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Ni-Catalyzed Reductive Allylation of Unactivated Alkyl Halides with Allylic Carbonates

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Allylation of alkyl substrates represents a very important reaction type in modern synthetic organic chemistry. Numerous elegant approaches to allylated alkanes have been developed, primarily based on the transition-metal-catalyzed addition of alkyl nucleophiles to allylic electrophiles.[1–3] This includes the recent Ni-catalyzed asymmetric Negishi coupling of primary alkylzinc reagents with allylic chlorides developed by Fu and co-workers.[2] There are also a few examples focusing on the catalytic coupling of allylic Grignard reagents with alkyl electrophiles.[3] On the other hand, the direct coupling of alkyl halides with allylic electrophiles, despite appearing to be a more convenient strategy because alkyl halides are, in general, more accessible and easier to use than alkyl nucleophiles, has not been well addressed. In addition to the Cu-catalyzed allylation of in situ alkyl Grignard reagents, radical allylation of alkyl halides has also been documented.[4–7] However, these methods are subject to either narrow substrate scope or regioselectivity issues. In particular, the classical radical addition and fragmentation process often requires toxic radical initiators or light irradiation, and suffers from poor *E*/*Z* selectivity. Therefore, development of a highly efficient reductive coupling between alkyl halides and allylic electrophiles is still widely sought. Very recently, a cobalt-catalyzed reductive coupling of alkyl halides with allylic acetate or carbonates was disclosed, for which moderate regioselectivity was observed for more hindered alkyl and allylic substrates.[8]

The catalytic reductive coupling of alkyl and/or aryl electrophiles has advanced rapidly since 2009.[8–10] In general, these coupling processes can be classified into two types, namely, in situ formation of organometallic nucleophiles and redox processes. Whereas the first category comprises Co-, Fe-, and Pd-catalyzed reductive couplings of alkyl and aryl halides,[9] the second reaction type has been demonstrated in the Co- and Ni-catalyzed reductive coupling of alkyl halides.[8,10] As part of an effort to develop cross-coupling approaches that use unactivated alkyl halides with other electrophiles, we recently discovered a direct coupling reaction of two different unactivated alkyl halides under Ni-catalyzed reductive conditions, for which the catalyst displays intriguing features in differentiating the alkyl substrates and subduing the competitive homocoupling side reactions.[10a] Extension of this strategy to the reductive coupling of unactivated alkyl halides with allylic electrophiles is therefore appealing because the allylic electrophiles can be viewed as activated alkyl species that possess very different reactivities from the unactivated alkyl halides.

In addition, recent studies on the Ni-catalyzed Negishi coupling of alkyl halides have suggested that the oxidative addition of alkyl halides to a Ni^{I} intermediate involves the generation of an alkyl radical and a Ni^{II} species prior to the formation of Ni^{III}.[11–13] This further prompted us to determine the feasibility of the Ni-catalyzed allylation of alkyl halides with allylic electrophiles in the presence of a terminal reductant, such as Zn. We reasoned that alkyl radical[10a,14] and allyl–Ni^{II} intermediates can be generated under these conditions, which may lead to allylated alkanes. Herein, we disclose the Ni-catalyzed allylation of various functionalized alkyl halides with substituted allylic carbonates by using environmentally benign Zn powder as the reductant to provide *E*-alkenes in good to excellent yields and excellent regioselectivities. Our preliminary mechanistic studies also suggest that a catalytic redox process may be involved in this method.

We initially examined the reaction of 4-iodo-1-tosylpiperidine (**1a**) with allyl methylcarbonate (**2a**) by employing [Ni(cod)$_2$] (10 mol%; cod = 1,5-cyclooctadiene)/*i*Pr-PyBox **4a** (15 mol%), Zn as the reductant,[15] and *N*,*N*-dimethylacetamide (DMA) as the solvent. Gratifyingly, the allylated product **3a** was obtained in a 67% yield (Table 1, entry 1). Addition of CuI (20 mol%) further enhanced the yield to 82% (Table 1, entry 2). The reactions went to completion after six hours either with or without CuI. The excess **2a** underwent slow homocoupling, and a substantial amount of **2a** was recovered after 12 h. The byproducts arising from **1a** in both cases were determined to be a 2:1 ratio of the hydrodehalogenation and β-hydride elimination products, along with a trace amount of the homocoupling product of **1a**. Therefore, CuI appears to inhibit the side reactions.[16] Raising the CuI loading or the temperature did not yield better results (Table 1, entries 3 and 4). Other ligands, such as **4b**, also did not generate better yields (Table 1, entry 5). Allylic

