JOC The Journal of Organic Chemistry

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Construction of Bulky Ligand Libraries by Ru(II)-Catalyzed P(III)-Assisted ortho-C−H Secondary Alkylation

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Cite This: https://doi.org/10.1021/acs.joc.1c01329 Read Online

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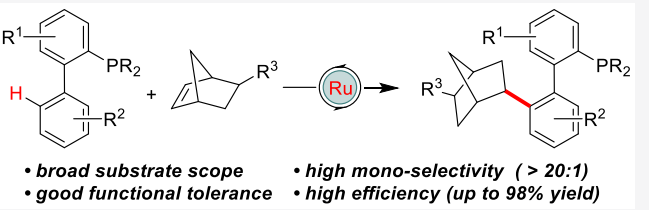
ABSTRACT: Modification of commercially available biaryl monophosphine ligands via ruthenium(II)-catalyzed P(III)-directed-catalyzed ortho C−H secondary alkylation is described. The use of highly ring-strained norbornene as a secondary alkylating reagent is the key to this transformation. A series of highly bulky ligands with a norbornyl group were obtained in excellent yields. The modified ligands with secondary alkyl group outperformed common substituted phosphines in the Suzuki−Miyaura cross-coupling reaction at a ppm mole level of Pd catalyst.



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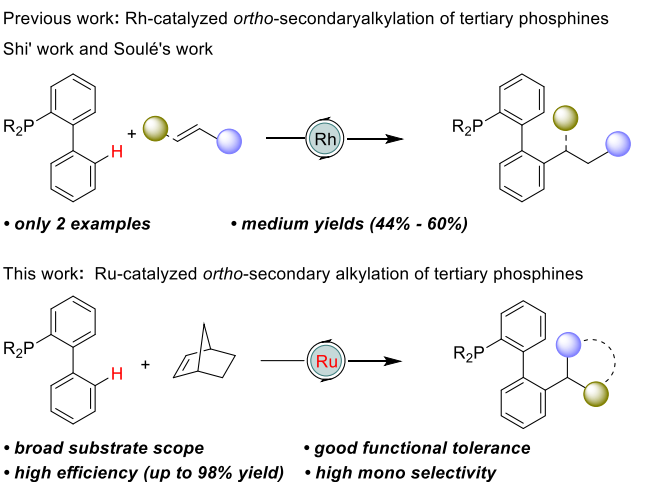
INTRODUCTION

Due to the important role of phosphine ligands in the field of metal catalysis, the design and synthesis of tertiary phosphine ligands have always been the focus and frontier of organic synthesis.[1] The introduction of bulky substituents in the ortho position of tertiary phosphine is a common and effective strategy for designing phosphine ligands, as the existence of highly sterically hindered substituents cannot only inhibit the ligand conversion but also improve the metal catalytic activity.[2] With this strategy, a series of general and efficient phosphine ligands, such as XPhos, BrettPhos, and RockPhos have been designed by Buchwald and others.[3] At present, synthesis of alkyl substituted phosphines mainly relies on the traditional multistep synthetic route,[4] which survived under harsh conditions, poor tolerance of functional groups, and low efficiency, thus limiting the efficient synthesis and development of new phosphines.

Late-stage diversification through regioselective C−H bond functionalization of phosphorus compounds has recently emerged as a suitable alternative to prepare new phosphines.[5] To avoid catalyst poisoning, the phosphorus atom has to be oxidized to act as a P(V) directing group.[6] In 2014, Clark et al. demonstrated that P(III) could act as a directing group in Ir-catalyzed C−H bond borylation of JohnPhos derivatives.[7] Since then, a series of novel ligands via ortho C−H borylation,[8] arylation,[9] alkylation,[10] alkenylation,[10a,11] and silylation[12] of phosphines have been successfully developed. However, direct installation of bulky secondary alkyl groups into phosphine ligands via P-directed ortho C−H activation remains a challenge because of the sterically hindered effect. As far as we know, there are only two examples reported about ortho secondary alkylated phosphine products, and the yields are not very high (44% and 60%).[10] Herein, we report a general and efficient synthesis of ortho secondary alkyl-substituted phosphine ligands via P-directed Ru(II)-catalyzed ortho C−H alkylation reaction (Scheme 1).

Norbornene is an effective alkylating reagent widely used in the field of C−H activation owing to its unique electronic and steric properties.[13] Inspired by these elegant work[14] and our recent studies on C−H functionalization,[15] especially tertiary

Scheme 1. Direct Synthesis of ortho Secondary Alkyl-Substituted Phosphines via Strategy of P-Directed C−H Activation



Received: June 7, 2021

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https://doi.org/10.1021/acs.joc.1c01329
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phosphines meta secondary alkylation,[15c] we envision that by selecting norbornene as the alkylating reagent, the selectivity of secondary alkylation reaction of phosphines may change from the meta to ortho position via ortho-metalation and subsequent insertion reaction. If this transformation can be achieved, a series of bulky ortho-secondary alkyl-substituted ligands would be efficiently prepared from commercially available phosphines. These highly sterically hindered phosphines will improve the efficiency of palladium catalyzed Suzuki coupling reaction by accelerating oxidative addition and reductive elimination steps.

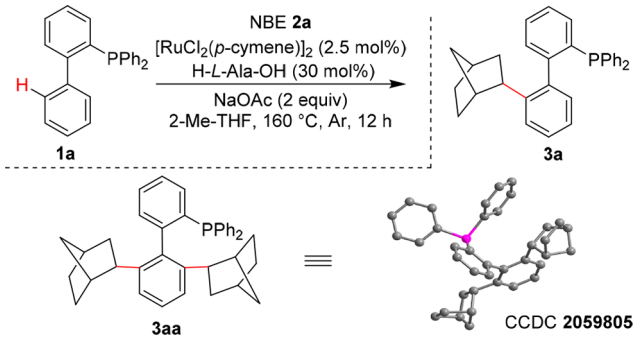
RESULTS AND DISCUSSION

To test our ideas, we initiated our study by choosing commercially available [1,1′-biphenyl]-2-yldiphenylphosphane (**1a**) and norbornene (**2a**) as model substrates. To our delight, the desired ortho secondary alkylated product **3a** was obtained in 98% yield with excellent monoselectivity (mono/di > 20:1) and high stereoselectivity (exo/endo > 20:1) by using 2.5 mol % $[RuCl_2(p\text{-cymene})]_2$, 30 mol % H-*L*-Ala-OH, and 2.0 equiv of NaOAc in 2-Me-THF at 160 °C for 12 h (Table 1, entry 1). The ortho-selectivity and exoaddition of the hydroarylation of norbornene **2a** was confirmed by X-ray analysis of disubstituted product **3aa**. Notably, this ruthenium-catalyzed alkylation of phosphines had excellent stereoselectivity giving two of the four possible isomers, which was confirmed by NMR characterization of **3a**. Unfortunately, the isomers could not be separated by column chromatography. When increasing the amount of norbornene, the ratio of mono- and disubstituted products reduced to 11:1, indicating the equivalent of NBE is significant to achieve high mono-selectivity (entry 2). Other ligands were investigated in this system (entries 3−6). Highly sterically hindered alkyl acid ligand (1-$AdCO_2H$) was also effective for this transformation, although with medium yield (60%) and high selectivity (mono/di = 15:1) (entry 3). Amino acid ligands, such as H-*L*-Phe-OH, H-*L*-Leu-OH and H-*L*-lle-OH were also tested, slightly lower yields (70−86%) of product were observed, perhaps due to their highly steric effects (entries 4−6). A low yield (52%) and selectivity (mono/di = 10:1) was observed in the absence of ligand, which showed that *L*-alanine played an important role in this reaction (entry 7). No product is generated without addition of NaOAc and ruthenium complex, highlighting both the base and ruthenium catalyst were essential in this transformation (entries 8 and 9). Finally, to demonstrate the irreplaceable norbornene, a series of other alkenes (**2b−2h**) were tested. Linear and cyclic alkenes such as 3-hexene (**2b**) and cyclohexene (**2c**) were ineffective for this reaction. Activated alkenes such as cyclohexanone (**2e** and **2f**), 1H-pyrrole-2,5-dione (**2g**), and cyclopropane (**2h**) had little activities for this transformation. These results highlighted the unique activity of norbornene and proved the key role of ring strain in achieving the ortho secondary alkylation.

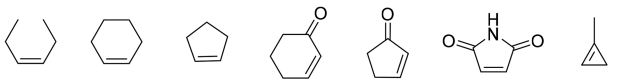
Having the optimized reaction conditions, the generality of this ortho secondary alkylation of tertiary phosphine was examined (Scheme 2). To our delight, the reaction had high stereoselectivity and provided exoalkylation products. For example, phosphines with diverse common groups such as MeO (**1b**, **1h**), Me (**1c**, **1j**, **1l**), F (**1d**, **1f**, **1i**, **1n**), Cl (**1e**, **1g**, **1k**, **1o**), Ph (**1m**), COMe (**1p**), and CO_2Me (**1q**) could react with norbornene **2a**, affording the corresponding exoalkylated products in moderate to high yields (**3b−3q**, 41−86%) and high selectivity (mono/di = 10:1−20:1). Substituted phosphines at the ortho, meta, or para positions could react smoothly, generating the desired products. Notably, biarylphosphines with an ortho-MeO (**1h**) group was also effective for this reaction, giving the desired monosecondary alkylated product in medium yield (**3h**, 44%). However, the binaphthyl- and dicyclohexyl-based phosphines had low activities for this reaction, probably due to the steric hindrance effect. Notably, the substituted norbornenes with Ac and CN groups could undergo this ortho-alkylation reaction smoothly, affording the corresponding products in moderate yields (**3r**, 58%; **3s**, 52%). The alkylated phosphine **3a** with Ad group at the ortho position could further react with norbornene **2a** but give a low yield of dialkylated product **3aa** due largely to steric hindrance. Thus, a series of new largely steric phosphines with different electronic properties were prepared for the first time. Unfortunately, substrates such as JohnPhos, CyJohnPhos, and CataCXium as well as norbornadiene had little activity in this transformation, giving a trace amount of products (**3t−3w**), probably due to unsuitable steric and electronic properties.

