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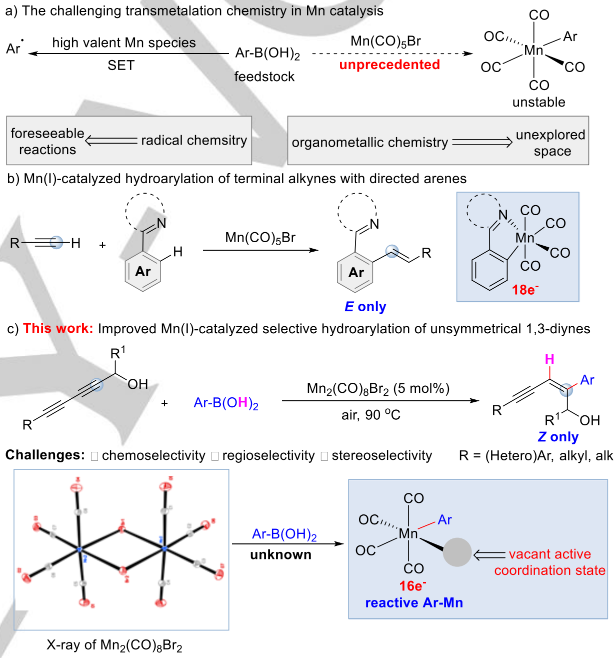
A Dimeric Mn-Catalyzed Completely Selective Hydroarylation of 1,3-Diynes for the Modular Synthesis of (*Z*)-Enynes Library

Zhongfei Yan, Xiang-Ai Yuan, Yue Zhao, Chengjian Zhu and Jin Xie*

Abstract: The transition-metal-catalyzed selective hydroarylation of unsymmetrical alkynes represents the state-of-art in organic chemistry, which still mainly relies on the use of precious late transition-metal catalysts. In this communication, we have developed an unprecedented Mn(I)-catalyzed hydroarylation of unsymmetrical 1,3-diyne alcohols with commercially available arylboronic acids in a predictive selectivity. This method well addresses the challenges in regio-, stereo- and chemoselectivity. It offers a general, convenient and practical strategy for the modular synthesis of multisubstituted (*Z*)-configurated conjugated enynes. This protocol is distinguished by its simple operation, complete selectivity, excellent functional group compatibility and gram-scale capacity. A dimeric Mn(I) species, $Mn_2(CO)_8Br_2$, was proven to be a much more efficient catalyst precursor than $Mn(CO)_5Br$.

The transition metal-catalyzed selective hydroarylation of C-C triple bonds with organometallic reagents,[1] particularly moisture and air-stable arylboronic acids,[2] is emerging as a reliable strategy for the streamlined synthesis of multisubstituted alkenes. Despite the important progress, regio- and chemoselective hydroarylation of unsymmetrical internal alkynes remains highly attractive. In comparison with Rh-[2a-f] and Pd-[2g-k] catalyzed hydroarylation, hydroarylation catalyzed by more earth-abundant and less toxic manganese has not yet been reported regardless of the potential importance of such a transformation. To date, the direct formation of Ar-Mn species from $Ar\text{-}B(OH)_2$ has remained a fundamentally unexplored topic.[3] The major barrier for this stems from the strong oxidation ability of high valent Mn-complexes[4a] and the low reactivity of Mn(I)-based catalysts toward transmetalation[4b] (Scheme 1a). Furthermore, almost all the known cases of alkyne insertion into C(aryl)-Mn bonds are based on the chelation-promoted 5-membered manganacycle model[5] because nonchelated $Ar\text{-}Mn(CO)_5$ species are prone to intramolecular rearrangement.[6] To the best of our knowledge, only chelation-controlled Mn(I)-catalyzed (*E*)-selective hydroarylation of terminal alkynes with directed arenes via C-H activation has been successfully reported by Wang's and Ackermann's group (Scheme 1b).[7] However, installing proximal directing groups onto arenes in advance is required, and the regioselectivity remains unsolved for internal alkynes. Therefore, the development of a general and highly selective hydroarylation of internal alkynes with commercially available $Ar\text{-}B(OH)_2$ is still a tremendous challenge in manganese catalysis.



