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Nickel-Catalyzed Cross-Coupling of Allyl Alcohols with Aryl- or Alkenylzinc Reagents

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ABSTRACT: Nickel-catalyzed cross-coupling of allyl alcohols with aryl- and alkenyl-zinc chlorides through C-O bond cleavage was performed. Reaction of (*E*)-3-phenylprop-2-en-1-ol and 1-aryl-prop-2-en-1-ols with aryl- or alkenylzinc chlorides gave linear cross-coupling products. Reaction of 1-phenyl- or 1-methyl-substituted (*E*)-3-phenylprop-2-en-1-ol with aryl- or alkenyl-zinc chlorides resulted in 3-aryl/alkenyl-substituted (*E*)-(prop-1-ene-1,3-diyl)dibenzenes or 3-aryl/alkenyl-substituted (*E*)-(but-1-enyl)benzene. Reaction of allyl alcohol with *p*-$Me_2NC_6H_4ZnCl$ resulted in a mixture of normal coupling product 4-allyl-*N*,*N*-dimethylaniline and its isomerized product *N*,*N*-dimethyl-4-(prop-1-en-1-yl)aniline.

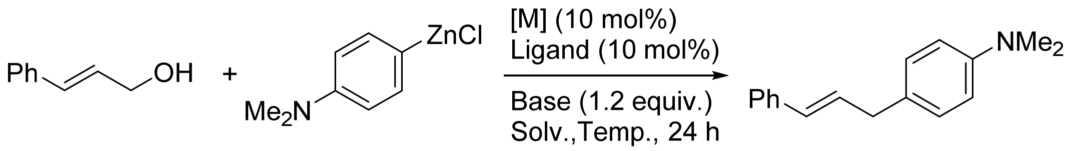
Introduction

Transition-metal-catalyzed allylation is a powerful tool to construct C-C bonds in organic synthesis.[1-3] Among the reactions allyl alcohol derivatives bearing a good leaving group such as allylic carboxylates, allylic carbonates, and allylic phosphates were often employed as electrophiles.[2-6] Allyl alcohols themselves were less used due to the poor leaving ability of hydroxide anion and the presence of acidic proton.[1] However, direct catalytic transformation of allyl alcohols is more step and atom economical because the activated allylic substrates were mostly prepared from allyl alcohols. Hence catalytic allylation using allyl alcohols as electrophiles attracted considerable attention in recent years.[1,7-11] For example, palladium-, rhodium-, and iridium-catalyzed cross-coupling of allyl alcohols with organoboron reagents have been achieved.[1,11] Transition-metal-catalyzed allylic alkylation of ketones, aldehydes, and other active methylene compounds using allyl alcohols were also carried out.[1,7] However, nucleophiles used in transformation of allyl alcohols are very limited. Among those nucleophiles often employed in cross-coupling reactions such as organo-magnesium, -zinc, -boron, -tin, and -silicon reagents,[12] only organoboron reagents were used to react with allyl alcohols. On the other hand, organozinc reagents show higher reactivity than organoboron, -silicon, and -tin reagents and better functional-group compatibility than organomagnesium reagents. Hence, it would be interesting to explore the reaction of allyl alcohols with organozinc reagents to construct C-C bonds. In addition, most of the reported reactions with allyl alcohols required palladium and iridium as catalysts. Inexpensive and earth-abundant nickel was rarely used in the transformations.[1] In a earlier study, we demonstrated that nickel can effectively catalyze cross-coupling of allyl methyl ethers with arylzinc reagents.[13] Here we report a nickel-catalyzed cross-coupling of allyl alcohols with aryl- and alkenylzinc reagents.

Results and discussion

Screening of catalyst and optimization of reaction conditions were carried out using coupling of (*E*)-3-phenylprop-2-en-1-ol (**1a**) with *p*-$Me_2NC_6H_4ZnCl$ (**2a**) as a model reaction. Due to the presence of the acidic proton in allyl alcohol, excess organozinc reagent was used or a strong base was added to convert the allyl alcohol to its salt prior to catalytic reaction. At first the pincer nickel complex and reaction conditions for coupling of allyl methyl ethers with aryl zinc reagents[13] were used to catalyze the coupling of **1a** with excess **2a** and the results showed that catalyst to be ineffective to current substrates. Hence we turned our attention to other nickel compounds. In the following tests, the reaction was first run in a mixed solvent of toluene and diisopropyl ether (3:1) at 120 °C (bath temperature) refering to reaction conditions of nickel-catalyzed coupling of phenolic salts or benzyl alcohols with Grignard reagents.[14] In the presence of 10 mol% $NiCl_2$(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane), reaction of **1a** with either 3.2 equiv. or 5 equiv. of **2a** resulted in 4-cinnamyl-*N,N*-dimethylaniline (**3a**) in 53% and 60% yields respectively (Table 1, entries 1 and 2). Reaction of sodium (*E*)-3-phenylprop-2-en-1-olate prepared from (*E*)-3-phenylprop-2-en-1-ol and NaH with 2 equiv. of **2a** gave a similar yield (Table 1, entry 3). However, marked improvements were observed if **1a** was pre-treated with MeLi, MeMgBr or MeZnCl (Table 1, entries 4-6). Next we examined other pre-catalysts including $NiCl_2$(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene), $NiCl_2$(dppp) (dppp = 1,3-bis(diphenylphosphino)propane), $NiCl_2(PPh_3)_2$ and $NiCl_2(PCy_3)_2$ and demonstrtated $NiCl_2$(dppe) to be most effective (Table 1, entries 7-10). We also examined the combination of simple nickel compounds and dppe and found that a combination of $Ni(OTf)_2$ and dppe resulted in highest product yield (Table 1, entries 11-14). In the absence of dppe, $Ni(OTf)_2$ can catalyze the reaction in relatively low efficiency. In the absence of any nickel catalyst the reaction also gave 28% product yield (Table 1, entries 15 and 16). In the latter case occurrence of the reaction may result from activation of Lewis acids such as $MgCl_2$ to the C-O bond of allyl alcohol. We did find that reaction of **1a** with **2a** gave trace amounts of coupling product in the absence of any Mg^{2+} ion and nickel catalyst (Table 1, entry 17). When 1.5 equiv. of **2a** were loaded or reaction time was shortened to 12 hours, the reactions gave lower yields (Table 1, entries 18 and 19). Reaction temperature is also an important factor. Lower temperatures than 120 °C led to lower product yields (Table 1, entries 20 and 21). Although the mixed solvent of toluene and diisopropyl ether led to good coupling results, we still tested other solvents including toluene, *i*-Pr_2O, THF, *n*-Bu_2O, dioxane, NMP, and a mixture of toluene and *n*-Bu$_2$O (3:1). The results showed that the mixture of toluene and *n*-Bu$_2$O (3:1) was as good as the mixed solvent of toluene and *i*-Pr$_2$O (3:1), and toluene alone was also a suitable solvent for the reaction (Table 1, entries 22-28). Finally, we tested the reaction in the mixed solvent of toluene and *n*-Bu$_2$O (3:1) using 5 mol% Ni(OTf)$_2$ and 5 mol% dppe loadings. Slightly lower product yield was obtained (Table 1, entry 29).

