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ARTICLE TYPE

Efficient Hydroarylation and Hydroalkenylation of Vinylarenes by Brønsted Acid Catalysis†

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Brønsted acid TF_2NH alone catalyzed both Friedel–Crafts-type hydroarylation and head-to-tail hydroalkenylation of vinylarenes under mild reaction conditions have been realized, providing a readily scalable, metal-free, and practical access to the 1,1-diarylalkane scaffolds and trans-1,3-diaryl-1-butenes in high yields and excellent regioselectivities.

The direct catalytic hydroarylation and hydroalkenylation of vinylarenes are highly atom-economical and fundamental methods for the synthesis of 1,1-diarylalkane (branched) scaffolds, which are core fragments existing in a number of complex natural and synthetic molecules. These compounds always display some biological activities and are potential therapeutic agents against cancer, smallpox, and insomnia, as well as other diseases (Figure 1).¹ Hence, much attention has been paid to achieve such transformations and numerous elegant developments have been reported (Scheme 1). According to the mechanism, the catalytic reactions can be classified into two major types: (1) hydroarylation through C-H activation by transition metal catalysts,^{2,3} and (2) Friedel–Crafts-type alkylation in the presence of Lewis or Brønsted acid.⁴ The former method usually requires a directing group on the arene and preferentially affords the linear adduct, with a few exceptions.⁵ In

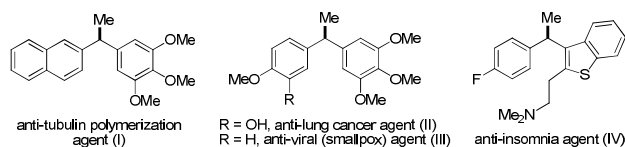


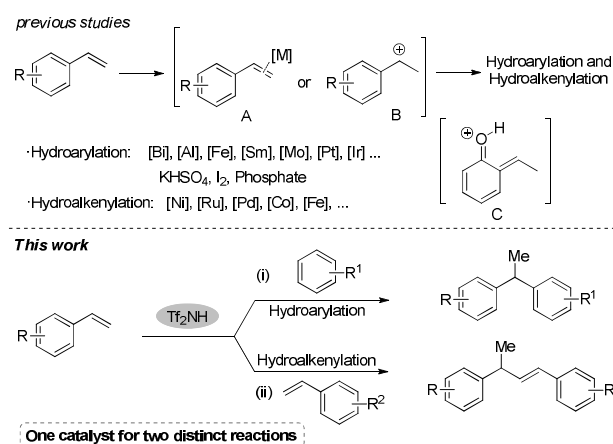
Figure 1 Representative Bioactive 1,1-diarylethanes.

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Scheme 1 Hydroarylation and Hydroalkenylation of Vinylarenes

contrast, 1,1-diarylethanes are generally obtained from Friedel–Crafts-type hydroarylation due to the stability of positive charge on the α -position of styrenethat develops upon Lewis acid coordination^{4a-g} or Brønsted acid protonation^{4h-k} (Scheme 1, A and B). Recently, Pospesch group reported a hydroarylation of styrene derivatives catalyzed by phosphate with indoles as reactive partner. However, the presence of hydroxyl group was necessary for forming more reactive quinonemethide-like intermediate to accomplish the whole reaction (Scheme 1, C).⁶ With the advent of modern ‘super acids’, especially triflimide (TF_2NH , $\text{pK}_a = 0.67$ in HOAc ⁷), we recognized that hydroarylation of simple vinyl arenes might be catalyzed by the strong Brønsted acid via the generation of the intermediate B (Scheme 1, i).

