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Investigating the microwave-accelerated Claisen rearrangement of allyl aryl ethers: Scope of the catalysts, solvents, temperatures, and substrates

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ABSTRACT

The microwave-accelerated Claisen rearrangement of allyl aryl ethers was investigated, in order to gain insight into the scope of the catalysts, solvents, temperatures, and substrates. Among the catalysts examined, phosphomolybdic acid (PMA) was found to greatly accelerate the reaction in NMP, at temperatures ranging from 220 to 300 °C. This method was found to be useful for preparing several intermediates previously reported in the literature using precious metal catalysts such as Au(I), Ag(I), and Pt(II). Additionally, substrates bearing bromo and nitro groups on the aryl portion required careful tailoring of the reaction conditions to avoid complex product profiles.

Substituted phenols or polyphenols (and their corresponding ethers) are a class of important compounds widely existing in natural products, pharmaceuticals, and synthetic intermediates [1]. One of the main methods to construct substituted phenols or polyphenols is the Claisen rearrangement [2]. Since its discovery in 1912, the Claisen rearrangement has been well studied and reviewed [3]. Typically, long reaction times and high temperatures are required when using conventional heating. Subsequent studies have found that a wide range of catalysts, such as protic acids (H_2SO_4, TFA, H_3PO_4), Lewis acids ($Bi(OTf)_3$, $AlCl_3$, $SnCl_4$, BCl_3), heteropoly acids, metal complexes, molecular sieves, and ionic liquids, could all accelerate the reaction [4].

The microwave-accelerated Claisen rearrangement has been reported by several research groups [5]. However, the reaction conditions vary from one research group to the other, and are often not reproducible using different substrates. For instance, Gupta used Zn dust to catalyze the reaction at temperatures as low as 55 °C, but we only observed trace amounts of product formation in the presence of Zn dust under microwave heating up to 160 °C [6]. Furthermore, each substrate's nature greatly affects the ease of rearrangement, and the optimal conditions often require careful tailoring.

In this work, we have investigated the Claisen rearrangement of a set of allyl aryl ethers, in order to identify the optimum catalyst and reaction conditions (solvent, temperature, reaction time, and the substrate effects). Among the catalysts examined, phosphomolybdic acid (PMA) was found to greatly accelerate the reaction in NMP, at temperatures ranging from 220 to 300 °C. These conditions were then applied to the synthesis of several key intermediates previously reported in the literature using precious metal catalysts.

Initially, we chose compound **1** [7] as a model substrate for the Claisen rearrangement studies. Under microwave irradiation in a capped vial, compound **1** was heated to a certain temperature, with or without catalyst, in commonly used organic solvents. The results are presented in Table 1. The reaction in dichloromethane at 130 °C did not produce any product after 60 min (Entry 1), while the reaction in ethanol gave **2** in 19% yield at 150 °C (no catalyst, 60 min, Entry 2). Water has been reported to accelerate the Claisen rearrangement by Wipf and co-workers [8]. However, when compound **1** was heated in water at 180 °C [9], only trace amounts of **2** was produced after 60 min, as suggested by TLC analysis. Switching from ethanol or water to other high thermal resistant solvents such as THF [6] (microwave 200 °C, 60 min, Entry 4), DMSO [5a] (240 °C, 60 min, Entry 5), and 1,4-dioxane (240 °C, 60 min, Entry 6) was not effective in accelerating the reaction or

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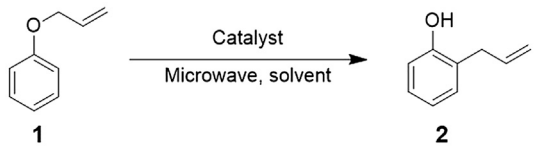
0040-4039/

Table 1
Effects of the solvents, temperatures, reaction time, and catalysts on the microwave-assisted Claisen rearrangement of **1**.[a]



