Direct, Oxidative Halogenation of Diaryl- or Dialkylphosphine oxides with (Dihaloiodo)arenes

Jasmin Eljo and Graham K. Murphy*
Department of Chemistry, University of Waterloo, 200 University Ave W., Waterloo, ON, Canada, N2L3G1

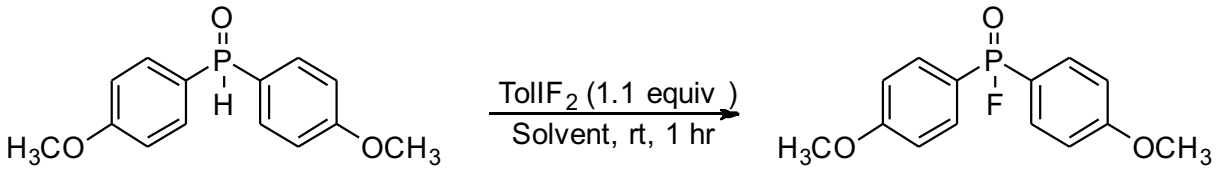
1. Experimental Details and Characterization Data

General Experimental Details: Reactions were carried out in oven-dried glassware under a positive nitrogen atmosphere. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes. Solvents were dried and purified using a JC Meyer solvent purification system, and were used without further purification. Thin layer chromatography was performed on glass plates pre-coated with 0.25 mm Kieselgel 60 F254 (Silicycle). Flash chromatography columns were packed with 230-400 mesh silica gel (Silicycle). Infrared spectra were recorded on

a Perkin Elmer FT-IR Spectrum Two with ATR Two. Proton NMR spectra (^{1}H NMR) were recorded at 300 or 500 MHz, and are reported (ppm) relative to the residual chloroform peak (7.26 ppm) and coupling constants (*J*) are reported in hertz (Hz). Carbon NMR spectra (^{13}C NMR) were recorded at 125 or 75 MHz and are reported (ppm) relative to the center line of the triplet from chloroform-d (77.00 ppm). Phosphorus NMR spectra (^{31}P NMR) were recorded at 121 or 202 MHz, and are reported (ppm) relative to the peak of 85% H_3PO_4 (0 ppm). Fluorine NMR spectra (^{19}F NMR) were recorded at 282 MHz, and are reported (ppm) relative to the peak of trifluoroacetic acid (-76.53 ppm). Mass spectra were performed on a ThermoFisher Scientific Q-Exactive hybrid mass spectrometer using positive electrospray ionization (ESI). ESI samples were infused at 5 μL/min in 1:1 CH_3OH/H_2O+0.1% formic acid.

2. Optimization Study for the Synthesis of P(O)F Compounds

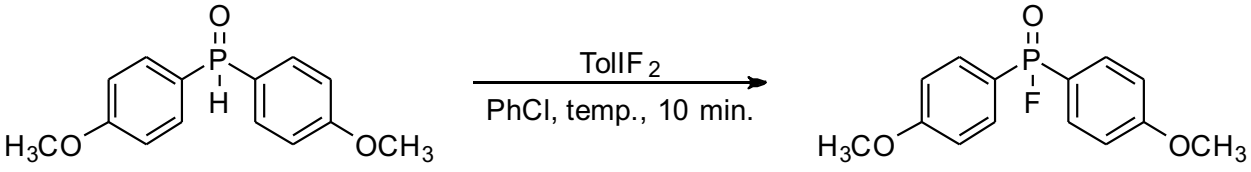
Table S1. Solvents screened in the oxidative fluorination reaction:



3a **4a**

entry	solvent	**4a** % yield
1	CH_2Cl_2	50%
2	DCE	53%
3	PhCl	58%
4	$CHCl_3$	46%
5	toluene	51%
6	Et_2O	49%
7	DMF	43%
8	CH_3CN	38%
9	THF	51%
10	acetone	31%

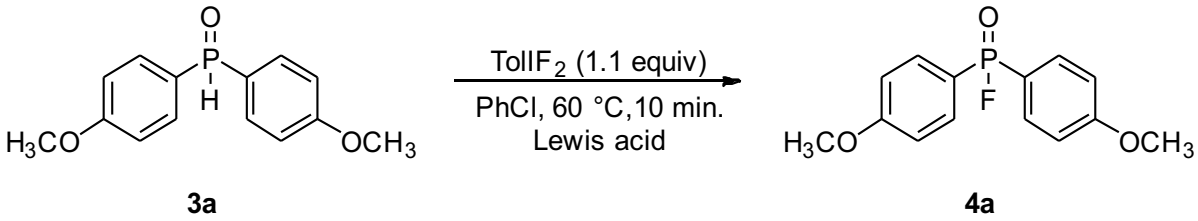
Table S2. Temperature and $TolIF_2$ loading screened in the oxidative fluorination reaction:



3a **4a**

entry	$TolIF_2$ (equiv)	temp. (°C)	**4a** % yield
1	1.1	40	64%
2	1.1	60	69%
3	1.1	80	69%
4	1.1	110	60%
5	1.1	reflux	64%
6	1.4	60	67%
7	1.02	60	55%

Table S3. Lewis Acids screened in the oxidative fluorination reaction:

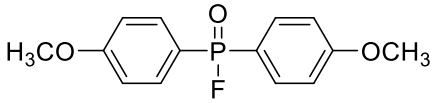


3a **4a**

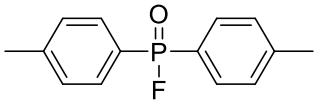
entry	Lewis acid	**4a** % yield
1	BF_3•OEt_2 (5 mol%)	67%
2	BF_3•OEt_2 (10 mol%)	67%
3	TiF_3 (10 mol%)	57%
4	TiF_4 (10 mol%)	52%
5	FeF_3 (10 mol%)	57%
6	InF_3 (10 mol%)	57%
7	AlF_3 (10 mol%)	60%
8	GaF_3 (10 mol%)	64%
9	BiF_3 (10 mol%)	57%

3. General Procedure A: Synthesis of P(O)F Compounds

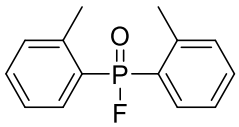
Into a round bottom flask was added *p*-(difluoroiodo)toluene (**1**, 0.17 mmol, 1.1 equiv) and PhCl (0.25 mL, 0.6M), followed by the secondary phosphine oxide (**3**, 0.15 mmol, 1.0 equiv). The resulting reaction mixture was stirred at 60 °C in a pre-heated oil bath for 10 minutes, by which time TLC analysis indicated consumption of the starting material. The crude reaction mixture was cooled to room temperature and directly purified by column chromatography (ether/pentane) without prior concentration.



Bis(4-methoxyphenyl)phosphinic fluoride (4a): Bis(4-methoxyphenyl)phosphine oxide (0.039 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The crude reaction mixture was purified via column chromatography (ether) to give **4a** (0.029 g, 69% yield) as a colourless oil which solidified upon standing. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.98 (d, *J* = 1006.7 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 43.02 (d, *J* = 1003.1 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75-7.68 (m, 4H), 6.99-6.95 (m, 4H), 3.83 (s, 6H). Spectral data were consistent with literature values.[1]

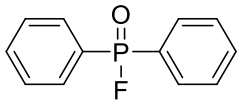


Di-*p*-tolylphosphinic fluoride (4b): Di-*p*-tolylphosphine oxide (0.035 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The crude reaction mixture was purified via column chromatography (50% ether/pentane) to give **4b** (0.023 g, 62% yield) as a white solid. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.64 (d, *J* = 1012.4 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 43.23 (d, *J* = 1011.6 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72-7.65 (m, 4H), 7.31-7.27 (m, 4H), 2.40 (s, 6H). Spectral data were consistent with literature values.[1]

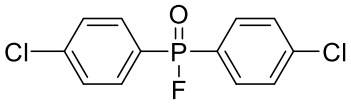


Di-*o*-tolylphosphinic fluoride (4c): Di-*o*-tolylphosphine oxide (0.035 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The crude reaction mixture was purified via column chromatography (50% ether/pentane) to give **4c** (0.025 g, 68% yield) as a colourless solid. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.44 (d, *J* = 1015.2 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 44.24 (d,

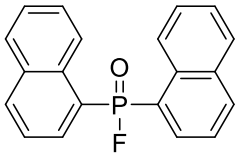
J = 1016.4 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82-7.75 (m, 2H), 7.49 (t, 2H, J = 7.5 Hz), 7.33-7.24 (m, 4H), 2.43 (s, 6H). Spectral data were consistent with literature values.[1]



