Boron Trichloride Mediated Regioselective Claisen Rearrangement of Resorcinol Derivatives: Application to Resorcinol Carvonyl Ethers

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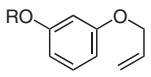
Abstract: Claisen rearrangement (CR) of resorcinol allyl ethers was examined. Although thermal CR gave low regioselectivity, the selectivity was much improved in the presence of a Lewis acid such as boron trichloride. This rearrangement was successfully applied to resorcinol carvonyl ethers for the regioselective introduction of a carvone unit into the resorcinol skeleton for the synthesis of phytoestrogenic miroestrols.

Key words: carvone, boron trichloride, rearrangement, regioselectivity, resorcinol

The Claisen rearrangement (CR)[1] is a versatile carbon–carbon bond-forming reaction whose aromatic version has been successfully used to introduce a C3-unit at the ortho position of phenols. However, the thermal CR of resorcinol derivatives (e.g., **1**, Figure 1) to give 6-isomers **2** and 2-isomers **3** as rearranged products (Scheme 1) usually proceeds with low regioselectivity.[2,3] Several examples of regioselective rearrangement have been reported: for example, the photo-CR of the methoxy-substituted derivative **1a** in the presence of α-cyclodextrin affords 6-allyl-3-methoxyphenol (**2a**) exclusively.[4] Regioselective Lewis acid mediated CR of allyl ethers has also been reported. For example, CR of the TBS-substituted derivative **1b** in the presence of diethylaluminum chloride (Et_2AlCl) gave a 6:1 mixture of **2b** and **3b**,[5] and $BF_3{\cdot}OEt_2$-mediated CR of the 1,1-dimethylallyl ether of the cinnamate derivative **4** gave a 10:1 mixture of **5** and **6**.[6] In these cases, 6-isomer **2b** or **5** was predominantly formed (Scheme 1).

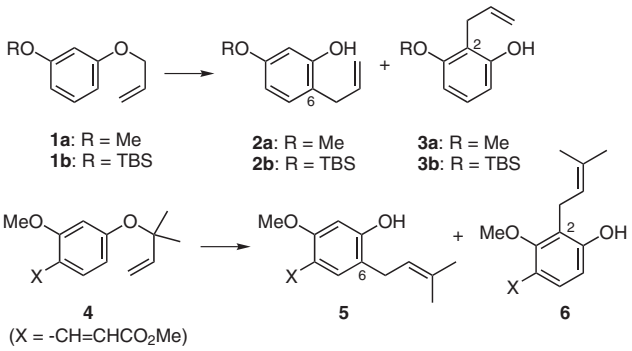


1

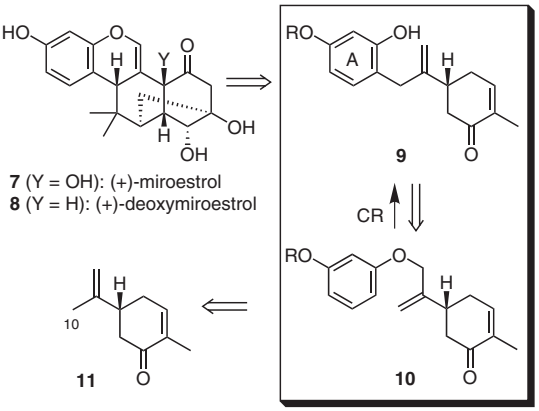
a: R = Me **e**: R = Bz
b: R = TBS **f**: R = H
c: R = TIPS
d: R = TBDPS

Figure 1 The structure of the substrate **1** for CR

As a part of our study of the chemical components of the Thai miracle herb 'kwao keur' (identified as *Pueraria mirifica*),[7] we have sought to synthesize the strongly phytoestrogenic compounds (+)-miroestrol (**7**)[8] and (+)-deoxymiroestrol (**8**). In our strategy, regioselective CR of the resorcinol carvonyl ether **10** is the key step for the introduction of (*R*)-carvone (**11**) to the A ring, as shown in Scheme 2.[9] In this article, we report in detail on our study of the regioselective CR of simple resorcinol derivatives and its application to carvonyl ethers for the synthesis of phytoestrogenic miroestrols.



Scheme 1 Reported CR of resorcinol derivatives **1** and **4**



Scheme 2 Retrosynthesis of (+)-miroestrol (**7**) and (+)-deoxymiroestrol (**8**)

Starting resorcinol allyl ethers **1** (shown in Figure 1) were prepared by conventional methods.[3] 1-Allyloxy-3-silyloxybenzenes **1b–d** were prepared by successive reactions of allylation of resorcinol monobenzoate (**12e**), hydrolysis of the corresponding benzoate **1e** to resorcinol **1f**, and silylation. TBDPS-substituted crotyl **13** (Z = H) and prenyl derivatives **13** (Z = Me) were obtained in a similar manner from **12e** using crotyl chloride or 3,3-dimethylallyl bromide, respectively (Figure 2).

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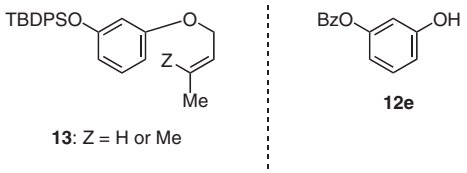
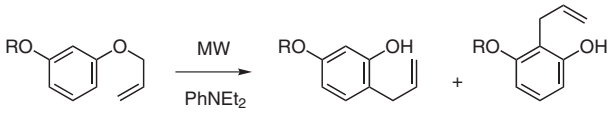


Figure 2 Structures of substrates **13** for CR and starting material **12e**

First we examined the microwave (MW)-mediated thermal CR[10] (Table 1). Reaction of allyl 3-methoxyphenyl ether (**1a**) at 250 °C in *N*,*N*-diethylaniline ($PhNEt_2$) as a solvent gave rearranged products **2a** and **3a** in 48 and 32% yield, respectively (entry 1). The regioselectivity was not improved by lowering the reaction temperature (entry 2), and CR of the corresponding silyloxy derivatives did not give improved regioselectivity (entries 3-5). However, effective conversions were observed in the latter rearrangements, independent of the size of silyloxy substituents.

Table 1 MW-Mediated Thermal CR of Resorcinol Allyl Ethers **1**

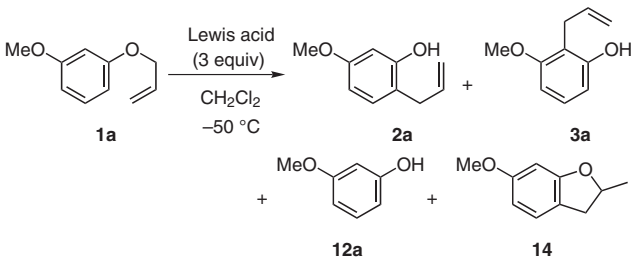


Entry	R in **1**	Conditions[a]	Yield (%)[b]		
			2	**3**	Total
1	**1a**: Me	250 °C, 30 min	48	32	80
2	**1a**: Me	100–180 °C, 75 min	17[c]	11[c]	28
3	**1b**: TBS	250 °C, 30 min	55	34	89
4	**1c**: TIPS	250 °C, 30 min	58	36	94
5	**1d**: TBDPS	250 °C, 30 min	61	34	95

[a] MW condition: Discover (CEM), 300 W, 47–48 psi.
[b] Isolated yield, unless otherwise noted.
[c] Estimated by ^1H NMR spectroscopy.

Next, we examined the Lewis acid-mediated CR of methyl ether **1a** (Table 2). High regioselectivity was observed in the presence of an excess (3 equiv) of boron trichloride, to give rearranged products **2a** and **3a** in 62 and 11% yield, respectively, albeit with concomitant generation of the deallylated product **12a** in 8% yield (entry 1). The reaction of **1a** with aluminum trichloride yielded **2a** as a major product with the better regioselectivity of 30:1, but the yield was slightly decreased due to the formation of byproducts such as **12a** (5%) and dihydrobenzofuran **14**[11] (6%) (entry 2). The weaker Lewis acid Et_2AlCl gave no by-products (entry 3), but the reaction did not go to completion and the selectivity was not better than that in the reaction with BCl_3. Thus, BCl_3 was found to be the most suitable reagent for this reaction.

Table 2 Effects of Lewis Acids on CR of Methyl Ether **1a**

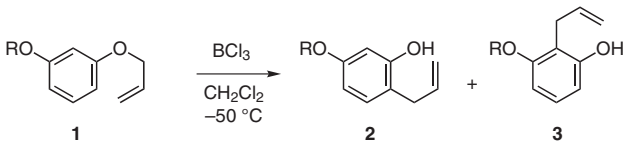


Entry	Lewis acid	Time (h)	Yield (%)[a]			
			1a	**2a**	**3a**	Others
1	BCl_3	1	0	62	11	**12a** (8%)
2	$AlCl_3$	1	0	59	2	**12a** (5%), **14** (6%)
3[b]	Et_2AlCl	5.5	35	44	6	–

[a] Isolated yield.
[b] The reaction mixture was gradually warmed to –20 °C.

Next, the BCl_3-mediated CR of allyl ethers **1** with various silyloxy substituents at the meta position was examined (Table 3). Compared with the result of methyl ether **1a**, both chemical yield and regioselectivity were improved in every case. As the bulkiness of the silyl group increased, the chemical yield increased and the regioselectivity improved (entries 2–4). For the CR of TBS ether **1b** (entry 2), the regioselectivity found was very similar to that observed previously using Et_2AlCl as a Lewis acid.[5] For the CR of TBDPS ether **1d** (entry 4), the total chemical yield and selectivity were up to 95% and 8.5:1, respectively.

Table 3 BCl_3-Mediated CR of **1** with Various Meta Substituents



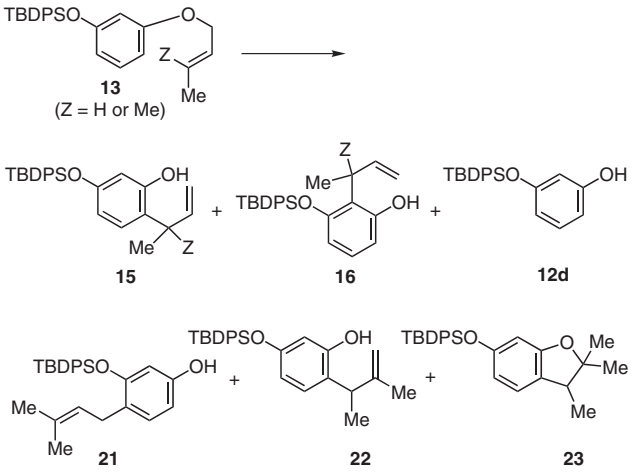
Entry	R in **1**	BCl_3 (equiv)	Time (h)	Yield (%)[a]		
				2	**3**	Total
1[b]	**1a**: Me	3	1	62	11	73
2	**1b**: TBS	3	1	75	13	88
3	**1c**: TIPS	3	1	77	11	88
4	**1d**: TBDPS	3	1	85	10	95
5	**1d**: TBDPS	1	1	84	8	92
6[c]	**1d**: TBDPS	1	5	77	5	82

[b] The data from entry 1 in Table 2.
[b] Isolated yield.
[c] The reaction was carried out at –78 °C.

Reaction with 1 equivalent of BCl_3 (entry 5) gave almost the same yield and selectivity as that with three equivalents of BCl_3 (entry 4). The selectivity was improved to 15:1 when the reaction was carried out at –78 °C (entry 6).

Furthermore, the CRs of the crotyl **13** (Z = H) and prenyl ethers **13** (Z = Me) with a silyloxy substituent were examined (Table 4). Under MW-mediated condition, the CR of **13** (Z = H) mainly afforded the 6-isomer **15** (Z = H) (entry 1). The regioselectivity was estimated to be 4:1, which was higher than that obtained for the simple allyl ether **1d** (see entry 5 in Table 1). BCl_3-mediated CR improved the regioselectivity to 10:1 (entry 2).