To prove the practicality of this protocol, a gram-scale reaction of 2-diphenylphosphinobiphenyl (**1a**) and norbornene

Table 1. Optimization of the Reaction Conditions[a]



Entry	Variation from the standard condition	3a/3aa[b]	Yield of 3a (%)[c]
1	no	>20:1	98[d]
2	NBE **2a** 3 equiv	11:1	89
3	1-$AdCO_2H$ instead of H-*L*-Ala-OH	15:1	60
4	H-*L*-Phe-OH instead of H-*L*-Ala-OH	18:1	86
5	H-leu-OH instead of H-*L*-Ala-OH	15:1	81
6	H-lle-OH instead of H-*L*-Ala-OH	15:1	70
7	without H-*L*-Ala-OH	10:1	52
8	without NaOAc	---	NP
9	without $[RuCl_2(p\text{-cymene})]_2$	---	NP



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), H-*L*-Ala-OH (30 mol %), and NaOAc (2.0 equiv) in 1 mL of 2-Me-THF at 160 °C under argon, 12 h. [b]Ratio of **3a**/**3aa** was determined by ^{31}P NMR using PPh_3 as an internal standard. [c]Yield of product was determined by ^1H NMR using CH_2Br_2 as an internal standard. [d]Diastereoselectivity (dr = 1:1) was determined by ^{31}P NMR.

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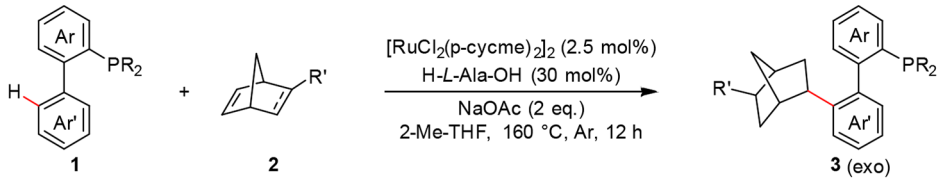
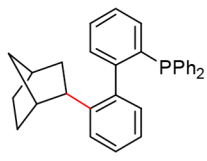
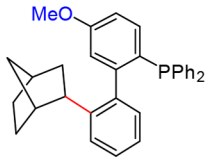
Scheme 2. Scope of ortho-Alkylation Reaction

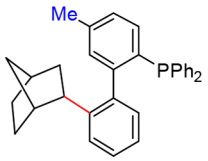




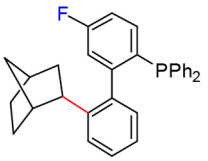
3a, 98% (m:d > 20:1)



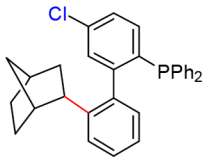
3b, 82% (m:d = 15:1)



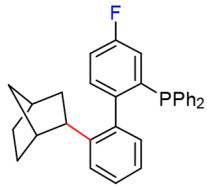
3c, 47% (m:d > 20:1)



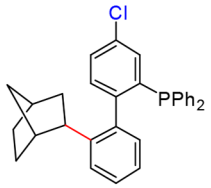
3d, 63% (m:d > 20:1)



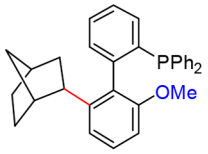
3e, 66% (m:d > 20:1)



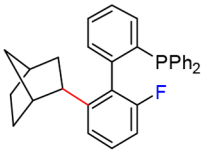
3f, 74% (m:d > 20:1)



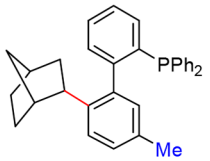
3g, 86% (m:d > 20:1)



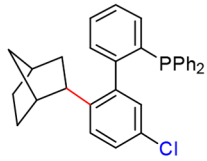
3h, 44% (m:d > 20:1)



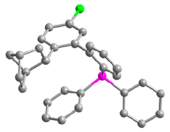
3i, 52% (m:d > 20:1)



3j, 47% (m:d > 20:1)



3k, 42% (m:d > 20:1)



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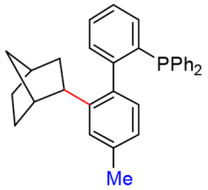
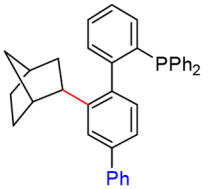
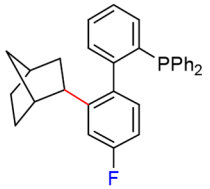


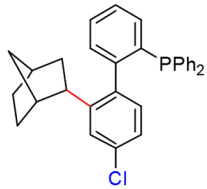
3l, 41% (m:d > 20:1)



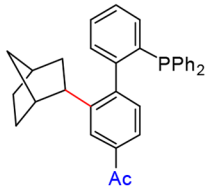
3m, 76% (m:d = 12:1)



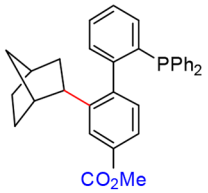
3n, 80% (m:d > 20:1)



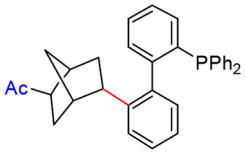
3o, 54% (m:d > 20:1)



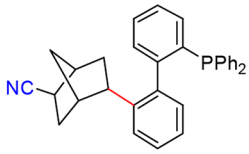
3p, 83% (m:d > 20:1)



3q, 74% (m:d = 10:1)

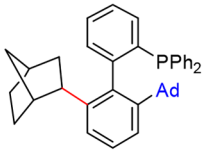


3r, 58% (m:d > 20:1)

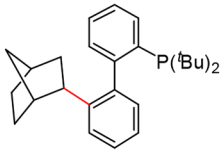


3s, 52% (m:d > 20:1)

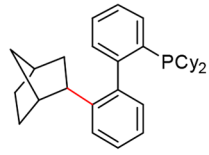
Failed examples



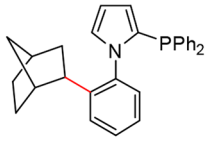
3aa, 34%[b]



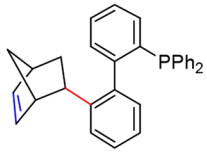
3t trace



3u, trace



3v, trace



3w, trace

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), H-*L*-Ala-OH (30 mol %), and NaOAc (2.0 equiv) in 1 mL of 2-Me-THF at 160 °C under argon, 12 h. Isolated yield. [b]^{31}P NMR yield.

(**2a**) was carried out under standard conditions. To our delight, 1.2 g of alkylated products was obtained in 88% yield (for details see the Supporting Information).

Palladium catalyzed Suzuki−Miyaura reaction is one of the most effective cross-coupling reactions for the construction of C−C bond.[16] However, the high cost and toxicity of the Pd-system limit its wide application in chemical and pharmaceutical. Using low catalyst loadings will decrease the cost of the catalyst and the toxicity of the reaction system, making the reaction more attractive to industry. When the palladium-loading at a level of 10 mol ppm, the price and toxicity of catalyst would remove the concern.[17] We expected with our highly sterically hindered Buchwald-phosphines, the palladium-catalyzed Suzuki−Miyaura reaction could be conducted at the mol ppm level (Scheme 3a). 4-Bromoanisole (**4a**) and phenylboronic acid (**5a**) were selected as substrates in the presence of 0.001 mol % $PdCl_2(PPh_3)_2$ (10 mol ppm). To our delight, our secondary alkyl-substituted phosphine (**3a**) showed excellent catalytic activity and provided the desired biaryl product (**6a**) in almost perfect yield (95%). In comparison, the unsubstituted biarylphosphine (**1a**) gave a low yield of product, indicating the importance of the alkyl group. Linear alkylated phosphine (**L1**)[15b] and arylated phosphine (**L4**)[15a] previously reported by our group as well as the common used XPhos (**L5**) were also tested in low catalyst loading, but they gave lower yields (81%, 75%, and 83%). This result showed that the large secondary alkyl group played a key role in promoting the activity of palladium

