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A Homogeneous, Recyclable Polymer Support for Rh(I)-Catalyzed C−C Bond Formation

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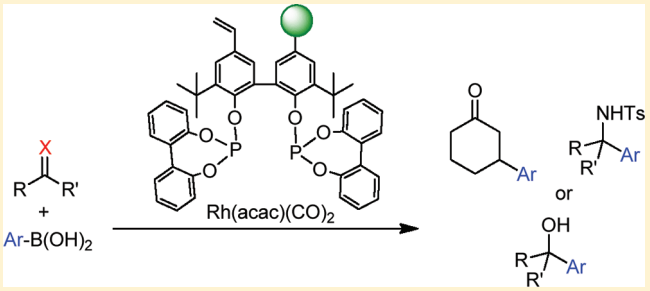
Supporting Information

ABSTRACT: A robust and practical polymer-supported, homogeneous, recyclable biphephos rhodium(I) catalyst has been developed for C−C bond formation reactions. Control of polymer molecular weight allowed tuning of the polymer solubility such that the polymer-supported catalyst is soluble in nonpolar solvents and insoluble in polar solvents. Using the supported rhodium catalysts, addition of aryl and vinylboronic acids to the electrophiles such as enones, aldehydes, *N*-sulfonyl aldimines, and alkynes occurs smoothly to provide products in high yields. Additions of terminal alkynes to enones and industrially relevant hydroformylation reactions have also been successfully carried out. Studies show that the leaching of Rh from the polymer support is low and catalyst recycle can be achieved by simple precipitation and filtration.



INTRODUCTION

Over the past decade, there has been considerable progress in the development of rhodium(I)-catalyzed carbon−carbon bond forming reactions.[1] Additionally, substantial attention has been given to the use of air−and moisture-stable organoboron reagents as reaction partners.[2] Rhodium(I)-catalyzed C−C bond formation reactions are often highly selective;[3] however, the high market price of rhodium and its propensity to fluctuate widely (e.g., 2008 $9500/oz; 2009 $1100/oz)[4] has motivated the development of procedures for nearly quantitative recycle and reuse of this costly metal. Previously, several groups developed different techniques for recycling of rhodium catalysts.[5] For example, immobilization of rhodium catalysts on solid supports such as silica[6] leads to a heterogeneous catalytic system that facilitates recycle but ultimately reduces the catalytic activity and selectivity. Herein we report the design, development, and synthesis of a homogeneous, recyclable polymer support for rhodium(I) and its successful application in C−C bond formation reactions. Exploiting the property of a polymer's differential solubility and phase trafficking by simple precipitation with an antisolvent can be used to recover and reuse the catalyst without appreciable loss of catalytic activity in subsequent runs.[7]

RESULTS AND DISCUSSION

Previously, several research groups[5b−d,8] have developed polystyrene supports that facilitate the recycle of rhodium catalysis. However, the typical polymer supports suffer from serious limitations such as poor solubility, gel formation, tedious procedures to swell the polymer, and limited loading of the ligand in the polymer backbone (e.g., 0.17 mmol/g).[6c] Most of the commercially available or synthesized resins are prepared by conventional radical polymerization of styrene and thus have high molecular weight and/or broad molecular weight distributions. Thus the polymer-supported catalysts derived from these resins often have low and nonuniform solubility. We directly encountered these issues during our initial efforts to synthesize a suitable copolymer to support rhodium catalysts. Specifically, radical copolymerization of styrene and comonomer **2** (10:1) (Figure 1) was initiated by AIBN in THF and carried out at 60 °C for 16 h. GPC analysis of the sample revealed that the molecular weight of the polymer was ∼135 000 and the molecular weight range was broad (PDI = 2.35−2.80). Because of this high molecular weight and wide MW distribution, the JanaPhos polymer existed in two phases, with some dissolved in toluene while much of it formed a gel phase at the bottom of the reactor which reduced the catalytic activity and made the polymer difficult to recycle (Figure 1).

In addition to the poor solubility characteristics of our first-generation support, the path used to synthesize comonomer **2** prevented us from large-scale synthesis of the polymer. Our initial effort to synthesize the comonomer involved a palladium-catalyzed Stille vinylation[9] of the bromo-bis-phenol **5** which was obtained from the oxidative dimerization of 4-bromo-2-*tert*-butylphenol (**4**) (Figure 2). Unfortunately, the oxidative dimerization of 4-bromo-2-*tert*-butylphenol (**4**) yielded only 12% of the desired product **5**. It was gratifying to find that a quantitative

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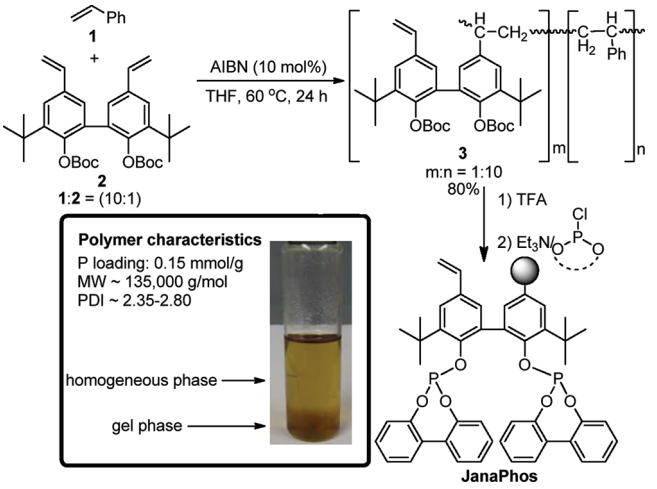

Figure 1. Original synthesis of JanaPhos.

conversion to the desired biphenol **7** was achieved when the electron-rich 2-*tert*-butyl-4-methoxyphenol (**6**) was used as a substrate.[10] Deprotection of the methyl ethers followed by regioselective triflation provided **8**, which was used as a substrate for the requisite Stille coupling after Boc protection of the phenol groups (Figure 2).[9]

With this improved monomer synthesis in hand, we chose to address the poor solubility characteristics of the polymer produced via conventional radical polymerization. We expected that the solubility problems associated with the supported ligand could be solved by synthesis of a polymer support that has a lower molecular weight and a narrow molecular weight distribution. Ultimately, we have been able to synthesize a polymer having comparatively low molecular weight and a narrow molecular weight distribution by utilizing nitroxyl radical-mediated living radical polymerization (Figure 3).[11] To do so, comonomer **2** was subjected to copolymerization with styrene (1:10) at 123 °C for 4 h in the presence of catalytic TEMPO and benzoyl peroxide initiator. Of note, further heating improves the yield of the polymer but leads to the formation of partially insoluble polymer. From the ^{1}H NMR spectrum of the resulting polymer, the comonomer incorporation into the polymer backbone was estimated as 10 mol %, the same as the initial concentration of the individual monomers; thus, the rate of incorporation of comonomer **2** is not very different from that of styrene. Interestingly, end group analysis of the resulting polymer suggests comonomer **2** does not act as a cross-linker under these conditions since only one vinyl group from the comonomer is incorporated into the polymer backbone.

After Boc-group deprotection of the ligand **2**, the polymer is allowed to react with 2 equiv of a chlorophosphite to introduce the chelating ligand onto the polymer backbone;[10a] for simplicity we have termed the resulting polymer-supported biphephos analogue JanaPhos. (Figure 1).[12] The maximum value that is calculated for the phosphorus loading onto the polymer backbone is 1.10 mmol/g, which corresponds to a ligand loading of 0.55 mmol/g. Using ^{31}P NMR spectroscopy we measure a phosphorus loading of 0.65 mmol/g (ligand loading = 0.325 mmol/g); this value was confirmed by ICP-OES analysis. The polymer-supported phosphite is quite soluble in tetrahydrofuran, dichloromethane, and toluene (e.g., 60 mg/mL in toluene) but insoluble in methanol. Thus, it is recovered quantitatively by simple precipitation with methanol followed by filtration.

