JOC The Journal of Organic Chemistry

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Generating Active "L-Pd(0)" via Neutral or Cationic π-Allylpalladium Complexes Featuring Biaryl/Bipyrazolylphosphines: Synthetic, Mechanistic, and Structure–Activity Studies in Challenging Cross-Coupling Reactions§

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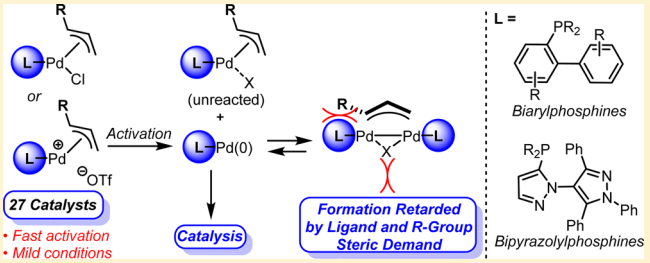
Supporting Information

ABSTRACT: Two new classes of highly active yet air- and moisture-stable π-R-allylpalladium complexes containing bulky biaryl- and bipyrazolylphosphines with extremely broad ligand scope have been developed. Neutral π-allylpalladium complexes incorporated a range of biaryl/bipyrazolylphosphine ligands, while extremely bulky ligands were accommodated by a cationic scaffold. These complexes are easily activated under mild conditions and are efficient for a wide array of challenging C–C and C–X (X = heteroatom) cross-coupling reactions. Their high activity is correlated to their facile activation to a 12-electron-based "L-Pd(0)" catalyst under commonly employed conditions for cross-coupling reactions, noninhibitory byproduct release upon activation, and suppression of the off-cycle pathway to form dinuclear $(\mu\text{-allyl})(\mu\text{-Cl})Pd_2(L)_2$ species, supported by structural (single crystal X-ray) and kinetic studies. A broad scope of C–C and C–X coupling reactions with low catalyst loadings and short reaction times highlight the versatility and practicality of these catalysts in organic synthesis.



INTRODUCTION

Pd-catalyzed cross-coupling reactions have become arguably the most practiced reactions of the 21st century in modern synthetic organic chemistry.[1] These reactions have been a benefactor to many areas of chemical research, because they are extensively utilized to prepare privileged structures for pharmaceutical, agrochemical, and electronics applications.[2] Traditionally the presumed active catalyst in these transformations, a ligated-Pd(0) complex, has been generated *in situ* by mixing a ligand with one of various Pd-precursors such as $Pd_2(dba)_3$ or $Pd(OAc)_2$. The drawbacks and limitations of these methods are well documented in the literature.[3] The original use[4] and development[5] of preformed $L_2Pd(0)$ complexes for cross-coupling applications by Dai and Fu and our group, respectively, have helped to alleviate some of these issues, although these catalysts are air-sensitive and contain an extra ligand that is often not necessary for many catalytic processes (Figure 1A).[6] Hartwig has introduced the use of a monoligated Pd(I)-dimer $\{[P(t\text{-}Bu)_3]PdBr\}_2$ for relatively challenging cross-coupling reactions.[7] However, this Pd(I) dimer complex is more air-sensitive in comparison to $[P(t\text{-}Bu)_3]_2Pd$ and has limitations with respect to ligand scope, which has hindered the development of a broad family of precatalysts.[8]

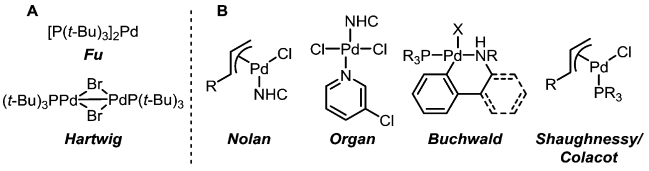


Figure 1. Examples of preformed Pd-complexes used in cross-coupling.

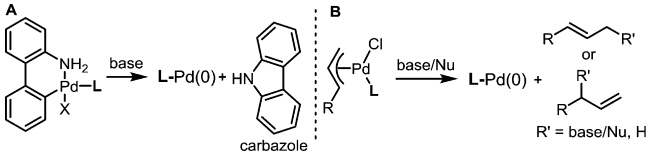
To address the issues described above, the development and use of air-stable, preformed monoligated-Pd complexes (Figure 1B) has become an emerging trend. These so-called "precatalysts" have been designed to generate the active *monoligated* 12-electron-based "L-Pd(0)" upon activation, ideally under the same conditions employed in cross-coupling reactions.[3a,b] For example, Nolan and co-workers have introduced NHC-ligated π-allylpalladium chloride (NHC = N-heterocyclic carbene) complexes for mild Suzuki–Miyaura and Buchwald–Hartwig amination reactions,[9] while Organ and co-workers have utilized pyridine stabilization to synthesize precatalysts with similar ligand types (PEPPSI catalysts).[10] Shaughnessy and Colacot and their co-workers, together[11a] and independently,[11b] described the preparation and use of phosphine-ligated π-allylpalladium chloride complexes, which were shown to be highly efficient and superior in a variety of C–C and C–N cross-coupling reactions in comparison to the *in situ* systems. Nolan and co-workers have additionally described a phosphine-ligated π-cinnamylpalladium complex

Received: May 5, 2015
Published: June 2, 2015

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794–6813

for aryl amination reactions.[12] Among the most versatile precatalysts available today are the ligated palladacycle precatalysts developed by Buchwald's group[13] and researchers at Merck.[14] These complexes have been prepared with a large scope of ligand types across several generations and are easily activated to generate "L-Pd(0)"[15] quantitatively with excellent reactivity in a broad range of cross-coupling reactions.[13,14,16] Despite these considerable advances, limitations still exist for certain applications/systems. For example, the synthesis and activation processes of aminobiphenyl-based palladacycles (second and third generation) involve suspected carcinogens aminobiphenyl (starting material) and carbazole (byproduct), respectively; the presence of which can complicate reaction workup from a product purification and safety point of view. Furthermore, the reductively eliminated carbazole (Scheme 1A) can consume the aryl-electrophile starting material and also

Scheme 1. Activation of (A) Palladacycle Precatalysts and (B) π-Allylpalladium Precatalysts

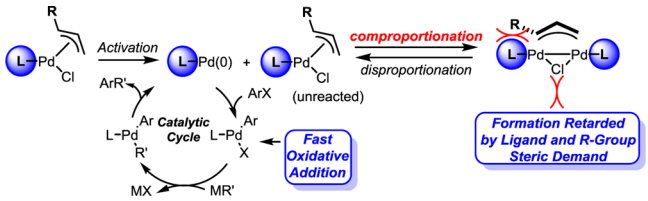


significantly retard the rate of some cross-coupling reactions (*vide infra*).[17] Recently, Buchwald et al. have introduced N-substituted aminobiphenyl-based precatalysts to address some of these issues.[13e] However, comparatively less toxicity data is available on N-substituted aminobiphenyls and N-substituted carbazoles, and the scope of ligands that could be incorporated into these complexes is not as vast as with their unsubstituted congeners. Herein, we report the synthesis and applications of two classes of highly active, yet air-stable π-allylpalladium precatalysts featuring either a neutral allylpalladium chloride or a cationic allylpalladium triflate platform, which together encompass an extremely broad ligand scope.[18] Upon activation, π-allylpalladium precatalysts release relatively benign substituted olefin byproducts (Scheme 1B).[9,19,20] These systems address many of the above issues from a practical and technological perspective. Mechanistic studies aimed at understanding the high efficiency of these precatalysts in accessing the active "L-Pd(0)" with respect to the effects of the ligand, substitution on the allyl group, and the counterions are also discussed in detail.

RESULTS AND DISCUSSION

Design and Synthesis of Pd(R-allyl)(L)Cl and [Pd(R-allyl)(L)]OTf Complexes. Prior studies have demonstrated that upon treatment of ligated allylpalladium chloride complexes with base, the resultant "L-Pd(0)" species can be consumed by the yet unreacted Pd(R-allyl)(L)Cl to form the (μ-allyl)(μ-Cl)-bridged dimer as shown in Scheme 2.[11,21] Recently, the groups of Balcells and Hazari[20] have elegantly studied the effects of allyl group substitution with respect to μ-allyl-bridged-dimer formation and catalytic activity with Nolan's Pd(R-allyl)(NHC)Cl complexes. They found that increased catalytic activity with substituted π-allylpalladium complexes was correlated to an increased barrier to dimer formation via comproportionation. Subsequent studies by Balcells, Hazari, and co-workers have revealed that the catalytic activity of Pd(R-allyl)(NHC)Cl complexes is inversely related to the relative

Scheme 2. Mechanistic Rationale for the High Activity of R-Allylpalladium Complexes with Biaryl/Bipyrazolylphosphine Ligands

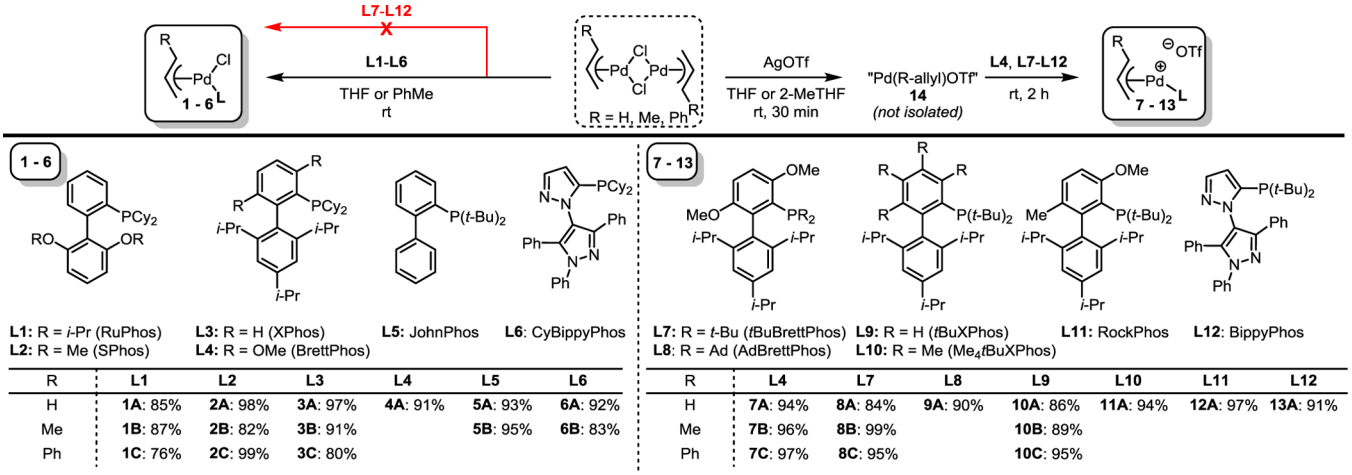


thermodynamic stability of the corresponding μ-allyl-bridged dimers.[22] Although μ-allyl-bridged Pd(I)-dimers do function well as precatalysts in certain catalytic applications,[11,20] dimer formation is a nonproductive off-cycle pathway, and disproportionation back to L-Pd(0) (and the ligated allylpalladium(II) complex) is required for catalytic activity. We therefore rationalized that the incorporation of very sterically bulky ligands such as biarylphosphines[23] or bipyrazolylphosphines[24] into the π-allylpalladium phosphine complex platform[25] should help to avoid the formation of μ-allyl-bridged Pd(I)-dimers upon activation through the intrinsic steric demand of these ligands, thereby providing highly active precatalysts. Additionally, the exceptionally high rate of oxidative addition[13a] of aryl halides to the catalysts generated using biarylphosphines should rapidly draw the active L-Pd(0) into the catalytic cycle, thus disfavoring the nonproductive comproportionation process.

Accordingly, we generated a library of allyl-, crotyl-, and cinnamyl-substituted[26] palladium complexes with biaryl- and bipyrazolyl-based ligands (Table 1, left) in uniformly high yields (76–99%) as air- and moisture-stable complexes (**1A**–**6B**) by reacting the appropriate ligand (**L1**–**L6**) with $[Pd(R\text{-allyl})Cl]_2$ (R = H, Me, Ph) at room temperature.[27,28] Although these complexes were easily synthesized in high yield with the smaller ligands from the biaryl/bipyrazolylphosphine series (**L1**–**L6**), attempts to incorporate the larger ligands of this class (**L7**–**L12**) were unsuccessful. It is known that Pd-centers bearing exceptionally sterically demanding ligands can, in some cases, force a counterion out of the metal coordination sphere.[29] Given this, we hypothesized that a cationic π-allyl-Pd precatalyst scaffold could potentially accommodate extremely bulky biaryl/bipyrazolylphosphines. Although some examples of cationic $[Pd(allyl)(L)_n]X$ (n = 1, 2, bidentate) complexes have been reported,[30] the synthetic procedures typically rely on either halide abstraction from the corresponding $Pd(allyl)(PR_3)Cl$ with an appropriate silver salt (e.g., AgOTf),[30a−k] or reacting a ligand with $[Pd(MeCN)_2(allyl)]$-OTf.[30l,m,31] The halide abstraction strategy was not feasible for our application because the required chloride complexes were challenging to prepare with extremely bulky ligands, while the instability of $[Pd(MeCN)_2(allyl)]OTf$ (unstable above −20 °C)[32] limited the practicality of the latter approach. Therefore, we turned our attention to preforming an allylpalladium complex functionalized with an easily dissociable counterion such as triflate, followed by an *in situ* reaction with an appropriate ligand. This technique obviates the need for synthesizing Pd(allyl)(L)Cl starting materials and avoids the isolation and handling of unstable "[Pd(R-allyl)]OTf" (**14**) intermediates. Indeed, stirring a mixture of $[Pd(allyl)Cl]_2$ with AgOTf for 30 min at room temperature, followed by the addition of a ligand (**L4**, **L7**–**L12**)[33] cleanly afforded R-allylpalladium triflate complexes **7A**–**13A** with high yields (84–

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794–6813

Table 1. Synthesis of R-Allylpalladium Precatalysts with Ligands L1−L12



R	L1	L2	L3	L4	L5	L6
H	**1A**: 85%	**2A**: 98%	**3A**: 97%	**4A**: 91%	**5A**: 93%	**6A**: 92%
Me	**1B**: 87%	**2B**: 82%	**3B**: 91%		**5B**: 95%	**6B**: 83%
Ph	**1C**: 76%	**2C**: 99%	**3C**: 80%			

R	L4	L7	L8	L9	L10	L11	L12
H	**7A**: 94%	**8A**: 84%	**9A**: 90%	**10A**: 86%	**11A**: 94%	**12A**: 97%	**13A**: 91%
Me	**7B**: 96%	**8B**: 99%		**10B**: 89%			
Ph	**7C**: 97%	**8C**: 95%		**10C**: 95%			

99%) as air- and moisture-stable solids (Table 1, right).[34] Using this synthetic approach, we incorporated both extremely bulky di-*tert*-butyl- (**L7**, **L9**−**L12**) and di-1-adamantyl-substituted (**L8**) ligands, including those with substitution on the phosphine-containing (top) aryl ring. Thus, utilizing either the chloride (neutral) or triflate (cationic) π-allylpalladium precatalyst scaffold, we synthesized and fully characterized 27 new precatalyst compounds, encompassing an extremely broad scope of ligands.

In order to gain more insight into the structure of these complexes, single crystal X-ray structures of allyl- and crotyl-substituted RuPhos complexes **1A** and **1B**, as well as of [Pd(allyl)(*t*BuBrettPhos)]OTf, **8A** (Figure 2), were deter-

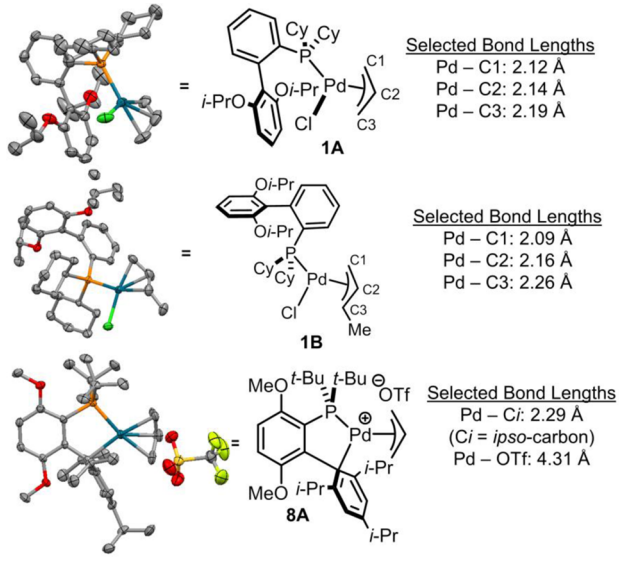


Figure 2. X-ray crystal structures of **1A**, **1B**, and **8A**. Thermal ellipsoid plot at 50% probability (hydrogen atoms, cocrystals, and solvent omitted for clarity).

mined. In accord with previous studies, the crotyl complex **1B** features an elongated Pd−C3 bond[35] relative to the analogous allyl complex **1A** (2.26 vs 2.19 Å), which has been previously correlated with more facile catalyst activation.[9c,11b] The X-ray structure of **8A** confirms the cationic nature of the Pd, as the triflate anion is dissociated from the metal center. (Pd−OTf distance = 4.31 Å) The Pd-center features a slightly distorted square planar geometry; however, in contrast to complexes of type **1**−**6** where the chloride occupies the fourth coordination site of the Pd, in **8A** the *ipso*-carbon of the triisopropylphenyl ring (C*i*) from **L7** occupies this site.[36]

Application Studies. The Pd(R-allyl)(L)Cl complexes were studied in a variety of cross-coupling reactions by comparing their reactivity with the corresponding palladacycles. We began our application studies by examining the amination of 4-chloroanisole with morpholine as a model reaction using RuPhos (**L1**)-based catalysts (Table 2) and reported reaction conditions.[13c] **L1** has been previously shown by Buchwald and co-workers to be an excellent ligand for aminations using secondary amines.[37] Although the RuPhos G1 precatalyst showed good reactivity, giving 66% conversion within 2 h (Table 2, entry 1), the G2 and G3 precatalysts provided ≤5% conversion (entries 2 and 3). Our π-allyl complexes **1A**−**1C** were highly active under the same conditions. In particular, crotyl (**1B**) and cinnamyl (**1C**) complexes gave the highest levels of conversion: 87% (100% at 2.5 h with added **L1**[38]) and 95%, respectively (entries 5−6).[26] It has been previously shown by Nolan as well as by our group that substituted π-allyl complexes can be more easily activated in comparison to their unsubstituted analogues.[9c,11b] Because G2 and G3 precatalysts release carbazole upon activation, we considered the possibility that this byproduct was inhibiting the reactions. To substantiate this hypothesis, 0.5 mol % of carbazole was added to the reactions employing RuPhos G1 or **1B** as precatalysts, and low conversions (≤6%) were again observed (entries 7−8).

We examined the versatility of catalyst **1B** in a variety of amination reactions, and the results are summarized in Table 3. Fast reaction rates with secondary amines were observed with 100% conversion reached within 1−2.5 h (Table 3, top). For **15e**, a milder base (K_2CO_3) was required, demonstrating that strongly basic conditions are not necessary for catalyst activation. Because BrettPhos (**L4**) has been demonstrated to be an excellent ligand for the monoarylation of primary amines,[39] we also studied the primary amination reactions using complex **7B** (Table 3, bottom). For the reaction of 4-chloroanisole with *n*-butylamine at 0.3 mol % catalyst loading, complete and rapid conversion to product (**15f**) was observed within 10 min. In contrast, the reaction catalyzed by the **L4**-3rd generation palladacycle precatalyst was noticeably slower, requiring 2 h for the reaction to reach completion.[40] Similar to what we observed in secondary amination, carbazole was

DOI: 10.1021/acs.joc.5b01005
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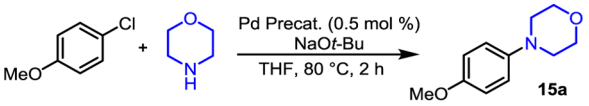
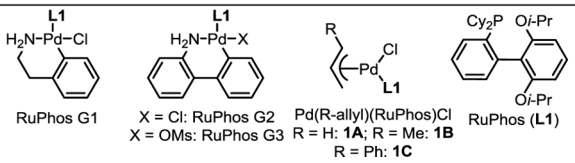
Table 2. Precatalyst Screen for the Amination of 4-Chloroanisole with Morpholine[a]

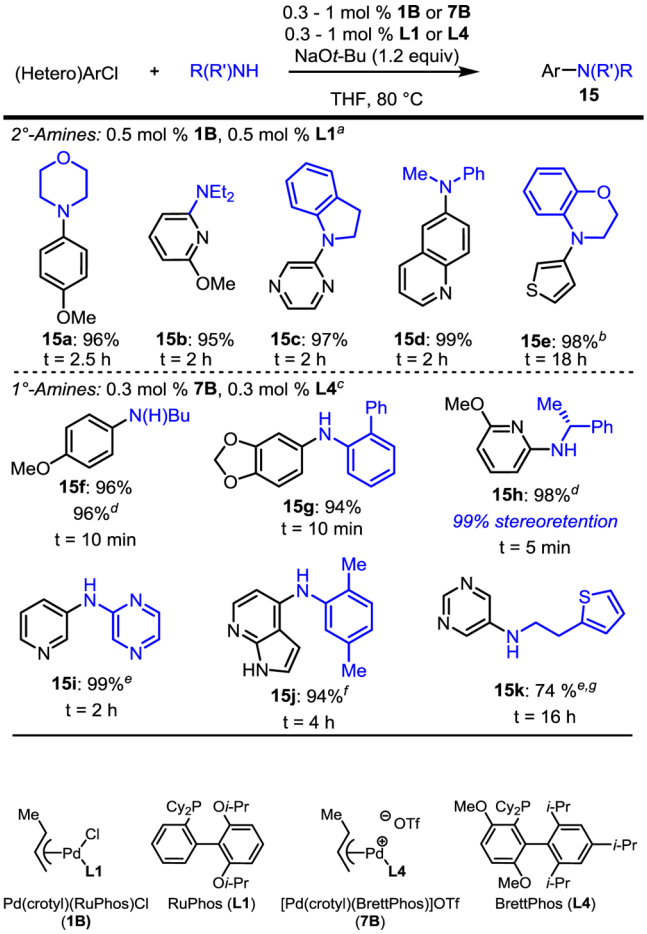


Entry	Catalyst	Conversion (%)[b]
1	RuPhos G1	66
2	RuPhos G2	4
3	RuPhos G3	5
4	**1A**	80
5	**1B**	87 / 97[d] / 100[d,e]
6	**1C**	95
7[c]	RuPhos G1	6
8[c]	**1B**	5



[a]Reaction conditions: 4-chloroanisole (1.0 mmol), morpholine (1.2 mmol), NaO*t*-Bu (1.2 mmol), catalyst (0.5 mol %), THF (2 mL). [b]Determined by GC using dodecane as an internal standard. [c]With 0.5 mol % carbazole added. [d]With 0.5 mol % additional RuPhos added. [e]Reaction time was 2.5 h.