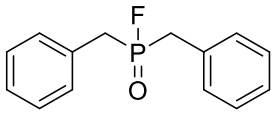
Diphenylphosphinic fluoride (4d): Diphenylphosphine oxide (0.030 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The crude reaction mixture was purified via column chromatography (80% ether/pentane) to give **4d** (15 mg, 46% yield) as a colourless oil. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.63 (d, J = 1018.0 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 41.90 (d, J = 1015.2 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.85-7.78 (m, 4H), 7.64-7.58 (m, 2H), 7.53-7.47 (m, 4H). Spectral data were consistent with literature values.[1]



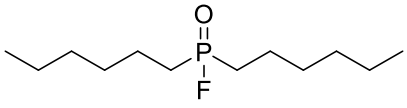
Bis(4-chlorophenyl)phosphinic fluoride (4e): Bis(4-chlorophenyl)phosphine oxide (0.041 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The crude reaction mixture was purified via column chromatography (50% ether/pentane), by rendering the stationary phase acidic with 1% acetic acid in pentane to give **4e** (0.020 g, 47% yield) as a colourless oil. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.27 (d, J = 1020.8 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 39.76 (d, J = 1016.4 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77-7.70 (m, 4H), 7.52-7.48 (m, 4H). Spectral data were consistent with literature values.[2]



Di(naphthalen-1-yl)phosphinic fluoride (4f): Di(naphthalen-1-yl)phosphine oxide (0.046 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The crude reaction mixture was purified via column chromatography (50% ether/pentane) to give **4f** (0.036 g, 75% yield) as a white solid. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -68.48 (d, J = 1018.0 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 45.47 (d, J = 1011.6 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.54-8.52 (m, 2H), 8.11-7.98 (m, 4H), 7.94-7.90 (m, 2H), 7.58-7.47 (m, 6H). Spectral data were consistent with literature values.[2]

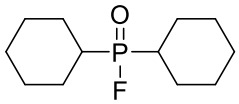


Dibenzylphosphinic fluoride (4g): Dibenzylphosphine oxide (0.034 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The crude reaction mixture was purified via column chromatography (ether) to give **4g** (0.012 g, 32% yield) as a colourless oil. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.06 (d, J = 1037.8 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 59.79 (d, J = 1034.6 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37-7.29 (m, 6H), 7.25-7.21 (m, 4H), 3.22 (dd, J = 16.5, J = 9 Hz, 4H). Spectral data were consistent with literature values.[2]

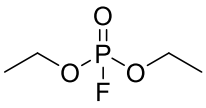


Dihexylphosphinic fluoride (4h): Dihexylphosphine oxide (0.033 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The reaction mixture was stirred at 60 °C in an oil bath for 30

minutes and the crude reaction mixture was purified via column chromatography (80% ether/pentane) by rendering the stationary phase acidic with 1% acetic acid in eluent to give **4h** (0.021 g, 60% yield) as a colourless oil which turned to a white solid gradually. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.67 (d, *J* = 1012.4 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 71.46 (d, *J* = 1012.8 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.88-1.76 (m, 4H), 1.69-1.55 (m, 4H), δ 1.44-1.25 (m, 12H), 0.87 (t, *J* = 6.0 Hz, 6H). Spectral data were consistent with literature values.[2]



Dicyclohexylphosphinic fluoride (4i): Dicyclohexylphosphine oxide (0.032 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The reaction mixture was stirred at 60 °C in an oil bath for 30 minutes and the crude reaction mixture was purified via column chromatography (ether) by rendering the stationary phase acidic with 1% acetic acid in 50% ether/pentane to give **4i** (0.019 g, 54% yield) as a colourless needle like crystals. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -95.11 (d, *J* = 1034.9 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ 72.04 (d, *J* = 1032.1 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.04-1.24 (m, 22H). Spectral data were consistent with literature values.[1]

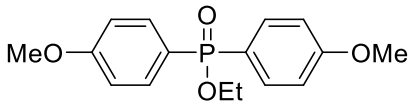


Diethyl phosphorofluoridate (6): Diethyl phosphite (19 µL, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **A**. The crude reaction mixture was purified via column chromatography

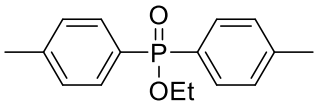
(ether) by rendering the stationary phase acidic with 1% acetic acid in 50% ether/pentane to give **6** (7.8 mg, 34% yield) as a colourless oil. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.24 (d, *J* = 975.7 Hz); **^{31}P NMR** (121 MHz, $CDCl_3$) δ -8.06 (d, *J* = 975.3 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.25 (q, *J* = 6.0 Hz, 4H), 1.38 (t, *J* = 6.0 Hz, 6H). Spectral data were consistent with literature values.[3,4]

4. General Procedure B: Synthesis of Phosphinates

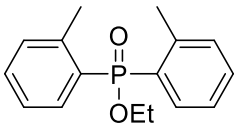
Into a round bottom flask was added (dichloroiodo)benzene (**2**, 0.15 mmol, 1.02 equiv), DCM (0.25 mL, 0.6M), and to this was added excess ethanol (0.1 mL, 10 equiv), followed by the secondary phosphine oxide (0.15 mmol, 1.0 equiv,). The reaction mixture was stirred at room temperature for the indicated length of time, then concentrated *in vacuo* and purified by column chromatography.



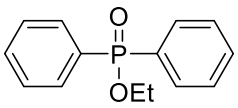
Ethyl bis(4-methoxyphenyl)phosphinate (7a): Bis(4-methoxyphenyl)phosphine oxide (0.039 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **B** for 30 minutes. The crude reaction mixture was purified via column chromatography (EtOAc) to give **7a** (0.040 g, 87% yield) as a colourless oil. **^{31}P NMR** (121 MHz, $CDCl_3$) δ 33.20; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.73-7.67 (m, 4H), 6.93-6.91 (m, 4H), 4.04 (*app.*quint, *J* = 6.0 Hz, 2H), 3.80 (s, 6H), 1.32 (t, *J* = 6.0 Hz, 3H). Spectral data were consistent with literature values.[5]



Ethyl di-*p*-tolylphosphinate (7b): Di-*p*-tolylphosphine oxide (0.035 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **B** for 30 minutes. The crude reaction mixture was purified via column chromatography (50% EtOAc/hexanes) to give **7b** (0.034 g, 83% yield) as a colourless oil. **^{31}P NMR** (121 MHz, $CDCl_3$) δ 33.22; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70-7.64 (m, 4H), 7.24-7.21 (m, 4H), 4.05 (*app.* quint, J = 6.0 Hz, 2H), 2.35 (s, 6H), 1.33 (t, J = 6.0 Hz, 3H). Spectral data were consistent with literature values.[5]

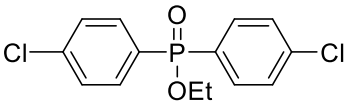


Ethyl di-*o*-tolylphosphinate (7c): Di-*o*-tolylphosphine oxide (0.035 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **B** for 1 hour. The crude reaction mixture was purified via column chromatography (50% EtOAc/hexanes) to give **7c** (0.028 g, 68% yield) as a colourless oil. **^{31}P NMR** (121 MHz, $CDCl_3$) δ 33.27; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.92-7.86 (m, 2H), 7.39 (t, J = 6.0 Hz, 2H) 7.29-7.25 (m, 2H), 7.19-7.15 (m, 2H), 4.13-4.04 (m, 2H), 2.35 (s, 6H), 1.37(t, J = 6.0 Hz, 3H). Spectral data were consistent with literature values.[6]

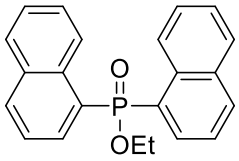


Ethyl diphenylphosphinate (7d): Diphenylphosphine oxide (0.031 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **B** for 30 minutes. The crude reaction mixture was purified via

column chromatography (80% EtOAc/hexanes) to give **7d** (0.030 g, 79% yield) as a colourless oil. **^{31}P NMR** (121 MHz, $CDCl_3$) δ 32.38; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.83-7.77 (m, 4H), 7.52-7.39 (m, 6H), 4.09 (*app.* quint, *J* = 6.0 Hz, 2H), 1.35 (t, *J* = 6.0 Hz, 3H). Spectral data were consistent with literature values.[2]

