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Nickel-Catalyzed, Regio- and Enantioselective Benzylic Alkenylation of Olefins with Alkenyl Bromide

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Abstract: A NiH-catalyzed migratory hydroalkenylation reaction of olefins with alkenyl bromides has been developed, affording benzylic alkenylation products with high yields and excellent chemoselectivity. The mild conditions of the reaction preclude olefinic products from undergoing further isomerization or subsequent alkenylation. Catalytic enantioselective hydroalkenylation of styrenes was achieved using a chiral bisoxazoline ligand.

A synergistic combination of a transition metal hydride[1,2] catalyzed alkene isomerization with transition metal-catalyzed cross-coupling enables migratory hydrofunctionalization.[3-8] The reaction uses easily available olefinic starting materials and is an attractive strategy for achieving formal C(sp^3)-H functionalization selectively at remote positions[9]. Owing to the low-cost and easy access to multiple oxidation states, and the well-developed cross-coupling chemistry,[10,11] it has recently been demonstrated that remote hydrofunctionalization of alkenes catalyzed by nickel hydride[2] can enable a range of functionalization reactions.[7,8] These include arylation, alkylation, thiolation, and amination at a distal or proximal C(sp^3)-H position (Figure 1a). In reductive processes,[7] selective functionalization depends upon the hypothesis that one of the alkylnickel intermediates generated by hydrometalation of an olefin, followed by chain-walking can be selectively captured by a cross-coupling partner. We recently questioned whether this general strategy could be expanded to remote alkenylation when a classic cross-coupling partner, a alkenyl bromide[12] is used (Figure 1b). We report the successful execution of this migratory hydroalkenylation strategy and demonstrate that by employing a chiral bisoxazoline ligand, enantioselective hydroalkenylation process can also be achieved.

As shown in Figure 1c, there are many potential challenges to this process. First, the alkene, the alkenyl halide and the migratory alkenylation product must all contain C=C double bonds and all could potentially undergo a chain-walking or alkenylation process with nickel hydrides. Second, isomeric mixtures of products may often be obtained due to the similar reactivity of different alkylnickel species. Third, it is possible that alkenyl bromides could be reduced by NiH. Consequently, a synthetically useful transformation requires 1) a hydrometalation process involving olefins with significantly different reactivities and 2) a alkenylation coupling process involving alkylnickel intermediates with significantly different reactivities.

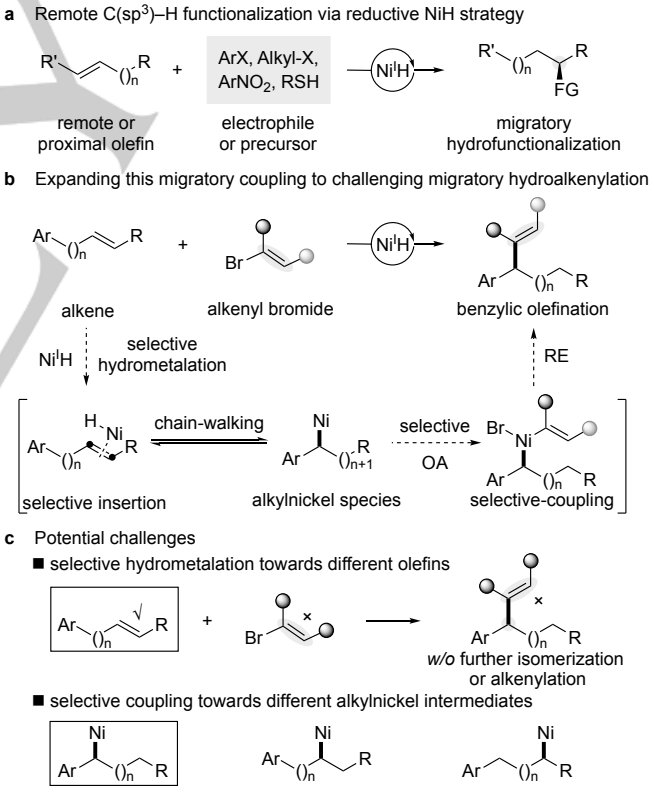

Figure 1. Ligated nickel-hydride catalyzed migratory hydroalkenylation. FG = functional group.