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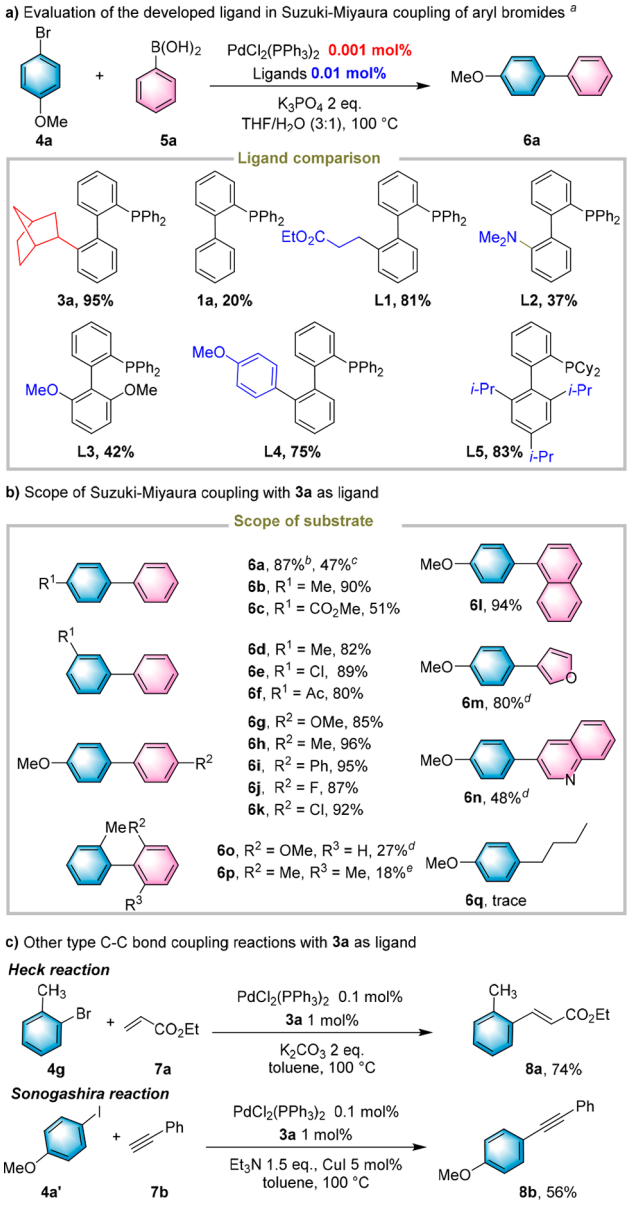
Scheme 3. Synthetic Application

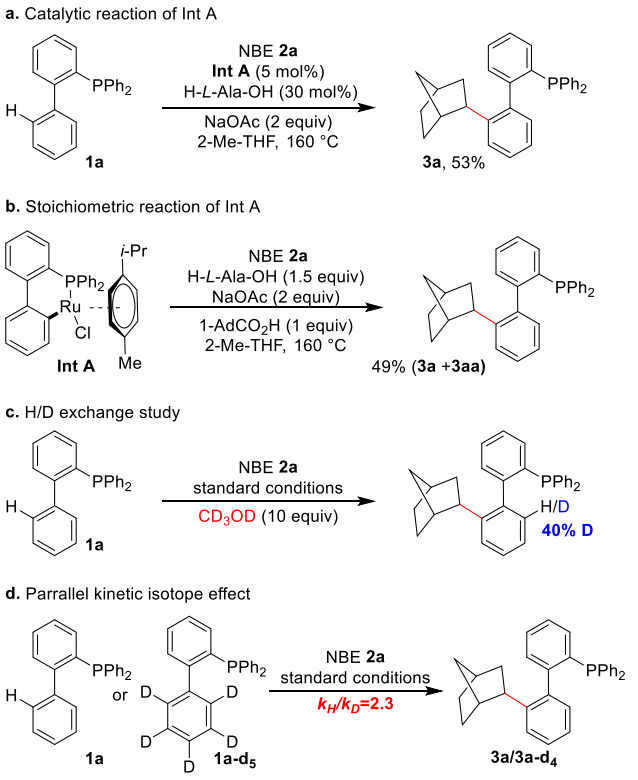


[a]Reaction conditions: **4** (0.5 mmol), **5** (0.65 mmol), $PdCl_2(PPh_3)_2$ (0.001 mol %), ligand (0.01 mol %), and K_3PO_4 (2.0 equiv) in 0.6 mL of THF and 0.4 mL of H_2O at 100 °C under argon, 10 h. [b]ArOTf as coupling reagent. [c]ArCl as coupling reagent, $PdCl_2(PPh_3)_2$ (0.01 mol %), **3a** (0.1 mol %). [d]$PdCl_2(PPh_3)_2$ (0.01 mol %), **3a** (0.1 mol %). [e]$PdCl_2(PPh_3)_2$ (1 mol %), **3a** (10 mol %).

catalyst. Other common ortho-substituted biarlyphosphines with Me_2N (PhDavePhos, **L2**) and OMe (**L3**) were also studied, but low activities were observed (37% and 42%) in 10 mol ppm of Pd-catalyst. These results demonstrated the high catalytic activity of our secondary alkylated phosphines. Using the phosphine product (**3a**) and 0.001 mol % of palladium catalyst, a series of biaryl compounds (**6a**–**6l**) with electron-withdrawing and electron-donating substituent groups were prepared in moderate to excellent yields (Scheme 3b). Notably, less active ArOTf and ArCl could be active using our phosphine ligand. Morever, the substrates containing heterocycle such as furan and quinoline were also tolerant with a higher load of Pd catalyst (**6m** and **6n**). Furthermore, ortho-substituted substrates for both aryl bromides and arylboronic acids could react in the presence of **3a**, affording largely steric di- or tri-substituted biaryls. To further prove the generality of our largely steric ligands, the phosphine of **3a** was further extended to Sonogashira and Heck reactions (Scheme 3c). To our delight, medium to high yields of alkenylated product **8a** and alkynylation product **8b** could be obtained under common conditions in the presence of **3a** ligand. These results proved that installation of a bulky secondary alkyl group into ligand could obviously improve the catalytic activity of phosphine and these ligands may have potential in the field of metal catalysis.

To gain insights into the mechanism of ruthenium catalyzed ortho secondary alkylation reaction of tertiary phosphines, the six-membered cycloruthenium complex (**Int A**) was prepared from **1a** and ruthenium catalyst first (for details see the Supporting Information).[15b] As we expected, **Int A** could replace the $[RuCl_2(p\text{-cymene})]_2$ as a catalyst for alkylation and deliver the product **3a** in 53% yield (Scheme 4a). When using

Scheme 4. Mechanistic Studies



a stoichiometric amount of **Int A** as the substrate, 49% yield of alkylated products (**3a** and **3aa**) were observed (Scheme 4b). These experimental results implicated the **Int A** may be an intermediate relating to the catalytic cycle. Next, a deuterium exchange experiment was conducted under standard conditions with addition of methanol-d_4, and 40% of deuterium substitution at the ortho position of isolated product was observed (Scheme 4c), indicating that the C–H bond cleavage is reversible. At last, parallel experiments of **1a** or **1a**-d_5 with **2a** revealed a kinetic isotope effect (KIE) of 2.3, suggesting that C–H bond cleavage might be the rate-determining step (Scheme 4d).

Based on these experimental results, we proposed a plausible mechanistic process for this C–H secondary alkylation (Scheme 5). First, the active Ru(II) species **I** is generated in

https://doi.org/10.1021/acs.joc.1c01329
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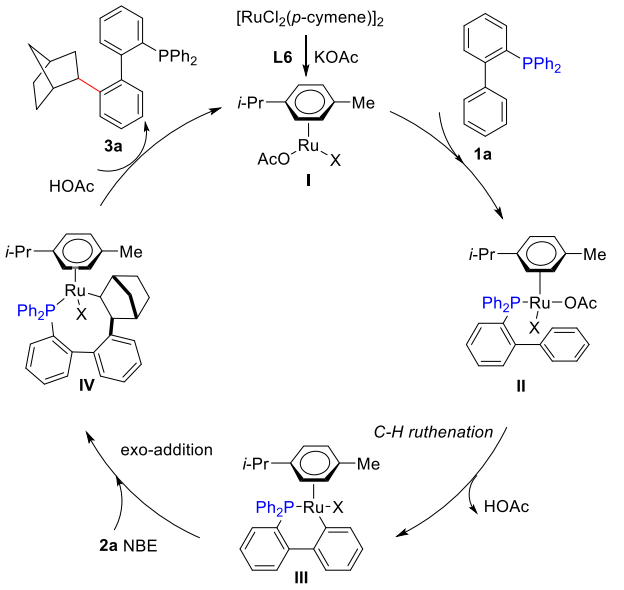
Scheme 5. Proposed Catalytic Cycle



the presence of H-*L*-Ala-OH and KOAc. Then, the phosphine **1a** coordinates with the Ru(II) species **I** to form the Ru complex **II**, which undergoes C−H activation generating the six-membered cycloruthenated complex **III**. Next, coordination of the NBE with complex **III** followed by exoinsertion into the Ru−C bond delivers the intermediate **IV**. Finally, the alkylation product **3a** generates after protonation of **IV** and regenerates the active complex **I**.

CONCLUSION

In summary, we have developed the first ruthenium-catalyzed $P^{(III)}$-directed ortho-selective C−H secondary alkylation, which provides straight and efficient access to highly sterically hindered tertiary phosphines. By selection of highly ring-tensioned norbornene as the alkylating reagent, we change the regioselectivity from the meta to the ortho position. A series of new highly steric biarylphosphines with norbornyl group were obtained with high yields and monoselectivity from commercially available starting materials. The excellent catalytic activities of these phosphine ligands were demonstrated in the palladium-catalyzed Suzuki−Miyaura cross-coupling reaction. This work will have significant potentials in the field of metal catalysis and ligand development. Other applications and more detailed mechanistic investigations are underway in our lab.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of argon. Analytical thin layer chromatography (TLC) was performed on silica gel plates with F-254 indicator, and compounds were visualized by irradiation with UV light. Flash column chromatography was carried out using silica gel (200−300 mesh) at increased pressure. The ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectroscopic data were recorded on Bruker Mercury Plus 400 MHz NMR spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for ^{31}P are reported relative to an external 85% H_3PO_4 standard. The diffraction data of crystals were collected on a Rigaku XtaLAB Synergy CCDC diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54056 Å) at 293 or 100 K. Absorption corrections were applied by SADABS. All the structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using SHELXTL-2014. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the ligand were generated geometrically. High-resolution mass spectra (HRMS) were recorded on the Thermo Scientific Exactive Plus (orbitrap) equipped with an electrospray ionization (ESI) ionization source.

