Harnessing Solvent-$^3O_2$ Charge Transfer Complex for Photochemical Conversion of Phosphines to Phosphine Oxides: The Synergy of Light and Ambient Air

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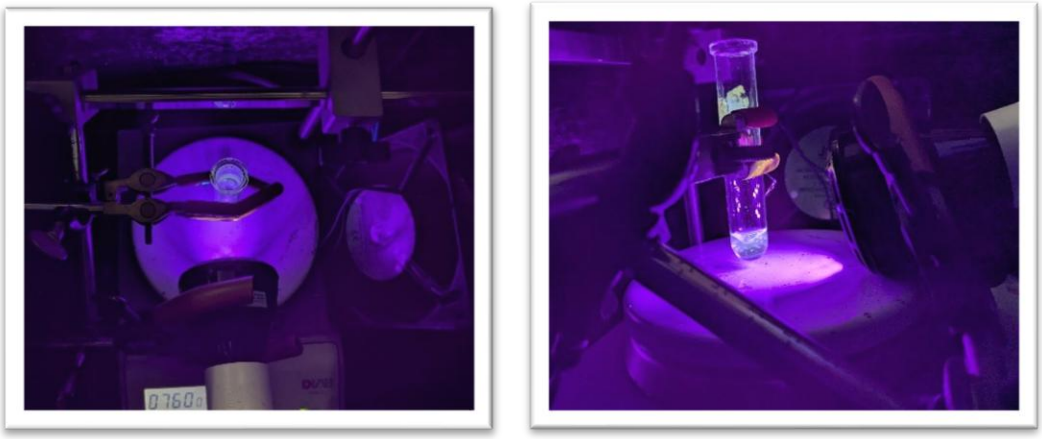
I. General Information

All chemicals were purchased either from Sigma Aldrich, TCI chemicals, Avra-chemicals, or BLD-Pharma and used without further purification unless mentioned. Reagent-grade solvents were purchased from Finar Chemicals (India) and used as it is. $CDCl_3$ and CD_2Cl_2 was purchased from either Cambridge Isotope Laboratories or Sigma Aldrich. All NMR spectra ^{1}H (400 MHz / 500 MHz), $^{13}C\{^{1}H\}$ (100 MHz / 125MHz), $^{31}P\{^{1}H\}$ (162 MHz / 202 MHz), ^{19}F (376 MHz / 470 MHz) were recorded by a Bruker Avance 400 MHz NMR/ 500 MHz spectrometer at an ambient temperature. ^{1}H NMR chemical shifts are reported relative to TMS and are referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm), whereas ^{13}C NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm, C_6D_6: 128.06 ppm). ^{31}P NMR, and ^{19}F NMR signals are quoted relative to H_3PO_4 and $CFCl_3$ respectively.

Waters Xevo G3-Q-TOF (LC-HRMS) was used. Jeol JES-X320 was used EPR measurements. For Gas chromatograph (GC) mass spectral analysis, Shimadzu GCMS-QP2010 SE was used. UV-Visible data was collected using Shimadzu UV-2600 instrument. Commercially available, pre-coated TLC-sheets ALUGRAM® Xtra Sil G/UV_{254} were purchased from MACHEREY-NAGEL GmbH & Co. KG. Column chromatography was performed using silica gel (100-200 mesh).

II. Procedure for the Photo-oxidation of Phosphines



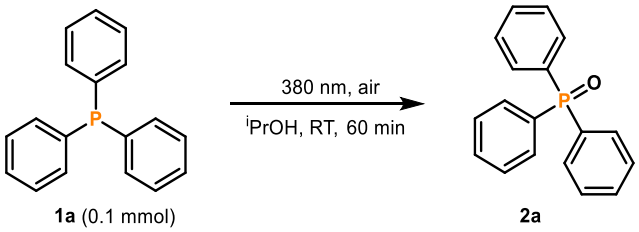
Top view Side view

Reaction Set Up

- Light-source detail (https://hepatochem.com/product/hck1012-01-013/): EvoluChem LED 380PF, Dominant wavelength of light source: λ_{max} = 380 nm (purple LED), LED input power: 18 Watt (max), Voltage: 110V-220V, Irradiance: 211 mW/cm^2.
- Material of the irradiation vessel: Borosilicate glass.
- No filter was used.
- Fan was used to maintain room temperature.

III. Optimization of the Reaction Conditions

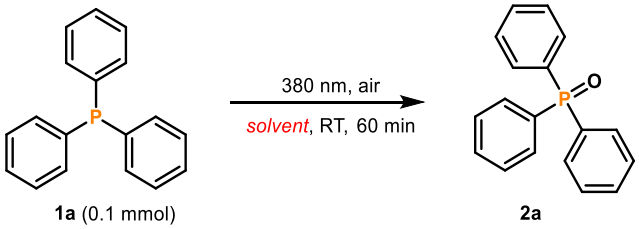
Scheme S1. Experimental procedure for the optimization of photo-oxidation of triphenylphosphine



1a (0.1 mmol) **2a**

To a flame-dried glass vial equipped with a magnetic stirring bar, triphenylphosphine (26.3 mg, 0.1 mmol), and 1.0 mL of isopropyl alcohol (^{i}PrOH) were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under open atmosphere for 60 minutes. The conversion of the crude product was calculated by ^{31}P-NMR.

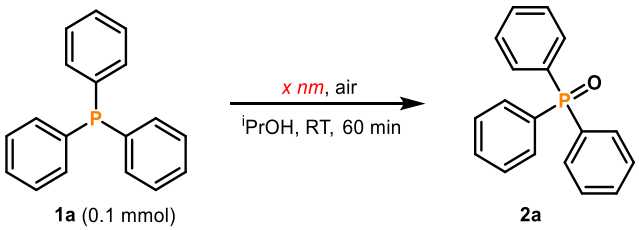
Table S1. Screening of solvents



Entry	Solvent	Conversion (%)
1	^{i}PrOH	100
2	EtOH	100
3	H_2O	trace
4	Acetone	100
5	MeCN	100
6	Ethyl acetate	31
7	2-Me THF	38
8	DMSO	93

Reaction conditions: Compound **1a** (0.1 mmol) in solvent (1.0 ml) under open atmosphere, rt, 60 min, 380 nm 18W EvoluChem LED. Conversions were determined by ^{31}P nuclear magnetic resonance (NMR) analysis of the crude reaction mixture.

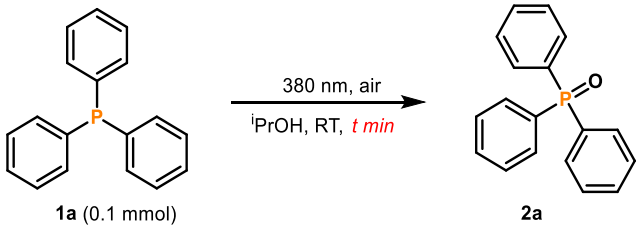
Table S2. Screening of light source



Entry	Light source (nm)	Conversion (%)
1	380 (18 W)	100
2	390 (40 W)	98
3	427 (40 W)	37
4	456 (40 W)	17
5	without light	0

Reaction conditions: Compound **1a** (0.1 mmol) in ^{i}PrOH (1.0 ml) under open atmosphere, rt, 60 min, x nm LED. Conversions were determined by ^{31}P nuclear magnetic resonance (NMR) analysis of the crude reaction mixture.

Table S3. Screening of time



Entry	Time (min)	Conversion (%)
1	60	100
2	40	100
3	30	94

Reaction conditions: Compound **1a** (0.1 mmol) in ^{i}PrOH (1.0 ml) under open atmosphere, rt, t min, 380 nm 18W EvoluChem LED. Conversions were determined by ^{31}P nuclear magnetic resonance (NMR) analysis of the crude reaction mixture.

IV. Substrate Scope and Characterization

General procedure A: Photo-oxidation of phosphines

To a flame-dried glass vial equipped with a magnetic stirring bar, phosphines (0.1 mmol), and 1.0 mL of isopropyl alcohol (^{i}PrOH) or, acetone were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under open atmosphere for 40 minutes. The conversion of the crude product was calculated by ^{31}P-NMR.

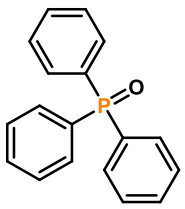
Method A. The crude reaction mixture was evaporated in vacuo to yield the pure product.

Method B. The residue was subjected to silica gel column chromatography to yield the pure product.

General procedure B: Photo-oxidation of phosphines (Scale-up reaction)

To a flame-dried glass vial equipped with a magnetic stirring bar, triphenylphosphine (**1a**) (1g, 3.8 mmol), and 15 mL of isopropyl alcohol (^{i}PrOH) were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under open atmosphere for 90 minutes. The conversion of the crude product was calculated by ^{31}P-NMR. The residue was purified *via* **Method A**.

Synthesis of Triphenylphosphine oxide (2a)



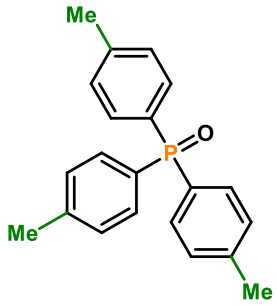
Following **Method A** for isolation, the pure product was obtained as a white solid (27.6 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.68-7.64 (m, 6H), 7.55-7.52 (m, 3H), 7.47-7.43 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 132.5 (d, J = 104.0 Hz), 132.2 (d, J = 9.9 Hz), 132.1 (d, J = 2.7 Hz), 128.6 (d, J = 12.4 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 29.3.

Synthesis of tri-p-tolylphosphine oxide (2b)



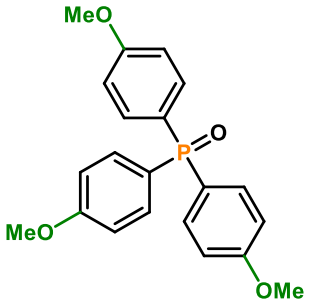
Following **Method A** for isolation, the pure product was obtained as a white solid (31.7 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.52 (dd, J = 11.4 Hz, 7.7 Hz, 6H), 7.23 (d, J = 7.8 Hz, 6H), 2.37 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 142.4 (d, J = 2.7 Hz), 132.2 (d, J = 10.3 Hz), 129.5 (d, J = 106.5 Hz), 129.2 (d, J = 12.6 Hz), 21.7.

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 29.9.

Synthesis of tris(4-methoxyphenyl)phosphine oxide (2c)



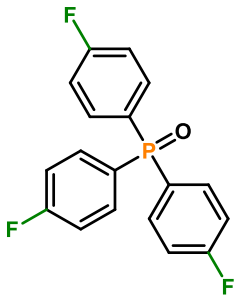
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (33.5 mg, 91 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.56-7.51 (m, 6H), 6.93-6.91 (m, 6H), 3.80 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 162.4 (d, J = 2.7 Hz), 133.9 (d, J = 11.3 Hz), 124.2 (d, J = 111.2 Hz), 114.1 (d, J = 13.2 Hz), 55.4.

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 29.6.

Synthesis of tris(4-fluorophenyl)phosphine oxide (2d)



Following **Method A** for isolation, the pure product was obtained as a white solid (32.9 mg, >99 % yield).

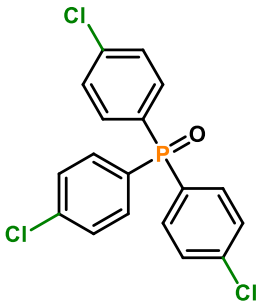
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.65-7.60 (m, 6H), 7.17-7.13 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 165.3 (dd, J = 254.4 Hz, 3.3 Hz), 134.6 (dd, J = 11.6 Hz, 9.0 Hz), 128.1 (dd, J = 108.6 Hz, 3.3 Hz), 116.2 (dd, J = 21.4 Hz, 13.4 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 27.1.

^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -105.9.

Synthesis of tris(4-chlorophenyl)phosphine oxide (2e)



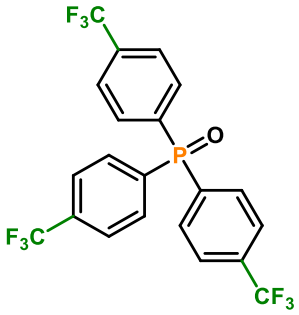
Following **Method A** for isolation, the pure product was obtained as a white solid (38.0 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.57-7.53 (m, 6H), 7.45-7.43 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 139.2 (d, J = 3.4 Hz), 133.4 (d, J = 10.9 Hz), 130.2 (d, J = 106.5 Hz), 129.2 (d, J = 12.9 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 27.1.

Synthesis of tris(4-(trifluoromethyl)phenyl)phosphine oxide (2f)



Following **Method A** for isolation, the pure product was obtained as a white solid (47.9 mg, >99 % yield).

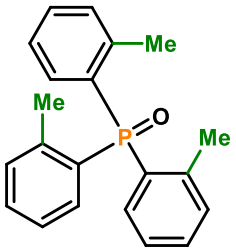
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84-7.77 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 135.4 (d, J = 103.3 Hz), 134.7 (dq, J = 33.2 Hz, 2.7 Hz), 132.6 (d, J = 10.2 Hz), 126.0 (qd, J = 11.3 Hz, 3.8 Hz), 123.4 (q, J = 273.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 25.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -63.3.

Synthesis of tri-o-tolylphosphine oxide (2g)



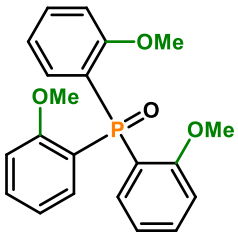
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (30.4 mg, 95 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.42 (t, J = 7.3 Hz, 3H), 7.32-7.30 (m, 3H), 7.16-7.07 (m, 6H), 2.49 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 143.6 (d, J = 7.8 Hz), 133.0 (d, J = 12.8 Hz), 132.1 (d, J = 10.5 Hz), 132.0 (d, J = 2.1 Hz), 130.6 (d, J = 101.5 Hz), 125.6 (d, J = 12.8 Hz), 22.1, 22.1.

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 37.4.

Synthesis of tris(2-methoxyphenyl)phosphine oxide (2h)



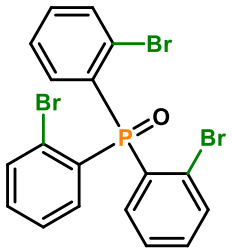
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (32.1 mg, 87 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.52-7.46 (m, 6H), 7.00-6.97 (m, 3H), 6.91 (dd, *J* = 8.2 Hz, 5.5 Hz, 3H), 3.58 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 161.7 (d, *J* = 2.4 Hz), 134.9 (d, *J* = 7.0 Hz), 134.7(d, *J* = 9.1 Hz), 133.8, 120.6 (d, *J* = 12.9 Hz), 111.5 (d, *J* = 6.6 Hz), 55.7.

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 26.7.

Synthesis of tris(2-bromophenyl)phosphine oxide (2i)



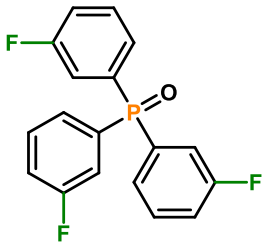
Following **Method A** for isolation, the pure product was obtained as a white solid (51.1 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.72-7.65 (m, 4H), 7.57-7.52 (m, 2H), 7.49-7.45 (m, 4H), 7.38-7.30 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 136.0 (d, *J* = 10.6 Hz), 134.9 (d, *J* = 7.4 Hz), 133.5 (d, *J* = 2.1 Hz), 133.0 (d, *J* = 105.1 Hz), 132.2 (d, *J* = 10.0 Hz), 132.1 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 108.0 Hz), 128.7 (d, *J* = 12.4 Hz), 128.6, 127.0 (d, *J* = 11.2 Hz), 127.0 .

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 30.7.

Synthesis of tris(3-fluorophenyl)phosphine oxide (2j)



Following **Method A** for isolation, the pure product was obtained as a white solid (33.0 mg, >99 % yield).

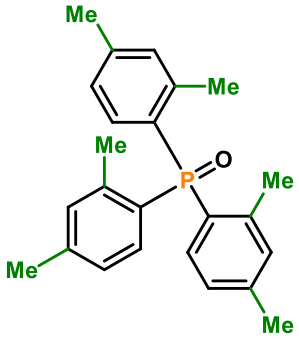
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.52-7.48 (m, 3H), 7.47-7.42 (m, 3H), 7.38-7.34 (m, 3H), 7.30-7.27 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 162.7 (dd, *J* = 251.4 Hz, 17.3 Hz), 134.1 (dd, *J* = 104.6 Hz, 5.5 Hz), 131.0 (dd, *J* = 14.2 Hz, 7.5 Hz), 127.8 (dd, *J* = 9.5 Hz, 3.2 Hz), 119.9 (dd, *J* = 21.3 Hz, 2.3 Hz), 119.0 (dd, *J* = 22.4 Hz, 10.9 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 26.2 (m).

^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -110.2 (d, *J* = 5.3 Hz).

Synthesis of tris(2,4-dimethylphenyl)phosphine oxide (2k)



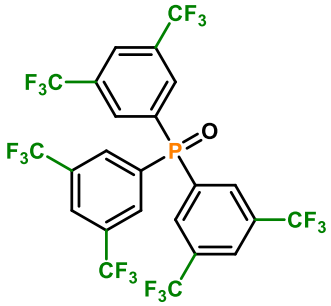
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (30.5 mg, 84 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.11 (d, *J* = 2.6 Hz, 3H), 6.99-6.93 (m, 6H), 2.43 (s, 9H), 2.35 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 143.4 (d, *J* = 8.1 Hz), 142.1 (d, *J* = 2.5 Hz), 133.2 (d, *J* = 13.3 Hz), 132.9 (d, *J* = 10.8 Hz), 127.7 (d, *J* = 103.8 Hz), 126.2 (d, *J* = 13.0 Hz), 22.0 (d, *J* = 3.9 Hz), 21.5.

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 37.6.

Synthesis of tris(3,5-bis(trifluoromethyl)phenyl)phosphine oxide (2l)



Following **Method A** for isolation, the pure product was obtained as a white solid (68.1 mg, >99 % yield).

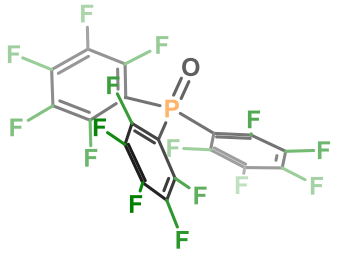
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.19 (s, 3H), 8.15 (s, 3H), 8.12 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 133.5 (dq, *J* = 34.5 Hz, 12.7 Hz), 133.0 (d, *J* = 105.6 Hz), 131.9 (d, *J* = 10.6 Hz), 127.6 (d, *J* = 3.2 Hz), 122.5 (q, *J* = 273.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 21.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -63.1.

Synthesis of tris(perfluorophenyl)phosphine oxide (2m)



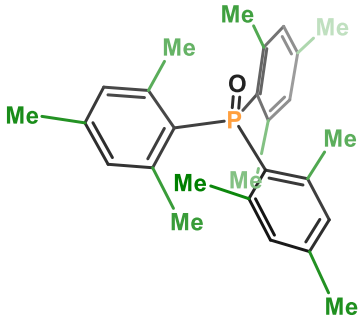
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (26.8 mg, 49 % yield).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.7 (d, J = 258.0 Hz), 144.5, 138.2 (d, J = 258.7 Hz), 106.8 (m).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) -8.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -131.3 (d, J = 20.5 Hz), -141.2 to -141.4 (m), -157.3 (m).

Synthesis of trimesitylphosphine oxide (2n)



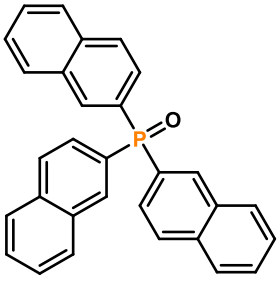
Following **Method A** for isolation, the pure product was obtained as a white solid (40.0 mg, >99 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.86-6.80 (m, 6H), 2.49-1.83 (m, 27H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 141.0 (d, J = 2.6 Hz), 132.3, 131.5, 131.2 (br), 23.7, 21.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.1.

Synthesis of tri(naphthalen-2-yl)phosphine oxide (2o)



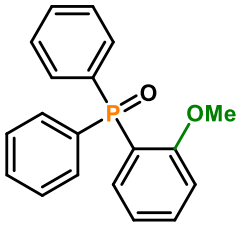
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (31.0 mg, 72 % yield).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.88 (d, *J* = 8.5 Hz, 3H), 8.06 (d, *J* = 8.1 Hz, 3H), 7.97 (d, *J* = 8.1 Hz, 3H), 7.56 (t, *J* = 7.5 Hz, 3H), 7.48-7.44 (m, 3H), 7.32-7.19 (m, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 134.7 (d, *J* = 7.9 Hz), 134.5 (d, *J* = 8.9 Hz), 134.0 (d, *J* = 12.2 Hz), 133.6(d, *J* = 2.8 Hz), 129.3 (d, *J* = 102.3 Hz), 129.3 (d, *J* = 1.6 Hz), 128.4 (d, *J* = 5.0 Hz), 127.6, 127.0, 124.8 (d, *J* = 14.5 Hz).

^{31}P NMR (162 MHz, CD_2Cl_2): δ (ppm) 39.7.

Synthesis of (2-methoxyphenyl)diphenylphosphine oxide (2p)



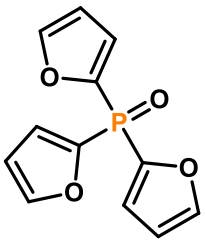
Following **Method A** for isolation, the pure product was obtained as a white solid (30.3 mg, 98 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.77 (dd, *J* = 13.4 Hz, 7.6 Hz, 1H), 7.73-7.69 (m, 4H), 7.55-7.49 (m, 3H), 7.44-7.41 (m, 4H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.92 (dd, *J* = 8.1 Hz, 5.5 Hz, 1H), 3.55 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.9 (d, *J* = 3.4 Hz), 135.0 (d, *J* = 7.1 Hz), 134.4 (d, *J* = 1.4 Hz), 133.1 (d, *J* = 107.4 Hz), 131.9 (d, *J* = 10.1 Hz), 131.5 (d, *J* = 2.7 Hz), 128.2 (d, *J* = 12.5 Hz), 121.0 (d, *J* = 11.7 Hz), 120.2 (d, *J* = 103.7 Hz), 111.5 (d, *J* = 6.4 Hz), 55.3.

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 27.6.

Synthesis of tri(furan-2-yl)phosphine oxide (2q)



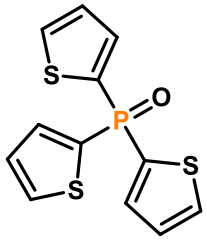
Following **Method A** for isolation, the pure product was obtained as a white solid (24.6 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.72-7.71 (m, 3H), 7.16-7.15 (m, 3H), 6.54-6.53 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 149.1 (d, *J* = 8.6 Hz), 145.8 (d, *J* = 159.6 Hz), 123.8 (d, *J* = 22.0 Hz), 111.2 (d, *J* = 9.4 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) -11.3.

Synthesis of tri(thiophen-2-yl)phosphine oxide (2r)



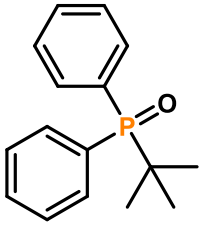
Following **Method A** for isolation, the pure product was obtained as a white solid (29.4 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.76-7.74 (m, 3H), 7.60-7.57 (m, 3H), 7.20-7.18 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 137.0 (d, J = 11.6 Hz), 134.7 (d, J = 128.0 Hz), 134.4 (d, J = 5.6 Hz), 128.4 (d, J = 15.2 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 6.6.

Synthesis of tert-butyldiphenylphosphine oxide (2s)



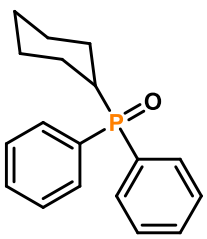
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (22.3 mg, 86 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96-7.91 (m, 4H), 7.52-7.43 (m, 6H), 1.23 (d, J = 15.0 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 132.3 (d, J = 8.2 Hz), 131.6 (d, J = 2.7 Hz), 131.0 (d, J = 90.4 Hz), 128.4 (d, J = 10.9 Hz), 34.0 (d, J = 70.6 Hz), 25.2.

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 39.2.

Synthesis of cyclohexyldiphenylphosphine oxide (2t)



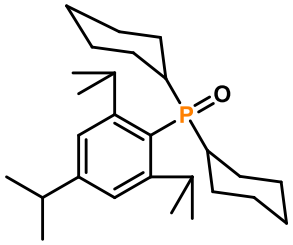
Following **Method A** for isolation, the pure product was obtained as a white solid (28.3 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.78-7.74 (m, 4H), 7.48-7.44 (m, 6H), 2.26-2.19 (m, 1H), 1.79-1.69 (m, 5H), 1.53-1.50 (m, 2H), 1.26 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 132.3, 131.6 (d, J = 2.6 Hz), 131.2 (d, J = 8.6 Hz), 128.6 (d, J = 11.1 Hz), 37.2 (d, J = 73.2 Hz), 26.4 (d, J = 13.5 Hz), 25.8, 24.8 (d, J = 2.7 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 35.0.

Synthesis of dicyclohexyl(2,4,6-triisopropylphenyl)phosphine oxide (2u)



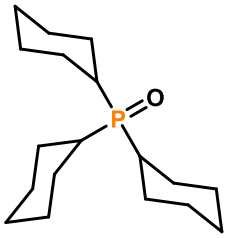
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (39.6 mg, 95 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.10-7.07 (m, 2H), 2.85 (sept, J = 6.9 Hz, 1H), 2.07-1.20 (m, 42 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.1, 123.2, 122.7, 122.4, 41.4 (d, J = 64.6 Hz), 34.0, 27.1 (d, J = 3.4 Hz), 26.9, 26.8, 26.7 (d, J = 2.9 Hz), 25.9, 23.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 53.3.

Synthesis of tricyclohexylphosphine oxide (2v)



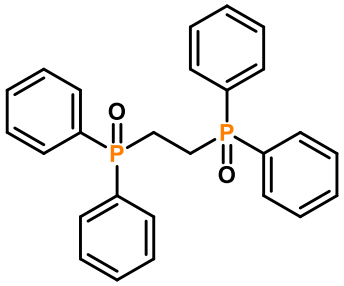
Following **Method B** for isolation, the residue was subjected to silica gel column chromatography (Hexane:EtOAc = 1:1), to yield the pure product as a white solid (27.2 mg, 92 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.90-1.70 (m, 18H), 1.41-1.22 (m, 15H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 35.3 (d, J = 60.6 Hz), 27.0 (d, J = 11.7 Hz), 26.4 (d, J = 2.7 Hz), 26.2.

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 49.1.

Synthesis of ethane-1,2-diylbis(diphenylphosphine oxide) (2w)



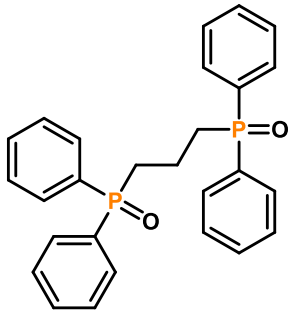
Following **Method A** for isolation, the pure product was obtained as a white solid (42.7 mg, >99 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68-7.67 (m, 8H), 7.47-7.41 (m, 12H), 2.49 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 132.1, 130.8 (t, J = 4.6 Hz), 128.9 (t, J = 5.9 Hz), 21.6 (dd, J = 64.3 Hz, 32.5 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 32.9.

Synthesis of propane-1,3-diylbis(diphenylphosphine oxide) (2x)



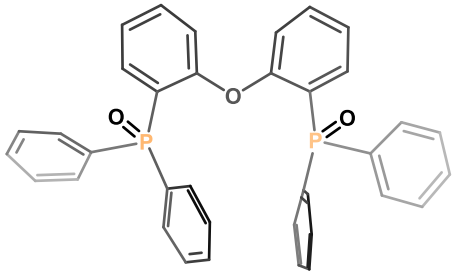
Following **Method A** for isolation, the pure product was obtained as a white solid (44.1 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.68-7.64 (m, 8H), 7.47-7.44 (m, 4H), 7.41-7.38 (m, 8H), 2.51-2.46 (m, 4H), 2.01-1.95 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 132.5 (d, J = 98.8 Hz), 131.9 (d, J = 2.4 Hz), 130.8 (d, J = 9.4 Hz), 128.8 (d, J = 11.8 Hz), 30.0 (dd, J = 71.3 Hz, 11.0 Hz), 15.0 (t, J = 3.2 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 32.9.

Synthesis of (oxybis(2,1-phenylene))bis(diphenylphosphine oxide) (2y)



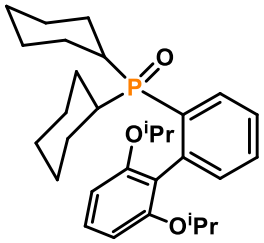
Following **Method A** for isolation, the pure product was obtained as a white solid (56.6 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.68-7.62 (m, 10H), 7.47-7.05 (m, 17H), 6.05 (dd, *J* = 7.8 Hz, 5.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 158.9 (d, *J* = 2.5 Hz), 134.2 (d, *J* = 7.2 Hz), 134.0, 132.2-131.6 (m), 128.5-128.1 (m), 124.0 (d, *J* = 101.2 Hz), 123.9 (d, *J* = 11.1 Hz), 120.1 (d, *J* = 6.2 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 26.3.

