A novel palladium-catalyzed hydroalkoxylation of alkenes with a migration of double bond†

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A novel palladium-catalyzed addition of alcohols to olefins was developed, in which a migration of double bond was involved. By this new method, a variety of allylic ethers were prepared with moderate to high yields under mild conditions.

Introduction

Carbon–oxygen bond structures are widely present in natural products and medicinally important compounds. The formation of carbon–oxygen bonds, therefore, has stimulated considerable interest in developing new methods and become one of the great aspects of organic synthesis. In the past few years, continuous efforts have been made in this field with various methods developed and strengthened. Ethers and esters with carbon–oxygen bonds are usually prepared under mild conditions *via* the addition of hydroxy groups of alcohols or carboxylic acids to olefins (hydroalkoxylation) catalyzed by Brønsted acids,[1] main group metals[2] or transitional metals such as platinum,[3] copper,[4] silver,[5] gold,[6] palladium[7] and lanthanides.[8] It is obvious that this method provides the potential of both regio- and enantiocontrol. In particular, palladium catalysts, due to their extraordinary catalytic activities and outstanding ability to tolerate a wide variety of functional groups, have received much attention.[9] In most cases, hydroalkoxylation of olefins catalyzed by palladium catalysts involves a process in which the cationic palladium first activates the unsaturated carbon–carbon bonds by coordination and then the desired compounds are formed by the subsequent nucleophilic addition of the O–H groups and protonation of the Pd–carbon bond.[2]

Results and discussion

In this communication, we disclose a novel approach toward the palladium-catalyzed combination of alcohols and homoallylic alcohols under mild conditions to afford a series of allylic ethers efficiently (Fig. 1). It was noted that a process in which rearrangement of the homoallylic alcohol occurs provides a delocalized allyl cation structure[10] and that subsequently a nucleophilic alcohol attacks this cation, forming a carbon–oxygen bond. Compared with the past research on palladium-catalyzed allylation with free allylic alcohols,[11] the π-allyl–palladium intermediate was formed twice in our research. Also, this reaction broadens the scope of Li *et al*.'s work on the isomerization of double bonds that occurs with ruthenium catalysts in water.[12]

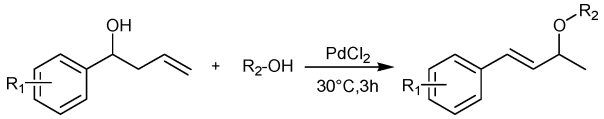

Fig. 1 Palladium-catalyzed addition of alcohols to olefins.

In our initial studies, many catalysts as well as ligands were investigated, as summarized in Table 1. The reaction conditions were optimized and the best conditions found were to use 10 mol% of $PdCl_2$ only, as shown in entry 1 of Table 1. By virtue of these optimized conditions, the reaction afforded **2a** with an isolated yield of 84%. The reactions under other palladium catalysts such as $Pd(OAc)_2$, $PdCl_2(CH_3CN)_2$ and $PdCl_2(PhCN)_2$ could also generate the desired products with fairly good yields (Table 1, entries 2–4). Subsequently, we attempted to improve the reaction by employing different ligands. Thus, aliphatic ligands, aryl amine ligands, pyridine-containing ligands and phosphorous ligands were examined. However, all of them had negative influences on this reaction to different degrees (Table 1, entries 5–11). Having gained some crucial insights of the effect of different catalysts, further optimization was performed on exploring the effects of the solvent as well as the additives (Table 2). It was obvious that methanol is the best solvent while other additives all disfavor this reaction to different degrees. Therefore, the best reaction conditions found are that the substrate **1a** is treated with catalytic $PdCl_2$ (10 mol%) in alcohols.

Subsequently, the optimized system was applied to the addition of various alcohols to **1a** and the results were listed in Table 3. It was found that the primary alcohols provided the desired products with moderate to good yields (Table 3, entries 1–3, 5 and 7) while the secondary alcohol gave the product with slightly lower yield, perhaps due to the steric effect (Table 3, entry 4). Nevertheless, the influence of steric hindrance on the reaction was limited. Even for *tert*-butyl alcohol, which has great steric hindrance, the desired products could be obtained with moderate yields (Table 3, entry 6). Moreover, we have expanded our investigation to acetic acid as the nucleophile and the additional product **2i** could also be obtained (Table 3, entry 9).

