# Synthesis of new chelating phosphines containing an aryl chloride group

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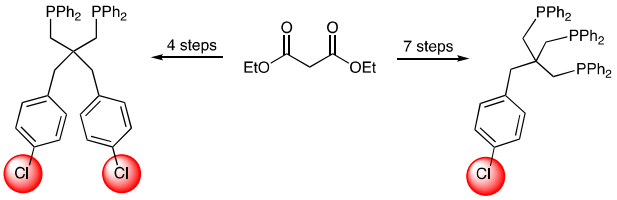


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**Abstract** The syntheses of bidentate and tripodal phosphine ligands containing aryl chlorides were achieved in 4 and 6 steps respectively, starting from diethylmalonate.

**Key words** Phosphines, aryl chloride, chelating ligands

Phosphines represent the most widely used ligand class in homogeneous catalysis. Their ability to bind strongly to metals and ease for tuning both steric and electronic properties has led to applications in metal-catalyzed transformations.[2] They have also emerged as efficient organocatalysts, further highlighting their importance in synthetic methodology.[3] Monodentate phosphines are synthetically accessible and versatile.[4] However, loss of these ligands can lead to catalyst decomposition, thus lowering yields and selectivity. One of the main strategies that has been employed to address these limitations has been to use chelating phosphine ligands.[5] In the context of converting natural abundant feedstocks to sustainable alternative fuels, multidentate phosphines have played a major role in the fields of Hydrogen Evolution Reactions (HER),[6] $CO_2$ Reduction Reactions ($CO_2$RR)[7] and Nitrogen Reduction Reactions (NRR).[8]

In recent years, catalysts immobilized on materials have attracted increasing interest since they offer enhanced activity, reduced loading, and convenient product separation.[9] The synthesis and stability of such heterogenized systems is dependent on bifunctional ligands that contain one site for metal binding and another site for surface attachment. For the latter, C($sp^2$)-halide moieties are among the most versatile functional group as they can be converted to a large variety of other functionalities that can be used for surface functionalization (*e.g.* organolithium[10], organomagnesium,[11] alkene,[12] alkyne,[11a, 13] trialkoxysilane,[14] phosphonic acid,[15] and silatrane[16]).

The synthesis of bifunctional phosphines in the context of NRR has been already investigated by several groups.[17] Notably, Tuczek and coworkers have developed the synthesis of a tetherable tripodal phosphine containing a triazatriangulene (TATA) group that can be deposited on a Au(111) surface.[17c]

Herein we describe the synthesis of both bidentate and tripodal phosphine ligands from diethyl malonate. The bidentate phosphine **4** possesses two C($sp^2$)–Cl functional groups in its backbone structure and the tripodal phosphine **10** possesses one (Figure 1). Because of the straightforward synthesis from inexpensive materials, we expect that the method disclosed here will be useful for various attachment protocols.

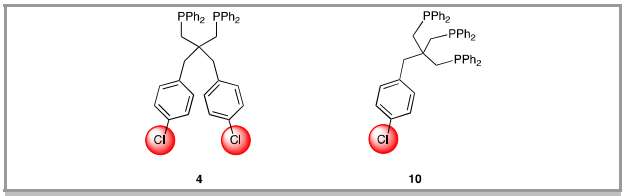
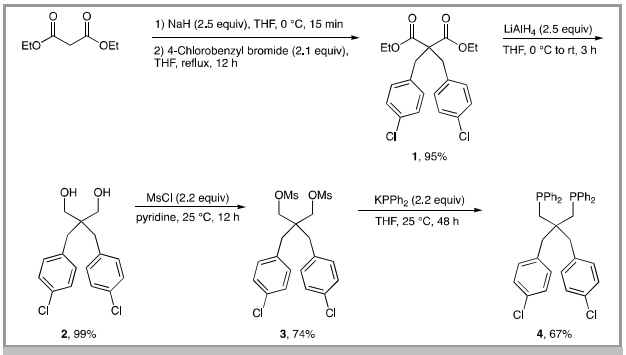



