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(DiMeIHept^{Cl})Pd: A Low-Load Catalyst for Solvent-Free (Melt) Amination

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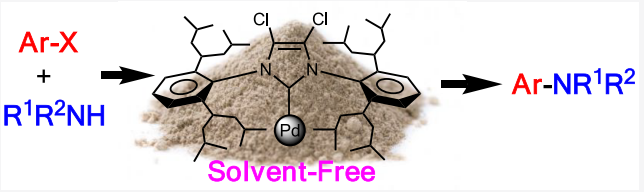
ABSTRACT: *(DiMeIHept^{Cl})Pd*, a hyper-branched N-aryl Pd NHC catalyst, has been shown to be efficient at performing amine arylation reactions in solvent-free ("melt") conditions. The highly lipophilic environment of the alkyl chains flanking the Pd center serves as lubricant to allow the complex to navigate through the paste-like environment of these mixtures. The protocol can be used on a multi-gram scale to make a variety of aniline derivatives, including substrates containing alcohol moieties.



INTRODUCTION

Organic solvents remain the major contributor to the E-Factor (Environmental Factor, defined as the ratio of the mass of waste generated per unit of product produced) for small-molecule, fine chemical manufacturing.[1,2] Perhaps the most straightforward approach to lowering solvent-related E-Factor is to eliminate reaction solvent altogether.[1,2] This technique has had some success in metal-catalyzed cross-coupling,[3−6] which encompasses a broad variety of bond-forming reactions that are widely employed in fine chemical synthesis. A reaction that is of particular interest in our group is metal-catalyzed amination.[7−13] In light of the intense interest in C−N bond formation in many different fine chemical sectors (e.g., pharmaceuticals, agrochemicals, electronics),[14] a number of teams have worked toward making this widely employed transformation solvent-free as there would be a notable impact on lowering the process's E-Factor.[15−31] In addition, performing reactions without solvent maximizes the reactants' concentration, hence the transformation rate.

By their nature, cross-coupling reactions contain significant amounts of solids. Bases, such as various metal carbonates or phosphates, and salt additives, such as LiBr, are generally solids and, in many cases, so too are the organic starting materials and/or products. Melts generally rely on at least one of the reagents being a liquid, thereby acting as the solvent/lubricant for the reaction. Even so, most reaction mixtures are more of a paste than a free-flowing liquid, which limits diffusion and slows or prevents/stalls transformations. This means that higher catalyst loads are necessary to ensure that there is some in all regions of the melt to drive the chemistry forward.[16,17,19−29] This serves to counteract the E-Factor gain associated with eliminating reaction solvent. From two articles[15,18] reporting 0.1 mol % Pd complex load for C−N coupling melt reactions, one explores the Pd(NHC) catalyst core,[15] which intersects with the work performed in our group.

Generally, NHC ligands are widely used and make Pd catalysis very efficient.[32−36] We reasoned that, if we could make the NHC suitably "greasy", it would improve its ability to migrate through the melt paste by creating its own liquid shell/environment in which coupling can occur. In this way, less catalyst could perform the same task as reactions with higher loads due to the enhanced mobility of the catalyst through the semi-solid matrix of the melt. Pd-*DiMeIHept^{Cl}* (Cl refers to the chlorines on the NHC (N-heterocyclic carbene) core), shown in Figure 1 in two precatalyst forms **1a** and **1b**, is decorated with eight isobutyl groups off the benzylic position of the N-aryl substituent on the NHC core, making it highly lipophilic. The Pd center is profoundly hindered, which will serve multiple purposes as a melt-catalyst candidate. The hindrance will ensure that the metal is primarily only ligated to the NHC, ensuring its high reactivity in oxidative addition and entering the amination catalytic cycle. Further, London dispersion interactions introduced by bulky alkyl chains about Pd(0) facilitate interaction with the oxidative addition partner[37] and help prevent catalyst death.[37,38] Taken together, these attributes stemming from the complex's dense placement of branched alkyl chains around the metal should reduce greatly the quantity of catalyst necessary for this purpose. Both **1a** and **1b** precatalysts were crystallized and characterized by SC-XRD (Figure 1 and the Supporting Information (SI)).

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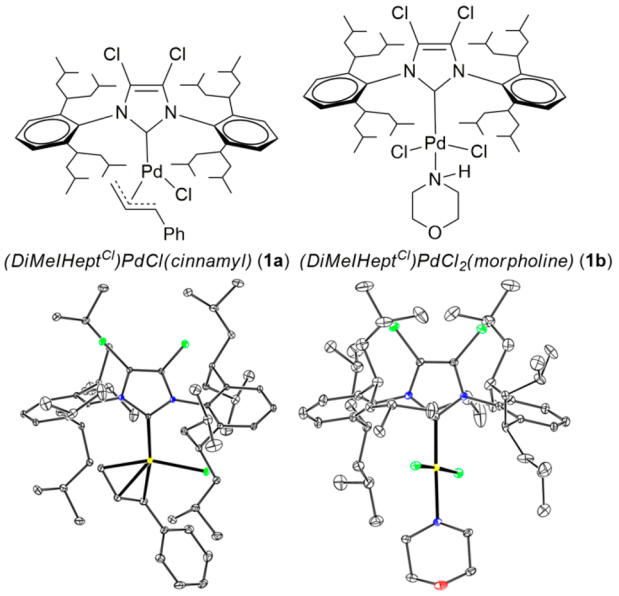
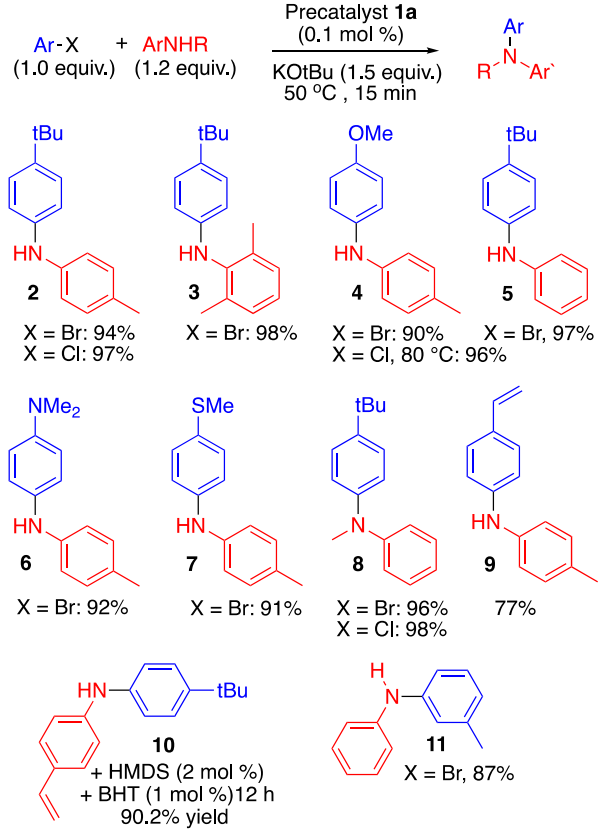


Figure 1. Structure of Pd precatalysts used in this study.

RESULTS AND DISCUSSION

We began our investigation with aniline nucleophiles employing 4-methylaniline (1.2 equiv) and 1-bromo-4-*tert*-butylbenzene as electrophile (product **2**, Table 1). With only 0.1 mol % of **1a**, the reaction was complete in just 15 min at 50 °C. These coupling conditions worked well with both aryl bromides and aryl chlorides, with only one example (**4**) working noticeably better at 80 °C. Compound **2** could be formed in 75 min at 0.01 mol % load of **1a**, or in 2 h at r.t. with 0.1 mol % load of **1a**, providing the initial mixture was well stirred. All results disclosed in this article were obtained with rigorous exclusion of air in a nitrogen-filled glovebox. We performed the transformation to prepare **2** under air and obtained the product in slightly lower yield (90%), but this was accompanied by some very minor air oxidation (see Experimental Section for details).

Table 1. Pd-Catalyzed Amination of Aryl Bromides and Chlorides with Aniline Nucleophiles under Melt Conditions Using (DiMeIHept^{Cl})Pd(cinnamyl)Cl (1a)[a]



[a]Yields are reported on material purified by column chromatography on silica gel or neutral alumina.

We next examined the coupling of aryl bromides to alkyl amines (**12**–**16**, Table 2). Although alkylamines are more nucleophilic, catalytic coupling also involves Pd(amine) deprotonation, which is faster for arylamines.[8,39] The latter effect must be dominating, as arylation of alkylamines in a melt required higher temperatures. We have found precatalyst **1b** was notably superior to **1a** under such conditions, although we have no concrete explanation for this at this time. Anilines (**17**–**20**, **22**), carbazole (**21**), and indole (**23**) also could be coupled effectively using **1b**. We examined representative aryl chlorides and found similar levels of conversion using NaOtAm as base, which helps suppress aryl ether[40,41] and phenol[42] formation. Further, coupling leading to TPD (*N*,*N*′-bis(3-mthylphenyl)-*N*,*N*′-diphenylbenzidine, compound **18**, Table 2) went well, which is of note due to the application of this compound in the hole transport layer of OLED devices.[43−46] In our experiments, we have found that KOtBu and NaOtBu were interchangeable for most reactions; only TPD (**18**) preparation required KOtBu as the reaction failed with NaOtBu. Coupling of styryl bromide with diarylamines is relevant for the manufacture of polymeric layers of photoelectronic devices;[47,48] in particular, the polymer containing the di(4-*tert*-butylphenyl)phenylamine group (as in compound **22**) was shown to be a p-type organic semiconductor and was employed to create a hole transport layer.[49] One can notice that coupling with diarylamines was performed either at 50 °C (**19**, **22**) or at 120 °C (**17**, **18**). Precatalyst **1b** was used for both cases, but at 50 °C, 0.1 mol % of **1b** gave maximum 60% conversion. To push the reaction further at 50 °C, we had to use 0.2 mol % of **1b**. An easy solution to this problem was to increase the reaction temperature; however, this was not tolerated by styrenes, which polymerized under these conditions.

We then explored the ability to couple the same aniline twice, i.e., diarylation (Scheme 1). Coupling leading to **24** with **1a** went very well, whereas, in the case of **22**, dicoupling proceeded to 51% yield. This reaction was complicated by competing Heck coupling of amino-styrenes with the bromoarene, and a similar result was observed on attempted coupling of **10** with 1-bromo-4-*tert*-butylbenzene.

Next, we thought it would be interesting to investigate the coupling of partners decorated with a reactive functional group. We have observed redox processes leading to formation of various products and we have found how this can be suppressed. The unwanted redox processes could be catalyzed by KOtBu, known to initiate SET reactions,[50,51] by a homogeneous Pd catalyst and heterogeneous elemental palladium. The latter is a product of Pd(NHC) complex decomposition[52] and was observed in our reaction mixtures after quenching. Elemental palladium is a known catalyst of transfer hydrogenation being able to extract hydrogen from all

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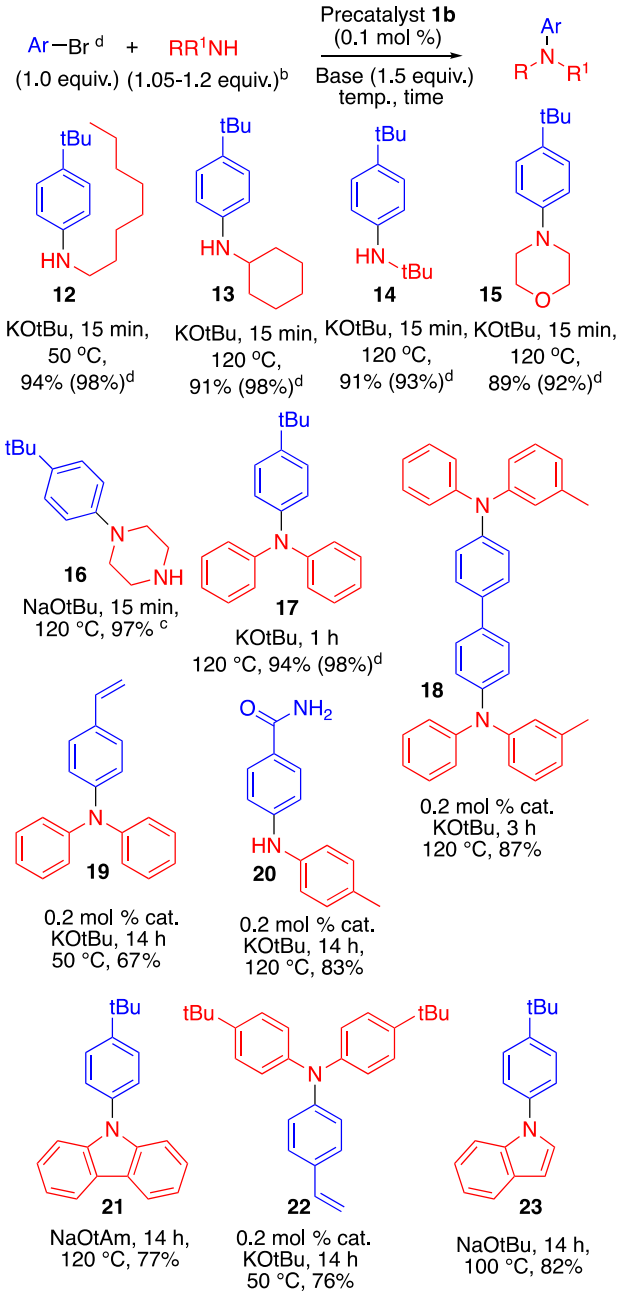
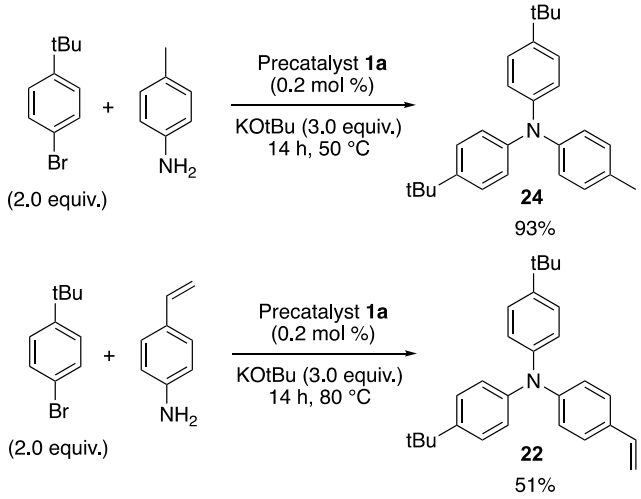
Table 2. Pd-Catalyzed Amination of Aryl Chlorides with Alkyl Amine, Aniline, and Heterocyclic Nucleophiles under Melt Conditions Using (DiMeIHept^{Cl})Pd(morpholine)Cl$_2$ (1b)[a]



[a]Yields are reported on material purified by column chromatography on silica gel, neutral alumina, or florisil. [b]For primary amines and aniline nucleophiles, 1.2 equiv of the amine is used. For secondary amine nucleophiles, 1.05 equiv of amine is used. [c]Four equivalents of piperazine was used. [d]Compounds **12**, **13**, **14**, **15**, and **17** were also prepared from 1-chloro-4-*tert*-butylbenzene under similar conditions (yields are given in brackets).

Scheme 1. Diarylations under Melt Conditions Using (DiMeIHept^{Cl})Pd(cinnamyl)Cl (1a)



available sources, thus oxidizing them, and transferring H_2 to other compounds.[53−55]

First, we considered aminations where the substrate had an acidic hydrogen to see if that posed any issues for the coupling under our melt conditions (Scheme 2). We performed three couplings of phenols, as both the oxidative addition partner (**25** and **26**) and the amine (**27**). Application of our standard coupling conditions resulted in formation of desired coupling products in low to modest yields, which was typically accompanied by the formation of redox-associated byproducts. The byproducts were identified by GC-MS to be N-aryl iminoquinones and biphenyls (derived from ArBr). As Pd complexes are known to be able to oxidize hydroquinones to quinones,[56] we suggest a similar oxidation of N-aryl-4-aminophenols could lead to N-aryl iminoquinones. The reduced compound in this case was the aryl bromide, which was partially transformed into the corresponding biphenyl. Another problem introduced by phenols is their nucleophilicity. In earlier experiments, we determined that O-nucleophiles slow this coupling when KOH or LiO*i*Pr was used as base. Deprotonation of phenol by KOtBu led to the same effect. We attribute slow coupling to the nucleophilic phenolate ion and coordinating N-aryl iminoquinone.

