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Nickel-Catalyzed Alkylation or Reduction of Allylic Alcohols with Alkyl Grignard Reagents

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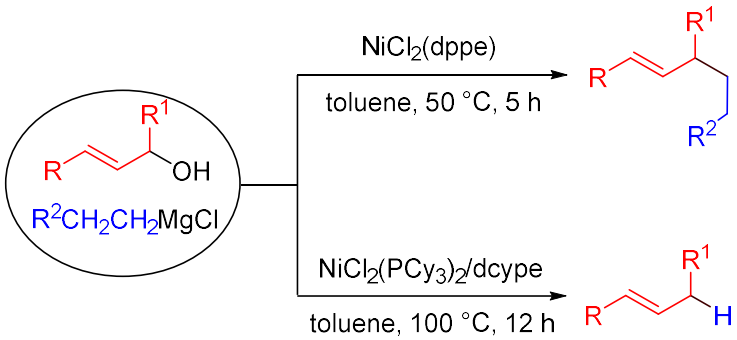


Abstract: By choosing different phosphine ligands nickel-catalyzed selective alkylation and reduction of allylic alcohols with alkyl Grignard reagents were performed. The reaction using Ni(dppe)Cl_2 as the catalyst resulted in the cross coupling of allylic alcohols with primary alkyl Grignard reagents and cyclopropylmagnesium bromide. The reaction catalyzed by the combination of Ni(PCy_3)$_2Cl_2$ and dcype led to the reduction of allylic alcohols. Secondary alkyl Grignard reagents except cyclopropylmagnesium bromide always led to reduction of allylic alcohols using either Ni(dppe)Cl_2 or Ni(PCy_3)$_2Cl_2$/dcype as the catalyst. In the reductive reaction β-H-containing alkyl Grignard reagents were required.

Introduction

Compounds containing allyl moiety are widely existent in natural products and bioactive molecules and often used as versatile building blocks in organic synthesis.[1] Hence synthesis and transformation of allyl compounds have attracted much attention. Transition-metal-catalyzed transformation of allyl compounds such as cross-coupling and hydrogenation is among the most widely investigated reactions. The allyl substrates employed in the transformations were often allylic halides and allylic alcohol derivatives.[2,3] However, direct use of allylic alcohols is more step- and atom-economical because the allylic substrates such as allylic halides, allylic carboxylates, allylic tosylates and allylic phosphates were mostly prepared from allylic alcohols. Hence catalytic transformation of allylic alcohols via C-O bond cleavage attracts considerable attention although the reaction is often more difficult due to the poor leaving ability of the hydroxy group.[4,5]

Kumada reaction has been extensively explored over the years.[6] Compared with aryl and alkenyl substrates, alkyl substrates involving electrophilic and nucleophilic substrates are less to use because alkyl metal intermediates are prone to unproductive β-H elimination although some examples have been reported.[6,7] Electrophilic substrates used in the successful examples are also limited, being mainly alkyl halides. The Kumada coupling employing an alcohol as the electrophile was rare as the reasons mentioned above.[8] On the other hand, the β-H elimination side reaction in the reaction of alkyl Grignard reagents with electrophiles might become a main reaction through choice of catalysts and conditions. Thus, reaction of alkyl Grignard reagents with electrophilic species can be utilized to perform reduction of the organic molecules. Several examples of transition-metal-catalyzed reduction reactions using alkyl Grignard reagents have been reported.[9] We describe here ligand-controlled nickel-catalyzed selective alkylation and

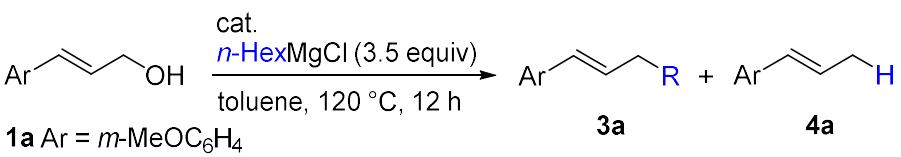
reduction of allylic alcohols with alkyl Grignard reagents.

Results and Discussion

We chose reaction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol (**1a**) with hexylmagnesium bromide to screen catalysts and conditions (Table 1). In the absence of a transition metal catalyst, the reaction cannot occur at all (entry 1). In the presence of 10 mol% $Fe(acac)_3$ and 20 mol% PCy_3, the reaction gave a reductive product **4a** in 13% yield. No cross-coupling product was obtained. A combination of $CoCl_2$ or $CoBr_2$ (10 mol%) and PCy_3 (20 mol%) as well as $Co(PPh_3)_2Cl_2$ (10 mol%) showed higher catalytic activity than the combination of $Fe(acac)_3$ and PCy_3 and each of the cobalt catalysts led to formation of **4a** in 47% yield (entries 2-4). Both $PdCl_2$(dppf) and $PdCl_2(PPh_3)_2$ cannot catalyze the reaction (entries 5 and 6). Several nickel complexes including $NiCl_2(PPh_3)_2$, $NiCl_2(PCy_3)_2$ and $NiCl_2(PMe_3)_2$ were demonstrated to be more active catalysts than the iron and cobalt catalysts. They catalyzed the reaction to yield reductive product **4a** without exception (entries 7-9). However, bidentate phosphine ligand coordinated nickel complexes such as $NiCl_2$(dppe) and $NiCl_2$(dppp) led to formation of cross-coupling product **3a**, along with a small amount of reductive product **4a** (entries 10 and 11). $NiCl_2$(dppf) and the combination of $NiCl_2$(DME), $Ni(OTf)_2$ or $Ni(acac)_2$ and dcype behaved different from $NiCl_2$(dppe) and $NiCl_2$(dppp). They drove the reaction to form reductive product **4a** (entries 12-15). Further tests showed that the combination of $NiCl_2(PCy_3)_2$ (10 mol%) and dcype (10 mol%) led to formation of **4a** in the highest yield (entry 16). Higher loading of dcype was unfavorable (entry 17). Next, we optimized other conditions including reaction temperature, solvent, loading amount of the catalysts, loading amount of *n*-HexMgBr, and reaction time employing $NiCl_2$(dppe) as the coupling catalyst and $NiCl_2(PCy_3)_2$/dcype as the reduction catalyst, respectively (Tables S1-S5 in the Supporting Information). The results showed that reaction of

1a with 3.0 equiv of *n*-HexMgBr in the presence of 10 mol% $NiCl_2$(dppe) in toluene at 50 °C for 5 h gave the optimal yield of the cross-coupling product. The reductive reaction required 3.5 equiv of *n*-HexMgBr and 10 mol% of $NiCl_2(PCy_3)_2$/dcype loadings to achieve the optimal results. Higher reaction temperature (100 °C) and longer reaction time (12 h) were necessary. Toluene was also suitable solvent for this transformation.

Table 1. Screening of transition-metal catalysts[a]



Entry	Cat. (mol%)	Yield (%)[b] (**3a**:**4a**)
1	–	0
2	$Fe(acac)_3$ (10) + PCy_3 (20)	13 (0:100)
3	CoX_2 (10) + PCy_3 (20) (X = Cl or Br)	47 (0:100)
4	$Co(PPh_3)_2Cl_2$ (10)	47 (0:100)
5[c]	$PdCl_2$(dppf)	–
6	$PdCl_2(PPh_3)_2$	–
7	$NiCl_2(PPh_3)_2$ (10)	57 (0:100)
8	$NiCl_2(PCy_3)_2$ (10)	60 (0:100)
9	$NiCl_2(PMe_3)_2$ (10)	50 (0:100)
10	$NiCl_2$(dppe) (10)	96 (95:5)
11	$NiCl_2$(dppp) (10)	96 (89:11)
12	$NiCl_2$(dppf) (10)	60 (0:100)
13	$NiCl_2$(DME) (10) + dcype (10)	16 (0:100)
14	$Ni(OTf)_2$ (10) + dcype (10)	13 (0:100)

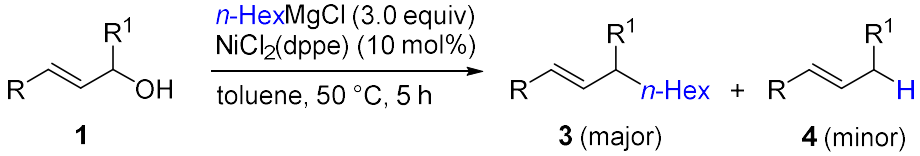
15	$Ni(acac)_2$ (10) + dcype (10)	60 (0:100)
16	$NiCl_2(PCy_3)_2$ (10) + dcype (10)	91 (0:100)
17	$NiCl_2(PCy_3)_2$ (10) + dcype (20)	39 (0:100)

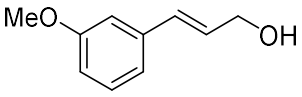
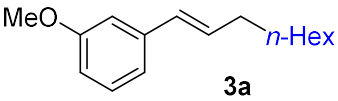
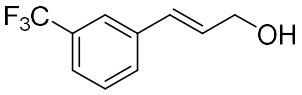
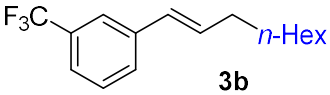
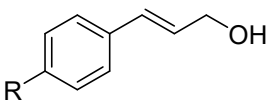
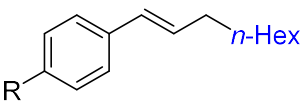
[a] The reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation. [b] Yields were determined by ^1H NMR spectra using $CHCl_2CHCl_2$ as an internal standard. [c] The reaction was carried out in toluene (120 °C), THF (80 °C) and Et_2O (50 °C), respectively.