Table 1. Catalyst screening and optimization of reaction conditions[a]



1a **2a** **3a**

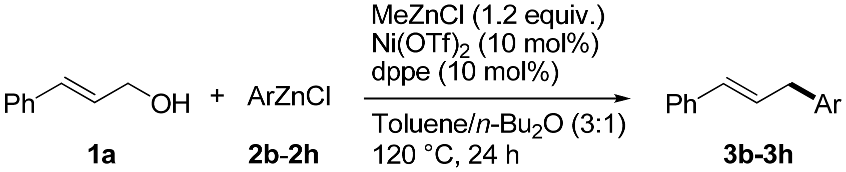
Entry	Amount of zinc reagent (equiv.)	Base	[M] (mol%)	Ligand (mol%)	T (°C)	Solvent	Yield (%)
1	3.2	–	NiCl$_2$(dppe)	–	120	Tolu/*i*-Pr$_2$O (3:1)	53
2	5	–	NiCl$_2$(dppe)	–	120	Tolu/*i*-Pr$_2$O (3:1)	60
3	2	NaH	NiCl$_2$(dppe)	–	120	Tolu/*i*-Pr$_2$O (3:1)	61
4	2	MeLi	NiCl$_2$(dppe)	–	120	Tolu/*i*-Pr$_2$O (3:1)	89
5	2	MeMgCl	NiCl$_2$(dppe)	–	120	Tolu/*i*-Pr$_2$O (3:1)	92
6	2	MeZnCl	NiCl$_2$(dppe)	–	120	Tolu/*i*-Pr$_2$O (3:1)	92
7	2	MeZnCl	NiCl$_2$(dppf)	–	120	Tolu/*i*-Pr$_2$O (3:1)	85
8	2	MeZnCl	NiCl$_2$(dppp)	–	120	Tolu/*i*-Pr$_2$O (3:1)	82
9	2	MeZnCl	NiCl$_2$(PPh$_3$)$_2$	–	120	Tolu/*i*-Pr$_2$O (3:1)	40
10	2	MeZnCl	NiCl$_2$(PCy$_3$)$_2$	–	120	Tolu/*i*-Pr$_2$O (3:1)	17
11	2	MeZnCl	Ni(COD)$_2$	dppe	120	Tolu/*i*-Pr$_2$O (3:1)	83
12	2	MeZnCl	Ni(acac)$_2$	dppe	120	Tolu/*i*-Pr$_2$O (3:1)	92
13	2	MeZnCl	NiCl$_2$(DME)	dppe	120	Tolu/*i*-Pr$_2$O (3:1)	83
14	2	MeZnCl	Ni(OTf)$_2$	dppe	120	Tolu/*i*-Pr$_2$O (3:1)	98
15	2	MeZnCl	Ni(OTf)$_2$	–	120	Tolu/*i*-Pr$_2$O (3:1)	72
16	2	MeZnCl	–	–	120	Tolu/*i*-Pr$_2$O (3:1)	28
17[b]	2	MeLi	–	–	120	Tolu/*i*-Pr$_2$O (3:1)	trace
18	1.5	MeZnCl	Ni(OTf)$_2$	dppe	120	Tolu/*i*-Pr$_2$O (3:1)	65
19[c]	2	MeZnCl	Ni(OTf)$_2$	dppe	120	Tolu/*i*-Pr$_2$O (3:1)	92
20	2	MeZnCl	Ni(OTf)$_2$	dppe	100	Tolu/*i*-Pr$_2$O (3:1)	95
21	2	MeZnCl	Ni(OTf)$_2$	dppe	80	Tolu/*i*-Pr$_2$O (3:1)	75

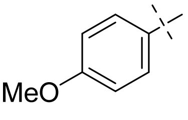
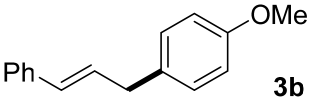
22	2	MeZnCl	$Ni(OTf)_2$	dppe	120	Tolu	96
23	2	MeZnCl	$Ni(OTf)_2$	dppe	reflux	*i*-Pr_2O	35
24	2	MeZnCl	$Ni(OTf)_2$	dppe	reflux	THF	8
25	2	MeZnCl	$Ni(OTf)_2$	dppe	120	*n*-Bu_2O	84
26	2	MeZnCl	$Ni(OTf)_2$	dppe	120	dioxane	23
27	2	MeZnCl	$Ni(OTf)_2$	dppe	120	NMP	trace
28	2	MeZnCl	$Ni(OTf)_2$	dppe	120	Tolu/*n*-Bu_2O (3:1)	98
29[d]	2	MeZnCl	$Ni(OTf)_2$	dppe	120	Tolu/*n*-Bu_2O (3:1)	92

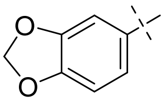
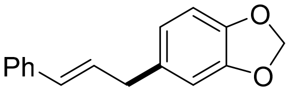
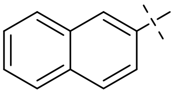
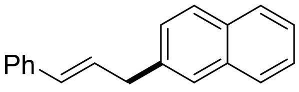
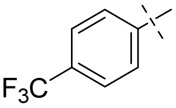
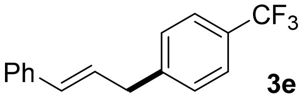
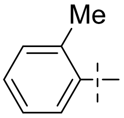
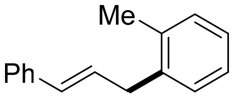
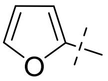
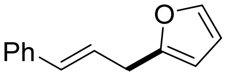
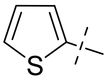
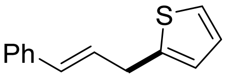
[a] Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation; *p*-$Me_2NC_6H_4ZnCl$ was prepared from *p*-$Me_2NC_6H_4MgBr$ and $ZnCl_2$ in the presence of 2 equiv. of LiCl. [b] *p*-$Me_2NC_6H_4ZnCl$ was prepared from *p*-$Me_2NC_6H_4Li$ and $ZnCl_2$ in the presence of 1 equiv. of LiCl. [c] The reaction time was 12 h. [d] 5 mol% $Ni(OTf)_2$ and 5 mol% dppe were employed.