We initiated our investigation by exploring the migratory hydroalkenylation of 4-phenyl-1-butene (**1a**) with *p*-(2-bromo)alkenyl anisole (**2a**) (Table 1). After extensive examination of nickel catalysts, hydride sources, bases and solvents, the desired migratory hydroalkenylation product (**3a**) was produced in 86% isolated yield at -10 °C with excellent

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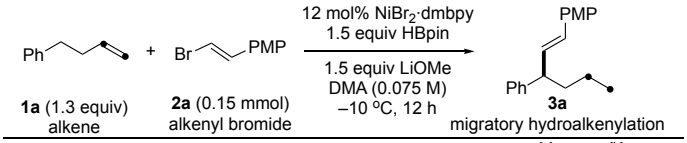
regioselectivity. The regioisomeric ratio (rr) or the proportion of benzylic product versus all other isomers was 95:5 (Table 1, entry 1). Using other nickel sources, such as $NiCl_2$·dmbpy (dmbpy = 6,6'-dimethyl-2,2'-bipyridine), led to diminished yields and regioselectivity (entry 2). With other ligands such as 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy) no desired alkenylation product was produced (entry 3). Reduction of catalyst loading to 10 mol% led to incomplete conversion (entry 4). Evaluation of hydride sources revealed that a borane dimethyl sulfide complex was comparably effective (entry 5) whereas polymethylhydrosiloxane (PMHS) offered only trace amounts of desired product (entry 6). Replacement of LiOMe by CsF led to diminished yield (entry 7). THF was shown to be an unsuitable solvent (entry 8). Conducting the reaction at 0 °C (entry 9) led to somewhat lower yield, whereas at -20 °C a comparable yield could be obtained (entry 10). Use of only 1 equiv of the alkene (**1a**) also gave inferior results (entry 11). In contrast, low yield and moderate rr was observed under our previous reaction conditions[7e] (entry 12).

Table 1: Variation of reaction parameters.



1a (1.3 equiv) alkene; **2a** (0.15 mmol) alkenyl bromide; **3a** migratory hydroalkenylation

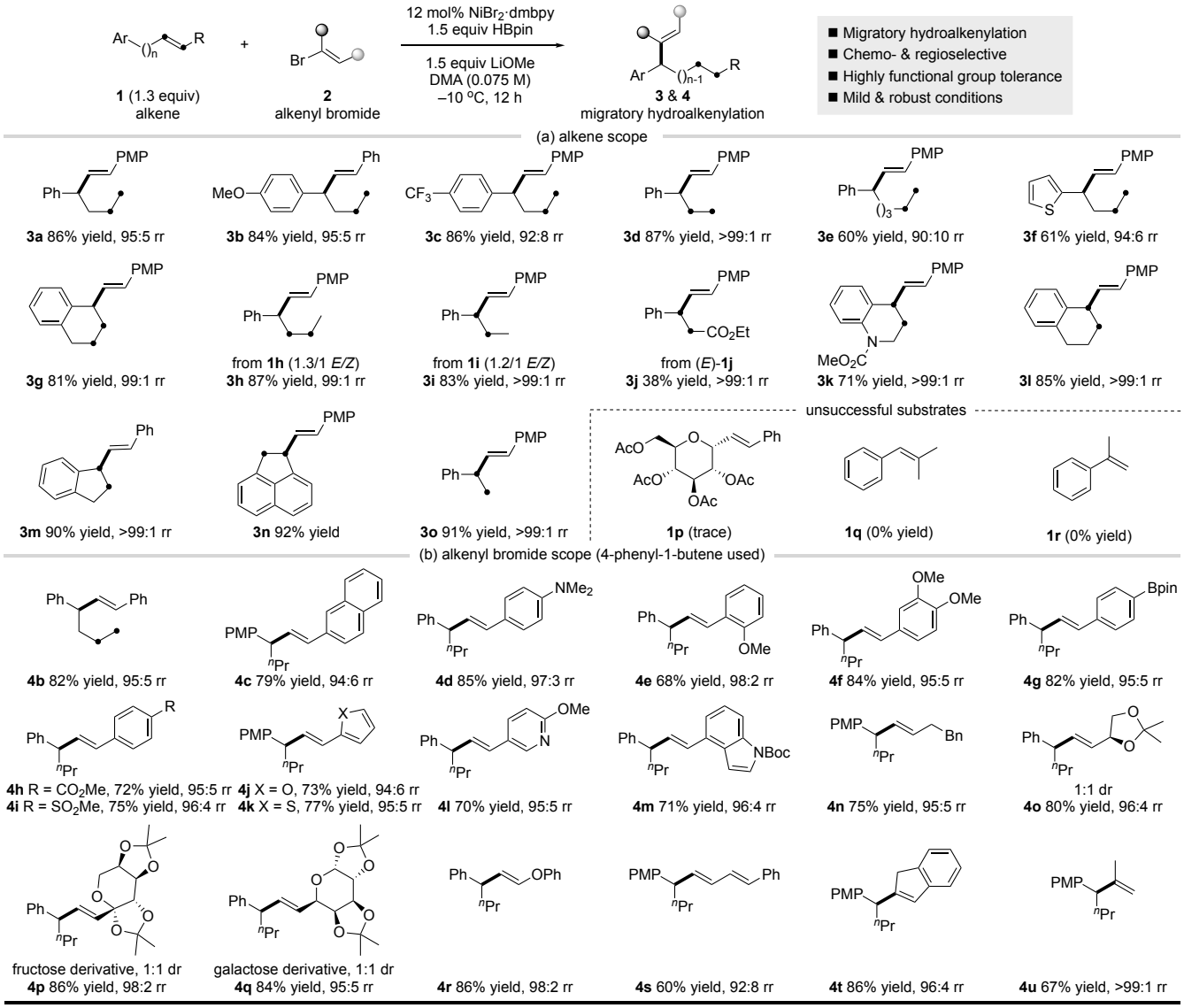
Entry	Variation from standard conditions	Yield [%][a]	rr[b]
1	none	87 (86)	95:5
2	$NiCl_2$·dmbpy, instead of $NiBr_2$·dmbpy	36	87:13
3	$NiBr_2$·dtbpy, instead of $NiBr_2$·dmbpy	0	–
4	10 mol% $NiBr_2$·dmbpy	72	94:6
5	$(CH_3)_2S{\cdot}BH_3$, instead of HBpin	80	97:3
6	PMHS, instead of HBpin	trace	ND
7	CsF, instead of LiOMe	33	93:7
8	THF, instead of DMA	0	–
9	0 °C	74	93:7
10	–20 °C	84	96:4
11	1.0 equiv **1a**	58	95:5
12	previous reaction conditions[7e]	42	86:14