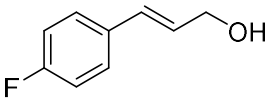
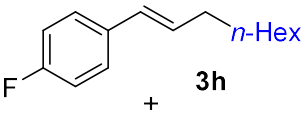
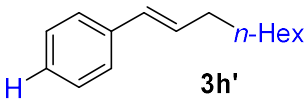
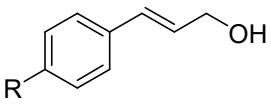
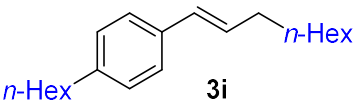
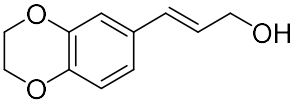
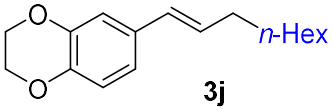
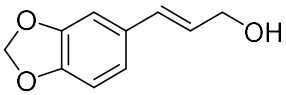
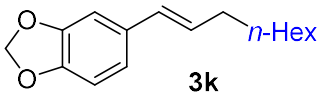
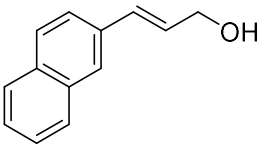
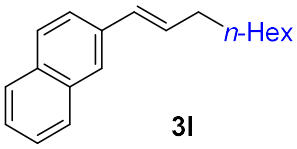
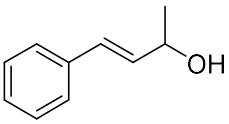
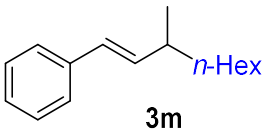
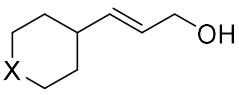
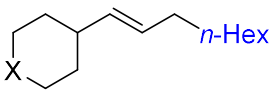
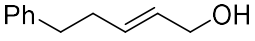
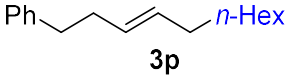
With the optimized conditions in hand, we first examined the scope of substrates of the cross-coupling reaction. Reaction of various allylic alcohols with *n*-HexMgCl was tested (Table 2). A series of 3-(substituted phenyl)prop-2-en-1-ols, $RC_6H_4CH=CHCH_2OH$ (R = *m*-OMe, *m*-CF_3, *p*-*t*-Bu, *p*-OMe, *p*-NMe_2, *p*-OCF_3 and *p*-CF_3), were demonstrated to react smoothly with *n*-HexMgCl, affording the cross-coupling products along with a small amount of reductive side products (entries 1-7). Reaction of the above subtrates with *m*-CF_3 and *p*-CF_3 groups on the phenyl rings gave relatively low product yields because of the existence of side reactions (entries 2 and 7). Reaction of the other substrates resulted in the desired products in excellent yields. The allylic alcohols with electron-poor phenyl substituents gave higher ratio of cross-coupling products (entries 2, 6 and 7). Reaction of (*E*)-3-(4-fluorophenyl)prop-2-en-1-ol with *n*-HexMgCl generated a mixture of (*E*)-1-fluoro-4-(non-1-en-1-yl)benzene (**3h**) and (*E*)-non-1-en-1-ylbenzene (**3h'**) in a ratio of 58 to 42 (entry 8). The latter was formed via catalytic reduction of the aromatic C-F bond by *n*-HexMgCl.[10] Reaction of both (*E*)-3-(4-chlorophenyl)prop-2-en-1-ol and (*E*)-3-(4-(methylthio)phenyl) prop-2-en-1-ol with *n*-HexMgCl gave (*E*)-1-hexyl-4-(non-1-en-1-yl)benzene (entries 9 and 10). This resulted from further alkylation of the aromatic C-Cl and C-SMe bonds under the current conditions.[11] Reaction of other 3-arylprop-2-en-1-ols including (*E*)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)prop-2-en-1-ol, (*E*)-3-(benzo[*d*][1,3]

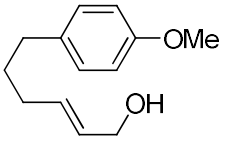
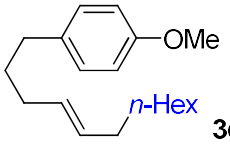
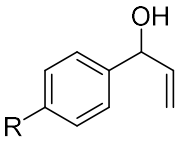
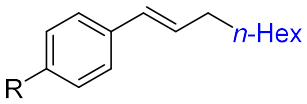
dioxol-5-yl)prop-2-en-1-ol, and (*E*)-3-(naphthalen-2-yl)prop-2-en-1-ol with *n*-HexMgCl resulted in the corresponding cross-coupling products along with a small amount of reductive products (entries 11-13). (*E*)-4-Phenylbut-3-en-2-ol exhibited lower reactivity than the (*E*)-3-arylprop-2-en-1-ols shown in entries 1-7. Its reaction with *n*-HexMgCl required higher temperature and longer time to reach completion and gave relatively low product yield (entry 14). Several (*E*)-3-alkylprop-2-en-1-ols were also tested (entries 15-18). They reacted smoothly with *n*-HexMgCl under the optimized conditions. Reaction of 1-arylprop-2-en-1-ols including 1-(4-methoxyphenyl)prop-2-en-1-ol and 1-(4-(dimethylamino)phenyl) prop-2-en-1-ol resulted in linear coupling products **3d** and **3e**, respectively. Small amount of reductive product was also observed in each case (entries 19 and 20).

Table 2. Cross-coupling of allylic alcohols with *n*-HexMgCl[a]



Entry	Allylic alcohol	Product (major)	Yield [%][b] (**3**:**4**)
1		 **3a**	97 (95:5)
2		 **3b**	79 (>99:1)
			
3		R = *t*-Bu **3c**	96 (96:4)
4		R = OMe **3d**	99 (97:3)

5		R = NMe_2 **3e**	91 (94:6)
6		R = OCF_3 **3f**	98 (>99:1)
7		R = CF_3 **3g**	79 (>99:1)
8		 **3h** +  **3h'**	99 (**3h**:**3h'** = 58:42)[c]
		 **3i**	
9	R = Cl		99 (98:2)[c]
10	R = SMe		92 (97:3)[c]
11		 **3j**	85 (95:5)
12		 **3k**	69 (95:5)[d]
13		 **3l**	99 (96:4)
14		 **3m**	53[e]
			
15		X= CH_2 **3n**	72 (α/γ = 95:5)
16		X = O **3o**	76 (α/γ = 98:2)
17		 **3p**	97 (α/γ = 86:14)

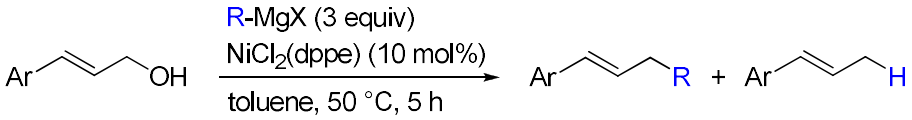
18		 **3q**	99 (α/γ = 85:15)
			
19		R = OMe **3d**	92 (95:5)
20		R = NMe_2 **3e**	94 (89:11)

[a] Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation. [b] Isolated yield. The product ratio was obtained by the ^{1}H NMR integration. [c] 3.5 equiv of *n*-HexMgCl were used. [d] 100 °C, 12 h. [e] 120 °C, 12 h.

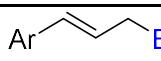
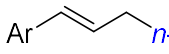
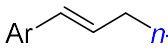
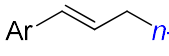
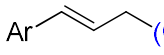
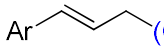
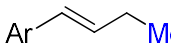
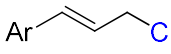
Next, various alkyl Grignard reagents were tested by reaction with **1a** (Table 3). Each of EtMgCl, *n*-PrMgBr, *n*-BuMgCl, and *n*-C_8H_{17}MgBr exhibited similar reactivity to *n*-HexMgCl. Their reaction with **1a** resulted in the desired cross-coupling products in very good yields along with a small amount of reductive species (entries 1-4). Reaction of both EtMgCl and *n*-PrMgBr gave the reductive species in a higher ratio than those of *n*-BuMgCl, *n*-C_6H_{13}MgCl and *n*-C_8H_{17}MgBr. Reaction of $Ph(CH_2)_2MgBr$ with **1a** gave a mixture of coupling product and reductive product in 74 to 26 ratio (entry 5). Relatively high ratio of reductive product is ascribed to the formation of stable styrene via β-H elimination of the alkylnickel intermediate. This is supported by reaction of $Ph(CH_2)_3MgBr$ with **1a**, which resulted in a mixture of coupling product and reductive product in 93 to 7 ratio (entry 6). Several β-H-free alkyl Grignard reagents including MeMgCl, $PhCH_2MgCl$, *t*-$BuCH_2MgBr$, and Me_3SiCH_2MgCl were also employed in the transformation (entries 7-10). Except *t*-$BuCH_2MgBr$ each of the Grignard reagents resulted in the desired cross-coupling product in excellent yield. Reaction of *t*-$BuCH_2MgBr$ with **1a** under catalysis of $NiCl_2$(dppe) gave the cross-coupling product (**3ai**) in 50% yield. However, the

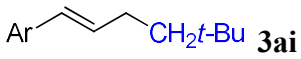
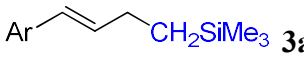
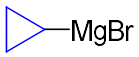
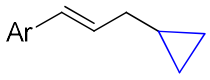
reaction under catalysis of $NiCl_2(PCy_3)$/dcype at 120 °C resulted in **3ai** in 85% yield (entry 9). Reaction of secondary alkyl Grignard reagent, cyclopropylmagnesium bromide, with **1a** required higher temperature and longer time, and gave the cross-coupling product in relatively low yield, along with a small amount of reductive species (entry 11). Other secondary alkyl Grignard reagents including cyclobutylmagnesium bromide, cyclopentylmagnesium bromide, cyclohexylmagnesium bromide, and isopropylmagnesium bromide were also examined. No cross-coupling reaction occurred under the standard conditions. When the reactions were performed at 120 °C, the reductive product **4a** was obtained in moderate yields (Scheme 1).

Table 3. Cross-coupling of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with RMgX[a]



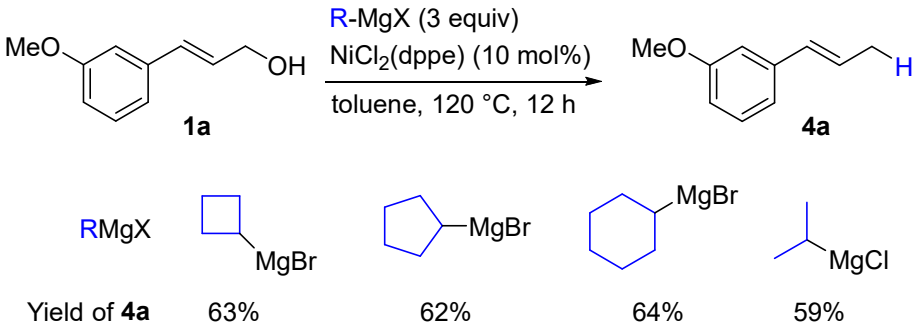
1a Ar = *m*-$MeOC_6H_4$ **3** **4a**

Entry	RMgX	Product (major)	Yield (%)[b] (**3**:**4a**)
1	EtMgCl	 **3aa**	95 (85:15)
2	*n*-PrMgBr	 **3ab**	93 (82:18)
3	*n*-BuMgCl	 **3ac**	99 (95:5)
4	*n*-C_8H_{17}MgBr	 **3ad**	99 (95:5)
5	$Ph(CH_2)_2MgBr$	 **3ae**	99 (74:26)[c]
6	$Ph(CH_2)_3MgBr$	 **3af**	99 (93:7)[d]
7	MeMgCl	 **3ag**	91[e]
8	$PhCH_2MgCl$	 **3ah**	94[e]

9	*t*-BuCH$_2$MgBr	 **3ai**	50[e] (85[f,g])
10	Me$_3$SiCH$_2$MgCl	 **3aj**	99[e]
11		 **3ak**	42 (92:8)[e]

[a] Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation. [b] Isolated yield. The product ratio was obtained by the ^{1}H NMR integration. [c] Yield of pure **3ae** was 73%. [d] Yield of pure **3af** was 92%. [e] 80 °C. [f] A combination of $NiCl_2(PCy_3)_2$ (10 mol%) and dcype (10 mol%) as catalyst. [g] 120 °C, 12 h.