Table 3. Scope of Amination Reactions using 1B (Secondary Amines) and 7B (Primary Amines)



[a]General conditions for secondary amination: ArCl/HetArCl (1.0 mmol), amine (1.2 mmol), NaO*t*-Bu (1.2 mmol), **1B** (0.5 mol %), **L1** (0.5 mol %), THF (2 mL). [b]1 mol % **1B**/1 mol % RuPhos, K_2CO_3, 2-methyl-2-butanol, 110 °C, 18 h. [c]General conditions for primary amination: ArCl/HetArCl (1.0 mmol), amine (1.2 mmol), NaO*t*-Bu (1.2 mmol), **7B** (0.3 mol %), **L4** (0.3 mol %), THF (2 mL), 80 °C. [d]**7C** (0.3 mol %) was used. [e]Base was K_2CO_3 (1.4 mmol), solvent was 2-methyl-2-butanol (2 mL), 110 °C. [f]Base was LiHMDS (2.4 mmol), **7B** (1.0 mol %), no added **L4**, 65 °C. [g]**7B** (1.2 mol %), **L4** (1.2 mol %).

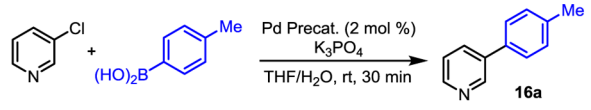
again identified as the cause of the rate retardation in primary amination, albeit to a lesser extent.[40] Secondary aryl amines **15f**–**15h** were formed with fast reaction times (5–10 min) using primary aliphatic (entry **15f**) and aromatic (entry **15g**) and optically active α-chiral (entry **15h**) amines at 0.3 mol % catalyst loading. Notably, **15h** was formed with high stereochemical fidelity (99% stereoretention), whereas erosion of enantiopurity of α-chiral amines in Buchwald–Hartwig amination reactions can be problematic.[41] Heterocyclic substrates that contain more than one nitrogen atom were efficiently coupled in good to high yields using **1B** or **7B** (entries **15c**, **15i**–**15k**) under slightly modified conditions. The similar yields of **15f** observed using **7B** and **7C** (96%) demonstrate the interchangeability of crotyl- and cinnamyl-substituted complexes.[26]

Previous work from our group demonstrated the effectiveness of π-allylpalladium chloride complexes of AmPhos, Q-Phos, P(*t*-Bu)$_3$, and (*t*-Bu)$_2$NpP (Np = neopentyl) in Suzuki–Miyaura reactions.[11b] Our group was the first to show that these complexes could be activated in the presence of weak bases.[11b] Thus, we investigated the **L3**-based (XPhos) precatalyst **3B**[26] for Suzuki–Miyaura coupling reactions under mild conditions. **L3** has previously been shown to be an extremely useful ligand for Suzuki–Miyaura reactions, even with challenging unstable boronic acid and derivatives.[42] Using precatalyst **3B**, the coupling of 3-chloropyridine with *p*-tolylboronic acid gave 91% conversion in 30 min, (Table 4, entry 1) while the XPhos G3 palladacycle was less active (65% conversion; entry 2) under reported conditions.[13b] Interestingly, under these reaction conditions, carbazole does not appear to have a negative effect on Suzuki–Miyaura reactions; the addition of 2 mol % carbazole to the reaction catalyzed by **3B** did not significantly affect the conversion (entry 3). Thus, the higher conversion observed with **3B** likely reflects the relative rates of catalyst activation.

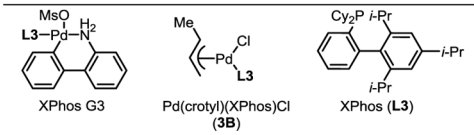
The fast generation of the active "L-Pd(0)" catalyst using **3B** has allowed a range of heteroaryl chlorides to be efficiently coupled with challenging aryl and heteroaryl boronic acids with uniformly high yields, including those that are prone to rapid protodeboronation,[13b] at or slightly above room temperature (Table 5). For example, 2-thienylboronic acid, 2-furanboronic acid, and 2,6-difluorophenylboronic acid (entries **16b**, **16c**, and **16d**) were all coupled in high yields within 1 h.

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794–6813

Table 4. Precatalyst Evaluation for the Suzuki−Miyaura Coupling[a]

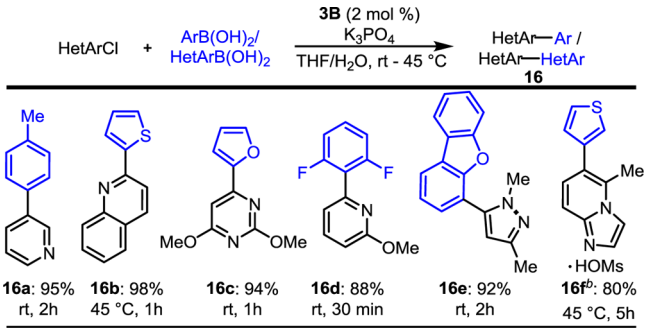


Entry	Catalyst	Conversion (%)[b]
1	Pd(crotyl)(XPhos)Cl (**3B**)	91 / 100[c]
2	XPhos G3	65
3	**3B**[d]	89



[a]Reaction conditions: 3-chloropyridine (1.0 mmol), *p*-tolylboronic acid (1.5 mmol), K_3PO_4 (2.0 mmol), catalyst (2 mol %), THF (2 mL), H_2O (4 mL). [b]Determined by GC analysis. [c]Run for 2 h. [d]With 2 mol % of carbazole added.

Table 5. Suzuki−Miyaura Coupling Reactions Using Precatalyst 3B[a]



[a]Reaction conditions: HetArCl (1.0 mmol), $ArB(OH)_2$ (1.5 mmol), K_3PO_4 (2.0 mmol), catalyst (2 mol %), THF (2 mL), H_2O (4 mL). [b]ArBr used, product isolated as the hydromethanesulfonate salt for ease of purification.

We also evaluated XPhos (**L3**) complexes **3A**−**3C**, as well as the XPhos G3 palladacycle, in the monoarylation of acetophenone (Figure 3).[43] Rapid conversion (≥95%) within 1 h to form **17a** was observed using **3A**−**3C**, of which the allyl complex **3A** was optimal (98% conversion). Similar to what we observed in amination, the rate of conversion was significantly lower when G3 XPhos was employed as the precatalyst; 34% conversion was observed at 1 h, and 4 h was necessary to reach high conversion (93%). Carbazole was again shown to retard the rate of the reaction as evidenced by the comparable lower activity of **3A** with 1 mol % of carbazole added relative to that of the XPhos G3 palladacycle. Four examples of ketone enolate arylations using **3A** are highlighted in Table 6.

Catalyst systems based on very bulky *t*BuBrettPhos (**L7**), *t*BuXPhos (**L9**), RockPhos (**L11**), and BippyPhos (**L12**) exhibit excellent reactivity in myriad challenging C−X (X = heteroatom) cross-coupling reactions, particularly those with difficult reductive elimination steps.[44] Therefore, we evaluated our π-allylpalladium catalysts **7**−**13** to effect such transformations utilizing known or modified reaction conditions,

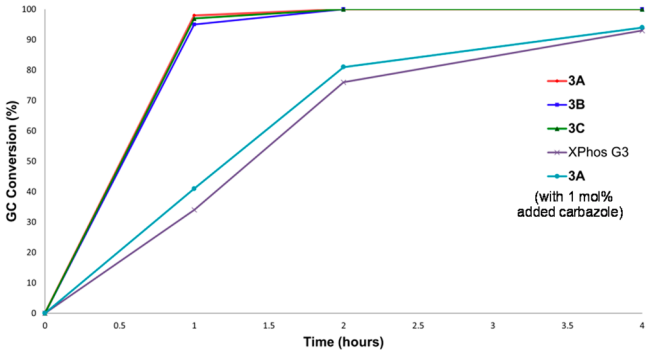
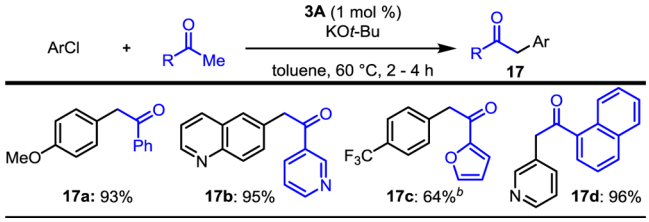


Figure 3. Catalyst comparison in the α-arylation of acetophenone with 4-chloroanisole. Reaction conditions: 4-chloroanisole (1.0 mmol), ketone (1.2 mmol), KO*t*-Bu (2.4 mmol), Pd catalyst (1 mol %), toluene (4 mL), 60 °C, 4 h.

Table 6. Ketone Enolate Arylation Reactions Using 3A[a]



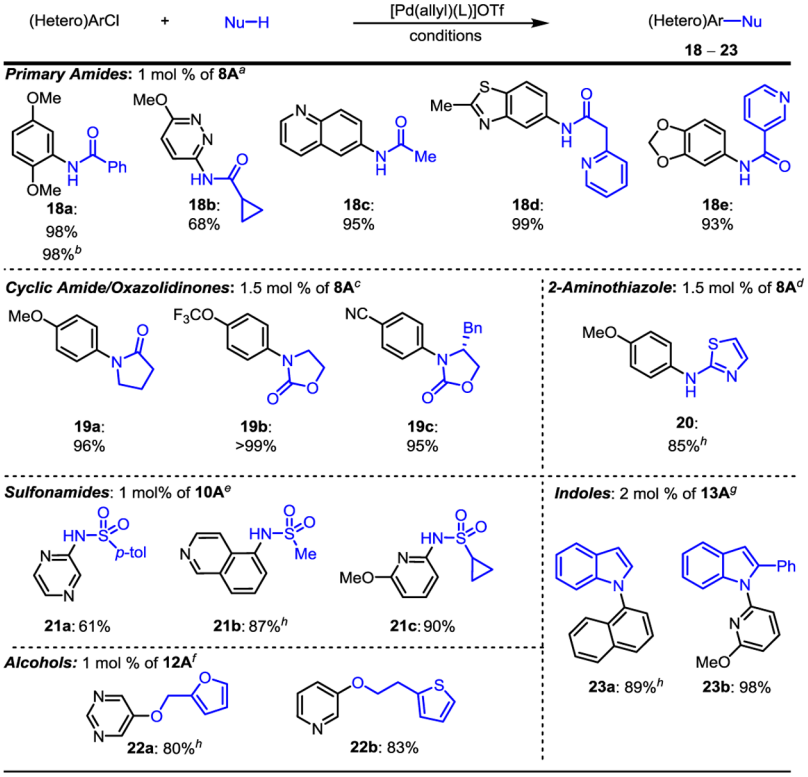
[a]Reaction conditions: Ar/HetArCl (1.0 mmol), ketone (1.2 mmol), KO*t*-Bu (2.4 mmol), **3A** (1 mol %), toluene (4 mL), 60 °C, 2−4 h. [b]2 mol % of **3A** used.

and the results are summarized in Table 7. The arylation of primary amides[44a] was highly efficient, giving aryl amide products **18a**−**18e** generally with high yields using 1.0 mol % of **8A**. Notably, in the reaction to form **18a**, the catalyst loading was lowered to 0.1 mol %, with no deleterious effect on yield, although a longer reaction time was required. Additionally, a cyclic secondary amide as well as cyclic oxazolidinones proved to be excellent substrates with a catalyst loading of 1.5 mol %, for producing **19a**−**19c** in ≥95% yields. Reported arylation reactions of 2-aminothiazoles using an **L7**-based catalyst required acetate additives to reach full conversion with unactivated aryl electrophiles.[45] However, our π-allyl catalyst **8A** provided a significant advantage: 2-aminothiazole was efficiently coupled with 4-bromoanisole to produce *N*-aryl-2-aminothiazole **20** with 85% yield in the absence of acetate. Sulfonamides were also efficiently coupled with nitrogen-containing heteroaryl halides in good yield at 1 mol % catalyst loading of **10A** (entries **21a**−**21c**). Previous examples of sulfonamidation of heteroaryl electrophiles were limited to activated heteroaryl chlorides[46] using high catalyst loadings (2−10 mol %) to achieve moderate yields or required the use of aryl nonaflates.[47] Various heterocycles were well tolerated in the C−O coupling of heteroaryl halides with primary alcohols using **12A** (entries **22a**,**22b**).[44c] Additionally the N-arylation of indoles proceeded in high yield using BippyPhos-based **13A** (entries **23a**,**23b**).[44d]

Mechanistic Studies on Carbazole Inhibition. In order to understand the negative effect of carbazole, we studied the cross-coupling of morpholine with chlorobenzene as a model system using RuPhos G3 (Scheme 3A). Even after 1 h at 80 °C, only 9% GC conversion was observed. ^{31}P NMR analysis of the crude reaction mixture indicated the presence of a single

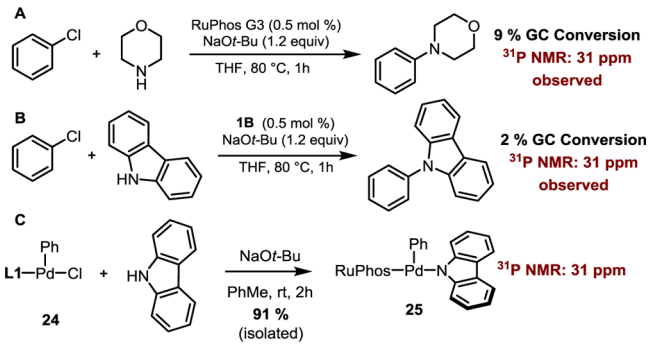
DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794−6813

Table 7. Challenging Cross-Coupling Reactions Using Various [Pd(allyl)(L)]OTf Complexes



[a]General conditions: (hetero)aryl chloride (1.0 mmol), amide (1.2 mmol), **8A** (1.0 mol %), K_3PO_4 (1.4 mmol), *t*-BuOH (2 mL), 110 °C. [b]0.1 mol % of **8A** used, 16 h reaction time. [c]General conditions: (hetero)aryl chloride (1.0 mmol), amide (1.2 mmol), **8A** (1.5 mol %), K_3PO_4 (1.4 mmol), *t*-BuOH (2 mL), 110 °C. [d]Reaction conditions: 4-bromoanisole (1.0 mmol), 2-aminothiazole (1.2 mmol), **8A** (1.5 mol %), K_2CO_3 (1.4 mmol), *t*-BuOH (2 mL), 110 °C. [e]General conditions: sulfonamide (1.0 mmol), heteroaryl chloride (1.2 mmol), **10A** (1.0 mol %), K_3PO_4 (1.5 mmol), 2-methyl-2-butanol (4 mL), 110 °C. [f]General conditions: heteroaryl chloride (1.0 mmol), alcohol (1.5 mmol), **12A** (1.0 mol %), K_3PO_4 (1.5 mmol), toluene (1 mL), 100 °C. [g]General conditions: (hetero)aryl chloride (1.0 mmol), indole (1.0 mmol), **13A** (2.0 mol %), **L12** (2.0 mol %), NaO*t*-Bu (1.4 mmol), toluene (4 mL), 110 °C. [h]Aryl bromide used.

Scheme 3. (A) Cross-Coupling of PhCl with Morpholine Catalyzed by RuPhos G3, (B) Cross-Coupling of PhCl with Carbazole Using 1B, and (C) Preparation of L1-Pd(Ph)carbazol-9-yl (25)



phosphorus-containing species at 31 ppm. An identical peak was also observed in the attempted cross-coupling of carbazole with chlorobenzene using **1B** (Scheme 3B). Hence, we postulated that this species was likely a stable L-Pd(Ar)-carbazolyl complex, generated in catalysis via a competitive "transmetallation"[48] between carbazole and the substrate (nucleophile) with the Pd(II)-oxidative addition intermediate. A high barrier to reductive elimination[49−51] from the resulting L-Pd(Ar)carbazolyl complex could be responsible for the observed diminished catalytic activity in the presence of carbazole.[52]

To substantiate this hypothesis, we independently synthesized Pd-carbazol-9-yl complex **25** from **24**[53] and carbazole as shown in Scheme 3C. The ^{31}P NMR shift (31 ppm) of **25** confirms the presence of this species in the reactions of Scheme 3A,B. The X-ray crystal structure of **25** was also determined, revealing that this complex contains a slightly distorted square planar Pd(II)-center (Figure 4), with a stabilizing interaction between the Pd and the *ipso*-carbon of the non-phosphine-containing aryl ring.[36] The Pd–N bond length (2.04 Å) closely resembles those of other tricoordinate monoligated Pd-amido complexes reported by Yamashita and Hartwig (2.07−2.09 Å).[54]

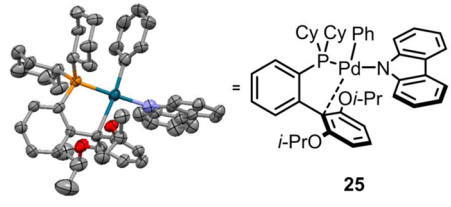


Figure 4. Crystal structure of **25**. Thermal ellipsoid plot at 50% probability (hydrogen atoms, cocrystal, and solvent omitted for clarity). Selected bond lengths: Pd–N, 2.04 Å; Pd–*ipso*-C, 2.49 Å; Pd–C_{Ph}, 2.00 Å.

DOI: 10.1021/acs.joc.5b01005
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The reductive elimination of 9-phenylcarbazole (**26**) from **25** was studied at 100 °C in toluene-d_8 (using PhBr to trap L-Pd(0)),[55] and first-order decay was observed (Figure 5).[40] The

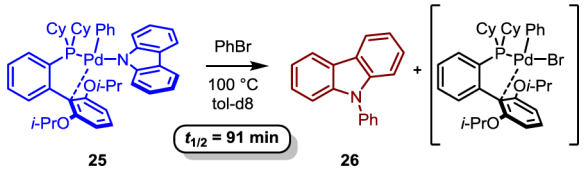


Figure 5. Thermal reductive elimination of 9-phenylcarbazole (**26**) from **25**.

half-life ($t_{1/2}$) was found to be 91 min with a first-order rate constant of k_{obs} = 1.17 × 10^{-4} s^{-1}, indicating a relatively slow rate of reductive elimination.[56] We note, however, that the rate of reductive elimination from complexes of type **25** (as well as the extent to which carbazole inhibits reaction rates) will depend on several factors including temperature, ligand, and substrate.

