Supplementary Information

Manganese (I)-Catalyzed Access to 1,2-Bisphosphine Ligands

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Table of contents

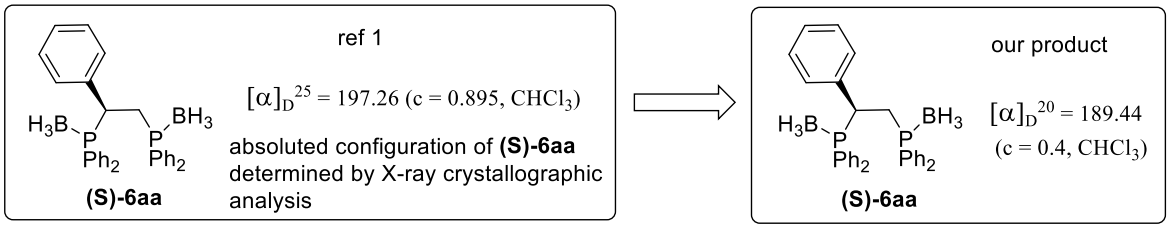
1. General experimental information

All reactions using oxygen- and/or moisture-sensitive materials were carried out with anhydrous and deoxygenated solvents under a nitrogen atmosphere using oven dried glassware and standard Schlenk techniques. Reactions of hydrophosphination using toluene as solvent were carried out using the glovebox. Reactions were monitored by ^{1}H NMR and ^{31}P NMR. Purification of the products was performed by flash-column chromatography using Merck 60 Å 230-400 mesh silica gel. NMR data was collected on Varian VXR400 (^{1}H at 400 MHz; ^{13}C at 100.58 MHz) equipped with a 5 mm *z*-gradient broadband probe. Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak ($CDCl_3$, ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm; Toluene-d_8, ^{1}H: 7.09 7.00 6.98 2.06 ppm, ^{13}C: 129.2 128.3 125.49 20.4 ppm). Coupling constants are reported in Hertz. Multiplicity is reported with the usual abbreviations (s: singlet, d: doublet, br s: broad singlet, dd: doublet of doublets, t: triplet, m: multiplet). Exact mass spectra were recorded on a LTQ Orbitrap XL apparatus with ESI ionization. Enantiomeric excess (*ee*) of all compounds was determined by Chiral HPLC analysis using a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector.

Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. Solvents not required to be dry were purchased as technical grade and used as received. Dry solvents were freshly collected from a dry solvent purification system prior to use. Inert atmosphere experiments were performed with standard Schlenk techniques with dried (P_2O_5) nitrogen gas or inside the glovebox (the levels of O_2 and H_2O were maintained under 0.1ppm). Acetylene derivatives (**S1**), diarylphosphine oxides (**S2**), diphenyl(vinyl) phosphine oxide (**1'b**), Phosphine reagents (**R_2PH**) were purchased from Sigma-Aldrich, TCI and ABCR. Unless otherwise noted substrates were prepared by literature reported methods (*vide infra*). All new compounds were fully characterized by ^{1}H, ^{13}C and ^{31}P NMR, HPLC and HRMS techniques.

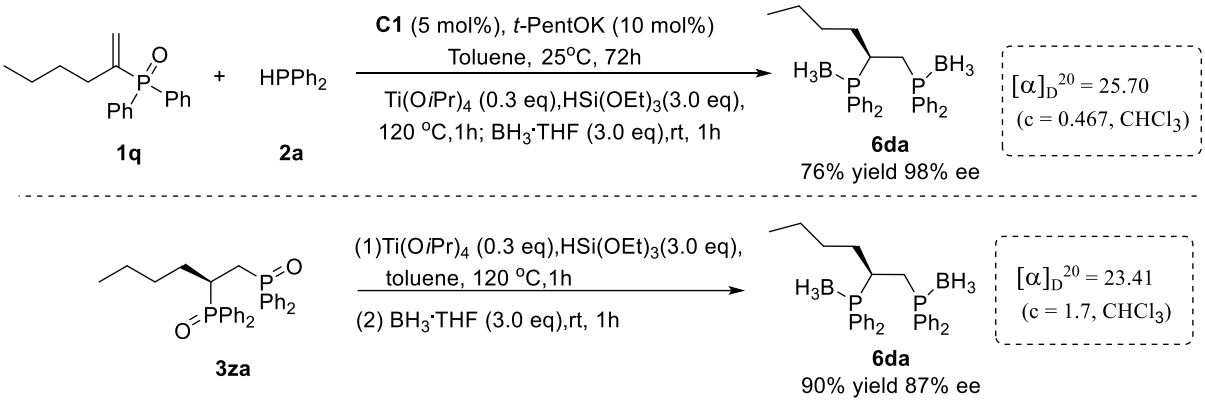
2. Determination of absolute configuration and NMR studies

2.1 Determination of the absolute configuration of 6aa



The absolute configuration of the product **6aa** has been determined by X-ray crystallographic analysis in Yin's work (*Angew. Chem., Int. Ed.* **2020**, *59*, 7057–7062).[1] In their report, the optical rotation of (S)-**6aa** is $[\alpha]_D^{25}$ = 197.26 (c = 0.895, $CHCl_3$). For our product **6aa**, the optical rotation is $[\alpha]_D^{20}$ = 189.44 (c = 0.4, $CHCl_3$). Thus, the product **6aa** obtained via our protocol with **(R_c, S_p)-C1** as the catalyst is S configuration. The absolute configuration of other products was assigned accordingly.

2.2 Determination of the absolute configuration of 3za

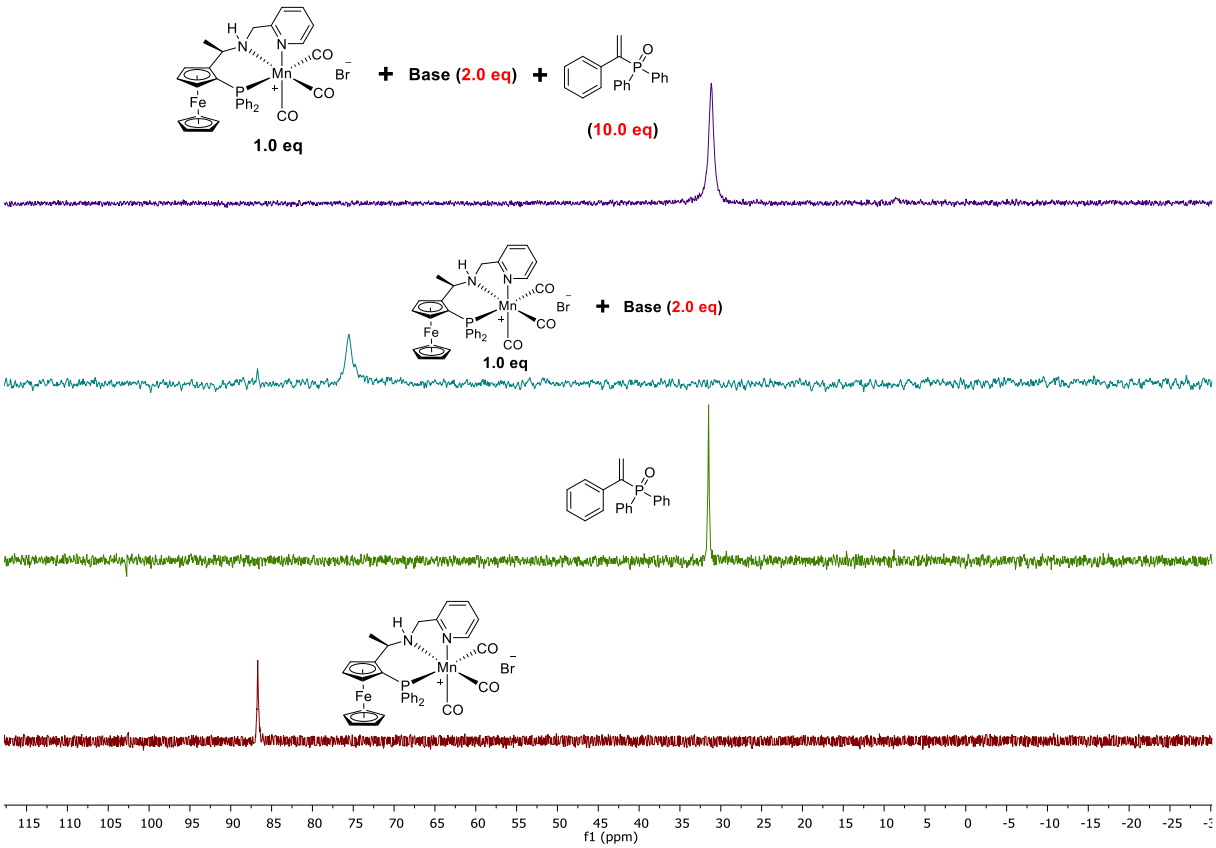


3za was transformed to **6da** through reduction, which led to the determination of the absolute configuration of **3za**.

2.3 NMR spectroscopic studies

NMR spectroscopic studies were performed to understand interactions between activated Mn-complex and phosphine oxide substrate. 31P NMR spectroscopy at rt temperature was used for this purpose. All the NMR tube samples were prepared in glove box using young valve NMR tubes and deuterated toluene as a solvent. As it can be seen from the figure below upon addition of 2.0 eq. of base to **Mn(I)-L** new compound, namely activated Mn-catalyst is being formed as it can be deduced by the disappearance of the original peak and the appearance of a new one. Upon addition of10 eq. of phosphine oxide **1a** which is completely soluble in toluene, the only peak that can be observed is from the oxide itself, while activated complex disappears. This process is also accompanied by large amount of precipitate formed which could not be characterized since it was decomposed upon attempts to isolate. This precipitate doesn't form

under reaction conditions when diphenylphosphine is also present and therefore it cannt be related to some intermediate that is involved in the reaction path. Further detailed studies are required to get clear mechanistic picture of this transformation.



Scheme S1: 31 P NMR in d-toluene from the bottom to the top: **Mn(I)-L**, **1a, Mn(I)-L** + 2.0 equiv. of tPentOK, **Mn(I)-L** + 2.0 eq. of tPentOK + 10.0 eq. of **1a**

3. Manganese (I)-Catalyzed Asymmetric Hydrophosphination/Protonation of α, β-unsaturated Phosphine Oxides

3.1 General procedure A

All the reactions performed with toluene as solvent were carried out inside the glovebox in order to ensure inert reaction conditions. In an oven-dried 4 mL vial equipped with a magnetic stirring bar, **Mn(I)-L** (0.0025 mmol, 2.5 mol%) was dissolved in 0.5 mL of deoxygenated toluene and stirred for 1 min. Then, a commercially available solution of *t*PentOK 1.7 M in dry, deoxygenated toluene (0.005 mmol, 5 mol%) or Barton's base (0.005 mmol, 5 mol%) was added and the mixture was stirred during 5 min, observing complete solubility of the catalyst and a change in color of the solution due to the activation of the catalyst. When toluene is used as solvent and *t*PentOK as a base, a color change of the solution from yellow to dark red is observed. This color change is indicative of the catalyst activation.* After 5 min stirring, the substrate **1** (0.1 mmol, 1.0 equiv) (dissolved in 0.5 mL of deoxygenated toluene) was added at once followed by the addition of the phosphine **2** (0.105 mmol, 1.05 equiv).** (when the reaction was carried out at 60 ^{o}C, after the addition of substrate **1** and phosphine **2**, the reaction mixture was taken out of the glovebox and heated to 60 ^{o}C). The reaction was monitored by analysing aliquots of the reaction mixture by ^{31}P NMR spectroscopy. After observing full consumption of the starting materials, the reaction mixture was loaded directly onto a column packed with silica gel, and eluted with pentane/ethyl acetate/methanol to give the desired product.

** If there is no colour change observed when toluene and tPentOK are used as the solvent and base, respectively, the catalyst has either decomposed or not enough base has been added to activate the catalyst. As a result, the reaction will not occur.*

*** High purity of the starting materials, catalyst and solvents used in the hydrophosphination reaction is of great importance for the reaction to work.*

3.2 General procedure B: One-pot synthesis of chiral 1,2-bisphosphine boranes (6aa-6da)

All the reactions performed with toluene as solvent were carried out inside the glovebox in order to ensure inert reaction conditions. In an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar, **Mn(I)-L** (0.005 mmol, 2.5 mol%) was dissolved in 0.5 mL of deoxygenated toluene and stirred for 1 min. Then, a commercially available solution of *t*PentOK 1.7 M in dry, deoxygenated toluene (0.01 mmol, 5 mol%) was added and the mixture was stirred during 5 min, observing complete solubility of the catalyst and a change in color of the solution due to the activation of the catalyst. When toluene is used as solvent and *t*PentOK as a base, a color change of the solution from yellow to dark red is observed. This color change is indicative of the catalyst activation. After 5 min stirring, the substrate **1** (0.2 mmol, 1.0 equiv) (dissolved in 1 mL of deoxygenated toluene) was added at once followed by the addition of phosphine **2** (0.21 mmol, 1.05 equiv). The reaction was monitored by analysing aliquots of the reaction mixture by ^{31}P NMR spectroscopy. After observing full consumption of the starting materials, $HSi(OEt)_3$ (0.6 mmol, 3.0 equiv) and $Ti(OiPr)_4$ (0.06 mmol, 30 mol%) were added sequentially via syringe. The reaction mixture was taken out of the glovebox and heated to 120 ^{o}C for an hour. After that, the reaction was cooled to room temperature and BH_3 (1 M in THF)

(0.8 mmol, 4.0 equiv) was added via syringe under N_2 atmosphere. The resulting reaction mixture was stirred at room temperature for an hour. After removal of the volatiles under reduced pressure, the crude was purified by silica gel column chromatography (pentane/dichloromethane = 2/1) to afford the desired product **6**.

3.3 General procedure C: Synthesis of chiral 1,2-bisphosphines (7aa-7da)*

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with chiral phosphine boranes **6** (0.10 mmol, 1.0 equiv), DABCO (0.40 mmol, 4.0 equiv) and degassed toluene (2.5 mL) under N_2 atmosphere. The reaction mixture was stirred at 50 ^oC for 12h. After that, the reaction was cooled to room temperature and the reaction mixture was washed with degassed water (5 x 2 mL) N_2 atmosphere. The organic phase was dried by $MgSO_4$, and then filtered under N_2 atmosphere. After removal of the volatiles in high vacuum (0.1mm Hg), the desired product **7** was obtained as a solid.

** Degassed toluene, water and N_2 atmosphere are of great importance for obtaining the pure product.*

3.4 Procedure for the synthesis of racemic product

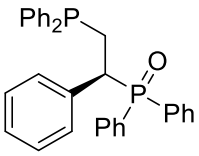
All the racemic hydrophosphination reactions were performed inside the glovebox to ensure inert reaction conditions. In an oven-dried 4 mL vial equipped with a magnetic stirring bar the substrate **1** (0.1 mmol, 1.0 equiv) were dissolved in toluene (1 mL). Then, a commercially available solution of *t*PentOK (1.7 M in toluene, 30 mol%) was added followed by the addition of $HPPh_2$ (0.105 mmol, 1.05 equiv). After stirring overnight at room temperature, the reaction mixture was loaded directly onto a column packed with silica gel, and eluted with pentane/ethyl acetate/methanol to give the desired product.

3.5 Procedure for the preparative scale (3 mmol, 1.0g) reaction

In an oven-dried round bottom flask, located inside the glovebox and equipped with a septum and a magnetic stirring bar, **Mn(I)-L** (0.015 mmol, 0.5 mol%) was added and it was dissolved in dry, deoxygenated toluene (15 mL). The mixture was stirred inside the glovebox for 5 min. Then, a commercially available solution of *t*PentOK 1.7 M in toluene (0.03 mmol, 1 mol%) was added and the mixture was stirred for 10 min to activate the catalyst. Upon activation of the catalyst, a change in the color of the solution from yellow to dark red was observed. The substrate **1b** (3.0 mmol, 1.0 equiv) was added at once, followed by the drop-wise addition of $HPPh_2$ (3.15 mmol, 1.05 equiv) over a period of 2 min. After stirring at room temperature for 48 h, the resulting mixture was evaporated and the residue was purified by column chromatography using pentane/ethyl acetate/methanol (1:1:0.05) to afford the desired product **3ba** with 91% yield and 98% ee.

Specific experimental details and product characterization

(S)-(2-(diphenylphosphaneyl)-1-phenylethyl)diphenylphosphine oxide (3aa)



Following general procedure A: The reaction was performed with **1a** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25 °C for 16 h. Product **3aa** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [96% yield, >99% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.52 (m, 3H, C*H*$_{Ar}$), 7.47-7.42 (m, 3H, C*H*$_{Ar}$), 7.38-7.30 (m, 4H, C*H*$_{Ar}$), 7.27-7.14 (m, 15H, C*H*$_{Ar}$), 3.30-3.25 (m, 1H, P(O)Ph_2C*H*), 2.90-2.85 (m, 1H, PPh_2CH*H*), 2.59-2.56 (m, 1H, PPh_2CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.8, 138.7, 137.3, 137.2, 135.3, 134.5, 134.4, 131.9, 131.7, 131.4, 131.3, 131.0, 130.1, 129.6, 128.8, 128.8, 128.7, 128.4, 128.3, 128.3, 128.1, 128.0, 128.0, 127.4, 43.6, 43.2, 29.0, 28.9. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (162 MHz, $CDCl_3$): δ 33.5 (d, *J* = 31.5 Hz), -19.7 (d, *J* = 31.5 Hz).
HRMS (ESI, m/Z): calcd. for $C_{32}H_{29}OP_2$ $[M+H]^+$: 491.1688, found: 491.1686.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 12.9 (minor) and 16.6 (major).

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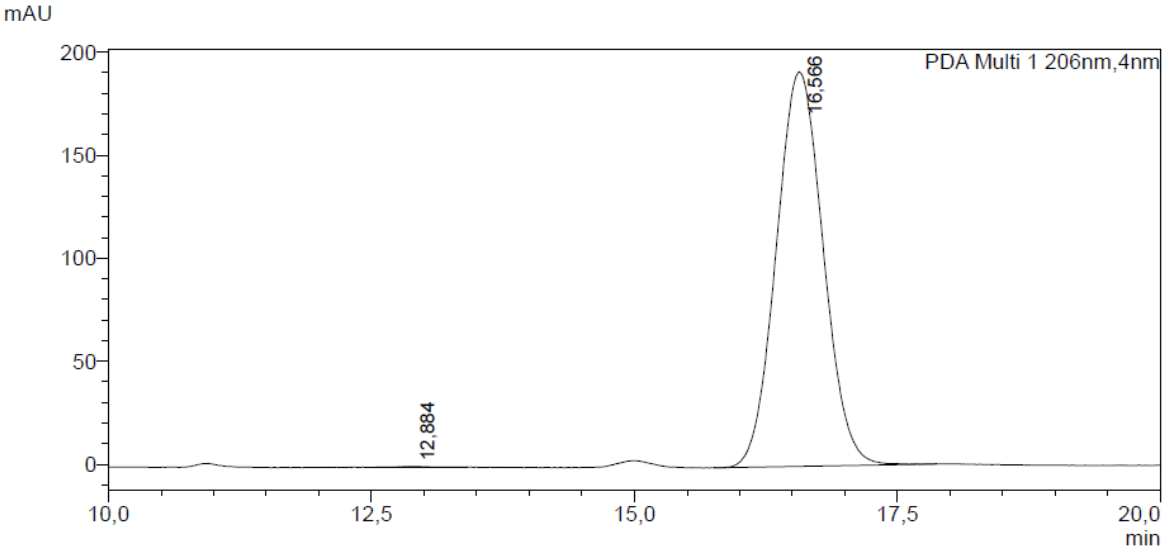

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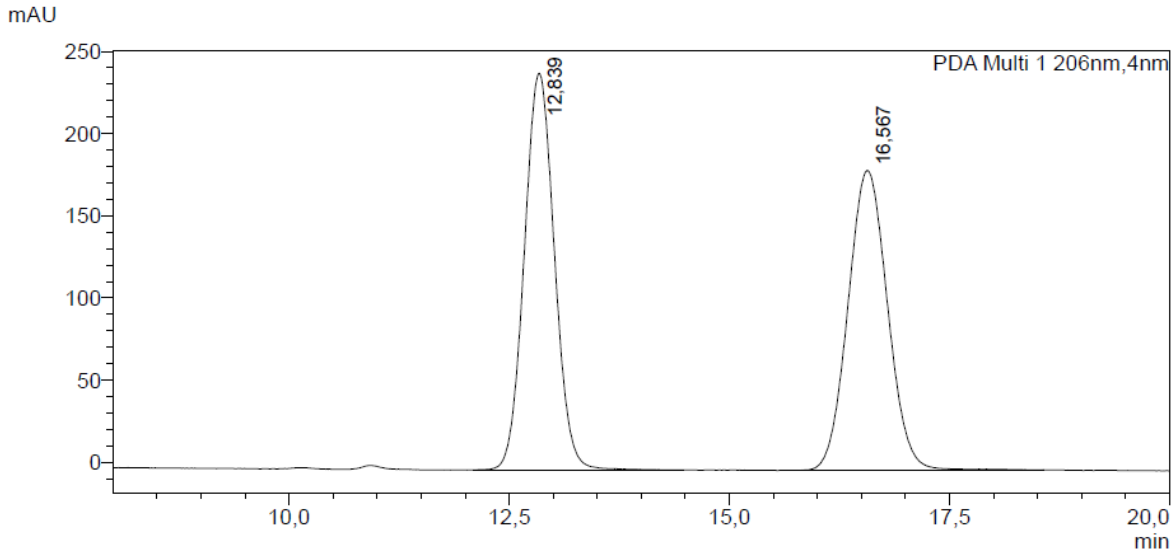

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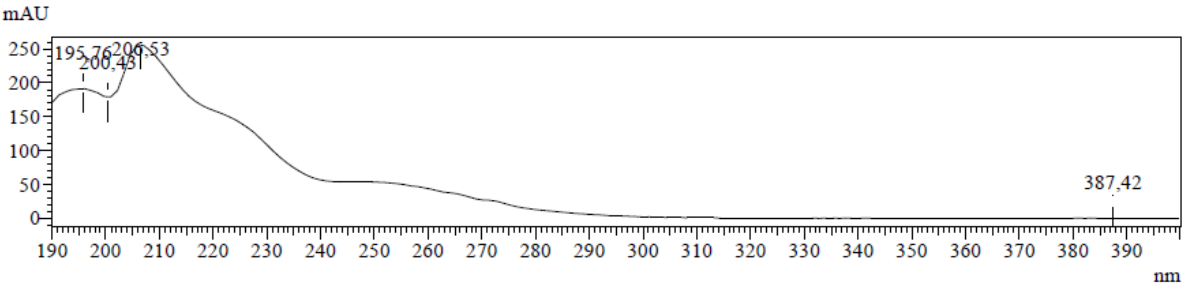

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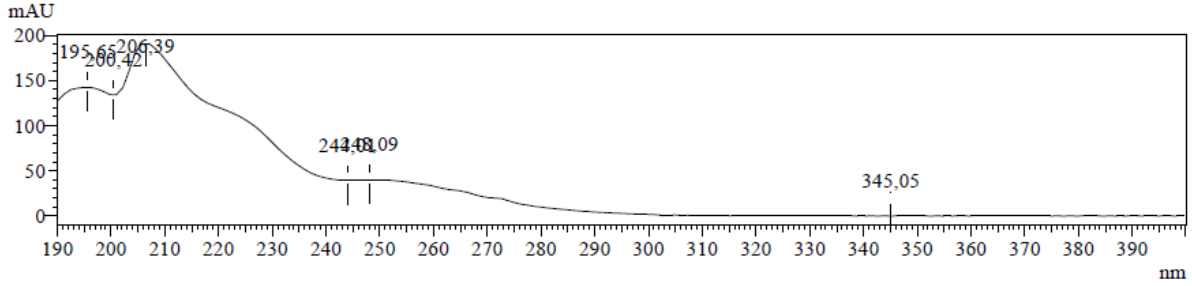
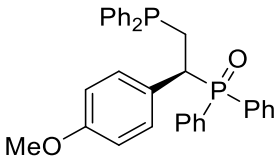


(S)-(2-(diphenylphosphaneyl)-1-(4-methoxyphenyl)ethyl)diphenylphosphine oxide (3ba)



Following general procedure A: The reaction was performed with **1b** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3ba** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [90% yield, 98% ee].

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.63 – 7.48 (m, 3H, C*H*$_{Ar}$), 7.46 – 7.20 (m, 10H, C*H*$_{Ar}$), 7.20 – 7.09 (m, 9H, C*H*$_{Ar}$), 6.71 (d, *J* = 8.2 Hz, 2H, C*H*$_{Ar}$), 3.73 (s, 3H, OC*H*$_3$), 3.32 – 3.16 (m, 1H, P(O)Ph$_2$C*H*), 2.87 – 2.78 (m, 1H, PPh$_2$CH*H*), 2.61 – 2.45 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR (CDCl$_3$, 101 MHz): δ 158.9, 158.9, 138.7, 138.5, 137.2, 137.0, 134.5, 134.3, 132.6, 131.9, 131.9, 131.8, 131.8, 131.6, 131.5, 131.4, 131.3, 131.3, 131.1, 131.1, 131.0, 130.9, 129.7, 128.9, 128.8, 128.7, 128.3, 128.3, 128.1, 128.0, 127.1, 127.1, 127.1, 127.0, 114.0, 113.9, 55.2, 42.8, 42.7, 42.2, 42.0, 29.2, 29.0. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (CDCl$_3$, 162 MHz): δ 30.6 (d, *J* = 31.6 Hz), -22.5 (d, *J* = 31.6 Hz).
HRMS (ESI, m/Z): calcd. for $C_{33}H_{31}O_2P_2$ $[M+H]^+$: 521.1794, found: 521.1794.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 21.7 (minor) and 31.7 (major).

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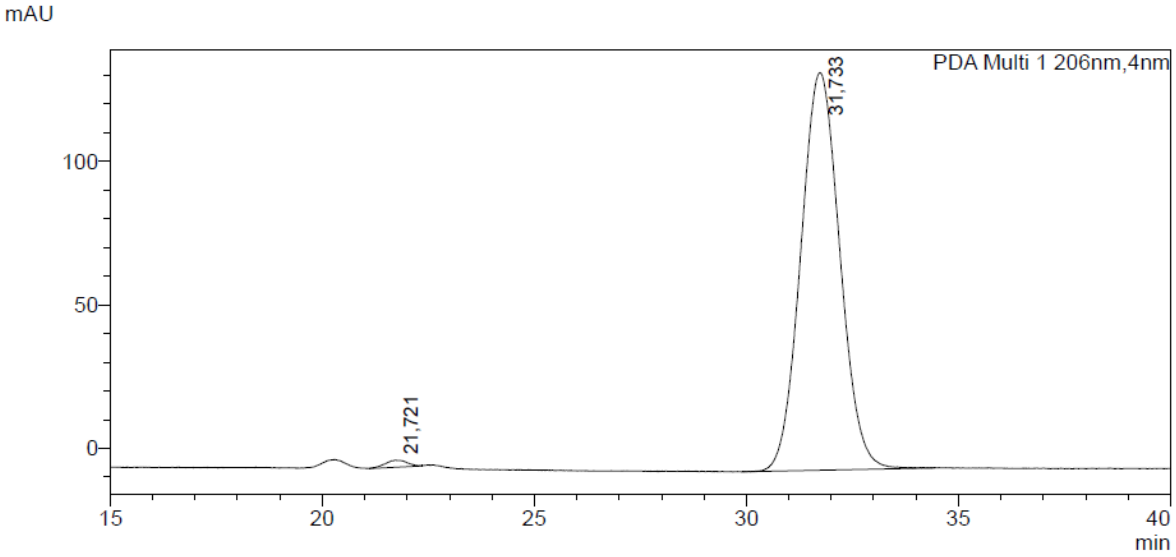

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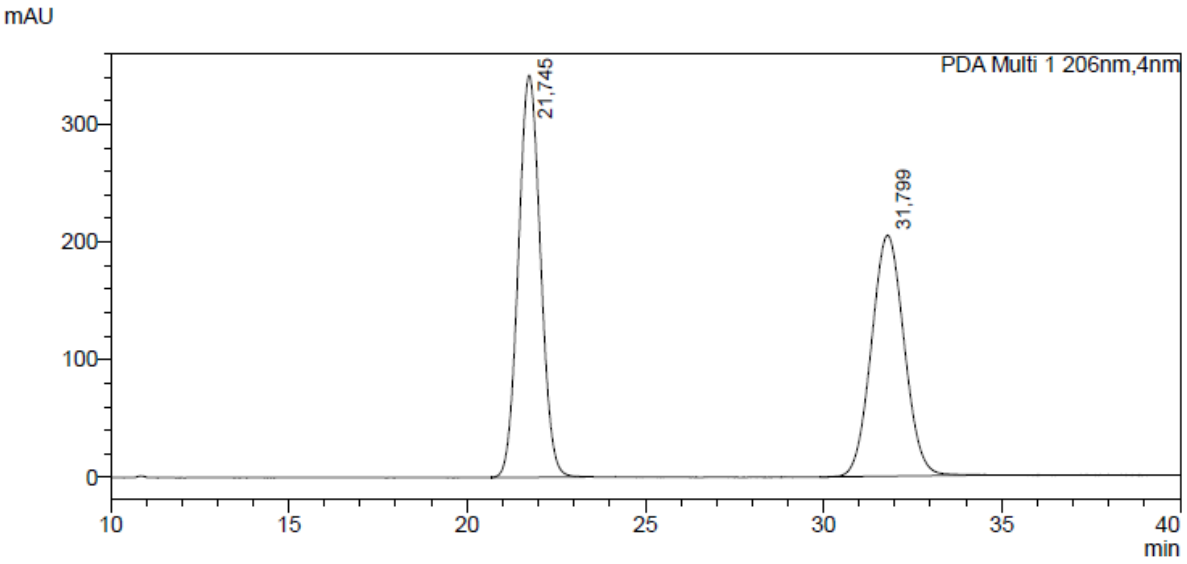

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UV Spectrum

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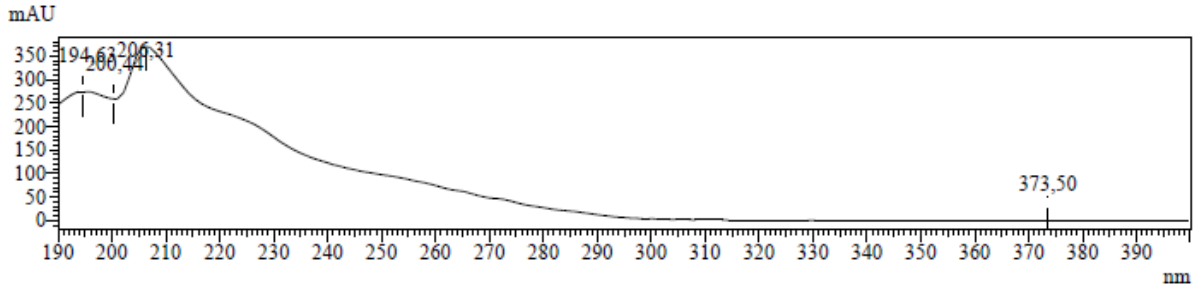

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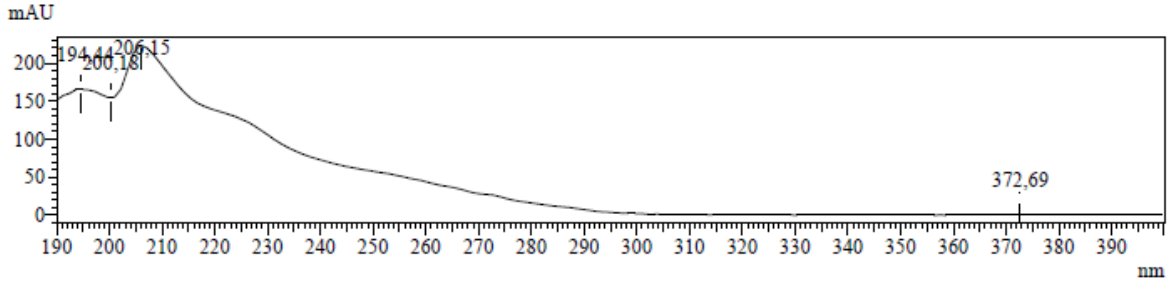
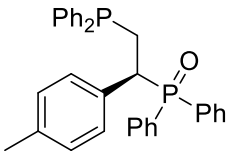


(S)-(2-(diphenylphosphaneyl)-1-(p-tolyl)ethyl)diphenylphosphine oxide (3ca)



Following general procedure A: The reaction was performed with **1c** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3ca** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [88% yield, 98% ee].

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.62 – 7.05 (m, 22H, C*H*$_{Ar}$), 6.99 – 6.97 (m, 2H, C*H*$_{Ar}$), 3.26 – 3.19 (m, 1H, P(O)Ph$_2$C*H*), 2.85 – 2.76 (m, 1H, PPh$_2$CH*H*), 2.56 – 2.50 (m, 1H, PPh$_2$CH*H*), 2.25 (s, 3H, C*H*$_3$).
^{13}C NMR (CDCl$_3$, 101 MHz): δ 141.4, 141.3, 141.1, 139.9, 139.7, 139.6, 137.1, 136.9, 135.2, 134.4, 134.3, 134.0, 133.9, 133.8, 133.6, 132.4, 132.2, 131.8, 131.4, 131.3, 130.8, 130.6, 130.5, 45.7, 45.2, 31.7, 31.5, 23.8. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (CDCl$_3$, 162 MHz) δ 30.3 (d, *J* = 31.2 Hz), -22.9 (d, *J* = 31.2 Hz).
HRMS (ESI, m/Z): calcd. for $C_{33}H_{31}OP_2$ $[M+H]^+$: 505.1845, found: 505.1846.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 15.0 (minor) and 18.9 (major).

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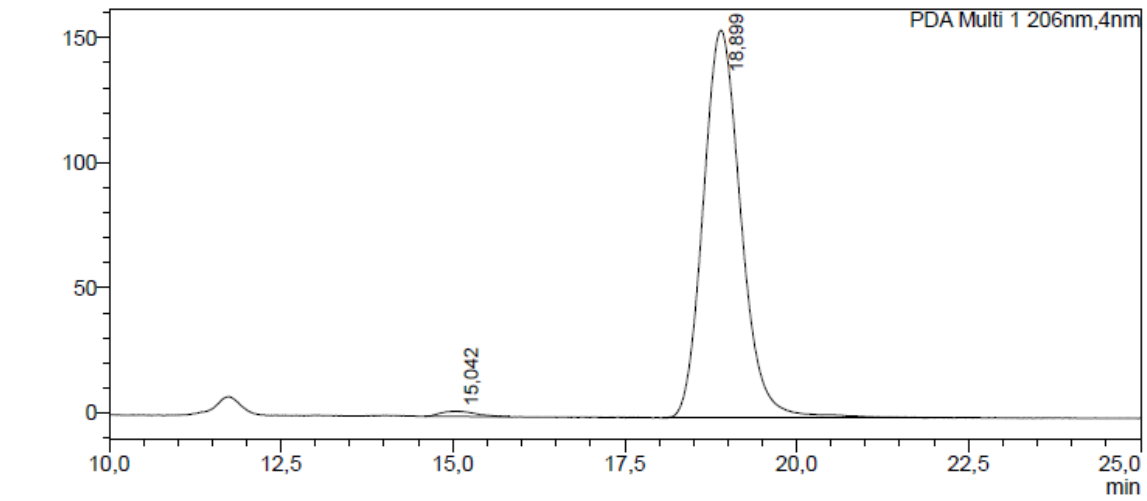

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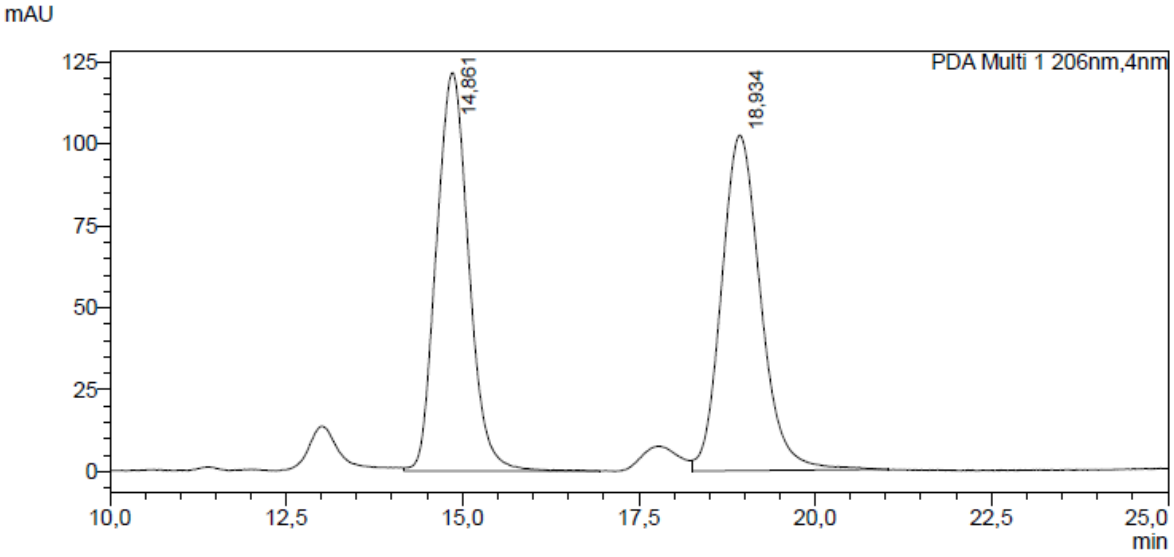

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UV Spectrum

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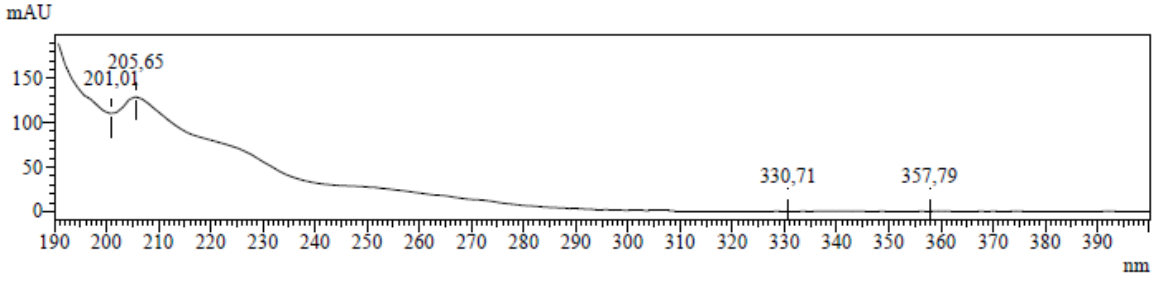

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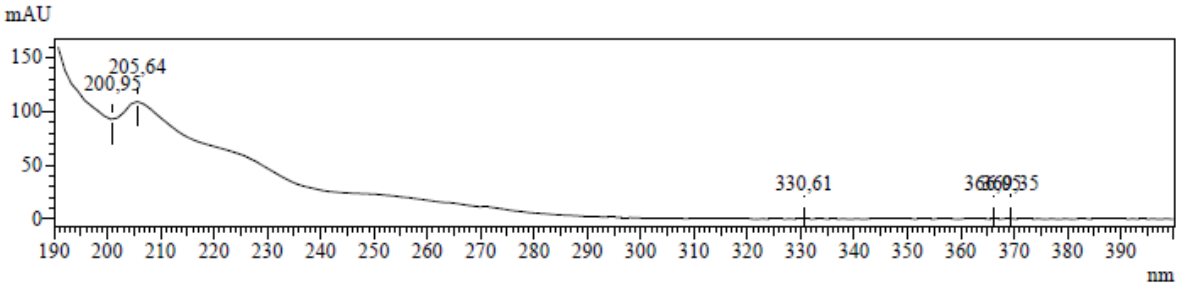
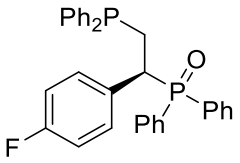


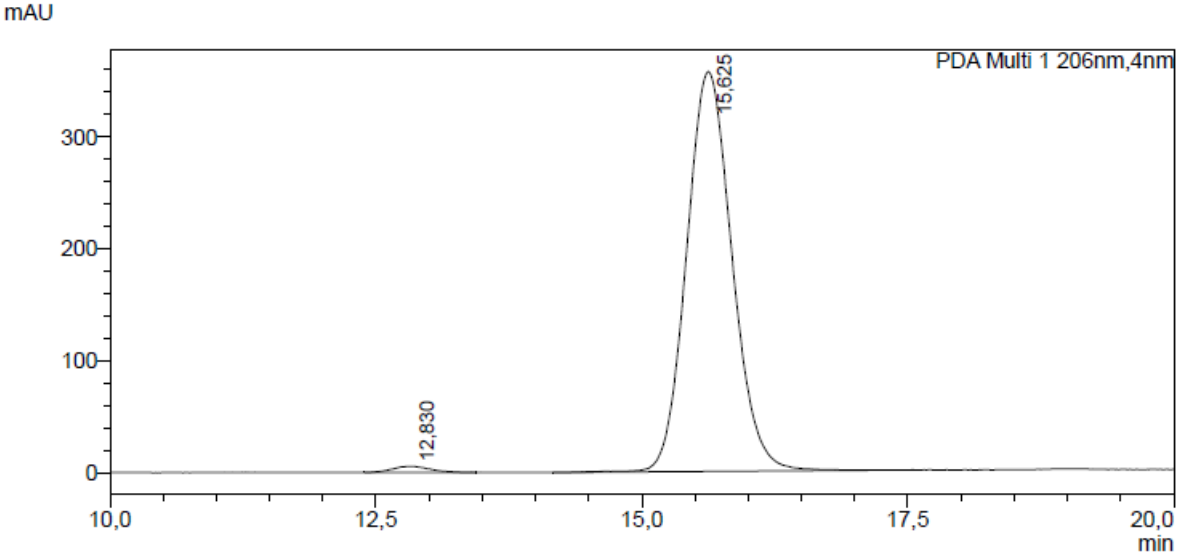
(S)-(2-(diphenylphosphaneyl)-1-(4-fluorophenyl)ethyl)diphenylphosphine oxide (3da)



Following general procedure A: The reaction was performed with **1d** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3da** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [98% yield, 98% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 – 7.55 (m, 3H, C*H*$_{Ar}$), 7.49 – 7.45 (m, 3H, C*H*$_{Ar}$), 7.43 – 7.37 (m, 2H, C*H*$_{Ar}$), 7.36 – 7.27 (m, 5H, C*H*$_{Ar}$), 7.24 – 7.17 (m, 9H, C*H*$_{Ar}$), 6.92 – 6.88 (m, 2H, C*H*$_{Ar}$), 3.35 – 3.27 (m, 1H, P(O)Ph$_2$C*H*), 2.90 – 2.80 (m, 1H, PPh$_2$CH*H*), 2.62 – 2.55 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3, 163.3, 160.8, 160.8, 138.4, 138.3, 137.1, 136.9, 134.3, 134.1, 132.3, 132.3, 131.9, 131.9, 131.8, 131.7, 131.5, 131.4, 131.4, 131.3, 131.3, 131.2, 131.1, 131.0, 131.0, 131.0, 131.0, 130.8, 130.7, 130.5, 130.2, 130.2, 129.6, 129.2, 129.1, 128.8, 128.8, 128.7, 128.7, 128.6, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 115.4, 115.4, 115.2, 115.2, 43.0, 42.9, 42.4, 42.2, 29.0, 28.9. (Due to C−P and C-F coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.0.
^{31}P NMR (162 MHz, $CDCl_3$): δ 30.6 (d, *J* = 31.6 Hz), -22.0 (d, *J* = 31.6 Hz).
HRMS (ESI, m/Z): calcd. for $C_{32}H_{28}FOP_2$ $[M+H]^+$: 509.1594, found: 509.1595.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 254 nm. Retention time (min): 12.8 (minor) and 15.6 (major).

<Chromatogram>

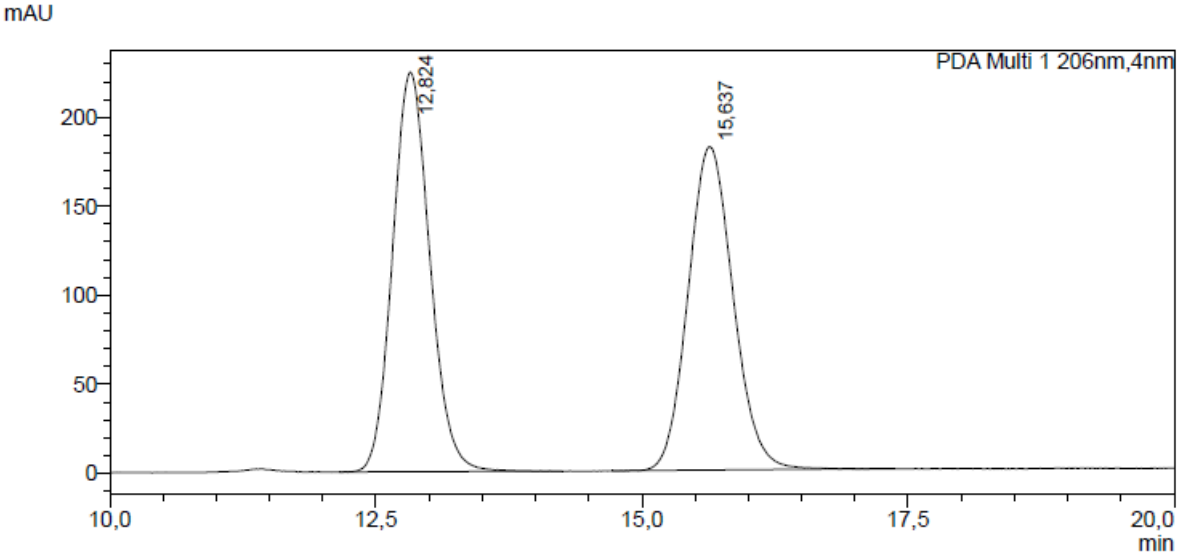


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	12,830	129313	5417	1,202
2	15,625	10627413	356864	98,798
Total		10756726	362281	100,000

<Chromatogram>



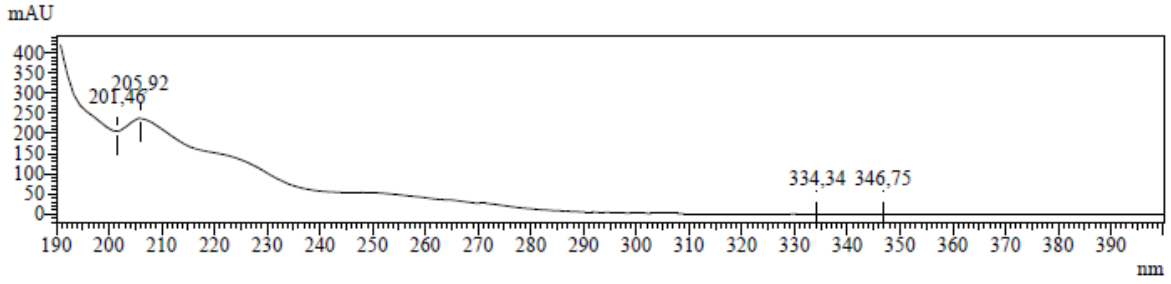
<Peak Table>

PDA Ch1 206nm

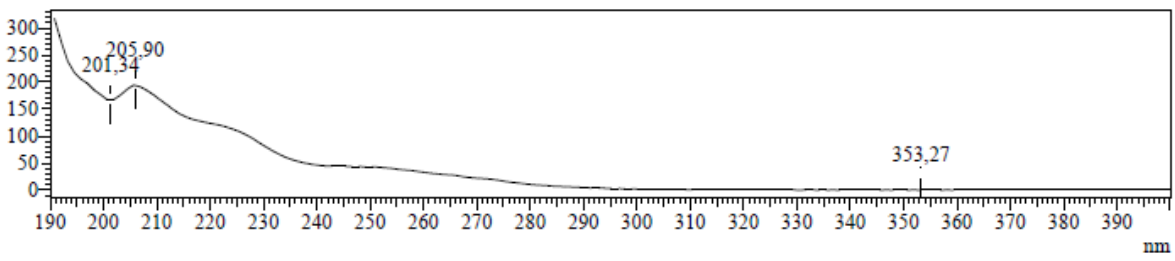
Peak#	Ret. Time	Area	Height	Area%
1	12,824	5479354	224566	50,567
2	15,637	5356499	181813	49,433
Total		10835853	406378	100,000

UV Spectrum

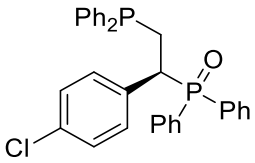
Peak# : 1
Retention Time : 12,824 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 15,637 min
Compound Name :
Spectrum Operation:



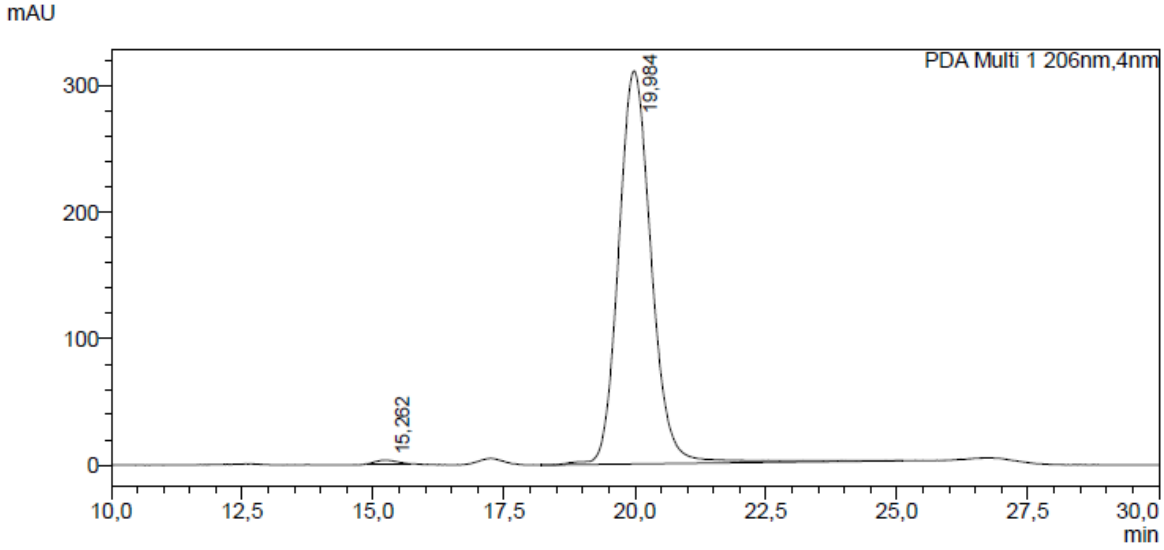
(S)-(1-(4-chlorophenyl)-2-(diphenylphosphaneyl)ethyl)diphenylphosphine oxide (3ea)



Following general procedure A: The reaction was performed with **1e** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3ea** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [93% yield, 99% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 – 7.50 (m, 3H, C*H*$_{Ar}$), 7.49 – 7.41 (m, 3H, C*H*$_{Ar}$), 7.41 – 7.33 (m, 2H, C*H*$_{Ar}$), 7.32 – 7.23 (m, 5H, C*H*$_{Ar}$), 7.22 – 7.09 (m, 11H, C*H*$_{Ar}$), 3.34 – 3.20 (m, 1H, P(O)Ph$_2$C*H*), 2.91 – 2.69 (m, 1H, PPh$_2$CH*H*), 2.64 – 2.45 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.4, 138.3, 137.2, 137.0, 134.4, 134.2, 133.3, 133.3, 132.3, 132.0, 131.8, 131.5, 131.4, 131.4, 130.9, 130.8, 130.6, 129.7, 129.0, 128.9, 128.8, 128.6, 128.4, 128.4, 128.3, 128.2, 43.4, 43.3, 42.8, 42.6, 29.1, 28.9. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.0 (d, *J* = 31.2 Hz), -19.7 (d, *J* = 31.2 Hz).
HRMS (ESI, m/Z): calcd. for $C_{32}H_{28}ClOP_2$ $[M+H]^+$: 525.1298, found: 525.1300.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 15.3 (minor) and 20.0 (major).

<Chromatogram>

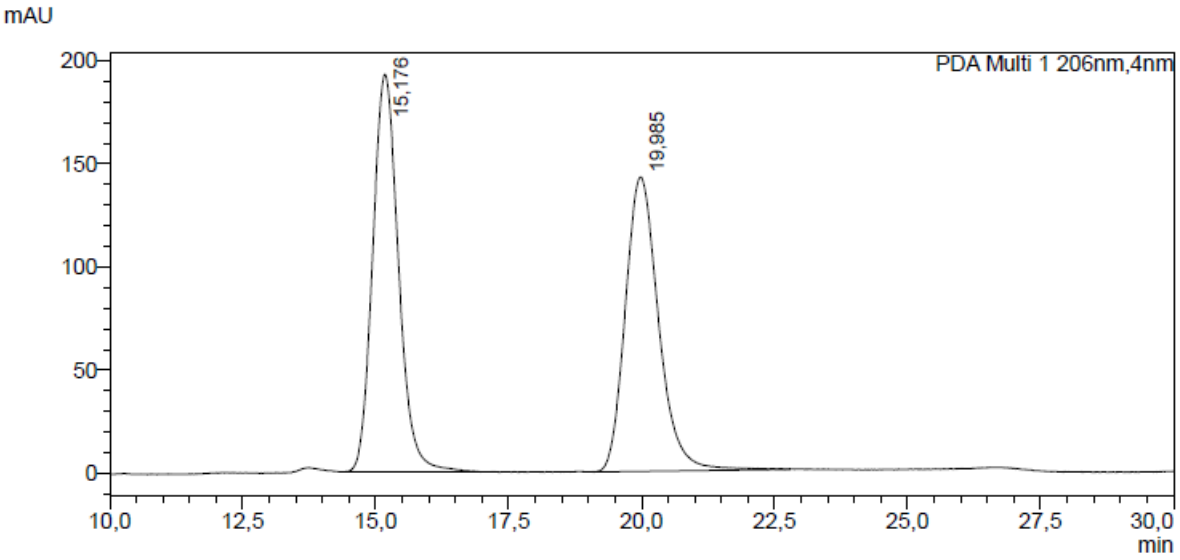


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	15,262	79508	2995	0,581
2	19,984	13596642	311115	99,419
Total		13676150	314109	100,000

<Chromatogram>



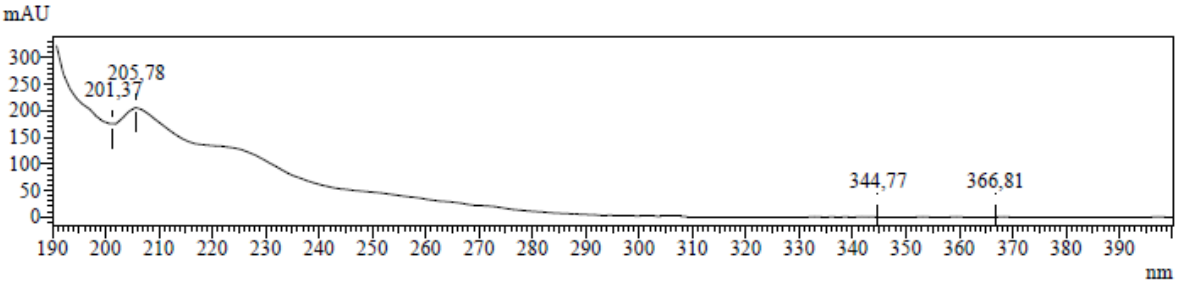
<Peak Table>

PDA Ch1 206nm

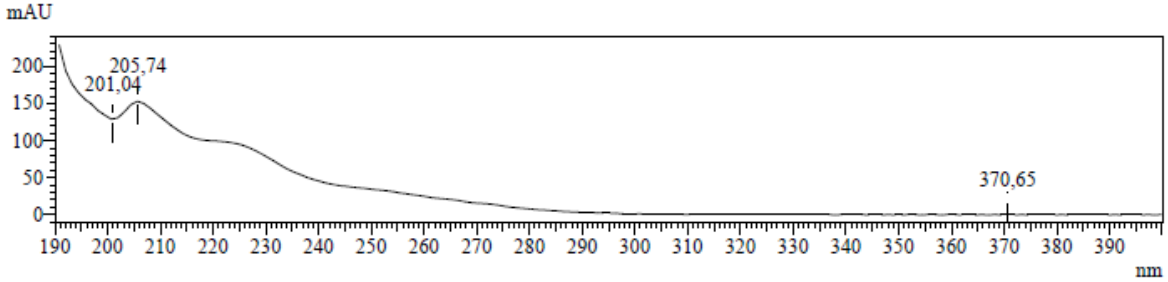
Peak#	Ret. Time	Area	Height	Area%
1	15,176	6515547	192614	51,124
2	19,985	6229099	142709	48,876
Total		12744646	335322	100,000

UV Spectrum

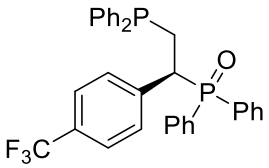
Peak# : 1
Retention Time : 15,176 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 19,985 min
Compound Name :
Spectrum Operation:



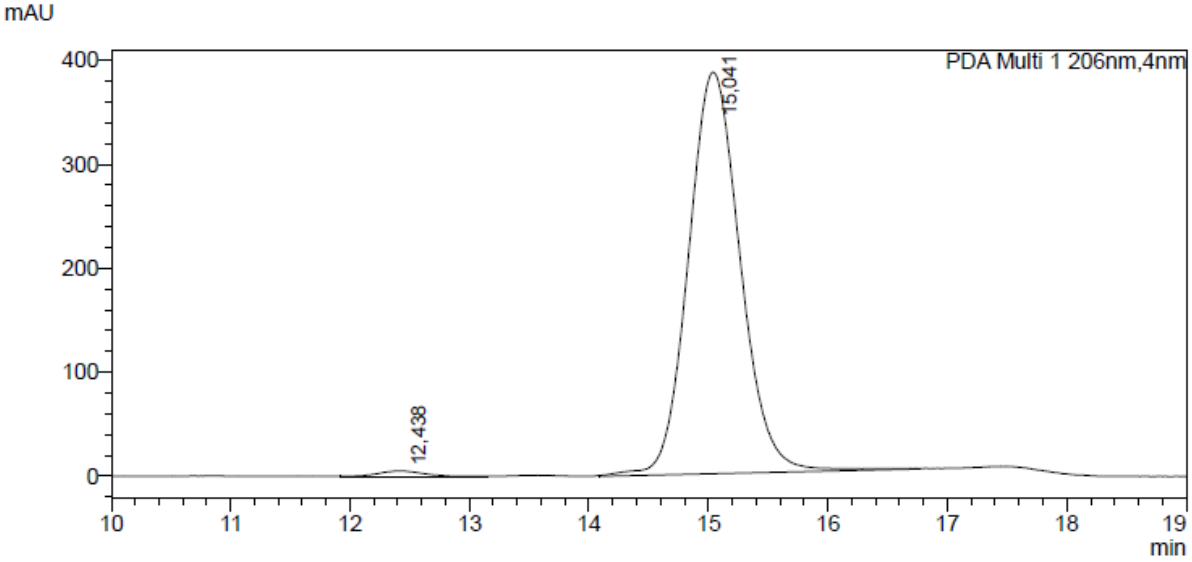
(S)-(2-(diphenylphosphaneyl)-1-(4-(trifluoromethyl)phenyl)ethyl)diphenylphosphine oxide (3fa)



Following general procedure A: The reaction was performed with **1f** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3fa** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [79% yield, 98% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 – 7.58 (m, 2H, C*H*$_{Ar}$), 7.59 – 7.51 (m, 1H, C*H*$_{Ar}$), 7.49 – 7.40 (m, 3H, C*H*$_{Ar}$), 7.41 – 7.33 (m, 4H, C*H*$_{Ar}$), 7.33 – 7.19 (m, 7H, C*H*$_{Ar}$), 7.19 – 7.11 (m, 7H, C*H*$_{Ar}$), 3.43 – 3.30 (m, 1H, P(O)Ph$_2$C*H*), 2.91 – 2.81 (m, 1H, PPh$_2$CH*H*), 2.60 – 2.53 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.8, 138.2, 138.0, 137.1, 136.9, 134.3, 134.1, 132.2, 132.2, 132.1, 131.9, 131.7, 131.6, 131.4, 131.4, 131.3, 131.1, 131.1, 130.8, 130.8, 130.4, 130.3, 129.8, 129.6, 129.6, 129.3, 129.3, 129.1, 128.9, 128.9, 128.4, 128.4, 128.4, 128.3, 128.2, 125.6, 125.3, 125.3, 125.3, 125.3, 125.2, 125.2, 122.9, 44.1, 44.0, 43.5, 43.3, 28.9, 28.7. (Due to C−P and C-F coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.0 (dd, *J* = 31.9, 2.3 Hz), -19.2 (d, *J* = 31.9 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.5.
HRMS (ESI, m/Z): calcd. for $C_{33}H_{28}F_3OP_2$ $[M+H]^+$: 559.1562, found: 559.1559.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 254 nm. Retention time (min): 12.4 (minor) and 15.0 (major).

<Chromatogram>

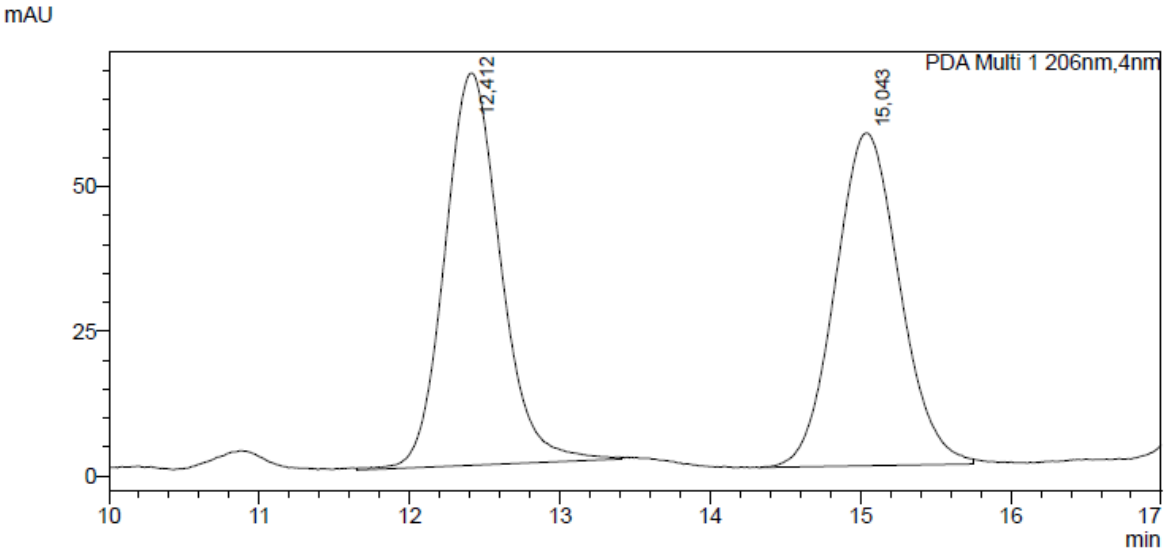


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	12,438	140156	5315	1,184
2	15,041	11695299	386342	98,816
Total		11835455	391657	100,000

<Chromatogram>



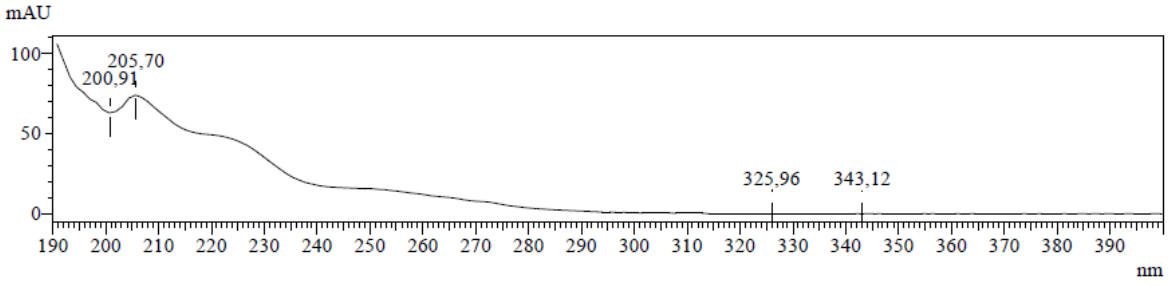
<Peak Table>

PDA Ch1 206nm

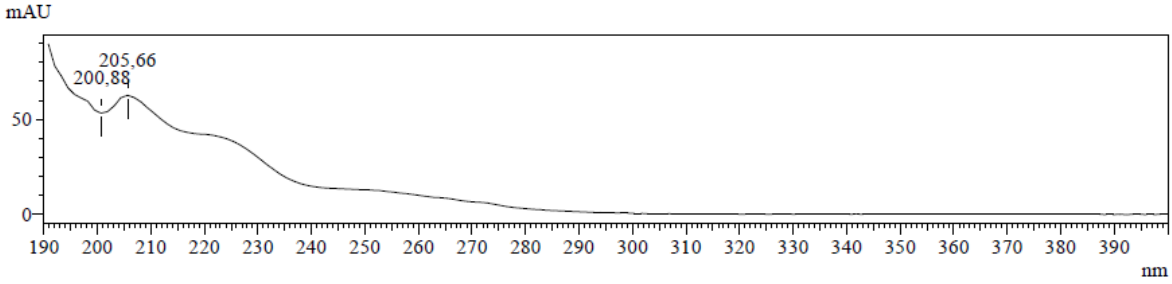
Peak#	Ret. Time	Area	Height	Area%
1	12,412	1753010	67795	50,522
2	15,043	1716814	57535	49,478
Total		3469824	125330	100,000

UV Spectrum

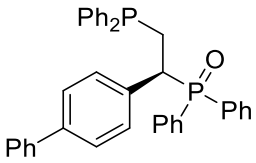
Peak# : 1
Retention Time : 12,409 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 15,042 min
Compound Name :
Spectrum Operation:



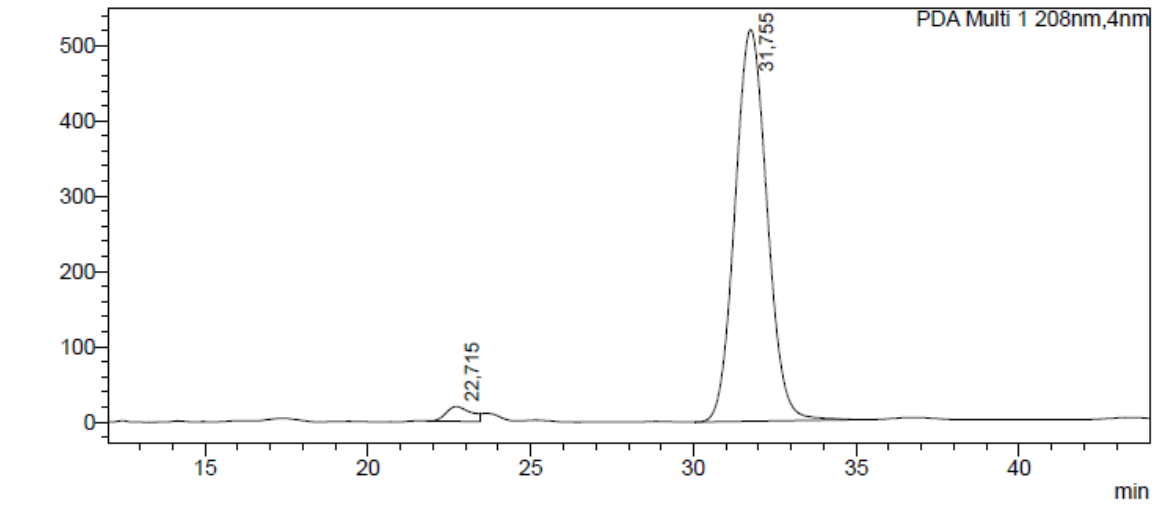
(S)-(1-([1,1'-biphenyl]-4-yl)-2-(diphenylphosphaneyl)ethyl)diphenylphosphine oxide (3ga)



Following general procedure A: The reaction was performed with **1g** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3ga** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [95% yield, 94% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 – 7.57 (m, 2H, C*H*$_{Ar}$), 7.56 – 7.50 (m, 3H, C*H*$_{Ar}$), 7.49 – 7.09 (m, 24H, C*H*$_{Ar}$), 3.43 – 3.26 (m, 1H, P(O)Ph$_2$C*H*), 2.99 – 2.82 (m, 1H, PPh$_2$CH*H*), 2.67 – 2.51 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.4, 142.6, 142.6, 141.2, 141.1, 140.0, 139.8, 137.0, 137.0, 137.0, 136.9, 136.9, 136.8, 135.1, 135.1, 134.6, 134.5, 134.4, 134.4, 134.3, 134.1, 134.1, 134.0, 134.0, 133.9, 133.9, 133.6, 133.5, 133.4, 133.0, 133.0, 132.2, 131.4, 131.4, 131.3, 131.3, 130.9, 130.8, 130.7, 130.6, 130.5, 129.8, 129.6, 46.2, 46.1, 45.6, 45.4, 31.6, 31.4. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.4 (d, *J* = 32.2 Hz), -22.3 (d, *J* = 32.2 Hz).
HRMS (ESI, m/Z): calcd. for $C_{32}H_{28}ClOP_2$ $[M+H]^+$: 567.2001, found: 567.2001.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 208 nm. Retention time (min): 22.7 (minor) and 31.8 (major).

<Chromatogram>

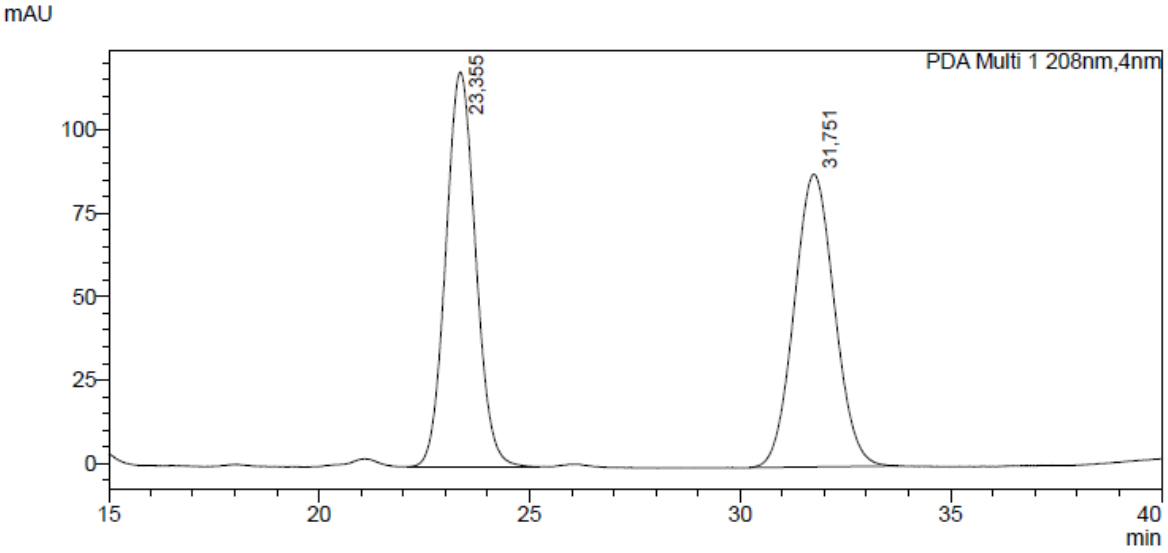


<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	22,715	1038027	19500	2,832
2	31,755	35611992	519888	97,168
Total		36650019	539388	100,000

<Chromatogram>



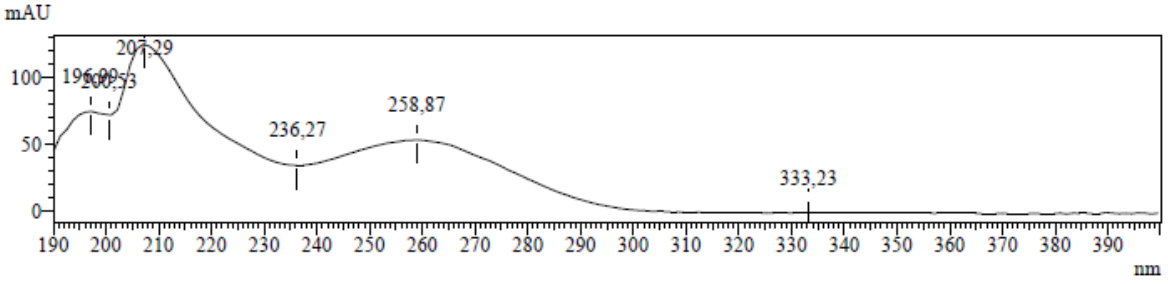
<Peak Table>

PDA Ch1 208nm

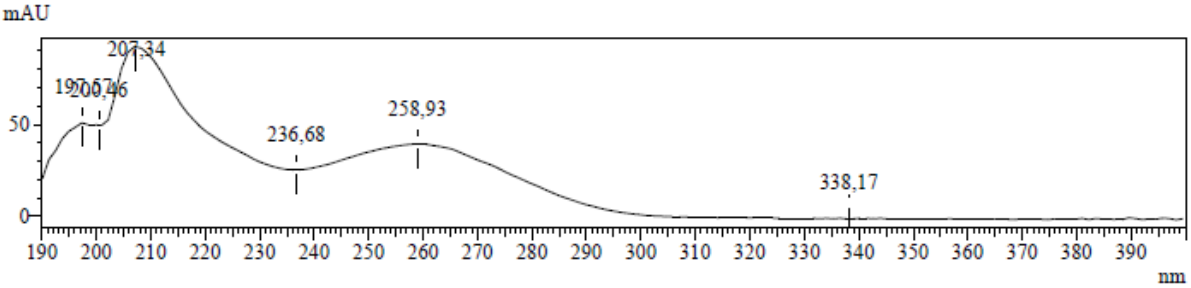
Peak#	Ret. Time	Area	Height	Area%
1	23,355	5827516	118274	49,970
2	31,751	5834400	87708	50,030
Total		11661916	205982	100,000

UV Spectrum

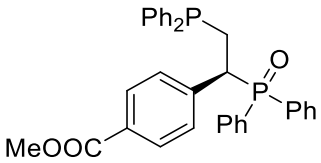
Peak# : 1
Retention Time : 23,355 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 31,751 min
Compound Name :
Spectrum Operation:



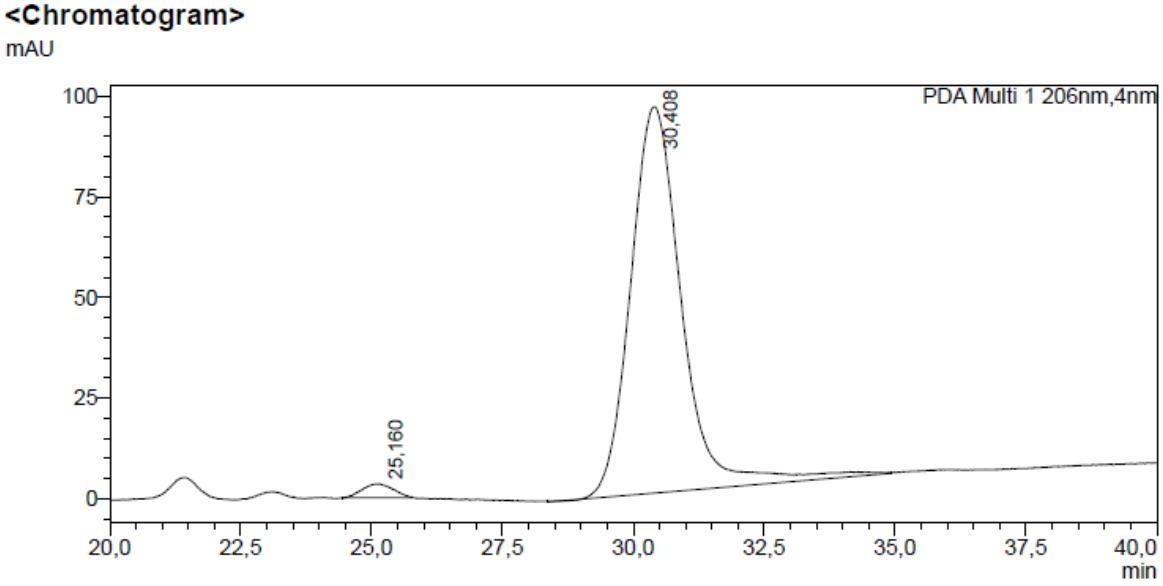
methyl (S)-4-(2-(diphenylphosphaneyl)-1-(diphenylphosphoryl)ethyl)benzoate (3ha)



Following general procedure A: The reaction was performed with **1h** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3ha** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [91% yield, 96% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, *J* = 8.1 Hz, 2H, C*H*$_{Ar}$), 7.65 – 7.56 (m, 2H, C*H*$_{Ar}$), 7.55 – 7.49 (m, 1H, C*H*$_{Ar}$), 7.47 – 7.39 (m, 3H, C*H*$_{Ar}$), 7.39 – 7.32 (m, 2H, C*H*$_{Ar}$), 7.31 – 7.20 (m, 7H, C*H*$_{Ar}$), 7.18 – 7.07 (m, 7H, C*H*$_{Ar}$), 3.86 (s, 3H, COOC*H*$_3$), 3.44 – 3.25 (m, 1H, P(O)Ph$_2$C*H*), 2.95 – 2.76 (m, 1H, PPh$_2$CH*H*), 2.64 – 2.46 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 166.9, 141.0, 141.0, 141.0, 141.0, 138.3, 138.2, 136.9, 136.7, 134.3, 134.1, 132.0, 131.9, 131.8, 131.6, 131.5, 131.4, 131.3, 131.2, 131.0, 131.0, 130.8, 130.7, 130.4, 130.0, 130.0, 129.7, 129.6, 129.5, 129.0, 129.0, 128.9, 128.8, 128.8, 128.7, 128.3, 128.2, 128.1, 128.1, 128.0, 52.0, 44.0, 43.9, 43.4, 43.3, 29.7. (Due to C–P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 29.8 (d, *J* = 30.7 Hz), -22.6 (d, *J* = 30.7 Hz).
HRMS (ESI, m/Z): calcd. for $C_{34}H_{31}O_3P_2$ $[M+H]^+$: 549.1743, found: 549.1743.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 25.2 (minor) and 30.5 (major).

<Chromatogram>

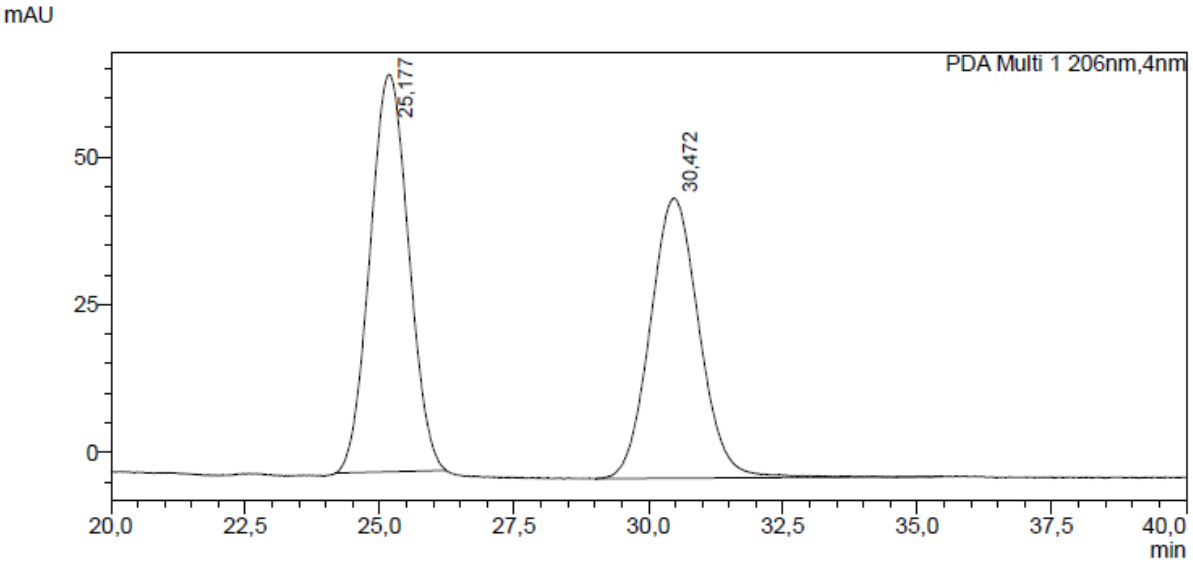


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	25,160	142695	3407	2,135
2	30,408	6542425	95983	97,865
Total		6685120	99390	100,000

<Chromatogram>



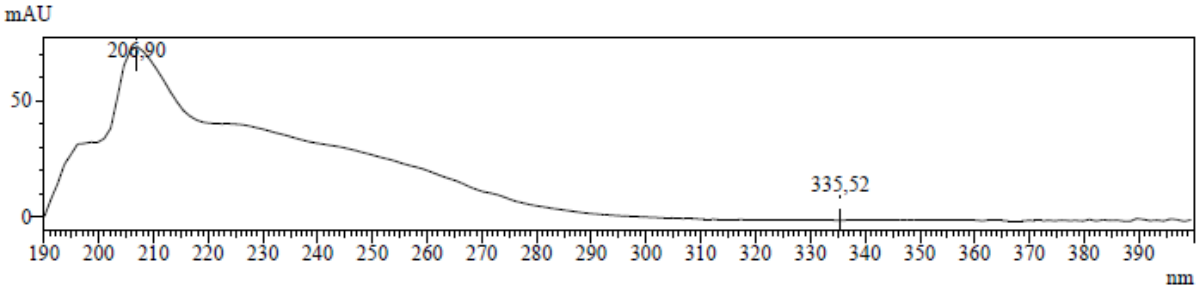
<Peak Table>

PDA Ch1 206nm

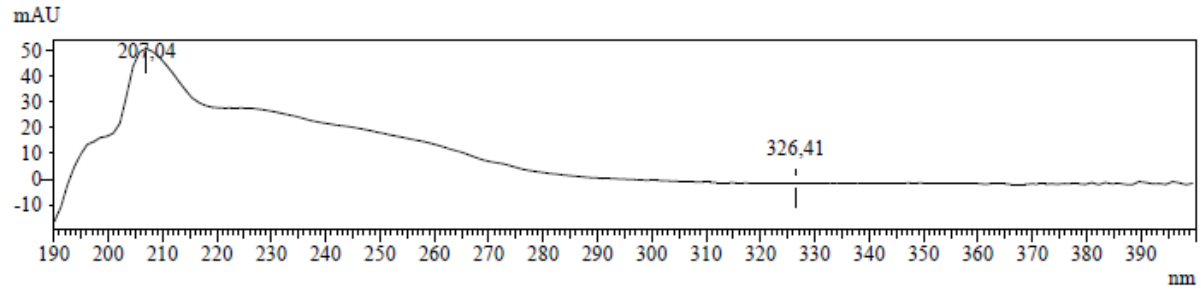
Peak#	Ret. Time	Area	Height	Area%
1	25,177	3366953	67260	52,908
2	30,472	2996800	47467	47,092
Total		6363753	114726	100,000

UV Spectrum

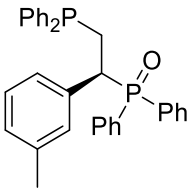
Peak# : 1
Retention Time : 25,177 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 30,472 min
Compound Name :
Spectrum Operation:



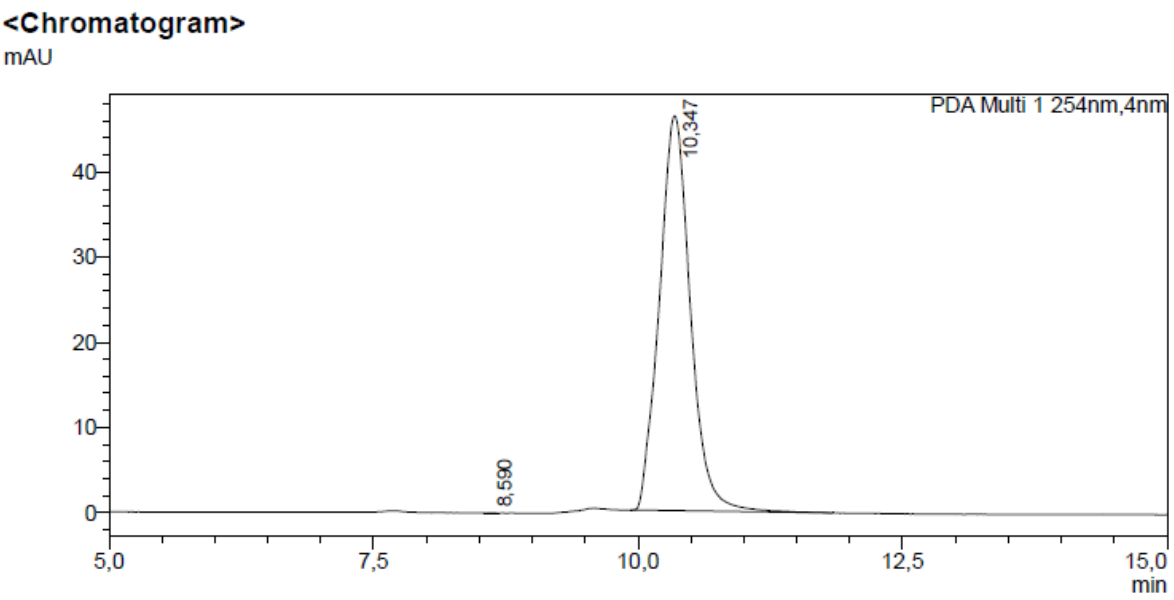
(S)-(2-(diphenylphosphaneyl)-1-(m-tolyl)ethyl)diphenylphosphine oxide (3ia)



Following general procedure A: The reaction was performed with **1i** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3ia** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [81% yield, >99% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 – 7.51 (m, 3H, C*H*$_{Ar}$), 7.46 – 7.15 (m, 17H, C*H*$_{Ar}$), 7.09 – 6.96 (m, 4H, C*H*$_{Ar}$), 3.29 – 3.22 (m, 1H, P(O)Ph$_2$C*H*), 2.92 – 2.82 (m, 1H, PPh$_2$CH*H*), 2.59 – 2.53 (m, 1H, PPh$_2$CH*H*), 2.23 (s, 3H, PhC*H*$_3$).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.8, 138.7, 137.9, 137.4, 137.3, 135.0, 134.5, 134.3, 132.6, 132.0, 131.8, 131.5, 131.4, 131.2, 131.1, 131.0, 130.7, 129.6, 128.8, 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 127.2, 43.8, 43.0, 28.9, 28.7, 21.5. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (162 MHz, $CDCl_3$): δ 30.5 (d, *J* = 32.2 Hz), -22.6 (d, *J* = 32.2 Hz).
HRMS (ESI, m/Z): calcd. for $C_{33}H_{31}OP_2$ $[M+H]^+$: 505.1845, found: 505.1845.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 254 nm. Retention time (min): 8.6 (minor) and 10.3 (major).

<Chromatogram>

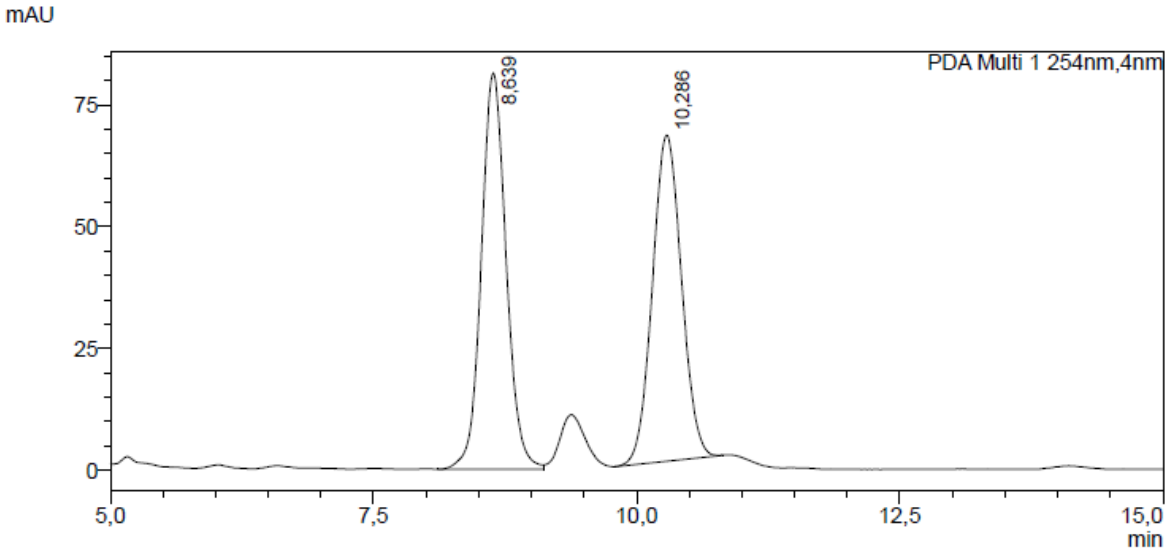


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8,590	63	21	0,007
2	10,347	946115	46379	99,993
Total		946177	46400	100,000

<Chromatogram>



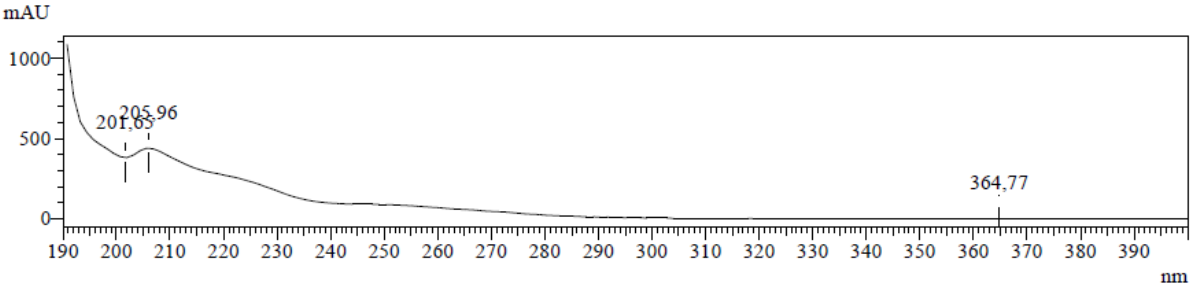
<Peak Table>

PDA Ch1 254nm

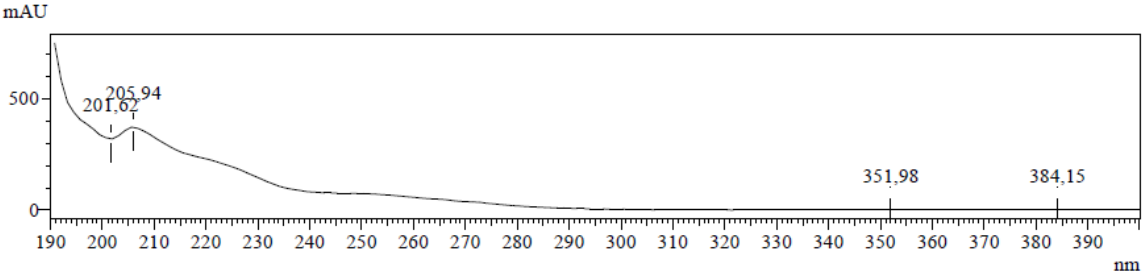
Peak#	Ret. Time	Area	Height	Area%
1	8,639	1334281	81263	50,886
2	10,286	1287818	66900	49,114
Total		2622098	148162	100,000

UV Spectrum

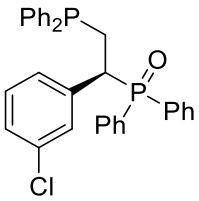
Peak# : 1
Retention Time : 8,639 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 10,286 min
Compound Name :
Spectrum Operation:



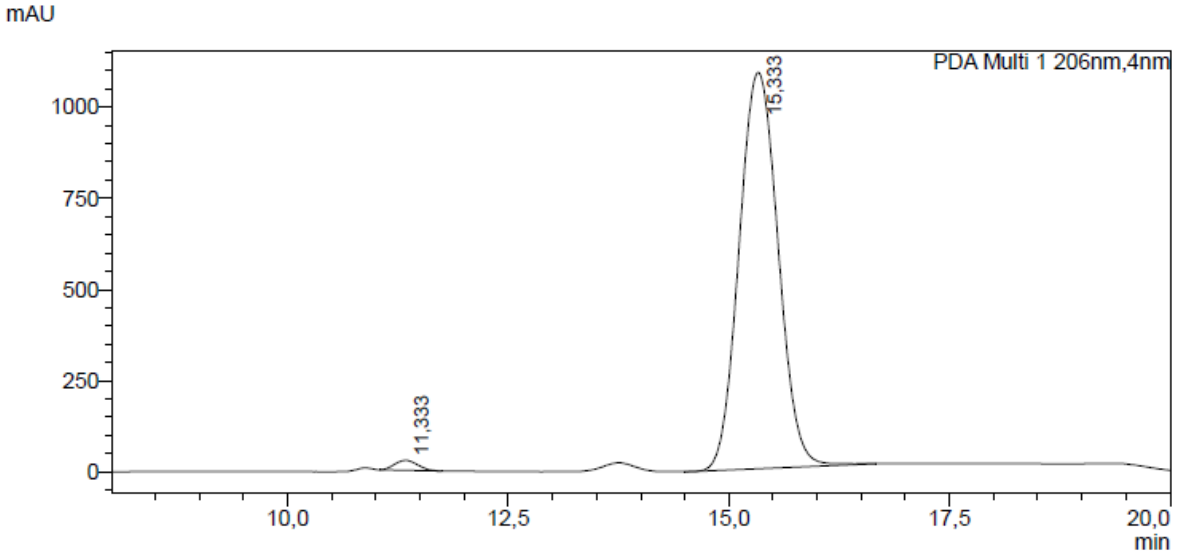
(S)-(1-(3-chlorophenyl)-2-(diphenylphosphaneyl)ethyl)diphenylphosphine oxide (3ja)



Following general procedure A: The reaction was performed with **1j** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3ja** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [90% yield, 97% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 – 7.49 (m, 3H, C*H*$_{Ar}$), 7.47 – 7.40 (m, 3H, C*H*$_{Ar}$), 7.39 – 7.32 (m, 2H, C*H*$_{Ar}$), 7.31 – 7.21 (m, 5H, C*H*$_{Ar}$), 7.21 – 7.07 (m, 11H, C*H*$_{Ar}$), 3.36 – 3.11 (m, 1H, P(O)Ph$_2$C*H*), 2.88 – 2.72 (m, 1H, PPh$_2$CH*H*), 2.61 – 2.44 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.4, 138.3, 137.7, 137.6, 137.6, 137.6, 137.2, 137.0, 134.4, 134.2, 132.2, 132.2, 132.1, 132.0, 132.0, 131.8, 131.6, 131.6, 131.4, 131.4, 131.2, 131.2, 130.9, 130.9, 130.5, 130.2, 130.2, 129.7, 129.6, 129.6, 129.0, 128.9, 128.9, 128.8, 128.4, 128.3, 128.2, 128.2, 128.1, 127.6, 127.6, 43.8, 43.7, 43.2, 43.0, 28.9, 28.9, 28.7, 28.7. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.1 (d, *J* = 31.3Hz), -22.5 (d, *J* = 31.3 Hz).
HRMS (ESI, m/Z): calcd. for $C_{32}H_{28}ClOP_2$ $[M+H]^+$: 525.1298, found: 525.1295.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 11.3 (minor) and 15.3 (major).

<Chromatogram>

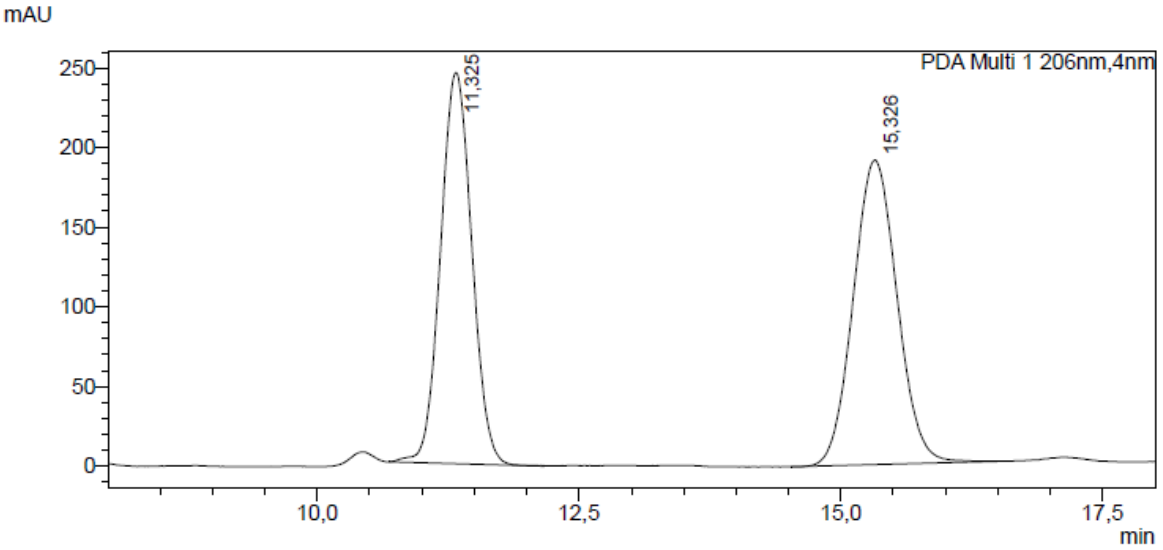


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	11,333	490156	27016	1,442
2	15,333	33497677	1086535	98,558
Total		33987832	1113551	100,000

<Chromatogram>



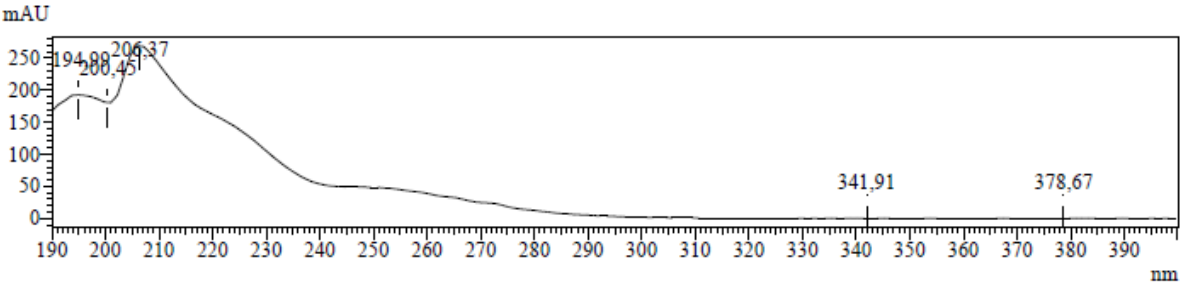
<Peak Table>

PDA Ch1 206nm

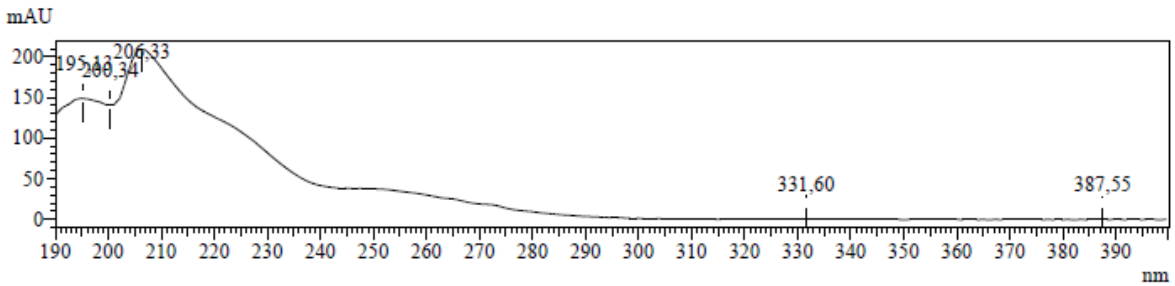
Peak#	Ret. Time	Area	Height	Area%
1	11,325	5116666	245728	47,927
2	15,326	5559394	191201	52,073
Total		10676060	436929	100,000

UV Spectrum

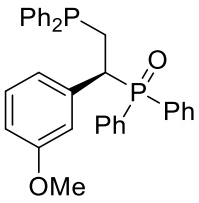
Peak# : 1
Retention Time : 11,325 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 15,326 min
Compound Name :
Spectrum Operation:



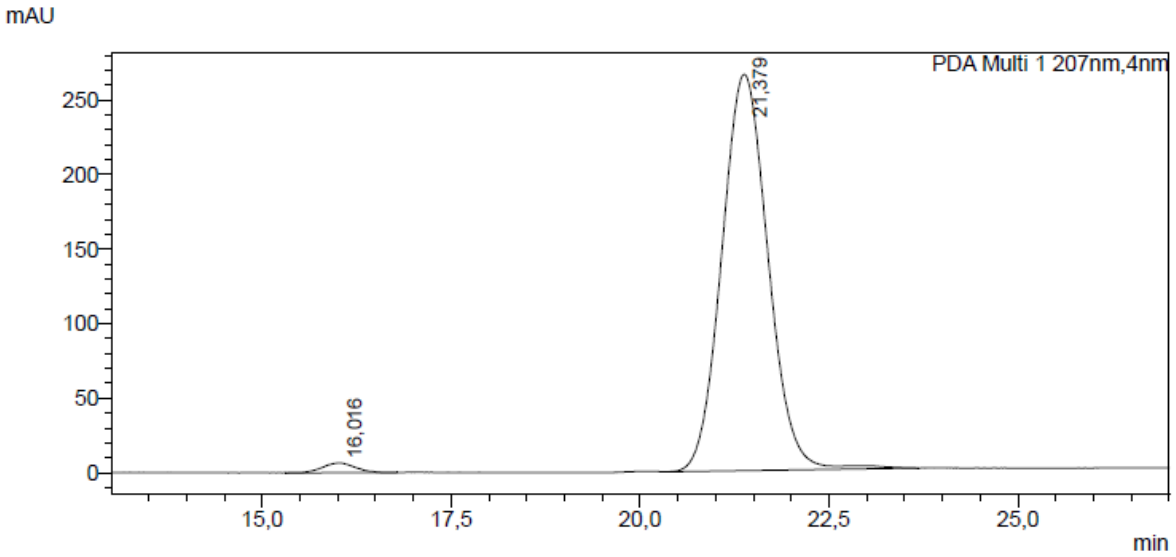
(S)-(2-(diphenylphosphaneyl)-1-(3-methoxyphenyl)ethyl)diphenylphosphine oxide (3ka)



Following general procedure A: The reaction was performed with **1k** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), barton's base (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 48 h. Product **3ka** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [82% yield, 97% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 – 7.49 (m, 3H, C*H*$_{Ar}$), 7.49 – 7.38 (m, 3H, C*H*$_{Ar}$), 7.39 – 7.24 (m, 7H, C*H*$_{Ar}$), 7.21 – 7.13 (m, 7H, C*H*$_{Ar}$), 7.12 – 7.08 (m, 1H, C*H*$_{Ar}$), 6.85 – 6.67 (m, 3H, C*H*$_{Ar}$), 3.69 (s, 3H, OC*H*$_3$), 3.32 – 3.16 (m, 1H, P(O)Ph$_2$C*H*), 2.92 – 2.78 (m, 1H, PPh$_2$CH*H*), 2.61 – 2.48 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.4, 138.7, 138.6, 137.3, 137.2, 136.8, 136.8, 136.7, 136.7, 134.4, 134.4, 134.2, 132.4, 132.4, 131.8, 131.8, 131.7, 131.7, 131.5, 131.4, 131.4, 131.3, 131.2, 131.2, 130.9, 130.8, 130.7, 129.5, 129.2, 129.2, 128.8, 128.7, 128.6, 128.6, 128.2, 128.1, 128.0, 128.0, 127.8, 122.6, 122.5, 115.2, 115.1, 113.4, 113.4, 55.1, 43.9, 43.7, 43.2, 43.1, 28.9, 28.9, 28.8, 28.7. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.3 (d, *J* = 31.8 Hz), -19.6 (d, *J* = 31.8 Hz).
HRMS (ESI, m/Z): calcd. for $C_{33}H_{31}O_2P_2$ $[M+H]^+$: 521.1794, found: 521.1786.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 207 nm. Retention time (min): 16.0 (minor) and 21.4 (major).

<Chromatogram>

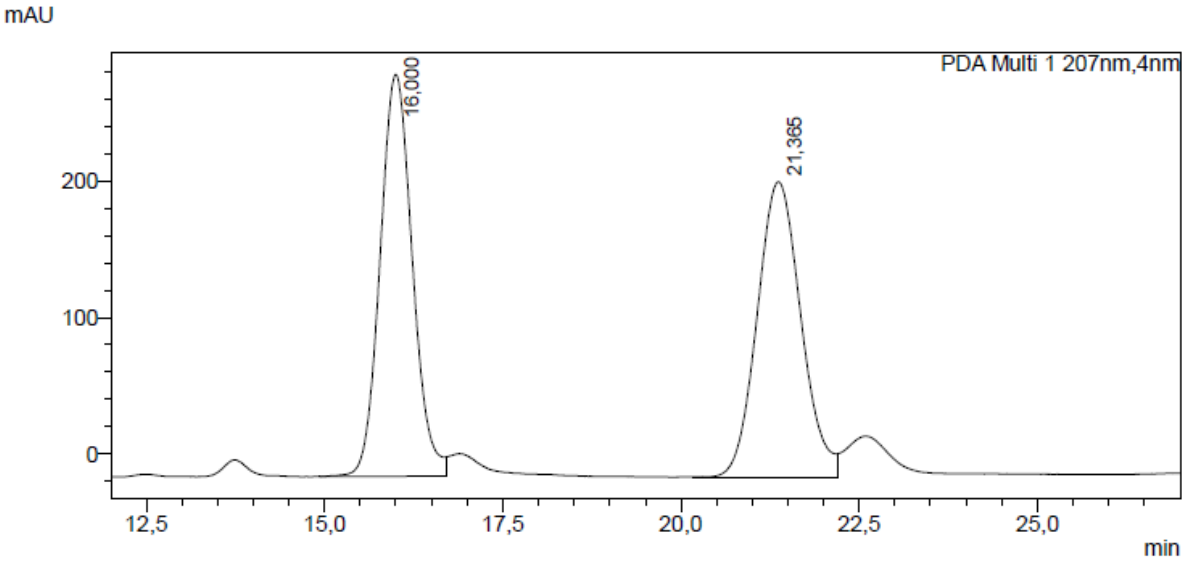


<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	16,016	196599	6460	1,707
2	21,379	11317547	265676	98,293
Total		11514146	272136	100,000

<Chromatogram>



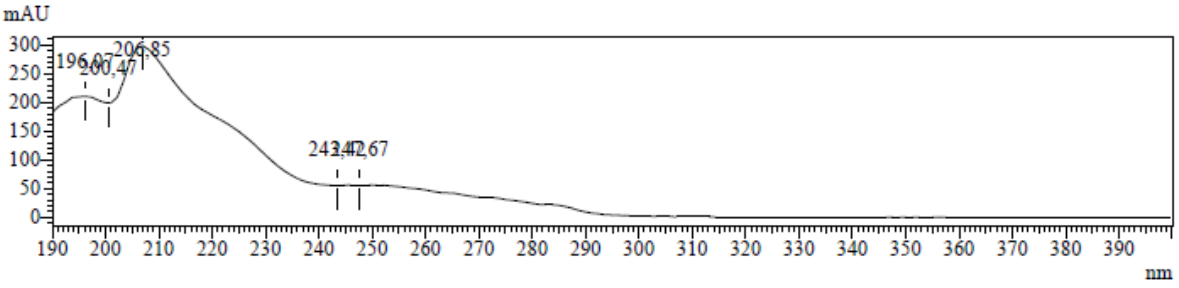
<Peak Table>

PDA Ch1 207nm

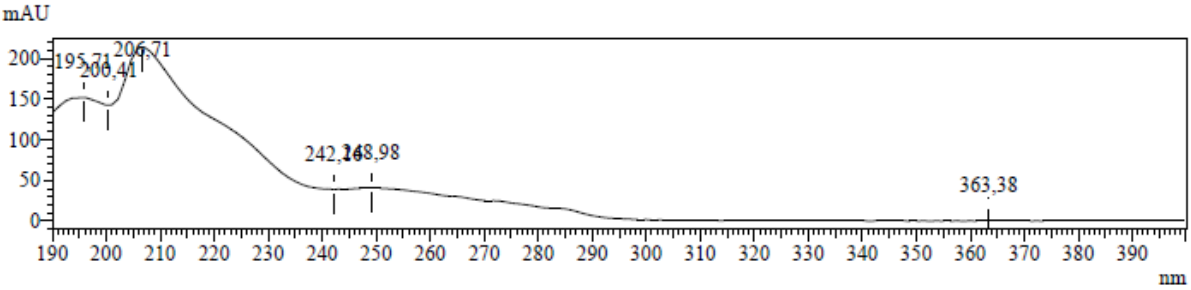
Peak#	Ret. Time	Area	Height	Area%
1	16,000	9264584	294327	50,097
2	21,365	9228832	216349	49,903
Total		18493416	510676	100,000

UV Spectrum

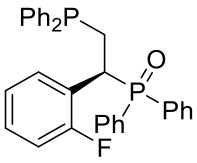
Peak# : 1
Retention Time : 16,000 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 21,365 min
Compound Name :
Spectrum Operation:



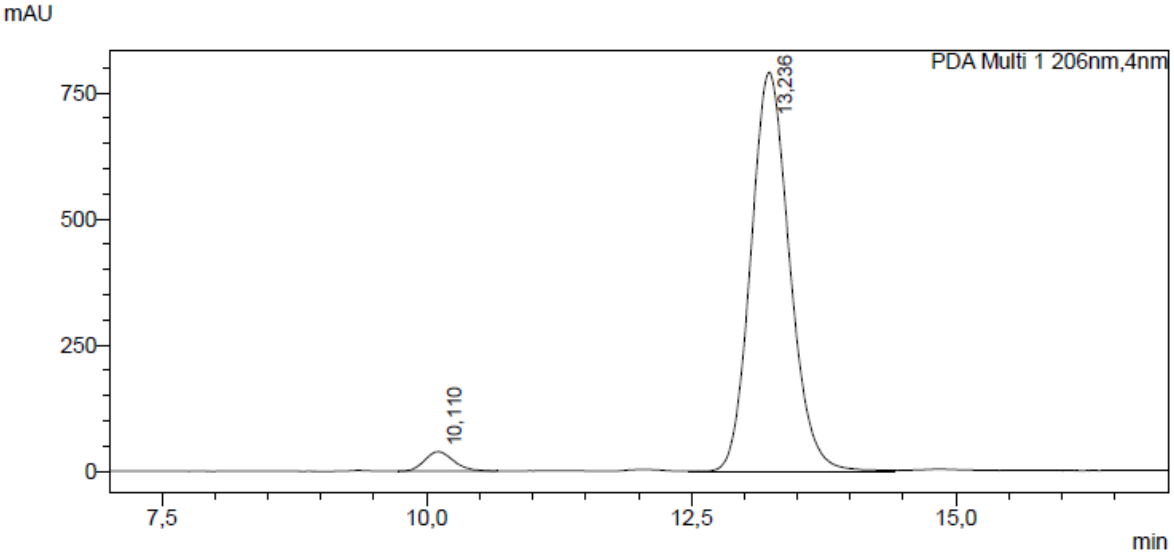
(S)-(2-(diphenylphosphaneyl)-1-(2-fluorophenyl)ethyl)diphenylphosphine oxide (3la)



Following general procedure A: The reaction was performed with **1l** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3la** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [94% yield, 93% ee].

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.94 – 7.72 (m, 1H, C*H*$_{Ar}$), 7.62 – 7.48 (m, 3H, C*H*$_{Ar}$), 7.49 – 7.07 (m, 19H, C*H*$_{Ar}$), 6.85 – 6.71 (m, 1H, C*H*$_{Ar}$), 3.92 – 3.74 (m, 1H, P(O)Ph$_2$C*H*), 2.92 – 2.73 (m, 1H, PPh$_2$CH*H*), 2.63 – 2.45 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR (CDCl$_3$, 101 MHz): δ 161.8, 159.3, 138.5, 138.3, 137.4, 137.2, 134.5, 134.3, 132.4, 132.0, 131.8, 131.4, 131.3, 131.2, 130.9, 130.7, 130.6, 130.4, 129.6, 128.9, 128.8, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 124.7, 123.4, 123.3, 114.9, 114.7, 34.0, 33.3, 29.1, 29.0. (Due to C−P, C-F coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (CDCl$_3$, 162 MHz): δ 33.4 (dd, *J* = 33.1, 4.2 Hz), -19.1 (dd, *J* = 33.1, 5.9 Hz).
^{19}F NMR (CDCl$_3$, 376 MHz) δ -116.8.
HRMS (ESI, m/Z): calcd. for $C_{32}H_{28}FOP_2$ $[M+H]^+$: 509.1594, found: 509.1592.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 10.1 (minor) and 13.2 (major).

<Chromatogram>

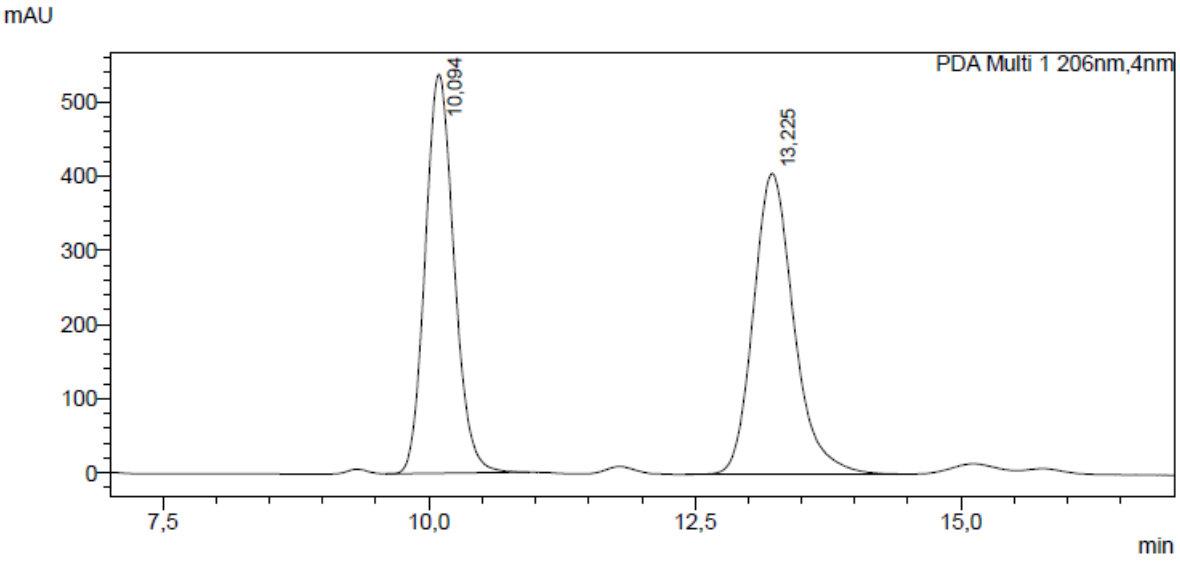


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	10,110	730368	38502	3,496
2	13,236	20161601	791032	96,504
Total		20891969	829534	100,000

<Chromatogram>



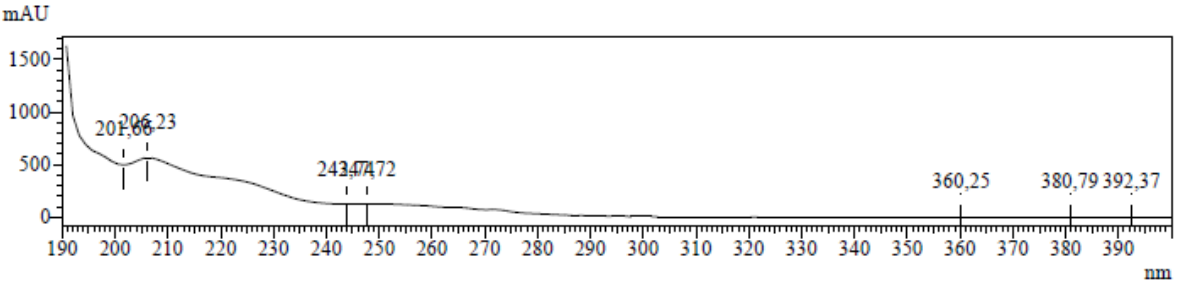
<Peak Table>

PDA Ch1 206nm

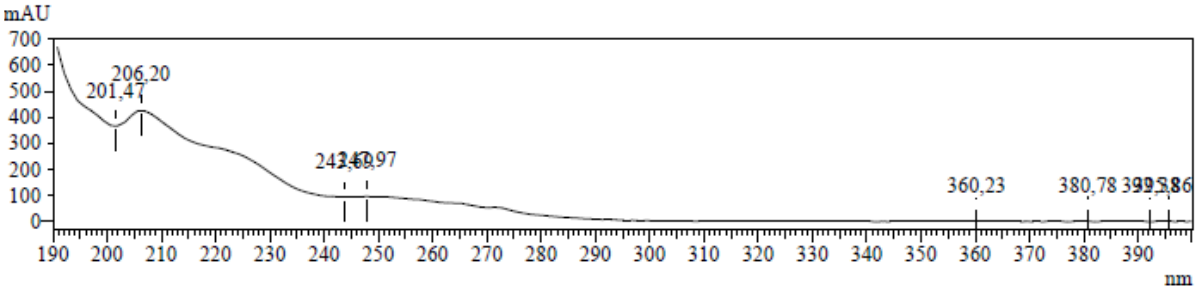
Peak#	Ret. Time	Area	Height	Area%
1	10,094	10156354	537787	48,560
2	13,225	10758855	405797	51,440
Total		20915209	943584	100,000

UV Spectrum

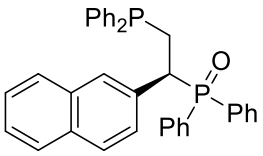
Peak# : 1
Retention Time : 10,094 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 13,225 min
Compound Name :
Spectrum Operation:



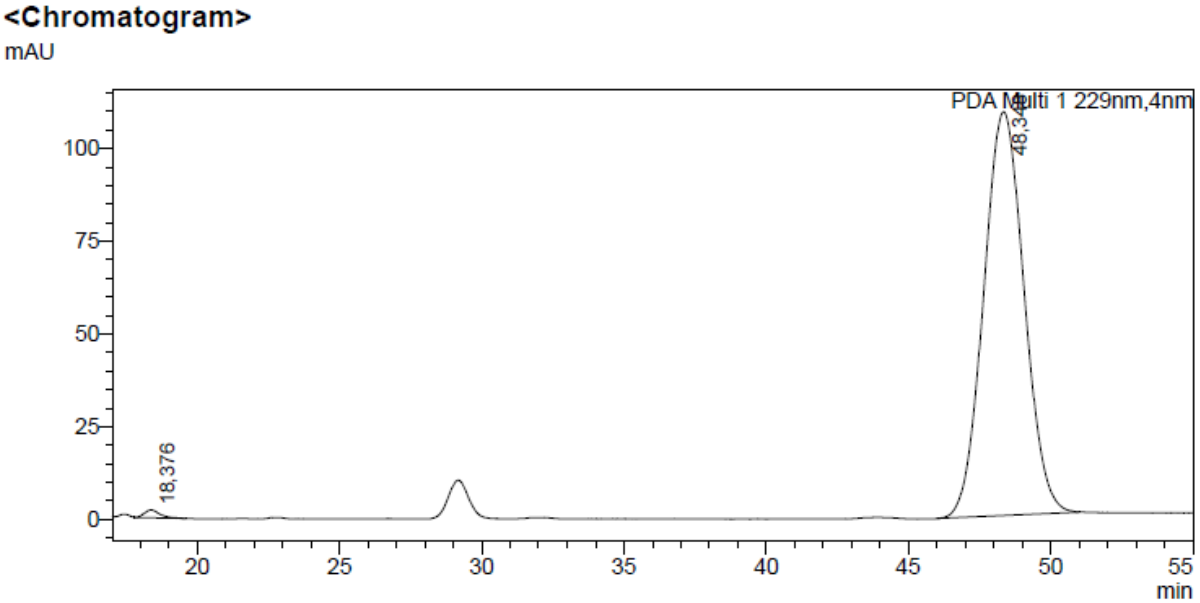
(S)-(2-(diphenylphosphaneyl)-1-(naphthalen-2-yl)ethyl)diphenylphosphine oxide (3ma)



Following general procedure A: The reaction was performed with **1m** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), barton's base (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 48 h. Product **3ma** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [80% yield, 99% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 – 7.61 (m, 7H, C*H*$_{Ar}$), 7.61 – 7.51 (m, 1H, C*H*$_{Ar}$), 7.48 – 7.06 (m, 19H, C*H*$_{Ar}$), 3.67 – 3.31 (m, 1H, P(O)Ph$_2$C*H*), 3.07 – 2.87 (m, 1H, PPh$_2$CH*H*), 2.74 – 2.48 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.8, 138.6, 137.4, 137.2, 134.5, 134.3, 133.4, 133.4, 133.1, 133.0, 133.0, 133.0, 132.8, 132.8, 132.5, 132.4, 132.0, 131.9, 131.9, 131.8, 131.5, 131.4, 131.4, 131.4, 131.0, 131.0, 131.0, 129.7, 129.7, 129.4, 129.3, 128.9, 128.9, 128.8, 128.8, 128.3, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 126.0, 125.8, 125.8, 44.1, 43.9, 43.4, 43.3, 29.3, 29.1. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.4 (d, *J* = 31.2 Hz), -19.7 (d, *J* = 31.2 Hz).
HRMS (ESI, m/Z): calcd. for $C_{36}H_{31}OP_2$ $[M+H]^+$: 541.1845, found: 541.1838.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 229 nm. Retention time (min): 18.4 (minor) and 48.3 (major).