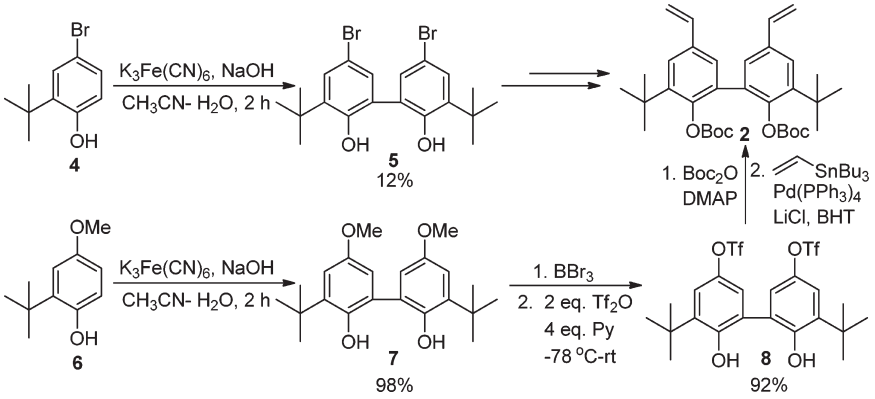

Figure 2. Improved procedure for the preparation of comonomer **2**.

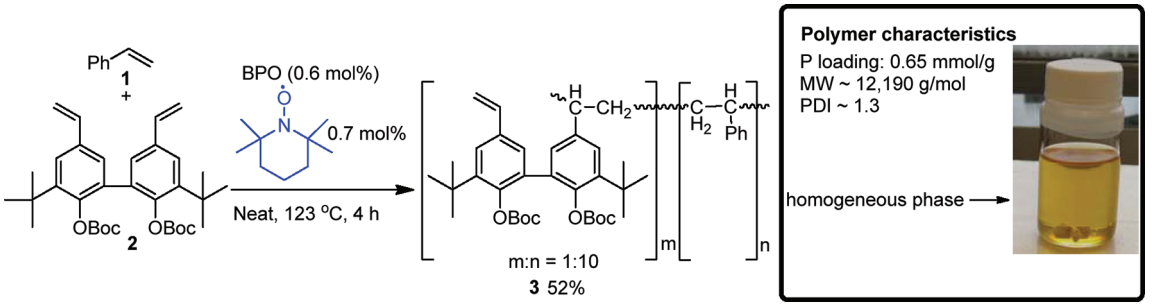

Figure 3. Synthesis of **3** by living radical polymerization.

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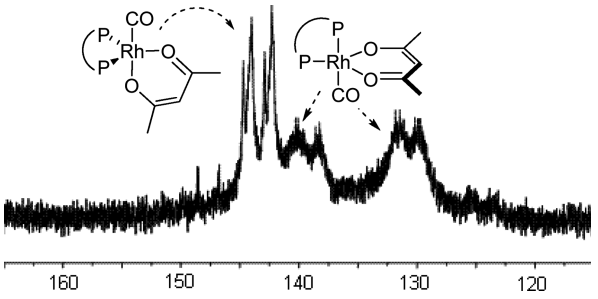


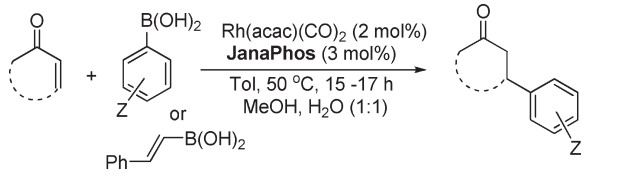
Figure 4. $^{103}Rh-^{31}P$ coupling in JanaPhos−Rh complex.

Next, a supported rhodium catalyst was easily prepared simply by treatment of the polymer support with $Rh(acac)(CO)_2$ for 1 h and the binding of rhodium to the phosphorus was confirmed by ^{31}P NMR spectroscopy. The ability to perform NMR spectroscopy on the supported catalyst highlights one advantage of soluble polymer supports, which allow typical solution-phase spectroscopies to be utilized. After the toluene solution of the polymer was treated with the $Rh(acac)(CO)_2$, the solution turned light yellow. Analysis of this solution by ^{31}P NMR spectroscopy (Figure 4) showed that three new doublets (J_{Rh-P} = 343, 291, 285 Hz) appeared at shifted positions (δ = 143.4, 138.1, 131.0); the rhodium-free polymer exhibits only a broad singlet at 143.4 ppm. The observed coupling constants are very similar to those observed for $^{103}Rh-^{31}P$ couplings in related complexes,[13] offering strong support for binding of the rhodium to the polymer. The simplest explanation for the observation of three doublets is the formation of two complexes with different geometries. The complex where diphosphite binds in the equatorial positions of a trigonal bipyramid would give rise to a single doublet because the P atoms are equivalent. However, binding of the ligand to an equatorial and apical position would lead to inequivalent P doublets. Thus, our tentative assignment is that the ligand binds with two different geometries.

To test the catalytic activity of the polymer-supported rhodium(I) catalyst, we turned our attention to the hydroarylation of enones.[1a−d,3a,12] Gratifyingly, we found that enals, aliphatic enones, chalcones, and cyclic enones all provide high yields of hydroarylation products with our ligand at 50 °C (Table 1). Importantly, these high yields are obtained when using just 1.3 equiv of boronic acid; related reactions using polymer-supported rhodium catalysts require 4−5-fold excess of boronic acids.[5b−d] The scope of the boronic acids that can be utilized was briefly examined. Simple aryl, substituted aryl, and vinyl boronic acids provided good yields of addition products. Moreover, additions to both γ,δ-unsaturated aldehydes and ketones provide hydroarylated products in good yields.

As compared to the rhodium-catalyzed conjugate addition of arylboronic acids,[1a,b] the addition of boronic acids to internal triple bonds has not received as much attention. The Hayashi group has reported the rhodium-catalyzed hydroarylation of alkynes with arylboronic acids and observed a 1,4-shift of rhodium from an alkenyl carbon to an aryl carbon.[3j] In addition, the Lautens group reported the rhodium-catalyzed regioselective hydroarylation of alkynes[14] and the Genêt group reported the addition of arylboronic acids to alkynes, employing water-soluble phosphines as ligands.[15] More recently, the Cheng group reported the phosphine-free rhodium-catalyzed hydroarylation of diarylacetylenes with boronic acids.[16] We were inclined to examine the catalytic activity of our ligand for the stereoselective hydroarylation

Table 1. Rhodium(I)-Catalyzed 1,4-Addition of Arylboronic Acids to Enones



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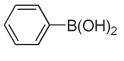
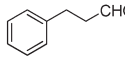
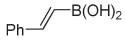
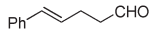
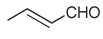
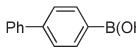
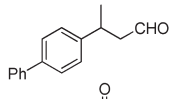
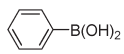
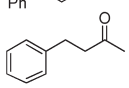
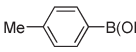
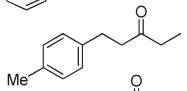
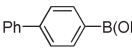
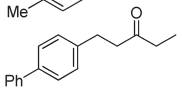
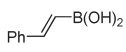
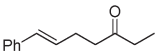
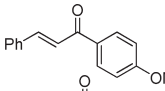
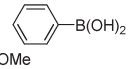
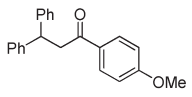
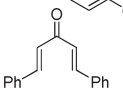
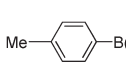
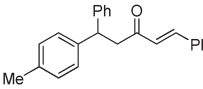
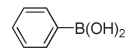
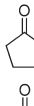
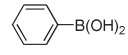
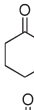
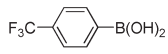
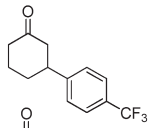
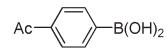
1				82
2				82
3				87
4				86
5				87
6				83
7				77
8				84
9				77
10				92
11				83
12				87
13				75[b]
14				86

[a] Yields refer to pure isolated products. [b] 2 equiv of the boronic acid was used.

of alkynes to get geometrically defined trisubstituted alkenes.[17] Using the JanaPhos−Rh combination, aryl boronic acids underwent addition to internal alkynes providing trisubstituted olefins in high yields at 90 °C (Table 2). As expected, the addition to the triple bond occurs in a syn fashion.[3j] Additions to both diphenylacetylene and dimethyl acetylenedicarboxylate occur in excellent yields with the JanaPhos under standard reaction condition. Importantly, a vinyl boronic acid generates a diene product in