Scheme 1. Mn(I)-catalyzed hydroarylation of alkynes and our design.

Conjugated enynes are prevalent structural motifs in a broad range of bioactive compounds[8a,8b] and also are versatile building blocks in synthetic chemistry.[8c] However, a general and completely selective strategy accessing to conjugated enynes remains challenging as the alkyne dimerization[8d, 8e] and cross-coupling strategies[8f, 8g] would potentially result in the formation of a mixture of regio- and stereoisomers. With this in mind, we selected unpolarized 1,3-diynes to start the study of Mn(I)-catalyzed hydroarylation with $Ar\text{-}B(OH)_2$ (Scheme 1c). Notably, for selective hydroarylation, the use of unsymmetrical 1,3-diynes faces more challenges than the use of terminal monoalkynes: (1) the regioselectivity in one alkyne unit for the insertion process into the C(aryl)-Mn σ bond; (2) the chemoselectivity between two unbiased alkyne moieties; (3) the stereoselectivity in the migratory insertion (*syn* vs *anti*), and (4) the ability to control whether single or double hydroarylation occurs. An improved manganese catalyst precursor, $Mn_2(CO)_8Br_2$ was considered,[9] as the resulting vacant active coordination state of Mn(I) intermediates could potentially coordinate with alkynes instead of ligand rearrangement and then rapidly undergo *syn*-

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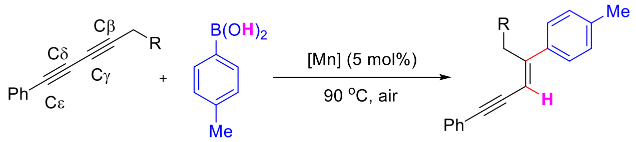
hydroarylation for the modular synthesis of multisubstituted (*Z*)-enynes (Scheme 1c).



1a-e **2a** **3a-e**

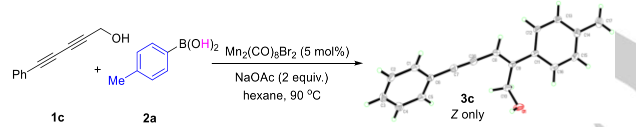
R	$Mn(CO)_5Br$ yield	$Mn_2(CO)_8Br_2$ yield
^{n}Bu (**1a**)	nd	trace
NHPh (**1b**)	nd	nd
OH (**1c**)	trace	16%
OMe (**1d**)	trace	15%
OAc (**1e**)	nd	nd

Reaction conditions: Mn (5 mol%), **1** (0.2 mmol), Ar-B(OH)$_2$ **2a** (1.5 equiv), NaOAc (1.5 equiv), DCE (2.0 mL), 90 °C, 12 h, air.

Scheme 2. Initial investigation of suitable 1,3-diyne type.

Initially, several substituted 1,3-diynes bearing different functional groups were employed to investigate the suitability of substrate type (Scheme 2). Fortunately, we found that diyne alcohol **1c** and its ether **1d** could undergo Mn(I)-catalyzed arylmetalation on the β-carbon only to afford the corresponding hydroarylation products (**3c** and **3d**) in 16% and 15% yields respectively, with complete regio-, stereo- and chemoselectivity by using $Mn_2(CO)_8Br_2$ as the catalyst precursor, whereas other substituted diynes (**1a**-**b** and **1e**) were rather recalcitrant to undergo the hydroarylation. It can clearly be concluded that $Mn_2(CO)_8Br_2$ is a much more efficient catalyst precursor than $Mn(CO)_5Br$, which is consistent with the mechanistic model hypothesis in Scheme 1c.

