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Article

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Selective Pd-Catalyzed Monoarylation of Small Primary Alkyl Amines through Backbone-Modification in Ylide-Functionalized Phosphines (YPhos)

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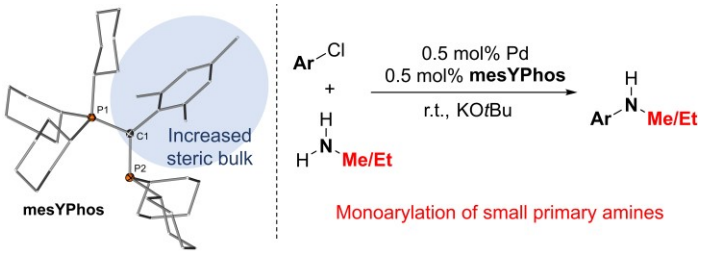
Supporting Information Placeholder



ABSTRACT: Ylide-substituted phosphines have shown to be excellent ligands for C-N coupling reactions under mild reaction conditions. Here, we report studies on the impact of the steric demand of the substituent in the ylide-backbone on the catalytic activity. Two new YPhos ligands with bulky *ortho*-tolyl (pinkYPhos) and mesityl substituents (mesYPhos) have been synthesized, which are slightly more sterically demanding than their phenyl analogue but considerably less flexible. This change in the ligand design leads to higher selectivities and yields in the arylation of small primary amines compared to previously reported YPhos ligands. Even $MeNH_2$ and $EtNH_2$ could be coupled at room temperature with a series of aryl chlorides in high yields.

INTRODUCTION

Transition metal catalyzed cross-coupling reactions have developed into a powerful tool in modern synthetic chemistry, allowing the synthesis of complex molecules under relatively mild reaction conditions from usually readily available starting materials. The C-N coupling reaction (Buchwald-Hartwig amination) of aryl electrophiles with amines is one of the most important methods due to the ubiquity of amine moieties in many pharmaceuticals, natural products, agrochemicals and fine chemicals used in materials chemistry and beyond.[1] The Buchwald-Hartwig amination has experienced remarkable advances in the last 25 years which are mainly connected with the development of new ancillary ligands. Electron-rich and sterically bulky monophosphines[2] as well as *N*-heterocyclic carbenes[3] have found to be particularly suited in that chemistry to generate and stabilize low-coordinated palladium species that readily undergo oxidative addition of C-X bonds, including the cheaper but more challenging aryl chlorides.

Small, unbranched primary alkyl amines such as methyl or ethylamine are one of the most challenging substrates in C-N coupling reactions. This is due to two inherent challenges connected with these substrates: (i) Due to their small size, selectivity between the mono and diarylation product is often problematic. Thus, very sterically hindered ligands are required to allow for selective monoarylation. (ii) Alkyl amines are prone to β-hydride elimination, which might lead to the formation of side products and thus requires a special ligand design to prevent the intramolecular C-H activation step. Because of these limitations comparably few synthetic protocols for the coupling of these amines have been reported in the past years. In case of palladium-catalyzed reactions, the first efficient protocol for methylamine coupling with aryl chlorides was described by Buchwald and coworkers in 2008 using a palladium precatalysts with the biarylphosphine BrettPhos, **A** (Figure 1).[4] Since then a number of other ligands have found to be highly efficient in this transformation. For example, Hartwig described the use of CyPF-^{t}Bu (**B**) both for ethyl and methylamine with a series of aryl bromides and chlorides.[5] Stradiotto and coworkers reported on the use of the DalPhos family of ligands (e.g. Me-DalPhos (**C**)[6] and Mor-DalPhos (**D**)[7]) as well as a phosphine-functionalised NHC ligand[8] as versatile ligands in a series of coupling reactions including

methylamine but also secondary amines. It must be noted that C-N coupling reactions including primary amines have recently also been reported with phosphine ligated nickel complexes,[9] including couplings under mild conditions[10] as well as copper-catalyzed protocols, which however require harsh reaction conditions or only allow for the amination of activated aryl electrophiles such as aryl iodides.[11] Despite these advances made in the past years, most of the catalysts still require higher reaction temperatures for the amination of aryl chlorides and/or make use of expensive ligands.

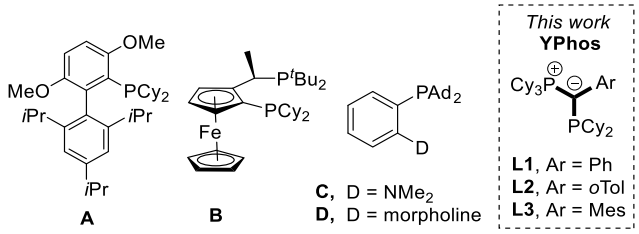
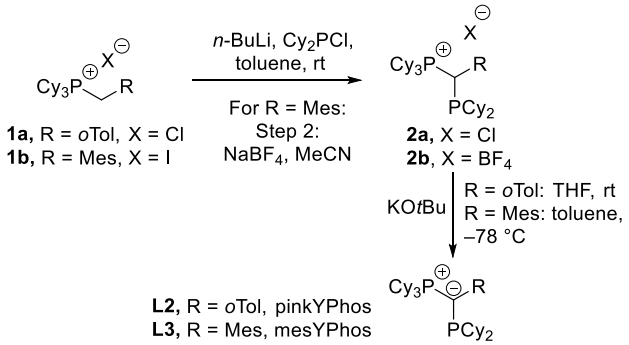


Figure 1. Phosphines used for the selective monoarylation of small primary alkylamines.

Recently, our group reported on the use of ylide-substituted phosphines (YPhos) as highly efficient ligands in gold catalysis[12] as well as Pd-catalyzed C-N and C-C coupling reactions.[13] YPhos ligands are in general electron-rich phosphines and easy-to-synthesis in few steps from cheap starting materials. Furthermore, modification of the ylide-backbone allowed for an additional tuning of the electronic and steric properties and hence of the catalytic activity of their metal complexes. For example, replacement of the methyl group in the ligand $Ph_3PC(Me)PCy_2$ with sulfonyl or cyano group led to an increase of catalytic activity in gold catalysed hydroaminations by orders of magnitude thus allowing catalysis with ppm-level catalyst loadings.[12] In palladium catalysis, the analogous PCy_3-substituted YPhos ligand joYPhos (**L1**) with a phenyl group in the ylide-backbone proved to be highly effective in Buchwald-Hartwig aminations of aryl chlorides at room temperature allowing for turnover frequencies greater than 10.000 h^{-1} with improved selectivities in comparison to its methyl-substituted analogue.[14] However, diarylation was observed as side-product with small primary amines. To address this limitation of **L1**, we became interested in the impact of the steric demand of the backbone substituent on the selectivity in mono versus diarylation reactions. Therefore, we addressed the synthesis of the *ortho*-tolyl (pinkYPhos, **L2**) and mesityl (mesYPhos, **L3**) substituted YPhos ligands. Here, we show that this modification indeed leads to a coherent structure-selectivity relationship and enables the selective monoarylation of methyl and ethyl amine with aryl chlorides at room temperature.

RESULTS AND DISCUSSION

Ligand synthesis and properties. The synthesis of the ligands **L2** and **L3** was attempted via the same protocol as used for the synthesis of ligand **L1**.[14] For the *ortho*-tolyl ligand $^{Cy}Y_{oTol}PCy_2$, formation of the phosphonium salt **2a** and subsequent deprotonation to **L2** revealed to be facile and allowed the isolation of the ligand as colorless solid in 84% from **1a**. (Scheme 1). In contrast, preparation of the mesityl ligand $^{Cy}Y_{Mes}PCy_2$ (**L3**) failed under the same reaction conditions. No complete conversion to the α-phosphino-phosphonium salt **2b** was observed when treating the phosphonium iodide **1b** with butyllithium and Cy_2PCl. We hypothesized that this might be due to an equilibrium between **1b** and **2b** as a consequence of the competing attack of the chloride at **2b**. This results in the reformation of the starting material and hence to mixtures of **2b** and **1b**. To prevent the attack of the halide, the chloride anion was replaced by addition of $NaBF_4$. Thus, α-phosphino phosphonium salt **2b** could be isolated in 62 % yield as colorless solid which is stable in solution. Due to the steric bulk of the mesityl group deprotonation also proved to be difficult but was accomplished by using potassium *tert*-butoxide at low temperatures. At higher temperatures, PCy3 elimination and formation of the C-C coupled diphosphine $(Mes(PCy_2)(H)C)_2$ was observed (see SI). Nonetheless, **L3** could be isolated as colorless solid and moderate yields of 41 %. The YPhos ligands **L2** and **L3** are characterized by two doublets in the $^{31}P\{^1H\}$ NMR at –0.5 and 19.3 ppm ($^2J_{PP}$ = 138.2 Hz) for **L2** and 6.1 and 13.8 ppm ($^2J_{PP}$ = 145.3 Hz) for **L3**.



Scheme 1. Preparation of ligands L2 and L3.

Single-crystals of both ligands could be obtained by slow evaporation of their saturated hexane solutions (Figure 2). The molecular structures of **L2** and **L3** are similar to the one reported for **L1**.[14] All ligands show similar bond lengths in the central P-C-P linkage and similar P-C-P angles between 112.5(1) (**L2**) and 113.7(1)° (**L1**). This is rather surprising, since the YPhos ligands in general were found to sensitively respond to steric pressure by changes in the P–C–P angle. For example, for the methyl-substituted ligand (keYPhos) changes of more than 15° in the P–C–P angle were observed in different Pd complexes depending on the demand of other co-ligands at the metal.[15] The similarity of the structures of **L1**-**L3** however, is probably the result of a change in the orientation of the aryl substituent relative to the P–C–P plane. While the corresponding P2–C1–C2–C3 angle in **L1** amounts to 75.3(1)°, it increases to 89.1(1) in **L3**. Thus, the latter features an almost ideal perpendicular arrangement of the mesityl group relative to the P-C-P linkage. Furthermore, the C1–C2 distances to the aryl substituents are longer in **L2** and **L3** (approx. 1.510 Å) in comparison to **L1** (1.489(2) Å), thus also slightly reducing the steric pressure.

