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Metal–Ligand Binding Interactions in Rhodium/Palladium-Catalyzed Synthesis of Dihydroquinolines

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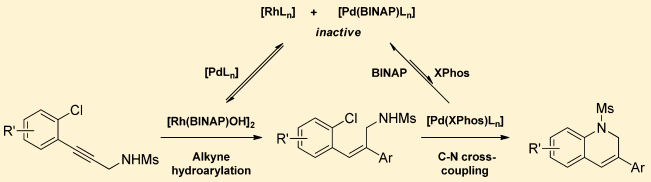
Supporting Information

ABSTRACT: A domino Rh- and Pd-catalyzed synthesis of dihydroquinolines is disclosed. Two metals and two ligands are placed in one reaction vessel along with the two reactive reagents to afford selective sequential coupling despite the potential for side reactions. In this report, we describe mechanistic investigations attempting to discern the catalyst–ligand interactions occurring in this domino reaction. Through these studies, the reactivity and relative catalyst ligand loadings were successfully tuned to efficiently access the heterocyclic products.



INTRODUCTION

Metal-catalyzed reactions play a central role in the synthesis of natural products, materials, and bioactive substances. The established approach is to conduct reactions one step at a time in sequence with a workup after each step and subsequent purification. We sought to develop a domino reaction sequence that can occur in one vessel containing more than one metal catalyst.[1,2] The implications of this approach include reduction of time, waste, and adverse environmental impact. These advantages may be useful in rapidly preparing structurally diverse compounds for biological screening or in the synthesis of a specific target on larger scale. Although the use of two metals in various modes of catalysis[2−6] (e.g., cooperative catalysis) has already yielded powerful reactions, issues of incompatibility of reagents and the added issues of ligand effects on multiple catalytic cycles have not been explored from a mechanistic perspective. Consequently, many examples of multimetal domino catalysis employ one ligand or ligand-less conditions.[6a−g,h,i] As ligands are integral in controlling regio-, stereo-, and enantioselectivity in metal-catalyzed reactions, their exclusion imposes significant limitations on reaction discovery and scope. Therefore, the development of multimetal–ligand domino catalysis may enable a broad range of useful transformations in a more practical way. The use of multiple ligands in multimetal catalysis can facilitate optimization, improve reaction efficiency, and allow systematic ligand screening to fine-tune reactivity. Perhaps due to the complex nature of catalyst–ligand interactions in multicatalytic systems, either the reports on multimetal and multiligand systems have simple metal–ligand interactions or no analysis of metal–ligand interactions was reported.[6k,l,m,n−p] Exploring the dynamics and relative reactivity of multiple-metal–ligand interactions may unlock the full potential of multimetal domino catalysis.

Following our recent report on an efficient synthesis of dihydroquinolines[6l] employing two different metals and two different ligands, we examined the nature of the metal–ligand interactions in the system in more detail. The reaction involves a domino Rh-catalyzed addition of arylboronic acids to alkynes, followed by a Pd-catalyzed C–N cross-coupling (Scheme 1). These studies have shown (1) the effect of metal–ligand exchange in catalysis, (2) the development of improved conditions based on a deeper understanding of ligand effects in multimetal domino catalysis, and (3) an application in the synthesis of heterocycles, such as dihydroquinolines and chromenes. We observed that, among the various metal–ligand species in the reaction vessel, the correct combinations of the metal–ligand complexes would catalyze two out of three possible reactions. We demonstrated that one of the two metals selectively binds one of the ligands while the other metal binds both. However, due to the superior reactivity of one of two metal–ligand species, a successful domino sequence is observed.

RESULTS AND DISCUSSION

We initiated our studies with the optimization of the Rh-catalyzed hydroarylation step (Table 1). The Rh-catalyzed addition of aryl boronic acids to alkynes and alkenes was first disclosed by Miyaura and Hayashi.[7] We were able to address issues of regioselectivity and reactivity of this formal hydroarylation reaction with directing groups such as pyridines and sulfones.[8] While Marinelli and co-workers have previously demonstrated regioselective Rh-catalyzed hydroarylation of aryl propargylamines,[9] achieving reactivity with a halogen substituent *ortho* to the alkyne proved to be challenging. For example, initial studies with 2-bromoaryl alkynes did not give the desired reactivity and significant decomposition was

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Scheme 1. Proposed Domino Catalytic Sequence

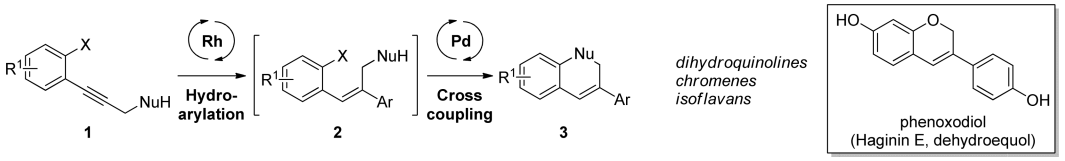
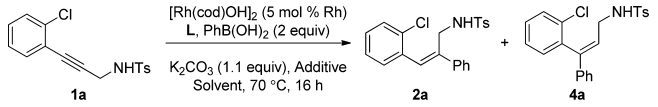


Table 1. Optimization of the Rh-Catalyzed Hydroarylation[a]



entry	ligand[b]	solvent	additive[c]	conv[d] (%)	NMR yield[e] (%) (2a:4a)	entry	ligand[b]	solvent	additive[c]	conv[d] (%)	NMR yield[e] (%) (2a:4a)
1	**L3**	EtOH (95%)		100	trace	7	**L4**	Diox	H_2O	0	
2	**L1**	THF	H_2O	100	40 (11:1)	8	**L2**	Diox	H_2O	0	
3	**L1**	PhMe	H_2O	100	45 (>25:1)	9	**L1**	Diox		100	44 (10:1)
4	**L1**	Diox[f]	H_2O	100	44 (10:1)	10[g]	**L1**	Diox	MeOH	100	65 (>25:1)
5	**L5**	Diox	H_2O	77	50 (>25:1)	11	**L1**	Diox	MeOH	100	77[h] (>25:1)
6	**L6**	Diox	H_2O	0		12[i]	**L1**	Diox	MeOH	100	69 (19:1)

[a]$[Rh(cod)OH]_2$ with ligand were mixed in 1 mL of dioxane for 15 min and then added to a vial containing **1a** (0.2 mmol), $PhB(OH)_2$, K_2CO_3, and 0.1 mL of additive. The mixture was stirred at 70 °C for 16 h. [b]5.2 mol % for bidentate ligands, 10.4 mol % for monodentate ligands. [c]10:1 solvent:additive. [d]conv = conversion. [e]Yield of **2a**. Yield and regioselectivity were determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard introduced into the crude mixture. [f]Diox = 1,4-dioxane. [g]Reaction conducted at 60 °C. [h]Isolated yield. [i]Reaction conducted at 80 °C.

observed. However, the less reactive 2-chloroaryl substrate **1a** underwent hydroarylation with good conversion.[10] While conducting an extensive ligand, solvent, and base screening, we looked for conditions in the hydroarylation step that would not interfere with conditions suitable for the subsequent C–N coupling. Employing $[Rh(cod)OH]_2$, BINAP (**L1**), $PhB(OH)_2$, and K_2CO_3, we observed favorable reactivity in either toluene or dioxane. Screening of ligands **L1**–**L6** (Figure 1, Table 1, entries 4–8) demonstrated BINAP **L1** as the ligand of choice for the hydroarylation. Although good regioselectivity was achieved, the yields were still moderate, and we explored the use of additives to increase the yield. There are a number of studies on Rh-catalyzed 1,4-conjugate additions that utilized additives such as methanol, which significantly enhanced the yield and enantioselectivity,[11] and we found that addition of methanol was very beneficial to the hydroarylation. A notable increase in yield was observed, and the regioselectivity of the hydroarylation was significantly enhanced as no arylation α to the arene was seen (>25:1 vs 10:1, Table 1, entries 10–12).

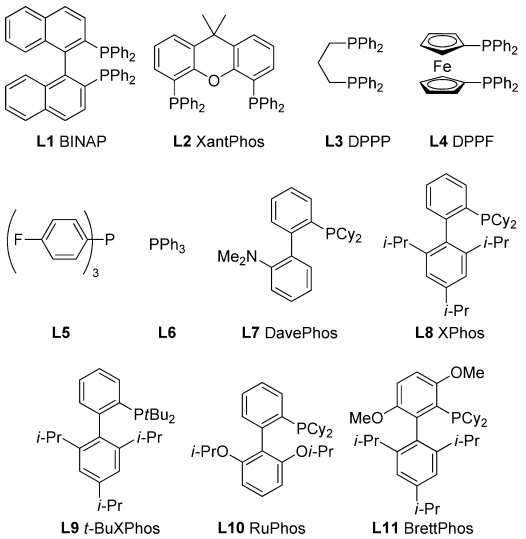


Figure 1. Ligands screened for hydroarylation and C–N/O cross-coupling.

We explored the hydroarylation to evaluate its scope (Table 2) and found that the reaction tolerated various substitution on the arylboronic acid, including electron rich (entry 7), electron poor (entry 5), and heteroarylboronic acids (entries 8, 9). Deactivated propargyl amines were tolerated. The unprotected amine did not participate well in the reaction. Substrates bearing the sulfonamide group gave the highest yields. Alcohols also exhibited good reactivity (entries 10, 11).

The adduct **2a** following the hydroarylation was shown to undergo a Pd-catalyzed intramolecular amidation (Table 3) to access dihydroquinolines of biological interest.[12] While the aryl chloride was tolerated in the hydroarylation step, its inherently low reactivity became a liability in the amidation step. Although intermolecular amination of aryl chlorides have been reported,[13,14] examples with deactivated amides such as sulfonamides were rare, and secondary sulfonamides even more uncommon.[15] Among these examples, the typical reaction used inorganic bases, polar aprotic solvents, and elevated temperatures, similar to that of the hydroarylation.[15] To effectively promote the amidation, we screened a number of ligands (Figure 1) that were suitable for coupling of aryl chlorides (Table 3). We noted that the ligand used in the hydroarylation reaction, BINAP (**L1**), was not capable of affecting the amidation (entries 1, 8). Using dioxane and carbonate bases, we were pleased to observe a smooth conversion of the hydroarylated intermediates **2a** and **2b** into dihydroquinolines **3a** and **3b** using $Pd(OAc)_2$ and XPhos (**L8**, dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, entries 4–6) as the catalyst system.

Establishing a two-step process provided access to dihydroquinolines **3a** and **3b** with a favorable overall yield of 61% and 71%, respectively. Subsequently, we shifted our focus

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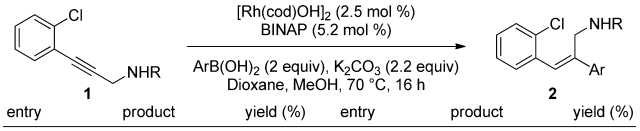
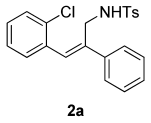
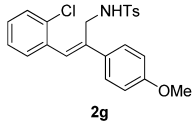
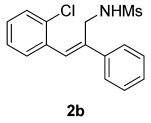
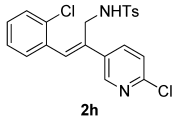
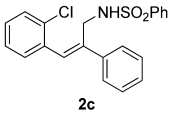
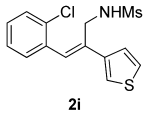
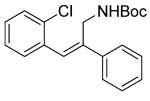
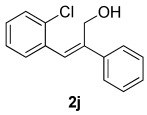
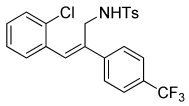
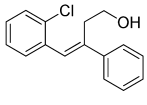
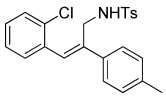
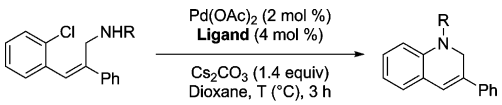
Table 2. Scope of Rh-Catalyzed Hydroarylation[a,b]



entry	product	yield (%)	entry	product	yield (%)
1	 **2a**	73	7	 **2g**	70
2	 **2b**	77[b]	8	 **2h**	77
3	 **2c**	70	9	 **2i**	77
4	 **2d**	49	10	 **2j**	51
5	 **2e**	69	11	 **2k**	51
6	 **2f**	64			

[a]See the Supporting Information for reaction procedures. Reactions conducted on 0.2 mmol scale. [b]Reaction conducted at 60 °C.

Table 3. Optimization of the Pd-Catalyzed Amidation[a]

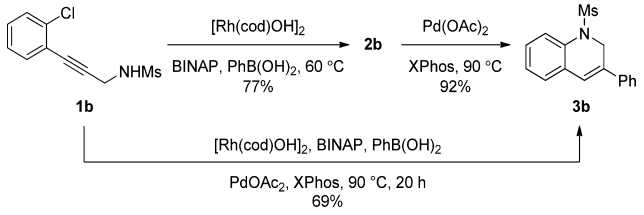


entry	R	ligand	T (°C)	conv[b] (%)	yield (%)
1	Ts	**L1**	100	0	0
2	Ts	**L2**	100	34	0
3	Ts	**L7**	100	53	6[b]
4	Ts	**L8**	100	100	70
5	Ts	**L8**	90	100	84[c]
6	Ms	**L8**	90	100	92[c]
7	Ts	**L9**	90	0	0[c]
8	Ms	**L1**	90	16	4[b,c]

[a]$Pd(OAc)_2$ and ligand were mixed in 1 mL of dioxane for 15 min and transferred to a vial containing **2** (0.2 mmol), and Cs_2CO_3 (91 mg, 1.4 equiv). The mixture was stirred at 90 °C for 3 h. [b]Determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c]With 10:1 dioxane:MeOH.

to determining the viability of a domino process, which would further increase the efficiency of this transformation. For consistency in the reaction protocol, we prepared the ligand–metal solutions separately and added them to the reactants prior to heating.[16] Performing the reaction without premixing the catalyst–ligand mixtures can achieve the desired transformation, but with ca. 5% diminished yield. The domino transformation proceeded smoothly in a comparable yield to the two-step reaction sequence (69% vs 71%, Scheme 2).

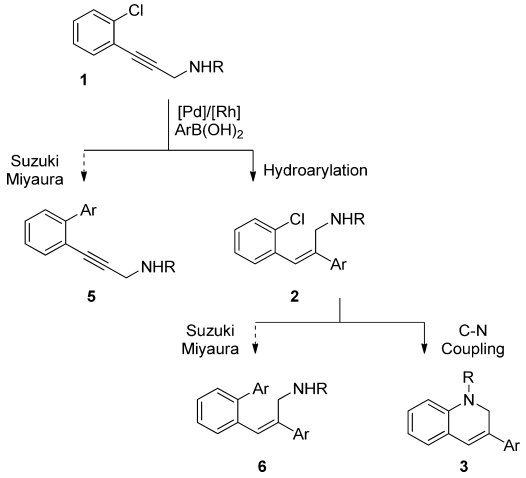
Scheme 2. Domino Rhodium and Palladium Catalysis[a]



[a]See Table 5 for domino reaction conditions.

Although this reaction was operationally simple, the selective formation of the desired dihydroquinoline product was rather fortuitous, since a number of problems could occur under the reaction conditions. For example, in the presence of two metals and two ligands, a scrambling of metal–ligand complexes and the formation of inactive or less active catalyst–ligand combinations are possible. Another concern is that the presence of arylboronic acids, arylhalides, and palladium in the domino reaction could lead to an undesired Suzuki–Miyaura transformation (Scheme 3).[17] Consequently, a time-resolved and

Scheme 3. Time-Resolved Domino Sequence and Competitive Reaction Pathways



controlled reaction sequence was clearly present in this domino process. Since Jeong's[6k] report, the development of a domino reaction with a rhodium–palladium multiligand system catalyzing mutually exclusive transformations has largely remained unexplored.

We probed the metal–ligand interactions of a domino process by ^{31}P NMR. In solution, we observed complexation of rhodium with BINAP. However, to our surprise, $[Rh(cod)OH]_2$ did not bind with XPhos, even with extended heating (Figure 2, entries 1, 2).[18,19] As a result, by adding BINAP to a solution of $[Rh(cod)OH]_2$ and XPhos, we observed selective binding of $[Rh(cod)OH]_2$ to BINAP (entry 4). This unanticipated specificity had implications in realizing a number of tandem/domino reactions, including enantioselective variants that we have recently reported (Scheme 4).[6m,p] We

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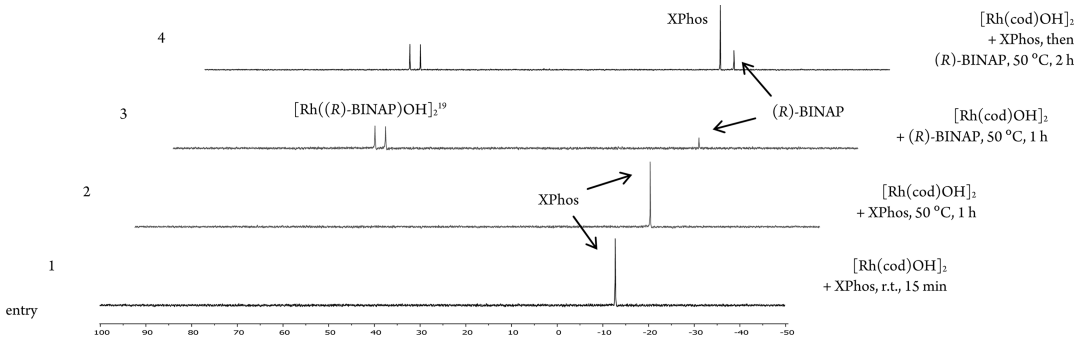


Figure 2. ^{31}P NMR spectra of Rh and ligand mixtures in benzene.

