Electronic Supplementary Material (ESI) for ChemComm.

Supplementary information

"Reductive coupling of two aldehydes to unsymmetrical *E*-alkenes *via* phosphaalkene and phosphinate intermediates"

*Juri Mai, Anna Arkhypchuk, Arvind Kumar Gupta, and Sascha Ott**

Department of Chemistry, Ångström laboratory, Uppsala University, Box 523,
75120 Uppsala, Sweden.

E-mail: sascha.ott@kemi.uu.se

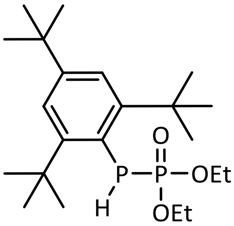
Contents

Materials and Methods

The formation of phosphaalkenes was carried out under an inert atmosphere of nitrogen using standard Schlenk techniques. All glassware was flame-dried, and aldehydes were dried/distilled prior to use. THF was freshly distilled over Na/benzophenone under nitrogen. NMR spectra were recorded on a JOEL (400YH magnet) Resonance ECZ 400 MHz spectrometer. Chemical shifts δ are reported in ppm and coupling constants J in Hz. ^{1}H NMR and ^{13}C NMR chemical shifts are referenced to the residual protic solvent signal and ^{31}P NMR spectra externally to 85% H_3PO_4(aq). Mass spectrometry analyses were performed in direct injection mode on a Thermo Finnigan LCQ Deca XP Max LC/MS spectrometer, and high-resolution mass spectra (HR-MS) were recorded on a Thermo Scientific Orbitrap LTQ XL or Bruker MicrOTof ESI spectrometer. DFT calculations were performed using Gaussian 09 (Revision D.01) at the B3LYP level of theory and 6-311G(d,p) as basis set. All molecules were geometry optimized and the optimized geometries were confirmed to be true minima on the PES with no negative frequencies.

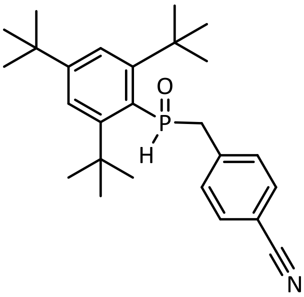
General procedures

A. Preparation of phosphanylphosphonate reagent Mes*P(H)-P(O)(OEt)$_2$ **1-H**[1]



Mes*PH$_2$ (24.4 mmol, 6.8 g) was refluxed with AIBN (1.4 mmol, 0.2 g) in CCl_4 (80 ml) under nitrogen atmosphere for 4 hours (full conversion to Mes*P(H)Cl was monitored by ^{31}P NMR). After cooling down, the volatiles were removed under vacuum using a cold trap. The crude product Mes*P(H)Cl was re-dissolved in water-free toluene (35 ml), followed by the addition of 1.1 equivalents of triethyl phosphite (26.9 mmol, 4.7 ml). The solution was stirred under reflux for 2 h after which the reaction progress was observed by ^{31}P NMR showing a complete conversion. All solvents were removed under vacuum using a cold trap. The residue was dissolved in Et_2O, washed with water and brine and dried over $MgSO_4$. Recrystallization from *n*-hexane furnished the pure product **1-H** as white crystals. Yield: 6.9 g, 68%. ^{1}H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 7.39 (s, 2H), 5.40 (dd, $^{1}J_{H–P}$ = 231.0 Hz, $^{2}J_{H–P}$ = 14.2 Hz), 3.82–3.61 (m, 2H), 3.54–3.40 (m, 2H), 1.58 (br s, coalescence, 18H), 1.29 (s, 9H), 1.12–1.03 (m, 6H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 300 K): δ = 156.7 (coalescence), 150.4 (d, $J_{C–P}$ = 5.3 Hz), 122.6 (coalescence), 120.7 (dd, $J_{C–P}$ = 31.2, 11.3 Hz), 61.8 (dd, $J_{C–P}$ = 7.7, 0.5 Hz), 61.7 (dd, $J_{C–P}$ = 7.2, 2.1 Hz), 35.0 (d, $J_{C–P}$ = 1.5 Hz), 33.9 (coalescence), 31.8, 31.4 (d, $J_{C–P}$ = 1.39 Hz), 16.5 (d, $J_{C–P}$ = 6.3 Hz), 16.4 (d, $J_{C–P}$ = 6.4 Hz). ^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz, 300 K): δ = 35.0 (d, $^{1}J_{P–P}$ = 222 Hz), −88.8 (d).

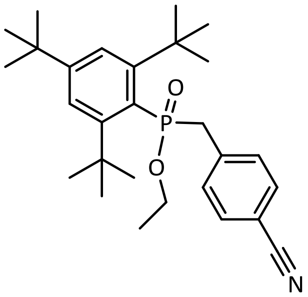
B. Synthesis of 4-(((2,4,6-tri-*tert*-butylphenyl)hydrophosphoryl)methyl)-benzonitrile (**5**)



Under a nitrogen atmosphere phosphaalkene (*E*)-(4-cyanobenzylidene)(2,4,6-tri-*tert*-butylphenyl)phosphane (400 mg, 1.02 mmol) was dissolved in 10 ml of water-free and degassed THF. 2 equivalents of an aqueous solution of NaOH (mass concentration ρ = 60 mg/ml) were added, and the mixture was stirred at room temperature under a nitrogen atmosphere for 14 days. After full consumption of phosphaalkene (monitored by ^{31}P NMR) all solvents were removed under reduced pressure and the residue was re-dissolved in degassed DCM and washed with water. The aqueous phase was extracted three times with DCM and the organic phases were combined. Evaporation of all solvents on vacuum afforded the crude product which was purified by silica gel column chromatography (ethyl acetate, R_f = 0.45). Colorless solid; isolated yield 43%. ^{1}H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 7.65 (ddd, $^1J_{H\text{-}P}$ = 494.9 Hz, $^3J_{H\text{-}H}$ = 6.7 Hz, $^3J_{H\text{-}H}$ = 1.9 Hz, 1H), 7.66 – 7.13 (br s, 2H), 7.36 – 7.29 (m, 2H), 6.56 – 6.43 (m, 2H), 3.50 – 3.29 (m, 2H), 1.56 (br s, 9H), 1.35 (br s, 9H), 1.30 (br s, 9H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 157.29 (br s), 153.83 (d, $J_{C\text{-}P}$ = 3.7 Hz), 138.56 (d, $J_{C\text{-}P}$ = 5.6 Hz), 132.12 (d, $J_{C\text{-}P}$ = 3.9 Hz), 130.16 (d, $J_{C\text{-}P}$ = 5.9 Hz), 125.99, 125.05, 123.19 (br s), 118.68 (d, $J_{C\text{-}P}$ = 2.9 Hz), 110.66 (d, $J_{C\text{-}P}$ = 4.4 Hz), 42.75, 42.18, 35.24, 33.81 (br s), 31.31 (br s). ^{31}P NMR ($CDCl_3$, 162 MHz, 300 K) δ = 24.43 (dt, $^1J_{H\text{-}P}$ = 495.3 Hz, $^2J_{H\text{-}P}$ = 15.8 Hz). HR-MS/ESI (+): m/z = 410.2606 [M+H]$^+$, calculated [$C_{26}H_{37}NOP$]$^+$ = 410.2589. Elemental analysis: calculated C = 76.25, H = 8.86, N=3.42; experimental C = 75.49, H = 8.87, N=3.39.

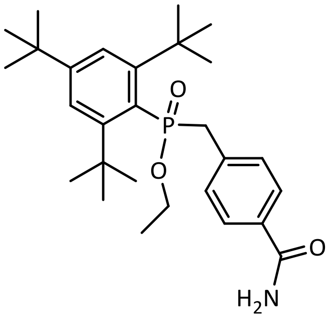
C. Synthesis of phosphinates (**9)**

ethyl(4-cyanobenzyl)(2,4,6-tri-*tert*-butylphenyl)phosphinate (with R = Et and R_1 = CN)



To a solution of (*E*)-(4-cyanobenzylidene)(2,4,6-tri-*tert*-butyl-phenyl)phosphane (1.7 g, 4.34 mmol) in 10 ml of water-free THF 1.1 equivalents of an ethanolic sodium ethoxide solution (1.78 ml, 4.78 mmol; 21% NaOEt in EtOH) were added at room temperature. The mixture was stirred for 5 minutes and 1.1 equivalents of *t*-BuOOH (0.87 ml, 4.78 mmol; 5.50 M solution in decane) were added. The reaction mixture was stirred for 5 hours at room temperature (conversion was monitored by ^{31}P NMR). All solvents were removed on vacuum, the residue was re-dissolved in ethyl acetate and washed with water. The crude pale yellow product was recrystallized from *n*-hexane to afford a colorless solid. Isolated yield 65%. ^{1}H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 7.59 – 7.53 (m, 2H), 7.36 – 7.32 (m, 4H), 3.90 – 3.75 (m, 2H), 3.70 – 3.46 (m, 2H), 1.53 (s, 18H), 1.30 (s, 9H), 0.88 (t, ^{3}J = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 151.96 (d, $J_{C\text{-}P}$ = 3.8 Hz), 139.79 (d, $J_{C\text{-}P}$ = 10.3 Hz), 132.00 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.02 (d, $J_{C\text{-}P}$ = 5.6 Hz), 127.33 (d, $J_{C\text{-}P}$ = 126.4 Hz), 124.09 (d, $J_{C\text{-}P}$ = 12.5 Hz), 119.11 (d, $J_{C\text{-}P}$ = 1.8 Hz), 110.28 (d, $J_{C\text{-}P}$ = 3.2 Hz), 60.76 (d, $J_{C\text{-}P}$ = 6.8 Hz), 41.30 (d, $J_{C\text{-}P}$ = 87.4 Hz), 40.35 (d, $J_{C\text{-}P}$ = 2.9 Hz), 33.95, 31.09, 16.04 (d, $J_{C\text{-}P}$ = 5.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz, 300 K) δ = 41.30 (br s). MS/ESI (+): *m/z* (%) = 454.17 (100) $[M+H]^+$, 906.98 (25) $[2M+H]^+$.

ethyl(4-carbamoylbenzyl)(2,4,6-tri-*tert*-butylphenyl)phosphinate (with R = Et and R_1 = $C(O)NH_2$)



To a solution of (*E*)-(4-cyanobenzylidene)(2,4,6-tri-*tert*-butyl-phenyl)phosphane (0.52 g, 1.33 mmol) in 10 ml of ethanol 1.3 equivalents of an ethanolic sodium ethoxide solution (0.65 ml, 1.73 mmol; 21% NaOEt in EtOH) were added at room temperature. The mixture was stirred for 5 minutes and 1.3 equivalents of an aqueous hydrogen peroxide solution were added at room temperature. A precipitate was formed, and the mixture was stirred for 10 minutes at room temperature. After full conversion (monitored by ^{31}P NMR), the solvents were removed under reduced pressure and the residue was re-dissolved in chloroform and washed with water. The combined organic phases were dried over $MgSO_4$ and the solvents were removed using a rotary evaporator. The product was obtained after washing of the residue with *n*-hexane. Colorless solid; isolated yield 67%. ^{1}H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 7.78 – 7.71 (m, 2H), 7.38 – 7.33 (m, 4H), 6.31 – 6.03 (br s, 1H), 5.68 – 5.42 (br s, 1H), 3.92 – 3.77 (m, 2H), 3.67 – 3.44 (m, 2H), 1.54 (s, 18H), 1.30 (s, 9H), 0.87 (t, ^3J = 6.7 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 169.22, 151.81, 151.78, 138.54, 138.44, 131.43 (d, $J_{C\text{-}P}$ = 3.1 Hz), 130.56 (d, $J_{C\text{-}P}$ = 5.7 Hz), 127.49 (d, $J_{C\text{-}P}$ = 2.6 Hz), 124.11 (d, $J_{C\text{-}P}$ = 12.2 Hz), 60.82 (d, $J_{C\text{-}P}$ = 7.0 Hz), 41.14 (d, $J_{C\text{-}P}$ = 87.8 Hz), 40.40 (d, $J_{C\text{-}P}$ = 3.0 Hz), 34.05, 31.16, 16.13 (d, $J_{C\text{-}P}$ = 5.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz, 300 K) δ = 42.48 (br s). MS/ESI (+): *m/z* (%) = 472.16 (100) $[M+H]^+$, 943.29 (90) $[2M+H]^+$.

D. Preparation of phosphaalkenes[1]

To a solution of the phosphanylphosphonate reagent **1-H** (250 mg, 0.603 mmol) in 15 ml water-free THF were added dropwise 1.2 equivalents (0.72 ml, 0.724 mmol) of a 1 M lithium diisopropylamide solution at room temperature. The dark yellow mixture was stirred for 5 minutes before the addition of aldehyde (1.2 equivalents, 0.724 mmol). Formation of phosphaalkene and full consumption of lithiated phosphanylphosphonate reagent was monitored by ^{31}P NMR. In here, the reaction times differ from several minutes (for R_1 = CN, Br) to over night (R_1 = H, OMe) in dependence on the *para*-substituent on the aldehyde. The reaction was then quenched with a saturated aqueous solution of NH_4Cl. The mixture was diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate and the organic phases were combined and dried over $MgSO_4$. The volatiles were removed on rotary evaporator and the crude product was then purified by column chromatography on silica gel.

E. Preparation of alkenes

In a Schlenk flask phosphanylphosphonate **1-H** (250 mg, 0.603 mmol) was dissolved in 15 ml of water-free THF and 1.15 equivalents (0.69 ml, 0.693 mmol) of a 1 M lithium diisopropylamide solution in THF were added at room temperature. 1.05 equivalents of the first aldehyde were added, and the formation of the phosphaalkene was monitored by ^{31}P NMR using an external C_6D_6 standard. After complete transformation, which is typically within several minutes, one equivalent of a tetrabutylammonium methoxide solution (20% TBAOMe in MeOH) was added,[1] and the mixture was stirred at room temperature for 30 minutes. After full conversion (followed by ^{31}P NMR) one equivalent of *t*-BuOOH (391 mg, 0.603 mmol, as a solution of 14%weight in benzene) was added at room temperature. The oxidation was performed open to air and was complete in 5-6 hours (monitored by ^{31}P NMR). 3 equivalents of a 1 M THF solution of KO^{t}Bu (1.80 ml, 1.80 mmol) were added simultaneously with the second aldehyde (0.603 mmol) and the mixture was stirred at room temperature. Conversion of the phosphinate intermediate **9** to the final phosphonate by-oproduct **10** was monitored by ^{31}P NMR. After completion of the coupling step, typically between 15-90 minutes, the reaction was quenched with a saturated aqueous solution of NH_4Cl. The crude mixture was diluted with ethyl acetate and washed with water. The aqueous phase was extracted with ethyl acetate for three times, and the combined organic phases were dried over $MgSO_4$. Evaporation of the solvents under reduced pressure afforded the crude product as a yellow solid. The olefinic products were purified by silica gel column chromatography.

---

[1] Alternatively, a tetrabutylammonium ethoxide solution (40% TBAOEt in EtOH) can be used.

Determination of crude yields (conversions)

A sample of crude product of known mass is dissolved in 1 ml of a $CDCl_3$ stock solution of cyclohexene (0.039 M) and added to an NMR tube. Integration of the olefinic peak of the product in the ^1H NMR spectrum against the reference peak of cyclohexene (5.67 ppm) (set as 1.00 reference integral value) allows the calculation of the product concentration in the sample. With this concentration and the known mass of the crude product, the total mass of the product in the crude reaction mixture can be calculated. Conversions are calculated relative to the amount of used phosphanylphosphonate **1-H**.

An example is shown below in Figure **S1** for the crude product of (*E*)-4-(4-(*tert*-butyl)styryl)-benzonitrile.

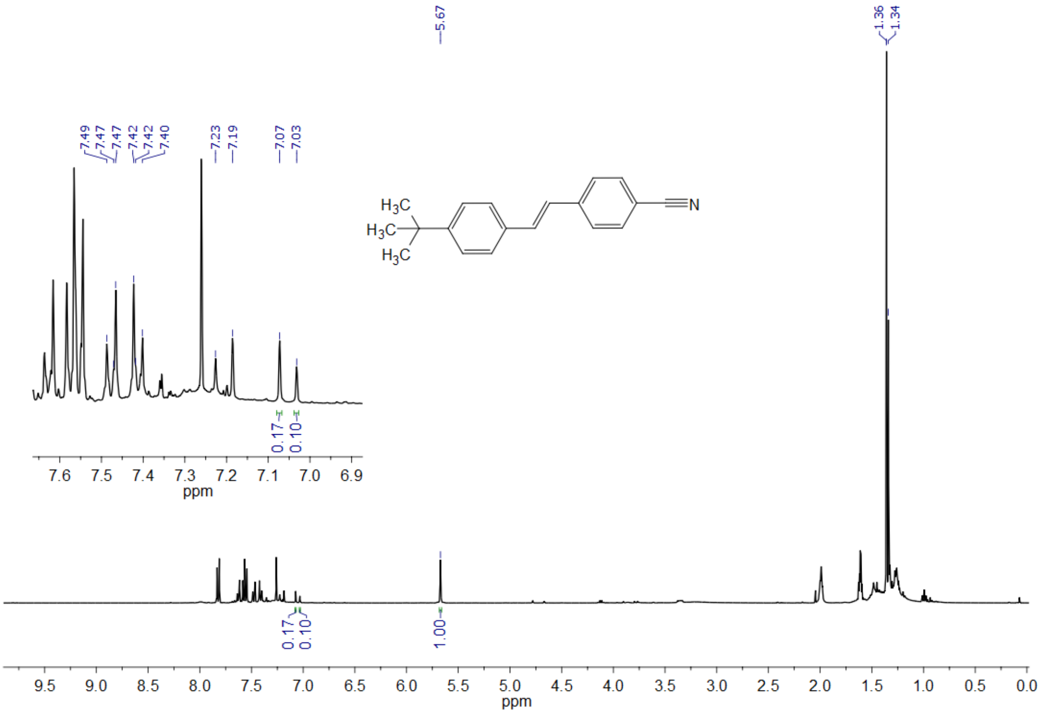


Figure S1: ^1H NMR spectrum of crude product of (*E*)-4-(4-(*tert*-butyl)styryl)benzonitrile (**Table 1**, **Entry 1**) in $CDCl_3$ (400 MHz, 300 K) with cyclohexene as a reference.

In the specific example the total mass of crude product is: *m*(crude product) = 446 mg.

27 mg were taken and dissolved in 1 ml of $CDCl_3$ stock solution of cyclohexene for the crude yield determination. Consequently, the mass factor is: 446 mg/27 mg = 16.52.

Integration of the olefinic protons (d at 7.05 ppm and 7.21 ppm) gives a value of 2 * 0.27 = 0.54 relative to the signal of the two olefinic protons in cyclohexene (Figure S1). With a concentration of the cyclohexene stock solution of 0.039 M, the concentration of the product for the NMR tube is calculated as:

c(product NMR tube) = 0.54 * 0.039 M = 0.021 M.

With the NMR sample volume being 1 ml, *n*(product NMR tube) = 0.021 mmol.

Multiplication by the mass factor gives the total amount of product in the crude reaction mixture. *n*(product) = 16.52 * 0.021 mmol = 0.347 mmol. Expected product amount was 0.584 mmol, which results in 59% crude yield (conversion).

^{31}P NMR investigation on intermediates **8** and **9**

Figure S2 shows the proton-coupled ^{31}P NMR spectra of the phosphinite **8** and phosphinate **9** intermediates during reaction monitoring. The signal pattern indicates a coupling to both protons of the corresponding methylene groups. This finding is in agreement with the finding that the acid/base equilibria are lying rather on the side of the protonated form of **8** and **9**.

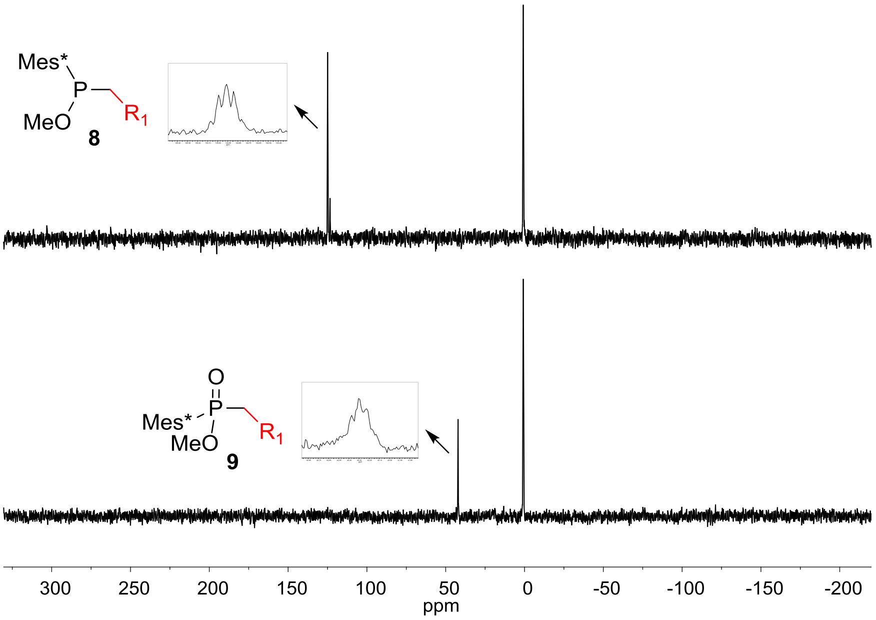
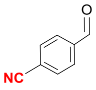
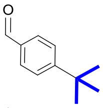
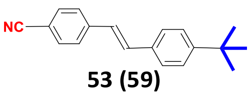
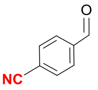
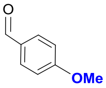
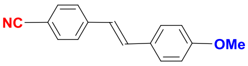
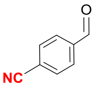
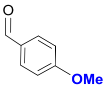
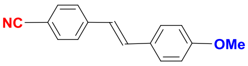
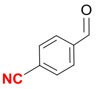
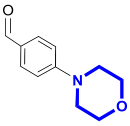
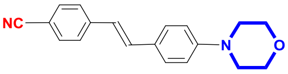
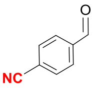
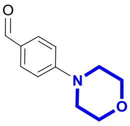
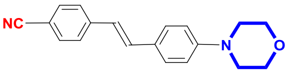
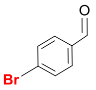
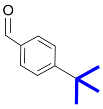
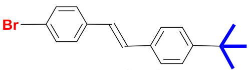
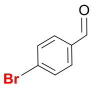
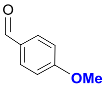
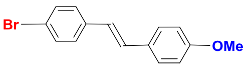
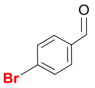
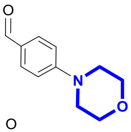
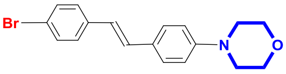
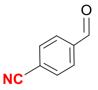
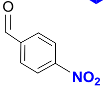
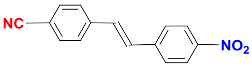


Figure S2: ^{31}P NMR spectra of intermediates **8** and **9** during reaction monitoring (insets show the zoom in of the signals).