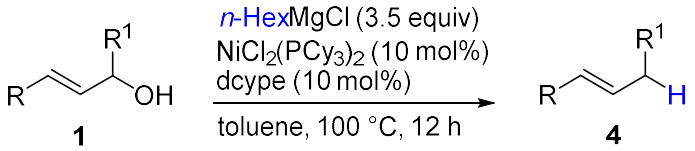
Scheme 1. Reaction of allylic alcohol **1a** with secondary alkyl Grignard reagents.



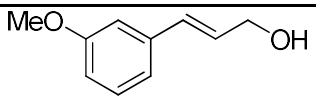
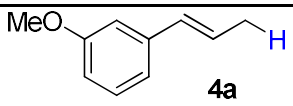
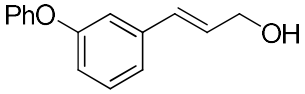
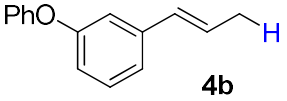
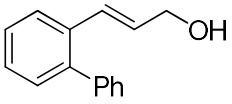
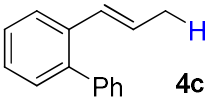
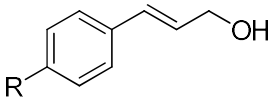
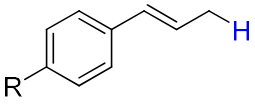
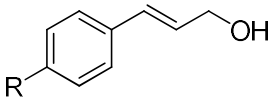
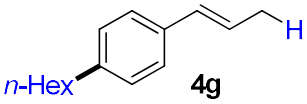
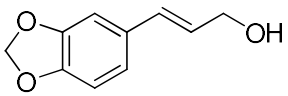
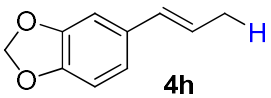
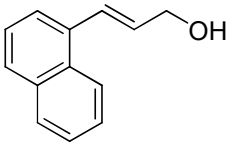
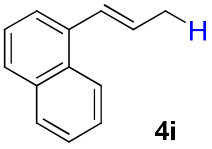
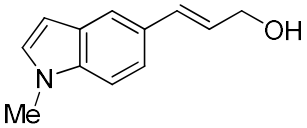
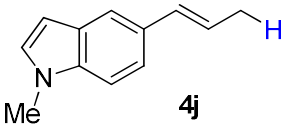
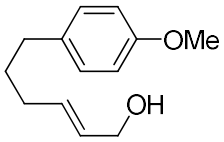
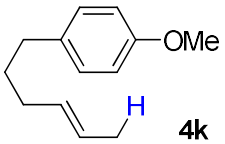
Reduction of various allylic alcohols was examined by reaction with *n*-HexMgCl under the optimized conditions (Table 4). 3-(*meta*-, *ortho*- and *para*-substituted phenyl)prop-2-en-1-ols showed good reactivity. Their reactions with *n*-HexMgCl gave the reductive products in very good yields (entries 1-6). Reaction of (*E*)-3-(3-phenoxyphenyl)prop-2-en-1-ol and (*E*)-3-(biphenyl-2-yl)prop-2-en-1-ol also gave small amount of γ-hydrogenated isomers besides the corresponding main products (entries 2 and 3). Several 3-(*para*-substituted phenyl)prop-2-en-1-ols including (*E*)-3-(4-(methylthio)phenyl)prop-2-en-1-ol, (*E*)-3-(4-fluorophenyl)prop-2-en-1-ol and (*E*)-3-(4-(trifluoromethoxy)phenyl)prop-2-en-1-ol showed different reactivity from the

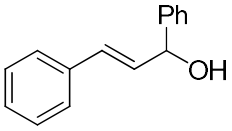
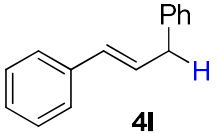
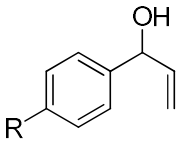
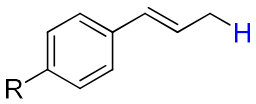
compounds mentioned above. Reaction of each of them with *n*-HexMgCl resulted in (*E*)-1-hexyl-4-(prop-1-en-1-yl)benzene, along with a small amount of 1-allyl-4-hexylbenzene. In these reactions, the SMe, F and OCF_3 groups on the aromatic rings were converted to *n*-C_6H_{13} group via nickel-catalyzed cross-coupling with *n*-HexMgCl. Meanwhile, the OH group in each molecule was catalytically reduced by *n*-HexMgCl (entries 7-9). Other aryl-substituted allylic alcohols such as (*E*)-3-(benzo[d][1,3]dioxol-5-yl)prop-2-en-1-ol, (*E*)-3-(naphthalen-1-yl)prop-2-en-1-ol and (*E*)-3-(1-methyl-1H-indol-5-yl)prop-2-en-1-ol resulted in normal reductive products when reaction with *n*-HexMgCl (entries 10-12). Reaction of (*E*)-3-(naphthalen-1-yl)prop-2-en-1-ol also formed a small amount of 1-allylnaphthalene as the side product (entry 11). Alkyl-substituted allylic alcohol, (*E*)-5-(4-methoxy phenyl)pent-2-en-1-ol, reacted with *n*-HexMgCl under the standard conditions to give a mixture of regio isomers (α/γ = 82:18) in 91% total yield (entry 13). 1,3-Disubstituted allylic alcohol, (*E*)-1,3-diphenylprop-2-en-1-ol, also reacted smoothly with *n*-HexMgCl to afford (*E*)-prop-1-ene-1,3-diyldibenzene in 64% yield (entry 14). Finally, we examined reaction of two 1-arylprop-2-en-1-ols, 1-(4-methoxyphenyl)prop-2-en-1-ol and 1-(4-(dimethylamino)phenyl)prop-2-en-1-ol. Reaction of each of them with *n*-HexMgCl gave terminal hydrogenation species in good yield (entries 15 and 16).

Table 4. Reduction of Allylic Alcohols with *n*-HexMgCl[a]



Entry	Allylic alcohol	Product	Yield (%)[b]

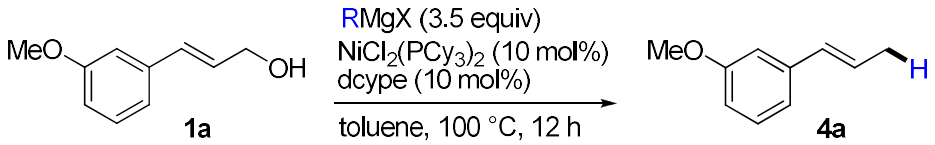
1		 **4a**	87
2		 **4b**	81 (α/γ = 94:6)[c]
3		 **4c**	89 (α/γ = 94:6)[c]
			
4	R = *t*-Bu **4d**		86
5	R = OMe **4e**		86
6	R = NMe_2 **4f**		89
		 **4g**	
7	R = SMe		44[d]
8	R = F		86[d]
9	R = OCF_3		50[d]
10		 **4h**	62
11		 **4i**	78 (α/γ = 94:6)[c]
12		 **4j**	50
13		 **4k**	91 (α/γ = 82:18)[c]

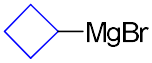
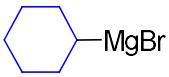
14		 **4l**	64
			
15		R = OMe **4e**	75%
16		R = NMe_2 **4f**	76%

[a] The reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation. [b] Isolated yield. [c] The isomer ratio was obtained by the ^{1}H NMR integration. [d] The products were a mixture of regio isomers (α/γ = 88:12).

We also examined the reductive reaction using other alkyl Grignard reagents under the optimized conditions (Table 5). Thus, reaction of (*E*)-3-(3-methoxyphenyl) prop-2-en-1-ol with 3.5 equiv of Grignard reagents was performed in the presence of $NiCl_2(PCy_3)_2$ (10 mol%)/dcype (10 mol%) in toluene at 100 °C for 12 h. The reductive product **4a** was obtained in 56% to 91% yields. Among the primary alkyl Grignard reagents EtMgCl led to relatively low yield of **4a**, and *n*-PrMgBr and *n*-BuMgCl led to excellent yields of **4a** (entries 1-3). Among the secondary alkyl Grignard reagents tested, *i*-PrMgCl exhibited good reactivity and led to formation of **4a** in very good yield; whereas cyclobutylmagnesium bromide, cyclopentyl magnesium bromide and cyclohexylmagnesium bromide led to the desired procucts in 72-74% yields (entries 4-7). Tertiary alkyl Grignard reagent, *t*-BuMgCl, showed very similar reactivity to *i*-PrMgCl. Its reaction under the standard conditions gave the reductive product in 83% yield (entry 8).

Table 5 Reduction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with various Grignard reagents[a]

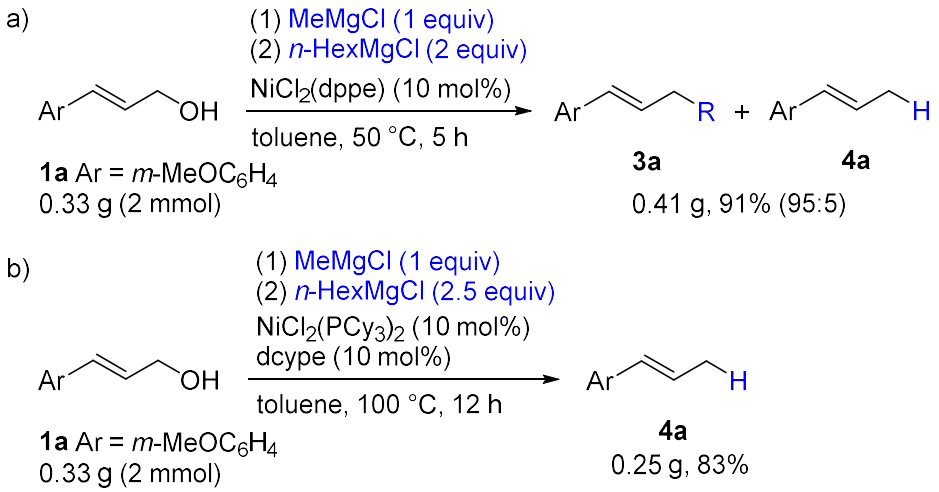


Entry	RMgX	Yield (%)[b]
1	EtMgCl	56
2	*n*-PrMgBr	91
3	*n*-BuMgCl	90
4	*i*-PrMgCl	83
5		73
6		72
7		74
8	*t*-BuMgCl	83

[a] The reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation. [b] Yields were determined by ^{1}H NMR spectra using $CHCl_2CHCl_2$ as an internal standard.