Synthesis of dicyclohexyl(2',6'-diisopropoxy-[1,1'-biphenyl]-2-yl)phosphine oxide (2z)



Following **Method A** for isolation, the pure product was obtained as a white solid (48.0 mg, >99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.88-7.84 (m, 1H), 7.42-7.39 (m, 1H), 7.37-7.34 (m, 1H), 7.22-7.18 (m, 1H), 6.58 (d, *J* = 8.3 Hz, 2H), 4.36 (sept, *J* = 5.9 Hz, 2H), 1.72-1.57 (m, 12H), 1.44-1.26 (m, 10H), 1.18 (d, *J* = 6.1 Hz, 6H), 0.99 (d, *J* = 6.0 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 156.9, 139.3 (d, *J* = 7.1 Hz), 132.8 (d, *J* = 4.9 Hz), 132.7 (d, *J* = 6.9 Hz), 131.9 (d, *J* = 83.5 Hz), 129.9 (d, *J* = 2.5 Hz), 128.8, 126.0 (d, *J* = 10.6 Hz), 123.4 (d, *J* = 1.4 Hz), 107.6, 71.5, 37.1 (d, *J* = 65.5 Hz), 26.8 (d, *J* = 12.9 Hz), 26.2 (dd, *J* = 9.7 Hz, 3.2 Hz), 25.5, 22.3 (d, *J* = 79.2 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 47.8.

V. Green Chemistry Metrics

Atom Economy (AE) (%) $= \frac{Molecular\ weight\ of\ product}{\sum Molecular\ weight\ of\ reactants} \times 100$

$= \frac{278.29}{262.29 + 16} \times 100$

$= 100$

Reaction Mass Efficiency (RME) (%) $= \frac{Mass\ of\ isolated\ product}{\sum Mass\ of\ reactants} \times 100$

$= \frac{27.6}{26.2 + 1.6} \times 100$

$= \frac{27.6}{27.8} \times 100$

$= 99.3$

Environmental Factor (E-factor) $= \frac{Total\ mass\ of\ waste}{Mass\ of\ isolated\ product}$

When solvent recovered, $= \frac{83.1}{27.6}$

$= 3.0$

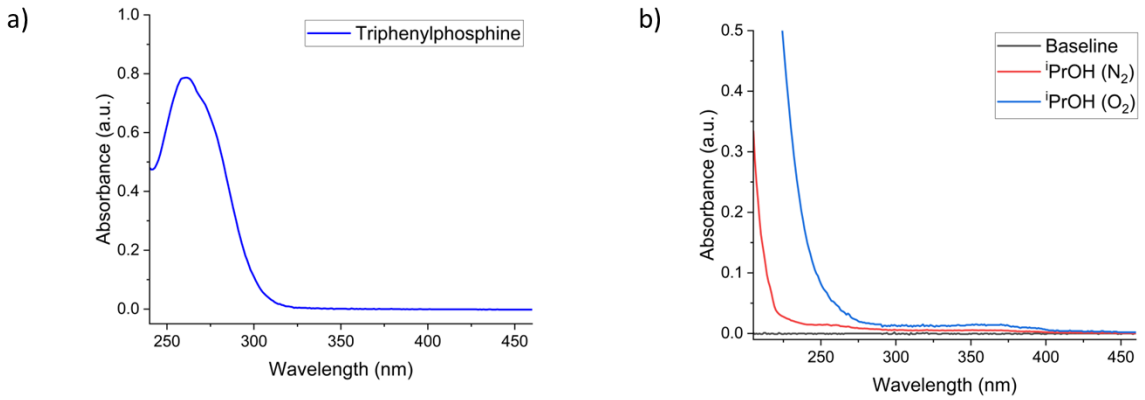
When solvent is not recovered, $= \frac{83.1 + 701.5}{27.6}$

$= \frac{784.6}{27.6}$

$= 28.4$

VI. Mechanistic Investigations

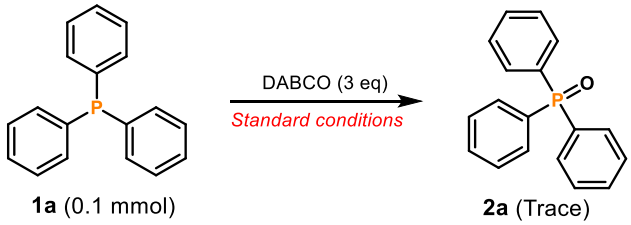
VI. I. UV -Visible experiments



(a) UV-Visible absorption spectrum of triphenylphosphine (**1a**) was recorded in isopropanol, revealing an absorption maximum (λ_{max}) at 260 nm. Notably, no significant absorption was observed beyond 330 nm, confirming that the substrate is transparent at 380 nm and thus incapable of direct photoexcitation under the experimental purple LED irradiation.

(b) Recording the UV-visible spectra of isopropanol under varying atmospheres showed that oxygen (O_2) leads to a markedly higher absorbance compared to nitrogen (N_2). Specifically, the spectra in O_2 displayed an extended absorption tail into the visible region (up to 400 nm), whereas the N_2 environment did not. This red-shifted absorption provides evidence for the existence of a solvent-$^3O_2$ charge-transfer complex.

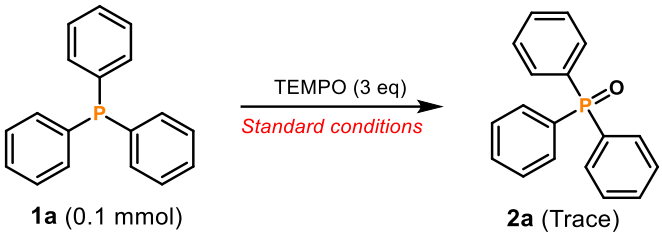
VI. II. $^1O_2$ Quenching Experiment



To a flame-dried glass vial equipped with a magnetic stirring bar, triphenylphosphine (**1a**) (0.1 mmol, 26.3 mg), DABCO (1,4-diazabicyclo[2.2.2]octane) (0.3 mmol, 33.6 mg) and 1.0 mL of

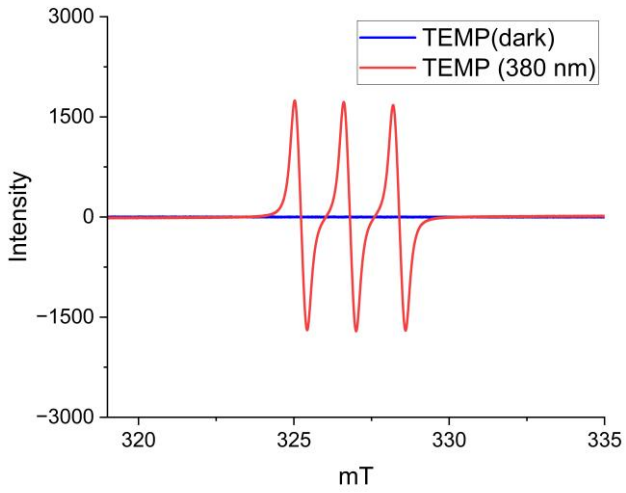
isopropyl alcohol (^{i}PrOH) were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under open atmosphere for 40 minutes. The conversion of the crude product was calculated by ^{31}P-NMR. Only trace amount of **2a** was detected, confirming the presence of $^{1}O_2$ in the reaction pathway.

VI. III. Radical Scavenging Experiment

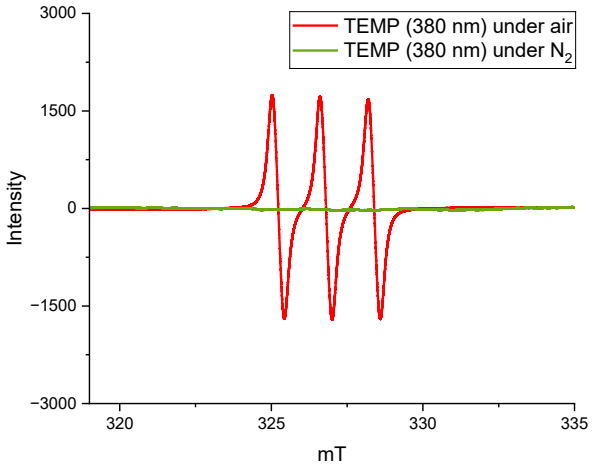


To a flame-dried glass vial equipped with a magnetic stirring bar, triphenylphosphine (**1a**) (0.1 mmol, 26.3 mg), TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) (0.3 mmol, 46.9 mg) and 1.0 mL of isopropyl alcohol (^{i}PrOH) were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under open atmosphere for 40 minutes. The conversion of the crude product was calculated by ^{31}P-NMR. Only trace amount of **2a** was detected, confirming the presence of radical in the reaction pathway.

VI. IV. EPR Studies with TEMP

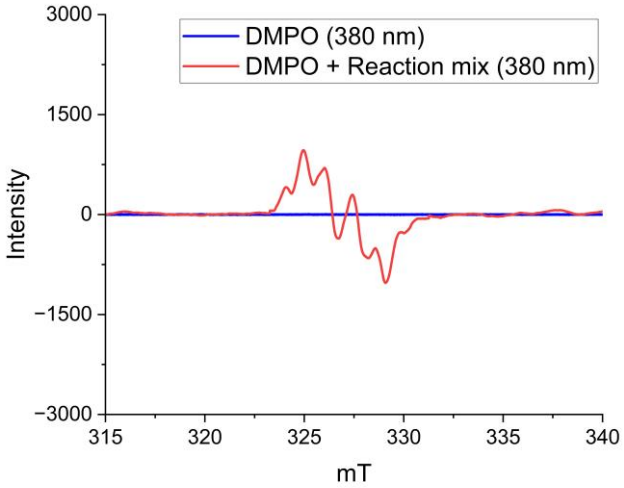


EPR spectra of TEMP (2,2,6,6-tetramethylpiperidine) (50 mM) were recorded under dark conditions and after irradiation at 380 nm for 15 minutes in isopropanol. While no paramagnetic signals were detected under dark conditions, the sample exhibited a characteristic 1:1:1 triplet EPR spectrum upon 15 minutes of irradiation at 380 nm. This signal is indicative of the formation of the TEMPO radical, resulting from the trapping of singlet oxygen ($^{1}O_2$) by TEMP.

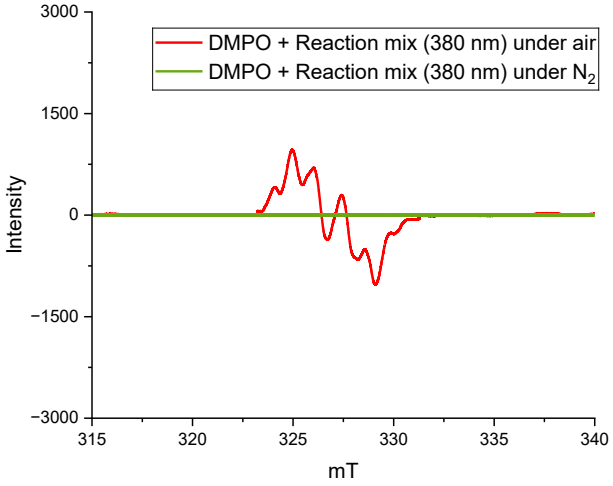


Furthermore, EPR spectrum was recorded after irradiation at 380 nm for 15 minutes under nitrogen atmosphere. No paramagnetic signals were observed, confirming the singlet oxygen arise from aerial oxygen activation.

VI. V. EPR Studies with DMPO

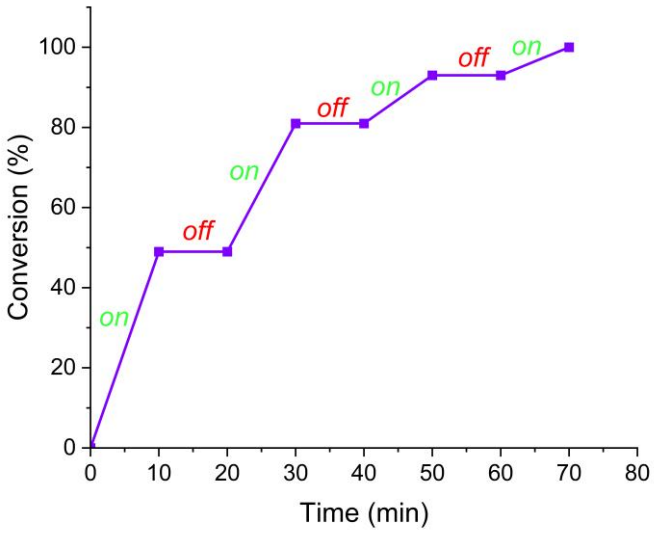


To identify radical intermediates, EPR spin-trapping was performed using DMPO (5,5-Dimethyl-1-pyrroline N-oxide) (50 mM). While pure DMPO remained EPR-silent under 380 nm light, DMPO in the presence of reaction mixture (380 nm irradiation for 10 minutes) under air exhibited a characteristic peak corresponding to a DMPO-trapped superoxide radical, further validating the presence of reactive oxygen species (ROS) during the course of the reaction.



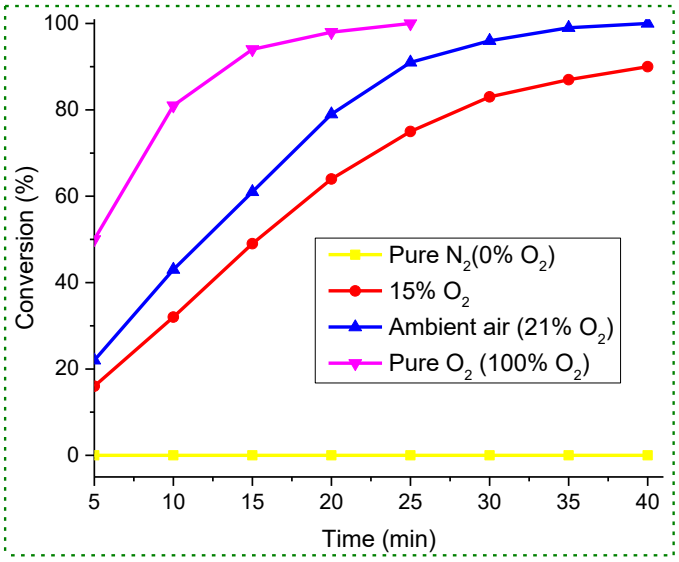
Additionally, DMPO in the presence of reaction mixture (380 nm irradiation for 10 minutes) under nitrogen atmosphere remained EPR-silent. This observation further clarifies ROS is generated only in presence of oxygen.

VI. VI. Light On/Off Experiment



To a flame-dried glass vial equipped with a magnetic stirring bar, triphenylphosphine (**1a**) (0.1 mmol, 26.3 mg), and 1.0 mL of isopropyl alcohol (^{i}PrOH) were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under open atmosphere. Aliquots of crude reaction mixture were subjected to ^{31}P NMR analysis at regular intervals of 10 minutes in the presence and absence of a 380 nm 18W EvoluChem LED. This study confirmed that the reaction proceeds only in the presence of light.

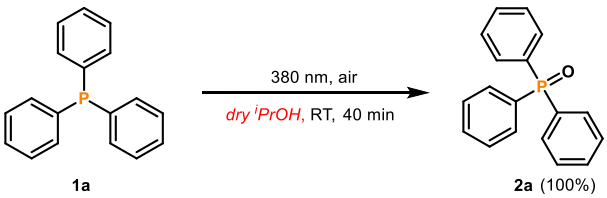
VI. VII. Oxygen Concentration Kinetics



	Conversion to 2a			
Time (min)	**Pure N_2 (0% O_2)**	**15% O_2**	**Ambient air (21% O_2)**	**Pure O_2 (100% O_2)**
5	0	16	22	50
10	0	32	43	81
15	0	49	61	94
20	0	64	79	98
25	0	75	91	100
30	0	83	96	-
35	0	87	99	-
40	0	90	100	-

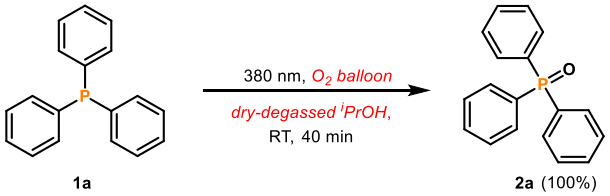
VI. VIII. Control Experiments

a) Reaction using dry solvent



To a flame-dried glass vial equipped with a magnetic stirring bar, triphenylphosphine (0.1 mmol), and 1.0 mL of dry isopropyl alcohol (^{i}PrOH) were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under open atmosphere for 40 minutes. The conversion of the crude product was calculated by ^{31}P-NMR. 100% conversion to **2a** was observed, indicating aerial oxygen is the source of oxygen in the product.

b) Reaction using dry and degassed solvent with pure O_2 balloon



To a flame-dried glass vial equipped with a magnetic stirring bar, triphenylphosphine (0.1 mmol), and 1.0 mL of dry and degassed isopropyl alcohol (^{i}PrOH) were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under O_2 atmosphere for 40 minutes. The conversion of the crude product was calculated by ^{31}P-NMR. 100% conversion to **2a** was observed, confirming aerial oxygen is the sole oxidant in our reaction pathway.

VII. Quantum Yield Measurement (*via* chemical actinometry)[1, 2]

a) Measurement of the photon flux

Solution A – Potassium ferrioxalate hydrate (737 mg, 1.5 mmol) was dissolved in aq. H_2SO_4 (0.05 M, 10 mL) to afford a 0.15 M ferrioxalate solution.

Solution B – 1,10-Phenanthroline monohydrate (20 mg, 0.1 mmol), NaOAc (4.5 g) were dissolved in aq. H_2SO_4 (0.5 M, 20 mL).

Both the solutions were stored in the dark. The photon flux of the 380 nm LED was determined first. For this, 1 mL of **solution A** was added to six glass vials. Three of the vials were stored in dark conditions, and three were irradiated using a 380 nm LED for 60 seconds. Then 300 µL of **solution B** was added to all the six vials, and they were left to stir in the dark for 60 minutes to facilitate the coordination of Fe(II) by phenanthroline.
The absorbance at 510 nm was then measured for all the six solutions. The difference in absorbance (ΔA_{510} nm) between the average absorbance of the three irradiated and the three non-irradiated samples at 510 nm was then determined.

The formed amount of Fe(II) was calculated according to the Beer-Lambert's law:

$$nFe(II) = \frac{V \times \Delta A}{l \times \varepsilon}$$

where, V (total volume of solution) = 1.3 mL (0.0013 L)

l (path length of the cuvette) = 1.0 cm

ε (molar extinction coefficient of the ferrioxalate actinometer at λ = 510 nm) = 11100 $L.mol^{-1}.cm^{-1}$

$$nFe(II) = \frac{0.0013 \times 2.04}{1 \times 11100}$$

$$nFe(II) = 2.39 \times 10^{-7}\ \text{mol}$$

The fraction of light which was absorbed by the actinometer at λ = 380 nm (*f*) was determined with following equation with the absorbance of the ferrioxalate stock solution at λ = 380 nm

$$f = 1 - 10^{-A_{380}}$$

$$f = 1 - 10^{-2.69} = 0.998$$

Photon flux was determined by the following equation with $\phi_f = 1.18$ (at λ = 380 nm).[3,4]

$$Photon\ flux\ (\phi_q) = \frac{nFe(II)}{\phi_f \times t \times f}$$

$$= \frac{2.39 \times 10^{-7}}{1.18 \times 60 \times 0.998}$$

$$= 3.38 \times 10^{-9}\ \text{mol.s}^{-1}$$

b) Measurement of quantum yield for the formation of product 2a

To a flame-dried glass vial equipped with a magnetic stirring bar, triphenylphosphine (0.1 mmol), and 1.0 mL of isopropyl alcohol (^{i}PrOH) were added. Then, the mixture was irradiated under 380 nm 18W EvoluChem LED at a distance of 4 cm at room temperature under open atmosphere for 5 minutes. The yield of the crude product was calculated by ^{31}P-NMR. The yield of the product **2a** was found to be 22% (2.2×10^{-5} mol).

The quantum yield (ϕ) was calculated as follows:

$$\text{Quantum yield } (\phi) = \frac{n_{product}}{\phi q \times t \times f_r}$$

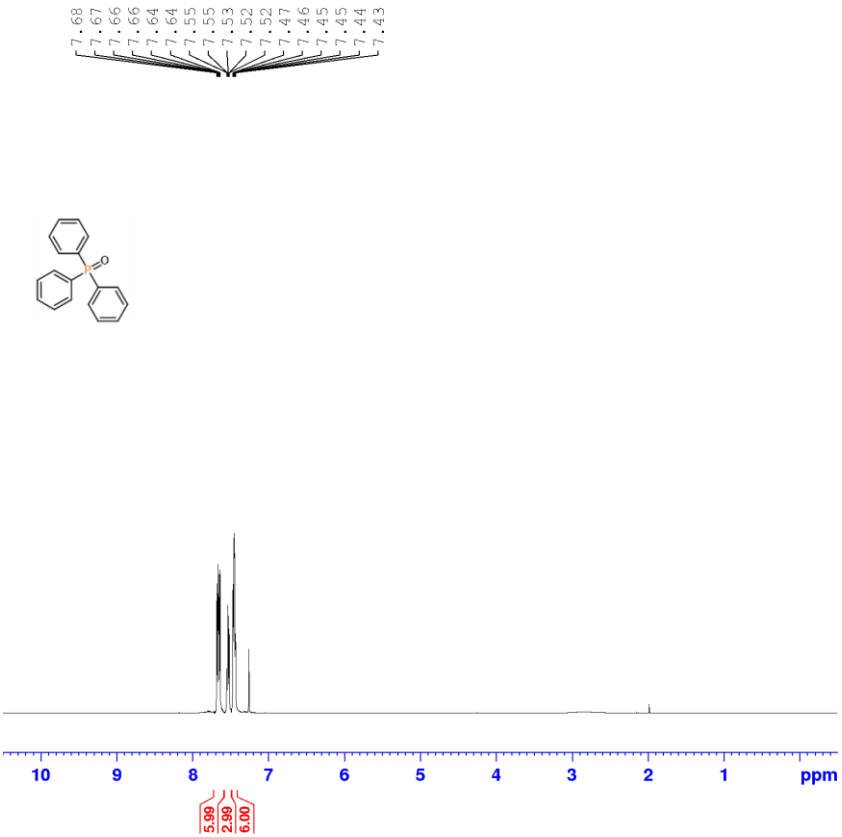
where the photon flux (ϕq) is 3.38×10^{-9} mol.s^{-1}, *t* is the reaction time (5 minutes = 300 s), and f_r is the fraction of light absorbed by the reaction mixture ($f_r = 1 - 10^{-A} = 1 - 10^{-0.14} = 0.28$).

The quantum yield has been calculated to be 77, indicating a radical chain propagation mechanism.

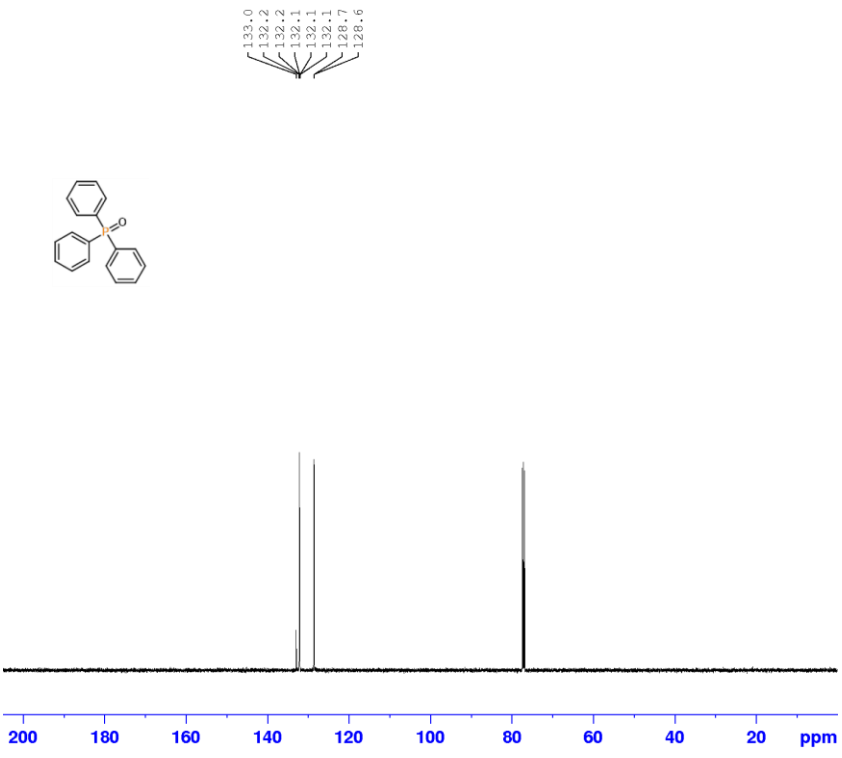
VIII. NMR Spectra

Triphenylphosphine oxide (2a)

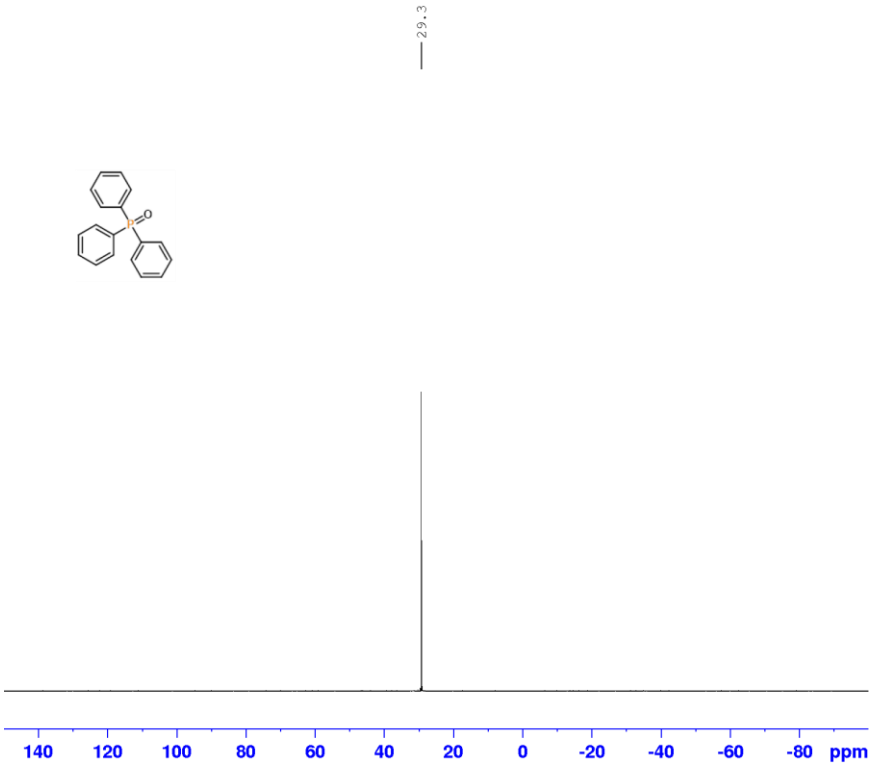
^{1}H NMR, $CDCl_3$, 500 MHz (2a)



^{13}C NMR, $CDCl_3$, 125 MHz (2a)

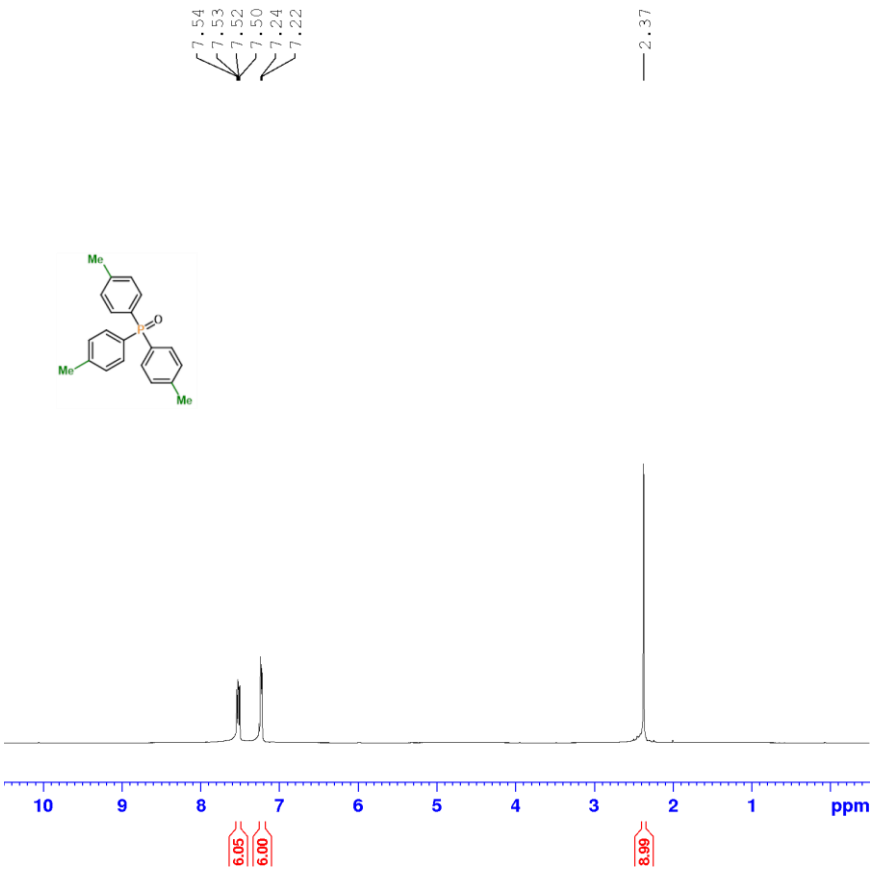


^{31}P NMR, $CDCl_3$, 202 MHz (2a)