To further evaluate the scope of this reaction, a range of homoallylic alcohol derivatives was subjected to the optimized reaction conditions (Table 4). In general, substitution (MeO, Br or Cl) at the *ortho*-position of the phenyl ring provided the corresponding adducts with higher yields than substitution at the *para*-position (Table 4, entries 1–3 and 5–7) regardless whether the substituent was electron-withdrawing or electron-donating.

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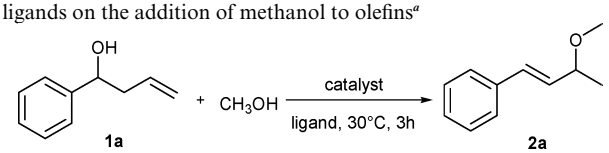
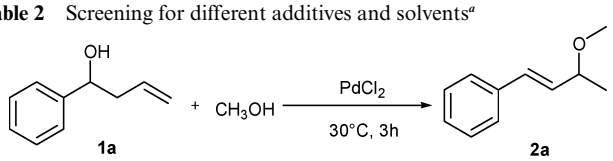
Table 1 Effect of different catalysts and ligands on the addition of methanol to olefins[a]



Entry	Catalyst	Ligand	Isolated yield (%)
1	$PdCl_2$	—	84
2	$Pd(OAc)_2$	—	75
3	$PdCl_2(CH_3CN)_2$	—	80
4	$PdCl_2(PhCN)_2$	—	82
5	$PdCl_2$	Pyridine	Trace
6	$PdCl_2$	2,2′-Bipyridine	Trace
7	$PdCl_2$	1,10-Phenanthroline	Trace
8	$PdCl_2$	Benzene-1,2-diamine	70
9	$PdCl_2$	N^1,N^1,N^2,N^2-Tetramethylethane-1,2-diamine	36
10	$PdCl_2$	1,4-Diaza-bicyclo[2.2.2]octane	83
11	$PdCl_2$	$P(Ph)_3$	65

[a] Reaction conditions: 1 mmol of **1a** in 5 mL of methanol with 10 mol% catalyst and 10 mol% ligand.

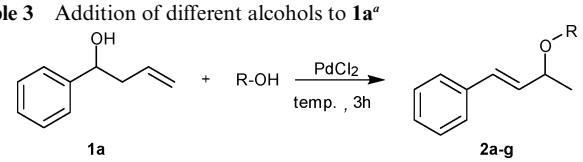
Table 2 Screening for different additives and solvents[a]



Entry	Catalyst	Additive	Solvent	Isolated yield (%)
1	$PdCl_2$	—	DMF	30
2	$PdCl_2$	—	Toluene	72
3	$PdCl_2$	—	Hexane	70
4	$PdCl_2$	—	Acetone	25
5	$PdCl_2$	K_2CO_3	Methanol	62
6	$PdCl_2$	HCl	Methanol	66
7	$PdCl_2$	CH_3COOH	Methanol	63
8	$PdCl_2$	Et_3N	Methanol	50

[a] 1 mmol of **1a** in 1 mL of methanol, in the presence of corresponding additive (1 mmol) and solvent (5 mL) with 0.1 mmol $PdCl_2$.

Table 3 Addition of different alcohols to **1a**[a]

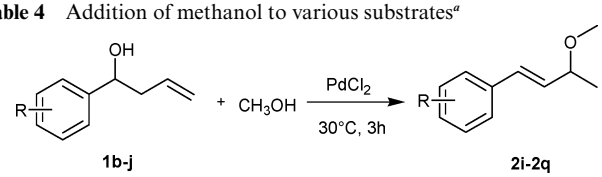


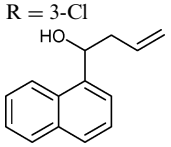
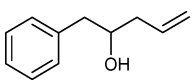
Entry	R-OH	Product	Isolated yield (%)
1	Methanol	**2a**	84
2	Ethanol	**2b**	77
3	1-Propanol	**2c**	78
4	2-Propanol	**2d**	72
5	1-Butanol	**2e**	73
6	*tert*-Butyl alcohol	**2f**	53
7	Benzyl alcohol	**2g**	52
8	Glycol	**2h**	72
9	Acetic acid	**2i**	57

[a] Reaction conditions: 0.2 M of **1a** in alcohol or carboxylic acid with 10 mol% catalyst. Reaction temperature for entries 6 and 7 was 50 °C while for others it was about 30 °C.