[a] Yields determined by crude ^{1}H NMR using 2,5-dimethylfuran as the internal standard. The yield in parentheses is the isolated yield. [b] Regioselectivity (rr) determined by GC and GCMS analysis. HBpin = pinacolborane, DMA = *N*,*N*-dimethylacetamide, PMP = *p*-methoxyphenyl.

Under the optimal reaction conditions, a fairly broad scope of alkenes and alkenyl bromides are suitable substrates (Table 2). As shown in Table 2a, both monosubstituted terminal alkenes (**3a**–**3f**) and less sterically hindered internal alkenes (**3g**, **3h**) undergo this migratory hydroalkenylation chemoselectively, producing the benzylic alkenylation products. In general, electron-donating substituents (**3b**) on the remote aryl ring showed higher rr than those with electron-withdrawing ones (**3c**), and terminal alkenes with a shorter alkyl chain (**3d**) showed higher rr than those with a longer alkyl chain (**3e**). Heterocycles such as thiophene (**3f**) are also compatible. Both the β-unsubstituted styrene (**3o**) and styrenes with different primary alkyl groups substituted at the β-position (**3i**–**3n**) are well tolerated. In contrast, styrenes with sterically hindered substituent at either α- or β-position are unsuitable substrates under current conditions (**1p**–**1r**).

As shown in Table 2b, a wide range of β-aryl-substituted (*E*)-alkenyl bromides bearing electron-rich (**4d**, **4e**) or electron-poor substituents (**4f**-**4i**) on the arene afford the desired product smoothly. Good migratory coupling results were also observed for β-heteroaromatic-substituted (*E*)-alkenyl bromides, containing for example a furan (**4j**), thiophene (**4k**), pyridine (**4l**) or indole (**4m**). β-alkyl-substituted (*E*)-alkenyl bromides (**4n**–**4q**), such as those containing a structurally complex fructose (**4p**) or galactose derivative (**4q**) were also shown to be viable substrate and β-phenoxy-substituted (*E*)-alkenyl bromide (**4r**) was also proved to be compatible. However, a slight decrease in the regioselectivity was observed when 1,3-dienyl bromide (**4s**) was used as the substrate. Notably, α-alkyl substituted alkenyl bromides (**4t**, **4u**) are also competent coupling partners.