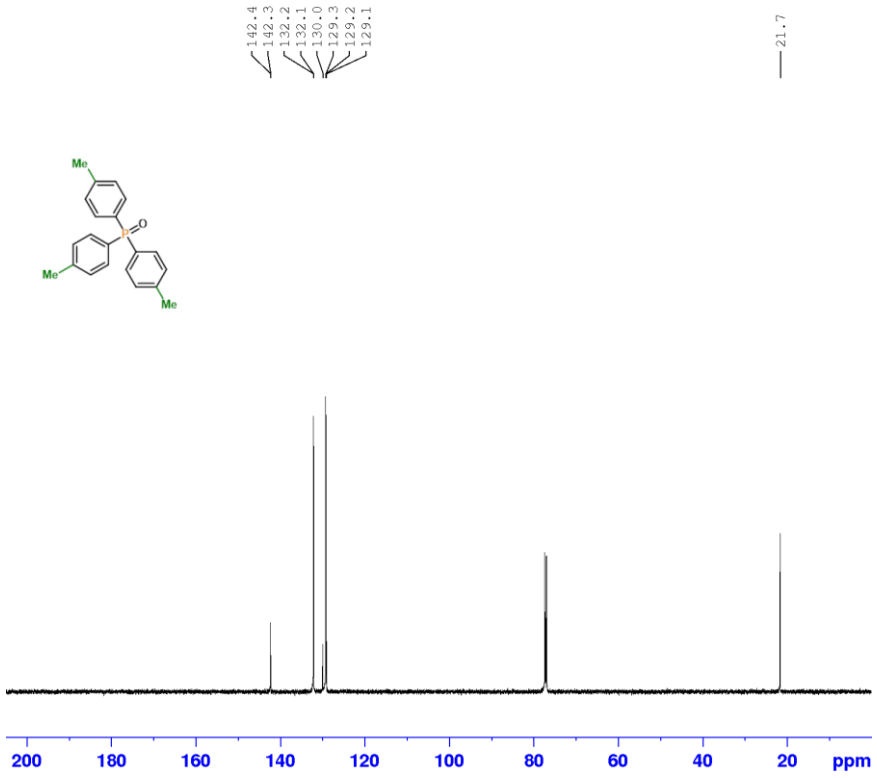


Tri-p-tolylphosphine oxide (2b)

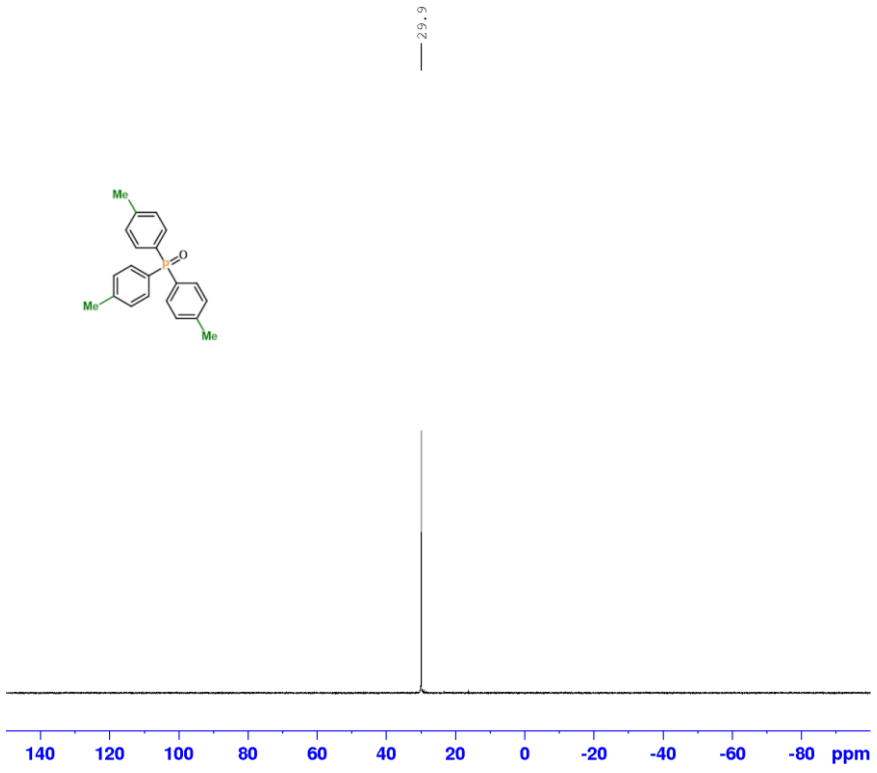
^{1}H NMR, $CDCl_3$, 500 MHz (2b)



^{13}C NMR, $CDCl_3$, 125 MHz (2b)

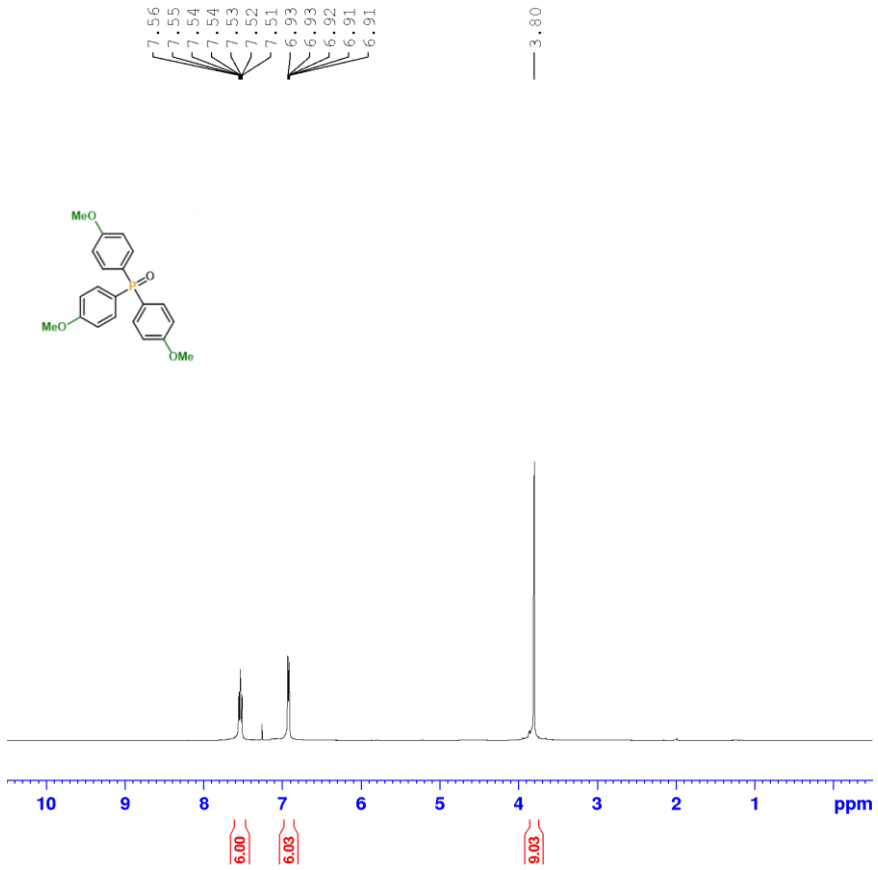


^{31}P NMR, $CDCl_3$, 202 MHz (2b)

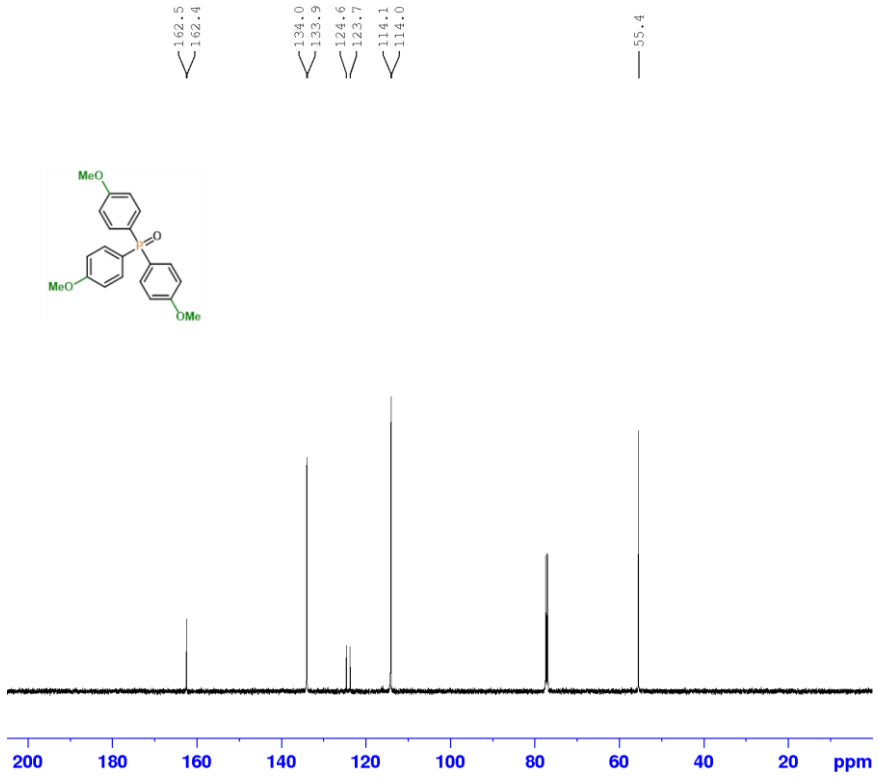


Tris(4-methoxyphenyl)phosphine oxide (2c)

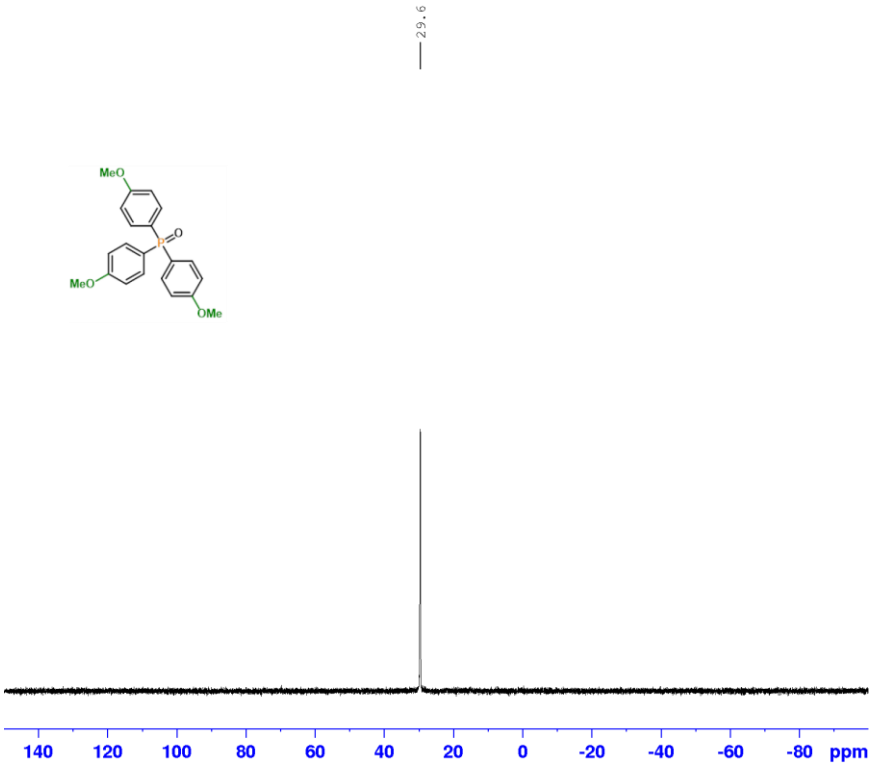
^{1}H NMR, $CDCl_3$, 500 MHz (2c)



^{13}C NMR, $CDCl_3$, 125 MHz (2c)

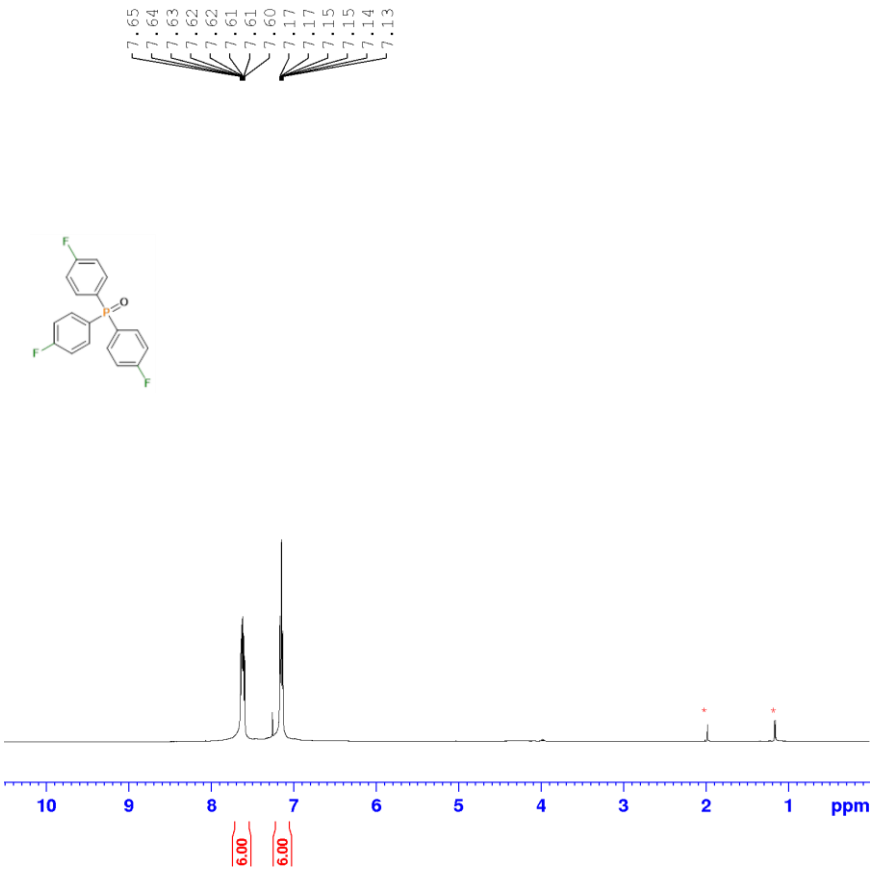


^{31}P NMR, $CDCl_3$, 202 MHz (2c)



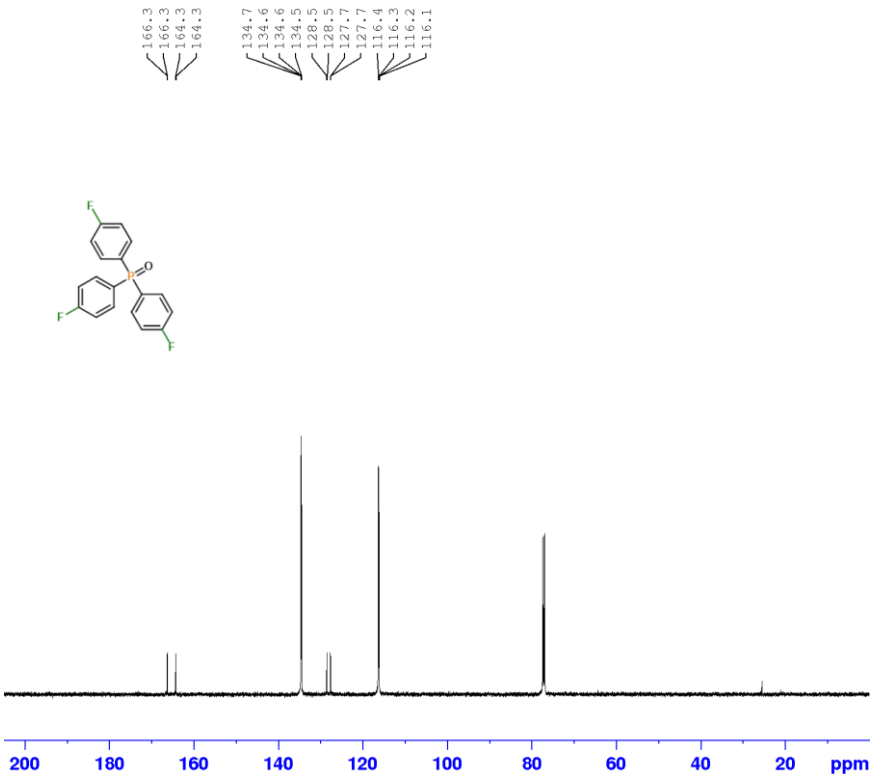
Tris(4-fluorophenyl)phosphine oxide (2d)

^{1}H NMR, $CDCl_3$, 500 MHz (2d)

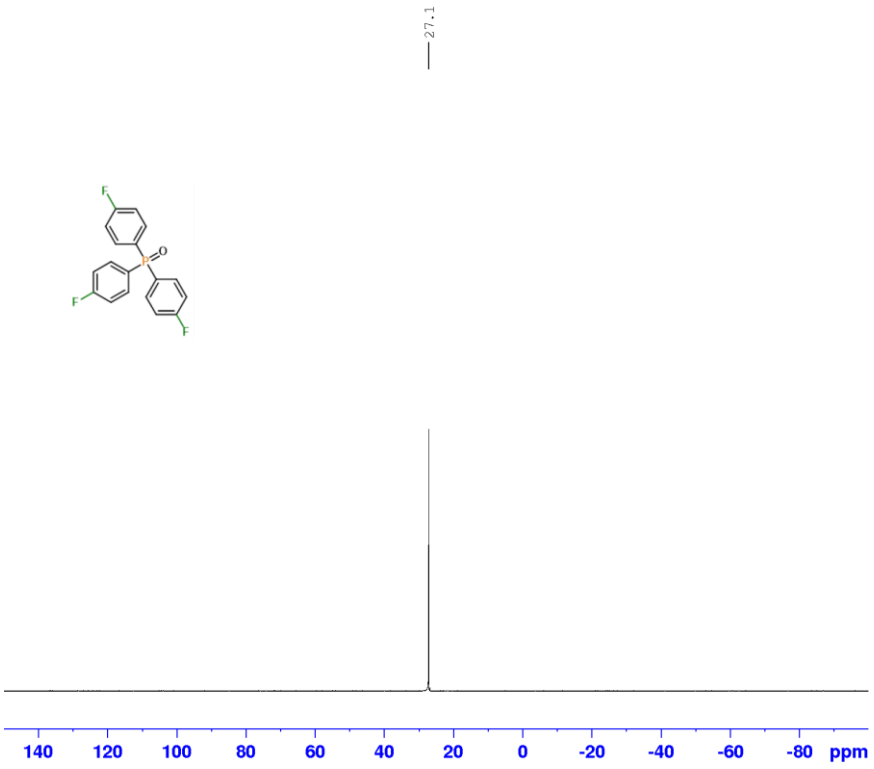


* = Solvent

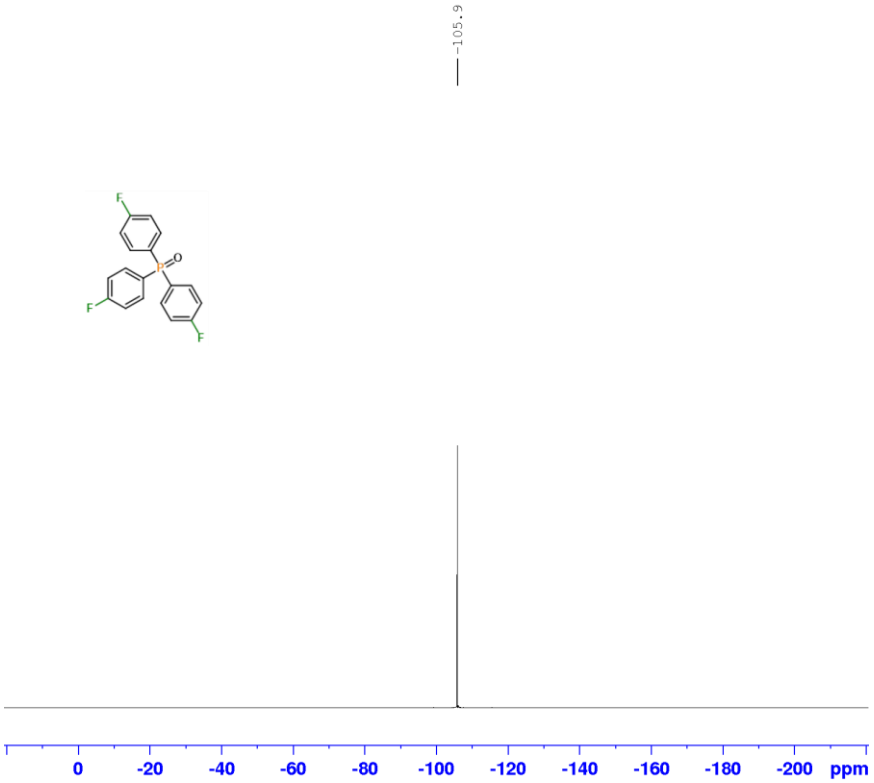
^{13}C NMR, $CDCl_3$, 125 MHz (2d)



^{31}P NMR, $CDCl_3$, 202 MHz (2d)

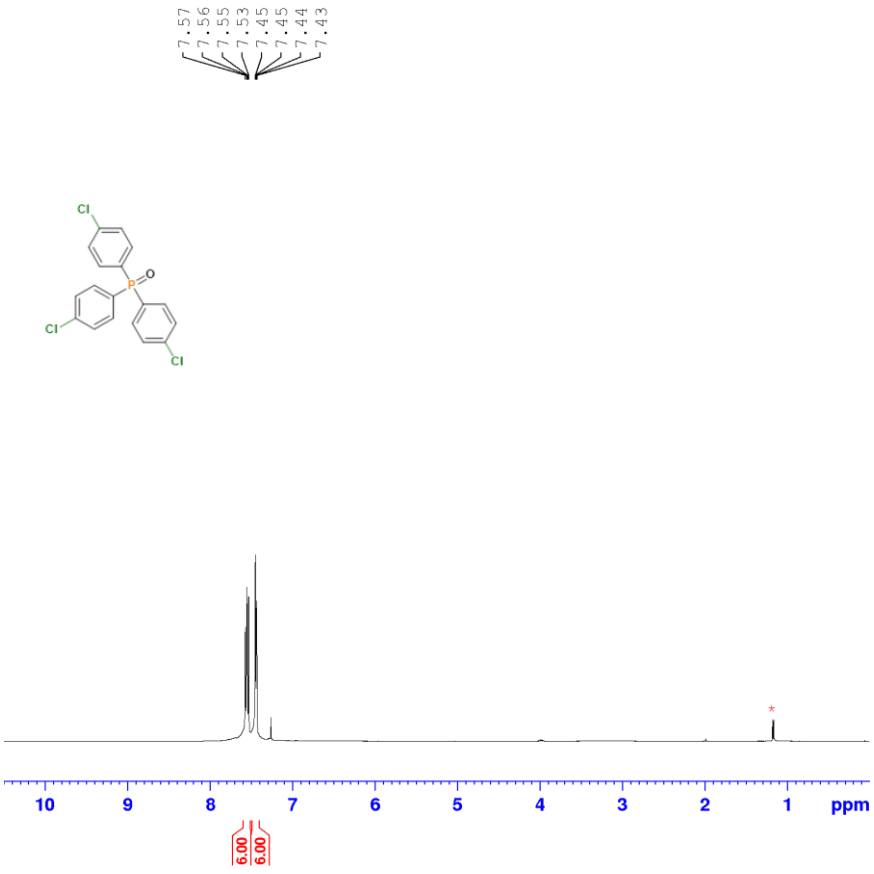


^{19}F NMR, $CDCl_3$, 470 MHz (2d)



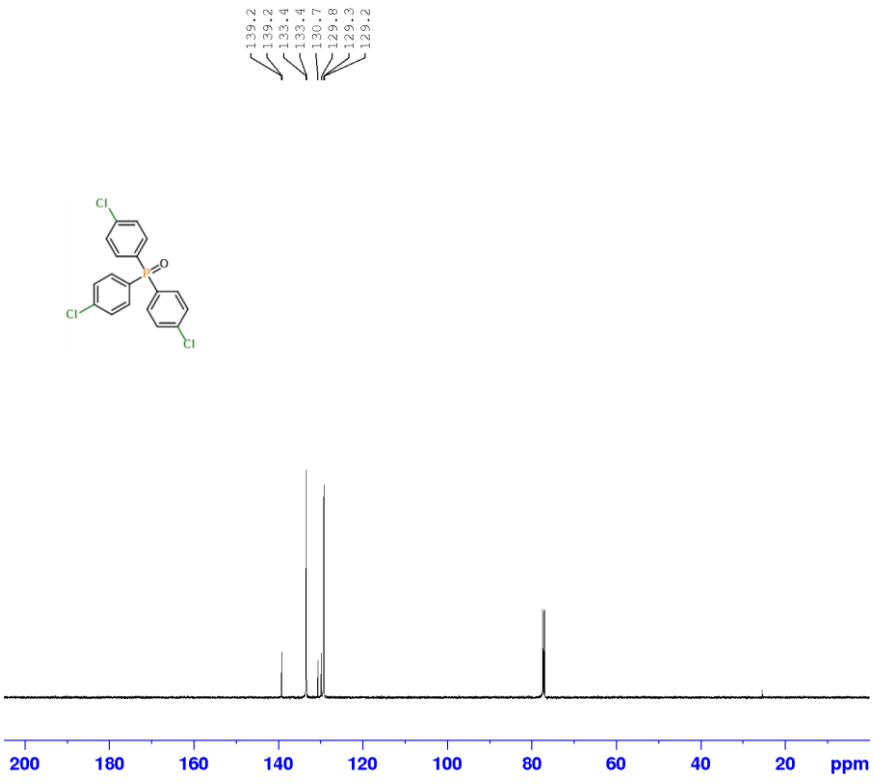
Tris(4-chlorophenyl)phosphine oxide (2e)

^{1}H NMR, $CDCl_3$, 500 MHz (2e)

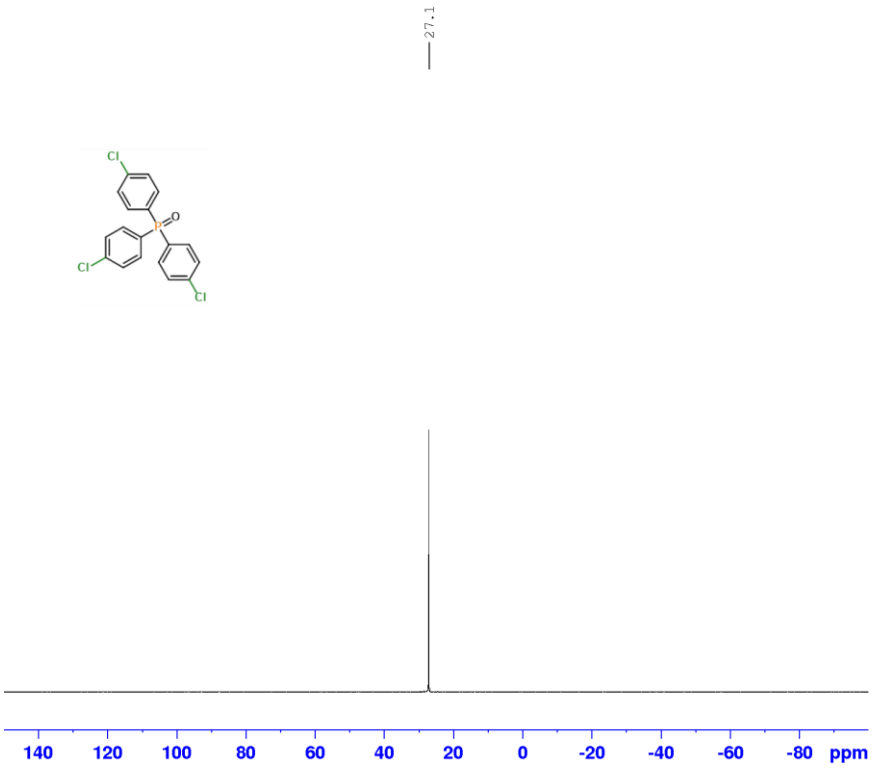


* = Solvent

^{13}C NMR, $CDCl_3$, 125 MHz (2e)