Table 4 CR of Crotyl **13** (Z = H) and Prenyl Ether **13** (Z = Me)



Entry	Z in **13**	Conditions[a]	Yield (%)[b]					
			15	**16**	**12d**	**21**	**22**	**23**
1	H[c]	A	64	14	0	0	0	0
2	H[c]	B	85	8	4	0	0	0
3	Me	A	0	0	10	58	14	7
4	Me	C	0	0	3	68	12	0
5	Me	B	26	0	32	0	0	0

[a] Conditions; A: in $PhNEt_2$, MW, 250 °C, 0.5 h; B: BCl_3 (1 equiv), in CH_2Cl_2, –50 °C, 1 h; C: in $PhNEt_2$, MW, 200 °C, 0.5 h.
[b] Isolated yield.
[c] A 5:1 *trans/cis* mixture.

The thermal CR of phenyl prenyl ether (**17**) has been reported to generate 4-isomer **18**, through a double rearrangement, and the abnormal Claisen product **19** in around 72 and 30% yield, respectively, without the formation of the normal Claisen product **20** (Figure 3).[12,13] Indeed, we found that thermal CR of the prenyl ether **13** (Z = Me) gave neither the 6-isomer **15** (Z = Me) nor the 2-isomer **16** (Z = Me); rather, the double rearranged 4-isomer **21** was formed as a major product in 58% yield together with three other products, namely the phenol **12d** (10%), the abnormal Claisen product **22** (14%), and its cyclized product **23** (7%) (entry 3). Generation of the abnormal Claisen product **22** was not suppressed in the CR of **13** (Z = Me) at lower temperature, but the yield of 4-isomer **21** increased (entry 4).[14] The ratio of normal/abnormal Claisen product was estimated to be 3:1 to 5:1, which is similar to the ratio obtained previously using the simple phenyl ether **17**.[12,13] Unexpectedly, the BCl_3-mediated CR of **13** (Z = Me) afforded the desired compound **15** (Z = Me) in a low yield of 26% (entry 5).

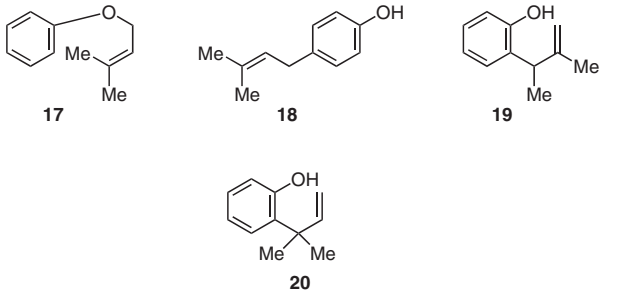
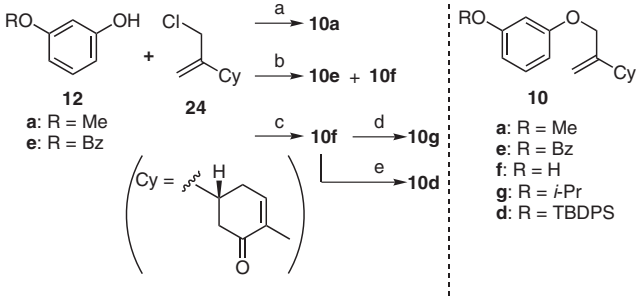


Figure 3 The structures of phenyl prenyl ether (**17**) and its rearranged products

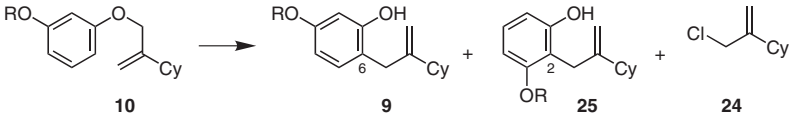
Finally, we subjected the resorcinol carvonyl ethers **10** to CR in order to introduce a carvone unit into the resorcinol skeleton. The starting carvonyl ethers **10** were prepared as follows: direct displacement of the chlorine atom of 10-chlorocarvone (**24**)[15] with resorcinol monomethyl ether (**12a**) in the presence of K_2CO_3 afforded the corresponding 3-methoxyphenyl ether **10a**. On the other hand, carvonylation of resorcinol monobenzoate (**12e**) yielded the desired benzoate **10e** and resorcinol carvonyl ether (**10f**) by partial hydrolysis of **10e** in the reaction course in 40 and 18% yield, respectively. Thus, complete hydrolysis of the crude mixture of the last reaction gave **10f** in 70% yield. The corresponding isopropyl **10g** and TBDPS derivatives **10d** were obtained by alkylation or silylation, respectively, of the phenol **10f** (Scheme 3).



Scheme 3 Synthesis of resorcinol carvonyl ethers **10**. *Reagents and conditions*: (a) from **12a**: K_2CO_3, DMF, 70 °C, 9 h, 77%; (b) from **12e**: K_2CO_3, DMF, 60 °C, 6 h, 40% for **10e**, 18% for **10f**; (c) from **12e**: 1. K_2CO_3, DMF, 60 °C, 6 h, 2. KOH, MeOH, 0 °C, 30 min, 70%; (d) 2-bromopropane, K_2CO_3, DMF, 50 °C, 4 h, 85%; (e) TBDPSCl, imidazole, DMF, r.t., 4 h.

Similar to the case of the simple resorcinol allyl ethers **1**, the MW-mediated CR of **10** gave 6-carvonyl resorcinols **9** and 2-carvonyl resorcinols **25** in unsatisfactory yield and regioselectivity. Hence, we examined BCl_3-mediated CR (Table 5). When the methoxy **10a** and phenolic **10f**

Table 5 BCl_3-Mediated CR of Resorcinol Carvonyl Ethers **10**



Entry	R in **10**	Conditions	Yield (%)[a]		
			9	**25**	**24**
1	**10a**: Me	–50 to –20 °C, 3 h	54	10	19
2	**10f**: H	–50 °C, 3 h	51	9	8
3	**10e**: Bn	–50 °C, 1 h	23	9	33
4	**10g**: *i*-Pr	–50 °C, 1 h	5[b]		17
5	**10d**: TBDPS	–50 °C, 1 h	76[c]	6[c]	0

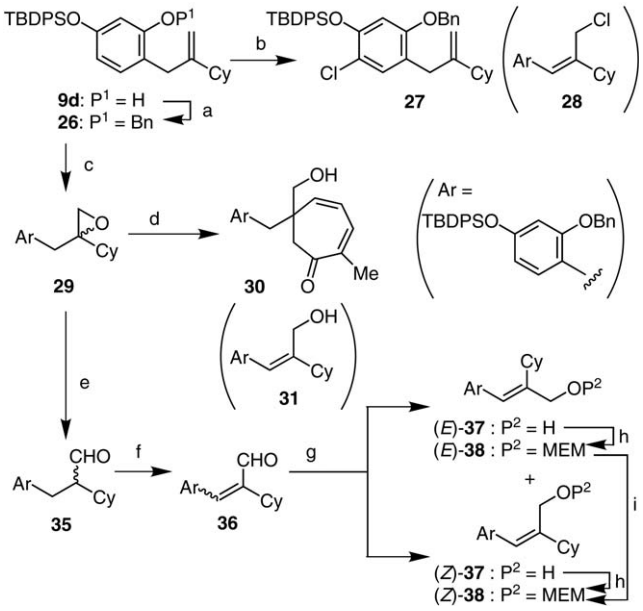
[a] Isolated yields from corresponding **10** unless otherwise noted.
[b] A 4: 1 mixture of **9g** and **25g**.
[c] Isolated yields from **10f** in two steps.

derivatives were used as substrates (entries 1,2), the regioselectivities were almost the same as that obtained in the CR of **1a**; by contrast, the reaction with the benzoyloxy-substituted ether **10e** (entry 3) proceeded with a lower regioselectivity than was observed for the CR of **1a**. The isopropyl derivative **10g** gave a complex mixture containing small amounts of **9g**, **25g** and **24** because of the lability of the isopropyl group under acidic conditions (entry 4). As expected, the yield and regioselectivity were improved (**9d**:**25d** = 13:1, 76% yield for **9d**) when the TBDPS ether **10d** was used (entry 5).

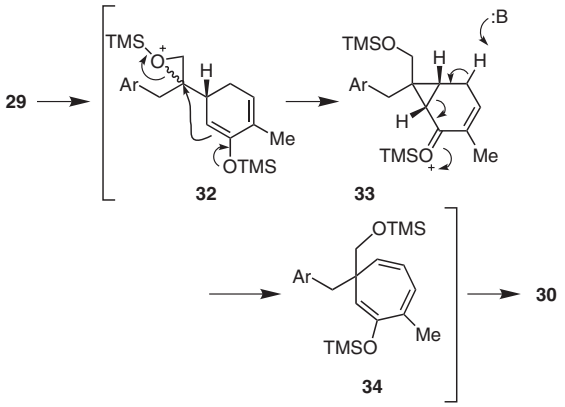
Introduction of a halogen or oxygen function into the carvone unit in the desired rearranged product **9d** was attempted, because these functions play an important role in later steps in our synthetic strategy (Scheme 4). Direct allylic chlorination on **26**, which was prepared by benzylation of the phenol **9d** via the same procedure as was used to prepare 10-chlorocarvone (**24**) from carvone (**11**), afforded the chlorobenzene **27** but not the desired allylic chloride **28**. Therefore, we tried a stepwise procedure via epoxide **29** starting from **26**.

Epoxidation of **26** with MCPBA afforded the corresponding epoxide **29** as a 1.2:1 mixture of diastereoisomers. First, the rearrangement of **29** to allyl alcohol **31** under basic conditions was examined. No reaction occurred when epoxide **29** was treated with two equivalents of LDA, and the addition of HMPA resulted in a complex mixture. Treatment of epoxide **29** with TMSOTf in the presence of Et_3N[16] followed by deprotection of the newly introduced TMS group afforded the eucarvone derivative **30**. The formation of **30** can be plausibly explained by the mechanism shown in Scheme 5, in which the silyl enol ether **32** is converted into the [4.1.0] bicyclic system **33** followed by expansion to the seven-membered ring product **34** accompanying desilylation.[17]

On the other hand, treatment of epoxide **29** with $BF_3{\cdot}OEt_2$ gave aldehyde **35** as a 1:1 mixture of diastereoisomers.[18] Dehydrogenation of **35** with DDQ yielded the enal **36** (*E*/*Z* = 1:3), which was subjected to selective reduction of the aldehyde moiety with sodium triacetoxyborohydride [$NaBH(OAc)_3$][19] followed by separation of diastereoisomers by column chromatography, to give the *Z*-alcohol (*Z*)-**37** and *E*-alcohol (*E*)-**37** in 60% and 13% yield, respectively. The relative configuration of each isomer was



Scheme 4 *Reagents and conditions*: (a) benzyl bromide, KI, K_2CO_3, DMF, r.t., 3 h, 94%; (b) from **26**: $Ca(OCl)_2$, CH_2Cl_2, H_2O, SiO_2, r.t., 6 h, 48%; (c) from **26**: MCPBA, CH_2Cl_2, –10 °C, 18 h, 67%; (d) 1. TMSOTf, Et_3N, CH_2Cl_2, 0 °C, 30 min, 2. alumina column chromatography, 3. $TsOH{\cdot}H_2O$, MeOH, r.t., 30 min, 47%; (e) $BF_3{\cdot}OEt_2$, CH_2Cl_2, –20 °C, 40 min, 49% from **26**; (f) DDQ, benzene, reflux, 7 h, 53%, *E*/*Z* = 1: 3; (g) $NaBH_4$, AcOH, benzene, reflux, 2.5 h, then separation, 60% for (*Z*)-**37**, 13% for (*E*)-**37** from **35**; (h) MEMCl, *i*-$PrNEt_2$, DMF, 60 °C, 2 h, 81% for (*Z*)-**38**, 91% for (*E*)-**38**; (i) *hν*, benzene, acetophenone, r.t., 1 h, 41% for (*Z*)-**38**, 29% recovery for (*E*)-**38**.



Scheme 5 Proposed mechanism for the ring expansion of **29** to **30**

determined from the NOE enhancements (Figure 4). The alcohols (*Z*)- and (*E*)-**37** were converted into the corresponding MEM ethers (*Z*)- and (*E*)-**38** in 81% and 91% yield, respectively. Irradiation of (*E*)-**38** with UV light caused it to be partially isomerized to (*Z*)-**38** (41% yield), with recovery of the starting (*E*)-**38** in 29% yield.