Our solution to this phenolate problem was addition of a Lewis acid. A common method to couple phenol-containing partners is with LiHMDS as base;[13,57] however, in melt conditions, this gave negligible yields. On the basis of the literature,[58−62] we propose that Lewis acids react with the phenol to form a neutral species of the type ArOAl(OAlk)$_2$ or ArOTi(OAlk)$_3$, thus masking nucleophilic phenolate and making oxidation to N-aryl iminoquinones impossible. On the other hand, Lewis acids could also promote reductive elimination.[63]

Coupling also proceeded nicely with benzyl alcohols (**28** and **29**). Benzyl alcohols are readily oxidized by Pd(II) complexes, which are intermediates of Pd-catalyzed C−N coupling.[64] In our standard reaction conditions, we observed the desired coupling product (2- or 4-(arylamino)benzyl alcohol), as well as its reduced (2- or 4-(arylamino)toluene) and oxidized (2- or 4-(arylamino)benzaldehyde) derivatives. The imine, formed *in situ* from excessive *o*-toluidine and 4-(*p*-tolylamino)benzaldehyde, was isolated and characterized (see the SI for details). Suppression of these unwanted side reactions was achieved by *in situ* O-silylation using a NaOtBu/HMDS mixture, thus making oxidation less favorable. Deprotection of the product happened on silica gel chromatography. Utilization of LiHMDS for this coupling was less efficient as the reaction initiated too fast and led to

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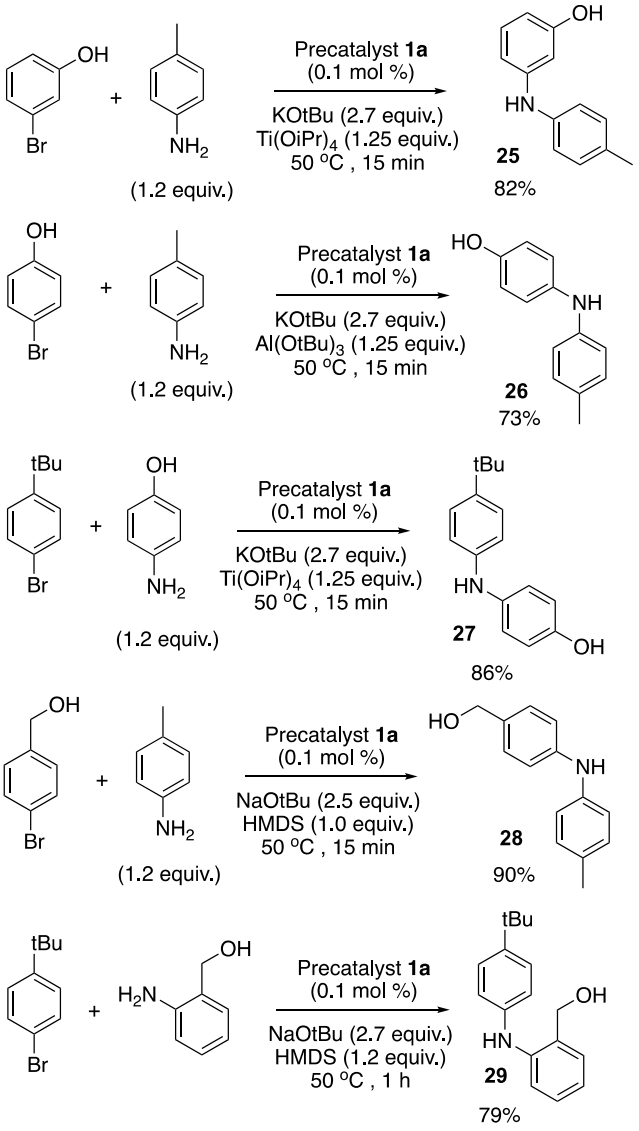
J. Org. Chem. 2021, 86, 10343−10359

Scheme 2. Coupling of Substrates Possessing OH Groups under Melt Conditions Using (DiMeIHept^{Cl})PdCl(cinnamyl) (1a)



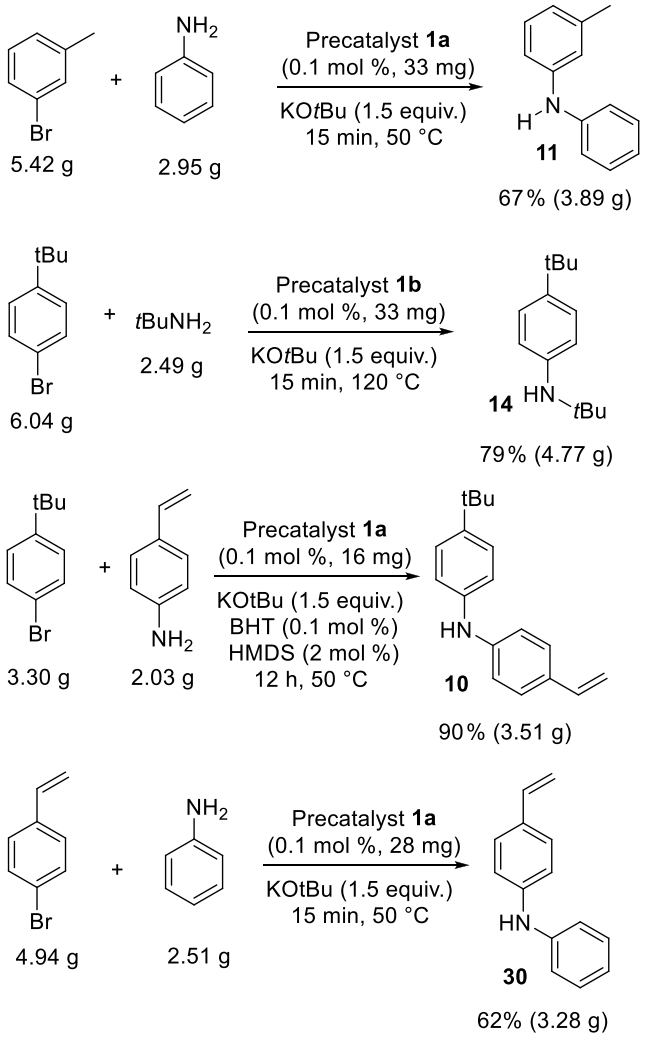
immediate cementation, making it impossible to push it to high conversion.

Finally, encouraged by the results above, we wanted to examine the scalability of this melt chemistry (Scheme 3). Conversion of the electrophile was quantitative when the crude product mixtures were assessed by ^{1}H NMR spectroscopy, and isolation provided multi-gram quantities of the target anilines. Compounds **11** and **14** were directly distilled from reaction mixtures, thus excluding any solvent usage though the whole synthetic procedure.

CONCLUSIONS

In summary, we have developed solvent-free (melt) amine arylation protocols to assemble aniline products using a hyperbranched Pd-NHC precatalyst [(DiMeIHept^{Cl})Pd) (**1**). The morpholine variant of this complex (**1b**) appears to tolerate higher temperatures associated with this procedure when compared to its π-allyl counterpart **1a**. The procedure accommodates aniline, alkylamine, carbazole, and indole nucleophiles, while being tolerant of both alkyl and aryl

Scheme 3. Multi-Gram Quantity Couplings under Melt Conditions Using (DiMeIHept^{Cl})PdCl(cinnamyl) (1a) or (DiMeIHept^{Cl})PdCl$_2$(morpholine) (1b)



alcohols in either coupling partner. The procedure is scalable to at least the multi-gram scale and was useful to prepare compounds of interest to a number of sectors including small molecule pharmaceutical, agrochemical, and materials (e.g., electronics) companies.

EXPERIMENTAL SECTION

General Information. Glovebox manipulations were performed in an MBraun Unilab glovebox under an atmosphere of dry nitrogen; to avoid static electrical effects on weighing powders, all vials were wrapped in aluminum foil. All reagents were purchased from Sigma-Aldrich, Alfa Aesar, Oakwood, AK Scientific, and Combi-Blocks and were used without further purification unless noted otherwise. The ligands for **1a** and **1b** were obtained from Total Synthesis Ltd., Toronto, Canada. All reaction vials and rare earth stir bars (egg shaped) were purchased from VWR. Analytical thin layer chromatography (TLC) was performed on 200 μm thick silica gel (Silicycle), or neutral alumina precoated aluminum plates, and spots were visualized with UV light (254 nm). Metal beads for the heating bath were purchased from Lab Armor. Preparative TLC (PTLC) was performed on Silicycle 20 × 20 cm plates with a 2 mm layer of 40−63 μm 60 Å silica gel, and bands were visualized with UV light (254 nm). Column chromatography purifications were carried out using Biotage Isolera or Biotage Isolera Four instruments on Santai iLOK-SL silica gel

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J. Org. Chem. 2021, 86, 10343−10359

(40−63 μm, 60 Å, 10 or 20 g), Santai iLOK neutral alumina (50−75 μm, 55 Å, 24 or 50 g), or Santali iLOK-SL neutral alumina (50−75 μm, 55 Å, 24 g) columns, observing UV absorption at 254 and 280 nm for fraction collection, unless noted otherwise.

NMR spectra were recorded on Bruker AVANCE III HD 500 or AVANCE III HD 600 spectrometers. No-D NMR spectra (using non-deuterated solvents in lock off conditions) were performed using proton gradient shimming on the most intensive solvent peak. Percent conversion was assessed either by ^{1}H NMR or quantitative ^{13}C{^{1}H} NMR spectroscopy by integration of products signals relative to those of residual starting material. Quantitative ^{13}C{^{1}H} NMR spectra were collected with inverse gated decoupling using a waltz65 decoupling pulse sequence; the 90° excitation pulse was followed by 1.1 s acquisition and 15 s relaxation (256 transients were collected). ^{1}H NMR spectra were internally referenced to TMS, ^{13}C{^{1}H} NMR spectra were internally referenced to the carbon signal(s) of the solvent, and ^{15}N NMR spectra were externally referenced to liquid ammonia (Bruker scale). The following abbreviations are used to describe peak multiplicities: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, spt = septet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, qd = quartet of doublets. For all isolated compounds, 2D NMR spectra (NOAH-BSC[65,66] where single FID is separated into ^{13}C−^{1}H HMBC, ^{13}C−^{1}H edited HSQC and ^{1}H−^{1}H COSY, ^{15}N−1H HMBC and ^{1}H−^{1}H NOESY for cases of separated spin systems) were collected to ensure atoms connectivity and identity of products; NMR peaks assignment was done with help of these 2D experiments.

All mono- and diarylamines presented in this article promote chloroform degradation by UV light or oxygen. Paramagnetic broadening of peaks in NMR spectra is not an indication of product poor quality. However, broadening can be avoided by using absolute $CDCl_3$ and protection of NMR samples from UV light (incl. sunlight), or by choosing a different solvent. Commercially available $CDCl_3$ was filtrated through basic alumina and stored in an amber-glass bottle over metallic silver; for most samples, this solvent gave excellent NMR spectra. In instances where poor spectra were obtained, $CDCl_3$ was degassed by bubbling nitrogen through it for 20 min, after which it was distilled over P_2O_5. Absolute $CDCl_3$ was stored over metallic silver in a light-protected Straus flask under nitrogen.

GC-MS analysis was performed on Agilent 6890N (GC) and 5975B (MS) instruments on an Agilent HP-5MS column (30 m × 0.250 mm, 0.25 μm film thickness).

High resolution mass spectrometry (HRMS) analysis was performed by the John L. Holmes Mass Spectrometry Facility at the University of Ottawa on Kratos Concept 2S (electron impact ionizer, magnetic sector analyzer) or Waters Global (electrospray ionizer, time-of-flight analyzer) instruments.

Elemental analysis was performed in Ján Veizer Stable Isotope Laboratory at the University of Ottawa on an Elementar Isotope Cube EA instrument. Silver capsules were used for halogen-containing compounds.

Single crystal X-ray data were collected on a Bruker KAPPA Apex II Diffractometer equipped with an Apex II CCD detector, using Mo Kα X-ray radiation. A single crystal of compound **1a** was grown by slow evaporation of toluene solution; a crystal of compound **1b** was grown by slow evaporation of pentane solution.

All solid reagents involved in melt reactions were ground in an agate mortar and stored in an inert atmosphere; only minor caking of these solids occurred on storage.

*[1,3-Bis[2,6-bis[3-methyl-1-(2-methylpropyl)butyl]phenyl]-4,5-dichloro-1,3-dihydro-2H-imidazol-2-ylidene]chloro[(1,2,3-η)-1-phenyl-2-propen-1-yl]palladium, [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**).* A 500 mL three-neck round-bottom flask equipped with a stir bar was flame-dried and cooled under nitrogen. To this were added NaO*t*Bu (1.19 g, 12.05 mmol), [(cinnamyl)PdCl]$_2$ (2.84 g, 5.30 mmol), and 1,3-bis(2,6-bis(2,6-dimethylheptan-4-yl)phenyl)-4,5-dichloro-1*H*-imidazol-3-ium chloride (8.0 g, 9.64 mmol). The flask was purged with argon, and dry THF (110 mL) was added. The mixture was placed in a preheated oil bath at 70 °C, stirred for 16 h, and then cooled to room temperature. Solvent was removed *in vacuo*, and the residue was redissolved in CH_2Cl_2 (20 mL). The mixture was then passed through a silica gel plug wetted with pentane, eluting with CH_2Cl_2 until the filtrate ran clear. The resulting orange solution was concentrated, and the solid was recrystallized from CH_2Cl_2 (minimal)/pentane using a rotavap. The precipitate was then isolated by filtration and washed with cold pentane. The recrystallization process was repeated twice more, or until no more solid could be isolated. The product was then dried under high vacuum to give a yellow solid (8.23 g, 81%).

Mp 190−191 °C (decomposition). δ 7.43 (t, J = 7.7 Hz, 2H, 4-CH), 7.30 (d, J = 7.7 Hz, 4H, 3-CH), 7.23 (m, 2H, 2-CH^{Ph}), 7.14−7.11 (m, 3H, indirectly assigned: 7.13 4-CH^{Ph}, 7.12 3-CH^{Ph}), 5.24 (m, 2-CH^{cinnamyl}), 4.61 (d, J = 13.2 Hz, 3-CH^{cinnamyl}), 2.82 (br s, 4H, 4′-CH), 1.82 (br s, 8H, 6′-CH and 5′-CH$_2$), 1.69 (br m, 8H, 3′-CH$_2$ and 5′-CH$_2$), 1.58 (br s, 4H, 2′-CH), 1.42 (m, 4H, 3′-CH$_2$), 0.96 (d, J = 6.2 Hz, 12H, 7′′-CH$_3$), 0.87 (d, J = 6.2 Hz, 12H, 7′-CH$_3$), 0.83 (d, J = 6.4 Hz, 12H, 1′′-CH$_3$), 0.79 (d, J = 6.4 Hz, 12H, 1′-CH$_3$) ppm, 1-CH$_2^{cinnamyl}$ is broadened to baseline; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 182.4 (CPd), 144.5 (2-C), 137.0 (1-C^{Ph}), 136.0 (1-C), 129.4 (4-CH), 128.2 (2-CH^{Ph}), 128.1 (3-CH^{Ph}), 127.2 (4-CH^{Ph}), 126.7 (3-CH), 120.2 (CCl), 108.3 (2-CH^{cinnamyl}), 93.3 (3-CH^{cinnamyl}), 49.0 (1-CH$_2^{cinnamyl}$), 43.9 (3′-CH$_2$), 42.2 (br s, 5′-CH$_2$), 36.6 (4′-CH), 25.4 (2C, 6′-CH and 7′-CH$_3$), 25.1 (2′-CH), 24.5 (7′′-CH$_3$), 24.3 (1′-CH$_3$), 23.2 (br s, 1′′-CH$_3$) ppm. HRMS (ESI/TOF) m/z: [M − Cl]$^+$ calcd for $C_{60}H_{91}Cl_2N_2^+$ 1015.5589; found 1015.5554.