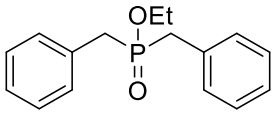


Ethyl bis(4-chlorophenyl)phosphinate (7e): Bis(4-chlorophenyl)phosphine oxide (0.040 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **B** for 30 minutes. The crude reaction mixture was purified via column chromatography (50% EtOAc/hexanes) to give **7e** (0.040 g, 85% yield) as a colourless oil. **^{31}P NMR** (121 MHz, $CDCl_3$) δ 30.52; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75-7.68 (m, 4H), 7.44-7.41 (m, 4H), 4.09 (*app.* quint, *J* = 6.0 Hz, 2H), 1.36 (t, *J* = 6.0 Hz, 3H). Spectral data were consistent with literature values.[2]

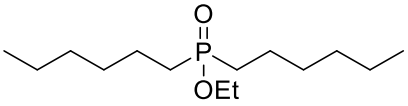


Ethyl di(naphthalen-1-yl)phosphinate (7f): Di(naphthalen-1-yl)phosphine oxide (0.046 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **B** for 2.5 hours. The crude reaction mixture was purified via column chromatography (50% EtOAc/hexanes) to give **7f** (0.047 g, 90% yield) as a colourless oil. **IR** (ATR) 3048, 2981, 1591, 1569, 1487, 1247, 1080, 788 cm^{-1}; **^{31}P NMR** (121 MHz, $CDCl_3$) δ 35.16; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.62-8.60 (m, 2H), 8.15 (dd, *J* = 15 Hz, *J* = 6.0 Hz, 2H), 8.01 (d, *J* = 9.0 Hz, 2H), 7.87-7.84 (m, 2H), 7.52-7.47 (m, 6H), 4.25-4.16 (m, 2H), 1.38 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 134.1 (d, *J* = 10.5 Hz), 133.7 (d, *J* = 10.5

Hz), 133.5 (d, *J* = 7.5 Hz), 133.0 (d, *J* = 9.8 Hz), 128.9, 128.9, 127.1, 126.9 (d, *J* = 78.8 Hz), 126.6 (d, *J* = 5.3 Hz), 124.7 (d, *J* = 14.3 Hz), 61.4 (d, *J* = 6.0 Hz), 16.5 (d, *J* = 6.8 Hz); **LRMS** (ESI) calcd for $C_{22}H_{19}O_2P$ $(M+H)^+$ 347.11; found 347.25.

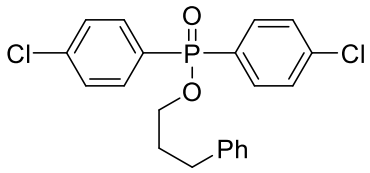


Ethyl dibenzylphosphinate (7g): Dibenzylphosphine oxide (0.034 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **B** for 1 hour. The crude reaction mixture was purified via column chromatography (80% EtOAc/hexanes) to give **7g** (0.024 g, 59% yield) as a colourless oil. **IR** (ATR) 3048, 3013, 2904, 1602, 1560, 1465, 1351, 1112, 1083, 881 cm^{-1}; **^{31}P NMR** (121 MHz, $CDCl_3$) δ 48.84; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30-7.22 (m, 10H), 3.87 (*app.* quint, *J* = 6.0 Hz, 2H), 3.07 (d, *J* = 15 Hz, 4H), 1.14 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 131.5 (d, *J* = 7.5 Hz), 129.9 (d, *J* = 6.0 Hz), 128.6 (d, *J* = 3.0 Hz), 126.9 (d, *J* = 3.0 Hz), 61.1 (d, *J* = 6.8 Hz), 36.1 (d, *J* = 86.3 Hz), 16.5 (d, *J* = 6.0 Hz); **LRMS** (ESI) calcd for $C_{16}H_{19}O_2P$ $(M+H)^+$ 275.11;found 275.17.



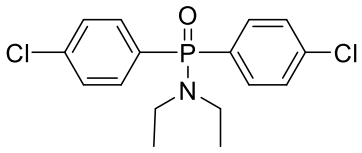
Ethyl dihexylphosphinate (7h): Dihexyllphosphine oxide (0.033 g, 0.15 mmol, 1.0 equiv) was subjected to General Procedure **B** for 3 hours. The crude reaction mixture was purified via column chromatography (2% MeOH/EtOAc) to give **7h** (19 mg, 48% yield) as a colourless oil. **IR** (ATR) 2884, 2859, 2064, 1720, 1426, 1331, 1126, 1038, 946 cm^{-1}; **^{31}P NMR** (121 MHz, $CDCl_3$) δ 59.32**;** **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.02 (*app.* quint, *J* = 6.0 Hz, 2H), 1.72-1.62 (m, 4H), 1.57-1.47 (m,

4H), 1.37-1.26 (m, 15H), 0.86 (t, J = 6.0 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 59.9 (d, J = 6.8 Hz), 31.2, 30.5 (d, J = 15.0 Hz), 28.1 (d, J = 88.5 Hz), 22.3, 21.7 (d, J = 3.8 Hz), 16.6 (d, J = 6.0 Hz), 13.9; **LRMS** (ESI) calcd for $C_{14}H_{31}O_2P$ $(M+H)^+$ 264.21;found 264.25.



3-Phenylpropyl bis(4-chlorophenyl)phosphinate (8a): Bis(4-chlorophenyl)phosphine oxide (0.041 g, 0.15mmol, 1.0 equiv) was subjected to General Procedure **B** for 1 hour using 3-phenylpropanol instead of ethanol. The crude reaction mixture was purified via column chromatography (50% EtOAc/hexanes) to give **8a** (0.042 g, 69% yield) as a colourless oil. **IR** (ATR) 3051, 2997, 1691, 1462, 1104, 1018, 806, 761, 622 cm^{-1}, **^{31}P NMR** (121 MHz, $CDCl_3$) δ 30.03; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72-7.66 (m, 4H), 7.44-7.40 (m, 4H), 7.29-7.24 (m, 2H), 7.20-7.13 (m, 3H), 4.01 (q, J = 6.0 Hz, 2H), 2.73 (t, J = 6.0 Hz, 2H), 2.09-2.00 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.6, 139.0 (d, J = 3.0 Hz), 133.1, 132.9, 129.7 (d, J = 139.5 Hz), 129.1 (d, J = 13.5 Hz), 128.5, (d, J = 6.8 Hz), 126.1, 64.6 (d, J = 6.0 Hz), 32.0 (d, J = 6.8 Hz), 31.9; **LRMS** (ESI) calcd for $C_{21}H_{19}Cl_2O_2P$ (M^+) 405.05; found 405.17 and 407.08.

5. Synthesis of *P,P*-bis(4-chlorophenyl)-*N,N*-diethylphosphinic amide (8c)



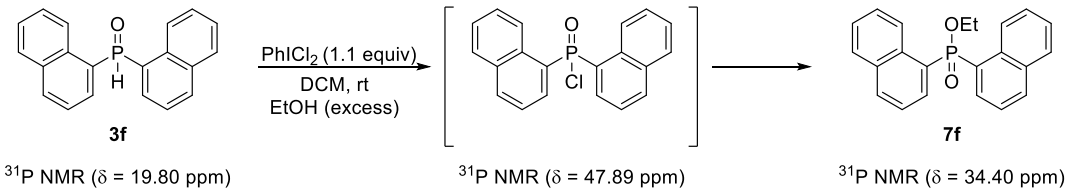
Into a round bottom flask was added (dichloroiodo(benzene (**2**, 0.043 g, 0.15 mmol, 1.02 equiv), DCM (0.25 mL, 0.6M), and to this was added secondary phosphine oxide **3e** (0.041 g, 0.15 mmol,

1.0 equiv). The reaction mixture was stirred at room temperature for 5 minutes and diethyl amine (0.15 mL, 1.5 mmol, 10 equiv) was added to this over two minutes and the resulting mixture stirred at room temperature for 1 hour. The crude reaction mixture was purified via column chromatography (EtOAc) to give **8c** (0.021 g, 41% yield) as a colourless oil. **IR** (ATR) 3012, 2976, 1583, 1481, 1019, 1013, 975, 732, 603 cm^{-1}; **^{31}P NMR** (121 MHz, $CDCl_3$) δ 29.81; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.81-7.77 (m, 4H), 7.46-7.44 (m, 4H), 3.10-3.03 (m, 4H), 1.12 (t, *J* = 6.0 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.4 (d, *J* = 3.8 Hz), 133.7 (d, *J* = 9.8 Hz), 130.7 (d, *J* = 130.5 Hz), 128.9 (d, *J* = 12.8 Hz), 39.3 (d, *J* = 3.8 Hz), 14.1 (d, *J* = 4.5 Hz); **LRMS** (ESI) calcd for $C_{16}H_{18}Cl_2NOP$ (M^+) 342.05; found 342.17 and 344.17.