The optimized conditions for coupling and reduction also suited for a larger scale of preparation. 2 mmol of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol was treated with an equiv of MeMgCl and then coupled with *n*-HexMgCl under the standard coupling conditions to afford cross-coupling product **3** in excellent yield, along with a small amount of reductive product **4a** (Scheme 2a). Similarly, 2 mmol of (*E*)-3-(3-methoxyphenyl) prop-2-en-1-ol was treated with an equiv of MeMgCl and then *n*-HexMgCl under the standard reduction conditions to give reductive species **4a** in 83% yield (Scheme 2b). These experimental results attested to the synthetic utility of the methods.

Scheme 2. Scale-up experiments.

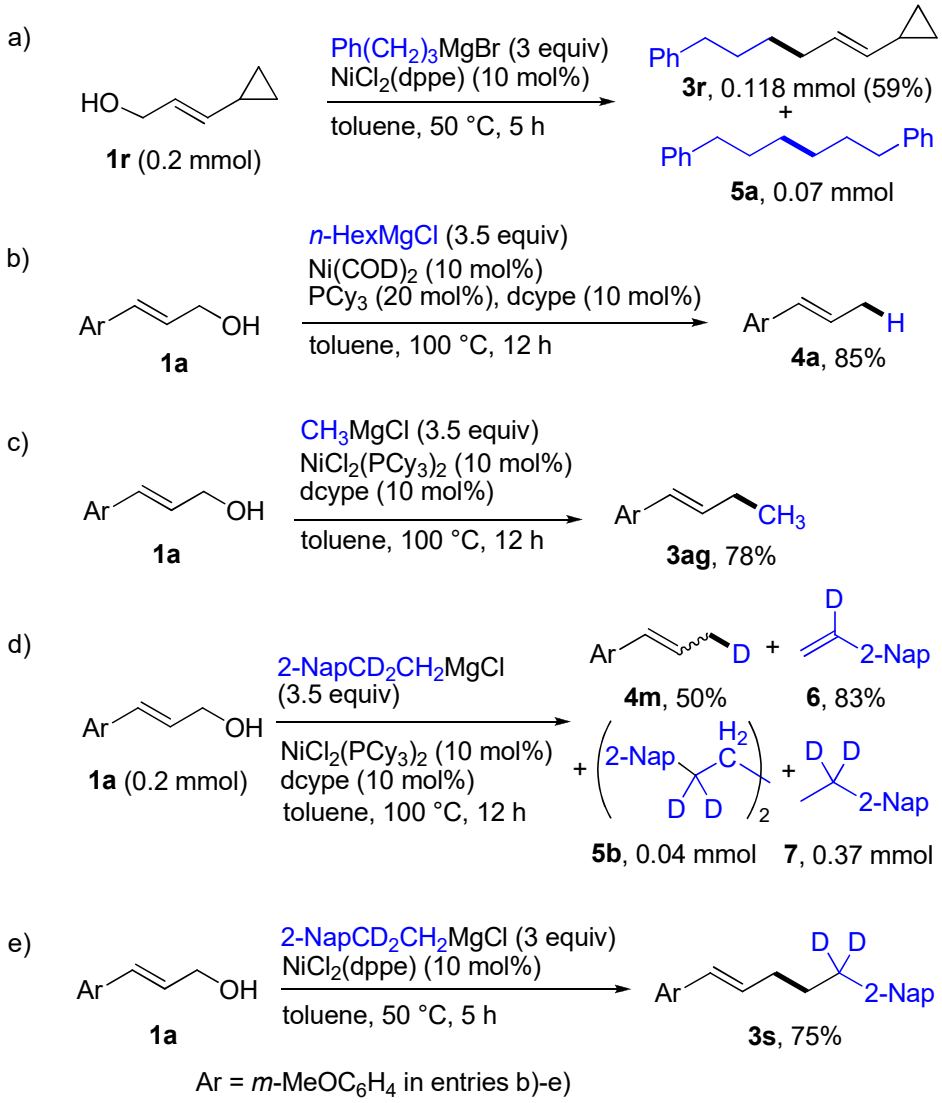


Preliminary mechanistic studies were performed. Reaction of (*E*)-3-cyclopropylprop-2-en-1-ol with 3 equiv of $Ph(CH_2)_3MgBr$ in the presence of $NiCl_2$(dppe) (10 mol%) afforded the cross-coupling product (*E*)-(6-cyclopropylhex-5-en-1-yl)benzene in 59% yield, along with homocoupling species of $Ph(CH_2)_3MgBr$. No products formed via ring-opening of cyclopropyl group were observed. This rules out the possibility of a free radical process (Scheme 3a). The homocoupling species of $Ph(CH_2)_3MgBr$ might be generated via reaction of the Grignard reagent with $NiCl_2$(dppe) which results in formation of a Ni(0) species. The catalytic activity of the combination of $Ni(COD)_2$ (10 mol%), PCy_3 (20 mol%) and dcype (10 mol%) towards the reaction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with *n*-HexMgCl is comparable to that of the combination of $NiCl_2(PCy_3)_2$ (10 mol%) and dcype (10 mol%). This implies that the reductive reaction might be through a Ni(0)/Ni(II) catalytic cycle (Scheme 3b). Under the optimized reductive conditions reaction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with MeMgCl generated a cross-coupling product (Scheme 3c). No reductive product was observed. This experimental fact shows that the reductive reaction cannot occur between a allylic alcohol and a

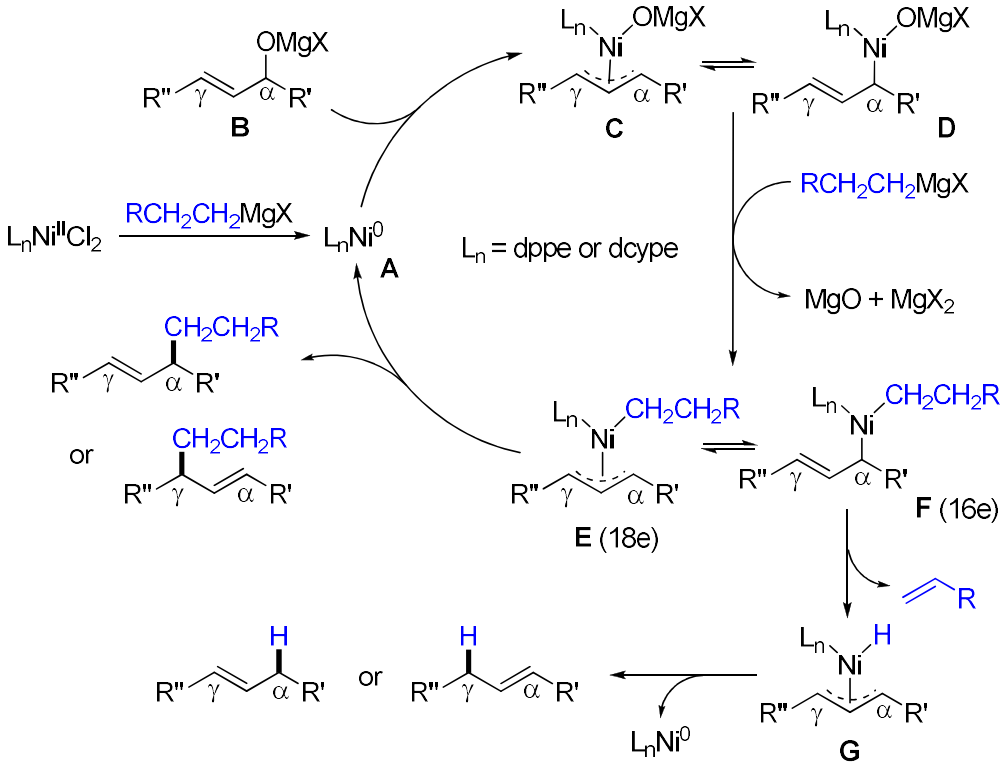
β-H-free alkyl Grignard reagent. When a β-deuterated alkyl Grignard reagent, 2-$NapCD_2CH_2MgCl$ (2-Nap = 2-naphthyl), was reacted with (*E*)-3-cyclopropylprop-2-en-1-ol under the standard reductive conditions, *m*-$MeOC_6H_4CH{=}CHCH_2D$ and 2-$NapC(D){=}CH_2$ were obtained in 50% and 83% yields, respectively (Scheme 3d). Under the coupling conditions reaction of 2-$NapCD_2CH_2MgCl$ with (*E*)-3-cyclopropylprop-2-en-1-ol afforded the cross-coupling product in 75% yield (Scheme 3e). Formation of α- and γ-isomers in the coupling reaction and reductive reaction of 3-alkyl allylic alcohols implies the existence of an η^3-allylnickel intermadiate in the catalytic process (Table 2, entries 15-18 and Table 4, entry 13). On the basis of above experimental facts, a Ni(0)/Ni(II) process might operate in the catalytic cycle. But a Ni(I)/Ni(III) mechanism cannot be ruled out. The possible mechanism via Ni(0)/Ni(II) process is proposed in Scheme 4. Thus, in the catalytic cycle a Ni(0) species **A** is first formed through reduction of Ni(II) with the Grignard reagent. Oxidative addition of the Ni(0) with allyloxomagnesium **B** produces allylnickel intermediates which involve **C** (η^3-allyl) and **D** (η^1-allyl) as an equilibrium mixture.[8a,12a-b] Subsequently, transmetalation of **C** and **D** with Grignard reagent forms allylnickel complexes **E** (η^3-allyl) and **F** (η^1-allyl) as another equilibrium mixture. If the ligand is not bulky enough (e.g. dppe), η^3-allylnickel **C** and **E** might be the major constituent in the respective equilibrium. Reductive elimination of **E** results in α- or γ-alkylated product of the allyl alcohol. When one of the R' and R" groups is an aryl group, the more stable aryl-alkenyl π-π conjugated product is preferred. If the ligand is bulky enough (e.g. dcype), η^1-allylnickel **D** and **F** might be the major constituent in the equilibriums. In addition, stronger electron-donation of ligand is better for the β-H elimination.[12c] Both steric and electronic factors promote β-H elimination of **F** which gives η^3-allylnickel hydride intermediate **G**. Reductive elimination of **G** results in α- or γ- hydrogenated product of the allyl alcohol, and

regenerates catalytically active Ni(0) species.

