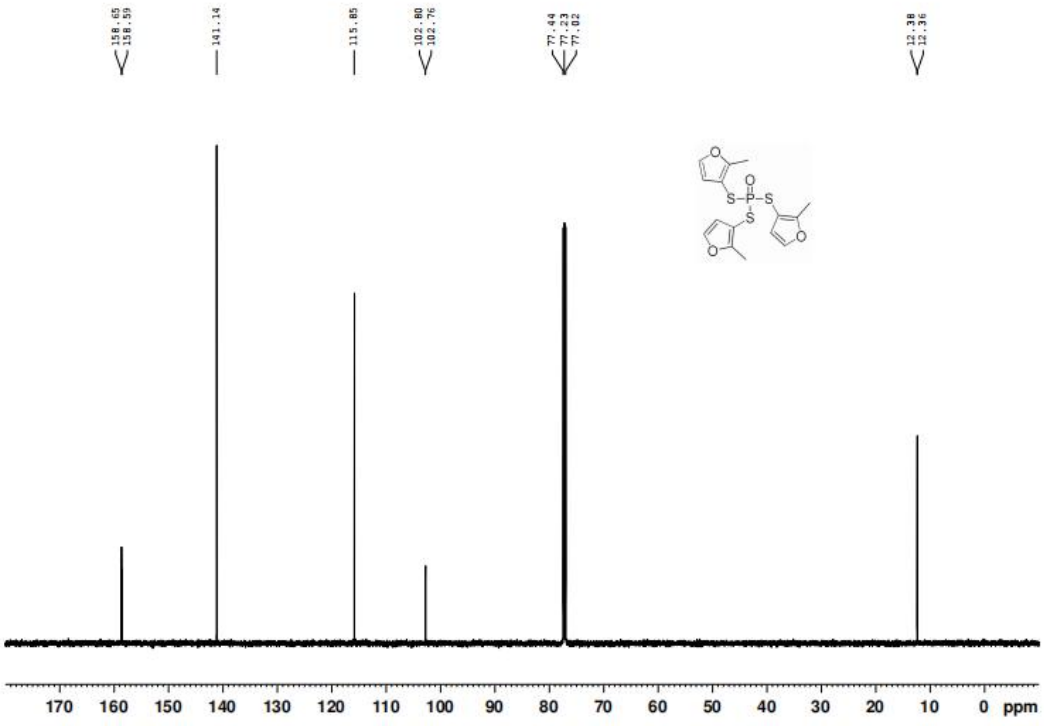
4r


55.45
400 300 200 100 0 -100 -200 -300 -400 ppm

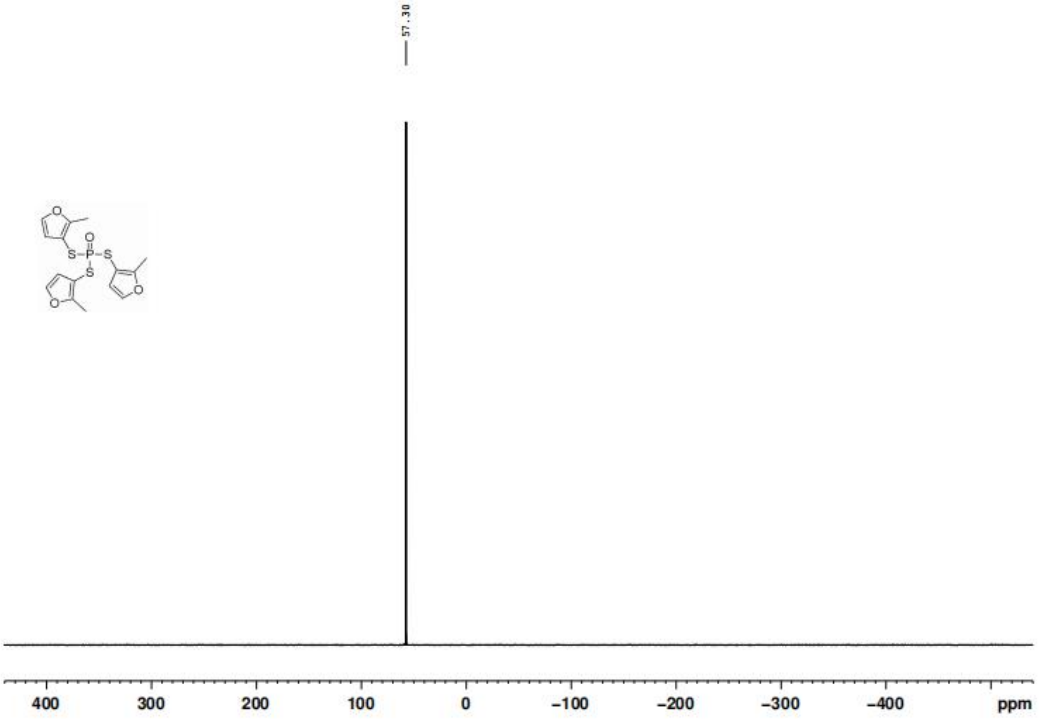
4s


7.314
7.311
6.425
6.422
2.317
2.309
9
8
7
6
5
4
3
2
1
0
ppm
3.00
2.97
9.00

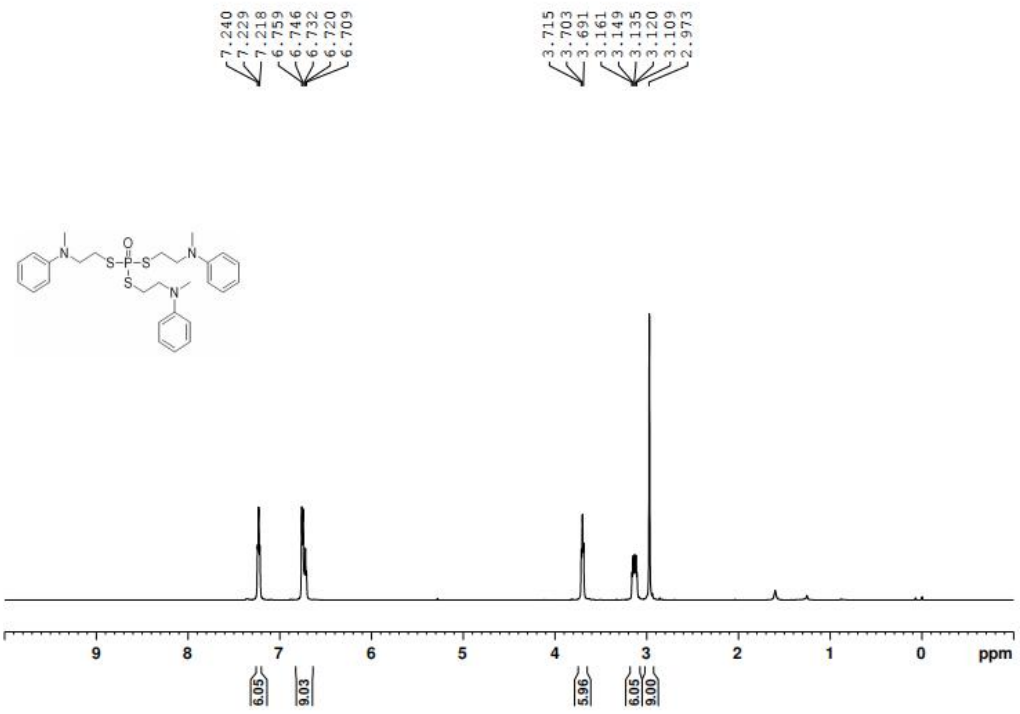
4s


158.65
158.59
141.14
115.85
102.80
102.76
77.44
77.23
77.02
12.38
12.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

