Supplementary Material

Cs_2CO_3-Mediated synthetic strategy for iprobenfos derivatives *via* thiophilic addition of *H*-phosphites on *in situ* generated thioaldehydes

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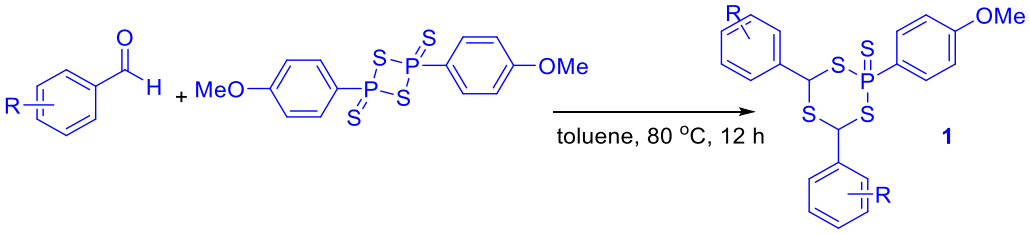
Table of Contents

1. General information

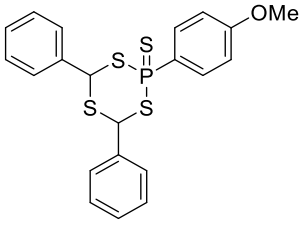
Reagents, substrates, and solvents were purchased from commercial suppliers and used without purification. Anhydrous toluene uses calcium hydride to remove water, dry, and distill. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F_{254} (Merck). Chromatography was performed using silica gel 60 (43-63 um) (Merck) and Aluminum oxide 90 neutral (MN). ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were using $CDCl_3$ on *J*eol 400 MHz spectrometers. Tetramethylsilane (TMS) served as an internal standard for ^{1}H and ^{13}C NMR analysis. Chemical shifts in ^{1}H NMR and ^{13}C NMR spectra are reported as follows: Chloroform-d (referenced to 7.26 ppm for ^{1}H and 77.10 ppm for ^{13}C). Coupling constants (*J*) are reported in hertz and peak multiplicities are reported using the following abbreviations: m = multiplet; s = singlet; d = doublet; t = triplet; q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets, tq = triplet of quartets, qd = quartet of doublets, br = broad signal. Low-Resolution Mass Spectrometry (LRMS) experiments were recorded on an Agilent Technologies 5977A with Agilent Technologies 7890B. High-Resolution Mass Spectrometry (HRMS) experiments were recorded on *J*eol *J*MS-HX-110 with EI (Electron Impact) method. All the phosphites 2a & 2b commercially purchased and used without purification and all the thioaldehydes 1a-m were prepared from known literature methods.[1]

Synthesis of trithiaphosphinanes.



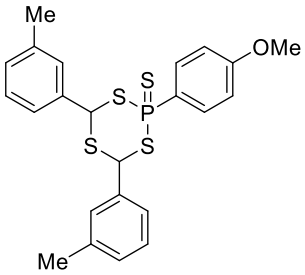
In a pre-dried 250 mL flask was added Lawesson's reagent (7 mmol, 2.8 g), Benzaldehydes (10 mmol, 1.061 g) and dry toluene (60 mL) The reaction mixture was vigorously stirred at 80 °C (oil bath) for 12 hours under nitrogen atmosphere. After completion of the reaction, the reaction mixture was filter and solvent was removed. Then the red oil crude was purified by flash aluminium oxide column chromatography (DCM/hexane = 15%) as eluent to afford the pure products **1**.

2-(4-Methoxyphenyl)-4,6-diphenyl-1,3,5,2-trithiaphosphinane 2-sulfide (1a)



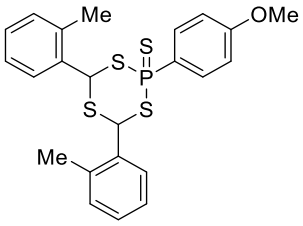
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J = 14.6 & 9.0 Hz, 2H), 7.50 (dd, J = 8.0 & 1.6 Hz, 4H), 7.40-7.34 (m, 6H), 7.09-7.06 (m, 2H), 6.29 (d, J = 9.2 Hz, 2H), 3.87 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.1, 137.7 (d, J = 8.0 Hz), 133.8 (d, J = 14.0 Hz), 129.2 (d, J = 14.0 Hz), 128.0, 123.1, 122.1, 114.8 (d, J = 16.0 Hz), 58.2, 55.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.8. HRMS (EI) calcd for $C_{21}H_{19}OPS_4$ $[M]^+$ 446.5958 found: 446.0059. M.P.: 78-83 °C

2-(4-Methoxyphenyl)-4,6-di-*m*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (1b)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J = 14.7 & 8.9 Hz, 2H), 7.32-7.23 (m, 6H), 7.15 (d, J = 7.0 Hz, 2H), 7.09-7.06 (m, 2H), 6.25 (d, J = 9.2 Hz, 2H), 3.88 (s, 3H), 2.34 (s, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.1, 139.1, 137.6 (d, J = 8.0 Hz), 133.7 (d, J = 13.0 Hz), 130.1, 128.8 (d, J = 43.0 Hz), 125.1, 123.2, 122.3, 114.6 (d, J = 16.0 Hz), 58.3, 55.6, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.7. HRMS (EI) calcd for $C_{23}H_{23}OPS_4$ $[M]^+$ 474.0369 found: 474.0379. M.P.: 79-83 °C

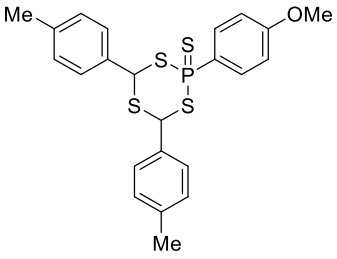
2-(4-Methoxyphenyl)-4,6-di-*o*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (1c)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.17 (m, 2H), 7.54-7.52 (m, 2H), 7.24-7.17 (m, 6H), 7.05-7.02 (m, 2H), 6.55 (d, J = 9.8 Hz, 2H), 3.80 (s, 3H), 2.49 (s, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.0 (d, J = 3.4 Hz), 136.1 (d, J = 8.0 Hz), 135.2, 133.5 (d, J = 14.0 Hz), 130.9, 129.1, 128.1, 126.9, 123.1, 122.2, 114.6 (d, J = 16.0 Hz), 55.4 (d, J = 19.7 Hz), 19.2; ^{31}P NMR

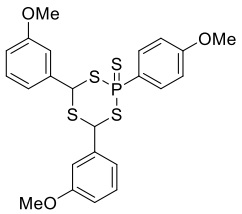
(162 MHz, $CDCl_3$): δ 74.6. HRMS (EI) calcd for $C_{23}H_{23}OPS_4$ $[M]^+$ 474.0369 found: 474.0379. M.P.: 63-68 °C.

2-(4-Methoxyphenyl)-4,6-di-*p*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (1d)



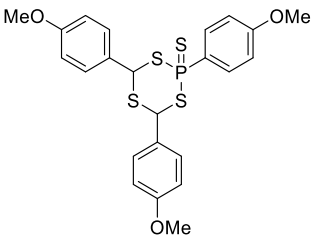
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J = 14.6 & 8.9 Hz, 2H), 7.38 (d, J = 8.1 Hz, 4H), 7.18 (d, J = 8.0 Hz, 4H), 7.08 (dd, J = 8.9, 3.3 Hz, 2H), 6.24 (d, J = 9.2 Hz, 2H), 3.89 (s, 3H), 2.34 (s, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.2 (d, J = 3.4 Hz), 139.4, 134.8 (d, J = 8.7 Hz), 133.6 (d, J = 13.5 Hz), 130.1, 129.9, 129.4 (d, J = 6.0 Hz), 128.5, 127.8 (d, J = 14.4 Hz), 127.5, 123.3, 122.3, 114.6 (d, J = 15.0 Hz), 58.1, 55.6, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.7. HRMS (EI) calcd for $C_{23}H_{23}OPS_4$ $[M]^+$ 474.0369 found: 474.0379. M.P.: 65-72 °C.

4,6-Bis(3-methoxyphenyl)-2-(4-methoxyphenyl)-1,3,5,2 trithia-phosphinane 2-sulfide (1e)



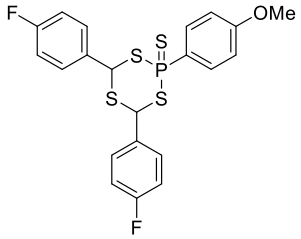
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.16 (m, 2H), 7.29-7.25 (m, 2H), 7.09-7.06 (m, 4H), 7.02-7.00 (m, 2H), 6.90-6.87 (m, 2H), 6.24 (d, J = 9.1 Hz, 2H), 3.89 (s, 3H), 3.81 (s, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.0 (d, J = 3.0 Hz), 160.0, 138.8 (d, J = 9.1 Hz), 133.5 (d, J = 13.1 Hz), 130.2, 122.9, 121.9, 115.3, 114.5 (d, J = 16.2 Hz), 113.1, 58.3, 55.5, 55.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.7. HRMS (EI) calcd for $C_{23}H_{23}O_3PS_4$ $[M]^+$ 506.0268 found: 506.0271.

2,4,6-Tris(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1f)



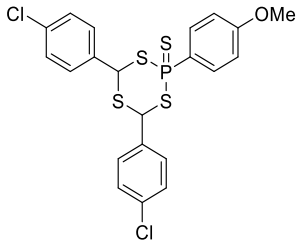
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.15 (m, 2H), 7.44-7.40 (m, 4H), 7.09-7.05 (m, 2H), 6.90-6.86 (m, 5H), 6.20 (d, J = 8 Hz, 2H), 3.88 (s, 3H), 3.79 (s, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.0 (d, J = 3.0), 160.2, 133.7 (d, J = 13.1 Hz), 131.9, 129.8 (d, J = 10.0 Hz), 129.3, 128.8, 123.2, 122.1, 114.6, 114.4, 57.8, 55.6, 55.4; ^{31}P NMR (162 MHz, $CDCl_3$); δ 72.7. HRMS (EI) calcd for $C_{23}H_{23}O_3PS_4$ $[M]^+$ 506.0268 found: 506.0276.

4,6-Bis(4-fluorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1g)



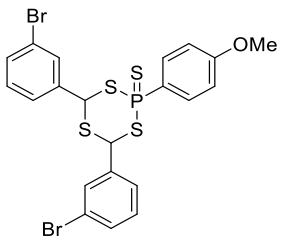
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.15 (m, 2H), 7.50-7.45 (m, 4H), 7.10-7.04 (m, 6H), 6.25 (d, J = 9.1 Hz, 2H), 3.88 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.3, 161.8, 133.7 (d, J = 14.0 Hz), 129.9 (d, J = 8.2 Hz), 122.8, 121.8, 116.3 (d, J = 21.7 Hz), 114.6 (d, J = 15.9 Hz), 57.4, 55.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.8. HRMS (EI) calcd for $C_{21}H_{17}F_2OPS_4$ $[M]^+$ 481.9868 found: 481.9871. M.P.: 130-135 ℃.

4,6-Bis(4-chlorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1h)



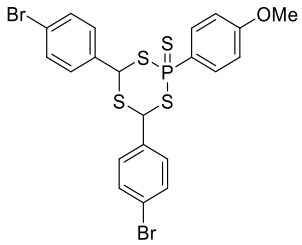
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.13 (m, 2H), 7.44-7.24 (m, 8H), 7.10-7.07 (m, 2H), 6.25 (d, J = 9.1 Hz, 2H), 3.88 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.4, 136.0 (d, J = 9.2 Hz), 135.3, 133.6 (d, J = 14.0 Hz), 129.4 (d, J = 7.0 Hz), 122.7, 121.7, 114.7 (d, J = 15.9 Hz), 57.6, 55.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.8. HRMS (EI) calcd for $C_{21}H_{17}Cl_2OPS_4$ $[M]^+$ 513.9277 found: 513.9282.

4,6-Bis(3-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1i)



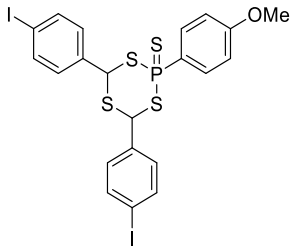
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.13 (m, 2H), 7.66 (t, J = 1.9 Hz, 2H), 7.48 (dq, J = 8.0 & 1.0 Hz, 2H), 7.43-7.40 (m, 2H), 7.26-7.22 (m, 2H), 7.10-7.06 (m, 2H), 6.23 (d, J = 9.1 Hz, 2H), 3.88 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.4, 139.3 (d, J = 8.0 Hz), 133.6 (d, J = 14.0 Hz), 132.6, 130.6 (d, J = 35.2 Hz), 126.7, 123.1, 122.6, 121.7, 114.7 (d, J = 16.4 Hz), 57.5, 55.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.7. HRMS (EI) calcd for $C_{21}H_{17}Br_2OPS_4$ $[M]^+$ 601.8267 found: 601.8274. M.P.: 86-90 °C.

4,6-Bis(4-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1j)



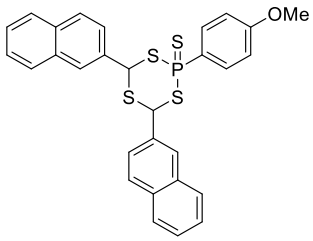
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.13 (m, 2H), 7.51-7.30 (m, 8H), 7.08-7.05 (m, 2H), 6.23 (d, J = 9.2 Hz, 2H), 3.85 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.2, 136.6 (d, J = 9.2 Hz), 133.7 (d, J = 14.0 Hz), 132.3 (d, J = 14.0 Hz), 123.5, 122.6, 121.6, 114.7 (d, J = 16.0 Hz), 57.7, 55.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.6. HRMS (EI) calcd for $C_{21}H_{17}Br_2OPS_4$ [M]+ 601.8274 found: 601.8262.

4,6-Bis(4-iodophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1k)



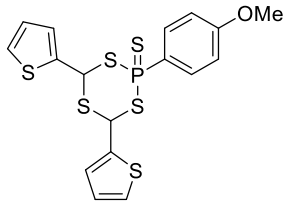
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.13 (m, 2H), 7.73-7.70 (m, 4H), 7.26-7.21 (m, 4H), 7.10-7.01 (m, 2H), 6.20 (d, J = 9.1 Hz, 2H), 3.90 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.3, 138.4, 137.1 (d, J = 9.0 Hz), 133.8 (d, J = 14.1 Hz), 130.9, 129.3, 114.8 (d, J = 16.0 Hz), 95.4, 57.7, 55.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.7. HRMS (EI) calcd for $C_{21}H_{17}I_2OPS_4$ $[M]^+$ 697.7989 found: 697.7981.

2-(4-Methoxyphenyl)-4,6-di(naphthalen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (1l)



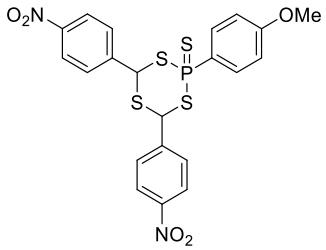
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27-8.21 (m, 2H), 8.02 (d, J = 1.5 Hz, 2H), 7.86 (s, 2H), 7.83-7.79 (m, 6H), 7.60 (dd, J = 8.5 & 1.9 Hz, 2H), 7.51-7.46 (m, 4H), 7.09-7.06 (m, 2H), 6.52 (d, J = 9.2 Hz, 2H), 3.86 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.2, 135.0, 133.8 (d, J = 9.2 Hz), 133.4 (d, J = 18.2 Hz), 129.2, 128.2, 127.8, 127.6, 126.9, 126.7, 125.4, 123.1, 122.1, 114.7 (d, J = 15.9 Hz), 58.6, 55.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.9 M.P.: 150-155 ℃

2-(4-Methoxyphenyl)-4,6-di(thiophen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (1m)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.13 (m, 2H), 7.32-7.29 (m, 2H), 7.25-7.23 (m, 2H), 7.09-6.97 (m, 4H), 6.56 (d, J = 12 Hz, 2H), 3.88 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.3, 139.0 (d, J = 11.0 Hz), 138.7, 133.7 (d, J = 14.0 Hz), 127.3 (d, J = 12.0 Hz), 127.1, 126.9, 126.3, 122.4, 121.4, 114.7 (d, J = 16.2 Hz), 55.7, 53.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.5.

2-(4-Methoxyphenyl)-4,6-bis(4-nitrophenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1n)

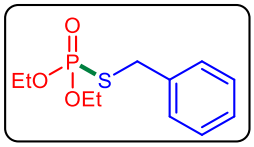


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29-8.24 (m, 5H), 7.72-7.68 (m, 4H), 7.14-7.10 (m, 2H), 6.42 (d, J = 8.0 Hz, 2H), 3.93 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 164.7, 148.3, 143.7 (d, J = 8.0 Hz), 133.7 (d, J = 14.0 Hz), 129.3, 124.7, 124.0, 114.9 (d, J = 16.2 Hz), 57.5, 55.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.9.

2. General procedure for table 1

In a sealed tube, 2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5,2-trithiaphosphinane 2-sulfide (**1a**) (267.9 mg, 0.6 mmol), base (40 mol %) was added in a glove box, followed by diethyl phosphites **2a** (55.24 mg, 0.4 mmol) and solvent (2 mL) were added, and stir at 80-100 ºC for 8-10 hours. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and filtered through a celite pad and concentrated under reduced pressure. The crude product thus obtained was then purified by column chromatography using silica gel (300-400 mesh) (15% ethyl acetate in hexanes) to obtain the pure product of **3a**.

Representative example of Table 1: *S*-Benzyl *O,O*-diisobutyl phosphorothioate (3a)[2]

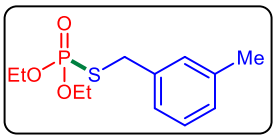


Yield: 77.66 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.24 (m, 5H), 4.16-3.96 (m, 6H), 1.28 (t, J=7.2 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 137.4 (d, J = 6.0 Hz), 128.9, 128.6, 127.6, 63.5 (d, J = 6.0 Hz), 34.9 (d, J = 3.0 Hz), 15.9 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.3.

3. General procedure for Table 2

In a sealed tube, added **1** (0.6 mmol), cesium carbonate (40 mol %) in a glove box, then dialkyl phosphites **2** (0.4 mmol) and ethyl acetate (2 mL) were added, the reaction mixture was then heated for 10 hours at 80 ºC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and filtered through a celite pad and concentrated under reduced pressure. The crude product thus obtained was purified by column chromatography using silica gel (300-400 mesh) (10-20% ethyl acetate in hexanes) to obtain the pure products **3**.

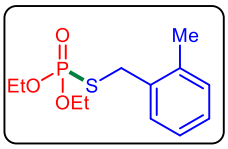
***O,O*-Diethyl *S*-(3-methylbenzyl) phosphorothioate (3b)[3]**



The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-*m*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (**1b)** (284.7 mg, 0.6 mmol), diethyl phosphite (**2a)** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3b**

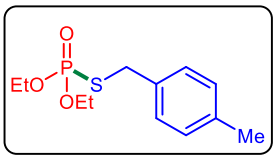
(66.92 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.14 (m, 3H), 7.08 (d, J = 7.2 Hz, 1H), 4.18-3.98 (m, 6H), 2.34 (s, 3H), 1.29 (t, J=7.2 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 138.2, 137.3 (d, J = 6.0 Hz), 129.6, 128.6, 128.4, 125.9, 63.5 (d, J = 5.0 Hz), 34.9 (d, J = 4.0 Hz), 21.3, 15.9 (d, J = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$); δ 27.4. HRMS (EI) calcd for $C_{12}H_{19}O_3PS$ $[M]^+$ 274.0793 found: 274.0784.

O,O-Diethyl *S*-(2-methylbenzyl) phosphorothioate (3c)[3]



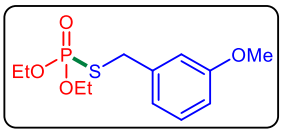
The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-*o*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (**1c)** (284.7 mg, 0.6 mmol), diethyl phosphite **2a** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3c** (65.82 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 6.8 Hz, 1H), 7.21-7.13 (m, 3H), 4.18-3.99 (m, 6H), 2.40 (s, 3H), 1.30 (td, J = 7.2 & 0.8 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 136.6, 135.1 (d, J = 6.0 Hz), 130.6, 130.0, 128.1, 126.2, 63.5 (d, J = 6.0 Hz), 33.1 (d, J = 3.0 Hz), 19.2, 16.0 (d, J = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.4.

O,O-diethyl *S*-(4-methylbenzyl) phosphorothioate (3d)[3]



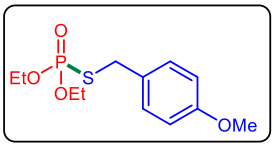
The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-*p*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (**1d)** (284.7 mg, 0.6 mmol), diethyl phosphite (**2a)** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3d** as a colorless liquid (66.92 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 4.73-3.98 (m, 6H), 2.32 (s, 3H), 1.29 (t, J = 7.2 Hz, 6H). ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 137.2, 134.2 (d, J = 6.0 Hz), 129.2, 128.7, 63.4 (d, J = 5.0 Hz), 34.6 (d, J = 4.0 Hz), 21.0 (s), 15.8 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.5. HRMS (EI) calcd for $C_{12}H_{19}O_3PS$ $[M]^+$ 274.0793 found: 274.0784.

O,O-diethyl *S*-(3-methoxybenzyl) phosphorothioate (3e)



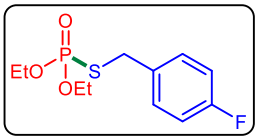
The title compound was prepared following the general procedure for table 2, using 4,6-bis(3-methoxyphenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1e)** (304.0 mg, 0.6 mmol), diethyl phosphite **2a** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3e** as a colorless liquid (40.66 mg, 35% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, J = 8.0 Hz, 1H), 6.95-6.90 (m, 2H), 6.80 (dd, J = 8.4 & 2.4 Hz, 1H), 4.17-3.98 (m, 6H), 3.80 (s, 3H), 1.29 (t, J = 7.2 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 159.6, 138.9 (d, J = 6.0 Hz), 129.6, 121.0, 114.3, 113.2, 63.4 (d, J = 6.0 Hz), 55.1, 34.8 (d, J = 4.0 Hz), 15.8 (d, J = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.3. HRMS (EI) calcd for $C_{12}H_{19}O_4$ PS $[M]^+$ 290.0742 found: 290.0743.

O,O-diethyl *S*-(4-methoxybenzyl) phosphorothioate (3f)[4]



The title compound was prepared following the general procedure for table 2, using 2,4,6-tris(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1f)** (304.0 mg, 0.6 mmol), diethyl phosphite (**2a)** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3f** (56.90 mg, 49% yield); ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.27 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.17-3.98 (m, 6H), 3.79 (s, 3H), 1.29 (t, J = 7.2 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 159.0, 130.1, 129.4 (d, J = 6.0 Hz), 114.0, 63.4 (d, J = 6.0 Hz), 55.3, 34.5 (d, J = 4.0 Hz), 15.9 (d, J = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.5.

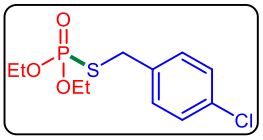
O,O-diethyl *S*-(4-fluorobenzyl) phosphorothioate (3g)[5]



The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-

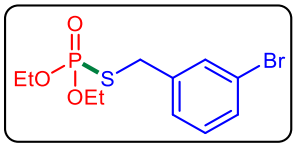
fluorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1g)** (289.4 mg, 0.6 mmol), diethyl phosphite **2a** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3g** (55.65 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.31 (m, 2H), 7.03-6.97 (m, 2H), 4.16-3.97 (m, 6H), 1.29 (td, J = 7.2 & 0.8 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 162.2 (d, J = 236.0 Hz), 133.4 (dd, J = 4.0 & 5.0 Hz), 130.4 (d, J = 9.0 Hz), 115.4 (d, J = 21.0 Hz), 63.5 (d, J = 6.0 Hz), 34.1 (d, J = 3.0 Hz), 15.8 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.5. HRMS (EI) calcd for $C_{11}H_{16}FO_3PS$ $[M]^+$ 278.0542 found: 278.0544.

S-(4-chlorobenzyl) *O,O*-diethyl phosphorothioate (3h)[3]



The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-chlorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1h)** (309.2 mg, 0.6 mmol), diethyl phosphite **2a** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3h** (35.28 mg, 30% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 4H), 4.16-3.97 (m, 6H), 1.29 (td, J = 3.2 & 0.8 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 136.2 (d, J = 5.0 Hz), 133.5, 130.3, 128.8, 63.6 (d, J = 5.0 Hz), 34.2 (d, J = 3.9 Hz), 15.9 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.0. HRMS (EI) calcd for $C_{11}H_{16}ClO_3PS$ $[M]^+$ 294.0246 found: 294.0238.

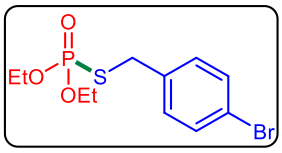
O,O-diethyl *S*-(3-bromobenzyl) phosphorothioate (3i)



The title compound was prepared following the general procedure for table 2, using 4,6-bis(3-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1i)** (362.6 mg, 0.6 mmol), diethyl phosphite (**2a)** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3i** (56.98 mg, 42% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 4.17-3.97 (m, 6H), 1.30 (t, J = 0.8 Hz, 6H);

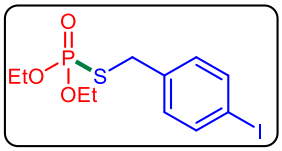
$^{13}C\{H\}$NMR (100 MHz, $CDCl_3$): δ 139.9 (d, J = 4.0 Hz), 131.8, 130.6, 130.1, 127.5, 122.4, 63.6 (d, J = 6.0 Hz), 34.2 (d, J = 4.0 Hz), 15.9 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.7. HRMS (EI) calcd for $C_{11}H_{16}BrO_3PS$ $[M]^+$ 337.9741 found: 337.9739.

_O,O_- diethyl _S_-(4-bromobenzyl) phosphorothioate (3j)[6]



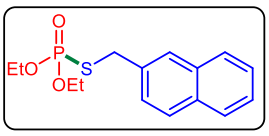
The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1j)** (362.6 mg, 0.6 mmol), diethyl phosphite (**2a)** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3j** (61.05 mg, 45% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.27-7.22 (m, 2H), 4.16-3.96 (m, 6H), 1.28 (td, J = 7.2 & 0.8 Hz, 6H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$): δ 136.6 (d, J = 5.0 Hz), 131.7, 130.6, 121.5, 63.6 (d, J = 6.0 Hz), 34.2 (d, J = 4.0 Hz), 15.9 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.9. HRMS (EI) calcd for $C_{11}H_{16}BrO_3PS$ $[M]^+$ 337.9741 found: 337.9739.

_O,O_- diethyl _S_-(4-iodobenzyl) phosphorothioate (3k)



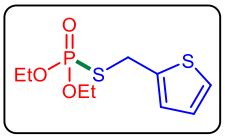
The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-iodophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1k)** (419.0 mg, 0.6 mmol), diethyl phosphite (**2a)** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3k** (77.2 mg, 50% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 4.15-3.94 (m, 6H), 1.28 (td, J =7.2 & 0.8 Hz, 6H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$): δ 137.6, 137.2 (d, J = 5.0 Hz), 130.7, 93.0, 63.5 (d, J = 6.0 Hz), 34.2, 15.8 (d, J = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.8; HRMS (EI) calcd for $C_{11}H_{16}IO_3PS$ $[M]^+$ 385.9602 found: 385.9599.

_O,O_-diethyl _S_-(naphthalen-2-ylmethyl) phosphorothioate (3l)



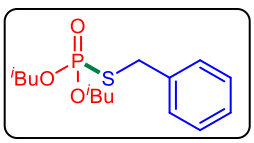
The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di(naphthalen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1l)** (328.0 mg, 0.6 mmol), diethyl phosphite (**2a)** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3l** (74.48 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.57-7.47 (m, 3H), 7.37 (t, J = 7.6 Hz, 1H), 4.49 (d, J = 12.4 Hz, 2H), 4.16-3.95 (m, 4H), 1.25 (t, J = 7.2 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 133.6, 132.6 (d, J = 6.0 Hz), 130.89, 128.8, 128.7, 127.6, 126.3, 125.8, 125.2, 123.4, 63.5 (d, J = 6.0 Hz), 32.7 (d, J = 3.0 Hz), 15.8 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.3. HRMS (EI) calcd for $C_{15}H_{19}O_3PS$ $[M]^+$ 310.0793 found: 310.0789.

O,O-diethyl *S*-(thiophen-2-ylmethyl) phosphorothioate (3m)[7]



The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di(thiophen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1m)** (275.1 mg, 0.6 mmol), diethyl phosphite (**2a)** (55.24 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3m** (44.69 mg, 42% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, J = 5.2 & 2.0 Hz, 1H), 7.03 (d, J = 3.2 Hz, 1H), 6.93-6.90 (m, 1H), 4.27 (d, J = 14.0 Hz, 2H), 4.20-4.01 (m, 4H), 1.31(t, J = 7.2 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 140.0 (d, J = 6.0 Hz), 127.1, 126.9, 125.7, 63.6 (d, J = 5.0 Hz), 29.5 (d, J = 3.0 Hz), 15.9 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.7. HRMS (EI) calcd for $C_9H_{15}O_3PS_2$ $[M]^+$ 266.0200 found: 266.0206.

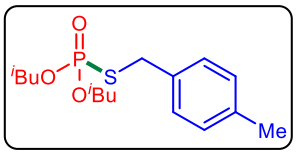
S-benzyl *O,O*-diisobutyl phosphorothioate (3n)[5]



The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5,2-trithiaphosphinane 2-sulfide (**1a)** (267.9 mg, 0.6 mmol),

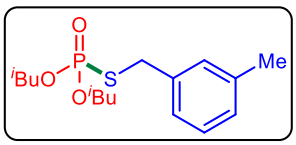
di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3n** (88.58 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.24 (m, 5H), 4.04 (d, J = 14.0 Hz, 2H), 3.84-3.78 (m, 2H), 3.73-3.67 (m, 2H), 1.95-1.85 (m, 2H), 0.92 (d, J = 1.2 Hz, 6H), 0.90 (d, J = 1.2 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 137.5 (d, J = 5.0 Hz), 128.9, 128.7, 127.6, 73.3 (d, J = 7.0 Hz), 34.9 (d, J = 3.0 Hz), 28.9 (d, J = 8.0 Hz), 18.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.4.

O,O-Diisobutyl *S*-(4-methylbenzyl) phosphorothioate (3o)[5]



The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-*p*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (**1d)** (284.7 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3o** (72.69 mg, 55% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 6.86-6.83 (m, 2H), 4.01 (d, J = 13.2 Hz, 2H), 3.84-3.79 (m, 5H), 3.74-3.58 (m, 2H), 1.96-1.85 (m, 2H), 0.93(d, J = 1.2 Hz, 6H), 0.91 (d, J = 1.2 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 159.0, 130.1, 129.4 (d, J = 6.0 Hz), 114.0, 73.3 (d, J = 7.0 Hz), 55.3, 34.4, (d, J = 4.0 Hz), 28.9 (d, J = 7.0 Hz), 18.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.5. HRMS (EI) calcd for $C_{16}H_{27}O_3PS$ $[M]^+$ 330.1419 found: 330.1422.

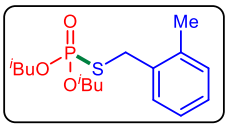
O,O-Diisobutyl *S*-(3-methylbenzyl) phosphorothioate (3p)



The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-*m*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (**1b)** (284.7 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (53.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3p** (76.65 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.91 (t, J = 2.0 Hz, 1H), 6.81 (dd, J = 8.4 & 2.4 Hz, 1H), 4.02 (d, J = 13.6 Hz,

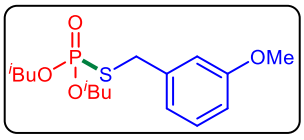
2H), 3.85-3.79 (m, 5H), 3.75-3.69 (m, 2H), 1.96-1.86 (m, 2H), 0.93 (d, J = 1.2 Hz, 6H), 0.91 (d, J = 1.2 Hz, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 159.7, 139.0 (d, J = 5.0 Hz), 129.7, 121.2, 114.4, 113.3, 73.4 (d, J = 6.0 Hz), 55.3, 34.9, (d, J = 4.0 Hz), 29.0 (d, J = 7.0 Hz), 18.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.4. HRMS (EI) calcd for $C_{16}H_{27}O_3$ PS $[M]^+$ 330.1419 found: 330.1422.

O,O-Diisobutyl *S*-(2-methylbenzyl) phosphorothioate (3q)



The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-*o*-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (**1c)** (284.7 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3q** (79.30 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.30 (m, 1H), 7.20-7.12 (m, 3H), 4.06 (d, J = 12.0 Hz, 2H), 3.85-3.80 (m, 2H), 3.75-3.70 (m, 2H), 2.40 (s, 3H), 1.97-1.87 (m, 2H), 0.93 (d, J = 1.2 Hz, 6H), 0.91 (d, J = 1.2 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 136.6, 135.1 (d, J = 6.0 Hz), 130.5, 129.9, 128.0, 126.2, 73.3 (d, J = 7.0 Hz), 33.0 (d, J = 3.0 Hz), 28.9 (d, J = 7.0 Hz), 19.1, 18.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.5. HRMS (EI) calcd for $C_{16}H_{27}O_3PS$ $[M]^+$ 330.1419 found: 330.1416.

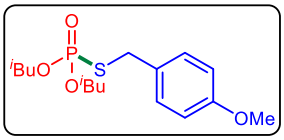
O,O-Diisobutyl S-(3-methoxybenzyl) phosphorothioate (3r)



The title compound was prepared following the general procedure for table 2, using 4,6-bis(3-methoxyphenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1e)** (304.0 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3r** (66.50 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, J = 8.0 Hz, 1H), 6.95-6.91 (m, 2H), 6.80 (dd, J = 8.0 & 2.0 Hz, 1H), 4.02 (d, J = 14.0 Hz, 2H), 3.83-3.79 (m, 5H), 3.75-3.71 (m, 2H), 1.96-1.86 (m, 2H), 0.92 (d, J = 1.2 Hz, 6H), 0.91 (d, J = 1.2 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 159.7, 138.9 (d, J = 6.0 Hz), 129.7, 121.2, 114.3, 113.2, 73.3 (d, J = 6.0 Hz), 55.2, 34.8 (d, J = 4.0 Hz), 28.9 (d, J = 7.0 Hz), 18.7. ^{31}P NMR (162 MHz,

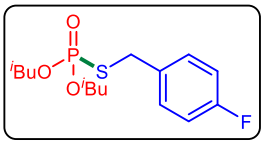
$CDCl_3$): δ 27.4. HRMS (EI) calcd for $C_{16}H_{27}O_4PS$ $[M]^+$ 346.1368 found: 346.1363.

O,O-Diisobutyl *S*-(4-methoxybenzyl) phosphorothioate (3s)[8]



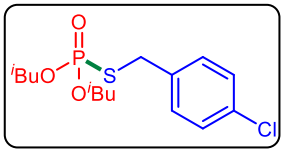
The title compound was prepared following the general procedure for table 2, using 2,4,6-tris(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1f**) (304.0 mg, 0.6 mmol), di-isobutyl phosphite (**2b**) (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3s** (88.67 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 6.87-6.82 (m, 2H), 4.02 (d, J = 13.2 Hz, 2H), 3.84-3.78 (m, 5H), 3.74-3.68 (m, 2H), 1.96-1.87 (m, 3H), 0.93 (d, J = 3.0 Hz, 6H), 0.91 (d, J = 3.0 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 159.0, 130.1, 129.4 (d, J = 5.0 Hz), 114.4, 73.3 (d, J = 7.0 Hz), 55.3 (s), 34.5 (d, J = 4.0 Hz), 28.9 (d, J = 8.0 Hz), 18.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.6. HRMS (EI) calcd for $C_{16}H_{27}O_4PS$ $[M]^+$ 346.1368 found: 346.1363.

S-(4-Fluorobenzyl) *O,O*-diisobutyl phosphorothioate (3t)



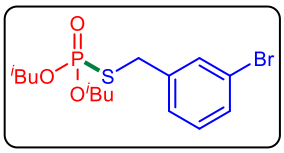
The title compound was prepared following the general procedure for table 2 using 4,6-bis(4-fluorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1g**) (289.4 mg, 0.6 mmol), di-isobutyl phosphite (**2b**) (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3t** (77.57 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 2H), 7.03-6.98 (m, 2H), 4.03 (d, J = 14.0 Hz, 2H), 3.84-3.78 (m, 2H), 3.74-3.68 (m, 2H), 1.95-1.87 (m, 2H), 0.92 (d, J = 6.8 Hz, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 161.6 (d, J = 170.0 Hz), 133.2 (d, J = 125.0 Hz), 130.4 (d, J = 9.0 Hz), 115.6 (d, J = 21.0 Hz), 73.4 (d, J = 7.0 Hz), 34.2 (d, J = 4.0 Hz), 29.0 (d, J = 7.0 Hz), 18.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.5. HRMS (EI) calcd for $C_{15}H_{24}FO_3PS$ $[M]^+$ 334.1168 found: 334.1172.

S-(4-Chlorobenzyl) *O,O*-diisobutyl phosphorothioate (3u)



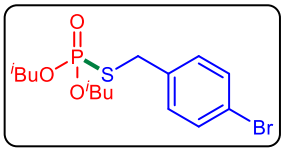
The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-chlorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1h)** (309.2 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3u** (70.16 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 4H), 4.01 (d, J = 14.4 Hz, 2H), 3.83-3.77 (m, 2H), 3.73-3.67 (m, 2H), 1.95-1.85 (m, 2H), 0.91 (d, J = 6.8 Hz, 12H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 136.2 (d, J = 5.0 Hz), 133.4, 130.3, 128.8, 73.4 (d, J = 7.0 Hz), 34.2 (d, J = 4.0 Hz), 28.9 (d, J = 7.0 Hz), 18.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.0. HRMS (EI) calcd for $C_{15}H_{24}ClO_3PS$ $[M]^+$ 350.0872 found: 350.0869.

_S_-(3-Bromobenzyl) _O,O_-diisobutyl phosphorothioate (3v)



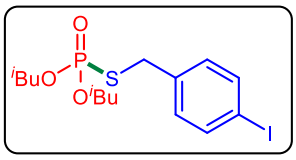
The title compound was prepared following the general procedure for table 2, using 4,6-bis(3-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1i)** (362.6 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3v** (102.77 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (t, J = 1.6 Hz, 1H), 7.40-7.37 (m, 1H), 7.31-7.27 (m, 1H), 7.19 (t, J = 8.0 Hz, 1H), 3.98 (d, J = 14.8 Hz, 2H), 3.84-3.79 (m, 2H), 3.74-3.67 (m, 2H), 1.95-1.85 (m, 2H), 0.92 (d, J = 0.8 Hz, 6H), 0.90 (d, J = 1.2 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 134.0 (d, J = 5.0 Hz), 125.8, 124.6, 124.1, 121.5, 116.4, 67.3 (d, J = 7.0 Hz), 28.1, 22.8 (d, J= 8.0 Hz), 12.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.85. HRMS (EI) calcd for $C_{15}H_{24}BrO_3PS$ $[M]^+$ 394.0367 found: 394.0358.

_S_-(4-bromobenzyl) _O,O_-diisobutyl phosphorothioate (3w)



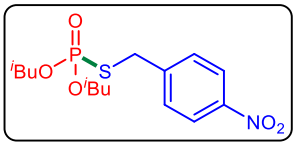
The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1j)** (362.6 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3w** (109.10 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.26-7.23 (m, 2H), 3.99 (d, J = 14.8 Hz, 2H), 3.83-3.77 (m, 2H), 3.73-3.67 (m, 2H), 1.95-1.85 (m, 2H), 0.91 (d, J = 6.8 Hz, 12H). ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 136.7 (d, J = 5.0 Hz), 131.7, 130.6, 121.5, 73.4 (d, J = 6.0 Hz), 34.2 (d, J = 4.0 Hz), 28.8 (d, J = 8.0 Hz), 18.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.9. HRMS (EI) calcd for $C_{15}H_{24}BrO_3PS$ $[M]^+$ 394.0367 found: 394.0364.

S-(4-Iodobenzyl) *O,O*-diisobutyl phosphorothioate (3x)



The title compound was prepared following the general procedure for table 2, using 4-iodobenzothialdehyde **1k** (148.8 mg, 0.6 mmol), di-isobutyl phosphite **2b** (419.0 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3x** (72.53 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dt, J = 8.8 & 2.4 Hz, 2H), 7.12 (dt, J = 8.8 & 2.4 Hz, 2H), 3.98 (d, J = 14.8 Hz, 2H), 3.82-3.77 (m, 2H), 3.72-3.66 (m, 2H), 1.94-1.84 (m, 2H), 0.91 (d, J = 0.8 Hz, 6H), 0.90 (d, J = 0.8 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 137.7, 137.5 (d, J = 5.0 Hz), 130.9, 93.0, 73.4 (d, J = 7.0 Hz), 34.4 (d, J = 4.0 Hz), 28.9 (d, J = 8.0 Hz), 18.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.9. HRMS (EI) calcd for $C_{15}H_{24}IO_3PS$ $[M]^+$ 442.0228 found: 442.0234.

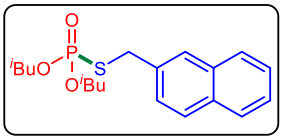
O,O-Diisobutyl *S*-(4-nitrobenzyl) phosphorothioate (3y)



The title compound was prepared following the general procedure for table 2, using 4-nitrobenzothialdehyde **1n** (100.3 mg, 0.6 mmol), di-isobutyl phosphite **2b** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3y** (43.36 mg, 30% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.16 (m, 2H), 7.58-7.55 (m, 2H), 4.12 (d, J = 15.6 Hz, 2H), 3.84-

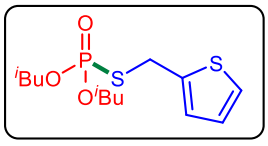
3.75 (m, 2H), 3.74-3.68 (m, 2H), 1.95-1.85 (m, 2H), 0.85 (d, J = 6.9 Hz, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 147.2, 145.4 (d, J = 4.0 Hz), 129.7, 123.8, 73.6 (d, J = 7.0 Hz), 34.0 (d, J = 4.0 Hz), 29.8 (d, J = 7.0 Hz), 18.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.2. HRMS (EI) calcd for $C_{15}H_{24}NO_5PS$ $[M]^+$ 361.1113 found: 361.1117.

_O,O_-diisobutyl S-(naphthalen-2-ylmethyl) phosphorothioate (3z)



The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di(naphthalen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1l)** (328.0 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3z** (89.41 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.57-7.47 (m, 3H), 7.39-7.35 (m, 1H), 4.51 (d, J = 12.4 Hz, 2H), 3.83-3.76 (m, 2H), 3.73-3.67 (m, 2H), 1.92-1.82 (m, 2H), 0.89 (d, J = 4.0 Hz, 6H), 0.87 (d, J = 4.0 Hz, 6H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 133.7, 132.6 (d, J = 6.0 Hz), 130.9, 128.77, 128.70, 127.6, 126.3, 125.8, 125.2, 123.5, 73.2 (d, J = 7.0 Hz), 32.6 (d, J = 4.0 Hz), 28.7 (d, J = 7.0 Hz), 18.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.4. HRMS (EI) calcd for $C_{19}H_{27}O_3PS$ $[M]^+$ 366.1419 found: 366.1416.

_O,O_-diisobutyl _S_-(thiophen-2-ylmethyl) phosphorothioate (3aa)



The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di(thiophen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (**1m)** (275.1 mg, 0.6 mmol), di-isobutyl phosphite (**2b)** (77.68 mg, 0.4 mmol), Cs_2CO_3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane) to provide **3aa** (54.16 mg, 42% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, J = 5.2 & 1.2 Hz, 1H), 7.03 (dd, J = 3.6 & 1.2 Hz, 1H), 6.91 (dd, J = 5.2 & 3.6 Hz, 1H), 4.28 (d, J = 13.6 Hz, 2H), 3.88-3.82 (m, 2H), 3.78-3.72 (m, 2H), 1.99-1.88 (m, 2H), 0.93 (d, J = 17.0 Hz, 12H); ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ 140.0 (d, J = 6.0 Hz), 127.1, 126.8, 125.6, 73.3 (d, J = 7.0

Hz), 29.4 (d, J = 3.0 Hz), 28.9 (d, J = 8.0 Hz), 18.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.7. HRMS (EI) calcd for $C_{13}H_{23}O_3PS_2$ $[M]^+$ 322.0826 found: 322.0819.

