CESIUM FLUORIDE-MEDIATED CLAISEN REARRANGEMENTS OF PHENYL PROPARGYL ETHERS: SUBSTITUENT EFFECTS OF AN *ORTHO*-ALKOXY GROUP ON THE BENZENE RING OR MODIFIED PROPARGYL RESIDUES

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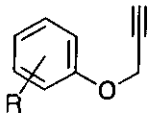
Abstract - The expected 7-alkoxy-2-methylbenzo[*b*]furans were effectively given in the CsF-mediated Claisen rearrangement of phenyl propargyl ethers with an *o*-alkoxy substituent on the benzene ring. On the other hand CsF did not affect the production of the corresponding benzo[*b*]furans when ethers, carrying a propargyl residue modified by either 1,1-dimethyl or 3-ethoxycarbonyl functions, were used as substrates in the rearrangement.

INTRODUCTION

We previously reported that the Claisen rearrangement of phenyl propargyl ethers (**1**) in the presence of cesium fluoride (CsF) (the CsF-mediated Claisen rearrangement)[1] led to the exclusive formation of 2-methylbenzo[*b*]furans (**2**), but not benzo[*b*]pyrans (**3**), and that the rearrangement was dependent upon both the nature and the location of substituents on the benzene ring.[2] As a continuous study we further examined the effects of substituents on the benzene ring or in the propargyl residue on the rearrangement. In this paper we present general effectivity of CsF on the cyclization of ethers with an *o*-alkoxy substituent on the benzene ring to 7-alkoxy-2-methylbenzo[*b*]furans in the CsF-mediated Claisen rearrangement, but ineffectivity of CsF on the formation of expected benzofurans when the ethers with 1- or 3-substituted propargyl residues were used as substrates.



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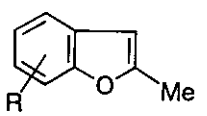

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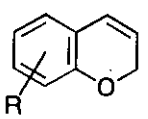

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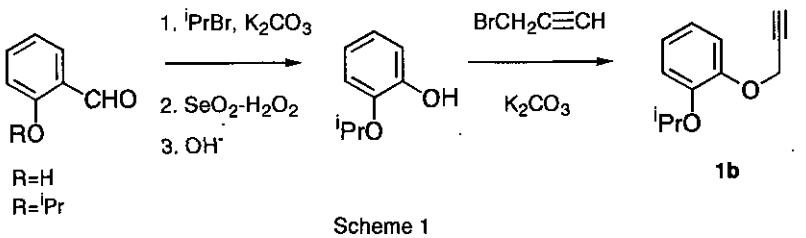
RESULTS AND DISCUSSION

On the Substituent Effect of an *o*-Alkoxy Group on the Benzene Ring on the Cyclization

The Claisen rearrangement of phenyl propargyl ethers smoothly gave cyclized products when a methoxy



Scheme 1

Table 1. The CsF-mediated Claisen rearrangements of phenyl propargyl ethers (**1**) without or with an alkoxy group at the *ortho* position

1 $\xrightarrow[PhNEt_2]{CsF,\ \Delta}$ **2**

entry	**1** (R)	time (h)	**2** (%)
1	**1a** (H)	10	23
2	**1b** (*o*-O^{i}Pr)	2.5	75
3	**1c** (*o*-OBzl)	6.5	76
4[a]	**1d** (*o*-OMe)	4.5	74

[a] The data in the ref 2.

(MeO) group was present at the *ortho* position of the benzene rings.[2] This fact encouraged us to investigate the Claisen rearrangement of other *o*-alkoxyphenyl propargyl ethers with more bulky isopropoxy (^{i}PrO) (**1b**) and a benzyloxy (BzlO) (**1c**) groups in addition to phenyl propargyl ether (**1a**) itself. The ^{i}PrO ether (**1b**) was prepared from salicylaldehyde by four step reactions as shown in Scheme 1.[3]

Phenyl propargyl ethers (**1**) were subjected to Claisen rearrangement under the condition of heating in diethylaniline ($PhNEt_2$) in the presence of CsF under argon (Ar) (Table 1). Although ineffective reaction was observed in the case of **1a** (entry 1), the expected benzofurans (**2b**, **2c**) were given in high yields from **1b** (entry 2) and **1c** (entry 3). Among the rearrangements examined here in addition to the reported rearrangement of the *o*-MeO derivative (**1d**)[2] (entry 4), the ^{i}PrO ether (**1b**) resulted in the most effective cyclization.

Harfenist *et al.*[4] reported that the reaction had been remarkably accelerated when phenyl 1,1-dimethylpropargyl ethers (**4**) were used as substrates in the thermal Claisen rearrangement (the absence of CsF). The acceleration of the reaction could be rationalized by the preference of a conformation A to a conformation B in the transition state of the rearrangement of **4**, in which both cyclizing positions were forced to be close to each other by a steric repulsion between the aromatic ring and the bulky 1,1-dimethyl group on the propargyl residue (*gem*-dimethyl effect)[4] (Figure 1). The effective cyclization in the CsF-mediated Claisen rearrangements of *o*-alkoxyphenyl propargyl ethers (**1**), especially the ^{i}PrO ether (**1b**), might be also caused by the contribution of a conformation C like the conformation A in **4** because of a