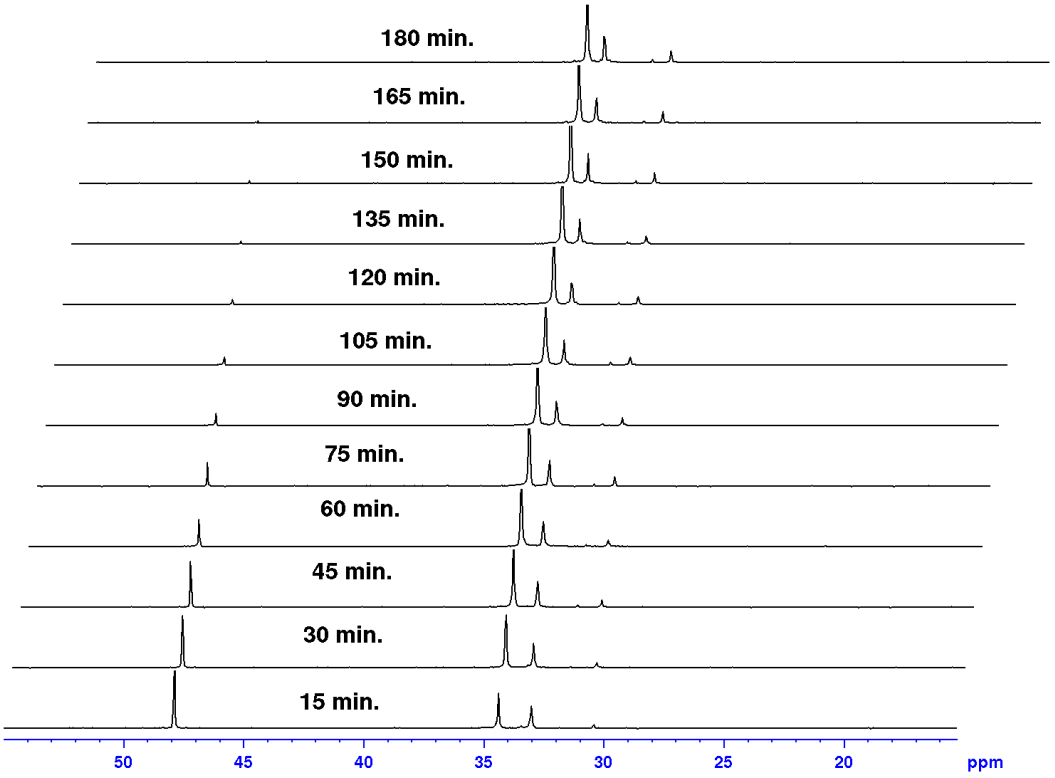
6. ^{31}P NMR experiment for the synthesis of ethyl di(naphthalen-1-yl)phosphinate **7f** via the phosphinic chloride

An experiment was conducted using ^{31}P NMR spectroscopy to monitor the conversion of secondary phosphine oxide **3f** to phosphinate **7f**. via the formation of the intermediate phosphinic chloride using triphenylphosphine oxide (^{31}P NMR, δ = 33.04 ppm) as internal standard. 1.0 equiv of **3f** was added to a round bottom flask containing 1.1 equiv of $PhICl_2$ and excess ethanol in DCM. The reaction mixture was stirred for 10 minutes at room temperature, transferred to an NMR tube and the ^{31}P NMR spectrum was then acquired at 15 minute intervals until the reaction was complete.

- Complete consumption of the starting material (**3f**) had occurred within 15 minutes, as none was observed in the initial NMR spectrum.
- The resulting phosphinic chloride was gradually consumed over the course of 150 minutes, being converted to phosphinate product **7f**.
- None of the acid was observed in the NMR spectra



Internal Standard Ph_3PO (^{31}P NMR, δ = 33.04 ppm)



7. References:

1. Liu, N.; Mao, L.; Yang, S. *Chem. Commun.* **2014**, *50*, 10879–10882.

2. Chen, Q.; Zeng, J.; Yan, X.; Huang, Y.; Wen, C.; Liu, X.; Zhang, K. *J. Org. Chem.* **2016**, *81* (20), 10043–10048.

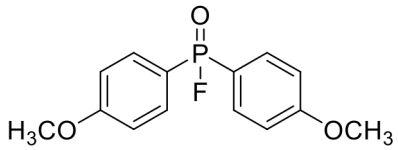
3. Chworos, A.; Wozniak, L. A. *Tetrahedron Lett.* **1999**, *40*, 9337–9340.

4. Sierakowski, T.; Kiddle, J. J. *Tetrahedron Lett.* **2005**, *46*, 2215–2217

5. Qi, N.; Zhang, N.; Allu, S. R.; Gao, J.; Guo, J.; He, Y. *Org. Lett.* **2016**, *18* (23), 6204–6207.

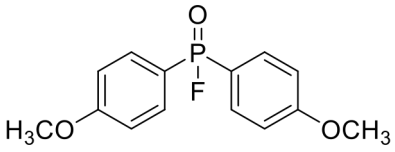
6. Park, S.; Seo, B.; Shin, S.; Son, J.-Y.; Lee, P. H. *Chem. Commun.* **2013**, *49* (77), 8671.

8. ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR Spectra of Compounds:



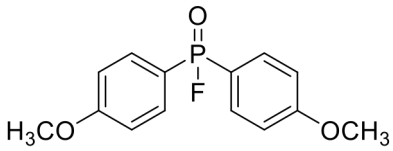
4a

^{19}F NMR (282 MHz, $CDCl_3$)



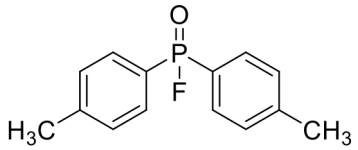
4a

^{31}P NMR (121 MHz, $CDCl_3$)



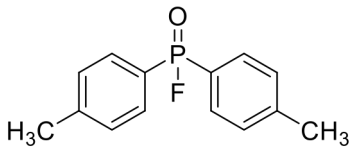
4a

^{1}H NMR (300 MHz, $CDCl_3$)



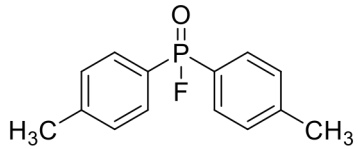
4b

^{19}F NMR (282 MHz, $CDCl_3$)



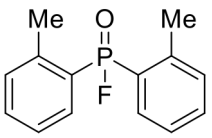
4b

^{31}P NMR (121 MHz, $CDCl_3$)



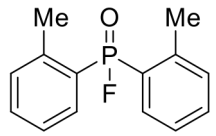
4b

^{1}H NMR (300 MHz, $CDCl_3$)



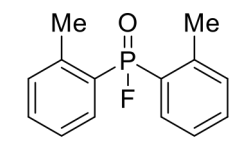
4c

^{19}F NMR (282 MHz, $CDCl_3$)



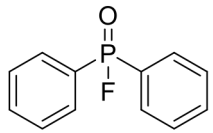
4c

^{31}P NMR (121 MHz, $CDCl_3$)



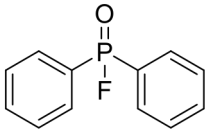
4c

^{1}H NMR (300 MHz, $CDCl_3$)



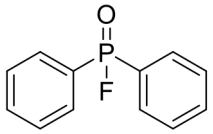
4d

^{19}F NMR (282 MHz, $CDCl_3$)



