Supporting Information

Synthesis of Alkenylphosphine Oxides via Tf_2O Promoted Addition-Elimination of Ketones and Secondary Phosphine Oxides

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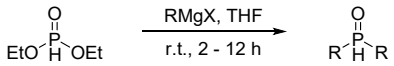
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All reactions were carried out in sealed tubes filled with argon. All reactions were monitored by TLC (thin layer chromatography) and visualized using UV light. The products were purified by column chromatography using 200-300 mesh silica. The elution solvent used for column chromatography was PE (petroleum ether, boiling point range 60 - 90 °C), EA (ethyl acetate) and DCM (dichloromethane). ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded using a Bruker AVANCE NEO 400M NMR spectrometer at Zhengzhou University (North Campus). Chemical shifts (δ) of ^{1}H NMR spectra were reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 101 MHz with complete proton decoupling spectrophotometers. ^{31}P NMR spectra were observed in the ^{1}H-decoupled mode. High-resolution mass spectra (HRMS) were obtained from Shimadzu LCMS-IT-TOF mass spectrometer and DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer.

2. General Procedure for the Synthesis of Substrates

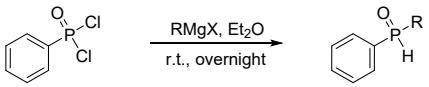
2.1 General procedure for the synthesis of secondary phosphine oxides



Secondary phosphine oxides **2** were synthesized according to the literature procedure.[1] A 250 mL round bottom flask equipped with an addition funnel was evacuated and backfilled with Ar and this operation was repeated three times. The solvent of RMgBr in THF (66 mL, 66 mmol, 3.3 equiv) was added to the bottle and cooled to 0 ℃ under Ar. A solution of diethylphosphite (2.6 mL, 20 mmol, 1.0 eq) in 10 mL THF was then added dropwise over 15 min. The mixture stirred for two hours at ambient temperature and then cooled again to 0 ℃. 75 mL 0.1 M HCl was added dropwise over 5 min. Subsequently, 50 mL MTBE was added, and stirring for further 5 minutes at 0 ℃. The organic layer was removed and the aqueous layer was extracted with DCM (3 × 40 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to give the compounds as white solids.

The substrates **2u - 2ah** were synthesized according to this procedure. Spectroscopic data in agreement with that reported previously.[2]

2.2 General procedure for the synthesis of asymmetric secondary phosphine oxides

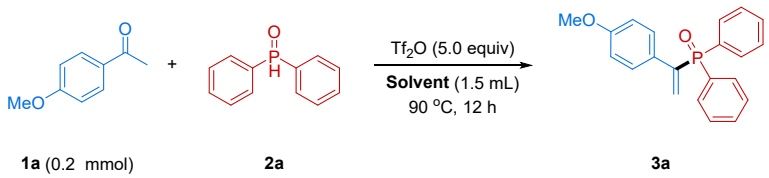


Asymmetric secondary phosphine oxides were synthesized following the literature procedure.[3] Alkyl or aryl magnesium bromide/chloride (1.0 M in Et_2O, 22 mL) was cooled to 0 °C under N_2, then a solution of dichlorophenylphospine (20 mmol) in dry Et_2O (10 mL) was dropwise added over 30 min. The mixture was stirred at r.t. overnight and then quenched with sat. aq. NH_4Cl solution. Subsequently, water (70 mL) was added and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic phases were dried over anhydrous $MgSO_4$, concentrated under vacuum, and the crude residue purified by silica gel column chromatography (PE/EA) to afford the desired asymmetric secondary phosphine oxide.

The substrates **2ai** and **2aj** were synthesized according to this procedure. Spectroscopic data in agreement with that reported previously.[3, 4]

3. Optimization Studies

Table S1. Screening of Solvent[a]

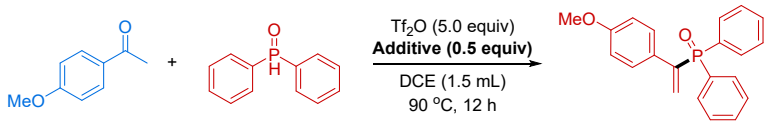


1a (0.2 mmol) **2a** **3a**

Entry	Solvent	Yield (%) [b]
1	**DCE**	**23**
2	DCM	12
3	Toluene	20
4	n-hexane	5
5	$CHCl_3$	8

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), Tf_2O (1.0 mmol, 5.0 equiv), Solvent (1.5 mL), 90 °C, 12 h, Argon atmosphere. [b]Determined by GC using naphthalene as an internal standard.

Table S2. Screening of Additive[a]

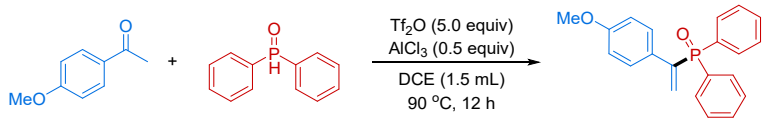


1a (0.2 mmol) **2a** **3a**

Entry	Additive	Yield (%) [b]
1	**$AlCl_3$**	**48**
2	$FeCl_3$	44
3	$BF_3{\cdot}Et_2O$	17
4	$Sc(OTf)_3$	7
5	$Yb(OTf)_3$	12

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), Additive (0.1 mmol, 0.5 equiv), Tf_2O (1.0 mmol, 5.0 equiv), DCE (1.5 mL), 90 °C, 12 h, Argon atmosphere. [b]Determined by GC using naphthalene as an internal standard.

Table S3. Screening of the amount of 2a[a]

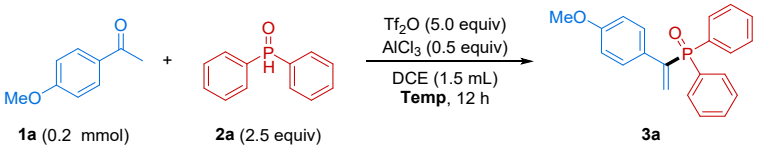


1a (0.2 mmol) **2a** **3a**

Entry	**2a**	Yield (%) [b]
1	1.1 equiv	14
2	1.5 equiv	29
3	2.0 equiv	48
4	**2.5 equiv**	**62**
5	3.0 equiv	60

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (x equiv), $AlCl_3$ (0.1 mmol, 0.5 equiv), Tf_2O (1.0 mmol, 5.0 equiv), DCE (1.5 mL), 90 °C, 12 h, Argon atmosphere. [b] Determined by GC using naphthalene as an internal standard.

Table S4. Screening of Tempreture[a]

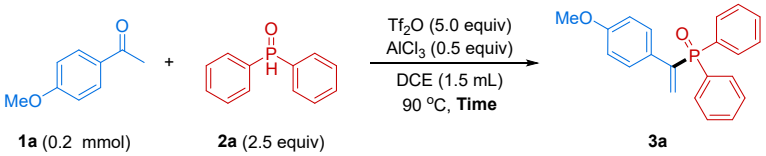


1a (0.2 mmol) **2a** (2.5 equiv) **3a**

Entry	Temperature (°C)	Yield (%)[b]
1	0	trace
2	30	16
3	50	22
4	70	37
5	80	53
6	**90**	**62**
7	100	59
8	110	56

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), $AlCl_3$ (0.1 mmol, 0.5 equiv), Tf_2O (1.0 mmol, 5.0 equiv), DCE (1.5 mL), Temperature, 12 h, Argon atmosphere. [b]Determined by GC using naphthalene as an internal standard.

Table S5. Screening of Time[a]

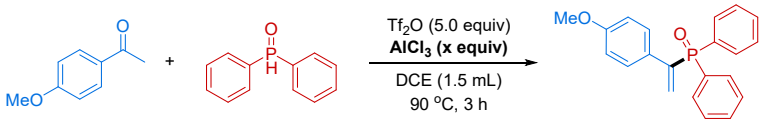


1a (0.2 mmol) **2a** (2.5 equiv) **3a**

Entry	Time	Yield (%) [b]
1	0.5 h	76
2	1 h	82 (77) [c]
3	**3 h**	**88 (82)** [c]
4	6 h	81

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), $AlCl_3$ (0.1 mmol, 0.5 equiv), Tf_2O (1.0 mmol, 5.0 equiv), DCE (1.5 mL), 90 °C, Time (x h), Argon atmosphere. [b] Determined by GC using naphthalene as an internal standard. [c]Isolated yield.

Table S6. Screening of the amount of $AlCl_3$[a]

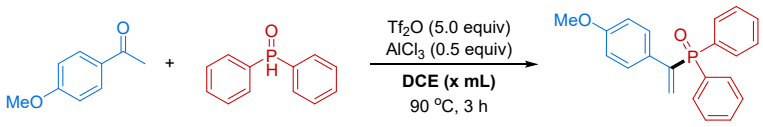


1a (0.2 mmol) **2a** (2.5 equiv) **3a**

Entry	$AlCl_3$	Yield (%)[b]
1	0.1 equiv	52
2	**0.5 equiv**	**88**
3	1.0 equiv	19

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), $AlCl_3$ (x equiv), Tf_2O (1.0 mmol, 5.0 equiv), DCE (1.5 mL), 90 °C, 3 h, Argon atmosphere. [b]Determined by GC using naphthalene as an internal standard.

Table S7. Screening of the amount of DCE[a]

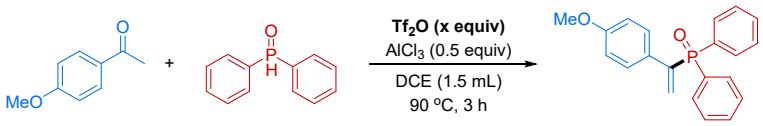


1a (0.2 mmol) **2a** (2.5 equiv) **3a**

Entry	DCE	Yield (%)[b]
1	1.0 mL	83
2	**1.5 mL**	**88**
3	2.0 mL	88

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), $AlCl_3$ (0.1 mmol, 0.5 equiv), Tf_2O (1.0 mmol, 5.0 equiv), DCE (x mL), 90 °C, 3 h, Argon atmosphere. [b]Determined by GC using naphthalene as an internal standard.

Table S8. Screening of the amount of Tf_2O[a]

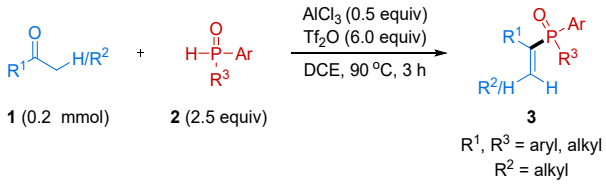


1a (0.2 mmol) **2a** (2.5 equiv) **3a**

Entry	Tf_2O	Yield (%) [b]
1	4.0 equiv	68
2	5.0 equiv	88
3	**6.0 equiv**	**99 (95)** [c]
4	7.0 equiv	79
5	8.0 equiv	77

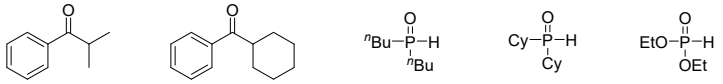
[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), $AlCl_3$ (0.1 mmol, 0.5 equiv), Tf_2O (x equiv), DCE (1.5 mL), 90 °C, 3 h, Argon atmosphere. [b]Determined by GC using naphthalene as an internal standard. [c]Isolated yield.

4. General Procedure for the Synthesis of *α*-Substituted Alkenylphosphine Oxides



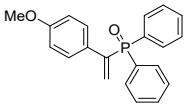
A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with ketones **1** (0.2 mmol, 1.0 equiv), secondary phosphorus oxides **2** (0.5 mmol, 2.5 equiv), and $AlCl_3$ (13.3 mg, 0.1 mmol, 0.5 equiv). The tube was deoxygenated with Argon for 3 times, followed by the addition of DCE (1.5 mL). Subsequently, the flask was stirred under Argon for 1 minute with the aim of fully dissolving secondary phosphorus oxides **2**. After a rapid addition of Tf_2O (201 μL, 1.2 mmol, 6.0 equiv) to the reaction system, the flask was sealed and reacted at 90 °C for 3 h. The resulting mixture was diluted with 5.0 mL DCM and quenched by 5.0 mL saturated $NaHCO_3$ aqueous solution. The mixture was poured into 15.0 mL water and extracted with DCM (15.0 mL × 3). The combined organic layer was dried over $MgSO_4$, filtrated and evaporated to give the crude product, which was then purified on silica gel to afford target compounds **3**.

Some unsuccessful examples:

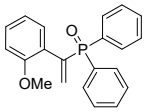


n.d. n.d. 28% NMR yield n.d. n.d.

5. Characterization of Products

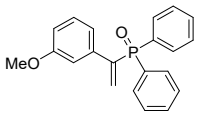


(1-(4-Methoxyphenyl)vinyl)diphenylphosphine oxide (3a):[5] The reaction was conducted on 0.2 mmol scale. The title product **3a** was purified by flash column chromatography (PE/EA = 1/2) to give as white solid (63.5 mg, 95% yield, m.p.: 128 - 130 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 4H), 7.47 – 7.37 (m, 8H), 6.74 (d, *J* = 12.0 Hz, 2H), 6.15 (d, *J* = 40.0 Hz, 1H), 5.60 (d, *J* = 20.0 Hz, 1H), 3.68 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 142.5 (d, *J* = 93.9 Hz), 130.9 (d, *J* = 9.1 Hz), 130.80 (d, *J* = 3.0 Hz), 130.79 (d, *J* = 103.0 Hz), 129.4 (d, *J* = 11.1 Hz), 128.8 (d, *J* = 10.1 Hz), 128.3 (d, *J* = 5.1 Hz), 127.4 (d, *J* = 12.1 Hz), 112.8, 54.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.4.

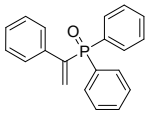


(1-(2-Methoxyphenyl)vinyl)diphenylphosphine oxide (3b): The reaction was conducted on 0.2 mmol scale. The product **3b** was purified by flash column chromatography (PE/EA = 1/2) to give as pale yellow oil (61.5 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 4H), 7.46 – 7.42 (m, 2H), 7.39 – 7.35 (m, 4H), 7.27 – 7.25 (m, 1H), 7.20 – 7.16 (m, 2H), 6.83 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.26 – 6.12 (m, 2H), 3.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3 (d, *J* = 4.0 Hz), 140.9 (d, *J*

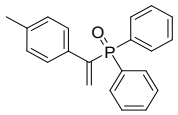
= 93.9 Hz), 133.0 (d, *J* = 8.1 Hz), 131.2 (d, *J* = 104.0 Hz), 130.9 (d, *J* = 10.1 Hz), 130.4 (d, *J* = 3.0 Hz), 129.4 (d, *J* = 4.0 Hz), 128.5, 127.0 (d, *J* = 12.1 Hz), 125.6 (d, *J* = 8.1 Hz), 119.3, 109.3, 53.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.5. **HRMS** (ESI) Calcd for $C_{21}H_{20}O_2P$ $[M + H]^+$ 335.1201, found 335.1207.



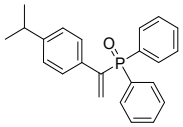
(1-(3-Methoxyphenyl)vinyl)diphenylphosphine oxide (3c): The reaction was conducted on 0.2 mmol scale. The product **3c** was purified by flash column chromatography (PE/EA = 1/2) to give as yellow oil (53.5 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 4H), 7.48 – 7.41 (m, 6H), 7.15 - 7.11 (m, 1H), 7.03 – 6.98 (m, 2H), 6.76 (d, *J* = 8.0, 1H), 6.23 (d, *J* = 40.0, 1H), 5.78 (d, *J* = 20.0, 1H), 3.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3, 143.1 (d, *J* = 92.9 Hz), 137.9 (d, *J* = 10.1 Hz), 131.1 (d, *J* = 10.1 Hz), 131.0 (d, *J* = 10.1 Hz), 130.9 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 104.0 Hz), 128.4, 127.5 (d, *J* = 13.1 Hz), 119.6 (d, *J* = 4.0 Hz), 113.2, 112.3 (d, *J* = 4.0 Hz), 54.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.6. **HRMS** (ESI) Calcd for $C_{21}H_{20}O_2P$ $[M + H]^+$ 335.1201, found 335.1206.



Diphenyl(1-phenylvinyl)phosphine oxide (3d):[6] The reaction was conducted on 0.2 mmol scale. The product **3d** was purified by flash column chromatography (PE/EA = 1/1) to give as white solid (45.6 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 4H), 7.52 – 7.41 (m, 8H), 7.24 – 7.23 (m, 3H), 6.24 (d, *J* = 40.0 Hz, 1H), 5.77 (d, *J* = 20.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4 (d, *J* = 91.9 Hz), 136.6 (d, *J* = 10.1 Hz), 131.0 (d, *J* = 10.1 Hz), 130.9 (d, *J* = 2.0 Hz), 130.6 (d, *J* = 104.0 Hz), 127.5, 127.4, 127.2, 127.1 (d, *J* = 5.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.9.

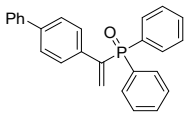


Diphenyl(1-(*p*-tolyl)vinyl)phosphine oxide (3e)[3]: The reaction was conducted on 0.2 mmol scale. The product **3e** was purified by flash column chromatography (PE/EA = 1/1) to give as pale yellow oil (52.8 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 4H), 7.39 – 7.34 (m, 8H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.15 (d, *J* = 40.0 Hz, 1H), 5.63 (d, *J* = 20.0 Hz, 1H), 2.17 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9 (d, *J* = 92.9 Hz), 137.0, 133.5 (d, *J* = 10.1 Hz), 130.9 (d, *J* =10.1 Hz), 130.6 (d, *J* = 102.0 Hz), 130.2 (d, *J* = 10.1 Hz), 128.1, 127.4 (d, *J* = 12.1 Hz), 126.9 (d, *J* = 4.0 Hz), 20.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.3.

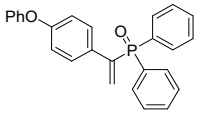


(1-(4-Isopropylphenyl)vinyl)diphenylphosphine oxide (3f): The reaction was conducted on 0.2 mmol scale. The product **3f** was purified by flash column chromatography (PE/EA = 1/1) to give as pale yellow solid (54 mg, 78% yield, m.p.: 98-100 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 4H), 7.50 –

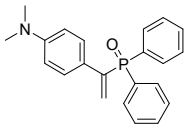
7.37 (m, 8H), 7.09 (d, J = 8.0 Hz, 2H), 6.22 (d, J = 40.0 Hz, 1H), 5.69 (d, J = 20.0 Hz, 1H), 2.86 – 2.79 (m, 1H), 1.18 (d, J = 4.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 143.1 (d, J = 92.9 Hz), 133.8 (d, J = 10.1 Hz), 131.0 (d, J = 10.1 Hz), 130.9 (d, J = 103.0 Hz), 130.8 (d, J = 3.0 Hz), 130.2 (d, J = 10.1 Hz), 127.4 (d, J = 12.0 Hz), 127.0 (d, J = 4.0 Hz), 125.5, 32.7, 22.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.2. **HRMS** (ESI) Calcd for $C_{23}H_{24}OP$ $[M + H]^+$ 347.1565, found 347.1564.



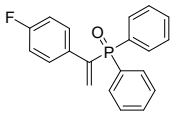
(1-([1,1'-Biphenyl]-4-yl)vinyl)diphenylphosphine oxide (3g):[7] The reaction was conducted on 0.2 mmol scale. The product **3g** was purified by flash column chromatography (PE/EA = 1/1) to give as white solid (32.7 mg, 43% yield, m.p.: 143 - 145 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 4H), 7.58 – 7.38 (m, 14H), 7.33 – 7.30 (m, 1H), 6.30 (d, J = 40.0 Hz, 1H), 5.75 (d, J = 20.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9 (d, J = 92.9 Hz), 139.9, 139.4, 135.4 (d, J = 10.1 Hz), 131.0 (d, J = 10.1 Hz), 130.9, 130.7 (d, J = 10.1 Hz), 130.6 (d, J = 104.0 Hz), 127.7, 127.50 (d, J = 5.1 Hz), 127.49 (d, J = 12.1 Hz), 126.4, 126.1, 125.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.4.



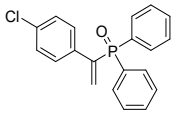
(1-(4-Phenoxyphenyl)vinyl)diphenylphosphine oxide (3h): The reaction was conducted on 0.2 mmol scale. The product **3h** was purified by flash column chromatography (PE/EA = 1/1) to give as pale yellow oil (56.3 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 4H), 7.53 – 7.41 (m, 8H), 7.32 – 7.28 (m, 2H), 7.10 – 7.06 (m, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 12.0 Hz, 2H), 6.21 (d, J = 40.0 Hz, 1H), 5.67 (d, J = 20.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5, 155.6, 142.5 (d, J = 92.9 Hz), 131.2 (d, J = 10.1 Hz), 131.0 (d, J = 9.1 Hz), 130.6 (d, J = 103.0 Hz), 128.7, 128.6 (d, J = 5.0 Hz), 127.5 (d, J = 12.1 Hz), 127.3 (d, J = 10.1 Hz), 122.6, 118.2, 117.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.3. **HRMS** (ESI) Calcd for $C_{26}H_{22}O_2P$ $[M + H]^+$ 397.1357, found 397.1350.



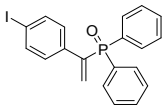
(1-(4-(Dimethylamino)phenyl)vinyl)diphenylphosphine oxide (3i):[8] The reaction was conducted on 0.2 mmol scale. The product **3i** was purified by flash column chromatography (PE/EA = 1/1) to give as red solid (34.7 mg, 50% yield, m.p.: 98 - 99 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 4H), 7.51 – 7.38 (m, 8H), 6.57 (d, J = 8.0 Hz, 2H), 6.15 (d, J = 40.0 Hz, 1H), 5.54 (d, J = 20.0 Hz, 1H), 2.90 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 142.3 (d, J = 92.9 Hz), 131.2 (d, J = 103.0 Hz), 131.0 (d, J = 10.1 Hz), 130.7 (d, J = 3.0 Hz), 127.9 (d, J = 5.1 Hz), 127.6 (d, J = 10.1 Hz), 127.4 (d, J = 12.1 Hz), 124.2 (d, J = 10.1 Hz), 111.1, 39.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.9.



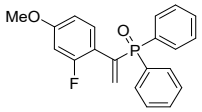
(1-(4-Fluorophenyl)vinyl)diphenylphosphine oxide (3j):[5] The reaction was conducted on 0.2 mmol scale. The product **3j** was purified by flash column chromatography (PE/EA = 1/1) to give as white solid (54.8 mg, 85% yield, m.p.: 98 - 99 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.50 – 7.39 (m, 8H), 6.90 (t, *J* = 8.0 Hz, 2H), 6.17 (d, *J* = 40.0 Hz, 1H), 5.67 (d, *J* = 20.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7 (d, *J* = 249.5 Hz), 142.4 (d, *J* = 93.9 Hz), 132.6 (dd, *J* = 10.1, 3.0 Hz), 131.8 (dd, *J* = 28.3, 7.1 Hz), 130.9 (d, *J* = 10.1 Hz), 130.7 (d, *J* = 10.1 Hz), 130.4 (d, *J* = 103.0 Hz), 128.9 (dd, *J* = 8.1, 5.1 Hz), 127.5 (d, *J* = 12.1 Hz), 114.4 (d, *J* = 21.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.2.



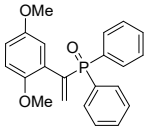
(1-(4-Chlorophenyl)vinyl)diphenylphosphine oxide (3k):[7] The reaction was conducted on 0.2 mmol scale. The product **3k** was purified by flash column chromatography (PE/EA = 1/1) to give as white solid (48.1 mg, 71% yield, m.p.: 102 - 103 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 4H), 7.53 – 7.43 (m, 8H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.21 (d, *J* = 40.0 Hz, 1H), 5.71 (d, *J* = 20.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4 (d, *J* = 92.9 Hz), 135.0 (d, *J* = 10.1 Hz), 133.4, 131.1, 131.0 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 10.1 Hz), 130.2 (d, *J* = 104.0 Hz), 128.4 (d, *J* = 5.1 Hz), 127.6 (d, *J* = 1.5 Hz), 127.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.1.



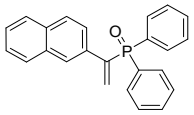
(1-(4-Iodophenyl)vinyl)diphenylphosphine oxide (3l): The reaction was conducted on 0.2 mmol scale. The product **3l** was purified by flash column chromatography (PE/EA = 1/1) to give as white solid (52.5 mg, 61% yield, m.p.: 164 - 166 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 4H), 7.57 – 7.40 (m, 8H), 7.25 – 7.23 (m, 2H), 6.21 (d, *J* = 40.0 Hz, 1H), 5.70 (d, *J* = 20.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6 (d, *J* = 92.9 Hz), 136.5, 136.1 (d, *J* = 10.1 Hz), 131.1, 131.0 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 10.1 Hz), 130.2 (d, *J* = 104.0 Hz), 128.9 (d, *J* = 4.0 Hz), 127.6 (d, *J* = 12.1 Hz), 93.6 (d, *J* = 1.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.0. **HRMS** (ESI) Calcd for $C_{20}H_{17}IOP$ $[M + H]^+$ 431.0062, found 431.0058.



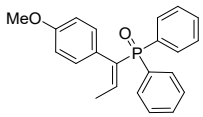
(1-(2-Fluoro-4-methoxyphenyl)vinyl)diphenylphosphine oxide (3m): The reaction was conducted on 0.2 mmol scale. The product **3m** was purified by flash column chromatography (PE/EA = 1/2) to give as yellow solid (56.4 mg, 80%, m.p.: 60 - 62 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 4H), 7.51 – 7.41 (m, 7H), 6.80 (d, *J* = 12.0 Hz, 2H), 6.50 (d, *J* = 40.0 Hz, 1H), 6.19 (d, *J* = 20.0 Hz, 1H), 3.97 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6 (d, *J* = 11.1 Hz), 159.3 (dd, *J* = 248.5, 6.1 Hz), 136.5 (d, *J* = 94.9 Hz), 133.8 (d, *J* = 10.1 Hz), 130.9 (d, *J* = 10.1 Hz), 130.7 (d, *J* = 4.0 Hz), 130.6 (d, *J* = 3.0 Hz), 130.4 (d, *J* = 103.0 Hz), 127.4 (d, *J* = 12.1 Hz), 116.1 (dd, *J* = 14.1, 11.1 Hz), 108.5 (d, *J* = 2.0 Hz), 101.1 (d, *J* = 27.3 Hz), 54.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.3. **HRMS** (ESI) Calcd for $C_{21}H_{19}FO_2P$ $[M + H]^+$ 353.1107, found 353.1102.



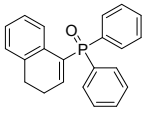
(1-(2,4-Dimethoxyphenyl)vinyl)diphenylphosphine oxide (3n): The reaction was conducted on 0.2 mmol scale. The product **3n** was purified by flash column chromatography (PE/EA = 1/2) to give as brown oil (29.9 mg, 41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 4H), 7.497– 7.38 (m, 6H), 6.79 – 6.70 (m, 2H), 6.63 – 6.60 (m, 1H), 6.26 – 6.12 (m, 2H), 3.63 (s, 3H), 3.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.1, 149.7 (d, *J* = 3.0 Hz), 140.7 (d, *J* = 93.9 Hz), 133.3 (d, *J* = 9.1 Hz), 131.3 (d, *J* = 103.0 Hz), 130.9 (d, *J* = 9.1 Hz), 130.5 (d, *J* = 3.0 Hz), 127.1 (d, *J* = 12.1 Hz), 126.4 (d, *J* = 9.1 Hz), 114.9 (d, *J* = 4.0 Hz), 113.5, 110.8, 54.7, 54.4.. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.8. **HRMS** (ESI) Calcd for $C_{22}H_{22}O_3P$ $[M + H]^+$ 365.1301, found 365.1306.



(1-(Naphthalen-2-yl)vinyl)diphenylphosphine oxide (3o):[9] The reaction was conducted on 0.2 mmol scale. The product **3o** was purified by flash column chromatography (PE/EA = 1/1) to give as yellow solid (28.4 mg, 40% yield, m.p.: 238 - 240 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.78 – 7.71 (m, 7H), 7.59 – 7.57 (m, 1H), 7.52 – 7.41 (m, 8H), 6.36 (d, *J* = 40.0 Hz, 1H), 5.84 (d, *J* = 20.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3 (d, *J* = 92.9 Hz), 135.1 (d, *J* = 10.1 Hz), 133.1, 133.0, 132.5 (d, *J* = 10.1 Hz), 132.1 (d, *J* = 10.1 Hz), 132.2, 132.0, 131.7 (d, *J* = 104.0 Hz), 128.6 (d, *J* = 12.1 Hz), 128.5, 128.2, 127.9 (d, *J* = 5.1 Hz), 127.6, 126.3 (d, *J* = 14.1 Hz), 125.8 (d, *J* = 4.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.0.

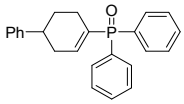


(*E*)-(1-(4-Methoxyphenyl)prop-1-en-1-yl)diphenylphosphine oxide (3p): The reaction was conducted on 0.2 mmol scale. The product **3p** was purified by flash column chromatography (PE/EA = 1/2) to give as colorless oil (61.3 mg, 88% yield, *E/Z* = 5/1). Major (*E*-configuration): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.45 – 7.29 (m, 6H), 6.92 – 6.89 (m, 2H), 6.72 – 6.70 (m, 3H), 3.69 (s, 3H), 1.72 – 1.70 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9 (d, *J* = 2.0 Hz), 143.3 (d, *J* = 10.1 Hz), 136.3 (d, *J* = 98.0 Hz), 133.7 (d, *J* = 103.0 Hz), 132.1 (d, *J* = 9.1 Hz), 131.6 (d, *J* = 2.0 Hz), 131.2 (d, *J* = 5.1 Hz), 128.2 (d, *J* = 12.1 Hz), 126.9 (d, *J* = 10.1 Hz), 113.7, 55.1, 15.9 (d, *J* = 15.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.4. **HRMS** (ESI) Calcd for $C_{22}H_{22}O_2P$ $[M + H]^+$ 349.1357, found 349.1352.

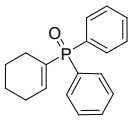


(3,4-Dihydronaphthalen-1-yl)diphenylphosphine oxide (3q):[10] The reaction was conducted on 0.2 mmol scale. The product **3q** was purified by flash column chromatography (PE/EA = 1/1) to give as white solid (60.7 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.63 (m, 5H), 7.59 – 7.34 (m,

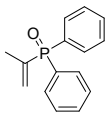
6H), 7.23 – 7.04 (m, 2H), 7.05 – 6.97 (m, 1H), 6.27 (dt, *J* = 19.5, 4.6 Hz, 1H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.48 – 2.18 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9 (d, *J* = 9.5 Hz), 135.6 (d, *J* = 7.7 Hz), 132.29 (d, *J* = 104.0 Hz), 132.25 (d, *J* = 102.0 Hz), 132.0 (d, *J* = 9.7 Hz), 131.8 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 9.1 Hz), 130.9, 128.6 (d, *J* = 12.0 Hz), 127.8, 127.3 (d, *J* = 3.7 Hz), 126.7, 27.3 (d, *J* = 2.1 Hz), 24.3 (d, *J* = 13.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.3.



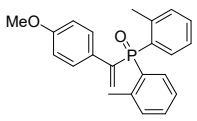
Diphenyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)phosphine oxide (3r): The reaction was conducted on 0.2 mmol scale. The product **3r** was purified by flash column chromatography (PE/EA = 1/1) to give as pale yellow oil (41.6 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 4H), 7.56 – 7.46 (m, 6H), 7.33 – 7.29 (m, 2H), 7.22 – 7.19 (m, 3H), 6.50 (dd, *J* = 20.0, 4.0 Hz, 1H), 2.87 – 2.86 (m, 1H), 2.56 – 2.51 (m, 1H), 2.44 – 2.31 (m, 3H), 2.06 – 2.02 (m, 1H), 1.86 – 1.76 (m, 1H). **^{13}C NMR (**101 MHz, $CDCl_3$) δ 144.8, 141.8 (d, *J* = 8.1 Hz), 131.0 (d, *J* = 5.1 Hz), 130.9 (d, *J* = 100.0 Hz), 130.87 (d, *J* = 3.0 Hz), 130.81, 127.53 (d, *J* = 12.1 Hz), 127.48 (d, *J* = 10.1 Hz), 125.8, 125.4, 38.2, 33.4 (d, *J* = 15.1 Hz), 28.4 (d, *J* = 9.1 Hz), 24.3 (d, *J* = 9.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.2. **HRMS** (ESI) Calcd for $C_{24}H_{24}OP$ $[M + H]^+$ 359.1565, found 359.1567.



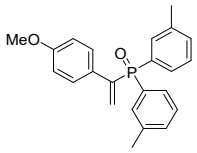
Cyclohex-1-en-1-yldiphenylphosphine oxide (3s):[11] The reaction was conducted on 0.2 mmol scale. The product **3s** was purified by flash column chromatography (PE/EA = 1/2) to give as colorless oil (40.1 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 4H), 7.50 – 7.38 (m, 6H), 6.35 (d, *J* = 20.0 Hz, 1H), 2.13 – 2.25 (m, 4H), 1.60 – 1.73 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6 (d, *J* = 9.1 Hz), 130.9 (d, *J* = 10.1 Hz), 130.7 (d, *J* = 3.0 Hz), 130.5 (d, *J* = 90.9 Hz), 130.3 (d, *J* = 104.0 Hz), 127.4 (d, *J* = 12.1 Hz), 25.4 (d, *J* = 14.1 Hz), 23.5 (d, *J* = 9.1 Hz), 21.1 (d, *J* = 8.1 Hz), 20.4 (d, *J* = 1.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.8.



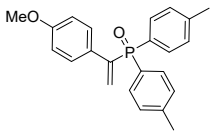
Diphenyl(prop-1-en-2-yl)phosphine oxide (3t):[12] The reaction was conducted on 0.2 mmol scale. The product **3t** was purified by flash column chromatography (PE/EA = 1/2) to give as white solid (29.6 mg, 61% yield, m.p.: 126 - 128 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 4H), 7.54 – 7.43 (m, 6H), 5.92 (d, *J* = 40.0 Hz, 1H), 5.62 (d, *J* = 20.0 Hz, 1H), 1.98 (d, *J* = 12.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4 (d, *J* = 92.9 Hz), 131.0 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 10.1 Hz), 130.0 (d, *J* = 103.0 Hz), 129.5 (d, *J* = 10.1 Hz), 127.5 (d, *J* = 12.1 Hz), 18.1 (d, *J* = 12.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.3.



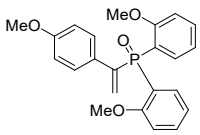
(1-(4-Methoxyphenyl)vinyl)di-*o*-tolylphosphine oxide (3u): The reaction was conducted on 0.2 mmol scale. The product **3u** was purified by flash column chromatography (PE/EA = 1/1) to give as orange oil (63.8 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.40 – 7.31 (m, 6H), 7.15 – 7.12 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.20 (d, *J* = 40.0, 1H), 5.49 (d, *J* = 20.0, 1H), 3.75 (s, 3H), 2.57 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 142.5 (d, *J* = 8.1 Hz), 141.8 (d, *J* = 91.9 Hz), 132.0 (d, *J* = 13.1 Hz), 131.0 (d, *J* = 10.1 Hz), 130.8 (d, *J* = 2.0 Hz), 129.33 (d, *J* = 101.0 Hz), 129.30 (d, *J* = 9.1 Hz), 128.5 (d, *J* = 5.1 Hz), 128.3 (d, *J* = 11.1 Hz), 124.3 (d, *J* = 13.1 Hz), 112.9, 54.2, 20.8 (d, *J* = 4.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 37.3. **HRMS** (ESI) Calcd for $C_{23}H_{24}O_2P$ $[M + H]^+$ 363.1514, found 363.1514.



(1-(4-Methoxyphenyl)vinyl)di-*m*-tolylphosphine oxide (3v): The reaction was conducted on 0.2 mmol scale. The product **3v** was purified by flash column chromatography (PE/EA = 1/1) to give as orange oil (26.1 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 12.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 4H), 7.30 – 7.28 (m, 4H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.16 (d, *J* = 40.0 Hz, 1H), 5.63 (d, *J* = 20.0 Hz, 1H), 3.74 (s, 3H), 2.35 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 142.6 (d, *J* = 90.9 Hz), 137.4 (d, *J* = 12.1 Hz), 131.6 (d, *J* = 2.0 Hz), 131.5 (d, *J* = 10.1 Hz), 130.6 (d, *J* = 103.0 Hz), 129.3 (d, *J* = 12.1 Hz), 129.0 (d, *J* = 10.1 Hz), 128.4 (d, *J* = 5.1 Hz), 128.0 (d, *J* = 10.1 Hz), 127.2 (d, *J* = 13.1 Hz), 112.8, 54.2, 20.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.0. **HRMS** (ESI) Calcd for $C_{23}H_{24}O_2P$ $[M + H]^+$ 363.1514, found 363.1511.

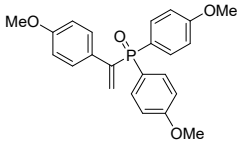


(1-(4-Methoxyphenyl)vinyl)di-*p*-tolylphosphine oxide (3w): The reaction was conducted on 0.2 mmol scale. The product **3w** was purified by flash column chromatography (PE/EA = 1/2) to give as dark yellow oil (52.2 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 4H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.21 (m, 4H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 40.0 Hz, 1H), 5.61 (d, *J* = 20.0 Hz, 1H), 3.73 (s, 3H), 2.36 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5, 142.7 (d, *J* = 93.9 Hz), 141.2 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 10.1 Hz), 129.2 (d, *J* = 10.1 Hz), 129.0 (d, *J* = 10.1 Hz), 128.3 (d, *J* = 5.1 Hz), 128.2 (d, *J* = 12.1 Hz), 127.5 (d, *J* = 106.1 Hz), 112.8, 54.2, 20.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.0. **HRMS** (ESI) Calcd for $C_{23}H_{24}O_2P$ $[M + H]^+$ 363.1514, found 363.1505.

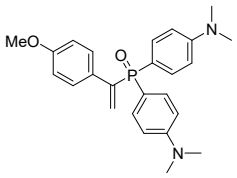


Bis(2-methoxyphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3x): The reaction was conducted on 0.2 mmol scale. The product **3x** was purified by flash column chromatography (PE/EA = 1/3) to give as orange solid (71.8 mg, 91% yield, m.p.: 99 - 100 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m,

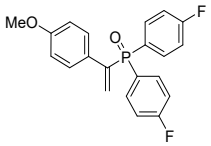
2H), 7.43 – 7.37 (m, 4H), 6.96 – 6.92 (m, 2H), 6.82 – 6.79 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.03 (d, *J* = 40.0, 1H), 5.80 (d, *J* = 20.0, 1H), 3.69 (s, 3H), 3.54 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2 (d, *J* = 2.0 Hz), 158.2, 142.7 (d, *J* = 99.9 Hz), 133.5 (d, *J* = 9.1 Hz), 132.6, 130.2 (d, *J* = 11.1 Hz), 128.1 (d, *J* = 4.0 Hz), 127.2 (d, *J* = 10.1 Hz), 119.6 (d, *J* = 107.1 Hz), 119.5 (d, *J* = 12.1 Hz), 112.4, 110.1 (d, *J* = 7.1 Hz), 54.3, 54.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.1. **HRMS** (ESI) Calcd for $C_{23}H_{24}O_4P$ $[M + H]^+$ 395.1412, found 395.1405.



Bis(4-methoxyphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3y): The reaction was conducted on 0.2 mmol scale. The product **3y** was purified by flash column chromatography (PE/EA = 1/2) to give as dark yellow oil (60.7 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.43 – 7.41 (m, 2H), 6.94 – 6.91 (m, 4H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.13 (dd, *J* = 40.0, 1H), 5.63 (dd, *J* = 20.0, 1H), 3.82 (s, 6H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 3.0 Hz), 158.6, 143.2 (d, *J* = 93.9 Hz), 132.8 (d, *J* = 10.1 Hz), 129.2 (d, *J* = 10.1 Hz), 128.9 (d, *J* = 10.1 Hz), 128.4 (d, *J* = 5.1 Hz), 122.3 (d, *J* = 111.1 Hz), 113.0 (d, *J* = 13.1 Hz), 112.8, 54.3, 54.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.2. **HRMS** (ESI) Calcd for $C_{23}H_{24}O_4P$ $[M + H]^+$ 395.1412, found 395.1409.

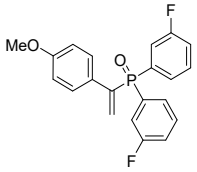


Bis(4-(dimethylamino)phenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3z): The reaction was conducted on 0.2 mmol scale. The product **3z** was purified by flash column chromatography (EA/CH_3OH = 80/1) to give as dark yellow solid (57.2 mg, 68% yield, m.p.: 153 - 155 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 6H), 6.77 – 6.65 (m, 6H), 6.09 (d, *J* = 40.0 Hz, 1H), 5.64 (d, *J* = 20.0 Hz, 1H), 3.74 (s, 3H), 2.98 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3, 151.2 (d, *J* = 2.0 Hz), 143.8 (d, *J* = 94.9 Hz), 132.3 (d, *J* = 11.1 Hz), 131.5 (d, *J* = 12.1 Hz), 129.8 (d, *J* = 10.1 Hz), 128.4 (d, *J* = 4.0 Hz), 116.2 (d, *J* = 116.2 Hz), 112.6, 110.2 (d, *J* = 13.1 Hz), 54.2, 38.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.9. **HRMS** (ESI) Calcd for $C_{25}H_{30}N_2O_4P$ $[M + H]^+$ 421.2045, found 421.2030.

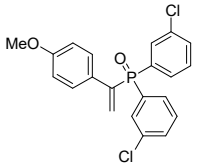


Bis(4-Fluorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3aa): The reaction was conducted on 0.2 mmol scale. The product **3aa** was purified by flash column chromatography (PE/EA = 1/1) to give as dark yellow oil (63.7 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 4H), 7.41 – 7.39 (m, 2H), 7.15 – 7.10 (m, 4H), 6.79 – 6.77 (m, 2H), 6.18 (d, *J* = 40.0 Hz, 1H), 5.64 (d, *J* = 20.0 Hz, 1H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1 (dd, *J* = 254.5, 3.0 Hz), 158.8, 142.5 (d, *J* = 93.9 Hz), 133.4 (dd, *J* = 11.1, 8.1 Hz), 129.6 (d, *J* = 10.1 Hz), 128.5 (d, *J* = 10.1 Hz), 128.3 (d, *J* = 5.1 Hz), 126.6

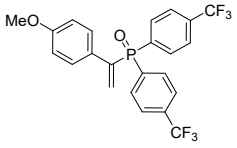
(dd, J = 106.1, 3.0 Hz), 115.0 (dd, J = 21.2, 13.1 Hz), 113.0, 54.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.7. **HRMS** (ESI) Calcd for $C_{21}H_{18}F_2O_2P$ $[M + H]^+$ 371.1012, found 371.1009.



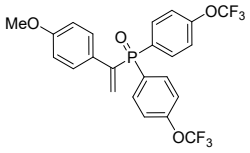
Bis(3-Fluorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ab): The reaction was conducted on 0.2 mmol scale. The product **3ab** was purified by flash column chromatography (PE/EA = 1/1) to give as white solid (59.3 mg, 80% yield, m.p.: 136 - 137 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 8H), 7.21 – 7.17 (m, 2H), 6.78 (d, J = 12.0 Hz, 2H), 6.21 (d, J = 40.0 Hz, 1H), 5.63 (d, J = 20.0 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.5 (dd, J = 251.5, 17.2 Hz), 158.9, 141.6 (d, J = 94.9 Hz), 133.0 (dd, J = 102.0, 5.1 Hz), 130.0 (d, J = 10.1 Hz), 129.6 (dd, J = 14.1, 7.1 Hz), 128.3 (d, J = 5.1 Hz), 128.2 (d, J = 10.1 Hz), 126.6 (dd, J = 9.1, 3.0 Hz), 118.3 (dd, J = 20.2, 3.0 Hz), 117.8 (dd, J = 22.2, 10.1 Hz), 113.0, 54.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.3. **HRMS** (ESI) Calcd for $C_{21}H_{18}F_2O_2P$ $[M + H]^+$ 371.1012, found 371.1010.



