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Binary-Acid Catalysis with Sc(OTf)$_3$/TfOH in the Alkenylation of Arenes with Alkynes

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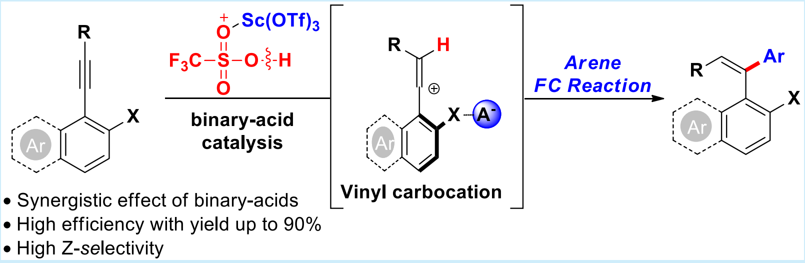
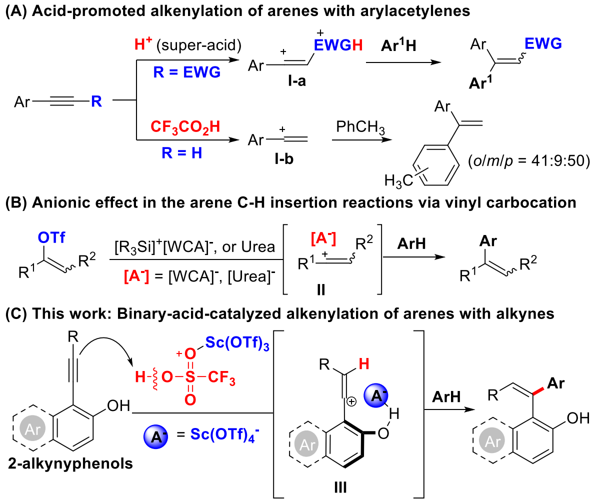


ABSTRACT: Herein we report binary acid Sc(OTf)$_3$/TfOH-catalyzed alkenylation of arenes with alkynes. In this system, the high-energy vinyl carbocations with activated and weakly coordinating trifluoromethanesulfonate anions by Lewis acid Sc(III) can undergo facile Friedel−Crafts reactions with arenes to give the desired adducts in up to 90% yield and with high *Z*-selectivity.

The alkenylation of arenes with alkynes is one of the most straightforward strategies to build versatile structural motifs of polysubstituted olefins.[1] A number of transition-metal catalysts have been reported to promote the alkenylation of (hetero)arenes with alkynes.[2−9] In addition, the Friedel−Crafts reaction of arenes with in situ generated vinyl carbocations **I-a** (Scheme 1, A), which is generally difficult to achieve and requires in combined acids (e.g., HF-SbF$_5$, TfOH-SbF$_5$) as dual super acids and solvents, has appeared as a complementary yet appealing strategy for alkenylation reaction.[10a,11] Kitamura found that stoichiometric amounts of CF$_3$CO$_2$H could promote the hydroarylation reaction of phenylacetylene with toluene via carbocations **I-b**, but with lower regioselectivity.[10b] Recently, Nelson has developed weakly coordinating anions (WCA) salts and thioureas catalysis for the functionalization of unactivated C−H bonds via vinyl carbocations **II** (Scheme 1, B).[12]

Scheme 1. Alkenylation Reaction of Arenes



In fact, 2-alkynyphenols are also one of the most attractive precursors for in situ generated vinylidene-quinone methides (**VQM**).[13] Recently, Tan developed chiral phosphoric acid catalysis for the asymmetric hydroarylation reaction of arylacetylenes with 2-naphthols.[13a] Previously, we developed enantioselective cationic functionalizations catalyzed by asymmetric binary acids (ABC) endowed with bi/multi-activation site (e.g., proton and metal center).[14] According to Yamamoto's combined acid principles, acidity/electrophilicity of Lewis acid, Brønsted acid, or both could be enhanced to activate inert substrates.[15] In fact, it was found that anionic ligands could stabilize the developing carbocations from simple olefins through anion-pair effect in binary acid systems.[14a] We describe herein an alkenylation reaction of arenes with 2-alkynyphenols that is mediated by Sc(OTf)$_3$/TfOH (Scheme 1, C). In this scenario, binary acids enhanced electrophilicity and acidity may facilitate the nucleophilic attack of 2-alkynyphenols to form vinyl carbocations **III** with a