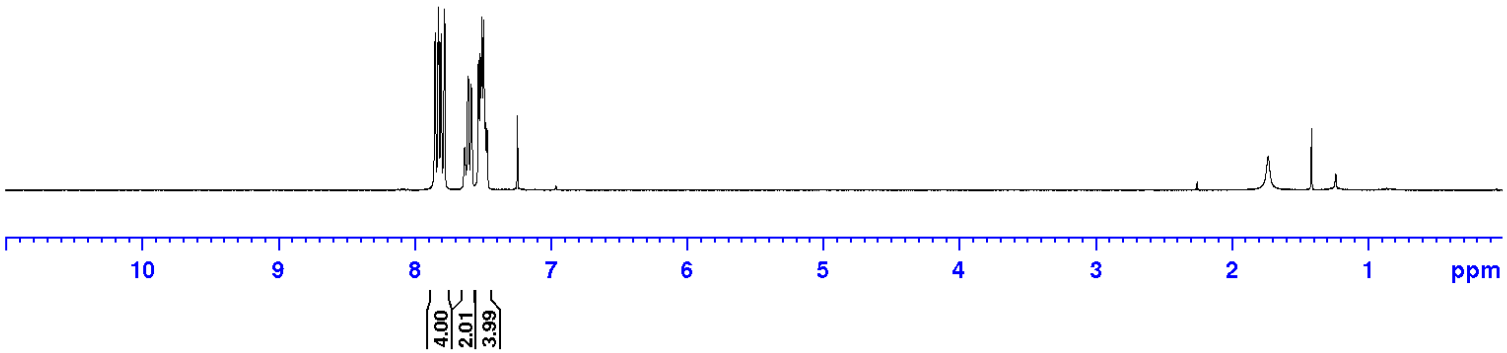
4d

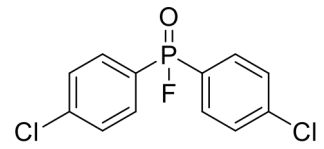
^{31}P NMR (121 MHz, $CDCl_3$)



4d

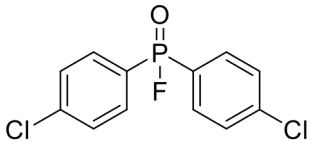
^{1}H NMR (300 MHz, $CDCl_3$)





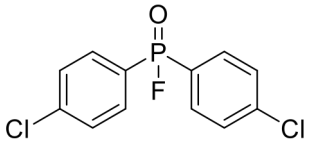
4e

^{19}F NMR (282 MHz, $CDCl_3$)



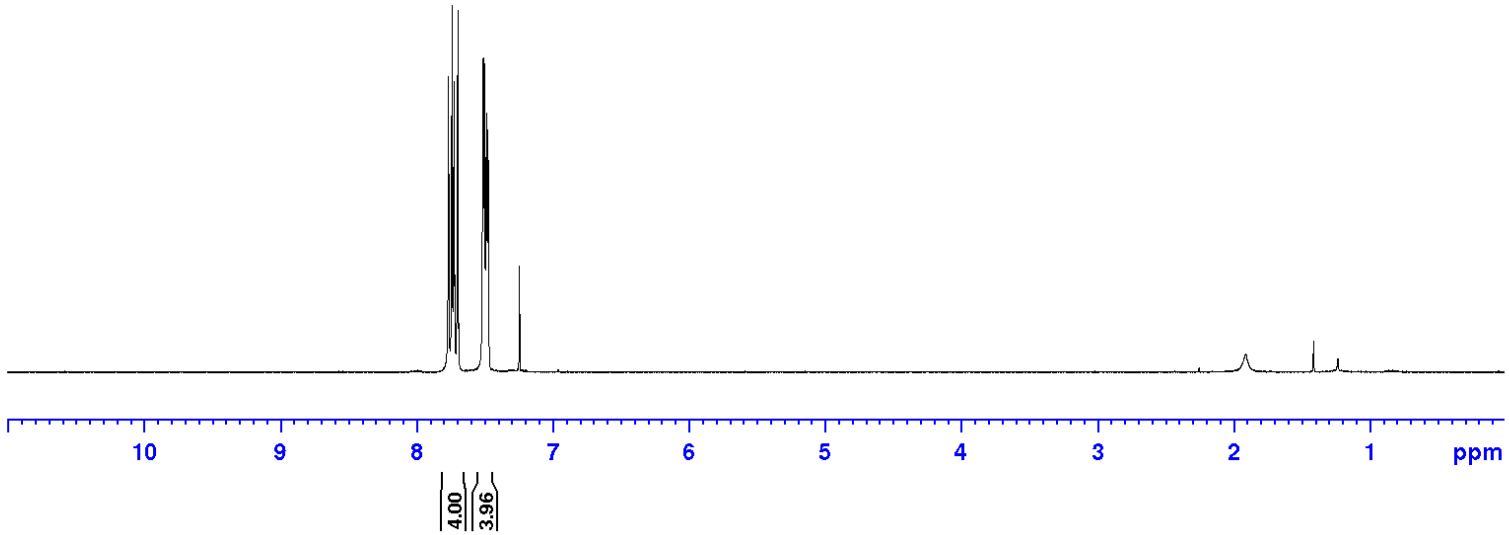
4e

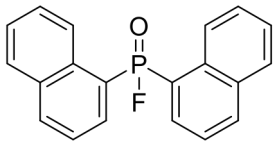
^{31}P NMR (121 MHz, $CDCl_3$)



4e

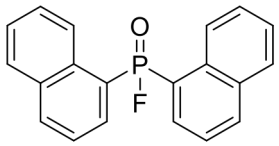
^{1}H NMR (300 MHz, $CDCl_3$)





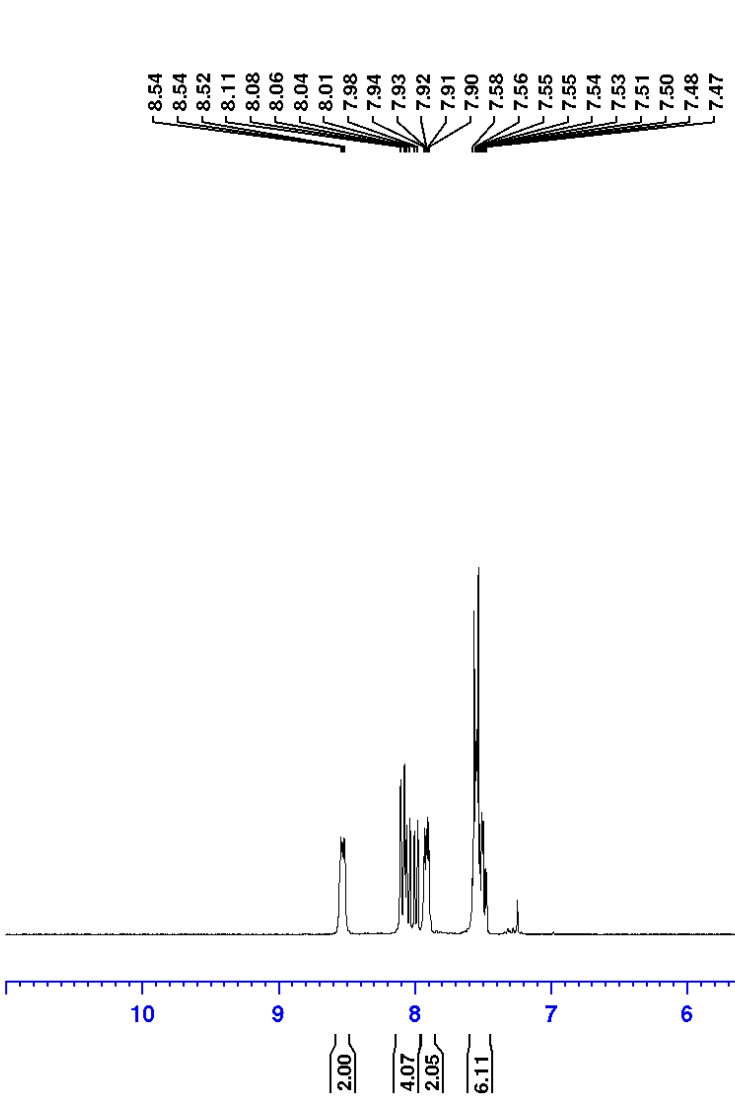
4f

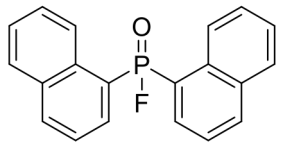
^{19}F NMR (282 MHz, $CDCl_3$)



4f

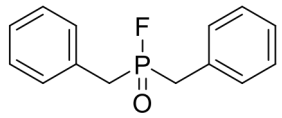
^{31}P NMR (121 MHz, $CDCl_3$)





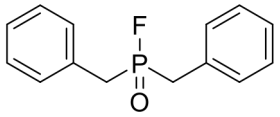
4f

^{1}H NMR (300 MHz, $CDCl_3$)