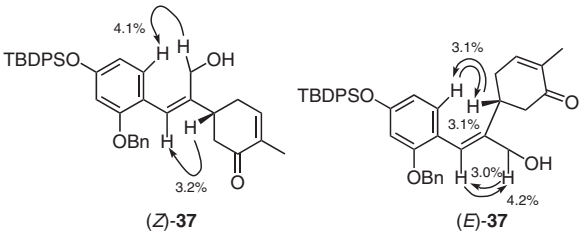


Figure 4 Selected NOE enhancements of (*Z*)- and (*E*)-**37**

In conclusion, we found that BCl_3 was a suitable Lewis acid for the regioselective CR of resorcinol allyl ethers **1a–d** to afford the 6-isomers **2a–d** as major products in good yield and with high regioselectivity (up to 15:1). The yield and regioselectivity of these reactions depended on the substituent at the meta position of **1** and the Lewis acid utilized. CR of the crotyl ether **13** (Z = H) gave the corresponding crotyl resorcinols **15** (Z = H) and **16** (Z = H) in a ratio of 4:1 under thermal conditions, and in a ratio of 10:1 under Lewis acid conditions. CR of the prenyl ether **13** (Z = CH_3) afforded mainly the 4-isomer **21** under thermal conditions, but afforded the 6-isomer **15** (Z = CH_3) under Lewis acid conditions, albeit in low yield. In the BCl_3-mediated CR of the carvonyl ether **10d** with a TBDPS function, the 6-isomer **9d** was preferentially formed with regioselectivity of up to 13:1. The rearranged product **9d** was transformed into the desired MEM ether (*Z*)-**38** in six steps. Further manipulations aimed at the total synthesis of miroestrols are under investigation in our laboratory.

All melting points were measured on a micro melting-point hot stage (Yanaco) and uncorrected. IR spectra were recorded on a JASCO FT/IR-300E spectrophotometer; ATR = attenuated total reflectance system. ^{1}H NMR spectra were recorded on JEOL JNM-GSX400A (400 MHz), -ECP400 (400 MHz) or -ECP600 (600 MHz), using tetramethysilane (0.00 ppm) as an internal standard; ^{13}C NMR spectra were recorded on JEOL JNM-ECP400 (100 MHz) or -ECP600 (150 MHz), using the middle resonance of $CDCl_3$ (77.0 ppm) as an internal standard; δ in ppm, *J* in Hz, dif. = diffused. EIMS were recorded on a JEOL GC-Mate with direct inlet. FABMS were recorded on a JMS-HX110 with *m*-nitrobenzyl alcohol as a matrix. SiO_2 60 F254 (Merck) was used for TLC, and SiO_2 60 (Kanto Chemicals, No. 375674-85) or Al_2O_3 (Merck, 1097) for column chromatography (CC). Biotage Horizon system was used for flash chromatography. Anhyd CH_2Cl_2, Et_2O, and DMF were purchased from Kanto Chemicals. Anhyd THF was purchased from Wako Chemicals. Microwave irradiation was done in a CEM Discover system in a sealed tube.

2-Allyoxyphenol (1f)

To a mixture of **12e** (507 mg, 2.32 mmol) and K_2CO_3 (672 mg, 4.87 mmol) in DMF (2 mL), was added allyl bromide (0.31 mL, 3.51 mmol) and the mixture was stirred at 60 °C for 2 h. After cooling, sat. aq NH_4Cl (5 mL) and H_2O (5 mL) were added and the mixture was extracted with Et_2O (3 × 20 mL). The organic layer was washed with H_2O (5 × 10 mL) and brine (1 × 10 mL), then dried ($MgSO_4$). The solvent was evaporated in vacuo to give crude **1e** as a yellow oil (578 mg). To the solution of crude **1e** in MeOH (2 mL), was added a solution of KOH in MeOH (2 mL) at r.t. and the whole was stirred at r.t. for 25 min. After evaporation in vacuo, the residue was dissolved in H_2O (5 mL), acidified with 10% HCl and extracted with Et_2O (3 × 20 mL). The organic layer was washed with sat. aq $NaHCO_3$ (3 × 20 mL) and brine (1 × 10 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 10:1) to give **1f** as a pale yellow oil (289 mg, 83%). Spectral data were identical with those in the literature.[5]

1-Allyloxy-3-silyloxybenzenes; 1-Allyloxy-3-*tert*-butyldiphenylsilyloxybenzene (1d); Typical Procedure

TBDPSCl (1.2 mL, 4.52 mmol) was added to a mixture of **1f** (507 mg, 3.38 mmol) and imidazole (473 mg, 6.81 mmol) in DMF (5 mL) and the mixture was stirred at r.t. for 20 h. H_2O (20 mL) was added and extracted with Et_2O (3 × 60 mL). The organic layer was washed with H_2O (5 × 50 mL) and brine (2 × 40 mL), and then dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 10:1–5:1) to give **1d** as a colorless oil (1.22 g, 93%).

IR (ATR): no characteristic absorption.

^{1}H NMR (400 MHz): δ = 1.10 (s, 9 H), 4.29 (d, *J* = 5.4 Hz, 2 H), 5.17 (dif. dd, *J* = 10.7, 1.8 Hz, 1 H), 5.26 (dif. dd, *J* = 17.4, 1.8 Hz, 1 H), 5.91 (ddt, *J* = 17.4, 10.7, 5.4 Hz, 1 H), 6.35–6.37 (m, 2 H), 6.44 (dif. d, *J* = 8.8 Hz, 1 H), 6.96 (t, *J* = 8.8 Hz, 1 H), 7.34–7.43 (m, 6 H), 7.70–7.73 (dif. d, *J* = 7.2 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 19.5, 26.5, 68.6, 106.5, 107.9, 112.4, 117.5, 127.7, 129.4, 129.8, 132.9, 133.2, 135.5, 156.6, 159.4.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{25}H_{28}O_2Si$: 388.1859; found: 388.1835.

1-Allyloxy-3-*tert*-butyldimethylsilyloxybenzene (1b)

This compound was prepared from **1f** in the same manner as for **1d** and was obtained as a colorless oil (86%). Spectral data were identical with those in the literature.[5]

1-Allyloxy-3-triisopropylsilyloxybenzene (1c)

This compound was prepared from **1f** in the same manner as for **1d** and was obtained as a colorless oil (89%).

IR (ATR): no characteristic absorption.

^{1}H NMR (400 MHz): δ = 1.10 (d, *J* = 7.2 Hz, 18 H), 1.24 (m, 3 H), 4.50 (ddd, *J* = 5.2, 1.5, 1.5 Hz, 2 H), 5.28 (ddt, *J* = 10.5, 1.6, 1.5 Hz,

1 H), 5.40 (ddt, *J* = 17.0, 1.6, 1.5 Hz, 1 H), 6.05 (ddt, *J* = 17.0, 10.5, 5.2 Hz, 1 H), 6.46–6.52 (m, 3 H), 7.09 (dd, *J* = 8.0, 8.0 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 12.7, 17.9, 68.8, 106.9, 107.4, 112.6, 117.6, 129.6, 133.4, 157.2, 159.7.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{18}H_{30}O_2Si$: 306.2015; found: 306.1995.

3-(But-2-enyloxyphenoxy)-*tert*-butyldiphenylsilane (13, Z = H)
This compound was prepared from **12e**, crotyl chloride (*trans*/*cis* = 5:1) and TBDPSCl following the procedure for **1f** and **1d** and was obtained as a colorless oil (75% in 3 steps, as 5:1 mixture of *trans* and *cis*).

IR (ATR): no characteristic absorption.

^{1}H NMR (400 MHz): δ (for *trans* isomer) = 1.09 (s, 9 H), 1.69 (d, *J* = 6.2 Hz, 3 H), 4.20 (dd, *J* = 6.2, 1.2 Hz, 2 H), 5.56–5.76 (m, 2 H), 6.34–6.36 (m, 2 H), 6.43 (dif. d, *J* = 8.4 Hz, 1 H), 6.96 (dif. dd, *J* = 8.4, 8.4 Hz, 1 H), 7.34–7.44 (m, 6 H), 7.71 (dif. d, *J* = 6.6 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 17.8, 19.5, 26.5, 68.5, 106.4, 107.9, 112.2, 126.0, 127.7, 129.4, 129.8, 130.4, 132.9, 135.5, 156.6, 159.5.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{26}H_{30}O_2Si$: 402.2015; found: 402.2044.

3-(3-Methylbut-2-enyloxyphenoxy)-*tert*-butyldiphenylsilane (13, Z = CH$_3$)
This compound was prepared from **12e**, 3,3-dimethylallyl bromide, and TBDPSCl in the same manner as for **13** (Z = H) and was obtained as a colorless oil (84% in 3 steps).

IR (ATR): no characteristic peak.

^{1}H NMR (400 MHz): δ = 1.10 (s, 9 H), 1.64 (s, 3 H), 1.74 (s, 3 H), 4.25 (d, 2 H, *J* = 6.8 Hz), 5.37 (dif. tqq, 1 H, *J* = 6.8, 1.4, 1.4 Hz), 6.33–6.36 (m, 2 H), 6.44 (dif. d, 1 H, *J* = 8.0 Hz), 6.96 (dif. dd, *J* = 8.0, 8.0 Hz, 1 H), 7.34–7.43 (m, 6 H), 7.71–7.73 (dif. d, *J* = 6.4 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 18.1, 19.5, 25.8, 26.5, 64.5, 106.3, 107.9, 112.1, 119.6, 127.7, 129.4, 129.8, 133.0, 135.5, 137.9, 156.6, 159.7.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{27}H_{32}O_2Si$: 416.2172; found: 416.2183.

Microwave-Mediated CR of Allyl Ether 1; Typical Procedure (Table 1, Entry 1)
A solution of **1a** (104 mg, 0.64 mmol) in $PhNEt_2$ (1 mL) was irradiated at 250 °C for 30 min. After cooling to r.t., the mixture was diluted with EtOAc (30 mL), washed 10% aq HCl (5 × 10 mL) and brine (1 × 10 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 20:1 to 10:1) to give **2a** (50 mg, 48%) and **3a** (34 mg, 32%) as colorless oils. Spectral data of **2a** and **3a** were identical with those reported in the literature.[4]

BCl_3-Mediated CR of Allyl Ether 1; Typical Procedure (Table 2, Entry 1)
BCl_3 (1 M solution in CH_2Cl_2, 1.8 mL, 1.8 mmol) was added to a solution of **15a** (104 mg, 0.63 mmol) in CH_2Cl_2 (1.0 mL) at –50 °C and the mixture was stirred at –50 °C for 1 h. H_2O (10 mL) was added and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were washed with brine (1 × 20 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 20:1 to 10:1) to give a colorless oil **2a** (64 mg, 62%), **3a** (11 mg, 11%), and **12a** (6 mg, 8%).

6-Allyl-3-(*tert*-butyldimethylsilyloxy)phenol (2b)
IR (ATR): 3463 cm^{-1}.

^{1}H NMR (400 MHz): δ = 0.19 (s, 6 H), 0.98 (s, 9 H), 3.34 (d, *J* = 6.3 Hz, 2 H), 4.89 (s, 1 H, D_2O-exch), 5.12–5.17 (m, 2 H), 6.00 (ddt, *J* = 17.5, 9.5, 6.3 Hz, 1 H), 6.35 (d, *J* = 2.3 Hz, 1 H), 6.38 (dd, *J* = 8.0, 2.3 Hz, 1 H), 6.92 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz): δ = –4.5, 18.2, 25.7, 34.6, 107.9, 112.6, 116.2, 118.0, 130.6, 136.8, 154.8, 155.4.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{15}H_{24}O_2Si$: 264.1546; found: 264.1529.

2-Allyl-3-(*tert*-butyldimethylsilyloxy)phenol (3b)
IR (ATR): 3484 cm^{-1}.

^{1}H NMR (400 MHz): δ = 0.22 (s, 6 H), 1.00 (s, 9 H), 3.46 (br d, *J* = 6.0 Hz, 2 H), 4.96 (s, 1 H, D_2O-exch), 5.08–5.14 (m, 2 H), 5.97 (ddt, *J* = 17.2, 10.2, 6.0 Hz, 1 H), 6.44 (d, *J* = 8.0 Hz, 1 H), 6.47 (d, *J* = 8.0 Hz, 1 H), 6.97 (dif. dd, *J* = 8.0, 8.0 Hz, 1 H).