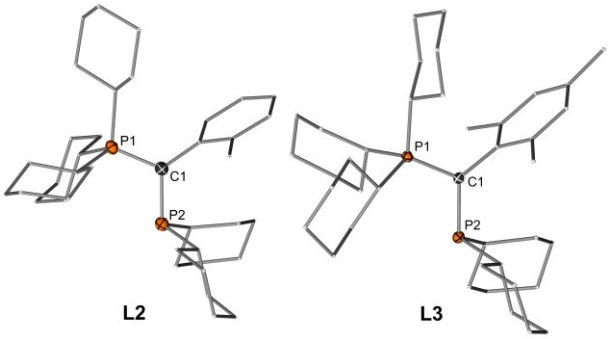


Figure 2: Molecular structures of $^{Cy}Y_{oTol}PCy_2$ (L2) and $^{Cy}Y_{Mes}PCy_2$ (L3). Crystallographic details are provided in the SI.

The steric and electronic properties of **L2** and **L3** were measured by determination of the Tolman electronic parameter (TEP) and the buried volume (%V_{bur}). The TEP value was derived from the CO stretching frequency in the corresponding L·Rh(acac)CO complexes in DCM. Crystals of [**L2**·Rh(CO)acac] were grown by cooling of a DCM solution of the complex to –30 °C and confirmed the formation of the rhodium complex for the tolyl ligand **L2** (Figure 3). With TEPs of 2048.0 (**L2**) and 2048.4 cm^{-1} (**L3**) both ligands are slightly stronger donors than **L1** (2050.1 cm^{-1})[13a] and similarly stronger than the commonly used *N*-heterocyclic carbenes IMes (TEP=2050.7 cm^{-1}) or IPr (TEP = 2051.5 cm^{-1}).[16]

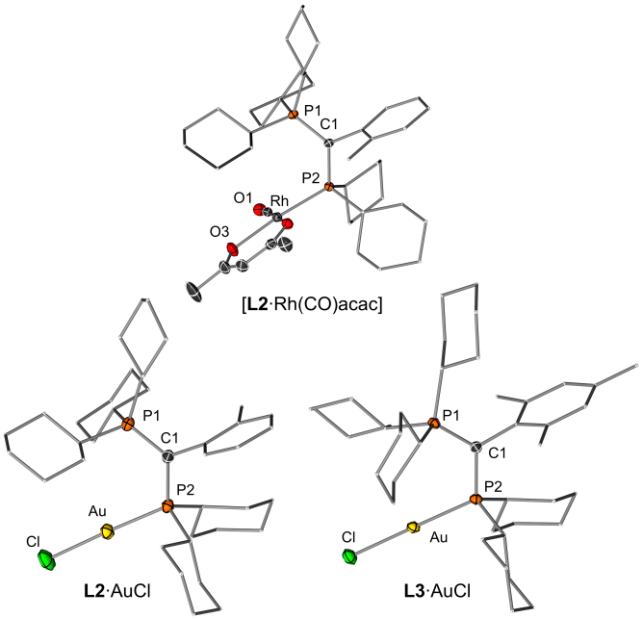


Figure 3. Molecular structure of [L2·Rh(CO)acac], L2·AuCl and L3·AuCl. Crystallographic details are provided in the SI.

To determine %V_{bur}, the corresponding L·AuCl complexes were prepared form the free ligands and (THT)AuCl (THT = tetrahydrothiophene) and isolated as colorless solids in moderate yields of approx. 55 %. Both crystals were grown by diffusion of pentane into a THF solution of the gold complex. The crystal structure (Figure 3) of $Y_{o\text{-}Tol}PCy_2$·AuCl yielded a buried volume of %V_{bur} = 49.4 % for **L2**, while a slightly higher value of %V_{bur} = 50.7 % was found for **L3**. Thus, both ligands cover approx. half the sphere around a metal center and are thus more sterically demanding than their phenyl analogue **L1**, which exhibits a buried volume of 47.9 %. In the gold complex, **L3** shows again an ideal perpendicular arrangement of the mesityl substituent relative to the P–C–P moiety, thus indicating an ideal protection of the ylidic carbon atom by the two *ortho*-methyl substituents. Interestingly, the tolyl ligand shows a disorder in the molecular structure of the free ligand as well as the gold complex, which concerns the geometry around the ylidic carbon atom C1. While a planar geometry around C1 was found in all structures of the YPhos ligands and their metal complexes, **L2** shows a slightly pyramidalized carbon atom in both crystal structures with sum of angles around C1 of approx. 355°. The pyramidalization always results in an opening of the pocket between the cyclohexyl groups to accommodate the *ortho*-methyl substituent. This flexibility is prevented in the mesityl ligand.

Pd-catalyzed C-N coupling of small alkyl amines. With successful synthesis of the ligands we turned our attention towards the impact of the backbone-substituent on the efficiency of the ligands in Pd-catalyzed amination reactions. We assumed that formation of the active species with $Pd_2(dba)_3$ might be slow, particularly with the bulky mesityl ligand. Thus, at first the formation of the L·Pd(dba) complex was investigated to get an estimation of the time required for catalyst preformation. To this end, the reaction of $Pd_2(dba)_3$ with an equiv. amount of ligand was followed by ^{31}P NMR spectroscopy. Both dba complexes exhibit distinct NMR features, giving rise to two doublets in the $^{31}P\{^1H\}$ NMR spectrum with coupling constants of approx. 90 Hz. Reaction monitoring revealed that **L2** requires only 1 h reaction time to completely convert into the L·Pd(dba) complex, while 16 h were needed for **L3** (see Figure S8 and S9).

With this information in hand, the catalytic ability of the ligands was tested. We focussed on the amination of aryl chlorides with small alkyl amines, which are usually difficult to be selectively monoarylated. We selected the coupling of *p*-tolyl chloride with the primary amines $MeNH_2$, $EtNH_2$, *n*$BuNH_2$, $BnNH_2$ (Bn = benzyl), *i*$PrNH_2$ and *t*$BuNH_2$ as test protocol. We also included three secondary amines (Et_2NH, piperidine and *N*-methylaniline) to examine whether also these substrates can be coupled. The reactions were conducted at room temperature with 0.5 mol% of ligand and 0.25 mol% Pd_2dba_3·dba. The results obtained after 1 h reaction time with **L2** and **L3** are given in Figure 4. Longer reaction times did not lead to a significantly change of the obtained yields. The activity of pinkyPhos and mesYPhos was compared with joYPhos (**L1**) as well as the P*t*Bu_2 ligand trYPhos (**L4**) to gain insights into structure-selectivity relationships. The comparison shows clear differences in the catalytic activity depending on the backbone-substituent. While the smaller phenyl-substituted joYPhos (**L1**) is the most efficient ligand for secondary amines, it is less efficient for primary

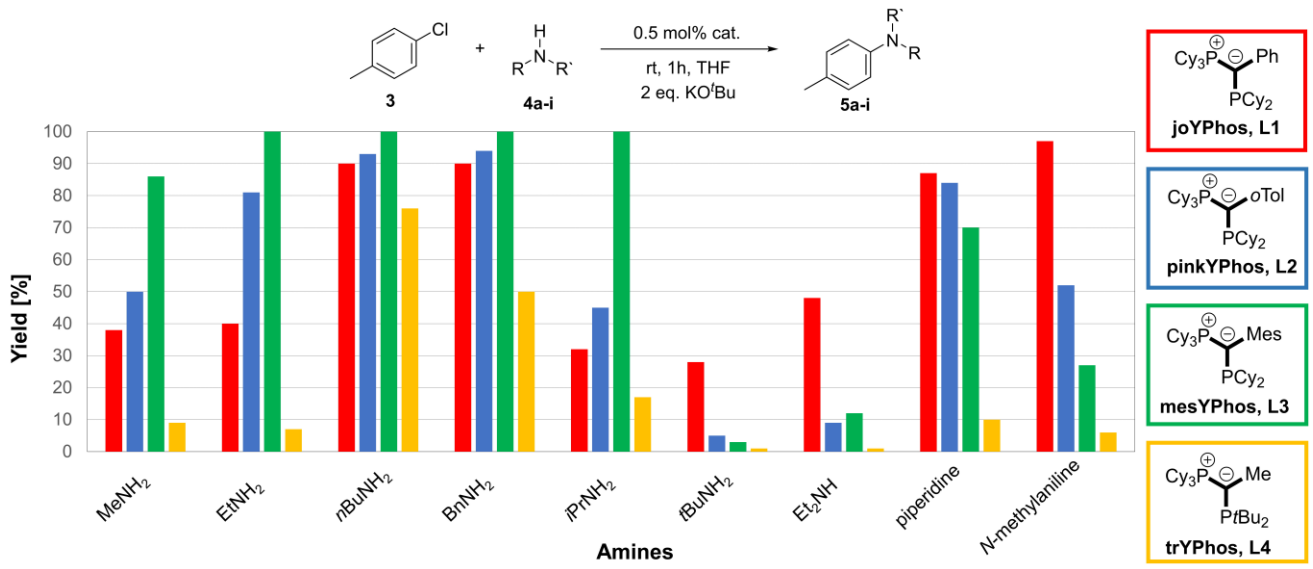


Figure 4. Comparison of the catalytic activity of **L1-L4.** Reaction conditions: 0.5 mol% cat, RT, 1h, aryl chloride:amine 1:1.1, yield determined by GC FID analysis with tetradecane as internal standard.

amines. In contrast, the *ortho*-tolyl and especially the mesityl-substituted ligands **L2** and **L3** are very efficient for the coupling of primary amines, with **L3** giving superior results. To our delight, also methylamine and ethylamine, which are particularly difficult substrates, could be selectively monoarylated. Likewise, *n*BuNH$_2$, BnNH$_2$ and *i*PrNH$_2$ were all fully converted into the corresponding aniline derivatives within only 1h reaction time. However, *tert*-butyl amine seems to be the limit in steric demand of primary amines and could not be coupled under these reaction conditions. The high selectivity for the monoarylation of small primary amines with **L2** and **L3** is reflected in low conversions observed for secondary amines. Here, **L3** led to considerably lower yields than joYPhos.

The results clearly demonstrate that the steric bulk of **L2** and **L3** is necessary to allow the selective monoarylation, particularly with MeNH$_2$. Here, the smaller **L1** delivers considerable amounts of the diarylation product (>10%). However, it is not only the steric bulk of the ligand that is important. This becomes clear from the fact that the *tert*-butyl ligand **L4** (%V_{bur} = 51.3%) which is of similar size than **L3** gives lower yields. This can be explained by the higher reactivity and lower stability of the **L4**-based palladium complexes, which was already observed in case of the α-arylation of ketones.[13c] In contrast to the methyl group in the backbone of **L4**, the *ortho*-tolyl and mesityl groups impart steric bulk but also protection of the carbanionic center, which stabilizes the catalytically active species and thus hampers catalysts decomposition.