Table 1: Optimization of reaction conditions.[a]

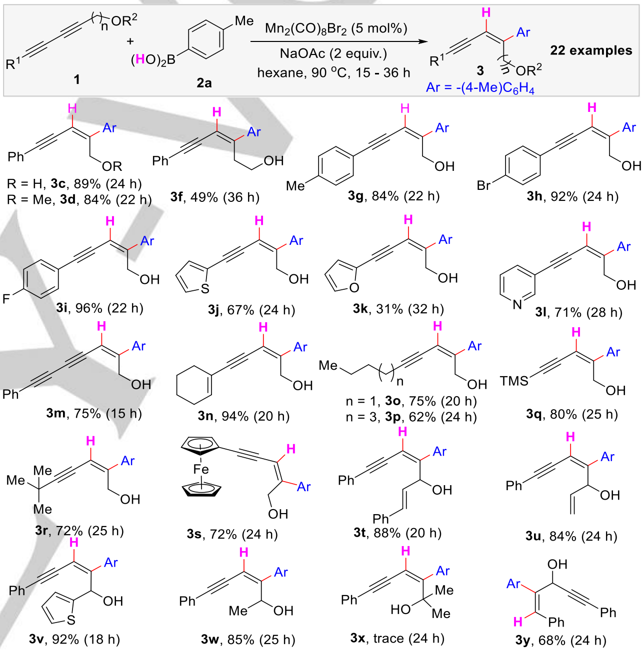


Entry	Variation in standard conditions	Yield[b](%)
1	none	89
2	DCE instead of hexane	73
3	benzene instead of hexane	48
4	LiOAc instead of NaOAc	65
5	Cy$_2$NH instead of NaOAc	nd
6[c]	Pd(PPh$_3$)$_4$ instead of $Mn_2(CO)_8Br_2$	trace
7[d]	[Rh(acaca)(C$_2$H$_4$)$_2$] instead of $Mn_2(CO)_8Br_2$	trace
8	without $Mn_2(CO)_8Br_2$	nd

[a] Standard reaction conditions: $Mn_2(CO)_8Br_2$ (5 mol%), **1c** (0.2 mmol), 4-MeC$_6$H$_4$B(OH)$_2$ (0.6 mmol), NaOAc (2 equiv), hexane (5 mL), 90 °C, air, 24 h. [b] Isolated yield. nd = not detected. [c] Pd(PPh$_3$)$_4$ (3 mol%), AcOH (10 mol%), 1,4-dioxane (1 mL), 60 °C, argon. [d] Rh(acac)(C$_2$H$_4$)$_2$ (3 mol%), dppf (6.6 mol%), 1,4-dioxane/H$_2$O (10:1, 1 mL), 100 °C, argon.

With these intriguing initial results, the reaction of 5-phenylpenta-2,4-diyn-1-ol (**1c**) and *p*-tolylboronic acid (**2a**) was chosen as a model reaction to optimize the reaction conditions (Table 1). We found that solvents and additives tremendously influenced the yield of **3c** (See Supporting Information for details). With 5 mol% $Mn_2(CO)_8Br_2$ as the catalyst precursor and NaOAc as additives, the selective hydroarylation reaction could smoothly occur to afford enyne alcohol (**3c**) in 89% yields when performed under air using hexane instead of DCE (entry 1). The solid-state molecular structure of **3c** was determined by single crystal X-ray structure analysis. The other solvents and bases resulted in lower yields (entries 2-5). Significantly, the use of Pd(PPh$_3$)$_4$[2h] and [Rh(acac)(C$_2$H$_4$)$_2$][2a] instead of $Mn_2(CO)_8Br_2$ resulted in only trace product as regio- and stereoisomers under reported hydroarylation conditions (entries 6 and 7), further underlining the unique catalytic reactivity of Mn(I)-based catalyst. The control experiment demonstrated that $Mn_2(CO)_8Br_2$ was crucial for a success (entry 8).

Table 2: Diyne scope.