**Figure 1** Structures of the bidentate phosphine **4** and tripodal phosphine **10**

The synthesis of the bidentate phosphine (Scheme 1) started from diethyl malonate, which was efficiently bis-benzylated using 4-chlorobenzyl bromide to give **1** in 95% yield. Compound **1** was then reduced using 2 equivalents of $LiAlH_4$ at room temperature for 3 hours to give diol **2** in 99% yield. Diol **2** was then treated with 2 equivalents of MsCl in pyridine at room temperature for 12 hours to afford the bis-mesylated product **3** in 74% yield. Last, the phosphines were installed by substitution of the mesylate groups using in situ generated $KPPh_2$ from the deprotonation of $HPP_2$ by KOtBu in THF. The substitution was completed after 24 hours at room temperature to afford diphosphine **4** in 67% yield. During the course of our investigation, tosylate was also tested as the leaving group.

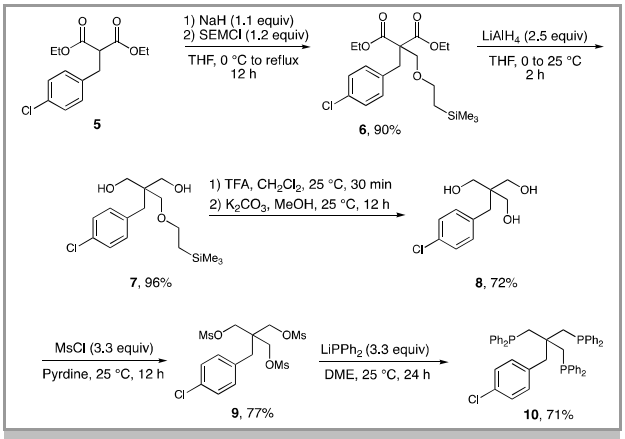
However, in this case the substitution reaction with $LiPPh_2$ or $KPPh_2$ did not proceed to completion at room temperature.




**Scheme 1** Synthesis of the bidentate phosphine

The synthesis of the brominated analogue was also investigated. Unfortunately, we observed that $KPPh_2$ or $LiPPh_2$ underwent competitive substitution reaction on C($sp^2$)-Br,[18] and therefore the bromide variant was not accessible through this route.

The synthesis of the tripodal phosphine **10** was also achieved starting from diethyl malonate (Scheme 2).




**Scheme 2** Synthesis of the tripodal phosphine

Diethyl 2-(4-chlorobenzyl)malonate **5** was prepared by monobenzylation of diethylmalonate using 4-chlorobenzyl bromide following a literature precedent.[19] The monobenzylated compound **5** was then deprotonated with NaH at 0 °C in THF and alkylated using 2-(trimethylsilyl)ethoxymethyl chloride (SEM-Cl) at reflux for 12 hours to afford **6** in 90% yield. The isolated compound **6** was then reduced using 2.5 equivalents of $LiAlH_4$ at room temperature to give diol **7** in 96% yield. The deprotection of the SEM group was achieved using a 2-step procedure. First, diol **7** was treated with trifluoroacetic acid in $CH_2Cl_2$ at room temperature for 5 min.[20] During that step, alongside the SEM group deprotection, we observed the formation of trifluoroacetylated triol **8**.[21] Therefore, after evaporating TFA and $CH_2Cl_2$, the crude mixture was then stirred with $K_2CO_3$ in methanol for 12 hours at room temperature to complete the formation of triol **8** in 72% yield.[22] Triol **8** was treated with 3.3 equivalents of MsCl in pyridine at room temperature for 12 hours to provide the triply mesylated intermediate **9** in 77% yield. Finally, the phosphines were installed by substitution of the OMs groups using $LiPPh_2$ (generated *in situ* from the deprotonation of $HPP_2$ with n-BuLi in DME). The substitution reaction was completed after 24 hours at room temperature and triphosphine **10** was obtained in 71% yield. Analogously to the synthesis of diphosphine **4**, we were not able to access the brominated analogue of ligand **10** due to competitive substitution of the C–Br by $KPPh_2$ or $LiPPh_2$ at room temperature.