A single crystal for XRD was grown by slow evaporation of toluene solution of this complex.

*(SP-4-1)-[1,3-Bis(2,6-bis(2,6-dimethylheptan-4-yl)phenyl)-4,5-dichloro-1H-imidazol-2-ylidene]dichloro(morpholine-κ-N4)-palladium, [Pd(DiMeIHept^{Cl})(morpholine)Cl$_2$] (**1b**).* For all cases, unstabilized Et$_2$O was used in this procedure. Under air, a 10 mL microwave vial was charged by 410.0 mg (1 equiv) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**) and 3.9 mL (20 equiv) of a 2 M HCl solution in Et$_2$O. This mixture was heated in a Biotage Initiator microwave to 70 °C for 10 h. These conditions are very important for suitable yield of the bridged chloride complex [Pd(DiMeIHept^{Cl})Cl$_2$]$_2$; lower temperature leads to low conversion, whereas higher temperature leads to decomposition. At this point, we did not try to isolate [Pd(DiMeIHept^{Cl})Cl$_2$]$_2$ and used it crude for morpholine coordination. Following forming the dimer, all volatiles were evaporated under a stream of nitrogen; then the residue was dried under 100 mTorr vacuum for 4 h to remove the last traces of HCl. Complex [Pd(DiMeIHept^{Cl})Cl$_2$]$_2$ was redissolved in 2 mL of Et$_2$O, and 0.17 mL (5 equiv) of morpholine was added. The mixture was stirred for 1 h, then adsorbed on silica gel PTLC plate. The plate was placed in a large desiccator and dried under 100 mTorr vacuum after which it was eluated for 1 min by DCM to make a sharp starting line of crude mixture, and again placed in the desiccator and dried under vacuum. After drying the plate, it was eluted to the top using a pentane-Et$_2$O mixture (4:1), doped with 3 vol % of morpholine (doping is essential to prevent the retro reaction to form [Pd(DiMeIHept^{Cl})Cl$_2$]$_2$ on silica gel). This gave a band with Rf 0.71, from which 66.1 mg of a side product was eluted with Et$_2$O. We could not assign a formula to this side product by NMR spectroscopy, nor could we obtain X-ray quality crystals. Et$_2$O elution of another band with Rf 0.55 gave 326.2 mg (79.2%) of the target complex after drying under 100 mTorr vacuum.

The isolated product contained variable quantities of morpholine or Et$_2$O in different batches, as well as some unidentified contaminants. We could roughly assess its purity to be 90% by mass, and the minor component was ignored in catalysis (i.e., for catalytic reaction was always assumed purity to be 100%).

Complex **1b** is air stable, and all operations with it can be performed at room temperature. Long time storage was at −20 °C, and we have not tested how stable it is on storage at r.t. This complex obtained by elution from silica gel scratched from the PTLC plate was smeared in a 100 mL flask, which made it difficult to work with. To simplify handling, we redissolved it in a minimal quantity of DCM and transferred it to a 1 dram vial. Solvent was evaporated under a

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J. Org. Chem. 2021, 86, 10343−10359

stream of nitrogen, and the residue was dried under vacuum. Then the content was redissolved in 1−2 mL of benzene, cooled to −196 °C, placed in a small desiccator, and lyophilized in a 100 mTorr vacuum overnight. Lyophilized **1b** was a light-yellow, fluffy powder that was easy to work with.

Mp 165−166 °C (decomposition). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (t, J = 7.8 Hz, 2H, 4-CH), 7.36 (d, J = 7.8 Hz, 4H, 3-CH), 3.63 (dd, J = 12.0, 3.0 Hz, 2H, OCH_2), 3.26 (td, J = 12.0, 1.8 Hz, 2H, OCH_2), 3.11 (qd, J = 12.9, 3.0 Hz, 2H, NCH_2), 2.94 (m, 4H, 4′-CH), 2.78 (t, J = 12.1 Hz, 1H, NH), 2.59 (d, J = 13.2 Hz, 2H, NCH_2), 2.06 (m, 4H, 3′-CH_2), 2.01−1.92 (m, 8H, indirectly assigned: 1.98 3′-CH_2, 1.92 2′-CH), 1.64−1.53 (m, 8H, indirectly assigned: 1.60 5′-CH_2, 1.55 6′-CH), 1.45 (m, 4H, 5′-CH_2), 1.00 (d, J = 6.6 Hz, 12H, 1′′-CH_3), 0.94 (d, J = 6.2 Hz, 12H, 1′-CH_3), 0.83 (d, J = 6.4 Hz, 12H, 7̀-CH_3), 0.74 (d, J = 6.4 Hz, 12H, 7′′-CH_3) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.7 (CPd), 145.4 (2-C), 134.5 (1-C), 129.4 (4-CH), 126.9 (3-CH), 120.8 (CCl), 67.9 (OCH_2), 47.9 (NCH_2), 44.2 (5′-CH_2), 43.2 (3′-CH_2), 36.9 (4′-CH), 26.1 (2′-CH), 25.3 (1′-CH_3), 25.0 (6′-CH), 24.3 (7′′-CH_3), 24.2 (1′′-CH_3), 23.1 (7′-CH_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 188.9 (N^{NHC}), 17.3 (NH) ppm. Anal. Calcd for $C_{55}H_{91}Cl_4N_3OPd$: C, 62.41; H, 8.67; N, 3.97. Found: C, 62.11; H, 8.32; N, 3.76

A single crystal for XRD was grown by slow evaporation of pentane solution of this complex.

General Procedure A for C−N Coupling, Applicable for Both Liquid Nucleophile and Electrophile. In a glovebox, a 2 dram vial (for reactions at 25−80 °C) or a 10 mL microwave vial (for reaction at higher temperature) was charged with 1−2 mg of solid catalyst. Quantities of other reagents were calculated based on the loading of the Pd precatalyst. Liquid electrophile and nucleophile were then added, and the vial was shaken for a few seconds, after which solid base was added. Immediately after this, a stir bar was added, the vial was sealed, and the contents were stirred vigorously for 30 s at r.t. In certain cases, mechanical stirring by spatula was necessary owing to rapid cementation of the mixture and magnetic stirring was not possible. The vial was then taken out of the glovebox and immersed in a preheated metal-bead bath, and the contents were stirred at 1200 rpm at the specified temperature for the time indicated.

General Procedure B for C−N Coupling, Applicable When Either Nucleophile or Electrophile Is Solid. In a glovebox, a 2 dram vial (for reactions at 25−80 °C) or a 10 mL microwave vial (for reactions requiring higher temperature) was charged with 1−2 mg of solid catalyst. Quantities of other reagents were calculated based on the loading of the Pd precatalyst. Then the vial was charged with solid base and solid reagent, and the contents were stirred by a metal spatula. The liquid reagent was added, followed immediately by the stir bar, after which the vial was sealed, and the contents were stirred vigorously for 30 s at r.t. In certain cases, mechanical stirring by a spatula was needed, as mixture cementation occurred very fast and magnetic stirring was not possible. The vial was then taken out of the glovebox and immersed in a preheated metal-bead bath, and the contents were stirred at 1200 rpm at the specified temperature for the time indicated.

General Procedure C for C−N Coupling, Applicable for Both Solid Nucleophile and Electrophile. For this case, the order of addition does not appear to be critical. Everything was done according to general procedure B, and after all solids were added, the contents were stirred well by metallic spatula. The stir bar was then added, and the vial sealed taken out of the glovebox and immersed in a preheated metal-bead bath. The content was stirred at 1200 rpm at the specified temperature for the time indicated.

Quenching Procedure D, Applicable for Products Soluble in Dichloromethane. The reaction was quenched by the addition of water (2 mL), followed by 2 mL of dichloromethane (DCM). The mixture was shaken, and the DCM layer was taken for No-D NMR analysis. If the reaction was selected for purification, the DCM layer was separated, and the aqueous layer was extracted by DCM (3 × 2 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated. Final purification was done by LC on silica gel or neutral aluminum oxide. Base-sensitive products were quenched by addition of $NaH_2PO_4{\cdot}2H_2O$ or KH_2PO_4 (equivalent quantity to base) before adding water and DCM.

Caution! *Quenching by water and $CDCl_3$ must be avoided!* We have observed unwanted reactivity between $CDCl_3$ with the base and crude products, which negatively impacted analysis.

Quenching Procedure E, Applicable for Products Insoluble, or Sparingly Soluble in Dichloromethane. The reaction was quenched by addition of 5 mL of water, after which the mixture was stirred or sonicated for 30 min, filtered, and washed well with water (ca. 80 mL). The solid together with frit was placed in a vacuum desiccator and dried under vacuum at 100 mTorr. Once dry, a small sample of the solid was dissolved in appropriate solvent (DCM, $CDCl_3$, THF, CD_3OD, or DMSO-d_6) and analyzed by NMR spectroscopy. For experiments selected for purification, the crude product was washed off from the frit with suitable solvent, adsorbed on silica gel or Celite, and purified by LC on silica gel or neutral aluminum oxide.

Base-sensitive products were quenched by addition of $NaH_2PO_4{\cdot}2H_2O$ or KH_2PO_4 (equivalent quantity to base) before adding water.

*4-(tert-Butyl)-N-(p-tolyl)aniline (**2**).* Following general procedures B and D, 1.0 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 202.4 mg (1 equiv) of 4-*tert*-butylbromobenzene, 122.1 mg (1.2 equiv) of *p*-toluidine, and 159.8 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min (or left running at r.t. for 2 h). After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and the product was eluted with a gradient of 100% hexane to 10% ethyl acetate in hexanes. After drying under vacuum at 200 mTorr, 214.5 mg of **2** (94%) was obtained as a yellow oil, which crystallized on storage.

The same procedure employing 1.4 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 224.2 mg (1 equiv) of 4-*tert*-butylchlorobenzene, 170.9 mg (1.2 equiv) of *p*-toluidine, and 223.7 mg (1.5 equiv) of KOtBu yielded 308.6 mg (97.0%) of after column chromatography.

*0.01 Mol% **1a** Coupling Reaction to Prepare **2**.* The experiment with 0.01% precatalyst was conducted in the following manner. [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**, 1.0 mg) was dissolved in 1 mL of benzene, and 0.1 mL of this solution was transferred to 2 dram vial, frozen, and lyophilized in vacuum (200 mTorr). This gave 100 μg of solid precatalyst, whose load with respect to the aryl bromide was 0.01 mol %. Further operations were conducted according to general procedures B and D employing 202.4 mg (1 equiv) of 4-*tert*-butylbromobenzene, 122.1 mg (1.2 equiv) of *p*-toluidine, and 159.8 mg (1.5 equiv) of KOtBu. After heating with stirring to 50 °C for 75 min, 215.7 mg of **2** (95%) was isolated as described above.

Performing reaction under air was done in a similar way, according to general procedures B and D. 1.4 mg of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 170.9 mg (1.2 equiv) of *p*-toluidine, and 223.7 mg (1.5 equiv) of KOtBu were charged to a 2 dram vial under air as quickly as possible and stirred by a metallic spatula for a few seconds. This resulted in mixture blackening. Then 4-*tert*-butylbromobenzene (283.3 mg, 1 equiv) was added, followed by a magnetic stir bar. The vial was corked, and the content was vigorously stirred at r.t. for 30 s. At this point, the content was totally black (vs green under an inert atmosphere). The vial was heated for 15 min at 50 °C; then workup and chromatographic purification were performed as described above. This gave 286.1 mg (90%) of the desired product as a dark orange oil (vs yellow oil obtained under an inert atmosphere).

For this compound, paramagnetic broadening was significant even after only a brief exposure in $CDCl_3$ to sunlight. To avoid this, the sample was kept in darkness; the use of absolute $CDCl_3$ was not necessary.

Mp 46−47 °C (lit. 48−50 °C).[67] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dt, J = 8.7, 2.5 Hz, 2H, 3-CH), 7.00 (d, J = 8.6 Hz, 2H, 3′-CH), 6.92−6.87 (m, 4H, indirectly assigned: 6.91 2-CH, 6.89 2′-CH), 5.39 (br s, NH), 2.24 (s, 3H, 4′-Me), 1.27 (s, 9H, 4-tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.4 (4-C), 141.2 (1-C), 140.9 (1′-C), 130.2 (4′-C), 129.9 (3′-CH), 126.1 (3-CH), 118.2 (2′-CH), 117.2 (2-CH), 34.1 (CMe_3), 31.6 (CMe_3), 20.7 (4′-Me) ppm; ^{15}N NMR

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J. Org. Chem. 2021, 86, 10343−10359

(^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 79.0 ppm. The spectral data are consistent with those reported in the literature.[68]

*N-(4-(tert-Butyl)phenyl)-2,6-dimethylaniline (**3**).* Following general procedures A and D, 1.5 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 303.5 mg (1 equiv) of 4-*tert*-butylbromobenzene, 207.1 mg (1.2 equiv) of 2,6-dimethylaniline, and 239.7 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and the product was eluted using a gradient of 100% hexane to 10% ethyl acetate in hexanes. After drying under vacuum at 200 mTorr, 315.9 mg of **3** (98%) was obtained as a colorless solid.

Mp 89−90 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (dt, J = 8.7, 2.5 Hz, 2H, 3′-CH), 7.10 (d, J = 7.3 Hz, 2H, 3-CH), 7.05 (m, 1H, 4-CH), 6.45 (dt, J = 8.7, 2.5 Hz, 2H, 2′-CH), 5.10 (br s, NH), 2.20 (s, 6H, 2-Me), 1.27 (s, 9H, 4′-tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.8 (4′-C), 141.1 (1′-C), 138.9 (1-C), 135.6 (2-*C*Me), 128.6 (3-CH), 126.0 (3′-CH), 125.5 (4-CH), 113.6 (2′-CH), 34.0 (*C*Me$_3$), 31.7 (C*Me*$_3$), 20.7 (2-C*Me*) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 71.3 ppm. The spectral data are consistent with those reported in the literature.[69]

*4-Methoxy-N-(p-tolyl)aniline (**4**).* Following general procedures B and D, 1.4 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 248.6 mg (1 equiv) of 4-bromoanisole, 170.9 mg (1.2 equiv) of *p*-toluidine, and 223.7 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min. After workup, the crude mixture was dissolved in DCM, adsorbed on silica gel, and evaporated. This silica gel was transferred on top of a 10 g silica gel column and eluted using a gradient of 100% hexane to 5% ethyl acetate in hexanes, followed by 5% ethyl acetate in hexanes until the product eluted. After drying under vacuum at 200 mTorr, 254.8 mg of **4** (90%) was obtained as an off-white solid.

The same procedure employing 2.4 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 325.0 mg (1 equiv) of 4-chloroanisole, 293.0 mg (1.2 equiv) of *p*-toluidine, and 383.6 mg (1.5 equiv) of KOtBu yielded 465.5 mg of **4** (96%). The coupling reaction was conducted at 80 °C for 15 min or at 50 °C for 12 h in this case.

