Electronic Supplementary Information for

Metal-free Oxidative Phosphinylation of Aryl Alkynes to *β*-Ketophosphine Oxides *via* Visible-Light Photoredox Catalysis

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1 Materials and equipment

Unless otherwise noted, reagents were commercially available and used without any further purification. The photocatalytic reactions were irradiated with a 23W household white LED lamp which was directly got from the supermarket. The products were purified by column chromatography using 100-200 mesh silica gel or preparative TLC using glass 0.25 mm silica gel plates. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel, and compounds were detected by visualization under an ultraviolet lamp (254 nm). ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on an AVANCE III 500 Bruker spectrometer operating at 500 MHz, 125 MHz, 202 MHz and 470 MHz, respectively. Chemical shifts were reported in ppm. Coupling constants (*J* values) were reported in Hz.

2 Typical experimental procedures

General procedure for the preparation of alkynes:

Compounds **2d**, **2e**, **2l**, **2m** were prepared according to the reported procedure.[1] Aryl bromide or iodide (5.0 mmol, 1 equiv.) was placed in a Schlenk flask under an argon atmosphere. Triethylamine (7 mL) was added by syringe followed by addition of trimethylsilylacetylene (1.0 mL, 7.08 mmol, 1.42 equiv.), bis(triphenylphosphine)palladium(II) dichloride (35.1 mg, 1.0 mol%), and copper(I) iodide (9.5 mg, 0.05 mmol). The mixture was stirred at 40 ℃ for 16 h. The reaction mixture was cooled to room temperature. The reaction mixture was filtered over a short pad of silica gel (hexane) and the solvent was removed under reduced pressure. The residue was diluted with methanol (25 mL) and stirred at room temperature for 2 h with an excess of potassium carbonate under argon. After complete conversion of the starting material the solution was filtered, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

General procedure for the synthesis of SPOs:

Substrates **1b**, **1c** were prepared according to the reported procedure.[2] Diethylphosphite (1.29 mL, 10.0 mmol) was added dropwise at 0 ºC to a solution of phenylmagnesium bromide in tetrahydrofuran which was prepared from aryl bromides (32.6 mmol) and magnesium (0.95 g, 39.6 mmol). The mixture was aged for 30 min at 0 ℃, then stirred at ambient temperature for 16 h. After that it was cooled again to 0 ℃, and 75 mL NH_4Cl aqueous was then added slowly. The mixture was extracted with diethyl ether and the organic phase was washed with $NaHCO_3$ aqueous and brine, then it was dried over Na_2SO_4. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel to give the product.

General procedure for the photocatalytic oxidative phosphinylation of alkynes:

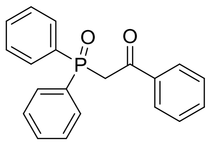
A 10 mL reaction vessel was equipped with rhodamine B (1 mg, 0.002 mmol, 0.5 mol%), SPO **1** (0.4 mmol) and a magnetic stirring bar. *i*-PrOH (0.4 mL) was added, followed by aryl alkyne **2** (1.2 mmol, 3 equiv.). The mixture was irradiated with a household white LED lamp (23 W) and stirred under O_2 (balloon) at room temperature for 12 h. After the reaction, the reaction was quenched by 10 mL ethyl acetate. The resulting mixture was passed through a plug of silica gel, concentrated under reduced pressure. Purification of the crude product was achieved by column chromatography or preparative TLC.

Experimental procedure for the radical capture experiment with TEMPO:
A 10 mL reaction vessel was equipped with rhodamine B (1 mg, 0.002 mmol, 0.5 mol%), SPO **1a** (81 mg, 0.4 mmol), TEMPO (94 mg, 0.6 mmol) and a magnetic stirring bar. *i*-PrOH (0.4 mL) was added, followed by phenylacetylene **2a** (123 mg, 1.2 mmol, 3 equiv.). The mixture was irradiated with a household white LED lamp (23 W) and stirred under O_2 (balloon) at room temperature for 12 h. After the reaction, the reaction was quenched by 10 mL ethyl acetate. And product **3a** was not detected.

Procedure for the experiment conducted in N_2:
A 10 mL reaction vessel was equipped with rhodamine B (1 mg, 0.002 mmol, 0.5 mol%), SPO **1a** (81 mg, 0.4 mmol), and a magnetic stirring bar. The vessel was evacuated and backfilled with dry nitrogen (this operation was repeated three times). *i*-PrOH (0.4 mL) was added, followed by phenylacetylene **2a** (123 mg, 1.2 mmol, 3 equiv.). The mixture was irradiated with a household white LED lamp (23 W) and stirred under O_2 (balloon) at room temperature for 12 h. After the reaction, the reaction was quenched by 10 mL ethyl acetate. And only trace product **3a** was detected.

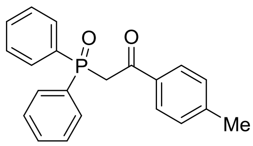
Procedure for the experiment conducted in presence of 4Å MS:
4Å molecular sieve was washed with ethanol, crushed to powder, and dried at 400 ℃ for 4 h. A 10 mL reaction vessel was equipped with rhodamine B (1 mg, 0.002 mmol, 0.5 mol%), SPO **1a** (81 mg, 0.4 mmol), 4Å molecular sieve (50 mg) and a magnetic stirring bar. Dry *i*-PrOH (0.4 mL) was added, followed by phenylacetylene **2a** (123 mg, 1.2 mmol, 3 equiv.). The mixture was irradiated with a household white LED lamp (23 W) and stirred under O_2 (balloon) at room temperature for 12 h. After the reaction, the reaction was quenched by 10 mL ethyl acetate. And product **3a** was isolated by column chromatography in the yield of 85%.

3 Analytical data



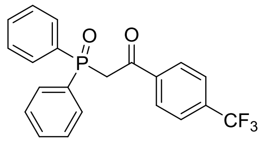
Chemical Formula: $C_{20}H_{17}O_2P$
Exact Mass: 320.10
Elemental Analysis: C, 74.99; H, 5.35; O, 9.99; P, 9.67

2-(Diphenylphosphoryl)-1-phenylethan-1-one (**3a**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.79 (dd, *J* = 12.0, 7.9 Hz, 4H), 7.51 (dd, *J* = 13.5, 6.7 Hz, 3H), 7.47 – 7.29 (m, 6H), 4.13 (d, *J* = 15.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 137.1, 133.7, 132.5, 132.3, 131.6, 131.3, 131.2, 129.3, 128.8, 128.7, 128.6, 43.6, 43.1. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.2.



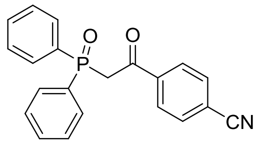
Chemical Formula: $C_{21}H_{19}O_2P$
Exact Mass: 334.11
Elemental Analysis: C, 75.44; H, 5.73; O, 9.57; P, 9.26

2-(Diphenylphosphoryl)-1-(p-tolyl)ethan-1-one (**3b**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.84 – 7.77 (m, 4H), 7.52 (td, *J* = 7.3, 1.6 Hz, 2H), 7.46 (td, *J* = 7.5, 2.5 Hz, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.12 (d, *J* = 15.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 144.7, 134.7, 132.6, 132.2, 131.7, 131.3, 131.2, 129.5, 129.3, 128.7, 128.6, 43.6, 43.1, 21.8. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.3.



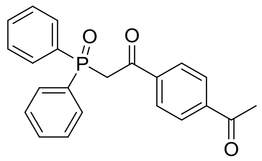
Chemical Formula: $C_{21}H_{16}F_3O_2P$
Exact Mass: 388.08
Elemental Analysis: C, 64.95; H, 4.15; F, 14.68; O, 8.24; P, 7.98

2-(Diphenylphosphoryl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**3c**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.1 Hz, 2H), 7.82 – 7.74 (m, 4H), 7.67 (d, J = 8.2 Hz, 2H), 7.53 (td, J = 7.3, 1.5 Hz, 2H), 7.46 (td, J = 7.6, 3.2 Hz, 4H), 4.16 (d, J = 15.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 139.6, 134.9, 134.7, 132.5, 132.1, 131.2, 131.1, 129.8, 128.9, 128.8, 125.7, 124.7, 122.6, 44.2, 43.8. ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.2.



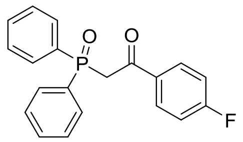
Chemical Formula: $C_{21}H_{16}NO_2P$
Exact Mass: 345.09
Elemental Analysis: C, 73.04; H, 4.67; N, 4.06; O, 9.27; P, 8.97

4-(2-(Diphenylphosphoryl)acetyl)benzonitrile (**3d**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 2H), 7.82 – 7.74 (m, 4H), 7.71 (d, J = 8.5 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.50 – 7.45 (m, 4H), 4.13 (d, J = 15.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9, 139.9, 132.6, 132.5, 132.0, 131.2, 131.1, 129.9, 129.0, 128.9, 118.0, 116.8, 44.4, 43.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.7.



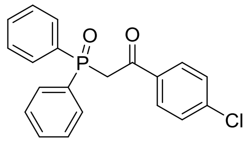
Chemical Formula: $C_{22}H_{19}O_3P$
Exact Mass: 362.11
Elemental Analysis: C, 72.92; H, 5.29; O, 13.25; P, 8.55

1-(4-Acetylphenyl)-2-(diphenylphosphoryl)ethan-1-one (**3e**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 7.5 Hz, 2H), 7.77 (m, J = 12.3, 7.3 Hz, 4H), 7.51 (t, J = 7.3 Hz, 2H), 7.48 – 7.40 (m, 4H), 4.14 (d, J = 15.2 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 192.5, 140.5, 140.1, 132.4, 132.3, 131.4, 131.2, 131.1, 129.6, 128.9, 128.8, 128.4, 44.1, 43.7, 27.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.8.



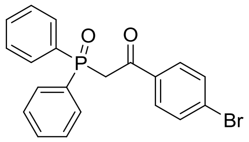
Chemical Formula: $C_{20}H_{16}FO_2P$
Exact Mass: 338.09
Elemental Analysis: C, 71.00; H, 4.77; F, 5.62; O, 9.46; P, 9.16

2-(Diphenylphosphoryl)-1-(4-fluorophenyl)ethan-1-one (**3f**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 2H), 7.85 – 7.77 (m, 4H), 7.54 (td, J = 7.3, 1.5 Hz, 2H), 7.51 – 7.42 (m, 4H), 7.09 (t, J = 8.6 Hz, 2H), 4.12 (d, J = 15.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.3, 167.2, 165.2, 133.5, 132.4, 132.3, 132.2, 131.4, 131.2, 131.1, 128.8, 128.7, 115.8, 115.7, 43.9, 43.4. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -104.1.



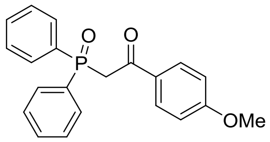
Chemical Formula: $C_{20}H_{16}ClO_2P$
Exact Mass: 354.06
Elemental Analysis: C, 67.71; H, 4.55; Cl, 9.99; O, 9.02; P, 8.73

1-(4-Chlorophenyl)-2-(diphenylphosphoryl)ethan-1-one (**3g**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.87 – 7.73 (m, 4H), 7.52 (td, J = 7.3, 1.5 Hz, 2H), 7.46 (ddd, J = 8.5, 6.8, 3.2 Hz, 4H), 7.41 – 7.32 (m, 2H), 4.10 (d, J = 15.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 140.3, 135.4, 132.4, 132.2, 131.4, 131.2, 131.1, 130.9, 128.9, 128.8, 128.8, 43.9, 43.5. ^{31}P NMR (202 MHz, CDCl$_3$) δ 26.9.



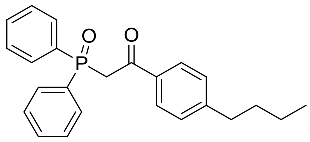
Chemical Formula: $C_{20}H_{16}BrO_2P$
Exact Mass: 398.01
Elemental Analysis: C, 60.17; H, 4.04; Br, 20.01; O, 8.02; P, 7.76

1-(4-Bromophenyl)-2-(diphenylphosphoryl)ethan-1-one (**3h**). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.87 (d, J = 8.5 Hz, 2H), 7.84 – 7.73 (m, 4H), 7.59 – 7.51 (m, 4H), 7.50 – 7.41 (m, 4H), 4.09 (d, J = 15.2 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 192.0, 135.8, 132.4, 132.3, 132.0, 131.4, 131.2, 131.2, 131.0, 129.2, 128.9, 128.8, 44.0, 43.5. ^{31}P NMR (202 MHz, CDCl$_3$) δ 26.9.



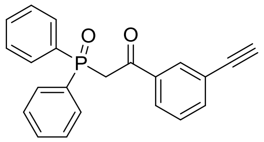
Chemical Formula: $C_{21}H_{19}O_3P$
Exact Mass: 350.11
Elemental Analysis: C, 71.99; H, 5.47; O, 13.70; P, 8.84

2-(Diphenylphosphoryl)-1-(4-methoxyphenyl)ethan-1-one (**3i**). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.00 – 7.93 (m, 2H), 7.82 – 7.75 (m, 4H), 7.54 – 7.47 (m, 2H), 7.44 (ddd, J = 8.5, 6.7, 3.1 Hz, 4H), 6.93 – 6.81 (m, 2H), 4.07 (d, J = 15.3 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 191.15, 164.10, 132.56, 132.22, 131.88, 131.73, 131.28, 131.20, 130.26, 128.76, 128.67, 113.84, 55.62, 43.47, 43.01. ^{31}P NMR (202 MHz, CDCl$_3$) δ 27.4.



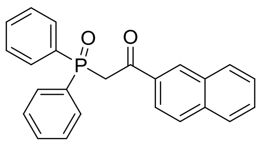
Chemical Formula: $C_{24}H_{25}O_2P$
Exact Mass: 376.16
Elemental Analysis: C, 76.58; H, 6.69; O, 8.50; P, 8.23

1-(4-Butylphenyl)-2-(diphenylphosphoryl)ethan-1-one (**3j**). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 (d, J = 7.9 Hz, 2H), 7.87 – 7.73 (m, 4H), 7.55 – 7.49 (m, 2H), 7.45 (td, J = 7.8, 3.2 Hz, 4H), 7.21 (d, J = 7.9 Hz, 2H), 4.13 (d, J = 15.4 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.34 (p, J = 7.4 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 192.4, 149.6, 134.8, 132.5, 132.2, 131.7, 131.3, 131.2, 129.5, 128.7, 128.6, 43.5, 43.0, 35.8, 33.2, 22.4, 14.0. ^{31}P NMR (202 MHz, CDCl$_3$) δ 27.5.



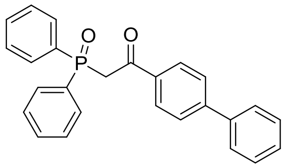
Chemical Formula: $C_{22}H_{17}O_2P$
Exact Mass: 344.10
Elemental Analysis: C, 76.74; H, 4.98; O, 9.29; P, 8.99

2-(Diphenylphosphoryl)-1-(3-ethynylphenyl)ethan-1-one (**3k**). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.02 (s, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.84 – 7.74 (m, 4H), 7.61 (d, J = 7.7 Hz, 1H), 7.51 (td, J = 7.3, 1.5 Hz, 2H), 7.48 – 7.41 (m, 4H), 7.36 (t, J = 7.8 Hz, 1H), 4.13 (d, J = 15.3 Hz, 2H), 3.10 (s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 192.2, 137.2, 136.9, 132.8, 132.4, 132.2, 131.3, 131.2, 129.6, 128.9, 128.8, 122.9, 82.5, 78.6, 43.6, 43.2. ^{31}P NMR (202 MHz, CDCl$_3$) δ 27.3.



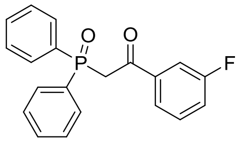
Chemical Formula: $C_{24}H_{19}O_2P$
Exact Mass: 370.11
Elemental Analysis: C, 77.83; H, 5.17; O, 8.64; P, 8.36

2-(Diphenylphosphoryl)-1-(naphthalen-2-yl)ethan-1-one (**3l**). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.55 (s, 1H), 7.99 – 7.93 (m, 2H), 7.82 (tt, J = 7.8, 4.2 Hz, 6H), 7.62 – 7.56 (m, 1H), 7.56 – 7.48 (m, 3H), 7.48 – 7.41 (m, 4H), 4.27 (d, *J* = 15.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 135.9, 134.5, 132.5, 132.3, 132.1, 131.7, 131.3, 131.3, 130.1, 129.0, 128.8, 128.7, 128.5, 127.8, 126.9, 124.3, 43.8, 43.4. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.3.



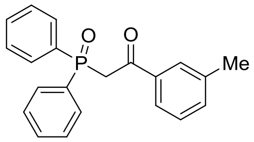
Chemical Formula: $C_{26}H_{21}O_2P$
Exact Mass: 396.13
Elemental Analysis: C, 78.78; H, 5.34; O, 8.07; P, 7.81

1-([1,1'-Biphenyl]-4-yl)-2-(diphenylphosphoryl)ethan-1-one (**3m**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.88 – 7.79 (m, 4H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.48 – 7.41 (m, 6H), 7.37 (t, *J* = 7.3 Hz, 1H), 4.17 (d, *J* = 15.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.4, 146.3, 139.9, 135.8, 132.5, 132.3, 131.7, 131.3, 131.2, 130.0, 129.1, 128.8, 128.7, 128.5, 127.4, 127.3, 43.7, 43.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.3.



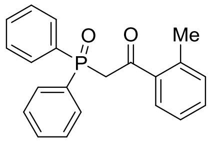
Chemical Formula: $C_{20}H_{16}FO_2P$
Exact Mass: 338.09
Elemental Analysis: C, 71.00; H, 4.77; F, 5.62; O, 9.46; P, 9.16

2-(Diphenylphosphoryl)-1-(3-fluorophenyl)ethan-1-one (**3n**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (m, *J* = 13.7, 8.0, 3.4 Hz, 5H), 7.62 (m, *J* = 9.6, 2.0 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.46 (m, *J* = 7.7, 2.9 Hz, 4H), 7.39 (m, *J* = 7.9, 5.4 Hz, 1H), 7.22 (m, *J* = 8.3, 2.5 Hz, 1H), 4.12 (d, *J* = 15.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.7, 162.6, 160.7, 138.0, 131.3, 131.1, 130.3, 130.1, 130.1, 129.3, 129.2, 127.8, 127.7, 124.4, 119.7, 119.6, 114.7, 114.6, 42.8, 42.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.8.



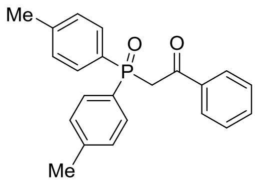
Chemical Formula: $C_{21}H_{19}O_2P$
Exact Mass: 334.11
Elemental Analysis: C, 75.44; H, 5.73; O, 9.57; P, 9.26

2-(Diphenylphosphoryl)-1-(m-tolyl)ethan-1-one (**3o**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.75 (m, 5H), 7.71 (s, 1H), 7.50 (m, 2H), 7.44 (m, 2.3 Hz, 4H), 7.35 – 7.25 (m, 2H), 4.12 (d, *J* = 15.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 138.4, 137.1, 134.5, 132.6, 132.2, 131.7, 131.3, 131.2, 129.7, 128.8, 128.7, 128.5, 126.7, 43.6, 43.1, 21.4. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.2.



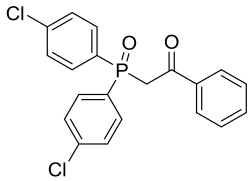
Chemical Formula: $C_{21}H_{19}O_2P$
Exact Mass: 334.11
Elemental Analysis: C, 75.44; H, 5.73; O, 9.57; P, 9.26

2-(Diphenylphosphoryl)-1-(o-tolyl)ethan-1-one (**3p**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.68 (m, 4H), 7.53 – 7.46 (m, 2H), 7.42 (ddd, *J* = 8.7, 5.2, 1.8 Hz, 4H), 7.30 (td, *J* = 7.5, 1.8 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 4.10 (d, *J* = 15.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.8, 139.0, 137.6, 132.7, 132.2, 132.1, 131.9, 131.9, 131.2, 131.2, 130.4, 128.8, 128.7, 125.9, 46.0, 45.5, 21.4. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.3.



Chemical Formula: $C_{22}H_{21}O_2P$
Exact Mass: 348.13
Elemental Analysis: C, 75.85; H, 6.08; O, 9.18; P, 8.89

2-(Di-p-tolylphosphoryl)-1-phenylethan-1-one (**3q**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.57 (dd, *J* = 12.0, 7.9 Hz, 4H), 7.46 – 7.41 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.13 (m, 4H), 4.01 (d, *J* = 15.3 Hz, 2H), 2.28 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 142.8, 137.2, 133.6, 131.3, 131.2, 129.5, 129.4, 128.6, 128.5, 43.9, 43.4, 21.7. ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.7.