1 **2**

Entry	Solvent	Temperature (℃)	Time (min)	Catalyst (amount)	Yield **2** (%)[a]
1	CH_2Cl_2	130	60	–	0[b, c]
2	EtOH	150	60	–	19[b]
3	H_2O	180	60	–	trace[c, d]
4	THF	200	60	–	7[b]
5	DMSO	240	60	–	21
6	1,4-dioxane	240	60	–	23
7	xylenes	250	60	–	80[b]
8	*N,N*-diethylaniline	250	60	–	87[b]
9	DMF	250	60	–	98
10	DMF	250	30	–	90
11	DMF	250	10	–	71
12	NMP	250	30	–	90
13	NMP	300	10	–	92
14	NMP	300	5	–	77
15	HMPT	300	10	–	72
16	NMP	160	30	A-45 ion exchange resin (0.15 equiv.)	trace[c, d]
17	NMP	300	2	$CeCl_3{\cdot}7H_2O$ (0.059 equiv.)	46
18	NMP	300	2	$Yb(OTf)_3$ (0.022 equiv.)	88
19	NMP	300	2	$AlCl_3$ (0.01 equiv.)	79
20	NMP	300	2	$BF_3{\cdot}Et_2O$ (0.004 equiv.)	77
21	**NMP**	**300**	**2**	**PMA (0.012 equiv.)**	**91**
22	NMP	300	2	PMA (0.006 equiv.)	85
23	NMP	300	1	PMA (0.012 equiv.)	81
24	NMP	250	2	PMA (0.012 equiv.)	57[b]
25	NMP	200	2	PMA (0.012 equiv.)	5[b, e]
26	NMP	150	2	PMA (0.012 equiv.)	4[b, e]

[a] Isolated yields unless otherwise indicated. [b]Yields were measured using HPLC. [c]95% of starting material was recovered. [d]TLC analysis. [e]89% of starting material was recovered.

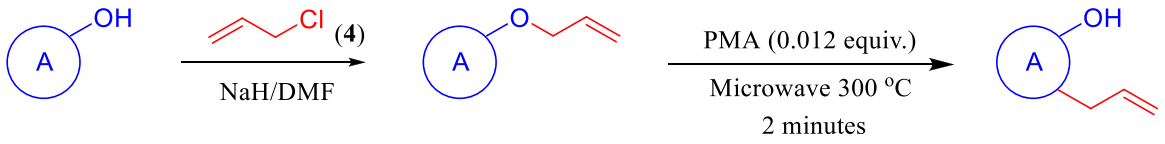
increasing the yield. Other higher boiling point solvents such as xylenes [10], *N,N*-diethylaniline [11], and DMF [12] were also examined. Reaction temperatures higher than 250 °C were avoided to prevent the decomposition of DMF. In poor microwave absorbing solvents such as xylenes, it was difficult to maintain the temperature higher than 250 °C, as the microwave magnetron is not set up to operate at full power for extended periods. Among these three solvents, DMF appears to be the best (Entry 9 vs Entries 7 and 8). Therefore, we further investigated the model reaction using DMF as the solvent. When the reaction time was reduced from 60 min to 30 min, then to 10 min, the yield decreased (Entries 10 and 11). Switching the solvent from DMF to NMP, gave a comparable yield (*ca.* 90%) at 250 °C for 30 min (Entry 12 vs Entry 10). Due to the decomposition of DMF at temperatures above 250 °C, we selected NMP as an alternative solvent to examine the effect of higher temperatures. The reaction in NMP at 300 °C produced an excellent yield after only 10 min (Entry 13). However, a further decrease of the reaction time to 5 min resulted in a significant decrease of the yield (77%, Entry 14). HPLC analysis indicates that the starting material **1** remained. Finally, HMPT was examined at 300 °C for 10 min, and the yield was moderate and comparable to that of the 5 min-reaction in NMP (Entry 15 vs Entry 14). It is clear that NMP stands out as the best solvent among those examined in Table 1.