Next we examined substrate scope under the optimized conditions. Thus, allyl alcohols were first treated with MeZnCl at room temperature and next the reaction was run in a mixed solvent of toluene and *n*-Bu_2O (3:1) at 120 °C for 24 h using a combination of $Ni(OTf)_2$ (10 mol%) and dppe (10 mol%) as pre-catalyst. To choose MeZnCl rather than MeLi or MeMgCl (cf. Table 1, entries 4-6) as a base is to prevent undesirable side reaction when the allyl alcohols containing reactive functional groups such as COOEt, $CONEt_2$, and CN were employed. Compound **1a** was demonstrated to react smoothly with various arylzinc chlorides including electron-rich and electron-poor ones (Table 2, entries 1-5). For example, the reactions with electron-rich arylzinc reagents including (4-(dimethylamino)phenyl)zinc chloride (**2a**), (4-methoxyphenyl)zinc chloride (**2b**) and benzo[*d*][1,3]dioxol-5-ylzinc chloride (**2c**) as well as naphthalen-2-ylzinc chloride (**2d**) gave almost quantitative yields (Table 1, entry 28 and Table 2, entries 1-3). Reaction of electron-poor zinc reagent, *p*-$CF_3C_6H_4ZnCl$ (**2e**), resulted in lower yield (Table 2, entry 4). This might be due to weaker nucleophilicity of **2e** and existence of side reactions as observation from TLC of the resultant reaction mixture. Reaction of *o*-MeC_6H_4ZnCl (**2f**) gave excellent product yield (Table 2, entry 5). It seems that steric hindrance of *o*-tolyl group affects the reaction in a very small degree. Two heteroarylzinc reagents, furan-2-ylzinc chloride (**2g**) and thiophen-2-ylzinc chloride (**2h**), can also react with **1a** to form 2-cinnamylfuran (**3g**) and 2-cinnamylthiophene (**3h**), respectively (Table 2, entries 6 and 7). We noted that LiCl and $MgCl_2$ additives can promote the coupling reaction. If furan-2-ylzinc chloride was prepared from furan-2-yllithium and an equiv. of $ZnCl_2$, the coupling reaction gave 47% product yield. If the zinc reagent was prepared from furan-2-yllithium and an equiv. of $ZnCl_2$ in the presence of 1.0 equiv. LiCl and 1.0 equiv. $MgCl_2$, the coupling reaction gave 62% product yield. The other reactions also required the existence of LiCl and $MgCl_2$ to achieve good yields. For example, catalytic reaction of **1a** with **2a** in the absence of any Mg^{2+} ion gave desired product in 72% yield which was markedly lower than that under standard conditions (Table 1, entry 28). The acceleration effect of LiCl and $MgCl_2$ to the reaction of organozinc reagents has been observed previously by us and other groups.[15] $MgCl_2$ as a stronger Lewis acid than $ZnCl_2$ may weaken C-O bond of the allyl alcohols by coordination of the oxygen atom to magnesium center. The role of LiCl may be to enhance reactivity of organozinc reagents through breaking the aggregation of the organozinc reagent with $MgCl_2$ and forming more nucleophilic lithium zincates.[15c,d] In addition, each of the reactions shown in Table 2 yielded linear cross-coupling product with a *trans*-double bond as shown by the CH=CH coupling constants of the ^1H NMR spectra ranging from 15.6 to 16 Hz.

Table 2. Ni-catalyzed reaction of (*E*)-3-phenylprop-2-en-1-ol with (hetero)arylzinc chlorides[a]



Entry	Ar	Product	Yield (%)
1		 **3b**	99

2		 **3c**	99
3		 **3d**	99
4		 **3e**	73
5		 **3f**	88
6		 **3g**	47[b] 62[c]
7		 **3h**	86[c]

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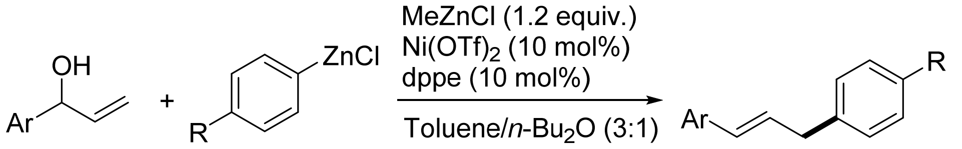
[a] The reactions were carried out using 0.5 mmol **1a** and 1.0 mmol of arylzinc chlorides according to the conditions indicated by above equation. Unless otherwise specified, the zinc reagents were prepared from Grignard reagents and $ZnCl_2$ in the presence of 2 equiv. of LiCl. [b] The zinc reagent was prepared from 1 equiv. of furan-2-yllithium and 1 equiv. of $ZnCl_2$. [c] The zinc reagents were prepared from 1 equiv. of furan-2-yllithium or thiophen-2-yllithium and 1 equiv. of $ZnCl_2$ in the presence of 1 equiv. of LiCl and 1 equiv. of $MgCl_2$.

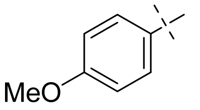
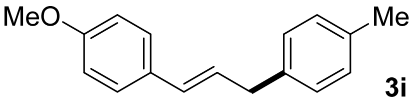
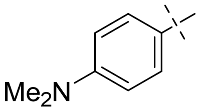
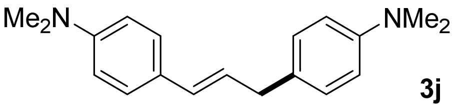
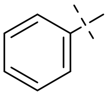
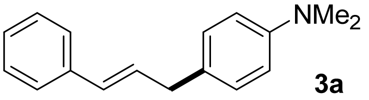
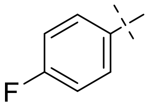
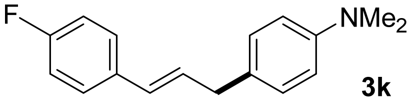
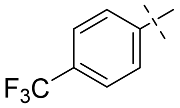
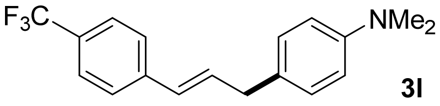
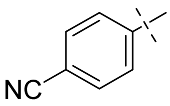
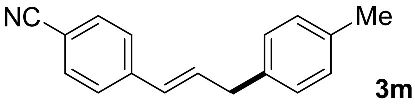
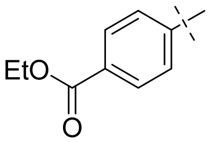
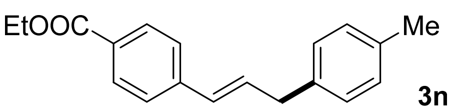
1-Aryl-prop-2-en-1-ols reacted smoothly with arylzinc chlorides to generate exclusively linear coupling products, (*E*)-1,3-diarylpropenes (Table 3, entries 1-8). The substituted phenyl groups attached on prop-2-en-1-ols can be electron-rich and electron-deficient ones. The reactions also tolerated functional groups on the phenyl groups including MeO, Me_2N, F, CF_3, CN, and $C(O)NEt_2$ (Table 3, entries 1, 2, and 4-8). When the substituted groups were CF_3 and CN, the reactions gave lower yields (Table 3, entries 5 and 6). It is surprising that reaction of ethyl 4-(1-hydroxyallyl)benzoate (**1h**) led to very low yield of desired product (Table 3, entry 7). We inferred that a side reaction between the hydroxy group of allyl alcohol and the C(O)OEt group may occur which complicated the catalytic process. Coupling of 1-heteroaryl-prop-2-en-