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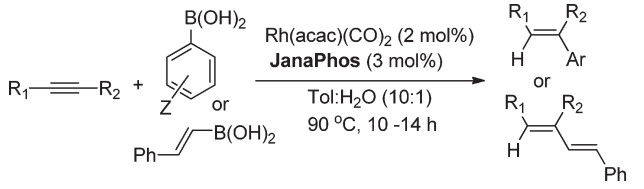
Table 2. Rhodium(I)-Catalyzed Addition of Boronic Acids to Internal Alkynes



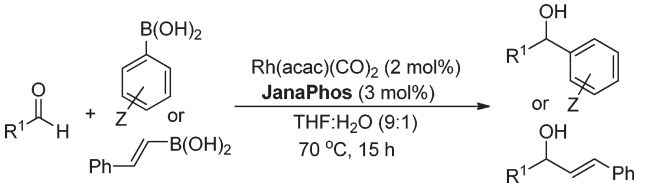
entry	acetylene	boronic acid	product	yield (%)
1	Ph—≡—Ph	Me—B(OH)$_2$	Ph, Ph / H, C$_6$H$_4$(*p*-Me)	87
2	Ph—≡—Ph	MeO—B(OH)$_2$	Ph, Ph / H, C$_6$H$_4$(*p*-OMe)	90
3	MeO$_2$C—≡—CO$_2$Me	B(OH)$_2$	MeO$_2$C, CO$_2$Me / H, Ph	92
4	MeO$_2$C—≡—CO$_2$Me	Ph—B(OH)$_2$	MeO$_2$C, CO$_2$Me / H, Ph	77
5	Ph—≡—Me	Me—B(OH)$_2$	Ph, Me / H, C$_6$H$_4$(*p*-Me)	91

high yield using only 1.5 equiv of boronic acid reaction partner (entry 4, Table 2). Lastly, the regioselectivity of hydroarylation was examined using phenylpropyne (entry 5, Table 2). The reaction was highly regioselective for addition of the aryl group to the less hindered alkyne carbon; such regioselectivity can also be explained by addition to form the more stable α-arylrhodium intermediate.[15b]

The facile transmetalation between boron and rhodium allows access to arylrhodium intermediates that may be useful for addition to many electrophiles.[2b,18] For example, the Miyaura group reported the rhodium-catalyzed addition of organoborornic acids to aldehydes in an aqueous solution.[3c] Later on, several research groups improved the protocol by ligand and catalyst modification.[19] For example, the Gois group has a remarkable development involving the combination of dirhodium precatalyst and NHC ligand for efficient arylation of aldehydes in aqueous solvent.[20]

Our previous successful use of JanaPhos in aqueous biphasic media led us to investigate the hydroarylation of aldehydes to form diaryl methanols, which are key structural elements in an array of pharmacologically active compounds.[21] Initially, a mixture of benzaldehyde, phenylboronic acid, and JanaPhos/(CO)$_2$Rh(acac) was heated at 50 °C in toluene combined with a 1:1 mixture of methanol/water cosolvent. Unfortunately, a very low yield of benzhydrol (20%) was isolated even after prolonged heating. After optimization of the reaction conditions, we were able to isolate a moderate yield (45%) of benzhydrol from a mixture of tetrahydrofuran and water (9:1) at 70 °C (entry 4, Table 3). Fortunately, electron-withdrawing substituents on the aromatic aldehyde facilitated the reaction and provided higher yields of the product alcohols (entry 5, Table 3). Interestingly, Miyaura reported no reaction with 4-nitrobenzaldehyde under their reaction conditions[3c] but we were able to isolate a high yield of product from addition to nitrobenzaldehyde under our conditions (entry 5, Table 3). The arylation of 4-acetylbenzaldehyde was accomplished in a chemoselective manner, resulting in selective

Table 3. Rhodium(I)-Catalyzed 1,2-Addition of Arylboronic Acids to Aldehydes



entry	R$_1$—CHO	boronic acid	product	yield (%)[a]
1	(CH$_2$)$_3$CHO	B(OH)$_2$	(CH$_2$)$_3$, OH	82
2	CHO	B(OH)$_2$	OH	72
3	CHO	Ph—B(OH)$_2$	OH, Ph	65
4	CHO	B(OH)$_2$	OH	45
5	O$_2$N—CHO	B(OH)$_2$	OH, O$_2$N	86
6	Br—CHO	Me—B(OH)$_2$	OH, Br, Me	75
7	H$_3$COC—CHO	H$_3$CO—B(OH)$_2$	OH, H$_3$COC, OCH$_3$	82

[a] Yields refer to isolated pure products.

addition to the aldehyde while the ketone functionality remains intact (entry 7, Table 3). Last, aliphatic aldehydes also underwent arylation under the reaction conditions, providing high yields of secondary alcohols (entries 1 and 2, Table 3).

In addition to the arylations of aldehydes, the JanaPhos−Rh complex catalyzes the 1,2-addition of arylboronic acids to *N*-sulfonyl aldimines.[22] Because *N*-sulfonyl aldimines are sensitive to water, the arylations were carried out in nonaqueous solvent. Ultimately, we found that when a mixture of *N*-sulfonyl aldimines and arylboronic acids are heated at 90 °C in dioxane, the corresponding amine is produced in good to high yields under neutral reaction conditions (Table 4). This allowed the formation of both tosyl and nosyl amines via addition of aryl and vinylboronic acids.

The 1,4-addition of terminal alkynes to enones is a challenging reaction that can suffer from limitations such as the use of stoichiometric transition metals or highly basic reaction conditions to generate acetylides. Moreover, dimerization of the intermediate metal acetylide can be problematic.[23] Nevertheless, the product γ,δ-alkynyl ketones generated from the 1,4-addition of alkynes are useful intermediates for organic synthesis providing ready access to 1,4-diketones,[24] furans,[25] and pyrrols.[26] In 1990, Kovalev published a rhodium-catalyzed addition of alkynes to methyl vinyl ketone.[27] While noteworthy, this methodology did not have practical applicability because of the long reaction times and the use of toxic, volatile, and air-sensitive materials to prepare the catalyst.

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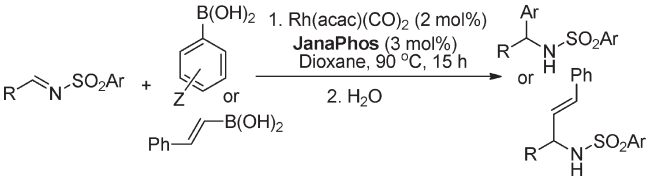
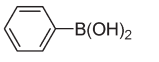
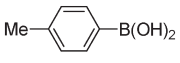
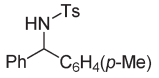
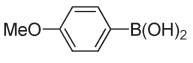
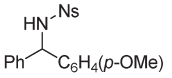
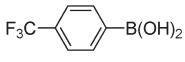
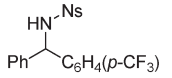
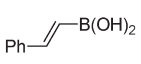
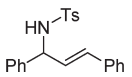
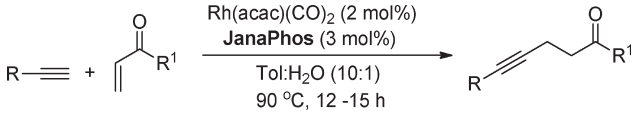
Table 4. Rhodium(I)-Catalyzed 1,2-Addition of Arylboronic Acids to *N*-Sulfonyl Aldimines

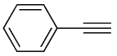
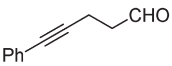
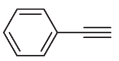
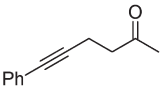
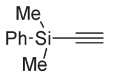
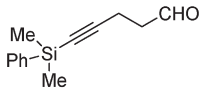
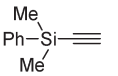
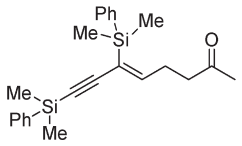


entry	$R{=}N{-}SO_2Ar$	boronic acid	product	yield (%)[a]
1				82
2				87
3				90
4				77
5				73

[a] Yields refer to isolated pure products.

Table 5. Rhodium(I)-Catalyzed 1,4-Addition of Terminal Alkynes to Enones



entry	acetylene	enone	product	yield (%)[a]
1				87
2				83
3				82
4				77[b]

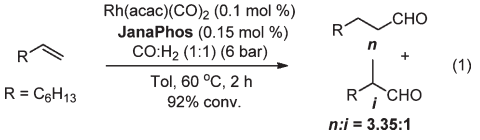
[a] Yields refer to pure isolated products.