For this compound, paramagnetic broadening was significant even after brief exposure of its $CDCl_3$ solution to sunlight. To avoid this, the sample was kept in darkness; the use of absolute $CDCl_3$ was not necessary. Mp 86−87 °C (lit. 82 °C).[70] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04−6.99 (m, 4H, indirectly assigned: 7.03 3′-CH, 7.01 2-CH), 6.86−6.82 (m, 4H, indirectly assigned: 6.85 2′-CH, 6.83 3-CH), 5.38 (br s, NH), 3.78 (s, 3H, OMe), 2.27 (s, 3H, 4′-Me) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 154.9 (4-C), 142.5 (1′-C), 136.7 (1-C), 129.9 (3′-CH), 129.4 (4′-*C*Me), 121.2 (2-CH), 116.7 (2′-CH), 114.8 (3-CH), 55.73 (OMe), 20.69 (4′-C*Me*) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 76.3 ppm. The spectral data are consistent with those reported in the literature.[70]

*4-(tert-Butyl)-N-phenylaniline (**5**).* Following general procedures A and D, 1.0 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 202.4 mg (1 equiv) of 4-*tert*-butylbromobenzene, 106.1 mg (1.2 equiv) of aniline, and 159.8 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and eluted with a gradient of 100% hexane gradient to 10% ethyl acetate in hexanes. After drying under vacuum at 200 mTorr, 208 mg of **5** (97%) was obtained as a colorless solid.

Mp 67−68 °C (lit. 66−67 °C).[71] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dt, J = 8.6, 2.5 Hz, 2H, 3-CH), 7.23 (m, 2H, 3′-CH), 7.03 (dt, J = 8.6, 2.5 Hz, 4H, 2-CH and 2′-CH), 6.88 (tt, J = 7.3, 0.9 Hz, 1H, 4′-CH), 5.61 (br s, NH), 1.31 (s, 9H, 4-tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.3 (4-C), 143.8 (1′-C), 140.4 (1-C), 129.4 (3′-CH), 126.3 (3-CH), 120.5 (4′-CH), 118.2 (2-CH), 117.2 (2′-CH), 34.3 (4-*C*Me$_3$), 31.6 (4-C*Me*$_3$) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 80.5 ppm. The spectral data are consistent with those reported in the literature.[71]

*N^1,N^1-Dimethyl-N^4-(p-tolyl)benzene-1,4-diamine (**6**).* Following general procedures C and D, 1.2 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 228.0 mg (1 equiv) of 4-bromo-*N*,*N*-dimethylaniline, 146.5 mg (1.2 equiv) of *p*-toluidine, and 191.8 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min. After workup, the crude mixture was dissolved in DCM, adsorbed on silica gel, and evaporated. This silica gel was transferred on top of a 10 g silica gel column and eluted with a gradient of 100% hexane to 2% ethyl acetate in hexanes, followed by 2% ethyl acetate in hexanes until the product eluted. Both eluents were doped by 3 vol % of NEt_3. After drying under vacuum at 200 mTorr, 236 mg of **6** (92%) was obtained as an off-white solid.

This compound catalyzes rapid photo- or oxidative decomposition of $CDCl_3$; this solvent was not suitable for NMR spectroscopy. There are indications that this compound has an available low lying triplet state, especially under action of acid. It is EPR active in the solid state (singlet with *g*-factor 2.0029) and turns deep blue on silica gel; the color disappears on elution. As well, **6** turns blue on UV irradiation of its methanol solution. Peaks in its ^{1}H NMR spectra were broad in CD_3OD and DMSO-d_6, but sharp in acetone-d_6 and absolute C_6D_6. Two articles[72,73] report NMR spectra of this compound in DMSO-d_6; we observed peak broadening in the ^{1}H NMR spectrum of this compound in DMSO-d_6, although chemical shifts were the same as those reported. The ^{13}C{^{1}H} NMR spectrum in acetone-d_6 showed satellites near 3-C, 4-C, 1′-C, and 2′-C, probably due to formation of metastable enamine (N^1,N^1-dimethyl-N^4-(prop-1-en-2-yl)-N^4-(*p*-tolyl)benzene-1,4-diamine). Also, the ^{1}H NMR spectrum in CH_2Cl_2 showed sharp signals, but only immediately after reaction quenching, when the CH_2Cl_2 solution was extracted from water containing KOH derived from excessive KOtBu.

Mp 94−95 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ 7.01 (dt, J = 8.7, 2.5 Hz, 2H, 3-CH), 6.96 (d, J = 8.4 Hz, 2H, 3′-CH), 6.83 (dt, J = 8.4, 2.5 Hz, 2H, 2′-CH), 6.74 (br dt, J = 8.7, 2.5 Hz, 3H, 2-CH and NH), 2.86 (s, 6H, NMe$_2$), 2.20 (s, 3H, 4′-CMe) ppm; ^{13}C{^{1}H} NMR (150 MHz, acetone-d_6) δ 147.4 (1-C), 144.78 and 144.71 (1′-C), 134.72 and 134.66 (4-C), 130.3 (3-CH), 127.9 (4′-*C*Me), 122.17 and 122.10 (3-CH), 115.97 and 115.93 (2′-CH), 114.9 (2-CH), 41.4 (NMe$_2$), 20.6 (4′-C*Me*) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, acetone-d_6) δ 76.4 (NH), 36.1 (NM$_e$). ^{1}H NMR (600 MHz, C_6D_6) δ 7.00 (dt, J = 8.8, 2.5 Hz, 2H, 3-CH), 6.98 (d, J = 8.4 Hz, 2H, 3′-CH), 6.83 (dt, J = 8.4, 2.5 Hz, 2H, 2′-CH), 6.60 (dt, J = 8.8, 2.5 Hz, 2H, 2-CH), 4.85 (br s, 1H, NH), 2.54 (s, 6H, NMe$_2$), 2.17 (s, 3H, 4′-CMe) ppm; ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 147.3 (1-C), 144.2 (1′-C), 133.8 (4-C), 130.1 (3-CH), 128.3−127.8 (C_6D_6, indirectly assigned 3-CH at 128.14), 122.9 (3-CH), 116.0 (2′-CH), 114.5 (2-CH), 41.0 (NMe$_2$), 20.7 (4′-C*Me*) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, C_6D_6) δ 75.3 (NH), 35.9 (NM$_e$). HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{19}N_2^+$ 227.1548; found 227.1534.

*4-Methyl-N-(4-(methylthio)phenyl)aniline (**7**).* Following general procedures B and D, 1.5 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 289.3 mg (1 equiv) of (4-bromophenyl)(methyl)sulfane, 183.1 mg (1.2 equiv) of *p*-toluidine, and 239.7 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min. After workup, the crude mixture was dissolved in DCM, adsorbed on silica gel, and evaporated. This silica gel was transferred on top of a 10 g silica gel column and eluted with a gradient of 100% hexane to 5% ethyl acetate in hexanes, followed by 5% ethyl acetate in hexanes until the product eluted. After drying under vacuum at 200 mTorr, 297 mg (91%) of **7** was obtained as an off-white solid.

Mp 86−87 °C (lit. 81−82 °C).[74] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dt, J = 8.8, 2.5 Hz, 2H, 3′-CH), 7.07 (d, J = 8.3 Hz, 2H, 3-CH), 6.97 (d, J = 8.3 Hz, 2H, 2-CH), 6.94 (br d, J = 8.8 Hz, 2H, 2′-CH), 5.57 (br s, NH), 2.43 (s, 3H, SMe), 2.29 (s, 3H, 4-Me) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 142.4 (1′-C), 140.2 (1-C), 131.2 (4-*C*Me), 130.3 (3′-CH), 130.0 (3-CH), 128.1 (4′-CS), 119.0 (2-CH), 117.7 (2′-CH), 20.8 (4-Me), 18.23 (4′-SMe) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 80.3 ppm. The spectral data are consistent with those reported in the literature.[75]

*4-(tert-Butyl)-N-methyl-N-phenylaniline (**8**).* Following general procedures A and D, 1.6 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 323.8 mg (1 equiv) of 1-bromo-4-(*tert*-butyl)benzene, 170.9 mg (1.05 equiv) of *N*-methylaniline, and 255.7 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min.

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J. Org. Chem. 2021, 86, 10343−10359

After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and eluted with 100% hexanes. After drying under vacuum at 200 mTorr, 350 mg (96%) of **8** was obtained as a yellow oil.

The same procedure employing 1.3 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 208.2 mg (1 equiv) of 4-*tert*-butylchlorobenzene, 138.9 mg (1.05 equiv) of *N*-methylaniline, and 207.8 mg (1.5 equiv) of KOtBu yielded 289 mg (98%) of **8** after chromatography.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dt, J = 8.7, 2.5 Hz, 2H, 3-CH), 7.24 (m, 3′-CH and $CHCl_3$), 7.00 (dt, J = 8.7, 2.5 Hz, 2H, 2-CH), 6.96 (m, 2H, 2′-CH), 6.89 (tt, J = 7.3, 1.0 Hz, 1H, 4′-CH), 3.29 (s, 3H, NMe), 1.31 (s, 9H, tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.3 (1′-C), 146.5 (1-C), 144.9 (4-C), 129.2 (3′-CH), 126.2 (3-CH), 121.4 (2-CH), 120.4 (4′-CH), 119.1 (2′-CH), 40.4 (NMe), 34.3 (CMe_3), 31.60 (CMe_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 64.8 ppm. The spectral data are consistent with those reported in the literature.[69]

*4-Methyl-N-(4-vinylphenyl)aniline (**9**).* For this reaction, we used 97% pure 4-bromostyrene stabilized by 3,5-di-*tert*-butylcatechol (0.1 mol %), supplied by AK Scientific. Following general procedures A and D, 1.9 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 330.2 mg (1 equiv) of 4-bromostyrene, 232.0 mg (1.2 equiv) of *p*-toluidine, and 303.7 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min. After workup, the combined DCM extracts after drying were adsorbed on Celite and dried in vacuum. This Celite was placed into a loading cartridge atop of a Santai neutral alumina column (24 g), and the product was eluted using a gradient of 100% hexane to 5% ethyl acetate in hexanes, followed by 5% ethyl acetate in hexanes until the product eluted. After drying under vacuum at 200 mTorr, 289 mg (77%) of **9** was obtained as a colorless solid.

This product rapidly decomposes on silica gel and is very sensitive to UV light. Unlike other products described above, **9** simply decomposes under UV irradiation. Decomposition products are not paramagnetic, and the decomposition rate strongly depends on solvent. It is very fast in DCM and $CDCl_3$, slower in EtOAc, and very slow in hexanes. We were able to use UV detection at 254 and 280 nm for chromatography at a flow rate of 18 mL/min, which minimizes exposure to UV light. Brief exposure does not result in significant decomposition. We also checked the stability of **9** in $CDCl_3$ where it remained intact after 24 h in darkness, whereas decomposition was very fast upon exposure to sunlight.

Mp 84−85 °C (lit. 71−73 °C).[76] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dt, J = 8.5, 2.2 Hz, 2H, 3′-CH), 7.09 (d, J = 8.1 Hz, 2H 3-CH), 7.00 (d, J = 8.1 Hz, 2H, 2-CH), 6.95 (dt, J = 8.5, 2.2 Hz, 2H, 2′-CH), 6.64 (dd, J = 17.6, 10.8 Hz, 1H, CH^{vinyl}), 5.65 (br s, 1H, NH), 5.59 (dd, J = 17.6, 0.7 Hz, 1H, CH_2^{vinyl}), 5.09 (dd, J = 10.8, 0.7 Hz, 1H, CH_2^{vinyl}), 2.31 (CH_3) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.8 (1′-C), 140.0 (1-C), 136.5 (CH^{vinyl}), 131.3 (4-C), 130.02 (3-CH), 129.97 (4′-C), 127.4 (3′-CH), 119.3 (2-CH), 116.6 (2′-CH), 110.9 (CH_2^{vinyl}), 20.9 (Me) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 81.4 ppm. The spectral data are consistent with those reported in the literature.[76]

*4-(tert-Butyl)-N-(4-vinylphenyl)aniline (**10**).* For this reaction, we used 97% pure 4-aminostyrene stabilized by KOH (0.5 mol %), supplied by Oakwood. KOH is an inhibitor of Pd-catalyzed coupling; thus it was inactivated by addition of HMDS. We also had to add BHT to the reaction mixture to inhibit polymerization. Addition order is very important for this reaction. In the glovebox, a 2 dram vial was wrapped in aluminum foil and charged with 1.2 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 2.5 mg (1 mol %) of BHT, 3.7 mg (2 mol %) of HMDS, 242.8 mg (1 equiv) of 4-*tert*-butylbromobenzene, and 162.9 mg (1.2 equiv) of 4-aminostyrene. The mixture was stirred briefly, 191.8 mg (1.5 equiv) of KOtBu was added, the vial was closed, and the content was immediately stirred magnetically at r.t. for a few seconds. The vial was taken out of the glovebox and inserted in a preheated metal-bead bath, and the mixture was stirred at 1200 rpm for 12 h at 50 °C. Quenching was performed according to the general procedure D. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 24 g neutral alumina column and eluted with a gradient of 100% hexane to 5% ethyl acetate in hexanes. After drying under vacuum at 200 mTorr, 268 mg (93%) of **10** was obtained as an orange oil, which crystallized on storage at −20 °C and remained solid on thawing to r.t.

*Large Scale Synthesis of **10**.* The synthesis was performed in the following manner. A 100 mL pear-shaped flask, stir bar, 10 cm Vigreux column, rubber septum, and balloon attached to a syringe needle were placed into the glovebox. The top joint of the Vigreux column was corked by a rubber septum and pierced by a needle equipped with a balloon. The flask was wrapped in aluminum foil and charged with 16.3 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)-Cl] (**1a**), 34.1 mg (1 mol %) of BHT, 50.0 mg (2 mol %) of HMDS, 3.2984 g (1 equiv) of 1-bromo-4-(*tert*-butyl)benzene, and 2.0287 g (1.1 equiv) of 4-aminostyrene. The content was stirred magnetically for a few seconds. KOtBu (2.6051 g, 1.5 equiv) was added to the reaction mixture as quickly as possible after which the flask was corked by a Vigreux column, and the content was immediately stirred magnetically. In 30−60 s, an exotherm was observed with gentle refluxing of tBuOH. The balloon mounted on top of the Vigreux column had to protect the glovebox atmosphere from these gases. The assembled apparatus was taken out of the glovebox and placed in a metal-bead bath preheated to 50 °C, and the mixture was stirred at 1200 rpm for 12 h. After cooling to r.t., the Vigreux column was removed and the reaction was quenched with water (20 mL) and DCM (20 mL). After separating the phases, the aqueous phase was washed with DCM (2 × 20 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, filtrated, and evaporated. The crude product was dissolved in hexanes (50 mL) and injected into a stack of consecutively connected two Santai iLOK 50 g neutral alumina columns. Elution was performed with hexanes, and after the BHT peak was fully eluted (observation on 280 nm; BHT does not absorb UV light at 254 nm), the solvent polarity was increased to 2% EtOAc, which eluted the target compound as a very broad peak. Evaporation of all fractions containing product and drying under vacuum at 200 mTorr provided 3.51 g (90%) of an orange oil, which crystallized on storage at −20 °C.

Mp 58−59 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dt, J = 8.6, 2.5 Hz, 4H, 3-CH and 3′-CH), 7.03 (dt, J = 8.6, 2.5 Hz Hz, 2H 2-CH), 6.97 (dt, J = 8.6, 2.5 Hz, 2H, 2′-CH), 6.64 (dd, J = 17.6, 10.8 Hz, 1H, CH^{vinyl}), 5.65 (br s, 1H, NH), 5.59 (dd, J = 17.6, 0.9 Hz, 1H, CH_2^{vinyl}), 5.09 (dd, J = 10.8, 0.9 Hz, 1H, CH_2^{vinyl}), 1.31 (tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.6 (4-C), 143.5 (1′-C), 140.1 (1-C), 136.5 (CH^{vinyl}), 130.0 (4′-C), 127.4 (3′-CH), 126.3 (3-CH), 118.5 (2-CH), 116.8 (2′-CH), 111.0 (CH_2^{vinyl}), 34.3 (4-CMe_3), 31.6 (4-CMe_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 81.8 ppm. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}N^+$ 252.1752; found 252.1773.