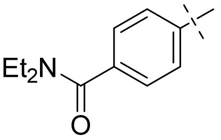
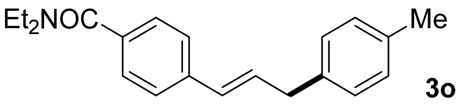
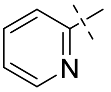
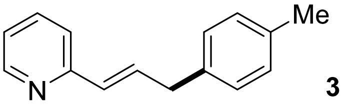
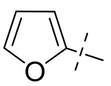
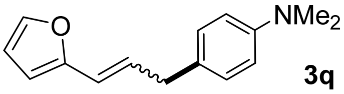
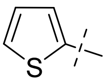
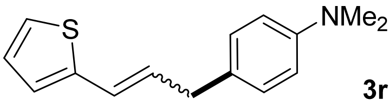
1-ols including 1-(pyridin-2-yl)prop-2-en-1-ol (**1j**), 1-(furan-2-yl)prop-2-en-1-ol (**1k**), and 1-(thiophen-2-yl)prop-2-en-1-ol (**1l**) with arylzinc chlorides also produced linear coupling products (Table 3, entries 9-11). Reaction of 1-(pyridin-2-yl)prop-2-en-1-ol with *p*-tolylzinc chloride afforded (*E*)-2-(3-(*p*-tolyl)prop-1- en-1-yl)pyridine (**3p**) in 77% yield. Respective reaction of 1-(furan-2-yl)prop-2-en-1-ol and 1-(thiophen-2-yl)prop-2-en-1-ol with (4-(dimethylamino)phenyl)zinc chloride formed mixtures of *Z* and *E* isomers of desired products **3q** and **3r** in excellent yields.

Table 3. Ni-catalyzed reaction of 1-aryl-prop-2-en-1-ols with arylzinc chlorides[a]



1b-1l **2** **3a, 3i-3r**

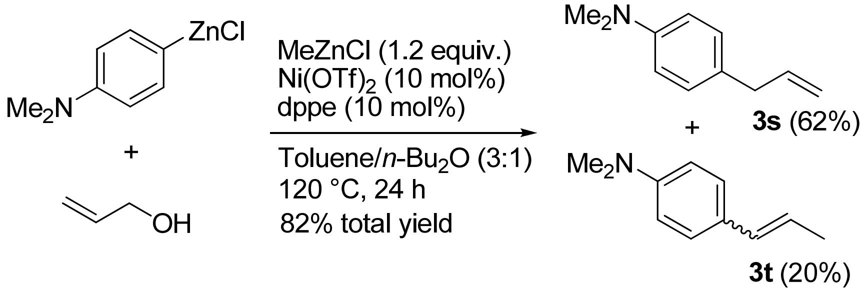
Entry	Ar	Product	Yield (%)
1			96%
2			83%
3			99%
4			94%
5			76%
6			64%
7			20% (25%[b])

8		 **3o**	89%
9		 **3p**	77%
10		 **3q**	87%[c]
11		 **3r**	96%[d]

[a] The reactions were carried out on a 0.5 mmol scale and 2 equiv. of zinc reagents were employed. The zinc reagents were prepared from corresponding Grignard reagents and $ZnCl_2$ in the presence of 2 equiv. of LiCl. [b] 20 mol% $Ni(OTf)_2$ and 20 mol% dppe were used. [c] *Z/E* = 9/91. [d] *Z/E* = 15/85.

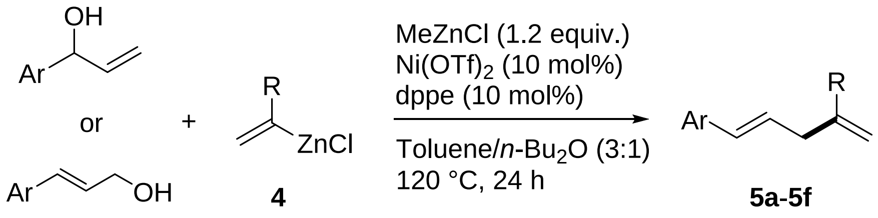
The catalyst system also suited for the coupling of non-aryl substituted allyl alcohols. For example, reaction of allyl alcohol with *p*-$Me_2NC_6H_4ZnCl$ under the standard conditions gave a mixture of 4-allyl-*N*,*N*-dimethylaniline (**3s**) and *N*,*N*-dimethyl-4-(prop-1-en-1-yl) aniline (**3t)** in 82% total yield (Scheme 1). The product **3t** should be from isomerization of **3s** during the process of reaction. In addition, **3t** is a mixture of *Z* and *E* isomers.

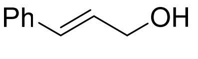
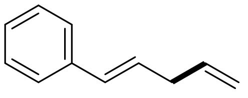
Scheme 1. Ni-catalyzed reaction of allylic alcohol with *p*-$Me_2NC_6H_4ZnCl$

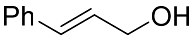
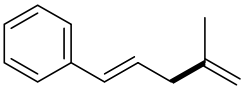
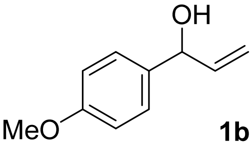
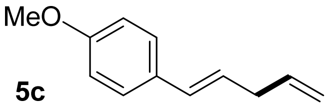
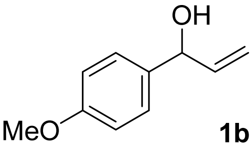
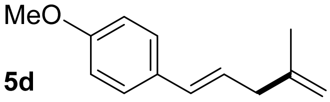
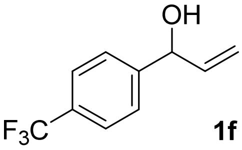
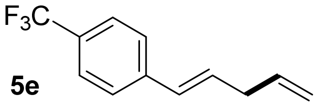
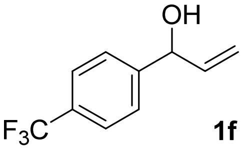
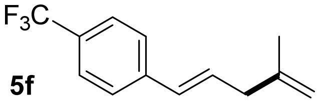


Reaction of alkenylzinc reagents with **1a** and 1-aryl-prop-2-en-1-ols was carried out under the same conditions as for reaction of arylzinc reagents. Reaction of vinylzinc chloride (**4a**) with **1a** gave a mixture of (*E*)-penta-1,4-dien-1-ylbenzene and its isomerization species (1*E*,3*E*)-penta-1,3-dien-1-ylbenzene in a ratio of 86 to 14 and 98% total yield. When the same reaction was run at 80 °C, (*E*)-penta-1,4-dien-1-ylbenzene (**5a**) was obtained as sole coupling product in 94% yield (Table 4, entry 1). Reaction of prop-1-en-2-ylzinc chloride (**4b**) with (*E*)-3-phenylprop-2-en-1-ol (**1a**) under the standard conditions resulted in (*E*)-(4-methylpenta-1,4-dienyl)benzene (**5b**) in 84% yield (Table 4, entry 2). No isomerization product was observed. Reaction of two 1-aryl-prop-2-en-1-ols, 1-(4-methoxyphenyl)prop-2-en-1-ol (**1b**) and 1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (**1f**), with alkenylzinc reagents afforded desired products **5c**-**5f** (Table 4, entries 3-6). The former gave excellent yields, and the latter gave lower yields. The yield difference may be due to the existence of side reactions for 1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol rather than electron effects of aryl groups in the allyl alcohol substrates. We did observe small amount of side products from TLC for the reaction of 1-(4-(trifluoromethyl)phenyl) prop-2-en-1-ol. Reaction of prop-1-en-2-ylzinc chloride gave lower yields in comparison with corresponding those of vinylzinc chloride. This may result from greater steric hindrance of prop-1-en-2-yl group than vinyl group. The above reactions also gave linear alkenes with (*E*)-geometry of C-C double bonds.