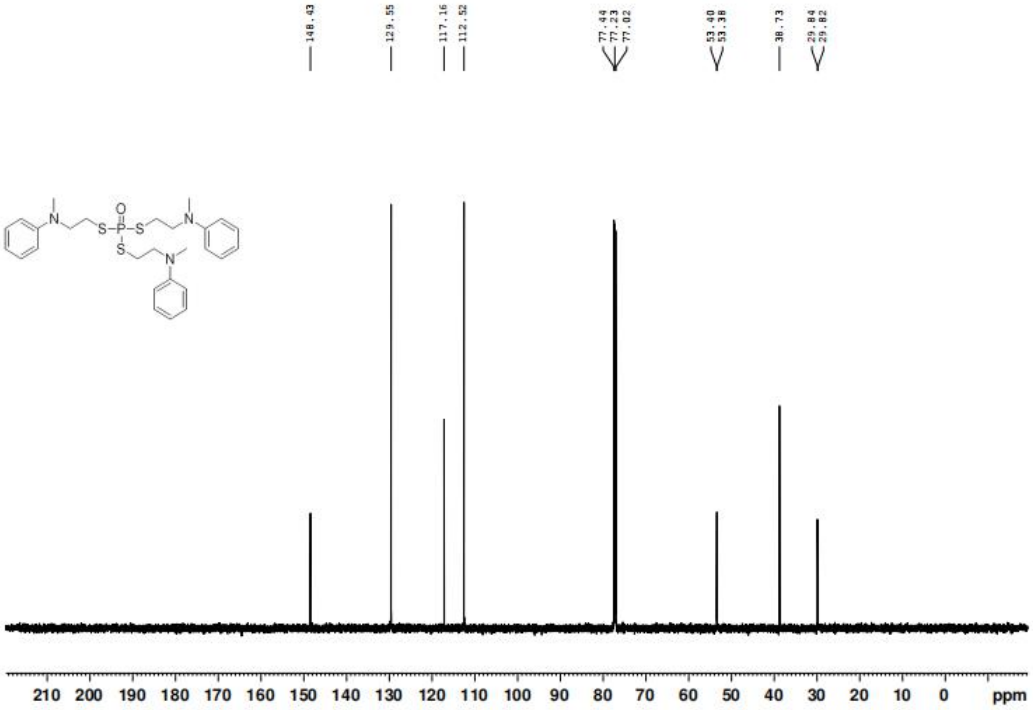
4s


57.30
400
300
200
100
0
−100
−200
−300
−400
ppm

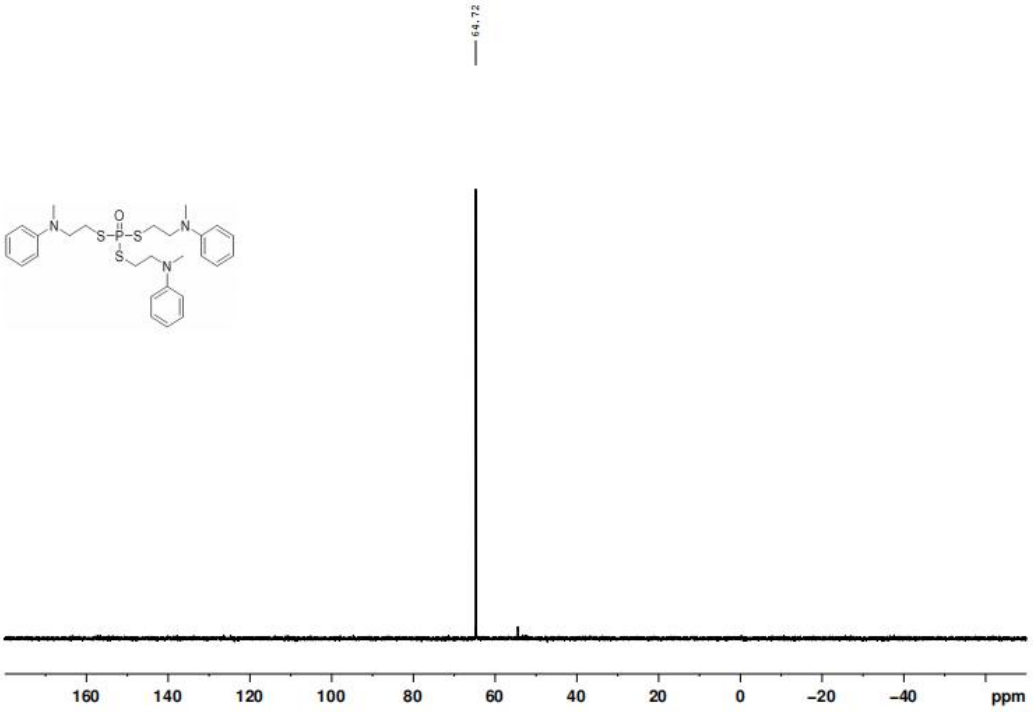
4t


7.240
7.229
7.218
6.759
6.746
6.732
6.720
6.709
3.715
3.703
3.691
3.161
3.149
3.135
3.120
3.109
2.973
9
8
7
6
5
4
3
2
1
0
ppm
6.05
9.03
5.96
6.05
9.00

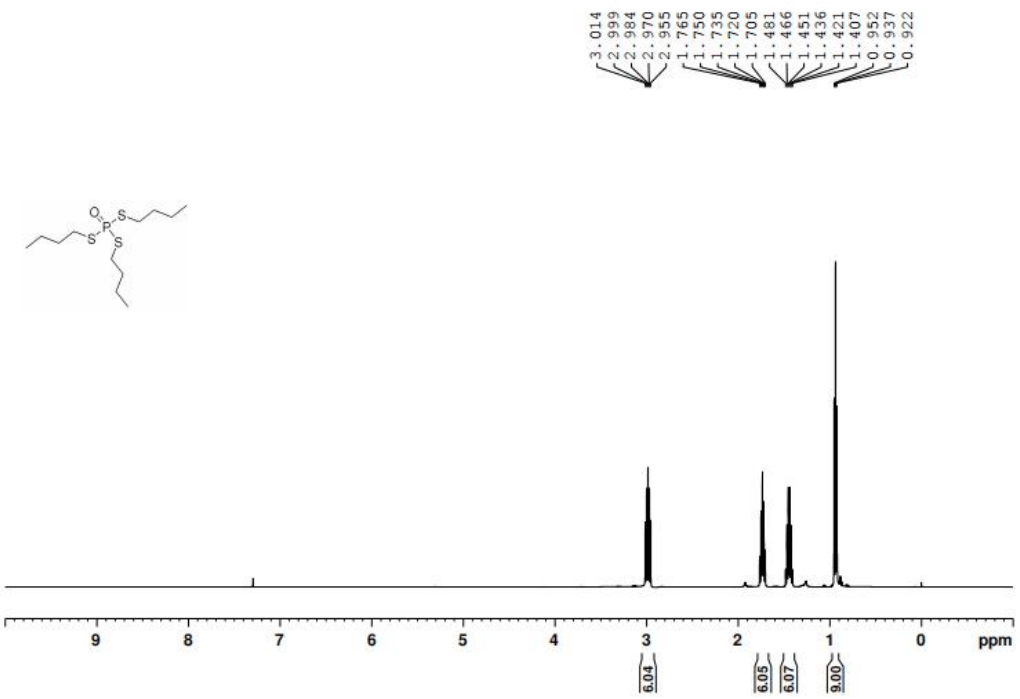
4t


148.43
129.55
117.16
112.52
77.49
77.23
77.02
53.40
53.38
38.73
29.84
29.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