Scheme 4. Ligand-Specific Binding of $[Rh(cod)OH]_2$ to BINAP[19]

$[Rh(cod)OH]_2$ + BINAP → $[Rh(BINAP)OH]_2$

$[Rh(cod)OH]_2$ + XPhos ⇢ $[Rh(XPhos)L_n]$

$[Rh(cod)OH]_2$ + BINAP + XPhos → $[Rh(BINAP)OH]_2$ + XPhos

also attempted to investigate the multiligand multicatalyst mixture with Rh/BINAP and Pd/XPhos directly via ^{31}P NMR. However, the mixture decomposed over time or with heating, posing difficulties in deducing the catalytic species present in the complex mixutre.

For the rhodium-catalyzed step, we also carried out several control experiments, and the outcomes corroborated with our ^{31}P NMR studies (Table 4). In the hydroarylation reaction, [Rh(BINAP)] was the agent responsible for catalysis (entry 2). BINAP was essential as no hydroarylation occurred in reactions with $[Rh(cod)OH]_2$ on its own or with added XPhos (entries 1, 3). $Pd(OAc)_2$ was not an effective catalyst for the hydroarylation (entry 4). In fact, if only palladium and XPhos were present with a mixture of the alkyne **1b** and phenylboronic acid, Suzuki–Miyaura cross-coupling was observed in high yield (entry 5). Since the hydroarylation reaction occurred at 70 °C while the C–N cross-coupling was sluggish at that temperature, the rate difference provided the "time-resolution" that was crucial to the success of the domino process.

Subsequently, we tested the impact of added $Pd(OAc)_2$ and XPhos on the efficiency of the hydroarylation step (Figure 3). The Rh-catalyzed addition gave 70% conversion in 30 min at 70

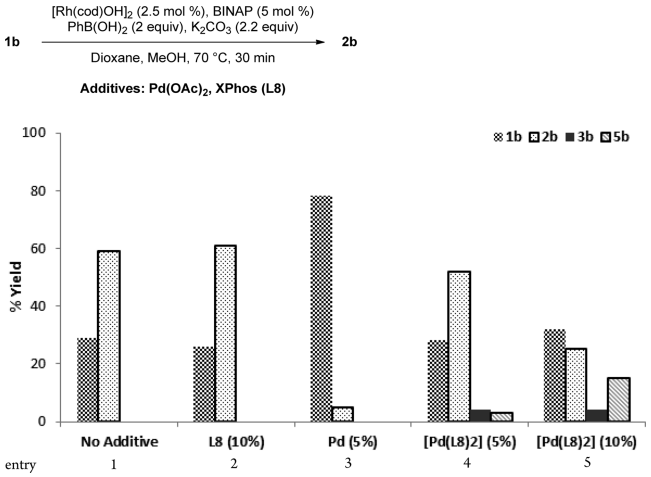
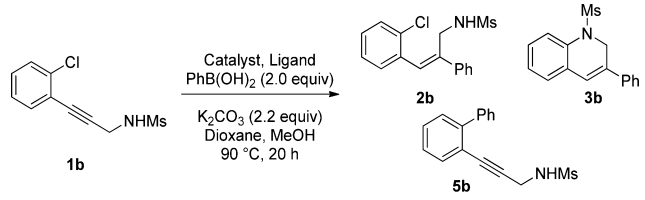


Figure 3. Effect of Pd and XPhos as additives in the hydroarylation step. Yields determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

°C (entry 1). The addition of XPhos had no effect, further supporting that this ligand has minimal interaction with rhodium. However, adding $Pd(OAc)_2$ to the reaction caused a significant decrease in conversion (entry 3). It appeared that palladium may competitively bind BINAP, thus stripping it from rhodium and diminishing the catalytic efficiency. Consequently, the addition of both $Pd(OAc)_2$ and XPhos to the reaction largely negated the competitive phosphine binding effect of added $Pd(OAc)_2$. As a result, high conversion was restored for the Rh-catalyzed hydroarylation (entry 4). At 5

Table 4. Control Reactions for Domino Catalysis[a]



entry[b]	catalyst (mol %)	ligand (mol %)	**1b** (%)	**2b** (%)	**3b** (%)	**5b** (%)
1	$[Rh(cod)OH]_2$ (2.5)		0[c]	0	0	0
2	$[Rh(cod)OH]_2$ (2.5)	**L1** (5)	0	77[d]	0	0
3	$[Rh(cod)OH]_2$ (2.5)	**L8** (10)	56	6	0	0
4	$Pd(OAc)_2$ (2)	**L1** (2)	96	0	0	0
5	$Pd(OAc)_2$ (2)	**L8** (4)	6	0	9	76

[a]See Table 5 for reaction procedures. [b]Yields determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c]Decomposition was observed. [d]>25:1 regioselectivity.

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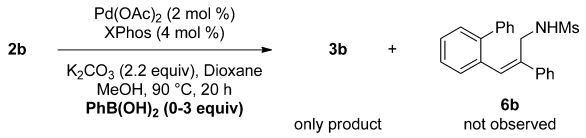
mol % $Pd(OAc)_2$ and 10 mol % XPhos loading (equivalent Rh:Pd loading), traces of the Suzuki cross-coupling **5b** and domino products **3b** appeared. As the loading of the palladium and XPhos increased, the amount of Suzuki coupling products **5b** became significant (entry 5). From the observations of reaction behavior, it appeared that, by fine-tuning the catalytic components, a domino reaction was feasible.

With these initial studies in hand, we examined the Pd-catalyzed amidation step and the influence of additives. Even in the presence of a boronic acid, full conversion of **2b** to the amidation product **3b** was observed without the formation of the Suzuki–Miyaura coupling product **6b** (Scheme 5). The intramolecular cyclization out-competed the intermolecular cross-coupling.

Scheme 5. Competition Reaction of Amidation and Suzuki–Miyaura Cross-Coupling



Driven by the control in selectivity observed during the amidation step in the presence of boronic acids, we proceeded to probe the catalyst–ligand interactions between palladium, XPhos, and BINAP. In the Pd-catalyzed amidation step, we observed that BINAP attenuated the reaction (Figure 4). As the loading of BINAP increased from 4 mol % (2:1 L:Pd) to 8 mol %, the reaction became so slow that no conversion was observed (entries 3, 4). The preferential binding of BINAP with palladium diminished the amount of the active [Pd(XPhos)] species in the reaction medium. However, even with premixing

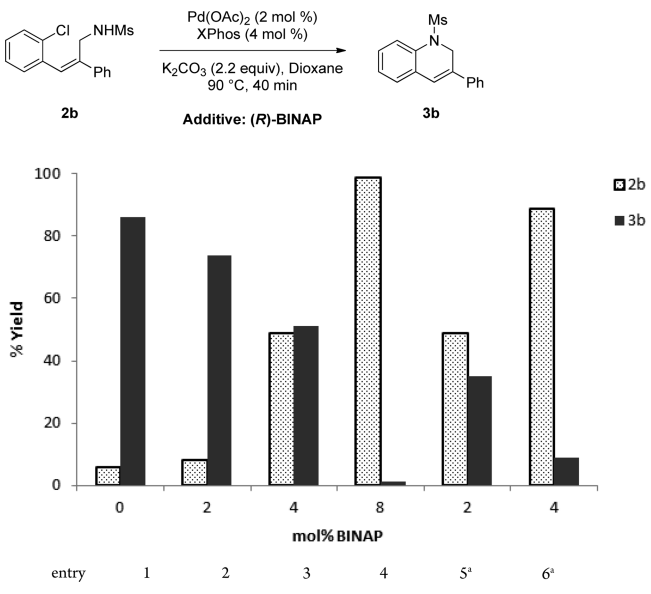
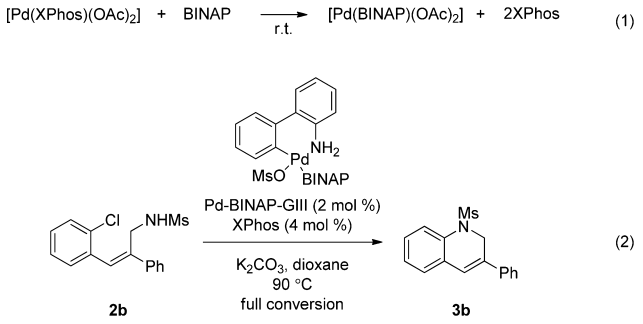


Figure 4. Effect of BINAP and ligand exchange on the amidation reaction. $Pd(OAc)_2$ and XPhos were premixed for 30 min to fully form the ligand-bound species (observed via ^{31}P NMR). BINAP was subsequently added, and the mixture was stirred for an additional 30 min. The catalyst–ligand mixture was then subjected to the reaction. [a] $Pd(OAc)_2$ and BINAP were premixed for 30 min to form $[Pd(BINAP)(OAc)_2]$ (^{31}P NMR), followed by addition of XPhos and stirring for an additional 30 min prior to subjecting to the reaction.

$Pd(OAc)_2$ and BINAP to form the $[Pd(BINAP)(OAc)_2]$[20] complex prior to the addition of XPhos, we still observed reactivity despite lowered conversion of **2b** to the amidation product **3b** (entries 5, 6). Using ^{31}P NMR to investigate the ligand exchange at the premixing stage (Scheme 6, eq 1), we

Scheme 6. BINAP–XPhos Interactions with Pd in the Amidation Step



observed that $Pd(OAc)_2$ preferentially bound BINAP, a bidentate ligand, over XPhos, a bulky monodentate ligand, at room temperature (see the Supporting Information). While BINAP could displace XPhos on [Pd(II)(XPhos)] species, we did not observe the reverse process. However, the preferential Pd-BINAP association was not necessarily static under the reaction conditions. In addition, although Pd(II) oxidation of BINAP to generate Pd(0) and BINAP(O) is a known process[20] and could offer an explanation for the observations made in Figure 4 (entries 5, 6), this was not a necessary mechanism responsible for ligand exchange. For instance, premixing $[Rh(cod)OH]_2$ with XPhos and $Pd(OAc)_2$ with BINAP could still lead to a successful domino reaction. Switching the palladium source to Pd-BINAP-GIII, a [Pd(0)-BINAP] precursor developed by the Buchwald group,[21] and adding XPhos gave full conversion to the amidation product **3b** (Scheme 6, eq 2). Buchwald and co-workers observed exchange between RuPhos **L9** and BrettPhos **L10** on palladium,[22] so we were intrigued by the possibility of a weak catalyst–ligand exchange occurring under our reaction conditions to generate sufficient amounts of the active [Pd(XPhos)] species to catalyze the amidation step.

Ultimately, the inhibitory effects of excess BINAP overwhelmed the weak Pd–XPhos interactions in the Pd-catalyzed amidation step and significantly hindered conversion. However, the addition of $[Rh(cod)OH]_2$ along with BINAP (Figure 5, entry 4) ameliorated the inhibitory properties of BINAP, similar to the beneficial effect of adding both $Pd(OAc)_2$ and XPhos in the hydroarylation step. This result suggested that rhodium can competitively and selectively bind BINAP. The active sequestration of BINAP by rhodium liberated palladium from the inactive [Pd(BINAP)] species and increased the amount of the [Pd(XPhos)] complex. However, the loading of rhodium and BINAP relative to palladium and XPhos is also important. When it was increased to 10 mol % (5:1 Rh:Pd), the amount of BINAP available to complex onto palladium increased as well, leading to inhibition (entry 5).

With a better understanding of metal–ligand interactions, we studied the effect of relative equivalents of the catalysts in the domino reaction. With an equivalent loading of the two catalysts, the domino product **3b** was formed in 50% yield with full consumption of starting material **1b** (Figure 6). It was

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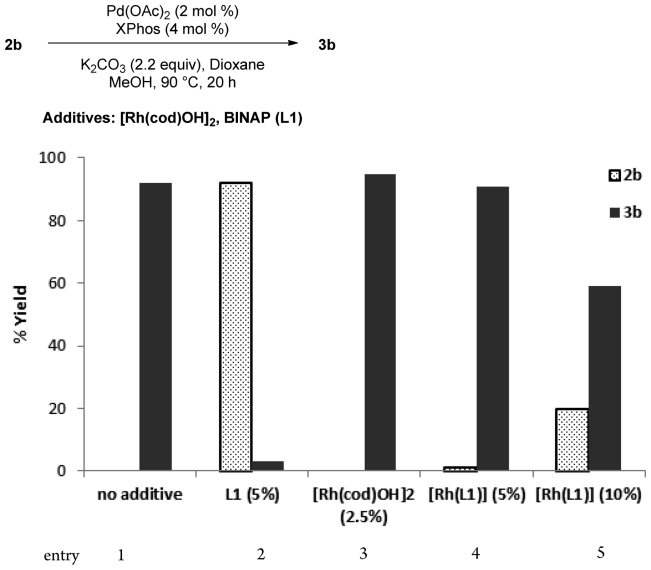

Figure 5. Influence of $[Rh(cod)OH]_2$ and BINAP in the amidation reaction.

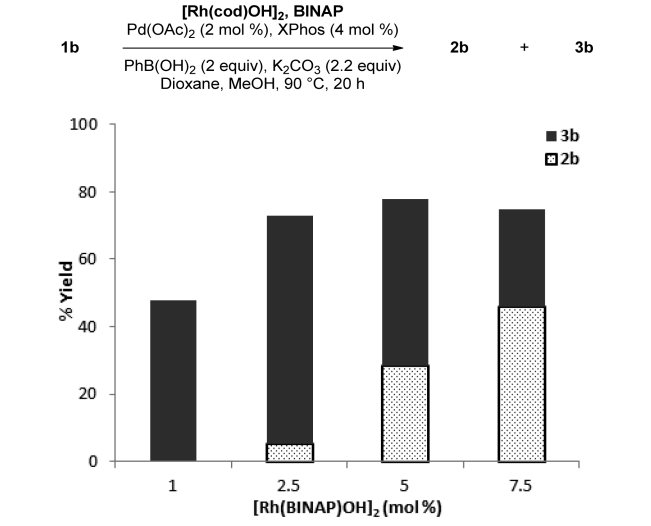

Figure 6. Determination of optimal catalyst ratios for the domino reaction.[24]

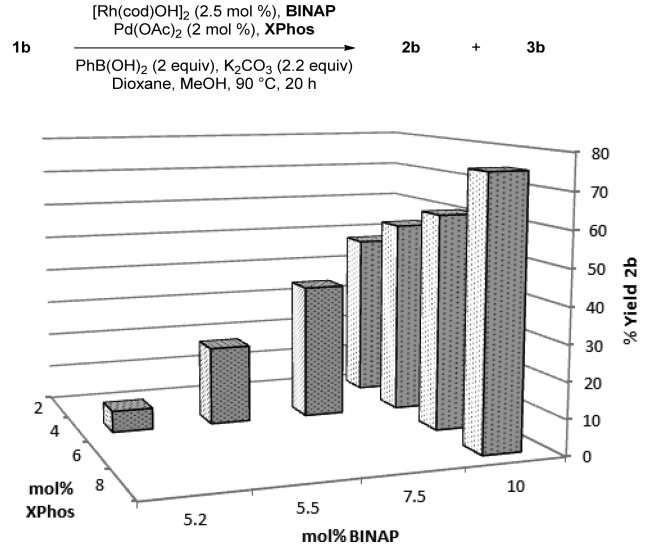

Figure 7. Effect of relative ligand loading on the formation of **2b** in the domino reaction. See Table 5 for reaction procedures.

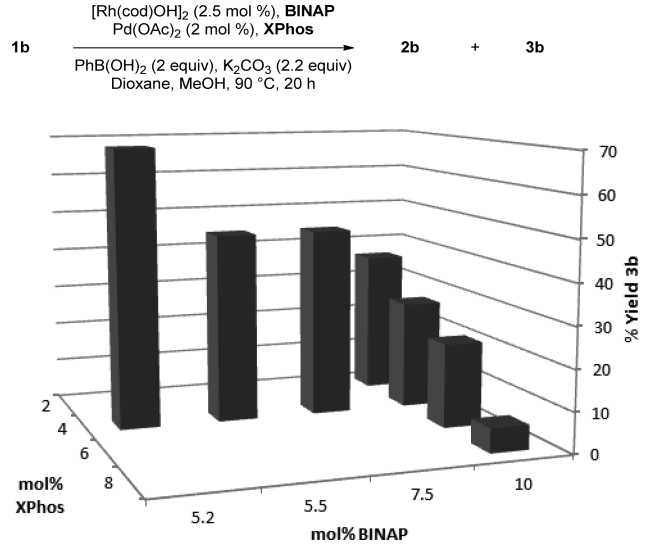

Figure 8. Effect of relative ligand loading on the formation of **3b** in the domino reaction.

apparent that a lower loading of rhodium and BINAP promoted Suzuki–Miyaura byproduct formation, whereas high loading inhibited the amidation step. The optimal loading was established at 2.5 mol % $[Rh(cod)OH]_2$ (5 mol % Rh), 5.2 mol % BINAP, 2 mol % $Pd(OAc)_2$, and 4 mol % XPhos. Keeping the metal catalyst loading at 5 mol % Rh and 2 mol % Pd, we varied the relative ligand loadings (Figures 7 and 8). With increased BINAP loadings, the reaction stalled at the intermediate **2b**. We attempted to out-compete BINAP at 10 mol % with increased loading of XPhos, but to no avail, observing even lower yields. The increased XPhos loading may result in coordinative saturation of palladium, decreasing its catalytic activity.[23]

From the insights gained from these metal–ligand interaction experiments, we propose that the two catalytic cycles occurred independently and no cooperative interactions between the two catalytic cycles existed (Scheme 7). The cycles commenced as the substrate **1** and arylboronic acid underwent rapid Rh-catalyzed formal hydroarylation to yield **2**. This intermediate then entered the second catalytic cycle through a Pd-catalyzed C–N coupling to yield the product **3**. The alternative undesired Suzuki–Miyaura cross-coupling of **1b** with the arylboronic acid could be observed. Additionally, inhibition of the hydroarylation and C–N coupling by $Pd(OAc)_2$ and BINAP, respectively, were observed. However, with optimized catalyst ratios, the alternative pathway and inhibition effects were suppressed.