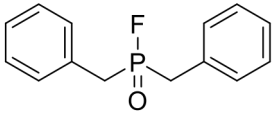
4g

^{19}F NMR (282 MHz, $CDCl_3$)



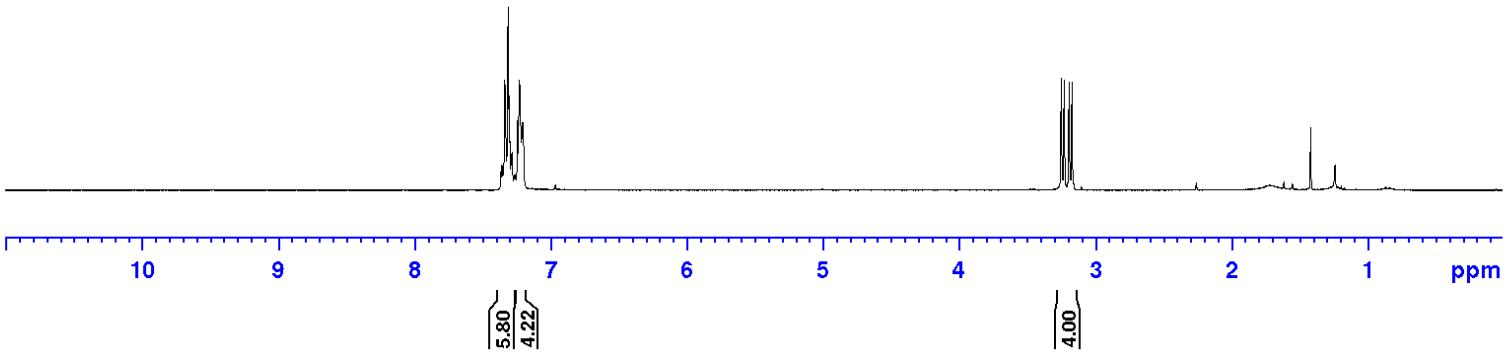
4g

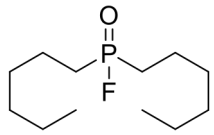
^{31}P NMR (121 MHz, $CDCl_3$)



4g

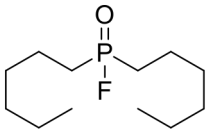
^{1}H NMR (300 MHz, $CDCl_3$)





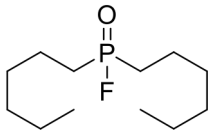
4h

^{19}F NMR (282 MHz, $CDCl_3$)



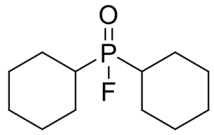
4h

^{31}P NMR (121 MHz, $CDCl_3$)



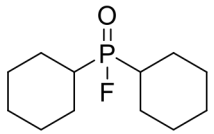
4h

^{1}H NMR (300 MHz, $CDCl_3$)



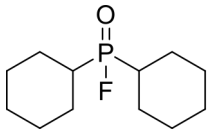
4i

^{19}F NMR (282 MHz, $CDCl_3$)



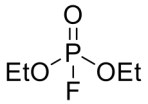
4i

^{31}P NMR (121 MHz, $CDCl_3$)



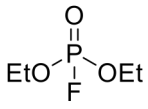
4i

^{1}H NMR (300 MHz, $CDCl_3$)



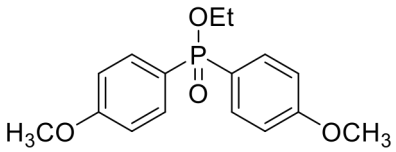
6

^{19}F NMR (282 MHz, $CDCl_3$)



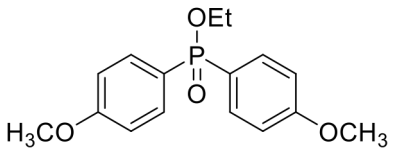
6

^{31}P NMR (121 MHz, $CDCl_3$)



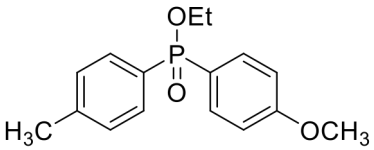
7a

^{31}P NMR (121 MHz, $CDCl_3$)



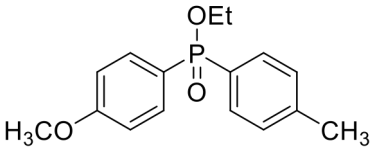
7a

^{1}H NMR (300 MHz, $CDCl_3$)



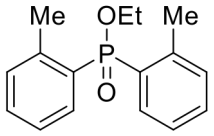
7b

^{31}P NMR (121 MHz, $CDCl_3$)



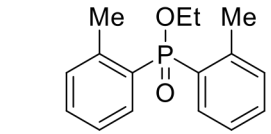
7b

^{1}H NMR (300 MHz, $CDCl_3$)



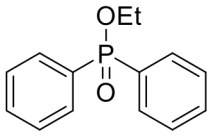
7c

^{31}P NMR (121 MHz, $CDCl_3$)



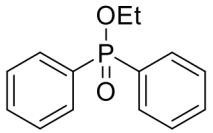
7c

^{1}H NMR (300 MHz, $CDCl_3$)



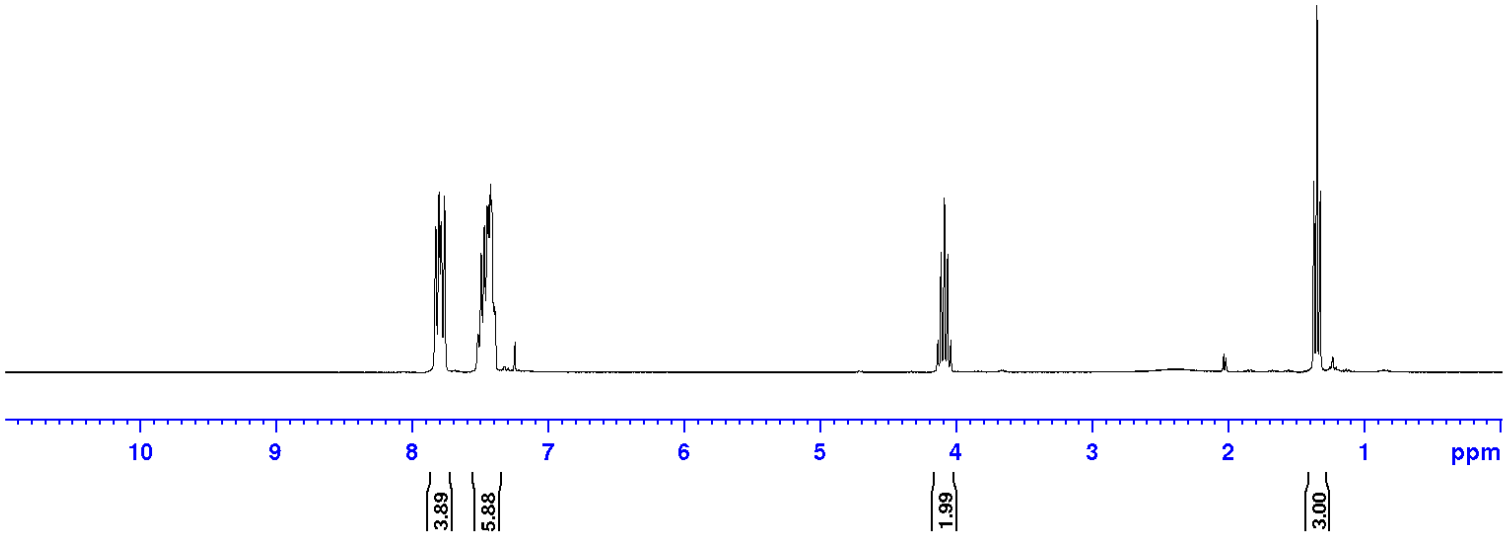
7d

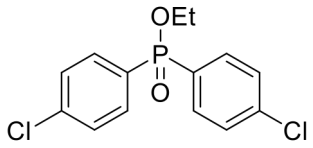
^{31}P NMR (121 MHz, $CDCl_3$)



7d

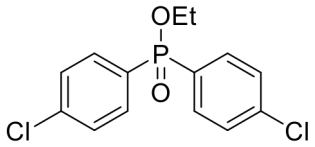
^{1}H NMR (300 MHz, $CDCl_3$)