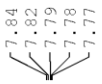


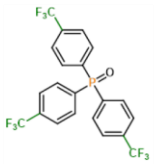
^{31}P NMR, $CDCl_3$, 202 MHz (2e)

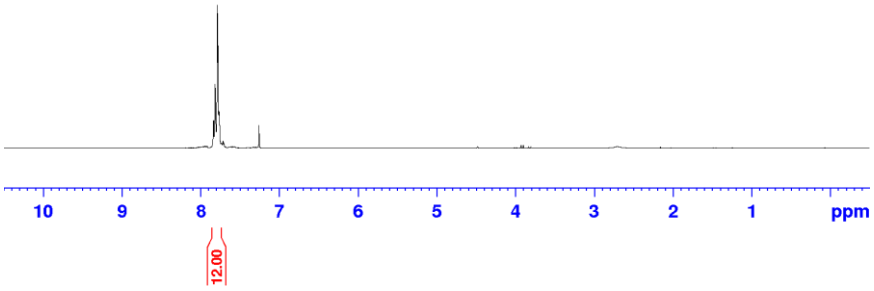


Tris(4-(trifluoromethyl)phenyl)phosphine oxide (2f)

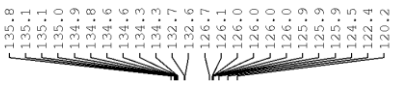
^{1}H NMR, $CDCl_3$, 400 MHz (2f)

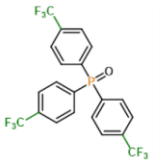


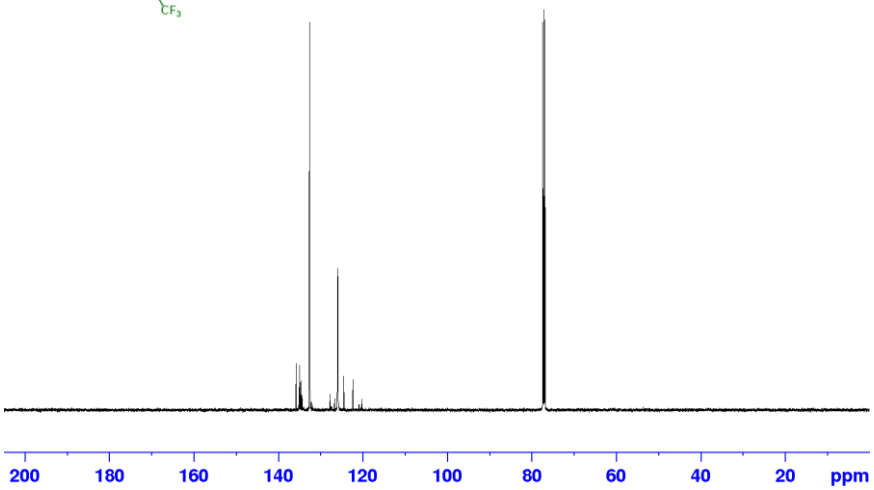




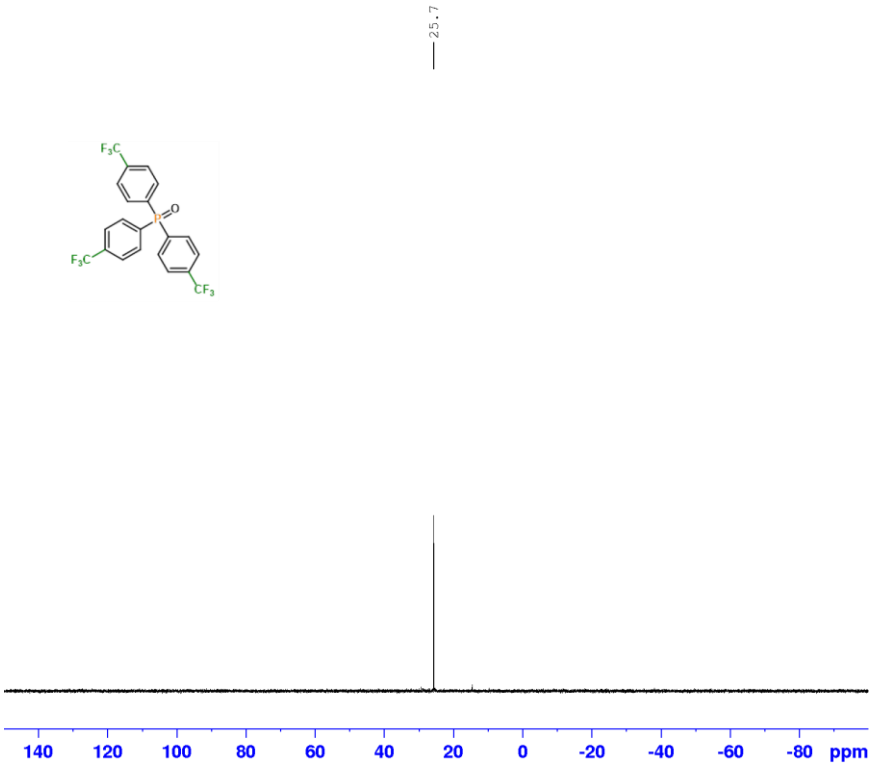
^{13}C NMR, $CDCl_3$, 125 MHz (2f)



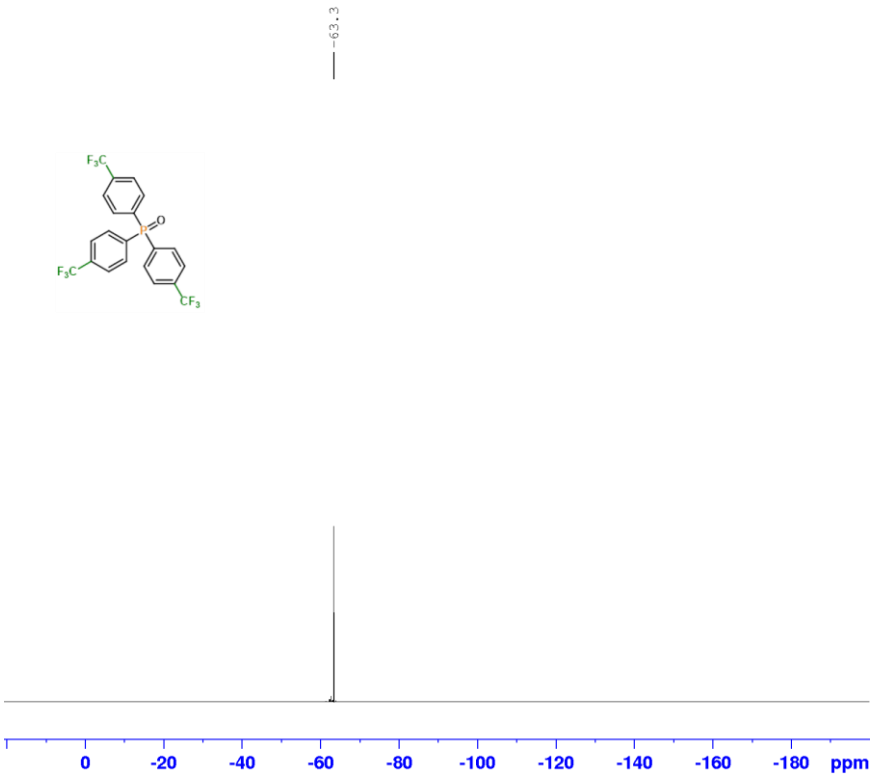




^{31}P NMR, $CDCl_3$, 162 MHz (2f)

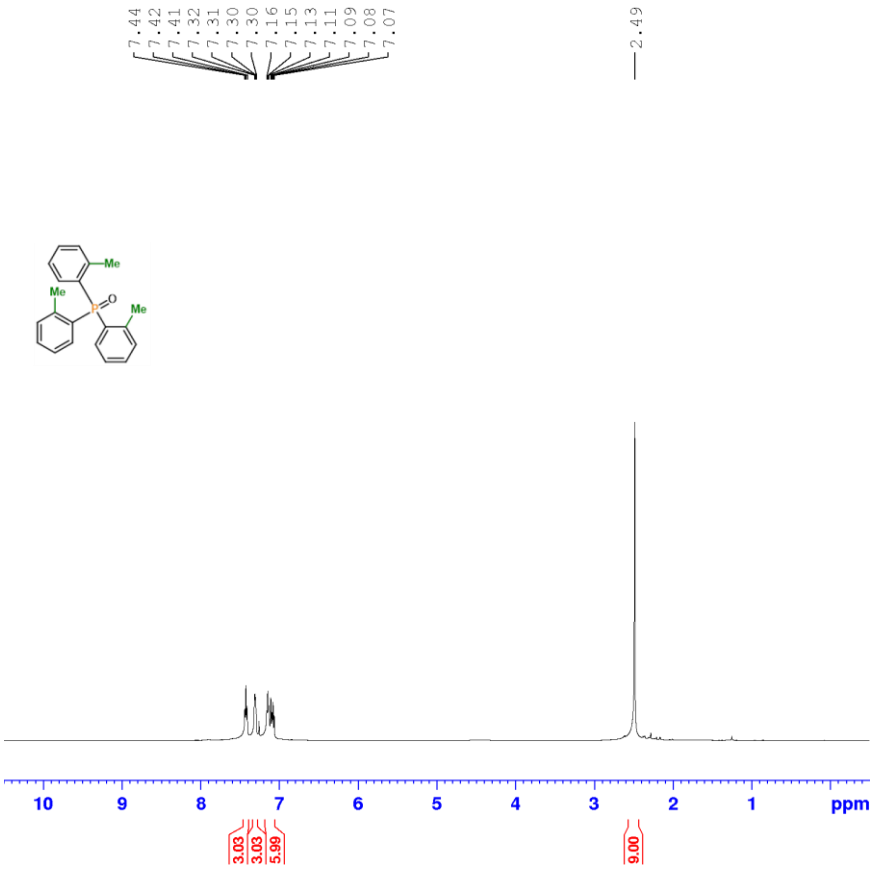


^{19}F NMR, $CDCl_3$, 376 MHz (2f)

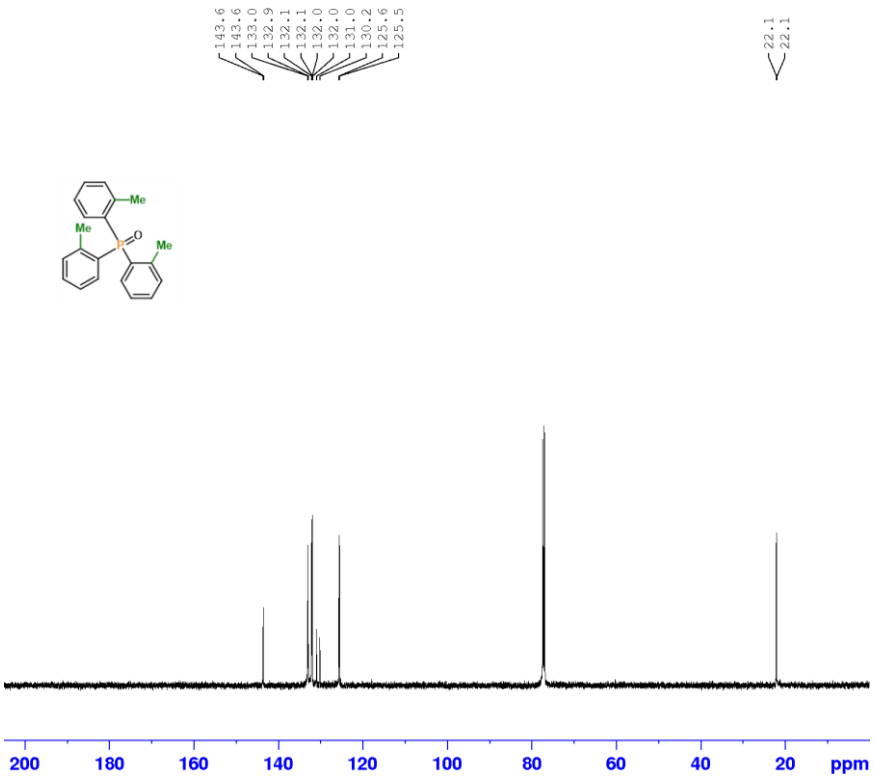


Tri-o-tolylphosphine oxide (2g)

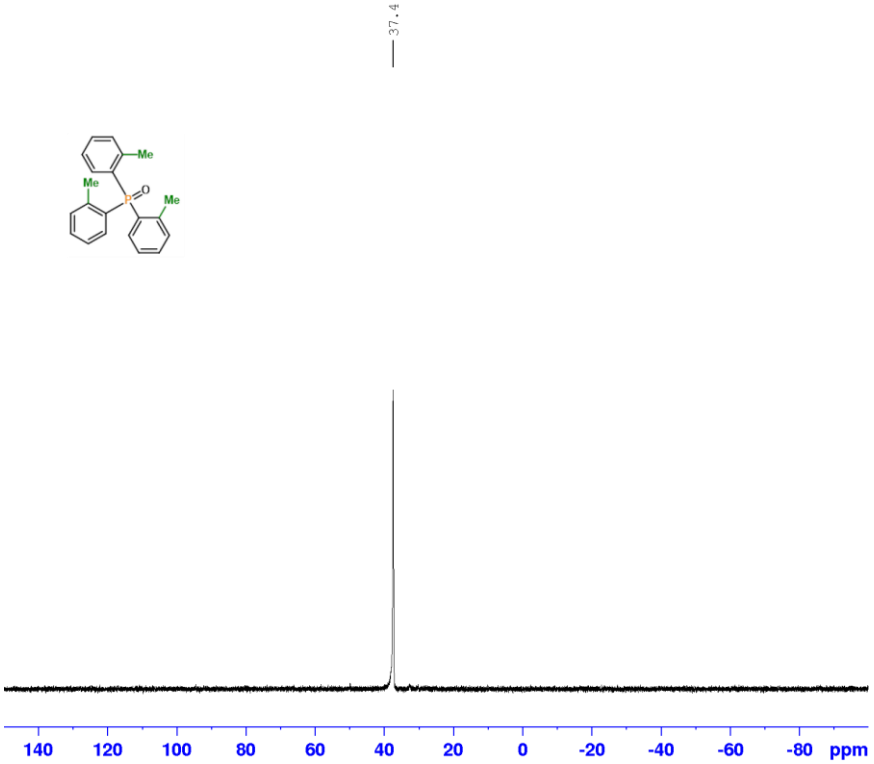
^{1}H NMR, $CDCl_3$, 500 MHz (2g)



^{13}C NMR, $CDCl_3$, 125 MHz (2g)

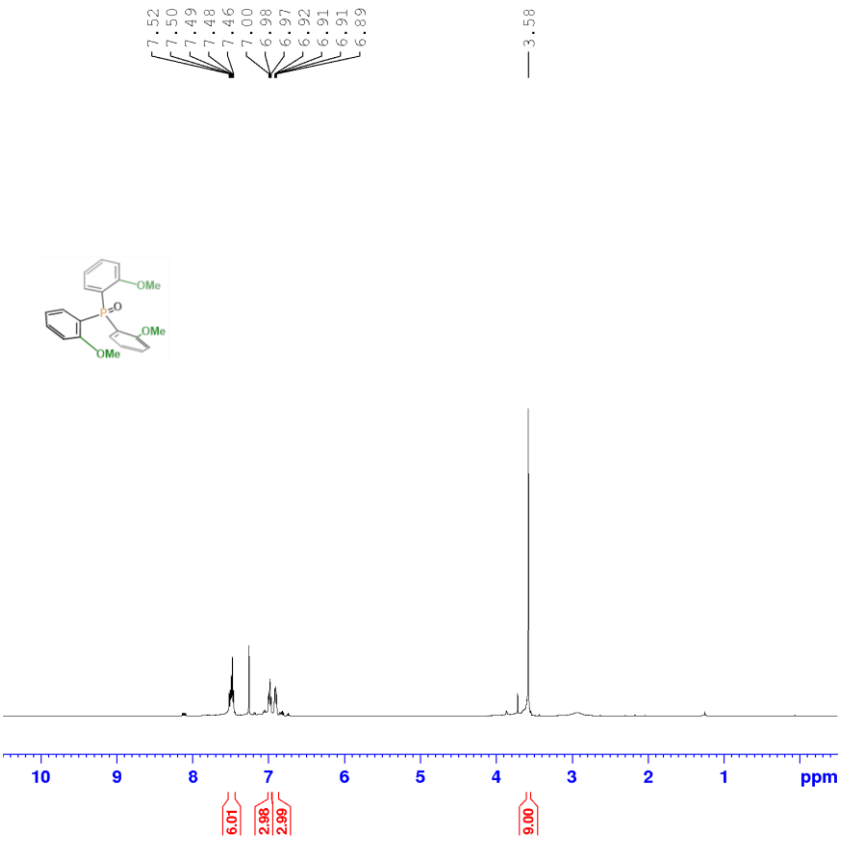


^{31}P NMR, $CDCl_3$, 202 MHz (2g)

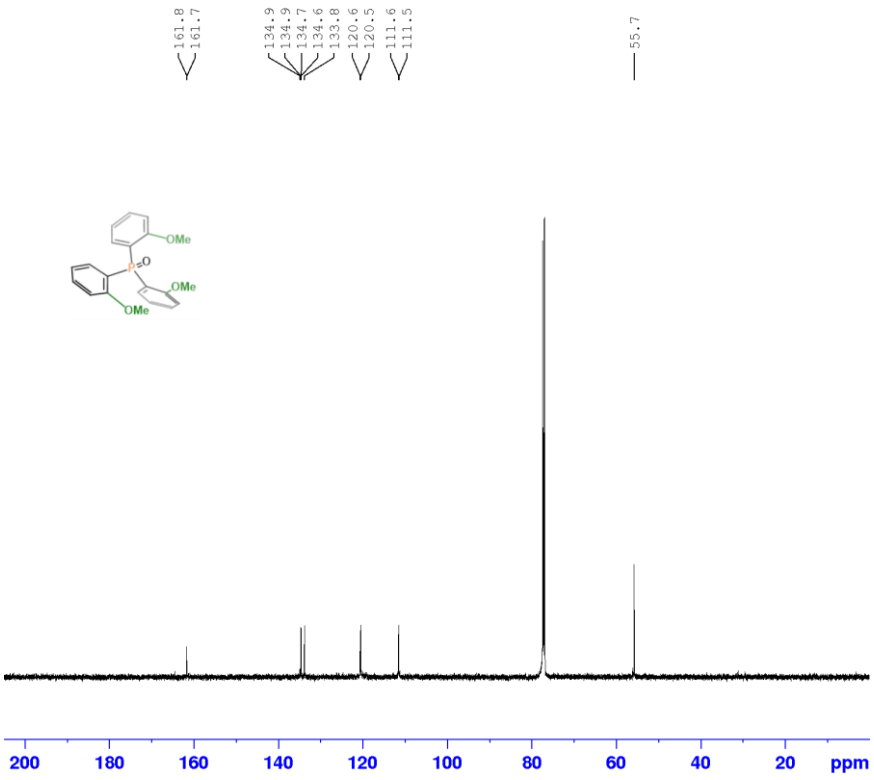


Tris(2-methoxyphenyl)phosphine oxide (2h)

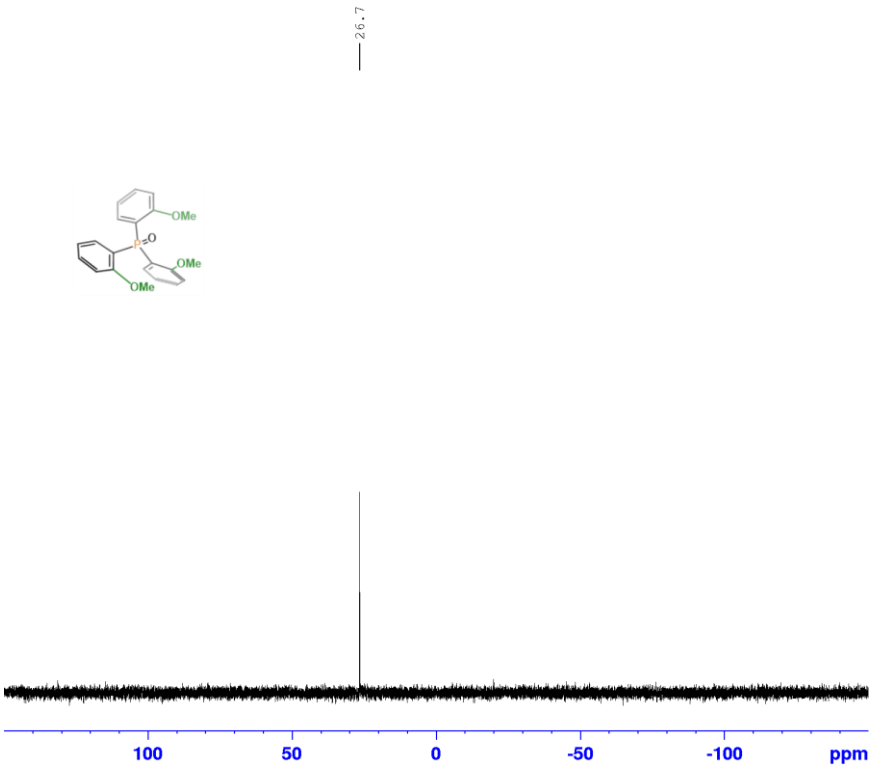
^{1}H NMR, $CDCl_3$, 500 MHz (2h)



^{13}C NMR, $CDCl_3$, 125 MHz (2h)

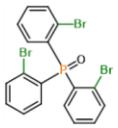


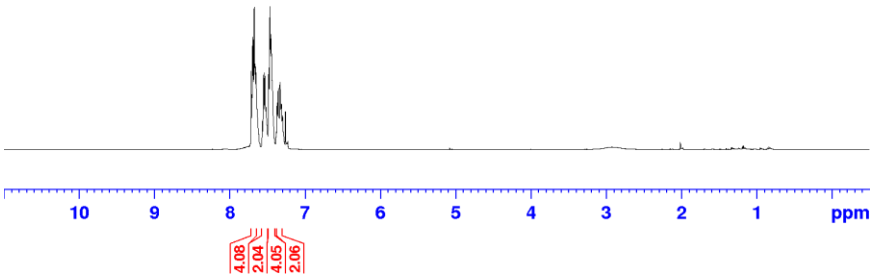
^{31}P NMR, $CDCl_3$, 202 MHz (2h)



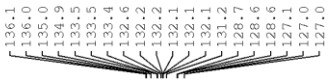
Tris(2-bromophenyl)phosphine oxide (2i)

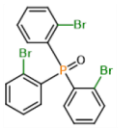
^{1}H NMR, $CDCl_3$, 500 MHz (2i)

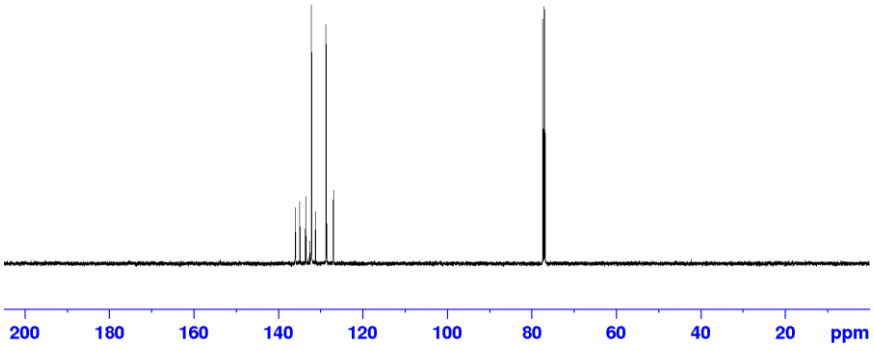




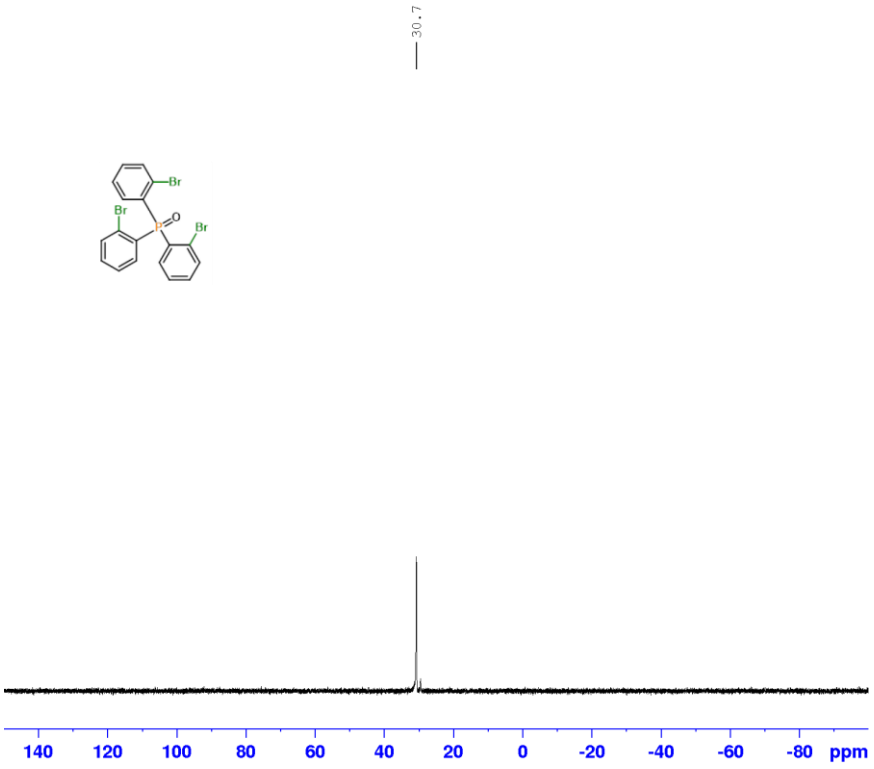
^{13}C NMR, $CDCl_3$, 125 MHz (2i)





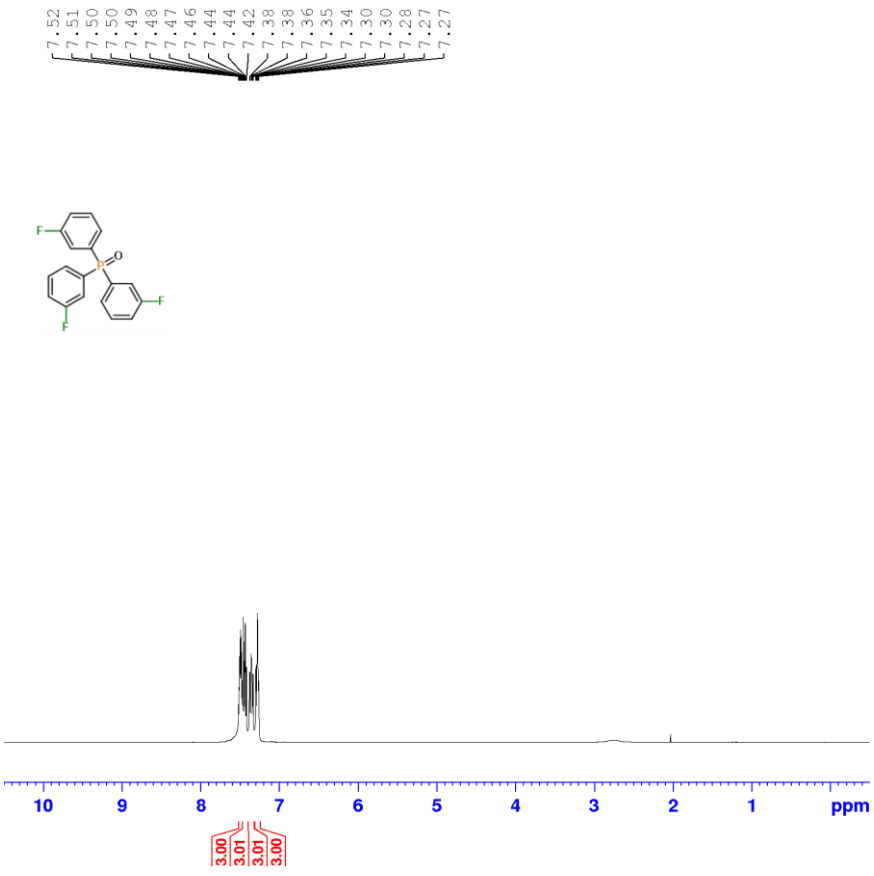


^{31}P NMR, $CDCl_3$, 202 MHz (2i)