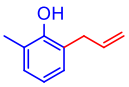
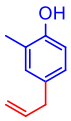
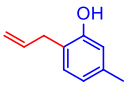
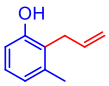
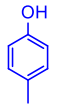
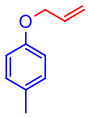
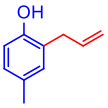
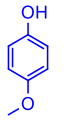
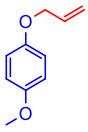
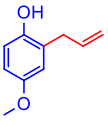
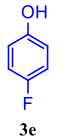
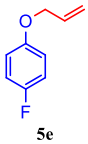
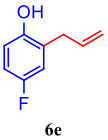
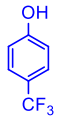
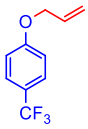
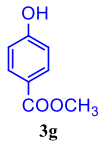
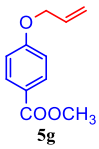
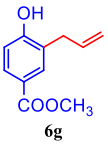
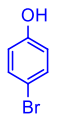
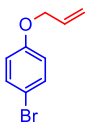
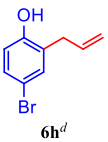
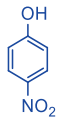
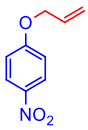
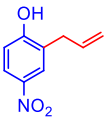
Next, we examined the effect of various catalysts for this model reaction. Amberlyst™ 45 Resin (A-45) is a macroporous sulfonic acid polymer catalyst designed for use in high-temperature (up to 160 °C without decomposition) heterogenous catalysis. However, the reaction using Amberlyst™ 45 at 160 °C in NMP gave only trace amounts of product **2**, and the starting material **1** remained (Entry 16). Other catalysts such as $CeCl_3{\cdot}7H_2O$ (0.059 equiv.), $Yb(OTf)_3$ (0.022 equiv.) [13], $AlCl_3$ (0.01 equiv.) [14] and $BF_3{\cdot}Et_2O$ (0.004 equiv.) [15] were found to accelerate the reaction within 2 min, with moderate yields varying from 46 to 88% (Entries 17–20). To our delight, the use of PMA significantly accelerated the reaction. At 300 °C, with as low as 0.012 equiv. of PMA, the reaction gave an excellent yield after 2 min (Entry 21), and a good yield after 1 min (Entry 23). The yield of **2** decreased slightly when the amount of PMA was reduced from 0.012 equiv. to 0.006 equiv. (Entries 22 vs. 21). Furthermore, when the reaction time (2 min) and catalyst amount (0.012 equiv. PMA) was kept constant, the yields decreased along with the reaction temperature (Entries 24–26). It is worth noting that the yield decreased dramatically when the reaction was performed at temperatures below 250 °C (Entries 25–26).

Based on the results from Table 1, PMA appeared to be the best catalyst among those examined. Next, we decided to synthesize a set of allyl aryl ethers to probe the substrate scope, using the optimised conditions described in Entry 21. Allyl aryl ethers **5** bearing different "A" motifs were synthesized *via* a standard alkylation reaction between the corresponding phenol **3** and allyl halide **4** in moderate to good yields. The Claisen rearrangement of **5** was carried out under the conditions described in Entry 21 (Table 1), unless otherwise indicated (Table 2).

Initially, substrates bearing a single substituent on the aryl portion were examined (Entries 1–7). The reaction of *ortho*-substituted phenyl ether **5a** gave a separable mixture of **6a-1** and **6a-2**, in which the allyl group migration favored the *ortho*-position over the *para*-position to the phenol group (Entry 1, Table 2). We obtained a slightly higher ratio of **6a-1** to **6a-2** and a similar overall

Table 2
Substrate scope for the microwave-assisted Claisen rearrangement of **5**.[a]