With the optimized reaction conditions (Table 1, entry 1) in hand, we next investigated the substrate scope with regard to the unsymmetrical 1,3-diynes (Table 2). Both homopropargylic alcohols (**3c** and **3f**) and ether (**3d**) were effective substrate types. All aryl- and heteroaryl-substituted 1,3-diynes tested could undergo Mn(I)-catalyzed selective hydroarylation to furnish **3g-l** in 31-96% yields. Importantly, the regioselectivity was not affected by the proximal heteroaryl substituents (**3j-l**). When the trialkyne and enediyne alcohols were employed under standard conditions, they gave the desired enediyne (**3m**) in 75% yield and dieneyne (**3n**) in 94% yield. Various undifferentiated aliphatic 1,3-diynes (**3o-r**) could uniformly proceed this hydroarylation reaction regardless of the steric and electronic effects of their substituents. The ferrocene-based diyne alcohol is a competent substrate, and the resulting ferrocenyl enyne (**3s**) may attract considerable interest in material science owing to the unique electronic property. Beside primary alcohols, several functionalized diyne secondary alcohols reacted smoothly with organoborons to give **3t-w** in 84-92% yields. Of note, the reactive alkene (**3n**, **3t** and **3u**) and electron-rich heteroaryl (**3j**, **3k**, **3s** and **3v**) units keep intact in Mn-catalyzed hydroarylation, which showcases a very attractive

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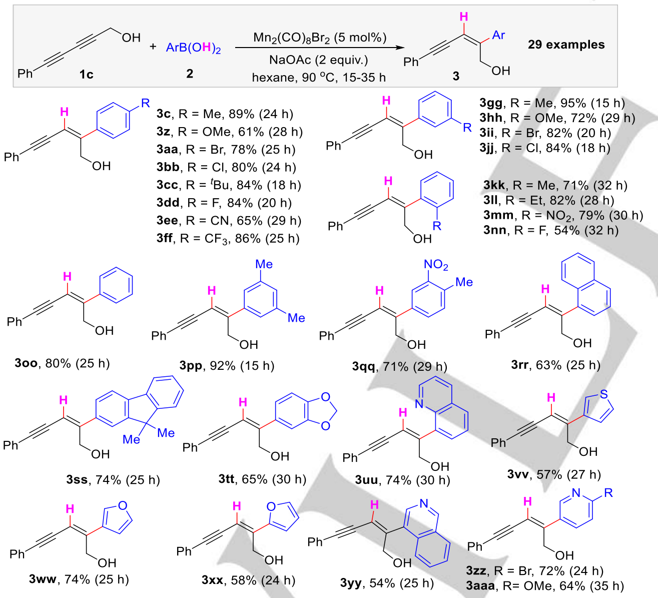
synthetic advantage in organometallic chemistry. However, the introduction of a tertiary alcohol moiety almost blocked the hydroarylation due to the steric hindrance effect (**3x**). In addition, Mn(I)-catalyzed hydroarylation of a skipped 1,4-diyne[10] provided an important alternative means of stereoselectively constructing skipped enyne alcohol (**3y**) in 68% yield. Notably, it appears that there is no significant effect of electronics (**3g-i**) and steric hindrance (**3t-w**) on the hydroarylation regioselectivity.

Subsequently, a wide range of commercially available arylboronic acids were evaluated (Table 3). In general, both electron-rich (-Me, -Et, -OMe, -^{t}Bu etc.) and electron-poor (-F, -Cl, -CN, -CF_3, -NO_2 etc.) functional groups in the *para-*, *meta-* and *ortho-*positions of the phenyl rings could tolerate the reaction conditions well, which suggests that the electronic and steric effect of substituents on arylboronic acids have little influence. The resulting enyne alcohols (**3c** and **3z-nn**) were isolated in 54-95% yields with exclusive *Z*-selectivity. The compatibility of bromo substituents further highlighted the synthetic advantages of this protocol (**3aa**, **3ii** and **3zz**). Meanwhile, 2-naphthylboronic acid and (9,9-dimethyl-9H-fluoren-2-yl)boronic acid proceeded the hydroarylation smoothly to afford **3rr** and **3ss** in 63% and 74% yield respectively. The heterocycle-containing boronic acids, including furan-, thiophen-, quinoline- and pyridine-based heteroarylboronic acids, were efficient coupling partners under Mn catalysis, affording the expected products (**3tt-aaa**) in synthetically useful yields.