Table 4. Ni-catalyzed reaction of (*E*)-3-phenylprop-2-en-1-ol or 1-aryl-prop-2-en-1-ols with alkenylzinc chlorides[a]



Entry	Alcohol	R	Product	Yield (%)
1	 **1a**	H	 **5a**	98[b] 94[c]

2	 **1a**	Me	 **5b**	84
3	 **1b**	H	 **5c**	99
4	 **1b**	Me	 **5d**	87
5	 **1f**	H	 **5e**	79
6	 **1f**	Me	 **5f**	70

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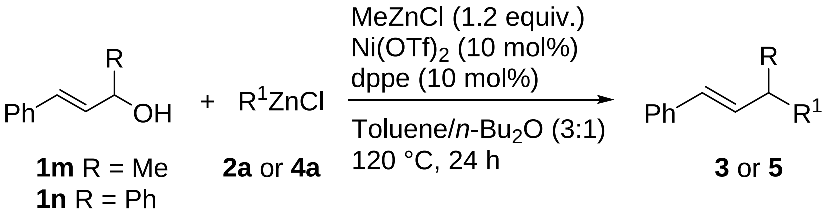
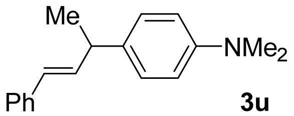
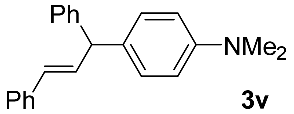
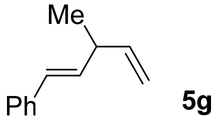
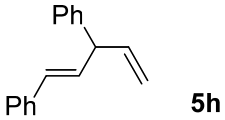
[a] The reactions were carried out on a 0.5 mmol scale and 2 equiv. of zinc reagents were employed. The zinc reagents were prepared from corresponding Grignard reagents and $ZnCl_2$ in the presence of 2 equiv. of LiCl. [b] (*E*)-penta-1,4-dien-1-ylbenzene/(1*E*,3*E*)- penta-1,3-dien-1-ylbenzene = 86/14. [c] The reaction temperature was 80 °C.

Both (*E*)-4-phenylbut-3-en-2-ol (**1m**) and (*E*)-1,3-diphenylprop-2-en-1-ol (**1n**) also reacted smoothly with *p*-$Me_2NC_6H_4ZnCl$ or CH_2=CHZnCl under the optimized conditions. In the reaction of (*E*)-4-phenylbut-3-en-2-ol with either *p*-$Me_2NC_6H_4ZnCl$ or CH_2=CHZnCl no allylic rearrangements were observed (Table 5, entries 1 and 3). Reactions of (*E*)-1,3-diphenylprop-2-en-1-ol gave lower yields of desired products (**3v** and **5h**) than those of (*E*)-4-phenylbut-3-en-2-ol (Table 5, entries 2 and 4). This is ascribed to greater steric hindrance of (*E*)-1,3-diphenylprop-2-en-1-ol than (*E*)-4-phenylbut- 3-en-2-ol.

Table 5. Ni-catalyzed reaction of (*E*)-4-phenylbut-3-en-2-ol and (*E*)-1,3-diphenylprop-2-en-1-ol with *p*-$Me_2NC_6H_4ZnCl$ or CH_2=CHZnCl[a]



Entry	R	R^1	Product	Yield (%)
1	Me	*p*-$Me_2NC_6H_4$	 **3u**	94
2	Ph	*p*-$Me_2NC_6H_4$	 **3v**	76
3	Me	CH_2=CH	 **5g**	96
4	Ph	CH_2=CH	 **5h**	86

[a] The reactions were carried out on a 0.5 mmol scale and 2 equiv. of zinc reagents were employed. The zinc reagents were prepared from corresponding Grignard reagents and $ZnCl_2$ in the presence of 2 equiv. of LiCl.

The reaction was not affected by 1,1-diphenylethene additive. In the presence of 1 equiv. of 1,1-diphenylethene, the catalytic reaction of **1a** with **2a** under standard conditions gave desired product in 99% yield. This ruled out the possibility of a free radical process. A combination of $Ni(COD)_2$ (10 mol%) and dppe (10 mol%) can catalyze coupling of **1a** with **2a** in 83% product yield (Table 1, entry 11). Based on these experimental results we inferred that the reaction may proceed through a Ni(0)/Ni(II) cycle. The allylic rearrangement shown in Tables 3 and 4 supports formation of a allylnickel intermediate in the reaction process. Attempts to prepare and isolate the intermediate through reaction of (*E*)-PhCH=CHCH$_2$OZnCl or (*E*)-PhCH=CHCH(Ph)OZnCl with an equiv. of $Ni(COD)_2$/dppe were unsuccessful. The ^1H NMR spectrum of the resultant species of reaction of (*E*)-PhCH=CHCH(Ph)OZnCl with an equiv. of

$Ni(COD)_2$/dppe exhibited complicated spectral signals rather than those of simple allylnickel. In Table 5 we showed that reaction of (*E*)-1,3-diphenylprop-2-en-1-ol with *p*-$Me_2NC_6H_4ZnCl$ under standard conditions gave cross-coupling product in 76% yield. However, the same reaction and conditions but employing an equiv. of $Ni(OTf)_2$/dppe gave only 28% product yield. This result made us realize that some other factors might steer the reaction process. We ran the reaction again in the presence of 13 equiv. of $ZnCl_2$, 25 equiv. of LiCl and 13 equiv. of $MgCl_2$ additives and the result showed that a 84% product yield was achieved. The experimental fact implies that a high molar ratio of Zn^{2+}, Li^{+} and Mg^{2+} ions to nickel is necessary for a successful catalytic process. Although we inferred that $MgCl_2$ as a strong Lewis acid may promote activation the C-O bond of allyl alcohols and LiCl may enhance reactivity of organozinc reagents, the concrete mode of action was still unclear. The reaction intermediate may be a complex cluster composed of zinc, lithium, magnesium, nickel ions and reaction substrates. Further studies will be needed to clarify the reaction mechanism.

Conclusions

In summary, $Ni(OTf)_2$/dppe has been demonstrated to effectively catalyze cross-coupling of allyl alcohols with aryl or alkenylzinc reagents through C-O bond cleavage. The reaction exhibits high regioselectivity, both (*E*)-3-phenylprop-2-en-1-ol and 1-aryl-prop-2-en-1-ol substrates resulting in linear coupling products. The reaction also shows high *E*/*Z*-selectivity for the new C-C double bond in most cases, the alkenes with (*E*)-geometry being formed except the reaction of 1-(furan-2-yl)prop-2-en-1-ol and 1-(thiophen-2-yl)prop-2-en-1-ol with arylzinc chlorides, which afforded a mixture of (*Z*)- and (*E*)-isomers. The catalyst system also suited for the coupling of more steric hindered secondary allyl alcohols such as (*E*)-4-phenylbut-3-en-2-ol and (*E*)-1,3-diphenylprop-2-en-1-ol with aryl or vinylzinc reagents to afford regioselective coupling products with (*E*)-C-C double bond geometry. The reaction may proceed through a Ni(0)/Ni(II) cycle, but lithium, magnesium and zinc ions play an important role in the catalytic process.