On the other hand, *meta*-substitution had little influence on the reaction. For instance, **1i** gave the corresponding adduct **2q** with a yield of 57% (entry 8). Even when the phenyl ring was replaced by a naphthyl ring, the desired product **2r** could also be obtained with a good yield (Table 4, entry 9). More importantly, homoallylic alcohol **1k** with an aliphatic substituent was also reactive. The reaction led to the desired product **2s** with a yield of 74% (Table 4, entry 10).

Table 4 Addition of methanol to various substrates[a]



Entry	Substrate	Product		Isolated yield (%)
1	R = 4-Cl	**1b**	**2J**	60
2	R = 4-Br	**1c**	**2l**	78
3	R = 4-MeO	**1d**	**2k**	70
4	R = 4-Me	**1e**	**2m**	74
5	R = 2-Cl	**1f**	**2n**	64
6	R = 2-Br	**1g**	**2o**	86
7	R = 4-MeO	**1h**	**2p**	80
8	R = 3-Cl	**1i**	**2q**	57
9		**1j**	**2r**	81
10		**1k**	**2s**	74

[a] Reaction conditions: 0.2 M of **1b–1k** in methanol with 10 mol% catalyst.

Afterwards, a tentative mechanism for this novel palladium-catalyzed reaction was proposed on the basis of our experimental results, as outlined in Fig. 2. Initially, the coordination of palladium(II) to **1a** activates the alkene toward the subsequent migration of hydride from the C2 position to the C4 position at the terminal of the chain. Then the structure of π-allyl–palladium[10] is built up through the departure of the hydroxyl group and the

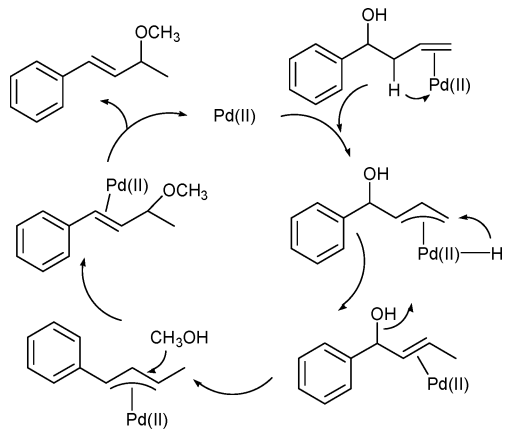


Fig. 2 Proposed mechanism for the addition of methanol to **1a** to form (*E*)-(3-methoxybut-1-enyl)benzene.

following methanol attack on this allyl–palladium complex forms the carbon–oxygen bond, finally giving the stable product. To support this mechanism, additional experiments were designed and performed (Fig. 3). When methanol was replaced with d_4-methanol, only d_3-**2a** was obtained, which indicated that C4 of d_3-**2a** did not catch the proton from the hydroxy group in methanol (Fig. 3, reaction 1). With this result in hand, **1l** was also synthesized (an intermediate mentioned in Li *et al*.'s mechanism[12]) to be reacted with methanol under the above-mentioned reaction conditions, and **2a** could be obtained quantitatively as well (Fig. 3, reaction 3). In addition, the result that (*E*)-buta-1,3-dienylbenzene (**1m**) could not be converted to **2a** under the same reaction conditions also offered evidence to support the proposed mechanism (Fig. 3, reaction 2). This palladium-catalyzed mechanism is similar to the mechanism proposed by Li *et al*., where the reaction was performed in water and catalyzed by a ruthenium complex.[12]

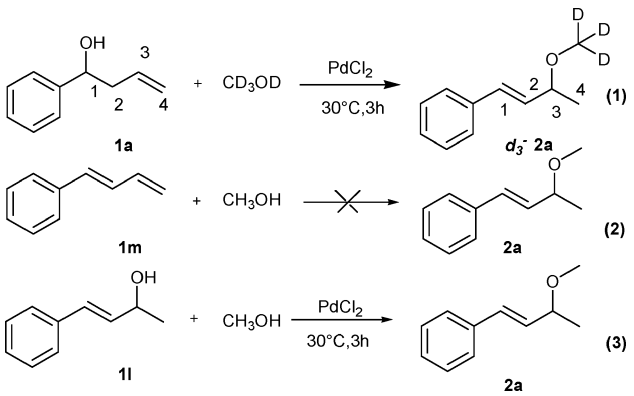


Fig. 3 Supporting experiments to investigate the mechanism.