In conclusion, we developed an efficient synthetic route that led to a new bidentate phosphine and a new tripodal phosphine. The bidentate phosphine was obtained in 4 steps from diethyl malonate with an overall yield of 47%. The tripodal phosphine was obtained in 6 steps from diethyl 2-(4-chlorobenzyl)malonate with an overall yield of 34%.

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All reagents purchased from commercial sources were degassed under dynamic vacuum at -78 °C, transferred into a $N_2$-filled glovebox and stored over 3 Å molecular sieves. Diethyl malonate (>98%), sodium hydride (60% dispersion in mineral oil), lithium aluminium hydride (95%), trifluoroacetic acid (99%), pyridine (99.8%), *n*-butyllithium (2.5 M in hexane) and anhydrous dimethoxyethane (99.5%) were obtained from Sigma-Aldrich. Potassium carbonate (99%), methanesulfonyl chloride (98%), diphenylphosphine (99%) and potassium tert-butoxide (97%) were obtained from Alfa Aesar. 4-Chlorobenzyl bromide (>98%) and (trimethylsilyl)ethoxymethyl chloride (>95%) were purchased from TCI. Methanol (electronic grade), ethyl acetate (HPLC grade), hexanes (HPLC grade), petroleum ether (certified ACS), and isopropyl alcohol (HPLC grade) were obtained from Fisher Scientific. Glassware was dried at 150 °C overnight. Tetrahydrofuran (THF) and dicholoromethane (DCM) were obtained from J.T. Baker, dried via passage through a column of activated alumina on an Inert Technologies PureSolv MD7 solvent purification system and subsequently stored under nitrogen. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. **Warning!** Lithium aluminum hydride is pyrophoric, and should be handled with caution.

NMR spectra were recorded on Agilent NMR spectrometers operating at 400.13 MHz. All resonances in the $^1$H NMR spectra are referenced to chloroform-$d_1$ (δ 7.26 ppm) or DCM-$d_2$ (δ 5.32 ppm) unless otherwise noted. Resonances were singlets unless otherwise noted. IR data were recorded on a Shimadzu FTIR spectrophotometer (IRTracer-100) with diamond ATR. High resolution mass spectrometry (HRMS) was obtained on a Shimadzu LCMS-9030 Quadrupole Time-of-Flight High-Performance Liquid Chromatograph Mass Spectrometer.

**Procedures**

Diethyl 2,2-bis(4-chlorobenzyl)malonate (1):

A dried 500 mL 2 neck round-bottom flask under $N_2$ equipped with a reflux condenser and a stir bar was charged with diethylmalonate (3.20 g, 20.0 mmol) and THF (100 mL). The mixture was cooled to 0°C and NaH (2.00 g, 50 mmol) was added in 5 portions over 5 min. After 30 min at 0°C, 4-chlorobenzyl bromide (8.40 g, 42 mmol) was added and the reaction was heated to reflux for 12 hours. The reaction mixture was then cooled to room temperature and quenched with 25 mL of saturated aqueous $NH_4Cl$. 50 mL of $Et_2O$ was added. The phases were separated and the aqueous phase was extracted with 2x50 mL of $Et_2O$. The combined organic phase was dried with $MgSO_4$ and solvents were evaporated under reduced pressure. The crude solid was washed with 15 mL of cold EtOAc/hexane (1:10) mixture and diethyl 2,2-bis(4-chlorobenzyl)malonate (**1**) was obtained as a white solid (7.78 g, 19.0 mmol, 95% yield).