Despite recent advancements,[28] an efficient catalytic system to recycle costly rhodium metal for this transformation is still needed.

Keeping these issues in mind, we were motivated to test our ligand and $Rh(acac)(CO)_2$ as a catalyst for the addition of alkynes to enals and enones. Initially, a stoichiometric amount of phenyl acetylene was allowed to undergo conjugate addition to methyl vinyl ketone at 90 °C in toluene and water (10:1), providing a moderate yield (62%) of addition product. The yield was substantially improved when the addition was performed in a sealed tube using 2 equiv of volatile MVK (entry 2, Table 5). Interestingly, when ethynyldimethyl(phenyl)silane was used as the alkyne for addition to MVK, the expected product was not observed. Instead, the expected product underwent a second addition of terminal alkyne to form an enyne product (entry 4, Table 5). This stereo—and regioselective mode of addition has been detailed in recent literature.[29] Interestingly, when acrolein was utilized as the reaction partner, the normal 1,4-addition product is formed in high yield from both phenylacetylene and ethynyldimethyl(phenyl)silane (entries 1 and 3, Table 5).

Finally, we tested the catalytic activity of our JanaPhos—Rh catalyst for the hydroformylation reaction. Hydroformylation chemistry is commercially practiced for the production of aldehyde compounds, which are used as precursors to surfactants and plasticizers. Current technology allows rhodium recycle by using an aqueous—biphase process.[30] However, this process is most useful for propylene hydroformylation and is limited by the low solubility of the long chain olefins in water. Although less expensive cobalt catalysts can be used, they also present serious limitations including the use of high syngas pressure and high temperature to produce linear aldehydes with relatively low selectivity.[31] Thus, a homogeneous recyclable rhodium-based catalyst that is more active and selective, yet operates under mild reaction conditions is still desired. Since JanaPhos provides an effective homogeneous polymer support for rhodium-catalyzed transformations, it was deemed worthwhile to examine the hydroformylation of 1-octene.

Therefore, $Rh(acac)(CO)_2$ and JanaPhos were dissolved in toluene under inert atmosphere. After the addition of 1-octene, syngas (CO: H_2, 1:1 v/v, 6 bar) was purged into the reactor and the whole system was heated at 60 °C. After 2 h, the mixture was cooled to room temperature and methanol (5 vol equiv) was added to it to effect precipitation of the catalyst, which was recovered (95%) by filtration. Under these conditions, the conversion was relatively high (92%), but the selectivity to normal aldehyde was only 3.35:1 (eq 1); this selectivity can be increased by running the reaction in a CO_2-expanded solvent.[33]



(1)

As detailed above, the catalyst can be easily recovered by precipitation using methanol as an antisolvent. Such recovery of the rhodium catalyst is useful not only for economic reasons, but also because contamination of a product by metal impurities is undesirable and must be limited to sub-ppm levels.[32] To further evaluate the recovery of the catalyst, the catalytic conjugate addition of phenylboronic acid to cyclohexenone was performed.[12] As observed for the hydroformylation reaction, addition of methanol to the reaction mixture precipitated the catalyst as a white solid, which was isolated by simple filtration. The recovered catalyst was then used for subsequent addition reactions (Figure 5). First, it was observed that performing the filtration under air was associated with the gradual loss of catalytic activity as gauged by the yield of product. However, filtration under an inert

dx.doi.org/10.1021/jo201476h |J. Org. Chem. 2011, 76, 8376–8385

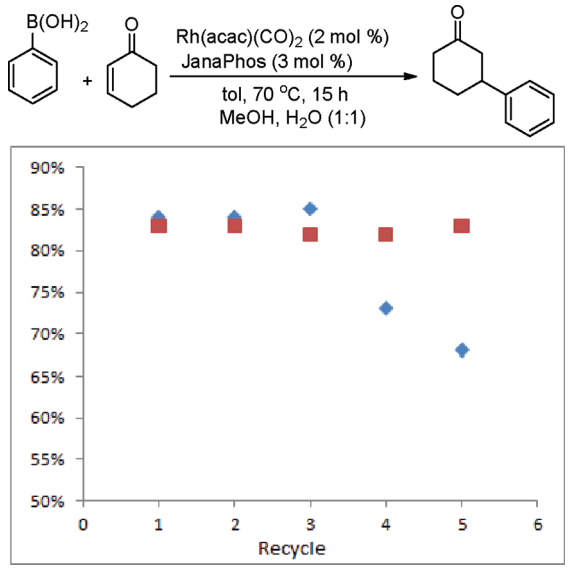


Figure 5. Yield of catalyst recycle via filtration (♦), under air (■), and under N_2.

atmosphere allowed recycle with no appreciable loss of catalytic activity. While the recovered white solid is somewhat unusual for a rhodium-containing catalyst, the $^{31}P-^{103}Rh$ coupling present in the ^{31}P NMR of the recovered catalyst confirms that Rh remains bound to the polymer. The binding of Rh to the recovered polymer has been further confirmed by leaching studies in conjunction with ICP-OES/MS.

Although the catalyst could be recycled by simple precipitation and filtration, such studies do not adequately quantify the leaching of catalyst from the polymer support. Thus, we analyzed the leaching of rhodium from the polymer using membrane nanofiltration.[34] Specifically, the polymer-supported rhodium catalyst dissolved in pure toluene was subjected to continuous filtration through a polyimide membrane for 7 h, and the leached rhodium in the effluent was quantified by ICP-OES. The membrane used had a nominal molecular weight cutoff of 400 Da, which allowed leached rhodium, but not polymer-supported rhodium, to pass through. Under these conditions, over 98% of the rhodium was retained on the polymer. Importantly, evaluation of Rh leaching vs time showed that leaching was initially significant (ca. 2% after 5 h). However, analysis of the filtrate after 7 h revealed that the effluent contained minimal (20 ppb) rhodium. These studies suggest that the polymer contains a small amount (ca. 2%) of loosely bound rhodium, while 98% of the rhodium exists in a bound state that is resistant to leaching. Similar experiments have revealed minimal leaching in the context of hydroformylation reactions.[33]

In summary, a robust and practical polymer-supported, recyclable rhodium(I) catalyst has been developed for C−C bond formation reactions. A series of rhodium(I)-catalyzed reactions have been investigated and high chemical yields of the corresponding products have been isolated, proving the general applicability of the JanaPhos ligand. Control of polymer molecular weight allowed the tuning of solubility such that the polymer-supported catalyst is soluble in nonpolar solvents and insoluble in polar solvents. The recyclability of the catalyst has been demonstrated, and nanofiltration experiments suggest that 98% of the rhodium does not easily leach from the polymer support. Ultimately a low rhodium leaching of 20 ppb can be obtained, allowing efficient recycle of the rhodium catalyst.

EXPERIMENTAL SECTION

Materials. Solvents were dried and purified by treatment with activated alumina (Puresolv, Innovative Technology. Inc.). Other reagents were used, as they were received. ^1H NMR spectra were referenced to residual protio solvent signals. Structural assignments are based on ^1H and ^{13}C for the known compounds, and melting point and ^1H, ^{13}C, DEPT-135, ^{13}P, and IR spectroscopies for the unknown compounds. 2xPLgel mixed D and an oligopore column were used for GPC analysis of the polymer-supported ligand.

*Synthesis of 5,5′-Dimethoxy-3,3′-di-tert-butylbiphenyl-2,2′-diol (**7**).*[35] A solution of 3-*tert*-butyl-4-hydroxyanisole (10.00 g, 55.5 mmol) in methanol (300 mL) was prepared, and a solution of KOH (11.07 g, 198 mmol) and $K_3Fe(CN)_6$ (18.32 g, 55.5 mmol) in water (300 mL) was added dropwise over 1 h at room temperature. The mixture was stirred for 2 h before the addition of 200 mL of water. The suspension was extracted with 500 mL of ethyl acetate twice. The aqueous solution was extracted with 150 mL of ether, and the organic phases were combined and washed with 200 mL of saturated brine. The organic phase was dried over Na_2SO_4. Removal of the solvents under vacuum afforded a light brown solid. Washing with *n*-hexane resulted in an off-white powder; yield: 9.80 g (98%). mp 220−222 °C; ^1H NMR (400 MHz, CD_2Cl_2) δ ppm 6.99 (d, J = 4.12 Hz, 2H), 6.66 (d, J = 4.12 Hz, 2H), 5.15 (s, br, 2H), 3.79 (s, 6H), 1.47 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 153.3, 145.82, 138.8, 123.6, 115.0, 111.9, 55.6, 35.0, 29.2; IR (CH_2Cl_2): ν 3533 (br), 3001, 2985, 1596, 1414, 1392, 1215, 1159 cm^{-1}; calcd HRMS for $C_{22}H_{30}O_4$ (M^+), 358.2144; found, 358.2123.