Additionally, hydroalkenylation of olefins is one of the current interesting and useful protocols to synthesize essential intermediates for fine and industrial chemicals.⁸ Generally, such reactions could be carried out following three ways to date: head-to-head (h-h),⁹ head-to-tail (h-t)¹⁰ and tail-to-tail (t-t)¹¹. Since a new allylic carbon stereogenic center is formed, the h-t dimerization is considered more attractive. Although a range of metal catalytic systems have been developed for this transformation: Dawans^{10a} and Yi¹⁰ⁱ disclosed that nickel-based

catalyst could catalyze dimerization of styrenes. Shirakawa^{10e} and Cheng^{10f} reported that the catalyst containing metal center of palladium and cobalt also showed highly catalytic activity to the reaction. Other development was linked to the discovery that the cooperation of iron and silver salts^{10k} to facilitate the formation of trans-1,3-diaryl-1-butenes. Although these methods are efficient, the need of expensive phosphorus ligands and additives, as well as generation of oligomers or polymers was a huge drawback. Therefore, in view of the demand for most simple and less expensive processes, the dimerization of styrenes catalyzed by organic catalyst, especially easily accessible Brønsted acids, is a very promising alternative to above-mentioned methodologies. And we suppose that the benzyl cation generated under the catalysis of Tf₂NH could be captured by vinylarenes themselves through nucleophilic addition, followed by deprotonation to form the dimerized product (Scheme 1, ii). In this paper, we describe the successful results obtained in both intramolecular Friedel–Crafts hydroarylation and hydroalkenylation of vinylarenes catalyzed by Tf₂NH alone under mild reaction conditions.¹²

The initial investigation was carried out using a model reaction between styrene **1a** and anisole **2a** (Table 1). We found

Table 1 Optimization of Reaction Conditions for the Hydroarylation^a

entry	substrate 2	Tf ₂ NH (%)	solvent	t (°C)	yield (%) ^b
1	2a	2	Et ₂ O	rt	trace
2	2a	2	THF	80	66
3	2a	2	Cyclohexane	80	62
4	2a	2	Dioxane	80	68
5	2a	4	Dioxane	80	71
6	2a	4	Dioxane	60	38
7	2b	4	Dioxane	80	68
8 ^c	2b	4	Dioxane	80	73
9 ^c	2b	4	Dioxane	90	75
10 ^d	2b	-	Dioxane	90	n.r.

^aReaction conditions: **1a** (0.2 mmol) and **2** (0.4 mmol) in 1.0 mL of solvent for 12 h in a sealed tube; ^bIsolated yield; ^cThe reaction was conducted in a 5:1 molar ratio of arene **2b** (0.5 mmol) to styrene **1a** (0.1 mmol). ^dIn the absence of acid, no reaction determined by GC.

that the Friedel–Crafts hydroarylation could take place with Tf₂NH as a catalyst. The screening of solvents showed that dioxane was superior to other solvent and the product was obtained in 71% yield at 80 °C with 4 mol % of Tf₂NH (entries 1-5). Lowering the temperature to 60 °C resulted in 38% yield (entry 6). Because of the challenge to separate two isomers **3a'** of 2- and 4-regioselectivities with anisole **2a**, and more importantly, for the development of a practical access to analogues of potential therapeutic agents **I-III** (figure 1),¹ we finally selected 1,2,3-trimethoxybenzene **2b** as the reactant to continue our study (entries 7-9), and the further improved reaction condition was obtained in a 5:1 molar ratio of arene **2b** to **1a** at 90 °C with a 4 mol % catalyst loading that led to 75% yield of product **3a** exclusively (entry 9). No reaction occurred in the absence of acid catalyst (entry 10).

With the optimized reaction conditions established, we then

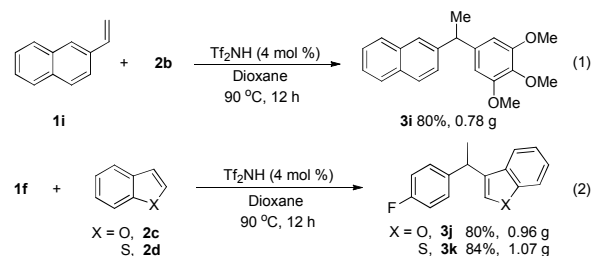
Table 2 Scope of Vinylarenes for the Hydroarylation^a

entry	R	3	yield (%) ^b
1	H	3a	75
2	2-Me	3b	86
3	4-Me	3c	82
4	4- <i>tert</i> -butyl	3d	88
5	2,5-dimethyl	3e	92
6	4-F	3f	75
7	4-Cl	3g	62
8	4-Br	3h	50

^aReaction conditions: **1** (0.10 mmol), **2b** (0.50 mmol), Tf₂NH (4 mol %), dioxane (1 mL), 90 °C, 12 h; ^bIsolated yield.