Conclusions

We have developed a novel palladium-catalyzed hydroalkoxylation of homoallylic alcohols with a double bond migration. More importantly, in this reaction a π-allyl–palladium complex was involved and a process of isomerization of homoallyic alcohols catalyzed by Pd(II) was determined. To the best of our knowledge, it represents the first example of the palladium-catalyzed addition of alcohols to olefins involving isomerization of homoallylic alcohols and migration of the double bond. Further investigation of the scope and mechanism of this reaction is ongoing in our laboratory.

Experimental

IR (Perkin-Elmer, 2000FTIR), ^{1}H NMR (CD_3Cl, 400 or 300 MHz), ^{13}C NMR ($CDCl_3$, 100 or 75 MHz) and MS-GC (HP 5890(II)/HP5972, EI. Analytical thin-layer chromatography (TLC) plates were commercially available. Solvents were reagent grade unless otherwise noted. All starting materials and reagents are commercially available and were used as received.

Typical procedure of the addition of alcohols to olefins

To a solution of **1a** (1 mmol) in 3 mL of MeOH, $PdCl_2$ (0.1 mmol) was added. Thereafter the mixture was heated at 30 °C under air for 3 h, the methanol was evaporated under reduced pressure, and the residual mixture was then purified by column chromatography over silica gel to afford product **2a** with high purity.

General procedure for allylation of carbonyl compounds in aqueous medium[13]

To a mixture of the carbonyl compound (1 mmol) in 2 mL of THF and 4 mL of saturated NH_4Cl solution was added zinc powder (0.130 g, 2 mmol) and allyl bromide (0.242 g, 2 mmol) at room temperature. After the mixture was stirred for 0.5 h it was extracted with ethyl acetate for three times. The combined organic extracts were dried using anhydrous Na_2SO_4 and evaporated under reduced pressure; the mixture was then purified by column chromatography over silica gel to afford products **1a**–**1k** with high purity.

(*E*)-(3-Methoxybut-1-enyl)benzene (2a)[14]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.41–7.22 (m, 5H), 6.54 (d, J = 15.9 Hz, 1H), 6.09 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 3.92–3.87 (m, 1H), 3.32 (s, 3H), 1.33 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 136.8, 131.6, 131.5, 128.7, 127.8, 126.6, 78.3, 56.2, 21.6. IR (liquid film, cm^{-1}): ν = 3027, 2975, 2927, 2820, 1686, 1494, 1450, 1369, 1199, 1139, 1111, 1084, 1042, 968, 748, 693. HRMS calc. $C_{11}H_{14}O$: 162.1045. Found: 162.1040.

(d_3-(*E*)-(3-Methoxybut-1-enyl)benzene (d_3-2a). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.41–7.21 (m, 5H), 6.53 (d, J = 15.9 Hz, 1H), 6.09 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.05–3.96 (m, 1H), 1.33 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 136.8, 131.6, 131.4, 128.7, 127.7, 126.6, 78.1, 21.6. IR (liquid film, cm^{-1}): ν = 3027, 2965, 2928, 2854, 2234, 2192, 2057, 1598, 1494, 1448, 1368, 1150, 1121, 1092, 1021, 968, 747, 693. HRMS calc. $C_{11}H_{11}D_3O$: 165.1233. Found: 165.1231.

(*E*)-(3-Ethoxybut-1-enyl)benzene (2b). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.38–7.21 (m, 5H), 6.51 (d, J = 15.9 Hz, 1H), 6.12 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.05–3.96 (m, 1H), 3.62–3.52 (m, 1H), 3.47–3.37 (m, 1H), 1.33 (d, J = 6.3 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 136.9, 132.3, 130.9, 128.7, 127.7, 126.6, 76.4, 63.7, 21.9, 15.6. IR (liquid film, cm^{-1}): ν = 3027, 2975, 2929, 2869, 1598, 1493, 1447, 1369, 1317, 1092, 967, 748, 693. HRMS calc. $C_{12}H_{16}O$: 176.1201. Found: 176.1223.