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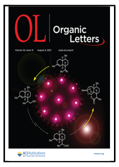

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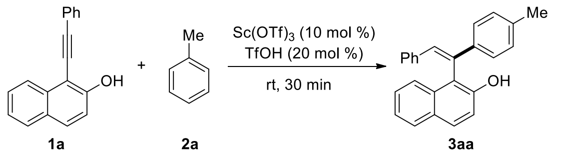
weakly coordinating Sc(III)-based trifluoromethanesulfonate anion (A^{-}), which undergo subsequent Friedel−Crafts reaction to afford final products.

Alkenylation of toluene **2a** with 1-(phenylethynyl)-naphthalene-2-ol **1a** was chosen as a model reaction to test the catalytic activity (Table 1). We were able to identify a viable complex composed of $Sc(OTf)_3$ (10 mol %) and TfOH (20 mol %) at room temperature. Under optimized conditions, the desired adduct **3aa** can be isolated in 76% yield ($Z/E > 19:1$) (entry 1). Interestingly, no reaction occurred in the absence of TfOH at room temperature (entry 2), but a reaction temperature 80 °C was found to give the adduct **3aa** in 32% yield (entry 3). However, the other Brønsted acids, such as $(PhO)_2PO_2H$, CF_3CO_2H, MsOH, and TsOH, were found to be inferior to TfOH (entries 4−7 vs entry 1). We hypothesized that trifluoromethanesulfonate anion by Lewis acid Sc(III) would help stabilize the developing carbocations through an ion-pair effect (like **III**) and suppress further decomposition of alkyne **1a** and product **3aa**. In addition, screening of various Lewis acids was carried out with TfOH (20 mol %) at room temperature. Other Lewis acids such as Ni(II), Cu(II), and In(III), or no Lewis acid, were less effective under these conditions (<72% yield, entries 8−11 vs entry 1). The impact of the ratio of $Sc(OTf)_3$ and TfOH was also examined. The activity was improved by increasing the ratio of $TfOH/Sc(OTf)_3$ from 2:1 to 4:1 (entry 12 vs entry 1); however, further increasing the ratio to 6:1 did not lead to further improvement in activity (entry 13 vs entry 12). Interestingly, it was found that an enhanced cationic nature of the scandium center (by the addition of NaBArF instead of OTf^{-} salt; BArF = $[3,5-(CF_3)_2C_6H_3]B$) is essential for reactivity of Sc(III) Lewis acid in the absence of TfOH, but it still required much longer reaction times (12 h) than the binary-acid system (entry 14 vs entry 12).

Table 1. Optimization of the Reaction Conditions[a]