Chemical Formula: $C_{20}H_{15}Cl_2O_2P$
Exact Mass: 388.02
Elemental Analysis: C, 61.72; H, 3.88; Cl, 18.22; O, 8.22; P, 7.96

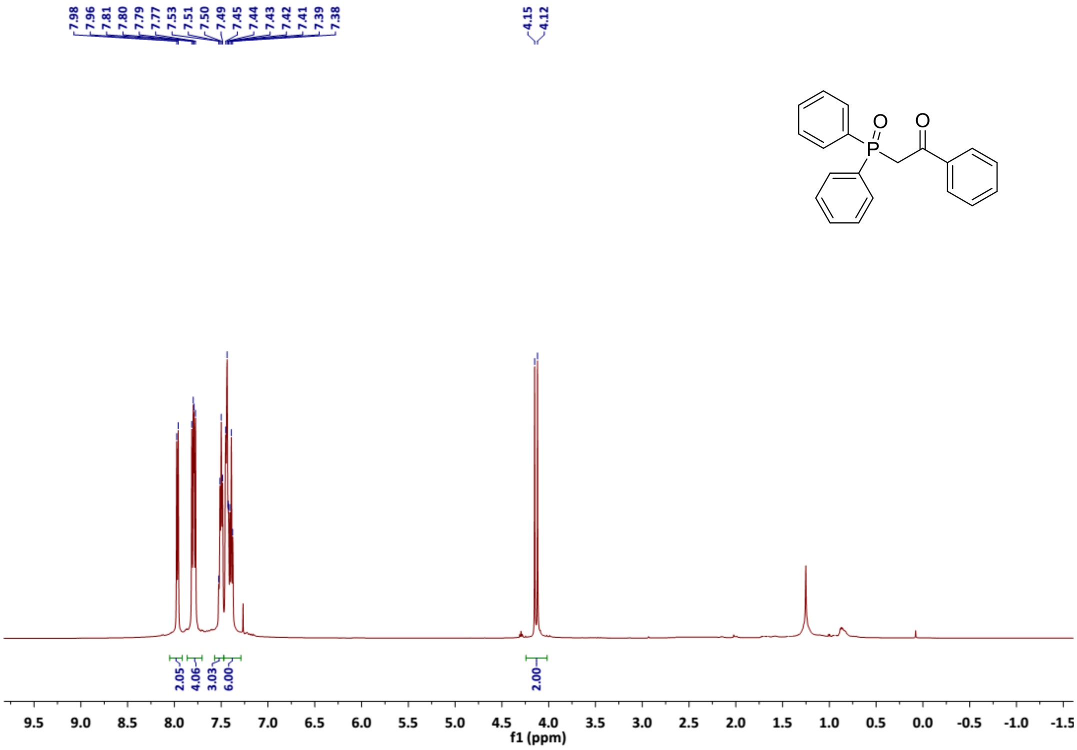
2-(Bis(4-chlorophenyl)phosphoryl)-1-phenylethan-1-one (**3r**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.72 (dd, *J* = 11.7, 8.2 Hz, 4H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (m, 6H), 4.12 (d, *J* = 15.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 139.2, 136.8, 134.0, 132.7, 132.6, 130.6, 129.8, 129.3, 129.2, 128.8, 43.5, 43.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.2.

4 References

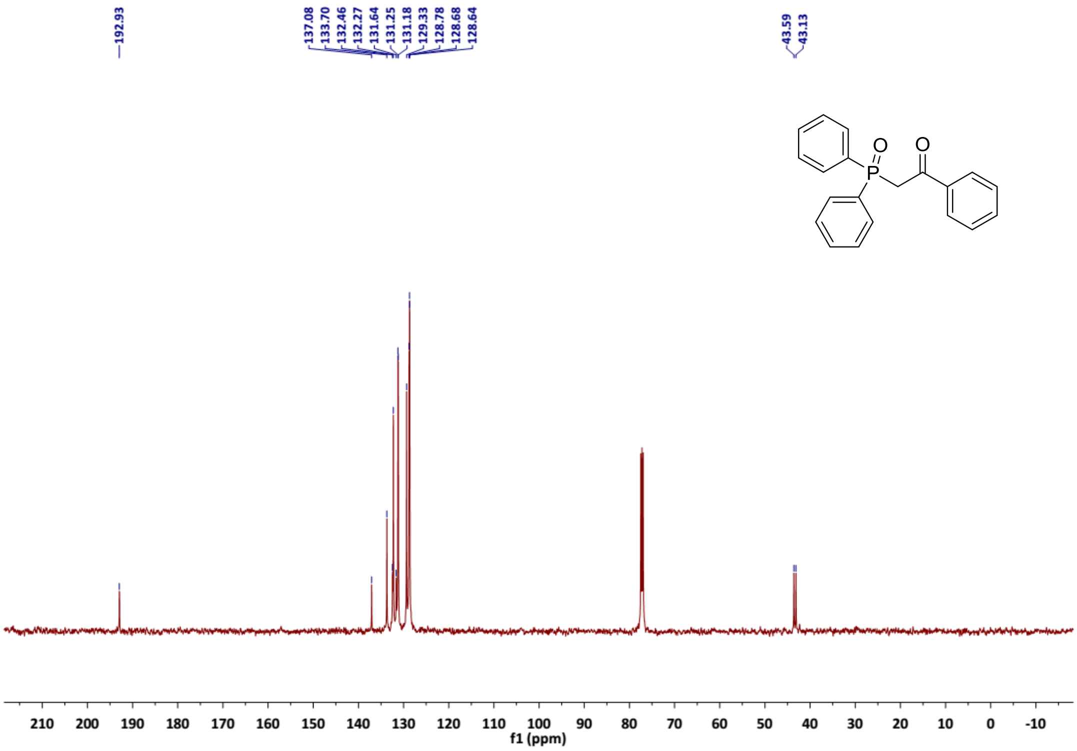
[1] (a) X. Shao, X. Wang, T. Yang, L. Lu and Q. Shen, *Angew. Chem. Int. Ed.*, 2013, **52**, 3457; (b) A. Miersch and G. Hilt, *Chem. Eur. J.*, 2012, **18**, 9798; (c) F. Punner and G. Hilt, *Chem. Commun.*, 2012, **48**, 3617.

[2] J. Ke, Y. Tang, H. Yi, Y. Li, Y. Cheng, C. Liu and A. Lei, *Angew. Chem. Int. Ed.*, 2015, **54**, 6604.

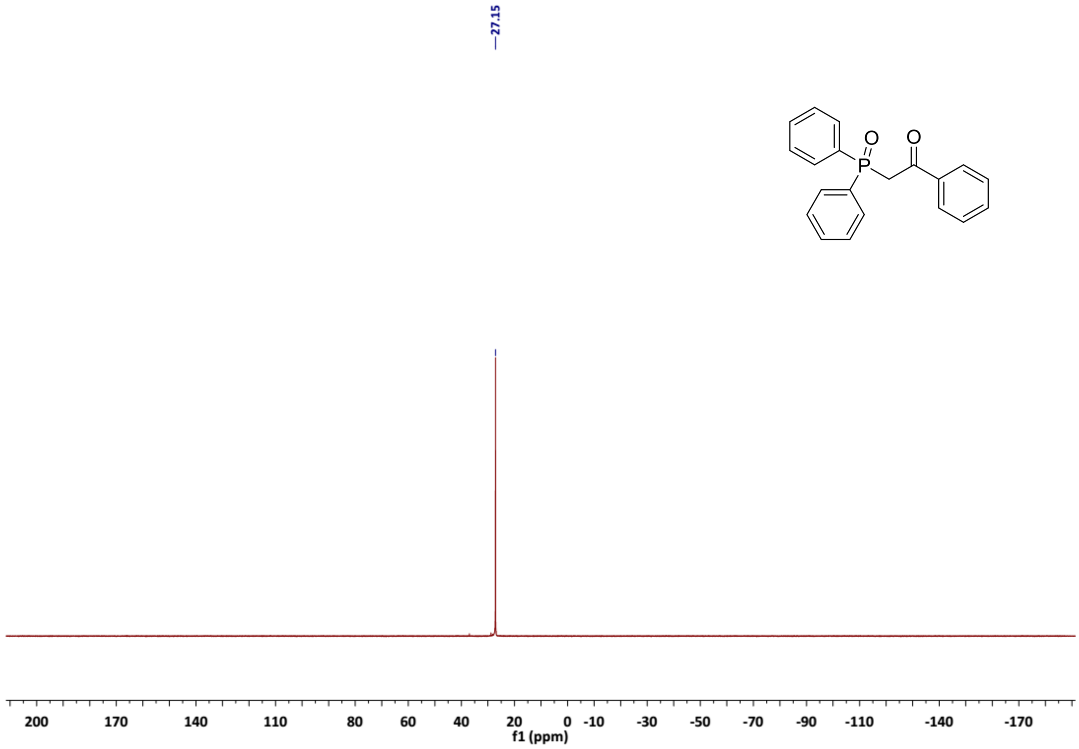
5 Spectra



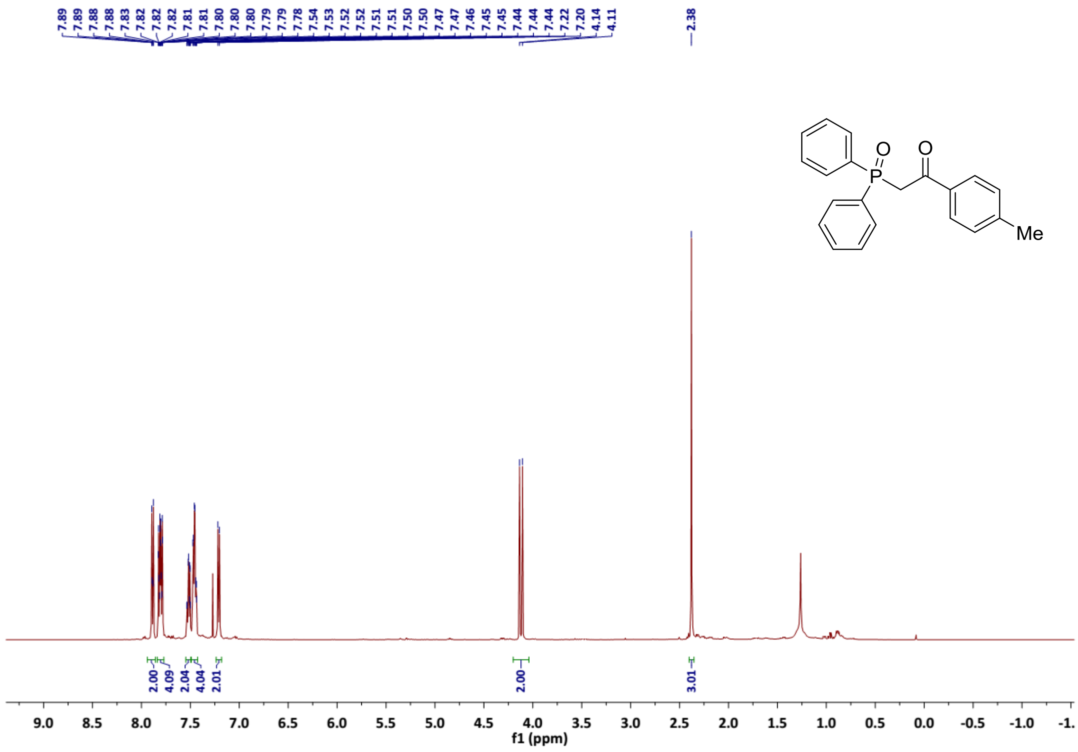
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3a**



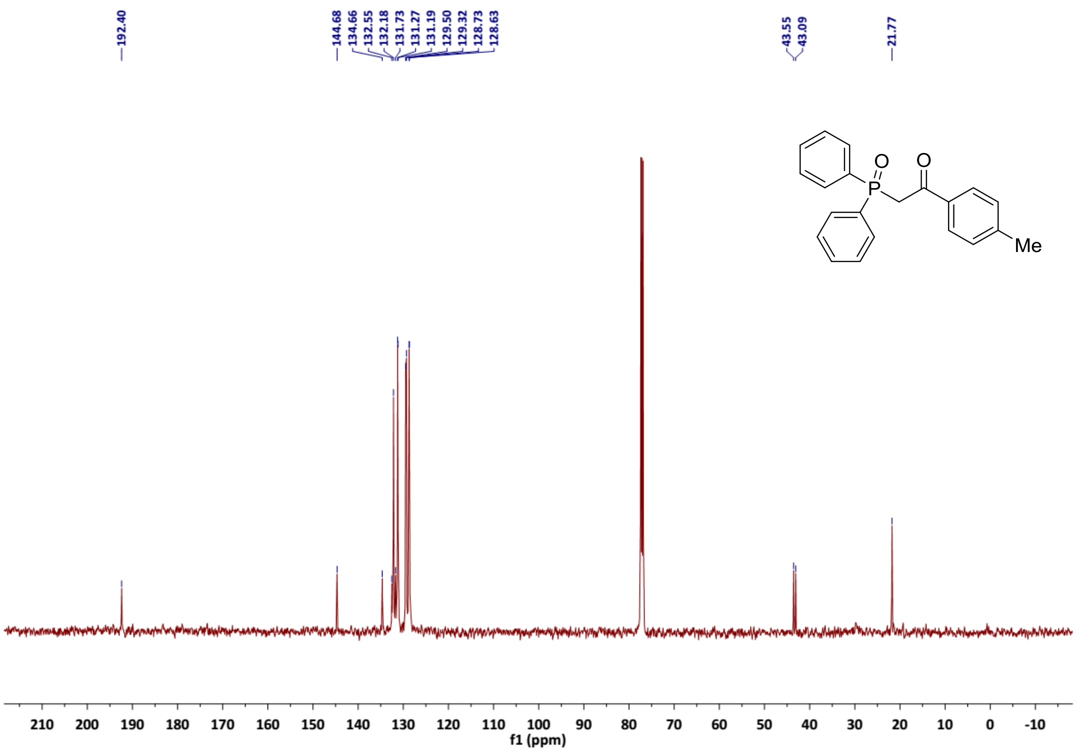
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3a**



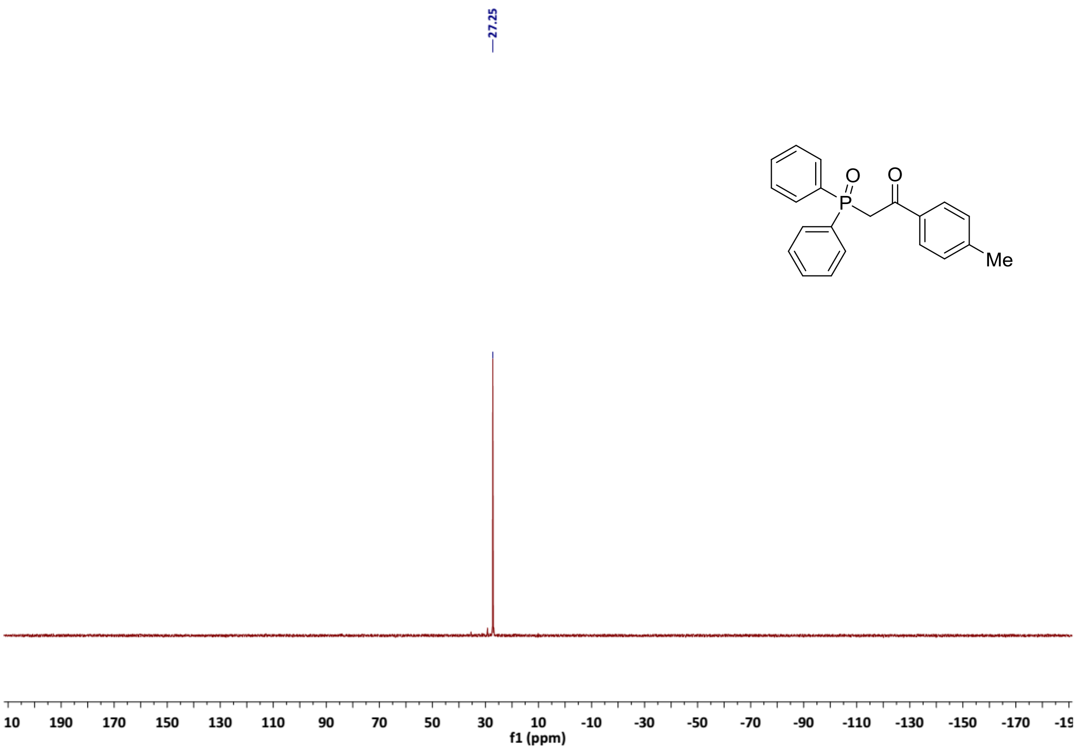
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3a**



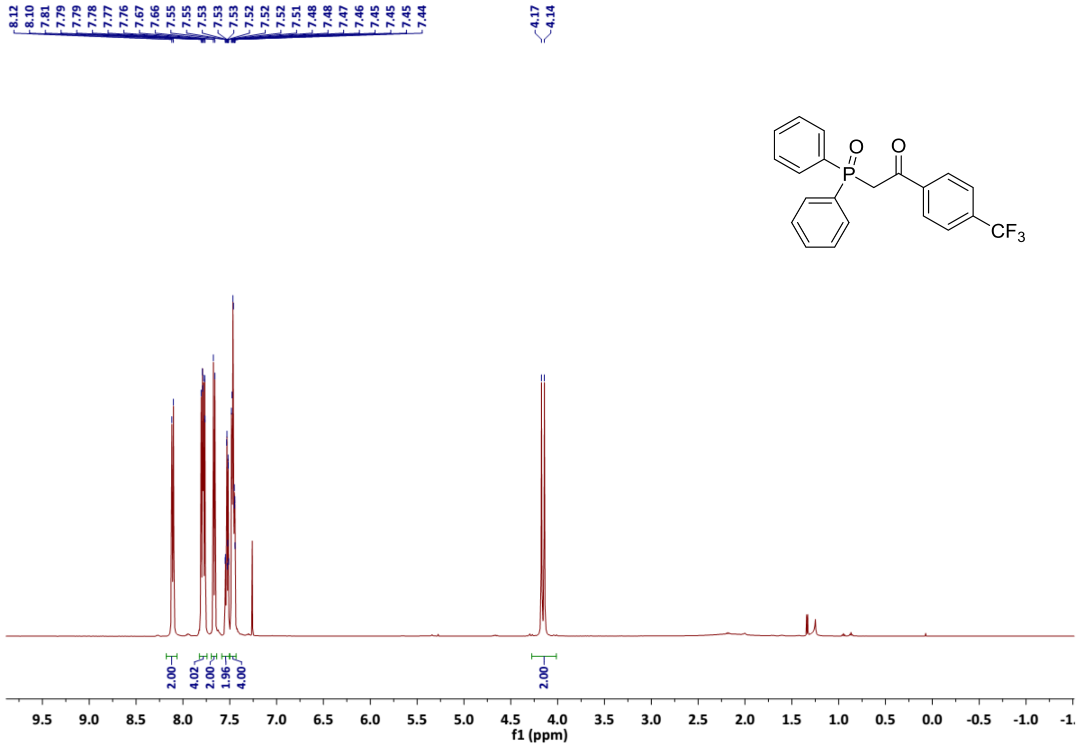
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3b**



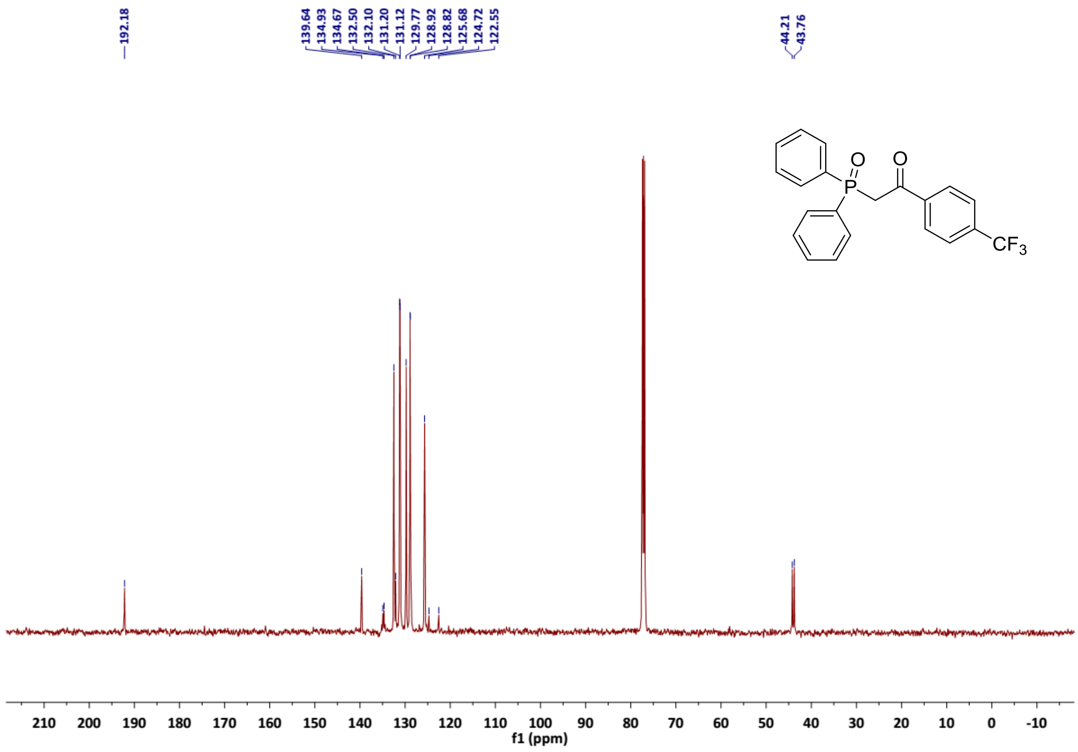
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3b**