FT-IR (solid, $cm^{-1}$): 2993 (w), 2976 (w), 2950 (w), 1731 (s), 1495 (m), 1305 (m), 1175 (s), 1042 (m), 827 (m), 809 (s), 532 (s).

$^1$H NMR ($CDCl_3$, 400 MHz): δ = 7.25 – 7.20 (m, 4H), 7.12 – 7.06 (m, 4H), 4.10 (q, *J* = 7.1 Hz, 4H), 3.16 (s, 4H), 1.15 (t, *J* = 7.1 Hz, 6H) ppm.

$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz): δ = 170.6, 134.8, 132.97, 131.5, 128.4, 61.5, 60.1, 39.0, 13.9 ppm.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{23}Cl_2O_4$: 409.0973; found: 409.0947.

2,2-Bis(4-chlorobenzyl)propane-1,3-diol (**2**):

A dried 250 mL Schlenk flask under $N_2$ was charged with **1** (5.00 g, 12.2 mmol) and THF (100 mL) with stirring, and cooled to 0 °C. $LiAlH_4$ (1.16 g, 30.5 mmol) was added in 5 portions over 10 min. The reaction mixture was then stirred for 4 hours at room temperature. $Et_2O$ (50 mL) was added and mixture was cooled to 0 °C. 1.2 mL of $H_2O$ was added dropwise, followed by 15% NaOH solution (1.2 mL). The mixture was stirred for 15 min at room temperature and 3.6 mL of $H_2O$ was added. About 4 g of $MgSO_4$ was added and the mixture was filtered through filter paper and the collected solid was washed with 20 mL of $Et_2O$. Solvents were removed under reduced pressure to give the product as a colorless oil (3.93 g, 12.1 mmol, 99% yield).

FT-IR (neat, $cm^{-1}$): 3375 (s), 3040 (w), 2945 (w), 2890 (w), 1495 (s), 1173 (m), 1095 (m), 1019 (s), 957 (m), 764 (m), 519 (m).

$^1H$ NMR ($CDCl_3$, 400 MHz): 7.28 – 7.23 (m, 4H), 7.18 – 7.13 (m, 4H), 3.47 (d, *J* = 3.5 Hz, 4H), 2.70 (s, 4H), 1.91 (s, 2H) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 136.1, 132.4, 132.0, 128.5, 66.4, 43.7, 38.5 ppm.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{19}Cl_2O_2$: 325.0762; found: 325.0745.

2,2-Bis(4-chlorobenzyl)propane-1,3-diyl bis(methanesulfonate) (**3**):

A dried 100 mL round-bottom flask under $N_2$ equipped with a stir bar was charged with **2** (3.93 g, 12.1 mmol) and pyridine (30 mL). The mixture was cooled to 0 °C and MsCl (2.1 mL, 26.8 mmol) was added dropwise. The reaction was then stirred for 12 hours at room temperature. The reaction mixture was quenched with $H_2O$ (20 mL) and $CH_2Cl_2$ (100 mL) was added. The phases were separated and the organic phase was then washed with 20 mL of 0.5 M aqueous $H_2SO_4$, followed by 20 mL of saturated $NaHCO_3$ solution and 20 mL of $H_2O$. The organic phase was dried over $Na_2SO_4$ and evaporated under reduced pressure. 10 mL of EtOAc/hexane (1:2) was added to the crude and the mixture was stored at -30 °C overnight. The product was collected by filtration and obtained as a white crystalline powder (4.31 g, 8.95 mmol, 74%).

FT-IR (neat, $cm^{-1}$): 3024 (w), 2945 (w), 2904 (w), 1495 (m), 1360 (s), 1118 (s), 977 (s), 952 (s), 828 (s), 573 (w) 526 (m).

$^1H$ NMR ($CDCl_3$, 400 MHz): 7.32 – 7.27 (m, 4H), 7.16 – 7.11 (m, 4H), 3.95 (s, 4H), 3.02 (s, 6H), 2.77 (s, 4H) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 133.4, 133.3, 132.0, 128.9, 69.2, 42.2, 37.5, 37.5 ppm.

HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{22}Cl_2NaO_6S_2$: 503.0133; found: 503.0102.

2,2-Bis(4-chlorobenzyl)propane-1,3-diyl bis(diphenylphosphane) (**4**):

Inside a glovebox, a Schlenk flask equipped with a stir bar was charged with $HPPh_2$ (1.23 g, 6.6 mmol) and THF (20 mL). The mixture was cooled to 0 °C and KOtBu (0.842 mg, 7.5 mmol) was added in 5 portions over 5 min. Then, the mixture was allowed to warm to room temperature and **3** (1.44 g, 3.0 mmol) was added in 5 portions over 5 min. After 48 h, the solvent was removed under reduced pressure. The mixture was dissolved in toluene (3 mL) and then placed in the freezer (-30 °C) for 12 hours. The solution was decantated from the solid and the solvent was evaporated under reduced pressure. The crude oil was redissolved in toluene (2 mL), layered with MeOH and stored at -35 °C for 24 hours. The product was collected by filtration and was obtained as white crystals (1.33 g, 2.01 mmol, 67%).

FT-IR (solid, $cm^{-1}$): 3063 (w), 3036 (w), 2922 (w), 1494 (m), 1337 (m), 1437 (w), 1073 (m), 1003 (m), 739 (m), 695 (s).

$^1H$ NMR ($CD_2Cl_2$, 400 MHz): 7.37 – 7.24 (m, 20H), 7.20 – 7.12 (m, 8H), 2.93 (s, 4H), 2.04 (d, *J* = 3.0 Hz, 4H) ppm.

$^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 101 MHz): δ = 140.1 (d, *J* = 12.2 Hz), 137.1, 133.3 (d, *J* = 20.0 Hz), 133.1 (d, J = 2.5 Hz), 132.4, 129.0, 128.9 (d, *J* = 7.2 Hz), 128.3, 44.1 (t, *J* = 7.4 Hz), 43.8 (t, *J* = 13.4 Hz), 37.0 (dd, *J* = 15.7, 7.3 Hz) ppm.

$^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 162 MHz): δ -27.77 ppm.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{41}H_{37}Cl_2NaP_2$: 661.1748; found: 661.1729.

Diethyl 2-(4-chlorobenzyl)-2-((2-(trimethylsilyl)ethoxy)methyl)-malonate (**6**):

A dried 500 mL two-neck round bottom flask under $N_2$ was fitted with a reflux condenser and a stir bar, and then charged with diethyl 2-(4-chlorobenzyl)malonate (7.77 g, 27.3 mmol) and THF (300 mL). The mixture was cooled to 0° C and NaH (1.31 g, 32.7 mmol) was added in 5 portions over 5 min and stirred for 30 min. 2-(trimethylsilyl)ethoxymethyl chloride (5.00 g, 30 mmol) was added dropwise at 0 °C, and the reaction mixture was heated to reflux for 12 hours. The reaction was cooled to room temperature and quenched with saturated aqueous $NH_4Cl$ (25 mL). $Et_2O$ (50 mL) was added. The phases were separated and the aqueous phase was extracted with $Et_2O$ (2 x 50 mL). The combined organic phase was dried with $MgSO_4$ and solvents were removed under reduced pressure. The crude oil was purified by flash column chromatography ($SiO_2$, 5% EtOAc in hexanes, $R_f$ = 0.58). The product was obtained as a colorless oil (10.20 g, 24.57 mmol, 90% yield).

FT-IR (neat, $cm^{-1}$): 2994 (w), 2949 (w), 1735 (s), 1498 (m), 1274 (m), 1151 (m), 1096 (m), 1035 (m), 861 (m), 532 (m).