^{13}C NMR (100 MHz): δ = –4.2, 18.3, 25.8, 28.1, 109.0, 111.3, 115.6, 116.3, 127.2, 136.2, 154.4, 155.7.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{15}H_{24}O_2Si$: 264.1546; found: 264.1523.

6-Allyl-3-(triisopropylsilyloxy)phenol (2c)
IR (ATR): 3461 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.10 (d, *J* = 7.3 Hz, 18 H), 1.24 (dif. sept, *J* = 7.3 Hz, 3 H), 3.33 (d, *J* = 6.2 Hz, 2 H), 4.86 (s, 1 H, D_2O-exch), 5.13 (m, 2 H), 6.00 (dif. ddt, *J* = 17.7, 9.5, 6.2 Hz, 1 H), 6.39 (d, *J* = 2.2 Hz, 1 H), 6.42 (dd, *J* = 8.1, 2.2 Hz, 1 H), 6.91 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 12.6, 17.9, 34.5, 107.8, 112.4, 116.1, 117.6, 130.6, 136.9, 154.7, 155.9.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{18}H_{30}O_2Si$: 306.2015; found: 306.2001.

2-Allyl-3-(triisopropylsilyloxy)phenol (3c)
IR (ATR): 3424 cm^{-1}.

^{1}H NMR (400MHz): δ = 1.11 (d, *J* = 7.3 Hz, 18 H), 1.30 (sept, *J* = 7.3 Hz, 3 H), 3.50 (ddd, *J* = 6.4, 1.6, 1.6 Hz, 2 H), 4.94 (s, 1 H, D_2O-exch), 5.07–5.15 (m, 2 H), 5.98 (ddt, *J* = 17.1, 10.1, 6.4 Hz, 1 H), 6.40 (d, *J* = 8.0 Hz, 2 H), 6.94 (dif. dd, *J* = 8.0, 8.0 Hz, 1 H).

^{13}C NMR (100MHz): δ = 13.0, 18.1, 28.1, 108.6, 110.8, 115.6, 115.7, 127.1, 136.3, 154.7, 155.6.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{18}H_{30}O_2Si$: 306.2015; found: 306.2011.

6-Allyl-3-(*tert*-butyldiphenylsilyloxy)phenol (2d)
IR (ATR): 3538 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.08 (s, 9 H), 3.25 (d, *J* = 6.4 Hz, 2 H), 5.01 (s, 1 H, D_2O-exch), 5.06–5.11 (m, 1 H), 5.95 (ddt, *J* = 17.5, 9.9, 6.3 Hz, 1 H), 6.27–6.30 (m, 2 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 7.33–7.42 (m, 6 H), 7.70–7.72 (dif. d, *J* = 7.8 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 19.4, 26.5, 34.5, 107.5, 112.3, 116.0, 117.9, 127.7, 129.8, 130.5, 133.0, 135.5, 136.8, 154.5, 155.3.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{25}H_{28}O_2Si$: 388.1859; found: 388.1870.

2-Allyl-3-(*tert*-butyldiphenylsilyloxy)phenol (3d)
IR (ATR): 3538 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.08 (s, 1 H), 3.66 (d, *J* = 5.8 Hz, 2 H), 4.92 (s, 1 H, D_2O-exch), 5.13–5.19 (m, 2 H), 6.03–6.13 (dif. ddt, *J* = 17.0, 10.0, 5.8 Hz, 1 H), 6.05 (dif. d, *J* = 8.0 Hz, 1 H), 6.38 (d, *J* = 8.0 Hz, 1 H), 6.65 (dd, *J* = 8.0, 8.0 Hz, 1 H), 7.34–7.44 (m, 6 H), 7.71 (dif. d, *J* = 7.3 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 19.5, 26.5, 28.1, 108.7, 111.8, 115.5, 115.8, 126.9, 127.8, 129.9, 132.7, 135.4, 136.2, 154.1, 155.3.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{25}H_{28}O_2Si$: 388.1859; found: 388.1885.

6-Methoxy-2-methyl-2,3-dihydrobenzofuran (14)
IR (ATR): no characteristic peak.

^{1}H NMR (400 MHz): δ = 1.45 (d, *J* = 6.5 Hz, 1 H), 2.74 (dd, *J* = 14.9, 7.3 Hz, 1 H), 3.38 (dd, *J* = 14.9, 7.8 Hz, 1 H), 3.76 (s, 3 H), 4.93 (dif. qdd, *J* = 7.8, 7.3, 6.5 Hz, 1 H), 6.36–6.39 (m, 2 H), 7.01 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 21.8, 36.5, 55.5, 80.5, 96.1, 105.6, 118.9, 124.8, 160.3, 160.7.

LRMS-EI: *m*/*z* = 160 (M$^+$).

3-*tert*-Butyldiphenylsilyloxy-6-(1-methyl)allylphenol (15, Z = H)
IR (ATR): 3537 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.08 (s, 9 H), 1.30 (d, *J* = 7.0 Hz, 3 H), 3.53 (qd, *J* = 7.0, 6.3 Hz, 1 H), 4.89 (s, 1 H, D_2O-exch), 5.08–5.13 (m, 2 H), 6.00 (ddd, *J* = 17.3, 10.4, 6.3 Hz, 1 H), 6.27 (d, *J* = 2.4 Hz, 1 H), 6.30 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.81 (d, *J* = 8.4 Hz, 1 H), 7.34–7.44 (m, 6 H), 7.71 (dif. d, *J* = 7.6 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 18.8, 19.4, 26.5, 37.0, 107.7, 112.2, 113.9, 122.9, 128.0, 129.8, 133.0, 135.5, 142.8, 154.1, 155.0.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{26}H_{30}O_2Si$: 402.2015; found: 402.2008.

3-*tert*-Butyldiphenylsilyloxy-2-(1-methyl)allylphenol (16, Z = H)
IR (ATR): 3496 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.48 (d, *J* = 7.0 Hz, 3 H), 4.49 (dif. qd, *J* = 7.0, 4.0 Hz, 1 H), 5.37–5.45 (m, 2 H), 5.64 (1 H, s, D_2O-exch), 6.05 (d, *J* = 8.4 Hz, 1 H), 6.33–6.41 (dif. ddd, *J* = 18.5, 11.6, 4.0 Hz, 1 H), 6.36 (dif. d, *J* = 8.0 Hz, 1 H), 6.65 (dif. dd, *J* = 8.0, 8.0 Hz, 1 H), 7.35–7.43 (m, 6 H), 7.71 (dif. dd, *J* = 6.4, 6.4 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 16.3, 19.5, 26.5, 32.5, 110.1, 111.6, 115.4, 119.9, 127.2, 127.8, 129.9, 132.5, 132.6, 135.4, 142.7, 153.2, 156.2.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{26}H_{30}O_2Si$: 402.2015; found: 402.1993.

3-*tert*-Butyldiphenylsilyloxy-4-(3,3-dimethyl)allylphenol (21)
IR (ATR): 3373 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.09 (s, 9 H), 1.72 (s, 3 H), 1.76 (s, 3 H), 3.42 (d, *J* = 7.2 Hz, 2 H), 4.39 (s, 1 H, D_2O-exch), 5.40 (dif. dqq, *J* = 7.2, 1.4, 1.4 Hz, 1 H), 5.91 (d, *J* = 2.4 Hz, 1 H), 6.27 (dd, *J* = 8.2, 2.4 Hz, 1 H), 6.96 (d, *J* = 8.2 Hz, 1 H), 7.33–7.42 (m, 6 H), 7.71 (dif. d, *J* = 8.0 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 17.9, 19.5, 25.8, 26.4, 28.2, 106.4, 107.8, 123.2, 124.1, 127.8, 129.9, 132.3, 132.2, 132.7, 135.4, 153.8, 153.8.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{32}O_2Si$: 416.2172; found: 416.2141.

5-(*tert*-Butyldiphenylsilyloxy)-2-(1,2-dimethylallyl)phenol (22)
IR (ATR): 3464 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.08 (s, 9 H), 1.33 (d, *J* = 7.2 Hz, 3 H), 1.59 (s, 3 H), 3.43 (q, *J* = 7.2 Hz, 1 H), 4.94 (s, 1 H), 5.00 (s, 1 H), 5.28 (s, 1 H, D_2O-exch), 6.26–6.29 (m, 2 H), 6.79 (d, *J* = 8.1 Hz, 1 H), 7.34–7.43 (m, 6 H), 7.70 (dif. d, *J* = 6.8 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 18.4, 19.4, 20.6, 26.5, 41.6, 107.9, 111.0, 112.1, 122.1, 127.7, 128.5, 129.6, 133.0, 135.5, 150.3, 155.0, 155.2.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{32}O_2Si$: 416.2172; found: 416.2141.

6-*tert*-Butyldiphenylsilyloxy-2,2,3-trimethyl-2,3-dihydrobenzofuran (23)
IR (ATR): no characteristic peak.

^{1}H NMR (400 MHz): δ = 1.08 (s, 9 H), 1.12 (d, *J* = 7.2 Hz, 3 H), 1.20 (s, 3 H), 1.40 (s, 3 H), 3.01 (q, *J* = 7.2 Hz, 1 H), 6.21–6.23 (m, 2 H), 6.74 (d, *J* = 8.4 Hz, 1 H), 7.33–7.42 (m, 6 H), 7.71 (m, 4 H).

^{13}C NMR (100 MHz): δ = 14.7, 19.5, 21.9, 26.5, 27.9, 45.1, 90.2, 102.0, 111.2, 123.5, 125.4, 127.7, 129.7, 133.1, 135.5, 155.8, 158.7.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{32}O_2Si$: 416.2172; found: 416.2141.

5-*tert*-Butyldiphenylsilyloxy-2-(1,1-dimethyl)allylphenol (15, Z = Me)
IR (ATR): 3485 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.08 (s, 9 H), 1.34 (s, 6 H), 5.24 (dd, *J* = 10.6, 1.2 Hz, 1 H), 5.28 (dd, *J* = 17.7, 1.2 Hz, 1 H), 5.69 (s, 1 H, D_2O-exch), 6.13 (dd, *J* = 17.7, 10.6 Hz, 1 H), 6.26 (dd, *J* = 8.5, 2.5 Hz, 1 H), 6.34 (d, *J* = 2.5 Hz, 1 H), 6.91 (d, *J* = 8.5 Hz, 1 H), 7.34–7.44 (m, 6 H), 7.72 (m, 4 H).

^{13}C NMR (125 MHz): δ = 19.4, 26.5, 27.0, 39.7, 109.0, 111.8, 113.1, 126.4, 127.7, 129.8, 133.1, 135.4, 135.5, 148.2, 155.3, 155.5.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{32}O_2Si$: 416.2172; found: 416.2141.

(*R*)-5-[3-(3-Methoxyphenoxy)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (10a); Typical Procedure
A mixture of **12a** (1.70 mL, 15.5 mmol) and K_2CO_3 (2.54 g, 18.4 mmol) in DMF (10 mL) was stirred at r.t. for 30 min. 10-Chlorocarvone (**24**; 2.22 g, 12.0 mmol) in DMF (10 mL) was added and the mixture was stirred at 60 °C for 7 h. After cooling to r.t., sat. aq NH_4Cl (60 mL) and H_2O (60 mL) were added and the mixture was extracted with EtOAc (1 × 50 mL). The combined organic layers were washed with H_2O (5 × 200 mL) and brine (1 × 60 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue purified by CC (hexane–EtOAc, 4: 1) to give **10a** as a colorless oil (2.53 g, 77%); $[\alpha]_D^{24}$ –30.5 (*c* 1.0, $CHCl_3$).