*3-Methyl-N-phenylaniline (**11**).* Following general procedures A and D, 1.8 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 292.3 mg (1 equiv) of 3-bromotoluene, 191.0 mg (1.2 equiv) of aniline, and 287.7 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and eluted with a gradient of 100% hexane gradient to 5% ethyl acetate in hexanes. After drying under vacuum at 200 mTorr, 273 mg (87%) was obtained as a colorless oil.

*Large Scale Synthesis of **11**.* The synthesis was performed in the following manner. A 50 mL pear-shaped flask, stir bar, 10 cm Vigreux column, rubber septum, and balloon attached to a syringe needle were placed into the glovebox. The top joint of the Vigreux column was corked by a rubber septum and pierced by a needle equipped with a balloon. The flask was wrapped in aluminum foil and charged with 33.4 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 5.4241 g (1 equiv) of 3-bromotoluene, and 2.9535 g (1 equiv) of aniline. The content was stirred magnetically for a few seconds. KOtBu (3.9145 g, 1.1 equiv) was added to the reaction mixture as quickly as possible after which the flask was corked by the Vigreux column, and the content was immediately stirred magnetically. In 30−60 s, an exotherm was observed with gentle refluxing of tBuOH. The

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J. Org. Chem. 2021, 86, 10343−10359

balloon mounted on top of the Vigreux column had to protect the glovebox atmosphere from any harmful gas. The assembled apparatus was taken out of the glovebox and placed in a metal-bead bath preheated to 50 °C, and the mixture was stirred at 1200 rpm for 15 min. After cooling to r.t., the Vigreux column was removed, and a small sample was removed with a metal spatula and washed into an NMR with CH_2Cl_2 to check conversion by No-D NMR tube, which was quantitative. A short path distillation head with an attached fractional distillation spider and flasks was mounted on the flask. The product was distilled off under vacuum, collecting a fraction with bp 127 °C (1200 mTorr). This gave 3.8846 g (66.8%) of the desired product as a colorless oil, which crystallized on storage.

Mp 35−36 °C (lit. 31−32 °C).[77] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (m, $CHCl_3$ and 3′-CH), 7.15 (td, J = 7.4, 1.0 Hz, 1H, 5-CH), 7.06 (m, 2H, 2′-CH), 6.92 (tt, J = 7.5, 1.0 Hz, 1H, 4′-CH), 6.90−6.87 (m, 2H, indirectly assigned: 6.89 2-CH, 6.88 6-CH), 6.75 (d, J = 7.4 Hz, 1H, 4-CH), 5.76 (br s, 1H, NH), 2.30 (s, 3H, 3-Me) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.3 (1′-C), 143.2 (1-C), 139.4 (3-C), 129.5 (3′-CH), 129.3 (5-CH), 122.1 (4-CH), 121.1 (4′-CH), 118.7 (2-CH), 118.0 (2′-CH), 115.1 (6-CH), 21.7 (3-Me) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 82.0 ppm. The spectral data are consistent with those reported in the literature.[78]

*4-(tert-Butyl)-N-octylaniline (**12**).* Following general procedures A and D, 1.3 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 261.7 (1 equiv) of 1-bromo-4-(*tert*-butyl)benzene, 190.5 mg (1.2 equiv) of *n*-octylamine, and 206.7 mg (1.5 equiv) of KOtBu were heated to 50 °C for 15 min. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and eluted with a gradient of 100% hexane to 10% ethyl acetate in hexanes. After drying under vacuum at 200 mTorr, 302.3 mg (94.2%) of **12** was obtained as a colorless oil.

A similar procedure employing 1.6 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 254.9 mg (1 equiv) of 4-*tert*-butylchlorobenzene, 234.4 mg (1.2 equiv) of *n*-octylamine, and 249.7 mg (1.5 equiv) of NaOtAm was performed at 120 °C for 1 h. After workup, the combined DCM extracts were passed through a florisil column while eluting with DCM. After drying under vacuum at 200 mTorr, 393.5 mg (98%) of **12** was obtained contaminated with a tiny amount of diaryloctylamine.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (dt, J = 8.6, 2.5 Hz, 2H, 3-CH), 6.56 (dt, J = 8.6, 2.5 Hz, 2H, 2-CH), 3.48 (br s, 1H, NH), 3.08 (t, J = 7.3 Hz, 2H, 1′-CH_2), 1.60 (q, J = 7.3 Hz, 2H, 2′-CH_2), 1.38 (m, 2H, 3′-CH_2), 1.34−1.23 (m, 17H, indirectly assigned: 1.31 4′-CH_2, 1.29 7′-CH_2, 1.28 5′-CH_2, 1.27 tBu, 1.26 6′-CH_2), 0.88 (t, J = 7.1 Hz, 3H, 8′-CH_3) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 146.4 (1-C), 139.93 (4-C), 126.1 (3-CH), 112.5 (2-CH), 44.4 (1′-CH_2), 34.0 (4′-CMe_3), 32.0 (6′-CH_2), 31.7 (4′-CMe_3), 29.8 (2′-CH_2), 29.6 (4′-CH_2), 29.4 (5′-CH_2), 27.3 (3′-CH_2), 22.8 (7′-CH_2), 14.3 (8′-CH_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 61.2 ppm. The spectral data are consistent with those reported in the literature.[79]

*4-(tert-Butyl)-N-cyclohexylaniline (**13**).* Following general procedures A and D, 1.2 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 241.6 (1 equiv) of 4-*tert*-butylbromobenzene, 134.9 mg (1.2 equiv) of cyclohexylamine, and 190.8 mg (1.5 equiv) of KOtBu were heated to 120 °C for 15 min. After workup, the combined DCM extracts were passed through a florisil column while eluting with DCM. After drying under vacuum at 200 mTorr for 2 h, 258.8 mg (99%) of **13** was obtained as a light yellow oil.

A similar procedure employing 1.1 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 175.3 mg (1 equiv) of 4-*tert*-butylchlorobenzene, 123.7 mg (1.2 equiv) of cyclohexylamine, and 171.7 mg (1.5 equiv) of NaOtAm was performed at 120 °C for 1 h. The same workup yielded 238.0 mg (98%) of **13** contaminated with a tiny amount of diarylcyclohexylamine.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, J = 8.8, 2.5 Hz, 2H, 3-CH), 6.54 (d, J = 8.8, 2.5 Hz, 2H, 2-CH), 3.42 (br s, 1H, NH), 3.22 (ttt, J = 10.2, 3.7 Hz, 1H, 1′-CH), 2.04 (m, 2H, 2′-CH_2), 1.75 (m, 2H, 3′-CH_2), 1.64 (m, 1H, 4′-CH_2), 1.36 (m, 2H, 3′-CH_2), 1.27 (s, 9H, tBu), 1.22 (m, 1H, 4′-CH_2), 1.14 (m, 2H, 2′-CH_2) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 145.2 (1-C), 139.7 (4-C), 126.1 (3-CH), 112.9 (2-CH), 52.0 (1′-CH), 33.9 (4-CMe_3), 33.8 (2′-CH_2), 31.7 (4-CMe_3), 26.1 (4′-CH_2), 25.2 (3′-CH_2) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 76.8 ppm. The spectral data are consistent with those reported in the literature.[80]

*N,4-Di-tert-butylaniline (**14**).* Following general procedures A and D, 1.0 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 201.3 (1 equiv) of 1-bromo-4-(*tert*-butyl)benzene, 82.9 mg (1.2 equiv) of *tert*-butylamine, and 159.0 mg (1.5 equiv) of KOtBu were heated to 120 °C for 15 min. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and eluted with 100% hexane until *N*,4-di-*tert*-butyl-*N*-(4-(*tert*-butyl)phenyl)aniline came out. Then a gradient to 10% ethyl acetate in hexanes was utilized to elute the product. After drying under vacuum at 5 mbar vacuum, 175.5 mg (91%) of **14** was obtained as a colorless oil that solidified on storage at −20 °C, along with 7.7 mg (4.8%) of the di-addition product (for characterization data, see below).

The same procedure employing 1.1 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 175.3 mg (1 equiv) of 4-*tert*-butylchlorobenzene, 91.2 mg (1.2 equiv) of *tert*-butylamine, and 171.7 mg (1.5 equiv) of NaOtAm was performed at 120 °C for 3 h. After workup, the combined DCM extracts were passed through a florisil column and eluated with DCM. Evaporation of eluates and drying under vacuum at 5 mbar provides 203.4 mg (93%) of **14** contaminated with a small amount of *N*,4-di-*tert*-butyl-*N*-(4-(*tert*-butyl)phenyl)aniline (2.0%) and 4-*tert*-butylphenol (0.6%).

*Large Scale Synthesis of **14**.* The synthesis was performed in the following manner. A 50 mL pear-shaped flask, stir bar, 10 cm Vigreux column, rubber septum, and balloon attached to a syringe needle were placed into the glovebox. The top joint of the Vigreux column was corked by a rubber septum and pierced by a needle equipped with a balloon. The top joint of the Vigreux column was corked by a rubber septum and pierced by a needle equipped with a balloon. The flask was wrapped in aluminum foil and charged with 30.0 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 6.0396 g (1 equiv) of 1-bromo-4-(*tert*-butyl)benzene, and 2.4874 g (1.2 equiv) of *tert*-butylamine. The content was stirred magnetically for a few seconds, and 4.7701 g (1.5 equiv) of KOtBu was added to the reaction mixture as quickly as possible. The flask was corked with the Vigreux column, and the mixture was immediately stirred magnetically. In 30−60 s, an exotherm was observed with gentle refluxing of of tBuOH and $tBuNH_2$. The balloon mounted on top of the Vigreux column protected the glovebox atmosphere from any harmful gas. The assembled apparatus was taken out of the glovebox and placed in an oil bath preheated to 120 °C. At this temperature, the reaction was stirred at 1200 rpm for 15 min, then cooled to r.t. Under air, the Vigreux column was changed to a short path distillation head with an attached fractional distillation spider and flasks. The product was distilled off under vacuum, collecting a fraction with bp 94 °C (750 mTorr) to 92 °C (500 mTorr) to 98 °C (820 mTorr). The pressure fluctuated during fraction collection, which led to an inconsistent boiling point. This gave 4.7703 g (79%) of **14** as a clear oil that contained a trace of 1-(*tert*-butoxy)-4-(*tert*-butyl)benzene according to NMR and GC-MS analysis.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (dt, J = 8.7, 2.5 Hz, 2H, 3-CH), 6.70 (dt, J = 8.7, 2.5 Hz, 2H, 2-CH), 3.33 (br s, 1H, NH), 1.31 (s, 9H, NtBu), 1.28 (s, 9H, CtBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.3 (1-CN), 141.4 (4-C), 125.8 (3-CH), 117.8 (2-CH), 51.6 (NCMe_3), 34.0 (CCMe_3), 31.7 (CCMe_3), 30.3 (NCMe_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 85.1 ppm. The spectral data are consistent with those reported in the literature.[81]

N,4-Di-tert-butyl-N-(4-(tert-butyl)phenyl)aniline was isolated as a byproduct (7.7 mg, 4.8% yield, colorless solid) in the small scale preparation of *N*,4-di-*tert*-butylaniline (**14**).

Mp 96−97 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dt, J = 8.7, 2.5 Hz, 2H, 3-CH), 6.91 (dt, J = 8.7, 2.5 Hz, 2H, 2-CH), 1.38 (s, 9H, NtBu), 1.28 (s, 18H, CtBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

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J. Org. Chem. 2021, 86, 10343−10359

δ 146.0 (1-CN), 144.6 (4-C), 126.0 (2-CH), 125.4 (3-CH), 55.6 ($NCMe_3$), 34.2 ($CCMe_3$), 31.6 ($CCMe_3$), 30.2 ($NCMe_3$) ppm; ^{15}N NMR ($^1H-^{15}N$ HMBC projection, 60 MHz, $CDCl_3$) δ 87.0 ppm. HRMS (ESI/TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{36}N^+$ 338.2848; found 338.2865.

*4-(4-(tert-Butyl)phenyl)morpholine (**15**).* Following general procedures A and D, 1.2 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 241.6 mg (1 equiv) of 1-bromo-4-(*tert*-butyl)benzene, 103.7 mg (1.05 equiv) of morpholine, and 190.8 mg (1.5 equiv) of KOtBu were heated to 120 °C for 15 min. After workup, the combined DCM extracts were passed through a florisil column and eluted with DCM. Evaporation of eluates and drying in a 200 mTorr vacuum yielded 226.9 mg (89%) of **15** as an off-white solid which contained a small amount of 4-*tert*-butyl-phenol.

The same procedure employing 1.3 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 207.1 mg (1 equiv) of 4-*tert*-butylchlorobenzene, 112.3 (1.05 equiv) of morpholine, and 206.7 mg (1.5 equiv) of KOtBu yielded 254.4 mg (92%) of **15** containing a small amount 4-*tert*-butyl-phenol.

Mp 65−66 °C (lit. 59−62 °C).[82] ^1H NMR (600 MHz, $CDCl_3$) δ 7.30 (dt, *J* = 8.9, 2.1 Hz, 2H, 3-CH), 6.86 (dt, *J* = 8.9, 2.1 Hz, 2H, 2-CH), 3.85 (t, *J* = 4.8 Hz, 4H, OCH_2), 3.13 (t, *J* = 4.8 Hz, 4H, NCH_2), 1.29 (tBu) ppm; $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 149.0 (1-C), 142.9 (4-C), 126.1 (3-CH), 115.5 (2-CH), 67.1 (OCH_2), 49.7 (NCH_2), 34.1 (CMe_3), 31.6 (CMe_3) ppm; ^{15}N NMR ($^1H-^{15}N$ HMBC projection, 60 MHz, $CDCl_3$) δ 56.8 ppm. The spectral data are consistent with those reported in the literature.[24]

*1-(4-(tert-Butyl)phenyl)piperazine (**16**).* Following general procedures B and D, 1.1 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 221.5 mg (1 equiv) of 4-*tert*-butylbromobenzene, 358.0 mg (4 equiv) of piperazine, and 149.8 mg (1.5 equiv) of NaOtBu were heated to 120 °C for 15 min. After workup, the crude mixture was dissolved in DCM and poured directly on top of a 10 g silica gel column (DCM does not eluate the product at all). Both eluents were doped by 3 vol % of NEt_3. The column was washed with EtOAc until the peak of the byproduct (1,4-bis(4-(*tert*-butyl)phenyl)-piperazine; for characterization data, see below) was fully eluted. This was followed by a gradient of EtOAc to 10% MeOH in EtOAc, after which 10% MeOH in EtOAc was used until the product eluted from the column. Evaporation of fractions and drying under a vacuum of 100 mTorr gave 219.8 mg (97%) of **16** as a colorless solid.

Mp 133−134 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.9 Hz, 2H, 3′-CH), 6.85 (d, *J* = 8.9 Hz, 2H, 2′-CH), 3.08 (m, 4H, 2-CH_2), 2.98 (m, 4H, 3-CH_2), 2.37 (br s, 1H, 4-NH), 1.27 (s, 9H, tBu) ppm; $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 149.2 (1′-CN), 142.2 (4′-C), 125.7 (3′-CH), 115.6 (2′-CH), 50.3 (2-CH_2), 45.9 (3-CH_2), 33.8 (4′-CMe_3), 31.3 (4′-CMe_3) ppm; ^{15}N NMR ($^1H-^{15}N$ HMBC projection, 60 MHz, $CDCl_3$) δ 59.2 (1-N), 29.4 (4-NH) ppm. The spectral data are consistent with those reported in the literature.[83]

1,4-Bis(4-(tert-butyl)phenyl)piperazine was isolated as a byproduct (5.6 mg yield, 3.1%, off-white solid) in preparation of 1-(4-(*tert*-butyl)phenyl)piperazine (**16**).