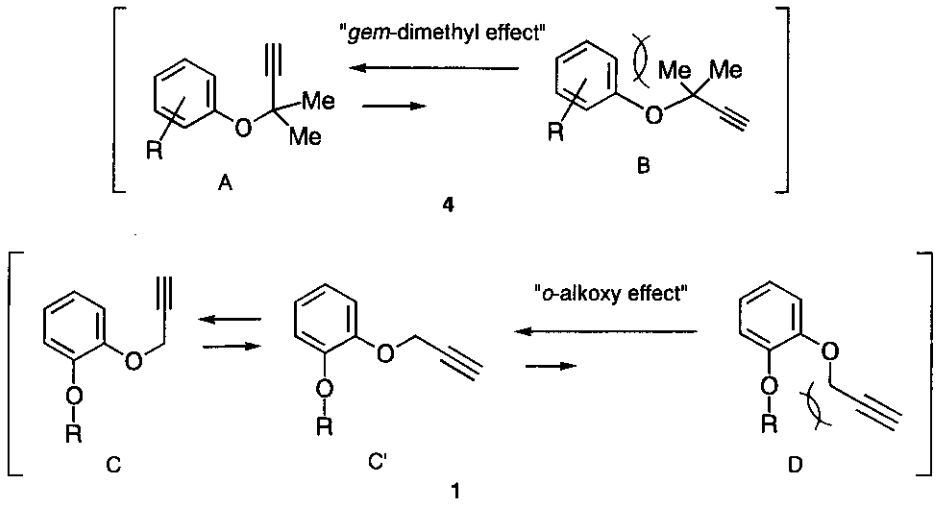
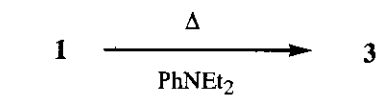


Figure 1. Possible conformations in the transition states of Claisen rearrangement of phenyl 1,1-dimethylpropargyl ether (**4**) or *o*-alkoxyphenyl propargyl ether (**1**)

possible steric repulsion between an alkoxy substituent at the *ortho* position of the benzene ring and the propargyl ether function in conformation D (*o*-alkoxy effect) (Figure 1).

Thermal Claisen rearrangement using **1a** and **1b** was also examined as comparable experiments (Table 2). As expected from the substituent effect in the CsF-mediated Claisen rearrangement mentioned above more smooth cyclization to the pyran (**3b**) was observed in the latter reaction (entry 2). We have already reported the effectiveness of the thermal reaction of the *o*-MeO derivative (**1d**)[2] (entry 3). Thus, it was found that an *o*-alkoxy substituent could play an important role for the product formation in the Claisen rearrangements of phenyl propargyl ethers (**1**), especially in the presence of CsF.

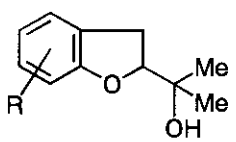
Table 2. Thermal Claisen rearrangements of phenyl propargyl ethers (**1**) with or without an alkoxy group at the *ortho* position



entry	**1** (R)	time (h)	**3** (%)
1	**1a** (H)	16	34
2	**1b** (*o*-O^{i}Pr)	2	55
3[a]	**1d** (*o*-OMe)	3.5	77

[a] The data in the ref 2.

On the Substituent Effect of Modified Propargyl Residues on the Cyclization A 2-(hydroxyisopropyl)dihydrobenzo[*b*]furan (**5**) skeleton as well as a 2,2-dimethyl-3-hydroxybenzo[*b*]pyran (**6**) is one of basic structures in aromatic hemiterpenes widely distributed in nature, such as coumarins or phenylpropanoids.[5] The CsF-mediated Claisen rearrangement of an ether (**4**) with a 1,1-dimethylpropargyl residue may produce a 2-isopropylbenzo[*b*]furan (**7**), which could be a possible synthetic precursor for **5**. We tried to examine the CsF-mediated Claisen rearrangement using 7-(1,1-dimethylpropargyloxy)coumarin



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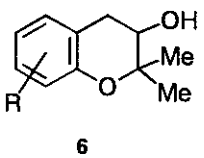

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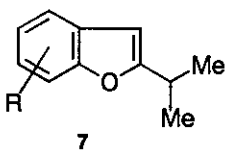

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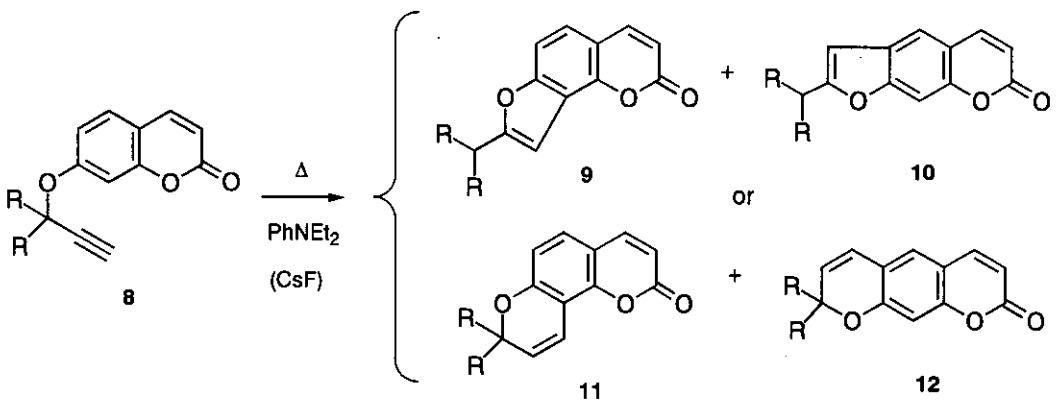
Table 3. The Claisen rearrangements of the propargyl ethers (**8**) derived from 7-hydroxycoumarin



entry	**8** (R)	CsF (M eq)	time	furans (%)		pyrans (%)	
				9	**10**	**11**	**12**
1	**a** (Me)	1.4	10 min	–	–	64	4
2		14	10 min	–	–	64	4
3		–	10 min	–	–	73	6
4	**b** (H)	1.4[a]	8 h	9	1	–	–
5		17[b]	9 h	4	1	–	–
6		–[b]	8 h	–	–	18	1

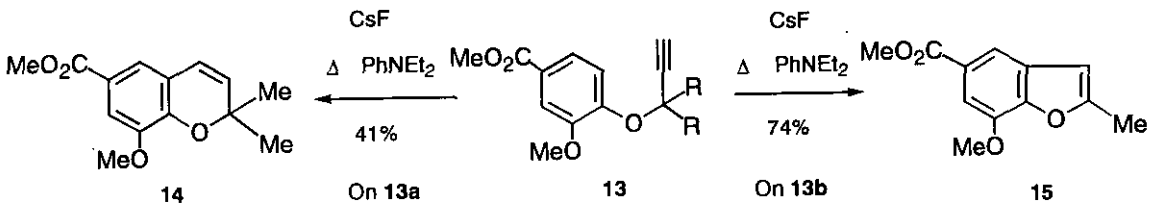
[a] The starting **8b** was recovered in 3 % yield. [b] The starting **8b** was recovered in 2 % yield.

(**8a**), in which (2-isopropylfurano)coumarins (**9a**, **10a**) could be the intended cyclized products (see Table 3). It is known that thermal rearrangement of **8a** smoothly gave angular-type natural (2,2-dimethylpyrano)coumarins, seselin (**11a**) and/or xanthyletin (**12a**), in high yield[6] due to the "*gem*-dimethyl effect"[4] mentioned above.

Treatment of **8a** in $PhNEt_2$ for 10 min under reflux in the presence of 1.4 molar amounts of CsF unexpectedly afforded the pyranocoumarins (**11a**, **12a**), but not the intended furanocoumarins (**9a**, **10a**) (entry 1). No production of **9a** and/or **10a** was observed even if the CsF-mediated Claisen rearrangement was carried out in the presence of a large amount of CsF (14 mol eq) (entry 2). Thermal rearrangement of **8a** afforded pyranocoumarins (**11a**, **12a**)[7] as reported in the literature[6] (entry 3).

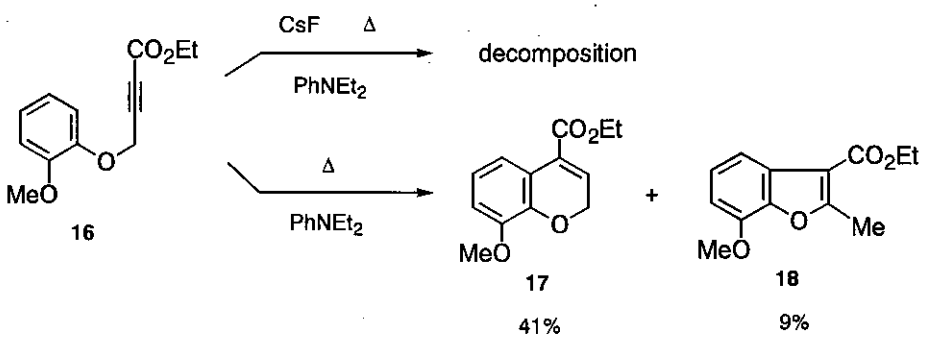
On the other hand furanocoumarins (**9b**, **10b**) were expectedly produced in the CsF-mediated Claisen rearrangement (entries 4, 5) when the ether (**8b**) without the 1,1-dimethyl substituent was used as a substrate, while the isomeric pyranocoumarins (**11b**, **12b**) in the thermal reaction (entry 6), albeit the less effective production of cyclized products in both rearrangements.

These facts suggest that the presence of a 1,1-dimethyl group on the propargyl residue could cause cyclization to a pyran ring even in the CsF-mediated Claisen rearrangement. This assumption was supported by the the CsF-mediated rearrangements using the alternative ethers (**13**) derived from methyl vanillate (Scheme 2). In the case of the 1,1-dimethylpropargyl ether (**13a**) the only isolable product was a benzopyran derivative (**14**), but an expected 2-methylbenzofuran (**15**) was given when used the ether (**13b**) lacking a 1,1-dimethyl group.



Scheme 2

Substitution at the 3 position of the propargyl residue may lead to the corresponding 3-functionalized 2-methylbenzo[*b*]furan in the CsF-mediated Claisen rearrangement. Thus, we next examined both the CsF-mediated and thermal Claisen rearrangements using a model ether (**16**) with an ethoxycarbonylpropargyl residue as a substrate, which could be given by ethoxycarbonylation of the *o*-MeO ether (**1d**).[2] However, only decomposition of **16** was observed in the presence of CsF, while the expected pyran (**17**) was produced in 41% yield in the absence of CsF, in which an isomeric furan derivative (**18**) was also formed in lower yield (9%). (Scheme 3) Thus, modification of the propargyl residue of phenyl propargyl ethers examined here resulted in no production of any benzofuran derivatives in the CsF-mediated Claisen rearrangement.



Scheme 3

CONCLUSION

The effective formation of 7-alkoxy-2-methylbenzo[*b*]furans due to "*o*-alkoxy effect" was observed in the rearrangement of *o*-alkoxyphenyl propargyl ethers. We have already succeeded in total synthesis of some natural products with a four sequentially substitued benzene ring in the molecules using 4-formyl-7-methoxy-2-methylbenzo[*b*]furan as a masked salicylaldehyde, derived from isovanillin through the CsF-mediated Claisen rearrangement of the corresponding propargyl ether.[8] Furthermore 7-benzyloxy-2-methylbenzo[*b*]furan (**2c**) prepared here had been used as a precursor for the basic nitrosation of phenolic compounds, giving potential antiviral-active quinone monoximes.[9] Thus, the CsF-mediated Claisen rearrangement of *o*-alkoxyphenyl propargyl ethers must be widely act as sources of synthetically available 7-alkoxy-2-methylbenzo[*b*]furans.

EXPERIMENTAL

All melting points were measured on a micro melting-point hot stage (Yanagimoto) and are uncorrected. IR spectra were recorded on a JASCO IR-700 spectrophotometer. NMR spectra were recorded in $CDCl_3$ with a Hitachi R-24B (60 MHz) and JEOL FX-270 (270 MHz) and JNM-GSX500A (500 MHz) spectrometers with tetramethylsilane (TMS) as an internal reference, unless otherwise stated. Diffused splitting pattern is abbreviated as dif. EIMS and HREIMS were measured with a Hitachi M-60 spectrometer using a direct inlet system and FABMS and HRFABMS with JEOL JMS-HX110 spectrometer. For column chromatography silica gel 60 (70-230 mesh ASTM; Merck) was used, while for TLC silica gel 60 F254 (Art. 5715, Merck) was used. CsF was heated and powdered under Ar before use.

Phenyl Propargyl Ether (1a) A mixture of phenol (20.2 g, 0.21 mol), propargyl bromide (27 mL, 0.36 mol), and K_2CO_3 (45.8 g, 0.33 mol) in DMF (146 mL) was stirred at rt overnight. After work-up **1a** was given as a colorless oil (26.0 g, 92%), which was purified by distillation [bp 75-80 °C/14 mmHg (lit.,[10] bp 50-51 °C/4 mmHg)].

***o*-Isopropoxyphenyl Propargyl Ether (1b)** (i) *o*-Isopropoxybenzaldehyde: A mixture of salicylaldehyde (6.15 g, 50.3 mmol), isopropyl bromide (9.4 mL, 100 mmol), and K_2CO_3 (13.84 g, 100

mmol) in DMF (50 mL) was stirred at rt for 2 days. After work-up 2-isopropoxybenzaldehyde was given as a pale brown oil (7.91 g, 96%). IR ν_{max} (neat): 1684 cm^{-1}. NMR (500 MHz) δ: 1.40 (6H, d, *J*=6.1 Hz, $CH(CH_3)_2$), 4.68 (1H, septet, *J*=6.1 Hz, $OCH(CH_3)_2$), 6.96-7.02 (2H, m, 3- and 5-H), 7.52 (1H, dt, *J*=7.8, 2.0 Hz, 4-H), 7.82 (1H, dd, *J*=7.8, 2.0 Hz, 6-H), 10.49 (1H, d, *J*=0.7 Hz, CHO). (ii) *o*-Isopropoxyphenol : Selenium dioxide (0.328 g, 2.96 mmol) and 30% H_2O_2 (9.7 mL, 94.9 mmol) were added to a stirred solution of *o*-isopropoxybenzaldehyde (6.01 g, 36.6 mmol) in CH_2Cl_2 (60 mL). The whole was stirred at rt for 3 days and then the excess reagent was decomposed by addition of $NaHSO_3$. After work-up a residual yellow oil (6.30 g) was dissolved in MeOH (56 mL). To the solution was added a solution of KOH (85%, 3.68 g, 55.7 mmol) in MeOH (37 mL) and then the whole was stirred at rt for 21 h. After work-up *o*-isopropoxyphenol was given as a pale brown oil (4.37 g, 78.5%). IR ν_{max} (neat): 3529 cm^{-1}. NMR (500 MHz) δ: 1.36 (6H, d, *J*=6.1 Hz, $CH(CH_3)_2$), 4.58 (1H, septet, *J*=6.1 Hz, $OCH(CH_3)_2$), 5.72 (1H, s, OH), 6.79-6.88 (3H, m, ArH), 6.93 (1H, dd, *J*=7.4, 1.8 Hz, 3-H). (iii) *o*-Isopropoxyphenyl Propargyl Ether (**1b**) : A mixture of *o*-isopropoxyphenol (0.98 g, 6.4 mmol), propargyl bromide (0.80 mL, 10.7 mmol), and K_2CO_3 (1.37 g, 9.93 mmol) in DMF (4.4 mL) was stirred at 50 °C for 2.5 h. After work-up **1b** was given as a colorless oil (1.18 g, 97%), which was purified by distillation (bp 90 °C/50 mmHg). FABMS *m/z*: 190 (M^+). IR ν_{max} (neat): 3290, 2118 cm^{-1}. NMR (500 MHz) δ: 1.35 (6H, d, *J*=6.1 Hz, $CH(CH_3)_2$), 2.48 (1H, t, *J*=2.4 Hz, $CH_2C{\equiv}CH$), 4.51 (1H, septet, *J*=6.1 Hz, $OCH(CH_3)_2$), 4.74 (2H, d, *J*=2.4 Hz, $OCH_2C{\equiv}CH$), 6.89-6.99 (3H, m, ArH), 7.06 (1H, dd, *J*=7.8, 1.7 Hz, ArH). HREIMS *m/z*: 190.1009 (Calcd for $C_{12}H_{14}O_2$: 190.0994).

***o*-Benzyloxyphenyl Propargyl Ether (1c)** A mixture of 2-benzyloxyphenol (0.099 g, 0.49 mmol), propargyl bromide (0.06 mL, 0.84 mmol), and K_2CO_3 (0.106 g, 0.77 mmol) in DMF (0.35 mL) was stirred at 50 °C for 3 h. After work-up purification of the crude product by column chromatography (ethyl acetate : hexane=1 : 20) afforded **1c** as a yellow oil (0.111 g, 95%), which solidified to give light brown prisms, mp 37-42 °C. IR ν_{max} (neat): 3290, 2118 cm^{-1}. NMR (500 MHz) δ: 2.49 (1H, t, *J*=2.5 Hz, $CH_2C{\equiv}CH$), 4.77 (2H, d, *J*=2.5 Hz, $OCH_2C{\equiv}CH$), 5.14 (2H, s, OCH_2Ph), 6.91-6.93 (3H, m, ArH), 7.06-7.09 (1H, m, ArH), 7.28 (1H, t, *J*=7.6 Hz, $CH_2\underline{Ph}$), 7.36 (2H, t, *J*=7.6 Hz, $CH_2\underline{Ph}$), 7.44 (2H, d, *J*=7.6 Hz, $CH_2\underline{Ph}$). HRFABMS *m/z*: 238.0989 (Calcd for $C_{16}H_{14}O_2$: 238.0994).

7-Coumaryl 1,1-Dimethylpropargyl Ether (8a) A mixture of 7-hydroxycoumarin (3.00 g, 18.5 mmol), 1-chloro-1,1-dimethyl-2-propyne[11] (6.32 g, 52.3 mmol), K_2CO_3 (10.8 g, 78.0 mmol), and KI (0.82 g, 4.95 mmol) in acetone (99 mL) and H_2O (29 mL) was stirred for 21 h under reflux. After work-up recrystallization of the crude product from acetone-hexane afforded **8a** as colorless prisms (2.87 g, 68%), mp 140-142 °C (lit.,[12] mp 137-139 °C).

7-Coumaryl Propargyl Ether (8b) A mixture of 7-hydroxycoumarin (2.00 g, 12.3 mmol), propargyl bromide (1.44 mL, 16.2 mmol), and K_2CO_3 (2.28 g, 16.5 mmol) in acetone (66 mL) was stirred for 3 h under reflux. After work-up recrystallization of the crude product from benzene-hexane afforded **8b** as colorless prisms (2.02 g, 82%), mp 119-120 °C (lit.,[13] mp 118 °C).

2-Methoxy-4-methoxycarbonylphenyl 1,1-Dimethylpropargyl Ether (13a) A mixture of methyl

vanillate (16.5 g, 0.091 mol), 1-chloro-1,1-dimethyl-2-propyne (37.1 g, 0.307 mol), K_2CO_3 (37.6 g, 0.271 mol), and tetrabutylammonium hydrosulfate (16.1 g, 0.047 mol) in CH_3CN (160 mL) and H_2O (41 mL) was stirred at 60 °C. After 30 h a mixture of the chloride (18.52 g, 0.153 mol), K_2CO_3 (19.1 g, 0.138 mol), CH_3CN (40 mL), and H_2O (10 mL) was added and then the whole was stirred at 60 °C. Further the chloride (18.02 g, 0.149 mol; 9.01 g, 0.075 mol), K_2CO_3 (19.3 g, 0.140 mol; 9.18 g, 0.066 mol), CH_3CN (60 mL; 40 mL), and H_2O (15 mL; 10 mL) were added to the reaction mixture after 30 h and 27 h, respectively, and then the whole was stirred at 60 °C for 20 h. After work-up purification of the crude product by column chromatography (ether : hexane=1 : 10) followed by recrystallization from ether afforded **13a** as colorless prisms (11.14 g, 49.5%), mp 99-101 °C. *Anal.* Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.69; H, 6.52. IR ν_{max} (nujol): 3244, 2152, 1707 cm^{-1}. NMR (500 MHz) δ: 1.72 (6H, s, CMe_2), 2.58 (1H, s, C≡CH), 3.88 (3H, s, OMe), 3.90 (3H, s, OMe), 7.51 (1H, d, *J*=8.5 Hz, 6-H), 7.57 (1H, d, *J* =2.0 Hz, 3-H), 7.62 (1H, dd, *J* =8.5, 2.0 Hz, 5-H).

2-Methoxy-4-methoxycarbonylphenyl Propargyl Ether (13b) A mixture of methyl vanillate (5.00 g, 27.5 mmol), propargyl bromide (2.48 mL, 32.9 mmol), and K_2CO_3 (4.58 g, 33.1 mmol) in DMF (25 mL) was stirred at rt for 3 h. After work-up purification of the crude product by column chromatography (ethyl acetate : hexane=1 : 20) afforded **9b** as colorless prisms (5.92 g, 98%), mp 81-82 °C, which were recrystallized from ether-hexane. *Anal.* Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.47; H, 5.42. IR ν_{max} (nujol): 3256, 2124, 1712 cm^{-1}. NMR (500 MHz) δ: 2.54 (1H, t, *J*=2.3 Hz, CH_2C-CH), 3.90 (3H, s, OMe), 3.93 (3H, s, OMe), 4.83 (2H, d, *J* =2.3 Hz, OCH_2C≡CH), 7.05 (1H, d, *J* =8.3 Hz, 6-H), 7.57 (1H, d, *J* =1.9 Hz, 3-H), 7.68 (1H, dd, *J* =8.3, 1.9 Hz, 5-H).

3-Ethoxycarbonylpropargyl *o*-Methoxyphenyl Ether (16) To a stirred solution of the *o*-MeO ether[2] (**1d**) (2.00 g, 12.3 mmol) in THF (20 mL) was added a 1.6 M solution of *n*-BuLi in hexane (9.0 mL, 14.4 mmol) at -78 °C under Ar and then the whole was stirred at -30 °C for 0.5 h. After recooled to -78 °C a solution of ethyl chloroformate (1.8 mL, 19 mmol) in THF (10 mL) was added and the whole was stirred at the same temperature for 2 h. After work-up purification of the crude product by column chromatography (benzene) followed by recrystallization from ether-hexane afforded **16** as yellow prisms (1.72 g, 60%), mp 40-41 °C. *Anal.* Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.90; H, 6.06. IR ν_{max} (nujol): 2242, 1700 cm^{-1}. NMR (60 MHz) δ: 1.30 (3H, t, *J*=7.0 Hz, CH_2CH_3), 3.90 (3H, s, OMe), 4.23 (2H, q, *J*=7.0 Hz, OCH_2CH_3), 4.88 (2H, s, OCH_2C≡C), 6.90-6.95 (2H, m, 3'-, 6'-H), 7.01-7.05 (2H, m, 4'-, 5'-H).

General Procedure for the CsF-Mediated Claisen Rearrangement A mixture of a phenyl propargyl ether and CsF in $PhNEt_2$ was heated under Ar. After diluted with ether insoluble materials were removed by decantation. The ethereal solution was washed with 5% HCl and brine, dried over K_2CO_3, and evaporated. The crude product(s) was purified by column chromatography, distillation, and/or recrystallization.

On Phenyl Propargyl Ether (1a): 2-Methylbenzo[*b*]furan (2a) Refluxing **1a** (0.989 g, 7.48 mmol) and CsF (1.48 g, 9.47 mmol) in $PhNEt_2$ (10 mL) for 10 h gave **2a** (0.225 g, 23%) as a colorless oil, bp 105 °C /22 mmHg (lit., [14] bp 105 °C/16 mmHg). *Anal.* Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.24; H, 5.88.

On *o*-Isopropoxyphenyl Propargyl Ether (1b): 7-Isopropoxy-2-methylbenzo[*b*]furan (2b) Refluxing **1b** (0.080 g, 0.42 mmol) and CsF (0.094 g, 0.62 mmol) in $PhNEt_2$ (0.9 mL) for 2.5 h gave **2b** (0.060 g, 75%) as a pale yellow oil. FABMS *m/z*: 190 (M^+). NMR (500 MHz) δ: 1.43 (6H, d, *J*=6.1 Hz, $OCH(CH_3)_2$), 2.47 (3H, d, *J*=1.2 Hz, 2-Me), 4.77 (1H, septet, *J*=6.1 Hz, $OCH(CH_3)_2$), 6.35 (1H, q, *J*=1.2 Hz, 3-H), 6.75 (1H, dd, *J*=6.8, 2.2 Hz, 6-H), 7.04-7.09 (2H, m, 4- and 5-H). HREIMS *m/z*: 190.1013 (Calcd for $C_{12}H_{14}O_2$: 190.0994).

On *o*-Benzyloxyphenyl Propargyl Ether (1c): 7-Benzyloxy-2-methylbenzo[*b*]furan (2c) Refluxing **1c** (0.500 g, 2.10 mmol) and CsF (0.544 g, 3.58 mmol) in $PhNEt_2$ (4.5 mL) for 6.5 h gave **2c** (0.379 g, 76%) as a pale yellow oil. EIMS *m/z*: 238 (M^+, 31.6%), 91 (100%). NMR (500 MHz) δ: 2.48 (3H, t, *J*=1.2 Hz, 2-Me), 5.30 (2H, s, OCH_2Ph), 6.36 (1H, q, *J*=1.2 Hz, 3-H), 6.76 (1H, dd, *J*=7.6, 1.5 Hz, 6-H), 7.04 (1H, t, *J*=7.6 Hz, 5-H), 7.06 (1H, dd, *J*=7.6, 1.5 Hz, 4-H), 7.30-7.40 (3H, m, $CH_2\underline{Ph}$), 7.49 (2H, d, *J*=7.0 Hz, $CH_2\underline{Ph}$). HRFABMS *m/z*: 238.0991 (Calcd for $C_{16}H_{14}O_2$: 238.0994).

On 7-Coumaryl 1,1-Dimethylpropargyl Ether (8a) **8a** (1.13 g, 4.96 mmol) was refluxed with CsF (1.05 g, 6.93 mmol) in $PhNEt_2$ (18 mL) for 10 min. After work-up two products were given: (i) **Seselin (11a)** (0.719 g, 64%), colorless prisms (from acetone-hexane), mp 118-120 °C (lit.,[12] mp 119-120 °C), was obtained as a less polar component and (ii) **Xanthyletin (12a)** (0.049 g, 4%), colorless prisms (from acetone-hexane), mp 130-132 °C (lit.,[15] mp 131-132 °C) was obtained as a more polar component.

On 7-Coumaryl Propargyl Ether (8b) **8b** (3.64 g, 18.2 mmol) was heated at 180 °C in $PhNEt_2$ (58 mL) with CsF (3.87 g, 25.5 mmol) for 8 h. After work-up two products were given: (i) **8-Methyl-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (9b)** (0.329 g, 9%), pale yellow prisms (from MeOH), mp 155-156 °C (lit.,[16] mp 153-154 °C). *Anal.* Calcd for $C_{12}H_8O_3$: C, 71.99; H, 4.03. Found: C, 71.82; H, 4.08. IR (nujol) 1730 cm^{-1}. NMR (270 MHz) δ: 2.51 (3H, d, *J*=1.2 Hz, 8-Me), 6.36 (1H, d, *J*=9.5 Hz, 3-H), 6.72 (1H, m, 9-H), 7.28 (1H, d, *J*=8.6 Hz, 5-H), 7.34 (1H, dd, *J*=8.6, 0.9 Hz, 6-H), 7.79 (1H, d, *J*=9.5 Hz, 4-H) and (ii) **7-Methyl-2*H*-furo[2,3-*g*]-1-benzopyran-2-one (10b)** (0.041 g, 1%), pale yellow prisms (from MeOH), mp 148-149 °C (lit.,[17] mp 151 °C). *Anal.* Calcd for $C_{12}H_8O_3$: C, 71.99; H, 4.03. Found: C, 71.89; H, 4.08. IR (nujol) 1730 cm^{-1}. NMR (270 MHz) δ: 2.48 (3H, d, *J*=0.9 Hz, 2-Me), 6.35 (1H, d, *J*=9.5 Hz, 6-H), 6.42 (1H, s, 3-H), 7.37 (1H, s, 9-H), 7.52 (1H, s, 4-H), 7.77 (1H, d, *J*=9.5 Hz, 5-H).

On 1,1-Dimethylpropargyl 2-Methoxy-4-methoxycarbonylphenyl Ether (13a): 2,2-Dimethyl-8-methoxy-6-methoxycarbonylbenzo[*b*]pyran (14) Heating **13a** (0.073 g, 0.29 mmol) and CsF (0.067 g, 0.44 mmol) in $PhNEt_2$ (0.7 mL) at 210 °C for 1 h gave **14** (0.030 g, 41%) as a colorless oil, bp 120-130 °C /5 mmHg. HRFABMS *m/z*: 248.1059 (Calcd for $C_{14}H_{16}O_4$: 248.1049). IR (neat) 1715 cm^{-1}. NMR (500 MHz) δ: 1.50 (6H, s, CMe_2), 3.88 (3H, s, OMe), 3.91 (3H, s, OMe), 5.66 (1H, d, *J*=9.8 Hz, 3-H), 6.33 (1H, d, *J*=9.8 Hz, 4-H), 7.38 (1H, d, *J*=1.9 Hz, 7-H), 7.45 (1H, d, *J*=1.9 Hz, 5-H).

On 2-Methoxy-4-methoxycarbonylphenyl Propargyl Ether (13b): 7-Methoxy-5-

methoxycarbonyl-2-methylbenzo[*b*]furan (15) Heating **13b** (2.12 g, 9.61 mmol) and CsF (2.19 g, 14.4 mmol) in $PhNEt_2$ (20 mL) at 210 °C for 48 h gave **15** (1.57 g, 74%) as colorless prisms (from hexane), mp 77-81 °C. *Anal.* Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.39; H, 5.46. IR (nujol) 1715 cm^{-1}. NMR (500 MHz) δ: 2.49 (3H, d, *J*=0.9 Hz, 2-Me), 3.93 (3H, s, OMe), 4.05 (3H, s, OMe), 6.43 (1H, br d, *J*=0.9 Hz, 3-H), 7.45 (1H, d, *J* =1.2 Hz, 6-H), 7.85 (1H, d, *J* =1.2 Hz, 4-H).

General Procedure for Thermal Claisen Rearrangement A solution of an aryl propargyl ether in $PhNEt_2$ was heated under Ar. After diluted with ether the ethereal solution was treated as in the CsF-mediated Claisen rearrangement.

On Phenyl Propargyl Ether (1a): Benzo[*b*]pyran (3a) Refluxing **1a** (1.029 g, 7.79 mmol) in $PhNEt_2$ (4 mL) for 16 h gave **3a** (0.353 g, 34%) as a colorless oil, bp 87-90 °C/14 mmHg (lit.,[9] bp 91-92 °C/14 mmHg). *Anal.* Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.74; H, 5.91.

On *o*-Isopropoxyphenyl Propargyl Ether (1b): 8-Isopropoxybenzo[*b*]pyran (3b) Refluxing **1b** (0.097 g, 0.51 mmol) in $PhNEt_2$ (0.5 mL) for 2 h gave **3b** (0.053 g, 55%) as a labile pale yellow oil. FABMS *m/z*: 190 (M^+). NMR (500 MHz) δ: 1.35 (6H, d, *J*=6.1 Hz, $CH(CH_3)_2$), 4.49 (1H, septet, *J*=6.1 Hz, $OCH(CH_3)_2$), 4.85 (2H, dd, *J*=3.7, 1.9 Hz, 2-H_2), 5.78 (1H, dt, *J*=9.8, 3.7 Hz, 3-H), 6.40 (1H, dt, *J*=9.8, 1.9 Hz, 4-H), 6.61 (1H, dd, *J*=6.3, 2.7 Hz, 7-H), 6.70-6.80 (2H, m, 5- and 6-H).

On 7-Coumaryl 1,1-Dimethylpropargyl Ether (8a) Refluxing **8a** (1.00 g, 4.38 mmol) in $PhNEt_2$ (16 mL) for 10 min gave seselin (**11a**) (0.730 g, 73%) and xanthyletin (**12a**) (0.059 g, 6%).

On 7-Coumaryl Propargyl Ether (8b) Refluxing **8b** (3.00 g, 15 mmol) in $PhNEt_2$ (48 mL) for 8 h gave two products: (i) **2*H*,8*H*-Benzo[1,2-*b*;3,4-*b*']dipyran-2-one (11b)** (0.554 g, 18%) was obtained as less polar colorless prisms (from ethyl acetate), mp160-162 °C (lit.,[18] mp 163 °C). *Anal.* Calcd for $C_{12}H_8O_3$: C, 71.99; H, 4.03. Found: C, 71.95; H, 4.11. IR (nujol) 1720 cm^{-1}. NMR (270 MHz) δ: 4.94 (2H, dd, *J*=3.5, 2.0 Hz, 8-H_2), 5.87 (1H, dt, *J*=10.1, 3.5 Hz, 9-H), 6.24 (1H, d, *J*=9.5 Hz, 3-H), 6.71 (1H, dd, *J*=8.4, 0.6 Hz, 6-H), 6.97 (1H, ddt, *J*=10.1, 2.0, 0.6 Hz, 10-H), 7.20 (1H, d, *J*=8.4 Hz, 5-H), 7.59 (1H, d, *J*=9.5 Hz, 4-H) and (ii) **2*H*,8*H*-Benzo[1,2-*b*;5,4-*b*']dipyran-2-one (12b)** (0.067 g, 2%) was obtained as more polar pale yellow prisms (from ethyl acetate), mp176-178 °C (lit.,[18] mp 173 °C). *Anal.* Calcd for $C_{12}H_8O_3$: C, 71.99; H, 4.03. Found: C, 71.82; H, 4.09. IR (nujol) 1720 cm^{-1}. NMR (270 MHz) δ: 4.94 (2H, dd, *J*=3.4, 1.8 Hz, 8-H_2), 5.81 (1H, dt, *J*=10.0, 3.4 Hz, 7-H), 6.23 (1H, d, *J*=9.5 Hz, 3-H), 6.42 (1H, dt, *J*=10.0, 1.8 Hz, 6-H), 6.70 (1H, s, 10-H), 7.00 (1H, s, 5-H), 7.57 (1H, d, *J*=9.5 Hz, 4-H).

On 3-Ethoxycarbonylpropargyl *o*-Methoxyphenyl Ether (16) Refluxing **16** (0.200 g, 0.85 mmol) in $PhNEt_2$ (2 mL) for 2 h gave two cyclized products: (i) **3-Ethoxycarbonyl-7-methoxy-2-methylbenzo[*b*]furan (18)** (0.018 g, 9%) was obtained as a less polar colorless oil, bp 120-130 °C /5 mmHg, which was solidified to give colorless prisms, mp 47-48 °C. HRFABMS *m/z*: 234.0898 (Calcd for $C_{13}H_{14}O_4$: 234.0892). IR (nujol) 1710 cm^{-1}. NMR (500 MHz) δ: 1.37 (3H, t, *J*=7.2 Hz, CH_2CH_3), 2.72 (3H, s, 2-Me), 3.94 (3H, s, OMe), 4.34 (2H, q, *J*=7.2 Hz, OCH_2CH_3), 6.74 (1H, d, *J*=7.6 Hz, 6-H), 7.15 (1H, t, *J*=7.6 Hz, 5-H), 7.48 (1H, d, *J*=7.6 Hz, 4-H) and (ii) **4-Ethoxycarbonyl-8-methoxy-2-**

methylbenzo[*b*]pyran (17) (0.081 g, 41%) was obtained as a more polar labile colorless oil, bp 130-140 °C /5 mmHg. IR (neat) 1720 cm^{-1}. NMR (500 MHz) δ: 1.36 (3H, t, *J*=7.1 Hz, CH_2CH_3), 3.89 (3H, s, OMe), 4.32 (2H, q, *J*=7.1 Hz, OCH_2CH_3), 4.89 (2H, d, *J*=4.1 Hz, 2-H_2), 6.83 (1H, t, *J*=4.1 Hz, 3-H), 6.85 (1H, t, *J*=8.0 Hz, 7-H), 6.92 (1H, t, *J*=8.0 Hz, 6-H), 7.52 (1H, d, *J*=8.0 Hz, 5-H).

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