4. References

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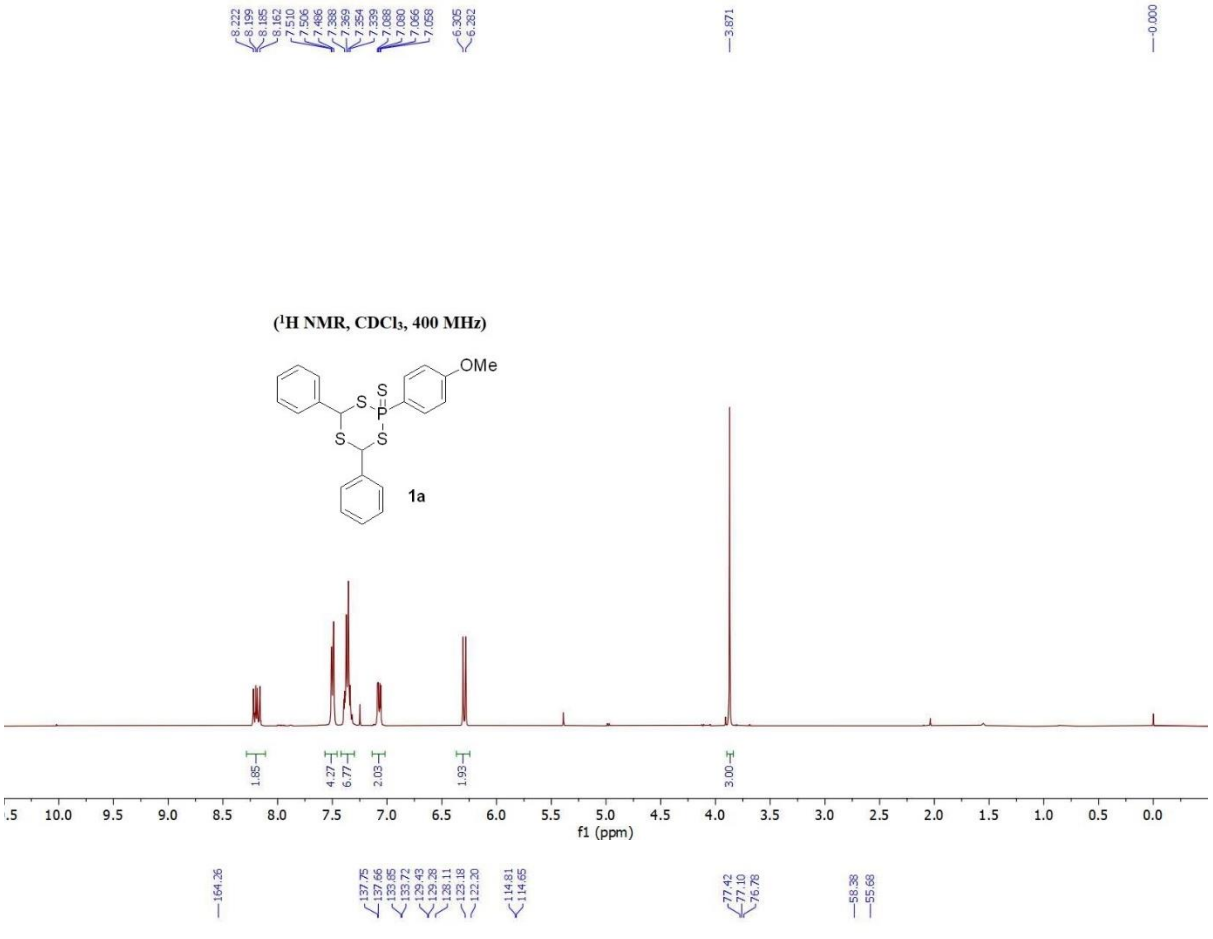
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8.199
8.185
8.162
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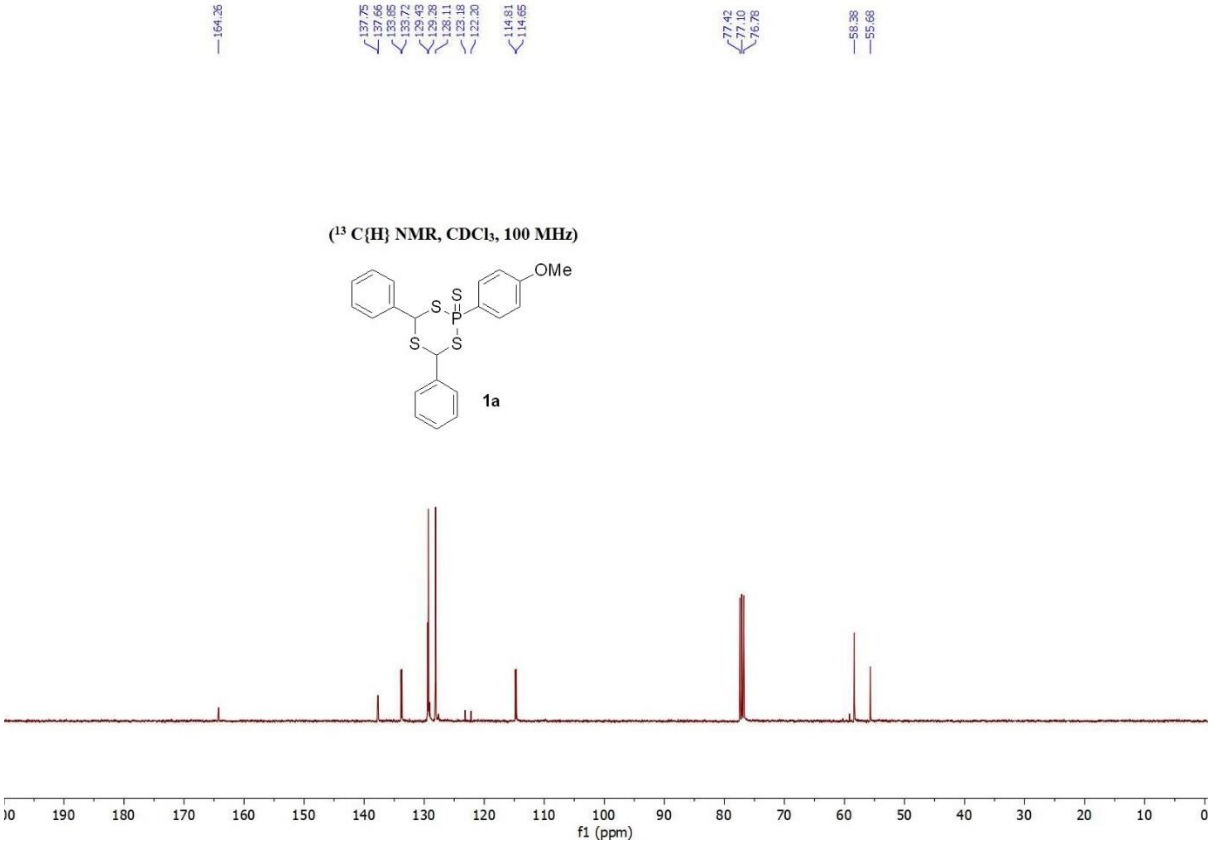
7.506
7.486
7.388
7.369
7.354
7.339
7.088
7.080
7.066
7.058
6.305
6.282
3.871
0.000
(1H NMR, CDCl3, 400 MHz)
OMe
S
S
P
S
S
1a
1.85
4.27
6.77
2.03
1.93
3.00
f1 (ppm)


164.26
137.75
137.66
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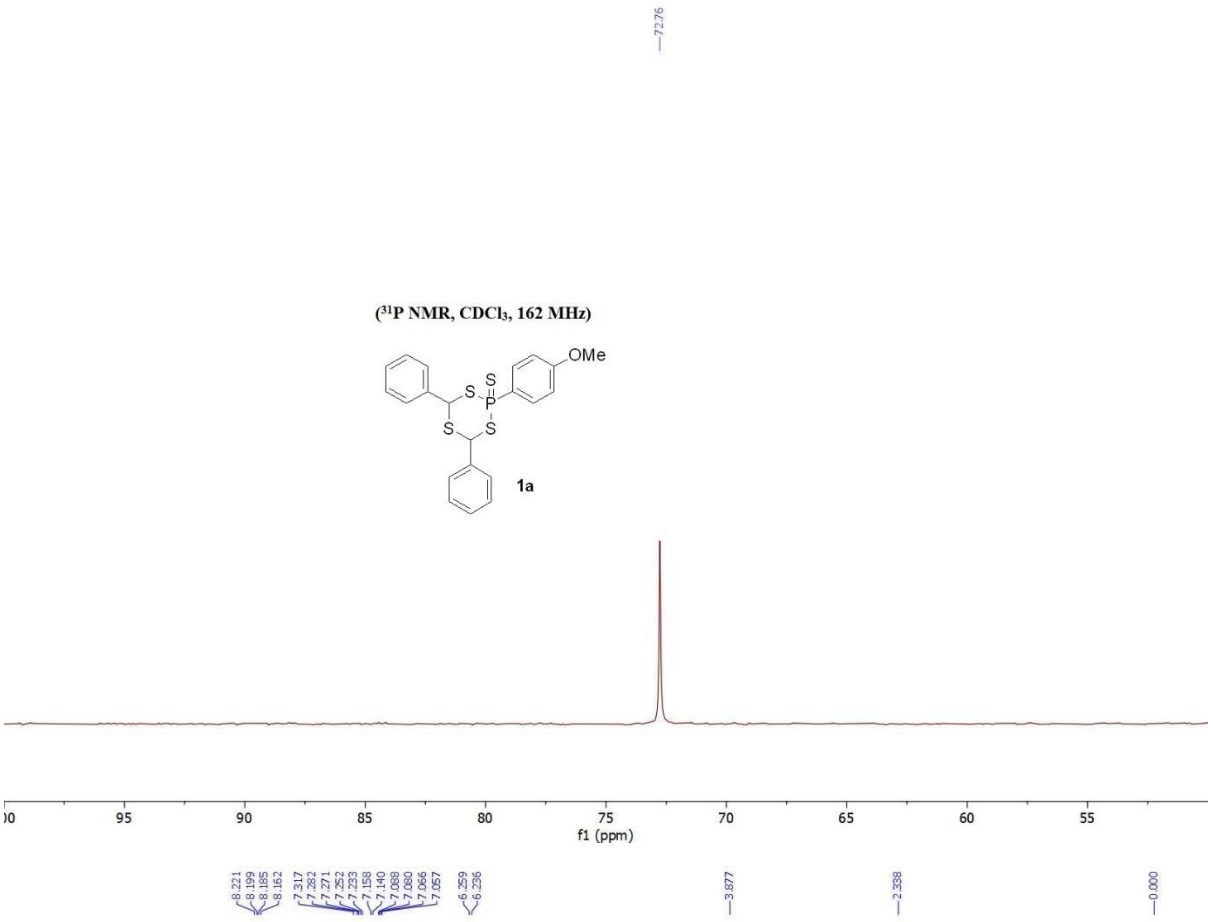
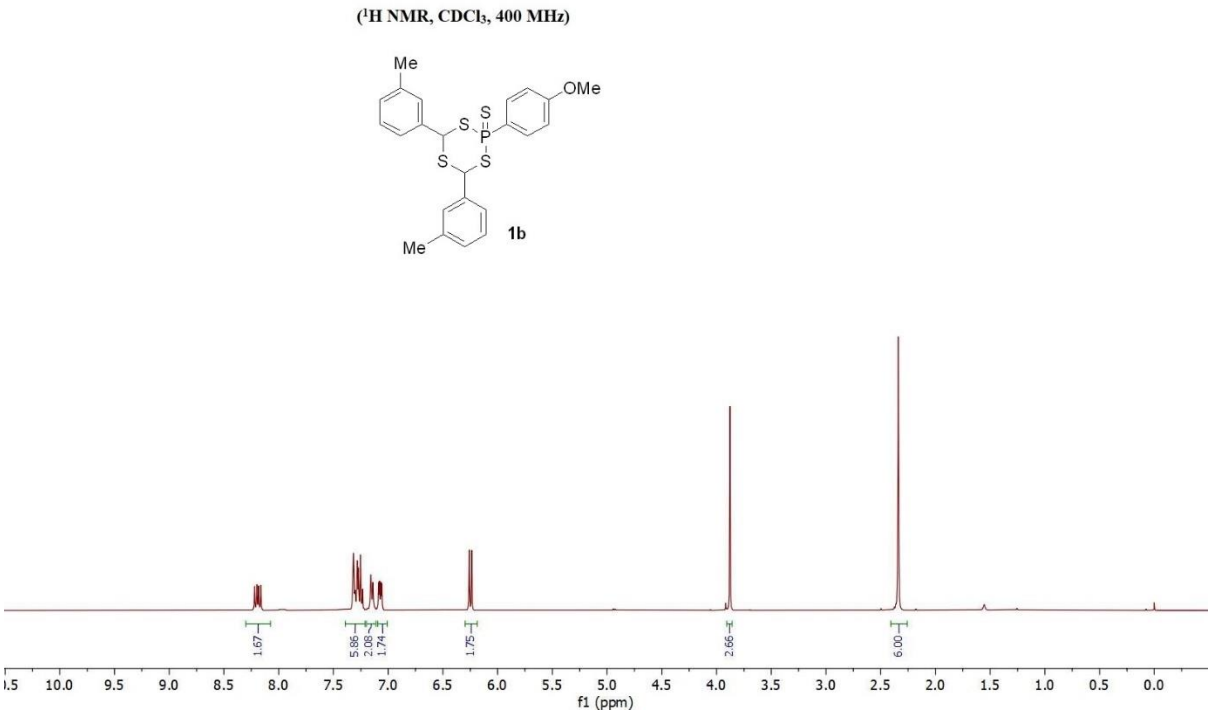
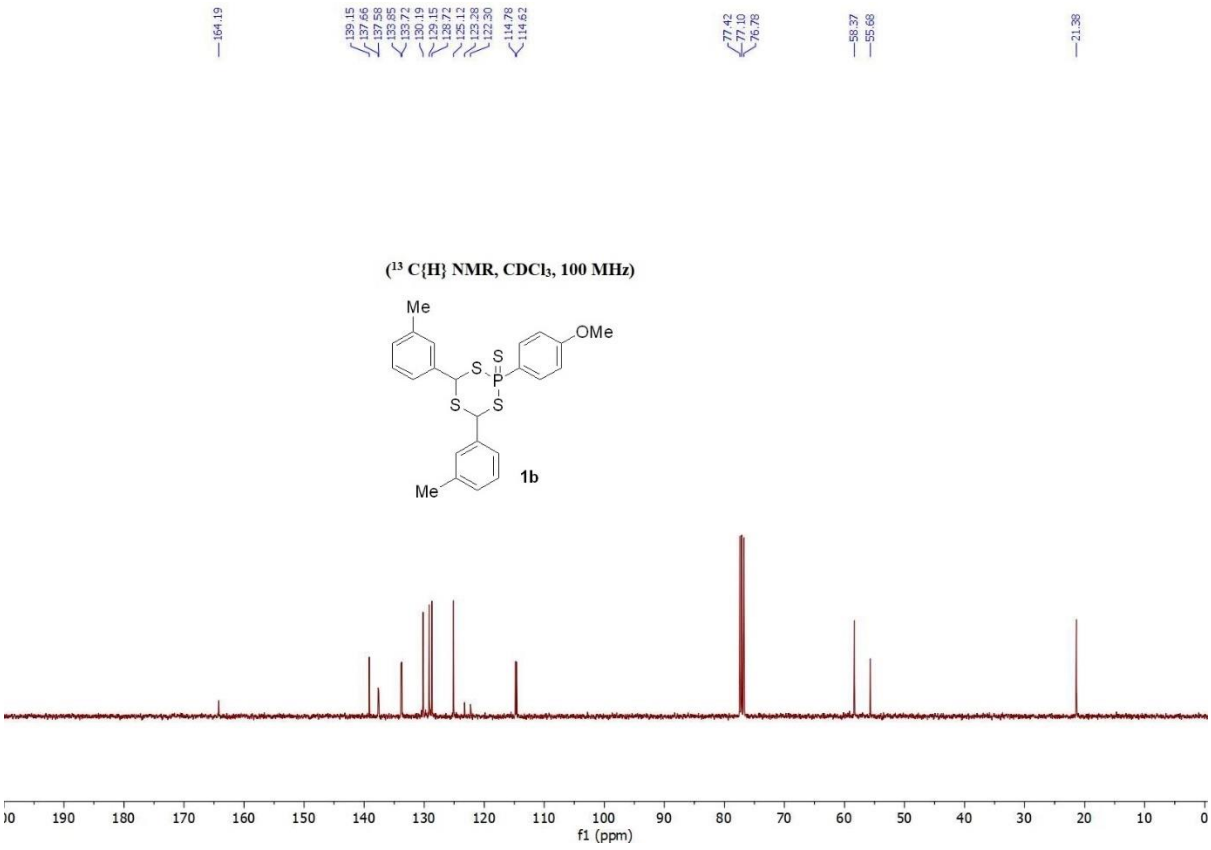
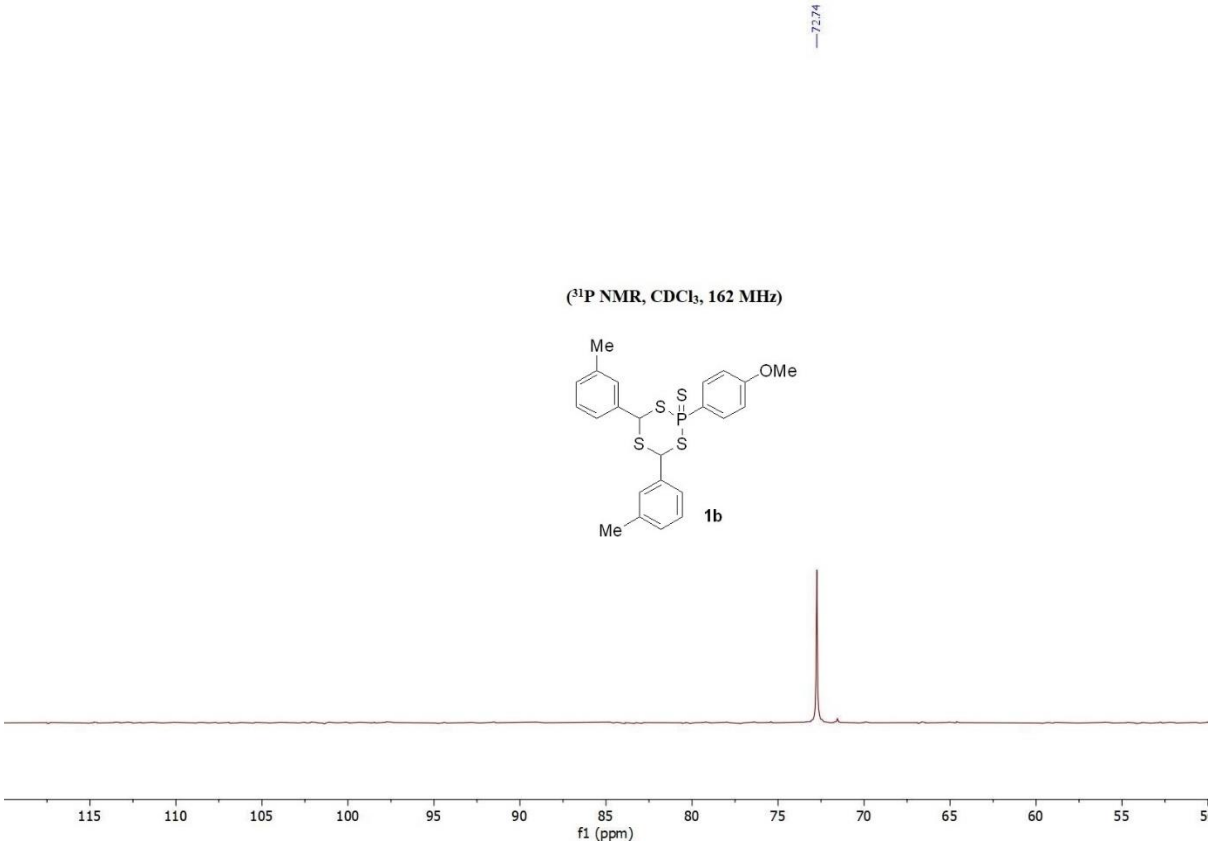
133.72
129.43
129.28
128.11
123.18
122.20
114.81
114.65
77.42
77.10
76.78
58.38
55.68
(13 C{H} NMR, CDCl3, 100 MHz)
OMe
S
S
P
S
S
1a
f1 (ppm)

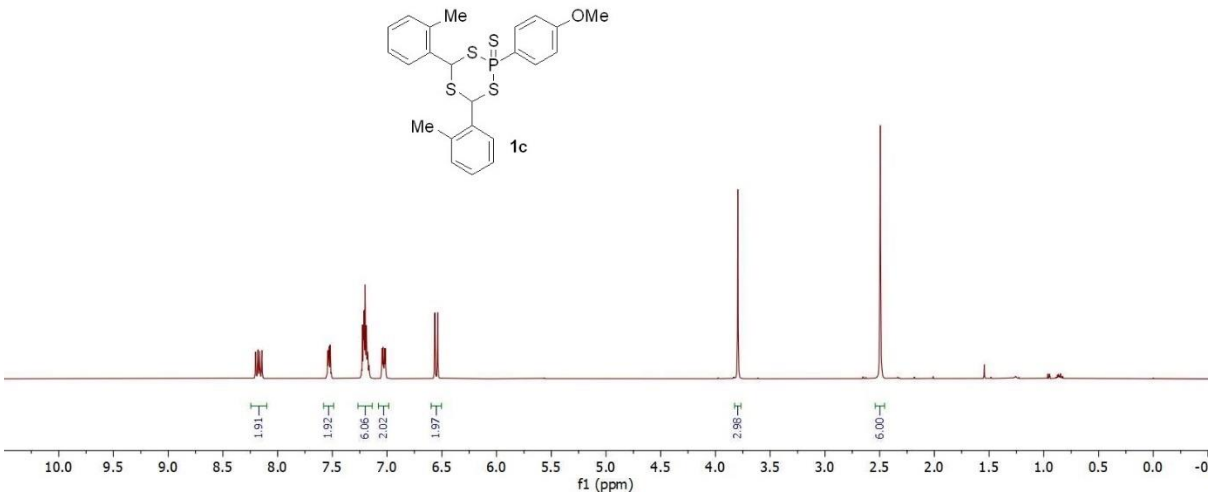

72.76
(31P NMR, CDCl3, 162 MHz)
OMe
S
S
P
S
S
1a
f1 (ppm)
8.221
8.199
8.185
8.162
7.317
7.282
7.271
7.252
7.233
7.158
7.140
7.088
7.080
7.066
7.057
6.259
6.236
3.877
2.338
0.000


(1H NMR, CDCl3, 400 MHz)
Me
OMe
S
S
P
S
S
Me
1b
f1 (ppm)
1.67
5.86
2.08
1.74
1.75
2.66
6.00

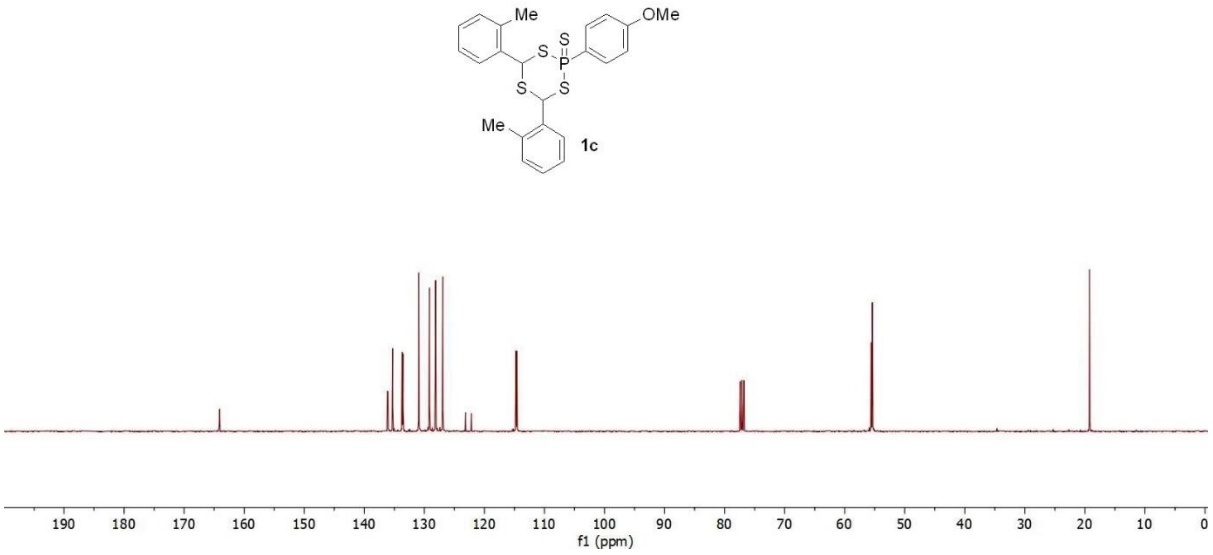

164.19
139.15
137.66
137.58
133.85
133.72
130.19
129.15
128.72
125.12
123.28
122.30
114.78
114.62
77.42
77.10
76.78
58.37
55.68
21.38
(13 C{H} NMR, CDCl3, 100 MHz)
Me
OMe
S
S
P
S
S
Me
1b
f1 (ppm)

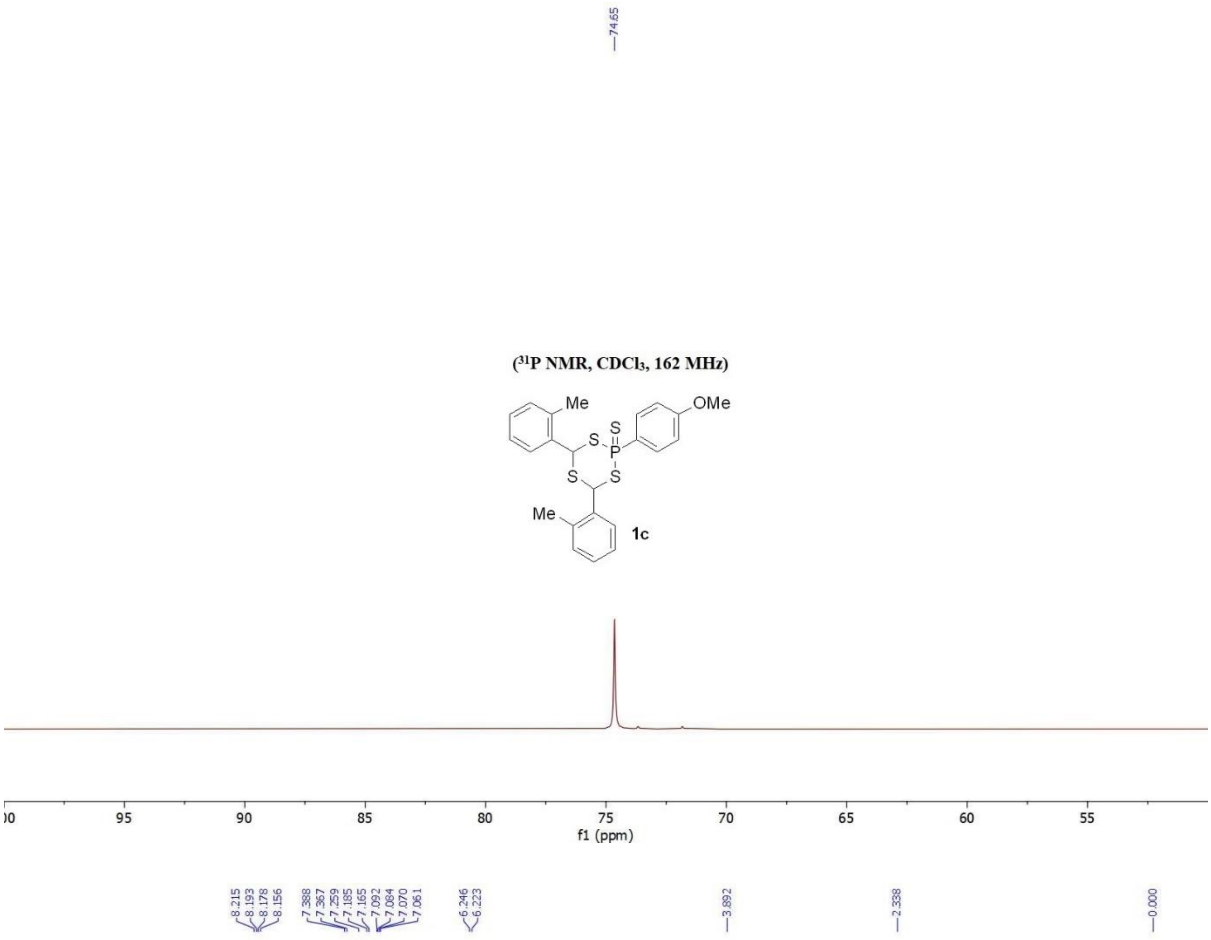

72.74
(31P NMR, CDCl3, 162 MHz)
Me
OMe
S
S
P
S
S
Me
1b
f1 (ppm)

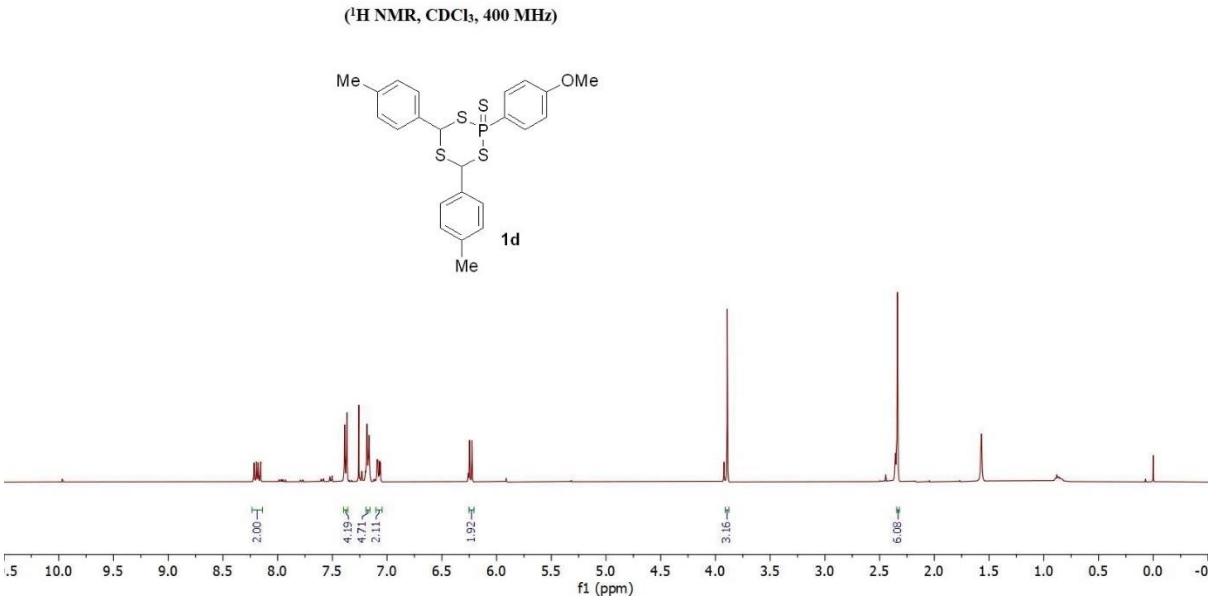
(¹H NMR, CDCl₃, 400 MHz)



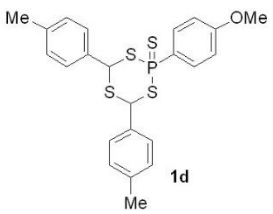
(¹³ C{H} NMR, CDCl₃, 100 MHz)



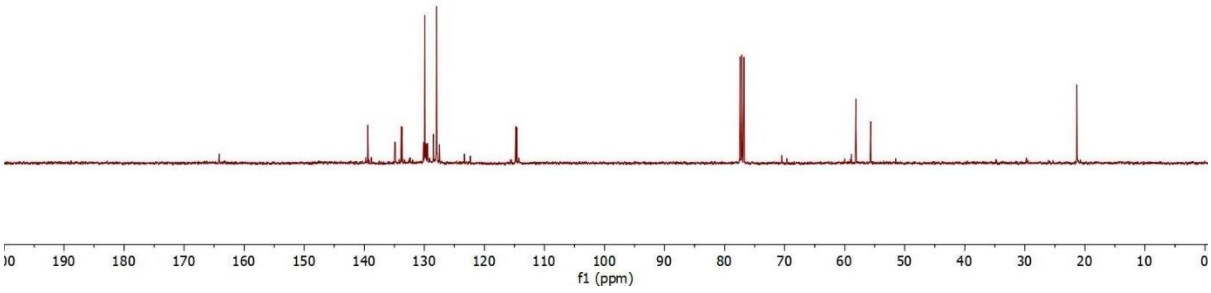

7.465
(31P NMR, CDCl3, 162 MHz)
Me
OMe
S
S
P
S
S
Me
1c
95
90
85
80
75
70
65
60
55
f1 (ppm)
8.215
8.193
8.178
8.156
7.388
7.367
7.259
7.185
7.165
7.092
7.084
7.070
7.061
6.246
6.223
3.892
2.338
0.000


(1H NMR, CDCl3, 400 MHz)
Me
OMe
S
S
P
S
S
1d
Me
2.00
4.19
4.71
2.11
1.92
3.16
6.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

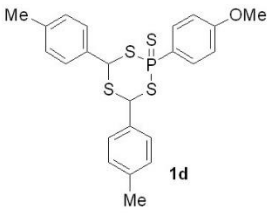
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



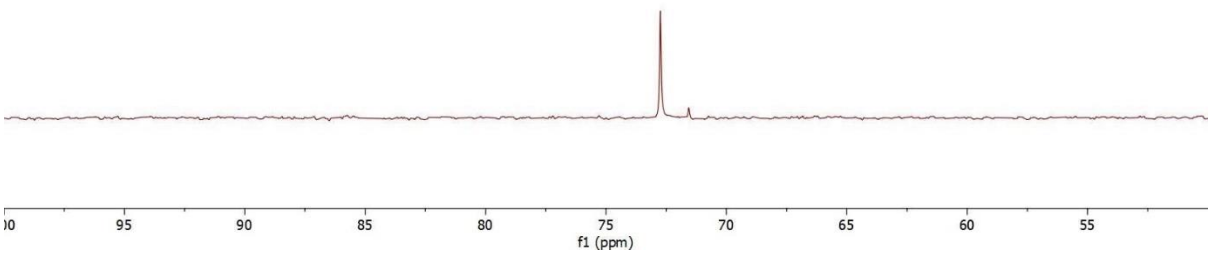
1d



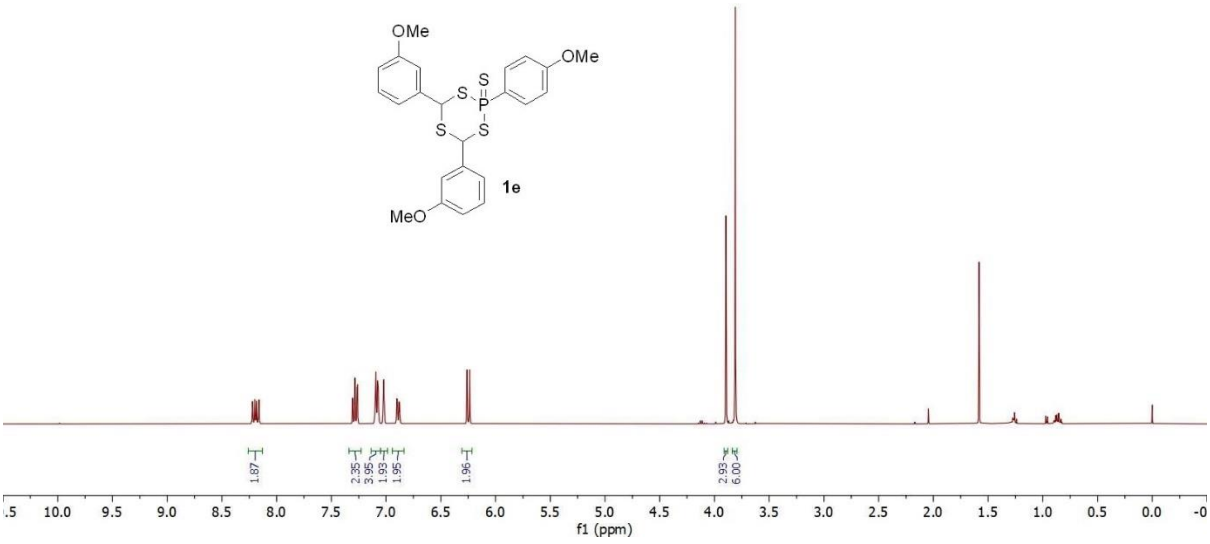
(^{31}P NMR, $CDCl_3$, 162 MHz)



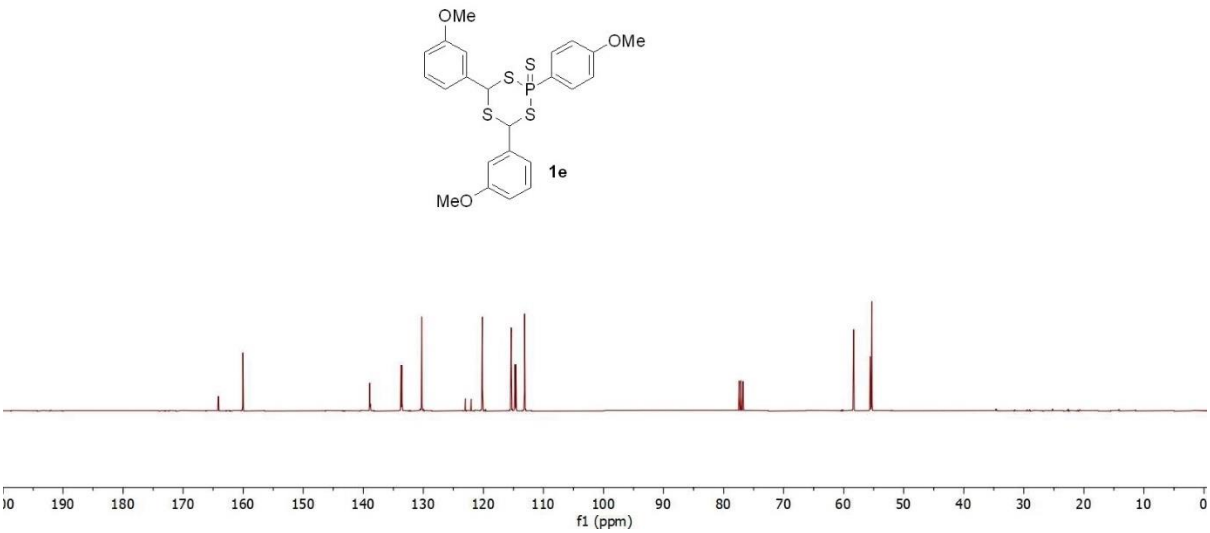
1d

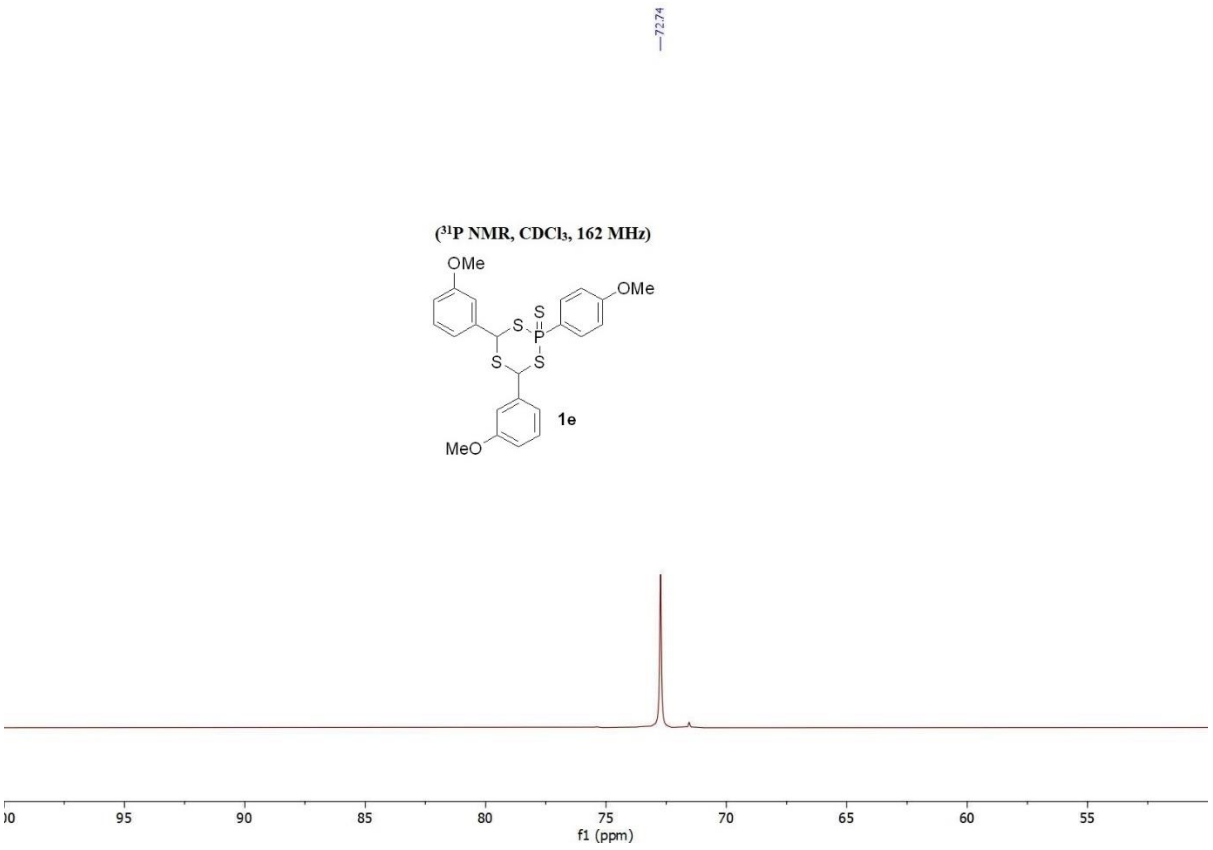


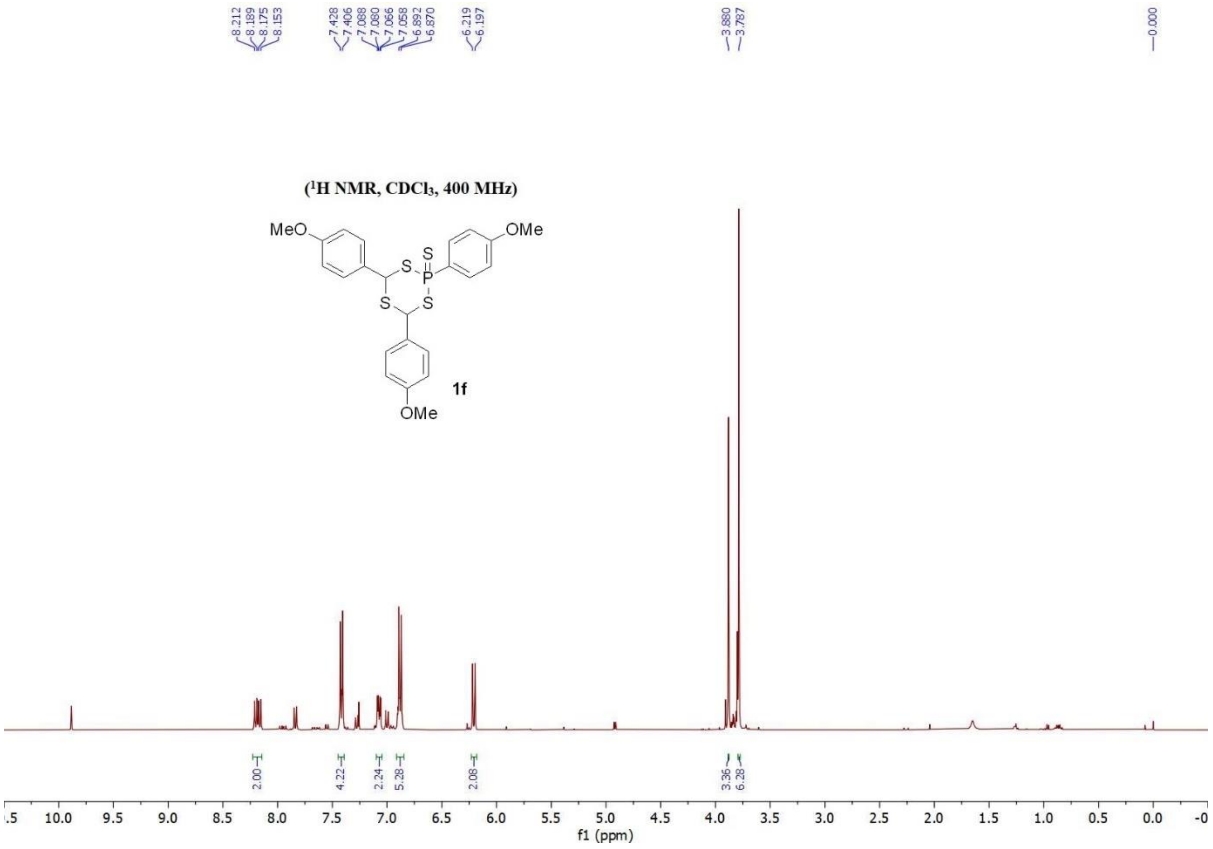
(¹H NMR, CDCl₃, 400 MHz)