Overview of olefinic products

The following Table S1 shows a list of olefinic products with the *E*/*Z* ratios, which were determined from crude products.

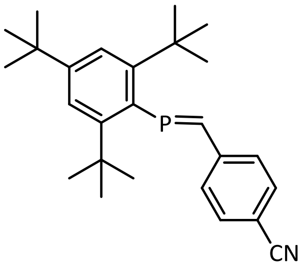
Table S1: List of aldehydes for the first and second coupling step with the corresponding unsymmetrically disubstituted olefinic products. The *E*/*Z* product ratio was determined from ^{1}H NMR spectrum of the crude product, respectively. ^{a}Coupling step was performed with 0.5 equivalent of 2nd aldehyde. The corresponding yield refers to the molarity of the 2nd aldehyde (entry **2’** and **3’**).

Entry	1st aldehyde	2nd aldehyde	Product isolated yield (crude yield)	*E/Z* product ratio
1			 **53 (59)**	99 / 1
2			 **51 (56)**	97 / 3
2’			 **79^a**	---
3			 **39 (45)**	95 / 5
3’			 **70^a**	---
4			 **50 (57)**	99 / 1
5			 **44 (51)**	98 / 2
6			 **35 (39)**	97 / 3
7			 **67**	---

NMR spectroscopic data

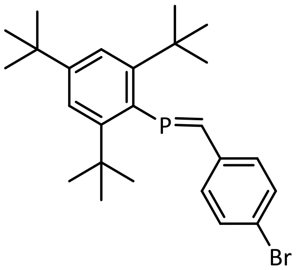
Phosphaalkenes

(*E*)-(4-cyanobenzylidene)(2,4,6-tri-*tert*-butylphenyl)phosphane:



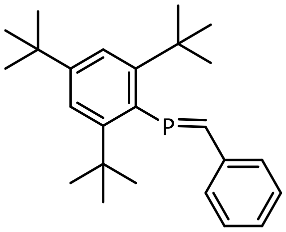
Purification by column chromatography (pentane:Et_2O = 9:1, R_f = 0.70). Pale yellow crystalline solid; isolated yield 72%. Analytical data of the compound are in agreement with the reported literature values.[2] For the *E*-isomer: ^1H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 8.06 (d, $^2J_{H\text{-}P}$= 25.0 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.58 – 7.56 (m, 2H), 7.46 (br s, 2H), 1.51 (s, 18H), 1.37 (s, 9H). ^{13}C {^1H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 172.73 (d, $J_{C\text{-}P}$ = 36.1 Hz), 154.13 (d, $J_{C\text{-}P}$ = 1.4 Hz), 150.38, 144.30 (d, $J_{C\text{-}P}$ = 14.6 Hz), 137.85 (d, $J_{C\text{-}P}$ = 53.2 Hz), 132.65 (d, $J_{C\text{-}P}$ = 3.2 Hz), 126.12 (d, $J_{C\text{-}P}$ = 22.5 Hz), 122.13 (d, $J_{C\text{-}P}$ = 1.1 Hz), 119.58, 110.67 (d, $J_{C\text{-}P}$ = 8.2 Hz), 38.34, 35.14, 34.00 (d, $J_{C\text{-}P}$ = 7.1 Hz), 31.48. ^{31}P NMR ($CDCl_3$, 162 MHz, 300 K) δ = 283.81 (d, $^2J_{H\text{-}P}$ = 25.0 Hz).

(*E*)-(4-bromobenzylidene)(2,4,6-tri-*tert*-butylphenyl)phosphane:



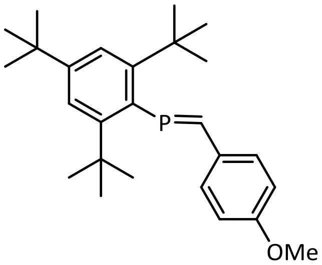
Purification by column chromatography (pentane, R_f = 0.55). Colorless crystalline solid; isolated yield 69%. Analytical data of the compound are in agreement with the reported literature values.[2] For the *E*-isomer: ^1H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 8.04 (d, $^2J_{H\text{-}P}$= 25.4 Hz, 1H), 7.48 – 7.40 (m, 6H), 1.52 (s, 18H), 1.37 (s, 9H). ^{13}C {^1H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 174.21 (d, $J_{C\text{-}P}$ = 34.9 Hz), 154.17 (d, $J_{C\text{-}P}$ = 1.5 Hz), 150.00, 139.14 (d, $J_{C\text{-}P}$ = 14.3 Hz), 138.62 (d, $J_{C\text{-}P}$ = 53.4 Hz), 131.96 (d, $J_{C\text{-}P}$ = 3.2 Hz), 127.31 (d, $J_{C\text{-}P}$ = 22.2 Hz), 122.01 (d, $J_{C\text{-}P}$ = 1.3 Hz), 119.62, 38.40, 35.15, 33.96 (d, $J_{C\text{-}P}$ = 7.2 Hz), 31.53. ^{31}P NMR ($CDCl_3$, 162 MHz, 300 K) δ = 262.2 (d, $^2J_{H\text{-}P}$ = 25.4 Hz).

(*E*)-benzylidene(2,4,6-tri-*tert*-butylphenyl)phosphane:



Purification by column chromatography (pentane, R_f = 0.60). Colorless crystalline solid; isolated yield 85%. Analytical data of the compound are in agreement with the reported literature values.[2] For the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 8.19 (d, $^2J_{H\text{-}P}$= 25.6 Hz, 1H), 7.61 (dd, ^3J = 7.5 Hz, ^4J = 3.0 Hz, 2H), 7.51 (br s, 2H), 7.38 – 7.27 (m, 3H), 1.59 (s, 18H), 1.42 (s, 9H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 175.99 (d, $J_{C\text{-}P}$ = 34.6 Hz), 154.21 (d, $J_{C\text{-}P}$ = 1.6 Hz), 149.79, 140.31 (d, $J_{C\text{-}P}$ = 13.7 Hz), 139.17 (d, $J_{C\text{-}P}$ = 53.6 Hz), 128.85 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.06 (d, $J_{C\text{-}P}$ = 7.6 Hz), 121.96 (d, $J_{C\text{-}P}$ = 1.4 Hz), 119.62, 38.44, 35.15, 33.98 (d, $J_{C\text{-}P}$ = 7.2 Hz), 31.57. ^{31}P NMR ($CDCl_3$, 162 MHz, 300 K) δ = 259.72 (d, $^2J_{H\text{-}P}$ = 25.6 Hz).

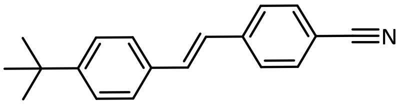
(*E*)-(4-methoxybenzylidene)(2,4,6-tri-*tert*-butylphenyl)phosphane:



Purification by column chromatography (heptane:Et_2O = 9:1, R_f = 0.50). Colorless crystalline solid; isolated yield 61%. Analytical data of the compound are in agreement with the reported literature values.[3] For the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 8.14 (d, $^2J_{H\text{-}P}$= 25.5 Hz, 1H), 7.56 (dd, ^3J = 8.7 Hz, ^4J = 3.1 Hz, 2H), 7.51 (br s, 2H), 6.90 (d, ^3J = 8.7 Hz, 2H), 3.85 (s, 3H), 1.58 (s, 18H), 1.42 (s, 9H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 175.71 (d, $J_{C\text{-}P}$ = 34.1 Hz), 159.81 (d, $J_{C\text{-}P}$ = 7.7 Hz), 154.28 (d, $J_{C\text{-}P}$ = 1.3 Hz), 149.62, 139.47 (d, $J_{C\text{-}P}$ = 53.4 Hz), 139.60 (d, $J_{C\text{-}P}$ = 13.7 Hz), 127.30 (d, $J_{C\text{-}P}$ = 21.9 Hz), 121.89 (d, $J_{C\text{-}P}$ = 1.1 Hz), 114.29 (d, $J_{C\text{-}P}$ = 2.9 Hz), 55.45, 38.46, 35.14, 33.96 (d, $J_{C\text{-}P}$ = 7.2 Hz), 31.57. ^{31}P NMR ($CDCl_3$, 162 MHz, 300 K) δ = 245.91 (d, $^2J_{H\text{-}P}$ = 25.5 Hz).

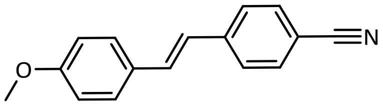
Alkenes

(*E*)-4-(4-(*tert*-butyl)styryl)benzonitrile (**Table 1**, **Entry 1**):



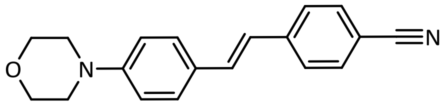
Purification by column chromatography (heptane:ethylacetate = 19:1, $R_f = 0.25$). Colorless crystalline solid; isolated yield 53%. Analytical data of the compound are in agreement with the reported literature values.[4] For the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 7.65 – 7.60 (m, 2H), 7.59 – 7.56 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.40 (m, 2H), 7.21 (d, ^3J = 16.3 Hz, 1H), 7.05 (d, ^3J = 16.3 Hz, 1H), 1.34 (s, 9H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 152.14, 142.20, 133.65, 132.60, 132.37, 126.89, 126.83, 126.06, 125.95, 119.25, 110.44, 34.88, 31.37.

(*E*)-4-(4-methoxystyryl)benzonitrile (**Table 1**, **Entry 2**):



Purification by column chromatography (heptane:DCM = 1:1, $R_f = 0.17$). Colorless crystalline solid; isolated yield 51%. Analytical data of the compound are in agreement with the reported literature values.[5] For the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 300 K): δ = 7.63 – 7.59 (m, 2H), 7.56 – 7.53 (m, 2H), 7.49 – 7.45 (m, 2H), 7.17 (d, ^3J = 16.3 Hz, 1H), 6.97 – 6.89 (m, 3H), 3.84 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 300 K) δ = 160.20, 142.34, 132.57, 132.07, 129.18, 128.39, 126.68, 124.65, 119.29, 114.42, 110.15, 55.48.

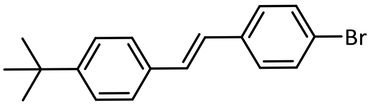
(*E*)-4-(4-morpholinostyryl)benzonitrile (**Table 1**, **Entry 3**):



Purification by column chromatography (DCM:ethylacetate = 19:1, $R_f = 0.51$). Pale yellow crystalline solid; isolated yield 39%. For the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 320 K): δ = 7.62 – 7.59 (m, 2H), 7.55 – 7.52 (m, 2H), 7.47 – 7.44 (m, 2H), 7.15 (d, ^3J = 16.2 Hz, 1H), 6.96 – 6.89 (m, 3H), 3.89 – 3.86 (m, 4H), 3.25 – 3.21 (m, 4H). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, 320 K) δ = 151.50, 142.54, 132.47, 132.21, 130.03, 129.52, 128.14, 126.52, 123.94, 115.32, 110.00, 66.82, 48.75. For the *Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 320 K): δ = 7.52 – 7.49 (m, 2H), 7.39

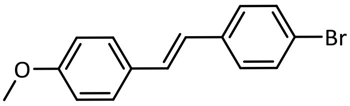
– 7.36 (m, 2H), 7.14 – 7.09 (m, 2H), 6.78 – 6.74 (m, 2H), 6.65 (d, ^3J = 12.2 Hz, 1H), 6.43 (d, ^3J = 12.2 Hz, 1H), 3.87 – 3.83 (m, 4H), 3.19 – 3.15 (m, 4H). ^{13}C {^{1}H} NMR (CDCl$_3$, 101 MHz, 320 K) δ = 150.84, 143.03, 133.11, 132.16, 130.15, 129.64, 127.54, 126.43, 119.16, 115.03, 110.38, 66.96, 48.87. HR-MS/ESI (+): m/z = 313.1317 [M+Na]$^+$, calculated [$C_{19}H_{18}N_2ONa$]$^+$ = 313.1311.

(*E*)-1-bromo-4-(4-(*tert*-butyl)styryl)benzene (**Table 1**, **Entry 4**):



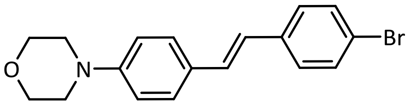
Purification by column chromatography (heptane:DCM = 8:2, R_f = 0.65). Colorless crystalline solid; isolated yield 50%. Analytical data of the compound are in agreement with the reported literature values.[6] For the *E*-isomer: ^{1}H NMR (CDCl$_3$, 400 MHz, 300 K): δ = 7.50 – 7.35 (m, 8H), 7.09 (d, ^3J = 16.3 Hz, 1H), 7.00 (d, ^3J = 16.3 Hz, 1H), 1.35 (s, 9H). ^{13}C {^{1}H} NMR (CDCl$_3$, 101 MHz, 300 K) δ = 151.27, 136.64, 134.32, 131.87, 129.38, 128.02, 126.76, 126.45, 125.82, 121.20, 34.80, 31.41.

(*E*)-1-bromo-4-(4-methoxystyryl)benzene (**Table 1**, **Entry 5**):



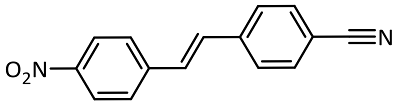
Purification by column chromatography (heptane:DCM = 1:1, R_f = 0.57). Colorless crystalline solid; isolated yield 44%. Analytical data of the compound are in agreement with the reported literature values.[7] For the *E*-isomer: ^{1}H NMR (CDCl$_3$, 400 MHz, 300 K): δ = 7.48 – 7.42 (m, 4H), 7.34 (d, ^3J = 8.4 Hz, 2H), 7.05 (d, ^3J = 16.3 Hz, 1H), 6.93 – 6.87 (m, 3H), 3.84 (s, 3H). ^{13}C {^{1}H} NMR (CDCl$_3$, 101 MHz, 300 K) δ = 159.78, 136.88, 131.90, 130.02, 129.22, 127.98, 127.89, 125.54, 120.98, 114.44, 55.49.

(*E*)-4-(4-(4-bromostyryl)phenyl)morpholine (**Table 1**, **Entry 6**):



Purification by column chromatography (DCM, R_f = 0.2). Colorless crystalline solid; isolated yield 35%. For the *E*-isomer: ^{1}H NMR (CDCl$_3$, 400 MHz, 320 K): δ = 7.48 – 7.40 (m, 4H), 7.37 – 7.31 (m, 2H), 7.02 (d, ^3J = 16.3 Hz, 1H), 6.93 – 6.85 (m, 3H), 3.89 – 3.84 (m, 4H), 3.23 – 3.18 (m, 4H). ^{13}C {^{1}H} NMR (CDCl$_3$, 101 MHz, 320 K) δ = 150.96, 137.02, 131.89, 129.29, 129.08, 127.83, 127.79, 125.03, 120.84, 115.74, 66.94, 49.24. HR-MS/ESI (+): *m/z* = 344.0647 [M+H]$^+$, calculated [$C_{18}H_{19}NOBr$]$^+$ = 344.0645.

(*E*)-4-(4-nitrostyryl)benzonitrile (**Table 1**, **Entry 7**):



Purification by column chromatography (DCM, R_f = 0.65). Yellow crystalline solid; isolated yield 67%. Analytical data of the compound are in agreement with the reported literature values.[8] For the *E*-isomer: ^{1}H NMR (CDCl$_3$, 400 MHz, 320 K): δ = 8.26 (d, ^3J = 8.7 Hz, 2H), 7.72 – 7.61 (m, 6H), 7.27 (s, 2H). ^{13}C {^{1}H} NMR (CDCl$_3$, 101 MHz, 320 K) δ = 147.61, 142.69, 140.66, 132.71, 131.20, 129.96, 127.43, 127.42, 124.29, 118.61, 112.07.

Appendix

NMR spectra

Phosphinoxide 5

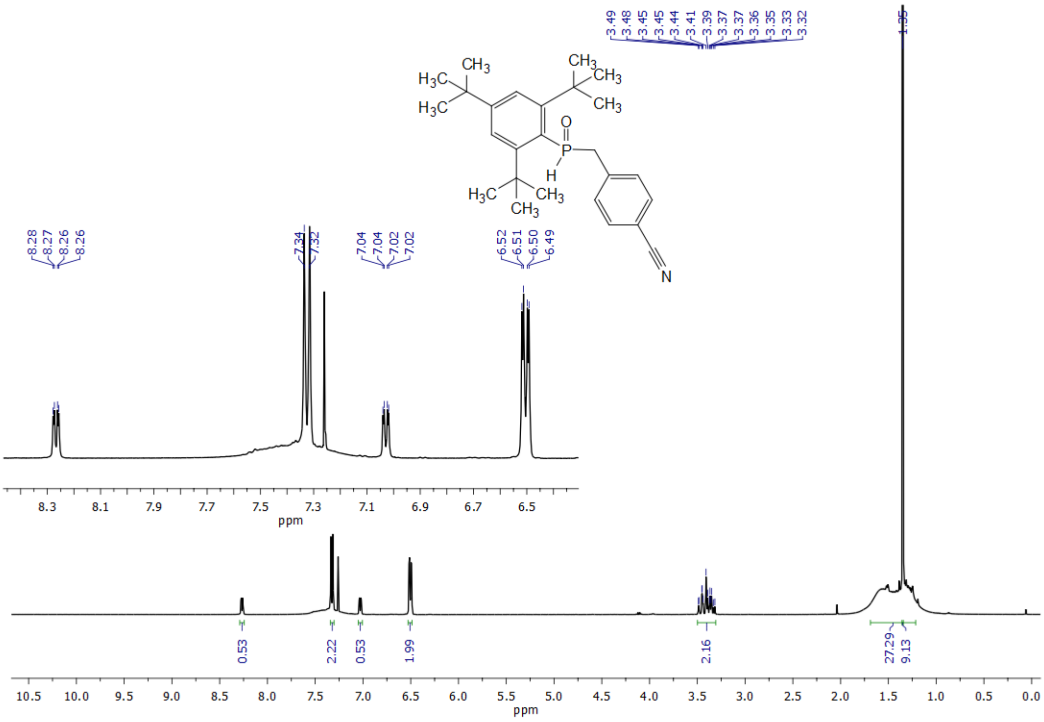


Figure S3: ^{1}H NMR spectrum of isolated 4-(((2,4,6-tri-*tert*-butylphenyl)hydrophosphoryl)methyl)-benzonitrile in $CDCl_3$ (400 MHz, 300 K).

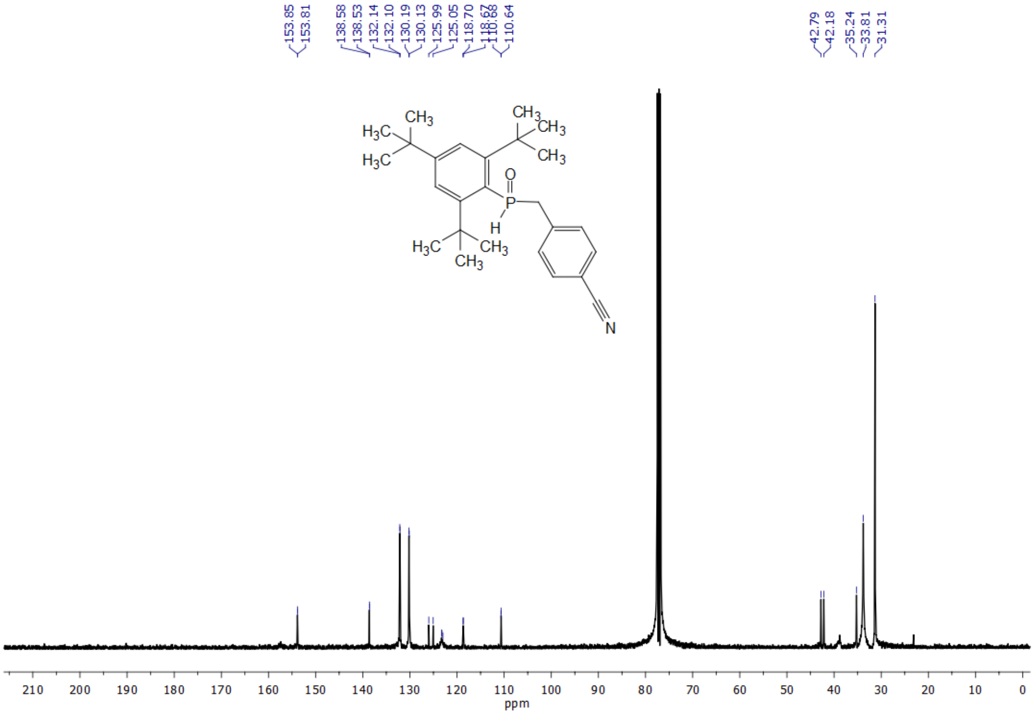


Figure S4: ^{13}C NMR spectrum of isolated 4-(((2,4,6-tri-*tert*-butylphenyl)hydrophosphoryl)methyl)-benzonitrile in $CDCl_3$ (101 MHz, 300 K).

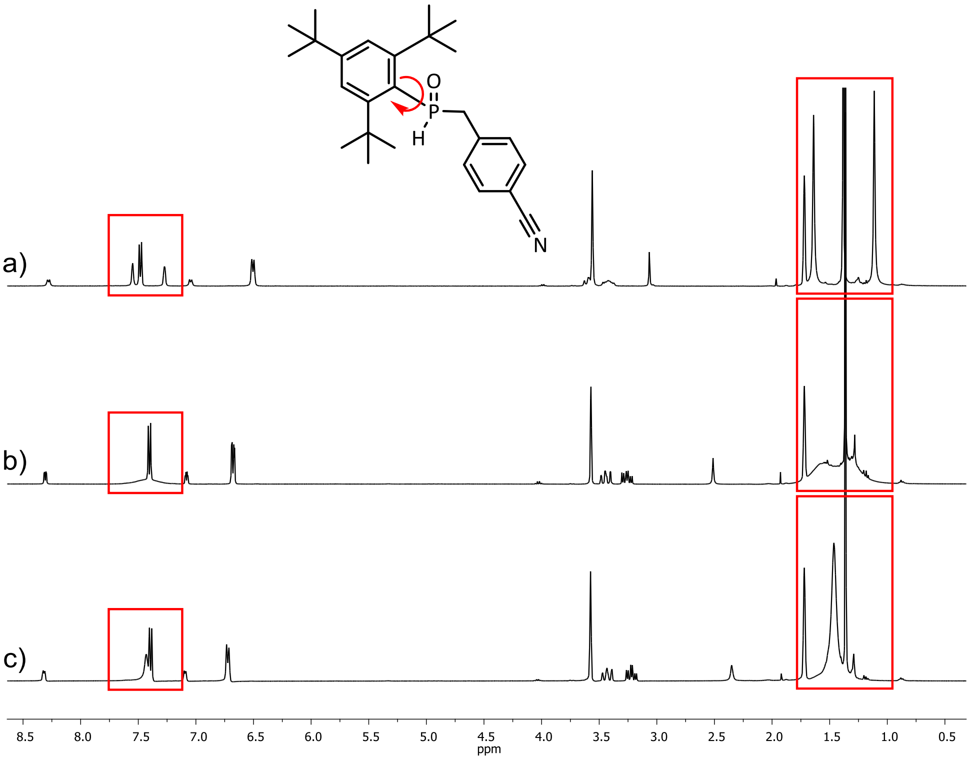


Figure S5: ^{1}H NMR spectrum of isolated 4-(((2,4,6-tri-*tert*-butylphenyl)hydrophosphoryl)methyl)-benzonitrile in THF-d_8 (400 MHz) at different temperatures: a) -80°C, b) 20°C and c) 50°C. Due to restricted bond rotation along the carbon atom from the Mes* substituent and the phosphorus atom dynamic exchange regimes are observed in ^{1}H NMR spectra at different temperatures. At low temperature (-80°C) the bond rotation is slow and the aromatic protons and protons on the *ortho* methyl groups of Mes* show two separate singlet signals, respectively. At 20°C and intermediate bond rotation a coalescence of the singlets is observed. An elevated temperature (50°C) leads to a slightly faster bond rotation. Due to the presence of a certain degree of restricted bond rotation, a signal broadening is observed at 50°C.