IR (neat): 1672 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.79 (ddd, *J* = 2.6, 1.5, 1.5 Hz, 3 H), 2.38 (dddq, *J* = 18.1, 10.8, 2.6, 2.6 Hz, 1 H), 2.45 (dd, *J* = 16.1, 13.2 Hz, 1 H), 2.56 (ddddq, *J* = 18.1, 5.9, 4.4, 1.5, 1.5 Hz, 1 H), 2.68 (ddd, *J* = 16.1, 3.8, 1.5 Hz, 1 H), 2.93 (m, 1 H), 3.79 (s, 3 H), 4.52, 4.49 (d each, *J* = 12.6 Hz, 1 H), 5.09, 5.27 (s each, 1 H), 6.47 (t, *J* = 2.4 Hz, 1 H), 6.50 (dd, *J* = 8.0, 2.4 Hz, 1 H), 6.52 (dd, *J* = 8.0, 2.4 Hz, 1 H), 6.76 (ddq, *J* = 5.7, 2.6, 1.5 Hz, 1 H), 7.17 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 15.7, 31.4, 38.3, 43.1, 55.2, 69.9, 101.2, 106.6, 106.8, 113.3, 129.9, 135.5, 144.3, 146.2, 159.7, 160.8, 199.3.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{21}O_3$: 273.1491; found: 273.1502.

(*R*)-5-[3-(3-Benzoyloxyphenoxy)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (10e) and (*R*)-5-[3-(3-Hydroxyphenoxy)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (10f)
Compounds **10e** and **10f** were prepared from **12e** and **24** by the same procedure as for **10a** and were obtained as a colorless oil in 40% (for **10e**) and as colorless minute crystals in 18% (for **10f**). Hydrolysis of crude product in this reaction gave **10f** in 70% yield.

10e
$[\alpha]_D^{24}$ –19.4 (*c* 1.0, $CHCl_3$).

IR (neat): 1735, 1671 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.79 (ddd, *J* = 2.7, 1.4, 1.4 Hz, 3 H), 2.37 (dddq, *J* = 18.1, 10.4, 2.8, 2.8 Hz, 1 H), 2.46 (dd, *J* = 16.1, 13.1 Hz, 1 H), 2.57 (ddddq, *J* = 18.1, 5.9, 4.6, 1.4, 1.4 Hz, 1 H), 2.69 (ddd, *J* = 16.1, 3.8, 1.4 Hz, 1 H), 2.90–2.98 (m, 1 H), 4.52, 4.55 (d each, *J* = 12.4 Hz, 1 H), 5.10 (s, 1 H), 5.28 (s, 1 H), 6.76 (ddq, *J* = 5.9, 2.7, 1.4 Hz, 1 H), 6.80 (t, *J* = 2.3 Hz, 1 H), 6.82–6.85 (m, 2 H), 7.32 (t, *J* = 8.2 Hz, 1 H), 7.52 (dif. t, *J* = 7.8 Hz, 2 H), 7.65 (dif. t, *J* = 7.7 Hz, 1 H), 8.20 (dif. dd, *J* = 8.3, 1.5 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 15.7, 31.4, 38.3, 43.0, 70.2, 108.5, 112.4, 113.6, 114.3, 128.6, 129.4, 129.9, 130.1, 133.6, 135.6, 144.3, 145.8, 151.8, 159.4, 165.0, 199.2.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}O_4$: 363.1596; found: 363.1607.

10f

Mp 50–51 °C; $[\alpha]_D^{24}$ –25.0 (*c* 1.0, $CHCl_3$).

IR (neat): 3371, 1655 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.79 (ddd, *J* = 2.7, 1.5, 1.5 Hz, 3 H), 2.37 (dddq, *J* = 18.3, 10.5, 2.7, 2.7 Hz, 1 H), 2.45 (dd, *J* = 16.1, 13.0 Hz, 1 H), 2.56 (ddddq, *J* = 18.3, 5.9, 4.4, 1.5, 1.5 Hz, 1 H), 2.69 (ddd, *J* = 16.1, 3.8, 1.5 Hz, 1 H), 2.89–2.97 (m, 1 H), 4.48, 4.51 (d each, *J* = 12.7 Hz, 1 H), 5.09 (s, 1H), 5.18 (br s, 1 H), 5.26 (s, 1 H), 6.41 (t, *J* = 2.4 Hz, 1 H), 6.44 (ddd, *J* = 8.2, 2.4, 0.8 Hz, 1 H), 6.48 (ddd, *J* = 8.2, 2.4, 0.8 Hz, 1 H), 6.77 (ddq, *J* = 5.8, 2.7, 1.5 Hz, 1 H), 7.12 (t, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 15.7, 31.4, 38.3, 43.0, 69.9, 102.3, 106.7, 108.3, 113.5, 130.1, 135.5, 145.3, 146.0, 157.1, 159.7, 200.2.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}O_3$: 259.1334; found: 259.1341.

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02; N, 0.00. Found: C, 74.23; H, 6.85; N, 0.25.

(*R*)-5-[3-(3-Isopropoxyphenoxy)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (10g)

A mixture of phenol **10f** (300 mg, 1.16 mmol), K_2CO_3 (567 mg, 4.09 mmol) and 2-bromopropane (0.33 mL, 3.51 mmol) in DMF (1.5 mL) was stirred at 50 °C for 4 h. After cooling to r.t., 10% aq HCl (2 mL) and H_2O (2 mL) were added and extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with H_2O (5 × 30 mL) and brine (1 × 20 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (hexane–EtOAc, 10:1) to give **10g** as a colorless oil (298 mg, 85%); $[\alpha]_D^{24}$ –28.4 (*c* 1.0, $CHCl_3$).

IR (neat): 1675 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.33 (d, *J* = 6.0 Hz, 1 H), 1.79 (ddd, *J* = 2.6, 1.5, 1.5 Hz, 3 H), 2.36 (dddq, *J* = 18.1, 10.8, 2.6, 2.6 Hz, 1 H), 2.45 (dd, *J* = 16.1, 13.2 Hz, 1 H), 2.56 (ddddq, *J* = 18.1, 5.9, 4.4, 1.5, 1.5 Hz, 1 H), 2.68 (ddd, *J* = 16.1, 3.8, 1.5 Hz, 1 H), 2.89–2.97 (m, 1 H), 4.48, 4.51 (d each, *J* = 12.3 Hz, 1 H), 4.52 (sept, *J* = 6.0 Hz, 1 H), 5.08, 5.26 (s each, 1 H), 6.45 (t, *J* = 2.2 Hz, 1 H), 6.47 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.50 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.75 (ddq, *J* = 5.9, 2.6, 1.5 Hz, 1 H), 7.15 (t, *J* = 8.3 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 15.6, 22.0, 31.4, 38.3, 43.0, 69.8, 69.9, 102.9, 106.6, 108.3, 113.2, 129.8, 135.5, 144.3, 146.2, 159.0, 159.7, 199.2.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{25}O_3$: 301.1804; found: 301.1776.

BCl_3-Mediated Claisen Rearrangement of 10a, 10e, 10f and 10g

These reactions were performed by the same procedure as that used for **1a** (Table 2, entry 1).

(*R*)-5-[3-(2-Hydroxy-4-methoxyphenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (9a)

Mp 109–110 °C; $[\alpha]_D^{24}$ –3.8 (*c* 1.0, $CHCl_3$).

IR (Nujol): 3209, 1649 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.77 (ddd, *J* = 2.4, 1.5, 1.5 Hz, 3 H), 2.32 (dddq, *J* = 18.1, 10.8, 2.6, 2.6 Hz, 1 H), 2.39 (dd, *J* = 16.3, 13.5 Hz, 1 H), 2.49 (ddddq, *J* = 18.1, 5.8, 4.2, 1.5, 1.5 Hz, 1 H), 2.63–2.72 (m, 2 H), 3.38 (s, 2 H), 3.76 (s, 3 H), 4.93, 4.95 (s each, 1 H), 5.49 (br s, 1 H), 6.40 (d, *J* = 2.4 Hz, 1 H), 6.44 (dd, *J* = 8.2, 2.4 Hz, 1 H), 6.73 (ddq, *J* = 5.8, 2.4, 1.5 Hz, 1 H), 6.97 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 15.7, 31.6, 35.6, 40.1, 43.3, 55.3, 102.1, 106.2, 111.4, 116.9, 131.4, 135.4, 144.9, 150.3, 155.2, 159.6, 200.0.

EIMS: *m*/*z* (%) = 273 (5.4), 272 (M$^+$, 29.2), 163 (25.0), 148 (70.4), 137 (100.0), 135 (23.8), 124 (20.3).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.88; H, 7.39.

(*R*)-5-[3-(6-Hydroxy-2-methoxyphenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (25a)

Mp 104–105 °C; $[\alpha]_D^{24}$ –12.0 (*c* 1.0, $CHCl_3$).

IR (Nujol): 3247, 1646 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.78 (ddd, *J* = 2.5, 1.4, 1.4 Hz, 3 H), 2.37 (dddq, *J* = 18.2, 10.6, 2.6, 2.6 Hz, 1 H), 2.39 (dd, *J* = 16.5, 13.7 Hz, 1 H), 2.49 (ddddq, *J* = 18.2, 5.8, 4.4, 1.4, 1.4 Hz, 1 H), 2.69–2.76 (m, 2 H), 3.47 (s, 2 H), 3.79 (s, 3 H), 4.83, 4.87 (s each, 1 H), 5.30 (br s, 1 H), 6.48 (dd, *J* = 8.1, 2.0 Hz, 2 H), 6.73 (ddq, *J* = 5.8, 2.5, 1.4 Hz, 1 H), 7.08 (t, *J* = 8.1 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 15.7, 28.6, 31.6, 40.7, 43.4, 55.8, 103.3, 108.8, 110.1, 113.4, 127.8, 135.4, 145.0, 150.0, 155.5, 158.4, 200.1.

EIMS: *m*/*z* (%) = 273 (7.2), 272 (M$^+$, 38.5), 163 (38.2), 148 (62.3), 137 (100.0), 135 (82.2), 124 (13.9).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.90; H, 7.20.

(*R*)-5-[3-(2,4-Dihydroxyphenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (9f)

Mp 122–125 °C; $[\alpha]_D^{24}$ +0.4 (*c* 1.0, MeOH).

IR (ATR): 3349, 1655 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.76 (ddd, *J* = 2.6, 1.4, 1.4 Hz, 3 H), 2.27–2.38 (m, 1 H), 2.38 (dd, *J* = 16.5, 13.6 Hz, 1 H), 2.48 (dif. ddd, *J* = 18.3, 5.8, 4.4 Hz, 1 H), 2.63–2.72 (m, 2 H), 3.33, 3.38 (d each, *J* = 16.0 Hz, 1 H), 4.92, 4.94 (s each, 1 H), 5.64 (br s, 2 H), 6.35 (d, *J* = 2.7 Hz, 1 H), 6.37 (dd, *J* = 8.1, 2.7 Hz, 1 H), 6.75 (ddq, *J* = 5.8, 2.6, 1.4 Hz, 1 H), 6.90 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD): δ = 15.4, 31.6, 34.1, 40.2, 43.2, 102.4, 106.8, 110.5, 116.8, 131.0, 134.9, 146.0, 150.4, 155.3, 155.8, 201.2.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{16}H_{18}O_3$: 258.1256; found: 258.1233.

(*R*)-5-[3-(2,6-Dihydroxyphenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (25f)

Mp 40–45 °C; $[\alpha]_D^{22}$ –13.5 (*c* 0.45, CH_3OH).

IR (ATR): 3352, 1647 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.77 (ddd, *J* = 2.7, 1.4, 1.4 Hz, 3 H), 2.32–2.44 (m, 2 H), 2.54 (ddddq, *J* = 18.1, 5.9, 4.5, 1.4, 1.4 Hz, 1 H), 2.67–2.80 (m, 2 H), 3.49, 3.58 (d each, *J* = 15.8 Hz, 1 H), 4.96, 4.99 (s each, 1 H), 5.43 (br s, 2 H), 6.42 (d, *J* = 8.1 Hz, 2 H), 6.76 (ddq, *J* = 5.9, 2.7, 1.4 Hz, 1 H), 6.97 (t, *J* = 8.1 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD): δ = 15.2, 27.9, 31.4, 40.8, 43.1, 106.6, 108.8, 112.6, 126.9, 134.7, 146.5, 149.5, 155.9, 201.6.

HREIMS: *m/z* $[M]^+$ calcd for $C_{16}H_{18}O_3$: 258.1256; found: 258.1250.

(*R*)-5-[3-(4-Benzoyloxy-2-hydroxyphenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (9e)
Mp 149–150 °C; $[\alpha]_D^{25}$ +0.9 (*c* 0.84, $CHCl_3$).

IR (Nujol): 3209, 1729, 1648 cm^{-1}.