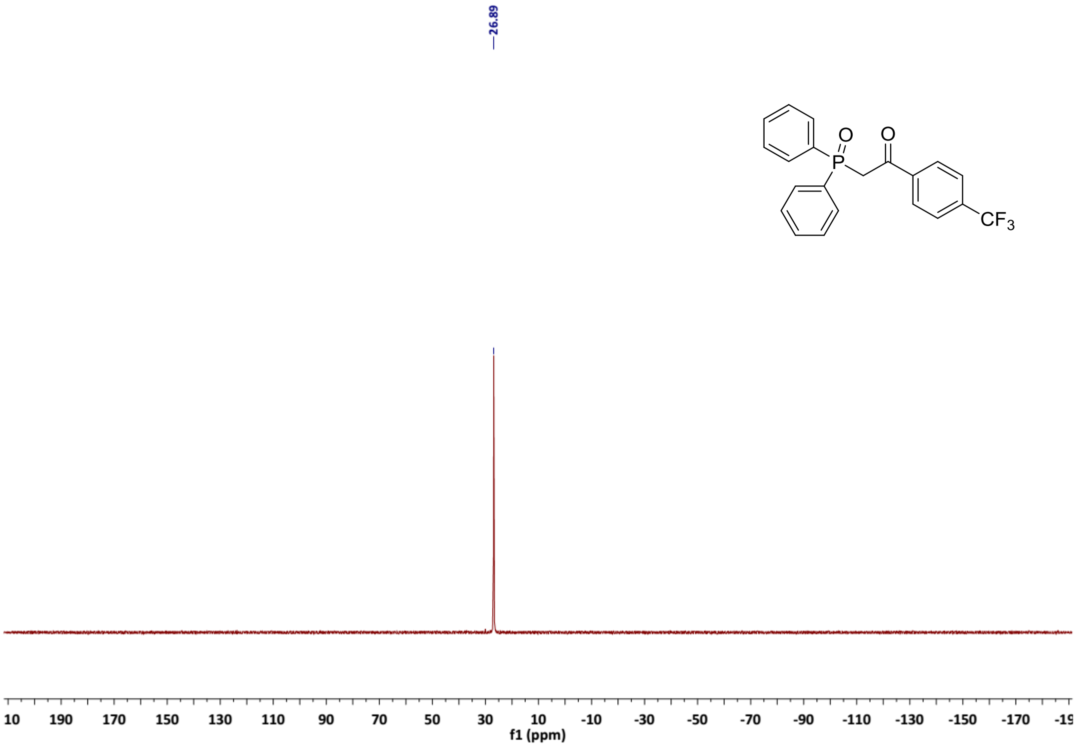
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3b**



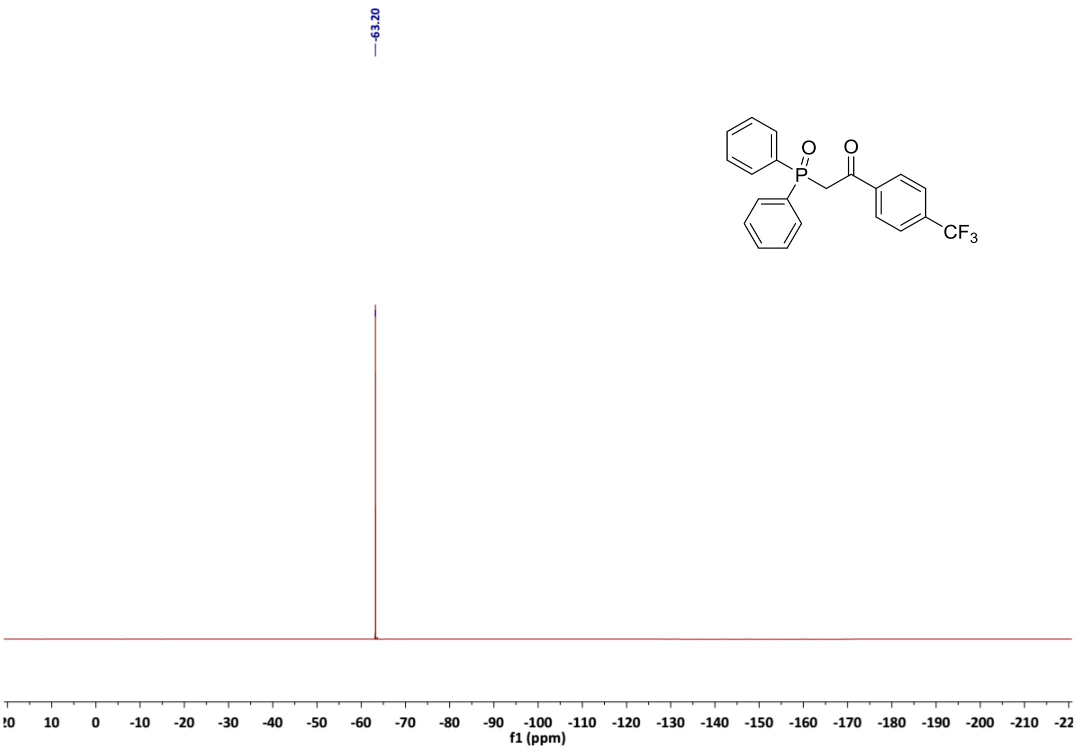
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **3c**



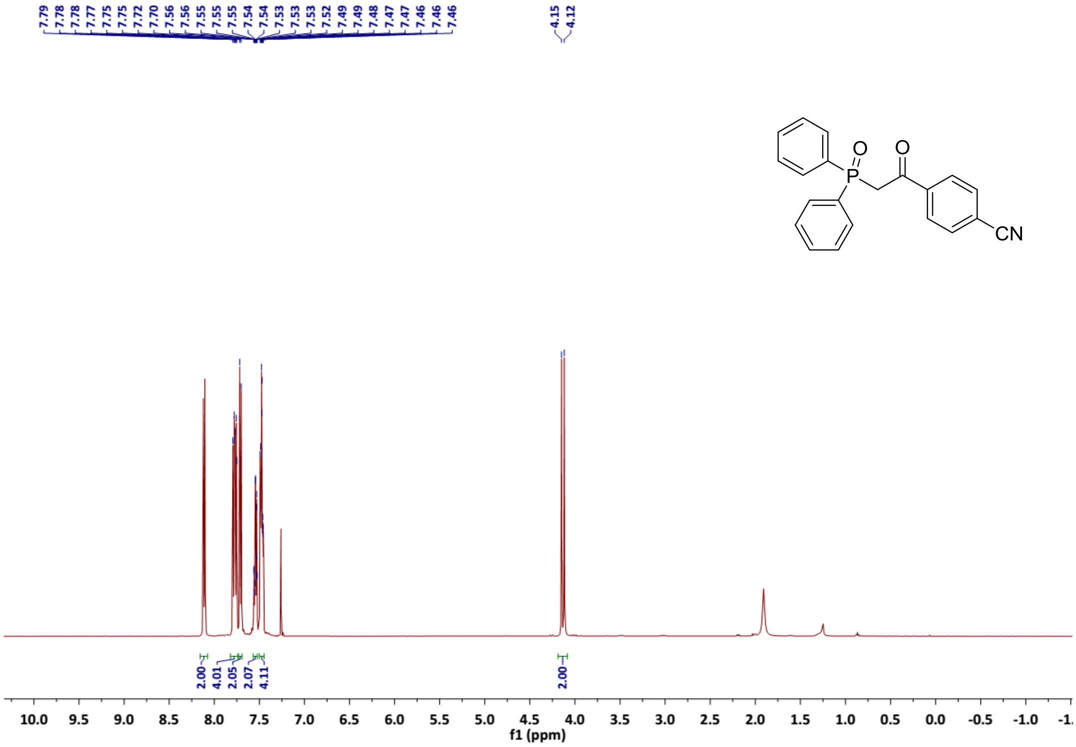
^{13}C NMR spectrum (125 MHz, CDCl$_3$) of **3c**



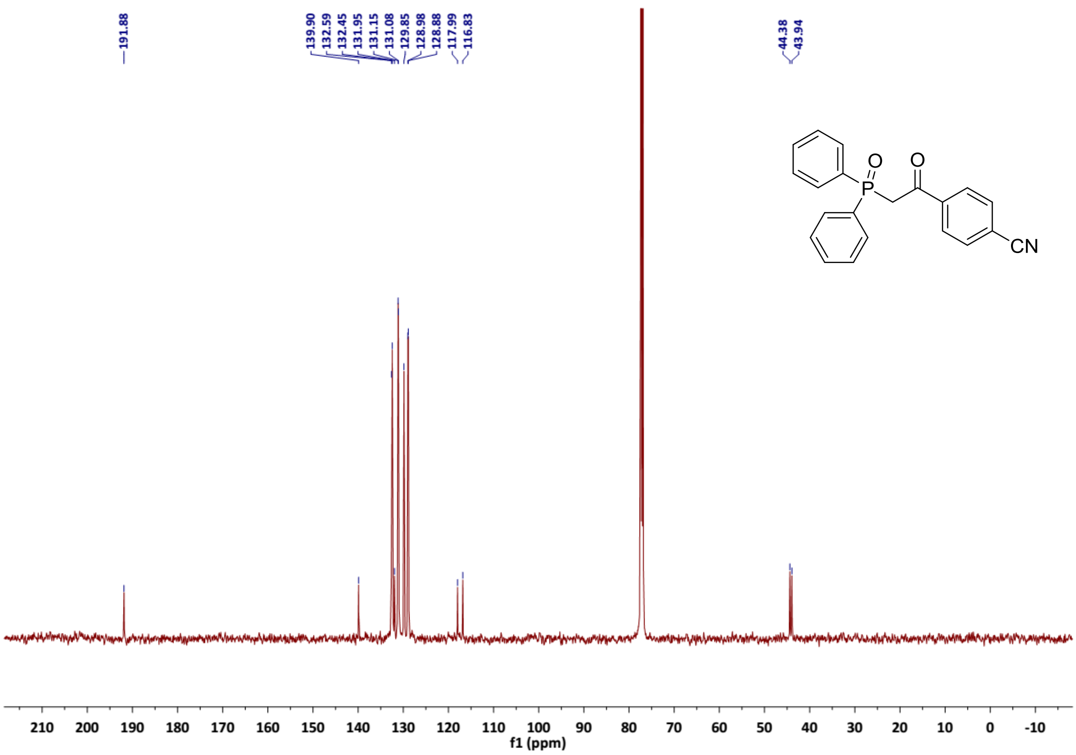
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3c**



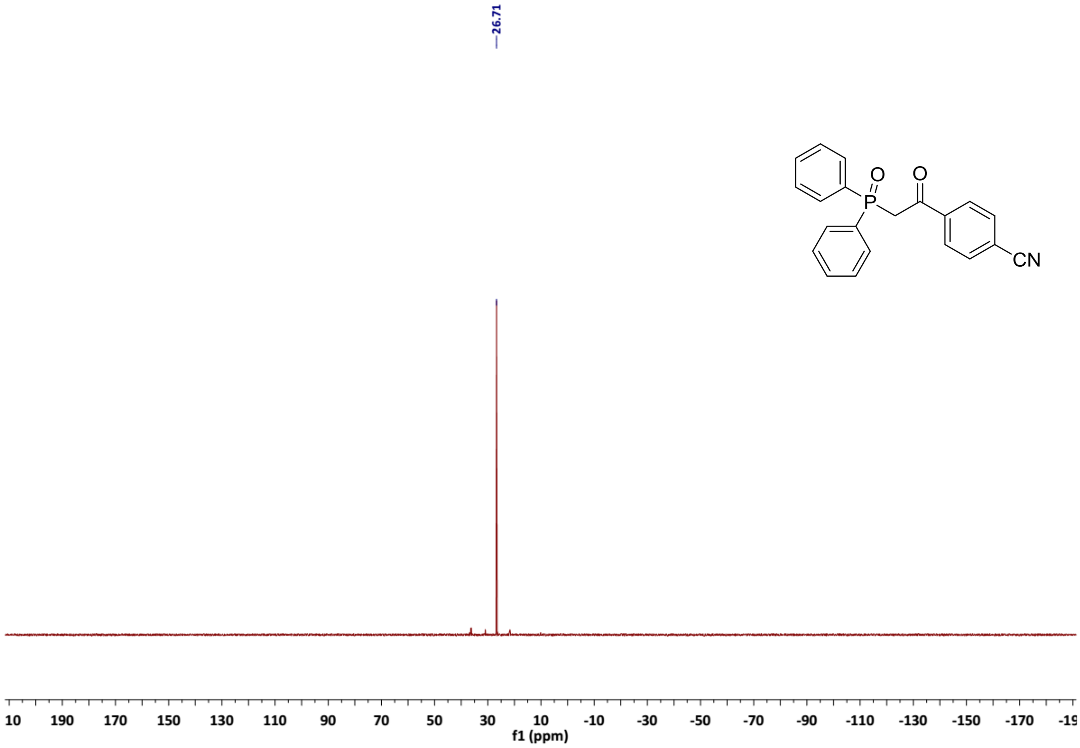
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **3c**



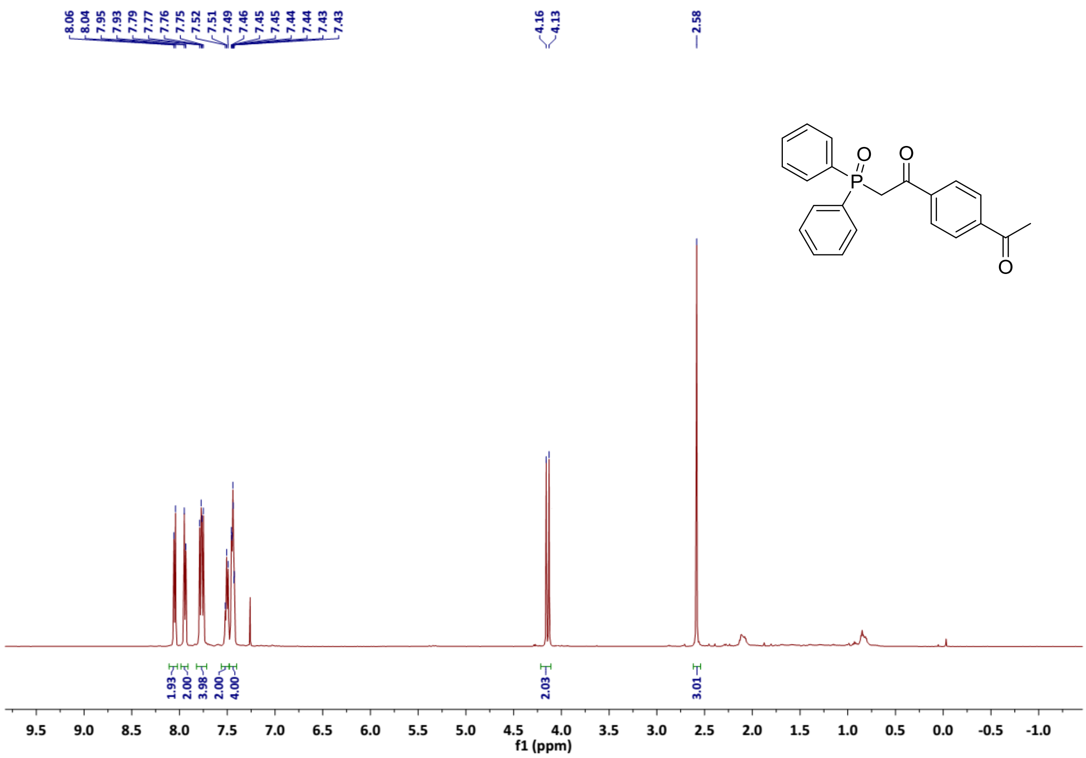
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3d**



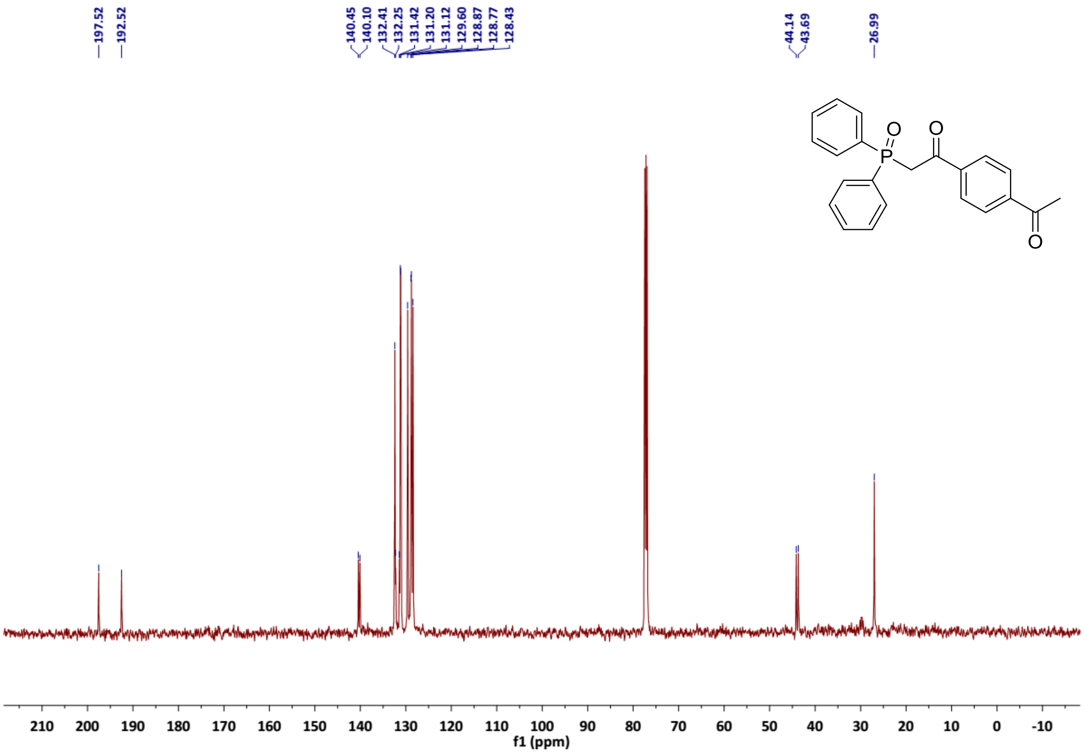
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3d**



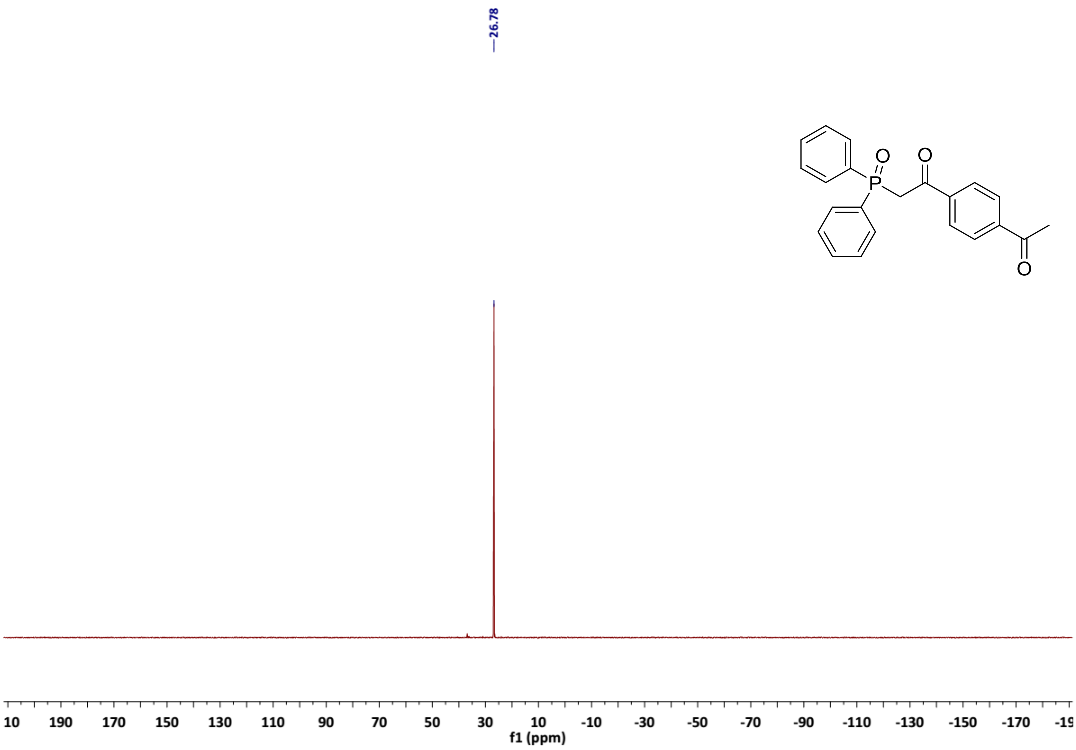
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3d**