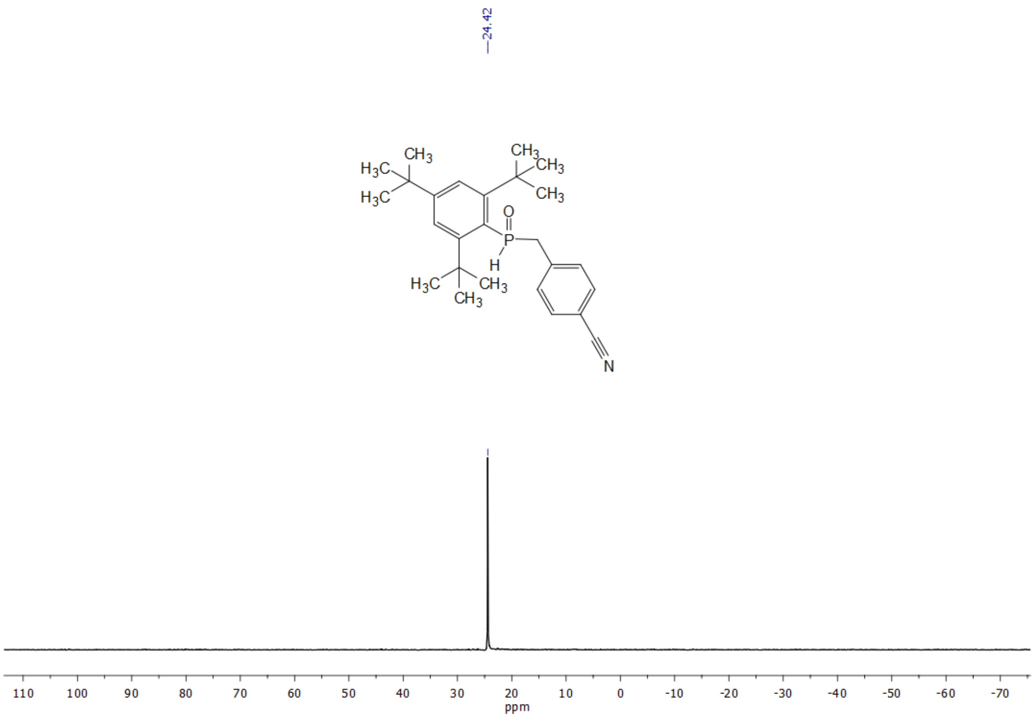


Figure S6: $^{31}P\ \{^{1}H\}$ NMR spectrum of isolated 4-(((2,4,6-tri-*tert*-butylphenyl)hydrophosphoryl)methyl)-benzonitrile in $CDCl_3$ (162 MHz, 300 K).

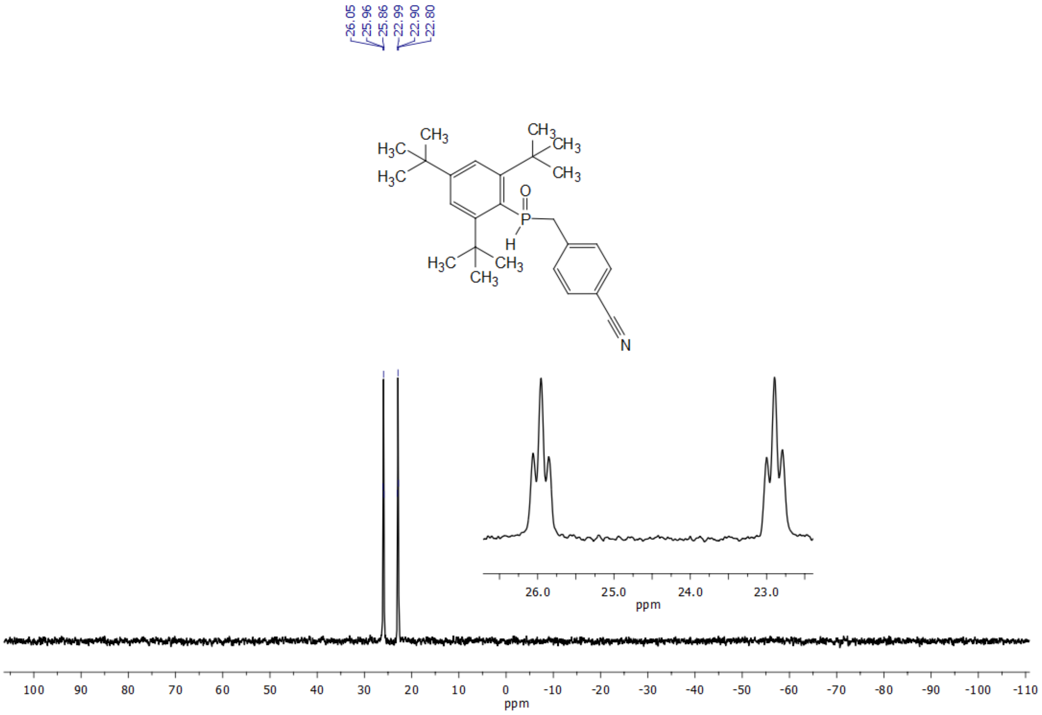


Figure S7: ^{31}P NMR spectrum of isolated 4-(((2,4,6-tri-*tert*-butylphenyl)hydrophosphoryl)methyl)-benzonitrile in $CDCl_3$ (162 MHz, 300 K).

Phosphinates 9

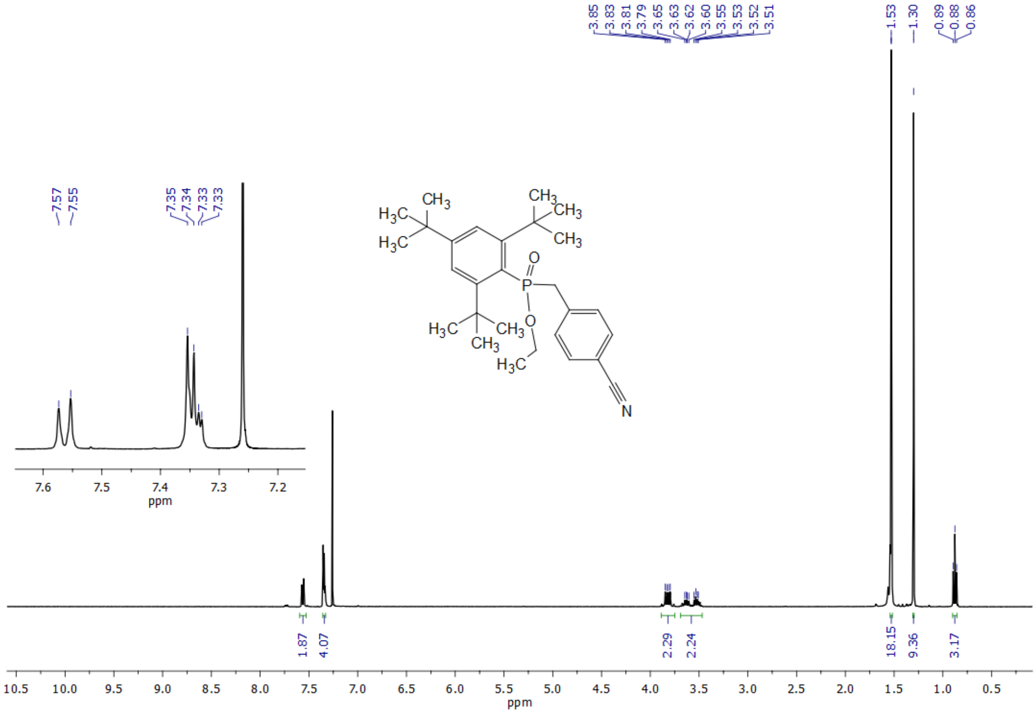


Figure S8: ^{1}H NMR spectrum of isolated ethyl(4-cyanobenzyl)(2,4,6-tri-*tert*-butylphenyl)phosphinate in $CDCl_3$ (400 MHz, 300 K).

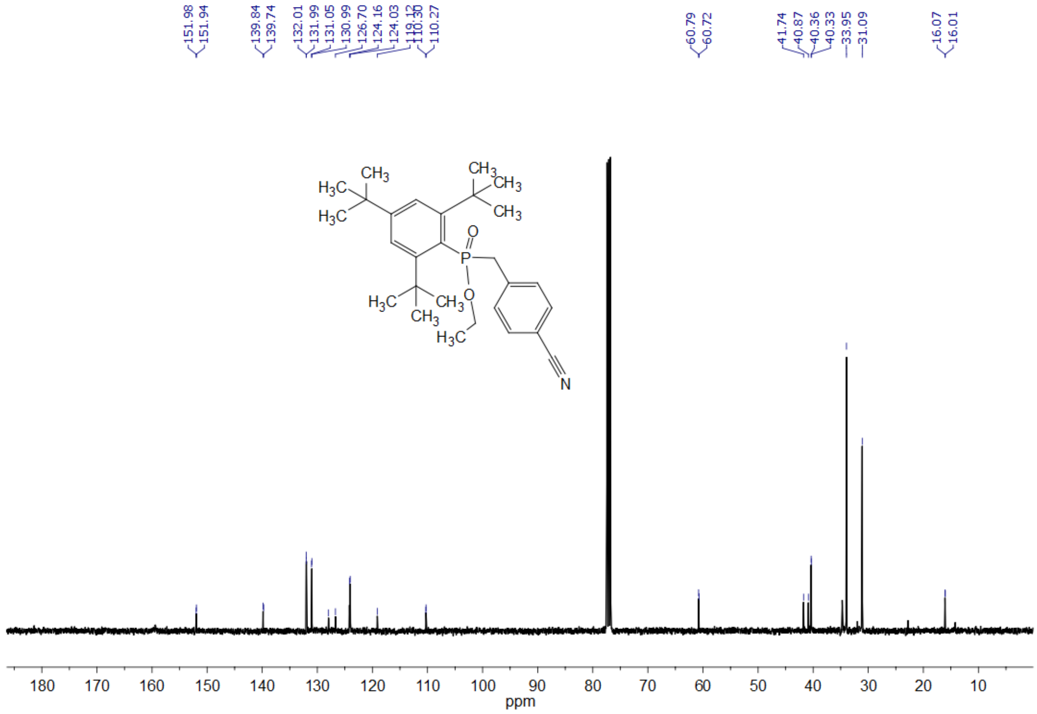


Figure S9: ^{13}C NMR spectrum of isolated ethyl(4-cyanobenzyl)(2,4,6-tri-*tert*-butylphenyl)phosphinate in $CDCl_3$ (101 MHz, 300 K).

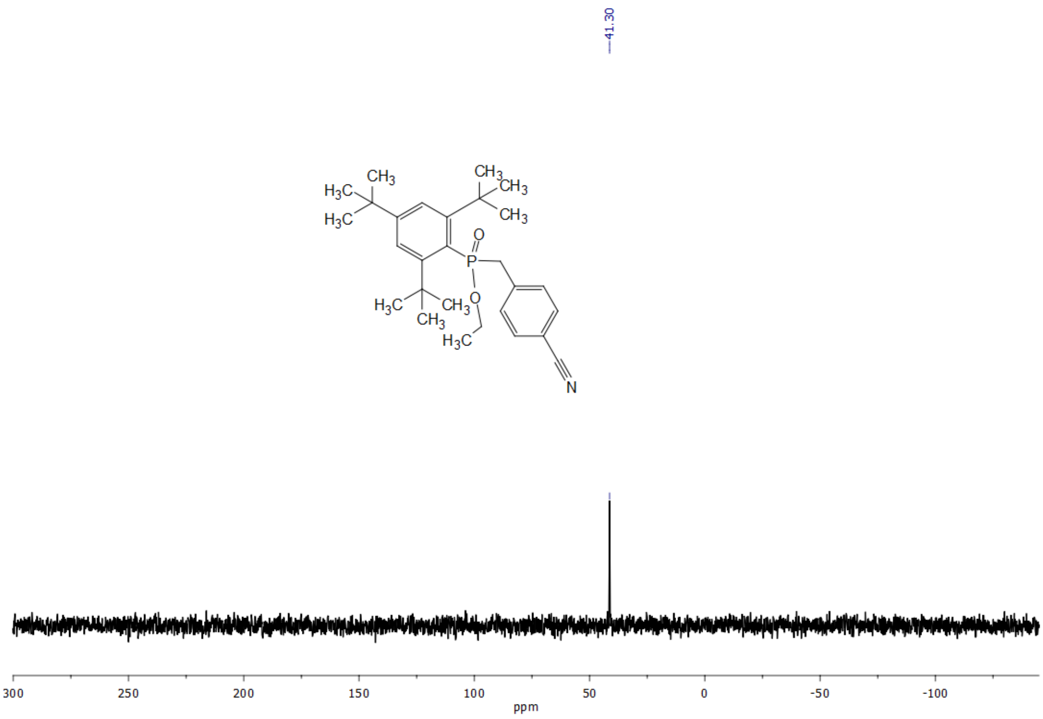


Figure S10: ^{31}P NMR spectrum of isolated ethyl(4-cyanobenzyl)(2,4,6-tri-*tert*-butylphenyl)phosphinate in $CDCl_3$ (162 MHz, 300 K).

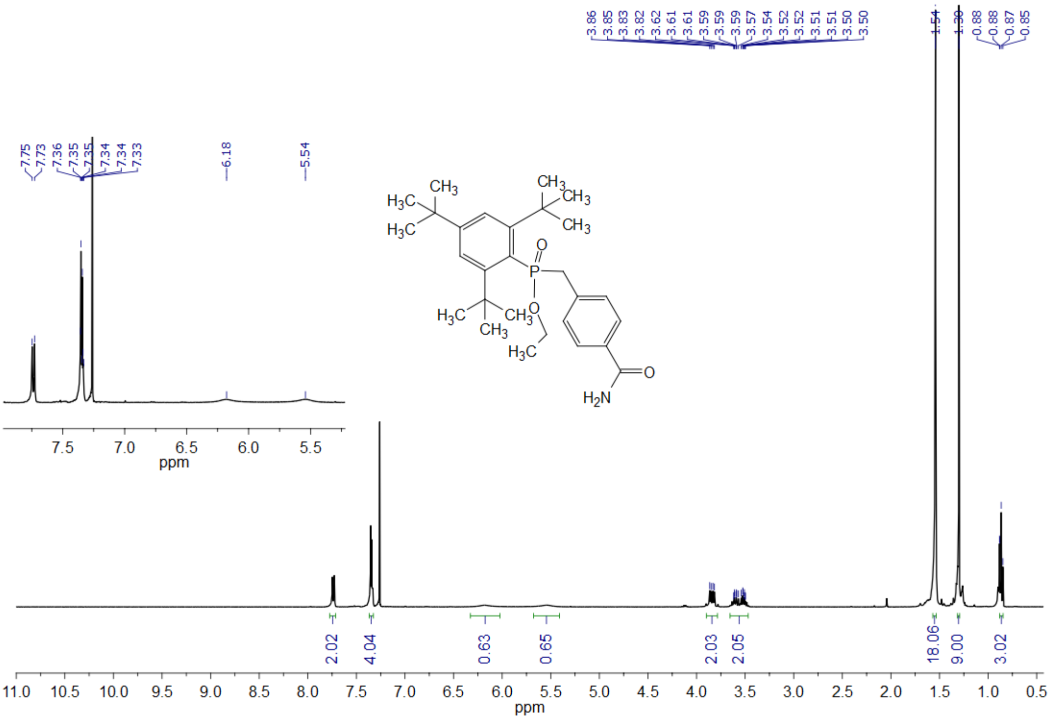


Figure S11: ^{1}H NMR spectrum of isolated ethyl(4-carbamoylbenzyl)(2,4,6-tri-*tert*-butylphenyl)-phosphinate in $CDCl_3$ (400 MHz, 300 K). Due to proton exchange processes with traces of water and HCl in $CDCl_3$ signal broadening of the amide protons are observed.

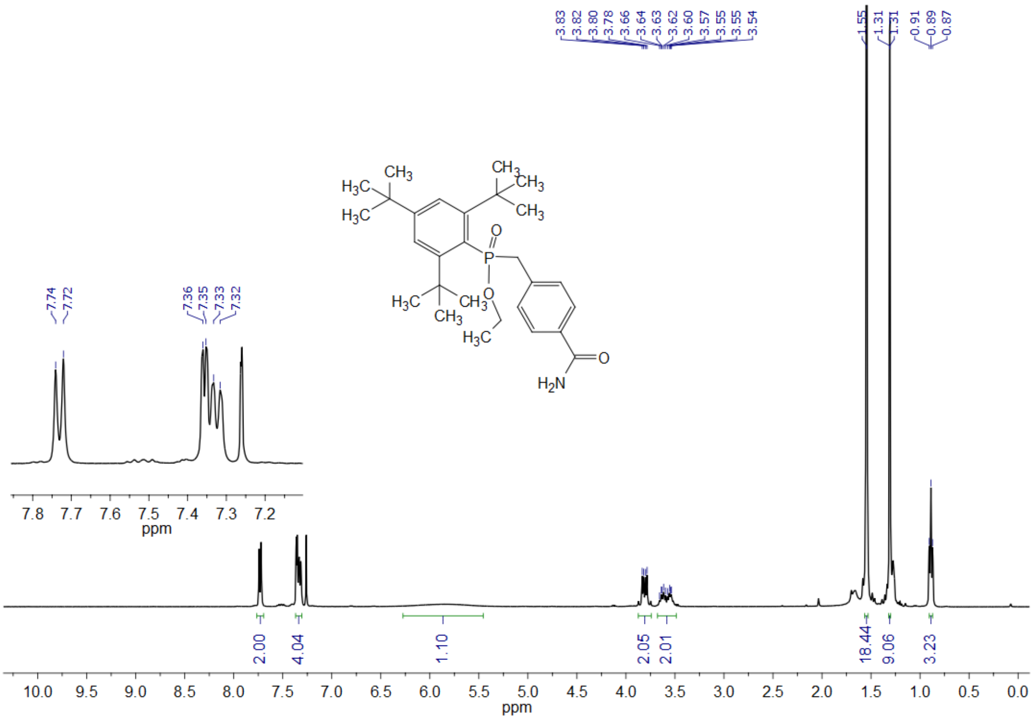


Figure S12: ^{1}H NMR spectrum of isolated ethyl(4-carbamoylbenzyl)(2,4,6-tri-*tert*-butylphenyl)-phosphinate in $CDCl_3$ (400 MHz, 320 K). Due to elevated temperature and increased intermolecular rate for the exchange of amide protons, coalescence of the signal occurs.

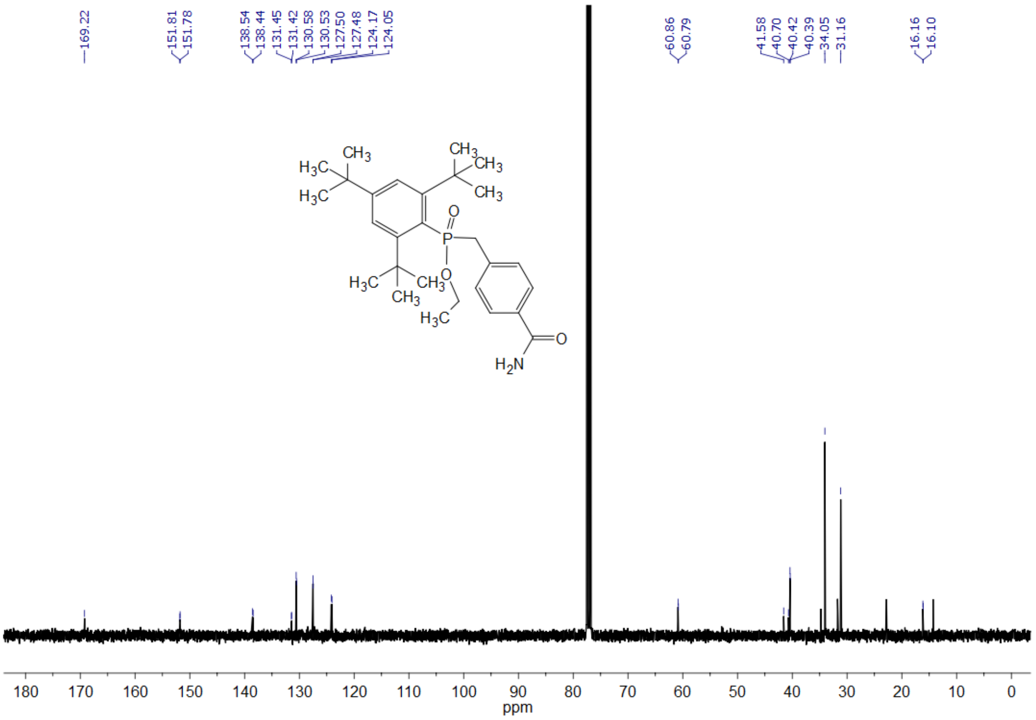


Figure S13: ^{13}C NMR spectrum of isolated ethyl(4-carbamoylbenzyl)(2,4,6-tri-*tert*-butylphenyl)-phosphinate in $CDCl_3$ (101 MHz, 300 K).