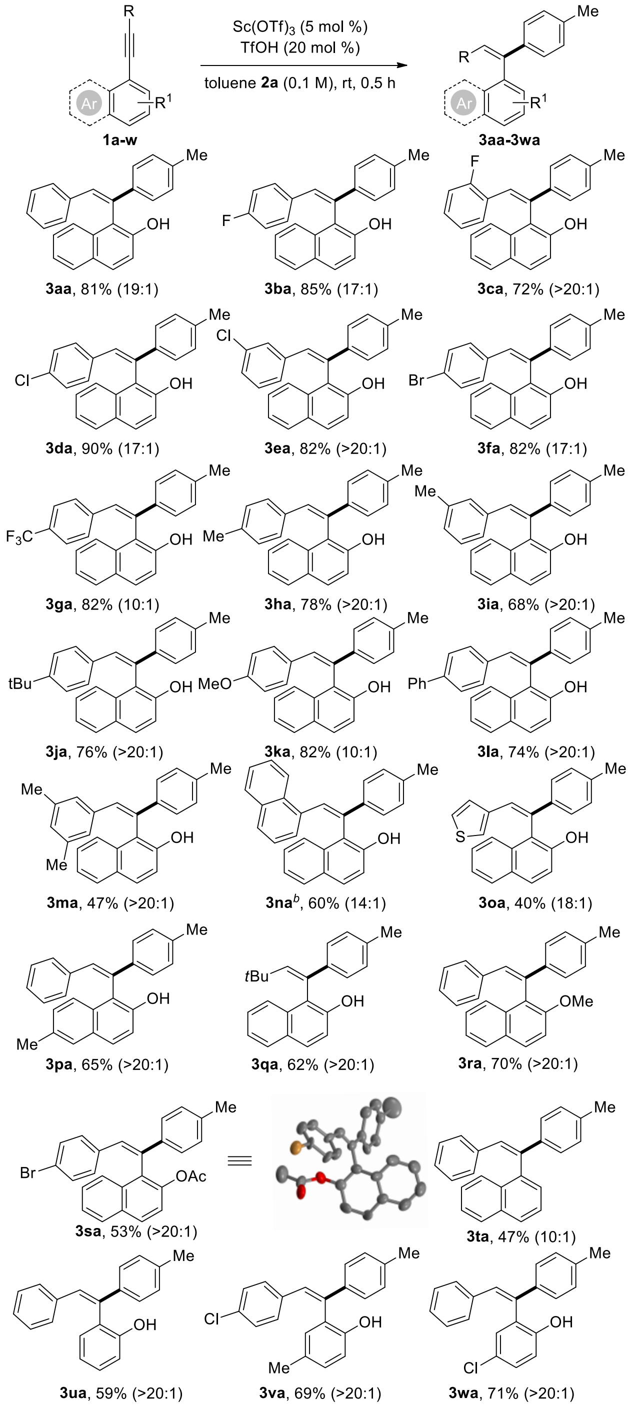


entry	variation from standard condition	yield (%)[b]
1	standard conditions	76
2	no TfOH	nr
3[c]	no TfOH, 80 °C	32
4	$(PhO)_2PO_2H$ instead of TfOH	38
5	CF_3CO_2H	trace
6	MsOH	59
7	TsOH	17
8	$Ni(OTf)_2$ instead of $Sc(OTf)_3$	72
9	$Cu(OTf)_2$	69
10	$In(OTf)_3$	55
11	no $Sc(OTf)_3$	53
12	5 mol % $Sc(OTf)_3$	81
13	30 mol % TfOH and 5 mol % $Sc(OTf)_3$	61
14[c]	5 mol % $Sc(OTf)_3$ and 5 mol % NaBArF	83

[a] Standard reaction condition: **1a** (0.1 mmol), $Sc(OTf)_3$ (10 mol %), and TfOH (20 mol %) at room temperature in $PhCH_3$ **2a** (1.0 mL) for 30 min. [b] Isolated yield, Z/E value of product **3aa** (>19:1). [c] 12 h. nr = no reaction.

The catalytic scope of the obtained optimal binary acid $Sc(OTf)_3$/TfOH was next explored in the alkenylation of toluene **2a** with alkynes **1** (Scheme 2). First, different substituent groups on the phenyl ring **1a−m** were investigated. Either electron-withdrawing groups (F, Cl, Br, and CF_3) or electron-donating groups (Me, *t*Bu, MeO, and Ph) at different

Scheme 2. Substrate Scope of Alkenylation of Toluene 2a with Alkynes 1[a]