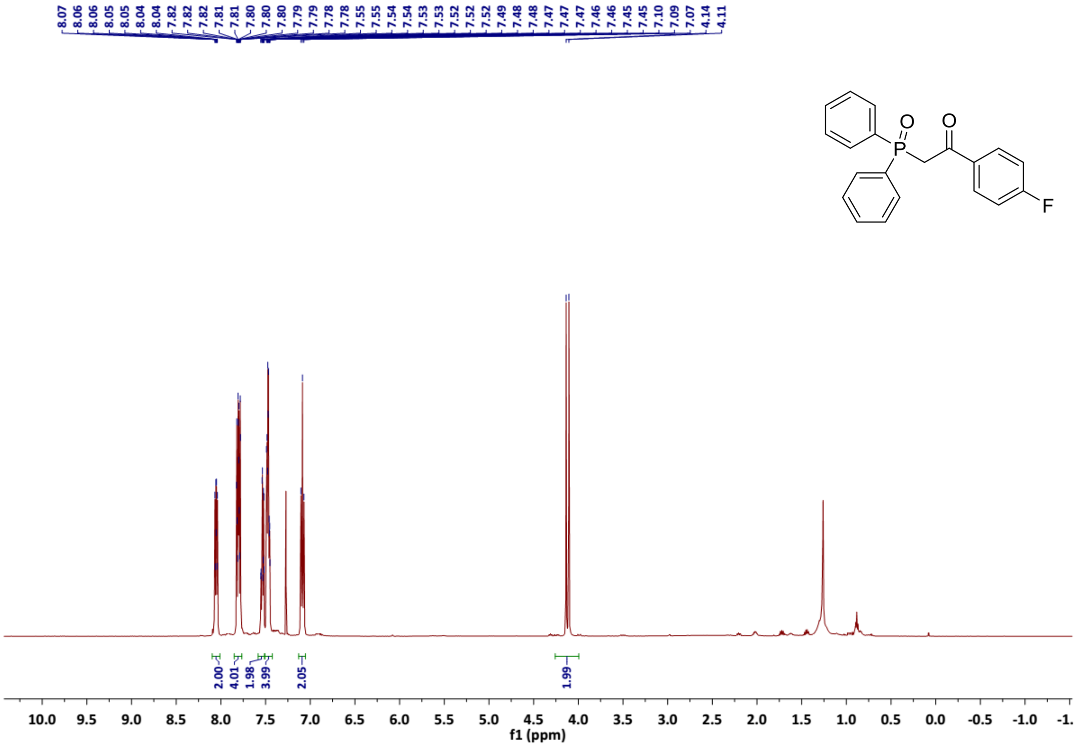
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3e**



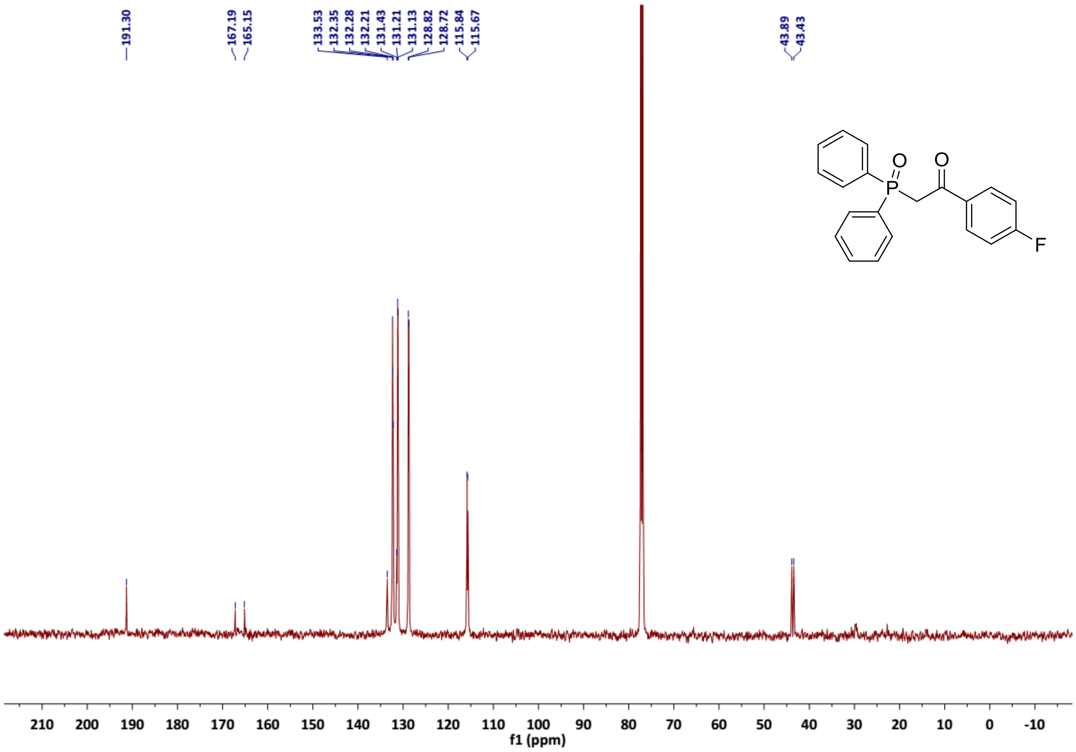
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3e**



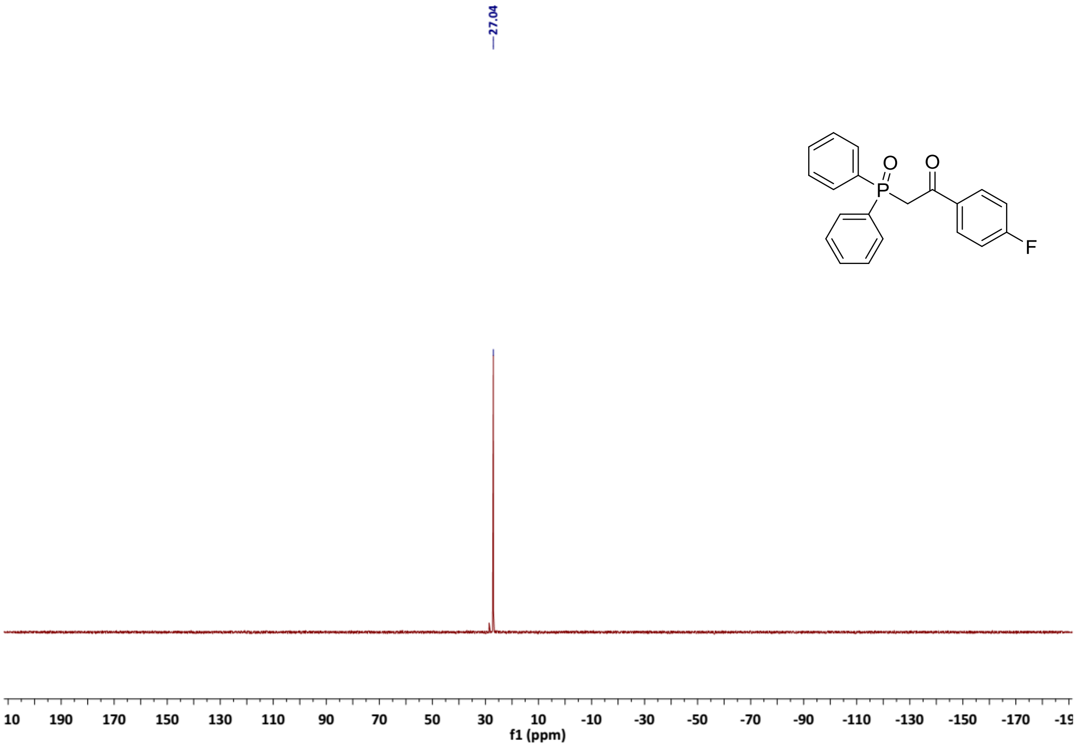
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3e**



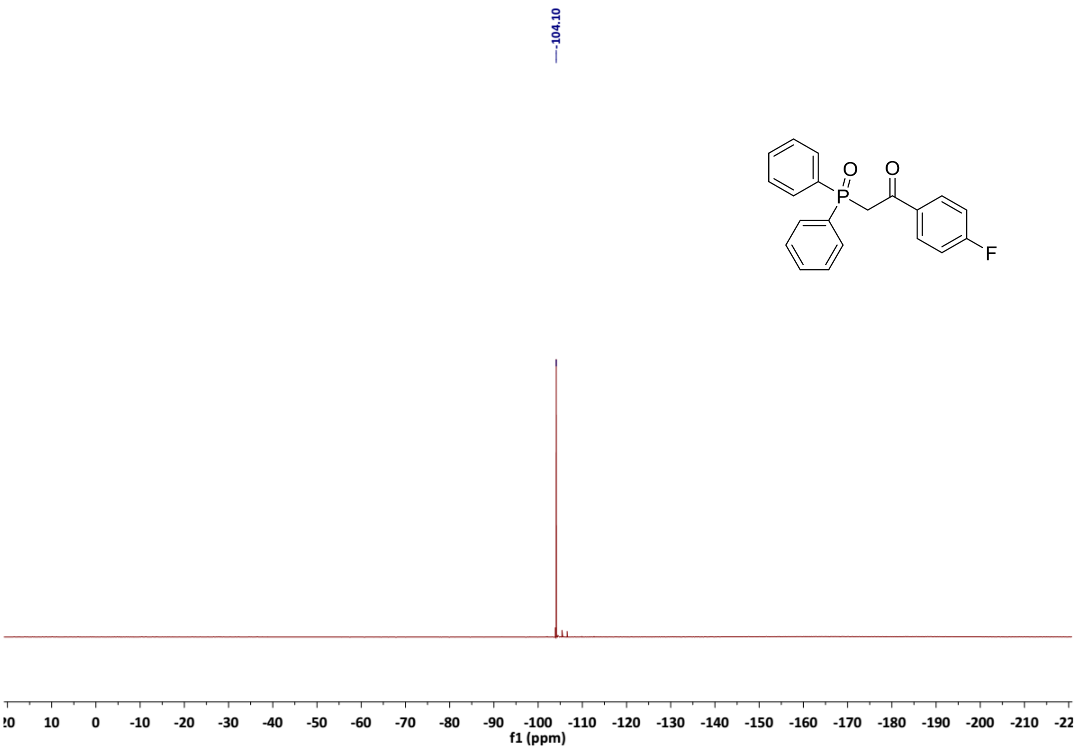
[1]H NMR spectrum (500 MHz, $CDCl_3$) of **3f**



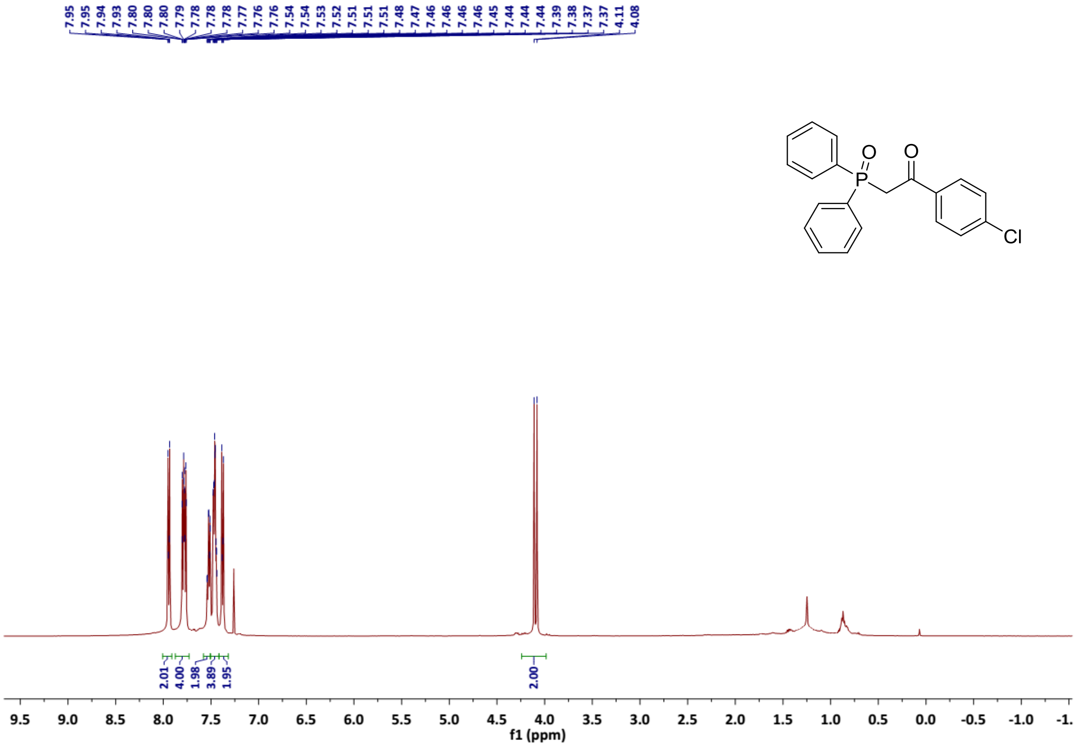
[13]C NMR spectrum (125 MHz, $CDCl_3$) of **3f**



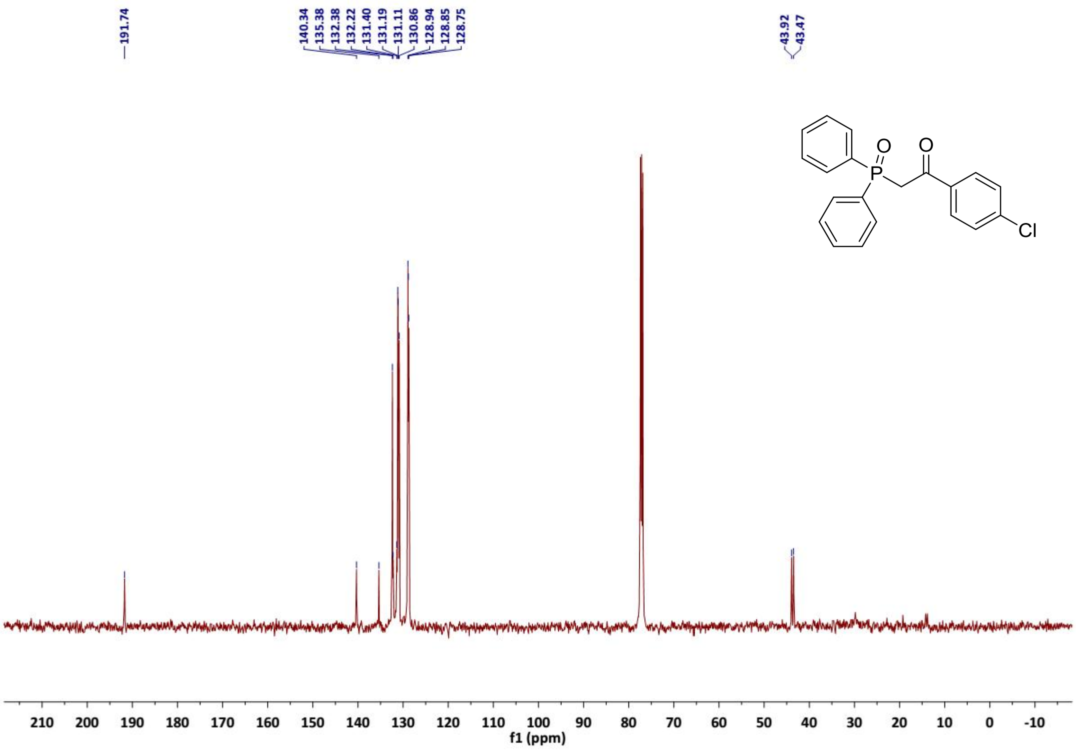
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3f**



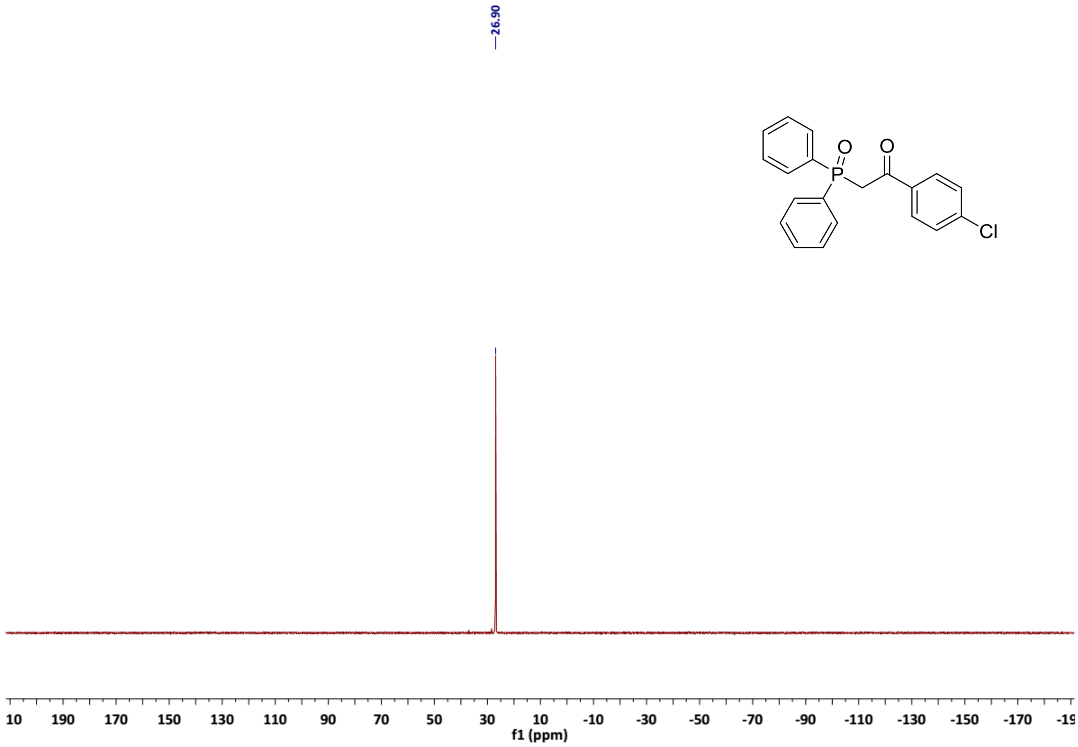
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **3f**



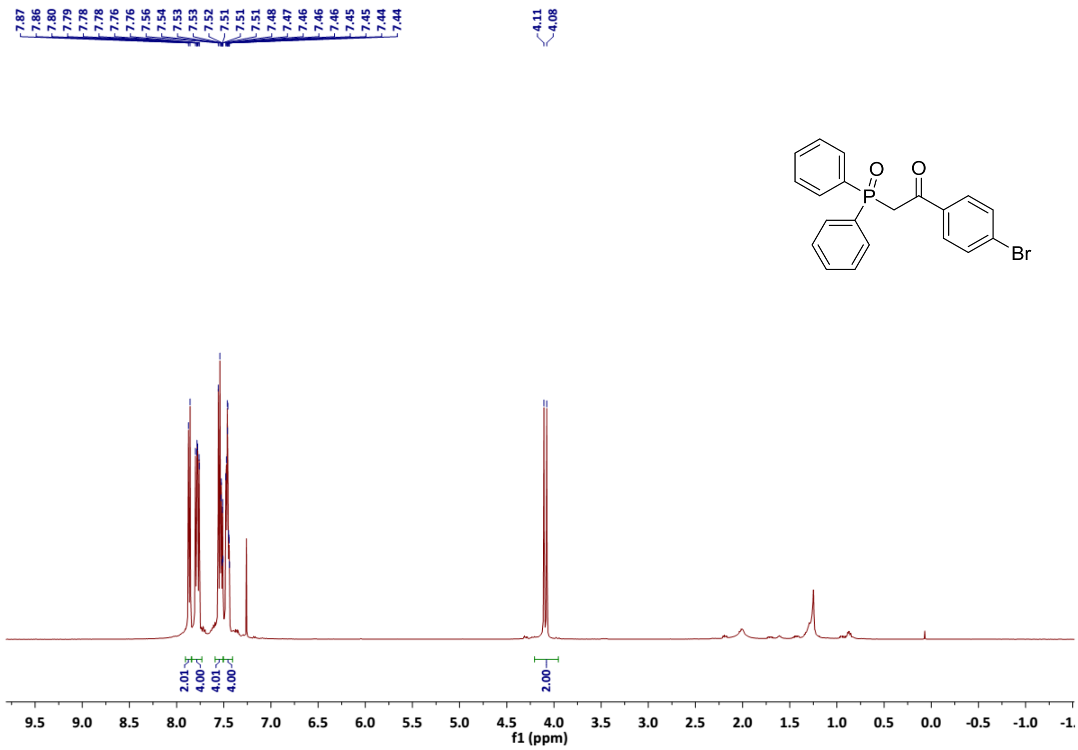
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3g**