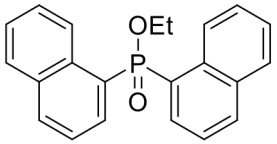
7e

^{31}P NMR (121 MHz, $CDCl_3$)



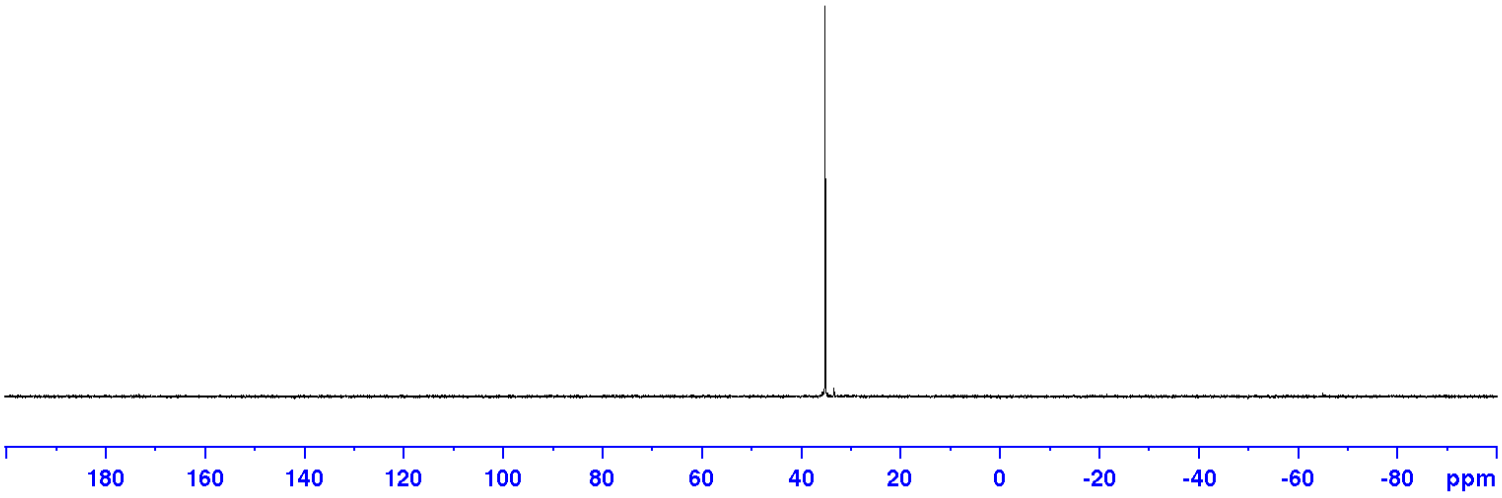
7e

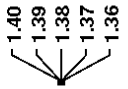
^{1}H NMR (300 MHz, $CDCl_3$)

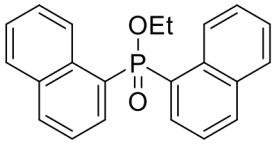


7f

^{31}P NMR (121 MHz, $CDCl_3$)

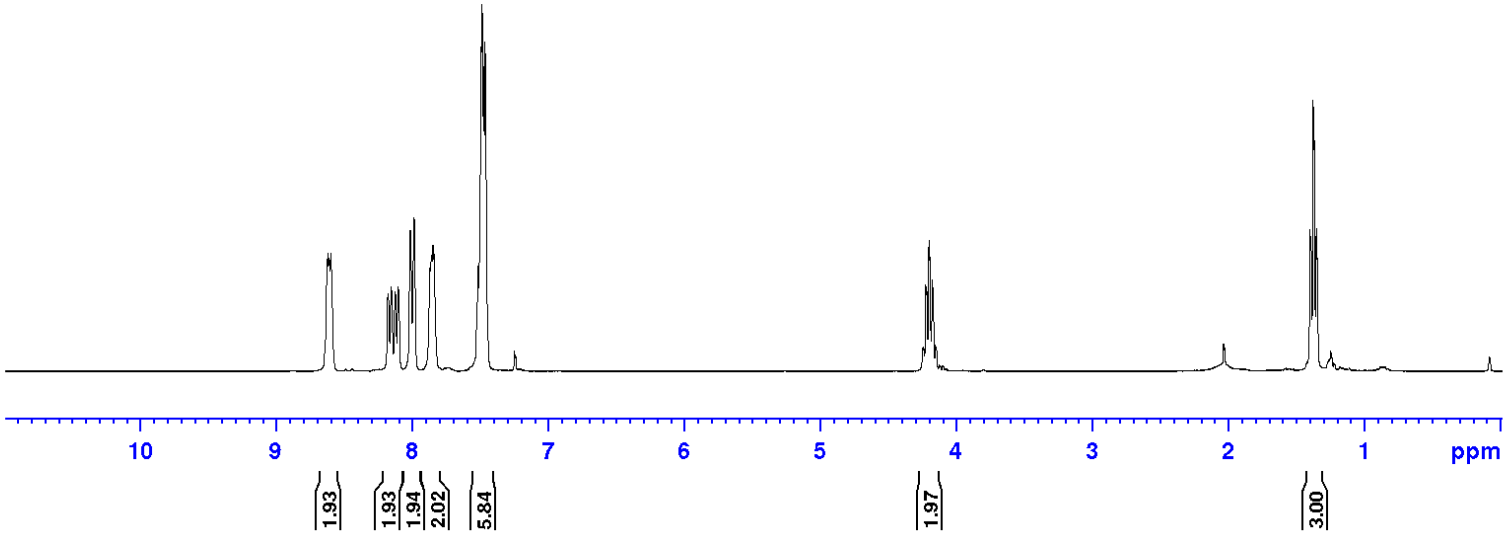


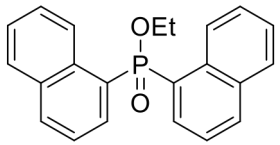




7f

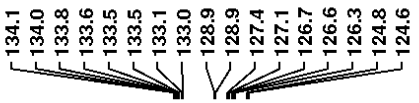
^{1}H NMR (300 MHz, $CDCl_3$)

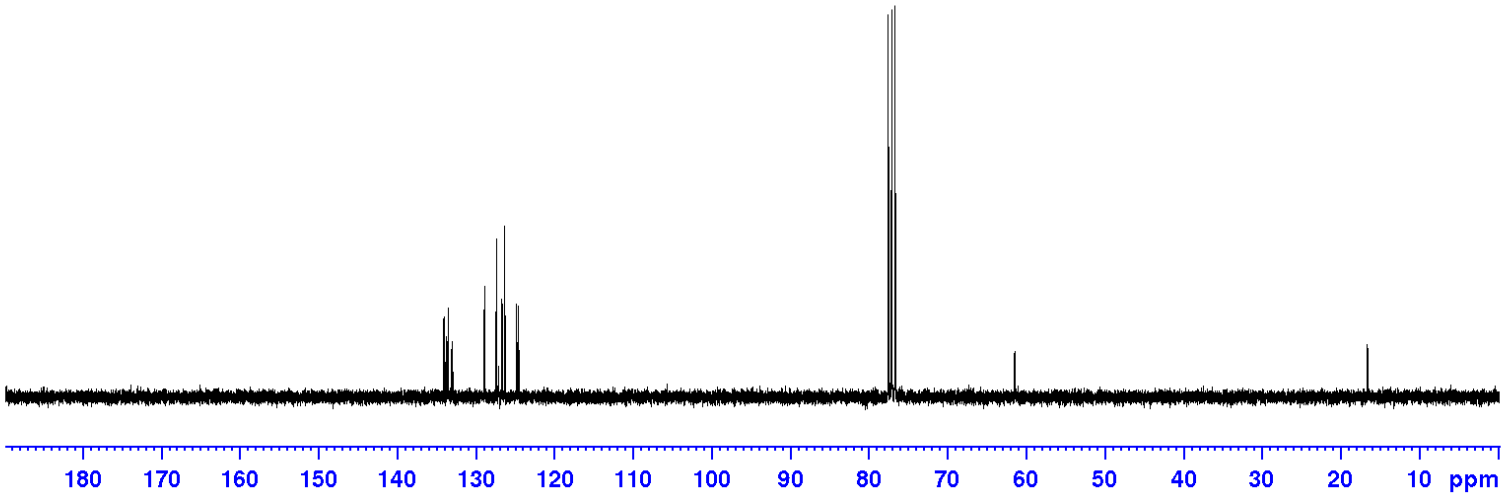


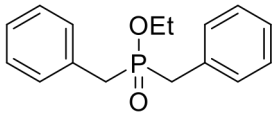


7f

^{13}C NMR (75 MHz, $CDCl_3$)