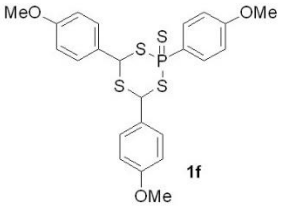
(¹³ C{H} NMR, CDCl₃, 100 MHz)



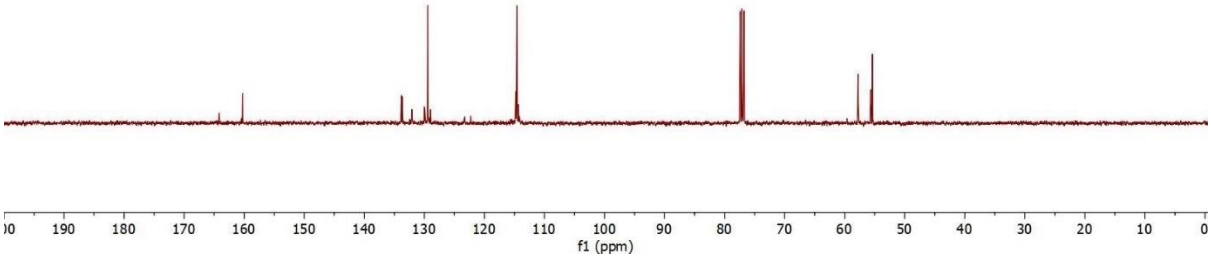

72.74
(31P NMR, CDCl3, 162 MHz)
OMe
OMe
S
S
P
S
S
1e
MeO
95
90
85
80
75
70
65
60
55
f1 (ppm)


8.212
8.189
8.175
8.153
7.428
7.406
7.088
7.080
7.066
7.058
6.892
6.870
6.219
6.197
3.880
3.787
0.000
(1H NMR, CDCl3, 400 MHz)
MeO
OMe
S
S
P
S
S
1f
OMe
2.00
4.22
2.24
5.28
2.08
3.36
6.38
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

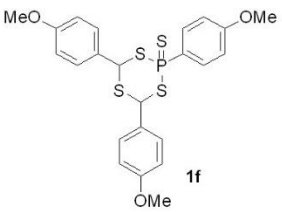
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



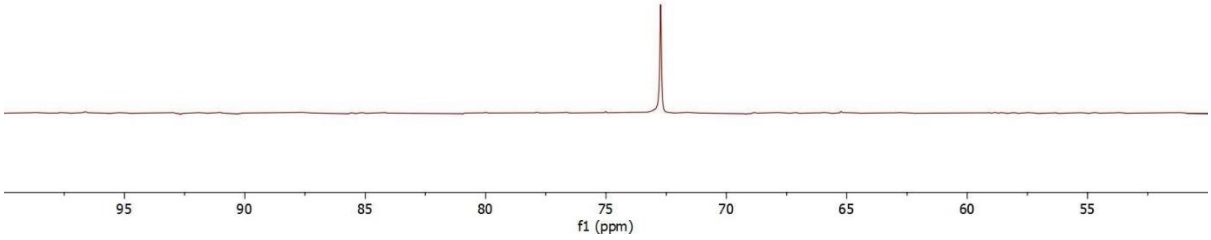
1f

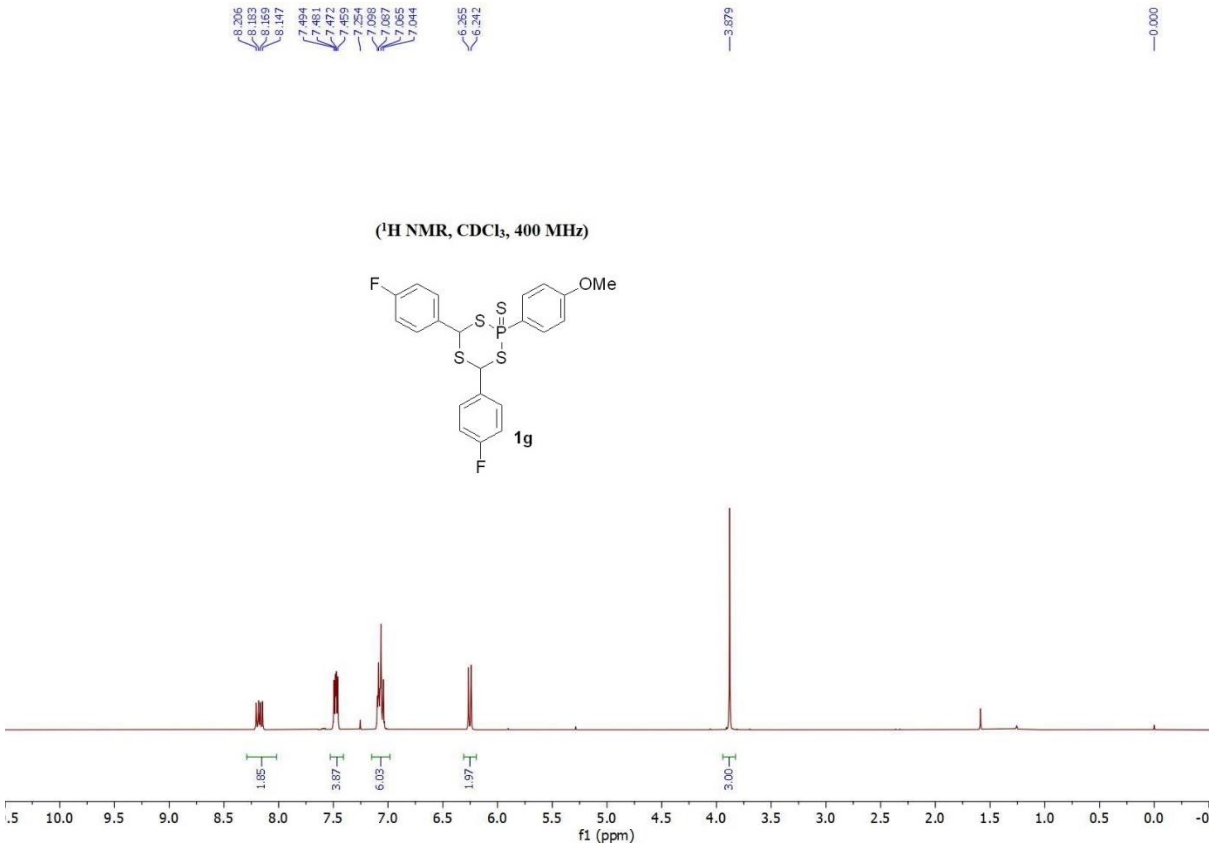


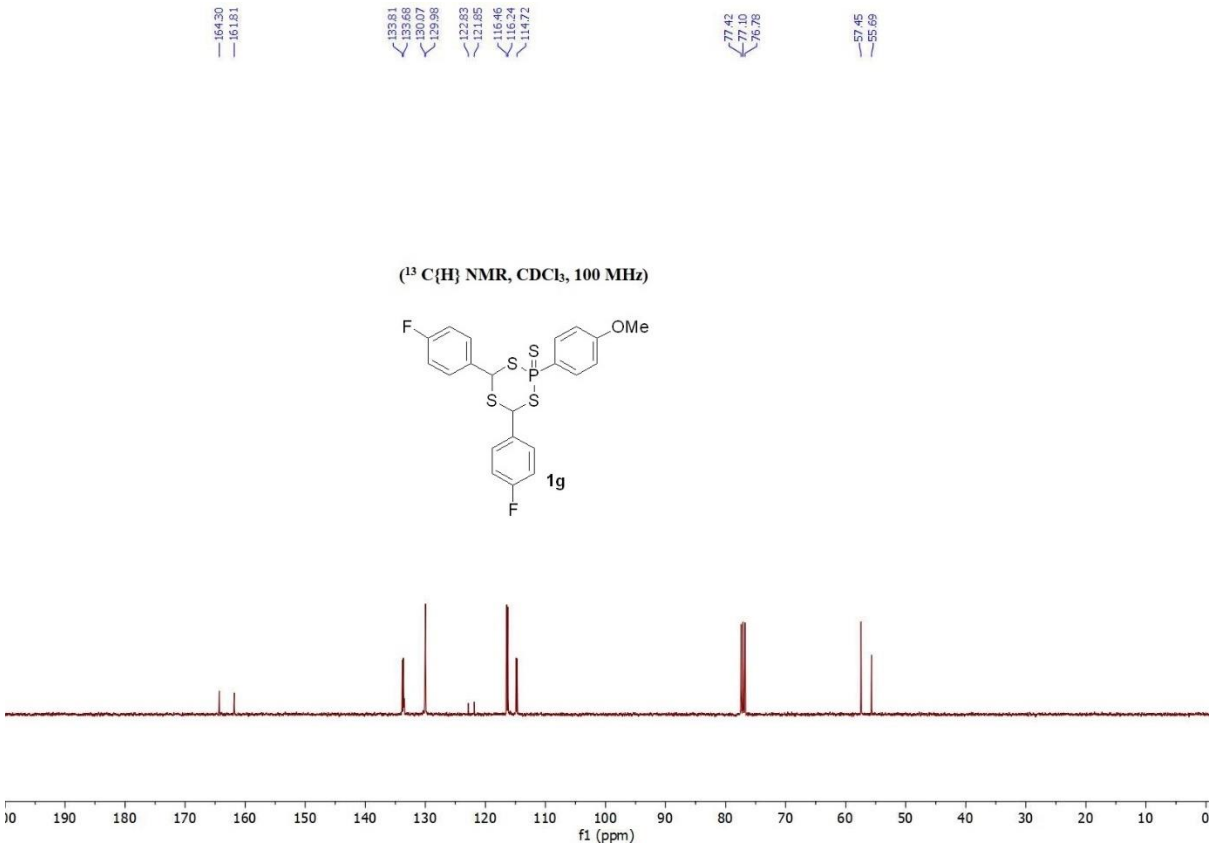
(^{31}P NMR, $CDCl_3$, 162 MHz)

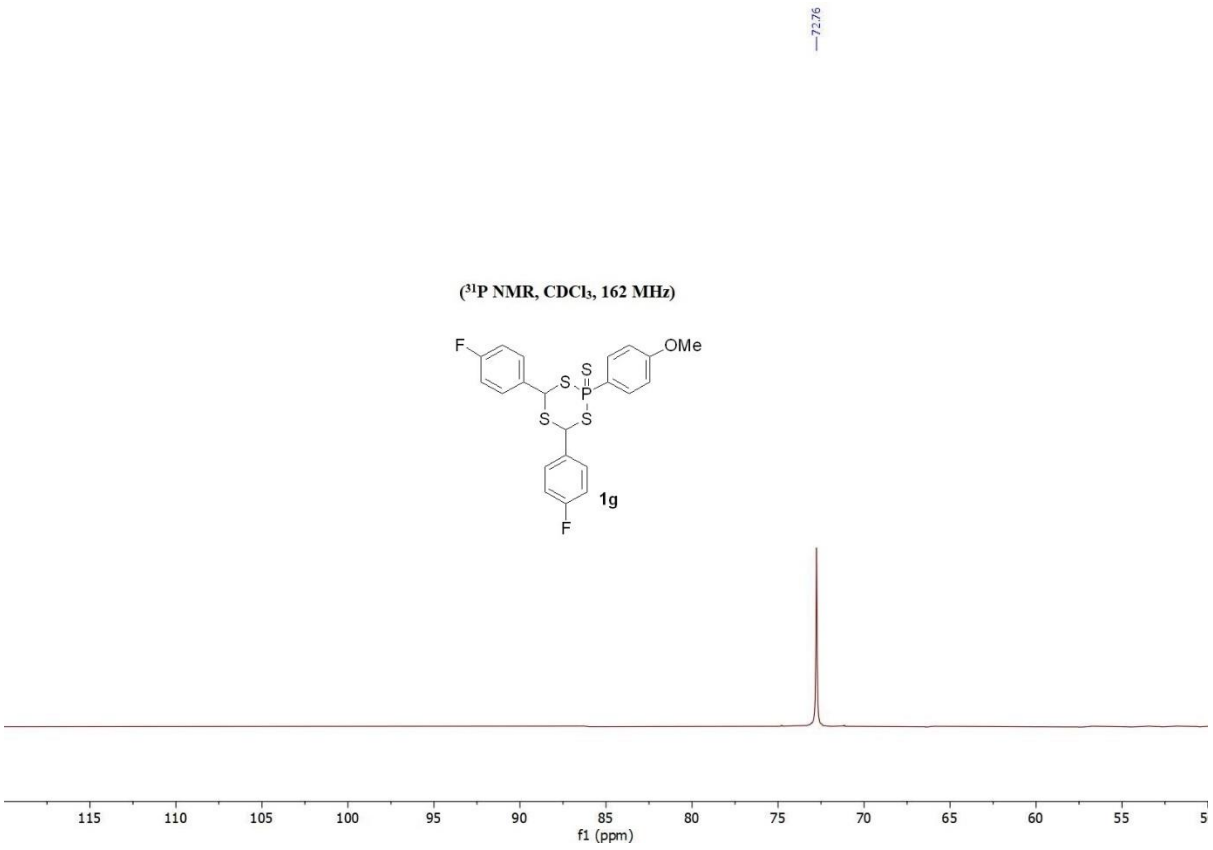


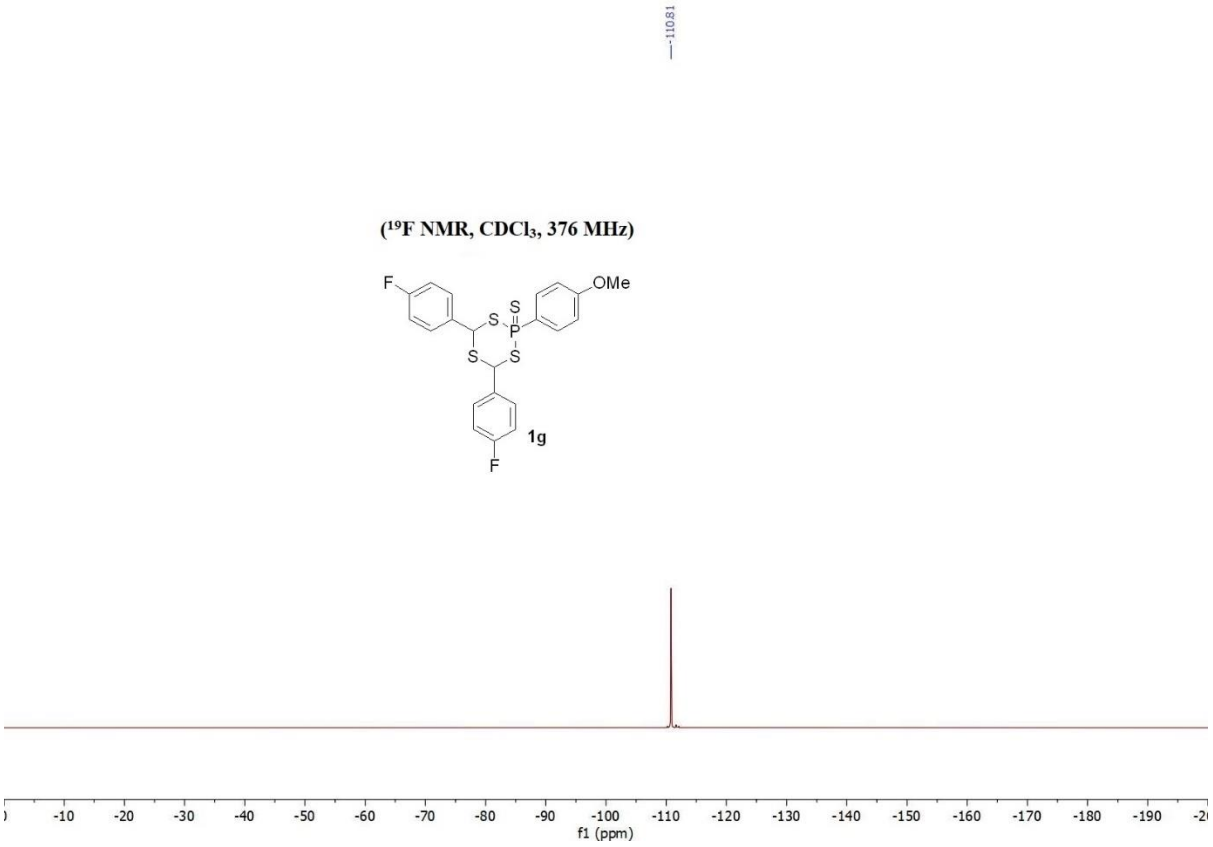
1f



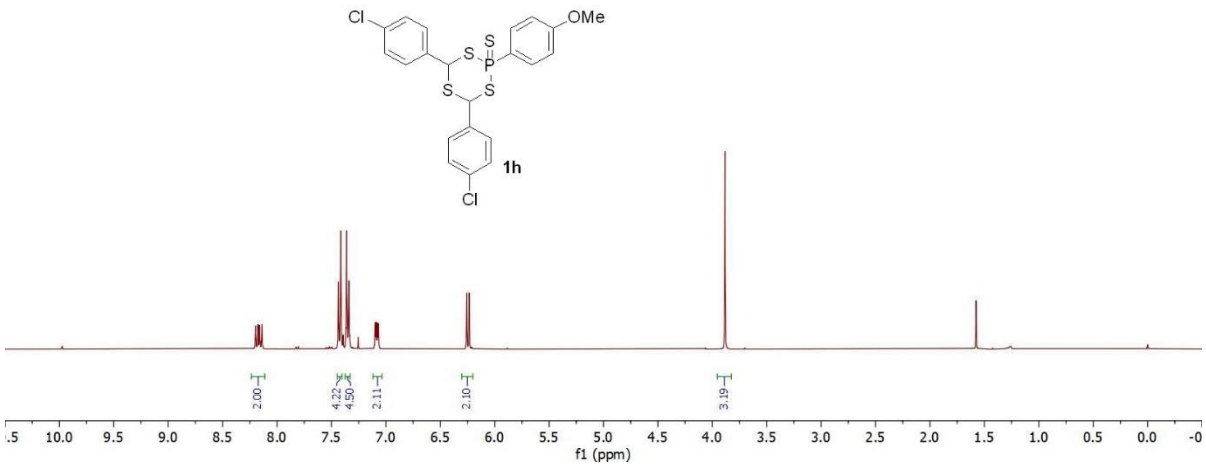

8.206
8.183
8.169
8.147
7.494
7.481
7.472
7.459
7.354
7.098
7.087
7.065
7.044
6.265
6.242
3.879
0.000
(1H NMR, CDCl3, 400 MHz)
F
OMe
S
S
P
S
S
1g
F
1.85
3.87
6.03
1.97
3.00
f1 (ppm)


164.30
161.81
133.81
133.68
130.07
129.98
122.83
121.85
116.46
116.24
114.72
77.42
77.10
76.78
57.45
55.69
(13 C{H} NMR, CDCl3, 100 MHz)
F
OMe
S
S
P
S
S
1g
F
f1 (ppm)

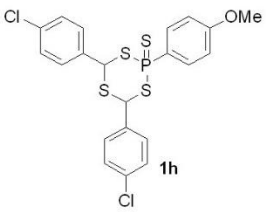

72.76
(31P NMR, CDCl3, 162 MHz)
F
OMe
S
S
P
S
S
S
1g
F
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)

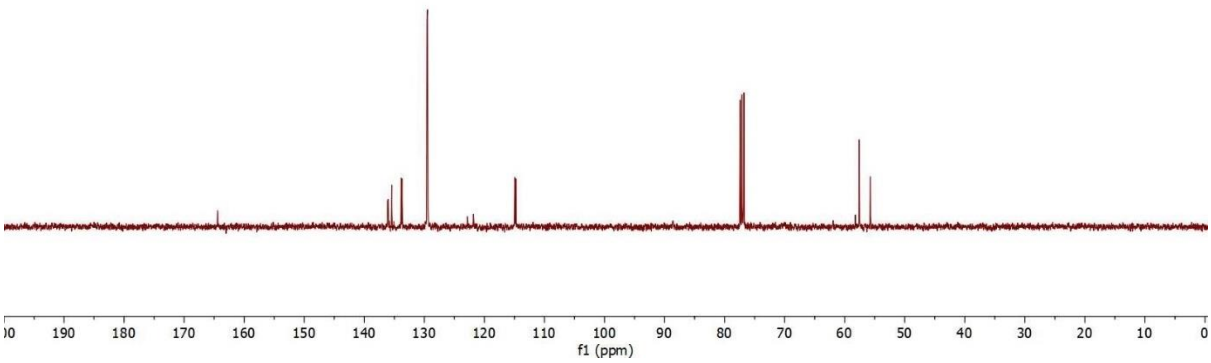

-110.81
(19F NMR, CDCl3, 376 MHz)
F
OMe
S
S
P
S
S
S
1g
F
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

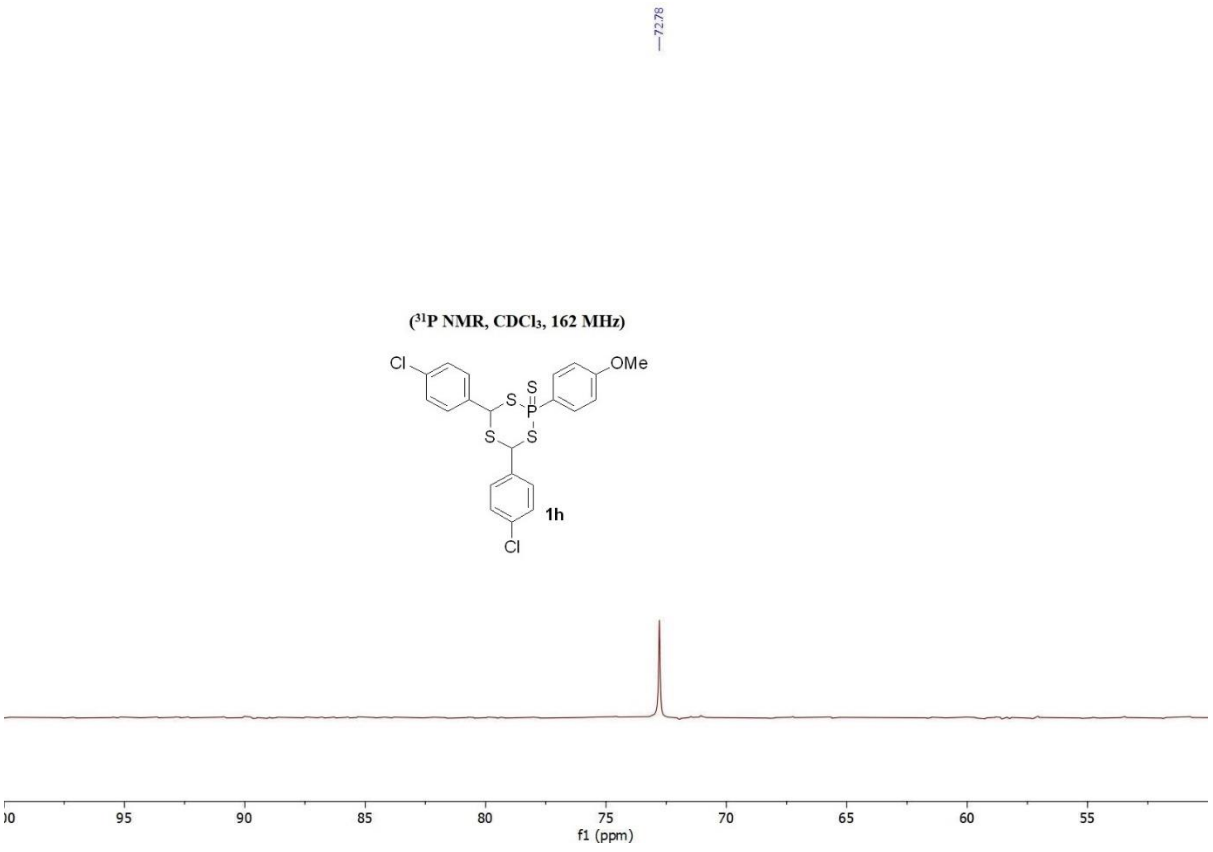
(¹H NMR, $CDCl_3$, 400 MHz)

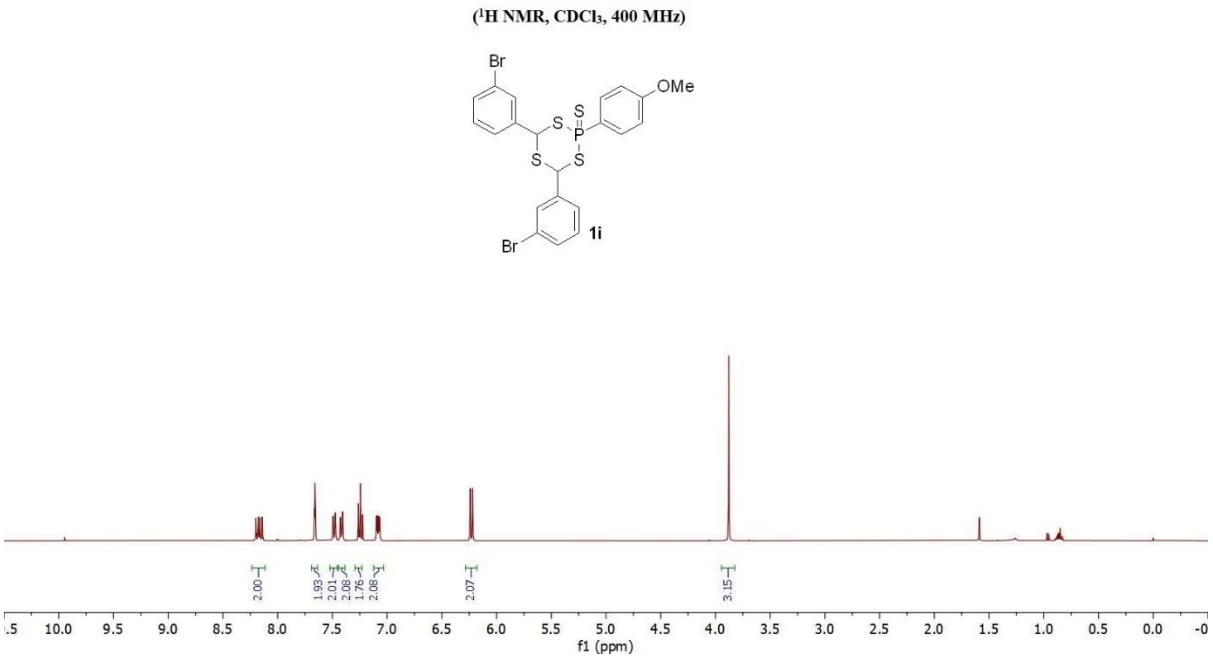


(¹³ C{H} NMR, $CDCl_3$, 100 MHz)

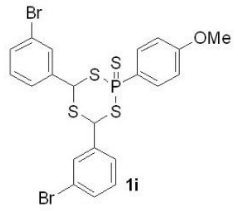


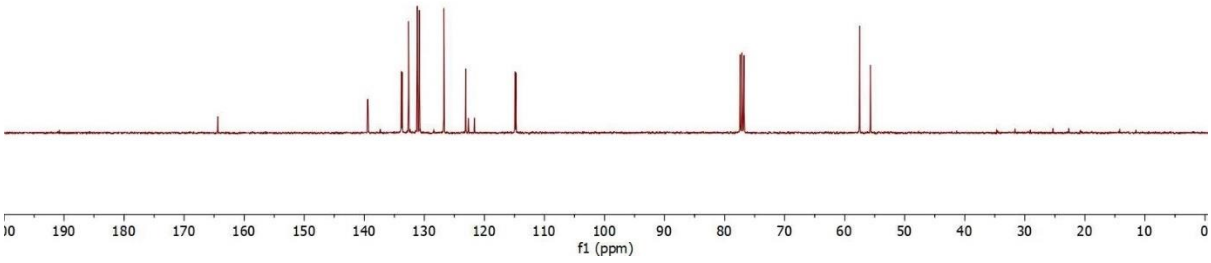



72.78
(31P NMR, CDCl3, 162 MHz)
Cl
OMe
S
S
P
S
S
S
1h
Cl
95
90
85
80
75
70
65
60
55
f1 (ppm)
8.199
8.177
8.162
8.140
7.664
7.659
7.655
7.496
7.491
7.489
7.476
7.471
7.469
7.429
7.427
7.423
7.410
7.406
7.403
7.363
7.343
7.223
7.098
7.089
7.075
7.067
6.241
6.218
3.878
0.000

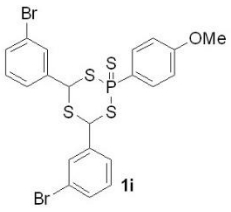

(1H NMR, CDCl3, 400 MHz)
Br
OMe
S
S
P
S
S
S
1i
Br
2.00
1.93
2.01
2.08
1.76
2.08
2.07
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

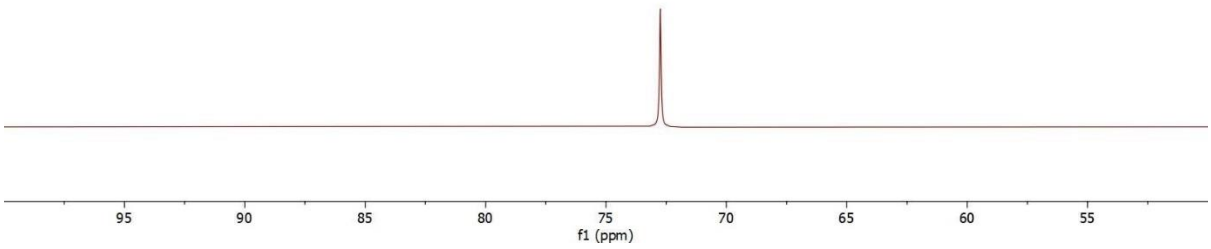
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



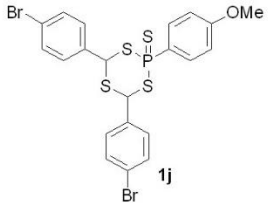


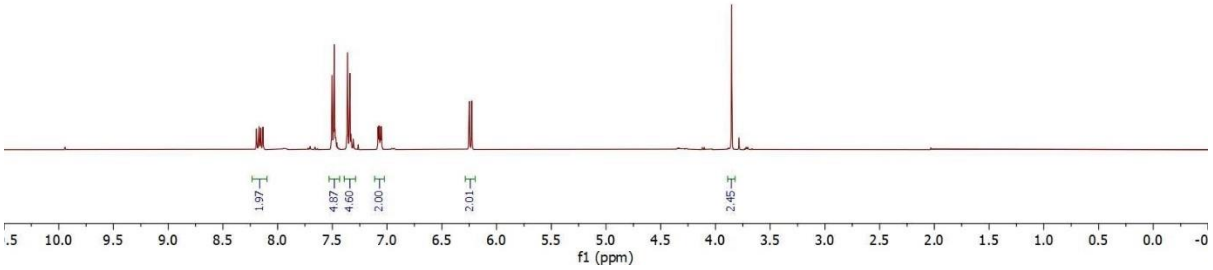
(^{31}P NMR, $CDCl_3$, 162 MHz)



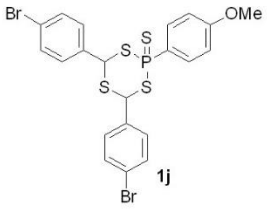


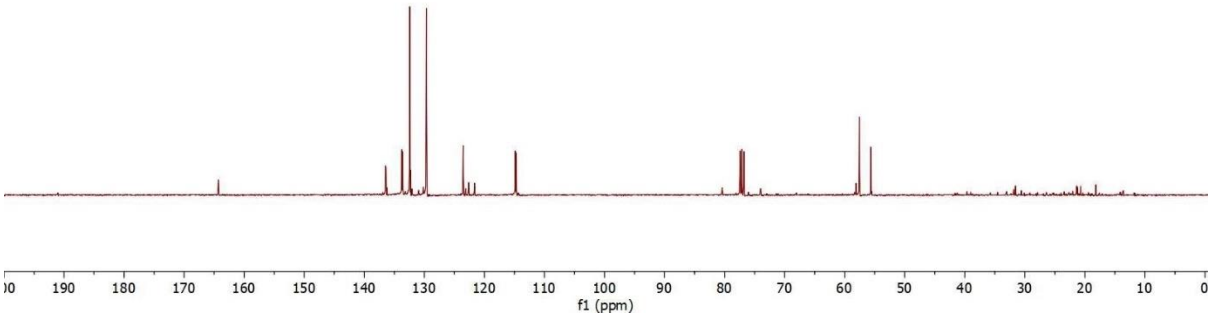
(^{1}H NMR, $CDCl_3$, 400 MHz)

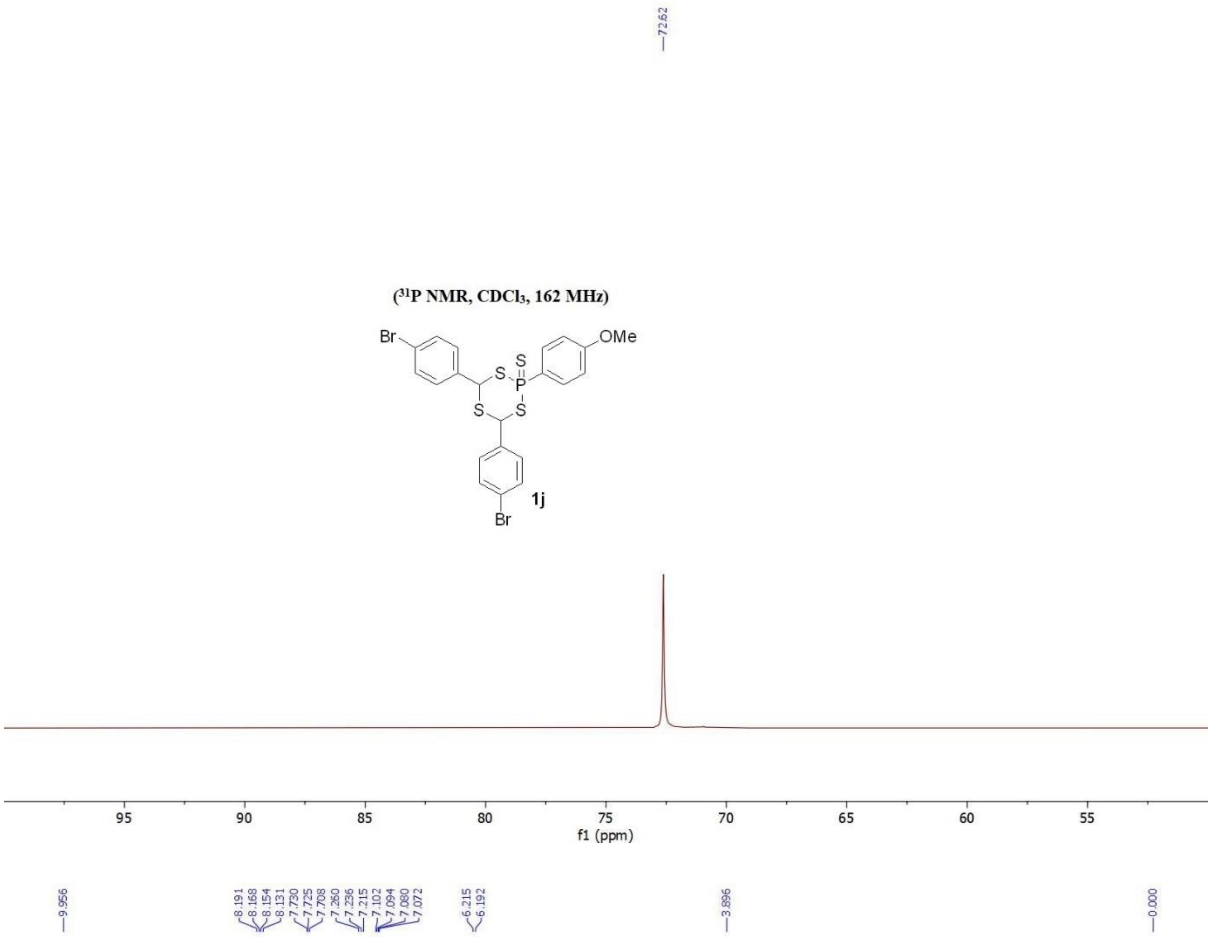


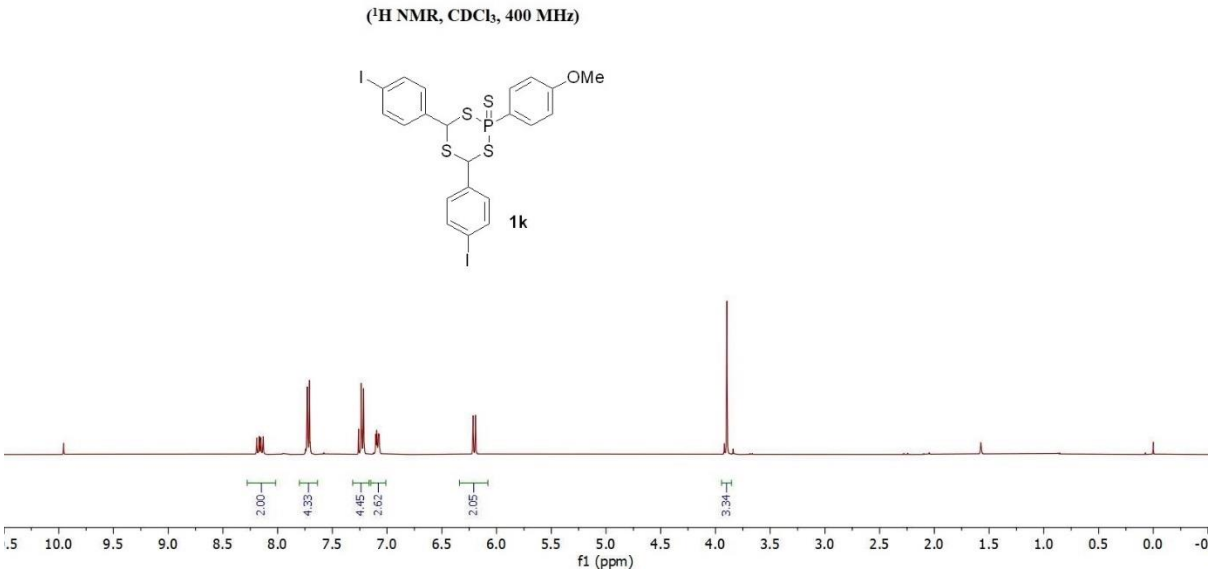


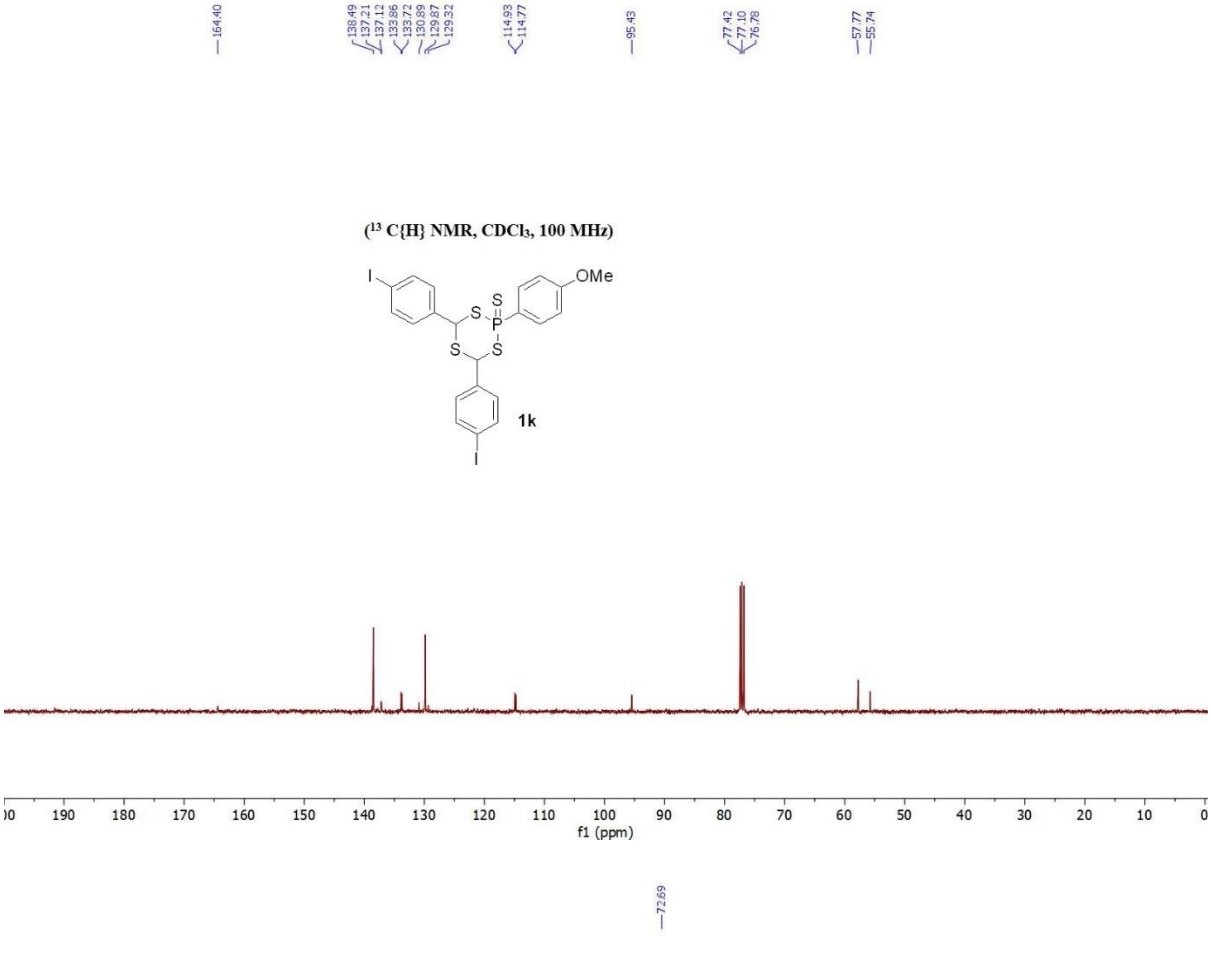
(^{13} C{H} NMR, $CDCl_3$, 100 MHz)