With the synthetic conditions optimized, we investigated the scope of the domino process with respect to various substitution patterns on the substrate and the arylboronic acid. We also investigated the nitrogen protecting group on the substrate **1** (Table 5) and observed the highest yields with mesyl and tosyl groups, though other sulfonyl groups were tolerated.

Using tosyl and mesyl protected substrates, we examined the scope of the arylboronic acid coupling partners (Table 6). From a two-step perspective, the yields were good (39–78%). A variety of arylboronic acids were tolerated. Both electron rich

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Scheme 7. Proposed Coexisting Domino Catalytic Cycles

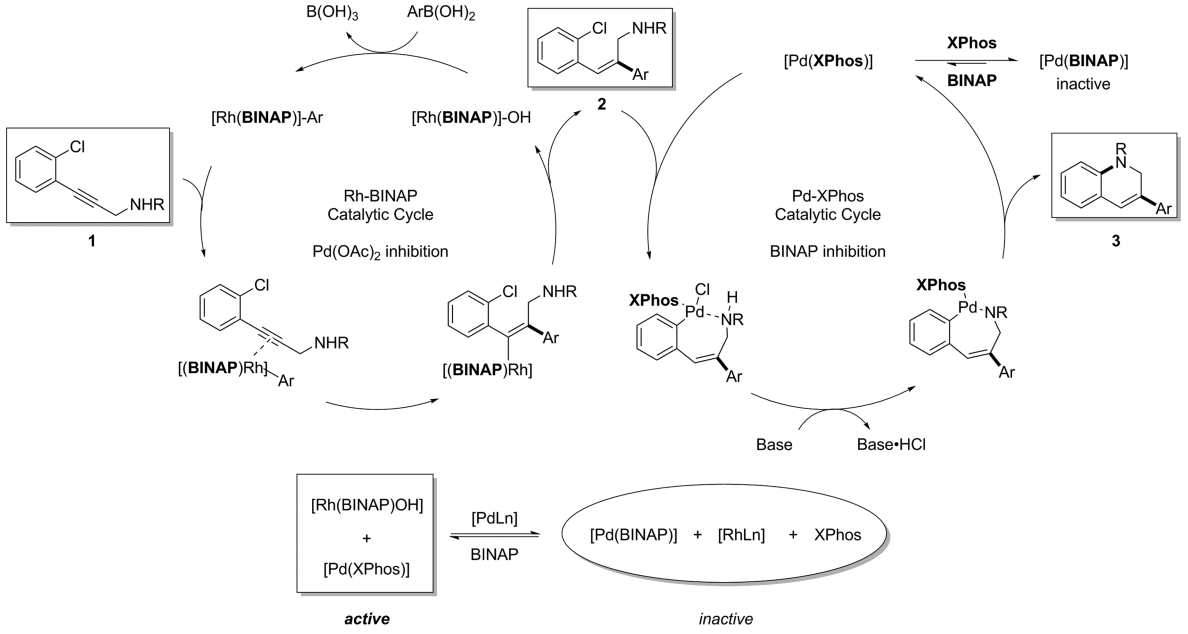
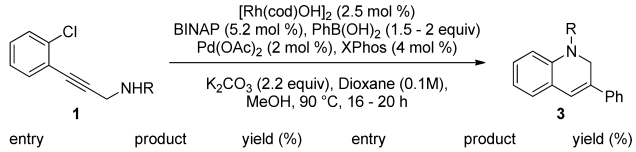
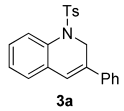
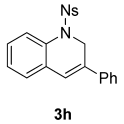
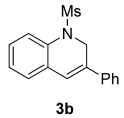
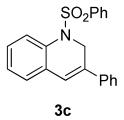
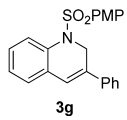


Table 5. Scope of Nitrogen Protecting Groups[a]



entry	product	yield (%)	entry	product	yield (%)
1	 **3a**	65	4	 **3h**	36
2	 **3b**	69	5	 **3c**	68
3	 **3g**	35			

[a]Stock catalyst solutions ([Rh(cod)OH]$_2$ (0.005 M) with BINAP (1.05 equiv to [Rh]) and Pd(OAc)$_2$ (0.008 M) with XPhos (2 equiv to [Pd])), were mixed separately in dioxane at 50 °C for 15 min. 0.5 mL of each solution was added to a vial containing **1** (0.2 mmol), ArB(OH)$_2$ (2 equiv), K_2CO_3 (2.2 equiv), and 0.1 mL of MeOH in 1 mL of dioxane. The mixture was stirred at 90 °C for 16–20 h.

to poor boronic acids gave similar yields (entries 10–13). Excellent regioselectivity was observed with respect to the alkyne for various boronic acids. Heteroaryl boronic acids also exhibited favorable reactivity. In particular, 3-thiophenyl boronic acid underwent the domino transformation with a 78% yield (entry 12).

As we investigated the effects of substitution on the arene (Table 7), we found improved yields with deactivated substrates (60–81%, entries 2–6). While electron rich arenes were slightly lower yielding, the high regioselectivity of the hydroarylation was retained. Various substitution patterns on the arene were well tolerated.

The hydroarylation–cross-coupling strategy could also be applied to the synthesis of aryl-2*H*-chromenes (Table 8). Switching the palladium catalyst to [Pd(allyl)Cl]$_2$ and the solvent to toluene resulted in an effective domino hydroarylation/C–O cross-coupling to afford the desired products with moderate yields.

The resulting dihydroquinoline products could be modified into the 3-substituted quinoline via elimination of the sulfonyl group in the presence of KO^{t}Bu at room temperature (Scheme 8, eq 1). The chromene **4h** could be dihydroxylated in high yield and ee (eq 2), and hydrogenation of the stilbene double bond can also be achieved under mild conditions.[25]

■ CONCLUSION

We have identified a synthesis of dihydroquinolines and chromenes via a two-metal, two-ligand domino process. This work demonstrated that, in spite of the potential complexity of metal–ligand interactions, applying multimetal–ligand domino reactions could yield powerful transformations in one step with high efficiency. Through our studies on the strength of the binding interactions, we gained valuable insight into the role of each individual component in this domino reaction. Although inhibitory effects and side reactivity existed, modifications in the reaction conditions could counter these problems. Our work provided an example of two transition-metal complexes with different phosphine ligands capable of association and dissociation, whereby the active metal–ligand complexes function independently to catalyze the desired reaction pathway.

■ EXPERIMENTAL SECTION

For general experimental methods, see the Supporting Information. Characterization data and experimental methods for **1j**,[26] **1b**, **1l**, **1n**, **1o**, **2b**, **2i**, **5b**, **3 lb**, **3qb**, **3rb**, **4c–f**, **4h**,[6l] and **7**[28] were reported previously.

Substrate Syntheses. *N-(3-(2-Chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**1a**).* A round-bottom flask containing

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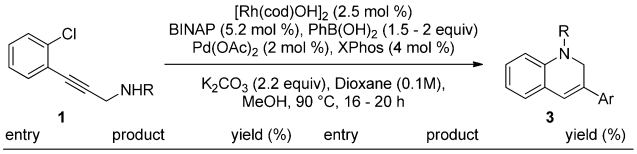
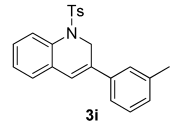
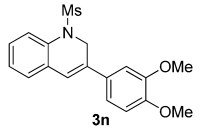
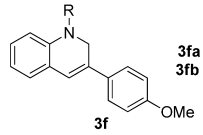
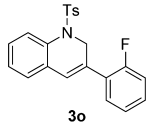
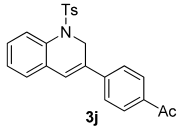
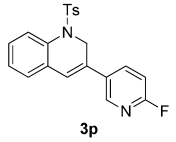
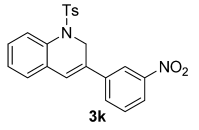
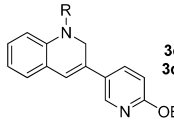
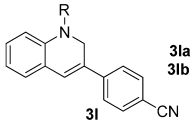
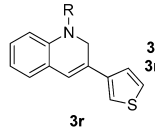
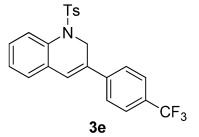
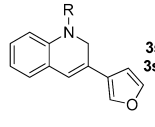
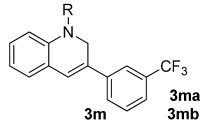
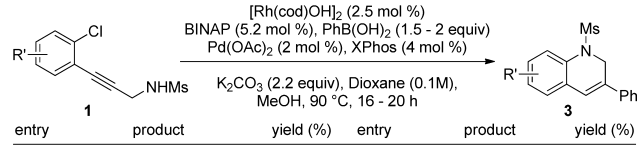
Table 6. Scope of Boronic Acids in the Domino Reaction[a]

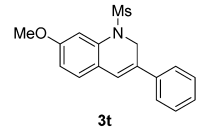
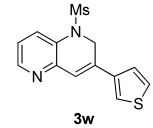
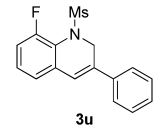
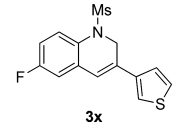
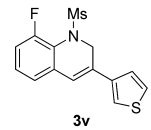
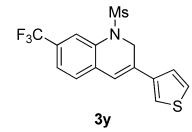
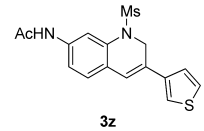


entry	product	yield (%)	entry	product	yield (%)
1	 **3i**	59	8	 **3n**	50
2	 **3f**	**3fa** R = Ts, 40 **3fb** R = Ms, 49	9	 **3o**	39
3	 **3j**	63	10	 **3p**	47
4	 **3k**	49	11	 **3qa** R = Ts, 47 **3qb** R = Ms, 65	
5	 **3l**	**3la** R = Ts, 56 **3lb** R = Ms, 68	12	 **3r**	**3ra** R = Ts, 46 **3rb** R = Ms, 78
6	 **3e**	64	13	 **3s**	**3sa** R = Ts, 42 **3sb** R = Ms, 64
7	 **3m**	**3ma** R = Ts, 63 **3mb** R = Ms, 55			

[a]See Table 5 for reaction conditions.

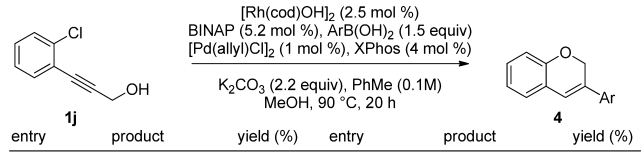
Table 7. Scope of Substitutions on Substrate[a]

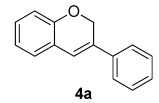
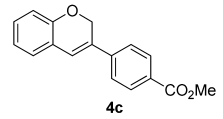
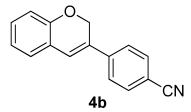


entry	product	yield (%)	entry	product	yield (%)
1	 **3t**	54	4	 **3w**	45
2	 **3u**	62	5	 **3x**	61
3	 **3v**	73	6	 **3y**	78 81[b]
			7	 **3z**	63

[a]See Table 5 for reaction conditions. [b]Reaction conducted at 60 °C for 90 min and at 90 °C for the rest of the reaction duration.

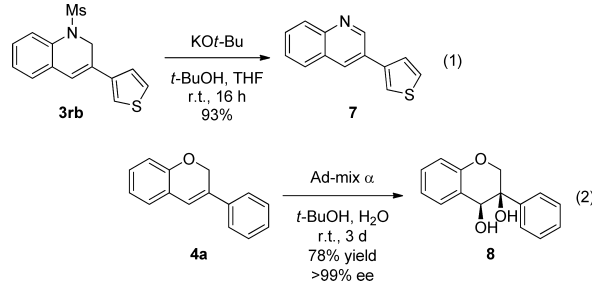
Table 8. Synthesis of Chromenes[a]



entry	product	yield (%)	entry	product	yield (%)
1	 **4a**	59	3	 **4c**	50
2	 **4b**	27			

[a]See Table 5 for reaction conditions.

Scheme 8. Post-modification of Domino Products



$Pd(PPh_3)_2Cl_2$ (71 mg, 1 mol %) and CuI (38 mg, 2 mol %) was purged with argon. *N*,*N*-Dimethylformamide (50 mL, 0.2 M) and triethylamine (10.1 g, 13.9 mL, 100 mmol, 10 equiv) were added, followed by 2-chloro-1-iodobenzene (2.62 g, 1.34 mL, 11 mmol, 1.1 equiv) and *N*-(prop-2-ynyl)toluenesulfonamide (2.09 g, 10 mmol, 1 equiv), and the flask was stirred at r.t. for 16 h. The reaction mixture was diluted with EtOAc and partitioned with water. The organic phase was separated and washed with water 2× and brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. Column chromatography (pentane:EtOAc 7:3) yielded the titled compound as an off-white solid in 70% yield (2.24 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.30–7.18 (m, 3H), 7.15 (d, J = 4.2 Hz, 2H), 4.72 (s, 1H), 4.14 (d, J = 6.1 Hz, 2H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.9, 136.9, 135.9, 133.5, 129.9, 129.7, 129.3, 127.6, 126.4, 122.2, 88.6, 81.7, 34.0, 21.6; **IR** (NaCl, neat): 3256, 2862, 1596, 1472, 1431, 1322, 1306, 1293, 1140, 1092, 1066, 963, 837, 819 cm^{-1}; **m.p.**: 134–136 °C; **HRMS** (TOF, ESI^+): calcd for $C_{16}H_{15}ClNO_2S$ $(M + H)^+$: 320.0506; Found: 320.0499.

*N-(3-(2-Chlorophenyl)prop-2-ynyl)methanesulfonamide (**1b**).* A round-bottom flask containing $Pd(PPh_3)_2Cl_2$ (100 mg, 2 mol %) and CuI (60 mg, 4 mol %) was purged with argon. Acetonitrile (30 mL, 0.2 M) and triethylamine (30 mL, 0.2 M) were added, followed by the 2-chloro-1-iodobenzene (1.81 g, 0.926 mL, 7.59 mmol, 1.1 equiv) and

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N-(prop-2-ynyl)methanesulfonamide **7** (918 mg, 6.9 mmol, 1 equiv), and the flask was stirred at 40 °C for 4 h, at which no starting material remained on TLC. The reaction crude was filtered through a Celite plug and concentrated under vacuum. Column chromatography (pentane:EtOAc 7:3) yielded the titled compound as an off-white solid in 75% yield (1.26 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (dd, J = 7.5, 1.8 Hz, 1H), 7.40 (dd, J = 8.0, 1.2 Hz, 1H), 7.29 (td, J = 7.8, 1.8 Hz, 1H), 7.23 (td, J = 7.5, 1.4 Hz, 1H), 4.70 (t, J = 5.6 Hz, 1H), 4.27 (d, J = 6.2 Hz, 2H), 3.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ136.1, 133. 130.1, 129.5, 126.8, 122.0, 89.3, 81.9, 41.8, 33.8; **IR** (NaCl, neat): 3280, 3016, 2961, 2930, 2879, 1473, 1432, 1417, 1243, 1166, 1156, 1070, 1063, 1034, 996, 971, 827, 761, 739, 715, 667, 667, 589, 547, 522 cm^{-1}; **m.p.**: 65−67 °C; **HRMS** (TOF, EI$^+$): calcd for $C_{10}H_{10}ClNO_2S$ $(M)^+$: 243.0121; Found: 243.0117.

*tert-Butyl 3-(2-Chlorophenyl)prop-2-ynylcarbamate (**1d**).* A round-bottom flask containing $Pd(PPh_3)_2Cl_2$ (354 mg, 1 mol %), CuI (192 mg, 2 mol %), and a stirring bar was purged with argon. Triethylamine (170 mL, 0.3 M) was added. Following this, 2-chloro-1-iodobenzene (12.0 g, 6.15 mL, 50.5 mmol, 1.01 equiv) was added, followed by *tert*-butyl prop-2-yn-1-ylcarbamate (7.76 g, 50 mmol, 1 equiv), and the reaction was allowed to stir at room temperature for 4 h, at which point no starting material could be observed by TLC. The reaction crude was filtered through a Celite plug and concentrated under vacuum. Column chromatography (pentane:EtOAc 9:1) yielded the titled compound as a colorless solid in 95% yield (12.6 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (dd, J = 7.4, 1.8 Hz, 1H), 7.35 (dd, J = 7.9, 1.2 Hz, 1H), 7.21 (td, J = 7.7, 1.9 Hz, 1H), 7.16 (td, J = 7.5, 1.4 Hz, 1H), 4.93 (s, 1H), 4.19 (d, J = 3.3 Hz, 2H), 1.45 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.4, 136.0, 133.5, 129.4, 129.3, 126.5, 122.7, 90.9, 80.1, 79.9, 31.4, 28.4; **IR** (NaCl, neat): 3343, 2979, 2933, 1712, 1679, 1505, 1475, 1368, 1274, 1249, 1168, 1064, 1049, 1033, 859, 755 cm^{-1}; **m.p.**: 58−60 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{14}H_{17}ClNO_2$ $(M + H)^+$: 266.09478; Found: 266.09413.