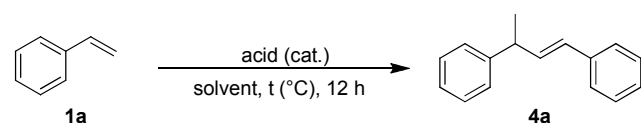
examined the substrate scope of the hydroarylation between various vinylarenes **1** and **2b** (Table 2). Significantly, besides **1a**, the transformations took place smoothly to assemble (1-(3,4,5-trimethoxyphenyl)ethyl)-arenes exclusively with other substituted vinylarenes and self-dimerization of **1** was tremendously suppressed. Basically, the relatively electron-rich styrenes were more reactive than electron-deficient ones. For instance, styrenes **1b** and **1c** with *ortho*-/*para*-methyl substituent converted into the corresponding adducts **3b** and **3c** in 86% and 82% yields, respectively (entries 2 and 3). Compound **3d** was readily obtained in 88% yield employing 4-*tert*-butyl styrene **1d** as the substrate (entry 4). The best result was obtained by introducing two methyl groups on 2,5-position of the benzene ring to furnish **3e** in 92% yield (entry 5). When electron-withdrawing halogen atom was attached to the aromatic ring in styrenes, the good outcomes was gained. 4-halogen-containing (F, Cl, and Br) styrenes **1f-h** were all compatible with this transformation and cleanly led to **3f-h** in 75-50% yields (entries 6-8).

To highlight the potential application of the highly atom-economic hydroarylation process, we conducted the reactions of 2-vinylnaphthalene **1i** with **2b** (Scheme 2, eq 1), and **1f** with benzofuran **2c** and benzo[*b*]thiophene **2d** to gram-scale (eq 2). Accordingly, treating **1i** (3.0 mmol, 0.462 g) with **2b** (15.0 mmol, 5 equiv), and **1f** (6.0 mmol, 0.73 g) with **2c** (5.0 mmol, 0.59 g) and **2d** (5.0 mmol, 0.67 g) to the standard reaction conditions, readily provided the potent of tubulin polymerization **3i**,^{1d} **3j**, and **3k** in 80-84% yields. Notably, **3k** is a very useful material for the synthesis of anti-insomnia agent benzothiophene IV.^{1d}



Scheme 2 Gram-Scale Hydroarylations

During the period of our studies on above hydroarylation between vinylarenes and anisole, it was found that a small quantity of homodimerized products generated. We reasoned that such dimerization of styrene derivatives might be also catalyzed by Brønsted acids (Table 3). Examination of usual Brønsted acids

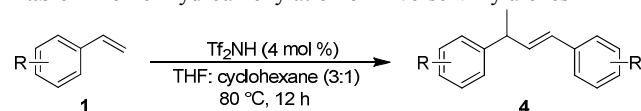
Table 3 Optimization of Reaction Conditions for the Hydroalkenylation^a

entry	acid (mol %)	solvent	t (°C)	yield (%) ^b
1	<i>p</i> -TSA (4)	THF	80	-
2	TFA (4)	THF	80	-
3	CF ₃ SO ₃ H (4)	THF	80	60
4	Tf ₂ NH (4)	THF	80	70
5	Tf ₂ NH (4)	THF: cyclohexane (3:1)	80	82
6	Tf ₂ NH (6)	THF: cyclohexane (3:1)	80	81
7	Tf ₂ NH (4)	THF: cyclohexane (3:1)	60	<10 ^c
8	Tf ₂ NH (4)	THF: cyclohexane (3:1)	90	80

^aReaction conditions: **1a** (0.2 mmol), acid (4-6 mol %), solvent (1 mL), 60-90 °C, 12 h; ^bIsolated yield; ^cDetected by GC analysis.