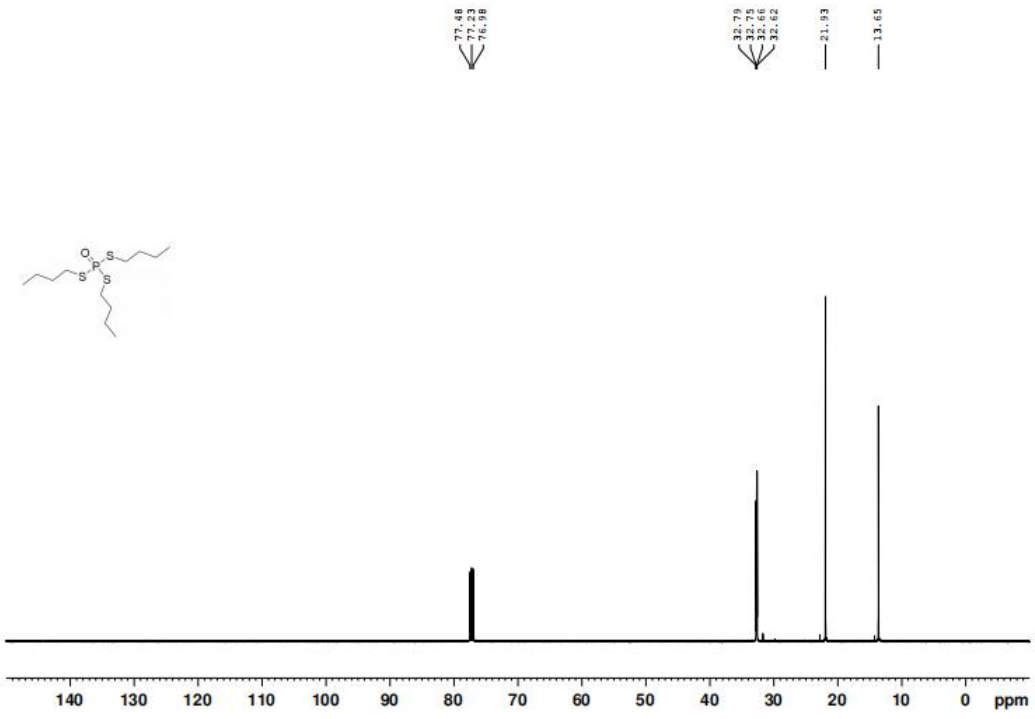
4t


64.72
160 140 120 100 80 60 40 20 0 -20 -40 ppm

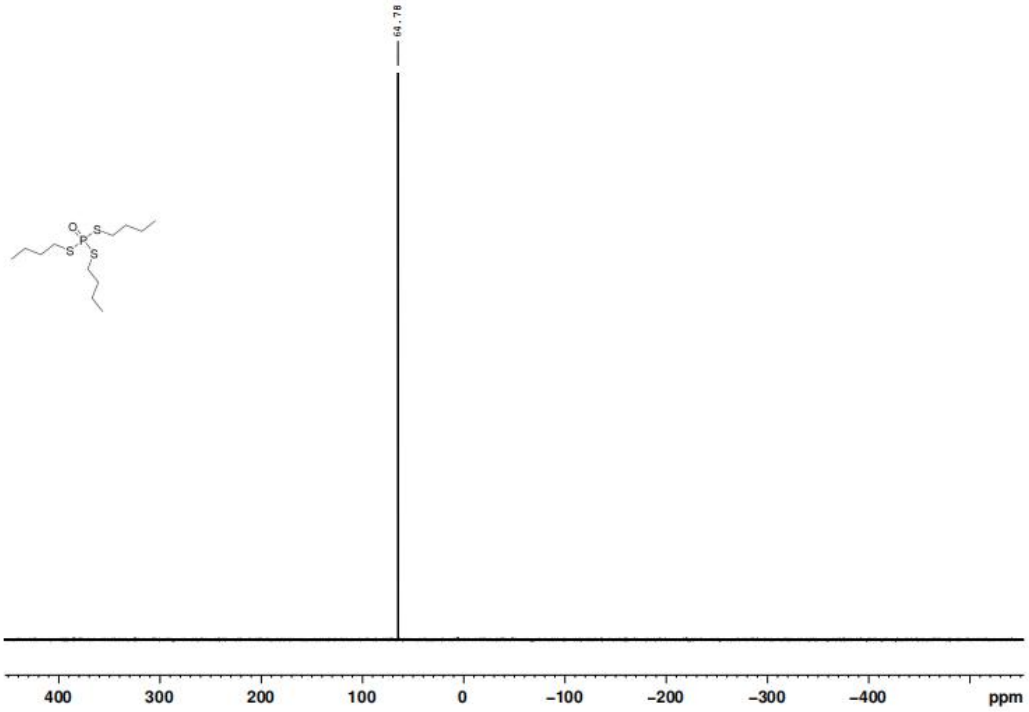
4u


3.014
2.999
2.984
2.970
2.955
1.765
1.750
1.735
1.720
1.705
1.481
1.466
1.451
1.436
1.421
1.407
0.952
0.937
0.922
9
8
7
6
5
4
3
2
1
0
ppm
6.04
6.05
6.07
9.00

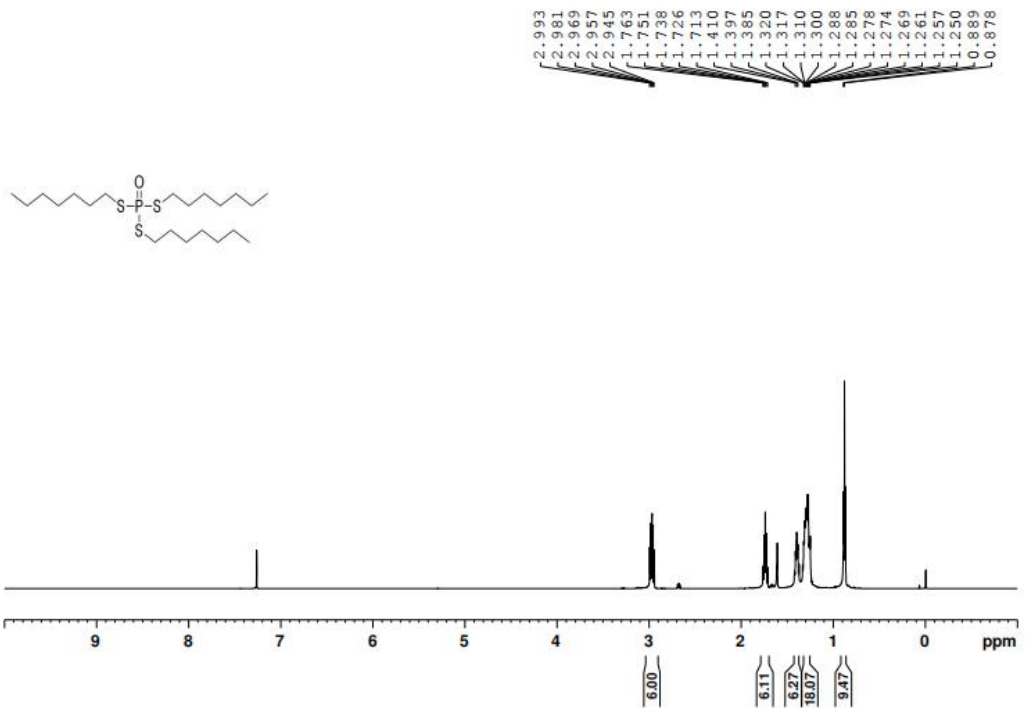
4u


77.48
77.23
76.98
32.79
32.75
32.66
32.62
21.93
13.65
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

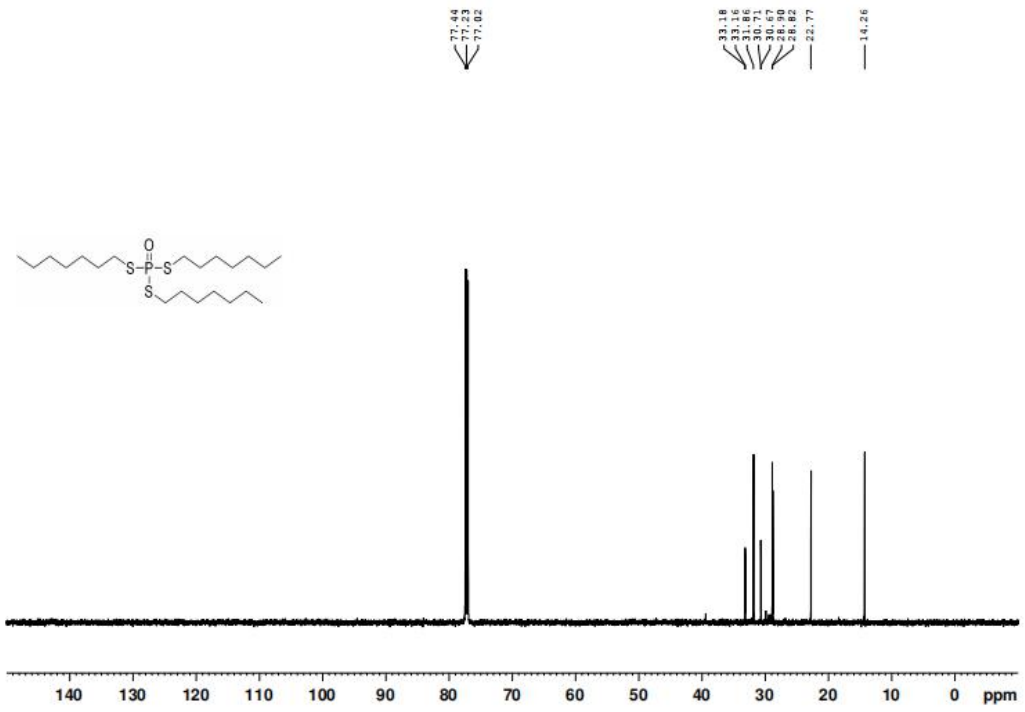
4u


64.78
400
300
200
100
0
-100
-200
-300
-400
ppm

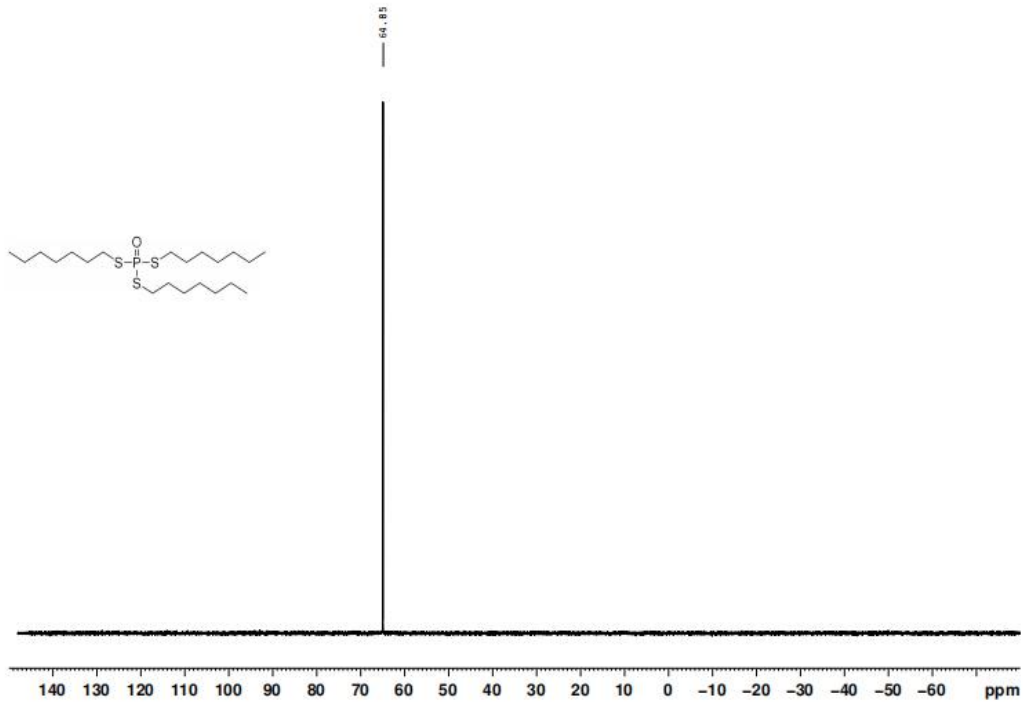
4v


2.993
2.981
2.969
2.957
2.945
1.763
1.751
1.738
1.726
1.713
1.410
1.397
1.385
1.320
1.317
1.310
1.300
1.288
1.285
1.278
1.274
1.269
1.261
1.257
1.250
0.889
0.878
9
8
7
6
5
4
3
2
1
0
ppm
6.00
6.11
6.27
18.07
9.47