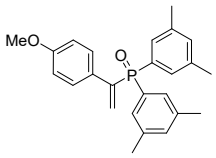
Bis(3-chlorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ac): The reaction was conducted on 0.2 mmol scale. The product **3ac** was purified by flash column chromatography (PE/EA = 2/1) to give as white solid (63.7 mg, 79% yield, m.p.: 111 - 113 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.55 – 7.34 (m, 8H), 6.79 – 6.77 (m, 2H), 6.21 (d, J = 40.0 Hz, 1H), 5.63 (d, J = 20.0 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 141.6 (d, J = 94.9 Hz), 134.2 (d, J = 16.2 Hz), 132.7 (d, J = 102.0 Hz), 131.3 (d, J = 2.0 Hz), 130.8 (d, J = 10.1 Hz), 130.1 (d, J = 10.1 Hz), 129.0 (d, J = 13.1 Hz), 128.9 (d, J = 9.1 Hz), 128.3 (d, J = 5.1 Hz), 128.1 (d, J = 10.1 Hz), 113.1, 54.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.2. **HRMS** (ESI) Calcd for $C_{21}H_{18}Cl_2O_2P$ $[M + H]^+$ 403.0421, found 403.0419.



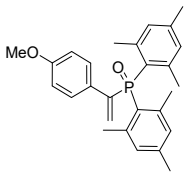
(1-(4-Methoxyphenyl)vinyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ad): The reaction was conducted on 0.2 mmol scale. The product **3ad** was purified by flash column chromatography (PE/EA = 1/1) to give as orange oil (85.6 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 12.0 Hz, 2H), 7.86 – 7.75 (m, 4H), 7.59 – 7.55 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.25 (d, J = 40.0 Hz, 1H), 5.68 (d, J = 20.0 Hz, 1H), 3.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 141.5 (d, J = 94.9 Hz), 134.1 (d, J = 10.1 Hz), 131.6 (d, J = 103.0 Hz), 130.7 (d, J = 10.1 Hz), 130.3 (q, J = 33.3 Hz), 130.2 (q, J = 33.3 Hz), 128.3 (d, J = 5.1 Hz), 128.2 (d, J = 12.1 Hz), 127.7 (d, J = 10.1 Hz), 122.5 (q, J = 273.7 Hz), 113.1, 54.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.0. **HRMS** (ESI) Calcd for $C_{23}H_{18}F_2O_2P$ $[M + H]^+$ 471.0949, found 471.0948.



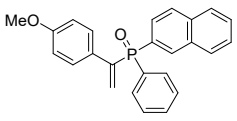
(1-(4-Methoxyphenyl)vinyl)bis(4-(trifluoromethoxy)phenyl)phosphine oxide (3ae): The reaction was conducted on 0.2 mmol scale. The product **3ae** was purified by flash column chromatography (PE/EA = 3/1) to give as pale yellow oil (90.4 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 4H), 7.42 – 7.28 (m, 6H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.22 (d, *J* = 40.0 Hz, 1H), 5.64 (d, *J* = 20.0 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 151.1 (dq, *J* = 3.0, 1.0 Hz), 141.9 (d, *J* = 94.9 Hz), 132.9 (d, *J* = 11.1 Hz), 130.0 (d, *J* = 10.1 Hz), 129.0 (d, *J* = 105.0 Hz), 128.3 (d, *J* = 5.1 Hz), 128.2 (d, *J* = 10.1 Hz), 119.5 (d, *J* = 13.1 Hz), 119.3 (q, *J* = 259.9 Hz), 113.1, 54.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.2. **HRMS** (ESI) Calcd for $C_{23}H_{18}F_6O_4P$ $[M + H]^+$ 503.0847, found 503.0843.



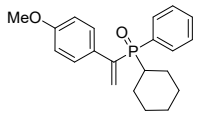
Bis(3,5-dimethylphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3af): The reaction was conducted on 0.2 mmol scale. The product **3af** was purified by flash column chromatography (PE/EA = 1/2) to give as orange oil (40.6 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.31 (d, *J* = 12.0, 4H), 7.11 (s, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.14 (dd, *J* = 40.0, 1H), 5.62 (dd, *J* = 20.0, 1H), 3.74 (s, 3H), 2.29 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 142.8 (d, *J* = 92.9 Hz), 137.0 (d, *J* = 12.1 Hz), 132.5 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 102.0 Hz), 129.2 (d, *J* = 10.1 Hz), 128.7 (d, *J* = 10.1 Hz), 128.6 (d, *J* = 9.1 Hz), 128.4 (d, *J* = 4.0 Hz), 112.8, 54.2, 20.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.2. **HRMS** (ESI) Calcd for $C_{25}H_{28}O_2P$ $[M + H]^+$ 391.1827, found 391.1828.



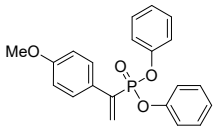
Dimesityl(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ag): The reaction was conducted on 0.2 mmol scale. The product **3ag** was purified by flash column chromatography (PE/EA = 1/1) to give as colorless oil (49.3 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 6.86 – 6.82 (m, 6H), 6.15 (d, *J* = 40.0 Hz, 1H), 5.57 (d, *J* = 20.0 Hz, 1H), 3.79 (s, 3H), 2.31 (s, 12H), 2.26 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 145.0 (d, *J* = 87.9 Hz), 141.3 (d, *J* = 9.1 Hz), 139.8 (d, *J* = 2.0 Hz), 129.9 (d, *J* = 11.1 Hz), 129.6 (d, *J* = 9.1 Hz), 129.2 (d, *J* = 98.0 Hz), 128.6 (d, *J* = 5.1 Hz), 125.9 (d, *J* = 13.1 Hz), 112.7, 54.2, 22.3 (d, *J* = 4.0 Hz), 19.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.8. **HRMS** (ESI) Calcd for $C_{27}H_{32}O_2P$ $[M + H]^+$ 419.2140, found 419.2137.



(1-(4-Methoxyphenyl)vinyl)(naphthalen-2-yl)(phenyl)phosphine oxide (3ah): The reaction was conducted on 0.2 mmol scale. The product **3ah** was purified by flash column chromatography (PE/EA = 1/1) to give as colorless oil (35.4 mg, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 16.0 Hz, 1H), 7.88 – 7.74 (m, 5H), 7.65 – 7.41 (m, 8H), 6.78 – 6.75 (m, 2H), 6.22 (d, *J* = 40.0 Hz, 1H), 5.69 (d, *J* = 20.0 Hz, 1H), 3.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 143.6 (d, *J* = 92.7 Hz), 134.7 (d, *J* = 2.5 Hz), 134.0 (d, *J* = 8.9 Hz), 132.5 (d, *J* = 13.1 Hz), 132.0 (d, *J* = 103.0 Hz), 131.98 (d, *J* = 9.6 Hz), 131.8 (d, *J* = 2.7 Hz), 130.4 (d, *J* = 10.4 Hz), 129.9 (d, *J* = 10.2 Hz), 129.5, 129.3 (d, *J* = 4.8 Hz), 128.9, 128.4 (d, *J* = 12.0 Hz), 128.1, 128.0, 127.8, 126.8, 126.7, 113.9, 55.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.3. **HRMS** (ESI) Calcd for $C_{25}H_{22}O_2P$ $[M + H]^+$ 385.1357, found 385.1354.



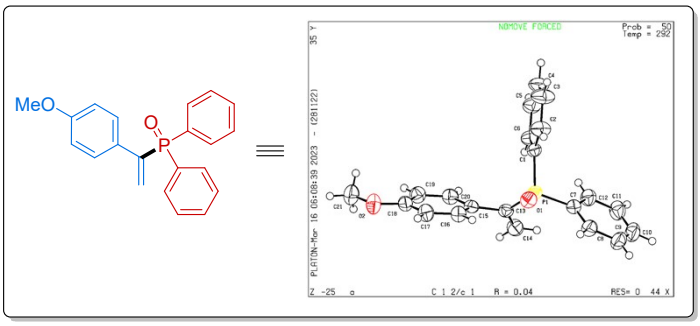
Cyclohexyl(1-(4-methoxyphenyl)vinyl)(phenyl)phosphine oxide (3ai): The reaction was conducted on 0.2 mmol scale. The product **3ai** was purified by flash column chromatography (PE/EA = 1/2) to give as colorless oil (44.3 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.49 – 7.37 (m, 3H), 7.12 – 7.10 (m, 2H), 7.80 – 7.78 (m, 2H), 6.18 (d, *J* = 20.0 Hz, 1H), 6.00 (d, *J* = 40.0 Hz, 1H), 3.78 (s, 3H), 2.06 – 1.40 (m, 11H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5, 142.9 (d, *J* =3.0 Hz), 129.7 (d, *J* = 93.9 Hz), 129.6 (d, *J* = 11.1Hz), 129.9 (d, *J* = 11.1 Hz), 129.4 (d, *J* = 7.1 Hz), 128.5 (d, *J* = 4.0 Hz), 127.2 (d, *J* = 9.1 Hz), 126.5, 112.7, 54.3, 34.7 (d, *J* = 72.7 Hz), 25.4, 25.3, 24.8, 24.1 (d, *J* = 2.0 Hz), 23.9 (d, *J* = 3.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.3. **HRMS** (ESI) Calcd for $C_{21}H_{26}O_2P$ $[M + H]^+$ 341.1670, found 341.1667.



Diphenyl (1-(4-methoxyphenyl)vinyl)phosphonate (3aj):[13] The reaction was conducted on 0.2 mmol scale. The product **3aj** was purified by flash column chromatography (PE/EA = 2/1) to give as brown oil (37.4 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.31 – 7.26 (m, 4H), 7.17 – 7.13 (m, 6H), 6.94 – 6.92 (m, 2H), 6.46 (d, *J* = 24.0, 1H), 6.24 (d, *J* = 48.0, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 149.3 (d, *J* = 8.1 Hz), 137.1 (d, *J* = 177.8 Hz), 131.7 (d, *J* = 9.1 Hz), 128.7, 128.0 (d, *J* = 6.1 Hz), 127.4 (d, *J* = 12.1 Hz), 124.1 (d, *J* = 1.0 Hz), 119.6 (d, *J* = 5.1 Hz), 113.0, 54.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 10.3.

6. X-ray Crystallographic Data

Single crystals of **3a** ($C_{21}H_{19}O_2P$) was obtained from DCM. A suitable crystal was selected and the crystal data of compound **3a** was collected on a 'Bruker APEX-II CCD' diffractometer using graphite-monochromatic Mo Kα radiation. The crystal was kept at 292.0 K during data collection. Using Olex2,[14] the structure was solved with the ShelXS[15] structure solution program using Direct Methods and refined with the ShelXL[16] refinement package using Least Squares minimisation. Crystallographic data for the structure has been deposited to the Cambridge Crystallographic Data Center (CCDC 2285977).



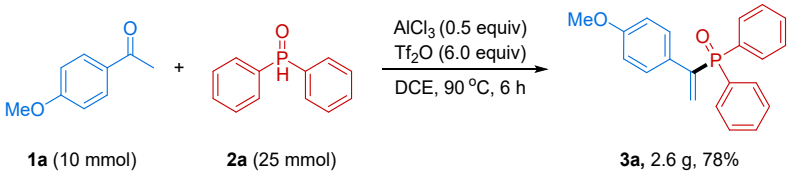
Scheme S1. Displacement ellipsoid plot of **3a** (50% probability level).

The crystallographic data are summarized in the following table.

Identification code	**3a**
Empirical formula	$C_{21}H_{19}O_2P$
Formula weight	334.33
Temperature/K	292.0
Crystal system	monoclinic
Space group	C2/c
a/Å	24.242(18)
b/Å	8.394(4)
c/Å	17.127(12)
α/°	90
β/°	99.39(4)
γ/°	90
Volume/Å^3	3438(4)
Z	8
ρ_{calc}g/cm^3	1.292
μ/mm^{-1}	0.169
F(000)	1408.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.822 to 52.744
Index ranges	-30 ≤ h ≤ 30, -10 ≤ k ≤ 10, -21 ≤ l ≤ 21
Reflections collected	36386
Independent reflections	3517 [R_{int} = 0.0959, R_{sigma} = 0.0436]
Data/restraints/parameters	3517/0/219
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.0995
Final R indexes [all data]	R_1 = 0.0579, wR_2 = 0.1081
Largest diff. peak/hole / e Å^{-3}	0.29/-0.24

7. Transformations of Product

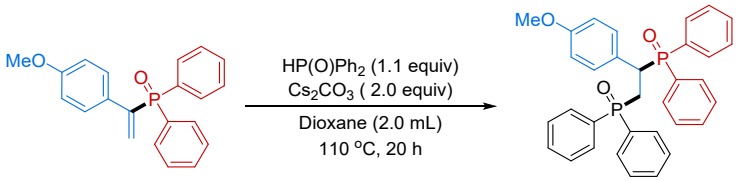
7.1 Gram-scale reaction



1a (10 mmol) **2a** (25 mmol) **3a,** 2.6 g, 78%

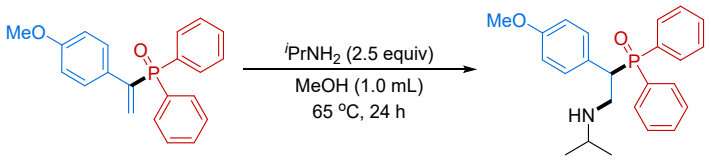
General Procedure for 10 mmol-scale reaction: Under an argon atmosphere, an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (1.5 g, 10.0 mmol, 1.0 equiv), **2a** (5.0 g, 25 mmol, 2.5 equiv), $AlCl_3$ (666 mg, 5 mmol, 0.5 equiv) and 60 mL of DCE. After stirring at room temperature for 1 minute, Tf_2O (12 mL, 60 mmol, 6.0 equiv) was added and the Schlenk tube was stirred at 90 ℃ for 6 h. After the reaction was completed (monitored by TLC analysis), the resulting mixture was quenched by saturated $NaHCO_3$ aqueous solution. The mixture was poured into 30 mL water and extracted with DCM (30 mL × 3). The combined organic layer was dried over $MgSO_4$, filtrated and evaporated to give the crude product, which was then purified on silica gel (PE/EA=1/1) to afford target compounds **3a** (2.6 g, 78% yield, white solid).

7.2 Transformations of 3a



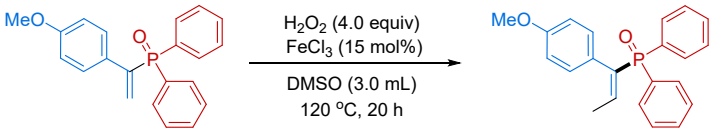
3a (0.4 mmol) **4a**, 60%

(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine oxide) (4a):[17] A 10 mL Schlenk tube equipped with a stir bar was charged with **3a** (133.6 mg, 0.4 mmol, 1.0 equiv), diphenylphosphine oxide (164.0 mg, 0.44 mmol, 1.1 equiv) and Cs_2CO_3 (262.8 mg, 0.8 mmol, 2.0 equiv). The tube was evacuated and backfilled with argon (three times), and then Dioxane (2.0 mL) was added sequentially via a syringe. The resulting mixture was stirred for 20 h at 110 ℃. After cooled to room temperature, the reaction was quenched with water (15.0 mL) and extracted with DCM (3 x 15.0 mL). The organic layer was washed with brine, and dried over $MgSO_4$ and volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (EA/MeOH = 50/1) to give the desired product **4a** (128.8 mg, 60% yield, white solid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.54 – 7.50 (m, 5H), 7.44 – 7.28 (m, 8H), 7.20 – 6.99 (m, 7H), 6.34 (d, J = 8.0 Hz, 2H), 4.27 – 4.19 (m, 1H), 3.68 (s, 3H), 3.14 – 3.07 (m, 1H), 2.83 – 2.73 (m, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 158.5 (d, J = 2.0 Hz), 134.7 (d, J = 100.0 Hz), 132.3, 132.1 (d, J = 2.0 Hz), 131.8 (d, J = 2.0 Hz), 131.7 (d, J = 101 Hz), 131.6 (d, J = 8.1 Hz), 131.4 (d, J = 2.0 Hz), 131.3 (d, J = 5.1 Hz), 131.0, 130.9 (d, J = 9.1 Hz), 130.8 (d, J = 10.1 Hz), 130.3 (d, J = 10.1 Hz), 129.1 (d, J = 12.1 Hz), 128.7 (d, J = 11.1 Hz), 128.1 (d, J = 11.1 Hz), 127.9 (d, J = 12.1 Hz), 126.0 (d, J = 5.1 Hz), 113.5, 55.1, 38.5 (dd, J = 66.7, 3.0 Hz), 30.4 (d, J = 69.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.0 (d, J = 48.6 Hz), 29.8 (d, J = 48.6 Hz).



3a (0.4 mmol) **4b**, 68%

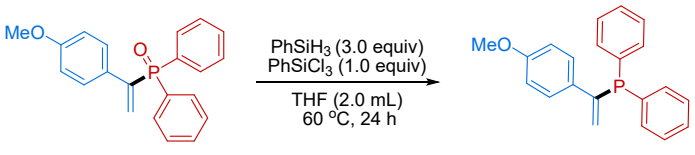
(2-(Isopropylamino)-1-(4-methoxyphenyl)ethyl)diphenylphosphine oxide (4b): Isopropylamine (1.0 mmol, 2.5 equiv) was added to **3a** (133.6 mg, 0.4 mmol) in CH_3OH (1 mL) and heated at 65 °C for 24 h in a sealed tube. After the reaction was completed (monitored by TLC analysis), the reaction was added with water (15.0 mL) and the resulting mixture was extracted with DCM (3 x 15.0 mL). The organic layer was washed with brine, and dried over $MgSO_4$ and volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (EA/CH_3OH = 10/1) to give the desired product **4b** (107 mg, 68% yield, colorless oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.47 – 7.28 (m, 6H), 7.21 – 7.08 (m, 4H), 6.66 (d, *J* = 8.0 Hz, 2H), 3.93 – 3.85 (m, 2H), 3.65 (s, 3H), 3.30 – 3.23 (m, 1H), 3.12 – 3.06 (m, 1H), 2.76 – 2.69 (m, 1H), 0.91 – 0.89 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1 (d, *J* = 2.0 Hz), 132.1 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 96.0 Hz), 131.59 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 100.0 Hz), 130.8 (d, *J* = 12.1 Hz), 131.3 (d, *J* = 13.1 Hz), 130.9 (d, *J* = 6.1 Hz), 128.9 (d, *J* = 11.1 Hz), 128.2 (d, *J* = 12.1 Hz), 125.6 (d, *J* = 4.0 Hz), 114.2 (d, *J* = 3.0 Hz), 55.2, 48.9, 46.4, 45.2 (d, *J* = 66.7 Hz), 21.8 (d, *J* = 3.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.6. **HRMS** (ESI) Calcd for $C_{24}H_{29}NO_2P$ $[M + H]^+$ 394.1936, found 394.1933.



3a (0.4 mmol) **4c**, 45%, *E*-isomers

(*E*)-(1-(4-Methoxyphenyl)prop-1-en-1-yl)diphenylphosphine oxide (4c): A 10 mL Schlenk tube equipped with a stir bar was charged with **3a** (133.6 mg, 0.4 mmol, 1.0 equiv) and $FeCl_3$ (9.73 mg, 15 mol%). The tube was evacuated and backfilled with argon (three times), and then H_2O_2 (164 μL, 1.6 mmol) and DMSO (3.0 mL) was added sequentially via a syringe. The resulting mixture was stirred for 20 h at 120 °C. After cooled to room temperature, the reaction was added with water (15.0 mL) and the resulting mixture was extracted with DCM (3 x 15.0 mL). The organic layer was washed with brine, and dried over $MgSO_4$ and volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (EA/PE = 2/1) to give the desired product **4c** (62.7 mg, 45% yield, *E*/*Z* >20:1, colorless oil). Spectroscopic data in agreement with **3p**.

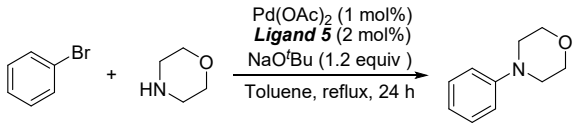
7.3 Application of 3a



3a (1.0 mmol) **5**, 66%

(1-(4-Methoxyphenyl)vinyl)diphenylphosphane (5):[18] A 10 mL oven-dried sealed tube equipped with a magnetic stir bar was charged with **3a** (334.1 mg, 1.0 mmol, 1.0 equiv). The tube was evacuated and backfilled with argon (three times) and then THF (2.0 mL), $PhSiH_3$ (3.0 mmol, 370 μL, 3.0 equiv) and $PhSiCl_3$ (1.0 mmol, 163 μL, 1.0 equiv) was added sequentially via a syringe. The resulting mixture was

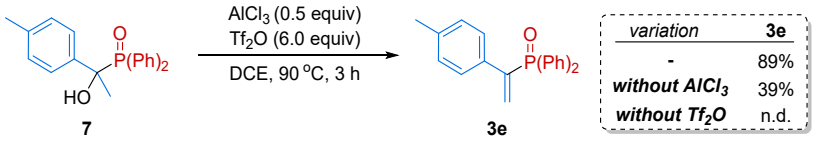
stirred for 24 h at 60 °C. After cooled to room temperature, the reaction was quenched with water (10.0 mL) and the resulting mixture was extracted with ethyl acetate (3 x 15.0 mL). The organic layer was washed with brine, and dried over $MgSO_4$ and volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA = 30/1) to give the desired product **5** (210.1 mg, 66% yield, white solid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 2H), 7.40 – 7.36 (m, 4H), 7.28 – 7.27 (m, 6H), 6.77 (d, *J* = 12.0 Hz, 2H), 5.89 (d, *J* = 16.0 Hz, 1H), 4.86 (d, *J* = 4.0 Hz, 1H), 3.68 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3 (d, *J* = 2.0 Hz), 147.8 (d, *J* = 16.2 Hz), 135.6 (d, *J* = 10.1 Hz), 134.4 (d, *J* = 19.2 Hz), 134.2 (d, *J* = 12.1 Hz), 133.3 (d, *J* = 10.1 Hz), 129.0, 128.5 (d, *J* = 8.1 Hz), 122.8 (d, *J* = 5.1 Hz), 113.8, 55.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -5.5.



4-Phenylmorpholine (6):[19] A 10 mL oven-dried sealed tube equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (0.8 mg, 1 mol%), **5** (2.5 mg, 2 mol%), NaO^tBu (46 mg, 1.2 equiv). The tube was evacuated and backfilled with argon (three times) and then PhBr (42 μL, 0.4 mmol, 1.0 equiv), morpholine (42 μL, 0.48 mmol, 1.2 equiv) and Toluene (2.0 mL) was added sequentially via a syringe. The resulting mixture was stirred at reflux for 24 h. After cooled to room temperature, the reaction was added with water (15.0 mL) and the resulting mixture was extracted with ethyl acetate (3 x 15.0 mL). The organic layer was washed with brine, and dried over $MgSO_4$ and volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA = 5/1) to give the desired product **6** (52.2 mg, 80% yield, white solid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 6.95 – 6.89 (m, 3H), 3.89 – 3.87 (m, 4H), 3.19 – 3.16 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 129.2, 120.1, 115.8, 67.0, 49.4.

8. Investigation of Reaction Mechanism

8.1 Transformation of intermediates

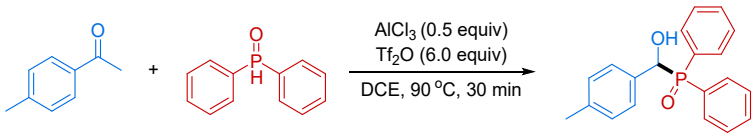


Under an argon atmosphere, an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged with **7** (67.2 mg, 0.2 mmol, 1.0 equiv), $AlCl_3$ (13.3 mg, 0.1 mmol, 0.5 equiv) and 1.5 mL of DCE. After stirring at room temperature for 1 minute, Tf_2O (201 μL, 1.2 mmol, 6.0 equiv) was added and the Schlenk tube was stirred at 90 °C for 3 h. After the reaction was completed (monitored by TLC analysis), the resulting mixture was quenched by saturated $NaHCO_3$ aqueous solution. The mixture was poured into 15.0 mL water and extracted with ethyl acetate (15.0 mL × 3). The combined organic layer was dried over $MgSO_4$, filtrated and evaporated to give the crude product, which was then purified on silica gel (PE/EA = 1/1) to afford target compounds **3e**.

*As shown in the figure above. The target product **3e** could be obtained in 89% yield when benzyl alcohol **7** was used under standard conditions. However, only 38% yield was obtained when the reaction was carried out in the absence of $AlCl_3$, and no product was detected in the absence of Tf_2O. These results*

suggest that 7 may be the intermediate of the reaction, and Tf_2O plays an important role in the dehydration of intermediate.

8.2 Detection of intermediates



1e **2a** **7**, *detected by HRMS*

HRMS
found: 359.1178

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-methylacetophenone **1e** (0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (0.5 mmol, 2.5 equiv), and $AlCl_3$ (13.3 mg, 0.1 mmol, 0.5 equiv). The tube was deoxygenated with Argon for 3 times, followed by the addition of DCE (1.5 mL). Subsequently, the flask was stirred under Argon for 1 minute with the aim of fully dissolving secondary phosphorus oxides **2a**. After a rapid addition of Tf_2O (201 μL, 1.2 mmol, 6.0 equiv) to the reaction system, the flask was sealed and reacted at 90 ℃ for 30 min. The resulting mixture was diluted with 5.0 mL DCM and quenched by 5.0 mL saturated $NaHCO_3$ aqueous solution. The mixture was poured into 15.0 mL water and extracted with DCM (15.0 mL × 3). The combined organic layer was dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The residue was detected by HRMS to confirmation of the presence of Intermediate **7**. **HRMS (ESI)**: calcd for $C_{21}H_{21}O_2PNa$ $[M + Na]^+$: 359.1171, found: 359.1178.

9. References

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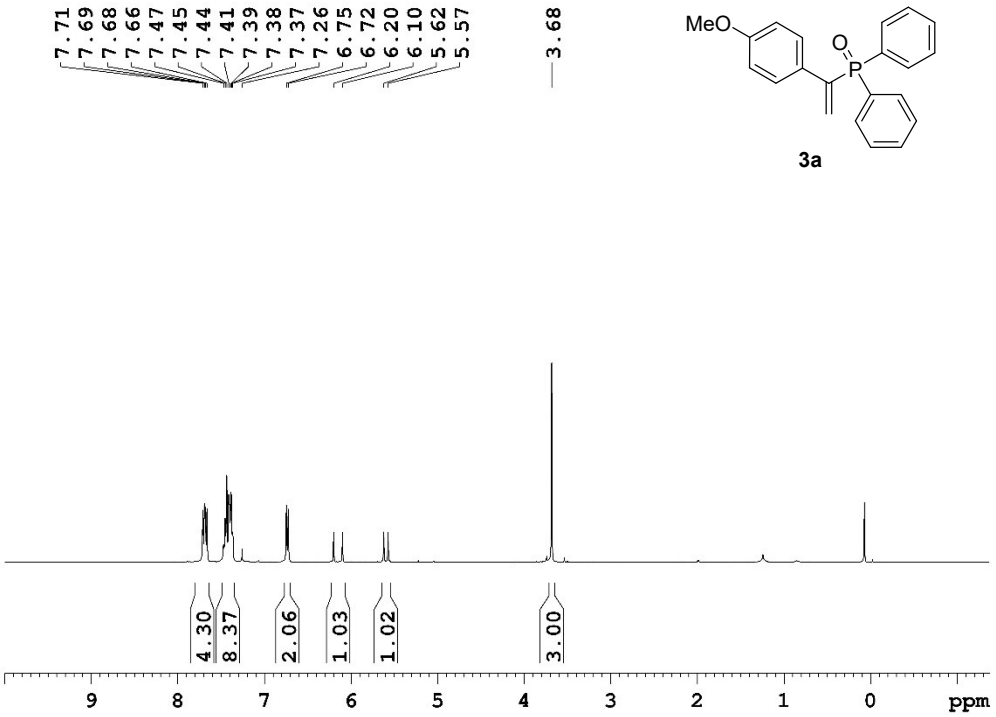
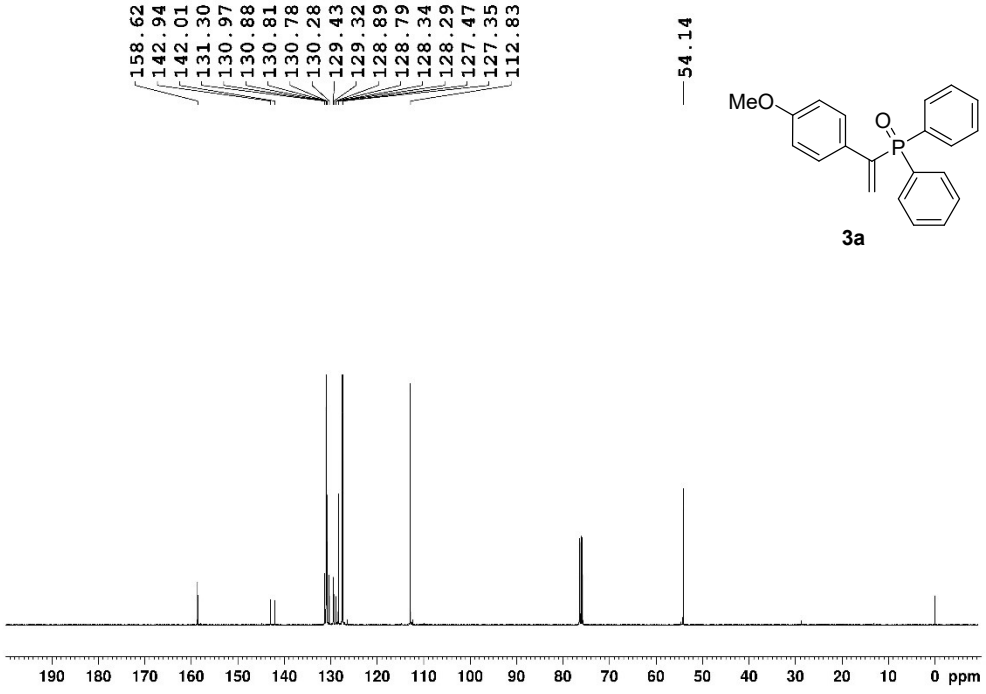
[19] B. Adhikari, M. Teimouri, J. W. Akin, S. Raju, S. L. Stokes, J. P. Emerson, *Eur. J. Org. Chem.* **2023**, e202300620.

10. NMR spectra of products: ^{1}H, ^{13}C and ^{31}P NMR

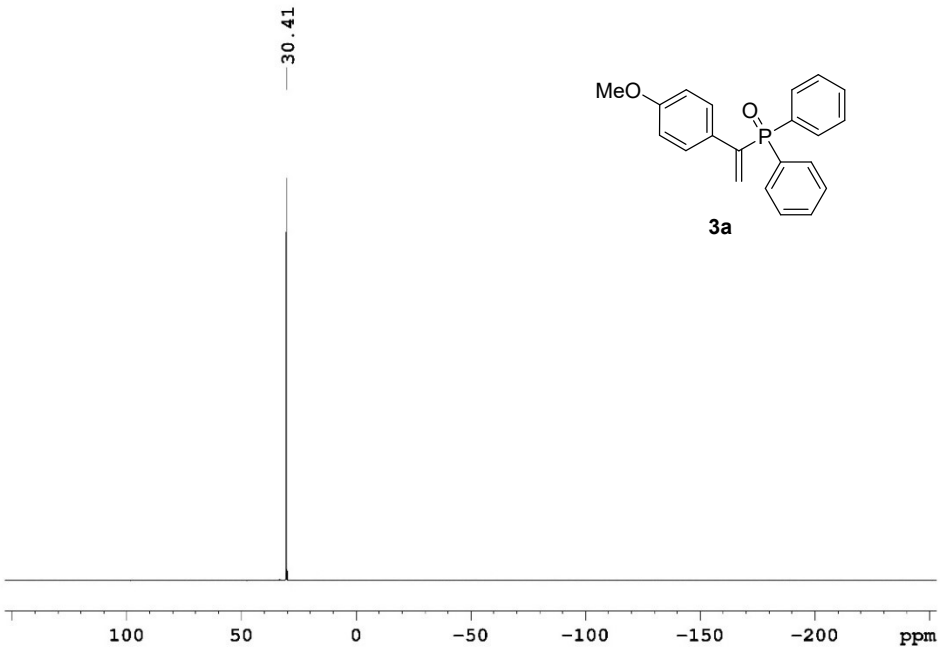
(1-(4-Methoxyphenyl)vinyl)diphenylphosphine oxide (3a): ^{1}H NMR (400 MHz, $CDCl_3$)



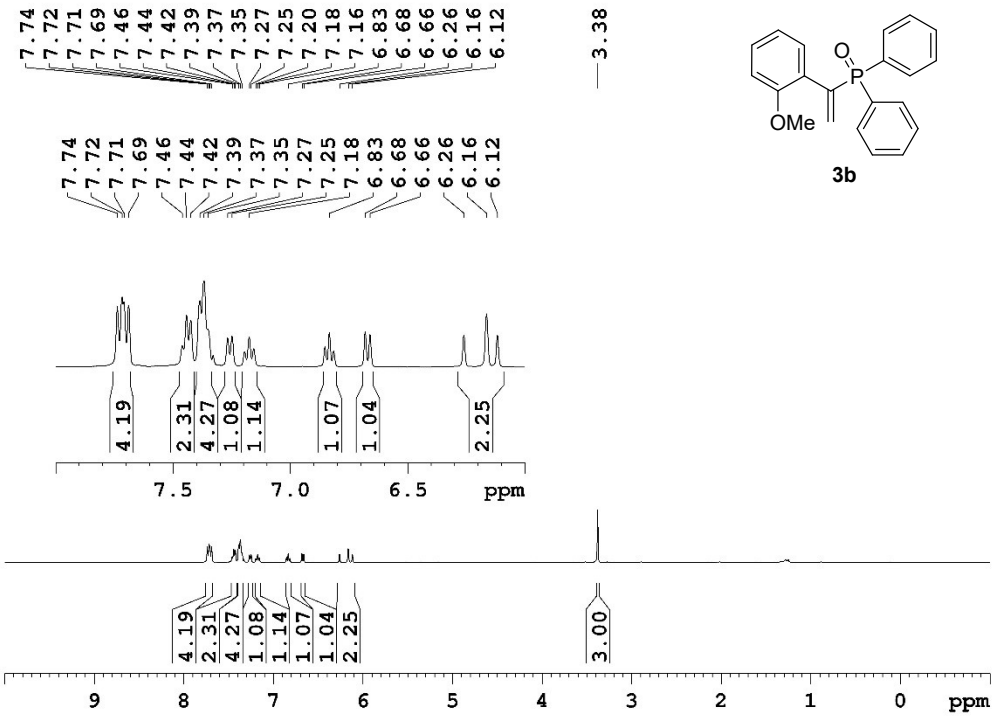
(1-(4-Methoxyphenyl)vinyl)diphenylphosphine oxide (3a): ^{13}C NMR (101 MHz, $CDCl_3$)



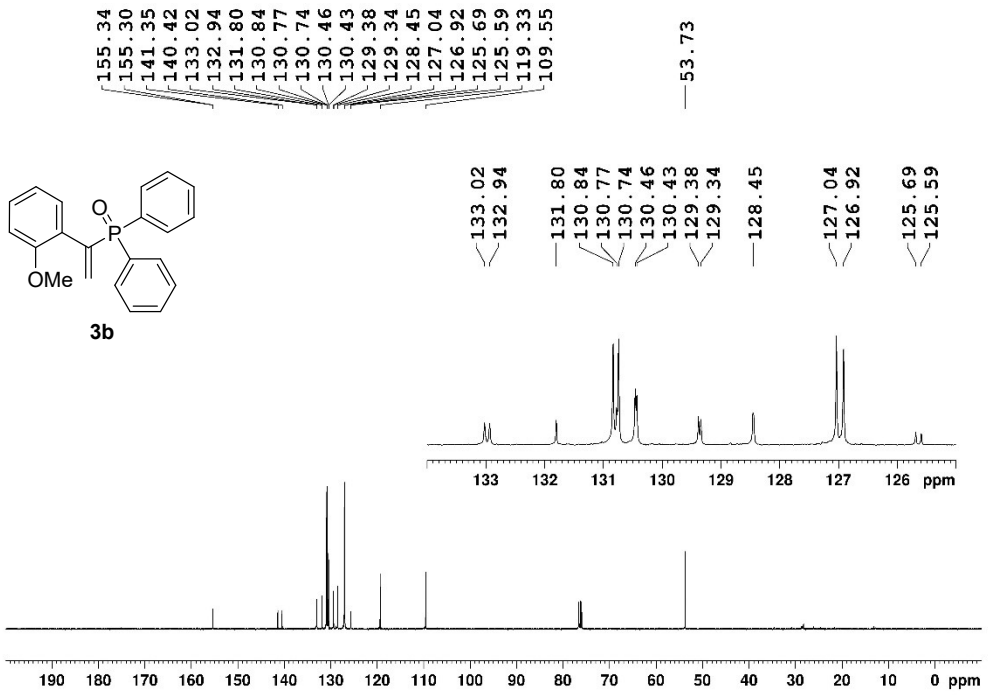
(1-(4-Methoxyphenyl)vinyl)diphenylphosphine oxide (3a): ^{31}P NMR (162 MHz, $CDCl_3$)



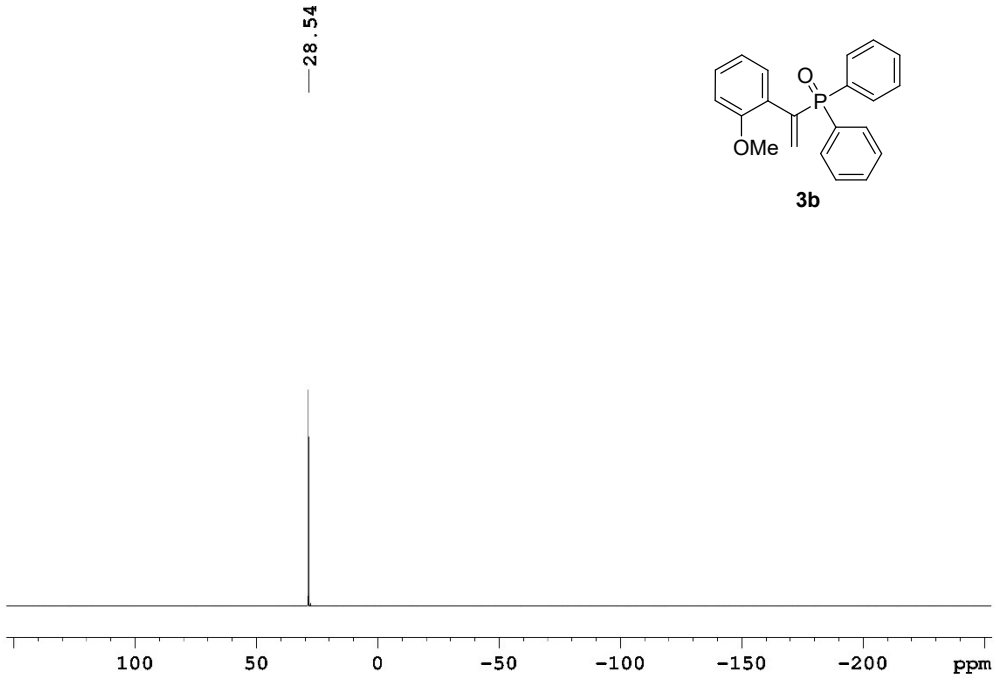
(1-(2-Methoxyphenyl)vinyl)diphenylphosphine oxide (3b): ^{1}H NMR (400 MHz, $CDCl_3$)



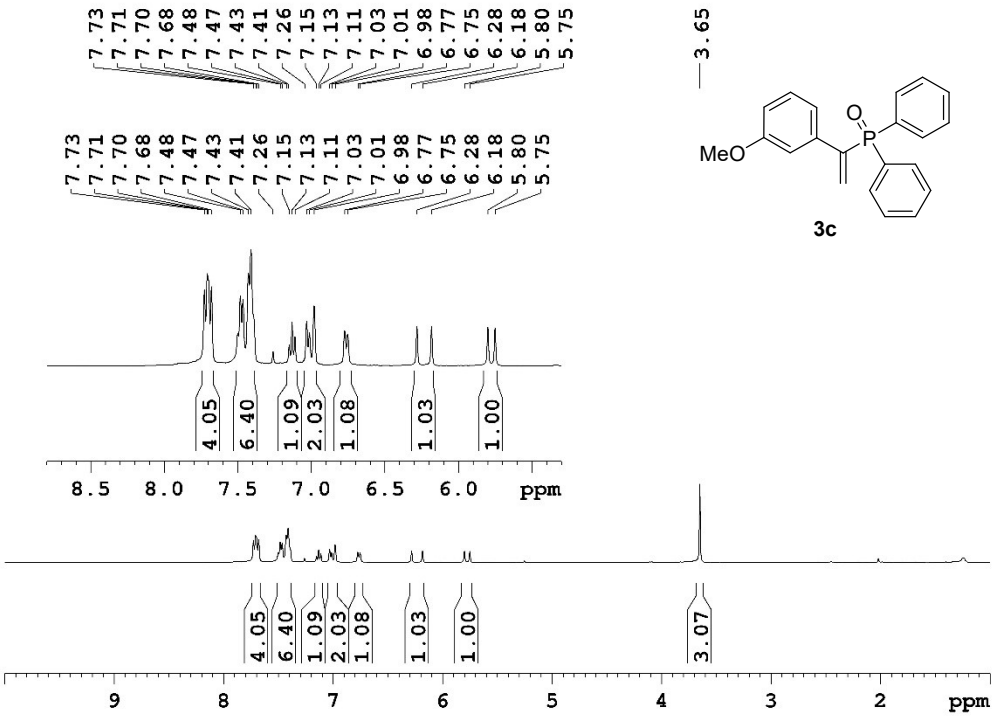
(1-(2-Methoxyphenyl)vinyl)diphenylphosphine oxide (3b): ^{13}C NMR (101 MHz, $CDCl_3$)



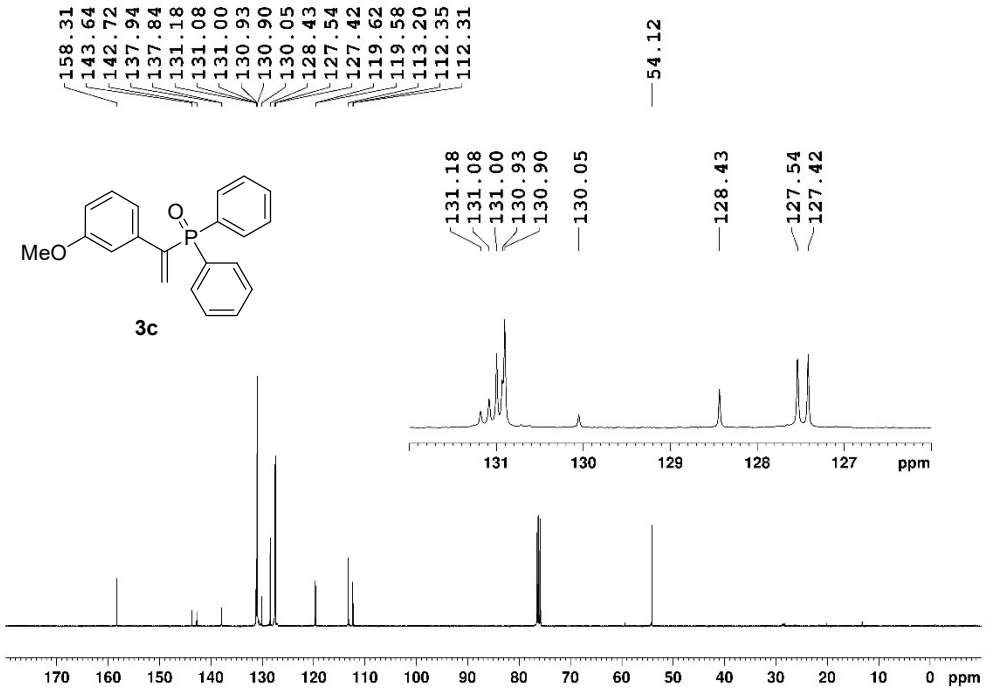
(1-(2-Methoxyphenyl)vinyl)diphenylphosphine oxide (3b): ^{31}P NMR (162 MHz, $CDCl_3$)