Entry	3	5	Yield 5 (%)[b]	6		Yield 6 (%)[b]
1	 **3a**	 **5a**	92%	 **6a-1**	 **6a-2**	55% (**6a-1**), 15% (**6a-2**) (70%, 2.4:1 ref. 5e)
2	 **3b**	 **5b**	57%	 **6b-1**	 **6b-2**	81% (**6b-1**:**6b-2** = 1:1)[c] (74%, 1.2:1 ref. 5e)
3	 **3c**	 **5c**	43%	 **6c**		81% (77%, ref.5e)
(77%, ref. 5e)						
4	 **3d**	 **5d**	71%	 **6d**		96% (73%, ref. 5e)
5	 **3e**	 **5e**	75%	 **6e**		88% (82%, ref. 16)
6	 **3f**	 **5f**	67%	 **6f**		79% (77%, ref. 16)
7	 **3g**	 **5g**	87%	 **6g**		90% (75%, ref. 11b)
8	 **3h**	 **5h**	88%	 **6h**[d]		76% (78%, ref. 6)
9	 **3i**	 **5i**	67%	 **6i**[e]		69% (83%, ref. 6)

(*continued on next page*)

Table 2 (*continued*)

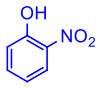
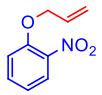
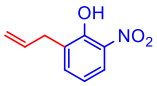
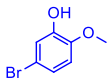
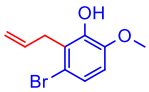
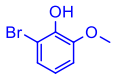
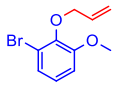
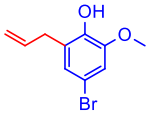
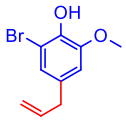
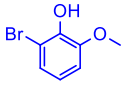
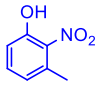
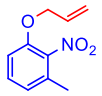
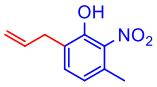
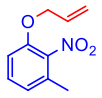
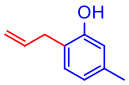
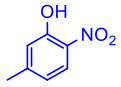
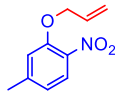
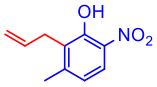
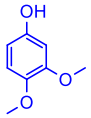
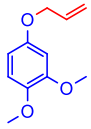
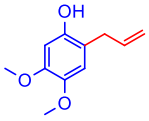
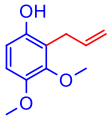
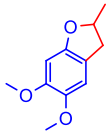
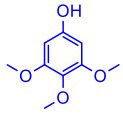
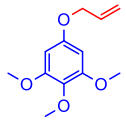
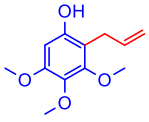
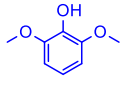
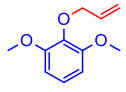
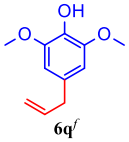
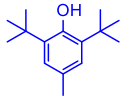
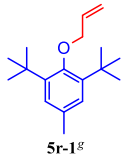
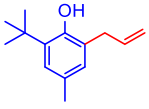
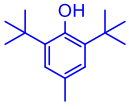
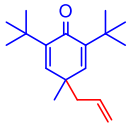
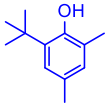
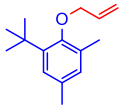
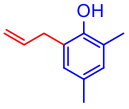
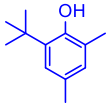
Entry	3	5	Yield **5** (%)[b]	6	Yield **6** (%)[b]
10	 **3j**	 **5j**	29%	 **6j**[e]	78% (77%, ref. 17)
11	 **3k**	 **5k**	63%	 **6k-1**[e]  **6k-2**[e]	54% (**6k-1**) (86%, ref. 18) 8% (**6k-2**)
12	 **3l**	 **5l**	50%	 **6l-1**[e]  **6l-2**[e]  **3l**[e]	21% (**6l-1**) 44% (**6l-2**:**3l** = 5:1)[c]
13	 **3m**	 **5m**	94%	 **6m**[e]	79%[d]
14		 **5m**		 **6b-1**	41%
15	 **3n**	 **5n**	88%	 **6n**[e]	73% (71%, ref. 19)
16	 **3o**	 **5o**	69%	 **6o-1**  **6o-2**  **6o-3**	53% (**6o-1**) 16% (**6o-2**) Trace (**6o-3**)
17	 **3p**	 **5p**	89%		70% (60%, ref. 20)
18	 **3q**	 **5q**	38%	 **6q**[f]	83% (85%, ref. 21)
19	 **3r**	 **5r-1**[g]	53%	 **6r**  **3r**	39% (**6r**) 15% (**3r**)

