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Tetrahedron
Tetrahedron 63 (2007) 6259–6286

Siloxyallenes revisited. A useful functional intermediate for the synthesis of (*Z*)-β-branched Morita–Baylis–Hillman type adducts and (*Z*)-chalcones

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Received 15 December 2006; revised 6 February 2007; accepted 7 February 2007
Available online 13 February 2007

Abstract—Siloxyallenes proved to be a useful functional intermediate in the preparation of (*Z*)-β-branched Morita–Baylis–Hillman type adducts by the reaction of aldehydes with silylacetylenes or siloxypropynes. Various (*Z*)-chalcones were stereoselectively synthesized from siloxypropynes via siloxyallenes.

1. Introduction

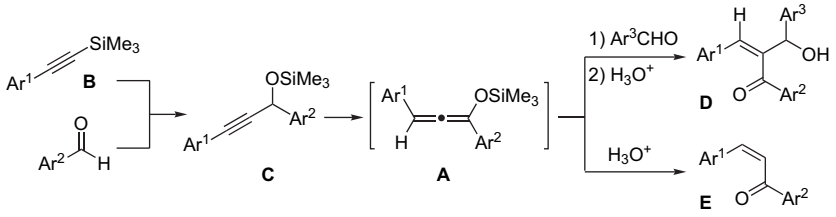
Siloxyallenes (allenyl silyl ethers or silyl allenolates) **A** have been recognized as useful functional intermediates in organic synthesis.[1] They have been synthesized in three ways: (1) isomerization of siloxypropynes (2-propynyl silyl ethers) with base,[1f–i] (2) coupling of silyl ketones with acetylides followed by a Brook rearrangement,[1a–e] and (3) reaction of α,β-alkynyl ketones with iodotrimethylsilane.[1j]

Recently, we found by chance that siloxyallenes **A** were formed as an intermediate in the synthesis of (*Z*)-β-branched Morita–Baylis–Hillman (MBH) type adducts **D**, as shown in Scheme 1. Reaction of silylacetylenes **B** with aldehydes catalyzed by a chiral ammonium fluoride gave (*Z*)-β-branched MBH type adducts **D** via siloxypropynes **C** and then siloxyallenes **A** as intermediates.[2] Formation of siloxyallenes **A** was also observed by treatment of siloxypropynes **C** with KO*t*-Bu, and siloxyallenes **A** reacted with other aldehydes to give (*Z*)-β-branched MBH type adducts **D**.[3] Acidic treatment of siloxyallenes **A** was revealed to produce (*Z*)-chalcone derivatives **E**.[4] We now report the details of the method for the preparation of (*Z*)-β-branched Morita–Baylis–Hillman type adducts **D** and (*Z*)-chalcone derivatives **E** via siloxyallenes **A**.

2. Results and discussion

2.1. Reaction of 1-phenyl-2-(trimethylsilyl)acetylene and aromatic aldehydes catalyzed with ammonium fluorides

In 1993, a chiral quaternary ammonium fluoride **5a** corresponding to a chiral version of tetrabutylammonium fluoride was prepared by our group[5] for the first time[6] from cinchonine. The fluoride has been revealed to be a good catalyst for a catalytic asymmetric silyl aldol reaction.[5] Since then, importance of chiral ammonium fluorides has been increasing in organic synthesis.[7]



Scheme 1.

Keywords: Siloxyallene; Morita–Baylis–Hillman type adduct; Silylacetylene; Siloxypropyne; (*Z*)-Chalcone.
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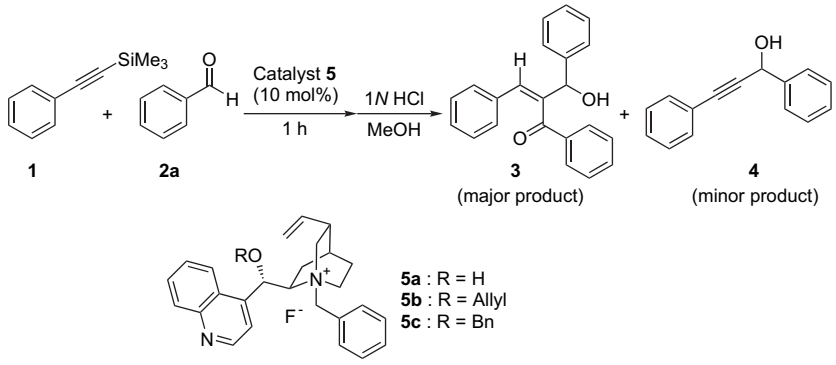
doi:10.1016/j.tet.2007.02.025