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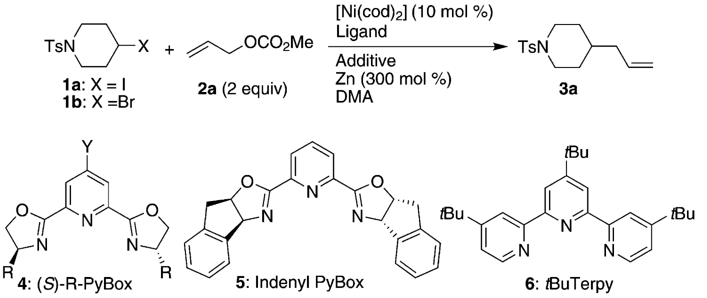
Table 1. Optimization of the coupling reaction of **1** with allyl carbonate **2a**.[a]



	X	Ligand ([mol %])	R	Y	Additive ([mol %])	T [°C]	t [h]	Yield [%][b]
1	I	**4a** (15)	*i*Pr	H	none	25	12	67
2	I	**4a** (15)	*i*Pr	H	CuI (20)	25	12	82
3	I	**4a** (15)	*i*Pr	H	CuI (50)	25	6	82
4	I	**4a** (15)	*i*Pr	H	CuI (30)	35	6	82
5	I	**4b** (15)	H	H	CuI (20)	25	12	5
6	Br	**4a** (15)	*i*Pr	H	none	25	12	n.d.[c]
7	Br	**4a** (15)	*i*Pr	H	none	80	12	7
8	Br	**4a** (15)	*i*Pr	H	CuI (20)	80	12	45
9	Br	**4b** (15)	H	H	CuI (20)	80	12	10
10	Br	**4c** (15)	Me	H	CuI (20)	80	12	20
11	Br	**4d** (15)	*s*Bu	H	CuI (20)	80	12	40
12	Br	**4e** (15)	*t*Bu	H	CuI (20)	80	12	n.d.[c]
13	Br	**5** (15)	–	–	CuI (20)	80	12	35
14	Br	**4a** (15)	*i*Pr	H	CuI (20)/$MgCl_2$ (1:1)	80	12	65
15	Br	**6** (15)	–	–	CuI (20)/$MgCl_2$ (1:1)	80	12	65
16	Br	**4a** (15)	*i*Pr	H	$MgCl_2$ (100)	80	12	76
17	Br	**4f** (15)	*i*Pr	OMe	$MgCl_2$ (100)	80	12	68
18	Br	**6** (15)	–	–	$MgCl_2$ (100)	80	12	91
19	Br	**6** (10)	–	–	$MgCl_2$ (150)	80	12	91

[a] Reaction conditions: **1** (100 mol%, 0.15 M in DMA), **2** (200 mol%), [Ni(cod)$_2$] (10 mol%), Zn (300 mol%), DMA (1 mL). Ligand, additive, temperature, and reaction time are variables. [b] Isolated yields. [c] n.d. = not detected.

substrates bearing leaving groups, such as acetate and *t*Bu-carbonates, resulted in low yields; no products were obtained for allyl bromide and phenyl sulfonate reagents.