General Procedure A for Protected Propargyl Amines. A round-bottom flask was charged with a stirring bar and *tert*-butyl 3-(2-chlorophenyl)prop-2-ynylcarbamate (11.93 g, 45 mmol, 1 equiv) and cooled to 0 °C in an ice bath. A solution of $HCl_{(aq)}$ in EtOAc (3 M, 30 mL) was added to this flask. The reaction was allowed to stir at room temperature, until no starting material was observed by TLC (2 h). The liquids were removed uder reduced pressure, leaving an orange flaky solid (prop-2-yn-1-aminium chloride, 8.54 g, 42.2 mmol), which was used without further purification. In order to synthesize the protected propargyl amines, the prop-2-yn-1-aminium chloride was treated with triethylamine and the appropriate electrophile in dichloromethane as described in each specific case.

*N-(3-(2-Chlorophenyl)prop-2-ynyl)benzenesulfonamide (**1c**).* According to the general procedure A, prop-2-yn-1-aminium chloride (500 mg, 2.474 mmol, 1 equiv) was placed into an oven-dried round-bottom flask with a stirring bar; dichloromethane (10 mL, 0.25 M) and triethylamine (550 mg, 0.757 mL, 5.4 mmol, 2.2 equiv) were added. The reaction was cooled to 0 °C in an ice bath. Benzenesulfonyl chloride (480 mg, 0.35 mL, 2.7 mmol, 1.1 equiv) was added dropwise over ∼3 min, and the reaction was allowed to warm to room temperature. When the reaction was complete, as observed by TLC (<1 h), the mixture was quenched with saturated $NH_4Cl_{(aq)}$, extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. Afterward, the solvent was removed under reduced pressure, and the crude was purified using column chromatography (pentane:EtOAc 9:1 to 8:2), yielding the title compound in 74% yield (560 mg) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97−7.92 (m, 2H), 7.56−7.44 (m, 3H), 7.36−7.30 (m, 1H), 7.22 (ddd, J = 8.0, 6.6, 2.5 Hz, 1H), 7.18−7.11 (m, 2H), 4.87 (t, J = 5.8 Hz, 1H), 4.16 (d, J = 6.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.9, 135.9, 133.5, 133.0, 129.8, 129.3, 129.3 (2), 127.5 (2), 126.4, 122.0, 88.4, 81.7, 34.0; **IR** (NaCl, neat): 3282, 3059, 2931, 2854, 1475, 1448, 1334, 1266, 1164, 1091, 1072, 1032, 967, 947, 844, 730 cm^{-1}; **m.p.**: 84−85 °C; **HRMS** (TOF, EI$^+$): calcd for $C_{15}H_{12}ClNO_2S$ $(M)^+$: 305.0277; Found: 305.0279.

*N-(3-(2-Chlorophenyl)prop-2-ynyl)-4-methoxybenzenesulfonamide (**1g**).* According to the general procedure A, prop-2-yn-1-aminium chloride (303 mg, 1.5 mmol, 1 equiv) was placed into an oven-dried round-bottom flask with a stirring bar; dichloromethane (5 mL, 0.3 M) and triethylamine (333.76 mg, 0.46 mL, 3.3 mmol, 2.2 equiv) were added. The reaction was cooled to 0 °C in an ice bath. 4-Methoxybenzene-1-sulfonyl chloride (341 mg, 1.1 equiv) in dichloromethane (1 mL) was added dropwise over ∼3 min, and the reaction was allowed to warm to room temperature. When the reaction was complete, as observed by TLC (<1 h), the mixture was quenched with saturated $NH_4Cl_{(aq)}$, extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. Afterward, the solvent was removed under reduced pressure, and the crude was purified using column chromatography (pentane:EtOAc 7:3 to 6:4), yielding the title compound in 70% yield (352 mg) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 7.9 Hz, 1H), 7.20 (ddd,J = 2.4, 6.8, 8.0 Hz, 1H), 7.17−7.08 (m, 2H), 6.89 (d, J = 8.9 Hz, 2H), 5.05 (t, J = 6.0 Hz, 1H), 4.11 (d, J = 6.1 Hz, 2H), 3.73 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$):δ 163.1, 135.8, 133.5, 131.3, 129.7 (2), 129.6, 129.2, 126.4, 122.2, 114.3 (2), 88.8, 81.5, 55.6, 33.9; **IR** (NaCl, neat): 3268, 3094, 3023, 2981, 2854, 1595, 1575, 1472, 1432, 1326, 1310, 1302, 1265, 1152 1073, 1022, 832, 763 cm^{-1}; **m.p.**: 105−107 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{16}H_{15}ClNO_3S$ $(M + H)^+$: 336.04612; Found: 336.04492.

*N-(3-(2-Chlorophenyl)prop-2-ynyl)-4-nitrobenzenesulfonamide (**1h**).* According to the general procedure A, prop-2-yn-1-aminium chloride (303 mg, 1.5 mmol, 1 equiv) was placed into an oven-dried round-bottom flask with a stirring bar; dichloromethane (5 mL, 0.3 M) and triethylamine (333.76 mg, 0.460 mL, 3.3 mmol, 2.2 equiv) were added. The reaction was cooled to 0 °C in an ice bath. 4-Nitrobenzene-1-sulfonyl chloride (366 mg, 1.1 equiv) in dichloromethane (1 mL) was added dropwise over ∼3 min, and the reaction was allowed to warm to room temperature. When the reaction was complete, as observed by TLC (<1 h), the mixture was quenched with saturated $NH_4Cl_{(aq)}$, extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. Afterward, the solvent was removed under reduced pressure, and the crude was purified using column chromatography (pentane:DCM:MeOH 47.5:47.5:5), yielding the title compound in 75% yield (385 mg) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (dt, J = 2, 9.2 Hz, 2H), 8.12 (dt, J = 2, 8.8 Hz, 2H), 7.31 (dd, J = 8.1, 0.8 Hz, 1H), 7.22 (ddd, J = 2, 7.2, 8 Hz 1H), 7.13 (td, J = 7.4, 1.2 Hz, 1H), 7.09 (dd, J = 2, 7.6 Hz, 1H), 5.06 (t, J = 6.0 Hz, 1H), 4.25 (d, J = 6.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.2, 146.0, 135.7, 133.2, 130.3, 129.5, 128.9 (2), 126.7, 124.4 (2), 121.5, 87.8, 82.4, 34.1; **IR** (NaCl, neat): 3285, 3101, 3076, 1520, 1471, 1432, 1344, 1159, 1053, 857, 766, 736, 622 cm^{-1}; **m.p.**: 128−129 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{15}H_{15}ClN_3O_4S$ $(M + NH_4)^+$: 368.04718; Found: 368.04750.

*4-(2-Chlorophenyl)but-3-yn-1-ol (**1k**).* A round-bottom flask containing $Pd(PPh_3)_2Cl_2$ (70 mg, 0.5 mol %), CuI (38 mg, 1 mol %), and a stirring bar was purged with argon. Triethylamine (40 mL, 0.5 M) was added. Following this, 2-chloro-1-iodobenzene (5.25 g, 2.69 mL, 22 mmol, 1.1 equiv) was added, followed by 3-butyn-1-ol (1.40 g, 1.51 mL, 20 mmol, 1 equiv), and the reaction mixture was degassed with argon. The mixture was stirred at room temperature for 16 h. The reaction crude was filtered through a Celite plug and concentrated under vacuum. Column chromatography (pentane:EtOAc 9:1) yielded the titled compound (2.85 g) as yellow oil in 79% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.49−7.41 (m, 1H), 7.41−7.35 (m, 1H), 7.28−7.14 (m, 2H), 3.84 (t, J = 6.2 Hz, 2H), 2.74 (t, J = 6.2 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 135.9, 133.3, 129.2, 129.1, 126.5, 123.2, 92.3, 79.6, 61.1, 24.1; **IR** (NaCl, $CDCl_3$): 3335, 2943, 2888, 2234, 1476, 1431, 1065, 1045, 1034, 754 cm^{-1}; **HRMS** (TOF, ESI$^+$): calcd for $C_{10}H_{10}ClO$:181.0420, Found: 181.0419.

*N-(3-(2-Chloro-3-fluorophenyl)prop-2-ynyl)methanesulfonamide (**1l**).* A round-bottom flask containing $Pd(PPh_3)_4$ (58 mg, 5 mol %), CuI (19 mg, 10 mol %), 1-bromo-2-chloro-3-fluorobonzene (210 mg, 1 mmol), and *N*-(prop-2-ynyl)methanesulfonamide (160 mg, 1.2 mmol, 1.2 equiv) was purged with argon. Acetonitrile (5 mL, 0.2 M) and diisopropylamine (5 mL, 0.2 M) were added. The reaction was sealed and stirred at 90 °C for 16 h. The reaction crude was filtered through a Celite plug and concentrated under vacuum. Column

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chromatography (hexane:EtOAc 9:1 to 8:2) yielded the titled compound as a colorless solid in 63% yield (165 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (d, J = 7.7 Hz, 1H), 7.20 (dt, J = 8.2, 5.1 Hz, 1H), 7.14 (dt, J = 8.6, 1.8 Hz, 1H), 5.11 (t, J = 6.0 Hz, 1H), 4.27 (d, J = 6.2 Hz, 2H), 3.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5 (d, J = 250 Hz), 129.0 (d, J = 3 Hz), 127.8 (d, J = 8 Hz), 123.4 (d, J = 18 Hz), 124.2 (s), 117.3 (d, J = 21 Hz), 90.5 (s), 80.8 (d, J = 4 Hz), 41.8 (s), 33.7 (s); **^{19}F NMR** (282 MHz, $CDCl_3$): δ −112.99 (dd, J = 8.4, 5.2 Hz); **IR** (NaCl, neat): 3285, 1569, 1468, 1440, 1320, 1247, 1153, 1076, 1036, 787 cm^{-1}; **m.p.**: 100−103 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{10}H_{10}ClFNO_2S$ (M + H)$^+$: 262.0105; found 262.0106.

*N-(3-(3-Chloropyridin-3-yl)prop-2-ynyl)methanesulfonamide (**1m**).* A round-bottom flask containing $Pd(PPh_3)_4$ (347 mg, 3 mol %) was purged with argon. Diisopropylamine (25 mL, 0.4 M) and 2-bromo-3-chloropyridine (1.924 g, 10 mmol, 1 equiv) were added, followed by *tert*-butyl prop-2-yn-1-ylcarbamate (1.86 g, 12 mmol, 1.2 equiv).The flask was stirred at 100 °C for 16 h. The reaction crude was filtered through a Celite plug and concentrated under vacuum. Column chromatography (pentane:EtOAc 7:3) yielded *tert*-butyl (3-(2-chloropyridin-3-yl)prop-2-yn-1-yl)carbamate in 67% (1.79 g) yield as a brown solid. This material was then placed in a round-bottom flask, cooled to 0 °C in an ice bath, and was treated with $HCl_{(aq)}$ in EtOAc (3 M, 30 mL). The reaction was monitored by TLC. Upon completion, the liquids were removed under vacuum to give a crystalline solid (3-(2-chloropyridin-3-yl)prop-2-yn-1-aminium chloride). This material (500 mg, 2.47 mmol, 1 equiv) was placed into a flame-dried round-bottom flask. Dichloromethane (12 mL, 0.2 M) and triethylamine (860 mg, 1.15 mL, 6.18 mmol, 2.5 equiv) were added. Upon cooling to 0 °C in an ice bath, methanesulfonyl chloride (340 mg, 227 μL, 2.96 mmol, 1.2 equiv) was added dropwise over ∼3 min. The reaction was allowed to warm to room temperature and monitored by TLC. Upon completion, the mixture was quenched with saturated $NH_4Cl_{(aq)}$, extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. Afterward, the solvent was removed under reduced pressure, and the crude was purified using column chromatography (pentane:EtOAc 1:1), yielding the title compound in 58% yield (351 mg, 39% overall) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.36 (dd, J = 4.4, 1.2 Hz, 1H), 7.77 (dd, J = 7.6, 1.2 Hz, 1H), 7.23 (dd, J = 7.6, 4.9 Hz, 1H), 4.86 (t, J = 5.3 Hz, 1H), 4.28 (d, J = 6.2 Hz, 2H), 3.16 (s, 3H); **^{13}C NMR**(101 MHz, $CDCl_3$): δ 152.4, 149.1, 141.9, 122.1, 119.4, 91.9, 80.0, 41.9, 33.7; **IR** (NaCl, neat): 3269, 2918, 2850, 1395, 1318, 1152, 1092, 1070, 808 cm^{-1}; **m.p.**: 113−114 °C; **HRMS** (TOF, DART$^+$): calcd for $C_9H_{10}ClN_2O_2S$ (M + H)$^+$: 245.01515; Found: 245.01471.

*N-(3-(2-Chloro-5-fluorophenyl)prop-2-ynyl)methanesulfonamide (**1n**).* A round-bottom flask containing $Pd(PPh_3)_4$ (58 mg, 5 mol %), CuI (19 mg, 10 mol %), 2-bromo-1-chloro-4-fluorobonzene (210 mg, 1 mmol), and *N*-(prop-2-ynyl)methanesulfonamide (160 mg, 1.2 mmol, 1.2 equiv) was purged with argon. Acetonitrile (5 mL, 0.2 M) and diisopropylamine (5 mL, 0.2 M) were added. The reaction was sealed and stirred at 90 °C for 16 h. The reaction crude was filtered through a Celite plug and concentrated under vacuum. Column chromatography (hexane:EtOAc 9:1 to 8:2) yielded the titled compound as a colorless solid in 56% yield (146 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.36 (dd, J = 8.9, 5.1 Hz, 1H), 7.16 (dd, J = 8.5, 3.0 Hz, 1H), 7.02 (ddd, J = 8.9, 7.9, 3.0 Hz, 1H), 4.72 (s, 1H), 4.27 (d, J = 6.2 Hz, 2H), 3.16 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 161.0 (d, J = 248 Hz), 131.5 (d, J = 4 Hz), 131.0 (d, J = 9 Hz), 123.6 (d, J = 10 Hz), 120.4 (d, J = 25 Hz), 117.8 (d, J = 23 Hz), 90.6 (s), 81.1 (d, J = 3 Hz), 42.0 (s), 33.8 (s); **^{19}F NMR** (282 MHz, $CDCl_3$): δ −115.33 (td, J = 8.1, 5.1 Hz); **IR** (NaCl, neat): 3281, 1602, 1577, 1469, 1405, 1320, 1154, 1120, 1000, 874, 817, 649 cm^{-1}; **m.p.**: 74−76 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{10}H_{10}ClFNO_2S$ (M + H)$^+$, 262.0104; found 262.0105.

*N-(3-(2-Chloro-4-(trifluoromethyl)phenyl)prop-2-ynyl)methanesulfonamide (**1o**).* A round-bottom flask containing $Pd(PPh_3)_2Cl_2$ (72 mg, 2 mol %) and CuI (44 mg, 4 mol %) was purged with argon. Acetonitrile (25 mL, 0.2 M) and triethylamine (25 mL, 0.2 M) were added, followed by 2-chloro-1-iodo-4-(trifluoromethyl)benzene (1.53 g, 5 mmol, 1 equiv) and *N*-(prop-2-ynyl)methanesulfonamide (732 mg, 5.5 mmol, 1.1 equiv), and the flask was stirred at 40 °C for 5 h when no starting material remained on TLC. The reaction crude was filtered through a Celite plug and concentrated under vacuum. Column chromatography (hexane:EtOAc 9:1 to 8:2) yielded the titled compound as a pale yellow solid in 63% yield (0.98 g). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 4.75 (br s, 1H), 4.29 (d, J = 6.2 Hz, 2H), 3.16 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 136.6 (s), 133.9 (s), 131.8 (q, J = 34 Hz), 126.5 (q, J = 4 Hz), 125.7 (s), 123.6 (q, J = 4 Hz), 123.0 (q, J = 273 Hz), 92.0 (s), 80.6 (s), 41.7 (s), 33.6 (s); **^{19}F NMR** (282 MHz, $CDCl_3$): δ −63.5; **IR** (NaCl, neat): 3281, 1391, 1320, 1141, 1082, 834, 723 cm^{-1}; **m.p.**: 73−75 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{11}H_{10}ClF_3NO_2S$: 312.0073; Found: 312.0074.