As an extension of the utilization of chiral ammonium fluorides to organic synthesis, the reaction of 1-phenyl-2-(trimethylsilyl)acetylene (**1**) with benzaldehyde (**2a**) was investigated by use of the quaternary ammonium fluoride **5a** derived from cinchonine.[5] To our surprise, the main product of the reaction, after acidic workup, was not the expected propargyl alcohol **4** but the MBH type adduct **3**. The latter **3** was probably formed by the reaction of another equivalent of benzaldehyde with the originally formed silyl derivative of the propargyl alcohol. The structure of **3** was identified by spectral comparison with the known compound,[8] but the exclusive formation of the (*Z*)-isomer was recognized. Tetrabutylammonium fluoride (TBAF) as well as other fluoride anion reagents were already utilized for the same reaction, but the main product was always reported to be the propargyl alcohol **4**,[9] contrary to our result. Furthermore, β-substituted MBH type adducts are not so easy to prepare by use of the MBH reaction though several alternative improved methods have been reported.[1a,c,d,h–j,8,10] Thus, we launched to explore the versatility of the unprecedented reaction.

The results are summarized in Table 1. The reaction rapidly proceeded at lower temperature in various solvents. Conversion of the hydroxyl function of the catalyst **5a** to the ether function, **5b** and **5c**, resulted in the decrease of the formation of **3** but increase of the formation of **4** (entries 7–9 in Table 1).

The order of the addition of the reactants and catalyst influenced the reaction. The reaction smoothly proceeded when the acetylene **1** was added to a mixture of benzaldehyde (**2a**) and the catalyst **5a**, while no reaction occurred when the acetylene was first mixed with the catalyst and then the aldehyde was added. Suitable quantities of benzaldehyde in CH_2Cl_2 were 1.25–1.5 equiv, but not 2 equiv (entries 10–13). The MBH type adduct **3** was preferentially formed even when less than 1 equiv of the aldehyde was used. The requisite concentration of the catalyst was 10 mol %. The use of TBAF in THF (commercially available, 1 M solution containing ca. 5% water) afforded the propargyl alcohol **4** as the major product as reported. A similar result was obtained when anhydrous TBAF[11] was used. These experiments clearly indicate that the reaction producing the β-substituted MBH type product will be specific to the cinchoninium ammonium fluoride and different from TBAF. The reaction proceeded in a complete diastereoselective manner to give the (*Z*)-isomer only, but, unfortunately, the enantioselectivity of the reaction was quite low, as shown in Table 1.

Table 1. Reaction of 1-phenyl-2-(trimethylsilyl)acetylene (**1**) with benzaldehyde (**2a**) catalyzed with benzylcinchoninium fluoride (**5a**) and its derivatives[a]



Entry	Catalyst	Solvent	Temperature (°C)	**2a** (equiv)	Yield (%)[b]; **3**[d]	ee%[c]; **4**[e]
1	**5a**	CH_2Cl_2	−20 to rt	1.1	90 (0)	—
2	**5a**	Toluene	−20 to rt	1.1	73 (3)	—
3	**5a**	THF	−20	1.1	73 (6)	—
4	**5a**	DMF	−20	1.1	78 (2)	—
5	**5a**	MeCN	−20	1.1	84 (0)	—
6	**5a**	THF	−40	1.1	73 (7)	13 (15)
7[f]	**5a**	THF	−20	1.1	80 (9)	—
8	**5b**	THF	−20	1.1	49 (16)	18 (28)
9	**5c**	THF	−20	1.1	45 (17)	27 (21)
10	**5a**	CH_2Cl_2	−20 to rt	0.8	46 (0)	9
11	**5a**	CH_2Cl_2	−20 to rt	1.25	86 (0)	2
12	**5a**	CH_2Cl_2	−20 to rt	1.5	83 (0)	2
13	**5a**	CH_2Cl_2	−20 to rt	2.0	58 (0)	4
14	**5a**[g]	CH_2Cl_2	−20 to rt	1.5	65 (3)	23
15[f]	**TBAF**[h]	THF	−20	1.1	10	63

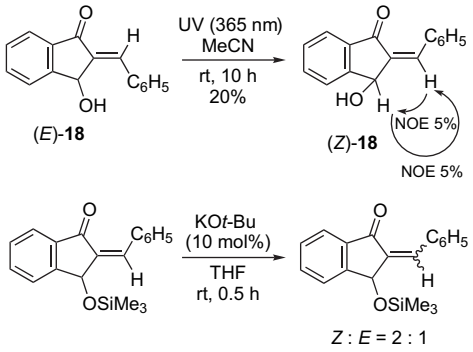
[a] To a mixture of the catalyst **5** and benzaldehyde (**2a**) was added the acetylene **1**.
[b] Isolated yield.
[c] Checked by DAICEL CHIRALCEL OD (hexane/*i*-PrOH=9:1, 1 mL/min, 254 nm).
[d] Yield based on **2a**.
[e] Yield based on **1**.
[f] To a mixture of the acetylene **1** and benzaldehyde (**2a**) was added the catalyst **5a**.
[g] The catalyst **5a** (5 mol %) was used.
[h] THF solution was purchased and used directly.