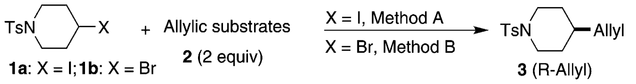
When 4-bromo-1-tosylpiperidine (**1b**) was subjected to the [Ni(cod)$_2$]/**4a**/Zn/DMA conditions at 25 °C, only hydro-dehalogenation and β-hydride elimination of **1b** were observed (Table 1, entry 6). Raising the temperature produced **3a** in a highest yield of only 7% at 80 °C (Table 1, entry 7 and Table S1 in the Supporting Information).[17] The addition of CuI (20 mol%) boosted the yield to 45% (Table 1, entry 8 and Table S2 in the Supporting Information).[17] Extensive examination of ligands (Table 1, entries 9–13) and solvents (Table S3 in the Supporting Information) did not result in any further improvements.[17] However, the addition of anhydrous $MgCl_2$ (20 mol%) promoted the yield to 65% by using **4a** as the ligand (Table 1, entry 14),[18] which is comparable to the yield found when using *t*Bu-Terpy (**6**; Table 1, entry 15) as the ligand. Further screening of different Ni sources and reductants did not provide better results (Tables S4 and S5 in the Supporting Information). Under the improved reaction conditions (Table 1, entry 14), **1b** was consumed after 8 h, whereas a substantial amount of **2a** was recovered; the byproducts derived from **1b** were from hydro-dehalogenation (≈10%), β-hydride elimination (≈10%), and homocoupling (≈10%). The side reactions, however, could be significantly suppressed by employing a stoichiometric amount of $MgCl_2$ as the sole additive (Table 1, entries 16–19). A combination of 1 equivalent of $MgCl_2$ and 15 mol% of **6** gave the highest yield (91%). The amount of **6** could be further reduced to 10 mol% without diminishing the yield by utilizing 1.5 equivalents of $MgCl_2$ (Table 1, entry 19).

By using the optimized conditions for **2a** (Table 1, entries 4 and 19), a diverse set of substituted allylic carbonates **2b**–**2m** were examined for the coupling reaction with **1a** and **1b** (Table 2). For the 3-alkyl-substituted allyl substrates **2b** (*trans*) and **2c** (*cis*), moderate to good yields were obtained with **1a** (Table 2, entries 1 and 3), whereas excellent yields were observed with **1b** (Table 2, entries 2 and 4). It should be noted that only the *trans*-product **3c** was isolated for the reaction of *cis*-3-ethyl carbonate **2c** (Table 2, entries 3 and 4). For *trans*-3-phenyl carbonate **2d**, both **1a** and **1b** delivered the allylated product **3d** in high yields, despite the fact that **1b** appears to be more efficient (Table 2, entries 5 and 6). The allylic carbonates bearing 2-methyl groups, as in **2e** and **2f**, generally displayed much lower reactivity, giving poor results for both **1a** and **1b** (Table 2, entries 7–10). The 2-phenyl carbonate **2g**, however, behaved differently from the 2-alkyl-substituted analogues, providing moderate and excellent yields for **1a** and **1b**, respectively (Table 2, entries 11 and 12). The coupling reactions of **1a** and **1b** with 1-alkyl-substituted allyl substrates **2h**–**2k** were generally highly efficient (Table 2, entries 13–20). Poor results were delivered for 1-phenyl allylic carbonate **2l** due to extensive homocoupling (Table 2, entries 21–22). Finally, the sterically more congested 1,3-diethyl compound **2m** provided **3m** in poor yields (Table 2, entries 23 and 24).

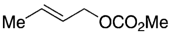
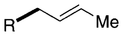
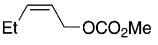
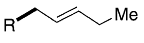
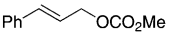
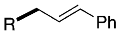
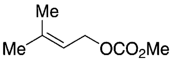
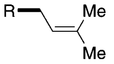
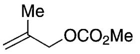
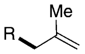
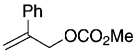
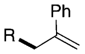
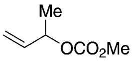
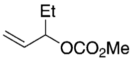
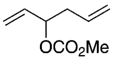
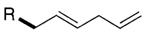
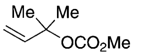
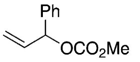
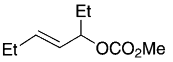
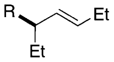
Interestingly, extensive screening of other ligands for the example reactions in Table 2 indicated that the coupling efficiency for **1a** with 3-alkyl and 2-aryl allylic carbonates, and **1b** with 2-alkyl and 3,3′-dimethyl allylic carbonates could be drastically improved by using ligand **4g** (Table 3). The generality of these scenarios was evident for **2b**, **2c**, and **2n** (Table 3, entries 1–3), **2e**, **2f**, and **2o** (Table 3, entries 4–6), and **2g** and **2p** (Table 3, entries 7 and 8).