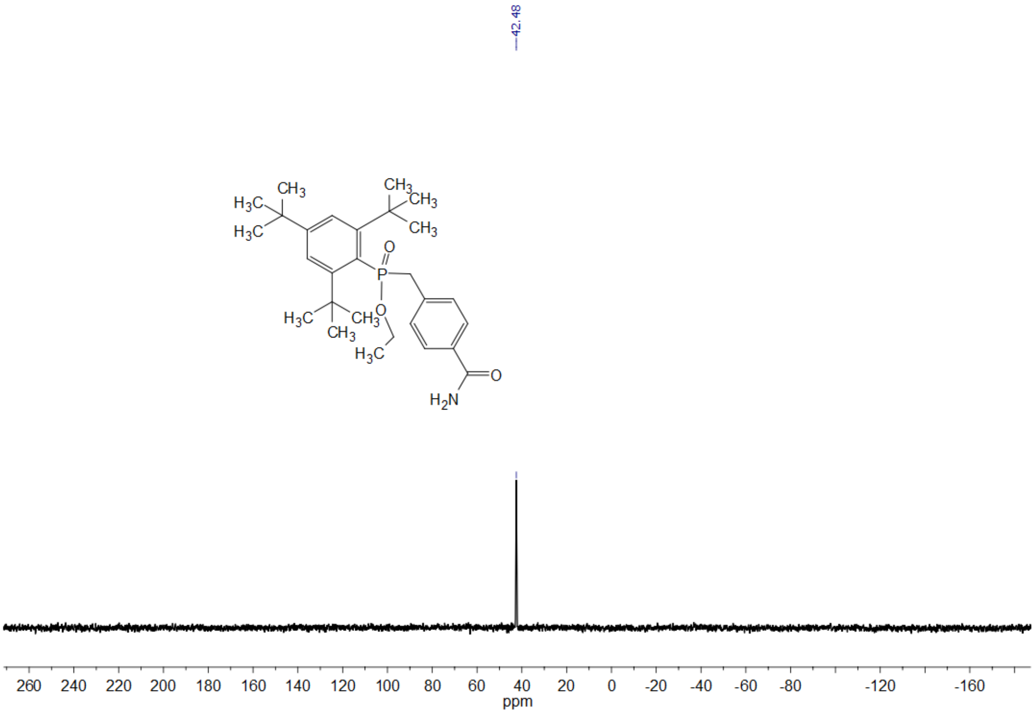


Figure S14: ^{31}P NMR spectrum of isolated ethyl(4-carbamoylbenzyl)(2,4,6-tri-*tert*-butylphenyl)-phosphinate in $CDCl_3$ (162 MHz, 300 K).

Phosphaalkenes

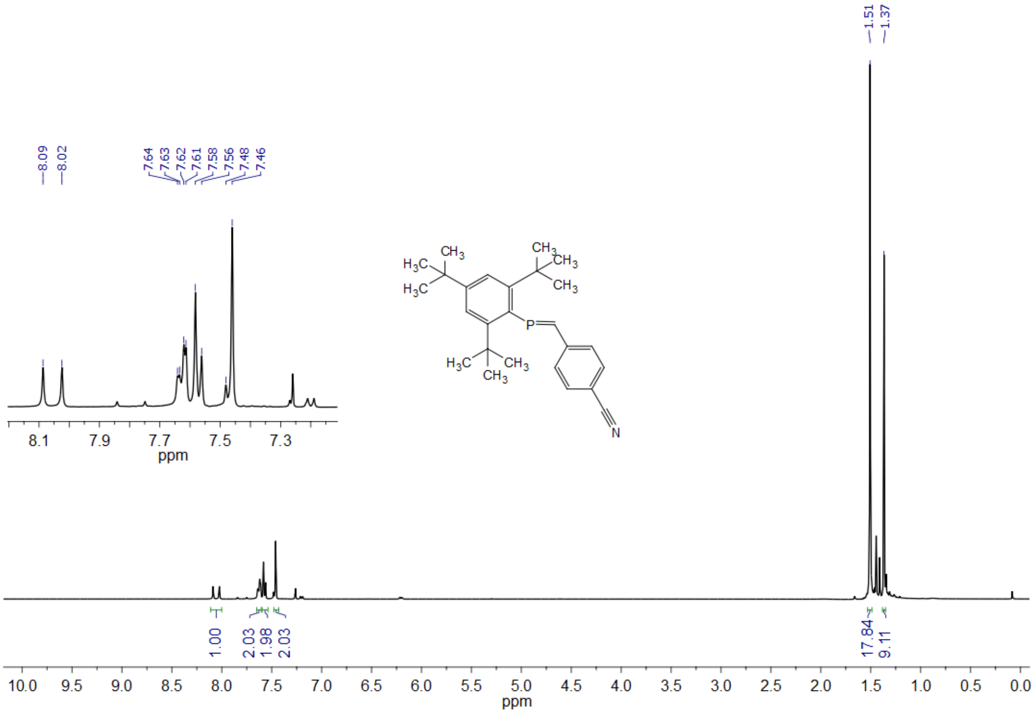


Figure S15: ^{1}H NMR spectrum of isolated (*E*)-(4-cyanobenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane (contains *Z*-isomer) in $CDCl_3$ (400 MHz, 300 K).

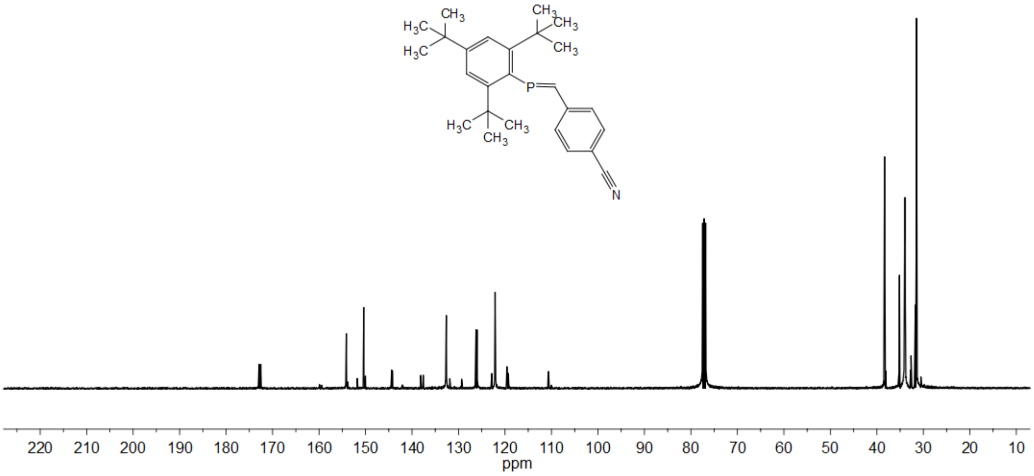


Figure S16: ^{13}C NMR spectrum of isolated (*E*)-(4-cyanobenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane (contains *Z*-isomer) in $CDCl_3$ (101 MHz, 300 K).

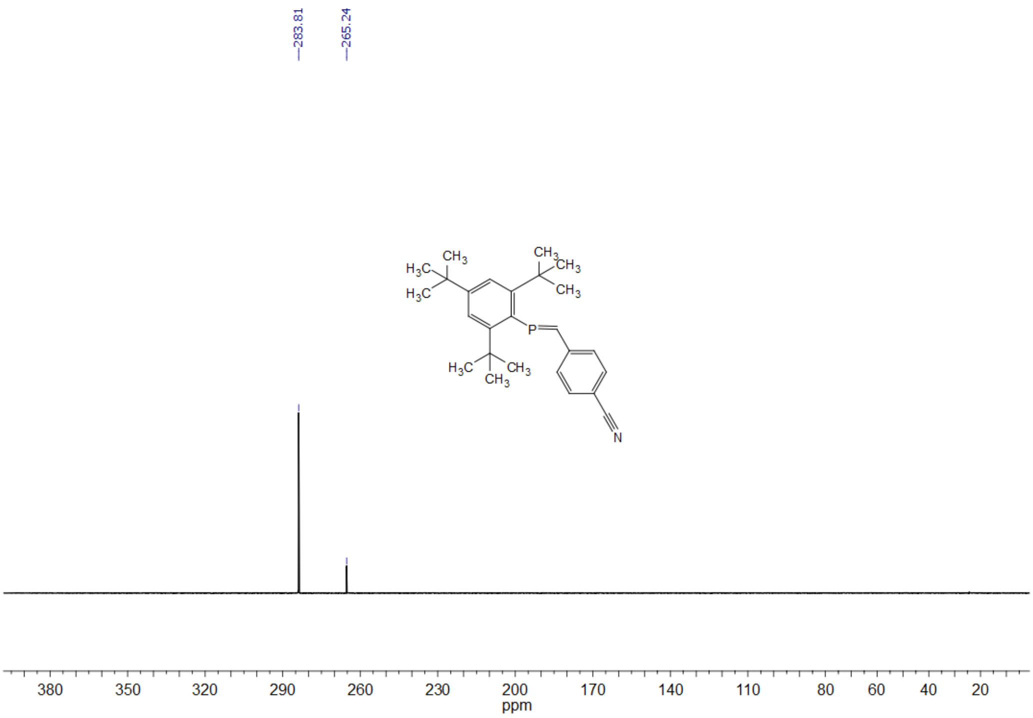


Figure S17: ^{31}P {^{1}H} NMR spectrum of isolated (*E*)-(4-cyanobenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane (contains *Z*-isomer) in CDCl$_3$ (162 MHz, 300 K).

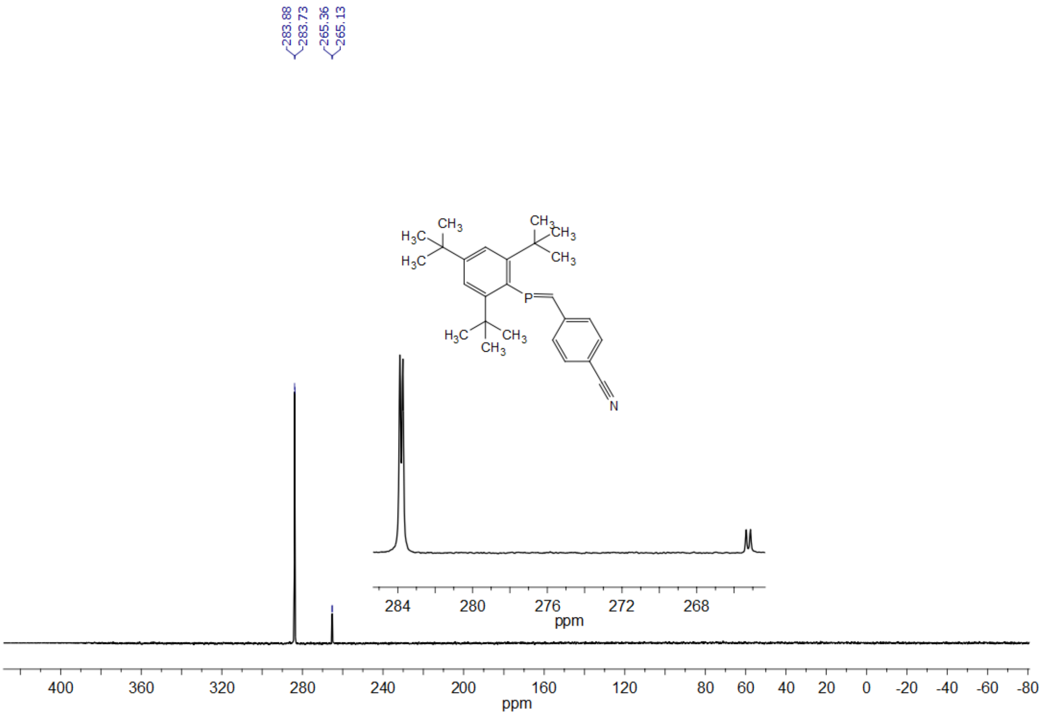


Figure S18: ^{31}P NMR spectrum of isolated (*E*)-(4-cyanobenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane (contains *Z*-isomer) in CDCl$_3$ (162 MHz, 300 K).

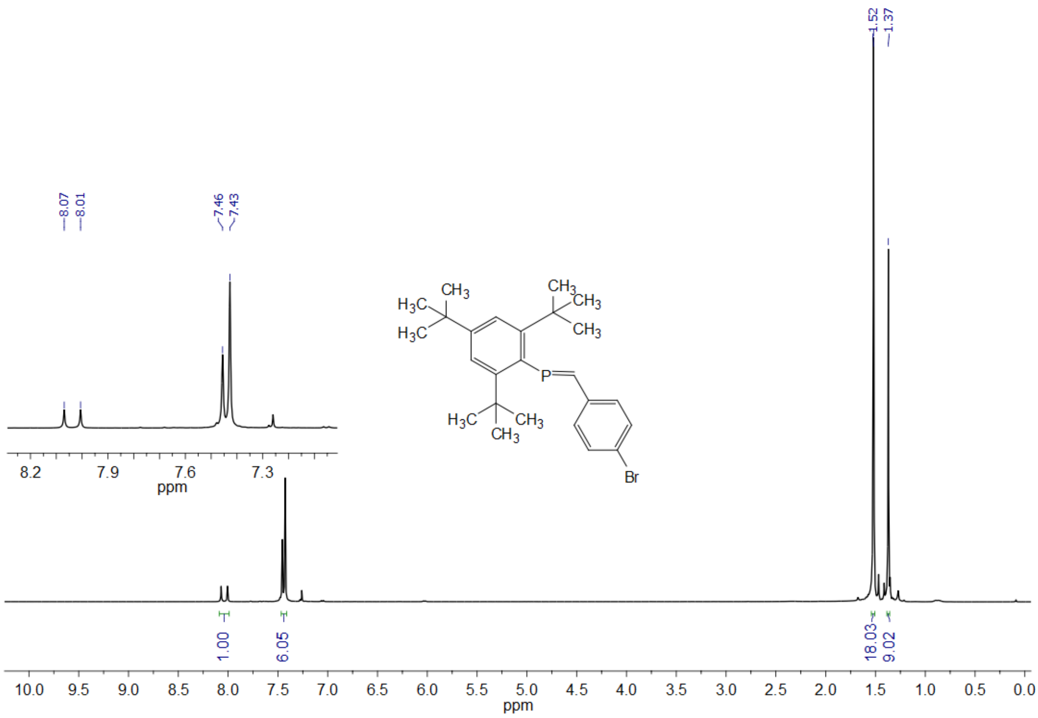


Figure S19: ^1H NMR spectrum of isolated (*E*)-(4-bromobenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane in $CDCl_3$ (400 MHz, 300 K).

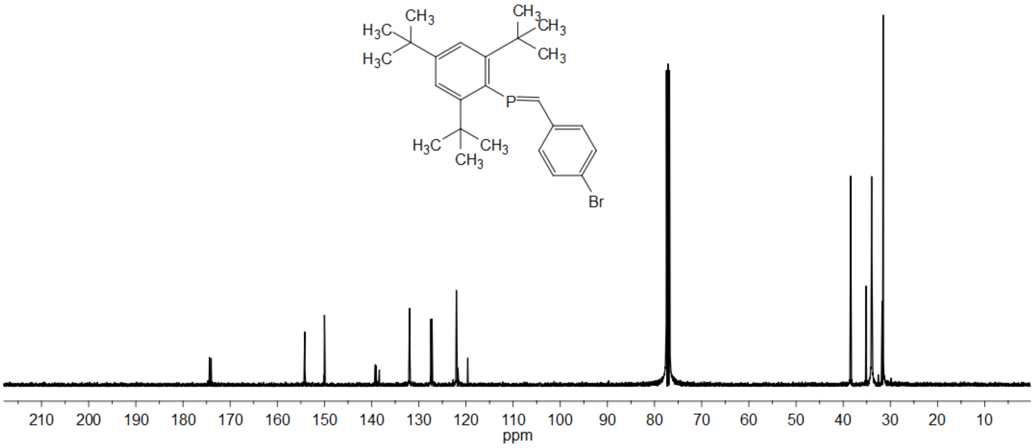


Figure S20: ^{13}C NMR spectrum of isolated (*E*)-(4-bromobenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane in $CDCl_3$ (101 MHz, 300 K).

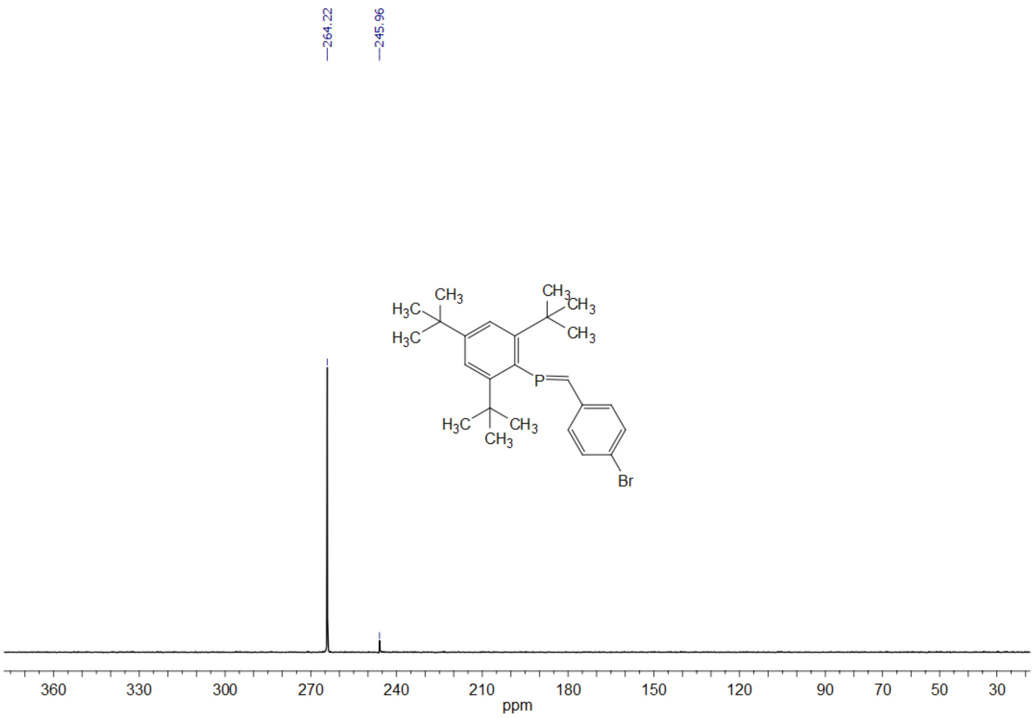


Figure S21: ^{31}P {^{1}H} NMR spectrum of isolated (*E*)-(4-bromobenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane in CDCl$_3$ (162 MHz, 300 K).

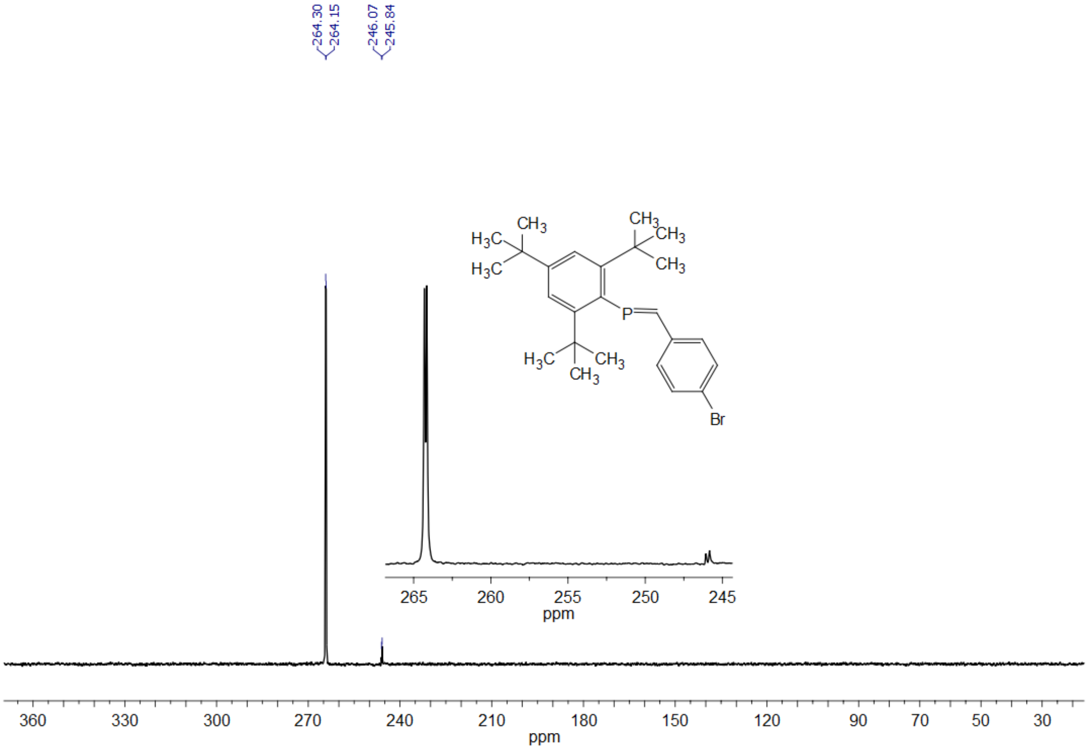


Figure S22: ^{31}P NMR spectrum of isolated (*E*)-(4-bromobenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane in CDCl$_3$ (162 MHz, 300 K).

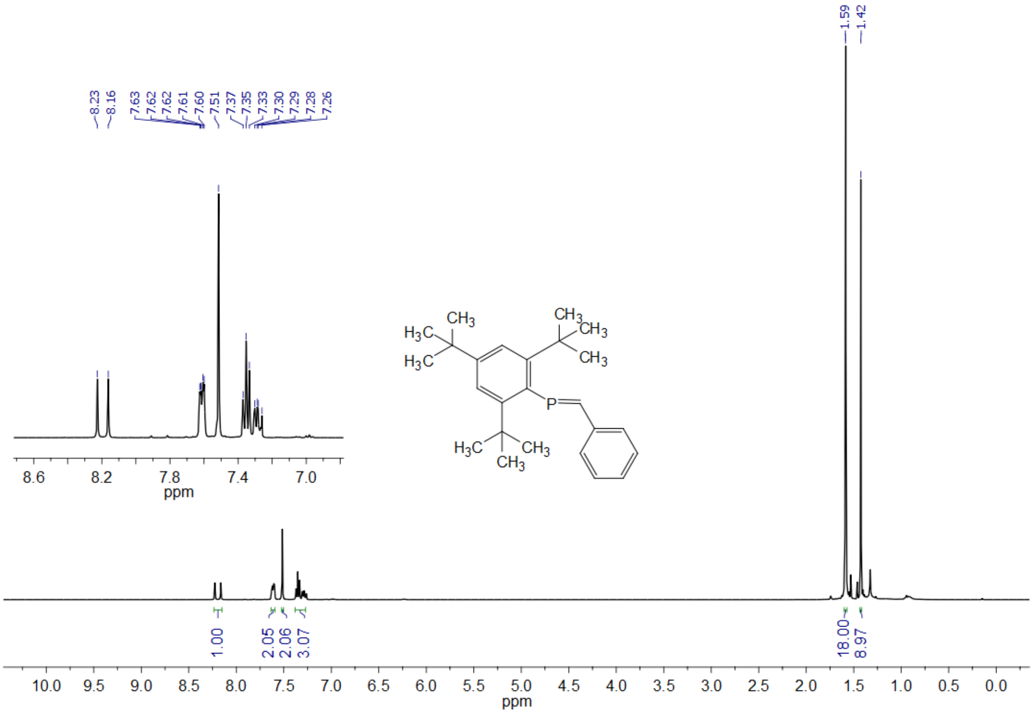


Figure S23: ^{1}H NMR spectrum of isolated (*E*)-benzylidene(2,4,6-tri-*tert*-butylphenyl)phosphane in $CDCl_3$ (400 MHz, 300 K).