Table 2 (*continued*)

Entry	3	5	Yield **5** (%)[b]	6	Yield **6** (%)[b]
		 **5r-2**[g]	28%		
20	 **3s**	 **5s**	67%	 **6s**[e]  **3s**[e]	42% (**6s**) 23% (**3s**)

[a] Reagents and conditions: Step 1:**3** (5 mmol), **4** (6 mmol), NaH (6 mmol), DMF (5 mL), r.t. Step 2: **5** (0.5 mmol), PMA (0.006 mmol), NMP (1 mL), microwave 300 °C, 2 min. [b]Isolated yields unless otherwise indicated. [c]Ratio was determined by intergration of ^{1}H NMR spectra. [d]Reaction without catalyst, microwave 230 °C, 20 min. [e]Reaction without catalyst, microwave 220 °C, 20 min. [f]Reaction without catalyst, microwave 250 °C, 10 min. [g]Compound **5r-1** was prepared from **3r** and allyl chloride in 53% yield using standard alkylation conditions. Compound **5r-2** was isolated as a by-product in 28% yield.

yield compared to the conditions reported by Chu and co-workers [5e]. When *meta*-substituted phenyl ether **5b** was used, the reaction produced an inseperable mixture of two products **6b-1** and **6b-2** in a 1:1 ratio (slightly higher overall yield than Chu and co-workers [5e]), with the migration proceeding to both of the *ortho*-positions (Entry 2). For substrates bearing *para*-substituents such as *para*-methyl (**5c**), *para*-methoxy (**5d**), *para*-fluoro (**5e**), *para*-trifluoromethyl (**5f**), and *para*-methylbenzoate (**5g**), the reaction proceeded smoothly to give *ortho*-rearrangement products (**6c-g**, Entries 3–7). It should be noted that our method produced better yields for selected substrates than what was reported in the literature. However, their bromo and nitro substituted arenes (**5h** and **5i**) gave mixtures of products under the above conditions (Entries 11–12). Subsequent investigation revealed that the substrates bearing bromo and nitro groups required lower reaction temperatures and the absence of PMA. Thus, compounds **5h** and **5i** underwent rearrangement at lower temperatures (230 °C or 220 °C respectively) to give **6h** and **6i**, respectively, in reasonable yields after 20 min (Entries 8 and 9). The *ortho*-nitro substrate **5j** gave a single rearrangement product where the allyl group migrated to the position next to phenol group (Entry 10). Other allyl aryl ethers bearing either bromo or nitro groups all required lower temperatures (220 °C) and the absence of PMA (Entries 11–13). It