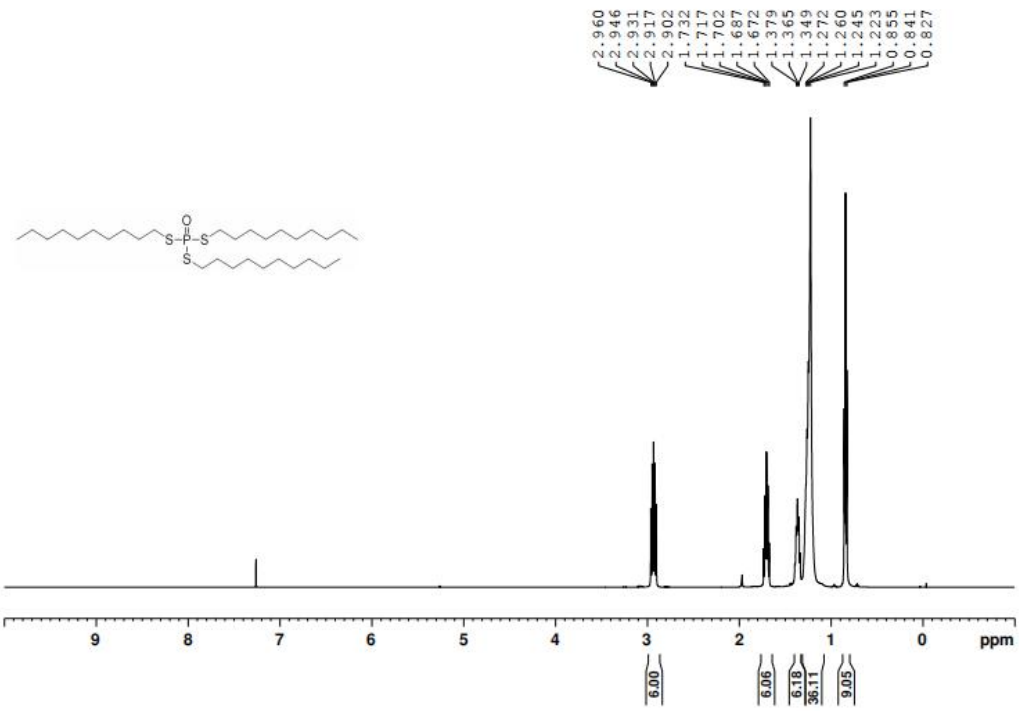
4v


77.44
77.23
77.02
33.18
33.16
31.86
30.71
30.67
28.90
28.82
22.77
14.26
O
S
P
S
S
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

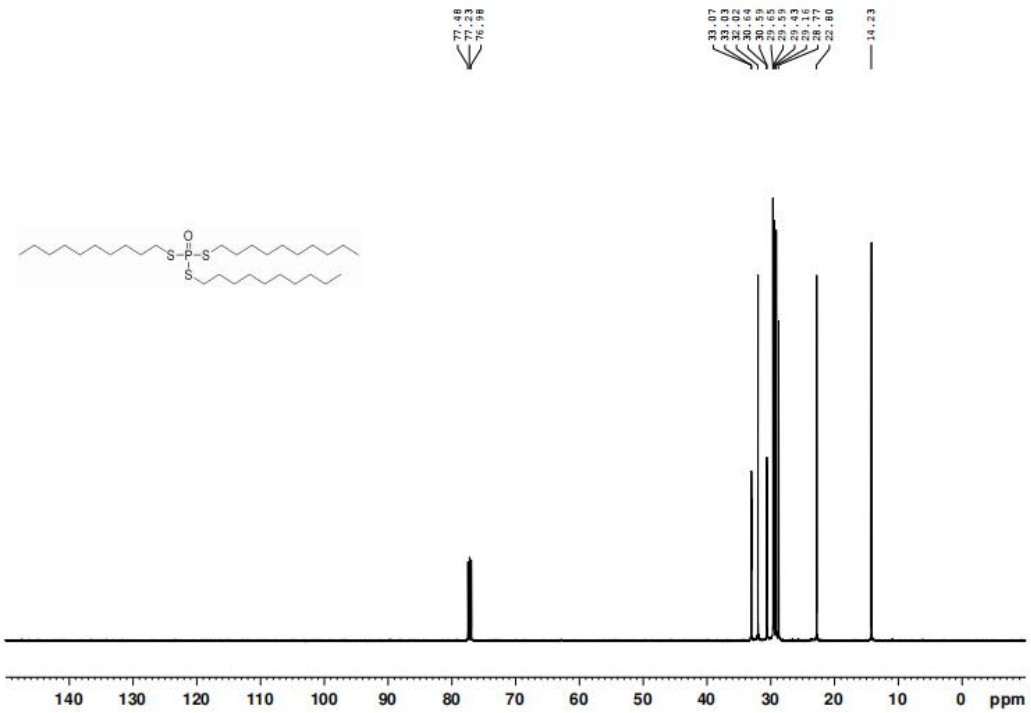
4v


64.85
O
S
P
S
S
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

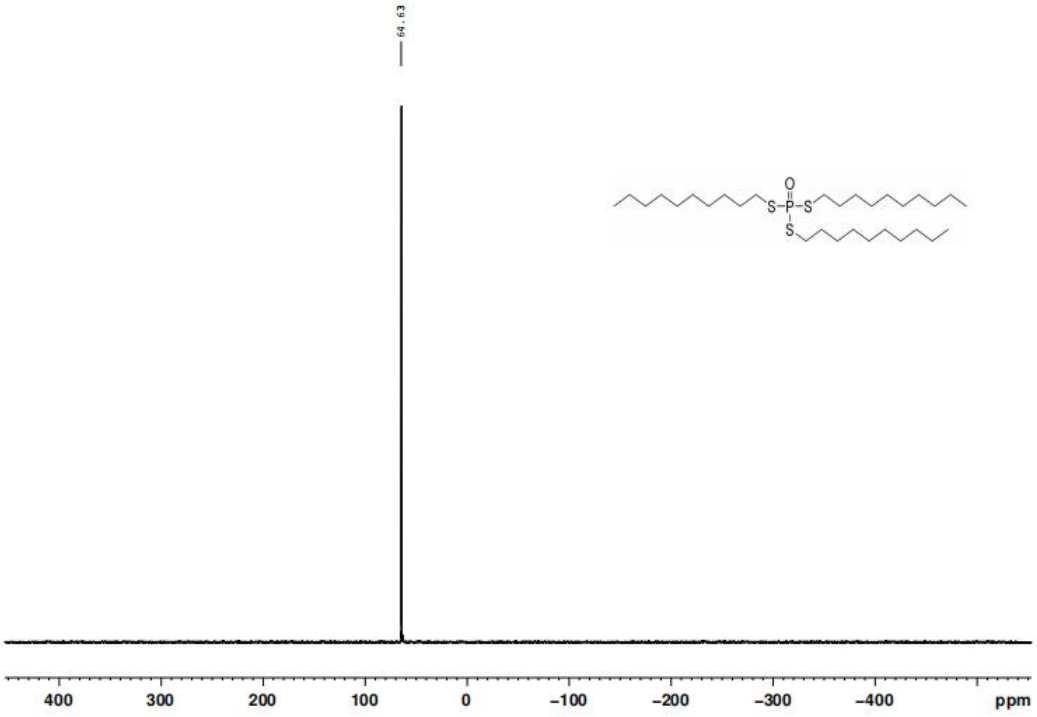
4w


2.960
2.946
2.931
2.917
2.902
1.732
1.717
1.702
1.687
1.672
1.379
1.365
1.349
1.272
1.260
1.245
1.223
0.855
0.841
0.827
9
8
7
6
5
4
3
2
1
0
ppm
6.00
6.06
6.18
36.11
9.05

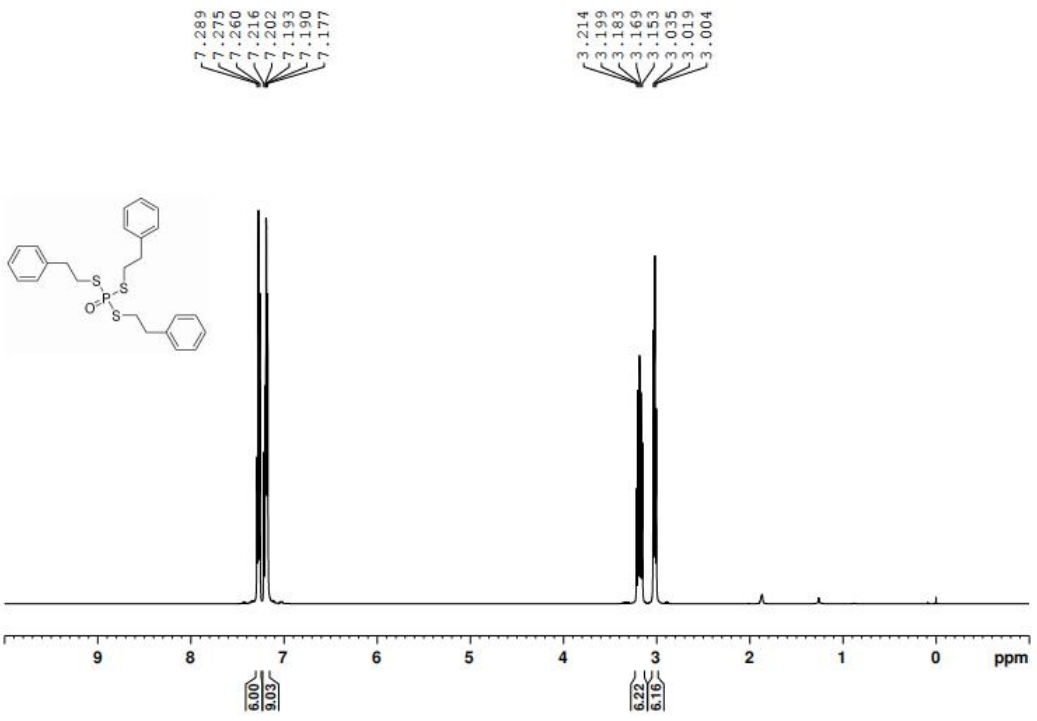
4w


77.48
77.23
76.98
33.07
33.03
32.02
30.64
30.59
29.65
29.55
29.43
29.16
28.77
22.80
14.23
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