Preparation of Starting Materials. Materials were purchased from Alfa-Aesar, Laajoo, Macklin, Adamas, Bidepharm, and Aladdin and used as received. All the solvents were purchased from commercial suppliers and purified by standard procedures as specified in *Purification of Laboratory Chemicals*.[20]

General Procedure for Ru(II)-Catalyzed Direct ortho-Selective Secondary Alkylation. To a 25 mL Schlenk tube was added **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 2.5 mol %), H-*L*-Ala-OH (5.3 mg, 30 mol %), and NaOAc (32.8 mg, 2.0 equiv). The tube was purged with Ar three times, followed by the addition of 2-Me-THF (1 mL). The mixture was stirred at 160 °C in the heating module for 12 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel affording the alkylated products **3**.

Evaluation of the Developed Ligands in Suzuki−Miyaura Couplings. A stock solution of $PdCl_2(PPh_3)_2$ (1.4 mg) with **3a** (8.6 mg) in THF (10 mL) was initially prepared with continuous stirring at room temperature under a nitrogen atmosphere for 5 min. To a 25 mL Schlenk tube was added the stock solution (25 μL), and the solvent was removed under vacuum directly. Then, 4-bromoanisole **4a** (0.5 mmol, 93.0 mg, 1.0 equiv), phenylboronic acid **5a** (0.65 mmol, 79.3 mg, 1.3 equiv), and K_3PO_4 (212 mg, 2.0 equiv) was added to the Schlenk tube. The tube was purged with Ar three times, followed by the addition of H_2O (0.4 mL) and THF (0.6 mL). The mixture was stirred at 100 °C in the heating module for 10 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (R_f = 0.4, hexane) affording the pure product **6a** (white solid, 87.4 mg, 95% yield).

Evaluation of the Developed Ligands in Heck Reaction. To a 25 mL Schlenk tube was added 1-bromo-2-methylbenzene **4g** (0.5 mmol, 85.0 mg, 1.0 equiv), ethyl acrylate **7a** (1.5 mmol, 150.1 mg, 3.0 equiv), $PdCl_2(PPh_3)_2$ (0.1 mol %), **3a** (1 mol %), and K_2CO_3 (2.0 equiv). The tube was purged with Ar three times, followed by the addition of toluene (0.5 mL). The mixture was stirred at 100 °C in the heating module for 10 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (R_f = 0.3, EA/hexane = 1/50) affording the pure product **8a** (colorless oil, 70.3 mg, 74% yield).

Evaluation of the Developed Ligands in Sonogashira Reaction. To a 25 mL Schlenk tube was added 1-methoxy-4-methylbenzene **4a′** (0.5 mmol, 61.0 mg, 1.0 equiv), ethynylbenzene **7b** (0.55 mmol, 56.1 mg, 1.1 equiv), $PdCl_2(PPh_3)_2$ (0.1 mol %), **3a** (1 mol %), CuI (5 mol %), and Et_3N (1.5 equiv). The tube was purged with Ar three times, followed by the addition of toluene (0.5 mL). The mixture was stirred at 100 °C in the heating module for 10 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (R_f = 0.7, hexane) affording the pure product **8b** (colorless oil, 58.3 mg, 56% yield).

Crystallography. Single crystals of **3aa** and **3k** suitable for X-ray diffraction were grown by layering methanol on the dichloromethane solutions. The diffraction data of crystals were collected on a Rigaku XtaLAB Synergy CCD diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54056 Å) at 293 or 100 K. Absorption corrections were applied by SADABS. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically with isotropic thermal parameters. All the structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using Olex2. The CCDC reference number is 2059805

https://doi.org/10.1021/acs.joc.1c01329
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for **3aa** and 2070266 for **3k**. The ellipsoid contour is 50% probability in the caption for the image of the **3aa** and **3k**.