***Table 3*:** Arylboronic acid scope.



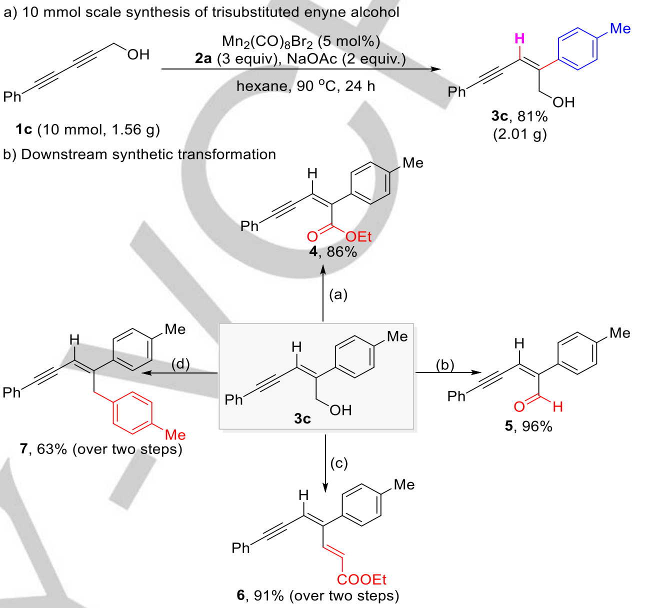
3c, R = Me, 89% (24 h)
3z, R = OMe, 61% (28 h)
3aa, R = Br, 78% (25 h)
3bb, R = Cl, 80% (24 h)
3cc, R = ^{t}Bu, 84% (18 h)
3dd, R = F, 84% (20 h)
3ee, R = CN, 65% (29 h)
3ff, R = CF_3, 86% (25 h)

3gg, R = Me, 95% (15 h)
3hh, R = OMe, 72% (29 h)
3ii, R = Br, 82% (20 h)
3jj, R = Cl, 84% (18 h)

3kk, R = Me, 71% (32 h)
3ll, R = Et, 82% (28 h)
3mm, R = NO_2, 79% (30 h)
3nn, R = F, 54% (32 h)

3oo, 80% (25 h)
3pp, 92% (15 h)
3qq, 71% (29 h)
3rr, 63% (25 h)
3ss, 74% (25 h)
3tt, 65% (30 h)
3uu, 74% (30 h)
3vv, 57% (27 h)
3ww, 74% (25 h)
3xx, 58% (24 h)
3yy, 54% (25 h)
3zz, R = Br, 72% (24 h)
3aaa, R= OMe, 64% (35 h)

As shown in Scheme 3a, when the model reaction was scaled-up to 10 mmol, a satisfying yield of 81% was obtained. Importantly, there are several synthetic advantages of using a readily transformable hydroxyl group in the substrates. It can not only avoid the requirement of installing and removing an external polarized directing group, but also is a versatile functional group for downstream synthetic transformations to deliver the corresponding ester (**4**) and aldehyde (**5**) in good yields. Additionally, enyne alcohol **3c** can be converted into a trisubstituted conjugated dieneyne (**6**) in excellent stereoselectivity and good yield. A Pd-catalyzed C(sp^2)-C(sp^3) coupling of enyne alcohol derivative with arylboronic acid to afford product **7** (63% over two steps) further illustrated the synthetic robustness in the modular synthesis of a wide range of substituted enynes.



Scheme 3. Synthetic application. For the reaction conditions please see Supporting Information for details.

As outlined in Scheme 4, some mechanistic experiments were carried out to elucidate the possible mechanism. According to the calculated NBO charge distribution results, the electronic effect of the alkyne may not be the key factor in Mn(I)-catalyzed hydroarylation because the arylation occurred only on the β-carbon even when the relatively more positive C(ε) was present (Scheme 4a).[11] Deuterium-labeling experiment demonstrated that the hydrogen atom at the vinyl position should come from protons in the reaction media (Eq. 1). Interestingly, switching the substrate from diyne alcohol **1c** to monoyne alcohol **8** allowed the desired product **9** to be obtained in 83% yield in a complete selectivity (Eq. 2 and 3). However, for unsymmetrical monoalkynes **10** and **13**, the regioselectivity of alkyne migratory insertion into the Mn-C(sp^2) σ bond significantly decreased,[12] which indicates that both the hydroxyl group and aryl or alkynyl group substituents in the substrates are crucial for the origin of selectivity in the present catalysis (Eq. 4 and 5).