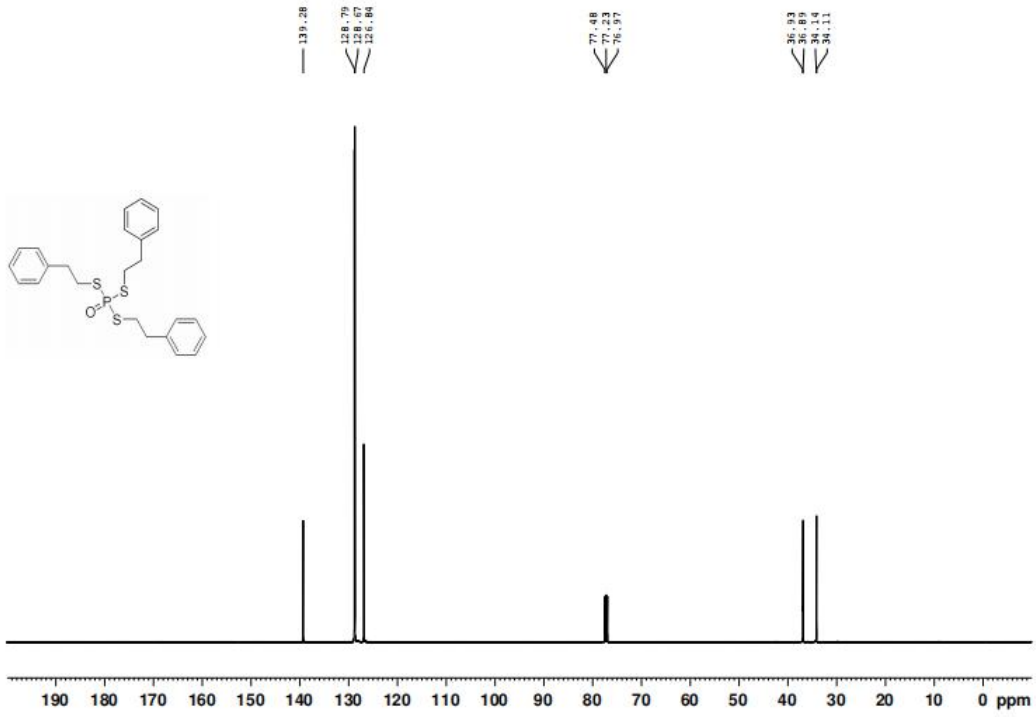
4w


64.63
400
300
200
100
0
−100
−200
−300
−400
ppm

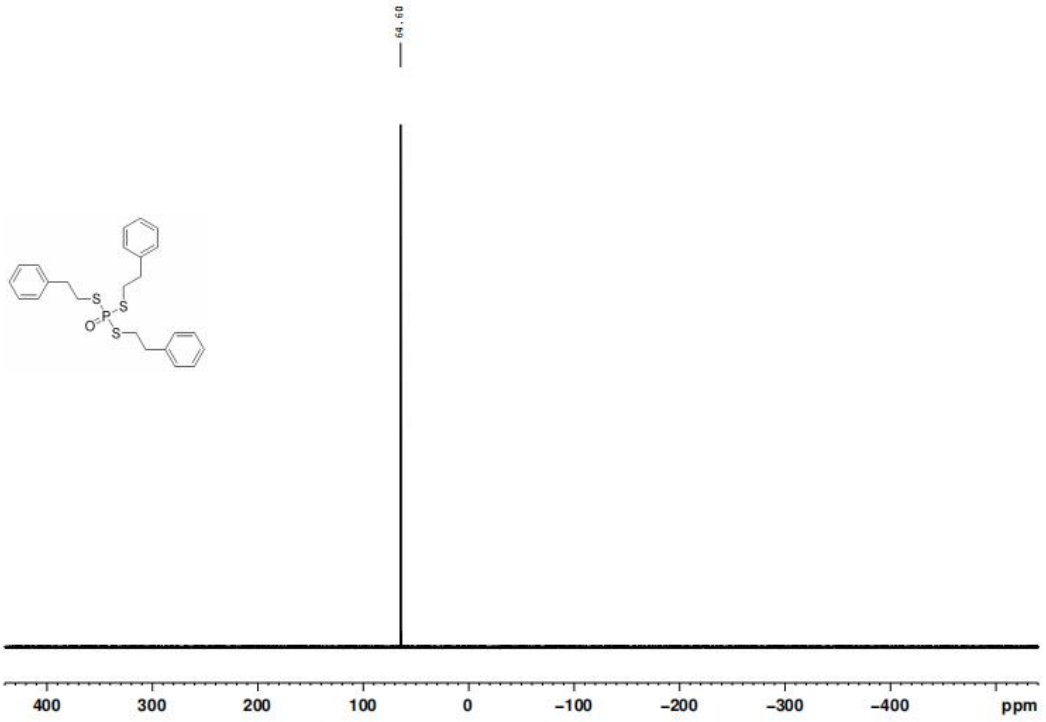
4x


7.289
7.275
7.260
7.216
7.202
7.193
7.190
7.177
3.214
3.199
3.183
3.169
3.153
3.035
3.019
3.004
9
8
7
6
5
4
3
2
1
0
ppm
6.00
9.03
6.22
6.16

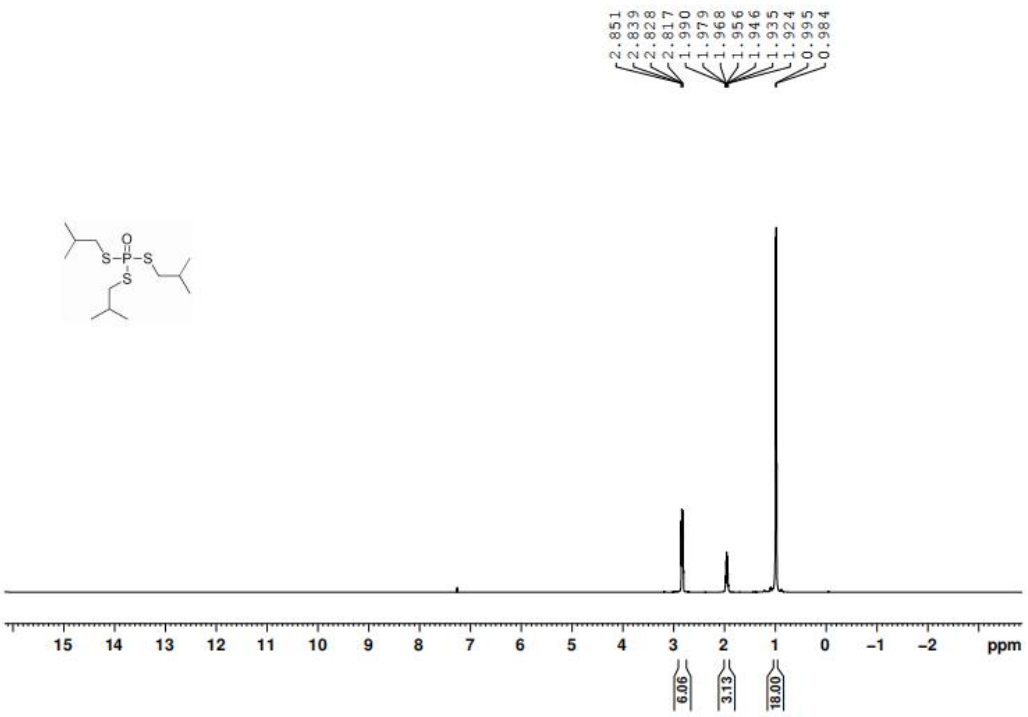
4x


139.28
128.79
128.67
126.84
77.48
77.23
76.97
36.93
36.89
34.14
34.11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