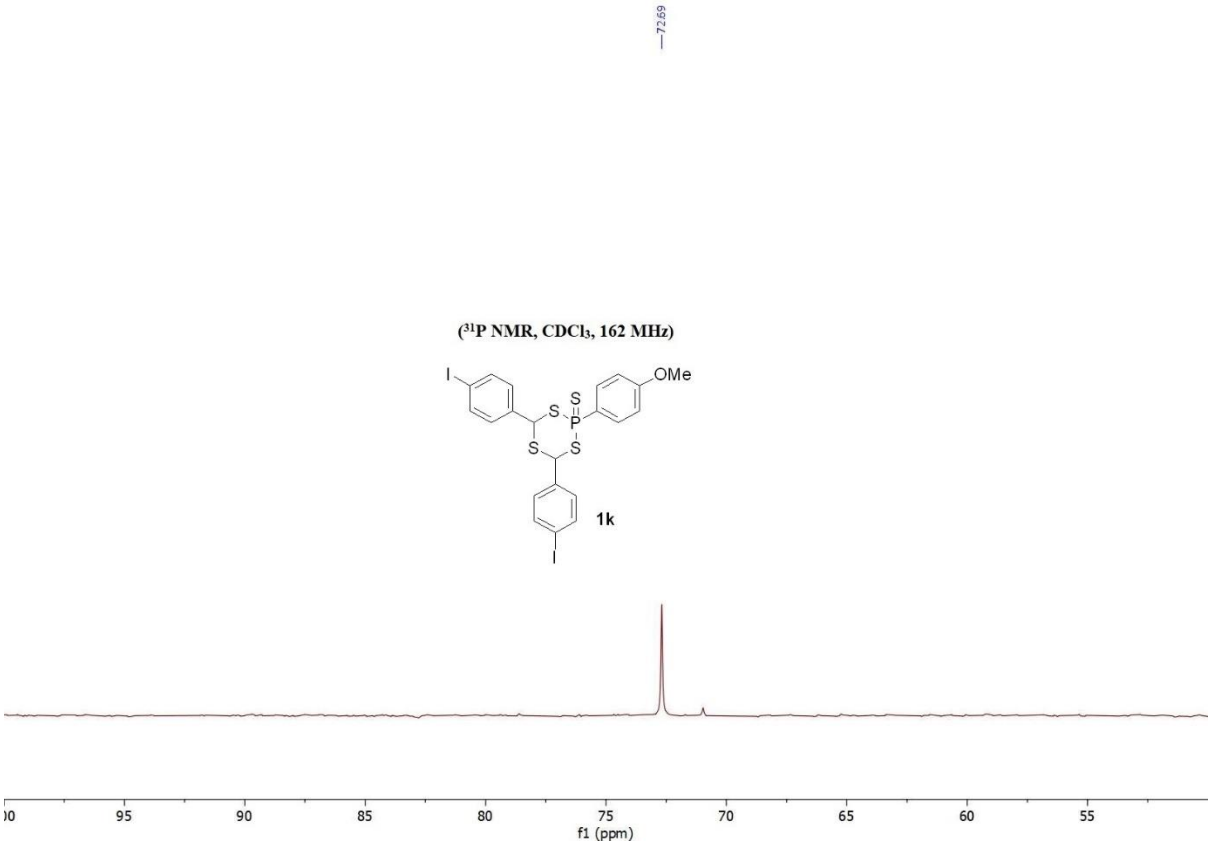


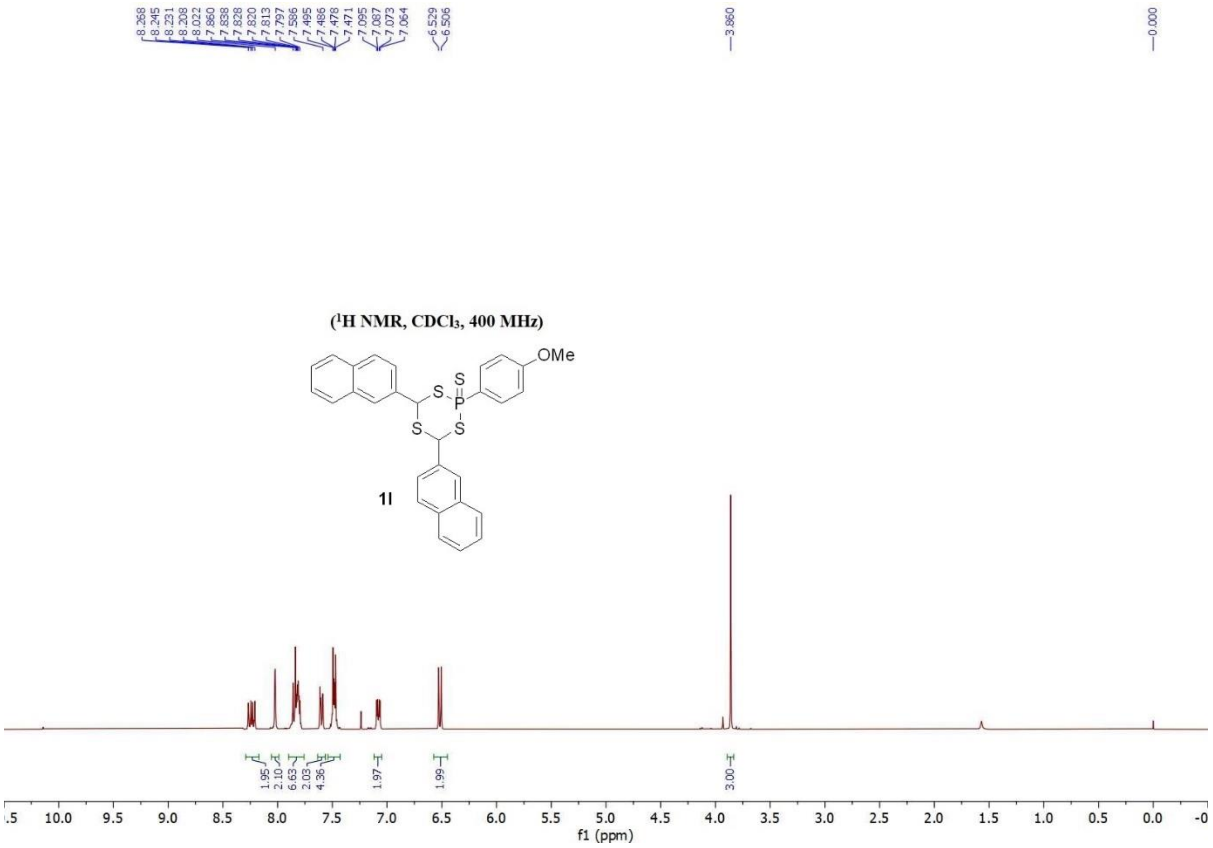


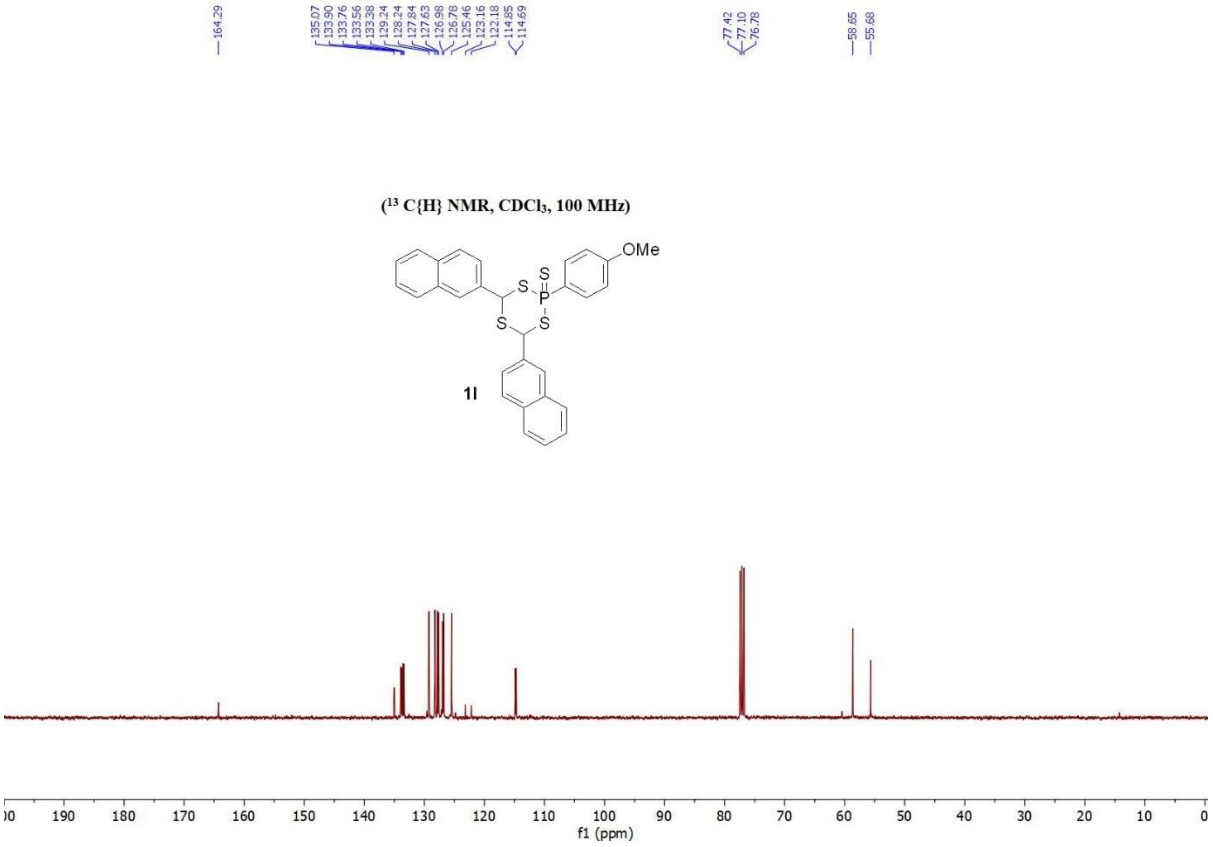

7.262
(31P NMR, CDCl3, 162 MHz)
Br
OMe
S
S
P
S
S
S
1j
Br
95
90
85
80
75
70
65
60
55
f1 (ppm)
9.956
8.191
8.168
8.154
8.131
7.730
7.725
7.708
7.360
7.236
7.215
7.102
7.094
7.080
7.072
6.215
6.192
3.896
0.000

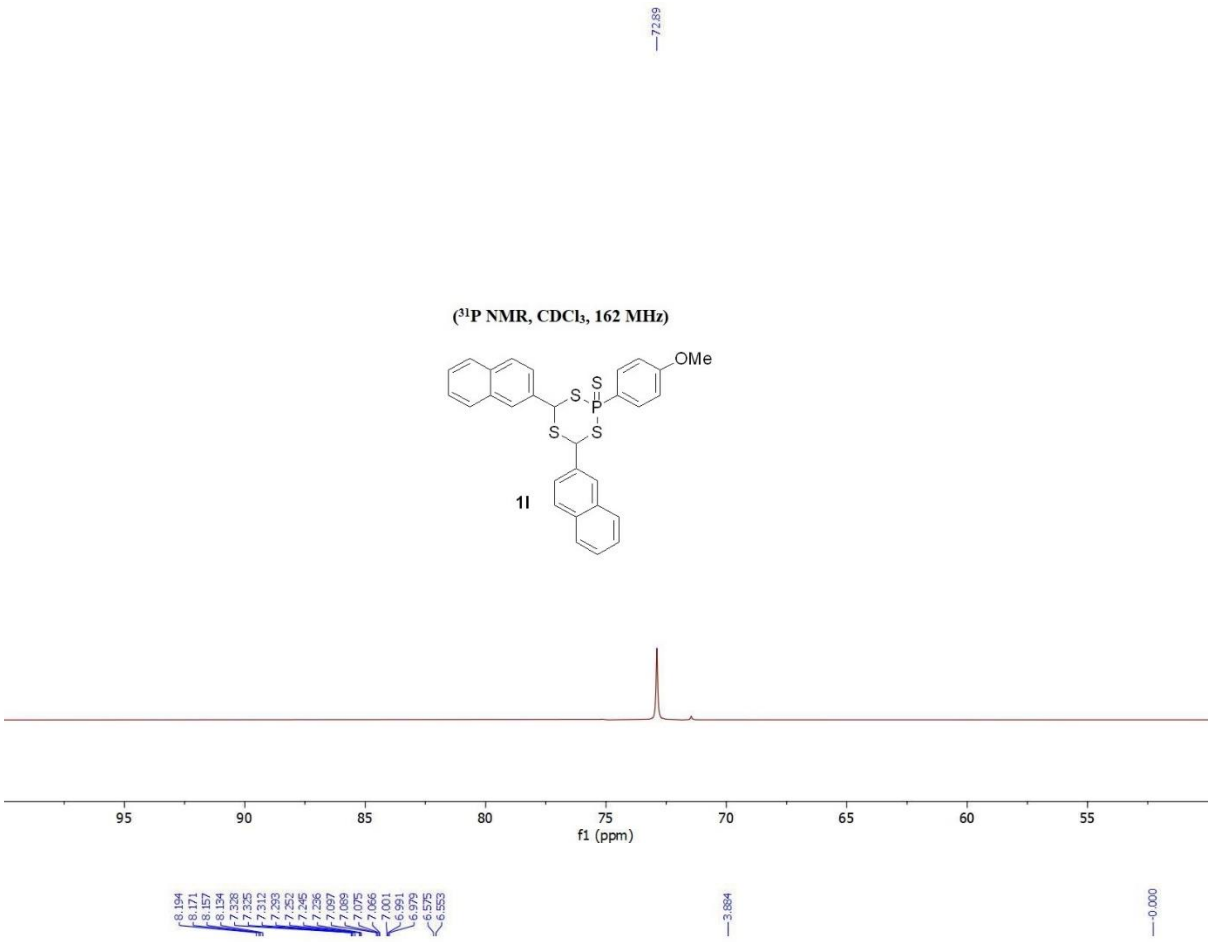

(1H NMR, CDCl3, 400 MHz)
I
OMe
S
S
P
S
S
S
1k
I
2.00
4.33
4.45
2.62
2.05
3.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

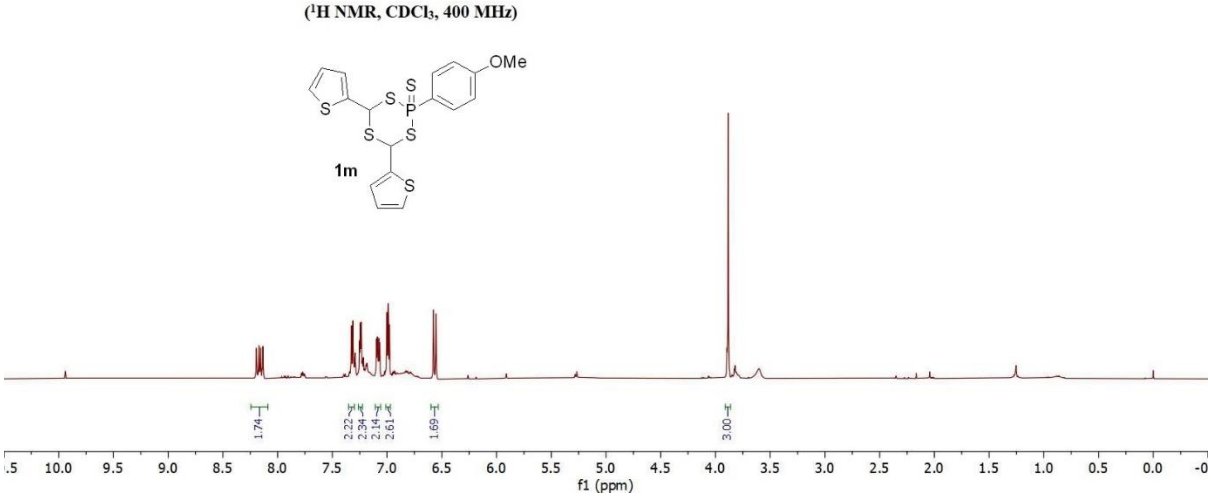

164.40
138.49
137.21
137.12
133.86
133.72
130.89
129.87
129.32
114.93
114.77
95.43
77.42
77.10
76.78
57.77
55.74
(13 C{H} NMR, CDCl3, 100 MHz)
I
OMe
S
S
P
S
S
1k
I
f1 (ppm)


72.69
(31P NMR, CDCl3, 162 MHz)
I
OMe
S
S
P
S
S
1k
I
f1 (ppm)

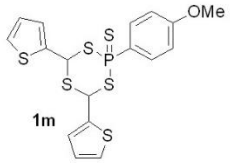

8.258
8.245
8.231
8.208
8.022
7.860
7.838
7.828
7.820
7.813
7.797
7.586
7.495
7.486
7.478
7.471
7.095
7.087
7.073
7.064
6.529
6.506
3.860
0.000
(1H NMR, CDCl3, 400 MHz)
OMe
S
S
P
S
S
1l
1.95
2.10
6.63
2.03
4.36
1.97
1.99
3.00
f1 (ppm)

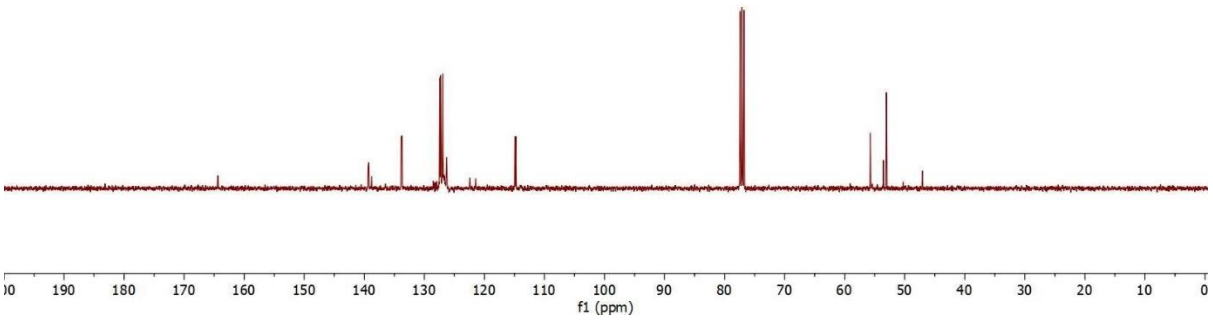

164.29
135.07
133.90
133.76
133.56
133.38
129.24
128.24
127.84
127.63
126.98
126.78
125.46
123.16
122.18
114.85
114.69
77.42
77.10
76.78
58.65
55.68
(13 C{H} NMR, CDCl3, 100 MHz)
OMe
S
S
P
S
S
1l
f1 (ppm)


72.89
(31P NMR, CDCl3, 162 MHz)
OMe
S
S
P
S
S
S
1l
95
90
85
80
75
70
65
60
55
f1 (ppm)
8.194
8.171
8.157
8.134
7.328
7.325
7.311
7.293
7.252
7.245
7.236
7.097
7.089
7.075
7.066
7.001
6.991
6.979
6.575
6.553
3.884
0.000

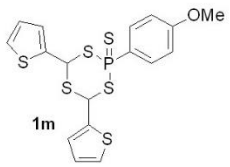

(1H NMR, CDCl3, 400 MHz)
OMe
S
S
P
S
S
S
1m
S
1.74
2.22
2.34
2.14
2.61
1.69
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

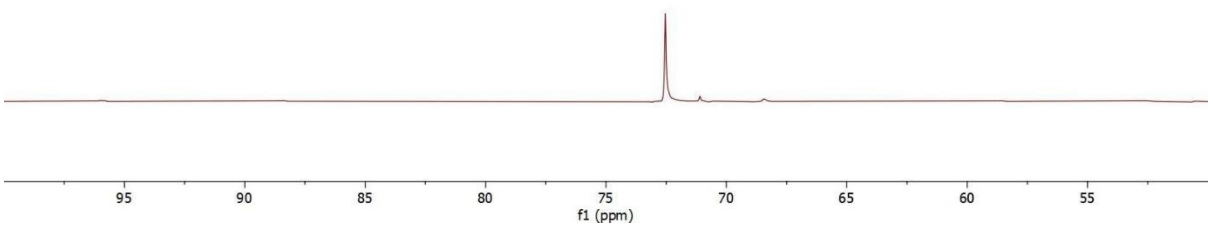
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)

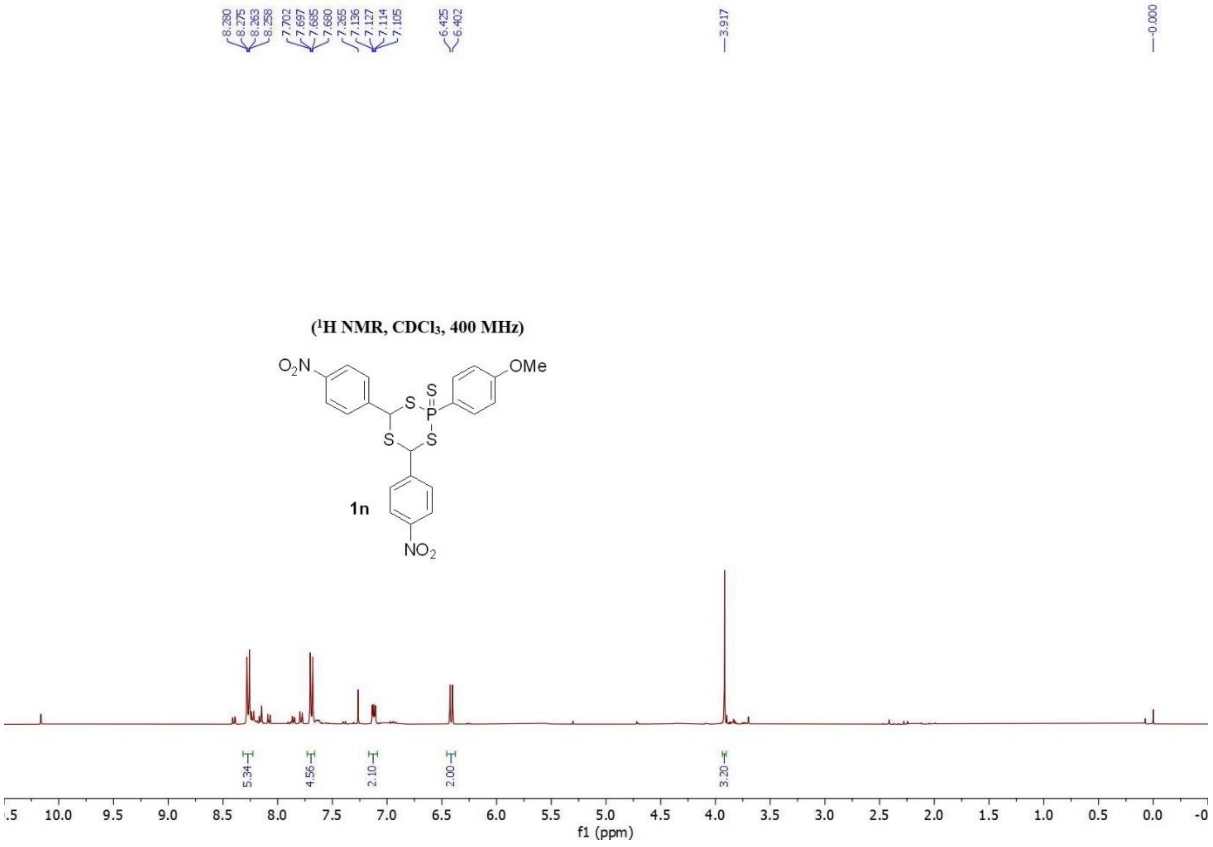


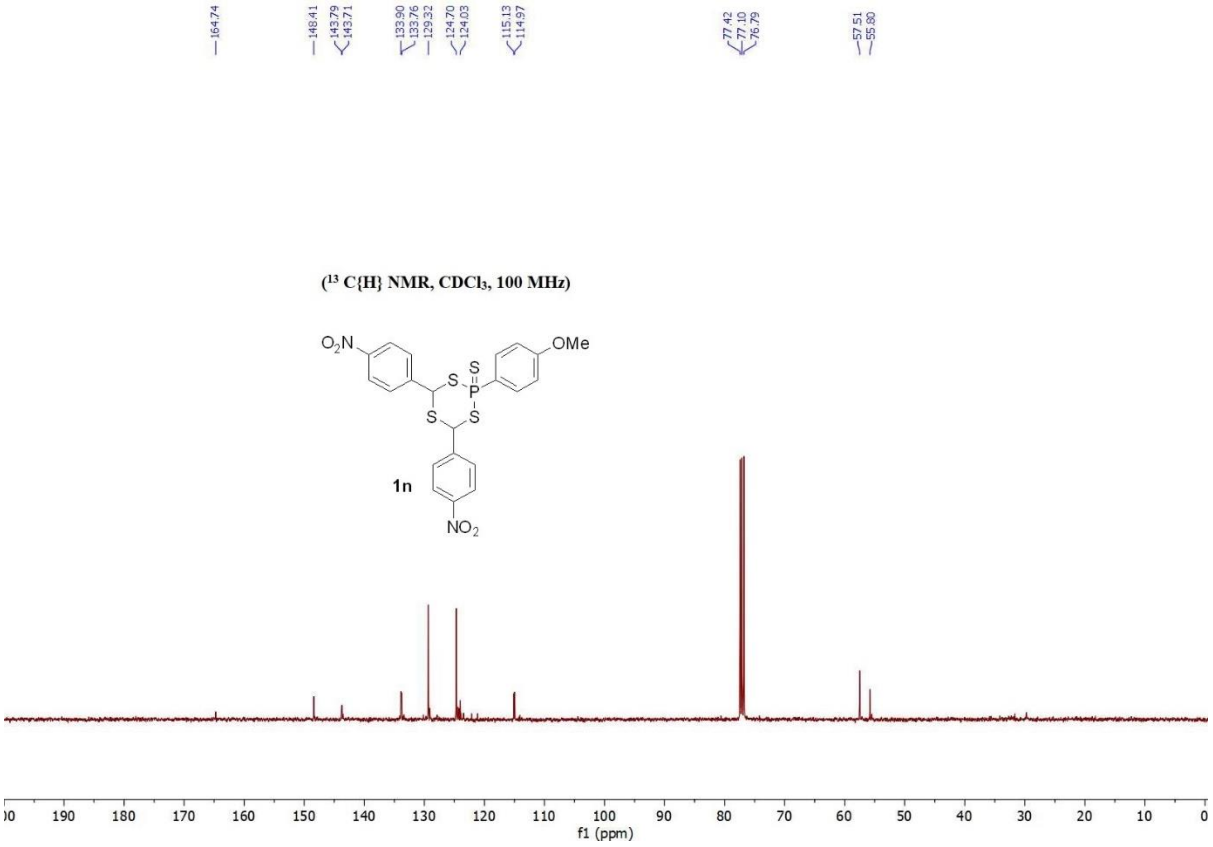


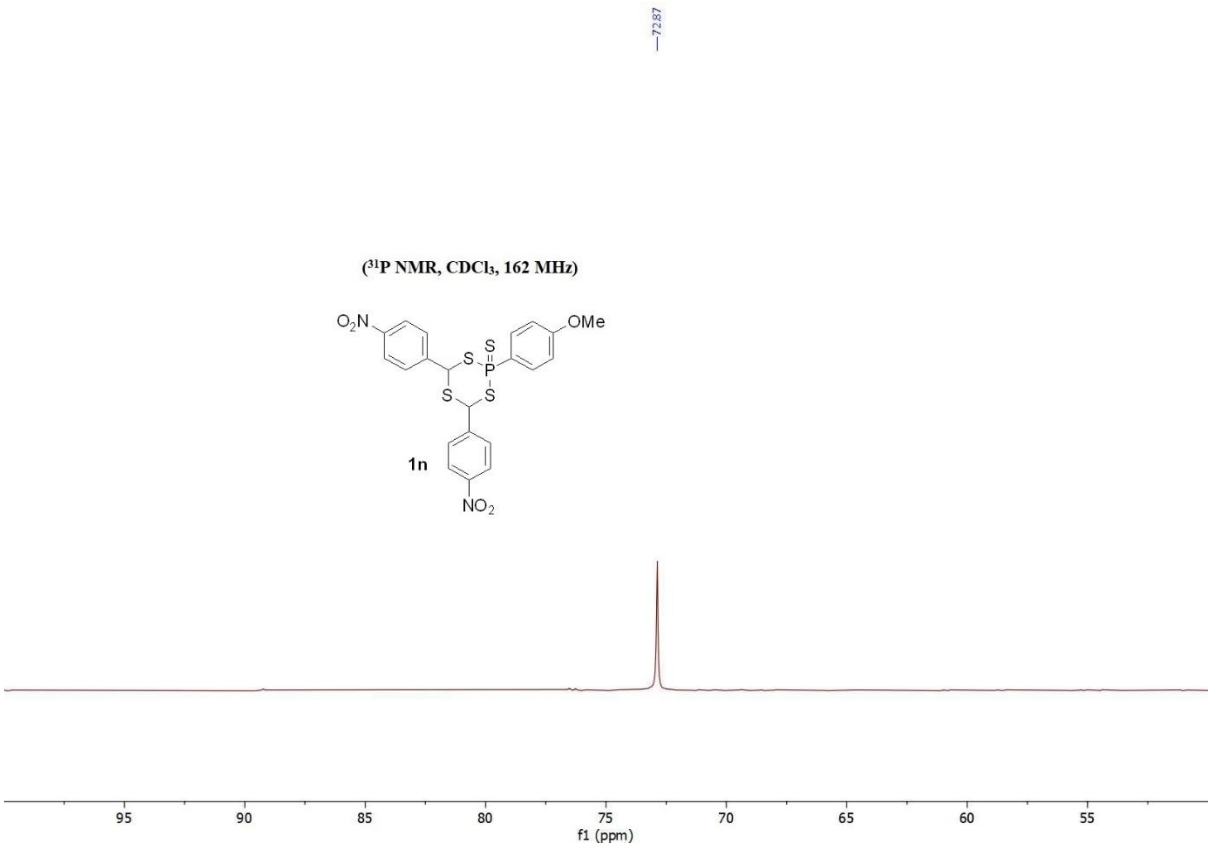
(^{31}P NMR, $CDCl_3$, 162 MHz)





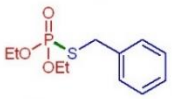

8.290
8.275
8.263
8.258
7.702
7.697
7.685
7.680
7.265
7.136
7.127
7.114
7.105
6.425
6.402
3.917
0.000
(1H NMR, CDCl3, 400 MHz)
O2N
OMe
S
S
P
S
S
S
1n
NO2
5.34
4.56
2.10
2.00
3.20
f1 (ppm)


164.74
148.41
143.79
143.71
133.90
133.76
129.32
124.70
124.03
115.13
114.97
77.42
77.10
76.79
57.51
55.80
(13 C{H} NMR, CDCl3, 100 MHz)
O2N
OMe
S
S
P
S
S
S
1n
NO2
f1 (ppm)

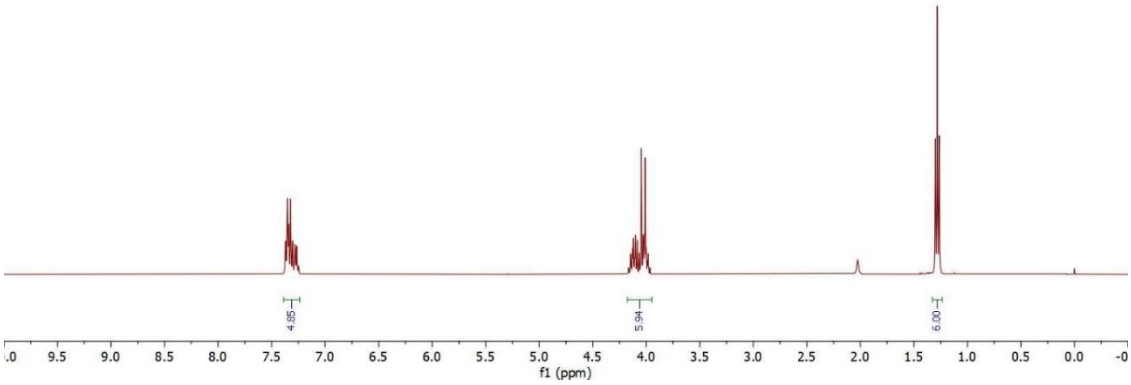

7287
(^{31}P NMR, $CDCl_3$, 162 MHz)
O_2N
OMe
S
S
P
S
S
1n
NO_2
95
90
85
80
75
70
65
60
55
f1 (ppm)

^{1}H, ^{13}C, ^{31}P & ^{19}F NMR spectra of compounds 3

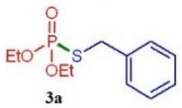
(^{1}H NMR, $CDCl_3$, 400 MHz)



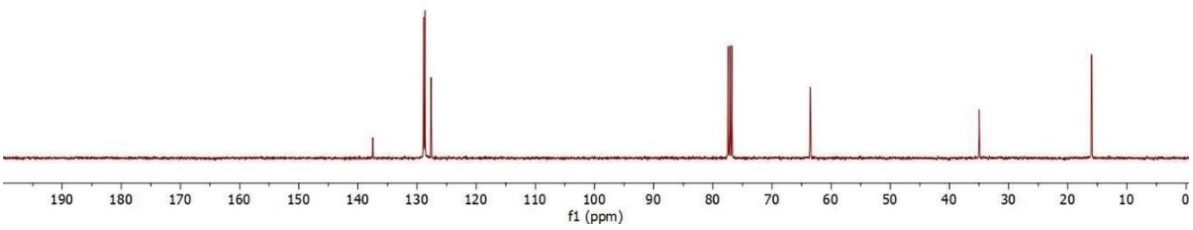
3a

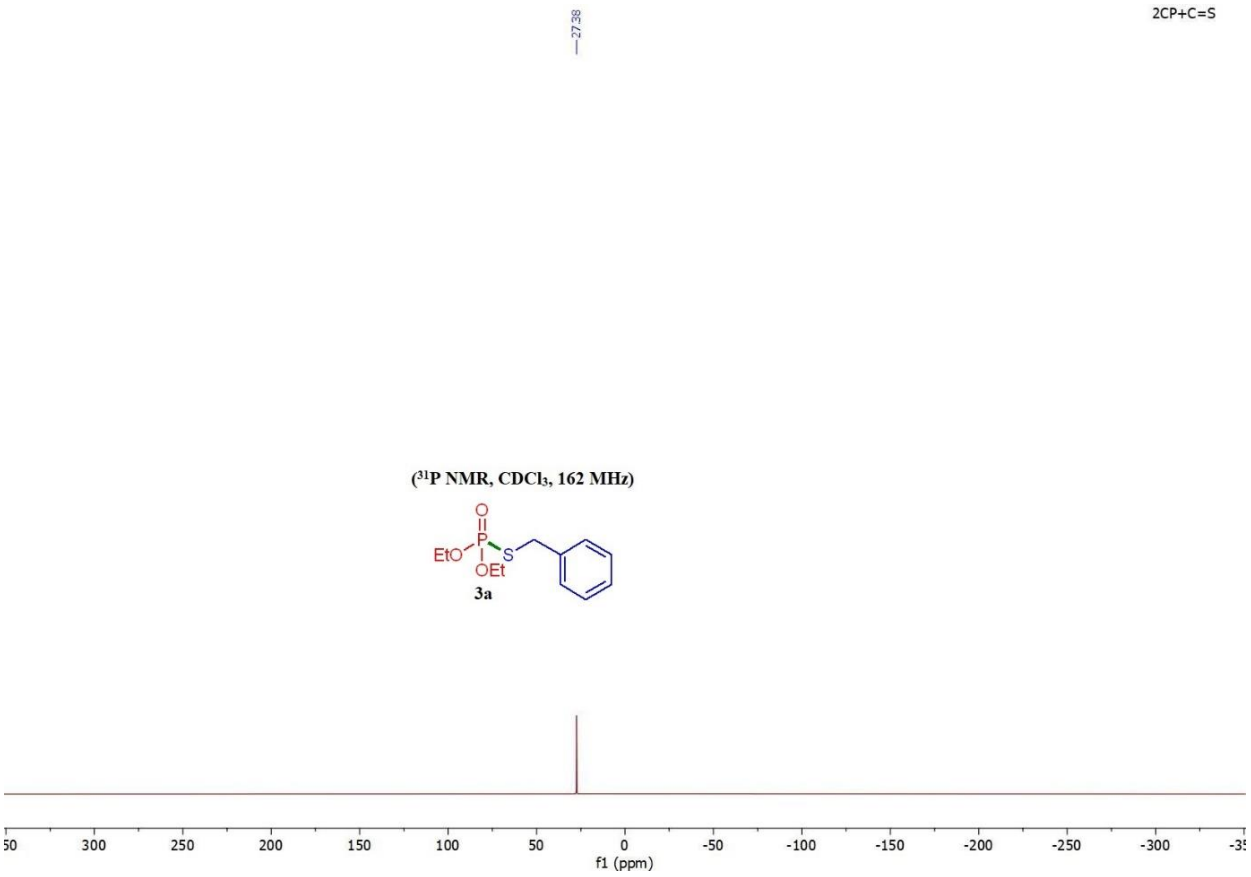


($^{13}C\{H\}$ NMR, $CDCl_3$, 100 MHz)



3a

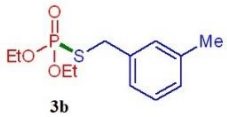




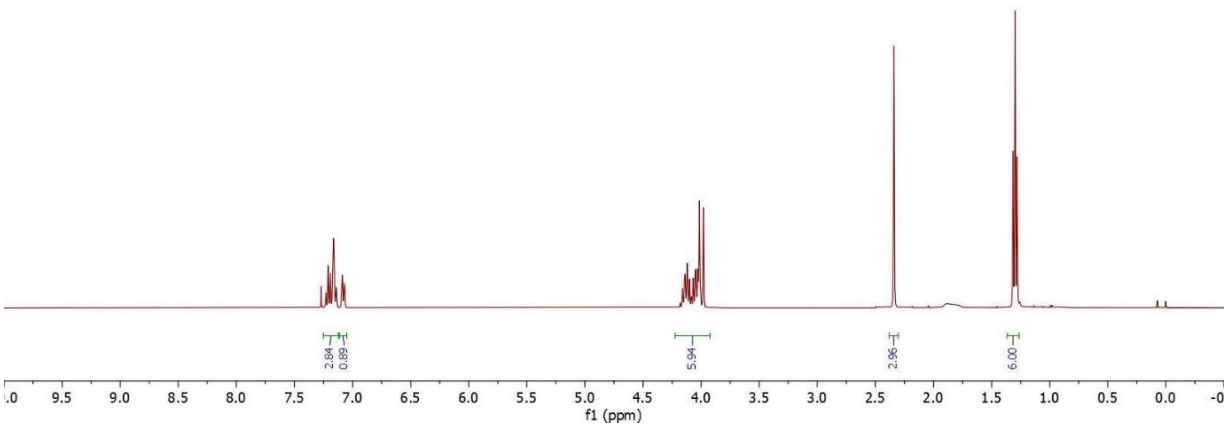
(^{31}P NMR, $CDCl_3$, 162 MHz)

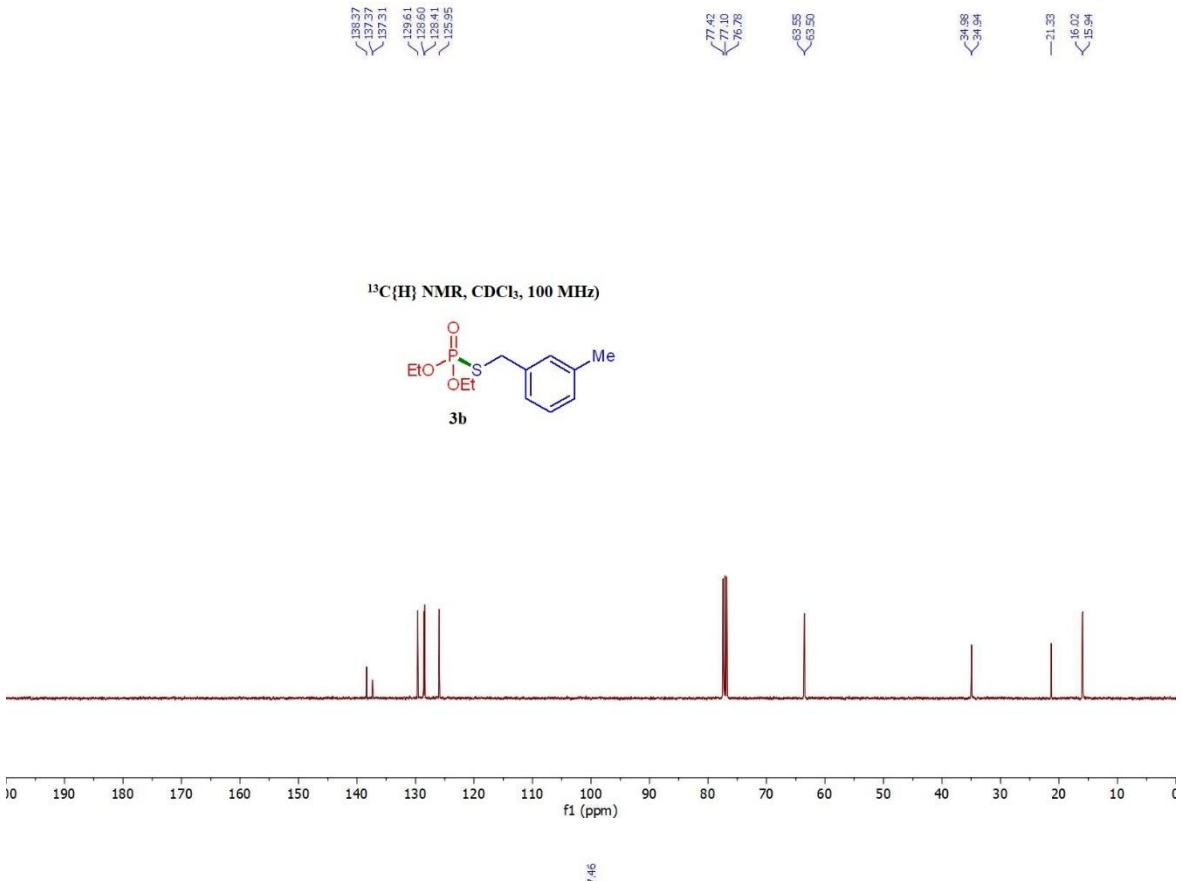
3a

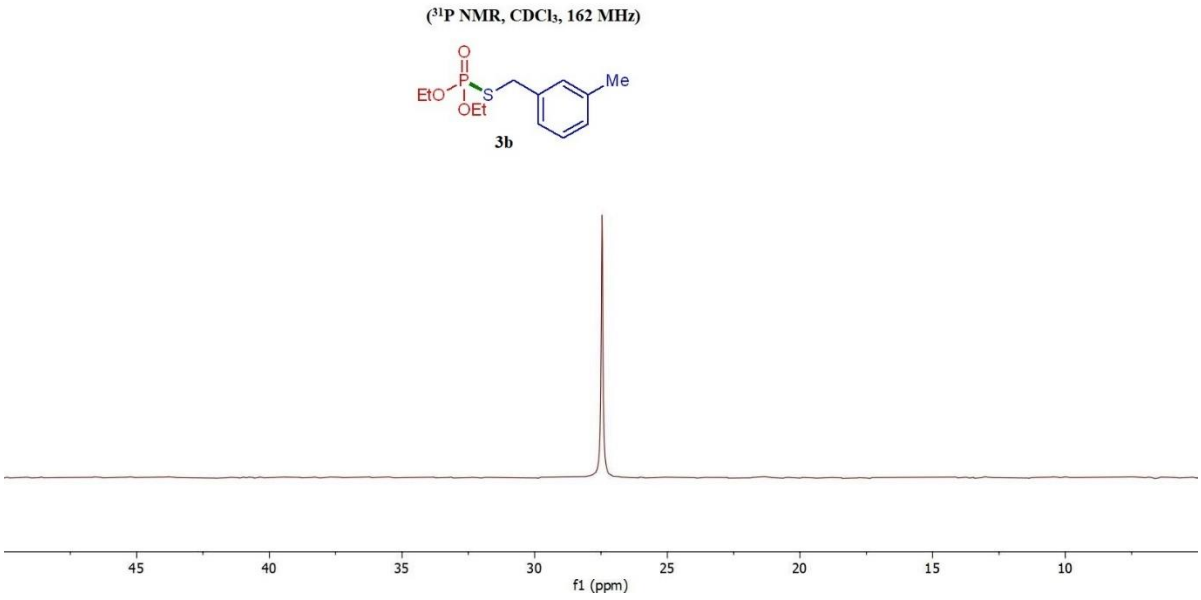
(^{1}H NMR, $CDCl_3$, 400 MHz)

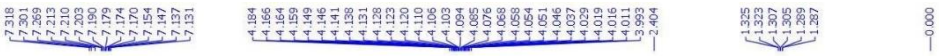


3b

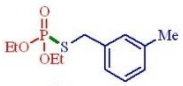



138.37
137.37
137.31
129.61
128.60
128.41
125.95
77.42
77.10
76.78
63.55
63.50
34.98
34.94
21.33
16.02
15.94
^{13}C{H} NMR, CDCl$_3$, 100 MHz)
EtO
P
O
OEt
S
Me
3b
f1 (ppm)
27.46

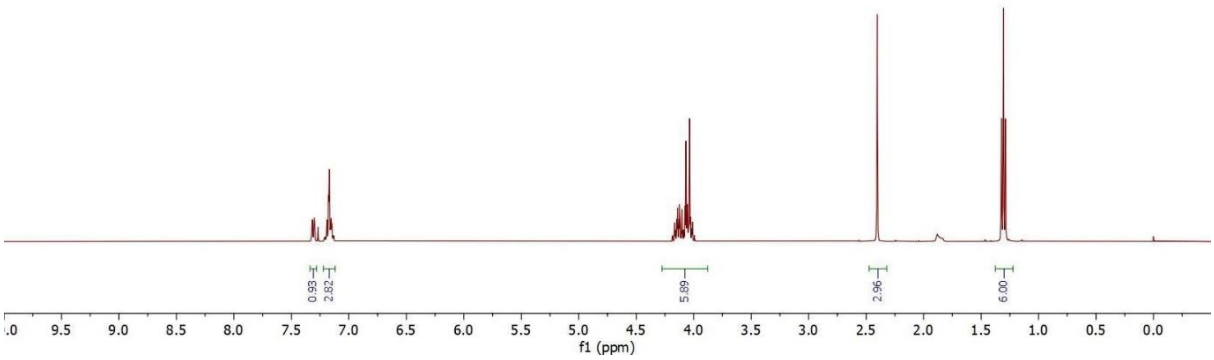

(^{31}P NMR, CDCl$_3$, 162 MHz)
EtO
P
O
OEt
S
Me
3b
f1 (ppm)



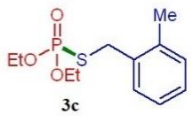
(¹H NMR, $CDCl_3$, 400 MHz)