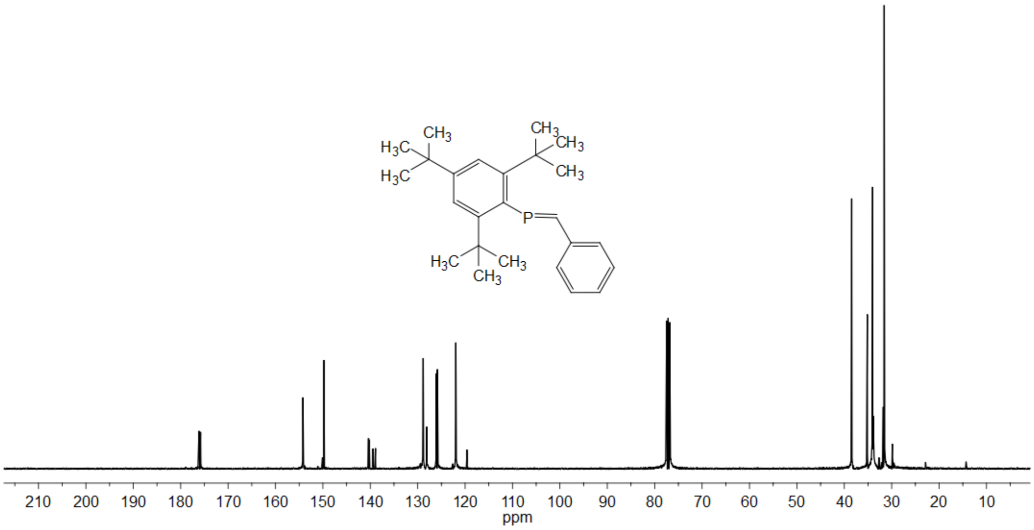


Figure S24: ^{13}C NMR spectrum of isolated (*E*)-benzylidene(2,4,6-tri-*tert*-butylphenyl)phosphane in $CDCl_3$ (101 MHz, 300 K).

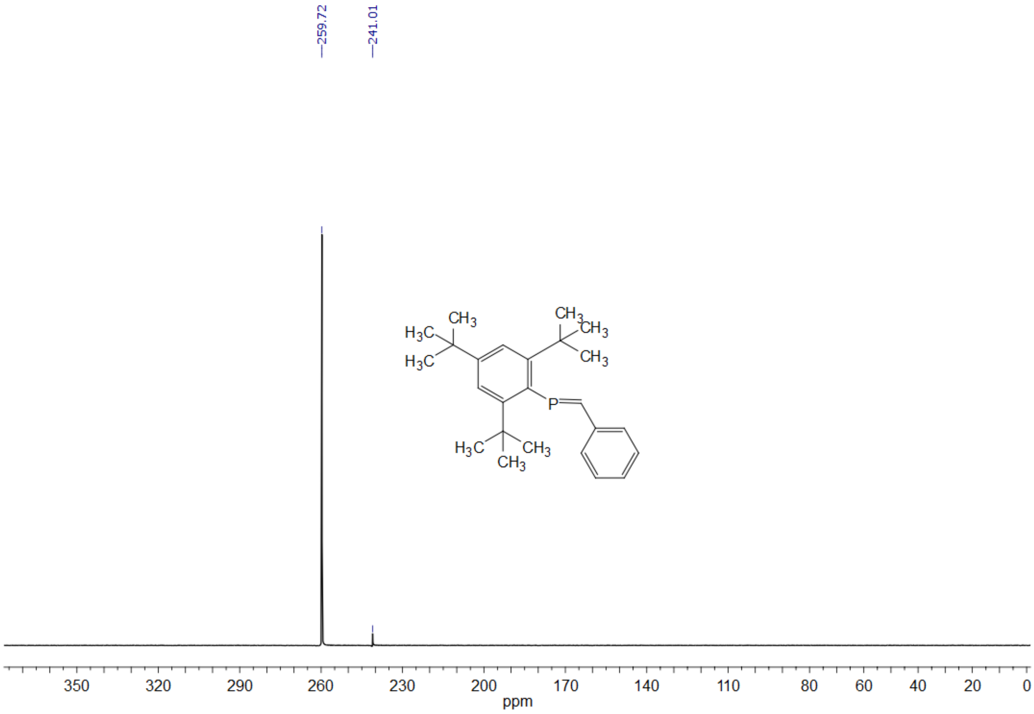


Figure S25: ^{31}P {^{1}H} NMR spectrum of isolated (*E*)-benzylidene(2,4,6-tri-*tert*-butylphenyl)phosphane in $CDCl_3$ (162 MHz, 300 K).

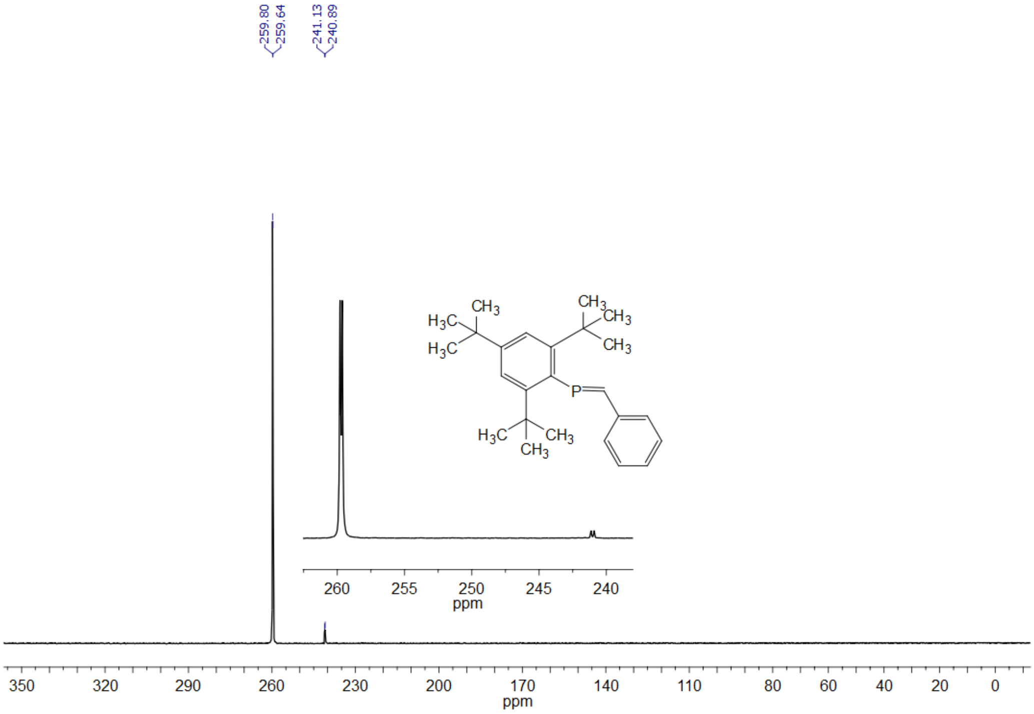


Figure S26: ^{31}P NMR spectrum of isolated (*E*)-benzylidene(2,4,6-tri-*tert*-butylphenyl)phosphane in $CDCl_3$ (162 MHz, 300 K).

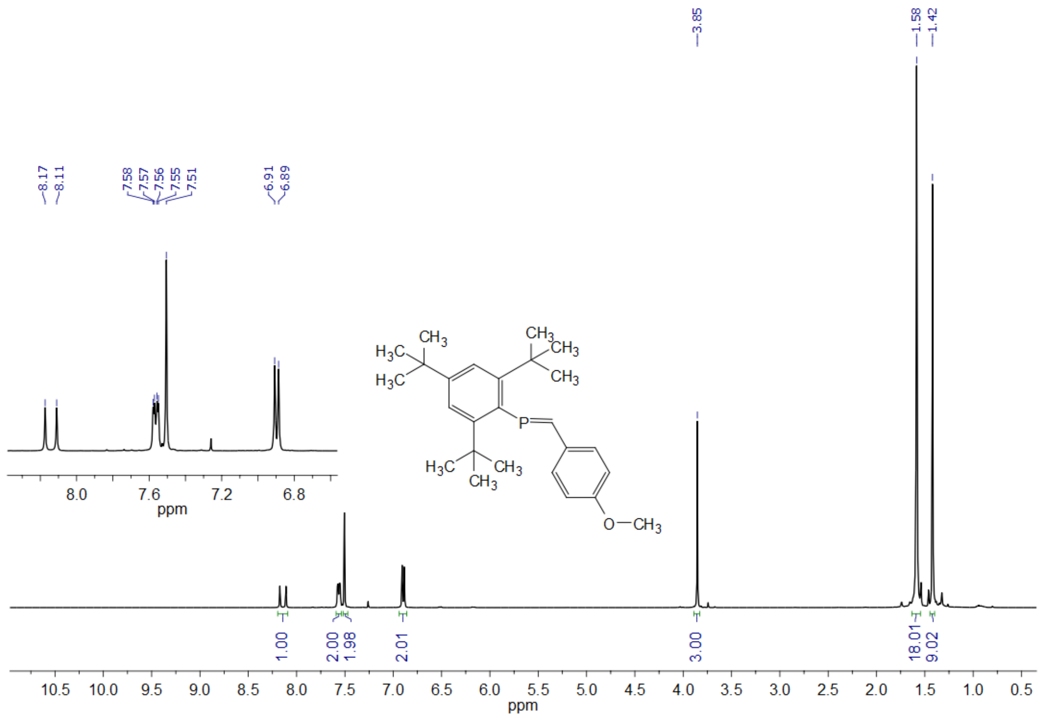


Figure S27: ^{1}H NMR spectrum of isolated (*E*)-(4-methoxybenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane in $CDCl_3$ (400 MHz, 300 K).

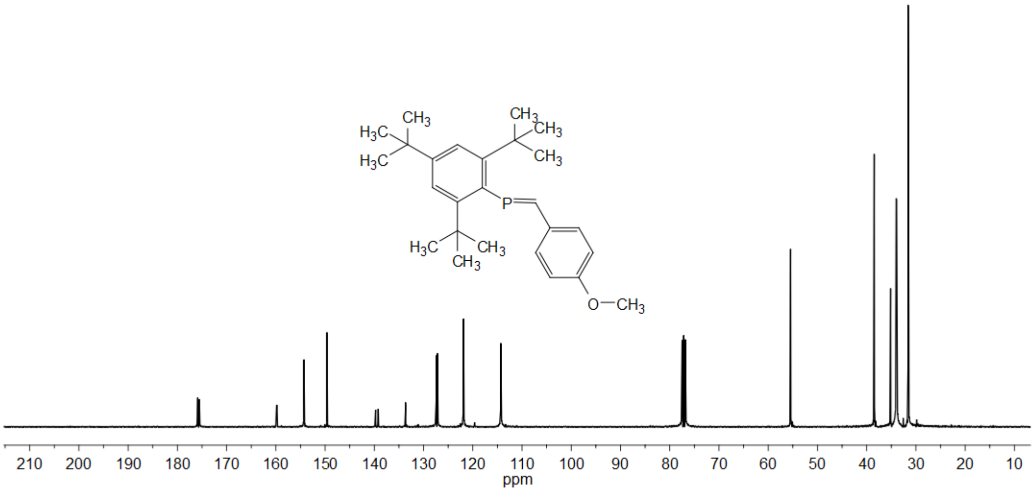


Figure S28: ^{13}C NMR spectrum of isolated (*E*)-(4-methoxybenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane in $CDCl_3$ (101 MHz, 300 K).

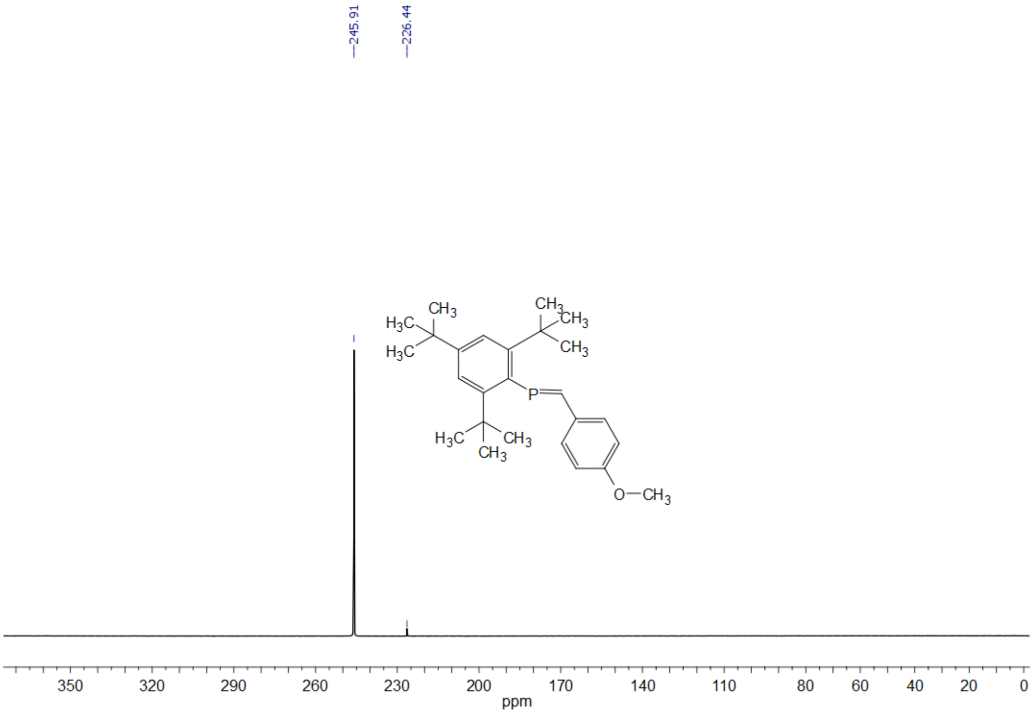


Figure S29: $^{31}P\ \{^{1}H\}$ NMR spectrum of isolated (*E*)-(4-methoxybenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane in $CDCl_3$ (162 MHz, 300 K).

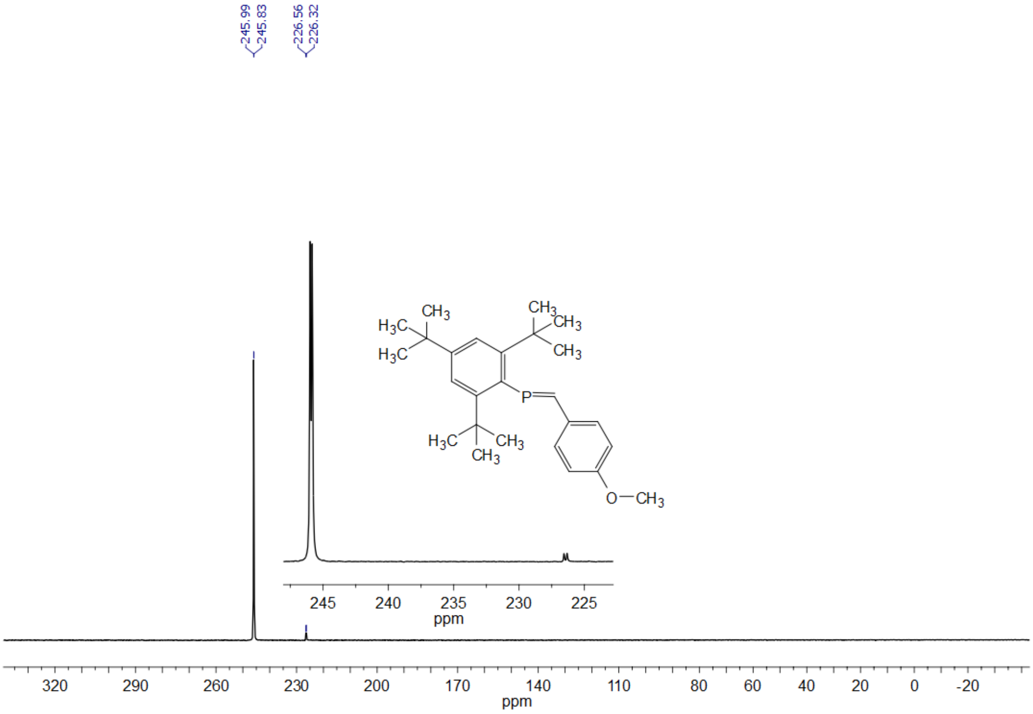


Figure S30: ^{31}P NMR spectrum of isolated (*E*)-(4-methoxybenzylidene)(2,4,6-tri-*tert*-butylphenyl)-phosphane in $CDCl_3$ (162 MHz, 300 K).

Alkenes

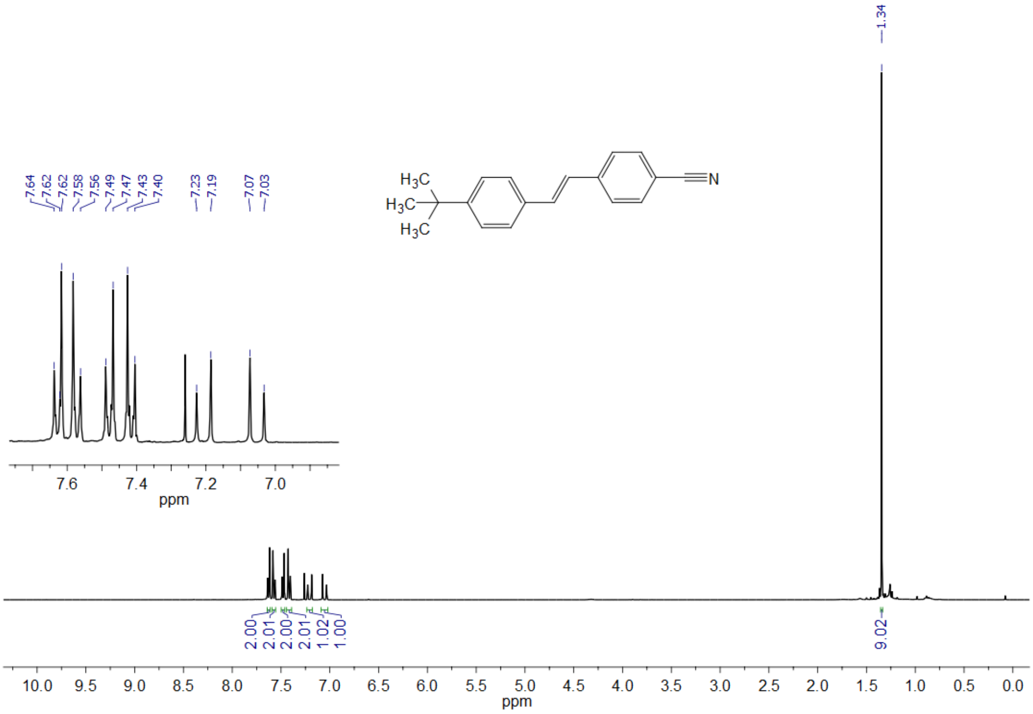


Figure S31: ^{1}H NMR spectrum of isolated (*E*)-4-(4-(*tert*-butyl)styryl)benzonitrile (**Table 1**, **Entry 1**) in CDCl3 (400 MHz, 300 K).

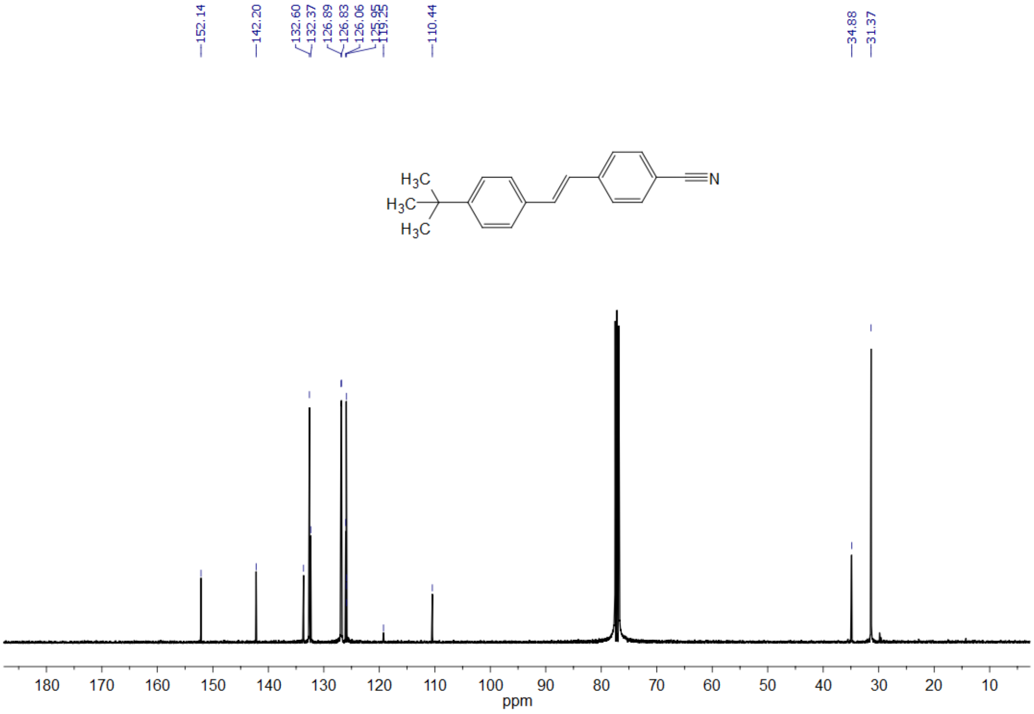


Figure S32: ^{13}C NMR spectrum of isolated (*E*)-4-(4-(*tert*-butyl)styryl)benzonitrile (**Table 1**, **Entry 1**) in CDCl3 (101 MHz, 300 K).

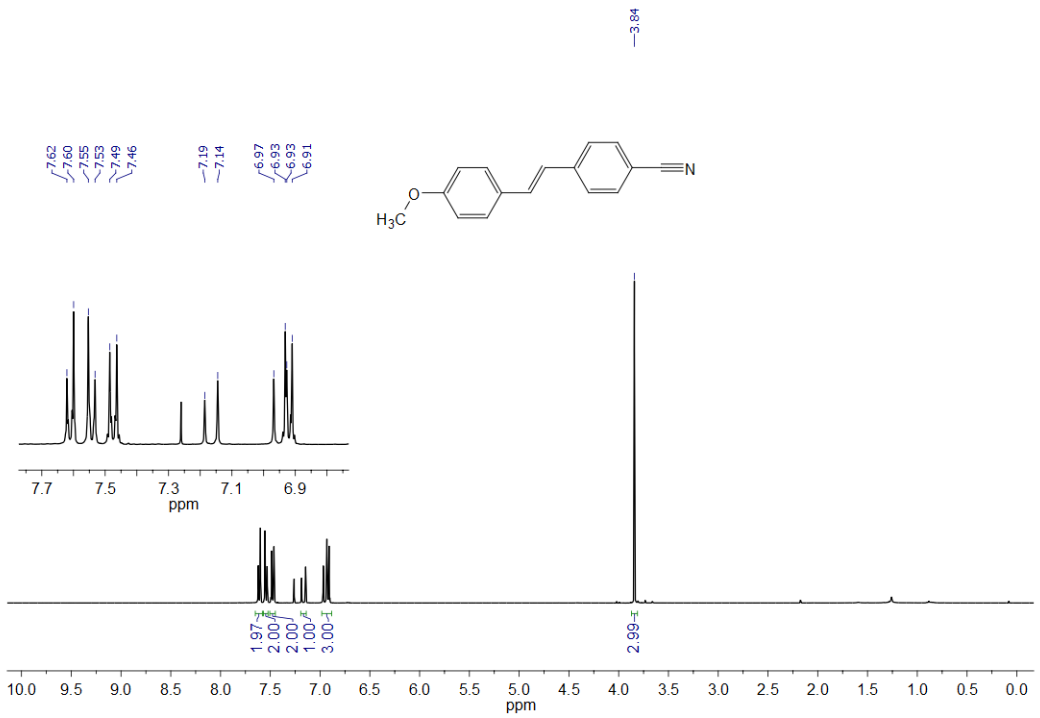


Figure S33: ^{1}H NMR spectrum of isolated (*E*)-4-(4-methoxystyryl)benzonitrile (**Table 1**, **Entry 2**) in $CDCl_3$ (400 MHz, 300 K).