Mp 227−228 °C (decomposition). ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (dt, *J* = 8.7, 2.5 Hz, 4H, 3-CH), 6.93 (dt, *J* = 8.7, 2.5 Hz, 2-CH), 3.31 (s, 8H, CH_2), 1.30 (s, 18H, tBu) ppm; $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 149.0 (1-C), 142.9 (4-C), 126.1 (3-CH), 116.2 (2-CH), 49.8 (CH_2), 34.1 (4-CMe_3), 31.6 (4-CMe_3) ppm; ^{15}N NMR ($^1H-^{15}N$ HMBC projection, 60 MHz, $CDCl_3$) δ 57.8 ppm. HRMS (ESI/TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{35}N_2^+$ 351.2800; found 351.2970.

*4-(tert-Butyl)-N,N-diphenylaniline (**17**).* Following general procedures B and D, 1.3 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 261.7 mg (1 equiv) of 4-*tert*-butylbromobenzene, 218.2 mg (1.05 equiv) of diphenylamine, and 206.7 mg (1.5 equiv) of KOtBu were heated to 120 °C for 1 h. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and eluted with hexanes. After drying under vacuum at 200 mTorr vacuum, 346.3 mg (94%) was obtained as a colorless solid.

The same procedure employing 1.5 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1b**), 239.0 mg (1 equiv) of 4-*tert*-butylchlorobenzene, 251.8 mg (1.05 equiv) of diphenylamine, and 238.5 mg (1.5 equiv) of KOtBu yielded 416.5 mg (98%) of **17**.

Mp 66−67 °C (lit. 52−53 °C,[84] 74−75 °C,[85] 77−79 °C).[7] ^1H NMR (600 MHz, $CDCl_3$) δ 7.26−7.20 (m, indirectly assigned: 7.24 $CHCl_3$, 7.24 3-CH, 7.22 3′-CH), 7.08 (d, *J* = 7.9 Hz, 4H, 2′-CH), 7.01 (dt, *J* = 8.6, 2.5 Hz, 2H, 2-CH), 6.97 (t, *J* = 7.2 Hz, 2H, 4′-CH), 1.31 (s, 9H, tBu) ppm; $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 148.1 (1′-C), 145.9 (4-C), 145.1 (1-C), 129.2 (3′-CH), 126.2 (3-CH), 124.1 (2-CH), 124.0 (2′-CH), 122.4 (4′-CH), 34.4 (4-CMe_3), 31.6 (4-CMe_3) ppm; ^{15}N NMR ($^1H-^{15}N$ HMBC projection, 60 MHz, $CDCl_3$) δ 94.0 ppm. The spectral data are consistent with those reported in the literature.[71]

*N^4,$N^{4'}$-Diphenyl-N^4,$N^{4'}$-di-m-tolyl-[1,1′-biphenyl]-4,4′-diamine (TPD, **18**).* Following general procedures B and D, 1.5 mg (0.2 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 221.1 mg (1 equiv) of 4,4′-dibromobiphenyl, 272.7 mg (2.1 equiv) of 3-methyl-*N*-phenyl-aniline, and 238.5 mg (3 equiv) of KOtBu were heated to 120 °C for 3 h. After workup, the combined DCM extracts were evaporated and the residue was redissolved in 10 mL of absolute DCM, 1 mL of NEt_3, and 1 mL of acetyl chloride. The flask was corked, the solution was stirred for 14 h, and the reaction was quenched with 10 mL of 2 M NaOH. The phases were separated, and the aqueous phase was extracted with DCM (2 × 10 mL). The combined organic extracts were adsorbed on silica gel and evaporated. This silica was placed on top of a 10 g silica gel column and eluted using a gradient of 100% hexanes to 5% EtOAc in hexanes, after which 5% EtOAc in hexanes was used until the product eluted. This provided 315.3 mg (87.1%) of **18** as a colorless solid after drying under vacuum at 100 mTorr.

On silica gel, acidic, neutral, and basic alumina, TPD is co-eluted with unreacted 3-methyl-*N*-phenylaniline. The only way to obtain **18** pure was to derivatize diarylamine with acetyl chloride. We have also investigated this coupling performed in a deficiency of 3-methyl-*N*-phenylaniline; this gave impure **18**, which we were unable to purify.

Mp 170−171 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.44 (dt, *J* = 8.6, 2.5 Hz, 4H, 2-$CH^{biphenyl}$), 7.25 (t, *J* = 7.5 Hz, $CHCl_3$ and 3-CH^{Ph}), 7.14 (t, *J* = 7.7 Hz, 2H, 5-CH^{mTol}), 7.12−7.09 (m, 8H, indirectly assigned: 7.10 3-$CH^{biphenyl}$, 7.10 2-CH^{Ph}), 7.00 (t, *J* = 7.5 Hz, 2H, 4-CH^{Ph}), 6.95 (s, 2H, 2-CH^{mTol}), 6.92 (d, *J* = 7.7 Hz, 6-CH^{mTol}), 6.84 (d, *J* = 7.7 Hz, 2H, 4-CH^{mTol}), 2.26 (s, 6H, 3-Me^{mTol}) ppm; $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.9 (1-CN^{Ph}), 147.8 (1-CN^{mTol}), 146.9 (4-$CN^{biphenyl}$), 139.3 (3-C^{mTol}), 134.7 (1-$C^{biphenyl}$), 129.3 (3-CH^{Ph}), 129.2 (5-CH^{mTol}), 127.4 (2-$CH^{biphenyl}$), 125.2 (2-CH^{mTol}), 124.3 (2-CH^{Ph}), 124.2 (3-$CH^{biphenyl}$), 124.0 (2-CH^{mTol}), 122.8 (4-CH^{Ph}), 121.8 (6-CH^{mTol}), 21.6 (3-Me^{mTol}) ppm; ^{15}N NMR ($^1H-^{15}N$ HMBC projection, 60 MHz, $CDCl_3$) δ 94.9 ppm. The spectral data are consistent with those reported in the literature.[86]

*N,N-Diphenyl-4-vinylaniline (**19**).* Following general procedures B and D, 1.9 mg (0.2 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2], 167.1 mg (1 equiv) of 4-bromostyrene, 159.5 mg (1.05 equiv) of diphenylamine, and 151.1 mg (1.5 equiv) of KOtBu were heated to 50 °C for 14 h. After workup, the combined DCM extracts were dried over anhydrous Na_2SO_4, filtrated, adsorbed on Celite, and dried in vacuum. This Celite was placed in a loading cartridge placed before a Santai neutral alumina column (24 g), and the product was eluted with hexanes. After drying under vacuum at 100 mTorr, 165 mg (67%) of **19** was obtained as a colorless solid.

Mp 94−95 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.25 (dt, *J* = 8.5, 2.5 Hz, 2H, 3-CH), 7.21 (br t, *J* = 7.4, Hz, 4H, 3′-CH), 7.07 (m, 4H, 2′-CH), 7.00 (dt, *J* = 8.5, 2.5 Hz, 2H, 2-CH), 6.98 (tt, 7.4, 1.0 Hz, 2H, 4′-CH), 6.63 (dd, *J* = 17.6, 10.8 Hz, 1H, CH^{vinyl}), 5.61 (dd, *J* = 17.6, 0.7 Hz, 1H, CH_2^{vinyl}), 5.12 (dd, *J* = 10.8, 0.7 Hz, 1H, CH_2^{vinyl}) ppm; $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.7 (1′-C), 147.6 (1-C), 136.3 (CH^{vinyl}), 132.0 (4-C), 129.4 (3′-CH), 127.2 (3-CH), 124.5 (2′-CH), 123.7 (2-CH), 123.0 (4′-CH), 112.3 (CH_2^{vinyl}) ppm; ^{15}N NMR ($^1H-^{15}N$ HMBC projection, 60 MHz, $CDCl_3$) δ 96.1 ppm. The spectral data are consistent with those reported in the literature.[87,88]

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J. Org. Chem. 2021, 86, 10343−10359

*4-(p-Tolylamino)benzamide (**20**).* Following general procedures C and E, 1.5 mg (0.2 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 141.7 mg (1 equiv) of 4-bromobenzamide, 91.1 mg (1.2 equiv) of *p*-toluidine, and 198.8 mg (2.5 equiv) of KOtBu were heated to 120 °C for 14 h. After workup, the crude product was diluted with MeOH, added to silica gel, and evaporated. This silica was placed on top of a 20 g silica gel column and eluted with a gradient of 100% hexane to 60% ethyl acetate in hexanes, after which 60% ethyl acetate in hexanes was used until the product eluted from the column. After drying under vacuum at 200 mTorr, 132.7 mg (83%) was obtained as a colorless solid. Although the crude product was well soluble in MeOD, once purified, **20** was sparingly soluble in MeOH, MeCN, and EtOAc; thus the NMR spectra in CD_3OD were recorded as a suspension.

Mp 208−209 °C. ^{1}H NMR (600 MHz, CD_3OD) δ (7.72, dt, J = 8.8, 2.5 Hz, 2H, 2-CH), 7.11 (d, J = 8.4 Hz, 2H, 3′-CH), 7.06 (d, J = 8.4 Hz, 2H, 2′-CH), 6.98 (dt, J = 8.8, 2.5 Hz, 2H, 3-CH), 2.29 (s, 3H, 4′-Me) ppm; ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 172.2 ($CONH_2$), 150.5 (4-CN), 140.8 (1′-CN), 133.3 (4′-C), 131.1 (3′-CH), 130.7 (2-CH), 124.0 (1-C), 121.7 (2′-CH), 115.1 (3-CH), 21.1 (4′-Me); ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, CD_3OD) δ 88.9 (4-NH) ppm, $CONH_2$ was not visible. S (ESI/TOF) found (calculated): [M + Na$^+$] 249.1012 (249.1004) Da.

*9-(4-(tert-Butyl)phenyl)-9H-carbazole (**21**).* Following general procedures B and D, 1.0 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 201.3 mg (1 equiv) of 4-*tert*-butylbromobenzene, 165.9 mg (1.05 equiv) of carbazole, and 156.1 mg (1.5 equiv) of NaOtAm were heated to 120 °C for 14 h. After workup, the crude mixture was dissolved in DCM, adsorbed on silica gel, and evaporated. This silica gel was transferred on top of a 20 g silica gel column and eluted with hexanes. After drying under vacuum at 100 mTorr, 217.6 mg (77%) of **21** was obtained as a white solid.

The same result was observed employing 0.2 mol % of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**) under the same conditions. The reaction yield depended very much on the carbazole supplier; the best was the 98% pure one, purchased from Combi-Blocks.

Mp 187−188 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 8.14 (dt, J = 7.7, 0.8 Hz, 2H, 4-CH), 7.60 (dt, J = 8.5, 2.5 Hz, 2H, 3′-CH), 7.48 (dt, J = 8.5, 2.5 Hz, 2H, 2′-CH), 7.42 (dt, J = 8.1, 0.9 Hz, 2H, 1-CH), 7.39 (m, 2H, 2-CH), 7.27 (m, 2H, 3-CH), 1.42 (s, 9H, tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 150.6 (4′-C), 141.1 (9a-CN), 135.1 (1′-CN), 126.9 (3′-CH), 126.7 (2′-CH), 125.9 (2-CH), 123.4 (4a-C), 120.4 (4-CH), 119.8 (3-CH), 110.0 (1-CH), 34.9 (4′-CMe_3), 31.6 (4′-CMe_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, CD_3OD) δ 126.1 ppm. The spectral data are consistent with those reported in the literature.[24]

*4-(tert-Butyl)-N-(4-(tert-butyl)phenyl)-N-(4-vinylphenyl)aniline (**22**).* Following general procedures B and D, 1.6 mg (0.2 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 138.3 mg (1 equiv) of 4-bromostyrene, 223.3 mg (1.05 equiv) of bis(4-(*tert*-butyl)phenyl)-amine, and 127.2 mg (1.5 equiv) of KOtBu were heated to 50 °C for 14 h. After workup, the combined DCM extracts were dried over anhydrous Na_2SO_4, filtered, adsorbed on Celite, and dried in vacuum. This Celite was placed in a loading cartridge atop of a Santai neutral alumina column (24 g), and the product was eluted with hexanes. After drying under vacuum at 100 mTorr, 220.2 mg (76%) of **22** was obtained as a colorless solid.

Mp 155−156 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (m, 6H, 2-CH$^{Ar\text{-}vinyl}$ and 3-CH$^{Ar\text{-}tBu}$), 7.00 (dt, J = 8.6, 2.5 Hz, 4H, 2-CH$^{Ar\text{-}tBu}$), 6.98 (br d, J = 8.6 Hz, 2H, 2-CH$^{Ar\text{-}vinyl}$), 6.62 (dd, J = 17.6, 10.8 Hz, 1H, CH^{vinyl}), 5.58 (d, J = 17.6 Hz, 1H, CH_2^{vinyl}), 5.09 (d, J = 10.8 Hz, 1H, $CH_2^{Ar\text{-}vinyl}$), 1.29 (s, 18H, tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.9 (1-CN$^{Ar\text{-}vinyl}$), 145.8 (4-C$^{Ar\text{-}tBu}$), 145.0 (1-CN$^{Ar\text{-}tBu}$), 136.5 (CH^{vinyl}), 131.2 (4-C$^{Ar\text{-}vinyl}$), 127.0 (3-CH$^{Ar\text{-}vinyl}$), 126.2 (3-CH$^{Ar\text{-}tBu}$), 124.1 (2-CH$^{Ar\text{-}tBu}$), 122.9 (2-CH$^{Ar\text{-}vinyl}$), 111.7 ($CH_2^{Ar\text{-}vinyl}$), 34.4 (CMe_3), 31.6 (CMe_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 94.1 ppm. The spectral data are consistent with those reported in the literature.[89]

*1-(4-(tert-Butyl)phenyl)-1H-indole (**23**).* Following general procedures B and D, 1.3 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(morpholine)Cl_2] (**1b**), 261.7 mg (1 equiv) of 4-*tert*-butylbromobenzene, 151.1 mg (1.05 equiv) of indole, and 177.0 mg (1.5 equiv) of NaOtBu were heated to 100 °C for 14 h (reaction performed at 120 °C for 1 h gave almost the same results). After workup, the combined DCM extracts were dried over anhydrous Na_2SO_4, filtered, adsorbed on silica gel, and dried in vacuum. This silica gel was transferred on top of a 10 g silica gel column. The column was eluted by hexanes (2 column volumes), then ramping polarity to 5% EtOAc (10 column volumes), then isocratic. The mixture of the two stated products was coeluated by 2% EtOAc in hexanes during gradient. The related fractions were evaporated, redissolved in DCM, and adsorbed on silica gel. This silica was reloaded on top of a 20 g silica gel column and eluted with hexanes, yielding **23** first, followed by 1,3-bis(4-(*tert*-butyl)phenyl)-1*H*-indole (for characterization data, see below). Evaporation of related fractions and drying under vacuum at 100 mTorr vacuum provided 250.8 mg (82%) of **23** as a colorless solid.

Mp 116−117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 7.9 Hz, 1H, 4-CH), 7.53 (d, J = 8.3 Hz, 1H, 7-CH), 7.44 (dt, J = 8.5, 2.5 Hz, 2H, 3′-CH), 7.35 (dt, J = 8.5, 2.5 Hz, 2H, 2′-CH), 7.25 (d, J = 3.2 Hz, 1H, 2-CH), 7.17 (m, 1H, 6-CH), 7.13 (m, 1H, 5-CH), 6.62 (d, J = 3.2 Hz, 1H, 3-CH), 1.33 (s, 9H, tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.5 (4′-C), 137.3 (1′-C), 136.0 (8-C), 129.3 (9-C), 128.1 (2-CH), 126.5 (3′-CH), 124.0 (2′-CH), 122.3 (6-CH), 121.2 (4-CH), 120.3 (5-CH), 110.7 (7-CH), 103.4 (3-CH), 34.7 (4′-CMe_3), 31.5 (4′-CMe_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 145.4 ppm. The spectral data are consistent with those reported in the literature.[71]

1,3-Bis(4-(tert-butyl)phenyl)-1H-indole was isolated as a byproduct (42.2 mg, 18.0%, colorless solid) in preparation of 1-(4-(*tert*-butyl)phenyl)-1*H*-indole (**23**).