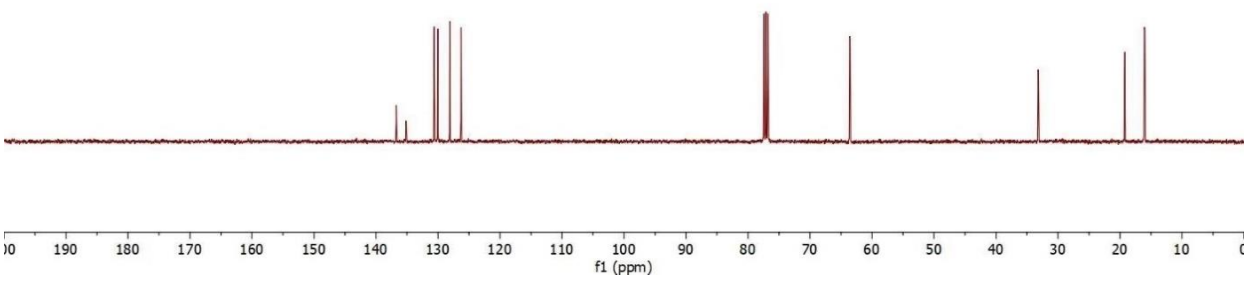
3c

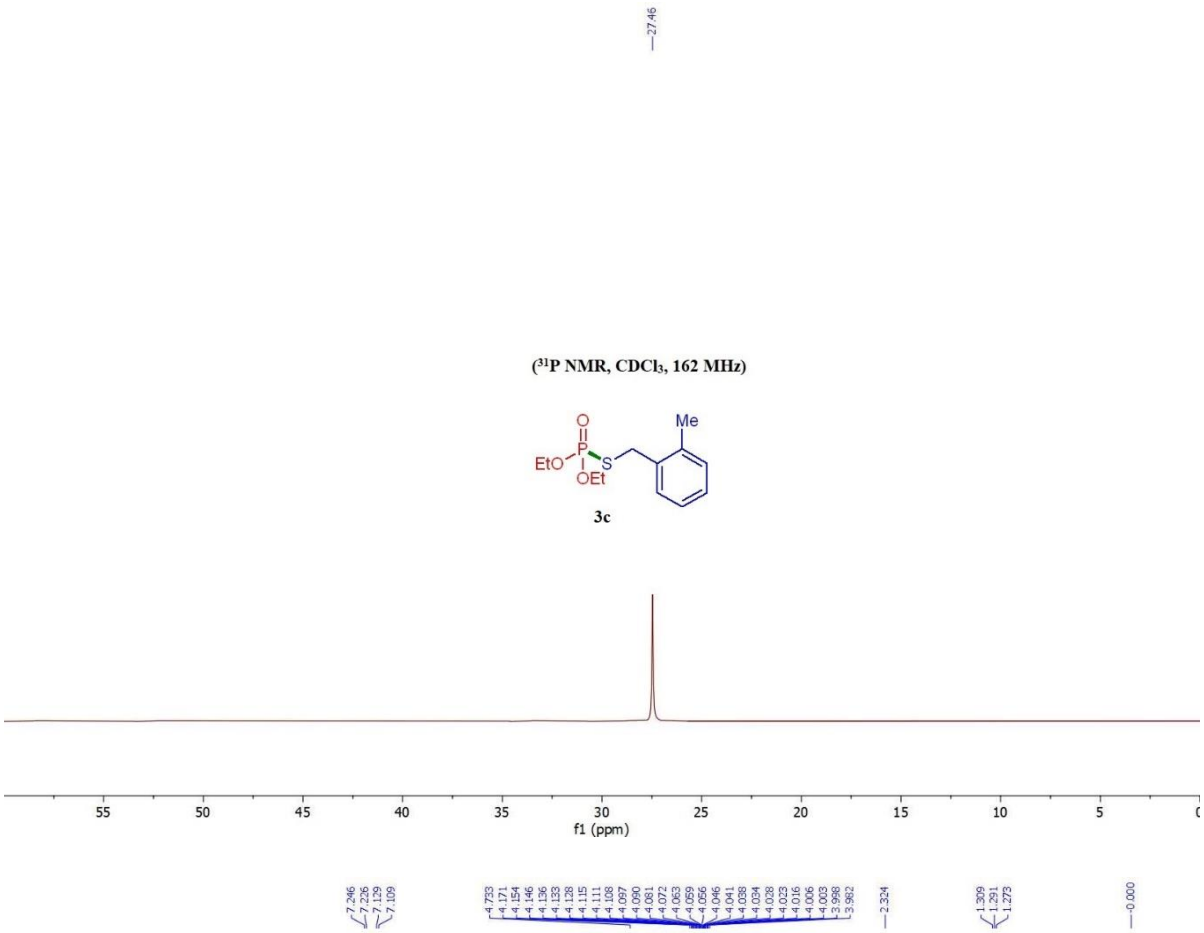


(¹³ C{H} NMR, $CDCl_3$, 100 MHz)



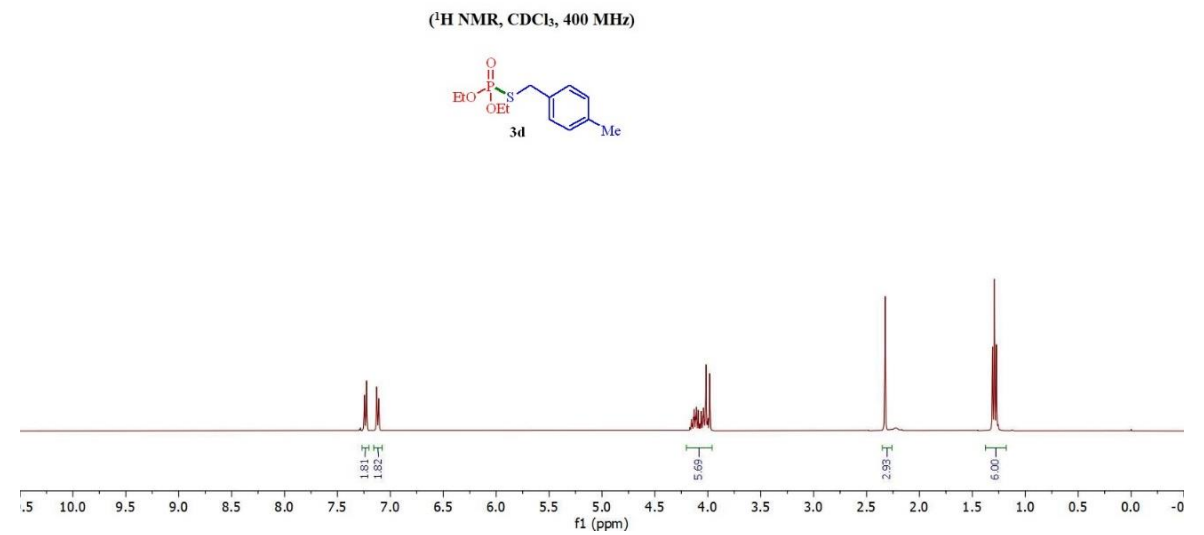
3c

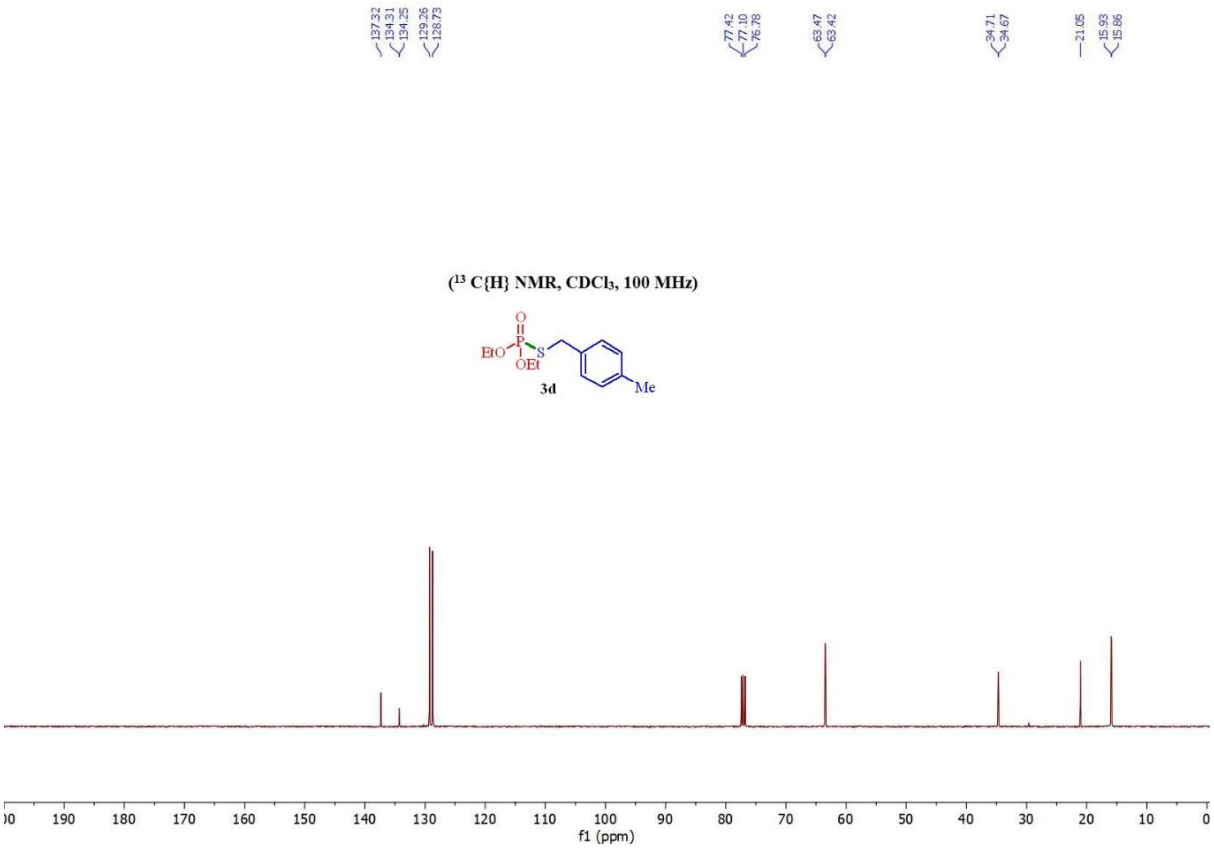


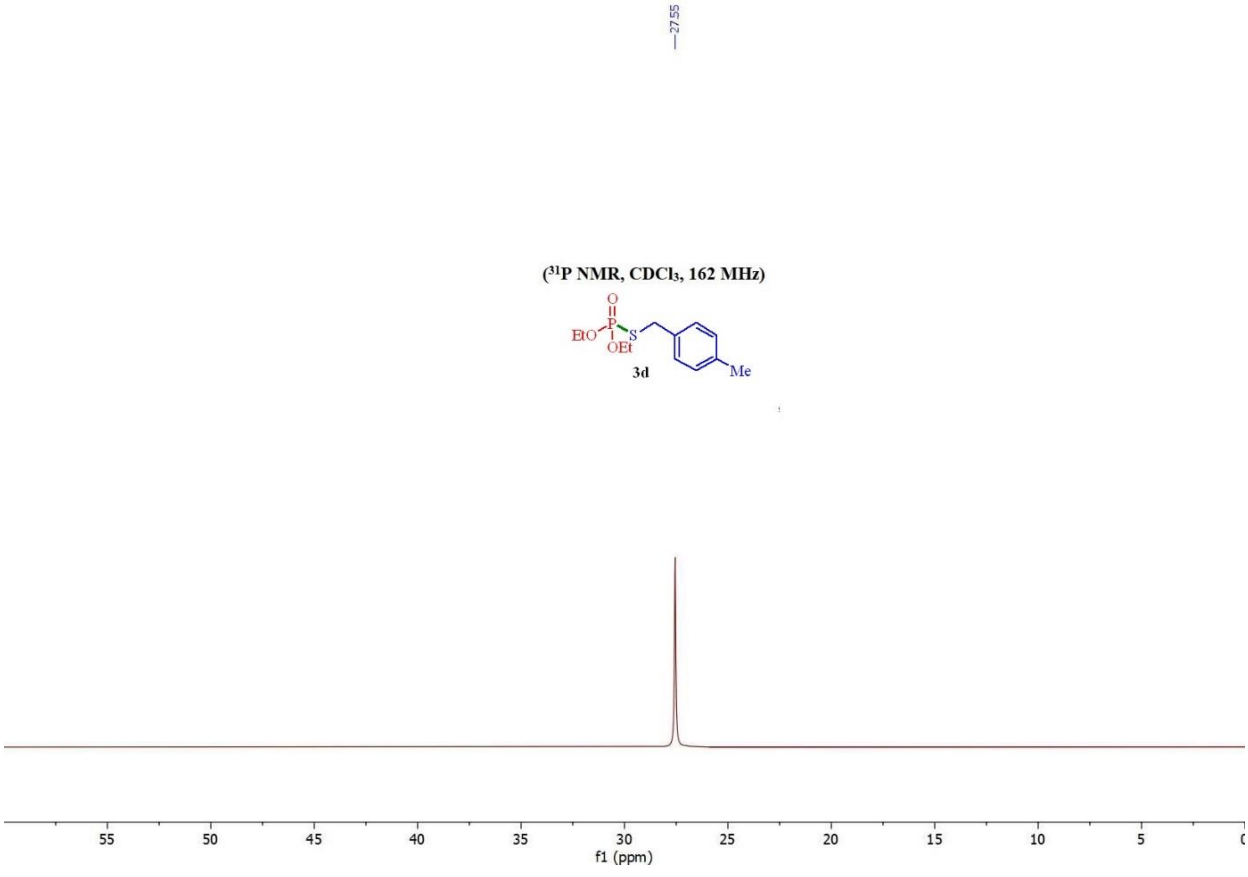


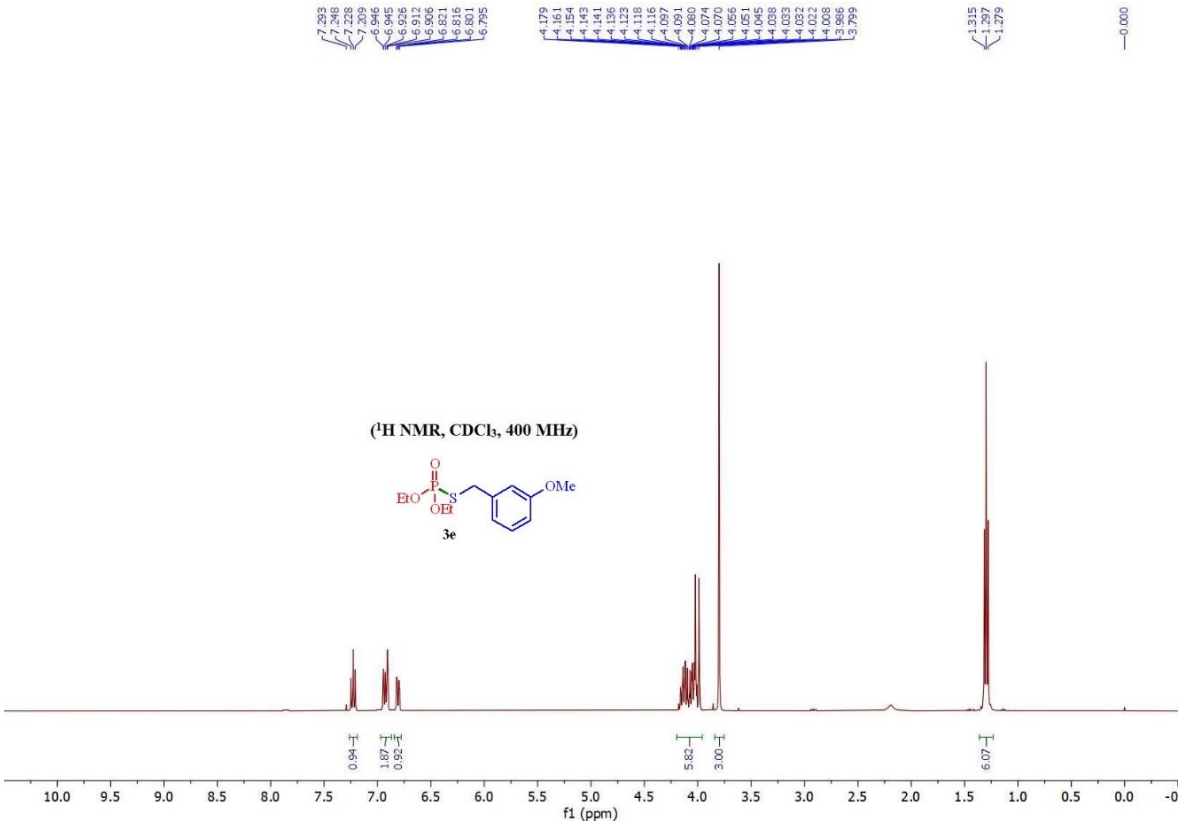
(^{31}P NMR, $CDCl_3$, 162 MHz)

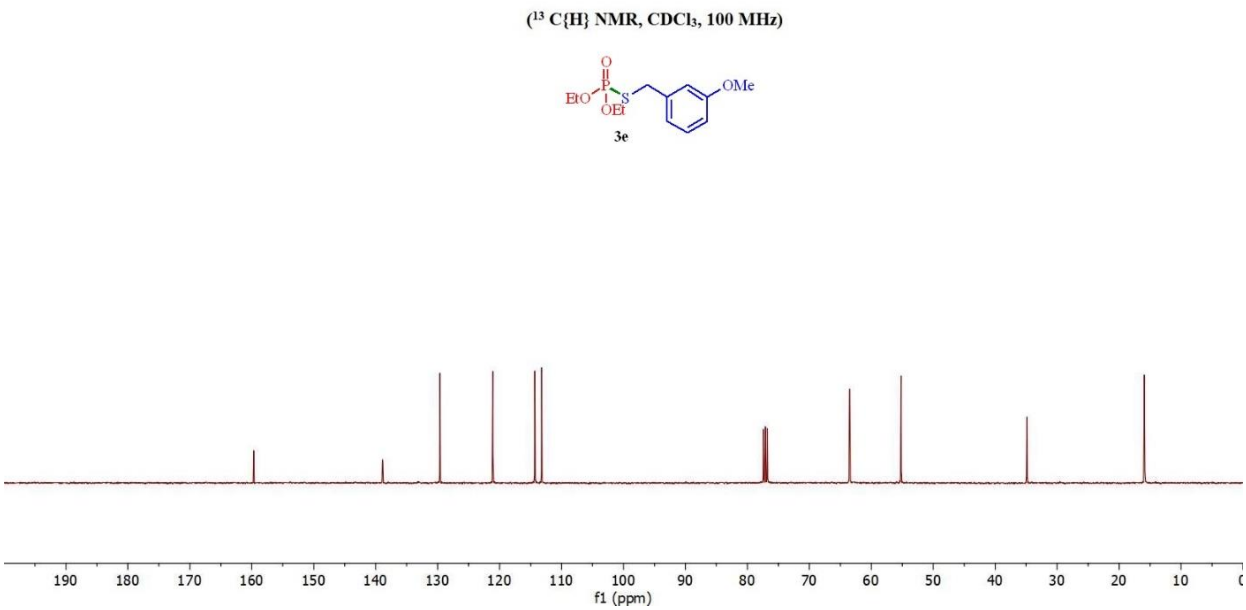
(^{1}H NMR, $CDCl_3$, 400 MHz)

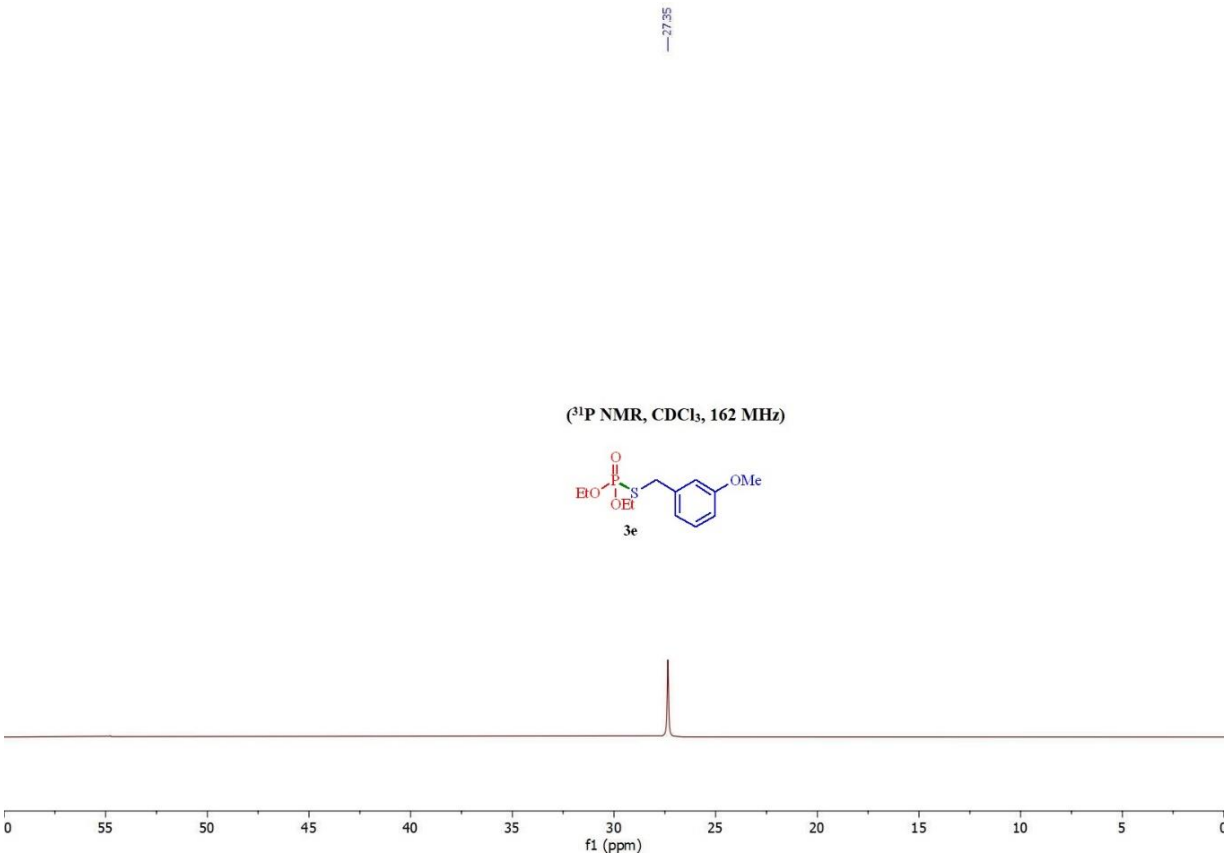



137.32
134.31
134.25
129.26
128.73
77.42
77.10
76.78
63.47
63.42
34.71
34.67
21.05
15.93
15.86
(13 C{H} NMR, CDCl3, 100 MHz)
EtO
O
P
S
OEt
3d
Me
f1 (ppm)


27.55
(31P NMR, CDCl3, 162 MHz)
EtO
O
P
S
OEt
3d
Me
f1 (ppm)


(1H NMR, CDCl3, 400 MHz)
EtO
OEt
OMe
3e
f1 (ppm)

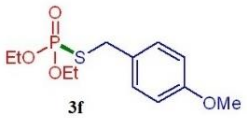

(13 C{H} NMR, CDCl3, 100 MHz)
EtO
OEt
OMe
3e
f1 (ppm)



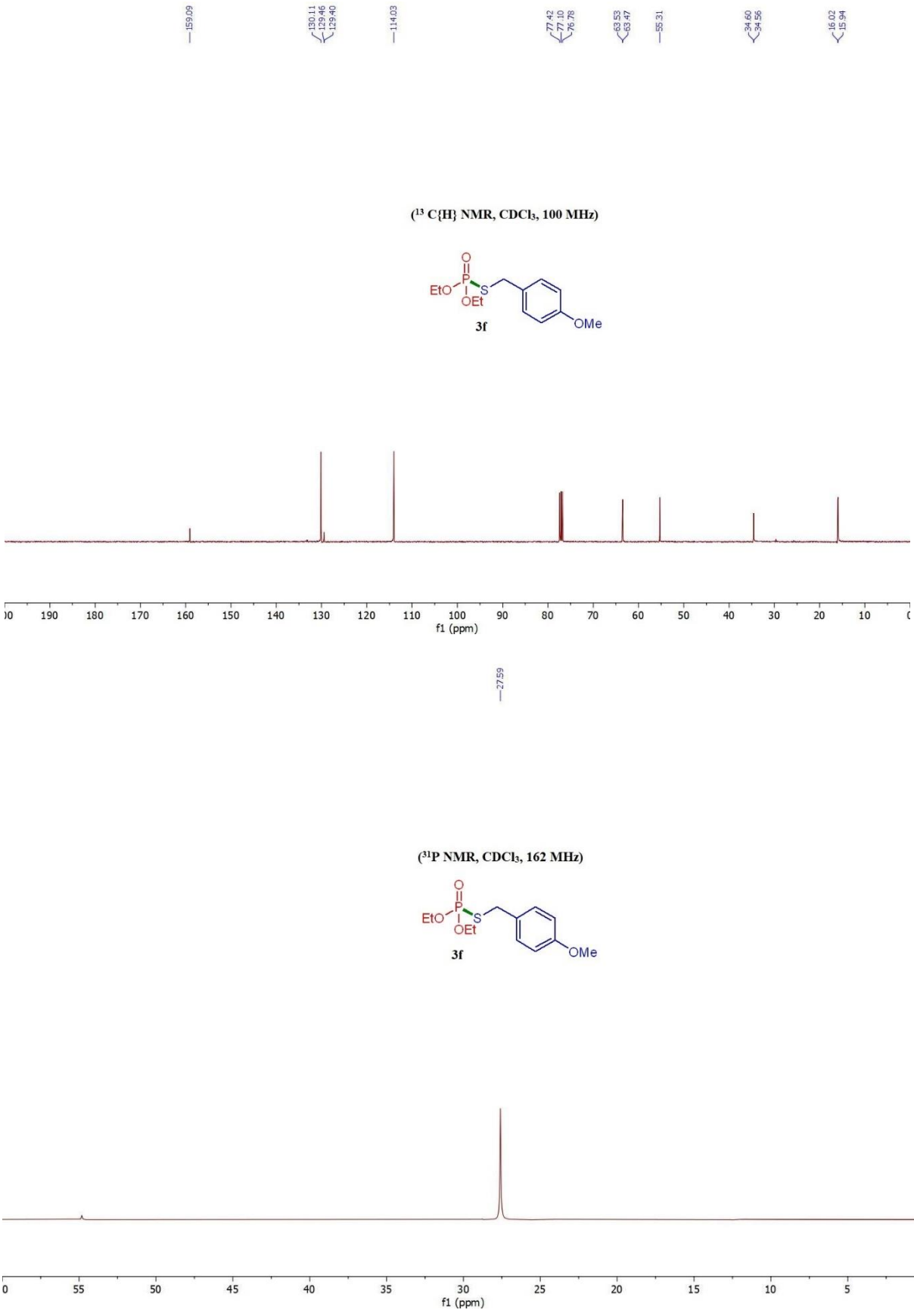
(^{31}P NMR, $CDCl_3$, 162 MHz)

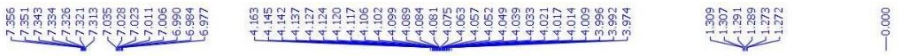
3e

(^{1}H NMR, $CDCl_3$, 400 MHz)

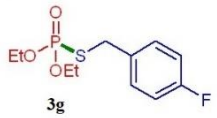


3f

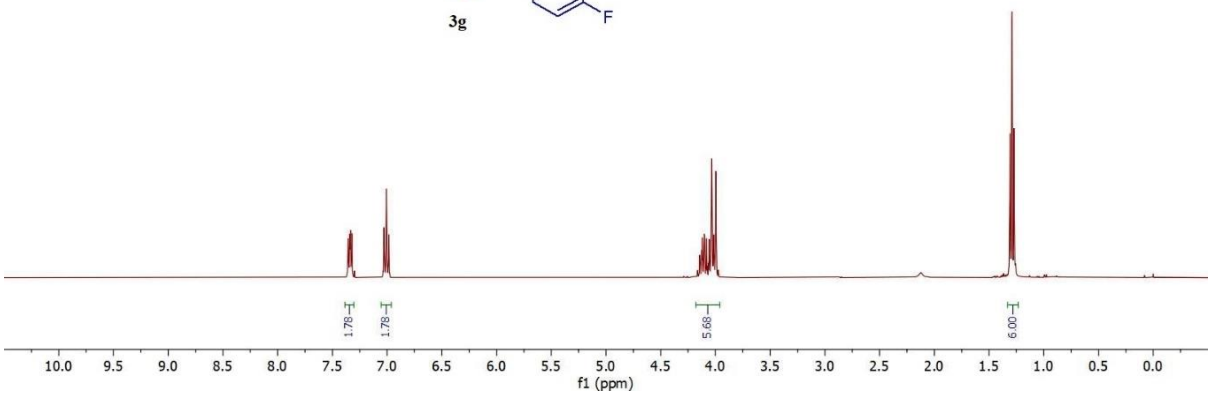

159.09
130.11
129.46
129.40
114.03
77.42
77.10
76.78
63.53
63.47
55.31
34.60
34.56
16.02
15.94
(13 C{H} NMR, CDCl3, 100 MHz)
EtO
P
O
OEt
S
OMe
3f
f1 (ppm)
27.59
(31P NMR, CDCl3, 162 MHz)
EtO
P
O
OEt
S
OMe
3f
f1 (ppm)



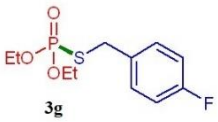
(¹H NMR, CDCl₃, 400 MHz)



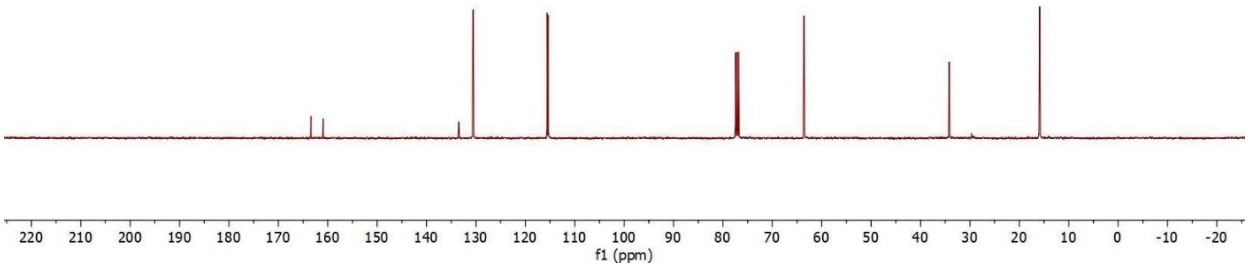
3g

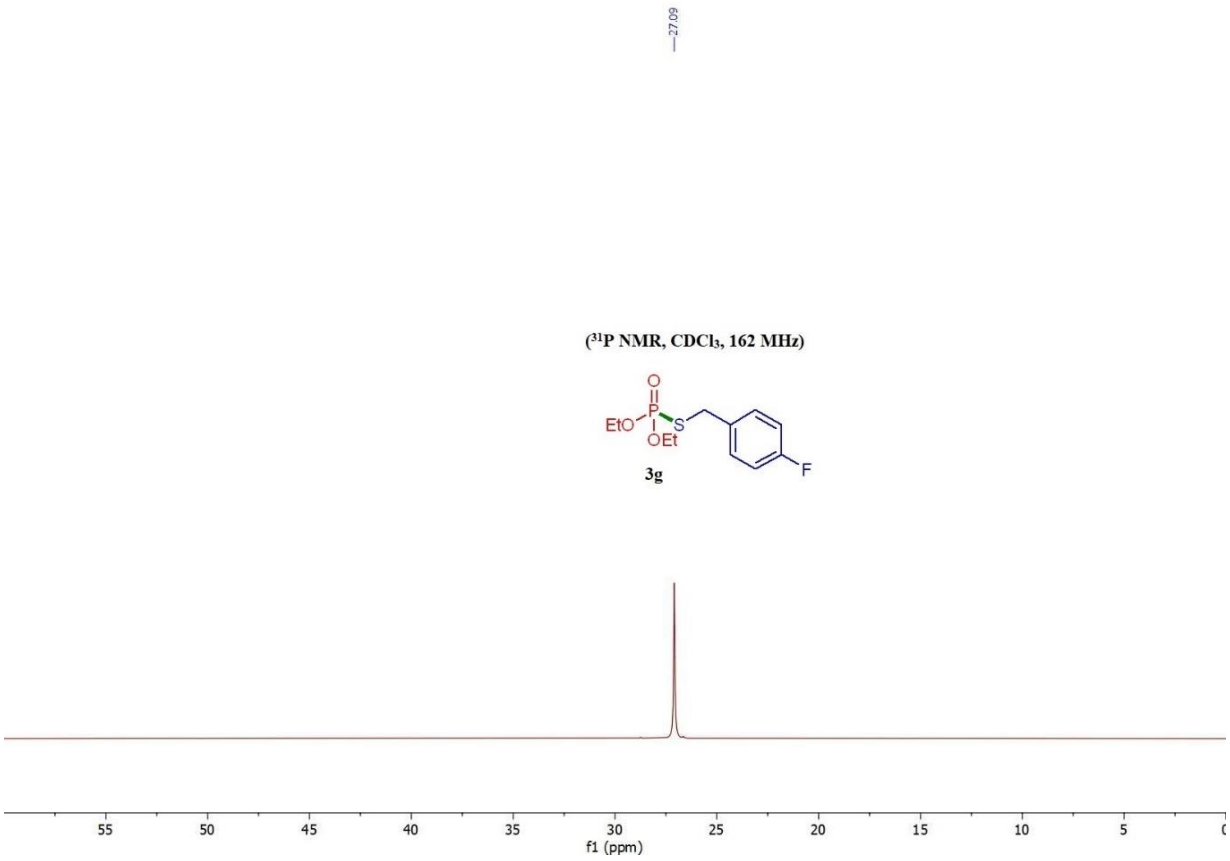


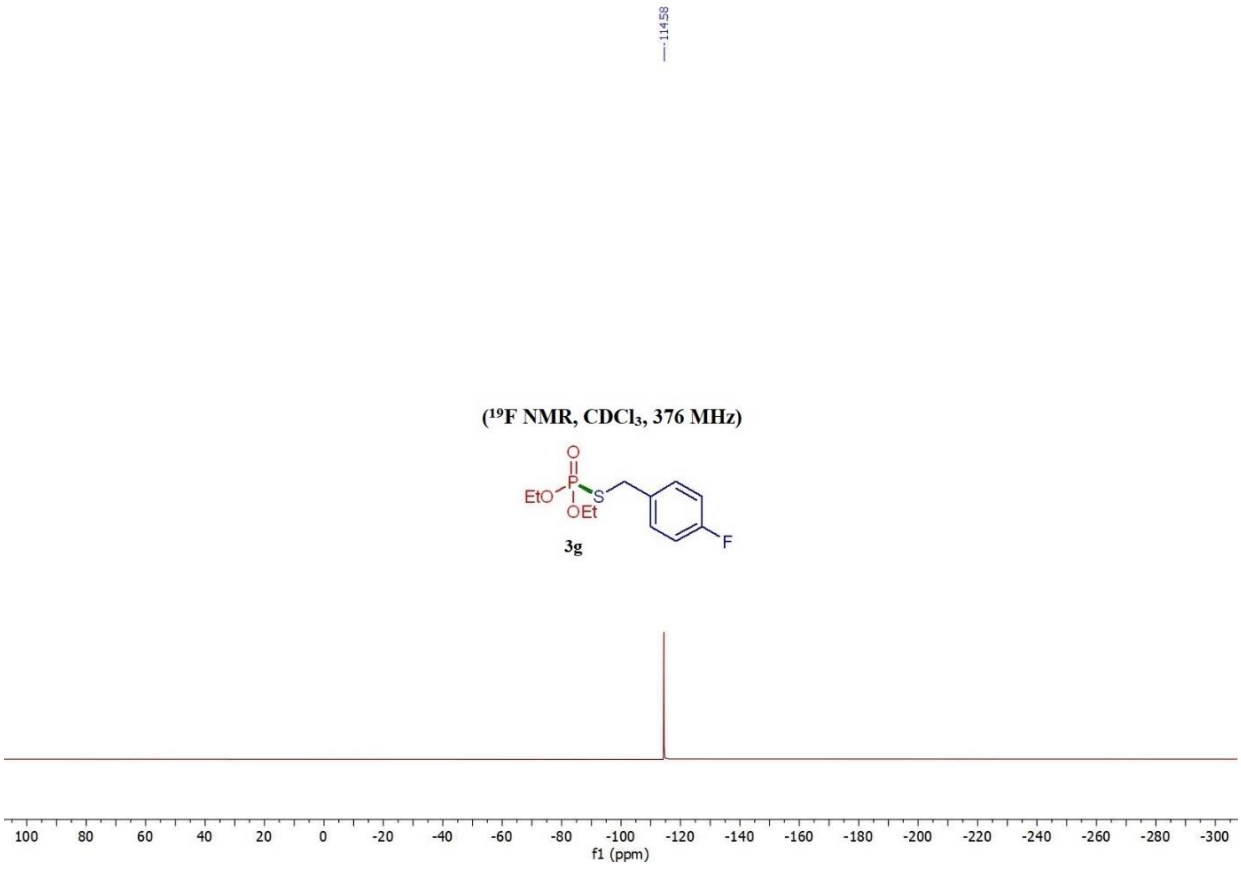
(¹³ C{H} NMR, CDCl₃, 100 MHz)



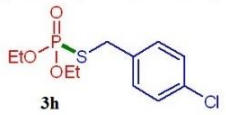
3g



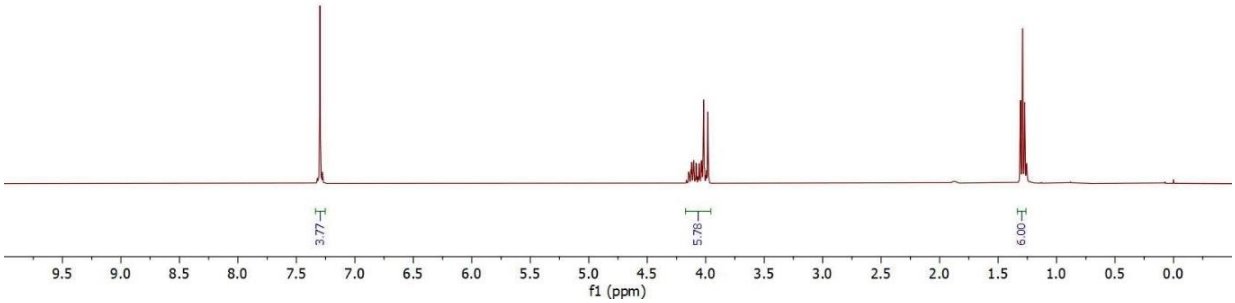

27.09
(31P NMR, CDCl3, 162 MHz)
O
EtO
P
S
OEt
F
3g
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)


11458
(19F NMR, CDCl3, 376 MHz)
O
EtO
P
S
OEt
F
3g
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

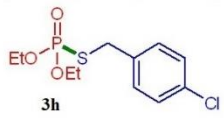
(¹H NMR, CDCl₃, 400 MHz)



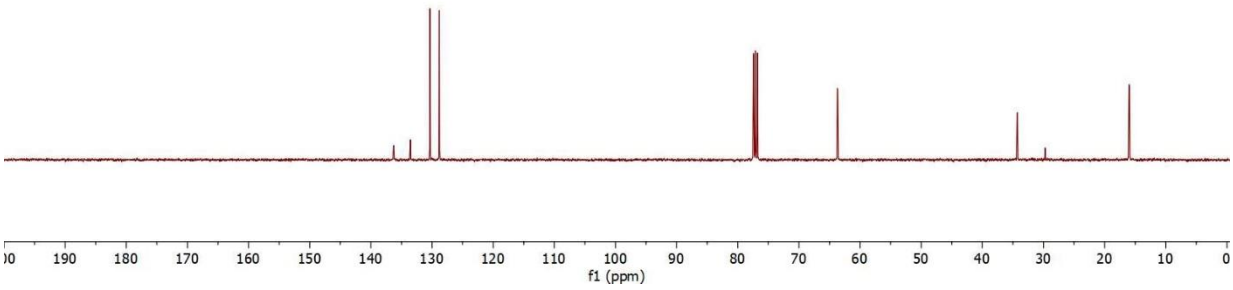
3h

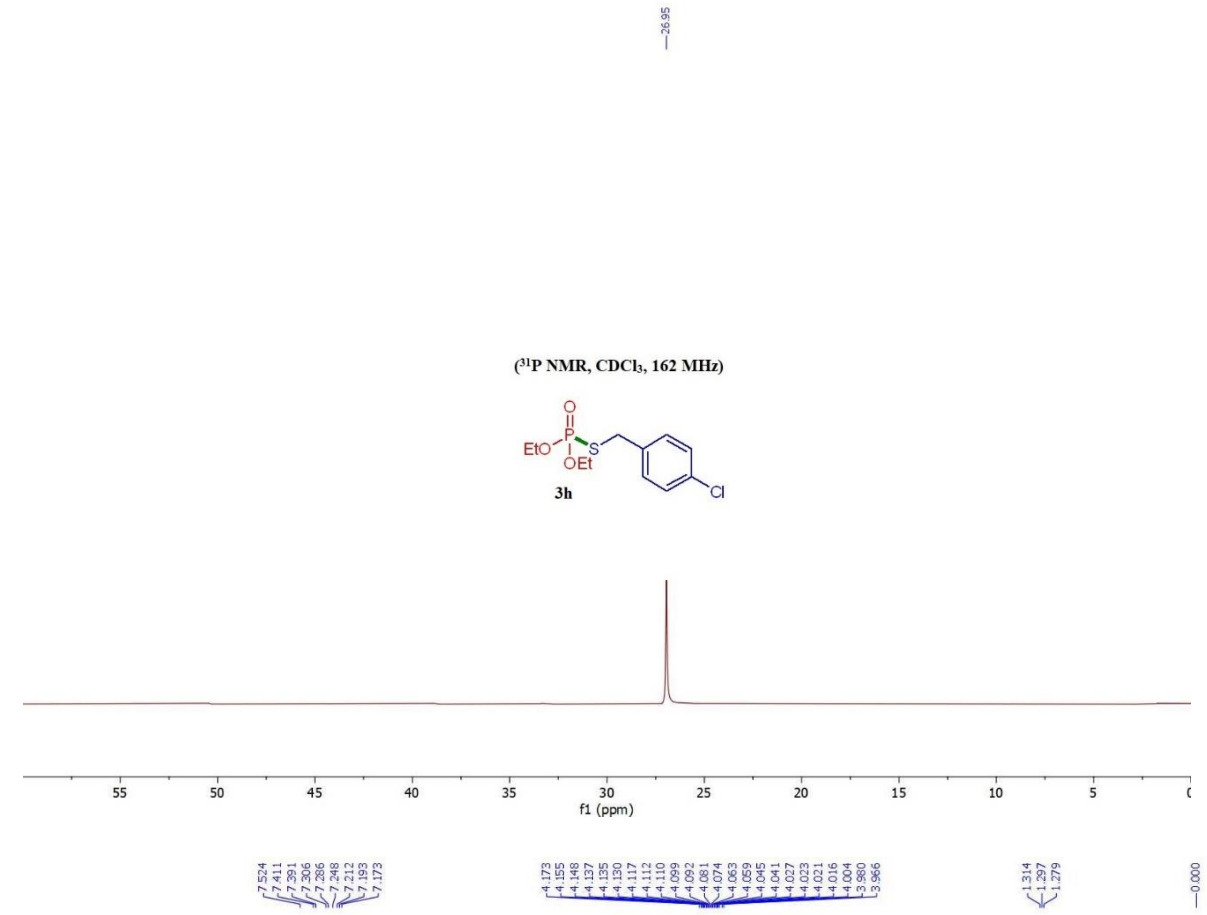


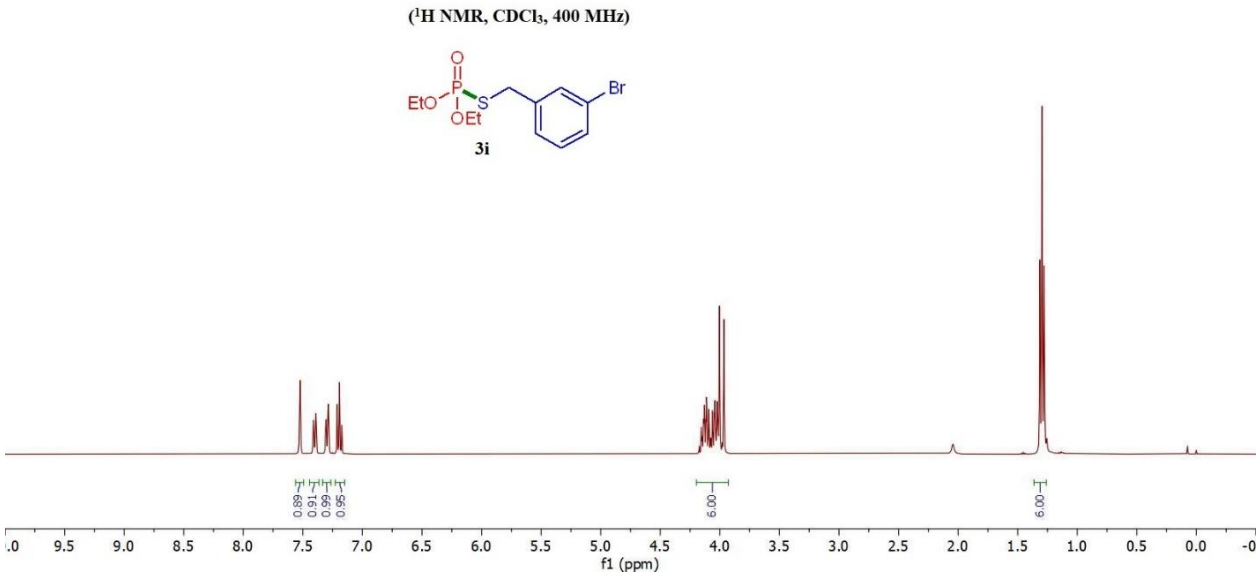
(¹³C{H} (100 MHz, CDCl₃)