^1H NMR (400 MHz): δ = 1.78 (ddd, *J* = 2.4, 1.4, 1.4 Hz, 3 H), 2.30–2.40 (m, 1 H), 2.43 (dd, *J* = 16.1, 13.4 Hz, 1 H), 2.47–2.54 (m, 1 H), 2.66–2.76 (m, 2 H), 3.41, 3.45 (d each, *J* = 16.1 Hz, 1 H), 4.93, 4.98 (s each, 1 H), 5.77 (br s, 1 H), 6.72–6.76 (m, 3 H), 7.12 (d, *J* = 7.9 Hz, 1 H), 7.50 (dif. t, *J* = 7.7 Hz, 2 H), 7.63 (dif. t, *J* = 7.5 Hz, 1 H), 8.18 (dif. dd, *J* = 8.4, 1.3 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 15.6, 31.5, 35.0, 40.2, 43.2, 109.4, 111.5, 113.3, 123.0, 128.5, 129.4, 130.1, 131.1, 133.6, 135.3, 145.4, 149.7, 150.1, 155.0, 165.4, 200.5.

EIMS: *m/z* (%) = 362 (M^+, 13.0), 105 (100.0), 77 (24.0).

Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 75.94; H, 5.97.

(*R*)-5-[3-(2-Benzoyloxy-6-hydroxyphenyl)-prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (25e)
Mp 145–146 °C; $[\alpha]_D^{25}$ –19.6 (*c* 0.17, $CHCl_3$)

IR (Nujol): 3169, 1722, 1636 cm^{-1}.

^1H NMR (400 MHz): δ = 1.75 (ddd, *J* = 2.7, 1.5, 1.5 Hz, 3 H), 2.24 (dddq, *J* = 18.2, 10.4, 2.7, 2.7 Hz, 1 H), 2.32 (dd, *J* = 16.1, 13.4 Hz, 1 H), 2.37–2.46 (m, 1 H), 2.63–2.71 (m, 2 H), 3.38, 3.45 (d each, *J* = 15.8 Hz, 1 H), 4.75, 4.81 (s each, 1 H), 5.95 (br s, 1 H), 6.66 (br d, *J* = 5.9 Hz, 1 H), 6.76 (dif. d, *J* = 8.1 Hz, 2 H), 7.17 (t, *J* = 8.1 Hz, 1 H), 7.52 (dif. t, *J* = 7.7 Hz, 2 H), 7.65 (dif. t, *J* = 7.6 Hz, 1 H), 8.18 (dif. dd, *J* = 8.4, 1.3 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 15.6, 29.5, 31.5, 40.4, 43.2, 110.7, 113.4, 114.6, 118.4, 127.6, 128.6, 129.3, 130.1, 133.7, 135.2, 145.4, 148.5, 150.5, 155.6, 165.2, 200.5.

HRFABMS: *m/z* $[M + H]^+$ calcd for $C_{23}H_{23}O_4$: 363.1596; found: 363.1611.

(*R*)-5-[3-(2-Hydroxy-4-isopropoxyphenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (9g)
Mp 78–79 °C; $[\alpha]_D^{24}$ –1.2 (*c* 1.1, $CHCl_3$).

IR (ATR): 3332, 1647 cm^{-1}.

^1H NMR (400 MHz): δ = 1.31 (d, *J* = 6.0 Hz, 6 H), 1.77 (ddd, *J* = 2.5, 1.4, 1.4 Hz, 3 H), 2.27–2.36 (m, 1 H), 2.39 (dd, *J* = 16.3, 13.5 Hz, 1 H), 2.48 (ddddq, *J* = 18.1, 5.7, 4.6, 1.4, 1.4 Hz, 1 H), 2.63–2.74 (m, 2 H), 3.37 (s, 2 H), 4.47 (sept, *J* = 6.0 Hz, 1 H), 4.93, 4.95 (s each, 1 H), 5.49 (br s, 1 H), 6.39 (d, *J* = 2.5 Hz, 1 H), 6.42 (dd, *J* = 8.2, 2.5 Hz, 1 H), 6.73 (ddq, *J* = 5.7, 2.5, 1.4 Hz, 1 H), 6.94 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 15.7, 22.1, 31.6, 35.6, 40.0, 43.3, 69.9, 103.8, 108.1, 111.3, 116.6, 131.3, 135.4, 144.8, 150.3, 155.2, 157.9, 199.9.

HRFABMS: *m/z* $[M]^+$ calcd for $C_{19}H_{25}O_3$: 301.1804; found: 301.1800.

Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.84; H, 7.98.

(*R*)-5-[3-(6-Hydroxy-2-isopropoxyphenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (25g)
Mp 80–81 °C; $[\alpha]_D^{22}$ –8.2 (*c* 0.30, $CHCl_3$).

IR (ATR): 3259, 1647 cm^{-1}.

^1H NMR (400 MHz): δ = 1.30 (d, *J* = 6.0 Hz, 6 H), 1.77 (ddd, *J* = 2.5, 1.4, 1.4 Hz, 3 H), 2.29–2.38 (m, 1 H), 2.40 (dd, *J* = 16.1, 13.4 Hz, 1 H), 2.56 (ddddq, *J* = 18.1, 5.8, 4.2, 1.4, 1.4 Hz, 1 H), 2.67–2.76 (m, 2 H), 3.48 (s, 2 H), 4.52 (sept, *J* = 6.0 Hz, 1 H), 4.86 (s, 1 H), 4.87 (br s, 1 H), 5.37 (br s, 1 H), 6.44 (d, *J* = 8.2 Hz, 1 H), 6.47 (d, *J* = 8.2 Hz, 1 H), 6.75 (ddq, *J* = 5.8, 2.5, 1.4 Hz, 1 H), 7.04 (t, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 15.7, 22.10, 22.14, 28.8, 31.6, 40.4, 43.3, 70.0, 105.4, 108.3, 110.1, 114.3, 127.5, 135.3, 145.0, 150.1, 155.8, 156.6, 200.1.

EIMS: *m/z* (%) = 301 (5.4), 300 (M^+, 25.5), 165 (95.8), 149 (62.1), 135 (100.0), 123 (79.4), 109 (28.3).

Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 76.21; H, 8.11.

BCl_3-Mediated Claisen Rearrangement of 10d via Introduction of TBDPS Group to Phenol 10f
To a solution of **10f** (302 mg, 1.17 mmol), imidazole (162 mg, 2.37 mmol) in DMF (1.5 mL), was added TBDPSCl (0.40 mL, 1.54 mmol) at r.t. and the mixture was stirred at r.t. for 4.5 h. H_2O (50 mL) was added and the mixture was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with H_2O (3 × 100 mL) and brine (1 × 100 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo. The crude **10d** was dissolved in CH_2Cl_2 (6 mL) and 1 M solution of BCl_3 (3.5 mL, 3.5 mmol) was added at –50 °C. The mixture was stirred at –50 °C for 1 h. H_2O (80 mL) was added and the mixture was extracted with $CHCl_3$ (2 × 100 mL). The combined organic layers were washed with H_2O (1 × 100 mL) and brine (1 × 100 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by flash CC (*n*-hexane–EtOAc, 98:2–90:10) to give **9d** (439 mg, 76%) and **25d** (35 mg, 6%).

(*R*)-5-{3-[4-(*tert*-Butyldiphenylsilyloxy)-2-hydroxyphenyl]prop-1-en-2-yl}-2-methylcyclohex-2-en-1-one (9d)
Mp 141–142 °C; $[\alpha]_D^{25}$ –1.7 (*c* 1.0, $CHCl_3$).

IR (Nujol): 3372, 1648 cm^{-1}.

^1H NMR (400 MHz): δ = 1.08 (s, 9 H), 1.76 (ddd, *J* = 2.5, 1.4, 1.4 Hz, 3 H), 2.25 (dddq, *J* = 18.2, 10.4, 2.5, 2.5 Hz, 1 H), 2.34 (dd, *J* = 16.1, 13.3 Hz, 1 H), 2.42 (dif. ddd, *J* = 18.2, 7.3, 5.8 Hz, 1 H), 2.59 (ddd, *J* = 16.1, 3.7, 1.4 Hz, 1 H), 2.62–2.68 (m, 1 H), 3.28 (s, 2 H), 4.84, 4.90 (s each, 1 H), 4.93 (s, 1 H), 6.25 (d, *J* = 2.4 Hz, 1 H), 6.29 (d, *J* = 8.2, 2.4 Hz, 1 H), 6.70 (ddq, *J* = 5.8, 2.8, 1.4 Hz, 1 H), 6.76 (d, *J* = 8.2 Hz, 1 H), 7.33–7.43 (m, 6 H), 7.70 (dif. dd, *J* = 8.0, 1.5 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 15.6, 19.4, 26.4, 31.5, 35.0, 40.1, 43.1, 107.5, 111.0, 112.0, 117.6, 127.6, 129.8, 130.8, 132.9, 135.2, 135.4, 145.3, 150.1, 154.7, 155.2, 200.3.

EIMS: *m/z* (%) = 497 (42.5), 496 (M^+, 98.6), 440 (91.2), 439 (100.0), 361 (91.6), 291 (71.7), 199 (62.8).

Anal. Calcd for $C_{32}H_{36}O_3Si$: C, 77.38; H, 7.31. Found: C, 77.56; H, 7.27.

(*R*)-5-{3-[2-(*tert*-Butyldiphenylsilyloxy)-6-hydroxyphenyl]prop-1-en-2-yl}-2-methylcyclohex-2-en-1-one (25d)
Mp 156–157 °C; $[\alpha]_D^{25}$ –6.6 (*c* 0.56, $CHCl_3$).

IR (Nujol): 3280, 1636 cm^{-1}.

^1H NMR (400 MHz): δ = 1.06 (s, 9 H), 1.79 (ddd, *J* = 2.7, 1.4, 1.4 Hz, 3 H), 2.39 (dddq, *J* = 18.1, 10.5, 2.7, 2.7 Hz, 1 H), 2.49 (dd, *J* = 16.1, 13.4 Hz, 1 H), 2.60 (dif. ddd, *J* = 18.1, 5.9, 4.6 Hz, 1 H), 2.72 (ddd, *J* = 16.1, 3.7, 1.4 Hz, 1 H), 2.81–2.90 (m, 1 H), 3.63, 3.68 (d each, *J* = 16.1 Hz, 1 H), 4.84, 4.96 (s each, 1 H), 5.33 (br s, 1 H), 6.05, 6.38 (d each, *J* = 8.1 Hz, 1 H), 6.66 (t, *J* = 8.1 Hz, 1 H), 6.73 (ddq, *J* = 5.9, 2.7, 1.4 Hz, 1 H), 7.33–7.45 (m, 6 H), 7.69 (dif. dd, *J* = 8.0, 1.4 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 15.7, 19.4, 26.5, 29.3, 31.9, 41.3, 43.4, 108.7, 110.0, 111.6, 115.3, 127.0, 127.8, 129.9, 132.4, 132.5, 135.3, 135.4, 145.0, 149.4, 154.3, 155.6, 200.1.

HRFABMS: *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{36}O_3Si$: 497.2512; found: 497.2469

(*R*)-5-[3-(2-Benzoyloxy-4-*tert*-Butyldiphenylsilyloxyphenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (26)

A mixture of **9d** (714 mg, 1.44 mmol), KI (120 mg, 0.72 mmol), K_2CO_3 (320 mg, 2.32 mmol) and benzyl bromide (0.26 mL, 2.19 mmol) in DMF (3 mL) was stirred at r.t. for 3 h. Sat. aq NH_4Cl (20 mL) was added and the mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H_2O (5 × 90 mL) and brine (1 × 30 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–Et_2O, 9:1) to give **26** as a colorless oil (797 mg, 94%); $[\alpha]_D^{23}$ –1.3 (*c* 1.0, $CHCl_3$).