*N-(3-Chloro-4-(3-(methylsulfonamido)prop-1-ynyl)phenyl)-acetamide (**1p**).* A round-bottom flask containing $Pd(PPh_3)_2Cl_2$ (58 mg, 5 mol %) and CuI (19 mg, 10 mol %) was purged with argon. Acetonitrile (5 mL, 0.2 M) and diisopropylamine (5 mL, 0.2 M) were added; following this, *N*-(4-bromo-3-chlorophenyl)acetamide (249 mg, 1 mmol, 1 equiv) was added, followed by *N*-(prop-2-ynyl)-methanesulfonamide (173 mg, 1.3 equiv). The reaction was allowed to stir at 90 °C for 16 h. The reaction crude was filtered through a Celite plug and concentrated under vacuum. Column chromatography (pentane:EtOAc 1:1) yielded the titled compound as a colorless solid in 50% yield (150 mg). **^{1}H NMR** (400 MHz, *DMSO*): δ 10.26 (bs, 1H), 7.89 (s, 1H), 7.66 (t, J = 5.3 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 4.10 (d, J = 5.5 Hz, 2H), 3.03 (s, 3H), 2.06 (s, 3H); **^{13}C NMR** (101 MHz, *DMSO*): δ 169.0, 140.7, 134.8, 134.0, 118.7, 117.4, 115.5, 90.0, 80.0, 40.7, 32.6, 24.1; **IR** (neat): 3331, 3096, 3010, 2929, 2886, 1676, 1583, 1515, 1493, 1455, 1385, 1320, 1255, 1150, 1051, 1005, 964, 884, 843 cm^{-1}; **m.p.**: 171−172 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{12}H_{14}ClN_2O_3S$ (M + H)$^+$: 301.04137; Found: 301.04054.

Rhodium-Catalyzed Hydroarylation. *General Procedure B for Rh-Catalyzed Alkyne Arylation. (Z)-N-(3-(2-Chlorophenyl)-2-phenylallyl)methanesulfonamide (**2b**).* $[Rh(cod)OH]_2$ (11.4 mg, 2.5 mol % (5 mol % [Rh])) and BINAP (32.4 mg, 5.2 mol %) were weighed into a 2-dram vial, which was fitted with a cap with a septum and purged with argon for 5 min. Dioxane (1 mL) was added to the vial, and the solution was allowed to stir for 15 min at 50 °C (Note 1). Substrate **1b** (244 mg, 1 mmol), phenylboronic acid (183 mg, 1.5 mmol, 1.5 equiv), and K_2CO_3 (166 mg, 1.2 mmol, 1.2 equiv) were weighed into a 25 mL round-bottom flask, which was fitted with a septum and purged with argon. 1,4-Dioxane (8 mL) and MeOH (0.8 mL) were added to the reaction. The catalyst solution was added to this reaction flask via syringe. The reaction was heated to 50 °C overnight (16 h), after which TLC showed complete consumption of phenylboronic acid. The reaction mixture was cooled to room temperature and filtered through a plug of silica (washing with EtOAc), and the solvent was removed under vacuum. The crude was purified using column chromatography (loading with toluene, pentane:EtOAc 8:2 to75:25) to yield a thick yellow oil, which slowly solidified upon standing (238 mg) in 74% yield (slightly higher yield (49.6 mg, 77%) was isolated on 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57−7.51 (m, 2H), 7.48−7.27 (m, 7H), 6.97 (s, 1H), 4.32−4.23 (m, 3H), 2.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.03, 138.39, 134.92, 134.02, 130.44, 129.86, 129.43, 129.38, 129.22 (2C), 128.77, 127.09, 126.99 (2C), 42.49, 40.53; **IR** (NaCl, neat): 3282, 3058, 3023, 2963, 2932, 1496, 1471, 1445, 1428, 1409, 1318, 1264, 1153, 1067, 1052, 1034, 967, 883, 862, 836, 763, 699 cm^{-1}; **m.p.**: 77−78 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{16}H_{20}ClN_2O_2S$ (M + NH_4)$^+$: 339.09340; Found: 339.09383.

Note 1: Premixing $[Rh(cod)OH]_2$ and BINAP was not crucial for the single step procedure, and similar yields (70−77%) were obtained if the catalyst and ligand were weighed as solids together with base and substrates.

*(Z)-N-(3-(2-Chlorophenyl)-2-phenylallyl)-4-methylbenzenesulfonamide (**2a**).* The product was synthesized according to general procedure B, using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), substrate **1a** (64 mg, 0.2 mmol, 1 equiv), phenylboronic acid (49 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1

equiv). The crude product was purified by flash chromatography with 0−10% EtOAc/hexanes to provide the title compound (58.1 mg) as an off-white solid 73%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.7 Hz, 1H), 7.21−7.13 (m, 4H), 7.13−7.06 (m, 1H), 6.83 (s, 1H), 4.44 (s, 1H), 4.02 (d, J = 5.6 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.5, 138.7, 137.3, 136.2, 134.8, 134.0, 130.2, 129.7, 129.6, 129.2, 129.0, 128.9, 128.5, 127.3, 126.8, 126.7, 42.4, 21.7; **IR** (NaCl, $CDCl_3$): 3266, 3057, 1660, 1599, 1471, 1445, 1404, 1327, 1163, 1094, 1067, 1053, 887, 814, 760, 698, 667 cm^{-1}; **m.p.**: 127−129 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{22}H_{21}NO_2SCl$: 398.0976; Found: 398.0985.

*(Z)-N-(3-(2-Chlorophenyl)-2-phenylallyl)benzenesulfonamide (**2c**).* The titled compound was synthesized using procedure B using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), substrate **1c** (61.2 mg, 0.2 mmol, 1 equiv), phenylboronic acid (49 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1 equiv). The product was isolated through column chromatography (pentane:EtOAc 9:1) as a pale yellow solid in 70% yield (48.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 7.8 Hz, 1H), 7.34−7.26 (m, 5H), 7.26−7.10 (m, 3H), 6.89 (s, 1H), 4.49 (t, J = 5.2 Hz, 1H), 4.10 (d, J = 5.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.2, 138.6, 137.2, 134.8, 134.0, 132.8, 130.2, 129.7, 129.3, 129.2(2), 129.0(2), 128.5, 127.3(2), 126.9, 126.7(2), 42.4; **IR** (NaCl, neat): 3260, 3061, 3023, 2917, 2849, 1471, 1447, 1321, 1166, 1095, 1066, 1049, 757, 721, 689 cm^{-1}; **m.p.**: 131−134 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{21}H_{19}ClNO_2S$ (M + H)$^+$: 384.08250; Found: 384.08289.

*(Z)-tert-Butyl 3-(2-Chlorophenyl)-2-phenylallylcarbamate (**2d**).* The titled compound was synthesized using procedure B using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), substrate **1d** (53.2 mg, 0.2 mmol, 1 equiv), phenylboronic acid (49 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1 equiv). The product was isolated through column chromatography (pentane:EtOAc 95:5) as a colorless solid (33.7 mg) in 45% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.4 Hz, 2H), 7.45−7.31 (m, 5H), 7.31−7.21 (m, 2H), 6.95 (s, 1H), 4.40 (s, 1H), 4.32 (d, J = 4.6 Hz, 2H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.6, 139.6, 139.4, 135.3, 134.0, 130.5, 129.5, 128.8, 128.7, 128.1, 128.0, 126.9, 126.7, 79.4, 39.7, 28.3 (3); **IR** (NaCl, neat): 3335, 3059, 3003, 2978, 2932, 1709, 1674, 1593, 1506, 1392, 1367, 1269, 1246, 1165, 1065, 1034, 860, 754 cm^{-1}; **m.p.**: 84−88 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{20}H_{23}ClNO_2$ (M + H)$^+$: 344.14173; Found: 344.14281.

*(Z)-N-(3-(2-Chlorophenyl)-2-(4-(trifluoromethyl)phenyl)allyl)-4-methylbenzenesulfonamide (**2e**).* The product was synthesized according to general procedure B, using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), substrate **1a** (64 mg, 0.2 mmol, 1 equiv), (4-(trifluoromethyl)phenyl)boronic acid (76 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1 equiv). The crude was purified by flash chromatography with 0−10% EtOAc/hexanes to provide the title compound (64.3 mg) as an off-white solid 69%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.2 Hz, 3H), 7.43 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 7.9 Hz, 1H), 7.28−7.13 (m, 5H), 6.93 (s, 1H), 4.61 (s, 1H), 4.07 (d, J = 5.8 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 143.72 (s), 142.54 (s), 136.56 (s), 136.15 (s), 134.32 (s), 134.02 (s), 131.15 (s), 130.09 (s), 129.76 (s), 129.73 (s), 129.42 (s), 127.21 (s), 127.15 (s), 126.93 (s), 125.69 (q, J = 3.8 Hz), 42.37 (s), 21.60 (s); **^{19}F NMR** (377 MHz, $CDCl_3$): δ 63.0 (s); **IR** (NaCl, $CDCl_3$): 3264, 1616, 1435, 1323, 1161, 1123, 1072, 748 cm^{-1}; **m.p.**: 129−131 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{23}H_{20}NO_2F_3SCl$: 466.0849; Found: 466.0835.

*(Z)-N-(3-(2-Chlorophenyl)-2-(p-tolyl)allyl)-4-methylbenzenesulfonamide (**2f**).* The product was synthesized according to general procedure B, using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), substrate **1a** (64 mg, 0.2 mmol, 1 equiv), (4-(methyl)phenyl)boronic acid (54 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1 equiv). The crude was purified by flash chromatography with 0−10% EtOAc/hexanes to provide the title compound (52.7 mg) as an off-white solid 64%. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.57 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 7.7 Hz, 1H), 7.26−7.08 (m, 9H), 6.85 (s, 1H), 4.39 (s, 1H), 4.05 (d, J = 5.6 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.6, 138.5, 137.1, 136.2, 135.7, 134.9, 134.1, 130.2, 129.7, 129.7, 129.6, 129.0, 128.4, 127.4, 126.8, 126.6, 77.5, 77.2, 76.8, 42.4, 21.7, 21.3; **IR** (NaCl, $CDCl_3$): 3244, 1435, 1316, 1165, 1096, 1065, 810, 748, 706 cm^{-1}; **m.p.**: 122−125 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{23}H_{23}NO_2SCl$: 412.1132; Found: 412.1142.

*(Z)-N-(3-(2-Chlorophenyl)-2-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide (**2g**).* The product was synthesized according to general procedure B, using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), substrate **1a** (64 mg, 0.2 mmol, 1 equiv), (4-methoxyphenyl)boronic acid (61 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1 equiv) and was purified by flash chromatography with 0−10% EtOAc/hexanes to provide the title compound (59.9 mg) as an off-white solid 70%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.3 Hz, 2H), 7.36 (dd, J = 7.8, 1.0 Hz, 1H), 7.28−7.11 (m, 7H), 6.89−6.78 (m, 3H), 4.28 (t, J = 5.5 Hz, 1H), 4.04 (d, J = 5.6 Hz, 2H), 3.84 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.9, 143. 5, 136.5, 136.1, 134.9, 134.0, 130.8, 130.1, 129.7, 129.5, 128.8, 127.8, 127.6, 127.3, 126.7, 114.3, 55.4, 42.3, 21.6; **IR** (NaCl, $CDCl_3$): 3264, 1616, 1435, 1323, 1161, 1123, 1072, 748 cm^{-1}; **m.p.**: 129−131 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{23}H_{20}NO_2F_3SCl$: 466.0849; Found: 466.0835.

*(Z)-N-(3-(2-Chlorophenyl)-2-(6-chloropyridin-3-yl)allyl)-4-methylbenzenesulfonamide (**2h**).* The titled compound was synthesized using procedure B using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), substrate **1a** (64 mg, 0.2 mmol, 1 equiv), (6-chloropyridin-3-yl)boronic acid (63 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv). The product was isolated through column chromatography (pentane:EtOAc 8:2) as a yellow solid in 77% yield (67 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.34 (d, J = 2.4 Hz, 1H), 7.64 (dd, J = 8.3, 2.5 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 7.8 Hz, 1H), 7.32−7.07 (m, 6H), 6.89 (s, 1H), 5.16 (t, J = 5.8 Hz, 1H), 4.02 (d, J = 5.8 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 150.88, 147.89, 143.84, 137.02, 136.09, 133.98, 133.95, 133.87, 131.28, 130.07, 129.80 (2), 129.72, 129.51, 127.09 (2), 126.89, 124.03, 42.18, 21.67; **IR** (NaCl, neat): 3265, 3062, 2922, 2852, 1582, 1469, 1377, 1326, 1160, 1109, 1094, 1067, 756 cm^{-1}; **m.p.**: 143−147 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{21}H_{19}Cl_2N_2O_2S$ (M + H)$^+$: 433.0538; Found: 433.0552.

*(Z)-N-(3-(2-Chlorophenyl)-2-(thiophen-3-yl)allyl)methanesulfonamide (**2i**).* The titled compound was synthesized using procedure B using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), substrate **1i** (48 mg, 0.2 mmol, 1 equiv), 3-thiophenylboronic acid (51 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1 equiv). The product was isolated as a colorless thick oil in 73% yield (48 mg). **^{1}H NMR** (399 MHz, $CDCl_3$): δ 7.50 (dd, J = 2.8, 1.4 Hz, 1H), 7.48−7.42 (m, 1H), 7.41−7.25 (m, 5H), 7.10 (s, 1H), 4.53 (t, J = 5.6 Hz, 1H), 4.20 (d, J = 5.8 Hz, 2H), 2.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.3, 134.8, 134.0, 132.7, 130.4, 129.8, 129.4, 128.1, 127.1, 126.8, 125.8, 122.5, 42.8, 40.3; **IR** (NaCl, neat): 3286, 3108, 2959, 2917, 2850, 1468, 1428, 1403, 1321, 1152, 1066, 1053, 1033, 963, 912, 785, 759, 739 cm^{-1}; **HRMS** (TOF, DART$^+$): calcd for $C_{14}H_{15}ClNO_2S_2$: 328.02327 (M + H)$^+$; Found: 328.02280.

*(Z)-3-(2-Chlorophenyl)-2-phenylprop-2-en-1-ol (**2j**).* The product was synthesized according to general procedure B, using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), substrate **1j** (33.3 mg, 0.2 mmol, 1 equiv), phenylboronic acid (48.8 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1 equiv). The crude was purified by flash chromatography with 0−10% EtOAc/hexanes to provide the title compound (25 mg) as an off-white solid 51%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.1 Hz, 2H), 7.47 (dd, J = 7.3, 1.9 Hz, 1H), 7.41 (t, J = 7.3 Hz, 3H), 7.34 (t, J = 7.3 Hz, 1H), 7.26 (pd, J = 7.2, 1.7 Hz, 2H), 7.00 (s, 1H), 4.60 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.5, 140.0, 135.5, 134.2, 130.8, 129.6, 128.9, 128.9, 128.2, 128.1, 126.9, 126.8, 77.5, 77.2, 76.8, 60.5; **IR** (NaCl, $CDCl_3$): 3363, 3057, 2924, 1495, 1470, 1435, 1053, 1032, 1017, 758, 696 cm^{-1}; **m.p.**: 69−70 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{15}H_{17}ClNO$ (M + NH_4^+): 262.0999; Found: 262.0998.

*(E)-4-(2-Chlorophenyl)-3-phenylbut-3-en-1-ol (**2k**).* The product was synthesized according to general procedure B, using [Rh(cod)-

$OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), substrate **1k** (36.1 mg, 0.2 mmol, 1 equiv), phenylboronic acid (49 mg, 0.4 mmol, 2 equiv), and K_2CO_3 (31 mg, 0.22 mmol, 1.1 equiv). The crude was purified by flash chromatography with 0−10% EtOAc/hexanes to provide the title compound (26.4 mg) as a white solid 51%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55−7.19 (m, 10H), 6.86 (s, 1H), 3.63 (t, J = 6.7 Hz, 2H), 2.91 (t, J = 6.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.6, 140.3, 136.3, 134.3, 130.7, 129.6, 128.7, 128.5, 128.4, 127.9, 126.9, 126.7, 77.5, 77.2, 76.8, 61.2, 33.6; **IR** (NaCl, $CDCl_3$): 3354, 3057, 3023, 2961, 2883, 1495, 1468, 1442, 1035, 758, 698 cm^{-1}; **m.p.**: 75−76 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{16}H_{19}ClNO$ ($M + NH_4^+$): 276.1155; Found: 276.1148.

Palladium-Catalyzed Suzuki−Miyaura Cross-Coupling of 2b. *N-(3-(Biphenyl-2-yl)prop-2-ynyl)methanesulfonamide (**5b**).* The substrate **1a** was reacted under standard C−N coupling reactions. **1a** (49 mg, 0.2 mmol), phenylboronic acid (36.6 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) were combined in a 2-dram vial equipped with a stirring bar and a septum. After purging with argon, dioxane (2 mL, 0.1 M) and methanol (0.05 mL) were added. The reaction was stirred at 90 °C for 1 h and then was allowed to cool, filtered through a silica plug, and concentrated. Column chromatography (hexane:EtOAc 7:3) gave the titled compound in 76% yield (44 mg) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54−7.29 (m, 9H), 4.49 (t, J = 5.9 Hz, 1H), 4.07 (d, J = 6.2 Hz, 2H), 2.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.3, 140.6, 133.1, 129.8, 129.3, 129.2, 128.3, 127.9, 127.3, 120.5, 86.8, 84.8, 77.6, 77.2, 76.7, 40.9, 33.7; **IR** (NaCl, neat): 3287, 3061, 3024, 2931, 2853, 1589, 1476, 1432, 1415, 1322, 1153, 1071, 1009, 996, 960, 912, 831, 762, 738, 701 cm^{-1}; **HRMS** (TOF, DART$^+$): calcd for $C_{16}H_{19}N_2O_2S$ ($M + NH_4$)$^+$: 303.11672; Found: 303.11580.