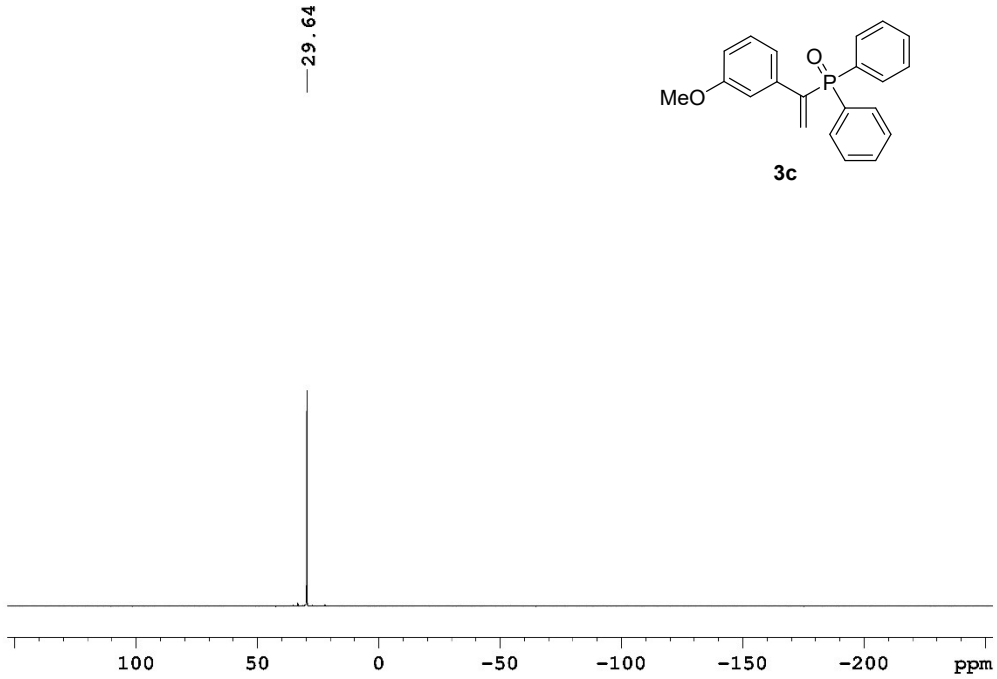
(1-(3-Methoxyphenyl)vinyl)diphenylphosphine oxide (3c): ^{1}H NMR (400 MHz, $CDCl_3$)



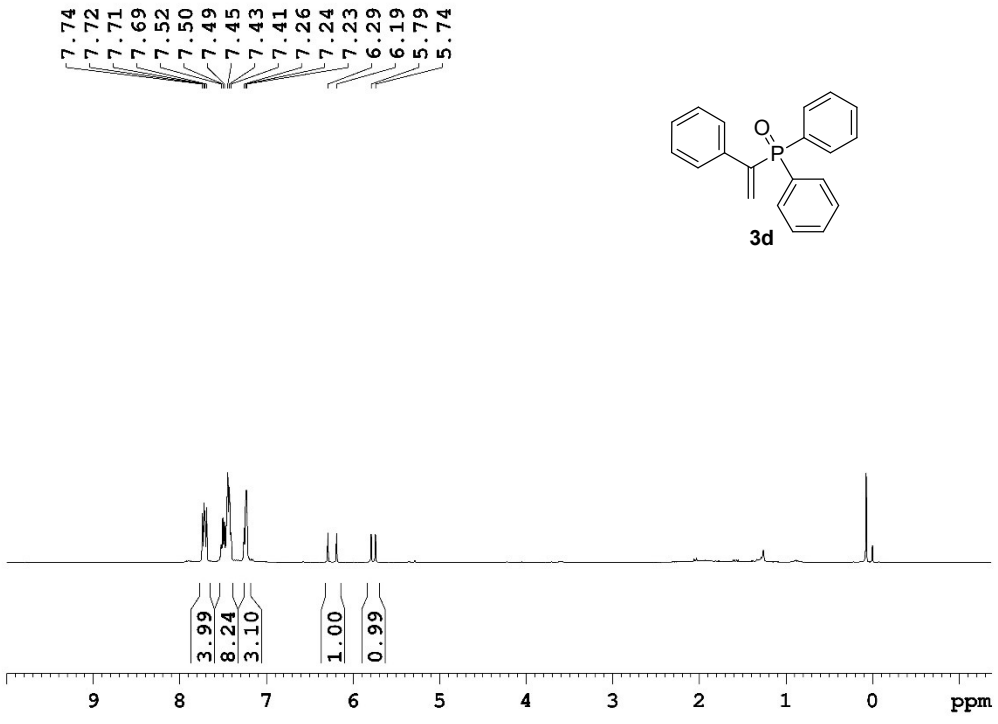
(1-(3-Methoxyphenyl)vinyl)diphenylphosphine oxide (3c): ^{13}C NMR (101 MHz, $CDCl_3$)



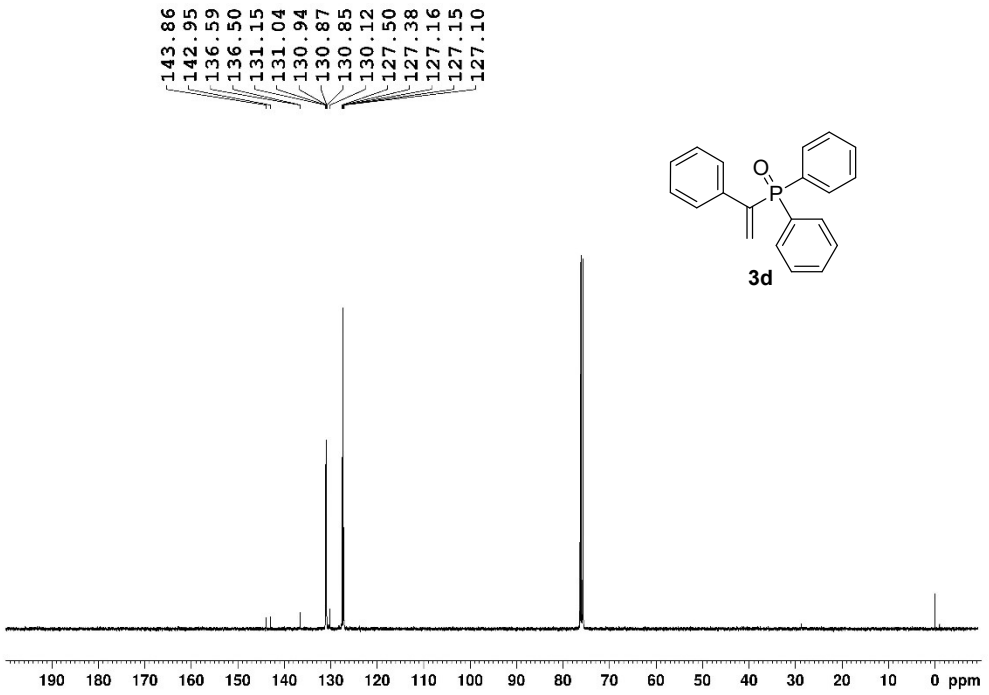
(1-(3-Methoxyphenyl)vinyl)diphenylphosphine oxide (3c): ^{31}P NMR (162 MHz, $CDCl_3$)



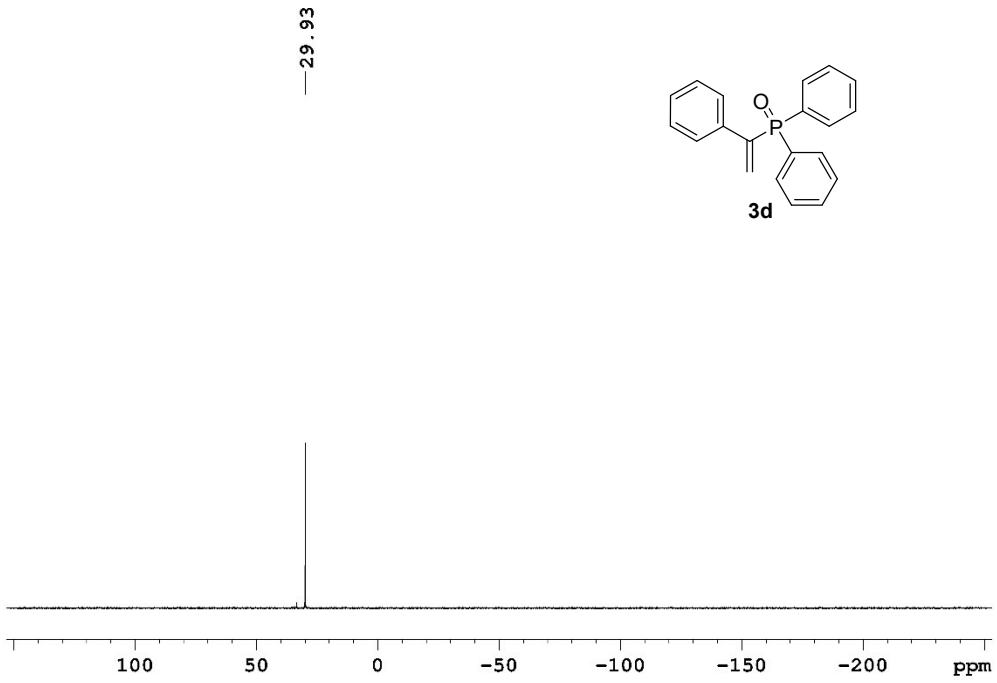
Diphenyl(1-phenylvinyl)phosphine oxide (3d): ^{1}H NMR (400 MHz, $CDCl_3$)



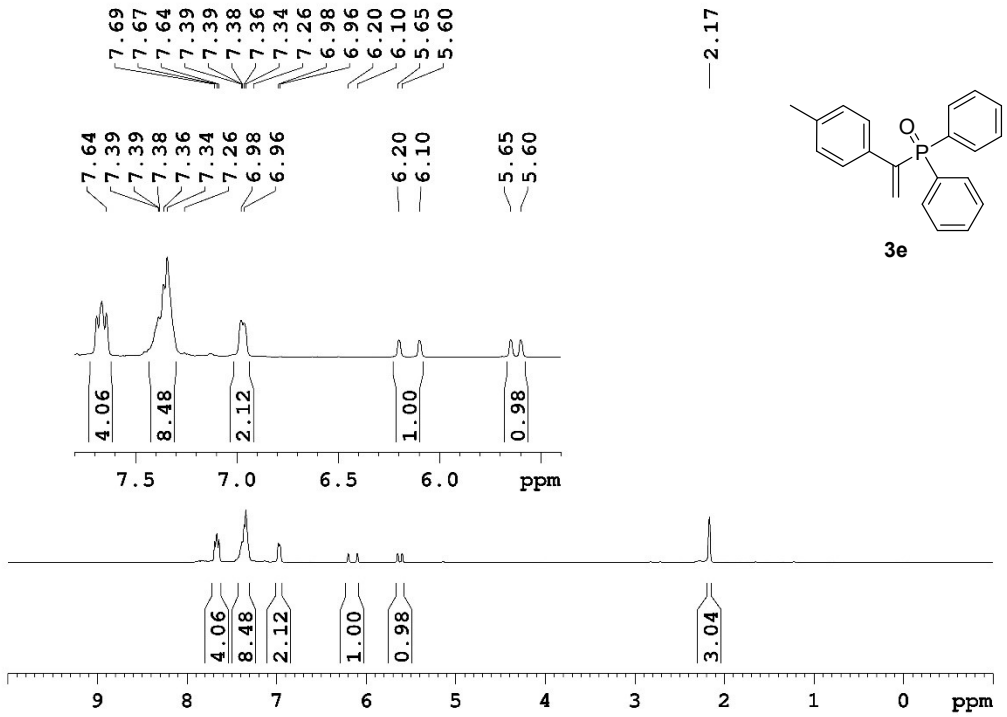
Diphenyl(1-phenylvinyl)phosphine oxide (3d): ^{13}C NMR (101 MHz, $CDCl_3$)



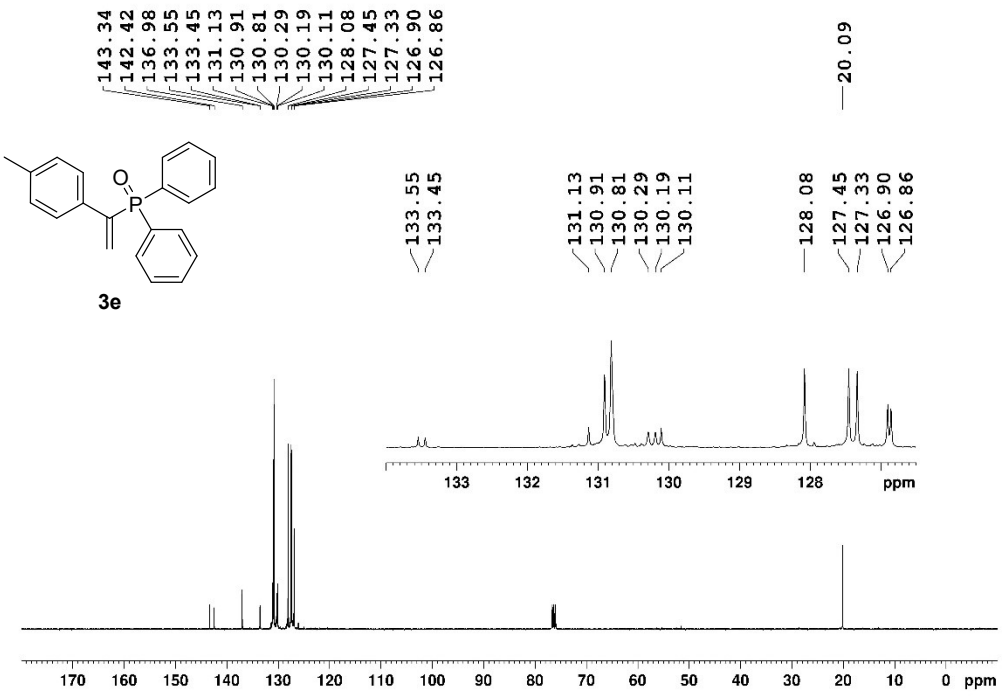
Diphenyl(1-phenylvinyl)phosphine oxide (3d): ^{31}P NMR (162 MHz, $CDCl_3$)



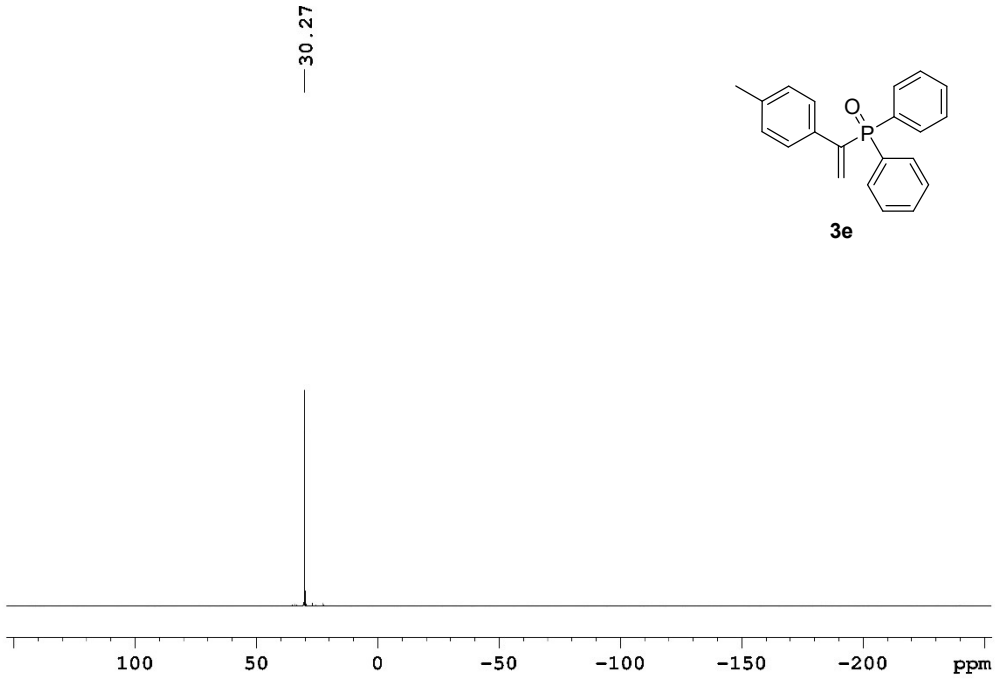
Diphenyl(1-(*p*-tolyl)vinyl)phosphine oxide (3e): ^{1}H NMR (400 MHz, $CDCl_3$)



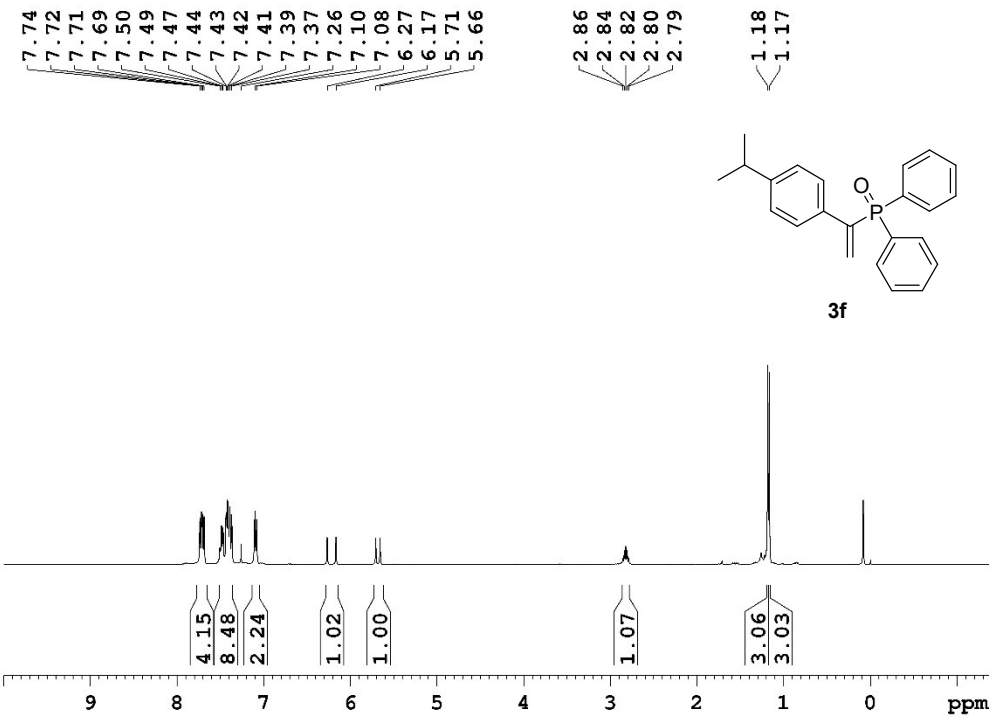
Diphenyl(1-(*p*-tolyl)vinyl)phosphine oxide (3e): ^{13}C NMR (101 MHz, $CDCl_3$)



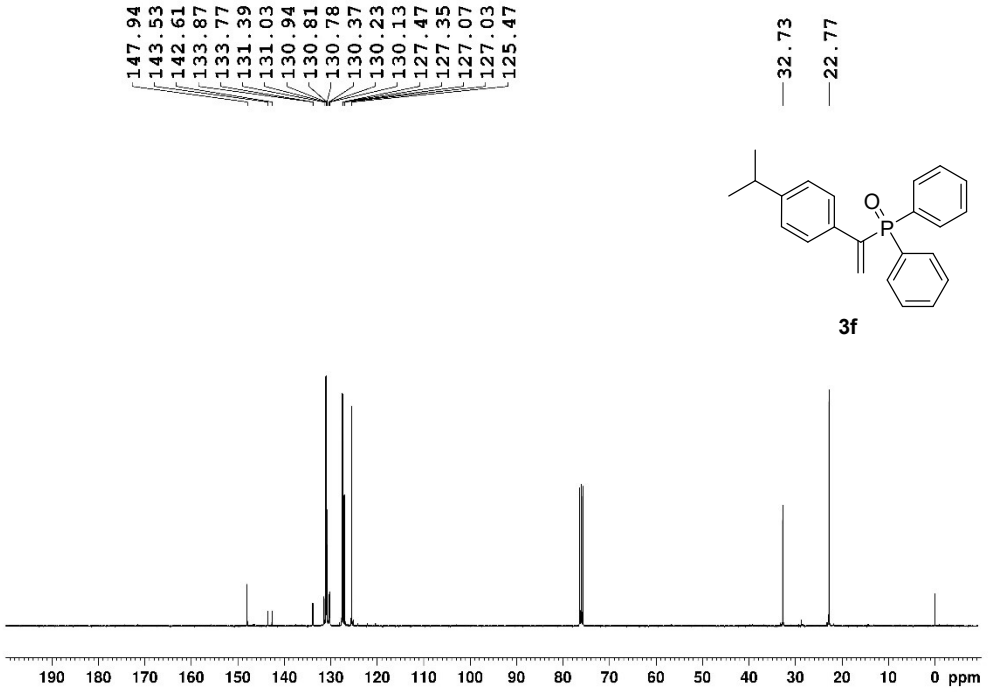
Diphenyl(1-(*p*-tolyl)vinyl)phosphine oxide (3e): ^{31}P NMR (162 MHz, $CDCl_3$)



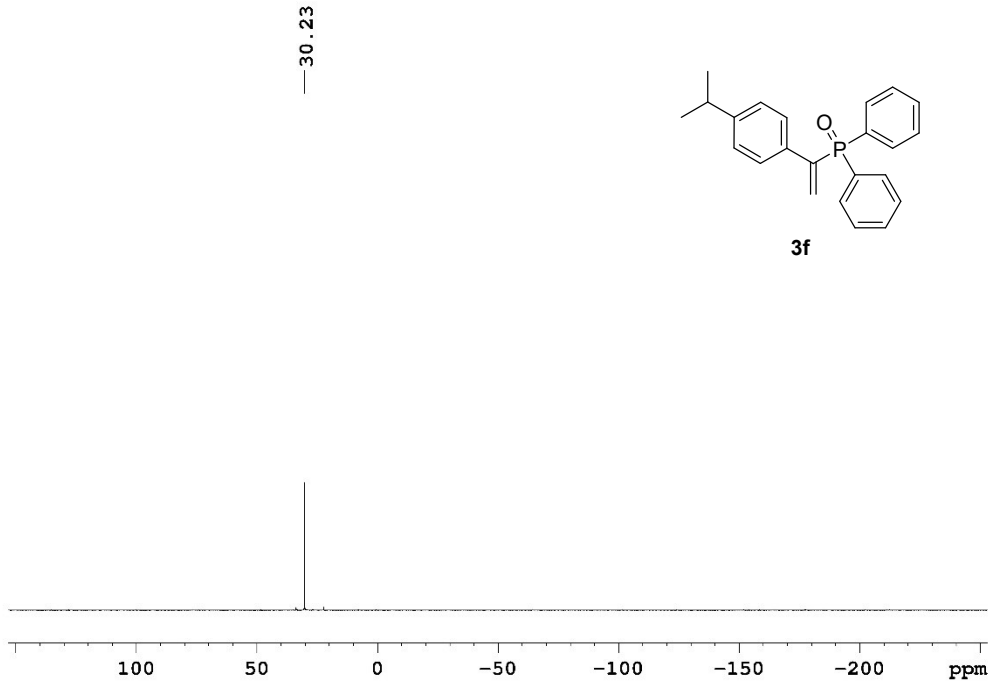
(1-(4-Isopropylphenyl)vinyl)diphenylphosphine oxide (3f): ^{1}H NMR (400 MHz, $CDCl_3$)



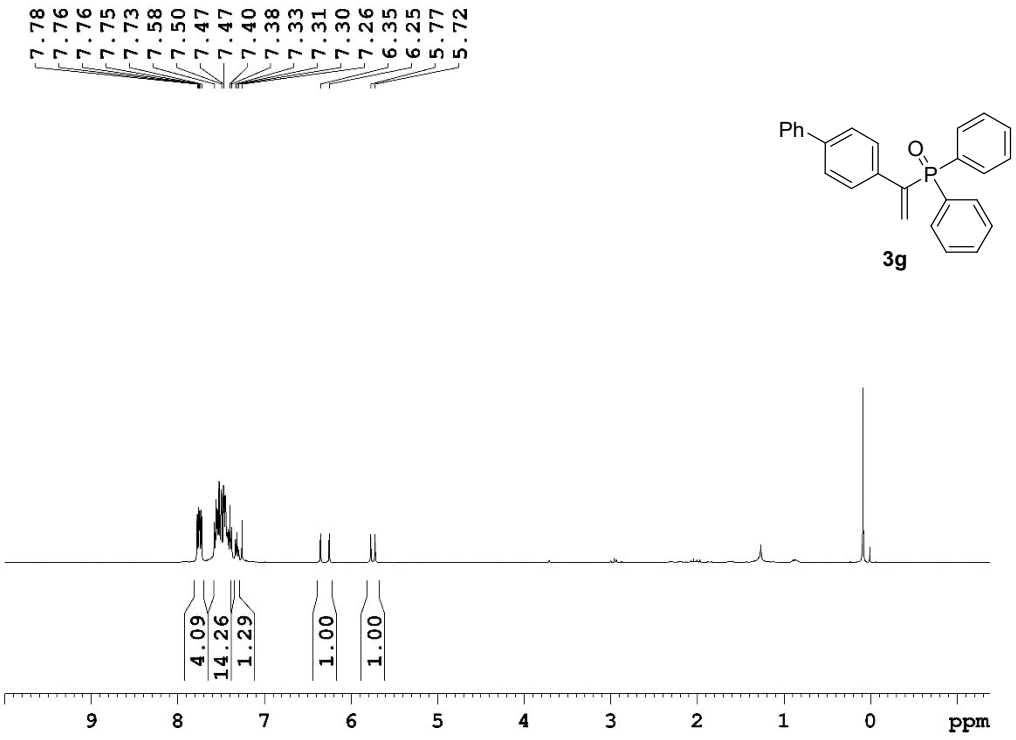
(1-(4-Isopropylphenyl)vinyl)diphenylphosphine oxide (3f): ^{13}C NMR (101 MHz, $CDCl_3$)



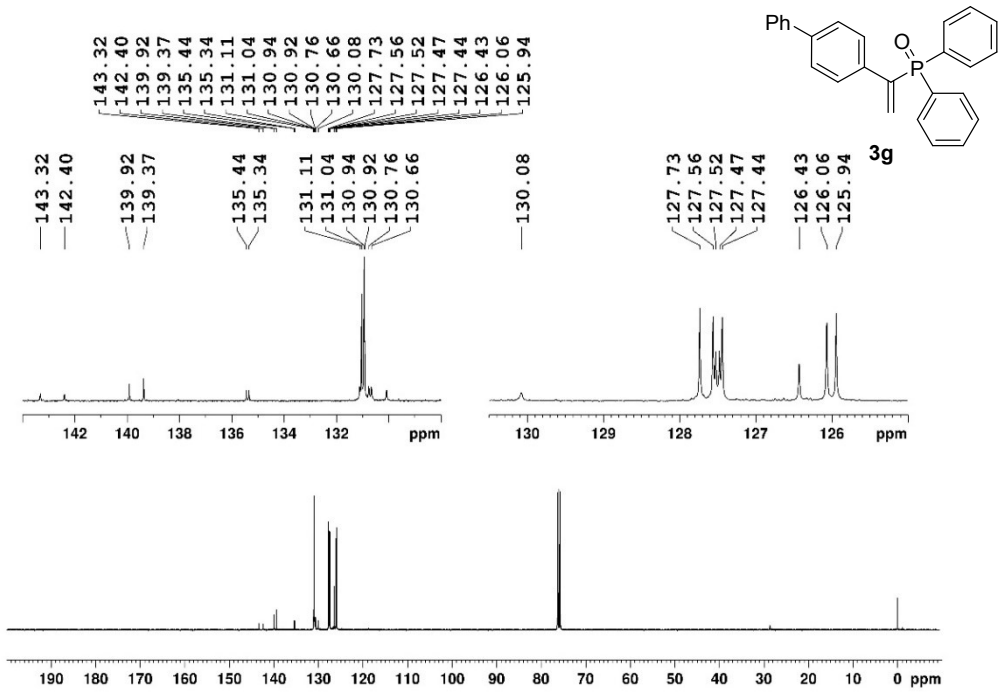
(1-(4-Isopropylphenyl)vinyl)diphenylphosphine oxide (3f): ^{31}P NMR (162 MHz, $CDCl_3$)



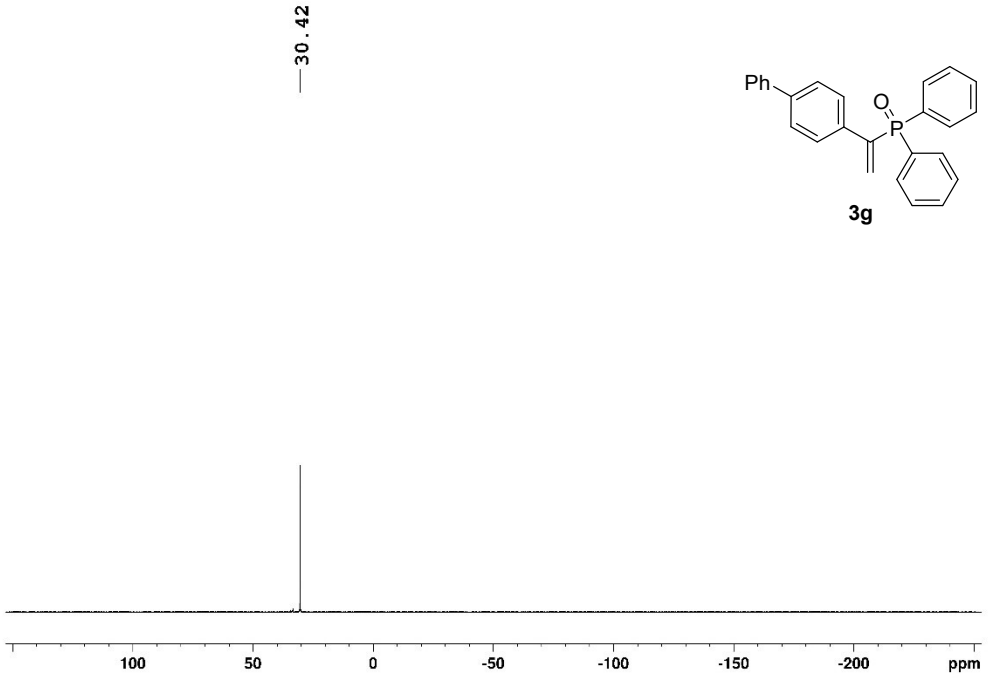
(1-([1,1'-Biphenyl]-4-yl)vinyl)diphenylphosphine oxide (3g): ^{1}H NMR (400 MHz, $CDCl_3$)



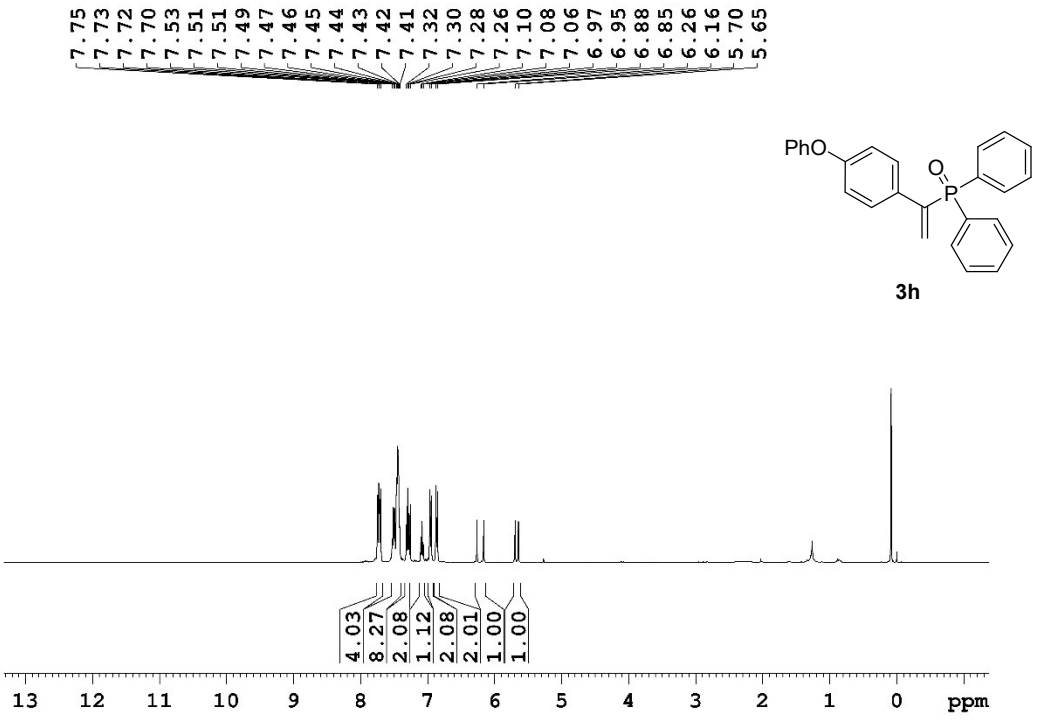
(1-([1,1'-Biphenyl]-4-yl)vinyl)diphenylphosphine oxide (3g): ^{13}C NMR (101 MHz, $CDCl_3$)



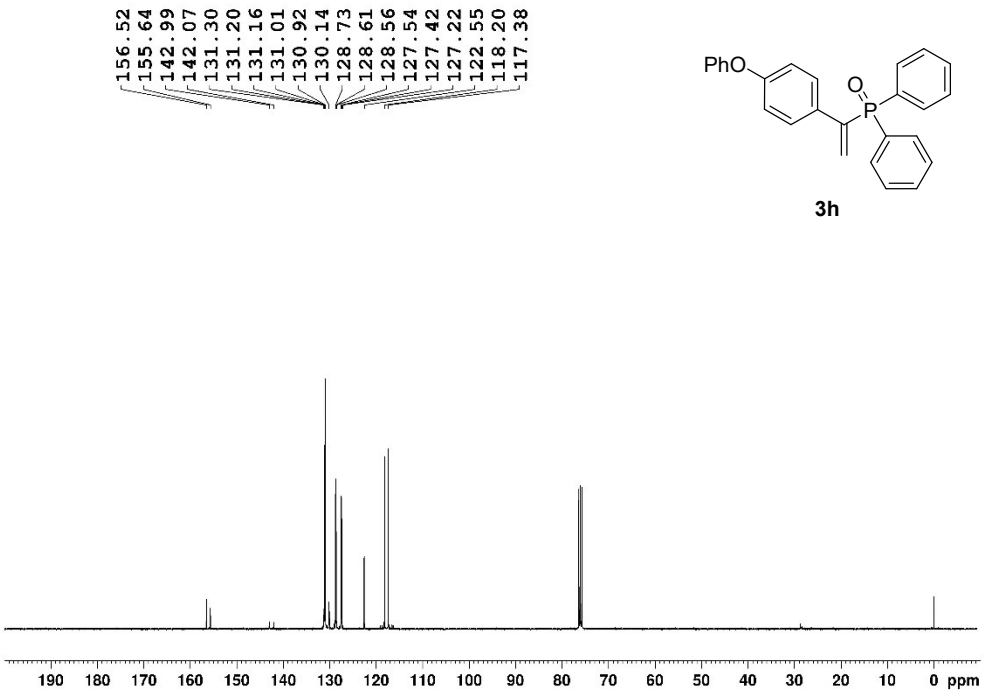
(1-([1,1'-Biphenyl]-4-yl)vinyl)diphenylphosphine oxide (3g): ^{31}P NMR (162 MHz, $CDCl_3$)



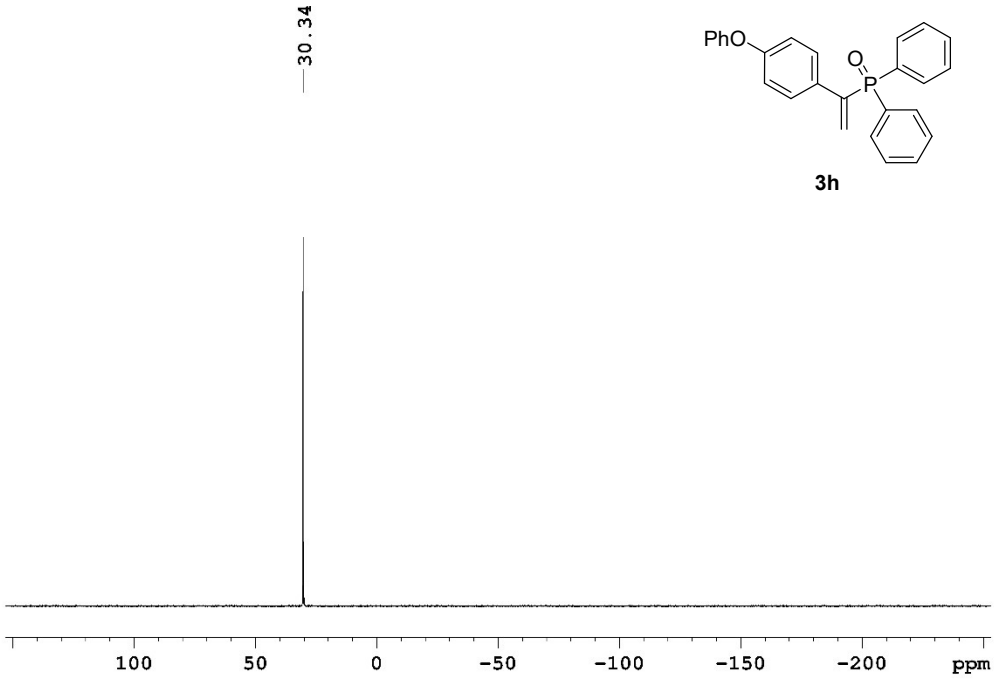
(1-(4-Phenoxyphenyl)vinyl)diphenylphosphine oxide (3h): ^{1}H NMR (400 MHz, $CDCl_3$)



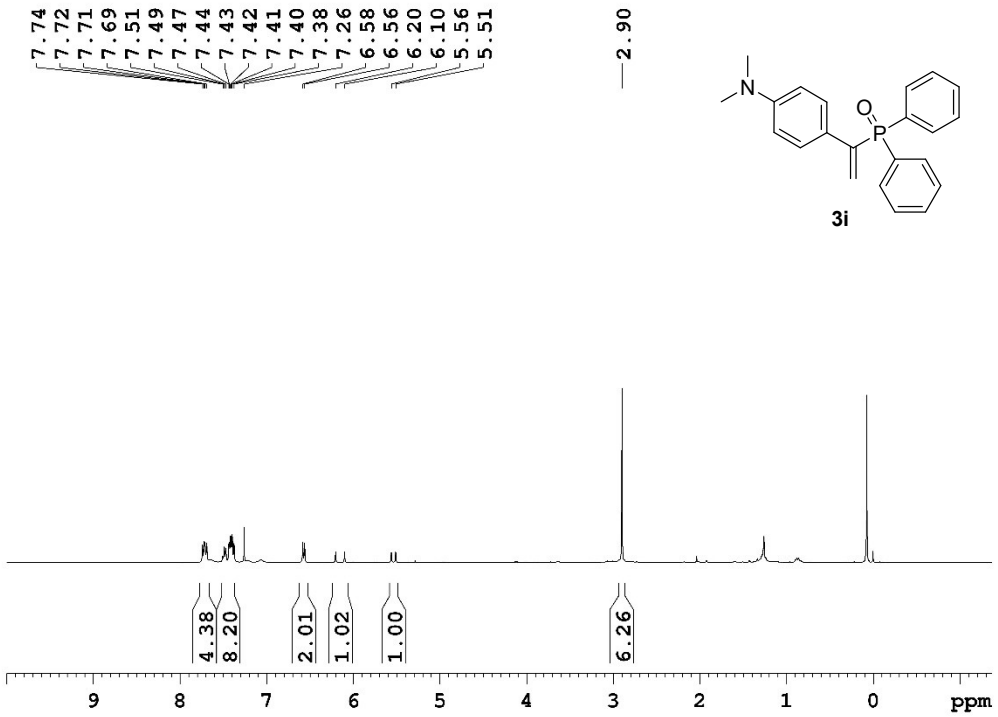
(1-(4-Phenoxyphenyl)vinyl)diphenylphosphine oxide (3h): ^{13}C NMR (101 MHz, $CDCl_3$)



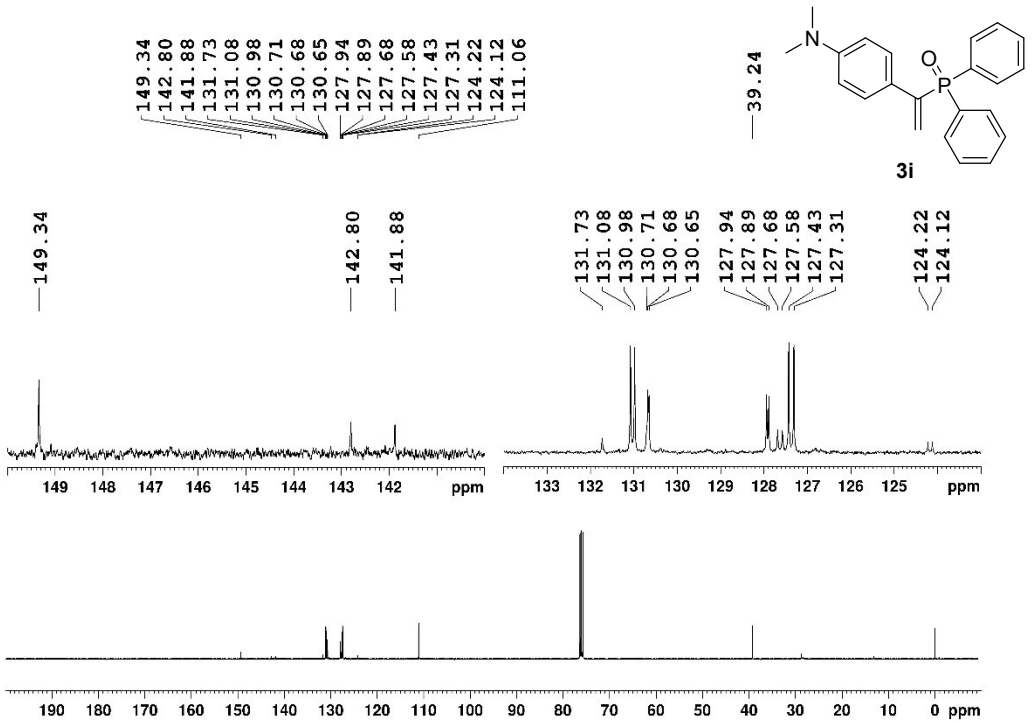
(1-(4-Phenoxyphenyl)vinyl)diphenylphosphine oxide (3h): ^{31}P NMR (162 MHz, $CDCl_3$)



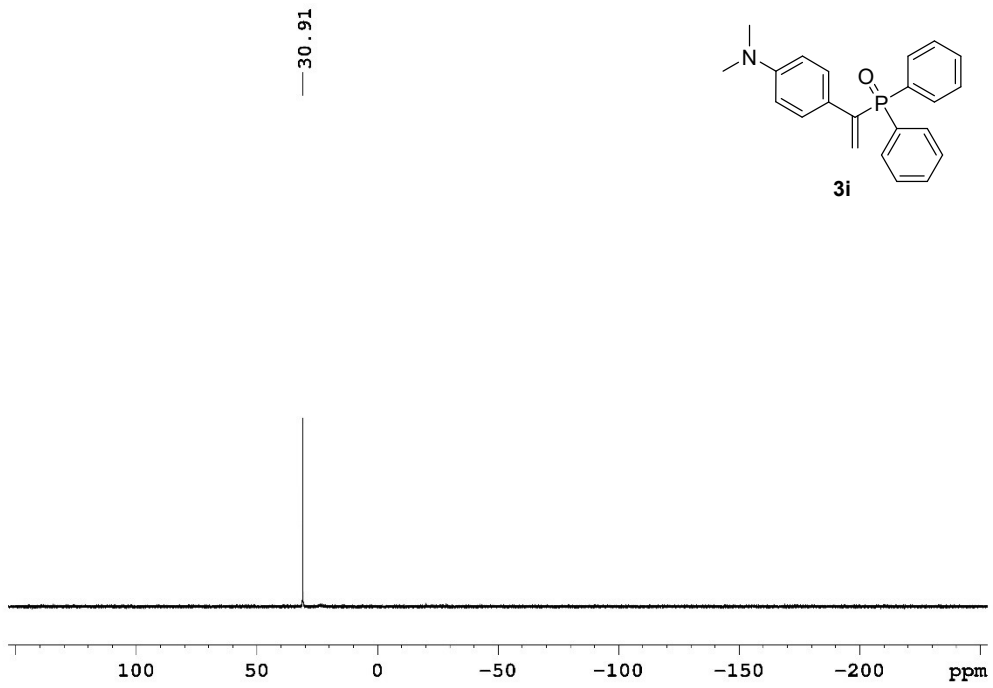
(1-(4-(Dimethylamino)phenyl)vinyl)diphenylphosphine oxide (3i): ^{1}H NMR (400 MHz, $CDCl_3$)