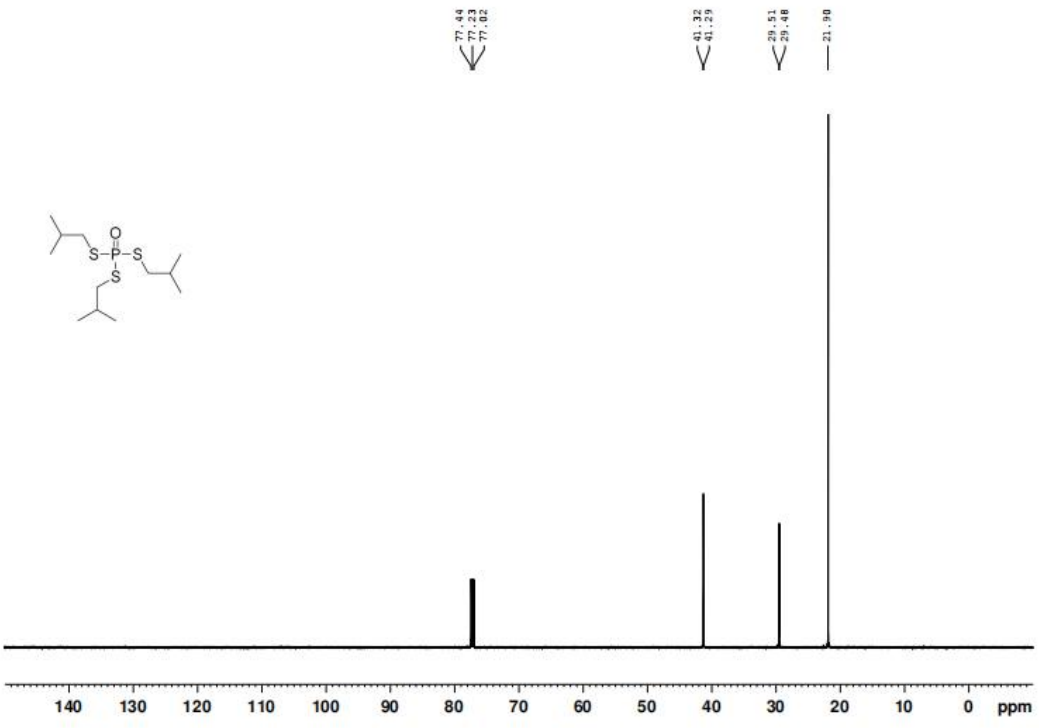
4x


64.60
400 300 200 100 0 −100 −200 −300 −400 ppm

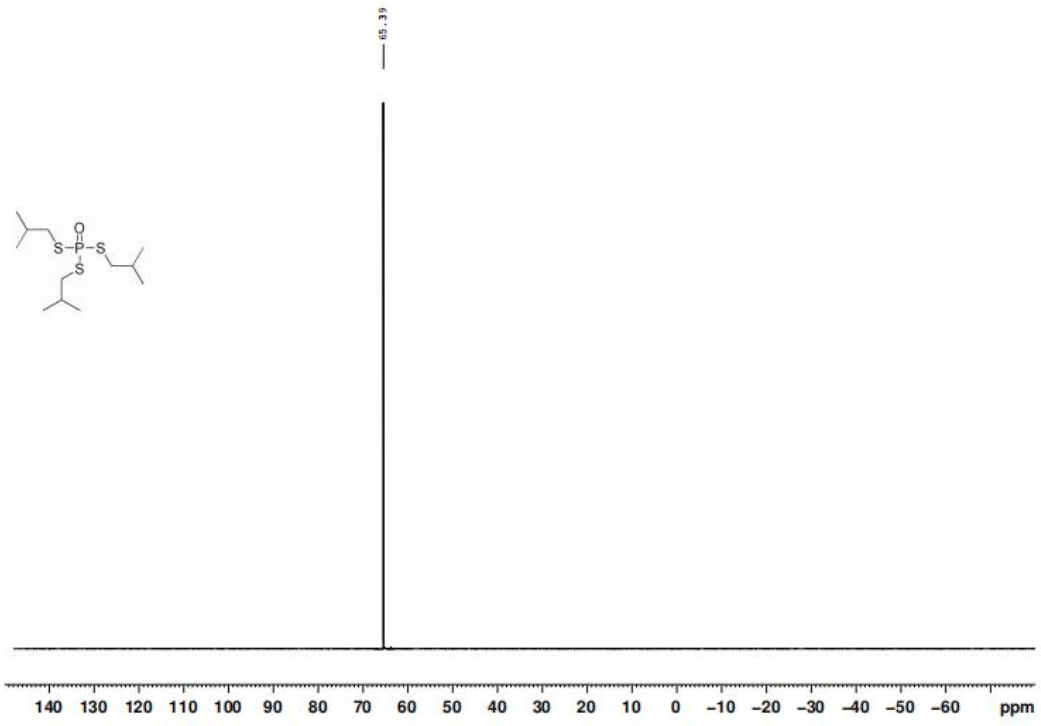
4y


2.851
2.839
2.828
2.817
1.990
1.979
1.968
1.956
1.946
1.935
1.924
0.995
0.984
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
6.06
3.13
18.00

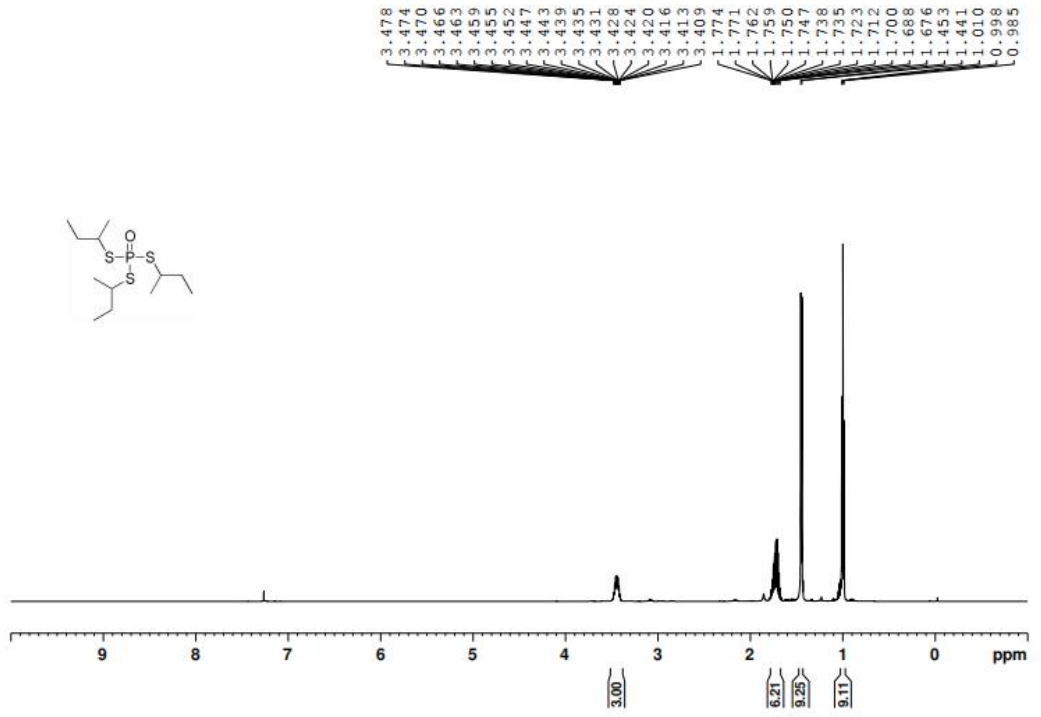
4y


77.44
77.23
77.02
41.32
41.29
29.51
29.48
21.90
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