(*E*)-(3-Propoxybut-1-enyl)benzene (2c)[15]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.41–7.23 (m, 5H), 6.51 (d, J = 15.9 Hz, 1H), 6.12 (dd, J = 15.9 Hz, 7.2 Hz, 1H), 4.01–3.97 (m, 1H), 3.48–3.42 (m, 1H), 3.35–3.30 (m, 1H), 1.64–1.56 (m, 2H), 1.32 (d, J = 6.0 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 137.0, 132.4, 130.8, 128.7, 127.7, 126.6, 76.5, 23.3, 21.8, 10.8. IR (liquid film, cm^{-1}): ν = 3060, 2969, 2931, 2874, 1598, 1494, 1451, 1369, 1318, 1090, 967, 748, 693. HRMS calc. $C_{13}H_{18}O$: 190.1358. Found: 190.1339.

(*E*)-(3-Isopropoxybut-1-enyl)benzene (2d)[15]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.40–7.20 (m, 5H), 6.50 (d, J = 16.2 Hz, 1H), 6.07 (dd, J = 15.9 Hz, 7.2 Hz, 1H), 4.16–4.10 (m, 1H), 3.75–3.67 (m, 1H), 1.31 (d, J = 6.3 Hz, 3H), 1.16 (d, J = 6.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 137.0, 133.0, 130.3, 128.7, 127.6, 126.6, 73.6, 68.6, 23.5, 22.3, 21.9. IR (liquid film, cm^{-1}): ν = 3056, 2921, 1644, 1459, 1374, 1258, 1102, 800. HRMS calc. $C_{13}H_{18}O$: 190.1358. Found: 190.1366.

(*E*)-(3-Butoxybut-1-enyl)benzene (2e). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.40–7.23 (m, 5H), 6.51 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.00–3.96 (m, 1H), 3.54–3.46 (m, 1H), 3.39–3.31 (m, 1H), 1.59–1.52 (m, 2H), 1.41–1.31 (m, 5H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 137.0, 132.5, 130.8, 128.7, 127.7, 126.6, 68.6, 32.2, 21.8, 19.6, 14.1. IR (liquid film, cm^{-1}): ν = 3026, 2957, 2871, 1459, 1369, 1243, 1090, 973, 747, 692. HRMS calc. $C_{14}H_{20}O$: 204.1514. Found: 204.1512.

(*E*)-(3-*tert*-Butoxybut-1-enyl)benzene (2f)[14]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.37–7.20 (m, 5H), 6.48 (d, J = 15.9 Hz, 1H), 6.23 (dd, J = 15.9 Hz, 6.0 Hz, 1H), 4.31–4.27 (m, 1H), 1.27 (d, J = 6.3 Hz, 3H), 1.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 137.5, 135.2, 128.6, 128.1, 127.3, 126.4, 74.1, 68.4, 28.7, 23.9. IR (liquid film, cm^{-1}): ν = 3027, 2975, 2929, 2868, 1688, 1598, 1494, 1449, 1369, 1316, 1153, 1092, 967, 748, 693. HRMS calc. $C_{14}H_{20}O$: 204.1514. Found: 204.1516.

(*E*)-[3-(Benzyloxy)but-1-enyl]benzene (2g)[16]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.41–7.22 (m, 10H), 6.54 (d, J = 15.9 Hz, 1H), 6.17 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.15–4.06 (m, 1H), 1.38 (d, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 138.9, 136.8, 131.9, 131.5, 128.7, 128.5, 127.8, 127.6, 126.6, 76.0, 70.2, 21.9. IR (liquid film, cm^{-1}): ν = 3029, 2972, 2925, 2855, 1599, 1494, 1452, 1369, 1145, 1072, 968, 746, 694. HRMS calc. $C_{17}H_{18}O$: 238.1358. Found: 238.1349.

(*E*)-2-(4-Phenylbut-3-en-2-yloxy)ethanol (2h). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.40–7.22 (m, 5H), 6.54 (d, J = 15.9 Hz, 1H), 6.11 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.10–4.01 (m, 1H), 3.74 (t, J = 7.5 Hz, 2H), 3.67–3.61 (m, 1H), 3.52–3.45 (m, 1H), 2.05 (br, 1H), 1.36 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 136.6, 131.5, 128.7, 127.8, 126.6, 77.2, 69.5, 62.1, 21.7. IR (liquid film, cm^{-1}): ν = 3433, 3027, 2974, 2929, 2866, 1494, 1450, 1371, 1147, 1106, 1061, 968, 750, 694. HRMS calc. $C_{13}H_{18}O_2$: 206.1307. Found: 206.1303.