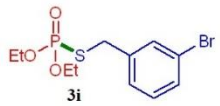
3h



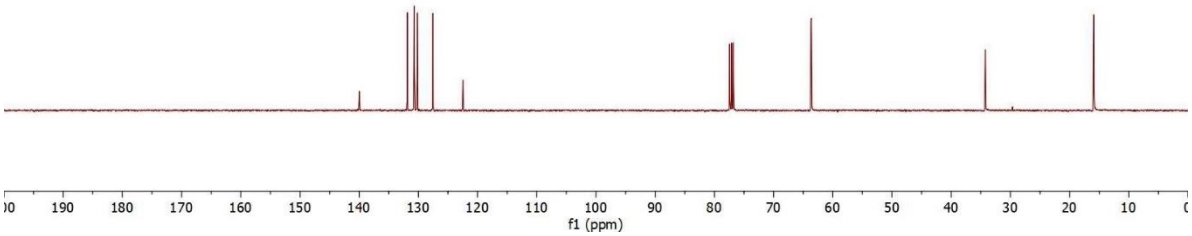

26.95
(31P NMR, CDCl3, 162 MHz)
EtO
OEt
S
Cl
3h
f1 (ppm)
7.524
7.411
7.391
7.306
7.286
7.248
7.212
7.193
7.173
4.173
4.155
4.148
4.137
4.135
4.130
4.117
4.112
4.110
4.099
4.092
4.081
4.074
4.063
4.059
4.045
4.041
4.027
4.023
4.021
4.016
4.004
3.980
3.966
1.314
1.297
1.279
0.000


(1H NMR, CDCl3, 400 MHz)
EtO
OEt
S
Br
3i
0.89
0.91
0.99
0.95
6.00
6.00
f1 (ppm)

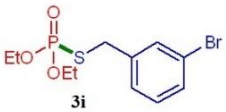
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



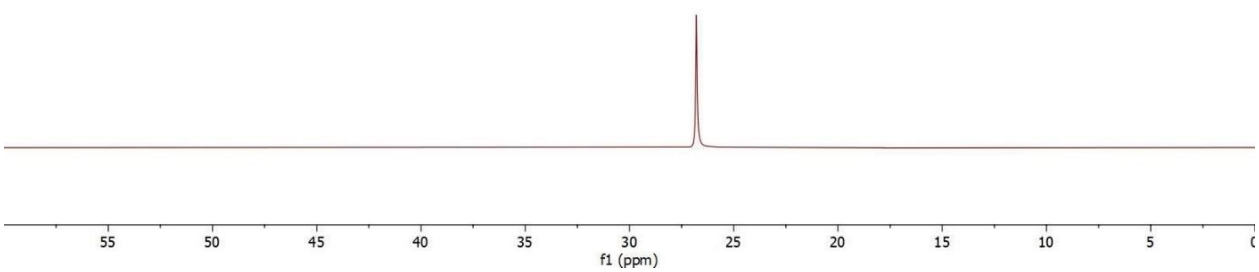
3i



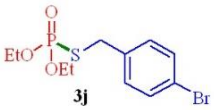
(^{31}P NMR, $CDCl_3$, 162 MHz)



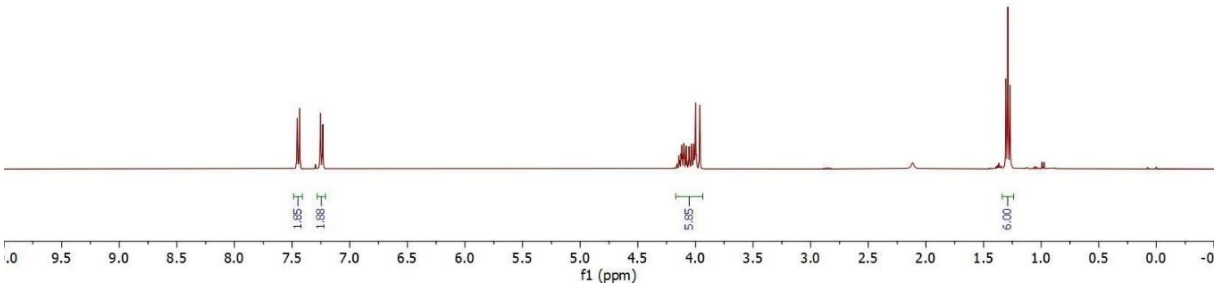
3i



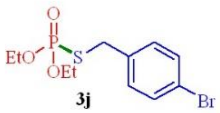
(^{1}H NMR, $CDCl_3$, 400 MHz)



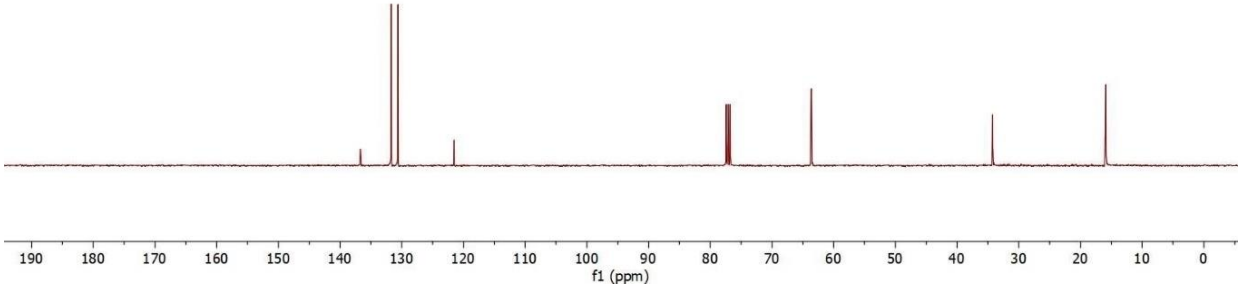
3j

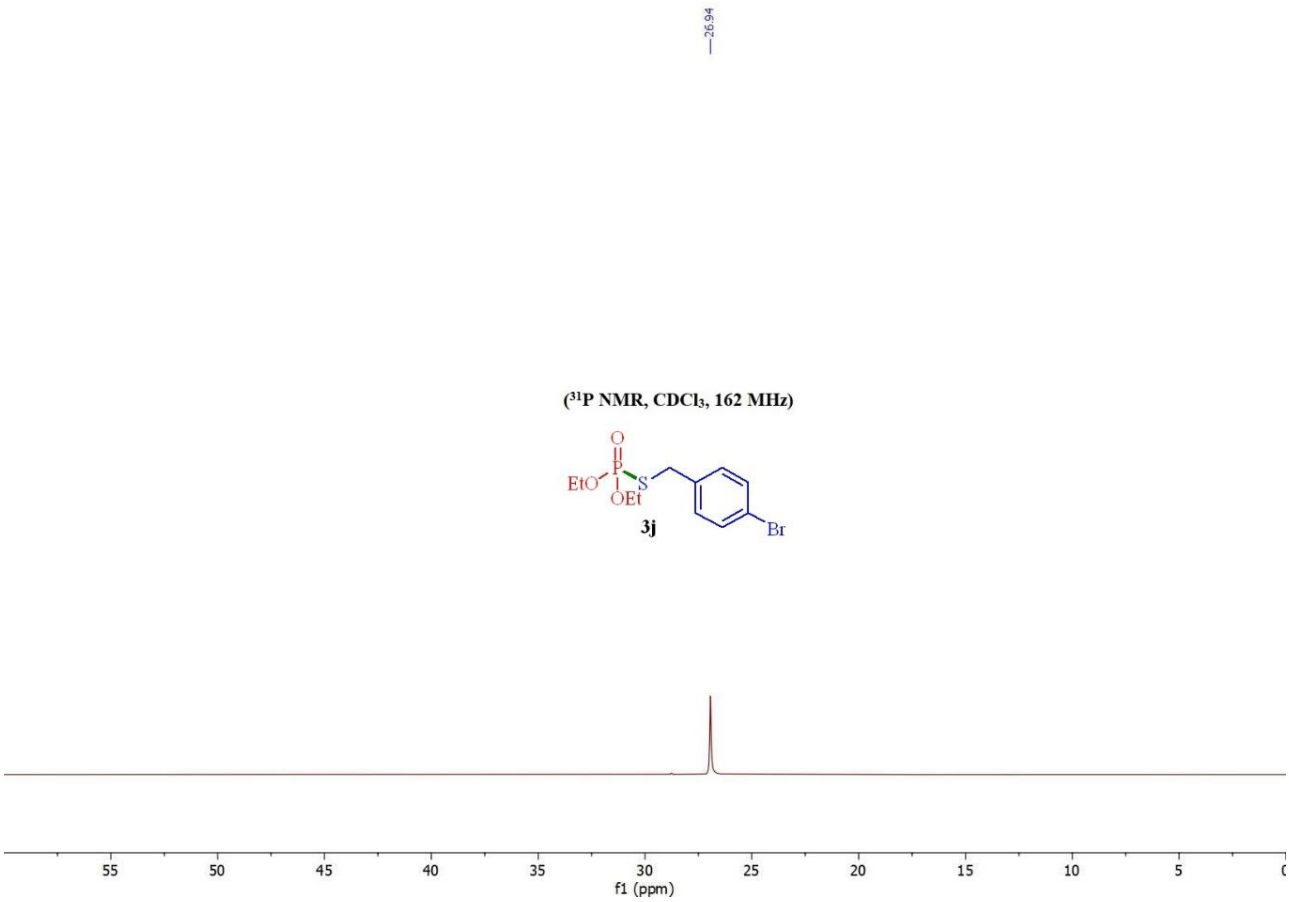


(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



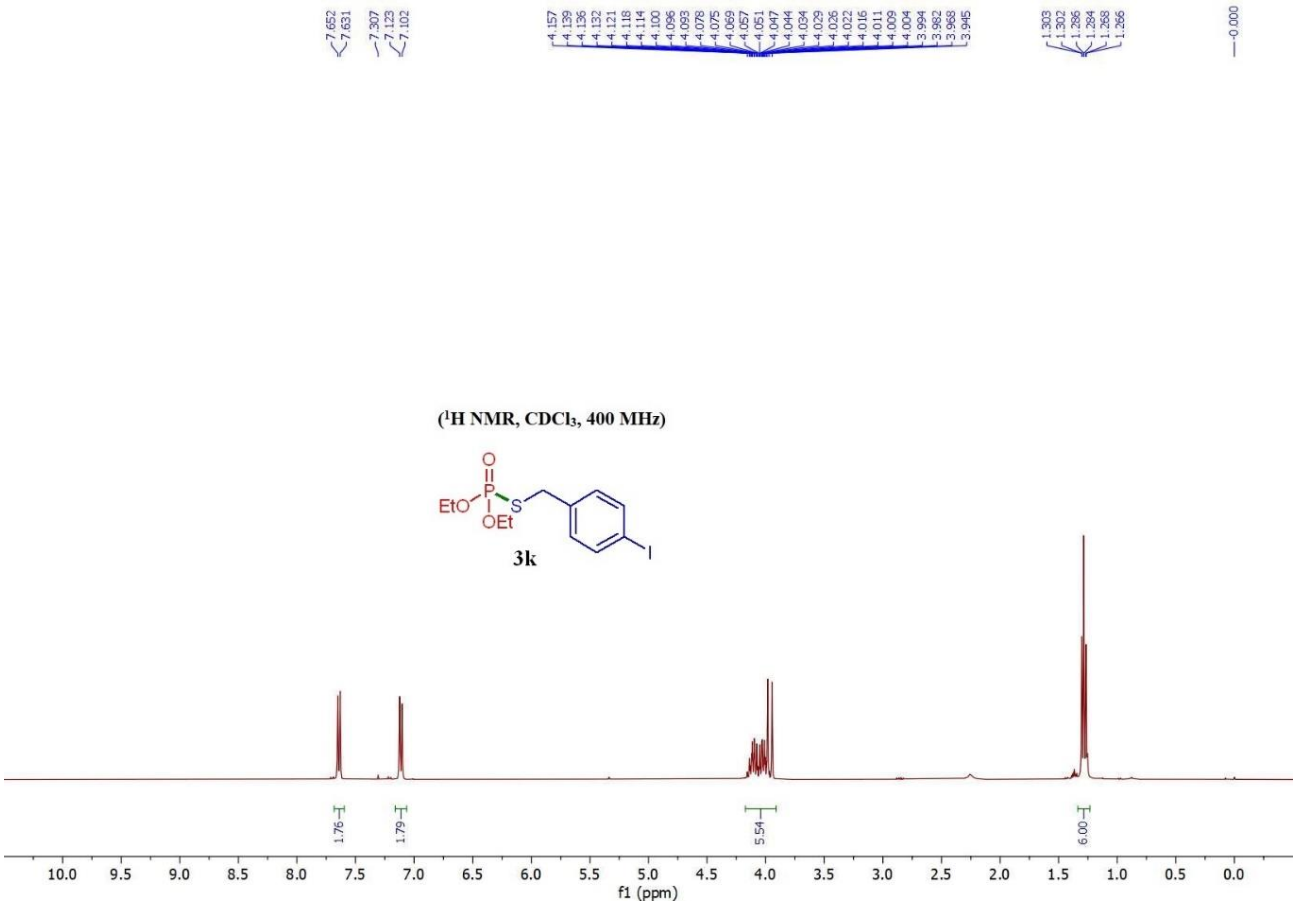
3j





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

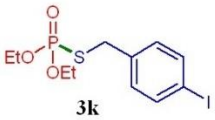
3j



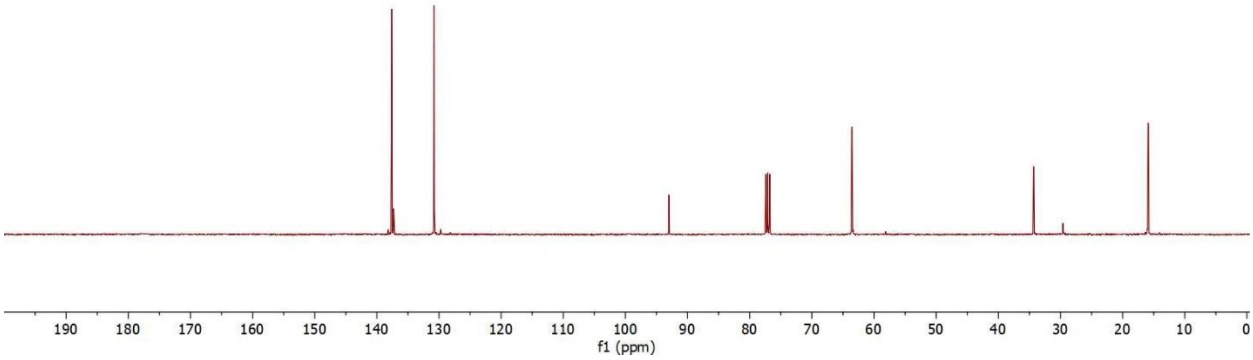
(^{1}H NMR, $CDCl_3$, 400 MHz)

3k

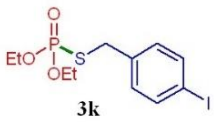
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



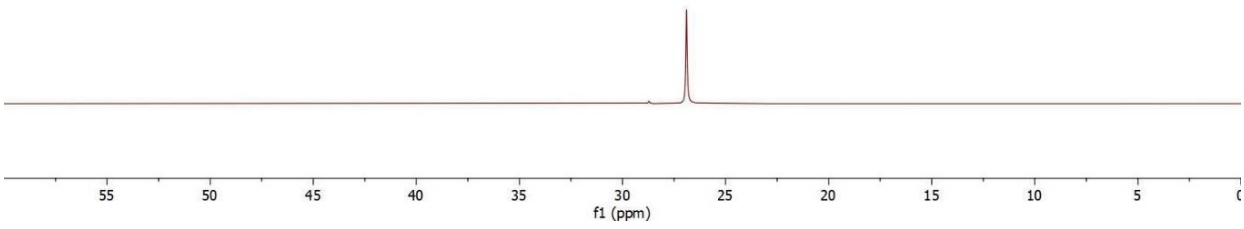
3k



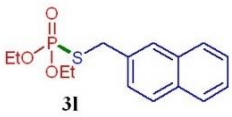
(^{31}P NMR, $CDCl_3$, 162 MHz)



3k

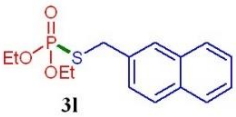


(¹H NMR, $CDCl_3$, 400 MHz)

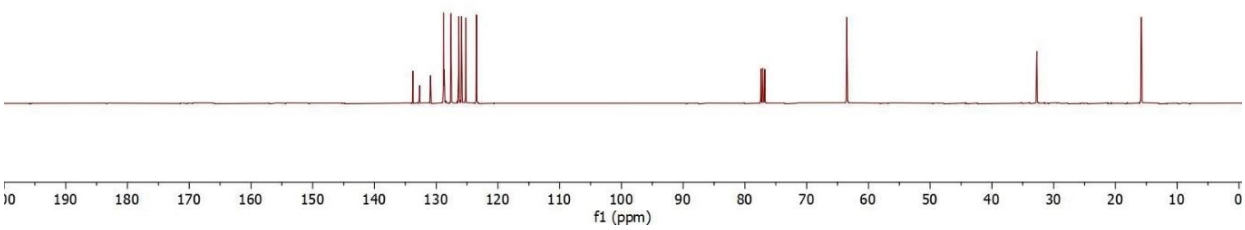


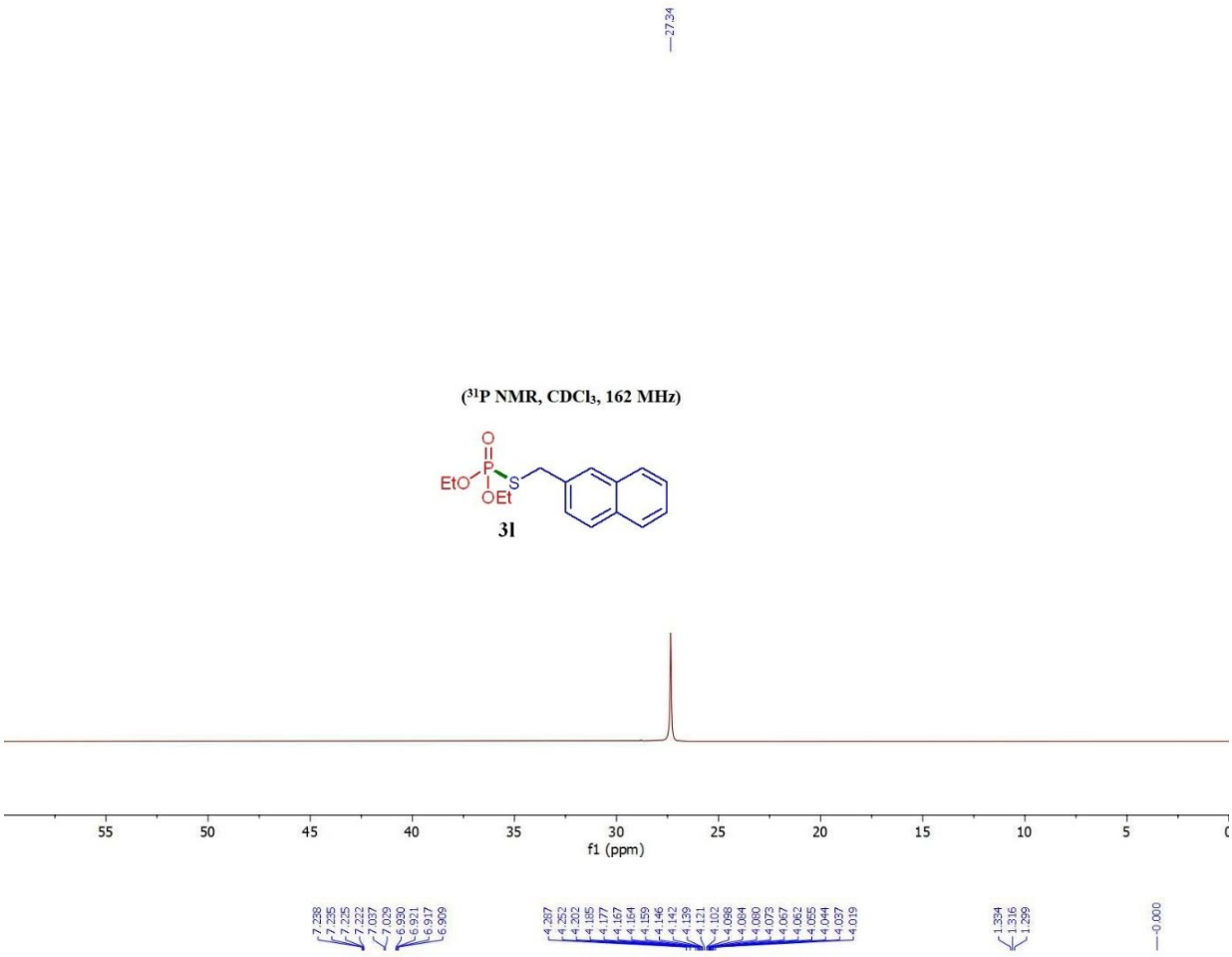
3l

(¹³ C{H} NMR, $CDCl_3$, 100 MHz)



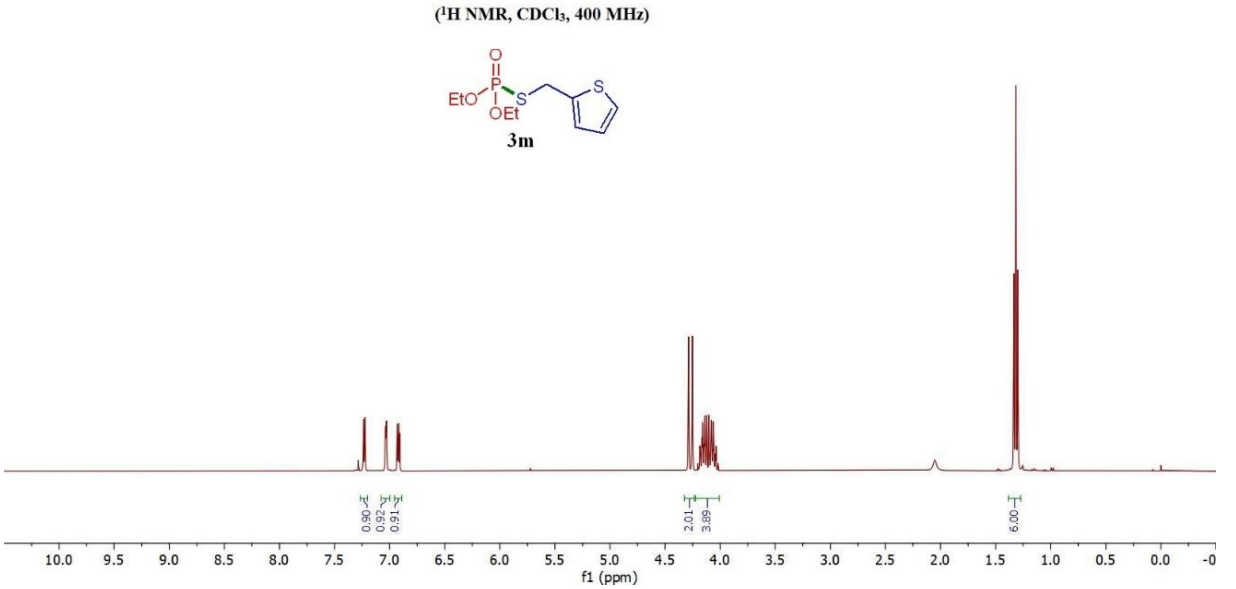
3l





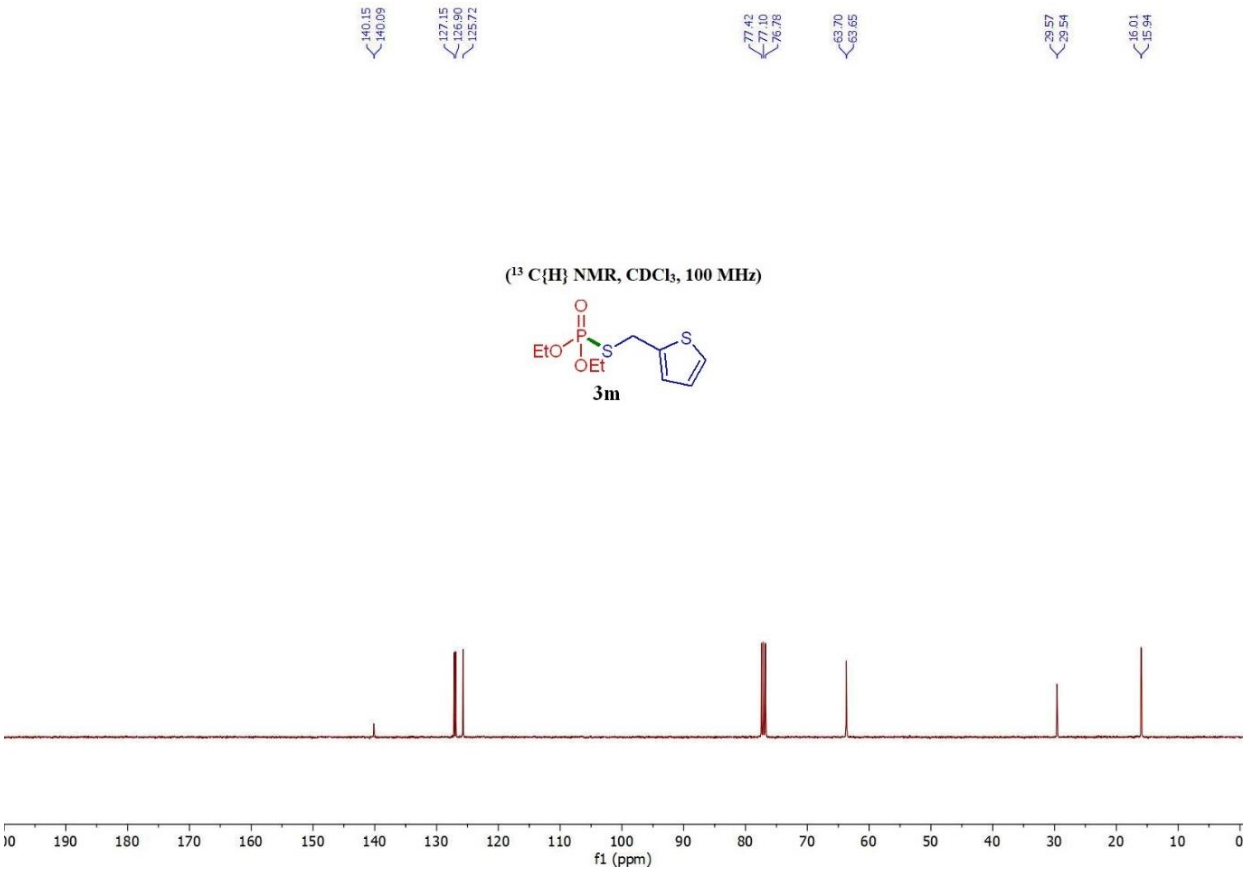
(^{31}P NMR, $CDCl_3$, 162 MHz)

3l



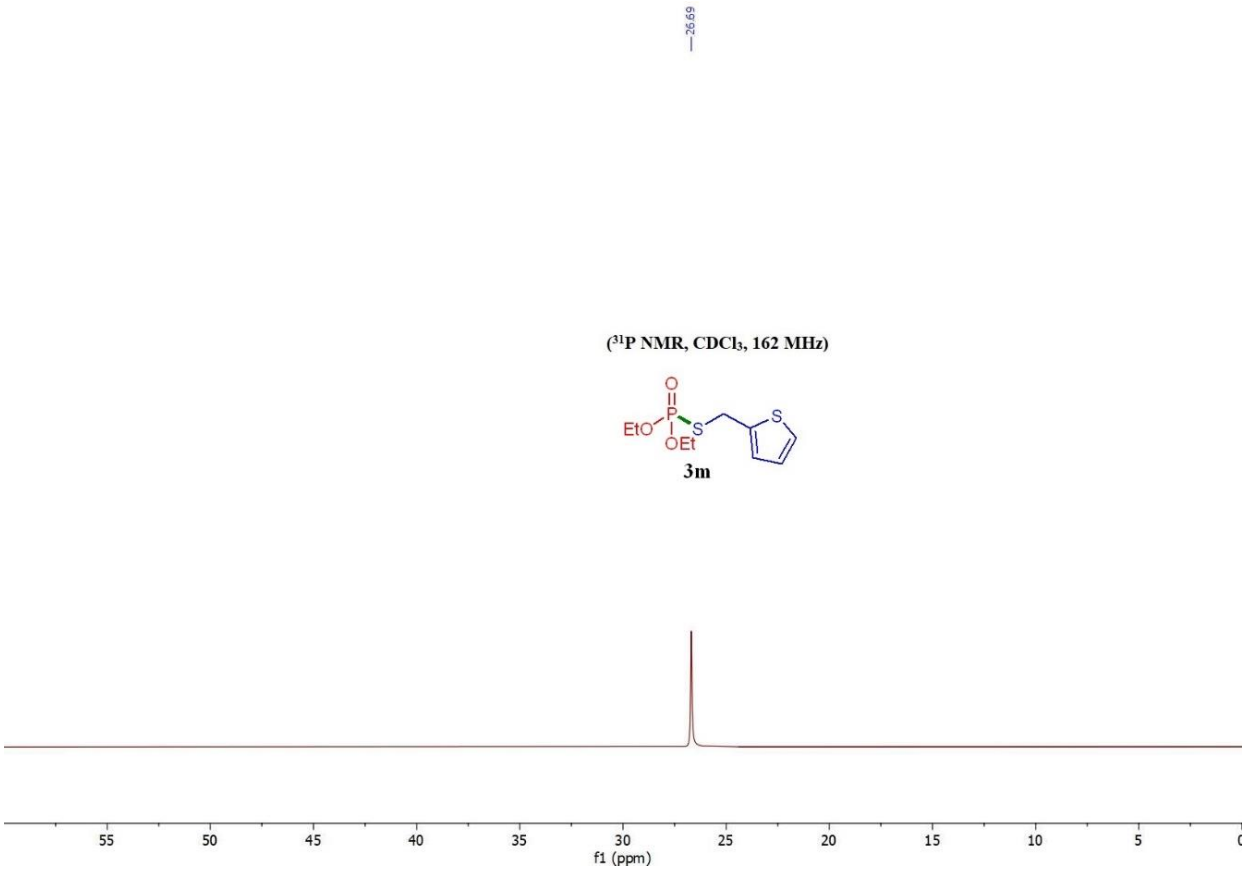
(^{1}H NMR, $CDCl_3$, 400 MHz)

3m



(^{13}C{H} NMR, $CDCl_3$, 100 MHz)

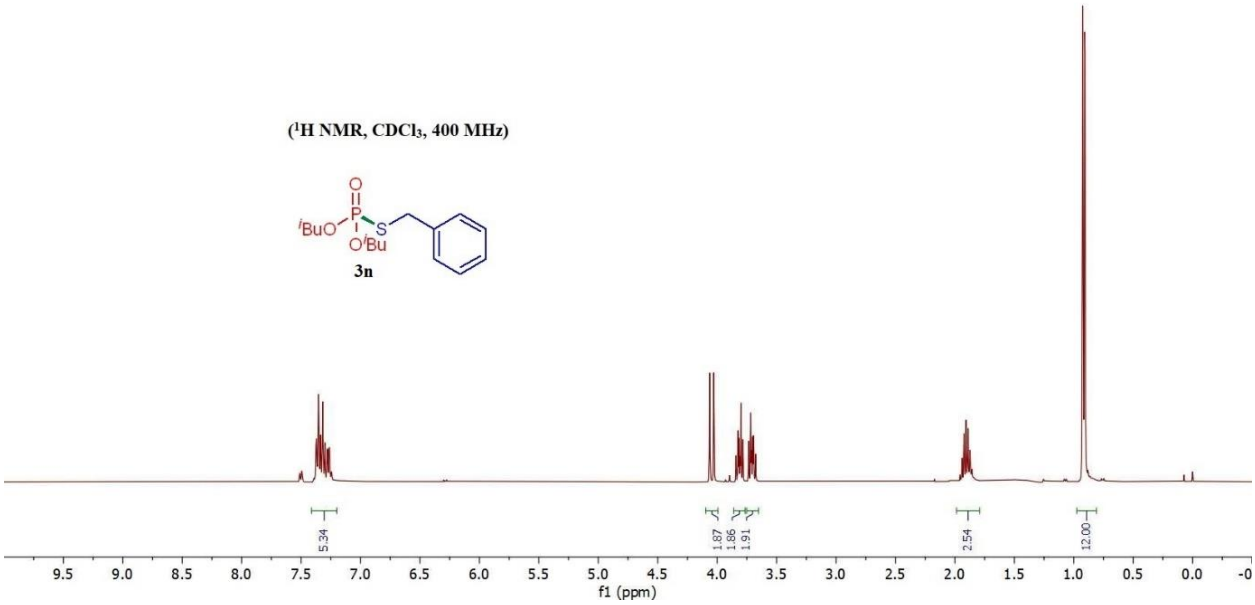
3m



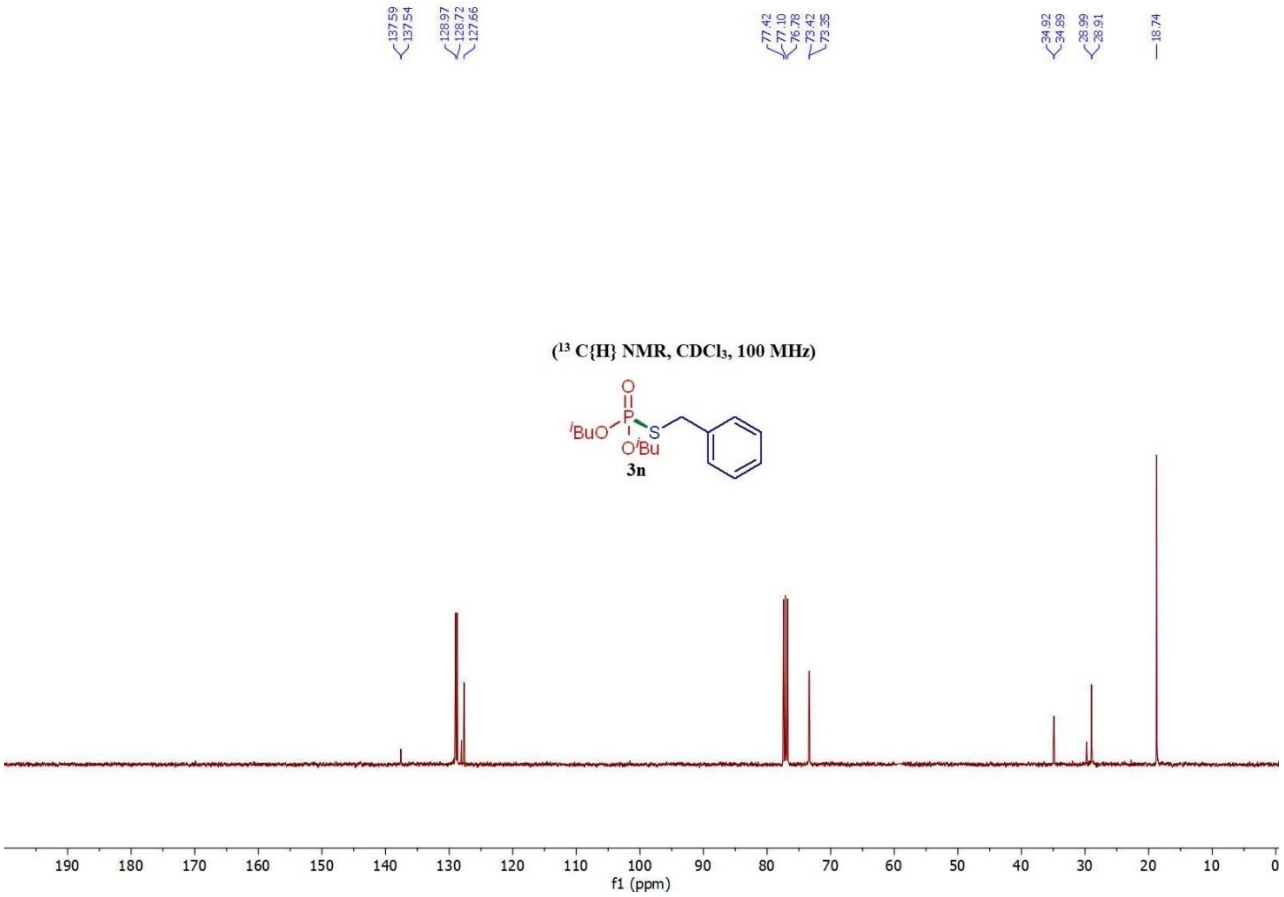
(^{31}P NMR, $CDCl_3$, 162 MHz)

3m

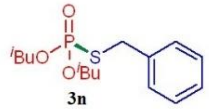
(^{1}H NMR, $CDCl_3$, 400 MHz)



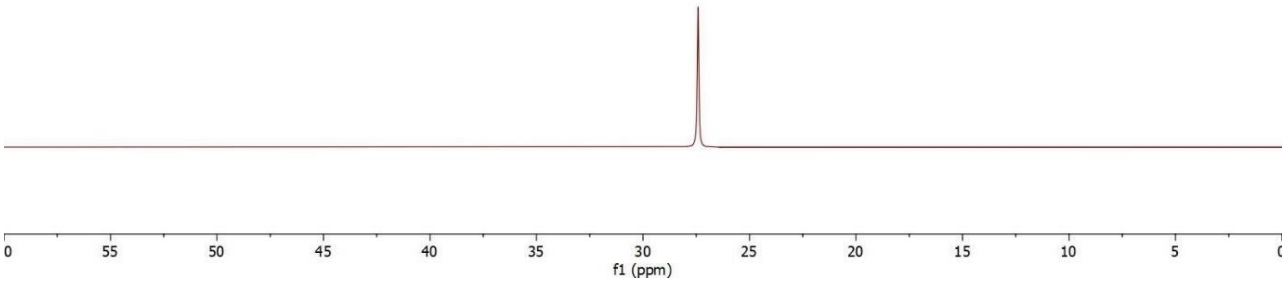
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



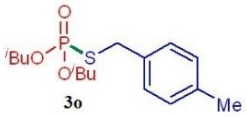
(^{31}P NMR, $CDCl_3$, 162 MHz)



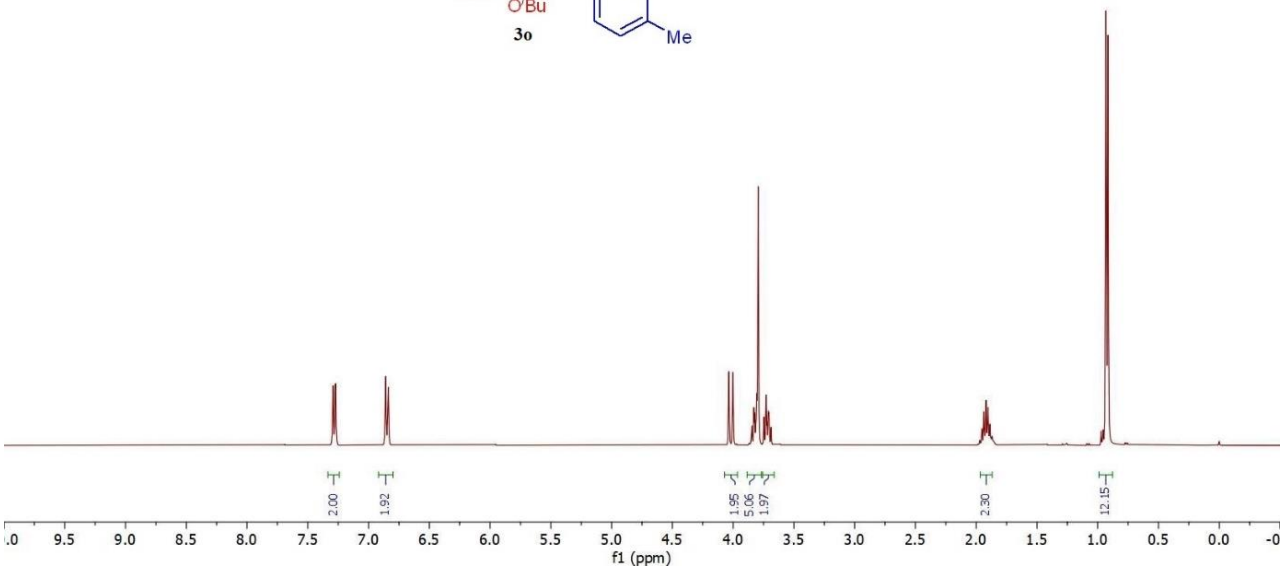
3n

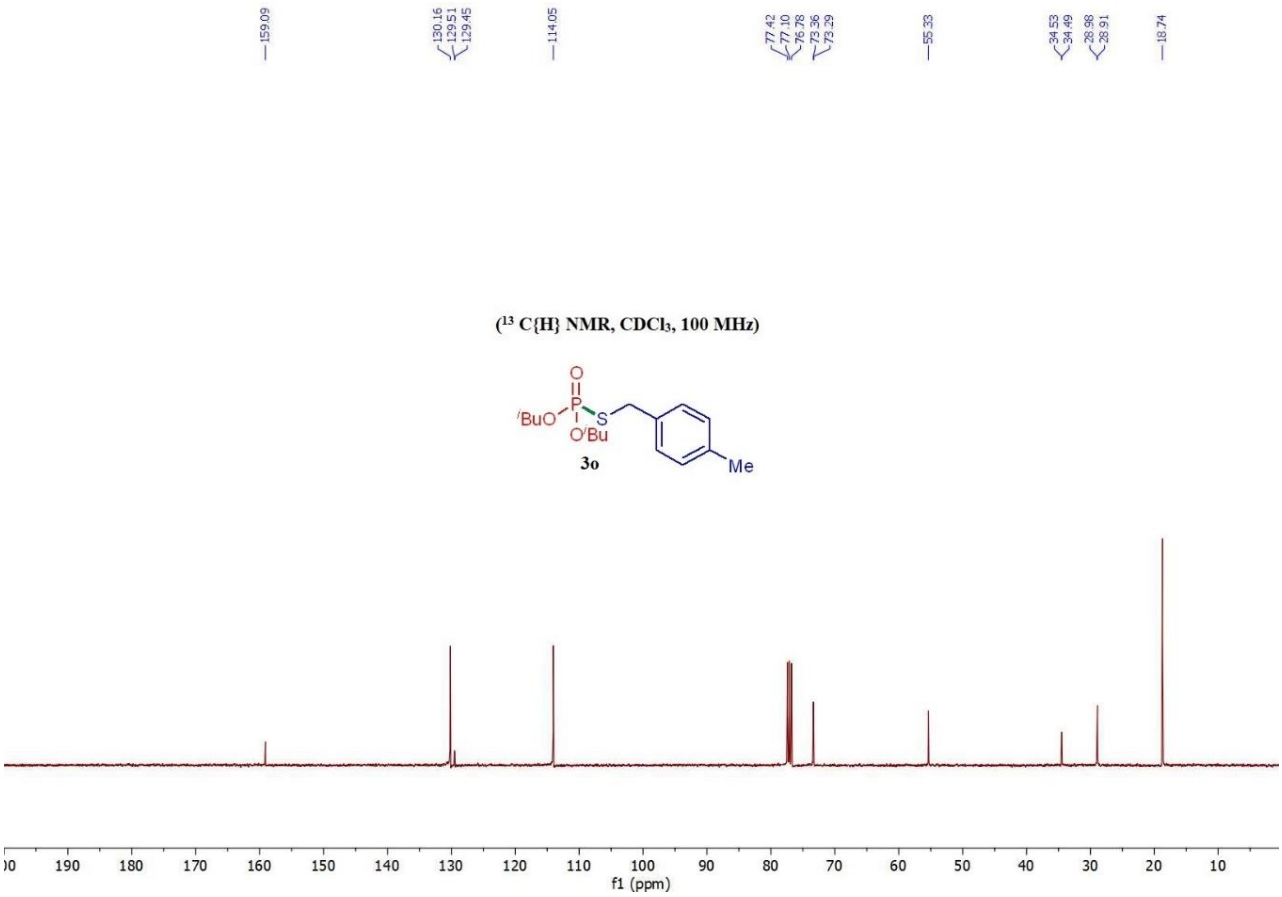


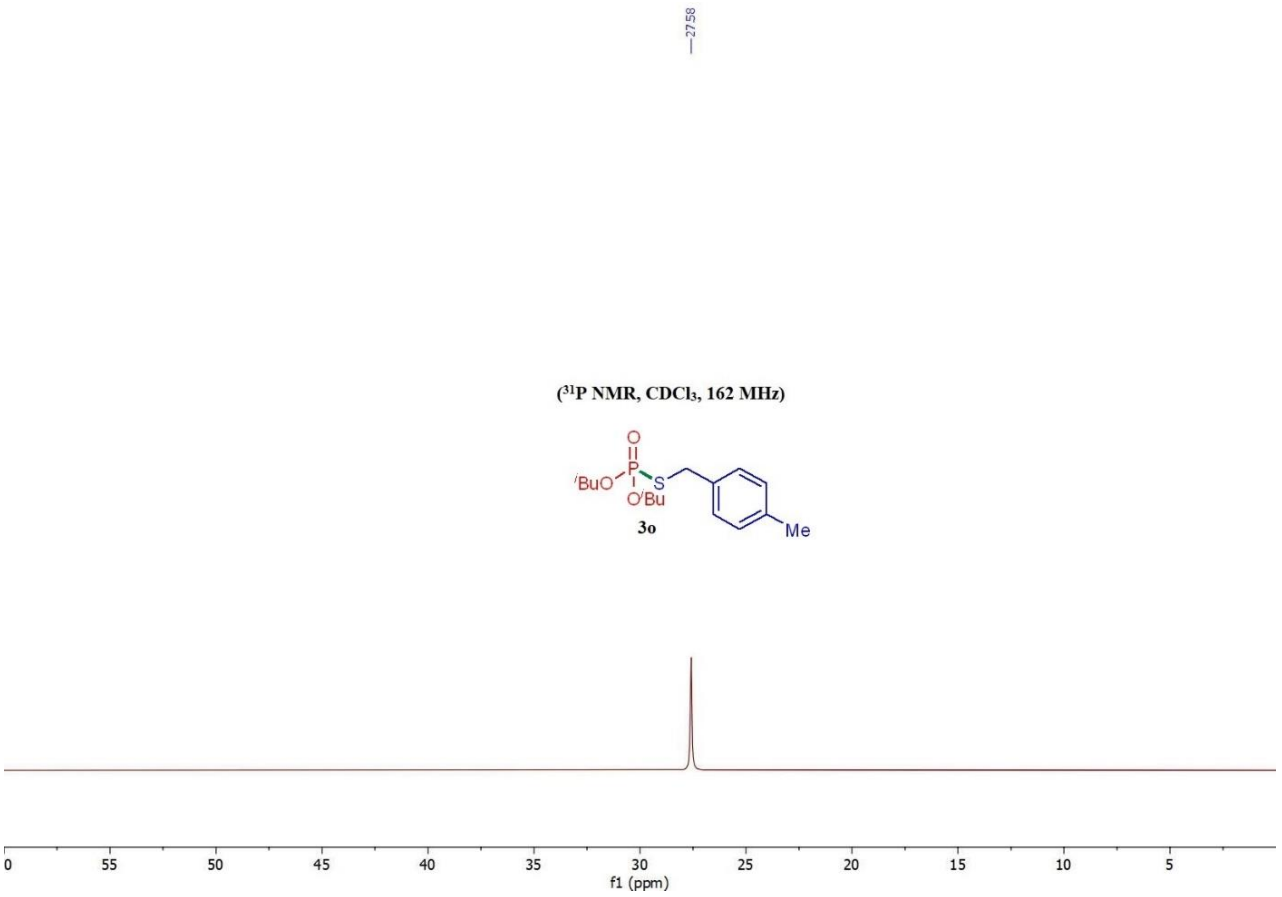
(^{1}H NMR, $CDCl_3$, 400 MHz)