Nonetheless, it is remarkable a simple modification of the ligand backbone from phenyl to *ortho*-tolyl and mesityl leads to such an impact on the selectivity of the catalysts towards different substrates. Presumably, this selectivity difference is not only the result of the different steric bulk of the ligands – note that the %V_{bur} values of the ligands **L1-L3** are within only 4 % – but also results from differences in the flexibility of the ligands. Thus, the larger substituents in the backbone prevent large changes in the P–C–P angles, which are necessary to move the PCy$_3$ moiety away from the metal in order to open the coordination sphere around the metal for larger substrates. While this flexibility is beneficial for fast catalysis, it leads to lower selectivities. Due to these structural features, joYPhos (**L1**) seems to be the ideal ligand for secondary amines, while mesYPhos (**L3**) is best for small unhindered primary amines.

Motivated by the excellent activity of ligand **L3** for the coupling of small unhindered primary amines at room temperature, we tested the isolation of these compounds as well as a broader substrate scope. We were pleased to see, that amines **5aa** to **5ae** could be isolated in good to excellent yields (Figure 5). Since methylamine and ethylamine are difficult substrates for which only a limited number of catalysts exist, we further focussed on these substrates. Aryl chlorides with electron-withdrawing as well as electron-donating substituents could be coupled in good to high yields. The same holds true for somewhat more sterically demanding substrates with *ortho*-substituents (**5ba**, **5bb** and **5ea**). Also, 2-chloropyridine could be successfully converted into the corresponding methyl- or ethylamines, albeit lower yields were observed with 0.5 mol% catalyst loading.

CONCLUSION

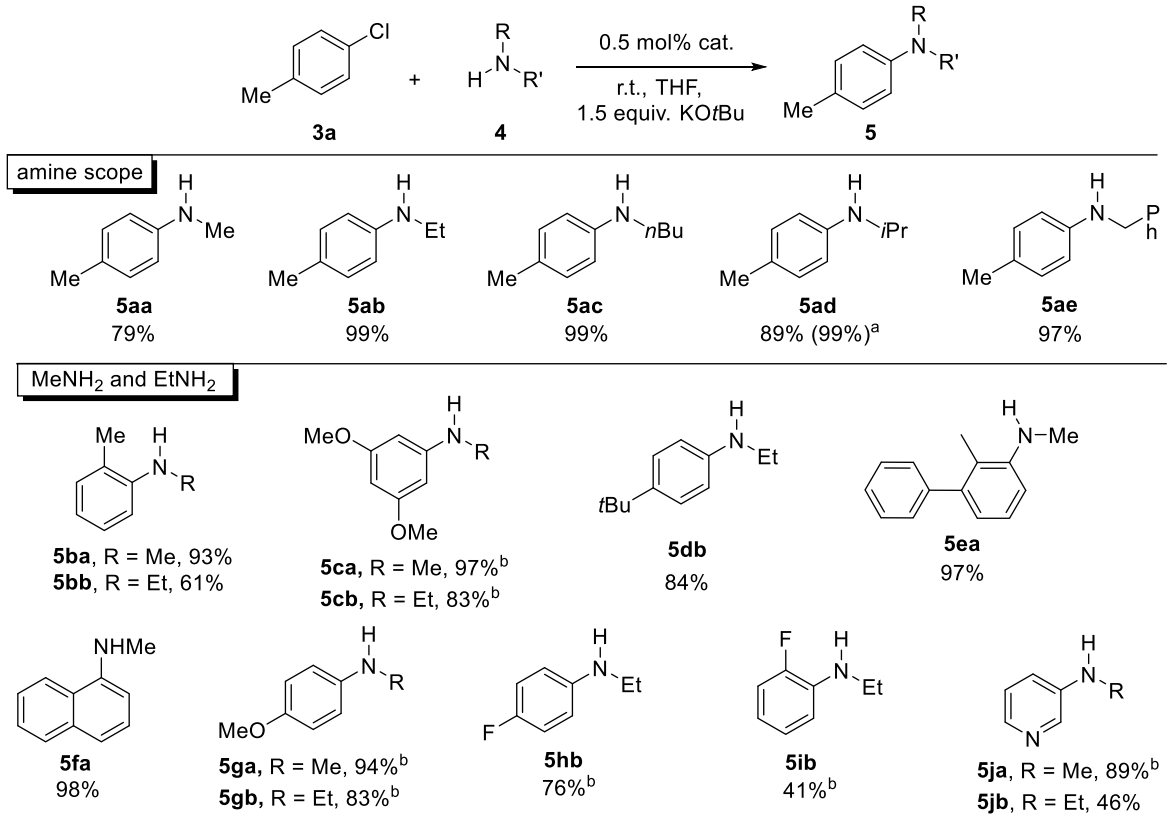
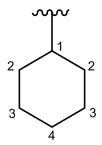


Figure 5. Substrate scope of the C-N coupling of primary amines with L3. Reaction conditions: 0.5 mol% cat, RT, 90 min, aryl chloride:amine 1:1.1, isolated yields. [b]GC yield. [c]1 mol % cat. X-ray crystallographic data for 5ea can be found in Supporting Information.

In conclusion, we reported on the preparation of two new YPhos ligands with a bulky *o*-tolyl (pinkYPhos) and mesityl substituent (mesYPhos) in the ylide-backbone. This modification led to a slight increase of the steric demand and a more rigid ligand structure compared to the joYPhos ligand with a phenyl group in the backbone. A comparison of the activity of the different YPhos ligands in the C–N coupling of aryl chlorides with different primary and secondary amines revealed that the increased bulk and the lower flexibility of the ligand structures allow for higher selectivities in the coupling of unhindered substrates. Particularly, mesYPhos gave high yields for the monoarylation of methyl and ethylamine at room temperature. These results demonstrate that the backbone substituent in ylide-substituted phosphines not only controls the donor properties of these ligands, but also provides a further handle to adjust the steric demand and particularly the flexibility of the ligand.

EXPERIMENTAL SECTION

General Methods. All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried using an MBraun SPS-800 (THF, DCM, toluene, acetonitrile, diethylether and pentane) or dried in accordance with standard procedures. Deuterated solvents were stored over molecular sieves in an argon-filled glovebox. $ClPCy_2$ was prepared according to published procedures.[17] $Pd_2(dba)_3$·dba and (tht)AuCl were donated by UMICORE AG & Co.[18] All other reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium or Acros Organics and used without further purification. NMR spectra were recorded on Avance-400 spectrometers at 25 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (*J*) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, br = broad signal. Signal assignment was supported by HSQC (^1H / ^{13}C), HMBC (^1H / ^{13}C, ^1H / ^{31}P) correlation experiments for all ligands, their precursors and their metal complexes, the isolated cross-coupling products were analyzed according to their shift. Cyclohexyl groups were assigned according to the scheme on the right-hand side. Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer. IR-Spectra were recorded on a Thermo Nicolet iS5 FT-IR in transmission mode with a Specac "Omni-cell" with KBr plates and a 0.1 mm spacer or with an ATR module at 22 °C. Column chromatography was performed on a Reveleris X2 (BÜCHI) Flash Chromatog-



raphy- System using Reveleris packed columns. Melting Points were collected on a Stuart SMP 30 with a heat up speed of 2 °C per minute.

Synthesis of Phosphonium Salt 1a. 4.7 mL (5.0 g, 35.6 mmol, 1.0 eq.) of 1-(chloromethyl)-2-methylbenzene and 11.0 g (39.1 mmol, 1.1 eq.) of tricyclohexylphosphine were suspended in 60 mL of dry toluene and stirred at room temperature overnight. The precipitated solid was filtered through a *Schlenk* frit and washed two times with 7 mL of dry toluene. The solid was dried for 5 hours, giving the product as a colorless solid (13.8 g, 32.8 mmol, 92 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.28 (m, 1H, C$H_{, oTol}$), 7.28 – 7.18 (m, 3H, C$H_{, oTol}$), 4.14 (d, $^{2}J_{HP}$ = 14.3, 2H, P–CH_2-Tol), 2.92 – 2.69 (m, 3H, C$H_{, Cy, H1}$), 2.50 (d, J = 1.4 Hz, 3H, CH_3), 2.05 – 1.93 (m, 6H, C$H_{2, Cy, H2}$), 1.93 – 1.83 (m, 6H, C$H_{2, Cy, H3}$), 1.82 – 1.72 (m, 3H, C$H_{2, Cy, H4}$), 1.63 – 1.45 (m, 6H, C$H_{2, Cy, H2}$), 1.46 – 1.35 (m, 6H, C$H_{2, Cy, H3}$), 1.33 – 1.19 (m, 3H, C$H_{2, Cy, H4}$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 30.8. Further spectroscopic and physical properties match with the literature report.[19]

Synthesis of 2-(iodomethyl)-1,3,5-trimethylbenzene. Here, we report an alternative synthesis route. A two-necked flask with 15 g (0.10 mol, 1.0 eq.) of 2,4,6-trimethylbenzyl alcohol was equipped with a dropping funnel. The solid was dissolved in 100 mL of DCM and 8.0 mL (13 g, 0.11 mol, 1.1 eq.) of thionyl chloride was filled into the dropping funnel. The reagent was added dropwise under vigorous stirring and the suspension was stirred for an additional hour. The reaction mixture was quenched with 50 mL of water and the organic phase was extracted three times with 50 mL of water in a separating funnel. The organic phase was dried over magnesium sulfate and the solvent was removed *in vacuo*. The successful formation of the intermediate 2-(chloromethyl)-1,3,5-trimethylbenzene was confirmed by NMR spectroscopy. The intermediate product (15.1 g, 0.09 mol, 1.0 eq.) and 14.8 mg (0.10 mol, 1.1 eq.) of sodium iodide were dissolved in 100 mL of acetonitrile and refluxed with an oil bath overnight. The solid was filtered over a filter paper and the solvent was removed *in vacuo*. The solid was dissolved in 100 mL of ethyl acetate and extracted three times with 50 mL of water in a separating funnel. The aqueous phase was extracted one more time with 100 mL of ethyl acetate. The organic phases were combined, and the solvent was removed at reduced pressure to yield the product as a light yellow solid (20.1 g, 0.8 mol, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, 2H, C$H_{, Mes, meta}$), 4.46 (s, 2H, I–CH_2-Mes), 2.32 (s, 6H, C$H_{3, Mes, ortho}$), 2.26 (s, 3H, C$H_{3, Mes, para}$). Further spectroscopic and physical properties match with the literature report.[20]