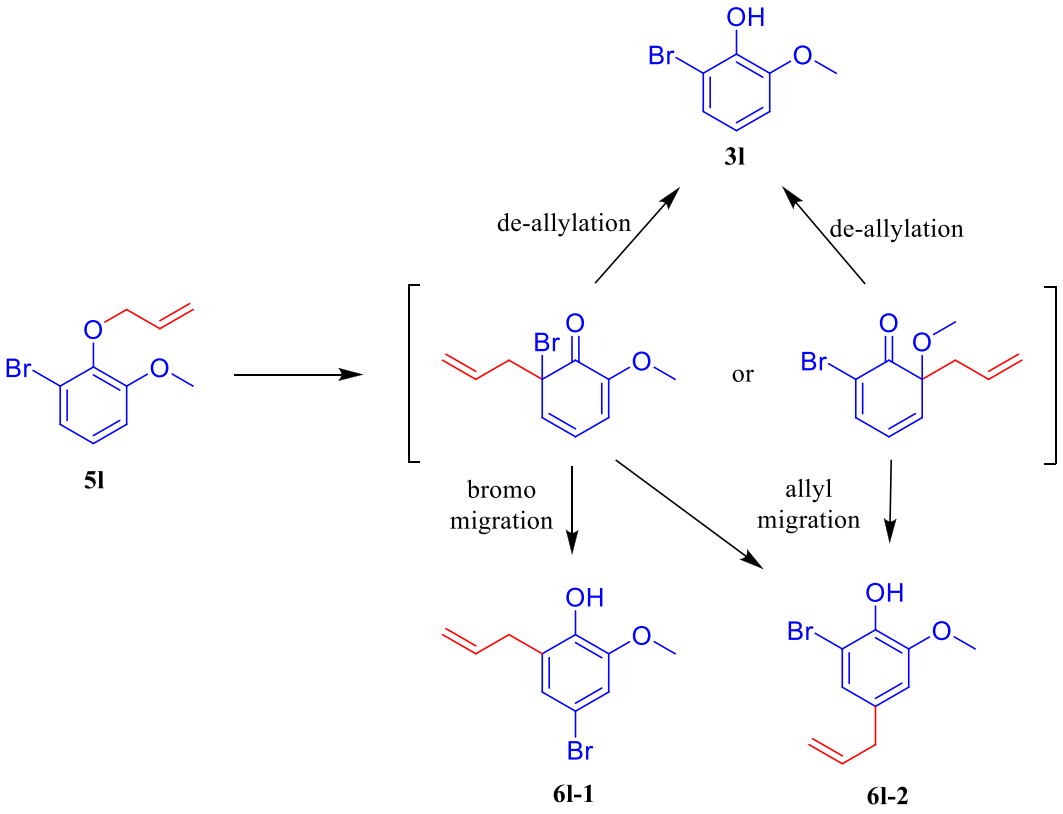
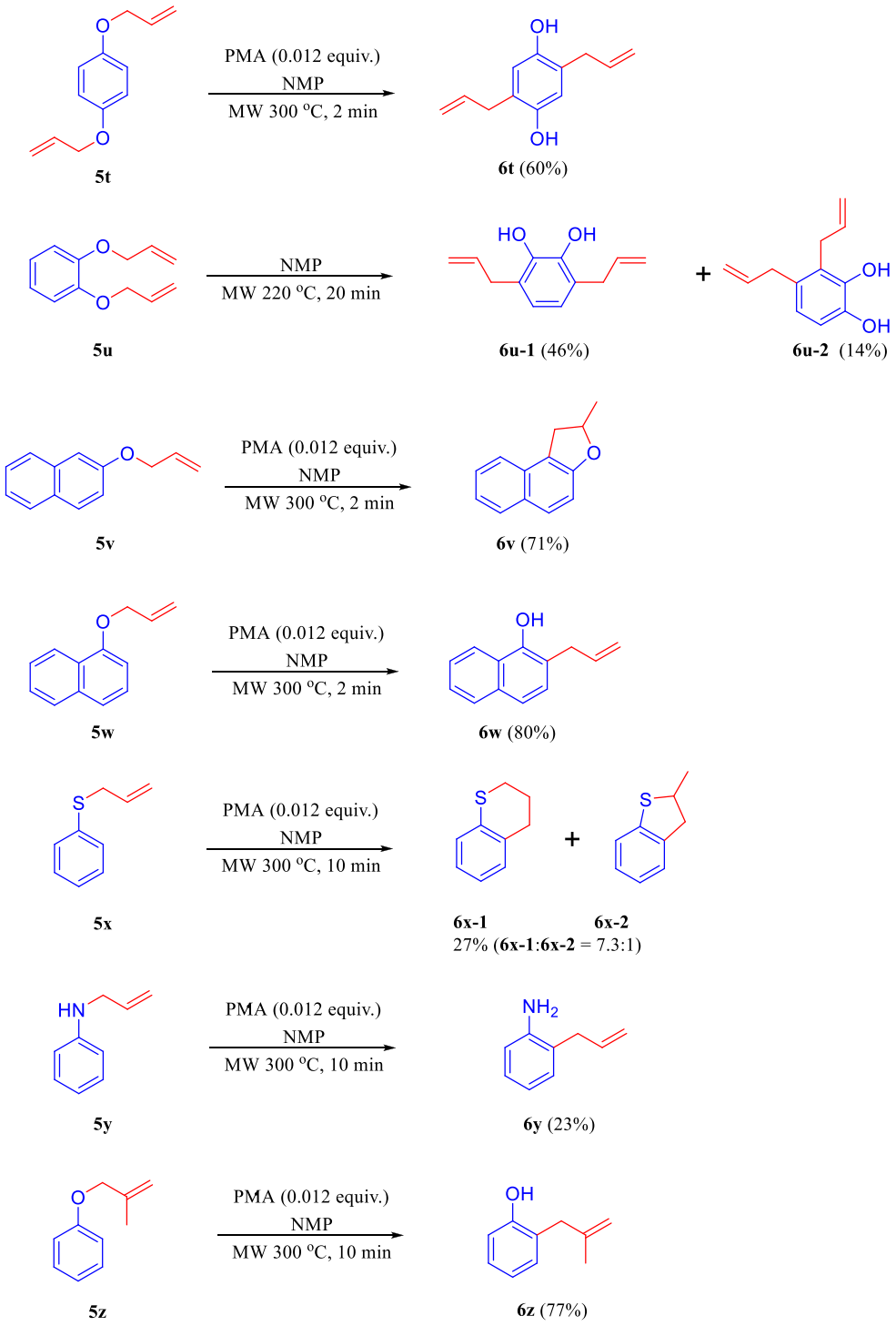