<Chromatogram>



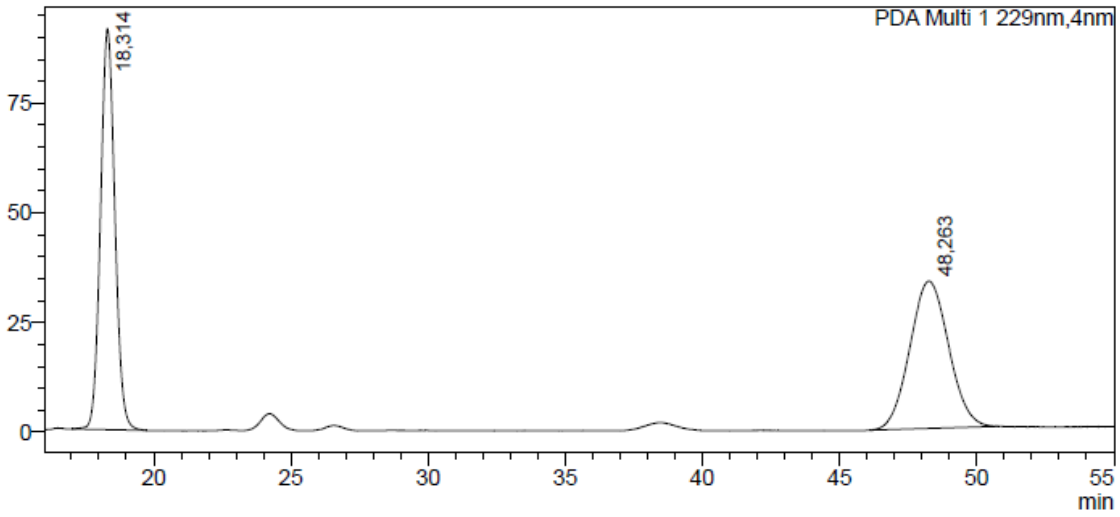
<Peak Table>

PDA Ch1 229nm

Peak#	Ret. Time	Area	Height	Area%
1	18,376	77223	2087	0,713
2	48,348	10754932	108898	99,287
Total		10832155	110985	100,000

<Chromatogram>

mAU



<Peak Table>

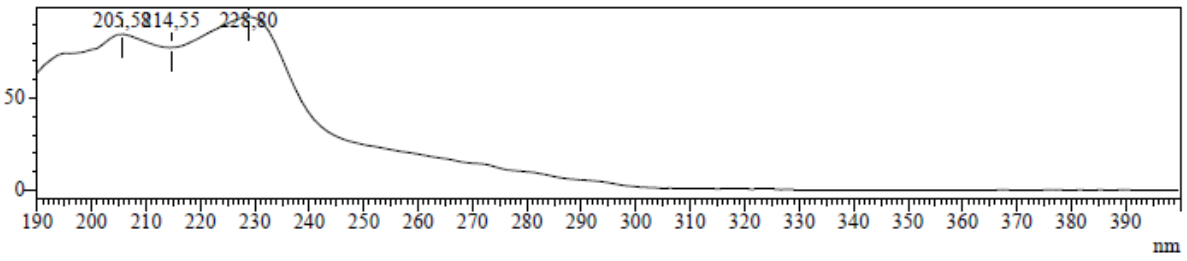
PDA Ch1 229nm

Peak#	Ret. Time	Area	Height	Area%
1	18,314	3350789	91343	50,346
2	48,263	3304761	33549	49,654
Total		6655551	124892	100,000

UV Spectrum

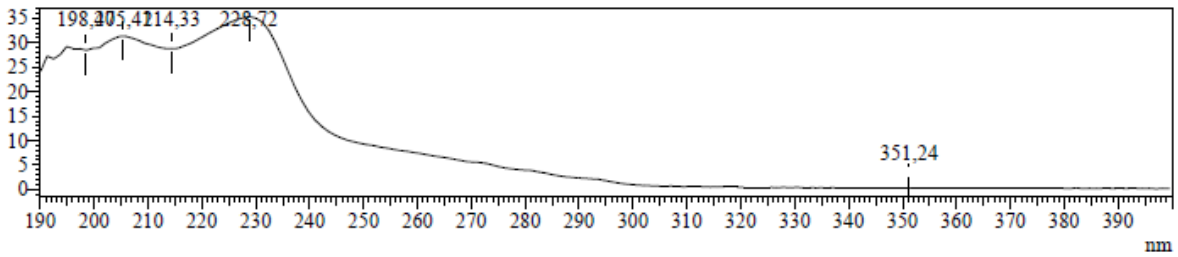
Peak# : 1
Retention Time : 18,314 min
Compound Name :
Spectrum Operation:

mAU

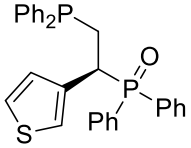


Peak# : 2
Retention Time : 48,263 min
Compound Name :
Spectrum Operation:

mAU



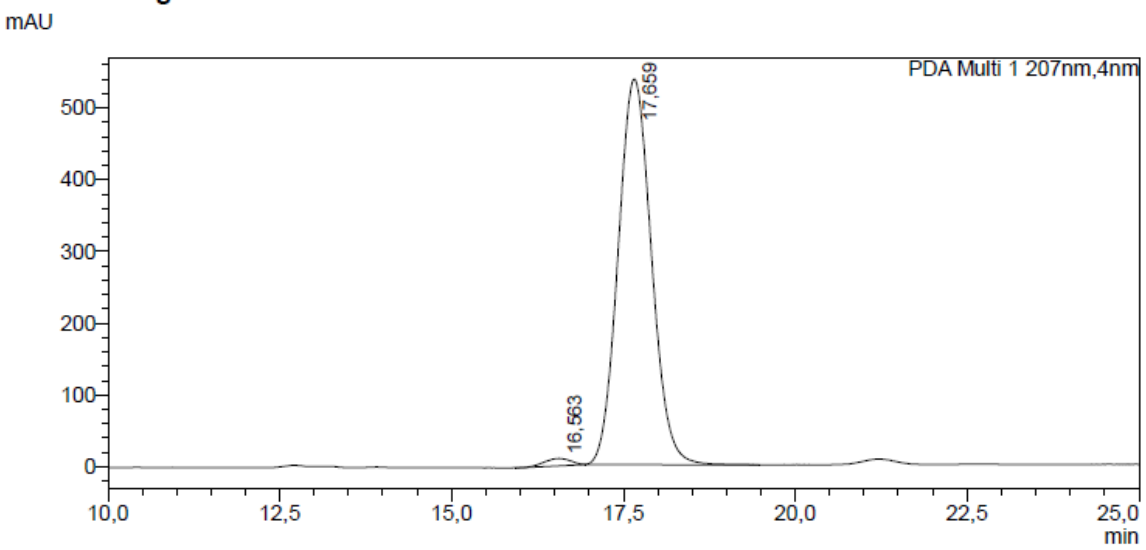
(S)-(2-(diphenylphosphaneyl)-1-(thiophen-3-yl)ethyl)diphenylphosphine oxide (3na)



Following general procedure A: The reaction was performed with **1n** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3na** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [97% yield, 97% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 – 7.08 (m, 21H, C*H*$_{Ar}$), 6.99 (s, 2H, C*H*$_{Ar}$), 3.52 – 3.45 (m, 1H, P(O)Ph_2C*H*), 2.82 – 2.74 (m, , 1H, PPh_2CH*H*), 2.54 – 2.50 (m, 1H, PPh_2CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.8, 138.6, 137.4, 137.2, 135.8, 134.4, 134.2, 132.6, 132.0, 131.8, 131.4, 130.9, 129.6, 128.8, 128.3, 128.2, 125.6, 124.2, 39.6, 38.8, 29.2, 29.0. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.0 (d, *J* = 31.5 Hz), -21.6 (d, *J* = 31.5 Hz).
HRMS (ESI, m/Z): calcd. for $C_{30}H_{27}OP_2S$ $[M+H]^+$: 497.1252, found: 497.1250.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 207 nm. Retention time (min): 16.6 (minor) and 17.7 (major).

<Chromatogram>

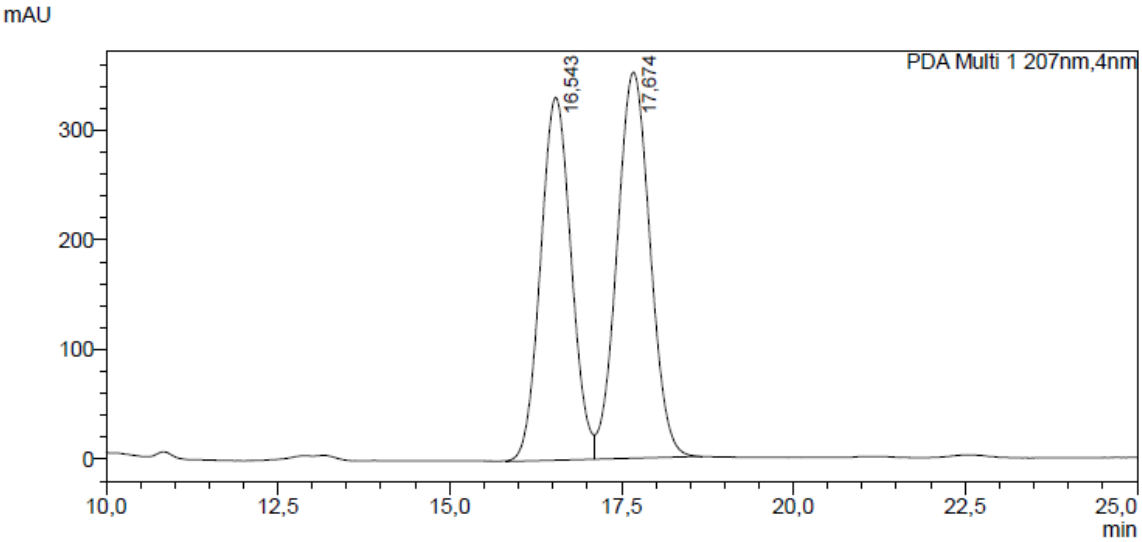


<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	16,563	278459	10345	1,516
2	17,659	18088698	536979	98,484
Total		18367157	547324	100,000

<Chromatogram>



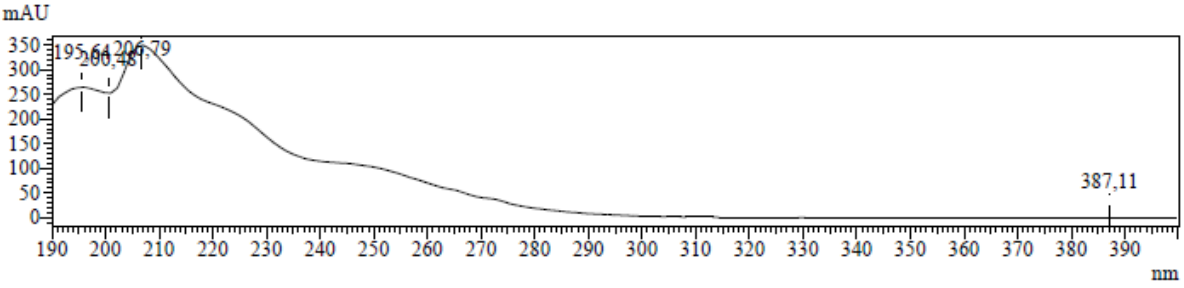
<Peak Table>

PDA Ch1 207nm

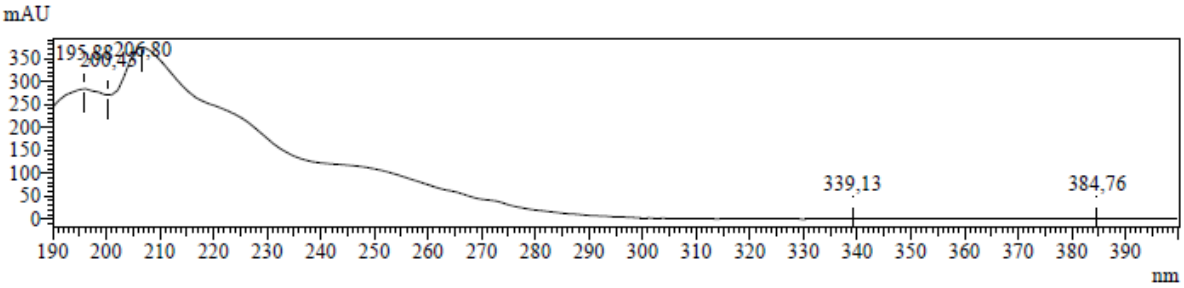
Peak#	Ret. Time	Area	Height	Area%
1	16,543	10280301	330944	46,636
2	17,674	11763508	352183	53,364
Total		22043809	683127	100,000

UV Spectrum

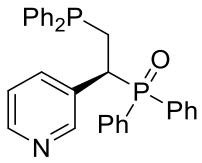
Peak# : 1
Retention Time : 16,543 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 17,674 min
Compound Name :
Spectrum Operation:



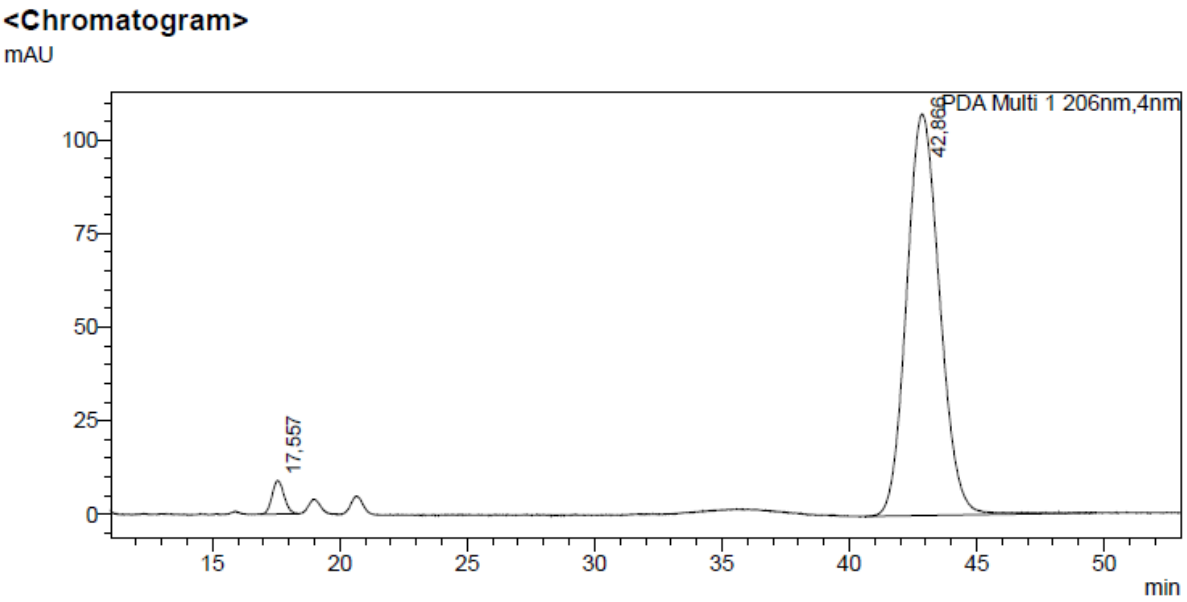
(S)-(2-(diphenylphosphaneyl)-1-(pyridin-3-yl)ethyl)diphenylphosphine oxide (3oa)



Following general procedure A: The reaction was performed with **1o** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3oa** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [80% yield, 94% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.36 (d, *J* = 4.7 Hz, 1H, C*H*$_{Ar}$), 8.08 (s, 1H, C*H*$_{Ar}$), 7.83 (d, *J* = 8.1 Hz, 1H, C*H*$_{Ar}$), 7.66 – 7.57 (m, 2H, C*H*$_{Ar}$), 7.57 – 7.50 (m, 1H, C*H*$_{Ar}$), 7.48 – 7.40 (m, 3H, C*H*$_{Ar}$), 7.39 – 7.33 (m, 2H, C*H*$_{Ar}$), 7.31 – 7.21 (m, 5H, C*H*$_{Ar}$), 7.20 – 7.11 (m, 8H, C*H*$_{Ar}$), 3.36 – 3.20 (m, 1H, P(O)Ph$_2$C*H*), 2.91 – 2.75 (m, 1H, PPh$_2$CH*H*), 2.63 – 2.46 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 151.3, 151.2, 148.7, 138.3, 138.1, 136.9, 136.8, 136.8, 136.7, 134.4, 134.2, 132.2, 132.2, 132.0, 131.8, 131.8, 131.7, 131.4, 131.3, 130.8, 130.7, 129.8, 129.1, 129.0, 129.0, 128.9, 128.5, 128.4, 128.4, 128.4, 128.3, 123.6, 41.3, 41.2, 40.7, 40.5, 28.7, 28.5. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.10(d, *J* = 30.6 Hz), -22.5 (d, *J* = 30.6 Hz).
HRMS (ESI, m/Z): calcd. for $C_{31}H_{28}NOP_2$ $[M+H]^+$: 492.1641, found: 492.1636.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 17.6 (minor) and 42.9 (major).

<Chromatogram>

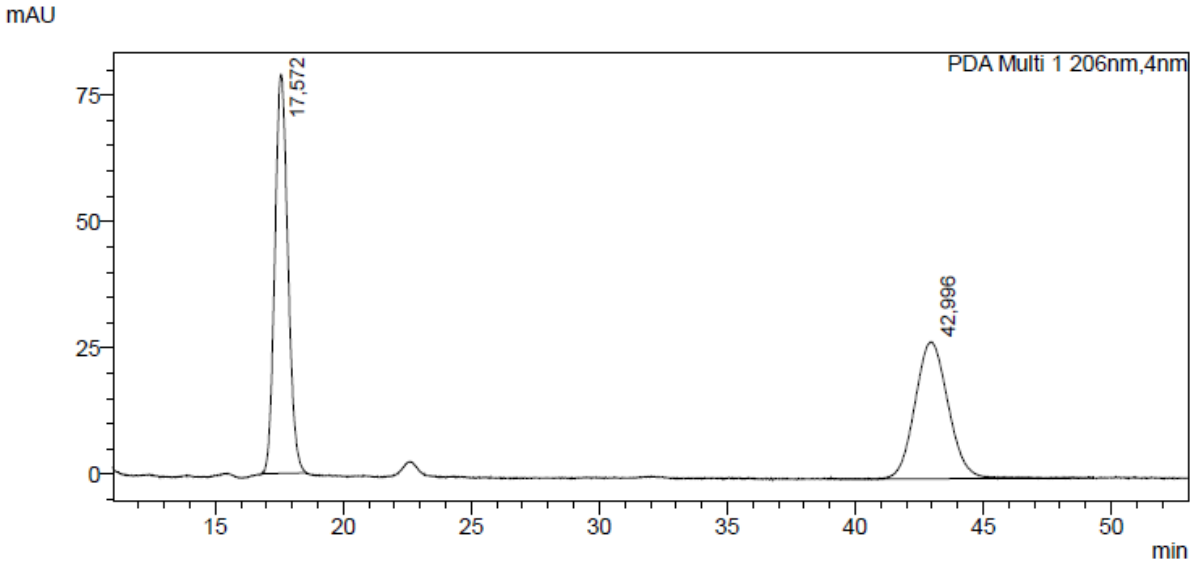


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	17,557	294681	8999	2,944
2	42,866	9716073	107295	97,056
Total		10010755	116294	100,000

<Chromatogram>



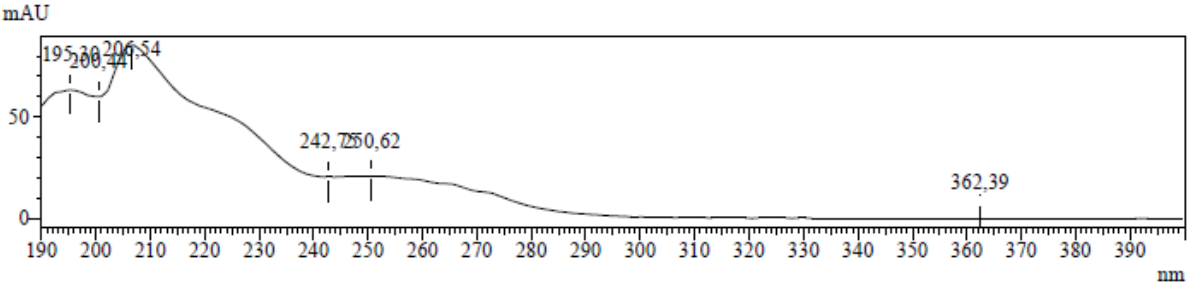
<Peak Table>

PDA Ch1 206nm

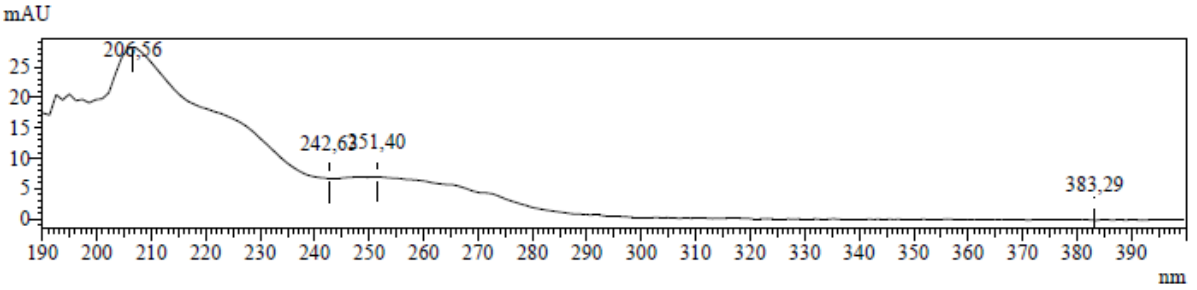
Peak#	Ret. Time	Area	Height	Area%
1	17,572	2804045	78935	53,236
2	42,996	2463152	27088	46,764
Total		5267197	106023	100,000

UV Spectrum

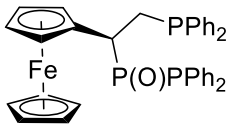
Peak# : 1
Retention Time : 17,572 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 42,996 min
Compound Name :
Spectrum Operation:



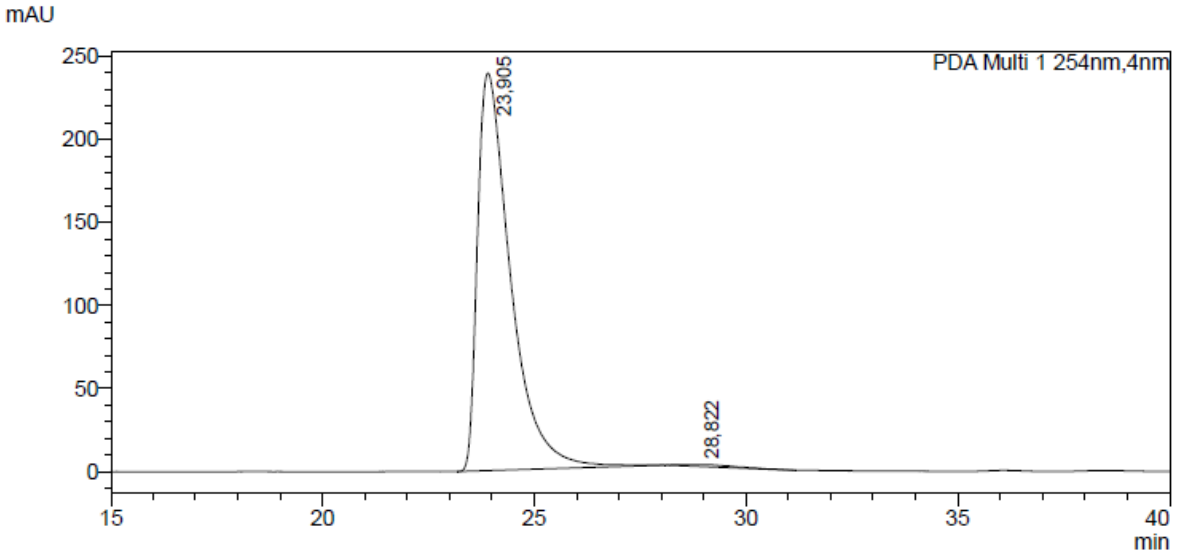
(S)-(2-(diphenylphosphaneyl)-1-ferrocenylethyl)diphenylphosphine oxide (3pa)



Following general procedure A: The reaction was performed with **1p** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **3pa** was obtained as an orange solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [92% yield, 98% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 – 7.56 (m, 2H, C*H*$_{Ar}$), 7.47 – 7.38 (m, 7H, C*H*$_{Ar}$), 7.37 – 7.24 (m, 11H, C*H*$_{Ar}$), 4.25 (d, *J* = 1.2 Hz, 1H, C*H*$_{Fe}$), 4.09 – 4.08 (m, 1H, C*H*$_{Fe}$), 4.05 (s, 5H, C*H*$_{Fe}$), 3.91 – 3.89 (m, 1H, C*H*$_{Fe}$), 3.51 (d, *J* = 1.3 Hz, 1H, C*H*$_{Fe}$), 3.46 – 3.37 (m, 1H, P(O)Ph$_2$C*H*), 3.06 – 2.97 (m, 1H, PPh$_2$CH*H*), 2.59 – 2.49 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.8, 139.7, 138.0, 137.8, 133.6, 133.4, 133.0, 132.8, 132.1, 132.0, 132.0, 131.7, 131.6, 131.6, 131.5, 131.4, 131.4, 130.7, 128.9, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.0, 127.9, 86.2, 86.2, 69.3, 69.2, 68.1, 68.1, 68.1, 67.5, 67.2, 38.4, 38.2, 37.8, 37.6, 28.1, 28.0. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.5 (d, *J* = 20.3 Hz), -17.5 (d, *J* = 20.3 Hz).
HRMS (ESI, m/Z): calcd. for $C_{36}H_{33}FeOP_2$ $[M+H]^+$: 599.1351, found: 599.1354.
HPLC: Chiracel-ODH, *n*-heptane/*i*-PrOH 95:05, 0.5 mL/min., 40 °C, detection at 254 nm. Retention time (min): 23.9 (major) and 28.8 (minor).

<Chromatogram>

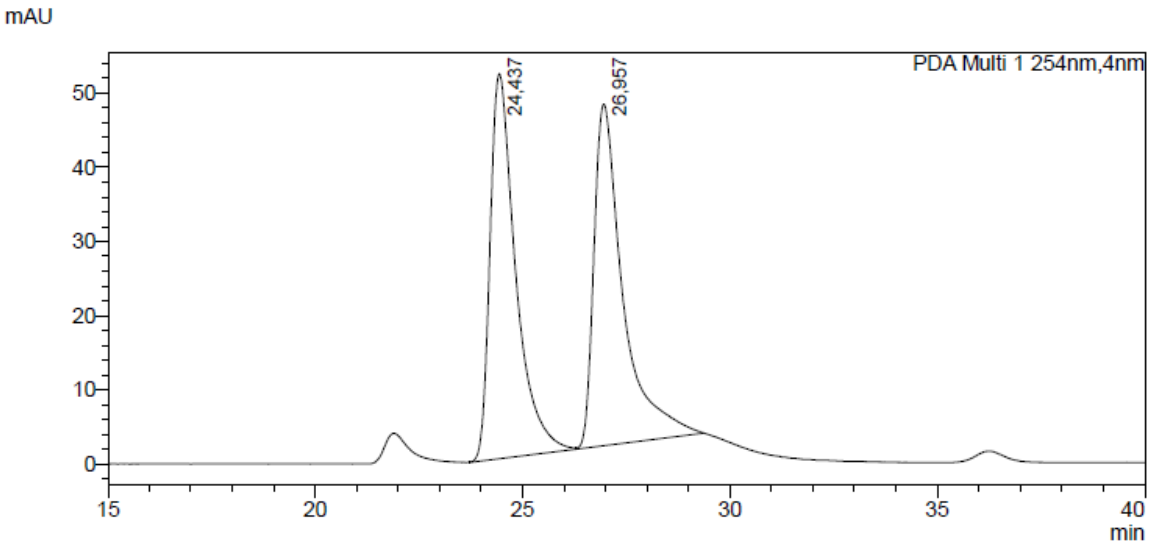


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23,905	13013279	239216	99,168
2	28,822	109220	1116	0,832
Total		13122499	240332	100,000

<Chromatogram>



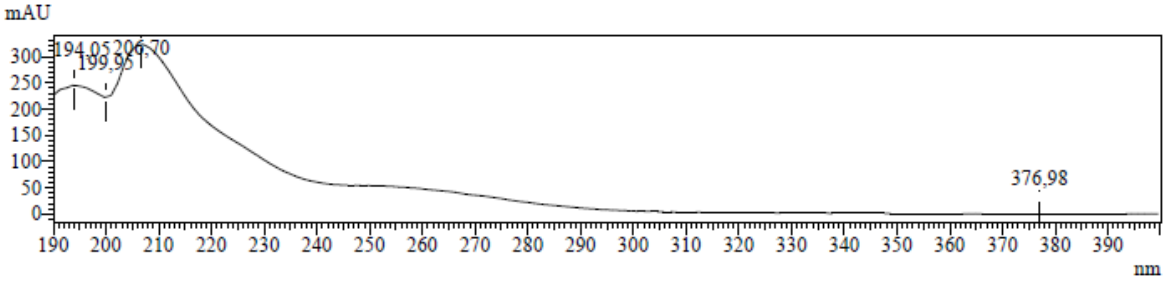
<Peak Table>

PDA Ch1 254nm

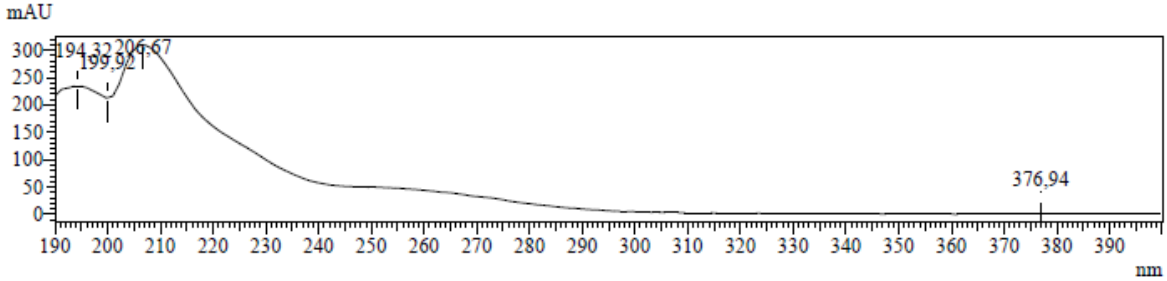
Peak#	Ret. Time	Area	Height	Area%
1	24,437	2234712	51887	49,871
2	26,957	2246236	46012	50,129
Total		4480948	97899	100,000

UV Spectrum

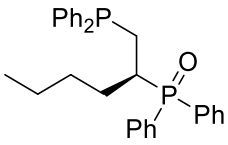
Peak# : 1
Retention Time : 24,437 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 26,957 min
Compound Name :
Spectrum Operation:



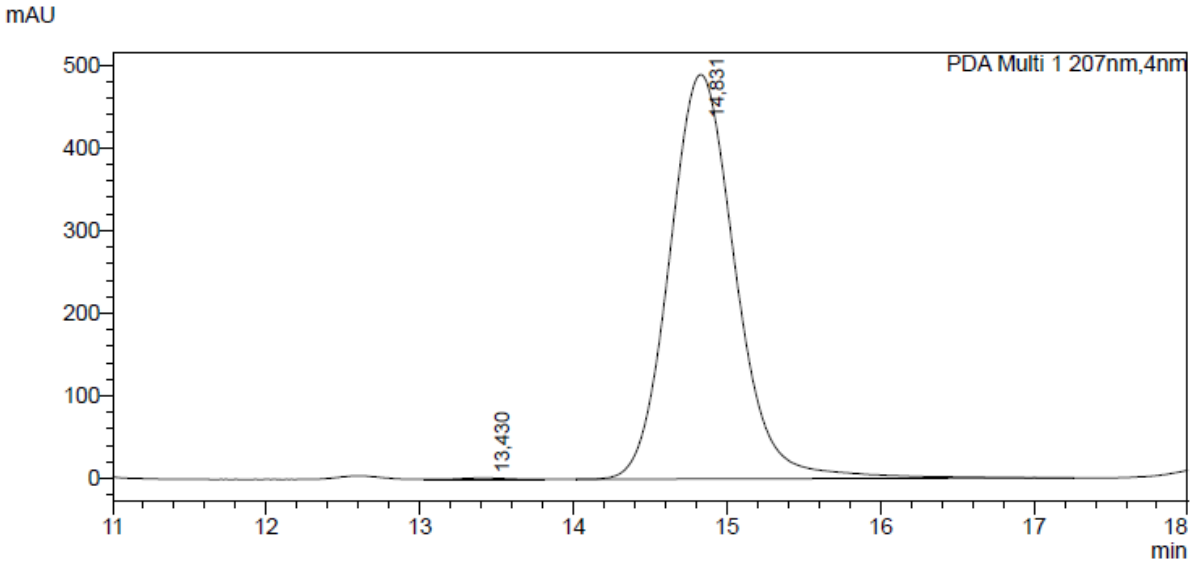
(S)-(1-(diphenylphosphaneyl)hexan-2-yl)diphenylphosphine oxide (3qa)



Following general procedure A: The reaction was performed with **1q** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **3qa** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [95% yield, >99% ee].

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.68 – 7.60 (m, 2H, C*H*$_{Ar}$), 7.53 – 7.19 (m, 18H, C*H*$_{Ar}$), 2.36 – 2.22 (m, 2H), 2.22 – 2.08 (m, 1H), 2.07 – 1.86 (m, 1H), 1.79 – 1.60 (m, 1H), 1.55 – 1.35 (m, 1H), 1.22 – 1.00 (m, 3H), 0.70 (t, *J* = 7.1 Hz, 3H, C*H*$_3$).
^{13}C NMR (CDCl$_3$, 101 MHz): δ 138.8, 138.6, 137.5, 137.3, 134.3, 134.1, 133.3, 132.7, 132.3, 132.2, 132.0, 131.8, 131.6, 131.6, 131.6, 131.2, 131.1, 131.0, 130.9, 129.5, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 34.5, 34.4, 33.8, 33.7, 30.2, 30.2, 30.2, 30.2, 28.2, 28.2, 28.1, 28.1, 27.4, 27.4, 27.2, 27.2, 22.9, 13.8. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (CDCl$_3$, 162 MHz): δ 33.4 (d, *J* = 32.2 Hz), -21.5 (d, *J* = 32.2 Hz).
HRMS (ESI, m/Z): calcd. for $C_{30}H_{33}OP_2$ $[M+H]^+$: 471.2001, found: 471.1998.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 13.4 (minor) and 14.8 (major).

<Chromatogram>

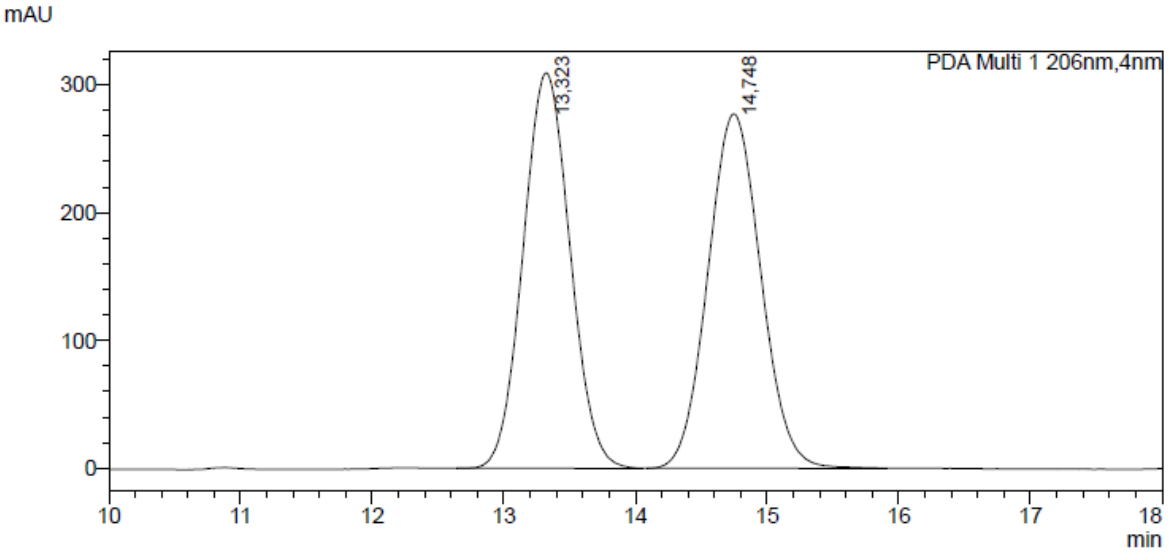


<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	13,430	33676	1495	0,230
2	14,831	14635416	489316	99,770
Total		14669092	490810	100,000

<Chromatogram>



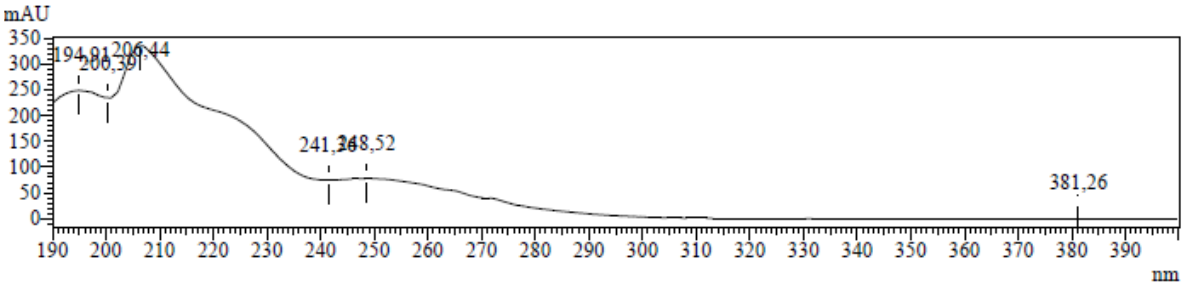
<Peak Table>

PDA Ch1 206nm

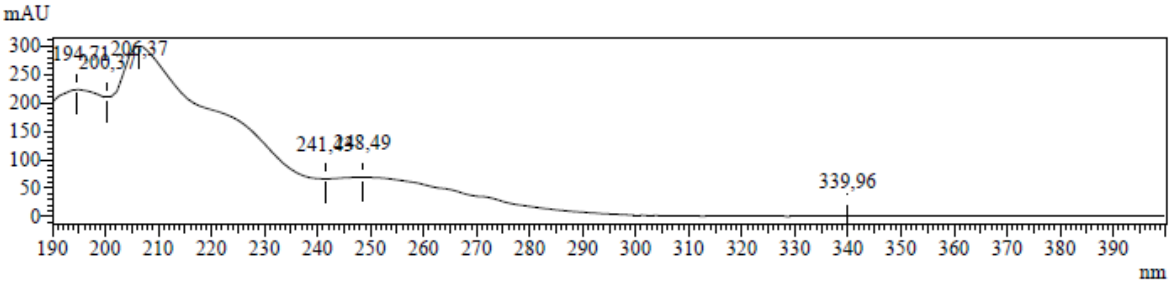
Peak#	Ret. Time	Area	Height	Area%
1	13,323	7676102	309232	49,751
2	14,748	7752827	277052	50,249
Total		15428928	586284	100,000

UV Spectrum

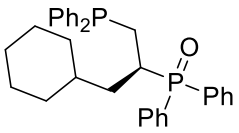
Peak# : 1
Retention Time : 13,323 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 14,748 min
Compound Name :
Spectrum Operation:



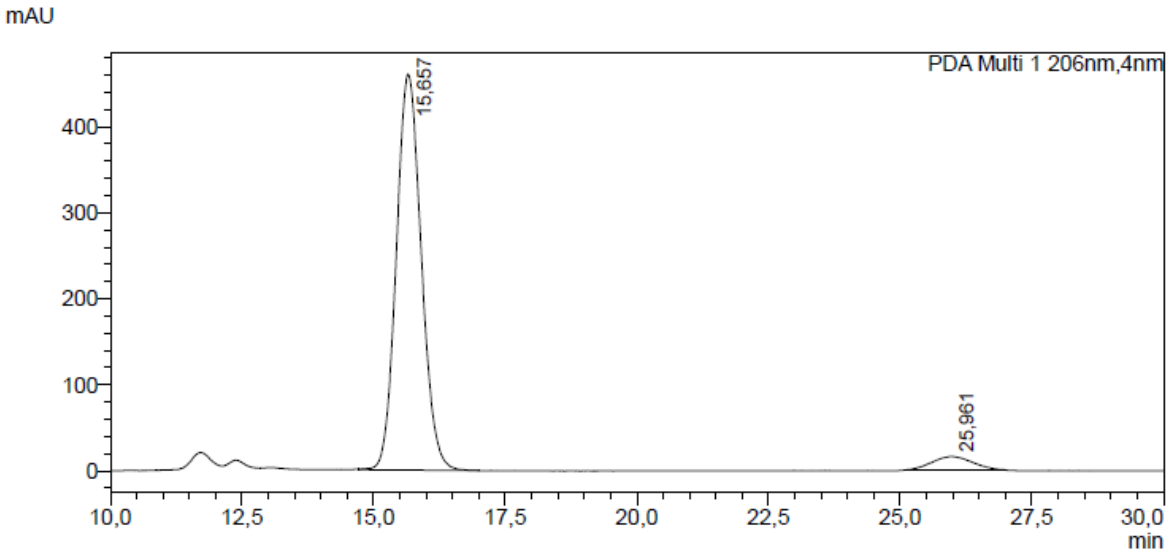
(S)-(1-(diphenylphosphaneyl)hexan-2-yl)diphenylphosphine oxide (3ra)



Following general procedure A: The reaction was performed with **1r** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **3ra** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [80% yield, 90% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 – 7.62 (m, 2H, C*H*$_{Ar}$), 7.58 – 7.49 (m, 2H, C*H*$_{Ar}$), 7.49 – 7.21 (m, 16H, C*H*$_{Ar}$), 2.48 – 2.35 (m, 1H, P(O)Ph$_2$C*H*), 2.34 – 2.22 (m, 1H, PPh$_2$CH*H*), 2.21 – 2.08 (m, 1H, PPh$_2$CH*H*), 1.83 – 1.65 (m, 2H), 1.62 – 1.36 (m, 5H), 1.14 – 0.67 (m, 5H), 0.61 – 0.45 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.0, 138.9, 137.8, 137.6, 134.4, 134.2, 133.5, 132.8, 132.6, 132.2, 132.1, 131.8, 131.6, 131.6, 131.5, 131.2, 131.2, 131.1, 131.0, 129.4, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 36.9, 36.9, 36.8, 36.8, 36.0, 35.9, 35.9, 35.9, 33.4, 33.1, 31.6, 31.5, 30.9, 30.8, 29.1, 29.1, 28.0, 28.9, 26.5, 26.3, 26.1. (Due to C–P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 36.4 (d, *J* = 31.0 Hz), -17.3 (d, *J* = 31.0 Hz).
HRMS (ESI, m/Z): calcd. for $C_{33}H_{37}OP_2$ $[M+H]^+$: 511.2314, found: 511.2312.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 15.7 (major) and 26.0 (minor).

<Chromatogram>

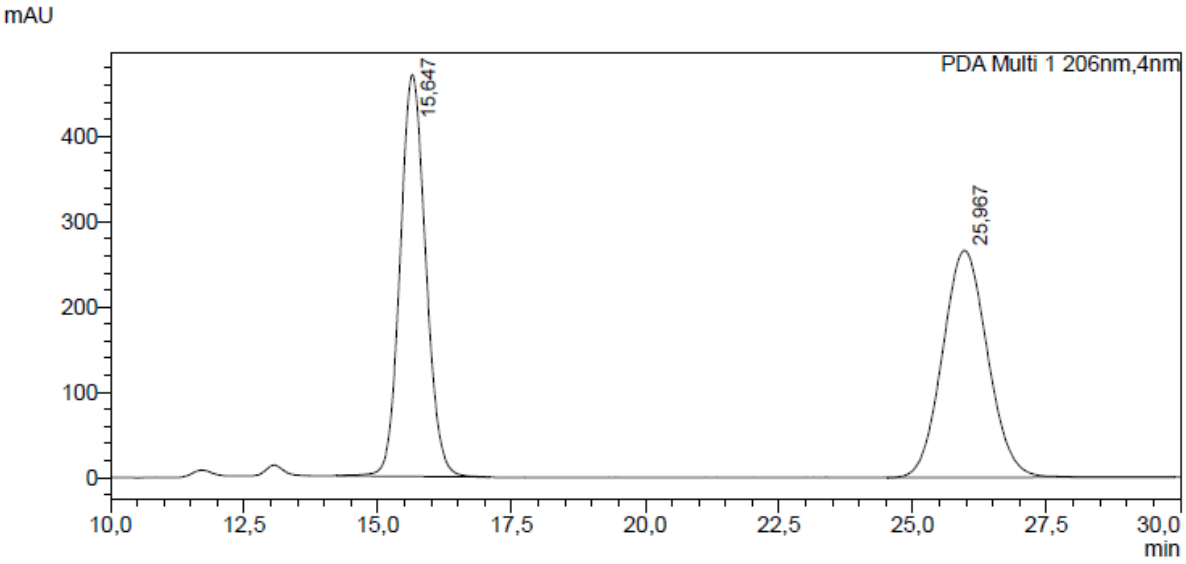


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	15,657	15177338	459969	94,761
2	25,961	839128	15579	5,239
Total		16016466	475547	100,000

<Chromatogram>



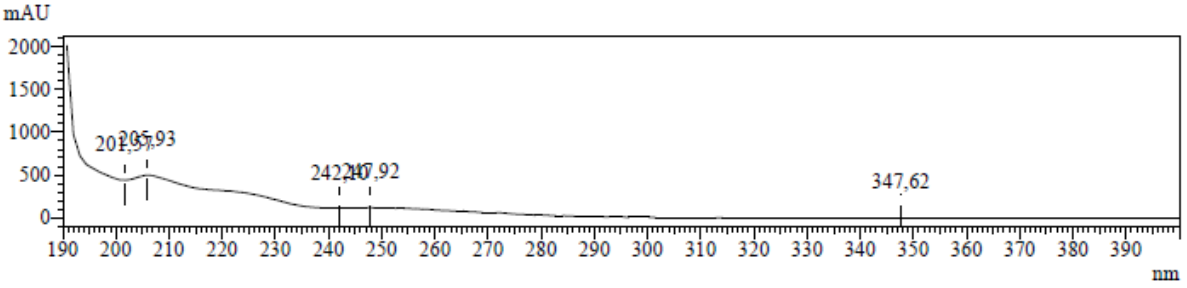
<Peak Table>

PDA Ch1 206nm

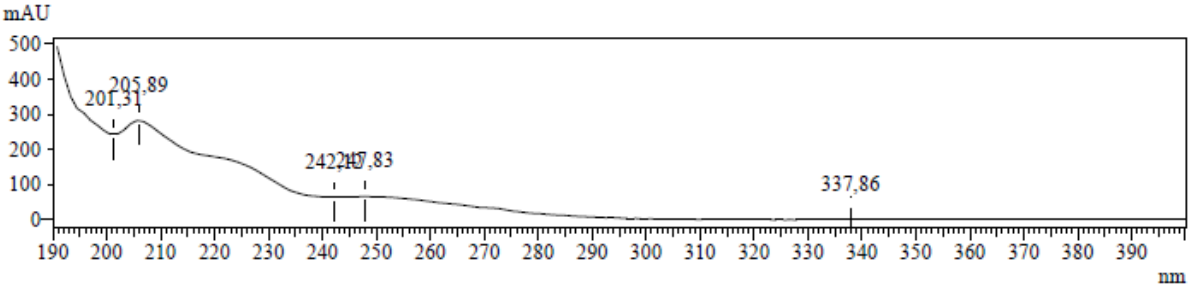
Peak#	Ret. Time	Area	Height	Area%
1	15,647	15681927	470262	50,178
2	25,967	15570938	265615	49,822
Total		31252866	735877	100,000

UV Spectrum

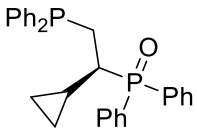
Peak# : 1
Retention Time : 15,647 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 25,967 min
Compound Name :
Spectrum Operation:



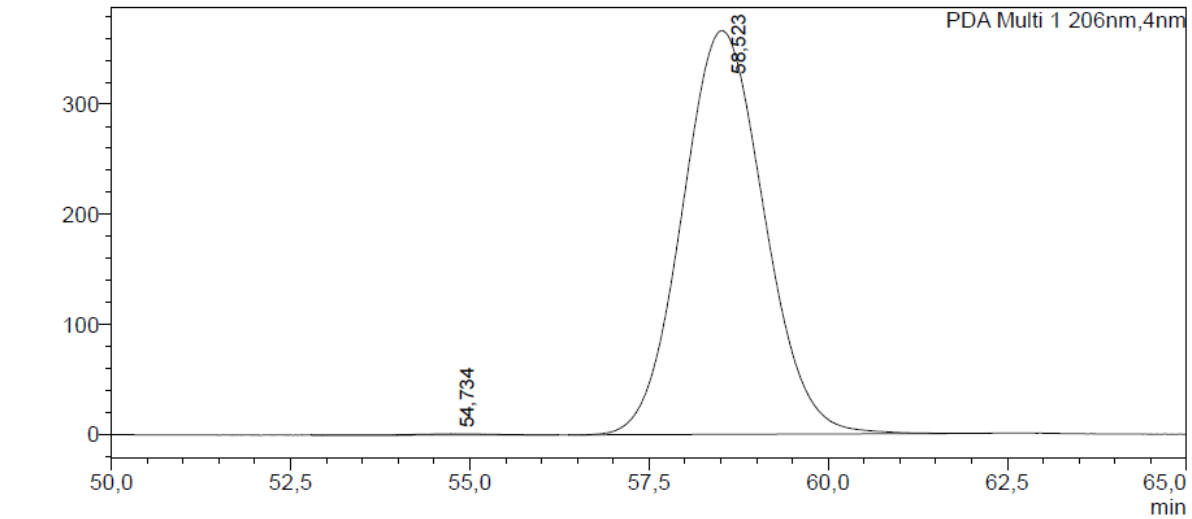
(S)-(1-cyclopropyl-2-(diphenylphosphaneyl)ethyl)diphenylphosphine oxide (3sa)



Following general procedure A: The reaction was performed with **1s** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **3sa** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [90% yield, >99% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 – 7.62 (m, 2H, C*H*$_{Ar}$), 7.62 – 7.51 (m, 2H, C*H*$_{Ar}$), 7.51 – 7.20 (m, 16H, C*H*$_{Ar}$), 2.55 – 2.37 (m, 2H), 1.75 – 1.50 (m, 1H), 1.11 – 0.91 (m, 1H), 0.60 – 0.46 (m, 1H), 0.42 – 0.27 (m, 1H), 0.19 – 0.04 (m, 1H), 0.37 – 0.54 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.2, 139.1, 138.1, 137.9, 134.1, 133.9, 133.6, 132.7, 132.6, 132.3, 132.1, 131.7, 131.7, 131.5, 131.5, 131.4, 131.3, 131.2, 131.1, 129.3, 128.8, 128.8, 128.7, 128.4, 128.4, 128.4, 128.3, 128.3, 41.0, 40.8, 40.3, 40.2, 29.1, 28.9, 11.0, 7.0, 6.9, 6.9, 6.8, 5.7. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 32.4 (d, *J* = 30.3 Hz), -20.4 (d, *J* = 30.3 Hz).
HRMS (ESI, m/Z): calcd. for $C_{29}H_{29}OP_2$ $[M+H]^+$: 455.1688, found: 455.1684.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 0.5 mL/min., 40 °C, detection at 206 nm. Retention time (min): 54.7 (minor) and 58.5 (major).

<Chromatogram>

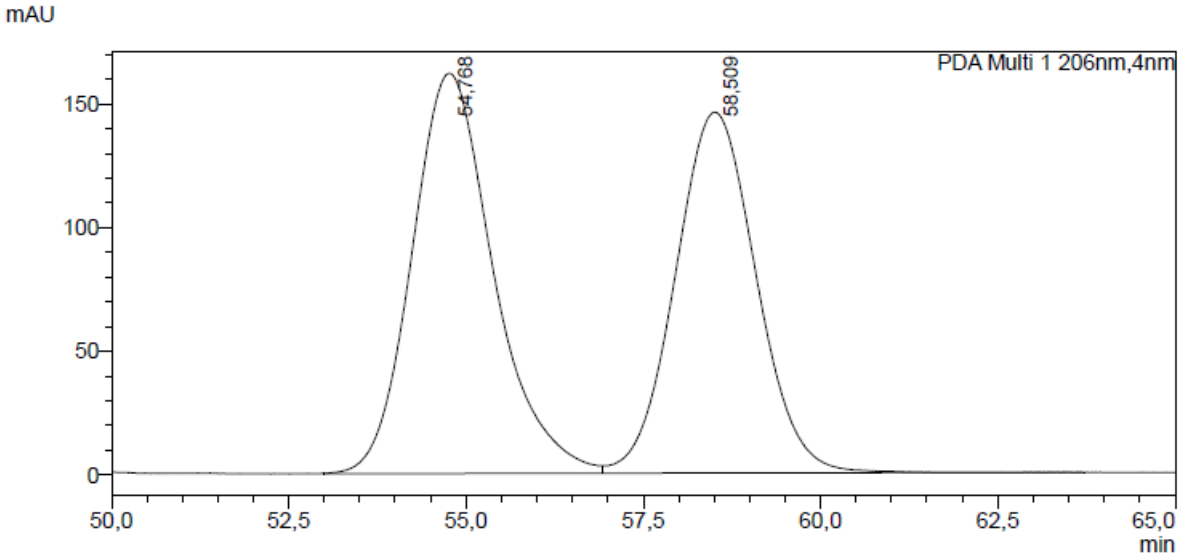


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	54,734	78033	1045	0,267
2	58,523	29167964	366445	99,733
Total		29245997	367489	100,000

<Chromatogram>



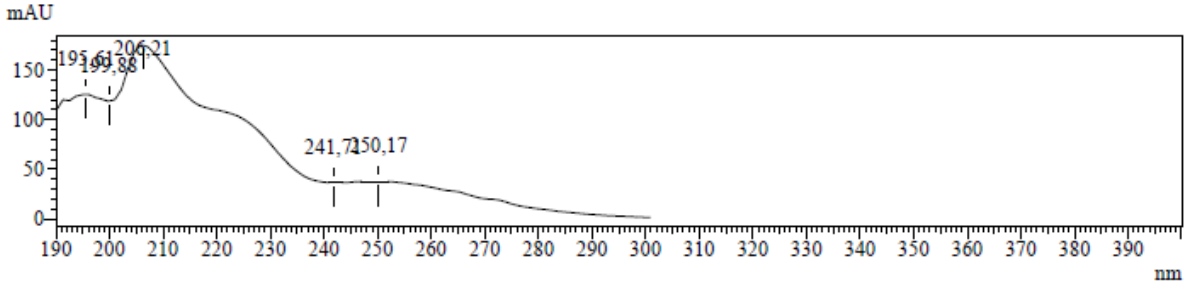
<Peak Table>

PDA Ch1 206nm

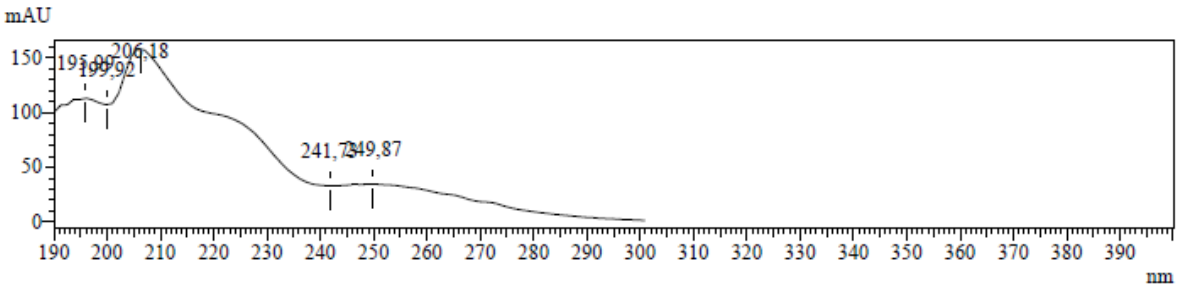
Peak#	Ret. Time	Area	Height	Area%
1	54,768	12910197	161748	52,756
2	58,509	11561427	145839	47,244
Total		24471624	307587	100,000

UV Spectrum

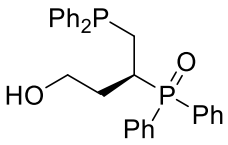
Peak# : 1
Retention Time : 54,768 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 58,509 min
Compound Name :
Spectrum Operation:



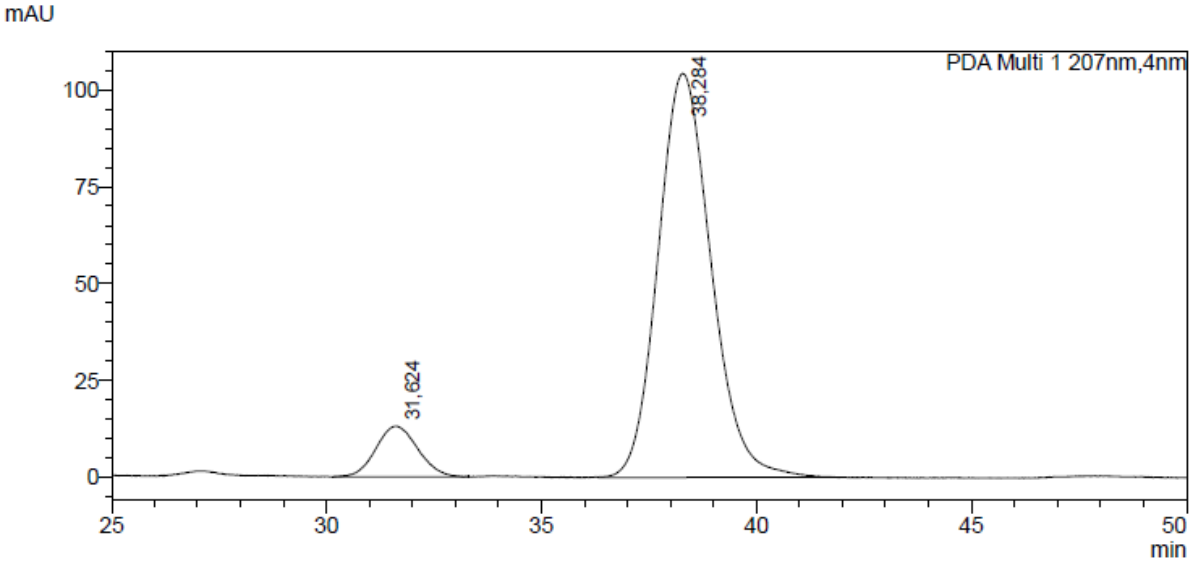
(S)-(1-(diphenylphosphaneyl)-5-hydroxypentan-2-yl)diphenylphosphine oxide (3ta)



Following general procedure A: The reaction was performed with **1t** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 5 days. Product **3ta** was obtained as a white solid after column chromatography (SiO_2, ethyl acetate/methanol =1:0.05) [61% yield, 82% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 – 7.31 (m, 13H, C*H*$_{Ar}$), 7.32 – 7.24 (m, 7H, C*H*$_{Ar}$), 4.66 (br s, 1H, O*H*), 3.97 – 3.80 (m, 1H, OHCH*H*), 3.78 – 3.56 (m, 1H, OHCH*H*), 2.55 – 2.38 (m, 1H, P(O)Ph$_2$C*H*), 2.37 – 2.17 (m, 3H), 2.13 – 1.90 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.0, 137.9, 136.6, 136.5, 134.2, 134.0, 131.9, 131.8, 131.7, 131.3, 131.2, 131.0, 130.9, 129.7, 128.8, 128.8, 128.5, 128.4, 58.5, 33.2, 33.1, 32.6, 32.4, 30.4, 30.3, 25.5, 25.3. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.7 (d, *J* = 30.0 Hz), -19.6 (d, *J* = 30.0 Hz).
HRMS (ESI, m/Z): calcd. for $C_{28}H_{29}O_2P_2$ $[M+H]^+$: 459.1637, found: 459.1638.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 207 nm. Retention time (min): 31.6 (minor) and 38.3 (major). (*Due to the poor separation of the product **3ta** in the HPLC, the ee of this compound was determined from the corresponding oxidized derivative.)*

<Chromatogram>

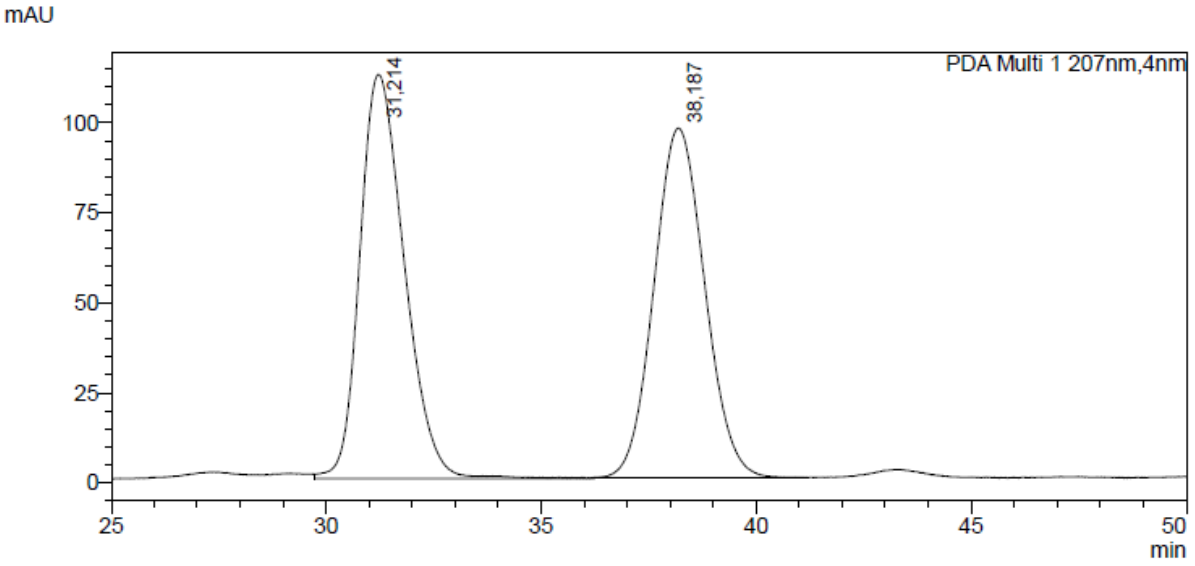


<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	31,624	884925	13047	8,999
2	38,284	8948920	104200	91,001
Total		9833845	117247	100,000

<Chromatogram>



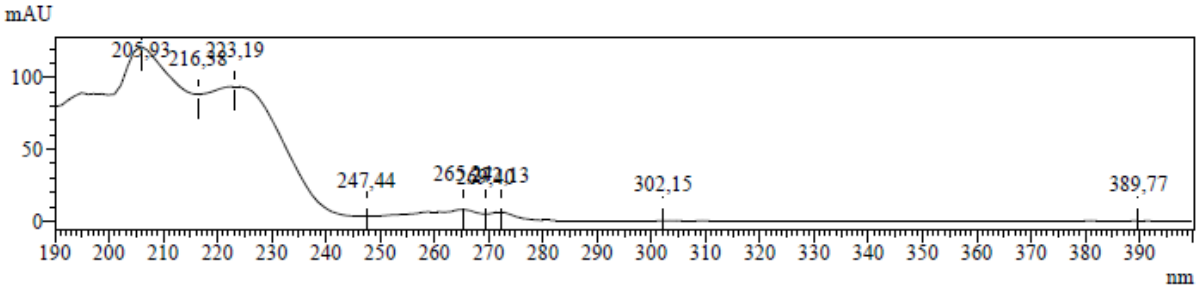
<Peak Table>

PDA Ch1 207nm

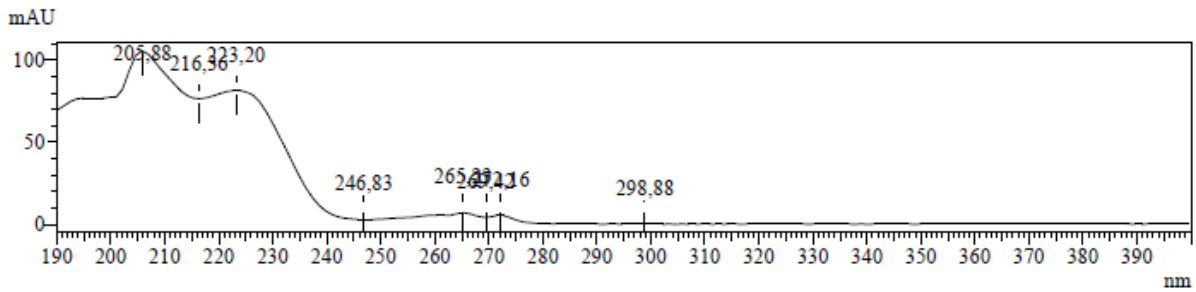
Peak#	Ret. Time	Area	Height	Area%
1	31,214	8067998	112164	50,305
2	38,187	7970298	97014	49,695
Total		16038296	209178	100,000

UV Spectrum

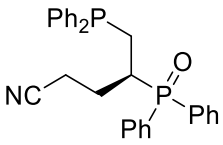
Peak# : 1
Retention Time : 31,214 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 38,187 min
Compound Name :
Spectrum Operation:



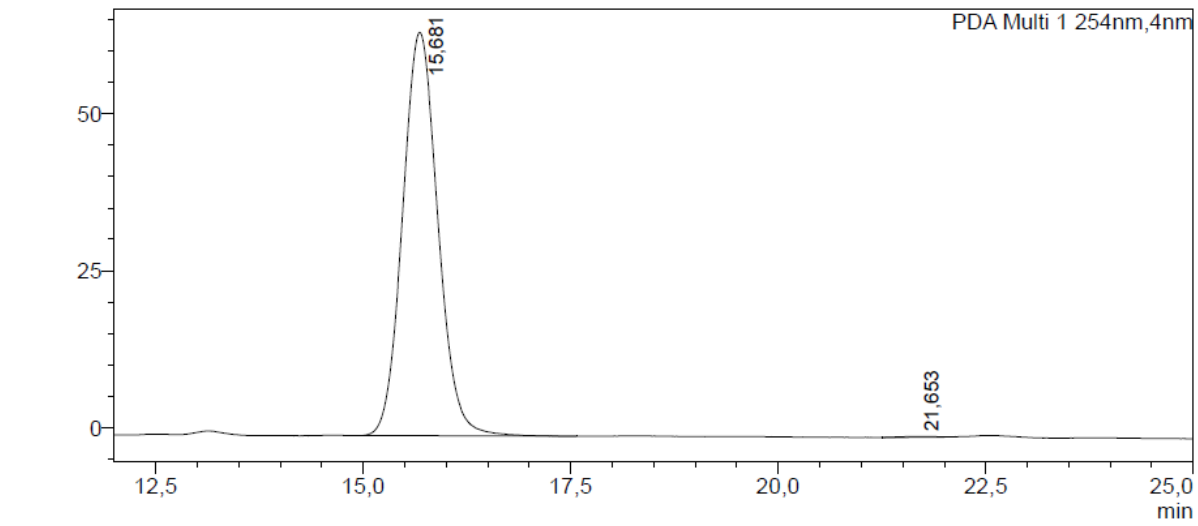
(S)-5-(diphenylphosphaneyl)-4-(diphenylphosphoryl)pentanenitrile (3ua)



Following general procedure A: The reaction was performed with **1u** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **3ua** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [93% yield, >99% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 – 7.59 (m, 2H, C*H*$_{Ar}$), 7.55 – 7.39 (m, 7H, C*H*$_{Ar}$), 7.41 – 7.22 (m, 11H, C*H*$_{Ar}$), 2.69 – 2.45 (m, 2H), 2.43 – 2.26 (m, 3H), 2.24 – 2.04 (m, 2H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 137.7, 137.6, 136.4, 136.2, 134.3, 134.1, 132.2, 132.1, 132.1, 131.9, 131.9, 131.9, 131.7, 131.4, 131.3, 130.9, 130.8, 130.7, 130.6, 130.4, 129.8, 129.1, 129.0, 128.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 119.3, 33.1, 33.0, 32.4, 32.3, 26.7, 26.6, 24.6, 24.5, 15.6, 15.6, 15.5. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 35.5 (d, *J* = 29.3 Hz), -19.9 (d, *J* = 29.3 Hz).
HRMS (ESI, m/Z): calcd. for $C_{29}H_{28}NOP_2$ $[M+H]^+$: 468.1641, found: 468.1640.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 207 nm. Retention time (min): 15.7 (major) and 21.7 (minor).

<Chromatogram>

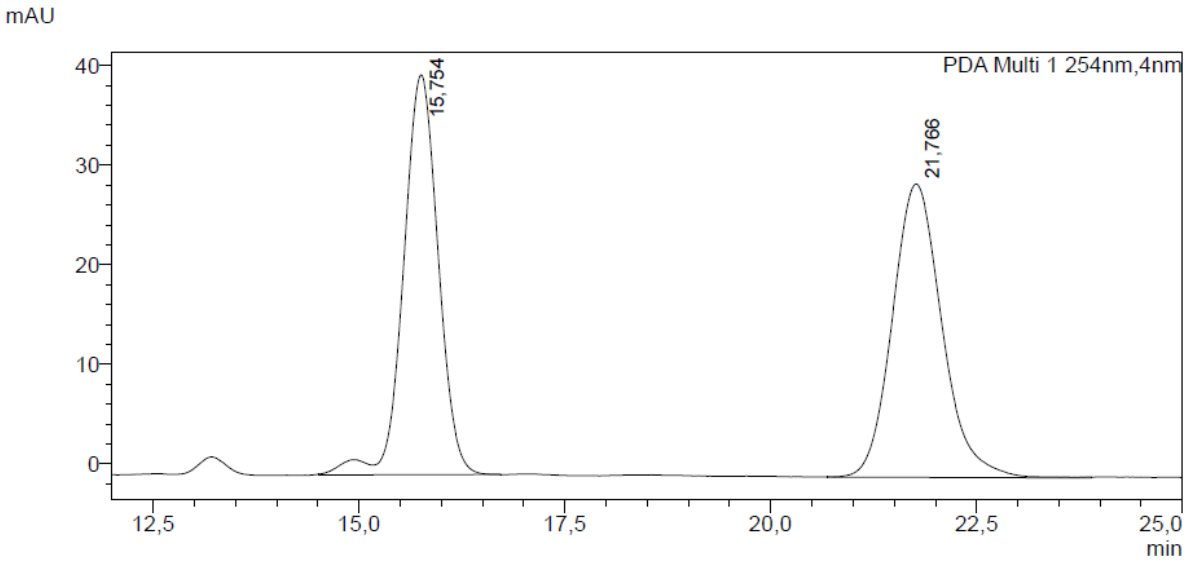


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15,681	1897116	64126	99,849
2	21,653	2861	114	0,151
Total		1899977	64239	100,000

<Chromatogram>



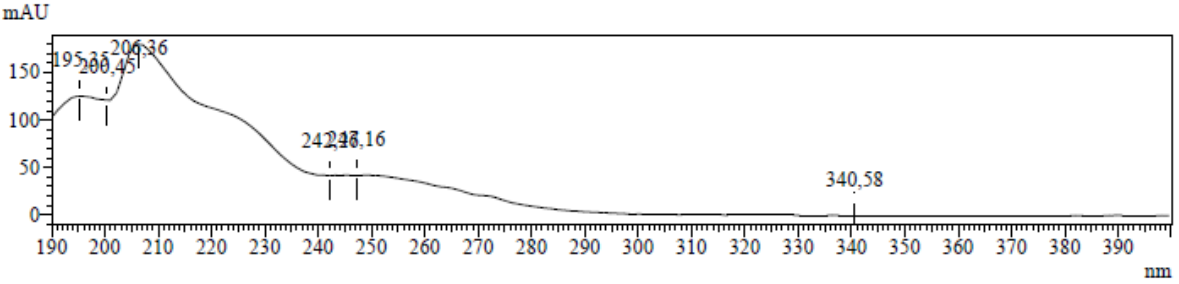
<Peak Table>

PDA Ch1 254nm

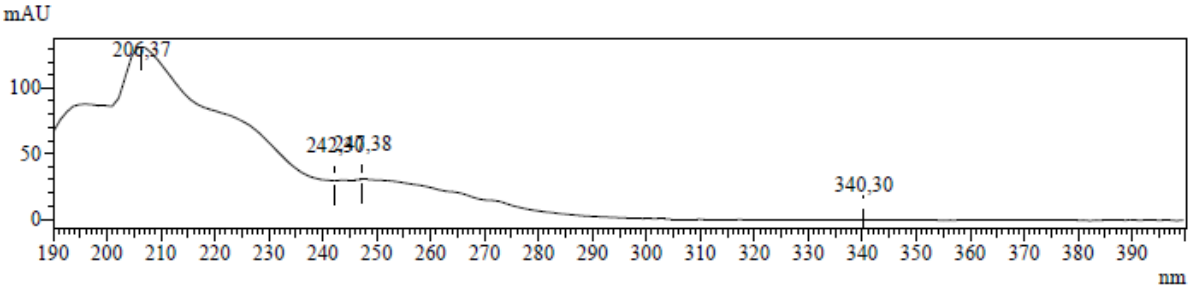
Peak#	Ret. Time	Area	Height	Area%
1	15,754	1188768	40188	49,028
2	21,766	1235917	29485	50,972
Total		2424684	69673	100,000

UV Spectrum

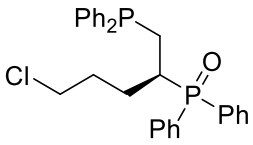
Peak# : 1
Retention Time : 15,753 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 21,764 min
Compound Name :
Spectrum Operation:



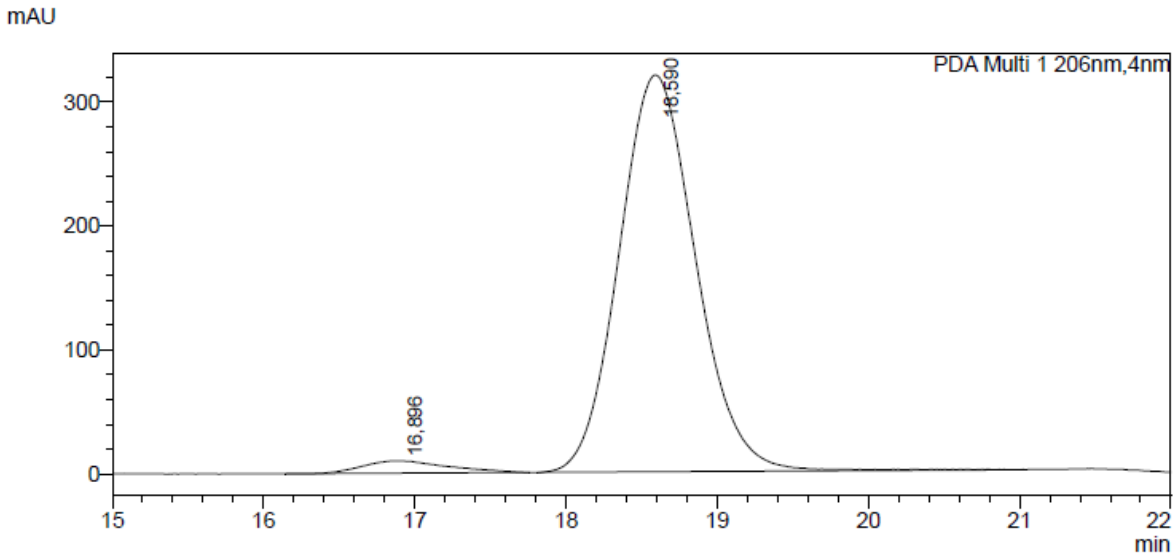
(S)-(5-chloro-1-(diphenylphosphaneyl)pentan-2-yl)diphenylphosphine oxide (3va)



Following general procedure A: The reaction was performed with **1v** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **3va** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [88% yield, 93% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 – 7.59 (m, 2H, C*H*$_{Ar}$), 7.56 – 7.21 (m, 18H, C*H*$_{Ar}$), 3.34 (t, *J* = 6.2 Hz, 2H,ClC*H*$_2$), 2.40 – 1.96 (m, 3H), 1.94 – 1.81 (m, 1H), 1.80 – 1.64 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.4, 138.3, 137.0, 136.8, 134.2, 134.0, 132.8, 132.2, 132.0, 131.8, 131.7, 131.7, 131.6, 131.6, 131.2, 131.0, 130.9, 130.9, 130.8, 129.5, 128.8, 128.7, 128.7, 128.6, 128.4, 128.4, 128.3, 44.9, 34.0, 33.9, 33.3, 33.2, 30.3, 30.3, 30.3, 26.8, 26.7, 25.8, 25.7, 25.7, 25.6. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 35.9 (d, *J* = 31.0 Hz), -19.2 (d, *J* = 31.0 Hz).
HRMS (ESI, m/Z): calcd. for $C_{29}H_{30}ClOP_2$ $[M+H]^+$: 491,1455, found: 491,1455.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 16.9 (minor) and 18.6 (major).

<Chromatogram>

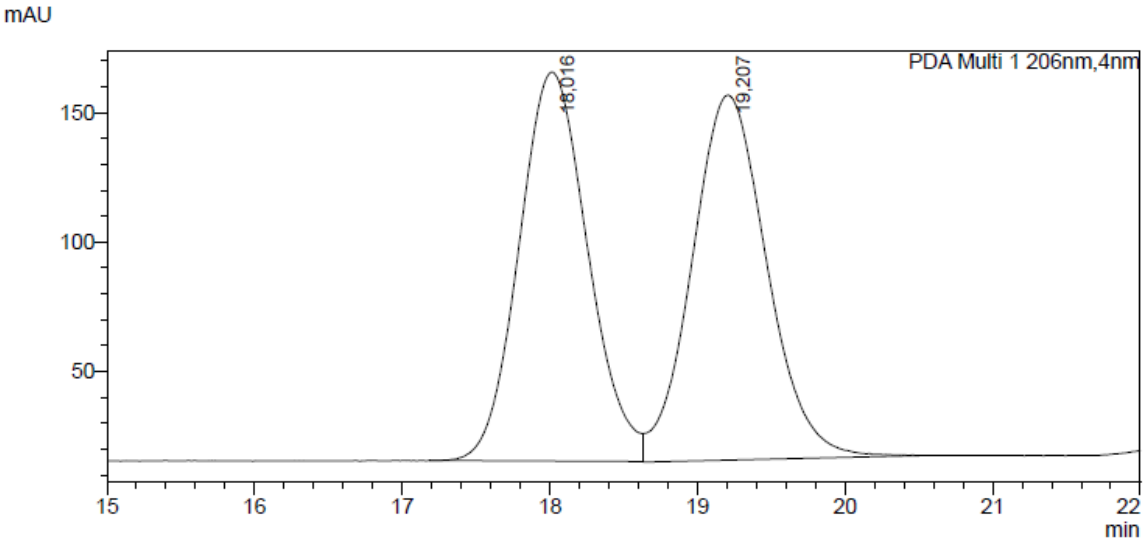


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	16,896	389883	9986	3,345
2	18,590	11265734	319743	96,655
Total		11655617	329729	100,000

<Chromatogram>



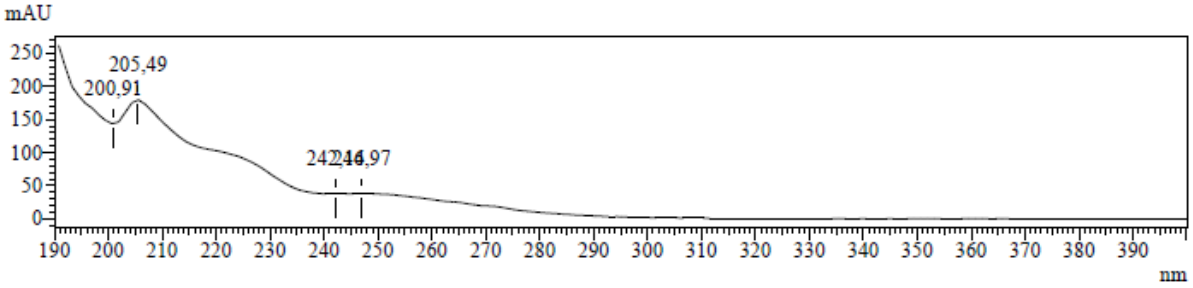
<Peak Table>

PDA Ch1 206nm

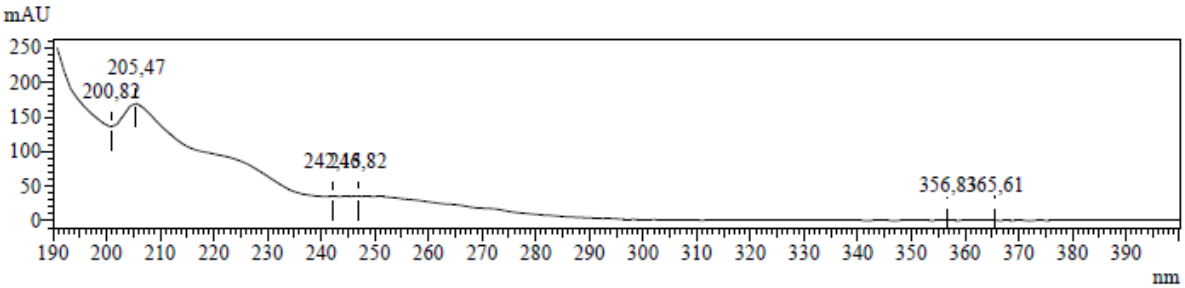
Peak#	Ret. Time	Area	Height	Area%
1	18,016	4865627	150228	49,463
2	19,207	4971235	140871	50,537
Total		9836862	291099	100,000

UV Spectrum

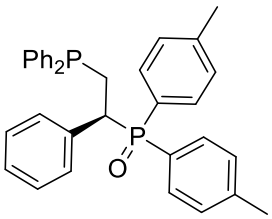
Peak# : 1
Retention Time : 18,016 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 19,207 min
Compound Name :
Spectrum Operation:



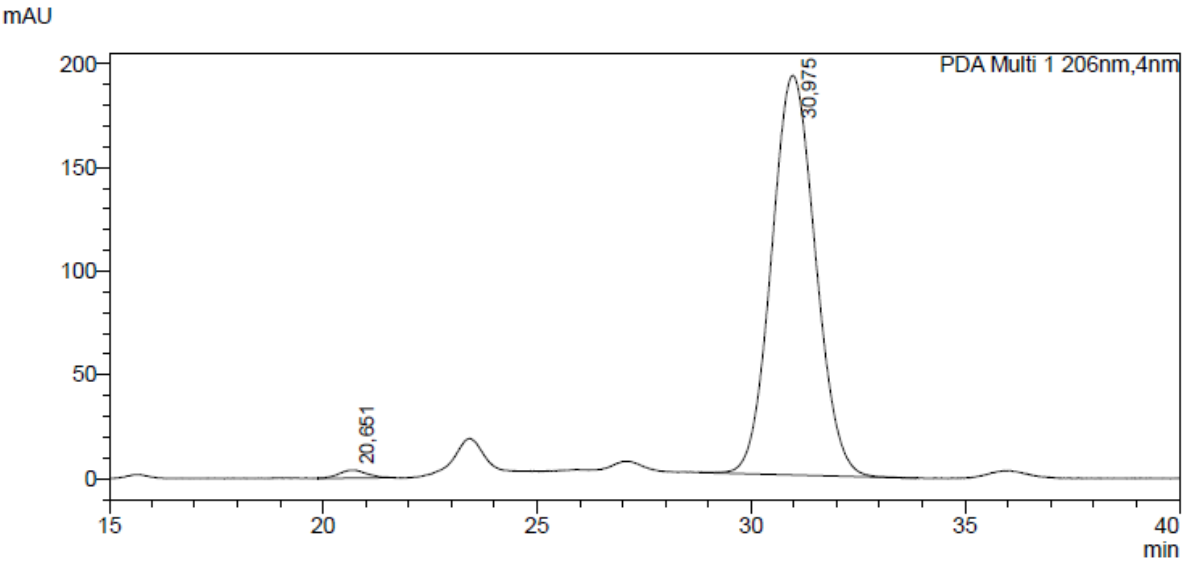
(S)-(2-(diphenylphosphaneyl)-1-phenylethyl)di-p-tolylphosphine oxide (3wa)



Following general procedure A: The reaction was performed with **1w** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **3wa** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [87% yield, 98% ee].

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.49 – 7.39 (m, 3H, C*H*$_{Ar}$), 7.38 – 7.25 (m, 4H, C*H*$_{Ar}$), 7.23 – 7.14 (m, 12H, C*H*$_{Ar}$), 7.12 – 7.02 (m, 2H, C*H*$_{Ar}$), 6.97 – 6.88 (m, 2H, C*H*$_{Ar}$), 3.28 – 3.12 (m, 1H, P(O)Ph$_2$C*H*), 2.93 – 2.72 (m, 1H, PPh$_2$CH*H*), 2.65 – 2.47 (m, 1H, PPh$_2$CH*H*), 2.40 (s, 3H, C*H*$_3$), 2.20 (s, 3H, C*H*$_3$).
^{13}C NMR (CDCl$_3$, 101 MHz): δ 142.2, 142.2, 141.6, 141.6, 139.1, 138.9, 137.4, 137.3, 135.8, 135.7, 135.7, 135.7, 134.6, 134.4, 131.9, 131.8, 131.5, 131.4, 131.1, 131.0, 130.2, 130.1, 129.6, 129.5, 128.8, 128.8, 128.7, 128.7, 128.4, 128.4, 128.3, 128.2, 128.0, 127.8, 127.4, 127.3, 44.0, 43.8, 43.3, 43.2, 29.2, 29.1, 29.0, 29.0, 21.8, 21.7, 21.6, 21.5. (Due to C–P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (CDCl$_3$, 162 MHz): δ 30.8 (d, *J* = 31.1 Hz), -22.6 (d, *J* = 31.1 Hz).
HRMS (ESI, m/Z): calcd. for $C_{34}H_{33}OP_2$ $[M+H]^+$: 519.2001, found: 519.2003.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 20.7 (minor) and 31.0 (major).

<Chromatogram>



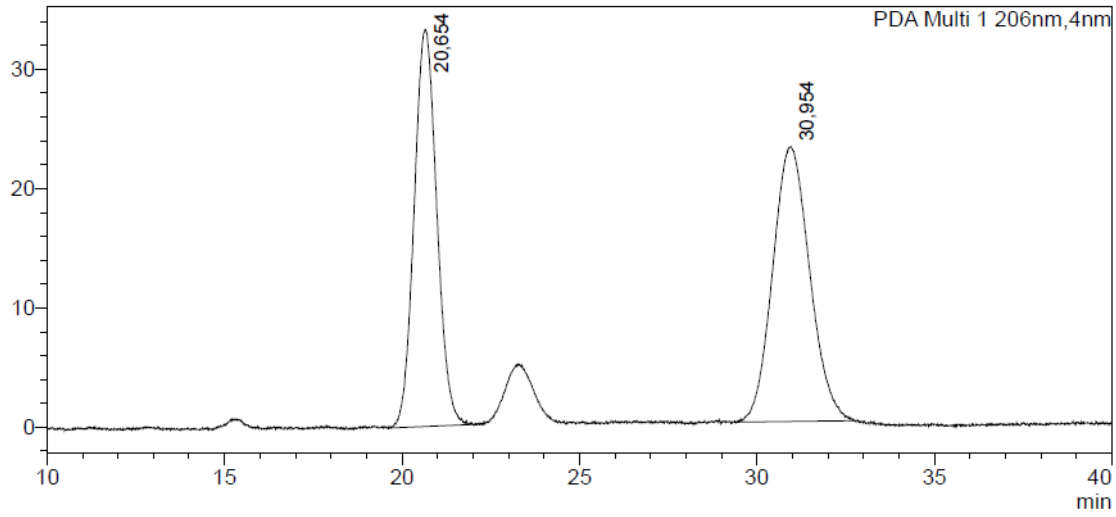
<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	20,651	171546	3840	1,231
2	30,975	13759361	192617	98,769
Total		13930906	196457	100,000

<Chromatogram>

mAU



<Peak Table>

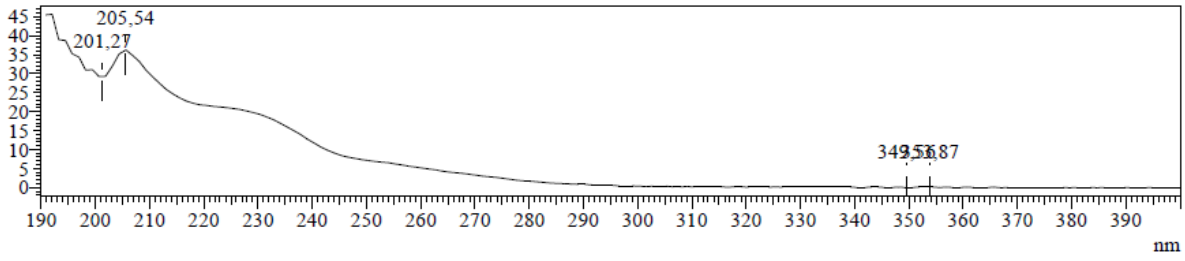
PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	20,654	1477393	33290	46,909
2	30,954	1672081	23072	53,091
Total		3149474	56362	100,000

UV Spectrum

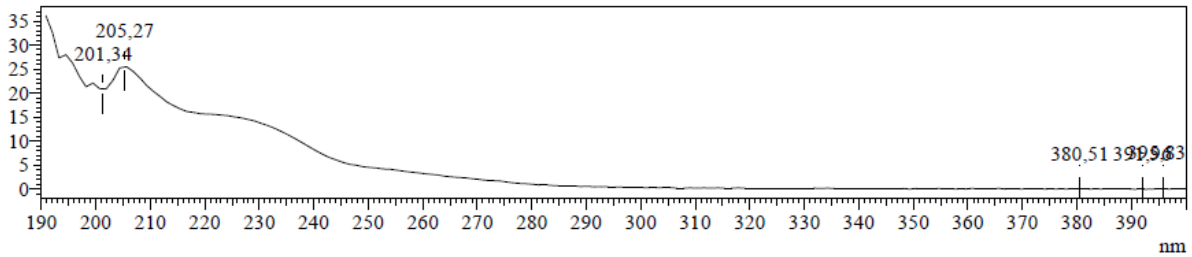
Peak# : 1
Retention Time : 20,654 min
Compound Name :
Spectrum Operation:

mAU

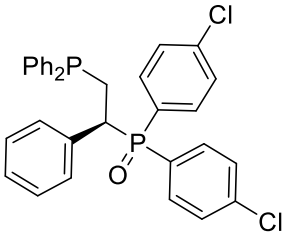


Peak# : 2
Retention Time : 30,954 min
Compound Name :
Spectrum Operation:

mAU



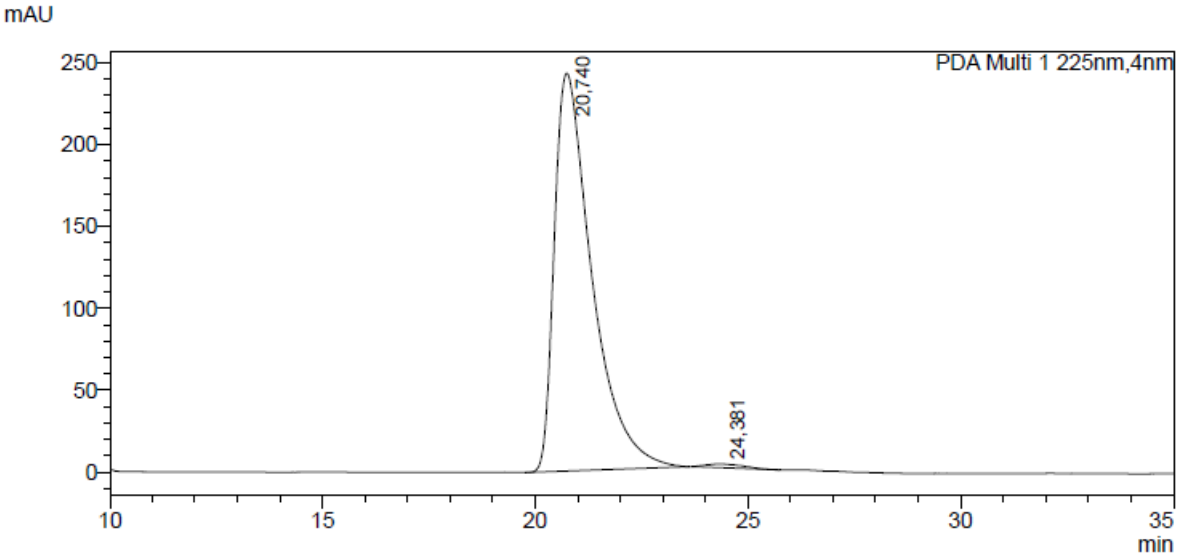
(S)-bis(4-chlorophenyl)(2-(diphenylphosphaneyl)-1-phenylethyl)phosphine oxide (3xa)



Following general procedure A: The reaction was performed with **1x** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **3xa** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [90% yield, 98% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 – 7.28 (m, 8H, C*H*$_{Ar}$), 7.27 – 7.07 (m, 15H, C*H*$_{Ar}$), 3.29 – 3.08 (m, 1H, P(O)Ph$_2$C*H*), 2.96 – 2.71 (m, 1H, PPh$_2$CH*H*), 2.59 – 2.37 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.6, 138.6, 138.3, 138.1, 138.0, 138.0, 137.3, 137.1, 134.8, 134.8, 134.7, 134.7, 134.4, 134.2, 132.6, 132.6, 132.2, 132.1, 131.8, 131.6, 130.7, 129.9, 129.9, 129.8, 129.7, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 43.7, 43.6, 43.1, 42.9, 29.1, 28.9. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 32.5 (d, *J* = 32.0 Hz), -19.9 (d, *J* = 32.0 Hz).
HRMS (ESI, m/Z): calcd. for $C_{32}H_{27}Cl_2OP_2$ $[M+H]^+$: 559.0909, found: 559.0910.
HPLC: Chiracel-ODH, *n*-heptane/*i*-PrOH 95:05, 0.5 mL/min., 40 °C, detection at 225 nm. Retention time (min): 20.7 (major) and 24.4 (minor). (*Due to the poor separation of the product **3xa** in the HPLC, the ee of this compound was determined from the corresponding oxidized derivative.)*

<Chromatogram>

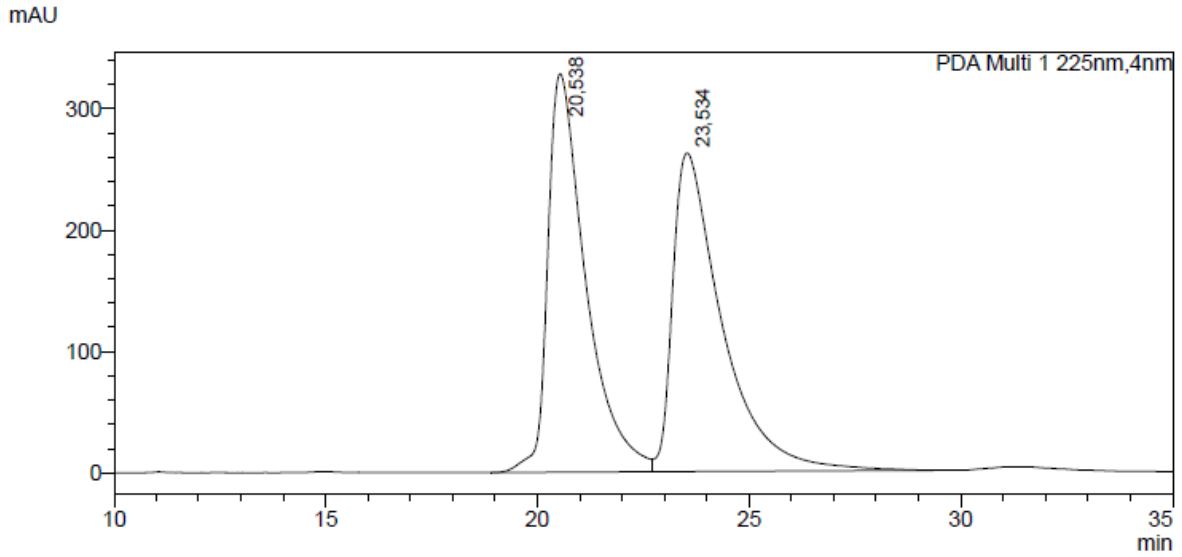


<Peak Table>

PDA Ch1 225nm

Peak#	Ret. Time	Area	Height	Area%
1	20,740	14942894	242870	99,071
2	24,381	140070	2279	0,929
Total		15082965	245149	100,000

<Chromatogram>



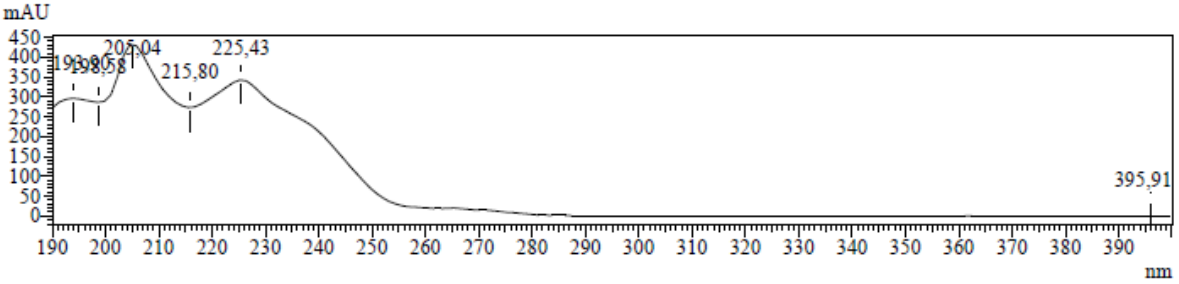
<Peak Table>

PDA Ch1 225nm

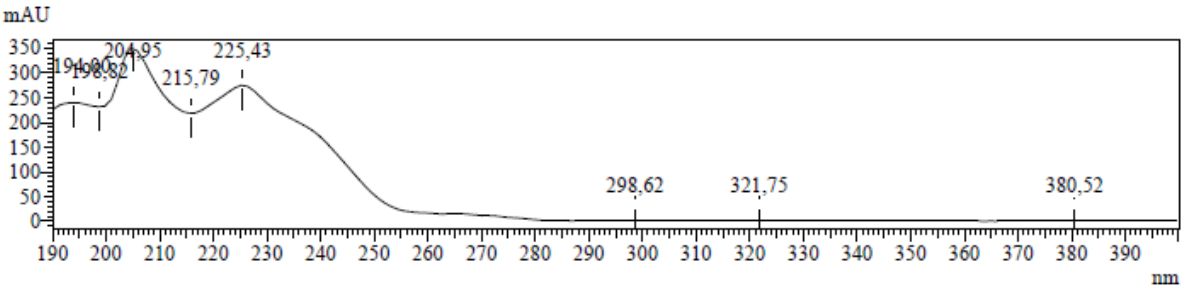
Peak#	Ret. Time	Area	Height	Area%
1	20,538	20500925	328160	49,037
2	23,534	21305933	262482	50,963
Total		41806858	590642	100,000

UV Spectrum

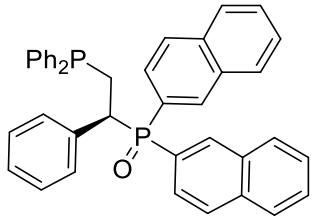
Peak# : 1
Retention Time : 20,538 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 23,534 min
Compound Name :
Spectrum Operation:



(S)-(2-(diphenylphosphaneyl)-1-phenylethyl)di(naphthalen-2-yl)phosphine oxide (3ya)

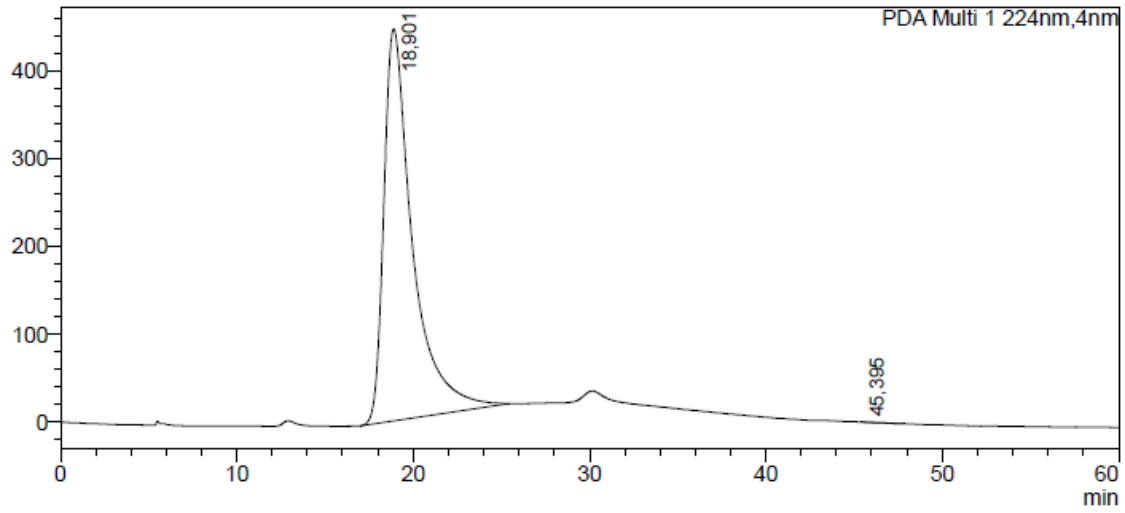


Following general procedure A: The reaction was performed with **1y** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **3ya** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [95% yield, >99% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41 (d, *J* = 12.5 Hz, 1H, C*H*$_{Ar}$), 7.94 – 7.84 (m, 4H, C*H*$_{Ar}$), 7.71 – 7.50 (m, 6H, C*H*$_{Ar}$), 7.48 – 7.36 (m, 3H, C*H*$_{Ar}$), 7.35 – 7.21 (m, 7H, C*H*$_{Ar}$), 7.20 – 7.10 (m, 8H, C*H*$_{Ar}$), 3.59 – 3.40 (m, 1H, P(O)Ph$_2$C*H*), 3.05 – 2.85 (m, 1H, PPh$_2$CH*H*), 2.75 – 2.58 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR (**$CDCl_3$, 101 MHz):** δ 138.9, 138.7, 137.3, 137.1, 135.5, 135.5, 135.4, 135.4, 134.8, 134.8, 134.3, 134.3, 133.8, 133.8, 133.3, 133.2, 132.8, 132.7, 132.3, 132.2, 131.9, 131.7, 130.2, 130.2, 129.9, 129.9, 129.7, 129.1, 129.1, 128.9, 128.9, 128.8, 128.7, 128.6, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.1, 126.6, 126.1, 126.0, 125.9, 125.8, 43.9, 43.7, 43.2, 43.1, 29.2, 29.1. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz) δ 30.8 (d, *J* = 31.0 Hz), -22.8 (d, *J* = 31.0 Hz).
HRMS (ESI, m/Z): calcd. for $C_{40}H_{33}OP_2$ $[M+H]^+$: 590.2001, found: 590.2008.
HPLC: Chiracel-OZH, *n*-heptane/*i*-PrOH 80:20, 0.5 mL/min., 40 °C, detection at 224 nm. Retention time (min): 18.9 (major) and 45.4 (minor). (*Due to the poor separation of the product **3ya** in the HPLC, the ee of this compound was determined from the corresponding oxidized derivative.)*

<Chromatogram>

mAU



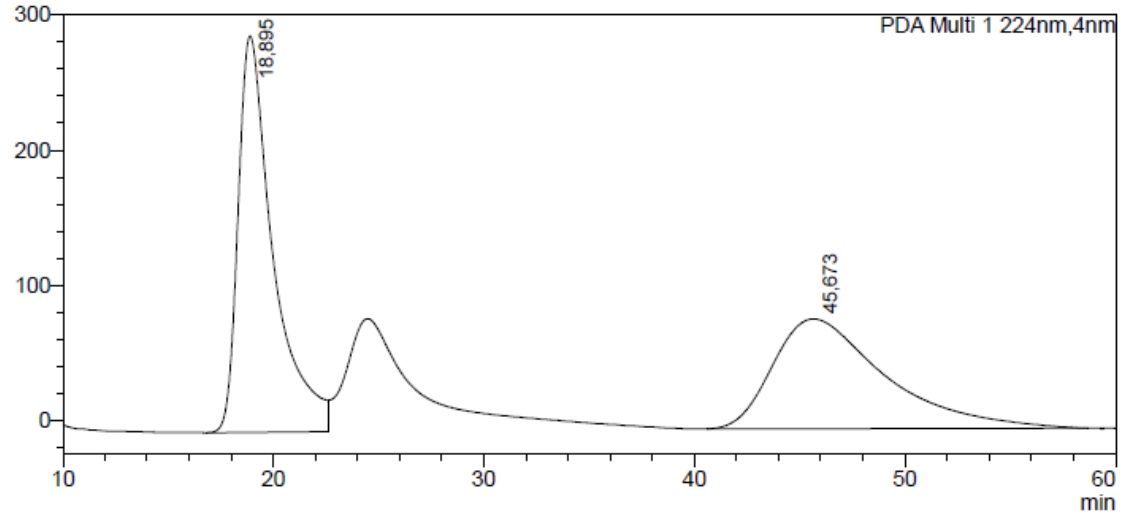
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Area%
1	18,901	50624455	446250	99,976
2	45,395	12373	131	0,024
Total		50636828	446381	100,000

<Chromatogram>

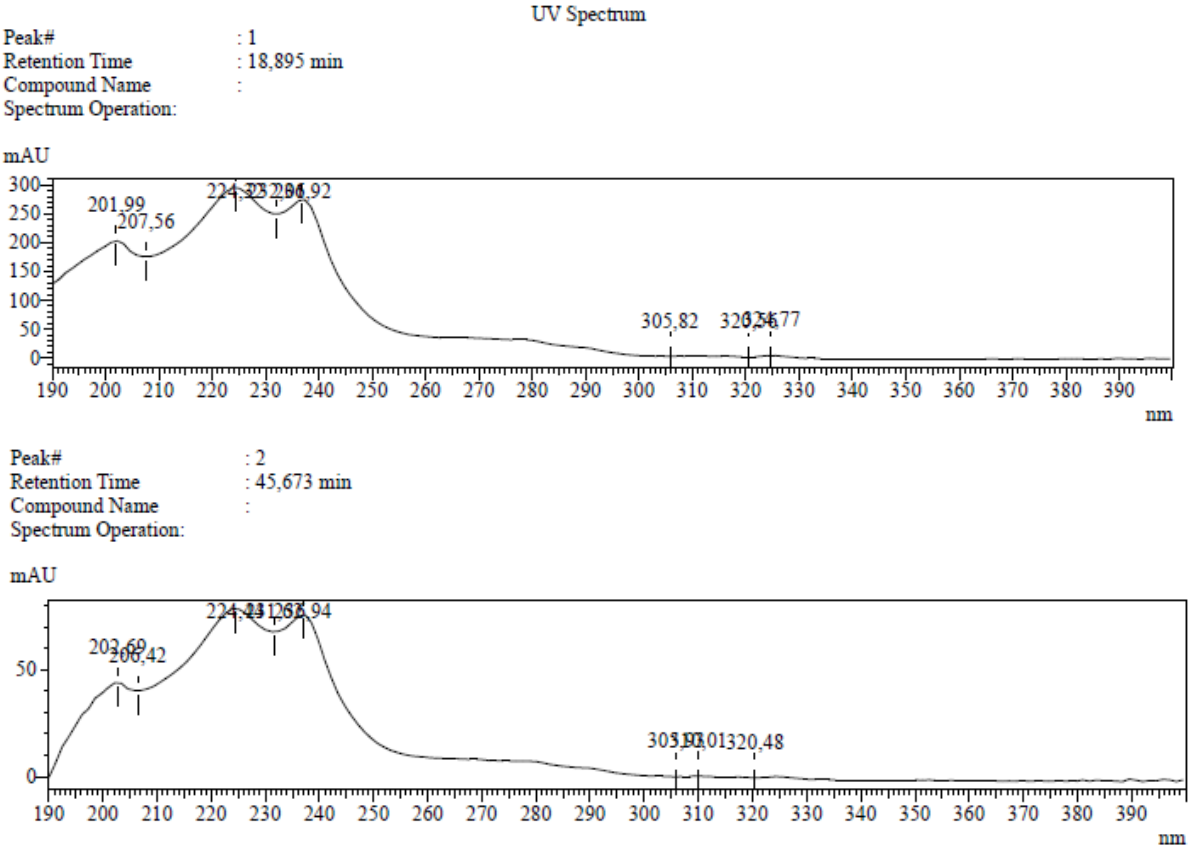
mAU



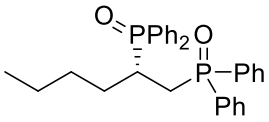
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Area%
1	18,895	33829336	292757	52,941
2	45,673	30070236	81148	47,059
Total		63899572	373905	100,000



(S)-hexane-1,2-diylbis(diphenylphosphine oxide) (3za)

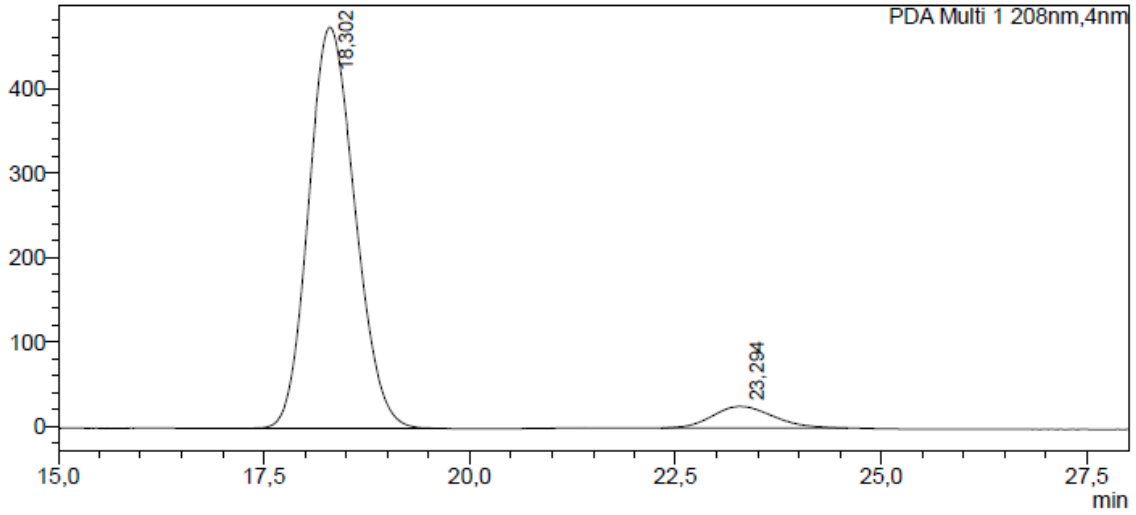


Following general procedure A: The reaction was performed with **1z** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.010 mmol, 10 mol%), **2a** (0.1 mmol, 1 equiv.), toluene (1.0 mL) at 60°C for 72 h. Then, the reaction mixture was quenched by 30% H_2O_2 aqueous solution (25 μL) and was stirred for additional 30 minutes at room temperature. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) to give product **3za** as a white solid [82% yield, 87% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 – 7.65 (m, 6H, C*H*$_{Ar}$), 7.54 – 7.30 (m, 14H, C*H*$_{Ar}$), 3.07 – 2.89 (m, 1H, P(O)Ph$_2$C*H*), 2.71 – 2.44 (m, 2H, P(O)Ph$_2$C*H*$_2$), 1.84 – 1.60 (m, 1H), 1.53 – 1.36 (m, 1H), 1.31 – 1.19 (m, 1H), 0.97 – 0.73 (m, 3H), 0.50 (t, *J* = 7.2 Hz, 3H, C*H*$_3$).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 134.0, 133.9, 133.0, 132.9, 132.7, 132.5, 131.9, 131.9, 131.8, 131.8, 131.7, 131.6, 131.3, 131.2, 131.1, 131.0, 130.9, 130.8, 130.8, 130.7, 31.7, 31.7, 31.0, 31.0, 29.2, 29.2, 28.1, 27.9, 27.2, 22.7, 13.5. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 37.0 (d, *J* = 47.4 Hz), 30.0 (d, *J* = 47.4 Hz).
HRMS (ESI, m/Z): calcd. for $C_{30}H_{32}O_2P_2Na$ $[M+Na]^+$: 509.1770, found: 509.1768.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 208 nm. Retention time (min): 18.3 (major) and 23.3 (minor).

<Chromatogram>

mAU



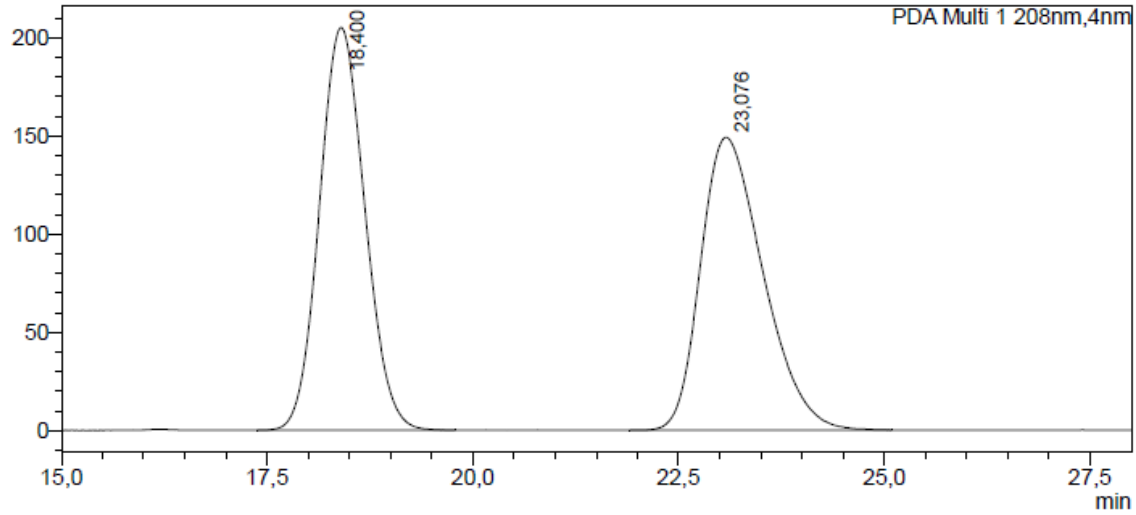
<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	18,302	18627278	474484	93,503
2	23,294	1294244	25449	6,497
Total		19921522	499932	100,000

<Chromatogram>

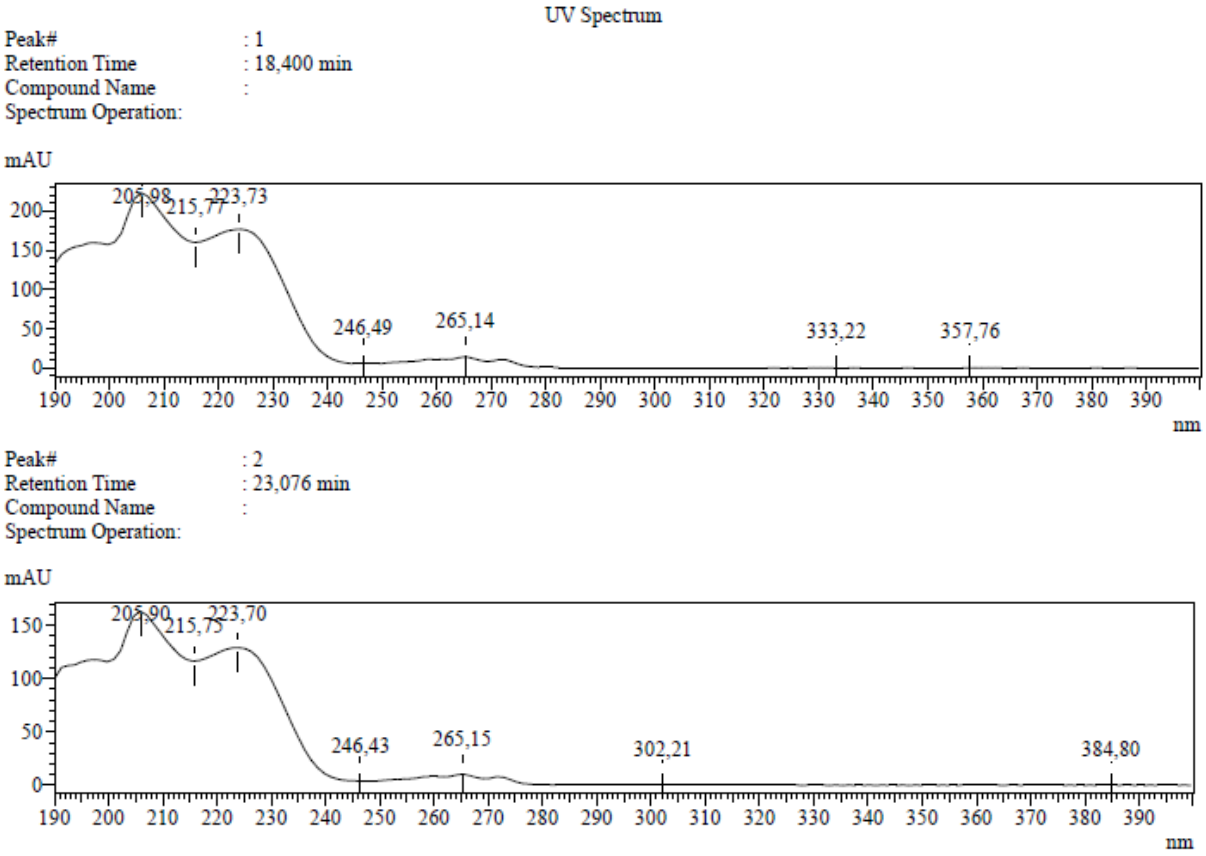
mAU



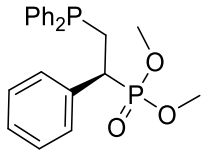
<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	18,400	7875796	204969	49,988
2	23,076	7879642	149129	50,012
Total		15755438	354098	100,000



dimethyl (S)-(2-(diphenylphosphaneyl)-1-phenylethyl)phosphonate (4a'a)

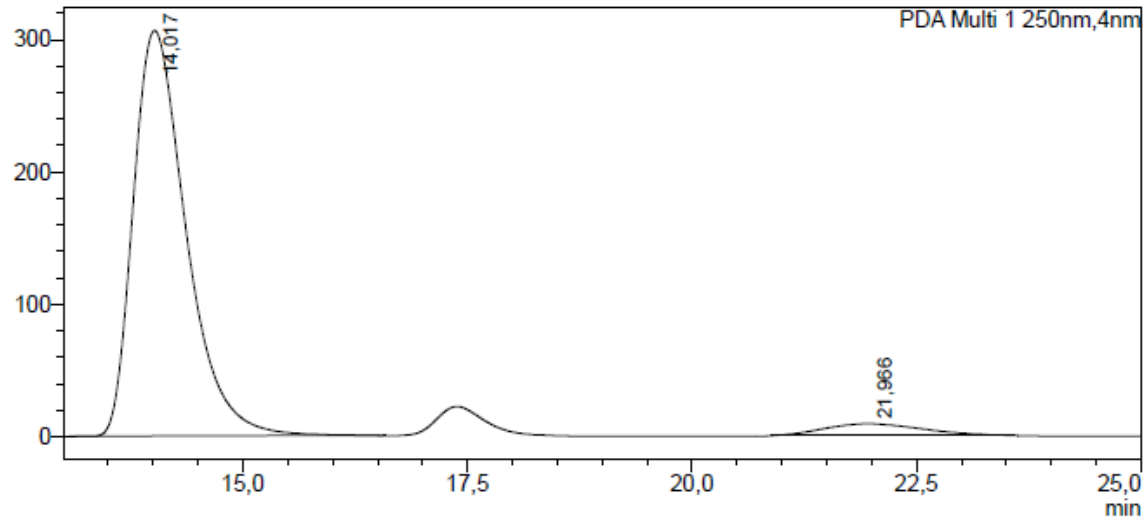


Following general procedure A: The reaction was performed with **1a'** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 24 h. Product **4a'a** was obtained as colorless oil after column chromatography (SiO_2, pentane/ethyl acetate = 1:1) [88% yield, 90% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 – 7.45 (m, 2H, C*H*$_{Ar}$), 7.43 – 7.37 (m, 3H, C*H*$_{Ar}$), 7.36 – 7.23 (m, 10H, C*H*$_{Ar}$), 3.68 (d, *J* = 10.6 Hz, 3H, OC*H*$_3$), 3.42 (d, *J* = 10.6 Hz, 3H, OC*H*$_3$), 3.08 – 2.96 (m, 1H, P(O)(OCH$_3$)$_2$C*H*), 2.93 – 2.83 (m, 1H, PPh$_2$CH*H*), 2.76 – 2.65 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR (CDCl$_3$, 101 MHz): δ 138.8, 138.7, 136.97, 136.9, 135.2, 135.2, 135.2, 135.2, 133.7, 133.6, 132.2, 132.1, 129.5, 129.5, 129.3, 128.7, 128.7, 128.6, 128.6, 128.3, 128.3, 127.6, 127.6, 53.6, 53.6, 52.7, 52.7, 41.5, 41.4, 40.6, 40.4, 29.2, 29.2, 29.1, 29.1. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (CDCl$_3$, 162 MHz): δ 30.4 (d, *J* = 43.3 Hz), -20.9 (d, *J* = 43.3 Hz).
HRMS (ESI, m/Z): calcd. for $C_{22}H_{25}O_3P_2$ $[M+H]^+$: 399.1273, found: 399.1280.
HPLC: Chiracel-OJH, *n*-heptane/*i*-PrOH 90:10, 0.5 mL/min., 40 °C, detection at 221 nm. Retention time (min): 14.0 (major) and 22.0 (minor).