IR (neat): 1673 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.09 (s, 9 H), 1.75 (ddd, *J* = 2.7, 1.4, 1.4 Hz, 3 H), 2.15 (dddq, *J* = 18.3, 10.5, 2.6, 2.6 Hz, 1 H), 2.31 (dd, *J* = 16.0, 13.4 Hz, 1 H), 2.23–2.39 (m, 1 H), 2.52 (ddd, *J* = 16.0, 3.7, 1.4 Hz, 1 H), 2.56–2.64 (m, 1 H), 3.22, 3.28 (d each, *J* = 15.6 Hz, 1 H), 4.63 (s, 1 H), 4.65 (s, 2 H), 4.77 (s, 1 H), 6.31 (d, *J* = 2.3 Hz, 1 H), 6.33 (dd, *J* = 8.1, 2.3 Hz, 1 H), 6.59 (ddq, *J* = 5.7, 2.7, 1.4 Hz, 1 H), 6.80 (d, *J* = 8.1 Hz, 1 H), 7.21 (dif. dd, *J* = 7.5, 2.0 Hz, 2 H), 7.27–7.44 (m, 9 H), 7.70 (dif. dd, *J* = 8.1, 1.5 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 15.7, 19.4, 26.6, 31.8, 34.3, 40.6, 43.4, 69.8, 104.6, 110.3, 111.8, 120.4, 127.3, 127.7, 128.3, 129.8, 130.5, 133.0, 134.8, 135.1, 135.6, 137.0, 144.8, 150.4, 155.1, 156.7, 200.0.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{39}H_{42}O_3Si$: 586.2903; found: 586.2874.

(*R*)-5-[3-(2-Benzyloxy-4-*tert*-butyldimethylsilyloxy-5-chlorophenyl)prop-1-en-2-yl]-2-methylcyclohex-2-en-1-one (27)

A solution of **26** (105 mg, 0.18 mmol) in CH_2Cl_2 (2 mL), and SiO_2 (33 mg) were added to a suspension of $Ca(OCl)_2$ (60%, 44 mg, 0.18 mmol) in H_2O (0.2 mL) and the mixture was stirred at r.t. for 5 h. The mixture was filtered and the filtrate was dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by flash CC (*n*-hexane–Et_2O, 100:1 to 90:10) to give **27** as a colorless oil (54 mg, 48%); $[\alpha]_D^{21}$ +1.3 (*c* 1.0, $CHCl_3$).

IR (ATR): 1670 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.13 (s, 9 H), 1.75 (ddd, *J* = 2.5, 1.3, 1.3 Hz, 1 H), 2.16 (dddq, *J* = 18.3, 10.4, 2.5, 2.5 Hz, 1 H), 2.31 (dd, *J* = 16.1, 13.2 Hz, 1 H), 2.32–2.39 (m, 1 H), 2.34 (dif. ddd, *J* = 16.1, 3.7, 1.5 Hz, 1 H), 2.58–2.63 (m, 1 H), 3.19, 3.23 (d each, *J* = 15.9 Hz, 1 H), 4.28, 4.31 (d each, *J* = 12.4 Hz, 1 H), 4.65, 4.82 (s each, 1 H), 6.06 (s, 1 H), 6.61 (ddq, *J* = 5.7, 2.8, 1.3 Hz, 1 H), 6.99 (dif. dd, *J* = 6.3, 2.8 Hz, 2 H), 7.04 (s, 1 H), 7.21 (dd, *J* = 5.1, 1.8 Hz, 2 H), 7.38 (dif. t, *J* = 7.3 Hz, 5 H), 7.45 (dif. t, *J* = 7.4 Hz, 2 H), 7.70 (dif. dd, *J* = 8.1, 1.4 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 15.7, 19.7, 26.5, 31.7, 33.9, 40.6, 43.3, 69.8, 105.2, 110.9, 115.9, 121.6, 127.0, 127.8, 128.3, 130.2, 130.8, 132.6, 134.8, 135.2, 135.6, 136.4, 144.7, 149.7, 150.3, 154.8, 199.8.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{39}H_{41}{}^{35}ClO_3Si$: 620.2513; found: 620.2496.

(*R*)-5-[3-(2-Benzyloxy-4-*tert*-butyldiphenylsilyloxyphenyl)-1,2-epoxypropan-2-yl]-2-methylcyclohex-2-en-1-one (29)

To a solution of **26** (308 mg, 0.52 mmol) in CH_2Cl_2 (3 mL), was added MCPBA (65%, 182 mg, 0.69 mmol) at –10 °C and the mixture was stirred at –10 °C for 18 h. Aq 10% $Na_2S_2O_3$ was added and the mixture was extracted with $CHCl_3$ (2 × 30 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (2 × 20 mL) and brine (1 × 20 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 8:1) to give **29** as a 1:1 mixture of diastereoisomers (211 mg, 67%); colorless oil .

IR (neat): 1675 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.09, 1.10 (s each, 9 H), 1.73 (br s, 6 H), 2.07–2.34 (m, 9 H), 2.35, 2.36 (d each, *J* = 4.6 Hz, 1 H), 2.49 (d, *J* = 4.6 Hz, 1 H), 2.52 (d, *J* = 12.6 Hz, 1 H), 2.54 (d, *J* = 4.6 Hz, 1 H), 2.56 (d, *J* = 14.5 Hz, 1 H), 2.69 (d, *J* = 14.5 Hz, 1 H), 2.98, 3.09 (d each, *J* = 14.5 Hz, 1 H), 4.60 (d, *J* = 11.7 Hz, 1 H), 4.64 (s, 2 H), 4.65 (d, *J* = 11.7 Hz, 1 H), 6.30, 6.31 (d each, *J* = 2.3 Hz, 1 H), 6.33 (dd, *J* = 8.1, 2.3 Hz, 2 H), 6.52, 6.56 (dif. d each, *J* = 5.4 Hz, 1 H), 6.83, 6.85 (d each, *J* = 8.1 Hz, 1 H), 7.21–7.24 (m, 4 H), 7.29–7.44 (m, 18 H), 7.67–7.71 (m, 8 H).

^{13}C NMR (100 MHz): δ = 15.6, 19.4, 26.5, 27.6, 27.9, 31.9, 32.5, 37.8, 39.1, 39.7, 50.5, 60.3, 60.6, 69.9, 104.3, 111.8, 117.1, 117.2, 127.5, 127.7, 127.7, 128.0, 128.5, 129.9, 131.4, 131.5, 132.9, 135.0, 135.3, 135.5, 136.6, 136.7, 144.2, 144.5, 155.6, 157.1, 199.1.

HREIMS: *m*/*z* [M]$^+$ calcd for $C_{39}H_{42}O_4Si$: 602.2852; found: 602.2856.

6-[2-Benzyloxy-4-(*tert*-butyldiphenylsilyloxy)benzyl]-6-hydroxymethyl-2-methylcyclohepta-2,4-dienone (30)

To a solution of **29** (105 mg, 0.17 mmol) in CH_2Cl_2 (1 mL), were added Et_3N (0.12 mL, 0.86 mmol) and TMSOTf (0.09 mL, 0.50 mmol) at 0 °C and the mixture was stirred at 0 °C for 30 min. The mixture was diluted with EtOAc (30 mL) and washed with H_2O (4 × 20 mL) and brine (1 × 20 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (Al_2O_3, *n*-hexane–EtOAc, 20: 1) to give crude **34** (61 mg), which was treated with TsOH·H_2O (3.3 mg, 17 μmol) in MeOH (3 mL) and the mixture was stirred at r.t. for 30 min. $NaHCO_3$ (27 mg, 0.32 mmol) was added and the mixture was stirred at r.t. for 30 min, and then filtered. The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 3:1) to give **30** as a colorless oil (50 mg, 47%).

IR (ATR): 3503, 1652, 1604 cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.10 (s, 9 H), 1.93 (s, 3 H), 2.55 (d, *J* = 13.7 Hz, 1 H), 2.62 (d, *J* = 13.7 Hz, 1 H), 2.65 (d, *J* = 13.7 Hz, 1 H), 2.79 (d, *J* = 13.7 Hz, 1 H), 2.82 (dd, *J* = 8.2, 7.1 Hz, 1 H, D_2O-exch), 3.10 (dd, *J* = 11.7, 8.2 Hz, 1 H; d, *J* = 11.6 Hz with added D_2O), 3.20 (dd, *J* = 11.7, 7.1 Hz, 1 H; d, *J* = 11.6 Hz with added D_2O), 4.63, 4.66 (d each, *J* = 11.6 Hz, 1 H), 5.76 (d, *J* = 11.8 Hz, 1 H), 5.91 (dd, *J* = 11.8, 8.1 Hz, 1 H), 6.33 (d, *J* = 2.3 Hz, 1 H), 6.37 (dd, *J* = 8.2, 2.3 Hz, 1 H), 6.50 (br dd, *J* = 8.1, 1.4 Hz, 1 H), 6.77 (d, *J* = 8.2 Hz, 1 H), 7.23 (m, 2 H), 7.30–7.45 (m, 9 H), 7.68 (d, *J* = 6.7 Hz, 4 H).

^{13}C NMR (150 MHz): δ = 19.5, 19.9, 26.6, 30.1, 42.6, 48.2, 65.9, 70.9, 104.8, 112.5, 117.8, 124.1, 127.81, 127.9, 128.5, 128.8, 130.0, 133.0, 133.3, 133.8, 135.6, 135.7, 138.6, 143.4, 155.5, 157.2, 200.5.

HRFABMS: *m*/*z* [M + Na]$^+$ calcd for $C_{39}H_{242}O_4Si$ + Na: 625.2750; found: 625.2728.

(*R*)-3-[2-Benzyloxy-4-(*tert*-butyldiphenylsilyloxy)phenyl]-2-cyclohexylpropionaldehyde (35)

BF_3·OEt_2 (0.66 mL, 5.21 mmol) was added to a solution of crude **29** (2.6 g), which was prepared from **26** (2.04 g, 3.48 mmol) and MCPBA (65%, 1.21 g, 4.55 mmol), in Et_2O (20 mL) at –20 °C and the mixture was stirred at –20 °C for 40 min. H_2O (50 mL) was added and the mixture was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with brine (1 × 50 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–acetone, 7:1) to give **35** as a colorless oil (1.02 g, 49% from **26**, a 1:1 mixture of diastereoisomers).

IR (ATR): 1772, 1672 cm^{-1}.

^1H NMR (400 MHz): δ = 1.088, 1.090 (s each, 9 H), 1.731, 1.734 (br s each, 3H), 2.09–2.26 (m, 6 H), 2.32–2.51 (m, 4 H), 2.53–2.60 (m, 2 H), 2.72–2.84 (m, 4 H), 4.64, 4.65 (s each, 2 H), 6.30 (dif. d, *J* = 2.4 Hz, 2 H), 6.31 (dif. dd, *J* = 6.8, 2.4 Hz, 2 H), 6.55–6.57, 6.60–6.63 (m each, 1 H), 6.81 (d, *J* = 8.6 Hz, 2 H), 7.21–7.25 (m, 4 H), 7.30–7.45 (m, 18 H), 7.68 (dif. dd, *J* = 8.1, 1.5 Hz, 8 H), 9.53, 9.54 (s each, 1 H).

^{13}C NMR (100 MHz): δ = 15.60, 15.62, 19.4, 26.5, 26.8, 26.9, 29.3, 29.7, 35.0, 35.3, 41.4, 41.7, 55.5, 55.7, 69.8, 104.35, 104.43, 111.8, 119.19, 119.20, 127.5, 127.6, 127.7, 128.0, 128.47, 128.48, 129.9, 130.8, 132.9, 135.4, 135.45, 135.50, 136.5, 144.3, 144.4, 155.5, 156.74, 156.75, 198.8, 198.9, 203.9, 204.0.

HREIMS: *m*/*z* $[M]^+$ calcd for $C_{39}H_{42}O_4Si$: 602.2852; found: 602.2765.

3-[2-Benzyloxy-4-(*tert*-butyldiphenylsilyloxy)phenyl]-2-cyclohexylpropenal (36)

A solution of **35** (6.24 g, 10.3 mmol) and DDQ (3.05 g, 13.4 mmol) in benzene (60 mL) was stirred under reflux for 7 h. After cooling, a mixture of EtOAc and *n*-hexane (10:1) was added and the mixture was washed with aq 10% NaOH (3 × 200 mL) and brine (1 × 200 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 7:1) to give **36** as a yellow oil (3.29 g, 53%, *E*/*Z* = 1:3) and recovered **35** (475 mg, 8%).

IR (ATR): 1670 cm^{-1}.