To verify whether the Mn-Ar species was generated via transmetalation during the catalytic cycle, we mixed stoichiometric $Mn_2(CO)_8Br_2$ with arylboronic acid under reaction conditions (Scheme 4d). As the proposed nonchelated Ar-Mn species are too reactive to obtain[13] (Eq. 6), (2-(pyridin-2-yl)phenyl)boronic acid (**16**) was subsequently employed with the aim to stabilize the resulting reactive Ar-Mn species (Eq. 7). To our delight, a stable 5-membered manganacycle (**17**) was successfully isolated in 21% yield and its structure was further determined by X-ray single crystal structure analysis, constituting

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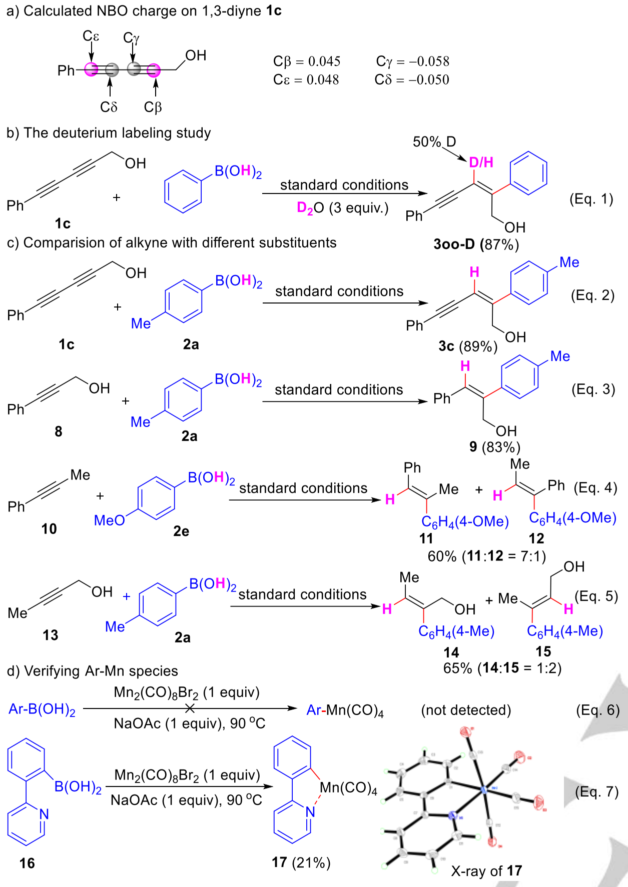
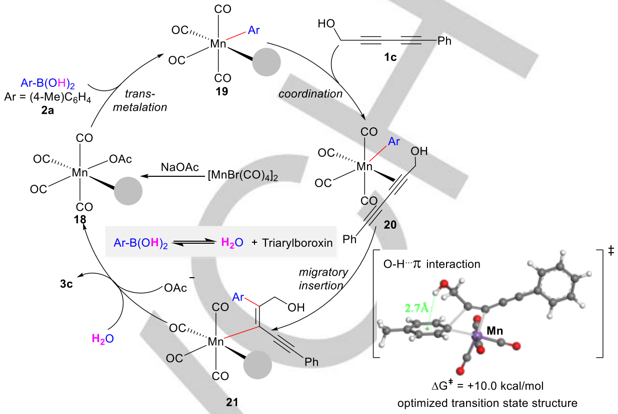
one solid evidence for the postulated intermediate via transmetalation.



Scheme 4. Mechanistic studies.