Mechanistic Study on Catalyst Activation Pathway. As previously mentioned, we hypothesized that the high reactivity of these allylpalladium complexes containing biaryl/bipyrazolylphosphines may be a consequence of the suppression of μ-allyl-bridged Pd(I)-dimer formation, a nonproductive pathway by which active Pd(0) is sequestered from the reaction mixture.[11,20] To test this theory, we independently synthesized the (μ-allyl)(μ-Cl)Pd_2(**L**)$_2$ complex with biarylphosphine **L2** (SPhos) using the method employed by Hazari et al. for synthesizing similar complexes with NHC ligands[20] (Figure 6A). The X-ray structure of **27a**, a (μ-allyl)(μ-Cl)-bridged

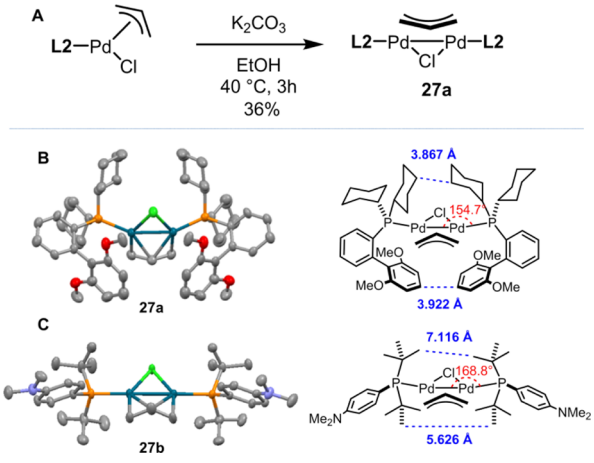
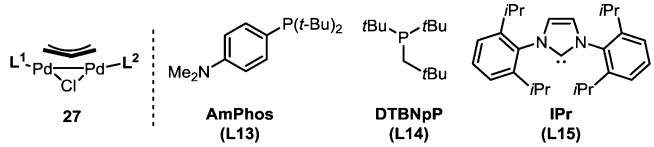


Figure 6. (A) Synthesis of (μ-allyl)Pd_2(L)$_2$(μ-Cl) complex **27a**. (B) X-ray structure of **27a**. Thermal ellipsoid plot at 50% probability. Hydrogen atoms omitted for clarity. (C) X-ray structure of **27b** (from ref 11b). Thermal ellipsoid plot at 50% probability (hydrogen atoms, cocrystals, and solvent omitted for clarity).

Pd(I)-dimer derived from **L2** (SPhos), one of the smallest ligands in the biarylphosphine family (cone angle = 240°),[57] provides some insight into understanding the catalyst activation pathway (Figure 6B). The complex crystallized in a conformation in which both cyclohexyl groups and the biaryl groups are eclipsed, because they are oriented away from the μ-allyl group and the chlorine atom. Relatively short distances were observed between the cyclohexyl groups (3.867 Å) and between the non-phosphine-containing aryl rings (3.922 Å) of the two SPhos ligands. Inspection of this structure reveals that replacement of cyclohexyl groups with more bulky groups (e.g., *t*-Bu) or increasing substitution on the non-phosphine-containing aryl ring (e.g., *i*-Pr) or the allyl moiety (e.g., Me) would result in increasingly unfavorable steric interactions. In contrast, in the X-ray crystal structure of (μ-allyl)(μ-Cl)-Pd_2(AmPhos)$_2$ **27b** (Figure 6C) that we previously reported[11b] featuring the smaller AmPhos ligand (cone angle 170°),[58] the closest points of contact between the two ligands are between the *tert*-butyl groups and are significantly more remote from one another (5.626 and 7.116 Å). Consistent with this trend, the μ-allyl-bridged Pd(I) dimer (**27c**)[11a] derived from DTBNpP (not shown), a ligand that features a cone angle between those of SPhos and AmPhos (198°),[59] has longer distances between the ligands than the SPhos-derived **27a** but shorter than those of the AmPhos-derived **27b** (closest contacts 4.186 and 4.980 Å). Complex **27a** is significantly bent as evidenced by the small Pd–Pd–P angles (154.7°), which is likely a result of minimization of the steric interactions between the ligands. Analogous Pd–Pd–L angles for related (μ-allyl)(μ-Cl)-bridged Pd(I)-dimer complexes are comparatively larger with AmPhos at 168.8°,[11b] DTBNpP at 156.3°–161.3°,[11a] and the NHC ligand IPr[60] at 164.8° (Table 8).[61] Thus, we believe

Table 8. Comparison of Pd–Pd–L Angles for μ-Allyl-Bridged Pd(I)-Complexes



entry	ligand (**L**^{1} = **L**^{2})	ligand cone angle (deg)	complex	∠Pd–Pd–**L**^{1} (deg)	∠Pd–Pd–**L**^{2} (deg)
1	SPhos (**L2**)	240	**27a**	154.7	154.7
2	AmPhos (**L13**)	170	**27b**	168.8	168.8
3	DTBNpP (**L14**)	198	**27c**	156.3	161.3
4	IPr (**L15**)		**27d**	164.8	164.8

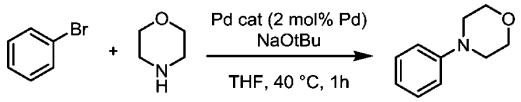
that (μ-allyl)(μ-Cl)Pd_2(**L**)$_2$ complexes will become increasingly destabilized with increasing ligand size or substitution on the allyl group due to steric strain, thereby retarding the nonproductive comproportionation process.

To demonstrate the low reactivity of a μ-allyl-bridged Pd(I)-dimer in a catalytic application, the amination reaction of bromobenzene with morpholine was studied using Pd(allyl)-(SPhos)Cl (**2A**), Pd(crotyl)(SPhos)Cl (**2B**), and (μ-allyl)-Pd_2(SPhos)$_2$(μ-Cl) (**27a**) as shown in Table 9. The difference in reactivity between **2B** and **27a** was striking: after 1 h at 40 °C, the reaction employing Pd(I)-dimer **27a** only reached 8% (entry 1), while full conversion was observed in the reaction catalyzed by **2B** (entry 2). Pd(allyl)(SPhos)Cl (**2A**) exhibited intermediate reactivity with 49% conversion (entry 3), which is expected because **2A** can comproportionate to form **27a** upon activation.

In order to gain a better understanding of the catalyst activation process, a series of stoichiometric activation experiments were carried out with selected R-allylpalladium complexes, and the results are summarized in Table 10. Thus, π-allylpalladium complexes were activated with a slight excess of NaO*t*-Am at room temperature in the presence of PhBr to trap "L-Pd(0)", and the relative amounts of oxidative addition

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794–6813

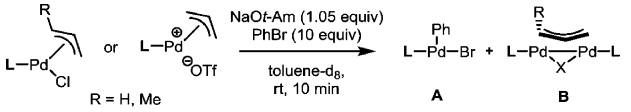
Table 9. Comparison of Pd(R-allyl)(SPhos)Cl and (μ-allyl)(μ-Cl)Pd_2(SPhos)$_2$ in Catalytic Aryl Amination[a]



entry	catalyst (2 mol % Pd)	GC conversion[b] (%)
1	(μ-allyl)(μ-Cl)Pd_2(SPhos)$_2$ (**27a**)	8
2	Pd(crotyl)(SPhos)Cl (**2B**)	100
3	Pd(allyl)(SPhos)Cl (**2A**)	49

[a]Reaction conditions: bromobenzene (1.0 mmol), morpholine (1.2 mmol), NaO*t*-Bu (1.2 mmol), dodecane (GC standard, 0.2 mmol), catalyst (2 mol % Pd), THF (1.5 mL), 40 °C, 1 h. [b]Determined by GC using dodecane as in internal standard.

Table 10. Stoichiometric Activation of R-Allylpalladium Precatalysts



entry	complex	yield **A**[a] (%)	yield **B**[a] (%)
1	Pd(allyl)(SPhos)Cl (**2A**)	11	44
2	Pd(crotyl)(SPhos)Cl (**2B**)	74	0
3	Pd(allyl)(BrettPhos)Cl (**4A**)	74	0
4	[Pd(allyl)(BrettPhos)]OTf (**7A**)	95	0
5	[Pd(allyl)(*t*BuXPhos)]OTf (**10A**)	92[b]	0
6	[Pd(allyl)(*t*BuBrettPhos)]OTf (**8A**)	100[b]	0

[a]Determined by relative ^{31}P NMR integration. [b]4-Bromobenzonitrile was used to trap the L-Pd(0) intermediate.

complex (**A**) and μ-allyl-bridged Pd(I)-dimer (**B**) were measured. In accord with our hypothesis, upon activation Pd(allyl)(SPhos)Cl (**2A**) gave only 11% of the oxidative addition product **A**; instead the (μ-allyl)(μ-Cl)-bridged Pd(I)-dimer **B** was the major product (44%), along with several as yet unidentified species (entry 1). However, the analogous crotyl-complex of SPhos (**2B**) reacted quickly to give 74% of the oxidative addition product (entry 2), demonstrating the significance of substitution on the allyl group for precluding dimer formation. The presence of even larger ligands can override the necessity for substitution on the allyl group, as the Pd(allyl)(BrettPhos)Cl complex (**4A**) is facilely activated with relatively clean formation (74%) of the oxidative addition product with no detectable amount of the (μ-allyl)-bridged dimer (entry 3). The analogous cationic complex to **4A**, [Pd(allyl)(BrettPhos)]OTf (**7A**), formed the oxidative addition product with higher efficiency (95%) (entry 4). π-Allyl-complexes bearing the extremely bulky ligands *t*BuXPhos and *t*BuBrettPhos rapidly and cleanly formed the oxidative addition products (92−100%) (entries 5−6) upon activation with NaO*t*-Am. In these experiments, 4-bromobenzonitrile was used to trap the transient Pd(0) species. Similar experiments using bromobenzene did in fact give rapid oxidative addition; however, the results were complicated by 3′-phenylation of the non-phosphine-containing aryl ring of the ligand.[62] These experiments substantiate our hypothesis that more sterically demanding phosphine ligands and substitution on the allyl group hinder the formation of μ-allyl-bridged Pd(I)dimers, thereby allowing facile formation of the active "L-Pd(0)" species. Although we have not studied the effects of cationic (OTf) vs neutral (Cl) complexes extensively, the enhanced reactivity with the former could be the consequence of the increased electrophilicity of the cationic complexes[30k,63] or the destabilization of the nonproductive μ-allyl-bridged species with the more labile triflate counterion.

CONCLUSIONS

In summary, we have developed two new classes of neutral and cationic π-allylpalladium precatalysts featuring biaryl- and bipyrazolylphosphines. A wide scope of Pd(R-allyl)(**L**)Cl complexes were synthesized with the less sterically encumbered members of this ligand class, while a cationic [Pd(R-allyl)(**L**)]OTf scaffold was engineered to accommodate extremely bulky ligands. These complexes were easily prepared in high yields as air- and moisture-stable solids and exhibit excellent reactivity in several challenging C−C and C−X cross-coupling processes, thus featuring key advantages over existing precatalyst technologies. Based on our mechanistic investigations, the high activity observed in reactions catalyzed by these new precatalysts is rationalized by (1) the fast activation of these complexes to the active "L-Pd(0)" catalyst under commonly employed catalytic conditions, (2) the release of noninhibitory byproducts, and (3) suppression of the comproportionation pathway to form stable dinuclear (μ-allyl)-bridged Pd(I) dimers. Supported by mechanistic and crystallographic studies, the diminished dimer formation is rationalized to be a consequence of the intrinsic steric demand of this ligand class in concert with the fast rate of oxidative addition that biarylphosphine-based catalysts exhibit. Additionally, substitution on the π-allyl group can disfavor the comproportionation pathway with less sterically biased ligands. We believe that this comprehensive strategy can be applied to generating precatalysts with many ligand systems that are not described in this report. Current studies aimed at exploring new reactions using these precatalysts as well as further understanding of their structure−activity relationships, in particular the role of the μ-allyl-bridged Pd(I)-complexes, are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Information. All reactions were performed in glassware that was dried in a vacuum oven (55−65 °C, 80 Torr) using standard Schlenk techniques unless noted otherwise. Anhydrous THF, toluene, 2-MeTHF, 2-methyl-2-butanol, and *tert*-butanol were purchased from commercial sources and used as received. For use in a glovebox, all solvents were further degassed by performing at least three freeze−pump−thaw cycles or by sparging with nitrogen for 30 min. All aryl halides, boronic acids, ketones, and solid amines were purchased from commercial sources and used as received unless otherwise noted. All liquid amines were passed through a plug of activated basic alumina prior to use in reactions. [(Allyl)PdCl]$_2$, [(crotyl)PdCl]$_2$, and [(cinnamyl)PdCl]$_2$, **L1**−**L12**, RuPhos G1, RuPhos G2, RuPhos G3, and XPhos G3 were obtained from our plant as most of them are commercially available from Johnson Matthey Catalysis and Chiral Technologies. AgOTf, NaO*t*-Bu, K_2CO_3, and anhydrous K_3PO_4 were purchased from commercial sources and used as received. The bulk containers of these bases were stored in a nitrogen-filled glovebox. Small amounts, up to 5 g, were removed and stored on the benchtop in a desiccator for up to 6 weeks. Chromatographic separations were performed using 12 g silica cartridges. All isolated materials were ≥95% pure as measured by ^{1}H NMR unless otherwise noted. Reactions were analyzed by gas chromatography using dodecane as an internal standard. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a 400 MHz NMR spectrometer. All chemical shifts are reported in ppm. ^{1}H and ^{13}C spectra were calibrated using residual solvent as an internal reference ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.16 ppm for

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794−6813

^{13}C NMR; C_6D_6, 7.16 ppm for ^{1}H NMR and 128.06 ppm ^{13}C NMR; DMSO-d_6, 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR; toluene-d_8, 2.08 ppm for ^{1}H NMR and 20.43 ppm for ^{13}C NMR). All ^{31}P NMR spectra were externally referenced to H_3PO_4 (0.00 ppm). All ^{19}F NMR spectra were externally referenced to $CFCl_3$ (0.00 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet, app t = apparent triplet, app d = apparent doublet, br = broad. High-resolution mass spectrometry (HRMS) was obtained on an oa-TOF spectrometer.

General Procedure for the Synthesis of 1A−6B. A dry Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with [(R-allyl)PdCl]$_2$ (0.50 equiv) followed by the appropriate ligand **L1**−**L6** (1.00 equiv). The flask was fitted with a rubber septum, and it was evacuated and backfilled with nitrogen. This evacuation/nitrogen backfill cycle was repeated two additional times. Solvent (THF or toluene) was added via syringe, and the reaction mixture was stirred at rt for the appropriate time. Pentane (or hexanes) was then added to fully precipitate the product. The solid materials were then collected by suction filtration, washed with additional pentane (or hexanes), and dried in vacuo.

*Pd(allyl)(RuPhos)Cl (**1A**).* The general procedure was followed using 503 mg (1.43 mmol) of [(allyl)PdCl]$_2$, 1.29 g (2.77 mmol) of RuPhos (**L1**), and 2 mL of anhydrous THF with a stir time of 30 min. The product was precipitated by the addition of 10 mL of pentane with cooling in an ice bath (0 °C) to give 1.52 g (2.34 mmol, 85%) of the title compound as a yellow solid. X-ray quality crystals were grown by slow vapor diffusion (THF/hexanes). ^{1}H NMR (400 MHz, C_6D_6, δ): 7.60 (t, J = 8.7 Hz, 1H), 7.18−7.05 (m, 3H), 6.96−6.86 (m, 1H), 6.92 (d, J = 7.7 Hz, 1H), 6.48 (dd, J = 7.5 Hz, 1H), 6.32 (d, J = 7.5 Hz, 1H), 5.03−4.91 (m, 1H), 4.49 (t, J = 7.4 Hz, 1H), 4.46−4.30 (m, 1H), 4.22−4.08 (m, 1H), 3.37−3.22 (m, 1H), 3.01 (dt, J = 9.7 Hz, 13.4 Hz, 1H), 2.55−2.04 (m, 5H), 2.03−0.80 (m, 29H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ): 157.2, 156.7, 141.3 (two peaks), 134.4, 134.3, 132.7, 132.6, 132.4, 132.1, 128.7 (two peaks), 128.3, 127.9, 125.4, 125.3, 122.5, 122.4, 115.3 (two peaks), 106.4, 105.5, 80.1, 79.8, 70.2, 69.9, 55.8, 36.2, 36.0, 35.5, 35.3, 29.5, 29.4, 27.1, 27.0, 26.2, 22.3, 22.2, 21.6, 21.3 [observed complexity due to C−P coupling]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 34.6 (br). Anal. Calcd for $C_{33}H_{48}ClO_2PPd$: C, 61.02; H, 7.45. Found: C, 60.87; H, 7.42.

*Pd(crotyl)(RuPhos)Cl (**1B**).* The general procedure was followed using 1.02 g (5.08 mmol) of [(crotyl)PdCl]$_2$, 2.37 g (10.2 mmol) of RuPhos (**L1**), and 2.5 mL of anhydrous THF with a stir time of 2 h. The product was precipitated by the addition of 10 mL of pentane to give 2.93 g (4.42 mmol, 87%) of the title compound as a light yellow solid. X-ray quality crystals were grown by slow vapor diffusion (THF/hexanes). ^{1}H NMR (400 MHz, C_6D_6, δ): 7.64 (t, J = 8.4 Hz, 1H), 7.24−7.09 (m, 3H), 7.06−7.00 (m, 1H), 6.50 (d, J = 7.9 Hz, 1H), 6.34 (d, J = 7.6 Hz, 1H), 4.90−4.80 (m, 1H), 4.58−4.45 (m, 1H), 4.31−4.18 (m, 1H), 3.82−3.70 (m, 1H), 3.34−3.26 (m, 1H), 2.57−0.80 (m, 38H). ^{13}C NMR{^{1}H} (100 MHz, C_6D_6, δ): 157.4, 156.9, 142.3, 142.2, 133.9, 133.8, 132.8 (two peaks), 132.5, 128.9 (two peaks), 128.2, 125.6, 125.5, 122.7 (two peaks), 114.7 (two peaks), 106.3, 105.4, 99.4, 99.1, 70.2, 70.0, 50.7, 37.5, 37.3, 36.7, 36.5, 30.0, 29.2, 27.4, 27.3, 27.1, 26.4, 22.5, 22.4, 21.6, 21.4, 17.4 (two peaks) [observed complexity due to C−P coupling]. ^{31}P NMR{^{1}H} (162 MHz, C_6D_6, δ): 33.2 (br). HRMS (ESI) m/z [M − Cl]$^+$ Calcd for $C_{34}H_{50}O_2PPd$: 627.2583. Found: 627.2554.

*Pd(cinnamyl)(RuPhos)Cl (**1C**).* The general procedure was followed using 1.00 g (1.93 mmol) of [(cinnamyl)PdCl]$_2$, 1.80 g (3.86 mmol) of RuPhos (**L1**), and 4 mL of anhydrous THF with a stir time of 2 h. The product was precipitated by the addition of 24 mL of pentane and was triturated for 1 h to give 2.13 g (2.94 mmol, 76%) of the title compound as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.78−7.68 (m, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.35−7.18 (m, 7H), 6.92−6.87 (m, 1H), 6.55 (d, J = 8.2 Hz, 2H), 5.72−5.58 (m, 1H), 4.91−4.77 (m, 1H), 4.52−4.39 (m, 1H), 3.00−2.50 (m, 1H), 2.31−2.19 (m, 2H), 2.05−1.94 (m, 2H), 1.74−1.49 (m, 8H), 1.44−0.89 (m, 24H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 156.9, 140.1, 137.1 (two peaks), 135.1, 132.8, 132.7, 131.8, 131.5, 128.7, 128.4, 127.5 (two peaks), 127.4, 125.2, 125.1, 122.4 (two peaks), 109.7, 109.6, 106.0, 100.3, 100.0, 70.4, 52.6, 35.0, 24.8, 30.0, 29.2. 27.0, 26.9, 26.8, 26.0, 22.4, 22.0, 21.8 [observed complexity due to C−P coupling]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 44.0 (br). HRMS (ESI) m/z [M − Cl]$^+$ Calcd for $C_{39}H_{52}O_2PPd$: 689.2740. Found: 689.2739.

*Pd(allyl)(SPhos)Cl (**2A**).* The general procedure was followed using 4.46 g (12.2 mmol) of [(allyl)PdCl]$_2$, 10.0 g (24.4 mmol) of SPhos (**L2**), and 30 mL of anhydrous THF with a stir time of 30 min. The product was precipitated by the addition of 30 mL of pentane to give 14.1 g (23.8 mmol, 98%) of the title compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.65 (t, J = 8.6 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.30−7.22 (m, 1H), 7.06 (dd, J = 3.5 Hz, 8.2 Hz, 1H), 6.70−6.44 (m, 2H), 5.24−5.08 (m, 1H), 4.47 (t, J = 7.1 Hz, 1H), 3.82−3.60 (m, 6H), 3.40−3.22 (m, 1H), 3.02 (dd, J = 9.4 Hz, 13.7 Hz, 1H), 2.41−2.00 (m, 3H), 2.00−0.90 (m, 20H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 257.7, 157.4, 140.3, 140.2, 132.6, 128.6, 125.5, 119.1 (two peaks), 115.6, 115.5, 103.8, 102.8, 81.7, 81.4, 67.6, 55.0, 54.5, 35.9, 35.6, 29.4, 28.7, 27.0, 26.9, 26.7, 25.8, 25.3 [observed complexity due to C−P coupling]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 31.9. Anal. Calcd for $C_{29}H_{40}ClO_2PPd$: C, 58.69; H, 6.79. Found: C, 58.68; H, 6.92.