Scheme 3. Mechanistic studies.



Scheme 4. Proposed catalytic cycle for the cross-coupling.



Conclusion

In summary, nickel-catalyzed reaction of allylic alcohols with alkyl Grignard reagents was performed, affording alkylation or reductive products of allylic alcohols depending on ligands. $Ni(dppe)Cl_2$ catalyst resulted in the cross coupling of allylic alcohols with alkyl Grignard reagents. The combination of $Ni(PCy_3)_2Cl_2$ and dcype led to the reduction of allylic alcohols by alkyl Grignard reagents. Under the alkylation conditions primary alkyl Grignard reagents including β-H-containing and β-H-free ones as well as secondary alkyl Grignard reagent, cyclopropylmagnesium bromide, were demonstrated to be practicable nucleophiles. Secondary alkyl Grignard reagents except cyclopropylmagnesium bromide made the reaction to form reductive products of allylic alcohols in fair yields even in the presence of $Ni(dppe)Cl_2$ catalyst. Primary, secondary and tertiary alkyl Grignard reagents can be used as the reducing agents in the presence of $Ni(PCy_3)_2Cl_2$/dcype. The presence of β-H was indispensable and primary alkyl

Grignard reagents such as *n*-PrMgBr, *n*-BuMgCl and *n*-HexMgCl were superior to the secondary and tertiary alkyl Grignard reagents. A range of allylic alcohols including 3-aryl and 3-alkyl allylic alcohols, 1,3-disubstituted allylic alcohols, and 1-aryl allylic alcohols can be used in the coupling or reductive reactions. No matter coupling or reductive reaction, 3-aryl allylic alcohols and 1-aryl allylic alcohols resulted in linear products, whereas 3-alkyl allylic alcohols led to a mixture of α- and γ-alkylation/hydrogenation isomers.

Experimental section

All reactions were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. All chemicals were purchased as reagent grade and used without further purification unless otherwise noted. Toluene, tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified by JC Meyer Phoenix Solvent Systems. Butyl ether (*n*-Bu_2O) was distilled under nitrogen over sodium and degassed prior to use. MeMgCl, EtMgCl, *n*-PrMgBr, *i*-PrMgCl, *n*-BuMgCl, *t*-BuMgCl, cyclopropylmagnesium bromide, cyclohexylmagnesium bromide and benzylmagnesium chloride were purchased from commercial vendors and used as received. Octylmagnesium bromide, phenethylmagnesium bromide, (3-phenylpropyl)magnesium bromide, neopentylmagnesium bromide, ((trimethylsilyl)methyl)magnesium chloride, cyclobutylmagnesium bromide and cyclopentylmagnesium bromide were prepared according to the general procedure reported by Watson.[13a] Each of these Grignard reagents are known.[13a-f] Their concentrations were titrated using Knochel's method.[14] Allylic alcohols were prepared according to reported procedure.[15] NMR spectra were recorded on a Bruker AV400 or Bruker AV300 spectrometer at 25 °C. The chemical shifts of the ^1H NMR spectra were referenced to TMS or internal solvent resonances and the chemical shifts of the ^{13}C 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 EI mode using an Orbitrap mass analyzer.

General procedure for the catalytic coupling of allylic alcohols with alkyl Grignard reagents. Allylic alcohol (1.0 mL, 0.2 M solution in THF, 0.2 mmol) and Ni(dppe)Cl_2 (10.6 mg, 10 mol %) were charged to a Schlenk tube under nitrogen. To the mixture was added alkyl Grignard reagent (0.6 mmol, THF solution) at room temperature. The mixture was stirred for 5 min. and then solvent was removed in vacuo. Toluene (2 mL) was added and the resultant mixture was stirred at 50 °C (oil bath) for 5 h. The mixture was cooled to room temperature, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and the residue was purified by silica gel chromatography to give the desired product.

*(E)-1-methoxy-3-(non-1-en-1-yl)benzene (**3a**).* Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 44.3 mg (97%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, J = 7.9 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.88 (t, J = 1.9 Hz, 1H), 6.75 (dd, J = 8.2, 2.6 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 6.23 (dt, J = 15.7, 6.8 Hz, 1H), 3.81 (s, 3H), 2.24–2.15 (m, 2H), 1.51–1.42 (m, 2H), 1.38–1.23 (m, 8H), 0.92–0.85 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 139.6, 131.8, 129.7, 129.6, 118.7, 112.5, 111.4, 55.3, 33.2, 32.0, 29.5, 29.4, 22.8, 14.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{24}O$ 232.1822; Found 232.1822.

*(E)-1-(non-1-en-1-yl)-3-(trifluoromethyl)benzene (**3b**).* Eluent: petroleum ether. Colorless oil, 42.7 mg (79%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.49 (d, J = 7.4 Hz, 1H), 7.46–7.34 (m, 2H), 6.41 (d, J = 15.9 Hz, 1H), 6.31 (dt, J = 15.8, 6.6 Hz, 1H), 2.27–2.17 (m, 2H), 1.53–1.43 (m, 2H), 1.38–1.23 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 138.9,

133.5, 131.0 (q, J = 32.0 Hz), 129.2, 129.0, 128.6, 124.4 (q, J = 272.3 Hz), 123.4 (q, J = 3.8 Hz), 122.7 (q, J = 3.8 Hz), 33.2, 32.0, 29.4, 29.3, 22.8, 14.2. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ –62.76. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{21}F_3$ 270.1590; Found 270.1589.

*(E)-1-(tert-butyl)-4-(non-1-en-1-yl)benzene (**3c**).* Eluent: petroleum ether. Colorless oil, 48.9 mg (96%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.5, 2H), 7.27 (d, J = 8.5, 2H), 6.35 (d, J = 15.8 Hz, 1H), 6.18 (dt, J = 15.8, 6.9 Hz, 1H), 2.25–2.13 (m, 2H), 1.49–1.40 (m, 2H), 1.34–1.25 (m, 17H), 0.88 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 149.9, 135.4, 130.6, 129.5, 125.7, 125.5, 34.6, 33.2, 32.0, 31.5, 29.6, 29.4, 29.3, 22.8, 14.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_{30}$ 258.2342; Found 258.2343.

*(E)-1-methoxy-4-(non-1-en-1-yl)benzene (**3d**).*[16] Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 45.5 mg (99%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.31 (d, J = 15.8 Hz, 1H), 6.07 (dt, J = 15.8, 6.8 Hz, 1H), 3.78 (s, 3H), 2.23–2.10 (m, 2H), 1.49–1.38 (m, 2H), 1.37–1.20 (m, 8H), 0.94–0.81 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.7, 131.0, 129.2, 129.1, 127.1, 114.0, 55.4, 33.2, 32.0, 29.7, 29.4, 22.8, 14.2.

*(E)-N,N-dimethyl-4-(non-1-en-1-yl)aniline (**3e**).* Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 43.7 mg (91%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.7 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 6.28 (d, J = 15.8 Hz, 1H), 6.01 (dt, J = 15.7, 6.9 Hz, 1H), 2.92 (s, 6H), 2.21–2.12 (m, 2H), 1.49–1.38 (m, 2H), 1.36–1.22 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 149.8, 129.5, 127.2, 127.0, 126.8, 112.8, 40.8, 33.2, 32.0, 29.9, 29.4, 29.3, 22.8, 14.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{27}N$ 245.2138; Found 245.2140.

*(E)-1-(non-1-en-1-yl)-4-(trifluoromethoxy)benzene (**3f**).* Eluent: petroleum ether. Colorless oil, 56.1 mg (98%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 6.35 (d, J = 15.9 Hz, 1H), 6.20 (dt, J = 15.8, 6.8 Hz, 1H), 2.26–2.14 (m, 2H), 1.51–1.41 (m, 2H),

1.35–1.25 (m, 8H), 0.89 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 148.1 (m), 136.9, 132.6, 128.4, 127.2, 121.2, 120.7 (q, J = 256.6 Hz), 33.2, 32.0, 29.4, 29.1, 22.8, 14.3. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ –57.91. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{21}OF_3$ 286.1539; Found 286.1541.

*(E)-1-(non-1-en-1-yl)-4-(trifluoromethyl)benzene (**3g**).* Eluent: petroleum ether. Colorless oil, 42.7 mg (79%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 6.40 (d, J = 16.0 Hz, 1H), 6.33 (dt, J = 15.8, 6.3 Hz, 1H), 2.28–2.18 (m, 2H), 1.52–1.43 (m, 2H), 1.38–1.22 (m, 8H), 0.89 (t, J = 6.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 141.6 (m), 134.3, 128.71 (q, J = 32.2 Hz), 128.69, 126.1, 125.6 (q, J = 3.8 Hz), 124.5 (q, J = 271.8 Hz), 33.2, 32.0, 29.4, 29.3, 22.8, 14.3. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –62.38. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{21}F_3$ 270.1590; Found 270.1592.

*(E)-1-fluoro-4-(non-1-en-1-yl)benzene (**3h**) and (E)-non-1-enylbenzene (**3h'**).*[17] ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.25 (m, 2.73H), 7.18 (t, J = 7.2 Hz, 0.42H), 6.97 (t, J = 8.7 Hz, 1.12H), 6.42–6.29 (m, 0.99H), 6.22 (dt, J = 15.8, 6.8 Hz, 0.42H), 6.13 (dt, J = 15.8, 6.9 Hz, 0.58H), 2.24–2.14 (m, 2H), 1.51–1.40 (m, 2H), 1.36–1.23 (m, 8 H), 0.89 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) for **3h**: δ 162.0 (d, J = 245.4 Hz), 134.2 (d, J = 3.3 Hz), 131.1 (d, J = 2.2 Hz), 128.6, 127.4 (d, J = 7.8 Hz), 115.4 (d, J = 21.5 Hz), 33.3, 32.2, 29.7, 29.6, 23.0, 14.5. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) for **3h'**: δ 138.3, 131.6, 130.0, 128.8, 127.1, 126.2, 33.4, 32.2, 29.8, 29.6, 23.0, 14.5. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ –116.00. HRMS (EI-TOF) for **3h**: m/z: $[M]^+$ Calcd for $C_{15}H_{21}F$ 220.1622; Found 220.1621.