Synthesis of phosphonium salt 1b. 9.77 g (37.6 mmol, 1.05 eq.) of 2-(iodomethyl)-1,3,5-trimethylbenzene and 10 g (35.6 mmol, 1.0 eq.) of tricyclohexylphosphine were suspended in 120 mL of dry toluene and stirred at room temperature overnight. The precipitated solid was filtered through a *Schlenk* frit and washed two times with 20 mL of dry toluene. The solid was dried for 5 hours, giving the product as a colorless solid (19.3 g, 35.6 mmol, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 2H, C$H_{, Mes, meta}$), 3.85 (d, $^{2}J_{HP}$ = 12.7 Hz, 2H, P–CH_2-Mes), 2.73 – 2.49 (m, 3H, C$H_{Cy, H1}$), 2.39 (s, 6H, C$H_{3, Mes, ortho}$), 2.24 (s, 3H, C$H_{3, Mes, para}$), 1.93 – 1.82 (m, 12H, C$H_{2, Cy, H2 + H3}$), 1.82 – 1.69 (m, 3H, C$H_{2, Cy, H4}$), 1.68 – 1.48 (m, 6H, C$H_{2, Cy, H2}$), 1.50 – 1.21 (m, 9H, C$H_{2, Cy, H3 + H4}$). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.3 (d, $^{5}J_{CP}$ = 3.6 Hz, $C_{, Mes, para}$), 137.1 (d, $^{3}J_{CP}$ = 4.5 Hz, $C_{, Mes, ortho}$), 130.4 (d, $^{4}J_{CP}$ = 3.0 Hz, C$H_{, Mes, meta}$), 123.5 (d, $^{2}J_{CP}$ = 8.5 Hz, $C_{, Mes, ipso}$), 32.9 (d, $^{1}J_{CP}$ = 36.8 Hz, C$H_{, Cy, C1}$), 27.6 (d, $^{2}J_{CP}$ = 4.4 Hz, C$H_{2, Cy, C2}$), 26.9 (d, $^{3}J_{CP}$ = 11.6 Hz, C$H_{2, Cy, C3}$), 25.4 (d, $^{4}J_{CP}$ = 1.8 Hz, C$H_{2, Cy, C4}$), 22.1 (d, $^{4}J_{CP}$ = 1.2 Hz, C$H_{3, Mes, ortho}$), 20.8 (d, $^{6}J_{CP}$ = 1.2 Hz, C$H_{3, Mes, para}$), 19.9 (d, $^{1}J_{CP}$ = 40.7 Hz, P–CH_2-Mes). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 31.6. IR (ATR): 2931 (s), 2849 (s), 1445 (s), 1397 (w), 1381 (w), 1179 (w), 1121 (w), 1045 (w), 1036 (w), 1009 (m), 887 (m), 869 (w), 851 (s), 828 (w), 791 (w), 740 (w), 564 (w), 532 (w), 521 (w). m.p.: 210.8 – 215.2 °C.

Synthesis of ligand L2. A *Schlenk* flask was filled with 4.0 g (9.5 mmol, 1.0 eq.) of phosphonium salt **1a**, which was suspended in 60 mL of dry THF. 6.5 mL (9.5 mmol, 1.46 M in hexane, 1 eq.) of *n*-butyllithium was added dropwise into the solution. After complete addition, a light-yellow solution was formed. To this solution 2.2 mL (2.3 g, 10.0 mmol, 1.05 eq.) chlorodicyclohexylphosphine was added dropwise and the solution was stirred overnight. The precipitated colorless solid was filtered through a glass frit and washed with 15 mL of dry THF. The solid was dried *in vacuo* and the intermediate phosphonium salt was isolated as a colorless solid (5.2 g, 8.4 mmol, 88 %). 5.19 g (8.41 mmol, 1.0 eq.) of the intermediate phosphonium salt and 1.04 g (9.25 mmol, 1.1 eq.) of sodium *tert*-butoxide was added into a *Schlenk* flask and suspended in 80 mL of THF. After one hour, a clear solution was formed. The solvent was removed and the solid was suspended in 60 mL of toluene. The solid was filtered off and washed with additional 10 mL of toluene. The filtrated solvent was removed and the remaining solid washed with 50 mL of dry acetonitrile. The product was obtained as a colorless solid (4.72 g, 8.13 mmol, 96 %, yield of two steps: 84 %). ^{1}H NMR (400 MHz, C_6D_6) δ 7.55 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, C$H_{Tol, ortho'}$), 7.28 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, C$H_{Tol, meta}$), 7.20 – 7.13 (m, 1H, C$H_{Tol, meta'}$), 7.09 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, C$H_{Tol, para}$), 2.71 (s, 3H, CH_3), 2.58 – 2.36 (m, 2H, C$H_{2, PCy2}$), 2.33 – 2.21 (m, 3H, C$H_{, PCy3, H1}$), 2.15 – 1.85 (m, 11H, C$H_{2, PCy3, H2 + PCy2}$ + C$H_{, PCy2, H1}$), 1.80 – 1.66 (m, 10H, C$H_{2, PCy3, H3 + PCy2}$), 1.63 – 1.43 (m, 13H, C$H_{2, PCy3, H2 + H4 + PCy2}$), 1.41 – 1.22 (m, 7H, C$H_{2, PCy2}$), 1.17 – 0.92 (m, 9H, C$H_{2, PCy3, H3 + H4}$). ^{13}C {^{1}H} NMR (101 MHz, C_6D_6) δ 143.7 (dd, $^{2}J_{CP}$ = 9.9 Hz, $^{2}J_{CP}$ = 2.6 Hz, $C_{Tol, ipso}$), 141.4 ($C_{Tol, ortho}$), 137.8 (d, $^{3}J_{CP}$ = 3.2 Hz, C$H_{Tol, ortho'}$), 130.6 (C$H_{Tol, meta}$), 124.5 (d, $^{4}J_{CP}$ = 2.0 Hz, C$H_{Tol, meta'}$), 124.1 (d, $^{5}J_{CP}$ = 2.1 Hz, C$H_{Tol, para}$), 40.1 (d, $^{1}J_{CP}$ = 14.0 Hz, C$H_{, PCy2, C1}$), 36.9 (dd, $^{1}J_{CP}$ = 48.1 Hz, $^{3}J_{CP}$ = 7.7 Hz, C$H_{, PCy3, C1}$), 36.9 – 36.4 (m, C$H_{, PCy2, C1}$), 33.7 (d, $^{2}J_{CP}$ = 23.4 Hz, C$H_{2, PCy2, C2}$), 32.9 (d, $^{2}J_{CP}$ = 20.6 Hz, C$H_{2, PCy2, C2}$), 31.2 (d, $^{2}J_{CP}$ = 11.7 Hz, C$H_{2, PCy2, C2}$), 29.8 (C$H_{2, PCy2, C3}$), 29.0 (d, $^{2}J_{PP}$ = 14.6 Hz, C$H_{2, PCy2, C2}$), 28.8 (m, C$H_{2, PCy3, C2}$), 28.1 (m, C$H_{2, PCy2, C3}$), 27.7 (m, C$H_{2, PCy3, C3 + PCy2, C3}$), 27.1 (m, C$H_{2, PCy2, C4}$), 26.6 (C$H_{2, PCy3, C4}$), 22.4 ($CH_3$), 17.9 (dd, $^{1}J_{CP}$ = 99.0 Hz, $^{1}J_{CP}$ = 29.7 Hz, P-C'-P). ^{31}P {^{1}H} NMR (162 MHz, C_6D_6) δ 19.3 (d, $^{2}J_{PP}$ = 138.2 Hz, PCy$_3$), -0.5 (d, $^{2}J_{PP}$ = 138.2 Hz, PCy$_2$). Anal. calc. For $C_{38}H_{62}P_2$: C 78.58, H 10.76; found: C 78.38, H 10.46. IR (ATR): 2915 (s), 2846 (s), 1590 (w), 1474 (w), 1445

(s), 1326 (w), 1282 (w), 1265 (w), 1217 (m), 1175 (w), 1129 (w), 1108 (w), 1074 (w), 1050 (w), 1006 (m), 974 (m), 899 (s), 885 (s), 846 (m), 813 (w), 791 (w), 747 (w), 725 (s), 569 (w), 543 (s), 523 (w), 512 (w). m.p.: 157.8 – 160.9 °C.