Notably, all reactions examined in Tables 2 and 3 gave *E*-alkenes only. The excellent regioselectivities (>20:1) for unsymmetrical allylic substrates were derived from the addition of the alkyl group to the sterically less hindered allylic terminus. In general, sterically more encumbered allylic substrates, such as **2m**, led to lower yields. When the allylation was less efficient, hydro-dehalogenation and homocoupling of **1a** or **1b** were usually the major factors accounting for poor results, with the latter being the main side reaction.

Table 2. Coupling of **1** with substituted allylic carbonates.[a]

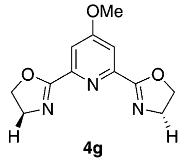


1a: X = I;**1b**: X = Br **2** (2 equiv) **3** (R-Allyl)

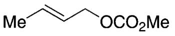
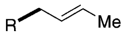
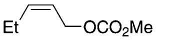
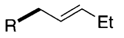
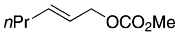
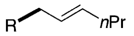
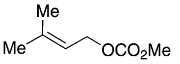
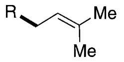
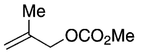
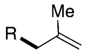
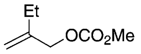
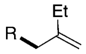
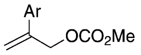
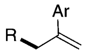
	R–X	Allylic Substrates		Product		Yield [%][b]
1	**1a**		**2b**		**3b**	65
2	**1b**					82
3	**1a**		**2c**		**3c**	40
4	**1b**					89
5	**1a**		**2d**		**3d**	75
6	**1b**					91
7	**1a**		**2e**		**3e**	trace
8	**1b**					35
9	**1a**		**2f**		**3f**	trace
10	**1b**					37
11	**1a**		**2g**		**3g**	49
12	**1b**					85
13	**1a**		**2h**	**3h**=**3b**		88
14	**1b**					90
15	**1a**		**2i**	**3i**=**3c**		85
16	**1b**					90
17	**1a**		**2j**		**3j**	82
18	**1b**					91
19	**1a**		**2k**	**3k**=**3e**		80
20	**1b**					70
21	**1a**		**2l**	**3l**=**3d**		trace
22	**1b**					14
23	**1a**		**2m**		**3l**	trace
24	**1b**					17

[a] Reaction conditions: **1** (100 mol %, 0.15 M in DMA), **2** (200 mol %), [Ni(cod)$_2$] (10 mol %), Zn (300 mol %), DMA (1 mL). For X=I, method A: **4a** (15 mol %), CuI (30 mol %) at 35 °C, 6 h; for X=Br, method B: **6** (10 mol %), MgCl$_2$ (150 mol %) at 80 °C, 12 h. [b] Isolated yields.

Table 3. Use of **4g** for the coupling of **1** and allylic substrates with certain substitution patterns.[a]



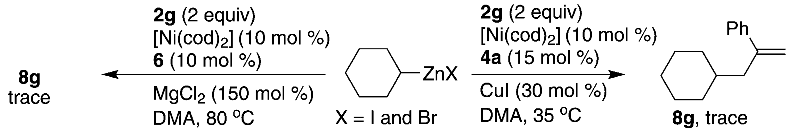
4g

	R–X	Allylic Substrates		Product		Yield [%][b]
1	**1a**		**2b**		**3b**	70
2	**1a**		**2c**		**3c**	74
3	**1a**		**2n**		**3n**	75
4	**1b**		**2e**		**3e**	90
5	**1b**		**2f**		**3f**	78
6	**1b**		**2o**		**3o**	83
						
7	**1a**	Ar=Ph	**2g**		**3g**	75
8	**1b**	Ar=4-MeO-C$_6$H$_4$	**2p**		**3p**	70

[a] Reaction conditions: **1** (100 mol %, 0.15 M in DMA), **2** (200 mol %), [Ni(cod)$_2$] (10 mol %), Zn (300 mol %), DMA (1 mL). For X=I, method A: **4g** (15 mol %), CuI (30 mol %) at 35 °C, 6 h; for X=Br, method B: **6** (10 mol %), MgCl$_2$ (150 mol %) at 80 °C, 12 h. [b] Isolated yields.