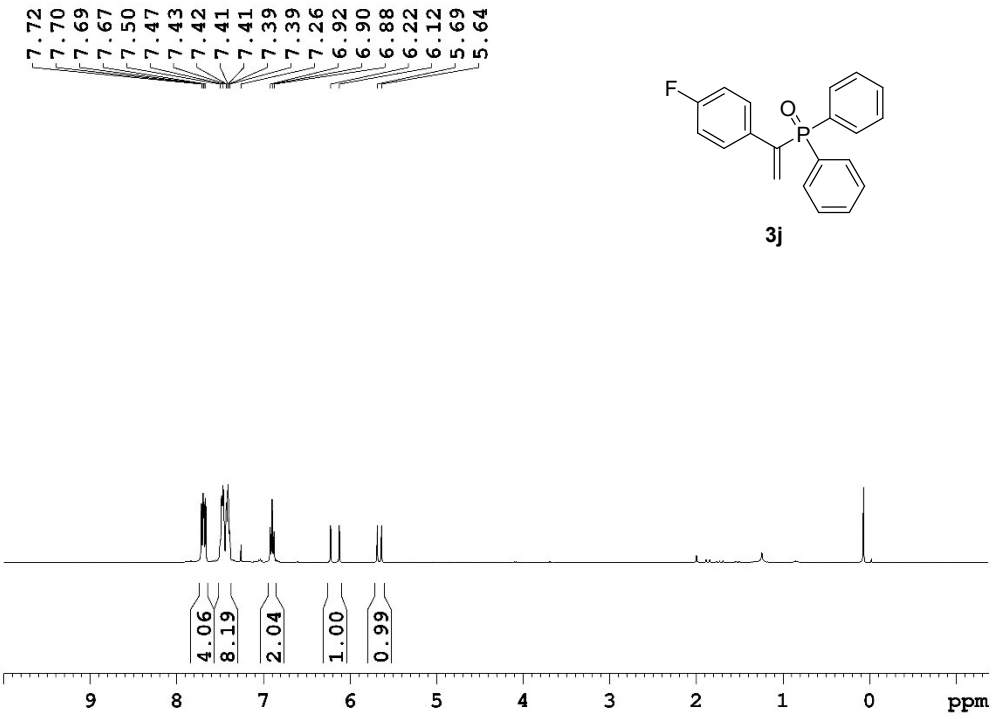
(1-(4-(Dimethylamino)phenyl)vinyl)diphenylphosphine oxide (3i): ^{13}C NMR (101 MHz, $CDCl_3$)



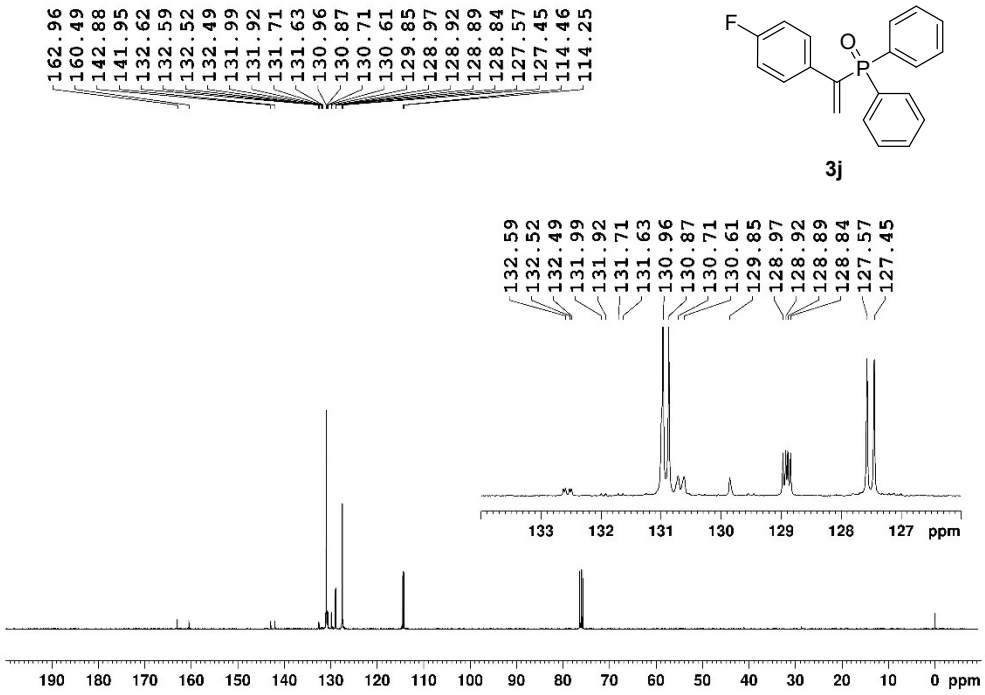
(1-(4-(Dimethylamino)phenyl)vinyl)diphenylphosphine oxide (3i): ^{31}P NMR (162 MHz, $CDCl_3$)



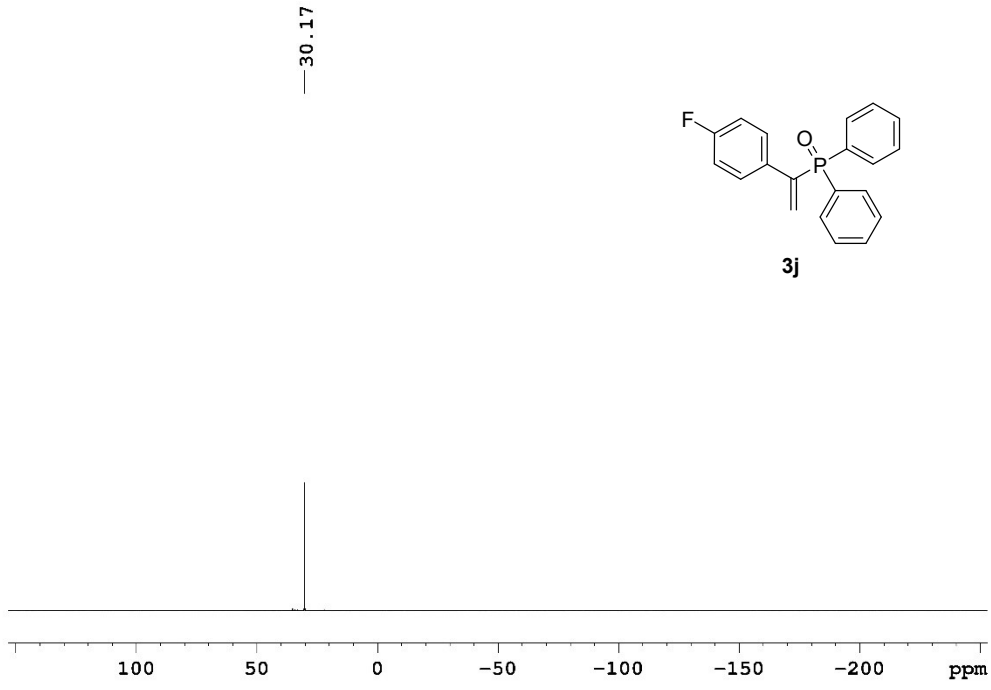
(1-(4-Fluorophenyl)vinyl)diphenylphosphine oxide (3j): ^{1}H NMR (400 MHz, $CDCl_3$)



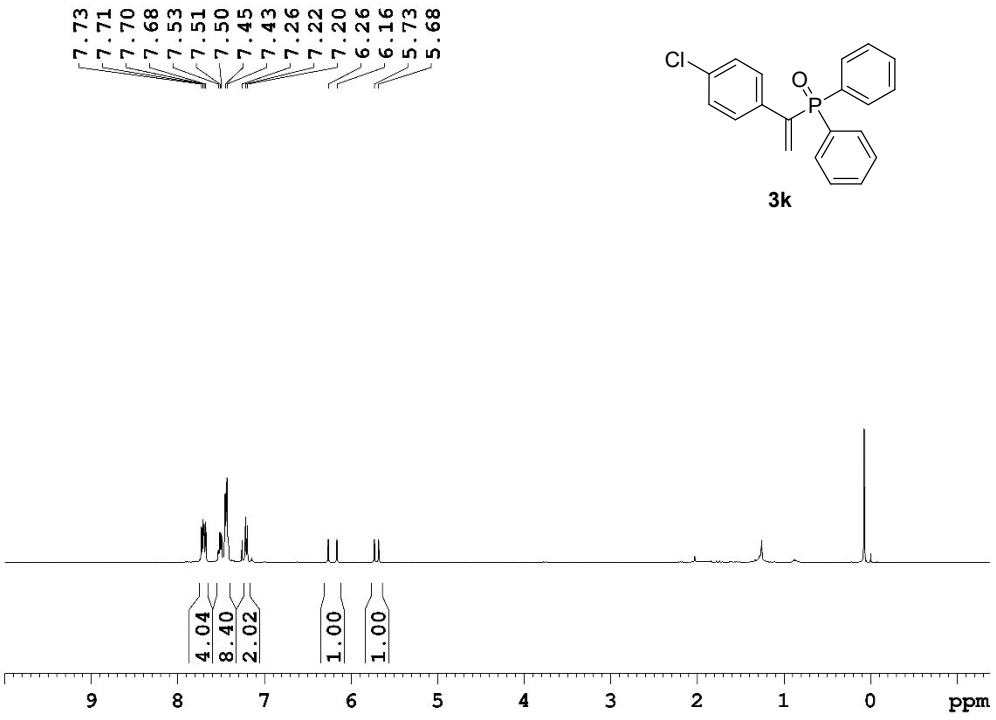
(1-(4-Fluorophenyl)vinyl)diphenylphosphine oxide (3j): ^{13}C NMR (101 MHz, $CDCl_3$)



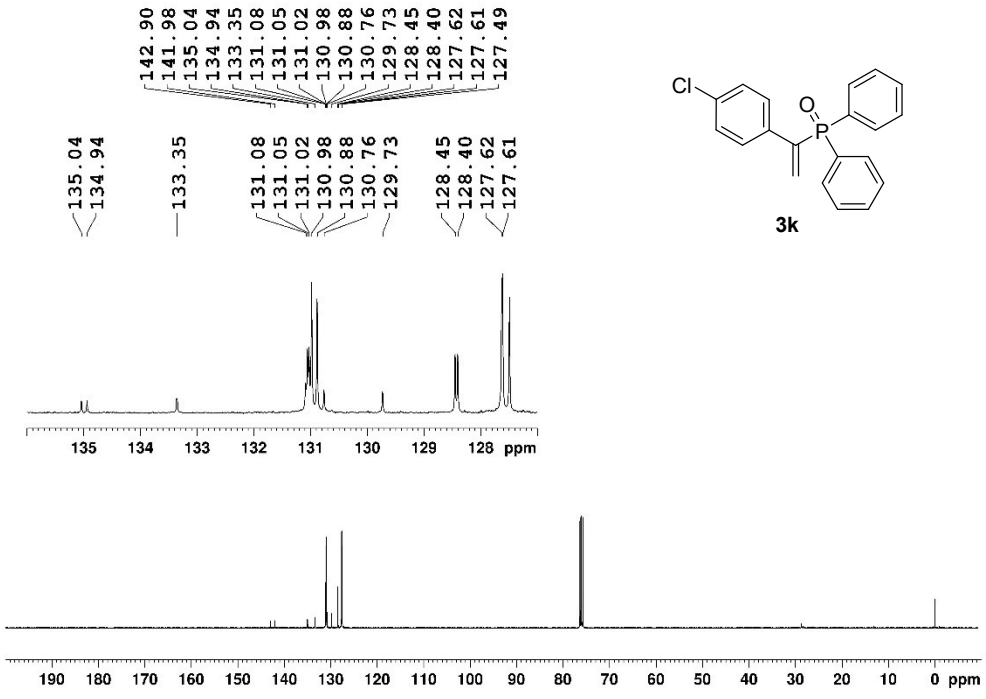
(1-(4-Fluorophenyl)vinyl)diphenylphosphine oxide (3j): ^{31}P NMR (162 MHz, $CDCl_3$)



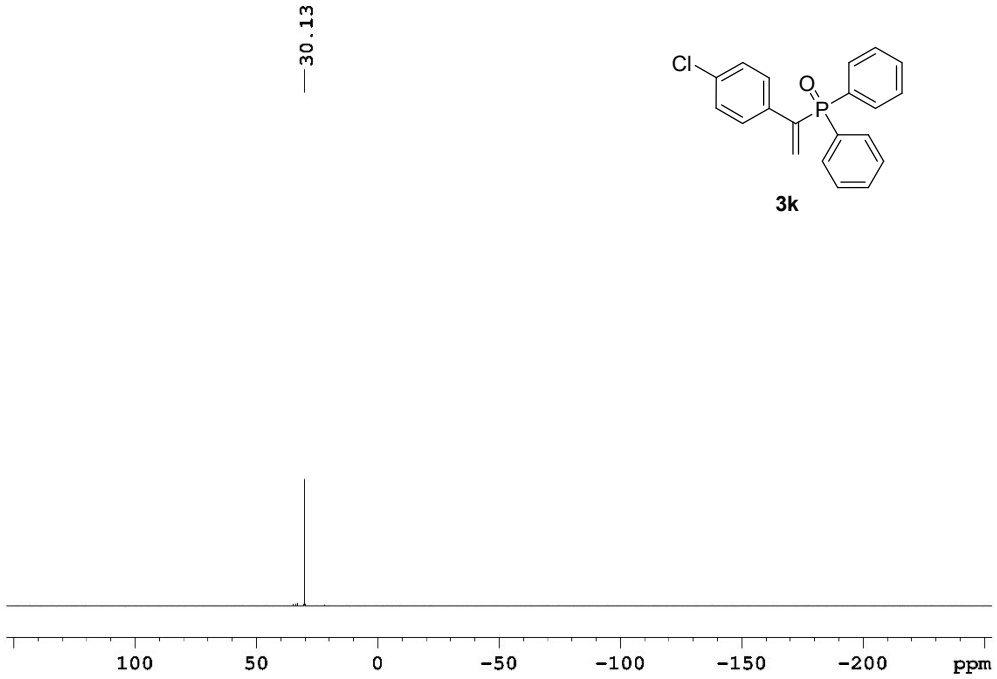
(1-(4-Chlorophenyl)vinyl)diphenylphosphine oxide (3k): ^{1}H NMR (400 MHz, $CDCl_3$)



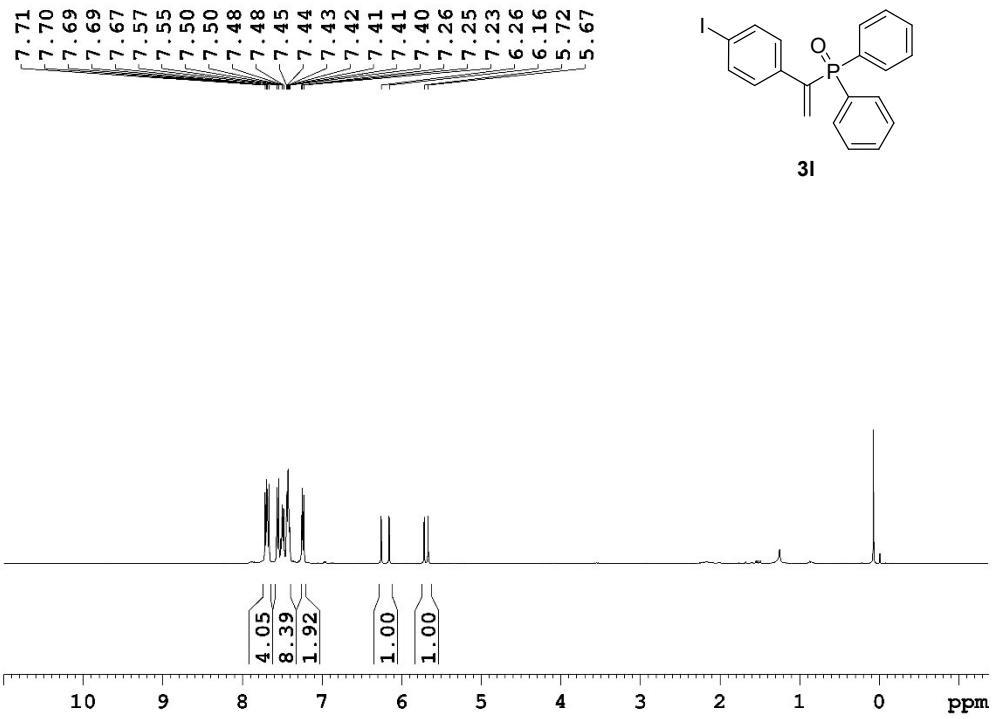
(1-(4-Chlorophenyl)vinyl)diphenylphosphine oxide (3k): ^{13}C NMR (101 MHz, $CDCl_3$)



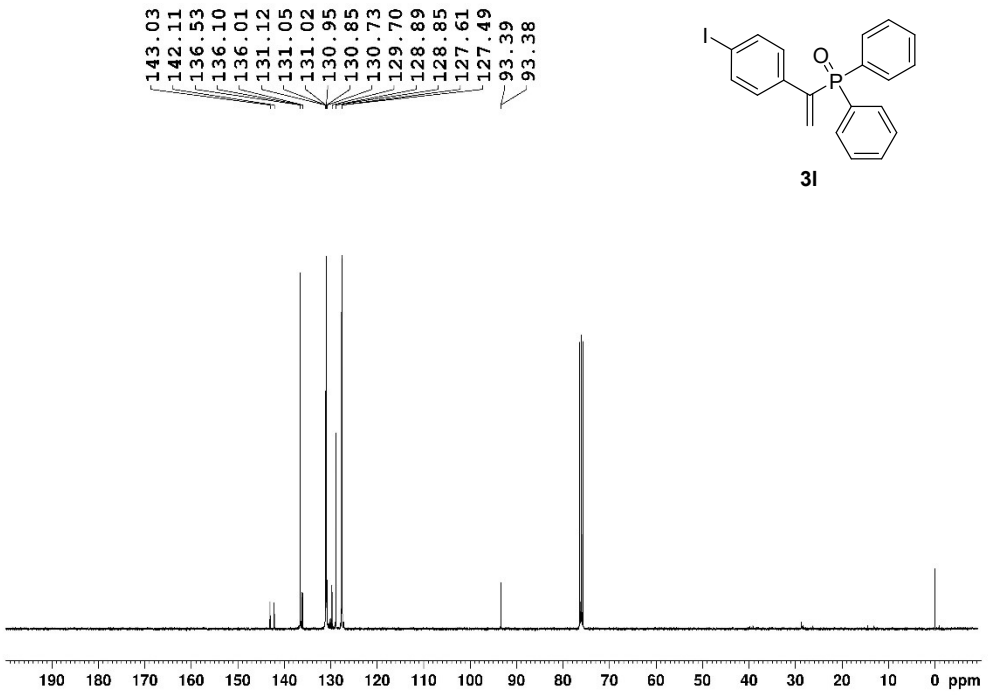
(1-(4-Chlorophenyl)vinyl)diphenylphosphine oxide (3k): ^{31}P NMR (162 MHz, $CDCl_3$)



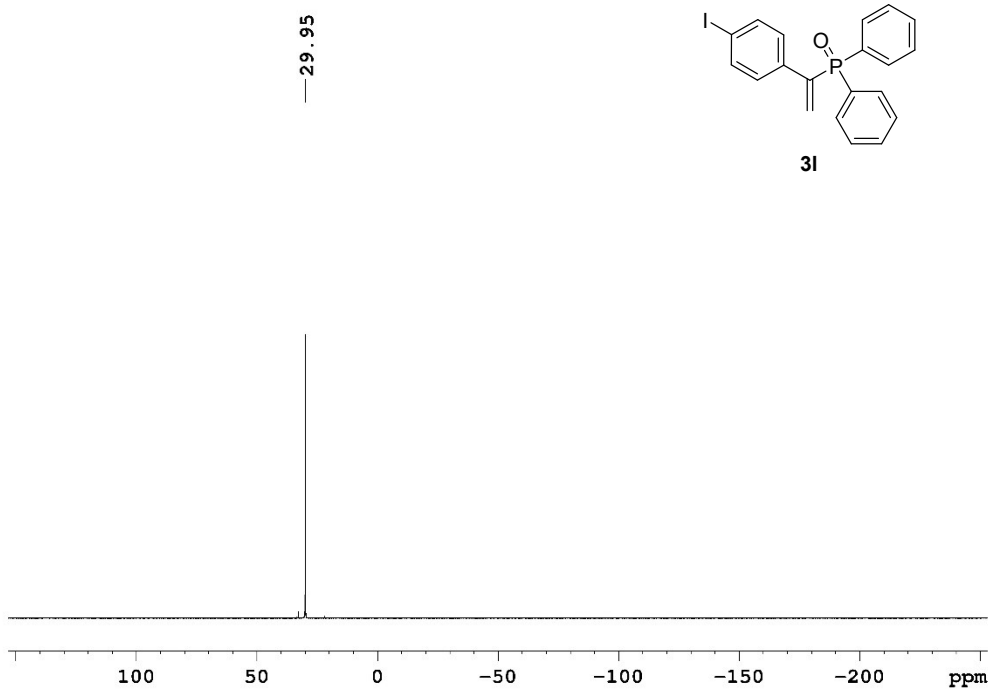
(1-(4-Iodophenyl)vinyl)diphenylphosphine oxide (3l): ^{1}H NMR (400 MHz, $CDCl_3$)



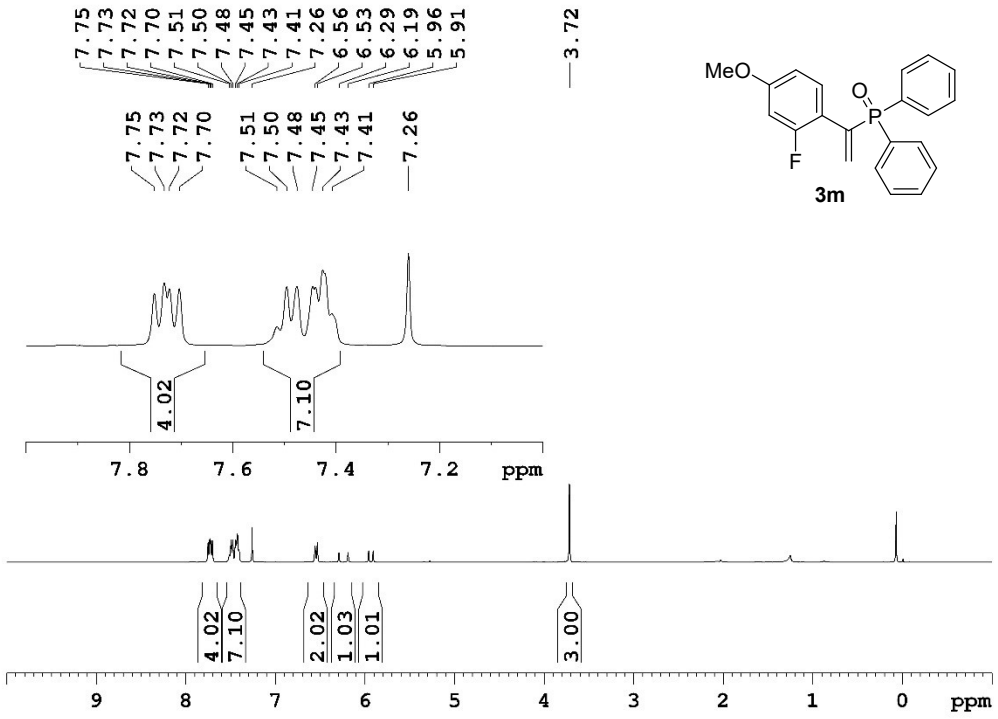
(1-(4-Iodophenyl)vinyl)diphenylphosphine oxide (3l): ^{13}C NMR (101 MHz, $CDCl_3$)



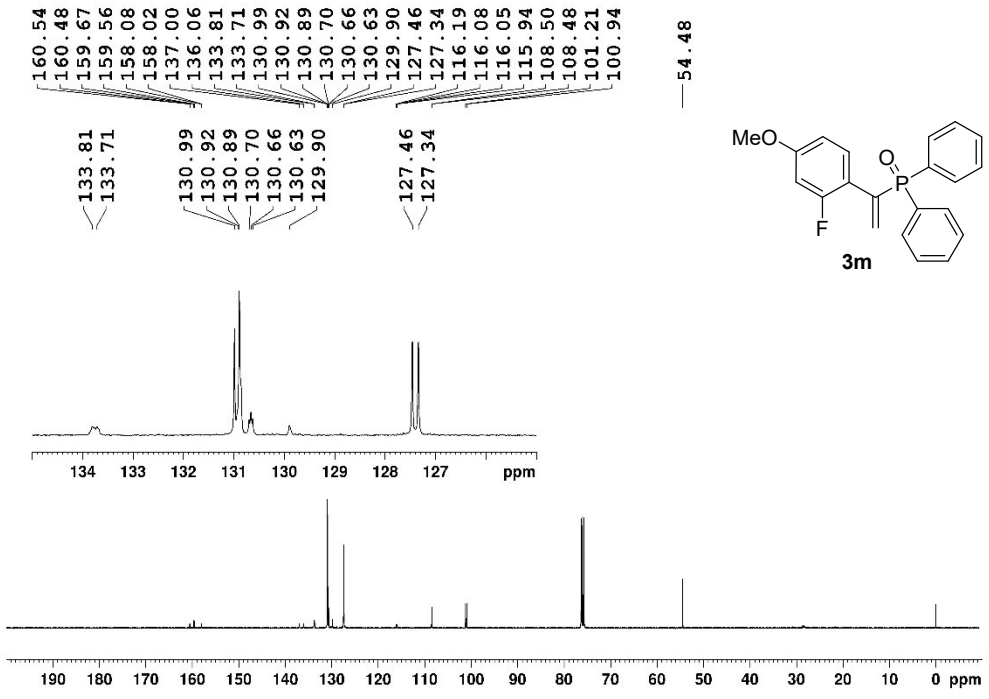
(1-(4-Iodophenyl)vinyl)diphenylphosphine oxide (3l): ^{31}P NMR (162 MHz, $CDCl_3$)



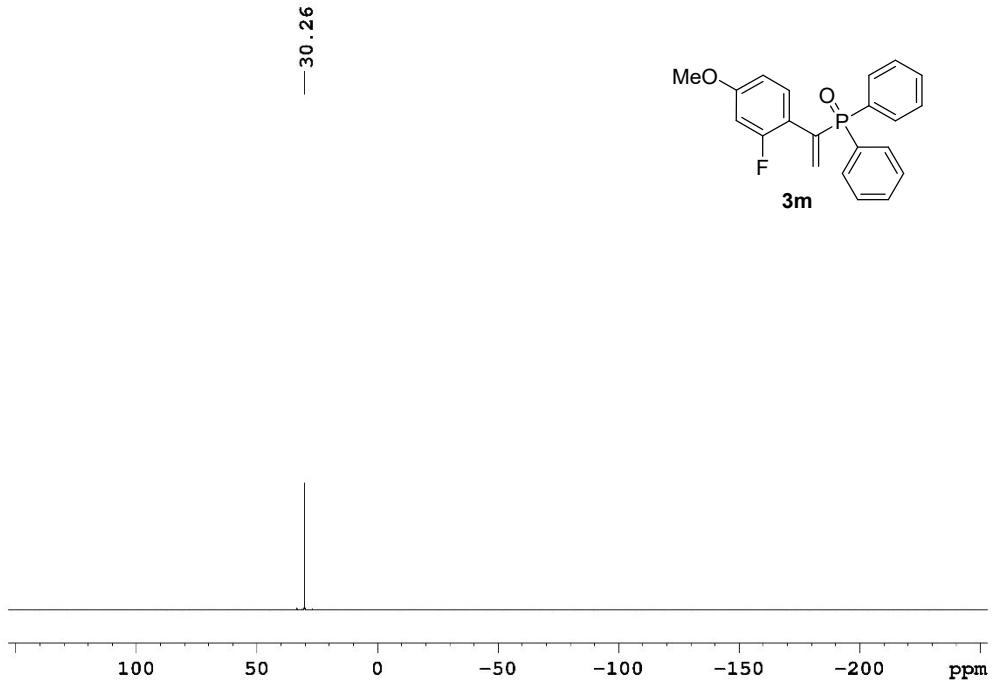
(1-(2-Fluoro-4-methoxyphenyl)vinyl)diphenylphosphine oxide (3m): ^{1}H NMR (400 MHz, $CDCl_3$)



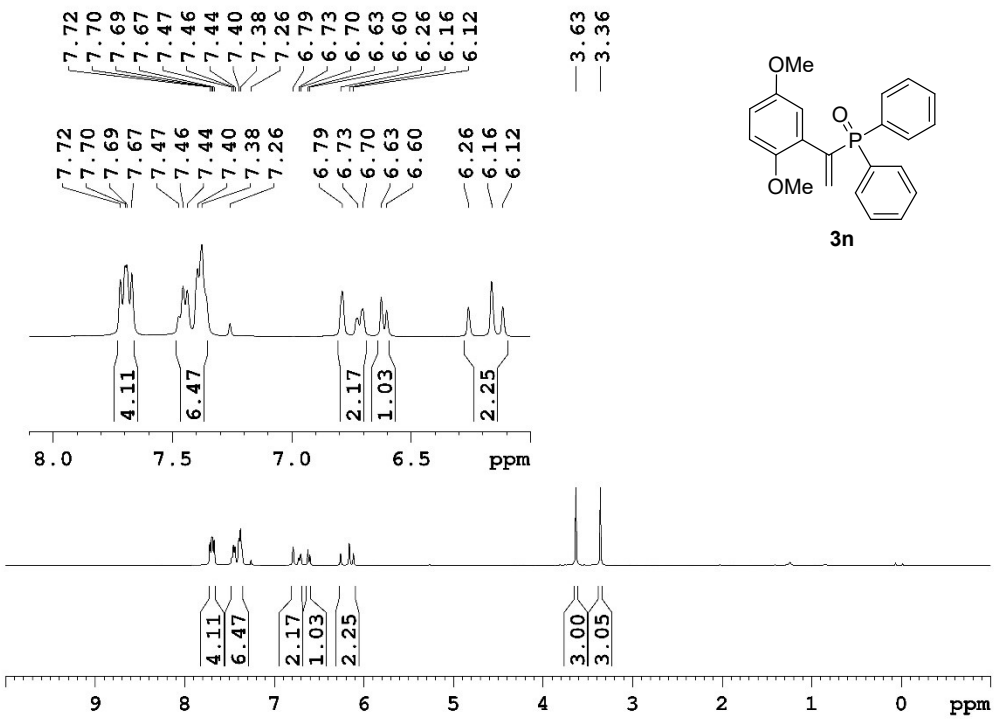
(1-(2-Fluoro-4-methoxyphenyl)vinyl)diphenylphosphine oxide (3m): ^{13}C NMR (101 MHz, $CDCl_3$)



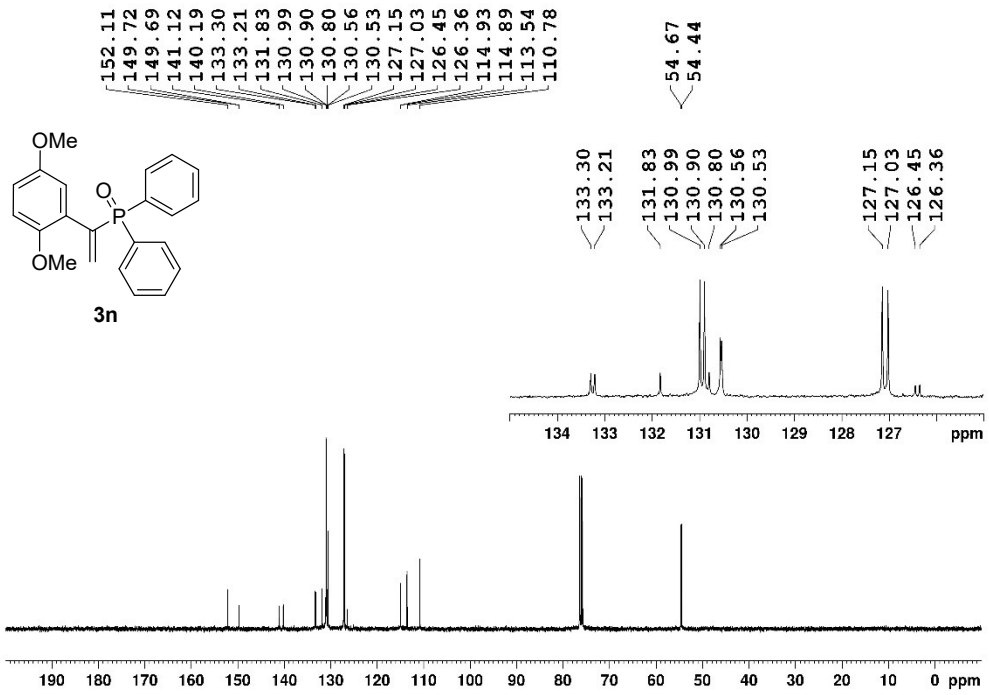
(1-(2-Fluoro-4-methoxyphenyl)vinyl)diphenylphosphine oxide (3m): ^{31}P NMR (162 MHz, $CDCl_3$)



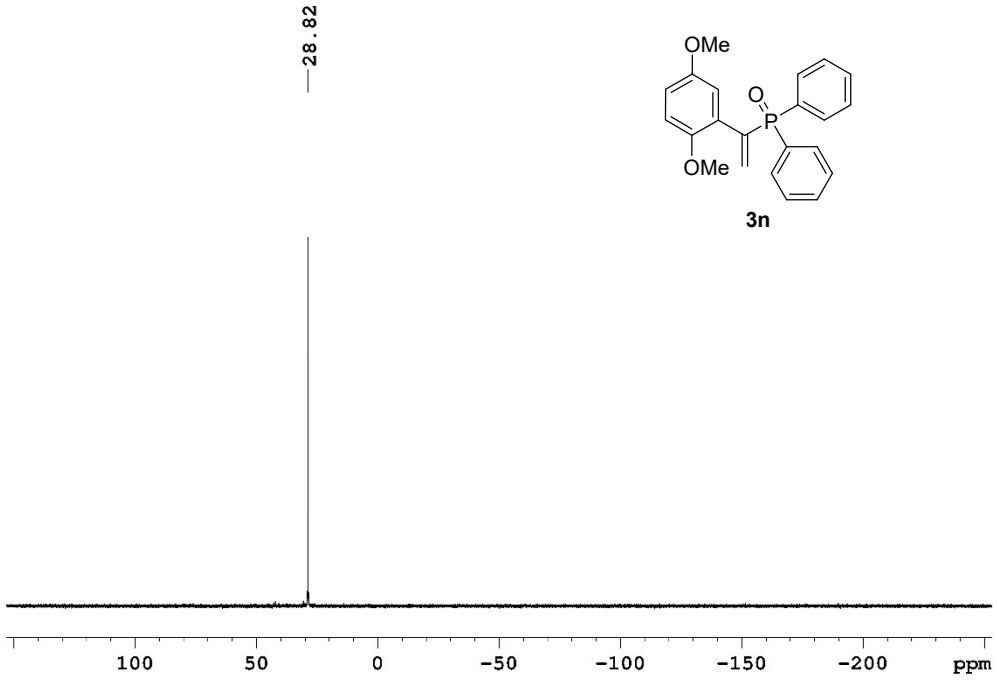
(1-(2,4-Dimethoxyphenyl)vinyl)diphenylphosphine oxide (3n): ^{1}H NMR (400 MHz, $CDCl_3$)



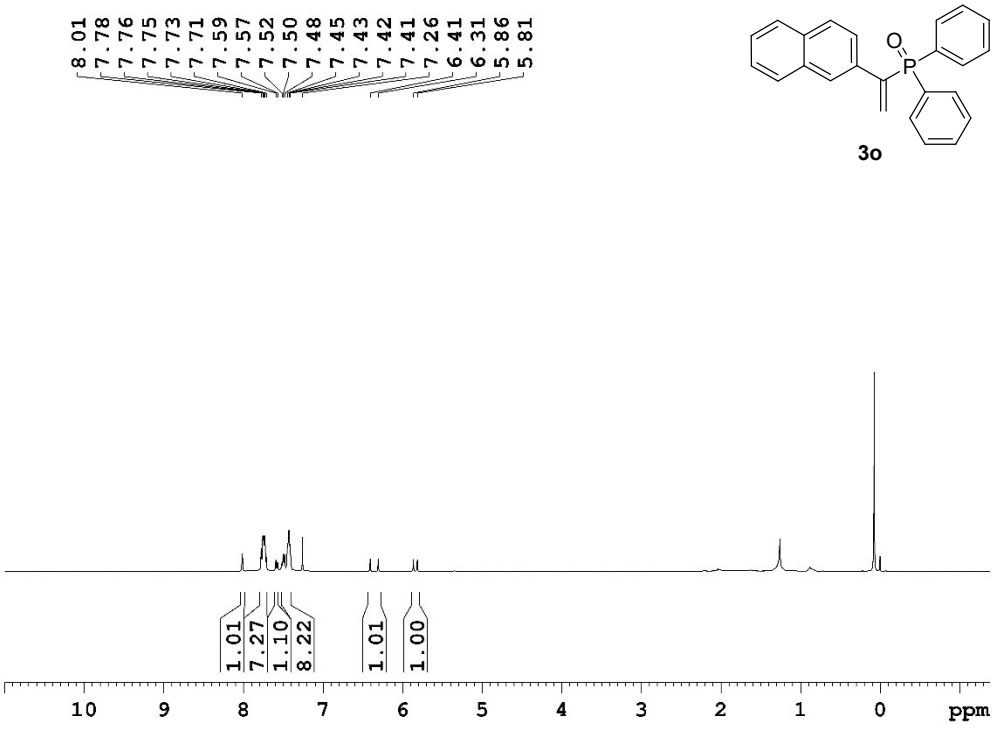
(1-(2,4-Dimethoxyphenyl)vinyl)diphenylphosphine oxide (3n): ^{13}C NMR (101 MHz, $CDCl_3$)



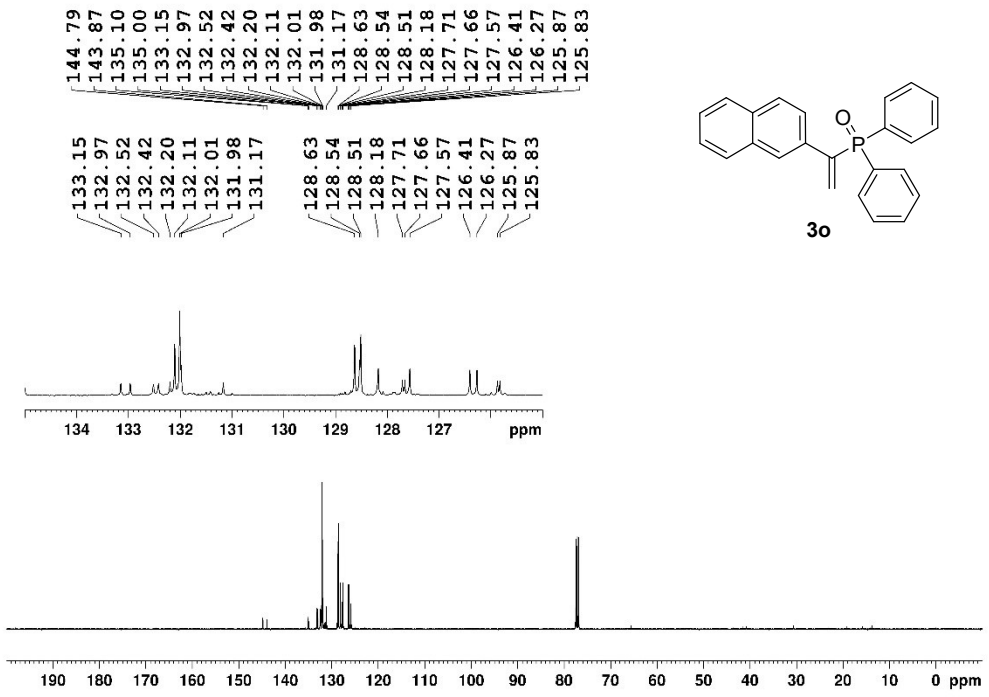
(1-(2,4-Dimethoxyphenyl)vinyl)diphenylphosphine oxide (3n): ^{31}P NMR (162 MHz, $CDCl_3$)



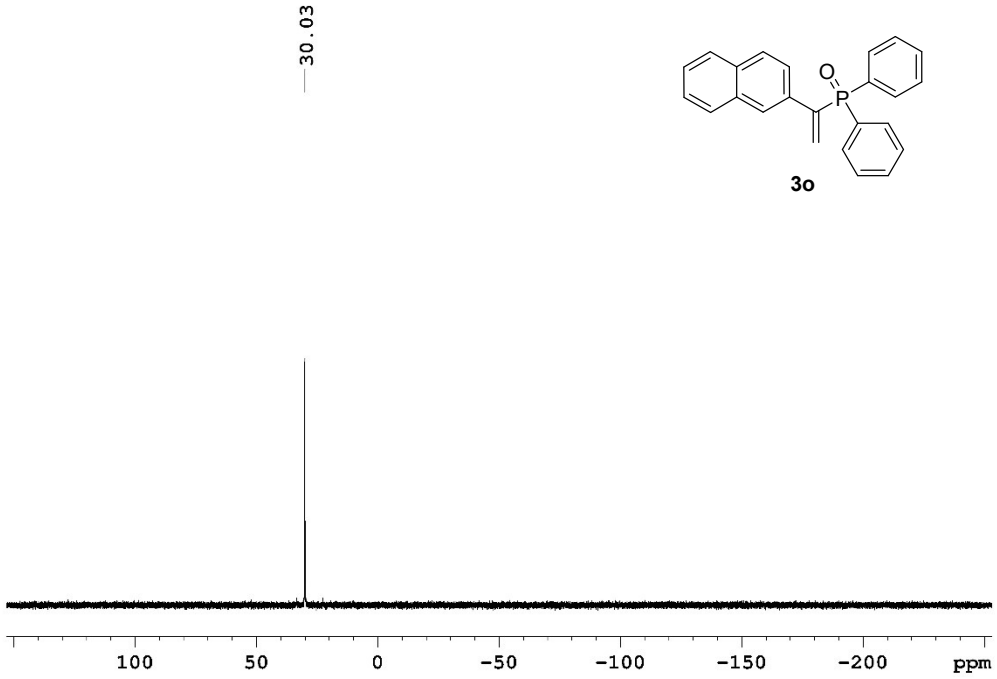
(1-(Naphthalen-2-yl)vinyl)diphenylphosphine oxide (3o): ^{1}H NMR (400 MHz, $CDCl_3$)