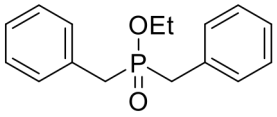






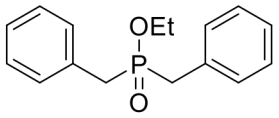
7g

^{31}P NMR (121 MHz, $CDCl_3$)



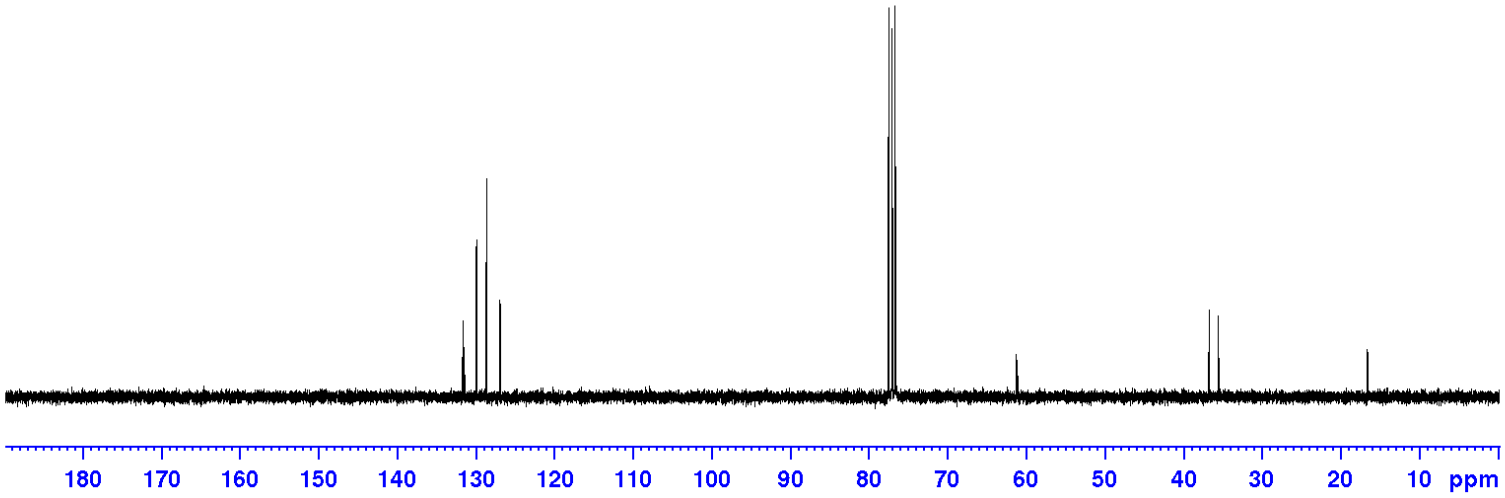
7g

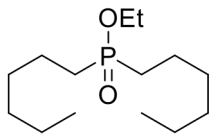
^{1}H NMR (300 MHz, $CDCl_3$)



7g

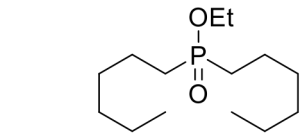
^{13}C NMR (75 MHz, $CDCl_3$)





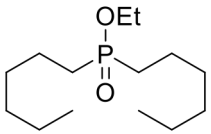
7h

^{31}P NMR (121 MHz, $CDCl_3$)



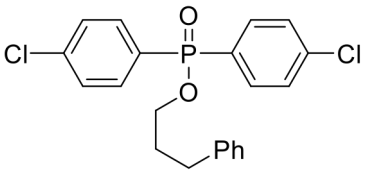
7h

^{1}H NMR (300 MHz, $CDCl_3$)



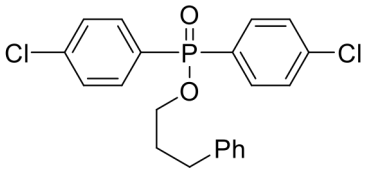
7h

^{13}C NMR (75 MHz, $CDCl_3$)



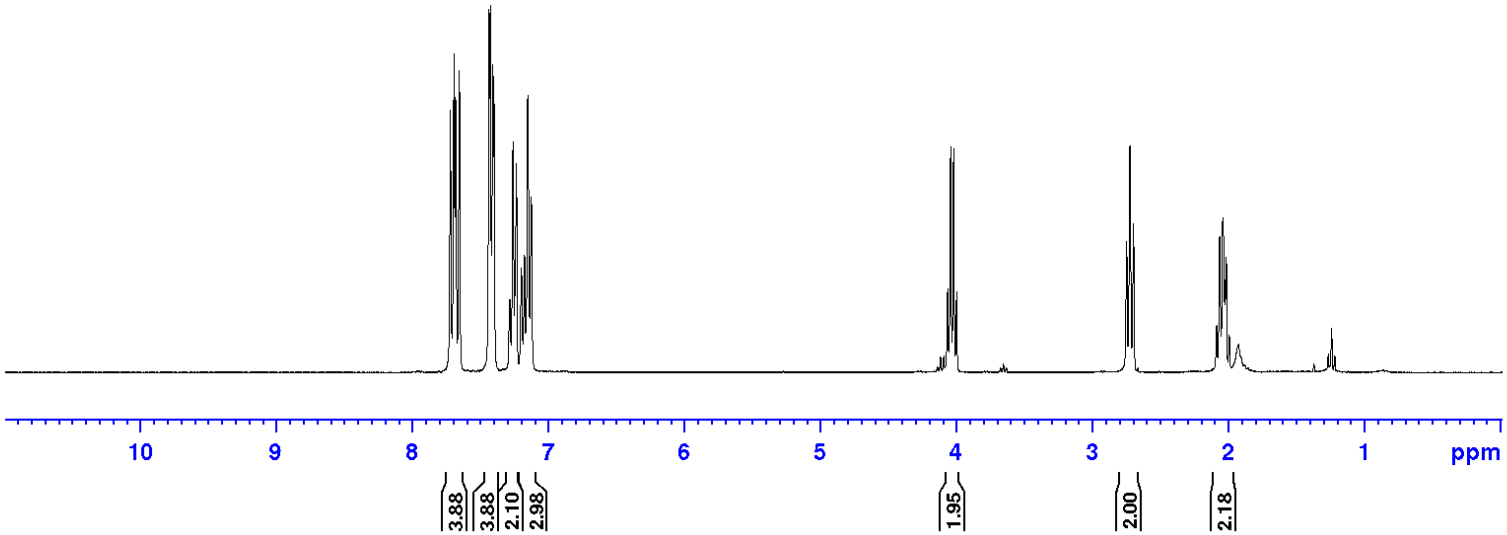
8a

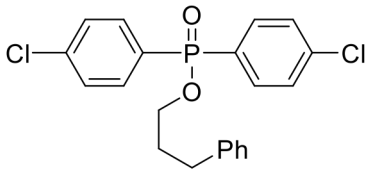
^{31}P NMR (121 MHz, $CDCl_3$)



8a

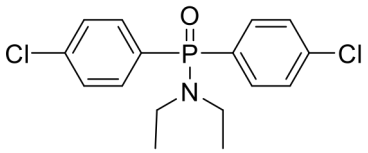
^{1}H NMR (300 MHz, $CDCl_3$)





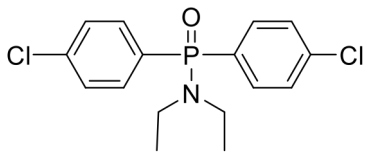
8a

^{13}C NMR (75 MHz, $CDCl_3$)



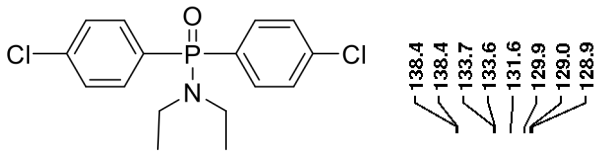
8c

^{31}P NMR (121 MHz, $CDCl_3$)



8c

^{1}H NMR (300 MHz, $CDCl_3$)



8c

^{13}C NMR (75 MHz, $CDCl_3$)