*Synthesis of 5,5′-Di-tert-butyl-6,6′-dihydroxybiphenyl-3,3′-diyl Bis(trifluoromethanesulfonate) (**8**).* To a stirring solution of **7** (3.6 g, 10 mmol) in CH_2Cl_2 (150 mL) was added boron tribromide (24 mL, 24 mmol, 1 M in DCM) dropwise over 30 min at 0 °C. After addition, the reaction mixture was taken to room temperature and stirred for 30 min. It was quenched by the addition of ice−water, and the white precipitate was dissolved by the addition of diethyl ether. The solution was placed in a separatory funnel and washed with 1 N HCl and brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left a white chalky solid (3.1 g, 93%), which was dissolved in 250 mL of dry dichloromethane. The solution was cooled to −78 °C, and pyridine (3.2 mL, 40 mmol) was added dropwise to it. A dilute solution of triflic anhydride (3.5 mL, 20 mmol) in dichloromethane (100 mL) was added to it over a period of 1 h. After addition, the reaction mixture was taken to room temperature and stirred for 30 min. Then the reaction mixture was partitioned between Et_2O, brine, and 1 N HCl. The organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. It was filtered and concentrated under vacuum. Purification by flash chromatography on silica gel provided a tan gummy liquid (5.24 g, 92% yield). ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.29 (d, J = 4.00 Hz, 2H), 7.04 (d, J = 4.0 Hz, 2H), 5.37 (s, br, 2H), 1.44 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 151.7, 142.9, 140.6, 122.3, 121.9, 121.2, 121.2, 120.4, 117.2, 114.2, 113.9, 35.5, 29.2; IR (CH_2Cl_2): ν 3554 (br), 2970, 1583, 1425, 1371, 1263, 1245, 1217, 745 cm^{-1}; calcd HRMS for $C_{22}H_{24}F_6O_8S_2$ (M + Na), 617.0714; found, 617.0716.

*Synthesis of tert-Butyl 3,3′-Di-tert-butyl-5,5′-divinylbiphenyl-2,2′-diyl Dicarbonate (**2**).* To a stirred solution of **8** (5.94 g, 10 mmol) in CH_2Cl_2 (120 mL) were added di-*tert*-butyl dicarbonate (5.5 mL, 24 mmol) and 4-dimethylaminopyridine (0.12 g, 1.0 mmol). The resulting solution was stirred overnight at 25 °C and then partitioned between Et_2O, brine, and 1 N HCl. The organic layer was washed twice with aqueous $NaHCO_3$ and once with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. Purification by flash chromatography on silica gel provided a colorless solid, which was recrystallized

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in hexane (7.62 g, 96% yield). The resulting solid was dissolved in 80 mL of dry 1,4-dioxane. Tri-*n*-butyl(vinyl)tin (4.2 mL, 13.2 mmol), Pd-$(PPh_3)_4$ (0.28 g, 0.24 mmol), lithium chloride (1.52 g, 36 mmol), and few crystals of 2,6-di-*tert*-butyl-4-methylphenol were added to this solution. The reaction mixture was refluxed at 98 °C for 4 h. After the reaction was complete, as indicated by TLC analysis, it was cooled to room temperature. After removal of dioxane, the residues were dissolved in Et_2O and then 5% aqueous KF was added. The resulting solution was stirred at 25 °C for 2 h. The solution was separated and followed by extraction with Et_2O (3 × 50 mL). The organic portions were combined, washed once with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, crude material was obtained which was purified by column chromatography on silica gel with ethyl acetate:hexane (10:90). A colorless solid was obtained by recrystallization in MeOH (2.8 g, 87% yield). mp 82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 (s, 2H), 7.29 (s, 2H), 6.71 (dd, J_1 = 16.0 Hz, J_2 = 12.0 Hz, 2H), 5.70 (d, J = 20.0 Hz, 2H), 5.22 (d, J = 12.0 Hz, 2H), 1.44 (s, 18H), 1.15 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 151.2, 146.9, 141.6, 136.5, 135.3, 133.1, 128.0, 125.0, 113.8, 82.3, 34.9, 30.6, 27.3; IR (CH_2Cl_2): ν 3088, 2877, 1757, 1580, 1475, 1456, 1397, 1275, 1216, 766 cm^{-1}; calcd HRMS for $C_{34}H_{47}O_6$ (M + 1), 551.3373; found, 551.3355.

*Synthesis of Poly[styrene-co-(2,2′-di-tert-butoxycarbonyloxy-3,3′-di-tert-butyl-5,5′-divinyl-1,1′-biphenyl)] (**3**).* A mixture of **2** (2.201 g, 4 mmol) and styrene (4.6 mL, 40 mmol) was placed in a Schlenk flask. TEMPO (40 mg, 0.25 mmol) and benzoyl peroxide, BPO (48 mg, 0.20 mmol) were added to it, and argon was bubbled through the mixture for 0.5 h prior to the heating. The mixture was then heated at 123 °C for 4 h. It was cooled to room temperature and poured slowly into a beaker containing MeOH (300 mL) to give a white solid precipitate. Further purification was performed by repeating the dissolution−precipitation twice with toluene solvent and MeOH antisolvent. The final product was dried under reduced pressure to give a white solid. (1.25 g, 52% yield).

Synthesis of Polystyrene-co-6,6′-(3,3′-di-tert-butyl-5,5′-divinylbiphenyl-2,2′-diyl)bis(oxy)didibenzo[1,3,2]dioxaphosphepine (JanaPhos). To a solution of copolymer **3** (2.0 g) in dry CH_2Cl_2 (60 mL) was added TFA (2.0 mL). The mixture was stirred over 48 h at 25 °C until IR and ^{1}H NMR showed that Boc was removed completely. Upon cooling to 0 °C, the saturated aqueous $NaHCO_3$ was added until the solution was neutral. The organic layer was separated from the biphasic solution and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed twice with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to give pale-brown solid. The resulting solid was dissolved in CH_2Cl_2 (50 mL) and 15 equiv of Et_3N and 10 equiv of 2,2′-bisphenoxyphosphorous chloride were added to the reaction vessel slowly at 0 °C. The reaction mixture was refluxed for 36 h. Upon cooling to 25 °C, the solution was poured into dry MeOH to give a white precipitate which was further purified by repeating dissolution−precipitation process three times with CH_2Cl_2/MeOH, toluene/MeOH, and THF/MeOH. The final product was dried under vacuum overnight. (86% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ ppm 7.46 (m, br, aromatic), 7.09 (m, br, aromatic), 6.63 (m, br, aromatic), 1.90 (m, br, CH−CH_2 polymer backbone), 1.48 (m, br, *tert*-butyl); ^{31}P NMR: δ ppm 145.4; IR ν (CH_2Cl_2) 3027, 2994, 2925, 2851, 1493, 1477, 1453, 1373, 1269, 1259, 1254, 1194, 768, 746, 723, 712, 697 cm^{-1}.

Representative Experimental Procedure for the 1,4-Addition of Arylboronic Acids to Enones. First, 2-cyclohexen-1-one (96 mg, 1 mmol) and phenylboronic acid (158 mg, 1.3 mmol) were added to a round-bottom flask. A toluene solution (5 mL) containing Rh(acac)$(CO)_2$ (5 mg, 0.02 mmol) and JanaPhos (70 mg, Rh/P = 1/3) was added under an inert atmosphere. A solution of methanol and water (1:1, 0.5 mL) was added to it via syringe, and the resulting mixture was heated at 50 °C for 15 h until the starting material was consumed as indicated by TLC. Then methanol (25 mL) was added, and the catalyst precipitated as a white solid. The catalyst was isolated under an inert atmosphere using a Schlenk filtration apparatus. Evaporation of the filtrate under reduced pressure provided the crude product, which was further purified by column chromatography (10% ethyl acetate in hexane) to obtain the pure product (144 mg, 83% yield). 3-Phenylcyclohexanone: Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36 (t, J = 8.17 Hz, 2H), 7.24−7.28 (m, 3H), 3.01−3.05 (m, 1H), 2.40−2.65 (m, 4H), 2.07−2.17 (m, 2H), 1.78−1.90 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 211.1, 144.4, 128.7, 126.7, 126.6, 49.0, 44.8, 41.2, 32.8, 25.6.