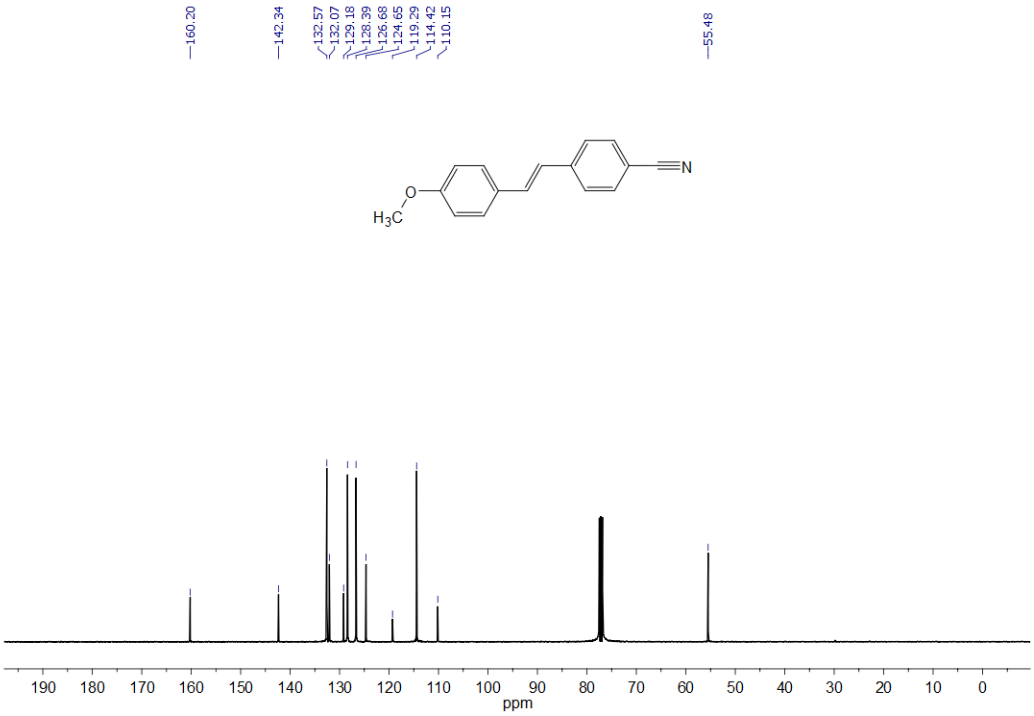


Figure S34: ^{13}C NMR spectrum of isolated (*E*)-4-(4-methoxystyryl)benzonitrile (**Table 1**, **Entry 2**) in $CDCl_3$ (101 MHz, 300 K).

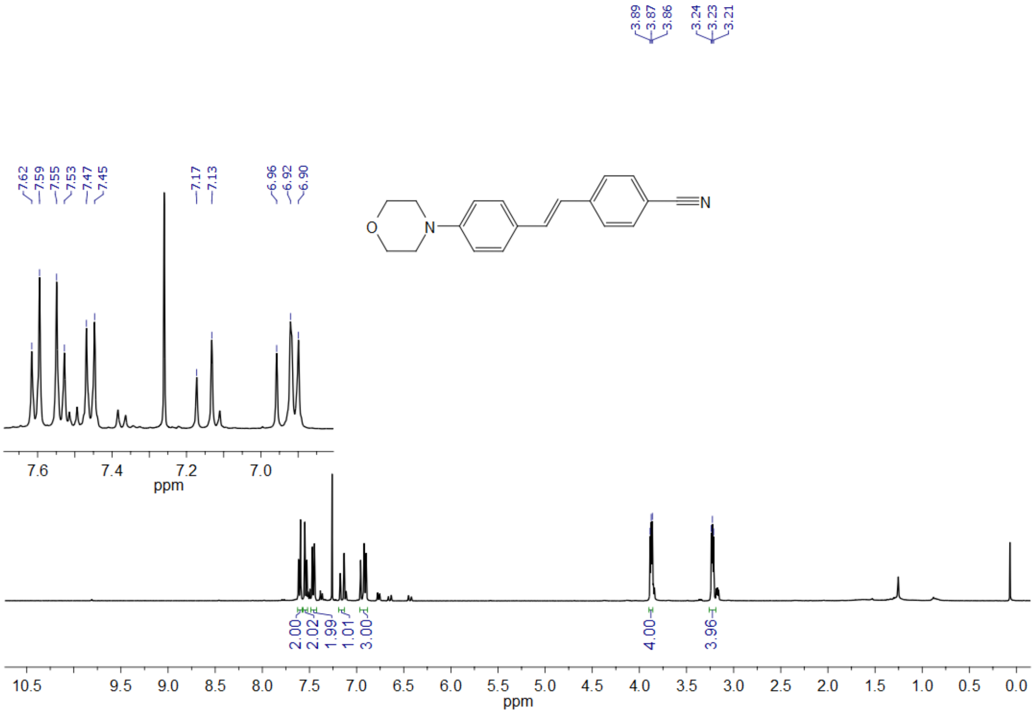


Figure S35: ^{1}H NMR spectrum of isolated (*E*)-4-(4-morpholinostyryl)benzonitrile (contains 9% of *Z*-isomer) (**Table 1**, **Entry 3**) in $CDCl_3$ (400 MHz, 320 K).

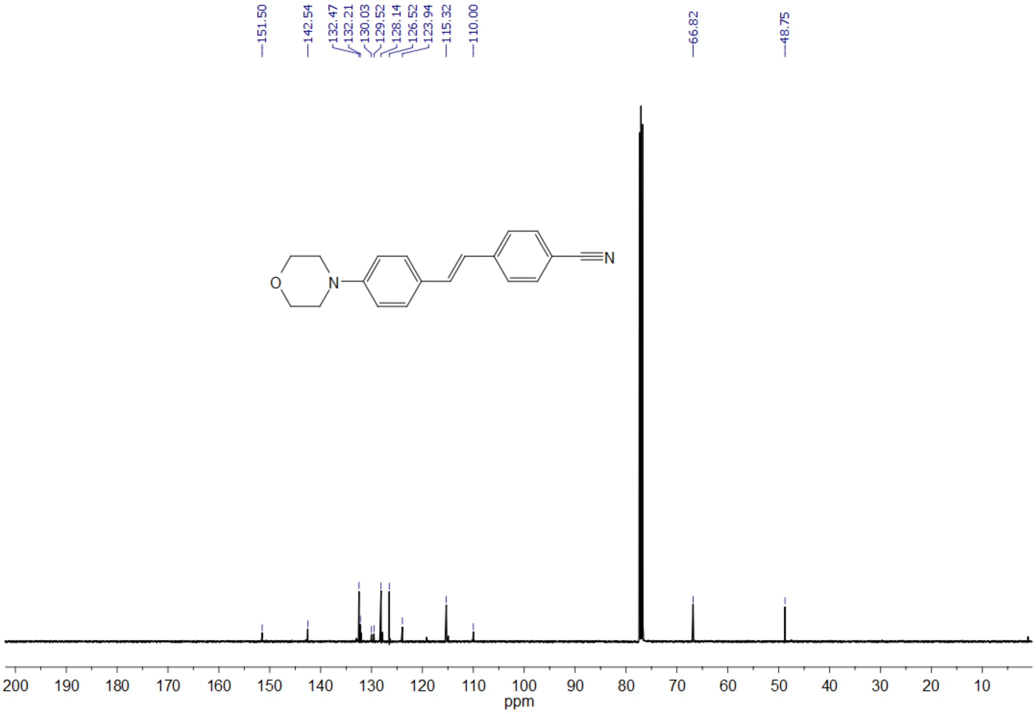


Figure S36: ^{13}C NMR spectrum of isolated (*E*)-4-(4-morpholinostyryl)benzonitrile (contains 9% of *Z*-isomer) (**Table 1**, **Entry 3**) in $CDCl_3$ (101 MHz, 320 K).

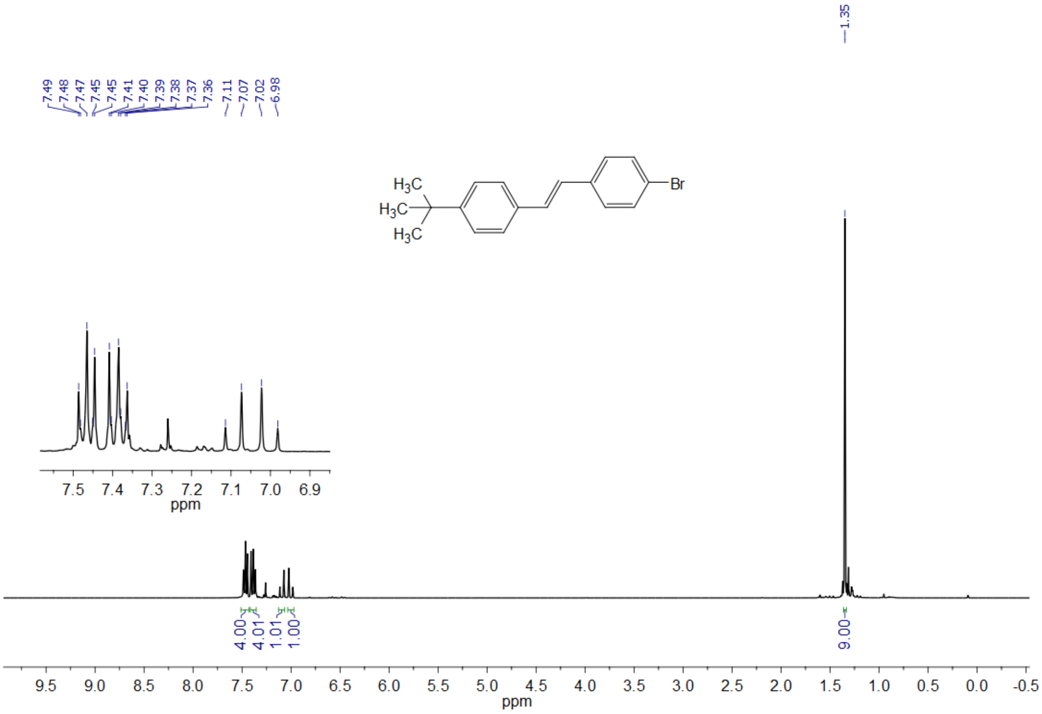


Figure S37: ^{1}H NMR spectrum of isolated (*E*)-1-bromo-4-(4-(*tert*-butyl)styryl)benzene (**Table 1, Entry 4**) in $CDCl_3$ (400 MHz, 300 K).

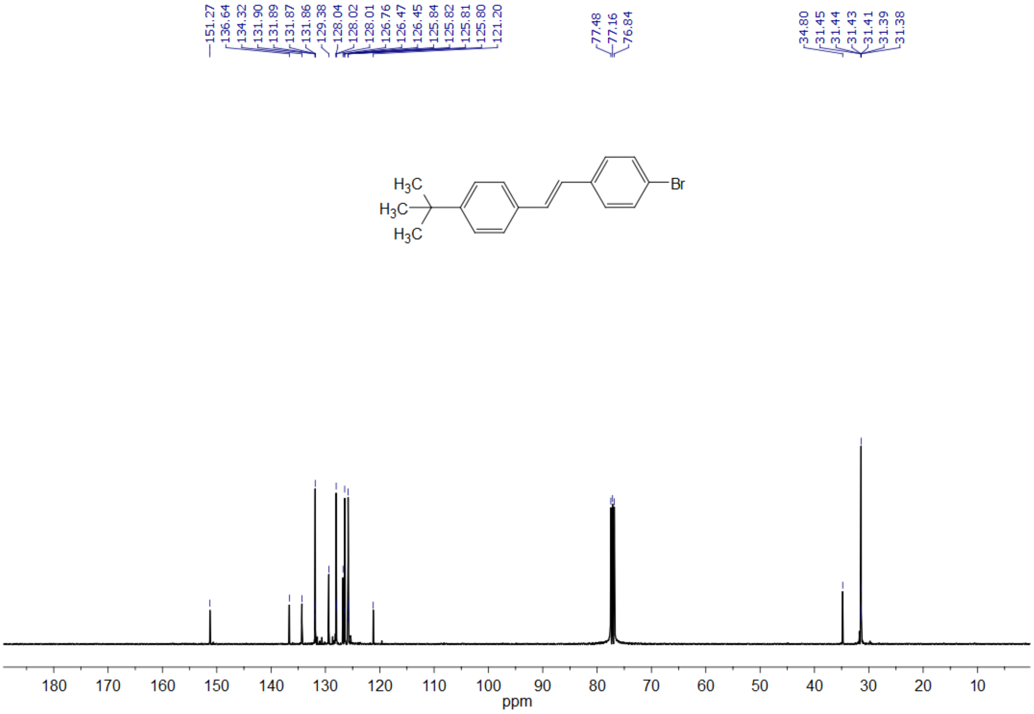


Figure S38: ^{13}C NMR spectrum of isolated (*E*)-1-bromo-4-(4-(*tert*-butyl)styryl)benzene (**Table 1, Entry 4**) in $CDCl_3$ (101 MHz, 300 K).

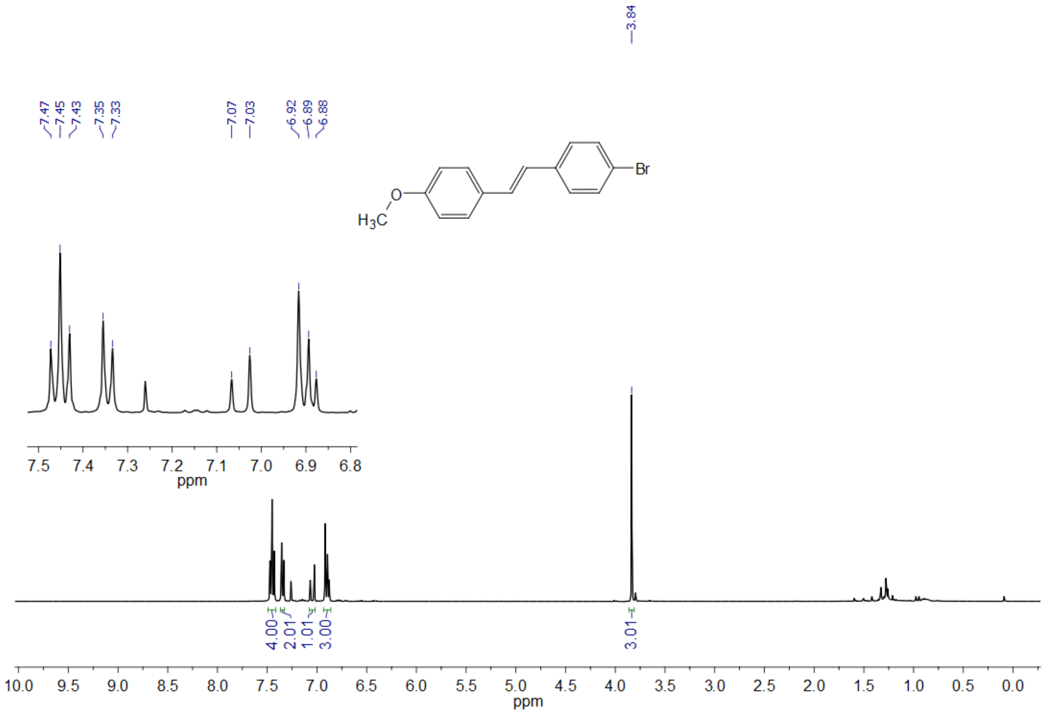


Figure S39: ^{1}H NMR spectrum of isolated (*E*)-1-bromo-4-(4-methoxystyryl)benzene (**Table 1**, **Entry 5**) in $CDCl_3$ (400 MHz, 300 K).

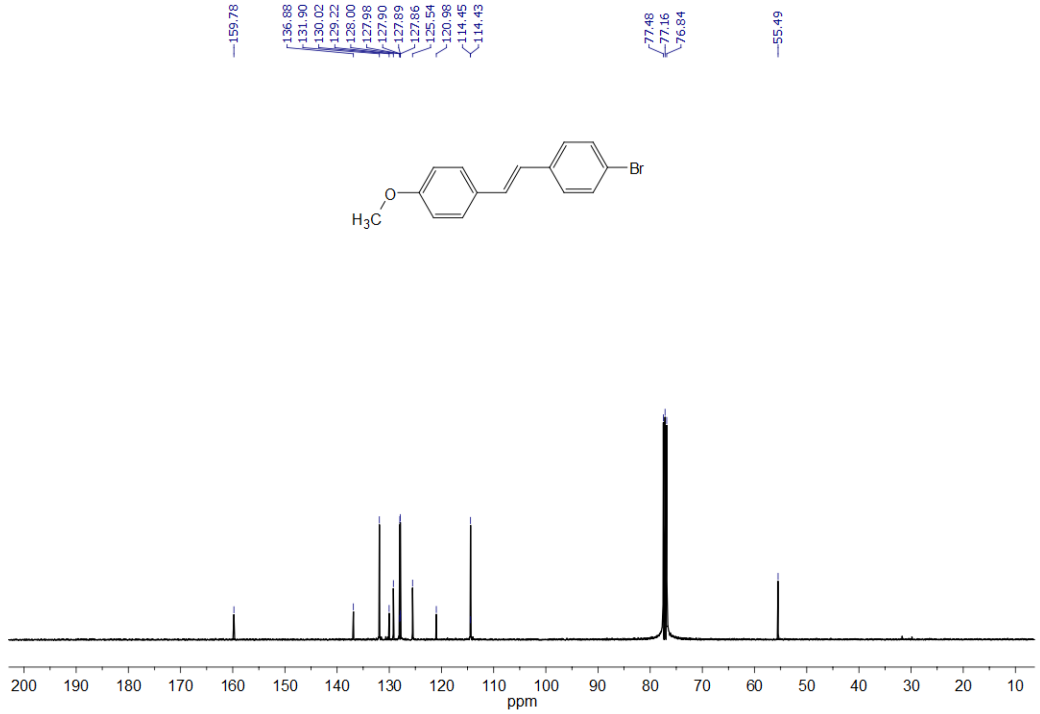


Figure S40: ^{13}C NMR spectrum of isolated (*E*)-1-bromo-4-(4-methoxystyryl)benzene (**Table 1**, **Entry 5**) in $CDCl_3$ (101 MHz, 300 K).

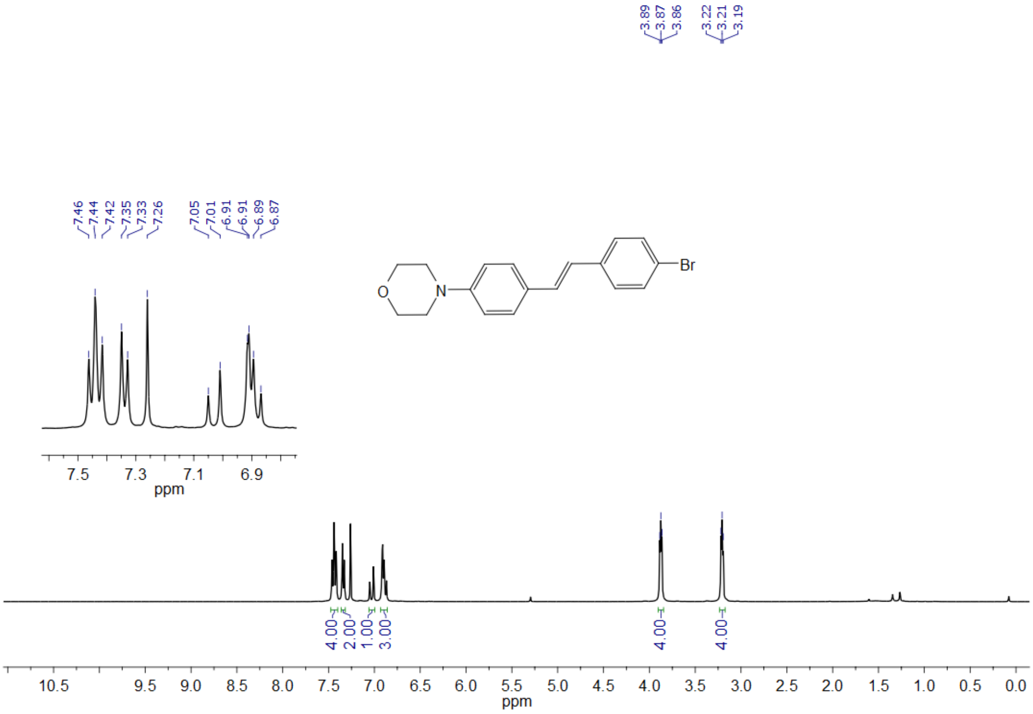


Figure S41: ^{1}H NMR spectrum of isolated (*E*)-4-(4-(4-bromostyryl)phenyl)morpholine (**Table 1**, **Entry 6**) in $CDCl_3$ (400 MHz, 320 K).

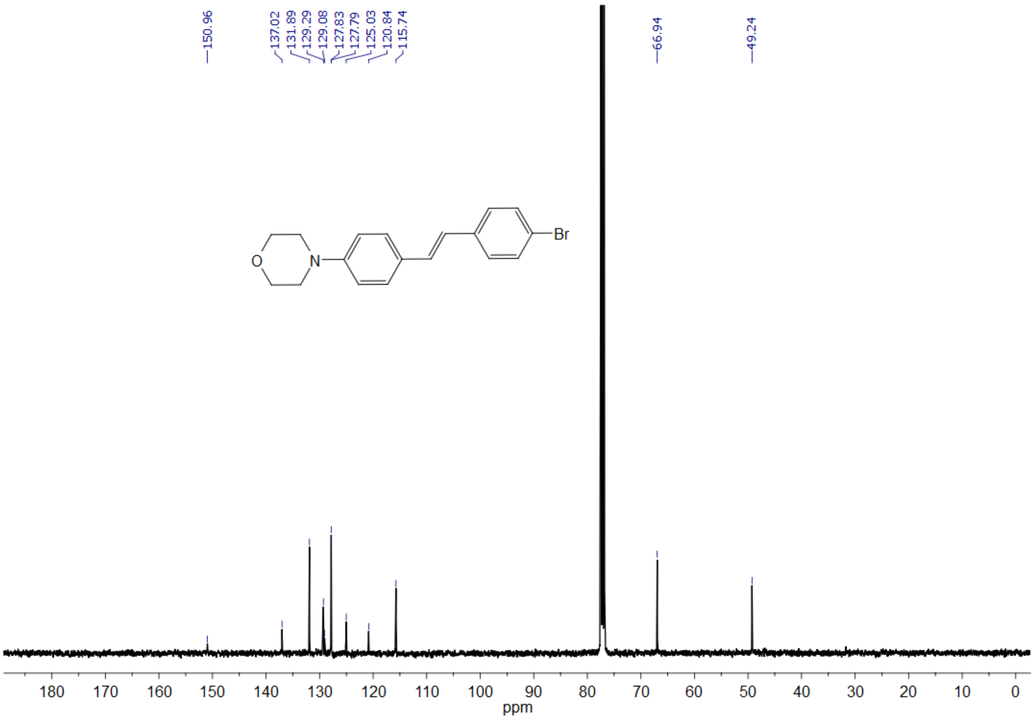


Figure S42: ^{13}C NMR spectrum of isolated (*E*)-4-(4-(4-bromostyryl)phenyl)morpholine (**Table 1**, **Entry 6**) in $CDCl_3$ (101 MHz, 320 K).