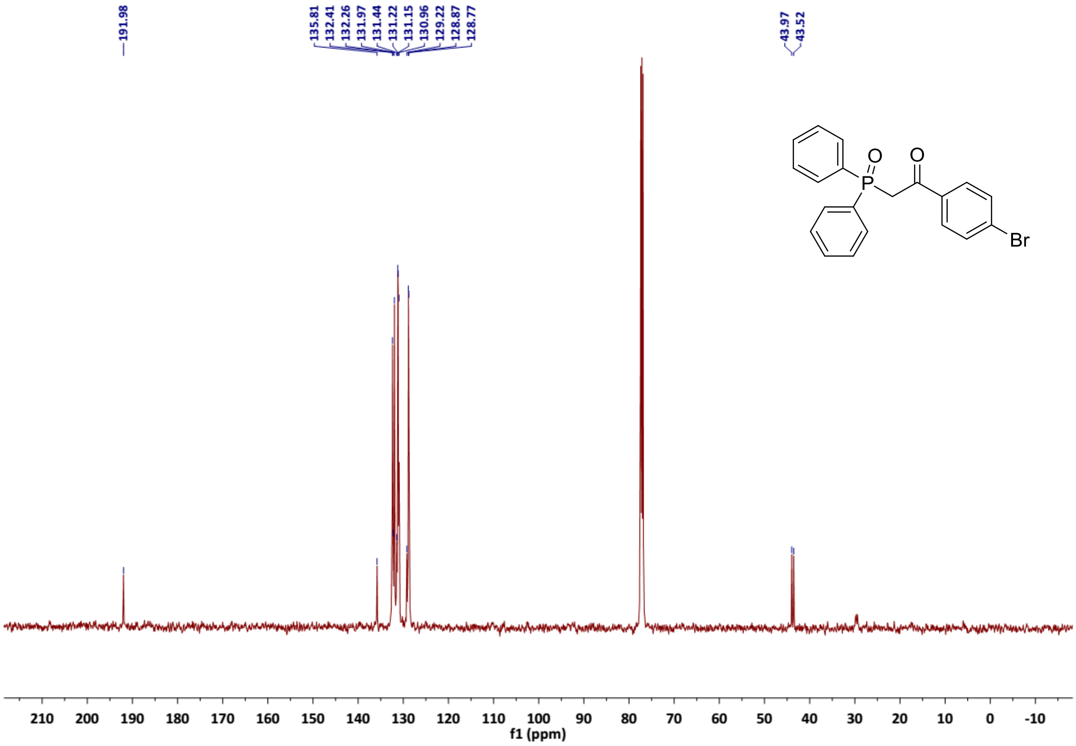
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3g**



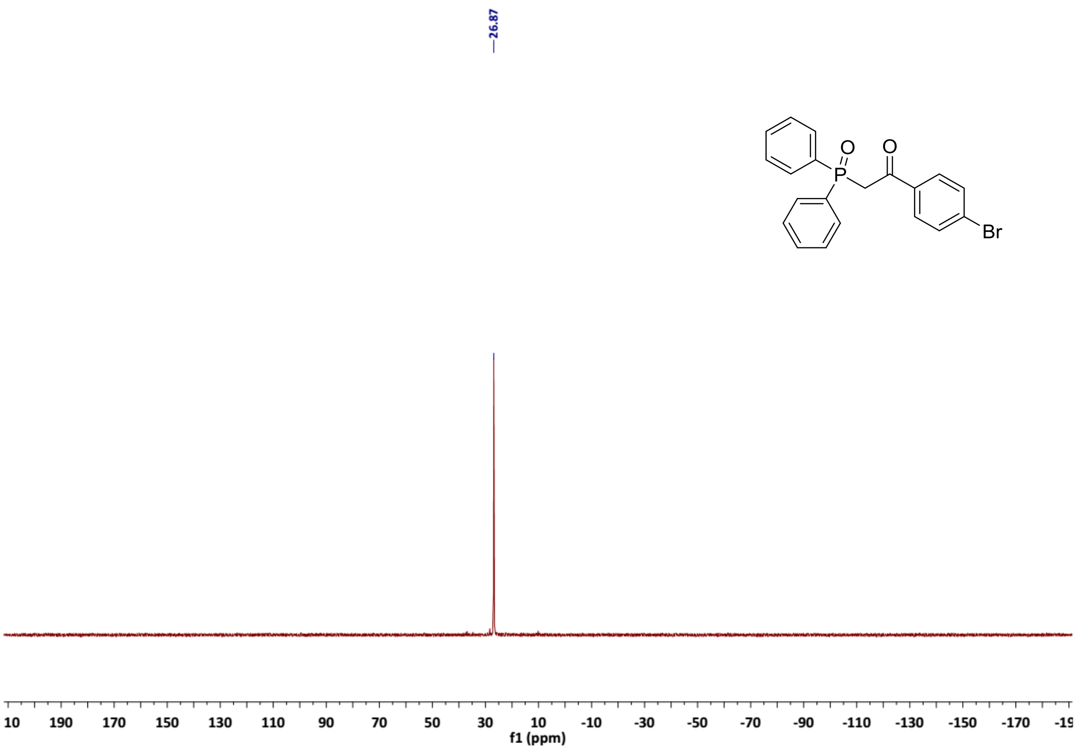
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3g**



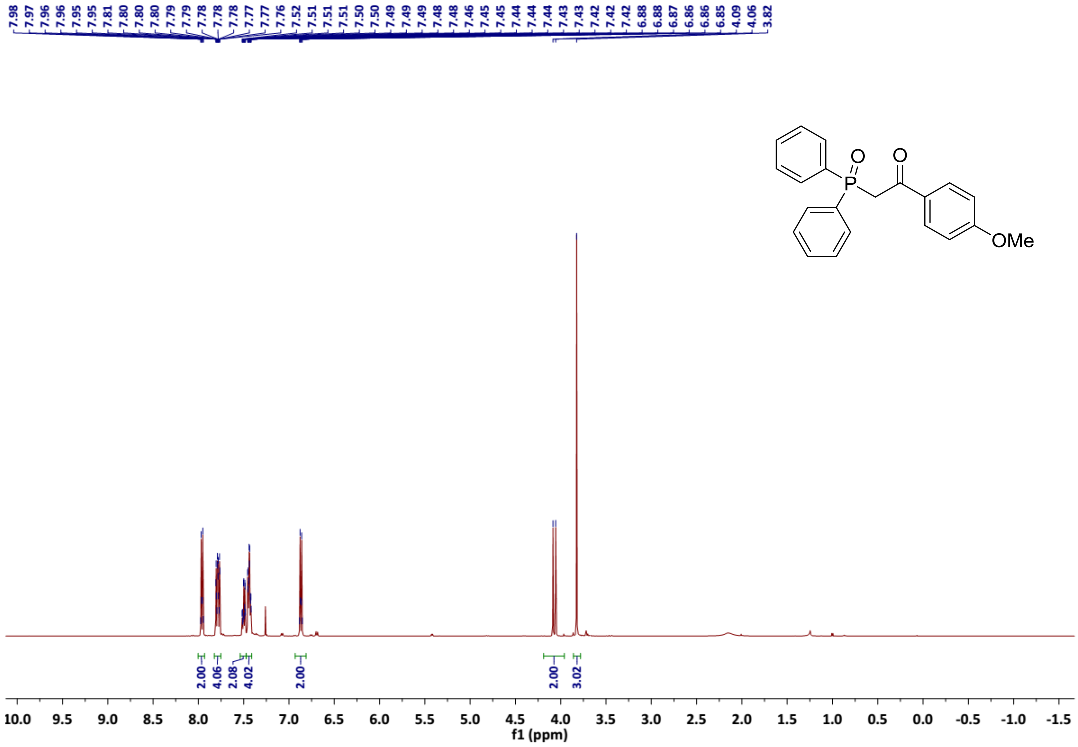
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3h**



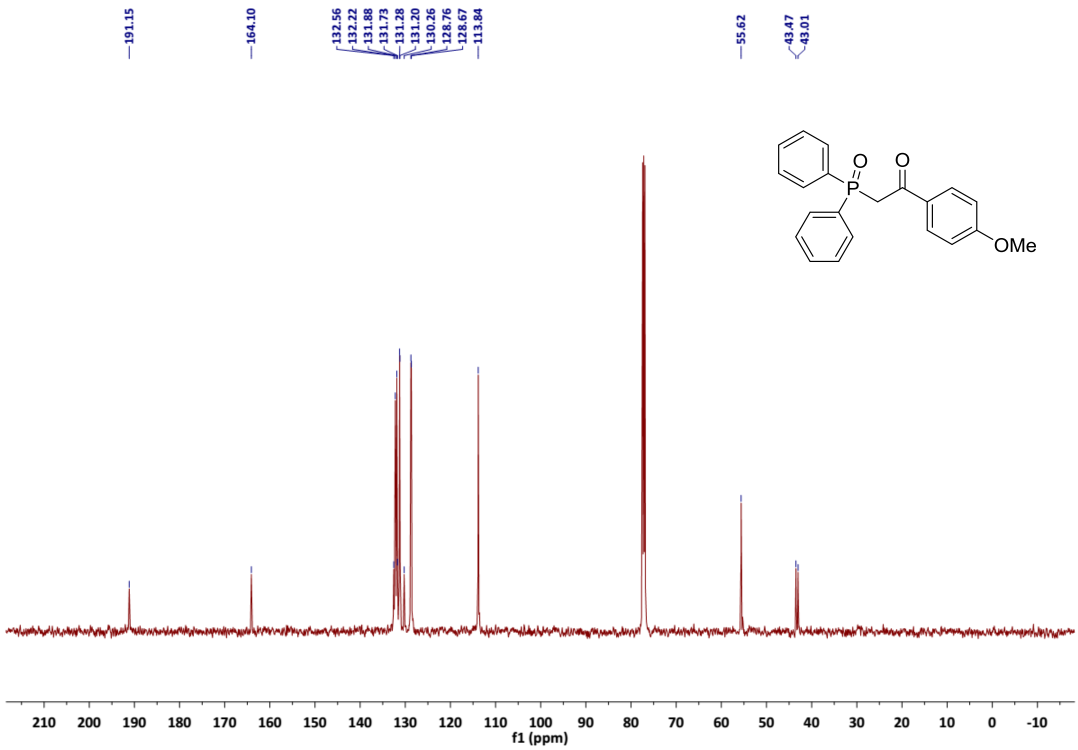
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3h**



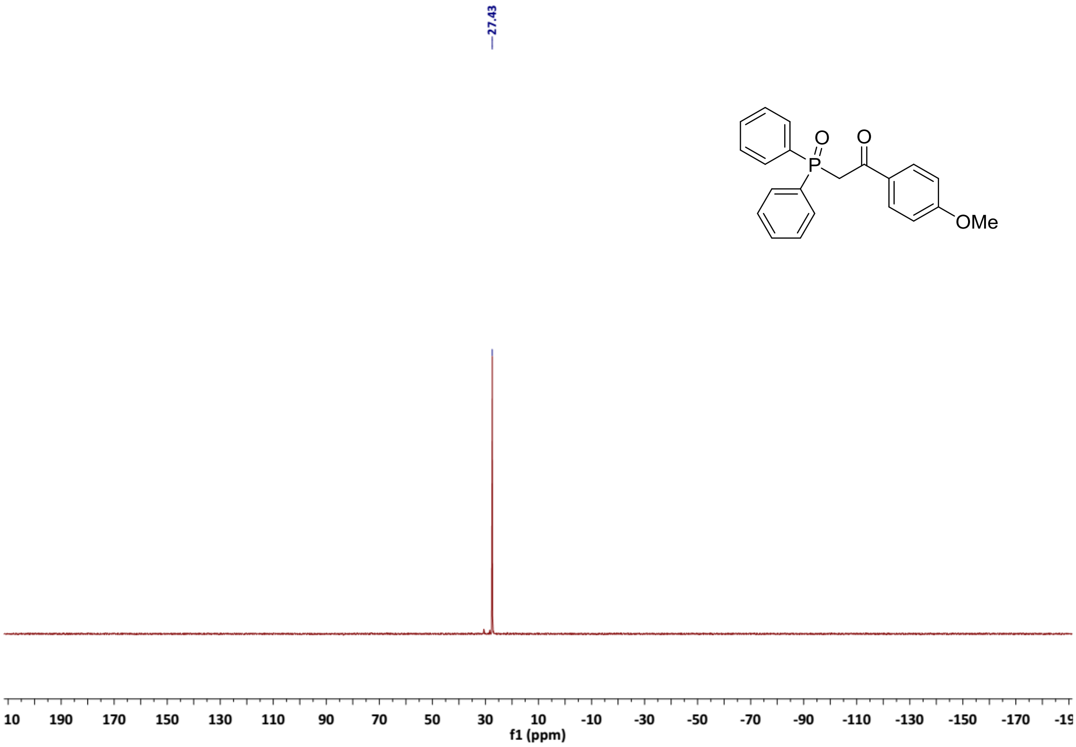
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3h**



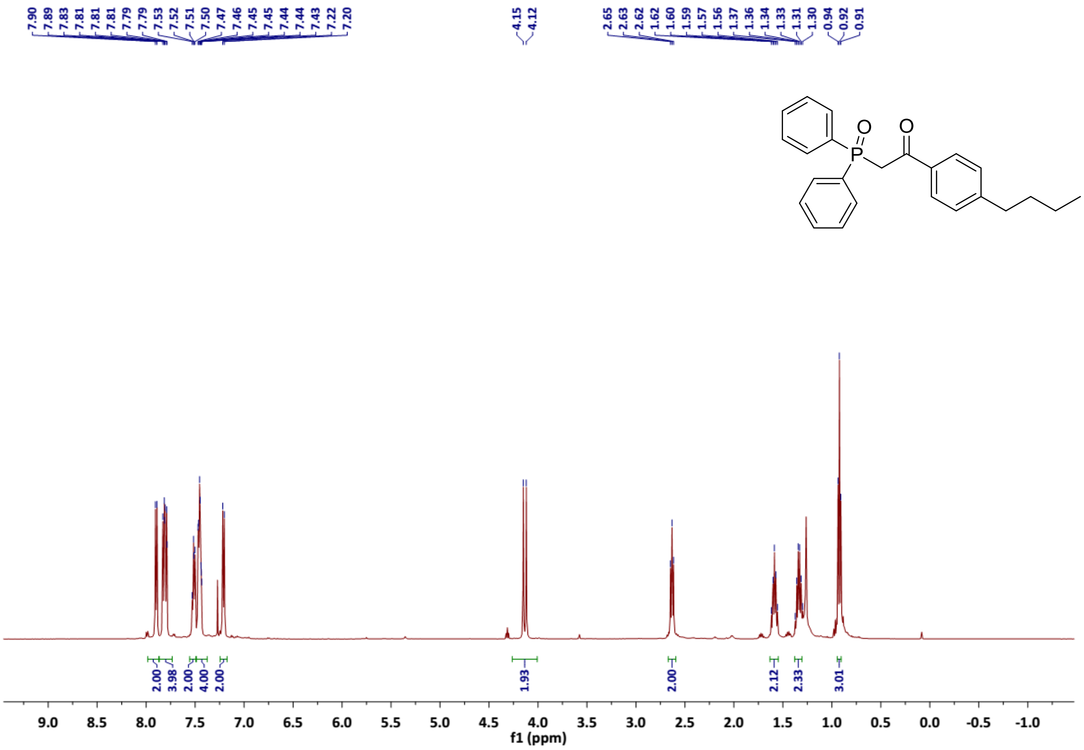
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3i**



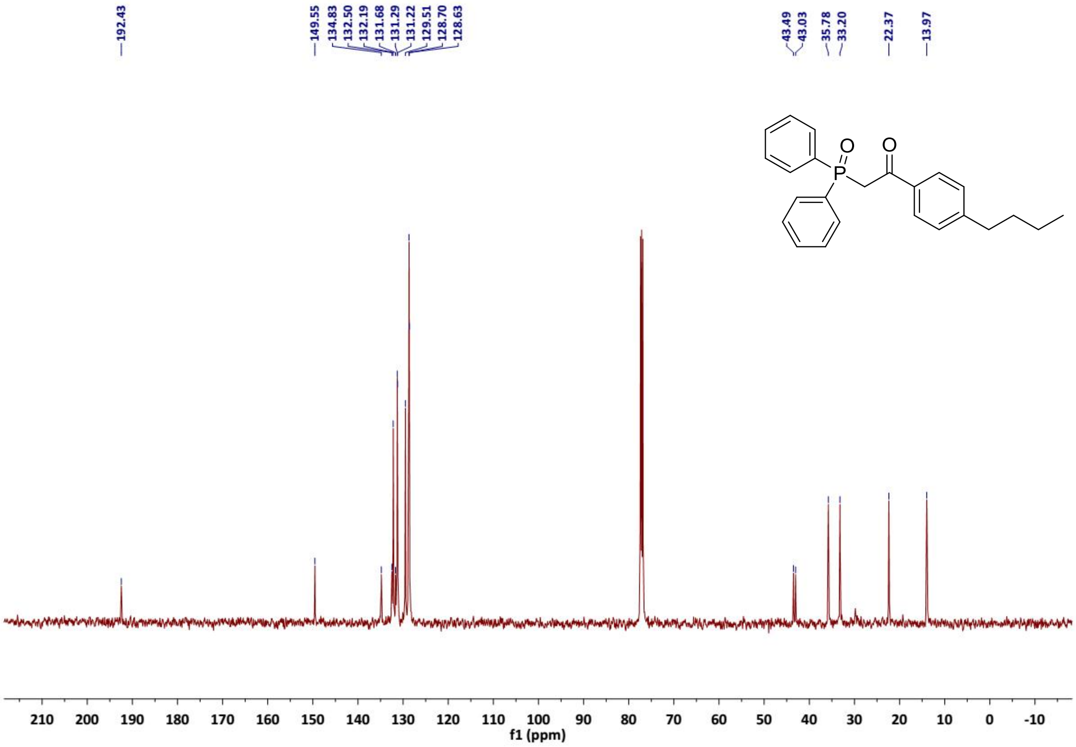
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3i**



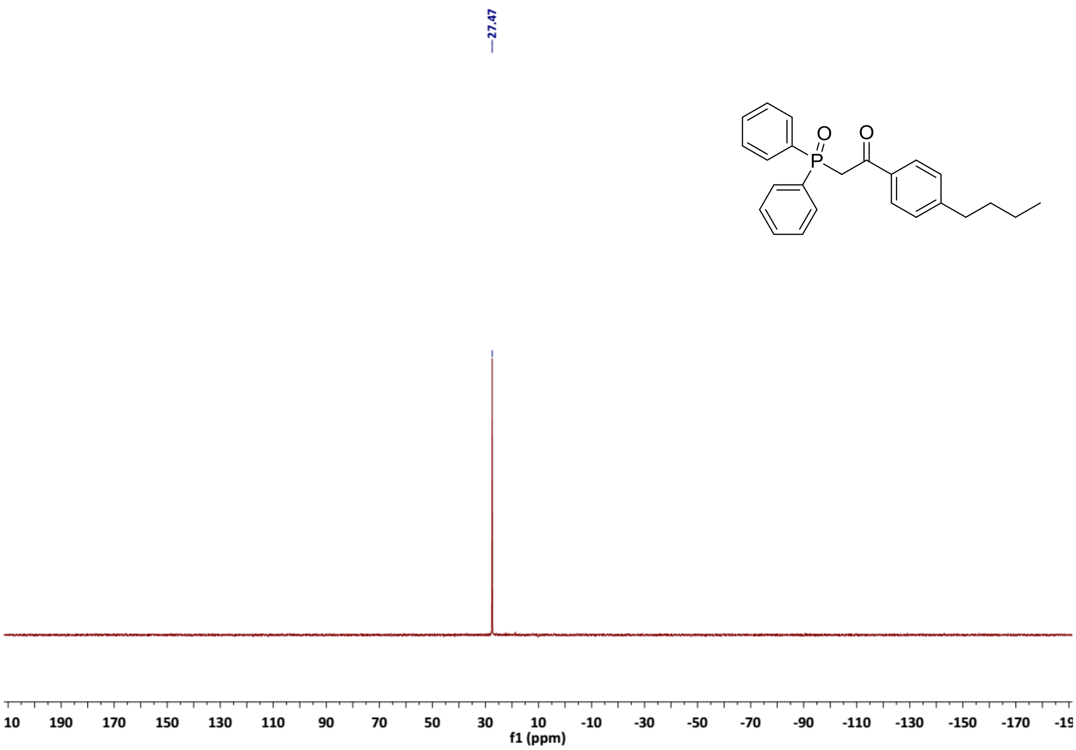
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3i**