3-Phenylpropanal (entry 1, Table 1):[36a] Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.85 (t, J = 4.00 Hz, 1H), 7.31−7.33 (m, 2H), 7.22−7.26 (m, 3H), 2.99 (t, J = 8.00 Hz, 2H), 2.80−2.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 201.7, 140.4, 128.7, 128.4, 126.4, 45.4, 28.2.

(E)-5-Phenylpent-4-enal (entry 2, Table 1):[36b] Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.83 (t, J = 4.00 Hz, 1H), 7.27−7.34 (m, 6H), 7.19−7.23 (m, 1H), 6.43 (d, J = 8.00 Hz, 1H), 6.17−6.24 (m, 1H), 2.62−2.66 (m, 2H), 2.53−2.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 202.0, 137.3, 131.2, 128.7, 128.3, 127.4, 126.2, 43.5, 25.6.

3-(Biphenyl-4-yl)butanal (entry 3, Table 1):[36c] Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.77 (t, J = 4.00 Hz, 1H), 7.57−7.62 (m, 4H), 7.47 (t, J = 8.00 Hz, 2H), 7.28−7.39 (m, 3H), 3.42−3.48 (m, 1H), 2.70−2.86 (m, 2H), 1.39 (d, J = 4.00 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 201.9, 144.6, 140.9, 139.6, 128.8, 127.5, 127.3, 127.1, 51.8, 34.0, 22.3.

4-Phenylbutan-2-one (entry 4, Table 1):[5b] Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.31 (d, J = 8.13 Hz, 2H), 7.21−7.24 (m, 3H), 2.93 (t, J = 8.00 Hz, 2H), 2.78 (t, J = 8.00 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 208.0, 141.0, 128.5, 128.3, 126.1, 45.2, 30.1, 29.7.

1-p-Tolylpentan-3-one (entry 5, Table 1):[36d] Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.10−7.15 (m, 4H), 2. 91 (t, J = 8.12 Hz, 2H), 2. 75 (t, J = 8.12 Hz, 2H), 2.44 (q, J = 8.12 Hz, 2H), 2.36 (s, 3H), 1.09 (t, J = 8.12 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 210.8, 138.1, 135.5, 129.2, 128.2, 44.1, 36.1, 29.5, 21.0, 7.8.

1-(Biphenyl-4-yl)pentan-3-one (entry 6, Table 1). Colorless solid, mp 62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (d, J = 8.12 Hz, 2H), 7.57 (d, J = 8.12 Hz, 2H), 7.48 (t, J = 8.00 Hz, 2H), 7.38−7.40 (m, 1H), 7.31 (d, J = 8.00 Hz, 2H), 3.00 (t, J = 8.00 Hz, 2H), 2.81 (t, J = 8.00 Hz, 2H), 2.47 (q, J = 8.00 Hz, 2H), 1.11 (t, J = 8.00 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 210.6, 141.0, 140.4, 139.1, 128.8, 128.8, 127.2, 127.2, 127.0, 43.8, 36.2, 29.5, 7.8; IR (CH_2Cl_2): ν 2979, 2939, 1712, 1519, 1487, 1409, 1377, 1363, 1112, 831, 765 cm^{-1}; calcd HRMS for $C_{17}H_{18}ONa$ (M + Na), 261.1255; found, 261.1294.

(E)-7-Phenylhept-6-en-3-one (entry 7, Table 1):[36e] Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28−7.37(m, 4H), 7.21−7.24 (m, 1H), 6.43 (d, J = 8.12 Hz, 1H), 6.19−6.26 (m, 1H), 2.63 (t, J = 4.13 Hz, 2H), 2.45−2.54 (m, 4H), 1.10 (t, J = 8.12 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 210.8, 137.5, 130.7, 129.1, 128.6, 127.1, 126.1, 41.9, 36.1, 27.3, 7.9.

1-(4-Methoxyphenyl)-3,3-diphenylpropan-1-one (entry 8, Table 1):[36f] Colorless solid, mp 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.96 (d, J = 8.13 Hz, 2H), 7.28−7.30 (m, 8H), 7.19−7.22(m, 2H), 6.94 (d, J = 8.13 Hz, 2H), 4.86 (t, J = 8.17 Hz, 1H), 3.88 (s, 3H), 3.72 (d, J = 4.13 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196.6, 163.6, 144.4, 130.4, 130.2, 128.6, 128.0, 126.4, 113.8, 55.6, 46.1, 44.4.

(E)-1,5-Diphenyl-5-p-tolylpent-1-en-3-one (entry 9, Table 2). Colorless solid, mp 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48−7.53 (m, 3H), 7.37−7.39 (m, 3H), 7.26−7.27 (m, 4H), 7.14−7.7.16 (m, 3H), 7.08 (d, J = 8.00 Hz, 2H), 6.69 (d, J = 16.0 Hz, 1H), 4.69 (d, J = 8.00 Hz, 1H), 3.41 (d, J = 8.00 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 198.3, 144.4, 142.9, 141.1, 136.0, 134.6, 130.6, 129.4,

129.0, 128.7, 128.4, 127.9, 127.8, 126.4, 126.4, 47.2, 45.9, 21.1; IR (CH_2Cl_2): ν 3060, 2350, 16087, 1604, 1589, 1421, 1367, 1259, 757 cm^{-1}; calcd HRMS for $C_{24}H_{22}ONa$ (M + Na), 349.1568; found, 349.1581.

3-Phenylcyclopentanone (entry 10, Table 1):[5c] Colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.36 (t, J = 8.13 Hz, 2H), 7.25−7.27 (m, 3H), 3.38−3.47 (m, 1H), 2.66 (dd, J = 8.12 Hz, 1H), 2.25−2.51 (m, 4H),1.94−2.05 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 218.5, 143.0, 128.7, 126.7, 45.8, 42.2, 38.9, 31.0.

3-(4-(Trifluoromethyl)phenyl)cyclohexanone (entry 12, Table 1):[3k] Colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, J = 8.00 Hz, 2H), 7.33 (d, J = 8.00 Hz, 2H), 3.05−3.08 (m, 1H), 2.38−2.62 (m, 4H), 2.14−2.19 (m, 1H), 2.07−2.11 (m, 1H), 1.72−1.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 210.4, 148.3, 129.3, 127.1, 125.8, 122.9, 48.6, 44.6, 41.2, 32.6, 25.5.

3-(4-Acetylphenyl)cyclohexanone (entry 13, Table 1):[3k] Colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.91 (d, J = 8.00 Hz, 2H), 7.31 (d, J = 8.00 Hz, 2H), 3.04−3.09 (m, 1H), 2.57 (s, 3H), 2.35−2.55 (m, 4H), 2.07−2.17 (m, 2H), 2.07−2.11 (m, 1H), 1.77−1.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 210.4, 197.7, 149.7, 135.8, 128.9, 126.9, 48.5, 44.7, 41.2, 32.5, 26.7, 25.5.

3-Phenylcycloheptanone (entry 14, Table 1):[5c] Colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.31−7.38 (m, 2H), 7.19−7.24 (m, 3H), 2.92−2.99 (m, 2H), 2.60−2.69 (m, 3H), 2.00−2.14 (m, 3H), 1.71−1.79 (m, 2H), 1.51−1.63 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 213.6, 147.0, 128.7, 126.5, 126.4, 51.4, 44.0, 42.8, 39.3, 29.3, 24.3.