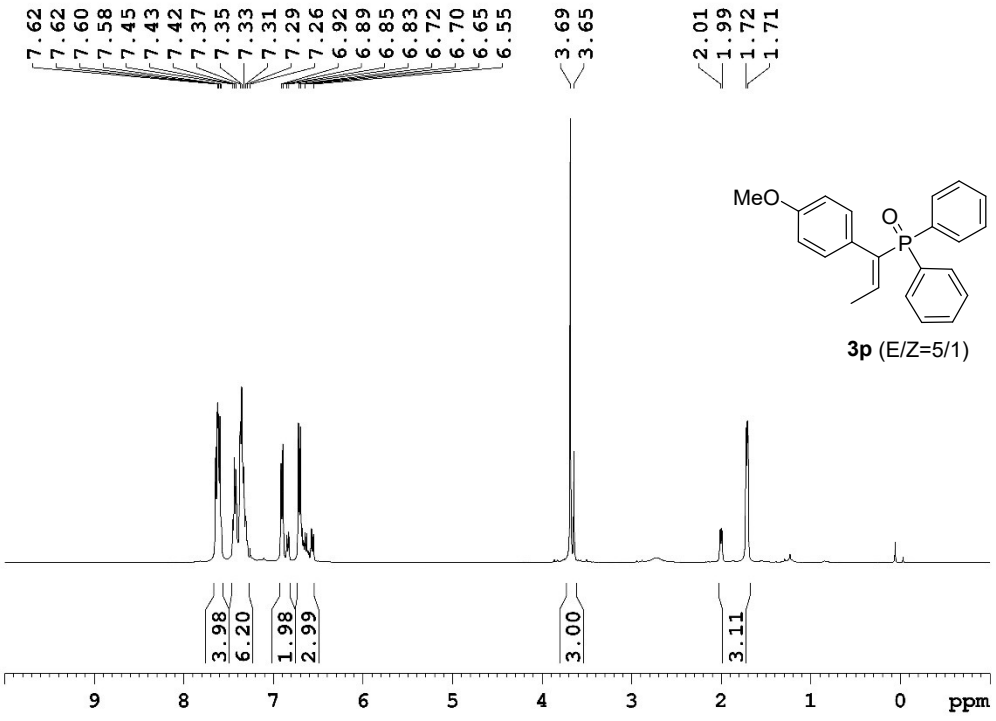
(1-(Naphthalen-2-yl)vinyl)diphenylphosphine oxide (3o): ^{13}CNMR (101 MHz, $CDCl_3$)



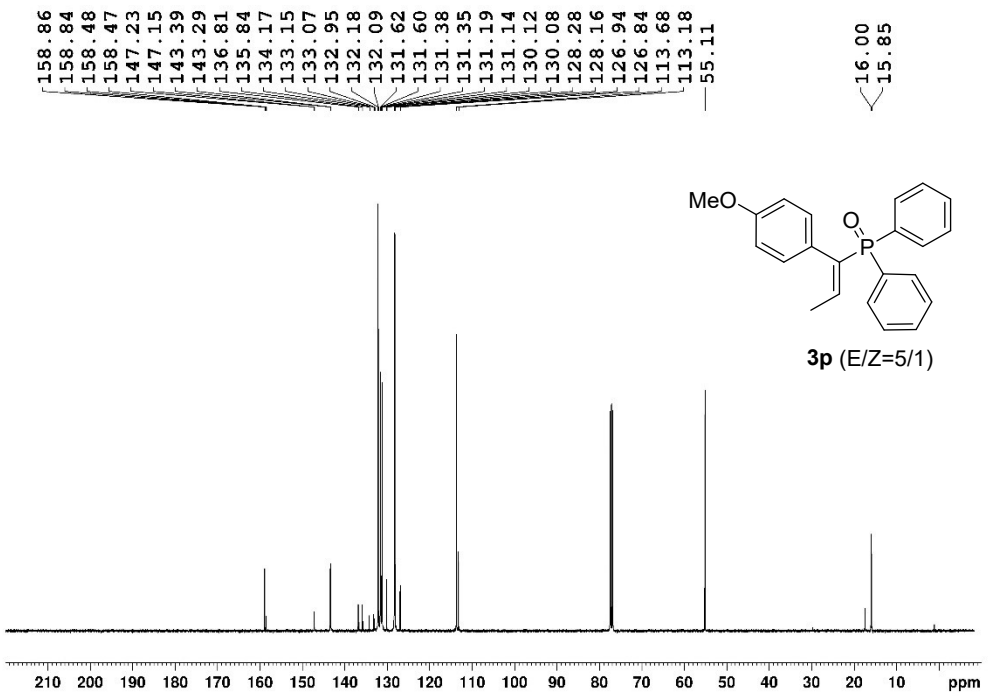
(1-(Naphthalen-2-yl)vinyl)diphenylphosphine oxide (3o): ^{31}P NMR (162 MHz, $CDCl_3$)



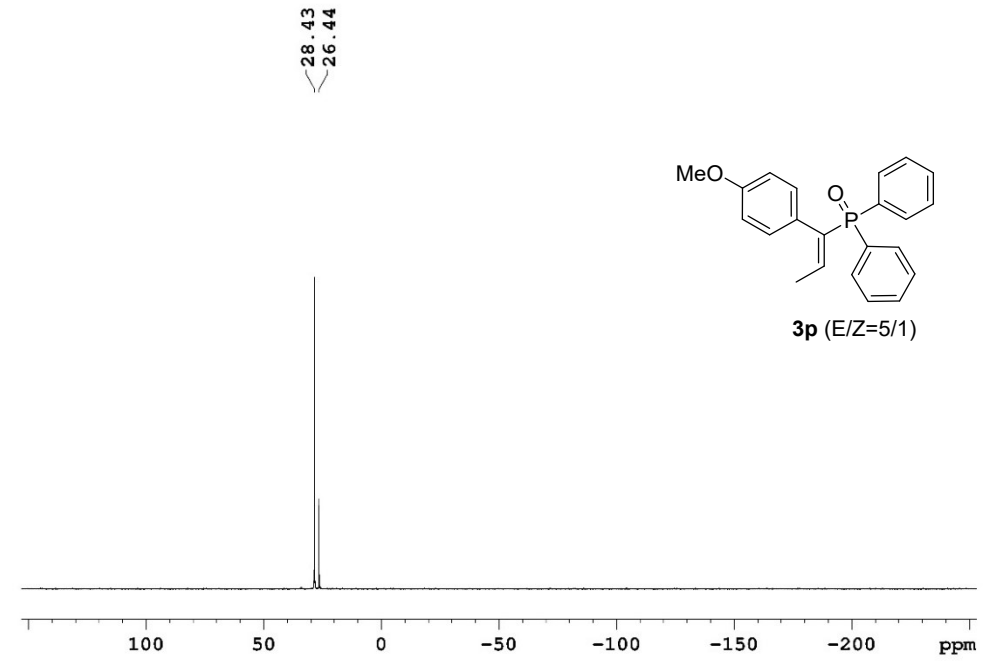
(*E*)-(1-(4-Methoxyphenyl)prop-1-en-1-yl)diphenylphosphine oxide (3p): ^{1}H NMR (400 MHz, $CDCl_3$)



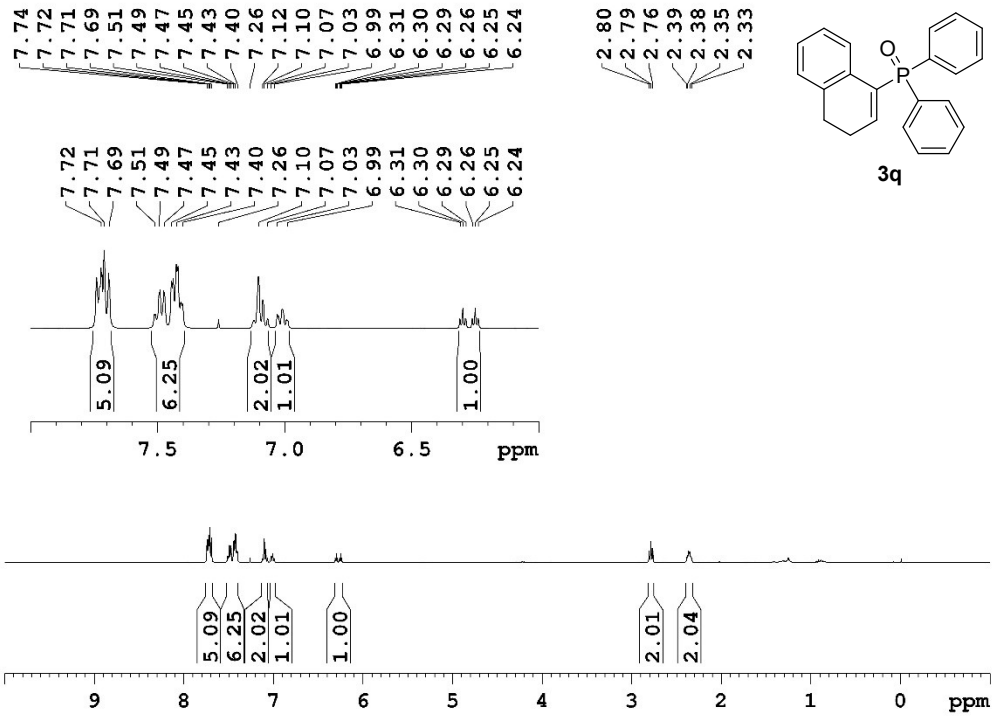
(*E*)-(1-(4-Methoxyphenyl)prop-1-en-1-yl)diphenylphosphine oxide (3p): ^{13}C NMR (101 MHz, $CDCl_3$)



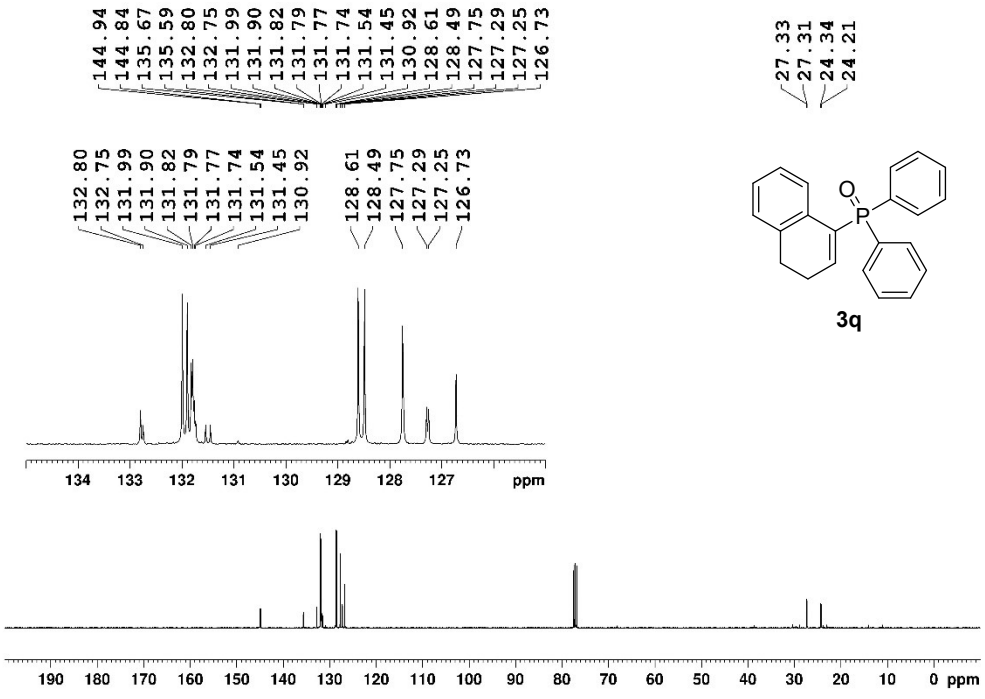
(*E*)-(1-(4-Methoxyphenyl)prop-1-en-1-yl)diphenylphosphine oxide (3p): ^{31}P NMR (162 MHz, $CDCl_3$)



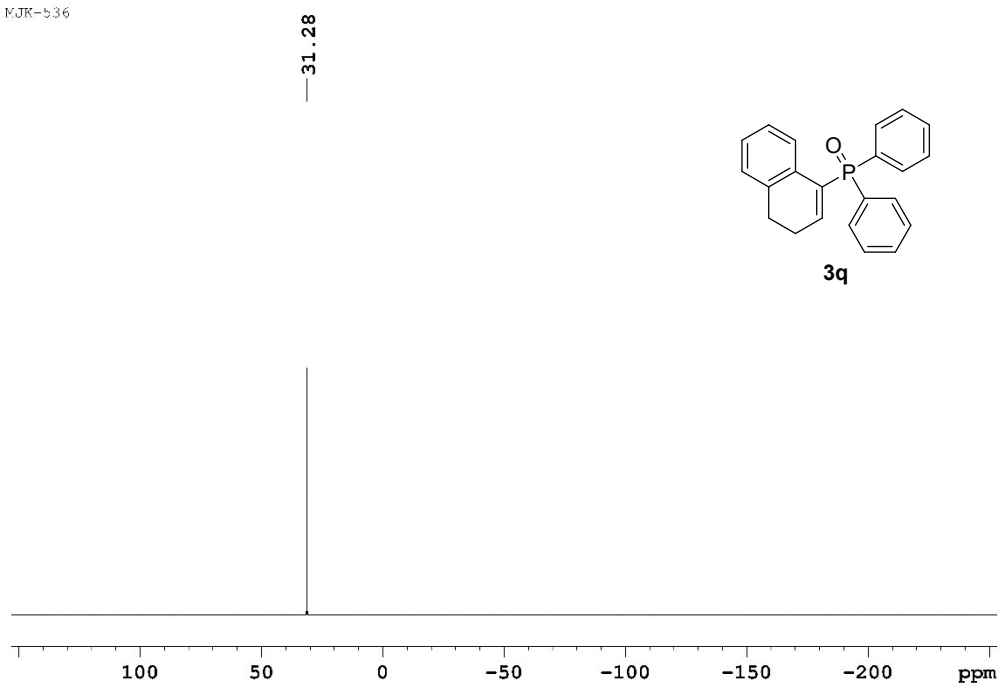
(1*H*-Inden-3-yl)diphenylphosphine oxide (3q): ^{1}H NMR (400 MHz, $CDCl_3$)



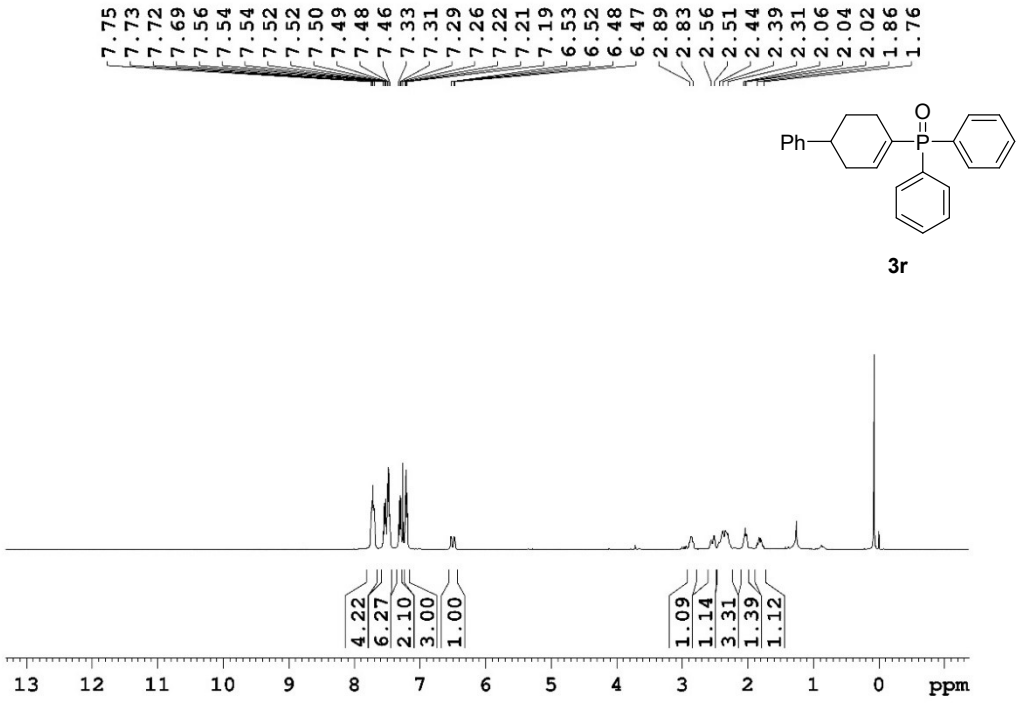
(1*H*-Inden-3-yl)diphenylphosphine oxide (3q): ^{13}C NMR (101 MHz, $CDCl_3$)



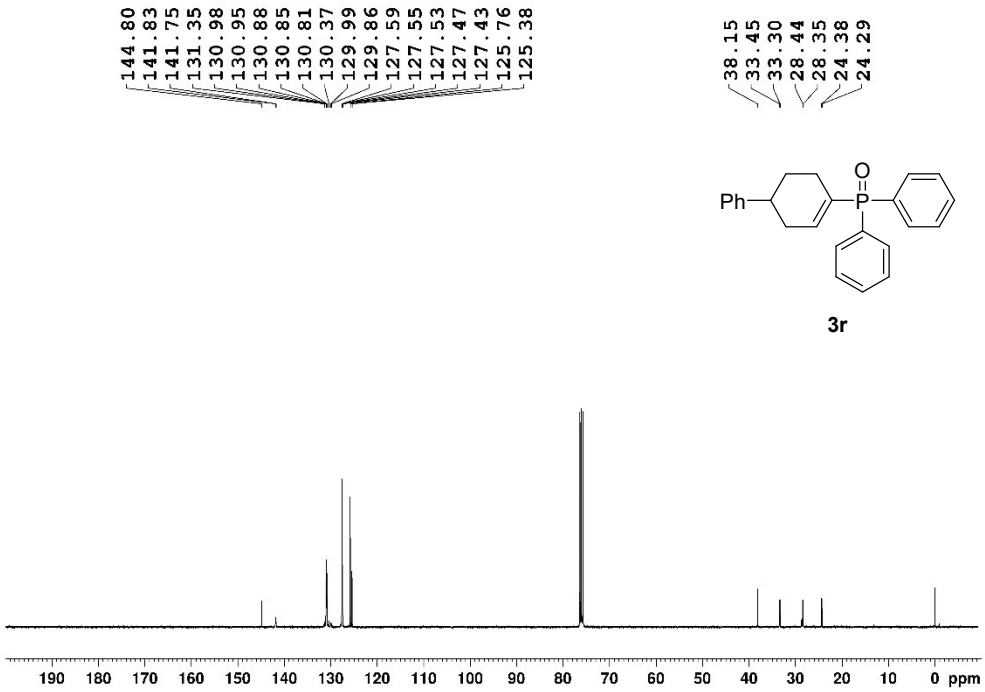
(1*H*-Inden-3-yl)diphenylphosphine oxide (3q): ^{31}P NMR (162 MHz, $CDCl_3$)



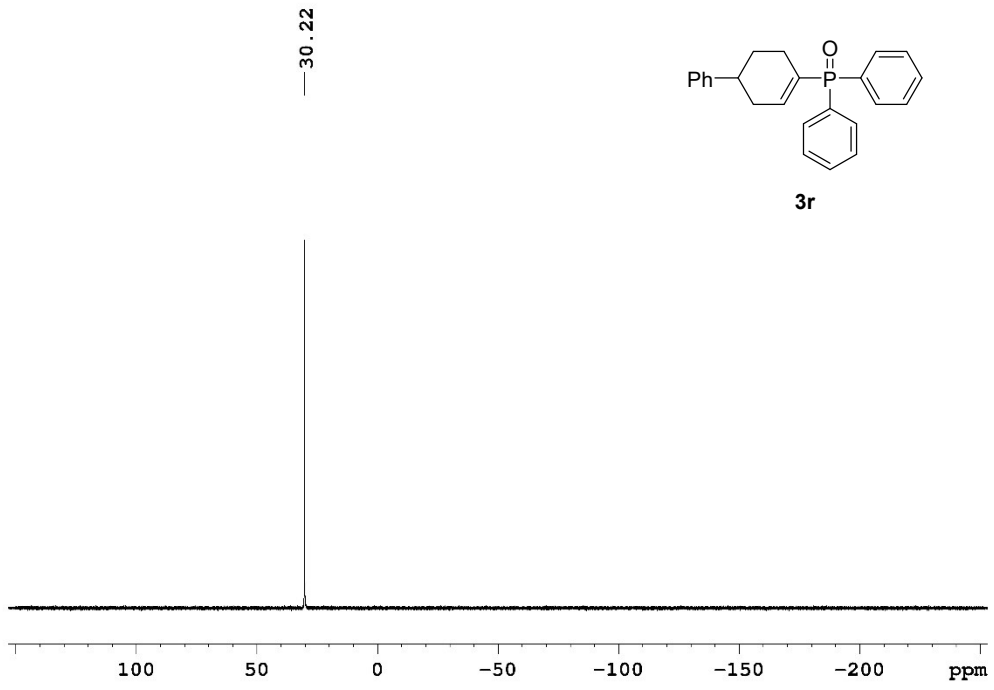
Diphenyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)phosphine oxide (3r): ^{1}H NMR (400 MHz, $CDCl_3$)



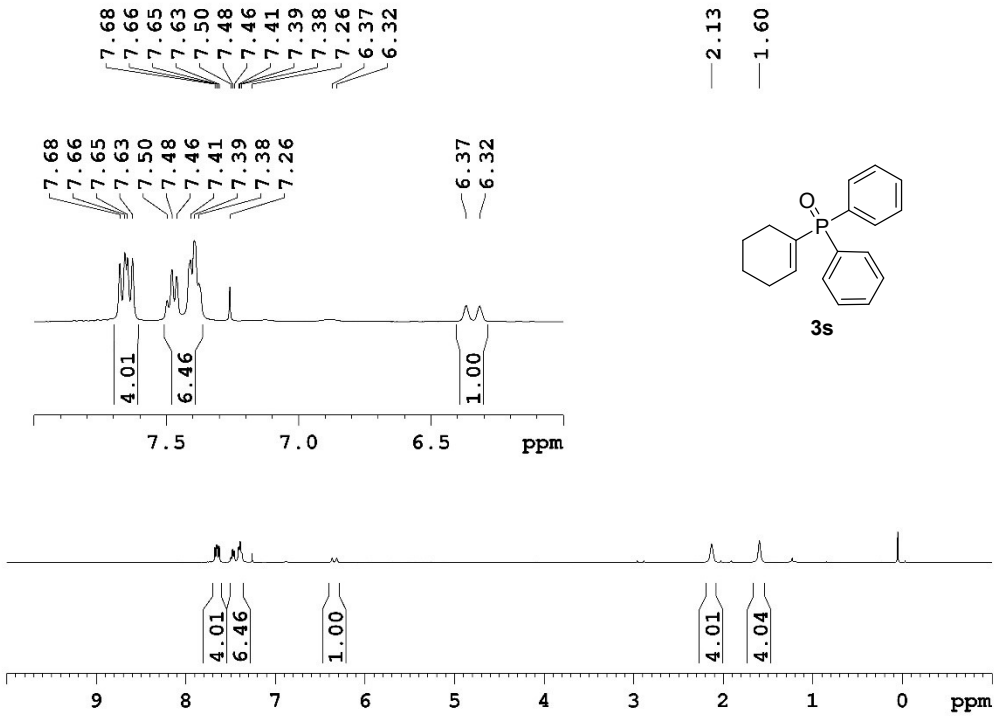
Diphenyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)phosphine oxide (3r): ^{13}C NMR (101 MHz, $CDCl_3$)



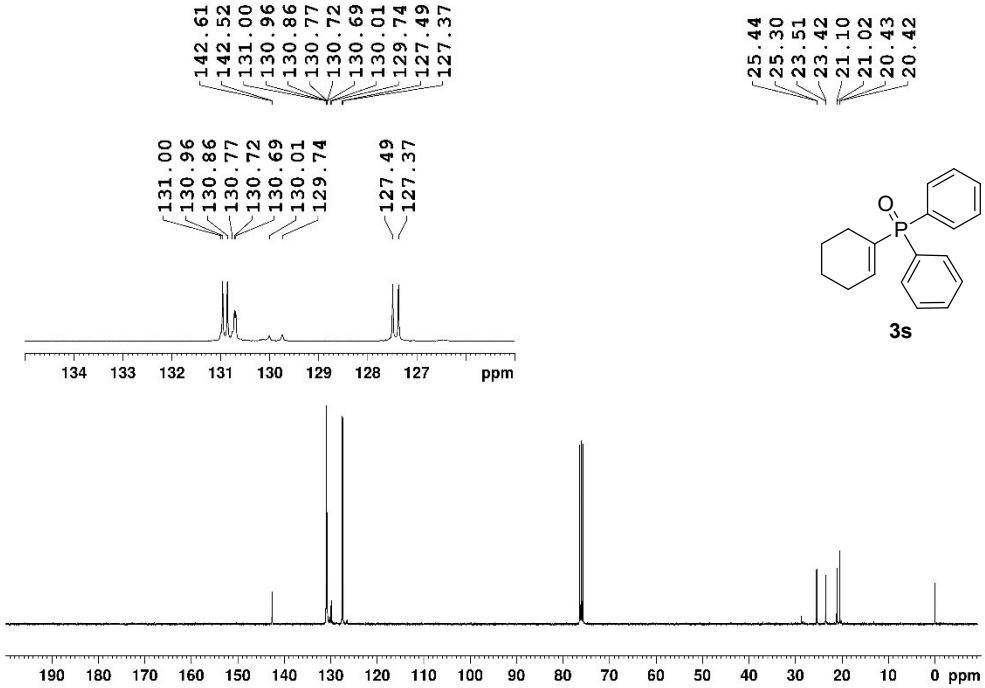
Diphenyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)phosphine oxide (3r): ^{31}P NMR (162 MHz, $CDCl_3$)



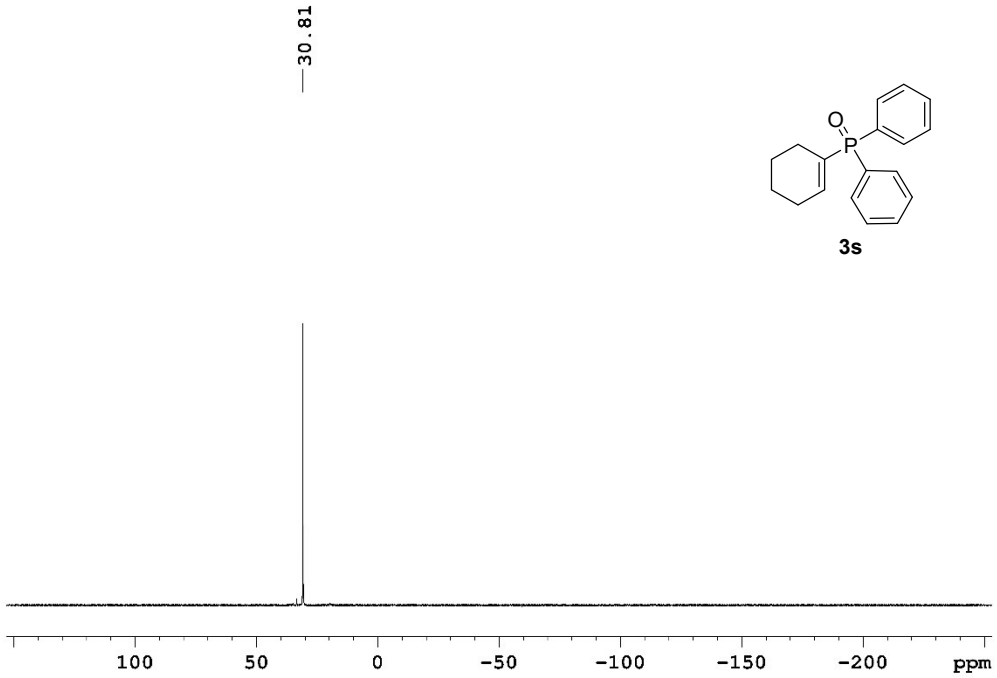
Cyclohex-1-en-1-yldiphenylphosphine oxide (3s): ^{1}H NMR (400 MHz, $CDCl_3$)



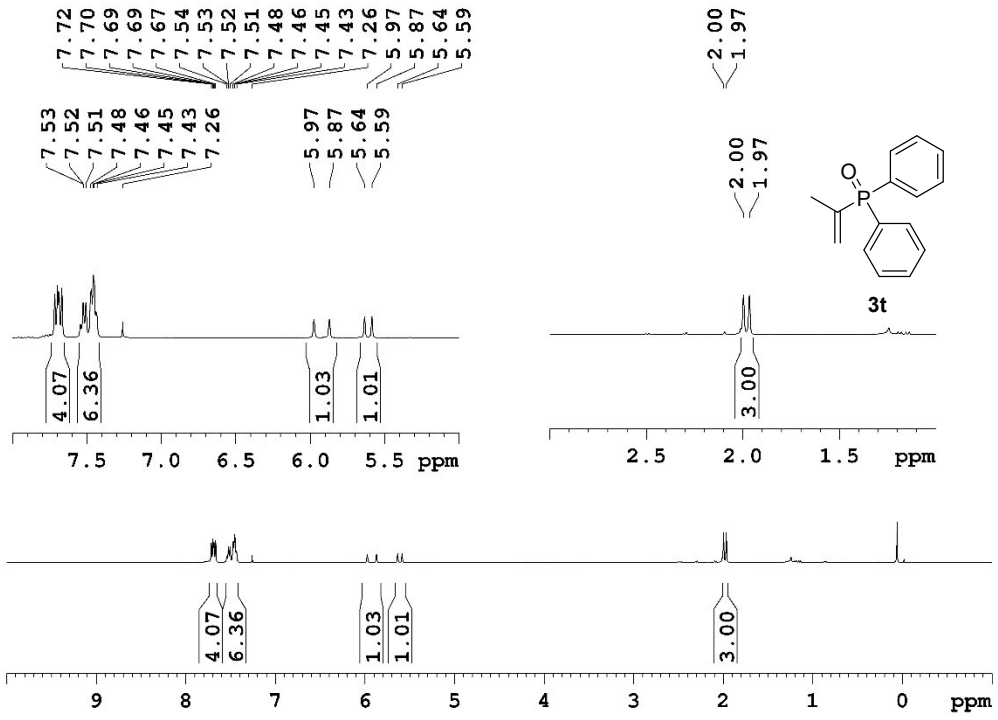
Cyclohex-1-en-1-yldiphenylphosphine oxide (3s): ^{13}C NMR (101 MHz, $CDCl_3$)



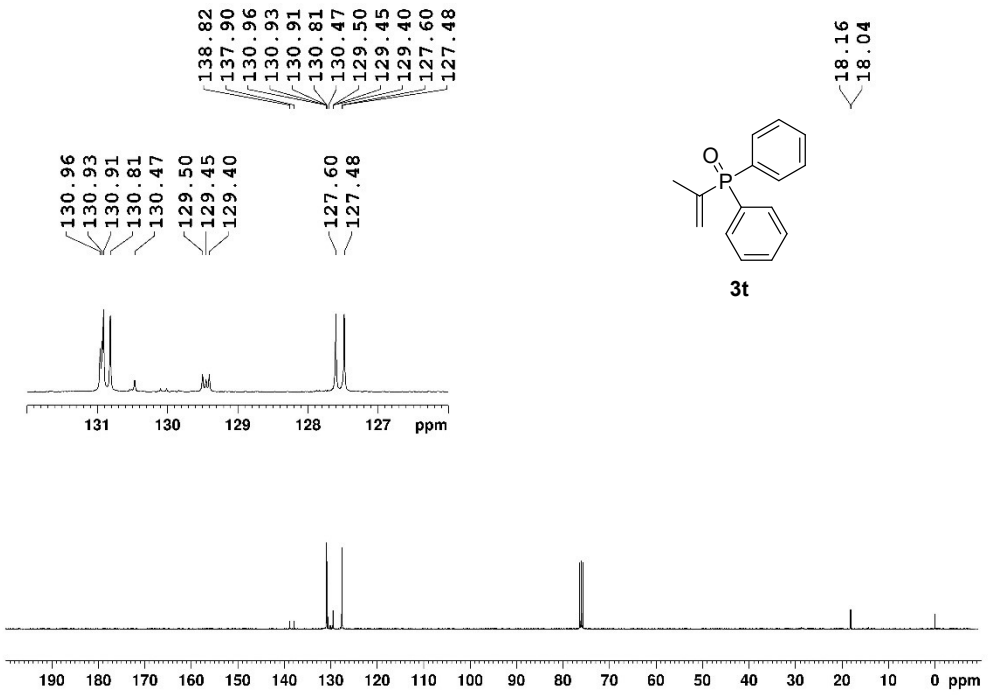
Cyclohex-1-en-1-yldiphenylphosphine oxide (3s): ^{31}P NMR (162 MHz, $CDCl_3$)



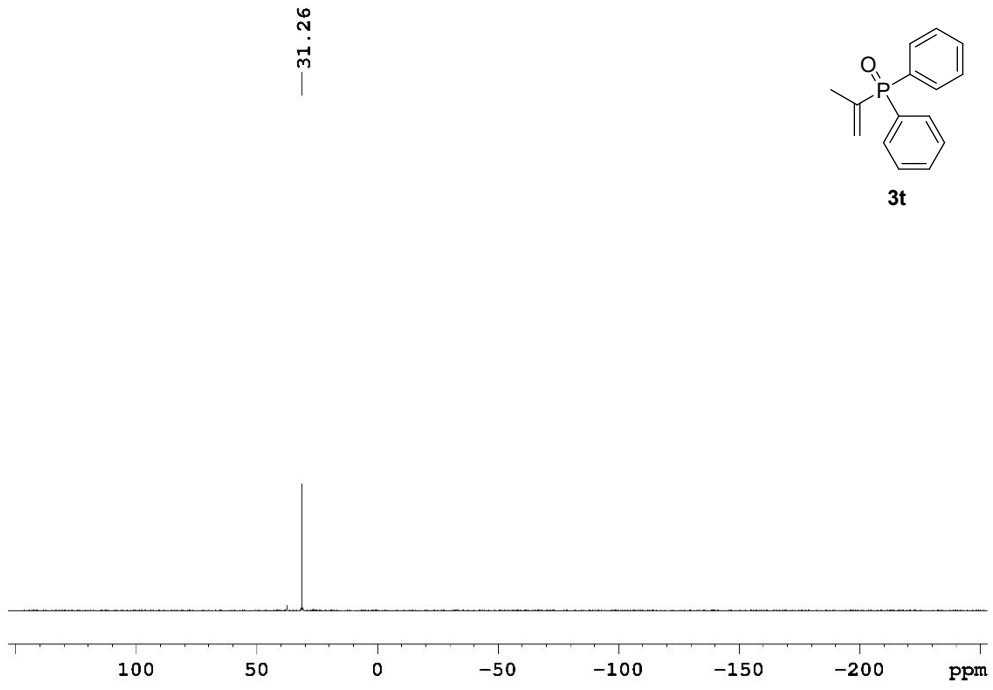
Diphenyl(prop-1-en-2-yl)phosphine oxide (3t): ^{1}H NMR (400 MHz, $CDCl_3$)



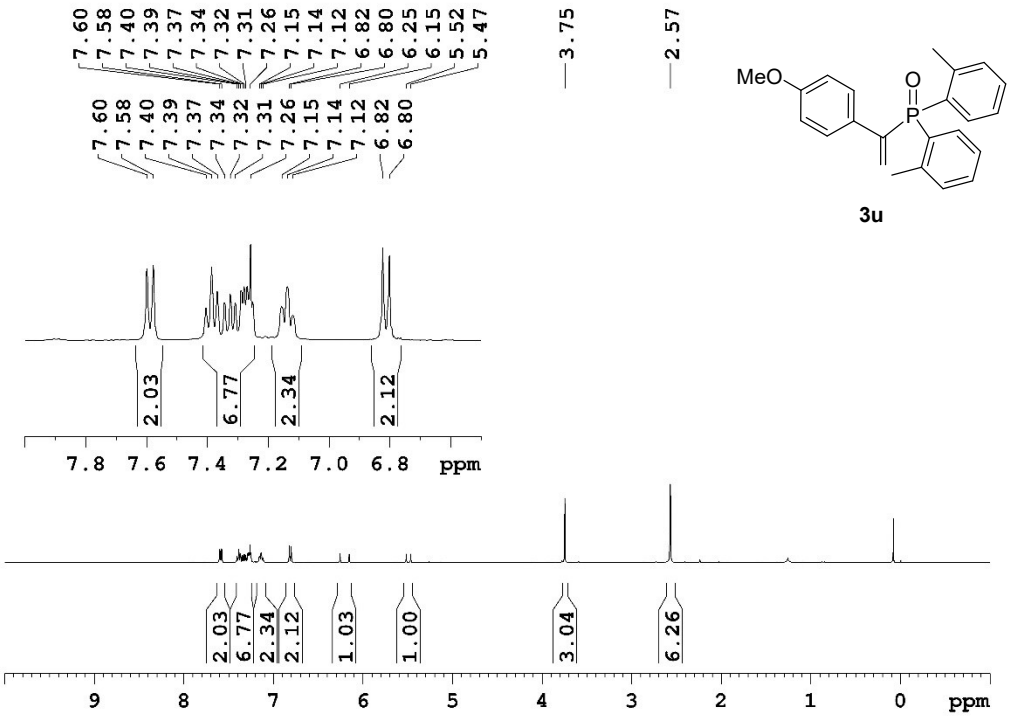
Diphenyl(prop-1-en-2-yl)phosphine oxide (3t): ^{13}C NMR (101 MHz, $CDCl_3$)



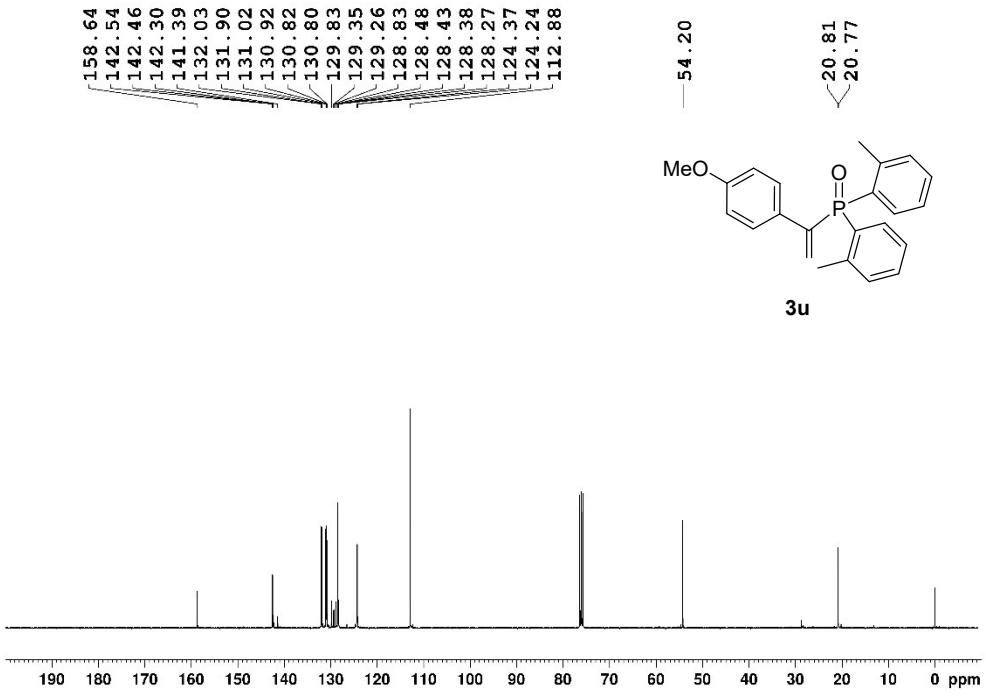
Diphenyl(prop-1-en-2-yl)phosphine oxide (3t): ^{31}P NMR (162 MHz, $CDCl_3$)



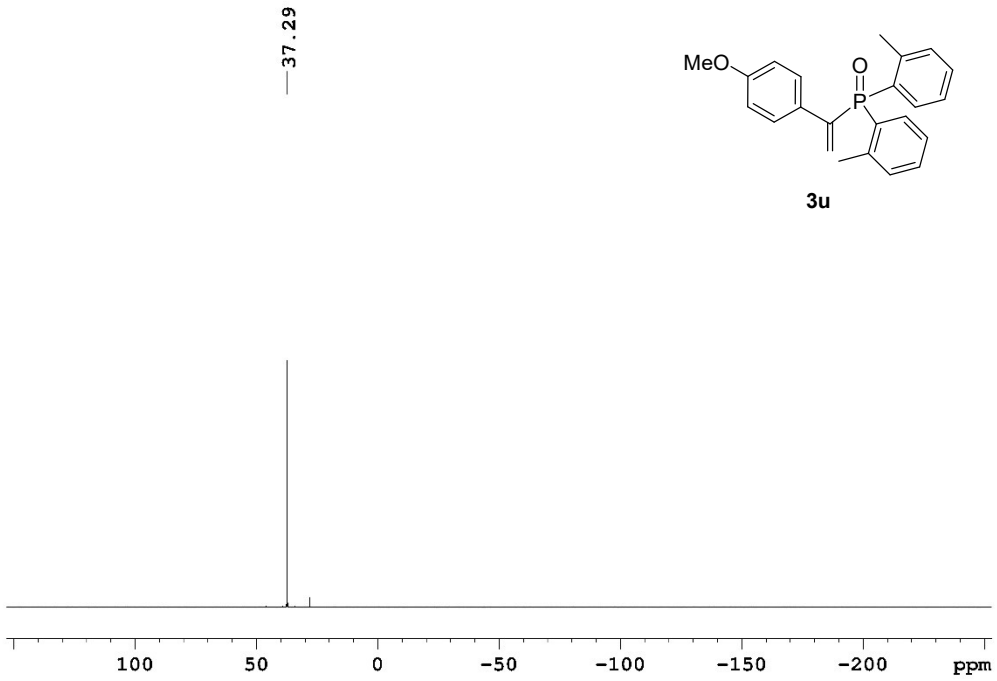
(1-(4-Methoxyphenyl)vinyl)di-*o*-tolylphosphine oxide (3u): ^{1}H NMR (400 MHz, $CDCl_3$)



(1-(4-Methoxyphenyl)vinyl)di-*o*-tolylphosphine oxide (3u): ^{13}C NMR (101 MHz, $CDCl_3$)

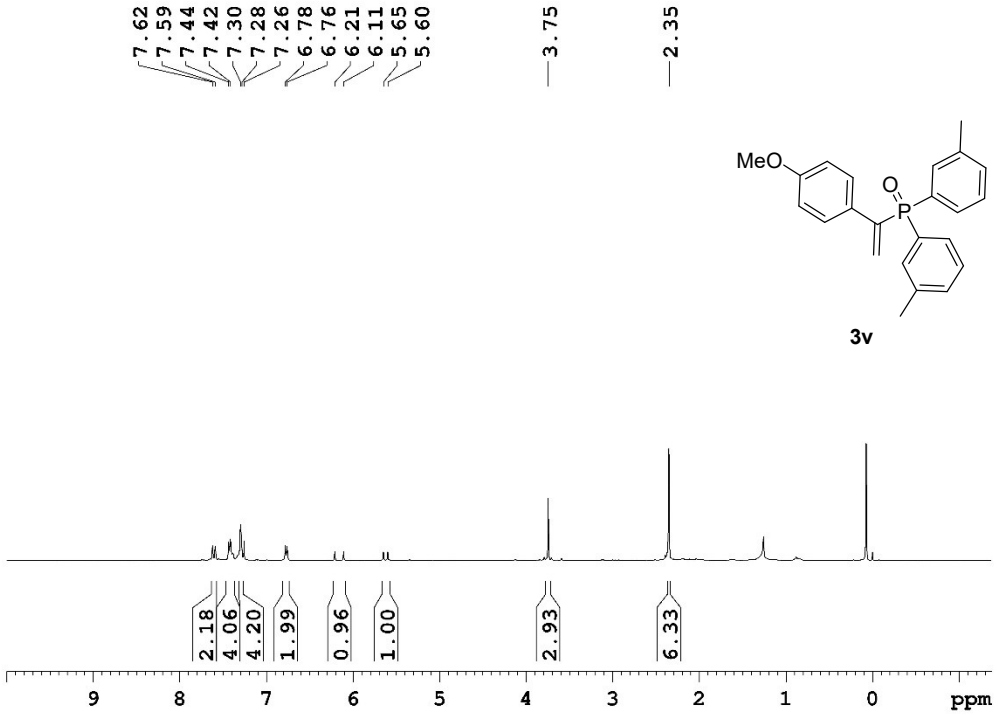


(1-(4-Methoxyphenyl)vinyl)di-*o*-tolylphosphine oxide (3u): ^{31}P NMR (162 MHz, $CDCl_3$)