Application of a catalytic amount of the reagent generated in situ from *N*-benzylcinchoninium bromide (**6**) and CsF to the reaction also smoothly afforded the MBH type adduct **3** in DMF, as shown in Table 2. Again, the *O*-benzyl derivative **7** did not give even a trace of the products.

Various aromatic aldehydes **2** underwent the reaction with the acetylene **1** to give the (*Z*)-MBH type adducts **D** as the major products under the reaction conditions shown in entry 12 of Table 1, as summarized in Table 3.

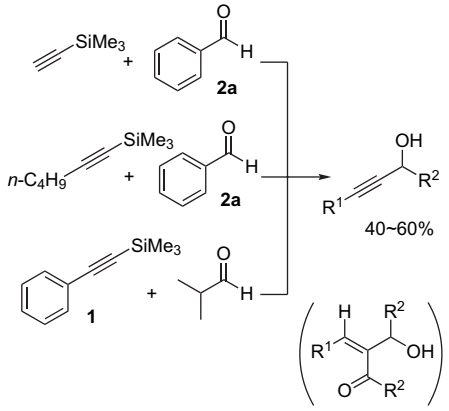
Although both 4-methyl- and 3,4-methylenedioxybenzaldehydes (**2b** and **2h**) solely afforded **8** and **15** in good yield, respectively, the methoxy and dimethoxy derivatives, **2c** and **2g**, respectively, furnished a mixture of the MBH type adducts, **9** and **12**, and the propargyl derivatives, **13** and **14**, in preference of the latter. The aromatic aldehydes **2d** and **2e** having halogen atoms smoothly afforded the MBH type adducts **10** and **11**, respectively. However, the reaction using 4-nitrobenzaldehyde (**2f**) and 4-pyridylaldehyde (**2k**) did not proceed at all, while the reaction with 4-dimethylaminobenzaldehyde (**2l**) gave a complicated mixture. In all the cases, the MBH type adducts **D** obtained proved to have (*Z*)-configuration.

Phthalaldehyde (**2m**) having two aldehyde functions afforded a mixture of the indanone **18** and dihydroisobenzofuran **19** in preference of the former. The major product **18** was revealed to be (*E*)-isomer while the crude product was a mixture of (*Z*)- and (*E*)-isomers in a ratio of 13:87. The (*Z*)-isomer was prepared by photoisomerization of the (*E*)-isomer according to the literature,[12] and its structure was confirmed by its NOE measurement, as shown in Scheme 2. The trimethylsilyl derivative of (*Z*)-**18** was isomerized to (*E*)-**18** silyl ether under basic conditions. Thus, the isolated major product (*E*)-**18** would be formed during the reaction by isomerization of the initially formed (*Z*)-**18**. The isomerization did not occur under acidic conditions for quenching the reaction. The minor product of the reaction proved to be the dihydroisobenzofuran **19**, which would be formed by the reaction of one of the aldehyde group with the acetylene **1** followed by cyclization and then methyl ether formation by acidic methanol treatment.



Scheme 2.

Application of the above method to aliphatic trimethylsilylacetylenes or aldehydes resulted in the formation of the propargyl alcohols, and no MBH type adducts could be detected in the products, as shown in Scheme 3.[13]

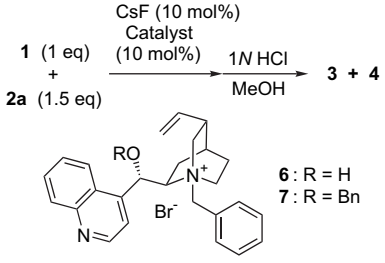


Scheme 3.

Two reaction routes would be possible for the formation of the MBH type adducts: the siloxyallene and oxetene routes, as shown in Scheme 4. If aldehydes having substituents on aromatic rings are used, two possible structurally isomeric adducts will be considered. The siloxyallene route will produce **G** while **H** will be obtained through the oxetene route.

This was clarified in the case of 4-fluorobenzaldehyde (**2d**) (Scheme 5). Thus, 4-fluorobenzaldehyde (**2d**) was subjected to the reaction with the propargyl alcohols **20** and **22**, respectively, by use of tris(triphenylsilyl)vanadate according to the procedure developed by Trost and Oi.[8] The reaction with **20** afforded a mixture of **10** and **21**,[14] in which the major product was identical to the MBH type adduct **10** obtained by use of the cinchonine catalyst **5a**. In contrast, the reaction with **22** afforded the compound **23**. All the products **10**, **21**, and **23** have (*Z*)-configuration, which was revealed by the characteristic *J*-value (ca. 4 Hz) at allylic position in their ^{1}H NMR spectra. The other MBH type adducts will have analogous structures **G**, as shown in Table 3.