General Experimental Procedure for the Addition of Arylboronic Acids to Internal Alkynes. Representative Experimental Procedure of 4-Tolylboronic Acid and Diphenylacetylene. A mixture of diphenylacetylene (178 mg, 1 mmol) and acrolein (112 mg, 2 mmol) was added to a round-bottom flask. An aqueous toluene mixture (Tol:H_2O, 10:1) (5 mL) containing Rh(acac)$(CO)_2$ (5 mg, 0.02 mmol) and JanaPhos (70 mg, Rh/P = 1/3) was added under an inert atmosphere. The reaction mixture was heated at 90 °C for 12 h until the starting material was consumed as indicated by TLC. Then 25 mL of methanol was added to the reaction mixture, and the catalyst precipitated as a white solid. The catalyst was isolated under an inert atmosphere using a Schlenk filtration apparatus. Evaporation of the filtrate under reduced pressure provided the crude product, which was further purified by column chromatography (10% ethyl acetate in hexane) to obtain the pure product (250 mg, 93% yield). **(*E*)-(1-*p*-Tolylethene-1,2-diyl)dibenzene:**[37a] Colorless solid (mp 93 °C), ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.28−7.37 (m, 3H), 7.23−7.27 (m, 4H), 7.12−1.18 (m, 5H), 7.04−7.06 (m, 2H), 6.98 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 142.6, 140.7, 140.6, 137.6, 137.5, 130.5, 129.6, 129.0, 128.7, 128.1, 127.6, 127.5, 126.7, 21.3.

(E)-(1-(4-Methoxyphenyl)ethene-1,2-diyl)dibenzene (entry 2, Table 2):[37a] Colorless viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.29−7.35 (m, 6H), 7.04−7.13 (m, 6H), 6.88−6.93 (m, 3H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 159.4, 142.3, 140.7, 137.7, 136.2, 130.5, 129.6, 128.9, 128.7, 128.1, 127.5, 126.7, 126.6, 113.7, 55.5.

Dimethyl 2-phenylmaleate (entry 3, Table 2):[37b] Colorless viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.50−7.52 (m, 2H), 7.42−7.46 (m, 3H), 6.35 (s, 1H), 3.98 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.5, 165.6, 149.1, 133.2, 130.8, 129.2, 126.9, 117.1, 52.9, 52.2.

Dimethyl 2-((E)-Styryl)maleate (entry 4, Table 2):[37c] Colorless solid, mp 84.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.43−7.46 (m, 2H), 7.32−7.38 (m, 3H), 6.78 (d, J = 1.32 Hz, 2H), 5.96 (s, 1H), 3.97 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.0, 165.7, 148.2, 138.6, 135.5, 130.5, 129.0, 124.3, 118.8, 52.9, 52.1.

(E)-1-Methyl-4-(1-phenylprop-1-en-2-yl)benzene (entry 5, Table 2):[37d] Colorless viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.25−7.34 (m, 5H), 7.07−7.15 (m, 4H), 6.72 (s, 1H), 2.27 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 141.2, 138.6, 137.4, 137.1, 129.3, 129.1, 128.3, 127.1, 126.5, 126.0, 21.2, 17.6.

Representative Experimental Procedure for the 1,2-Addition of Arylboronic Acids to Aldehydes. A mixture of 4-nitrobenzaldehyde (150 mg, 1 mmol) and phenylboronic acid (158 mg, 1.3 mmol) was added to a round-bottom flask. An aqueous THF solution (THF:H_2O, 9:1) (5 mL) containing Rh(acac)$(CO)_2$ (5 mg, 0.02 mmol) and JanaPhos (70 mg, Rh/P = 1/3) was added. The resulting reaction mixture was heated at 70 °C for 15 h until the starting material was consumed as indicated by TLC. Then methanol (25 mL) was added to the mixture, and the catalyst precipitated as a white solid. The catalyst was isolated under an inert atmosphere using a Schlenk filtration apparatus. Evaporation of the filtrate under reduced pressure provided the crude product, which was further purified by column chromatography (20% ethyl acetate in hexane) to obtain the pure product (198 mg, 86% yield). **(4-Nitrophenyl)(phenyl)methanol:** Colorless solid (mp 82 °C), ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.18 (d, J = 8.12 Hz, 2H), 7.57 (d, J = 8.12 Hz, 2H), 7.31−7.38 (m, 5H), 5.92 (d, J = 4.00 Hz, 1H), 2.43 (d, J = 4.00 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 150.8, 147.3, 142.8, 129.1, 128.5, 127.2, 126.8, 123.8, 75.6.

1-Phenylhexan-1-ol (entry 1, Table 3):[38a] Colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.30−7.38 (m, 5H), 4.63 (t, J = 8.00 Hz, 1H), 2.59 (s, 1H), 1.69−1.84 (m, 2H), 1.29−1.44 (m, 6H), 0.94 (t, J = 8.00 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 145.1, 128.4, 127.4, 126.0, 74.6, 39.1, 31.8, 25.6, 22.6, 14.1.

1-Phenylhexan-1-ol (entry 2, Table 3):[38b] Colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.36−7.39 (m, 4H), 7.30−7.34 (m, 3H), 7.22−7.24 (m, 3H), 4.70 (dd, J = 8.00 Hz, 1H), 2.65−2.82 (m, 2H), 2.04−2.17 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 144.6, 141.9, 128.6, 128.5, 128.5, 127.7, 126.0, 125.9, 73.9, 40.5, 32.1.

(E)-1,3-Diphenylprop-2-en-1-ol (entry 3, Table 3):[38c] Colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.38−7.48 (m, 6H), 7.26−7.35 (m, 4H), 6.73 (d, J = 16.22 Hz, 1H), 6.42 (dd, J = 8.13 Hz, 1H), 5.43 (dd, J = 4.10 Hz, 1H), 2.05 (d, J = 4.10 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 142.8, 136.6, 131.6, 130.7, 128.7, 128.7, 127.9, 128.9, 126.7, 126.4, 75.3.

Diphenylmethanol (entry 4, Table 3). Colorless solid, mp 66 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.30−7.43 (m, 10H), 5.84 (s, 1H), 2.51 (s, br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 143.9, 128.6, 127.6, 126.6, 76.3.

(4-Bromophenyl)(p-tolyl)methanol (entry 6, Table 3):[38d] Colorless solid, mp 82 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 (d, J = 8.11 Hz, 2H), 7.20 (d, J = 8.11 Hz, 2H), 7.17 (d, J = 8.10 Hz, 2H), 7.11 (d, J = 8.10 Hz, 2H), 5.68 (d, J = 4.12 Hz, 1H), 2.32 (d, J = 4.12 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 143.0, 140.6, 147.7, 131.6, 129.4, 128.2, 126.6, 121.4, 75.5, 21.2.

1-(4-(Hydroxy(4-methoxyphenyl)methyl)phenyl)ethanone (entry 7, Table 3):[38e] Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.87 (d, J = 8.32 Hz, 2H), 7.44 (d, J = 8.16 Hz, 2H), 7.23 (d, J = 8.60 Hz, 2H), 6.83 (d, J = 8.72 Hz, 2H), 5.79 (s, 1H), 3.75 (s, 3H), 2.98 (s, br, 1H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 198.2, 159.3, 149.5, 136.0, 135.7, 128.6, 128.1, 126.4, 114.1, 75.4, 55.3, 26.7.

Representative Experimental Procedure for the 1,2-Addition of Arylboronic Acids to N-Sulfonyl Aldimines. A mixture of freshly recrystallized (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide (260 mg, 1 mmol) and phenylboronic acid (158 mg, 1.3 mmol) was placed in a round-bottom flask. A dioxane (5 mL) solution containing Rh(acac)$(CO)_2$ (5 mg, 0.02 mmol) and JanaPhos (70 mg, Rh/P = 1/3) was added. The reaction mixture was heated at 90 °C for 15 h until the starting material was consumed as indicated by TLC. Then 25 mL of methanol was added to the mixture, and the catalyst precipitated as a white solid. The catalyst was isolated under an inert atmosphere using a Schlenk filtration apparatus. Evaporation of the filtrate under reduced pressure provided the crude product, which was further purified by column chromatography (30% ethyl acetate in hexane) to obtain the pure product (293 mg, 87% yield). Colorless solid, mp 142−144 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.56 (d, J = 8.30 Hz, 2H),

7.19−7.21 (m, 6H), 7.08−7.13 (m, 6H), 5.57 (d, J = 7.16 Hz, 1H), 5.22 (d, J = 7.08 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 143.3, 140.6, 137.4, 129.5, 128.7, 127.7, 127.5, 127.3, 61.4, 21.6.