^1H NMR (400 MHz): δ = 1.10 (s, 3.6 H), 1.11 (s, 9 H), 1.76–1.78 (m, 4.2 H), 2.14 (br ddd, *J* = 19.0, 5.1, 5.1 Hz, 0.4 H), 2.29–2.39 (m, 1.4 H), 2.47–2.57 (m, 3 H), 3.11 (dddq, *J* = 19.0, 11.7, 2.6, 2.6 Hz, 0.4 H), 3.25 (dd, *J* = 15.8, 14.3 Hz, 0.4 H), 3.29–3.35 (m, 1 H), 3.45 (br dd, *J* = 3.1, 3.1 Hz, 0.4 H), 4.71 (s, 2 H), 4.72 (s, 0.8 H), 6.35 (d, *J* = 2.2 Hz, 1.4 H), 6.40 (dd, *J* = 8.2, 2.2 Hz, 1 H), 6.42 (dd, *J* = 8.4, 2.2 Hz, 0.4 H), 6.70–6.73 (m, 1.4 H), 6.90 (d, *J* = 8.2 Hz, 1 H), 6.97 (d, *J* = 8.4 Hz, 0.4 H), 7.18 (dif. d, *J* = 7.9 Hz, 2.8 H), 7.30 (dif. t, *J* = 7.5 Hz, 4.2 H), 7.38 (dif. t, *J* = 7.1 Hz, 5.6 H), 7.45–7.47 (m, 3.2 H), 7.57 (s, 1 H), 7.67–7.71 (m, 5.6 H), 9.46 (d, *J* = 2.0 Hz, 0.4 H), 9.72 (s, 1 H).

^{13}C NMR (100 MHz): δ = 15.7, 15.8, 19.4, 26.4, 29.4, 31.8, 34.4, 35.9, 41.3, 42.7, 60.3, 70.2, 104.9, 112.0, 112.4, 116.0, 116.69, 127.02, 127.1, 127.9, 128.0, 128.5, 129.9, 130.1, 132.3, 132.4, 133.1, 134.9, 135.35, 135.42, 136.07, 136.11, 140.6, 140.7, 142.0, 144.5, 145.3, 148.6, 157.5, 157.7, 158.6, 158.7, 192.7, 195.8, 199.2, 199.6.

HREIMS: *m*/*z* $[M]^+$ calcd for $C_{39}H_{40}O_4Si$: 600.2696; found: 600.2734.

(*R*)-5-{3-[2-Benzyloxy-4-(*tert*-butyldiphenylsilyloxy)phenyl]-1-hydroxyprop-2-en-2-yl}-2-methylcyclohex-2-en-1-one (37)

AcOH (2.75 mL, 48.0 mmol) was added to a suspension of $NaBH_4$ (550 mg, 14.5 mmol) in benzene (10 mL) at r.t. and the mixture was refluxed for 20 min. Compound **36** (2.19 g, 3.64 mmol, *E*/*Z* = 1:3) in benzene (15 mL) was added at r.t. and the mixture was refluxed for 2.5 h. After cooling to 0 °C, sat. aq $NaHCO_3$ (30 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (1 × 50 mL) and brine (1 × 50 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 3:1) to give (*Z*)-**37** (1.31 g, 60%) and (*E*)-**37** (291 mg, 13%) as colorless oils.

***Z*-Isomer**

$[\alpha]_D^{24}$ -25.5 (*c* 1.0, $CHCl_3$).

IR (ATR): 3419, 1666 cm^{-1}.

^1H NMR (400 MHz): δ = 1.10 (s, 9 H), 1.73 (br s, 1 H), 1.77 (br s, 3 H), 2.39 (dddq, *J* = 18.2, 10.5, 2.7, 2.7 Hz, 1 H), 2.48 (dd, *J* = 16.0, 13.3 Hz, 1 H), 2.48–2.55 (m, 1 H), 2.64 (ddd, *J* = 16.0, 3.7, 1.2 Hz, 1 H), 2.98–3.06 (m, 1 H), 4.10 (br s, 2 H), 4.66 (s, 2 H), 6.35 (d, *J* = 2.2 Hz, 1 H), 6.37 (s, 1 H), 6.39 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.74 (ddq, *J* = 5.6, 2.7, 1.2 Hz, 1 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 7.21 (dif. d, *J* = 7.7 Hz, 2 H), 7.30 (dif. t, *J* = 8.0 Hz, 3 H), 7.37 (dif. t, *J* = 7.9 Hz, 4 H), 7.43 (dif. t, *J* = 7.4 Hz, 2 H), 7.70 (dif. d, *J* = 8.1 Hz, 4 H).

^{13}C NMR (150 MHz): δ = 15.6, 19.4, 26.5, 32.2, 40.3, 43.7, 60.3, 70.3, 105.1, 112.1, 119.0, 123.8, 127.1, 127.8, 127.9, 128.5, 129.9, 130.5, 132.8, 135.2, 135.5, 136.5, 141.7, 144.9, 156.0, 156.4, 199.9.

HRFABMS: *m*/*z* $[M + H]^+$ calcd for $C_{39}H_{42}O_4Si$: 602.2852; found: 602.2823.

***E*-Isomer**

$[\alpha]_D^{24}$ +96.7 (*c* 1.2, $CHCl_3$).

IR (ATR): 3447, 1668 cm^{-1}.

^1H NMR (400 MHz): δ = 1.08 (s, 9 H), 1.46 (t, *J* = 6.0 Hz, 1 H), 1.75 (ddd, *J* = 2.5, 1.3, 1.3 Hz, 3 H), 2.20 (dif. ddd, *J* = 18.3, 5.8, 4.8 Hz, 1 H), 2.40 (ddd, *J* = 16.1, 3.8, 1.3 Hz, 1 H), 2.53–2.63 (m, 1 H), 2.61 (dd, *J* = 16.1, 14.4 Hz, 1 H), 3.32 (dddd, *J* = 14.4, 11.1, 4.0, 4.0 Hz, 1 H), 4.25 (d, *J* = 6.0 Hz, 2 H), 4.66, 4.69 (d each, *J* = 12.5 Hz, 1 H), 6.30 (d, *J* = 2.3 Hz, 1 H), 6.35 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.52 (s, 1 H), 6.67 (dif. d, *J* = 5.8 Hz, 1 H), 6.80 (d, *J* = 8.3 Hz, 1 H), 7.18 (dif. dd, *J* = 7.4, 1.9 Hz, 2 H), 7.26–7.32 (m, 3 H), 7.35 (dif. t, *J* = 7.9 Hz, C_6H_5, 4 H), 7.42 (dif. t, *J* = 7.9 Hz, 2 H), 7.67 (dif. d, *J* = 8.0 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 15.7, 19.4, 26.5, 31.3, 36.4, 43.1, 64.8, 69.9, 105.0, 111.9, 118.8, 125.0, 127.0, 127.7, 127.7, 128.4, 129.7, 129.9, 132.8, 135.0, 135.5, 136.7, 141.0, 145.3, 156.0, 156.6, 199.6.

HRFABMS: *m*/*z* $[M + H]^+$ calcd for $C_{39}H_{42}O_4Si$: 602.2852; found: 602.2808.

(*R*,*Z*)-5-{3-[2-Benzyloxy-4-(*tert*-butyldiphenylsilyloxy)phenyl]-1-(2-methoxyethoxy)methoxy-2-propen-2-yl}-2-methylcyclohex-2-en-1-one (38)

To a solution of (*Z*)-**37** (3.02 g, 5.02 mmol) in DMF (10 mL), were added *i*-Pr_2EtN (2.6 mL, 14.9 mmol) and MEMCl (1.4 mL, 12.3 mmol) and the mixture was stirred at 90 °C for 2 h. After cooling to r.t., aq 5% HCl (50 mL) was added and the mixture was extracted with EtOAc (2 × 300 mL). The organic layer was washed with aq 5% HCl (4 × 100 mL) and brine (1 × 200 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 4:1) to give (*Z*)-**38** as a colorless oil (2.82 g, 81%). Compound (*E*)-**38** was prepared by the same procedure from (*E*)-**37** in 91% yield.

(*Z*)-38

$[\alpha]_D^{24}$ –21.1 (*c* 1.2, $CHCl_3$).

IR (ATR): 1672 cm^{-1}.

^1H NMR (400 MHz): δ = 1.09 (s, 9 H), 1.78 (br s, 3 H), 2.34–2.43 (m, 1 H), 2.47 (dd, *J* = 16.0, 13.5 Hz, 1 H), 2.46–2.56 (m, 1 H), 2.67 (ddd, *J* = 16.0, 3.7, 0.9 Hz, 1 H), 2.97–3.05 (m, 1 H), 3.33 (s, 3 H), 3.46 (dif. t, *J* = 4.6 Hz, 2 H), 3.64 (dif. t, *J* = 4.6 Hz, 2 H), 4.12 (s, 2 H), 4.67 (s, 4 H), 6.31 (d, *J* = 2.2 Hz, 1 H), 6.36 (dd, *J* = 8.2, 2.2 Hz, 1 H), 6.55 (s, 1 H), 6.75 (m, 1 H), 6.99 (d, *J* = 8.2 Hz, 1 H), 7.21 (dif. d, *J* = 7.7 Hz, 2 H), 7.26–7.45 (m, 9 H), 7.69 (dif. d, *J* = 7.5 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 15.7, 19.5, 26.5, 32.1, 40.6, 43.7, 59.0, 65.7, 67.1, 69.9, 71.7, 95.4, 104.7, 111.7, 118.9, 125.2, 126.9, 127.7, 127.8, 128.4, 130.0, 130.4, 132.9, 135.3, 135.5, 136.9, 138.1, 144.9, 156.2, 156.8, 199.9.

HREIMS: *m/z* $[M]^+$ calcd for $C_{42}H_{50}O_6Si$: 690.3376; found: 690.3318.

(*E*)-38

$[\alpha]_D^{26}$ +81.8 (*c* 1.0, $CHCl_3$).

IR (ATR): 1672 cm^{-1}.

^1H NMR (400 MHz): δ = 1.08 (s, 9 H), 1.75 (br s, 3 H), 2.17 (dif. ddd, *J* = 18.1, 4.9, 4.9 Hz, 1 H), 2.39 (ddd, *J* = 16.1, 3.7, 1.1 Hz, 1 H), 2.51–2.60 (m, 1 H), 2.61 (dd, *J* = 16.1, 14.3 Hz, 1 H), 3.26–3.35 (m, 1 H), 3.37 (s, 3 H), 3.52 (dif. t, *J* = 4.6 Hz, 2 H), 3.68 (dif. t, *J* = 4.6 Hz, 2 H), 4.20 (s, 2 H), 4.67 (s, 2 H), 4.72 (s, 2 H), 6.29 (d, *J* = 2.2 Hz, 1 H), 6.35 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.55 (s, 1 H), 6.66 (dif. d, *J* = 5.9 Hz, 1 H), 6.81 (d, *J* = 8.3 Hz, 1 H), 7.19 (dif. d, *J* = 7.5 Hz, 2 H), 7.27–7.30 (m, 3 H), 7.35 (dif. t, *J* = 7.6 Hz, 4 H), 7.42 (dif. t, *J* = 7.3 Hz, 2 H), 7.67 (dif. d, *J* = 8.0 Hz, 4 H).

^{13}C NMR (100 MHz): δ = 15.7, 19.4, 26.5, 31.1, 36.5, 43.0, 59.0, 67.0, 69.2, 69.8, 71.7, 94.2, 104.9, 111.8, 118.8, 127.0, 127.6, 127.7, 128.3, 129.7, 129.9, 129.9, 132.8, 135.0, 135.5, 136.8, 137.2, 145.2, 156.0, 156.6, 199.7.

HREIMS: *m/z* $[M]^+$ calcd for $C_{43}H_{50}O_6Si$: 690.3376; found: 690.3392.

Isomerization of (*E*)-38 to (*Z*)-38

A solution of (*E*)-**38** (526 mg, 0.76 mmol) and acetophenone (0.01 mL, 85.7 mmol, 0.11 mequiv) in benzene (15 mL) was irradiated by UV light (400 W high pressure Hg lump, Pyrex filter) for 1 h. The solvent was evaporated in vacuo and the residue was purified by CC (*n*-hexane–EtOAc, 3:1) to give (*E*)-**38** (150 mg, 29%) and (*Z*)-**38** (215 mg, 41%).

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