Palladium-Catalyzed C−N Cross-Coupling of 2b. *1-(Methylsulfonyl)-3-phenyl-1,2-dihydroquinoline (**3b**).* (*Z*)-*N*-(3-(2-Chlorophenyl)-2-phenylallyl)methanesulfonamide (**2b**) (64.4 mg, 0.2 mmol), K_2CO_3 (39 mg, 0.28 mmol, 1.4 equiv), $Pd(OAc)_2$ (0.9 mg, 2 mol %, Note 1), and XPhos (2.8 mg, 4 mol %, Note 1) were weighed into a 2-dram vial, which was fitted with a screw cap with a septum and purged with argon. Dioxane was added (2 mL), and the septum was replaced with a Teflon-lined screw cap (Note 2). The reaction was heated to 90 °C for 16 h, upon which the crude was filtered through a silica plug and concentrated. Column chromatography (pentane:EtOAc 9:1) yielded the titled compound in 91% yield as a colorless solid (most of the dihydropyridine compounds were highly fluorescent under UV light).

Note 1: Oftentimes, Pd-XPhos was added as a stock solution prepared by stirring the $Pd(OAc)_2$ and XPhos for 10−15 min (or until homogeneous) at room temperature or 50 °C.

Note 2: Alternatively, the argon inlet was removed and the vial septum was wrapped with parafilm.

Rh/Pd-Catalyzed Domino Dihydroquinoline Synthesis. *General Procedure C: Domino Synthesis of 3-Aryl-1,2-dihydroquinolines **3** from Arylpropargyl Alkynes **1**.* Substrates **1** (0.2 mmol, 1 equiv), arylboronic acid (1.1−2 equiv) (Note 1), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) were weighed into a 2-dram vial (Note 2) equipped with a stirring bar and fitted with a septum. The reaction vial was purged with argon, and then 1,4-dioxane (1 mL, 0.2 M) and MeOH (0.1 mL) were added. The catalyst solutions (0.5 mL of each, Note 3) were added to this reaction vessel. The septum was exchanged with a Teflon-lined screw cap, and the reaction was heated at 90 °C for 16 h. The crude was filtered through a plug of silica, concentrated under reduced pressure, and purified through column chromatography.

Note 1: 1.5 equiv of arylboronic acid was used for the majority of arylboronic acids (similar results were seen with 1.1 equiv or 2 equiv). Two equivalents of heteroaromatic boronic acids were used due to more facile proteodemetalation reaction.

Note 2: Microwave vials could be used instead of screw-cap vials with similar results.

Note 3: The catalyst solutions were prepared as follows:

$[Rh(cod)OH]_2$ (2.5 mol %; 5 mol % [Rh]) and BINAP (5.2 mol %) were weighed into a screw-cap vial. $Pd(OAc)_2$ (2 mol %) and XPhos (4 mol %) were weighed into a screw-cap vial. Both vials were equipped with a septum and purged with argon. Dioxane (0.5 mL, 0.01 M for $[Rh]_2$ (0.005 M for [Rh]), 0.008 M for [Pd]) was added to both vials, and the catalyst solutions were stirred at 50 °C for 15 min, after which these solutions were added to the reaction flask. More conveniently, for small-scale reactions, stock solutions of known concentration (usually: 0.01 mmol/mL for $[Rh]_2$ and 0.008 mmol/mL for [Pd]) were prepared and used in several parallel reactions. Sometimes, a colorless precipitate (excess BINAP) was observed in the rhodium catalyst mixture. In this case, the precipitate was allowed to settle (∼5 min), and only the supernatant was transferred to the reaction vessel.

*3-Phenyl-1-tosyl-1,2-dihydroquinoline (**3a**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 9:1) in 65% yield (47 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.9 Hz), 7.43−7.18 (m), 7.16 (d, J = 8.4 Hz), 7.03 (dd, J = 7.5, 1.5 Hz), 6.91 (d, J = 8.5 Hz), 6.30 (s), 4.80 (d, J = 1.1 Hz), 2.28 (s); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.49, 137.52, 135.73, 134.63, 134.34, 130.56, 128.97, 128.79, 128.35, 128.00, 127.19, 127.09, 127.07, 126.93, 125.25, 121.36, 77.48, 77.16, 76.84, 47.68, 21.60; **IR** (NaCl, neat): 2361, 1597,1481, 1346, 1165, 1088, 810, 760 cm^{-1}; **m.p.**: 177−179 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{22}H_{19}NO_2NaS$ ($M + Na^+$): 384.1028; Found: 384.1031.

*1-(Methylsulfonyl)-3-phenyl-1,2-dihydroquinoline (**3b**).* According to the general procedure C, substrate **1b** (49 mg, 0.2 mmol) and phenylboronic acid (36.6 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv). The product was isolated using column chromatography (pentane:EtOAc 9:1) in 69% yield (39.5 mg) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69−7.63 (m, 1H), 7.59−7.53 (m, 2H), 7.47−7.40 (m, 2H), 7.40−7.33 (m, 1H), 7.34−7.26 (m, 3H), 6.94 (s, 1H), 4.78 (d, J = 1.0 Hz, 2H), 2.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ137.2, 135.9, 134.6, 123.0, 129.2 (2C), 128.8, 128.5, 127.5, 127.3, 126.5, 125.5 (2C), 122.0, 47.5, 37.7; **IR** (NaCl, neat): 3070, 3031, 2930, 2891, 2853, 1589, 1496, 1484, 1455, 1344, 1321, 1203, 1154, 1083, 1037, 959, 912, 882, 845, 831, 761, 731, 693 cm^{-1}; **m.p.**: 119−121 °C; **HRMS** (TOF, EI): calcd for $C_{16}H_{15}NO_2S$: 285.0824; Found: 285.0816.

*3-Phenyl-1-(phenylsulfonyl)-1,2-dihydroquinoline (**3c**).* According to the general procedure C, substrate **1c** (61.1 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 8:2) in 54% yield (37.4 mg) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.78 (d, J = 7.9 Hz, 1H), 7.42−7.18 (m, 10H), 7.13 (t, J = 7.9 Hz, 2H), 7.02 (dd, J = 7.5, 1.1 Hz, 1H), 6.27 (s, 1H), 4.81 (d, J = 0.5 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 138.55, 137.44, 134.66, 134.24, 132.75, 130.63, 128.83(2), 128.40, 128.34(2), 128.05, 127.21, 127.15(2), 127.10, 126.99, 125.22(2), 47.72; **IR** (NaCl, neat): 3062, 3035, 2919, 2850, 1484, 1447, 1350, 1168, 1091, 1072, 757 cm^{-1}; **m.p.**: 135−138 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{21}H_{18}NO_2S$ ($M + H$)$^+$: 348.10582; Found: 348.10636.

*1-(4-Methoxyphenylsulfonyl)-3-phenyl-1,2-dihydroquinoline (**3g**).* According to the general procedure C, substrate **1g** (67.2 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 8:2) in 35% yield (26 mg) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 1H), 7.43−7.27 (m, 6H), 7.22 (dt, J = 7.6, 1.2 Hz, 1H), 7.20

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(d, J = 8.9 Hz, 2H), 7.03 (dd, J = 7.5, 1.3 Hz, 1H), 6.59 (d, J = 8.9 Hz, 2H), 6.34 (s, 1H), 4.80 (s, 2H), 3.74 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.00, 137.52, 134.71, 134.48, 130.63, 130.56, 129.31 (2), 128.82 (2), 128.38, 128.02, 127.10, 127.09, 127.08, 125.29 (2), 121.34, 113.52 (2), 55.60, 47.69; **IR** (NaCl, neat): 3063, 2966, 2839, 1595, 1580, 1497, 1348, 1304, 1260, 1157, 1026 cm^{-1}; **HRMS** (TOF, DART$^+$): calcd for $C_{22}H_{20}NO_3S$ (M + H)$^+$: 378.11639; Found: 378.11693.

*1-(4-Nitrophenylsulfonyl)-3-phenyl-1,2-dihydroquinoline (**3h**).* According to the general procedure C, substrate **1h** (70.2 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 9:1) in 36% yield (28 mg) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (dt, J = 8.9, 2.2 Hz, 2H), 7.79 (d, J = 7.9 Hz, 1H), 7.45−7.33 (m, 6H), 7.31−7.22 (m, 3H), 7.06 (dd, J = 7.5, 1.4 Hz, 1H), 6.31 (s, 1H), 4.83 (d, J = 0.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.1, 144.0, 136.9, 134.5, 133.5, 130.5, 129.2 (2), 128.9, 128.5, 128.4 (2), 127.9, 127.5, 127.0, 125.0 (2), 123.5 (2), 121.3, 47.8; **IR** (NaCl, neat): 3104, 3067, 2926, 2855, 1530, 1350, 1311, 1169, 1090 cm^{-1}; **m.p.**: 190−192 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{21}H_{20}N_3O_4S$ (M + NH_4)$^+$: 410.11745; Found: 410.11870.

*3-(m-Tolyl)-1-tosyl-1,2-dihydroquinoline (**3i**).* The product was synthesized according to general procedure C; substrate **1a** (64 mg, 0.2 mmol) and *m*-tolylboronic acid (41 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The crude was purified by flash chromatography with 0−5% EtOAc/hexanes to provide the title compound (44.3 mg) as an off-white solid 59%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.9 Hz, 1H), 7.33−7.10 (m, 6H), 7.09−6.98 (m, 3H), 6.92 (d, J = 8.1 Hz, 2H), 6.29 (s, 1H), 4.79 (d, J = 0.8 Hz, 2H), 2.38 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.3, 138.3, 137.5, 135.7, 134.7, 134.3, 130.5, 129.0, 128.9, 128.6, 127.8, 127.1, 126.9, 126.8, 125.9, 122.3, 121.1, 47. 7, 21.6, 21.5; **IR** (NaCl, $CDCl_3$): 1348, 1200, 1163, 1090, 1074, 1032, 785, 762, 711, 694, 671, 650, 584, 557 cm^{-1}; **m.p.**: 167−168 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{23}H_{22}NO_2S$ (M + H)$^+$: 376.1371; Found: 376.1381.

*3-(4-Methoxyphenyl)-1-tosyl-1,2-dihydroquinoline (**3fa**).* The product was synthesized according to general procedure C; substrate **1a** (64 mg, 0.2 mmol) and (4-methoxyphenyl)boronic acid (46 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The crude was purified by flash chromatography with 0−10% Et_2O/hexanes to provide the title compound (31.3 mg) as a white solid 40%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.9 Hz, 1H), 7.30−7.16 (m, 4H), 7.15 (d, J = 8.3 Hz, 2H), 6.99 (dd, J = 7.5, 1.5 Hz, 1H), 6.94−6.85 (m, 4H), 6.21 (s, 1H), 4.75 (s, 2H), 3.84 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.8, 143.4, 135.8, 134.2, 134.1, 130.8, 130.1, 128.9, 127.6, 127.2, 127.0, 126.9, 126.8, 126.5, 119.6, 114.2, 55.5, 47.6, 21.6; **IR** (NaCl, $CDCl_3$): 1609, 1516, 1456, 1348, 1290, 1252, 1182, 1165, 1120, 1032, 1008, 831, 816, 756, 682, 667, 567 cm^{-1}; **m.p.**: 109−110 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{23}H_{22}NO_3S$ (M + H)$^+$: 392.1320; Found: 392.1331.

*3-(4-Methoxyphenyl)-1-(methylsulfonyl)-1,2-dihydroquinoline (**3fb**).* The product was synthesized according to general procedure C; substrate **1b** (48.8 mg, 0.2 mmol) and (4-methoxyphenyl)boronic acid (46 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The crude was purified by flash chromatography with 0−20% Et_2O/hexanes to provide the title compound (30.9 mg) as a white solid 49%. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.69−7.59 (m, 1H), 7.51 (d, J = 9.0 Hz, 2H), 7.32−7.23 (m, 2H), 6.96 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 0.6 Hz, 1H), 4.74 (d, J = 1.2 Hz, 2H), 3.85 (s, 3H), 2.62 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 160.2, 135.4, 134.3, 130.3, 129.6, 128.0, 127.2, 127.2, 126.8, 126.5, 120.2, 114.6, 77.6, 77.2, 76.7, 6.56, 47.4, 37.7; **IR** (NaCl, $CDCl_3$): 2359, 2342, 1684, 1653, 1607, 1562, 1516, 1506, 1481. 1456. 1344. 1249, 1182, 1155, 1080, 1034, 957, 827, 770 cm^{-1}; **m.p.**: 127−130 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{17}H_{21}N_2O_3S$ (M + NH_4)$^+$: 333.1273; Found: 333.1278.

*1-(4-(1-Tosyl-1,2-dihydroquinolin-3-yl)phenyl)ethanone (**3j**).* The product was synthesized according to general procedure C; substrate **1a** (64 mg, 0.2 mmol) and (4-acetylphenyl)boronic acid (49 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The crude was purified by flash chromatography with 0−20% Et_2O/hexanes to provide the title compound (50.8 mg) as a white solid 63%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 7.9 Hz, 1H), 7.37−7.31 (m, 3H), 7.24 (td, J = 7.5, 1.1 Hz, 1H), 7.13 (d, J = 8.3 Hz, 2H), 7.07 (dd, J = 7.5, 1.3 Hz, 1H), 6.91 (d, J = 8.1 Hz, 2H), 6.43 (s, 1H), 4.82 (s, 2H), 2.63 (s, J = 6.7 Hz, 3H), 2.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.4, 143.5, 141.7, 136.4, 135.6, 134.6, 133.1, 129.9, 128.9, 128.8, 128.6, 127.4, 127.1, 127.0, 126.9, 125.1, 123.3, 47.3, 26.6, 21.5; **IR** (NaCl, $CDCl_3$): 1680, 1599, 1483, 1450, 1412, 1349, 1269, 1165, 1090, 1074, 810, 762, 716 cm^{-1}; **m.p.**: 179−180 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{24}H_{22}NO_3S$ (M + H)$^+$: 404.1320; Found: 404.1336.

*3-(3-Nitrophenyl)-1-tosyl-1,2-dihydroquinoline (**3k**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and 3-nitrophenylboronic acid (50 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was purified by flash chromatography with 0−10% Et_2O/hexanes to provide the title compound as a yellow solid 49%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20−8.12 (m, 1H), 7.95 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.61−7.53 (m, 2H), 7.37 (td, J = 7.8, 1.5 Hz, 1H), 7.28 (td, J = 7.4, 1.7 Hz, 1H), 7.16−7.03 (m, 3H), 6.95 (d, J = 8.1 Hz, 2H), 6.43 (s, 1H), 4.80 (s, 2H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148. 6, 143.9, 139.3, 135.6, 134.6, 131.9, 130.7, 129.8, 129.6, 129.1, 128.9, 127.5, 127.2, 127.1, 127.0, 123.9, 122.7, 120.1, 77.4, 77.0, 76.7, 47.3, 21.5; **IR** (NaCl, $CDCl_3$): 1597, 1526, 1483, 1348, 1163, 1090, 880, 808, 762, 735 cm^{-1}; **m.p.**: 196−197 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{22}H_{22}N_3O_4S$ (M + H)$^+$: 424.1331; Found: 424.1327.

*4-(1-Tosyl-1,2-dihydroquinolin-3-yl)benzonitrile (**3la**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and 4-(cyano)phenylboronic acid (44 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 95:5 to 9:1) in 56% yield (41 mg) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.40−7.30 (m, 3H), 7.25 (dt, J = 1.2, 7.2 Hz, 1H), 7.13 (d, J = 8.3 Hz, 2H), 7.07 (dd, J = 7.5, 1.1 Hz, 1H), 6.93 (d, J = 8.1 Hz, 2H), 6.43 (s, 1H), 4.79 (s, 2H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.80, 141.76, 135.75, 134.79, 132.66 (2), 132.50, 129.71, 129.12, 129.09 (2), 127.66, 127.29, 127.13 (2), 127.03, 125.66 (2), 124.34, 118.72, 111.66, 47.19, 21.62; **IR** (NaCl, neat): 3040, 2960, 2918, 2850, 2227, 1600, 1345, 1166, 1091, 840, 811, 759, 710 cm^{-1}; **m.p.**: 220−222 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{23}H_{19}N_2O_2S$ (M + H)$^+$: 387.11672; Found: 387.11675.

*4-(1-(Methylsulfonyl)-1,2-dihydroquinolin-3-yl)benzonitrile (**3lb**).* According to the general procedure C, substrate **1b** (48.7 mg, 0.2 mmol) and (4-cyanophenyl)boronic acid (44 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 7:3) in 68% yield (42.3 mg) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2H), 7.69−7.63 (m,

3H), 7.40−7.28 (m, 3H), 7.06 (s, 1H), 4.78 (s, 2H), 2.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.4, 134.8, 133.6, 132.9 (2), 129.5, 129.1, 128.1, 127.3, 126.2, 125.9 (2), 124.9, 118.6, 112.0, 47.0, 37.9; **IR** (NaCl, neat): 3060, 3015, 2931, 2855, 2230, 1603, 1506, 1480, 1456, 1340, 1234, 1154, 1082, 1036, 960, 842, 773, 763, 734 cm^{-1}; **m.p.**: 105−110 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{17}H_{18}N_3O_2S$ (M + NH_4)$^+$: 328.11197; Found: 328.11138.