5 in THF at 80 °C revealed that Tf₂NH is optimal which promoted the homodimerization successfully to provide the desired product **4a** in 70% (entries 1-4). Changing the solvent THF to a mixed solvent of THF and cyclohexane in a 3:1 volume ratio increased the yield up to 82% (entry 5). Enlarging the Tf₂NH-loading to 6 mol % didn't improve the reaction (entry 6). A sharp decrease of yield was observed from 80 °C to 60 °C, while raising the temperature to 90 °C didn't afford improvement in the yield (entries 7 and 8).

15 Next, the scope and generality of this homodimerization were explored using various commercially available vinylarenes (Table 4). Besides styrene, both alkyl-substituted and halogenated

Table 4 Homo-Hydroalkenylation of Diverse Vinylarenes^a

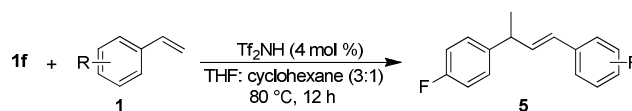
entry	substrate	product	yield (%) ^b
1	2-Me, 1b	4b	82
2	4-Me, 1c	4c	91
3	4- <i>tert</i> -butyl, 1d	4d	82
4	2-F, 1j	4j	78
5	3-F, 1k	4k	70
6	4-F, 1f	4f	90
7	4-Cl, 1g	4g	60
8	4-Br, 1h	4h	85
9	2-vinylnaphthalene, 1l	4l	80
10	prop-1-en-2-ylbenzene, 1m	4m	84
11	1,2-dihydronaphthalene, 1n	4n	75
12 ^c	1 <i>H</i> -indene, 1o	4o	76

^aReaction conditions: **1** (0.2 mmol), Tf₂NH (4 mol %), 1.0 mL mixed solvent of THF and cyclohexane with a 3:1 volume ratio, 80 °C, 12 h; ^bIsolated yield; ^c10 mmol of **1o** run the reaction to give 0.88 g of **4o**.

25 vinylarenes were all able to participate in the dimerization to provide smoothly the corresponding products. Methyl group in *ortho*- and *para*-position had no apparent effect on the yields of products (entries 1-2). Notably, *tert*-butyl substituent could also tolerate the reaction conditions and provided **4d** in 82% yield (entry 3). Gratifyingly, the fluorinated substrates underwent well

the process, and gave the *trans*-1,3-diaryl-1-butenes **4f**, and **4j-k** in good yields regard less of the substituted position (entries 4-6). Yields of more than 60% were obtained when Cl and Br substituted vinylarenes were used as reaction substrates (entries 7 and 8). With 1-vinylnaphthalene **1l** as substrate, the satisfied yield was achieved (entry 9). Prop-1-en-2-ylbenzene **1m** and the bicyclic compounds **1n** and 1*H*-indene **1o** are also compatible with this transformation, providing **4m-o** in acceptable yields (entries 10-12). It is noteworthy that the current homo-hydroalkenylation of **1o** is easily scaled up to 10 mmol scale, producing 0.88 g of **4o** in 76% yield (entry 12).

40 Remarkably, the cross-hydroalkenylation process occurred efficiently (Table 5). Treatment of **1f** (5.0 equiv) with another vinylarenes, including **1b**, **1d**, **1p**, and **1g**, to the standard reaction conditions afforded the desired products **5b-e** in 55-89% yields.

Table 5 Cross-Hydroalkenylation of Vinylarenes^a

entry	1	5	yield (%) ^b
1	4-Me, 1b	5b	86
2	4- <i>tert</i> -butyl, 1d	5c	78
3	2,5-dimethyl, 1p	5d	89
4	4-Cl, 1g	5e	55

^aReaction conditions: **1f** (1.0 mmol), **1** (0.2 mmol), acid (4 mol %), mixed solvent of THF/cyclohexane (3:1, 1 mL), 80 °C, 12 h; ^bIsolated yield.

45 In conclusion, we described a readily scalable, mild, and efficient method for hydroarylation and head-to-tail hydroalkenylation of vinylarenes with Brønsted acid Tf₂NH as the same only catalyst, which provides an easy access to bioactive 1,1-diaryllkane scaffold and *trans*-1,3-diaryl-1-butenes. This is the first example of highly regioselective hydroarylation and hydroalkenylation with only one organic catalyst.

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