Analytical Characterization Data of Products. *(2′-(Bicyclo[2.2.1]heptan-2-yl)-[1,1′-biphenyl]-2-yl)diphenylphosphane (**3a**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3a** (84.7 mg, 98%) as a colorless oil. m/d > 20:1, dr = 1.2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.38 (m, 1.5H), 7.36−7.32 (m, 9H), 7.25−7.17 (m, 5.5H), 7.05−6.97 (m, 1H), 6.85 (d, J = 7.6 Hz, 0.5H), 6.78 (d, J = 6.8 Hz, 0.5H), 2.56 (t, J = 6.8 Hz, 1H), 2.46 (s, 0.5H), 2.27 (s, 1H), 2.20 (s, 0.5H), 1.75−1.66 (m, 1.5H), 1.50−1.38 (m, 3H), 1.27 (d, J = 9.6 Hz, 0.5H), 1.15−0.88 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 148.3 (d, J = 32.3 Hz), 148.2 (d, J = 32.3 Hz), 145.7, 145.0, 141.2 (d, J = 7.1 Hz), 140.9 (d, J = 7.1 Hz), 138.0, 137.8 (d, J = 12.1 Hz), 137.5 (d, J = 12.1 Hz), 136.8 (d, J = 11.1 Hz), 136.6 (d, J = 11.1 Hz), 134.2, 134.1, 134.0, 133.9, 133.8, 133.7, 133.6, 130.8, 130.7, 130.6, 130.5, 130.4, 128.6, 128.5, 128.4, 128.3, 127.7 (d, J = 9.1 Hz), 127.4 (d, J = 8.1 Hz), 125.5, 125.1, 124.5, 124.4, 44.3, 43.6, 41.8, 41.7, 41.5, 38.4, 38.3, 37.4, 36.9, 36.8, 36.1, 31.1, 30.6, 28.6, 28.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.4, −15.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{30}P$ 433.2080; found 433.2076.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-5-methoxy-[1,1′-biphenyl]-2-yl)diphenylphosphane (**3b**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3b** (75.8 mg, 82%) as a colorless oil. m/d = 15:1, dr = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 0.5H), 7.34−7.30 (m, 7.5H), 7.24−7.19 (m, 4H), 7.12−6.99 (m, 2H), 6.90−6.87 (m, 2H), 6.83−6.77 (m, 1H), 3.83 (s, 3H), 2.59 (s, 1H), 2.45 (s, 0.5H), 2.28 (s, 1H), 2.45 (s, 0.5H), 1.75−1.67 (m, 1.5H), 1.49−1.42 (m, 3H), 1.28 (d, J = 7.6 Hz, 0.5H), 1.16−0.86 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 159.8, 159.7, 150.1 (d, J = 34.3 Hz), 145.6, 145.0, 141.3 (d, J = 7.1 Hz), 141.1 (d, J = 6.1 Hz), 138.7, 138.6, 138.5, 138.4, 138.3, 136.0, 135.6, 133.8, 133.7, 133.6, 133.5, 133.4, 130.5 (d, J = 3.0 Hz), 130.4 (d, J = 4.0 Hz), 128.4, 128.3, 128.2, 127.8 (d, J = 9.1 Hz), 127.6 (d, J = 9.1 Hz), 127.5, 125.6, 125.2, 124.6, 124.4, 116.0 (d, J = 6.1 Hz), 115.6 (d, J = 6.1 Hz), 113.8, 113.7, 55.4, 44.2, 43.8, 41.9, 41.7, 38.5, 37.4, 36.9, 36.8, 36.1, 31.1, 30.7, 28.6, 28.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −16.4, −17.4, −18.9, −19.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{32}OP$ 463.2185; found 463.2179.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-5-methyl-[1,1′-biphenyl]-2-yl)diphenylphosphane (**3c**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3c** (41.9 mg, 47%) as a colorless oil. m/d > 20:1, dr = 1.2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.6 Hz, 0.5H), 7.30−7.26 (m, 7.5H), 7.20−7.13 (m, 4H), 7.11−7.09 (m, 1.5H), 7.01−6.93 (m, 2.5H), 6.83 (d, J = 7.2 Hz, 0.5H), 6.75 (d, J = 7.6 Hz, 0.5H), 2.51 (t, J = 8.0 Hz, 1H), 2.41 (s, 0.5H), 2.36 (d, J = 3.6 Hz, 3H), 2.23 (s, 1H), 2.16 (s, 0.5H), 1.71−1.62 (m, 1.5H), 1.47−1.35 (m, 3H), 1.22 (d, J = 9.6 Hz, 0.5H), 1.11−0.83 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 148.4 (d, J = 32.3 Hz), 148.3 (d, J = 33.3 Hz), 145.7, 145.1, 141.4 (d, J = 7.1 Hz), 141.2 (d, J = 6.1 Hz), 138.5, 138.4, 138.3, 138.2, 138.1, 137.9, 134.4, 134.0, 133.9, 133.8, 133.7, 133.6, 133.5, 133.2, 133.1, 133.0, 131.5 (d, J = 6.1 Hz), 131.3 (d, J = 6.1 Hz), 130.7, 130.6, 128.4, 128.3, 128.2, 127.7, 127.6, 125.5, 125.1, 124.5, 124.4, 44.3, 44.2, 43.8, 41.8, 41.6, 38.5, 37.5, 36.9, 36.8, 36.1, 31.1, 30.5, 28.6, 28.5, 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −15.4, −16.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{32}P$ 447.2236; found 447.2227.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-5-fluoro-[1,1′-biphenyl]-2-yl)diphenylphosphane (**3d**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3d** (56.7 mg, 63%) as a colorless oil. m/d > 20:1, dr = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 0.5H), 7.33−7.29 (m, 7H), 7.20−7.10 (m, 5.5H), 7.04−6.99 (m, 2H), 6.97−6.91 (m, 1H), 6.79 (d, J = 7.6 Hz, 0.5H), 6.73 (dd, J = 7.6, 1.2 Hz, 0.5H), 2.55−2.50 (m, 1H), 2.44 (s, 0.5H), 2.27 (s, 1H), 2.18 (s, 0.5H), 1.73−1.63 (m, 1.5H), 1.46−1.44 (m, 2.5H), 1.27 (s, 0.5H), 1.14 (d, J = 9.6 Hz, 0.5H), 1.10−0.86 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 162.9 (d, J = 251.5 Hz), 162.8 (d, J = 250.5 Hz), 150.8 (d, J = 19.2 Hz), 150.5 (d, J = 19.2 Hz), 145.5, 144.9, 140.2, 140.1, 139.9, 139.8, 137.9, 137.8, 137.7, 137.6, 137.5, 137.4, 136.3 (d, J = 8.1 Hz), 135.9 (d, J = 8.1 Hz), 133.9, 133.7, 133.6, 133.5, 132.6, 132.5, 132.5, 132.4, 130.5 (d, J = 3.0 Hz), 130.4 (d, J = 3.0 Hz), 128.6, 128.5, 128.4, 128.2, 128.1, 125.6, 125.2, 124.7, 124.5, 117.9, 117.8, 117.7, 117.6, 117.5, 117.4, 117.3, 114.7 (d, J = 20.2 Hz), 114.6 (d, J = 20.2 Hz), 44.3, 43.6, 41.8, 41.6, 38.4, 37.4, 37.0, 36.8, 36.1, 31.1, 30.6, 28.6, 28.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −16.0, −17.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ −112.9, −113.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}FP$ 451.1985; found 451.1979.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-5-chloro-[1,1′-biphenyl]-2-yl)diphenylphosphane (**3e**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3e** (61.5 mg, 66%) as a colorless oil. m/d > 20:1, dr = 1.2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.6 Hz, 0.5H), 7.31−7.29 (m, 7.5H), 7.20−7.12 (m, 5H), 7.08−7.05 (m, 1H), 7.01−6.93 (m, 1H), 6.76 (d, J = 7.2 Hz, 0.5H), 6.70 (dd, J = 7.6, 1.2 Hz, 0.5H), 2.52−2.44 (m, 1.5H), 2.27 (s, 1H), 2.17 (s, 0.5H), 1.72−1.63 (m, 1.5H), 1.47−1.42 (m, 3H), 1.27 (s, 0.5H), 1.15−0.88 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 149.9 (d, J = 33.3 Hz), 149.8 (d, J = 32.3 Hz), 145.6, 144.9, 139.9 (d, J = 7.1 Hz), 139.6 (d, J = 7.1 Hz), 137.5, 137.4, 137.3, 137.2, 137.0, 136.9, 135.9, 135.7, 135.6, 135.2, 134.7, 134.6, 134.0, 133.8, 133.6, 130.7, 130.6 (d, J = 3.0 Hz), 130.5 (d, J = 3.0 Hz), 130.4, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7, 127.5, 125.6, 125.2, 124.6, 124.5, 44.4, 44.3, 43.7, 41.8, 41.6, 38.5, 38.4, 37.5, 37.0, 36.8, 36.1, 31.2, 30.6, 28.6, 28.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −15.5, −16.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}ClP$ 467.1690; found 467.1682.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-4-fluoro-[1,1′-biphenyl]-2-yl)diphenylphosphane (**3f**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3f** (66.6 mg, 74%) as a colorless oil. m/d > 20:1, dr = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.28 (m, 8H), 7.20−7.06 (m, 6H), 7.00−6.92 (m, 1H), 6.84−6.80 (m, 1H), 6.75 (d, J = 7.2 Hz, 0.5H), 6.70 (dd, J = 7.6, 0.8 Hz, 0.5H), 2.48 (t, J = 8.0 Hz, 1H), 2.43 (s, 0.5H), 2.28−2.25 (m, 1H), 2.15 (s, 0.5H), 1.72−1.63 (m, 1.5H), 1.47−1.38 (m, 3H), 1.27 (s, 0.5H), 1.13−0.89 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 162.0 (d, J = 248.5 Hz), 146.0, 145.3, 144.0 (d, J = 31.3 Hz), 143.8 (d, J = 30.3 Hz), 140.1, 140.0, 139.9, 139.8, 139.7, 137.1, 137.0, 136.7, 136.6, 134.1 (d, J = 6.1 Hz), 133.9, 133.7 (d, J = 6.1 Hz), 132.3 (d, J = 12.1 Hz), 132.0 (d, J = 13.1 Hz), 131.0 (d, J = 3.0 Hz), 130.9 (d, J = 3.0 Hz), 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 125.6, 125.1, 124.5, 124.4, 120.3 (d, J = 20.2 Hz), 119.9 (d, J = 21.2 Hz), 115.7 (d, J = 15.2 Hz), 115.5 (d, J = 15.2 Hz), 44.4, 44.3, 43.6, 41.7, 38.4, 37.5, 37.0, 36.8, 36.1, 31.2, 30.6, 28.6, 28.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −13.7, −14.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}FP$ 451.1985; found 451.1982.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-4-chloro-[1,1′-biphenyl]-2-yl)diphenylphosphane (**3g**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3g** (80.2 mg, 86%) as a colorless oil. m/d > 20:1, dr = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.30 (m, 8.5H), 7.23−7.08 (m, 6.5H), 7.00−6.93 (m, 1H), 6.74 (d, J = 7.6 Hz, 0.5H), 6.68 (d, J = 7.6 Hz, 0.5H), 2.51−2.43 (m, 1.5H), 2.28−2.25 (m, 1H), 2.16 (s, 0.5H), 1.72−1.64 (m, 1.5H), 1.47−1.39 (m, 3H), 1.28 (s, 0.5H), 1.15−0.89 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 146.5 (d, J = 31.3 Hz), 146.4 (d, J = 31.3 Hz), 145.8, 145.1, 139.9, 139.8, 139.7, 139.6, 139.5, 136.9, 136.9 (d, J = 12.1 Hz), 136.6 (d, J = 12.1 Hz), 134.1, 133.9, 133.7, 133.5, 133.4, 133.0, 132.1 (d, J = 6.1 Hz), 131.8 (d, J = 5.1 Hz), 130.8 (d, J = 3.0 Hz), 130.7 (d, J = 4.0 Hz), 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 125.6, 125.2, 124.6, 124.5, 44.4, 44.3, 43.6, 41.7, 38.5, 38.4, 37.5, 37.0, 36.8, 36.1, 31.2, 30.6, 28.6, 28.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −13.6, −14.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}ClP$ 467.1690; found 467.1683.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-6′-methoxy-[1,1′-biphenyl]-2-yl)diphenylphosphane (**3h**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3h** (40.7 mg, 44%) as a colorless oil. m/d > 20:1, dr = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.40 (m, 1H), 7.34−7.27 (m, 7.5H), 7.25−7.14 (m, 6.5H), 7.03 (d, J = 8.0 Hz, 0.5H), 6.95 (d, J = 8.0 Hz, 0.5H), 6.68 (d, J = 8.4 Hz, 0.5H), 6.63 (d, J = 8.0 Hz, 0.5H), 3.24 (d, J = 23.6 Hz, 3H), 2.33−2.30 (m, 1.5H), 2.22 (s, 1H), 2.14 (d, J = 3.2 Hz, 0.5H), 1.73 (d, J =