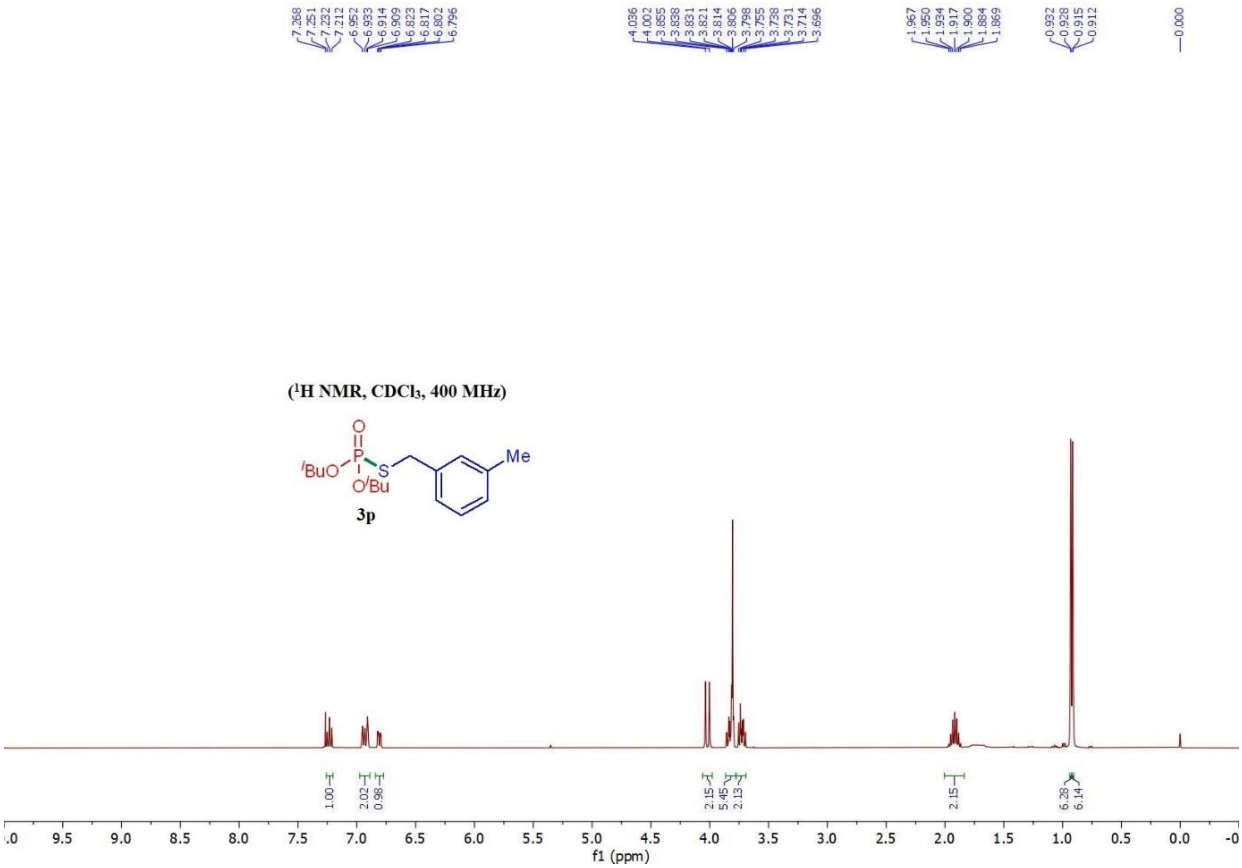


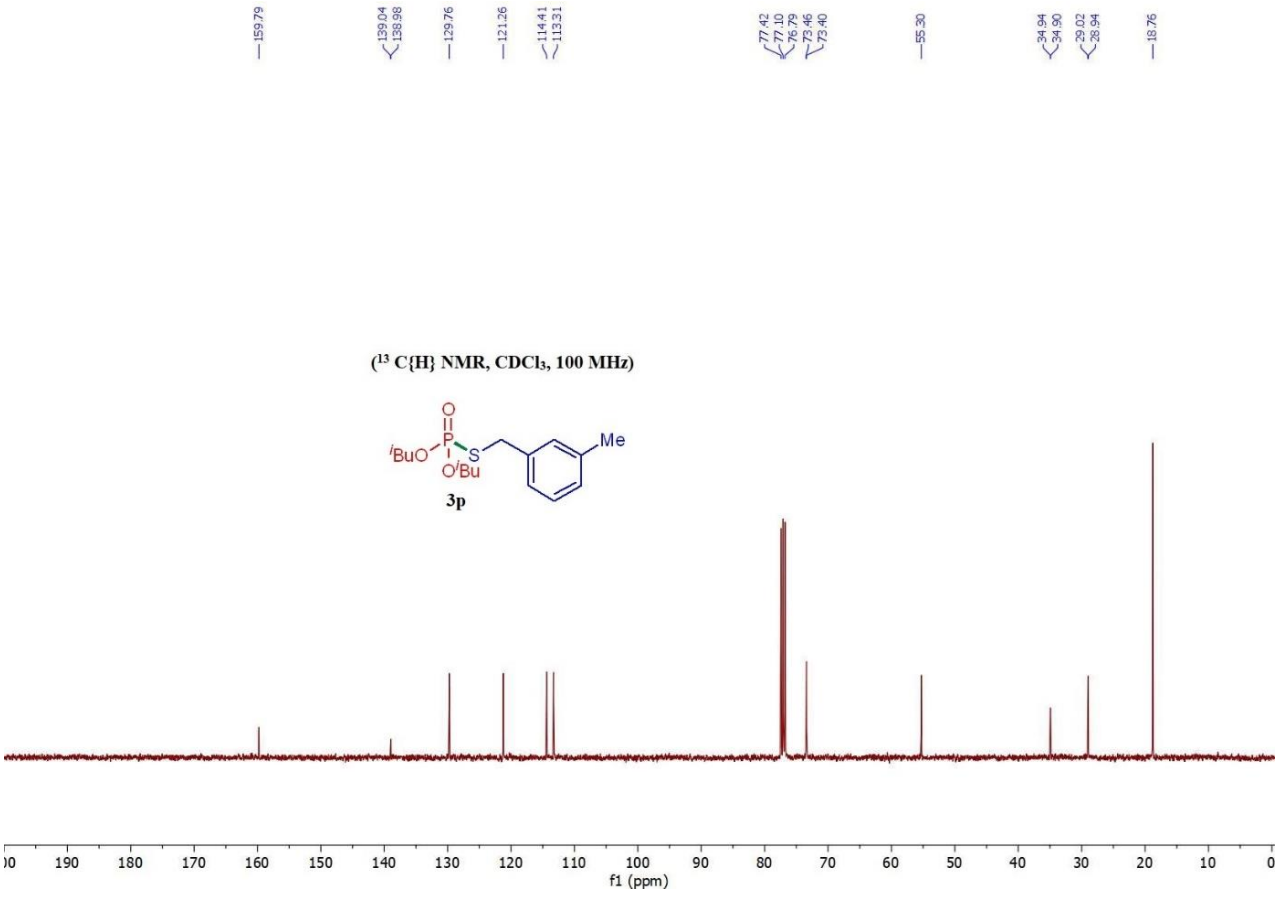
3o

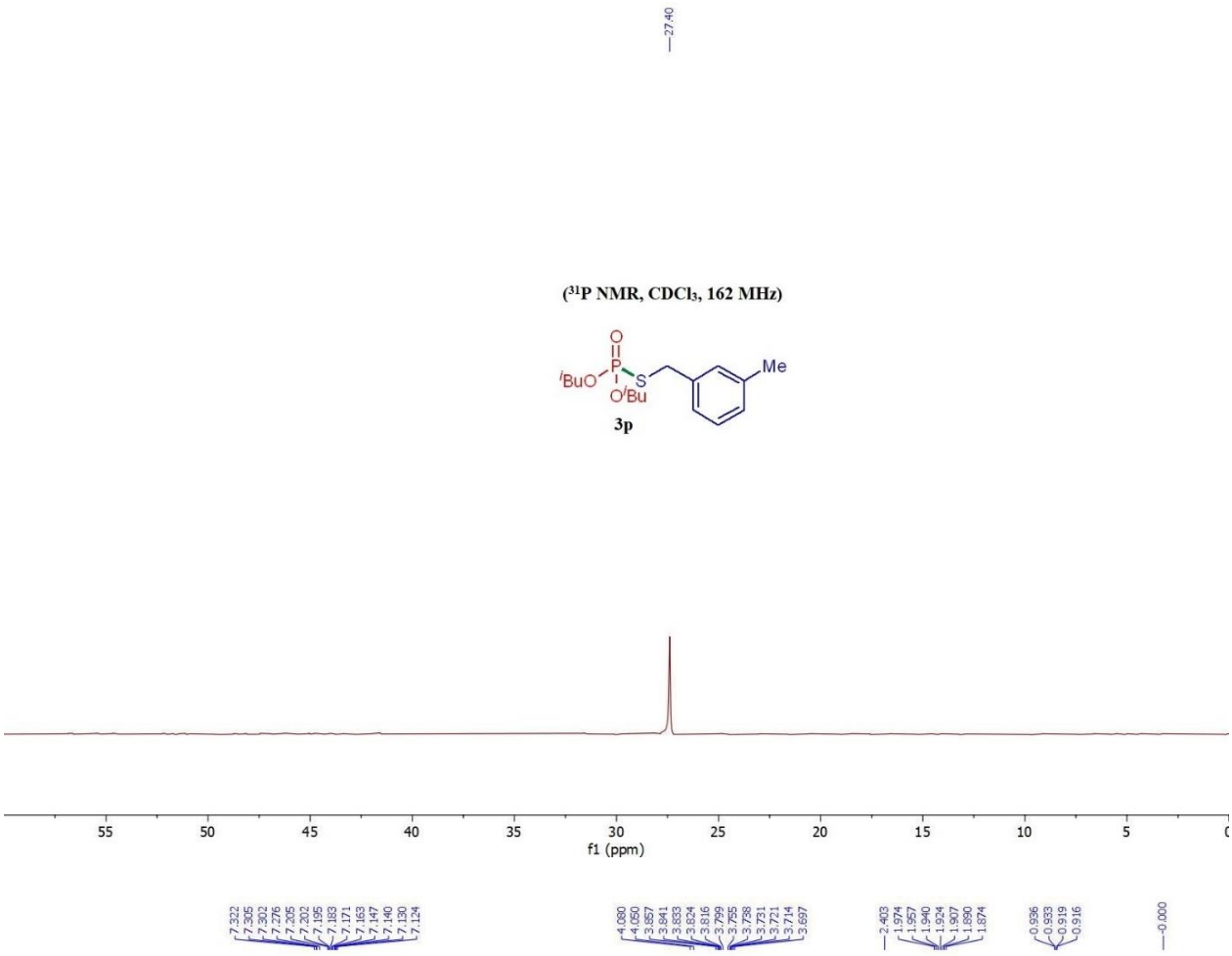



159.09
130.16
129.51
129.45
114.05
77.42
77.10
76.78
73.36
73.29
55.33
34.53
34.49
28.98
28.91
18.74
(^{13}C{H} NMR, CDCl$_3$, 100 MHz)
^{t}BuO
O^{t}Bu
3o
Me
f1 (ppm)


27.58
(^{31}P NMR, CDCl$_3$, 162 MHz)
^{t}BuO
O^{t}Bu
3o
Me
f1 (ppm)


7.368
7.351
7.232
7.212
6.952
6.933
6.914
6.909
6.823
6.817
6.802
6.796
4.036
4.002
3.855
3.838
3.831
3.821
3.814
3.806
3.798
3.755
3.738
3.731
3.714
3.696
1.967
1.950
1.934
1.917
1.900
1.884
1.869
0.932
0.928
0.915
0.912
0.000
(1H NMR, CDCl3, 400 MHz)
tBuO
O
P
S
OtBu
Me
3p
1.00
2.02
0.98
2.15
5.45
2.13
2.15
6.28
6.14
f1 (ppm)

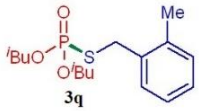

159.79
139.04
138.98
129.76
121.26
114.41
113.31
77.42
77.10
76.79
73.46
73.40
55.30
34.94
34.90
29.02
28.94
18.76
(13 C{H} NMR, CDCl3, 100 MHz)
tBuO
O
P
S
OtBu
Me
3p
f1 (ppm)



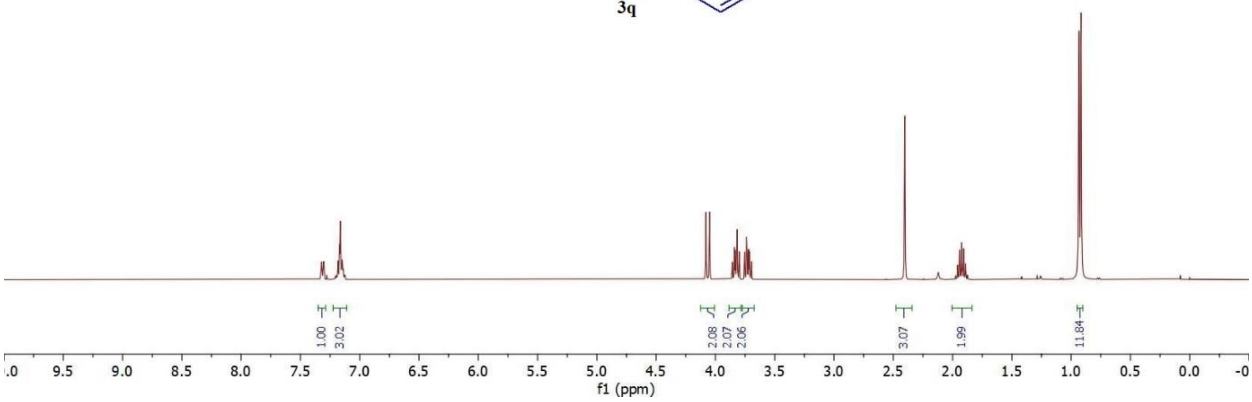
(^{31}P NMR, $CDCl_3$, 162 MHz)

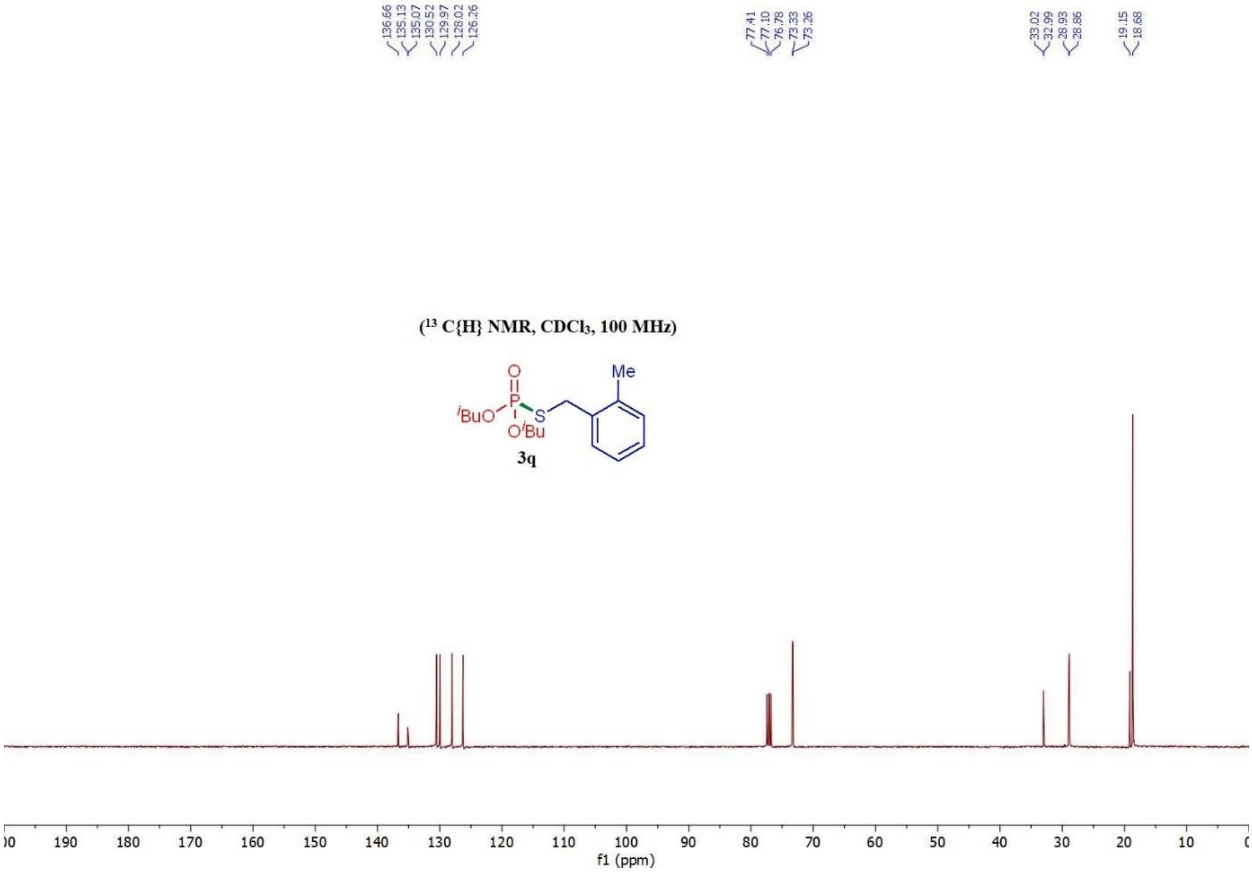
3p

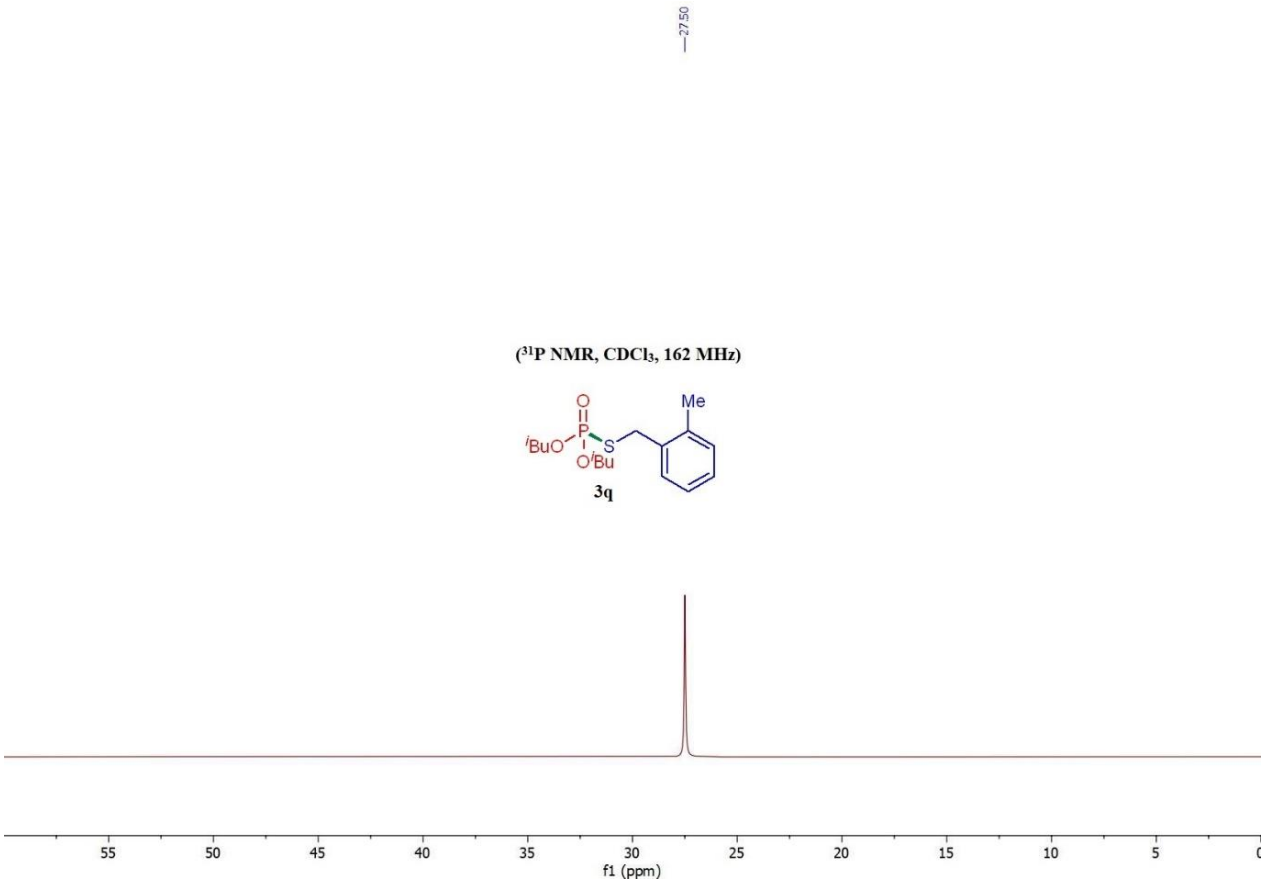
(^{1}H NMR, $CDCl_3$, 400 MHz)



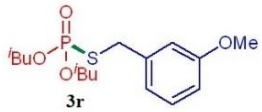
3q



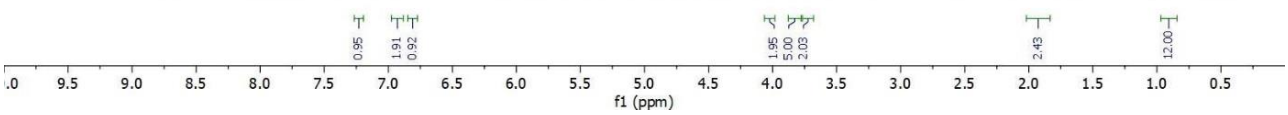

136.66
135.13
135.07
130.52
129.97
128.02
126.26
77.41
77.10
76.78
73.33
73.26
33.02
32.99
28.93
28.86
19.15
18.68
(13 C{H} NMR, CDCl3, 100 MHz)
Me
tBuO
O
P
S
OtBu
3q
f1 (ppm)


27.50
(31P NMR, CDCl3, 162 MHz)
Me
tBuO
O
P
S
OtBu
3q
f1 (ppm)

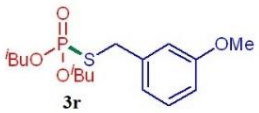
(^{1}H NMR, $CDCl_3$, 400 MHz)



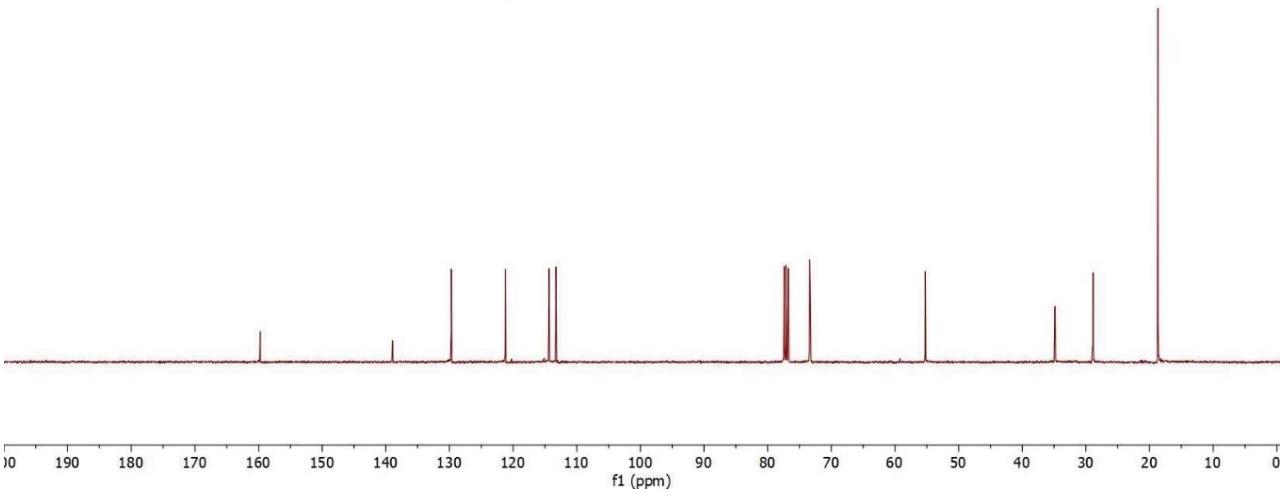
3r



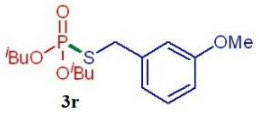
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



3r

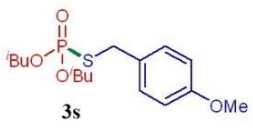


(^{31}P NMR, $CDCl_3$, 162 MHz)

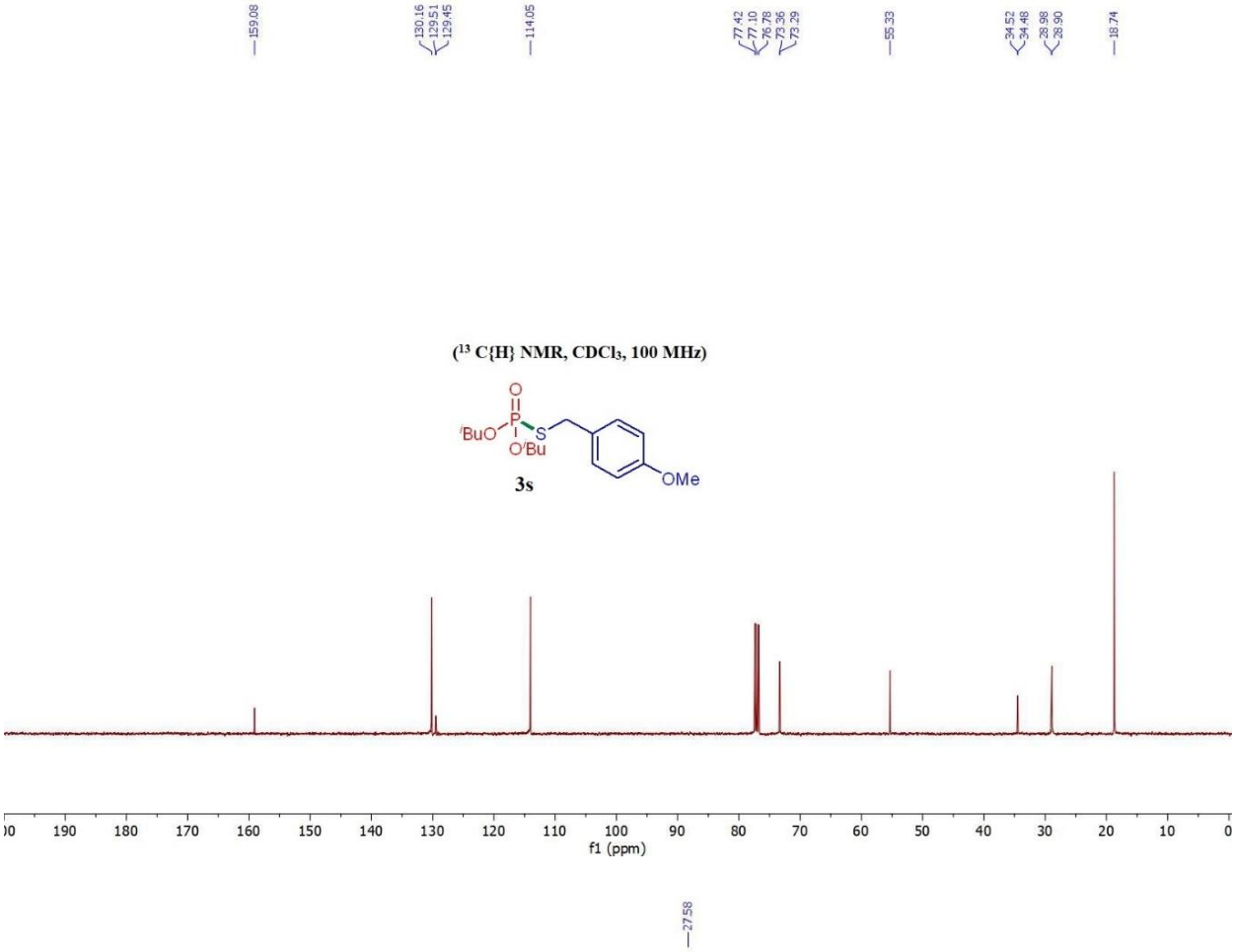


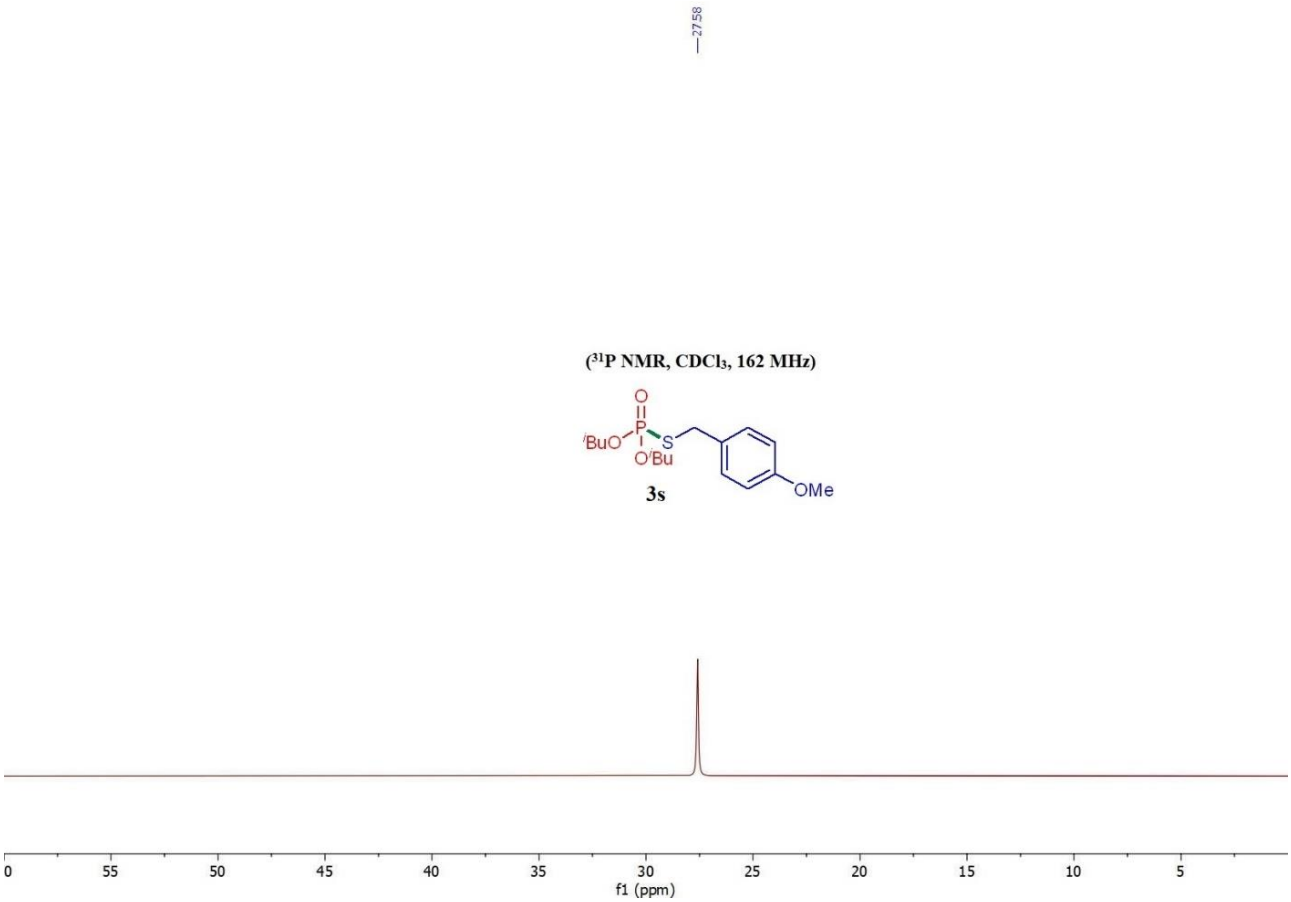
3r

(^{1}H NMR, $CDCl_3$, 400 MHz)

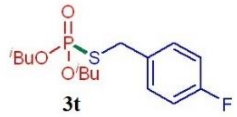


3s


159.08
130.16
129.51
129.45
114.05
77.42
77.10
76.78
73.36
73.29
55.33
34.52
34.48
28.98
28.90
18.74
(13 C{H} NMR, CDCl3, 100 MHz)
tBuO
O
P
S
OtBu
OMe
3s
f1 (ppm)

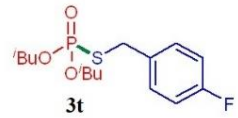

27.58
(31P NMR, CDCl3, 162 MHz)
tBuO
O
P
S
OtBu
OMe
3s
f1 (ppm)

(^{1}H NMR, $CDCl_3$, 400 MHz)



3t

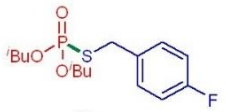
(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



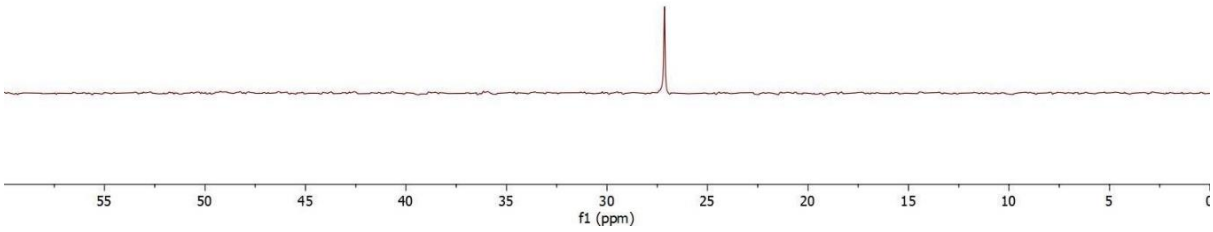
3t

27.14

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

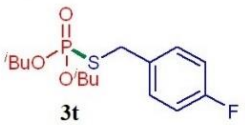


3t

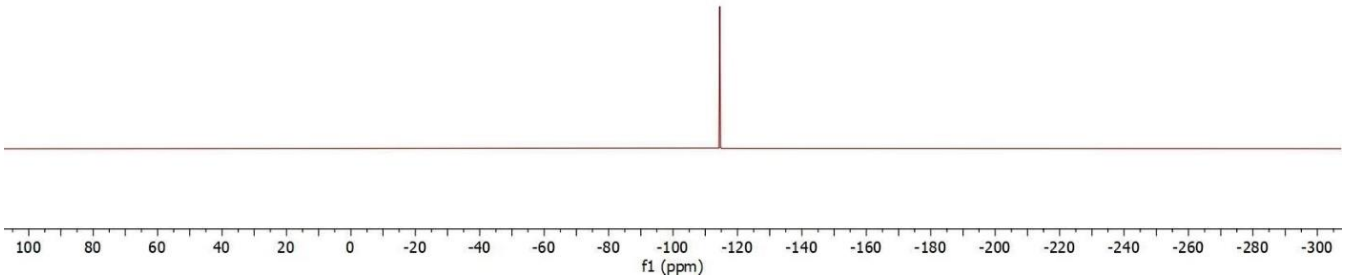


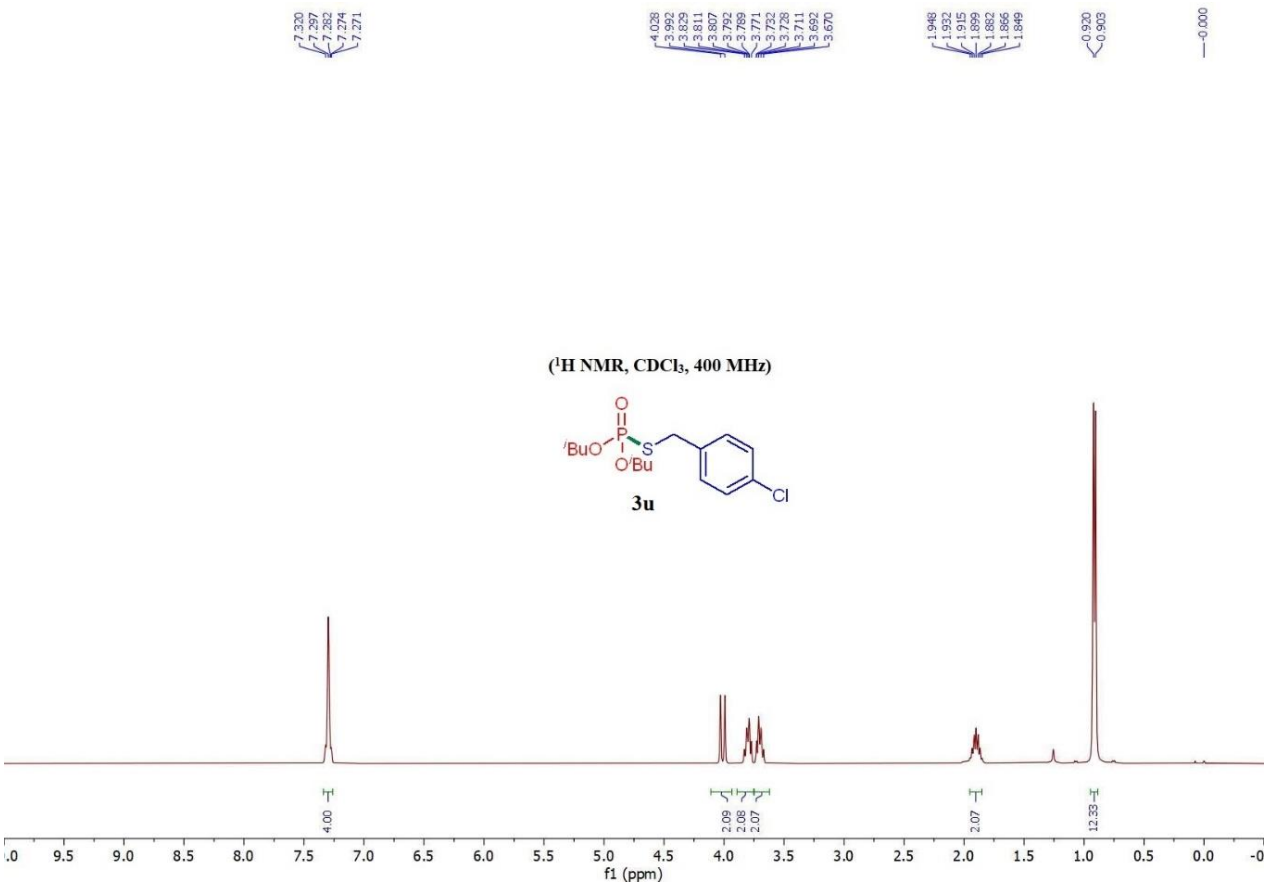
-114.51

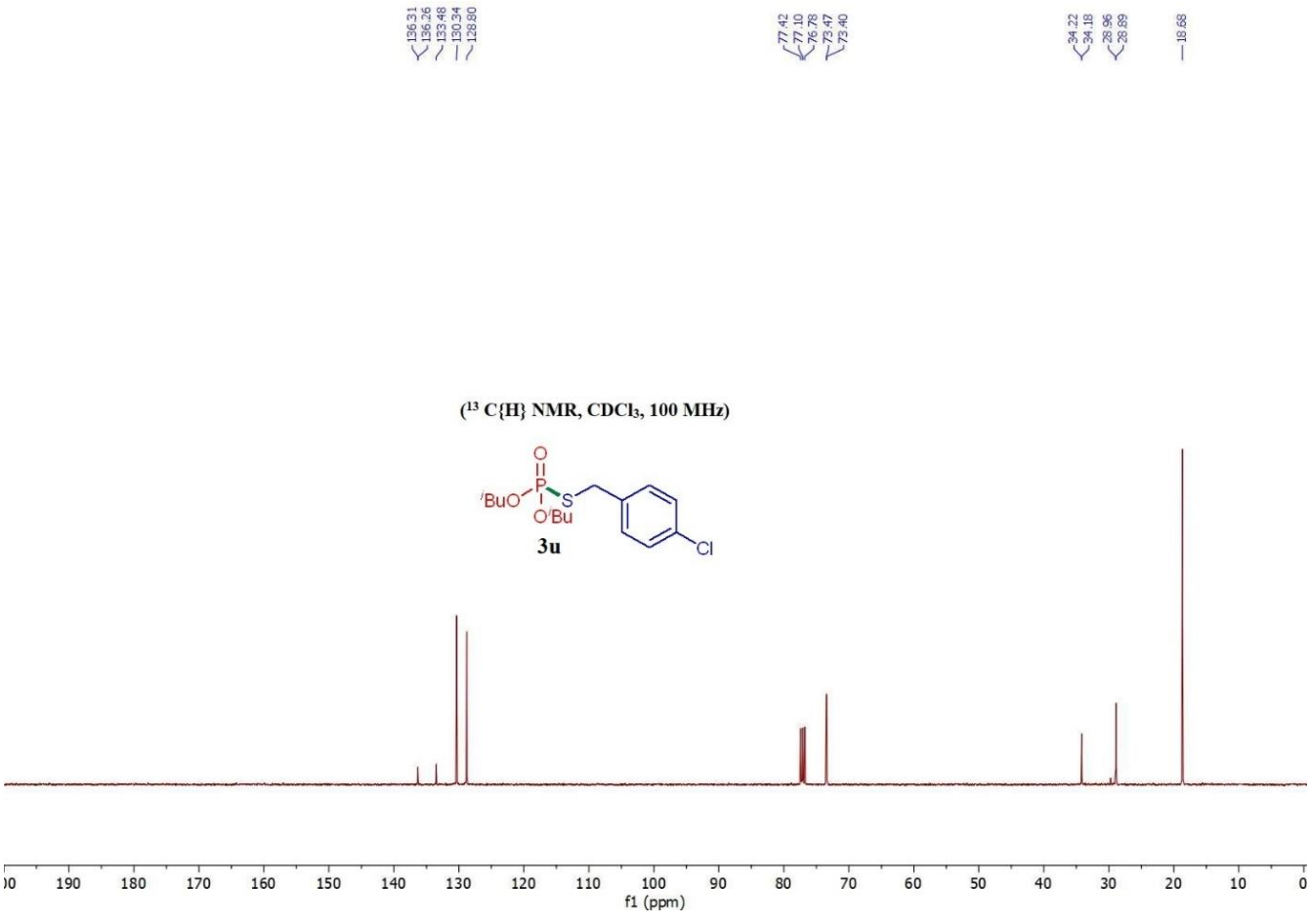
(^{19}F NMR, $CDCl_3$, 376 MHz)