*Pd(crotyl)(SPhos)Cl (**2B**).* The general procedure was followed using 501 mg (1.27 mmol) of [(crotyl)PdCl]$_2$, 1.05 g (2.56 mmol) of SPhos (**L2**), and 5 mL of anhydrous THF with a stir time of 6 h (reaction time not optimized). The product was precipitated by the addition of 10 mL of pentane to give 1.28 g (2.11 mmol, 82%) of the title compound as a light yellow solid. ^{1}H NMR (400 MHz, C_6D_6, δ): 7.58 (t, J = 7.7 Hz, 1H), 7.47−7.04 (m, 4H), 6.42 (d, J = 8.5 Hz, 1H), 6.28 (d, J = 8.3 Hz, 1H), 4.69−4.58 (m, 1H), 3.77−3.62 (m, 1H), 3.53 (s, 3H), 3.25 (s, 3H), 3.20 (d, J = 6.6 Hz, 1H), 2.52−2.29 (m, 2H), 2.20−1.15 (m, 24H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ): 158.0, 157.7, 141.8, 141.7, 133.4 (two peaks), 133.2, 133.1, 132.0, 131.7, 129.1 (two peaks), 128.2, 125.6, 125.5, 119.8, 119.7, 114.1 (two peaks), 103.7, 102.8, 99.8, 99.6, 54.8, 54.6, 48.4, 38.0, 37.8, 37.3, 37.1, 29.9, 28.5, 28.3, 27.4 (two peaks), 27.3, 27.1, 27.0 (two peaks), 26.9, 26.1, 17.1 (two peaks) [observed complexity due to C−P coupling]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ): 28.9. Anal. Calcd for $C_{30}H_{42}ClO_2PPd$: C, 59.31; H, 6.97. Found: C, 59.15; H, 7.17.

*Pd(cinnamyl)(SPhos)Cl (**2C**).* The general procedure was followed using 1.00 g (1.93 mmol) of [(cinnamyl)PdCl]$_2$, 1.59 g (3.86 mmol) of SPhos (**L2**), and 4.3 mL of anhydrous toluene with a stir time of 1 h. The product was precipitated by the addition of 10 mL of pentane to give 2.56 g (3.82 mmol, 99%) of the title compound as a bright yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.68 (t, J = 8.5 Hz, 1H), 7.48−7.20 (m, 8H), 7.08−7.02 (m, 1H), 6.60 (d, J = 8.3 Hz, 2H), 5.53−5.42 (m, 1H), 4.78−4.67 (m, 1H), 3.67 (s, 6H), 3.43−2.20 (m, 4H), 2.01−1.88 (m, 2H), 1.80−1.51 (m, 8H), 1.46−1.05 (m, 10H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 157.8, 140.3, 140.2, 136.9, 136.8, 135.0, 134.9, 133.0 (two peaks), 131.3, 131.0, 129.3, 129.0, 128.4, 128.4, 128.1, 127.6 (two peaks), 127.5, 125.7, 125.6, 119.4 (two peaks), 109.3, 109.2, 103.6, 101.7, 101.4, 55.3, 50.0, 36.1, 35.9, 29.8, 29.7, 29.2, 27.3, 27.2, 27.0, 26.9, 26.1 [observed complexity due to C−P coupling]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 37.4. Anal. Calcd for $C_{35}H_{44}ClO_2PPd$: C, 62.78; H, 6.62. Found: C, 62.66; H, 6.54.

*Pd(allyl)(XPhos)Cl (**3A**).* The general procedure was followed using 858 mg (2.36 mmol) of [(allyl)PdCl]$_2$, 2.26 g (4.74 mmol) of XPhos (**L3**), and 5 mL of anhydrous THF with a stir time of 3 h. The product was precipitated by the addition of 10 mL of pentane to give 3.04 g (4.62 mmol, 97%) of the title compound as a light yellow solid. Product contains ∼5 mol % THF. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.98−7.84 (m, 1H), 7.40−7.27 (m, 2H), 7.07−6.99 (m, 3H), 5.47−5.26 (m, 1H), 4.54 (t, J = 7.1 Hz, 1H), 3.51 (dd, J = 9.3 Hz, 13.6 Hz, 1H), 3.12−3.01 (m, 1H), 3.00−2.88 (m, 1H), 2.70−2.42 (m, 2H), 2.41−2.10 (m, 3H), 1.92−0.73 (m, 38H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 148.7, 146.2, 142.1, 136.6, 136.4, 136.3, 133.7, 133.6, 131.8, 131.6, 128.0 (two peaks), 125.5, 125.4, 120.7, 116.0, 116.0, 79.3, 79.0, 55.7, 34.4, 34.1, 33.9, 31.3, 30.4, 29.0, 27.1, 27.0, 26.8, 26.7, 25.6, 25.4, 23.9, 22.3 [observed complexity due to C−P coupling], peaks attributable to THF were observed at 67.7, 25.8. ^{31}P{^{1}H} NMR (162

DOI: 10.1021/acs.joc.5b01005
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MHz, $CDCl_3$, δ): 48.2 (br). Anal. Calcd for $C_{36}H_{54}ClPPd$: C, 65.55; H, 8.25. Found: C, 65.79; H, 8.01.

*Pd(crotyl)(XPhos)Cl (**3B**).* The general procedure was followed using 1.00 g (2.54 mmol) of $[(crotyl)PdCl]_2$, 2.42 g (5.08 mmol) of XPhos (**L3**), and 30 mL of anhydrous toluene with a stir time of 3 h. Pentane (60 mL) was added, and the mixture was concentrated in vacuo. The residue was dissolved in 5 mL of toluene and precipitated by the addition of 20 mL of pentane to give 3.11 g (4.61 mmol, 91%) of the title compound as an off-white solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.99−7.86 (m, 1H), 7.38−7.29 (m, 2H), 7.18−6.99 (m, 3H), 5.19−5.03 (m, 1H), 4.32−4.13 (m, 1H), 3.00−2.80 (m, 2H), 2.71−2.42 (m, 2H), 2.31−2.02 (m, 3H), 1.95−0.74 (m, 41H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 148.7, 146.3, 142.1, 136.9, 136.7, 136.5, 133.7, 133.6, 132.3, 132.0, 128.8, 128.0 (two peaks), 125.5, 125.4, 120.8, 115.0 (two peaks), 98.5, 98.2, 50.9, 34.8, 34.2, 31.4, 30.5 (two peaks), 29.2, 27.2, 27.1, 27.0, 26.9, 26.8, 25.8, 25.7, 24.0, 22.4, 17.2, 17.1 [observed complexity due to C−P coupling]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 50.8 (br). HRMS (ESI) m/z $[M - Cl]^+$ Calcd for $C_{37}H_{56}PPd$: 637.3154. Found: 637.3153.

*Pd(cinnamyl)(XPhos)Cl (**3C**).* The general procedure was followed using 1.00 g (1.93 mmol) of $[(cinnamyl)PdCl]_2$, 1.84 g (3.86 mmol) of XPhos (**L3**), and 5 mL of anhydrous toluene with a stir time of 1 h. The product was precipitated by the addition of 10 mL of pentane to give 2.27 g (3.09 mmol, 80%) of the title compound as a bright yellow solid. Product contains trace residual toluene. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.10−7.95 (m, 1H), 7.52 (d, J = 7.5 Hz, 2H), 7.42−7.23 (m, 5H), 7.11−7.01 (m, 3H), 5.87−5.69 (m, 1H), 5.20−5.06 (m, 1H), 3.08−2.90 (m, 2H), 2.73−0.70 (m, 43H), peaks attributable to toluene were observed at 7.17 and 2.36. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 148.9, 146.4, 142.1, 137.2, 136.9, 136.8, 136.7, 136.6, 133.8, 133.7, 132.4, 132.2, 129.0, 128.6, 128.4, 128.1, 127.6 (two peaks), 125.7, 125.6, 125.2, 121.0, 109.7, 109.6, 99.4, 99.1, 51.9, 34.5, 34.3, 31.7, 30.6, 29.2, 27.3, 27.2, 27.0, 26.9, 26.0, 25.7, 24.1, 22.5 [observed complexity due to C−P coupling], peaks attributable to toluene were observed at 137.7, 21.4. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 54.3 (br). Anal. Calcd for $C_{42}H_{58}ClPPd$: C, 68.56; H, 7.95. Found: C, 68.85; H, 7.93.

*Pd(allyl)(BrettPhos)Cl (**4A**).* The general procedure was followed using 502 mg (1.38 mmol) of $[(allyl)PdCl]_2$, 1.48 g (2.76 mmol) of BrettPhos (**L4**), and 6 mL of anhydrous THF with a stir time of 1.5 h. The product was precipitated by the addition of 6 mL of pentane to give 1.81 g (2.52 mmol, 91%) of the title compound as an off-white solid. ^1H NMR (400 MHz, $CDCl_3$, δ): Complex spectrum, see Supporting Information. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 154.8, 153.4, 152.2, 151.6, 151.4, 150.9, 135.0, 134.8, 131.3, 124.8, 124.1, 123.8, 119.3, 119.2, 115.4, 113.8, 113.0, 112.9, 100.5, 100.2, 56.04, 54.8, 51.9, 38.5, 38.3, 33.8, 32.2, 31.6, 30.5, 30.1, 27.2, 27.1, 26.8, 26.7, 25.8, 25.6, 25.0, 24.2, 23.9 [observed complexity due to C−P coupling]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 51.5. Anal. Calcd for $C_{38}H_{58}ClO_2PPd$: C, 63.42; H, 8.12. Found: C, 63.31; H, 8.31.

*Pd(allyl)(JohnPhos)Cl (**5A**).* The general procedure was followed using 1.00 g (2.75 mmol) of $[(allyl)PdCl]_2$, 1.64 g (5.50 mmol) of JohnPhos (**L5**), and 13 mL of anhydrous toluene with a stir time of 1.25 h. The product was precipitated by the addition of 26.5 mL of pentane to give 2.46 g (5.11 mmol, 93%) of the title compound as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.93−7.82 (m, 1H), 7.71−7.57 (m, 2H), 7.50−7.19 (m, 6H), 4.85−2.60 (br m, 5H), 1.90−1.10 (m, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 149.0, 148.8, 142.2 (two peaks), 134.8, 134.6, 133.6 (two peaks), 130.4, 129.8, 129.7, 129.6, 128.1, 126.3, 125.4, 125.3, 113.3, 113.2, 81.7 (br), 57.6 (br), 37.2, 30.9 [observed complexity due to C−P coupling]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 57.3. Anal. Calcd for $C_{23}H_{32}ClPPd$: C, 57.39; H, 6.70. Found: C, 57.35; H, 6.53.

*Pd(crotyl)(JohnPhos)Cl (**5B**).* The general procedure was followed using 1.00 g (2.54 mmol) of $[(crotyl)PdCl]_2$, 1.52 g (5.08 mmol) of JohnPhos (**L5**), and 12.5 mL of anhydrous toluene with a stir time of 1.25 h. The product was precipitated by the addition of 25 mL of pentane to give 2.40 g (4.84 mmol, 95%) of the title compound as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.87 (s, 1H), 7.75−7.50 (m, 2H), 7.50−7.10 (m, 6H), 4.23−3.98 (m, 1H), 3.83−3.60 (m, 1H), 3.11−2.99 (m, 1H), 1.76−1.20 (m, 22H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 149.0, 148.8, 142.1 (two peaks), 135.0, 133.9 (two peaks), 130.4, 130.0, 129.8, 129.7, 127.9, 126.4, 125.2 (two peaks), 112.7 (two peaks), 100.3, 100.0, 52.2, 37.7, 37.6, 37.3, 37.2, 31.7, 31.6, 30.5, 30.4, 17.7, 17.6 [observed complexity due to C−P coupling]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 57.1. Anal. Calcd for $C_{24}H_{34}ClPPd$: C, 58.19; H, 6.92. Found: C, 57.91; H, 6.74.

*Pd(allyl)(CyBippyPhos)Cl (**6A**).* A dry 20 mL scintillation vial was charged with 245 mg (0.67 mmol) of $[(allyl)PdCl]_2$ and transferred into a nitrogen-filled glovebox. The vial was then charged with 750 mg (1.34 mmol) of CyBippyPhos (**L6**). Four milliliters of toluene was added, and the mixture was stirred at rt for 30 min. During the stir time, the mixture became thick and stirring was difficult. An additional 4 mL of toluene was added to allow stirring to continue. The product was fully precipitated by the addition of 8 mL of hexanes. The solid was collected by vacuum filtration in air and washed with 3 × 10 mL of hexanes. The solid was dried in vacuo to give 913 mg (1.23 mmol, 92%) of the title compound as an off-white solid. The product contains <2 wt % of residual toluene. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.99 (s, 1H), 7.44−7.18 (m, 15H), 6.68−6.55 (m, 1H), 5.30−4.99 (m, 1H), 4.60−4.50 (m, 1H), 3.54−3.33 (m, 1H), 2.88−2.78 (m, 1H), 2.20−0.77 (m, 22H), 0.48−0.30 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 147.8, 147.5, 141.9, 140.6, 139.9, 139.8, 137.9, 137.1, 131.3, 131.1, 130.3, 129.3, 129.2, 129.1 (two peaks), 128.7, 128.4, 128.3, 127.6, 127.4, 126.2, 126.1, 125.9, 125.3, 120.1, 117.2, 117.0, 116.8, 116.6, 80.6, 80.3, 57.5, 56.2, 34.2, 33.9, 33.5, 33.3, 31.6, 30.7, 29.7, 29.5, 28.4, 28.2, 27.7, 27.1, 27.0, 26.9, 26.8, 26.6, 25.8, 25.3 [observed complexity due to C−P coupling]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 22.7 (br), 20.6 (br). Anal. Calcd for $C_{39}H_{44}ClN_4PPd$: C, 63.16; H, 5.98; N, 7.55. Found: C, 63.13; H, 5.93; N, 7.30.

*Pd(crotyl)(CyBippyPhos)Cl (**6B**).* A dry Schlenk flask was charged with 264 mg (0.67 mmol) of $[(crotyl)PdCl]_2$ and transferred into a nitrogen-filled glovebox. The flask was then charged with 750 mg (1.34 mmol) of CyBippyPhos (**L6**). Eight milliliters of toluene was added, and the mixture was stirred at rt for 1 h. The product was precipitated by the addition of 20 mL of pentane with cooling in an ice bath. The solid was collected by vacuum filtration in air, washed with 3 × 10 mL of hexanes, and dried in vacuo to give 904 mg (1.10 mmol, 83%) of the title compound as an off-white solid. The product is a 2/3 toluene adduct, which was broken by the dissolution in CH_2Cl_2 and evaporation of the solvent under reduced pressure at 60 °C. In solution, **10** exists as a 1:1 mixture of diastereomers. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.03 (app s, 1H, both diastereomers), 7.49−7.12, m, 15H, both diastereomers), 6.62−6.55 (m, 1H, both diastereomers), 5.10−4.90 (m, 1H), 4.75−4.67 (m, 1H), 4.30−4.10 (m, 1H, both diastereomers), 2.75−2.70 (m, 1H, both diastereomers), 2.20−0.75, m, 25H, both diastereomers), 0.70−0.40 (m, 1H, both diastereomers). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 147.2, 142.2, 142.0, 140.5, 140.4, 140.0, 139.9, 137.9, 137.6, 137.3, 137.1, 131.4, 131.3, 130.4, 129.1 (two peaks), 129.0, 128.7, 128.6 (two peaks), 128.5, 128.2 (two peaks), 127.6, 127.5, 126.2 (two peaks), 126.1, 125.3, 120.1, 119.8, 116.9, 116.8, 116.4, 116.3, 115.8 (two peaks), 115.3 (two peaks), 100.9, 100.6, 100.4, 52.0, 50.6, 34.9, 34.7, 34.4, 34.1, 30.6, 29.9 (two peaks), 29.6, 29.5, 28.5, 28.3, 27.9, 27.7, 27.2, 27.0, 26.9, 26.8, 26.7, 26.6, 26.0, 25.8, 22.4, 21.5 [observed complexity due to C−P coupling]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 22.6 (br), 19.8 (br). HRMS (ESI) m/z $[M - Cl]^+$ Calcd for $C_{40}H_{46}N_4PPd$: 719.2495. Found: 719.2510.

General Procedures for the Synthesis of 7A−13A. A dry Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with $[(R\text{-}allyl)PdCl]_2$ (0.50 mmol, 0.50 equiv) followed by AgOTf (257 mg, 1.00 mmol, 1.00 equiv). The flask was fitted with a rubber septum, evacuated, and backfilled with nitrogen. This evacuation/nitrogen backfill cycle was repeated two additional times. Solvent (10 mL of THF or 2-MeTHF) was added, and the reaction mixture was stirred at rt for 30 min while protected from light. A second dry Schlenk flask was equipped with a magnetic stir bar, fitted with a Schlenk frit, and charged with the appropriate ligand **L4** or **L7**−**L12** (1.00 mmol, 1.00 equiv). The flask was fitted with a rubber septum, and it was evacuated and backfilled with nitrogen. This

DOI: 10.1021/acs.joc.5b01005
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evacuation/nitrogen backfill cycle was repeated two additional times. The solution from the first Schlenk flask was transferred via cannula through the Schlenk frit (to remove AgCl) and into the second Schlenk flask containing the ligand, rinsing with 5 mL of additional solvent (THF or 2-MeTHF). This mixture was stirred at rt for 2 h. Thirty milliliters of hexanes was then added to fully precipitate the product. The solid materials were then collected by suction filtration, washed with additional pentane (or hexanes), and dried in vacuo.

*[Pd(allyl)(BrettPhos)]OTf (**7A**).* The general procedure was followed using 183 mg (0.50 mmol) of $[(allyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, and 537 mg (1.00 mmol) of BrettPhos (**L4**) in anhydrous THF to give 803 mg (0.94 mmol, 94%) of the title compound as a yellow solid. The material contains ∼3 wt % of THF. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (s, 1H), 7.23 (s, 1H), 7.07−6.98 (m, 1H), 6.96−6.87 (m, 1H), 5.45 (sept, J = 7.52 Hz, 1H), 4.14 (d, J = 6.8 Hz, 1H), 3.84 (s, 3H), 3.42 (dd, J = 8.2, 13.1 Hz, 1H), 3.29 (s, 3H), 2.90 (sept, J = 8.2 Hz, 1H), 2.79−2.63 (m, 1H), 2.59 (d, J = 13.2 Hz, 1H), 2.55−2.41 (m, 1H), 2.40−2.25 (m, 2H), 2.14 (sept, J = 7.8 Hz, 1H), 1.98−1.82 (m, 2H), 1.81−0.93 (m, 29H), 0.92−0.66 (m, 7H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 154.8 (two peaks), 153.3, 151.4, 150.5, 135.0, 134.8, 125.6, 124.9, 124.8, 124.2, 123.9, 122.4, 119.5, 119.4, 119.3, 115.2, 113.7, 112.7 (two peaks), 100.7, 100.5, 55.8, 54.7, 52.0, 38.5, 38.4, 38.3, 38.1, 33.7, 32.5, 31.5, 30.0, 27.2, 26.7, 26.6, 24.3, 24.0, 23.9, 23.8 [observed complexity due to C−P and C−F coupling]; peaks attributable to THF were observed at 67.7 and 25.4. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 51.4. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.4 (s, 3F). Anal. Calcd for $C_{39}H_{58}F_3O_5PPdS$: C, 56.21; H, 7.02. Found: C, 56.46; H, 7.05.

*[Pd(crotyl)(BrettPhos)]OTf (**7B**).* The general procedure was followed using 1.97 g (5.00 mmol) of $[(crotyl)PdCl]_2$, 2.57 g (10.0 mmol) of AgOTf, and 5.37 g (10.0 mmol) of BrettPhos (**L4**) in anhydrous THF (100 mL) to give 8.04 g (9.48 mmol, 95%) of the title compound as a yellow solid. The material contains ∼2 wt % of THF. In solution, **7B** exists as a mixture of four isomers in a 57:26:13:4 ratio as judged by ^{31}P NMR (X-ray crystallographic analysis indicates the presence of both *trans*-crotyl and *cis*-crotyl isomers). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35−7.00 (m, 3H), 6.80 (d, J = 9.5 Hz, 1H), 5.48−5.37 (m, 0.09 H), 5.37−5.19 (m, 0.39 H), 4.90−4.78 (m, 0.50 H), 4.23 (d, J = 6.7 Hz, 0.51H), 3.97 (d, J = 7.7 Hz, 0.30 H), 3.90−3.80 (m, 3H), 3.53−3.25 (m, 4H), 3.20−3.05 (m, 0.70 H), 3.04−2.75 (m, 1.44 H), 2.74−2.20 (m, 3H), 2.20−1.50 (m, 11H), 1.49−0.84 (m, 24 H), 0.83−0.68 (m, 8 H) (observed complexity due to the presence of multiple isomers). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 154.7 (two peaks), 152.7, 152.5, 152.1, 151.8 (two peaks), 151.6, 148.9, 148.6, 125.2, 125.1, 122.8, 122.6, 115.2, 113.8 (two peaks), 112.7 (two peaks), 108.4, 108.1, 55.9 (two peaks), 54.8, 54.7 (two peaks), 50.9, 39.2, 39.0 (two peaks), 38.8, 33.9, 33.6, 32.5, 32.4, 32.0, 31.7, 31.3, 30.3, 30.2, 30.1, 27.3 (two peaks), 27.2 (two peaks), 27.1, 27.0, 26.9 (three peaks), 26.8 (three peaks), 26.7, 25.7, 25.5, 25.4, 25.3, 25.0, 24.2 (two peaks), 24.1, 24.0 (two peaks), 23.9, 23.8, 23.6, 23.0, 15.6, 15.5 (observed complexity due to C−P coupling, C−F coupling, and the presence of multiple isomers). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 54.0, 52.2, 45.7, 43.3. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.2 (s, 3F). Anal. Calcd for $C_{40}H_{60}F_3O_5PPdS$: C, 56.70; H, 7.14. Found: C, 56.86; H, 7.42.