Experimental

All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Toluene, THF, *i*-Pr_2O, *n*-Bu_2O and 1,4-dioxane were distilled under nitrogen over sodium and degassed prior to use. NMP was dried over 4 Å molecular sieves, fractionally distilled under reduced pressure, and stored under a nitrogen atmosphere. $ZnCl_2$, and LiCl were purchased from commercial vendors and dried under vacuum at 140 °C for 12 h prior to use. MeMgCl, CH_2=CHMgCl, and *p*-$Me_2NC_6H_4MgBr$ were purchased from commercial vendors and used as received. The other Grignard reagents were prepared according to reported procedures.[16] Organozinc reagents were prepared from $ZnCl_2$ and an equiv. of Grignard reagents in the presence of 2 equiv. of LiCl. Various allyl alcohols including 1-phenyl-prop-2-en-1-ol, 1-(4-methoxyphenyl)prop-2-en-1-ol, 1-(4-(dimethyl amino)phenyl)prop-2-en-1-ol, 1-(4-fluorophenyl)prop-2-en-1-ol, 1-(4-(trifluoromethyl) phenyl)prop-2-en-1-ol, 4-(1-hydroxyallyl)benzonitrile, 1-(furan-2-yl)prop-2-en-1-ol, 1-(thiophen-2-yl)prop-2-en-1-ol, 1-(pyridin-2-yl)prop-2-en-1-ol), (*E*)-4-phenylbut-3-en-2-ol, (*E*)-1,3-diphenyl-prop-2-en-1-ol, ethyl 4-(1-hydroxyallyl)benzoate and *N,N*-diethyl-4-(1- hydroxyallyl)benzamide were prepared according to reported procedures.[7h,13,17] All other chemicals were obtained from commercial vendors and used as received. NMR spectra were recorded on a 400 MHz NMR spectrometer at ambient temperature. The chemical shifts of the ^1H NMR spectra were referenced to TMS and the chemical shifts of the $^{13}C\{^1H\}$ NMR spectra were referenced to internal solvent resonances. The chemical shifts of the ^{19}F NMR spectra were referenced to external CF_3COOH. High-resolution mass spectra (HR-MS) were acquired in the ESI or APCI mode using an Orbitrap mass analyzer.

General procedure for the catalytic coupling

$Ni(OTf)_2$ (17.8 mg, 10 mol%), dppe (19.9 mg, 10 mol%), and allyl alcohol (0.5 mL, 1.0 M solution in THF, 0.5 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture MeZnCl (1.2 mL, 0.5 M solution in THF, 0.6 mmol) was added at room temperature. After stirred for 5 min., a solution of aryl- or alkenylzinc reagent (2.0 mL, 0.5 M solution in THF, 1.0 mmol) was added and the solution was stirred for additional 5 min. Solvent was removed in vacuo. Toluene (3 mL) and *n*-Bu_2O (1 mL) were successively added. The resultant mixture was stirred at 120 °C for 24 h and then cooled to room temperature. A 20% aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

*4-cinnamyl-N,N-dimethylaniline (**3a**).*[18] Elute: EtOAc/petroleum ether: 1/60 (v/v), pale yellow oil, yield 116.3 mg (98%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.7, 6.5 Hz, 1H), 3.46 (d, *J* = 6.4 Hz, 2H), 2.92 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 149.5, 137.8, 130.5, 130.3, 129.4, 128.6, 128.3, 127.0, 126.2, 113.2, 41.0, 38.5.

*1-cinnamyl-4-methoxybenzene (**3b**).*[18] Elute: EtOAc/petroleum ether: 1/100 (v/v), colorless oil, yield 111.1 mg (99%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.3 Hz, 2H), 7.28 (t, *J* = 6.9 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.33 (dt, *J* = 15.7, 6.5 Hz, 1H), 3.79 (s, 3H), 3.49 (d, *J* = 6.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.2, 137.6, 132.3, 130.9, 129.8, 129.7, 128.6, 127.2, 126.2, 114.0, 55.4, 38.6.

*5-cinnamylbenzo[d][1,3]dioxole (**3c**).*[18] Elute: EtOAc/petroleum ether: 1/150 (v/v), colorless oil, yield 118.1 mg (99%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.77-6.66 (m, 3H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.7, 6.7 Hz, 1H), 5.91 (s, 2H), 3.45 (d, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 147.8, 146.1, 137.5, 134.1, 131.1, 129.5, 128.6, 127.3, 126.3, 121.5, 109.3, 108.4, 101.0, 39.2.

*2-cinnamylnaphthalene (**3d**).*[18] Elute: petroleum ether, white solid, yield 121.1 mg (99%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79 (t, *J* = 8.7 Hz, 3H), 7.66 (s, 1H), 7.40-7.46 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 3H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.23-7.16 (m, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.42 (dt, *J* = 15.6, 6.3 Hz, 1H), 3.69 (d, *J* = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 137.8, 137.6, 133.8, 132.3, 131.5, 129.2, 128.7, 128.2, 127.8, 127.7, 127.6, 127.3, 126.9, 126.3, 126.1, 125.5, 39.6.

*1-cinnamyl-4-(trifluoromethyl)benzene (**3e**).*[11b] Elute: petroleum ether, colorless oil, yield 95.7 mg (73%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.39-7.33 (m, 3H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.24-7.20 (m, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.32 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.60 (d, *J* = 6.8 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 144.4, 137.3, 132.1, 129.1, 128.7 (q, *J* = 32.4 Hz), 128.7, 128.0, 127.5, 126.3, 125.6 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 271.8 Hz), 39.2. ^{19}F NMR (376 MHz, CDCl$_3$): δ −62.33.

*1-cinnamyl-2-methylbenzene (**3f**).*[18] Elute: petroleum ether, colorless oil, yield 92.1 mg (88%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.22-7.13 (m, 5H), 6.41-6.28 (m, 2H), 3.53 (d, *J* = 4.8 Hz, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 138.4, 137.7, 136.6, 131.0, 130.4, 129.4, 128.7, 128.6, 127.2, 126.6, 126.2, 126.2, 37.0, 19.6.

*2-cinnamylfuran (**3g**).*[19] Elute: petroleum ether, colorless oil, yield 57.1g (62%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38-7.31 (m, 3H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.23-7.17 (m, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.34-6.25 (m, 2H), 6.06 (d, *J* = 3.1 Hz, 1H), 3.54 (d, *J* = 6.8 Hz, 2H). ^{13}C{^{1}H}

NMR (101 MHz, $CDCl_3$): δ 154.0, 141.5, 137.3, 132.1, 128.6, 127.4, 126.3, 125.7, 110.4, 105.8, 31.9.