<Chromatogram>

mAU



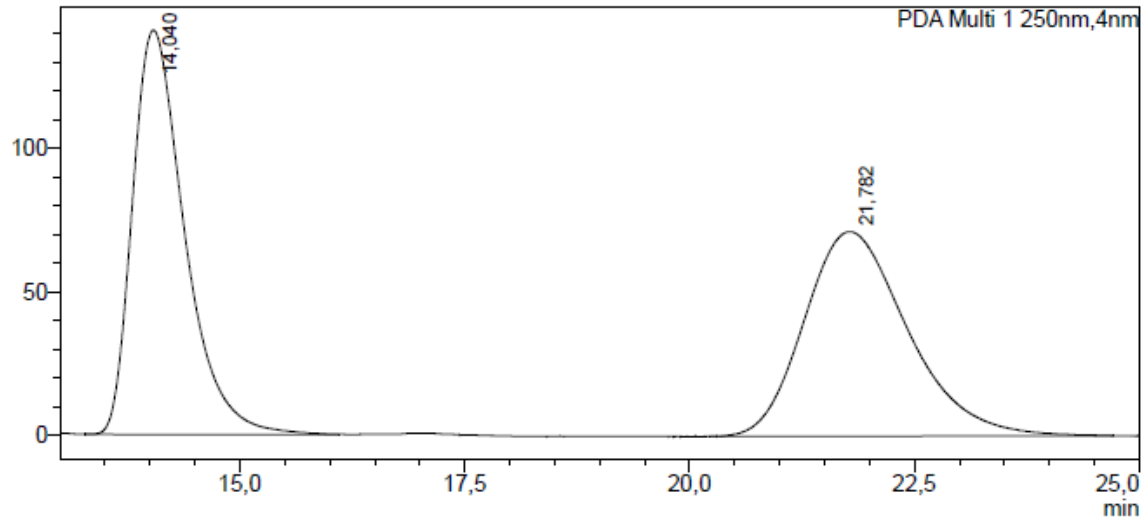
<Peak Table>

PDA Ch1 250nm

Peak#	Ret. Time	Area	Height	Area%
1	14,017	12494368	306203	95,783
2	21,966	550104	8066	4,217
Total		13044472	314270	100,000

<Chromatogram>

mAU

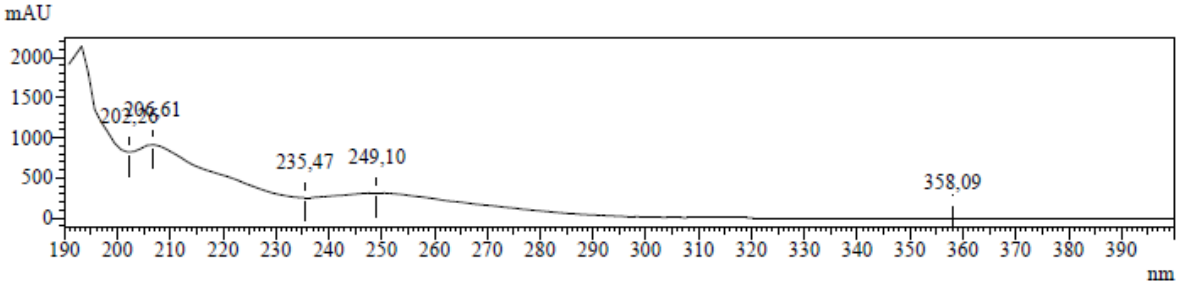


<Peak Table>

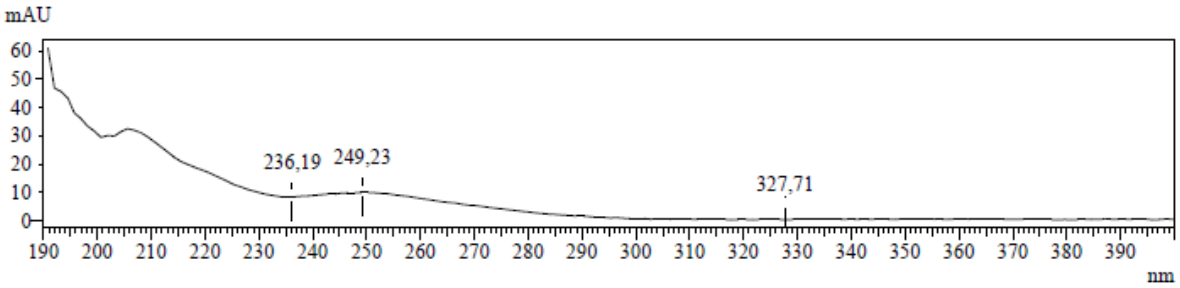
PDA Ch1 250nm

Ret. Time	Area	Height	Area%
14,040	5681470	140933	49,892
21,782	5706021	71312	50,108
	11387491	212245	100,000

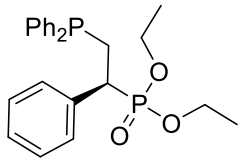
Peak# : 1
Retention Time : 14,031 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 21,954 min
Compound Name :
Spectrum Operation:

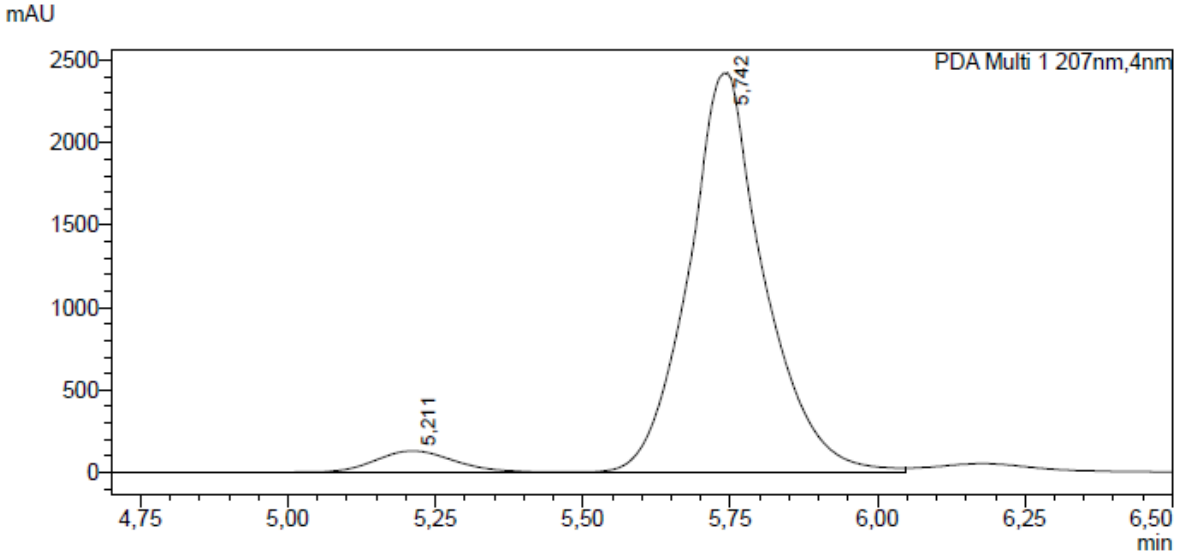


diethyl (S)-(2-(diphenylphosphaneyl)-1-phenylethyl)phosphonate (4b'a)



Following general procedure A: The reaction was performed with **1 b'** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 24 h. Product **4b'a** was obtained as colorless oil after column chromatography (SiO_2, pentane/ethyl acetate = 1:1) [75% yield, 89% ee].
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 – 7.45 (m, 2H, C*H*$_{Ar}$), 7.43 – 7.36 (m, 3H, C*H*$_{Ar}$), 7.35 – 7.22 (m, 10H, C*H*$_{Ar}$), 4.11 – 4.03 (m, 1H, CH_3CHCH), 4.03 – 3.95 (m, 1H, CH_3CHCH), 3.91 – 3.82 (m, 1H, CH_3CHCH), 3.68 – 3.57 (m, 1H, CH_3CHCH), 3.03 – 2.94 (m, 1H, $P(O)(OCH_2CH_3)_2CH$), 2.94 – 2.87 (m, 1H, PPh_2CHH), 2.74 – 2.62 (m, 1H, PPh_2CHH), 1.29 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.05 (t, *J* = 7.1 Hz, 3H, CH_2CH_3).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.0, 138.9, 137.1, 137.0, 135.5, 135.5, 135.5, 135.5, 133.8, 133.6, 132.2, 132.0, 129.6, 129.5, 129.3, 128.7, 128.6, 128.5, 128.5, 128.3, 128.3, 128.2, 127.5, 127.5, 62.8, 62.8, 61.9, 61.9, 41.9, 41.8, 41.0, 40.9, 29.3, 29.3, 29.2, 29.2, 16.4, 16.4, 16.2, 16.2. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 28.0 (d, *J* = 43.9 Hz), -20.8 (d, *J* = 43.9 Hz).
HRMS (ESI, m/Z): calcd. for $C_{24}H_{29}O_3P_2$ $[M+H]^+$: 427.1586, found: 427.1594.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 207 nm. Retention time (min): 5.2 (minor) and 5.7 (major).

<Chromatogram>

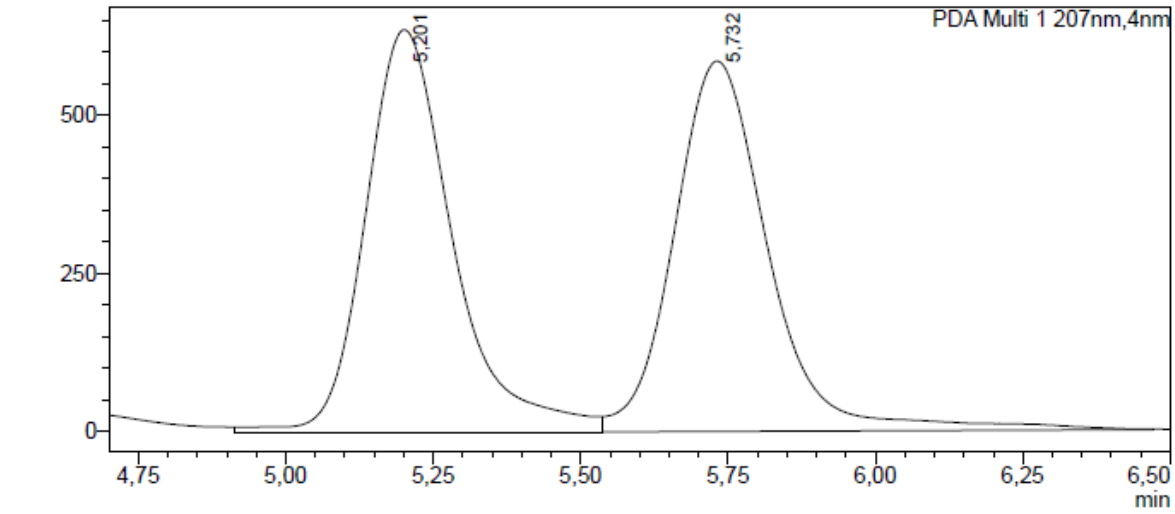


<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	5,211	1296062	132007	5,629
2	5,742	21729204	2420890	94,371
Total		23025265	2552897	100,000

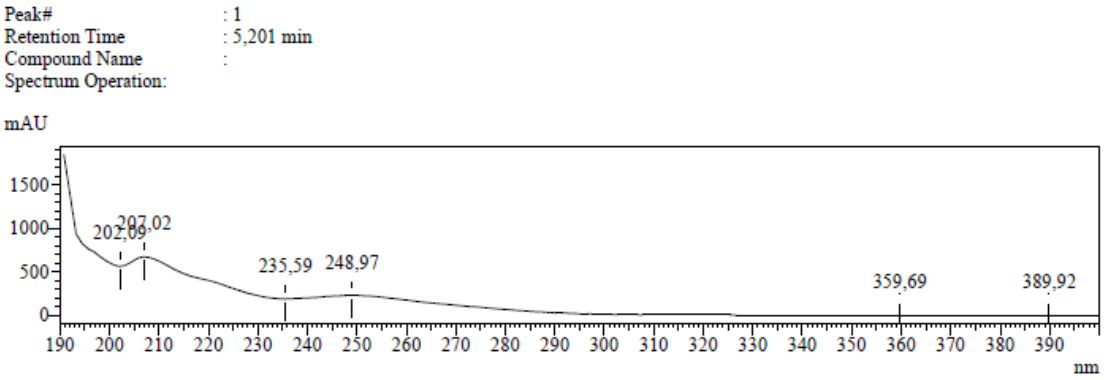
<Chromatogram>

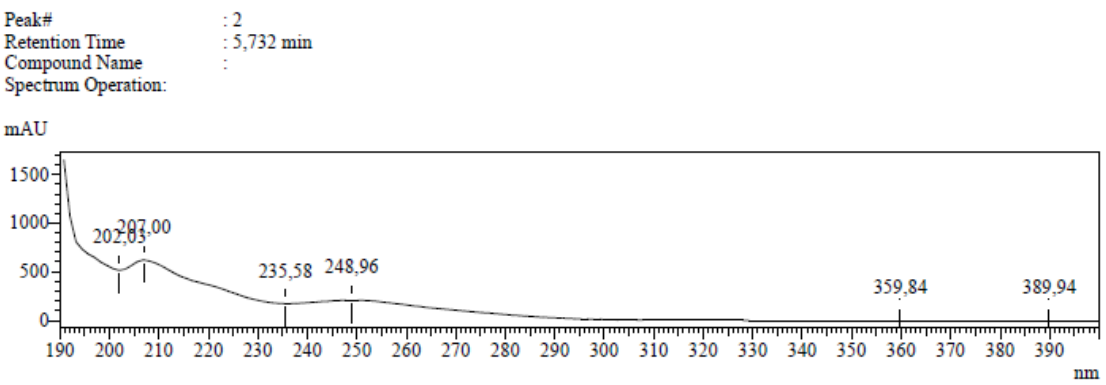


<Peak Table>

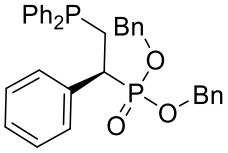
PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	5,201	6556204	634994	50,008
2	5,732	6554120	585460	49,992
Total		13110325	1220453	100,000



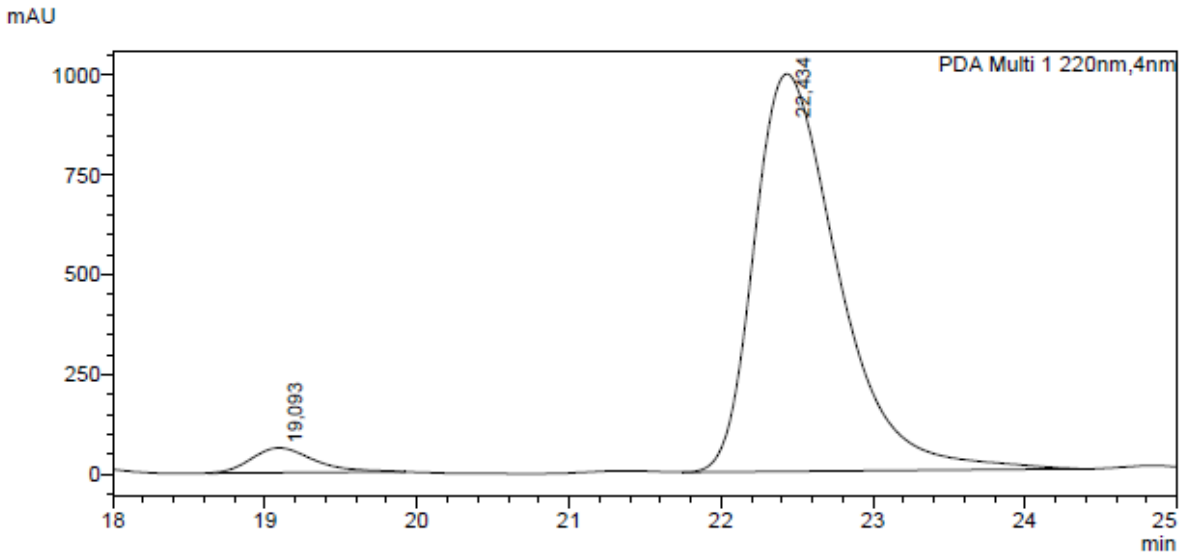


dibenzyl (S)-(2-(diphenylphosphaneyl)-1-phenylethyl)phosphonate (4c'a)



Following general procedure A: The reaction was performed with **1 c'** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 24 h. Product **4c'a** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate = 2:1) [78% yield, 91% ee].
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 – 7.11 (m, 23H, C*H*$_{Ar}$), 7.10 – 6.96 (m, 2H, C*H*$_{Ar}$), 5.01 (dd, *J* = 11.8, 9.0 Hz, 1H, PhCHC*H*), 4.87 (dd, *J* = 11.8, 7.6 Hz, 1H, PhCHC*H*), 4.75 (dd, *J* = 11.8, 6.8 Hz, 1H, PhCHC*H*), 4.48 (dd, *J* = 11.8, 8.0 Hz, 1H, PhCHC*H*), 3.10 – 2.95 (m, 1H, P(O)(OBn)$_2$C*H*), 2.90 – 2.80 (m, 1H, PPh$_2$CH*H*), 2.69 – 2.56 (m, 1H, PPh$_2$CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.3, 139.3, 139.2, 139.2, 137.3, 137.1, 136.9, 136.8, 136.8, 136.7, 135.7, 135.7, 135.6, 135.6, 134.2, 134.0, 132.6, 132.4, 130.1, 130.0, 129.7, 129.1, 129.0, 129.0, 129.0, 128.8, 128.8, 128.7, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 68.7, 68.6, 67.9, 67.8, 42.8, 42.6, 41.4, 41.2, 29.6, 29.5, 29.4, 29.4. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.9 (d, *J* = 44.6 Hz), -24.2 (d, *J* = 44.6 Hz).
HRMS (ESI, m/Z): calcd. for $C_{34}H_{33}O_3P_2$ $[M+H]^+$: 551.1899, found: 551.1898.
HPLC: Chiracel-ODH, *n*-heptane/*i*-PrOH 90:10, 0.5 mL/min., 40 °C, detection at 250 nm. Retention time (min): 19.1 (minor) and 22.4 (major).

<Chromatogram>

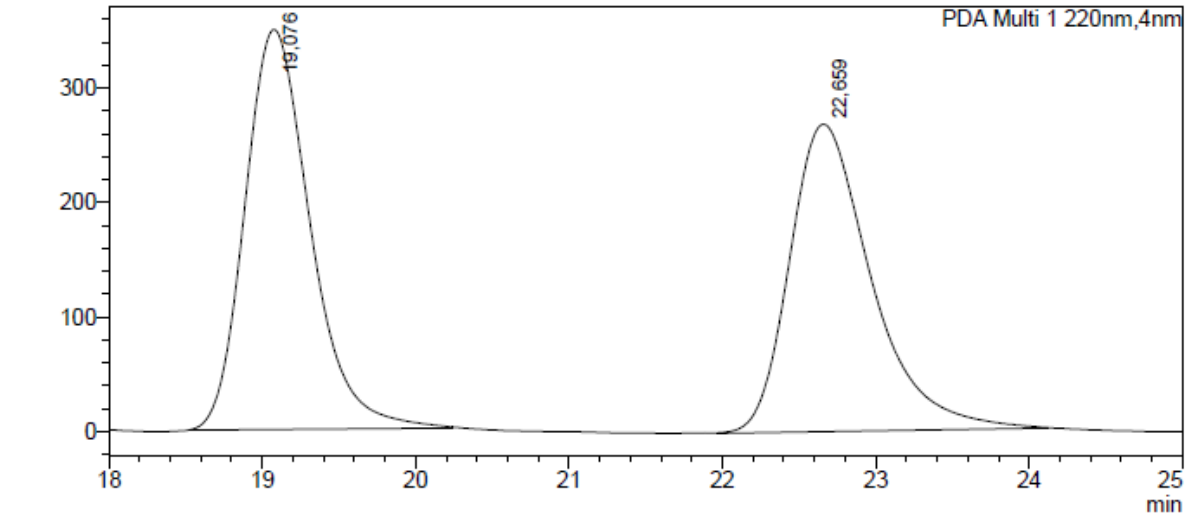


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	19,093	1795013	62148	4,465
2	22,434	38403152	996123	95,535
Total		40198165	1058271	100,000

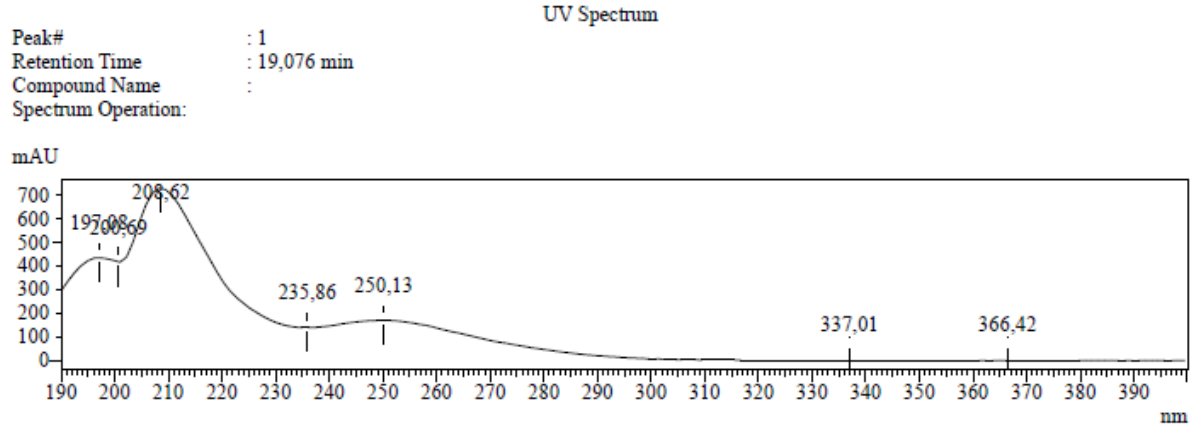
<Chromatogram>

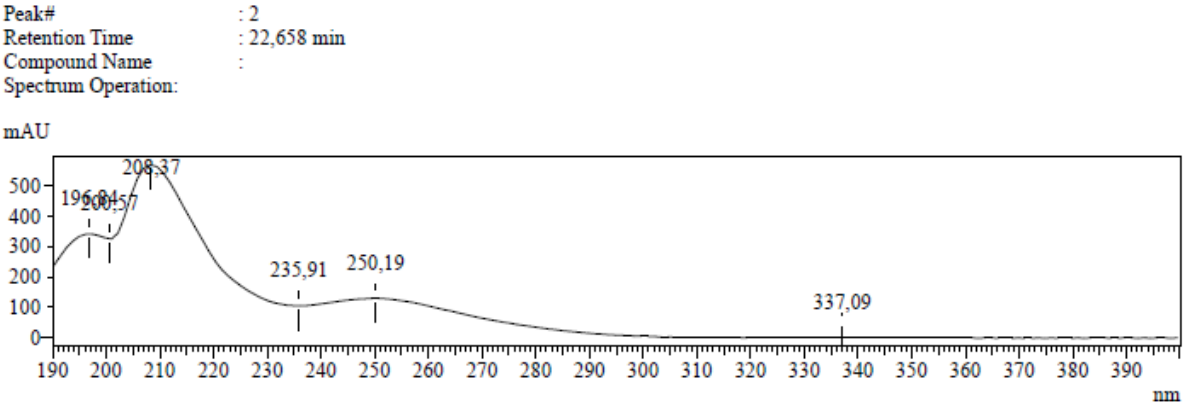


<Peak Table>

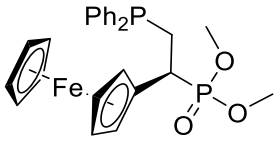
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	19,076	10350974	349197	50,973
2	22,659	9955942	268544	49,027
Total		20306915	617740	100,000



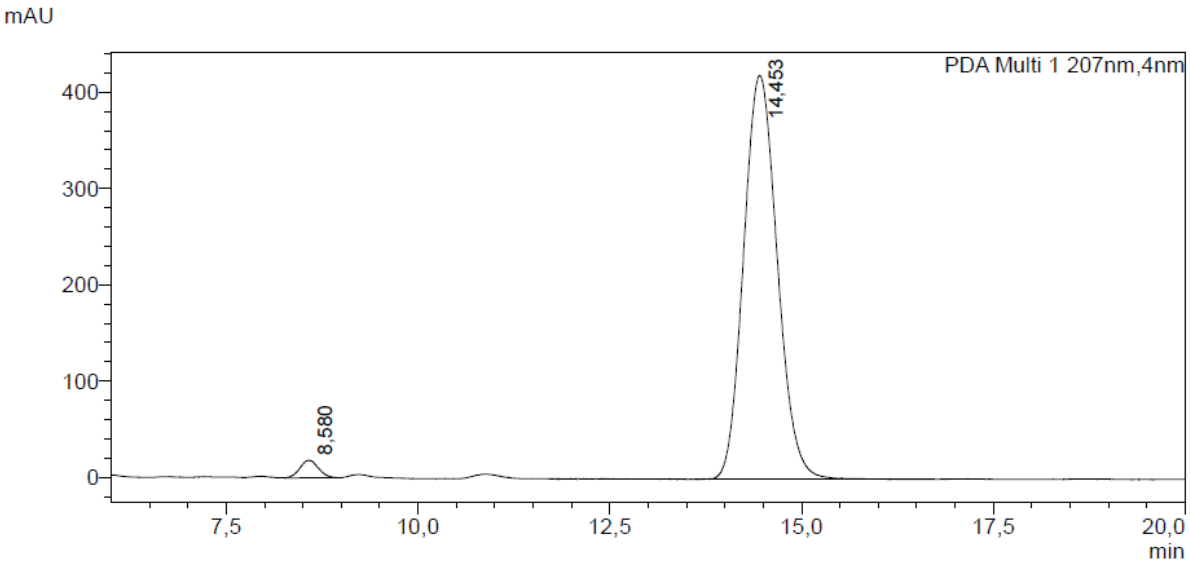


dimethyl (S)-(2-(diphenylphosphaneyl)-1-ferrocenylethyl)phosphonate (4d'a)



Following general procedure A: The reaction was performed with **1 d'** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **4d'a** was obtained as an oringe solid after column chromatography (SiO_2, pentane/ethyl acetate = 1:1) [98% yield, 95% ee].
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 – 7.55 (m, 2H, C*H*$_{Ar}$), 7.52 – 7.46 (m, 2H, C*H*$_{Ar}$), 7.43 – 7.31 (m, 6H, C*H*$_{Ar}$), 4.30 – 4.27 (m, 1H, C*H*$_{Fe}$), 4.24 – 4.20 (m, 1H, C*H*$_{Fe}$), 4.16 – 4.12 (m, 2H, C*H*$_{Fe}$), 4.04 – 3.97 (m, 5H, C*H*$_{Fe}$), 3.56 (d, *J* = 10.7 Hz, 1H, OC*H*$_3$), 3.49 (d, *J* = 10.5 Hz, 1H, OC*H*$_3$), 3.00 – 2.80 (m, 2H, P(O)(OCH$_3$)$_2$C*H*, PPh$_2$CHC*H*), 2.70 – 2.55 (m, 1H, PPh$_2$CHC*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.7, 139.5, 138.3, 138.1, 133.3, 133.1, 132.9, 129.0, 128.8, 128.8, 128.7, 128.7, 128.6, 86.0, 86.0, 86.0, 86.0, 69.3, 69.3, 69.3, 69.2, 69.0, 69.0, 67.8, 67.7, 67.5, 67.5, 67.5, 67.4, 53.3, 53.2, 53.2, 52.7, 52.7, 52.6, 52.6, 35.8, 35.6, 34.4, 34.2, 29.9, 29.8, 29.7, 29.7. (Due to C–P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.7 (d, *J* = 15.0 Hz), -19.3 (d, *J* = 15.0 Hz).
HRMS (ESI, m/Z): calcd. for $C_{26}H_{29}FeO_3P_2$ $[M+H]^+$: 507.0936, found: 507.0934.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 207 nm. Retention time (min): 8.6 (minor) and 14.5 (major).

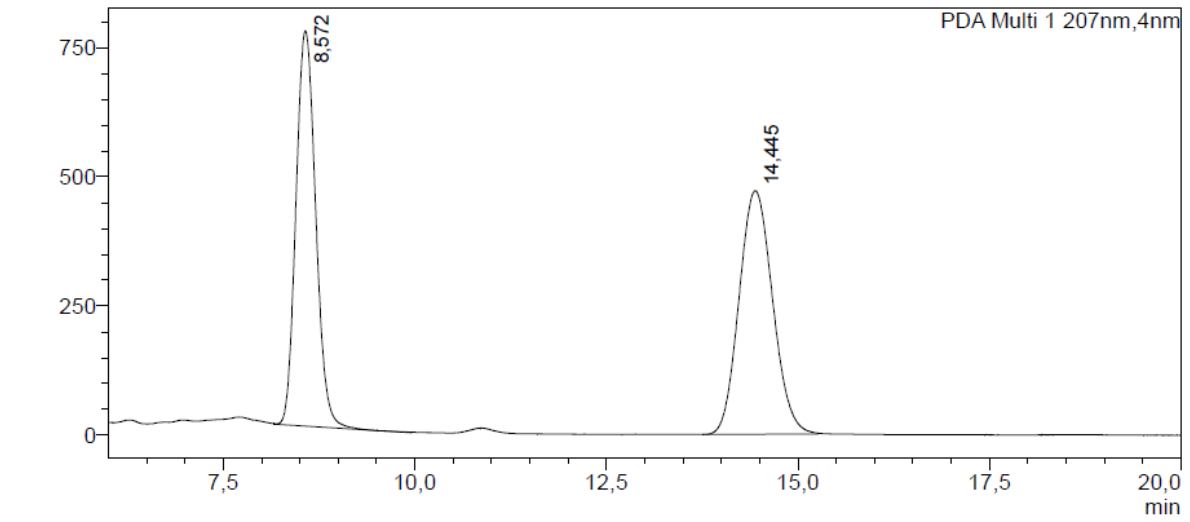
<Chromatogram>



PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	8,580	304262	18190	2,317
2	14,453	12827681	419380	97,683
Total		13131943	437570	100,000

<Chromatogram>

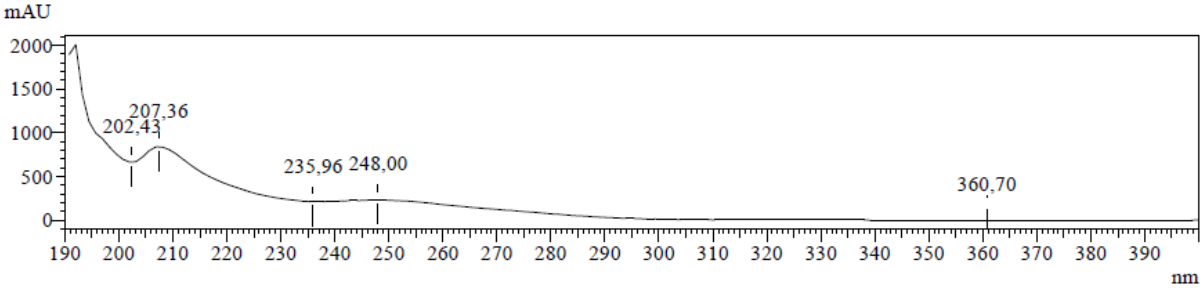


PDA Ch1 207nm

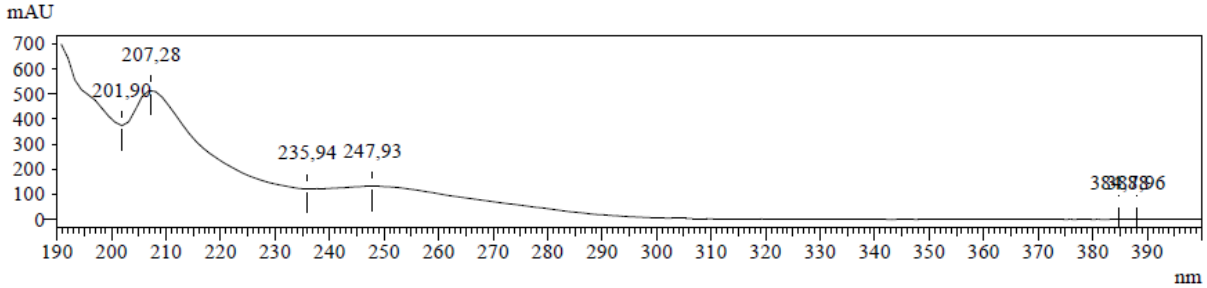
Peak#	Ret. Time	Area	Height	Area%
1	8,572	13707933	764334	48,845
2	14,445	14355942	471232	51,155
Total		28063875	1235566	100,000

UV Spectrum

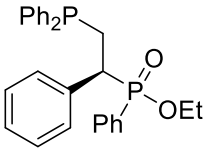
Peak# : 1
Retention Time : 8,572 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 14,445 min
Compound Name :
Spectrum Operation:



ethyl ((S)-2-(diphenylphosphaneyl)-1-phenylethyl)(phenyl)phosphinate (4e'a)



Following general procedure A: The reaction was performed with **1 e'** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Product **4e'a** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate = 1:1) [88% yield, 99% (80%) ee, 1:1 dr].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 – 7.41 (m, 2H, C*H*$_{Ar}$), 7.41 – 7.30 (m, 4H, C*H*$_{Ar}$), 7.30 – 7.14 (m, 11H, C*H*$_{Ar}$), 7.13 – 7.04 (m, 2H, C*H*$_{Ar}$), 7.03 – 6.90 (m, 1H, C*H*$_{Ar}$), 4.20 – 3.67 (m, 2H, CH_3CH_2), 3.16 – 2.50 (m, 3H, PPh_2CH_2, PhP(O)(OEt)C*H*), 1.37 – 0.90 (m, 3H, CH_2CH_3).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.8, 141.7, 139.7, 139.6, 139.2, 139.1, 138.0, 138.0, 137.7, 137.6, 137.6, 136.5, 136.3, 136.3, 136.1, 134.9, 134.9, 134.8, 134.8, 134.8, 134.7, 134.7, 134.6, 134.6, 134.4, 133.1, 132.8, 132.6, 132.5, 132.5, 132.4, 132.3, 131.9, 131.8, 131.3, 131.3, 131.2, 131.0, 131.1, 131.0, 130.9, 130.9, 130.9, 130.8, 130.8, 130.8, 130.7, 130.6, 130.0, 130.0, 129.8, 129.7, 129.2, 63.9, 63.8, 63.7, 47.8, 47.6, 47.4, 47.3, 46.8, 46.7, 46.5, 46.4, 30.7, 30.6, 30.3, 30.3, 30.2, 30.1, 19.2, 19.1, 18.9, 18.9. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)

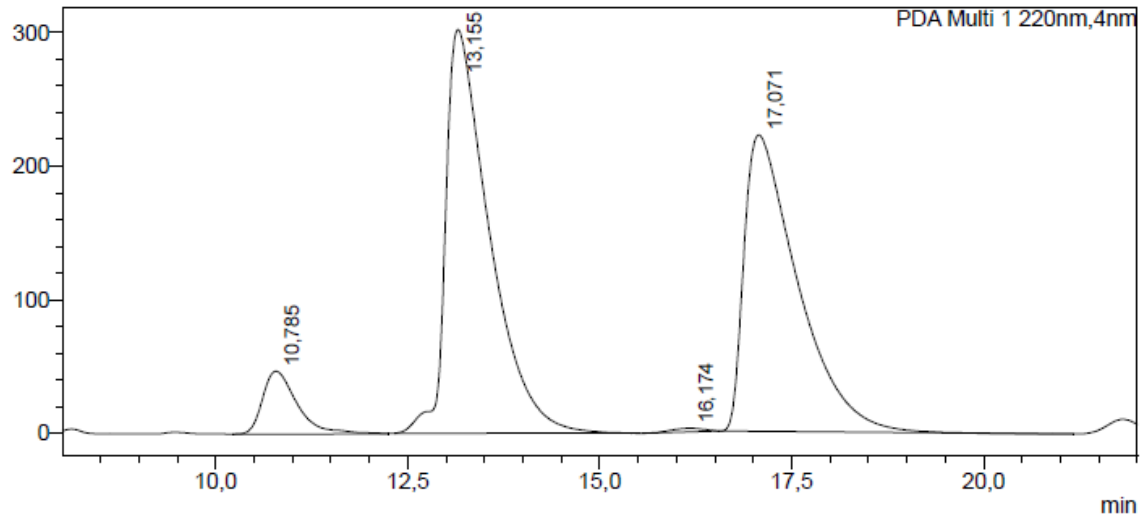
^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.8 (d, *J* = 37.0 Hz), 38.3 (d, *J* = 37.0 Hz), -23.2 (d, *J* = 37.0 Hz), -23.7 (d, *J* = 37.0 Hz).

HRMS (ESI, m/Z): calcd. for $C_{28}H_{29}O_2P_2$ $[M+H]^+$: 459.1637, found: 459.1638.

HPLC: Chiracel-ODH, *n*-heptane/*i*-PrOH 92:8, 1.0 mL/min., 40 °C, detection at 220 nm. Retention time (min): 10.8 (minor),13.2 (major), 16.2 (minor),17.1 (major). (*Due to the poor separation of the product **4e'a** in the HPLC, the ee of this compound was determined from the corresponding oxidized derivative.)*

<Chromatogram>

mAU



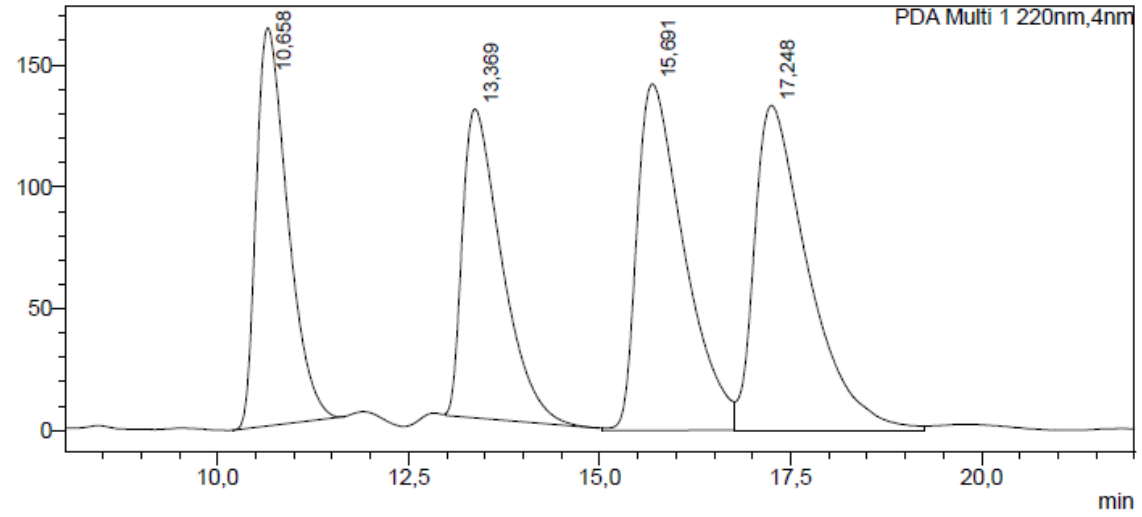
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	10,785	1478948	47084	6,070
2	13,155	12011693	302002	49,298
3	16,174	79927	2705	0,328
4	17,071	10794669	221661	44,304
Total		24365237	573452	100,000

<Chromatogram>

mAU



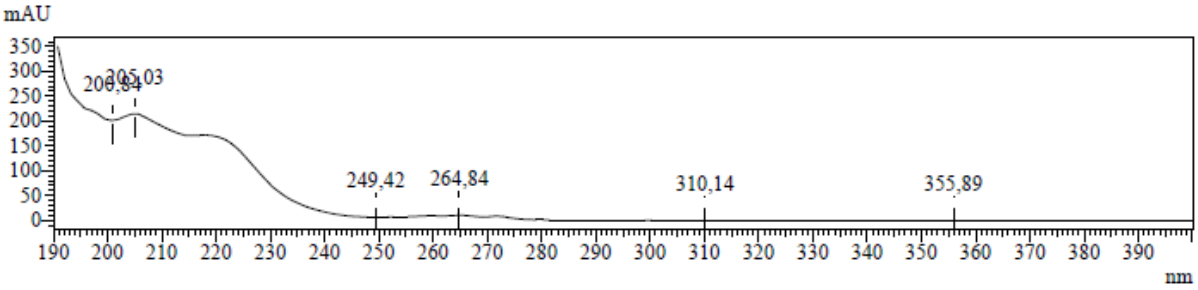
<Peak Table>

PDA Ch1 220nm

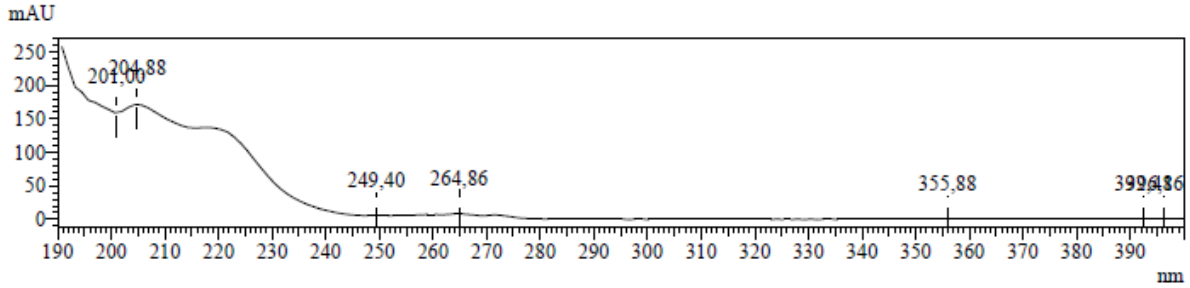
Peak#	Ret. Time	Area	Height	Area%
1	10,658	4678650	163164	21,400
2	13,369	4543525	126607	20,782
3	15,691	6104986	142014	27,924
4	17,248	6535528	133163	29,894
Total		21862689	564948	100,000

UV Spectrum

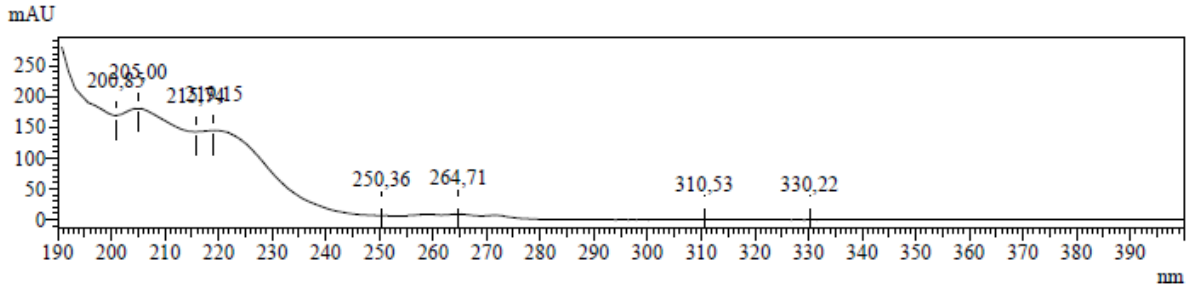
Peak# : 1
Retention Time : 10,658 min
Compound Name :
Spectrum Operation:



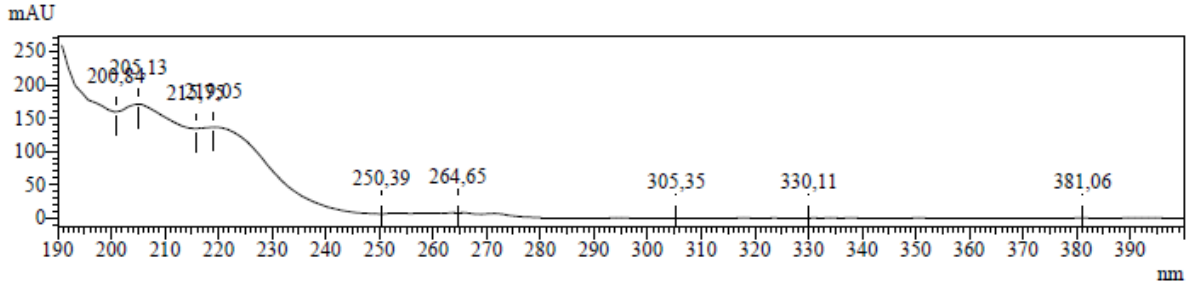
Peak# : 2
Retention Time : 13,369 min
Compound Name :
Spectrum Operation:



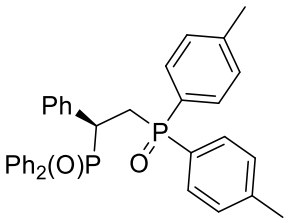
Peak# : 3
Retention Time : 15,691 min
Compound Name :
Spectrum Operation:



Peak# : 4
Retention Time : 17,248 min
Compound Name :
Spectrum Operation:

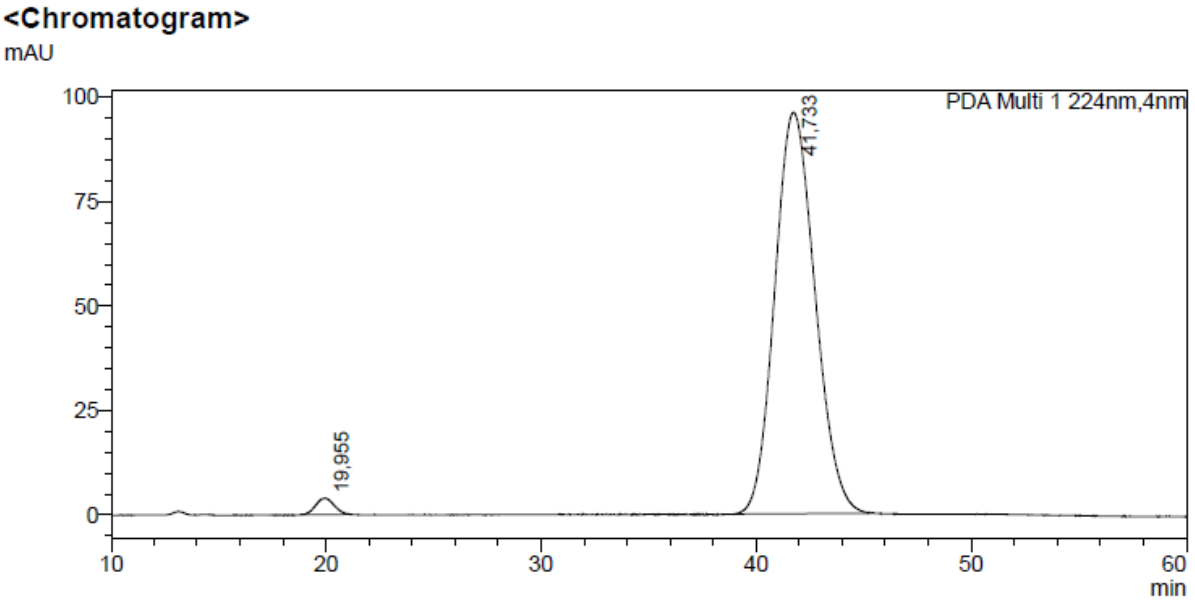


(S)-(2-(di-p-tolylphosphoryl)-1-phenylethyl)diphenylphosphine oxide (5ab)



Following general procedure A: The reaction was performed with **1a** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2b** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Then, the reaction mixture was quenched by 30% H_2O_2 aqueous solution (25 μL) and was stirred for additional 30 minutes at room temperature. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) to give product **5ab** as a white solid [82% yield, 96% ee].

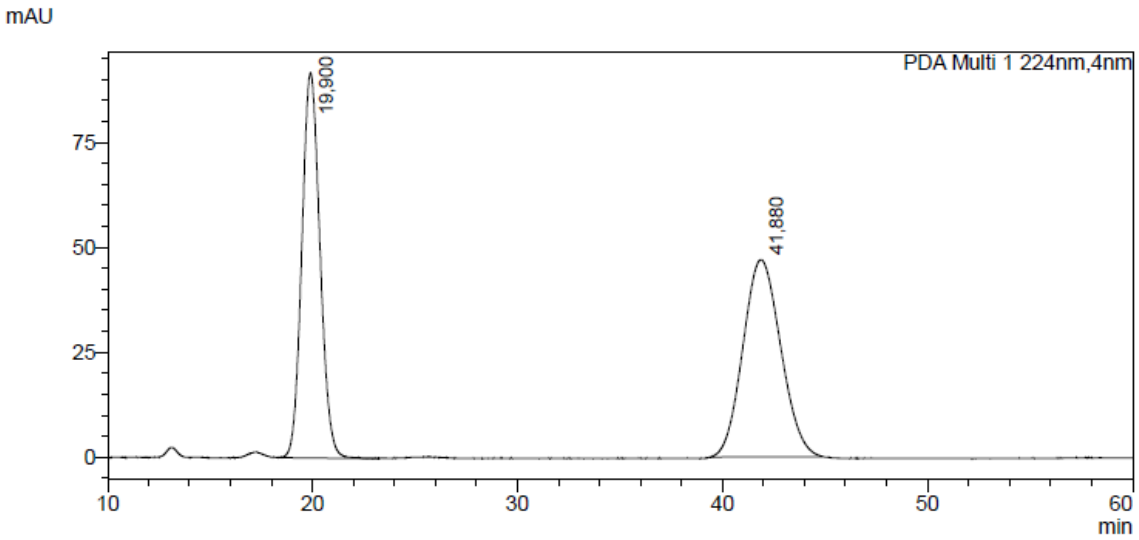
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 – 7.96 (m, 2H, C*H*$_{Ar}$), 7.58 – 7.46 (m, 3H, C*H*$_{Ar}$), 7.44 – 7.34 (m, 2H, C*H*$_{Ar}$), 7.33 – 7.19 (m, 3H, C*H*$_{Ar}$), 7.18 – 7.07 (m, 6H, C*H*$_{Ar}$), 7.06 – 6.96 (m, 2H, C*H*$_{Ar}$), 6.89 – 6.73 (m, 5H, C*H*$_{Ar}$), 4.31 – 4.14 (m, 1H, P(O)Ph$_2$C*H*), 3.14 – 2.96 (m, 1H, P(O)Ph$_2$CHCH*H*), 2.91 – 2.70 (m, 1H, P(O)Ph$_2$CHCH*H*), 2.29 (s, 3H, C*H*$_3$), 2.17 (s, 3H, C*H*$_3$).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.2, 142.2, 141.3, 141.3, 134.5, 134.4, 132.2, 132.1, 132.1, 131.8, 131.7, 131.5, 131.4, 131.3, 131.2, 131.0, 130.9, 130.8, 130.5, 130.4, 130.4, 130.2, 130.2, 129.5, 129.3, 129.2, 129.1, 128.9, 128.8, 128.6, 128.0, 127.9, 127.9, 127.9, 126.7, 126.7, 39.7, 39.7, 39.1, 39.0, 30.7, 30.0, 21.6, 21.4. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 32.1 (d, *J* = 46.7 Hz), 27.1 (d, *J* = 46.7 Hz).
HRMS (ESI, m/Z): calcd. for $C_{34}H_{33}O_2P_2$ $[M+H]^+$: 535.1950, found: 535.1953.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 70:30, 1.0 mL/min., 40 °C, detection at 224 nm. Retention time (min): 20.0 (minor) and 41.7 (major).



PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Area%
1	19,955	233663	3939	1,832
2	41,733	12521067	96024	98,168
Total		12754730	99962	100,000

<Chromatogram>

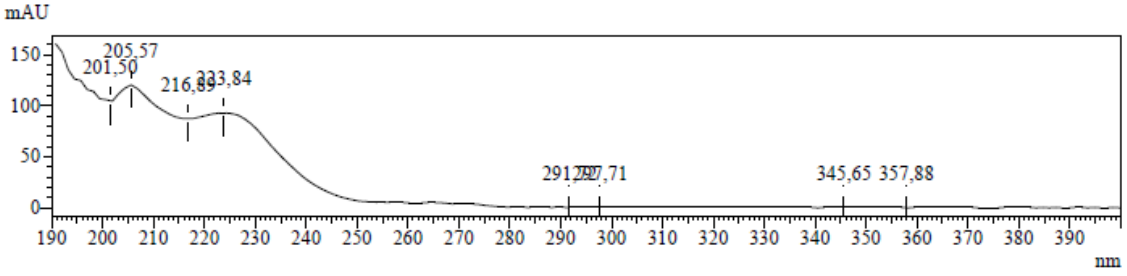


PDA Ch1 224nm

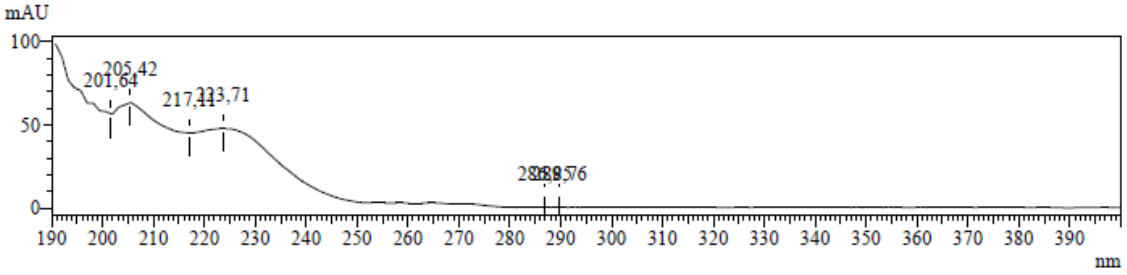
Peak#	Ret. Time	Area	Height	Area%
1	19,900	5654503	91696	48,439
2	41,880	6019049	46969	51,561
Total		11673552	138665	100,000

UV Spectrum

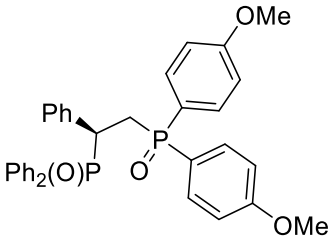
Peak# : 1
Retention Time : 19,900 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 41,880 min
Compound Name :
Spectrum Operation:



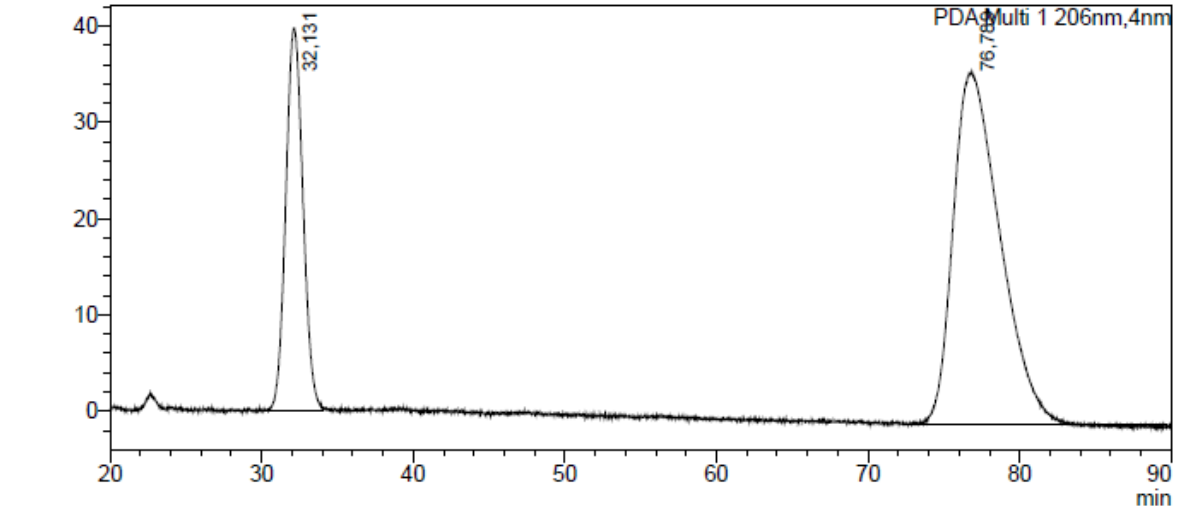
(S)-(2-(bis(4-methoxyphenyl)phosphoryl)-1-phenylethyl)diphenylphosphine oxide (5ac)



Following general procedure A: The reaction was performed with **1a** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2c** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h. Then, the reaction mixture was quenched by 30% H_2O_2 aqueous solution (25 μL) and was stirred for additional 30 minutes at room temperature. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) to give product **5ac** as a white solid [76% yield, 42% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 – 8.03 (m, 2H), 7.56 (s, 3H), 7.44 – 7.40 (m, 2H), 7.31 – 7.11 (m, 7H), 7.05 – 7.03 (m, 2H), 6.88 – 6.83 (m, 5H), 6.56 – 6.54 (m, 2H), 4.26 – 4.18 (m, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.06 – 3.00 (m, 1H), 2.86 – 2.75 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.2, 161.6, 134.5, 134.4, 132.7, 132.6, 132.2, 132.1, 131.7, 131.6, 131.2, 131.1, 130.9, 130.8, 130.4, 130.1, 130.0, 129.1, 129.0, 127.9, 127.8, 126.7, 114.2, 114.1, 113.6, 113.5, 55.3, 55.2, 39.6, 39.0, 30.8, 30.1. (Due to C–P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 35.3 (d, *J* = 46.5 Hz), 30.1 (d, *J* = 46.5 Hz).
HRMS (ESI, m/Z): calcd. for $C_{34}H_{33}O_4P_2$ $[M+H]^+$: 567.1849, found: 567.1853.
HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 70:30, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 32.1 (minor) and 76.8 (major).

<Chromatogram>

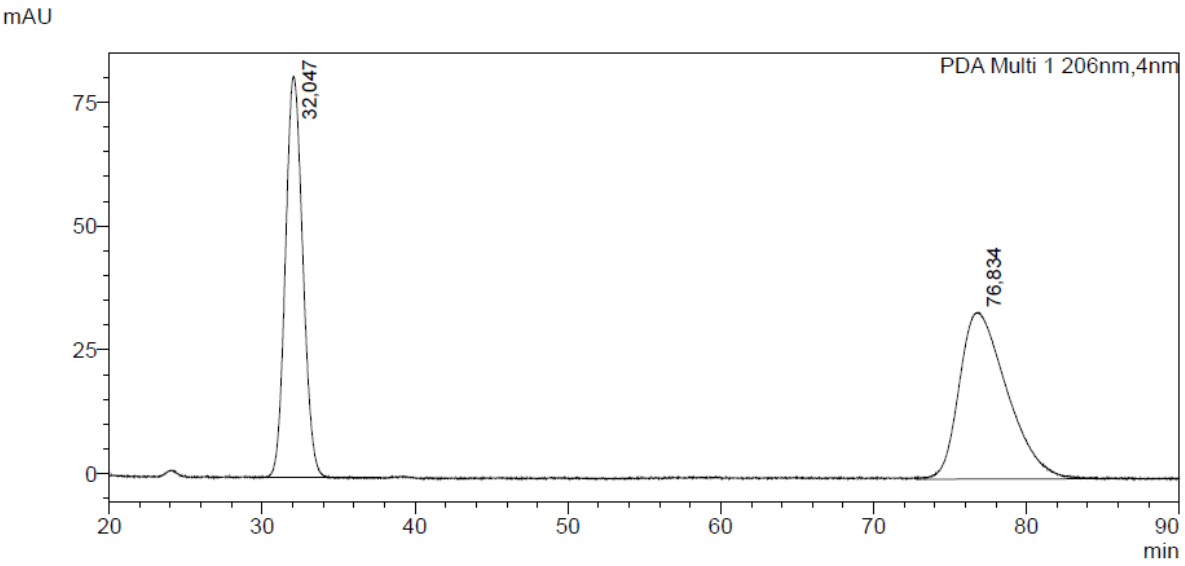


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	32,131	3159840	39779	28,908
2	76,789	7770940	36521	71,092
Total		10930780	76300	100,000

<Chromatogram>



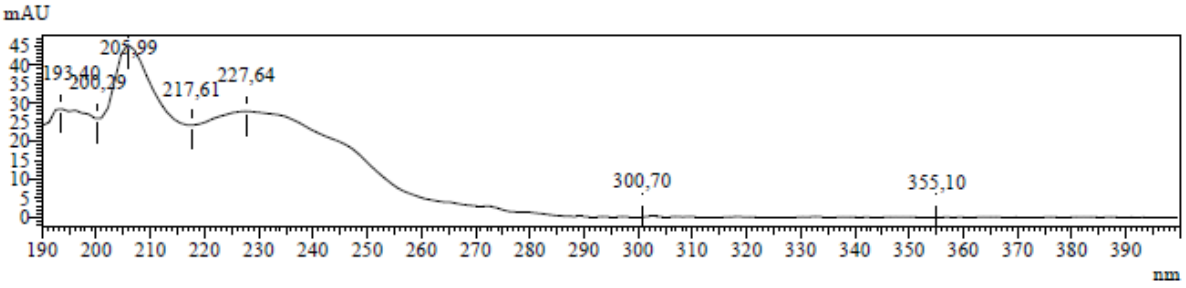
<Peak Table>

PDA Ch1 206nm

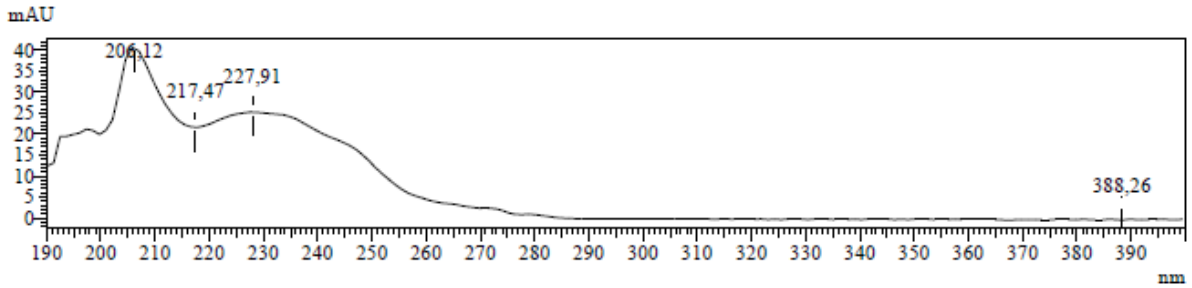
Peak#	Ret. Time	Area	Height	Area%
1	32,047	6374204	81006	46,574
2	76,834	7312090	33610	53,426
Total		13686294	114616	100,000

UV Spectrum

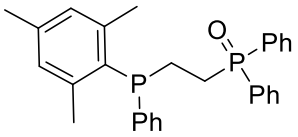
Peak# : 1
Retention Time : 32,131 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 76,789 min
Compound Name :
Spectrum Operation:



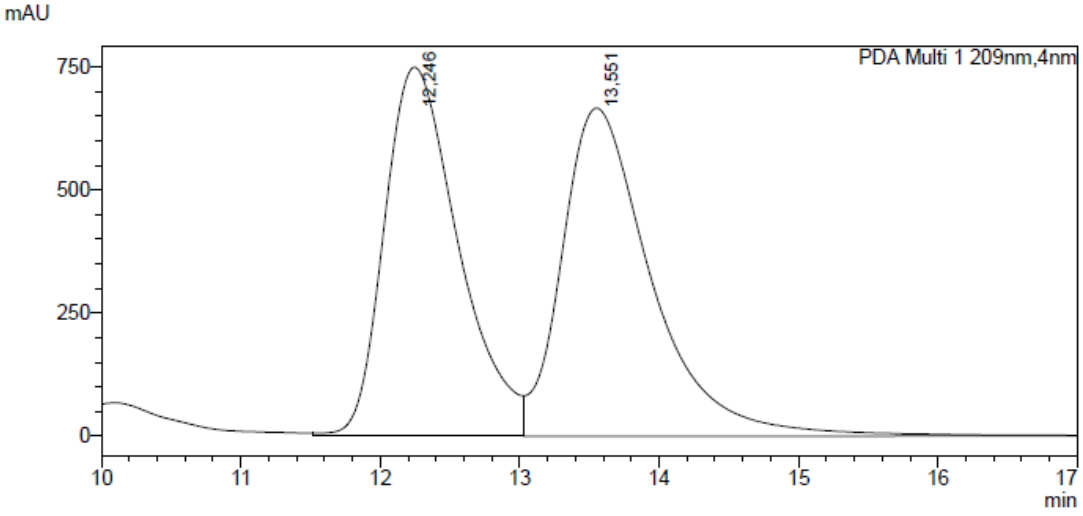
(2-(mesityl(phenyl)phosphaneyl)ethyl)diphenylphosphine oxide (5a'h)



Following general procedure A: The reaction was performed with **1'b** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2h** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h. Product **5b'h** was obtained as a white solid after column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) [86% yield, 0% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 – 7.60 (m, 4H), 7.53 – 7.39 (m, 6H), 7.22 – 7.11 (m, 5H), 6.85 (s, 2H), 2.55 – 2.36 (m, 3H), 2.28 (s, 3H), 2.21 (s, 6H), 2.15 – 2.03 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.8, 145.6, 140.7, 140.6, 140.5, 140.5, 140.1, 140.1, 133.6, 132.8, 132.6, 132.0, 131.9, 131.9, 131.9, 131.1, 131.0, 131.0, 130.9, 130.1, 130.0, 129.4, 129.2, 128.9, 128.8, 128.8, 128.7, 128.5, 128.5, 128.2, 128.0, 126.8, 126.8, 27.1, 26.9, 26.4, 26.2, 25.7, 23.4, 23.3, 21.2, 16.9, 16.9, 16.7, 16.7. (Due to C–P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 29.6 (d, *J* = 55.3 Hz), -25.0 (d, *J* = 55.3 Hz).
HRMS (ESI, m/Z): calcd. for $C_{29}H_{31}OP_2$ $[M+H]^+$: 457.1845, found: 457.1851.
HPLC: Chiracel-ASH, *n*-heptane/*i*-PrOH 90:10, 0.5 mL/min., 40 °C, detection at 209 nm. Retention time (min): 12.2 and 13.6.

<Chromatogram>

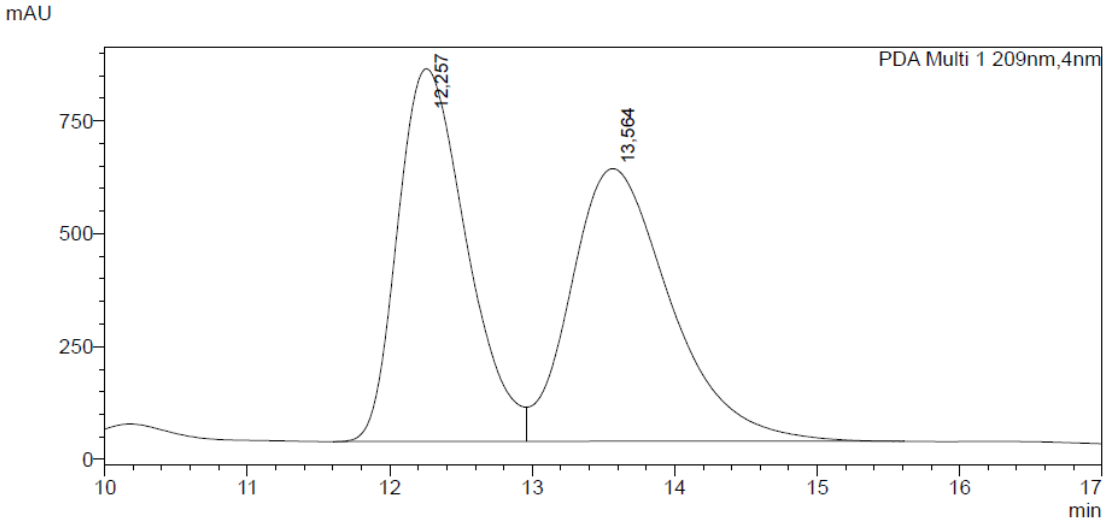


<Peak Table>

PDA Ch1 209nm

Peak#	Ret. Time	Area	Height	Area%
1	12,246	27731692	749362	48,004
2	13,551	30037348	666168	51,996
Total		57769040	1415531	100,000

<Chromatogram>



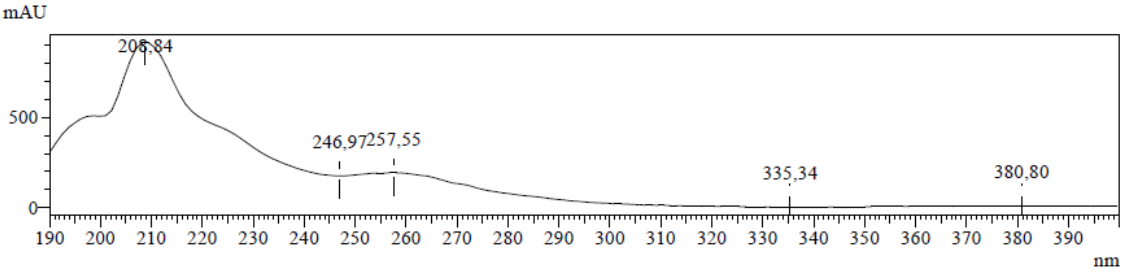
<Peak Table>

PDA Ch1 209nm

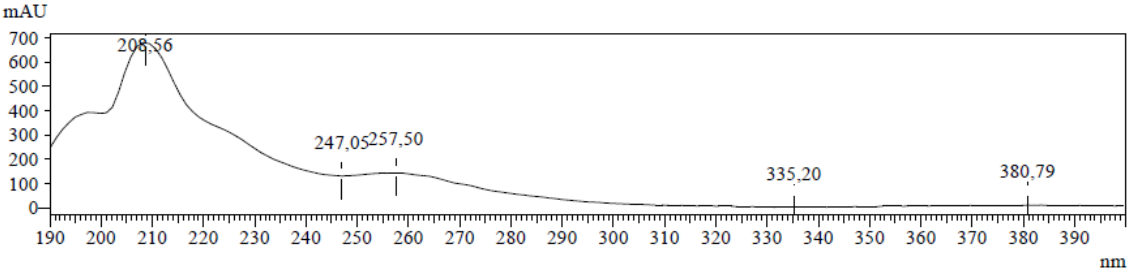
Peak#	Ret. Time	Area	Height	Area%
1	12,257	27682684	825392	48,567
2	13,564	29316155	604058	51,433
Total		56998839	1429450	100,000

UV Spectrum

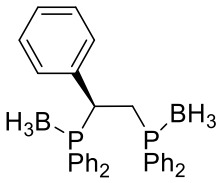
Peak# : 1
Retention Time : 12,257 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 13,564 min
Compound Name :
Spectrum Operation:



(S)-(1-phenylethane-1,2-diyl)bis(diphenylphosphane) borane complex (6aa)[1]



Following general procedure B: The reaction was performed with **1a** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h, then $Ti(OiPr)_4$ (0.03 mmol, 0.3 equiv), $HSi(OEt)_3$ (0.3 mmol, 3.0 equiv) at 120°C for 1h; finally, BH_3·THF (0.3 mmol, 3.0 equiv) at rt for 1h. Product **6aa** was obtained as a white solid after column chromatography (SiO_2, pentane/ dichloromethane = 2:1) [86% yield, 96% ee].

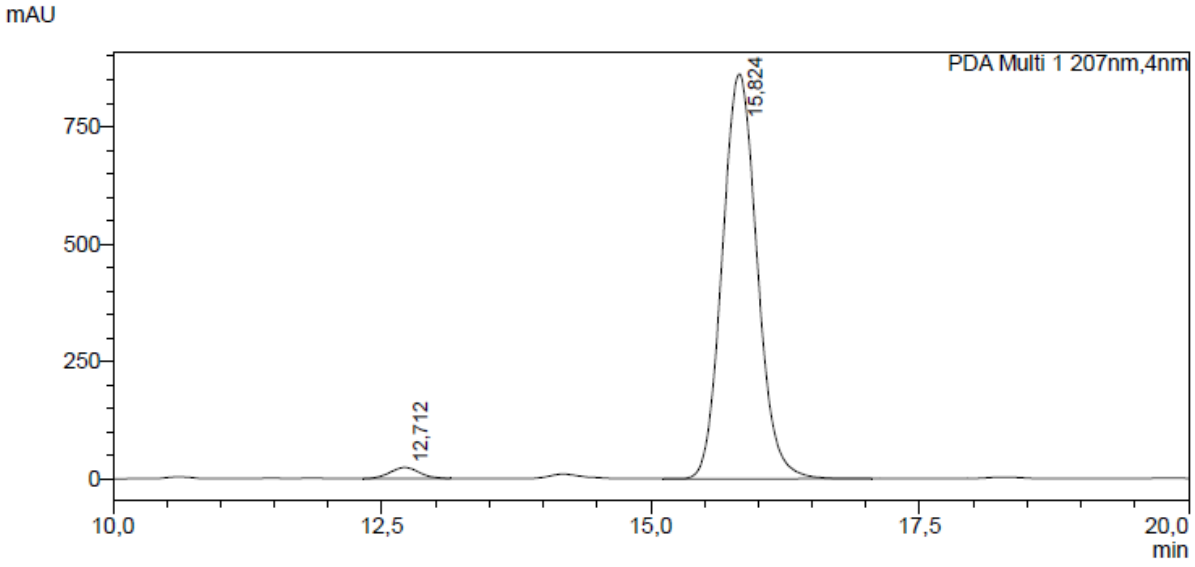
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 – 8.07 (m, 2H, C*H*$_{Ar}$), 7.65 – 7.57 (m, 3H, C*H*$_{Ar}$), 7.56 – 7.49 (m, 2H, C*H*$_{Ar}$), 7.48 – 7.43 (m, 1H, C*H*$_{Ar}$), 7.43 – 7.36 (m, 2H, C*H*$_{Ar}$), 7.34 – 7.26 (m, 3H, C*H*$_{Ar}$), 7.25 – 7.12 (m, 5H, C*H*$_{Ar}$), 7.09 – 7.01 (m, 2H, C*H*$_{Ar}$), 6.97 – 6.90 (m, 2H, C*H*$_{Ar}$), 6.89 – 6.82 (m, 1H, C*H*$_{Ar}$), 6.81 – 6.74 (m, 2H, C*H*$_{Ar}$), 4.61 – 4.49 (m, 1H, C*H*), 3.4 – 3.28 (m, 1H, CH*H*), 2.61 – 2.48 (m, 1H, CH*H*), 1.55 – 0.53 (m, 6H, 2xB*H*$_3$) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): δ 133.8, 133.4, 133.0, 132.9, 132.8, 132.5, 132.2, 131.8, 131.5, 131.3, 131.1, 131.0, 130.7, 130.4, 130.0, 129.8, 129.6, 129.6, 129.2, 129.1, 129.0, 128.8, 128.7, 128.4, 128.1, 128.0, 127.6, 127.5, 127.3, 127.0, 126.9, 126.7, 126.6, 37.9, 37.6, 27.1, 26.8. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)

^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.8, 13.8.

HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 0.5 mL/min., 40 °C, detection at 207 nm. Retention time (min): 12.7 (minor) and 15.8 (major).

<Chromatogram>

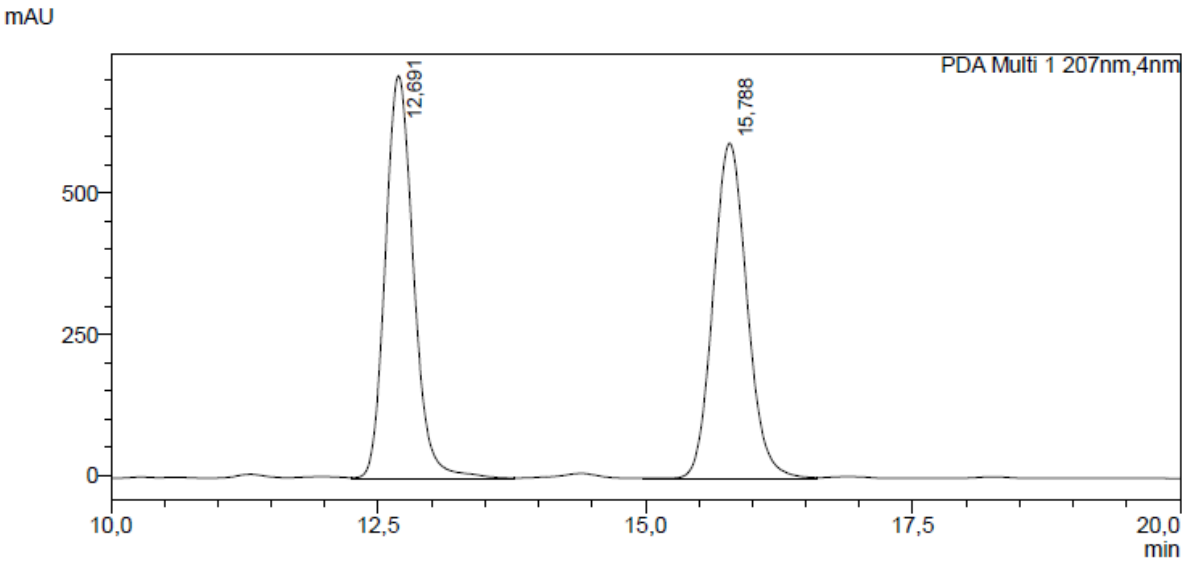


<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	12,712	438201	23439	2,208
2	15,824	19403996	861747	97,792
Total		19842197	885186	100,000

<Chromatogram>



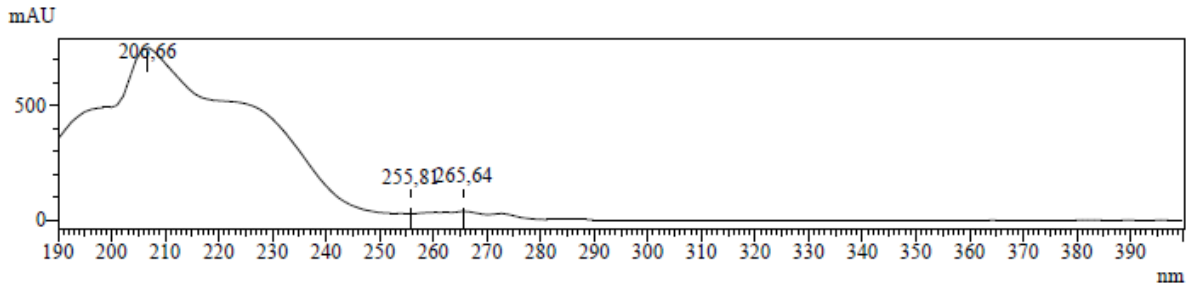
<Peak Table>

PDA Ch1 207nm

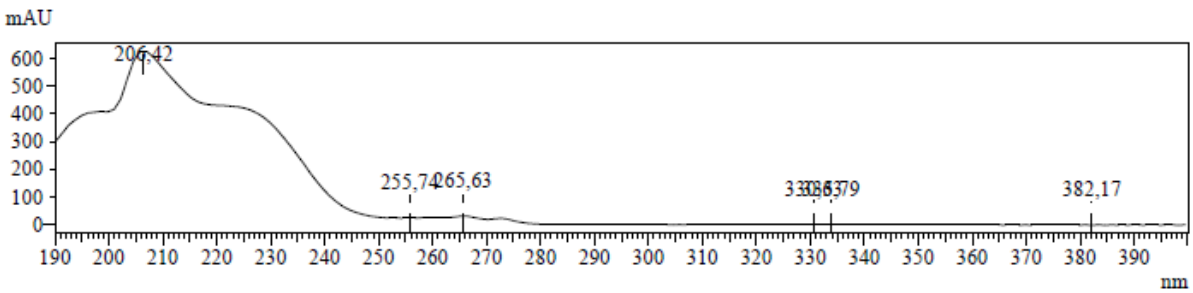
Peak#	Ret. Time	Area	Height	Area%
1	12,691	13106260	711796	50,020
2	15,788	13095910	593075	49,980
Total		26202171	1304871	100,000

UV Spectrum

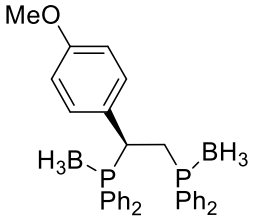
Peak# : 1
Retention Time : 12,691 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 15,788 min
Compound Name :
Spectrum Operation:



(S)-(1-(4-methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphane) borane complex (6ba)



Following general procedure B: The reaction was performed with **1b** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h, then Ti(O*i*Pr)$_4$ (0.03 mmol, 0.3 equiv), HSi(OEt)$_3$ (0.3 mmol, 3.0 equiv) at 120°C for 1h; finally, BH$_3$·THF (0.3 mmol, 3.0 equiv) at rt for 1h. Product **6ba** was obtained as a white solid after column chromatography (SiO_2, pentane/dichloromethane = 2:1) [80% yield, 97% ee].

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.15 – 8.05 (m, 2H, C*H*$_{Ar}$), 7.64 – 7.56 (m, 3H, C*H*$_{Ar}$), 7.54 – 7.48 (m, 2H, C*H*$_{Ar}$), 7.48 – 7.42 (m, 1H, C*H*$_{Ar}$), 7.42 – 73.6 (m, 2H, C*H*$_{Ar}$), 7.33 – 7.14 (m, 8H), 7.12 – 7.04 (m, 2H), 6.84 (d, *J* = 7.5 Hz, 2H, C*H*$_{Ar}$). 6.30 (d, *J* = 8.3 Hz, 2H, C*H*$_{Ar}$), 4.61 – 4.42 (m, 1H, C*H*), 3.65 (s, 3H, OC*H*$_3$), 3.35 – 3.20 (m, 1H, CH*H*), 2.58 – 2.43 (m, 1H, CH*H*), 1.47 – 0.56 (m, 6H, 2xB*H*$_3$).

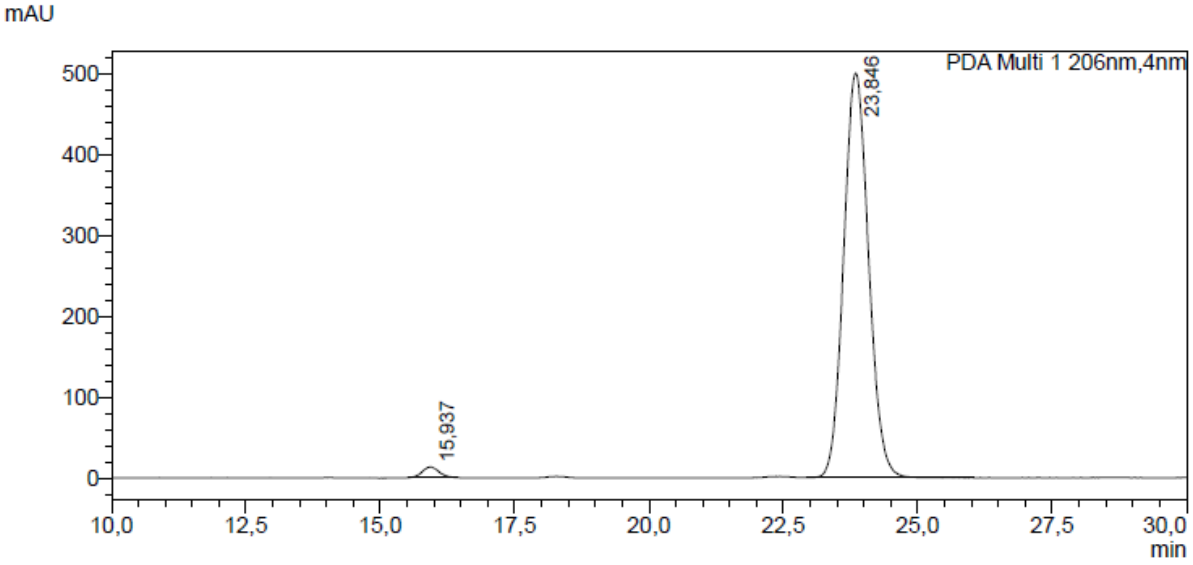
^{13}C NMR (CDCl$_3$, 101 MHz): δ 158.6, 158.6, 133.3, 133.2, 132.7, 132.7, 132.6, 132.5, 131.8, 131.8, 131.5, 131.5, 131.5, 131.4, 131.1, 131.1, 131.0, 131.0, 130.6, 130.6, 130.4, 130.0, 129.3, 129.23, 128.9, 128.8, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.0, 126.7, 124.6, 113.0, 112.9, 55.1, 37.0, 36.9, 36.7, 36.7, 27.4, 27.4, 27.2, 27.1. (Due to C–P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)

^{31}P NMR (CDCl$_3$, 162 MHz): δ 25.8, 16.7.

HRMS (ESI, m/Z): calcd. for $C_{33}H_{36}OP_2Na$ $[M+Na]^+$: 555.2320, found: 555.2319.

HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 0.5 mL/min., 40 °C, detection at 206 nm. Retention time (min): 15.9 (minor) and 23.8 (major).

<Chromatogram>

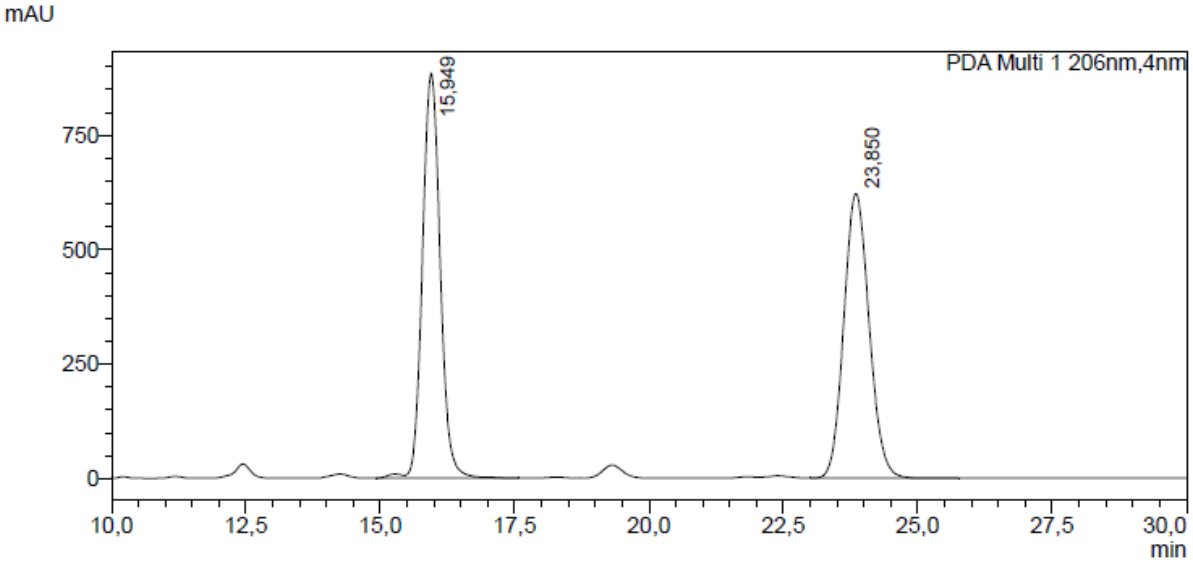


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	15,937	279342	12995	1,704
2	23,846	16111266	499695	98,296
Total		16390609	512690	100,000

<Chromatogram>



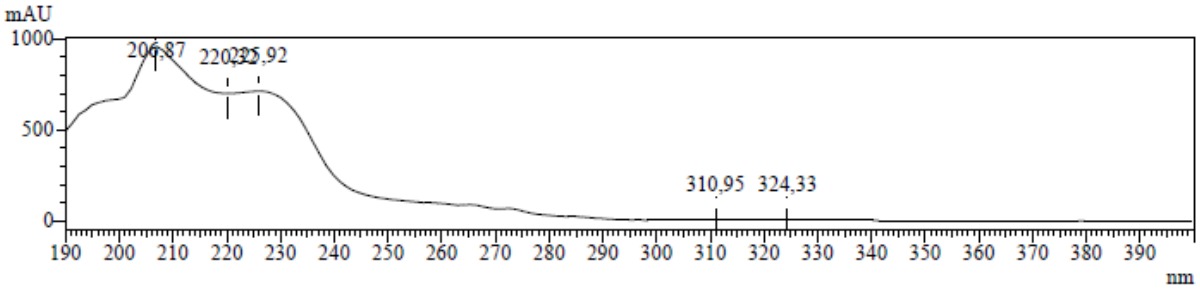
<Peak Table>

PDA Ch1 206nm

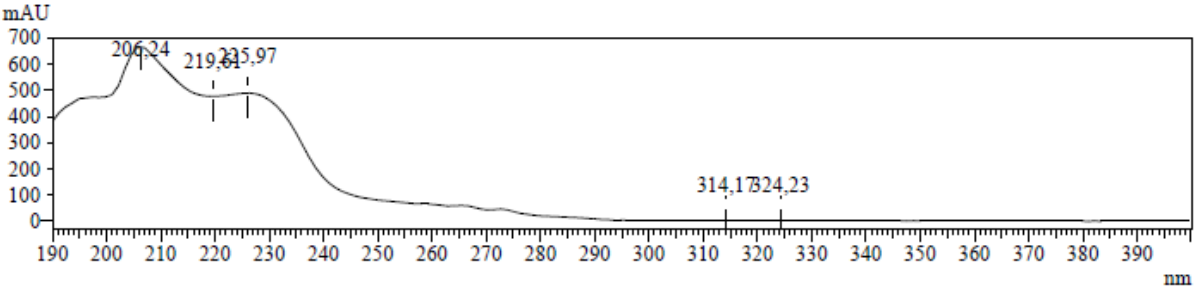
Peak#	Ret. Time	Area	Height	Area%
1	15,949	20377422	884022	50,037
2	23,850	20347611	621388	49,963
Total		40725032	1505411	100,000

UV Spectrum

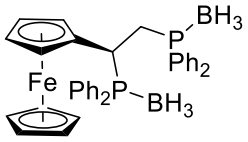
Peak# : 1
Retention Time : 15,949 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 23,850 min
Compound Name :
Spectrum Operation:



(S)-(1-ferrocenylethane-1,2-diyl)bis(diphenylphosphane) borane complex (6ca)



Following general procedure B: The reaction was performed with **1p** (0.1 mmol, 1 equiv.), manganese catalyst (0.0025 mmol, 2.5 mol%), *t*PentOK (0.005 mmol, 5 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 16 h, then Ti(O*i*Pr)$_4$ (0.03 mmol, 0.3 equiv), HSi(OEt)$_3$ (0.3 mmol, 3.0 equiv) at 120°C for 1h; finally, BH$_3$·THF (0.3 mmol, 3.0 equiv) at rt for 1h. Product **6ca** was obtained as an orange solid after column chromatography (SiO_2, pentane/dichloromethane = 2:1) [81% yield, 98% ee].

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.91 – 7.78 (m, 2H, C*H*$_{Ar}$), 7.73 – 7.62 (m, 2H, C*H*$_{Ar}$), 7.58 – 7.05 (m, 16H, C*H*$_{Ar}$), 4.43 – 4.30 (m, 1H, C*H*), 4.20 (s, br, 1H, C*H*$_{Fe}$), 3.94 (s, br, 6H, C*H*$_{Fe}$), 3.76 (s, br, 1H, C*H*$_{Fe}$), 3.59 (s, br, 1H, C*H*$_{Fe}$), 3.44 – 3.29 (m, 1H, CH*H*), 3.27 – 3.10 (m, 1H, CH*H*), 1.70 – 0.54 (m, 6H, 2xB*H*$_3$).

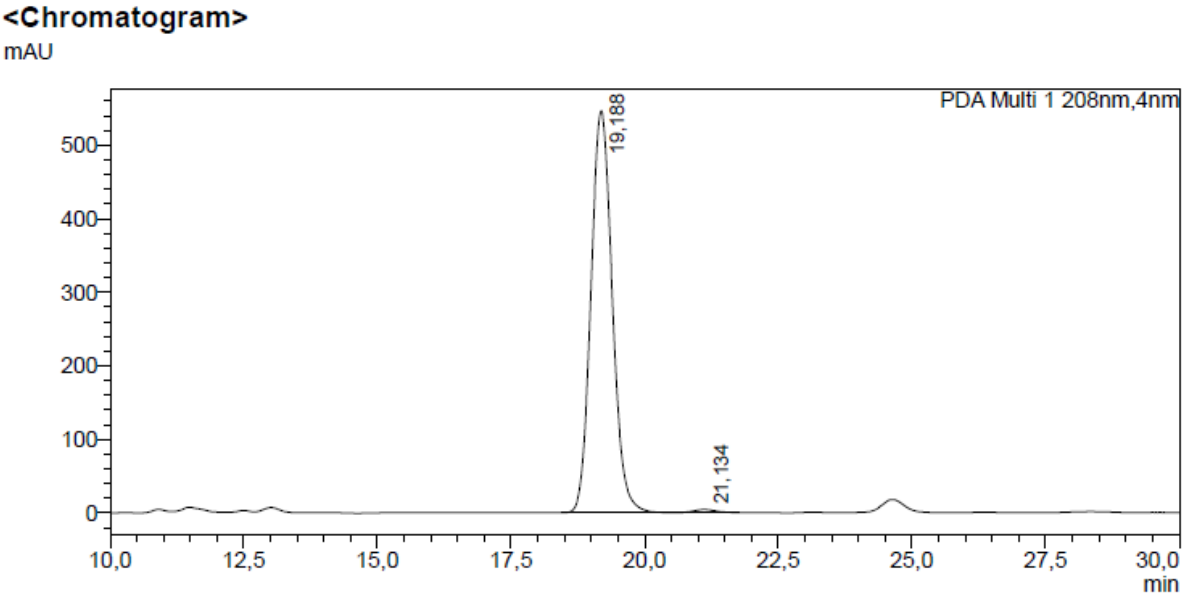
^{13}C NMR (CDCl$_3$, 101 MHz): δ 133.5, 133.5, 133.0, 133.0, 132.9, 132.8, 132.0, 131.9, 131.8, 131.7, 131.7, 131.4, 131.4, 131.1, 131.1, 131.0, 130.9, 130.9, 130.7, 130.7, 130.6, 129.3, 129.2, 129.1, 128.9, 128.8, 128.8, 128.6, 128.6, 128.5, 128.4, 128.2, 128.2, 127.3, 127.0, 89.1, 89.1, 89.1, 89.1, 69.6, 68.8, 68.6, 68.6, 67.3, 67.0, 31.2, 31.2, 31.0, 30.9, 29.9, 29.9, 29.7, 29.6. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)

^{31}P NMR (CDCl$_3$, 162 MHz): δ 25.0, 16.2.

HRMS (ESI, m/Z): calcd. for $C_{36}H_{38}B_2P_2Na$ $[M+Na]^+$: 633.1876, found: 633.1867.

HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 0.5 mL/min., 40 °C, detection at 208 nm. Retention time (min): 19.2 (major) and 21.1 (minor).

<Chromatogram>

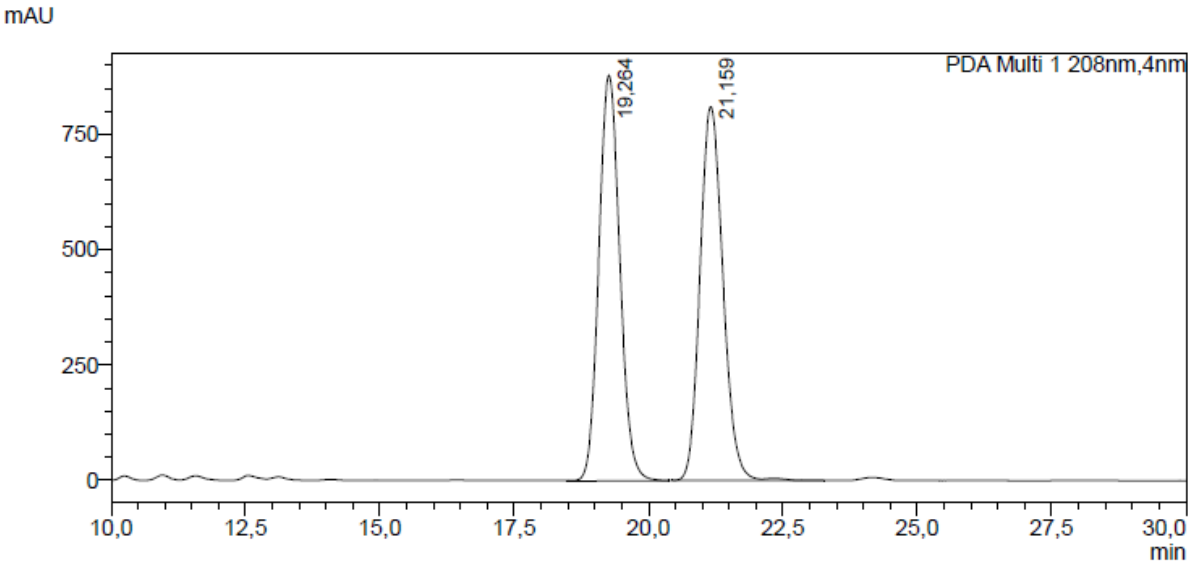


<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	19,188	15165953	546257	99,262
2	21,134	112803	4023	0,738
Total		15278756	550280	100,000

<Chromatogram>



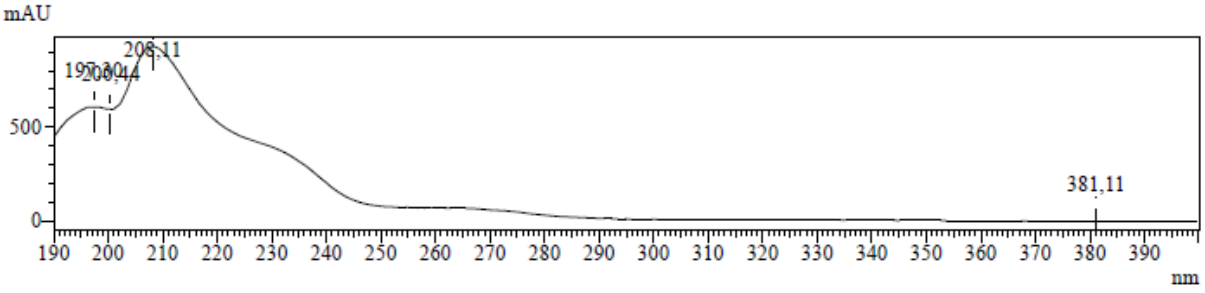
<Peak Table>

PDA Ch1 208nm

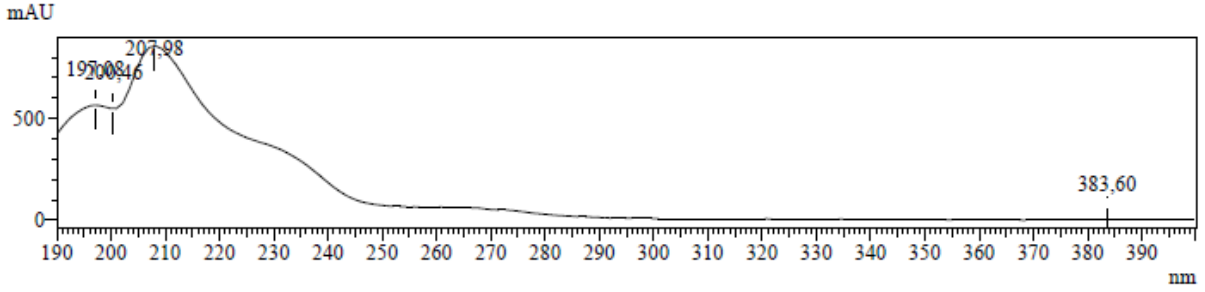
Peak#	Ret. Time	Area	Height	Area%
1	19,264	23970477	879790	49,848
2	21,159	24117061	810542	50,152
Total		48087538	1690332	100,000

UV Spectrum

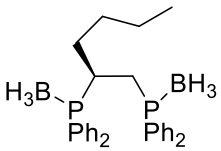
Peak# : 1
Retention Time : 19,264 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 21,159 min
Compound Name :
Spectrum Operation:



(S)-hexane-1,2-diylbis(diphenylphosphane) borane complex (6da)



Following general procedure B: The reaction was performed with **1q** (0.1 mmol, 1 equiv.), manganese catalyst (0.005 mmol, 2.5 mol%), *t*PentOK (0.01 mmol, 10 mol%), **2a** (0.105 mmol, 1.05 equiv.), toluene (1.0 mL) at 25°C for 72 h, then Ti(O*i*Pr)$_4$ (0.03 mmol, 0.3 equiv), HSi(OEt)$_3$ (0.3 mmol, 3.0 equiv) at 120°C for 1h; finally, BH_3·THF (0.3 mmol, 3.0 equiv) at rt for 1h. Product **6da** was obtained as a white solid after column chromatography (SiO_2, pentane/ dichloromethane = 2:1) [76% yield, 98% ee].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 – 7.82 (m, 2H, C*H*$_{Ar}$), 7.81 – 7.70 (m, 4H, C*H*$_{Ar}$), 7.55 – 7.28 (m, 14H, C*H*$_{Ar}$), 3.31 – 3.12 (m, 1H, C*H*), 2.74 – 2.57 (m, 1H, CH_2CHCH*H*), 2.32 – 2.17 (m, 1H, CH_2CHCH*H*), 1.69 – 1.46 (m, 2H), 1.30 – 1.17 (m, 5H), 0.98 – 0.83 (m, 3H), 0.67 – 0.60 (m, 2H, CH_3C*H*$_2$), 0.41 (t, *J* = 7.3 Hz, 3H, CH_2C*H*$_3$).

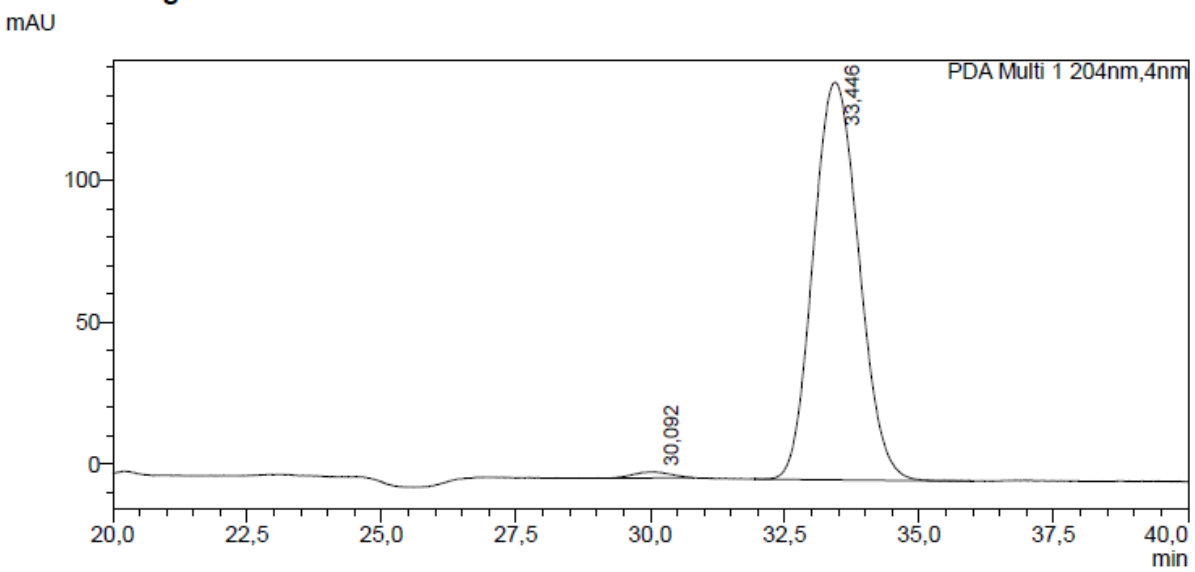
^{13}C NMR ($CDCl_3$, 101 MHz): δ 133.2, 133.1, 133.0, 132.9, 132.9, 132.8, 132.8, 131.8, 131.8, 131.7, 131.6, 131.6, 131.6, 131.5, 131.2, 131.2, 130.6, 130.1, 129.4, 129.3, 129.2, 129.2, 129.1, 129.1, 129.0, 129.0, 128.9, 128.9, 128.9, 128.8, 128.5, 128.5, 128.4, 127.9, 30.2, 30.2, 29.7, 29.7, 29.5, 29.5, 29.2, 29.1, 27.4, 27.4, 27.1, 27.1, 22.5, 13.4. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)

^{31}P NMR ($CDCl_3$, 162 MHz): δ 22.0, 13.9.

HRMS (ESI, m/Z): calcd. for $C_{30}H_{38}B_2P_2K$ $[M+K]^+$: 521.2266, found: 521.2275.

HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 98:02, 0.5 mL/min., 40 °C, detection at 204 nm. Retention time (min): 30.1 (minor) and 33.4 (major).

<Chromatogram>



<Peak Table>

PDA Ch1 204nm

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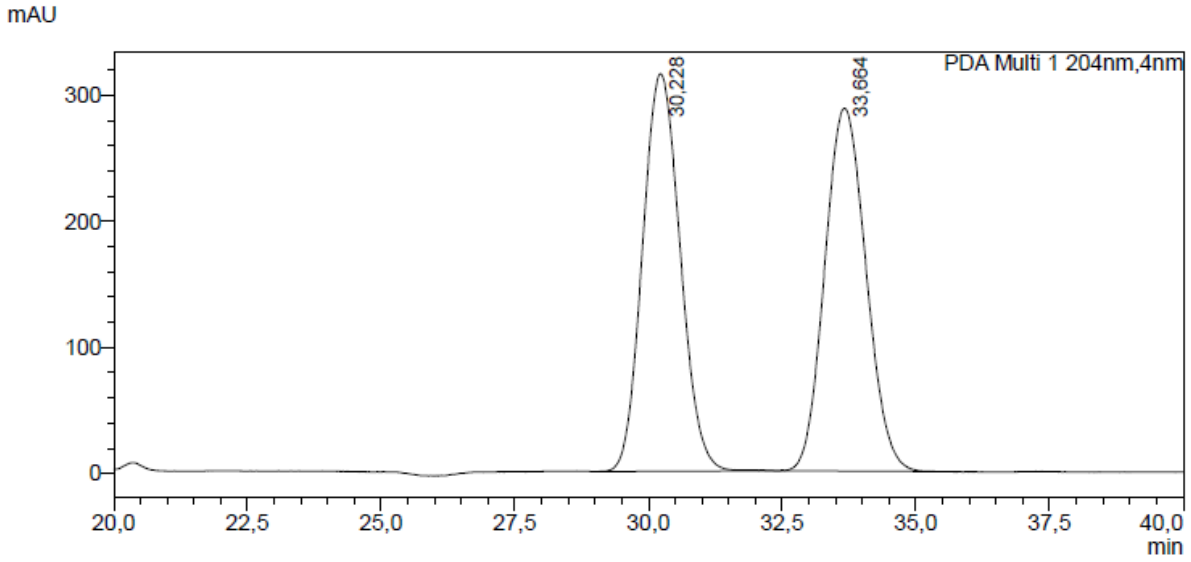
1	30,092	101049	2144	1,203
2	33,446	8299164	140172	98,797
Total		8400214	142317	100,000

<Chromatogram>



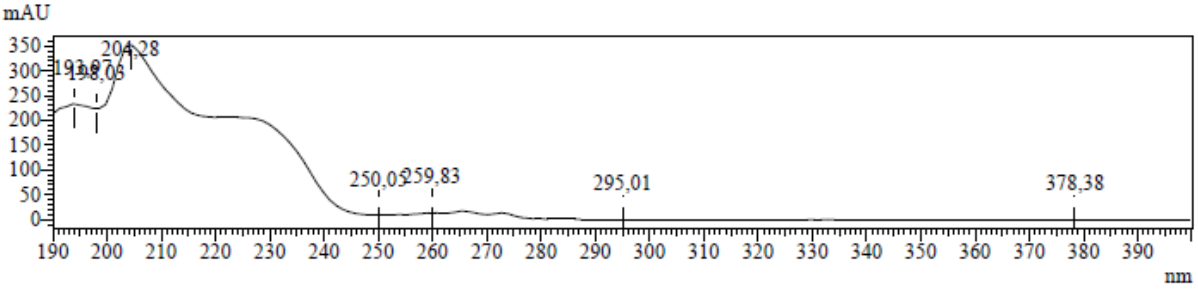
<Peak Table>

PDA Ch1 204nm

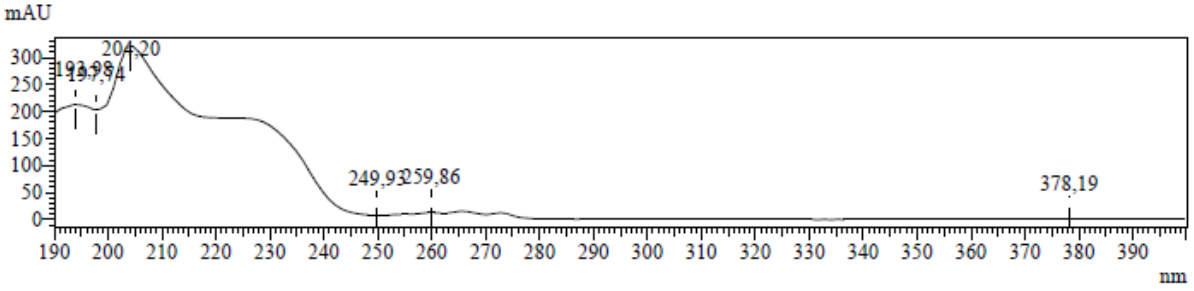
Peak#	Ret. Time	Area	Height	Area%
1	30,228	15454050	315432	49,979
2	33,664	15467254	287895	50,021
Total		30921304	603327	100,000

UV Spectrum

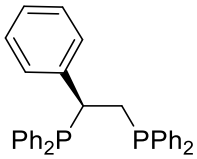
Peak# : 1
Retention Time : 30,228 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 33,664 min
Compound Name :
Spectrum Operation:



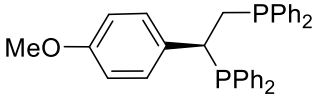
(S)-(1-phenylethane-1,2-diyl)bis(diphenylphosphane) (7aa)



Following general procedure C: The reaction was performed with **6aa** (0.1 mmol, 1 equiv.), DABCO (0.40 mmol, 4.0 equiv) and degassed toluene (2.5 mL) at 50°C for 12 h. Product **7aa** was obtained as a white solid with 92% yield.

^{1}H NMR (Toluene-d_8, 400 MHz): δ 7.46 – 7.40 (m, 2H, C*H*$_{Ar}$), 7.35 – 7.28 (m, 2H, C*H*$_{Ar}$), 7.20 – 7.15 (m, 2H, C*H*$_{Ar}$), 7.15 – 7.05 (m, 8H, C*H*$_{Ar}$), 7.06 – 6.98 (m, 4H, C*H*$_{Ar}$), 7.00 – 6.87 (m, 4H, C*H*$_{Ar}$), 6.86 – 6.76 (m, 3H, C*H*$_{Ar}$), 3.56 – 3.48 (m, 1H, PPh$_2$C*H*), 2.69 – 2.59 (m, 2H, PPh$_2$CH*H*).
^{13}C NMR (**Toluene-d_8, 101 MHz**) δ 141.2, 141.2, 141.2, 141.1, 139.9, 139.8, 139.0, 138.9, 137.8, 137.7, 137.6, 137.4, 137.3, 137.2, 134.6, 134.5, 134.5, 134.4, 133.6, 133.5, 132.5, 132.3, 129.9, 129.9, 129.3, 129.1, 128.8, 128.4, 128.4, 128.4, 128.4, 128.2, 128.0, 128.0, 126.6, 126.6, 42.8, 42.7, 42.6, 33.8, 33.7, 33.7, 33.6. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (**Toluene-d_8, 162 MHz**) δ 2.5 (d, *J* = 17.5 Hz), -21.0 (d, *J* = 17.5 Hz).
HRMS (ESI, m/Z): calcd. for $C_{32}H_{29}P_2$ $[M+H]^+$: 475.1739, found: 475.1743.

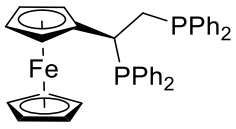
(S)-(1-(4-methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphane) (7ba)



Following general procedure C: The reaction was performed with **6ba** (0.1 mmol, 1 equiv.), DABCO (0.40 mmol, 4.0 equiv) and degassed toluene (2.5 mL) at 50°C for 12 h. Product **7ba** was obtained as a white solid with 95% yield.

^{1}H NMR (Toluene-d_8, 400 MHz): δ 7.50 – 7.40 (m, 2H, C*H*$_{Ar}$), 7.38 – 7.28 (m, 2H, C*H*$_{Ar}$), 7.20 – 7.04 (m, 12H, C*H*$_{Ar}$), 7.00 – 6.96 (m, 1H, C*H*$_{Ar}$), 6.95 – 6.79 (m, 5H, C*H*$_{Ar}$), 6.67 – 6.59 (m, 2H, C*H*$_{Ar}$), 3.58 – 3.44 (m, 1H, PPh$_2$C*H*), 3.28 (s, 3H, OC*H*$_3$), 2.73 – 2.53 (m, 2H, PPh$_2$CH*H*).
^{13}C NMR (Toluene-d_8, 101 MHz): δ 158.8, 158.8, 140.2, 140.0, 139.1, 139.0, 138.1, 138.1, 137.9, 137.9, 137.7, 134.7, 134.5, 134.5, 134.3, 133.7, 133.5, 132.9, 132.9, 132.8, 132.8, 132.5, 132.3, 130.8, 130.7, 129.3, 129.2, 128.8, 128.7, 128.4, 128.4, 128.0, 128.0, 128.0, 114.0, 54.5, 41.9, 41.8, 41.6, 34.3, 34.1, 34.1, 33.9. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (Toluene-d_8, 162 MHz): δ -1.4 (d, *J* = 17.2 Hz), -24.0 (d, *J* = 17.2 Hz).
HRMS (ESI, m/Z): calcd. for $C_{33}H_{31}OP_2$ $[M+H]^+$: 505.1845, found: 505.1857.

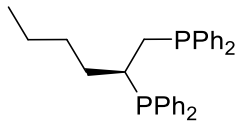
(S)-(1-ferrocenylethane-1,2-diyl)bis(diphenylphosphane) (7ca)



Following general procedure C: The reaction was performed with **6ca** (0.1 mmol, 1 equiv.), DABCO (0.40 mmol, 4.0 equiv) and degassed toluene (2.5 mL) at 50°C for 12 h. Product **7ca** was obtained as an yellow solid with 98% yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 – 7.51 (m, 2H, C*H*$_{Ar}$), 7.47 – 7.42 (m, 2H, C*H*$_{Ar}$), 7.41 – 7.35 (m, 6H, C*H*$_{Ar}$), 7.33 – 7.27 (m, 6H, C*H*$_{Ar}$), 7.24 – 7.19 (m, 2H, C*H*$_{Ar}$), 7.19 – 7.13 (m, 2H, C*H*$_{Ar}$), 4.05 – 3.86 (m, 7H, C*H*$_{Fe}$), 3.79 (s, 1H, C*H*$_{Fe}$), 3.61 (s, 1H, C*H*$_{Fe}$), 3.32 – 3.13 (m, 1H, PPh_2C*H*), 2.81 – 2.63 (m, 1H, PPh_2CH*H*), 2.37 – 2.27 (m, 1H, PPh_2CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.2, 139.1, 139.0, 139.0, 137.8, 137.8, 137.7, 137.6, 135.6, 135.4, 134.2, 134.1, 133.5, 133.3, 132.9, 132.8, 132.8, 132.7, 129.1, 128.8, 128.5, 128.5, 128.4, 128.4, 128.0, 128.0, 127.8, 127.7, 127.7, 91.1, 91.0, 68.5, 68.0, 67.5, 67.0, 66.3, 36.5, 36.4, 36.4, 36.2, 32.5, 32.4, 32.4, 32.3. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 6.1 (d, *J* = 64.7 Hz), -19.6 (d, *J* = 64.7Hz).
HRMS (ESI, m/Z): calcd. for $C_{36}H_{33}FeP_2$ $[M+H]^+$: 583.1401, found: 583.1394.

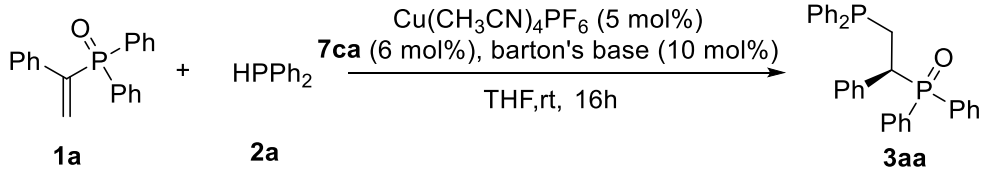
(S)-hexane-1,2-diylbis(diphenylphosphane (7da)



Following general procedure C: The reaction was performed with **6da** (0.1 mmol, 1 equiv.), DABCO (0.40 mmol, 4.0 equiv) and degassed toluene (2.5 mL) at 50°C for 12 h. Product **7da** was obtained as a white solid with 96% yield.

^{1}H NMR (Toluene-d_8, 400 MHz): δ 7.42 – 7.31 (m, 6H, C*H*$_{Ar}$), 7.30 – 7.23 (m, 2H, C*H*$_{Ar}$), 7.12 – 6.94 (m, 12H, C*H*$_{Ar}$), 2.49 – 2.34 (m, 2H), 2.12 – 2.06 (m, 1H), 2.00 – 1.87 (m, 1H), 1.84 – 1.75 (m, 1H), 1.72 – 1.61 (m, 1H), 1.56 – 1.46 (m, 1H), 1.29 – 1.17 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H, C*H*$_3$).
^{13}C NMR (Toluene-d_8, 101 MHz): δ 140.1, 140.0, 139.3, 139.2, 138.1, 138.0, 137.6, 137.6, 137.3, 137.3, 134.6, 134.4, 134.4, 134.2, 133.8, 133.7, 132.7, 132.6, 129.2, 129.1, 128.9, 128.6, 128.6, 128.6, 128.5, 128.1, 128.5, 128.2, 33.2, 33.1, 33.1, 33.0, 31.2, 31.2, 31.1, 31.1, 31.1, 31.0, 29.6, 29.6, 29.5, 23.4, 14.2. (Due to C−P coupling and the complexity of the spectrum, doublets cannot be assigned and they are listed as singlets)
^{31}P NMR (Toluene-d_8, 162 MHz): δ -3.8 (d, *J* = 21.2 Hz), -20.5 (d, *J* = 21.2 Hz).
HRMS (ESI, m/Z): calcd. for $C_{30}H_{33}P_2$ $[M+H]^+$: 455.2052, found: 455.2052.

4. Application of 7ca in the catalytic asymmetric hydrophosphination of 1a and 8



1a **2a** **3aa**

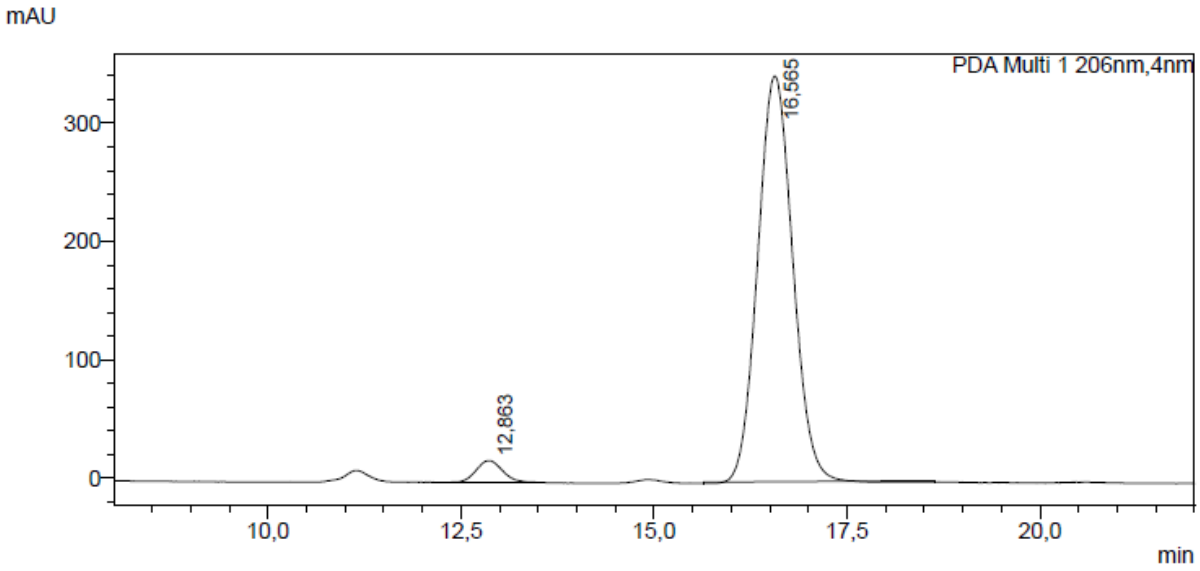
90% yield, 92% ee

General Procedure for hydrophosphination of 1a: In a 4 mL oven dried vial equipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (0.005 mmol, 5 mol%) and **7ca**

(0.005 mmol, 6 mol%) in a glove box under N_2 atmosphere. Anhydrous THF (1.0 mL) was added. The mixture was stirred at room temperature for 15 minutes to give a yellow catalyst solution. Then **1a** (0.1 mmol, 1.0 equiv) and **2a** (0.1 mmol, 1.0 equiv) were added sequentially and stirred for 2 min. Barton's Base (0.01 mmol, 10 mol%) was added. The resulting reaction mixture was stirred at room temperature for 16 hours. Then, the reaction mixture was concentrated under reduced pressure, the residue was purified by silica gel column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) to give the desired product **3aa** [90% yield, 92% ee].

HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 206 nm. Retention time (min): 12.9 (minor) and 16.6 (major).

<Chromatogram>

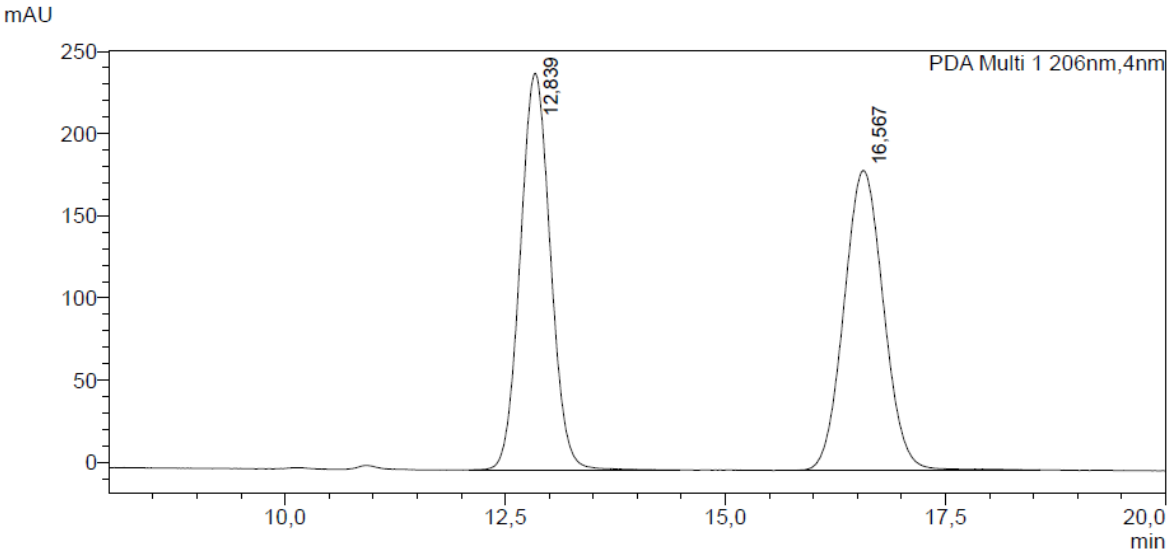


<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Area%
1	12,863	438078	18481	3,923
2	16,565	10728322	342696	96,077
Total		11166400	361178	100,000

<Chromatogram>



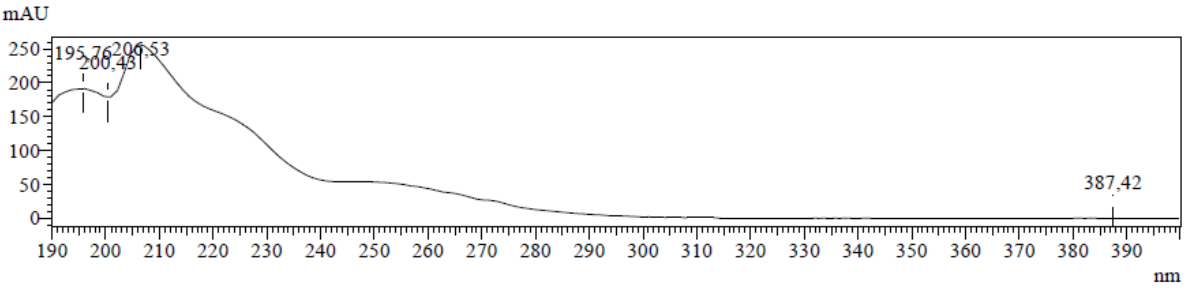
<Peak Table>

PDA Ch1 206nm

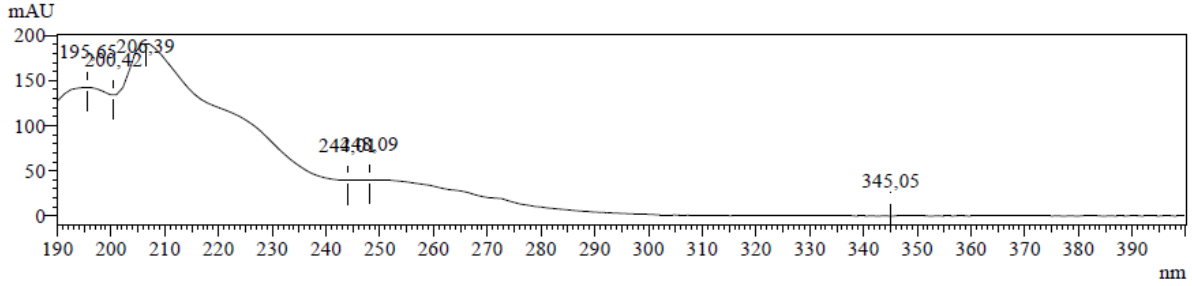
Peak#	Ret. Time	Area	Height	Area%
1	12,839	5752588	241197	50,190
2	16,567	5709111	182401	49,810
Total		11461699	423597	100,000

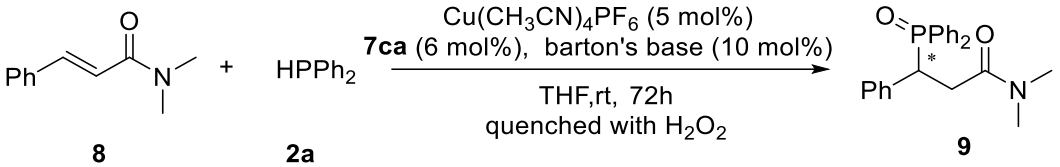
UV Spectrum

Peak# : 1
Retention Time : 12,839 min
Compound Name :
Spectrum Operation:



Peak# : 2
Retention Time : 16,567 min
Compound Name :
Spectrum Operation:





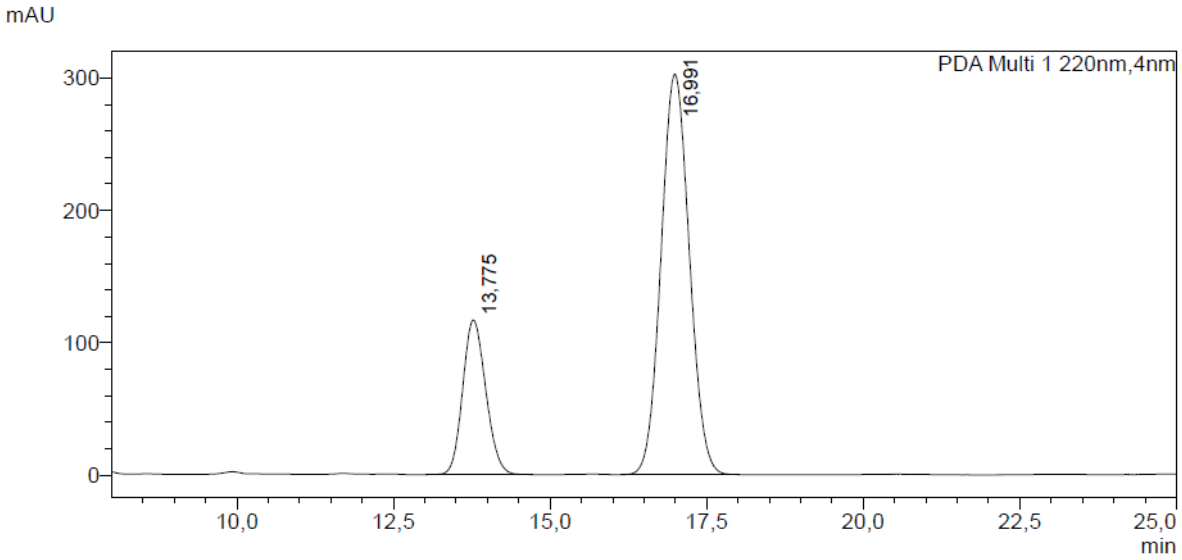
General Procedure for hydrophosphination of 8: In a 4 mL oven dried vial equipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (0.005 mmol, 5 mol%) and **7ca** (0.005 mmol, 6 mol%) in a glove box under N_2 atmosphere. Anhydrous THF (1.0 mL) was added. The mixture was stirred at room temperature for 15 minutes to give a yellow catalyst solution. Then **8** (0.1 mmol, 1.0 equiv) and **2a** (0.1 mmol, 1.0 equiv) were added sequentially and stirred for 2 min. Barton's Base (0.01 mmol, 10 mol%) was added. The resulting reaction mixture was stirred at room temperature for 72 hours. Then, the reaction mixture was quenched by 30% H_2O_2 aqueous solution (25 μL) and was stirred for additional 30 minutes at room temperature. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (SiO_2, pentane/ethyl acetate/methanol = 1:1:0.05) to give the desired product **9** [82% yield, 52% ee].

The NMR data are in agreement with the one present in literature.[2]

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 – 7.93 (m, 2H, C*H*$_{Ar}$), 7.53 – 7.50 (m, 3H, C*H*$_{Ar}$), 7.41 – 7.36 (m, 2H, C*H*$_{Ar}$), 7.33 – 7.31 (m, 2H, C*H*$_{Ar}$), 7.28 – 7.24 (m, 1H, C*H*$_{Ar}$), 7.19 – 7.06 (m, 5H, C*H*$_{Ar}$), 4.36 – 4.31 (m, 1H), 3.21 – 3.13 (m, 1H), 2.84 – 2.71 (m, 7H).

HPLC: Chiracel-ADH, *n*-heptane/*i*-PrOH 80:20, 1.0 mL/min., 40 °C, detection at 220 nm. Retention time (min): 13.8 (minor) and 17.0 (major).

<Chromatogram>



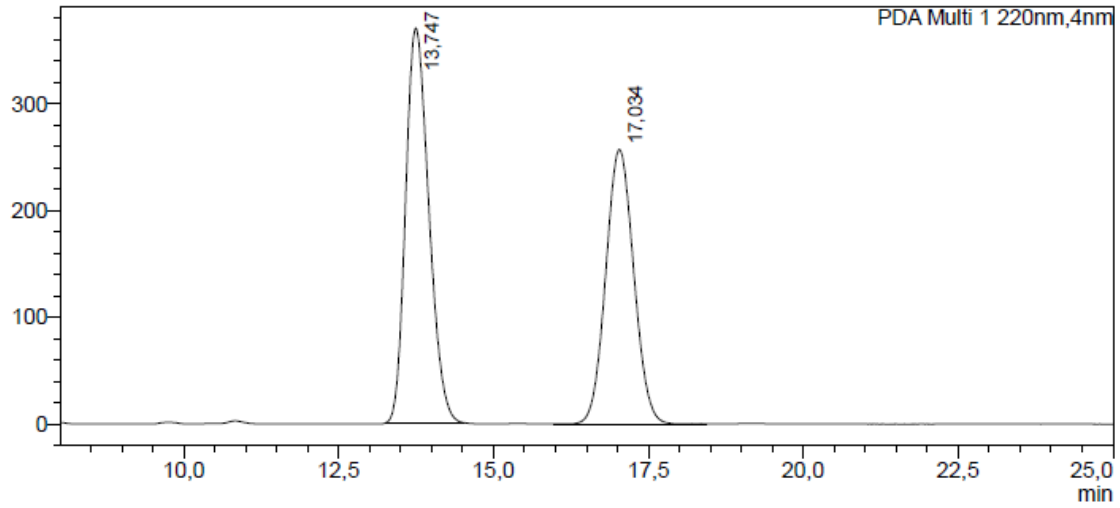
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	13,775	3005867	116797	24,024
2	16,991	9506153	302684	75,976
Total		12512020	419481	100,000

<Chromatogram>

mAU



<Peak Table>

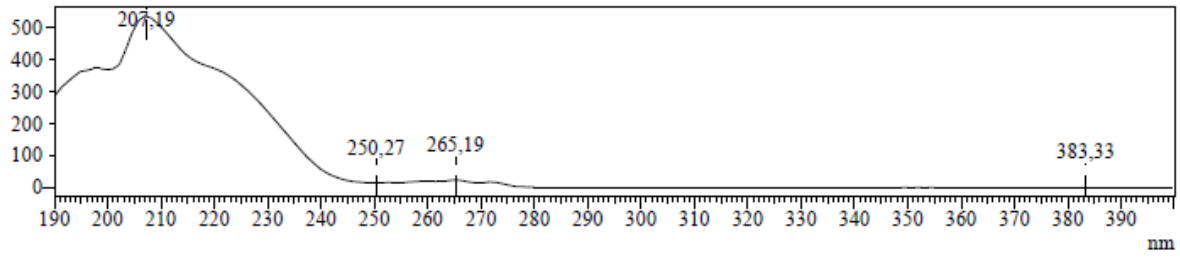
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	13,747	9643914	370014	54,350
2	17,034	8100020	257258	45,650
Total		17743934	627272	100,000

UV Spectrum

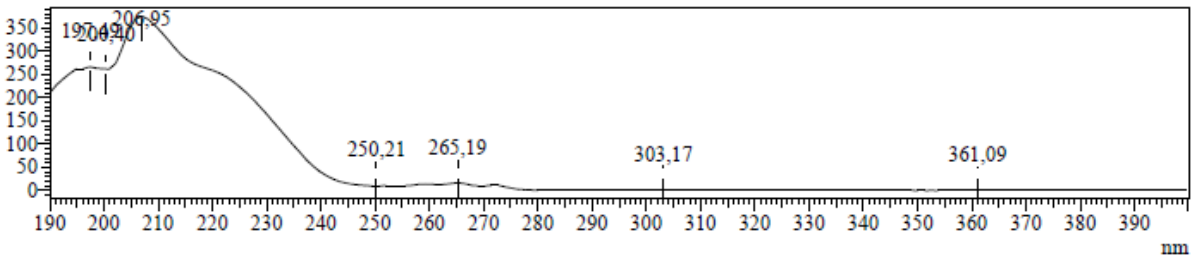
Peak# : 1
Retention Time : 13,747 min
Compound Name :
Spectrum Operation:

mAU



Peak# : 2
Retention Time : 17,034 min
Compound Name :
Spectrum Operation:

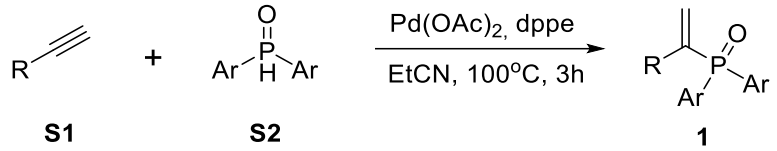
mAU



5. Substrate Synthesis

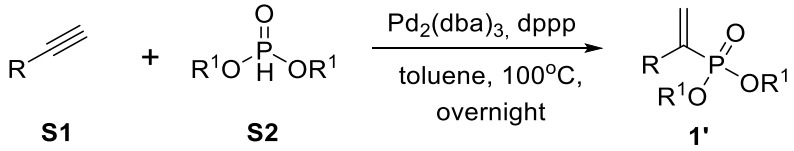
α, β-unsaturated phosphine oxides **1a−1y** were synthesized by a known literature procedure (Method A),[3] among them **1g-1l, 1n, 1o, 1q-1s, 1u,** and **1w-1y** are new compounds. α, β-unsaturated phosphonates **1'a−1'e** were synthesized by a known literature procedure (Method B).[4] α, β-unsaturated phosphine oxide **1z** was synthesized by a known literature procedure (Method C).[5] The mesityl(phenyl)phosphane (**2h**) was synthesized by a known literature procedure.[6] The spectroscopic data of new compounds are shown below.

Method A:



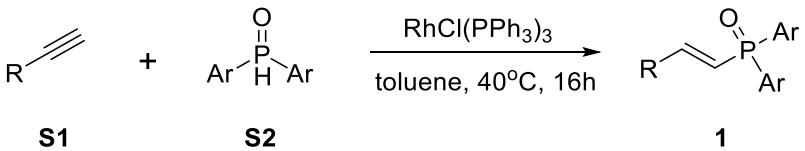
A mixture of $Pd(OAc)_2$ (5 mol%), dppe (7.5 mol%), diarylphosphine oxide **S2** (1.0 equiv), and acetylene derivative **S1** (1.1 equiv) dissolved in propionitrile (3 ml/mmol) was heated at 100 °C for 3 h. The resulting mixture was evaporated and the residue was purified by column chromatography using pentane/ethyl acetate (1/1) afforded the product **1**.

Method B:



An oven-dried schlenck tube containing a Teflon-coated stir bar was charged with 0.5 mol% $Pd_2(dba)_3$, 1 mol% dppp and toluene (2 ml/mmol) under N_2 atmosphere and stirred at room temperature for 10 min, then H-phosphonate **S2** (1.0 equiv) and alkyne **S1** (1.0 equiv) were added and the mixture was stirred at 100 °C overnight. The resulting mixture was evaporated and the residue was purified by column chromatography using pentane /ethyl acetate (3/1) afforded the product **1'**.

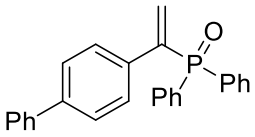
Method C:



Diarylphosphine oxide **S2** (1.0 equiv), alkyne **S1** (1.1 equiv) and $RhCl(PPh_3)_3$ (3 mol %) were dissolved in dry toluene (2 ml/mmol) under N_2 atmosphere. The resulting transparent yellow

solution was heated at 40 °C for 16h. The solvent was evaporated under reduced pressure to give a yellow semisolid. The crude product was then purified by column chromatography using pentane /ethyl acetate (2/1) afforded the product **1**.

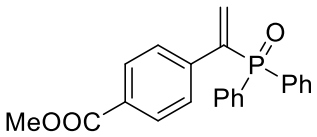
(1-([1,1'-biphenyl]-4-yl)vinyl)diphenylphosphine oxide (1g)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 46% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 – 7.70 (m, 4H, C*H*$_{Ar}$), 7.61 – 7.36 (m, 14H, C*H*$_{Ar}$), 7.35 – 7.30 (m, 1H, C*H*$_{Ar}$), 6.30 (dd, *J* = 40.4, 1.1 Hz, 1H, CH*H*), 5.74 (dd, *J* = 19.8, 1.1 Hz, 1H, CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 144.0 (d, *J* = 92.6 Hz), 141.1, 140.5 136.6 (d, *J* = 9.9 Hz), 132.2, 132.1, 132.0, 131.9 (d, *J* = 103.5 Hz), 131.8 (d, *J* = 10.0 Hz), 128.9, 128.6 (d, *J* = 12.1 Hz), 128.6 (d, *J* = 4.7 Hz), 127.6, 127.2 (d, *J* = 12.5 Hz).
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.3.
HRMS (ESI, m/Z): calcd. for $C_{26}H_{22}OP$ $[M+H]^+$: 381.1403, found: 381.1407.

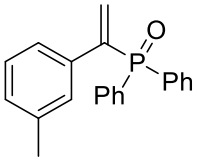
methyl 4-(1-(diphenylphosphoryl)vinyl)benzoate (1h)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 46% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 – 7.85 (m, 2H, C*H*$_{Ar}$), 7.77 – 7.64 (m, 4H, C*H*$_{Ar}$), 7.60 – 7.54 (m, 2H, C*H*$_{Ar}$), 7.54 – 7.47 (m, 2H, C*H*$_{Ar}$), 7.47 – 7.38 (m, 4H, C*H*$_{Ar}$), 6.29 (d, *J* = 39.6 Hz, 1H, CH*H*), 5.79 (d, *J* = 19.6 Hz, 1H, CH*H*), 3.86 (s, 3H, COOC*H*$_3$).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 166.8, 144.0 (d, *J* = 92.4 Hz), 142.3 (d, *J* = 9.9 Hz), 133.1 (d, *J* = 9.3 Hz), 132.2 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 9.8 Hz), 131.2 (d, *J* = 104.0 Hz), 129.8, 129.8, 128.7 (d, *J* = 12.3 Hz), 128.2 (d, *J* = 4.6 Hz), 52.2.
^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.8.
HRMS (ESI, m/Z): calcd. for $C_{22}H_{20}O_3P$ $[M+H]^+$: 363.1145, found: 363.1147.

diphenyl(1-(m-tolyl)vinyl)phosphine oxide (1i)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 57% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 – 7.64 (m, 4H, C*H*$_{Ar}$), 7.53 – 7.46 (m, 2H, C*H*$_{Ar}$), 7.45 – 7.36 (m, 4H, C*H*$_{Ar}$), 7.27 – 7.19 (m, 2H, C*H*$_{Ar}$), 7.12 – 7.09 (m, 1H, C*H*$_{Ar}$), 7.03 (d, *J* = 7.6 Hz,

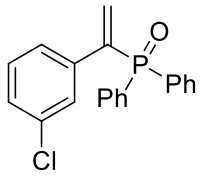
1H, C*H*$_{Ar}$), 6.21 (dd, *J* = 40.2, 1.2 Hz, 1H, CH*H*), 5.73 (dd, *J* = 19.7, 0.9 Hz, 1H, CH*H*), 2.24 (s, 3H, C*H*$_3$).

^{13}C NMR (CDCl$_3$, 101 MHz): δ 144.5 (d, *J* = 92.3 Hz), 138.1, 137.6 (d, *J* = 9.9 Hz), 132.1 (d, *J* = 9.5 Hz), 132.0, 132.0, 131.8 (d, *J* = 103.5 Hz), 129.1, 128.9 (d, *J* = 4.5 Hz), 128.8 (d, *J* = 13.5 Hz). 128.4, 125.4 (d, *J* = 4.7 Hz), 21.5.

^{31}P NMR (162 MHz, CDCl$_3$): δ 27.0.

HRMS (ESI, m/Z): calcd. for $C_{21}H_{20}OP$ $[M+H]^+$: 319.1246, found: 319.1243.

(1-(3-chlorophenyl)vinyl)diphenylphosphine oxide (1j)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 66% of yield.

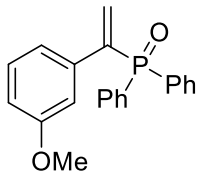
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.78 – 7.64 (m, 4H, C*H*$_{Ar}$), 7.57 – 7.35 (m, 8H, C*H*$_{Ar}$), 7.25 – 7.08 (m, 2H, C*H*$_{Ar}$), 6.23 (d, *J* = 39.6 Hz, 1H, CH*H*), 5.74 (d, *J* = 19.5 Hz, 1H, CH*H*).

^{13}C NMR (CDCl$_3$, 101 MHz): δ 143.5 (d, *J* = 92.6 Hz), 139.4 (d, *J* = 9.9 Hz), 134.4, 132.8 (d, *J* = 9.6 Hz), 132.2 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 9.8 Hz), 131.3 (d, *J* = 104.1 Hz), 129.8, 128.7 (d, *J* = 12.1 Hz), 128.4, 128.1 (d, *J* = 4.9 Hz), 126.6 (d, *J* = 4.4 Hz).

^{31}P NMR (CDCl$_3$, 162 MHz): δ 26.9.

HRMS (ESI, m/Z): calcd. for $C_{20}H_{17}ClOP$ $[M+H]^+$: 339.0700, found: 339.0701.

(1-(3-methoxyphenyl)vinyl)diphenylphosphine oxide (1k)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 70% of yield.

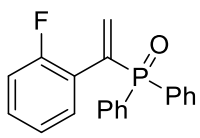
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.78 – 7.64 (m, 4H, C*H*$_{Ar}$), 7.56 – 7.47 (m, 2H, C*H*$_{Ar}$), 7.47 – 7.39 (m, 4H, C*H*$_{Ar}$), 7.17 – 7.13 (m, 1H, C*H*$_{Ar}$), 7.06 – 6.96 (m, 2H, C*H*$_{Ar}$), 6.83 – 6.74 (m, 1H, C*H*$_{Ar}$), 6.25 (dd, *J* = 39.8, 0.8 Hz, 1H, CH*H*), 5.85 – 5.73 (m, 1H, CH*H*), 3.67 (s, 3H, OC*H*$_3$).

^{13}C NMR (CDCl$_3$, 101 MHz): δ 159.3, 144.2 (d, *J* = 92.4 Hz), 138.9 (d, *J* = 10.3 Hz), 132.1, 132.0 (d, *J* = 9.6 Hz), 131.9, 131.1, 129.4, 128.4 (d, *J* = 12.1 Hz), 120.6 (d, *J* = 4.8 Hz), 114.2, 113.3 (d, *J* = 4.6 Hz), 55.1.

^{31}P NMR (CDCl$_3$, 162 MHz): δ 29.5.

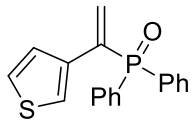
HRMS (ESI, m/Z): calcd. for $C_{21}H_{20}O_2P$ $[M+H]^+$: 335.1195, found: 335.1197.

(1-(2-fluorophenyl)vinyl)diphenylphosphine oxide (3l)



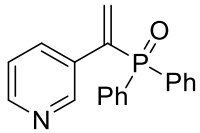
The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 70% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 – 7.69 (m, 4H, C*H*$_{Ar}$), 7.55 – 7.47 (m, 3H, C*H*$_{Ar}$), 7.47 – 7.38 (m, 4H, C*H*$_{Ar}$), 7.24 – 7.12 (m, 1H, C*H*$_{Ar}$), 7.03 – 6.92 (m, 2H, C*H*$_{Ar}$), 6.29 (d, *J* = 40.1 Hz, 1H, CH*H*), 6.03 (d, *J* = 19.8 Hz, 1H, CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.6 (dd, *J* = 247.7, 5.6 Hz), 138.0 (d, *J* = 94.3 Hz), 135.7 (dd, *J* = 8.8, 3.4 Hz), 132.1, 132.1, 132.0, 131.7, 131.3, 131.3, 131.3, 130.7, 129.8 (dd, *J* = 8.3, 1.4 Hz), 128.6 (d, *J* = 12.2 Hz), 125.0 (dd, *J* = 14.2, 10.4 Hz), 124.0 (dd, *J* = 3.7, 1.3 Hz), 115.9 (d, *J* = 22.6 Hz).
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.0.
^{19}F NMR (**$CDCl_3$, 376 MHz**) δ -115.4.
HRMS (ESI, m/Z): calcd. for $C_{20}H_{16}FOP$ $[M+H]^+$: 323.0996, found: 323.0999.
diphenyl(1-(thiophen-3-yl)vinyl)phosphine oxide (1n)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 71% of yield.

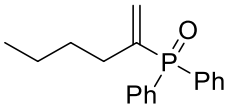
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 – 7.65 (m, 4H, C*H*$_{Ar}$), 7.56 – 7.48 (m, 3H, C*H*$_{Ar}$), 7.48 – 7.40 (m, 4H, C*H*$_{Ar}$), 7.24 – 7.16 (m, 2H, C*H*$_{Ar}$), 6.29 (d, *J* = 40.7 Hz, 1H, CH*H*), 5.58 (d, *J* = 20.0 Hz, 1H, CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.5 (d, *J* = 94.9 Hz), 137.2, 132.0, 131.9, 131.0, 129.4 (d, *J* = 9.3 Hz), 128.5 (d, *J* = 12.2 Hz), 126.5 (d, *J* = 6.0 Hz), 125.6, 124.8 (d, *J* = 3.5 Hz).
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.7.
HRMS (ESI, m/Z): calcd. for $C_{18}H_{16}OPS$ $[M+H]^+$: 311.0654, found: 311.0653.
diphenyl(1-(pyridin-3-yl)vinyl)phosphine oxide (1o)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 66% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.62 (s, 1H, C*H*$_{Ar}$), 8.47 (d, *J* = 4.9 Hz, 1H, C*H*$_{Ar}$), 7.98 – 7.89 (m, 1H, C*H*$_{Ar}$), 7.78 – 7.64 (m, 4H, C*H*$_{Ar}$), 7.56 – 7.49 (m, 2H, C*H*$_{Ar}$), 7.49 – 7.41 (m, 4H, C*H*$_{Ar}$), 7.16 (dd, *J* = 8.0, 4.8 Hz, 1H, C*H*$_{Ar}$), 6.27 (d, *J* = 39.5 Hz, 1H, CH*H*), 5.77 (d, *J* = 19.5 Hz, 1H, CH*H*).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 149.3 (d, *J* = 1.3 Hz), 148.6 (d, *J* = 5.5 Hz), 141.7 (d, *J* = 92.7 Hz), 136.0 (d, *J* = 3.6 Hz), 133.8 (d, *J* = 9.8 Hz), 133.0 (d, *J* = 9.4 Hz), 132.3 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 9.7 Hz), 130.9 (d, *J* = 104.2 Hz), 128.8 (d, *J* = 12.3 Hz), 123.2.
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.0.
HRMS (ESI, m/Z): calcd. for $C_{19}H_{16}NOP$ $[M+H]^+$: 306.1042, found: 306.1046.

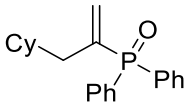
hex-1-en-2-yldiphenylphosphine oxide (1q)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 67% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 – 7.63 (m, 4H, C*H*$_{Ar}$), 7.59 – 7.35 (m, 6H, C*H*$_{Ar}$), 5.93 (d, *J* = 43.1 Hz, 1H, CH_2CCH*H*), 5.60 (d, *J* = 20.9 Hz, 1H, CH_2CCH*H*), 2.30 (q, *J* = 8.6 Hz, 2H), 1.54 – 1.38 (m, 2H), 1.33 – 1.19 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H, C*H*$_3$).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 144.2 (d, *J* = 91.5 Hz), 132.1, 132.0, 131.0, 128.8, 128.6 (d, *J* = 12.0 Hz), 31.4 (d, *J* = 10.4 Hz), 30.3 (d, *J* = 5.4 Hz), 22.4, 14.0.
^{31}P NMR ($CDCl_3$, 162 MHz): δ 28.8.
HRMS (ESI, m/Z): calcd. for $C_{18}H_{22}OP$ $[M+H]^+$: 285.1403, found: 285.1406.

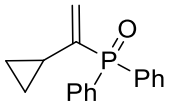
(3-cyclohexylprop-1-en-2-yl)diphenylphosphine oxide (1r)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 86% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 – 7.63 (m, 4H, C*H*$_{Ar}$), 7.57 – 7.40 (m, 6H, C*H*$_{Ar}$), 5.88 (dd, *J* = 43.2, 1.1 Hz, 1H,C=CH*H*), 5.63 (d, *J* = 20.8 Hz, 1H, C=CH*H*), 2.19 (dd, *J* = 12.0, 7.0 Hz, 2H, CH_2=CC*H*$_2$), 1.74 – 1.51 (m, 5H), 1.50 – 1.35 (m, 1H), 1.17 – 0.99 (m, 3H), 0.84 – 0.67 (m, 2H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.1 (d, *J* = 91.0 Hz), 131.9 (d, *J* = 9.6 Hz), 131.8 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 101.3 Hz), 129.8 (d, *J* = 10.1 Hz), 128.4 (d, *J* = 12.0 Hz), 39.9 (d, *J* = 10.1 Hz), 35.8 (d, *J* = 4.0 Hz), 33.0, 26.4, 26.1.
^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.6.
HRMS (ESI, m/Z): calcd. for $C_{21}H_{26}OP$ $[M+H]^+$: 325.1716, found: 325.1720.

(1-cyclopropylvinyl)diphenylphosphine oxide (1s)

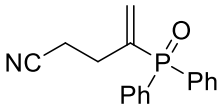


The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 56% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 – 7.69 (m, 4H, C*H*$_{Ar}$), 7.57 – 7.48 (m, 2H, C*H*$_{Ar}$), 7.49 – 7.42 (m, 4H, C*H*$_{Ar}$), 5.65 (d, *J* = 40.5 Hz, 1H, C=CH*H*), 5.60 (d, *J* = 20.0 Hz, 1H, C=CH*H*), 1.62 – 1.48 (m, 1H, CH_2CH_2CH), 0.80 – 0.67 (m, 2H, $CHCH_2CH_2$), 0.60 – 0.52 (m, 2H, $CHCH_2CH_2$).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.8 (d, *J* = 93.5 Hz), 132.0 (d, *J* = 9.8 Hz), 131.8 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 102.0 Hz), 128.4 (d, *J* = 11.9 Hz), 124.6 (d, *J* = 9.9 Hz), 12.8 (d, *J* = 16.2 Hz), 8.9 (d, *J* = 3.7 Hz).
^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.2.

HRMS (ESI, m/Z): calcd. for $C_{17}H_{18}OP$ $[M+H]^+$: 269.1090, found: 269.1091.

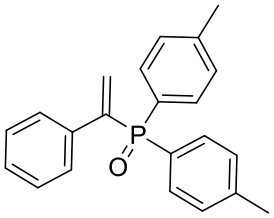
4-(diphenylphosphoryl)pent-4-enenitrile (1u)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 83% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 – 7.64 (m, 4H, C*H*$_{Ar}$), 7.62 – 7.42 (m, 6H, C*H*$_{Ar}$), 6.07 (d, *J* = 41.4 Hz, 1H, C=CH*H*), 5.58 (d, *J* = 19.7 Hz, 1H, C=CH*H*), 2.77 – 2.56 (m, 4H, C*H*$_2$C*H*$_2$).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 140.5 (d, *J* = 93.3 Hz), 132.4 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 9.8 Hz), 131.7 (d, *J* = 9.9 Hz), 130.4 (d, *J* = 102.8 Hz), 128.8 (d, *J* = 12.1 Hz), 118.8, 28.7 (d, *J* = 11.4 Hz), 17.2 (d, *J* = 3.9 Hz).
^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.9.
HRMS (ESI, m/Z): calcd. for $C_{17}H_{17}NOP$ $[M+H]^+$: 282.1042, found: 282.1046.

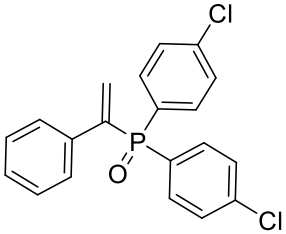
(1-phenylvinyl)di-p-tolylphosphine oxide (1w)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 70% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 – 7.52 (m, 4H, C*H*$_{Ar}$), 7.48 – 7.40 (m, 2H, C*H*$_{Ar}$), 7.26 – 7.16 (m, 7H, C*H*$_{Ar}$), 6.19 (d, *J* = 39.9 Hz, 1H, CH*H*), 5.72 (d, *J* = 19.6 Hz, 1H, CH*H*), 2.35 (s, 6H, 2xC*H*$_3$).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 144.7 (d, *J* = 92.4 Hz), 142.4 (d, *J* = 2.9 Hz), 137.8 (d, *J* = 9.9 Hz), 132.1 (d, *J* = 9.9 Hz), 131.7 (d, *J* = 9.7 Hz), 129.3 (d, *J* = 12.5 Hz), 128.5, 128.6 (d, *J* = 106.0 Hz), 128.2 (d, *J* = 4.7 Hz), 128.2 (d, *J* = 0.9 Hz), 21.7 (d, *J* = 1.4 Hz).
^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.4.
HRMS (ESI, m/Z): calcd. for $C_{22}H_{22}OP$ $[M+H]^+$: 333.1403, found: 333.1404.

bis(4-chlorophenyl)(1-phenylvinyl)phosphine oxide (1x)

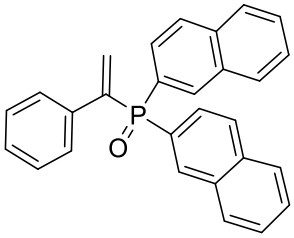


The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 54% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 – 7.54 (m, 4H, C*H*$_{Ar}$), 7.50 – 7.36 (m, 6H, C*H*$_{Ar}$), 7.33 – 7.19 (m, 3H, C*H*$_{Ar}$), 6.27 (d, *J* = 40.8 Hz, 1H, CH*H*), 5.77 (d, *J* = 20.2 Hz, 1H, CH*H*).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 144.0 (d, *J* = 94.3 Hz), 138.9 (d, *J* = 2.8 Hz), 137.1 (d, *J* = 9.8 Hz), 133.4 (d, *J* = 10.4 Hz), 132.5 (d, *J* = 9.4 Hz), 129.9 (d, *J* = 105.2 Hz), 129.1 (d, *J* = 12.8 Hz), 128.7, 128.7, 128.2 (d, *J* = 4.7 Hz).
^{31}P NMR ($CDCl_3$, 162 MHz): δ 28.5.
HRMS (ESI, m/Z): calcd. for $C_{20}H_{16}Cl_2OP$ $[M+H]^+$: 373.0310, found: 373.0312.

di(naphthalen-2-yl)(1-phenylvinyl)phosphine oxide (1y)



The product was synthesized following **Method A** obtained after column chromatography (SiO_2, EA:Pentane = 1:1) as a white solid 50% of yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, *J* = 13.6 Hz, 2H), 7.92 – 7.82 (m, 6H), 7.75 – 7.67 (m, 2H), 7.62 – 7.48 (m, 6H), 7.27 – 7.21 (m, 3H), 6.32 (dd, *J* = 40.4, 0.8 Hz, 1H), 5.87 (dd, *J* = 19.9, 0.8 Hz, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 144.5 (d, *J* = 92.7 Hz), 137.7 (d, *J* = 9.9 Hz), 134.8 (d, *J* = 2.3 Hz), 134.2 (d, *J* = 9.0 Hz), 132.6 (d, *J* = 13.4 Hz), 132.3 (d, *J* = 9.9 Hz), 129.1, 129.0 (d, *J* = 103.8 Hz), 128.6, 128.4, 128.4, 128.3, 128.3, 128.2 (d, *J* = 3.3 Hz), 127.0 (d, *J* = 0.7 Hz), 126.9 (d, *J* = 10.5 Hz).
^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.0.
HRMS (ESI, m/Z): calcd. for $C_{28}H_{22}OP$ $[M+H]^+$: 405.1403, found: 405.1402.

6. References

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(2) Y.-B. Li, H. Tian and L. Yin, *J. Am. Chem. Soc.* 2020, **142**, 20098–20106.

(3) N. Dobashi, K. Fuse, T. Hoshino, J. Kanada, T. Kashiwabara, C. Kobata, S. K. Nune and M. Tanaka, *Tetrahedron Lett.* 2007, **48**, 4669–4673.

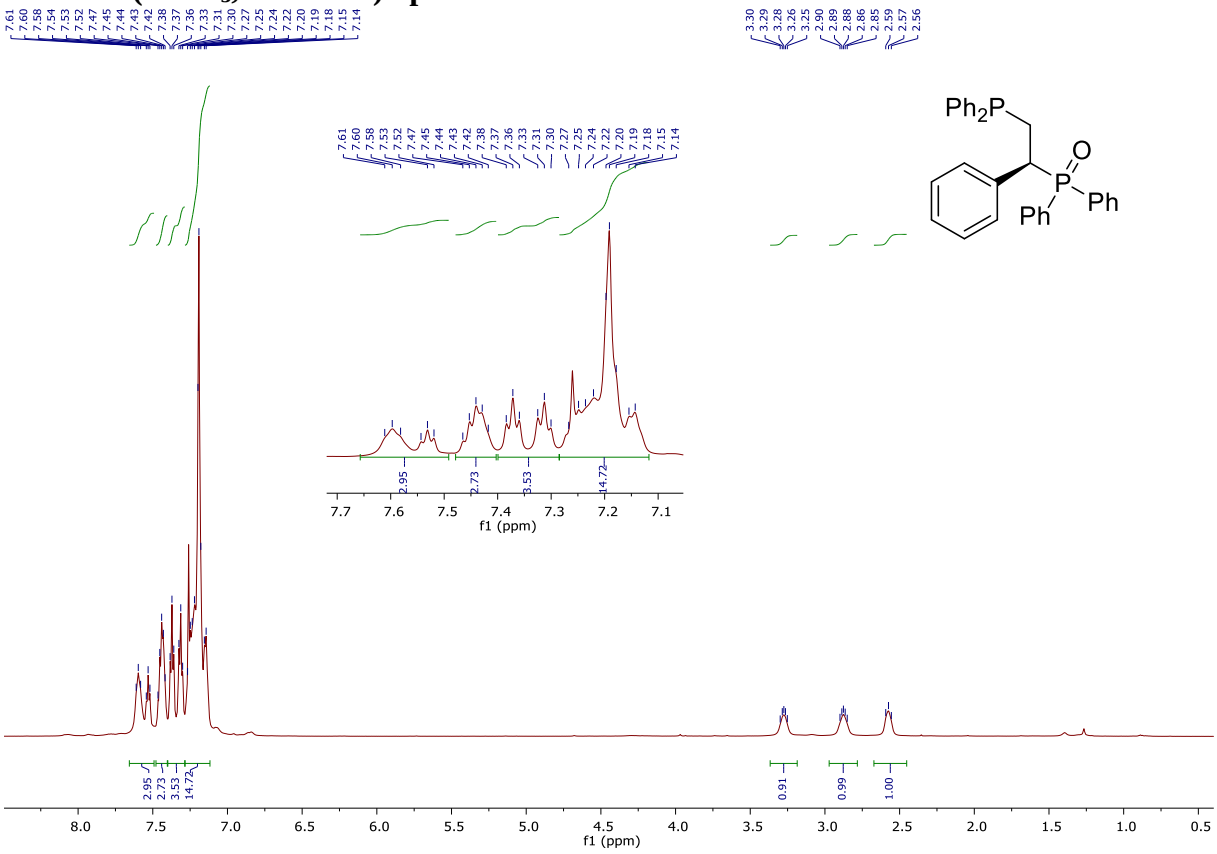
(4) T. Chen, C. Q. Zhao and L. B. Han, *J. Am. Chem. Soc.* 2018, **140**, 3139–3155.

(5) V. Hornillos, C. Vila, E. Otten and B. L. Feringa, *Angew. Chem., Int. Ed.* 2015, **54**, 7867–7871.

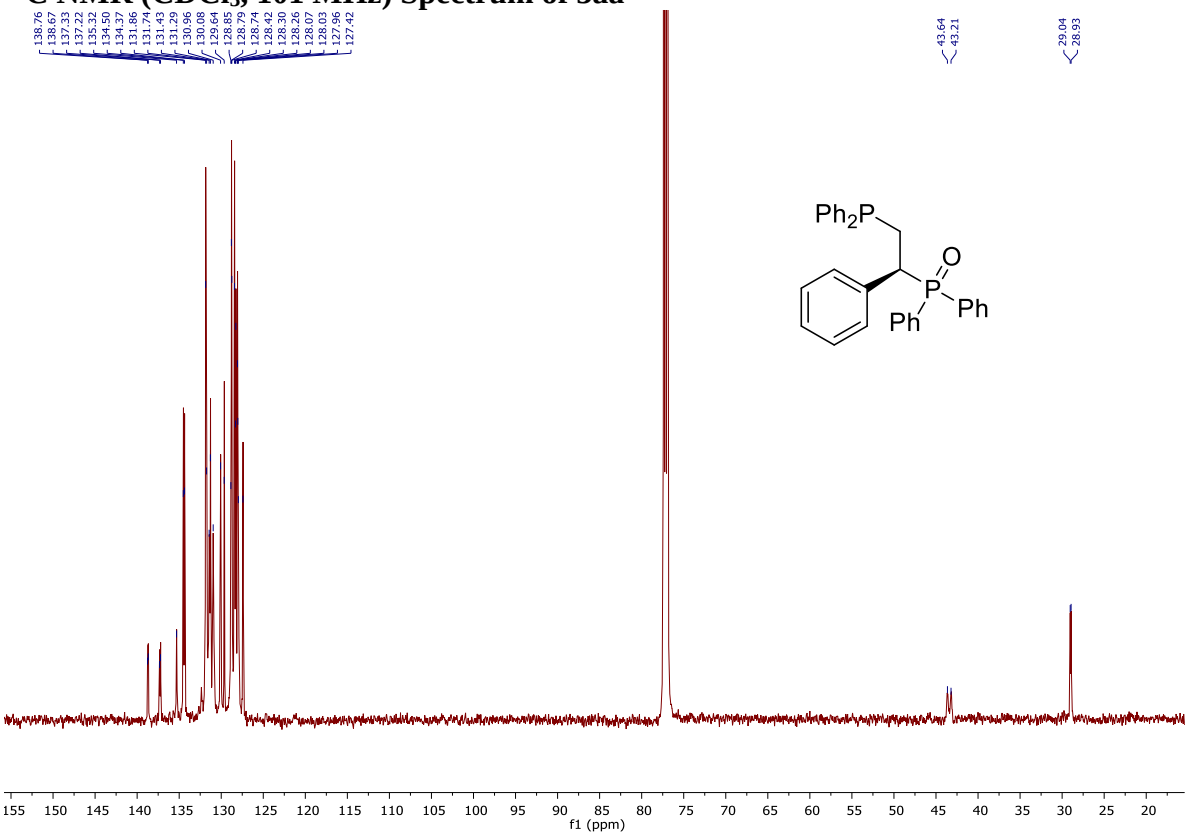
(6) Y.-B. Huang, Y.-X. Li, P.-H. Leung and T. Hayashi, *J. Am. Chem. Soc.* 2014, **136**, 4865–4868

7. NMR spectra

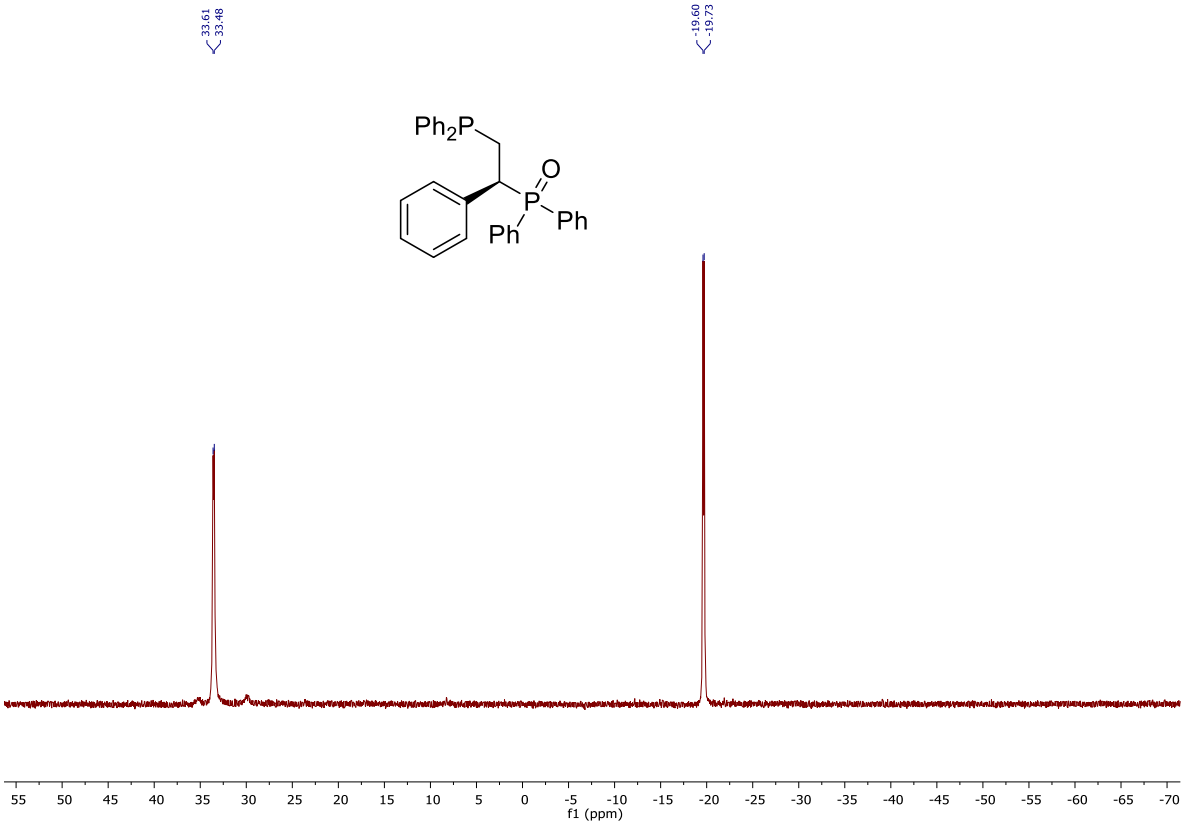
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3aa



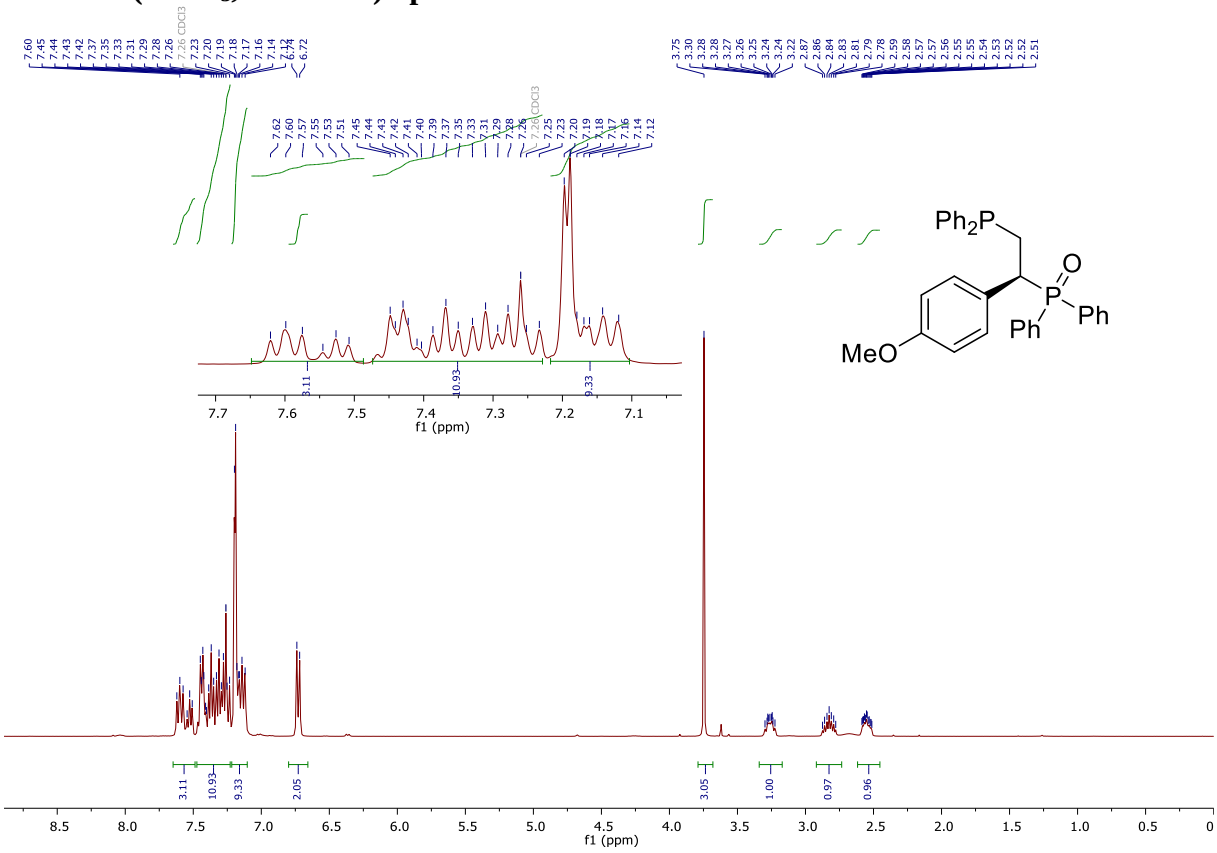
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3aa



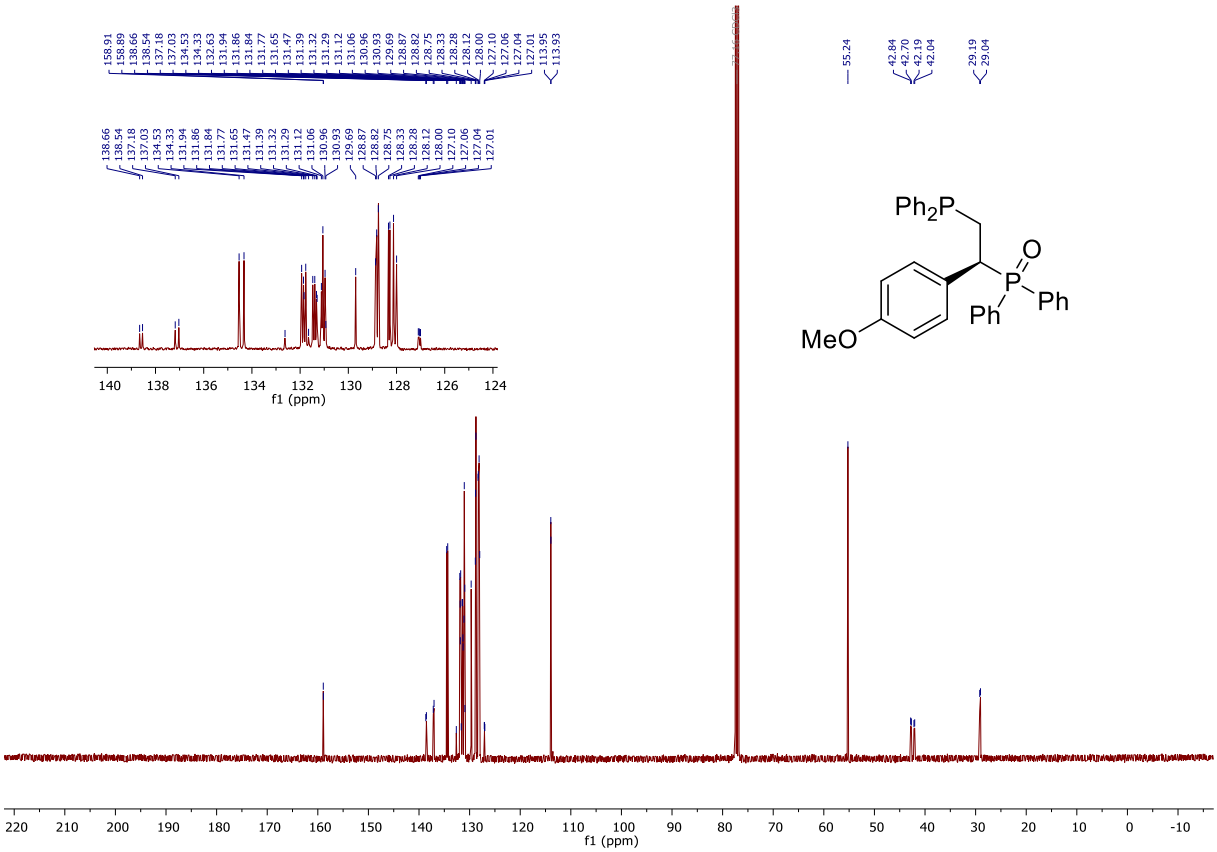
^{13}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3aa



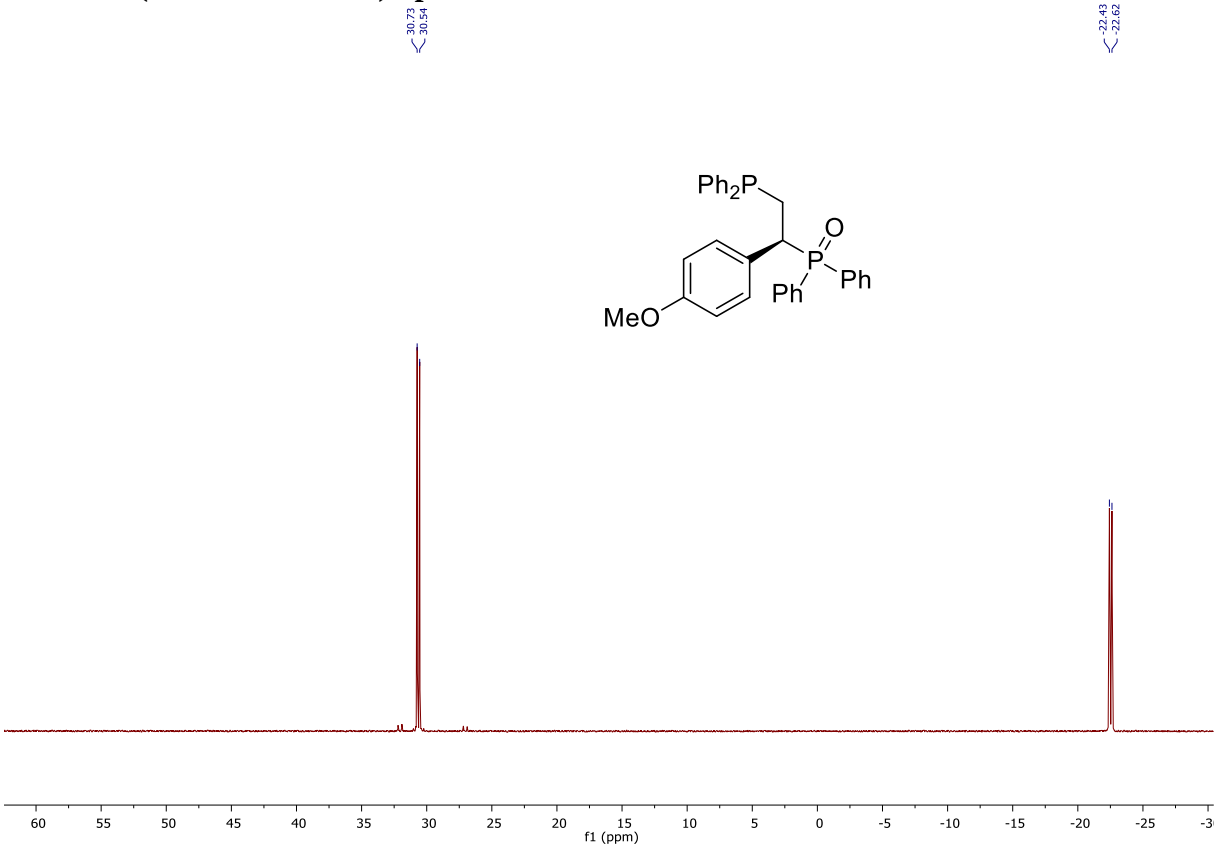
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ba



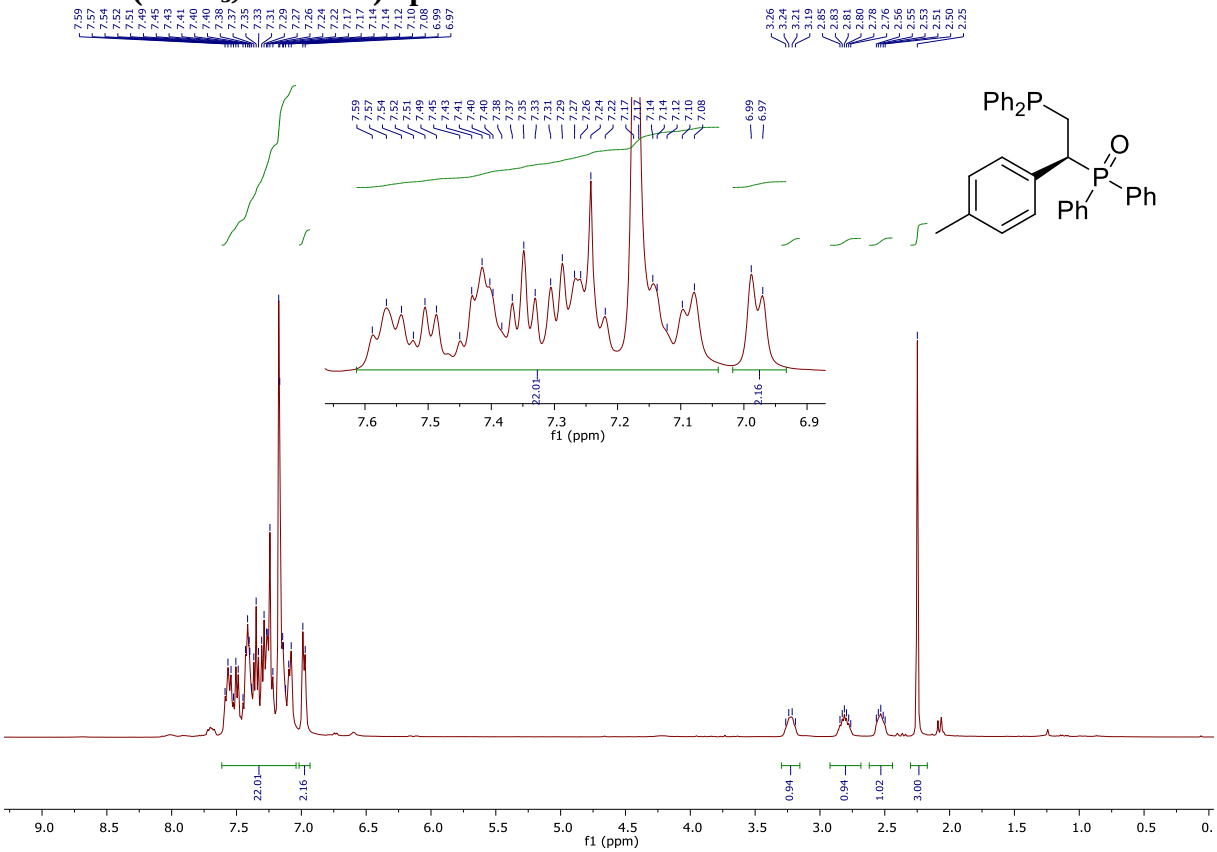
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ba



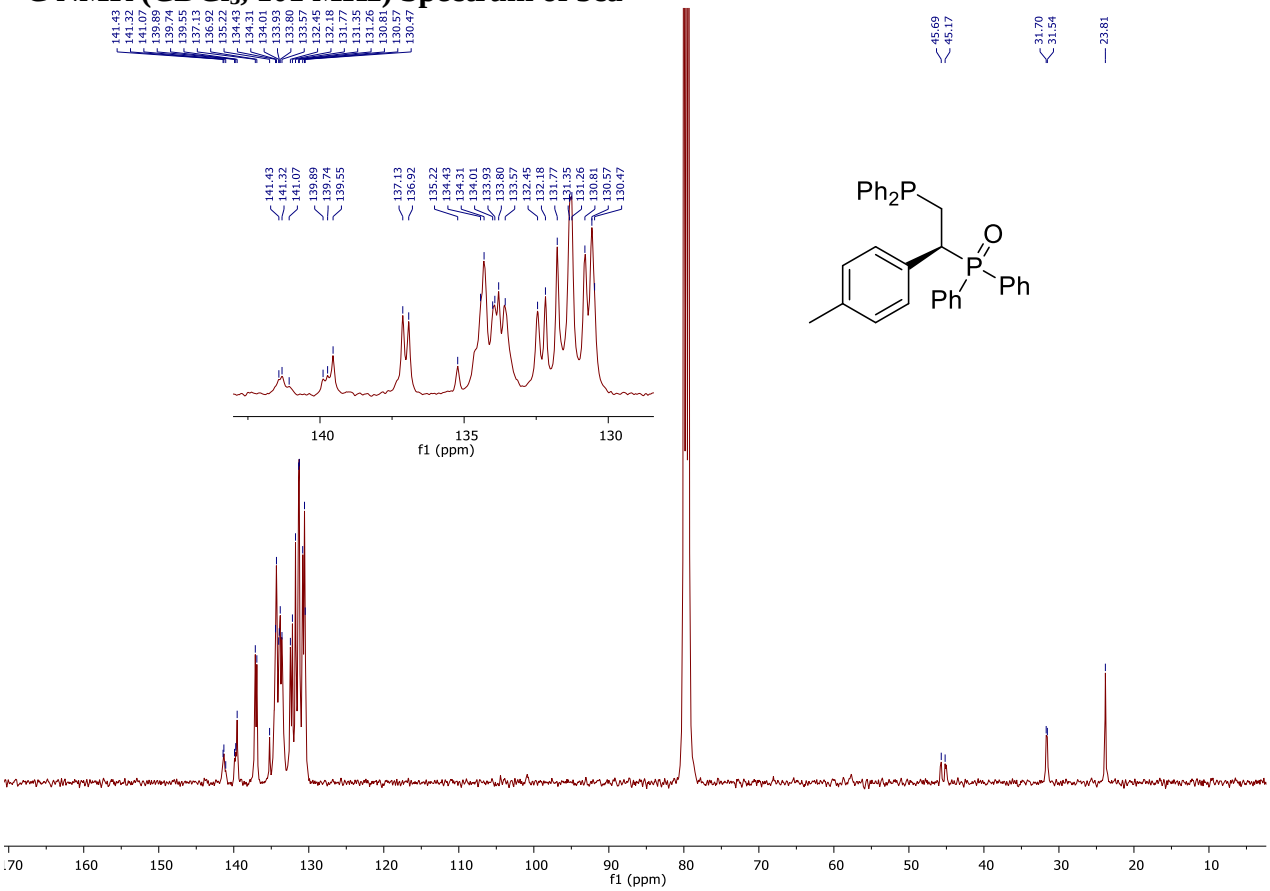
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ba



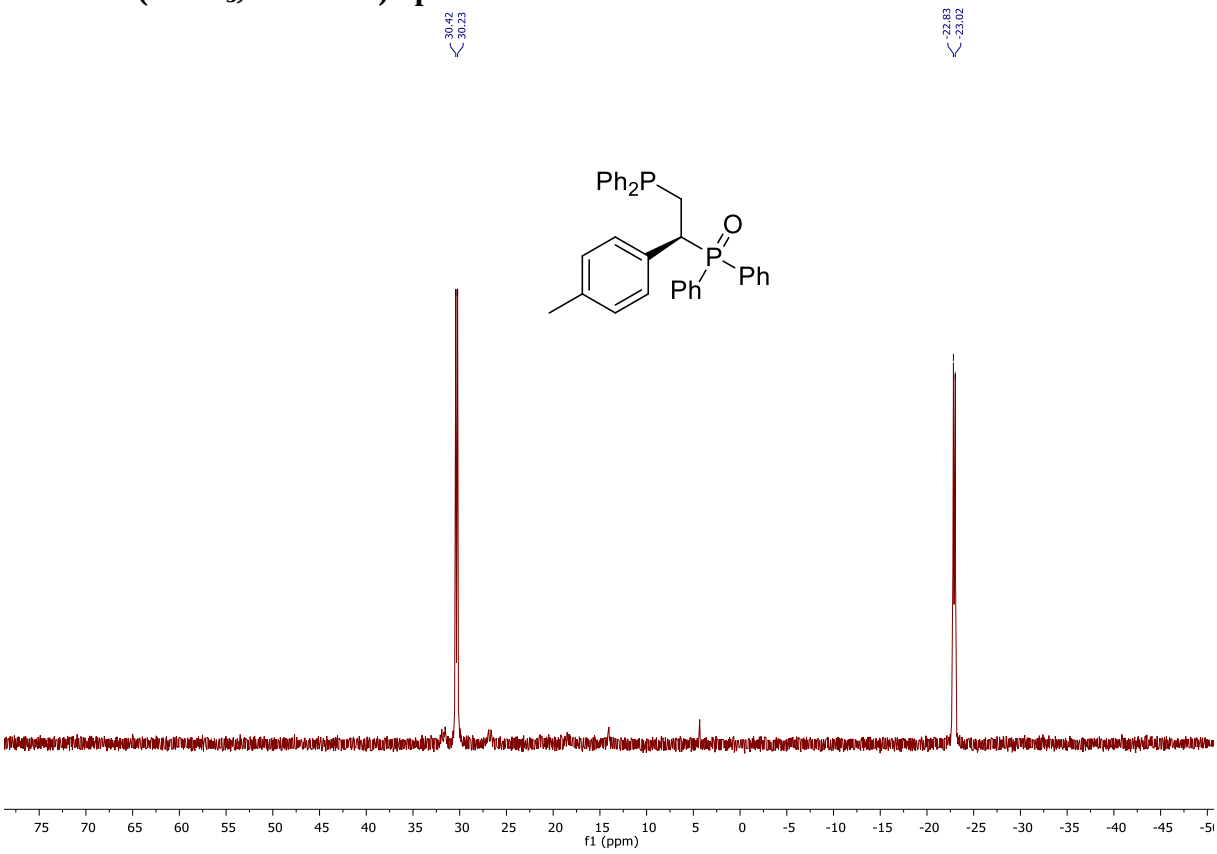
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ca



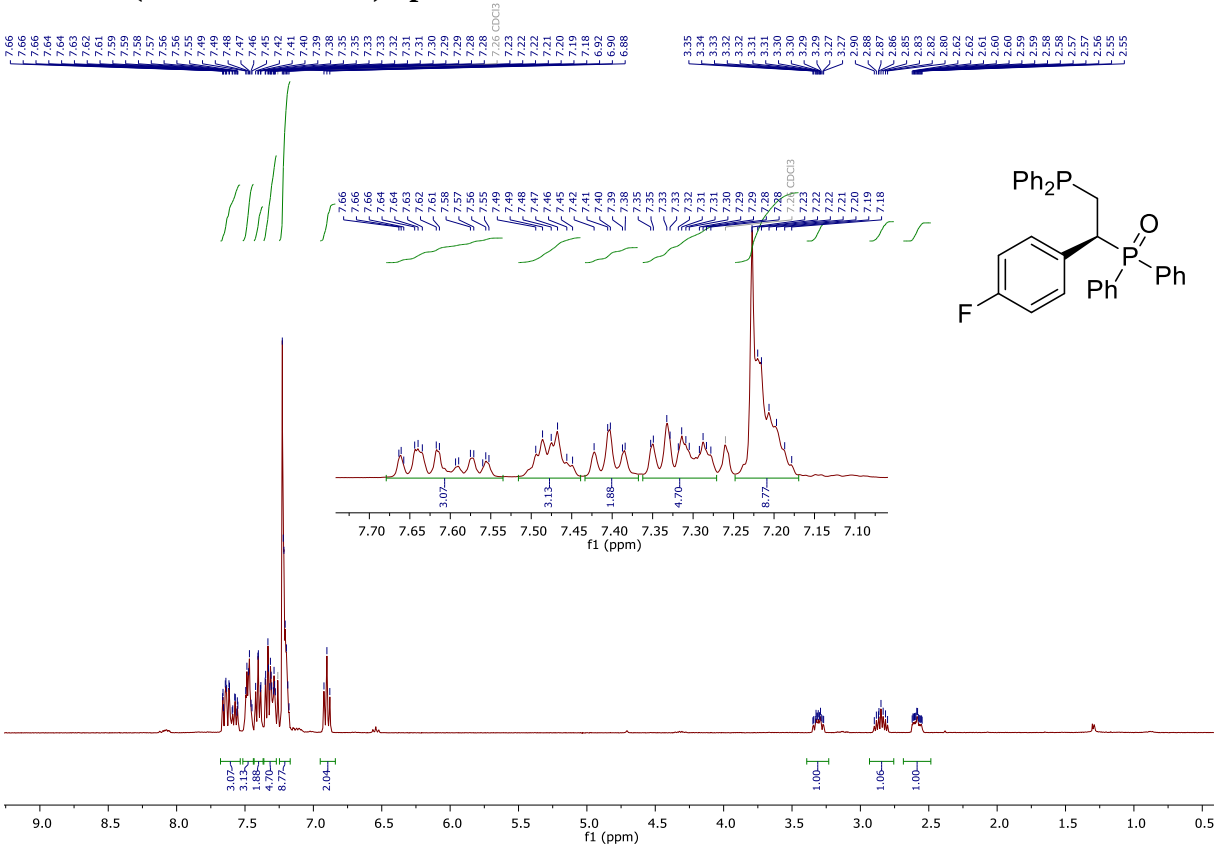
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ca



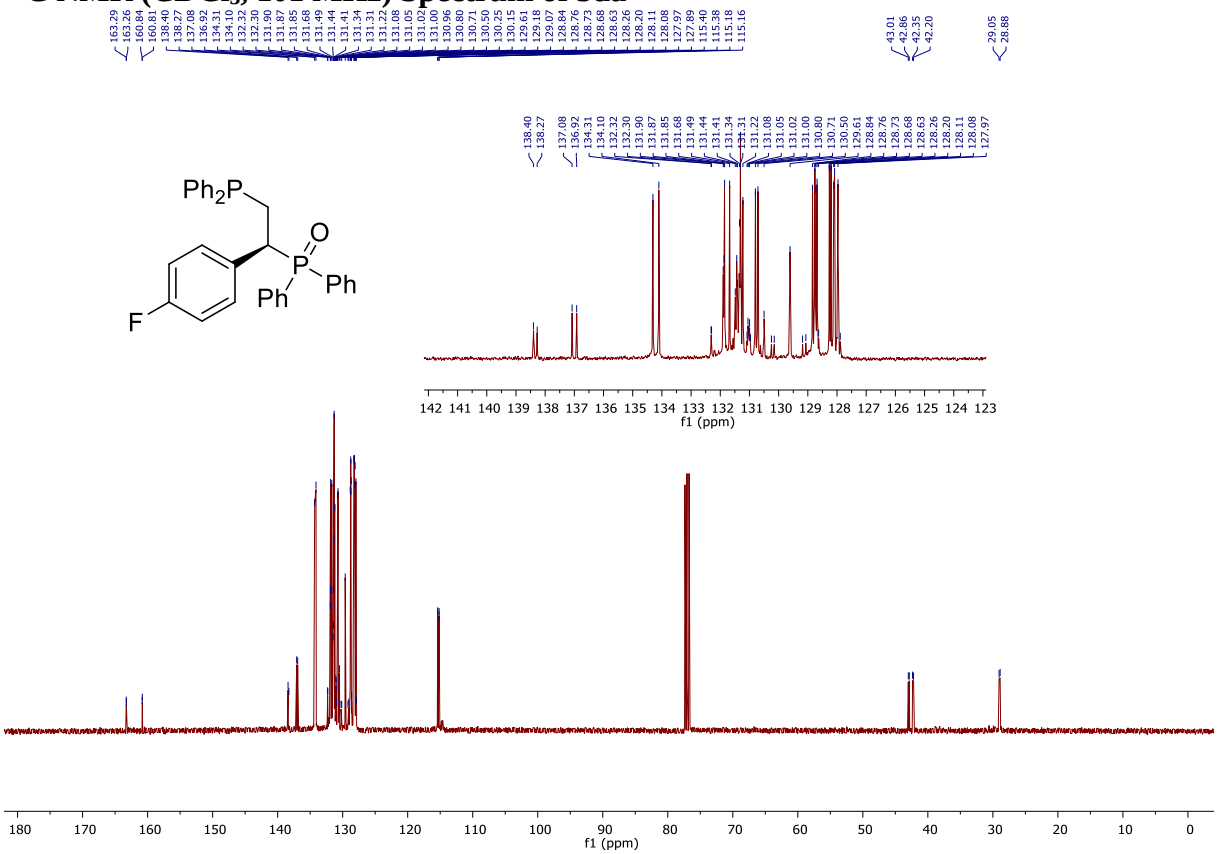
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ca



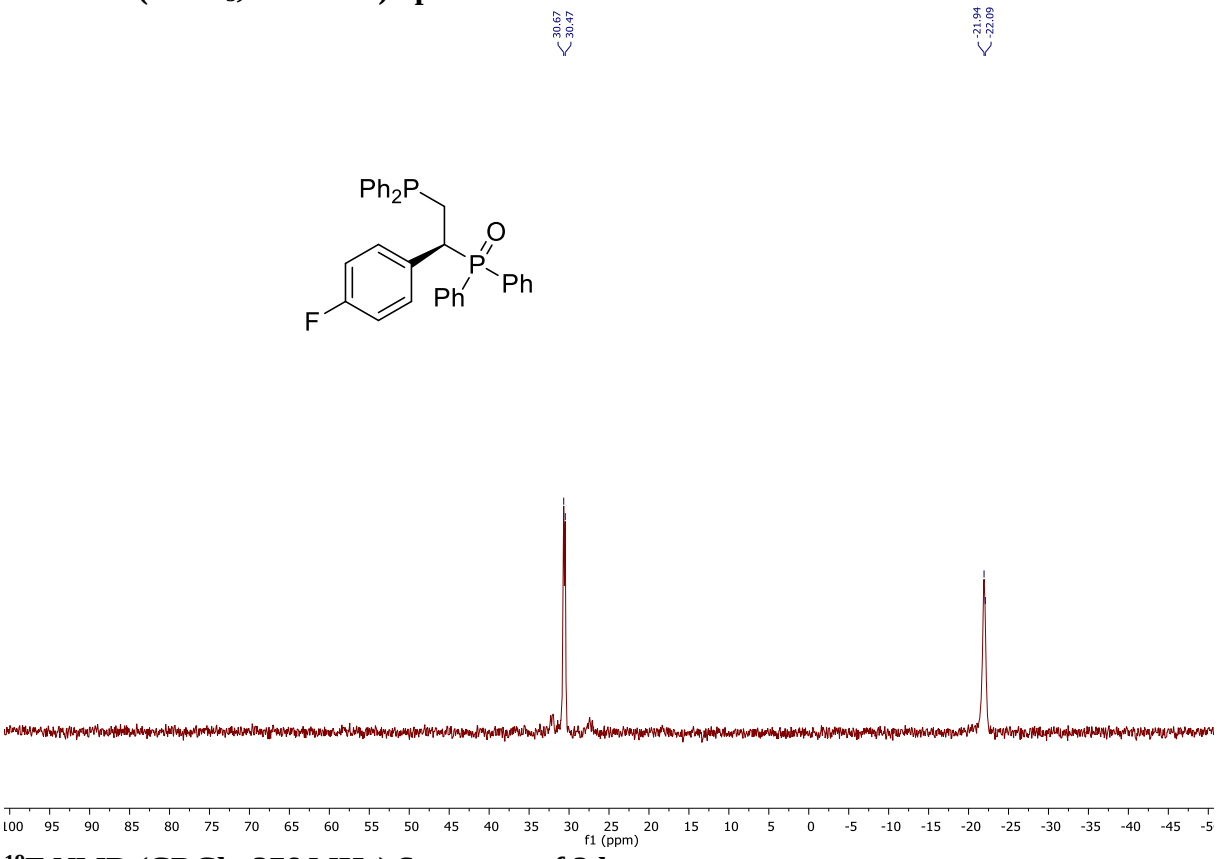
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3da



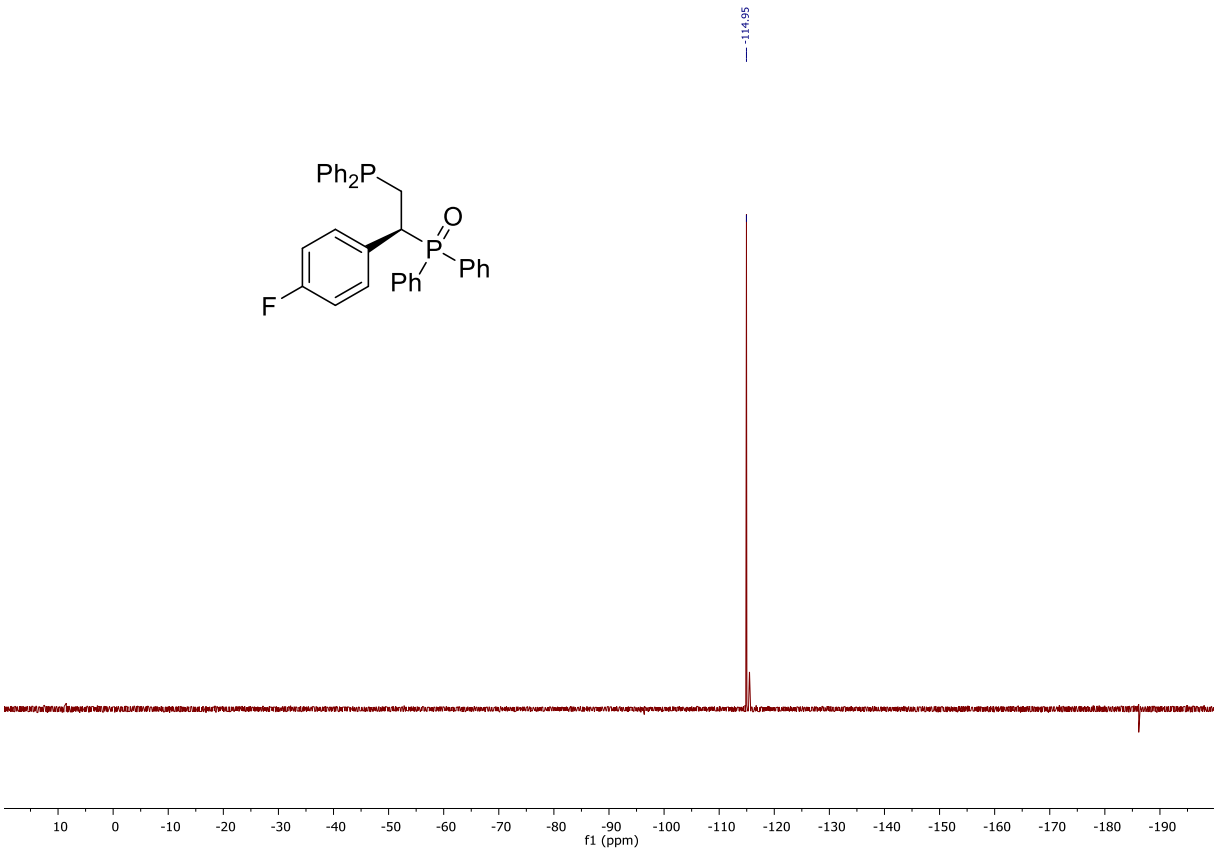
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3da



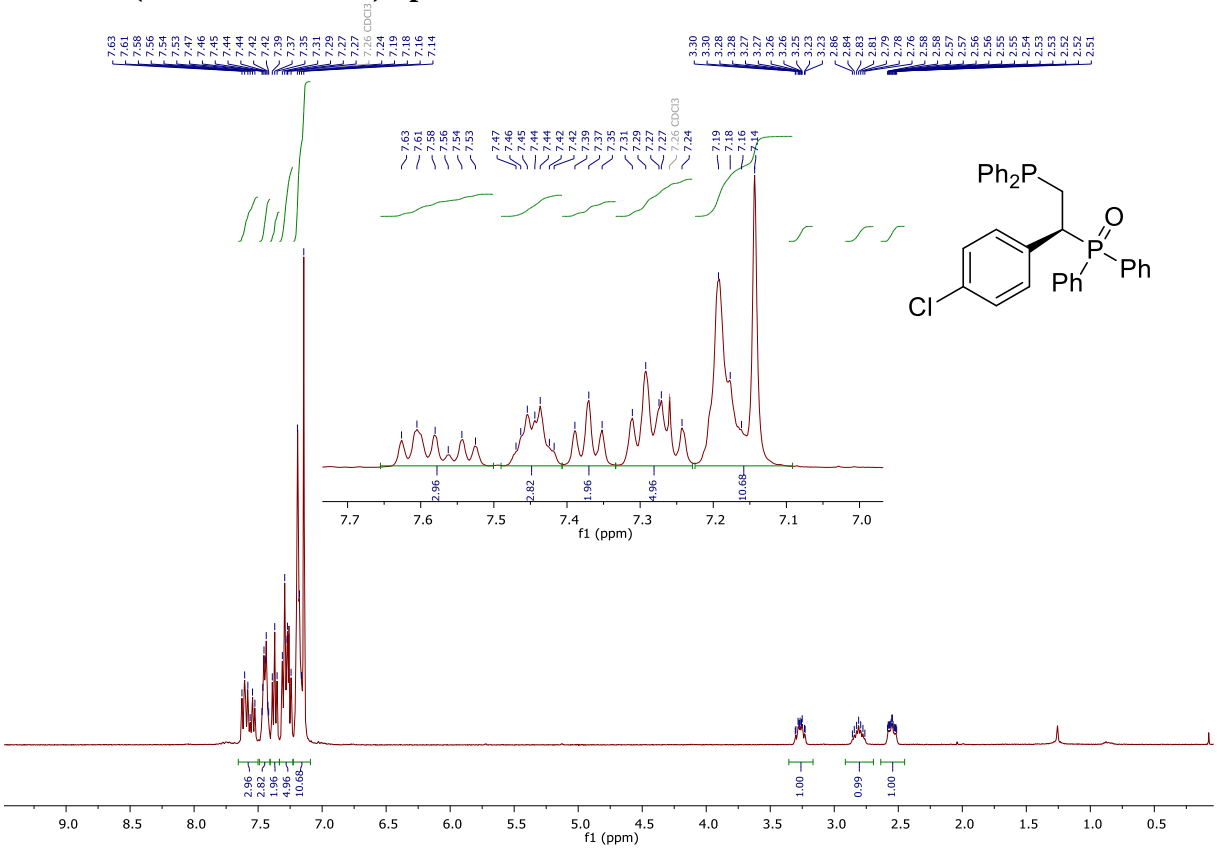
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3da



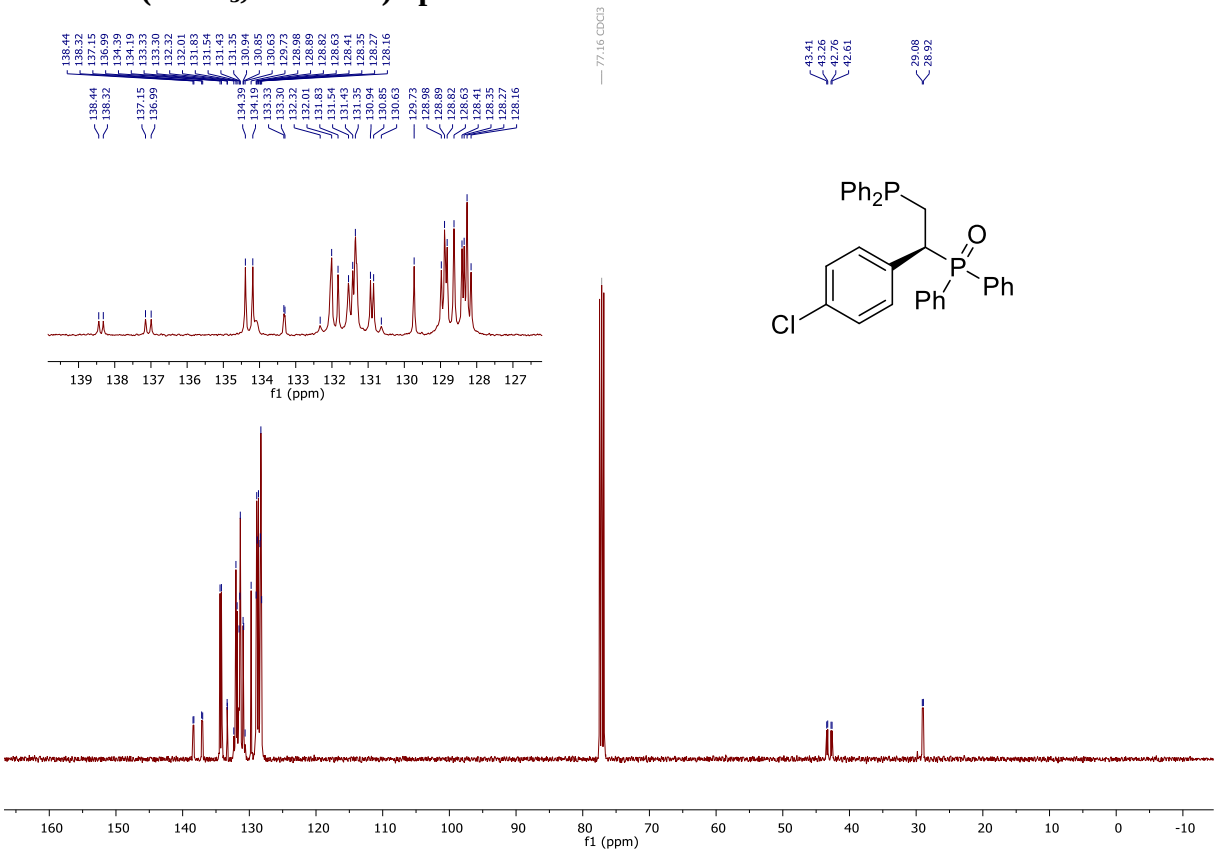
^{19}F NMR ($CDCl_3$, 376 MHz) Spectrum of 3da



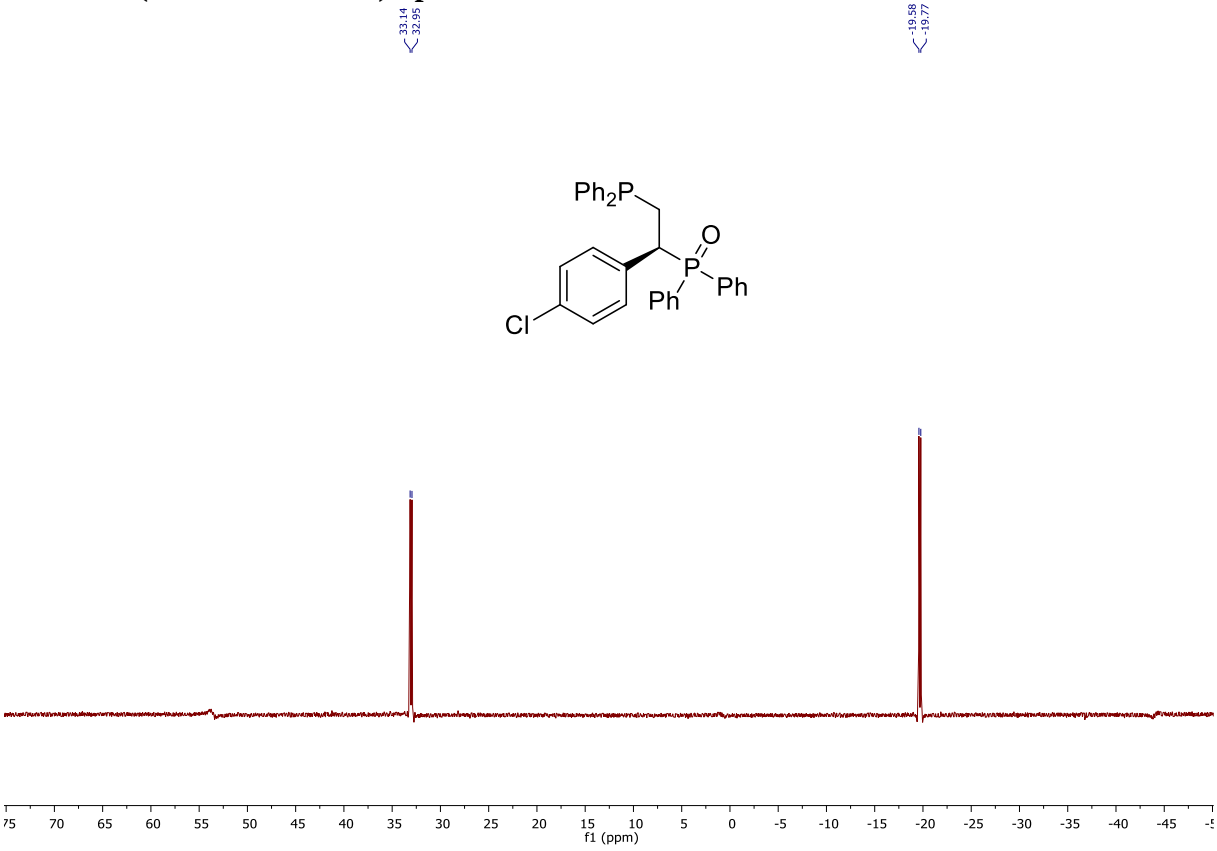
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ea



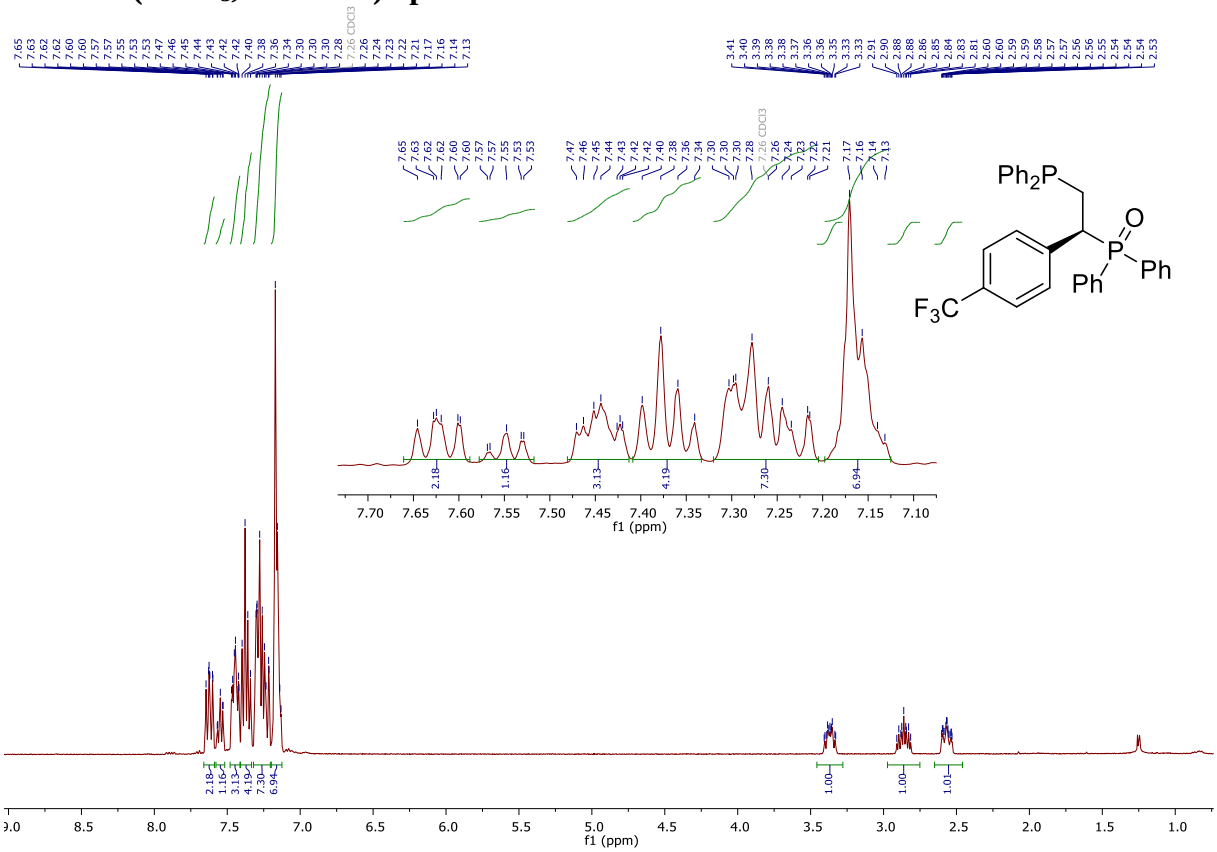
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ea



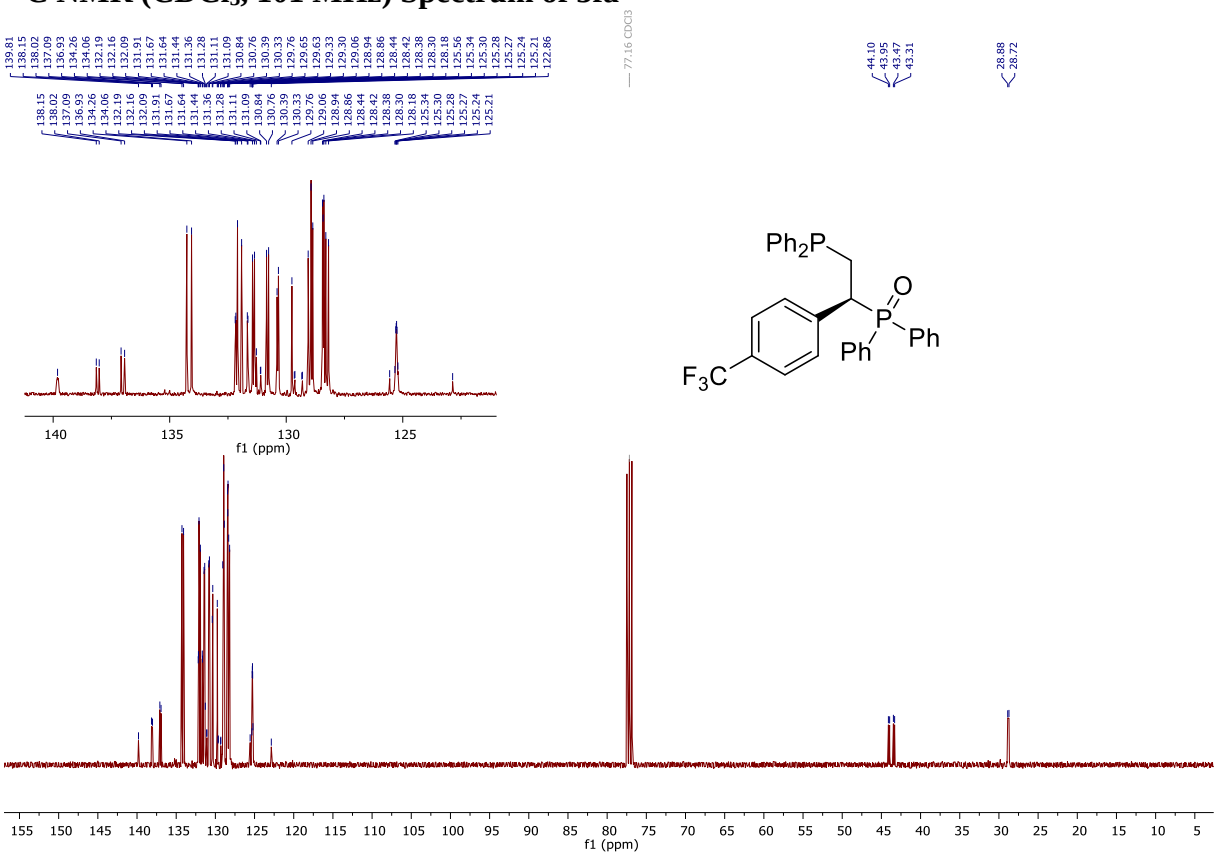
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ea



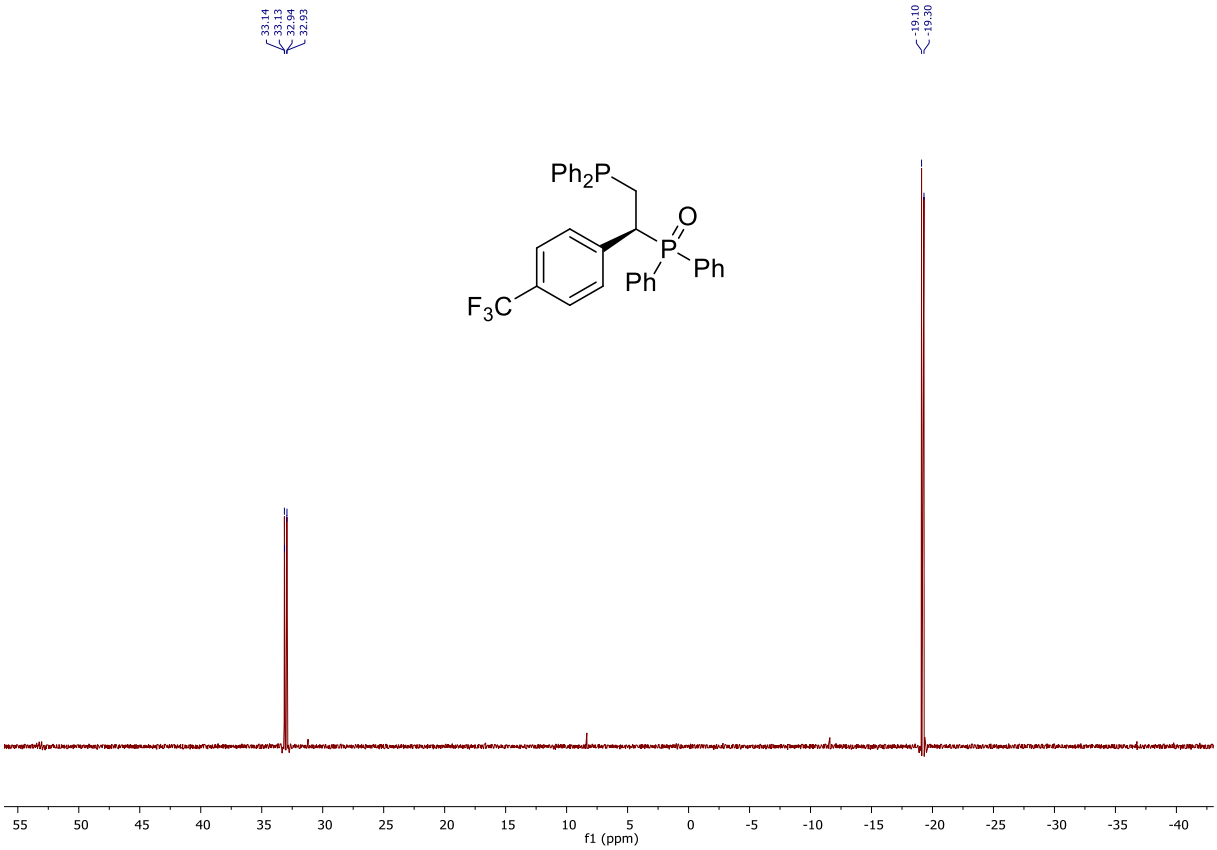
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3fa



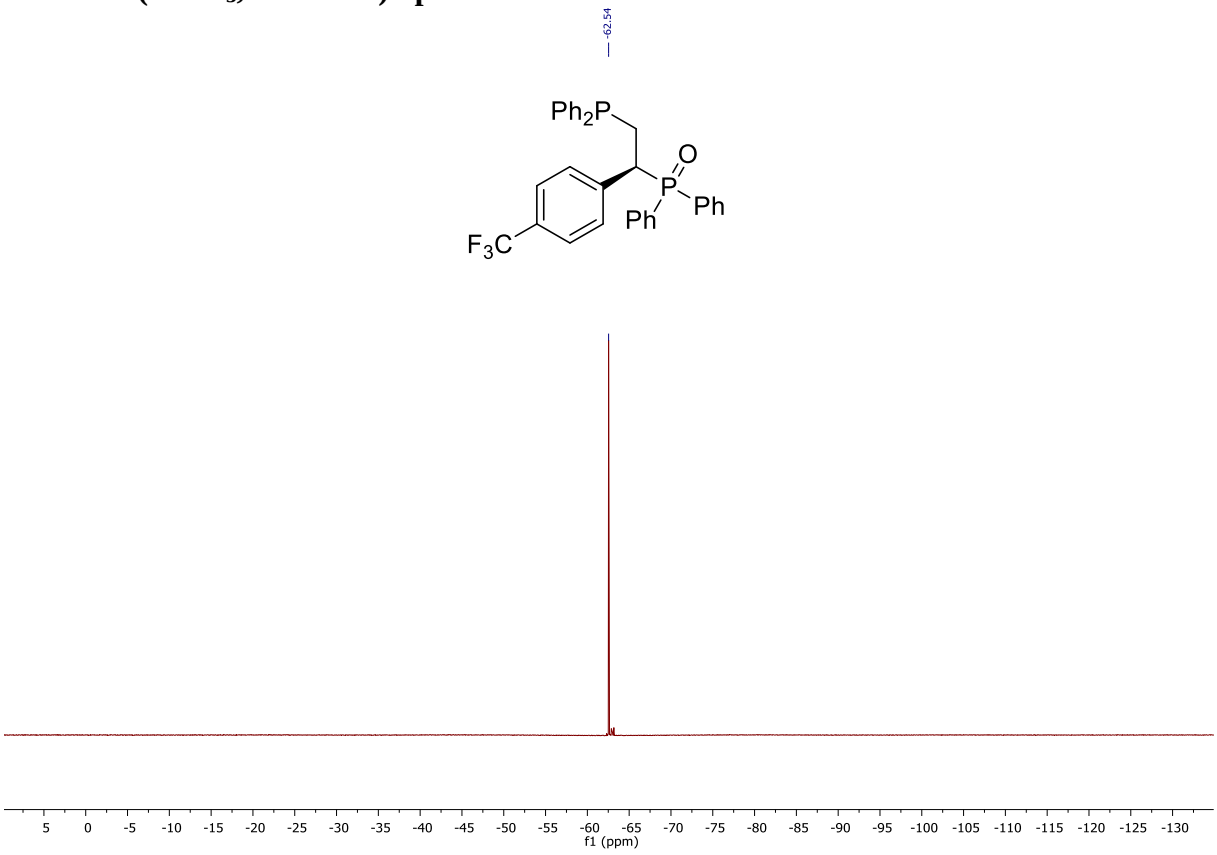
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3fa



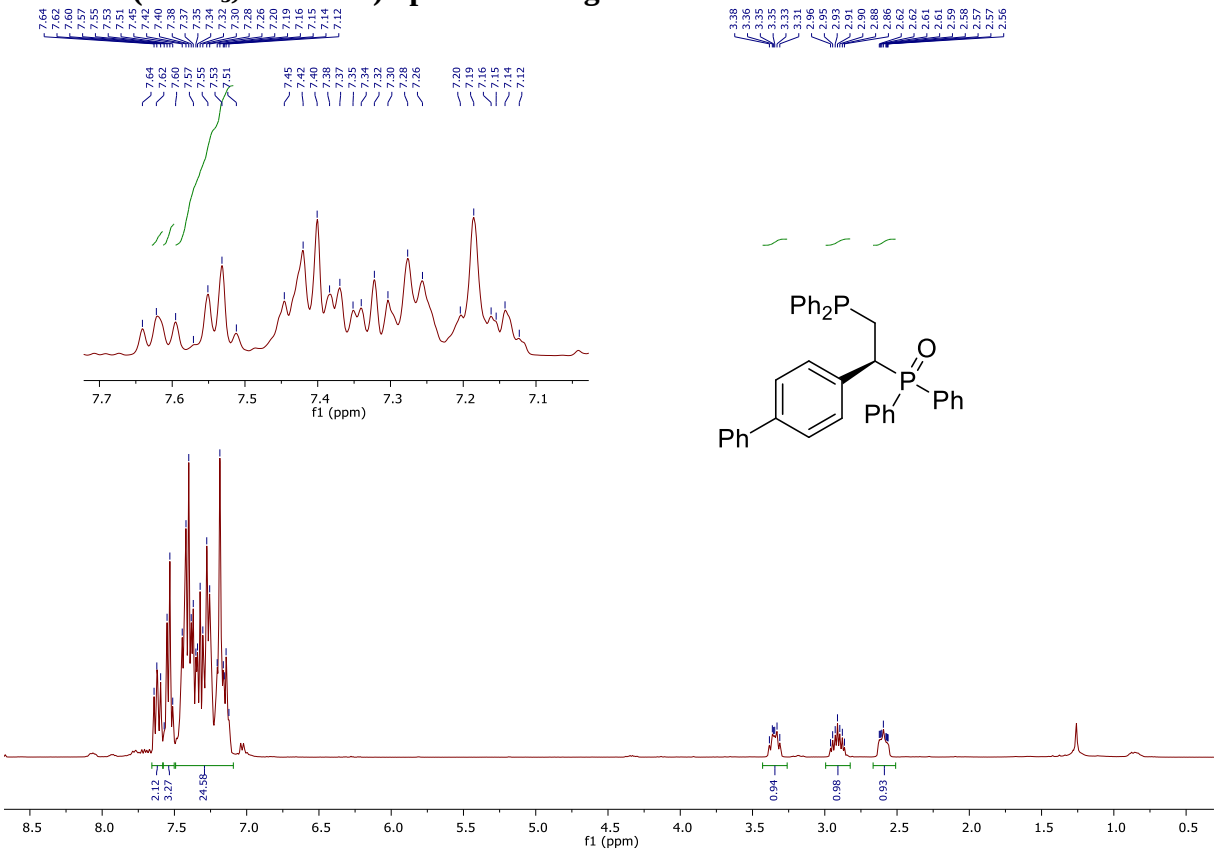
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3fa



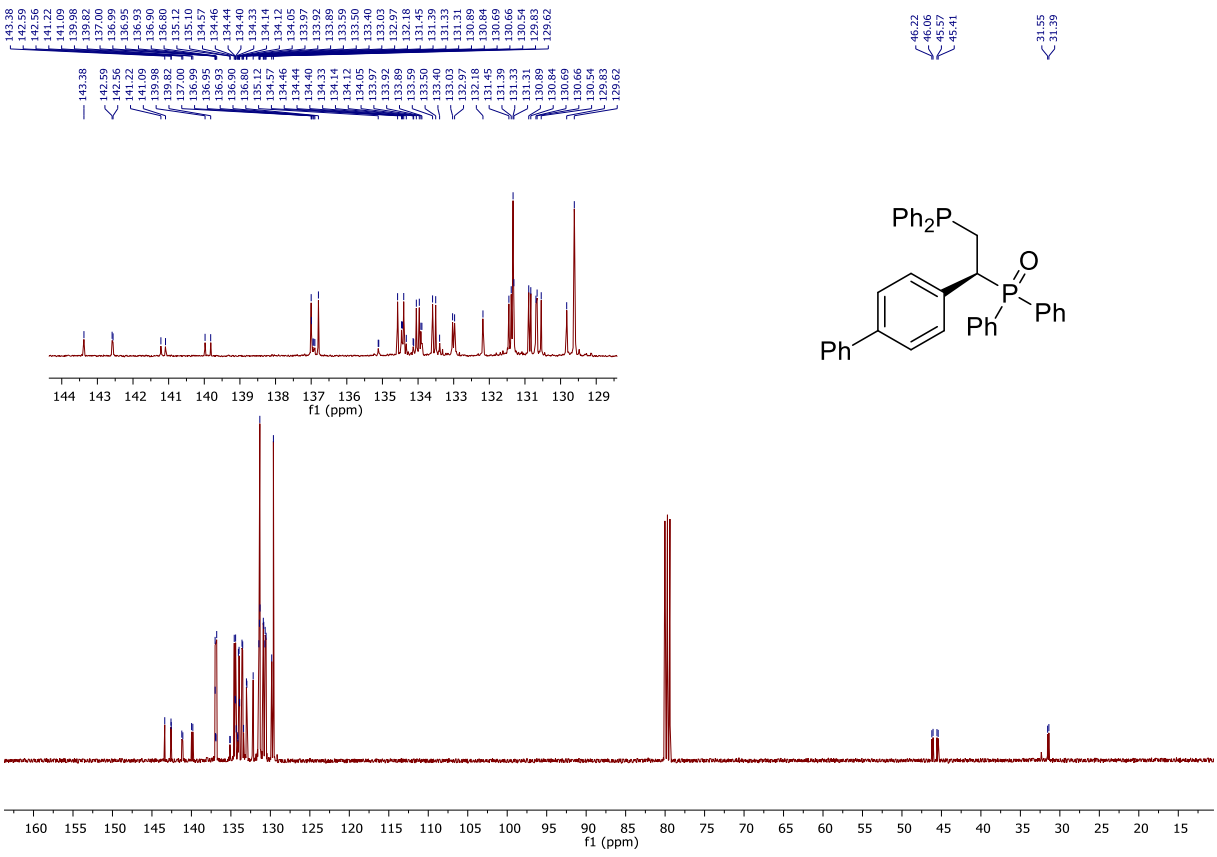
^{19}F NMR ($CDCl_3$, 376 MHz) Spectrum of 3fa



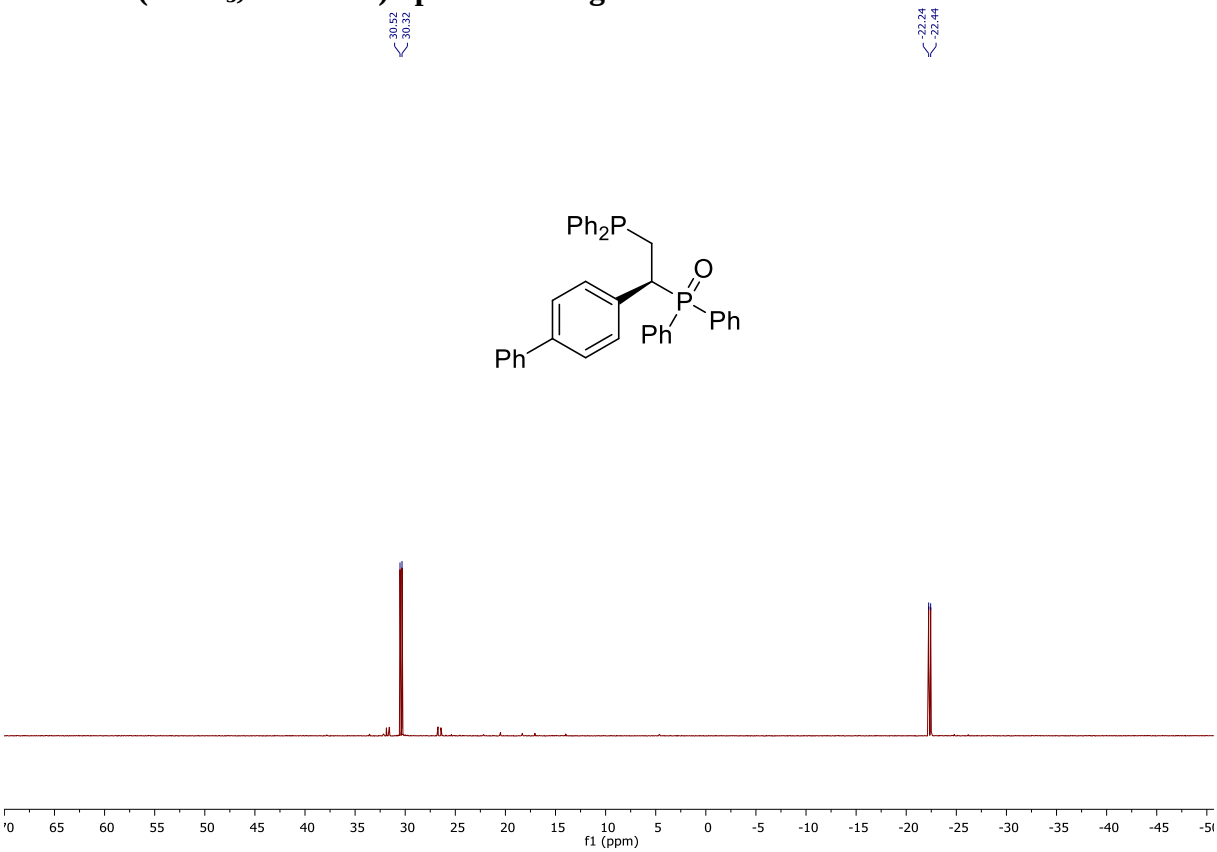
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ga



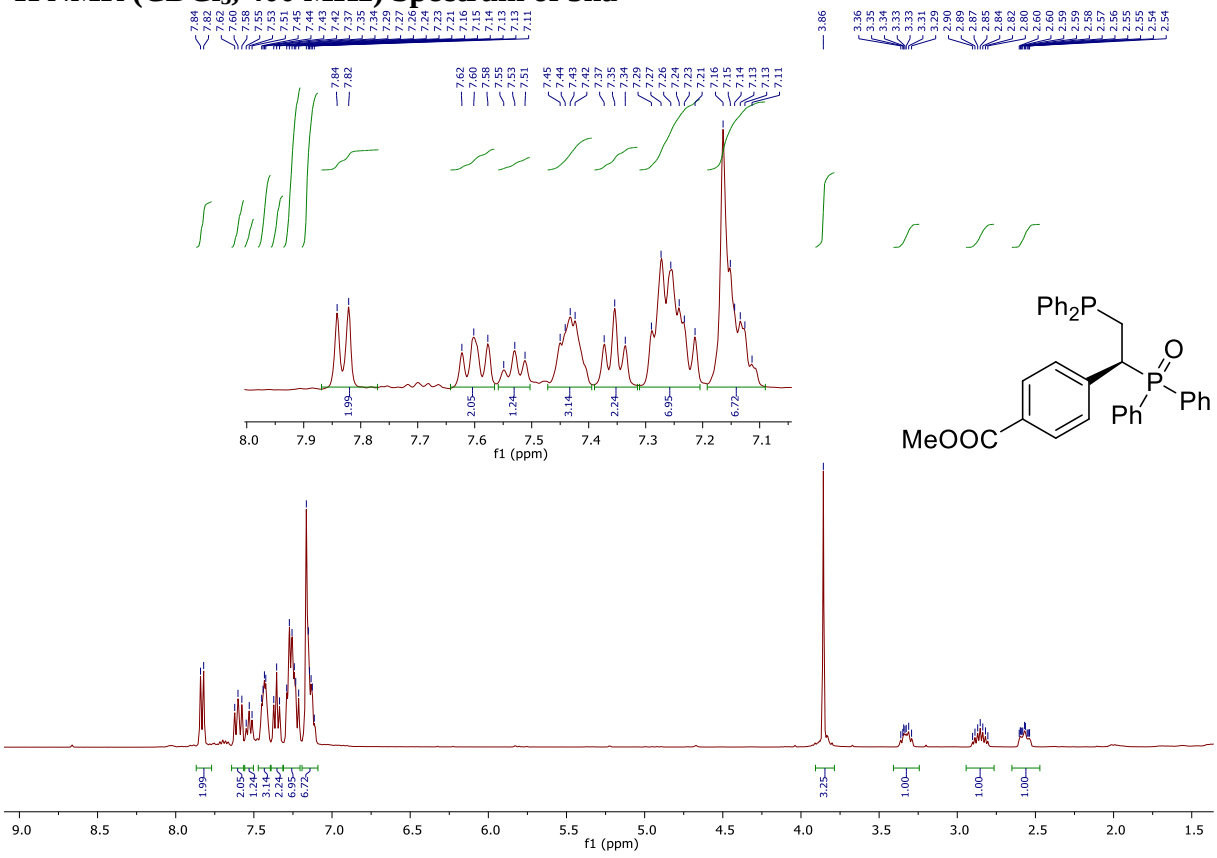
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ga



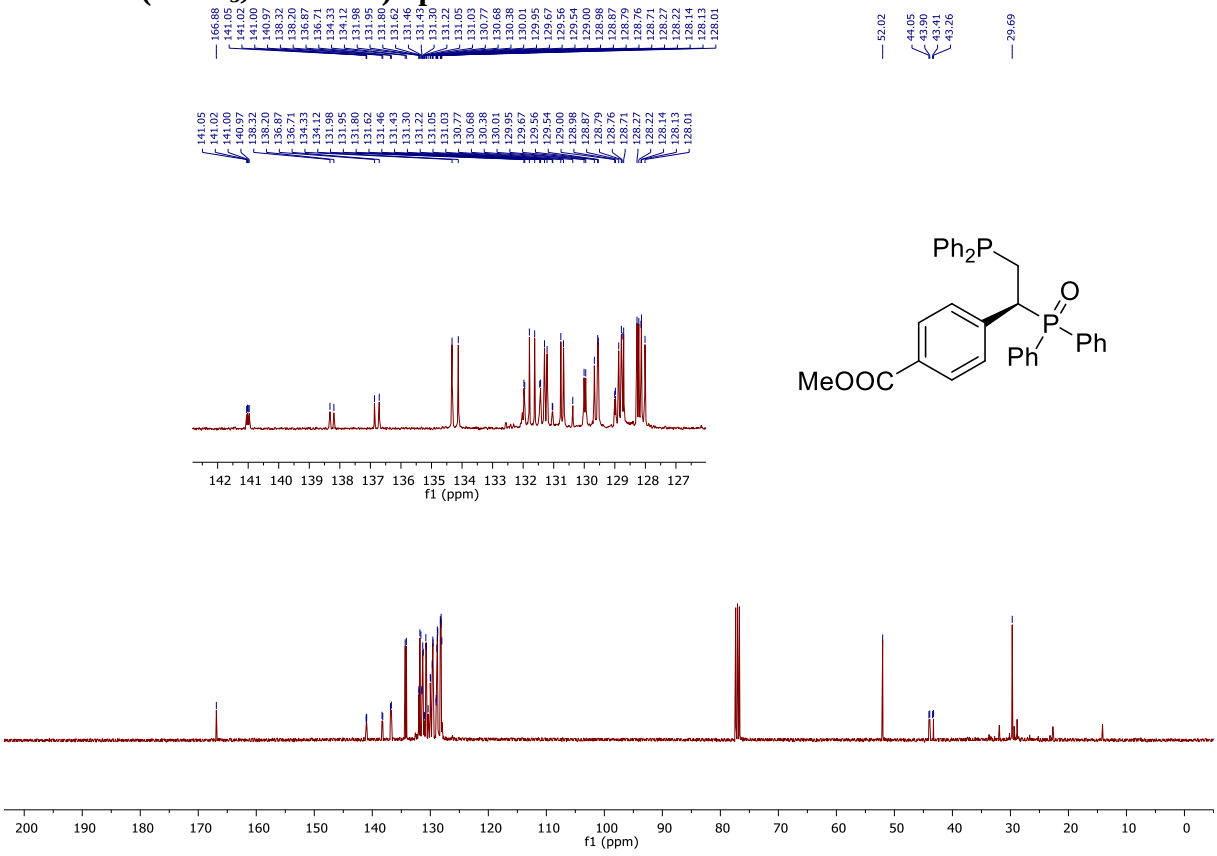
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ga