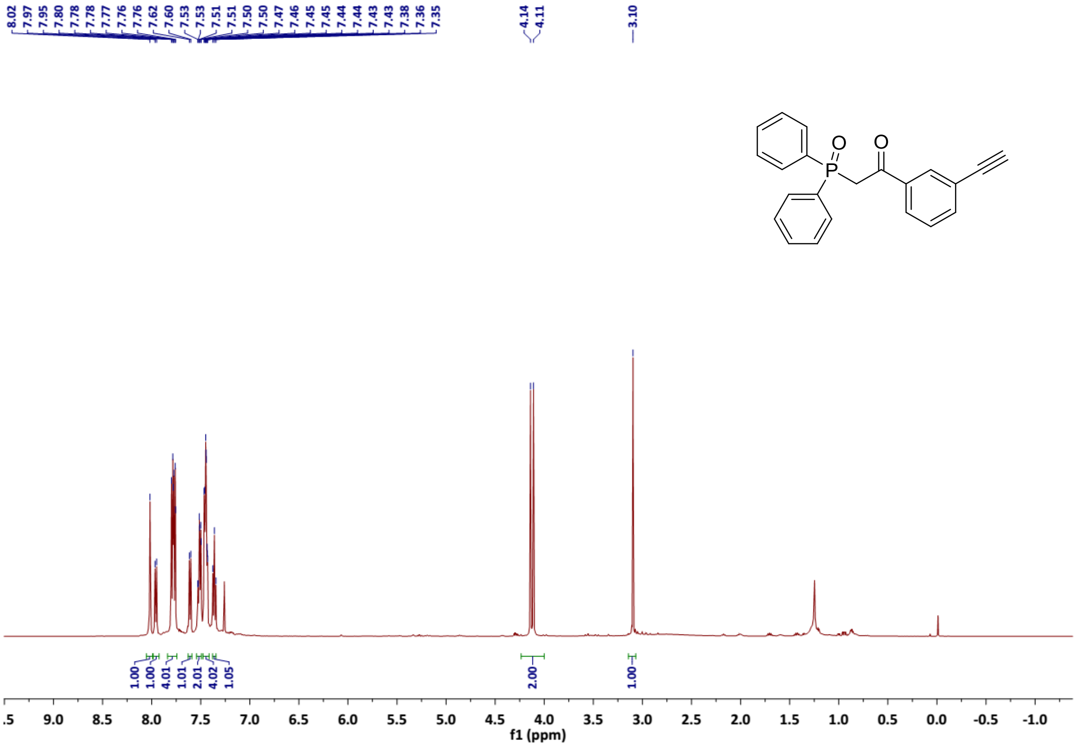
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3j**



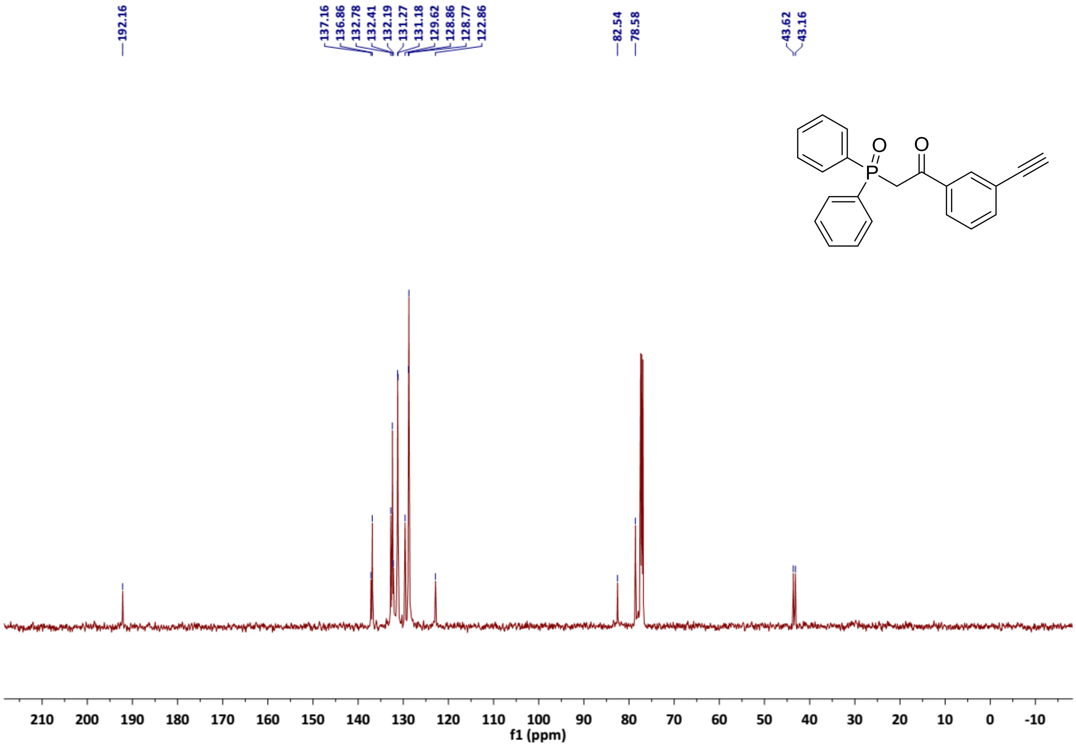
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3j**



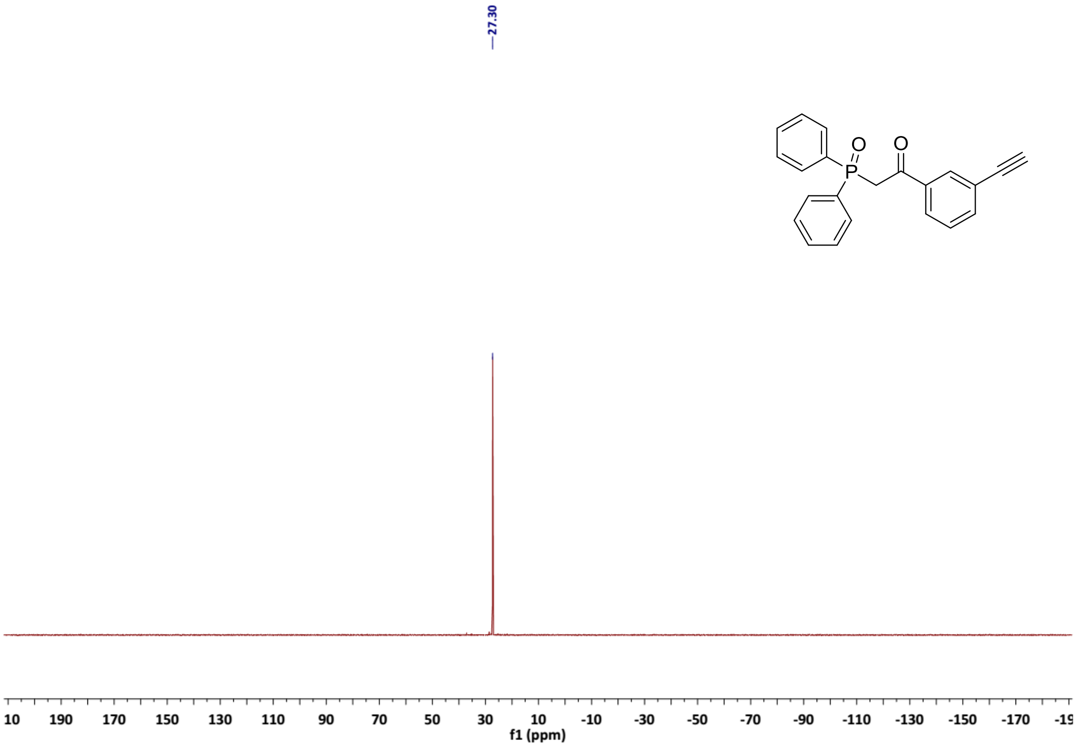
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3j**



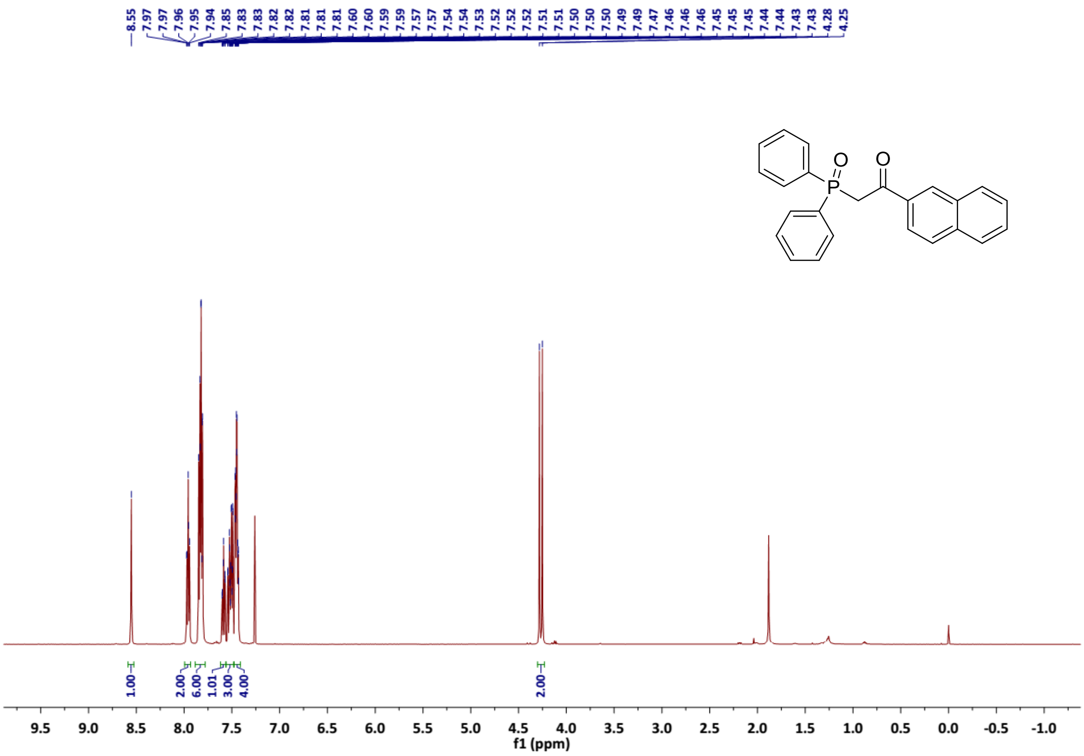
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3k**



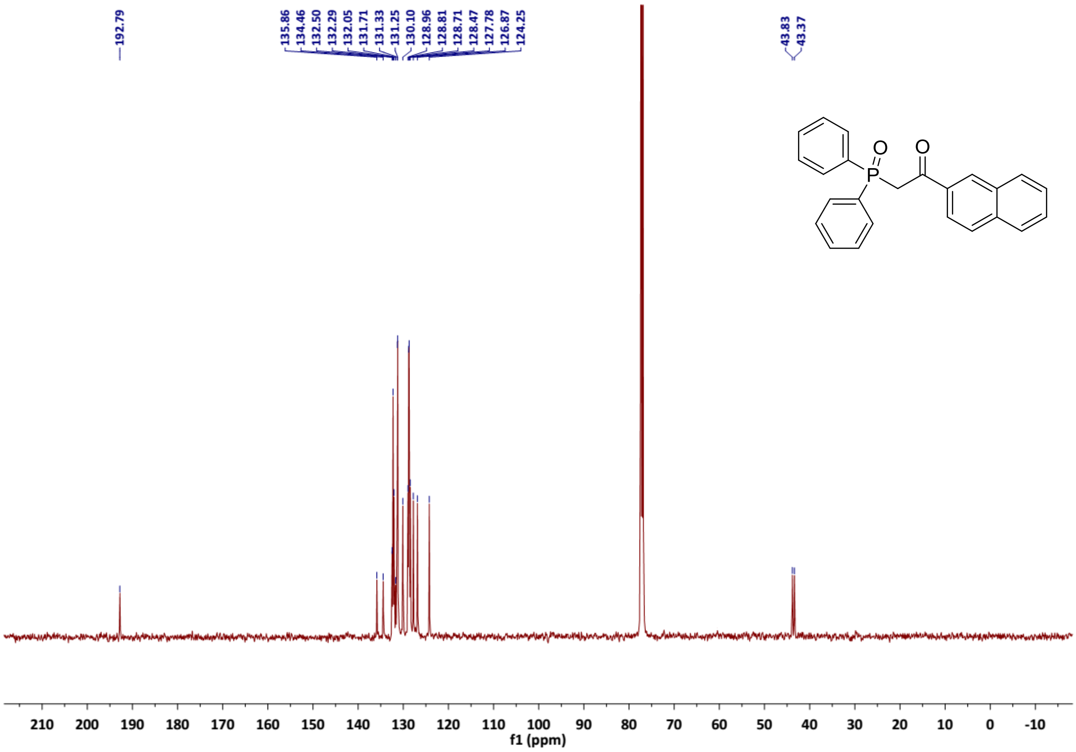
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3k**



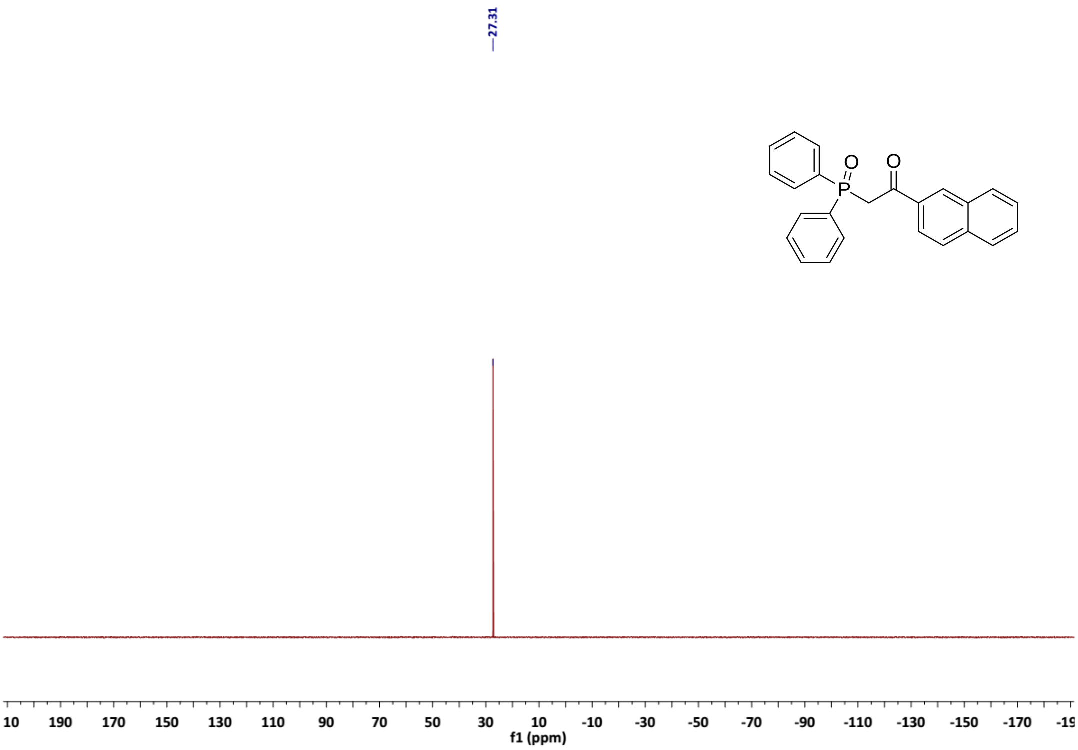
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3k**



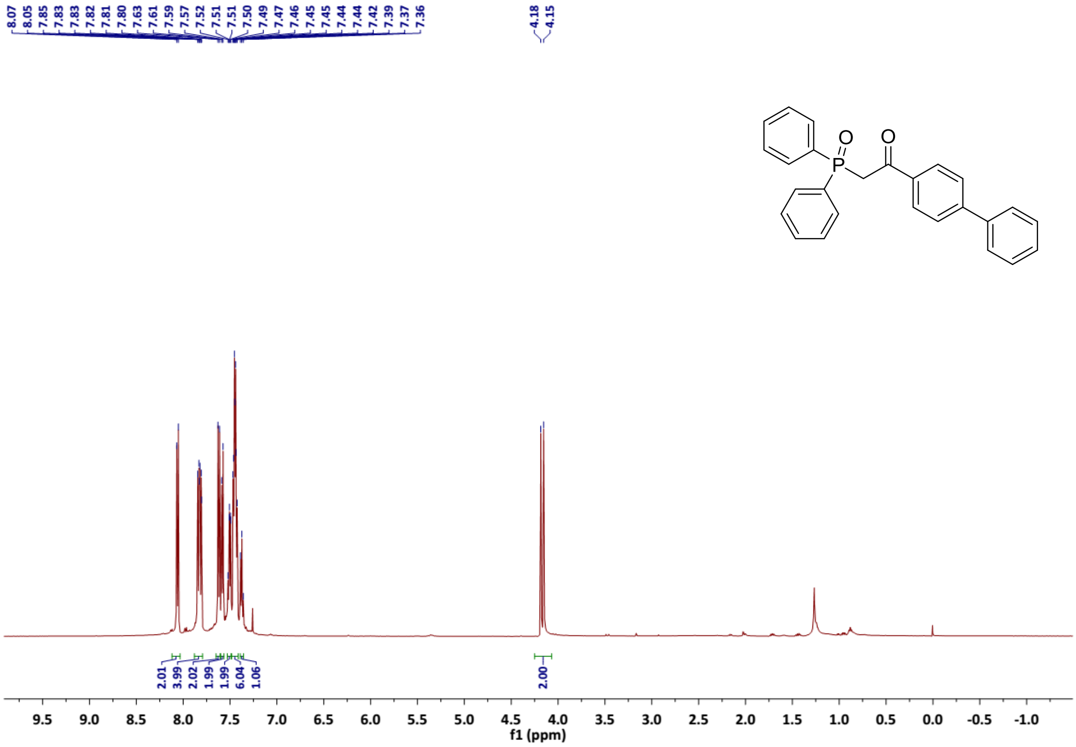
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3l**



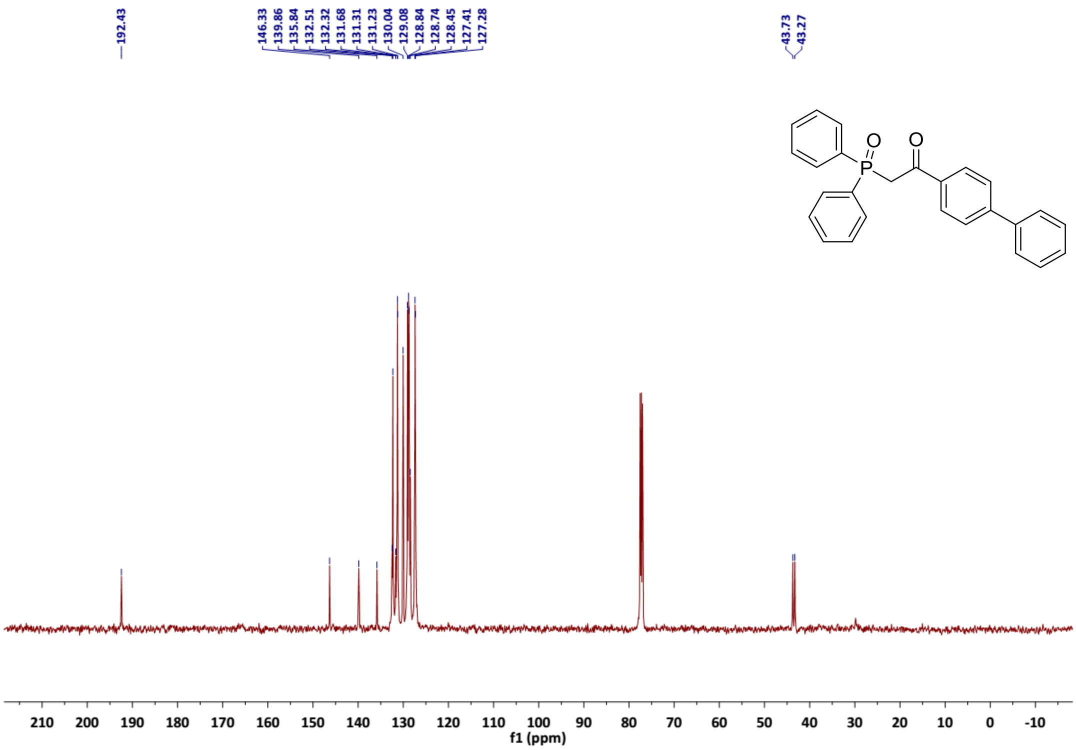
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3l**



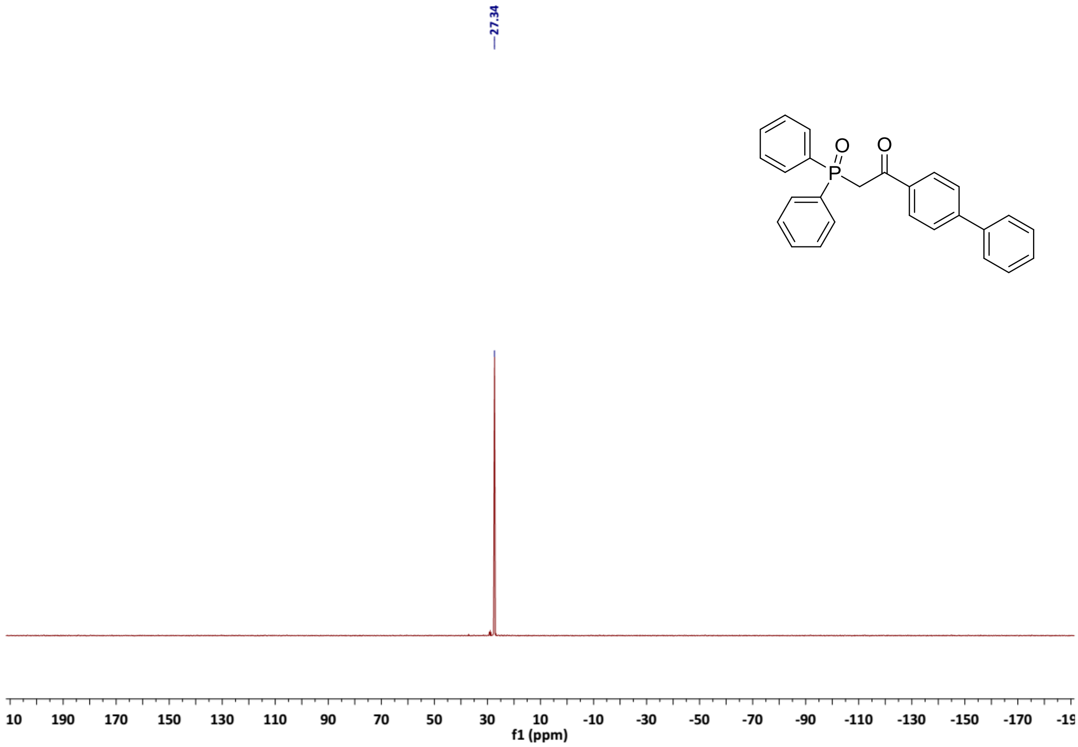
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3l**