Mp 163−164 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (br d, J = 7.3 Hz, 1H, 4-CH, NOE with 7.64 ppm peak), 7.64 (dt, J = 8.4, 2.5 Hz, 2H, 2-CH^{CAr}, NOE with 7.99 ppm peak), 7.59 (br d, J = 7.7 Hz, 1H, 7-CH NOE with 7.45 ppm peak), 7.52 (dt, J = 8.6, 2.5 Hz, 2H, 3-CH^{NAr}), 7.49 (dt, J = 8.4, 2.5 Hz, 2H, 3-CH^{CAr}), 7.45 (m, 3H, 2-CH^{NAr} and 2-CH, NOE with 7.59 ppm peak), 7.24 (m, 1H, 6-CH), 7.21 (m, 1H, 5-CH), 1.384 (s, 9H, 4-tBu^{NAr}), 1.380 (s, 9H, 4-tBu^{CAr}) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.8 (4-C^{NAr}), 149.1 (4-C^{CAr}), 137.1 (1-CN^{NAr}), 136.8 (8-C), 132.4 (1-C^{CAr}), 127.4 (2-CH^{CAr}), 127.3 (9-C), 126.6 (3-CH^{NAr}), 125.9 (3-CH^{CAr}), 125.6 (2-C), 124.2 (2-CH^{NAr}), 122.7 (6-CH), 120.7 (5-CH), 120.3 (4-CH), 118.8 (3-C), 111.0 (7-CH), 34.8 (4-CMe_3^{NAr}), 34.7 (4-CMe_3^{CAr}), 31.58 (4-CMe_3^{NAr}), 31.55 (4-CMe_3^{CAr}) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 144.4 ppm. HRMS (EI) m/z: [M]$^+$ calcd for $C_{28}H_{31}N^+$ 381.2457; found 381.24444.

*4-(tert-Butyl)-N-(4-(tert-butyl)phenyl)-N-(p-tolyl)aniline (**24**).* Following general procedures B and D, 1.7 mg (0.2 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 344.0 mg (2 equiv) of 4-*tert*-butylbromobenzene, 86.5 mg (1 equiv) of *p*-toluidine, and 271.7 mg (3 equiv) of KOtBu were heated to 50 °C for 14 h. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 10 g silica gel column and eluted with a gradient of 100% hexane to 10% ethyl acetate in hexanes. After drying under vacuum at 200 mTorr, 278.9 mg yield (93.0%) of **24** was obtained as a white solid.

Mp 121−122 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dd, J = 8.6, 2.5 Hz, 4H, 3-CH), 7.04 (d, J = 8.3 Hz, 2H, 3′-CH), 7.01−6.96 (m, 6H, indirectly assigned: 6.99 2′-CH, 6.98 2-CH), 2.30 (s, 3H, 4′-Me), 1.30 (s, 18H, 4-tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 145.7 (1′-CN), 145.5 (1-CN), 145.0 (4-C), 132.1 (4′-C), 129.9 (3′-CH), 126.0 (3-CH), 124.5 (2′-CH), 123.2 (2-CH), 34.4 (4-CMe_3), 31.6 (4-CMe_3), 21.0 (4′-Me) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 91.4 ppm. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{27}H_{37}N^+$ 372.2691; found 372.2689.

Attempt of 4-Styrylamine Diarylation by 4-tert-Butylbromobenzene. For this reaction, we used 97% pure 4-aminostyrene stabilized by KOH (0.5 mol %), supplied by Oakwood. KOH is an inhibitor of Pd-catalyzed coupling; thus it was deactivated by the addition of HMDS. We also had to add BHT to the reaction mixture to inhibit

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J. Org. Chem. 2021, 86, 10343−10359

polymerization. Addition order is very important for this reaction. In the glovebox, a 2 dram vial was wrapped in aluminum foil and charged with 1.2 mg (0.2 mol %) of [Pd(DiMeiHept^{Cl})(cinnamyl)Cl] (**1a**), 2.5 mg (1 mol %) of BHT, 3.7 mg (2 mol %) of HMDS, 242.8 mg (2 equiv) of 4-*tert*-butylbromobenzene, and 67.9 mg (1 equiv) of 4-aminostyrene. The mixture was stirred for a few seconds after which 191.8 mg (3 equiv) of KOtBu was added, the vial was closed, and the content was immediately stirred magnetically at r.t. for a few seconds. The vial was taken out of the glovebox and inserted in a preheated metal-bead bath, and the mixture was stirred at 1200 rpm at 80 °C for 14 h. Quenching was performed according to general procedure D. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 24 g neutral alumina column. The column was eluted by hexanes (7 column volumes), then ramping polarity to 5% EtOAc (6 column volumes), then isocratic. The first compound eluted by hexanes was the desired product; evaporation and drying under vacuum at 100 mTorr provided 112.2 mg (51.3%) of *4-(tert-butyl)-N-(4-(tert-butyl)phenyl)-N-(4-vinylphenyl)aniline* (**22**). The second compound was also eluted by hexanes, which, following the same solvent removal process, provided 51.8 mg (17.6%) of *N,N-bis(4-tert-butylphenyl)-4-[2-(4-tert-butylphenyl)ethenyl]benzenamine*. The third compound (7.2 mg, 5.0%) eluted at the end of the gradient ramp was *4-(tert-butyl)-N-(4-vinylphenyl)aniline* (**10**). Immediately following **10** came the forth compound 11.7 mg (8.2%), which was identified to be *4-tert-butyl-N-[4-[2-(4-tert-butylphenyl)ethenyl]phenyl]benzenamine*.

N,N-Bis(4-*tert*-butylphenyl)-4-[2-(4-*tert*-butylphenyl)ethenyl]-benzenamine, light brown solid.

Mp 172−173 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H, 2′′-CH^{CAr}), 7.35 (d, J = 8.5 Hz, 2H, 3′′-CH^{CAr}), 7.34 (d, J = 8.8 Hz, 2H, 3-CH), 7.25 (dt, J = 8.8, 2.5 Hz, 4H, 3′-CH^{NAr}), 7.04−6.99 (m, 7H, indirectly assigned: 7.02 2-CH and 2′-CH^{NAr}, 7.01 1-CH^{ethenyl}), 6.95 (d, J = 16.0 Hz, 1H, 2-CH^{ethenyl}), 1.32 (4′′-tBu^{CAr}), 1.30 (4′-tBu^{NAr}); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.4 (4′′-C^{CAr}), 147.6 (1-C), 145.9 (4′-C^{NAr}), 145.0 (1′-C^{NAr}), 135.1 (1-C^{CAr}), 131.1 (4-C), 127.7 (1-CH^{ethenyl}), 127.3 (3-CH), 126.5 (2-CH^{ethenyl}), 126.2 (3′-CH^{NAr}), 126.1 (2′′-CH^{CAr}), 125.7 (3′′-CH^{CAr}), 124.2 (2′-CH^{NAr}), 123.0 (2-CH), 34.7 (4′′-*C*Me$_3^{CAr}$), 34.4 (4′-*C*Me$_3^{NAr}$), 31.6 (4′-C*Me*$_3^{NAr}$), 31.5 (4′′-C*Me*$_3^{CAr}$) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 94.4 ppm. HRMS (EI) m/z: [M]$^+$ calcd for $C_{38}H_{45}N^+$ 515.3552; found 515.35773.

4-*tert*-Butyl-*N*-[4-[2-(4-*tert*-butylphenyl)ethenyl]phenyl]-benzenamine, light brown solid.

Mp 148−149 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H, 2′′-CH^{CAr}), 7.40 (d, J = 8.4 Hz, 2H, 3′-CH), 7.36 (d, J = 8.4 Hz, 2H, 3′′-CH^{CAr}), 7.31 (dt, J = 8.4, 2.5 Hz, 2H, 3-CH^{NAr}), 7.05 (dt, J = 8.4, 2.5 Hz, 2H, 2-CH^{NAr}), 7.02 (d, J = 8.4 Hz, 2H, 2′-CH), 7.02 (d, J = 16.3 Hz, 1H, 1-CH^{ethenyl}), 6.95 (d, J = 16.3 Hz, 1H, 2-CH^{ethenyl}), 5.70 (br s, 1H, NH), 1.33 (s, 9H, 4′′-tBu^{CAr}), 1.32 (s, 9H, 4-tBu^{NAr}) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.2 (4-C^{NAr}), 144.5 (4′′-C^{CAr}), 143.2 (1′-CN), 139.9 (1-CN^{NAr}), 135.1 (1′′-C^{CAr}), 129.9 (4′-C), 127.7 (1-CH^{ethenyl}), 127.5 (3′-CH), 126.2 (3-CH^{NAr}), 125.9 (2′′-CH^{CAr}), 125.7 (2-CH^{ethenyl}), 125.6 (3′′-CH^{CAr}), 118.4 (2-CH^{NAr}), 116.9 (2′-CH), 34.6 (4′′-*C*Me$_3^{CAr}$), 34.2 (4-*C*Me$_3$), 31.5 (4-C*Me*$_3$), 31.4 (4′′-C*Me*$_3^{CAr}$) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 82.2 ppm. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{28}H_{34}N^+$ 384.2691; found 384.2709.

Attempt of 4-(tert-Butyl)-N-(4-vinylphenyl)aniline (10) N-Arylation. In the glovebox, a 2 dram vial was wrapped in aluminum foil and charged with 1.5 mg (0.1 mol %) of [Pd(DiMeiHept^{Cl})(morpholine)-Cl$_2$] (**1b**), 3.1 mg (1 mol %) of BHT, 238.5 mg (1.5 equiv) of KOtBu, and 374.0 mg (1.0 equiv) of 4-(*tert*-butyl)-*N*-(4-vinylphenyl)aniline. The mixture was stirred by a spatula; then 302.0 mg (1 equiv) of 4-*tert*-butylbromobenzene was added. A stir bar was placed in the vial, and it was corked. For a few seconds, the mixture was stirred magnetically at r.t.; then the vial was taken out of glovebox and inserted in a preheated metal-bead bath. The mixture was stirred at 1200 rpm at 120 °C for 1 h. Quenching was performed according to general procedure D. After workup, the crude mixture was dissolved in hexanes and poured directly on top of a 24 g neutral alumina column. Chromatographic purification and drying in the same manner as described for the previous experiment provided 114.5 mg (21.1%) *of 4-(tert-butyl)-N-(4-(tert-butyl)phenyl)-N-(4-vinylphenyl)aniline* (**22**), 183.8 mg (50.3%) of *N,N-bis(4-tert-butylphenyl)-4-[2-(4-tert-butylphenyl)ethenyl]benzenamine*, 95.6 mg (25.6%) of unreacted *4-(tert-butyl)-N-(4-vinylphenyl)aniline* (**10**), and 129.6 mg (23.8%) of *4-tert-butyl-N-[4-[2-(4-tert-butylphenyl)ethenyl]phenyl]benzenamine*.

3-(p-Tolylamino)phenol (25). Addition order is important for this experiment. In a nitrogen filled glovebox, a 2 dram vial was wrapped in aluminum foil and charged with 1.6 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 426.2 mg (2.5 equiv) of KOtBu, and 195.3 mg (1.2 equiv) of *p*-toluidine. The content was stirred by a metal spatula, and then 453.4 mg (1.05 equiv) of Ti(OiPr)$_4$ was added, followed by 262.8 mg (1 equiv) of 3-bromophenol. Immediately after addition, the mixture was stirred magnetically for a few seconds until exothermic initiation and cementation happened. Following this, the vial was taken out of the glovebox and placed in a preheated metal-bead bath. The content was stirred at 1200 rpm at 50 °C for 15 min and was quenched by addition of 517 mg (2.7 equiv) of KH_2PO_4, water, and DCM. The content was stirred by a spatula. The mixture was filtered, and the filter cake was washed well with DCM. The phases were separated, and the aqueous phase was washed with DCM (3 × 2 mL). The combined DCM extracts were dried over anhydrous Na_2SO_4, concentrated, adsorbed on Celite, evaporated, and dried. This Celite was placed in a loading cartridge placed before a Santai neutral alumina column (24 g), and the product was eluted by a gradient of 100% hexane to 30% ethyl acetate in hexanes, then isocratic. The product was dried under vacuum at 100 mTorr vacuum to a constant mass, providing 257.1 mg (82%) of **25** as a light brown oil. NMR has shown some residual EtOAc, which could not be removed in vacuum. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11−7.06 (m, 3H, indirectly assigned: 7.09 3′-CH, 7.07 5-CH), 7.01 (dt, J = 8.4, 2.5 Hz, 2H, 2′-CH), 6.54 (ddd, J = 8.1, 2.2, 0.6 Hz, 1H, 4-CH), 6.49 (t, J = 2.2 Hz, 1H, 2-CH), 6.32 (ddd, J = 8.1, 2.2, 0.6 Hz, 1H, 6-CH), 5.59 (br s, 1H, NH), 4.71 (br s, 1H, OH), 2.31 (s, 3H, 4′-Me) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 156.7 (1-CO), 145.9 (3-CN), 139.8 (1′-CN), 131.6 (4′-C), 130.5 (5-CH), 130.0 (3′-CH), 119.9 (2′-CH), 109.3 (4-CH), 107.1 (6-CH), 103.1 (2-CH), 20.9 (4′-Me); ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 81.0 ppm. The spectral data are consistent with those reported in the literature.[90]

4-(p-Tolylamino)phenol (26). Addition order is important for this experiment. In the glovebox, a 2 dram vial was wrapped in aluminum foil and charged with 1.2 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})-(cinnamyl)Cl] (**1a**), 197.1 mg (1 equiv) of 4-bromophenol, and 467.8 mg (1.5 equiv) of 90% (technical grade) Al(OtBu)$_3$. The content was stirred by a metal spatula for a few seconds, and then by a magnetic stir bar at r.t. for 10 min, which resulted in the formation of white cemented solid. Following this, 191.8 mg (1.5 equiv) of KOtBu and 146.5 mg (1.2 equiv) of *p*-toluidine were added and the mixture was stirred by a spatula. Within a few seconds, the mixture melted and the color changed to ochre. The vial was taken out of the glovebox and placed in a preheated metal-bead bath. The content was stirred at 1200 rpm at 50 °C for 15 min, after which the reaction was quenched with the addition of 2 mL of sat. aqueous NH_4Cl and DCM. The mixture was then sonicated in an ultrasound bath for 5 min and stirred magnetically for 5 min, which resulted in separation of the DCM layer from the aqueous gel. 10 mL of 0.9 M aqueous Rochelle salt was added, which disrupted the gel. The phases were separated, and the aqueous layer was extracted by DCM (3 × 5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated, adsorbed on Celite, evaporated, and dried. This Celite was placed atop of a Santai neutral alumina column (20 g). Elution began with hexanes, and the polarity was ramped to 30% EtOAc in hexanes over 5 column volumes (CV) and then continued isocratically with 30% EtOAc. Immediately following the elution of unreacted *p*-toluidine, the eluent polarity was ramped to 100% EtOAc within 1 CV, 100% EtOAc was left running for 1 CV, and then the polarity was ramped to 10% MeOH in EtOAc within 1 CV, after which isocratic elution with 10% MeOH in EtOAc was continued.

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J. Org. Chem. 2021, 86, 10343−10359

The desired product started to elute by 100% EtOAc, but we knew it is partially adsorbed irreversibly until MeOH is added, which is the reason this elution procedure was developed. The product was eluted in two fractions, one when 100% EtOAc has hit the column, and the second when MeOH has reached it. Both fractions were combined, evaporated, and dried under vacuum at 100 mTorr, providing 170.3 mg (73%) of **26** as a light-brown solid containing a tiny quantity of 4-bromophenol.