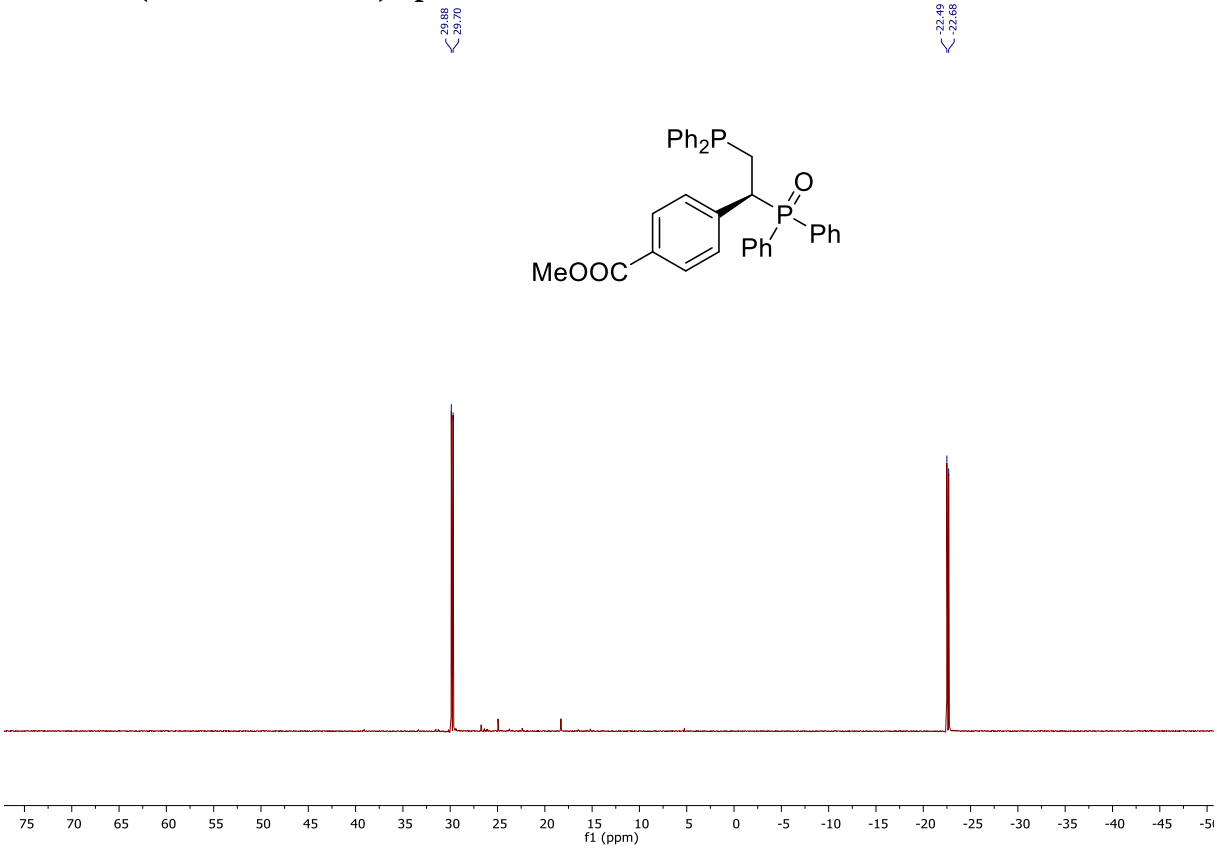
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ha



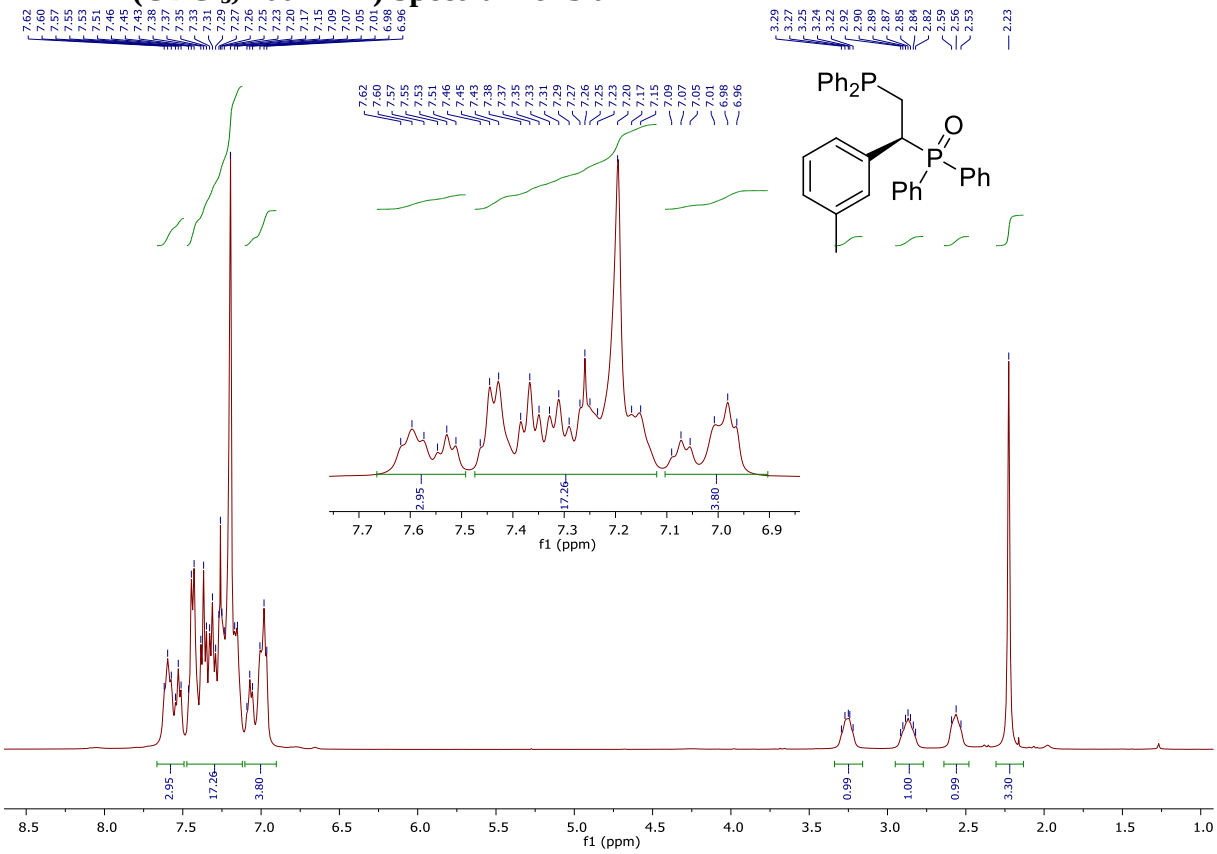
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ha



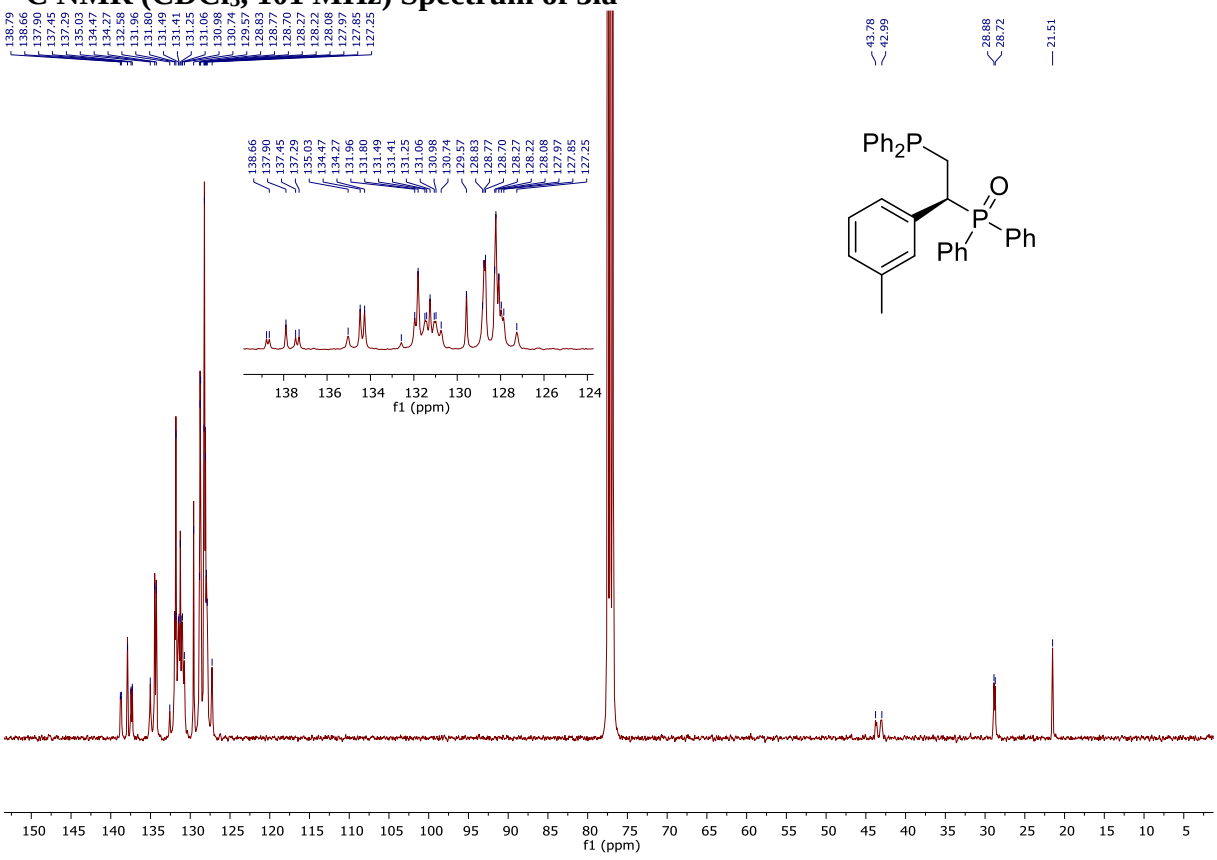
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ha



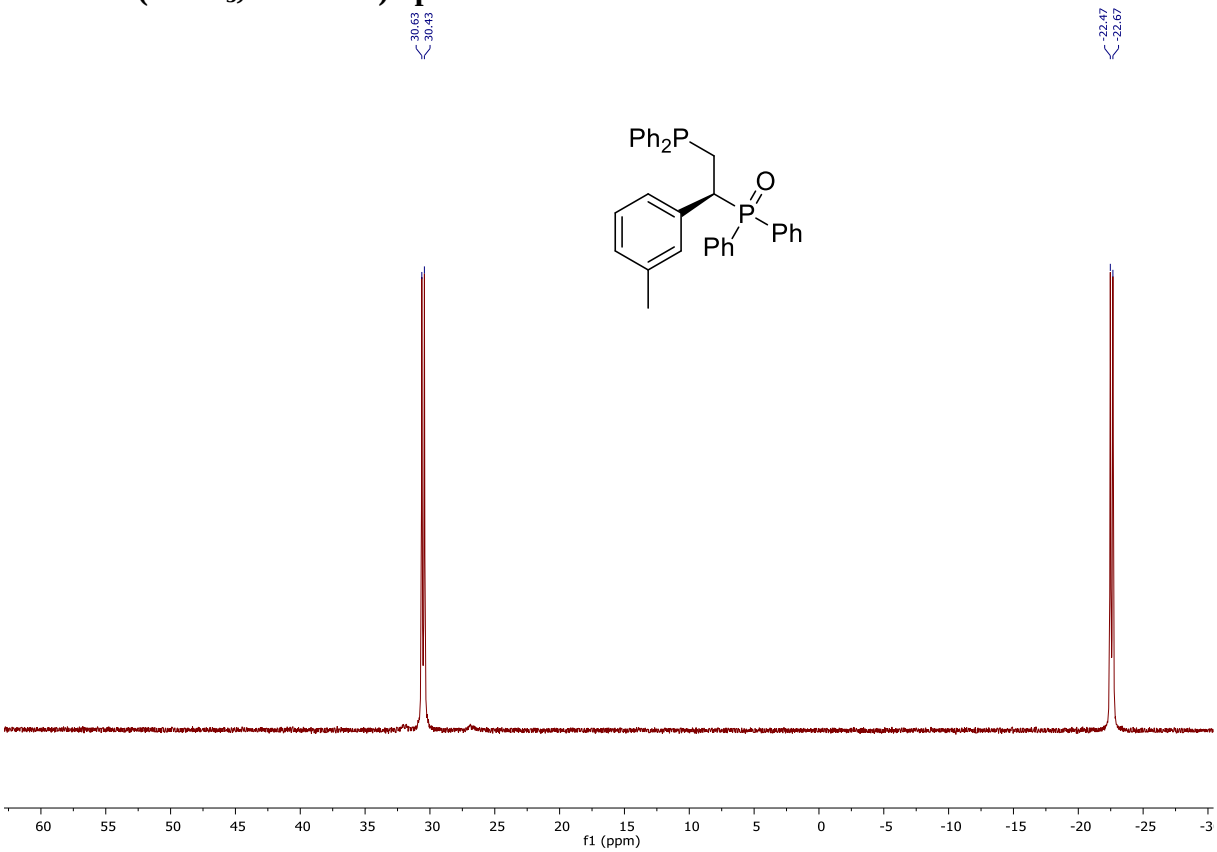
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ia



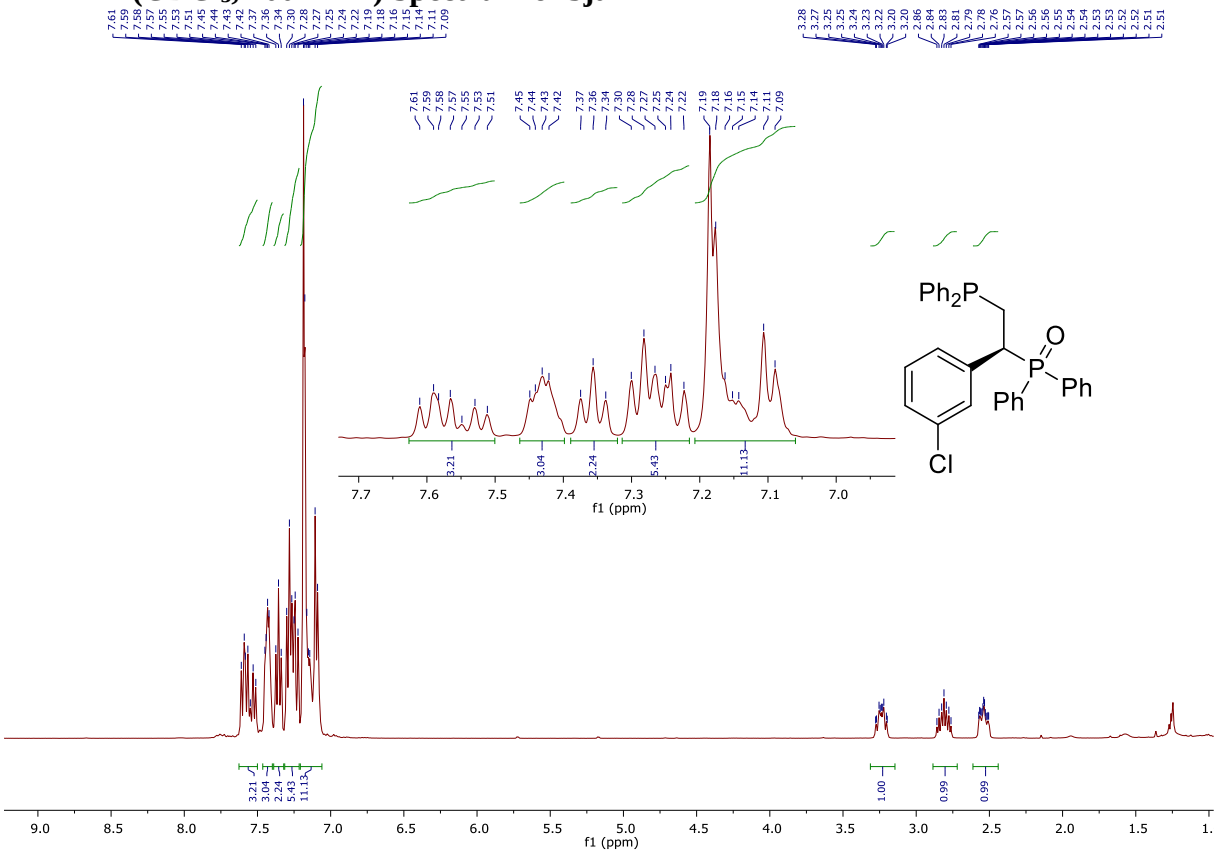
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ia



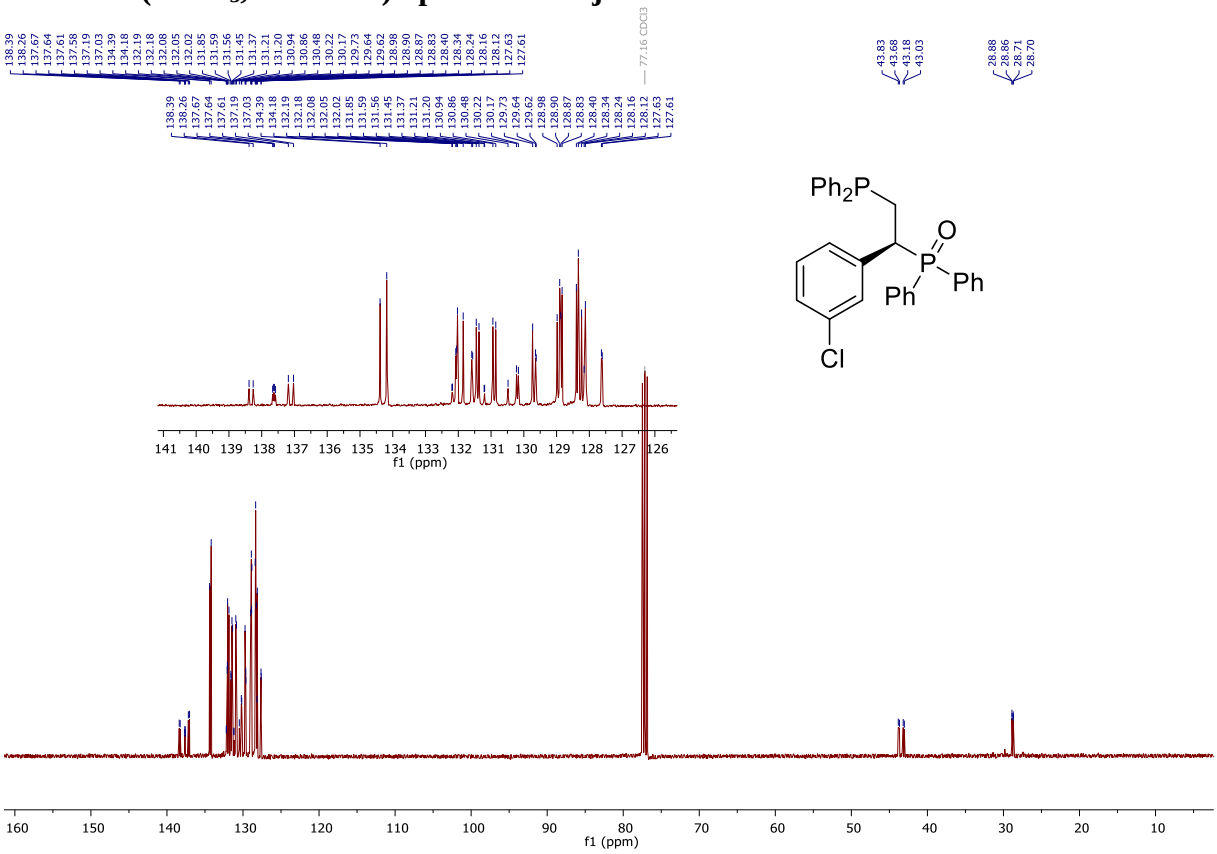
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ia



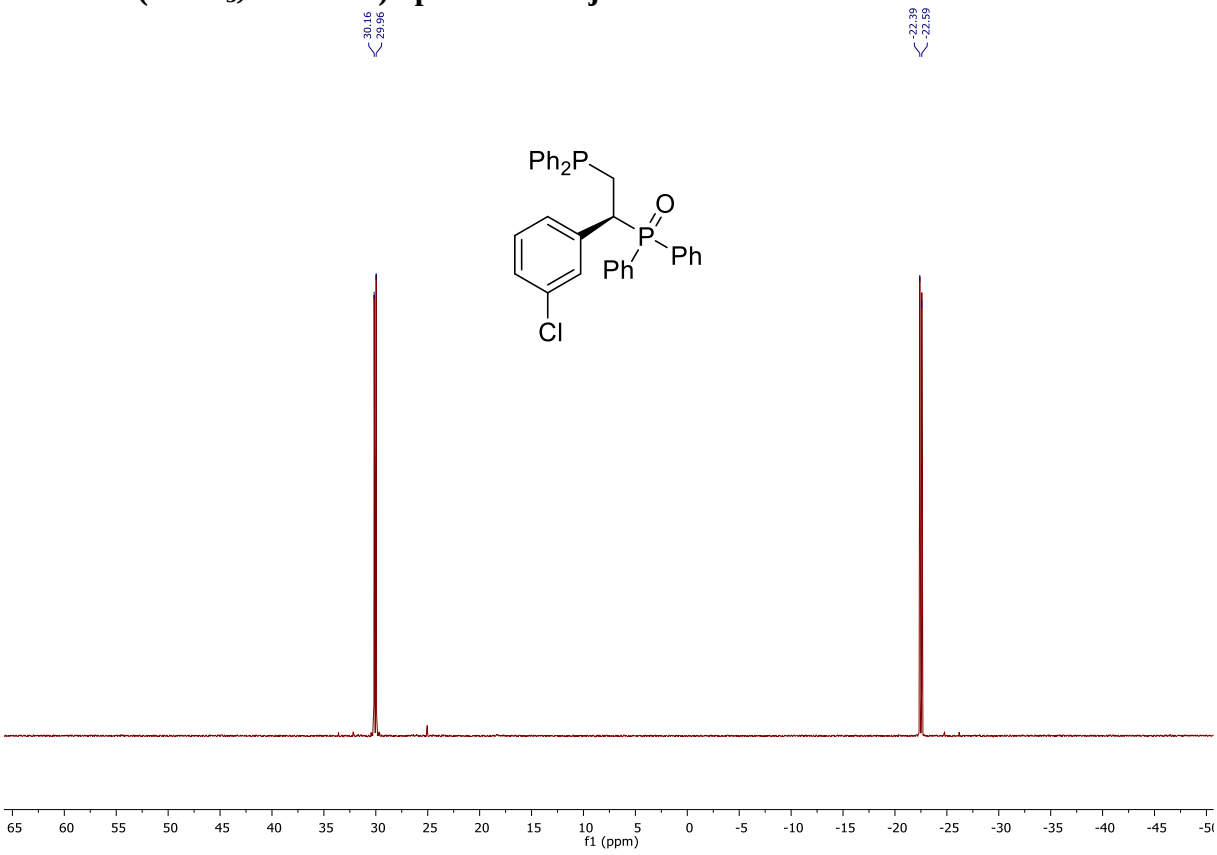
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ja



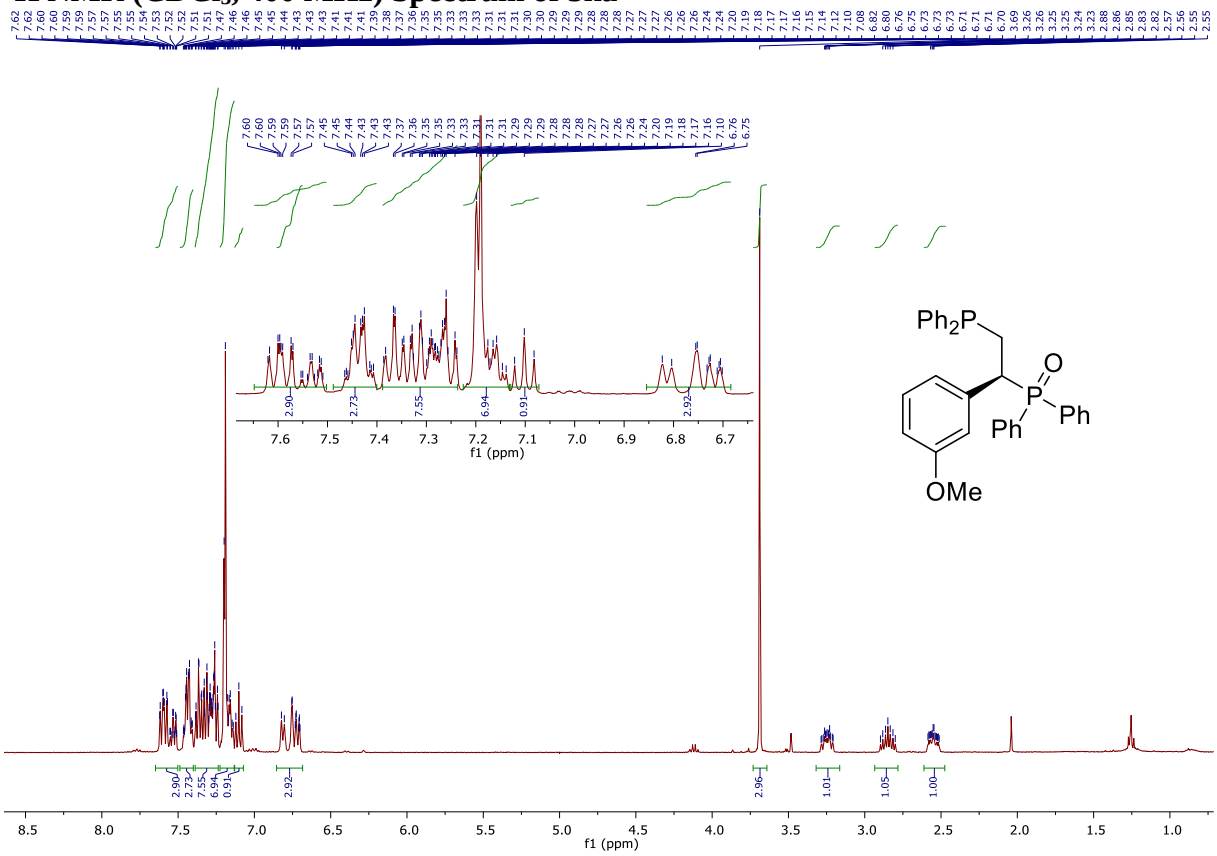
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ja



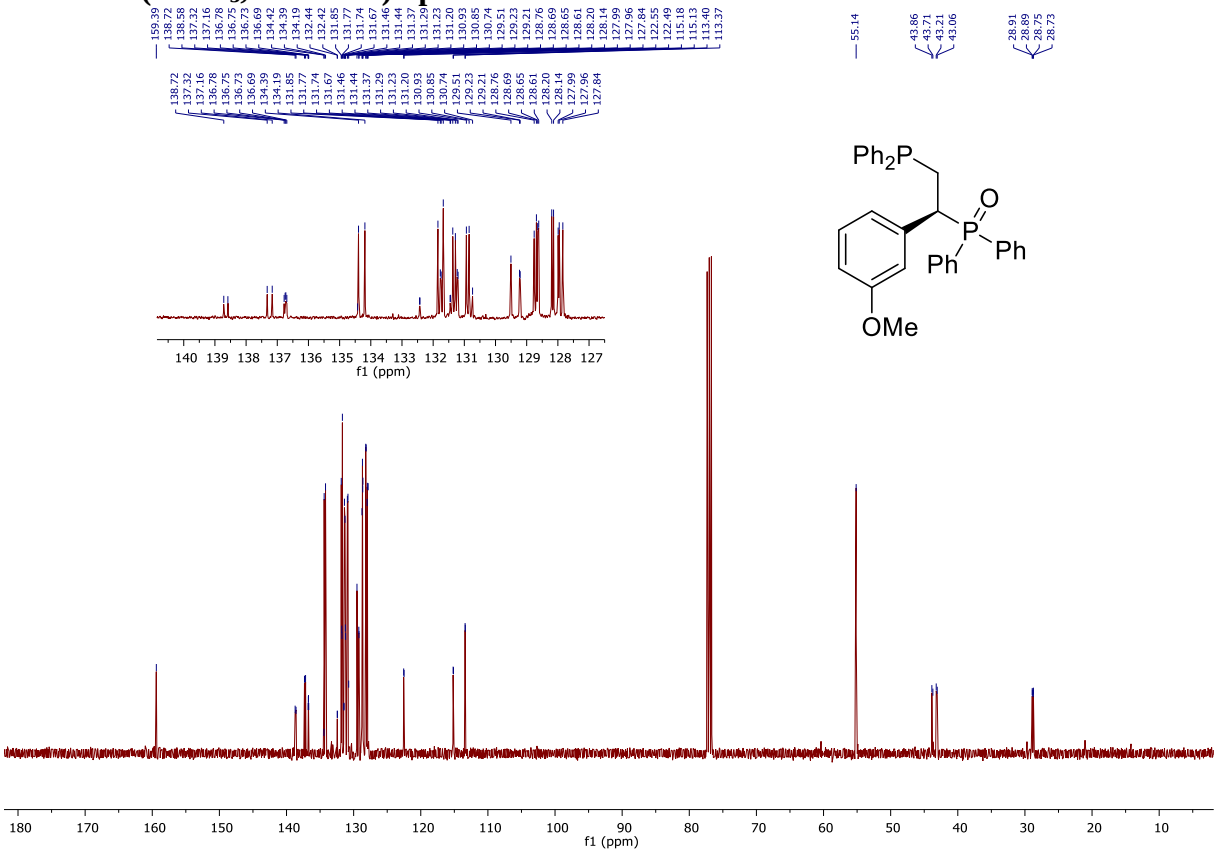
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ja



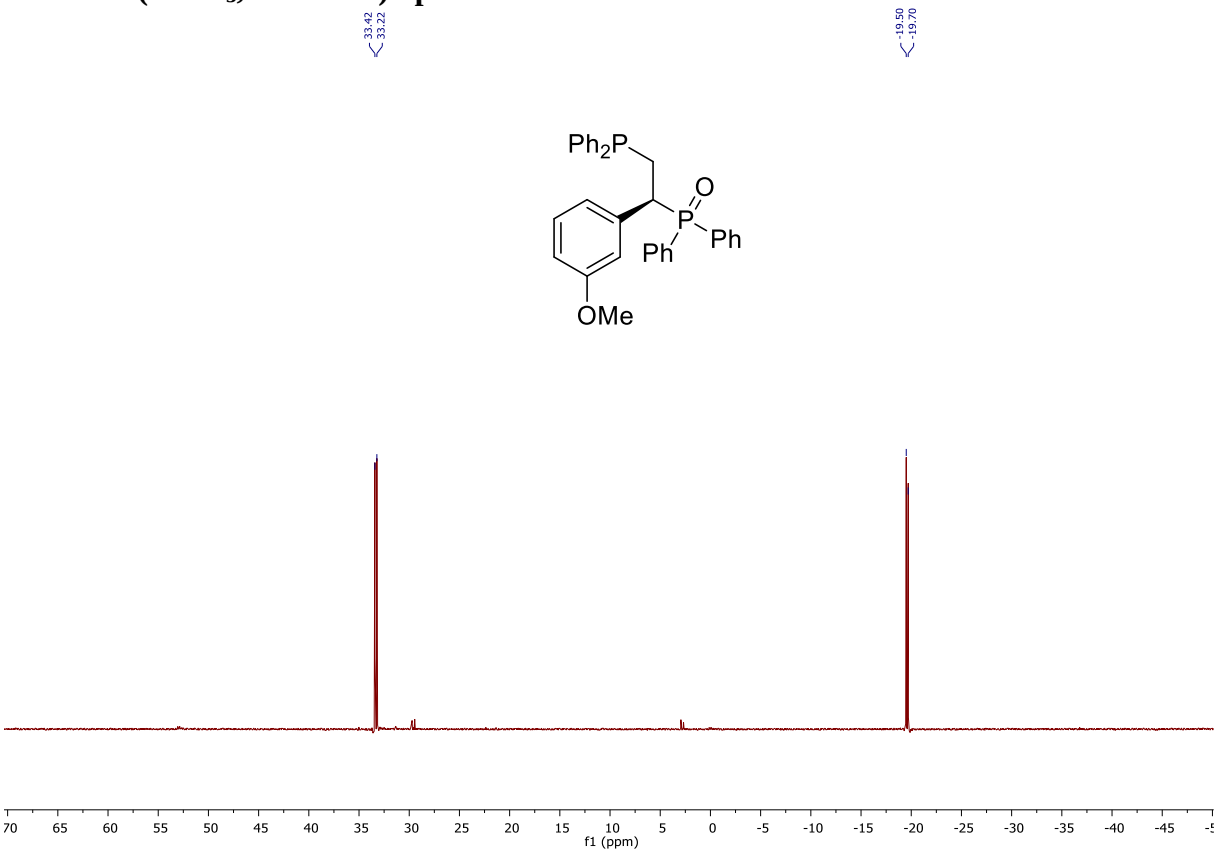
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ka



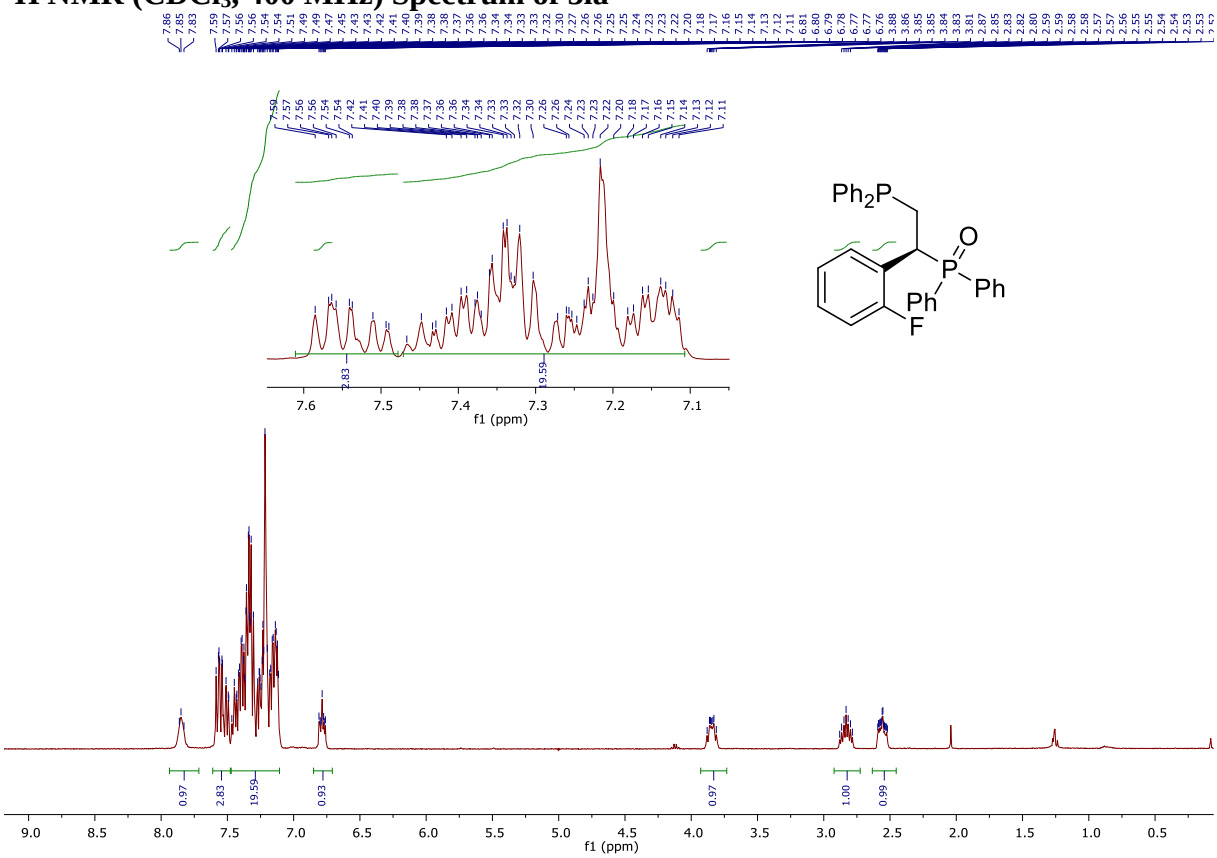
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ka



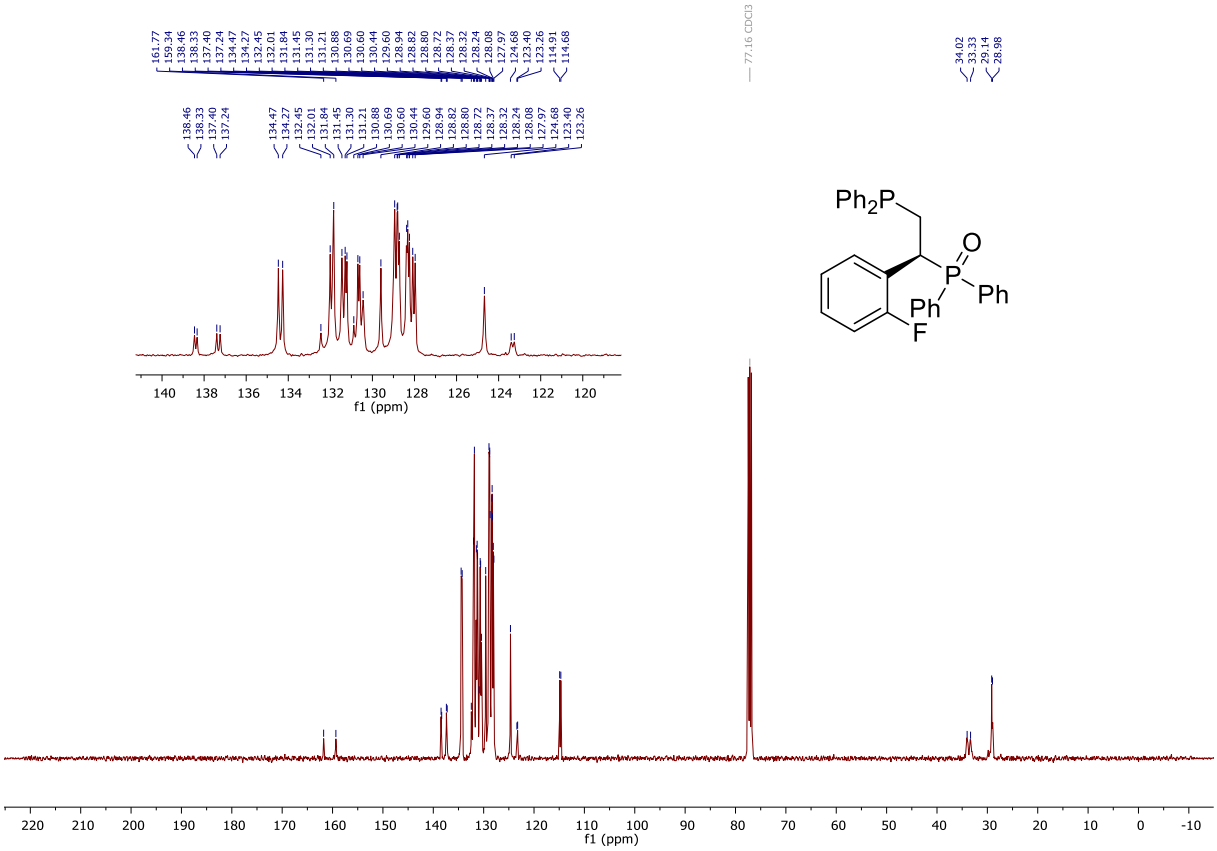
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ka



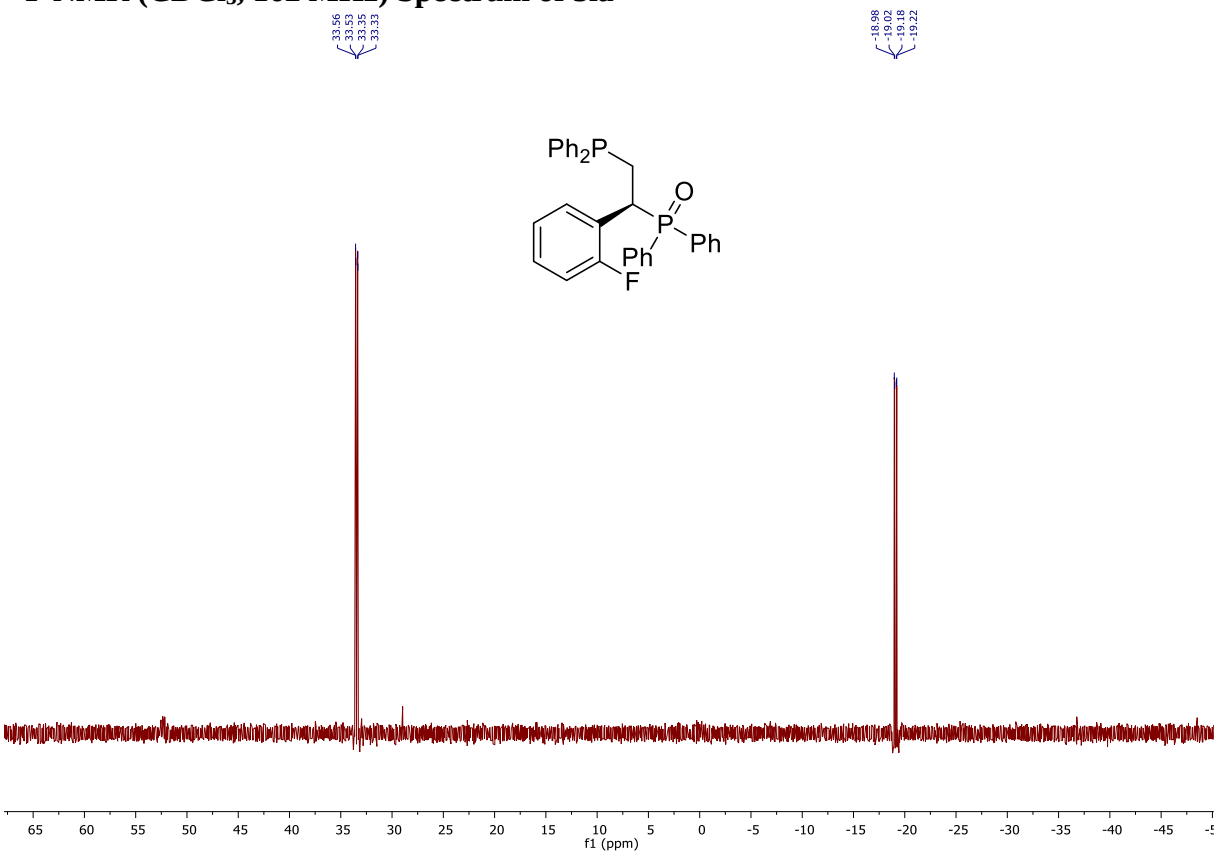
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3la



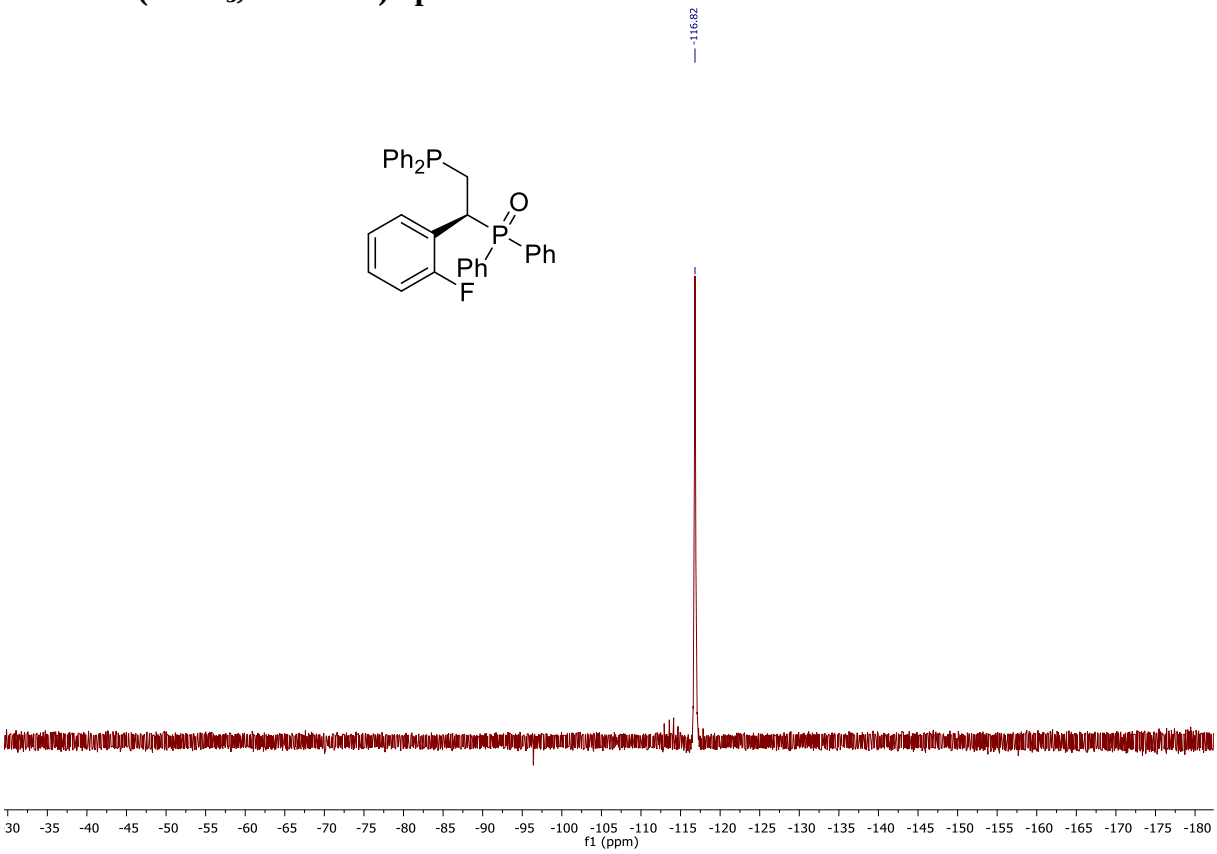
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3la



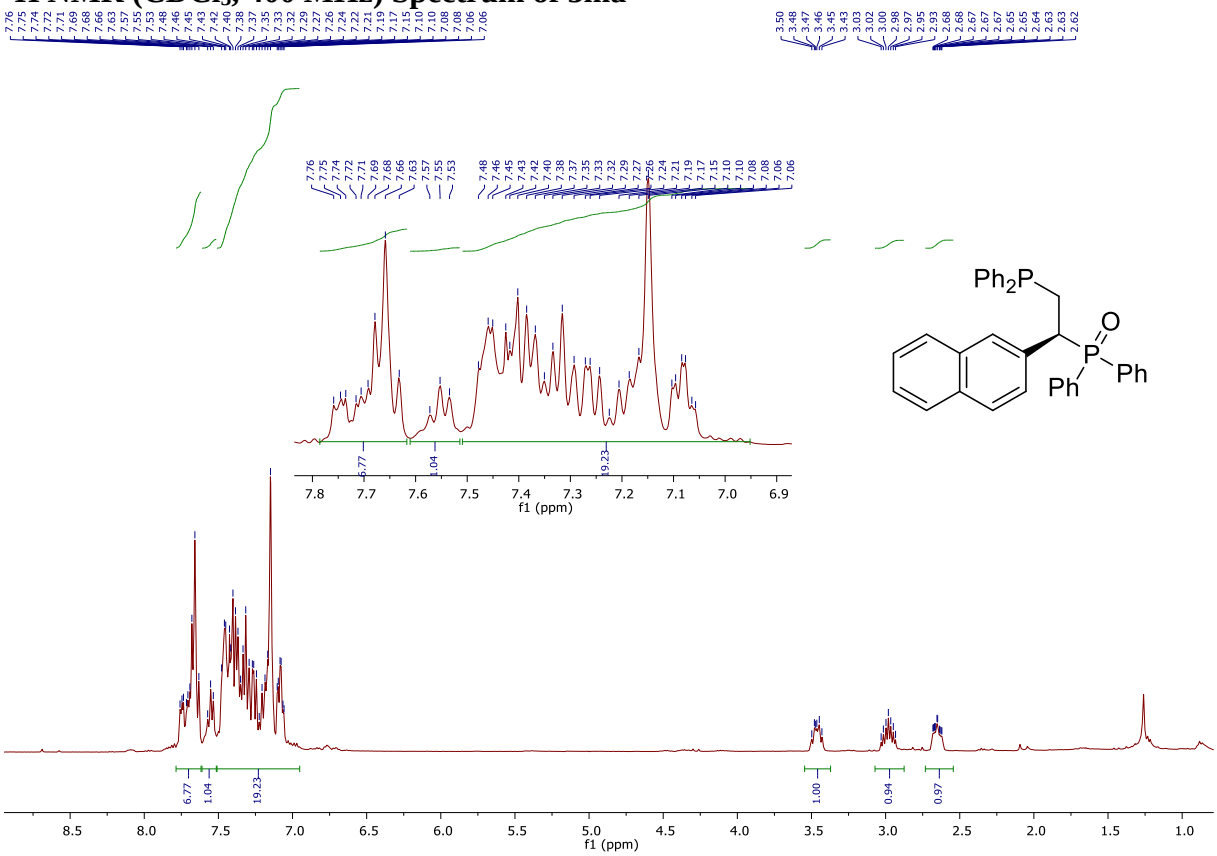
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3la



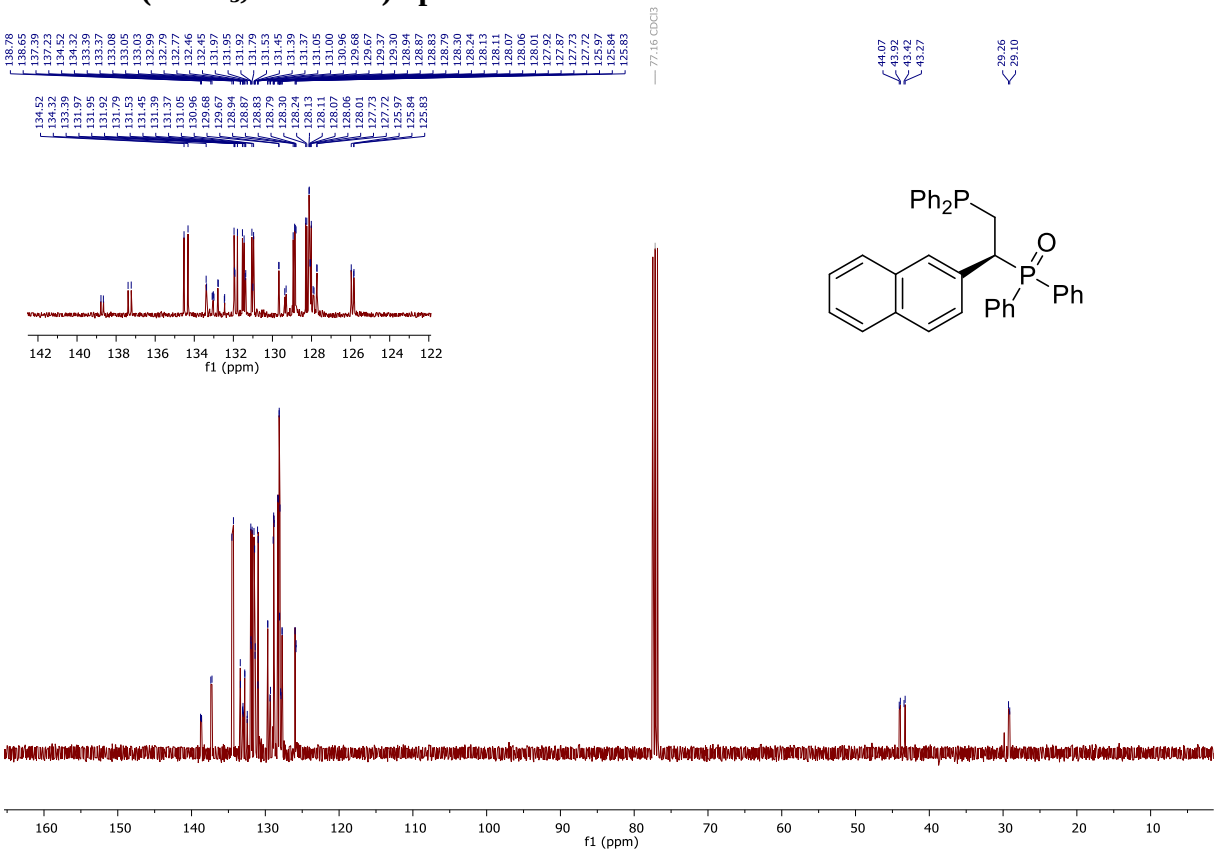
^{19}F NMR ($CDCl_3$, 376 MHz) Spectrum of 3la



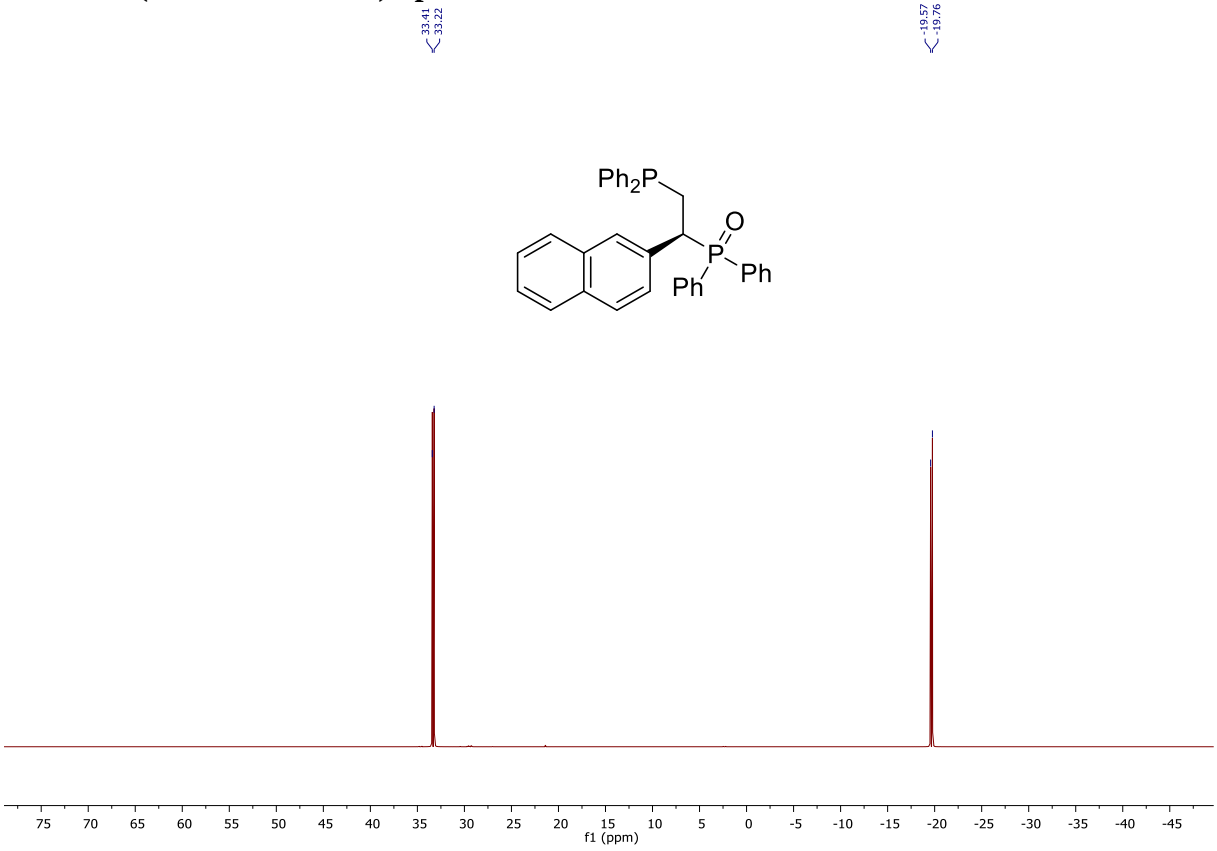
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ma



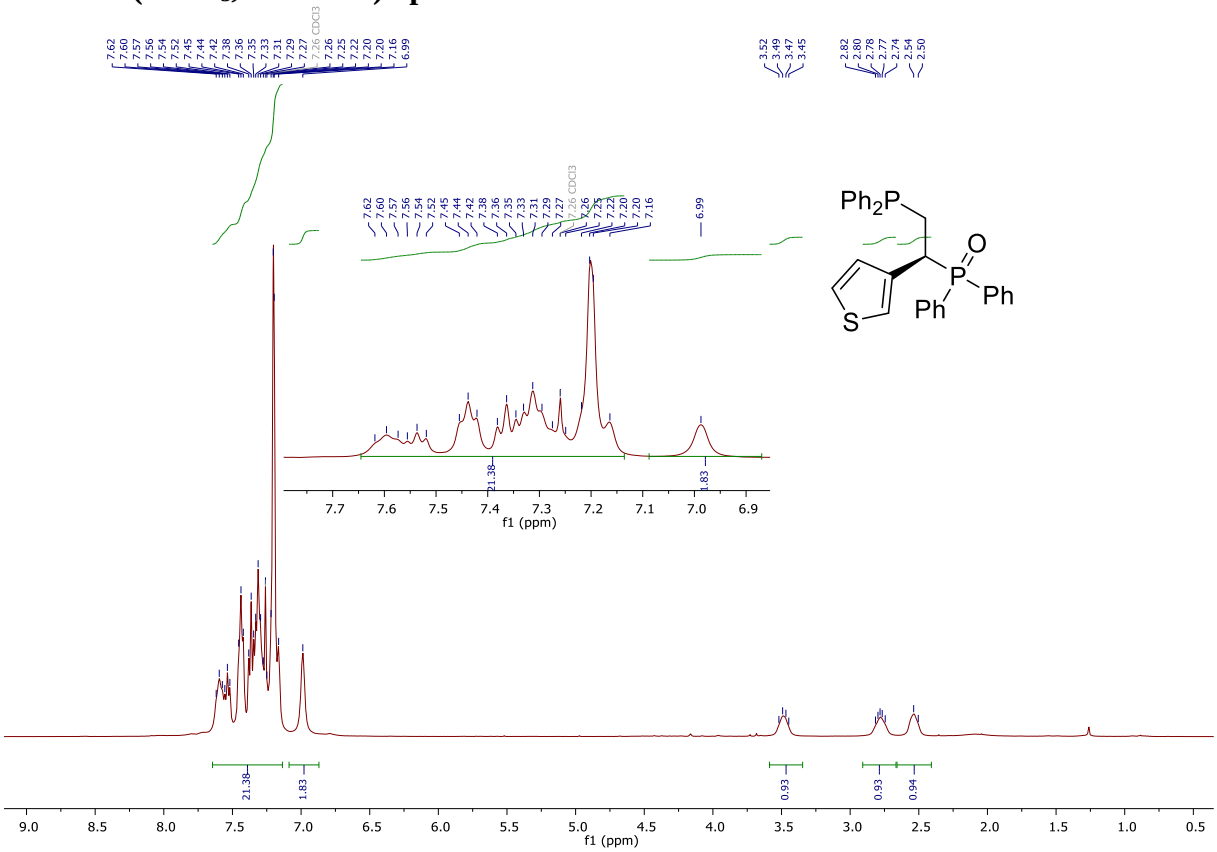
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ma



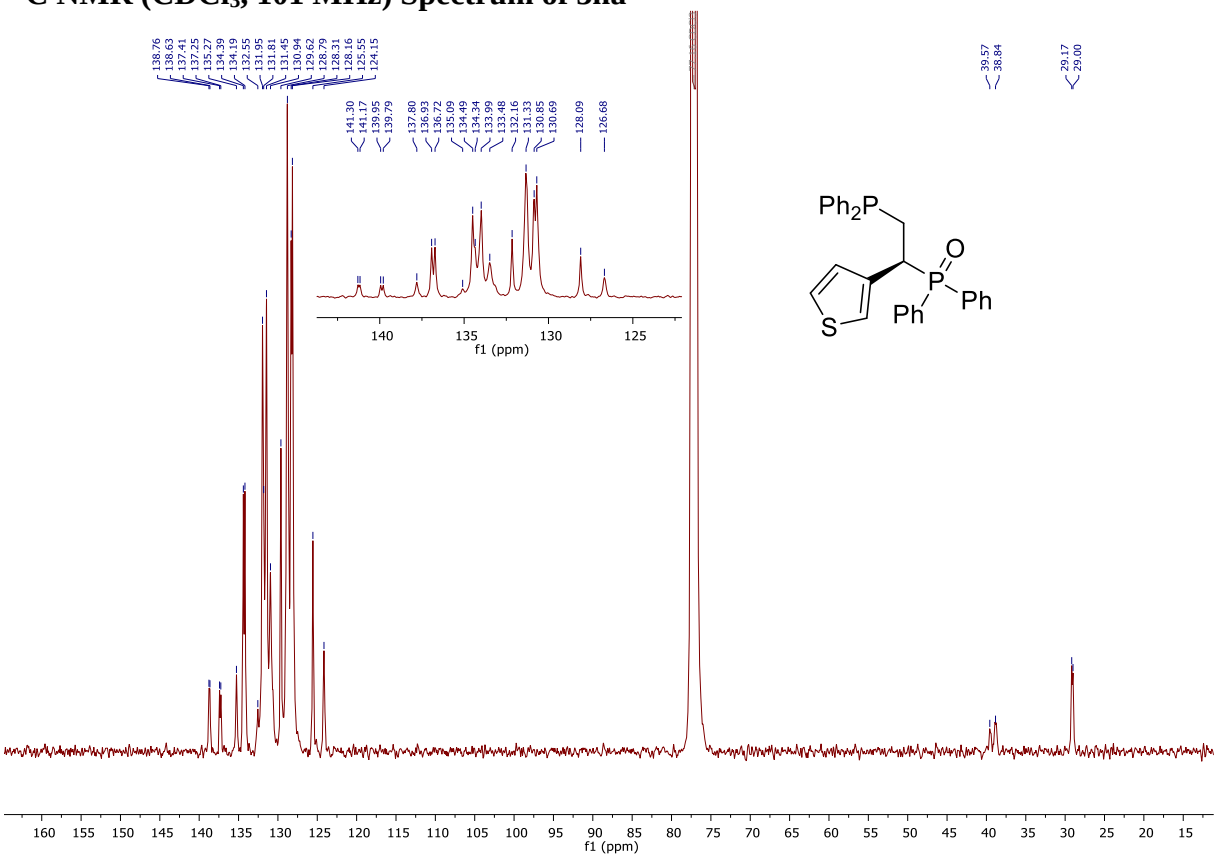
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ma



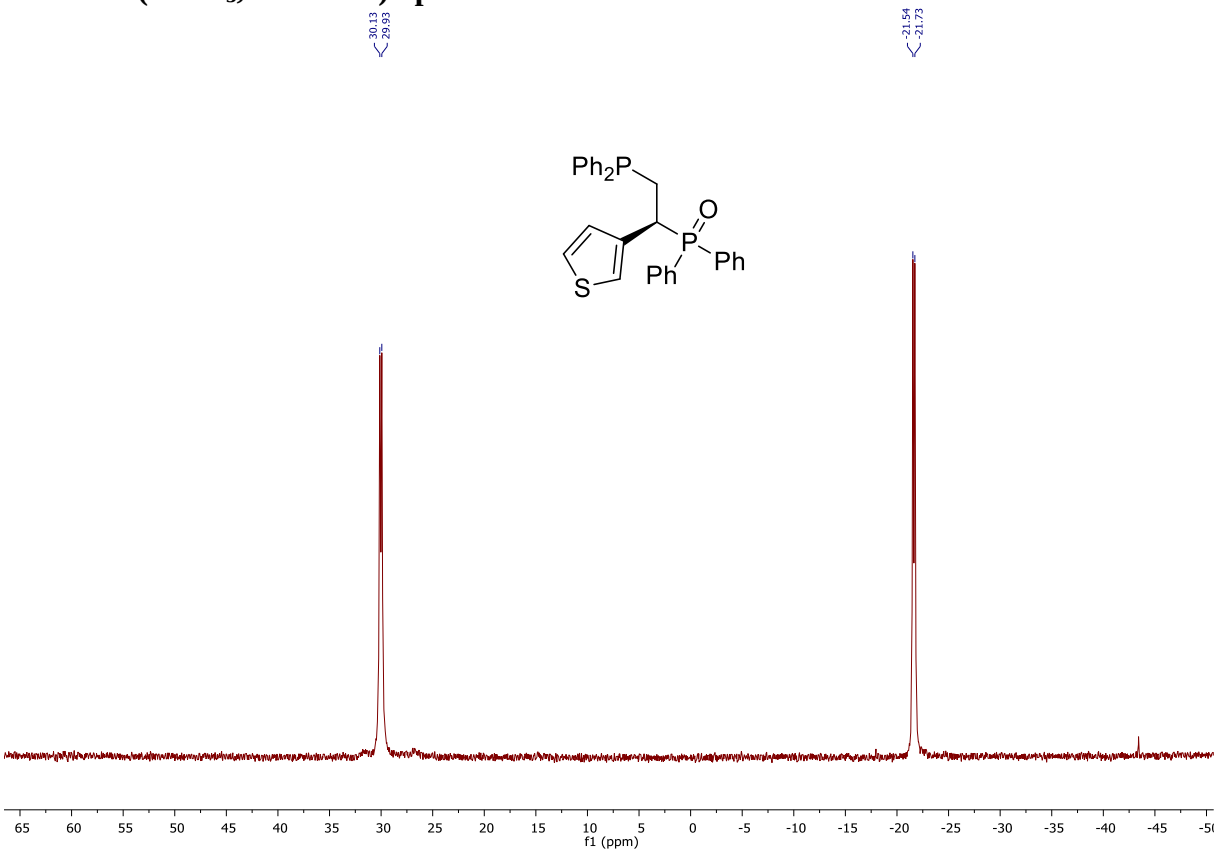
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3na



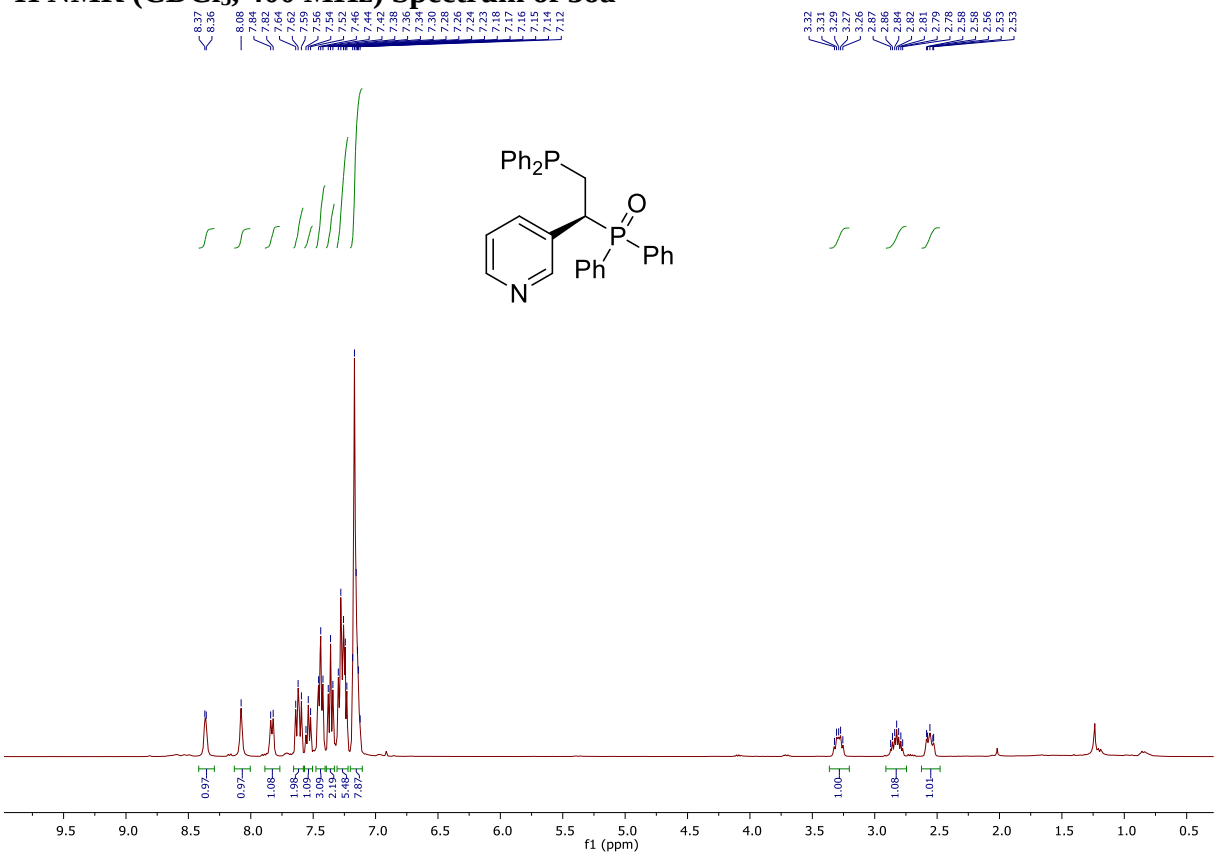
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3na



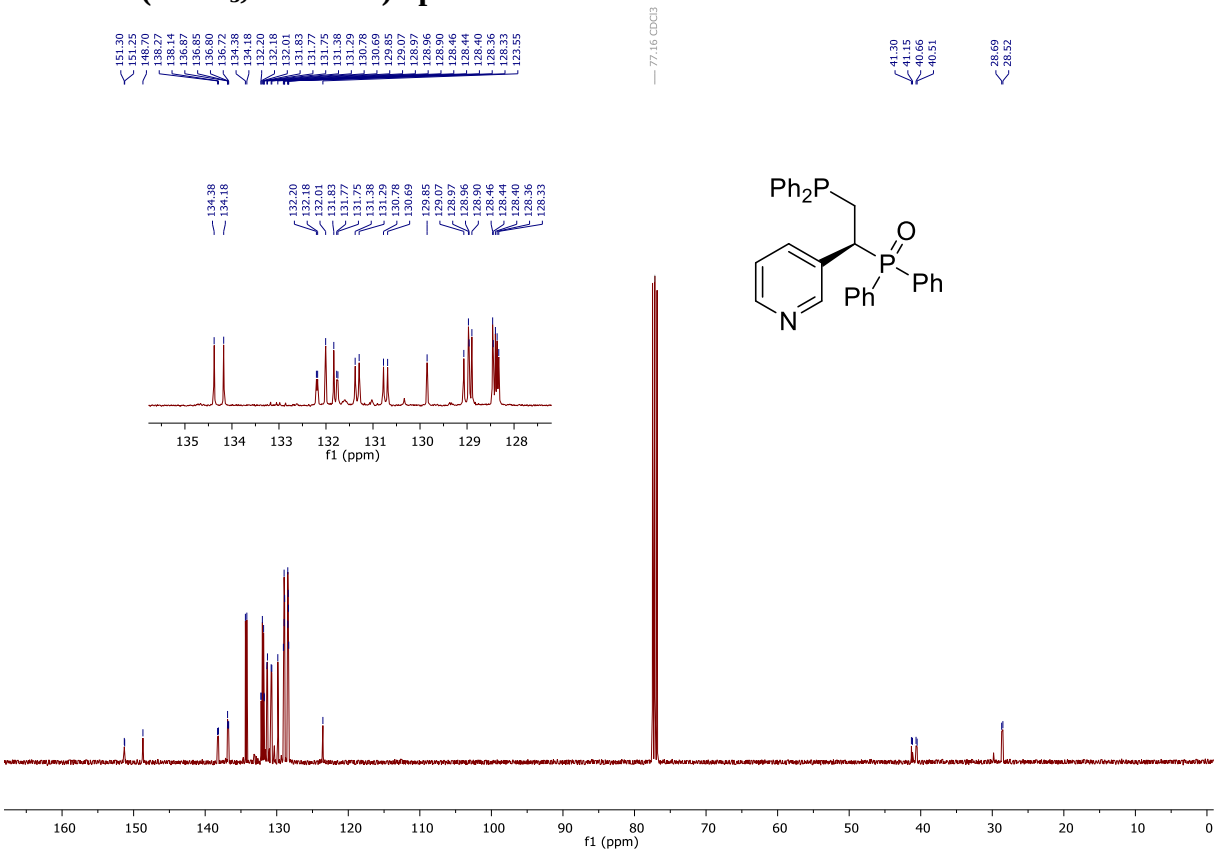
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3na



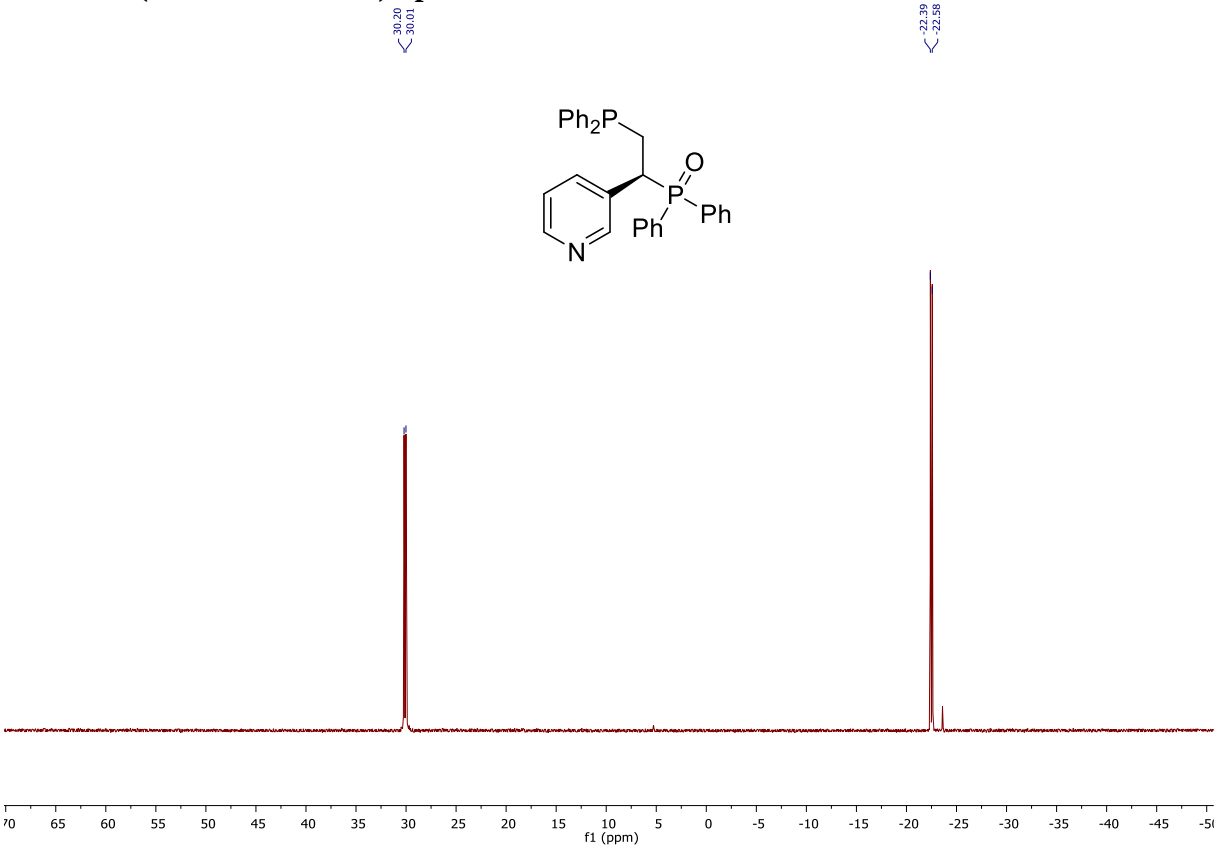
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3oa



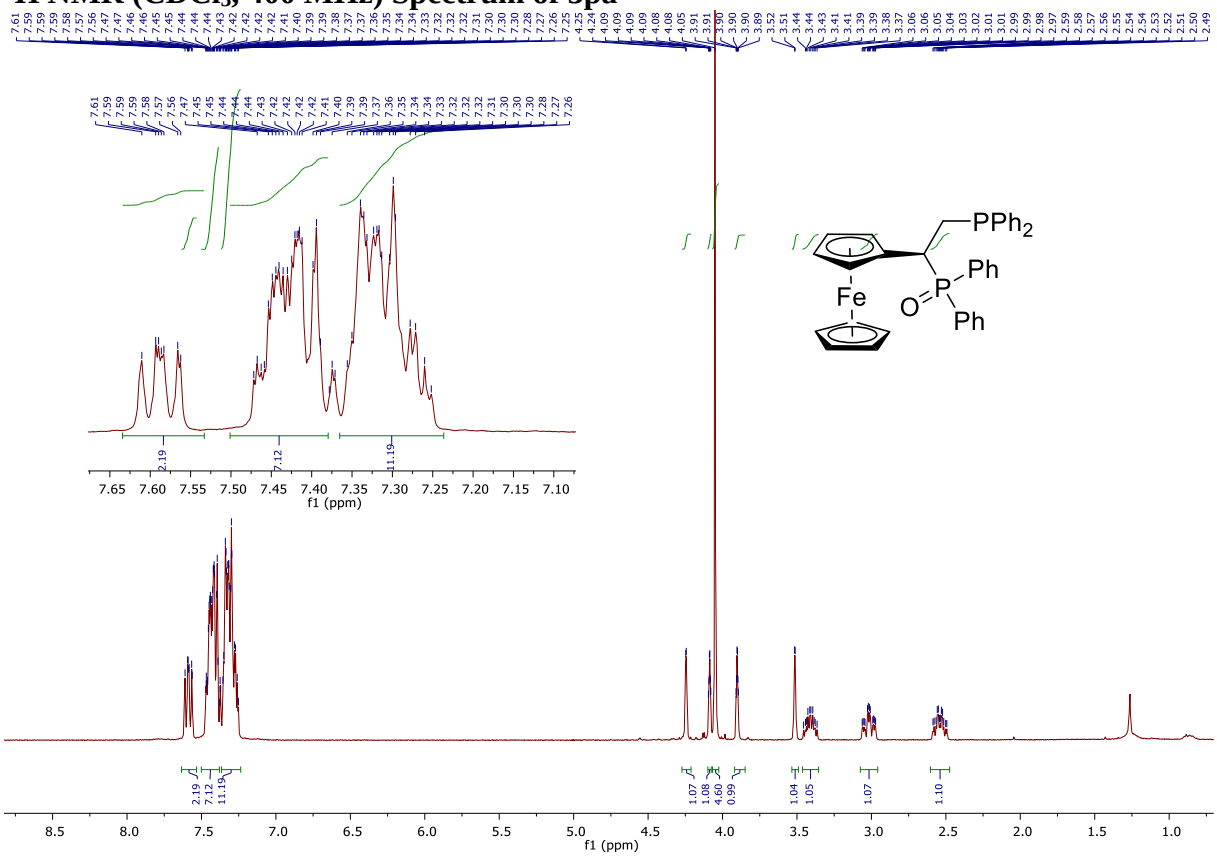
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3oa



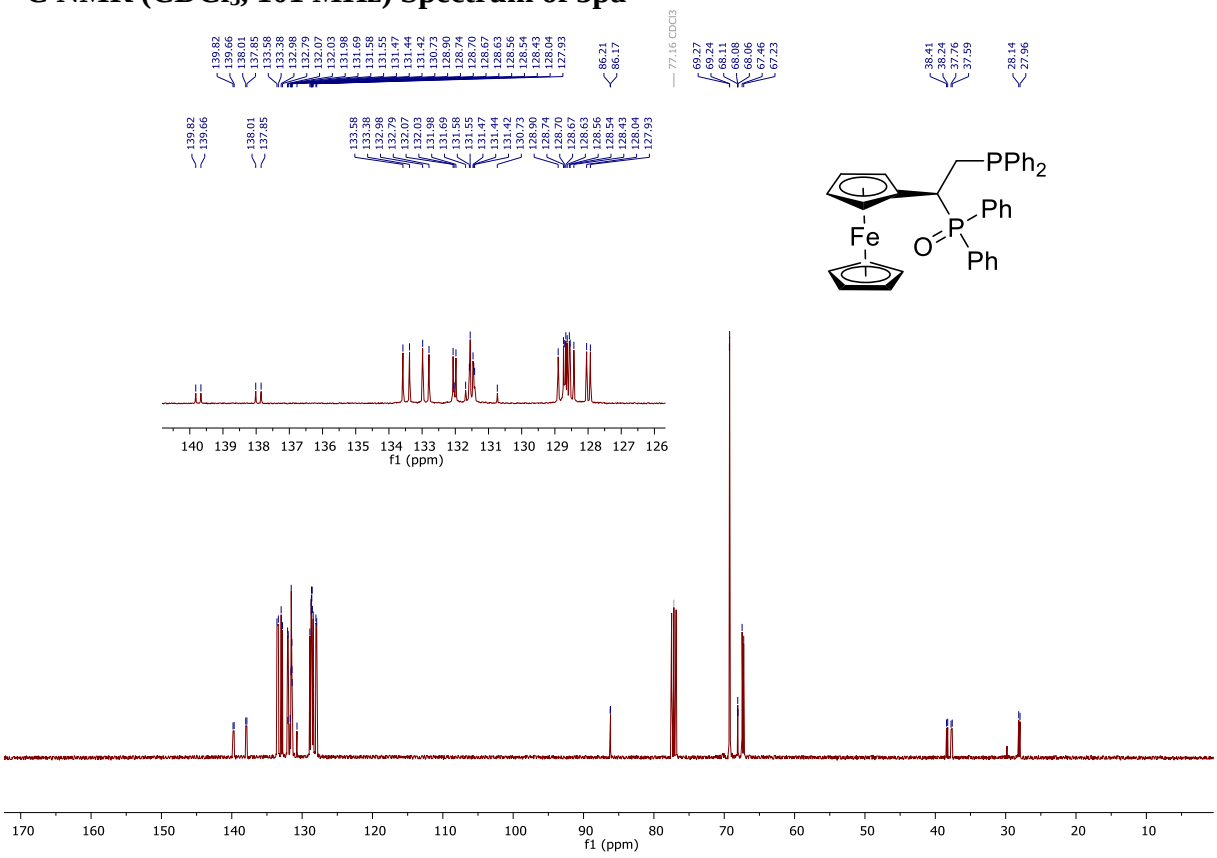
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3oa



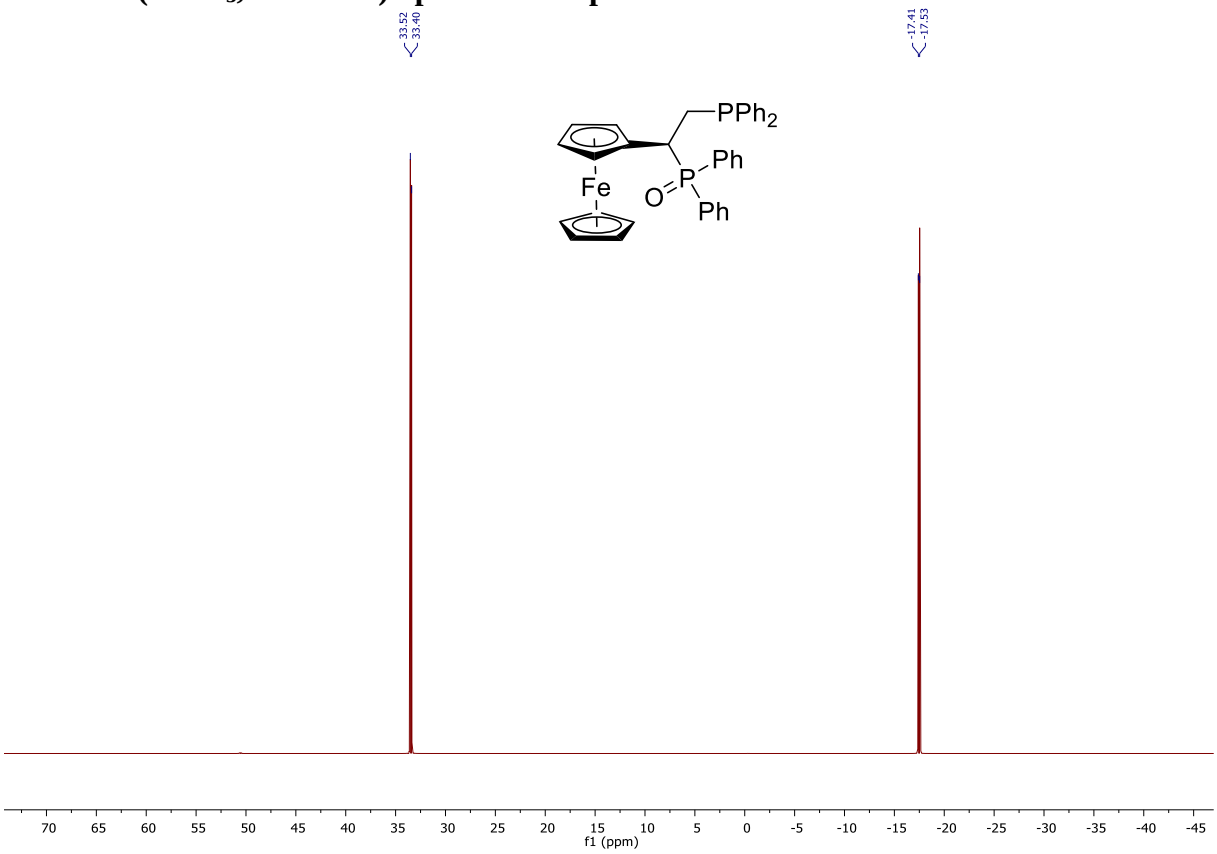
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3pa



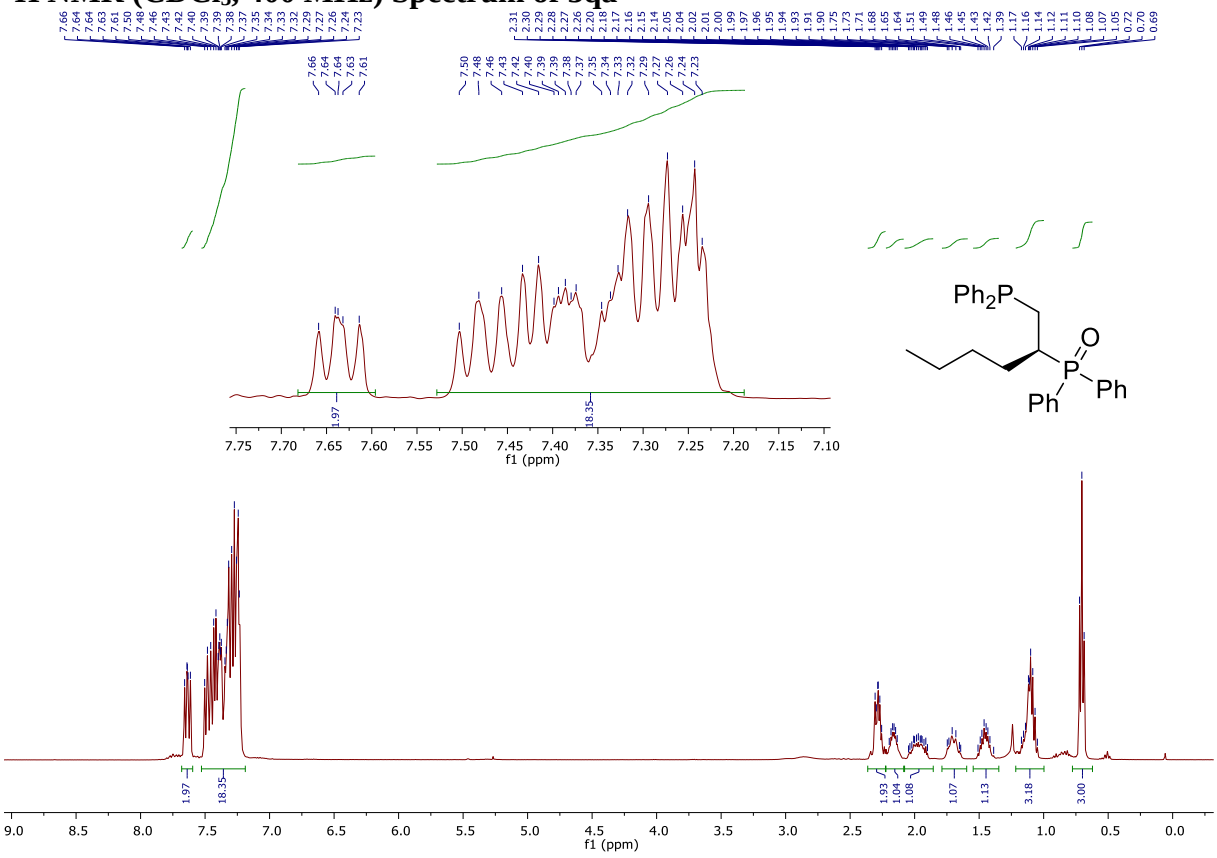
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3pa



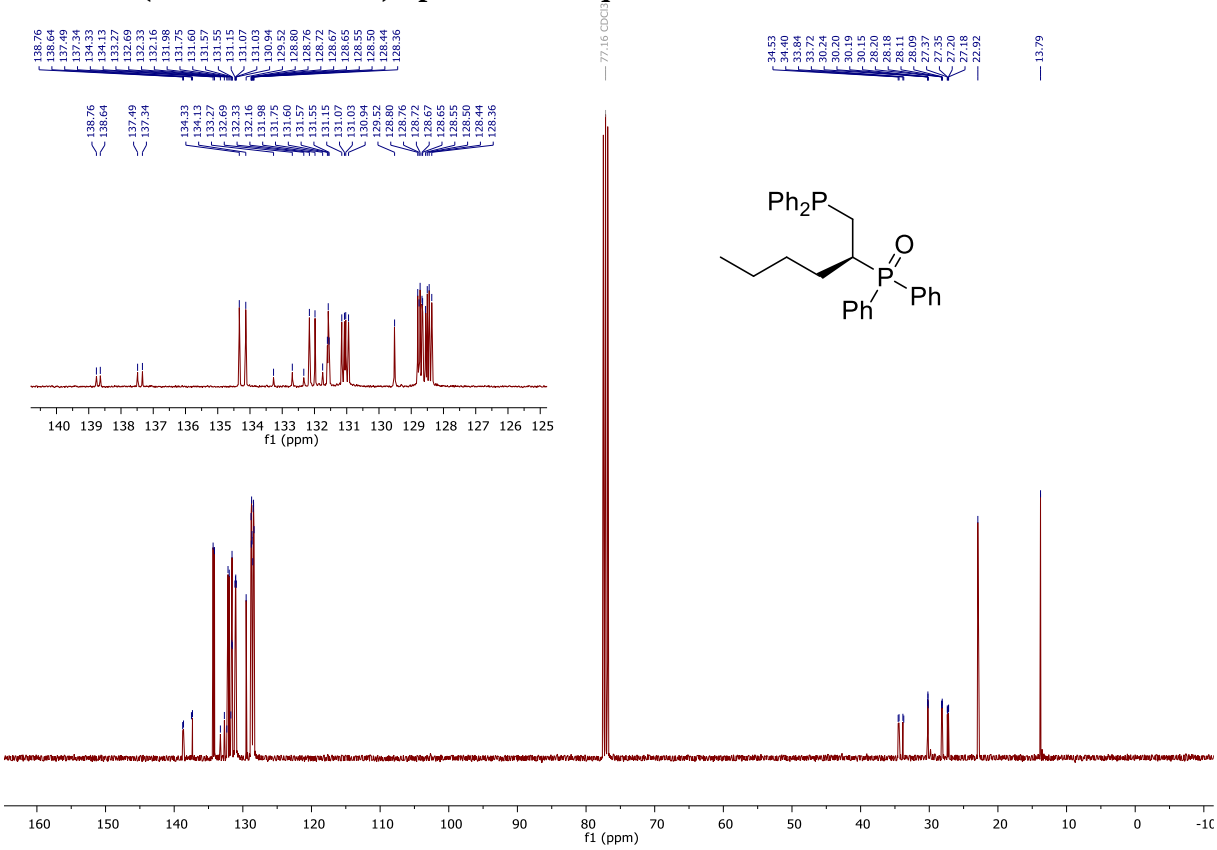
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3pa



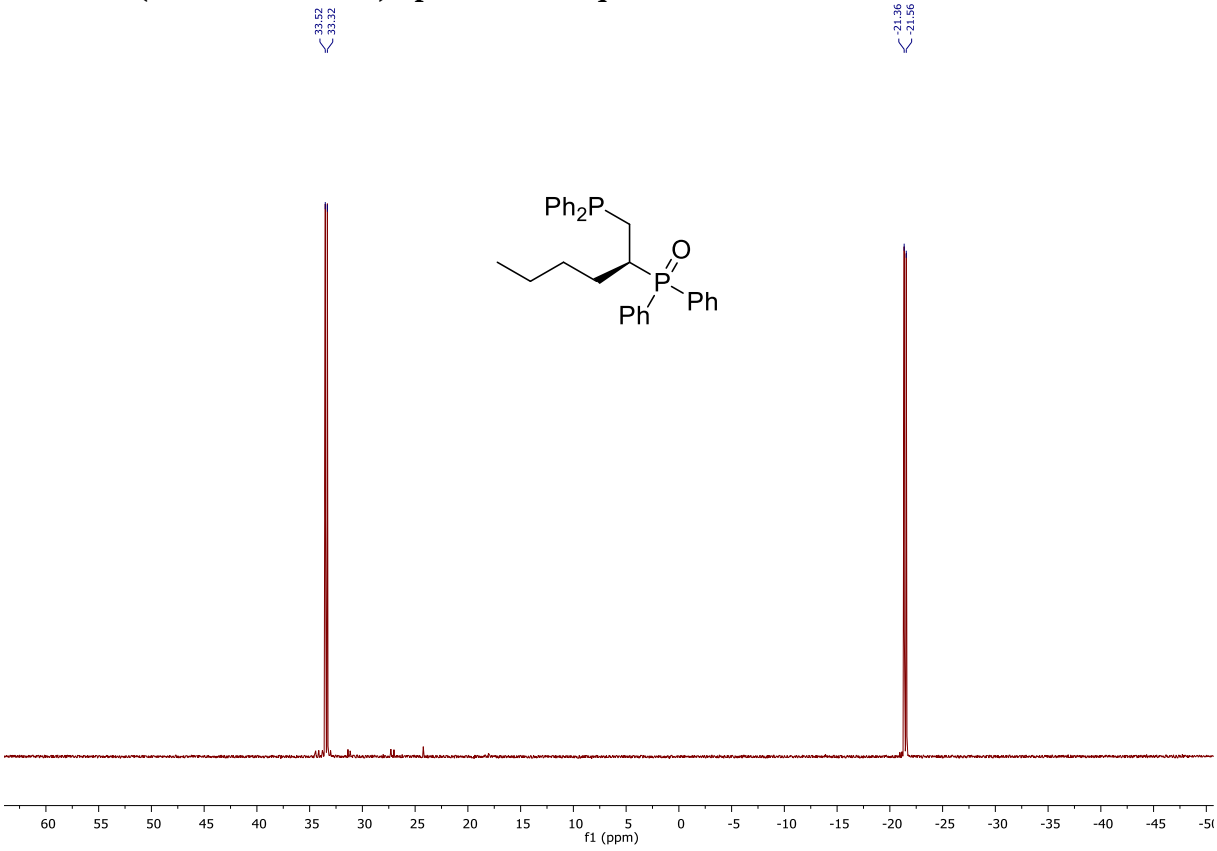
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3qa



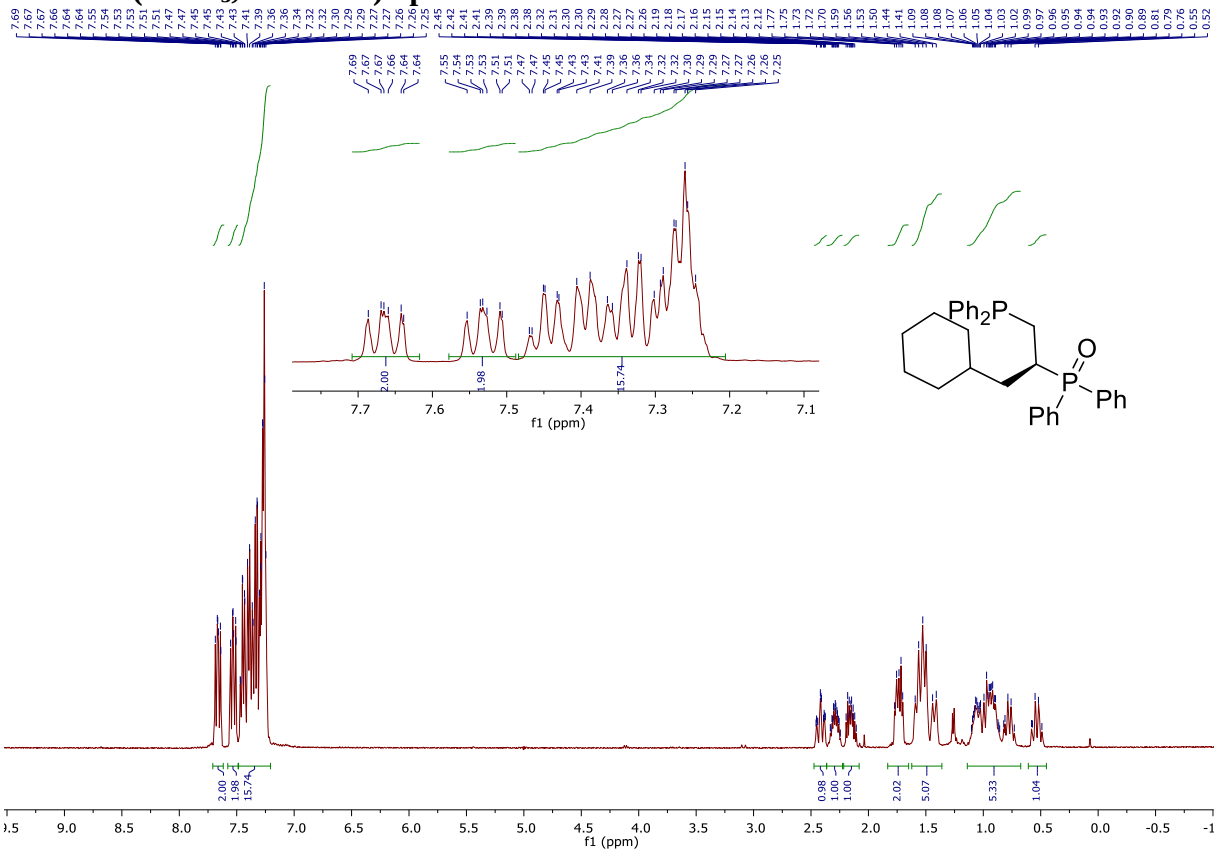
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3qa



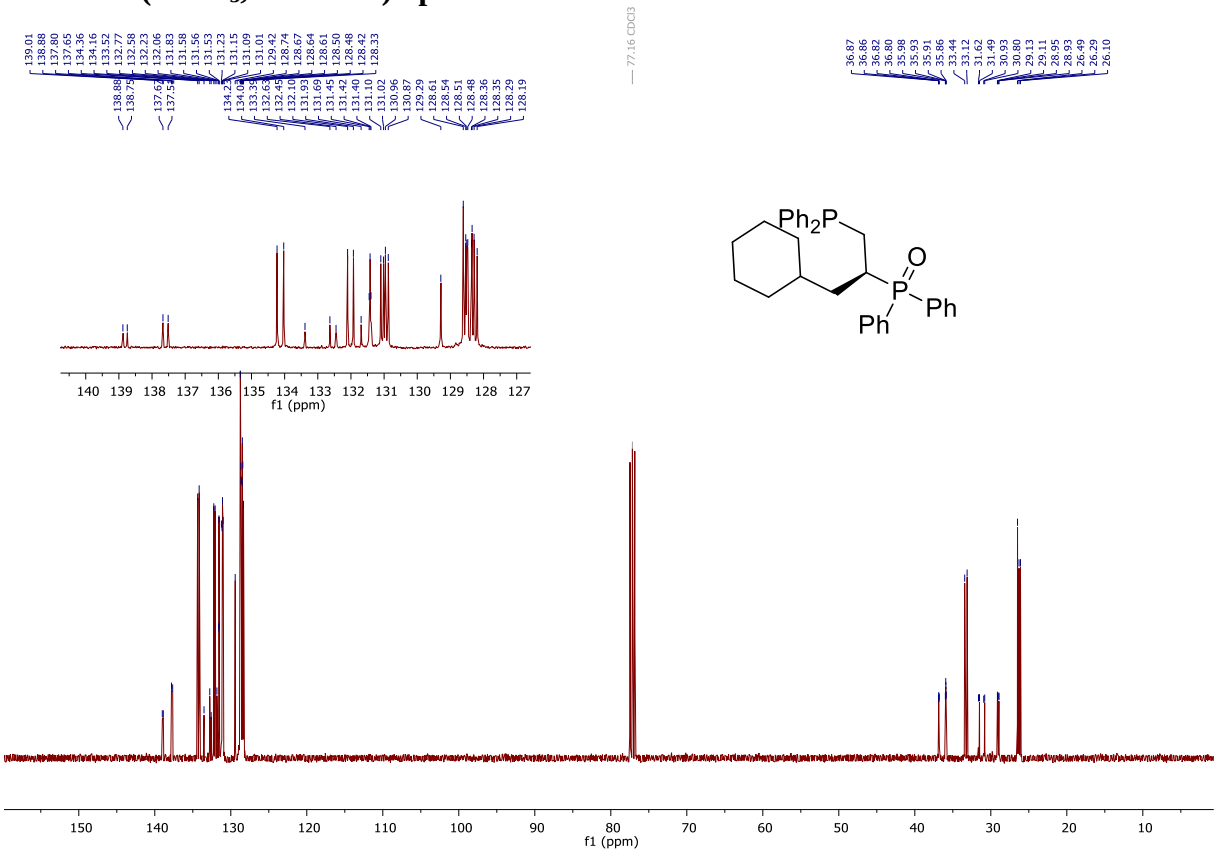
^{31}P NMR ($CDCl_3$, 101 MHz) Spectrum of 3qa



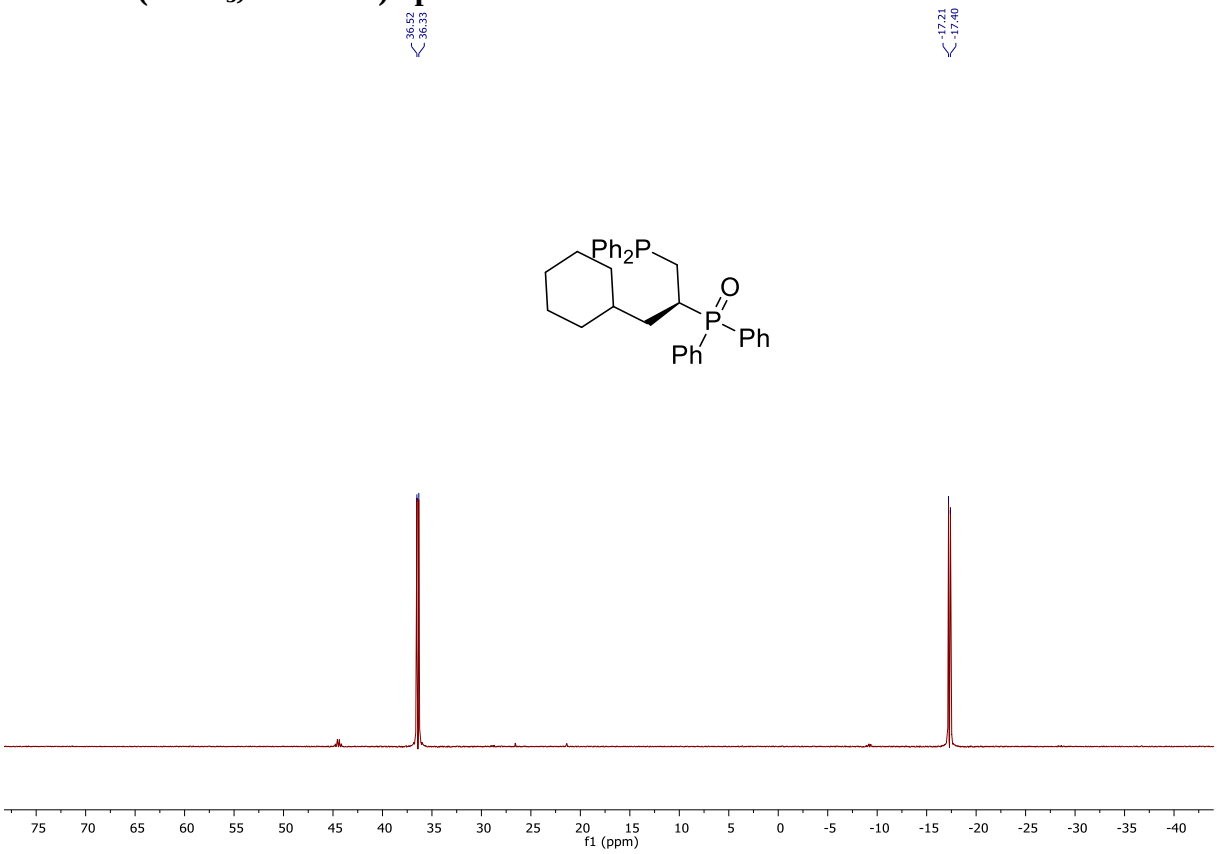
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ra



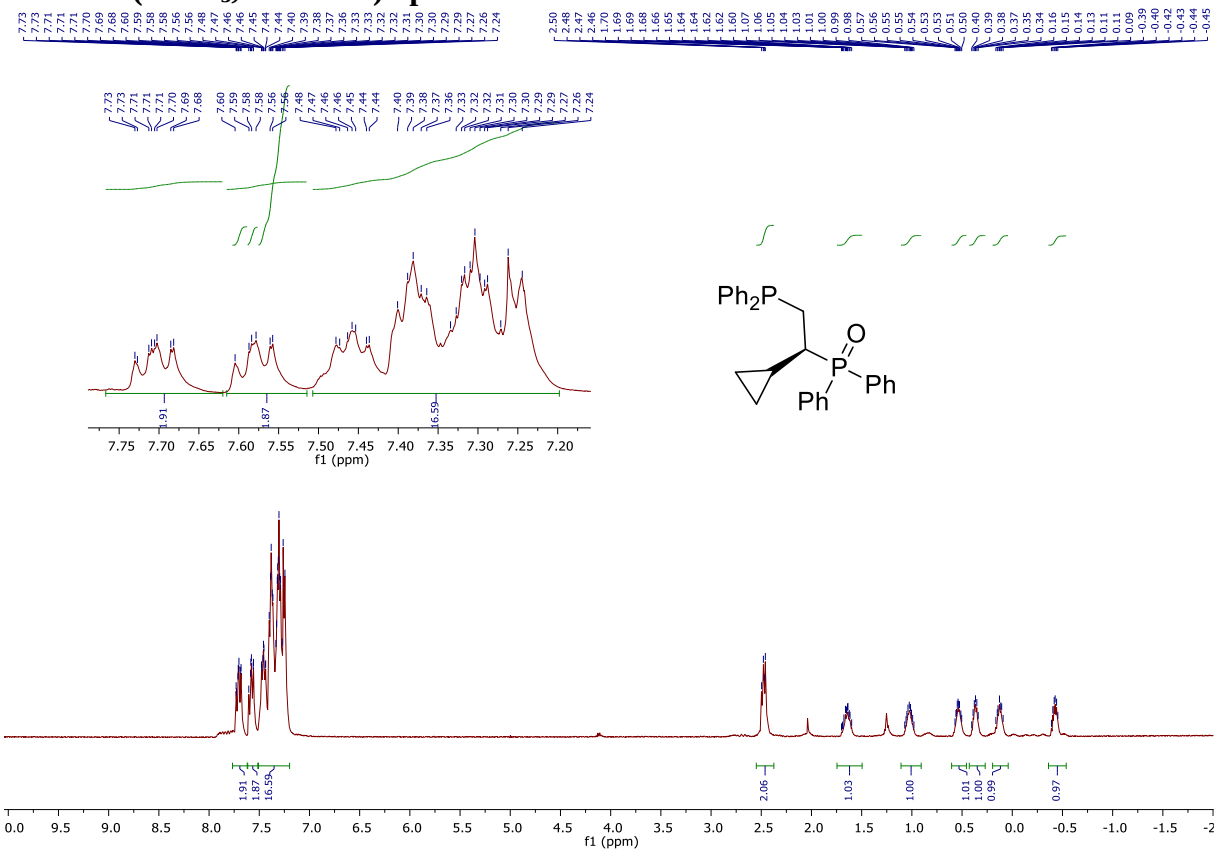
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ra



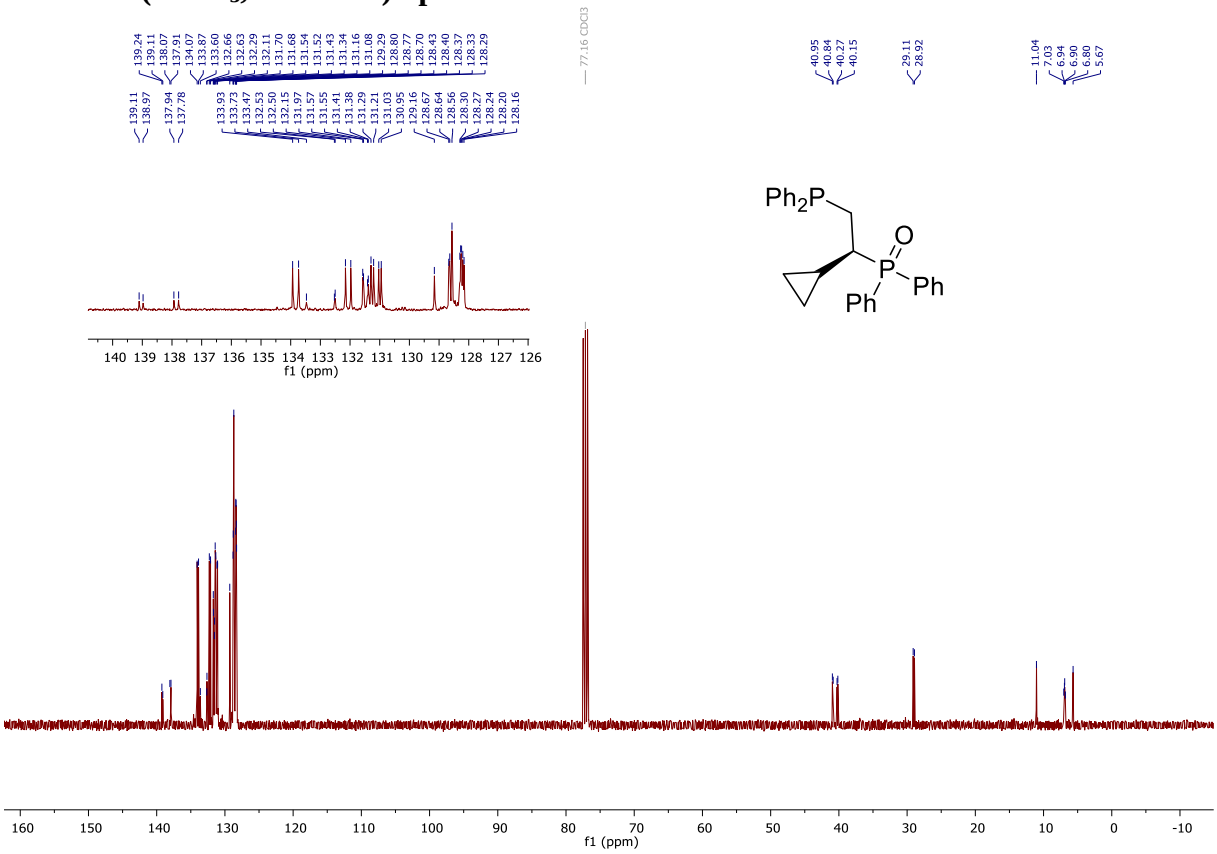
^{31}P NMR ($CDCl_3$, 101 MHz) Spectrum of 3ra



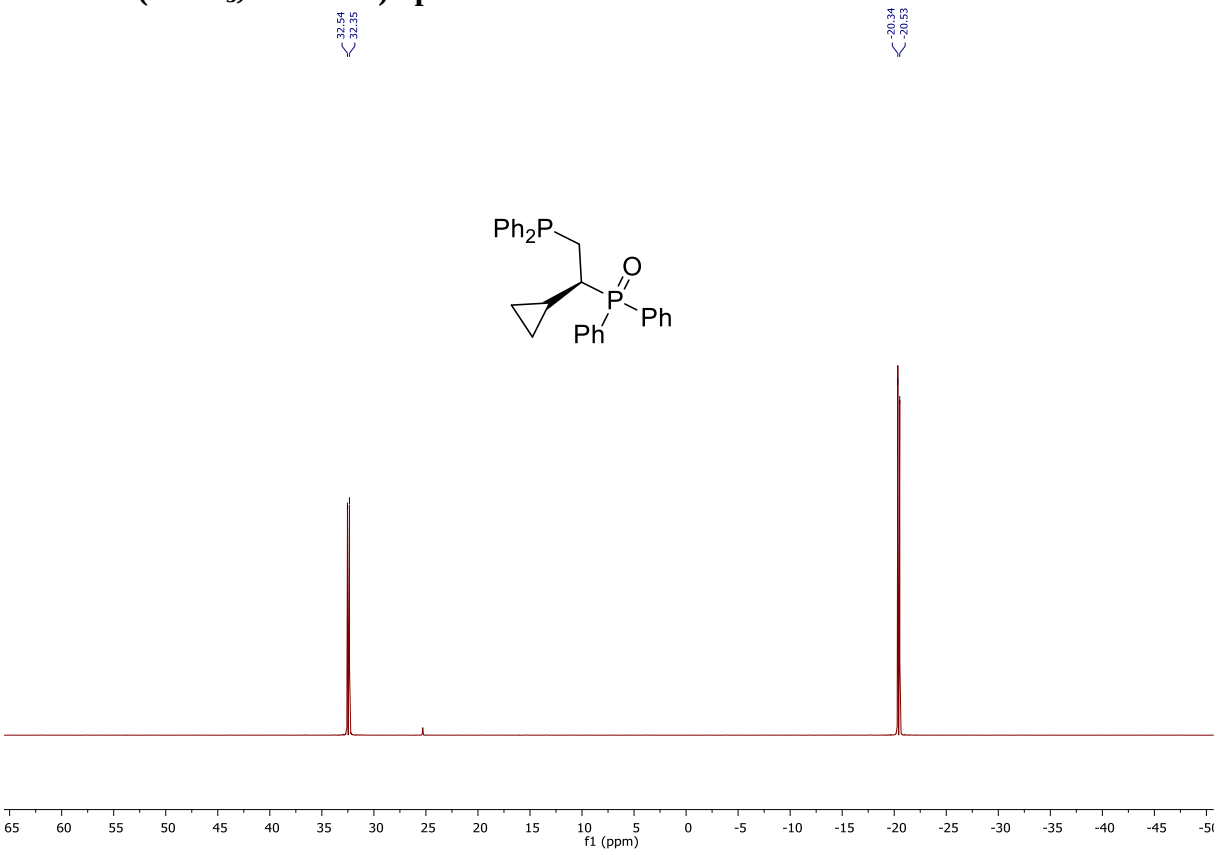
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3sa



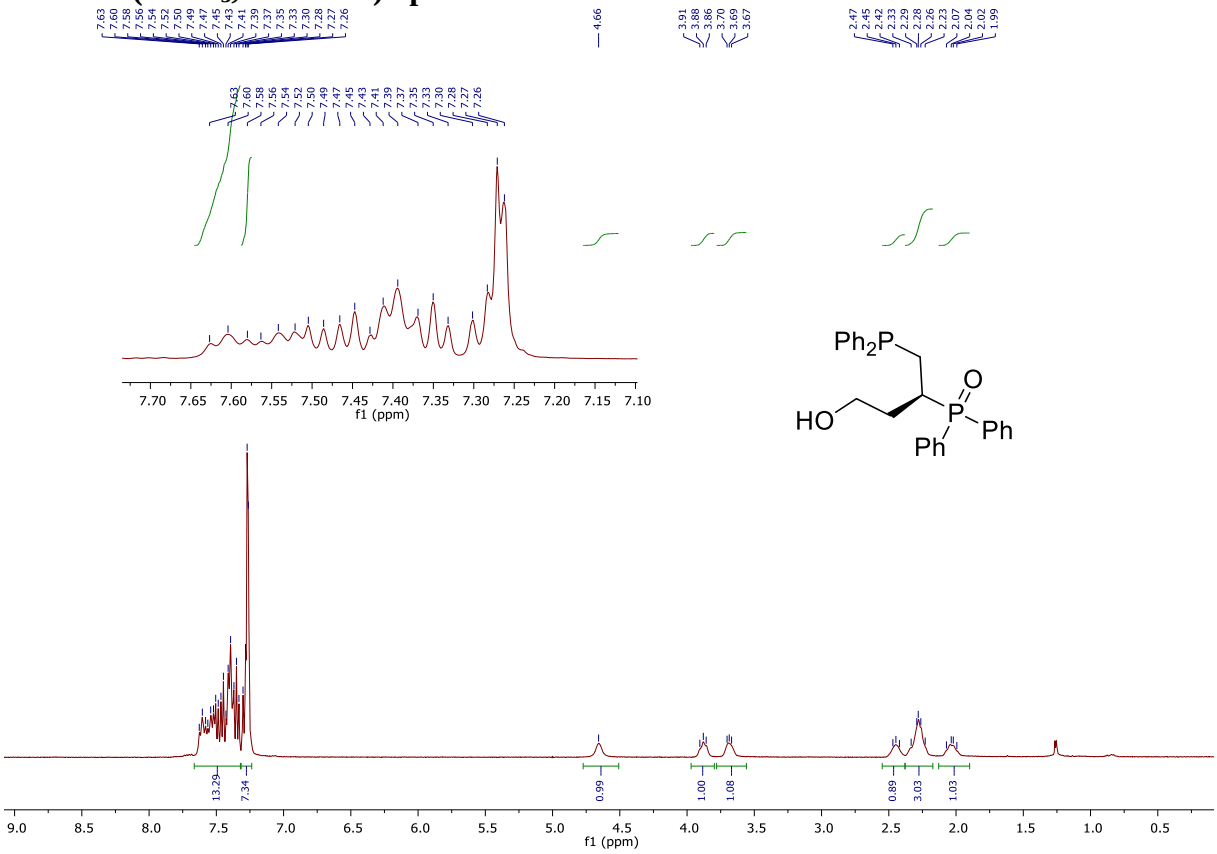
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3sa



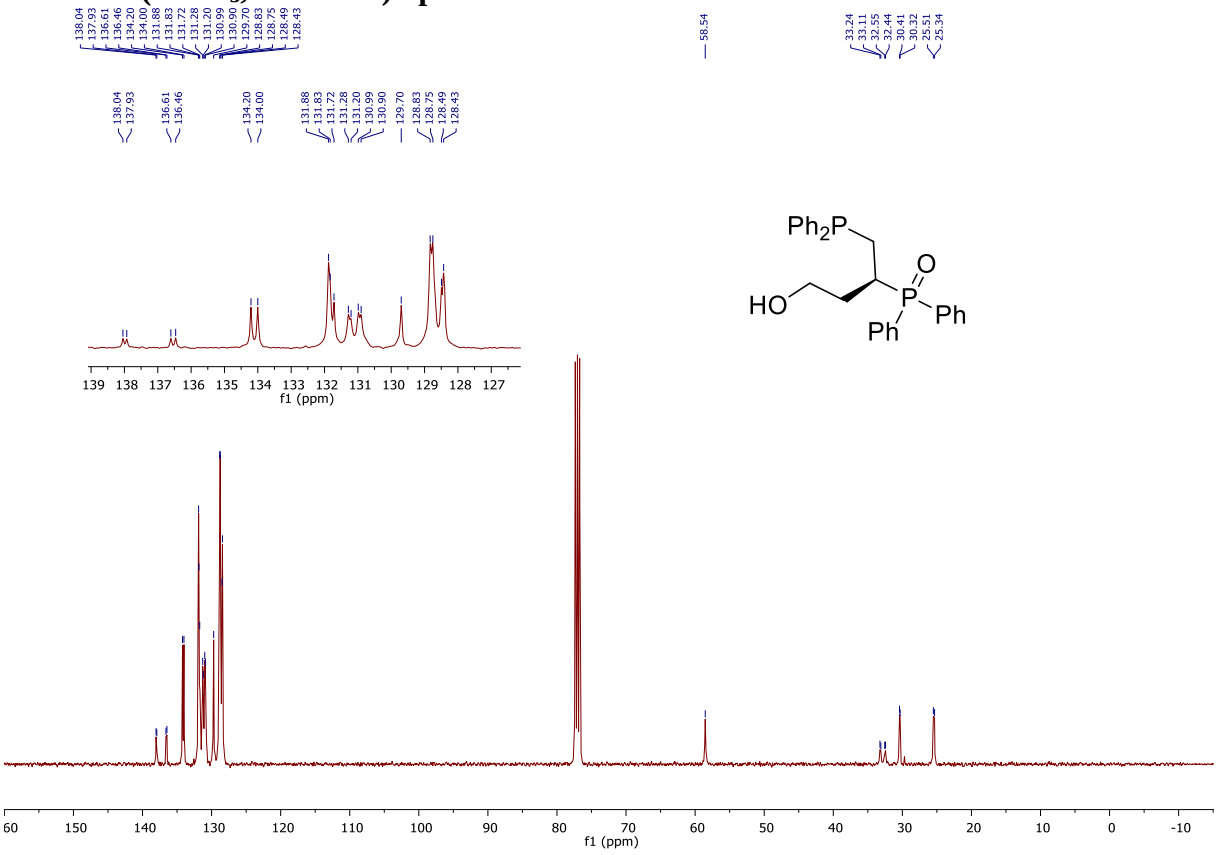
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3sa