$^1H$ NMR ($CDCl_3$, 400 MHz): 7.25 – 7.19 (m, 2H), 7.07 – 7.02 (m, 2H), 4.23 – 4.13 (m, 4H), 3.60 (s, 2H), 3.55 – 3.46 (m, 2H), 3.31 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 6H), 0.96 – 0.89 (m, 2H), 0.02 (s, 9H) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 169.6, 134.9, 132.9, 131.5, 128.5, 68.80, 68.78, 61.5, 59.5, 35.6, 18.1, 14.2, -1.2 ppm.

HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{31}ClNaO_5Si$: 437.1527; found: 437.1516.

2-(4-Chlorobenzyl)-2-((2-(trimethylsilyl)ethoxy)methyl)propane-1,3-diol (**7**):

A dried 500 mL Schlenk flask under $N_2$ equipped with a stir bar, was charged with **6** (10.00 g, 24.0 mmol) and THF (150 mL). The mixture was cooled to 0 °C and $LiAlH_4$ (2.27 g, 60.0 mmol) was added in 5 portions over 10 min. The reaction mixture was then stirred for 3 hours at room temperature. $Et_2O$ (100 mL) was added and the mixture was cooled to 0 °C. $H_2O$ (2.3 mL) was added dropwise, followed by 15% NaOH solution (2.3 mL). The mixture was stirred for 15 min at room temperature and $H_2O$ (4.6 mL) was added. $MgSO_4$ (5 g) was added and the mixture was filtered through filter paper, and the collected solid was washed with $Et_2O$ (20 mL). Solvents were removed under reduced pressure to give the product as a colorless oil (7.62 g, 23.04 mmol, 96% yield).

FT-IR (neat, $cm^{-1}$): 3398 (s), 2962 (m), 2874 (m), 1495 (m), 1253 (m), 1099 (m), 1036 (m), 862 (s), 839 (s).

$^1H$ NMR ($CDCl_3$, 400 MHz): 7.26 – 7.21 (m, 2H), 7.17 – 7.12 (m, 2H), 3.66 – 3.59 (m, 2H), 3.56 – 3.50 (m, 2H), 3.49 – 3.43 (m, 2H), 3.28 (s, 2H), 2.79 – 2.73 (m, 2H), 2.66 (s, 2H), 0.96 – 0.91 (m, 2H), 0.02 (s, 9H) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 135.9, 132.3, 131.9, 128.3, 74.0, 69.3, 65.6, 44.1, 35.4, 18.4, -1.2 ppm.

HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{16}H_{27}ClNaO_3Si$: 353.1316; found: 353.1313.

2-(4-Chlorobenzyl)-2-(hydroxymethyl)propane-1,3-diol (**8**):

A dried 100 mL Schlenk flask under $N_2$ equipped with a stir bar, was charged with **7** (4.95 g, 15 mmol), $CH_2Cl_2$ (30 mL) and trifluoroacetic acid (15 mL). The mixture was stirred for 5 min at room temperature. The solvents were removed under reduced pressure and the crude colorless oil was dissolved in MeOH (50 mL). $K_2CO_3$ (10.30 g, 75.0 mmol) was added, and the mixture was stirred for 12 hours at room temperature. The solvent was removed under reduced pressure and EtOAc (50 mL) was added to the crude product. The mixture was then filtered through a pad of silica gel and washed with EtOAc (100 mL). The solvent was removed

under reduced pressure to give the pure product as a colorless oil (2.49 g, 10.8 mmol, 72%).

FT-IR (neat, $cm^{-1}$): 3392 (s), 2962 (m), 2873 (m), 1496 (m), 1253 (m), 1097 (m).

$^1H$ NMR ($CDCl_3$, 400 MHz): 7.28 – 7.23 (m, 2H), 7.21 – 7.15 (m, 2H), 3.60 (s, 6H), 2.62 (s, 2H), 2.26 (bs, 2H) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 36.36, 132.38, 132.27, 128.53, 66.02, 44.62, 35.48 ppm.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{16}ClO_3$: 231.0788; found: 231.0774.