https://doi.org/10.1021/acs.joc.1c01329
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9.6 Hz, 0.5H), 1.65−1.58 (m, 1H), 1.47−1.32 (m, 3H), 1.22 (d, J = 9.6 Hz, 0.5H), 1.09 (d, J = 10.0 Hz, 0.5H), 0.96−0.76 (m, 2.5H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.0 (d, J = 14.1 Hz), 157.0 (d, J = 15.2 Hz), 147.6, 147.0, 144.8 (d, J = 35.4 Hz), 144.6 (d, J = 34.3 Hz), 138.5 (d, J = 13.1 Hz), 138.2 (d, J = 13.1 Hz), 137.9, 137.8, 137.5 (d, J = 9.1 Hz), 137.3 (d, J = 10.1 Hz), 134.7, 134.4, 133.9, 133.8, 133.7, 133.6, 133.5, 131.3 (d, J = 6.1 Hz), 130.9 (d, J = 6.1 Hz), 130.0 (d, J = 7.1 Hz), 129.7 (d, J = 7.1 Hz), 129.1, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.3, 127.2, 118.1, 117.6, 107.4, 107.2, 54.9, 54.8, 44.3, 44.1, 42.0, 41.9, 41.8, 38.4, 37.6, 36.8, 36.7, 36.1, 31.2, 30.7, 28.6, 28.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.6, −15.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{32}OP$ 463.2185; found 463.2176.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-6′-fluoro-[1,1′-biphenyl]-2-yl)-diphenylphosphane (**3i**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3i** (46.8 mg, 52%) as a colorless oil. m/d > 20:1, dr = 1:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.37 (m, 1H), 7.35−7.23 (m, 10.5H), 7.20−7.11 (m, 4H), 7.03 (d, J = 7.6 Hz, 0.5H), 6.87 (t, J = 8.4 Hz, 0.5H), 6.80 (t, J = 8.4 Hz, 0.5H), 2.30−2.16 (m, 2.5H), 2.01 (d, J = 3.2 Hz, 0.5H), 1.64 (d, J = 9.6 Hz, 0.5H), 1.52−1.27 (m, 4H), 1.20 (d, J = 9.6 Hz, 0.5H), 1.03−0.70 (m, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.0 (d, J = 243.4 Hz), 159.8 (d, J = 244.4 Hz), 149.1, 148.3, 141.8 (d, J = 28.3 Hz), 141.4 (d, J = 27.3 Hz), 137.9 (d, J = 11.1 Hz), 137.8 (d, J = 12.1 Hz), 137.7, 137.5, 137.4, 137.1 (d, J = 13.1 Hz), 136.8 (d, J = 13.1 Hz), 134.6, 134.2, 134.1 (d, J = 10.1 Hz), 133.9 (d, J = 10.1 Hz), 133.6 (d, J = 11.1 Hz), 133.4 (d, J = 11.1 Hz), 131.3 (d, J = 5.1 Hz), 130.9 (d, J = 6.1 Hz), 129.2 (d, J = 8.1 Hz), 129.0, 128.9 (d, J = 9.1 Hz), 128.8, 128.7, 128.6, 128.5, 128.3 (d, J = 7.1 Hz), 128.2 (d, J = 6.1 Hz), 128.1, 128.0, 121.3, 121.2, 120.7, 120.6, 112.4, 112.2, 112.0, 44.5, 44.3, 44.2, 42.1, 41.6, 37.8, 37.6, 36.9, 36.5, 35.7, 30.9, 30.5, 28.5, 28.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −13.7, −13.8, −14.7, −14.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −110.9, −111.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}FP$ 451.1985; found 451.1982.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-5′-methyl-[1,1′-biphenyl]-2-yl)-diphenylphosphane (**3j**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3j** (41.9 mg, 47%) as a colorless oil. m/d > 20:1, dr = 1.1:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.35 (m, 1H), 7.32−7.28 (m, 7.5H), 7.25−7.08 (m, 7.5H), 6.49 (s, 0.5H), 6.43 (d, J = 1.2 Hz, 0.5H), 2.55 (t, J = 8.4 Hz, 1H), 2.47 (s, 0.5H), 2.26−2.19 (m, 1.5H), 2.06 (d, J = 6.4 Hz, 3H), 1.72−1.65 (m, 1.5H), 1.47−1.39 (m, 3H), 1.23 (d, J = 9.6 Hz, 0.5H), 1.14−0.90 (m, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.3 (d, J = 32.3 Hz), 148.2 (d, J = 31.3 Hz), 142.5, 142.0, 141.0 (d, J = 7.1 Hz), 140.8 (d, J = 7.1 Hz), 138.1 (d, J = 7.1 Hz), 138.0 (d, J = 7.1 Hz), 137.8, 137.6, 137.5, 137.1 (d, J = 11.1 Hz), 136.9 (d, J = 11.1 Hz), 134.3 (d, J = 9.1 Hz), 134.1 (d, J = 9.1 Hz), 134.0, 133.8, 133.7, 133.6, 131.9, 131.8, 130.6 (d, J = 5.1 Hz), 130.4 (d, J = 6.1 Hz), 128.6, 128.5, 128.4, 128.3, 128.2, 127.3, 127.2, 125.3, 125.0, 44.0, 43.9, 43.5, 42.0, 41.9, 41.4, 38.6, 37.3, 36.9, 36.8, 36.2, 31.1, 30.6, 28.7, 28.6, 20.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.0, −15.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{32}P$ 447.2236; found 447.2235.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-5′-chloro-[1,1′-biphenyl]-2-yl)-diphenylphosphane (**3k**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3k** (39.1 mg, 42%) as a colorless oil. m/d > 20:1, dr = 1.1:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.28 (m, 8H), 7.25 (s, 0.5H), 7.22−7.10 (m, 7.5H), 6.66 (d, J = 1.6 Hz, 0.5H), 6.59 (d, J = 2.4 Hz, 0.5H), 2.51−2.47 (m, 1H), 2.41 (s, 0.5H), 2.25−2.23 (m, 1H), 2.11 (d, J = 2.8 Hz, 0.5H), 1.65−1.56 (m, 1.5H), 1.44−1.35 (m, 3H), 1.24 (d, J = 9.6 Hz, 0.5H), 1.12−0.84 (m, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.7 (d, J = 31.3 Hz), 146.5 (d, J = 32.3 Hz), 144.4, 143.7, 142.7 (d, J = 7.1 Hz), 142.4 (d, J = 7.1 Hz), 137.4 (d, J = 13.1 Hz), 137.3 (d, J = 12.1 Hz), 137.2, 137.1, 136.9, 136.7, 134.3 (d, J = 7.1 Hz), 134.1 (d, J = 6.1 Hz), 134.0, 133.9, 133.8, 133.7, 133.6, 133.5, 130.8 (d, J = 3.0 Hz), 130.6 (d, J = 3.0 Hz), 130.5, 130.3, 130.2, 130.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 127.8, 127.7, 127.6, 126.8, 126.5, 43.9, 43.6, 41.7, 41.6, 38.4, 38.4, 37.4, 37.0, 36.8, 36.0, 31.1, 30.5, 28.6, 28.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −13.6, −14.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}ClP$ 467.1690; found 467.1687.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-4′-methyl-[1,1′-biphenyl]-2-yl)-diphenylphosphane (**3l**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3l** (36.6 mg, 41%) as a colorless oil. m/d > 20:1, dr = 1.1:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.34 (m, 1H), 7.30−7.28 (m, 7H), 7.21−7.09 (m, 7H), 6.84−6.78 (m, 1H), 6.71 (d, J = 7.6 Hz, 0.5H), 6.65 (d, J = 7.6 Hz, 0.5H), 2.50 (t, J = 7.6 Hz, 1H), 2.41 (s, 0.5H), 2.37 (s, 3H), 2.24 (s, 1H), 2.17 (s, 0.5H), 1.72−1.63 (m, 1.5H), 1.48−1.36 (m, 3H), 1.22 (d, J = 9.2 Hz, 0.5H), 1.12−0.85 (m, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.5 (d, J = 33.3 Hz), 148.4 (d, J = 32.3 Hz), 145.3, 144.8, 138.5 (d, J = 7.1 Hz), 138.2 (d, J = 7.1 Hz), 138.1, 138.0, 137.8, 137.7, 137.2, 137.1, 136.8 (d, J = 11.1 Hz), 136.6 (d, J = 10.1 Hz), 134.4, 134.0, 133.9, 133.8, 133.7, 133.6, 131.0 (d, J = 5.1 Hz), 130.7 (d, J = 5.1 Hz), 130.6, 130.5, 128.6, 128.5, 128.4, 128.3, 127.3 (d, J = 9.1 Hz), 126.4, 126.0, 125.2 (d, J = 12.1 Hz), 44.2, 44.2, 43.5, 41.8, 41.4, 38.4, 37.4, 36.9, 36.8, 36.1, 31.1, 30.6, 28.6, 21.9, 21.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.9, −15.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{32}P$ 447.2236; found 447.2234.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-[1,1′:4′,1″-terphenyl]-2-yl)-diphenylphosphane (**3m**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3m** (77.2 mg, 76%) as a colorless oil. m/d = 12:1, dr = 1.1:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 1.6 Hz, 0.5H), 7.54 (d, J = 1.2 Hz, 0.5H), 7.48−7.31 (m, 11H), 7.25−7.17 (m, 7H), 6.90 (d, J = 7.6 Hz, 0.5H), 6.83 (d, J = 7.6 Hz, 0.5H), 2.61 (t, J = 8.4 Hz, 1H), 2.52 (s, 0.5H), 2.31−2.26 (m, 1.5H), 1.80−1.72 (m, 1.5H), 1.55−1.42 (m, 3H), 1.31 (s, 0.5H), 1.15−0.91 (m, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.0 (d, J = 32.3 Hz), 147.9 (d, J = 31.3 Hz), 146.1, 145.5, 141.8, 141.7, 140.4, 140.3, 140.1, 137.8 (d, J = 9.1 Hz), 137.7 (d, J = 9.1 Hz), 137.7, 137.5, 137.4, 136.9 (d, J = 11.1 Hz), 136.7 (d, J = 11.1 Hz), 134.2, 134.1, 134.0, 133.9, 133.8, 133.7, 131.2 (d, J = 13.1 Hz), 131.1 (d, J = 14.1 Hz), 130.9 (d, J = 6.1 Hz), 130.6 (d, J = 5.1 Hz), 128.8, 128.5, 128.4, 128.3, 127.5, 127.4, 127.3, 127.2, 124.4, 124.0, 123.3, 123.2, 44.4, 43.7, 41.8, 41.6, 38.5, 37.6, 37.0, 36.8, 36.2, 31.1, 30.6, 28.7, 28.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.1, −15.2, −16.9, −17.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{34}P$ 509.2393; found 509.2395.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-4′-fluoro-[1,1′-biphenyl]-2-yl)-diphenylphosphane (**3n**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3n** (72.1 mg, 80%) as a colorless oil. m/d > 20:1, dr = 1:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.35 (m, 1H), 7.30−7.28 (m, 7H), 7.24−7.10 (m, 6H), 7.06−6.98 (m, 1H), 6.75−6.60 (m, 2H), 2.48 (t, J = 8.0 Hz, 1H), 2.38 (s, 0.5H), 2.26−2.24 (m, 1H), 2.14 (s, 0.5H), 1.67−1.58 (m, 1.5H), 1.45−1.39 (m, 3H), 1.24 (s, 0.5H), 1.13−0.82 (m, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.6 (d, J = 245.4 Hz), 162.5 (d, J = 245.4 Hz), 148.5 (d, J = 7.1 Hz), 147.8 (d, J = 7.1 Hz), 147.3 (d, J = 15.2 Hz), 147.0 (d, J = 15.2 Hz), 137.6 (d, J = 4.0 Hz), 137.5 (d, J = 4.0 Hz), 137.4, 137.3, 137.2, 137.1, 137.0, 136.9, 136.8, 136.6, 136.5, 134.2, 134.1, 133.9, 133.7, 132.2 (d, J = 3.0 Hz), 132.1 (d, J = 3.0 Hz), 132.0 (d, J = 3.0 Hz), 131.9 (d, J = 3.0 Hz), 131.0 (d, J = 6.1 Hz), 130.7 (d, J = 5.1 Hz), 128.6, 128.5, 128.4, 127.6, 127.5, 112.7 (d, J = 22.2 Hz), 112.2 (d, J = 22.2 Hz), 111.3 (d, J = 12.1 Hz), 111.0 (d, J = 12.1 Hz), 44.4, 43.6, 41.7, 41.6, 38.4, 37.4, 36.9, 36.7, 36.0, 31.0, 30.5, 28.5, 28.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.2, −15.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.4, −114.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}FP$ 451.1985; found 451.1982.