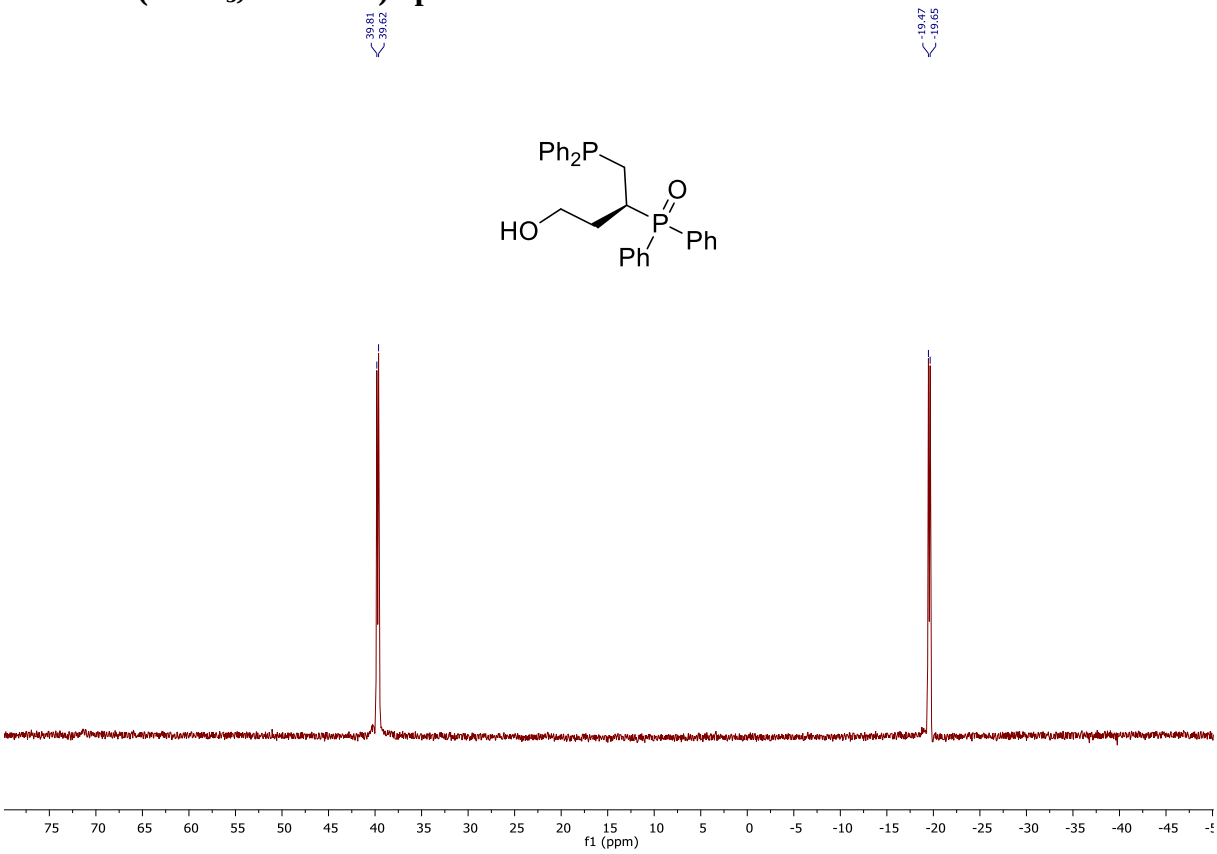
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ta



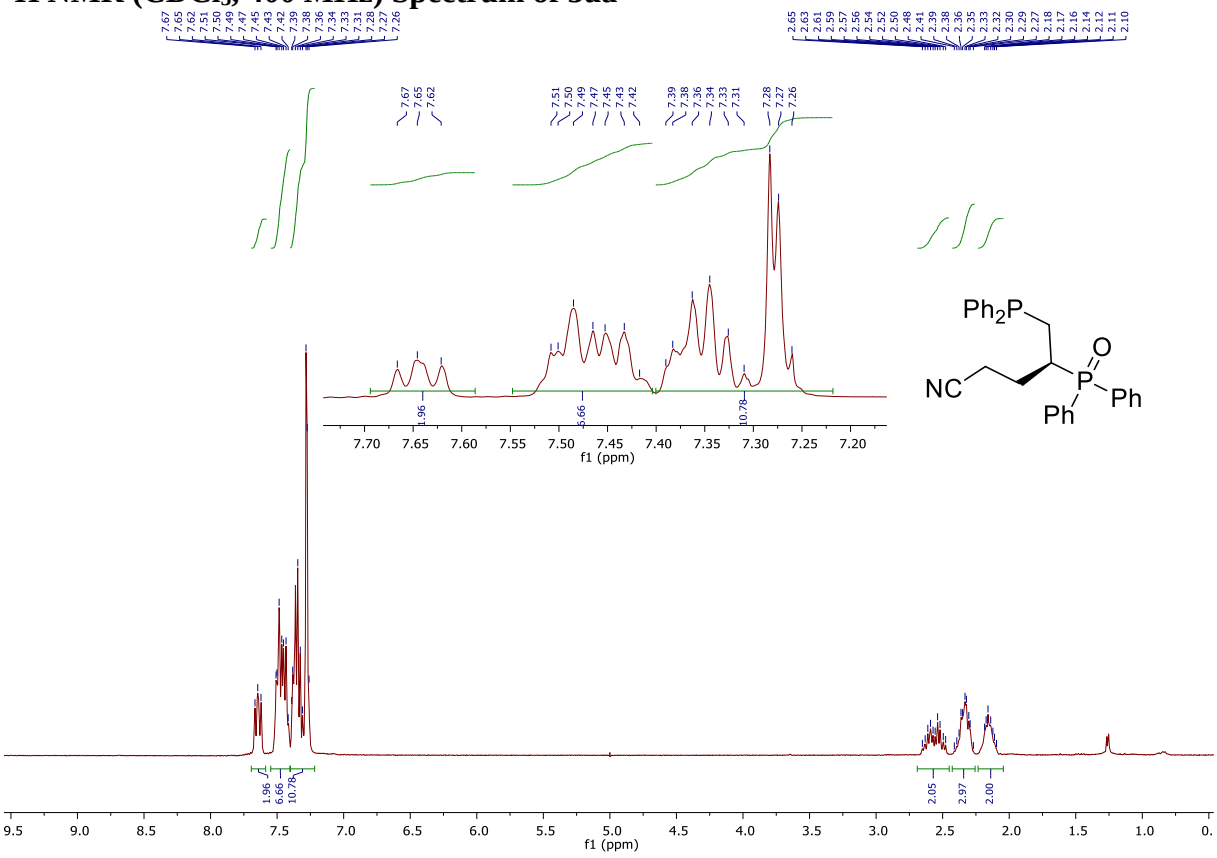
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ta



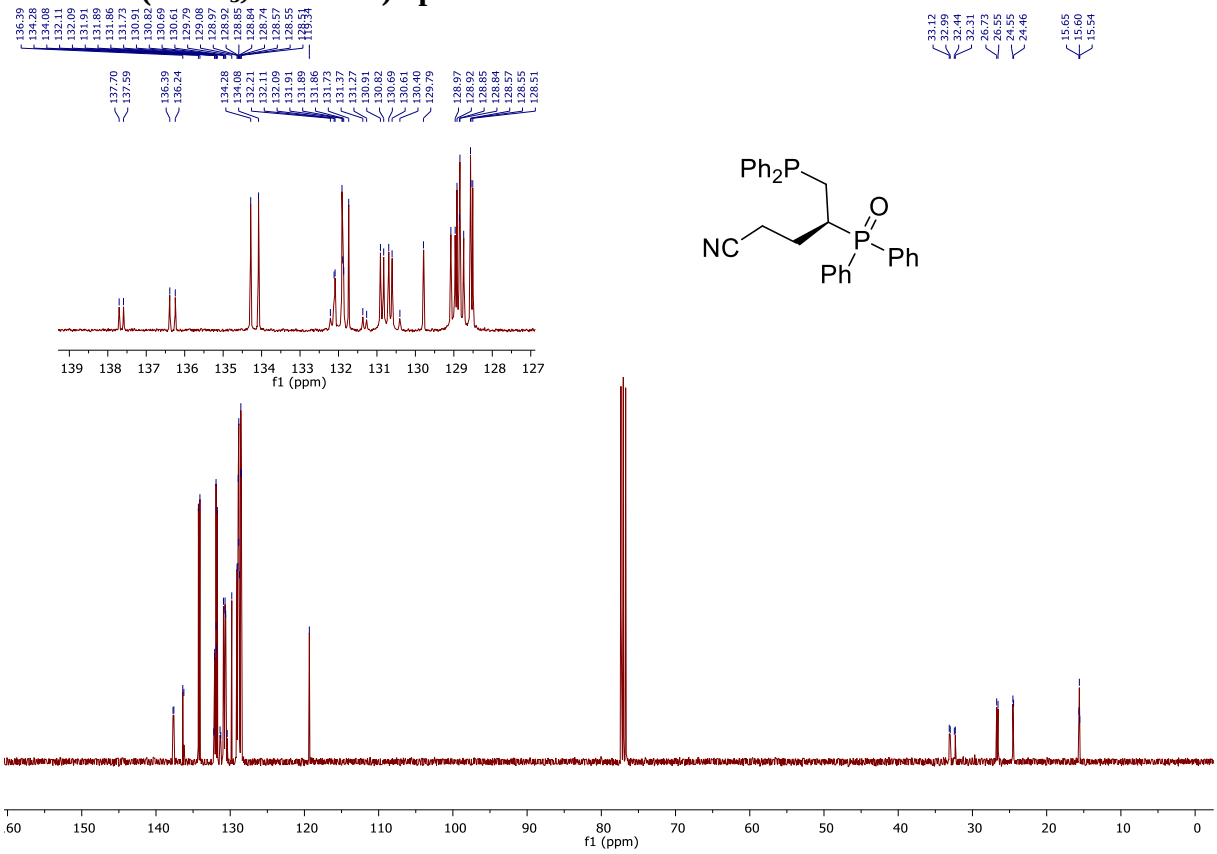
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ta



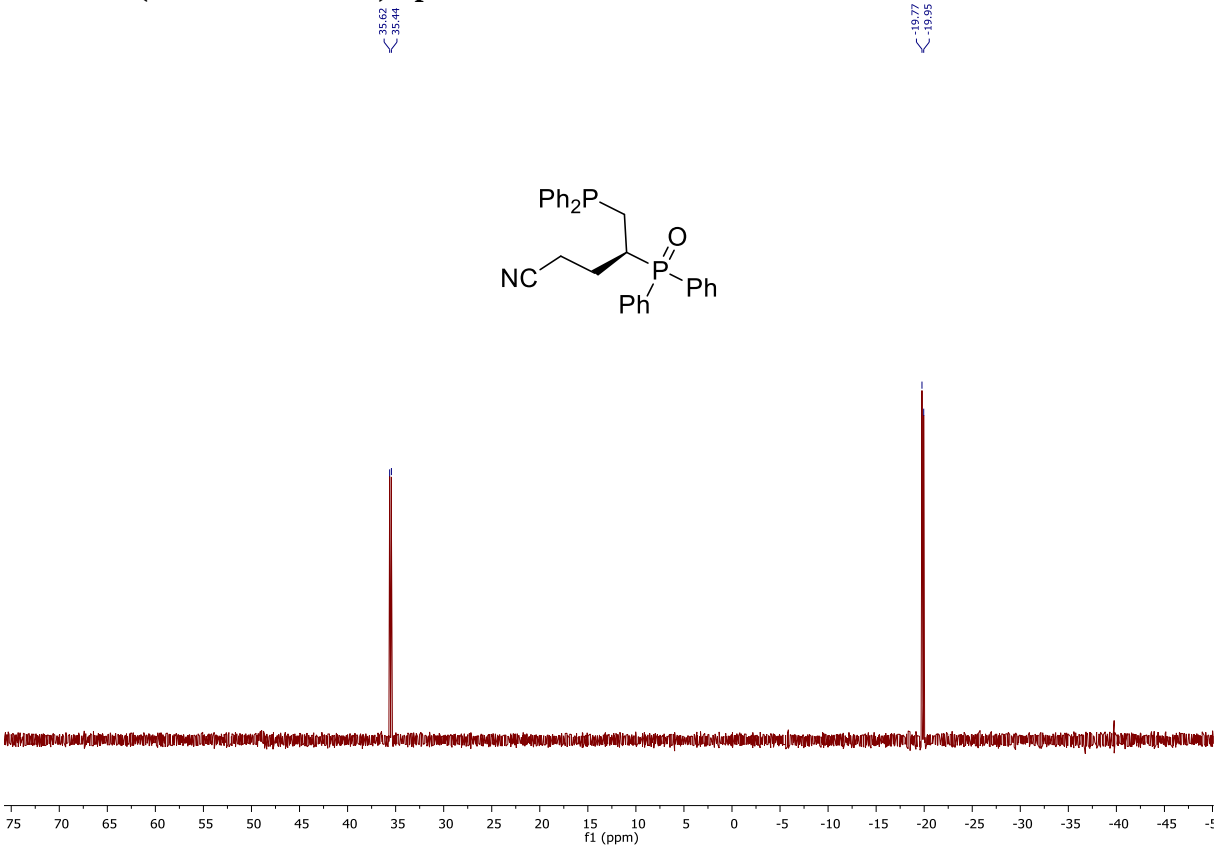
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ua



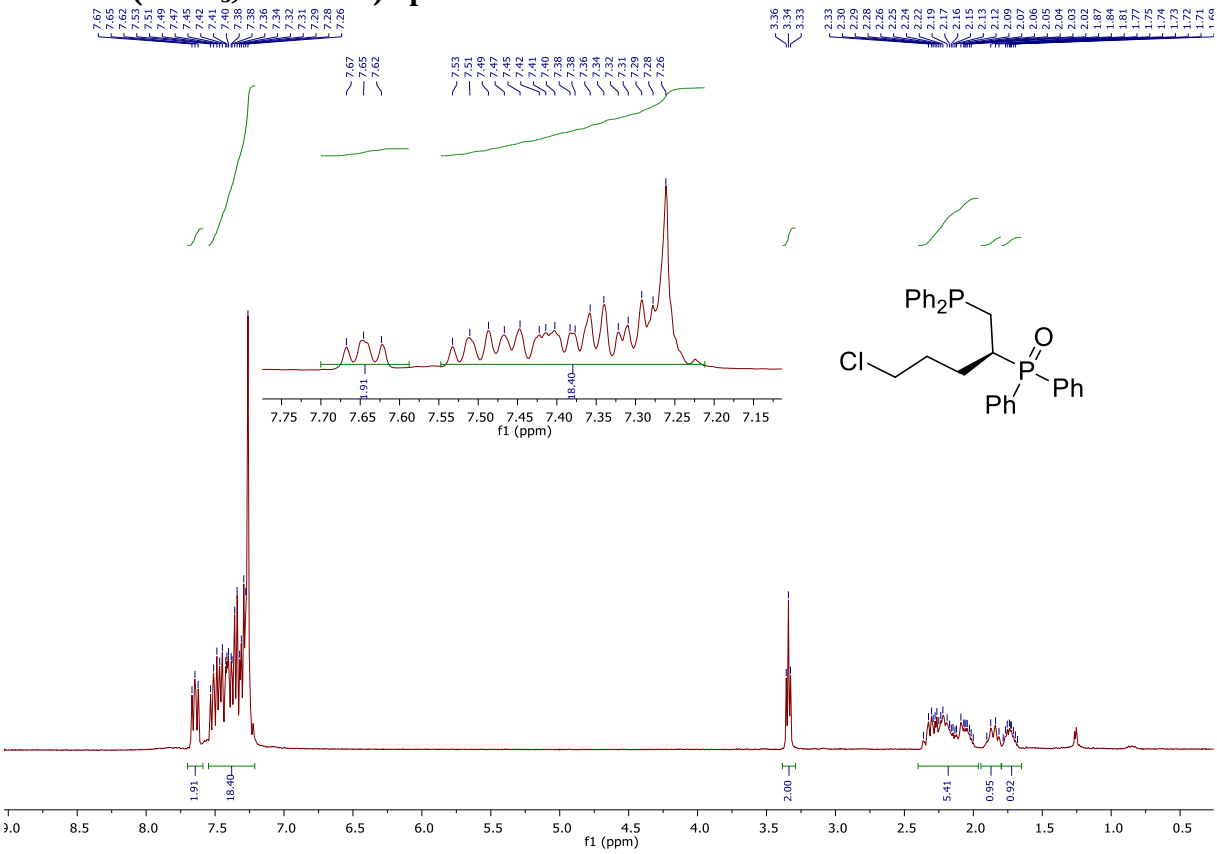
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ua



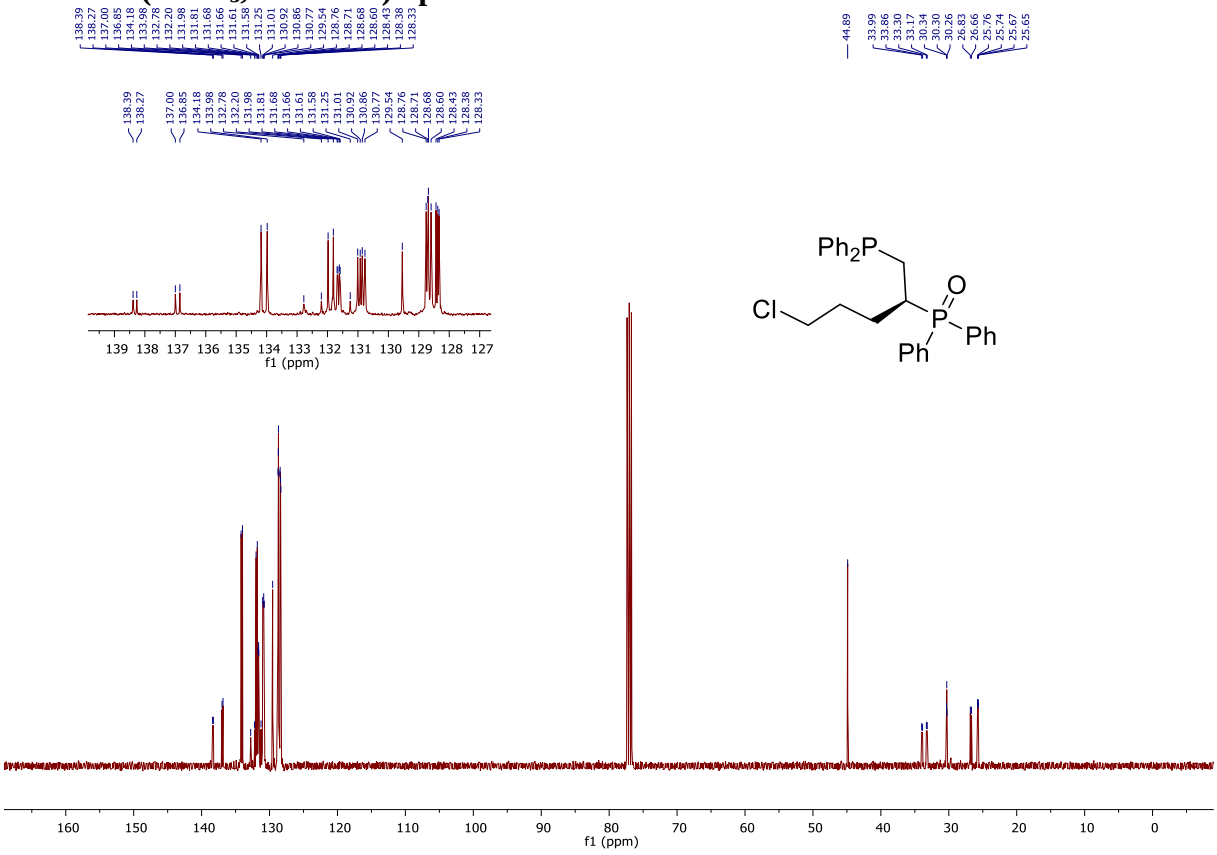
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ua



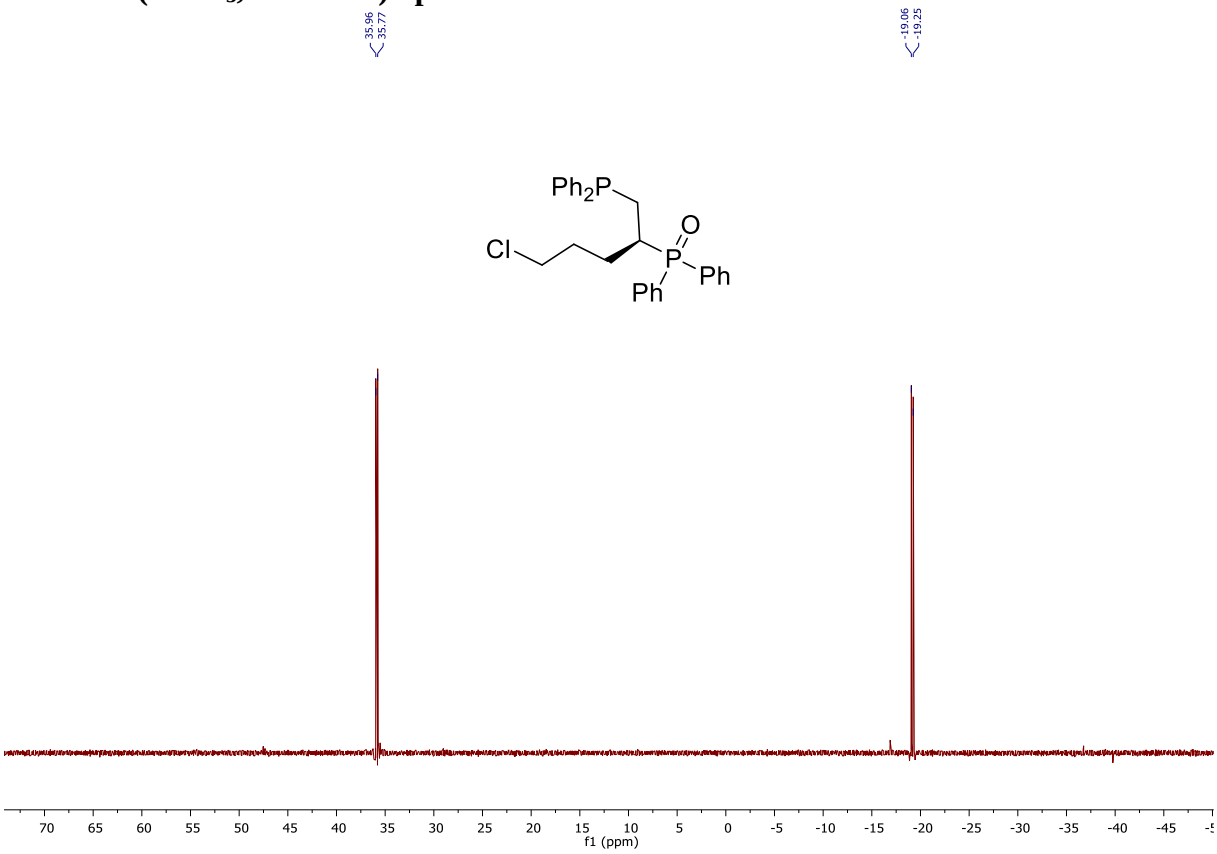
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3va



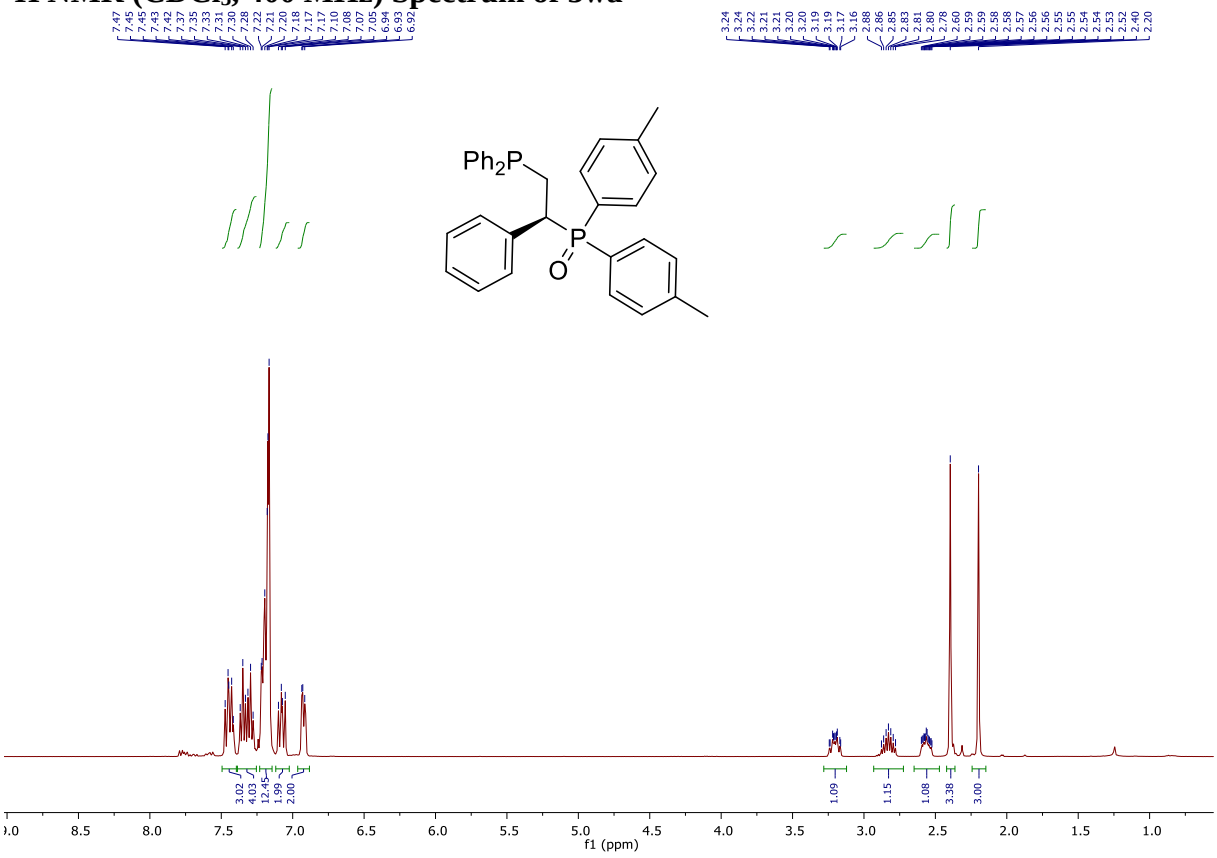
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3va



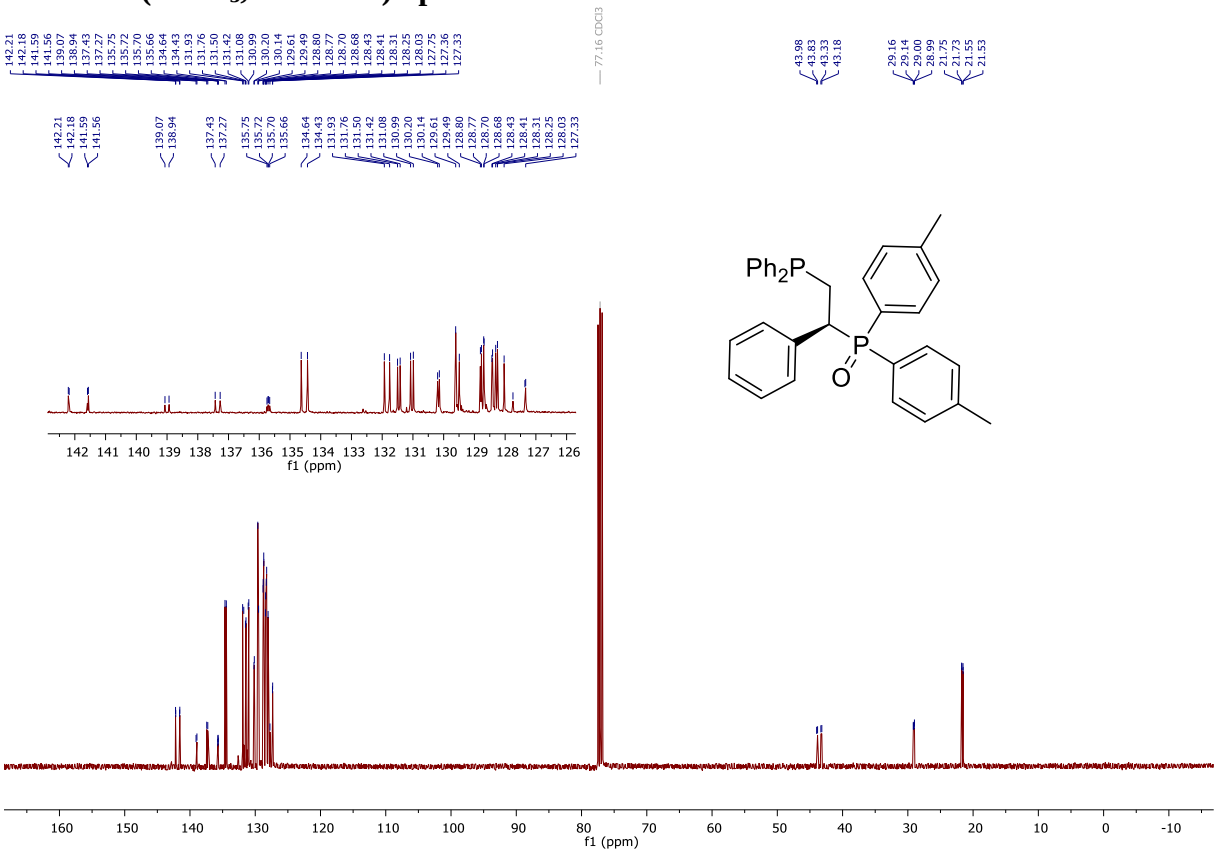
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3va



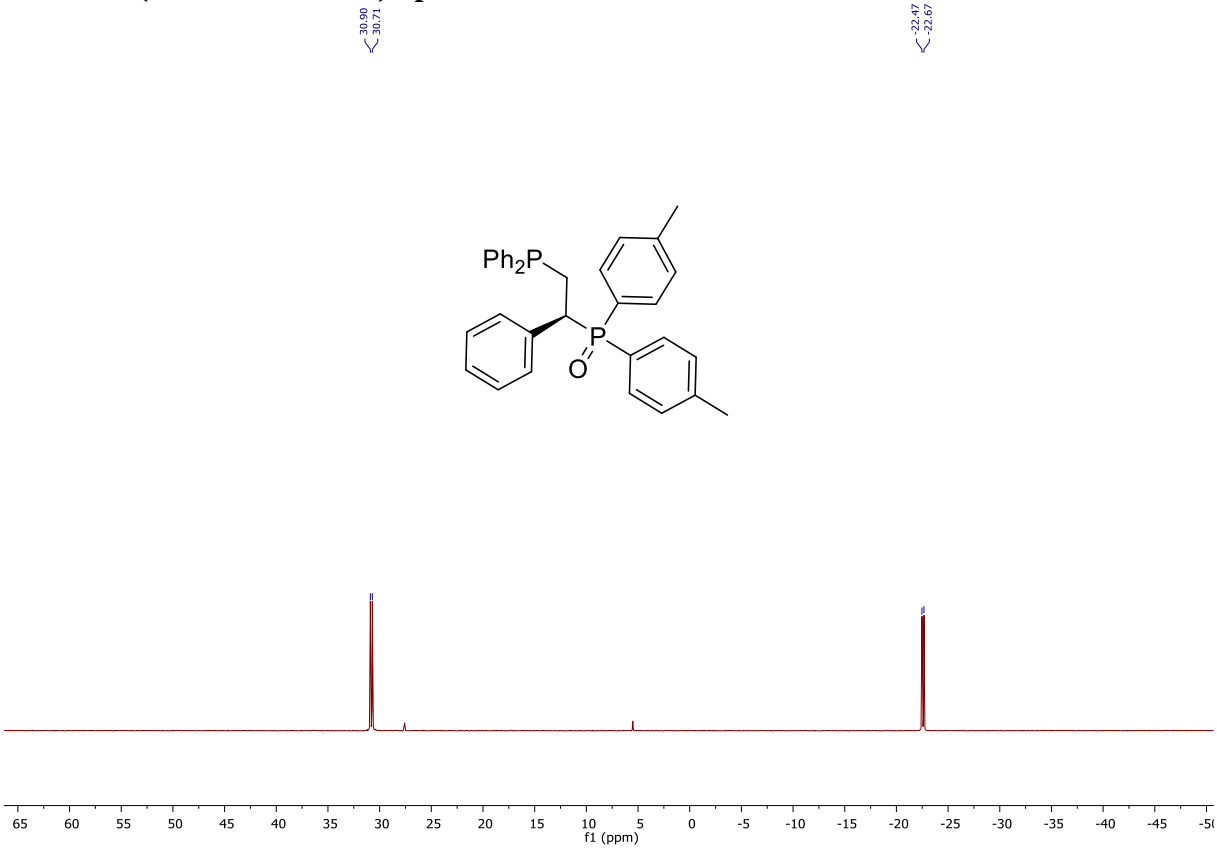
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3wa



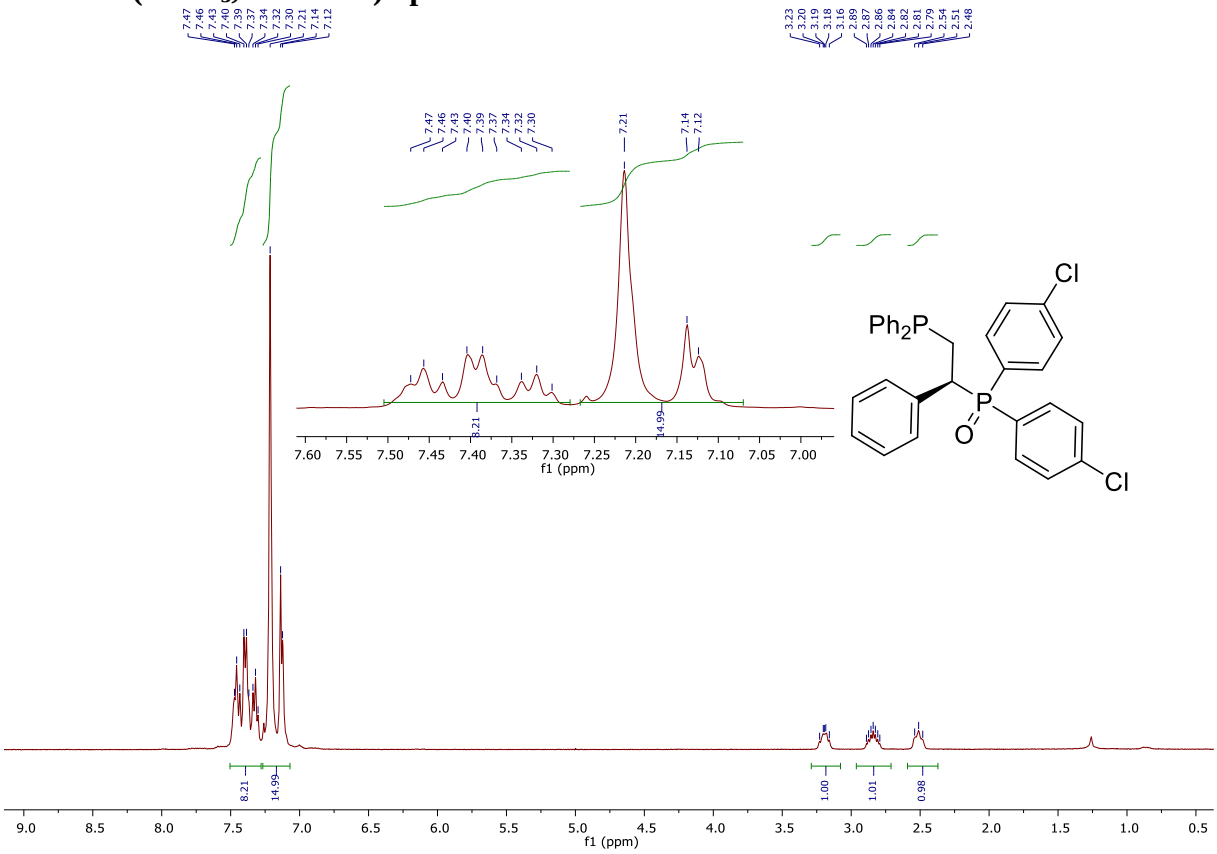
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3wa



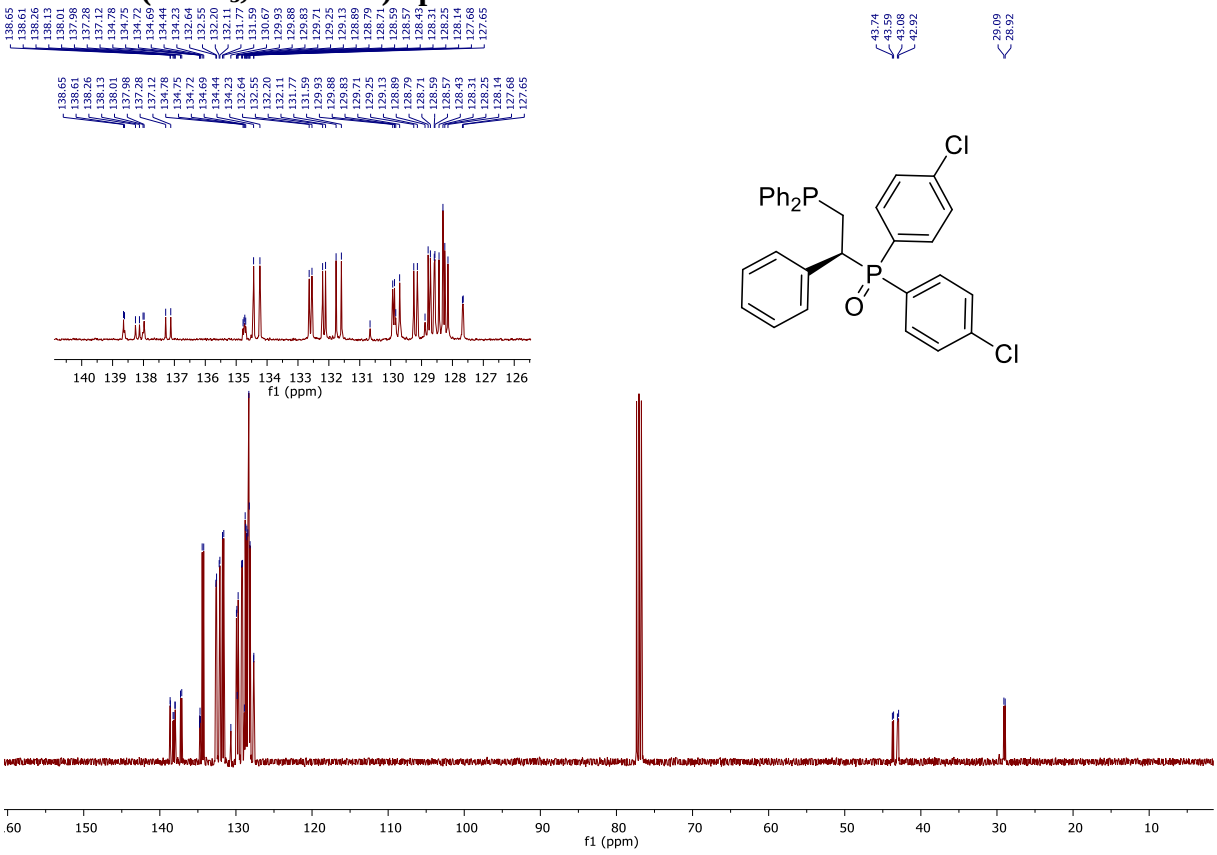
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3wa



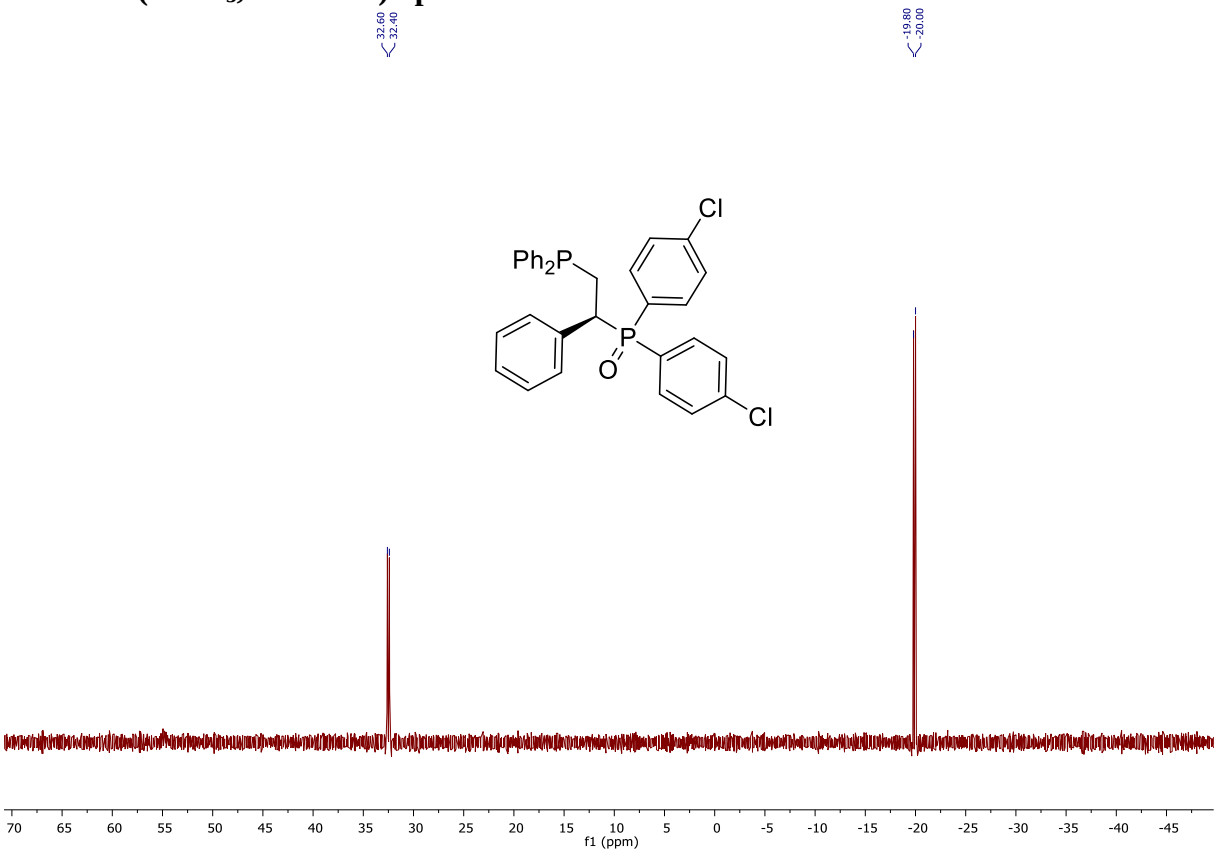
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3xa



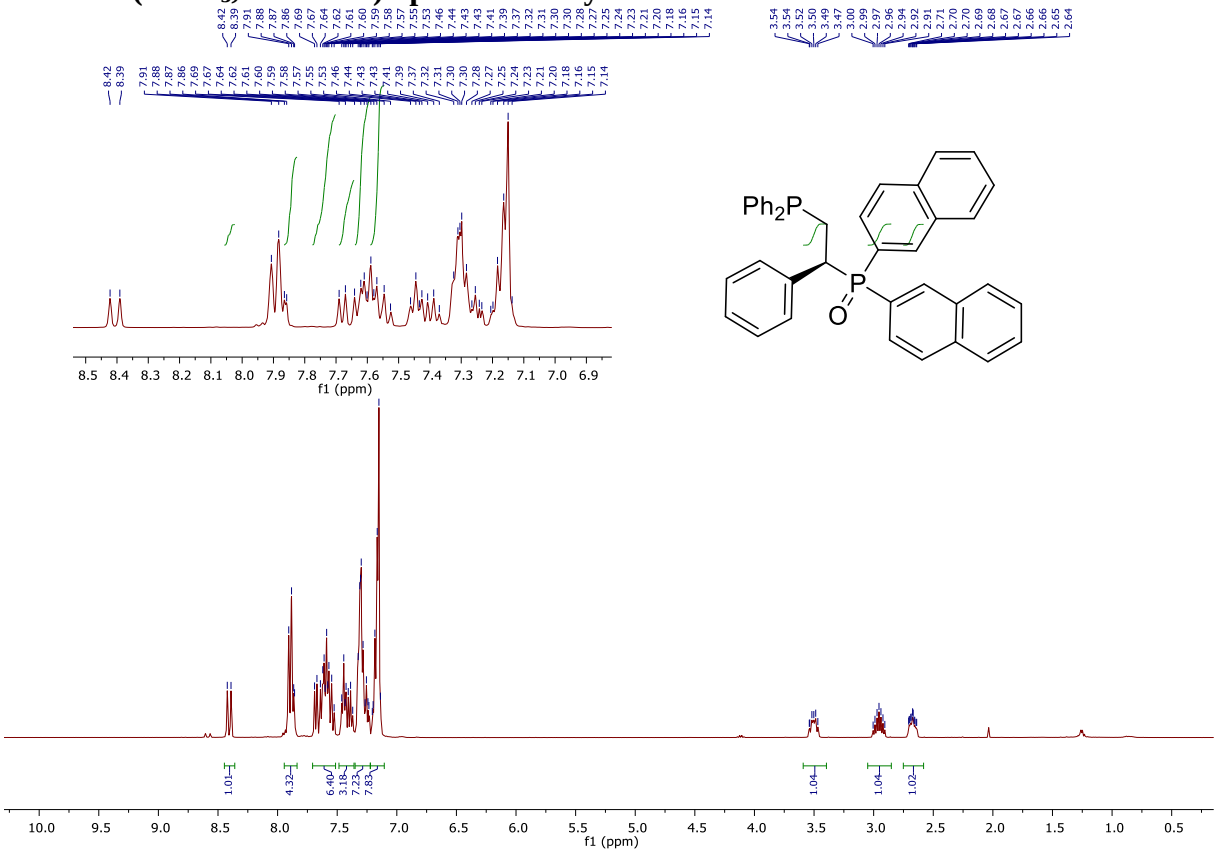
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3xa



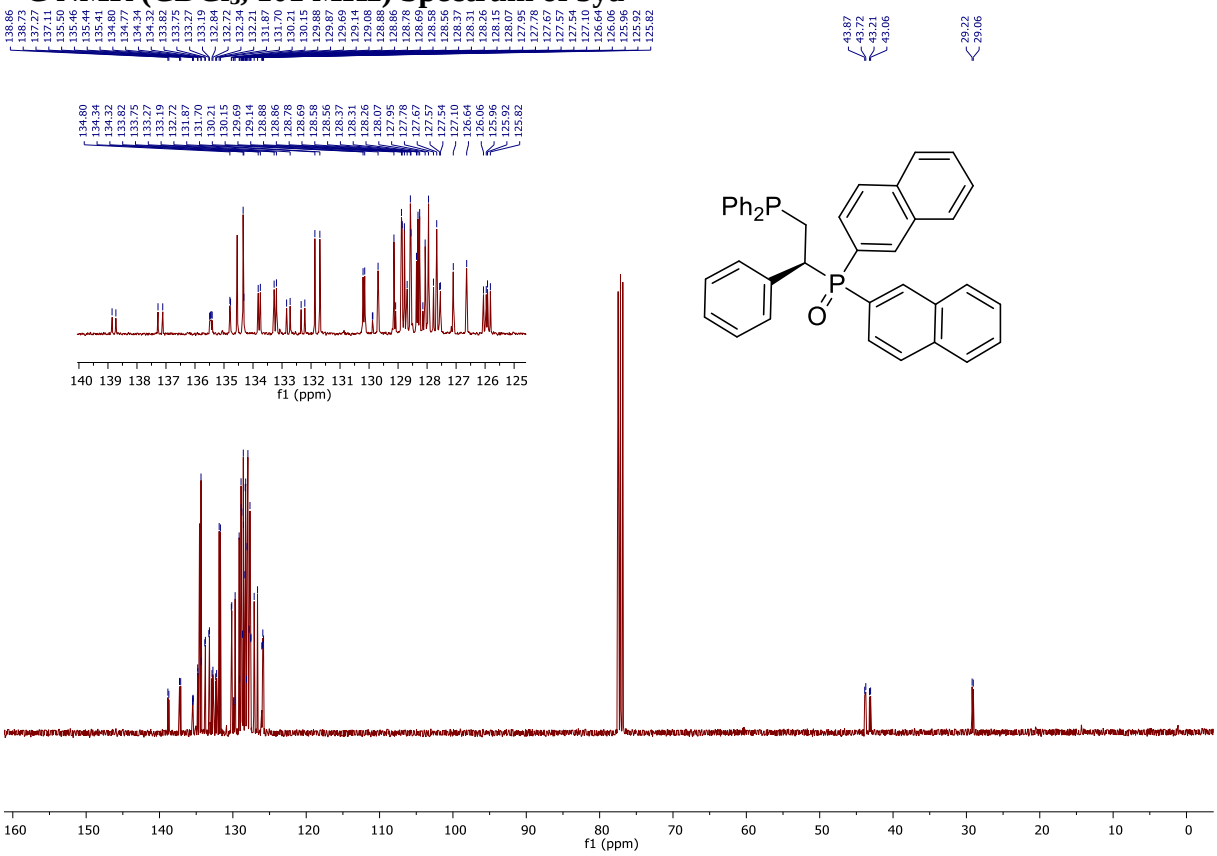
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3xa



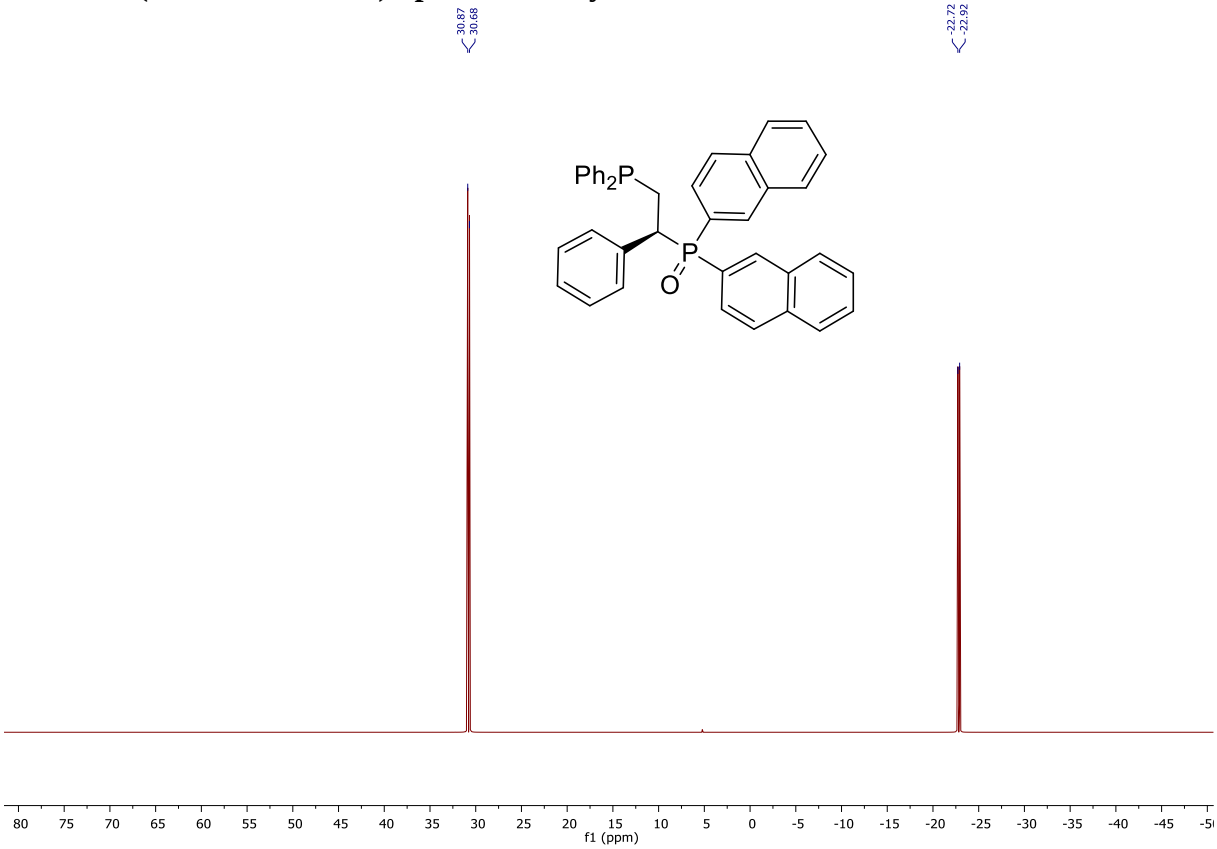
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3ya



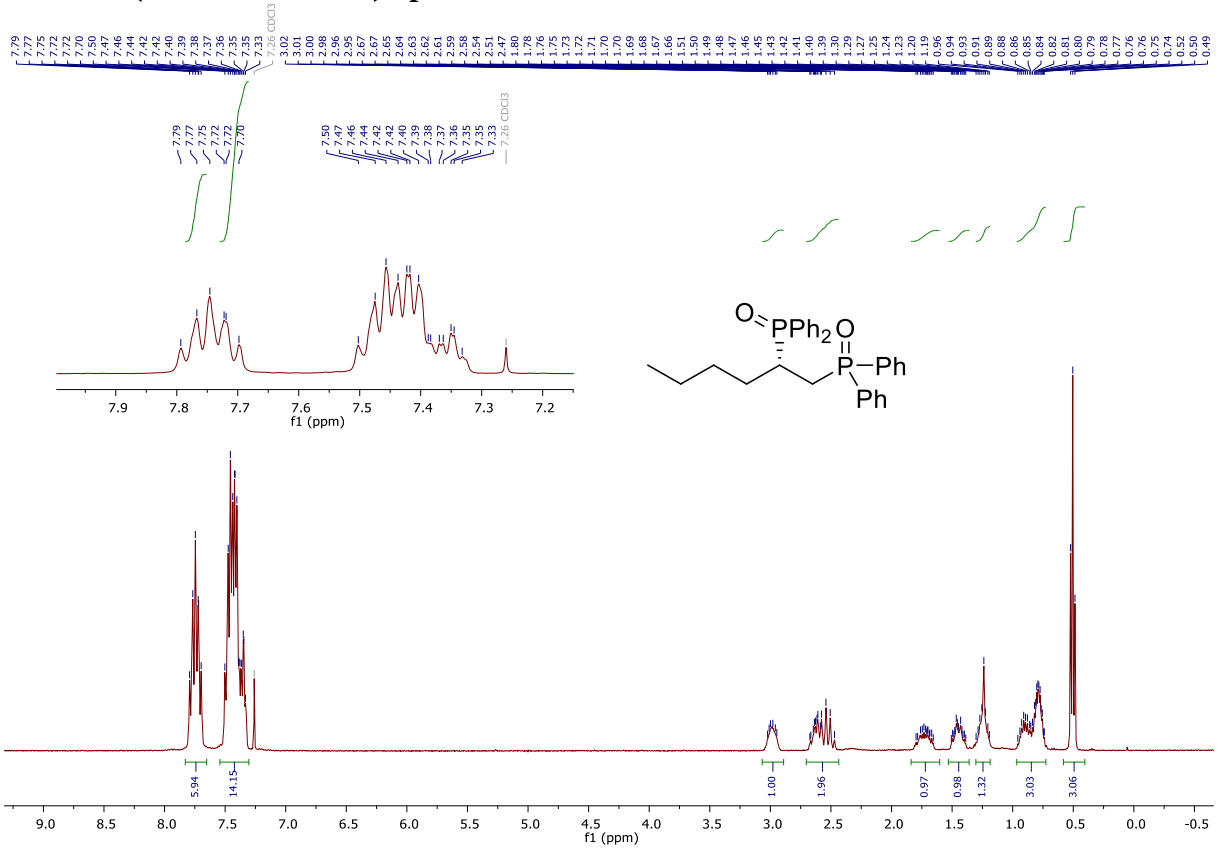
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3ya



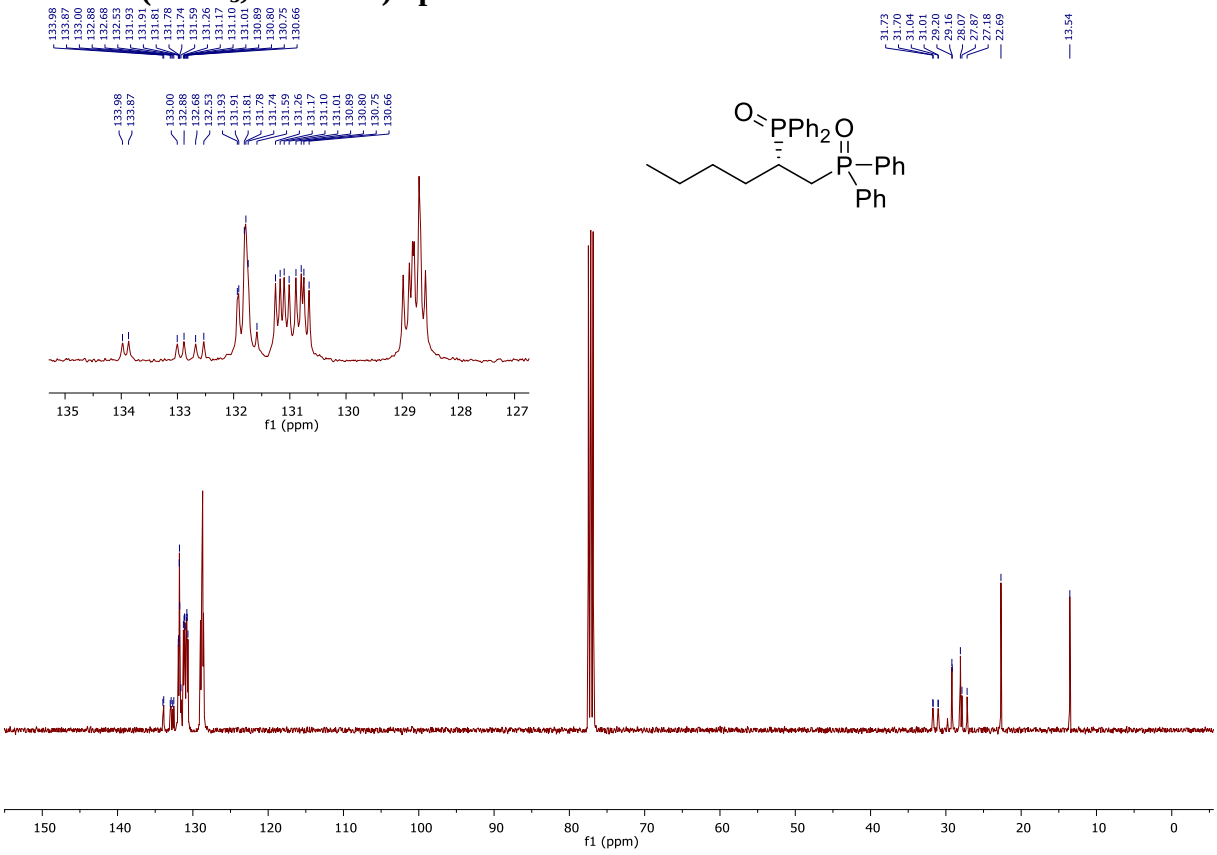
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3ya



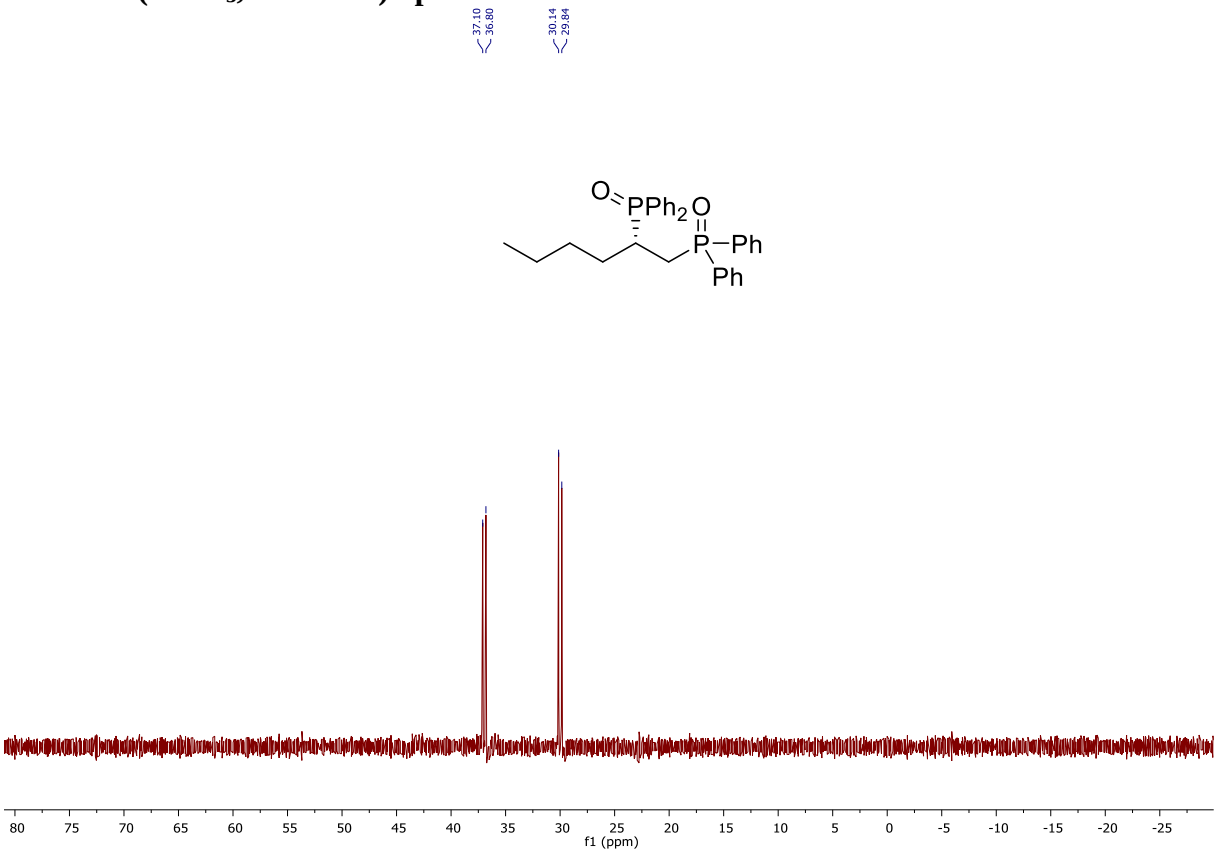
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 3za



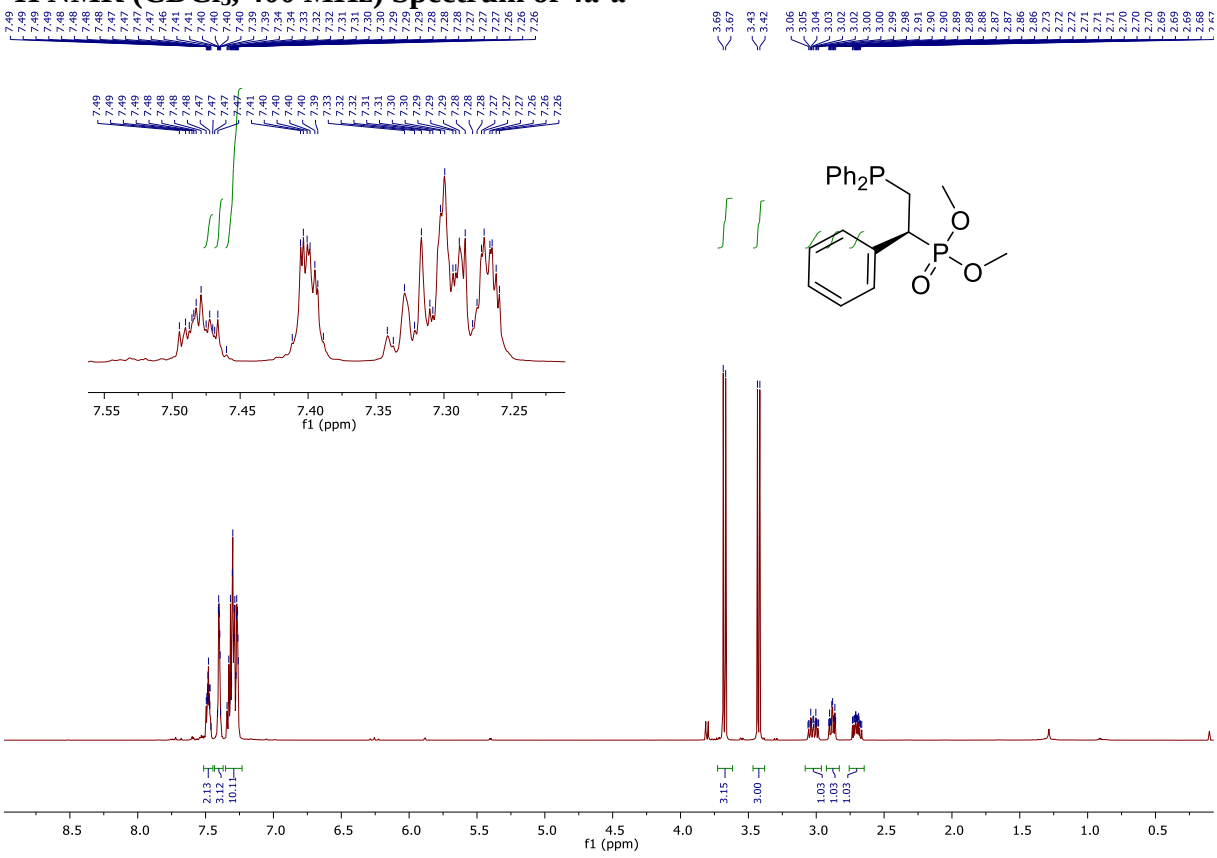
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 3za



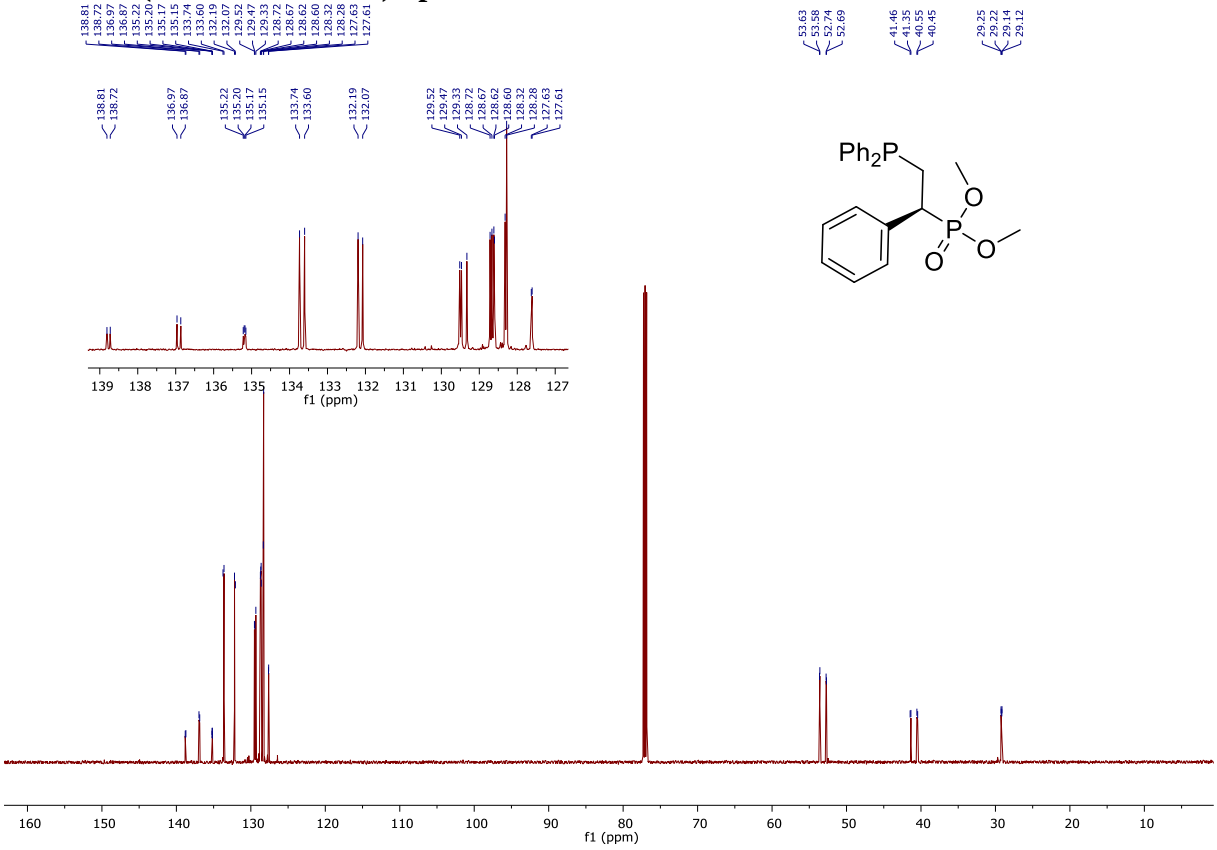
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 3za



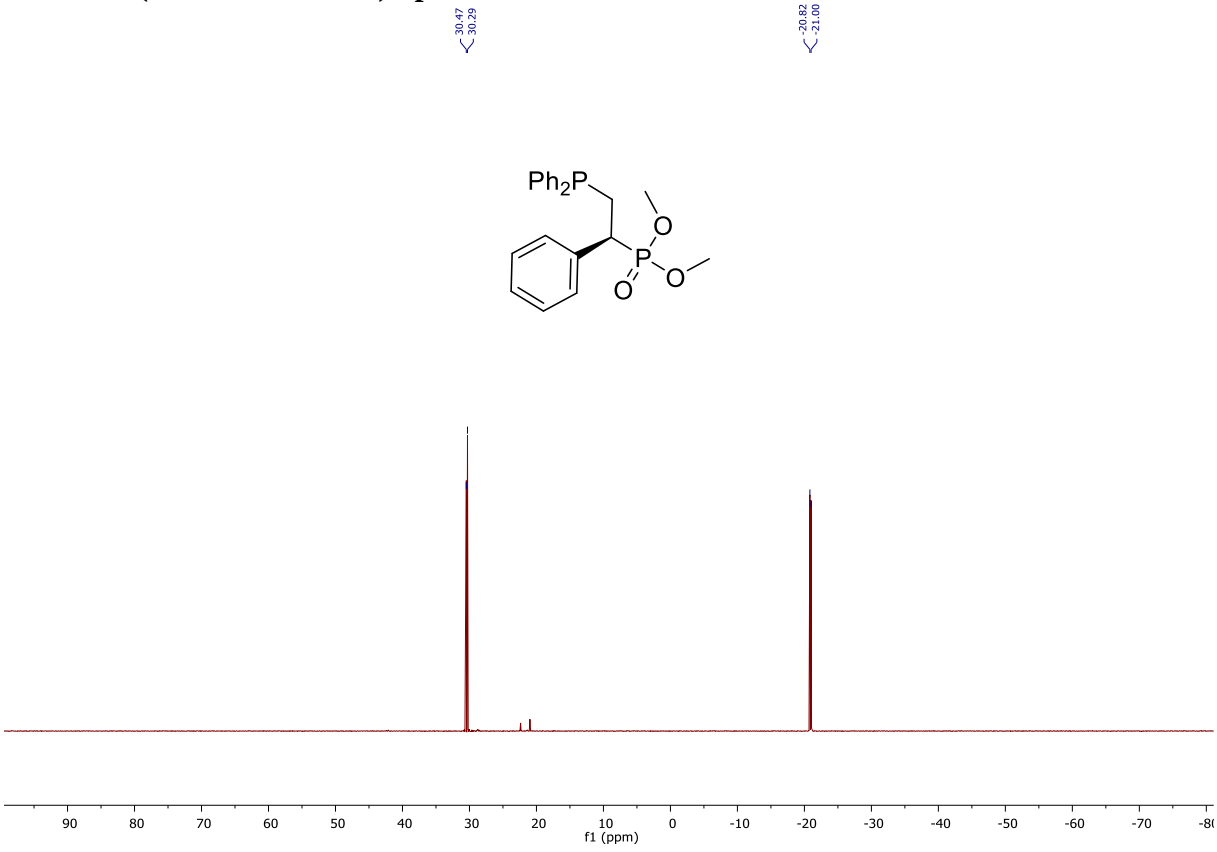
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4a'a



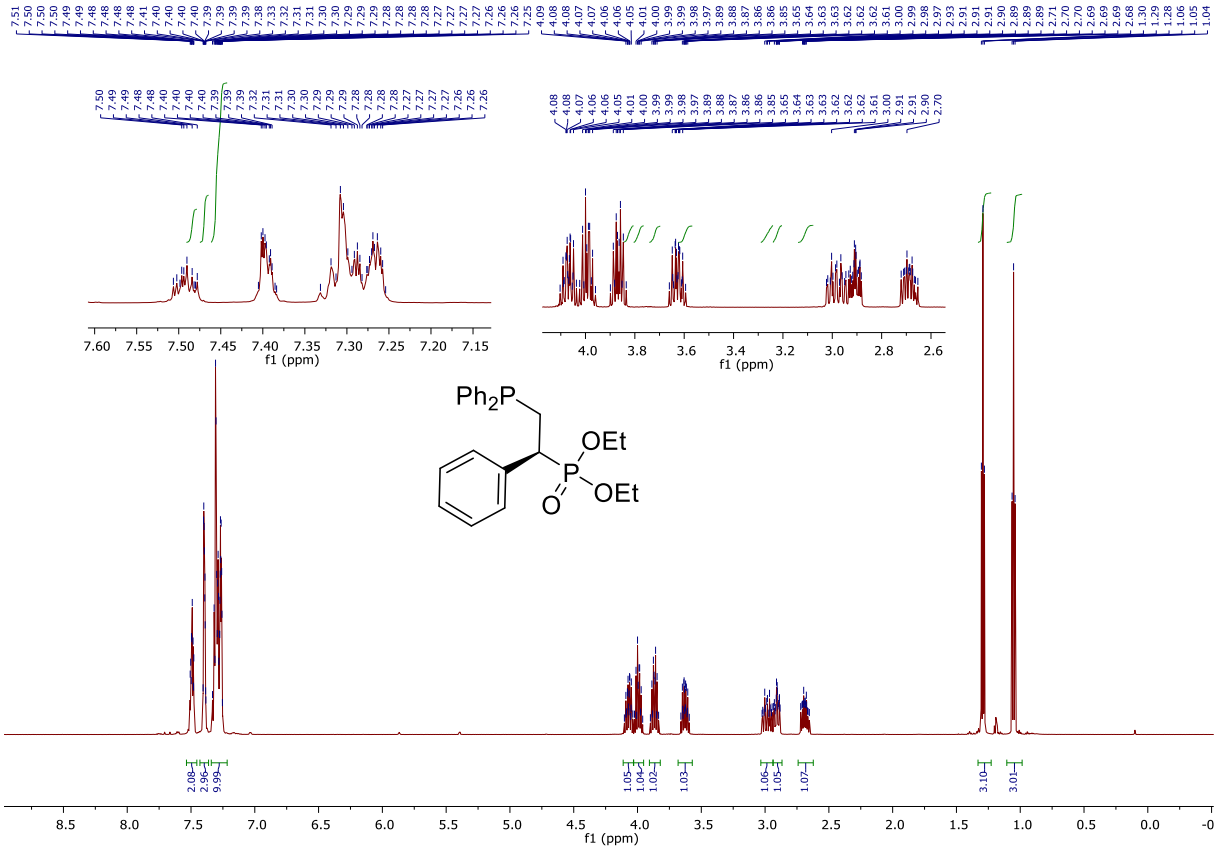
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 4a'a



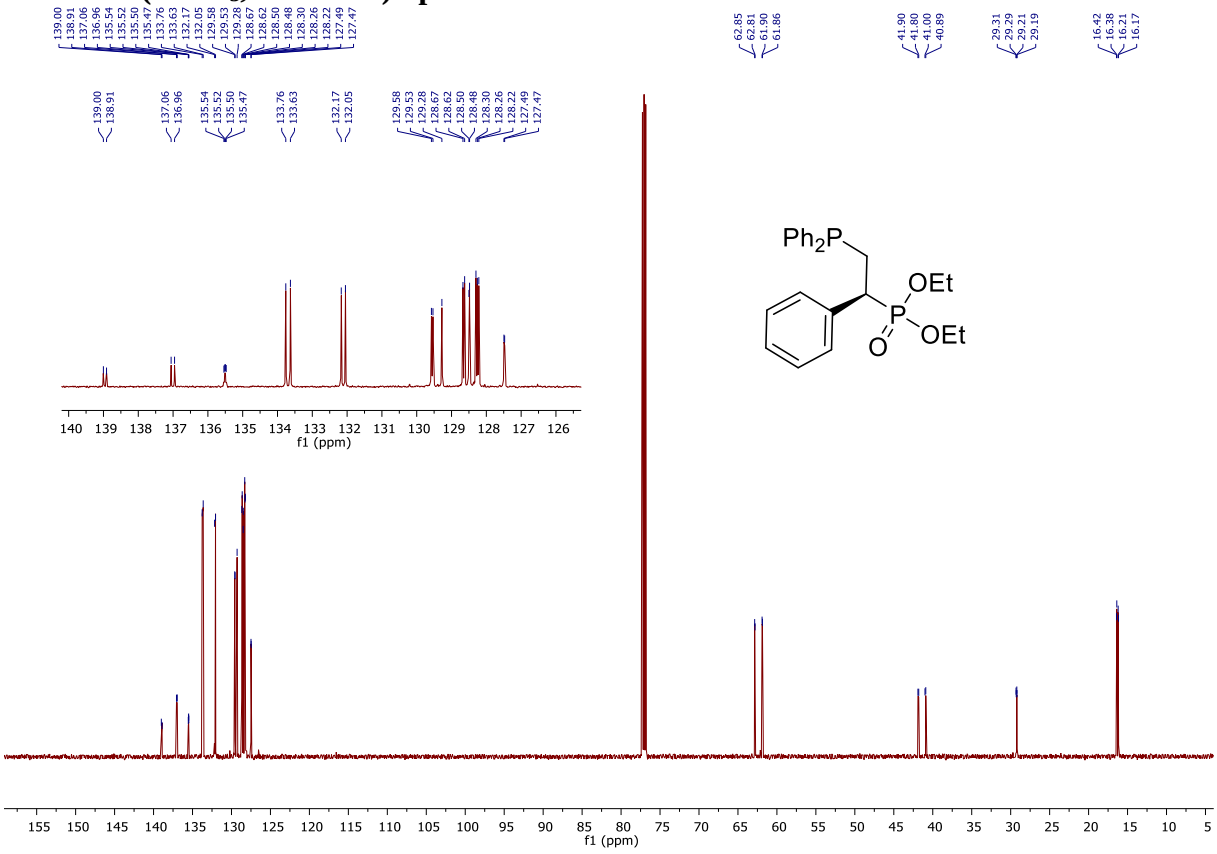
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 4a'a



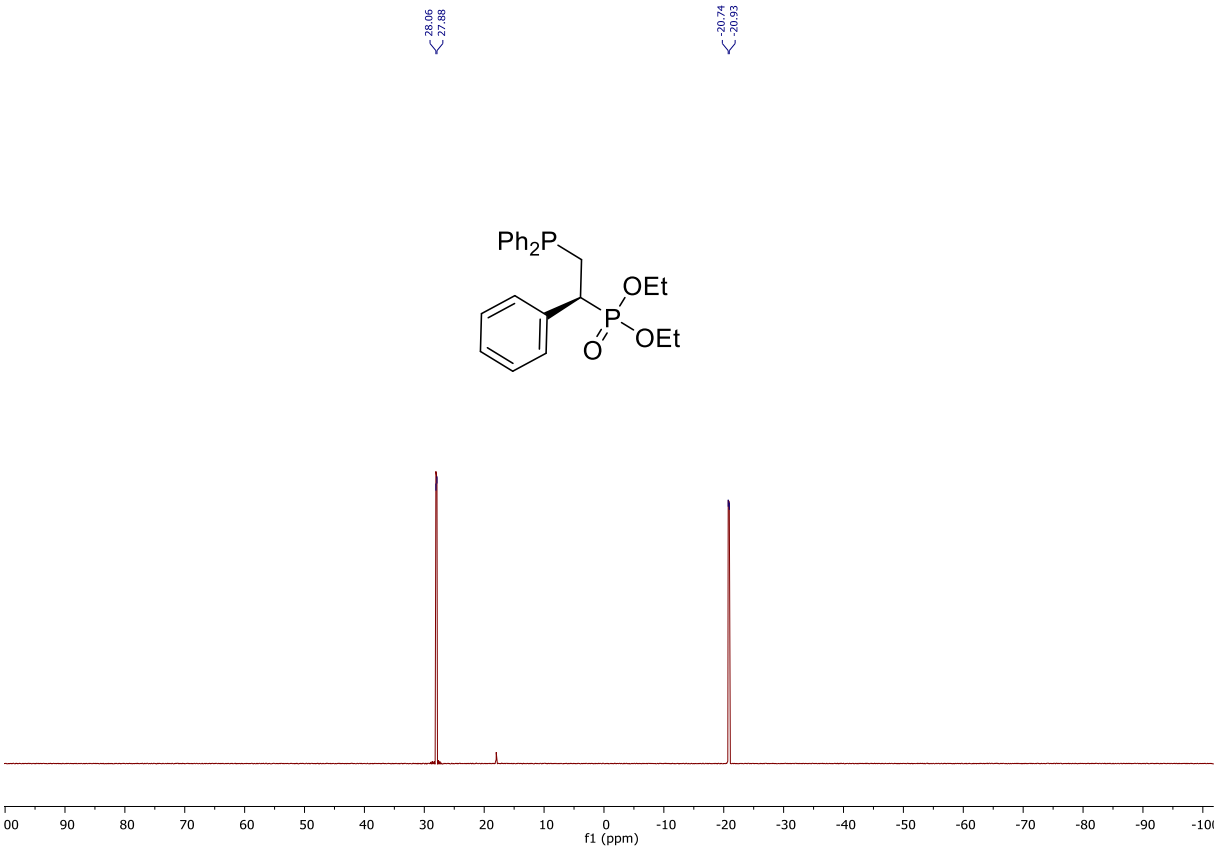
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4b'a



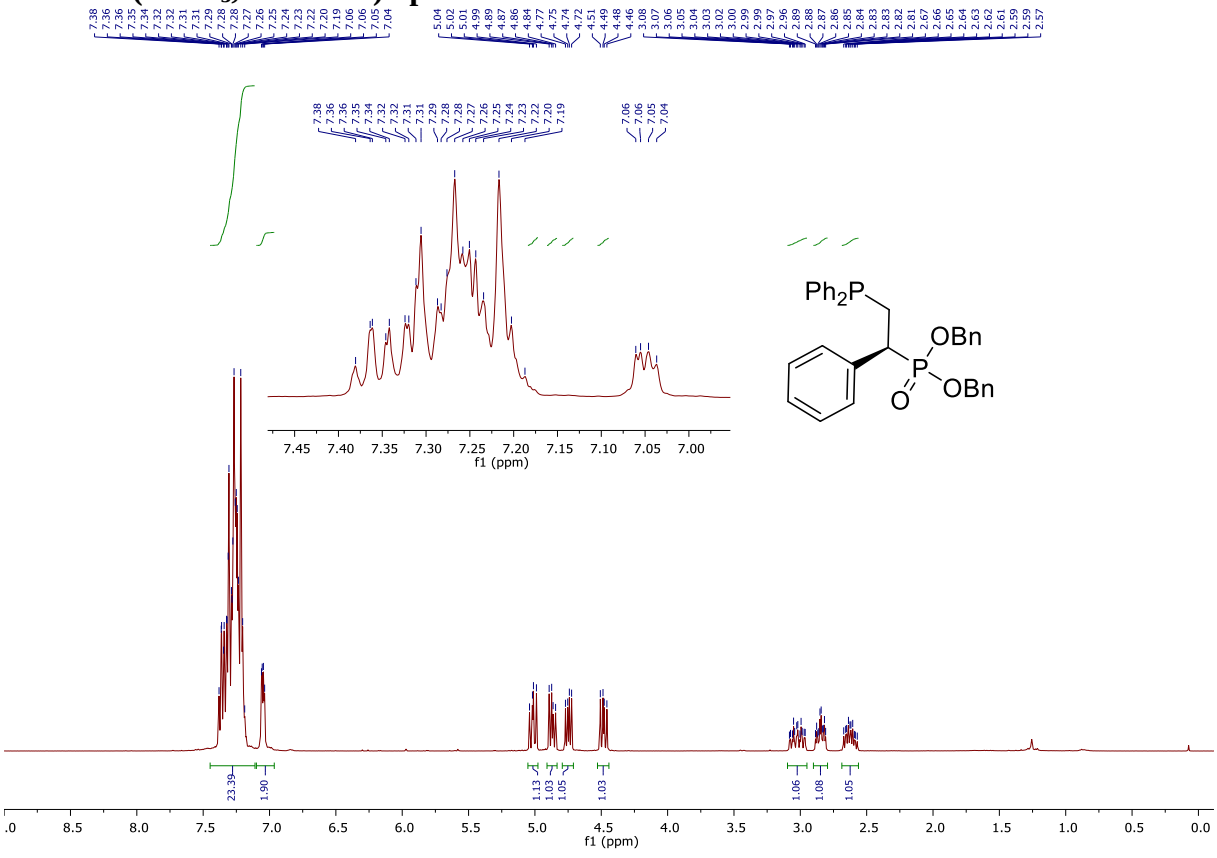
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 4b'a



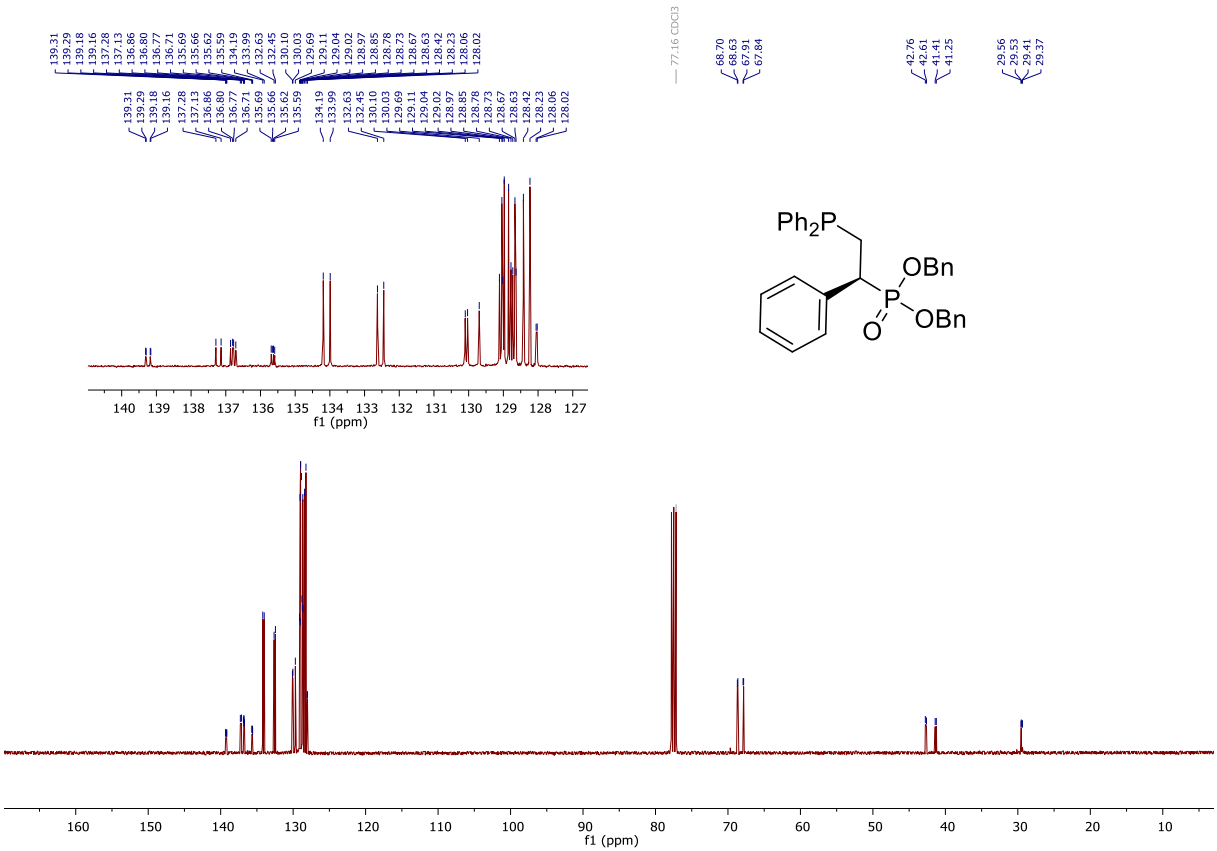
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 4b'a



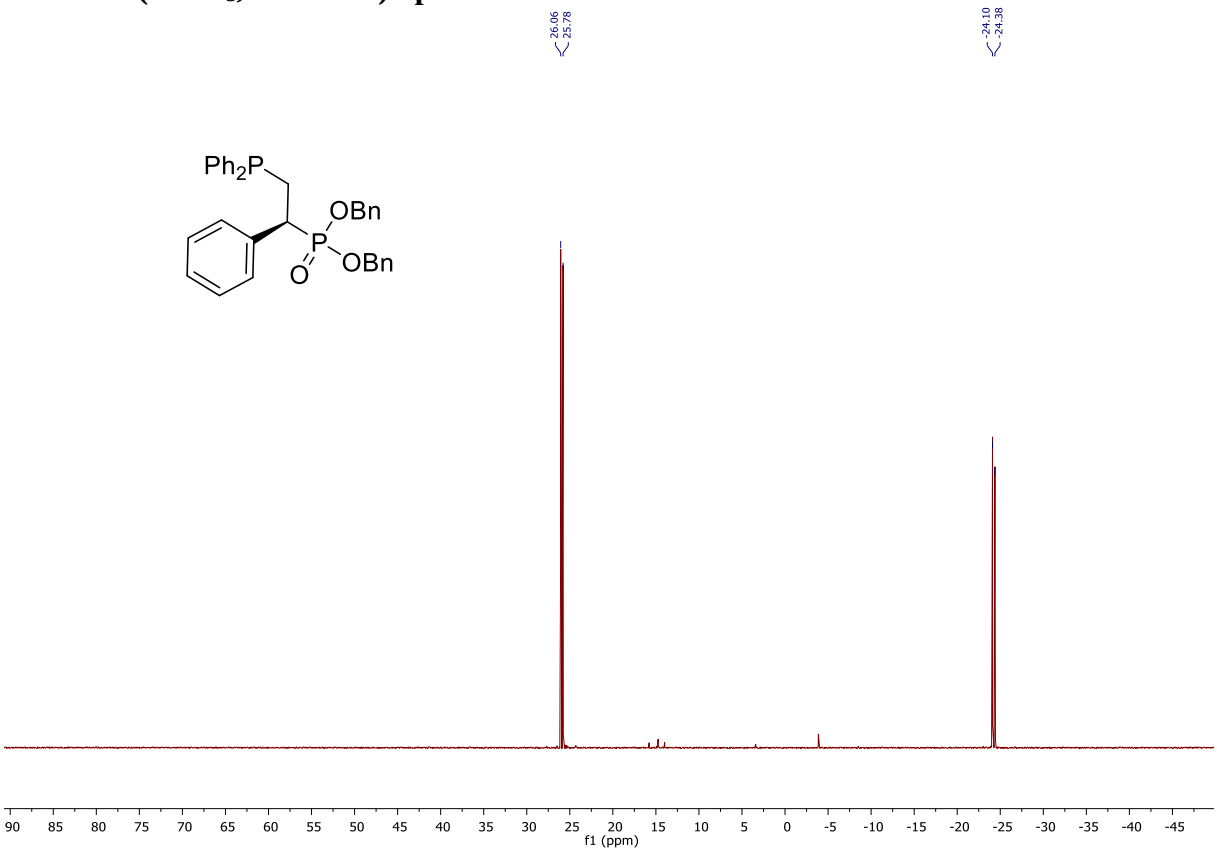
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4c'a



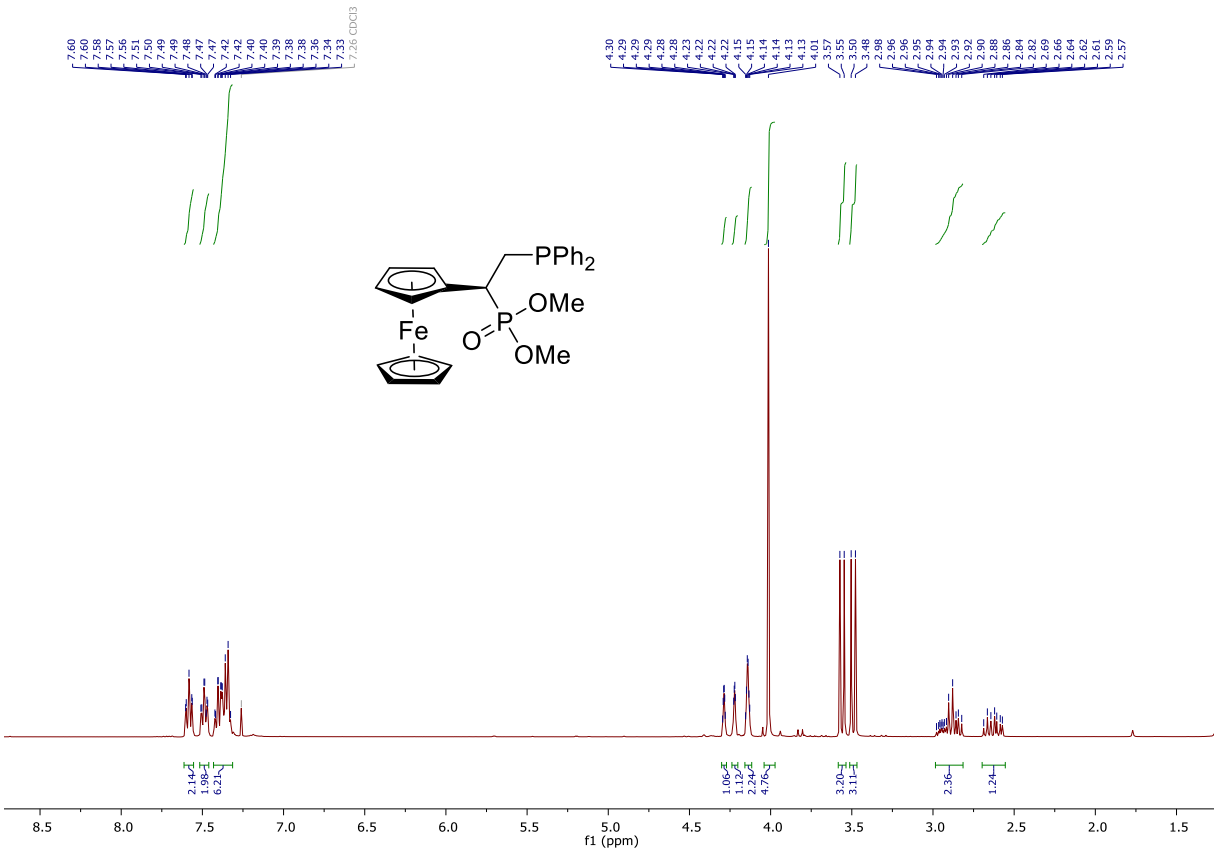
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 4c'a



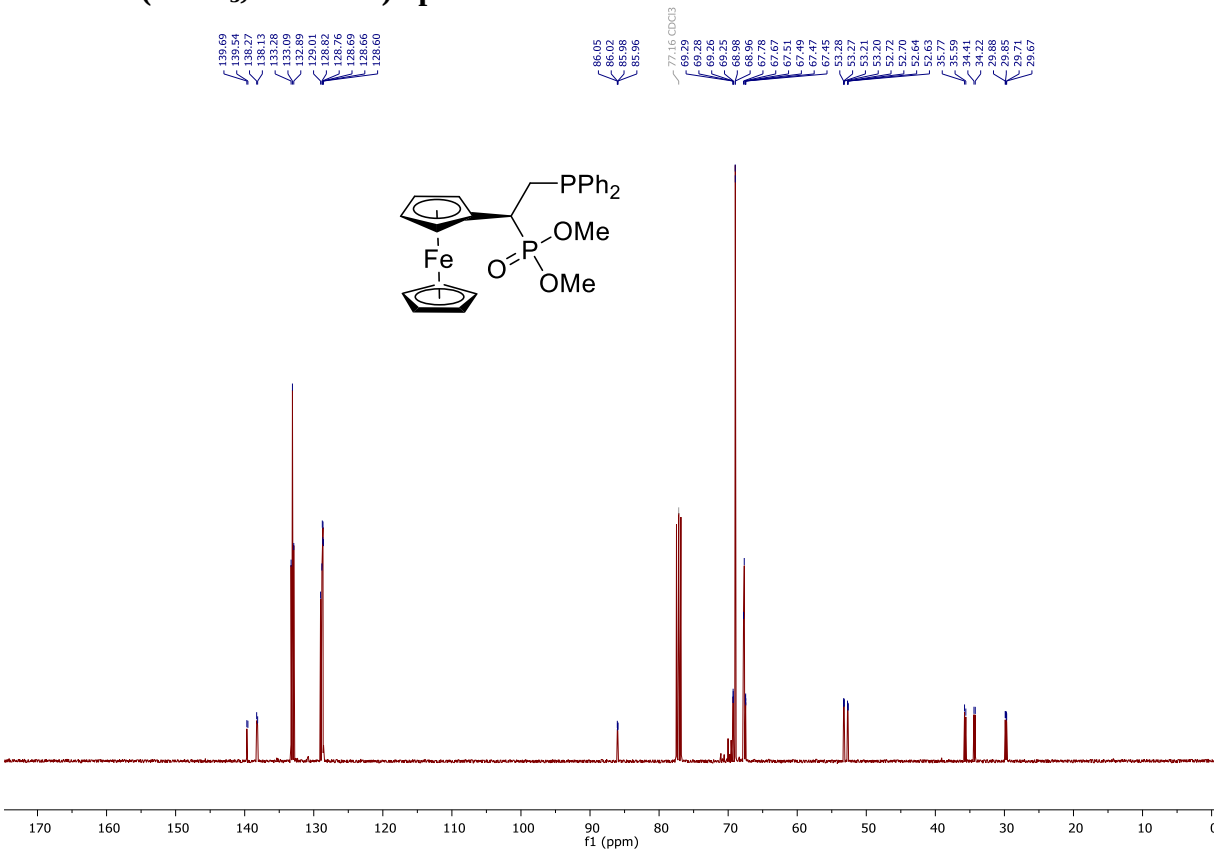
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 4c'a



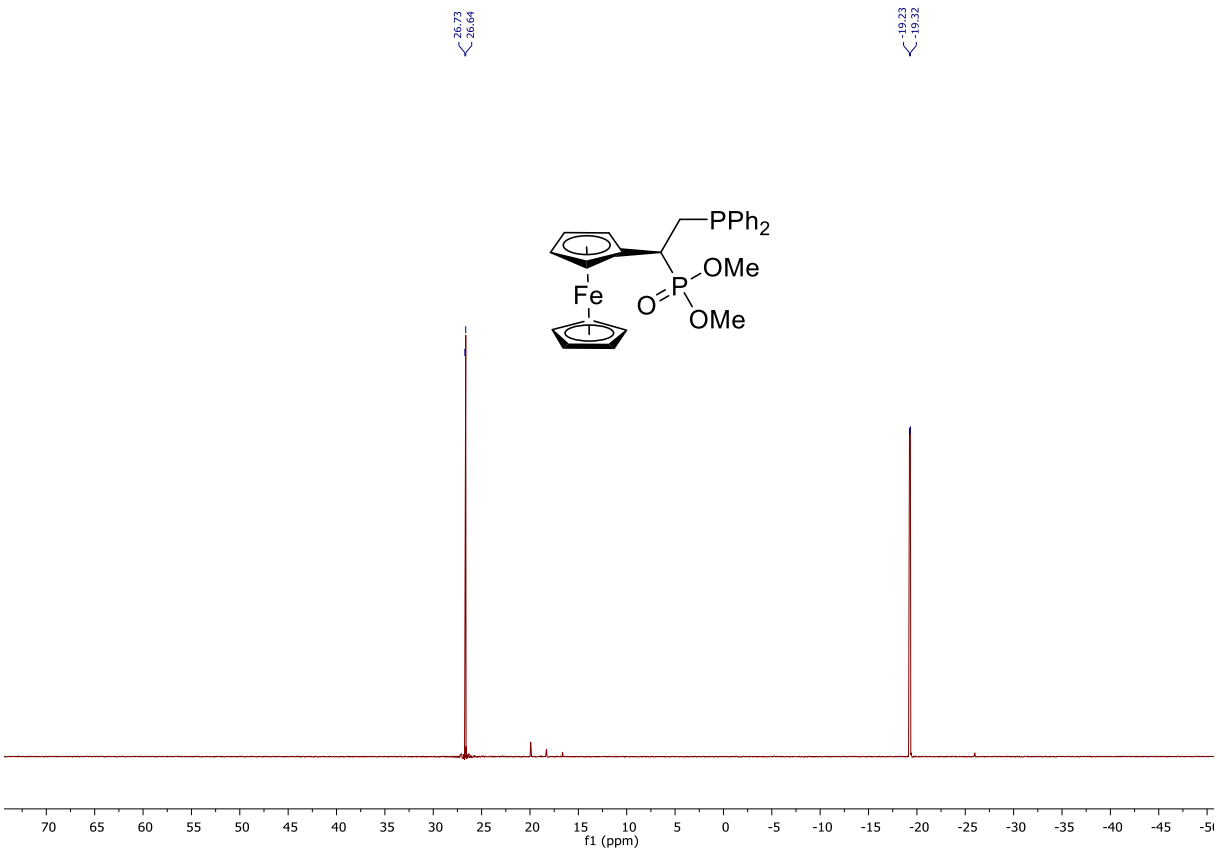
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4d'a



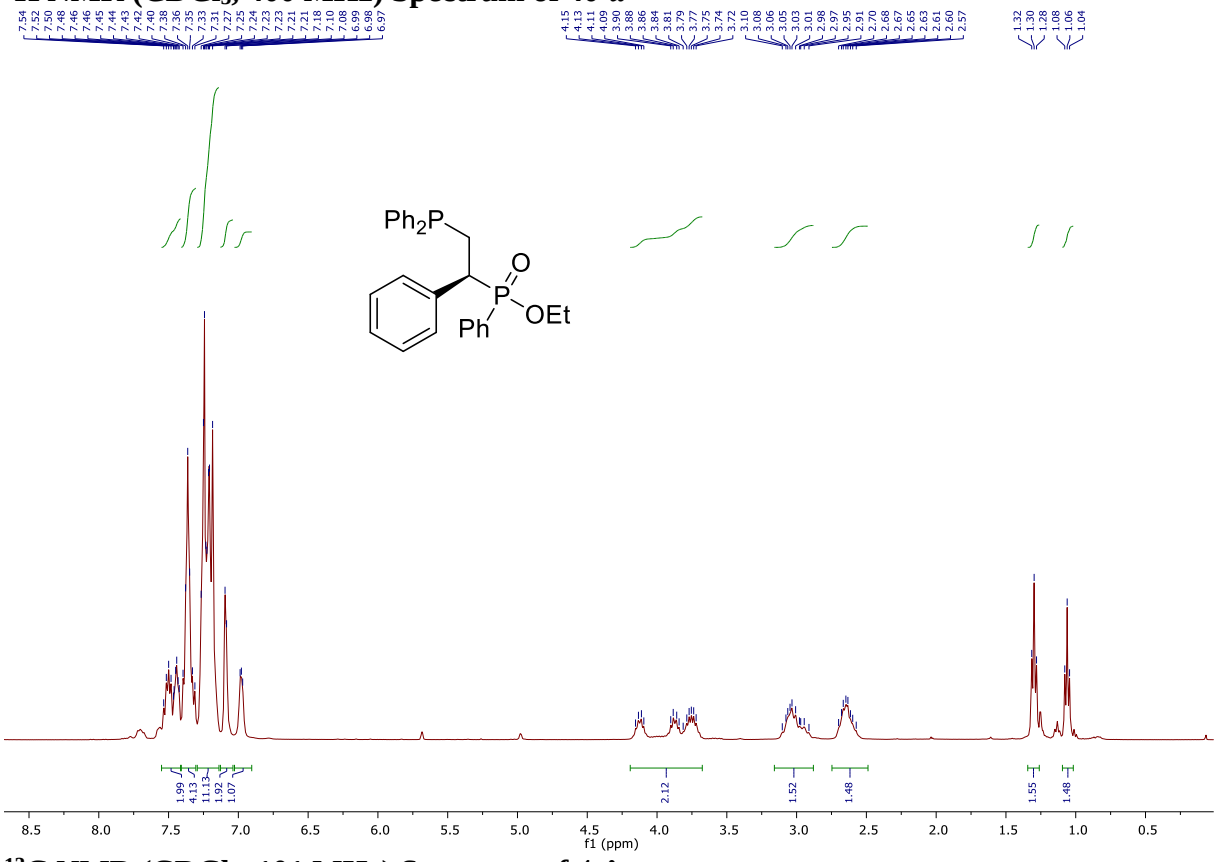
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 4d'a



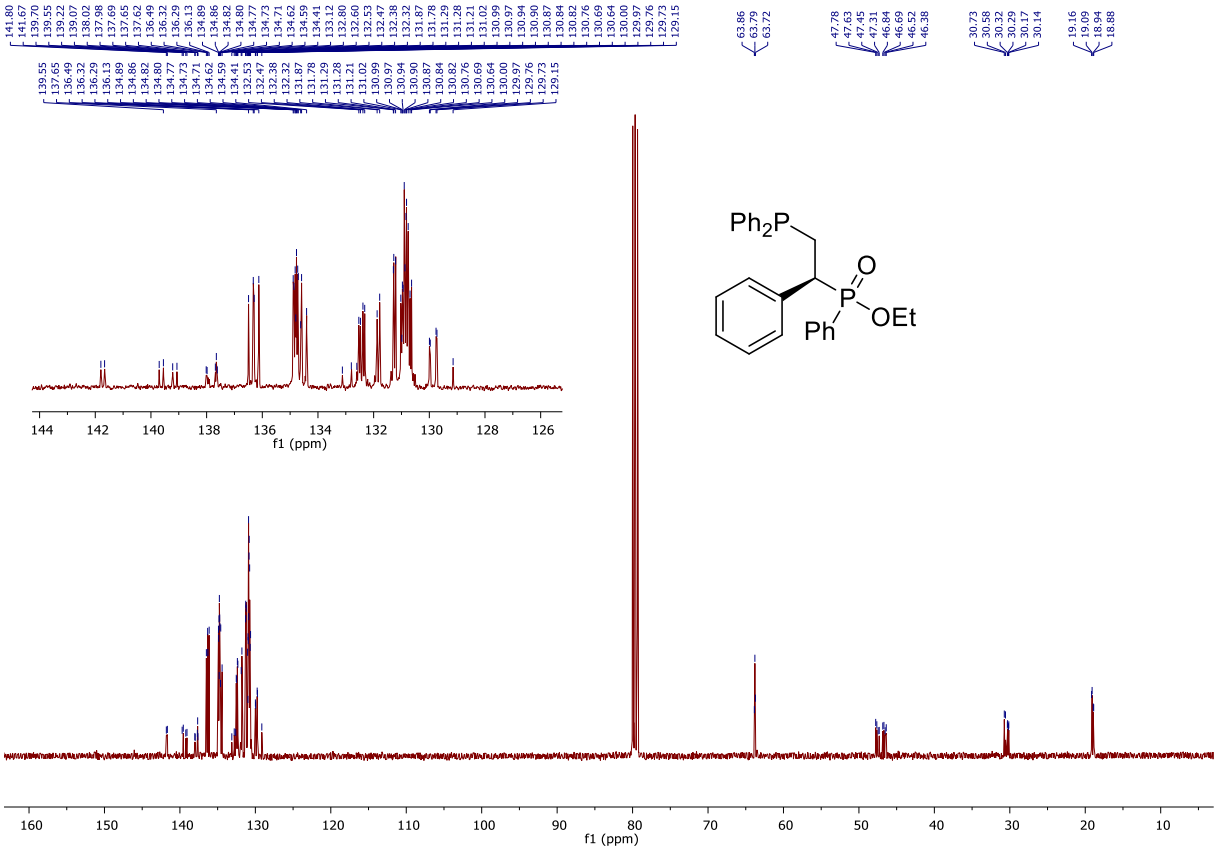
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 4d'a



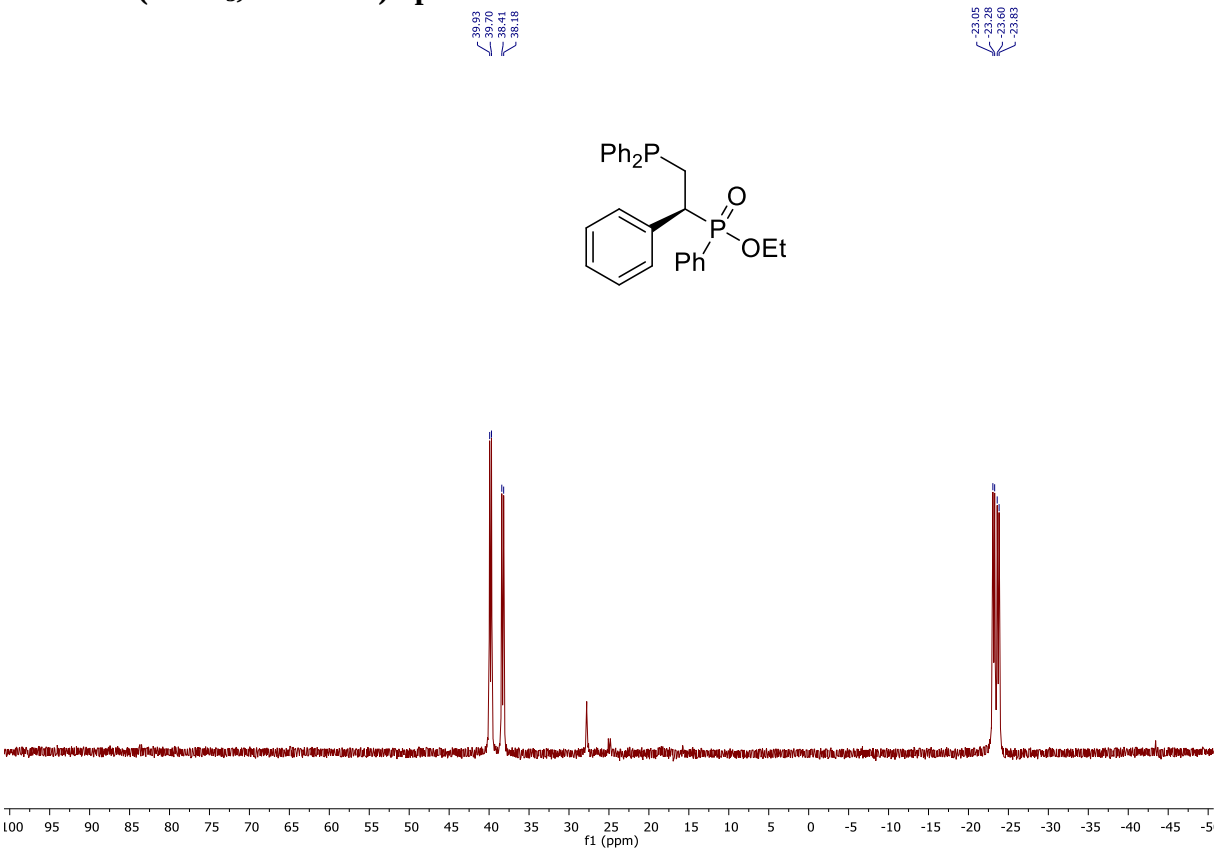
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4e'a



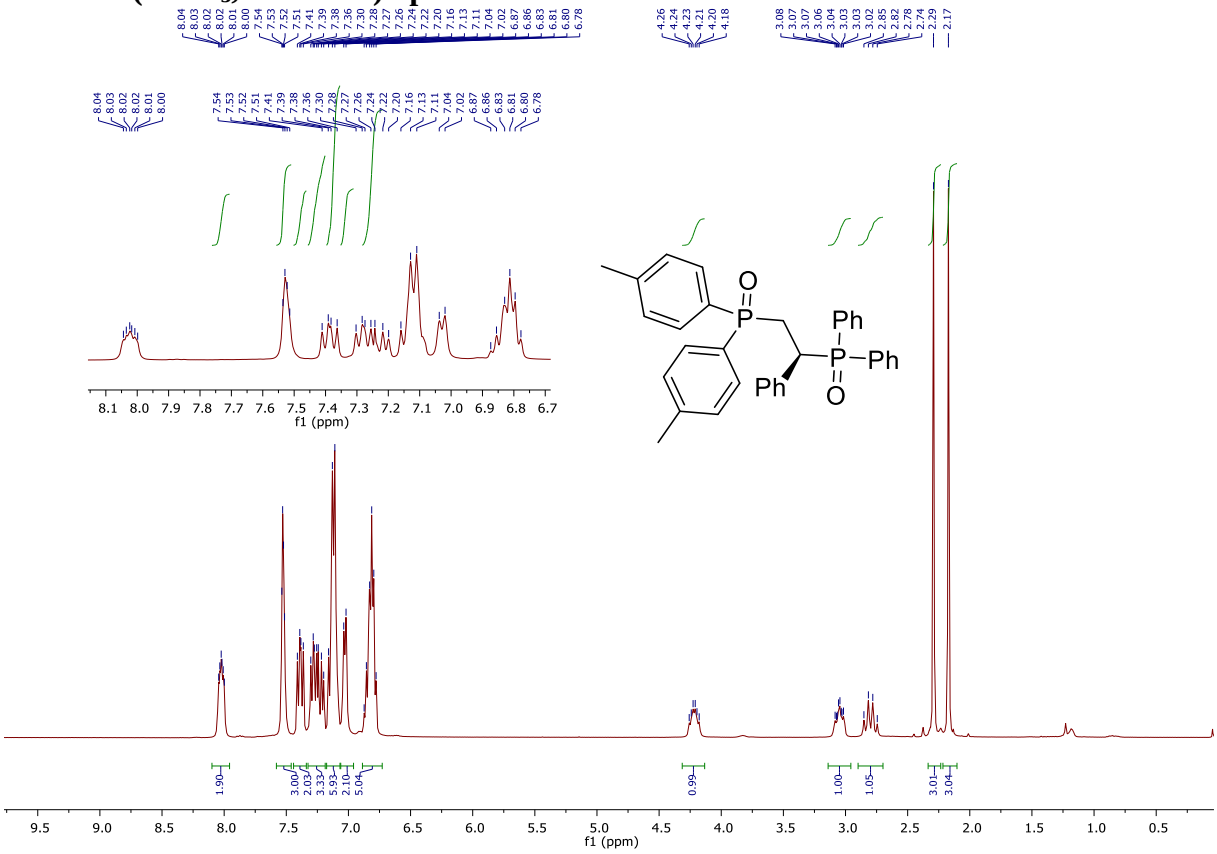
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 4e'a



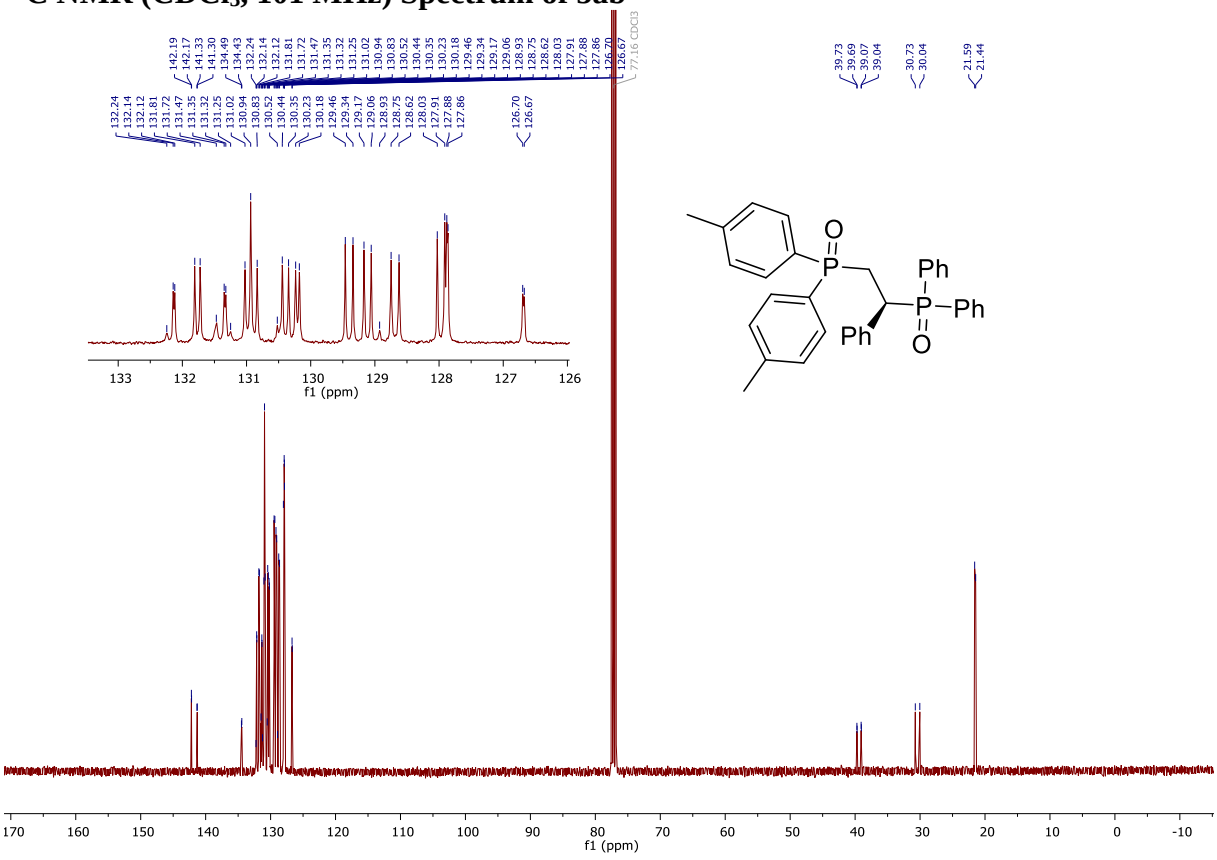
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 4e'a



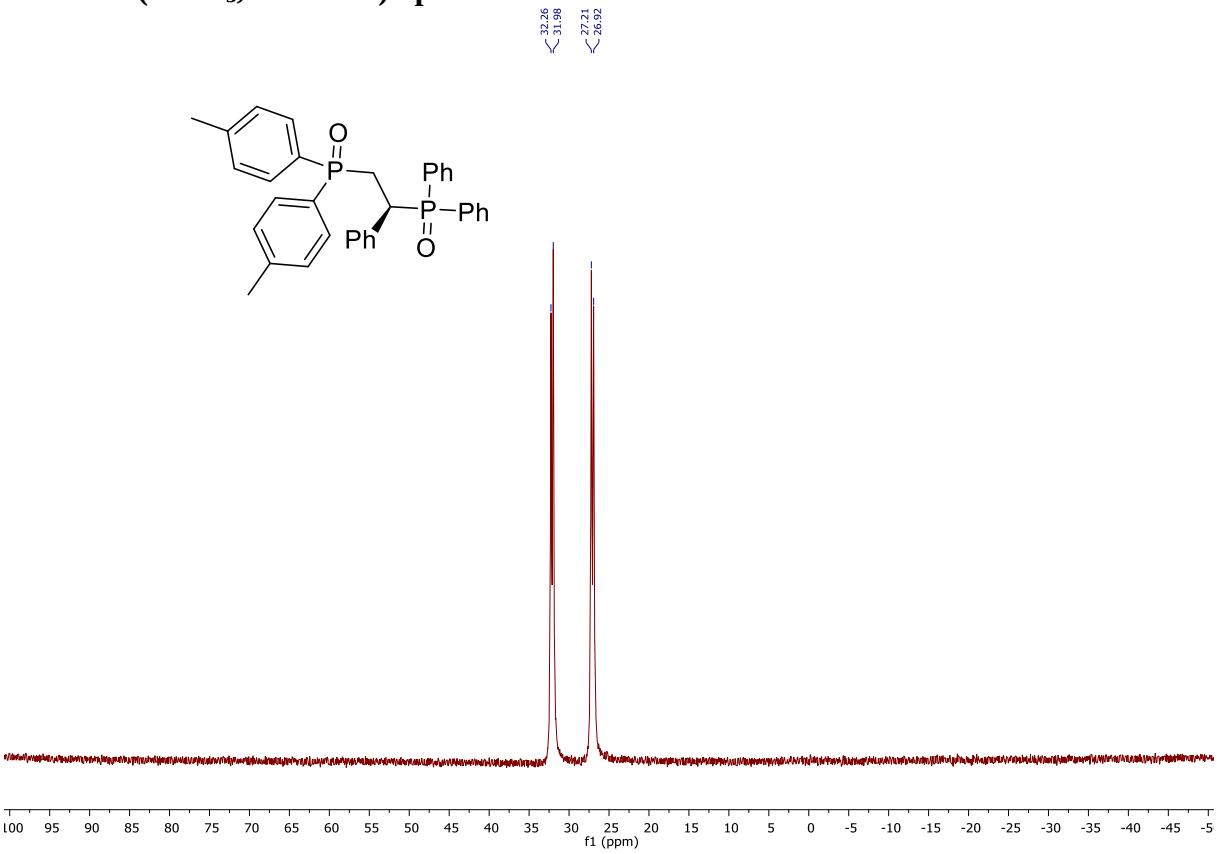
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 5ab