*[Pd(cinnamyl)(BrettPhos)]OTf (**7C**).* The general procedure was followed using 259 mg (0.50 mmol) of $[(cinnamyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, and 537 mg (1.00 mmol) of BrettPhos (**L4**) in anhydrous 2-MeTHF to give 884 mg (0.97 mmol, 97%) of the title compound as a yellow solid. The structure was confirmed by X-ray crystallographic analysis. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.60−7.20 (m, 4H), 7.16−6.80 (m, 4H), 6.48 (s, 0.71 H), 5.91−5.77 (m, 0.17 H), 5.50−5.39 (m, 0.73 H), 4.80 (d, J = 10.5 Hz, 0.16 H), 4.51 (app t, J = 10.5 Hz, 0.74 H), 4.26 (d, J = 5.5 Hz, 0.76 H), 4.13−4.02 (m, 0.24 H), 4.00−3.77 (m, 3H), 3.40−3.29 (m, 3H), 3.10−2.92 (m, 1H), 2.78−2.28 (m, 3 H), 2.20−0.45 (m, 38.2 H) (observed complexity due to the presence of isomers). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ):155.1, 154.8, 154.1, 152.8, 152.0, 151.8, 151.7, 148.4, 136.3, 136.1, 133.3, 133.2, 130.0, 129.9, 129.5, 125.9, 125.3, 124.7, 124.4, 124.2, 122.7, 121.8, 119.5, 116.2, 115.3, 115.1, 113.9, 113.6, 112.8, 112.7 (two peaks), 112.4, 109.0, 108.9, 56.1, 55.6, 54.8, 49.2, 39.5, 39.3 (two peaks), 39.1, 34.1, 33.1, 32.7, 31.9, 31.7, 31.4, 31.1, 30.5, 30.3, 29.2, 28.9, 28.6, 27.6, 27.4, 27.3, 27.2 (two peaks), 27.1, 27.0, 26.5, 26.0, 25.8, 25.7, 24.3, 24.2, 22.4, 21.0 (observed complexity due to C−P and C−F coupling and presence of multiple isomers). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 57.6, 39.5. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.1 (s, 3F). Anal. Calcd for $C_{45}H_{62}F_3O_5PPdS$: C, 59.43; H, 6.87. Found: C, 59.26; H, 6.68.

*[Pd(allyl)(tBuBrettPhos)]OTf (**8A**).* The general procedure was followed using 183 mg (0.50 mmol) of $[(allyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, and 485 mg (1.00 mmol) of tBuBrettPhos (**L7**) in anhydrous THF to give 653 mg (0.84 mmol, 84%) of the title compound as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (d, J = 2.5 Hz, 1H), 7.27 (d, J = 1.8 Hz, 1H), 7.09 (dd, J = 2.9 Hz, 9.0 Hz, 1H), 6.97 (d, J = 9.4 Hz, 1H), 5.53 (sept, J = 7.1 Hz, 1H), 4.37 (app d, J = 6.3 Hz, 1H), 3.83 (s, 3H), 3.35 (dd, J = 9.2 Hz, 13.9 Hz, 1H), 3.32 (s, 3H); 2.96 (sept, J = 6.9 Hz, 1H), 2.79 (app d, J = 12.4 Hz, 1H), 2.55 (sept, J = 6.7 Hz, 1H), 2.31−2.12 (m, 2H), 1.44−1.26 (m, 24H), 1.22 (dd, J = 6.9 Hz, 11.8 Hz, 6H), 0.85 (d, J = 6.9 Hz, 3H), 0.71 (d, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 156.3, 154.6 (two peaks), 154.5, 152.2, 151.5, 151.4, 136.5, 136.2, 125.8, 125.7, 125.6, 125.4, 125.2, 122.6, 119.7, 119.6, 119.4, 116.2, 115.5 (two peaks), 112.8, 112.0 (two peaks), 99.8, 99.5, 58.4 (two peaks), 54.7, 54.6, 39.9, 39.8, 39.3, 39.1, 34.0, 32.1, 32.0, 31.9, 31.8, 31.6 (two peaks), 25.7, 25.5, 24.6, 24.5, 24.2 [observed complexity due to C−P and C−F coupling]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 86.8. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −77.9 (s, 3F). Anal. Calcd for $C_{35}H_{54}F_3O_5PPdS$: C, 53.81; H, 6.97. Found: C, 53.79; H, 7.10.

*[Pd(crotyl)(tBuBrettPhos)]OTf (**8B**).* The general procedure was followed using 197 mg (0.50 mmol) of $[(crotyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, 485 mg (1.00 mmol) of tBuBrettPhos (**L7**) in anhydrous 2-MeTHF to give 784 mg (0.99 mmol, 99%) of the title compound as a light yellow solid. A minor impurity detected at 44.0 ppm integrating to 1% was observed in the ^{31}P NMR spectrum. In solution, **8B** exists as a mixture of three isomers in a 55:31:14 as judged by ^{31}P NMR. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38−7.05 (m, 3H), 6.95 (d, J = 7.6 Hz, 1H), 5.52−5.31 (m, 0.77 H), 4.98−4.85 (m, 0.29 H), 4.45−4.38 (m, 0.25 H), 4.18 (d, J = 7.7 Hz, 0.50 H), 3.71−3.68 (m, 3H), 3.39−3.22 (m, 3.75 H), 3.11 (d, J = 12.6 Hz, 0.86 H), 3.06−2.85 (m, 0.79 H), 2.65−2.45 (m, 1.36 H), 2.30−2.03 (m, 1H), 1.48−0.67 (m, 35.5 H) [observed complexity due to the presence of multiple isomers]. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 155.8, 155.4, 154.6 (two peaks), 154.5 (two peaks), 153.3, 151.7, 151.5, 151.4, 151.2, 149.1, 136.7, 136.5, 126.0, 125.9, 125.6, 125.1, 124.9, 123.7, 122.6, 121.3, 121.1, 119.4, 115.4, 114.6 (two peaks), 113.2 (two peaks), 112.7 (two peaks), 112.6, 54.7, 54.6 (two peaks), 54.5, 50.6, 50.5, 40.6, 39.4, 39.3, 39.2, 39.1, 34.1, 33.8, 32.2, 32.1 (two peaks), 32.0, 31.9 (two peaks), 31.8 (two peaks), 31.6, 31.4, 31.3 (two peaks), 31.2, 26.3, 26.1, 25.6, 25.4, 25.1, 24.6, 24.4, 24.4, 24.3, 24.1, 24.0, 23.6, 17.1 (two peaks) (observed complexity due to C−P and C−F coupling and the presence of multiple isomers). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 90.1, 88.4, 83.9. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.0 (s, 3F). Anal. Calcd for $C_{36}H_{56}F_3O_5PPdS$: C, 54.37; H, 7.10. Found: C, 54.58; H, 7.01.

*[Pd(cinnamyl)(tBuBrettPhos)]OTf (**8C**).* The general procedure was followed using 259 mg (0.50 mmol) of $[(cinnamyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, and 485 mg (1.00 mmol) of tBuBrettPhos (**L7**) in anhydrous 2-MeTHF to give 812 mg (0.95 mmol, 95%) of the title compound as a dark yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.60−7.47 (m, 1H), 7.36−7.27 (m, 2H), 7.15−6.80 (m, 5H), 6.50−4.30 (m, 3H), 3.85 (s, 3H), 3.28 (s, 3H), 2.95−1.98 (m, 3H), 1.90−1.66 (m, 1H), 1.61−0.50 (m, 37 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 161.8, 154.5, 153.7, 151.7, 151.6, 149.9, 143.6, 137.5, 137.2, 133.4, 129.5, 125.7, 122.6, 119.4, 115.4, 112.9, 112.6 (two peaks), 110.6, 109.0, 88.9, 72.8, 55.0, 54.6, 54.4, 41.2, 41.1, 40.3, 40.1, 32.1, 30.9, 25.8, 25.5, 25.1, 24.7, 24.4, 24.3, 22.3 [observed complexity due to C−P coupling and C−F coupling]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 94.5. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −77.9 (s, 3F). Anal. Calcd for $C_{41}H_{58}F_3O_5PPdS$: C, 57.44; H, 6.82. Found: C, 57.04; H, 6.77.

DOI: 10.1021/acs.joc.5b01005
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*[Pd(allyl)(AdBrettPhos)]OTf (**9A**).* The general procedure was followed using 57.1 mg (0.156 mmol) of $[(allyl)PdCl]_2$, 80.2 mg (0.312 mmol) of AgOTf, and 200 mg (0.312 mmol) of AdBrettPhos (**L8**) in anhydrous THF to give 265 mg (0.281 mmol, 90%) of the title compound as a tan solid. The product contained ∼2 wt % of THF. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 (s, 1H), 7.35 (s, 1H), 7.17 (dd, J = 2.3 Hz, 8.7 Hz, 1H), 7.04 (app d, J = 9.1 Hz, 1H), 5.60 (sept, J = 6.8 Hz, 1H), 4.54 (d, J = 6.2 Hz, 1H), 3.94 (s, 3H), 3.45−3.35 (m, 4H), 3.04 (quint, J = 7.0 Hz, 1H), 2.85 (d, J = 12.0 Hz, 1H), 2.63 (quint, J = 6.3 Hz, 1H), 2.39−1.91 (m, 18H), 1.81−1.60 (m, 12H), 1.42−1.19 (m, 13H), 0.99−0.82 (m, 4H), 0.78 (d, J = 6.7 Hz, 3H). Resonances attributable to THF were observed at 3.76 and 1.83 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 157.1, 154.8, 154.6, 152.6, 151.7, 151.5, 137.1, 136.8, 125.9, 125.3, 124.6, 124.4, 119.3 (two peaks), 115.4, 112.9, 112.8, 112.0 (two peaks), 100.2, 99.9, 58.1, 54.7, 45.6, 44.8, 44.7, 42.0, 36.3, 36.2, 34.4, 31.7, 29.2, 26.0, 25.6, 25.5, 24.9, 24.6, 24.3 (two peaks). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 88.9. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −77.9 (s, 3F). HRMS (ESI) m/z: $[M - OTf + H]^+$ Calcd for $C_{46}H_{66}O_2PPd$: 787.3835. Found: 787.3832.

*[Pd(allyl)(tBuXPhos)]OTf (**10A**).* A dry Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 3.66 g (10.0 mmol) of $[(allyl)PdCl]_2$ and 5.14 g (20.0 mmol) of AgOTf. The flask was fitted with a rubber septum and evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. Anhydrous THF (40 mL) was added, and the mixture was stirred at rt for 30 min while protected from light. A second dry Schlenk flask was charged with 8.49 g (20.0 mmol) of tBuXPhos (**L9**) and fitted with a rubber septum. The flask was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. Anhydrous THF (40 mL) was added, the contents were swirled, and all of **L9** dissolved. This solution was transferred into the first Schlenk flask via cannula rinsing with 5 mL of additional anhydrous THF. The mixture was stirred at rt for 1.5 h, and the contents were then filtered through a disposable frit (to remove AgCl) into a round-bottomed flask. To the resulting clear solution was added 170 mL of hexanes with agitation as solids precipitated. The solid was collected by vacuum filtration, washed (2 × 50 mL of hexanes), and dried in vacuo to give 12.5 g (17.2 mmol, 86%) of the title compound as a light yellow solid. Product contains ∼0.5 wt % of THF. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.92 (t, J = 7.3 Hz, 1H), 7.59−7.45 (m, 3H), 7.42 (s, 1H), 6.80 (dd, J = 3.2 Hz, 7.5 Hz, 1H), 5.71 (sept, J = 7.2 Hz, 1H), 4.49 (d, J = 6.7 Hz, 1H), 3.54 (dd, J = 9.0 Hz, 14.0 Hz, 1H), 3.03 (quint, J = 7.1 Hz, 1H), 2.93 (d, J = 12.9 Hz, 1H), 2.69−2.61 (m, 1H), 2.50 (quint, J = 7.1 Hz, 1H), 2.26 (J = 6.9 Hz, 1H), 1.52−1.41 (m, 9H), 1.41−1.27 (m, 21H), 0.96 (d, J = 6.7 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 153.6, 152.7, 149.2, 146.0, 145.8, 135.1 (two peaks), 134.9, 133.7, 133.6, 131.7, 131.6, 128.3, 128.2, 126.6, 126.2, 125.8, 122.6, 120.3 (two peaks), 120.1 (two peaks), 119.4, 116.2, 101.3, 101.1, 55.5, 38.3 (two peaks), 38.2, 38.1, 33.9, 32.0, 31.7, 31.2, 31.1, 30.9, 30.8, 25.9, 25.4, 24.9, 24.5 (two peaks), 24.1 [observed complexity due to C−P and C−F coupling]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 70.1. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.1 (s, 3F). Anal. Calcd for $C_{33}H_{50}F_3O_3PPdS$: C, 54.96; H, 6.99. Found: C, 54.72; H, 6.79.

*[Pd(crotyl)(tBuXPhos)]OTf (**10B**).* A dry Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 1.97 g (5.00 mmol) of $[(crotyl)PdCl]_2$ and 2.57 g (10.0 mmol) of AgOTf. The flask was fitted with a rubber septum and evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. Anhydrous 2-MeTHF (20 mL) was added, and the mixture was stirred at rt for 30 min while protected from light. A second dry Schlenk flask was charged with 4.25 g (10.0 mmol) of tBuXPhos (**L9**) and fitted with a rubber septum. The flask was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. Anhydrous 2-MeTHF (20 mL) was added, the contents were swirled, and all of **L9** dissolved. This solution was transferred into the first Schlenk flask via cannula rinsing with 5 mL of additional anhydrous 2-MeTHF. The mixture was stirred at rt for 2 h, and the contents were then filtered through a disposable frit (to remove AgCl) into a round-bottomed flask. To the resulting clear solution was added 90 mL of heptane with agitation as solids precipitated over 1 h. The solid was collected by vacuum filtration, washed (2 × 20 mL of heptane), and dried in vacuo to give 6.55 g (8.90 mmol, 89%) of the title compound as a yellow solid. In solution, **10B** exists as a mixture of three isomers in a 67:24:9 ratio as judged by ^{31}P NMR and ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.99−7.89 (m, 1H), 7.60−7.28 (m, 4H), 6.87−6.74 (m, 1H), 5.71−5.53 (m, 0.81 H), 5.23−5.10 (m, 0.32 H), 4.62−3.89 (m, 0.26 H), 4.38 (d, J = 6.8 Hz, 0.59 H), 3.89−3.79 (m, 0.62 H), 3.75−3.59 (m, 0.33 H), 3.30−3.14 (m, 1H), 3.13−3.03 (m, 0.72H), 2.80 (d, J = 8.2 Hz, 0.39H), 2.60−2.49 (m, 0.41 H), 2.47−2.34 (m, 0.57 H), 2.33−2.11 (m, 1H), 1.61−0.75 (m, 39 H) [observed complexity due to presence of multiple isomers]. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 153.7, 153.4, 152.8, 152.3, 151.9, 146.4, 146.2, 146.0, 145.8, 144.1, 135.0, 134.9, 134.7, 134.4, 134.1, 133.7, 133.5, 133.3, 133.2, 131.5, 131.4 (two peaks), 128.1 (two peaks), 128.0, 126.4, 125.7, 124.1, 122.9, 121.4, 120.4, 119.7, 119.3, 117.4, 116.1, 112.9, 112.8, 48.3, 38.9, 38.8, 38.1, 37.5, 37.3, 33.8, 33.5, 32.9, 31.6, 31.3, 31.1 (two peaks), 31.0 (two peaks), 30.7 (two peaks), 26.2, 24.9, 24.8, 24.5, 24.3, 24.2, 24.0 (two peaks), 23.7, 23.4, 22.8, 20.8, 17.0, 16.4 (two peaks) [observed complexity due to C−P coupling, C−F coupling, and the presence of multiple isomers]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 72.1, 71.7, 66.7. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −77.9 (s, 3F). Anal. Calcd for $C_{34}H_{52}F_3O_3PPdS$: C, 55.54; H, 7.13. Found: C, 55.71; H, 6.96.

*[Pd(cinnamyl)(tBuXPhos)]OTf (**10C**).* The general procedure was followed using 259 mg (0.50 mmol) of $[(cinnamyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, and 485 mg (1.00 mmol) of tBuXPhos (**L9**) in anhydrous THF to give 725 mg (0.91 mmol, 91%) of the title compound as a yellow solid. The structure was confirmed by X-ray crystallographic analysis. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.91 (t, J = 6.7 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.42 (t, J = 7.7 Hz, 1H), 7.29 (t, J = 7.7 Hz, 2H), 7.22−6.98 (m, 3H), 6.61 (dd, J = 3.2 Hz, 7.6 Hz, 2H), 5.71−4.00 (m, 2H), 3.20−2.11 (m, 2H), 1.95−0.55 (m, 39H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 153.1, 151.5, 146.8, 146.6, 135.4, 135.11, 135.0, 134.1, 133.6, 133.5, 131.5, 130.3 (two peaks), 129.6 (two peaks), 128.1, 128.0, 125.2, 123.3, 122.6, 119.4, 118.9, 116.2, 110.2, 39.3, 39.1, 32.1, 31.5, 31.3 (two peaks), 31.0, 25.7, 25.5, 24.9, 24.8, 24.4, 22.6, 22.5, 14.1 [observed complexity due to C−P and C−F coupling]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 76.0. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.6 (s, 3F). Anal. Calcd for $C_{39}H_{54}F_3O_3PPdS$: C, 58.75; H, 6.83. Found: C, 58.81; H, 6.76.

*[Pd(allyl)(Me$_4$tBuPhos)]OTf (**11A**).* The general procedure was followed using 183 mg (0.50 mmol) of $[(allyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, and 485 mg (1.00 mmol) of Me$_4$tBuXPhos (**L10**) in anhydrous THF to give 727 mg (0.94 mmol, 94%) of the title compound as a pale yellow solid. The product contains ∼0.5 wt % THF. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 (s, 1H), 7.32 (s, 1H), 5.58 (sept, J = 7.1 Hz, 1H), 4.53 (d, J = 6.5 Hz, 1H), 3.31 (dd, J = 9.5, 13.4 Hz, 1H), 3.00 (sept, J = 7.3 Hz, 1H), 2.91 (d, J = 12.8 Hz, 1H), 2.61 (sept, J = 6.8 Hz, 1H), 2.60 (s, 3H), 2.31 (sept, J = 6.6 Hz, 1H), 2.25 (s, 3H), 2.16−2.08 (m, 4H), 1.52−1.37 (m, 18H), 1.32 (d, J = 7.0 Hz, 6H), 1.24 (t, J = 7.6 Hz, 6H), 0.88 (d, J = 6.8 Hz, 3H), 0.82 (s, 3H), 0.74 (d, J = 6.6 Hz, 3H), peaks attributable to THF were observed at 3.76 and 1.85 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 155.1, 154.6, 151.4, 143.3, 143.0, 141.5 (two peaks), 139.2, 138.5, 138.4, 137.1, 137.0, 133.6, 133.4, 125.8, 125.6, 125.5, 122.6, 120.0, 119.9, 119.4, 116.2, 116.1, 98.3, 98.0, 62.7 (two peaks), 40.9, 40.8, 40.1, 40.0, 34.0, 33.4 (two peaks), 32.9 (two peaks), 32.2, 32.0, 26.9, 26.3, 26.2, 24.8, 24.6, 24.3 (two peaks), 18.7, 17.5, 17.3 [observed complexity due to C−P and C−F coupling], peaks attributable to THF were observed at 67.9 and 25.6 ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 93.5. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.1 (s, 3F). Anal. Calcd for $C_{37}H_{58}F_3O_3PPdS$: C, 57.17; H, 7.52. Found: C, 57.19; H, 7.64.