[1]H NMR spectrum (500 MHz, $CDCl_3$) of **3m**



[13]C NMR spectrum (125 MHz, $CDCl_3$) of **3m**



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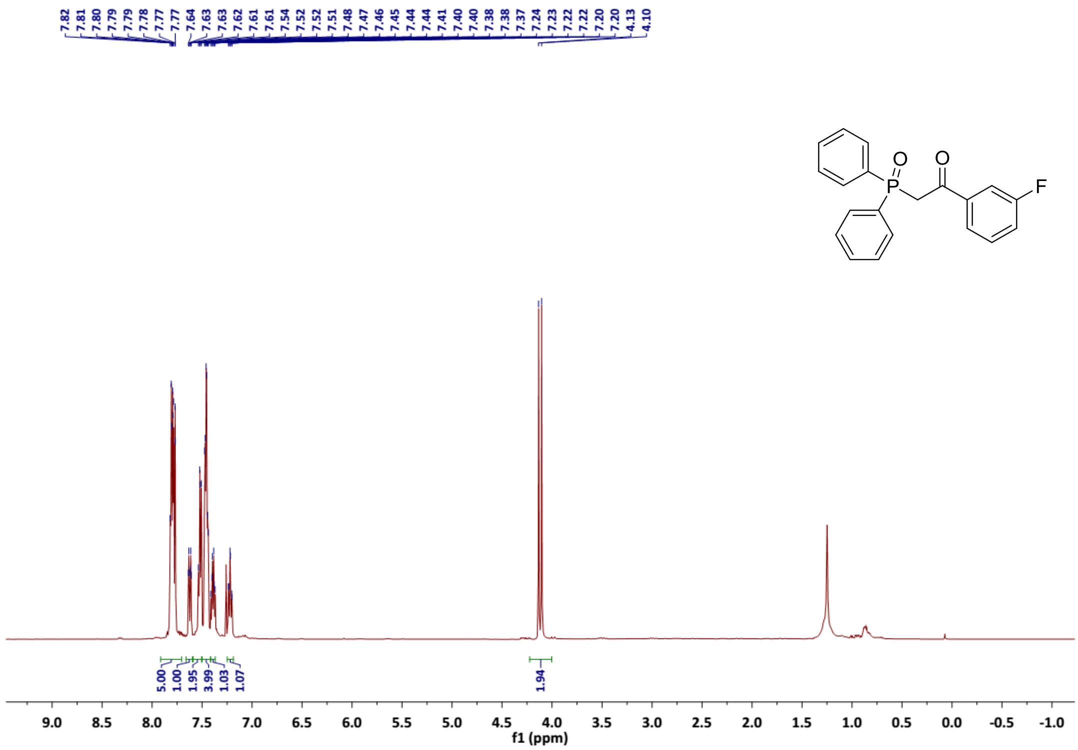
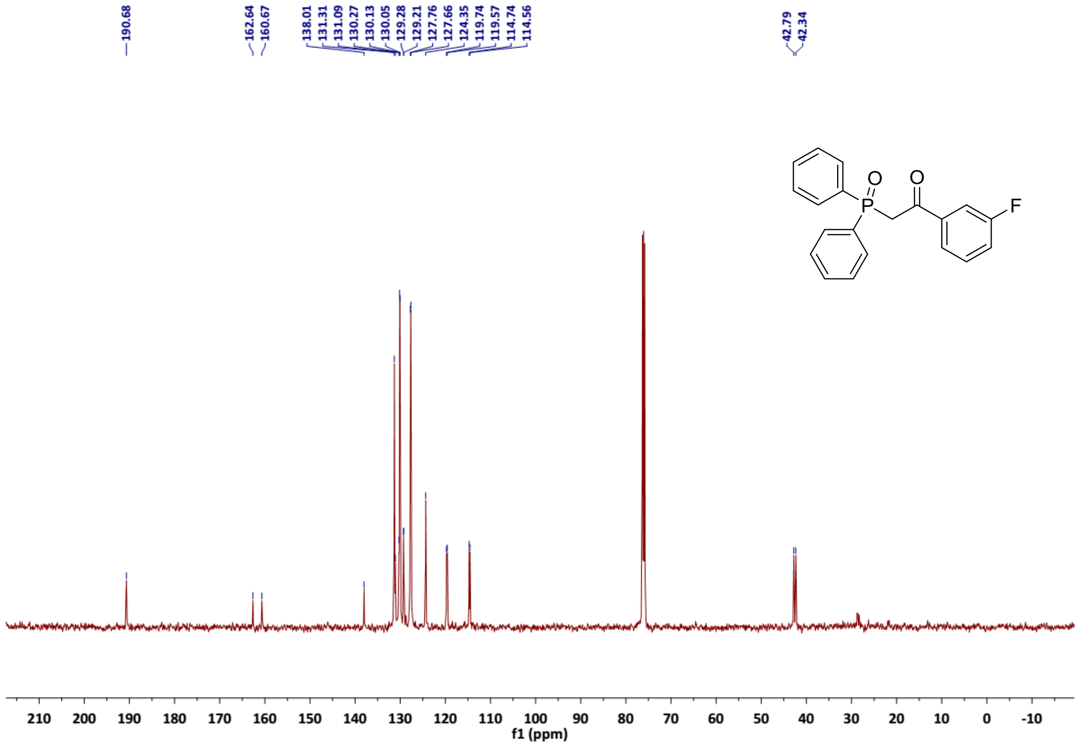
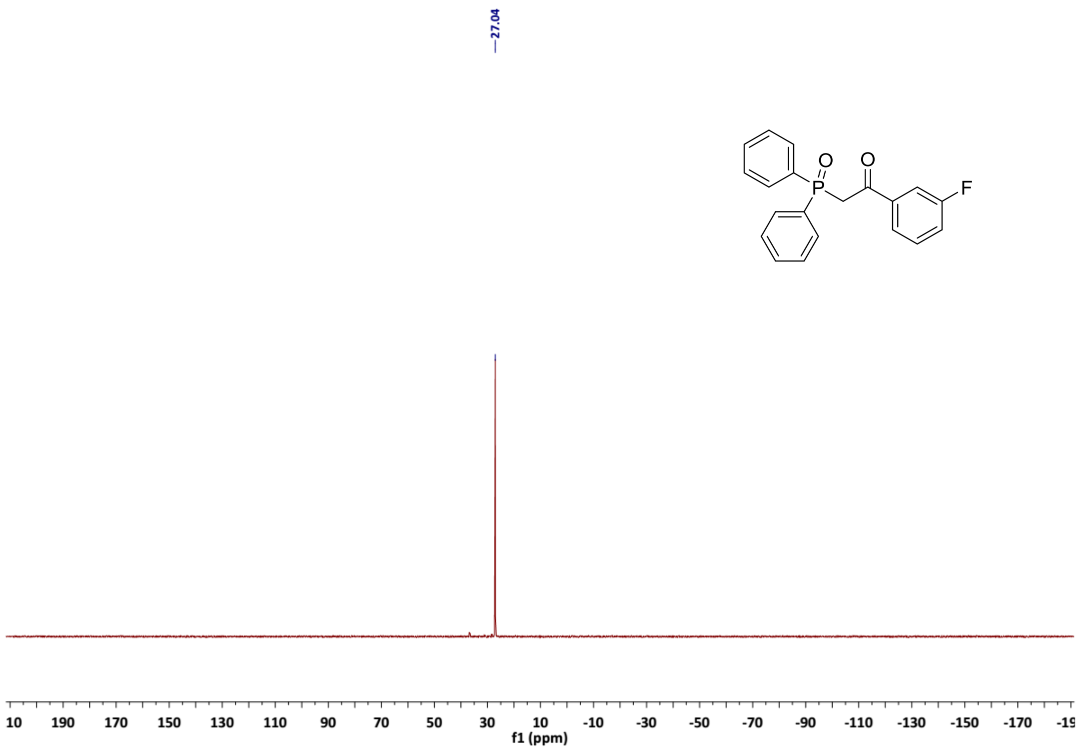


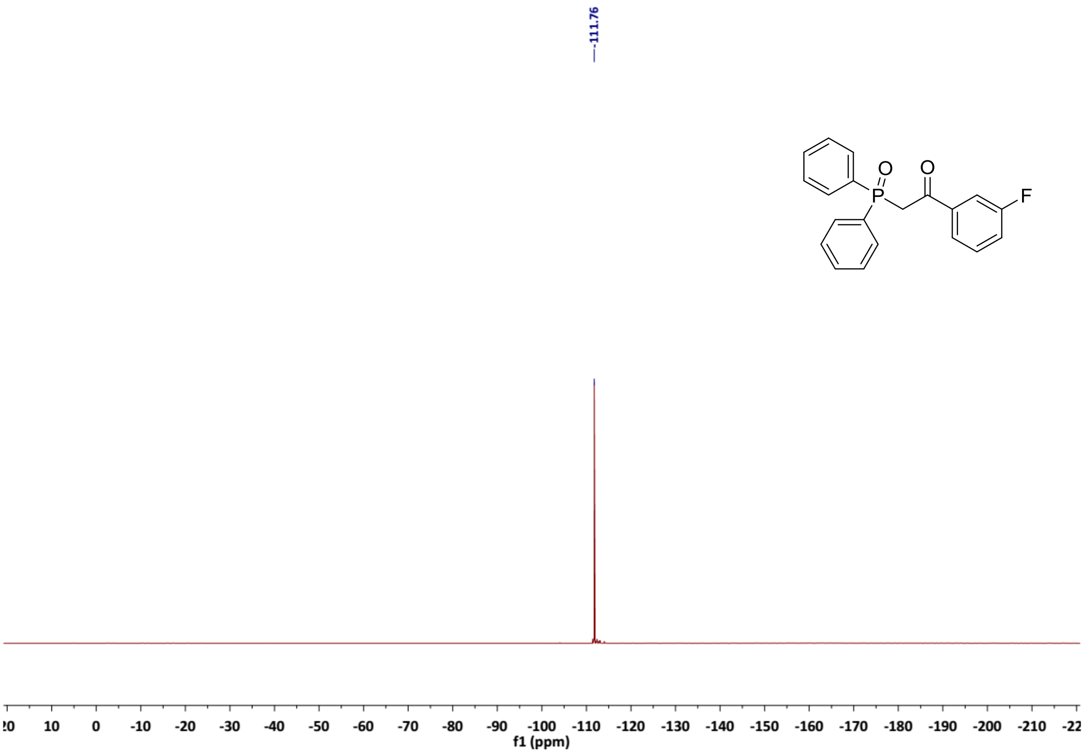
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3n**



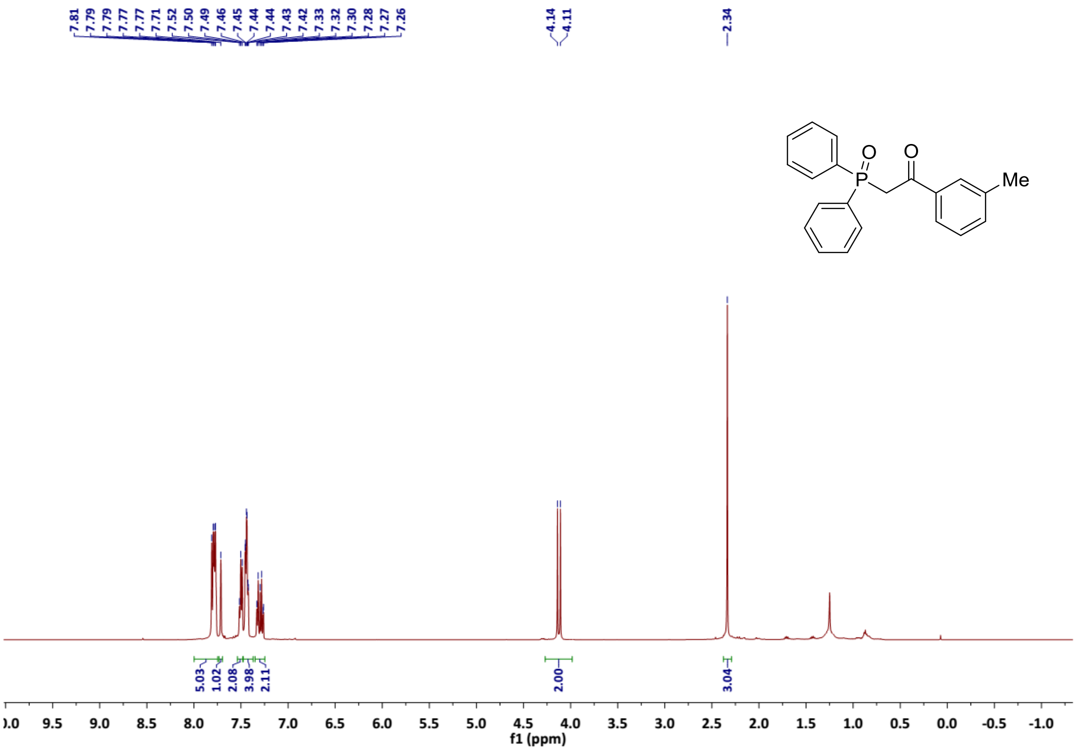
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3n**



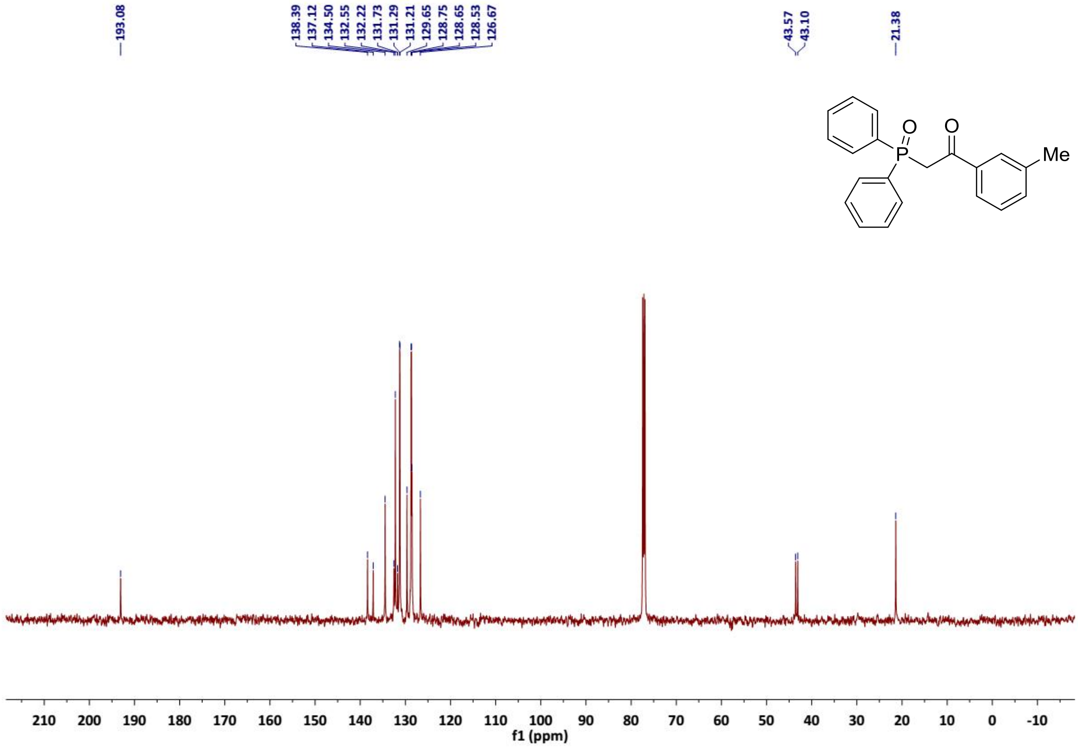
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3n**



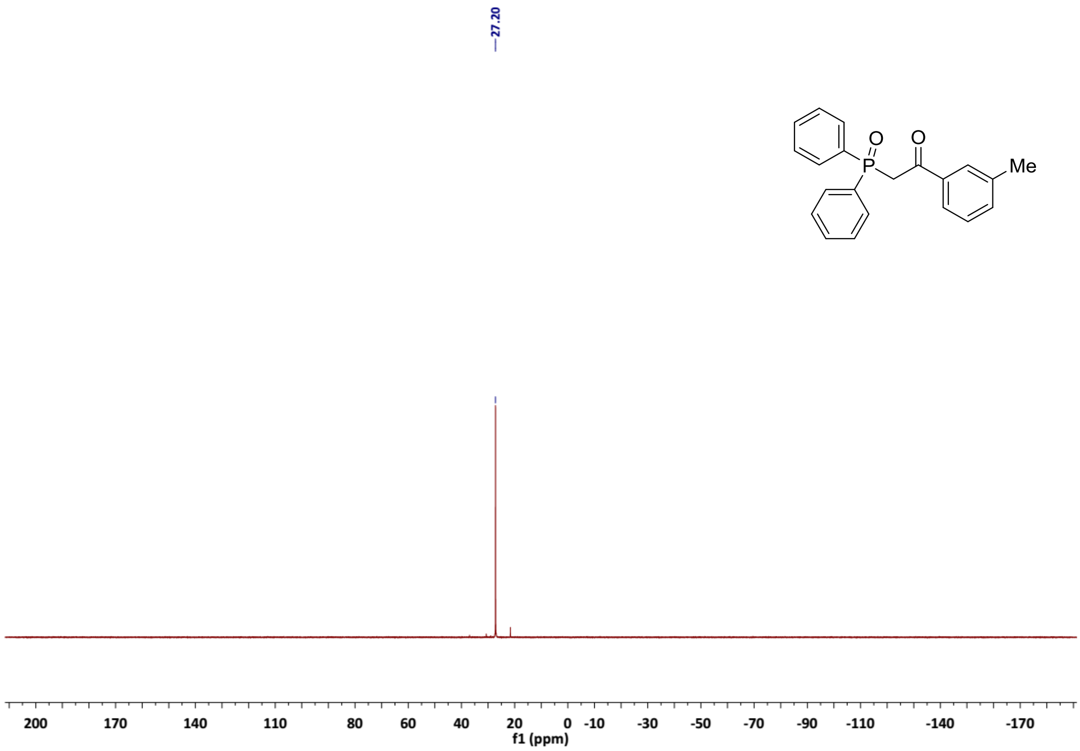
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **3n**



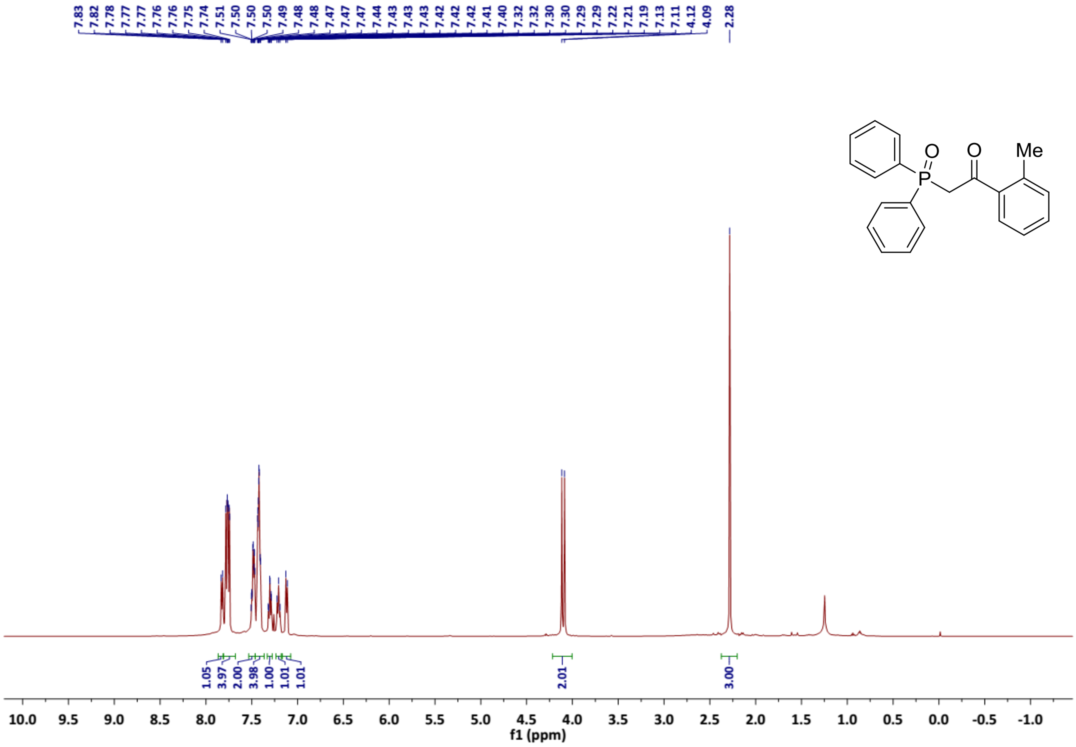
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3o**