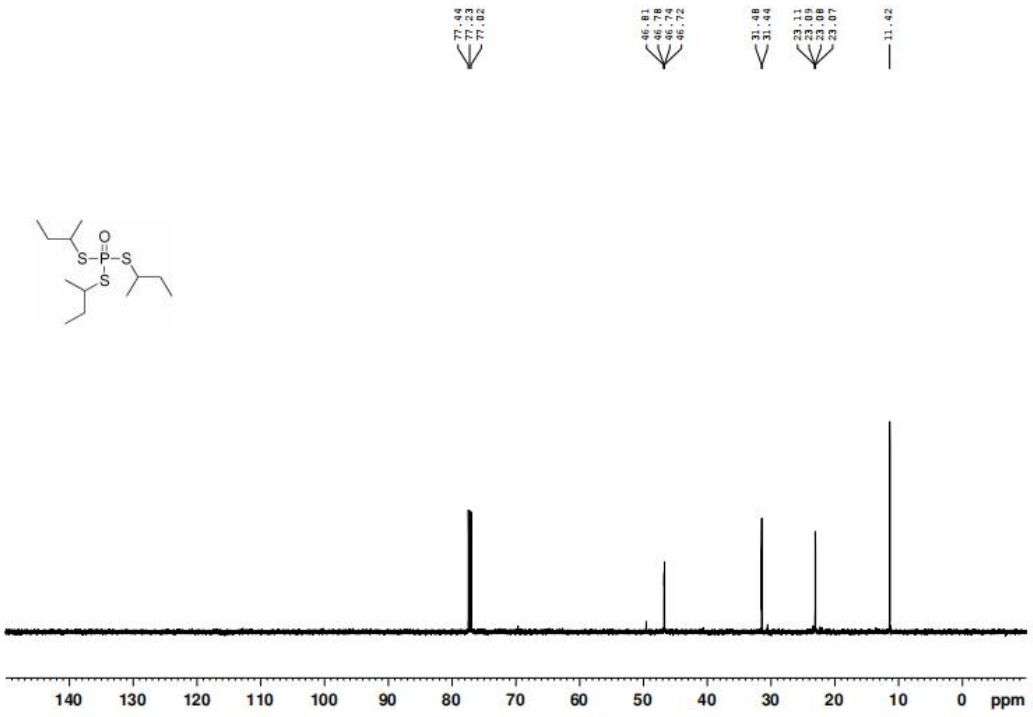
4y


65.39
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

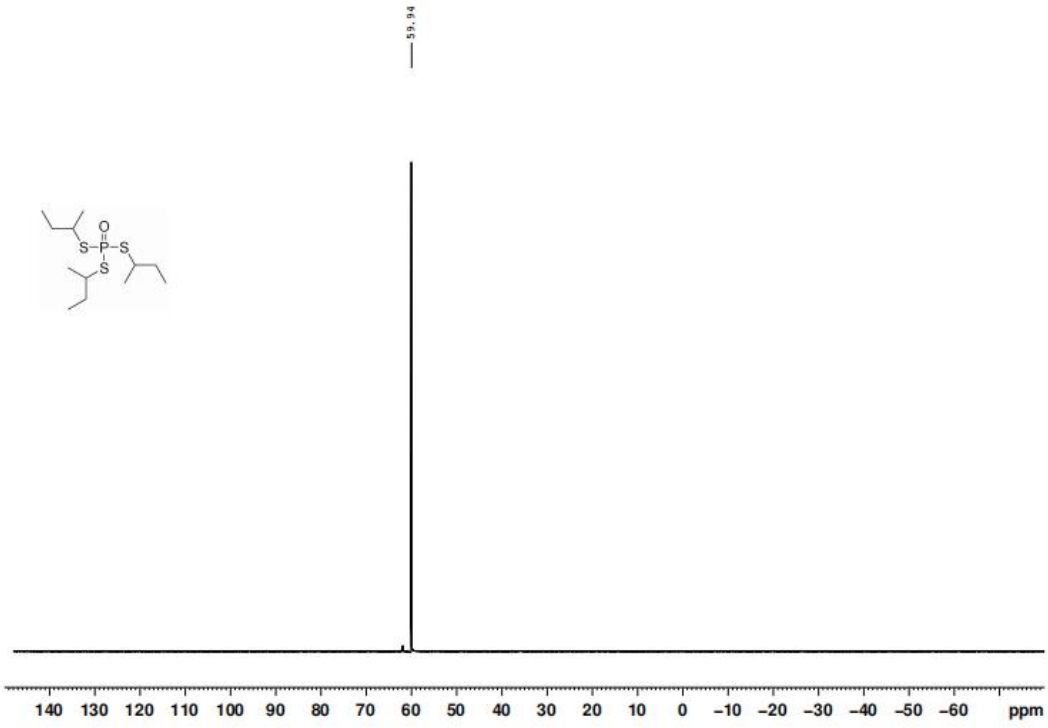
4z


3.478
3.474
3.470
3.466
3.463
3.459
3.455
3.452
3.447
3.443
3.439
3.435
3.431
3.428
3.424
3.420
3.416
3.413
3.409
1.774
1.771
1.762
1.759
1.750
1.747
1.738
1.735
1.723
1.712
1.700
1.688
1.676
1.453
1.441
1.010
0.998
0.985
9 8 7 6 5 4 3 2 1 0 ppm
3.00
6.21
9.25
9.11

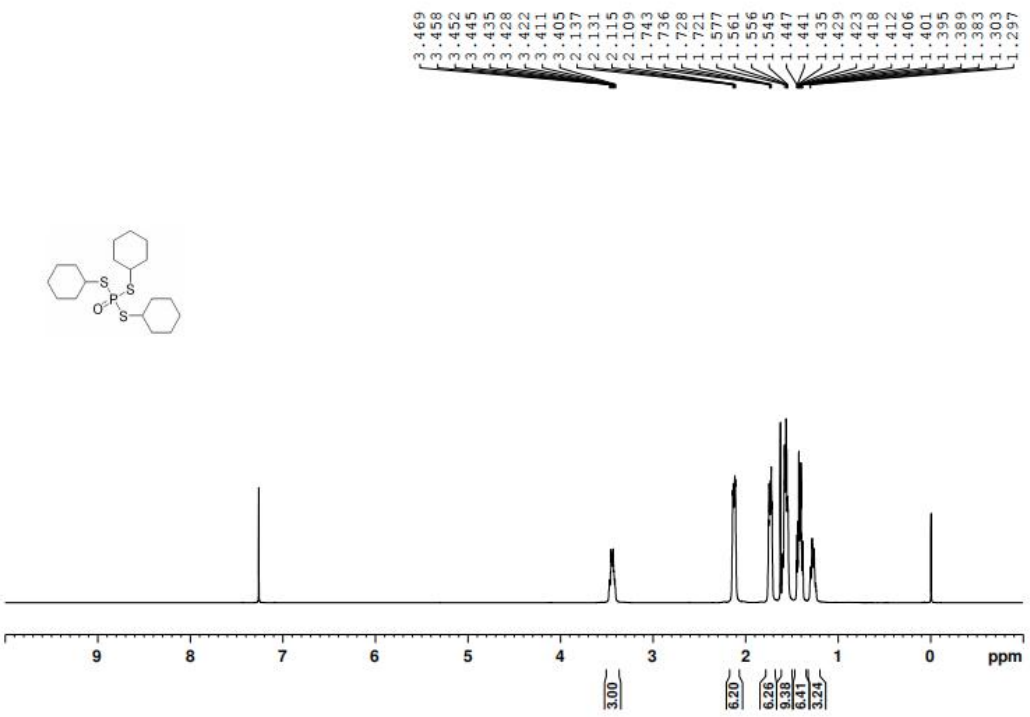
4z


77.44
77.23
77.02
46.81
46.78
46.74
46.72
31.48
31.44
23.11
23.09
23.08
23.07
11.42
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