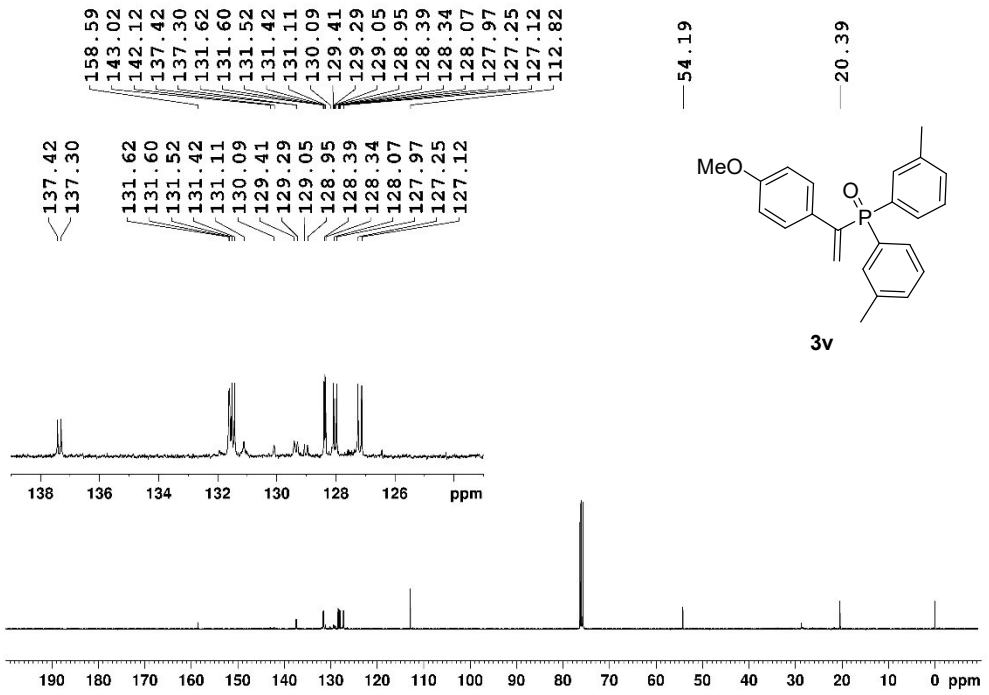
3u

(1-(4-Methoxyphenyl)vinyl)di-*m*-tolylphosphine oxide (3v): ^{1}H NMR (400 MHz, $CDCl_3$)

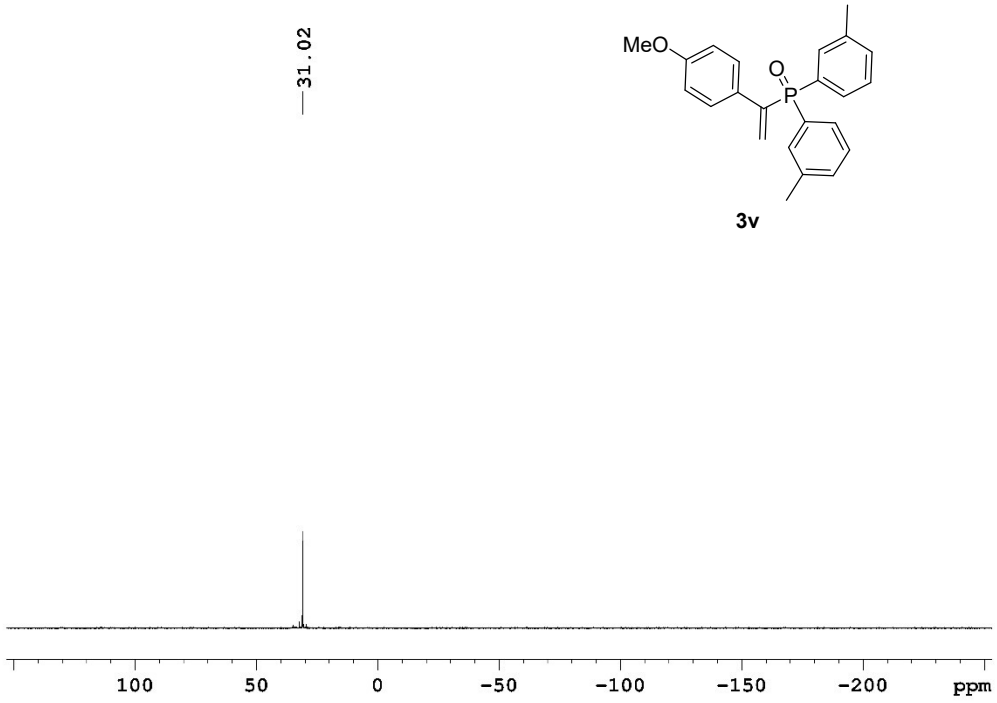


3v

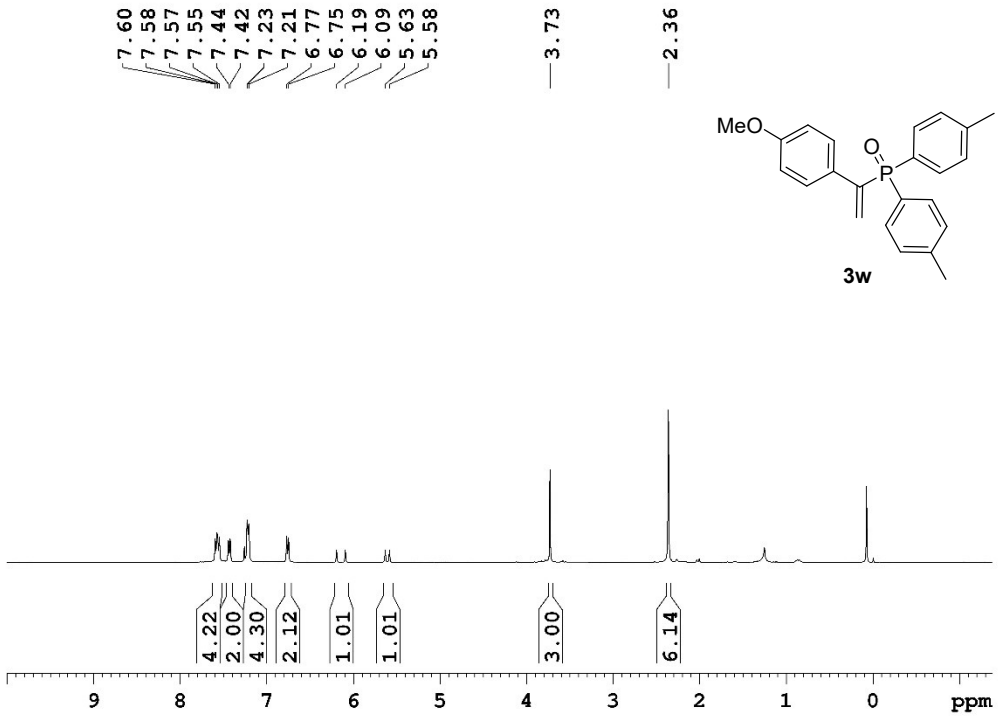
(1-(4-Methoxyphenyl)vinyl)di-*m*-tolylphosphine oxide (3v): ^{13}C NMR (101 MHz, $CDCl_3$)



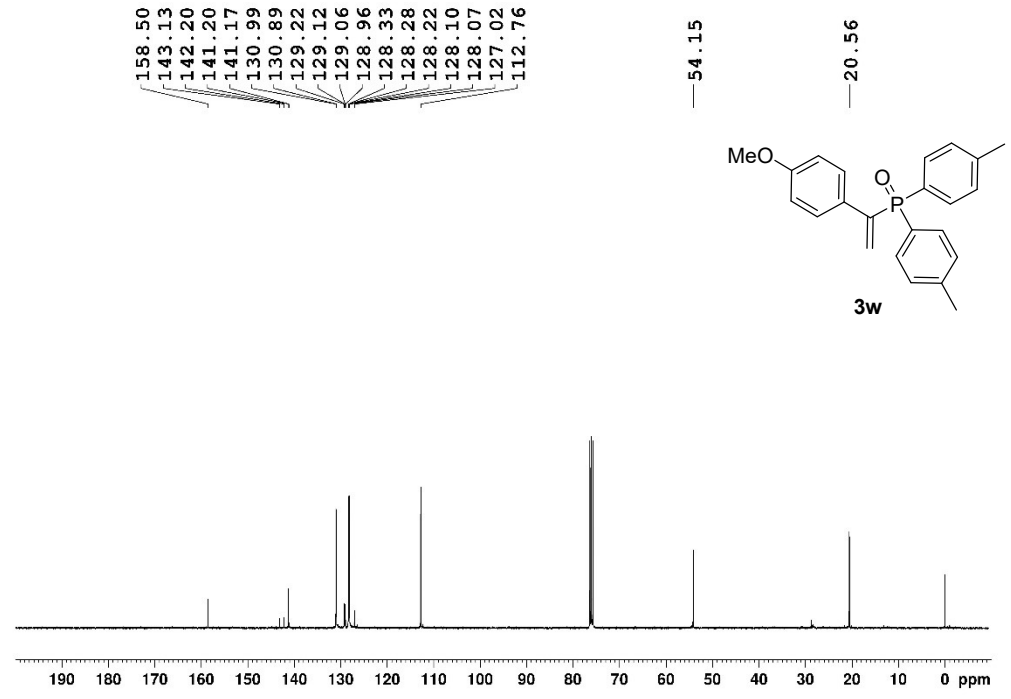
(1-(4-Methoxyphenyl)vinyl)di-*m*-tolylphosphine oxide (3v): ^{31}P NMR (162 MHz, $CDCl_3$)



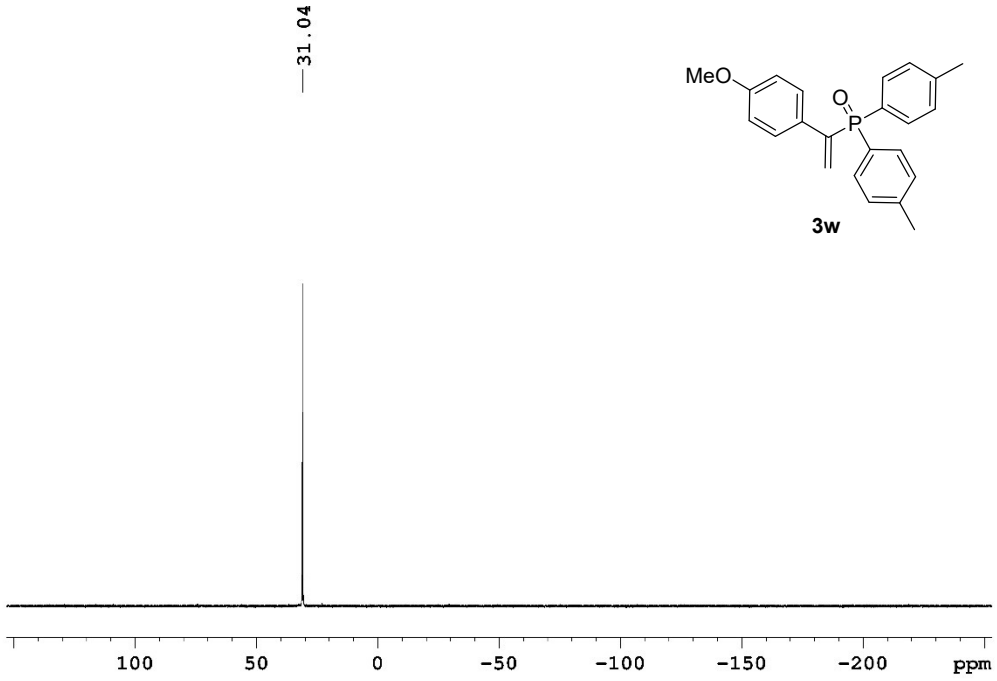
(1-(4-Methoxyphenyl)vinyl)di-*p*-tolylphosphine oxide (3w): ^{1}H NMR (400 MHz, $CDCl_3$)



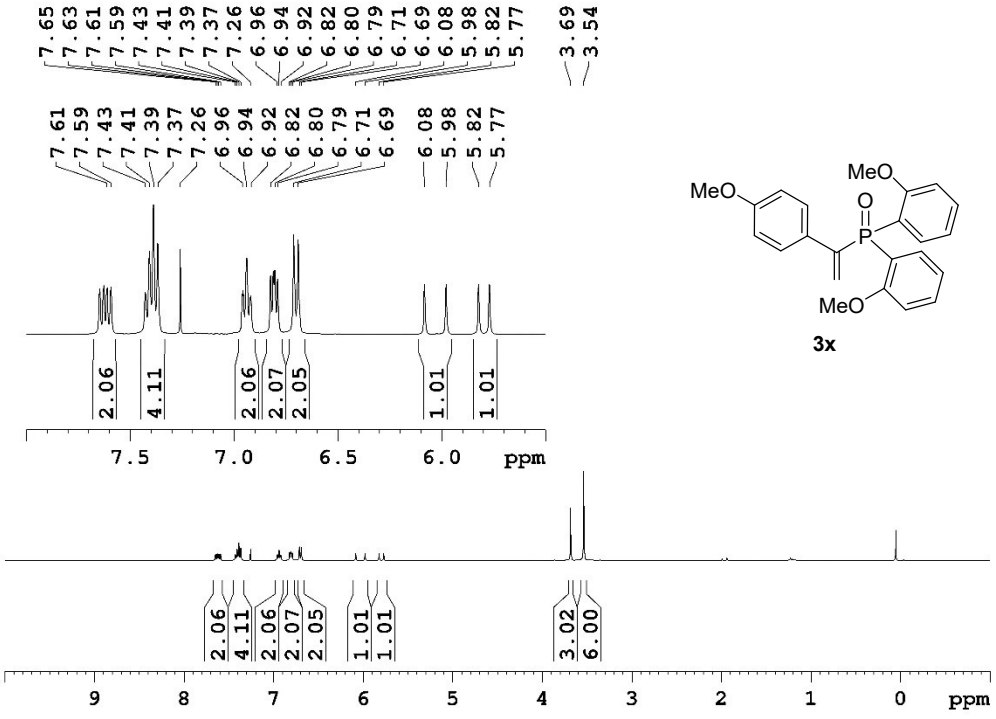
(1-(4-Methoxyphenyl)vinyl)di-*p*-tolylphosphine oxide (3w): ^{13}C NMR (101 MHz, $CDCl_3$)



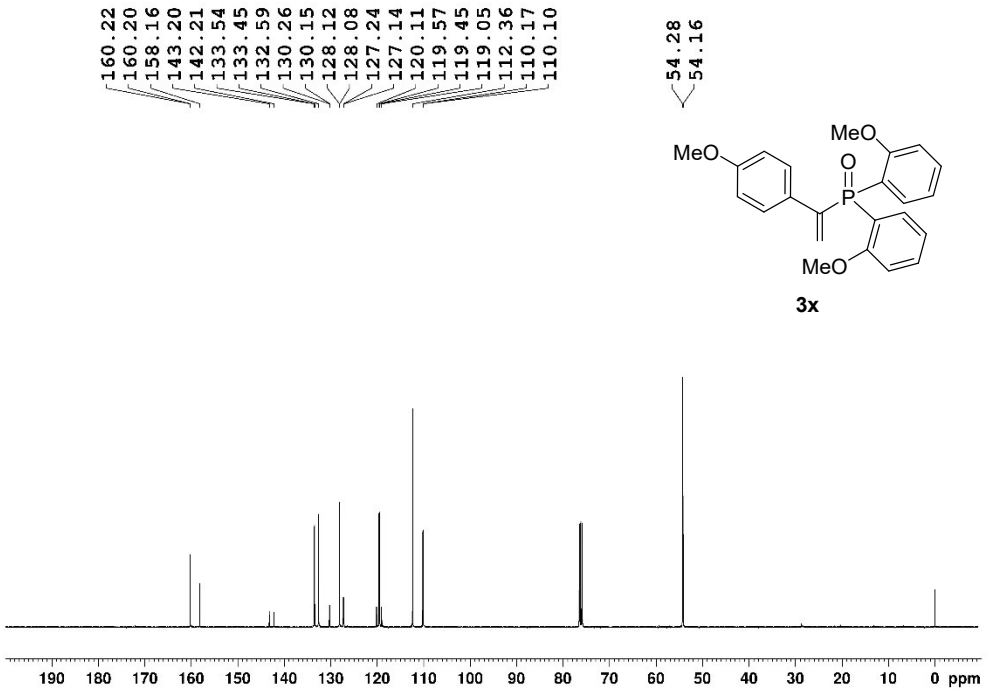
(1-(4-Methoxyphenyl)vinyl)di-*p*-tolylphosphine oxide (3w): ^{31}P NMR (162 MHz, $CDCl_3$)



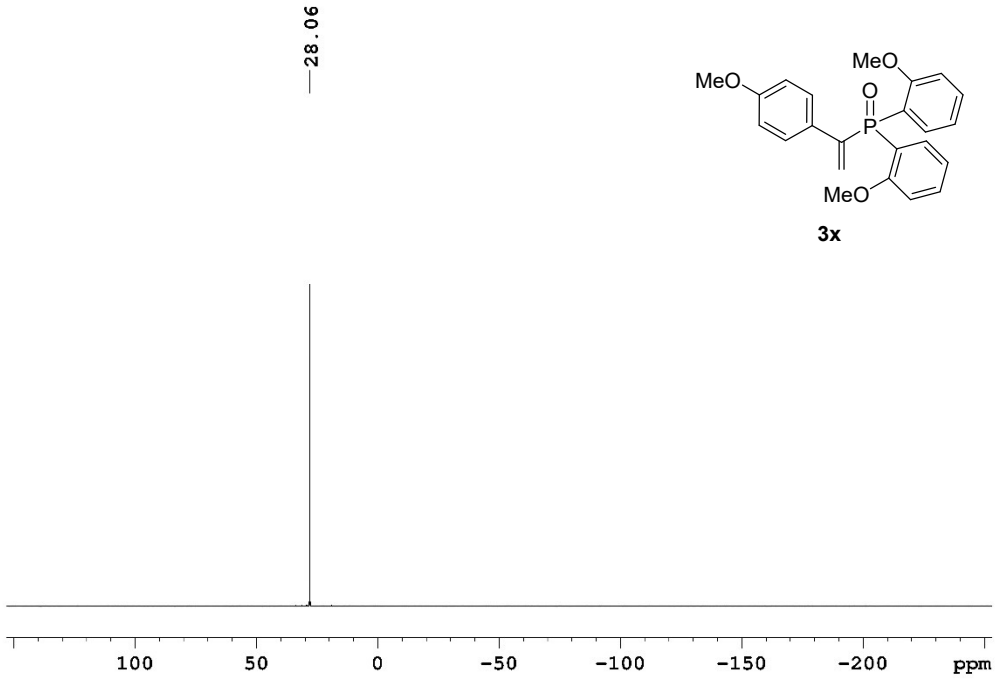
Bis(2-methoxyphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3x): ^{1}H NMR (400 MHz, $CDCl_3$)



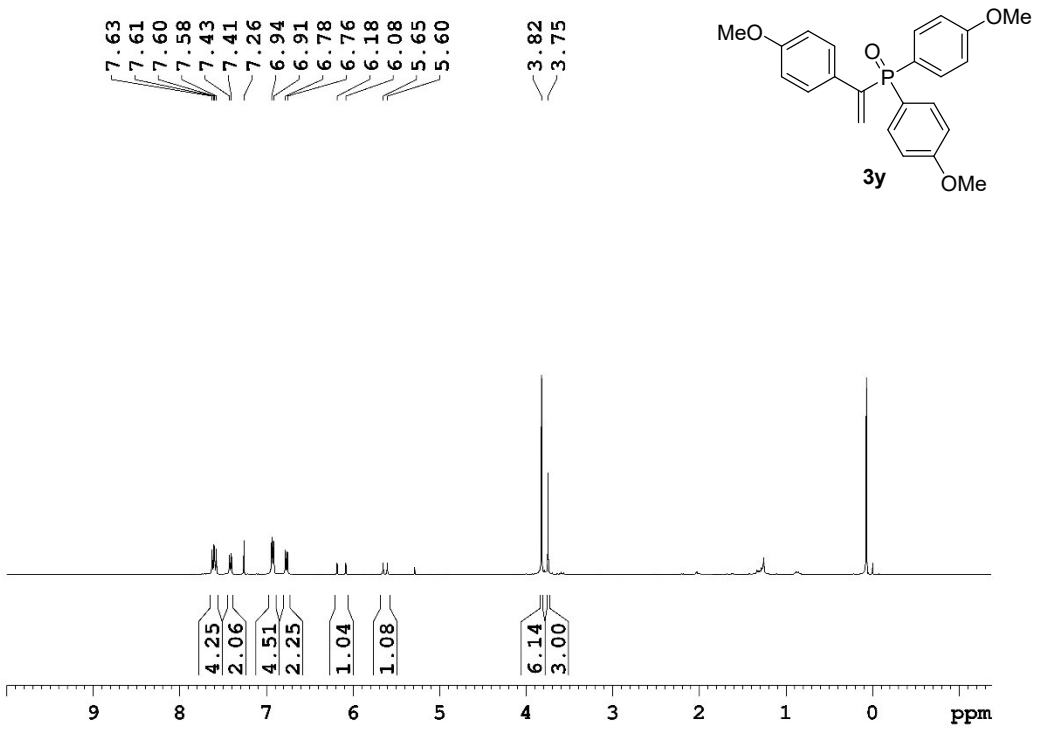
Bis(2-methoxyphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3x): ^{13}C NMR (101 MHz, $CDCl_3$)



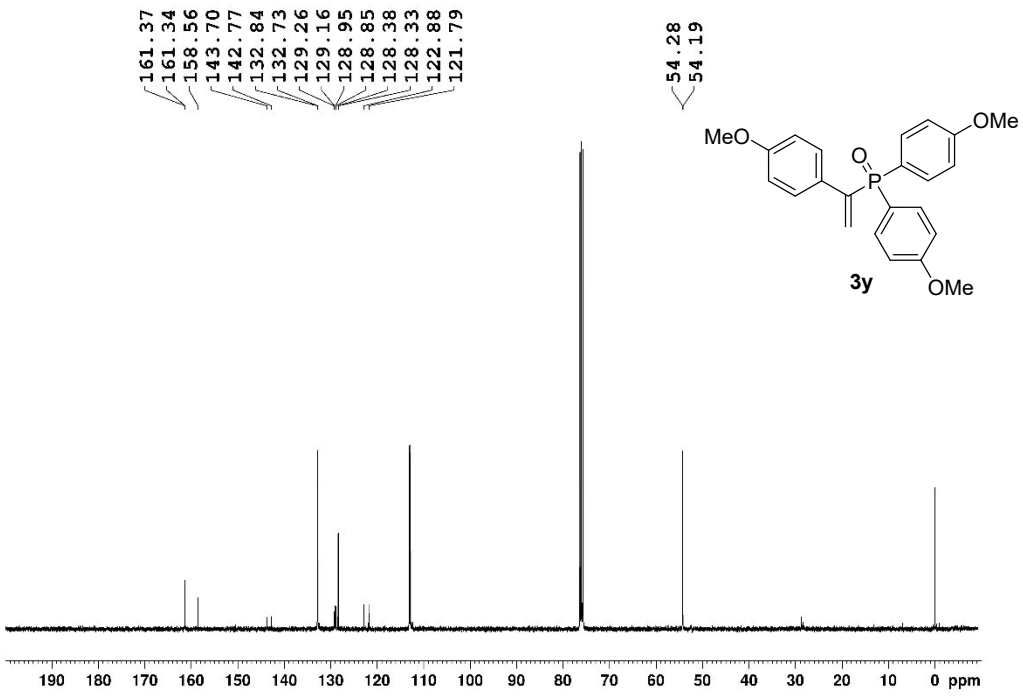
Bis(2-methoxyphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3x): ^{31}P NMR (162 MHz, $CDCl_3$)



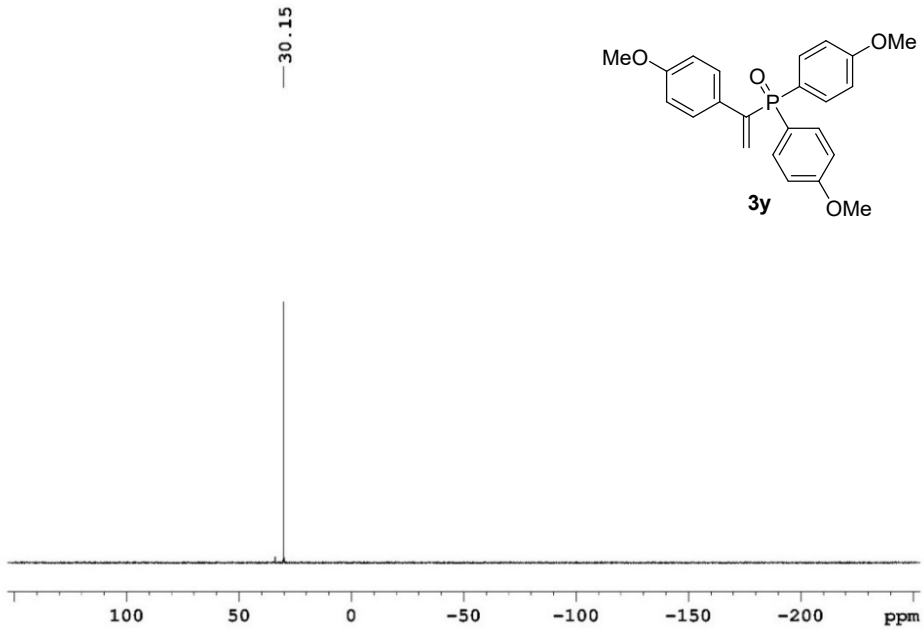
Bis(4-methoxyphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3y): ^{1}H NMR (400 MHz, $CDCl_3$)



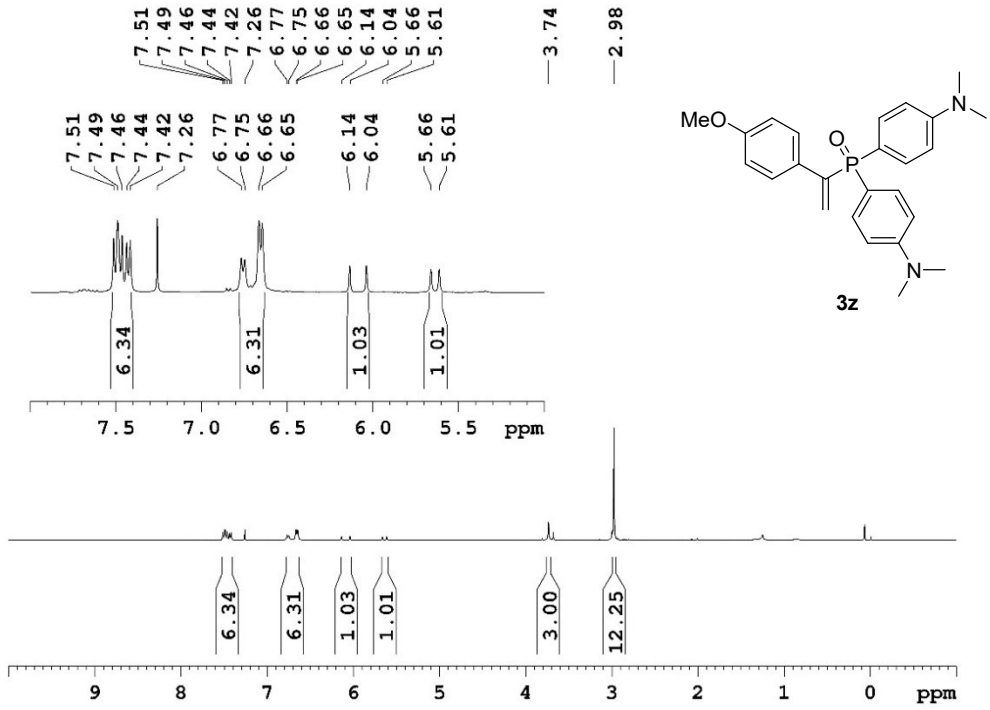
Bis(4-methoxyphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3y): ^{13}C NMR (101 MHz, $CDCl_3$)


161.37
161.34
158.56
143.70
142.77
132.84
132.73
129.26
129.16
128.95
128.85
128.38
128.33
122.88
121.79
54.28
54.19
MeO
OMe
O
P
OMe
3y
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

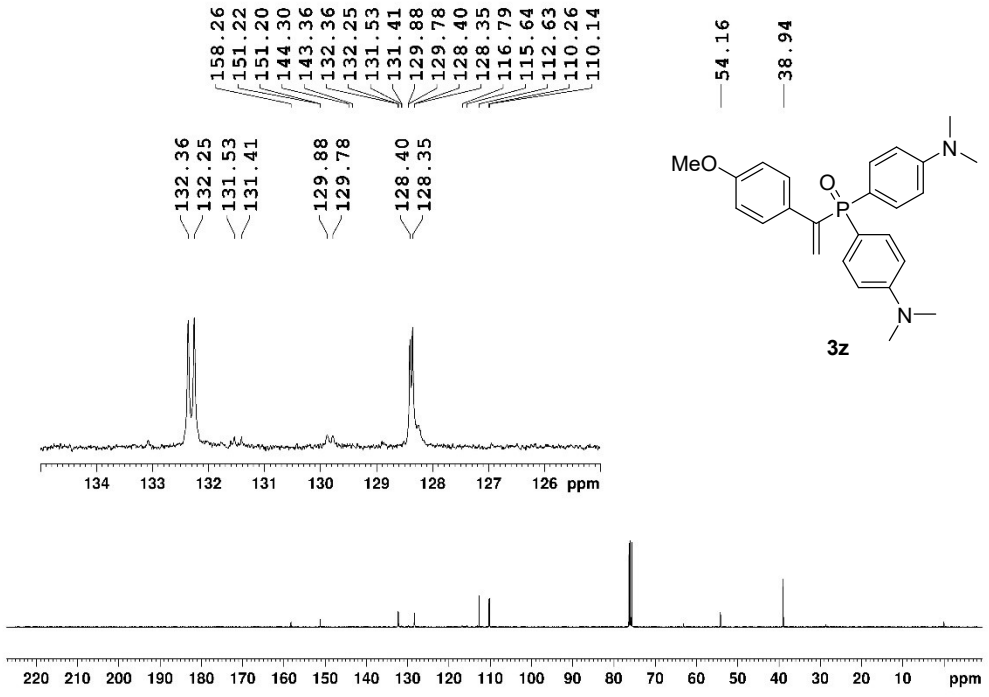
Bis(4-methoxyphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3y): ^{31}P NMR (162 MHz, $CDCl_3$)



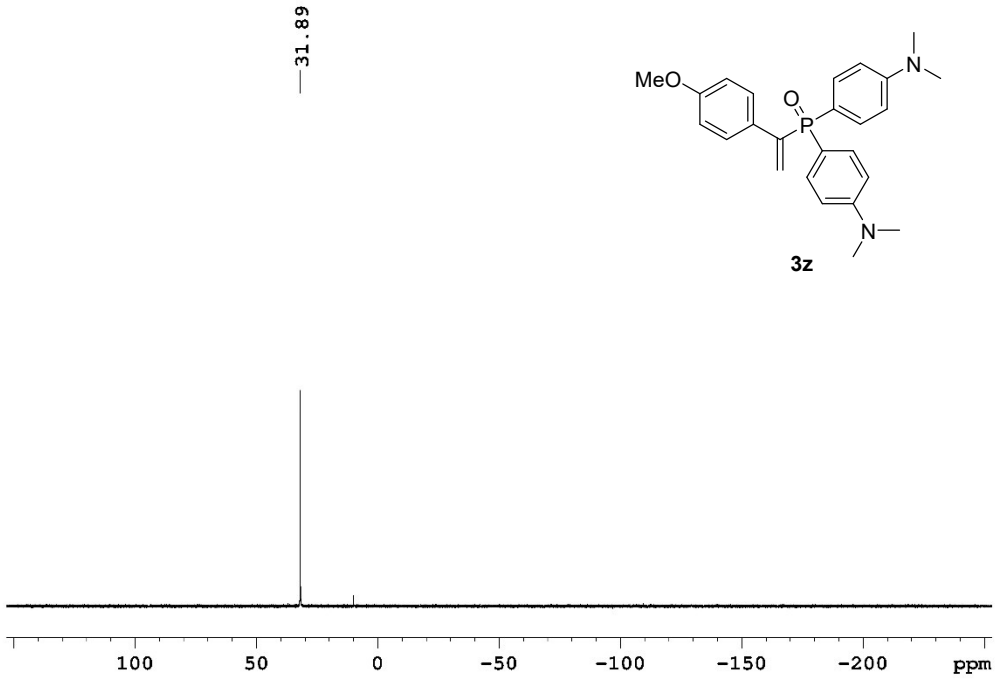
Bis(4-(dimethylamino)phenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3z): ^{1}H NMR (400 MHz, $CDCl_3$)



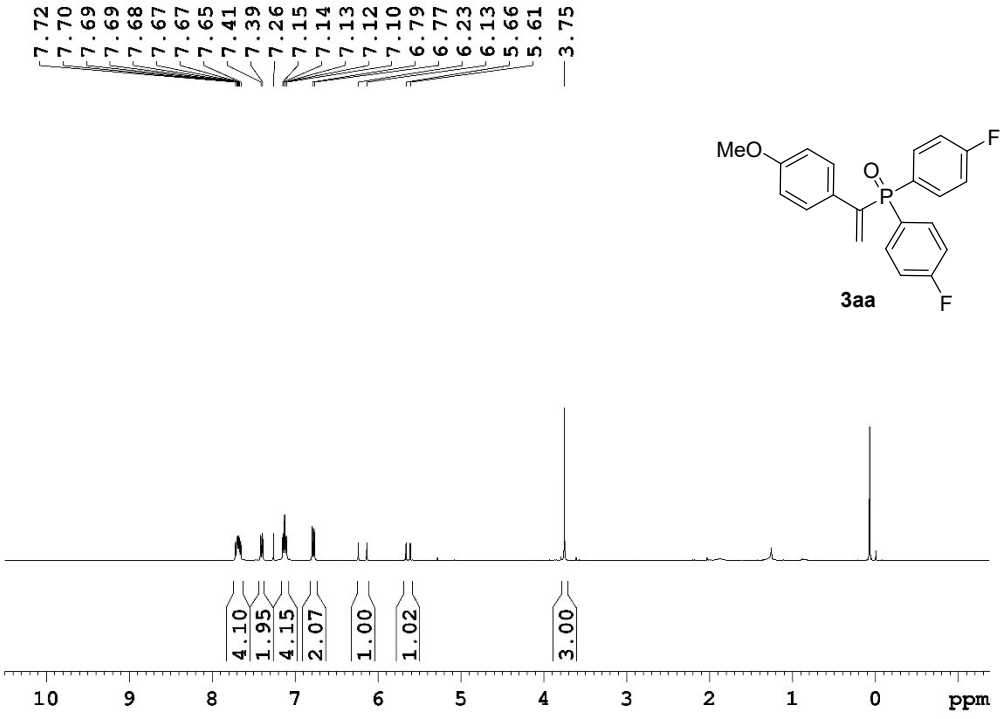
Bis(4-(dimethylamino)phenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3z): ^{13}C NMR (101 MHz, $CDCl_3$)



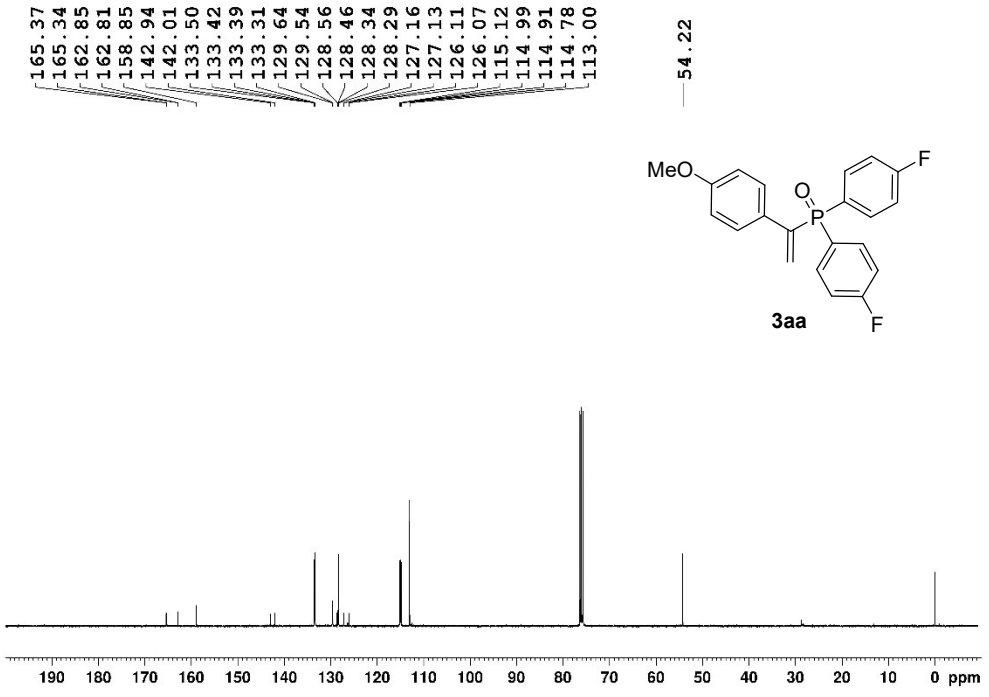
Bis(4-(dimethylamino)phenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3z): ^{31}P NMR (162 MHz, $CDCl_3$)



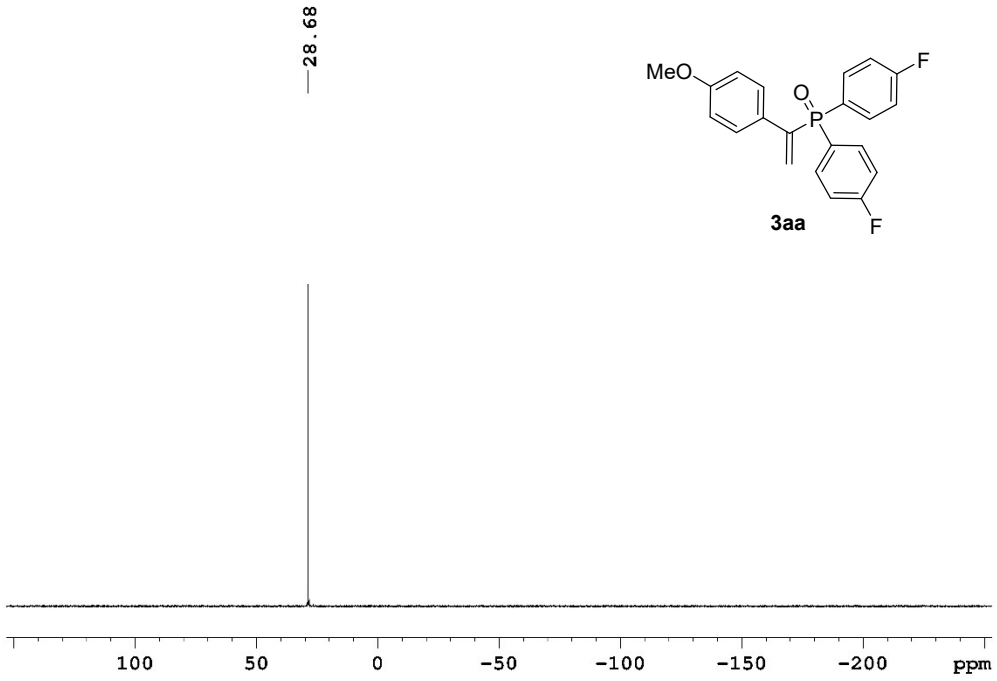
Bis(4-Fluorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3aa): ^{1}H NMR (400 MHz, $CDCl_3$)



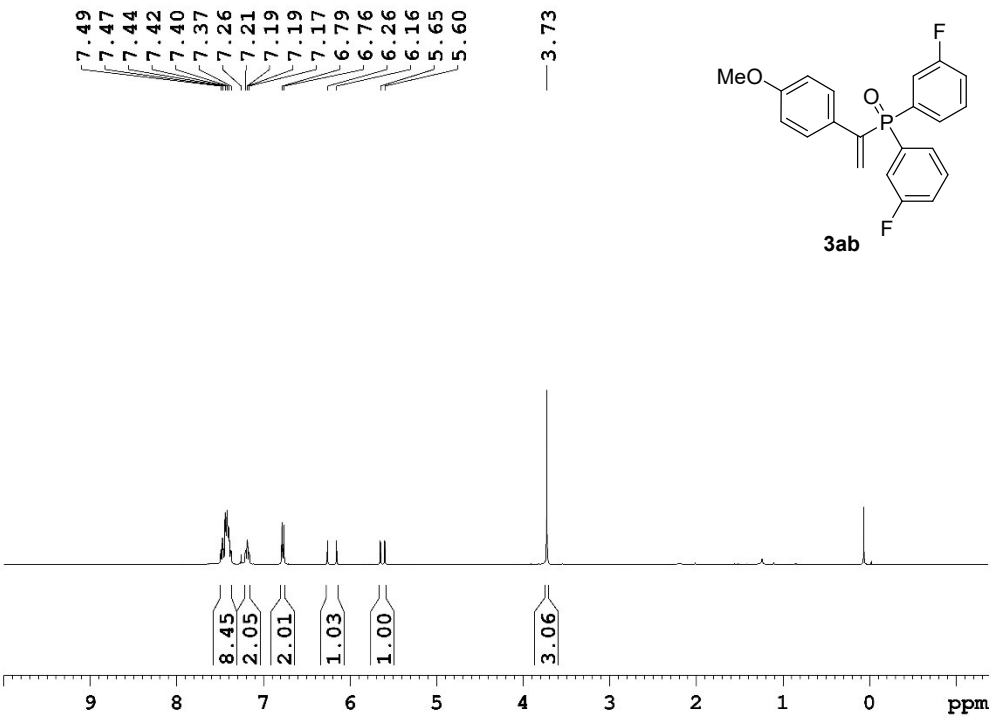
Bis(4-Fluorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3aa): ^{13}C NMR (101 MHz, $CDCl_3$)



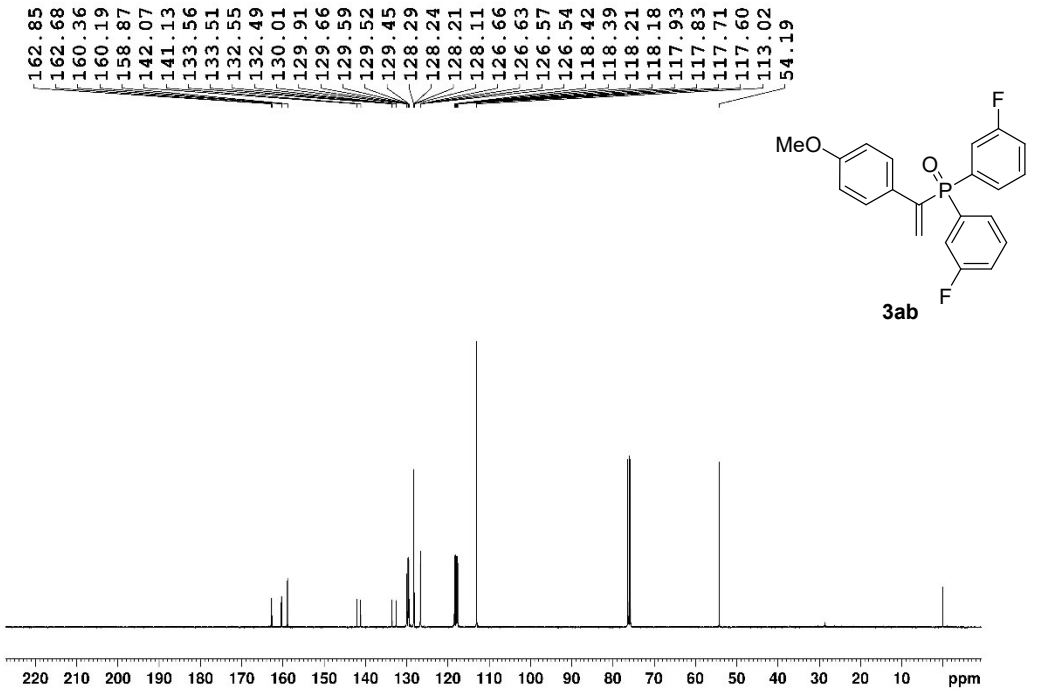
Bis(4-Fluorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3aa): ^{31}P NMR (162 MHz, $CDCl_3$)