*[Pd(allyl)(RockPhos)]OTf (**12A**).* The general procedure was followed using 183 mg (0.50 mmol) of $[(allyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, and 469 mg (1.00 mmol) of RockPhos (**L11**) in anhydrous THF to give 744 mg (0.97 mmol, 97%) of the title compound as a yellow solid. The product contains ∼0.8 wt % THF. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.44 (d, J = 1.3 Hz, 1H), 7.37 (d, J = 1.3 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.01 (dd, J = 2.2, 8.4 Hz, 1H),

DOI: 10.1021/acs.joc.5b01005
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5.57 (sept, J = 6.9 Hz, 1H), 4.44 (d, J = 6.6 Hz, 1H), 3.88 (s, 3H), 3.38 (dd, J = 9.4, 13.7 Hz, 1H), 3.01 (sept, J = 7.1 Hz, 1H), 2.86 (d, J = 12.7 Hz, 1H), 2.63 (sept, J = 6.7 Hz, 1H), 2.31 (sept, J = 6.8 Hz, 1H), 2.23 (dt, J = 2.3, 7.5 Hz, 1H), 1.45−1.20 (m, 30H) 1.08 (s, 3H), 0.97 (d, J = 6.5 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H), peaks attributable to THF were observed at 3.76 and 1.85 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 160.0, 159.9, 154.8, 154.7, 151.4, 146.8, 146.5, 137.2, 137.1, 132.2, 132.1, 125.9, 125.8, 125.7, 124.1, 123.9, 122.6, 120.0, 119.9, 119.4, 116.2, 116.1, 112.0 (two peaks), 99.0, 98.8, 59.2 (two peaks), 54.6, 40.2, 40.1, 39.6, 39.4, 34.1, 32.3 (two peaks), 32.0 (two peaks), 31.8, 27.0, 26.7, 24.7, 24.6, 24.3, 24.2, 19.0, [observed complexity due to C−P and C−F coupling], peaks attributable to THF were observed at 67.9 and 25.6 ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 84.8. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.2 (s, 3F). Anal. Calcd for $C_{35}H_{54}F_3O_4PPdS$: C, 54.93; H, 7.11. Found: C, 54.92; H, 7.25.

*[Pd(allyl)(BippyPhos)]OTf (**13A**).* The general procedure was followed with the following modifications: Using 183 mg (0.50 mmol) of $[(allyl)PdCl]_2$, 257 mg (1.00 mmol) of AgOTf, and 507 mg (1.00 mmol) of BippyPhos (**L12**) in anhydrous THF gave 786 mg (0.91 mmol, 91%) of the title compound as a pale yellow solid after precipitation with 1:3 hexanes/MTBE. The product is a 2/3 MTBE adduct. Note: This compound slowly changed color over the course of several months when stored on the benchtop. However, we have found that it is stable indefinitely when stored in the refrigerator. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.15−8.05 (m, 1H), 7.49−7.08 (m, 15H), 7.71−7.60 (m, 1H), 6.10−5.79 (m, 1H), 4.52−4.29 (m, 2H), 4.06−3.96 (m, 0.4H), 3.85−3.75 (m, 0.6H), 3.37−3.30 (m, 0.4H), 3.02−2.92 (m, 0.6H), 0.91−0.50 (m, 18H), peaks attributable to MTBE were observed at 3.10 and 1.05 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 156.4, 154.8, 150.5, 148.0, 146.3 (two peaks), 146.1, 146.0, 141.9, 141.5, 137.7, 137.6, 131.2, 130.5, 130.3, 129.8, 129.7, 129.4 (two peaks), 129.2, 129.1, 129.0, 128.9, 127.9, 127.7, 125.6, 125.2, 124.6, 122.6 (two peaks), 122.4, 121.8 (two peaks), 119.2, 116.0, 114.9, 104.0, 103.9, 93.4, 93.2, 90.1, 89.9, 57.8, 56.9, 36.4. 36.2, 36.1 (two peaks), 36.0, 35.9, 35.8, 29.0 (two peaks), 28.9 (two peaks), 28.5 (two peaks) [observed complexity due to C−F and C−P coupling], peaks attributable to MTBE were observed at 72.5, 49.2, and 26.8 ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 50.4, 49.5. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −78.8 (s, 3F). Anal. Calcd for $C_{36}H_{40}F_3N_4O_3PPdS\cdot(2/3)C_5H_{12}O$: C, 54.81; H, 5.61; N, 6.50. Found: C, 54.97; H, 5.70; N, 6.31.

General Procedure for the Secondary Amination Reactions in Table 3. An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1B** (0.5−1 mol % as indicated), **L1** (0.5−1 mol % as indicated), aryl chloride (1.00 mmol, if solid), and NaO*t*-Bu (1.20 mmol). The tube was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. Dodecane (GC standard, 0.20 mmol), the amine (1.20 mmol), aryl chloride (1.00 mmol, if liquid), and anhydrous THF (2 mL) were added sequentially via syringe. The tube was placed in a preheated oil bath and the contents were stirred for the indicated time. The tube was then removed from the oil bath and allowed to cool to room temperature. The reaction mixture was diluted with 10 mL of EtOAc and filtered through a pad of Celite. The solution was concentrated in vacuo, and the residue was chromatographed on silica gel.

*4-(4-Methoxyphenyl)morpholine (**15a**).* According to the general procedure, a mixture of 4-chloroanisole (123 μL, 1.00 mmol), morpholine (105 μL, 1.20 mmol), NaO*t*-Bu (115 mg, 1.20 mmol), **1B** (3.3 mg, 0.005 mmol), **L1** (2.3 mg, 0.005 mmol), and 2 mL of THF was stirred at 80 °C for 2.5 h. The crude material was chromatographed on silica gel with a gradient of 0−20% EtOAc/hexanes as the eluent to give 186 mg (0.96 mmol, 96%) of **15a** as a colorless solid. The spectroscopic data matched those previously reported.[37a] ^1H NMR (400 MHz, $CDCl_3$, δ): 6.85 (dd, J = 9.4 Hz, 16.2 Hz, 4H), 3.84 (app t, J = 4.7 Hz, 4H), 3.75 (s, 3H), 3.04 (app t, J = 4.7 Hz, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 154.3, 146.0, 118.1, 114.8, 67.3, 55.8, 51.1.

*N,N-Diethyl-6-methoxypyridin-2-amine (**15b**).* According to the general procedure, a mixture of 2-chloro-6-methoxypyridine (119 μL, 1.00 mmol), diethylamine (124 μL, 1.20 mmol), NaO*t*-Bu (115 mg, 1.20 mmol), **1B** (3.3 mg, 0.005 mmol), **L1** (2.3 mg, 0.005 mmol), and 2 mL of THF was stirred at 80 °C for 70 min. The crude material was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 171 mg (0.95 mmol, 95%) of **15b** as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.33 (t, J = 7.5 Hz, 1H), 5.99 (d, J = 7.8 Hz, 1H), 5.93 (d, J = 7.8 Hz, 1H), 3.86 (s, 3H), 3.49 (q, J = 7.0 Hz, 4 H), 1.81 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 163.4, 156.7, 139.8, 96.8, 95.2, 52.9, 42.7, 13.2. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{10}H_{17}N_2O$: 181.1341. Found: 181.1318.

*1-(Pyrazin-2-yl)indoline (**15c**).* According to the general procedure, a mixture of 2-chloropyrazine (89 μL, 1.00 mmol), indoline (135 μL, 1.20 mmol), NaO*t*-Bu (115 mg, 1.20 mmol), **1B** (3.3 mg, 0.005 mmol), **L1** (2.3 mg, 0.005 mmol), and 2 mL of THF was stirred at 80 °C for 1 h. The crude material was chromatographed on silica gel with a gradient of 0−50% EtOAc/hexanes as the eluent to give 191 mg (0.97 mmol, 97%) of **15c** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.28−8.14 (m, 3H), 8.00 (app d, J = 2.6 Hz, 1H), 7.27−7.13 (m, 2H), 6.93−6.88 (m, 1H), 4.05 (t, J = 8.7 Hz, 2H), 3.24 (t, J = 8.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 151.6, 144.1, 141.8, 134.3, 132.0, 131.3, 127.5, 124.8, 121.6, 114.2, 48.7, 27.9. Anal. Calcd for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.30. Found: C, 73.17; H, 5.63; N, 21.42.

*N-Methyl-N-phenylquinolin-6-amine (**15d**).* According to the general procedure, a mixture of 6-chloroquinoline (164 mg, 1.00 mmol), *N*-methylaniline (130 μL, 1.20 mmol), NaO*t*-Bu (115 mg, 1.20 mmol), **1B** (3.3 mg, 0.005 mmol), **L1** (2.3 mg, 0.005 mmol), and 2 mL of THF was stirred at 80 °C for 1 h. The crude material was chromatographed on silica gel with a gradient of 0−50% EtOAc/hexanes as the eluent to give 231 mg (0.99 mmol, 99%) of **15d** as a yellow oil. The spectroscopic data matched those previously reported.[64] ^1H NMR (400 MHz, $CDCl_3$, δ): 8.71 (dd, J = 1.4 Hz, 4.1 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 9.3 Hz, 1H), 7.40−7.33 (m, 3H), 7.30 (dd, J = 4.3 Hz, 8.3 Hz, 1H), 7.17 (app d, J = 7.5 Hz, 2H), 7.15−7.08 (m, 2H), 3.43 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 148.7, 147.7, 147.1, 144.2, 134.6, 130.0, 129.7 (two peaks), 124.0, 123.6, 123.4, 121.5, 111.2, 40.8.

*4-(Thiophen-3-yl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**15e**).* The general procedure was followed with the following modifications: a mixture of 3-chlorothiophene (93 μL, 1.00 mmol), benzomorpholine (140 μL, 1.20 mmol), K_2CO_3 (194 mg, 1.40 mmol), **1B** (6.6 mg, 0.01 mmol), **L1** (4.7 mg, 0.01 mmol), and 2 mL of 2-methyl-2-butanol was stirred at 110 °C for 20 h. The crude material was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 212 mg (0.98 mmol, 98%) of **15e** as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.30 (dd, J = 3.2 Hz, 5.2 Hz, 1H), 7.07 (dd, J = 1.4 Hz, 5.2 Hz, 1H), 6.98−6.92 (m, 1H), 6.91−6.85 (m, 1H), 6.81 (dd, J = 1.4 Hz, 3.2 Hz, 1H), 6.81−6.73 (m, 2H), 4.33 (t, J = 4.5 Hz, 2H), 3.69 (t, J = 4.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 146.1, 144.5, 133.1, 125.4, 124.1, 121.2, 120.1, 117.0, 116.3, 112.3, 64.5, 49.0. Anal. Calcd for $C_{12}H_{11}NOS$: C, 66.33; H, 5.10; N, 6.45. Found: C, 66.42; H, 5.24; N, 6.42.

General Procedure for the Primary Amination Reactions in Table 3. An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **7B** (0.3−1.2 mol % as indicated), **L4** (0.3−1.2 mol % as indicated), aryl chloride (1.00 mmol, if solid), and NaO*t*-Bu (1.20 mmol). The tube was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. Dodecane (GC standard, 0.20 mmol), the amine (1.20 mmol), aryl chloride (1.00 mmol, if liquid), and anhydrous THF (2 mL) were added sequentially via syringe. The tube was placed in a preheated oil bath, and the contents were stirred for the indicated time. The tube was then removed from the oil bath and allowed to cool to room temperature. The reaction mixture was diluted with 10 mL of EtOAc and filtered through a pad of Celite. The solution was concentrated in vacuo, and the residue was chromatographed on silica gel.

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794−6813

*N-Butyl-4-methoxyaniline (**15f**).* According to the general procedure, a mixture of 4-chloroanisole (123 μL, 1.00 mmol), n-butyalmine (119 μL, 1.20 mmol), NaO*t*-Bu (115 mg, 1.20 mmol), **7B** (2.5 mg, 0.003 mmol), **L4** (1.6 mg, 0.003 mmol), and 2 mL of THF was stirred at 80 °C for 10 min. The crude material was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 171 mg (0.96 mmol, 96%) of **15f** as a colorless oil. The spectral properties matched those previously reported.[65] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.79 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.33 (br s, 1H), 3.07 (t, *J* = 7.1 Hz, 2H), 1.65−1.55 (m, 2H), 1.49−1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 152.1, 143.1, 115.1, 114.2, 56.0, 44.9, 32.0, 20.5, 14.1.

*N-([1,1′-Biphenyl]-2-yl)benzo[d][1,3]dioxol-5-amine (**15g**).* According to the general procedure, a mixture of 5-chloro-1,3-benzodioxole (117 μL, 1.00 mmol), 2-aminobiphenyl (203 mg, 1.20 mmol), NaO*t*-Bu (115 mg, 1.20 mmol), **7B** (2.5 mg, 0.003 mmol), **L4** (1.6 mg, 0.003 mmol), and 2 mL of THF was stirred at 80 °C for 10 min. The crude material was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 272 mg (0.94 mmol, 94%) of **15g** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.53−7.43 (m, 4H), 7.42−7.34 (m, 1H), 7.28−7.15 (m, 3H), 7.01−6.90 (m, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 2.3 Hz, 1H), 6.53 (dd, *J* = 2.3 Hz, 8.3 Hz, 1H), 5.93 (s, 2H), 5.51 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 148.3, 143.1, 141.9, 139.2, 137.7, 130.9, 130.3, 129.5, 129.1, 128.5, 127.6, 120.1, 115.8, 113.6, 108.7, 103.2, 101.2. Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.91; H, 5.29; N, 4.79.

*(R)-6-Methoxy-N-(1-phenylethyl)pyridin-2-amine (**15h**).* According to the general procedure, a mixture of 2-chloro-6-methoxypyridine (119 μL, 1.00 mmol), (*R*)-(+)-α-methylbenzylamine (98% ee, 153 μL, 1.20 mmol), NaO*t*-Bu (115 mg, 1.20 mmol), **7C** (2.7 mg, 0.003 mmol), **L4** (1.6 mg, 0.003 mmol), and 1 mL of THF was stirred at 80 °C for 5 min. The crude material was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 223 mg (0.98 mmol, 98%) of **15h** as a colorless oil. $[\alpha]_D^{25} = -38.2°$ (*c* 1.03 $CHCl_3$). The enantiomeric excess was measured to be 97% by chiral HPLC analysis (Chiracel OD-H column, 5% IPA/hexanes, 1 mL/min, 254 nm). Racemic material was prepared in an identical experiment using racemic α-methylbenzylamine. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.41−7.29 (m, 4H), 7.28−7.19 (m, 2H), 6.00 (d, *J* = 8.0 Hz, 1H), 5.77 (d, *J* = 8.1 Hz, 1H), 4.89−4.63 (m, 2H), 3.81 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 163.6, 157.0, 145.2, 140.1, 128.7, 127.0, 126.0, 98.2, 97.9, 53.2, 52.1, 24.4. Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06. Found: C, 73.96; H, 6.97.

*N-(Pyridin-3-yl)pyrazin-2-amine (**15i**).* The general procedure was followed with the following modifications: A mixture of 3-chloropyridine (95 μL, 1.00 mmol), 2-aminopyrazine (114 mg, 1.20 mmol), K_2CO_3 (194 mg, 1.40 mmol), **7B** (2.5 mg, 0.003 mmol), **L4** (1.6 mg, 0.003 mmol), and 2 mL of 2-methyl-2-butanol was stirred at 110 °C for 2 h. The crude material was chromatographed on silica gel with a gradient of 0−5% MeOH/CH_2Cl_2 as the eluent to give 170 mg (0.99 mmol, 99%) of **15i** as a white solid. The spectral properties match those previously reported.[37b] ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.68 (s, 1H), 8.82 (d, *J* = 1.6 Hz, 1H), 8.27 (app s, 1H), 8.22−8.13 (m, 3H), 7.98 (app d, *J* = 2.4 Hz, 1H), 7.33 (dd, *J* = 4.7, 8.3 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, δ): 152.0, 142.2, 141.0, 140.2, 137.3, 135.1, 134.2, 124.7, 123.5.

*N-(2,5-Dimethylphenyl)-1H-pyrrolo[2,3-b]pyridin-4-amine (**15j**).* An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **7B** (8.5 mg, 1.2 mol) and 4-chloro-7-azaindole (153 mg, 1.00 mmol). The tube was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. 2,5-Dimethylaniline (150 μL, 1.20 mmol) and 2.4 mL of LiHMDS solution in THF (2.4 mmol) were added sequentially via syringe. The tube was placed in a preheated oil bath (65 °C), and the contents were stirred for 4 h. The tube was then removed from the oil bath and allowed to cool to room temperature, and 2 mL of 1 M HCl (aq) was added followed by 15 mL of EtOAc. The contents of the tube were then poured into a separatory funnel containing 20 mL of sat. $NaHCO_3$. The aqueous was extracted with EtOAc (3 × 15 mL), and the combined extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo, and the residue was chromatographed on silica gel using a gradient of 0−10% MeOH/CH_2Cl_2 as the eluent to give 223 mg (0.94 mmol, 94%) of **15j** as a light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 12.2 (br, s, 1H), 8.10 (d, *J* = 5.1 Hz, 1H), 7.37−7.11 (m, 3H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 5.7 Hz, 1H), 6.38 (d, *J* = 2.5 Hz, 1H), 6.08 (s, 1H), 2.36 (s, 3H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 150.2, 145.7, 143.9, 138.3, 136.7, 131.0, 129.6, 126.1, 125.3, 122.4, 108.8, 99.3, 96.9, 21.1, 17.6. HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{15}H_{16}N_3$: 238.1344. Found: 238.1341.

*N-(2-(Thiophen-2-yl)ethyl)pyrimidin-5-amine (**15k**).* The general procedure was followed with the following modifications: A mixture of 5-bromopyrimidine (159 mg, 1.00 mmol), 2-thiopheneethylamine (140 μL, 1.20 mmol), K_2CO_3 (194 mg, 1.40 mmol), **7B** (10.2 mg, 0.012 mmol), **L4** (6.4 mg, 0.012 mmol), and 2 mL of 2-methyl-2-butanol was stirred at 110 °C for 19 h. The crude material was chromatographed on silica gel with a gradient of 25−75% EtOAc/hexanes as the eluent to give 152 mg (0.74 mmol, 74%) of **15k** as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.60 (s, 1H), 8.10 (s, 2H), 7.19 (dd, *J* = 1.2 Hz, 3.2 Hz, 1H), 6.97 (dd, *J* = 7.4 Hz, 5.3 Hz, 1H), 6.89−6.83 (m, 1H), 3.89 (br s, 1H), 3.47 (q, *J* = 6.5 Hz, 2H), 3.16 (app t, *J* = 6.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 148.9, 141.5, 141.2, 140.7, 127.3, 125.8, 124.5, 44.4, 29.5. Anal. Calcd for $C_{10}H_{11}N_3S$: C, 58.51; H, 5.40; N, 20.47. Found: C, 58.28; H, 5.43; N, 20.42.

General Procedure for the Suzuki−Miyaura Couplings in Table 5. An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **3B** (2 mol %), heteroaryl chloride (1.00 mmol, if solid), and aryl/heteroarylboronic acid (1.5 mmol). The tube was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. The heteroaryl chloride (1.00 mmol, if liquid), anhydrous THF (2 mL), and aqueous 0.5 M K_3PO_4 (4.0 mL) were added sequentially via syringe. The contents of the tube were stirred at room temperature, or the tube was placed in a preheated oil bath at 45 °C as indicated, and the contents were stirred for the indicated time. If heated, the tube was then removed from the oil bath and allowed to cool to room temperature. The reaction mixture was diluted with 10 mL of EtOAc and 10 mL of H_2O, and then the aqueous phase was extracted with 3 × 10 mL of EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel, unless otherwise noted.

*3-(4-Tolyl)pyridine (**16a**).* According to the general procedure, a mixture of 3-chloropyridine (95 μL, 1.00 mmol), *p*-tolylboronic acid (204 mg, 1.50 mmol), **3B** (14 mg, 0.02 mmol), 2 mL of THF, and 4 mL of 0.5 M aqueous K_3PO_4 was stirred at room temperature for 2 h. The crude material was chromatographed on silica gel with a gradient of 10−40% EtOAc/hexanes as the eluent to give 160 mg (0.95 mmol, 95%) of **16a** as a colorless solid. The spectroscopic data matched those previously reported.[66] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.80 (s, 1H), 8.52 (d, *J* = 4.6 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.38−7.22 (m, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 148.1 (two peaks), 137.9, 136.5, 134.9, 134.0, 129.7, 126.9, 123.4, 21.1.

*2-(Thiophen-2-yl)quinoline (**16b**).* According to the general procedure, a mixture of 2-chloroquinoline (164 mg, 1.00 mmol), 2-thienylboronic acid (192 mg, 1.50 mmol), **3B** (14 mg, 0.02 mmol), 2 mL of THF, and 4 mL of 0.5 M aqueous K_3PO_4 was stirred at 45 °C for 2 h. The crude material was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 208 mg (0.99 mmol, 99%) of **16b** as a colorless solid. The spectroscopic data matched those previously reported.[67] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.12 (dd, *J* = 4.6 Hz, 8.6 Hz, 2H), 7.83−7.64 (m, 4H), 7.51−7.43 (m, 2H), 7.17 (t, *J* = 4.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 152.5, 148.3, 145.5, 136.7, 129.9, 129.4, 128.7, 128.2, 127.6, 127.3, 126.2, 126.0, 117.8.