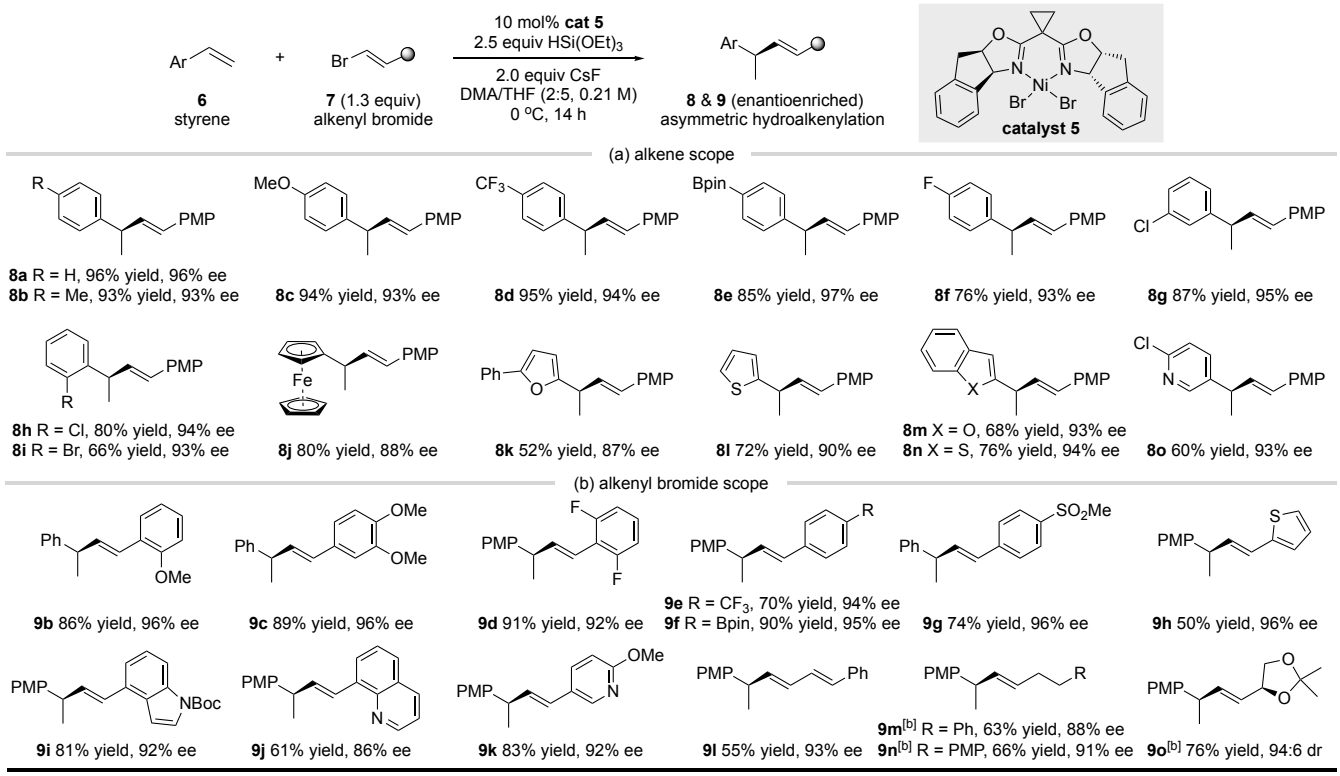
Table 2: Nickel hydride-catalyzed migratory hydroalkenylation of alkenes with alkenyl bromides.[a,b]



[a] Yield under each product refers to isolated yield of purified product (0.15 mmol scale, average of two runs). [b] rr determined by GC and GCMS analysis.