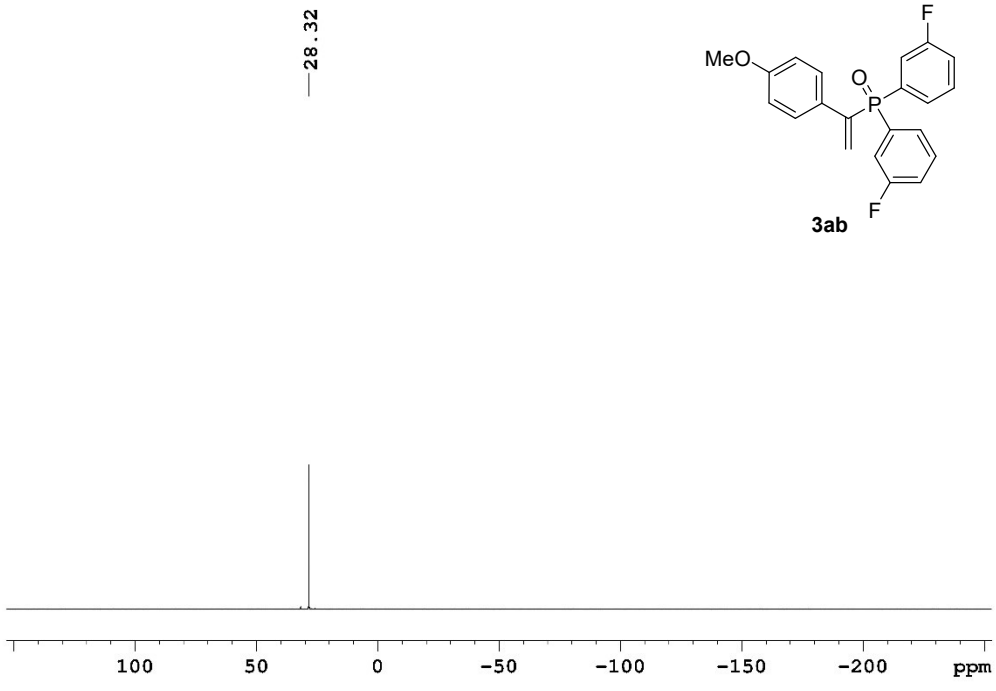
Bis(3-Fluorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ab): ^{1}H NMR (400 MHz, $CDCl_3$)



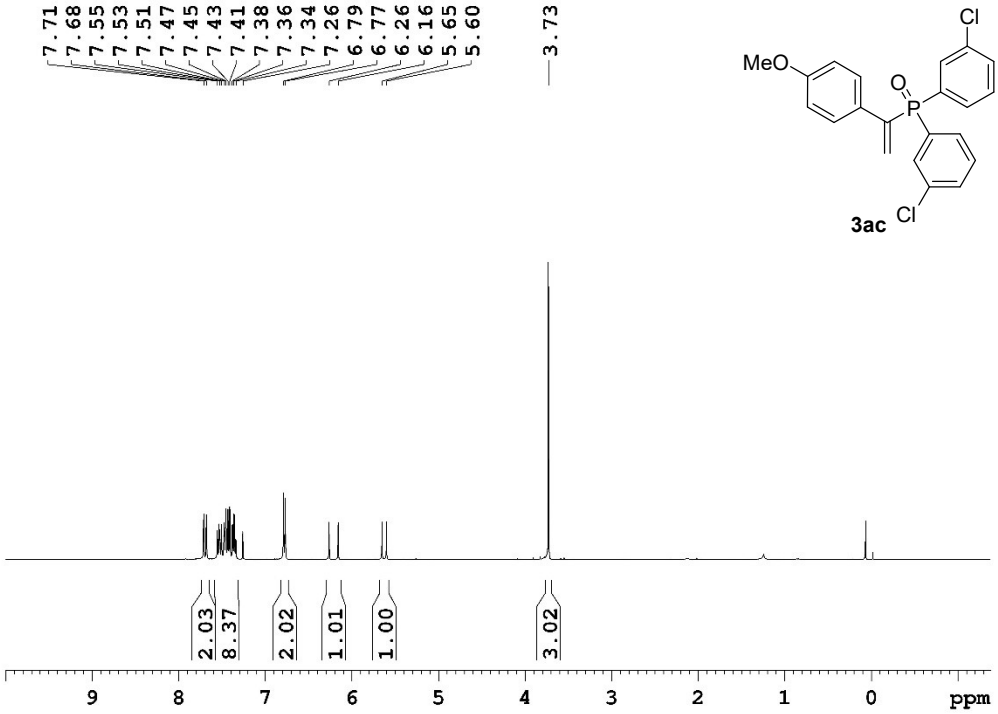
Bis(3-Fluorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ab): ^{13}C NMR (101 MHz, $CDCl_3$)



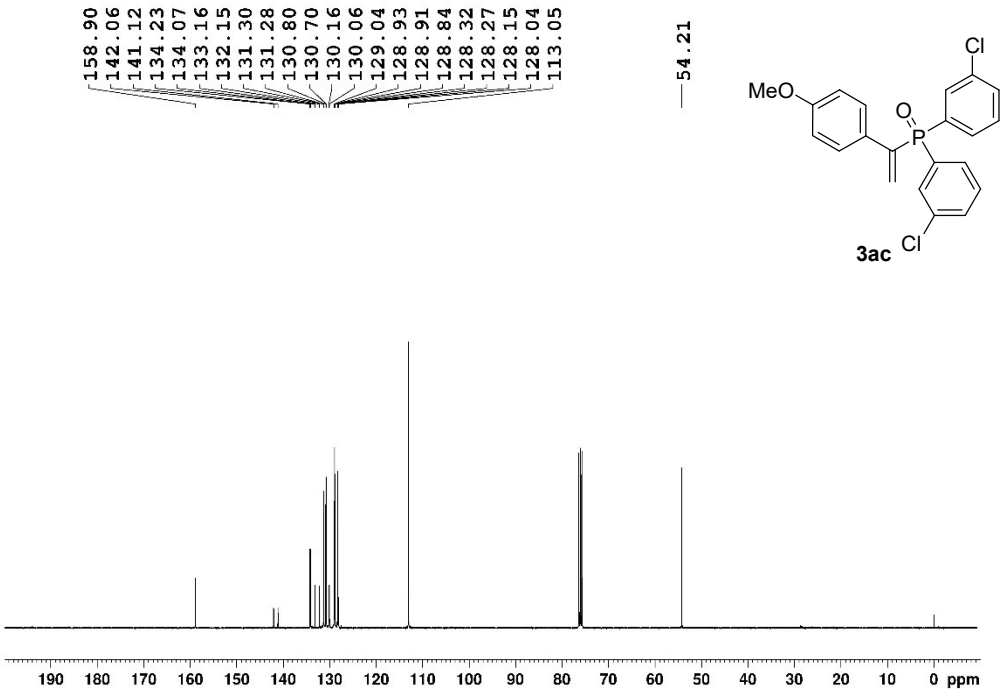
Bis(3-Fluorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ab): ^{31}P NMR (162 MHz, $CDCl_3$)



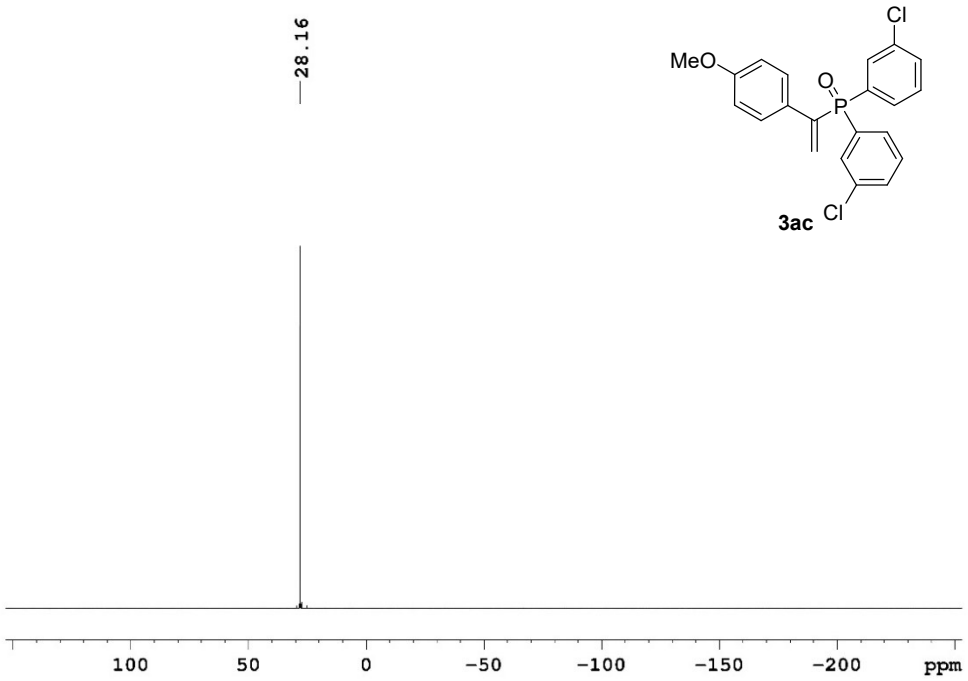
Bis(3-chlorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ac): ^{1}H NMR (400 MHz, $CDCl_3$)



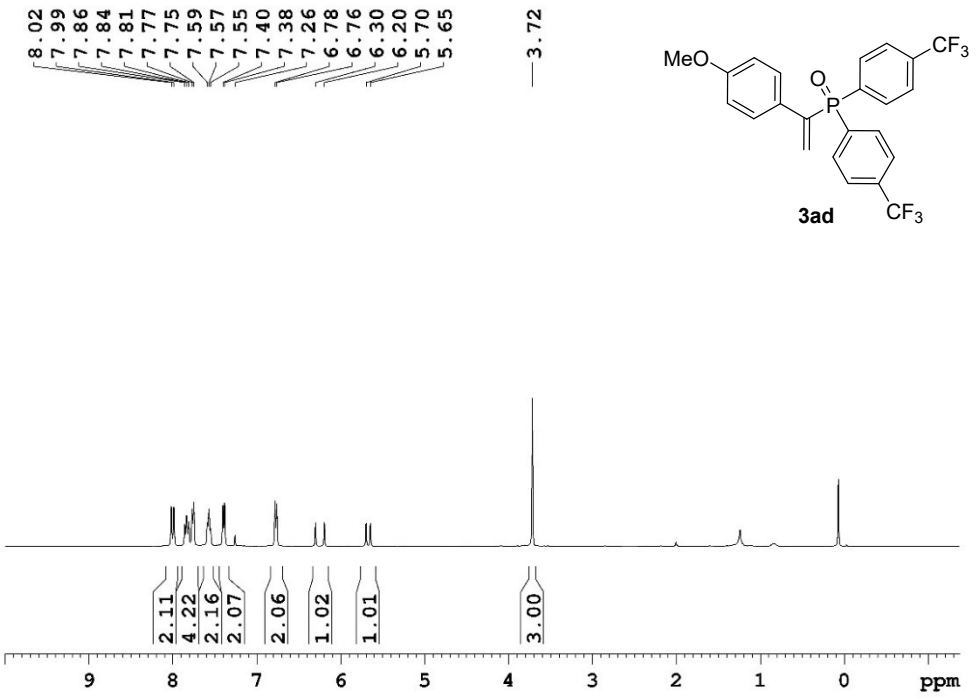
Bis(3-chlorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ac): ^{13}C NMR (101 MHz, $CDCl_3$)



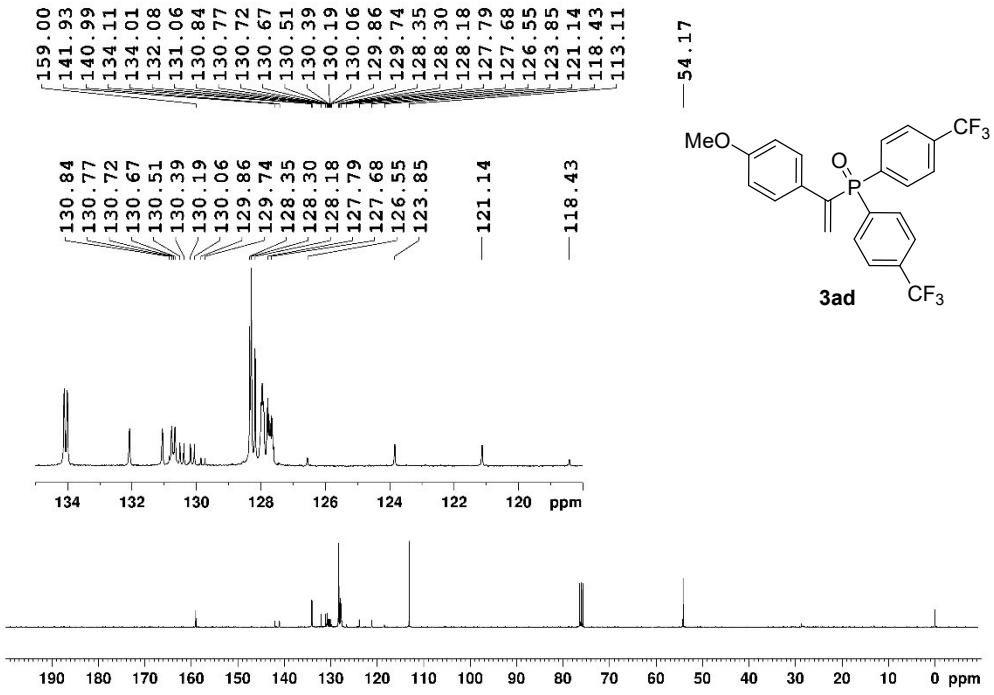
Bis(3-chlorophenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ac): ^{31}P NMR (162 MHz, $CDCl_3$)



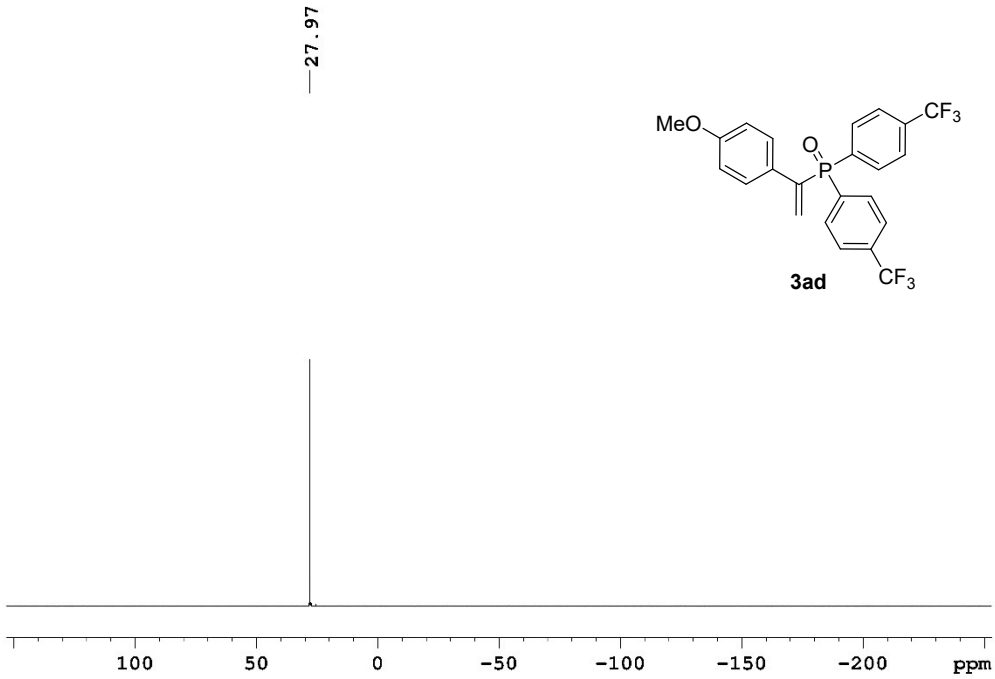
(1-(4-Methoxyphenyl)vinyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ad): ^{1}H NMR (400 MHz, $CDCl_3$)



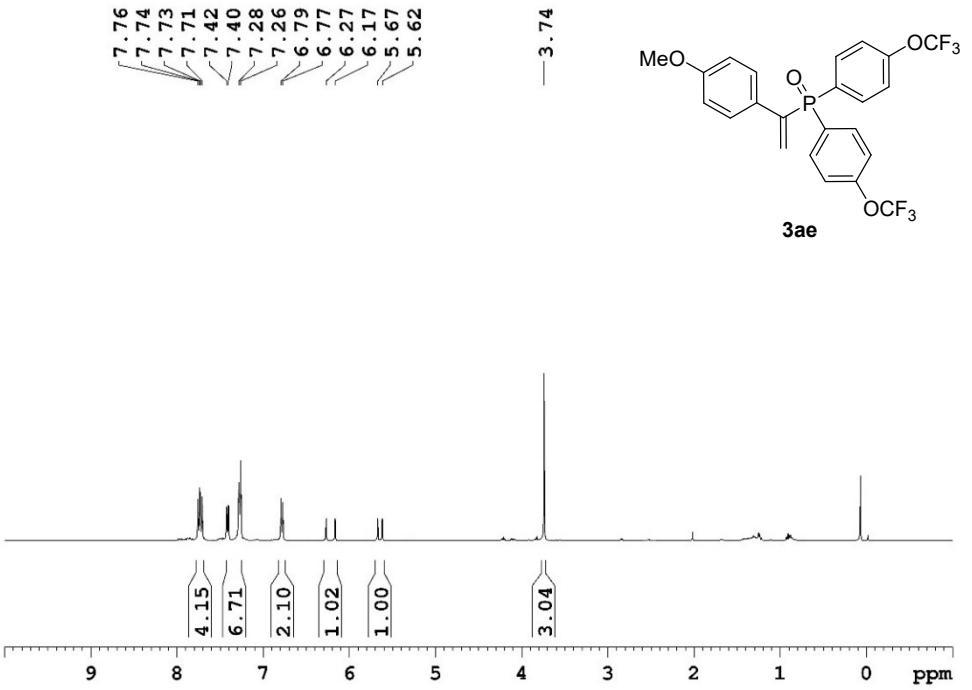
(1-(4-Methoxyphenyl)vinyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ad): ^{13}C NMR (101 MHz, $CDCl_3$)



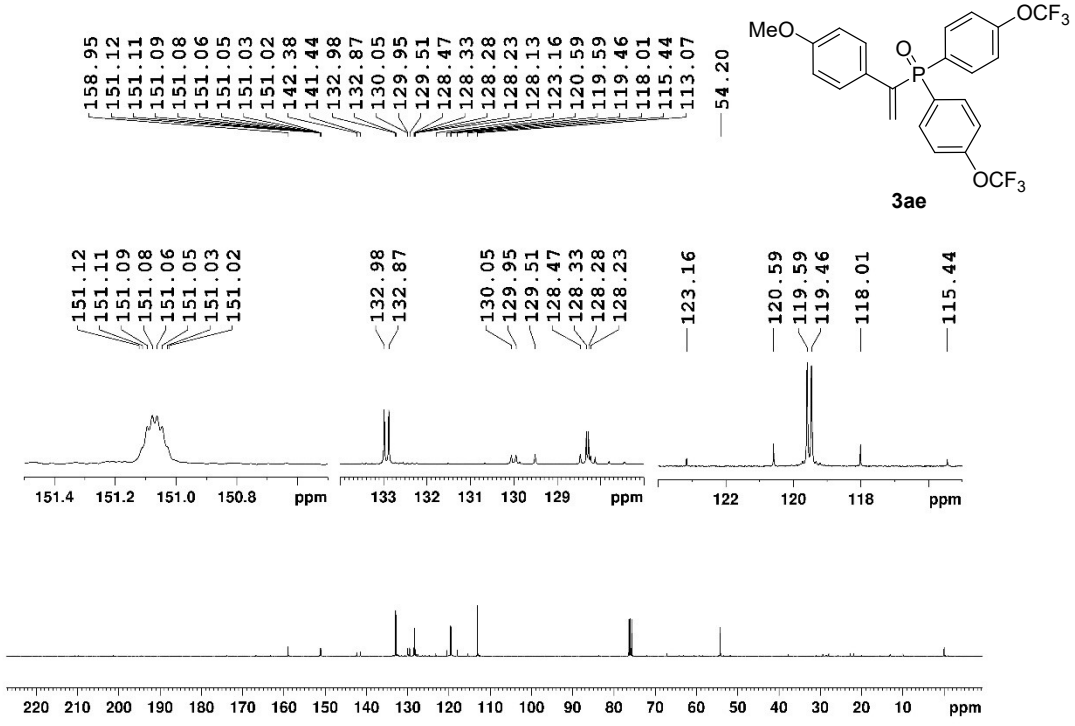
(1-(4-Methoxyphenyl)vinyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ad): ^{31}P NMR (162 MHz, $CDCl_3$)



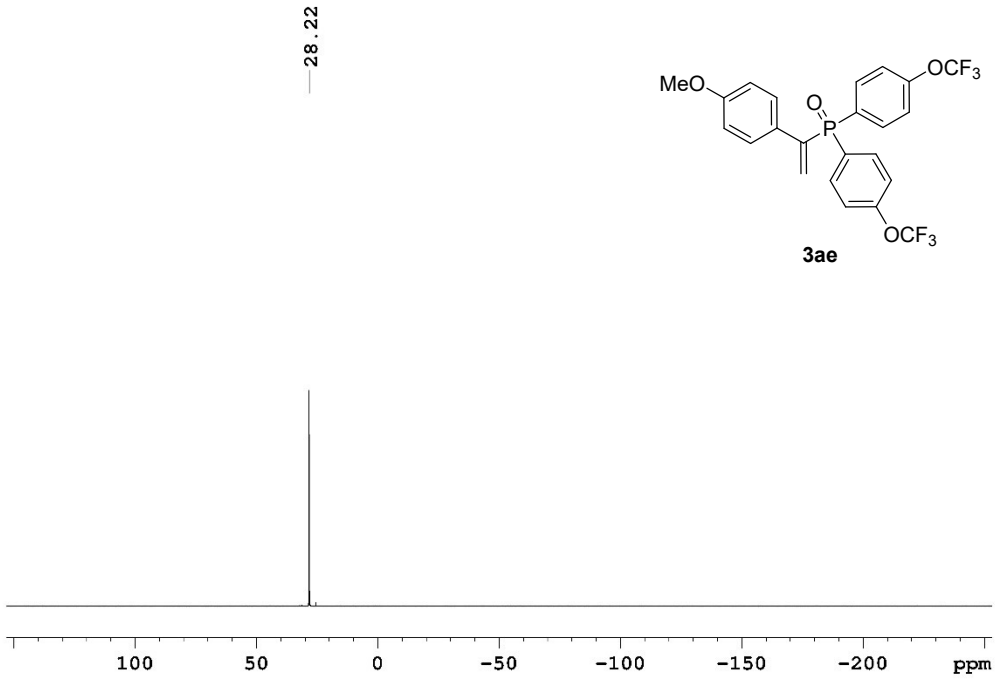
(1-(4-Methoxyphenyl)vinyl)bis(4-(trifluoromethoxy)phenyl)phosphine oxide (3ae): ^{1}H NMR (400 MHz, $CDCl_3$)



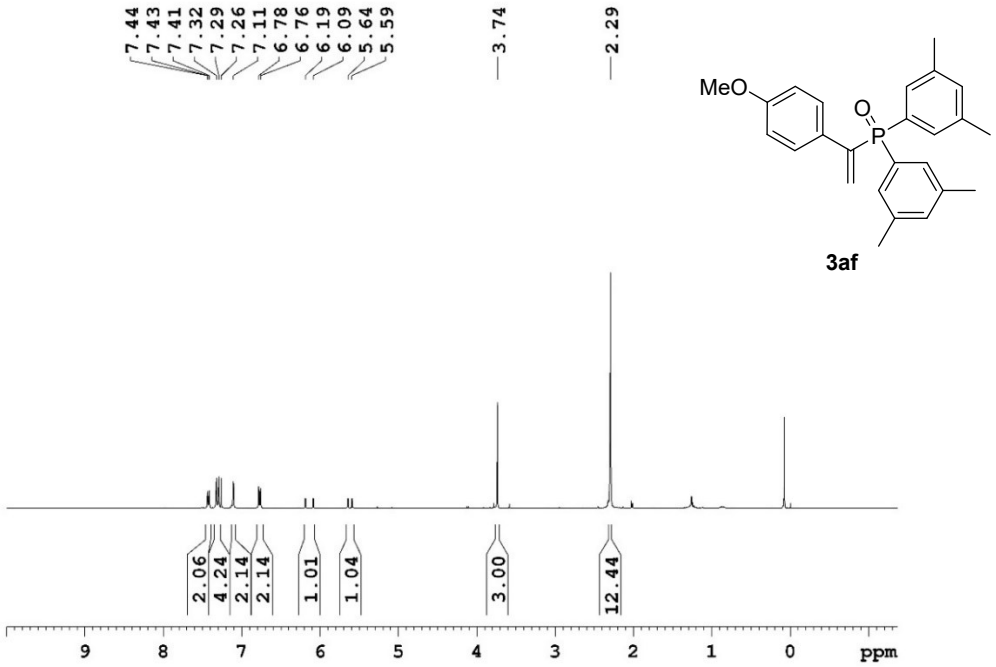
(1-(4-Methoxyphenyl)vinyl)bis(4-(trifluoromethoxy)phenyl)phosphine oxide (3ae): ^{13}C NMR (101 MHz, $CDCl_3$)



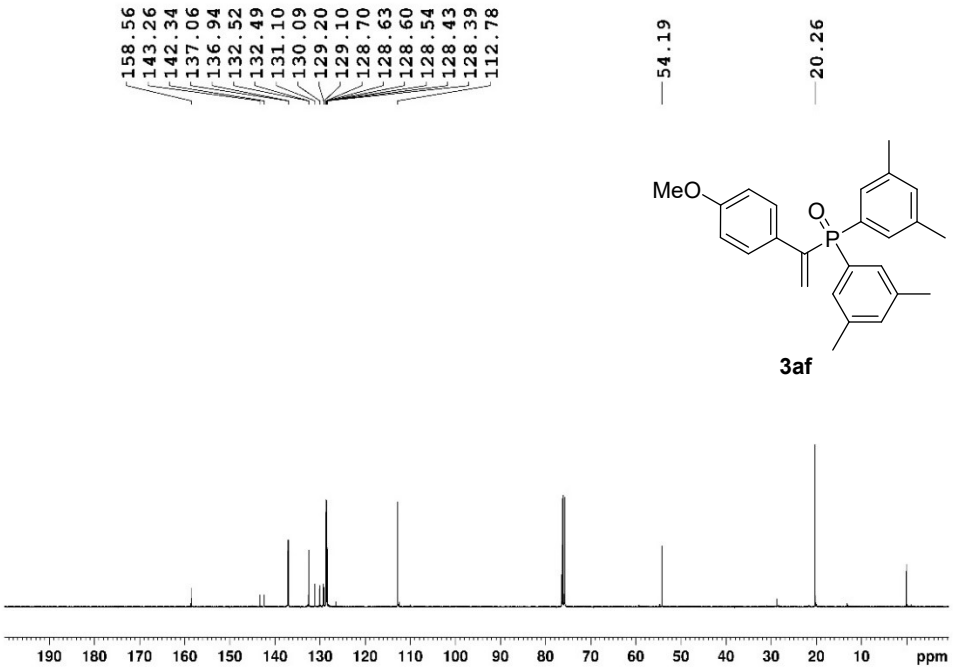
(1-(4-Methoxyphenyl)vinyl)bis(4-(trifluoromethoxy)phenyl)phosphine oxide (3ae): ^{31}P NMR (162 MHz, $CDCl_3$)



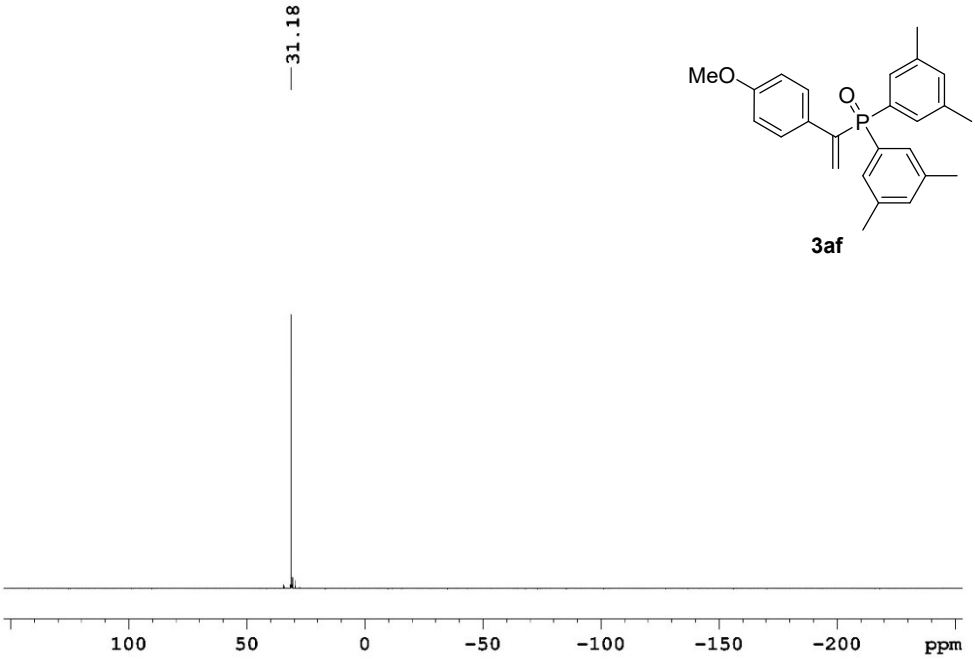
Bis(3,5-dimethylphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3af): ^{1}H NMR (400 MHz, $CDCl_3$)



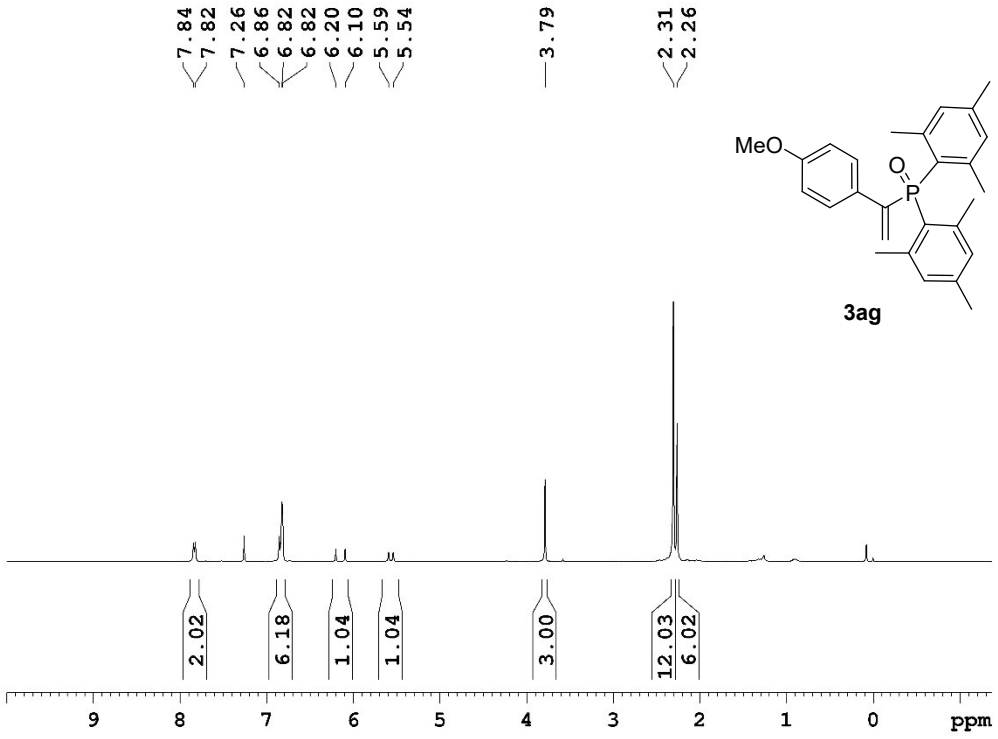
Bis(3,5-dimethylphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3af): ^{13}C NMR (101 MHz, $CDCl_3$)



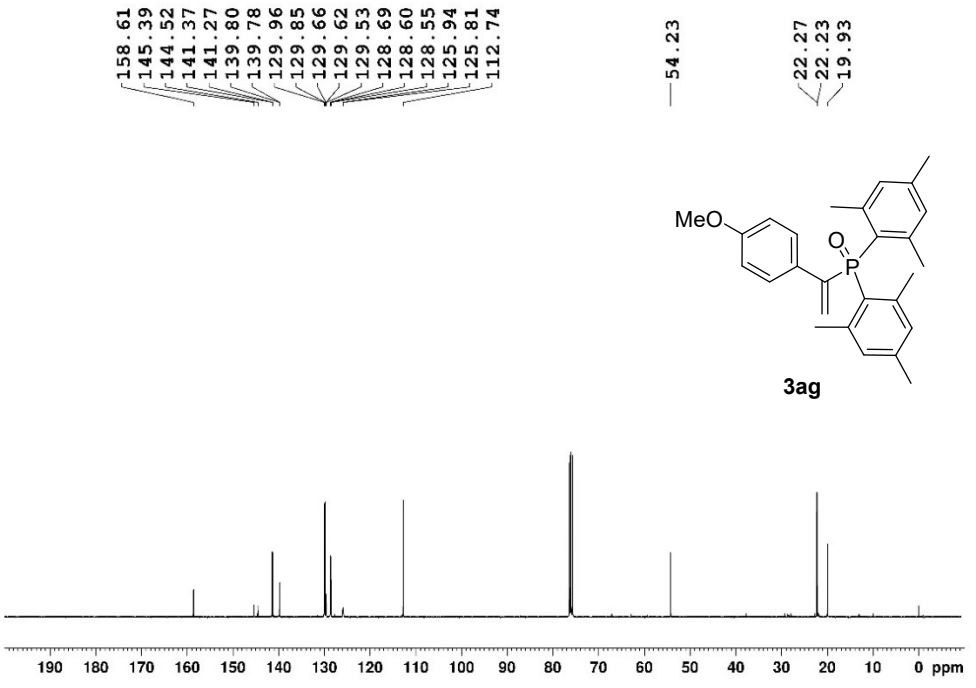
Bis(3,5-dimethylphenyl)(1-(4-methoxyphenyl)vinyl)phosphine oxide (3af): ^{31}P NMR (162 MHz, $CDCl_3$)



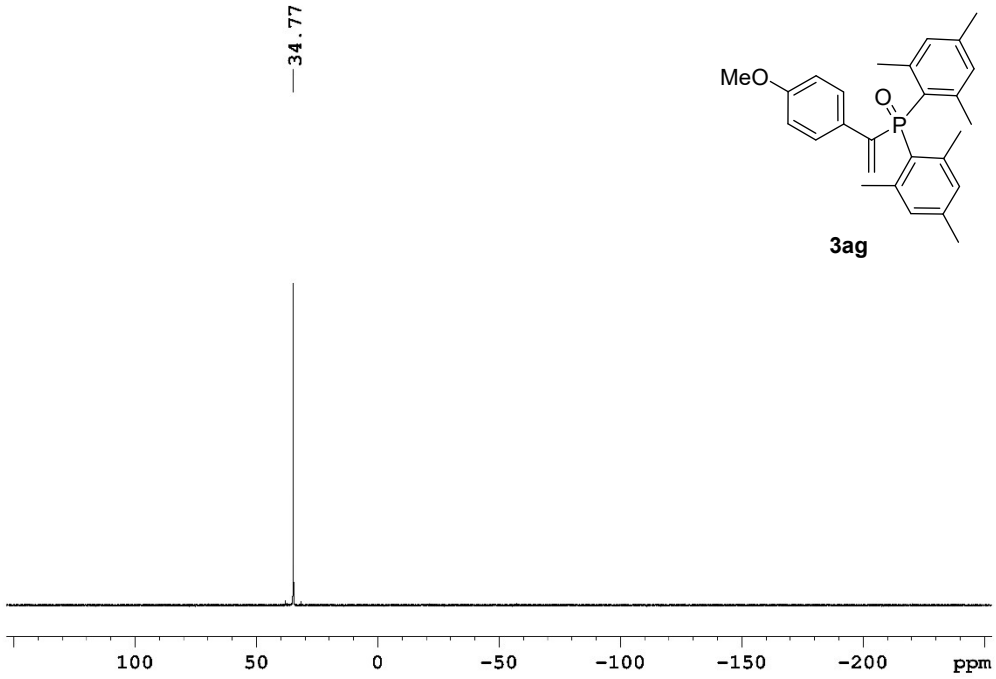
Dimesityl(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ag): ^{1}H NMR (400 MHz, $CDCl_3$)



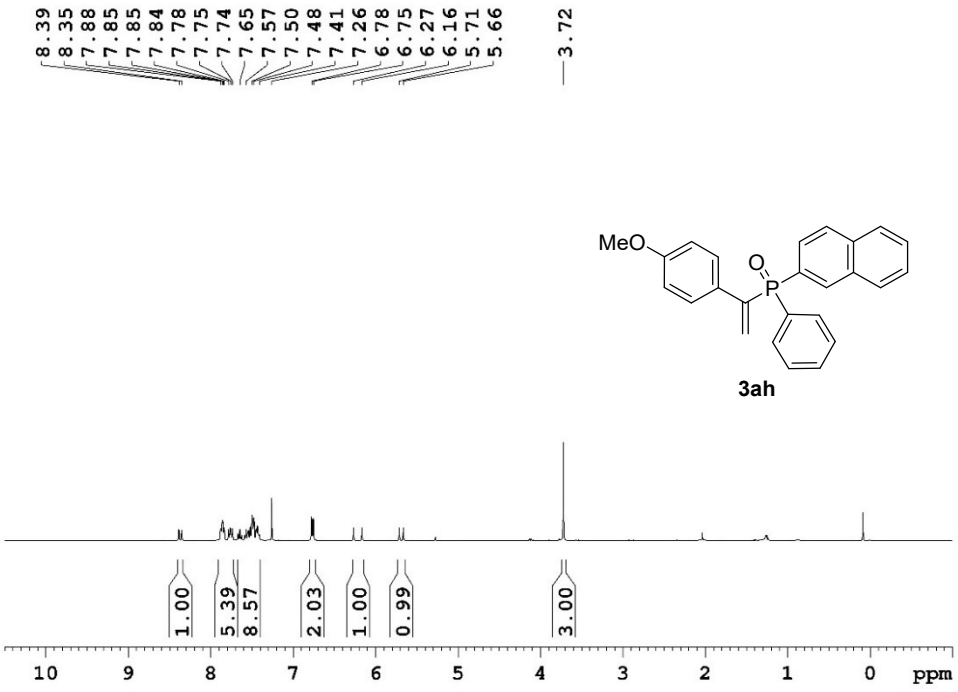
Dimesityl(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ag): ^{13}C NMR (101 MHz, $CDCl_3$)



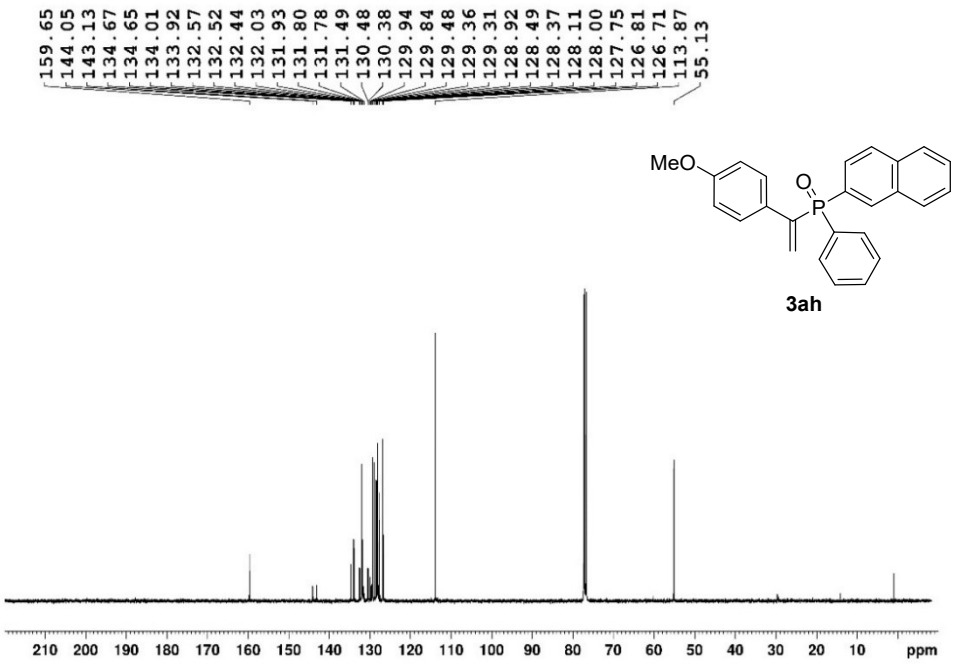
Dimesityl(1-(4-methoxyphenyl)vinyl)phosphine oxide (3ag): ^{31}P NMR (162 MHz, $CDCl_3$)



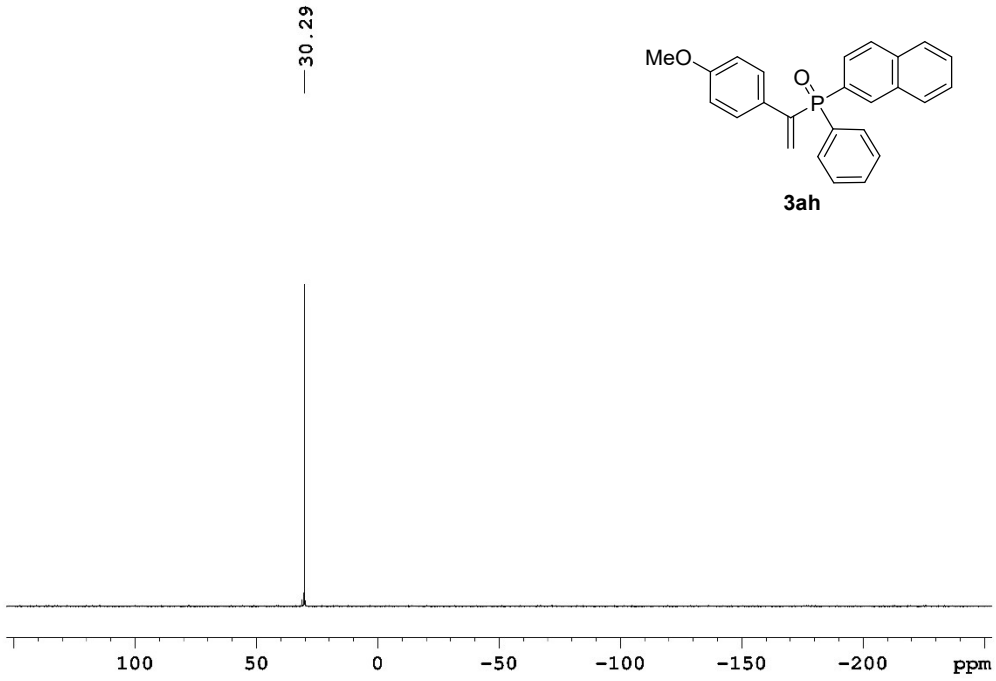
(1-(4-Methoxyphenyl)vinyl)(naphthalen-2-yl)(phenyl)phosphine oxide (3ah): ^{1}H NMR (400 MHz, $CDCl_3$)