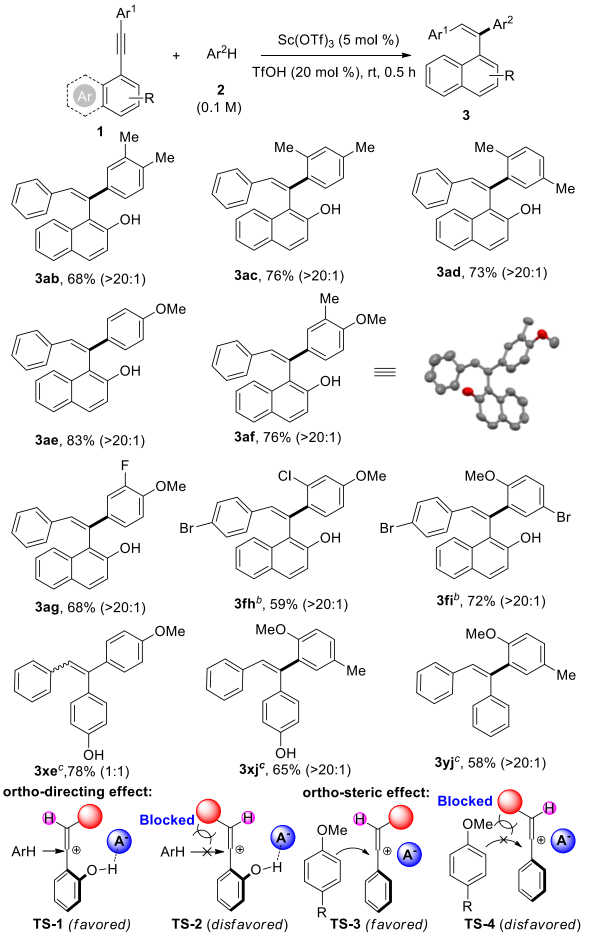
[a] Reaction condition: **1** (0.2 mmol), $Sc(OTf)_3$ (5 mol %), and TfOH (20 mol %) at room temperature in $PhCH_3$ **2a** (2.0 mL) for 0.5 h. Isolated yield for **3**, Z/E ratio of **3** in parentheses determined by ^1H NMR. [b] At room temperature for 2 h.

positions on the phenyl ring were tolerated well, giving the desired adducts **3aa**−**3la** in moderate to high yields and with high *Z*-selectivity. In addition, a dimethyl substituted group **1m** could also react with toluene **2a**, giving much lower yield (47%, *Z*/*E* >20:1). Moreover, the reaction could work well with naphthyl- and heteroaromatic substituted *o*-alkynylnaphthols **1n** and **1o**, affording the desired products **3na** and **3oa** in 40−60% yields and with high *Z*-selectivity (up to 18:1). Furthermore, we found that a substrate **1p** with a substituent (Me) on the naphthalene ring was also tolerated in this catalytic system, affording the adduct **3pa** in 65% yield (*Z*/*E* > 20:1). Satisfyingly, the reaction of alkyl substituted *ortho*-alkynylnaphthol **1q** also worked well, giving the product **3qa** in 62% yield (*Z*/*E* > 20:1). Significantly, *O*-protected alkynes **1r**−**s** also reacted with **2a** under the optimal conditions with excellent *Z*-selectivity, albeit in lower yields (70% yield for **3ra**, 53% yield for **3sa**), thus indicating that the formation of **VQM** was not crucial for this transformation. Surprisingly, 1-(phenylethynyl)naphthalene **1t** was also tolerated, affording the product **3ta** in 47% yield (*Z*/*E* = 10:1) and high regioselectivity (*p*/*o* > 99:1) like other alkynes containing the naphtholic OH. Although we still have no clear experimental evidence now, we think that this result may be caused by the steric hindrance of naphthalene ring shielding the *ortho*-attack of toluene. Next, a series of substituted 2-(phenylethynyl)-phenols **1u**−**w** were reacted with toluene **2a** under optimized reaction conditions. Compared with 2-(phenylethynyl)phenol **1u**, the reaction of arylalkynes bearing substitution on either the benzene ring or the phenol moiety gave much better yields (69% yield for **3va** and 71% yield for **3wa**). The relative configuration of **3sa** was assigned by X-ray diffraction analysis, and other adducts with toluene **2a** can therefore be assigned by analogy.[16]