(*E*)-4-Phenylbut-3-en-2-yl acetate (2i)[17]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.37–7.22 (m, 5H), 6.60 (d, J = 15.9 Hz, 1H), 6.19 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 5.58–5.48 (m, 1H), 2.07 (s, 1H), 1.41 (d, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 170.4, 136.5, 131.6, 128.9, 128.7, 128.0, 126.7, 71.1, 21.5, 20.5. IR (liquid film, cm^{-1}): ν = 3028, 2981, 2932, 1736, 1494, 1448, 1371, 1241, 1149, 1042, 966, 749, 693. HRMS calc. $C_{12}H_{14}O_2$: 190.0994. Found: 190.1003.

(*E*)-1-Chloro-4-(3-methoxybut-1-enyl)benzene (2j). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.33–7.26 (m, 4H), 6.49 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 3.90–3.87 (m, 1H), 3.32 (s, 3H), 1.32 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 135.3, 133.3, 132.3, 130.1, 128.8, 127.7, 78.0, 56.2, 21.4. IR (liquid film, cm^{-1}): ν = 3029, 2977, 2928, 1593, 1491, 1370, 1352, 1199, 1110, 1090, 969, 854, 809. HRMS calc. $C_{11}H_{13}ClO$: 196.0655. Found: 196.0646.

(*E*)-1-Bromo-4-(3-methoxybut-1-enyl)benzene (2k). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.45–7.43 (m, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 15.9 Hz, 1H), 6.09 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 3.91–3.86 (m, 1H), 3.32 (s, 3H), 1.32 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 135.7, 132.5, 131.8, 130.1, 128.1 121.5, 78.0, 56.3, 21.4. IR (liquid film, cm^{-1}): ν = 2926, 1728, 1487, 1462, 1423, 1371, 1259, 1109, 1075, 1038, 1011, 970, 804. HRMS calc. $C_{11}H_{13}BrO$: 240.0150. Found: 240.0139.

(*E*)-1-Methoxy-4-(3-methoxybut-1-enyl)benzene (2l)[15]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.35–7.31 (m, 2H), 6.87–6.85 (m, 2H), 6.47 (d, J = 15.9 Hz, 1H), 5.95 (dd, J = 16.2 Hz, 7.8 Hz, 1H), 3.89–3.81 (m, 1H), 3.79 (s, 3H), 3.31 (s, 3H), 1.32 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 159.4, 131.0, 129.6, 129.4, 127.8, 114.1, 78.4, 56.1, 55.4, 21.7. IR (liquid film, cm^{-1}): ν = 2960, 2928, 1608, 1512, 1462, 1300, 1248, 1176, 1108, 1082, 1036, 969, 819. HRMS calc. $C_{12}H_{16}O_2$: 192.1150. Found: 192.1159.

(*E*)-1-(3-Methoxybut-1-enyl)-4-methylbenzene (2m). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.29 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 6.50 (d, J = 15.9 Hz, 1H), 6.02 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 3.90–3.85 (m, 1H), 3.31 (s, 3H), 2.34 (s, 3H), 1.32 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 137.6, 134.0, 131.4, 130.6, 129.4, 126.5, 78.3, 56.1, 21.6, 21.3. IR (liquid film, cm^{-1}): ν = 3023, 2975, 2926, 2855, 2819, 1513, 1459, 1370, 1198, 1139, 1110, 1082, 969, 800. HRMS calc. $C_{12}H_{16}O$: 176.1201. Found: 176.1199.

(*E*)-1-Chloro-2-(3-methoxybut-1-enyl)benzene (2n). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.55–7.53 (m, 1H), 7.36–7.34 (m, 1H), 7.23–7.17 (m, 2H), 6.92 (d, J = 15.9 Hz, 1H), 6.08 (dd, J = 15.9 Hz, 7.6 Hz, 1H), 3.96–3.92 (m, 1H), 3.34 (s, 3H), 1.34 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 135.0, 134.4, 133.2, 129.8, 128.7, 127.7, 127.0, 126.9, 78.1, 56.2, 21.5. IR (liquid film, cm^{-1}): ν = 3063, 2977, 2929, 2821, 1591, 1470, 1441, 1369, 1354, 1200, 1143, 1110, 1083, 1037, 969, 751, 693. HRMS calc. $C_{11}H_{13}ClO$: 196.0655. Found: 196.0653.