*(2′-(Bicyclo[2.2.1]heptan-2-yl)-4′-chloro-[1,1′-biphenyl]-2-yl)-diphenylphosphane (**3o**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3o** (50.3 mg, 54%) as a colorless oil. m/d > 20:1, dr = 1.1:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.35 (m, 1H), 7.32−7.28 (m, 7.5H), 7.23−7.10 (m, 6.5H), 6.97−6.90 (m, 1H), 6.70 (d, J = 8.0 Hz, 0.5H), 6.64 (d, J = 8.0 Hz, 0.5H), 2.48 (t, J = 8.0 Hz, 1H), 2.40 (s, 0.5H), 2.26−2.24 (m, 1H), 2.14 (s, 0.5H), 1.68−1.61 (m, 1.5H), 1.48−1.36 (m, 3H), 1.27 (s, 0.5H), 1.14−0.84 (m, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.9, 147.1 (d, J = 33.3 Hz), 146.9 (d, J = 31.3 Hz), 139.6 (d, J = 7.1 Hz), 139.3 (d, J = 6.1 Hz), 137.6, 137.5, 137.4, 137.1 (d, J = 12.1 Hz), 136.9 (d, J = 12.1 Hz), 136.8, 136.7, 134.2, 134.1, 133.9, 133.8, 133.7, 133.5, 132.0 (d, J = 3.0 Hz), 131.8 (d, J = 3.0 Hz), 130.8 (d, J = 6.1

https://doi.org/10.1021/acs.joc.1c01329
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Hz), 130.5 (d, J = 5.1 Hz), 128.7, 128.6, 128.5, 128.4, 127.7, 127.6, 125.9, 125.5, 124.6, 124.5, 44.4, 43.6, 41.6, 41.5, 38.3, 37.4, 36.9, 36.7, 36.1, 31.1, 30.6, 28.5, 28.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.2, −15.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}ClP$ 467.1690; found 467.1688.

*1-(2-(Bicyclo[2.2.1]heptan-2-yl)-2′-(diphenylphosphanyl)-[1,1′-biphenyl]-4-yl)ethan-1-one (**3p**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3p** (78.7 mg, 83%) as a colorless oil. m/d > 20:1, dr = 1.2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 21.2, 1.6 Hz, 1H), 7.60−7.54 (m, 1H), 7.44−7.27 (m, 8H), 7.25−7.13 (m, 6H), 6.93 (d, J = 8.0 Hz, 0.5H), 6.86 (d, J = 8.0 Hz, 0.5H), 2.61 (d, J = 1.2 Hz, 3H), 2.57−2.54 (m, 1H), 2.48 (s, 0.5H), 2.30−2.27 (m, 1H), 2.17 (d, J = 2.8 Hz, 0.5H), 1.76−1.65 (m, 2H), 1.50−1.31 (m, 3H), 1.16−0.85 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 198.4, 198.3, 147.3 (d, J = 32.3 Hz), 147.2 (d, J = 32.3 Hz), 146.5 (d, J = 7.1 Hz), 146.4, 146.3 (d, J = 6.1 Hz), 145.8, 137.4, 137.3, 137.2, 137.0, 136.4 (d, J = 13.1 Hz), 136.4 (d, J = 12.1 Hz), 136.3, 136.2, 134.4, 134.3, 134.0, 133.9 (d, J = 3.0 Hz), 133.8, 133.7 (d, J = 3.0 Hz), 133.6, 131.0, 130.9, 130.2 (d, J = 6.1 Hz), 130.0 (d, J = 6.1 Hz), 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.8, 125.4, 125.1, 124.9, 124.8, 44.3, 43.7, 41.7, 41.5, 38.3, 38.2, 37.5, 37.0, 36.8, 36.0, 31.1, 30.6, 28.6, 28.5, 26.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.4, −15.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{32}OP$ 475.2185; found 475.2184.

*Methyl 2″-(dicyclohexylphosphanyl)-[1,1′:2′,1″-terphenyl]-3-carboxylate (**3q**).* Purification by column chromatography on silica gel (EA/hexane = 1/100) yielded **3q** (72.5 mg, 74%) as a colorless oil. m/d = 10:1, dr = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 21.2, 1.2 Hz, 1H), 7.69−7.62 (m, 1H), 7.43−7.28 (m, 8H), 7.24−7.14 (m, 6H), 6.88 (d, J = 7.6 Hz, 0.5H), 6.81 (d, J = 8.0 Hz, 0.5H), 3.92 (s, 3H), 2.58−2.53 (m, 1H), 2.48 (s, 0.5H), 2.29−2.26 (m, 1H), 2.16 (d, J = 2.8 Hz, 0.5H), 1.77−1.66 (m, 1.5H), 1.46−1.36 (m, 3H), 1.30 (s, 0.5H), 1.15−0.88 (m, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 167.5, 147.3 (d, J = 32.3 Hz), 147.2 (d, J = 32.3 Hz), 146.2, 146.1, 145.9, 145.5, 137.5, 137.3, 137.2, 137.0, 136.4 (d, J = 12.1 Hz), 136.3 (d, J = 12.1 Hz), 134.2, 134.0, 133.9, 133.8, 133.7, 133.6, 130.9 (d, J = 3.0 Hz), 130.7 (d, J = 3.0 Hz), 130.2 (d, J = 6.1 Hz), 130.0 (d, J = 5.1 Hz), 129.4, 129.3, 128.7, 128.6, 128.5, 128.4, 127.8, 127.7, 126.8, 126.5, 125.8, 125.7, 52.1, 44.3, 44.2, 43.6, 41.7, 41.4, 38.2, 37.4, 36.9, 36.8, 36.0, 31.1, 30.5, 28.6, 28.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.3, −15.4, −17.1, −18.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{32}O_2P$ 491.2134; found 491.2131.

*1-(5-(2′-(Diphenylphosphanyl)-[1,1′-biphenyl]-2-yl)bicyclo-[2.2.1]heptan-2-yl)ethan-1-one (**3r**).* Purification by column chromatography on silica gel (EA/hexane = 1/20) yielded **3r** (54.8 mg, 58%) as a colorless oil. m:d > 20:1, dr = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.36 (m, 1H), 7.33−7.28 (m, 9H), 7.22−7.11 (m, 6H), 7.02−6.95 (m, 1H), 6.80 (d, J = 7.2 Hz, 0.5H), 6.76 (dd, J = 7.6, 1.2 Hz, 0.5H), 2.57−2.47 (m, 2.5H), 2.32−2.21 (m, 1.5H), 2.11 (d, J = 2.0 Hz, 3H), 1.78−1.61 (m, 2H), 1.56−1.42 (m, 1.5H), 1.32 (d, J = 10.0 Hz, 0.5H), 1.21−0.96 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 210.2, 148.1 (d, J = 32.3 Hz), 148.0 (d, J = 32.3 Hz), 144.9, 144.1, 141.2 (d, J = 7.1 Hz), 140.9 (d, J = 7.1 Hz), 137.8 (d, J = 6.1 Hz), 137.7 (d, J = 5.1 Hz), 137.7, 137.5, 137.4, 137.0 (d, J = 11.1 Hz), 136.7 (d, J = 12.1 Hz), 134.2, 134.0, 133.8, 130.9 (d, J = 3.0 Hz), 130.8 (d, J = 3.0 Hz), 130.7 (d, J = 6.1 Hz), 130.5 (d, J = 5.1 Hz), 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.5, 127.4, 125.3, 124.8, 124.7, 54.1, 54.0, 43.9, 43.8, 43.4, 41.5, 41.3, 40.4, 40.2, 38.0, 35.4, 34.0, 33.8, 33.5, 29.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.4, −15.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{32}OP$ 475.2180; found 475.2185.