To further expand the substrate scope, we next tested other simple arenes (Scheme 3). *m*- and *p*-xylene **2c**,**d** worked well, providing much better yields than their *ortho*-substituted counterpart **2b**. Gratifyingly, anisole could react with 1-(phenylethynyl)-naphthalen-2-ol **1a**, giving the product **3ae** in 83% yield. Different substituents of anisole were also tested, and it was found that an electron-donating group (CH_3) was preferred to an electron-withdrawing group (F, Cl, and Br). In the presence of Et_3N, treatment of **3fh** and **3fi** with acetyl chloride in DCM at 0 °C led to the desired product *O*-protected *α*-alkynynaphthalen-2-ols **4** and **5** in 87% and 85% yields, respectively (Scheme 4, A). The relative configuration of **3af**, **4**, and **5** was assigned as *Z*-selective olefins by X-ray diffraction analysis, and other adducts with arenes **2b**−**i** can therefore be assigned by analogy.[16] In addition, 4-(phenylethynyl)phenol **1x** could also reacted with anisole to give the adduct **3xe** in 78% yield and with lower *Z*/*E* value (1:1, **3xe** vs **3ae**).[17] These results show that the *ortho*-hydroxyl group may not only increase the nucleophilicity of the alkyne via resonance donation but also tune the developing anion by an *ortho*-directing group (Scheme 3, **TS-1** vs **TS-2**). To our surprise, when 1-methoxy-4-methylbenzene **2j** was used, the reactions of **1x** and **1y** gave the products **3xj** and **3yj** with excellent *Z*/*E* value (>20:1), respectively, due to the effect of *ortho*-steric hindrance on the arenes (Scheme 3, **TS-3** vs **TS-4**).

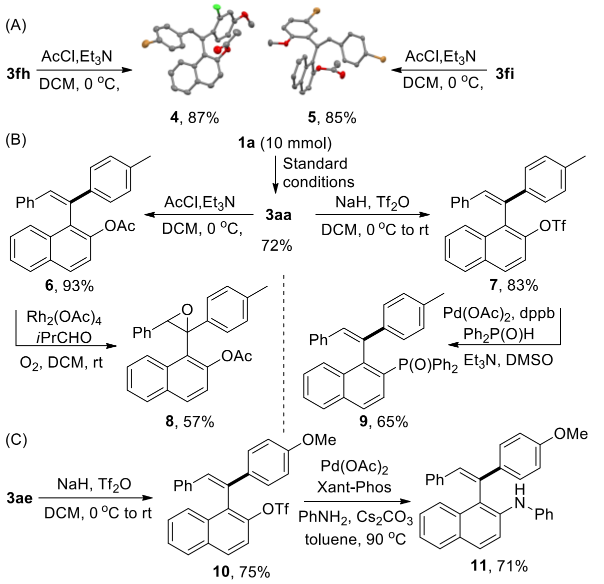
The developed alkenylation could be performed on a gram scale. Under the standard conditions, trisubstituted olefin **3aa** was obtained in 72% yield (*Z*/*E* = 19:1, Scheme 4, B). Next, the olefins **3aa** or **3ae** could also be easily converted into the

Scheme 3. Substrate Scope of Alkenylation of Arenes 2 with Alkynes 1[a]



[a]Reaction condition: **1** (0.2 mmol), $Sc(OTf)_3$ (5 mol %), and TfOH (20 mol %) at room temperature in Ar^1H **2** (2.0 mL) for 0.5 h. Isolated yield for **3**, *Z*/*E* ratio of **3** in parentheses determined by ^1H NMR. [b]50 °C for 3 h. [c]At room temperature for 12 h.

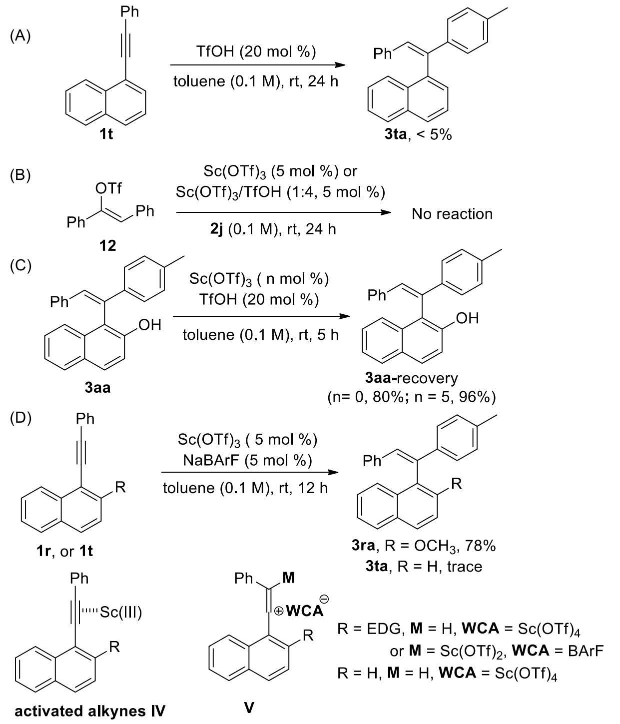
Scheme 4. Gram-Scale Reaction and Transformation of Trisubstituted Olefins 3