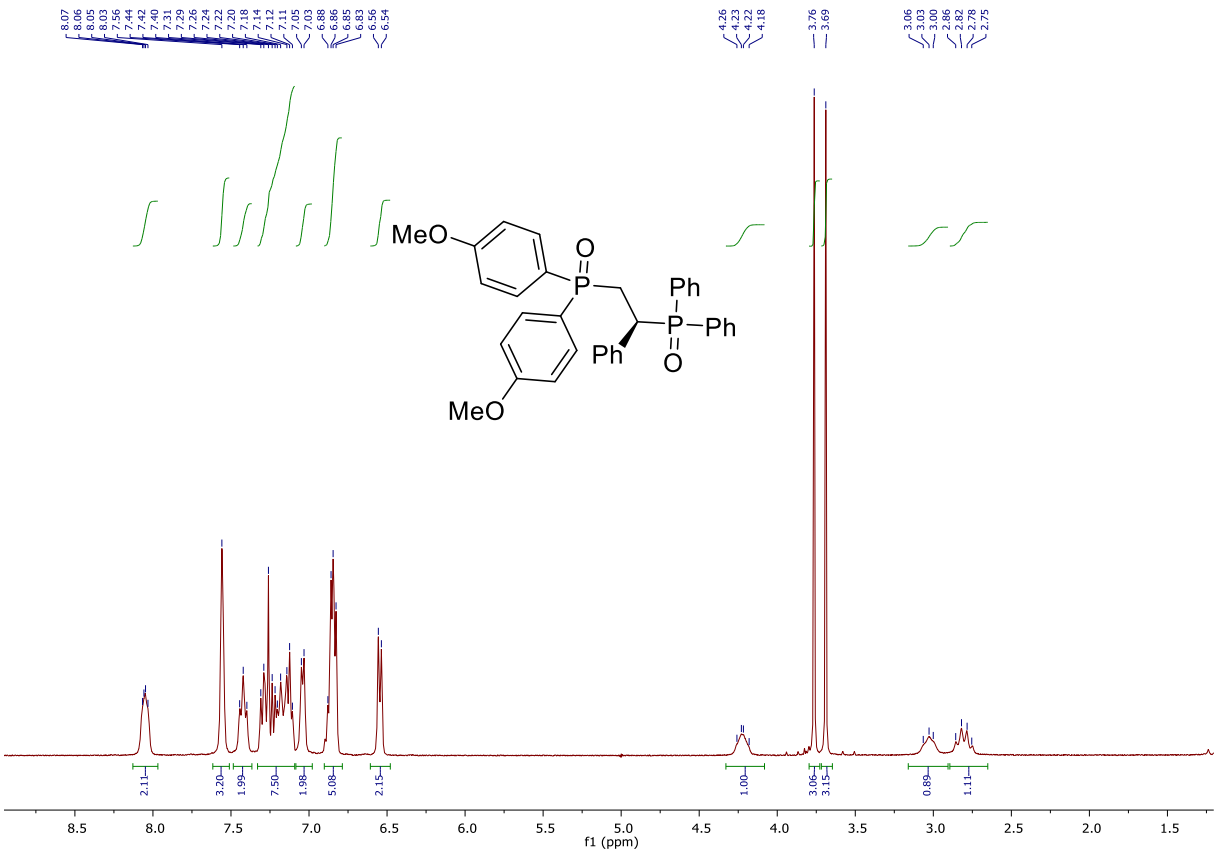
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 5ab



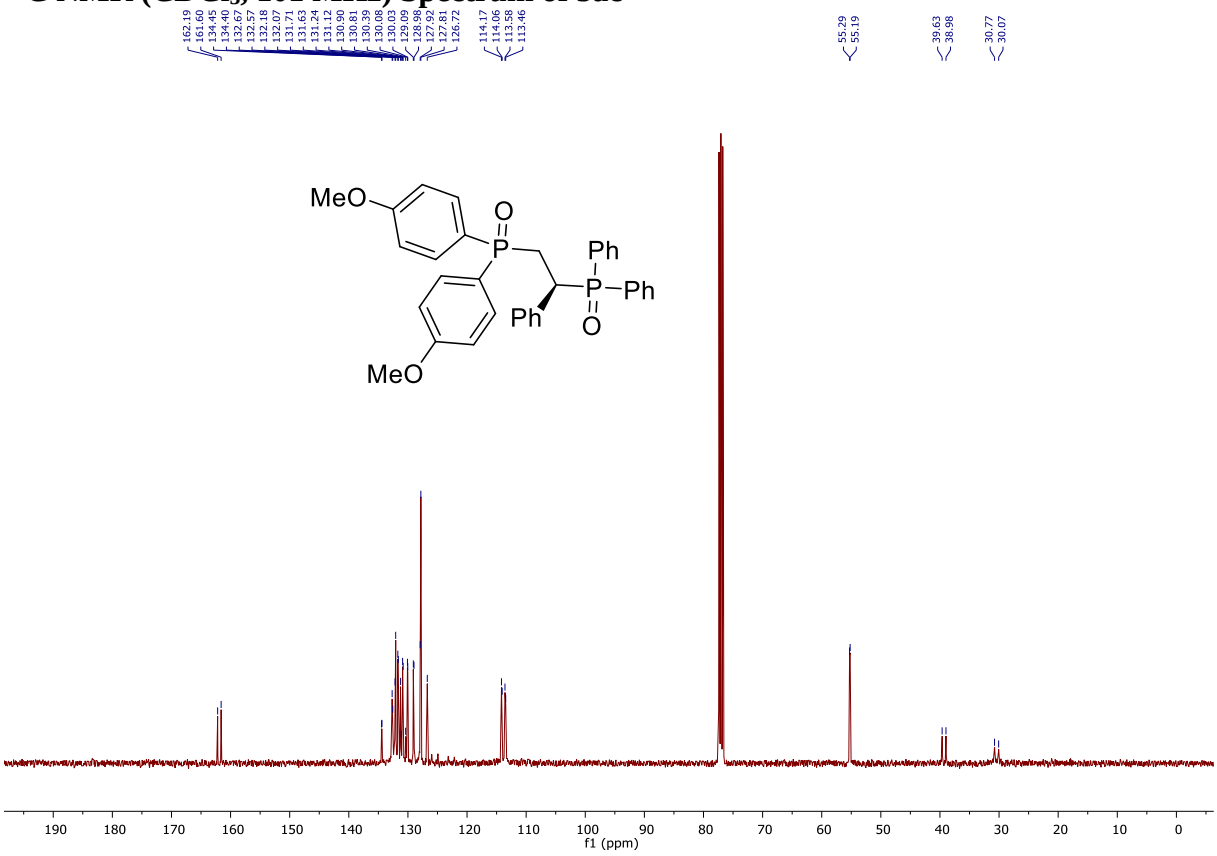
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 5ab



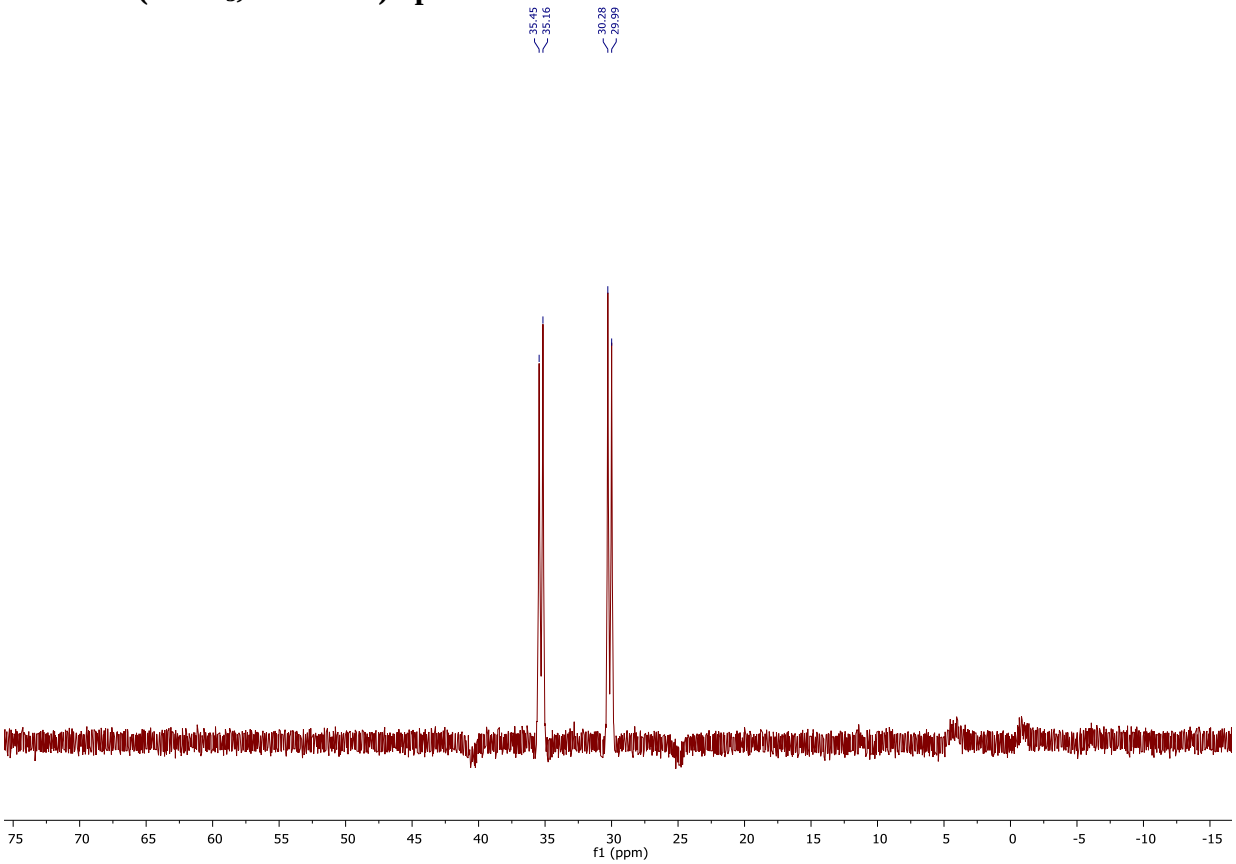
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 5ac



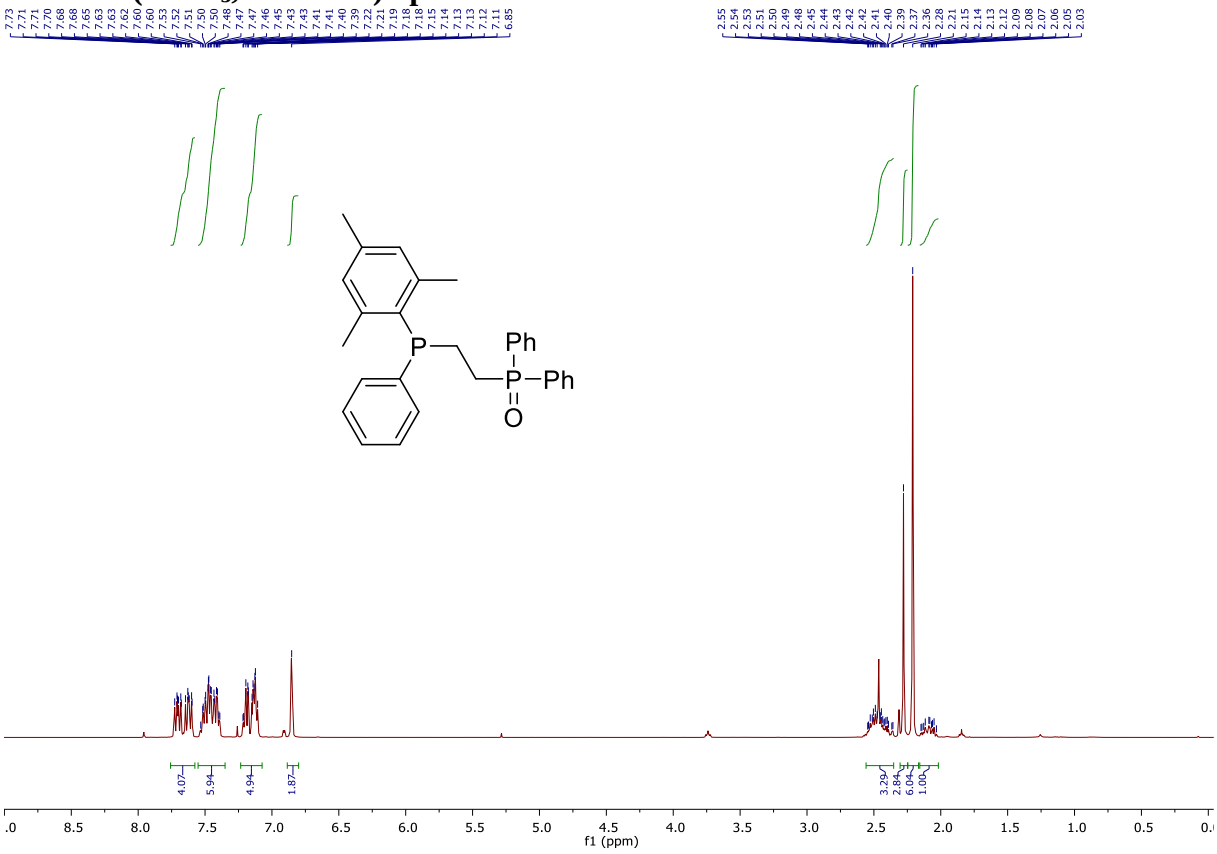
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 5ac



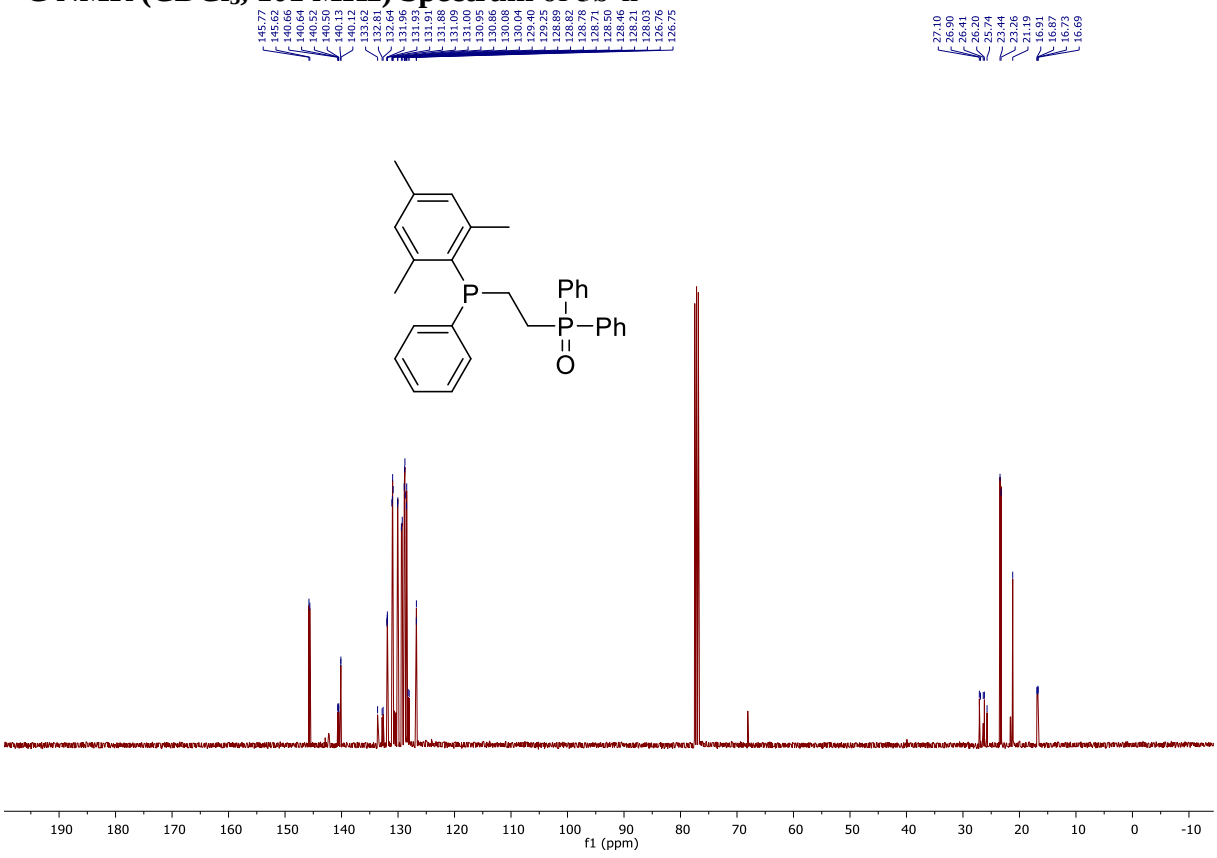
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 5ac



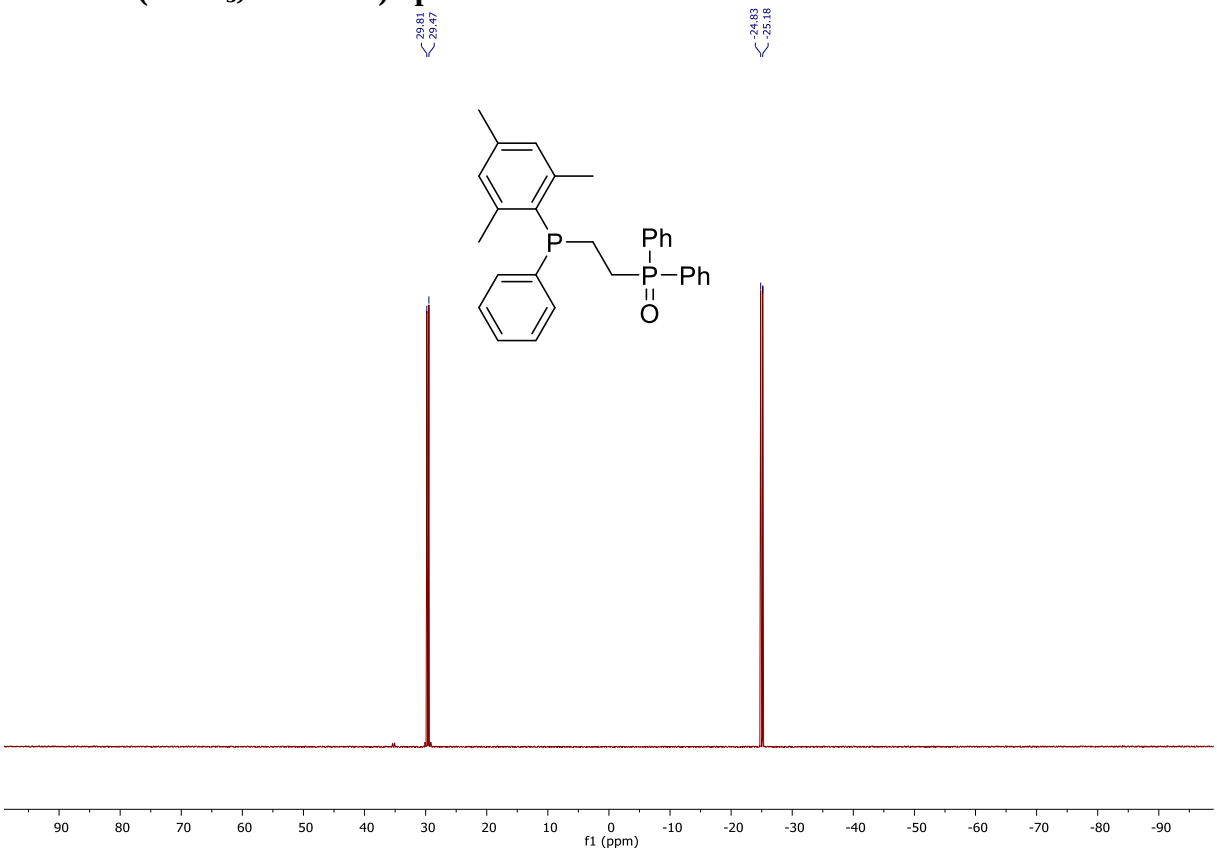
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 5b'h



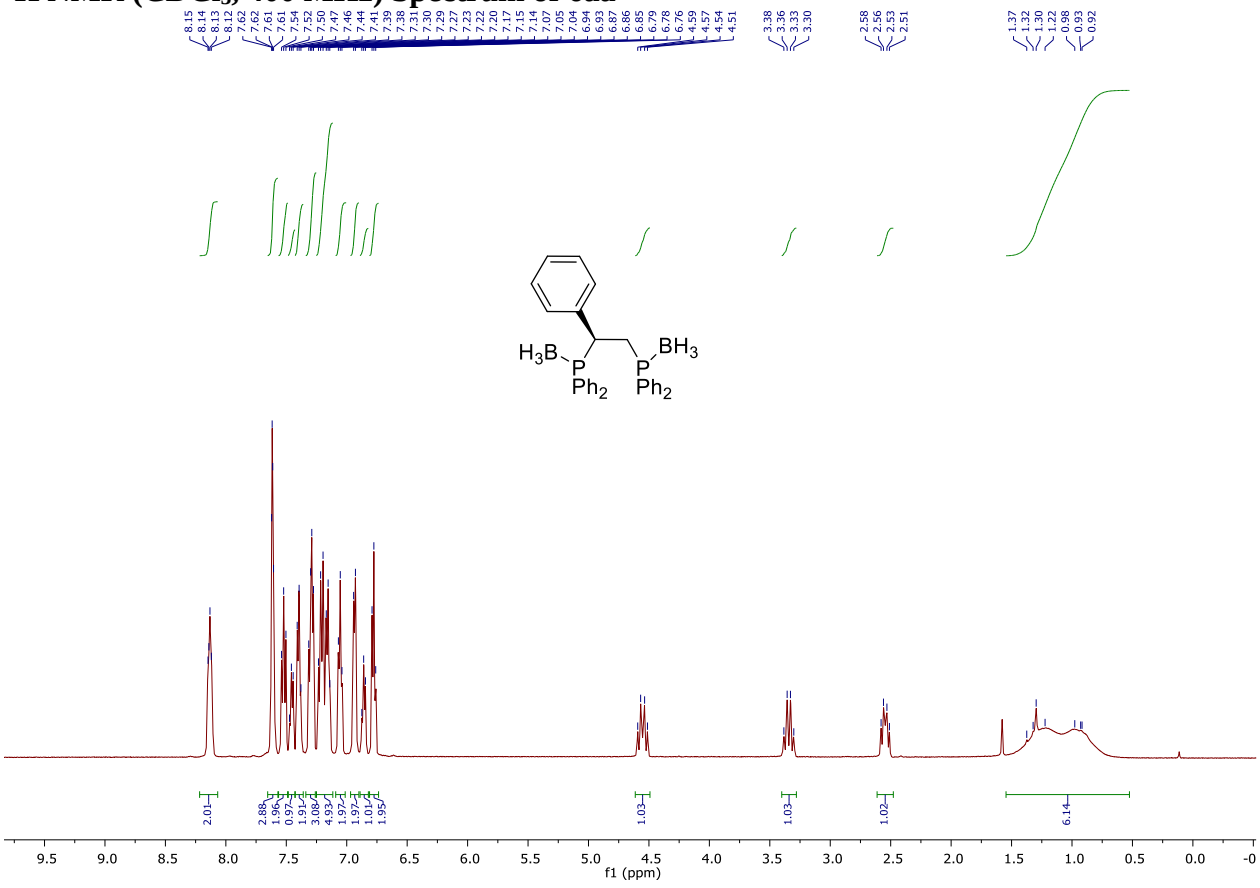
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 5b'h



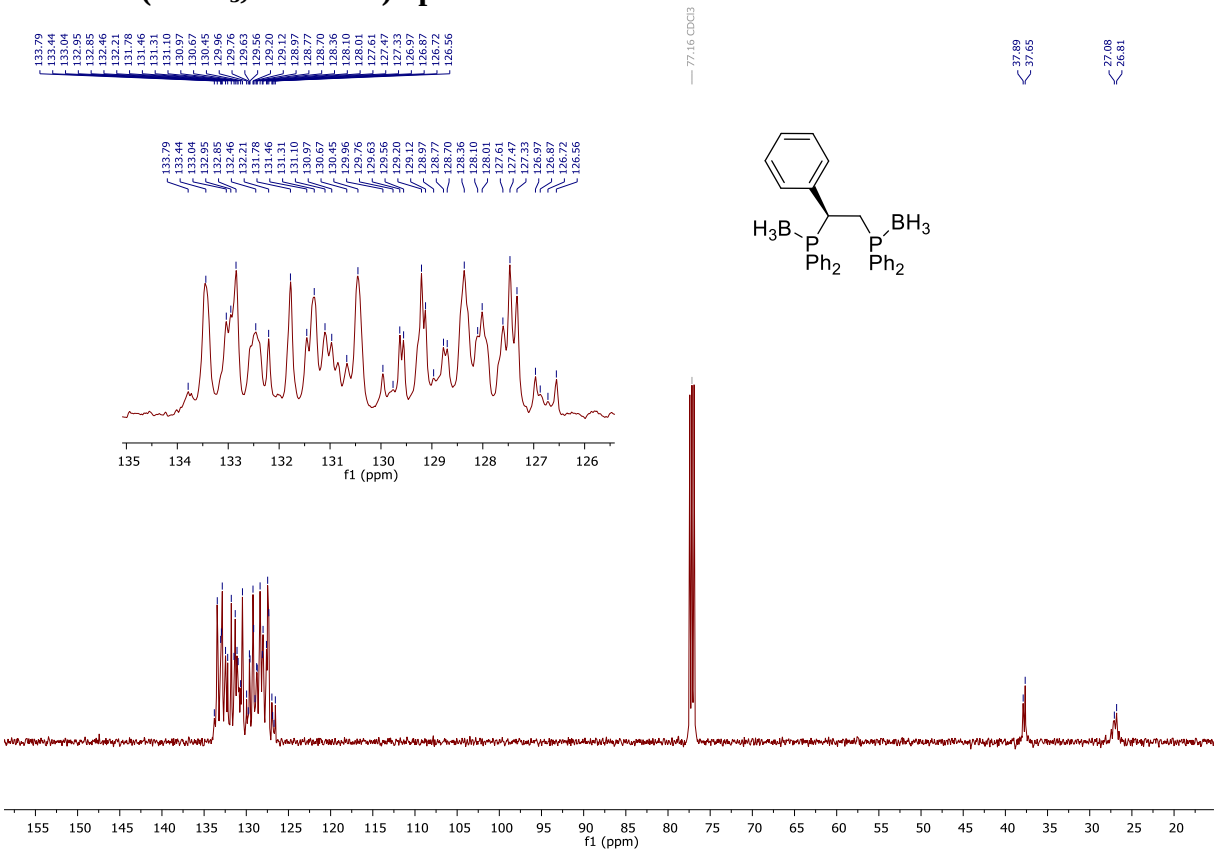
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 5b'h



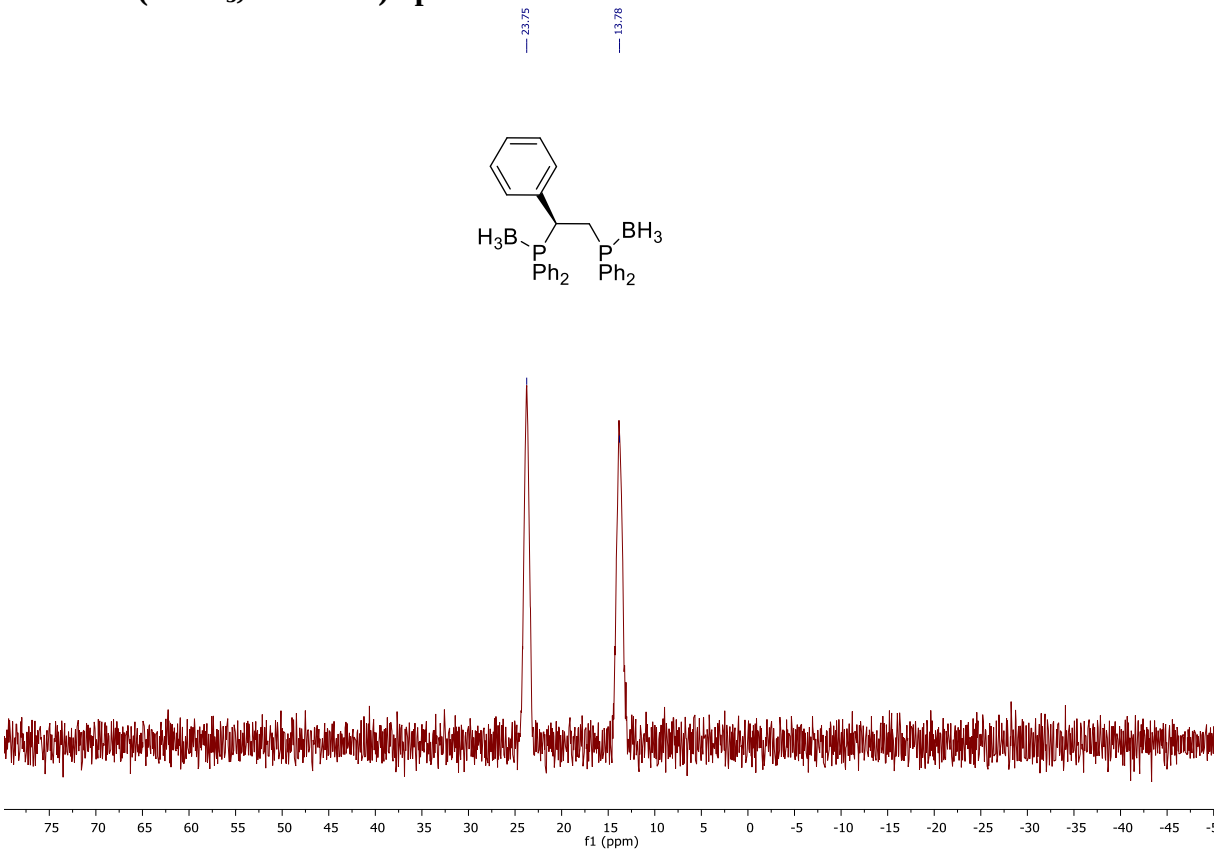
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 6aa



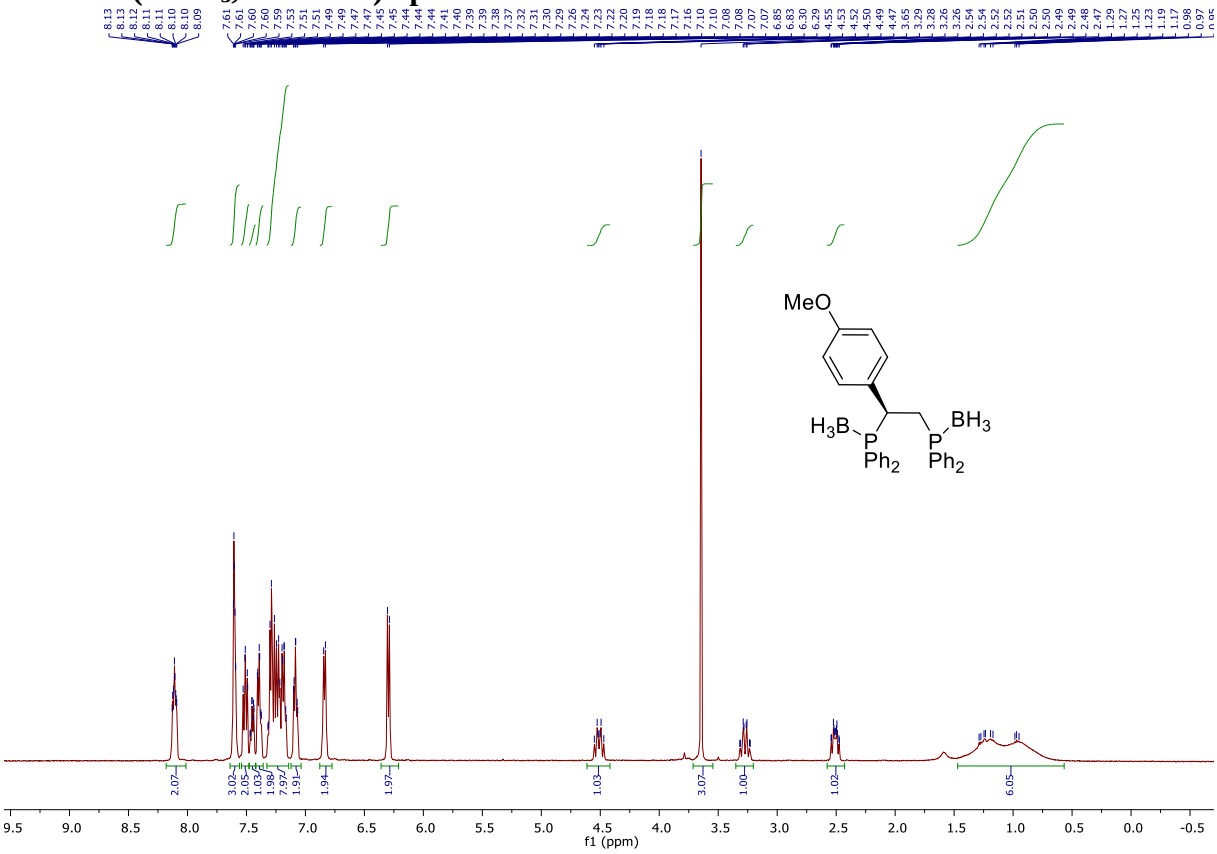
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 6aa



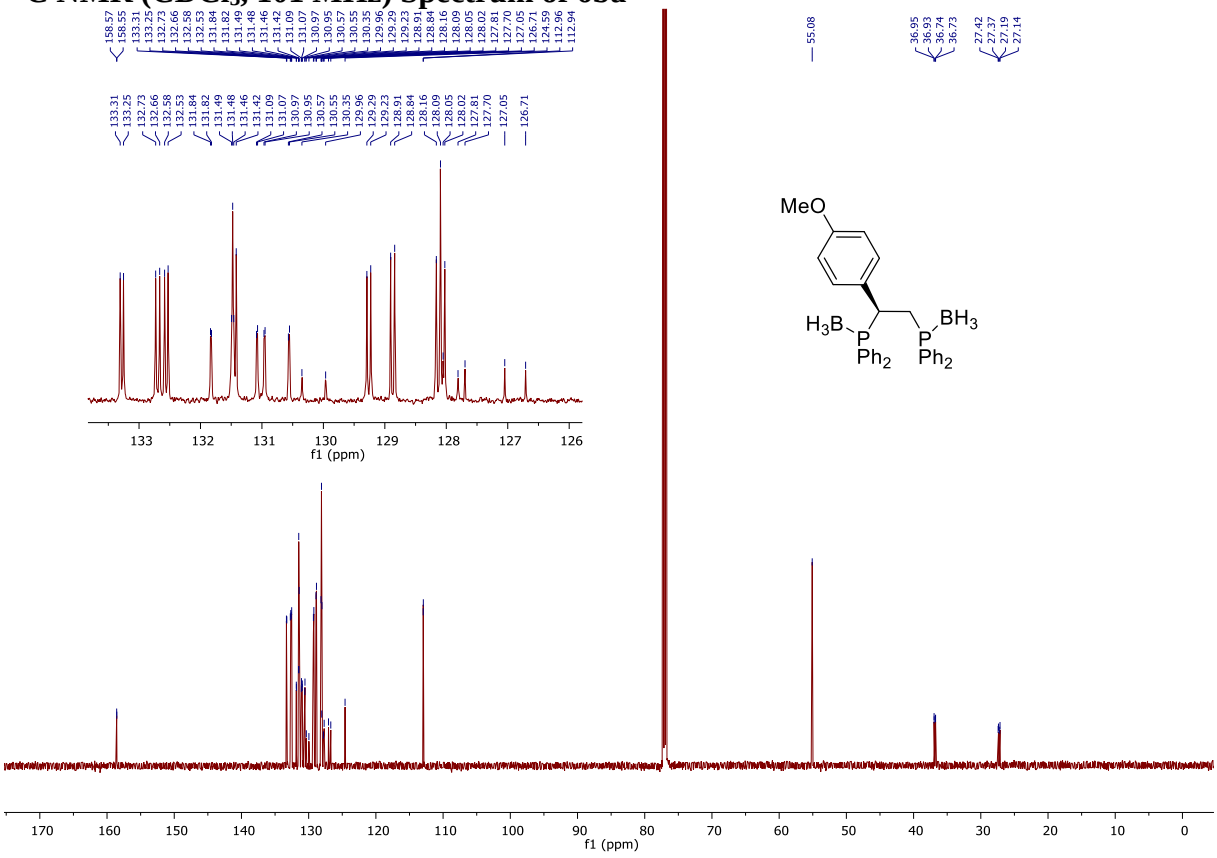
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 6aa



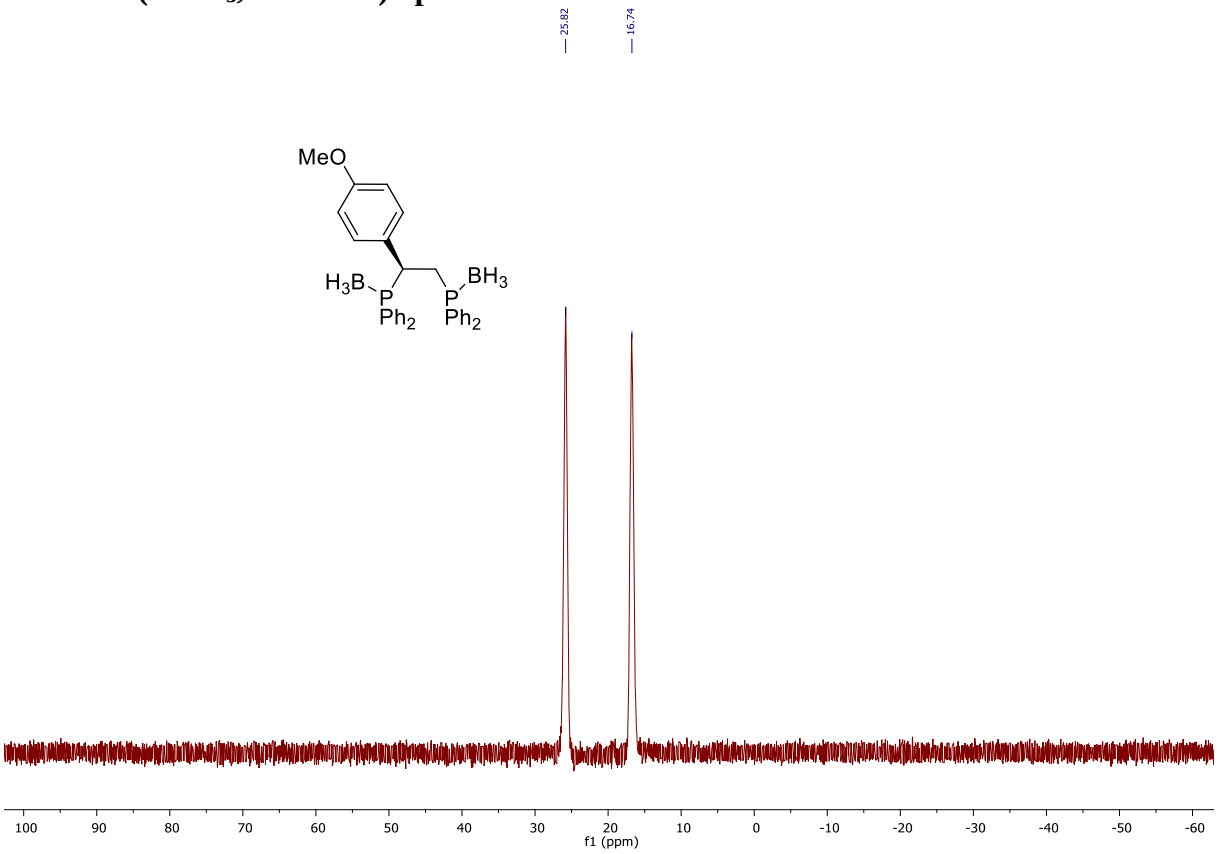
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 6ba



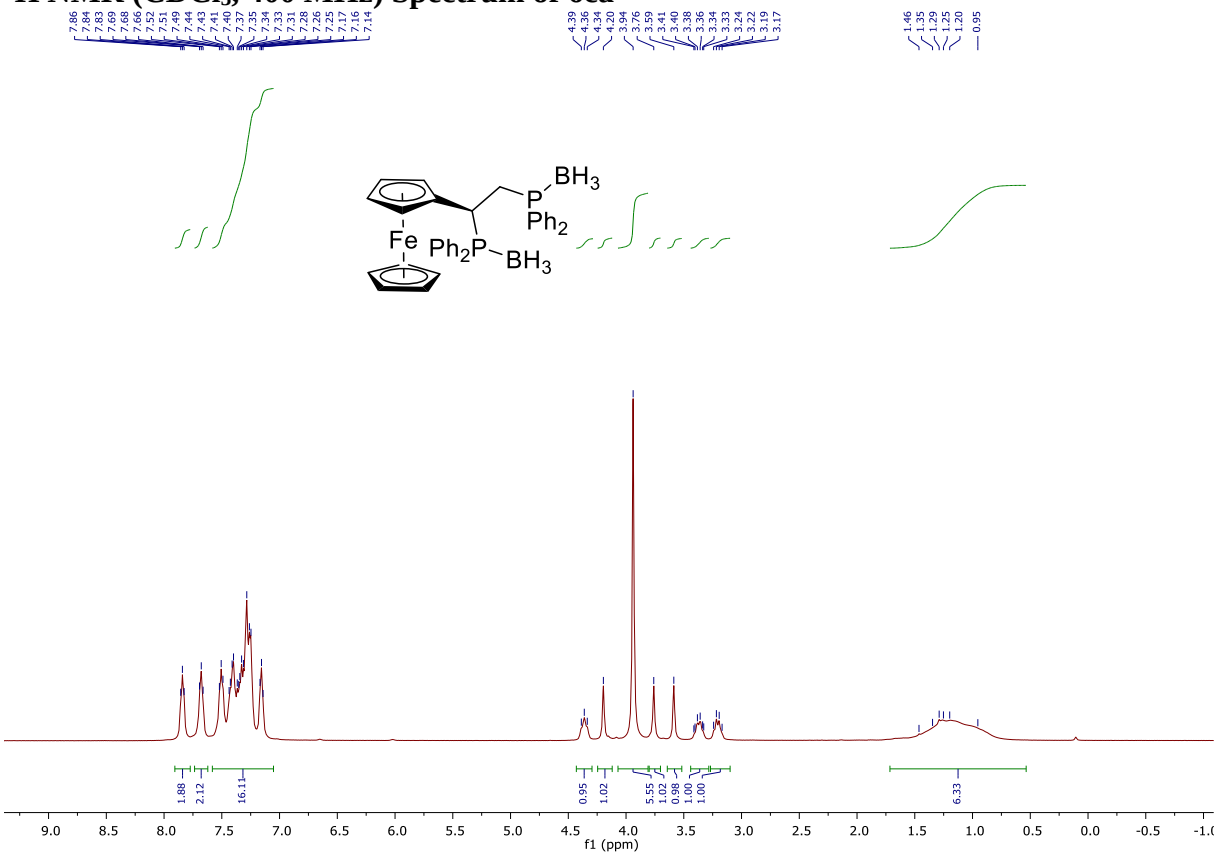
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 6ba



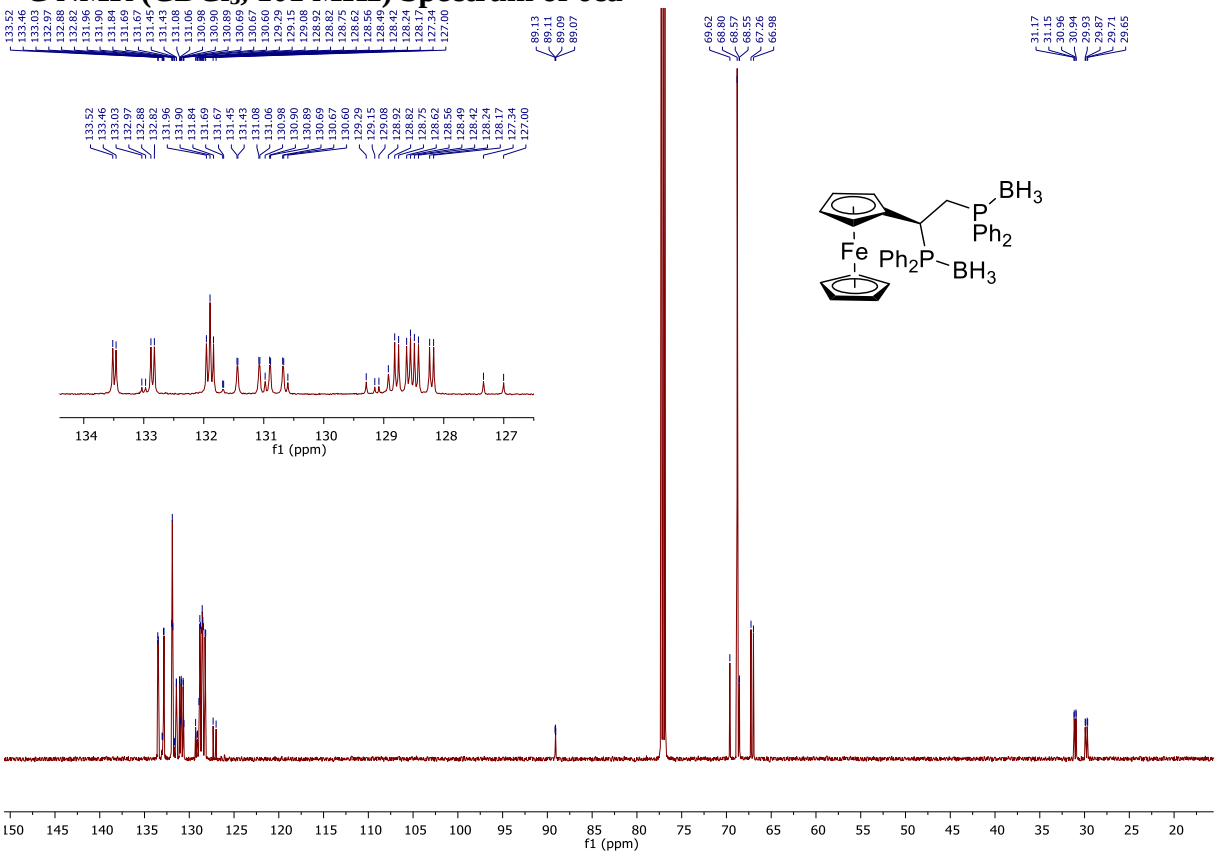
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 6ba



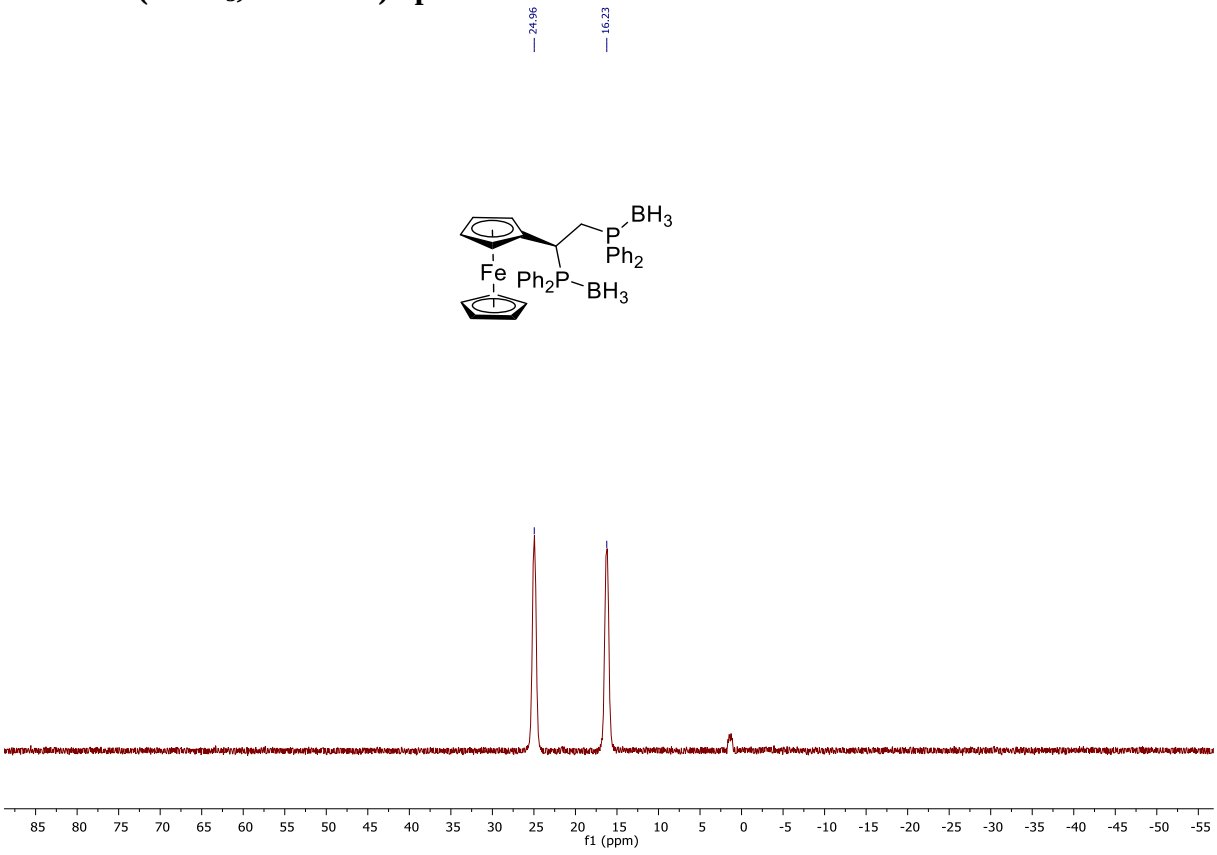
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 6ca



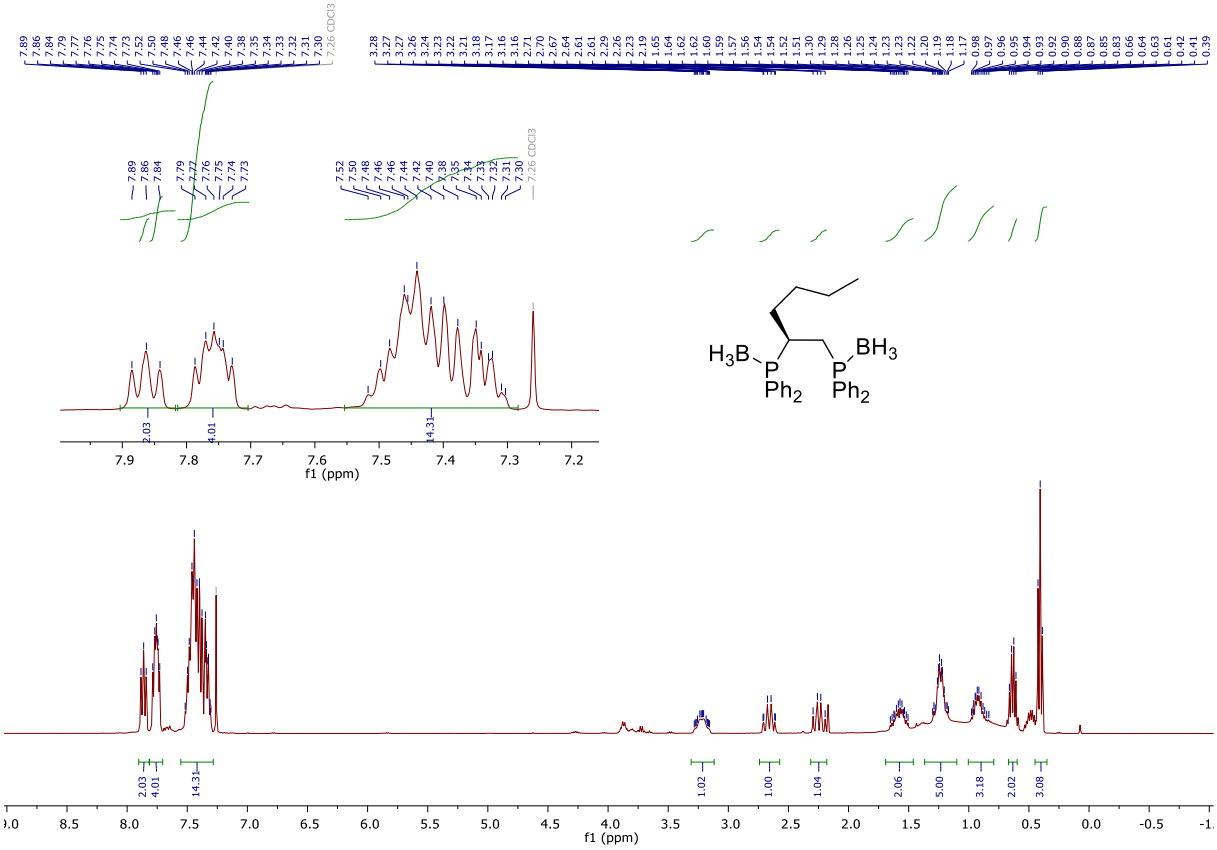
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 6ca



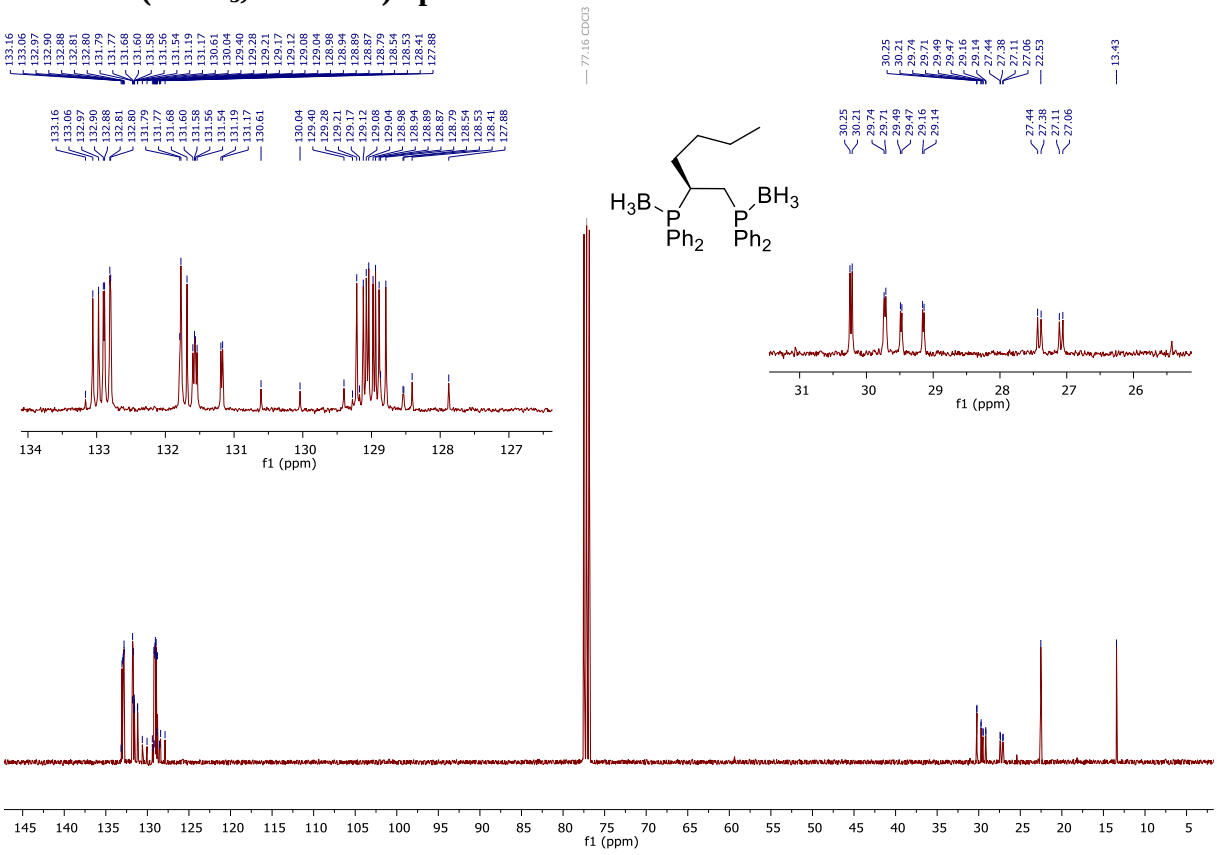
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 6ca



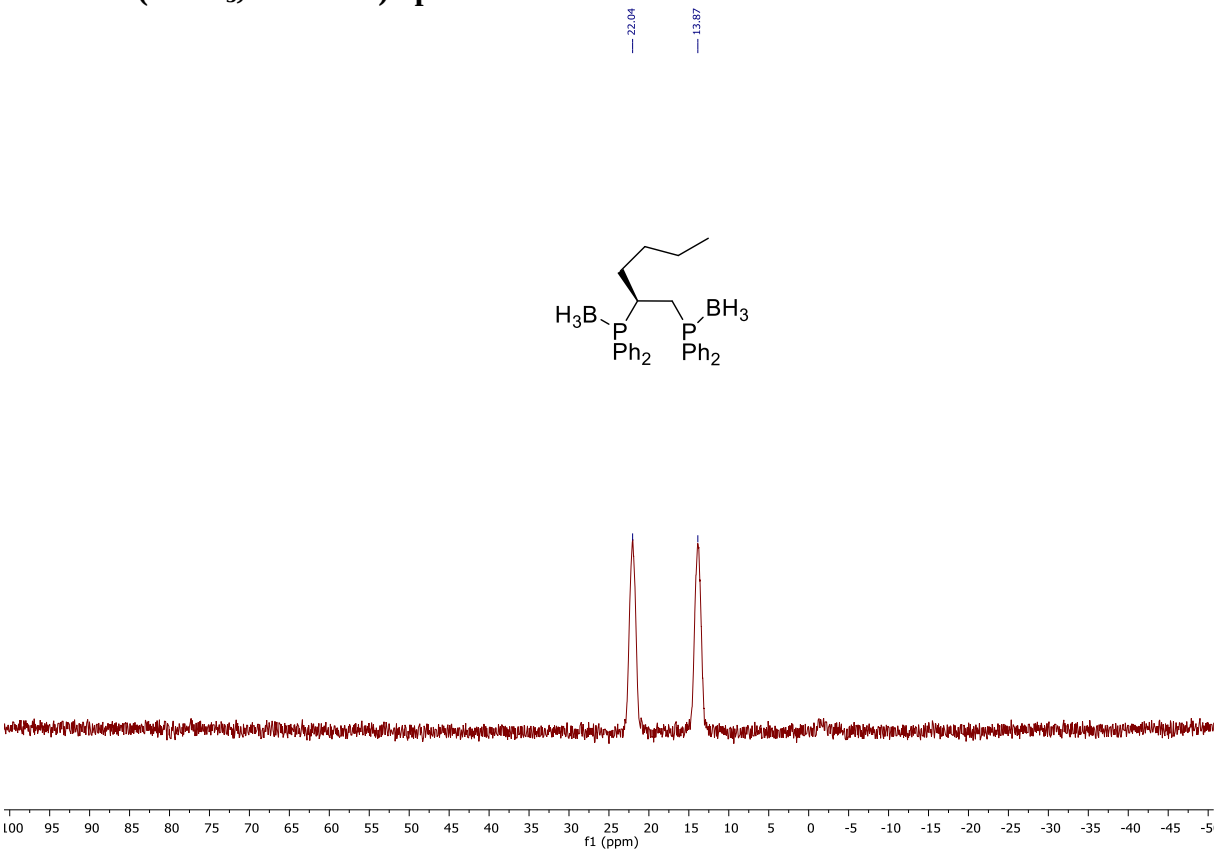
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 6da



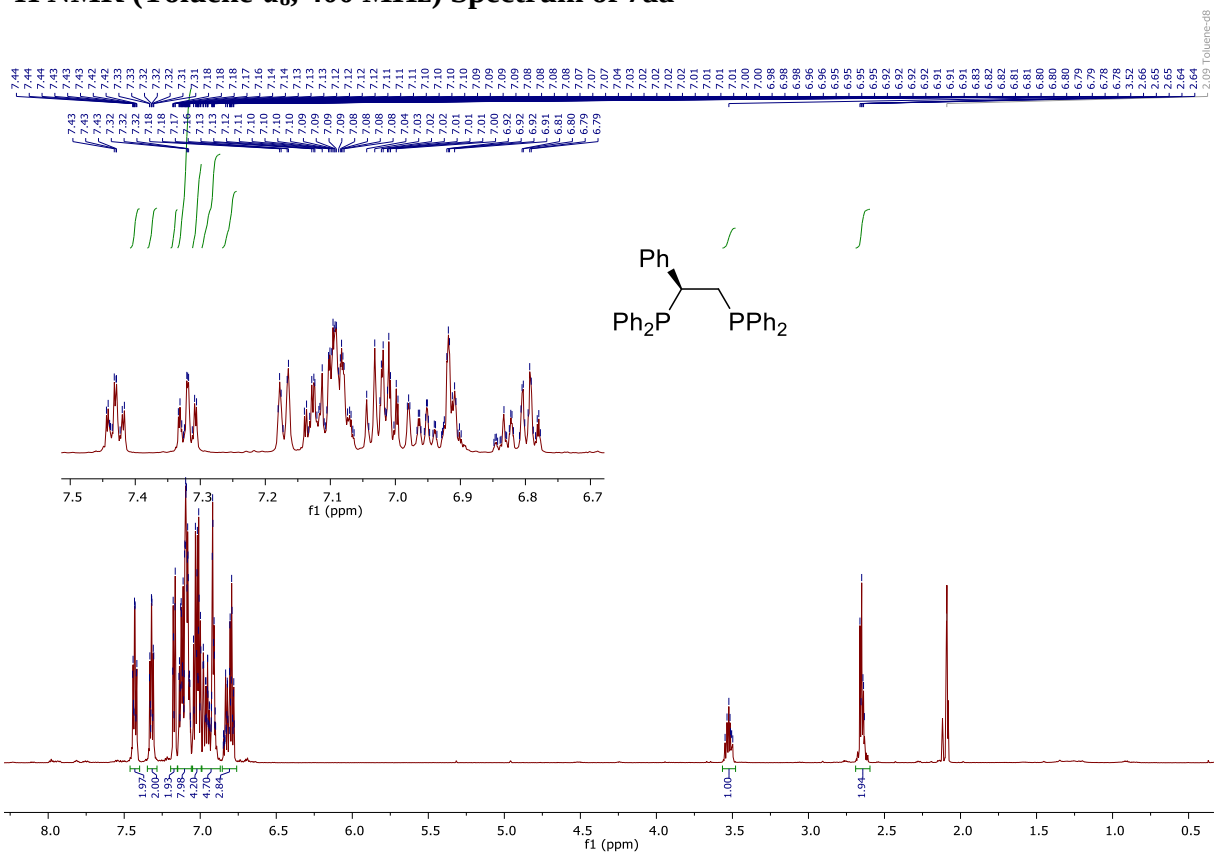
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 6da



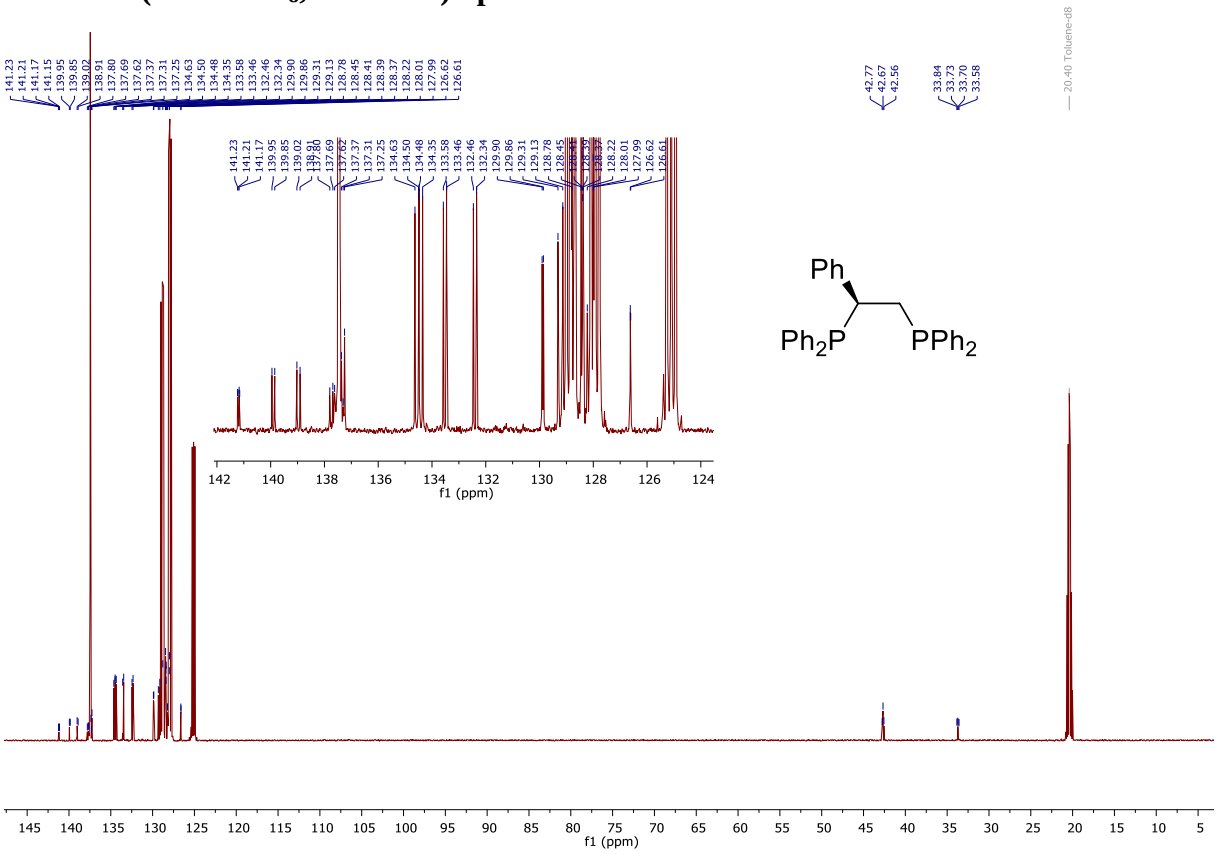
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 6da



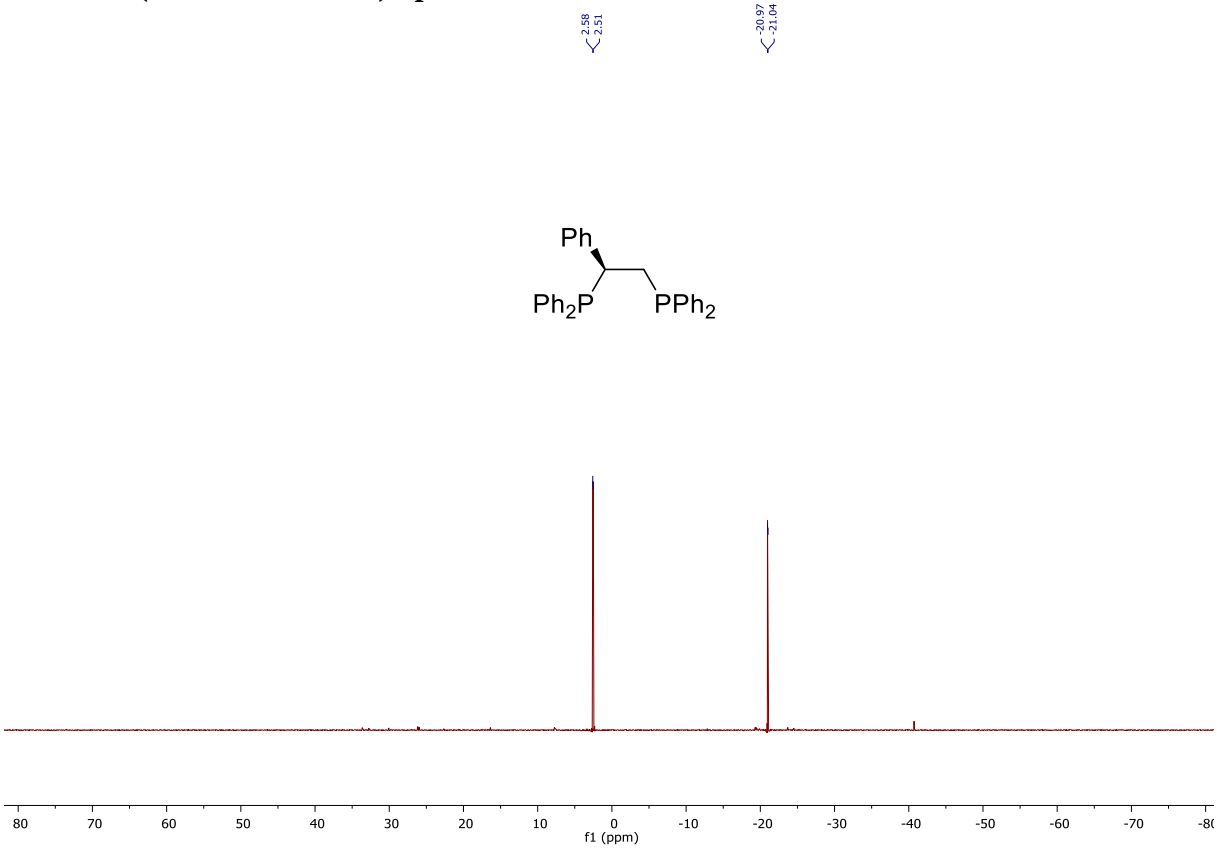
^{1}H NMR (Toluene-d_8, 400 MHz) Spectrum of 7aa



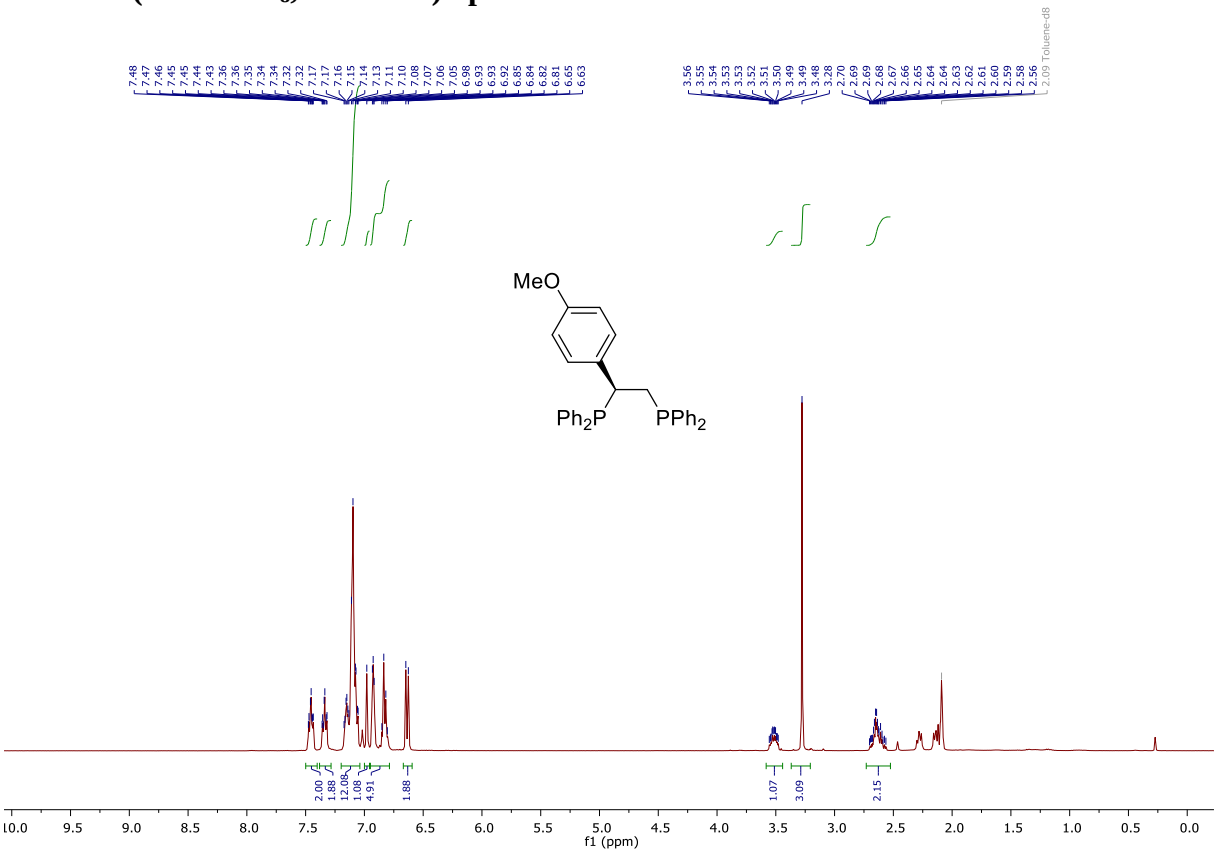
^{13}C NMR (Toluene-d_8, 101 MHz) Spectrum of 7aa



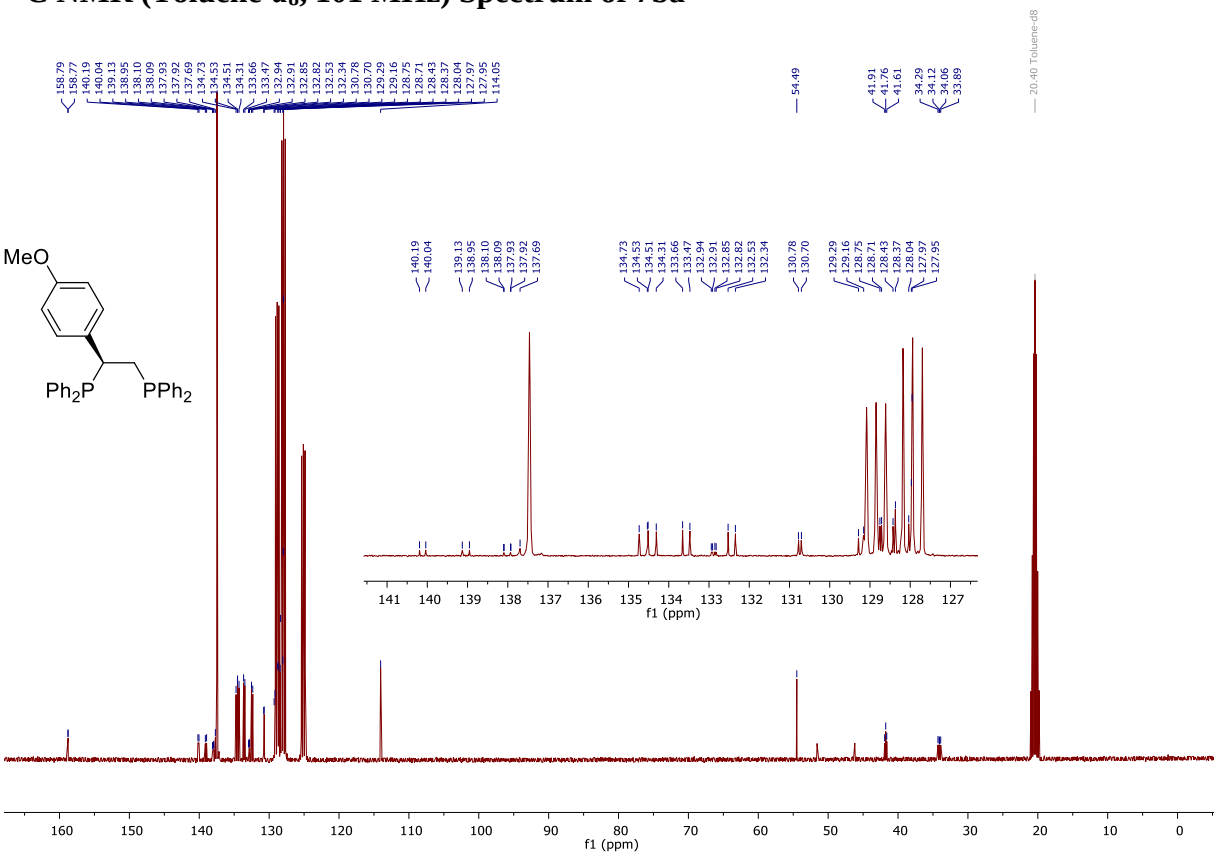
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 7aa



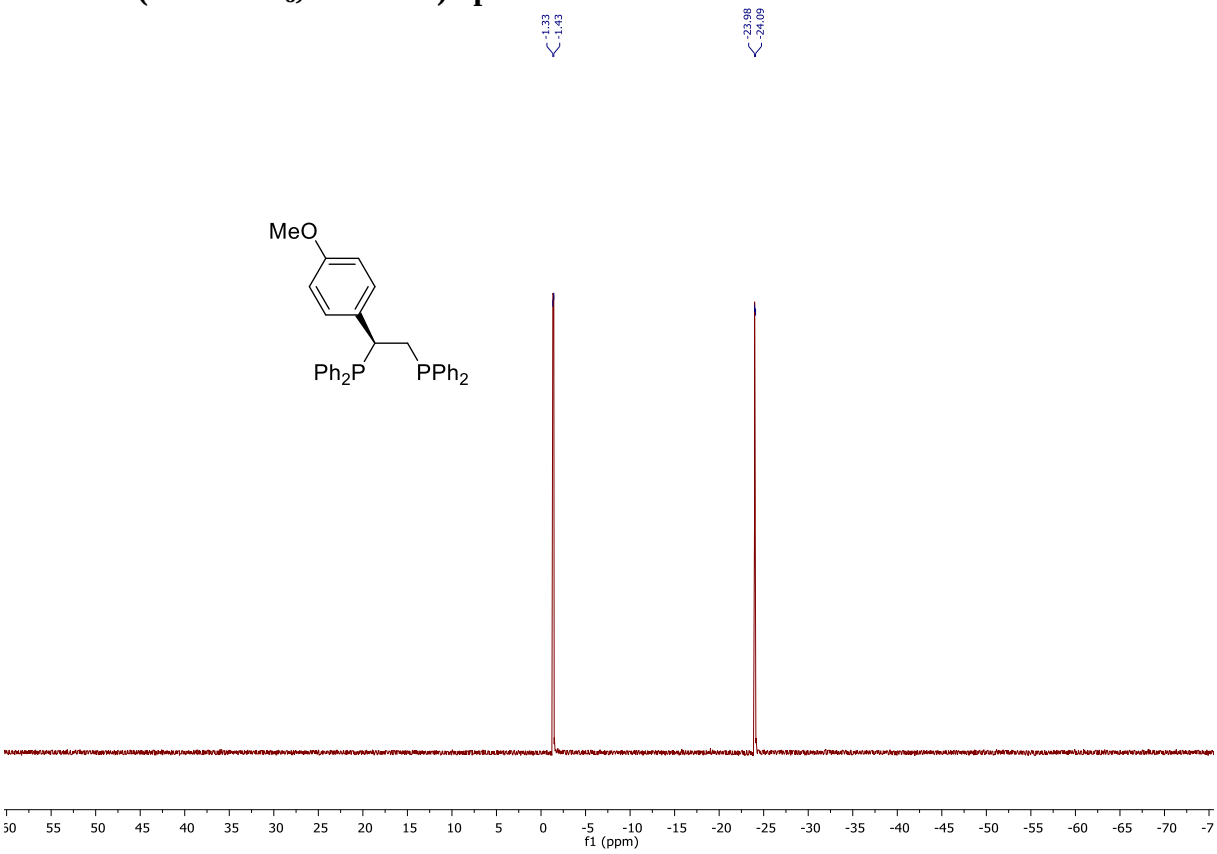
^{1}H NMR (Toluene-d_8, 400 MHz) Spectrum of 7ba



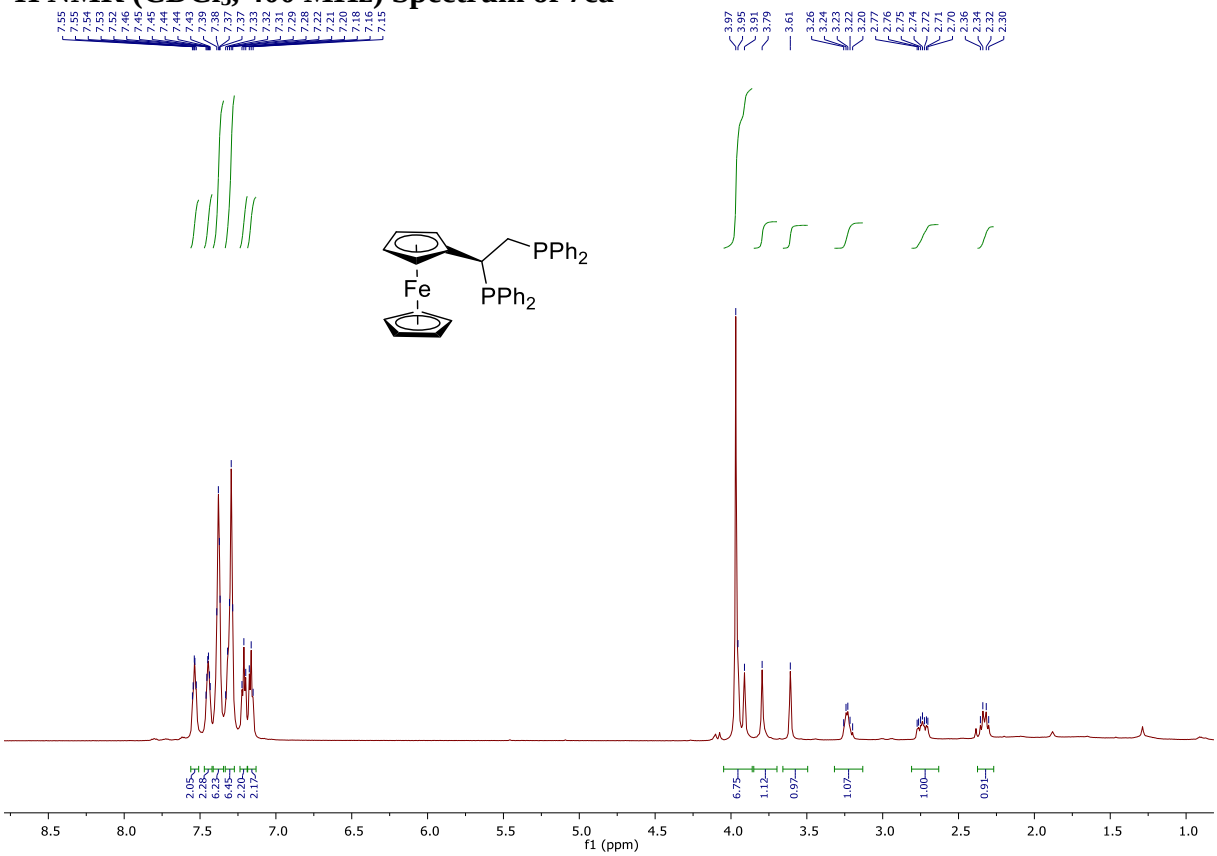
^{13}C NMR (Toluene-d_8, 101 MHz) Spectrum of 7ba



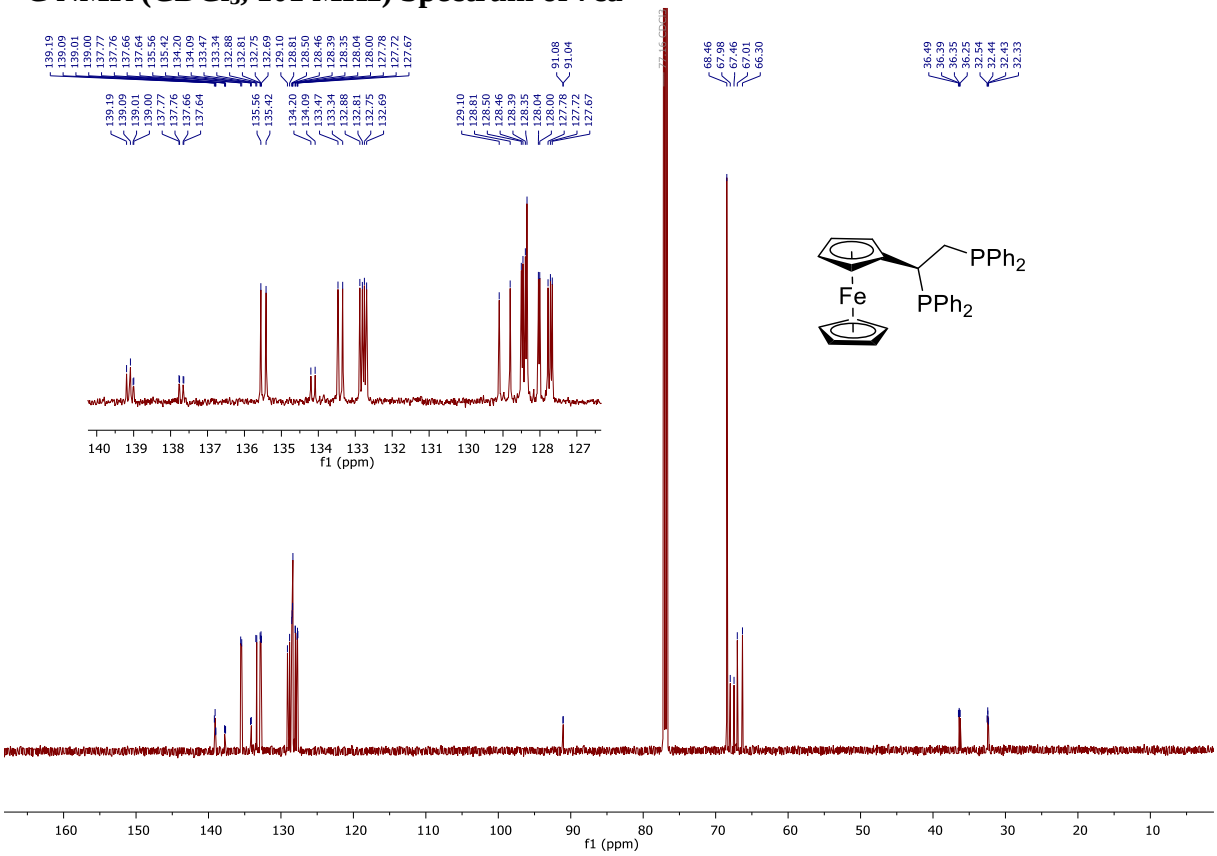
^{31}P NMR (Toluene-d_8, 162 MHz) Spectrum of 7ba



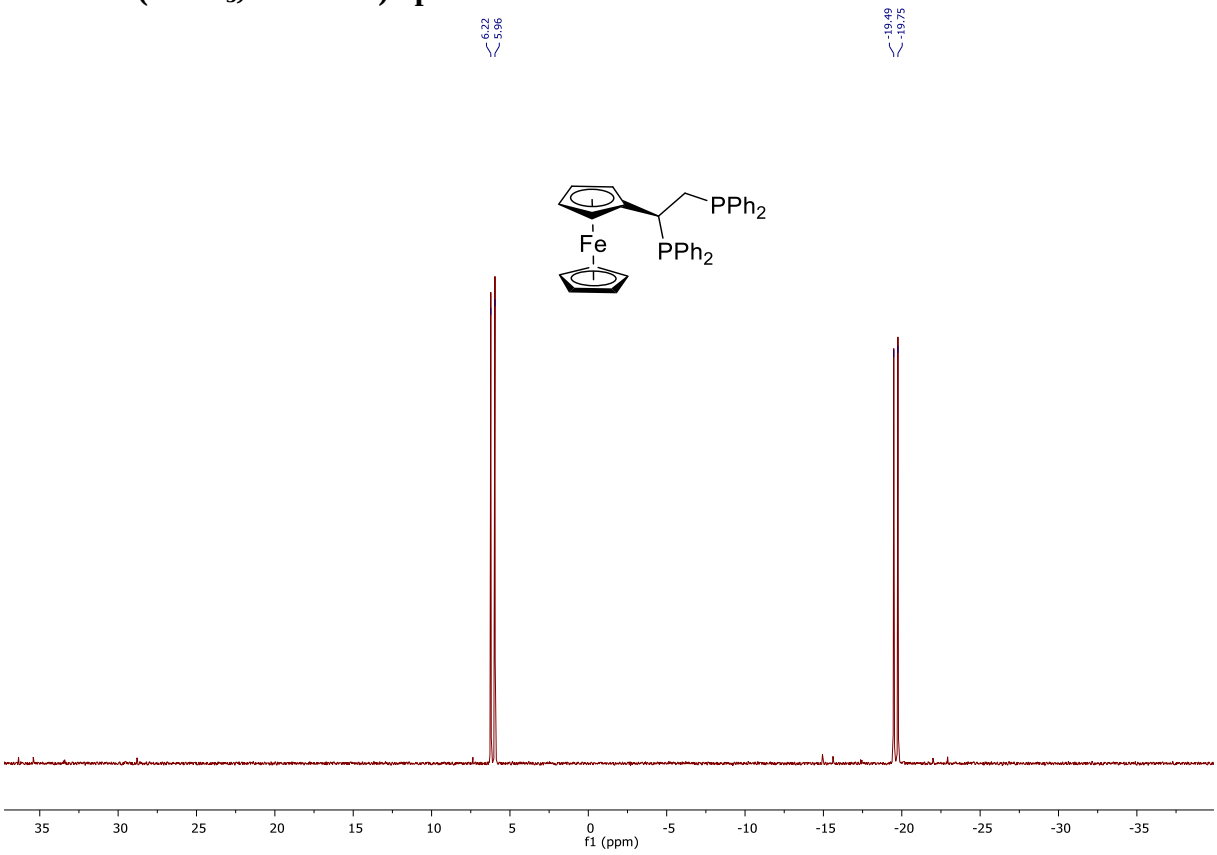
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 7ca



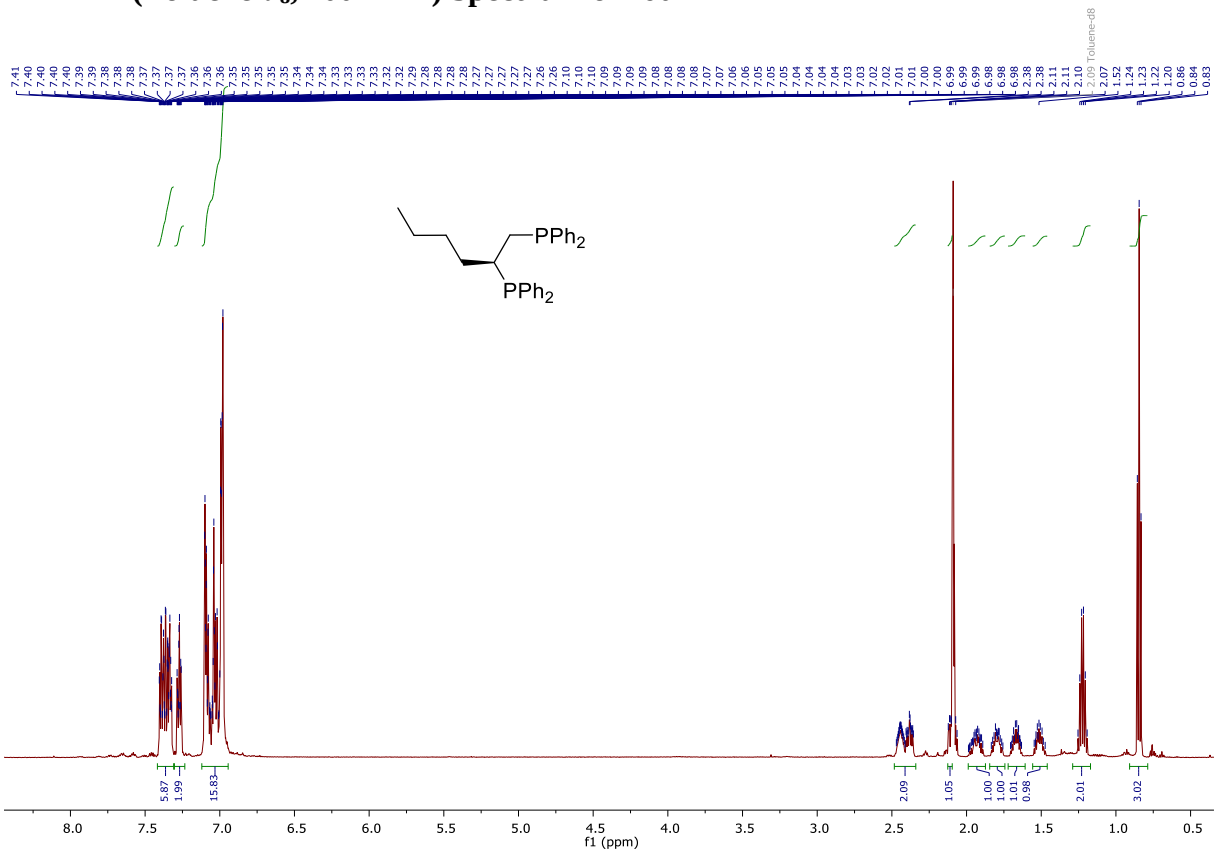
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 7ca



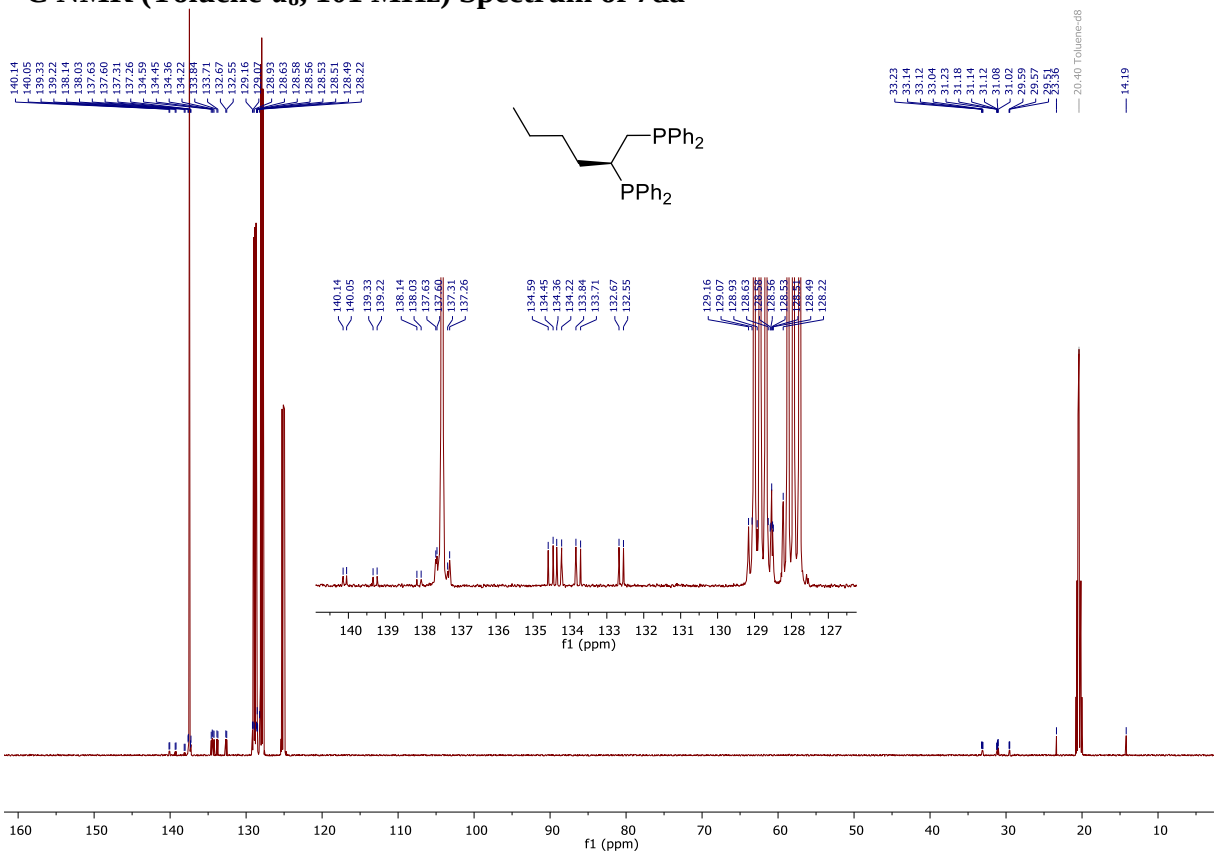
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 7ca



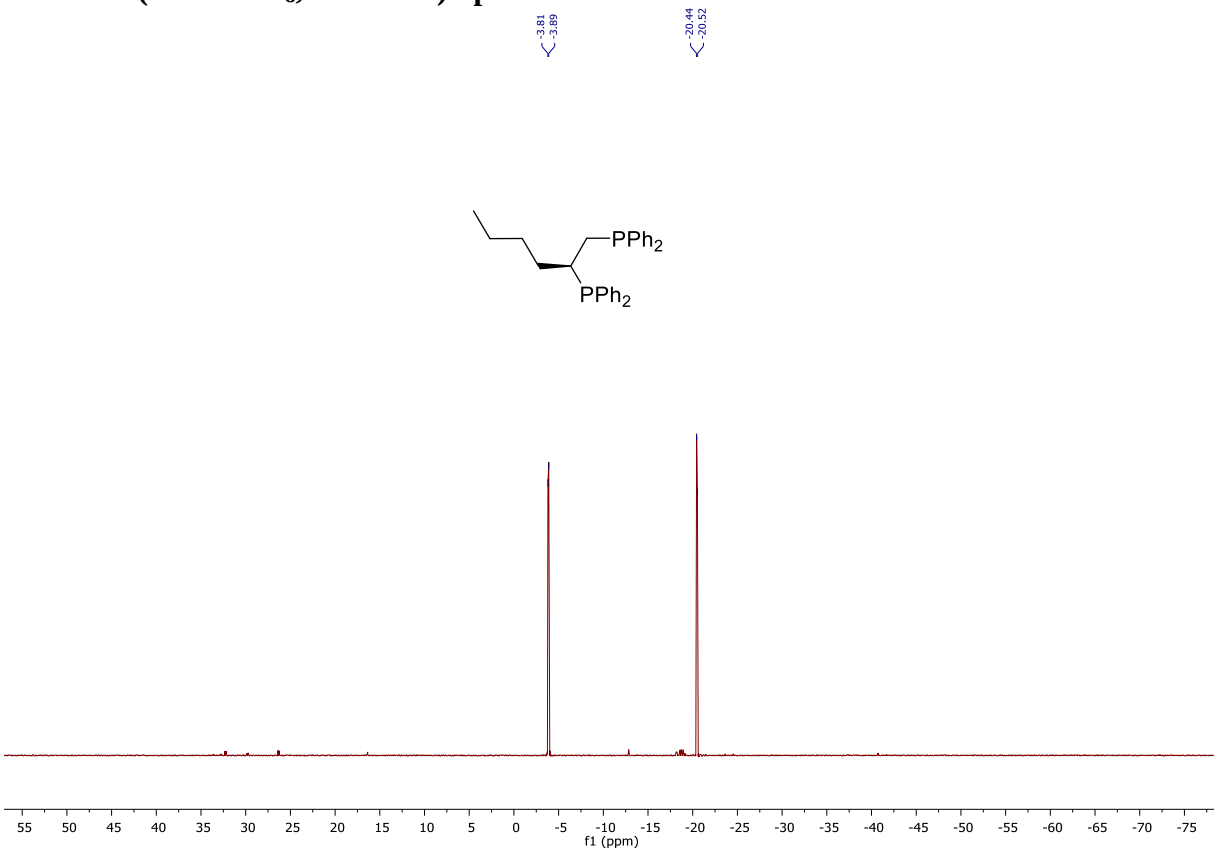
^{1}H NMR (Toluene-d_8, 400 MHz) Spectrum of 7da



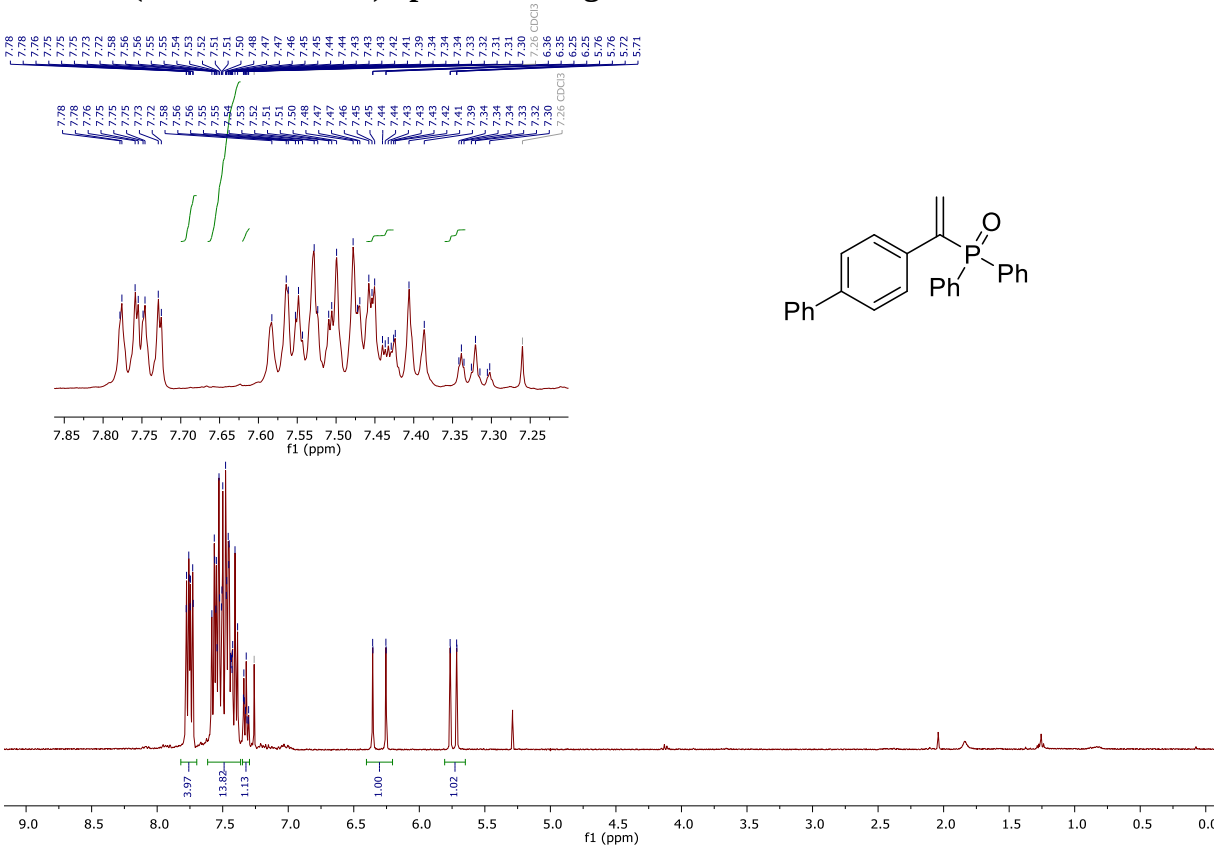
^{13}C NMR (Toluene-d_8, 101 MHz) Spectrum of 7da



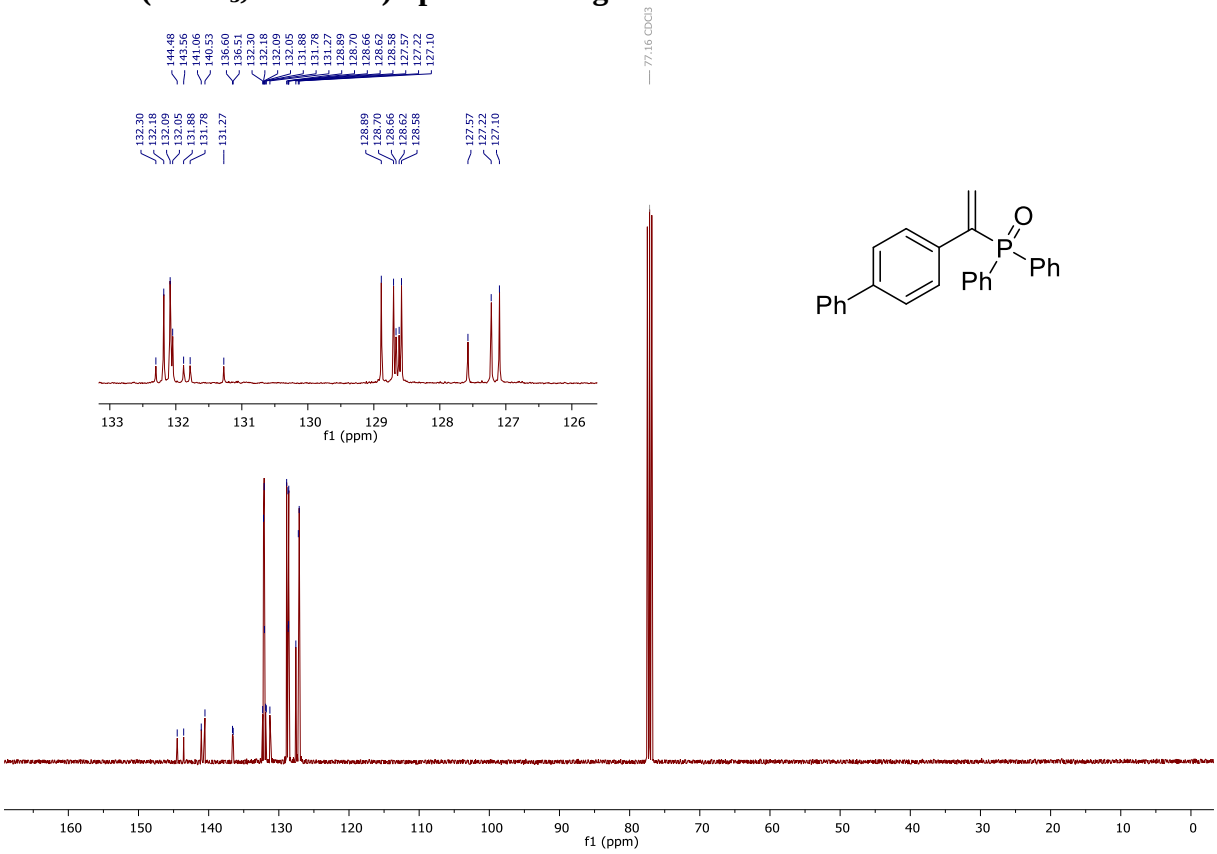
^{31}P NMR (Toluene-d_8, 162 MHz) Spectrum of 7da



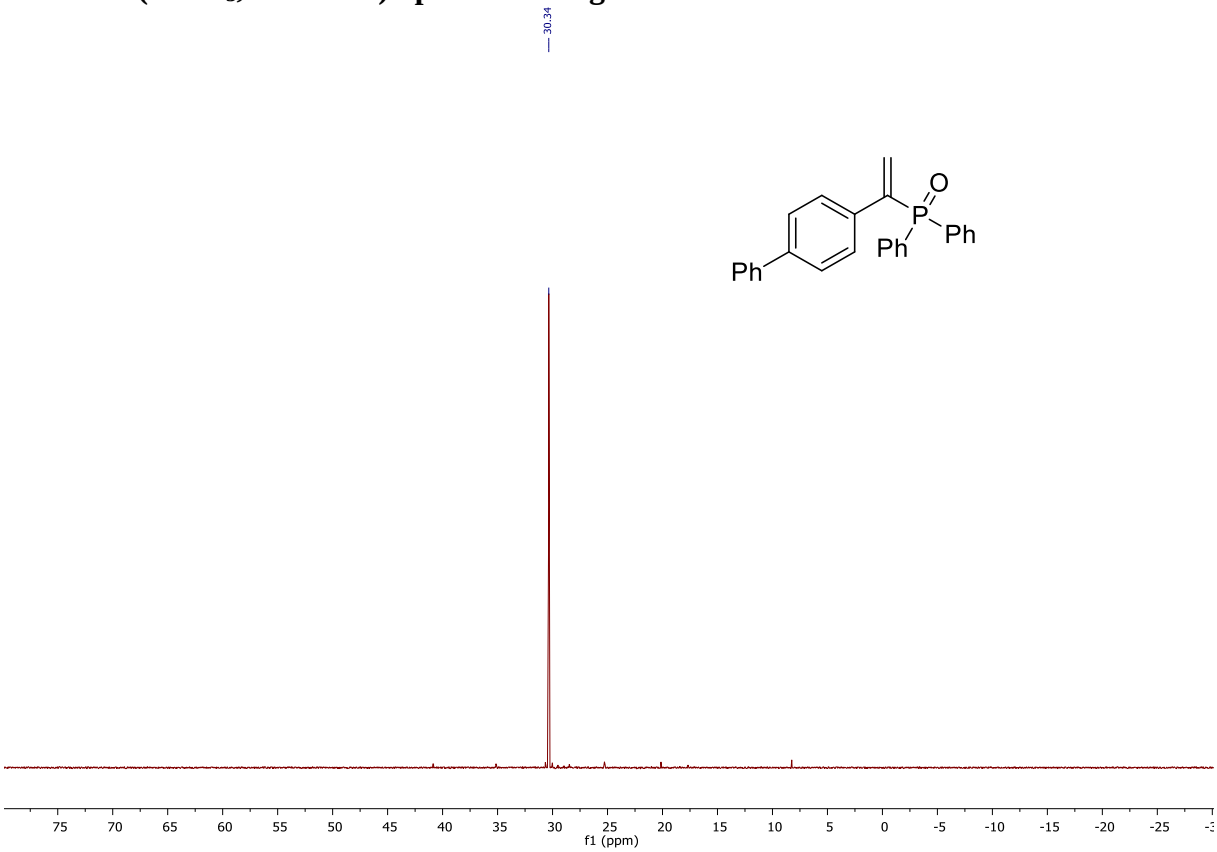
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1g



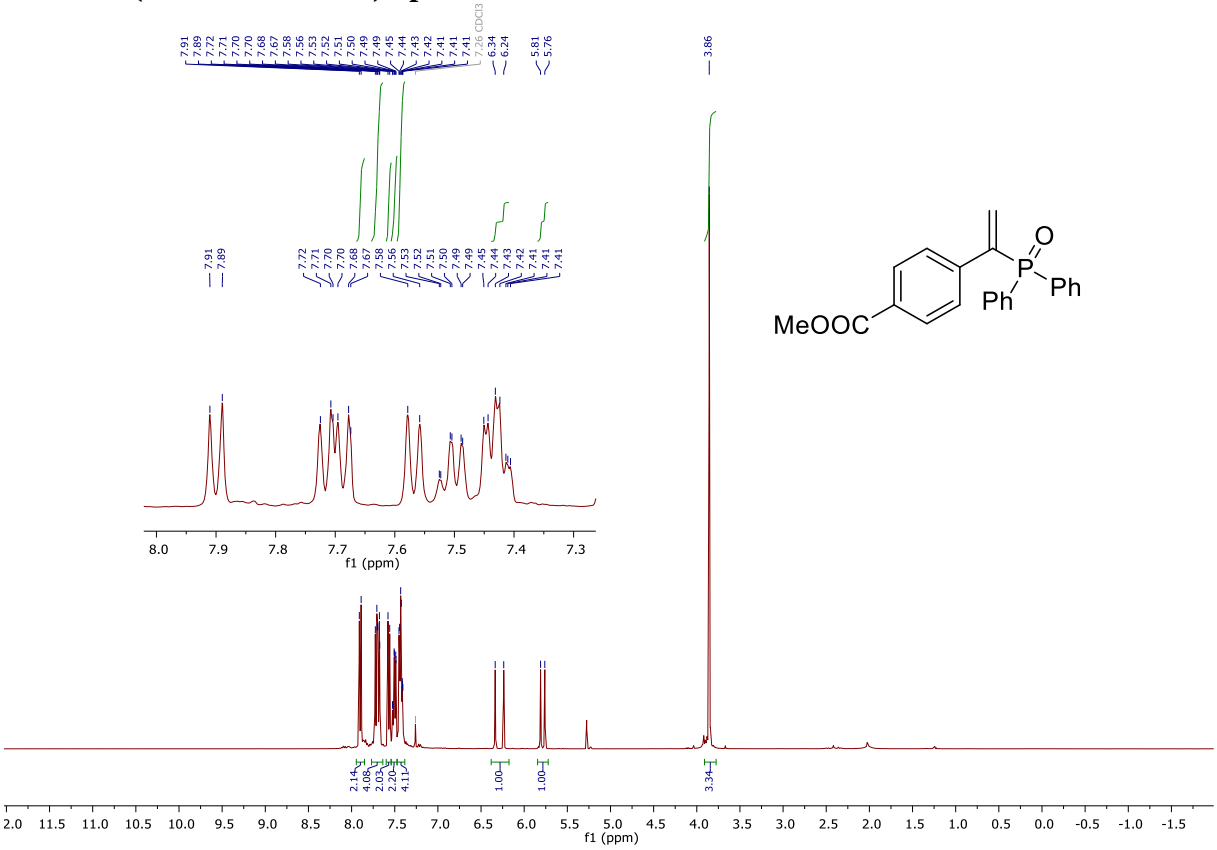
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1g



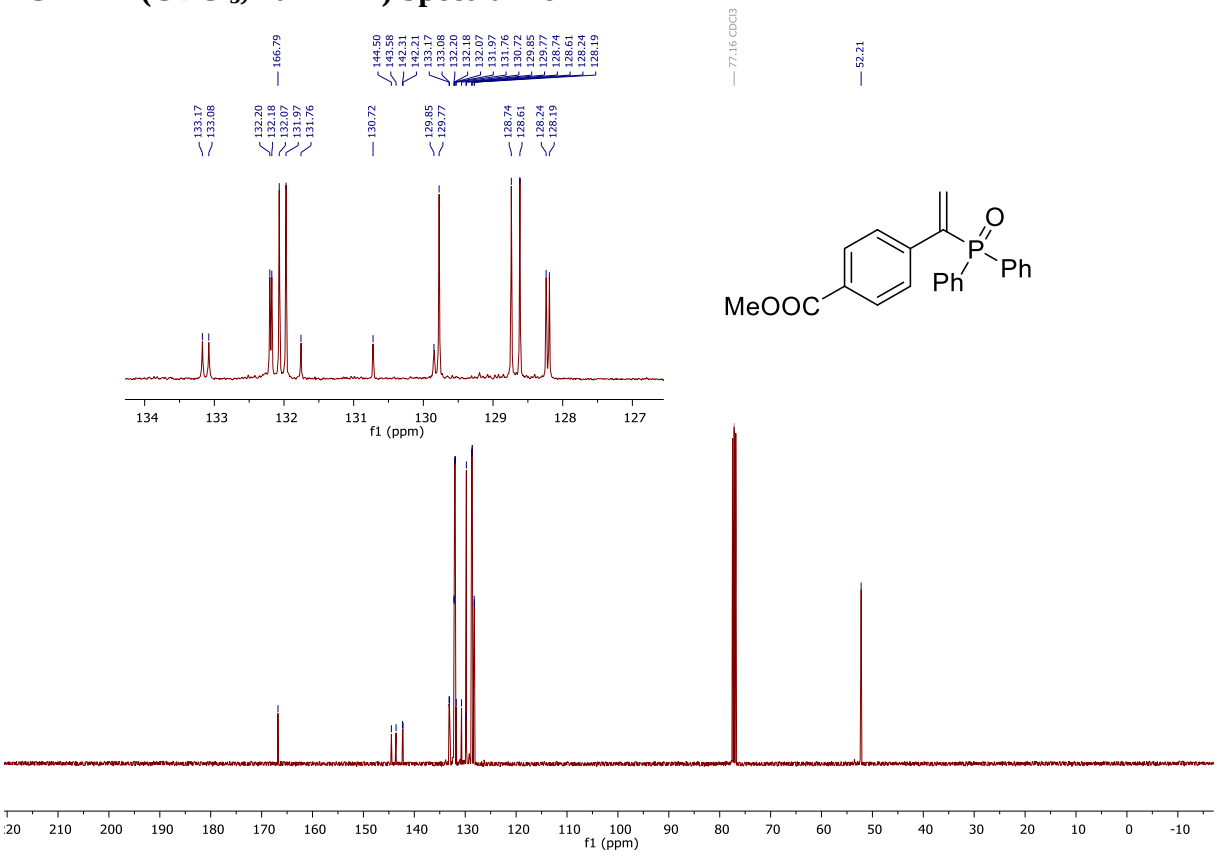
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1g



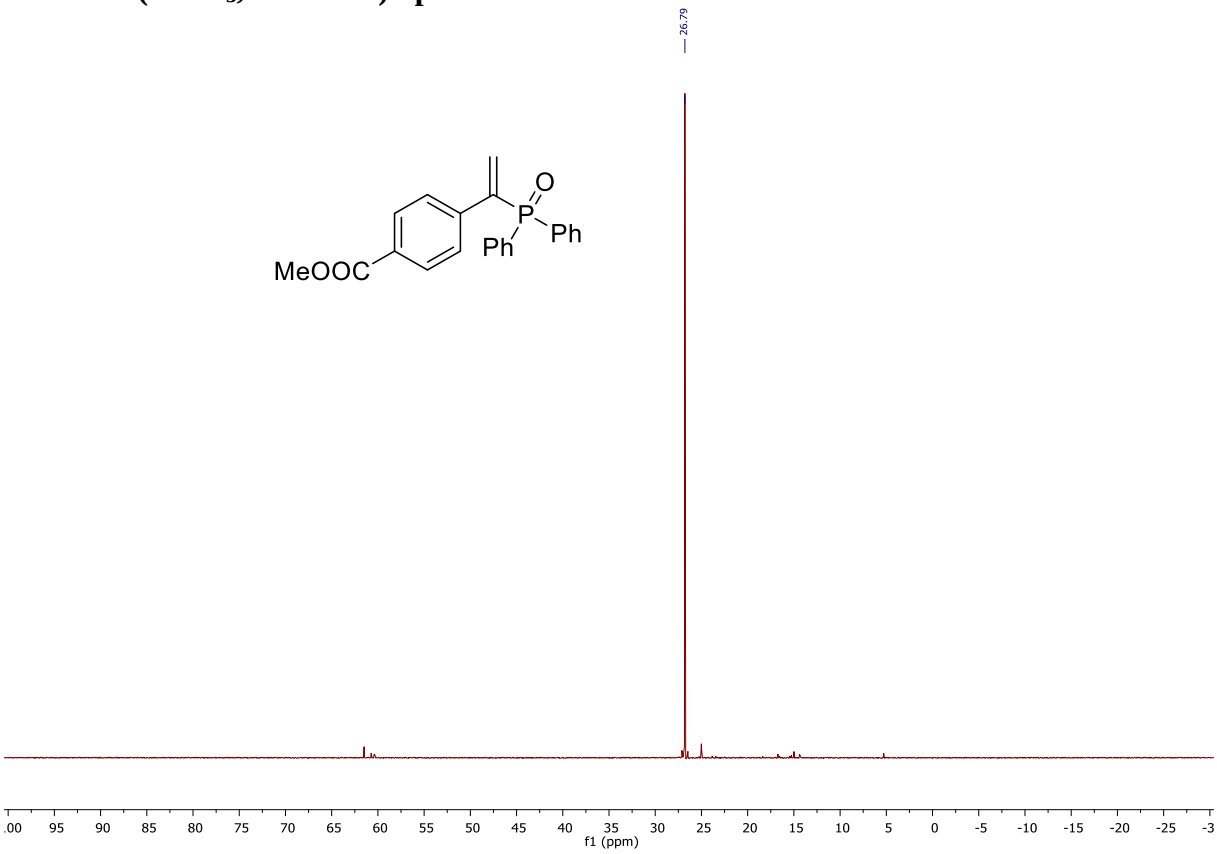
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1h



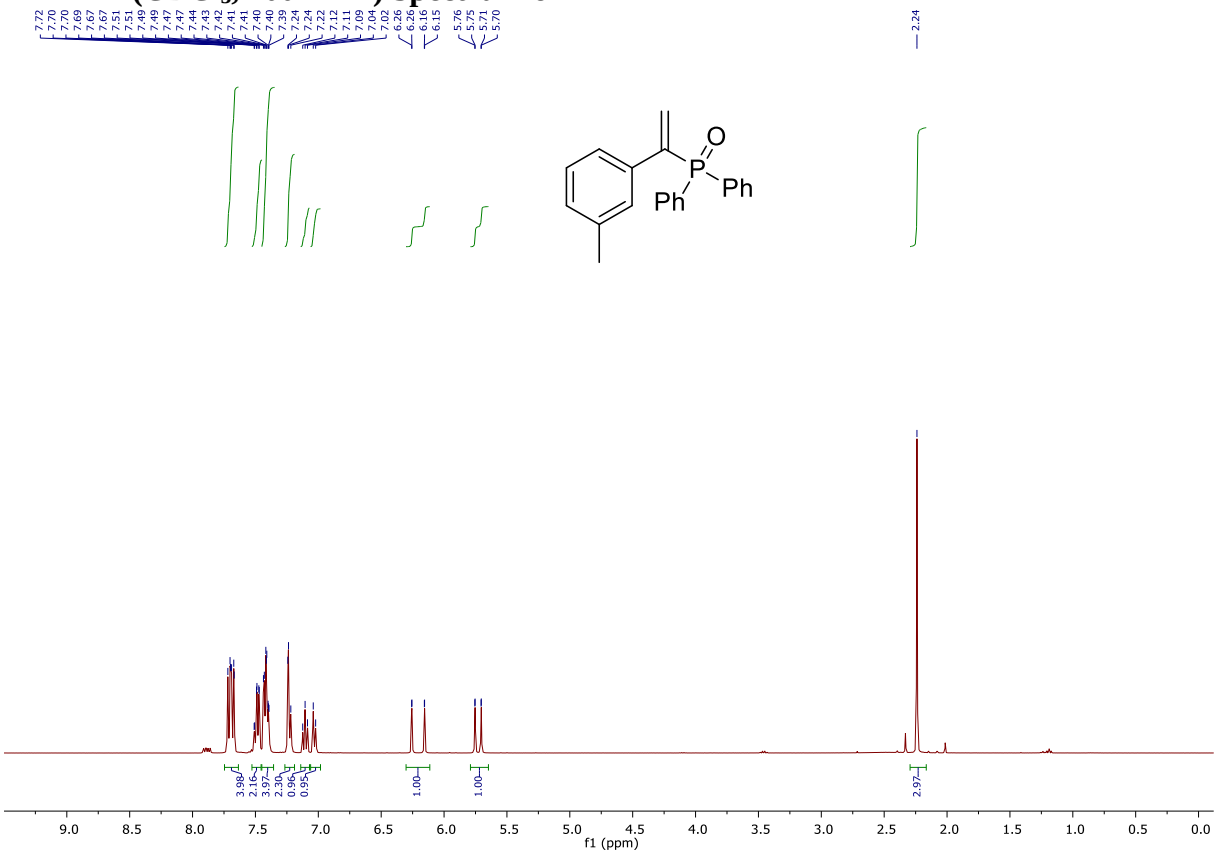
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1h