Synthesis of ligand L3. Phosphonium salt **1b** (5.0 g, 9.3 mmol, 1.0 eq.) was suspended in 70 mL of toluene and 5.82 mL of *n*-butyllithium (1.59 M in hexane, 1.0 eq.) was added dropwise. The remaining solid was filtered off and washed with 10 mL of toluene. Half of the solvent was removed at reduced pressure and 2.1 mL (2.2 g, 1.0 eq.) of chlorodicyclohexylphosphine were added. The solution was stirred for 3 days at room temperature and the resulting colorless solid was filtered off and washed with pentane (2 x 10 mL), dried *in vacuo*, thus giving the intermediate phosphonium salt (4.3 g, 5.8 mmol, 63 %). 0.64 mg (5.8 mmol, 1.0 eq.) of $NaBF_4$ was added to the phosphonium salt and the mixture was redissolved in 50 mL of acetonitrile and stirred overnight at room temperature. The resulting solid was filtered off, washed several times with MeCN (3 x 5 mL) and the solvent was removed at reduced pressure. The oily residue was suspended in 80 mL of diethyl ether and the suspension was stirred overnight until a white solid precipitated from the solution. The colorless BF_4 salt was filtered off and dried *in vacuo*. (4.0 g, 5.7 mmol, 98 %). 0.50 g (0.7 mmol, 1.0 eq.) of the BF_4 salt were suspended in 40 mL of toluene and 0.081 g (0.7 mmol, 1.0 eq.) of potassium *tert*-butoxide were dissolved in a second flask in 40 mL of toluene. Both solutions were cooled to –78 °C (dry ice/acetone bath) and stirred for 30 minutes at that temperature. The potassium *tert*-butoxide solution was transferred into the suspension and the mixture was allowed to warm to room temperature slowly overnight. The residue was filtered off and the solvent was removed *in vacuo*. The solid was washed with 20 mL of acetonitrile and dried *in vacuo* to yield the ligand as a colorless solid (0.29 g, 0.5 mmol, 66 %, overall yield: 41 %). ^{1}H NMR (400 MHz, C_6D_6) δ 6.99 (s, 2H, C*H*$_{\text{Mes, meta}}$), 2.76 (d, $^5J_{HH}$ = 1.4 Hz, 6H, C*H*$_{3, \text{Mes, ortho}}$), 2.49 – 2.32 (m, 2H, C*H*$_{2, \text{PCy2, H2}}$), 2.21 (s, 3H, C*H*$_{3, \text{Mes, para}}$), 2.22 – 2.12 (m, 6H, C*H*$_{2, \text{PCy3, H2}}$), 2.14 – 4.98 (m, 5H, C*H*$_{, \text{PCy2, H1} + \text{PCy3, H1}}$), 1.98 – 1.80 (m, 4H, C*H*$_{2, \text{PCy2, H2} + \text{H3}}$), 1.82 – 1.65 (m, 10H, C*H*$_{2, \text{PCy3, H3}}$ + C*H*$_{2, \text{PCy2, H3} + \text{H4}}$), 1.66 – 1.40 (m, 15H, C*H*$_{2, \text{PCy3, H2} + \text{H4}}$ + C*H*$_{2, \text{PCy2, H2} + \text{H3}}$), 1.38 – 1.22 (m, 4H, C*H*$_{2, \text{PCy2, H3} + \text{H4}}$), 1.20 – 0.91 (m, 9H, C*H*$_{2, \text{PCy3, H3} + \text{H4}}$). ^{13}C {^{1}H} NMR (101 MHz, C_6D_6) δ 142.7 (d, $^4J_{CP}$ = 4.6 Hz, *C*H$_{, \text{Mes, meta}}$), 140.8 (d, $^2J_{CP}$ = 9.5 Hz, *C*$_{, \text{Mes, ipso}}$), 133.4 (d, $^5J_{CP}$ = 2.7 Hz, *C*$_{, \text{Mes, para}}$), 129.0 (d, $^3J_{CP}$ = 1.9 Hz, *C*$_{, \text{Mes, ortho}}$), 41.4 (dd, $^1J_{CP}$ = 17.8 Hz, $^3J_{CP}$ = 6.2 Hz, *C*H$_{2, \text{PCy2, C1}}$), 39.6 (dd, $^1J_{CP}$ = 46.5 Hz, $^3J_{CP}$ = 6.3 Hz, *C*H$_{2, \text{PCy3, C1}}$), 35.0 (d, $^2J_{CP}$ = 24.8 Hz, *C*H$_{2, \text{PCy2, C2}}$), 32.1 (d, $^2J_{CP}$ = 3.6 Hz, *C*H$_{2, \text{PCy2, C2}}$), 29.5 (d, $^3J_{CP}$ = 15.4 Hz, *C*H$_{2, \text{PCy2, C3}}$), 29.3 (dd, $^2J_{CP}$ = 5.8 Hz, $^4J_{CP}$ = 3.6 Hz, *C*H$_{2, \text{PCy3, C2}}$), 29.0 (d, $^3J_{CP}$ = 4.3 Hz, *C*H$_{2, \text{PCy2, C3}}$), 28.2 (d, $^3J_{CP}$ = 10.4 Hz, *C*H$_{2, \text{PCy3, C3}}$), 27.6 (*C*H$_{2, \text{PCy2, C4}}$), 26.9 (*C*H$_{2, \text{PCy3, C4}}$), 24.1 (*C*H$_{3, \text{Mes, ortho}}$), 21.0 (*C*H$_{3, \text{Mes, para}}$), 14.5 (dd, $^1J_{CP}$ = 103.4 Hz, $^1J_{CP}$ = 30.2 Hz, P-*C*-P). ^{31}P {^{1}H} NMR (162 MHz, C_6D_6) δ 13.8 (d, $^2J_{PP}$ = 145.3 Hz, *P*Cy_3), 6.1 (d, $^2J_{PP}$ = 145.3 Hz, *P*Cy_2). CHNS: Anal. calc. For $C_{40}H_{66}P_2$: C 78.90, H 10.93; found: C 78.68, H 10.88. IR (ATR): 2922 (s), 2849 (m), 1444 (m), 1262 (w), 1216 (w), 1202 (w), 1154 (w), 1105 (w), 1071 (w), 1048 (w), 1005 (w), 969 (s), 942 (m), 897 (w), 883 (w), 870 (m), 851 (m), 808 (w), 742 (w), 730 (m), 693 (w), 569 (m), 519 (w), 502 (w). m.p.: 177.0 – 181.5 °C.

Synthesis of L2·AuCl. To ligand **L2** (150 mg, 0.27 mmol, 1.05 eq.) and (THT)AuCl (82.7 mg, 0.26 mmol, 1 eq.), 5 mL of pentane was added. The suspension was stirred for 3 days at room temperature. The solid was filtered and washed with 5 mL of pentane. The solid was dried at 50°C with an oil bath *in vacuo*. The product was obtained as a colorless solid (116 mg, 0.14 mmol, 55 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C*H*$_{\text{Tol, ortho'}}$), 7.20 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C*H*$_{\text{Tol, meta}}$), 7.10 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C*H*$_{\text{Tol, meta'}}$), 7.02 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C*H*$_{\text{Tol, para}}$), 2.56 – 2.85 (m, 3H, C*H*$_{, \text{PCy3, H1}}$), 2.50 (s, 3H, C*H*$_3$), 2.41 – 2.32 (m, 1H, C*H*$_{2, \text{PCy2, H2}}$), 2.32 – 2.23 (m, 1H, C*H*$_{2, \text{PCy2, H2}}$), 2.17 – 2.00 (m, 6H, C*H*$_{2, \text{PCy3, H2}}$), 1.99 – 1.41 (m, 26H, C*H*$_{2, \text{PCy3, H2} + \text{H3} + \text{H4} + \text{PCy2, H2} + \text{H3} + \text{H4}}$ + C*H*$_{, \text{PCy2, H1}}$), 1.35 – 1.02 (m, 18H, C*H*$_{2, \text{PCy3, H3} + \text{H4} + \text{PCy2, H2} + \text{H3} + \text{H4}}$). ^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2) δ 143.7 (dd, $^3J_{CP}$ = 5.7 Hz, $^3J_{CP}$ = 2.9 Hz, *C*$_{\text{Tol, ortho}}$), 140.9 (d, $^3J_{CP}$ = 2.6 Hz, *C*H$_{\text{Tol, ortho'}}$), 139.5 (dd, $^2J_{CP}$ = 4.8 Hz, $^2J_{CP}$ = 3.0 Hz, *C*$_{\text{Tol, ipso}}$), 131.4 (dd, $^4J_{CP}$ = 1.9 Hz, $^4J_{CP}$ = 1.9 Hz, *C*H$_{\text{Tol, meta}}$), 126.9 (d, $^5J_{CP}$ = 2.2 Hz, $^5J_{CP}$ = 2.2 Hz, *C*H$_{\text{Tol, para}}$), 125.3 (dd, $^4J_{CP}$ = 2.3 Hz, $^4J_{CP}$ = 2.3 Hz, *C*H$_{\text{Tol, meta'}}$), 42.0 (d, $^1J_{CP}$ =37.0 Hz, *C*H$_{, \text{PCy2, C1}}$), 40.5 (dd, $^1J_{CP}$ = 38.8 Hz, $^3J_{CP}$ = 3.8 Hz, *C*H$_{, \text{PCy2, C1}}$), 38.4 (dd, $^1J_{CP}$ = 47.7 Hz, $^3J_{CP}$ = 1.8 Hz, *C*H$_{, \text{PCy3, C1}}$), 34.1 (d, $^2J_{CP}$ = 2.5 Hz, *C*H$_{2, \text{PCy2, C2}}$), 34.0 (d, $^2J_{CP}$ = 2.8 Hz, *C*H$_{2, \text{PCy2, C2}}$), 31.2 (*C*H$_{2, \text{PCy2, C2}}$), 30.6 (*C*H$_{2, \text{PCy2, C2}}$), 29.6 (dd, $^2J_{CP}$ = 8.7 Hz, $^4J_{CP}$ = 3.3 Hz, *C*H$_{2, \text{PCy3, C2}}$), 28.5 (d, $^3J_{CP}$ = 13.8 Hz, *C*H$_{2, \text{PCy2, C3}}$), 28.2 (d, $^3J_{CP}$ = 11.4 Hz, *C*H$_{2, \text{PCy3, C3}}$), 28.0 – 27.6 (m, *C*H$_{2, \text{PCy2, C3}}$), 26.9 – 26.4 (m, *C*H$_{2, \text{PCy3, C4} + \text{PCy2, C4}}$), 22.7 (*C*H$_3$), 14.8 (dd, $^1J_{CP}$ = 97.8 Hz, $^1J_{CP}$ = 60.4 Hz). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2) δ 34.4 (d, $^2J_{PP}$ = 60.5 Hz, *P*Cy_3), 25.7 (d, $^2J_{PP}$ = 60.5 Hz, *P*Cy_2). Anal. calc. For $C_{38}H_{62}P_2ClAu$: C 56.12, H 7.68; found: C 55.63, H 7.82. IR(ATR): 2917 (s), 2846 (s), 1739 (s), 1447 (s), 1365 (m), 1228 (s), 1217 (s), 1205 (s), 1108 (w), 1009 (s), 990 (s), 919 (m), 888 (s), 846 (m), 738 (m), 729 (m), 545 (s), 510 (m). m.p.: 214.1 – 219.3 °C (decomposition).