Mp 123−124 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (d, J = 8.2 Hz, 2H, 3′-CH), 6.96 (dt, J = 8.8, 2.8 Hz, 2H, 3-CH), 6.84 (d, J = 8.2 Hz, 2H, 2′-CH), 6.76 (dt, J = 8.8, 2.8 Hz, 2H, 2-CH), 5.37 (br s, 1H, NH), 4.61 (br s, 1H, OH), 2.27 (s, 3H, 4′-Me) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.6 (1-CO), 142.5 (1′-CN), 136.9 (4-CN), 130.0 (3′-CH), 129.6 (4′-C), 121.4 (3-CH), 116.8 (2′-CH), 116.2 (2-CH), 20.7 (4′-Me) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 76.0 ppm. The spectral data are consistent with those reported in the literature.[90]

*4-((4-(tert-Butyl)phenyl)amino)phenol (**27**).* Addition order is important for this experiment. In the glovebox, a 2 dram vial was wrapped in aluminum foil and charged with 1.5 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 239.7 mg (1.5 equiv) of KOtBu, and 186.5 mg (1.2 equiv) of 4-aminophenol. The content was stirred by a metal spatula after which 506.0 mg (1.25 equiv) of $Ti(OiPr)_4$ was added, and the mixture was stirred magnetically for a few seconds. Thereafter, 303.5 mg (1 equiv) of 4-*tert*-butylbromophenol was added and the content was stirred magnetically for a few seconds. The vial was taken out of the glovebox and placed in a preheated metal-bead bath. The content was stirred at 1200 rpm at 50 °C for 15 min, and the reaction was quenched with the addition of 2 mL of sat. aqueous NH_4Cl and DCM. The mixture was filtrated through Celite, and the filter cake was washed well with DCM. A sample was taken from the DCM extract and subjected to No-D NMR, showing the product (90.2 mol %) and *tert*-butylbenzene (reduced educt, 9.8 mol %). The organic phase was dried over anhydrous Na_2SO_4, filtrated through a 1 cm plug of Na_2SO_4, and then washed well with DCM. The filtrate was concentrated, adsorbed on silica gel, and dried in vacuum. This silica was placed on top of a 10 g silica gel column and eluted with hexanes (1 column volume), followed by ramping the polarity to 10% EtOAc over 5 column volumes, then isocratic with 10% EtOAc, providing 294.3 mg (86%) g of **27** as a light brown solid after drying under vacuum at 200 mTorr until a constant mass. NMR has shown some residual EtOAc, which could not be removed in vacuum.

This reaction also could be done in the absence of Lewis acid, but with lower conversion. We have observed the formation of 4-((4-(*tert*-butyl)phenyl)imino)cyclohexa-2,5-dienone (iminoquinone) in this case, which inhibits further Pd coupling. The formation of iminoquinone is caused by undesired Pd-catalyzed redox processes, as quenching of the reaction in the glovebox with deoxygenated aqueous KH_2PO_4 and DCM also resulted in iminoquinone formation. Other Lewis acids including aluminum *tert*-butoxide, boron *tert*-butoxide, titanium *tert*-butoxide, tetrakis((trimethylsilyl)oxy)titanium, and *tert*-butyl borate led to worse results.

Mp 100−101 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (dt, J = 8.6, 2.5 Hz, $CHCl_3$ and 3′-CH), 6.99 (dt, J = 8.8, 2.9 Hz, 2H, 3-CH), 6.87 (dt, J = 8.6, 2.5 Hz, 2H, 2′-CH), 6.76 (dt, J = 8.8, 2.9 Hz, 2H, 2-CH), 5.40 (br s, 1H, NH), 4.58 (br s, 1H, OH), 1.29 (s, 9H, tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.7 (1-CO), 142.9 (4′-C), 142.5 (1′-CN), 136.6 (4-CN), 126.2 (3′-CH), 121.7 (3-CH), 116.2 (2-CH), 116.0 (2′-CH), 34.19 (4′-CMe_3), 31.6 (4′-CMe_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 76.0 ppm. MS (ESI/TOF) found (calculated): HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{19}N_2^+$ 242.1545; found 242.1538.

*(4-(p-Tolylamino)phenyl)methanol (**28**).* In the glovebox, a 2 dram vial was wrapped in aluminum foil and was charged consecutively with 1.6 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})-(cinnamyl)Cl] (**1a**), 294 mg (1 equiv) of 4-bromobenzyl alcohol, 195.3 mg (1.2 equiv) of *p*-toluidine, and 255 mg (1 equiv) of HMDS. The content was stirred for a few seconds, and then the vial was charged as quickly as possible with 365.0 mg (2.5 equiv) of NaOtBu. Immediately after that, the vial was corked and the content was vigorously stirred magnetically for ca. 30 s, until exothermic initiation happened, which resulted in reaction mixture cementation. Following this, the flask was taken out of the glovebox and placed in a preheated metal-bead bath and the mixture was stirred at 1200 rpm at 50 °C for 15 min. The reaction was quenched with 2 mL of water and 2 mL of DCM. The DCM layer was separated and analyzed by No-D NMR, which illustrated the product to be 4-methyl-*N*-(4-(((trimethylsilyl)-oxy)methyl)phenyl)-aniline. The remaining aqueous phase was extracted by DCM (3 × 2 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4, filtrated, and adsorbed on silica gel. This silica was placed on top of a 10 g silica gel column and eluted with a gradient of 100 hexanes to 30% EtOAc in hexanes, then isocratic, providing 302.6 mg (90%) of **28** as off-white solid. 4-Methyl-*N*-(4-(((trimethylsilyl)oxy)methyl)phenyl)aniline and 4-methyl-*N*-(4-(*p*-tolylamino)benzylidene)aniline were also isolated as byproducts (see characterization data below).

Mp 103−104 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dt, J = 8.4, 2.5 Hz, 2H, 2-CH), 7.09 (d, J = 8.3 Hz, 2H, 3′-CH), 7.00−6.96 (m, 4H, indirectly assigned: 6.99 2′-CH, 6.97 3-CH), 5.64 (br s, 1H, NH), 4.57 (s, 2H, OCH_2), 2.30 (s, 3H, 4′-Me), 1.68 (OH and water) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.8 (4-CN), 140.2 (1′-CN), 132.7 (1-C), 131.2 (4′-C), 130.0 (3′-CH), 128.5 (2-CH), 119.1 (2′-CH), 116.9 (3-CH), 65.3 (OCH_2), 20.8 (4′-Me) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 80.5 ppm. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}NO^+$ 214.1232; found 214.1223.

4-Methyl-N-(4-(((trimethylsilyl)oxy)methyl)phenyl)aniline was isolated as a byproduct (22.1 mg, 4.9%, brown oil) in preparation of (4-(*p*-tolylamino)phenyl)methanol (**28**). This substance is not stable on storage under air and is quickly desilylated by atmospheric moisture.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dt, J = 8.4, 2.5 Hz, 2H, 3′-CH), 7.08 (d, J = 8.3 Hz, 2H, 3-CH), 7.03−6.97 (m, 4H, indirectly assigned: 7.00 2-CH, 6.99 2′-CH), 5.61 (br s, 1H, NH), 4.63 (s, 2H, 4′-CH_2O), 2.32 (s, 3H, 4-Me), 0.17 (s, 9H, $SiMe_3$) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.1 (1′-CN), 140.6 (1-C), 133.0 (4′-C), 130.8 (4-C), 130.0 (3-CH), 128.3 (3′-CH), 118.7 (2-CH), 117.2 (2′-CH), 64.7 (4′-CH_2O), 20.8 (4-Me), −0.2 ($SiMe_3$) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 80.0 ppm. HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{23}NOSi^+$ 285.1549; found 285.15377.

4-Methyl-N-(4-(p-tolylamino)benzylidene)aniline was isolated as a byproduct (5.1 mg, 1.1%, brick red solid) in preparation of (4-(*p*-tolylamino)phenyl)methanol (**28**).

Mp 117−118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H, N=CH), 7.75 (dt, J = 8.6, 2.5 Hz, 2H, 3′-CH), 7.18 (d, J = 8.2 Hz, 2H, 3-CH^{NTol}), 7.15 (d, J = 8.3 Hz, 2H, 3-CH^{NHTol}), 7.11 (d, J = 8.2 Hz, 2H, 2-CH^{NTol}), 7.08 (d, J = 8.3 Hz, 2H, 2-CH^{NHTol}), 7.00 (dt, J = 8.6, 2.5 Hz, 2H, 2′-CH), 5.90 (br s, 1H, NH), 2.36 (s, 3H, 4-Me^{NTol}), 2.34 (s, 3H, 4-Me^{NHTol}) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 159.3 (N=CH), 150.2 (1-CN^{NTol}), 147.3 (1′-C), 138.7 (1-CN^{NHTol}), 135.2 (4-C^{NTol}), 132.8 (4-C^{NHTol}), 130.6 (3′-CH), 130.2 (3-CH^{NHTol}), 129.8 (3-CH^{NTol}), 128.2 (4′-C), 120.94 (2-CH^{NTol}), 120.88 (2-CH^{NHTol}), 115.2 (2′-CH), 21.1 (4-Me^{NTol}), 21.0 (4-Me^{NHTol}) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 84.9 (NH), 308.3 (N=CH) ppm. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{21}N_2^+$ 301.1705; found 301.1717.

*(2-((4-(tert-Butyl)phenyl)amino)phenyl)methanol (**29**).* In the glovebox, a 2 dram vial was wrapped in aluminum foil and was charged consecutively with 1.6 mg (0.1 mol %) of [Pd-(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 323.8 mg (1 equiv) of 4-*tert*-butylbromobenzene, 224.5 mg (1.2 equiv) of 2-aminobenzyl alcohol, and 294.2 mg (1.2 equiv) of HMDS. The content was stirred for a few seconds, and then the vial was charged as quickly as possible with 394.2 mg (2.7 equiv) of NaOtBu. Immediately after that, the vial was corked and the content was vigorously stirred magnetically for ca. 30 s until exothermic initiation happened, which resulted in reaction mixture cementation. Following this, the flask was taken out of the glovebox, placed in a preheated metal-bead bath, and stirred at 1200

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J. Org. Chem. 2021, 86, 10343−10359

rpm at 50 °C for 15 min. The reaction was quenched with 2 mL of water and 2 mL of DCM. The DCM layer was separated and analyzed by No-D NMR, confirming the presence of *N*-(4-(*tert*-butyl)phenyl)-2-(((trimethylsilyl)oxy)methyl)aniline. The remaining aqueous phase was extracted with DCM (3 × 2 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4, filtrated, and evaporated. The crude product was dissolved in hexanes and poured on top of a 20 g silica gel column. The product was eluted using a gradient of 100% hexanes to 100% DCM, then isocratic, providing 305.8 mg (79%) of **29** as a brown solid after drying under vacuum at 200 mTorr.

Mp 75−76 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, J = 8.1 Hz, 1H, 3-CH), 7.28 (dd, J = 8.6, 2.5 Hz, 2H, 3′-CH), 7.19 (td, J = 7.7, 1.5 Hz, 1H, 4-CH), 7.15 (dd, J = 7.3, 1.1 Hz, 1H, 6-CH), 7.01 (dd, J = 8.6, 2.5 Hz, 2H, 2′-CH), 6.83 (t, J = 7.3 Hz, 5-CH), 6.73 (br s, 1H, NH), 4.66 (s, 2H, OCH_2), 1.92 (br s, 1H, OH), 1.31 (s, 9H, tBu) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.1 (4′-C), 143.7 (2-CN), 140.3 (1′-CN), 129.7 (3-CH), 129.3 (4-CH), 128.0 (1-C), 126.2 (3′-CH), 120.0 (5-CH), 118.4 (2′-CH), 116.6 (3-CH), 64.7 (OCH_2), 34.3 (4′-CMe_3), 31.6 (4′-CMe_3) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 77.5 ppm. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}NO^+$ 278.1521; found 278.1546.

*N-Phenyl-4-vinylaniline (**30**).* Large scale preparation. For this reaction, we used 97% pure 4-bromostyrene stabilized by 3,5-di-*tert*-butylcatechol (0.1 mol %), supplied by AK Scientific.

A 100 mL pear-shaped flask, stir bar, 10 cm Vigreux column, rubber septum, and balloon attached to a syringe needle were placed into the glovebox. The top joint of the Vigreux column was corked by a rubber septum and pierced by a needle equipped with a balloon. The flask was wrapped in aluminum foil and charged with 28.4 mg (0.1 mol %) of [Pd(DiMeIHept^{Cl})(cinnamyl)Cl] (**1a**), 4.9362 g (1 equiv) of 4-bromostyrene, and 2.5114 g (1 equiv) of aniline. The content was stirred magnetically for a few seconds, followed by the rapid addition of 3.3285 g (1.1 equiv) of KOtBu. Immediately after that, the flask was corked by the Vigreux column, and the content was immediately stirred magnetically. In 30−60 s, this resulted in initiation of a mild exotherm with refluxing of tBuOH. The balloon mounted on top of the Vigreux column protected the glovebox atmosphere from any gas evolved. The assembled apparatus was taken out of glovebox and placed in a metal-bead bath preheated to 50 °C. After stirring at 1200 rpm for 15 min, the mixture was cooled to r.t. and the reaction was quenched with water (20 mL) and EtOAc (20 mL). This formed a stable emulsion that was broken by the addition of aqueous saturated Na_2SO_4 solution. The layers were separated, and the organic phase was washed with aqueous saturated Na_2SO_4 (50 mL). The organic extract was dried over anhydrous Na_2SO_4, filtrated, and washed with EtOAc. 50 g of neutral aluminum oxide was added to this solution, which was then evaporated and dried under vacuum at 100 mTorr. This alumina was transferred to a paper thimble and placed to a Soxhlet extractor. The desired product was extracted by boiling pentane for 24 h. To the receiving flask (where pentane was boiling) was added 6 mg of BHT before extraction started to inhibit polymerization. The product is sensitive to overheating, so we used a flat bottom Erlenmeyer flask as receiving flask and placed it directly on a hot plate, setting the temperature to 90 °C. The whole apparatus was wrapped in aluminum foil to insulate the contents, which led to a gentle boil, thus avoiding overheating during extraction. After extraction completed, the apparatus was cooled to r.t. and the pentane extract was evaporated and dried under vacuum at 100 mTorr for 48 h, providing 3.2774 g (62.2%) of **30** as light yellow solid. Diffusion NMR spectroscopy conducted on the product did not reveal any noticeable quantity of polymeric material. The remaining thimble was further extracted with boiling Et_2O for 24 h; however, this provided only a mixture of unidentified compounds. Thus, most of the product was extracted by pentane. Drying for 48 h was needed to remove traces of aniline.

For this compound, all properties, respectively, stability and disposition to decomposition are the same as those for 4-methyl-*N*-(4-vinylphenyl)aniline (**9**).

Mp 68−69 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (dt, J = 8.6, 2.2 Hz, 2H, 3-CH), 7.27 (m, 2H, 3′-CH), 7.07 (m, 2H, 2′-CH), 7.01 (dt, J = 8.6, 2.2 Hz, 2H, 2-CH), 6.94 (tt, J = 7.4, 1.0 Hz, 1H, 4′-CH), 6.65 (dd, J = 17.6, 10.8 Hz, 1H, CH^{vinyl}), 5.73 (br s, 1H, NH), 5.61 (dd, J = 17.6, 0.8 Hz, 1H, CH_2^{vinyl}), 5.11 (dd, J = 10.8, 0.8 Hz, 1H, CH_2^{vinyl}) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 142.94 (1-CN), 142.85 (1′-CN), 136.5 (CH^{vinyl}), 130.6 (4-C), 129.5 (3′-CH), 127.4 (3-CH), 121.4 (4′-CH), 118.2 (2′-CH), 117.5 (2-CH), 111.3 (CH_2^{vinyl}) ppm; ^{15}N NMR (^{1}H−^{15}N HMBC projection, 60 MHz, $CDCl_3$) δ 83.0 ppm. The spectral data are consistent with those reported in the literature.[91]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01057.

^{1}H and ^{13}C NMR spectra of isolated compounds and byproducts. Detailed crystallographic data for complexes **1a** and **1b** PDF)

Accession Codes

CCDC 2071914 and 2071915 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare the following competing financial interest(s): The PI receives royalty payments for the sales of catalysts in this manuscript.

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