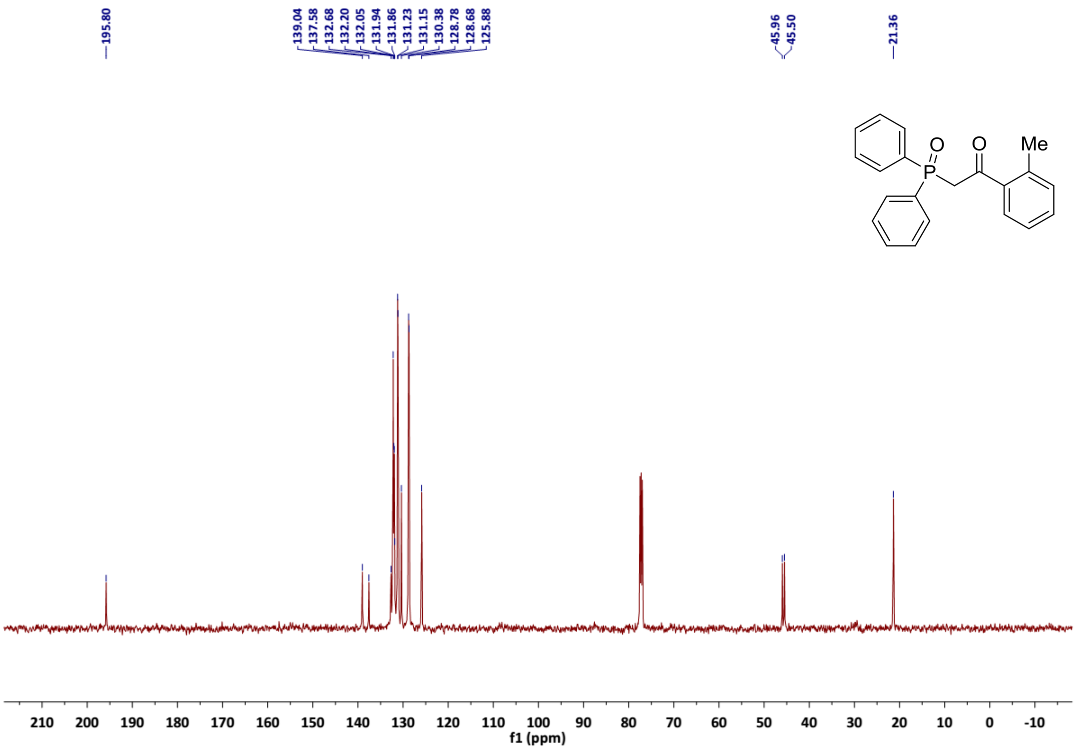
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3o**



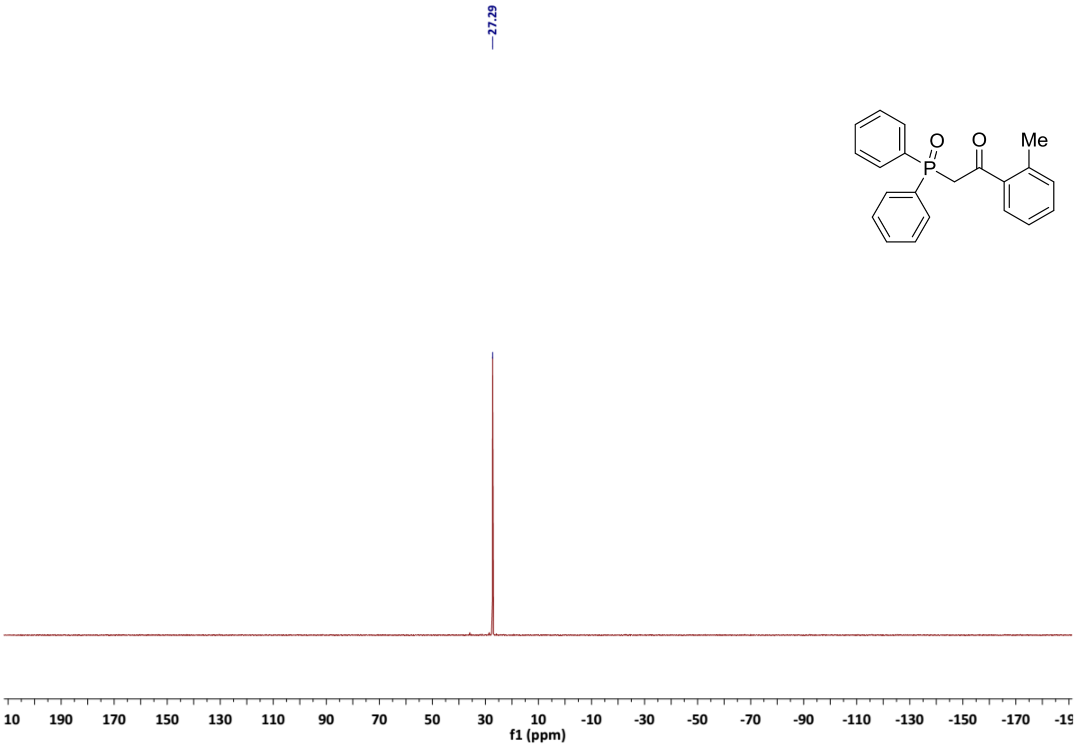
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3o**



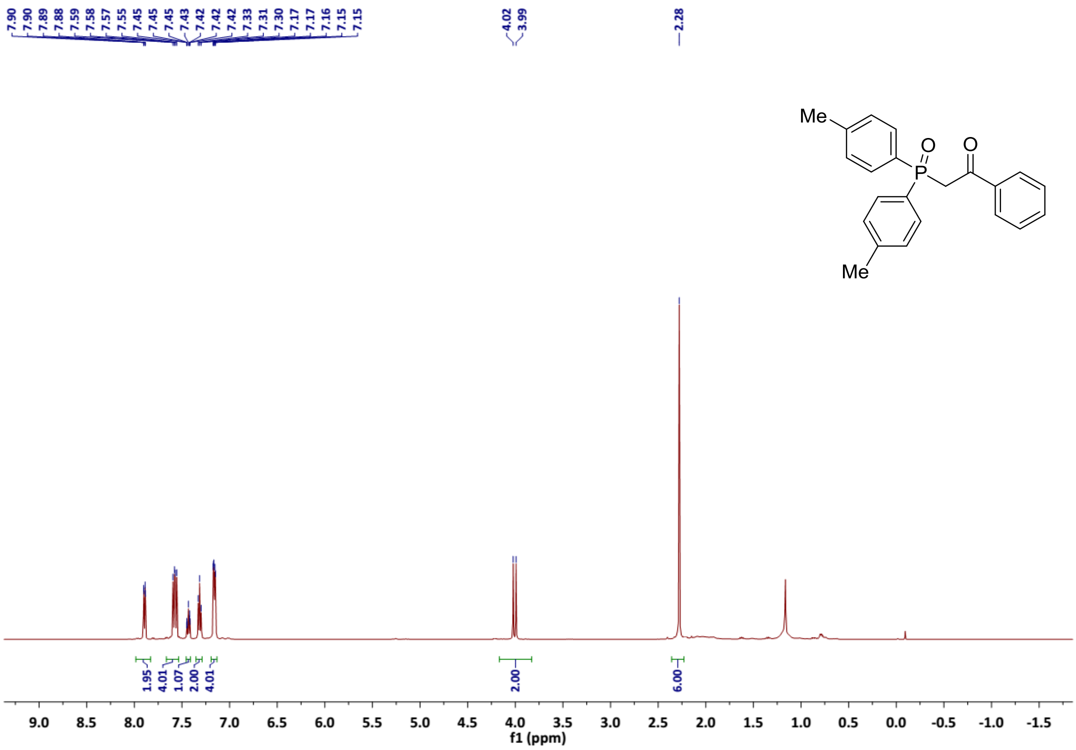
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3p**



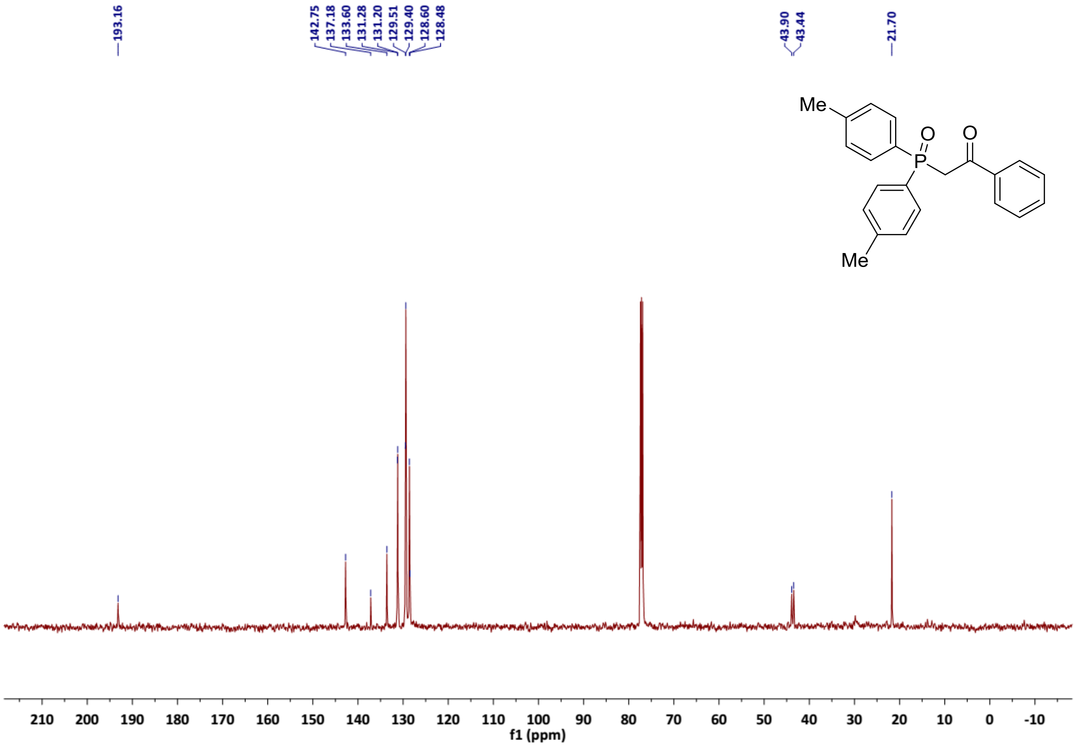
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3p**



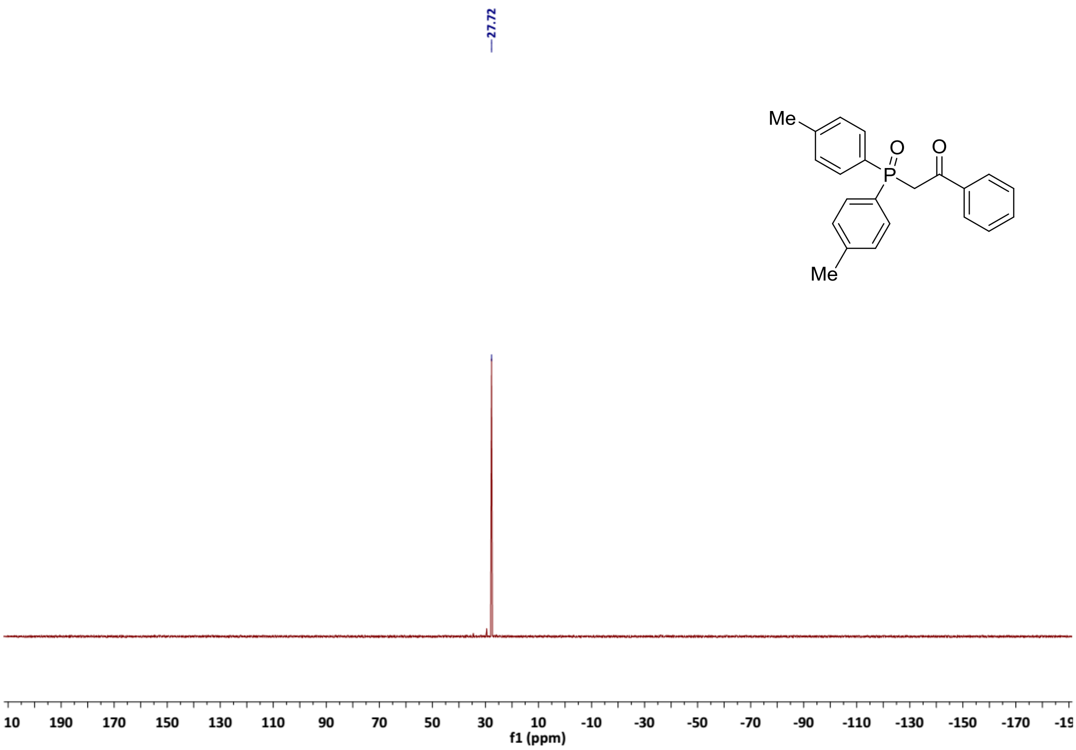
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3p**



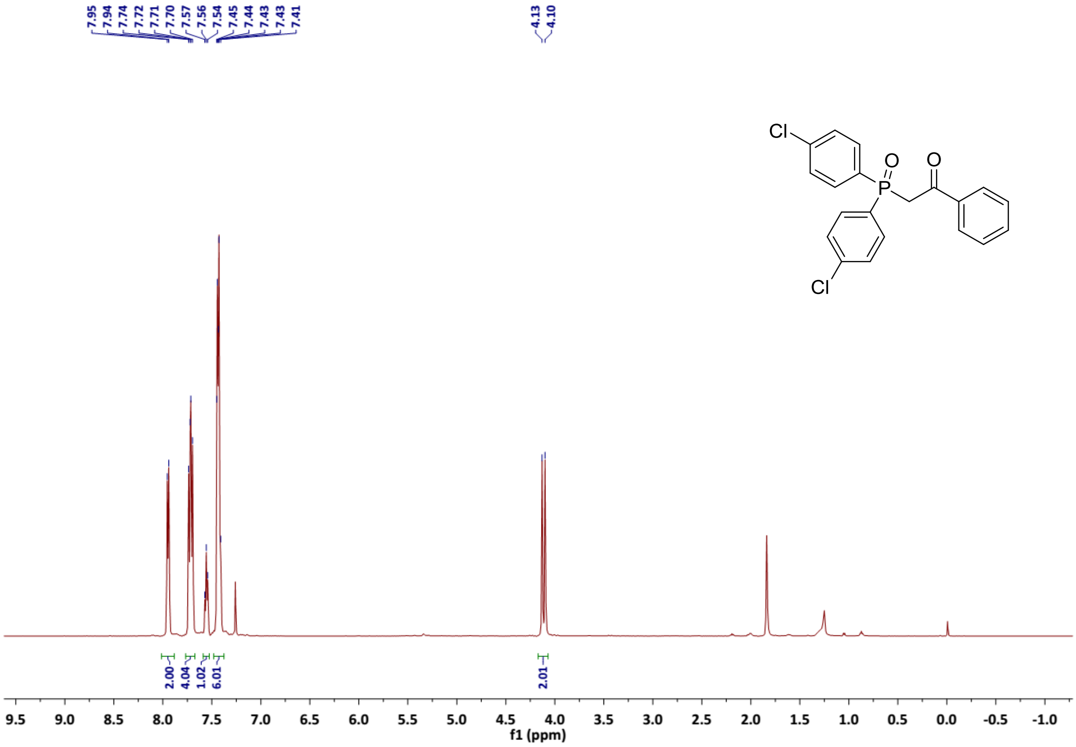
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3q**



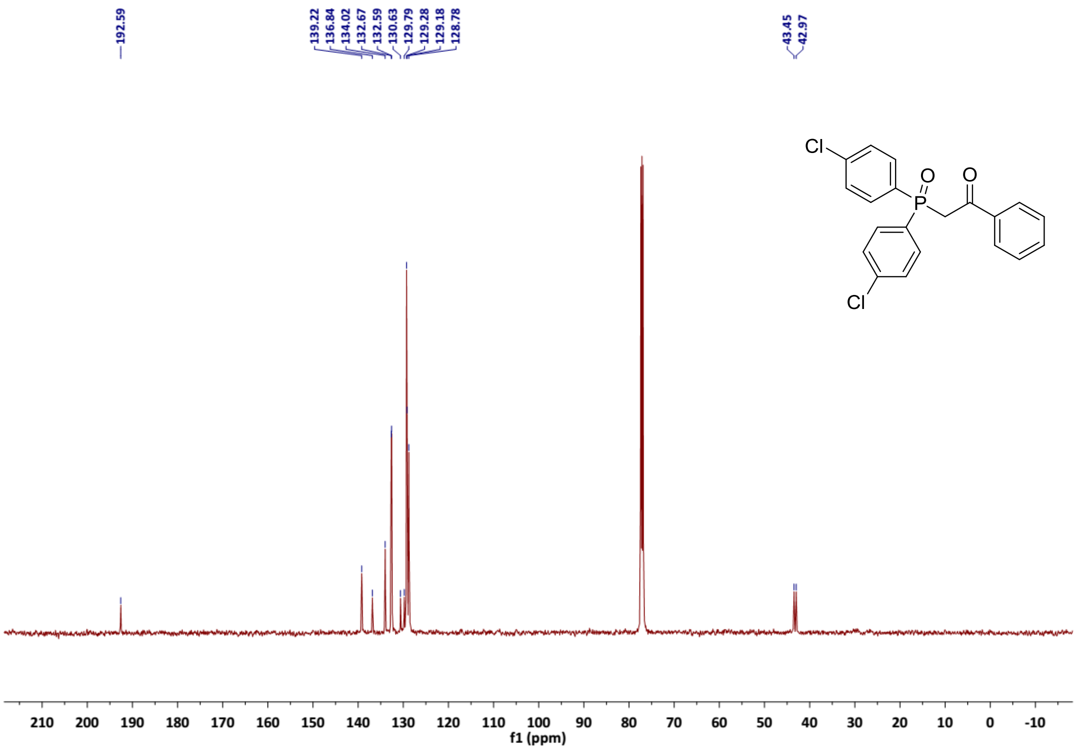
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3q**



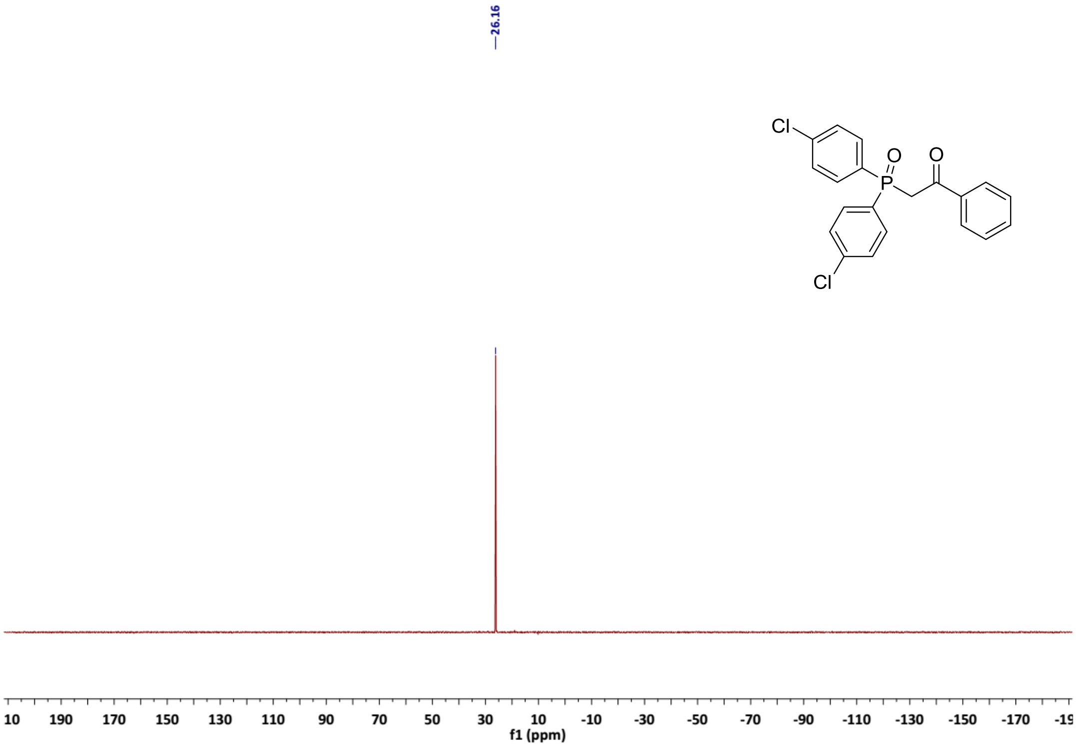
^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3q**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3r**



^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3r**



^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **3r**