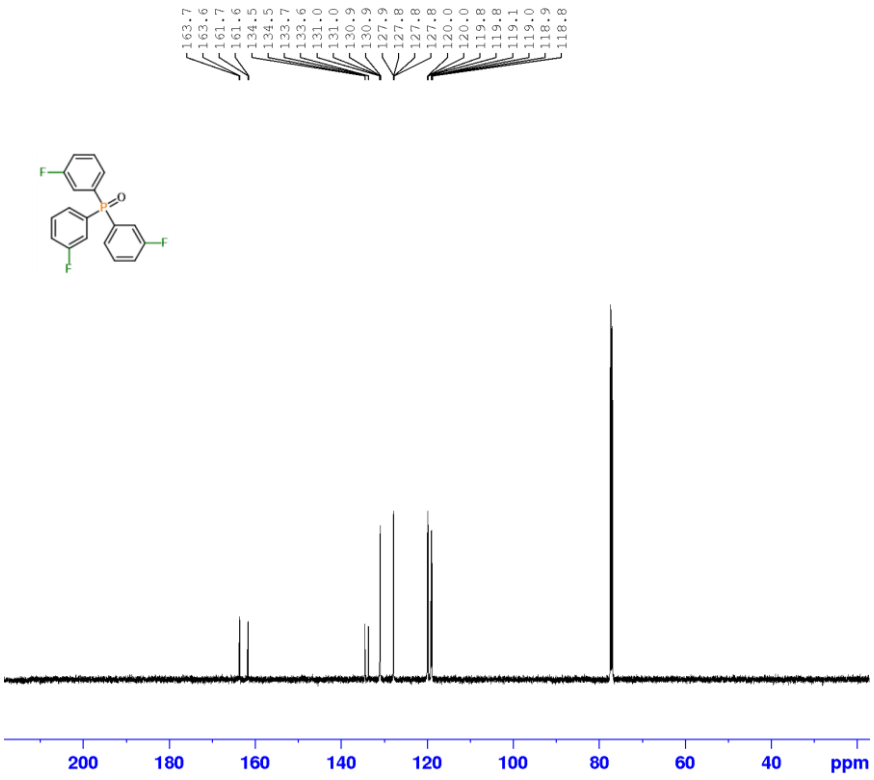


Tris(3-fluorophenyl)phosphine oxide (2j)

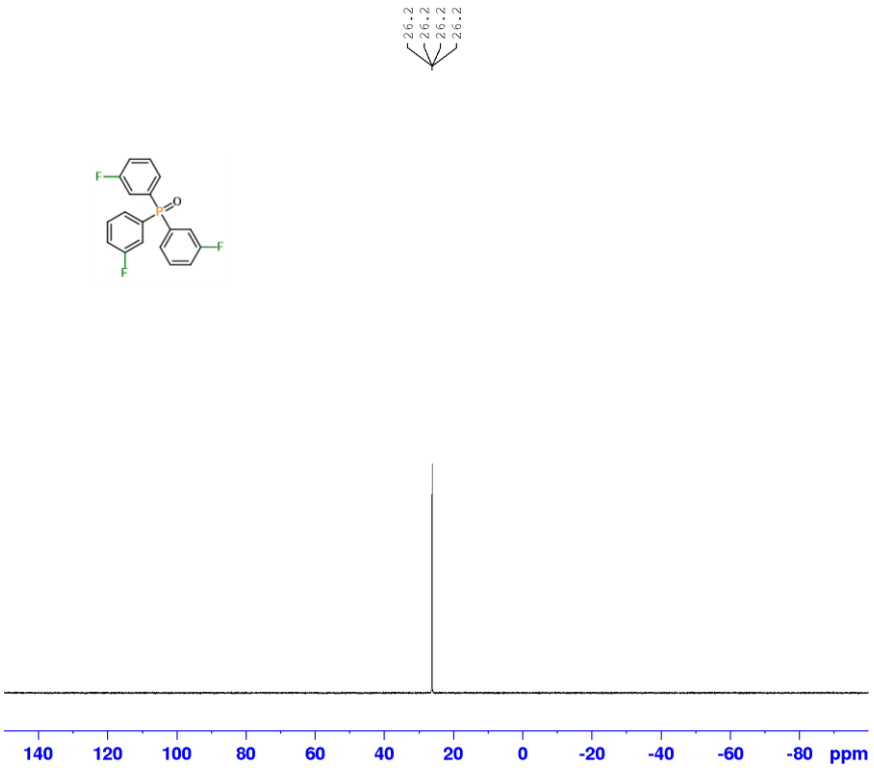
^{1}H NMR, $CDCl_3$, 500 MHz (2j)



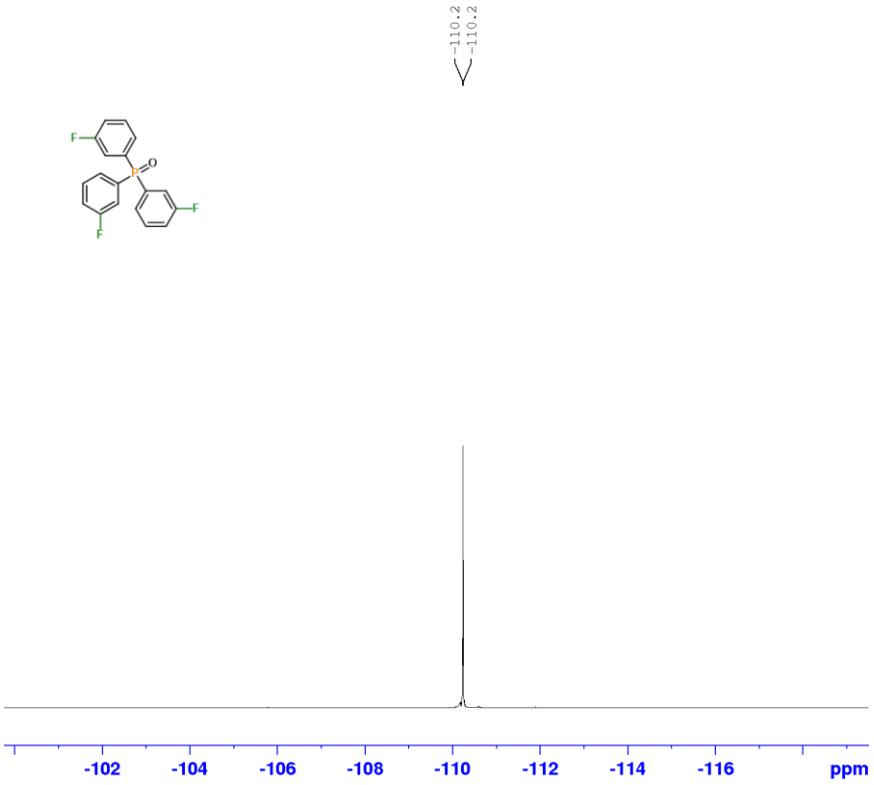
^{13}C NMR, $CDCl_3$, 125 MHz (2j)



^{31}P NMR, $CDCl_3$, 202 MHz (2j)

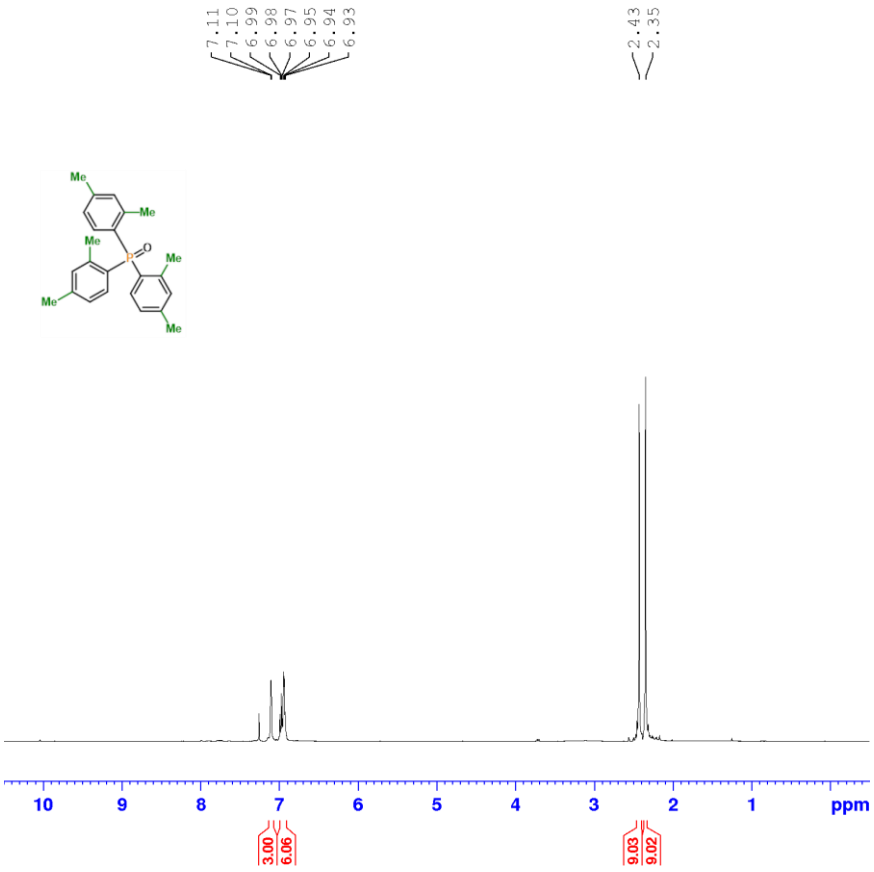


^{19}F NMR, $CDCl_3$, 470 MHz (2j)

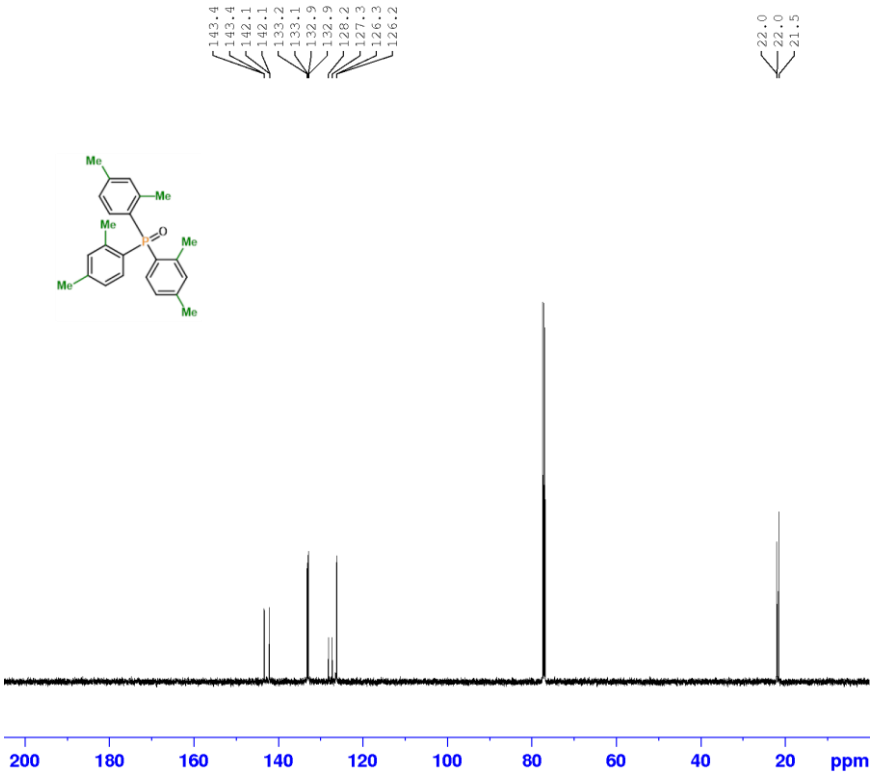


Tris(2,4-dimethylphenyl)phosphine oxide (2k)

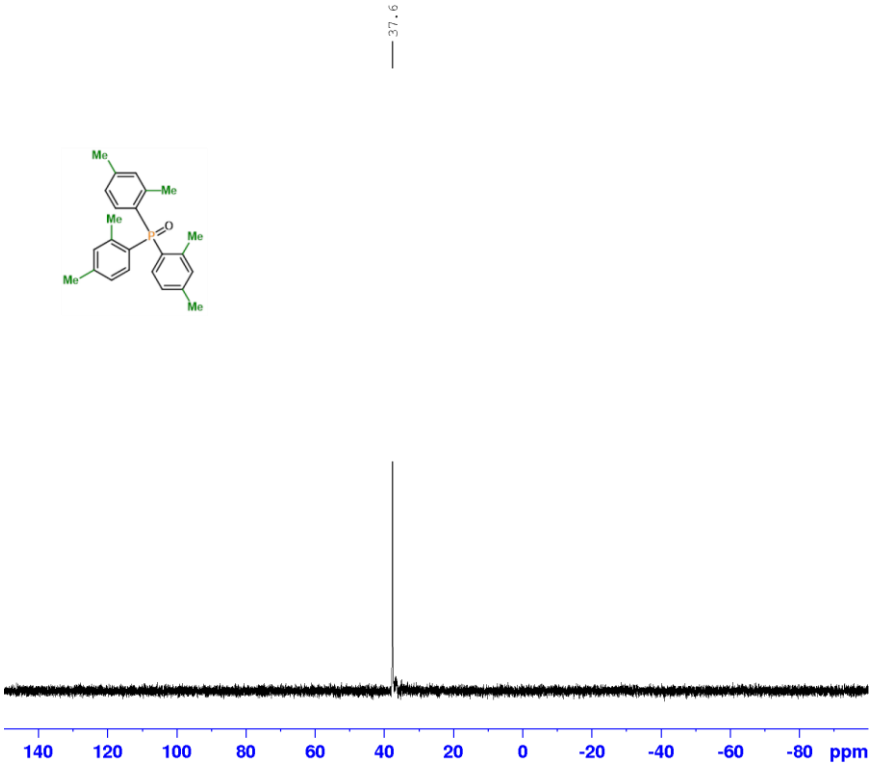
^{1}H NMR, $CDCl_3$, 500 MHz (2k)



^{13}C NMR, $CDCl_3$, 125 MHz (2k)

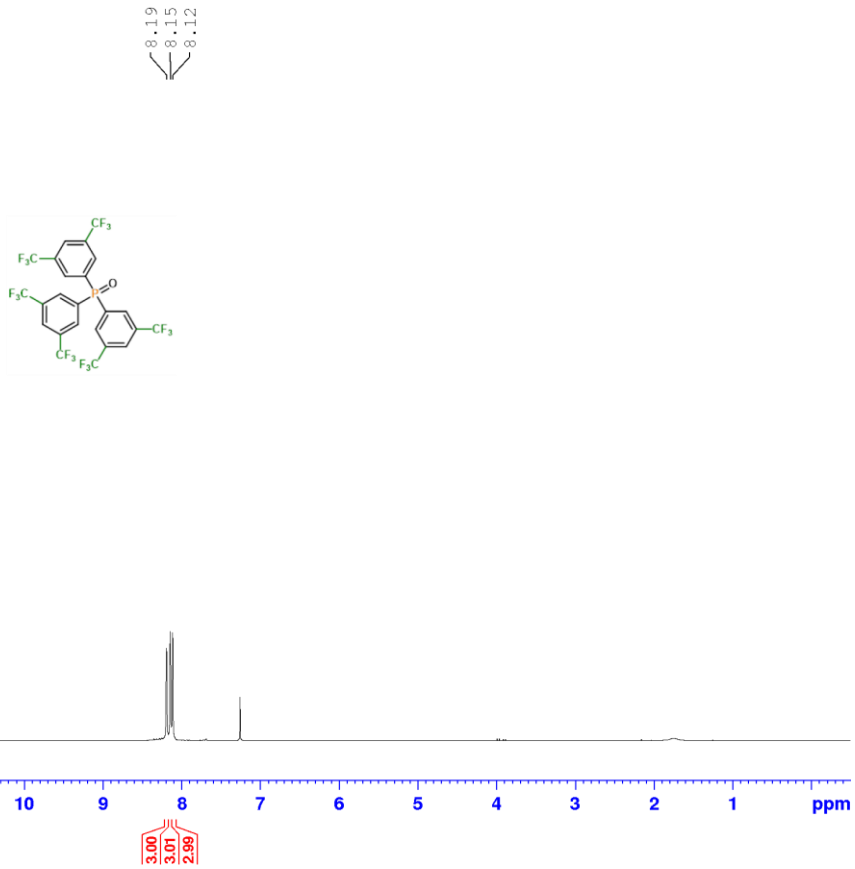


^{31}P NMR, $CDCl_3$, 202 MHz (2k)

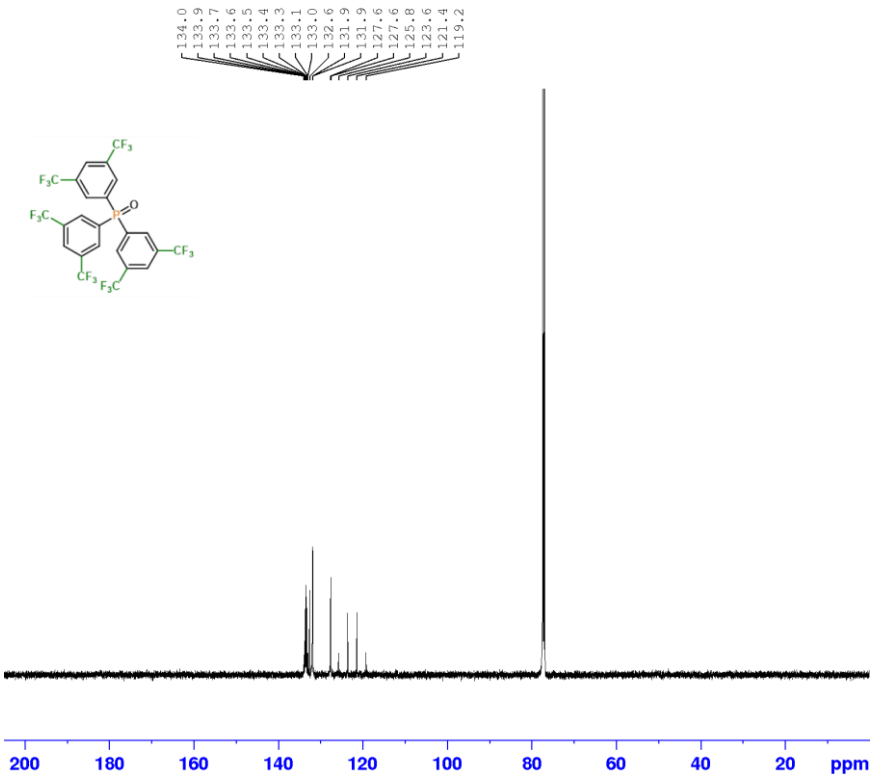


Tris(3,5-bis(trifluoromethyl)phenyl)phosphine oxide (2l)

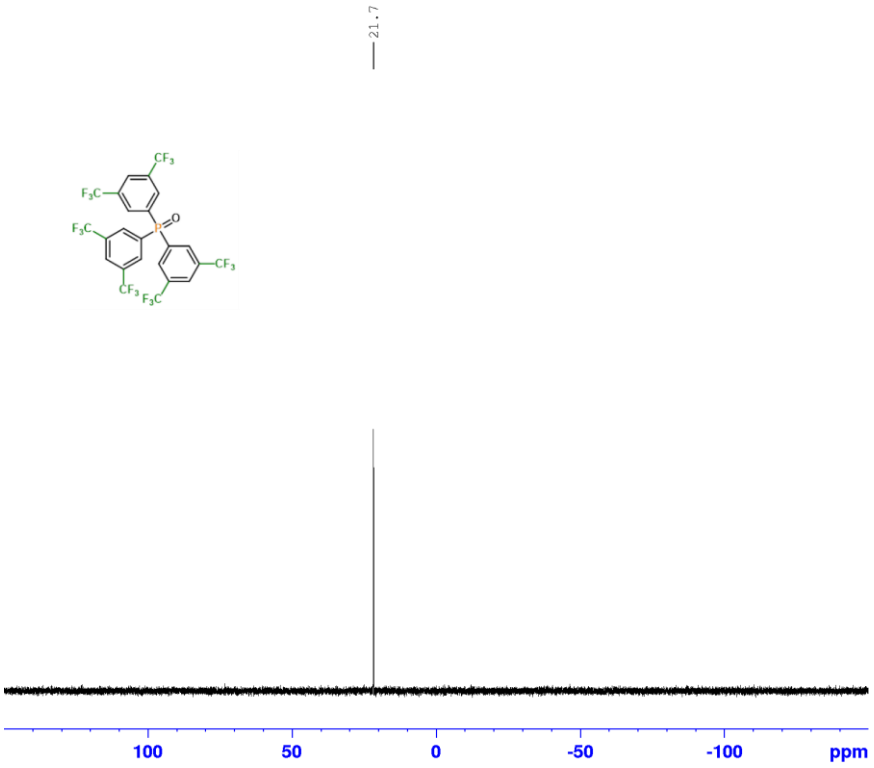
^{1}H NMR, $CDCl_3$, 400 MHz (2l)



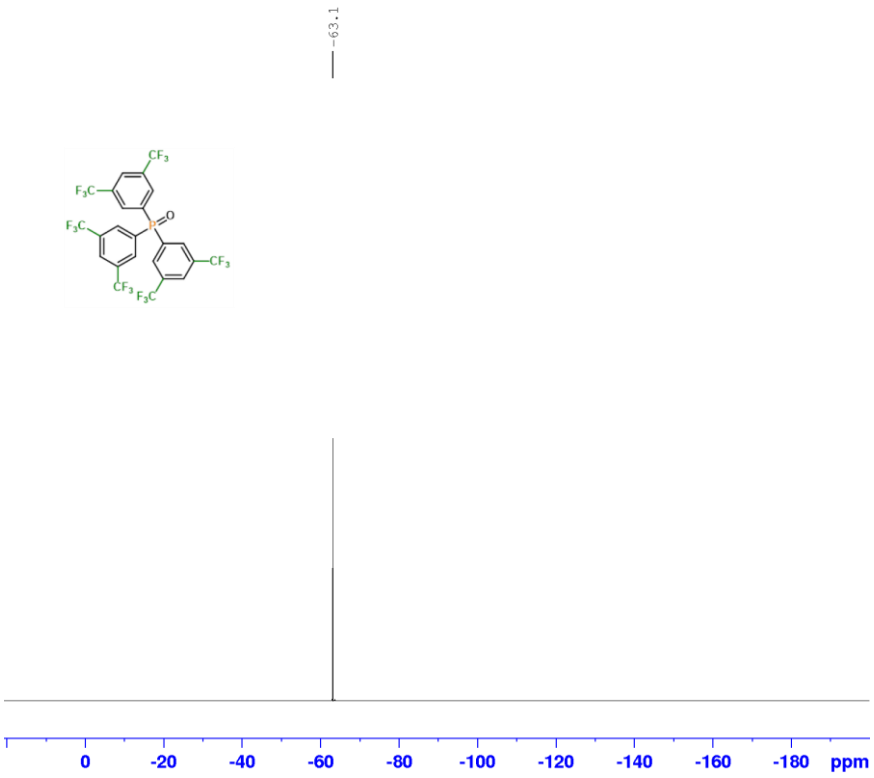
^{13}C NMR, $CDCl_3$, 125 MHz (2l)



^{31}P NMR, $CDCl_3$, 162 MHz (2l)

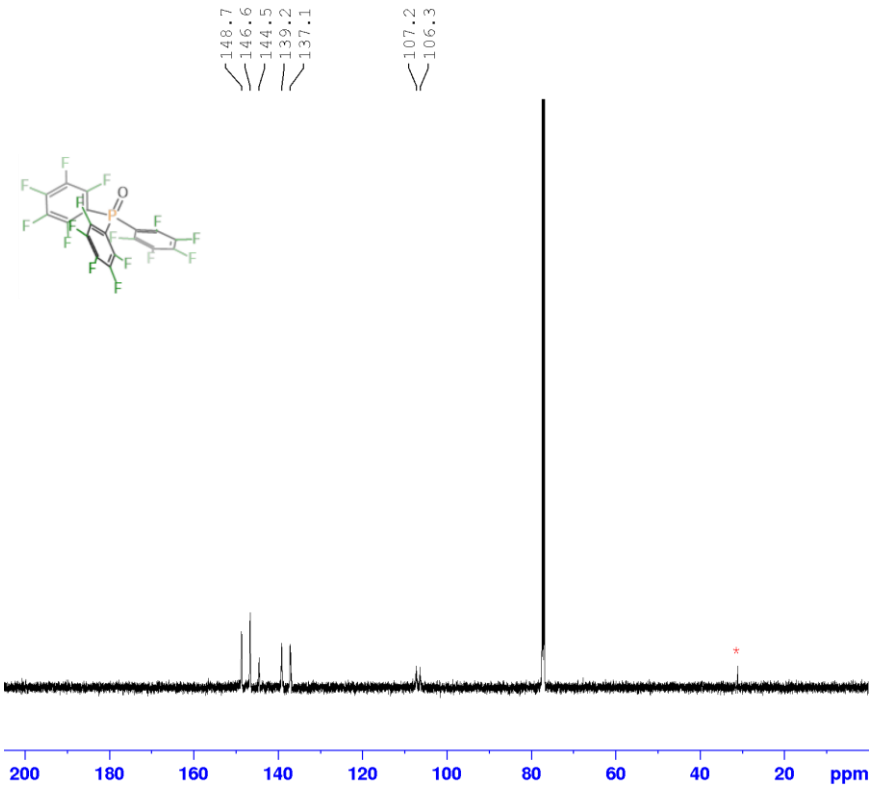


^{19}F NMR, $CDCl_3$, 376 MHz (2l)



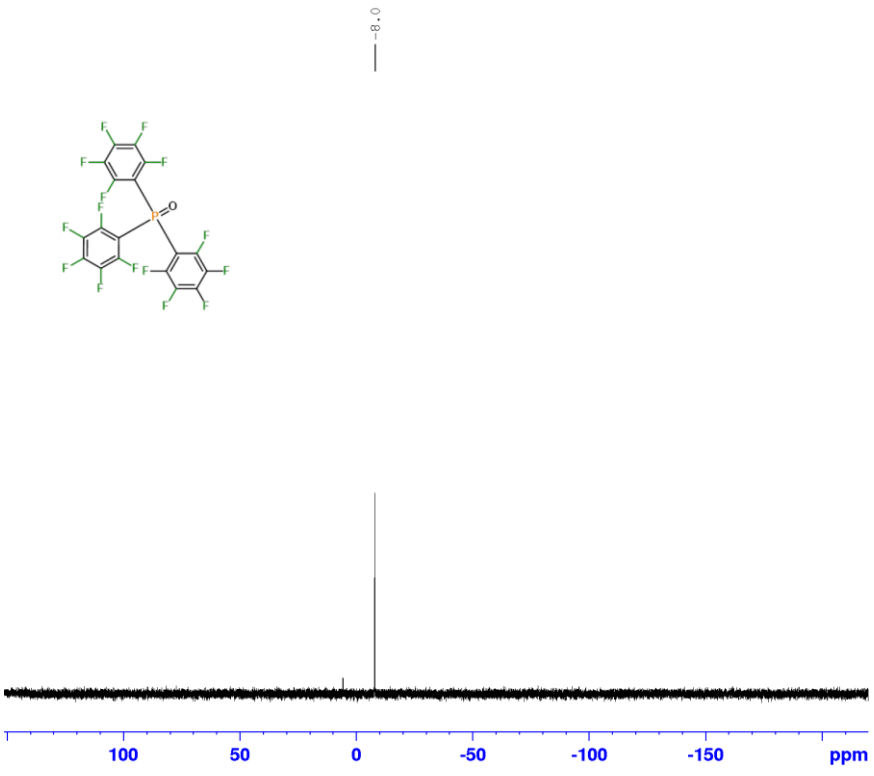
Tris(perfluorophenyl)phosphine oxide (2m)

^{13}C NMR, $CDCl_3$, 125 MHz (2m)

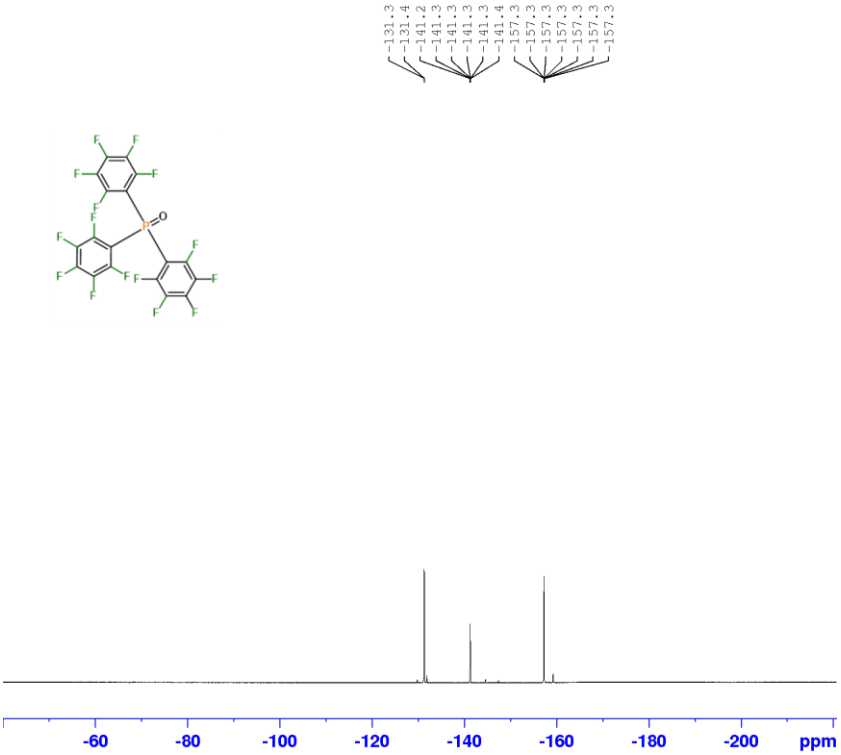


* = Solvent

^{31}P NMR, $CDCl_3$, 202 MHz (2m)