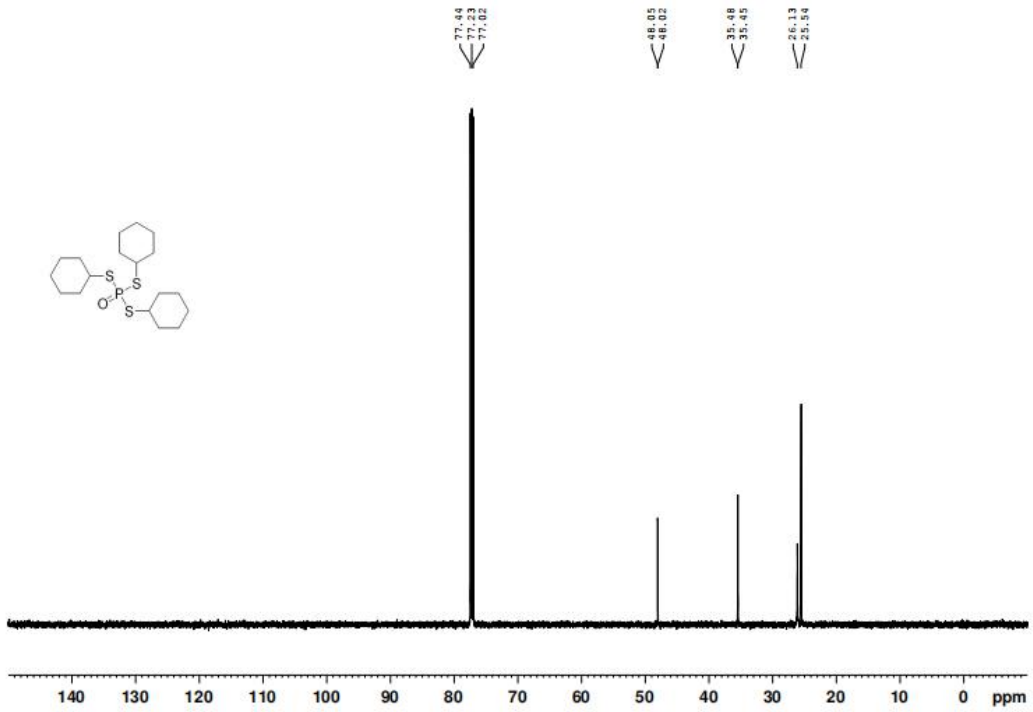
4z


59.94
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

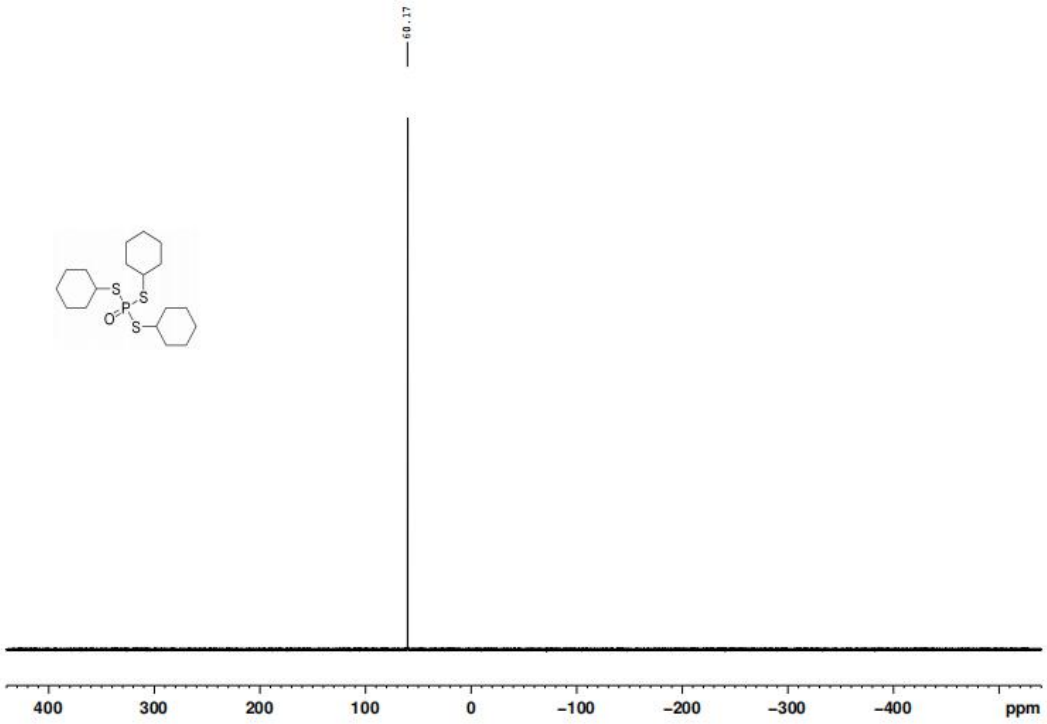
4aa


3.469
3.458
3.452
3.445
3.435
3.428
3.422
3.411
3.405
2.137
2.131
2.115
2.109
1.743
1.736
1.728
1.721
1.577
1.561
1.556
1.545
1.447
1.441
1.435
1.429
1.423
1.418
1.412
1.406
1.401
1.395
1.389
1.383
1.303
1.297
9
8
7
6
5
4
3
2
1
0
ppm
3.00
6.20
6.26
9.38
6.41
3.24

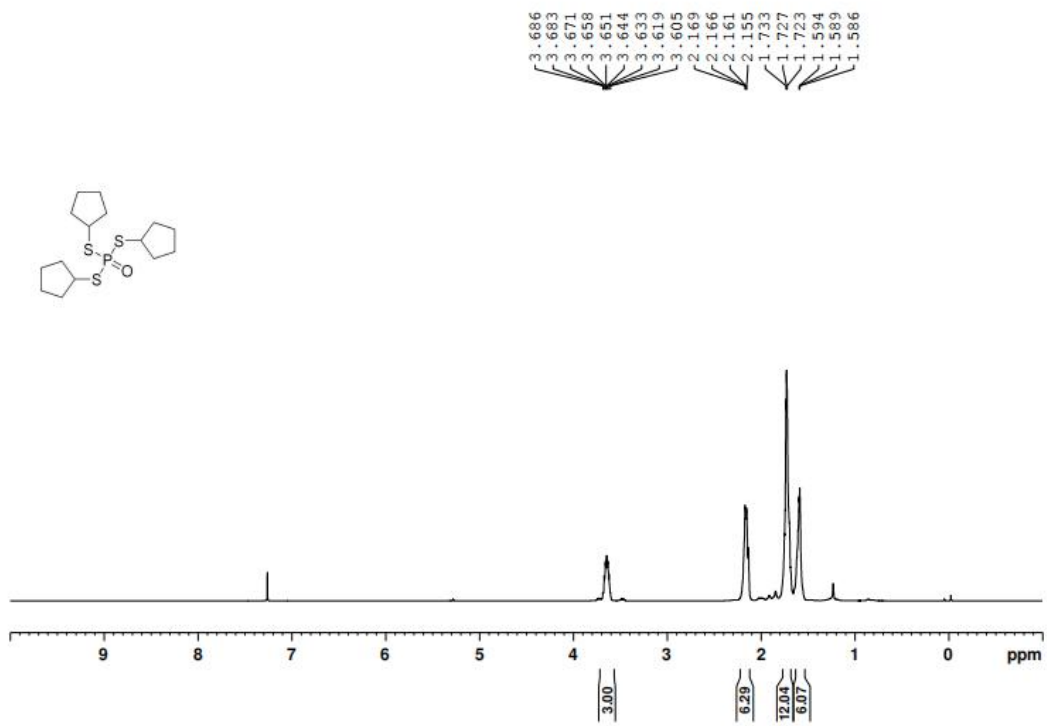
4aa


77.44
77.23
77.02
48.05
48.02
35.48
35.45
26.13
25.54
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

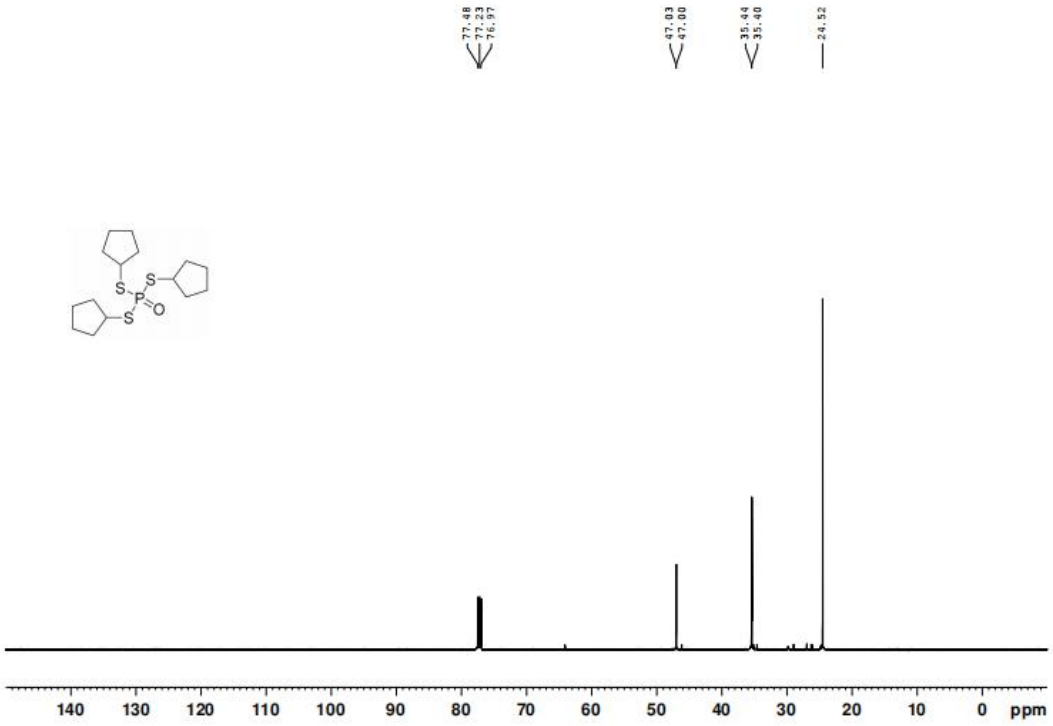
4aa


60.17
400
300
200
100
0
−100
−200
−300
−400
ppm

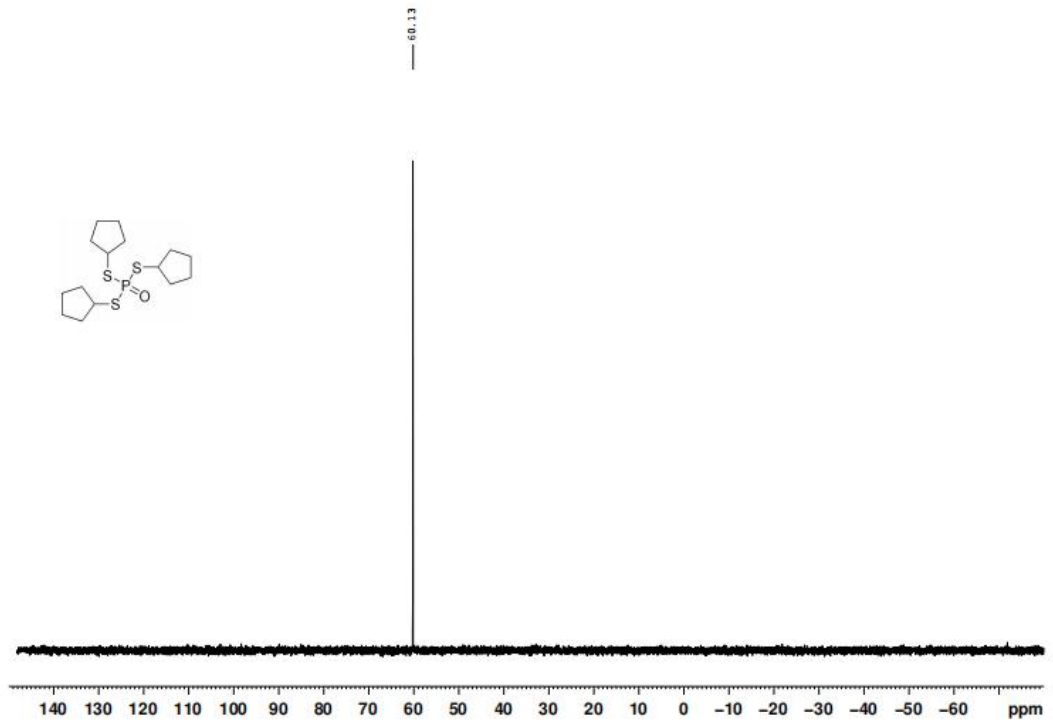
4ab


3.686
3.683
3.671
3.658
3.651
3.644
3.633
3.619
3.605
2.169
2.166
2.161
2.155
1.733
1.727
1.723
1.594
1.589
1.586
9
8
7
6
5
4
3
2
1
0
ppm
3.00
6.29
12.04
6.07

4ab


77.48
77.23
76.97
47.03
47.00
35.44
35.40
24.52
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

4ab


60.13
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm