



# MICROWAVE INDUCED LEWIS ACID CATALYZED CLAISEN REARRANGEMENT OF O-ALLYLARYL ETHERS

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## ABSTRACT

Microwave assisted Lewis acid catalyzed Claisen rearrangements of allylaryl ethers (**1a-r**) were investigated. Lewis acid ( $ZnCl_2$  and  $BF_3 \cdot OEt_2$ ) catalyzed microwave assisted Claisen rearrangement yielded 2-allylphenols (**2a-r**) from o-allylaryl ethers (**1a-r**) in excellent yields.

**Key words** : Claisen rearrangement, Microwave induced, O-Allylaryl ether, O-Allylphenol.

## INTRODUCTION

The Claisen rearrangement of o-allylaryl ethers to 2-allylphenols is important in view of its synthetic utility and mechanistic aspects<sup>1,2</sup>. Its widespread application is due to the less number of steps, which it requires in the synthesis of target molecules, moderate reaction rate and satisfactory yield of the desired products. As a result of this, the literature is replete with numerous examples of Claisen rearrangement on aromatic systems.

2-Allylphenols, which result from the Claisen rearrangement of o-allylaryl ethers, are important precursors in palladium induced heteroannulation to give benzofurans<sup>3</sup>. In a quest to examine the application of palladium catalyzed heteroannulations of highly substituted phenol substrates in benzofuran synthesis, We required a variety of 2-allylphenols (**2a-r**). The  $BF_3 \cdot OEt_2$  induced Claisen rearrangement of o-allylaryl ethers (**1a-r**) under microwave conditions appeared a most simple and convenient method for their synthesis.

## EXPERIMENTAL

All the melting points are uncorrected. IR spectra on KBr were recorded on FTIR-

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8400S (SHIMADZU).  $^1\text{H}$  NMR spectra were recorded on Model AC-300F (Bruker) using  $\text{CDCl}_3/\text{DMSO-d}_6$  as solvent and TMS as an internal standard. Microwave reactions were carried out on LG MC-808 WAR Model, operating at 720 W, generating 2450 MHz frequency.

Our initial attempt to obtain **2** from **1** through the Claisen rearrangement using an uncatalyzed thermal reaction ( $250^\circ\text{C}$ ) resulted in very low yield of **2** (Table 1). Hence, the use of the catalyst seemed inevitable in carrying out such thermally difficult reactions.

### Thermal rearrangement

A solution of *o*-allylaryl ether (**1a-r**) (25 mmol) in decalin (25 mL) was placed in a 100 mL round bottomed flask and heated at  $250^\circ\text{C}$  (in a silicon oil bath) for 5 h. In accord to earlier precedence in literature<sup>4</sup>, We examined the protic acid catalyzed reaction with  $\text{H}_2\text{SO}_4$  and TFA. The use of these catalysts in Claisen rearrangement of *o*-allylaryl ethers (**1a-r**) gave 2-allylphenols (**2a-r**) in low to moderate yields (Table 2).

**Table 1: Different conventional methods**

Method employed	Solvent / Bronsted acid	Temp <sup>d</sup> ( $^\circ\text{C}$ )	Time (h)
Thermal rearrangement	(A) Decalin <sup>a</sup>	250	5
Bronsted acid induced rearrangement	(B) $\text{H}_2\text{SO}_4^b$ (0.2N)	170-180	14
	(C) $\text{H}_2\text{SO}_4^b$ (0.5N)	170-180	22
	(D) $\text{H}_2\text{SO}_4^b$ (0.1N)	170-180	12
	(E) Trifluoro-acetic acid/ water/ dioxan (TWD) (2 : 1 : 1) <sup>c</sup>	170-175	1.5-2.0

<sup>a</sup>The reactions were run in decalin at 1 M,

<sup>b</sup>  $\text{H}_2\text{SO}_4$  at 0.15 M

<sup>c</sup> TWD at 0.32 M

<sup>d</sup>The temperature of silicon oil bath was noted.

In order to improve the yield of **2**, Claisen rearrangement of **1**, the reaction was carried out with Lewis acid catalyst ( $\text{ZnCl}_2$  and  $\text{BF}_3\cdot\text{OEt}_2$ ), which gave satisfactory results

but the process was time consuming. The reaction under microwave condition curtailed the time factor and the results, which have emanated from this study are summarized in this paper.

**Table 2 : The thermal and Bronsted acid induced Claisen rearrangement of allylaryl ethers**

Substrate	Product	Method employed <sup>a</sup> and yield(%) <sup>b</sup>				
		A	B	C	D	E
<b>1a</b>	<b>2a</b>	18	28	c	c	c
<b>1b</b>	<b>2b</b>	c	c	c	c	28
<b>1c</b>	<b>2c</b>	15	22	c	c	c
<b>1d</b>	<b>2d</b>	17	24	c	c	c
<b>1e</b>	<b>2e</b>	c	c	27	c	c
<b>1f</b>	<b>2f</b>	c	c	c	c	23
<b>1g</b>	<b>2g</b>	c	c	c	25	c
<b>1h</b>	<b>2h</b>	16	c	c	c	22
<b>1i</b>	<b>2i</b>	c	27	c	c	c
<b>1j</b>	<b>2j</b>	15	c	c	23	c
<b>1k</b>	<b>2k</b>	14	28	c	c	c
<b>1l</b>	<b>2l</b>	18	c	c	21	c
<b>1m</b>	<b>2m</b>	c	c	c	c	26
<b>1n</b>	<b>2n</b>	15	c	21	c	c
<b>1o</b>	<b>2o</b>	19	23	c	c	c
<b>1p</b>	<b>2p</b>	14	c	28	c	c
<b>1q</b>	<b>2q</b>	c	c	c	c	22
<b>1r</b>	<b>2r</b>	16	c	c	26	c

<sup>a</sup>For methods (A-E) see Table 1

<sup>b</sup>Isolated yield of the product is given, it is not fully optimized.

<sup>c</sup>No reaction, starting material was recovered unchanged.

### Bronsted acid induced rearrangement

In a 250 mL round bottomed flask fitted with reflux condenser, o-allylaryl ether (**1a-r**) (25 mmol) and H<sub>2</sub>SO<sub>4</sub> (0.2N, 165ml) were placed and heated at 170-180°C (in a silicon oil bath) for 4 h. The solution was made alkaline with NaHCO<sub>3</sub> solution and was extracted with ethylacetate, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to give 2-allylphenol (**2a-r**), which was purified by column chromatography on silica gel in the solvent system ( hexane-ethylacetate, 10 : 1) (yield 21-28%, Table 2)

**Table 3 : Reaction conditions used for the Lewis acid induced Claisen rearrangement of allyl aryl ethers to 2-allylphenols**

Reaction conditions	Allylaryl ethers	Lewis acid (BF <sub>3</sub> .OEt <sub>2</sub> )	Solvent
A	1.0 Equiv.	0.5 Equiv	Sulfolane <sup>a</sup>
B	1.0 Equiv	0.5 Equiv	Xylene <sup>b</sup>

<sup>a</sup>The reactions were run in sulfolane at 3M,

<sup>b</sup>in xylene at 0.5M.

**Table 4 : The Lewis acid induced Claisen rearrangement of allylaryl ethers**

Substrate	Product	Reaction condition <sup>a</sup> and yield % <sup>b</sup>				
		A			B	
<b>1a</b>	<b>2a</b>	190°C,	1.5h,	54%	12.0h,	61%
<b>1b</b>	<b>2b</b>		c		8.0h,	61%
<b>1c</b>	<b>2c</b>	160°C,	2.5h,	54%	5.5h,	60%
<b>1d</b>	<b>2d</b>	180°C,	1.0h,	45%	3.5h,	63%
<b>1e</b>	<b>2e</b>		c		6.0h,	59%
<b>1f</b>	<b>2f</b>		c		4.5h,	65%
<b>1g</b>	<b>2g</b>	155°C,	2.0h,	49%	8.0h,	61%
<b>1h</b>	<b>2h</b>	140°C,	1.5h,	44%	10.0h,	65%

Cont...

Substrate	Product	Reaction condition <sup>a</sup> and yield % <sup>b</sup>				
		A			B	
<b>1i</b>	<b>2i</b>	185°C,	2.0h,	47%	12.0h,	61%
<b>1j</b>	<b>2j</b>	170°C,	1.0h,	46%	3.0h,	60%
<b>1k</b>	<b>2k</b>	145°C,	3.0h,	43%	5.5h,	65%
<b>1l</b>	<b>2l</b>	160°C,	2.0h,	48%	7.0h,	62%
<b>1m</b>	<b>2m</b>	150°C,	1.5h,	54%	10.0h,	59%
<b>1n</b>	<b>2n</b>	175°C,	1.0h,	51%	14.0h,	58%
<b>1o</b>	<b>2o</b>	200°C,	2.5h,	53%	18.0h,	61%
<b>1p</b>	<b>2p</b>	185°C,	2.0h,	55%	24.0h,	61%
<b>1q</b>	<b>2q</b>	170°C,	1.0h,	50%	8.0h,	58%
<b>1r</b>	<b>2r</b>	190°C,	1.5h,	50%	6.5h,	58%

<sup>a</sup>For reaction conditions (A-B), see Table 3

<sup>b</sup>Isolated yield of the product is given, it is not fully optimized.

<sup>c</sup>No reaction, starting material was recovered unchanged.

### Lewis acid induced rearrangement

In a 50 mL round bottomed flask equipped with a reflux condenser and take off to the bubbler, o-allylaryl ether (**1a-r**) (25 mmol), sulfolane (10.0 mL), BF<sub>3</sub>.OEt<sub>2</sub> (2.92 mmol) were heated at 190°C for 1.5 h, cooled and poured into ice-cold water (15 mL). It was made acidic (pH 1) by adding 10% HCl solution and extracted with Et<sub>2</sub>O (5 mL x 3). The combined ether extracts were washed with water (50 mL), dried (MgSO<sub>4</sub>) and concentrated to give a crude brown oily residue, which was subjected to column chromatography on silica gel (hexane- ethylacetate, 10 : 1) to give 2-allylphenol (**2a-r**) (yield 43-62%, Table 4).

### Microwave assisted rearrangement using BF<sub>3</sub>.OEt<sub>2</sub>

A solution of o-allylaryl ether (**1a-r**) (12.5 mmol) and BF<sub>3</sub>.OEt<sub>2</sub> (17.5 mmol) in minimum amount of xylene was placed in a 100 mL borosil flask fitted with a funnel as a loose top. The reaction mixture was subjected to microwave irradiation at 720W with 30 sec/cycle. The number of cycle in turn depend on the completion of the reaction, which

was checked by TLC. The reaction timing varied from 5-8 min. After cooling to room temperature, the mixture was poured into water (80 mL) and extracted with ethylacetate (30 mL x 3). The solvent layer was washed with water, dried ( $\text{MgSO}_4$ ) and concentrated to give 2-allylphenol (**2a-r**). The crude product was subjected to column chromatography on silica gel in the solvent system (hexane-ethylacetate, 10 : 1) (yield 75-81%, Table 5 and 6).

**Table 5: Reaction conditions used for microwave assisted Claisen rearrangement of allyl aryl ethers to 2-allylphenols**

Reaction condition	Allylaryl ethers	Lewis acid	Solvent
A	1.0 Equiv.	$\text{BF}_3 \cdot \text{OEt}_2$ (1.0 Equiv)	Xylene <sup>a</sup>
B	1.0 Equiv	$\text{ZnCl}_2$ (3.0 Equiv)	Xylene <sup>a</sup>

<sup>a</sup>The reactions were run in xylene at 0.5M.

### Microwave assisted rearrangement using zinc chloride

A solution of o-allylaryl ether (**1a-r**) (12.5 mmol) in xylene (5.0 mL) and fused  $\text{ZnCl}_2$  (44.7 mmol) were placed in a 100 mL borosil flask fitted with a funnel as a loose top. The reaction mixture was subjected to microwave irradiation at 720W with 30 sec/cycle. The number of cycle in turn depend on the completion of the reaction, which was checked by TLC. The reaction timing varied from 5-8 min. After cooling to room temperature, the mixture was poured into water (80 mL) and extracted with ethylacetate (30 mL x 3). The solvent layer was washed with brine (30 mL), dried ( $\text{MgSO}_4$ ) and concentrated to give 2-allylphenol (**2a-r**). The crude product was subjected to column chromatography on silica gel in the solvent system (hexane-ethylacetate, 10 : 1) to give 2-allylphenol (**2a-r**) (yield 85-92%, Tables 5 and 6).

**Table 6 : Microwave assisted Claisen rearrangement of allyl aryl ethers**

Substrate	Product	Reaction condition <sup>a</sup> and yield % <sup>b</sup>			
		A		B	
<b>1a</b>	<b>2a</b>	5.0 min,	79%	5.5 min,	85%
<b>1b</b>	<b>2b</b>	6.0 min,	78	6.5 min,	86%

Cont...

Substrate	Product	Reaction condition <sup>a</sup> and yield % <sup>b</sup>			
		A		B	
<b>1c</b>	<b>2c</b>	5.5 min,	79%	5.0 min,	89%
<b>1d</b>	<b>2d</b>	6.5 min,	81%	6.0 min,	85%
<b>1e</b>	<b>2e</b>	5.0 min	77%	7.5 min,	87%
<b>1f</b>	<b>2f</b>	7.0 min.	80%	5.0 min,	91%
<b>1g</b>	<b>2g</b>	6.5 min,	79%	6.5 min,	88%
<b>1h</b>	<b>2h</b>	7.5 min,	77%	8.0 min,	92%
<b>1i</b>	<b>2i</b>	5.5 min,	75%	5.0 min,	87%
<b>1j</b>	<b>2j</b>	5.0min,	81%	7.5 min,	90%
<b>1k</b>	<b>2k</b>	8.0 min,	78%	5.0 min,	89%
<b>1l</b>	<b>2l</b>	5.5 min,	80%	7.0 min,	88%
<b>1m</b>	<b>2m</b>	5.0 min,	77%	8.0 min,	92%
<b>1n</b>	<b>2n</b>	6.5 min,	81%	5.0 min,	90%
<b>1o</b>	<b>2o</b>	8.0 min,	79%	6.0 min,	88%
<b>1p</b>	<b>2p</b>	5.5 min	77%	8.0 min,	86%
<b>1q</b>	<b>2q</b>	5.0 min,	76%	5.5 min,	89%
<b>1r</b>	<b>2r</b>	6.0 min,	78%	7.0 min,	91%

<sup>a</sup>For reaction conditions (A-B) see Table 5.

<sup>b</sup>Isolated yield of the product is given, it is not fully optimized.

**Table 7: Melting points and spectroscopic data of 2-allylphenol (2a- r)**

Product	M. P. (°C)	IR (cm <sup>-1</sup> )	<sup>1</sup> H NMR (δ ppm)
	Reported <sup>7-11</sup> (Observed)		
<b>2a</b>	126 (127)	3595, 1635, 1606, 1589, 1475, 988, 912, 888, 835, 589	5.09 (br, s, 1H, OH), 3.33 (d, 2H, CH <sub>2</sub> ), 6.30 (m, 1H, CH), 4.924.97 (m, 2H, CH <sub>2</sub> ), 7.07-6.50 (m, 3H, ArH)

Product	M. P. (°C) Reported <sup>7-11</sup> (Observed)	IR (cm <sup>-1</sup> )	<sup>1</sup> H NMR (δ ppm)
<b>2b</b>	126 (128)	3605, 1628, 1597, 1506, 1469, 999, 910, 790, 695, 591	5.11 (br, s, 1H, OH), 3.35 (d, 2H, CH <sub>2</sub> ), 6.33 (m, 1H, CH), 4.93-4.96 m, H, CH <sub>2</sub> ), 7.07-6.59 (m, 3H, ArH)
<b>2c</b>	97 (98.6)	3698, 1639, 1609, 1578, 1489, 989, 909, 883, 845, 738	5.10 (br, s, 1H, OH), 3.36 (d, 2H, CH <sub>2</sub> ), 6.34 (m, 1H, CH), 4.92-4.98 (m, 2H, CH <sub>2</sub> ), 6.91-6.55 (m, 3H, ArH)
<b>2d</b>	78 (78.7)	3593, 1629, 1604, 1584, 1496, 994, 913, 2924, 894, 852	5.09 (br, s, 1H, OH), 3.32 (d, 2H, CH <sub>2</sub> ), 6.35 (m, 1H, CH), 4.94- 4.99 (m, 2H, CH <sub>2</sub> ), 6.70-6.49 (m, 3H, ArH), 2.35 (s, 3H, - CH <sub>3</sub> )
<b>2e</b>	132 (133)	3607, 1634, 1610, 1575, 1542, 1358, 995, 907, 892, 855	5.11 (br, s, 1H, OH), 3.35 (d, 2H, CH <sub>2</sub> ), 6.32 (m, 1H, =CH), 4.914.99 (m, 2H, CH <sub>2</sub> ), 7.83-6.87 (m, 3H, ArH)
<b>2f</b>	132 (131)	3392, 1640, 1612, 1581, 1455, 987, 913, 1548, 1347, 795, 690	5.09 (br, s, 1H, OH), 3.32 (d, 2H, CH <sub>2</sub> ), 6.34 (m, 1H, CH), 4.90-4.98 (m, 2H, CH <sub>2</sub> ), 7.83-6.90 (m, 3H, ArH)
<b>2g</b>	78 (77)	3592, 1645, 1608, 1589, 1501, 2925, 994, 910, 790, 696	5.10 (br, s, 1H, OH), 3.33 (d, 2H, CH <sub>2</sub> ), 6.37 (m, 1H, CH), 4.92- 4.97 (m, 2H, CH <sub>2</sub> ), 6.78-6.42 (m, 3H, ArH), 2.35 (s, 3H, -CH <sub>3</sub> )
<b>2h</b>	78 (77)	3580, 1638, 1604, 1578, 1496, 998, 920, 2928, 792, 690	5.11 (br, s, 1H, OH), 3.31 (d, 2H, CH <sub>2</sub> ), 6.33 (m, 1H, CH), 4.91- 4.98 (m, 2H, CH <sub>2</sub> ), 6.78-6.58 (m, 3H, ArH), 2.35 (s, 3H, -CH <sub>3</sub> )



Product	M. P. (°C) Reported <sup>7-11</sup> (Observed)	IR (cm <sup>-1</sup> )	<sup>1</sup> H NMR (δ ppm)
<b>2i</b>	101 (102)	3395, 1635, 1610, 1594, 1448, 1012, 915, 1280, 789, 698	5.10 (br, s, 1H, OH), 3.36 (d, 2H, CH <sub>2</sub> ) 6.31 (m, 1H, CH), 4.90- 4.99 (m, 2H, CH <sub>2</sub> ), 6.91 -6.55 (m, 3H, ArH), 3.73 (s, 3H, OCH <sub>3</sub> )
<b>2j</b>	143 (144)	3385, 1642, 1016, 918, 160, 1510, 1455, 1680, 805, 685	5.09 (br, s, 1H, OH), 3.32 (d, 2H, CH <sub>2</sub> ), 6.30 (m, 1H, CH), 4.93- 4.97 (m, 2H, CH <sub>2</sub> ), 6.9 -16.55 (m, 3H, ArH), 4.29 (q, 2H, COOC <sub>2</sub> H <sub>5</sub> ), 1.30 (t, 3H, COOC <sub>2</sub> H <sub>5</sub> )
<b>2k</b>	131 (133)	3378, 1628, 1685, 1618, 1581, 1459, 995, 920, 790, 710	5.11 (br, s, 1, OH), 3.30 (d, 2H, CH <sub>2</sub> ), 6.33 (m, 1H, CH), 4.91- 4.99 (m, 2H, CH <sub>2</sub> ), 7.61 - 6.81 (m, 3H, ArH), 3.88 (s, 3H, COOCH <sub>3</sub> )
<b>2l</b>	120 (121)	3383, 1634, 1710, 1607, 1585, 1456, 1010, 908, 785, 694	5.12 (br, s, 1H, OH), 3.33 (d, 2H, CH <sub>2</sub> ), 6.31 (m, 1H, CH), 4.94- 4.98 (m, 2H, CH <sub>2</sub> ), 6.91 -6.55 (m, 3H, ArH), 10.24 (s, 1H, CHO)
<b>2m</b>	198 (199)	3375, 1629, 1615, 1590, 1460, 1014, 912, 889, 595	5.10 (br, s, 1H, OH), 3.31 (d, 2H, CH <sub>2</sub> ), 6.35 (m, 1H, CH), 4.92- 4.97 (m, 2H, CH <sub>2</sub> ), 6.91 -6.55 (m, 3H, ArH)
<b>2n</b>	101 (102)	3581, 1641, 2924, 1012, 912, 1603, 1585, 1465, 885	5.09 (br, s, 1H, OH), 3.34 (d, 2H, CH <sub>2</sub> ), 6.30 (m, 1H, CH), 4.90- 4.98 (m, 2H, CH <sub>2</sub> ), 6.91 -6.55 (m, 3H, ArH), 2.35 (s, 3H, CH <sub>3</sub> )
<b>2o</b>	198 (199.4)	3595, 1633, 1598, 1485, 1445, 598, 892	5.10 (br, s, 1H, OH), 3.33 (d, 2H, CH <sub>2</sub> ) 6.33 (m, 1H, CH), 4.91- 4.99 (m, 2H, CH <sub>2</sub> ), 6.91 -6.55 (m, 3H, ArH)

Product	M. P. (°C) Reported <sup>7-11</sup> (Observed)	IR (cm <sup>-1</sup> )	<sup>1</sup> H NMR (δ ppm)
<b>2p</b>	144 (145)	3589, 1630, 1610, 1584, 1462, 1015, 915, 805, 735	5.11 (br, s, 1H, OH), 3.31 (d, 2H, CH <sub>2</sub> ) 6.37 (m, 1H, CH) 4.90-4.97 (m, 2H, =CH <sub>2</sub> ), 8.05 - 7.25 (m, 3H, ArH)
<b>2q</b>	190 (192)	3595, 1641, 1608, 1589, 1454, 1011, 912, 1275, 808, 755	5.11 (br, s, 1H, OH), 3.30 (d, 2H, CH <sub>2</sub> ), 6.35 (m, 1H, CH), 4.92- 4.97 (m, 2H, CH <sub>2</sub> ), 7.75 -6.63 (m, 3H, ArH), 3.73 (s, 3H, OCH <sub>3</sub> )
<b>2r</b>	144 (143)	3598, 1625, 1010, 910, 160, 1592, 1456, 855, 820, 745	5.10 (br, s, 1H, OH), 3.35 (d, 2H, CH <sub>2</sub> ), 6.30 (m, 1H, CH), 4.91- 4.99 (m, 2H, CH <sub>2</sub> ), 7.60 -7.20 (m, 3H, ArH)

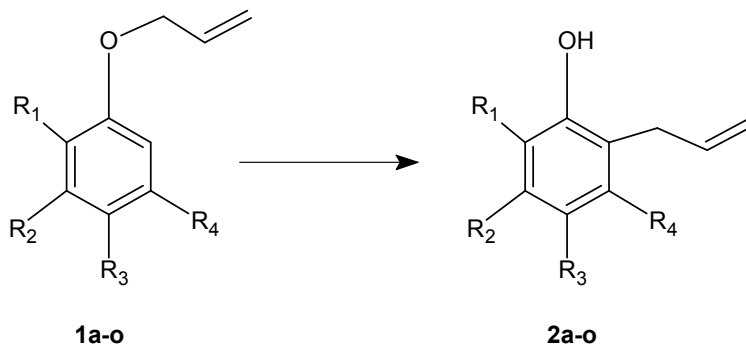
## RESULTS AND DISCUSSION

The protic acid 0.5N H<sub>2</sub>SO<sub>4</sub> and trifluoroacetic acid : water : dioxane (2 : 1 : 1) (TWD) were used as catalysts in the rearrangement of a series of o-allylaryl ethers (**1a-r**), which resulted in very low yield (Tables 1 and 2). These results corroborates to the earlier observations that the hydration of allyl chain probably occur during the rearrangement, which forms the side products<sup>5,6</sup>.

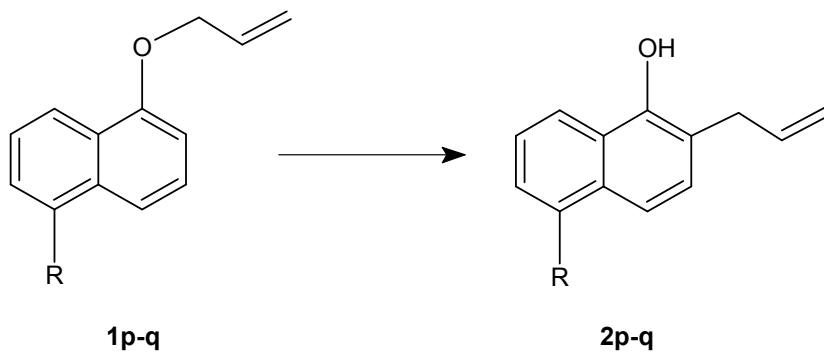
This problem was circumvented by the use of Lewis acid catalysts, which formed a better choice than Bronsted acid in effecting these rearrangements (Tables 3 and 4). Microwave assisted rearrangement of the solution of o-allylaryl ethers (**1a-r**) in xylene in presence of Lewis acid catalyst (BF<sub>3</sub>.OEt<sub>2</sub> / ZnCl<sub>2</sub>) afforded 2-allyl phenols (**2a-r**) in excellent yields (75-92%) (Tables 5 and 6), (**Scheme 1**).

Our results demonstrate that Lewis acid induced rearrangement under MW conditions tolerates a variety of substituents in the substrate and the reaction is slow with electron withdrawing substituents.

All the products (**2a-r**) were characterized on the basis of elemental analysis, IR <sup>1</sup>H NMR (Table 7) and by comparison of these data with authentic samples<sup>7-11</sup>.

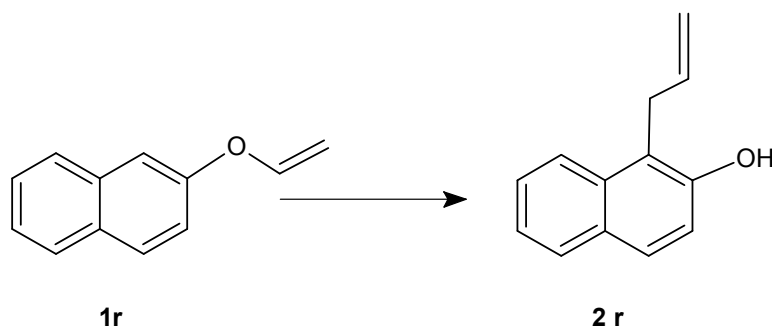


	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>		R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
<b>a</b>	H	H	Br	H	<b>i</b>	OMe	H	H	H
<b>b</b>	Br	H	H	H	<b>j</b>	COOEt	H	H	H
<b>c</b>	H	H	Cl	H	<b>k</b>	COOMe	H	H	H
<b>d</b>	H	H	CH <sub>3</sub>	H	<b>l</b>	CHO	H	H	H
<b>e</b>	H	H	NO <sub>2</sub>	H	<b>m</b>	Br	H	Br	H
<b>f</b>	NO <sub>2</sub>	H	H	H	<b>n</b>	CH <sub>3</sub>	H	CH <sub>3</sub>	H
<b>g</b>	H	CH <sub>3</sub>	H	H	<b>o</b>	H	Br	H	Br
<b>h</b>	CH <sub>3</sub>	H	H	H					



**p**, R = H

**q**, R = OMe



Scheme 1

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