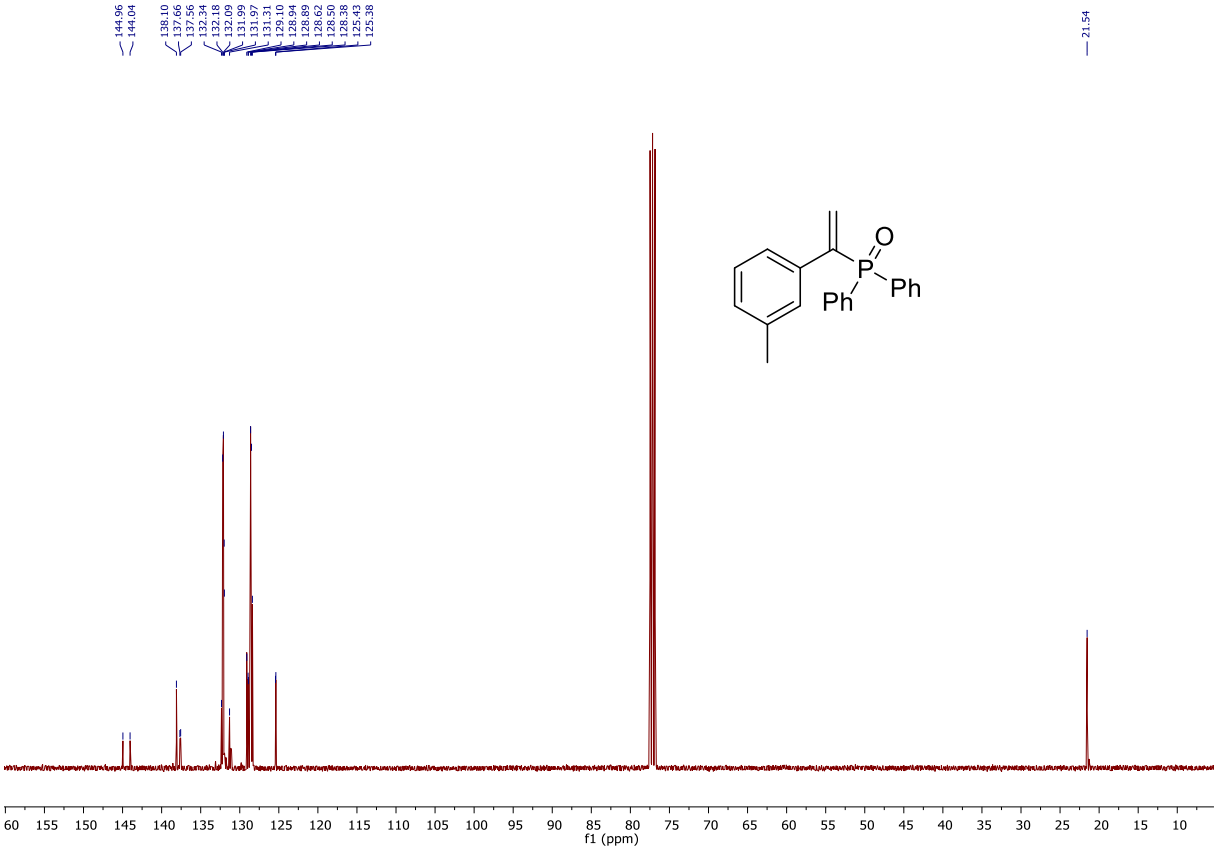
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1h



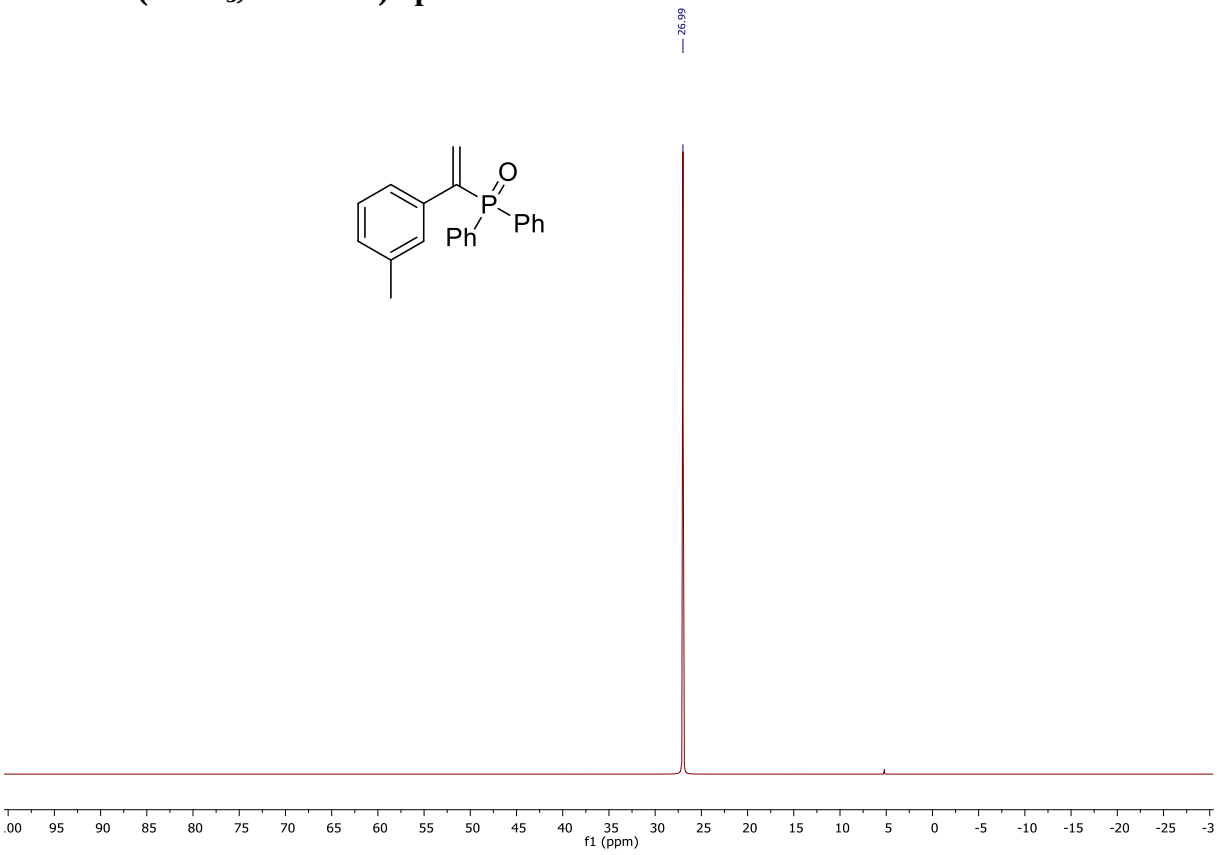
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1i



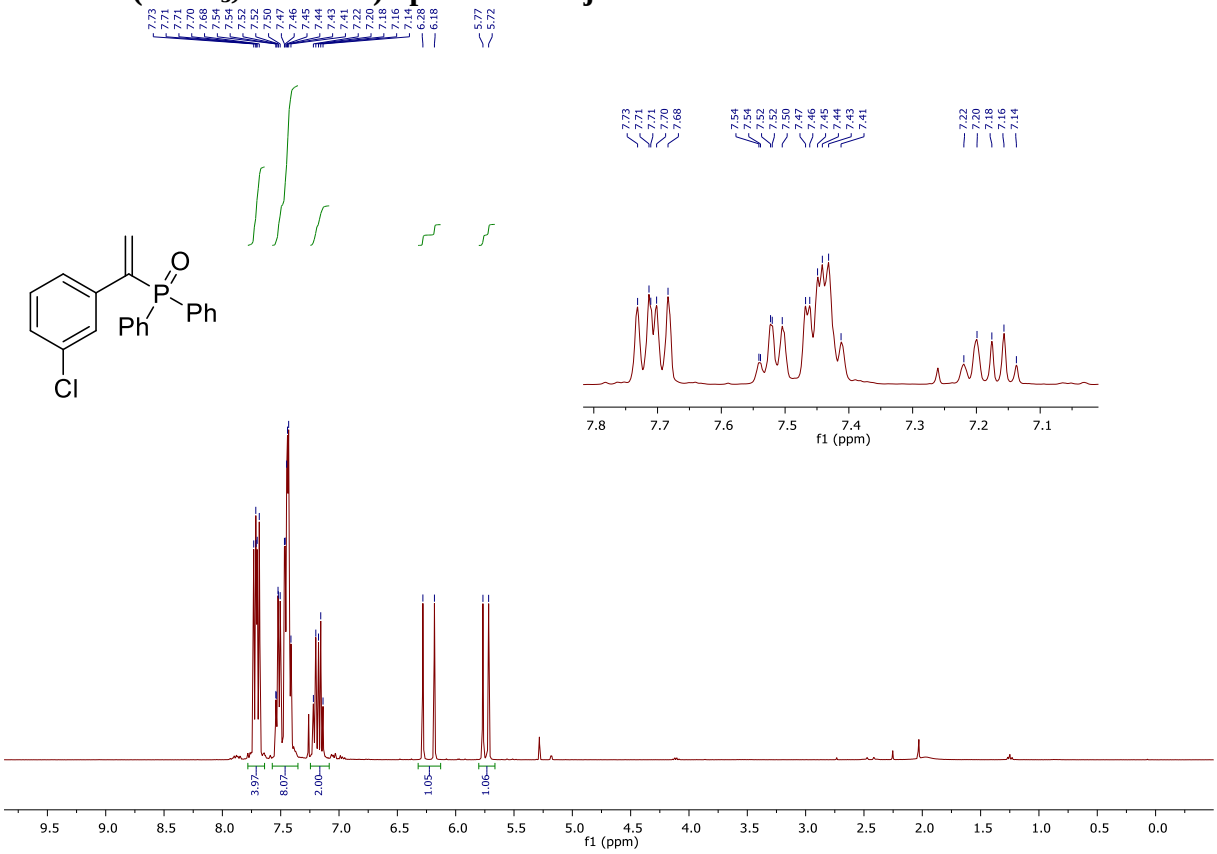
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1i



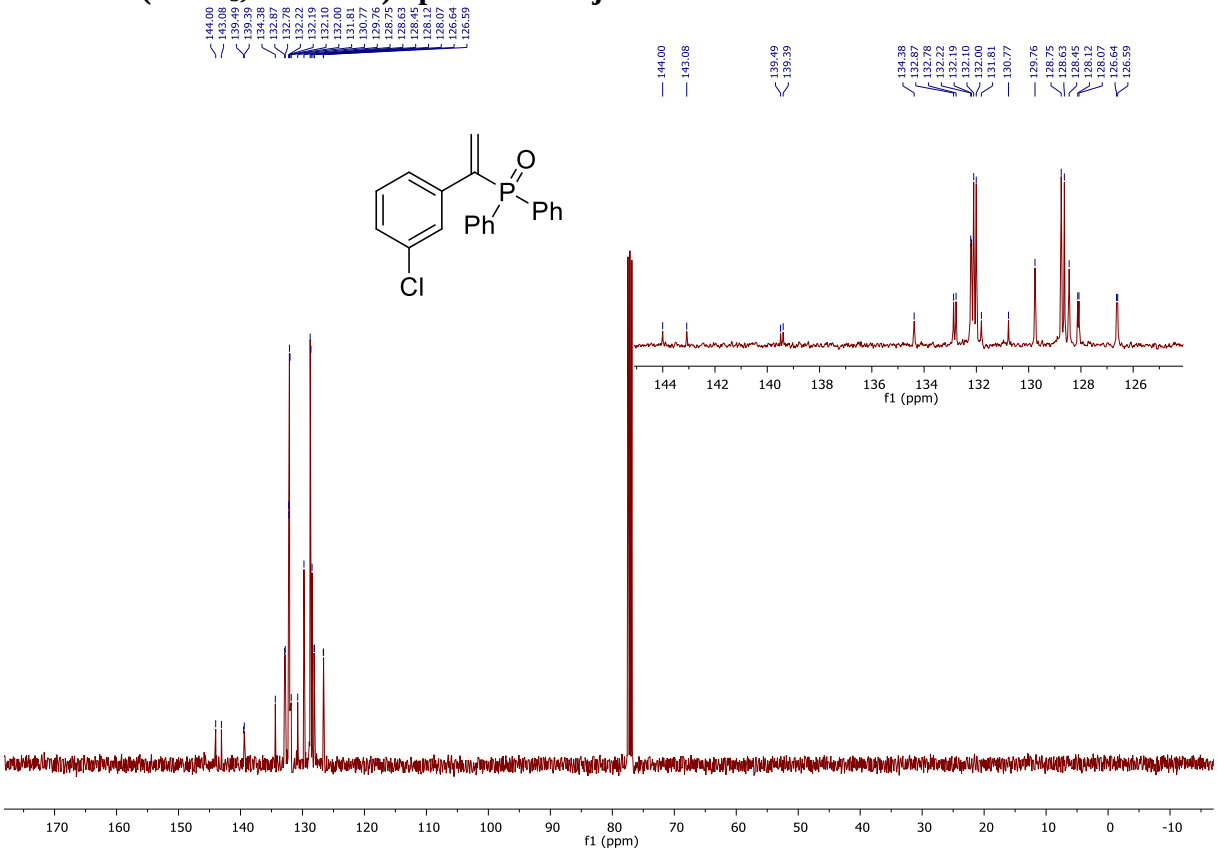
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1i



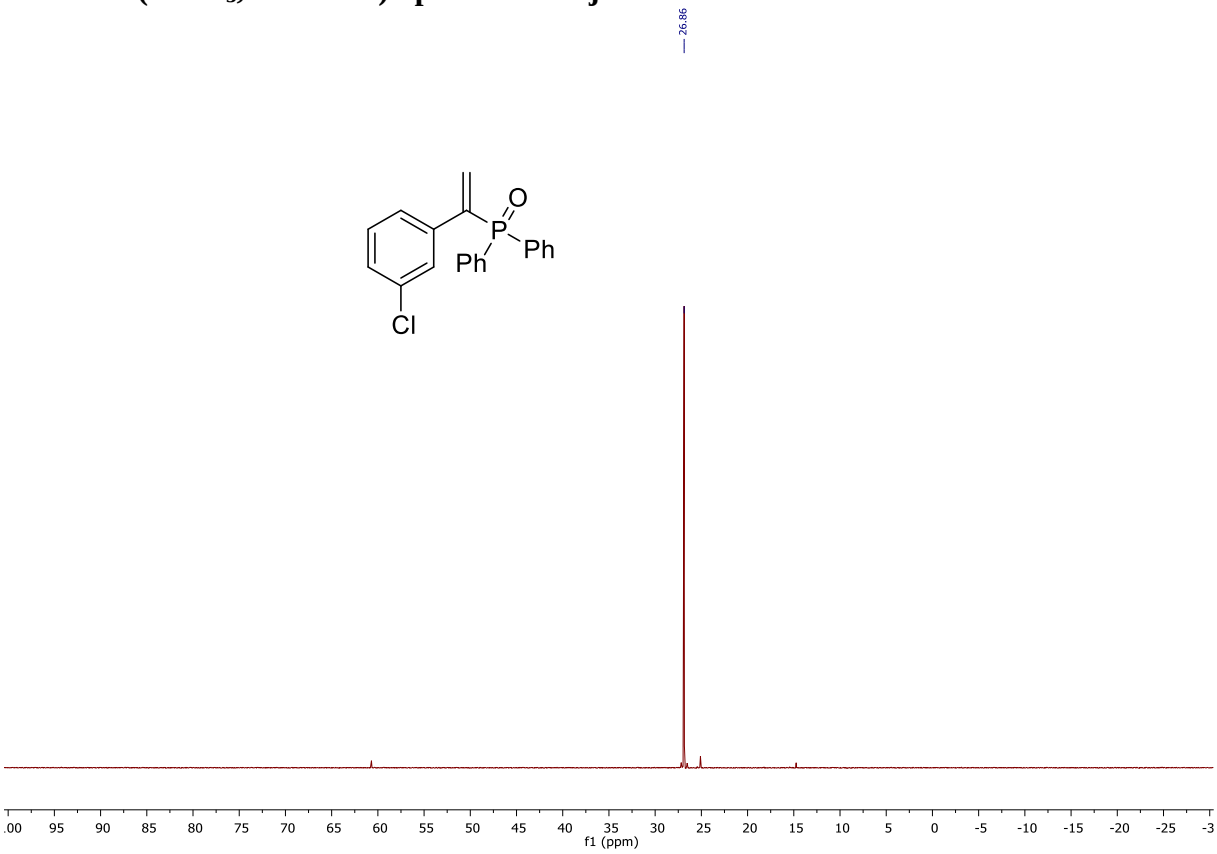
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1j



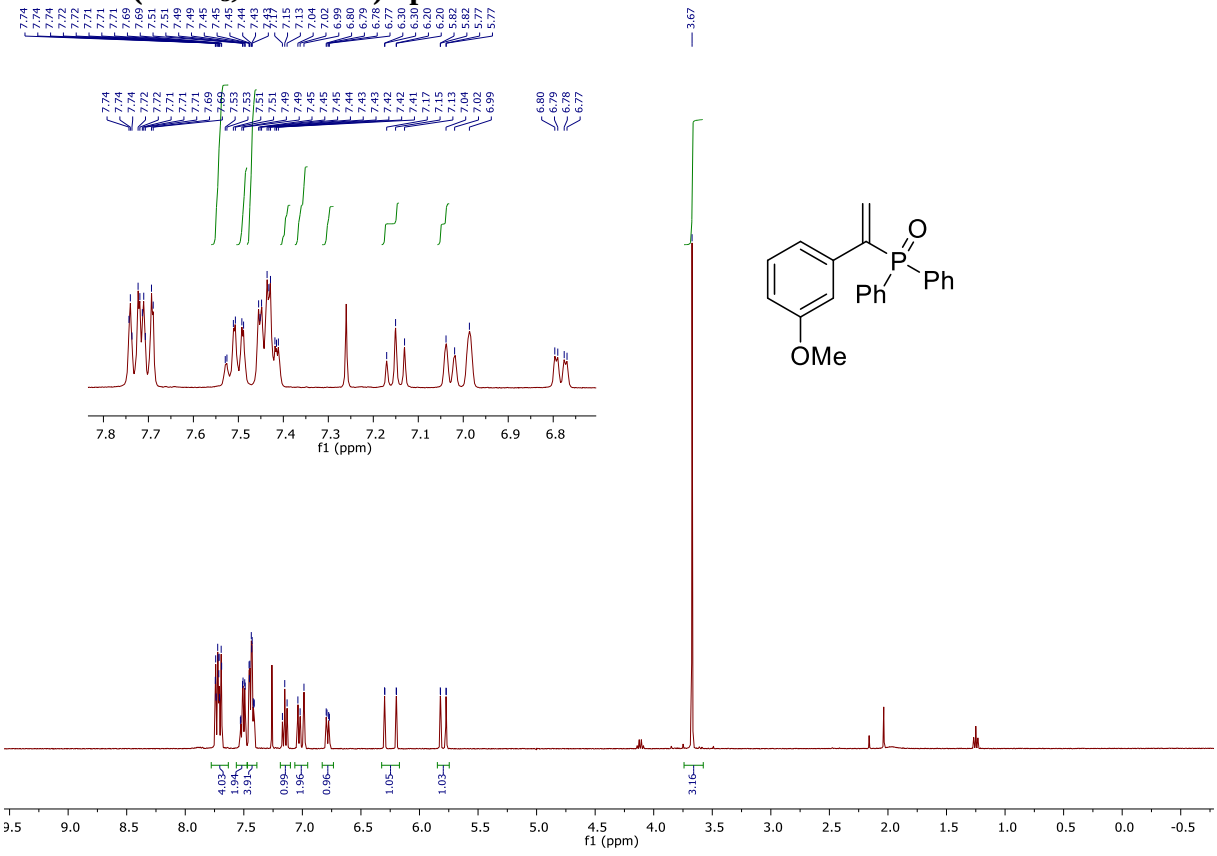
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1j



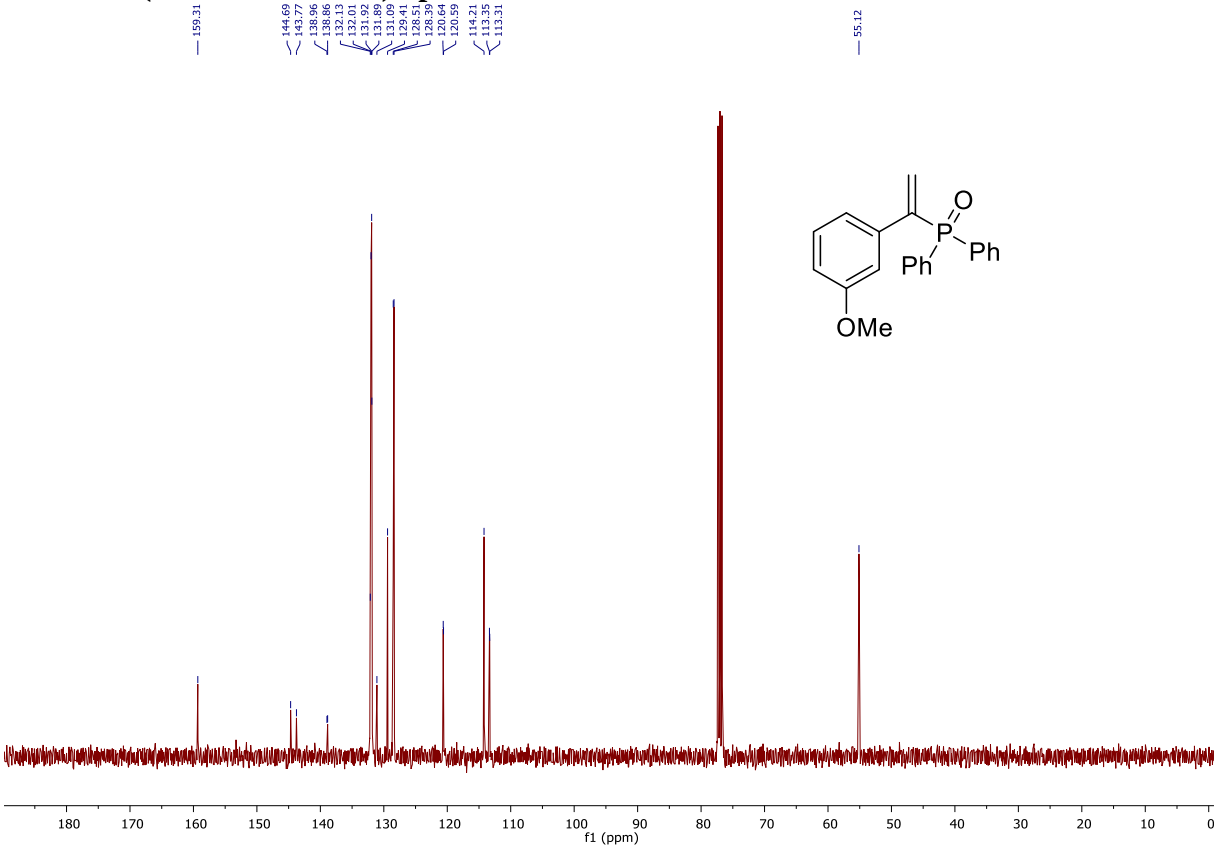
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1j



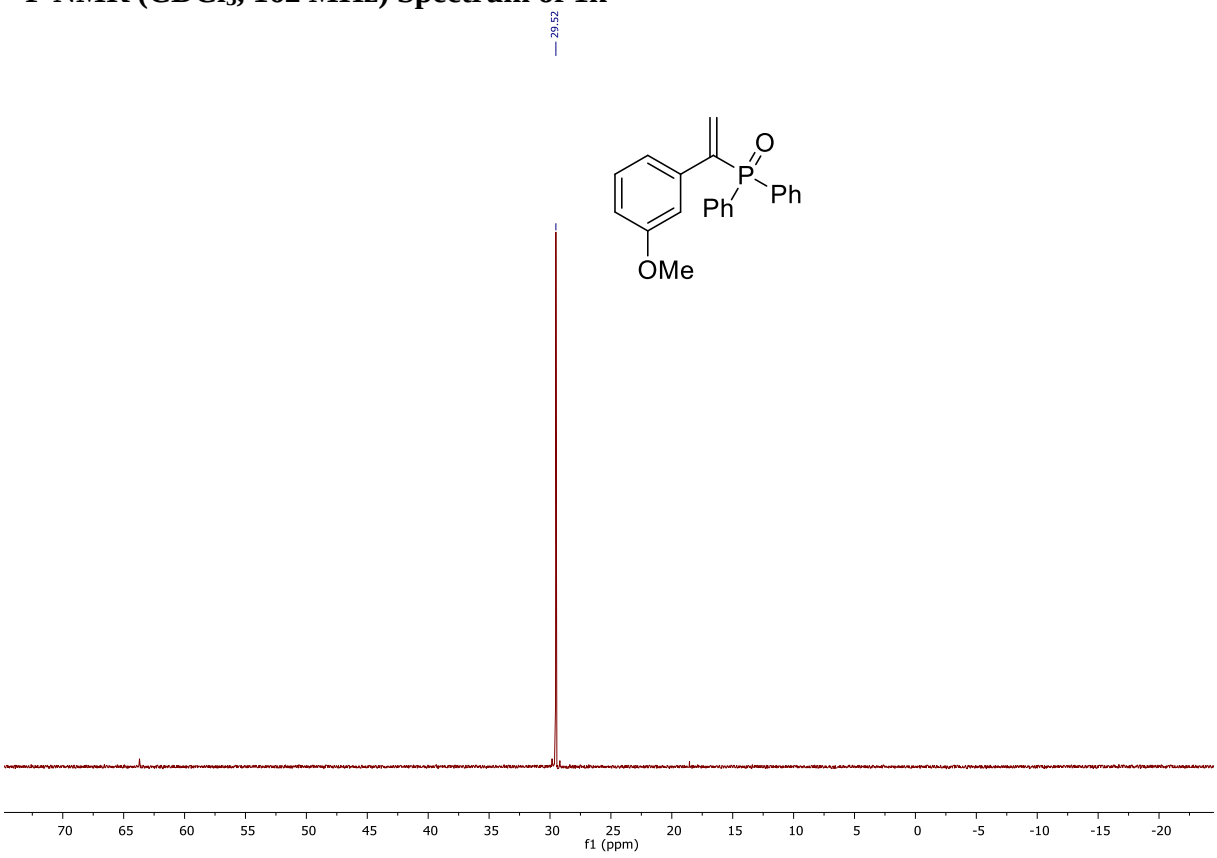
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1k



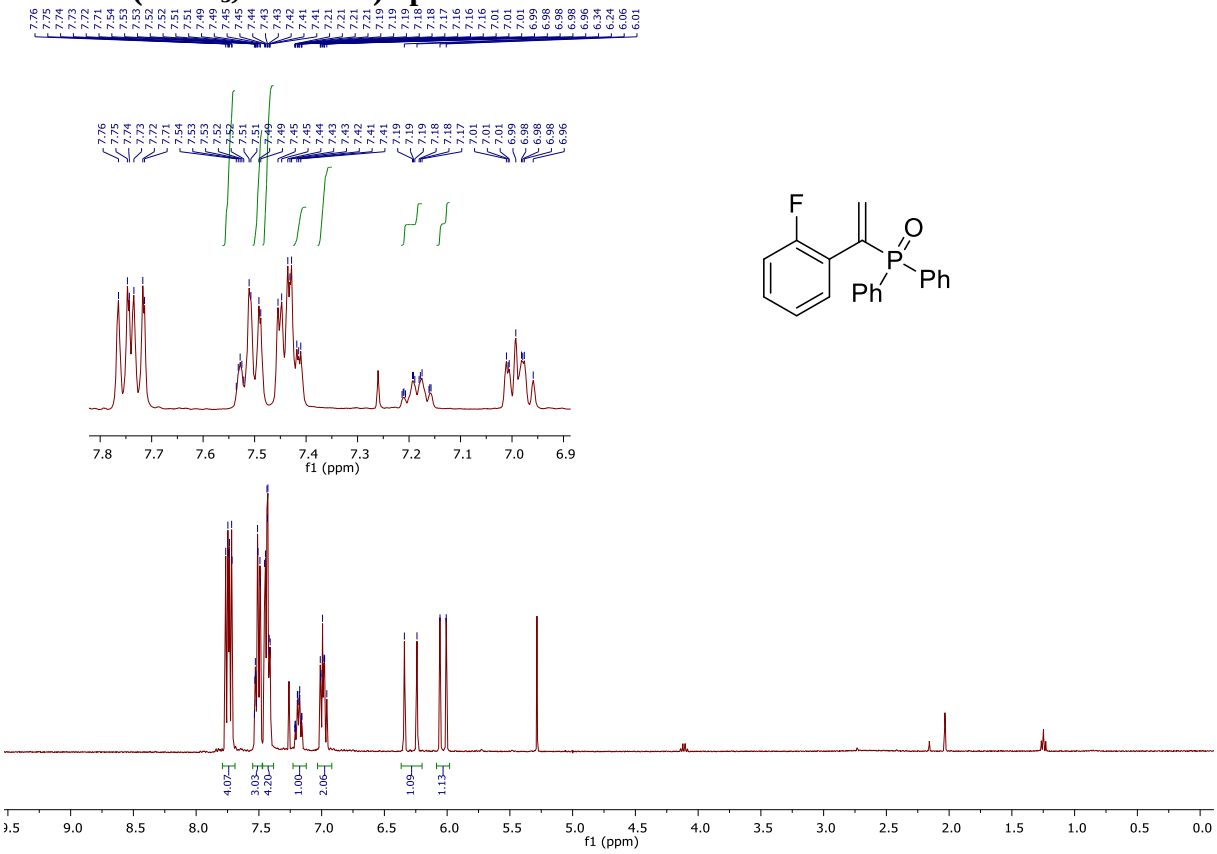
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1k



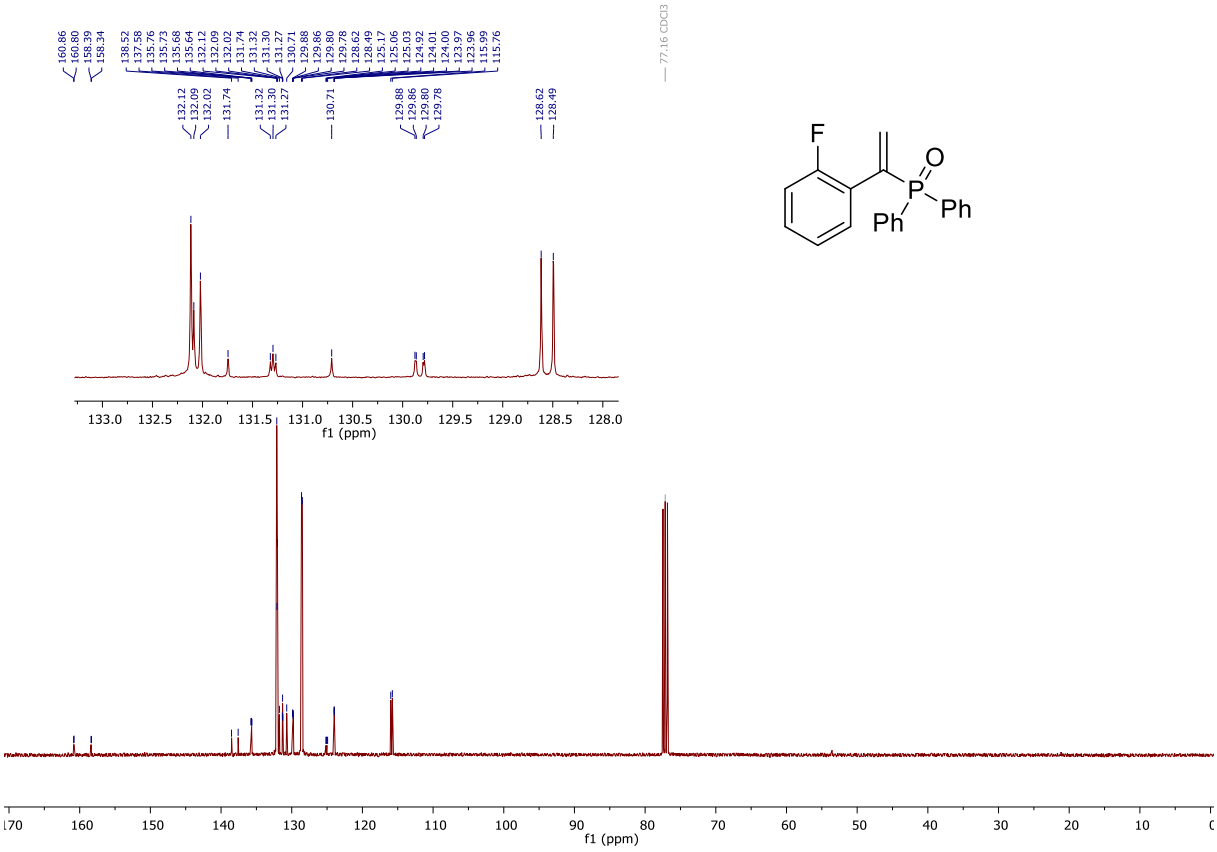
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1k



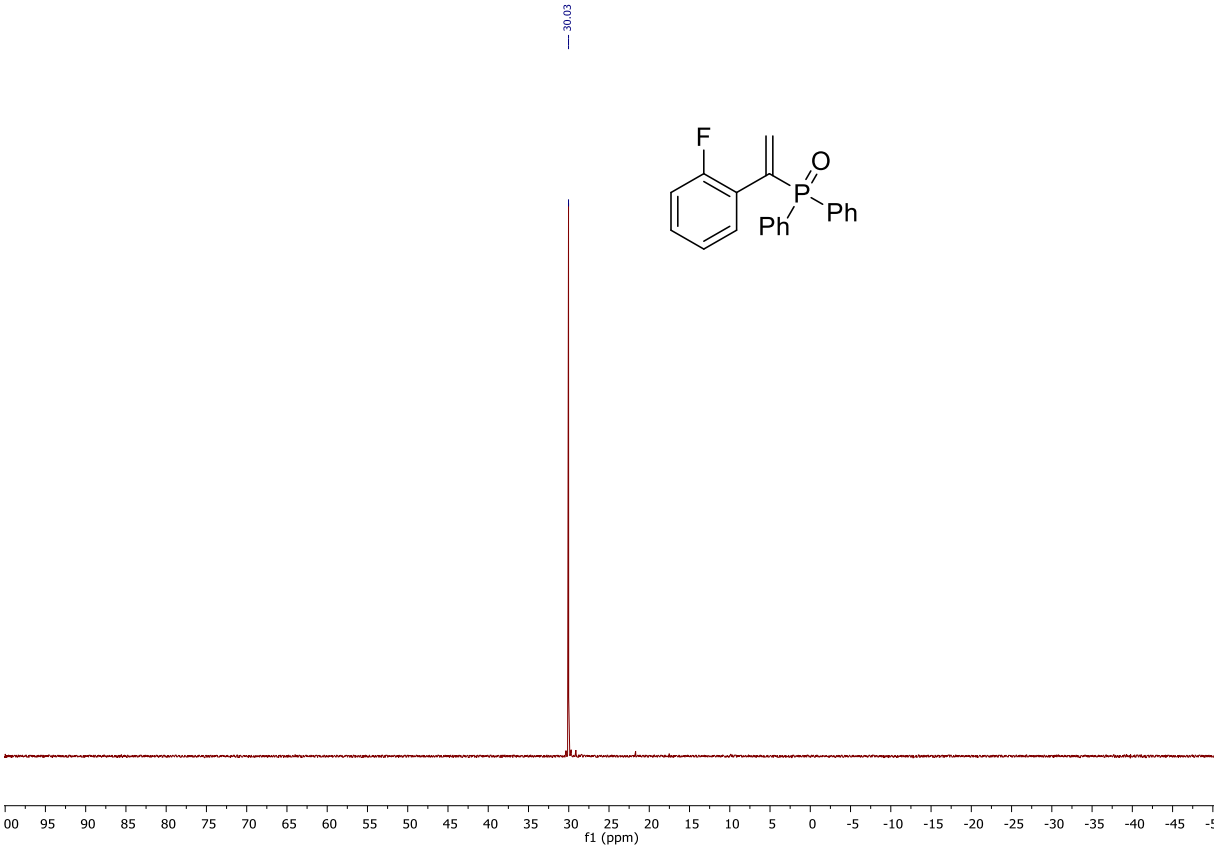
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1l



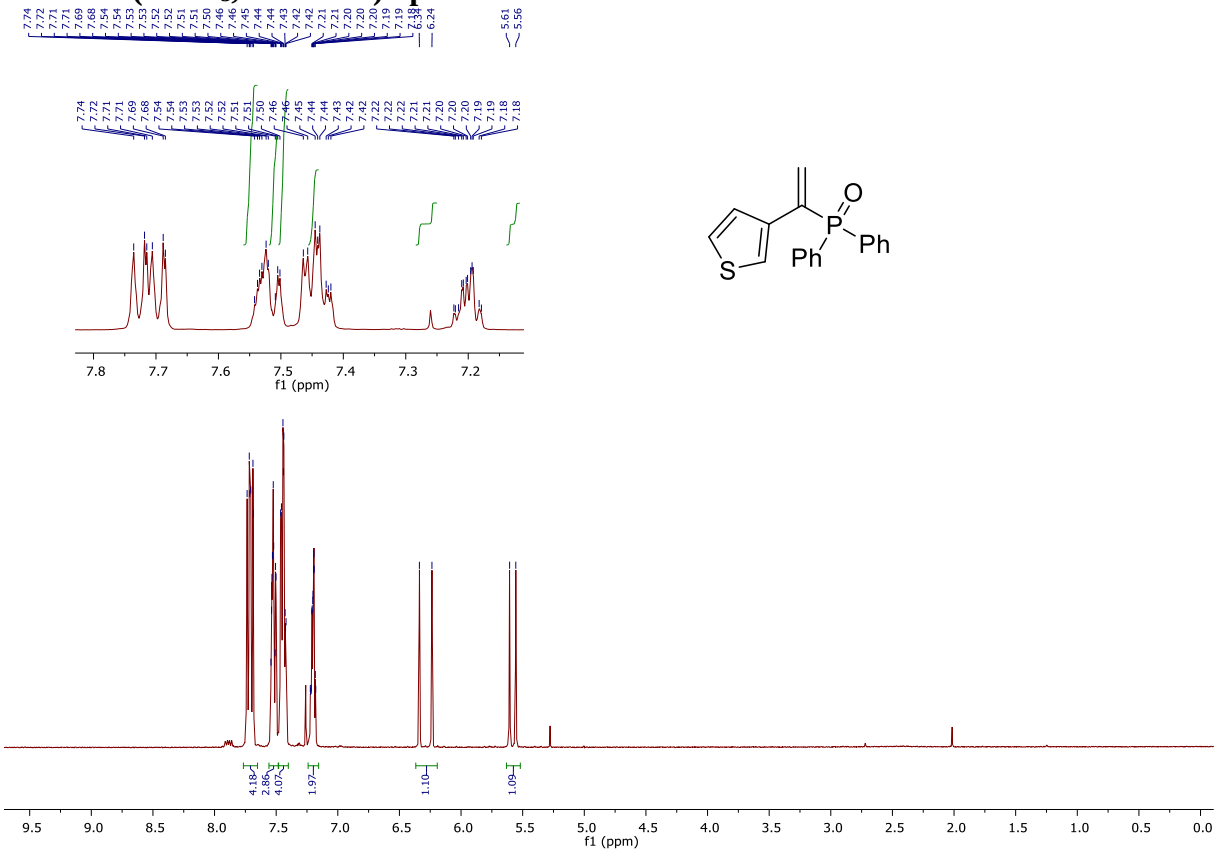
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1l



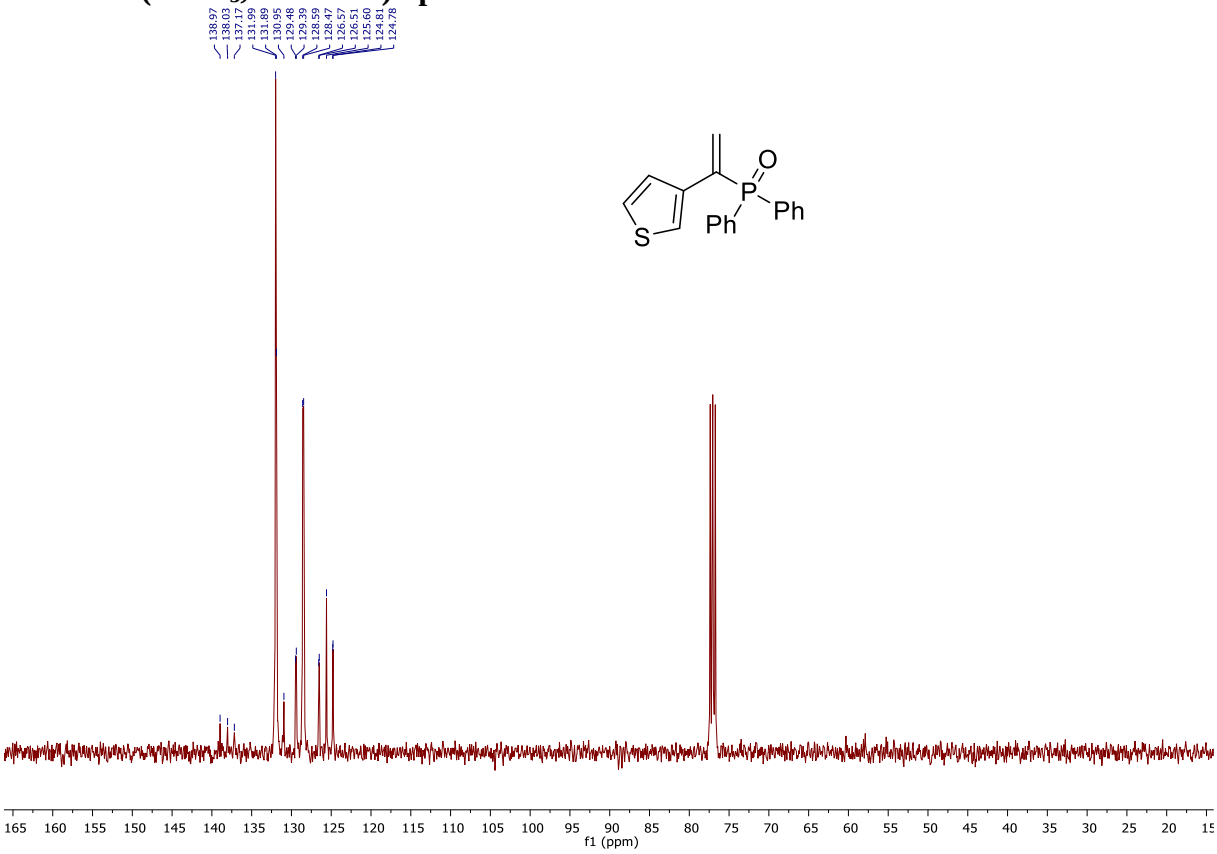
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1l



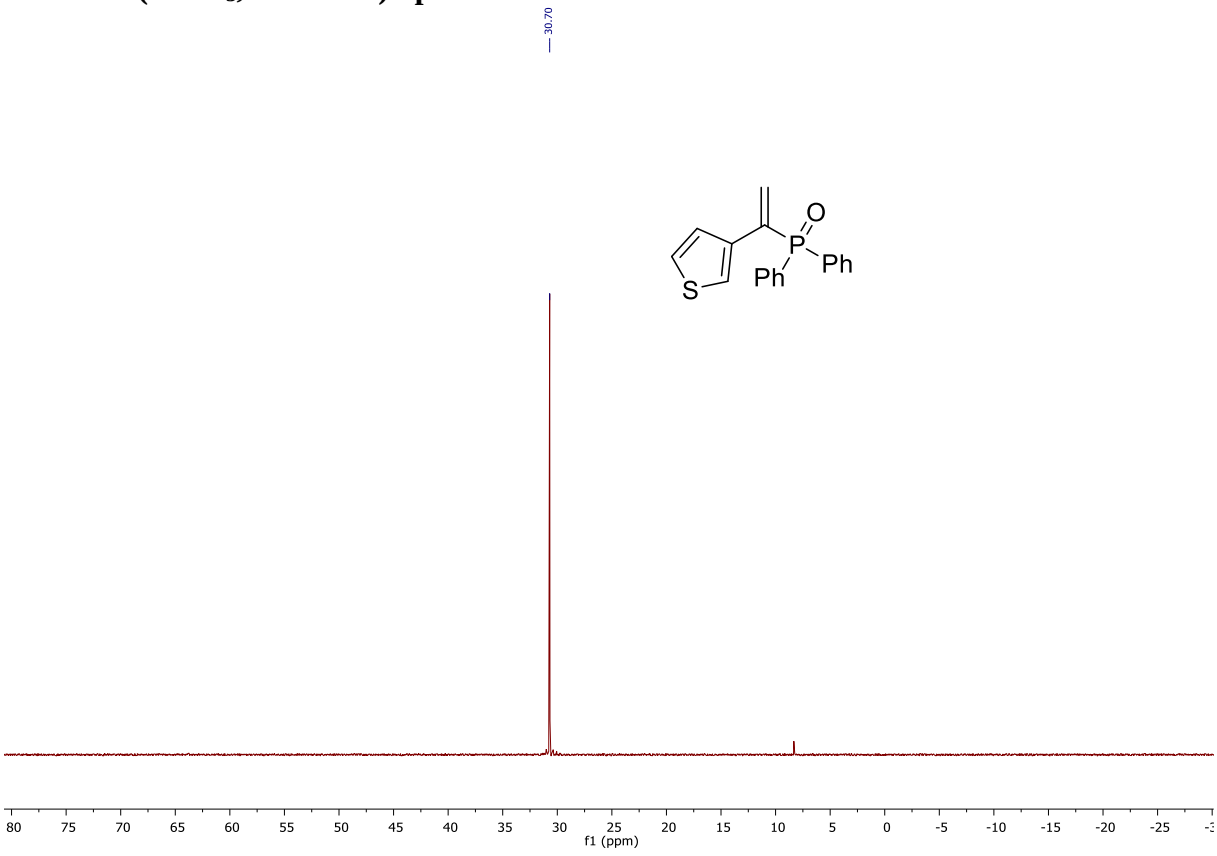
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1n



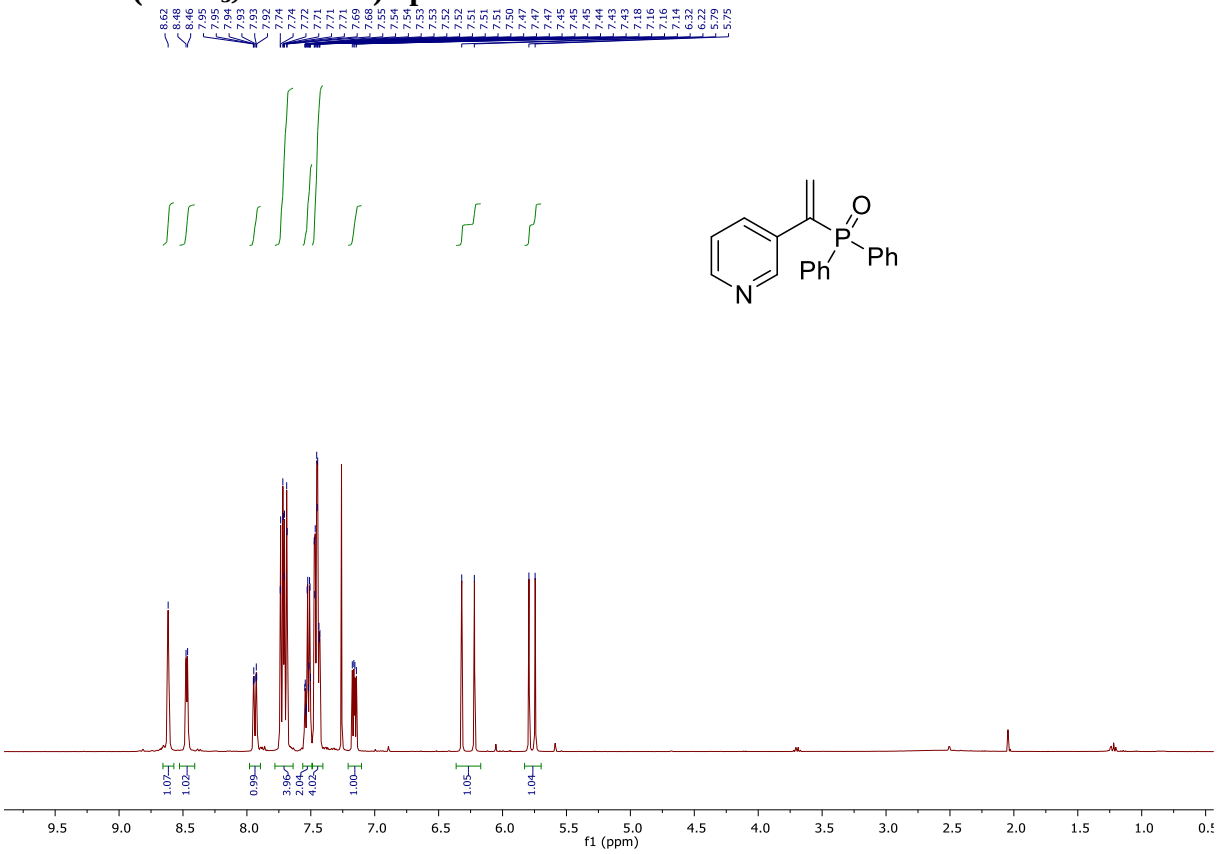
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1n



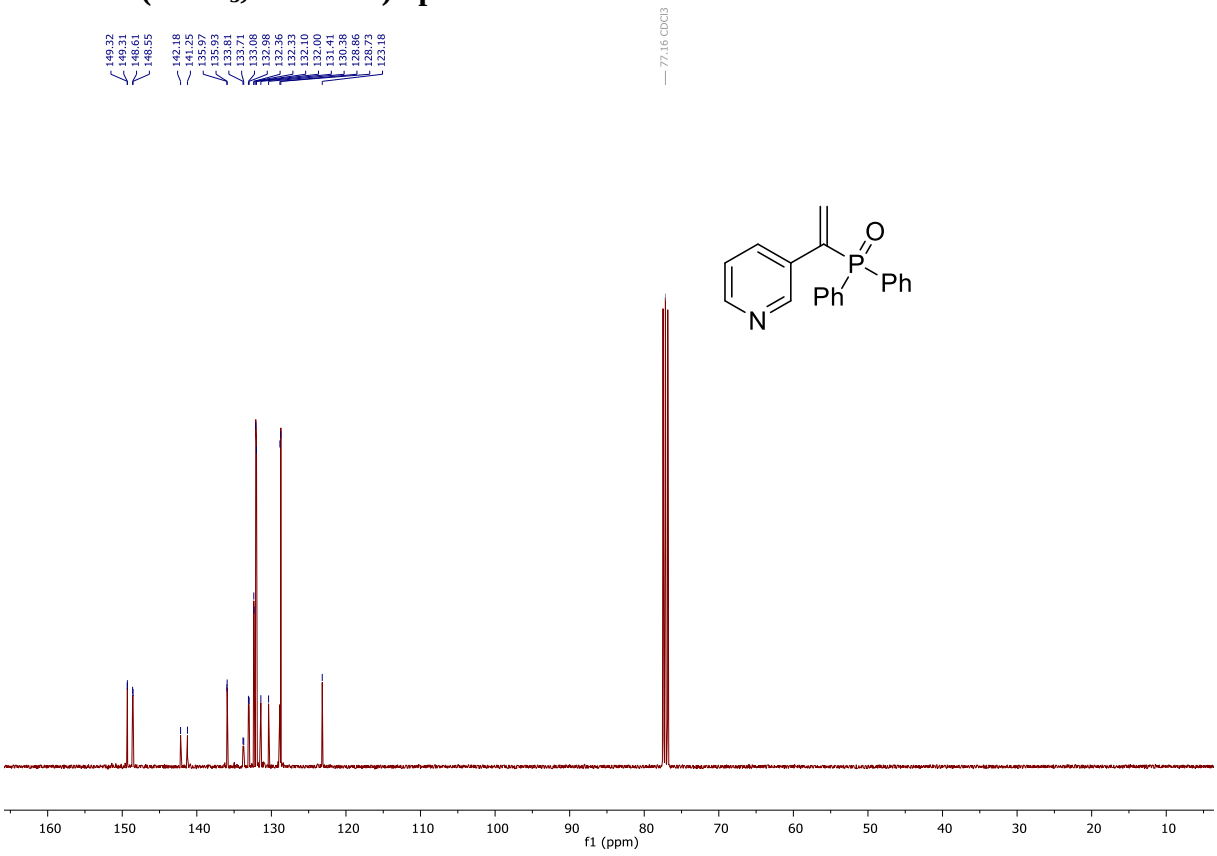
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1n



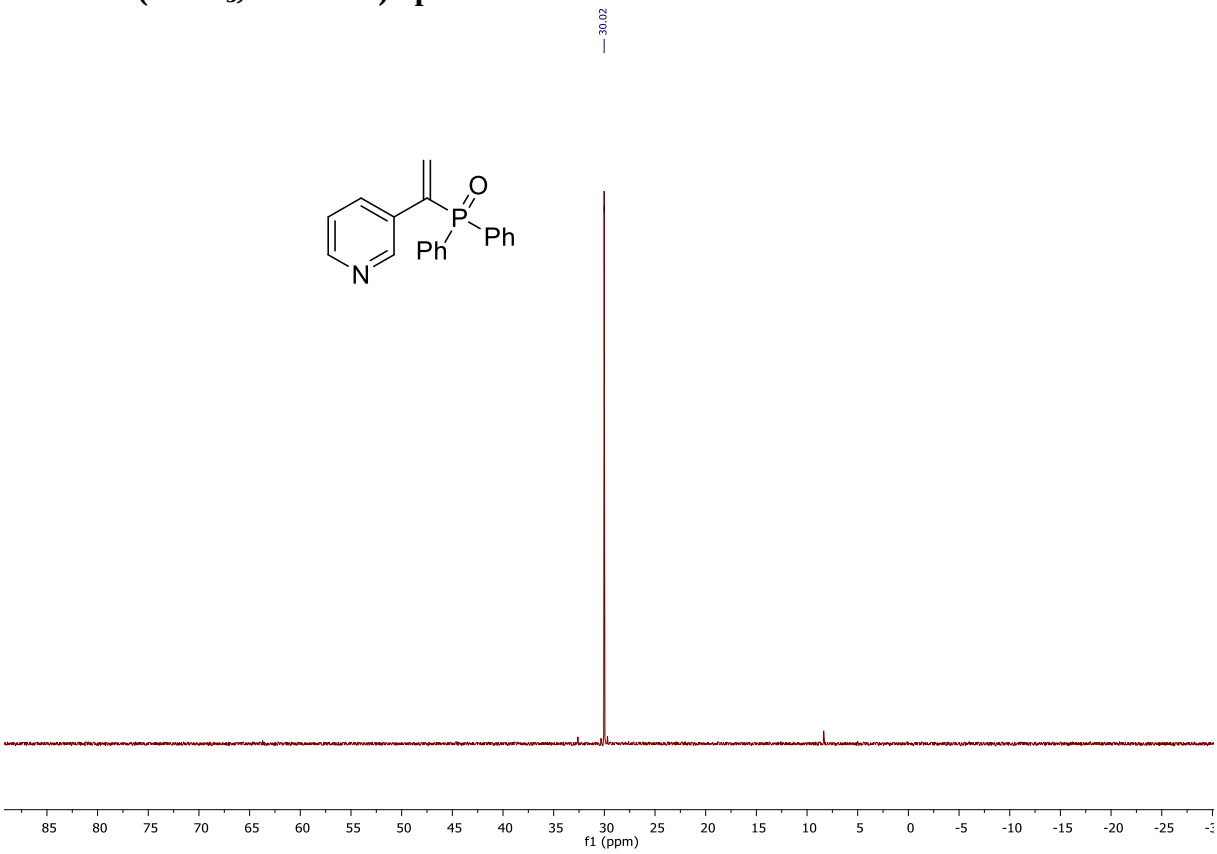
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1o



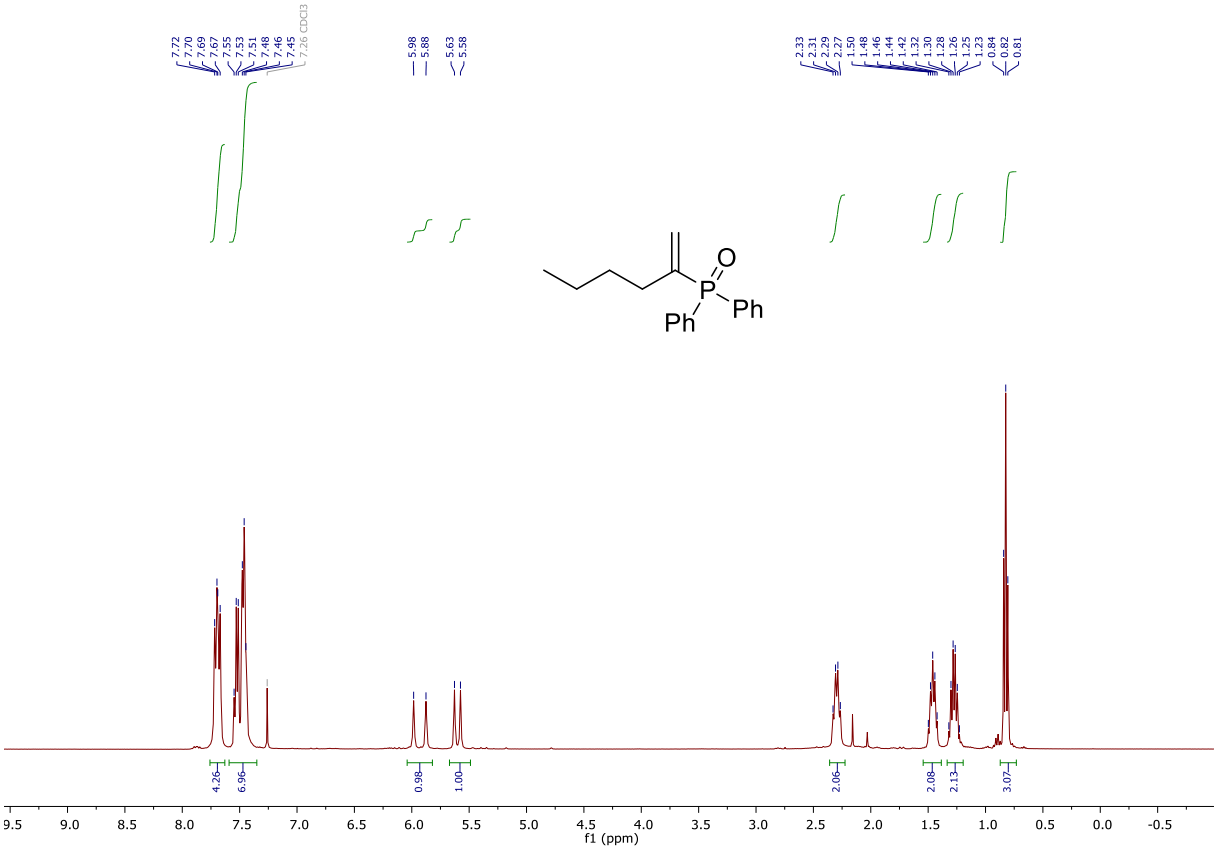
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1o



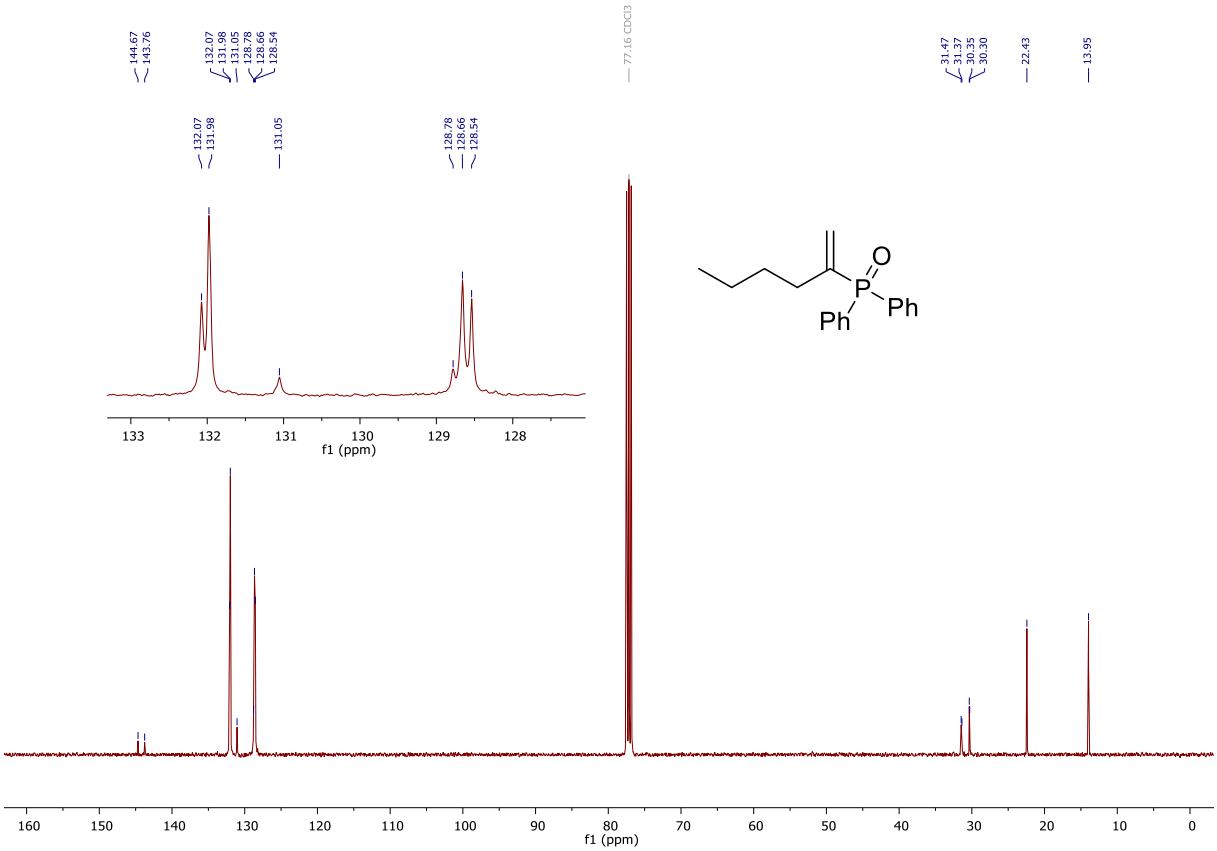
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1o



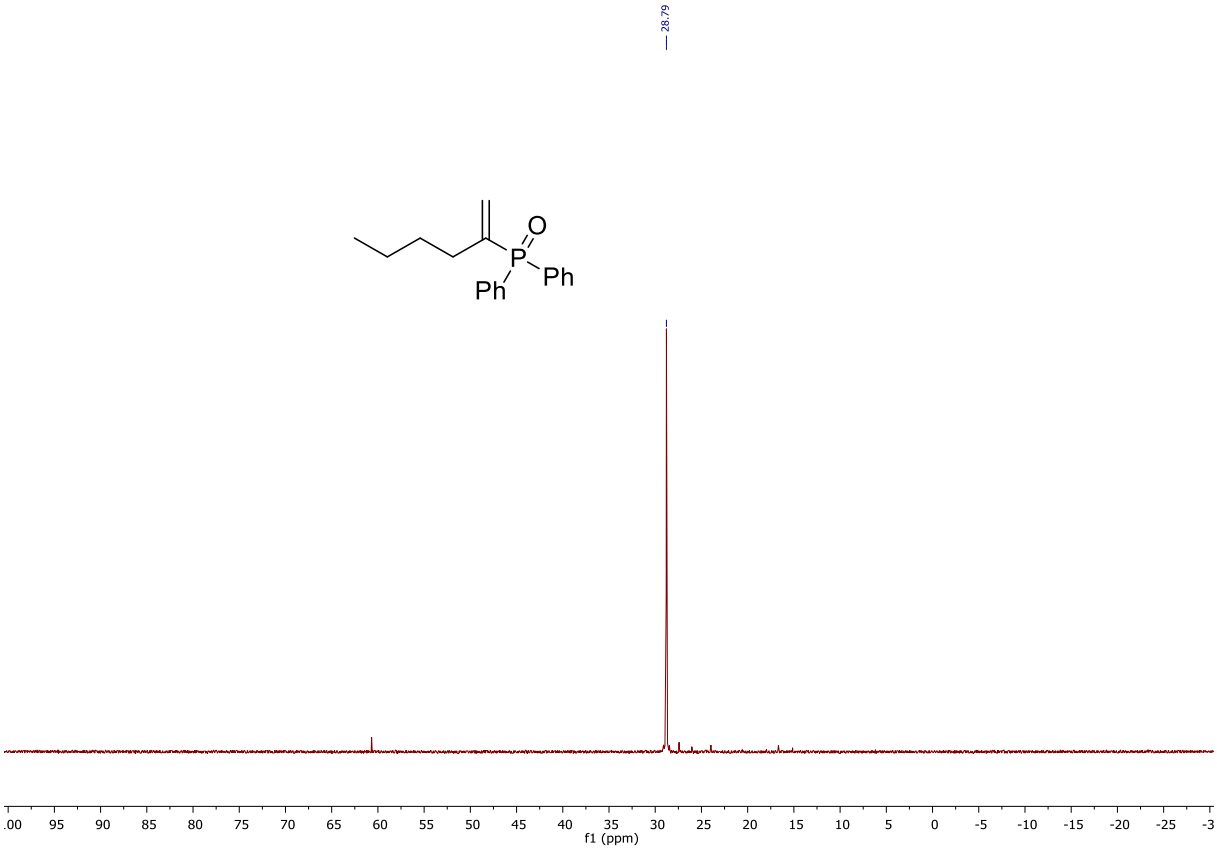
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1q



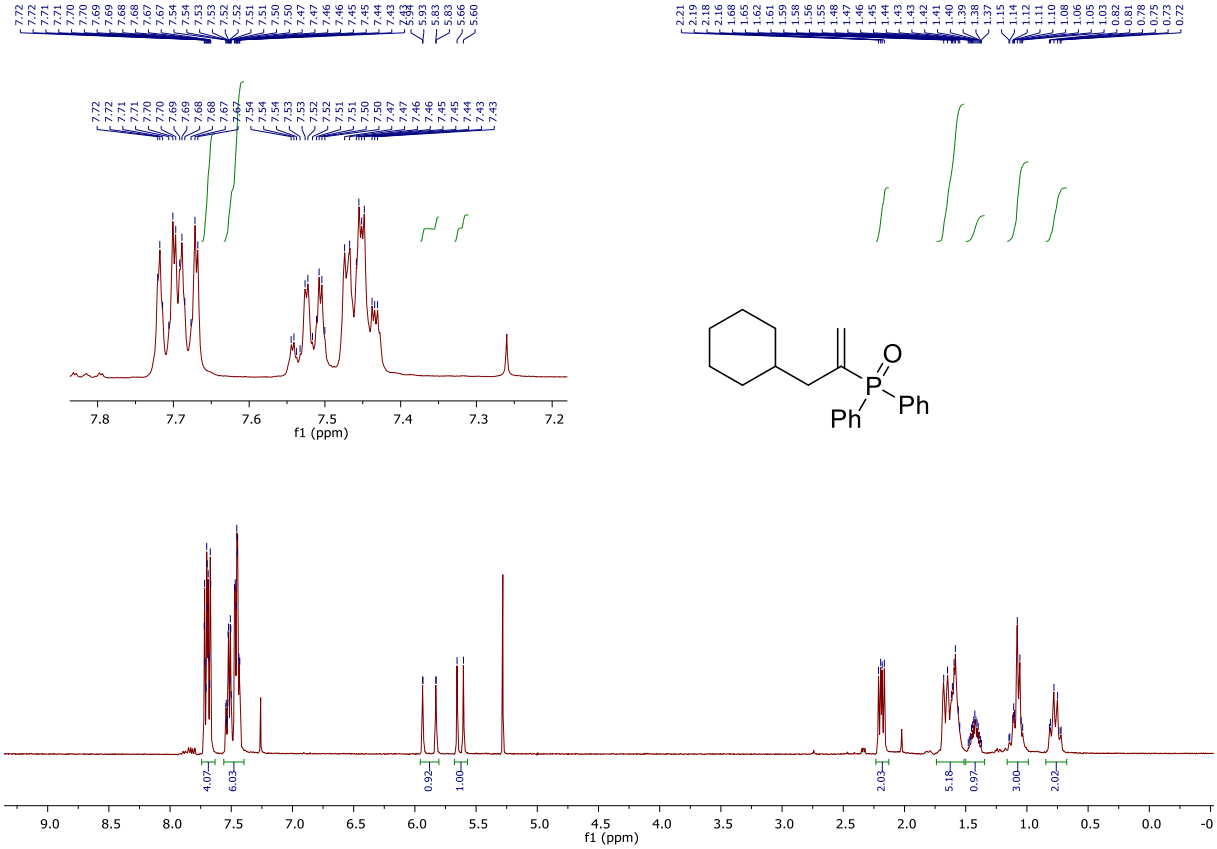
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1q



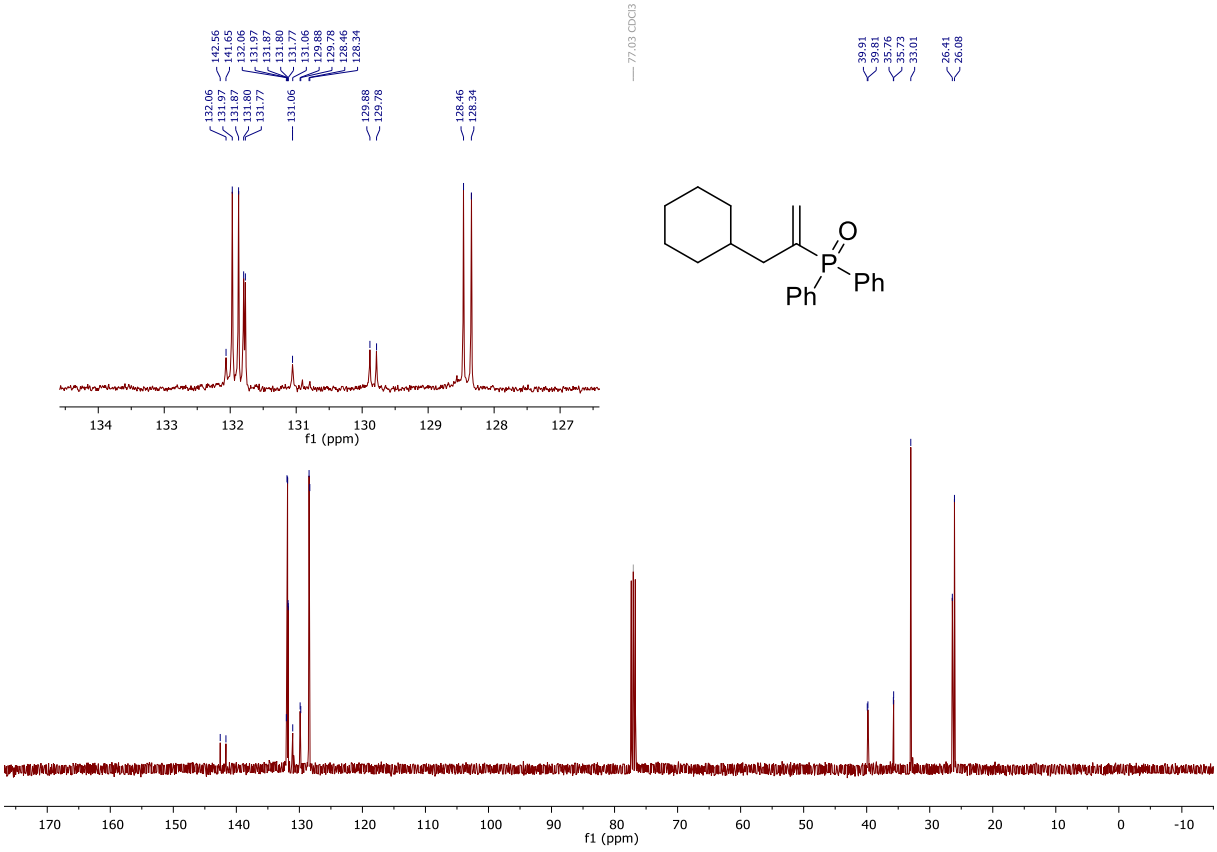
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1q



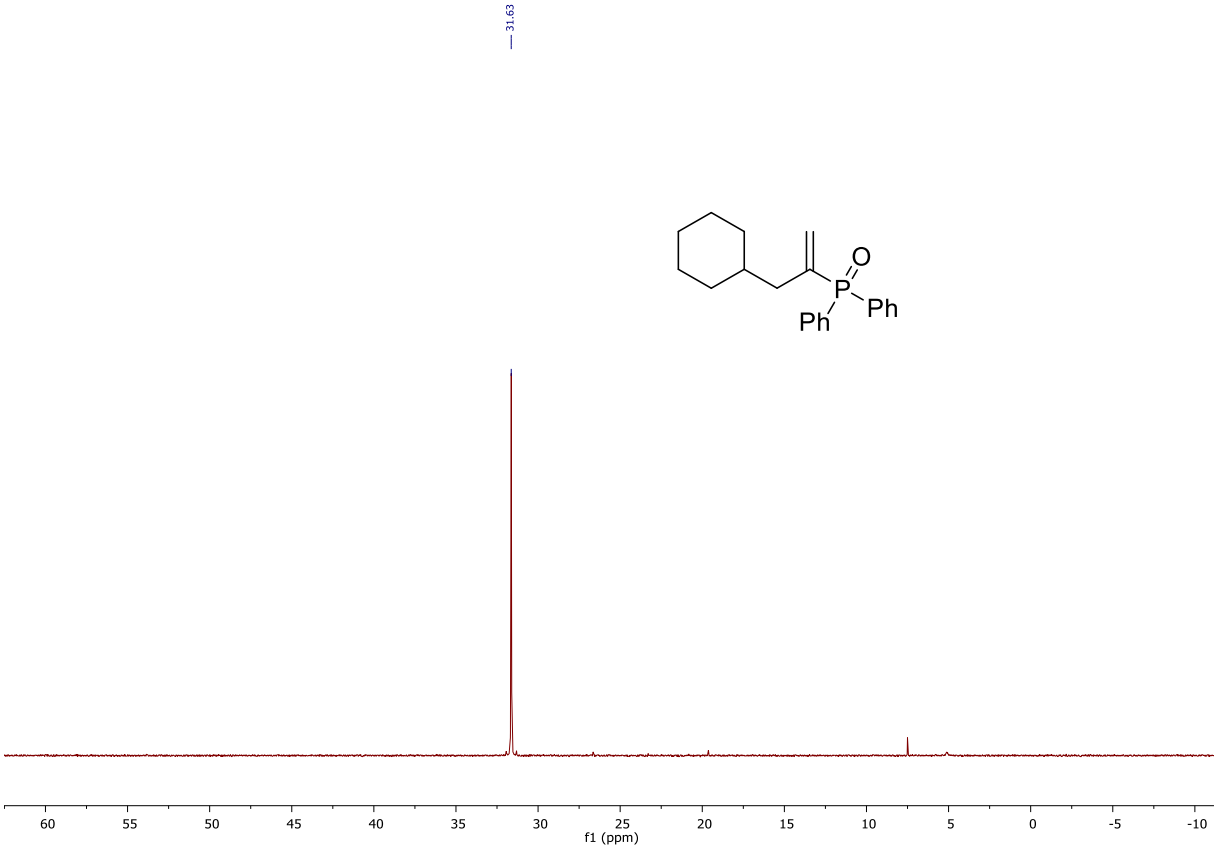
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1r



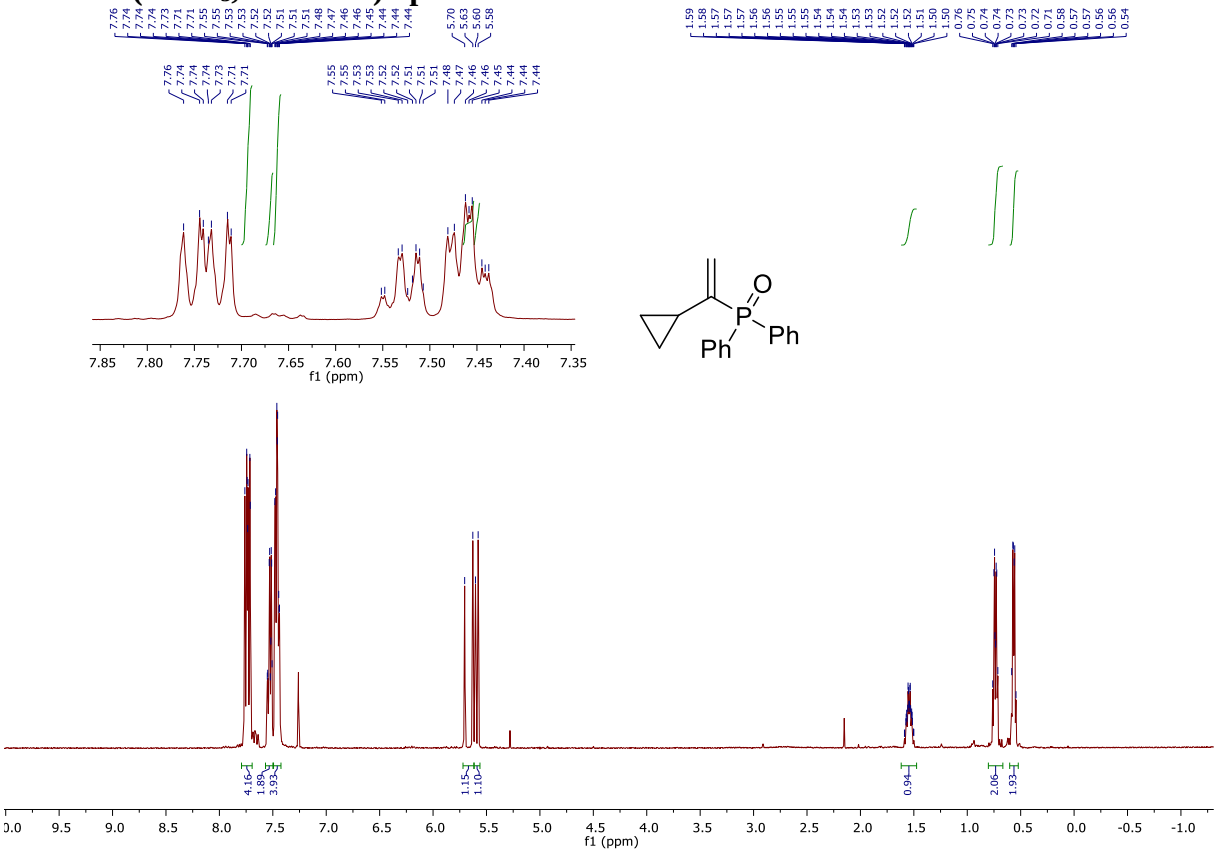
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1r



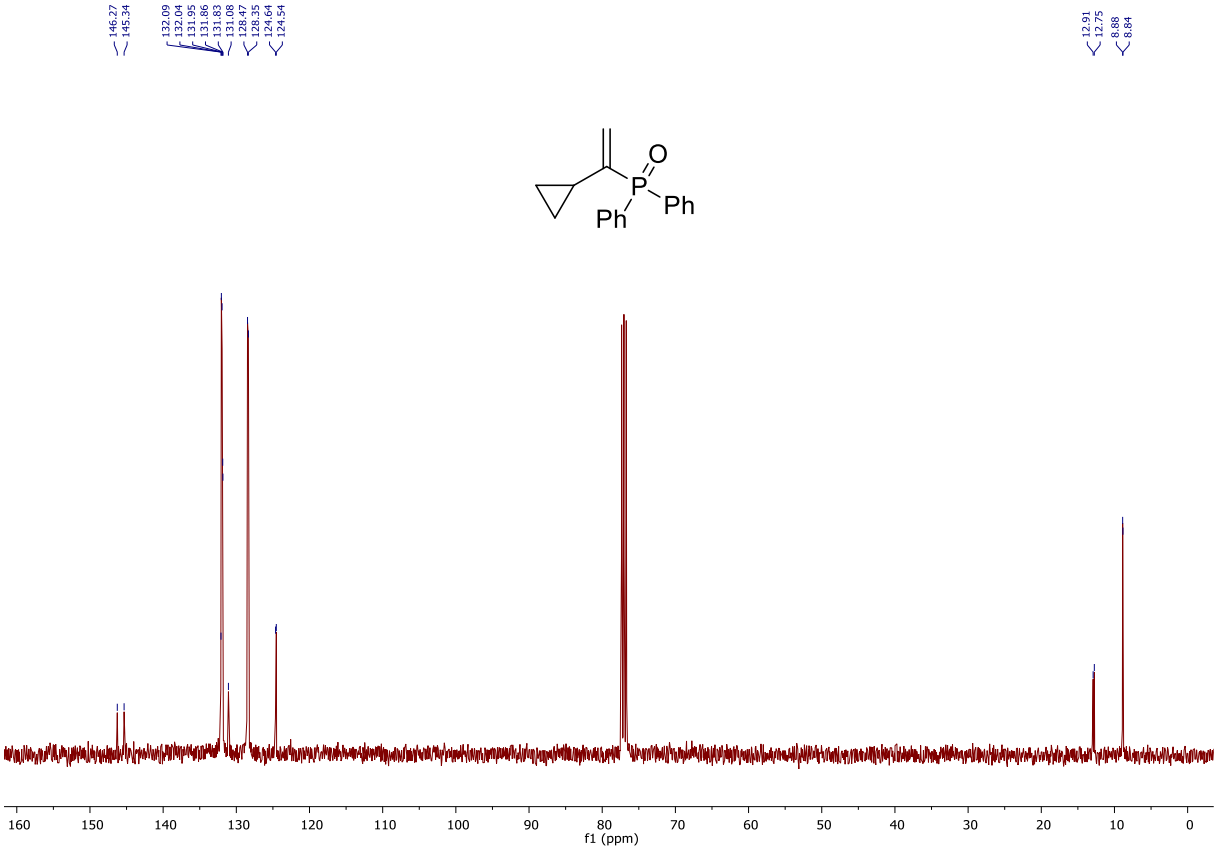
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1r



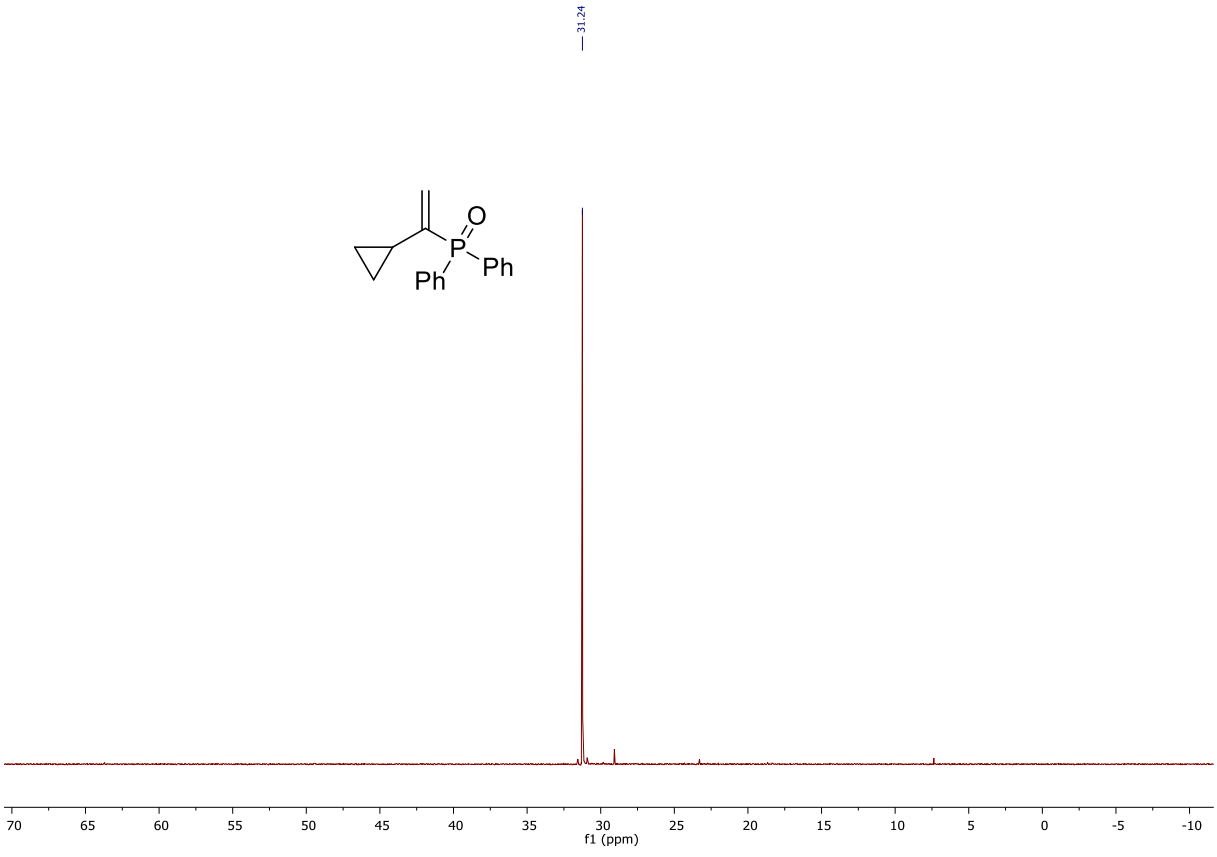
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1s



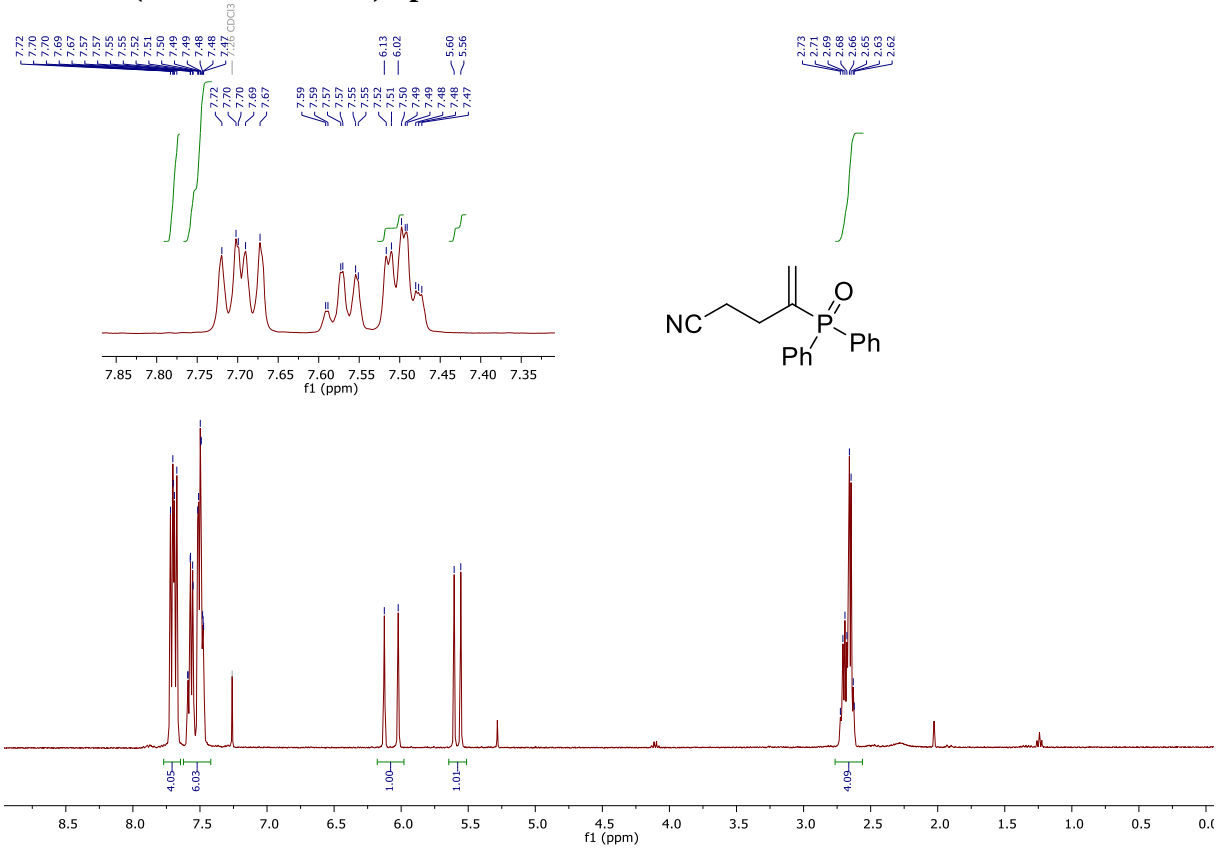
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1s



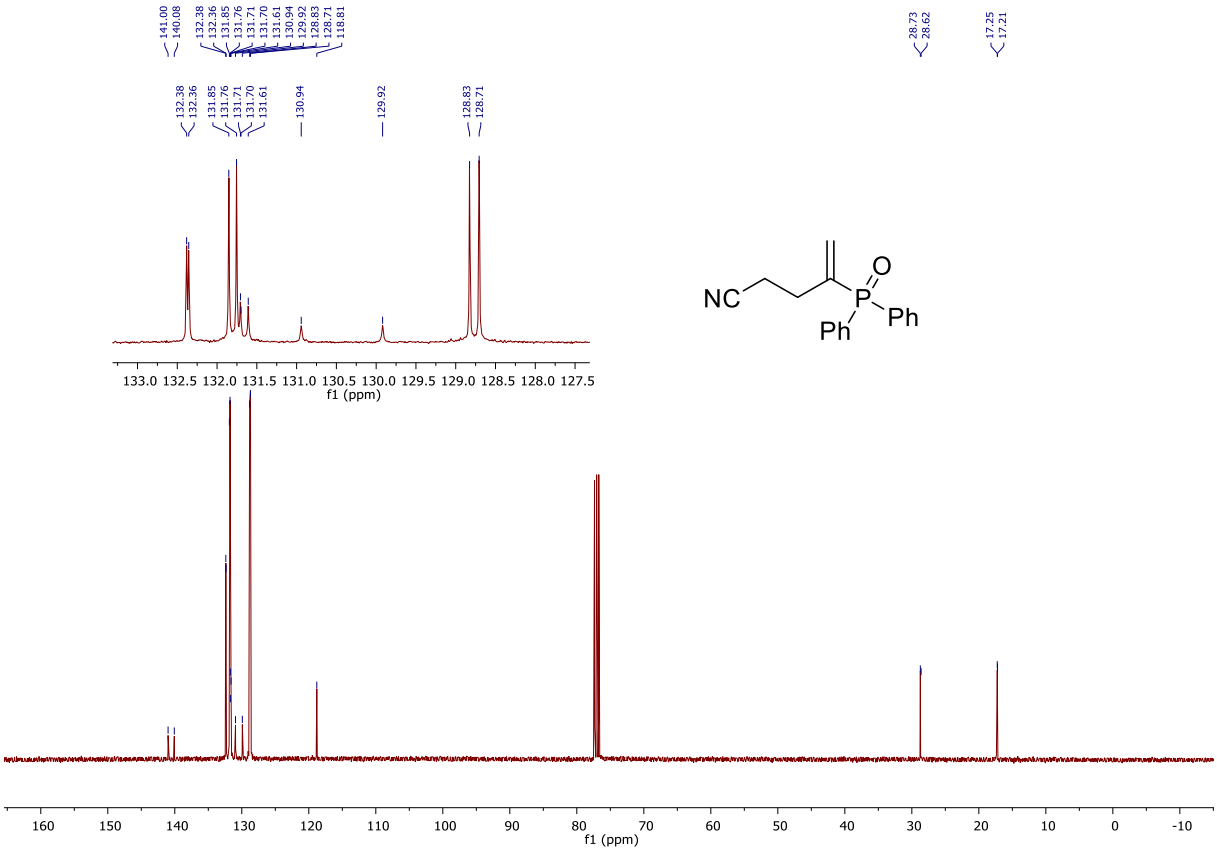
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1s



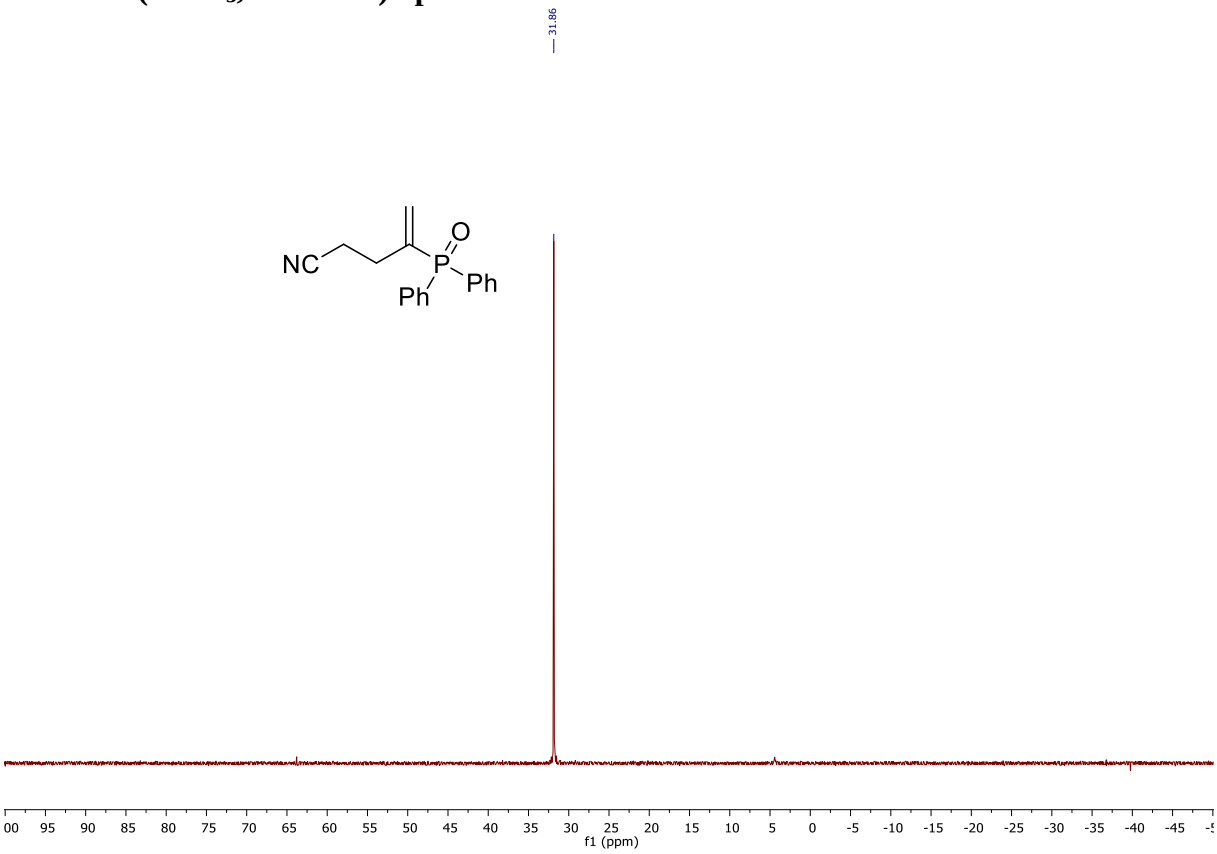
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1u



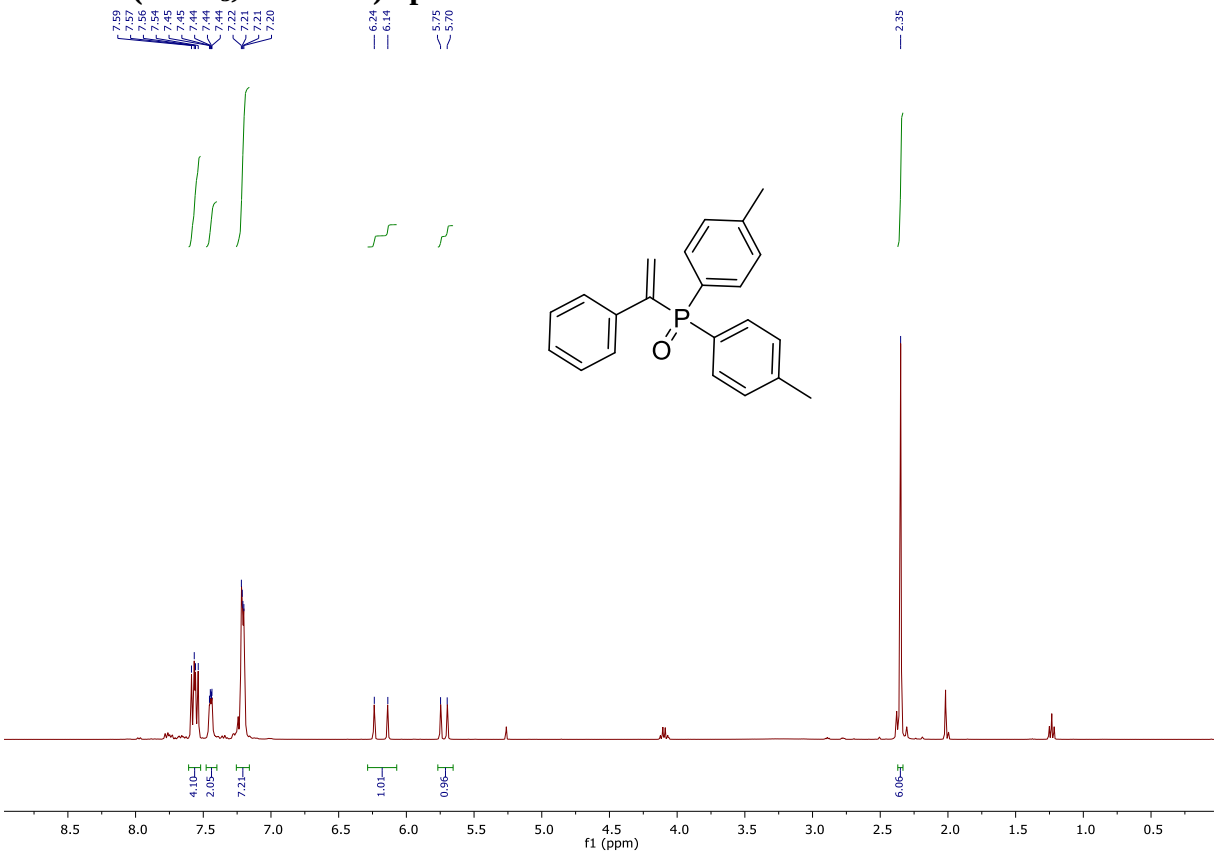
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1u



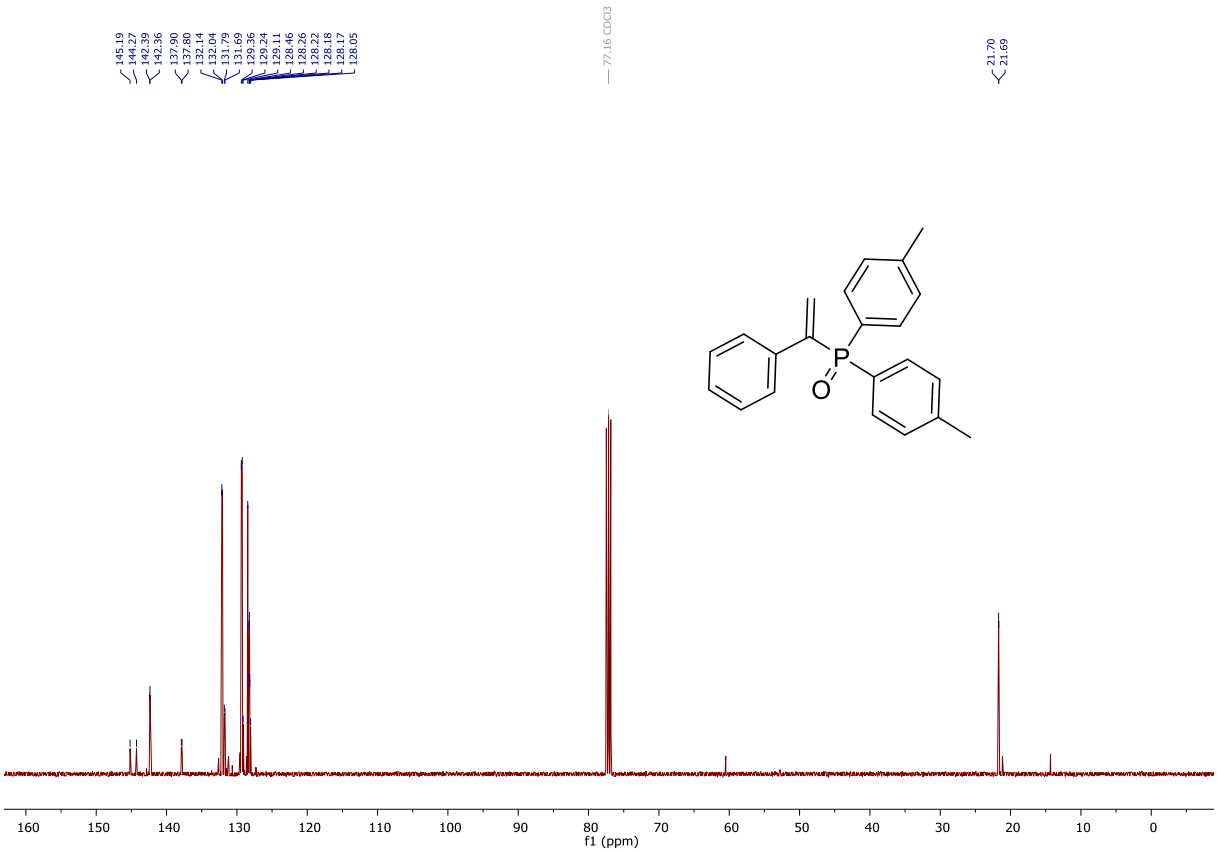
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1u



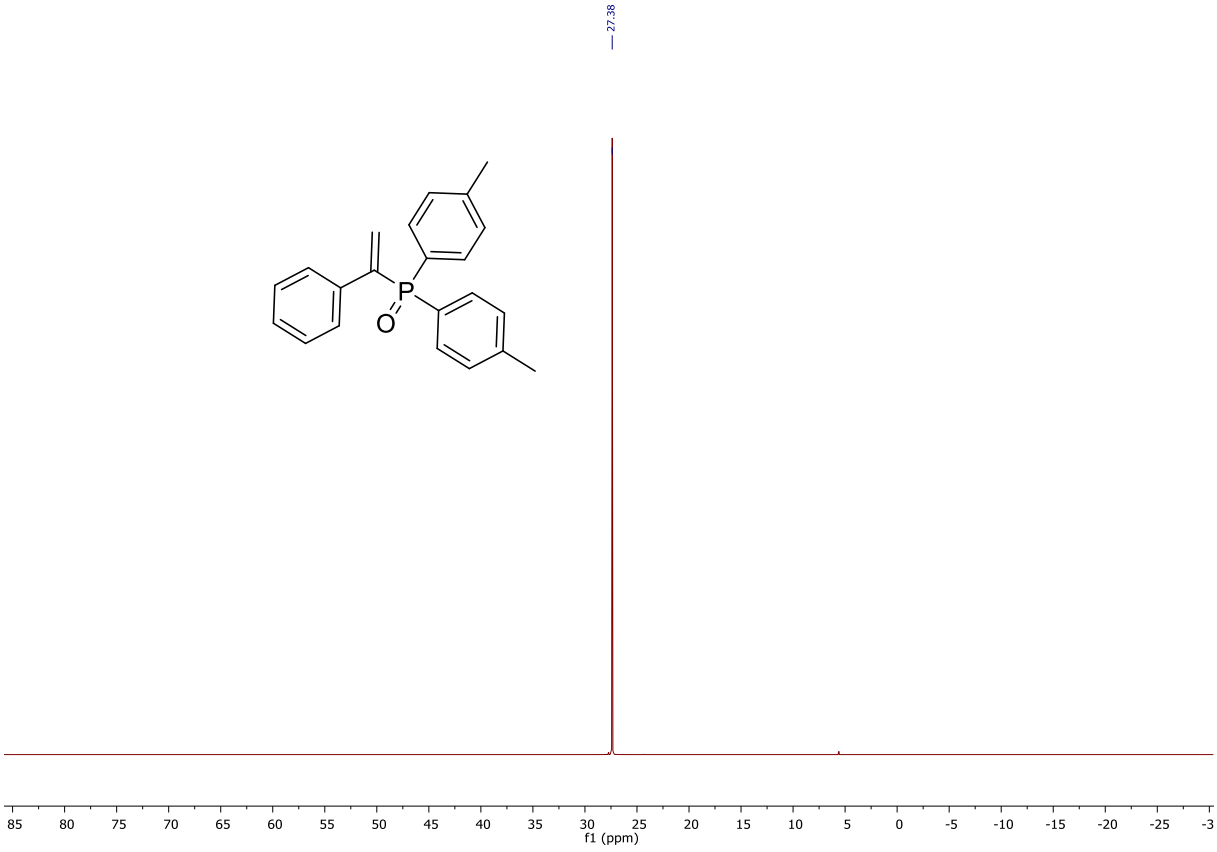
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1w



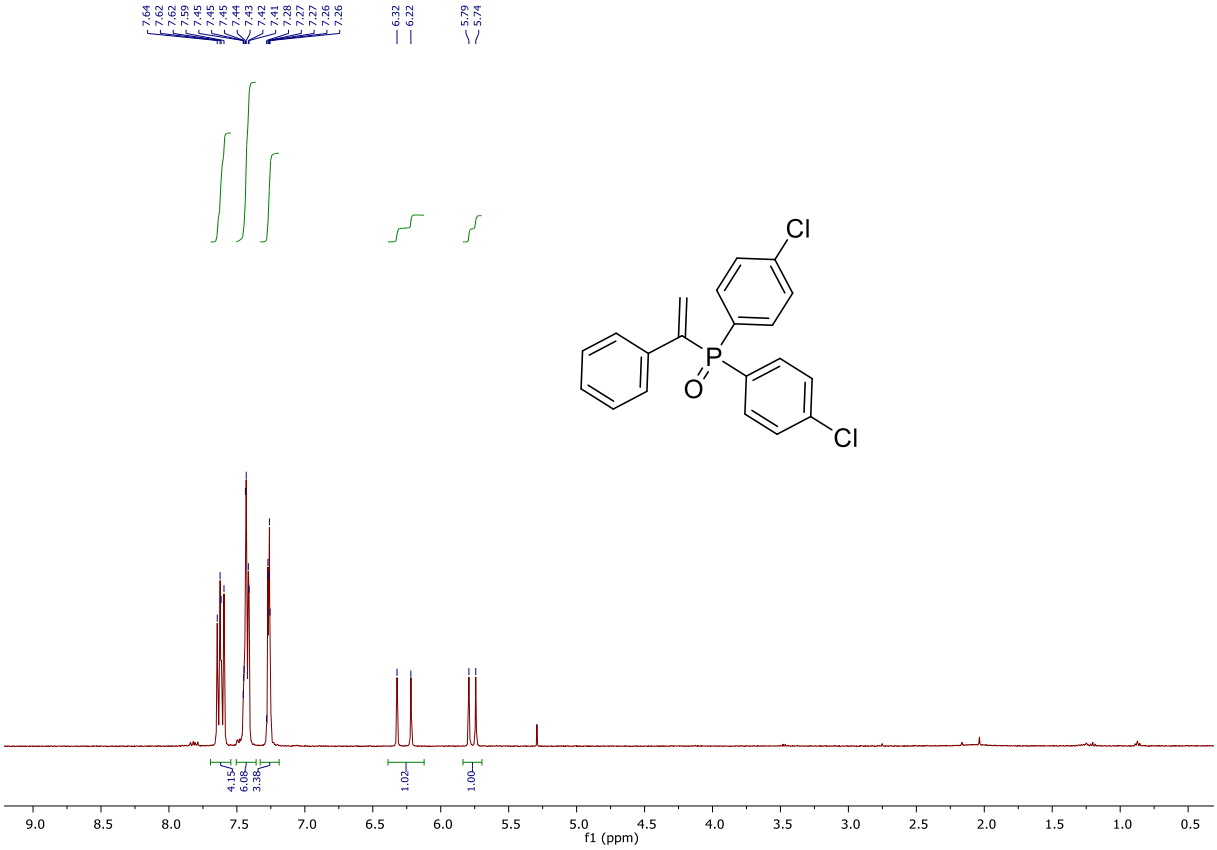
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1w



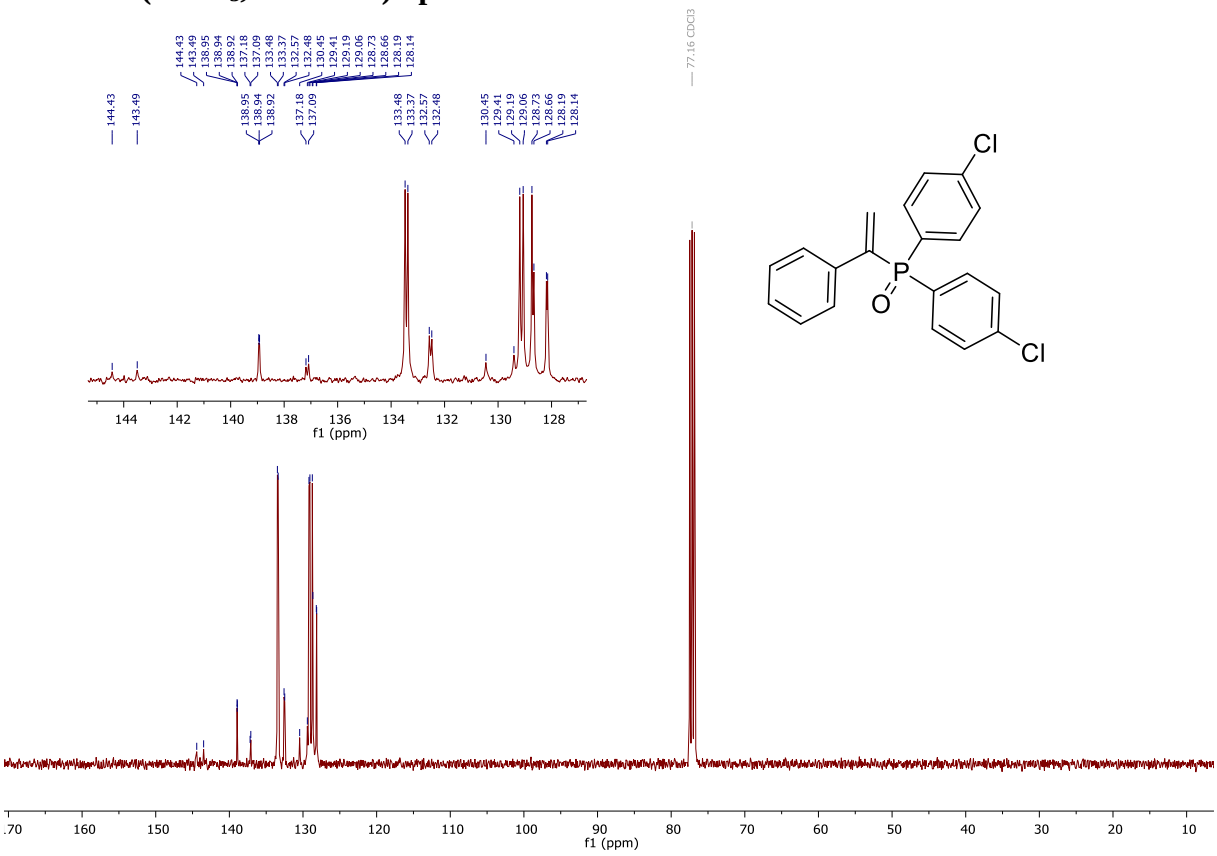
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1w



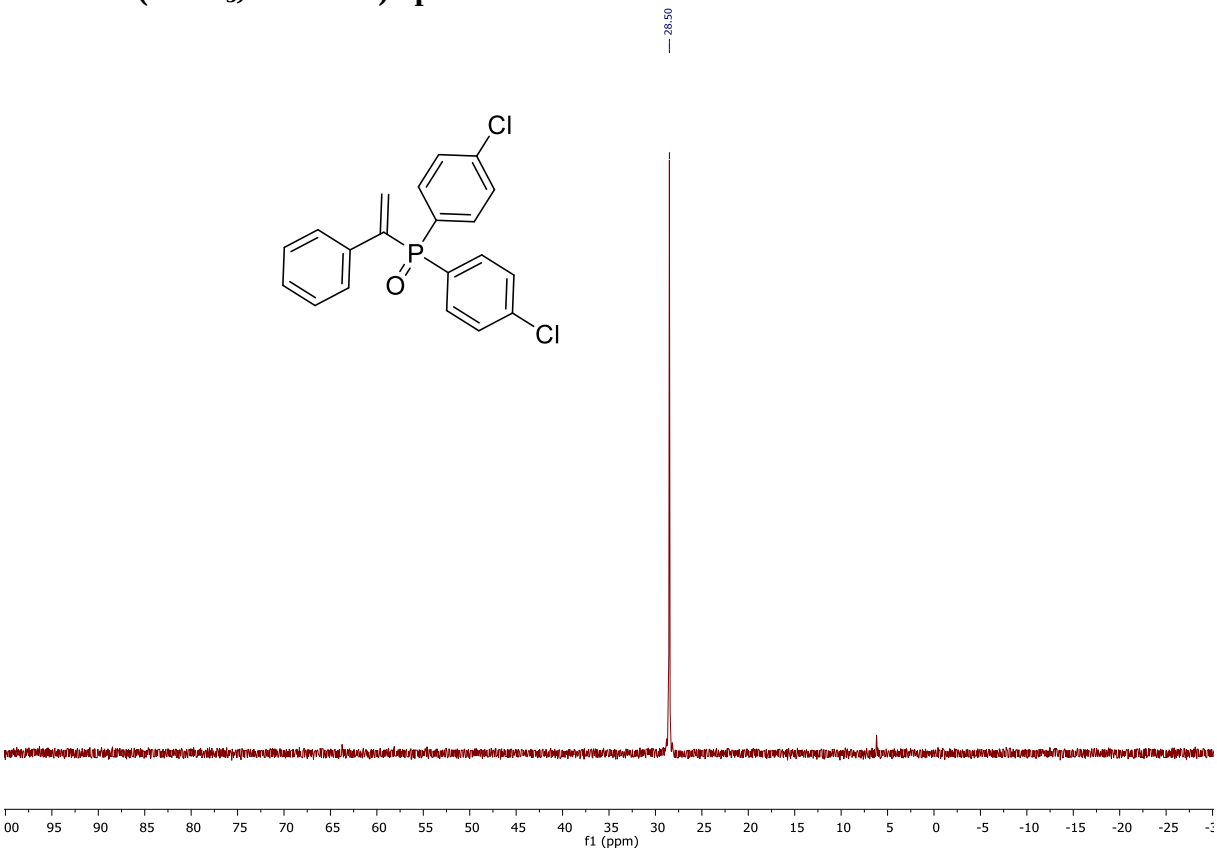
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1x



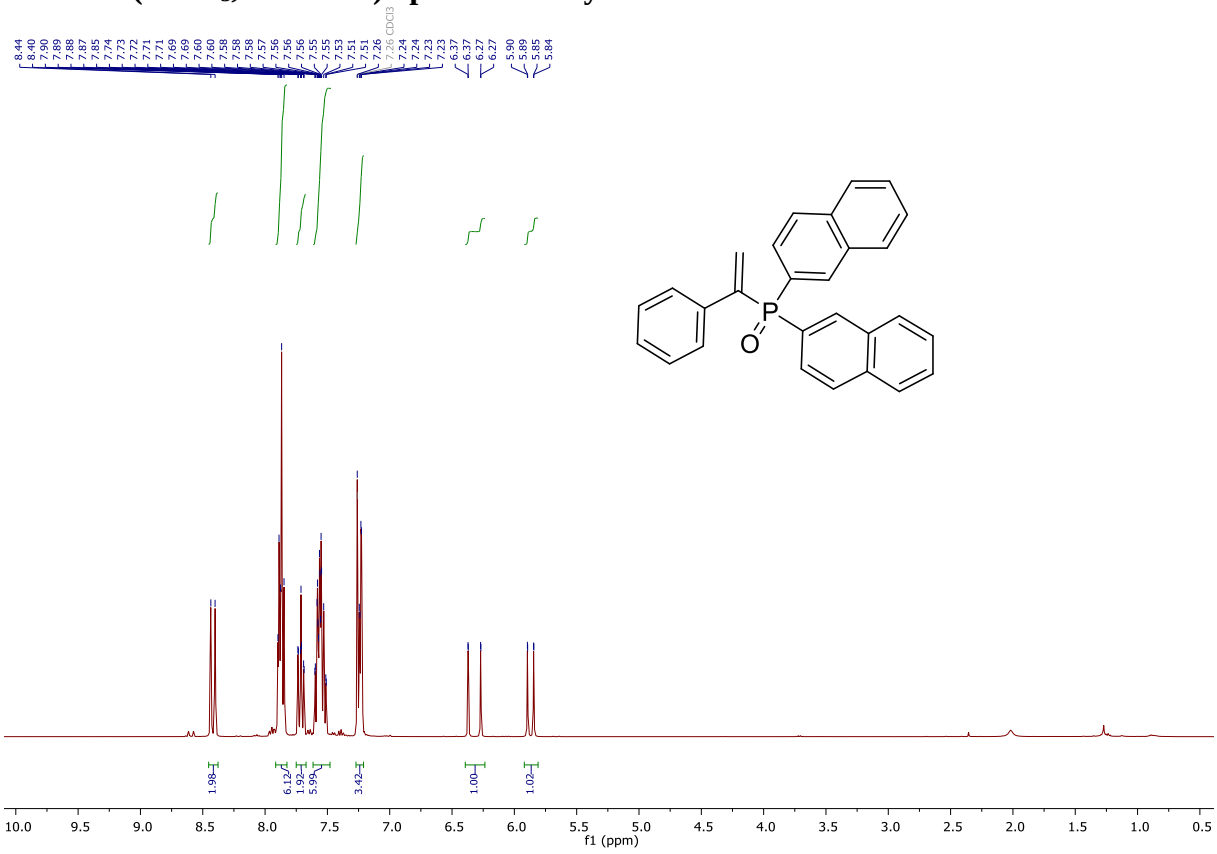
^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1x



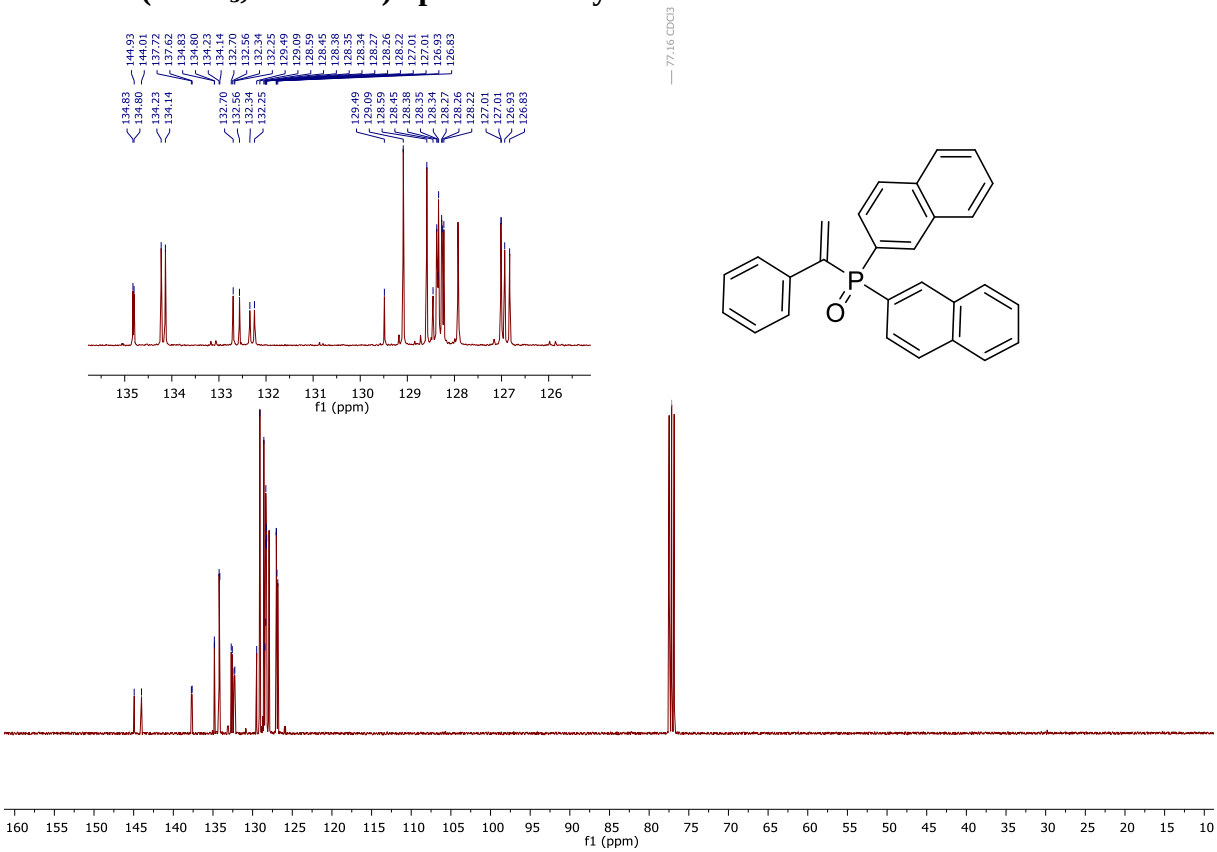
^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1x



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



^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1y



^{31}P NMR ($CDCl_3$, 162 MHz) Spectrum of 1y