Extension of the allylation approach to other alkyl halides **7a**–**7n** was also pursued (Table 4). The reaction tolerated a wide array of functional groups, including amide, aryl halide, ketal, ether, nitrile, ester, and even alcohol groups. Excellent regioselectivities (> 20:1) were also observed, with addition of the alkyl group to the less hindered allylic carbon terminus (Table 4, entries 1–7, 12 and 16). In general, secondary cyclic alkyl halides **7a**–**7k** provided the allylated alkanes **8a**–**8k** in good to excellent yields (Table 4, entries 1–13), with the exception of only a 53 % yield of **8j** due to substantial homocoupling of **7j** (X=I, Table 4, entry 12). Of special note is the high yield obtained for **8k**, containing a free hydroxyl group. The open chain secondary alkyl halides were also compatible with the optimized reaction conditions, offering **8l** and **8m** in good to excellent yields (Table 4, entries 14 and 15). No enantioselectivity was observed for **8l** (Table 4, entry 14, see the Supporting Information).[19] Finally, primary alkyl halide **7n** also produced the allylated product **8n** in a 62 % yield (Table 4, entry 16), for which a combination of **4a**, CuI, and MgCl$_2$ was determined to be the optimal reaction mixture.

To obtain insight into the reaction mechanism, we first examined whether the in situ formation of alkylzinc reagents was a possible reaction route,[20] by attempting the coupling of cyclohexylzinc halides with **2g** under the optimized reaction conditions in the absence of Zn. However, this reaction only produced trace amounts of **8g** at 35 or 80 °C (Scheme 1). This provides direct evidence that the allylation process is unlikely to proceed through an in situ alkylzinc/Negishi pathway.[2,21]

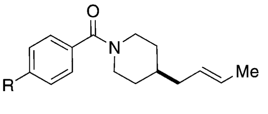
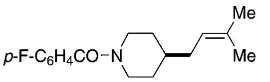
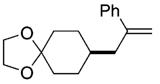
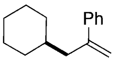
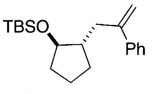
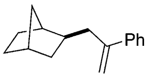
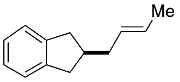
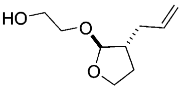
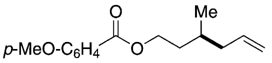
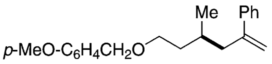
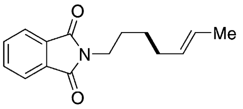


Scheme 1. Coupling of an organozinc reagent with **2g**.

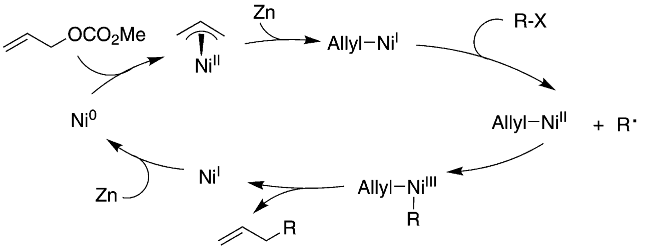
Additionally, under the allylation conditions, compound **9** underwent intramolecular cyclization followed by allylation with **2g** to give **10** in high *endo* diastereoselectivity, indicating that a radical intermediate was probably involved in the oxidative-addition step (Scheme 2).[13c,22] A mechanism implicating radical addition to allyl carbonate, followed by fragmentation to generate the allylated product, can be ruled out based on previous studies.[23]

Table 4. Scope and limitation of alkyl halides.[a]

$$\underset{\textbf{7a-7n}\ (X = Br, I)}{R_{alkyl}{-}X} + \underset{\textbf{2}\ (2\ equiv)}{\text{Allylic carbonate}} \xrightarrow[X = Br,\ Method\ B]{X = I,\ Method\ A} \underset{\textbf{8a-8n}}{R_{alkyl}{-}Allyl}$$

	X	Ligand	2	Product		Yield [%][b]
1	I	**4a**	**2h**		**8b**, R=F	90
2	I	**4a**	**2h**		**8b**, R=Cl	94
3	I	**4a**	**2h**		**8c**, R=Br	67
4	Br	**6**	**2h**		**8a**, R=F	91
5	Br	**6**	**2h**		**8b**, R=Cl	90
6	Br	**6**	**2b**		**8d**, R=CN	62
7	Br	**4a**	**2e**		**8e**	80
8	Br	**6**	**2g**		**8f**	85
9	Br	**6**	**2g**		**8g**	72
10	Br	**6**	**2g**		**8h**	56[c]
11	Br	**6**	**2g**		**8i**	75[c]
12	I	**4a**	**2h**		**8j**	53[d]
13	Br	**6**	**2a**		**8k**	82[c]
14	I	**4a**	**2a**		**8l**	64[e]
15	Br	**6**	**2g**		**8m**	85
16	Br	**4a**	**2b**		**8n**	62[f]