*(E)-1-hexyl-4-(non-1-en-1-yl)benzene (**3i**).* Eluent: petroleum ether. Colorless oil, 56.4 mg (99%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.34 (d, J = 15.8 Hz, 1H), 6.17 (dt, J = 15.8, 6.9 Hz, 1H), 2.56 (t, J = 7.7 Hz, 2H), 2.22–2.14 (m, 2H), 1.63–

1.54 (m, 2H), 1.50–1.40 (m, 2H), 1.36–1.24 (m, 14H), 0.92–0.84 (m, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 141.7, 135.5, 130.4, 129.7, 128.7, 125.9, 35.8, 33.2, 32.0, 31.9, 31.6, 29.6, 29.4, 29.3, 29.1, 22.83, 22.77, 14.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{21}H_{34}$ 286.2655; Found 286.2657.

(E)-6-(non-1-en-1-yl)-2,3-dihydrobenzo[b][1,4]dioxine ***(3j)***. Eluent: petroleum ether / ethyl acetate = 60:1. Colorless oil, 43.5 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 1H), 6.84 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.26 (d, *J* = 15.8 Hz, 1H), 6.07 (dt, *J* = 15.7, 6.9 Hz, 1H), 4.25 (s, 4H), 2.17 (q, *J* = 7.2 Hz, 2H), 1.50–1.40 (m, 2H), 1.38–1.23 (m, 8H), 0.90 (t, *J* = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 143.6, 142.7, 132.0, 129.8, 129.0, 119.4, 117.3, 114.5, 64.53, 64.50, 33.1, 32.0, 29.6, 29.34, 29.32, 22.8, 14.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{24}O_2$ 260.1771; Found 260.1770.

(E)-5-(non-1-en-1-yl)benzo[d][1,3]dioxole ***(3k)***. Eluent: petroleum ether/ethyl acetate = 60:1. Colorless oil, 33.4 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (s, 1H), 6.79–6.71 (m, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.05 (dt, *J* = 15.7, 6.9 Hz, 1H), 5.93 (s, 2H), 2.22–2.11 (m, 2H), 1.49–1.39 (m, 2H), 1.36–1.23 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 148.0, 146.6, 132.6, 129.7, 129.3, 120.3, 108.3, 105.5, 101.0, 33.1, 32.0, 29.6, 29.3, 22.8, 14.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{22}O_2$ 246.1614; Found 246.1614.

(E)-2-(non-1-en-1-yl)naphthalene ***(3l)***. Eluent: petroleum ether. Colorless oil, 49.3 mg (99%) (coupling product:reductive product = 96:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.70 (m, 3H), 7.65 (s, 1H), 7.56 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.45–7.35 (m, 2H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.30–2.19 (m, 2H), 1.54–1.44 (m, 2H), 1.39–1.27 (m, 8H), 0.94–0.86 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 135.6, 133.9, 132.8, 131.9, 129.9, 128.2, 127.9, 127.8, 126.2, 125.5, 125.4, 123.7, 33.4, 32.0, 29.6, 29.4, 29.38, 22.8, 14.3. HRMS (EI-TOF) m/z:

$[M]^+$ Calcd for $C_{19}H_{24}$ 252.1873; Found 252.1873.

*(E)-(3-methylnon-1-en-1-yl)benzene (**3m**)*.[18] Eluent: petroleum ether. Colorless oil, 22.9 mg (53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.32 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21–7.16 (m, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.09 (dd, *J* = 15.9, 8.0 Hz, 1H), 2.31–2.23 (m, 1H), 1.31–1.22 (m, 10H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 138.1, 137.3, 128.6, 128.0, 126.9, 126.1, 37.4, 37.3, 32.0, 29.6, 27.5, 22.8, 20.8, 14.3.

*(E)-non-1-en-1-ylcyclohexane (**3n**)*.[19] Eluent: petroleum ether. Colorless oil, 30.0 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.40–5.28 (m, 2H), 2.00–1.93 (m, 2H), 1.76–1.63 (m, 5H), 1.34–1.19 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 136.5, 127.9, 40.9, 33.5, 32.8, 32.0, 29.9, 29.4, 29.3, 26.4, 26.3, 22.8, 14.3.

*(E)-4-(non-1-en-1-yl)tetrahydro-2H-pyran (**3o**)*. Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 31.9 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.47–5.27 (m, 2H), 4.00–3.89 (m, 2H), 3.40 (dt, *J* = 11.7, 2.2 Hz, 2H), 2.22–2.07 (m, 1H), 2.02–1.94 (m, 2H), 1.63–1.54 (m, 2H), 1.50–1.39 (m, 2H), 1.36–1.22 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 134.5, 129.1, 67.9, 38.0, 33.1, 32.7, 32.0, 29.7, 29.3, 29.2, 22.8, 14.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{14}H_{26}O$ 210.1978; Found 210.1973.

*(E)-undec-3-en-1-ylbenzene (**3p**)*.[20] Eluent: petroleum ether. Colorless oil, 44.7 mg (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.24 (m, 2H), 7.21–7.13 (m, 3H), 5.50–5.37 (m, 2H), 2.70–2.62 (m, 2H), 2.35–2.25 (m, 2H), 2.02–1.92 (m, 2H), 1.32–1.22 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 142.3, 131.3, 129.4, 128.6, 128.4, 125.8, 36.3, 34.6, 32.7, 32.0, 29.7, 29.4, 29.3, 22.8, 14.3.

*(E)-1-(dodec-4-en-1-yl)-4-methoxybenzene (**3q**)*. Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 54.3 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J*

= 8.7 Hz, 2H), 5.45–5.35 (m, 2H), 3.78 (s, 3H), 2.60–2.49 (m, 2H), 2.09–1.88 (m, 4H), 1.70–1.58 (m, 2H), 1.34–1.20 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 157.8, 134.9, 131.1, 129.9, 129.4, 113.8, 55.4, 34.6, 32.8, 32.2, 32.0, 31.7, 29.8, 29.4, 29.3, 22.8, 14.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_{30}O$ 274.2291; Found 274.2294.

(E)-2-(5-(3-methoxyphenyl)pent-4-en-1-yl-1,1-d2)naphthalene ***(3s)***. Eluent: petroleum ether/ethyl acetate = 60:1. Colorless oil, 45.6 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.77 (m, 3H), 7.65 (d, *J* = 1.0 Hz, 1H), 7.50–7.40 (m, 2H), 7.36 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.93–6.87 (m, 1H), 6.81–6.74 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.27 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.82 (s, 3H), 2.35–2.25 (m, 2H), 1.90 (t, *J* = 7.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 139.9, 139.4, 133.8, 132.1, 131.0, 130.3, 129.6, 128.0, 127.7, 127.54, 127.52, 126.6, 126.0, 125.2, 118.8, 112.6, 111.4, 55.3, 32.6, 30.8. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{22}H_{20}D_2O$ 304.1791; Found 304.1793.

(E)-1-methoxy-3-(pent-1-en-1-yl)benzene ***(3aa)***.[21] Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 32.7 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.75 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.81 (s, 3H), 2.24–2.13 (m, 2H), 1.54–1.43 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 139.6, 131.5, 129.9, 129.6, 118.7, 112.5, 111.4, 55.3, 35.2, 22.7, 13.9.

(E)-1-(hex-1-en-1-yl)-3-methoxybenzene ***(3ab)***. Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 34.2 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 6.74 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.80 (s, 3H), 2.25–2.16 (m, 2H), 1.48–1.40 (m, 2H), 1.40–1.32 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 139.6, 131.7, 129.7, 129.5,

118.7, 112.5, 111.4, 55.3, 32.8, 31.6, 22.4, 14.1. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_{18}O$ 190.1352; Found 190.1351.

*(E)-1-(hept-1-en-1-yl)-3-methoxybenzene (**3ac**).* Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 39.9 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.75 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.35 (d, J = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.80 (s, 3H), 2.24–2.15 (m, 2H), 1.51–1.41 (m, 2H), 1.37–1.29 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 139.6, 131.7, 129.7, 129.5, 118.7, 112.5, 111.4, 55.3, 33.1, 31.6, 29.2, 22.7, 14.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{14}H_{20}O$ 204.1509; Found 204.1508.

*(E)-1-methoxy-3-(undec-1-en-1-yl)benzene (**3ad**).*[22] Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 50.3 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.74 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.7, 6.7 Hz, 1H), 3.80 (s, 3H), 2.26–2.14 (m, 2H), 1.51–1.40 (m, 2H), 1.36–1.20 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 139.6, 131.7, 129.7, 129.5, 118.7, 112.5, 111.4, 55.3, 33.2, 32.1, 29.74, 29.69, 29.5, 29.49, 29.4, 22.8, 14.3.

*(E)-1-methoxy-3-(5-phenylpent-1-en-1-yl)benzene (**3ae**).* Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 36.9 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.25 (m, 2H), 7.23–7.14 (m, 4H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.75 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.80 (s, 3H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.29–2.21 (m, 2H), 1.86–1.75 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.0, 142.5, 139.5, 131.0, 130.3, 129.6, 128.6, 128.5, 125.9, 118.8, 112.7, 111.5, 55.3, 35.5, 32.6, 31.1. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{20}O$ 252.1509; Found 252.1508.

*(E)-1-methoxy-3-(6-phenylhex-1-en-1-yl)benzene (**3af**).* Eluent: petroleum ether/ethyl acetate =

100:1. Colorless oil, 49.2 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.6 Hz, 2H), 7.23–7.13 (m, 4H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.75 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.6, 6.8 Hz, 1H), 3.80 (s, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.28–2.17 (m, 2H), 1.73–1.63 (m, 2H), 1.54–1.45 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.9, 142.7, 139.5, 131.3, 130.0, 129.6, 128.6, 128.4, 125.8, 118.7, 112.6, 111.4, 55.3, 36.0, 33.0, 31.2, 29.1. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_{22}O$ 266.1665; Found 266.1666.

*(E)-1-(but-1-en-1-yl)-3-methoxybenzene (**3ag**).* Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 29.6 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.88 (s, 1H), 6.74 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.1 Hz, 1H), 3.80 (s, 3H), 2.30–2.15 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.9, 139.5, 133.1, 129.5, 128.8, 118.7, 112.5, 111.3, 55.3, 26.2, 13.7. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{11}H_{14}O$ 162.1039; Found 162.1038.