corresponding acetate **6** and triflates **7** or **10**, respectively. Epoxidation[18] of olefin **6** were catalyzed by $Rh_2(OAc)_4$ to give the corresponding product **8** in 57% yield. In addition, palladium catalyzed-coupling reactions[13c] between the corresponding triflates and diphenyl phosphine oxide or aniline furnished **9** and **11** in 65% and 71% yields, respectively.

To gain insights into the mechanism of this methodology, several control experiments were carried out. From our studies, it was found that TfOH was actually a viable catalyst for the model reaction; however, the combination of TfOH with $Sc(OTf)_3$ could further improve the catalysis with better yield (Table 1, entry 11 vs 12), although the substrate **1a** is completely consumed almost at the same time under two different conditions. The difference in reactivity between TfOH alone and $Sc(OTf)_3$/TfOH, however, was more significant when the substrate did not contain the phenolic OH found in the model substrate **1a** (or another EDG). As such, when **1t** was treated with TfOH (20 mol %), alkenylation was only observed in <5% yield (Scheme 5, A). This result shows the importance of the binary acid system to efficient generation of vinyl carbocation species, particularly in less activated systems. In addition, we found that $Sc(OTf)_3$ or the binary acid catalyzed reaction of vinyl triflate **12** with arene **2j** could not work (Scheme 5, B), excluding the possibility of a vinyl triflate as an active intermediate in this reaction. When isolated adduct **3aa** was treated under binary acid catalytic conditions, **3aa** can be recovered quantitatively, while the recovery is only 80% of **3aa** in the absence of $Sc(OTf)_3$ (Scheme 5, C), thus suggesting product **3aa** should be more stable under the standard condition. Moreover, when only 10 equiv of **2a** was used in the binary-acid system, it was found that a survey of different solvents, such as $CHCl_3$, MeCN, and THF, resulted in poor yields (Table S5, entries 1−3), and no product **3aa** was obtained when using 1 equiv of TfOH alone in toluene (entry 4). Unknown byproducts were observed in these cases (Figure S1), which might be resulting from the failure of in situ redundant vinyl carbocation to be captured by toluene in time. Furthermore, 5 mol % of cationic Lewis acid $Sc(OTf)_2(BArF)$ could also promote the alkenylation of toluene **2a** with *O*-protected alkyne **1r** to give adduct **3ra** in 78% yield in the absence of TfOH for 12 h; however, only trace product **3ta** was observed when 1-(phenylethynyl)-naphthalene **1t** was used (Scheme 5, D), thus suggesting that alkynes bearing an electron-donating group at 2-position on the naphthyl ring may be more easily activated to form a vinyl carbocation **V** that has a weakly coordinating anion, such as $BArF^-$, and $Sc(OTf)_4^-$ through π-coordination (**IV**) by Scandium(III).[19] It is noteworthy that more electrophilicity of $Sc(OTf)_3$/TfOH is crucial to generate vinyl carbocations from neutral alkynes.

Scheme 5. Control Experiments



The characteristic absorption of carbocation can be clearly observed by UV−visible spectra.[20] Thus, the UV−vis spectroscopy of **1a** has been examined in CH_2Cl_2 in the presence of different acids (Figure S2), respectively, showing peak absorption at 303−355 nm, which tails above 400 nm (ε_{400} = 3882, ε_{450} = 2243 for the mixture of **1a**, and $Sc(OTf)_3$/TfOH). Upon in situ mixing **1a** and the binary acids, the colorless solution became red (Figure S2, inset). In order to exclude the new absorption at $\lambda > 400$ nm due to presence of **VQM**, the UV−vis experiments with *O*-protected alkyne **1r** were also conducted (Figure S3), giving similar results as the use of **1a**. These observations suggest that $Sc(OTf)_3$/TfOH should more effectively generate vinyl carbocation than either TfOH or $Sc(OTf)_2(BArF)$.