[a] Reaction conditions: **1** (100 mol%, 0.15 M in DMA), **2** (200 mol%), [Ni(cod)$_2$] (10 mol%), Zn (300 mol%), DMA (1 mL). For X=I, method A: **4a** (15 mol%), CuI (30 mol%) at 35 °C, 6 h; for X=Br, method B: **4g** or **6** (10 mol%), MgCl$_2$ (150 mol%) at 80 °C, 12 h. [b] Isolated yields. [c] >20:1 diastereoselectivity. [d] 20 °C. [e] No enantioselectivity was obtained. [f] Use of **4a** (15 mol%)/CuI (20 mol%)/MgCl$_2$ (20 mol%) at 80 °C.

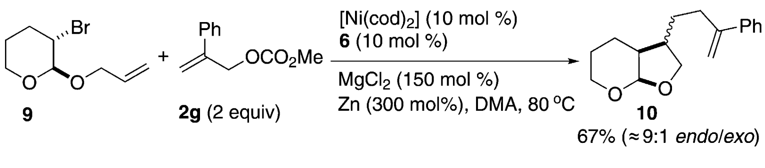


Scheme 3. Proposed reaction mechanism for the allylic alkylation.

Although more experiments are required to further understand the allylation mechanism, we propose that the reaction is likely to proceed first by oxidative addition of Ni^0 to allyl carbonate to produce a π-allyl–Ni^{II} species (Scheme 3). Single-electron reduction by Zn leads to an allyl–Ni^I intermediate,[24] which enables one-electron reduction of alkyl halides to give an alkyl radical and a second allyl–Ni^{II} complex. This hypothesis is in agreement with the stoichiometric allylic coupling of allylnickel(I) complexes with alkyl halides through a possible electron-transfer radical chain process.[25] Combination of the alkyl radical and the Ni^{II} intermediates generates an R–Ni^{III}–allyl species. Reductive elimination delivers the allylated alkane, along with a second Ni^I intermediate that is reduced to Ni^0 by Zn, allowing for the catalytic cycle to proceed. Although not directly relevant, Ni^I/Ni^{III} catalytic transformations have also been suggested in the Ni-catalyzed reductive coupling of aryl and alkyl halides.[10,11c,26]

An alternative pathway involving reductive transmetalation of allyl–Ni^{II} to allyl–Zn followed by a Negishi transformation is possible.[27] However, this notion seems to contradict the failure of the coupling of allylzinc bromide with **1a** and **1b** under the optimized reaction conditions in the absence of **2a** and zinc, for which the reduction of the C–X bonds accounted for the major product.

In conclusion, an efficient Ni-catalyzed method for the allylation of alkyl halides has been developed. Allylic substrates with various substitution patterns, and alkyl halides decorated with different functional groups are tolerated. Alkylation of unsymmetrical allylic carbonates provides exclusively *E*-alkenyl products. For less congested allylic carbonates, this method displays excellent regioselectivities by addition of alkyl groups to the less hindered allylic carbon atom. In addition, although more evidence is required, this unprecedented Ni-catalyzed allylation process appears to be mechanistically in agreement with a Ni^I/Ni^{III} redox process that has been proposed for the stoichiometric coupling of allyl-Ni^I with alkyl halides.[25] Future work will focus on detailed mechanistic studies, including reaction kinetics, as well as extending this protocol to sterically more encumbered reactants.



Scheme 2. Coupling of compound **9** with **2g**.

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Keywords: alkyl halides · allylation · allylic compounds · nickel · reductive coupling

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[19] Control of enantioselectivity for the newly formed stereocenter residing on the alkyl electrophiles appears to be a challenge. However, it should be noted that asymmetric alkylation of allyl electrophiles with racemic alkyl metallic nucleophiles has not been well addressed. Rather, achiral hard alkyl nucleophiles have been predominantly utilized to create chirality on allylic carbons. For an example, see Ref. [2].

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