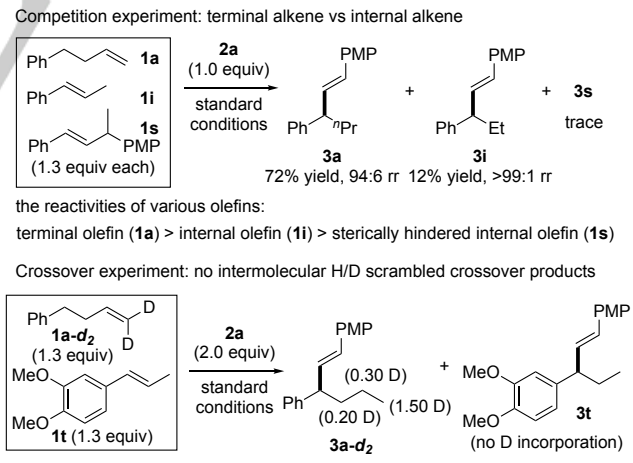
The asymmetric version of nickel-catalyzed hydroalkenylation was next explored using optically active ligands (Table 3). Systematic evaluation of various chiral ligands, showed that both high enantiomeric excess and yields were observed with a chiral nickel-bis(oxazoline) catalyst **5**[12a,c] for a range of styrenes[13,14] with alkenyl bromides. As shown in Table 3a, styrenes with a variety of substituents on the aromatic ring, both electron-rich (**8b**, **8c**) and electron-deficient (**8d**-**8i**), underwent this enantioselective hydroalkenylation smoothly with high levels of enantiocontrol. Ortho-substituted styrenes (**8h**, **8i**) were also suitable substrates. Notably, this catalyst system couples an alkenyl bromide in the presence of an aryl halide with high selectivity (**8f**-**8i**). Under these exceptionally mild reaction conditions, even a sensitive functional group like a boronic acid pinacol ester (**8e**) remained intact. Alkenylferrocene (**8j**) could also undergo the reaction, providing access to highly enantioenriched ferrocene derivatives. Heterocycles such as furan (**8k**), thiophene (**8l**), benzofuran (**8m**), benzothiophene (**8n**), and pyridine (**8o**) were also competent coupling partners. The scope of the alkenyl bromide component was explored (Table 3b), and a range of structurally diverse β-aryl substituted (*E*)-alkenyl bromides bearing electron-rich (**9b**) or electron-poor (**9c**-**9g**) substituents on the arene as well as β-heteroaryl substituted (*E*)-alkenyl bromides (**9h**-**9k**) were shown to participate in the reaction. In addition, 1,3-dienyl bromide (**9l**) reacted smoothly, and β-alkyl substituted (*E*)-alkenyl bromides (**9m**-**9o**) were also suitable substrates but with slightly reduced ee.

Table 3: Nickel hydride-catalyzed asymmetric hydroalkenylation of styrenes with alkenyl bromides.[a]



[a] Yield under each product refers to isolated yield of purified product (0.15 mmol scale, average of two runs), >99:1 regioisomeric ratio (rr) unless otherwise noted, enantioselectivities were determined by chiral HPLC analysis; the absolute configuration was assigned by chemical correlation or by analogy. [b] at 10 °C, DMA/NMP (2:8, 0.15 M) used.

A competition experiment was conducted to compare the relative reactivities of different types of C=C bond (Scheme 1a). The hydroalkenylation protocol described here exhibited excellent chemoselectivity when equal amounts of three olefins were present. In general, the steric effect is the dominant factor and the observed order is monosubstituted alkene (**1a**) > internal alkene (**1i**) > sterically hindered internal alkene (**1s**), which is consistent with the excellent chemoselectivity observed in the model reaction. Moreover, crossover experiment using a 1:1 mixture of deuterium-labeled alkene (**1a-d_2**) and undeuterated alkene (**1t**) was carried out (Scheme 1b). No H/D scrambled crossover products were obtained which indicates that chain-walking proceeds without dissociation of NiH from olefin.



Scheme 1. Competition experiment: terminal alkene vs internal alkene.

In conclusion, we have realized a nickel-catalyzed reductive alkenylation of remote and proximal olefins with benzylic selectivity. Excellent regio- and chemoselectivity were observed for a broad scope of alkenes and alkenyl bromides as starting materials. Critical to the success of the reaction is the highly selective hydrometalation and alkenylation. Alkenylation only takes place at benzylic position and the olefinic products are left intact with no further isomerization or subsequent alkenylation.

Catalytic enantioselective hydroalkenylation of styrenes was also observed when a chiral bisoxazoline ligand was used. The development of a migratory asymmetric version of this transformation and detailed mechanistic studies are currently in progress in our laboratory.

Acknowledgements

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Keywords: alkenes • asymmetric catalysis • isomerization • nickel • alkenylation

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[13] For β-substituted styrenes, no desired product was obtained.

[14] For vinylarenes with moderate yields (**8k**, **9h**, **9l**), the major by-products were the reduction of the corresponding vinylarenes.

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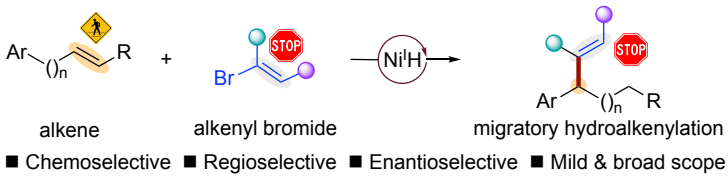

A nickel hydride-catalyzed highly selective migratory hydroalkenylation proceeds through competitive hydrometalation and oxidative addition. Employing a chiral bisoxazoline ligand, a catalytic enantioselective hydroalkenylation of styrenes was observed. The mild conditions of the reaction produced the benzylic alkenylation products exclusively, leaving the olefinic product intact.