Synthesis of L3·AuCl. To ligand **L3** (70 mg, 1.05 eq., 0.12 mmol) and (THT)AuCl (35.1 mg, 1 eq., 0.11 mmol), 5 mL of THF was added and the colorless suspension was stirred for 2 days at room temperature. To the solution, toluene (5 mL) was added and the suspension was stirred for another 30 min. The resulting solid was filtered and washed with pentane (3 x 5 mL) to yield the gold complex as a colorless solid (50 mg, 0.06 mmol, 54 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.88 (s, 2H, C*H*$_{, \text{Mes, meta}}$), 2.75 – 2.52 (m, 3H, C*H*$_{, \text{PCy3, H1}}$), 2.51 (s, 6H, C*H*$_{3, \text{Mes, para}}$), 2.41 – 2.24 (m, 8H, C*H*$_{2, \text{PCy3, H2}}$ + C*H*$_{2, \text{PCy2, H2}}$), 2.22 (s, 3H, C*H*$_{3, \text{Mes, para}}$), 1.96 – 1.84 (m, 2H, C*H*$_{, \text{PCy2, H1}}$), 1.90 – 1.73 (m, 9H, C*H*$_{2, \text{PCy3, H3} + \text{H4}}$), 1.73 – 1.65 (m, 4H, C*H*$_{2, \text{PCy2, H3} + \text{H4}}$), 1.64 – 1.53 (m, 4H, C*H*$_{2, \text{PCy2, H3} + \text{H4}}$), 1.52 – 1.38 (m, 2H, C*H*$_{2, \text{PCy2, H2}}$), 1.36 – 1.00 (m, 23H, C*H*$_{2, \text{PCy3, H2} + \text{H3} + \text{H4}}$ + C*H*$_{2, \text{PCy2, H2} + \text{H3}}$). ^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2) δ 145.6 – 142.7 (m, *C*$_{, \text{Mes, ortho}}$), 137.6 – 136.3 (m, *C*$_{, \text{Mes, ipso}}$), 136.2 – 135.5 (m, *C*$_{, \text{Mes, para}}$), 129.7 (t, $^3J_{CP}$ = 2.1 Hz, *C*H$_{, \text{Mes, meta}}$), 40.5 (dd, $^1J_{CP}$ = 37.0 Hz, $^3J_{CP}$ = 1.7 Hz, *C*H$_{, \text{PCy2, C1}}$), 40.4 – 38.7 (br, *C*H$_{, \text{PCy3, C1}}$), 35.4 (d, $^2J_{CP}$ = 3.9 Hz, *C*H$_{2, \text{PCy2, C2}}$), 30.5 (*C*H$_{2, \text{PCy2, C2}}$), 29.6 (*C*H$_{2, \text{PCy3, C2}}$), 28.3 (d, $^3J_{CP}$ = 14.4 Hz, *C*H$_{2, \text{PCy2, C3}}$), 28.0 (d, $^3J_{CP}$ = 11.0 Hz, *C*H$_{2, \text{PCy3, C3}}$), 27.8 (d, $^3J_{CP}$ = 11.3 Hz, *C*H$_{2, \text{PCy2, C3}}$), 26.7 (d, $^4J_{CP}$ = 1.6 Hz, *C*H$_{2, \text{PCy2, C4}}$), 26.6 (d, $^4J_{CP}$ = 1.7 Hz, *C*H$_{2, \text{PCy3, C4}}$), 24.3 (d,

$^4J_{CP}$ = 1.5 Hz, $CH_{3,\ Mes,\ ortho}$), 20.8 ($CH_{3,\ Mes,\ para}$), 12.5 (dd, $^1J_{CP}$ = 99.5 Hz, $^1J_{CP}$ = 62.3 Hz, P-*C*-P). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2) δ 37.5 (d, $^2J_{PP}$ = 64.7 Hz, *P*Cy$_3$), 22.2 (d, $^2J_{PP}$ = 64.7 Hz, *P*Cy$_2$). Anal. calc. For $C_{40}H_{66}P_2ClAu$: C: 57.10, H: 7.94. Measured: C: 57.37, H: 7.95. IR (ATP): 2922 (s), 2849 (m), 1444 (m), 1323 (w), 1268 (w), 1198 (m), 1172 (w), 1108 (w), 1072 (w), 1004 (m), 1004 (s), 952 (m), 852 (s), 816 (w), 742 (m), 595 (m), 566 (m). m.p.: 224.5 – 227.8 °C (decomposition).

Preparation of L2·Pd(dba). 10.0 mg (0.02 mmol, 1 eq.) of ligand **L2** and 11.7 mg (0.02 mmol, 1 eq.) of Pd_2dba_3·dba was dissolved in 0.6 mL of THF-d_8 and shaken for 1 hour. The reaction progress was monitored by ^{31}P{^{1}H} NMR and applied for further applications. ^{1}H NMR (THF-d_8, 400 MHz): δ 7.95 – 6.80 (m, 34H, C*H*$_{,\ dba\ +\ Tol}$), 2.42 (s, 3H, C*H*$_3$), 2.37 – 2.16 (m, 3H, C*H*$_{,\ PCy3}$), 2.18 – 0.73 (m, 52H, C*H*$_{2,\ PCy3}$ + C*H*$_{,\ PCy2}$ + C*H*$_{2,\ PCy2}$). ^{31}P {^{1}H} NMR (162 MHz, THF-d_8) δ 25.2 (d, $^2J_{PP}$ = 89.4 Hz, *P*Cy$_3$), 22.6 (d, $^2J_{PP}$ = 89.4 Hz, *P*Cy$_2$).

Preparation of L3·Pd(dba). 10.0 mg (0.02 mmol, 1 eq.) of ligand **L3** and 11.2 mg (0.02 mmol, 1 eq.) of Pd_2dba_3·dba was dissolved in 0.6 mL of THF-d_8 and shaked for 19 hours. The reaction progress was monitored by ^{31}P{^{1}H} NMR spectroscopy and the solution applied in further reactions. ^{1}H NMR (THF-d_8, 400 MHz): δ 8.07 – 7.05 (m, 14H, C*H*$_{,\ dba}$), 6.79 (s, 2H, C*H*$_{,\ Mes,\ meta}$), 2.45 (s, 6H, C*H*$_{3,\ Mes,\ ortho}$), 2.15 (s, 3H, C*H*$_{3,\ Mes,\ para}$), 3.09 – 0.51 (m, 55H, C*H*$_{,\ PCy3}$ + C*H*$_{2,\ PCy3}$ + C*H*$_{,\ PCy2}$ + C*H*$_{2,\ PCy2}$),. ^{31}P {^{1}H} NMR (162 MHz, THF-d_8) δ 30.6 (d, $^2J_{PP}$ = 91.8 Hz, *P*Cy$_3$), 20.0 (d, $^2J_{PP}$ = 91.8 Hz, *P*Cy$_2$).

Procedure of the C–N Coupling Reaction Screening. A 5 mL vial with a rubber cap and stirring bar was charged with 142.2 mg (1.27 mmol, 1.5 eq.) of potassium *tert*-butoxide and 143.0 mg (0.85 mmol, 1.0 eq.) of 1,3,5-trimethoxy benzene (NMR standard) in the glovebox. Outside, 0.10 mL (107.0 mg, 1.0 eq.) of 4-chlorotoluene and 0.92 mmol (1.1 eq.) of a primary amine were added into the vial *via* syringe. The mixture was filled up to a volume of 4 mL with THF. A second vial was charged with 4.22 µmol (0.005 eq.) of ligand **L2** or **L3** and 2.88 mg (4.22 µmol, 0.005 eq.) of Pd_2dba_3·dba. 0.5 mL of THF was added to the vial and the mixture was stirred for 1 h (**L2**) or 16 h (**L3**). The catalyst solution was added into the first vial. For reaction monitoring, 0.1 mL of reaction solution was quenched with 0.1 mL of water after a certain period. After extraction, the organic phase was dried in a flow of pressurized air. The residue was dissolved in $CDCl_3$ and solution was filtered into an NMR tube to remove remaining salt.

Procedure for Compound Isolation. A *Schlenk* tube was charged with 712.5 mg (6.35 mmol, 1.5 eq.) of potassium *tert*-butoxide in the glovebox and 4.23 mmol (1.0 eq.) of the chloroarene and 4.62 mmol (1.1 eq.) of the primary amine were added into the tube. The mixture was filled up to 20 mL of THF. A 5 mL vial was charged in the glovebox with 12.9 mg (0.02 mmol, 0.005 eq.) of **L3** and 14.4 mg (0.02 mmol, 0.005 eq.) of Pd_2dba_3·dba. The catalyst mixture was dissolved in 2.5 mL of THF and stirred overnight at room temperature. The catalytic solution was added into the *Schlenk* tube. After 90 minutes of reaction time, the mixture was quenched with 5 mL of a saturated NaCl solution and poured into a separating funnel. To the mixture, 10 mL of ethyl acetate was added, and organic phase was extracted three times with 1 mL HCl (37 % solution) in 10 mL distilled water. The aqueous phases were combined, and the solution was neutralized with Na_2CO_3 until reaching pH = 8. Then the aqueous phase was extracted with three portions of 10 mL ethyl acetate. The organic phases were combined, and the solvent was removed *in vacuo*. The purity was checked by NMR, if not pure, the crude product was purified *via* column chromatography (4 g silica-packed weld column, 0-30 % EtOAc in hexane).