Fig. 1. Possible rearrangement mechanism for substrate **5l**.



Scheme 1. Applications of the microwave-accelerated Claisen rearrangement in the synthesis of useful intermediates.

is worth noting that the effect of PMA is profound with nitro-bearing substrates such as compound **5m**. The reaction conditions with or without PMA produced different products (**6b-1** vs **6m**, Entry 14 vs Entry 13). Apparently, PMA causes the loss of the nitro group during the rearrangement. Thus, compound **5n** underwent rearrangement in the absence of PMA to give **6n** in good yield (Entry 15). Similarly, *ortho*-bromo bearing substrate **5l** underwent rearrangement under modified conditions (220 °C, 20 min, in the absence of PMA) to give two separable rearrangement products, **6l-1** and **6l-2**, in a ratio of approximately 1:1.7 (Entry 12). Compound **6l-1** was formed from double migration of the both bromo group and the allyl group. In addition, approximately 7% of the de-allyl product **3l** (starting material for **5l**) was detected. This result suggests that the reaction might involve multiple stepwise rearrangements. The allyl group of **5l** presumably first migrates to positions *ortho*- to the phenolic hydroxyl group. The high energy intermediates then proceed to a lower energy aromatic system *via* different pathways to furnish **6l-1**, **6l-2**, and **3l**, respectively (Fig. 1).

Other substrates with available *ortho*- and/or *para*- positions generally follow the same rule. Thus, **5o** underwent rearrangement to give **6o-1** and **6o-2** in a ratio of approximately 3.4:1 with trace amounts of **6l-3** detected (Entry 16). The complexity of the product profile is generally due to more than one available migration position leading to competion. For substrates with only one position available for migration, the reaction tends to be cleaner and proceeds in higher yields, i.e. Entries 17–18.