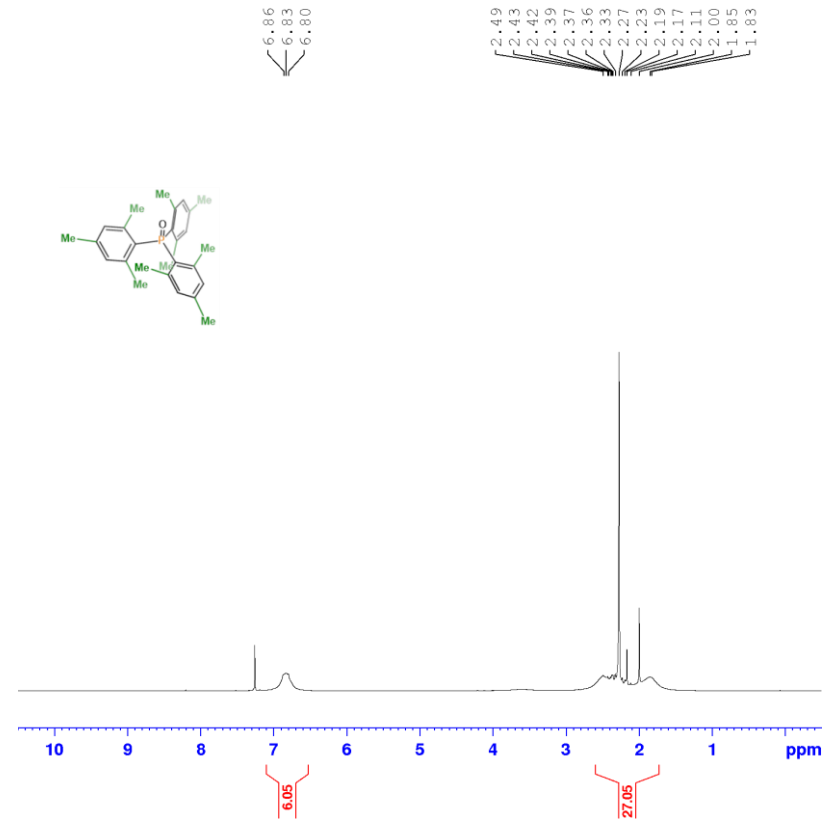


^{19}F NMR, $CDCl_3$, 470 MHz (2m)

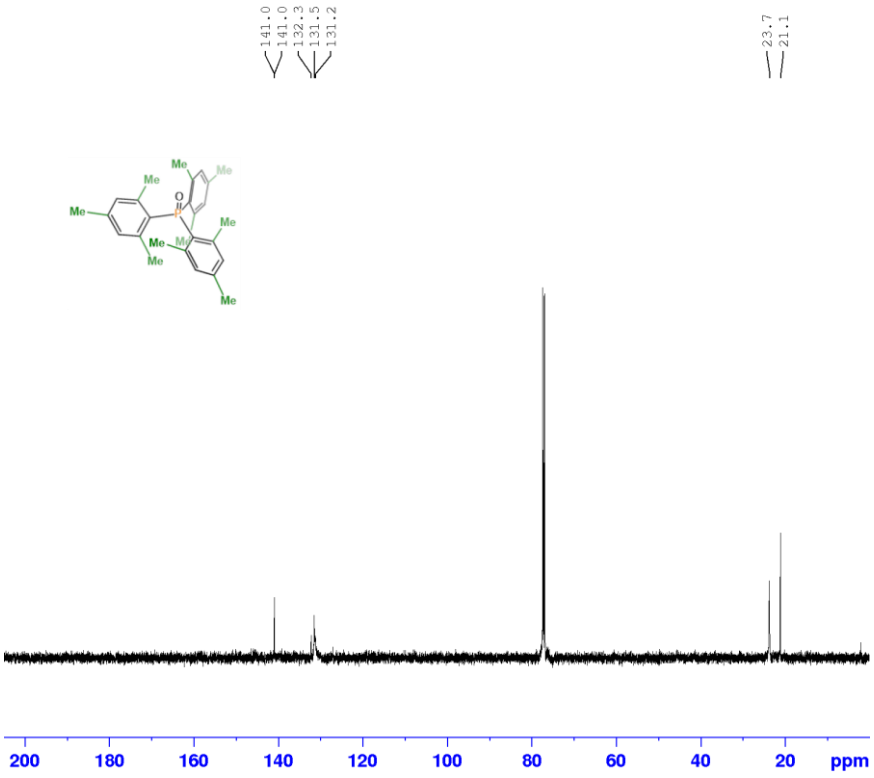


Trimesitylphosphine oxide (2n)

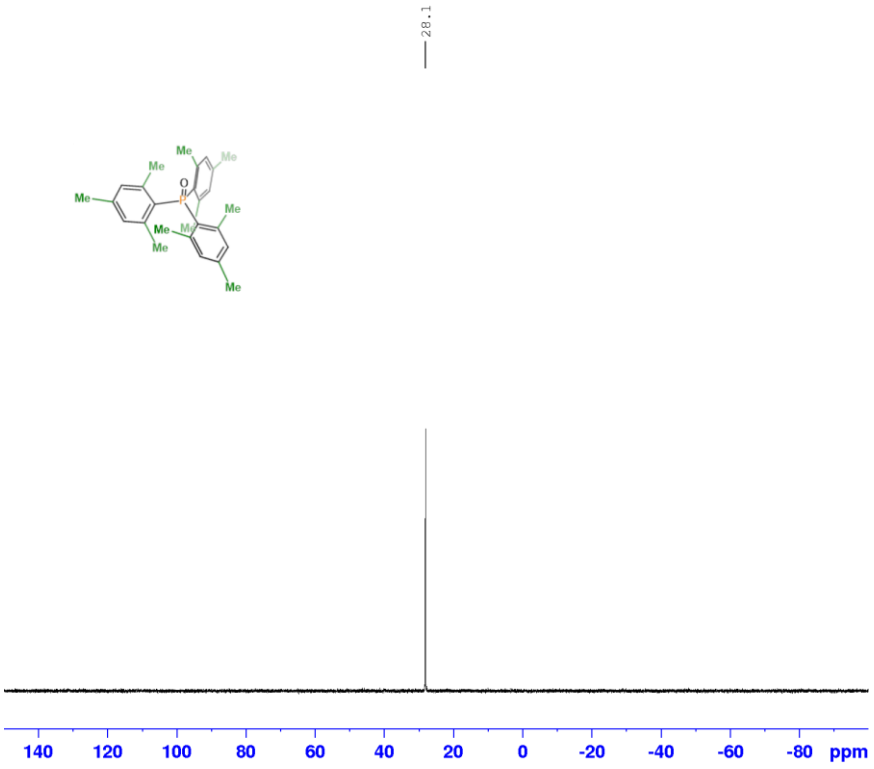
^{1}H NMR, $CDCl_3$, 400 MHz (2n)



^{13}C NMR, $CDCl_3$, 125 MHz (2n)

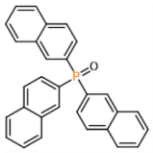


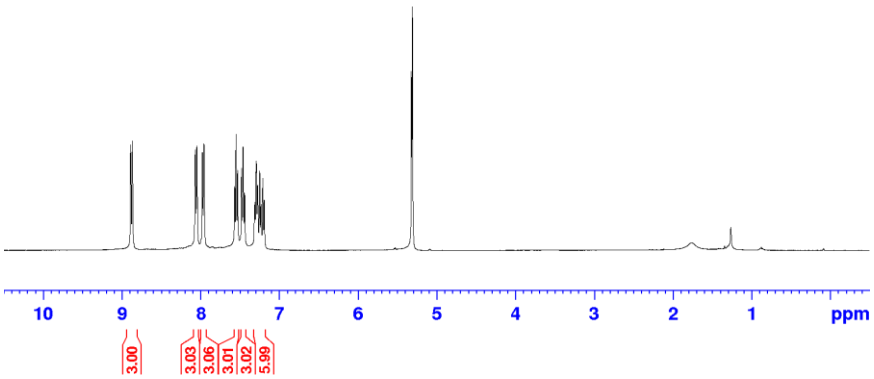
^{31}P NMR, $CDCl_3$, 162 MHz (2n)



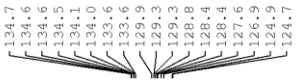
Tri(naphthalen-2-yl)phosphine oxide (2o)

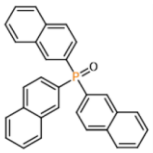
^{1}H NMR, CD_2Cl_2, 400 MHz (2o)



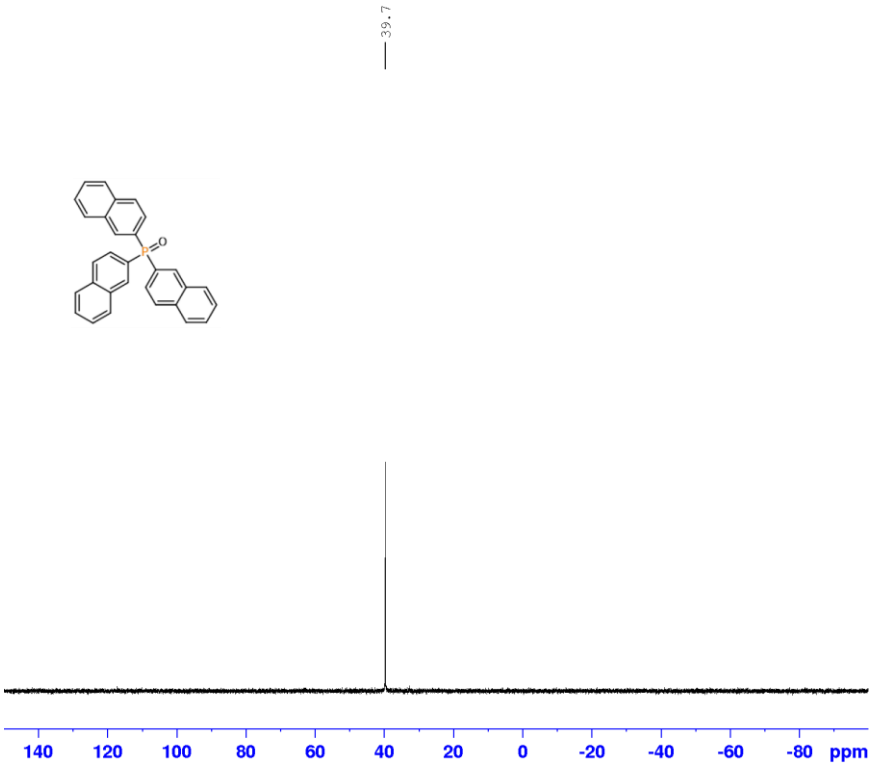


^{13}C NMR, CD_2Cl_2, 100 MHz (2o)



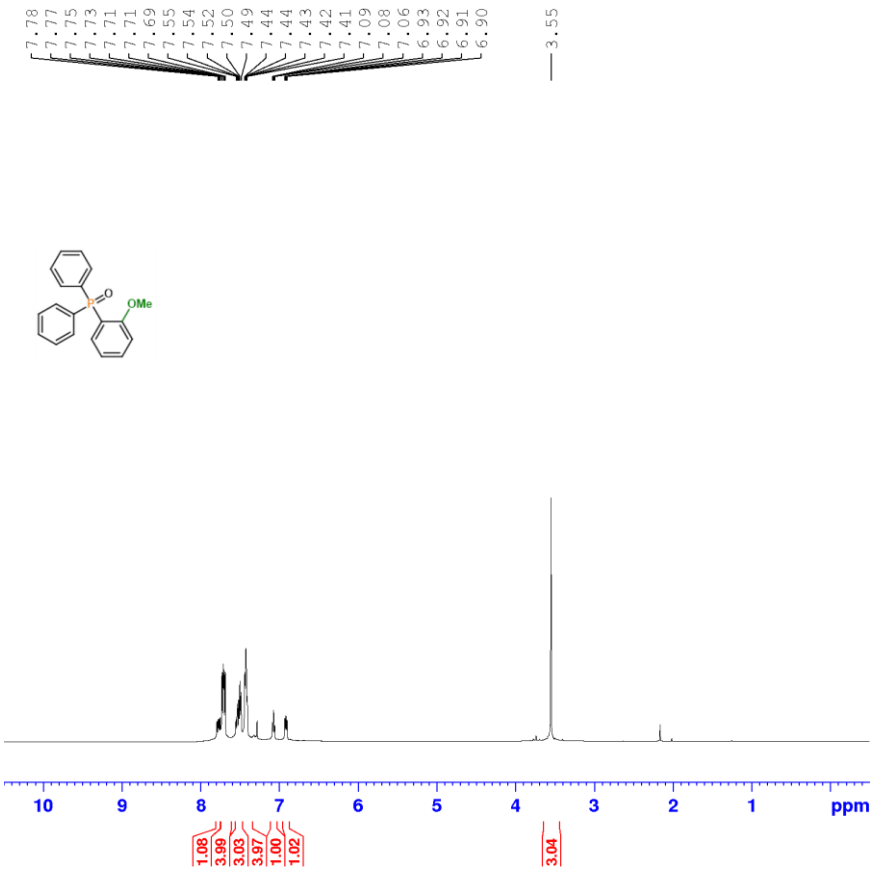


^{31}P NMR, $CDCl_3$, 162 MHz (2o)

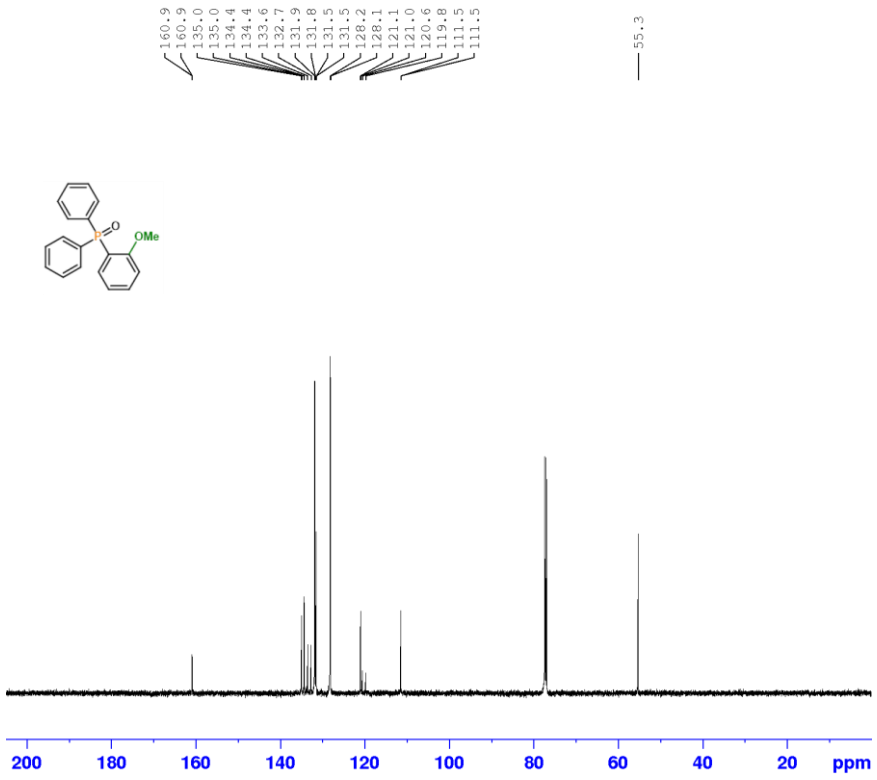


(2-methoxyphenyl)diphenylphosphine oxide (2p)

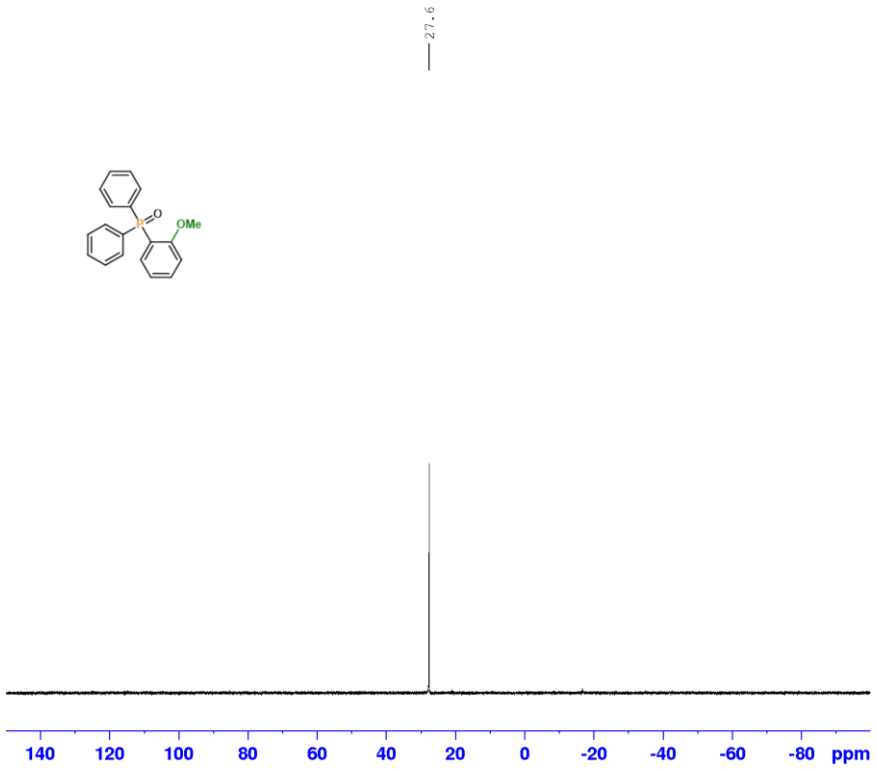
^{1}H NMR, $CDCl_3$, 500 MHz (2p)



^{13}C NMR, $CDCl_3$, 125 MHz (2p)

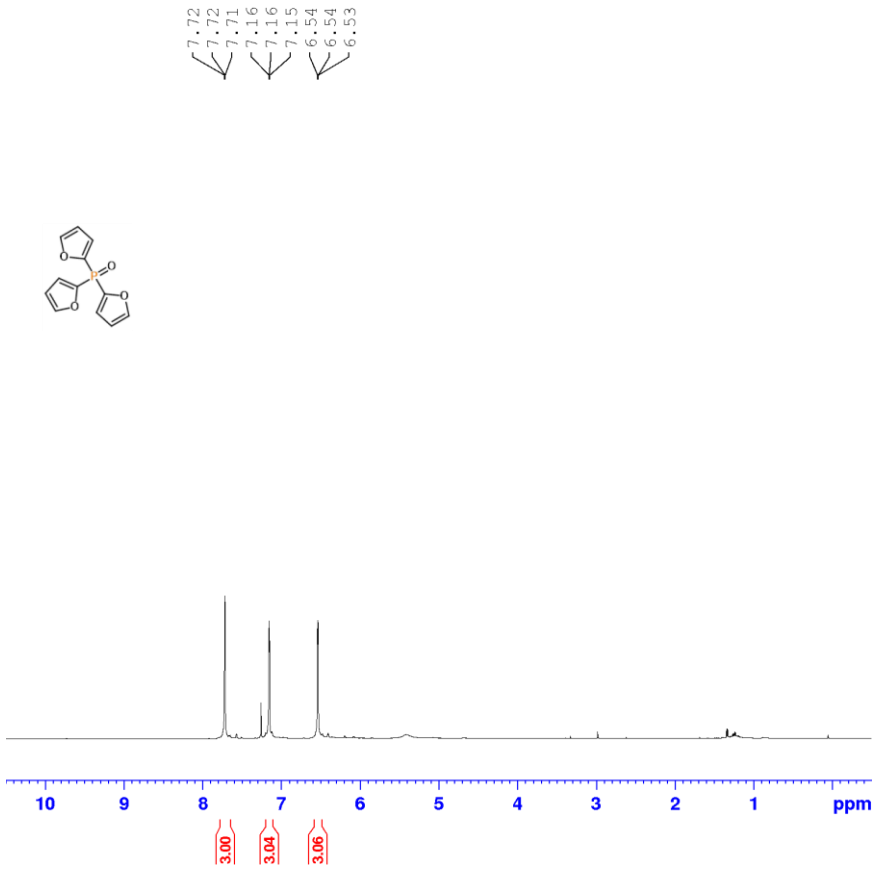


^{31}P NMR, $CDCl_3$, 202 MHz (2p)

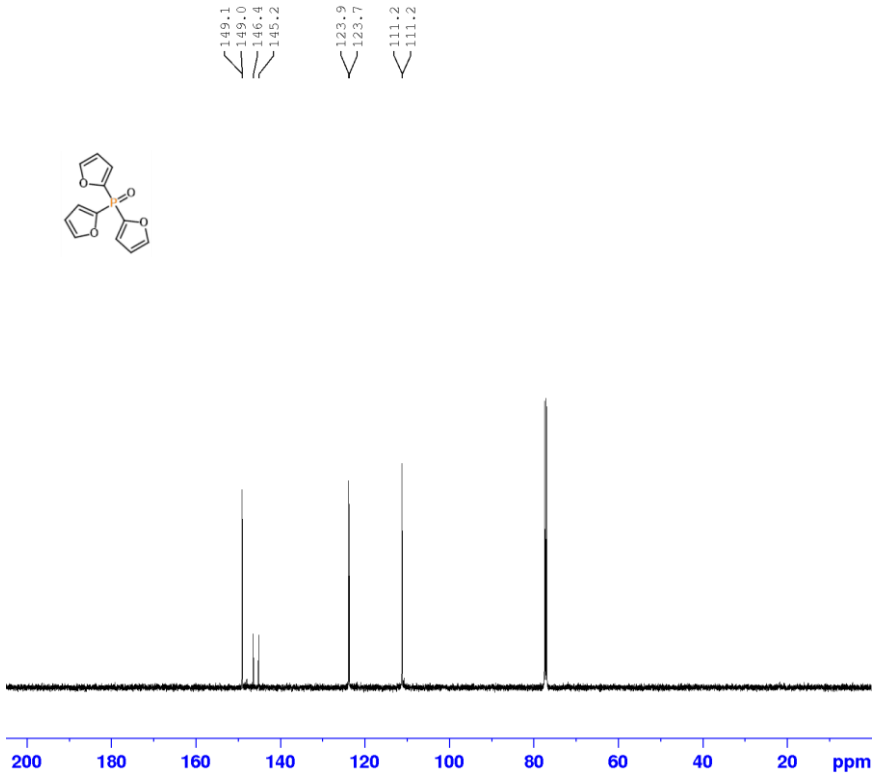


Tri(furan-2-yl)phosphine oxide (2q)

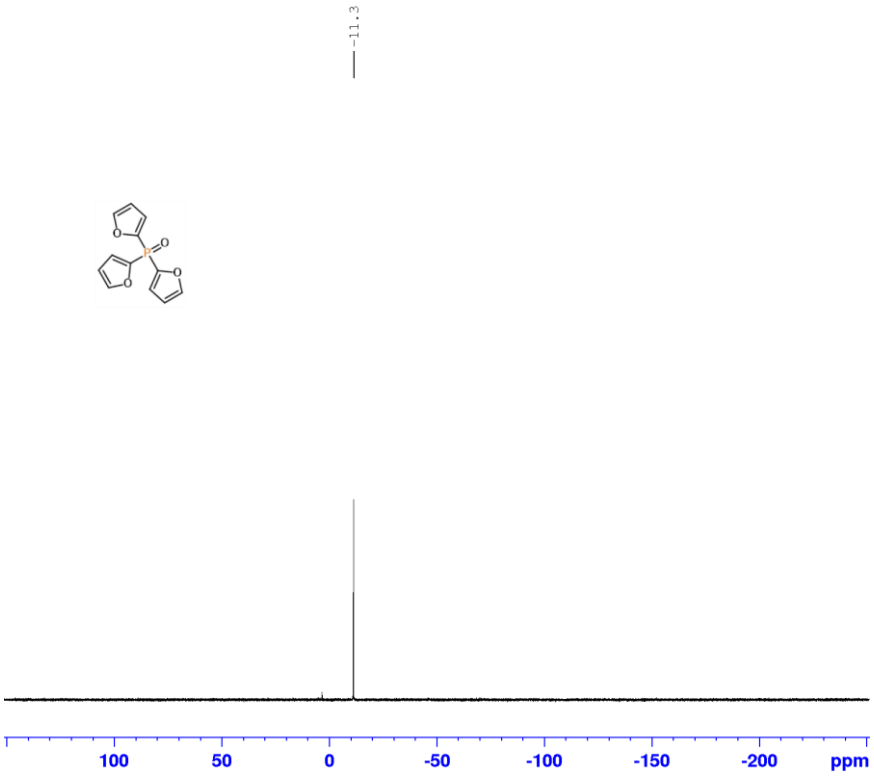
^{1}H NMR, $CDCl_3$, 500 MHz (2q)



^{13}C NMR, $CDCl_3$, 125 MHz (2q)

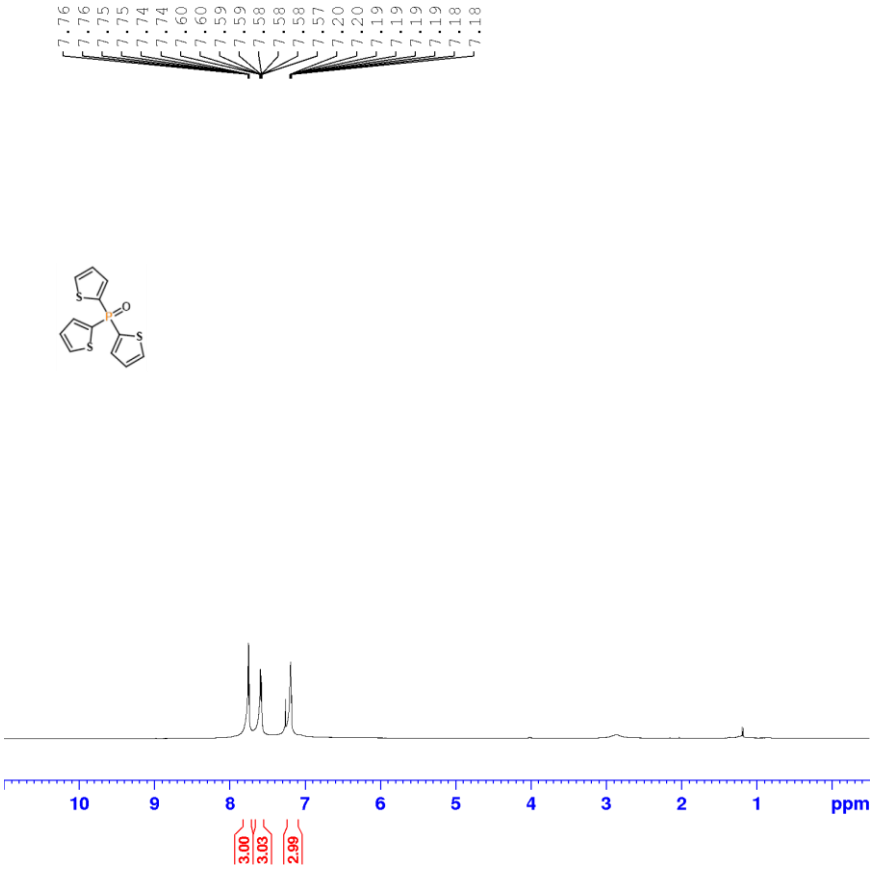


^{31}P NMR, $CDCl_3$, 202 MHz (2q)