*1-Tosyl-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroquinoline (**3e**).* The product was synthesized according to general procedure C; substrate **1a** (64 mg, 0.2 mmol) and (3-(trifluoromethyl)phenyl)-boronic acid (57 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The crude was purified by flash chromatography with 0−5% Et_2O/hexanes to provide the title compound (55.0 mg) as a white solid 64%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 8.6 Hz, 2H), 7.41−7.29 (m, 3H), 7.24 (td, J = 7.5, 1.1 Hz, 1H), 7.14 (d, J = 8.3 Hz, 2H), 7.06 (dd, J = 7.5, 1.2 Hz, 1H), 6.93 (d, J = 8.1 Hz, 2H), 6.39 (s, 1H), 4.80 (s, 2H), 2.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.71 (s), 140.94 (s), 135.75 (s), 134.64 (s), 133.07 (s), 129.99 (s), 129.06 (s), 128.73 (s), 127.46 (s), 127.22 (s), 127.16 (s), 127.01 (s), 125.80 (q, J = 3.8 Hz), 125.44 (s), 123.39 (s), 47.45 (s), 21.60 (s); **^{19}F NMR** (377 MHz, $CDCl_3$): δ 63.6 (s); **IR** (NaCl, $CDCl_3$): 1614, 1599, 1483, 1450, 1412, 1325, 1165, 1117, 1090, 1071, 831, 810, 762, 716, 679, 654 cm^{-1}; **m.p.**: 152−155 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{23}H_{19}F_3NO_2S$ (M + H)$^+$: 430.1089; Found: 430.1084.

*1-Tosyl-3-(3-(trifluoromethyl)phenyl)-1,2-dihydroquinoline (**3ma**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and 3-(trifluoromethyl)phenyl)boronic acid (57 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 9:1) in 63% yield (54 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.35 (td, J = 7.8, 1.5 Hz, 1H), 7.31 (s, 1H), 7.26 (td, J = 7.5, 1.2 Hz, 1H), 7.13 (d, J = 8.3 Hz, 2H), 7.08 (dd, J = 7.5, 1.3 Hz, 1H), 6.94 (d, J = 8.1 Hz, 2H), 4.79 (d, J = 0.7 Hz, 2H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.8 (s), 138.5 (s), 135.8 (s), 134.6 (s), 132.9 (s), 131.2 (q, J = 32.3 Hz), 130.0 (s), 129.4 (s), 129.1 (2), 128.6 (s), 128.3 (q, J = 1.2 Hz), 127.4 (s), 127.3 (s), 127.2 (s), 127.1 (2), 124.8 (q, J = 3.8 Hz), 124.1 (q, J = 273.7 Hz) 123.0 (s), 122.1 (q, J = 3.8 Hz), 47.5 (s), 21.5 (s); **^{19}F NMR** (377 MHz, $CDCl_3$): δ −61.82; **IR** (NaCl, neat): 3066, 2960, 2922, 2850, 1647, 1598, 1489, 1453, 1336, 1241, 1160, 1122, 1032, 1009, 895, 815, 738, 701, 682 cm^{-1}; **m.p.**: 97−100 °C; **HRMS** (TOF, EI$^+$): calcd for $C_{23}H_{18}F_3NO_2S$ (M)$^+$: 429.1010; Found: 429.1017.

*1-(Methylsulfonyl)-3-(3-(trifluoromethyl)phenyl)-1,2-dihydroquinoline (**3mb**).* According to the general procedure C, substrate **1b** (48.7 mg, 0.2 mmol) and (3-(trifluoromethyl)phenyl)boronic acid (57 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 85:15) in 55% yield (39 mg) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.1 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.7 Hz, 1H), 7.37−7.27 (m, 3H), 7.01 (s, 1H), 4.79 (s, 2H), 2.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.0 (s), 134.7 (s), 134.2 (s), 131.7 (q, J = 32.4 Hz), 129.8 (s), 129.4 (s), 129.1 (s), 128.6 (q, J = 1.1 Hz), 127.8 (s), 127.3 (s), 126.3 (s), 125.3 (q, J = 3.7 Hz), 124.2 (q, J = 310 Hz) 123.6, 122.1 (q, J = 3.8 Hz), 47.3 (s), 37.8 (s); **^{19}F NMR** (377 MHz, $CDCl_3$): δ −63.73; **IR** (NaCl, neat): 3070, 3037, 2930, 2854, 1593, 1484, 1451, 1432, 1343, 1332, 1278, 1268, 1156, 1126, 1076, 959 cm^{-1}; **HRMS** (TOF, DART$^+$): calcd for $C_{17}H_{18}F_3N_2O_2S$ (M + NH_4)$^+$: 371.10411; Found: 371.10396.

*3-(3,4-Dimethoxyphenyl)-1-(methylsulfonyl)-1,2-dihydroquinoline (**3n**).* According to the general procedure C, substrate **1b** (48.7 mg, 0.2 mmol) and (3,4-dimethoxyphenyl)boronic acid (55 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 8:2) in 50% yield (34.7 mg) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68−7.61 (m, 1H), 7.31−7.23 (m, 3H), 7.13 (dd, J = 8.3, 2.2 Hz, 1H), 7.08 (d, J = 2.1 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.86 (s, 1H), 4.74 (d, J = 0.9 Hz, 2H), 3.97 (s, 3H), 3.93 (s, 3H), 2.63 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.97, 149.59, 135.56, 134.42, 130.20, 129.94, 128.15, 127.27, 127.23, 126.50, 120.41, 118.43, 111.49, 108.45, 56.20, 56.18, 47.49, 37.69; **IR** (NaCl, neat): 3061, 3003, 2957, 2928, 2852, 1601, 1516, 1456, 1342, 1252, 1155, 1080, 1024, 959, 763 cm^{-1}; **HRMS** (TOF, DART$^+$): calcd for $C_{18}H_{23}N_2O_4S$ (M + NH_4)$^+$: 363.13785; Found: 363.13923.

*3-(2-Fluorophenyl)-1-tosyl-1,2-dihydroquinoline (**3o**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and 2-fluorophenylboronic acid (40 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 95:5 to 9:1) in 39% yield (27.8 mg) as an orange oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 1H), 7.37−7.20 (m, 3H), 7.18 (d, J = 8.2 Hz, 2H), 7.14−7.01 (m, 3H), 6.98 (d, J = 8.1 Hz, 2H), 6.92 (td, J = 7.7, 1.6 Hz, 1H), 6.31 (s, 1H), 4.78 (s, 2H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.33 (d, J = 249.6 Hz), 143.50 (s), 136.05 (s), 134.49 (s), 130.73 (d, J = 2.5 Hz), 130.09 (s), 129.79 (d, J = 8.4 Hz), 129.10 (2), 128.39 (s), 128.34 (d, J = 4.2 Hz), 127.25 (2), 127.23 (s), 127.04 (s), 127.02 (s), 126.03 (d, J = 13.6 Hz), 124.85 (d, J = 4.3 Hz), 124.33 (d, J = 3.4 Hz), 116.24 (d, J = 22.4 Hz), 48.24 (d, J = 7.2 Hz), 21.62 (s); **^{19}F NMR** (377 MHz, $CDCl_3$): δ −111.28 to −111.38 (m); **IR** (NaCl, neat): 3063, 2957, 2921, 2850, 1598, 1580, 1496, 1451, 1348, 1220, 1165, 1122, 1032, 1008, 815, 761, 679, 614 cm^{-1}; **HRMS** (TOF, EI$^+$): calcd for $C_{22}H_{18}NO_2FS$ (M)$^+$: 379.1042; Found: 379.1040.

*3-(6-Fluoropyridin-3-yl)-1-tosyl-1,2-dihydroquinoline (**3p**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and (6-fluoropyridin-3-yl)boronic acid (56 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 9:1) as a yellow solid in 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.27 (t, J = 7.3 Hz, 1H), 7.18 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 7.3 Hz, 1H), 6.88 (d, J = 8.1 Hz, 3H), 6.24 (s, 1H), 4.67 (s, 2H), 2.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.3 (d, J = 241.2 Hz), 144.6 (s), 144.5 (s), 143.9 (s), 137.7 (d, J = 8.0 Hz), 135.7 (s), 134.5 (s), 131.5 (d, J = 4.9 Hz), 130.2 (s), 129.7 (s), 129.1 (s), 128.8 (s), 127.3 (d, J = 6.3 Hz), 127.1 (s), 122.9 (d, J = 1.4 Hz), 109.7 (d, J = 37.6 Hz), 47.2 (s), 21.6 (s); **^{19}F NMR** (377 MHz, $CDCl_3$): δ −67.32, −67.33; **IR** (NaCl, $CDCl_3$): 1582, 1485, 1472, 1346, 1258, 1167, 1020, 833, 762, 712, 664 cm^{-1}; **m.p.**: 114−115 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{21}H_{18}N_2O_2FS$ (M)$^+$: 381.1073; Found: 381.1074.

*3-(6-Ethoxypyridin-3-yl)-1-tosyl-1,2-dihydroquinoline (**3qa**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and (6-ethoxypyridin-3-yl)boronic acid (67 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 9:1) in 47% yield (38.5 mg) as an orange solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, J = 2.4 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.45 (dd, J = 8.7, 2.6 Hz, 1H), 7.29 (td, J = 7.8, 1.4 Hz, 1H), 7.21 (td, J = 7.5, 1.0 Hz, 1H), 7.15 (d, J = 8.2 Hz, 2H), 7.01 (dd, J =

7.4, 1.1 Hz, 1H), 6.93 (d, J = 8.1 Hz, 2H), 6.72 (d, J = 8.7 Hz, 1H), 6.21 (s, 1H), 4.73 (s, 2H), 4.38 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.80, 143.84, 143.64, 135.73, 135.43, 134.24, 131.58, 130.35, 128.99 (2), 128.03, 127.14 (3), 126.99, 126.98, 126.48, 120.51, 111.08, 62.19, 47.27, 21.59, 14.76; **IR** (NaCl, neat): 3059, 2981, 2926, 2870, 1605, 1498, 1475, 1383, 1346, 1293, 1245, 1164, 1122, 1091, 1033, 1009, 925, 816, 735, 681 cm^{-1}; **m.p.**: 92−95 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{23}H_{23}N_2O_3S$ (M + H)$^+$: 407.14294; Found: 407.14393.

*3-(6-Ethoxypyridin-3-yl)-1-(methylsulfonyl)-1,2-dihydroquinoline (**3qb**).* According to the general procedure C, substrate **1b** (49 mg, 0.2 mmol) and 6-ethoxypyridin-3-ylboronic acid (67 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv). The product was isolated using column chromatography (pentane:EtOAc 7:3) in 66% yield (44 mg) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.36 (d, J = 2.4 Hz, 1H), 7.76 (dd, J = 8.7, 2.6 Hz, 1H), 7.67−7.61 (m, 1H), 7.33−7.23 (m, 3H), 6.86 (s, 1H), 6.79 (dd, J = 8.53, 0.34 Hz, 1H), 4.73 (d, J = 1.1 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ164.13, 144.09, 135.58, 134.38, 132.82, 129.76, 128.43, 127.34, 127.26, 126.37, 125.96, 120.98, 111.51, 62.23, 47.07, 37.72, 14.73; **IR** (NaCl, neat): 3070, 3053, 3025, 2975, 2932, 2896, 2861, 1602, 1569, 1501, 1481, 1454, 1401, 1380, 1342, 1292, 1268, 1155, 1083, 1040, 956, 925, 842, 816, 771, 544 cm^{-1}; **m.p.**: 137−140 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{17}H_{19}N_2O_3S$ (M + H)$^+$: 331.11164; Found: 331.11134.

*3-(Thiophen-3-yl)-1-tosyl-1,2-dihydroquinoline (**3ra**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and thiophen-3-ylboronic acid (51 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 9:1) in 46% yield (33.7 mg) as a pale yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.76 (d, J = 7.8 Hz, 1H), 7.35−7.12 (m, 6H), 7.07 (dd, J = 5.0, 1.4 Hz, 1H), 7.01 (dd, J = 7.4, 1.5 Hz, 1H), 6.89 (d, J = 8.1 Hz, 2H), 6.27 (s, 1H), 4.74 (d, J = 0.9 Hz, 2H), 2.27 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 143.50, 139.23, 135.58, 134.29, 130.43, 129.79, 128.86 (2), 127.76, 127.13 (2), 127.05, 126.94, 126.92, 126.52, 124.55, 121.08, 120.03, 47.53, 21.58; **IR** (NaCl, neat): 3110, 3070, 3037, 2921, 2851, 1596, 1480, 1456, 1343, 1162, 1090, 1078, 811, 769, 707, 694 cm^{-1}; **m.p.**: 175−177 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{20}H_{17}NO_2NaS_2$ (M + Na)$^+$: 390.0592; Found: 390.0603.

*1-(Methylsulfonyl)-3-(thiophen-3-yl)-1,2-dihydroquinoline (**3rb**).* According to the general procedure C, substrate **1b** (49 mg, 0.2 mmol) and 3-thiophenylboronic acid (51 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv). The product was isolated using column chromatography (pentane:EtOAc 85:15) in 78% yield (45.5 mg) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.67−7.61 (m, 1H), 7.44−7.36 (m, 3H), 7.30−7.22 (m, 3H), 6.90 (s, 1H), 4.71 (s, 2H), 2.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ138.69, 134.38, 130.85, 129.84, 128.20, 127.29, 127.23, 127.19, 126.51, 124.64, 121.77, 120.56, 47.33, 37.62; **IR** (NaCl, neat): 3105, 3066, 3018, 2929, 2853, 1625, 1599, 1482, 1455, 1409, 1342, 1322, 1203, 1155, 1118, 1078, 1036, 959, 909, 877, 819, 773, 760, 731 cm^{-1}; **m.p.**: 101−103 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{14}H_{17}N_2O_2S_2$ (M + NH_4)$^+$: 309.07314; Found: 309.07257.

*3-(Furan-3-yl)-1-tosyl-1,2-dihydroquinoline (**3sa**).* According to the general procedure C, substrate **1a** (64 mg, 0.2 mmol) and fur-3-ylboronic acid (45 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 9:1) in 42% yield (29.4 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.9 Hz, 1H), 7.60 (s, 1H), 7.42 (t, J = 1.6 Hz, 1H),7.27 (td, J = 7.7, 1.6 Hz, 1H), 7.21 (dd, J = 7.5, 1.3 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 6.98 (dd, J = 7.5, 1.4 Hz, 1H), 6.93 (d, J = 8.1 Hz, 2H), 6.38 (dd, J = 1.8, 0.7 Hz, 1H), 6.12 (s, 1H), 4.59 (d, J = 0.9 Hz, 2H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.18, 143.54, 139.53, 135.54, 134.32, 130.34, 128.90 (2), 127.64, 127.11 (2), 127.07, 127.02, 126.69, 126.68, 124.31, 119.34, 107.13f, 47.16, 21.58; **IR** (NaCl, neat): 3067, 2921, 2850, 1761, 1597, 1492, 1451, 1348, 1224, 1164, 1122, 1033, 1010, 815, 735, 682 cm^{-1}; **m.p.** (decomp): 138−148 °C; **HRMS** (TOF, EI$^+$): calcd for $C_{20}H_{17}NO_3S$ (M)$^+$: 351.0929; Found: 351.0931.

*3-(Furan-3-yl)-1-(methylsulfonyl)-1,2-dihydroquinoline (**3sb**).* According to the general procedure C, substrate **1b** (48.7 mg, 0.2 mmol) and furan-3-ylboronic acid (45 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 85:15) in 51% yield (28.3 mg) as a pale yellow solid. **^{1}H NMR** (399 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.66−7.60 (m, 1H), 7.49 (t, J = 2 Hz, 1H), 7.30−7.19 (m, 3H), 6.76 (s, 1H), 6.67 (dd, J = 1.8, 0.8 Hz, 1H), 4.57 (d, J = 1.0 Hz, 2H), 2.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.6, 139.9, 134.4, 129.7, 128.1, 127.7, 127.3, 127.1, 126.6, 123.9, 119.8, 107.2, 47.0, 37.6; **IR** (NaCl, neat) 3160, 3057, 3018, 3009, 2928, 2855, 1484, 1336, 1323, 1151, 1079, 1035, 967, 958, 872, 889, 820, 786, 767 cm^{-1}; **m.p.**: 163−167 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{14}H_{14}NO_3S$ (M + H)$^+$: 276.06944; Found: 276.06845.

*7-Methoxy-1-(methylsulfonyl)-3-phenyl-1,2-dihydroquinoline (**3t**).* The product was synthesized according to general procedure C; substrate **1g** (54.7 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was purified by flash chromatography with 0−10% Et_2O/hexanes to provide the title compound in 54% yield (34.1 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.3 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 2.5 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H), 6.89 (s, 1H), 6.84 (dd, J = 8.4, 2.6 Hz, 1H), 4.75 (d, J = 0.8 Hz, 2H), 3.86 (s, 3H), 2.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.7, 137.4, 136.0 132.6, 129.2, 128.4, 128.4, 125.3, 123.1, 121.7, 113.9, 111.5, 77.5, 77.2, 76.8, 55.8, 47.5, 37.8; **IR** (NaCl, $CDCl_3$): 3011, 2362, 1616, 1600, 1496, 1328, 1270, 1213, 1155, 1039, 761, 698, 554 cm^{-1}; **m.p.**: 119−187 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{17}H_{17}NO_3SNa$ (M + Na)$^+$: 338.0821; Found: 338.0823.