*(E)-1-methoxy-3-(4-phenylbut-1-en-1-yl)benzene (**3ah**).* Eluent: petroleum ether/ethyl acetate = 60:1. Colorless oil, 44.7 mg (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.25–7.16 (m, 4H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.87 (s, 1H), 6.75 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.80 (s, 3H), 2.79 (t, *J* = 9.8 Hz, 2H), 2.59–2.46 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.9, 141.9, 139.3, 130.5, 130.4, 129.6, 128.6, 128.5, 126.0, 118.8, 112.6, 111.5, 55.3, 36.0, 35.0. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{18}O$ 238.1352; Found 238.1352.

*(E)-1-(5,5-dimethylhex-1-en-1-yl)-3-methoxybenzene (**3ai**).* Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 36.9 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.74 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.80 (s, 3H), 2.25–2.11 (m, 2H), 1.41–1.31 (m, 2H), 0.93 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 139.6, 132.4, 129.6, 129.3, 118.7, 112.5, 111.3, 55.3, 43.8, 30.5, 29.5 28.5. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_{22}O$ 218.1665; Found 218.1665.

(E)-(4-(3-methoxyphenyl)but-3-en-1-yl)trimethylsilane ***(3aj)***. Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 46.5 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.90 (s, 1H), 6.76 (dd, *J* = 7.9, 2.2 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.7, 6.0 Hz, 1H), 3.82 (s, 3H), 2.32–2.15 (m, 2H), 0.78–0.65 (m, 2H), 0.04 (s, 9H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 160.0, 139.7, 134.3, 129.5, 128.4, 118.8, 112.5, 111.5, 55.3, 27.5, 16.4, –1.4. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{14}H_{22}OSi$ 234.1434; Found 234.1432.

(E)-1-(3-cyclopropylprop-1-en-1-yl)-3-methoxybenzene ***(3ak)***. Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 15.5 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.91 (s, 1H), 6.76 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.4 Hz,1H), 3.82 (s, 3H), 2.12 (t, *J* = 6.5 Hz, 2H), 0.91–0.77 (m, 1H), 0.56–0.45 (m, 2H), 0.15 (q, *J* = 4.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 139.5, 130.6, 129.8, 129.6, 118.8, 112.6, 111.4, 55.3, 37.8, 10.5, 4.4. HR-MS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_{16}O$ 188.1196; Found 188.1195.

General procedure for the catalytic reduction of allylic alcohols with *n*-HexMgCl. Allylic alcohol (1.0 mL, 0.2 M solution in THF, 0.2 mmol), $Ni(PCy_3)Cl_2$ (13.8 mg, 10 mol %), and dcype (8.5 mg, 10 mol%) were successively charged to a Schlenk tube under nitrogen. To the mixture was added *n*-HexMgCl (0.35 mL, 2 M solution in THF, 0.7 mmol) at room temperature. The mixture was stirred for 5 min. and then solvent was removed in vacuo. Toluene (2 mL) was added and the resultant mixture was stirred at 100 °C for 12 h. The mixture was cooled to room temperature, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was

rinsed with EtOAc (20 mL). The filtrate was concentrated and the residue was purified by silica gel chromatography to give the desired product.

*(E)-1-methoxy-3-(prop-1-en-1-yl)benzene (**4a**)*.[23] Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 25.9 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.87 (t, *J* = 2.0 Hz, 1H), 6.75 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.37 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.24 (dq, *J* = 15.7, 6.5 Hz, 1H), 3.81 (s, 3H), 1.88 (dd, *J* = 6.5, 1.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.9, 139.5, 131.0, 129.6, 126.2, 118.6, 112.5, 111.3, 55.3, 18.6.

*(E)-1-phenoxy-3-(prop-1-en-1-yl)benzene (**4b**)*. Eluent: petroleum ether/ethyl acetate = 60:1. Colorless oil, 34.2 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.29 (m, 2H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.12–7.04 (m, 2H), 7.04–6.95 (m, 3H), 6.84 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.35 (dd, *J* = 15.8, 1.2 Hz, 1H), 6.21 (dq, *J* = 15.7, 6.5 Hz, 1H), 1.86 (dd, *J* = 6.5, 1.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.53, 157.45, 140.0, 130.6, 129.8, 126.8, 123.3, 121.1, 118.9, 117.4, 116.3, 18.6. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_{14}O$ 210.1039 ; Found 210.1038.

*(E)-2-(prop-1-en-1-yl)-1,1'-biphenyl (**4c**)*. Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 34.6 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.45–7.38 (m, 2H), 7.37–7.32 (m, 3H), 7.32–7.28 (m, 1H), 7.28–7.21 (m, 2H), 6.37 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.16 (dq, *J* = 15.7, 6.6 Hz, 1H), 1.79 (dd, *J* = 6.6, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) : δ 141.3, 140.2, 136.0, 130.3, 129.9, 129.9, 128.1, 127.5, 127.0, 126.8, 126.6, 125.9, 18.8. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_{14}$ 194.1090; Found 194.1088.

*(E)-1-(tert-butyl)-4-(prop-1-en-1-yl)benzene (**4d**)*.[24] Eluent: petroleum ether. Colorless oil, 30.3 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.37 (dd, *J* = 15.7, 1.3 Hz, 1H), 6.19 (dq, *J* = 15.7, 6.6 Hz, 1H), 1.86 (dd, *J* = 6.6, 1.5 Hz, 3H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.8, 135.3, 130.9, 125.7, 125.5, 125.0, 34.6,

31.5, 18.6.

*(E)-1-methoxy-4-(prop-1-en-1-yl)benzene (**4e**)*.[25] Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 25.5 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.34 (dd, *J* = 15.7, 1.1 Hz, 1H), 6.09 (dq, *J* = 15.7, 6.6 Hz, 1H), 3.79 (s, 3H), 1.85 (dd, *J* = 6.6, 1.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.7, 130.9, 130.4, 127.0, 123.6, 114.0, 55.4, 18.6.

*(E)-N,N-dimethyl-4-(prop-1-en-1-yl)aniline (**4f**)*.[23] Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 28.7 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.31 (dd, *J* = 15.7, 1.2 Hz, 1H), 6.02 (dq, *J* = 15.7, 6.6 Hz, 1H), 2.93 (s, 6H), 1.84 (dd, *J* = 6.6, 1.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.8, 130.8, 126.9, 126.8, 121.6, 112.8, 40.8, 18.6.

*(E)-1-hexyl-4-(prop-1-en-1-yl)benzene (**4g**)*. Eluent: petroleum ether. Colorless oil, 34.9 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 6.37 (dd, *J* = 15.8, 1.4 Hz, 1H), 6.18 (dq, *J* = 15.7, 6.6 Hz, 1H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.86 (dd, *J* = 6.6, 1.6 Hz, 3H), 1.64–1.53 (m, 2H), 1.37–1.24 (m, 6H), 0.91–0.82 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 141.7, 135.5, 131.0, 128.7, 125.8, 124.8, 35.8, 31.9, 31.6, 29.1, 22.8, 18.6, 14.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_{22}$ 202.1716; Found 202.1713.

*(E)-5-(prop-1-en-1-yl)benzo[d][1,3]dioxole (**4h**)*.[24] Eluent: petroleum ether/ethyl acetate = 60:1. Colorless oil, 20.3 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (s, 1H), 6.73 (s, 2H), 6.31 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.07 (dq, *J* = 15.7, 6.4 Hz, 1H), 5.93 (s, 2H), 1.85 (dd, *J* = 6.6, 1.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 148.0, 146.6, 132.6, 130.6, 124.1, 120.2, 108.3, 105.4, 101.0, 18.5.

*(E)-1-(prop-1-en-1-yl)naphthalene (**4i**)*.[26] Eluent: petroleum ether/ethyl acetate = 100:1.

Colorless oil, 26.7 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.58–7.38 (m, 4H), 7.13 (d, *J* = 15.5 Hz, 1H), 6.32–6.18 (m, 1H), 2.00 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) : δ 135.9, 133.7, 131.2, 129.1, 128.6, 128.3, 127.3, 125.9, 125.8, 125.75, 124.1, 123.6, 19.1.

*(E)-1-methyl-5-(prop-1-en-1-yl)-1H-indole (**4j**).* Eluent: petroleum ether/ethyl acetate = 60:1. Colorless oil, 17.1 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.30–7.23 (m, 2H), 7.00 (d, *J* = 3.1 Hz, 1H), 6.51 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.43 (dd, *J* = 3.1, 0.7 Hz, 1H), 6.17 (dq, *J* = 15.7, 6.6 Hz, 1H), 3.76 (s, 3H), 1.89 (dd, *J* = 6.6, 1.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 136.2, 132.1, 129.7, 129.2, 128.8, 122.7, 119.8, 118.6, 109.3, 101.2, 33.0, 18.7. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_{13}N$ 171.1043; Found 171.1041.

*(E)-1-(hex-4-en-1-yl)-4-methoxybenzene (**4k**).* Eluent: petroleum ether/ethyl acetate = 100:1. Colorless oil, 34.7 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.58–5.33 (m, 2H), 3.78 (s, 3H), 2.62–2.49 (m, 2H), 2.11–1.96 (m, 2H), 1.71–1.55 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.8, 134.9, 131.3, 129.4, 125.2, 113.8, 55.4, 34.6, 32.2, 31.7, 18.1. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_{18}O$ 190.1352; Found 190.1351.

*(E)-prop-1-ene-1,3-diyldibenzene (**4l**).*[27] Eluent: petroleum ether. Colorless oil, 24.7 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.14 (m, 10H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.40–6.30 (m, 1H), 3.54 (d, *J* = 6.5 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 140.3, 137.7, 131.3, 129.4, 128.8, 128.6, 127.2, 126.32, 126.28, 39.5.

Catalytic coupling of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with *n*-HexMgCl on a 2 mmol scale. Ni(dppe)Cl_2 (106 mg, 10 mol %), (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol (5 mL, 0.4 M in THF, 2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeMgCl (0.67 mL, 3 M solution in THF, 2 mmol, 1.0 equiv) at room temperature. After the

mixture was stirred for 10 min, *n*-HexMgCl (2 mL, 2 M in THF, 4 mmol, 2.0 equiv) was added, and the solution was stirred for an additional 5 min. After the mixture was stirred for 5 min, solvent was removed in vacuo. Toluene (15 mL) was successively added. The resultant mixture was stirred at 50 °C (oil bath) for 5 h. After cooling to room temperature, a 20% aqueous solution of NH_4Cl (20 mL) was added. The mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography on silica gel (elution with petroleum ether/ethyl acetate 100:1 (v/v)) to give (*E*)-1-methoxy-3-(non-1-en-1-yl)benzene as colorless oil (412 mg, 91%).