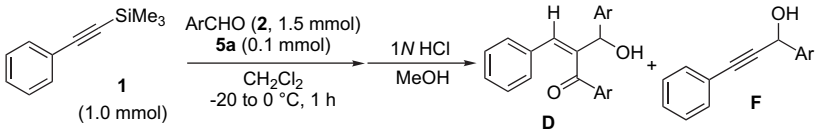
Table 2. Reaction of the silylacetylene **1** with the aldehyde **2a** using CsF and the bromides

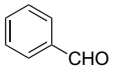
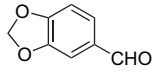
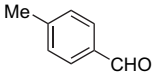
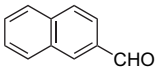
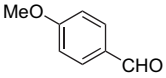
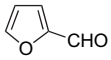
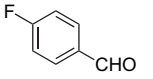
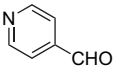
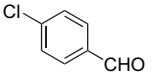
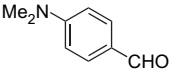
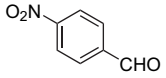
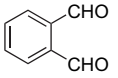
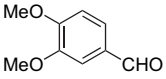


Entry	Catalyst	Solvent	Temperature/time	Yield (%)[a]	
				3[b]	**4**[c]
1	**6**	CH_2Cl_2	rt/0.5 h	72	19
2	**7**	CH_2Cl_2	rt/1 h	—[d]	—[d]
3	—	CH_2Cl_2	rt/0.5 h	—[d]	—[d]
4	**6**	CH_2Cl_2	0 °C/1 h	—[d]	—[d]
5	**6**	DMF	rt/0.5 h	91	—
6	—	DMF	rt/0.5 h	—	Trace

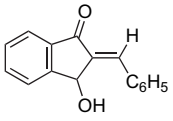
[a] Isolated yield.
[b] Based on **2a**.
[c] Based on **1**.
[d] Starting material was recovered.

Table 3. Synthesis of β-substituted Morita–Baylis–Hillman type adducts from the silylacetylene **1** and various aldehydes **2**

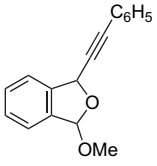


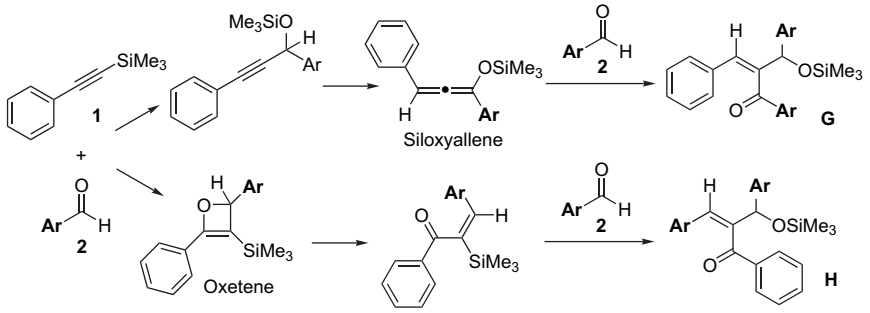
Entry	ArCHO	2	Yield (%)[a]				Entry	ArCHO	2	Yield (%)[a]			
			D[b]		F[c]					D[b]		F[c]	
1		**2a**	**3**	92	**4**	7	8		**2h**	**15**	87		—
2		**2b**	**8**	87		—	9		**2i**	**16**	85		—
3		**2c**	**9**	37	**13**	52[d]	10		**2j**	**17**	54		—
4		**2d**	**10**	89		—	11		**2k**		—		—
5		**2e**	**11**	89		—	12		**2l**		—		—
6		**2f**		—		—	13[f]		**2m**	**18**	49[g]	**19**	27[h]
7[e]		**2g**	**12**	23	**14**	26							

[a] Isolated yield.
[b] Based on **2**.
[c] Based on **1**.
[d] The propargyl derivative **13** was obtained as a mixture of OH and OMe derivatives.
[e] Quenched in MeCN instead of MeOH.
[f] Phthalaldehyde (0.75 mmol) was used. The crude product was a mixture of stereoisomers (*Z*/*E*=13:87).
[g] Product **18**:

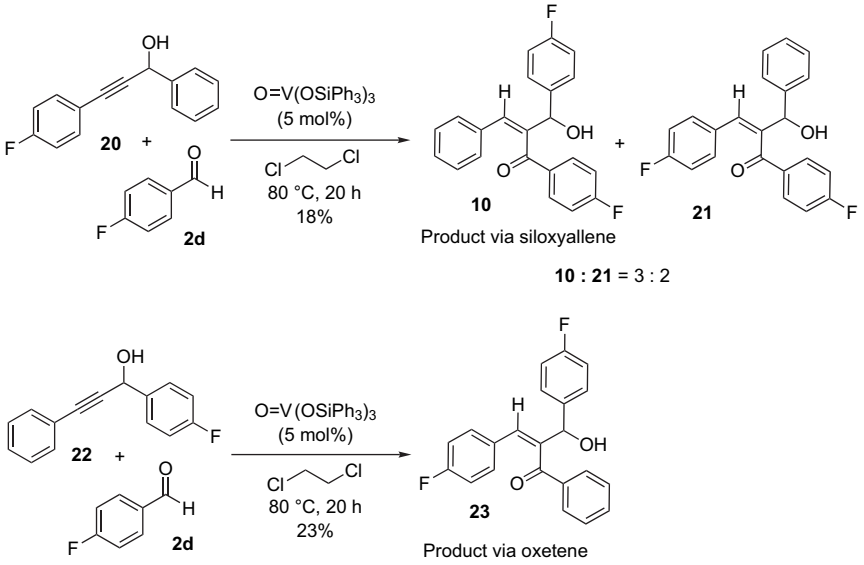


[h] Product **19**:





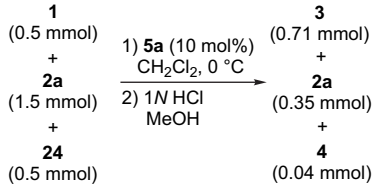
Scheme 4.



Scheme 5.

Thus, the reaction mechanism for the formation of the MBH type adducts **G** would be as shown in Scheme 6. The silylacetylene **1** would first add to the aldehyde **2** by the catalytic action of the fluoride **5a** to give the siloxypropyne **24**. Isomerization of the acetylenic triple bond to the allene bond would furnish the siloxyallene intermediate **25**, which would add the second aldehyde at the central carbon of the allene function. The (*Z*)-geometry preference in the product would be explained by the preferred chair form transition state **I** in which the reaction exclusively would occur from the less hindered site of the siloxyallene.

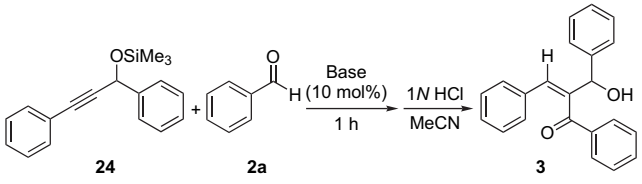
Although no isomerization of **24** occurred by the action of the ammonium fluoride **5a**, treatment of a mixture of **1**, **2a**, and **24** with the catalyst **5a** gave evidence of the conversion of **24**, as shown in Scheme 7. The base, e.g., phenylacetylide anion, probably generated in situ would participate in the deprotonation of **24** to induce the isomerization to the allene intermediate.



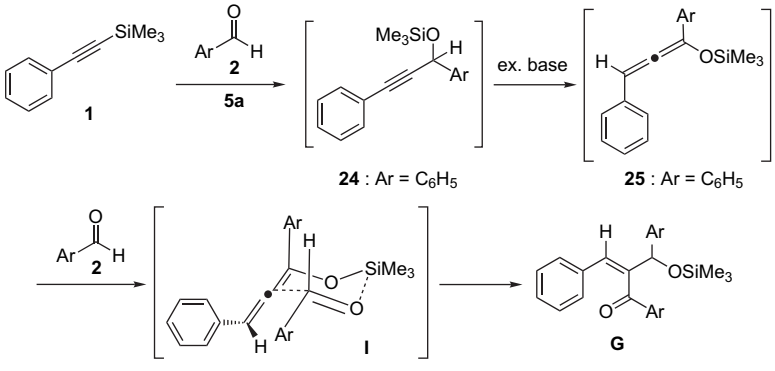
Scheme 7.

2.2. Reaction of 1,3-diaryl-2-propynyl trimethylsilyl ethers and aldehydes using potassium *tert*-butoxide

The above consideration of the reaction mechanism suggested that a base in addition to the fluoride ion might play a key role in the reaction. In fact, addition of a catalytic amount of potassium *tert*-butoxide (KO*t*-Bu) to a mixture of the siloxypropyne **24** and benzaldehyde (**2a**) in DMF afforded the MBH type adduct **3** after acid treatment, as shown in Scheme 8. Obviously, the reaction intermediate will be the siloxyallene formed by isomerization of the siloxypropyne[1a,c,d,h–j] As shown in Table 4, a combination of KO*t*-Bu and DMF gave the superior result, and the reaction



Scheme 8.



Scheme 6.

Table 4. Reaction of the siloxypropyne **2a** with the aldehyde **2a** using base[a]

Entry	Catalyst	Solvent	Temperature (°C)	Yield (%)[b]
1	KO*t*-Bu	DMF	−20	82
2	KO*t*-Bu[c]	DMF	−20	76
3	KO*t*-Bu	THF	−20	33
4	KO*t*-Bu[c]	THF	−20	57
5	KO*t*-Bu	THF	rt	68
6	KO*t*-Bu	CH_2CI_2	rt	2
7	KO*t*-Bu	DMF	−65	—
8	NaO*t*-Bu	DMF	−20	79
9	LiO*t*-Bu	DMF	−20	13
10	*i*-Pr_2NEt[d]	DMF	rt	—

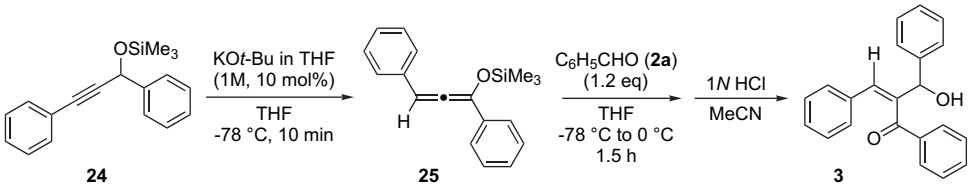
[a] Reaction time of all was 1 h.
[b] Yields of **3** were assayed by HPLC analysis using YMC Pro C 18 (4.6 mm×150 mm) column (UV 254 nm; flow rate, 1.0 mL/min; eluent, MeCN/H_2O/70% aq $HClO_4$=600:400:1 (v/v/v)).
[c] KO*t*-Bu in THF (1 M) was used.
[d] An excess (100 mol %) was used.

quickly proceeded at −20 °C within 1 h. NaO*t*-Bu afforded the comparable result while LiO*t*-Bu and Hünig base were not suitable for the reaction.

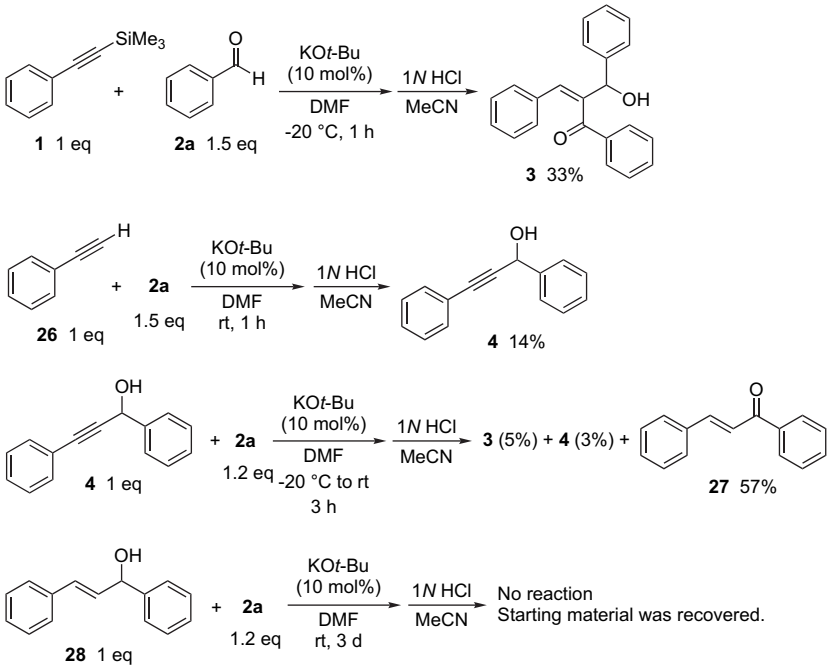
Isolation of the siloxyallene **25** was accomplished through the reaction of KO*t*-Bu with the siloxypropyne **24** without the aldehyde **2a** in THF. The crude product proved to be the siloxyallene **25** by ^1H NMR and IR spectra, the latter of which exhibited absorption of the allene moiety at 1928 cm^{-1},[15] as shown in Scheme 9. Purification of the crude product by silica gel column chromatography failed, and (*Z*)-chalcone was obtained. This observation led us to an exploration of the method for the synthesis of (*Z*)-chalcones, which will be described later in this paper. Attempted isolation of the siloxyallene failed in DMF probably because of higher reactivity of the siloxyallene and its decomposition. The siloxyallene was revealed to be quickly formed within 10 min at −78 °C in THF, and 10 mol % of KO*t*-Bu was sufficient to conduct the reaction.