Isolation of 5aa. 403 mg (3.3 mmol, 79 %) of a yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19 – 6.88 (m, 2H), 6.76 – 6.37 (m, 2H), 3.77 – 3.47 (br, 1H, N*H*), 2.82 (s, 3H, C*H*$_{3,\ NMe}$), 2.25 (s, 3H, C*H*$_{3,\ Tol}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 147.3 (*C*$_{,\ Tol}$), 129.8 (*C*H$_{,\ Tol}$), 126.7 (*C*$_{,\ Tol}$), 112.8 (*C*H$_{,\ Tol}$), 31.3 (*C*H$_{3,\ NMe}$), 20.5 (*C*H$_{3,\ Tol}$). Spectral data obtained for the compound are in good agreement with the reported data.[21]

Isolation of 5ab. 570 mg (4.2 mmol, 99 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.00 (d, 2H, $^3J_{HH}$ = 8.3 Hz, C*H*$_{,\ Tol}$), 6.56 (d, 2H, $^3J_{HH}$ = 8.3 Hz, C*H*$_{,\ Tol}$), 3.62 – 3.29 (br, 1H, N*H*), 3.15 (q, 2H, $^3J_{HH}$ = 7.2 Hz, C*H*$_{2,\ NEt}$), 2.25 (s, 3H, C*H*$_{3,\ Tol}$), 1.26 (t, 3H, $^3J_{HH}$ = 7.2 Hz, C*H*$_{3,\ NEt}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 146.3 (*C*$_{,\ Tol}$), 129.8 (*C*H$_{,\ Tol}$), 126.6 (*C*$_{,\ Tol}$), 113.1 (*C*H$_{,\ Tol}$), 39.0 (*C*H$_{2,\ NEt}$), 20.5 (*C*H$_{3,\ Tol}$), 15.1 (*C*H$_{3,\ NEt}$). Spectral data obtained for the compound are in good agreement with the reported data.[22]

Isolation of 5ac. 685 mg (4.2 mmol, 99 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.01 (d, 2H, $^3J_{HH}$ = 8.5 Hz, C*H*$_{,\ Tol}$), 6.56 (d, 2H, $^3J_{HH}$ = 8.5 Hz, C*H*$_{,\ Tol}$), 3.61 – 3.38 (br, 1H, N*H*), 3.11 (t, 2H, $^3J_{HH}$ = 7.1 Hz, C*H*$_{2,\ Bu}$), 2.27 (s, 3H, C*H*$_{3,\ Tol}$), 2.02 – 1.54 (m, 2H, C*H*$_{3,\ NBu}$), 1.53 – 1.27 (m, 2H, C*H*$_{2,\ NBu}$), 1.12 – 0.82 (m, 3H, C*H*$_{3,\ NBu}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 146.4 (*C*$_{,\ Tol}$), 129.8 (*C*H$_{,\ Tol}$), 126.4 (*C*$_{,\ Tol}$), 113.0 (*C*H$_{,\ Tol}$), 44.2 (*C*H$_{2,\ Bu}$), 31.9 (*C*H$_{2,\ Bu}$), 20.5 (*C*H$_{2,\ Bu}$), 20.4 (*C*H$_{3,\ Tol}$), 14.0 (*C*H$_{3,\ Bu}$). Spectral data obtained for the compound are in good agreement with the reported data.[23]

Isolation of 5ad. 561 mg (3.8 mmol, 89 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.99 (d, 2H, $^3J_{HH}$ = 8.1 Hz, C*H*$_{,\ Tol}$), 6.53 (d, 2H, $^3J_{HH}$ = 8.1 Hz, C*H*$_{,\ Tol}$), 3.61 (sept, 1H, $^3J_{HH}$ = 6.3 Hz, C*H*$_{,\ PiPr}$), 3.32 – 3.03 (br, 1H, N*H*), 2.24 (s, 3H, C*H*$_{3,\ Tol}$), 1.21 (d, 6H, $^3J_{HH}$ = 6.3 Hz, C*H*$_{3,\ NiPr}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 145.4 (*C*$_{,\ Tol}$), 129.9 (*C*H$_{,\ Tol}$), 126.4 (*C*$_{,\ Tol}$), 113.7 (*C*H$_{,\ Tol}$), 44.7 (*C*H$_{,\ iPr}$), 23.2 (*C*H$_{3,\ iPr}$), 20.5 (*C*H$_{3,\ Tol}$). Spectral data obtained for the compound are in good agreement with the reported data.[24]

Isolation of 5ae. 805 mg (4.1 mmol, 97 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 – 7.34 (m, 4H, C*H*$_{,\ NBz}$), 7.33 – 7.27 (m, 1H, C*H*$_{,\ NBz}$), 7.02 (d, 2H, $^3J_{HH}$ = 8.2 Hz, C*H*$_{,\ Tol}$), 6.60 (d, 2H, $^3J_{HH}$ = 8.2 Hz, C*H*$_{,\ Tol}$), 4.34 (s, 2H, C*H*$_{2,\ NBz}$), 4.05 – 3.89 (br, 1H, N*H*), 2.27 (s, 3H, C*H*$_{3,\ Tol}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 146.0 (*C*$_{,\ Tol}$), 139.7 (*C*$_{,\ NBz}$), 129.8 (*C*H$_{,\ Tol}$), 128.6 (*C*H$_{,\ NBz}$), 127.5 (*C*H$_{,\ NBz}$), 127.2 (*C*H$_{,\ NBz}$), 126.8 (*C*$_{,\ Tol}$), 113.1 (*C*H$_{,\ Tol}$), 48.7 (*C*H$_{2,}$

NBz), 20.4 (*C*H$_{3,\ Tol}$). Spectral data obtained for the compound are in good agreement with the reported data.[25]

Isolation of 5ba. 475 mg (3.9 mmol, 93 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 – 7.13 (m, 1H, C*H*$_{,\ Tol}$), 7.13 – 6.93 (m, 1H, C*H*$_{,\ Tol}$), 6.79 – 6.65 (m, 1H, C*H*$_{,\ Tol}$), 6.65 – 6.58 (m, 1H, C*H*$_{,\ Tol}$), 3.93 – 3.58 (br, 1H, N*H*), 2.90 (s, 3H, C*H*$_{3,\ NMe}$), 2.15 (s, 3H, C*H*$_{3,\ Tol}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 147.3 (*C*$_{,\ Tol}$), 130.1 (*C*H$_{,\ Tol}$), 127.3 (*C*H$_{,\ Tol}$), 122.1 (*C*$_{,\ Tol}$), 117.1 (*C*H$_{,\ Tol}$), 109.4 (*C*H$_{,\ Tol}$), 31.0 (*C*H$_{3,\ NMe}$), 17.5 (*C*H$_{3,\ Tol}$). Spectral data obtained for the compound are in good agreement with the reported data.[26]

Isolation of 5bb. 350 mg (2.6 mmol, 61 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.14 (m, 1H, C*H*$_{,\ Tol}$), 7.07 (m, 1H, C*H*$_{,\ Tol}$), 6.78 – 6.60 (m, 2H, C*H*$_{,\ Tol}$), 3.66 – 3.30 (br, 1H, N*H*), 3.22 (q, $^3J_{HH}$ = 7.1 Hz, 2H, C*H*$_{2,\ NEt}$), 2.15 (s, 3H, C*H*$_{3,\ Tol}$), 1.32 (t, $^3J_{HH}$ = 7.1 Hz, 3H, C*H*$_{3,\ NEt}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 146.5 (*C*$_{,\ Tol}$), 130.2 (*C*H$_{,\ Tol}$), 127.3 (*C*H$_{,\ Tol}$), 121.9 (*C*$_{,\ Tol}$), 116.9 (*C*H$_{,\ Tol}$), 109.8 (*C*H$_{,\ Tol}$), 38.6 (*C*H$_{2,\ NEt}$), 17.6 (*C*H$_{3,\ Tol}$), 15.1 (*C*H$_{3,\ NEt}$). Spectral data obtained for the compound are in good agreement with the reported data.[22]

Isolation of 5ca. Reaction was performed with 25.8 mg (0.04 mmol, 0.01 eq.) of L3 and 28.8 mg (0.04 mmol, 0.01 eq.) of Pd_2dba_3·dba. 683 mg (4.1 mmol, 97 %) of a dark-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.89 (t, $^4J_{HH}$ = 2.2 Hz, 1H, C*H*$_{,\ arom,\ para}$), 5.81 (d, $^4J_{HH}$ = 2.2 Hz, 2H, C*H*$_{,\ arom,\ ortho}$), 3.93 – 3.79 (br, 1H, N*H*), 3.76 (s, 6H, C*H*$_{3,\ OMe}$), 2.81 (s, 3H, C*H*$_{3,\ NMe}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 161.9 (*C*$_{,\ arom}$), 151.3 (*C*$_{,\ arom}$), 91.5 (*C*H$_{,\ arom,\ ortho}$), 89.9 (*C*H$_{,\ arom,\ para}$), 55.3 (O*C*H$_3$), 30.9 (NH*C*H$_3$). Spectral data obtained for the compound are in good agreement with the reported data.[27]

Isolation of 5cb. Reaction was performed with 25.8 mg (0.04 mmol, 0.01 eq.) of **L3** and 28.8 mg (0.04 mmol, 0.01 eq.) of Pd_2dba_3·dba. 637 mg (3.5 mmol, 83 %) of a dark-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.88 (t, $^4J_{HH}$ = 2.2 Hz, 1H, C*H*$_{,\ arom,\ para}$), 5.81 (d, $^4J_{HH}$ = 2.2 Hz, 2H, C*H*$_{,\ arom,\ ortho}$), 3.79 – 3.71 (br, 1H, N*H*), 3.75 (s, 6H, C*H*$_{3,\ OMe}$), 3.13 (q, $^3J_{HH}$ = 7.1 Hz, 2H, C*H*$_{2,\ NEt}$), 1.24 (t, $^3J_{HH}$ = 7.1 Hz, 3H, C*H*$_{3,\ NEt}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 161.9 (*C*$_{,\ arom}$), 150.4 (*C*$_{,\ arom}$), 91.8 (*C*H$_{,\ arom,\ ortho}$), 89.8 (*C*H$_{,\ arom,\ para}$), 55.3 (*C*H$_{3,\ OMe}$), 38.7 (*C*H$_{2,\ NEt}$), 14.9 (*C*H$_{3,\ NEt}$). Spectral data obtained for the compound are in good agreement with the reported data.[28]

Isolation of 5db. 630 mg (3.6 mmol, 84 %) of a redish oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 – 7.17 (m, 2H, CH$_{,\ arom}$), 6.63 – 6.55 (m, 2H, CH$_{,\ arom}$), 4.05 – 3.40 (br, 1H, NH), 3.15 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH$_{2,\ NEt}$), 1.29 (s, 9H, CH$_{3,\ tBu}$), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_{3,\ NEt}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 146.2 (C$_{,\ arom}$), 140.3 (C$_{,\ arom}$), 126.1 (CH$_{,\ arom}$), 112.8 (CH$_{,\ arom}$), 39.0 (CH$_{2,\ NEt}$), 34.0 (C$_{,\ tBu}$), 31.7 (CH$_{3,\ tBu}$), 15.1 (CH$_{3,\ NEt}$). Spectral data obtained for the compound are in good agreement with the reported data.[29]