*5-(2′-(Diphenylphosphanyl)-[1,1′-biphenyl]-2-yl)bicyclo[2.2.1]-heptane-2-carbonitrile (**3s**).* Purification by column chromatography on silica gel (EA/hexane = 1/30) yielded **3s** (47.5 mg, 52%) as a colorless oil. m/d > 20:1, dr = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.35 (m, 1H), 7.33−7.28 (m, 8H), 7.24−7.09 (m, 7H), 7.06−6.98 (m, 1H), 6.84 (d, J = 6.4 Hz, 0.5H), 6.77 (dd, J = 7.2 Hz, 0.5H), 2.61 (s, 1H), 2.54 (d, J = 3.6 Hz, 0.5H), 2.46 (t, J = 7.2 Hz, 1H), 2.29 (d, J = 3.6 Hz, 0.5H), 2.22−2.10 (m, 1H), 1.88−1.63 (m, 3H), 1.54−1.49 (m, 1H), 1.36−1.26 (m, 1.5H), 0.97−0.91 (m, 0.5H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 147.8 (d, J = 31.3 Hz), 147.7 (d, J = 32.3 Hz), 143.8, 143.1, 141.3 (d, J = 8.1 Hz), 141.0 (d, J = 6.1 Hz), 137.7, 137.5, 137.4, 137.3, 136.9 (d, J = 12.1 Hz), 136.7 (d, J = 12.1 Hz), 134.3, 134.1, 134.0, 133.9, 133.8, 133.7, 131.1 (d, J = 3.0 Hz), 130.9 (d, J = 3.0 Hz), 130.6 (d, J = 5.1 Hz), 130.3 (d, J = 6.1 Hz), 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 125.3, 125.1, 125.0, 124.6, 123.7, 123.6, 43.2, 43.1, 42.4, 42.3, 41.2, 40.0, 37.4, 37.0, 36.7, 36.3, 34.9, 30.3, 30.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ −14.5, −15.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{29}NP$ 458.2028; found 458.2032.

*4-Methoxy-1,1′-biphenyl (**6a**).*[18a] Purification by column chromatography on silica gel (EA/hexane = 1/50) yielded **6a** (87.4 mg, 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.55 (m, 4H), 7.45 (t, J = 7.2 Hz, 2H), 7.34 (tt, J = 7.2, 1.2 Hz, 1H), 7.03−6.99 (m, 2H), 3.87 (s, 3H).

*4-Methyl-1,1′-biphenyl (**6b**).*[18a] Purification by column chromatography on silica gel (hexane) yielded **6b** (75.6 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.67 (m, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.54−7.50 (m, 2H), 7.42 (tt, J = 7.2, 1.2 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H).

*Methyl [1,1′-Biphenyl]-4-carboxylate (**6c**).*[18b] Purification by column chromatography on silica gel (EA/hexane = 1/20) yielded **6c** (54.1 mg, 51%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dt, J = 8.4, 1.6 Hz, 2H), 7.68−7.61 (m, 4H), 7.49−7.45 (m, 2H), 7.42−7.38 (m, 1H), 3.95 (s, 3H).

*3-Methyl-1,1′-biphenyl (**6d**).*[18b] Purification by column chromatography on silica gel (hexane) yielded **6d** (68.9 mg, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.68 (m, 2H), 7.55−7.49 (m, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 7.6 Hz, 1H), 2.52 (s, 3H).

*3-Chloro-1,1′-biphenyl (**6e**).*[18c] Purification by column chromatography on silica gel (hexane) yielded **6e** (83.7 mg, 89%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.58 (m, 3H), 7.52−7.47 (m, 3H), 7.44−7.35 (m, 3H).

*1-([1,1′-Biphenyl]-3-yl)ethan-1-one (**6f**).*[18d] Purification by column chromatography on silica gel (EA/hexane = 1/20) yielded **6f** (78.4 mg, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.02 (m, 2H), 7.69−7.62 (m, 4H), 7.49−7.46 (m, 2H), 7.43−7.39 (m, 1H), 2.64 (s, 3H).

*4,4′-Dimethoxy-1,1′-biphenyl (**6g**).*[18a] Purification by column chromatography on silica gel (EA/hexane = 1/20) yielded **6g** (91.0 mg, 85%) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dt, J = 8.8, 2 Hz, 4H), 6.98 (dt, J = 8.8, 2 Hz, 4H), 3.86 (s, 6H).

*4-Methoxy-4′-methyl-1,1′-biphenyl (**6h**).*[18e] Purification by column chromatography on silica gel (EA/hexane = 1/50) yielded **6h** (95.0 mg, 96%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.54 (m, 4H), 7.32 (d, J = 7.6 Hz, 2H), 7.07−7.05 (m, 2H), 3.91 (s, 3H), 2.49 (s, 3H).

*4-Methoxy-1,1′:4′,1″-terphenyl (**6i**).*[18f] Purification by column chromatography on silica gel (EA/hexane = 1/50) yielded **6i** (123.5 mg, 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.58 (m, 8H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H).

*4-Fluoro-4′-methoxy-1,1′-biphenyl (**6j**).*[18e] Purification by column chromatography on silica gel (EA/hexane = 1/50) yielded **6j** (87.9 mg, 87%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.46 (m, 4H), 7.11 (tt, J = 8.8, 2 Hz, 2H), 6.98 (dt, J = 8.8, 2 Hz, 2H), 3.86 (s, 3H).

*4-Chloro-4′-methoxy-1,1′-biphenyl (**6k**).*[18e] Purification by column chromatography on silica gel (EA/hexane = 1/50) yielded **6k** (100.3 mg, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.47 (m, 4H), 7.40−7.38 (m, 2H), 7.01−6.97 (m, 2H), 3.86 (s, 3H).

*1-(4-Methoxyphenyl)naphthalene (**6l**).*[18g] Purification by column chromatography on silica gel (EA/hexane = 1/50) yielded **6l** (110.0 mg, 94%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−7.91 (m, 3H), 7.61−7.49 (m, 6H), 7.12 (d, J = 8.8 Hz, 2H), 3.95 (s, 3H).

*3-(4-Methoxyphenyl)furan (**6m**).*[18a] Purification by column chromatography on silica gel (EA/hexane = 1/25) yielded **6m** (69.6 mg, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67

https://doi.org/10.1021/acs.joc.1c01329
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(s, 1H), 7.47 (s, 1H), 7.44−7.42 (m, 2H), 6.95−6.91 (m, 2H), 6.67 (s, 1H), 3.83 (s, 3H).

3-(4-Methoxyphenyl)quinoline (**6n**).[18h] Purification by column chromatography on silica gel (EA/hexane = 1/25) yielded **6n** (56.4 mg, 48%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, J = 2.4 Hz, 1H), 8.25 (d, J = 2.4 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.72−7.65 (m, 3H), 7.59−7.55 (m, 1H), 7.08−7.04 (m, 2H), 3.88 (s, 3H).

2-Methoxy-2′-methyl-1,1′-biphenyl (**6o**).[18g] Purification by column chromatography on silica gel (EA/hexane = 1/50) yielded **6o** (26.7 mg, 27%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 1H), 7.27−7.13 (m, 5H), 7.03−6.45 (m, 2H), 3.76 (s, 3H), 2.14 (s, 3H).

2,2′,6-Trimethyl-1,1′-biphenyl (**6p**).[18b] Purification by column chromatography on silica gel (hexane) yielded **6p** (17.6 mg, 18%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.25 (m, 2H), 7.24−6.99 (m, 5H), 1.97 (s, 3H), 1.95 (s, 6H).

Ethyl (E)-3-(o-Tolyl)acrylate (**8a**).[19a] Purification by column chromatography on silica gel (EA/hexane = 1/50) yielded **8a** (70.3 mg, 74%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 16.0 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.28−7.25 (m, 1H), 7.23−7.19 (m, 2H), 6.36 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H).

1-Methoxy-4-(phenylethynyl)benzene (**8b**).[19b] Purification by column chromatography on silica gel (hexane) yielded **8b** (58.3 mg, 56%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.46 (m, 4H), 7.37−7.31 (m, 3H), 6.89 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H).

Scale Up Synthesis. To a 50 mL Schlenk tube was added 2-diphenylphosphinobiphenyl **1a** (3 mmol, 1.02 g, 1.0 equiv), norbornene **2a** (9 mmol, 0.85 g, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (45.8 mg, 0.025 equiv), H-*L*-Ala-OH (80.1 mg, 0.3 equiv), and NaOAc (492 mg, 2.0 equiv). The tube was purged with Ar three times, followed by the addition of 2-Me-THF (9 mL). The mixture was stirred at 160 °C in an oil bath for 24 h. The solution was then cooled to room temperature and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (R_f = 0.8, EA/hexane = 1/50) affording the alkylated products **3a** and **3aa** (white solid, 1.2 g, 83% yield, m/d = 1:1). The ratio of **3a** and **3aa** was about 1:1 by ^{31}P NMR yield analyzed with PPh_3 as an internal standard.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01329.

Copies of ^{1}H, ^{13}C{1H}, ^{31}P NMR, ^{19}F NMR, and single-crystal X-ray analysis of **3aa** and **3k** (PDF)

Accession Codes

CCDC 2059805 and 2070266 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the NSF of Guangxi Province (Grant No. 2017GXNSFDA198040) and the BAGUI talent program (Grant No. 2019AC26001).

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