According to the aforementioned mechanistic studies, a plausible mechanism was proposed in Scheme 5. First, in the presence of NaOAc at 90 °C, the dimeric $Mn_2(CO)_8Br_2$ catalyst precursor breaks into reactive Mn(I) species **18**, which can undergo transmetalation with arylboronic acid **2a** to generate nonchelated Ar-Mn intermediate **19** (16 e^-). The vacant active coordination state of **19** readily coordinates to substrate **1c** to form complex **20**. To better understand the origin of regioselectivity, we computed the possible transition state of alkyne migratory insertion step. It was found that the weak O-H···π interaction between the hydroxyl group in substrate **1c** and aryl group in Ar-Mn species would promote the β-carbon selectivity.[14] Then, *syn*-1,2-migratory insertion of the alkyne unit adjacent to the hydroxyl group to the Ar-Mn σ bond can give intermediate **21**, in which the alkyne motif may stabilize this intermediate via conjugative effect. Finally, protodemetalation with H_2O which can be generated *in situ* during the formation of the triarylboroxin species[15] regenerates the reactive Mn(I) species **18**. The DFT calculation results indicate that (*Z*)-enyne **3c** might be the kinetically controlled product because the free energy of (*E*)- and (*Z*)-isomers are very comparable (ΔE < 0.5 kcal/mol). Alternatively, the coordination of diyne **1c** to the vacant coordination state of Mn(I) center could occur prior to transmetalation with $Ar\text{-}B(OH)_2$.



Scheme 5. Proposed mechanism.

In conclusion, a highly efficient Mn(I)-catalyzed regio-, stereo- and chemoselective hydroarylation of unsymmetrical 1,3-diynes with commercially available arylboronic acids has been described. It affords a general, practical and convenient access to the streamlined construction of a wide array of trisubstituted (*Z*)-configurated conjugated enyne alcohols in moderate to excellent yields. The resulting products are versatile building blocks that can participate in a series of useful downstream synthetic transformations to rapidly populate a complex small-molecule enyne library. Although an excess of arylboronic acids is still necessary for good yield at present, this protocol represents an important step-forward toward fundamentally rarely explored transmetalation and nonchelation-controlled alkyne insertion chemistry in manganese catalysis. The exploration of new reactions catalyzed by dimeric Mn(I)-complex and of mechanistic studies is currently ongoing in our group.

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Keywords: manganese • homogeneous catalysis • alkyne • arylation • enynes

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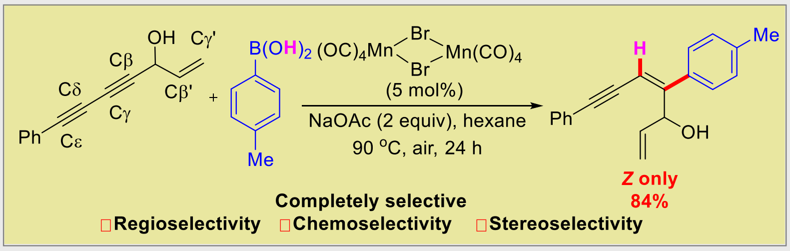
[12] To facilitate isolation of products **11** and **12**, *p*-methylphenylboronic acid **2a** was replaced with *p*-OMe-phenylboronic acid **2e**.

[13] In general, the more efficient a catalyst is, the more difficult it will be to isolate intermediates. The protodemetalation byproduct anisole was isolated in 21% yield during the synthesis of **3z**, which may indicate the involvement of Ar-Mn(I) intermediate during the catalytic cycle.

[14] The weak C-H$\cdots\pi$ interaction was observed for the ether-type substrate **1d**. A key review about these weak interactions, see: R. Hobza, Z. Havlas, *Chem. Rev*. **2000**, *100*, 4253-4264.

[15] The use of triarylboroxin and 3 equiv D_2O can furnish the D-labeled product **3oo-D** in 72% yield with 60% D atom at the vinyl position, see Supporting Information.

COMMUNICATION



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A Dimeric Mn-Catalyzed Completely Selective Hydroarylation of 1,3-Diynes for the Modular Synthesis of (Z)-Enynes Library

Two Mn are better than one: The first dimeric Mn(I)-catalyzed hydroarylation of unsymmetrical 1,3-diyne alcohols with arylboronic acids has been achieved in a predictive regio-, stereo- and chemoselectivity. It offers a general, convenient and practical strategy for the modular synthesis of multisubstituted (*Z*)-configurated conjugated enynes library.