Catalytic reduction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with *n*-HexMgCl on a 2 mmol scale. $Ni(PCy_3)Cl_2$ (138 mg, 10 mol %), dcype (85 mg, 10 mol%), (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol (5 mL, 0.4 M in THF, 2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeMgCl (0.67 mL, 3 M solution in THF, 2 mmol, 1.0 equiv) at room temperature. After the mixture was stirred for 10 min, *n*-HexMgCl (2.5 mL, 2 M in THF, 5 mmol, 2.5 equiv) was added, and the solution was stirred for an additional 5 min. After the mixture was stirred for 5 min, solvent was removed in vacuo. Toluene (15 mL) was successively added. The resultant mixture was stirred at 100 °C (oil bath) for 12 h. After cooling to room temperature, a 20% aqueous solution of NH_4Cl (20 mL) was added. The mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography on silica gel (elution with petroleum ether/ethyl acetate 100:1 (v/v)) to give (*E*)-1-methoxy-3-(prop-1-en-1-yl)benzene as colorless oil (253 mg, 83%).

Mechanism studies

Catalytic coupling of (*E*)-3-cyclopropylprop-2-en-1-ol with (3-phenylpropyl)magnesium bromide (Scheme 3a). Ni(dppe)Cl_2 (10.6 mg, 10 mol %), (*E*)-3-cyclopropylprop-2-en-1-ol (19.6 mg, 0.2 mmol) and THF (1 mL) were charged to a Schlenk tube under nitrogen. To the mixture was added (3-phenylpropyl)magnesium bromide (0.43 mL, 1.4 M in THF, 0.6 mmol) at room temperature. The mixture was stirred for 5 min. and then solvent was removed in vacuo. Toluene (2 mL) was added into the Schlenk tube and the resultant mixture was stirred at 50 °C (oil bath) for 5 h. Then the reaction mixture was cooed to room temperature, diluted with EtOAc (5 mL), and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and then purified by silica gel chromatography (eluent: petroleum ether) to give the mixture of (*E*)-(6-cyclopropylhex-5-en-1-yl)benzene (**3r**) (59% NMR yield) and 1,6-diphenylhexane (**5a**) (0.07 mmol based on NMR integral) using $CHCl_2CHCl_2$ (16.8 mg, 0.1 mmol) as an internal standard. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.22 (m, 3.54H), 7.22–7.12 (m, 4.88H), 5.94 (s, 1.69H), 5.49 (dt, *J* = 15.2, 6.8 Hz, 0.99H), 4.95 (dd, *J* = 15.2, 8.4 Hz, 1.04H), 2.64–2.55 (m, 3.22H), 2.05–1.95 (m, 2H), 1.67–1.57 (m, 3.41H), 1.45–1.23 (m, 5.57H), 0.68–0.59 (m, 1.97H), 0.36–0.23 (m, 1.92H). HRMS for **3r** (EI-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_{20}$ 200.1560; Found 200.1559. HRMS for **5a** (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{22}$ 238.1716; Found 238.1717.

Reaction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with *n*-HexMgCl using Ni(0) catalyst (Scheme 3b). Ni(COD)$_2$ (5.5 mg, 10 mol %), PCy_3 (11.2 mg, 20 mol%), dcype (8.5 mg, 10 mol%) and THF (1 mL) were charged to a Schlenk tube under nitrogen. The mixture was stirred for 5 min and then (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol (1 mL, 0.2 M in THF, 0.2 mmol) and *n*-HexMgCl (0.35 mL, 2 M in THF, 0.7 mmol, 3.5 equiv) were successively added. The mixture was stirred for 5 min and then solvent was removed in vacuo. Toluene (2 mL) was added to the

Schlenk tube and the resultant mixture was stirred at 100 °C (oil bath) for 12 h. The reaction mixture was cooled to room temperature, diluted with EtOAc (5 mL), and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and then purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 100:1) to give (*E*)-1-methoxy-3-(prop-1-en-1-yl)benzene (**4a**) as a colorless oil (25.3 mg, 85% yield).

Reaction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with CH_3MgCl in the presence of $NiCl_2(PCy_3)_2$ and dcype (Scheme 3c). $Ni(PCy_3)Cl_2$ (13.8 mg, 10 mol %), dcype (8.5 mg, 10 mol%) and (*E*)-3-(3-methoxy- phenyl)prop-2-en-1-ol (1 mL, 0.2 M in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the mixture was added MeMgCl (0.23 mL, 3 M in THF, 0.7 mmol) at room temperature. The mixture was stirred for 5 min and then solvent was removed in vacuo. Toluene (2 mL) was added and the resultant mixture was stirred at 100 °C (oil bath) for 12 h. Then the reaction mixture was cooled to room temperature, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and then purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 100:1) to give (*E*)-1-(but-1-en-1-yl)-3-methoxybenzene (**2h**) as a colorless oil (25.4 mg, 78% yield).

Catalytic reaction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with (2-(naphthalen-2-yl)ethyl-2,2-d_2) magnesium chloride (Scheme 3d).

(a) Preparation of (2-(naphthalen-2-yl)ethyl-2,2-d_2)magnesium chloride. In a Schlenk tube were placed 2-(naphthalen-2-yl)acetic acid (2.79 g, 15 mmol), NaOD (1.42 mL, 21 mmol, 40% wt in D_2O) and D_2O (5 mL). The mixture was heated at 100 °C (oil bath) for 24 h with stirring. After cooling to room temperature, the reaction mixture was acidified with 4 N hydrochloric acid. The solution was extracted with CH_2Cl_2 and the organic phases were dried with Na_2SO_4. The

solution was concentrated by rotary evaporation to give 2-(naphthalen-2-yl) acetic-2,2-d_2 acid as a white solid (2.56 g, 91% yield).

To a stirred suspension of $LiAlH_4$ (0.62 g, 16.3 mmol) in THF (20 mL) was added dropwise a solution of 2-(naphthalen-2-yl)acetic-2,2-d_2 acid (2.56 g, 13.6 mmol) in THF (15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. Then the mixture was acidified with 0.5 N hydrochloric acid, filtered and rinsed by EtOAc. The organic layer was successively washed with H_2O and brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (elution with petroleum ether/ethyl acetate 5:1 (v/v)) to give 2-(naphthalen-2-yl)ethan-2,2-d_2-1-ol as a white solid (1.92 g, 81% yield).

2,4,6-Trichloro-[1,3,5]-triazine (2.13 g, 11.6 mmol) was added to DMF (2.3 mL). After the formation of white solid, the reaction was monitored (TLC) until complete disappearance of 2,4,6-Trichloro-[1,3,5]-triazine. CH_2Cl_2 (25 mL) was added, followed by 2-(naphthalen-2-yl)ethan-2,2-d_2-1-ol (1.92 g, 11 mmol). The resultant mixture was stirred at room temperature until reaction completion (4 h, monitored by TLC). Water (20 mL) was added and then the organic phase was separated and washed with 15 mL of a saturated solution of Na_2CO_3, followed by 1 N hydrochloric acid and brine. The organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (elution with petroleum ether) to give 2-(2-chloroethyl-1,1-d_2)naphthalene as white solid (1.14 g, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.76 (m, 3H), 7.67 (s, 1H), 7.51–7.41 (m, 2H), 7.33 (dd, J = 8.4, 1.7 Hz, 1H), 3.78 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 135.6, 133.6, 132.5, 128.4, 127.8, 127.7, 127.6, 127.1, 126.3, 125.8, 44.9. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_9D_2Cl$ 192.0669; Found 192.0667.

Magnesium turnings (0.15 g, 6.25 mmol), 2-(2-chloroethyl-1,1-d_2)naphthalene (0.96 g, 5 mmol) and THF (5 mL) were added to a Schlenk tube under nitrogen. The mixture was stirred at 65 °C (oil bath) for 5 h. After cooling to room temperature, the reaction mixture was titrated according to the literature procedure to give a 0.63 M solution of (2-(naphthalen-2-yl)ethyl-2,2-d_2)magnesium chloride.

(b) Catalytic reduction of (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol with (2-(naphthalen-2-yl)ethyl-2,2-*d*$_2$)magnesium chloride. $Ni(PCy_3)Cl_2$ (13.8 mg, 10 mol %), dcype (8.5 mg, 10 mol%) and (*E*)-3-(3-methoxyphenyl)prop-2-en-1-ol (1 mL, 0.2 M in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the mixture was added (2-(naphthalen-2-yl)ethyl-2,2-d_2)magnesium chloride (1.1 mL, 0.63 M in THF, 0.7 mmol) at room temperature. The mixture was stirred for 5 min and then solvent was removed in vacuo. Toluene (2 mL) was added. The resultant mixture was stirred at 100 °C (oil bath) for 12 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and the residue was purified by silica gel chromatography (eluent: petroleum ether) to give the mixture of 2-(ethyl-1,1-d_2)naphthalene (0.37 mmol based on NMR integral) and 2-(vinyl-1-*d*)naphthalene (83% NMR yield using CH_2Br_2 (17.4 mg, 0.1 mmol) as an internal standard), and the mixture of 1-methoxy-3-(prop-1-en-1-yl-3-*d*)benzene (50% NMR yield) and 1,4-di(naphthalen-2-yl)butane-1,1,4,4-d_4 (0.04 mmol based on NMR integral using CH_2Br_2 (17.4 mg, 0.1 mmol) as an internal standard).

Catalytic coupling of (*E*)-3-(3-methoxy-phenyl)prop-2-e-n-1-ol with (2-(naphthalen-2-yl)ethyl-2,2-*d*$_2$)magnesium chloride (Scheme 3e). $Ni(dppe)Cl_2$ (10.6 mg, 10 mol %), (*E*)-3-(3-methoxyphenyl)prop-2-e-n-1-ol (1 mL, 0.2 M in THF, 0.2 mmol) were charged to a Schlenk tube

under nitrogen. To the mixture was added (2-(naphthalen-2-yl)ethyl-2,2-d_2) magnesium chloride (1.0 mL, 0.63 M in THF, 0.6 mmol) at room temperature. The mixture was stirred for 5 min and then solvent was removed in vacuo. Toluene (2 mL) was added and the resultant mixture was stirred at 50 °C (oil bath) for 5 h. The reaction mixture was cooled to room temperature, diluted with EtOAc (5 mL) and filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and then purified by silica gel chromatography (eluent: petroleum ether / ethyl acetate = 60:1) to give (*E*)-2-(5-(3-methoxyphenyl)pent-4-en-1-yl-1,1-d_2)naphthalene (**3s**) as a colorless oil, 45.6 mg (75% yield).

ASSOCIATED CONTENT

Supporting Information

Optimization details of reaction conditions and copies of NMR spectra of the reaction products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org website at DOI:

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Notes

The authors declare no competing financial interest.

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