When all the *ortho*- and *para*- positions of the aryl phenol group were occupied, the rearrangement occured differently. For instance, **5r-1** underwent the rearrangement to give **6r** and **3r** (Entry 19). The allyl group might first migrate to the *ortho*- position to form a high energy intermediate, followed by the expulsion of isobutene to produce **6r**. In addition, the phenol ally ether **5r-1** might decompose to form **3r**, which is the starting material for preparation of **5r-1**. Similarly, **5s** underwent the rearrangement to form **6s** and **3s** a ratio of approximately 2:1 (Entry 20).

The developed method was then used to prepare several key intermediates for organic synthesis and pharmaceuticals (Scheme 1). Compound **5t** underwent double rearrangement to give **6t** in 60% yield under the standard conditions (0.012 equiv. PMA, NMP, 300 °C, 2 min). However, the reaction of **5u**, a substrate also bearing two allyl ether groups, proceeded under modified conditions (220 °C, 20 min, NMP, in the absence of PMA) to give **6u-1 (**46%) and **6u-2** (14%). The results were consistent with the literature, but the reaction was complete in a much shorter time (20 min vs 585 min) [22]. Compound **6u-1** was a key intermediate for the preparation of a PI3K inhibitor [23]. Interestingly, 2-naphthalenyl ether **5v** underwent rearrangement and cyclization within 2 min to afford **6v** in 71% yield. Previously, several groups have reported the synthesis of **6v** involving precious metal catalysts such as $AuClPPh_3$, utilizing long reaction times and several synthetic steps [24]. 1-Naphthalenyl ether **5w** proceeds smoothly to give the rearrangement product **6w** in 80% yield. Unlike the reaction of **5v**, there was no cyclization product detected for **5w**. The synthesis of **6w** reported in the literature involved long reaction times at high temperatures [25]. Furthermore, the substrate scope for this method was further expanded. For example, allylic thio ether **5x** underwent rearrangement and cyclization in a single step to afford two products **6x-1** and **6x-2**, in a ratio of 7.3:1. Previously, compound **5x** was used by Dai and Yadav to synthesize **6x-2** [26]. Allyl aniline **5y** [27] underwent the rearrangement to afford *ortho*- product **6y** in 23% yield. Finally, 2-methylpropenyl phenyl ether **5z** (bearing a substituent on the allyl portion) rearranged to afford **6z** in good yield.

In summary, the Claisen rearrangement reaction under microwave irradiation was investigated in order to gain a better understanding of the scope of the catalysts, solvents, temperatures, and substrates. Catalytic PMA (as low as 0.012 equiv.) was found to be superior to the other catalysts examined, and to significantly accelerate the reaction greatly. NMP also appears to be the best solvent. In general, the reaction is complete within 2–10 min at 300 °C. The substrate scope was also investigated. In general, when *ortho*- and *para*- positions are both available, the allyl group can migrate to both positions, with preference for the *ortho*- position over the *para*- position. When both *ortho*-positions are blocked by substituents, allyl migration occurs to the available *para*- position. If all possible *ortho*- and *para*-positions are occupied, the substrates will either decompose to the phenol or swap one of the occupied *ortho*-groups with the allyl group. Bromo (but not fluoro) and nitro groups are sensitive substituents in this reaction. For substrates bearing these two groups, the use of PMA complicates the reaction profiles, resulting in either the loss, or the rearrangement, of the sensitive groups. In the absence of PMA and at a lower temperature, the sensitive groups (bromo and nitro) can be tolerated, but the reaction requires longer times. The substrate scope was further expanded to include allyl thiophenol ether, allyl aniline, propynyl phenol ether, and a substituted propenyl phenol ether. Finally, the method was employed to access several intermediates previously synthesized using precious metal catalysts such as Au(I), Ag(I), and Pt(II).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data (experimental procedures, NMR spectrum) can be found online at https://doi.org/10.1016/j.tetlet.2020.151995.

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