*4-(Furan-2-yl)-2,6-dimethoxypyrimidine(**16c**).* According to the general procedure, a mixture of 6-chloro-2,4-dimethoxypyrimidine

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794−6813

(175 mg, 1.00 mmol), 2-furanboronic acid (168 mg, 1.50 mmol), **3B** (14 mg, 0.02 mmol), 2 mL of THF, and 4 mL of 0.5 M aqueous K_3PO_4 was stirred at room temperature for 1 h. The crude material was chromatographed on silica gel with a gradient of 0−10% EtOAc/hexanes as the eluent to give 194 mg (0.94 mmol, 94%) of **16c** as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.53 (dd, J = 0.9 Hz, 1.9 Hz, 1H), 7.19 (dd, J = 0.7 Hz, 3.5 Hz, 1H), 6.69 (s, 1H), 6.53 (dd, J = 1.7 Hz, 3.4 Hz, 1H) 4.02 (s, 3H), 3.99 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 172.6, 165.6, 157.4, 152.2, 144.6, 112.3, 111.9, 95.0, 54.8, 54.0. Anal. Calcd for $C_{10}H_{10}N_2O_3$: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.19; H, 4.72; N, 13.42.

*2-(2,6-Difluorophenyl)-6-methoxypyridine (**16d**).* According to the general procedure, a mixture of 2-chloro-6-methoxypyridine (119 μL, 1.00 mmol), 2,6-difluorophenylboronic acid (237 mg, 1.50 mmol), **3B** (14 mg, 0.02 mmol), 2 mL of THF, and 4 mL of 0.5 M aqueous K_3PO_4 was stirred at room temperature for 30 min. The crude material was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 195 mg (0.88 mmol, 88%) of **16d** as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.64 (t, J = 7.8 Hz, 1H), 7.35−7.26 (m, 1H), 7.05 (d, J = 7.1 Hz, 1H), 7.00−6.92 (m, 2H), 6.75 (d, J = 8.3 Hz, 1H), 3.95 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 163.8, 160.5 (dd, J = 250.7 Hz, 6.97 Hz), 146.7, 138.6, 129.8 (t, J = 10.23 Hz), 118.8 (t, J = 1.95 Hz), 118.2 (t, J = 17.23 Hz), 111.8 (dd, J = 26.1 Hz, 6.6 Hz), 110.3, 53.6. Anal. Calcd for $C_{12}H_9F_2NO$: C, 65.16; H, 4.10; N, 6.33. Found: C, 65.14; H, 4.37; N, 6.46.

*5-(Dibenzo[b,d]furan-4-yl)-1,3-dimethyl-1H-pyrazole (**16e**).* According to the general procedure, a mixture of 5-chloro-1,3-dimethyl-1*H*-pyrazole (115 μL, 1.00 mmol), dibenzo[*b*]furan-4-boronic acid (318 mg, 1.50 mmol), **3B** (14 mg, 0.02 mmol), 2 mL of THF, and 4 mL of 0.5 M aqueous K_3PO_4 was stirred at room temperature for 2 h. The crude material was chromatographed on silica gel with a gradient of 0−10% EtOAc/hexanes as the eluent to give 240 mg (0.92 mmol, 92%) of **16e** as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.02−7.97 (m, 2H), 7.57 (d, J = 8.8 Hz, 1H), 7.58−7.36 (m, 4H), 6.33 (s, 1H), 3.85 (s, 3H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 156.2, 153.3, 147.9, 139.1, 128.0, 127.7, 125.0, 124.0, 123.2, 123.0, 121.1, 120.9, 115.6, 112.0, 107.1, 37.4, 13.7. Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.93; H, 5.29; N, 10.56.

*5-Methyl-6-(thiophen-3-yl)imidazo[1,2-a]pyridine hydromethanesulfonate (**16f**).* According to the general procedure, a mixture of 6-bromo-5-methylimidazo[1,2-*a*]pyridine (167 mg, 1.00 mmol), 3-thienylboronic acid (152 mg, 1.50 mmol), **3B** (14 mg, 0.02 mmol), 2 mL of THF, and 4 mL of 0.5 M aqueous K_3PO_4 was stirred at 45 °C for 5 h. The crude material was taken up in 10 mL of isopropyl acetate and stirred. Methanesulfonic acid (0.08 mL) was added slowly as a precipitate developed, and the mixture was stirred at rt for 30 min. The solid was collected by vacuum filtration, washed (3 × 5 mL isopropyl acetate, 1 × 10 mL hexanes), and dried in vacuo give 194 mg (0.80 mmol, 80%) of **16f** as a tan solid. ^{1}H NMR (400 MHz, 4:1 D_2O/DMSO-d_6, δ): 8.18 (s, 1H), 8.06 (s, 1H), 7.97 (d, J = 9.3 Hz, 1H), 7.85 (d, J = 9.3 Hz, 1H), 7.70−7.60 (m, 2H), 7.32 (d, J = 4.6 Hz, 1H), 2.87−2.77 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, 4:1 D_2O/DMSO-d_6, δ): 140.4, 137.8, 137.3, 137.2, 130.1, 128.5, 127.3, 126.5, 123.9, 114.7, 110.4, 40.1, 17.4. HRMS (ESI) m/z [M + H − OMs]$^+$ Calcd for $C_{12}H_{10}N_2S$: 215.0643. Found: 215.0644.

General Procedure for the Ketone Enolate Arylation Reactions in Table 6. An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **3A** (1−2 mol %, as indicated), aryl chloride (1.00 mmol, if solid), and KO*t*-Bu (2.00−2.40 mmol, as indicated). The tube was capped with a rubber septum and was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. Dodecane (GC standard, 0.20 mmol), the ketone (1.20 mmol), aryl chloride (1.00 mmol, if liquid), and anhydrous toluene (4 mL) were added sequentially via syringe. The tube was placed in a preheated oil bath (60 °C), and the contents were stirred for the indicated time. The tube was then removed from the oil bath and allowed to cool to room temperature. Saturated NH_4Cl (4 mL) and EtOAc (10 mL) were added, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The organic extracts were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel.

*2-(4-Methoxyphenyl)-1-phenylethan-1-one (**17a**).* According to the general procedure, a mixture of 4-chloroanisole (123 μL, 1.00 mmol), acetophenone (140 μL, 1.20 mmol), KO*t*Bu (224 mg, 2.00 mmol), **3A** (6.6 mg, 0.01 mmol), and 4 mL of toluene was stirred at 60 °C for 2 h. The crude material was chromatographed on silica gel with a gradient of 0−4% EtOAc/hexanes as the eluent to give 210 mg (0.93 mmol, 93%) of **17a** as a colorless solid. The spectroscopic data matched those previously reported.[43] ^{1}H NMR (400 MHz, $CDCl_3$, δ):8.02 (d, J = 6.8 Hz, 2H), 7.59−7.51 (m, 1H), 7.48−7.40 (m, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.24 (s, 2H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 199.0, 158.7, 136.8, 133.2, 130.6, 128.7 (two peaks), 126.6, 114.3, 55.4, 44.7.

*1-(Pyridin-3-yl)-2-(quinolin-6-yl)ethan-1-one (**17b**).* According to the general procedure, a mixture of 6-chloroquinoline (164 mg, 1.00 mmol), 3-acetylpyridine (132 μL, 1.20 mmol), KO*t*Bu (269 mg, 2.40 mmol), **3A** (6.6 mg, 0.01 mmol), and 4 mL of toluene was stirred at 60 °C for 4 h. The crude material was chromatographed on silica gel with EtOAc as the eluent to give 236 mg (0.95 mmol, 95%) of **17b** as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.29 (s, 1H), 8.90 (d, J = 3.5 Hz, 1H), 8.88 (d, J = 3.5 Hz, 1H), 8.29 (d, J = 8.2 Hz, 1H), 8.17−8.02 (m, 2H), 7.72 (s, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.47−7.31 (m, 2H), 4.50 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 196.1, 153.8, 150.6, 150.1, 147.6, 135.9, 135.8, 132.1, 131.8, 131.2, 130.1, 128.4, 128.2, 123.9, 121.5, 45.7. HRMS (ESI) m/z [M + H]$^+$ Calcd for $C_{16}H_{13}N_2O$: 249.1028. Found: 249.1020.

*1-(Furan-2-yl)-2-(4-(trifluoromethyl)phenyl)ethan-1-one (**17c**).* According to the general procedure, a mixture of 4-chlorobenzotrifluoride (133 μL, 1.00 mmol), 2-acetylfuran (132 μL, 1.20 mmol), KO*t*Bu (269 mg, 2.40 mmol), **3A** (13.2 mg, 0.02 mmol), and 4 mL of toluene was stirred at 60 °C for 4 h. The crude material was chromatographed on silica gel with EtOAc as the eluent to give 236 mg (0.95 mmol, 95%) of **17c** as a pale yellow solid. The spectroscopic data matched those previously reported.[68] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.64−7.53 (m, 3H), 7.45 (d, J = 8.0 Hz, 2H), 7.28−7.22 (m, 1H), 6.53 (dd, J = 1.6 Hz, 3.6 Hz, 1H), 4.21 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 185.7, 152.4, 146.9, 138.1, 130.0, 129.5 (q, ^2J (C−F) = 32 Hz), 125.7, 124.3 (q, ^1J (C−F) = 271 Hz), 118.1, 112.8, 45.1.

*1-(Naphthalen-1-yl)-2-(pyridin-3-yl)ethan-1-one (**17d**).* According to the general procedure, a mixture of 3-chloropyridine (95 μL, 1.00 mmol), 1-acetonaphthalene (182 μL, 1.20 mmol), KO*t*Bu (269 mg, 2.40 mmol), **3A** (13.2 mg, 0.02 mmol), and 4 mL of toluene was stirred at 60 °C for 4 h. The crude material was chromatographed on silica gel with 50% EtOAc/hexanes as the eluent to give 237 mg (0.96 mmol, 96%) of **17d** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.61−8.49 (m, 3H), 8.01−7.94 (m, 2H), 7.89 (dd, J = 1.6 Hz, 7.9 Hz, 1H), 7.63 (dt, J = 1.8 Hz, 7.8 Hz, 1H), 7.60−7.48 (m, 3H), 7.29−7.23 (m, 1H), 4.38 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 200.3, 150.8, 148.5, 137.2, 135.0, 134.1, 133.4, 130.4 (two peaks), 128.6, 128.3, 128.2, 126.8, 125.8, 124.4, 123.6, 45.7. HRMS (ESI) m/z [M + H]$^+$ Calcd for $C_{17}H_{14}NO$: 248.1075. Found: 248.1075.

General Procedure for the Arylation Reactions of Primary Amides in Table 7. An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **8A** (7.8 mg, 0.01 mmol, 1 mol %), aryl chloride (1.00 mmol, if solid), amide (1.20 mmol), and K_3PO_4 (297 mg, 1.40 mmol). The tube was capped with a rubber septum and was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. The aryl chloride (1.00 mmol, if liquid) and anhydrous *t*-BuOH (2 mL) were added sequentially via syringe. The tube was placed in a preheated oil bath (110 °C) and sealed, and the contents were stirred for 1.5 h unless otherwise indicated. The tube was then removed from the oil bath and allowed to cool to room temperature. H_2O (5 mL) was added, and the aqueous phase was extracted with EtOAc (3 × 5 mL). The organic extracts were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel.

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794−6813

*N-(2,5-Dimethoxyphenyl)benzamide (**18a**).* According to the general procedure, a mixture of 2-chloro-1,4-dimethoxybenzene (143 μL, 1.00 mmol), benzamide (145 mg, 1.20 mmol), K_3PO_4 (297 mg, 1.40 mmol), **8A** (7.8 mg, 0.01 mmol), and 2 mL of anhydrous *t*-BuOH was stirred at 110 °C for 1.5 h. The crude material was chromatographed on silica gel with 10% EtOAc/hexanes as the eluent to give 252 mg (0.98 mmol, 96%) of **18a** as a near-colorless oil. The spectroscopic properties matched those previously reported.[44a] A similar experiment using 0.8 mg of **8A** (0.001 mmol, 0.1 mol %) and a 16 h stir time gave 251 mg (0.98 mmol, 98%) of **18a** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.59 (br s, 1H), 8.27 (d, *J* = 3.2 Hz, 1H), 7.83 (app d, *J* = 6.8 Hz, 2H), 7.56−7.45 (m, 3H), 6.79 (d, *J* = 8.9 Hz, 1H), 6.60 (dd, *J* = 3.0 Hz, 8.9 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 165.3, 154.1, 142.5, 135.3, 131.9, 128.9, 128.6, 127.2, 110.9, 109.1, 106.0, 56.5, 56.0.

*N-(6-Methoxypyridazin-3-yl)cyclopropanecarboxamide (**18b**).* According to the general procedure, a mixture of 3-chloro-6-methoxypyridazine (145 mg, 1.00 mmol), cyclopropanecarboxamide (102 mg, 1.20 mmol), K_3PO_4 (297 mg, 1.40 mmol), **8A** (7.8 mg, 0.01 mmol), and 2 mL of anhydrous *t*-BuOH was stirred at 110 °C for 2 h. The crude material was chromatographed on silica gel with a gradient of 0−2.5% MeOH/CH_2Cl_2 as the eluent to give 132 mg (0.68 mmol, 68%) of **18b** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 11.2 (br s, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 3.98 (s, 3H), 2.57−2.46 (m, 1H), 1.14−1.06 (m, 2H), 0.93−0.84 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 174.0, 162.4, 152.9, 123.8, 119.8, 54.4, 15.5, 8.79. Anal. Calcd for $C_9H_{11}N_3O_2$: C, 55.95; H, 5.74; N, 21.75. Found: C, 56.18; H, 5.76; N, 21.70.

*N-(Quinolin-6-yl)acetamide (**18c**).* According to the general procedure, a mixture of 6-chloroquinoline (164 mg, 1.00 mmol), acetamide (71 mg, 1.20 mmol), K_3PO_4 (297 mg, 1.40 mmol), **8A** (7.8 mg, 0.01 mmol), and 2 mL of anhydrous *t*-BuOH were stirred at 110 °C for 1.5 h. The crude material was chromatographed on silica gel with a gradient of 0−4% MeOH/CH_2Cl_2 as the eluent to give 132 mg (0.95 mmol, 95%) of **18c** as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.86−8.64 (m, 2H), 8.38 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 9.5 Hz, 1H), 7.59 (dd, *J* = 2.5 Hz, 9.1 Hz, 1H), 7.34 (dd, *J* = 3.9 Hz, 8.6 Hz, 1H), 0.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 169.3, 149.2, 145.4, 136.4, 136.2, 129.8, 129.0, 123.5, 121.7, 116.3, 24.7. Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.66; H, 5.51; N, 14.94.

*N-(2-Methylbenzo[d]thiazol-5-yl)-2-(pyridin-2-yl)acetamide (**18d**).* According to the general procedure, a mixture of 5-chloro-2-methylbenzothiazole (184 mg, 1.00 mmol), 2-(pyridine-2-yl)-acetamide (143 mg, 1.20 mmol), K_3PO_4 (297 mg, 1.40 mmol), **8A** (7.8 mg, 0.01 mmol), and 2 mL of anhydrous *t*-BuOH was stirred at 110 °C for 1.5 h. The crude material was chromatographed on silica gel with a gradient of 0−2% MeOH/CH_2Cl_2 as the eluent to give 279 mg (0.99 mmol, 99%) of **18d** as a pale yellow-green solid. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 10.4 (br s, 1H), 8.51 (d, *J* = 4.6 Hz, 1H), 8.32 (d, *J* = 1.8 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.76 (td, *J* = 1.5 Hz, 7.4 Hz, 1H), 7.57 (dd, *J* = 1.5 Hz, 8.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 4.9 Hz, 7.4 Hz, 1H), 3.90 (s, 2H), 2.76 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, δ): 168.3, 167.9, 156.0, 153.5, 149.0, 137.6, 136.5, 129.5, 124.0, 121.9, 121.8, 117.0, 111.9, 45.9, 19.8. HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{15}H_{14}N_3OS$: 284.0858. Found: 284.0861.

*N-(Benzo[d][1,3]dioxol-5-yl)nicotinamide (**18e**).* According to the general procedure, a mixture of 6-chloroquinoline (164 mg, 1.00 mmol), acetamide (71 mg, 1.20 mmol), K_3PO_4 (297 mg, 1.40 mmol), **8A** (7.8 mg, 0.01 mmol), and 2 mL of anhydrous *t*-BuOH was stirred at 110 °C for 1.5 h. The crude material was chromatographed on silica gel with a gradient of 0−4% MeOH/CH_2Cl_2 as the eluent to give 225 mg (0.93 mmol, 93%) of **18e** as a pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, δ):10.3 (br s, 1H), 9.08 (d, *J* = 1.7 Hz, 1H), 8.75 (dd, *J* = 1.6 Hz, 4.9 Hz, 1H), 8.26 (td, *J* = 1.9 Hz, 8.1 Hz, 1H), 7.44 (dd, *J* = 4.7 Hz, 7.9 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.18 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.02 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, δ): 163.7, 152.0, 148.6, 147.0, 143.5, 135.3, 133.1, 130.6, 123.5, 113.4, 108.0, 102.5, 101.1. Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.60; H, 4.37; N, 11.16.

General Procedure for the Arylation Reactions of Cyclic Amide/Oxazolidinones in Table 7. An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **8A** (11.7 mg, 0.015 mmol, 1.5 mol %), aryl chloride (1.00 mmol, if solid), amide/oxazolidinone (1.20 mmol, if solid), and K_3PO_4 (297 mg, 1.40 mmol). The tube was capped with a rubber septum and was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. The amide (1.20 mmol, if liquid), aryl chloride (1.00 mmol, if liquid), and anhydrous *t*-BuOH (2 mL) were added sequentially via syringe. The tube was placed in a preheated oil bath (110 °C) and sealed, and the contents were stirred for 3 h. The tube was then removed from the oil bath and allowed to cool to room temperature. H_2O (5 mL) was added, and the aqueous phase was extracted with EtOAc (3 × 5 mL). The organic extracts were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel.

*1-(4-Methoxyphenyl)pyrrolidin-2-one (**19a**).* According to the general procedure, a mixture of 4-chloroanisole (123 μL, 1.00 mmol), 2-pyrolidinone (91 μL, 1.20 mmol), K_3PO_4 (297 mg, 1.40 mmol), **8A** (11.7 mg, 0.015 mmol), and 2 mL of anhydrous *t*-BuOH was stirred at 110 °C for 3 h. The crude material was chromatographed on silica gel with a gradient of 40−100% EtOAc/hexanes as the eluent to give 183 mg (0.96 mmol, 96%) of **19a** as a white solid. The spectroscopic properties matched those previously reported.[69] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.49 (d, *J* = 9.4 Hz, 2H), 6.88 (d, *J* = 9.4 Hz, 2H), 3.85−3.72 (m, 5H), 2.57 (t, *J* = 8.3 Hz, 2H), 2.20 (quint, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 174.0, 156.7, 132.8, 121.9, 114.2, 55.6, 49.3, 32.6, 18.1.

*3-(4-(Trifluoromethoxy)phenyl)oxazolidin-2-one (**19b**).* According to the general procedure, a mixture of 1-chloro-4-trifluoromethoxybenzene (144 μL, 1.00 mmol), 2-oxazolidinone (105 mg, 1.20 mmol), K_3PO_4 (297 mg, 1.40 mmol), **8A** (11.7 mg, 0.015 mmol), and 2 mL of anhydrous *t*-BuOH was stirred at 110 °C for 3 h. The crude material was chromatographed on silica gel with a gradient of 0−40% EtOAc/hexanes as the eluent to give 247 mg (1.00 mmol, 100%) of **19b** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.55 (app d, *J* = 9.5 Hz, 2H), 7.20 (app d, *J* = 8.8 Hz, 2H), 4.51−4.40 (m, 2H), 4.07−3.98 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 155.3, 145.2, 137.1, 121.8, 120.6 (q, J_{C-F} = 256 Hz), 119.4, 61.4, 45.2. HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{10}H_9F_3NO_3$: 248.0535. Found: 248.0537.

*(S)-4-(4-Benzyl-2-oxooxazolidin-3-yl)benzonitrile (**19c**).* According to the general procedure, a mixture of 4-chlorobenzonitrile (138 mg, 1.00 mmol), (*S*)-(−)-4-benzyl-2-oxazolidinone (186 mg, 1.20 mmol), K_3PO_4 (297 mg, 1.40 mmol), **8A** (11.7 mg, 0.015 mmol), and 2 mL of anhydrous *t*-BuOH was stirred at 110 °C for 3 h. The crude material was chromatographed on silica gel with a gradient of 0−40% EtOAc/hexanes as the eluent to give 265 mg (0.95 mmol, 95%) of **19c** as a brown solid. The spectroscopic properties matched those previously reported.[70] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.79−7.65 (m, 4H), 7.42−7.23 (m, 3H), 7.19 (app d, *J* = 6.3 Hz, 2H), 4.75−4.65 (m, 1H), 4.35 (t, *J* = 8.5 Hz, 1H), 4.25 (dd, *J* = 3.9 Hz, 9.0 Hz, 1H), 3.20 (dd, *J* = 4.5 Hz, 14.3 Hz, 1H), 2.82 (dd, *J* = 9.2 Hz, 14.3 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 154.7, 141.1, 134.5, 133.4, 129.2 (two peaks), 127.7, 120.1, 118.6, 107.6, 66.0, 56.5, 37.5.