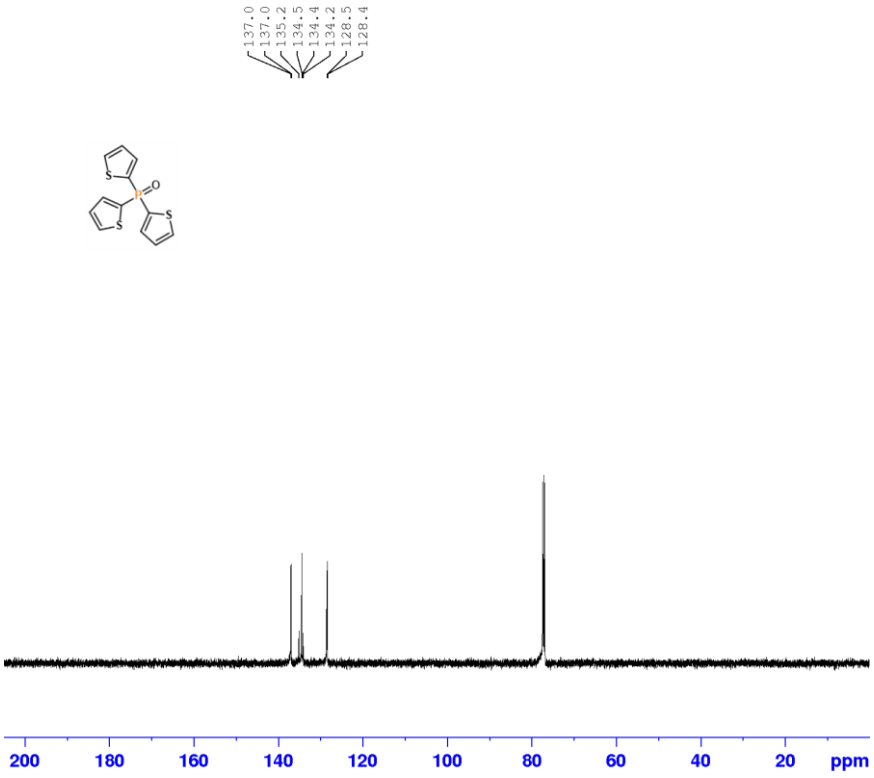


Tri(thiophen-2-yl)phosphine oxide (2r)

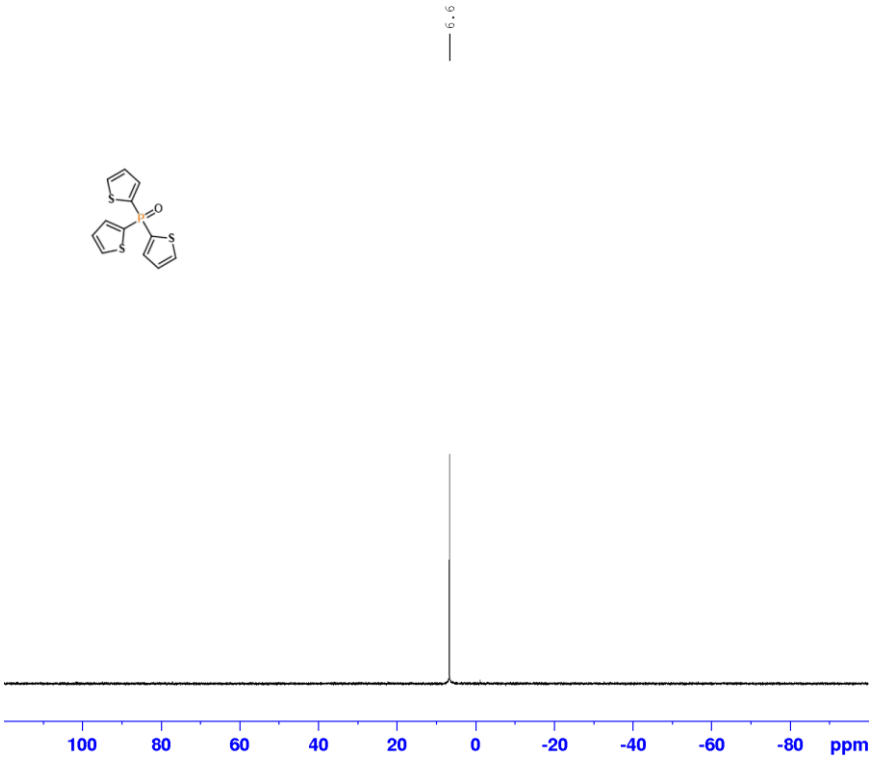
^{1}H NMR, $CDCl_3$, 500 MHz (2r)



^{13}C NMR, $CDCl_3$, 125 MHz (2r)

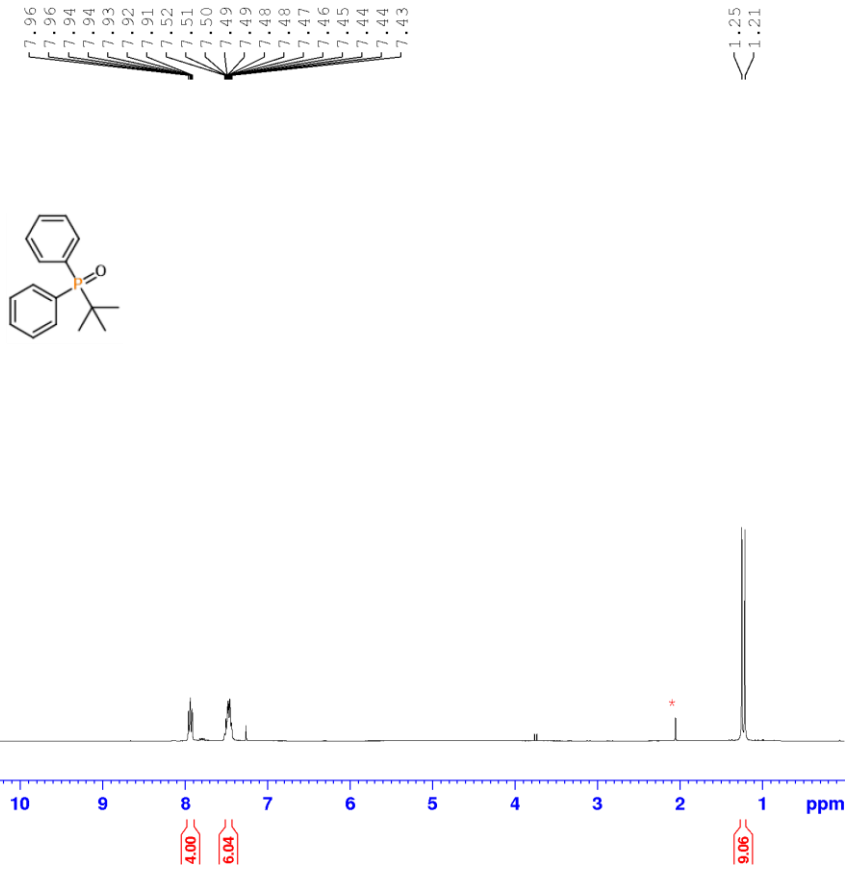


^{31}P NMR, $CDCl_3$, 202 MHz (2r)



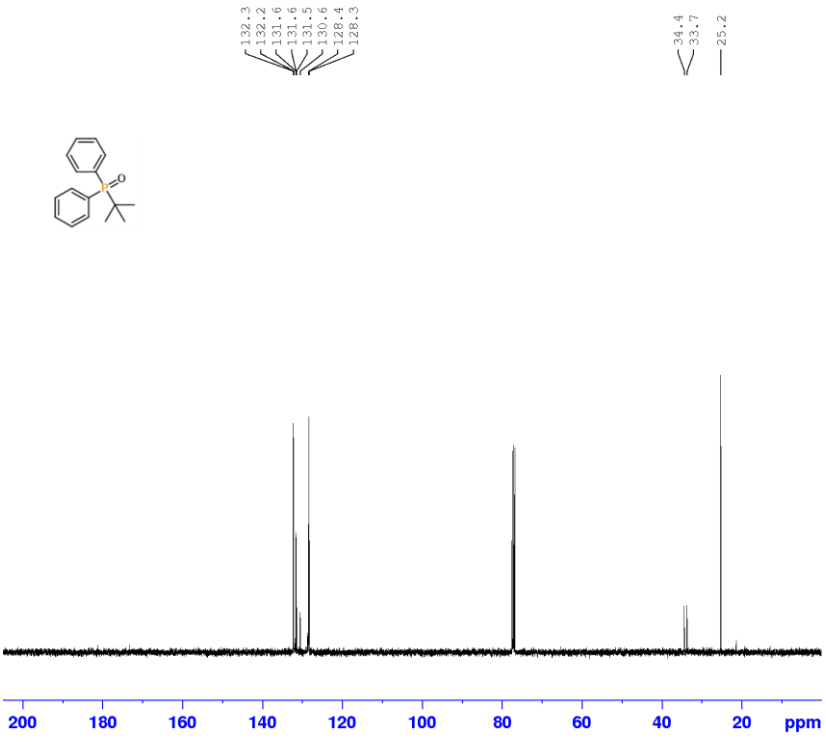
Tert-butyldiphenylphosphine oxide (2s)

^{1}H NMR, $CDCl_3$, 400 MHz (2s)

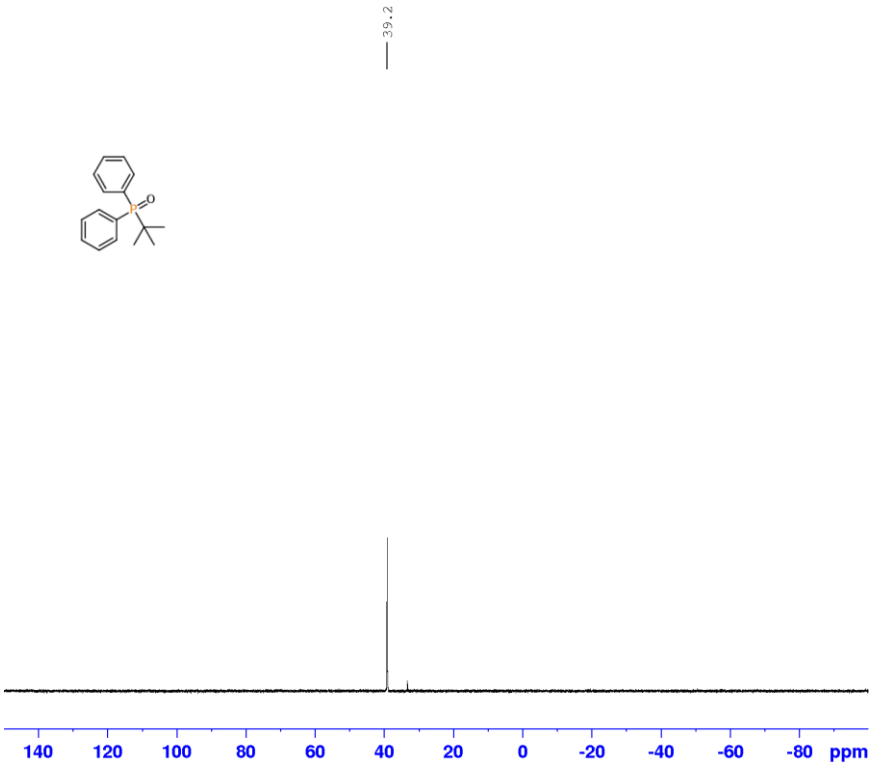


* = Solvent

^{13}C NMR, $CDCl_3$, 100 MHz (2s)

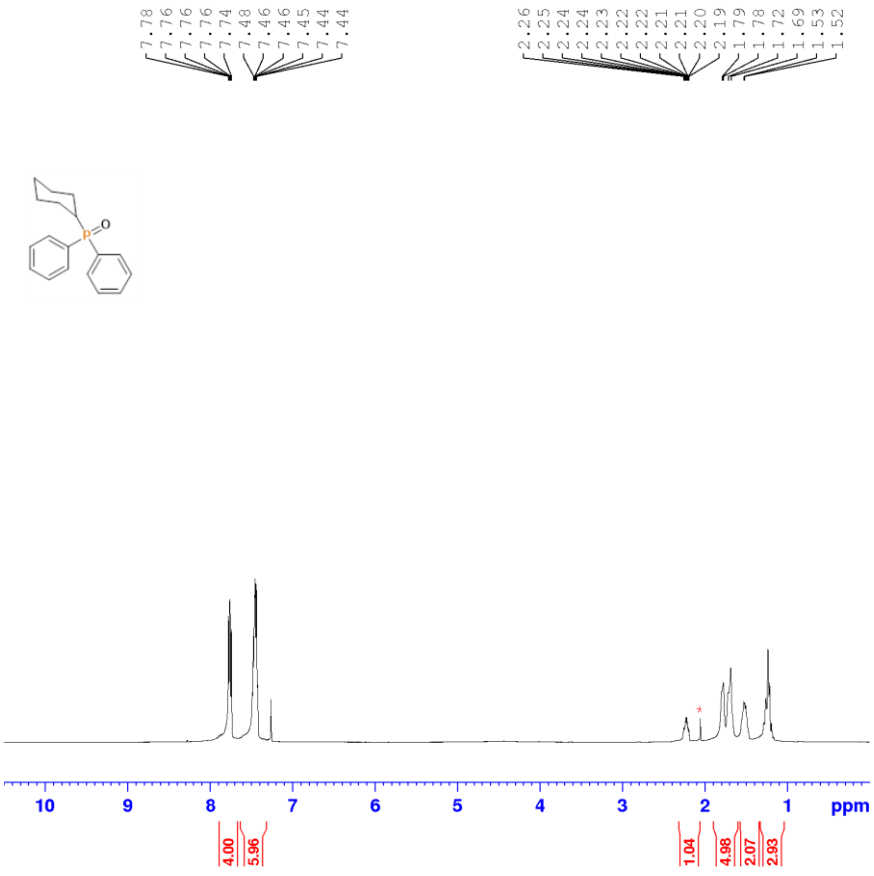


^{31}P NMR, $CDCl_3$, 202 MHz (2s)



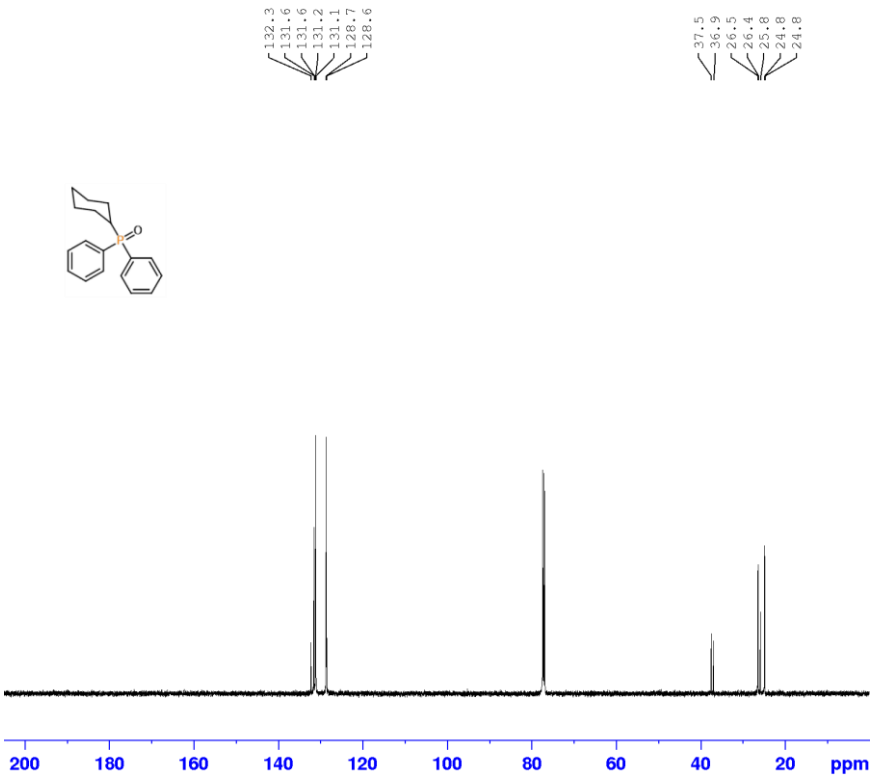
Cyclohexyldiphenylphosphine oxide (2t)

^{1}H NMR, $CDCl_3$, 500 MHz (2t)

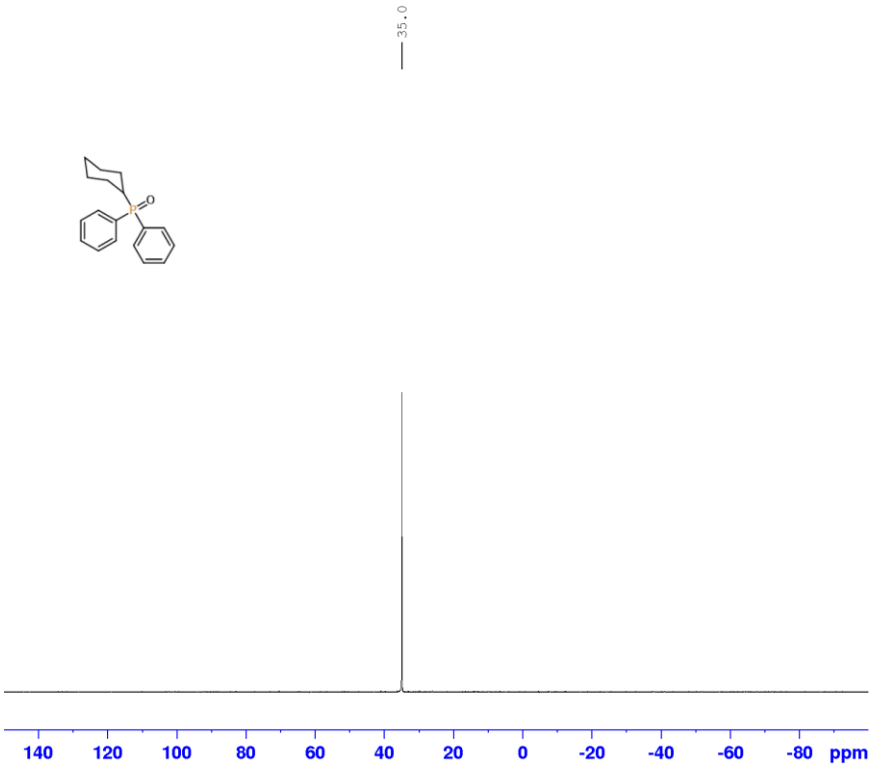


* = Solvent

^{13}C NMR, $CDCl_3$, 125 MHz (2t)

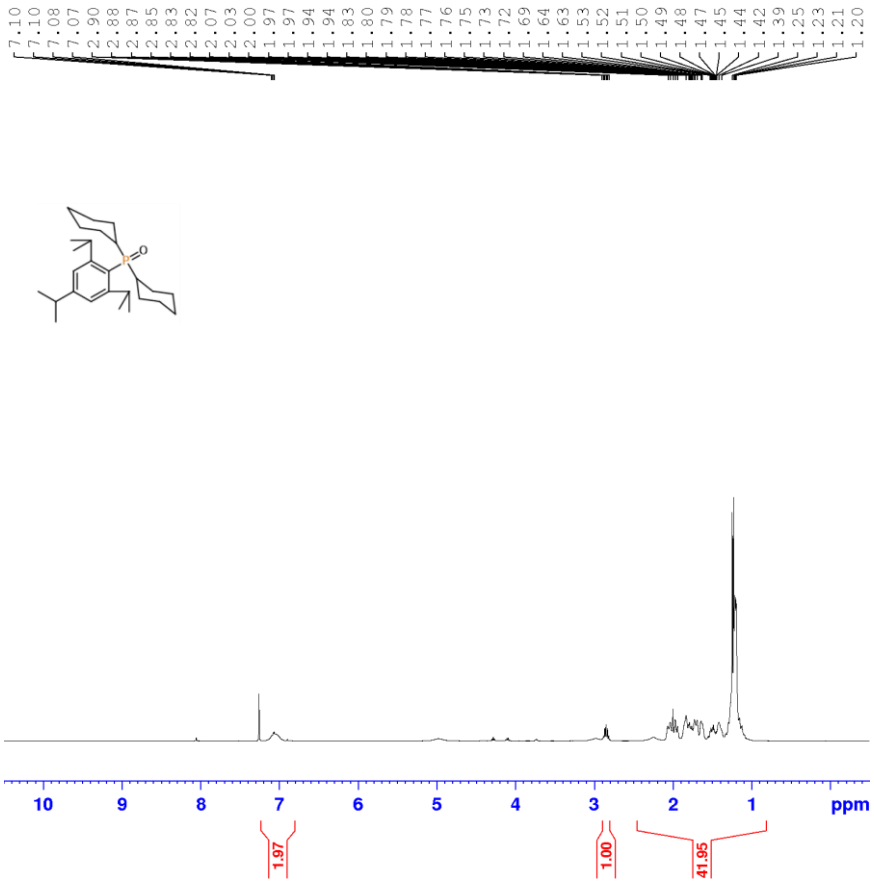


^{31}P NMR, $CDCl_3$, 202 MHz (2t)

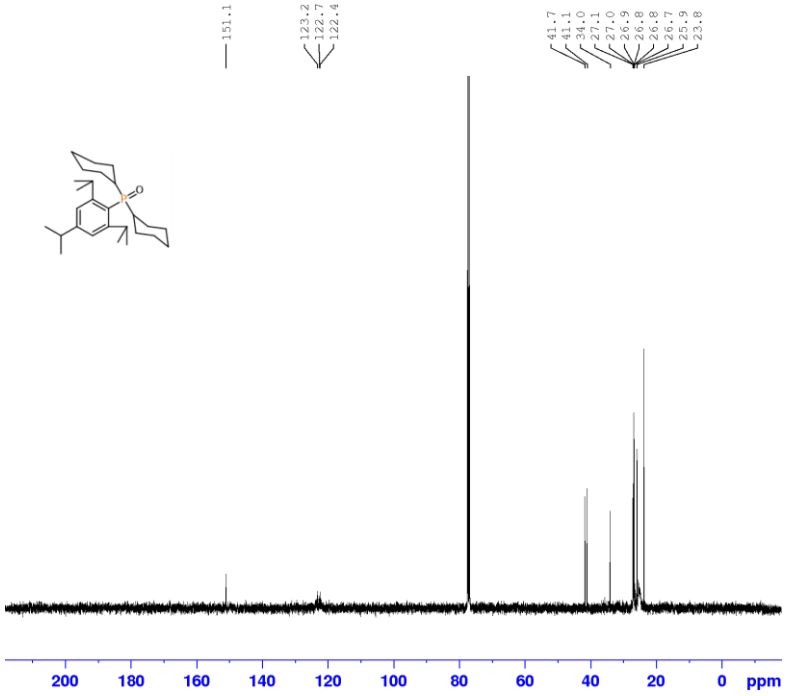


Dicyclohexyl(2,4,6-triisopropylphenyl)phosphine oxide (2u)

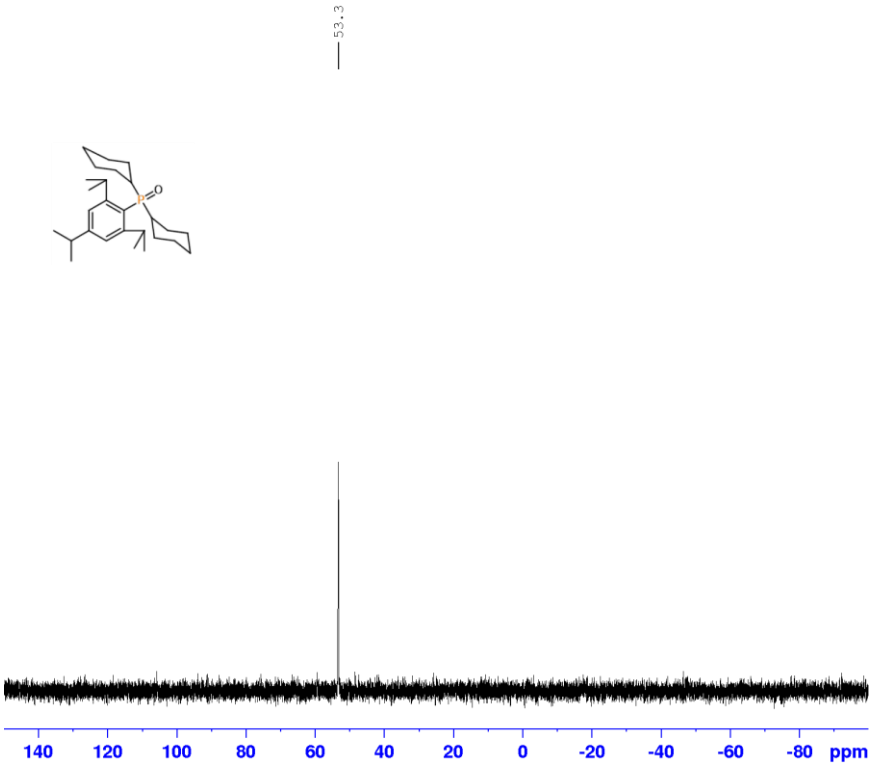
^{1}H NMR, $CDCl_3$, 400 MHz (2u)



^{13}C NMR, $CDCl_3$, 100 MHz (2u)

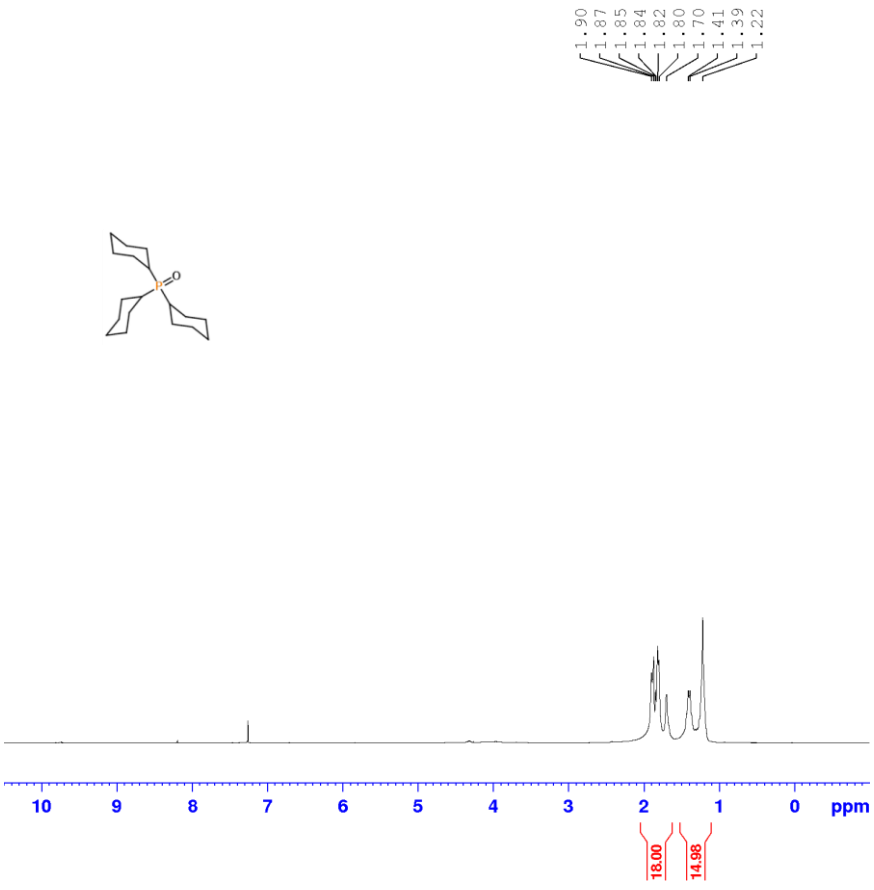


^{31}P NMR, $CDCl_3$, 162 MHz (2u)

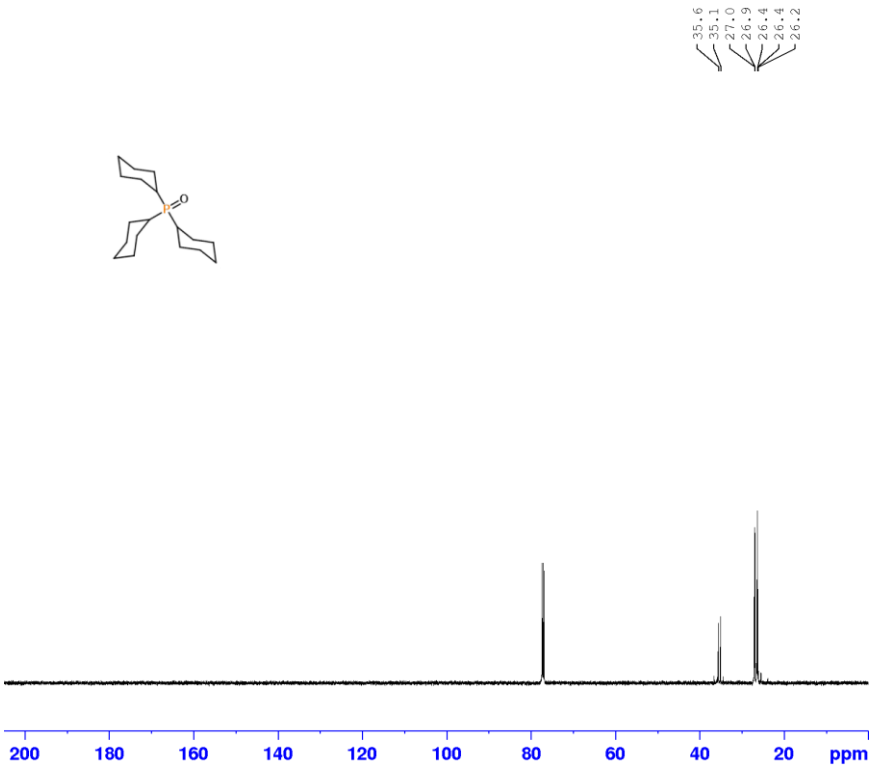


Tricyclohexylphosphine oxide (2v)