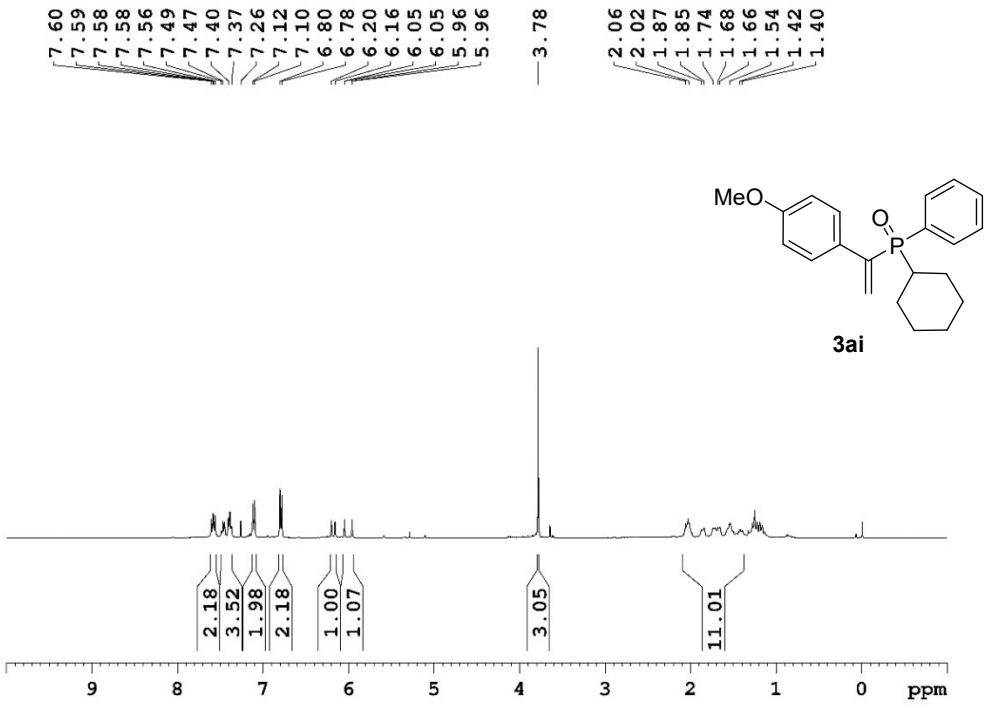
(1-(4-Methoxyphenyl)vinyl)(naphthalen-2-yl)(phenyl)phosphine oxide (3ah): ^{13}C NMR (101 MHz, $CDCl_3$)



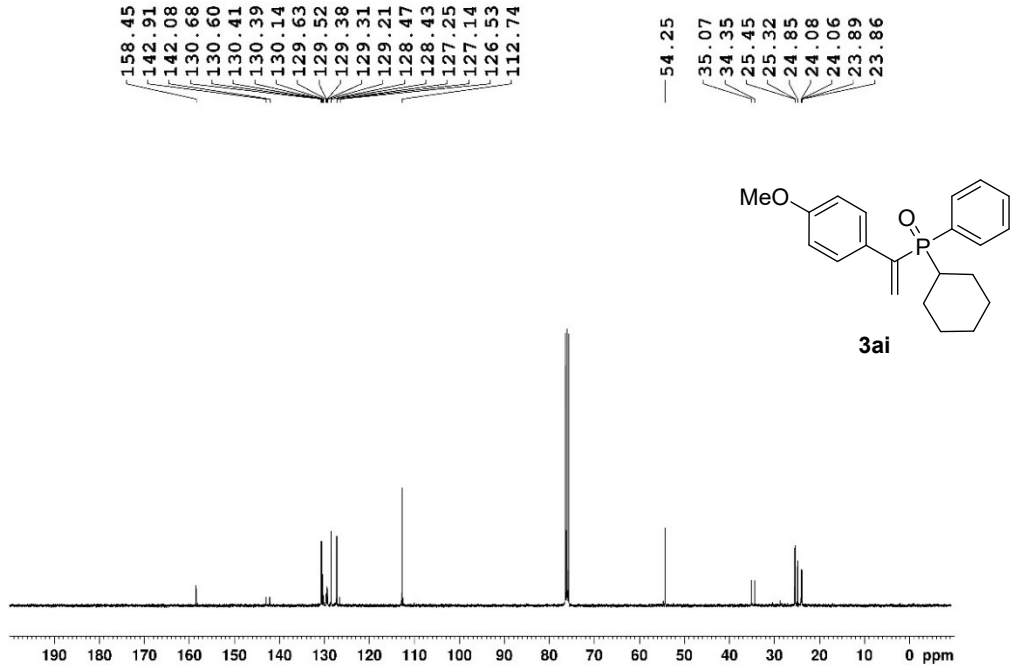
(1-(4-Methoxyphenyl)vinyl)(naphthalen-2-yl)(phenyl)phosphine oxide (3ah): ^{31}P NMR (162 MHz, $CDCl_3$)



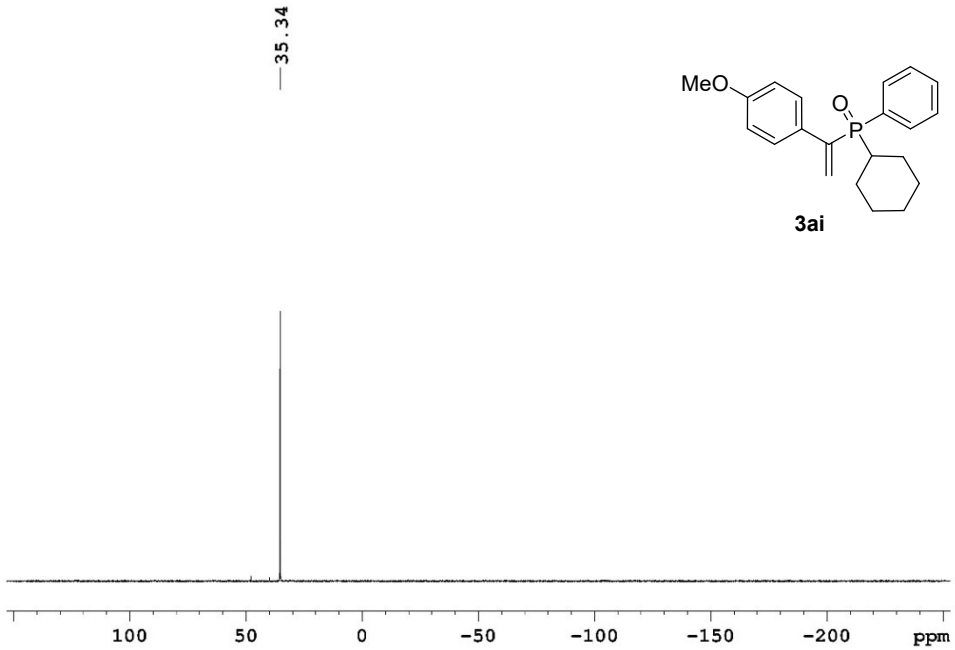
Cyclohexyl(1-(4-methoxyphenyl)vinyl)(phenyl)phosphine oxide (3ai): ^{1}H NMR (400 MHz, $CDCl_3$)



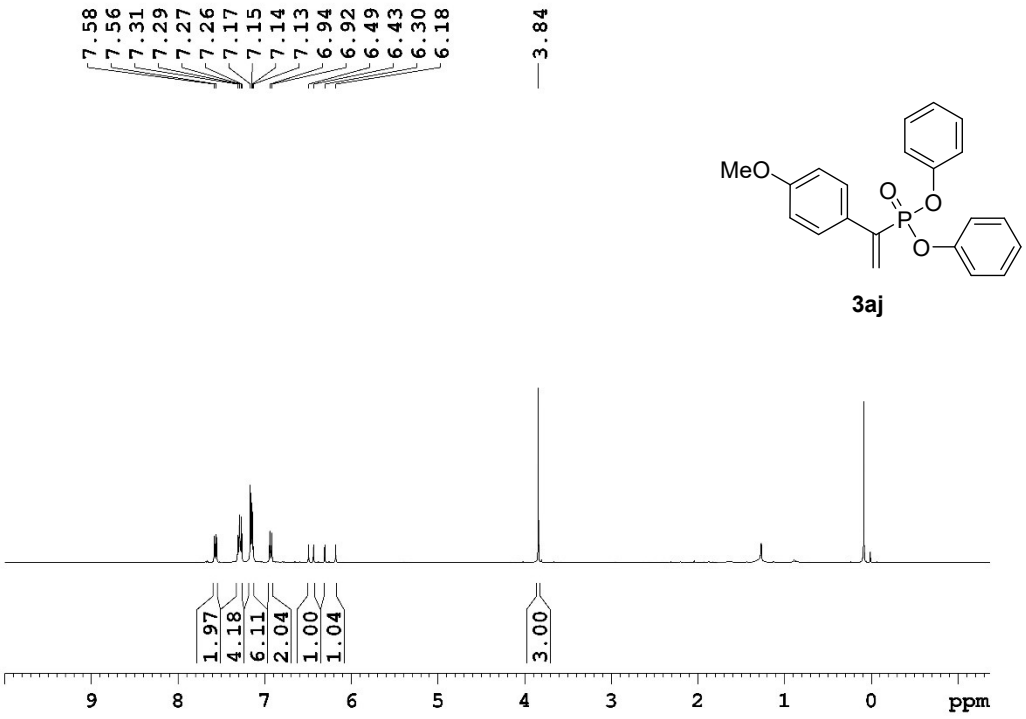
Cyclohexyl(1-(4-methoxyphenyl)vinyl)(phenyl)phosphine oxide (3ai): ^{13}C NMR (101 MHz, $CDCl_3$)



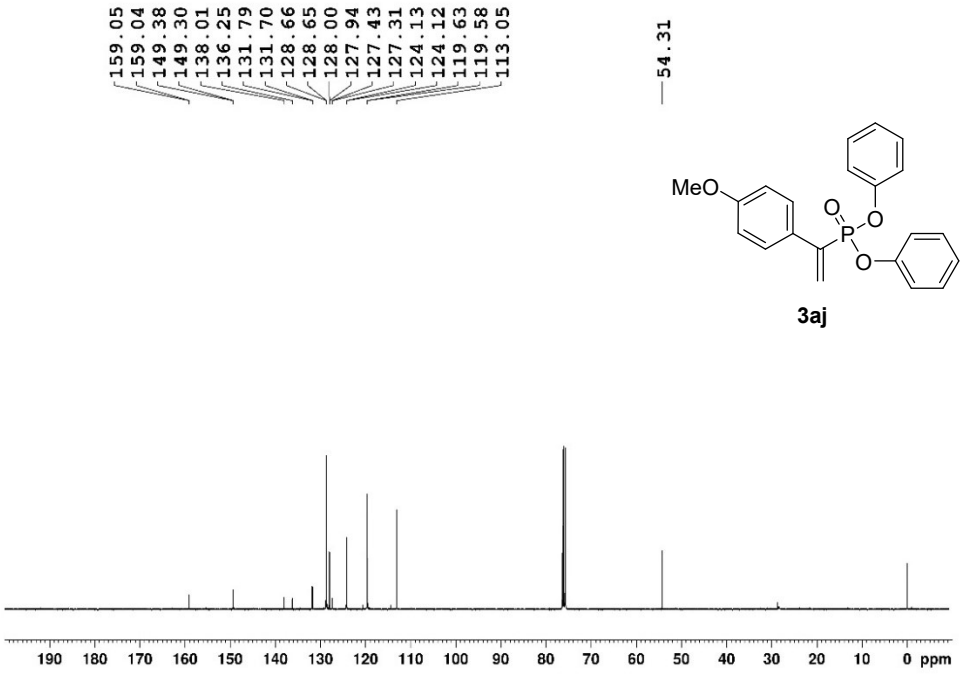
Cyclohexyl(1-(4-methoxyphenyl)vinyl)(phenyl)phosphine oxide (3ai): ^{31}P NMR (162 MHz, $CDCl_3$)



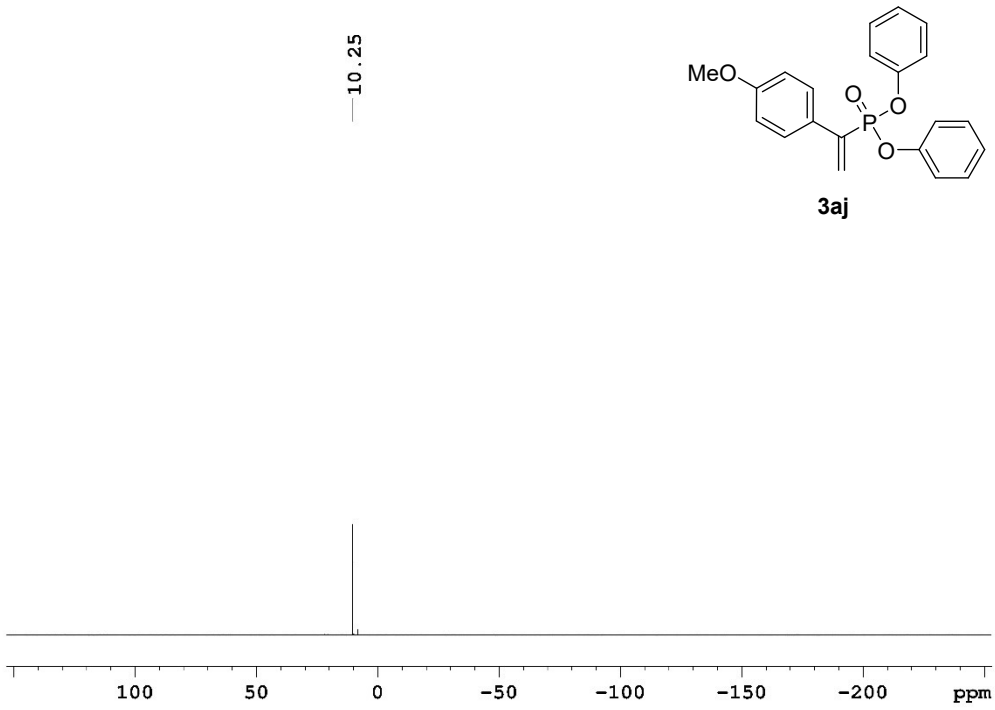
Diphenyl (1-(4-methoxyphenyl)vinyl)phosphonate (3aj): ^{1}H NMR (400 MHz, $CDCl_3$)



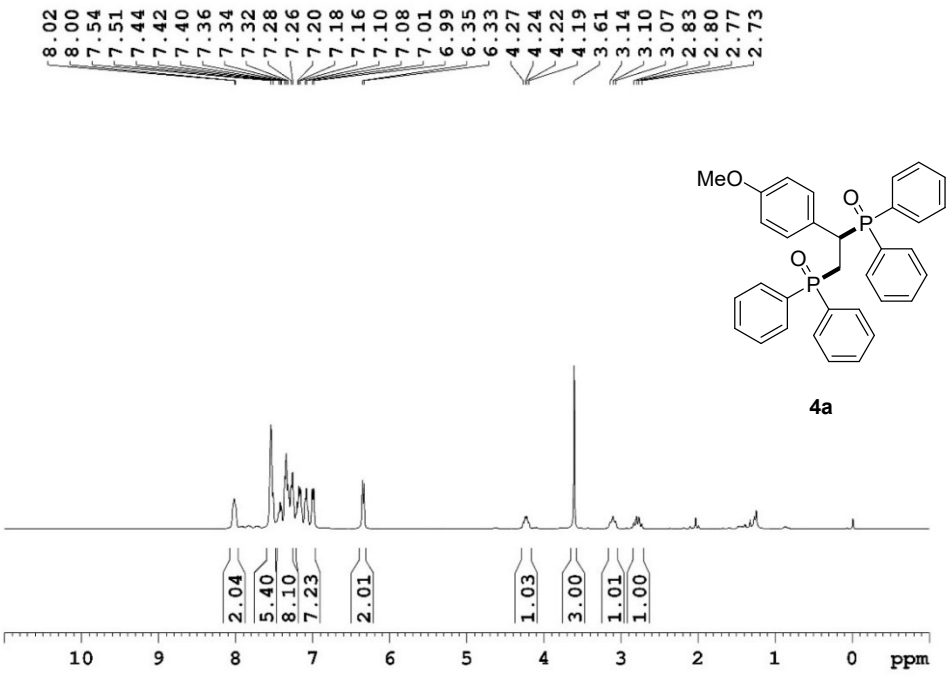
Diphenyl (1-(4-methoxyphenyl)vinyl)phosphonate (3aj): ^{13}C NMR (101 MHz, $CDCl_3$)



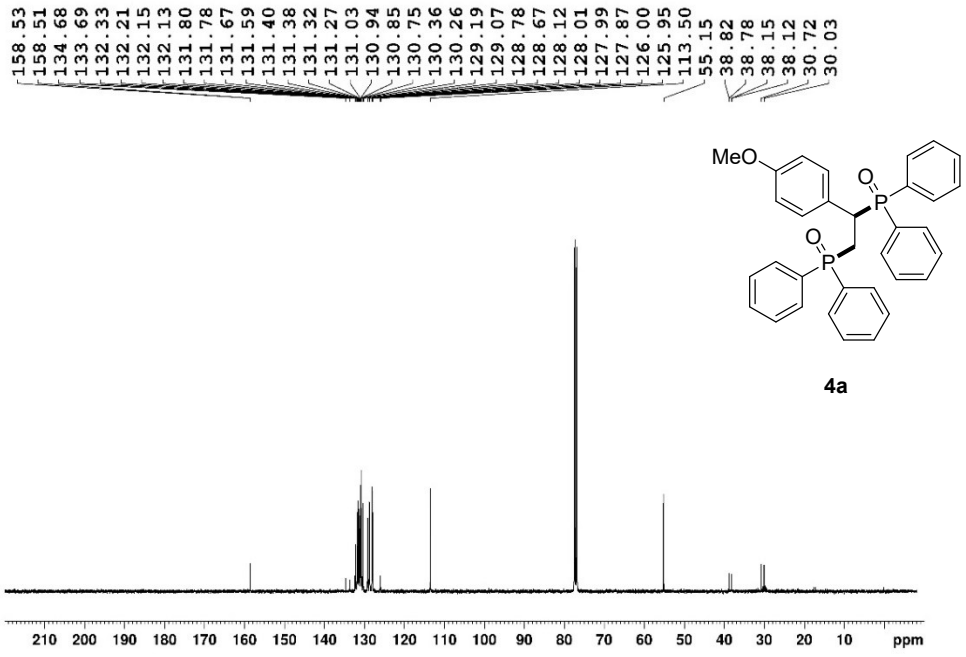
Diphenyl (1-(4-methoxyphenyl)vinyl)phosphonate (3aj): ^{31}P NMR (162 MHz, $CDCl_3$)



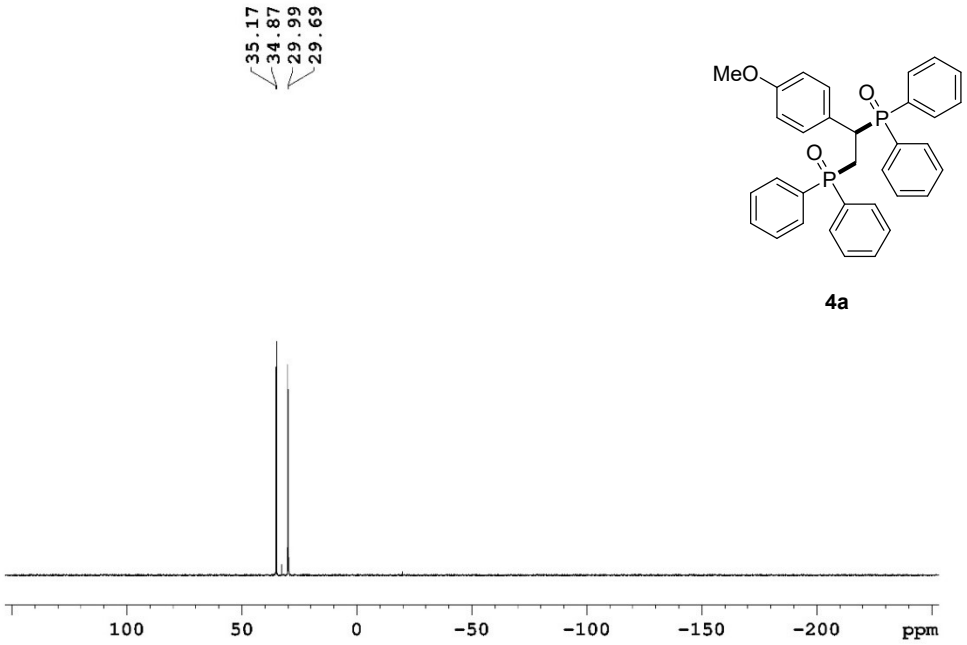
(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine oxide) (4a): ^{1}H NMR (400 MHz, $CDCl_3$)



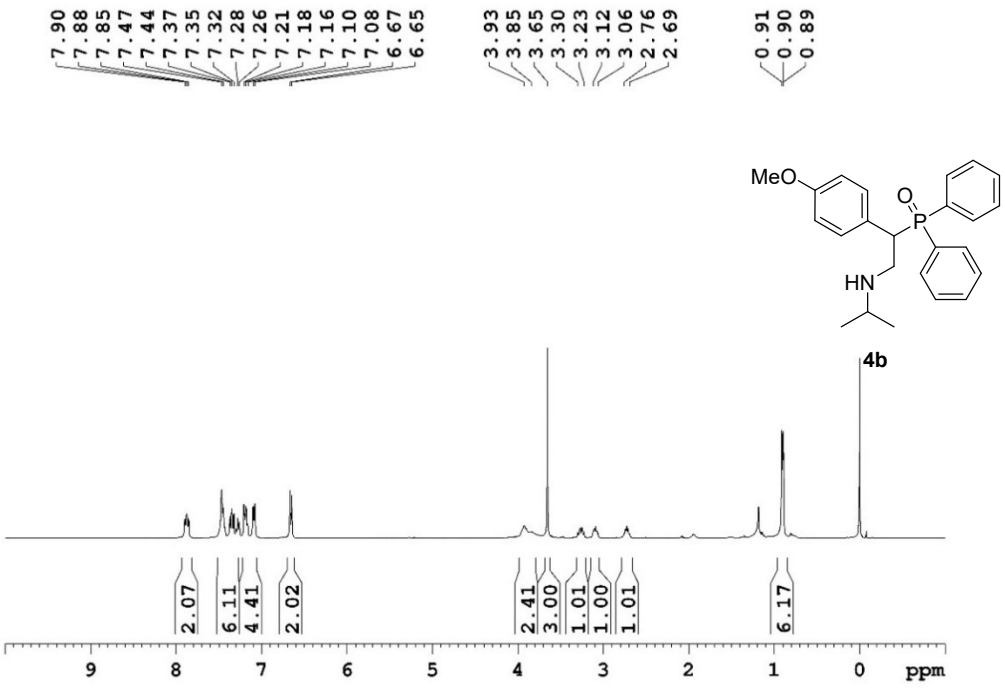
(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine oxide) (4a): ^{13}C NMR (101 MHz, $CDCl_3$)



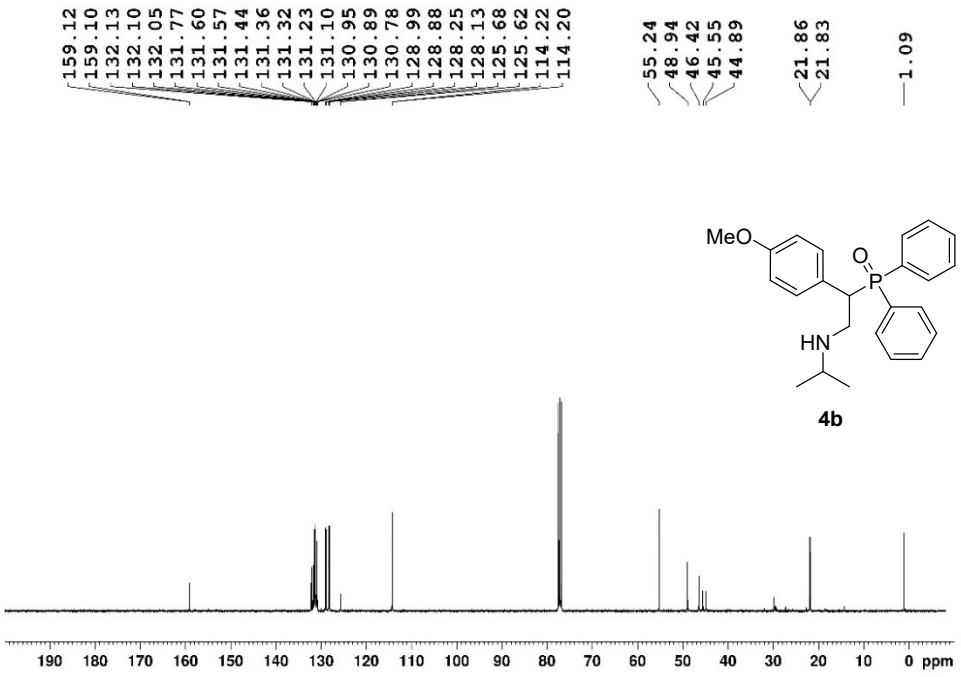
(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine oxide) (4a): ^{31}P NMR (162 MHz, $CDCl_3$)



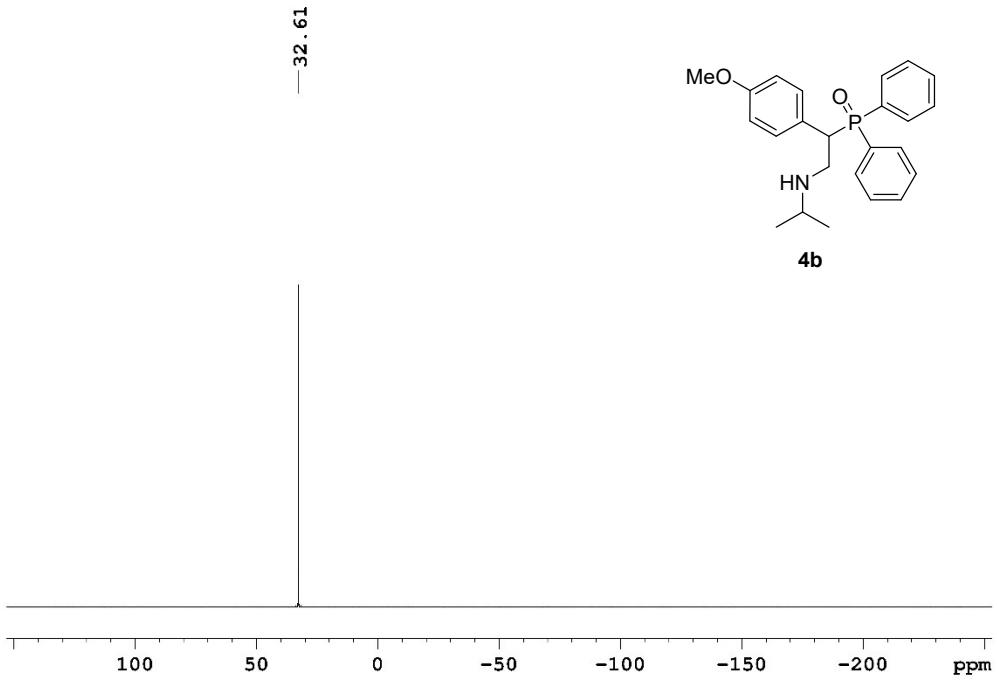
(2-(Isopropylamino)-1-(4-methoxyphenyl)ethyl)diphenylphosphine oxide (4b): ^{1}H NMR (400 MHz, $CDCl_3$)



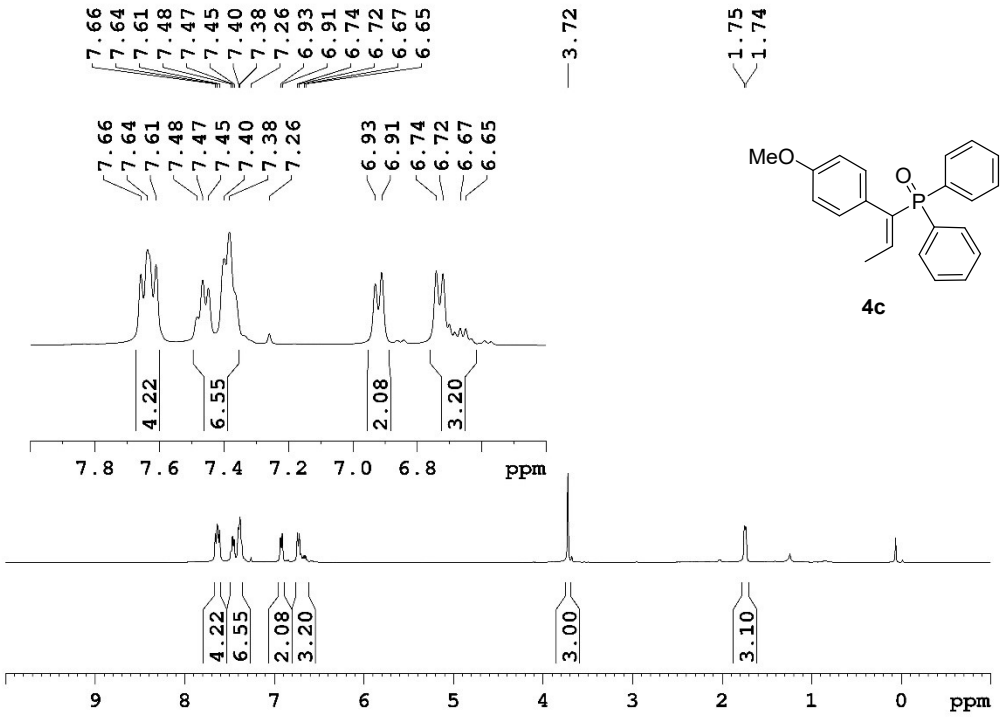
(2-(Isopropylamino)-1-(4-methoxyphenyl)ethyl)diphenylphosphine oxide (4b): ^{13}C NMR (101 MHz, $CDCl_3$)



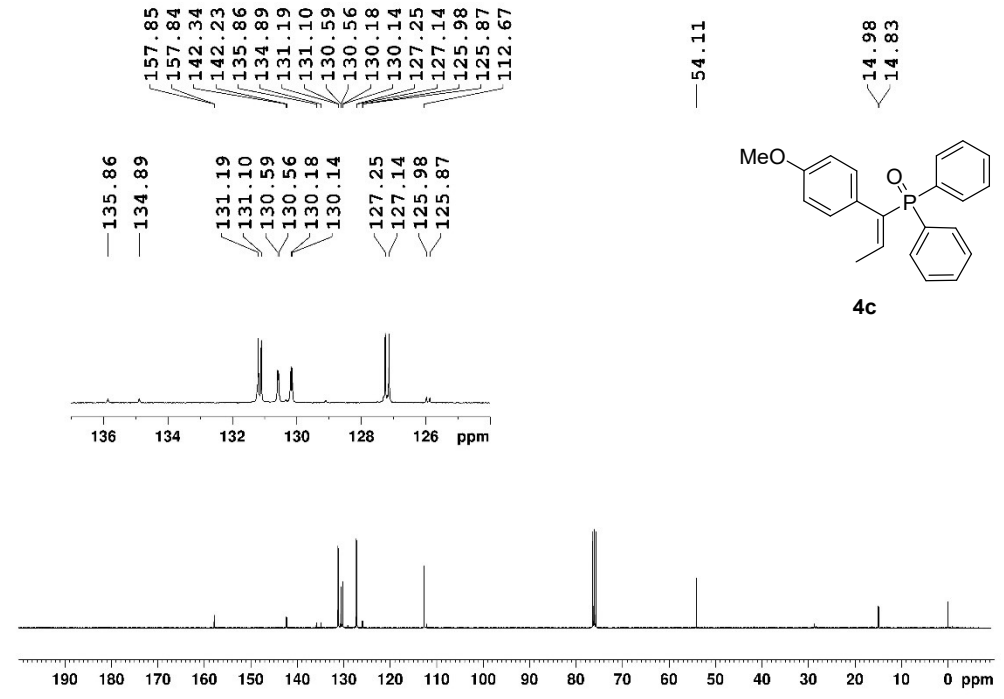
(2-(Isopropylamino)-1-(4-methoxyphenyl)ethyl)diphenylphosphine oxide (4b): ^{31}P NMR (162 MHz, $CDCl_3$)



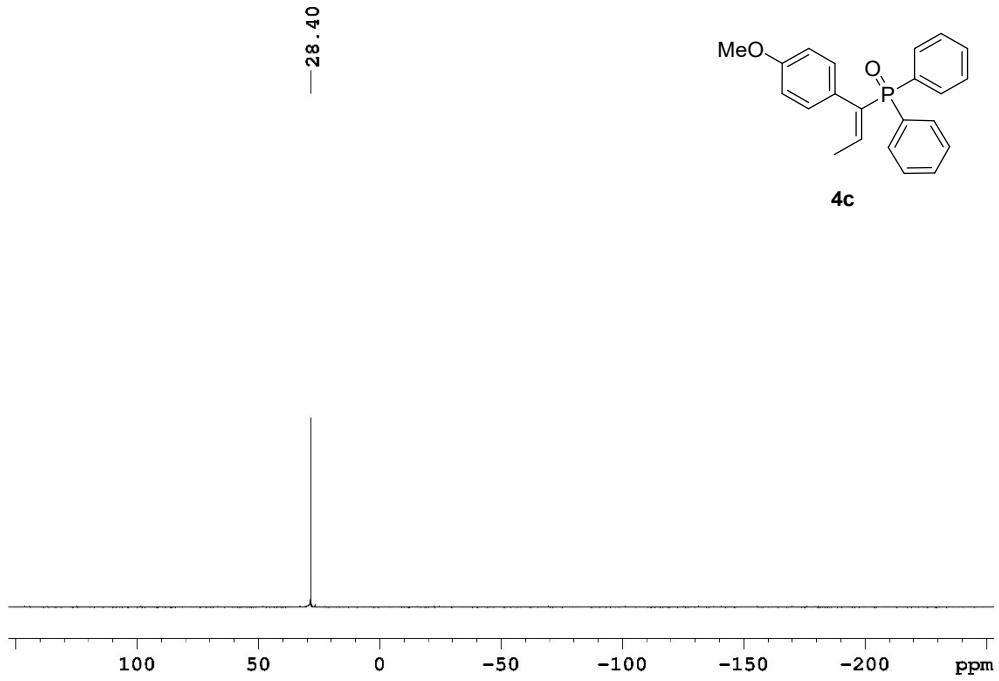
(*E*)-(1-(4-Methoxyphenyl)prop-1-en-1-yl)diphenylphosphine oxide (4c): ^{1}H NMR (400 MHz, $CDCl_3$)



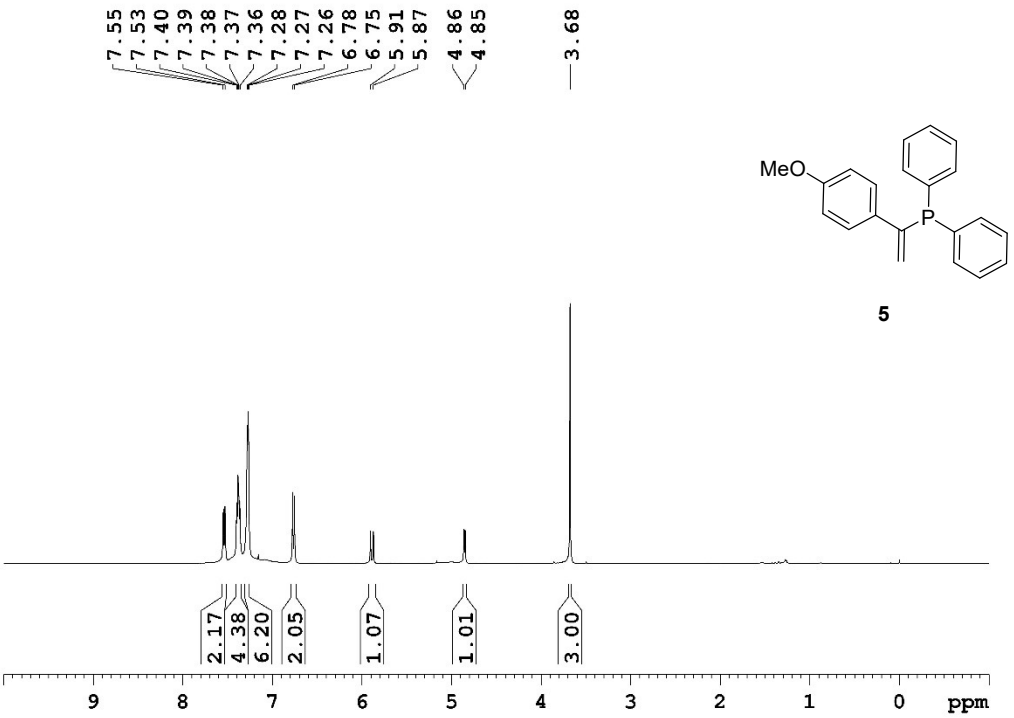
(*E*)-(1-(4-Methoxyphenyl)prop-1-en-1-yl)diphenylphosphine oxide (4c): ^{13}C NMR (101 MHz, $CDCl_3$)



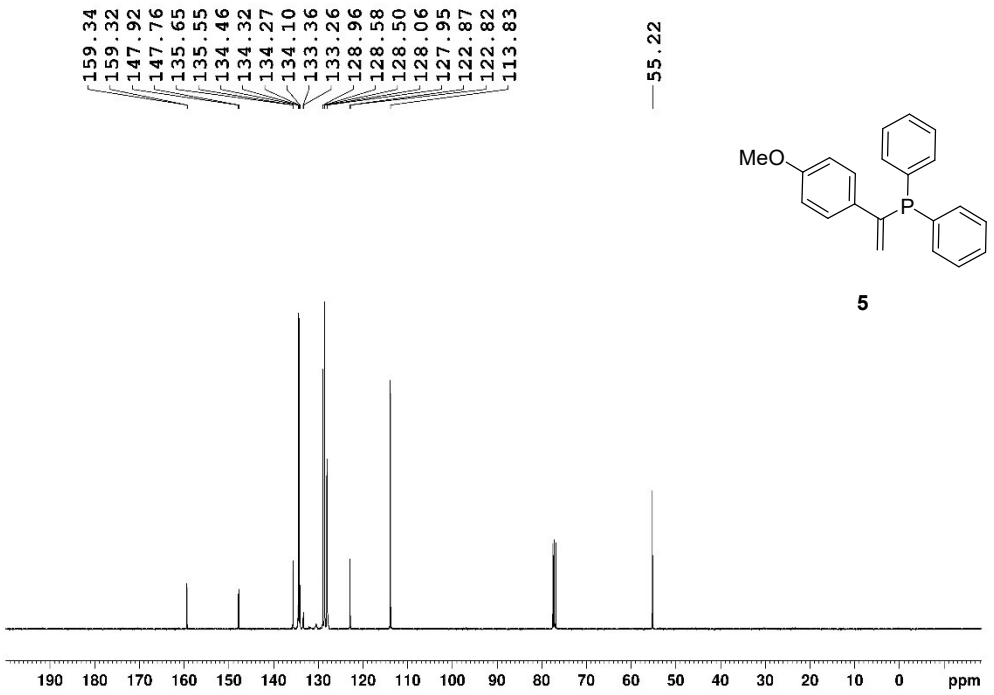
(*E*)-(1-(4-Methoxyphenyl)prop-1-en-1-yl)diphenylphosphine oxide (4c): ^{31}P NMR (162 MHz, $CDCl_3$)



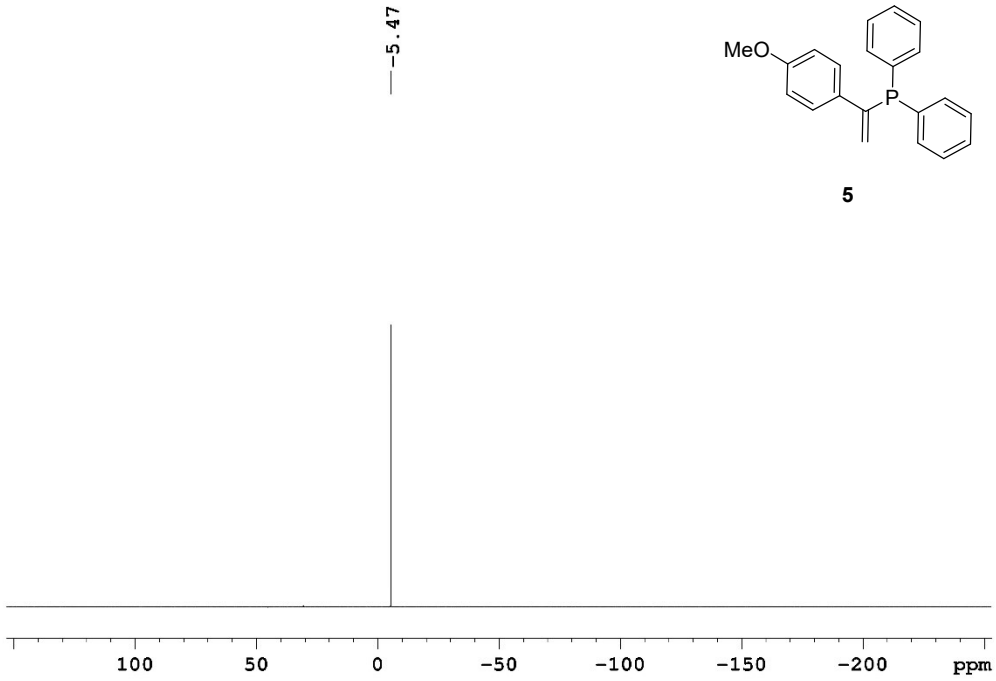
(1-(4-Methoxyphenyl)vinyl)diphenylphosphane (5): ^{1}H NMR (400 MHz, $CDCl_3$)



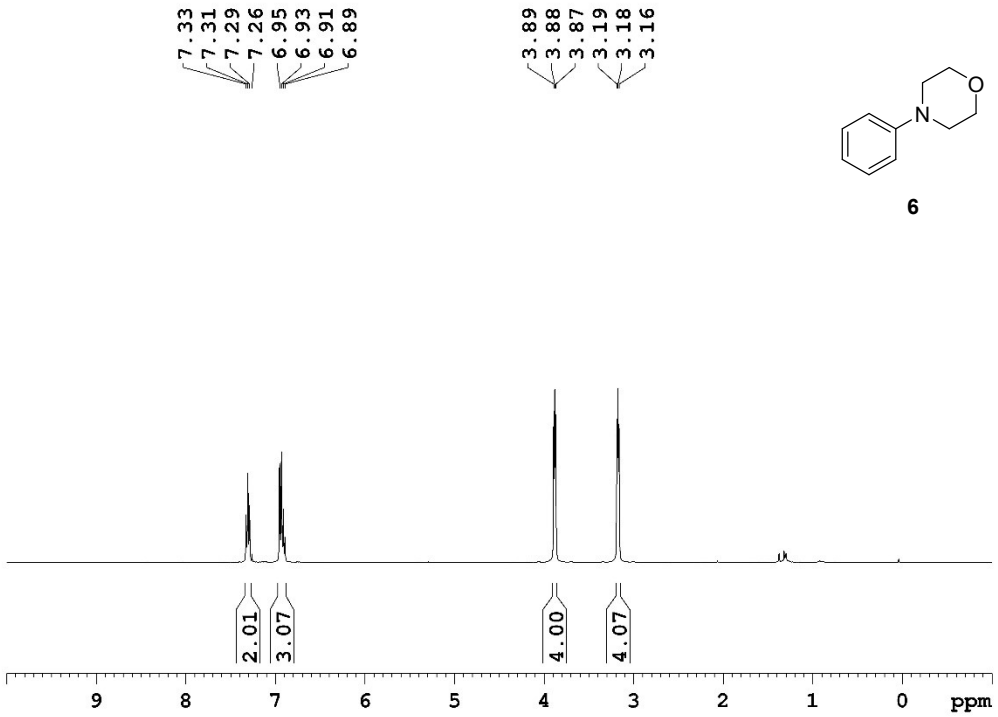
(1-(4-Methoxyphenyl)vinyl)diphenylphosphane (5): ^{13}C NMR (101 MHz, $CDCl_3$)



(1-(4-Methoxyphenyl)vinyl)diphenylphosphane (5): ^{31}P NMR (162 MHz, $CDCl_3$)



4-Phenylmorpholine (6): ^{1}H NMR (400 MHz, $CDCl_3$)



4-Phenylmorpholine (6): ^{13}C NMR (101 MHz, $CDCl_3$)