Next, the reaction was conducted in two-step procedure: the formation of the siloxyallene and then addition of the aldehyde. After acidic treatment, the desired MBH adduct was obtained in good yield comparable to the one-step procedure. Furthermore, it was found that addition of KO*t*-Bu to a mixture of benzaldehyde (**2a**) and 1-phenyl-2-(trimethylsilyl)acetylene (**1**), a precursor of the siloxypropyne, afforded the MBH adduct **3** though the yield was much lower (33% yield). No or little amount of **3** was formed by the reaction of benzaldehyde (**2a**) with phenylacetylene (**26**), 1,3-diphenylpropargyl alcohol (**4**), or 1,3-diphenylallyl alcohol (**28**), as shown in Scheme 10.

The synthesis of the MBH type adducts catalyzed with KO*t*-Bu was investigated using various substrates by two methods: method A in which KO*t*-Bu was added to a mixture



Scheme 9.

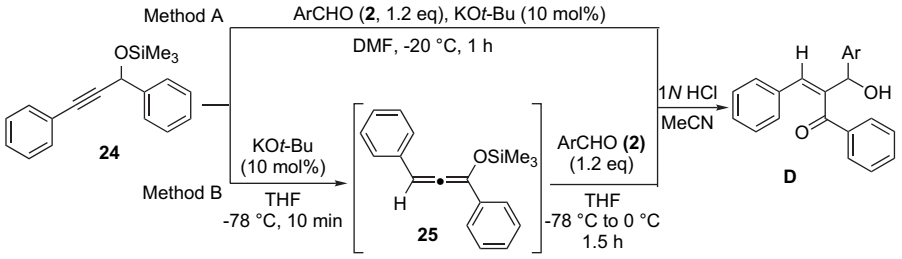


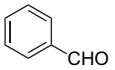
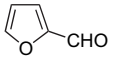
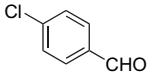
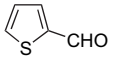
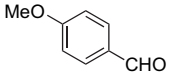
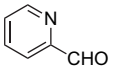
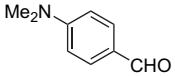
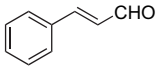
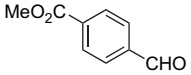
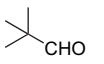
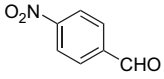
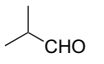
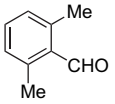
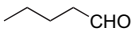
Scheme 10.

of the siloxypropyne **24** and the aldehyde **2** in DMF and method B in which the siloxyallene **25** was first formed by reaction of the siloxypropyne **24** with KO*t*-Bu in THF and then the aldehyde **2** was added. As summarized in Table 5, the siloxypropyne **24** rapidly reacted with various aldehydes **2** by use of a catalytic amount (10 mol %) of KO*t*-Bu to give the MBH type adducts **D** with (*Z*)-configuration in good to moderate yields. In general, method B gave a better result than method A. As in the reaction using the fluoride catalyst **5a** (entry 6 in Table 3), the reaction with 4-nitrobenzaldehyde (**3f**) resulted in the recovery of the starting aldehyde by use of method A. In contrast, the MBH type adduct **33** was obtained in 67% yield using method B. Although 4-dimethylaminobenzaldehyde (**2l**) did not give any products when cinchoninium fluoride **5a** was used (see entry 12 in Table 3), the MBH type adduct **31** was obtained in 35% yield by method A and the application of method B increased the yield to 74%. The ester function of the aldehyde **2n** and the sterically hindered case such as **2o** did not cause any trouble and the MBH type products **32** and **34** were obtained in 83 and 68% yields, respectively. Method B proved to be superior in the reaction with 2-pyridylaldehyde (**2q**) and cinnamaldehyde (**2r**), the latter of which did not give any 1,4-adduct. A striking contrast between the reaction catalyzed with the ammonium fluoride **5** and that using KO*t*-Bu was observed in the reactions utilizing aliphatic aldehydes. Pivalaldehyde (**2s**) afforded the MBH type adduct **39** by method A while only method B was effective for the reaction with the aldehydes **2t** and **2u** having α-proton.