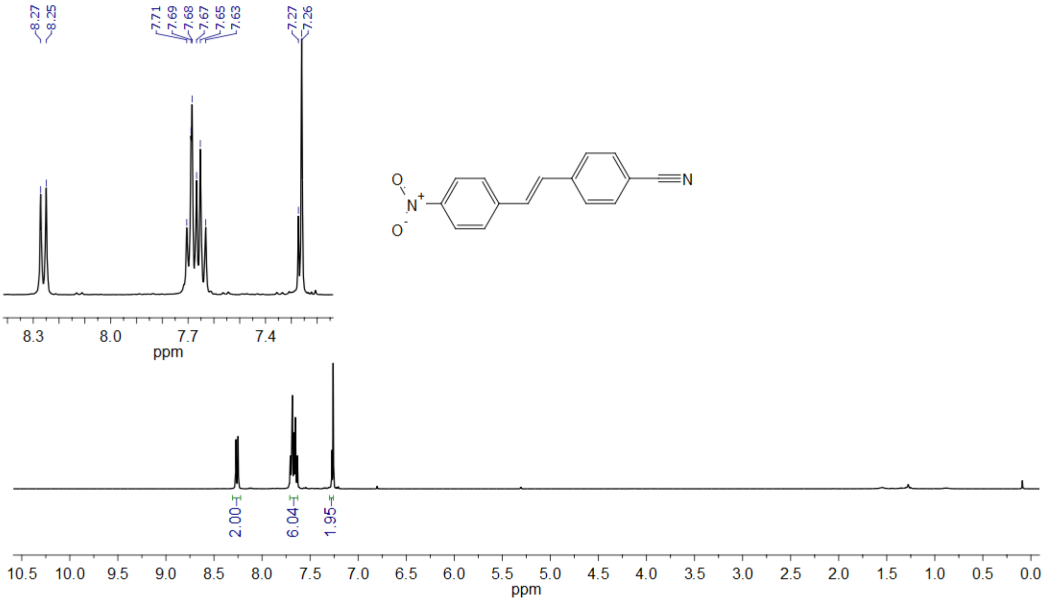


Figure S43: ^{1}H NMR spectrum of isolated (*E*)-4-(4-nitrostyryl)benzonitrile (**Table 1**, **Entry 7**) in $CDCl_3$ (400 MHz, 320 K).

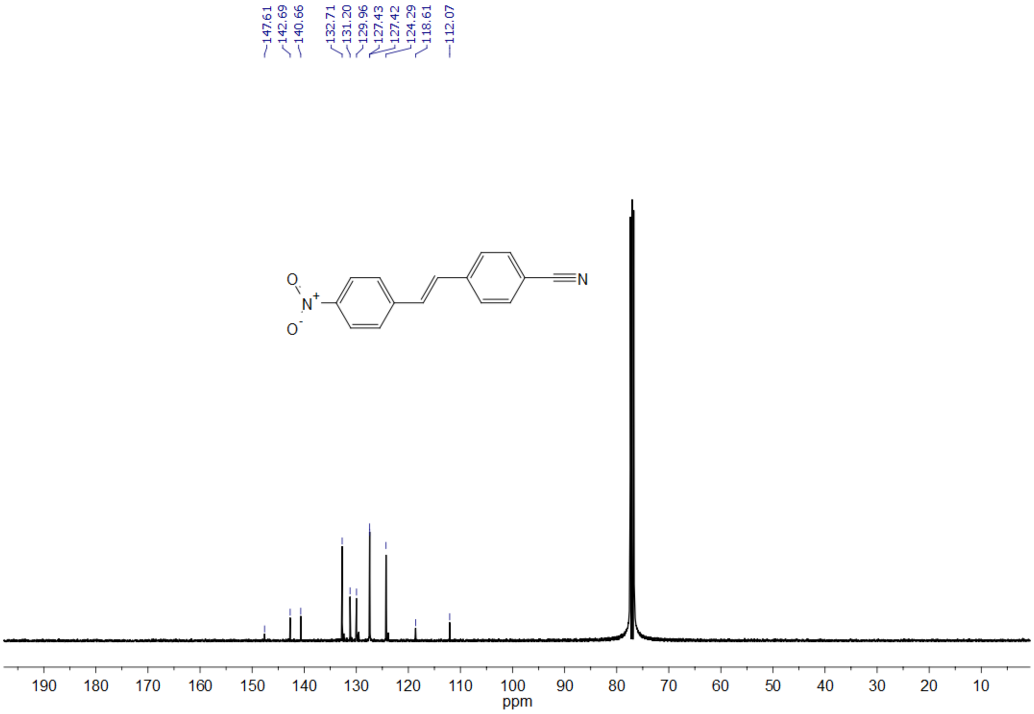


Figure S44: ^{13}C NMR spectrum of isolated (*E*)-4-(4-nitrostyryl)benzonitrile (**Table 1**, **Entry 7**) in $CDCl_3$ (101 MHz, 320 K).

DFT calculations

Phosphin oxide (**5**):

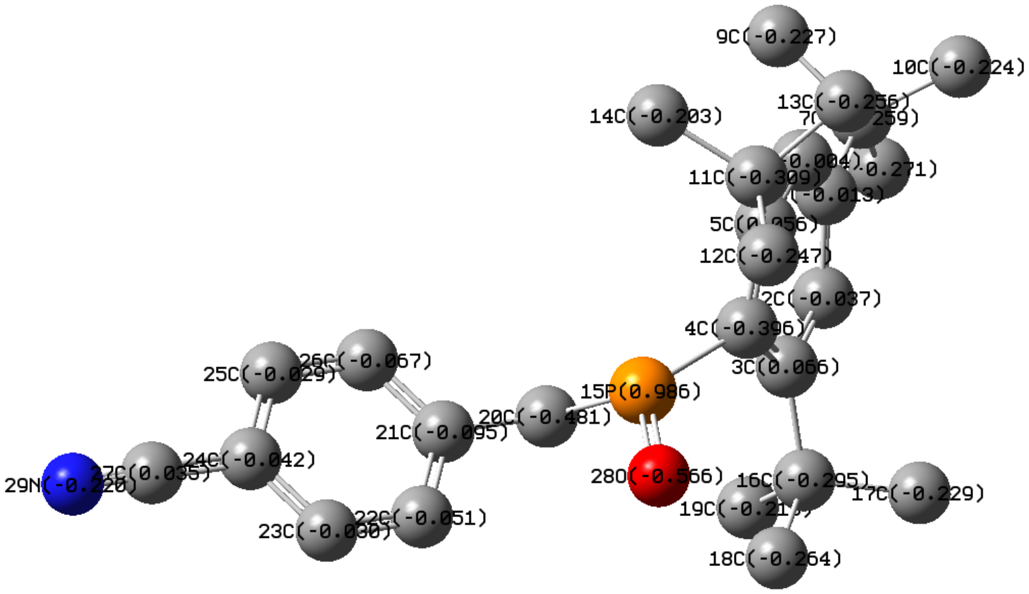


Figure S45: Optimized geometry structure (B3LYP and 6-311G(d,p)) with the corresponding Mulliken charges for each atom. Hydrogen atoms are omitted for clarity.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.221576	0.174611	-0.818822
2	6	0	2.714536	-1.072760	-0.479428
3	6	0	1.590664	-1.251383	0.340856
4	6	0	0.903325	-0.088858	0.788030
5	6	0	1.537176	1.190328	0.654779
6	6	0	2.652185	1.276847	-0.178286
7	6	0	4.407233	0.367008	-1.779891
8	6	0	4.853824	-0.954372	-2.432440
9	6	0	3.998822	1.343852	-2.906979
10	6	0	5.610465	0.953096	-1.004252
11	6	0	1.154602	2.491789	1.438601

12	6	0	0.438321	2.209028	2.780665
13	6	0	2.457764	3.240276	1.838590
14	6	0	0.326198	3.468067	0.569548
15	15	0	-0.922269	-0.076433	1.077290
16	6	0	1.317980	-2.733404	0.748439
17	6	0	2.614511	-3.252229	1.433524
18	6	0	0.197233	-2.957850	1.778735
19	6	0	1.029784	-3.608748	-0.493361
20	6	0	-1.632659	-0.851178	-0.458789
21	6	0	-3.080702	-0.472991	-0.642142
22	6	0	-4.063826	-0.947222	0.237971
23	6	0	-5.395840	-0.598860	0.068033
24	6	0	-5.774584	0.239440	-0.990953
25	6	0	-4.798241	0.726496	-1.869512
26	6	0	-3.467687	0.371724	-1.688873
27	6	0	-7.147583	0.596634	-1.173353
28	8	0	-1.560255	-0.533280	2.353818
29	7	0	-8.256160	0.885714	-1.323084
30	1	0	3.206749	-1.954002	-0.862080
31	1	0	3.108822	2.243947	-0.328292
32	1	0	5.672629	-0.759290	-3.129735
33	1	0	5.219731	-1.673052	-1.694263
34	1	0	4.042976	-1.423257	-2.996720
35	1	0	4.833785	1.493245	-3.597830
36	1	0	3.712995	2.322631	-2.515513
37	1	0	3.152805	0.950649	-3.477261
38	1	0	5.920218	0.281882	-0.198696
39	1	0	6.462490	1.092318	-1.676609
40	1	0	5.375211	1.922830	-0.559911
41	1	0	0.352821	3.145128	3.339183
42	1	0	-0.569702	1.810091	2.696262

```
    43          1          0       1.016187    1.509936    3.390107
    44          1          0       2.201323    4.061963    2.511688
    45          1          0       2.978545    3.680910    0.987099
    46          1          0       3.152793    2.579251    2.361851
    47          1          0      -0.660154    3.077524    0.313391
    48          1          0       0.176371    4.409263    1.107155
    49          1          0       0.847396    3.695089   -0.364429
    50          1          0      -1.195616    1.264522    0.747653
    51          1          0       2.469541   -4.289372    1.748816
    52          1          0       3.483409   -3.223452    0.775166
    53          1          0       2.845172   -2.658190    2.321573
    54          1          0       0.239026   -3.998540    2.112008
    55          1          0      -0.804278   -2.800073    1.384971
    56          1          0       0.303648   -2.320034    2.656221
    57          1          0       0.125799   -3.283969   -1.014199
    58          1          0       1.850127   -3.588421   -1.213833
    59          1          0       0.882890   -4.649012   -0.188772
    60          1          0      -1.030998   -0.512782   -1.305316
    61          1          0      -1.523154   -1.933388   -0.383227
    62          1          0      -3.774461   -1.573228    1.073123
    63          1          0      -6.148834   -0.968383    0.752981
    64          1          0      -5.087754    1.375137   -2.686977
    65          1          0      -2.719785    0.748843   -2.378012
---------------------------------------------------------------------------------------
```

Phosphinate (**9**):

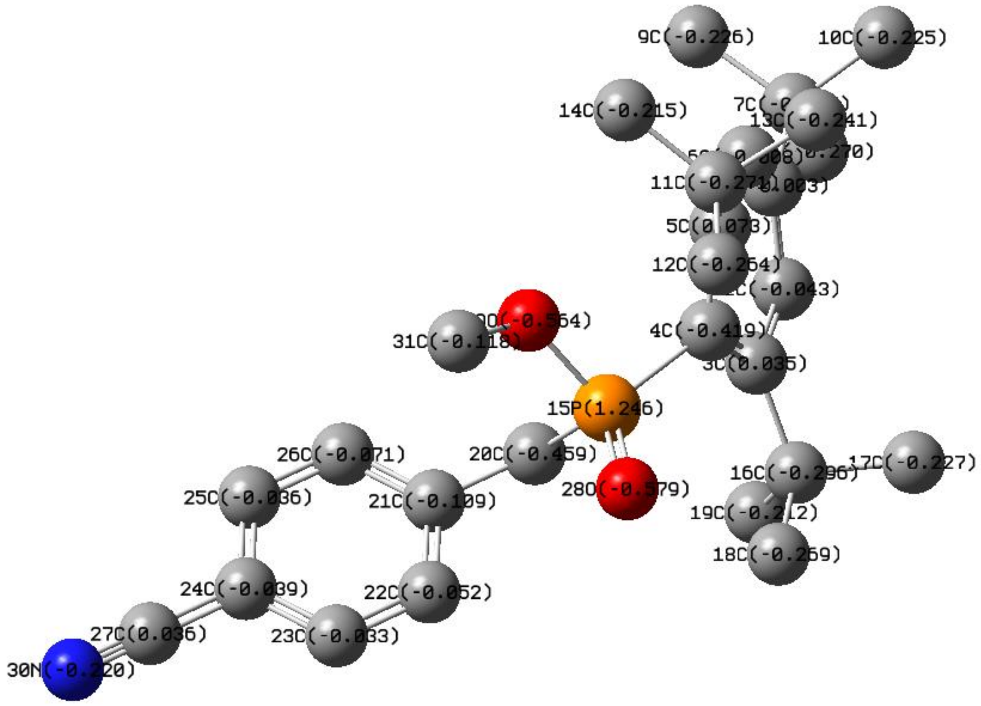


Figure S46: Optimized geometry structure (B3LYP and 6-311G(d,p)) with the corresponding Mulliken charges for each atom. Hydrogen atoms are omitted for clarity.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.272319	-0.423031	-0.888567
2	6	0	2.625251	-1.415054	-0.159981
3	6	0	1.536897	-1.160856	0.685630
4	6	0	1.023423	0.171061	0.727109
5	6	0	1.858008	1.232047	0.251772
6	6	0	2.921107	0.893113	-0.585500
7	6	0	4.386597	-0.716852	-1.906441
8	6	0	4.604430	-2.226504	-2.116647
9	6	0	3.999773	-0.092759	-3.267846
10	6	0	5.718293	-0.099326	-1.419955

11	6	0	1.796551	2.725655	0.699143
12	6	0	0.895907	2.980902	1.925603
13	6	0	3.224904	3.126124	1.170348
14	6	0	1.396667	3.652065	-0.469171
15	15	0	-0.802633	0.428672	0.877130
16	6	0	1.158027	-2.347134	1.633429
17	6	0	2.444683	-2.646340	2.458416
18	6	0	0.069440	-2.059591	2.686263
19	6	0	0.777273	-3.626318	0.853514
20	6	0	-1.518375	-0.911062	-0.192655
21	6	0	-2.990247	-0.722517	-0.462556
22	6	0	-3.932332	-0.828031	0.570281
23	6	0	-5.287025	-0.668836	0.315527
24	6	0	-5.731210	-0.397424	-0.986911
25	6	0	-4.796893	-0.285720	-2.025460
26	6	0	-3.443682	-0.446465	-1.757806
27	6	0	-7.126888	-0.235308	-1.254699
28	8	0	-1.487786	0.576114	2.193788
29	8	0	-1.030809	1.708062	-0.116184
30	7	0	-8.253873	-0.103387	-1.472619
31	6	0	-2.168595	2.578467	0.054088
32	1	0	2.984022	-2.430681	-0.234140
33	1	0	3.510934	1.694458	-1.008979
34	1	0	5.371977	-2.383060	-2.879023
35	1	0	4.946214	-2.722317	-1.203962
36	1	0	3.692482	-2.724330	-2.457472
37	1	0	4.781631	-0.285327	-4.008679
38	1	0	3.867259	0.989016	-3.195695
39	1	0	3.064919	-0.519290	-3.641660
40	1	0	6.012457	-0.516800	-0.453237
41	1	0	6.516595	-0.309366	-2.138201

42	1	0	5.648498	0.984981	-1.309080
43	1	0	1.076828	3.995918	2.289920
44	1	0	-0.165534	2.903605	1.718903
45	1	0	1.129569	2.291194	2.739973
46	1	0	3.199768	4.148443	1.557860
47	1	0	3.964531	3.102282	0.369358
48	1	0	3.572713	2.469615	1.972278
49	1	0	0.419107	3.382445	-0.864219
50	1	0	1.368303	4.692877	-0.131533
51	1	0	2.119638	3.590623	-1.287306
52	1	0	2.243777	-3.456192	3.165599
53	1	0	3.283857	-2.949330	1.831439
54	1	0	2.750209	-1.765551	3.028623
55	1	0	0.061692	-2.885160	3.403154
56	1	0	-0.937997	-1.990105	2.282696
57	1	0	0.261642	-1.139156	3.238006
58	1	0	-0.125270	-3.490908	0.253409
59	1	0	1.572203	-3.951375	0.179652
60	1	0	0.587520	-4.443384	1.555521
61	1	0	-0.951411	-0.909893	-1.124915
62	1	0	-1.348379	-1.868367	0.296815
63	1	0	-3.595023	-1.010145	1.583093
64	1	0	-6.007542	-0.750336	1.119942
65	1	0	-5.136758	-0.077133	-3.032408
66	1	0	-2.727232	-0.358501	-2.567028
67	1	0	-1.843652	3.583154	-0.217486
68	1	0	-2.973525	2.260924	-0.610114
69	1	0	-2.516441	2.565567	1.087883

Crystallographic data

Single crystals were coated with Paratone-N oil, mounted on the loop and frozen in the cold nitrogen stream. The data collections for all crystals were performed at 150(2) K. Reflections were collected on a Bruker APEXII CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction was performed with SAINT.[9] Absorption corrections for the area detector were performed using SADABS (empirical multi-scan method).[10] Structures were determined by direct methods and refined by least-squares methods on F^2 using the SHELX suit of programs.[11] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained in geometrical positions to their parent atoms.

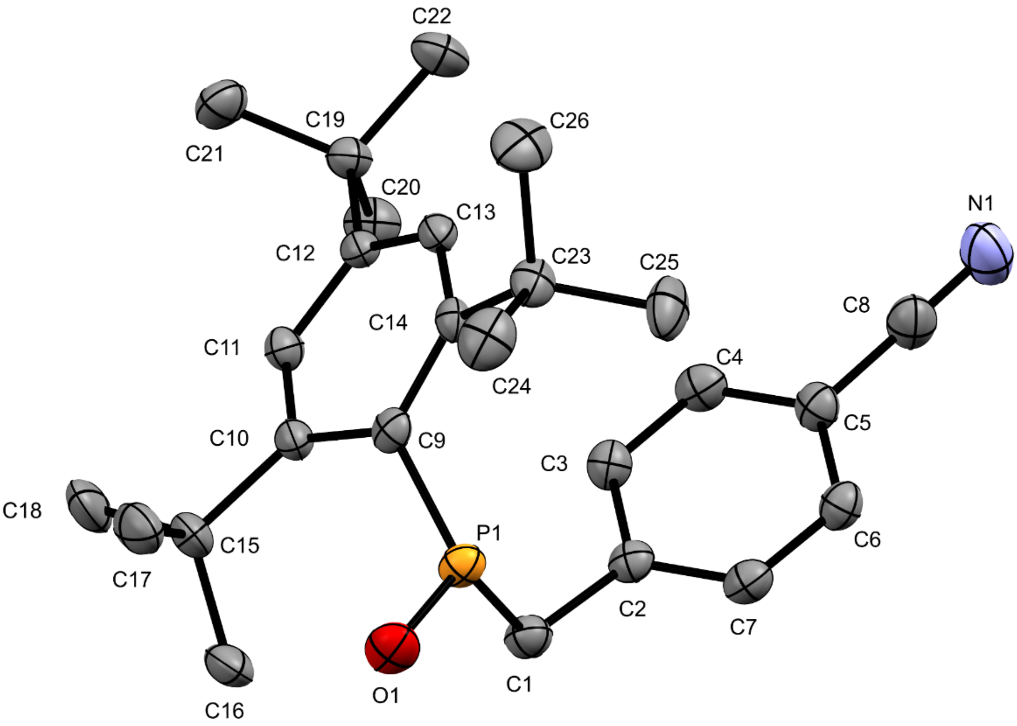


Figure S47: ORTEP plot of phosphine oxide **5** (with R_1 = CN) at 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table S2: Crystal data and structure refinement for compound **5** (CCDC 1832099).

Identification code	CCDC 1832099
Empirical formula	C26 H36 N O P
Formula weight	410.53
Temperature	150(2) K
Wavelength	0.71073 Å

Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.0822(4) Å	α= 106.883(3)°.
	b = 10.8747(4) Å	β= 90.592(3)°.
	c = 12.0033(5) Å	γ = 103.900(2)°.
Volume	1217.90(9) Å^3	
Z	2	
Density (calculated)	1.119 Mg/m^3	
Absorption coefficient	0.129 mm^{-1}	
F(000)	446	
Crystal size	0.63 x 0.40 x 0.12 mm^3	
Theta range for data collection	1.780 to 25.248°.	
Index ranges	-12<=h<=12, -13<=k<=13, -12<=l<=14	
Reflections collected	8831	
Independent reflections	4389 [R(int) = 0.0354]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6590	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4389 / 0 / 275	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1181	
R indices (all data)	R1 = 0.0657, wR2 = 0.1315	
Extinction coefficient	n/a	

Largest diff. peak and hole	0.254 and -0.797 e.Å^{-3}

Table S3: Bond lengths [Å] and angles [°] for CCDC 1832099.