Isolation of 5ea. 806 mg (4.1 mmol, 97 %) of a light-yellow oil, which crystallized upon standing over night. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 – 7.37 (m, 2H, C*H*$_{,\ arom}$), 7.37 – 7.29 (m, 3H, C*H*$_{,\ arom}$), 7.25 – 7.16 (m, 1H, C*H*$_{,\ arom}$), 6.92 – 6.58 (m, 2H, C*H*$_{,\ arom}$), 4.09 – 3.78 (br, 1H, N*H*), 2.95 (s, 3H, C*H*$_{3,\ NMe}$), 2.04 (s, 3H, C*H*$_{3,\ Me}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 147.6 (*C*$_{,\ arom}$), 142.8 (*C*$_{,\ arom}$), 142.6 (*C*$_{,\ arom}$), 129.6 (*C*H$_{,\ arom}$), 128.1 (*C*H$_{,\ arom}$), 126.7 (*C*H$_{,\ arom}$), 126.5 (*C*H$_{,\ arom}$), 119.5 (*C*$_{,\ arom}$), 119.2 (*C*H$_{,\ arom}$), 108.4 (*C*H$_{,\ arom}$), 31.2 (*C*H$_{3,\ NMe}$), 14.3 (*C*H$_{3,\ Me}$). Anal. calc. For $C_{14}H_{15}N$: C 85.24, H 7.66, N 7.10; found: C 85.12, H 7.67, N 7.18. IR(ATR): 3445 (w), 3051 (w), 2993 (w), 2905 (w), 2819 (w), 1904 (w), 1587 (m), 1570 (m), 1511 (m), 1490 (m), 1470 (s), 1441 (m), 1428 (m), 1377 (w), 1324 (m), 1287 (s), 1193 (m), 1167 (m), 1121 (w), 1072 (m), 1057 (m), 1028 (m), 1000 (m), 986 (m), 920 (w), 845 (w), 803 (w), 789 (s), 759 (s), 720 (s), 703 (s), 609 (m). m.p.: 56.6 – 58.3 °C.

Isolation of 5fa. 653 mg (4.2 mmol, 98 %) of a dark-brown oil were isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 – 7.75 (m, 2H, C*H*$_{,\ arom}$), 7.51 – 7.34 (m, 3H, C*H*$_{,\ arom}$), 7.30 – 7.22 (m, 1H, C*H*$_{,\ arom}$), 6.75 – 6.40 (m, 1H, C*H*$_{,\ arom}$), 4.62 – 4.46 (br, 1H, N*H*), 3.04 (s, 3H, C*H*$_{3,\ NMe}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 144.6 (*C*$_{,\ arom}$), 134.4 (*C*$_{,\ arom}$), 128.8 (*C*H$_{,\ arom}$), 126.8 (*C*H$_{,\ arom}$), 125.8 (*C*H$_{,\ arom}$), 124.8 (*C*H$_{,\ arom}$), 123.6 (*C*$_{,\ arom}$), 119.9 (*C*H$_{,\ arom}$), 117.5 (*C*H$_{,\ arom}$), 104.0 (*C*H$_{,\ arom}$), 31.2 (*C*H$_{3,\ NMe}$). Spectral data obtained for the compound are in good agreement with the reported data.[30]

Isolation of 5ga. Reaction was performed with 25.8 mg (0.04 mmol, 0.01 eq.) of **L3** and 28.8 mg (0.04 mmol, 0.01 eq.) of Pd_2dba_3·dba. 543 mg (4.0 mmol, 94 %) of a dark-yellow oil were isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.86 – 6.76 (m, 2H, C*H*$_{,\ arom}$), 6.65 – 6.57 (m, 2H, C*H*$_{,\ arom}$), 3.75 (s, 3H, C*H*$_{3,\ OMe}$), 3.73 – 3.26 (br, 1H, N*H*), 2.81 (s, 3H, C*H*$_{3,\ NMe}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 152.3 (*C*$_{,\ arom}$), 143.7 (*C*$_{,\ arom}$), 115.1 (*C*H$_{,\ arom}$), 113.9 (*C*H$_{,\ arom}$), 56.0 (*C*H$_{3,\ OMe}$), 31.8 (*C*H$_{3,\ NMe}$). Spectral data obtained for the compound are in good agreement with the reported data.[31]

Isolation of 5gb. Reaction was performed with 25.8 mg (0.04 mmol, 0.01 eq.) of **L3** and 28.8 mg (0.04 mmol, 0.01 eq.) of Pd_2dba_3·dba. 532 mg (3.5 mmol, 83 %) of a dark-yellow oil were isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.83 – 6.74 (m, 2H, C*H*$_{,\ arom}$), 6.64 – 6.55 (m, 2H, C*H*$_{,\ arom}$), 3.75 (s, 3H, C*H*$_{3,\ OMe}$), 3.50 – 3.33 (br, 1H, N*H*), 3.12 (q, $^3J_{HH}$ = 7.1 Hz, 2H, C*H*$_{2,\ NEt}$), 1.24 (t, $^3J_{HH}$ = 7.1 Hz, 3H, C*H*$_{3,\ NEt}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 152.3 (*C*$_{,\ arom}$), 142.8 (*C*$_{,\ arom}$), 115.0 (*C*H$_{,\ arom}$), 114.3 (*C*H$_{,\ arom}$), 56.0 (*C*H$_{3,\ OMe}$), 39.7 (*C*H$_{2,\ NEt}$), 15.1 (*C*H$_{3,\ NEt}$). Spectral data obtained for the compound are in good agreement with the reported data.[22]

Isolation of 5hb: Reaction was performed with 25.8 mg (0.04 mmol, 0.01 eq.) of **L3** and 28.8 mg (0.04 mmol, 0.01 eq.) of Pd_2dba_3·dba. 445 mg (3.2 mmol, 76 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.94 – 6.83 (m, 2H, C*H*$_{,\ arom}$), 6.59 – 6.49 (m, 2H, C*H*$_{,\ arom}$), 3.62 – 3.36 (br, 1H, N*H*), 3.12 (q, $^3J_{HH}$ = 7.1 Hz, 2H, C*H*$_{2,\ NEt}$), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3H, C*H*$_{3,\ NEt}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 155.9 (d, $^1J_{CP}$ = 234.5 Hz, *C*$_{,\ arom}$), 144.9 (*C*$_{,\ arom}$), 115.8 (d, J_{CF} = 22.3 Hz, *C*H$_{,\ arom}$), 113.7 (d, J_{CF} = 7.4 Hz, *C*H$_{,\ arom}$), 39.3 (*C*H$_{2,\ NEt}$), 15.0 (*C*H$_{3,\ NEt}$). Spectral data obtained for the compound are in good agreement with the reported data.[32]

Isolation of 5ib. Reaction was performed with 25.8 mg (0.04 mmol, 0.01 eq.) of **L3** and 28.8 mg (0.04 mmol, 0.01 eq.) of Pd_2dba_3·dba. 241 mg (1.7 mmol, 41 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06

– 6.91 (m, 2H, C*H*, arom), 6.76 – 6.66 (m, 1H, C*H*, arom), 6.65 – 6.55 (m, 1H, C*H*, arom), 3.84 – 3.74 (br, 1H, N*H*), 3.19 (q, $^3J_{HH}$ =, 2H, CH_2, NEt), 1.29 (t, $^3J_{HH}$ =, 3H, CH_3, NEt). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 151.7 (d, $^1J_{CF}$ = 238.0 Hz, *C*, arom), 137.1 (d, J_{CF} = 11.5 Hz, *C*, arom), 124.7 (d, J_{CF} = 3.4 Hz, *C*H, arom), 116.5 (d, J_{CF} = 7.0 Hz, *C*H, arom), 114.4 (d, J_{CF} = 18.4 Hz, *C*H, arom), 112.1 (d, J_{CF} = 3.6 Hz, *C*H, arom), 38.3 (*C*H_2, NEt), 15.0 (*C*H_3, NEt). Spectral data obtained for the compound are in good agreement with the reported data.[32]

Isolation of 5ja. Reaction was performed with 25.8 mg (0.04 mmol, 0.01 eq.) of **L3** and 28.8 mg (0.04 mmol, 0.01 eq.) of Pd_2dba_3·dba. 405 mg (3.7 mmol, 89 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (dd, 1H, J_{HH} = 5.1 Hz, J_{HH} = 1.9 Hz, *C*H, arom), 7.43 (ddd, 1H, J_{HH} = 8.7 Hz, J_{HH} = 7.1 Hz, J_{HH} = 1.9 Hz, *C*H, arom), 6.57 (dd, 1H, J_{HH} = 7.1 Hz, J_{HH} = 5.1 Hz, *C*H, arom), 6.38 (d, 1H, J_{HH} = 8.4 Hz, *C*H, arom), 4.65 – 4.33 (br, 1H, N*H*), 2.92 (d, 3H, $^3J_{HH}$ = 3.8 Hz, CH_3, NMe). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 159.6 (*C*H, arom), 148.1 (*C*H, arom), 137.4 (*C*H, arom), 112.7 (*C*H, arom), 106.2 (*C*H, arom), 29.1 (*C*H_3, NMe). Spectral data obtained for the compound are in good agreement with the reported data.[33]

Isolation of 5jb. 235 mg (3.3 mmol, 46 %) of a light-yellow oil was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (ddd, J_{HH} = 5.1 Hz, J_{HH} = 1.9 Hz, J_{HH} = 1.0 Hz, 1H, *C*H, arom), 7.38 (ddd, J_{HH} = 8.4 Hz, J_{HH} = 7.2 Hz, J_{HH} = 1.9 Hz, 1H, *C*H, arom), 6.52 (ddd, J_{HH} = 7.2 Hz, J_{HH} = 5.1 Hz, J_{HH} = 1.0 Hz, 1H, *C*H, arom), 6.34 (d, J_{HH} = 8.4 Hz, 1H, *C*H, arom), 4.79 – 4.41 (br, 1H, N*H*), 3.60 – 3.08 (m, 2H, CH_2, NEt), 1.22 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3, NEt). ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 159.0 (*C*, arom), 148.2 (*C*, arom), 137.4 (*C*H, arom), 112.7 (*C*H, arom), 106.4 (*C*H, arom), 36.9 (*C*H_2, NEt), 14.9 (*C*H_3, NEt). Spectral data obtained for the compound are in good agreement with the reported data.[34]

ASSOCIATED CONTENT

Supporting Information

Full analysis data for all new compounds, crystallographic details and copies of NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors have filed patent WO2019030304 covering the YPhos ligands and precatalysts discussed, which is held by UMICORE AG & Co. KG and products will be made commercially available from.

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