2-cinnamylthiophene ***(3h)****.*[20] Elute: petroleum ether, colorless oil, yield 86.3 mg (86%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.33 (m, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.14 (dd, J = 5.1, 0.9 Hz, 2H), 6.94 (dd, J = 5.1, 3.5 Hz, 1H), 6.85 (dd, J = 3.4, 0.9 Hz, 1H), 6.50 (d, J = 15.7 Hz, 1H), 6.35 (dt, J = 15.7, 6.8 Hz, 1H), 3.72 (d, J = 6.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 143.2, 137.3, 131.5, 128.7, 128.3, 127.4, 127.1, 126.4, 124.8, 123.9, 33.5.

(E)-1-methoxy-4-(3-(p-tolyl)prop-1-en-1-yl)benzene ***(3i)****.*[21] Elute: EtOAc/petroleum ether: 1/150 (v/v), white solid, yield 114.5 mg (96%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (dd, J = 8.7, 2.0 Hz, 2H), 7.11 (s, 4H), 6.82 (dd, J = 8.8, 2.1 Hz, 2H), 6.38 (d, J = 15.8 Hz, 1H), 6.26-6.12 (m, 1H), 3.78 (s, 3H), 3.48 (d, J = 6.8 Hz, 2H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.0, 137.5, 135.7, 130.6, 130.4, 129.3, 128.7, 127.5, 127.4, 114.1, 55.4, 39.1, 21.2.

(E)-4,4'-(prop-1-ene-1,3-diyl)bis(N,N-dimethylaniline) ***(3j)****.*[18] Elute: EtOAc/petroleum ether: 1/60 (v/v), colorless oil, yield 116.4 mg (83%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 6.71 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 6.35 (d, J = 15.7 Hz, 1H), 6.13 (dt, J = 15.6, 6.9 Hz, 1H), 3.42 (d, J = 6.9 Hz, 2H), 2.93 (s, 6H), 2.91 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 149.8, 149.4, 130.3, 129.4, 129.1, 127.1, 126.6, 126.1, 113.2, 112.7, 41.1, 40.8, 38.5.

(E)-4-(3-(4-fluorophenyl)allyl)-N,N-dimethylaniline ***(3k)****.*[18] Elute: EtOAc/petroleum ether: 1/60 (v/v), colorless oil, yield 119.9 mg (94%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J = 8.6, 5.5 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.96 (t, J = 8.7 Hz, 2H), 6.72 (d, J = 8.6 Hz, 2H), 6.38 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.7, 6.7 Hz, 1H), 3.44 (d, J = 6.7 Hz, 2H), 2.92 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 162.1 (d, J = 245.7 Hz), 149.5, 134.0 (d, J = 3.2 Hz),

130.1 (d, J = 2.2 Hz), 129.4, 129.2, 128.1, 127.6 (d, J = 7.9 Hz), 115.4 (d, J = 21.5 Hz), 113.2, 41.0, 38.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ –115.65.

(E)-N,N-dimethyl-4-(3-(4-(trifluoromethyl)phenyl)allyl)aniline ***(3l)***. Elute: EtOAc/petroleum ether: 1/60 (v/v), white solid, yield 115.7 mg (76%), mp 106-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 6.47-6.41 (m, 2H), 3.47 (d, J = 5.0 Hz, 2H), 2.92 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.6, 141.3, 133.3, 129.5, 129.2, 128.8 (q, J = 32.5 Hz), 127.5, 126.3, 125.5 (q, J = 3.8 Hz), 124.4 (d, J = 271.7 Hz), 113.2, 41.0, 38.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.36. IR (KBr): ν 3456, 2888, 2813, 1614, 1520, 1417, 1333, 1165, 1109, 1067, 856, 815 cm^{-1}. HR-MS (ESI): m/z 306.1460 [M+H]$^+$, calcd for $C_{18}H_{19}NF_3$: 306.1464.

(E)-4-(3-(p-tolyl)prop-1-en-1-yl)benzonitrile ***(3m)***. Elute: EtOAc/petroleum ether: 1/60 (v/v), greenish oil, yield 74.8 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.18-7.06 (m, 4H), 6.50 (dt, J = 15.8, 6.2 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 3.54 (d, J = 6.2 Hz, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 142.2, 136.2, 136.18, 134.0, 132.5, 129.5, 128.7, 126.7, 119.2, 110.4, 100.1, 39.1, 21.2. IR (KBr): ν 3452, 3020, 2922, 1633, 1508, 1407, 974, 808 cm^{-1}. HR-MS (ESI): m/z 234.1271 [M+H]$^+$, calcd for $C_{17}H_{16}N$: 234.1277.

(E)-ethyl 4-(3-(p-tolyl)prop-1-en-1-yl)benzoate ***(3n)***. Elute: EtOAc/petroleum ether: 1/150 (v/v), colorless oil, yield 35.0 mg (25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.13 (s, 4H), 6.51-6.43 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.62 – 3.44 (m, 2H), 2.33 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.5, 142.0, 136.5, 135.9, 132.4, 130.0, 129.9, 129.3, 128.9, 128.6, 125.9, 60.9, 39.0, 21.1, 14.4. IR (KBr): ν 2987, 2914, 1714, 1608, 1508, 1448, 1278, 1178, 1110, 1021, 964, 807, 765 cm^{-1}. HR-MS (APCI): m/z 281.1524 [M+H]$^+$, calcd for $C_{19}H_{21}O_2$: 281.1536.

(E)-N,N-diethyl-4-(3-(p-tolyl)prop-1-en-1-yl)benzamide ***(3o)***. Elute: EtOAc/petroleum ether:

1/4 (v/v), colorless oil, yield 136.7 mg (89%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.12 (s, 4H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.38 (dt, *J* = 15.6, 6.0 Hz, 1H), 3.64-3.40 (m, 4H), 3.26 (b, 2H), 2.33 (s, 3H), 1.23 (b, 3H), 1.11 (b, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 171.3, 138.5, 136.8, 135.9, 135.8, 130.9, 130.2, 129.3, 128.7, 126.7, 126.1, 43.4, 39.4, 39.0, 21.1, 14.3, 13.0. IR (KBr): *ν* 2982, 2927, 1637, 1517, 1464, 1430, 1089, 964, 805 cm^{-1}. HR-MS (ESI): m/z 308.2004 [M+H]$^+$, calcd for $C_{21}H_{26}ON$: 308.2009.

(E)-2-(3-(p-tolyl)prop-1-en-1-yl)pyridine ***(3p)****.* Elute: EtOAc/petroleum ether: 1/20 (v/v), yellowish oil, yield 80.5 mg (77%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.51 (d, *J* = 5.6 Hz, 1H), 7.56 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.16-7.04 (m, 5H), 6.84 (dt, *J* = 15.6, 6.9 Hz, 1H), 6.50 (dt, *J* = 15.6, 1.4 Hz, 1H), 3.54 (d, *J* = 6.9 Hz, 2H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 155.9, 149.4, 136.44, 136.43, 135.8, 134.5, 130.9, 129.3, 128.7, 121.8, 121.1, 38.8, 21.1. IR (KBr): *ν* 3008, 2923, 1659, 1586, 1511, 1469, 1431, 1301, 1205, 1155, 1050, 979, 808, 762 cm^{-1}. HR-MS (ESI): m/z 210.1274 [M+H]$^+$, calcd for $C_{15}H_{16}N$: 210.1277.