*8-Fluoro-1-(methylsulfonyl)-3-phenyl-1,2-dihydroquinoline (**3u**).* The product was synthesized according to general procedure C; substrate **1l** (52.4 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol, 1.5 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was purified by flash chromatography with 0−5% Et_2O/hexanes to provide the title compound in 62% (37.6 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.29−7.21 (m, 1H), 7.11−7.04 (m, 2H), 6.93 (s, 1H), 4.69 (s, 2H), 2.94 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.3 (s), 155.8 (s), 138.5 (s), 136.9 (s), 132.8 (d, J = 1.6 Hz), 129.1 (s), 128.9 (s), 128.1 (d, J = 8.5 Hz), 125.6 (s), 122.7 (d, J = 3.2 Hz), 122.5 (d, J = 12.3 Hz), 121.6 (d, J = 3.4 Hz), 116.0 (d, J = 21.1 Hz), 47.7 (s), 39.6 (d, J = 3.7 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ −118.85 (dd, J = 10.1, 4.8 Hz); **IR** (NaCl, $CDCl_3$): 3063, 3030, 2934, 1615. 1574, 1476, 1343, 1155, 1080, 1042, 968, 872, 835, 746, 696 cm^{-1}; **m.p.**: 58−60 °C; **HRMS** (TOF, EI$^+$): calc'd for $C_{16}H_{14}FNO_2S$ (M + H)$^+$: 303.0729; Found: 303.0728.

*8-Fluoro-1-(methylsulfonyl)-3-(thiophen-3-yl)-1,2-dihydroquinoline (**3v**).* According to the general procedure C, substrate **1l** (52.4 mg, 0.2 mmol) and 3-thiophenylboronic acid (51 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8

mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv). The product was isolated using column chromatography (pentane:EtOAc 8:2) in 73% yield (45.2 mg) as a colorless oil. **^{1}H NMR** (399 MHz, $CDCl_3$): δ 7.44 (dd, J = 2.7, 1.3 Hz, 1H), 7.40 (dd, J = 5.1, 2.8 Hz, 1H), 7.37 (dd, J = 5.1, 1.4 Hz, 1H), 7.23 (ddd, J = 12.7, 7.2, 3.2 Hz, 1H), 7.09−7.00 (m, 2H), 6.91 (d, J = 1.0 Hz, 1H), 4.63 (d, J = 1.0 Hz, 2H), 2.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.2 (d, J = 252.4 Hz), 138.4 (s), 133.4 (s), 132.8 (d, J = 1.7 Hz), 128.2 (d, J = 8.5 Hz), 127.2 (s), 124.8 (s), 122.6 (d, J = 3.2 Hz), 122.3 (d, J = 12.5 Hz), 122.2 (s), 120.2 (d, J = 3.4 Hz), 115.9 (d, J = 21.1 Hz), 47.6 (s), 39.5 (d, J = 3.7 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$): δ −118.17 (dd, J = 10.0, 4.7 Hz); **IR** (NaCl, neat): 3104, 3025, 2930, 2896, 2850, 1611, 1572, 1471, 1342, 1296, 1271, 1220, 1156, 1079, 1006, 961, 909, 863, 836, 794, 730 cm^{-1}; **HRMS** (TOF, EI$^+$): calcd for $C_{14}H_{12}NO_2S_2F$ (M + H)$^+$: 309.0294; Found: 309.0291.

*1-(Methylsulfonyl)-3-(thiophen-3-yl)-1,2-dihydro-1,5-naphthyridine (**3w**).* According to the general procedure C, substrate **1m** (49 mg, 0.2 mmol) and 3-thiophenylboronic acid (51 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv). The product was isolated using column chromatography (pentane:EtOAc 1:1) in 45% yield (26.3 mg) as a colorless solid, which turned dark green upon standing. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (dd, J = 4.8, 1.5 Hz, 1H), 7.91 (ddd, J = 8.1, 1.5, 0.7 Hz, 1H), 7.53−7.49 (m, 1H), 7.45−7.41 (m, 2H), 7.19 (dd, J = 8.1, 4.8 Hz, 1H), 7.10 (s, 1H), 4.78 (d, J = 1.2 Hz, 2H), 2.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.9, 148.1, 138.0, 135.3, 133.4, 131.3, 127.6, 124.9, 123.1, 122.5, 121.7, 47.0, 38.0; **IR** (NaCl, neat): 3105, 3007, 2927, 2850, 1620, 1580, 1435, 1188, 1157, 960, 910, 875, 820, 776, 730 cm^{-1}; **m.p.**: 128−130 °C; **HRMS** (TOF, EI$^+$): calcd for $C_{13}H_{12}N_2O_2S_2$ (M + H)$^+$: 292.0340; Found: 292.0347.

*6-Fluoro-1-(methylsulfonyl)-3-(thiophen-3-yl)-1,2-dihydroquinoline (**3x**).* According to the general procedure C, substrate **1n** (52.4 mg, 0.2 mmol) and 3-thiophenylboronic acid (51 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv). The product was isolated using column chromatography (pentane:EtOAc 9:1) in 70% yield (43.3 mg) as an off-white solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.60 (dd, J = 9.9, 5.1 Hz), 7.50−7.34 (m), 7.03−6.91 (m), 6.85 (s), 4.71 (d, J = 1.1 Hz), 2.61 (s); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 161.5 (d, J = 246 Hz), 138.3 (s), 132.3 (s), 131.6 (d, J = 9 Hz), 130.2 (d, J = 3 Hz), 128.5 (d, J = 9 Hz), 127.5 (s), 124.6 (s), 122.5 (s), 119.8 (d, J = 2 Hz), 114.9 (d, J = 23 Hz), 113.4 (d, J = 23 Hz), 47.5 (s), 37.6 (s); **^{19}F NMR** (282 MHz, $CDCl_3$) δ −115.05 (td, J = 8.4, 5.1 Hz); **IR** (NaCl, $CDCl_3$): 3091, 1485, 1338, 1156, 1076, 964, 827, 806, 769, 558 cm^{-1}; **m.p.**: 185−187 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{14}H_{13}FNO_2S_2$ (M + H)$^+$: 310.0360; Found: 310.0372.

*1-(Methylsulfonyl)-3-(thiophen-3-yl)-7-(trifluoromethyl)-1,2-dihydroquinoline (**3y**).* According to the general procedure C, substrate **1o** (62.3 mg, 0.2 mmol) and 3-thiophenylboronic acid (51 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.5 mg, 5.2 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv). The product was isolated using column chromatography (pentane:EtOAc 8:2) in 78% yield (56.1 mg) as a pale yellow solid. Alternatively, this compound was synthesized by the above procedure, heating at 60 °C for 1.5 h, then to 90 °C for 14.5 h to give 81% yield (58.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93−7.86 (m, 1H), 7.53−7.47 (m, 2H), 7.44 (dd, J = 5.1, 2.8 Hz, 1H), 7.41 (dd, J = 5.1, 1.4 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 6.94 (s, 1H), 4.75 (d, J = 0.9 Hz, 2H), 2.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.1 (s), 134.6 (s), 133.3 (s), 132.9 (s), 129.9 (q, J = 32.8 Hz), 127.6 (s), 127.5 (s), 124.6 (s), 123.9 (q, J = 3.8 Hz), 123.8 (q, J = 272.2 Hz), 123.5 (q, J = 4.0 Hz), 122.9 (s), 119.3 (s), 47.2 (s), 38.0 (d, J = 2.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$): δ −62.84 (s); **IR** (NaCl, neat):3106, 3051, 3014, 2932, 2896, 2852, 1614, 1569, 1502, 1346, 1330, 1297, 1270, 1253, 1225, 1158, 1125, 1071, 1032, 960, 916, 875, 847, 828, 778.763, 740, 663, 633, 556, 536 cm^{-1}; **m.p.**: 122−123 °C; **HRMS** (TOF, ESI$^+$): calcd for $C_{15}H_{16}F_3N_2O_2S_2$ (M + NH_4)$^+$: 377.06053; Found: 377.05937.

*N-(1-(Methylsulfonyl)-3-(thiophen-3-yl)-1,2-dihydroquinolin-7-yl)acetamide (**3z**).* According to the general procedure C, substrate **1p** (60.2 mg, 0.2 mmol) and 3-thiophenylboronic acid (51 mg, 0.4 mmol, 2 equiv) were reacted using $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %), BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), XPhos (3.8 mg, 4 mol %), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) in dioxane:MeOH (1 mL:0.1 mL). The product was isolated using column chromatography (pentane:EtOAc 7:3) in 63% yield (43.9 mg) as a colorless solid. **^{1}H NMR** (399 MHz, *DMSO*): δ 10.11 (s, 1H), 7.74 (s, 1H), 7.70 (s, 1H), 7.64 (dd, J = 5.0, 2.8 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.54 (d, J = 5.0 Hz, 1H), 7.27 (d, J = 8.3 Hz, 1H), 7.10 (s, 1H), 4.63 (s, 2H), 2.72 (s, 3H), 2.05 (s, 3H); **^{13}C NMR** (100 MHz, *DMSO*): δ 168.4, 138.7, 138.6, 134.5, 128.5, 127.5, 127.4, 124.9, 124.5, 121.7, 119.9, 117.0, 115.6, 46.5, 37.8, 24.0; **IR** (NaCl, neat): 3341, 2956, 2922, 2850, 1665, 1585, 1532, 1322, 1155, 1075, 1024, 875, 723 cm^{-1}; **m.p.**: 218−220 °C; **HRMS** (TOF, DART$^+$): calcd for $C_{16}H_{17}N_2O_3S_2$ (M + H)$^+$: 349.06806; Found: 349.06860.

General Procedure D: Domino Synthesis of Chromenes from Arylpropargyl Alkynes 1j. Substrate **1j** (33.3 mg, 0.2 mmol, 1 equiv), arylboronic acid (0.3 mmol, 1.5 equiv), and K_2CO_3 (61 mg, 0.44 mmol, 2.2 equiv) were weighed into a 2-dram vial (Note 2) equipped with a stirring bar and fitted with a septum. The reaction vial was purged with argon, and then toluene (1 mL, 0.2 M) and MeOH (0.1 mL) were added. The catalyst solutions (0.5 mL of each) containing $[Rh(cod)OH]_2$ (2.3 mg, 2.5 mol %) and BINAP (6.23 mg, 5 mol %), $Pd(OAc)_2$ (0.9 mg, 2 mol %), and XPhos (3.8 mg, 4 mol %) were added to this reaction vessel. The septum was exchanged with a Teflon-lined screw cap, and the reaction was heated at 90 °C for 16 h. The crude mixture was filtered though at plug of silica, concentrated under reduced pressure, and purified through column chromatography.

*3-Phenyl-2H-chromene (**4a**).* The product was synthesized according to general procedure D, using phenylboronic acid (36.6 mg, 0.3 mmol, 1.5 equiv) and purified by flash chromatography with 0−3% Et_2O/hexanes to provide the title compound in 59% yield (24.6 mg) as a yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.46−7.26 (m, 5H), 7.17−7.04 (m, 2H), 6.95−6.82 (m, 2H), 6.80 (s, 1H), 5.16 (d, J = 1.4 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 153.4, 136.9, 131.9, 129.2, 128.9, 128.2, 127.2, 124.9, 123.1, 121.7, 120.3, 115.6, 77.6, 77.2, 76.7, 67.3; Spectral data is in accord with the literature.[27]

*4-(2H-Chromen-3-yl)benzonitrile (**4b**).* The product was synthesized according to general procedure D, using (4-cyanophenyl)boronic acid (44 mg, 0.3 mmol, 1.5 equiv) and purified by flash chromatography with 0−3% Et_2O/hexanes to provide the title compound in 27% yield (12.6 mg) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73−7.63 (m, 2H), 7.55−7.48 (m, 2H), 7.19 (td, J = 7.9, 1.6 Hz, 1H), 7.13 (dd, J = 7.5, 1.5 Hz, 1H), 6.98−6.91 (m, 2H), 6.88 (d, J = 8.1 Hz, 1H), 5.15 (d, J = 1.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.7, 141.2, 132.7, 130.3, 129.8, 127.8, 125.3, 123.5, 122.4, 122.1, 118.9, 115.9, 111.3, 77.5, 77.2, 76.8, 66.7; **IR** (NaCl, $CDCl_3$): 2224, 1614, 1599, 1483, 1451, 1412, 1348, 1215, 1090, 1074, 831, 762, 716, 660 cm^{-1}; **m.p.**: 104−105 °C; **HRMS** (TOF, EI$^+$): calc'd for $C_{16}H_{10}NO$ (M + H)$^+$: 232.0762; Found: 232.0760.

*Methyl 4-(2H-Chromen-3-yl)benzoate (**4c**).* The product was synthesized according to general procedure D, using (4-(methoxycarbonyl)phenyl)boronic acid (54 mg, 0.3 mmol, 1.5 equiv) and purified by flash chromatography with 0−3% Et_2O/hexanes to provide the title compound in 50% yield (26.6 mg) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.19−7.13 (m, 1H), 7.11 (dd, J = 7.5, 1.6 Hz, 1H), 6.93 (ddd, J = 7.4, 6.7, 1.1 Hz, 2H), 6.87 (d, J = 8.0 Hz, 1H), 5.18 (s, 2H), 3.93 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.8, 153.6, 141.4, 130.7, 130.2, 129.9, 129.5, 127.6, 124.75, 122.7, 122.4, 121.9, 115.8, 67.0, 52.3; **IR** (NaCl, $CDCl_3$): 2359, 2340, 1724, 1487, 1456, 1431, 1415, 1321, 1279, 1211, 1192, 1107, 1015, 934, 853, 769, 746, 737, 696, 667 cm^{-1}; **m.p.**: 129−132 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{17}H_{15}O_3$ (M + H)$^+$: 267.1021; Found: 267.1018.

Product Derivatizations. *3-(Thiophen-3-yl)quinoline (7).* To the substrate **3rb** (58 mg, 0.2 mmol) in a dry round-bottom flask under a N_2 atmosphere was added anhydrous THF (3.5 mL) and *t*-BuOH (73 mg, 0.6 mmol, 3 equiv), followed by KO*t*-Bu (45 mg, 0.4 mmol, 2 equiv) at r.t. The mixture was stirred at r.t. for 16 h. Upon reaction completion, 10% NaOH (10 mL) was added and the mixture was extracted with EtOAc (2×), washed with water and brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product. The product was purified by flash chromatography with 0−10% Et_2O/hexanes to provide the title compound in 93% yield (39.3 mg) as a white solid 93%. **^{1}H NMR** (400 MHz, *CDCl*$_3$): δ 9.21 (d, J = 2.3 Hz, 1H), 8.29 (d, J = 2.1 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.86 (dd, J = 8.1, 1.4 Hz, 1H), 7.70 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.67 (dd, J = 2.9, 1.4 Hz, 1H), 7.57 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.54 (dd, J = 5.0, 1.4 Hz, 1H), 7.50 (dd, J = 5.0, 2.9 Hz, 1H); Spectral data is in accord with the literature.[4]

(3S,4R)-3-Phenylchroman-3,4-diol (8). To a round-bottom flask equipped with a magnetic stir bar was added AD-mix α (282 mg), followed by 4 mL of a 1:1 mixture of H_2O:*t*-BuOH. With vigorous stirring, the flask was cooled to 0 °C in an ice bath and the substrate **4a** (42 mg, 0.2 mmol) was added at once. The flask was gradually warmed to r.t. and stirred vigorously for 3 d. To the mixture was partitioned with EtOAc and water. The organic phase was washed with water, then brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product. The product was purified by flash chromatography with 0−10% EtOAc/hexanes to provide the title compound as a white solid (38 mg, 78%). The opposite enantiomer was synthesized using the same procedure employing AD-mix β. The enantiomers were separated on HPLC with Chiracel ODH column. 90:10 (hexanes:2-propanol). 0.8 mL/min flow rate. 210 nm. Retention times:13.5 (**8**) and 14.9 min. >99% ee was obtained. $[\alpha]_D^{20}$ = 28.8° cm^2/g (c = 1.0, >99% ee, $CHCl_3$). **^{1}H NMR** (400 MHz, *CDCl*$_3$): δ 7.57−7.47 (m, J = 8.9, 3.7 Hz, 3H), 7.40 (t, J = 7.4 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 5.08 (s, J = 5.4 Hz, 1H), 4.22 (d, J = 11.9 Hz, 1H), 4.14 (d, J = 11.9 Hz, 1H), 2.99 (s, 1H), 2.48 (s, 1H); **^{13}C NMR** (100 MHz, *CDCl*$_3$): δ 153.3, 140.6, 129.5, 129.3, 128.8, 128.2, 125.8, 123.8, 121.7, 116.6, 71.7, 71.0, 70.3; **IR** (NaCl, *CDCl*$_3$): 3408, 1611, 1586, 1489, 1460, 1447, 1229, 1200, 1045, 1026, 964, 910, 787, 756, 733, 700, 607 cm^{-1}; **m.p.**: 76−77 °C; **HRMS** (TOF, ESI$^+$): calc'd for $C_{15}H_{18}NO_3$ (M + H)$^+$: 260.1288; Found: 260.1287.

■ ASSOCIATED CONTENT

Supporting Information

General experimental procedures, NMR spectra of new products, and ^{31}P NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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