In summary, we have developed Sc(III)/TfOH-catalyzed alkenylation of arenes with alkynes via the vinyl cation, affording trisubstituted olefins **3** in high yields and with high *Z*-selectivity. Salient features of the alkenylation include binary-acid catalysis in carbocation transformation. Further studies on the challenging enantioselective synthesis of axial chirality by asymmetric binary-acid-catalyzed alkenylation of arene with alkynes are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02065.

Experiment procedures, and characterization data for compounds (PDF)

Accession Codes

CCDC 2040079, 2040082, 2040089, and 2040509 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.

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(16) The olefins **3fa** could also be easily converted into the corresponding acetate (Supporting Information), of which ^1H and ^{13}C NMR was the same as the compound **3sa**. In addition to X-ray diffraction analysis, the relative configurations of **3** were established by ^1H NMR analysis according to ref 15, and (a) Lesieur, M.; Bidal, Y.

D.; Lazreg, F.; Nahra, F.; Cazin, C. S. J. Versatile Relay and Cooperative Palladium(0) *N*-Heterocyclic Carbene/Copper(I) *N*-Heterocyclic Carbene Catalysis for the Synthesis of Tri- and Tetrasubstituted Alkenes. *ChemCatChem* **2015**, *7*, 2108−2112. (b) Terao, Y.; Nomoto, M.; Satoh, T.; Miura, M.; Nomura, M. Palladium-Catalyzed Dehydroarylation of Triarylmethanols and Their Coupling with Unsaturated Compounds Accompanied by C-C Bond Cleavage. *J. Org. Chem.* **2004**, *69*, 6942−6944. Analysis of previously reported trisubstituted olefins with naphthalen-2-ol or naphthalene ring indicates that they all demonstrate reliable chemical shift differences for the *Z* and *E* isomers. The alkene hydrogen for the *E* isomer is always located around 6.8−7.0 ppm. The resonance for the *Z* isomer alkene hydrogen can overlap with other signals and appear over 7.0 ppm, whereas the alkene hydrogen of adduct **3** was located around 7.31−7.59 ppm. According to these results of X-ray diffraction and ^{1}H NMR data, adducts **3** were determined as *Z*-olefins.

(17) The *Z*/*E* mixture of olefins **3xe** could also be easily converted into the corresponding methyl ether **13** (Supporting Information), which is a known compound; see: Wang, T.; Hu, Y.; Zhang, S. A Novel and Efficient Method for the Olefination of Carbonyl Compounds with Grignard Reagents in the Presence of Diethyl Phosphite. *Org. Biomol. Chem.* **2010**, *8*, 2312−2315.

(18) Shabashov, D.; Doyle, M. P. Rhodium Acetate-Catalyzed Aerobic Mukaiyama Epoxidative of Alkenes. *Tetrahedron* **2013**, *69*, 10009−10013.

(19) For a selected example of *π*-coordination of alkyne by Scandium(III) salts, see: Mandal, S.; Verma, P. K.; Geetharani, K. Lewis Acid Catalysis: Regioselective Hydroboration of Alkynes and Alkenes Promoted by Scandium Triflate. *Chem. Commun.* **2018**, *54*, 13690−13693.

(20) Some selected examples of UV−visible spectra of carbocation, see: (a) Byrne, P. A.; Kobayashi, S.; Würthwein, E.-U.; Ammer, J.; Mayr, H. Why Are Vinyl Cations Sluggish Electrophiles? *J. Am. Chem. Soc.* **2017**, *139*, 1499−1511. (b) Lv, J.; Zhang, Q.; Zhong, X.; Luo, S. Asymmetric Latent Carbocation Catalysis with Chiral Trityl Phosphate. *J. Am. Chem. Soc.* **2015**, *137*, 15576−15583. (c) Cozens, F. L.; Kanagasabapathy, V. M.; McClelland, R. A.; Steenken, S. Lifetimes and UV-visible Absorption Spectra of Benzyl, Phenethyl, and Cumyl Carbocations and Corresponding Vinyl Cations. A Laser Flash Photolysis Study. *Can. J. Chem.* **1999**, *77*, 2069−2082.