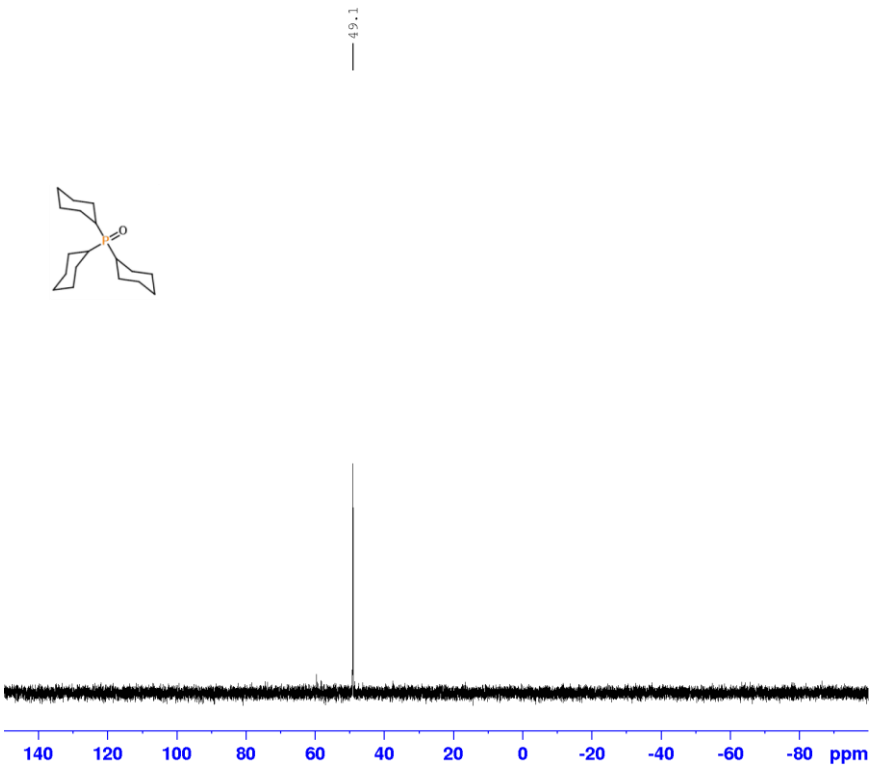
^{1}H NMR, $CDCl_3$, 500 MHz (2v)



^{13}C NMR, $CDCl_3$, 125 MHz (2v)

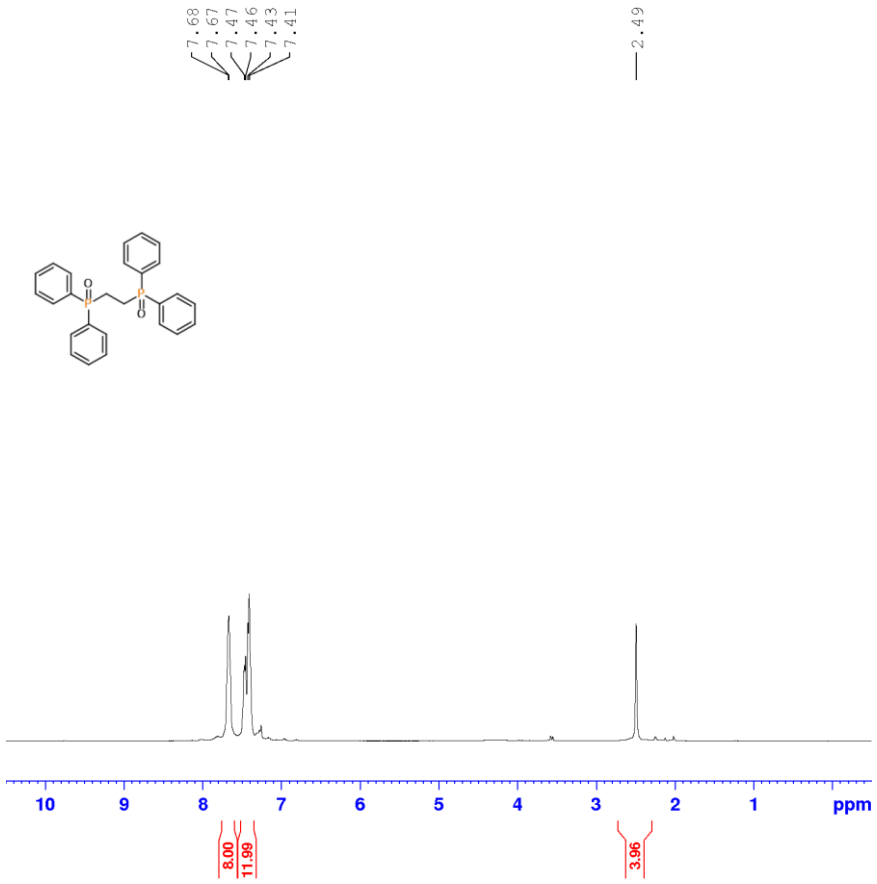


^{31}P NMR, $CDCl_3$, 202 MHz (2v)

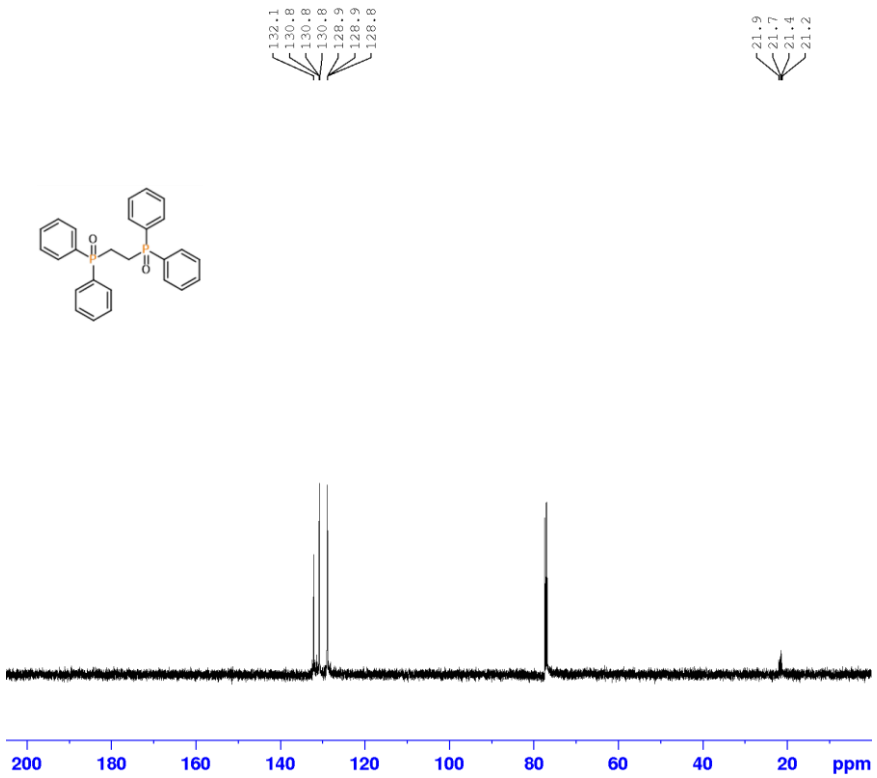


Ethane-1,2-diylbis(diphenylphosphine oxide) (2w)

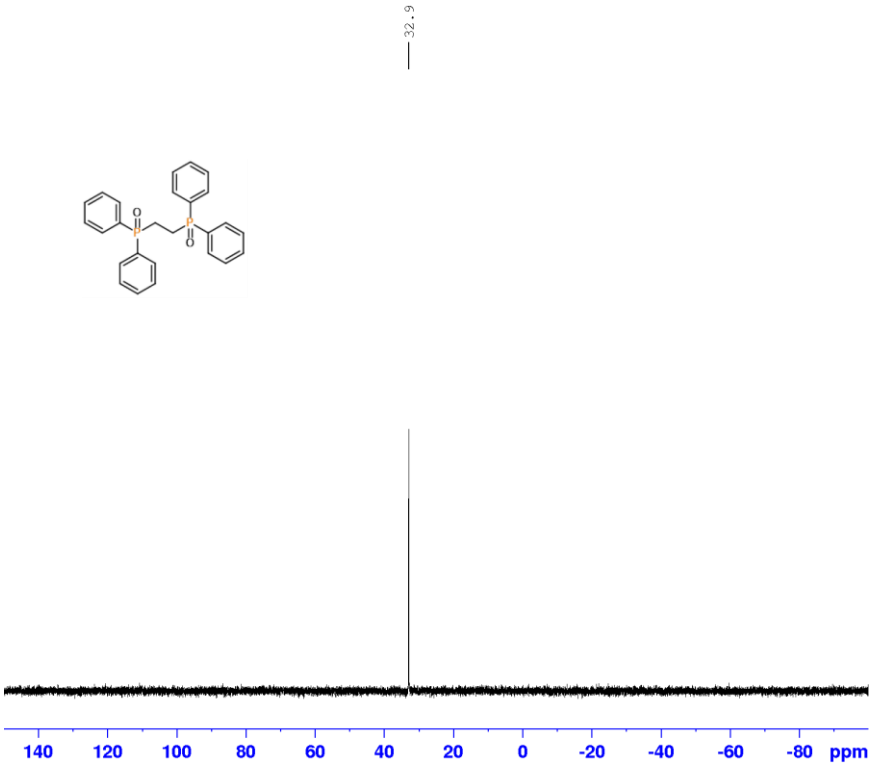
^{1}H NMR, $CDCl_3$, 400 MHz (2w)



^{13}C NMR, $CDCl_3$, 125 MHz (2w)

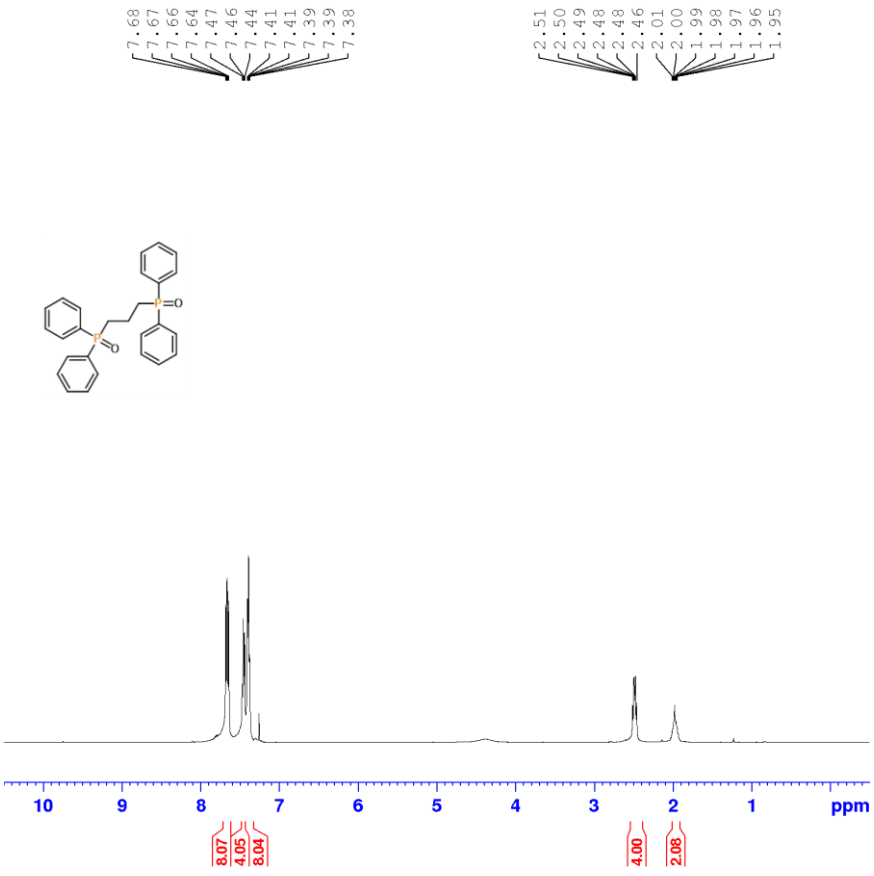


^{31}P NMR, $CDCl_3$, 202 MHz (2w)

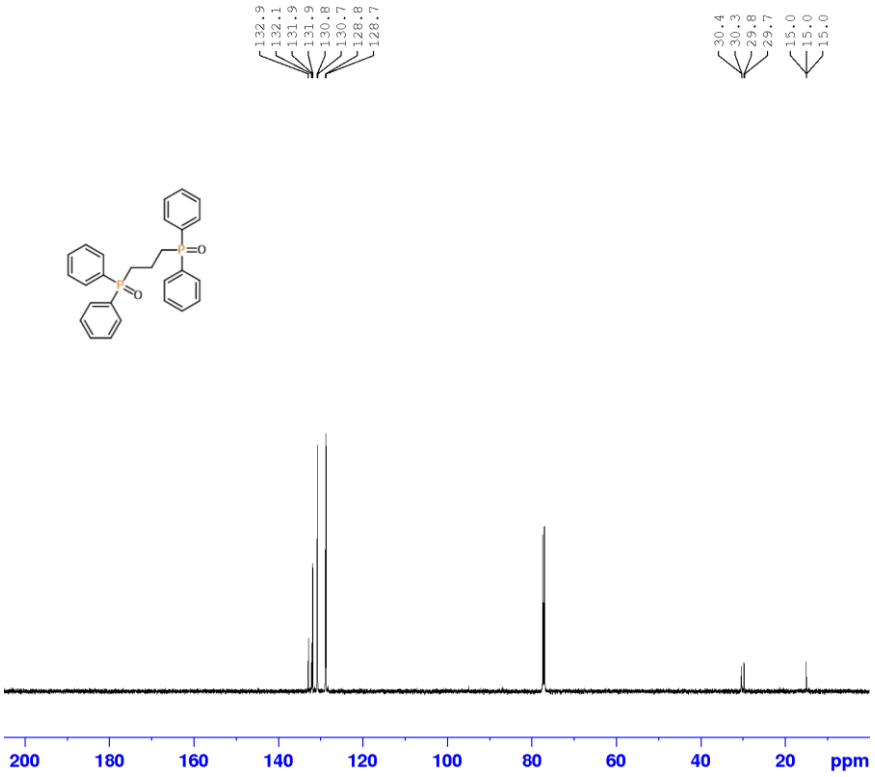


Propane-1,3-diylbis(diphenylphosphine oxide) (2x)

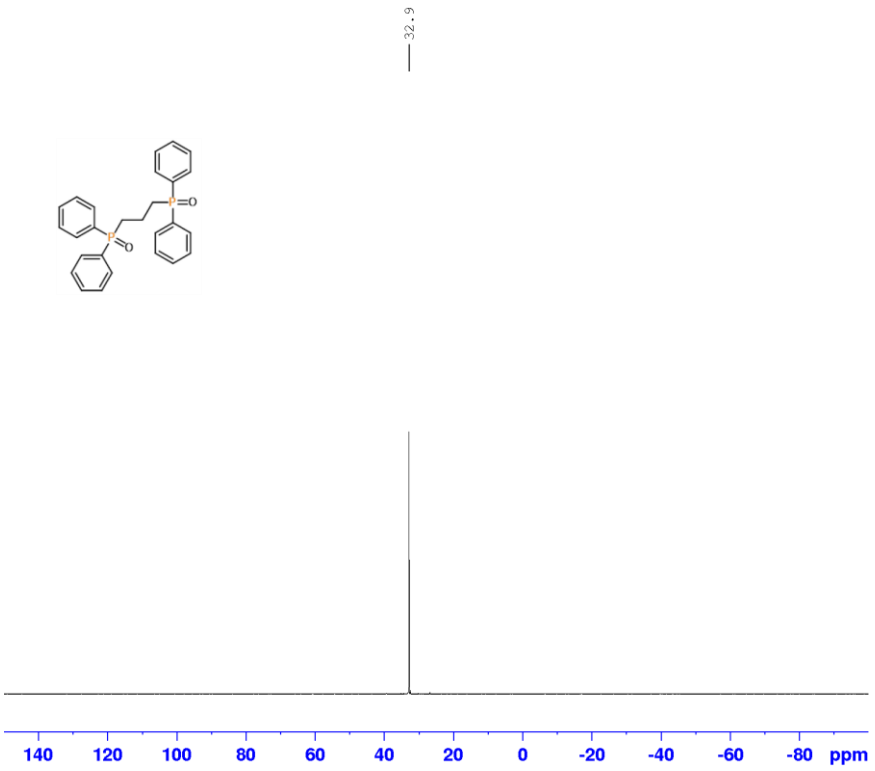
^{1}H NMR, $CDCl_3$, 500 MHz (2x)



^{13}C NMR, $CDCl_3$, 125 MHz (2x)

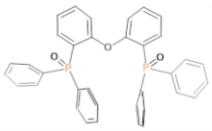


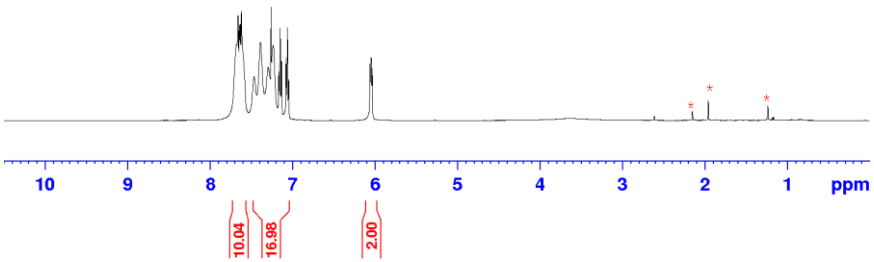
^{31}P NMR, $CDCl_3$, 202 MHz (2x)



(Oxybis(2,1-phenylene))bis(diphenylphosphine oxide) (2y)

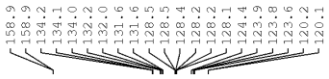
^{1}H NMR, $CDCl_3$, 500 MHz (2y)

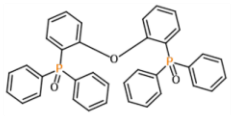


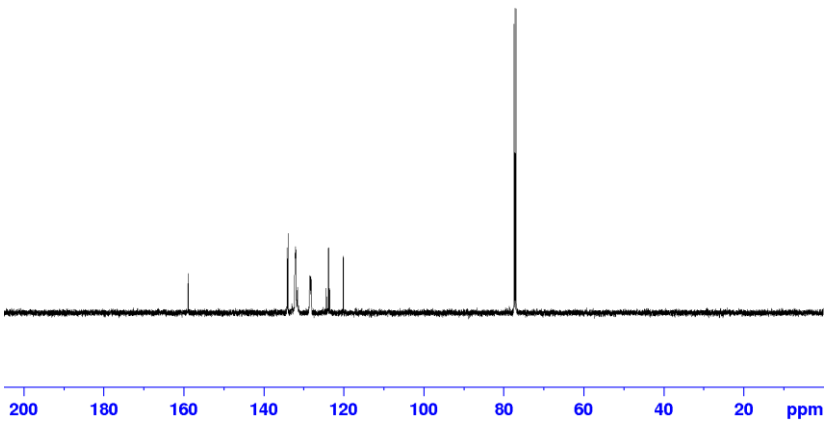


* = Solvent

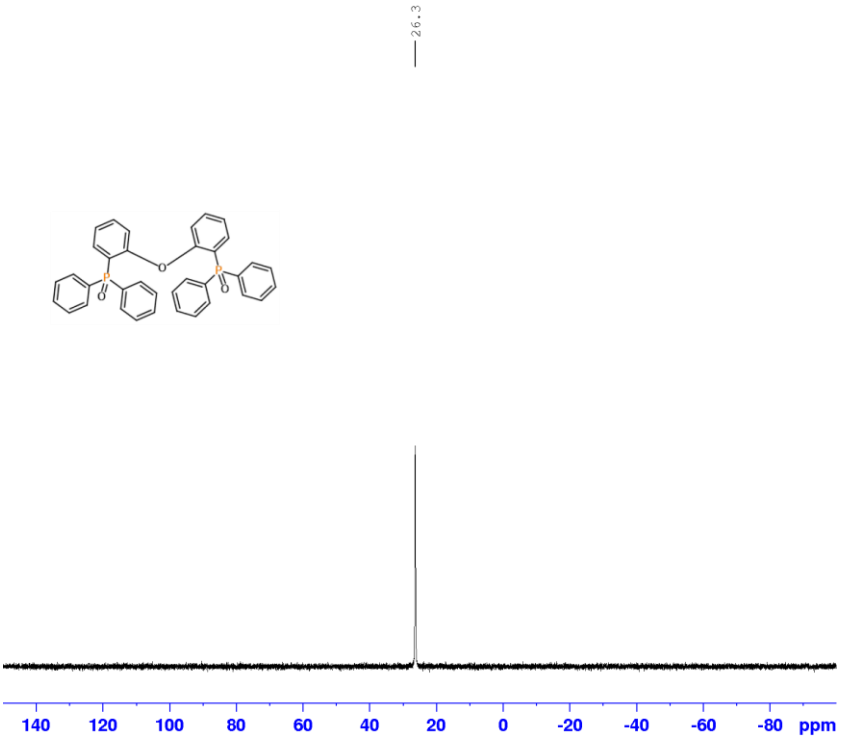
^{13}C NMR, $CDCl_3$, 125 MHz (2y)





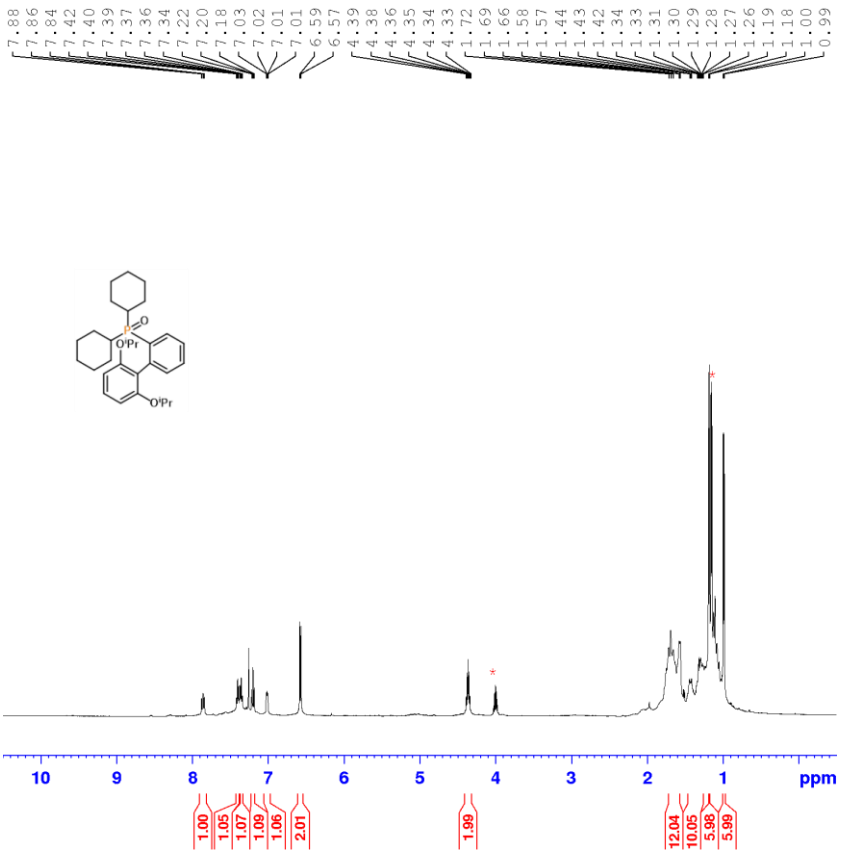


^{31}P NMR, $CDCl_3$, 202 MHz (2y)



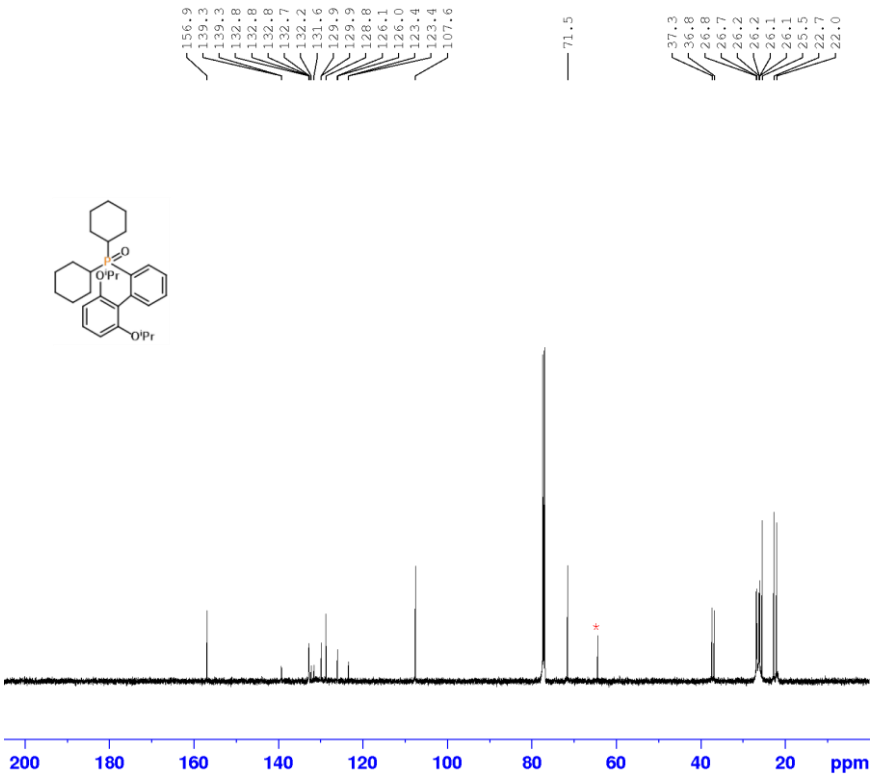
Dicyclohexyl(2',6'-diisopropoxy-[1,1'-biphenyl]-2-yl)phosphine oxide (2z)

^{1}H NMR, $CDCl_3$, 500 MHz (2z)



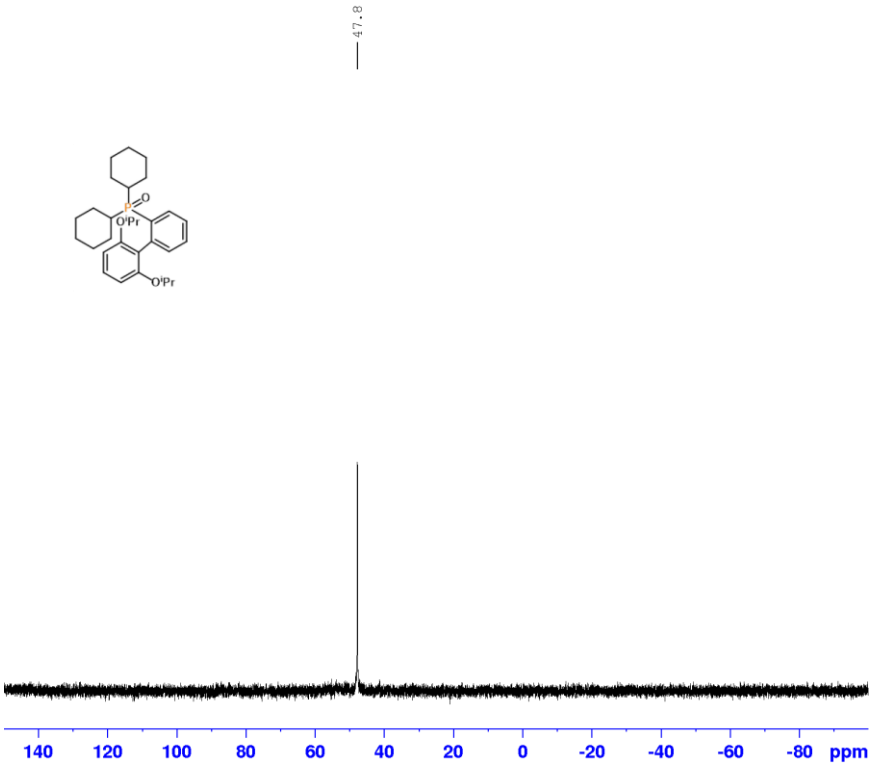
* = Solvent

^{13}C NMR, $CDCl_3$, 125 MHz (2z)



* = Solvent

^{31}P NMR, $CDCl_3$, 202 MHz (2z)



IX. References

1) B. Ghorai, B. Sahana, D. P. Hari*, Angew. Chem. Int. Ed.,* 2025, e202506747.

2) J. Patra, A. M. Nair, C.M.R. Volla, *Chem. Sci.,* 2024, **15**, 7136.

3) C. G. Hatchard and C.A. Parker, *Proc. R. Soc. Lond.,* 1956, **235**, 518.

4) H. J. Kuhn, S.E. Braslavsky and R. Schmidt, *Pure Appl. Chem.,* 2004, **76**, 2105.