(*E*)-1-Bromo-2-(3-methoxybut-1-enyl)benzene (2o). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.56–7.52 (m, 2H), 7.30–7.24 (m, 1H), 7.13–7.08 (m, 1H), 6.87 (d, J = 15.9 Hz, 1H), 6.02 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 3.97–3.92 (m, 1H), 3.35 (s, 3H), 1.34 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 136.8, 134.6, 133.1, 130.0, 129.0, 127.6, 127.3, 123.8, 78.0, 56.3, 21.5. IR (liquid film, cm^{-1}): ν = 3060, 2975, 2928, 2820, 1588, 1466, 1438, 1369, 1353, 1200, 1142, 1109, 1042, 1024, 967, 751, 667. HRMS calc. $C_{11}H_{13}BrO$: 240.0150. Found: 240.0153.

(*E*)-1-Methoxy-2-(3-methoxybut-1-enyl)benzene (2p). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.48–7.45 (m, 1H), 7.22 (d, J = 7.5 Hz, 1H), 6.95–6.83 (m, 3H), 6.10 (dd, J = 15.9 Hz, 7.8 Hz, 1H), 3.90–3.83 (m, 4H), 3.32 (s, 3H), 1.33 (d, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 156.9, 132.1, 128.8, 127.0, 126.4, 125.8, 120.8, 111.1, 78.7, 56.1, 55.6, 21.7. IR (liquid film, cm^{-1}): ν = 2974, 2931, 1597, 1490, 1463, 1291, 1244, 1107, 1082, 1029, 975, 751. HRMS calc. $C_{12}H_{16}O_2$: 192.1150. Found: 192.1143.

(*E*)-1-Chloro-3-(3-methoxybut-1-enyl)benzene (2q). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.38–7.37 (m, 1H), 7.26–7.22 (m, 3H), 6.48 (d, J = 15.9 Hz, 1H), 6.11 (dd, J = 15.9 Hz, 7.4 Hz, 1H), 3.91–3.87 (m, 1H), 3.32 (s, 3H), 1.32 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 138.7, 134.6, 133.2, 129.90, 129.86, 127.6, 126.4, 124.7, 77.9, 56.2, 21.4. IR (liquid film, cm^{-1}): ν = 3062, 2978, 2923, 2821, 1594, 1566, 1475, 1370, 1352, 1111, 968, 779, 685. HRMS calc. $C_{11}H_{13}ClO$: 196.0655. Found: 196.0659.

(*E*)-1-(3-Methoxybut-1-enyl)naphthalene (2r). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.13–8.11 (m, 1H), 7.86–7.84 (m, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 6.8 Hz, 1H), 7.52–7.43 (m, 3H), 7.29 (d, J = 15.7 Hz, 1H), 6.13 (dd, J = 15.7 Hz, 7.6 Hz, 1H), 4.04–4.01 (m, 1H), 3.41 (s, 3H), 1.41 (d, J = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 134.9, 134.6, 133.8, 131.3, 128.71, 128.65, 128.1, 126.2, 125.9, 125.8, 124.1, 123.8, 78.4, 56.3, 21.7. IR (liquid film, cm^{-1}): ν = 3058, 2976, 2928, 2819, 1590, 1447, 1395, 1369, 1198, 1141, 1111, 1087, 969, 794, 775. HRMS calc. $C_{15}H_{16}O$: 212.1201. Found: 212.1209.

(*E*)-(4-Methoxypent-2-enyl)benzene (2s)[18]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.32–7.17 (m, 5H), 5.80–5.72 (m, 1H), 5.42 (dd, J = 15.3 Hz, 7.5 Hz, 1H), 3.73–3.67 (m, 1H), 3.39 (d, J = 6.6 Hz, 2H), 3.26 (s, 3H), 1.41 (d, J = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 140.4, 133.4, 131.6, 128.7, 128.6, 128.4, 78.0, 56.0, 38.8, 21.5. IR (liquid film, cm^{-1}): ν = 3028, 2977, 2929, 2819, 1494, 1452, 1370, 1200, 1114, 1090, 1044, 972, 844, 745, 699. HRMS calc. $C_{12}H_{16}O$: 176.1201. Found: 176.1200.

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