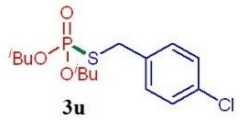
3t



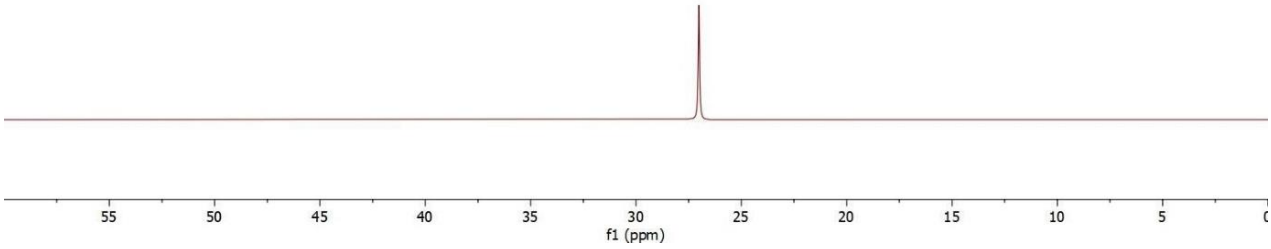

7.330
7.297
7.282
7.274
7.271
4.038
3.992
3.829
3.811
3.807
3.792
3.789
3.771
3.732
3.728
3.711
3.692
3.670
1.948
1.932
1.915
1.899
1.882
1.866
1.849
0.920
0.903
0.000
(1H NMR, CDCl3, 400 MHz)
tBuO
O
P
S
OtBu
Cl
3u
4.00
2.09
2.08
2.07
2.07
12.33
f1 (ppm)


136.31
136.26
133.48
130.34
128.80
77.42
77.10
76.78
73.47
73.40
34.22
34.18
28.96
28.89
18.68
(13 C{H} NMR, CDCl3, 100 MHz)
tBuO
O
P
S
OtBu
Cl
3u
f1 (ppm)

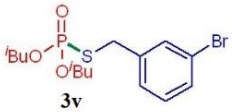
(^{31}P NMR, $CDCl_3$, 162 MHz)



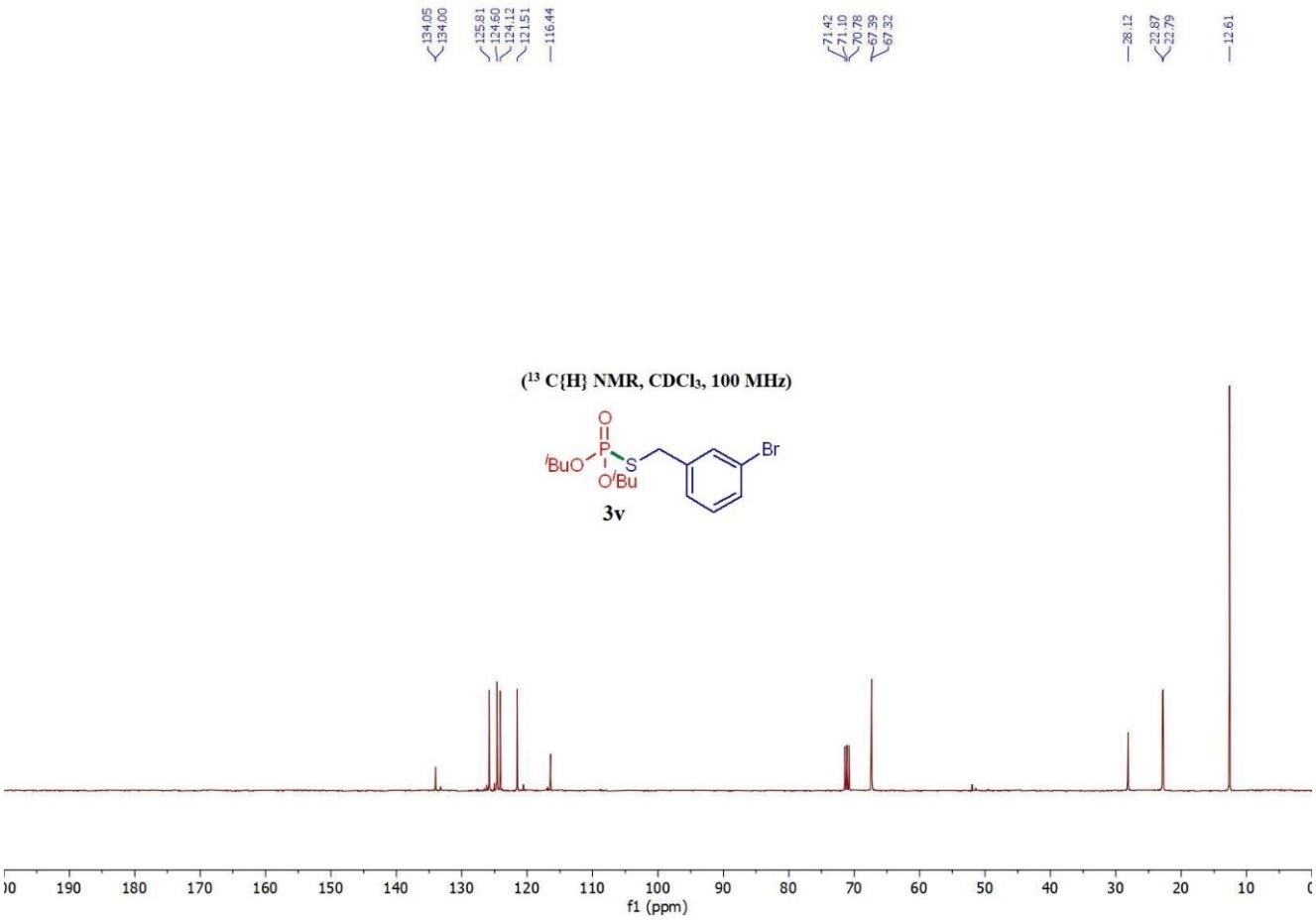
3u

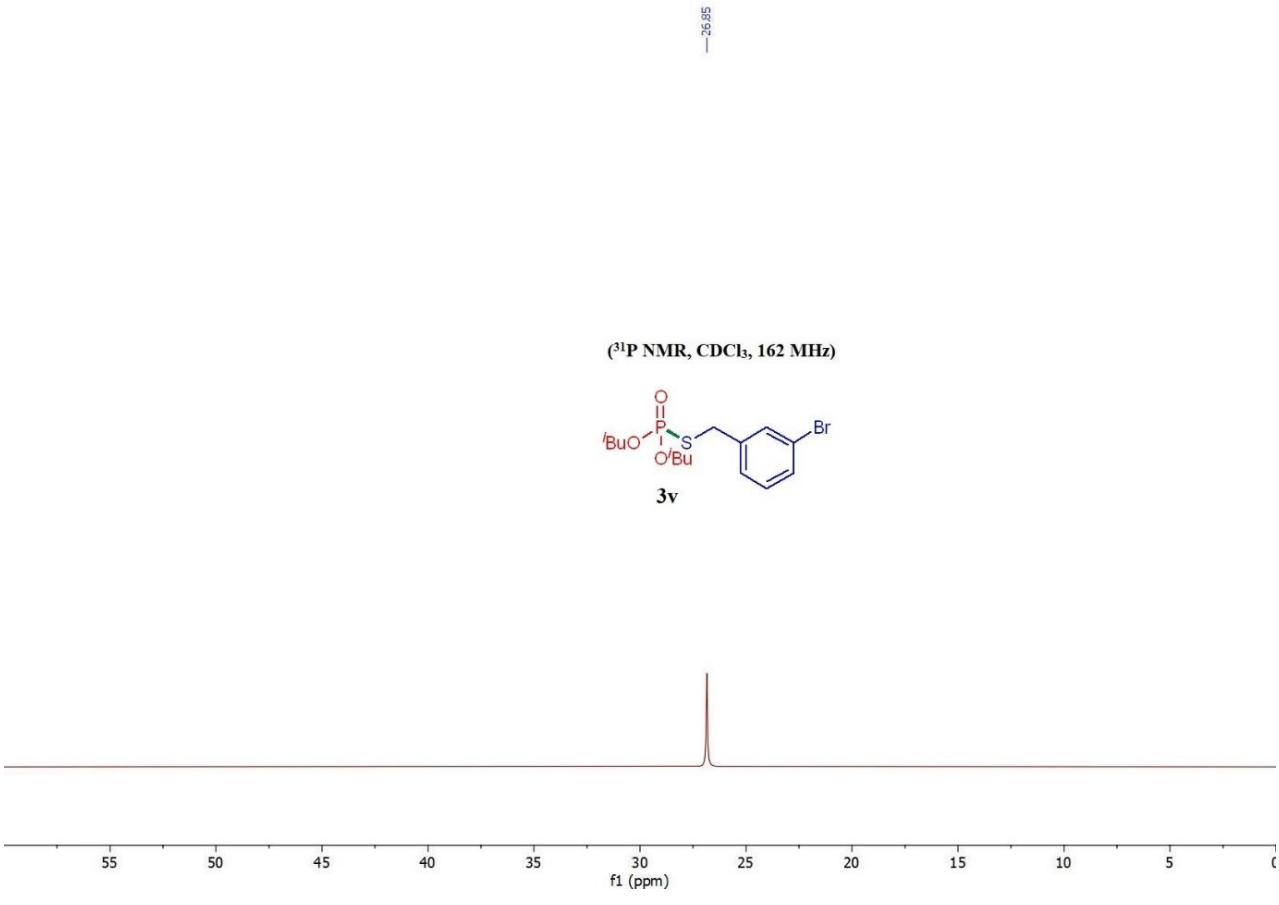


(^{1}H NMR, $CDCl_3$, 400 MHz)

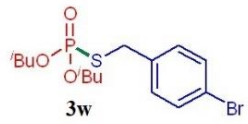


3v


134.05
134.00
125.81
124.60
124.12
121.51
116.44
71.42
71.10
70.78
67.39
67.32
28.12
22.87
22.79
12.61
(13 C{H} NMR, CDCl3, 100 MHz)
iBuO
O
P
S
OiBu
Br
3v
f1 (ppm)

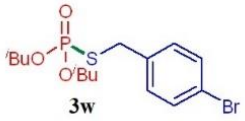

26.85
(31P NMR, CDCl3, 162 MHz)
iBuO
O
P
S
OiBu
Br
3v
f1 (ppm)

(¹H NMR, CDCl₃, 400 MHz)

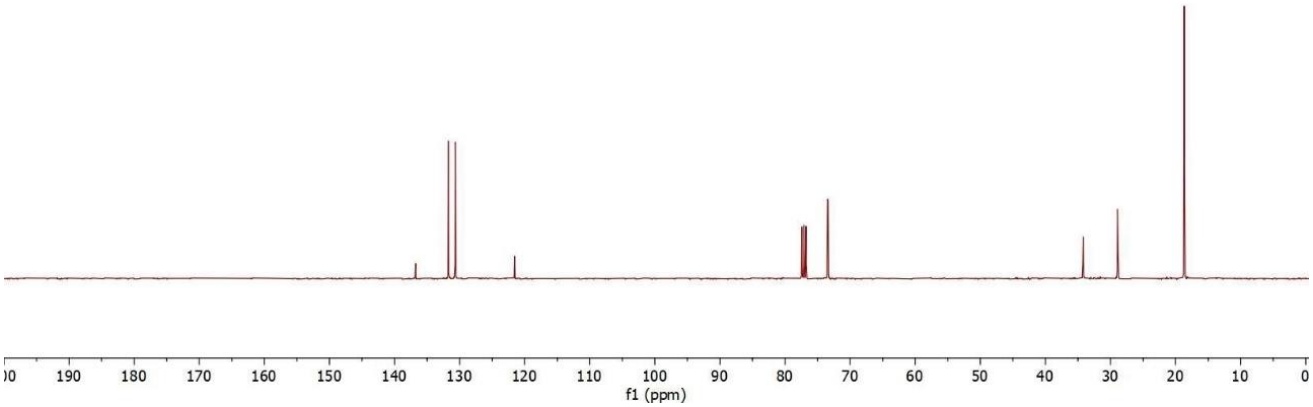


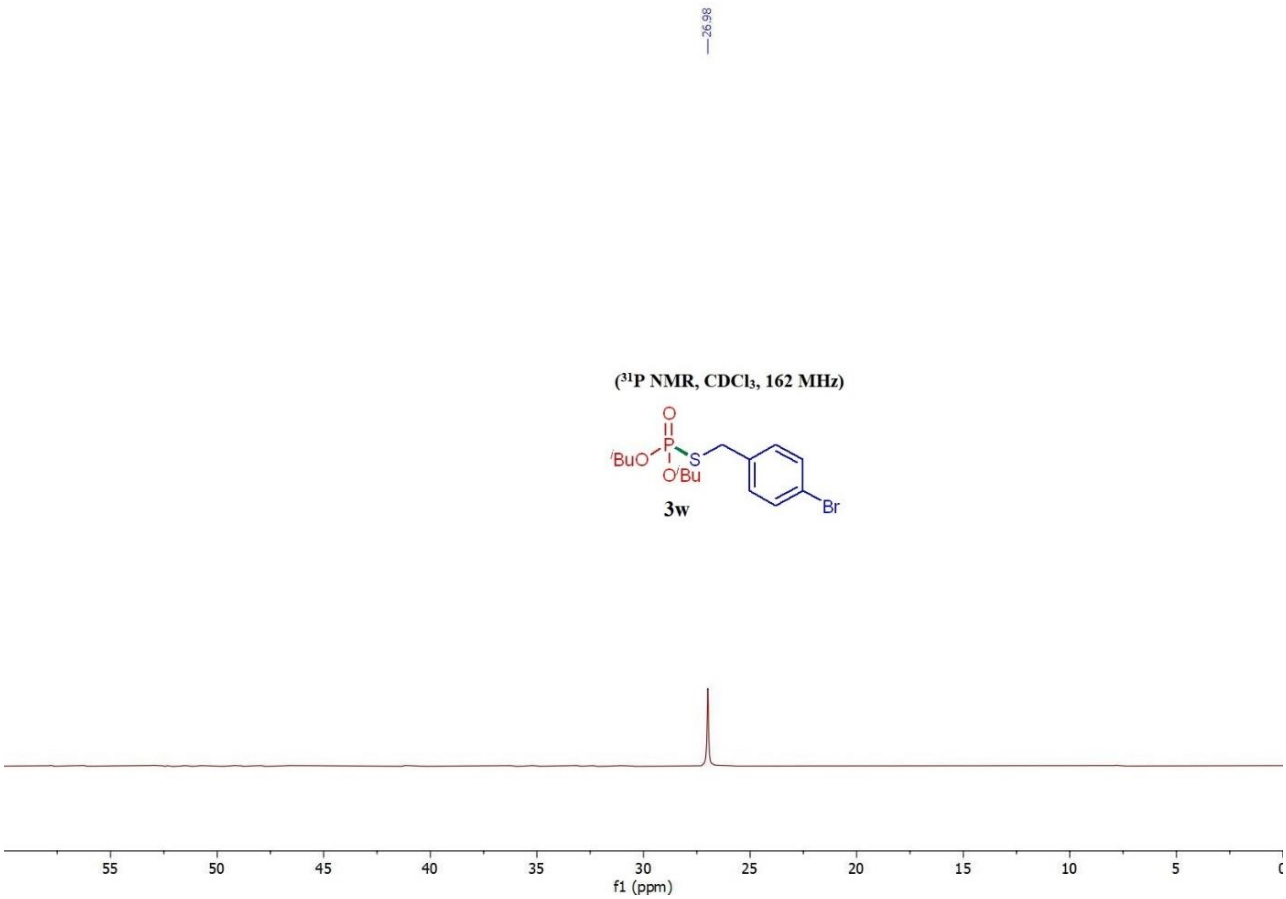
3w

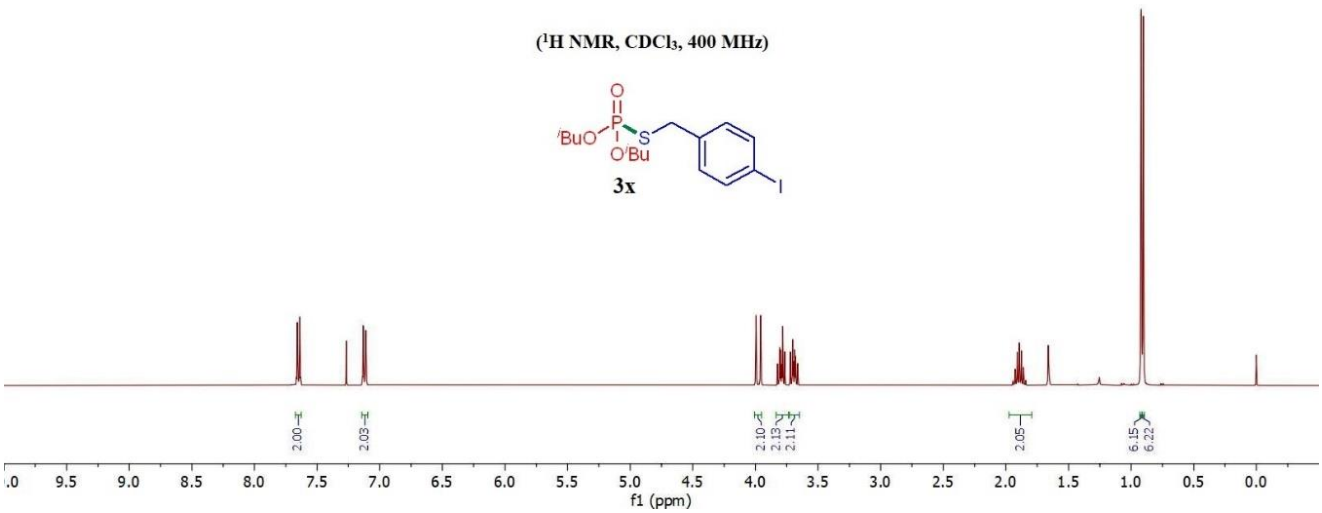
(¹³ C{H} NMR, CDCl₃, 100 MHz)

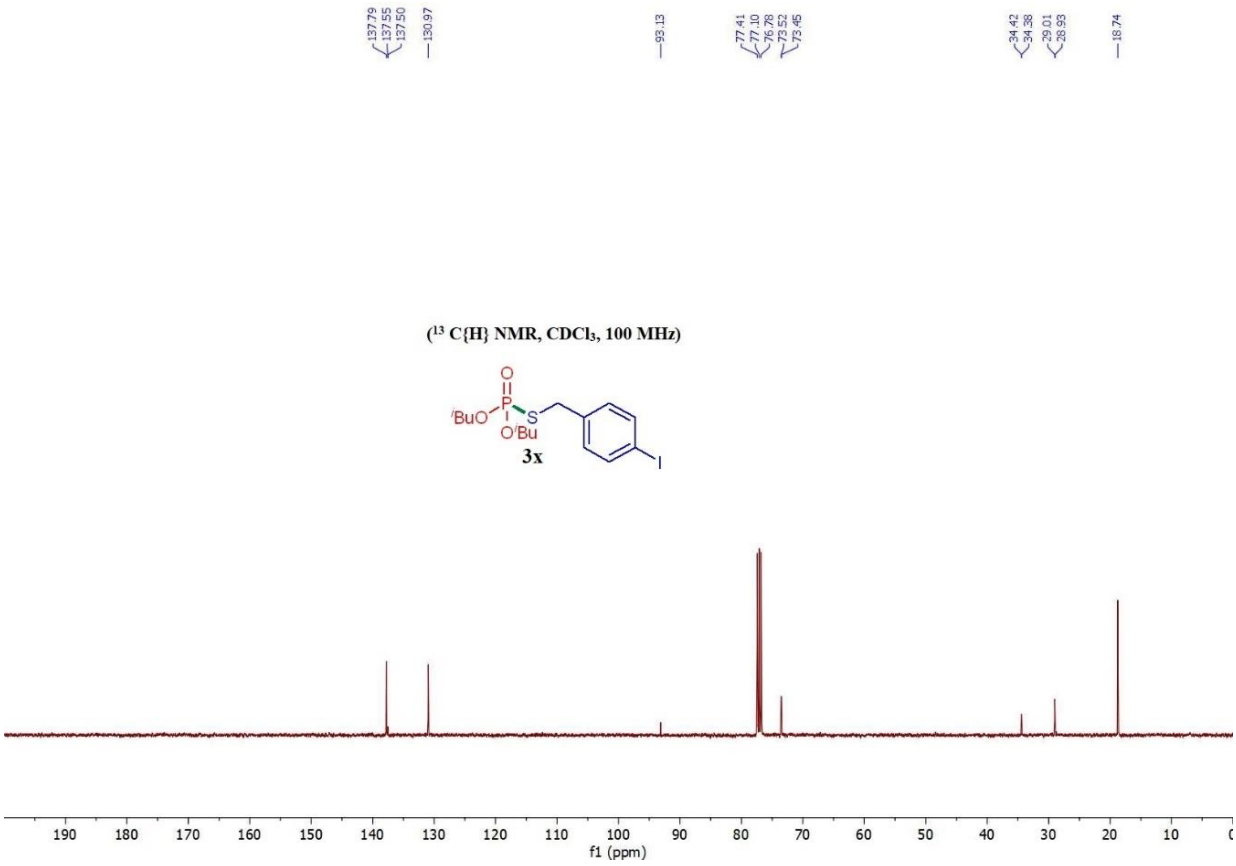


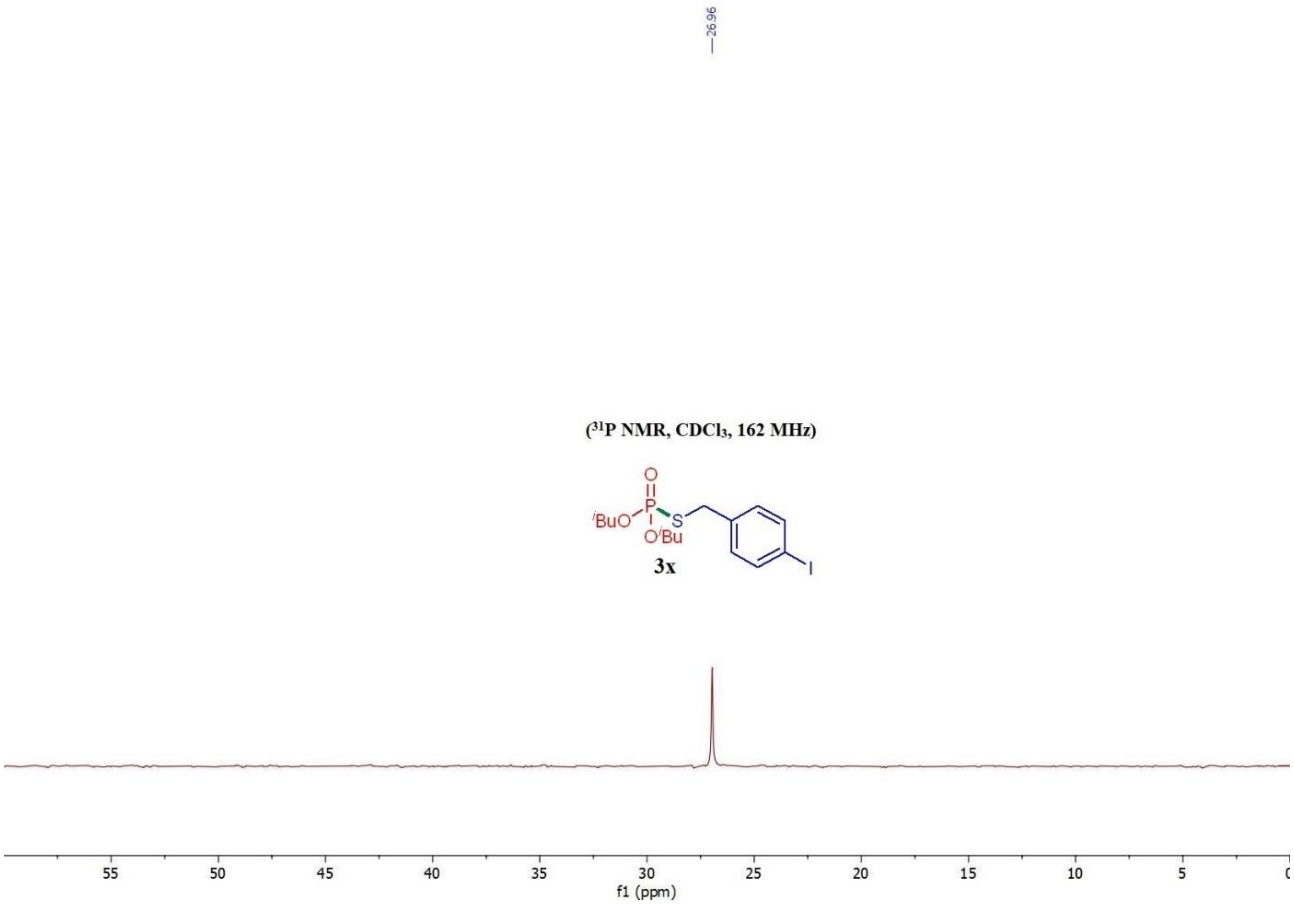
3w



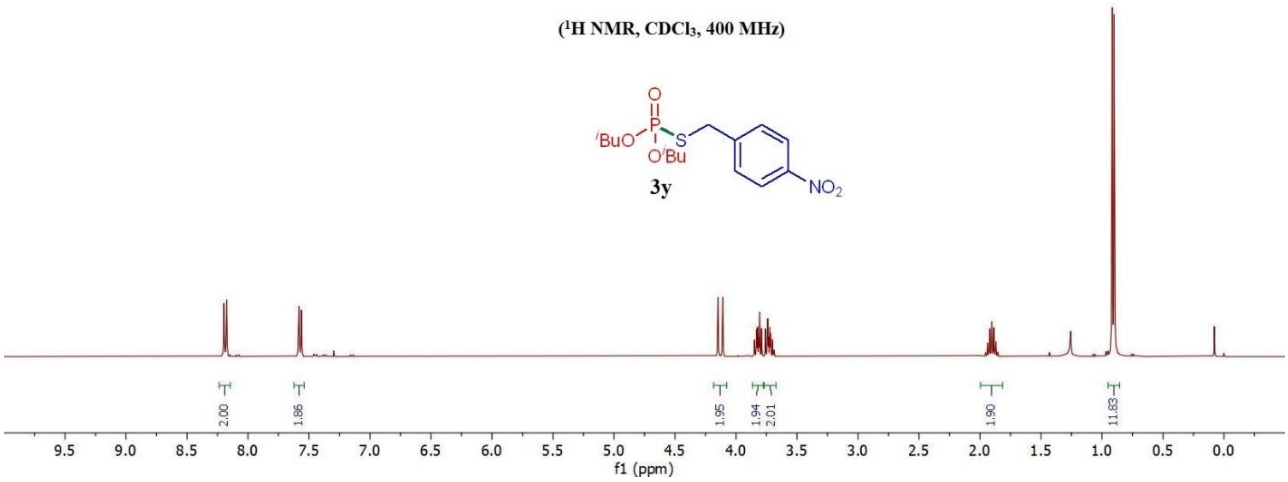

26.98
(31P NMR, CDCl3, 162 MHz)
tBuO
O
P
S
O tBu
Br
3w
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)
7.664
7.658
7.653
7.642
7.637
7.631
7.267
7.138
7.132
7.127
7.116
7.111
7.105
3.995
3.958
3.823
3.807
3.799
3.782
3.766
3.721
3.704
3.686
3.679
3.662
1.943
1.926
1.909
1.893
1.876
1.859
1.843
0.921
0.919
0.904
0.902
0.000


(1H NMR, CDCl3, 400 MHz)
tBuO
O
P
S
O tBu
I
3x
2.00
2.03
2.10
2.13
2.11
2.05
6.15
6.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

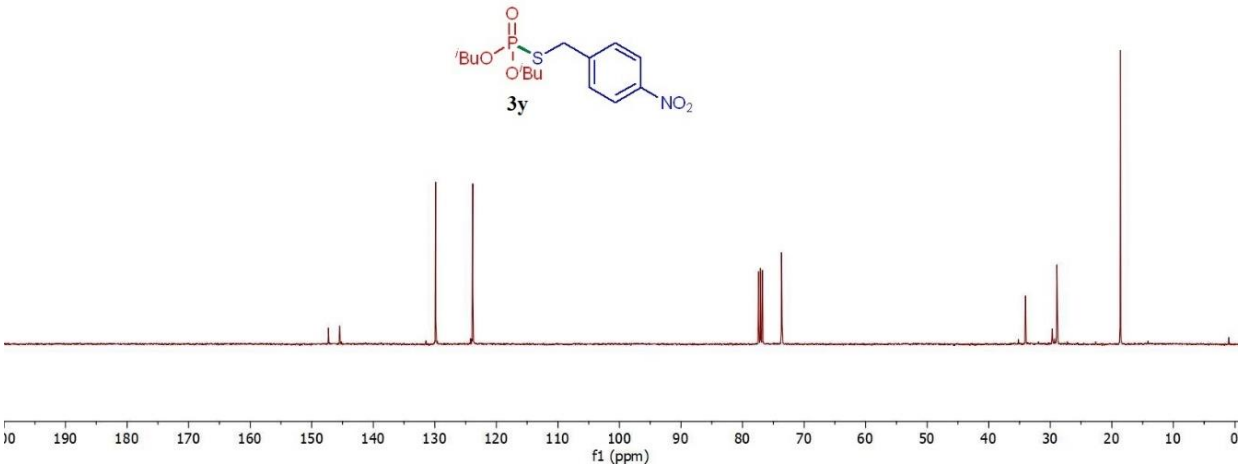

137.79
137.55
137.50
130.97
93.13
77.41
77.10
76.78
73.52
73.45
34.42
34.38
29.01
28.93
18.74
(13 C{H} NMR, CDCl3, 100 MHz)
3x
f1 (ppm)

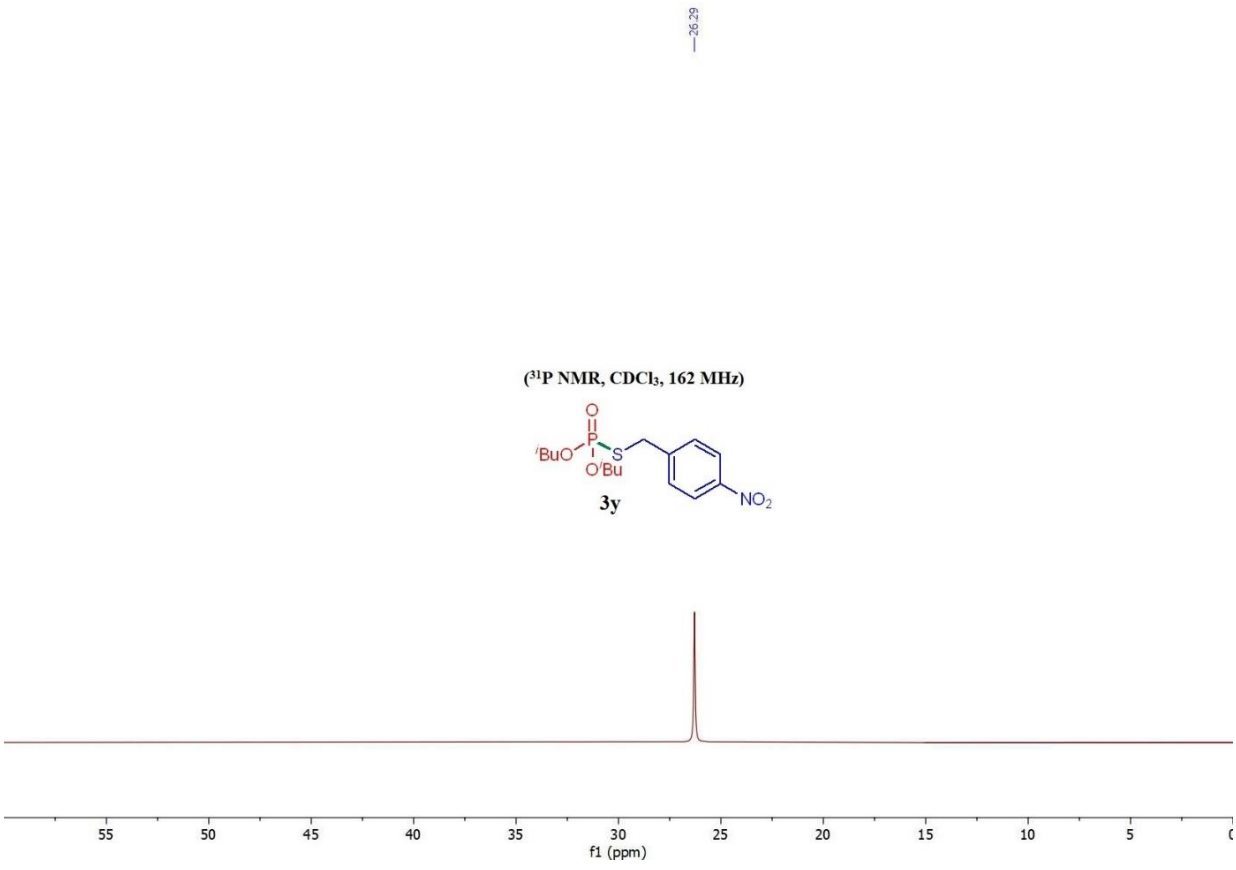

26.96
(31P NMR, CDCl3, 162 MHz)
3x
f1 (ppm)

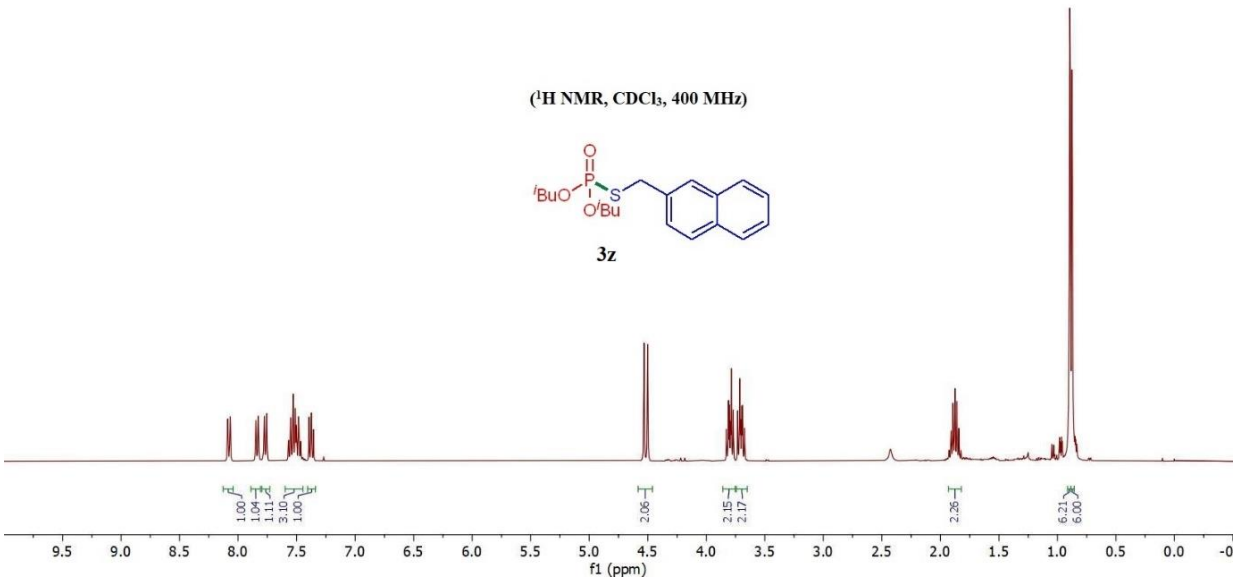
(¹H NMR, CDCl₃, 400 MHz)



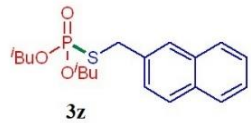
(¹³ C{H} NMR, CDCl₃, 100 MHz)



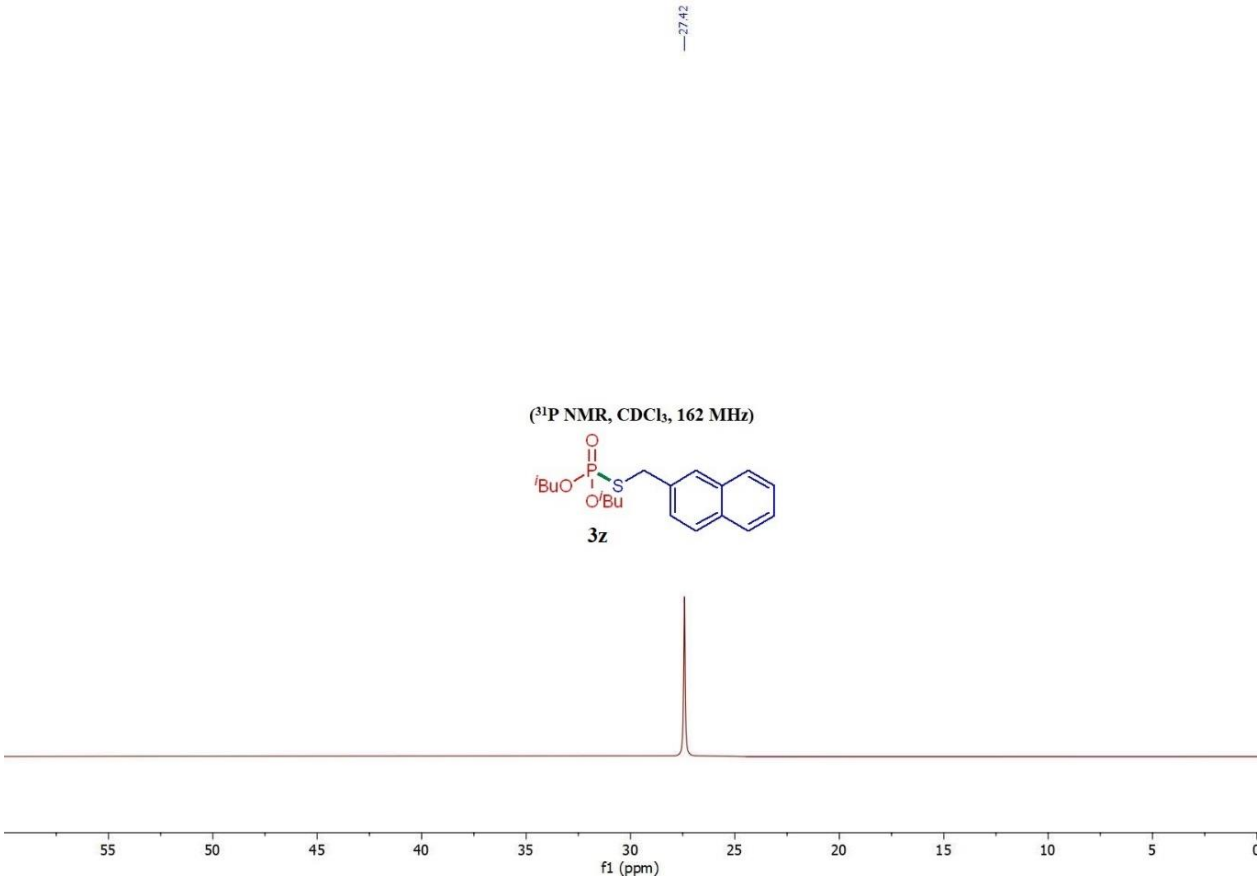

26.29
(31P NMR, CDCl3, 162 MHz)
iBuO
O
P
S
OiBu
NO2
3y
f1 (ppm)


(1H NMR, CDCl3, 400 MHz)
iBuO
O
P
S
OiBu
3z
f1 (ppm)

(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



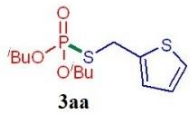
3z



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

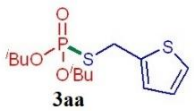
3z

(^{1}H NMR, $CDCl_3$, 400 MHz)

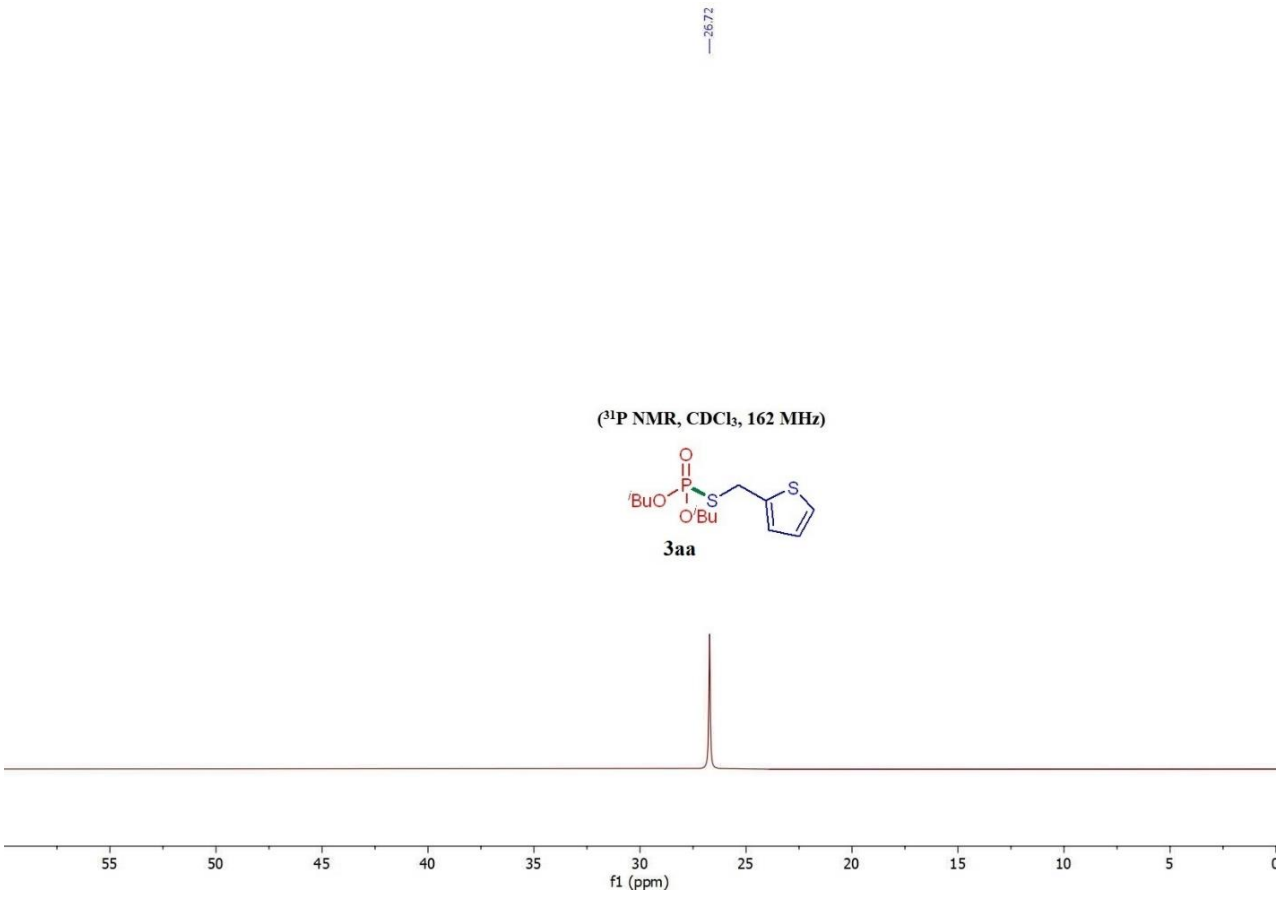


3aa

(^{13}C{H} NMR, $CDCl_3$, 100 MHz)



3aa


26.72
(31P NMR, CDCl3, 162 MHz)
tBuO
O
P
S
OtBu
S
3aa
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