4-Methyl-N-(phenyl(p-tolyl)methyl)benzenesulfonamide (entry 2, Table 4):[39a] Colorless solid, mp 132−134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.56 (d, J = 8.30 Hz, 2H), 7.18−7.19 (m, 3H), 7.10−7.13 (m, 4H), 6.97−7.01 (m, 4H), 5.53 (d, J = 7.25 Hz, 1H), 5.35 (d, J = 7.25 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 143.2, 140.8, 137.8, 137.5, 137.4, 129.4, 129.3, 128.6, 127.5, 127.4, 127.4, 127.3, 61.2, 21.6, 21.1.

N-((4-Methoxyphenyl)(phenyl)methyl)-4-nitrobenzenesulfonamide (entry 3, Table 4):[39b] Colorless solid, mp 167−169 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.11 (d, J = 8.95 Hz, 2H), 7.75 (d, J = 9.00 Hz, 2H), 7.20−7.21 (m, 3H), 7.08−7.10 (m, 2H), 7.01 (d, J = 6.50 Hz, 2H), 6.73 (d, J = 6.50 Hz, 2H), 5.68 (d, J = 7.15 Hz, 1H), 5.20 (d, J = 7.15 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.5, 149.8, 146.5, 139.7, 131.7, 128.8, 128.5, 128.1, 127.4, 123.9, 114.2, 61.3, 55.4.

4-Nitro-N-(phenyl(4-(trifluoromethyl)phenyl)methyl)benzenesulfonamide (entry 4, Table 4):[39c] Colorless solid, mp 187−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.16 (d, J = 8.76 Hz, 2H), 7.80 (d, J = 8.80 Hz, 2H), 7.52 (d, J = 8.08 Hz, 2H), 7.32 (d, J = 8.08 Hz, 2H), 7.25−7.28 (m, 3H), 7.05−7.07 (m, 2H), 5.77 (d, J = 7.28 Hz, 1H), 5.44 (d, J = 7.28 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 150.0, 146.1, 143.6, 138.8, 129.2, 128.7, 128.4, 127.9, 127.4, 125.83, 125.80, 124.1, 61.4.

(E)-N-(1,3-Diphenylallyl)-4-methylbenzenesulfonamide (entry 5, Table 4):[39c] Colorless solid, mp 112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.65 (d, J = 8.30 Hz, 2H), 7.14−7.27 (m, 12H), 6.35 (d, J = 15.8 Hz, 1H), 6.07 (dd, J = 15.80, 6.75 Hz, 1H), 5.11 (t, J = 6.65 Hz, 1H), 4.91 (d, J = 7.05 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.4, 139.7, 137.8, 136.1, 132.3, 129.6, 128.9, 128.6, 128.3, 128.1, 128.0, 127.5, 127.2, 126.7, 59.9, 21.6.

Representative Experimental Procedure for the 1,4-Addition of Terminal Alkynes to Enones. A mixture of phenylacetylene (102 mg, 1 mmol) and acrolein (158 mg, 1.3 mmol) was added to a thick glass-walled reaction tube. An aqueous toluene mixture (Tol:H_2O, 10:1) (5 mL) containing Rh(acac)$(CO)_2$ (5 mg, 0.02 mmol) and JanaPhos (70 mg, Rh/P = 1/3) was added under an inert atmosphere. The reaction mixture was heated at 90 °C for 13 h until the starting material was consumed as indicated by TLC. Then 25 mL methanol was added to the reaction mixture, and the catalyst precipitated as a white solid. The catalyst was isolated under an inert atmosphere using a Schlenk filtration apparatus. Evaporation of the filtrate under reduced pressure provided the crude product, which was further purified by column chromatography (10% ethyl acetate in hexane) to obtain the pure product (143 mg, 91% yield). 5-Phenylpent-4-ynal:[40a] Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.88 (t, J = 1.90 Hz, 1H), 7.39−7.42 (m, 2H), 7.28−7.32 (m, 3H), 2.75−2.81 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 200.63, 131.7, 128.3, 128.0, 123.4, 87.8, 81.6, 42.7, 12.8.

6-Phenylhex-5-yn-2-one (entry 2, Table 5):[40b] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.38−7.40 (m, 2H), 7.28−7.30 (m, 3H), 2.79 (t, J = 7.10 2H), 2.69 (t, J = 7.10 2H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 206.8, 131.7, 128.54, 128.51, 127.9, 88.6, 81.1, 42.7, 30.1, 14.2.

5-(Dimethyl(phenyl)silyl)pent-4-ynal (entry 3, Table 5). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.81 (t, J = 1.16 Hz, 1H), 7.59−7.62 (m, 2H), 7.37−7.39 (m, 3H), 2.73 (t, J = 6.64 Hz, 2H), 2.59 (t, J = 6.65 Hz, 2H), 0.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 201.1, 138.0, 134.4, 130.2, 128.7, 107.4, 84.6, 43.3, 14.0, 0.0, −0.2; IR (CH_2Cl_2): ν 3060, 2227, 1716, 1604, 1589, 1421, 1367, 1259, 757 cm^{-1}; calcd HRMS for $C_{13}H_{17}OSi$ (M + H), 217.1049; found, 217.1053.

8-(Dimethyl(phenyl)silyl)-6-((dimethyl(phenyl)silyl)ethynyl)oct-5-en-7-yn-2-one (entry 4, Table 5). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53−7.58 (m, 4H), 7.32−7.38 (m, 6H), 6.15 (t, J = 7.01 Hz, 2H), 2.69 (t, J = 7.04 Hz, 2H), 2.54 (t, J = 7.04 Hz, 2H), 2.11 (s, 3H), 0.42 (s, 6H), 0.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 207.9, 152.1, 137.5, 136.9, 134.1, 133.7, 129.3, 129.2, 127.8, 127.7, 124.5, 105.7, 101.5, 42.4, 29.7, 27.1, −0.7, −3.4; IR (CH_2Cl_2): ν 3060, 2225, 1713, 1615, 1604, 1589, 1421, 1368, 1259, 751 cm^{-1}; calcd HRMS for $C_{24}H_{31}OSi_2$ (M + H), 391.1913; found, 391.1917.

Experimental Procedure for the Hydroformylation of 1-Octene:[33] In a stainless steel high pressure reactor with thick-walled glass window and magnetic stirring bar, Rh(acac)$(CO)_2$ (2.6 mg, 0.01 mmol) and JanaPhos (Rh/P = 1/3) was dissolved in toluene (3.6 mL) under inert atmosphere. The solution was stirred overnight at 25 °C. After the addition of 1-octene (1.5 mL, 10.0 mmol) under an inert atmosphere, the reactor was connected to syngas (CO: H_2, 1:1 v/v). The reactor was heated via a thermocoil wrapping. After a temperature of 60 °C (ca. 12 min) was achieved, the reaction mixture was flushed five times with syngas and maintained at a constant syngas pressure of 6 bar. After 2 h, the reaction mixture was cooled to room temperature and depressurized by the slow release of syngas inside an efficient fume cupboard. After addition of methanol (5 mL), a white precipitation of the catalyst was separated by filtration. [The isolated catalyst was effective for subsequent hydroformylations and provided identical activity and selectivity.] The product aldehydes were characterized by gas chromatography in combination with ^{1}H NMR spectroscopy. **(Nonanal + 2-Methyloctanal):** Colorless liquid, linear/branched ratio, 2.1:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.76 (t, J = 4.00 Hz, 1H), 9.61 (d, J = 4.00 Hz, 1H), 2.42 (dt, J_1 = 8.00 Hz, J_2 = 4.00 Hz, 2H) 2.34 (t, J = 8.00 Hz, 2H), 1.59−1.64 (m, 5H), 1.27−1.30 (m, 28H), 1.17 (d, J = 4.00 Hz, 1H), 1.09 (d, J = 4.00 Hz, 1H), 0.88 (t, J = 8.00 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 205.5, 203.0, 183.2, 180.0, 46.3, 43.9, 39.4, 34.1, 33.5, 31.8, 31.65, 30.5, 29.4, 29.30, 29.27, 29.2, 29.15, 29.08, 29.05, 27.1, 26.9, 24.7, 22.61, 22.57, 22.55, 18.11, 18.09.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and complete compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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