4-(3-(furan-2-yl)allyl)-N,N-dimethylaniline ***(3q)****.* Elute: EtOAc/petroleum ether: 1/60 (v/v), yellow oil, yield 98.3 mg (87%).

NMR spectra for the *E*-isomer:

^{1}H NMR (400 MHz, CDCl$_3$): 7.29 (d, *J* = 1.6 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.36-6.25 (m, 2H), 6.20 (d, *J* = 16.0 Hz, 1H), 6.13 (d, *J* = 3.6 Hz, 1H), 3.42 (d, *J* = 6.4 Hz, 2H), 2.91 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 153.4, 149.5, 141.4, 129.5, 129.2, 128.0, 119.1, 113.2, 111.2, 106.4, 41.0, 38.2. HR-MS (ESI): m/z 228.1378 [M+H]$^+$, calcd for $C_{15}H_{18}ON$: 228.1383.

N,N-dimethyl-4-(3-(thiophen-2-yl)allyl)aniline ***(3r)****.*[18] Elute: EtOAc/petroleum ether: 1/60 (v/v), yellow oil, yield 117.2 mg (96%).

NMR spectra for the *E*-isomer:

^{1}H NMR (400 MHz, CDCl$_3$): 7.09 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 5.2 Hz, 1H), 6.91 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.87 (d, *J* = 3.2 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.19 (dt, *J* = 15.6, 6.8 Hz, 1H), 3.41 (d, *J* = 6.8 Hz, 2H), 2.91 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 149.5, 143.1, 130.3, 129.5, 127.9, 127.3, 124.6, 123.7, 123.4, 113.2, 41.0, 38.3. HR-MS (ESI): m/z 244.1148 [M+H]$^+$, calcd for $C_{15}H_{18}NS$: 244.1155.

*(E)-penta-1,4-dien-1-ylbenzene (**5a**).*[22] Elute: petroleum ether, colorless oil, yield 67.8 mg (94%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38-7.32 (m, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.97-5.84 (m, 1H), 5.15-5.02 (m, 2H), 2.96 (dt, *J* = 6.5, 1.4 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 137.7, 136.6, 131.0, 128.6, 128.3, 127.2, 126.2, 115.8, 37.2.

*(E)-(4-methylpenta-1,4-dien-1-yl)benzene (**5b**).*[23] Elute: petroleum ether, colorless oil, yield 66.5 mg (84%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.39-7.33 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23-7.17 (m, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.81-4.75 (m, 2H), 2.90 (d, *J* = 7.0 Hz, 2H), 1.77 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 144.7, 137.7, 131.5, 128.6, 128.3, 127.2, 126.2, 111.2, 41.6, 22.7.

*(E)-1-methoxy-4-(penta-1,4-dien-1-yl)benzene (**5c**).*[24] Elute: EtOAc/petroleum ether: 1/150 (v/v), yellowish oil, yield 86.3 mg (99%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.08 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.97-5.83 (m, 1H), 5.14-5.07 (m, 1H), 5.07-5.02 (m, 1H), 3.80 (s, 3H), 2.94 (td, *J* = 6.6, 1.4 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 158.9, 136.9, 130.6, 130.3, 127.3, 126.1, 115.6, 114.0, 55.4, 37.2.

*(E)-1-methoxy-4-(4-methylpenta-1,4-dien-1-yl)benzene (**5d**).*[25] Elute: EtOAc/petroleum ether: 1/150 (v/v), colorless oil, yield 81.7 mg (87%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.7, 7.1 Hz, 1H),

4.77 (s, 2H), 3.79 (s, 3H), 2.87 (d, *J* = 7.0 Hz, 2H), 1.76 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.9, 145.0, 130.8, 130.6, 127.3, 126.1, 114.0, 111.0, 55.4, 41.6, 22.6.

(E)-1-(penta-1,4-dien-1-yl)-4-(trifluoromethyl)benzene ***(5e)****.*[26] Elute: petroleum ether, colorless oil, yield 83.4 mg (79%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.97-5.83 (m, 1H), 5.17-5.06 (m, 2H), 3.03-2.95 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 141.2, 136.1, 131.2, 130.0, 129.0 (q, *J* = 32.4 Hz), 126.3, 125.6 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.6 Hz), 116.3, 37.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.43.

(E)-1-(4-methylpenta-1,4-dien-1-yl)-4-(trifluoromethyl)benzene ***(5f)****.*[27] Elute: petroleum ether, colorless oil, yield 79.2 mg (70%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.80 (d, *J* = 14.7 Hz, 2H), 2.92 (d, *J* = 6.9 Hz, 2H), 1.77 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.1, 141.2, 131.2, 130.3, 129.0 (q, *J* = 32.3 Hz), 126.3, 125.6 (q, *J* = 3.8 Hz, 6H), 124.4 (q, *J* = 271.7 Hz), 111.6, 41.6, 22.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.42.

(E)-N,N-dimethyl-4-(4-phenylbut-3-en-2-yl)aniline ***(3u)****.*[18] Elute: EtOAc/petroleum ether: 1/60 (v/v), colorless oil, yield 118.1 mg (94%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.30 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.20-7.12 (m, 3H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.42-6.32 (m, 2H), 3.61-3.49 (m, 1H), 2.90 (s, 6H), 1.42 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 149.4, 137.9, 136.2, 133.8, 128.6, 128.0, 128.0, 127.0, 126.2, 113.1, 41.7, 41.0, 21.4.

(E)-4-(1,3-diphenylallyl)-N,N-dimethylaniline ***(3v)****.*[28] Elute: EtOAc/petroleum ether: 1/60 (v/v), yellow oil, yield 119.1 mg (76%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.33-7.27 (m, 5H), 7.25-7.18 (m, 3H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.66-6.62 (m, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 4.81 (d, *J* = 7.4 Hz, 1H), 2.92 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 149.4, 144.3, 137.6, 133.5, 131.6, 130.9, 129.4, 128.8, 128.6, 128.5, 127.2, 126.4, 126.3, 112.9, 53.4, 40.9.

(E)-(3-methylpenta-1,4-dien-1-yl)benzene ***(5g)****.*[29] Elute: petroleum ether, colorless oil, yield 76.0 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.32 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.93-5.80 (m, 1H), 5.11-4.97 (m, 2H), 3.09-2.96 (m, 1H), 1.20 (d, *J* = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 142.6, 137.8, 134.4, 128.8, 128.6, 127.1, 126.2, 113.5, 40. 8, 19.9.

(E)-penta-1,4-diene-1,3-diyldibenzene ***(5h)****.*[30] Elute: petroleum ether, colorless oil, yield 94.9 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.17 (m, 10H), 6.50-6.33 (m, 2H), 6.19-6.03 (m, 1H), 5.25-5.07 (m, 2H), 4.22 (t, *J* = 5.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 142.8, 140.2, 137.5, 131.9, 130.8, 128.7, 128.7, 128.2, 127.4, 126.7, 126.4, 115.8, 52.5.

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Supporting Information

Copies of ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the cross-coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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