C(1)-C(2)	1.504(3)
C(1)-P(1)	1.835(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(7)	1.391(3)
C(2)-C(3)	1.397(3)
C(3)-C(4)	1.380(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.389(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.401(3)
C(5)-C(8)	1.439(3)
C(6)-C(7)	1.378(3)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-N(1)	1.146(3)
C(9)-C(14)	1.408(3)
C(9)-C(10)	1.434(3)
C(9)-P(1)	1.819(2)
C(9)-H(9)	1.0000
C(10)-C(11)	1.385(3)
C(10)-C(15)	1.557(3)
C(11)-C(12)	1.394(3)

C(11)-H(11)	0.9500
C(12)-C(13)	1.376(3)
C(12)-C(19)	1.538(3)
C(13)-C(14)	1.401(3)
C(13)-H(13)	0.9500
C(14)-C(23)	1.564(3)
C(15)-C(16)	1.532(3)
C(15)-C(18)	1.541(3)
C(15)-C(17)	1.544(3)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(20)	1.531(3)
C(19)-C(22)	1.533(3)
C(19)-C(21)	1.538(3)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(25)	1.538(3)
C(23)-C(24)	1.538(3)
C(23)-C(26)	1.543(3)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
O(1)-P(1)	1.4846(16)
P(1)-H(1)	1.326(19)

C(2)-C(1)-P(1)	109.86(14)
C(2)-C(1)-H(1A)	109.7
P(1)-C(1)-H(1A)	109.7

C(2)-C(1)-H(1B)	109.7
P(1)-C(1)-H(1B)	109.7
H(1A)-C(1)-H(1B)	108.2
C(7)-C(2)-C(3)	119.0(2)
C(7)-C(2)-C(1)	120.66(19)
C(3)-C(2)-C(1)	120.20(19)
C(4)-C(3)-C(2)	120.8(2)
C(4)-C(3)-H(3)	119.6
C(2)-C(3)-H(3)	119.6
C(3)-C(4)-C(5)	119.8(2)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	119.9(2)
C(4)-C(5)-C(8)	120.4(2)
C(6)-C(5)-C(8)	119.7(2)
C(7)-C(6)-C(5)	119.8(2)
C(7)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(6)-C(7)-C(2)	120.7(2)
C(6)-C(7)-H(7)	119.6
C(2)-C(7)-H(7)	119.6
N(1)-C(8)-C(5)	178.8(3)
C(14)-C(9)-C(10)	119.68(18)
C(14)-C(9)-P(1)	118.13(15)

C(10)-C(9)-P(1)	120.19(15)
C(14)-C(9)-H(9)	94.7
C(10)-C(9)-H(9)	94.7
P(1)-C(9)-H(9)	94.7
C(11)-C(10)-C(9)	116.82(18)
C(11)-C(10)-C(15)	119.06(18)
C(9)-C(10)-C(15)	123.63(18)
C(10)-C(11)-C(12)	123.45(19)
C(10)-C(11)-H(11)	118.3
C(12)-C(11)-H(11)	118.3
C(13)-C(12)-C(11)	117.10(19)
C(13)-C(12)-C(19)	123.11(18)
C(11)-C(12)-C(19)	119.67(18)
C(12)-C(13)-C(14)	122.76(19)
C(12)-C(13)-H(13)	118.6
C(14)-C(13)-H(13)	118.6
C(13)-C(14)-C(9)	117.76(18)
C(13)-C(14)-C(23)	116.59(18)
C(9)-C(14)-C(23)	125.55(18)
C(16)-C(15)-C(18)	105.74(19)
C(16)-C(15)-C(17)	109.32(18)
C(18)-C(15)-C(17)	107.3(2)
C(16)-C(15)-C(10)	115.47(18)
C(18)-C(15)-C(10)	110.63(18)

C(17)-C(15)-C(10)	108.10(18)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20)-C(19)-C(22)	108.18(18)
C(20)-C(19)-C(21)	110.28(18)
C(22)-C(19)-C(21)	108.55(18)
C(20)-C(19)-C(12)	108.85(17)
C(22)-C(19)-C(12)	112.30(18)

C(21)-C(19)-C(12)	108.68(18)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(25)-C(23)-C(24)	112.0(2)
C(25)-C(23)-C(26)	106.45(19)
C(24)-C(23)-C(26)	104.63(19)
C(25)-C(23)-C(14)	112.55(17)
C(24)-C(23)-C(14)	111.95(18)

C(26)-C(23)-C(14)	108.78(18)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(23)-C(26)-H(26A)	109.5
C(23)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
O(1)-P(1)-C(9)	120.02(9)
O(1)-P(1)-C(1)	114.98(10)
C(9)-P(1)-C(1)	103.38(9)
O(1)-P(1)-H(1)	114.6(8)
C(9)-P(1)-H(1)	102.4(8)

C(1)-P(1)-H(1)	98.5(8)

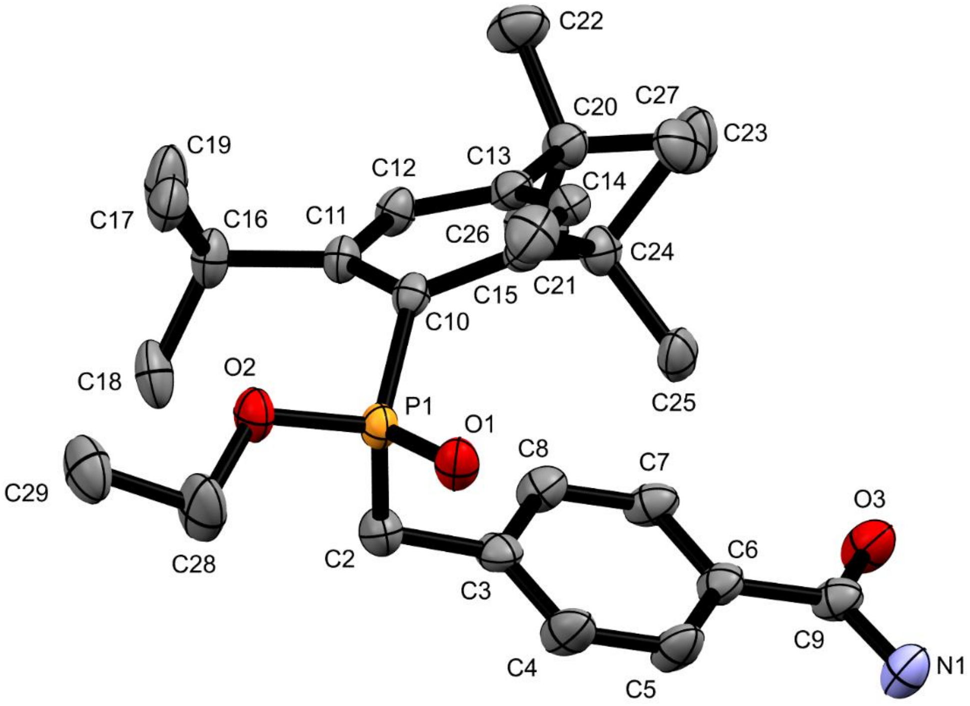


Figure S48: ORTEP plot of phosphinate **9** (with R = Et and R_1 = C(O)NH_2) at 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table S4: Crystal data and structure refinement for phosphinate **9** (CCDC 1832100).

Identification code	CCDC 1832100	
Empirical formula	C57 H85 Cl3 N2 O6 P2	
Formula weight	1062.55	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.7916(10) Å	α= 90.205(2)°.
	b = 17.0045(17) Å	β= 96.705(2)°.
	c = 17.0443(17) Å	γ = 106.832(2)°.
Volume	2971.0(5) Å^3	

Z	2
Density (calculated)	1.188 Mg/m^3
Absorption coefficient	0.256 mm^{-1}
F(000)	1140
Crystal size	0.10 x 0.04 x 0.02 mm^3
Theta range for data collection	1.204 to 25.250°.
Index ranges	-12<=h<=12, -20<=k<=20, -20<=l<=20
Reflections collected	40210
Independent reflections	10744 [R(int) = 0.0577]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7084
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10744 / 18 / 651
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0827, wR2 = 0.2224
R indices (all data)	R1 = 0.1232, wR2 = 0.2608
Extinction coefficient	n/a
Largest diff. peak and hole	1.808 and -0.819 e.Å^{-3}

Table S5: Bond lengths [Å] and angles [°] for CCDC 1832100.

P(1)-O(1)	1.478(3)
P(1)-O(2)	1.578(3)
P(1)-C(2)	1.810(5)
P(1)-C(10)	1.827(4)
P(2)-O(4)	1.476(3)
P(2)-O(5)	1.579(3)
P(2)-C(30)	1.800(5)
P(2)-C(38)	1.821(4)
O(2)-C(28)	1.462(6)
O(3)-C(9)	1.236(5)
O(5)-C(56)	1.428(7)
O(6)-C(37)	1.233(5)
N(1)-C(9)	1.332(6)
N(1)-H(1A)	0.8800
N(1)-H(1B)	0.8800
N(2)-C(37)	1.329(5)
N(2)-H(2A)	0.8800
N(2)-H(2B)	0.8800
C(2)-C(3)	1.506(6)
C(2)-H(2C)	0.9900
C(2)-H(2D)	0.9900
C(3)-C(8)	1.385(6)
C(3)-C(4)	1.388(6)

C(4)-C(5)	1.375(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.392(6)
C(5)-H(5)	0.9500
C(6)-C(7)	1.387(6)
C(6)-C(9)	1.494(6)
C(7)-C(8)	1.381(6)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(10)-C(15)	1.425(6)
C(10)-C(11)	1.452(5)
C(11)-C(12)	1.382(6)
C(11)-C(16)	1.565(6)
C(12)-C(13)	1.394(6)
C(12)-H(12)	0.9500
C(13)-C(14)	1.375(6)
C(13)-C(20)	1.529(6)
C(14)-C(15)	1.390(6)
C(14)-H(14)	0.9500
C(15)-C(24)	1.553(5)
C(16)-C(19)	1.539(6)
C(16)-C(17)	1.541(6)
C(16)-C(18)	1.544(7)
C(17)-H(17A)	0.9800

C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(22)	1.527(6)
C(20)-C(21)	1.529(7)
C(20)-C(23)	1.532(6)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(26)	1.534(6)
C(24)-C(25)	1.539(6)
C(24)-C(27)	1.555(6)
C(25)-H(25A)	0.9800

C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(29)	1.494(7)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-C(31)	1.516(6)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-C(36)	1.372(7)
C(31)-C(32)	1.379(7)
C(32)-C(33)	1.368(7)
C(32)-H(32)	0.9500
C(33)-C(34)	1.384(6)
C(33)-H(33)	0.9500
C(34)-C(35)	1.380(6)

C(34)-C(37)	1.495(6)
C(35)-C(36)	1.382(7)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(38)-C(43)	1.425(6)
C(38)-C(39)	1.442(6)
C(39)-C(40)	1.386(6)
C(39)-C(44)	1.574(6)
C(40)-C(41)	1.388(6)
C(40)-H(40)	0.9500
C(41)-C(42)	1.381(6)
C(41)-C(48)	1.522(6)
C(42)-C(43)	1.390(6)
C(42)-H(42)	0.9500
C(43)-C(52)	1.548(6)
C(44)-C(47)	1.536(7)
C(44)-C(45)	1.545(7)
C(44)-C(46)	1.552(7)
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800

C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-C(3A)	1.383(10)
C(48)-C(1A)	1.451(11)
C(48)-C(2A)	1.548(14)
C(52)-C(54)	1.531(7)
C(52)-C(53)	1.544(8)
C(52)-C(55)	1.545(7)
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(56)-C(57)	1.402(10)
C(56)-H(56A)	0.9900
C(56)-H(56B)	0.9900
C(57)-H(57A)	0.9800
C(57)-H(57B)	0.9800
C(57)-H(57C)	0.9800

C(1S)-Cl(3)	1.702(8)
C(1S)-Cl(1)	1.714(9)
C(1S)-Cl(2)	1.731(11)
C(1S)-H(1S)	1.0000
C(1A)-H(1A1)	0.9800
C(1A)-H(1A2)	0.9800
C(1A)-H(1A3)	0.9800
C(2A)-H(2A1)	0.9800
C(2A)-H(2A2)	0.9800
C(2A)-H(2A3)	0.9800
C(3A)-H(3A1)	0.9800
C(3A)-H(3A2)	0.9800
C(3A)-H(3A3)	0.9800

O(1)-P(1)-O(2)	112.20(17)
O(1)-P(1)-C(2)	107.8(2)
O(2)-P(1)-C(2)	107.81(19)
O(1)-P(1)-C(10)	118.43(18)
O(2)-P(1)-C(10)	106.35(17)
C(2)-P(1)-C(10)	103.5(2)
O(4)-P(2)-O(5)	112.39(18)
O(4)-P(2)-C(30)	107.3(2)
O(5)-P(2)-C(30)	107.3(2)
O(4)-P(2)-C(38)	118.0(2)

O(5)-P(2)-C(38)	106.55(18)
C(30)-P(2)-C(38)	104.6(2)
C(28)-O(2)-P(1)	120.1(3)
C(56)-O(5)-P(2)	122.5(3)
C(9)-N(1)-H(1A)	120.0
C(9)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0
C(37)-N(2)-H(2A)	120.0
C(37)-N(2)-H(2B)	120.0
H(2A)-N(2)-H(2B)	120.0
C(3)-C(2)-P(1)	111.4(3)
C(3)-C(2)-H(2C)	109.4
P(1)-C(2)-H(2C)	109.4
C(3)-C(2)-H(2D)	109.4
P(1)-C(2)-H(2D)	109.4
H(2C)-C(2)-H(2D)	108.0
C(8)-C(3)-C(4)	117.9(4)
C(8)-C(3)-C(2)	120.6(4)
C(4)-C(3)-C(2)	121.5(4)
C(5)-C(4)-C(3)	121.6(4)
C(5)-C(4)-H(4)	119.2
C(3)-C(4)-H(4)	119.2
C(4)-C(5)-C(6)	120.3(4)
C(4)-C(5)-H(5)	119.8

C(6)-C(5)-H(5)	119.8
C(7)-C(6)-C(5)	118.4(4)
C(7)-C(6)-C(9)	118.5(4)
C(5)-C(6)-C(9)	123.1(4)
C(8)-C(7)-C(6)	120.8(4)
C(8)-C(7)-H(7)	119.6
C(6)-C(7)-H(7)	119.6
C(7)-C(8)-C(3)	121.0(4)
C(7)-C(8)-H(8)	119.5
C(3)-C(8)-H(8)	119.5
O(3)-C(9)-N(1)	121.2(4)
O(3)-C(9)-C(6)	120.5(4)
N(1)-C(9)-C(6)	118.3(4)
C(15)-C(10)-C(11)	117.4(3)
C(15)-C(10)-P(1)	118.3(3)
C(11)-C(10)-P(1)	120.3(3)
C(12)-C(11)-C(10)	117.7(4)
C(12)-C(11)-C(16)	116.9(4)
C(10)-C(11)-C(16)	125.0(4)
C(11)-C(12)-C(13)	123.8(4)
C(11)-C(12)-H(12)	118.1
C(13)-C(12)-H(12)	118.1
C(14)-C(13)-C(12)	116.0(4)
C(14)-C(13)-C(20)	123.3(4)

C(12)-C(13)-C(20)	120.5(4)
C(13)-C(14)-C(15)	124.1(4)
C(13)-C(14)-H(14)	118.0
C(15)-C(14)-H(14)	118.0
C(14)-C(15)-C(10)	118.2(4)
C(14)-C(15)-C(24)	115.6(4)
C(10)-C(15)-C(24)	126.2(4)
C(19)-C(16)-C(17)	105.3(4)
C(19)-C(16)-C(18)	105.0(4)
C(17)-C(16)-C(18)	111.4(4)
C(19)-C(16)-C(11)	110.6(4)
C(17)-C(16)-C(11)	109.0(4)
C(18)-C(16)-C(11)	115.1(4)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5

H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(22)-C(20)-C(21)	109.5(4)
C(22)-C(20)-C(13)	108.9(3)
C(21)-C(20)-C(13)	108.6(4)
C(22)-C(20)-C(23)	109.6(4)
C(21)-C(20)-C(23)	108.5(4)
C(13)-C(20)-C(23)	111.7(4)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5

H(22B)-C(22)-H(22C)	109.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(26)-C(24)-C(25)	113.4(4)
C(26)-C(24)-C(15)	111.8(3)
C(25)-C(24)-C(15)	111.1(3)
C(26)-C(24)-C(27)	104.5(4)
C(25)-C(24)-C(27)	105.9(4)
C(15)-C(24)-C(27)	109.6(4)
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5

H(26B)-C(26)-H(26C)	109.5
C(24)-C(27)-H(27A)	109.5
C(24)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(24)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
O(2)-C(28)-C(29)	107.8(4)
O(2)-C(28)-H(28A)	110.2
C(29)-C(28)-H(28A)	110.2
O(2)-C(28)-H(28B)	110.2
C(29)-C(28)-H(28B)	110.2
H(28A)-C(28)-H(28B)	108.5
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(31)-C(30)-P(2)	113.2(3)
C(31)-C(30)-H(30A)	108.9
P(2)-C(30)-H(30A)	108.9
C(31)-C(30)-H(30B)	108.9
P(2)-C(30)-H(30B)	108.9

H(30A)-C(30)-H(30B)	107.8
C(36)-C(31)-C(32)	117.8(4)
C(36)-C(31)-C(30)	121.8(4)
C(32)-C(31)-C(30)	120.4(4)
C(33)-C(32)-C(31)	121.2(4)
C(33)-C(32)-H(32)	119.4
C(31)-C(32)-H(32)	119.4
C(32)-C(33)-C(34)	121.2(4)
C(32)-C(33)-H(33)	119.4
C(34)-C(33)-H(33)	119.4
C(35)-C(34)-C(33)	117.7(4)
C(35)-C(34)-C(37)	123.9(4)
C(33)-C(34)-C(37)	118.4(4)
C(34)-C(35)-C(36)	120.7(4)
C(34)-C(35)-H(35)	119.7
C(36)-C(35)-H(35)	119.7
C(31)-C(36)-C(35)	121.4(4)
C(31)-C(36)-H(36)	119.3
C(35)-C(36)-H(36)	119.3
O(6)-C(37)-N(2)	121.6(4)
O(6)-C(37)-C(34)	119.8(4)
N(2)-C(37)-C(34)	118.7(4)
C(43)-C(38)-C(39)	117.8(4)
C(43)-C(38)-P(2)	117.8(3)

C(39)-C(38)-P(2)	120.8(3)
C(40)-C(39)-C(38)	117.5(4)
C(40)-C(39)-C(44)	116.6(4)
C(38)-C(39)-C(44)	125.1(4)
C(39)-C(40)-C(41)	124.1(4)
C(39)-C(40)-H(40)	118.0
C(41)-C(40)-H(40)	118.0
C(42)-C(41)-C(40)	115.8(4)
C(42)-C(41)-C(48)	121.3(4)
C(40)-C(41)-C(48)	122.7(4)
C(41)-C(42)-C(43)	124.0(4)
C(41)-C(42)-H(42)	118.0
C(43)-C(42)-H(42)	118.0
C(42)-C(43)-C(38)	117.9(4)
C(42)-C(43)-C(52)	115.7(4)
C(38)-C(43)-C(52)	126.3(4)
C(47)-C(44)-C(45)	110.2(4)
C(47)-C(44)-C(46)	105.3(4)
C(45)-C(44)-C(46)	105.2(4)
C(47)-C(44)-C(39)	116.6(4)
C(45)-C(44)-C(39)	108.2(4)
C(46)-C(44)-C(39)	110.8(4)
C(44)-C(45)-H(45A)	109.5
C(44)-C(45)-H(45B)	109.5

H(45A)-C(45)-H(45B)	109.5
C(44)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(44)-C(46)-H(46A)	109.5
C(44)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(44)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(44)-C(47)-H(47A)	109.5
C(44)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(44)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(3A)-C(48)-C(1A)	124.1(7)
C(3A)-C(48)-C(41)	114.8(5)
C(1A)-C(48)-C(41)	112.4(5)
C(3A)-C(48)-C(2A)	96.4(9)
C(1A)-C(48)-C(2A)	97.8(9)
C(41)-C(48)-C(2A)	106.0(6)
C(54)-C(52)-C(53)	106.9(4)
C(54)-C(52)-C(55)	112.5(4)

C(53)-C(52)-C(55)	104.3(4)
C(54)-C(52)-C(43)	111.8(4)
C(53)-C(52)-C(43)	108.8(4)
C(55)-C(52)-C(43)	112.0(4)
C(52)-C(53)-H(53A)	109.5
C(52)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53B)	109.5
C(52)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
C(52)-C(54)-H(54A)	109.5
C(52)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
C(52)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(52)-C(55)-H(55A)	109.5
C(52)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(52)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(57)-C(56)-O(5)	109.5(6)
C(57)-C(56)-H(56A)	109.8

O(5)-C(56)-H(56A)	109.8
C(57)-C(56)-H(56B)	109.8
O(5)-C(56)-H(56B)	109.8
H(56A)-C(56)-H(56B)	108.2
C(56)-C(57)-H(57A)	109.5
C(56)-C(57)-H(57B)	109.5
H(57A)-C(57)-H(57B)	109.5
C(56)-C(57)-H(57C)	109.5
H(57A)-C(57)-H(57C)	109.5
H(57B)-C(57)-H(57C)	109.5
Cl(3)-C(1S)-Cl(1)	114.5(6)
Cl(3)-C(1S)-Cl(2)	108.4(5)
Cl(1)-C(1S)-Cl(2)	109.7(5)
Cl(3)-C(1S)-H(1S)	108.0
Cl(1)-C(1S)-H(1S)	108.0
Cl(2)-C(1S)-H(1S)	108.0
C(48)-C(1A)-H(1A1)	109.5
C(48)-C(1A)-H(1A2)	109.5
H(1A1)-C(1A)-H(1A2)	109.5
C(48)-C(1A)-H(1A3)	109.5
H(1A1)-C(1A)-H(1A3)	109.5
H(1A2)-C(1A)-H(1A3)	109.5
C(48)-C(2A)-H(2A1)	109.5
C(48)-C(2A)-H(2A2)	109.5

H(2A1)-C(2A)-H(2A2)	109.5
C(48)-C(2A)-H(2A3)	109.5
H(2A1)-C(2A)-H(2A3)	109.5
H(2A2)-C(2A)-H(2A3)	109.5
C(48)-C(3A)-H(3A1)	109.5
C(48)-C(3A)-H(3A2)	109.5
H(3A1)-C(3A)-H(3A2)	109.5
C(48)-C(3A)-H(3A3)	109.5
H(3A1)-C(3A)-H(3A3)	109.5
H(3A2)-C(3A)-H(3A3)	109.5

References

1 K. Esfandiarfard, A. I. Arkhypchuk, A. Orthaber and S. Ott, *Dalton Trans.*, 2016, **45**, 2201.

2 A. Termaten, M. van der Sluis and F. Bickelhaupt, *Eur. J. Org. Chem.*, 2003, **2003**, 2049.

3 S. Shah and J. D. Protasiewicz, *Chem. Comm.*, 1998, **0**, 1585.

4 H. A. Elazab, A. R. Siamaki, S. Moussa, B. F. Gupton and M. S. El-Shall, *Appl. Cat. A: Gen.*, 2015, **491**, 58.

5 Y.-C. Duan, Y.-Y. Guan, X.-Y. Zhai, L.-N. Ding, W.-P. Qin, D.-D. Shen, X.-Q. Liu, X.-D. Sun, Y.-C. Zheng and H.-M. Liu, *Eur. J. Med. Chem.*, 2017, **126**, 246.

6 T. Luo, R. Zhang, W. Zhang, X. Shen, T. Umemoto and J. Hu, *Org. Lett.*, 2014, **16**, 888.

7 A. Skhiri, R. B. Salem, J.-F. Soulé and H. Doucet, *Synthesis*, 2016, **48**, 3097.

8 Z. Fang, C. Cao and G. Chen, *J. Phys. Org. Chem.*, 2012, **25**, 1343.

9 SAINT, Bruker AXS Inc. Madison, WI, 2007.

10 SADABS, Bruker AXS Inc. Madison, WI, 2001.

11 G. M. Sheldrick, short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, **64**, 112.