*N-(4-Methoxyphenyl)thiazol-2-amine (**20**).* An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **8A** (11.7 mg, 0.015 mmol, 1.5 mol %), 2-aminothiazole (100 mg, 1.00 mmol), and K_2CO_3 (194 mg, 1.40 mmol). The tube was capped with a rubber septum and was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. 4-Bromoanisole (125 μL, 1.00 mmol) and anhydrous *t*-BuOH (4 mL) were added sequentially via syringe. The tube was placed in a preheated oil bath (110 °C) and sealed, and the contents were stirred for 3 h. The tube was then removed from the oil bath and diluted with 10 mL of EtOAc and H_2O (5 mL). The aqueous phase was extracted (3 × 5 mL of EtOAc). The combined extracts were washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with a gradient

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794−6813

of 0−3% MeOH/CH_2Cl_2 as the eluent to give 176 mg (0.85 mmol, 85%) of **20** as a tan solid. The spectroscopic properties match those previously reported.[45] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.73 (br s, 1H), 7.32 (app d, J = 9.4 Hz, 2H), 7.23 (d, J = 3.8 Hz, 1H), 6.87 (app d, J = 9.5 Hz, 2H), 6.50 (d, J = 3.8 Hz, 1H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 168.7, 156.1, 138.4, 134.5, 121.5, 114.8, 106.2, 55.6.

General Procedure for the Sulfonamidation Reactions in Table 7. An oven-dried threaded 2 dram, 17 mm × 60 mm reaction vial equipped with a Teflon-coated magnetic stir bar was charged with **10A** (7.2 mg, 0.01 mmol, 1 mol %), aryl halide (1.20 mmol, if solid), sulfonamide (1.00 mmol), and K_3PO_4 (318 mg, 1.50 mmol). The vial was capped with a polypropylene cap with PTFE-faced silicone septum and was evacuated and backfilled with nitrogen through a needle. This evacuation/backfill cycle was repeated two additional times. Anhydrous 2-methyl-2-butanol (4 mL) and the aryl halide (1.20 mmol, if liquid) were added sequentially via syringe. The nitrogen needle was removed and the vial was placed on a preheated aluminum block (110 °C), and the contents were stirred for 3 h. The vial was then removed from the heating block and allowed to cool to room temperature. Saturated ammonium chloride (10 mL) was added, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The organic extracts were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel.

*4-Methyl-N-(pyrazin-2-yl)benzenesulfonamide (**21a**).* According to the general procedure, a mixture of 2-chloropyrazine (107 μL, 1.20 mmol), *p*-toluenesulfonamide (171 mg, 1.00 mmol), K_3PO_4 (318 mg, 1.50 mmol), **10A** (7.2 mg, 0.01 mmol), and 4 mL of anhydrous 2-methyl-2-butanol was stirred at 110 °C for 3 h. The crude material was chromatographed on silica gel with a gradient of 0−100% EtOAc/hexanes as the eluent to give 152 mg (0.61 mmol, 61%) of **21a** as a white solid. The spectroscopic properties match those previously reported.[71] ^{1}H NMR (400 MHz, DMSO-d_6, δ): 11.47 (s, 1H), 8.36 (s, 1H), 8.21 (app s, 2H), 7.83 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, δ): 148.1, 143.7, 142.1, 138.8, 137.1, 134.8, 129.6, 127.1, 21.0.

*N-(Isoquinolin-5-yl)methanesulfonamide (**21b**).* According to the general procedure, a mixture of 5-bromoisoquinoline (250 mg, 1.20 mmol), methanesulfonamide (95 mg, 1.00 mmol), K_3PO_4 (318 mg, 1.50 mmol), **10A** (7.2 mg, 0.01 mmol), and 4 mL of anhydrous 2-methyl-2-butanol was stirred at 110 °C for 3 h. The crude material was chromatographed on silica gel with a gradient of 0−5% MeOH/CH_2Cl_2 as the eluent to give 194 mg (0.87 mmol, 87%) of **21b** as an off-white solid. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.92 (s, 1H), 9.34 (s, 1H), 8.58 (app d, J = 5.9 Hz, 1H), 8.12 (app d, J = 5.9 Hz, 1H), 8.03 (app d, J = 8.1 Hz, 1H), 7.78 (app d, J = 7.4 Hz, 1H), 7.69 (app t, J = 7.9 Hz, 1H), 3.06 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, δ): 152.4, 143.1, 132.3, 131.7, 129.0, 127.4, 126.6, 125.9, 116.0, 39.92. Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.54; N, 12.60. Found: C, 54.05; H, 4.26; N, 12.38.

*N-(6-Methoxypyridin-2-yl)cyclopropanesulfonamide (**21c**).* According to the general procedure, a mixture of 2-chloro-6-methoxypyridine (143 μL, 1.20 mmol), cyclopropanesulfonamide (121 mg, 1.00 mmol), K_3PO_4 (318 mg, 1.50 mmol), **10A** (7.2 mg, 0.01 mmol), and 4 mL of anhydrous 2-methyl-2-butanol was stirred at 110 °C for 3 h. The crude material was chromatographed on silica gel with a gradient of 0−40% EtOAc/hexanes as the eluent to give 207 mg (0.90 mmol, 90%) of **21c** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.54 (t, J = 7.9 Hz, 1H), 7.02 (bs, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.47 (d, J = 8.1 Hz, 1H), 3.88 (s, 3H), 2.81−2.75 (m, 1H), 1.32−1.28 (m, 2H), 1.05−1.00 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 163.7, 149.1, 141.0, 105.8, 103.6, 53.9, 31.3, 6.1. Anal. Calcd for $C_9H_{12}N_2O_3S$: C, 47.36; H, 5.30; N, 12.27. Found: C, 47.42; H, 5.27; N, 12.19.

General Procedure for the C−O Coupling Reactions in Table 7. An oven-dried threaded 2 dram, 17 mm × 60 mm reaction vial equipped with a Teflon-coated magnetic stir bar was charged with **12A** (7.7 mg, 0.01 mmol, 1 mol %), aryl halide (1.00 mmol, if solid), and K_3PO_4 (318 mg, 1.50 mmol). The vial was capped with a polypropylene cap with PTFE-faced silicone septum and was evacuated and backfilled with nitrogen through a needle. This evacuation/backfill cycle was repeated two additional times. Anhydrous toluene (1 mL), the aryl halide (1.00 mmol, if liquid), and alcohol (1.50 mmol) were added sequentially via syringe. The nitrogen needle was removed, the vial was placed on a preheated aluminum block (100 °C), and the contents were stirred for 16 h. The vial was then removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with 10 mL of EtOAc, filtered through a pad of Celite, and concentrated in vacuo. The residue was chromatographed on silica gel.

*5-(Furan-2-ylmethoxy)pyrimidine (**22a**).* According to the general procedure, a mixture of 5-bromopyrimidine (159 mg, 1.00 mmol), furfuryl alcohol (130 μL, 1.50 mmol), K_3PO_4 (318 mg, 1.50 mmol), **12A** (7.7 mg, 0.01 mmol), and 1 mL of anhydrous toluene was stirred at 100 °C for 16 h. The crude material was chromatographed on silica gel with a gradient of 0−50% EtOAc/hexanes as the eluent to give 141 mg (0.80 mmol, 80%) of **22a** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.85 (s, 1H), 8.48 (s, 2H), 7.45 (s, 1H), 6.47 (app d, J = 2.9 Hz, 1H), 6.39−6.38 (m, 1H), 5.10 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 152.6, 152.1, 148.8, 144.4, 143.9, 111.4, 110.9, 63.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_9N_2O_2$: 177.0664. Found: 177.0661.

*3-(2-(Thiophen-2-yl)ethoxy)pyridine (**22b**).* According to the general procedure, a mixture of 3-chloropyridine (94 μL, 1.00 mmol), 2-thiopheneethanol (167 μL, 1.50 mmol), K_3PO_4 (318 mg, 1.50 mmol), **12A** (7.7 mg, 0.01 mmol), and 1 mL of anhydrous toluene was stirred at 100 °C for 16 h. The crude material was chromatographed on silica gel with a gradient of 0−100% EtOAc/hexanes as the eluent to give 170 mg (0.83 mmol, 83%) of **22b** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.33 (s, 1H), 8.22 (s, 1H), 7.20−7.17 (m, 3H), 6.97−6.92 (m, 2H), 4.23 (t, J = 6.7 Hz, 2H), 3.33 (t, J = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 155.0, 142.6, 140.0, 138.3, 127.1, 125.9, 124.3, 124.0, 121.4, 68.9, 30.1. Anal. Calcd for $C_{11}H_{11}NOS$: C, 64.36; H, 5.40; N, 6.82. Found: C, 64.31; H, 5.64; N, 6.91.

Indole Arylation Reactions in Table 7. *1-(Naphthalen-1-yl)-1H-indole (**23a**).* An oven-dried threaded 2 dram, 17 mm × 60 mm reaction vial equipped with a Teflon-coated magnetic stir bar was charged with **13A** (8.0 mg, 0.01 mmol, 2 mol %), BippyPhos (**L12**) (5.1 mg, 0.01 mmol, 2 mol %), indole (58.6 mg, 0.50 mmol), and NaO*t*-Bu (67.3 mg, 0.70 mmol). The vial was capped with a polypropylene cap with PTFE-faced silicone septa and was evacuated and backfilled with nitrogen through a needle. This evacuation/backfill cycle was repeated two additional times. Anhydrous toluene (2 mL) and 1-bromonaphthalene (70.0 μL, 0.50 mmol) were added sequentially via syringe. The nitrogen needle was removed, the vial was placed on a preheated aluminum block (110 °C), and the contents were stirred for 16 h. The tube was then removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with 5 mL of EtOAc, filtered through a pad of Celite, and concentrated in vacuo. The residue was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 109 mg (0.45 mmol, 89%) of **23a** as a white solid. The spectroscopic properties match those previously reported.[72] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.98 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 7.8 Hz, 1H), 7.63−7.51 (m, 3H), 7.49−7.36 (m, 3H), 7.22−7.11 (m, 2H), 7.05 (d, J = 8.1 Hz, 1H), 6.79 (app d, J = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 138.2, 136.2, 134.6, 130.7, 129.9, 128.6 (two peaks), 128.3, 127.1, 126.8, 125.6, 125.3, 123.5, 122.3, 121.0, 120.2, 111.0, 103.0.

*1-(6-Methoxypyridin-2-yl)-2-phenyl-1H-indole (**23b**).* An oven-dried threaded 2 dram, 17 mm × 60 mm reaction vial equipped with a Teflon-coated magnetic stir bar was charged with **13A** (16 mg, 0.02 mmol, 2 mol %), BippyPhos (**L12**) (10 mg, 0.02 mmol, 2 mol %), 2-phenylindole (193 mg, 1.00 mmol), and NaO*t*-Bu (135 mg, 1.40 mmol). The vial was capped with a polypropylene cap with PTFE-faced silicone septum and was evacuated and backfilled with nitrogen. This evacuation/backfill cycle was repeated two additional times. Anhydrous toluene (4 mL) and 2-chloro-6-methoxypyridine (119 μL, 1.00 mmol) were added sequentially via syringe. The nitrogen needle

DOI: 10.1021/acs.joc.5b01005
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was removed, the vial was placed on a preheated aluminum block (110 °C), and the contents were stirred for 16 h. The tube was then removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with 10 mL of EtOAc, filtered through a pad of Celite, and concentrated in vacuo. The residue was chromatographed on silica gel with a gradient of 0−5% EtOAc/hexanes as the eluent to give 293 mg (0.98 mmol, 98%) of **23b** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.33−7.22 (m, 7H), 6.82 (s, 1H), 6.69−6.64 (m, 2H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 163.7, 149.6, 140.6, 140.1, 138.4, 133.5, 129.0, 128.9, 128.3, 127.5, 123.0, 121.5, 120.8, 113.6, 111.7, 108.6, 105.6, 53.8. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{17}N_2O$: 301.1341. Found: 301.1345.

Synthesis of Complex ***24***. A literature procedure was followed.[52] Thus, in a nitrogen-filled glovebox, a 20 mL scintillation vial equipped with a Teflon-coated magnetic stir bar was charged with 250 mg (0.54 mmol, 1 equiv) of **L1**. Chlorobenzene (109 μL) was added. Cyclohexane was added dropwise until the solution became homogeneous. of COD-Pd(CH_2TMS)$_2$[73] (208 mg, 0.54 mmol, 1 equiv) was added in a single portion, and the mixture was stirred overnight. To the resulting thick white suspension was added 5 mL of pentane, and the mixture was shaken briefly. The solid was collected by vacuum filtration, washed with 5 mL of additional pentane, and dried under a flow of nitrogen to give 355 mg (0.52 mmol, 97%) of **24** as a white solid. ^{1}H NMR (400 MHz, C_6D_6, δ): 7.80−7.60 (m, 1H), 7.52−7.40 (m, 2H), 7.40−7.30 (m, 1H), 7.19−7.05 (m, 1H), 7.04−6.81 (m, 5H), 6.70−6.47 (m, 2H), 4.45−4.26 (m, 2H), 2.80−2.69 (m, 0.4 H), 2.28−2.00 (m, 2.6 H), 1.99−1.44 (m, 12H), 1.38−0.78 (m, 19H) (observed complexity due to the monomeric/dimeric species in equilibrium). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ): 157.4, 144.5, 138.2, 137.1, 137.0, 133.9, 132.0, 132.6, 132.2, 132.1, 130.1, 129.4, 126.4, 126.2, 125.6 (two peaks), 122.7, 107.3, 70.0, 33.0, 32.7, 27.7, 27.1, 26.7, 26.6, 26.4, 26.3, 26.2, 25.5, 21.3, 20.7 (observed complexity due C−P coupling and monomeric/dimeric species in equilibrium). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ): 47.5, 30.1 (monomeric/dimeric species in equilibrium). Anal. Calcd for $C_{36}H_{48}ClO_2PPd$: C, 63.07; H, 7.06; Found: C, 62.63; H, 6.86.

Synthesis of Complex ***25***. In a nitrogen-filled glovebox, a 20 mL scintillation vial was charged with 500 mg (0.73 mmol, 1 equiv) of **24**, 122 mg (0.73 mmol, 1 equiv) of carbazole, and 70 mg (0.73 mmol, 1 equiv) of NaO*t*-Bu. Toluene (7.3 mL) was added, and the mixture was stirred at rt for 2 h. The resulting suspension was filtered to remove salts. To the filtrate was added 25 mL of pentane, and the mixture was placed in a −30 °C freezer overnight to induce crystallization. The crystals were collected by vacuum filtration, washed (2 × 5 mL of pentane), and dried in vacuo to give 566 mg (0.66 mmol, 91%) of **25** as a yellow solid. The product is a 1/2 pentane adduct. X-ray quality crystals were grown by slow vapor diffusion (toluene/hexanes). ^{1}H NMR (400 MHz, C_6D_6, δ): 8.35 (d, J = 7.6 Hz, 2H), 8.06 (d, J = 8.3 Hz, 2H), 7.73 (app t, J = 7.4 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.48 (app t, J = 7.4 Hz, 1H), 7.37 (app t, J = 7.2 Hz, 2H), 7.19 (app t, J = 7.6 Hz, 1H), 7.15−7.08 (m, 1H), 6.74−6.65 (m, 3H), 6.58−6.53 (m, 1H), 5.91 (app d, J = 8.3 Hz, 2H), 5.87−5.79 (m, 1H), 4.52 (sept, J = 5.8 Hz, 2H), 2.36−2.20 (m, 4H), 1.99−1.76 (m, 8H), 1.73−1.61 (m, 2H), 1.44 (d, J = 6.1 Hz, 6H), 1.44−1.29 (m, 2H), 1.28−1.04 (m, 6H), 0.81 (d, J = 6.0 Hz, 6H), peaks attributable to pentane were observed at 0.86 and 1.26 ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ): 158.7, 150.0, 147.1, 146.9, 141.3, 141.2, 137.2, 136.8, 135.9, 135.8, 135.0, 131.8, 131.7, 131.3, 130.8, 127.4, 127.0, 126.5 (two peaks), 126.2 (two peaks), 123.8, 123.0, 120.3, 115.2, 115.0, 109.8 (two peaks), 106.7, 70.8, 34.2, 34.0, 28.9, 28.7, 27.6, 27.4, 27.3, 27.2, 26.5, 22.7, 21.3 [observed complexity due to C−P coupling]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ): 31.3. HRMS (ESI) m/z [M − $C_{12}H_8$ (loss of carbazolyl)]$^+$ Calcd for $C_{36}H_{48}O_2PPd$: 649.2427. Found: 649.2433.

(μ-Allyl)(μ-Cl)Pd$_2$(SPhos)$_2$ ***(27a)***. In a nitrogen-filled glovebox, two dry 20 mL scintillation vials equipped with Teflon-coated magnetic stir bars were charged with 500 mg (×2, 1.68 mmol) of (allyl)Pd(SPhos)-Cl and 175 mg (×2, 2.53 mmol) of K_2CO_3 each. EtOH (16.8 mL) was added to each, the vials were placed in a preheated (40 °C) aluminum block, and the contents were stirred for 3 h. The contents were combined, and the solids were collected by vacuum filtration. The filter cake was extracted with THF (10 mL) and filtered, and the solvent was removed in vacuo at 30 °C to give 340 mg (0.31 mmol, 36%) of **27a** as a yellow-orange solid. ^{1}H NMR (400 MHz, THF-d_8, δ): 7.97−7.84 (m, 2H), 7.50−7.40 (m, 4H), 7.19 (app t, J = 8.9 Hz, 2H), 6.60 (d, J = 8.3 Hz, 2H), 6.52 (d, J = 8.5 Hz, 2H), 3.91−3.68 (m, 14H), 2.69−2.46 (m, 2H), 2.42−0.91 (m, 45H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ): 158.2, 157.8, 143.6, 143.5, 143.4, 134.3, 134.2, 134.1, 133.2 (two peaks), 132.4, 129.3, 120.5, 120.4 (two peaks), 104.0, 103.2, 67.8, 63.4, 55.2, 55.0, 39.9, 39.8 (two peaks), 38.3, 38.2, 38.1, 34.4, 30.6, 30.0, 28.4, 28.0 (two peaks), 27.9, 27.8, 27.7, 27.6, 27.6, 26.8, 26.6, 25.8 [observed complexity due to C−P coupling]. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, δ): 19.0. Anal. Calcd for $C_{55}H_{75}ClO_4P_2Pd_2$: C, 59.49; H, 6.81. Found: C, 59.16; H, 7.00.

(μ-Allyl)(μ-Cl)Pd$_2$(AmPhos)$_2$ ***(27b)***. In a nitrogen-filled glovebox, a dry 40 mL scintillation vial equipped with a Teflon-coated magnetic stir bar was charged with 500 mg (1.12 mmol) of (allyl)Pd(AmPhos)Cl and 231 mg (1.67 mmol) of K_2CO_3. EtOH (22.4 mL) was added, and the mixture was placed in a preheated (40 °C) aluminum block and stirred for 3 h. Pentane (20 mL) was added to precipitate, and the mixture was filtered through a disposable frit. The frit was removed from the glovebox, and the solids were extracted with 10 mL of CH_2Cl_2. Hexanes (10 mL) was added, and the solution was placed in the freezer for 16 h as crystals developed. The crystals were collected by vacuum filtration, washed (3 × 5 mL hexanes), and dried in vacuo to give 328 mg (0.36 mmol, 72%) of **27b** (yellow solid) as a CH_2Cl_2 adduct. The CH_2Cl_2 adduct was broken by drying in a vacuum oven at 50 °C for 16 h. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.76−7.66 (m, 4H), 6.67 (d, J = 8.6 Hz, 4H), 3.03−2.96 (m, 2H), 3.00 (s, 12H), 2.65−2.50 (m, 1H), 1.47−1.29 (m, 38H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 150.9, 137.6 (t, J = 7.5 Hz), 118.2 (t, J = 14.5 Hz), 110.9 (t, J = 5.4 Hz), 62.4 (t, J = 4.8 Hz), 40.2, 38.0, 35.4 (t, J = 6.2 Hz,), 35.0 (t, J = 5.4 Hz), 31.1 (t, J = 4.2 Hz), 30.1 (t, J = 4.2 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ): 67.2. Anal. Calcd for $C_{35}H_{61}ClN_2P_2Pd_2$: C, 51.26; H, 7.50; N, 3.42; Found: C, 51.42; H, 7.40; N, 3.38.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra for new compounds, complete catalyst comparison studies, and CIF files for **1A**, **1B**, **7B**, **7C**, **8A**, **10C**, **25**, and **27a**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01005.

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Notes

The authors declare the following competing financial interest(s): The allyl-, crotyl-, and cinnamyl-palladium precatalysts described in this work will soon be commercially available from Johnson Matthey Catalysis and Chiral Technologies (JMCCT) and are the intellectual property of Johnson Matthey PLC. Many of the biaryl ligands and palladacycle catalysts described herein are intellectual property of MIT and are commercially available from JMCCT through a licensing agreement.

■ ACKNOWLEDGMENTS

We thank Mr. Anuj Prakash for experimental assistance.

■ DEDICATION

§Dedicated to Fred Hancock on the occasion of his retirement from Johnson Matthey after 30 years of valuable service.

DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794−6813

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DOI: 10.1021/acs.joc.5b01005
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DOI: 10.1021/acs.joc.5b01005
J. Org. Chem. 2015, 80, 6794−6813