2-(4-Chlorobenzyl)-2-(((methylsulfonyl)oxy)methyl)propane-1,3-diyl bis(methanesulfonate) (**9**):

A dried 100 mL round-bottom flask under $N_2$ equipped with a stir bar was charged with **8** (1.00 g, 4.33 mmol) and pyridine (15 mL). The mixture was cooled to 0 °C and MsCl (1.1 mL, 14.20 mmol) was added dropwise. The reaction was then stirred for 12 hours at room temperature. The reaction was quenched with $H_2O$ (10 mL) and $CH_2Cl_2$ (75 mL) was added. Phases were separated and the organic phase was then washed subsequently with 0.5 M $H_2SO_4$ solution (15 mL), followed by saturated $NaHCO_3$ solution (15 mL) and $H_2O$ (15 mL). The mixture was dried over $Na_2SO_4$ and solvents were removed under reduced pressure. Then EtOAc/hexane (1:2, 10 mL) was added to the crude material and the mixture was stored at -30 °C overnight. The product was collected by filtration and was obtained as white crystals (1.55 g, 3.33 mmol, 77%).

FT-IR (neat, $cm^{-1}$): 3041 (w), 2951 (w), 1496 (w), 1334 (s), 956 (s), 793 (s), 559 (s).

$^1H$ NMR ($CDCl_3$, 400 MHz): 7.35 – 7.30 (m, 2H), 7.19 – 7.14 (m, 2H), 4.08 (s, 6H), 3.09 (s, 9H), 2.80 (s, 2H) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 133.9, 131.9, 131.8, 129.3, 66.7, 43.1, 37.6, 33.8 ppm.

HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{14}H_{21}ClNaO_9S_3$: 486.9934; found: 486.9914.

(2-(4-Chlorobenzyl)-2-((diphenylphosphanyl)methyl)propane-1,3-diyl) bis(diphenylphosphane) (**10**):

Inside a glovebox, a Schlenk flask equipped with a stir bar was charged with $HPPh_2$ (307 mg, 1.65 mmol) and DME (10 mL). The mixture was cooled to 0 °C and *n*-BuLi (2.5 M, 0.66 mL, 1.6 mmol) was added dropwise. The mixture was allowed to warm to room temperature and **9** (232 mg, 0.5 mmol) was added in 5 portions over 5 min. After 24 h, the solvent was removed under reduced pressure. The mixture was dissolved in toluene (2 mL) and layered with hexane (1 mL) then placed in the freezer (-30 °C) for 12 hours. The solution was decanted and evaporated under reduced pressure. The crude oil was redissolved in toluene (2 mL), layered with MeOH and stored at -35 °C for 24 hours. The product was collected by filtration and was obtained as a white crystalline powder (264 mg, 0.36 mmol, 71%).

FT-IR (solid, $cm^{-1}$): 3079 (m), 3010 (w), 2918 (w), 1590 (m), 1486 (m), 1437 (m), 1094 (m), 739 (s), 696 (s).

$^1H$ NMR ($CD_2Cl_2$, 400 MHz): 7.35 – 7.21 (m, 30H), 7.16 – 7.09 (m, 4H), 2.85 (s, 2H), 2.34 (s, 6H).

$^{13}C$ NMR ($CD_2Cl_2$, 126 MHz): δ = 140.2 (AB spin system, *J* = 12 Hz), 137.2, 133.37 (AB spin system, *J* = 20.4 Hz), 132.89 (AB spin system, *J* = 1.7 Hz), 132.36, 128.9, 128.8 (AB spin system, *J* =7.3 Hz), 45.80 (q, *J* = 7.3 Hz), 43.50 (q, *J* = 12.8 Hz), 39.82 – 39.47 (m).

$^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 162 MHz): δ -27.84.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{47}H_{43}ClP_3$: 735.2266; found: 735.2290.

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## Supporting Information

YES

## Primary Data

NO

## Conflict of Interest

The authors declare no competing financial interest.

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