Then, the reaction procedure of method B was applied to the reaction with ketones. Although 3-pentanone (**42**), acetophenone (**43**), and ethyl acetoacetate (**44**) did not give any MBH type adducts, the reaction with trifluoroacetophenone (**45**) and α-ketoesters **46** and **47** proceeded to give the MBH type adducts **J**, as shown in Table 6. In the latter cases, the carbonyl functions of the ketones may be activated by the electron-withdrawing functions, CF_3 and esters, or the reaction may proceed via a robust bicyclic transition state **51**.[16]

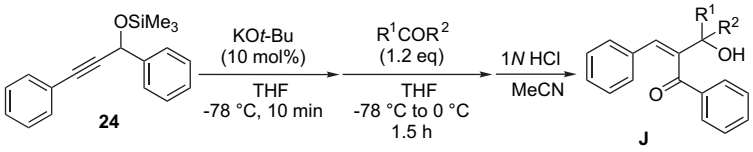
Table 5. Synthesis of β-substituted Morita–Baylis–Hillman type adducts **D** from the siloxypropyne **24** and various aldehydes **2**

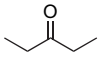
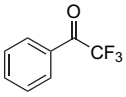
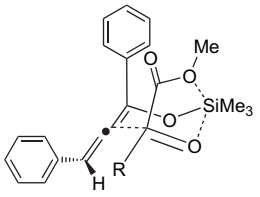
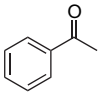
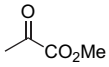
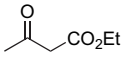
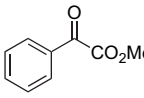


RCHO	2	Method	D	Yield (%)[a]	RCHO	2	Method	D	Yield (%)[a]
	**2a**	A B	**3**	82 85		**2j**	A	**35**	95
	**2e**	A	**29**	76		**2p**	A	**36**	83
	**2c**	A	**30**	72		**2q**	A B	**37**	35 54
	**2l**	A B	**31**	35 74		**2r**	A B	**38**	52 66
	**2n**	B	**32**	83		**2s**	A	**39**	67
	**2f**	A B	**33**	— 67		**2t**[b]	A B	**40**	— 69
	**2o**	A	**34**	68		**2u**[b]	A B	**41**	— 69

Method A: To a mixture of **24** and RCHO **2** in DMF was added KO*t*-Bu at −20 °C. After being stirred at −20 °C for 1 h, the mixture was quenched with 1 N aq HCl.
Method B: To a solution of **24** in THF was added KO*t*-Bu at −78 °C. After 10 min, RCHO **2** was added at −78 °C. The mixture was warmed to 0 °C during 0.5 h, stirred at 0 °C for 1 h, and quenched with 1 N aq HCl.
[a] Isolated yield.
[b] The aldehyde (1.5 equiv) was used.

Table 6. Synthesis of β-substituted Morita–Baylis–Hillman type adducts **J** from the siloxypropyne **24** and ketones



R^1COR^2	Yield (%)[a]	R^1COR^2	J	Yield (%)[a]	
 **42**[b]	—	 **45**[b]	**48**	78[c]	 **51**
 **43**[b]	—	 **46**	**49**	11	
 **44**[b]	—	 **47**	**50**	60[c]	

[a] Isolated yield.
[b] R^1COR^2 (1.5 equiv) was used.
[c] Trimethylsilyl ether was obtained.

Next, the reaction was carried out by use of various siloxypropynes **C** and aromatic aldehydes **2**. The starting siloxypropynes **C** were prepared by (1) lithiation of acetylenes with BuLi, (2) coupling with aldehydes, and then (3) *O*-silylation with Me_3SiCl–Et_3N. As expected, almost all the reactions proceeded to give the MBH type adducts **D** by use of method A, as shown in Table 7. Although method A afforded the adducts in lower yield in the reaction with the siloxypropynes **56** and **57**, method B improved the yields. The reaction with the alkyl derivatives **58** and **59** sluggishly proceeded. This will be due to the lower acidity of the propargylic proton, and no or little proton abstraction or isomerization occurred.

The MBH type adducts **D** obtained by use of KO*t*-Bu were (*Z*)-isomers, and no peaks of (*E*)-isomers were detected in their ^1H NMR spectra. NOE was observed in **63** and **64** as shown in Figure 1, which further confirmed the (*Z*)-configuration. The (*Z*)-configuration of the olefin part of the other adducts could be assigned by analogy.

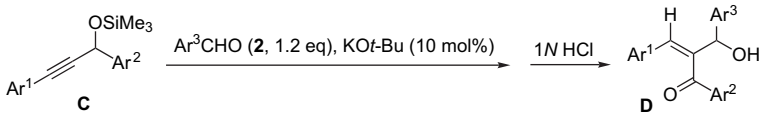
The mechanism for the formation of the MBH type adducts **D** will be as shown in Scheme 11. Abstraction of the proton from the propargyl position of the siloxypropyne **C** with KO*t*-Bu would afford the propargyl anion **69** together with *t*-BuOH. The propargyl anion **69** would be isomerized to the allenyl anion **70**, which would exchange the proton with the other siloxypropyne **C** to give the siloxyallene **A** and to regenerate the propargyl anion **69**. The siloxyallene **A** thus formed would react with the aldehyde **2** to produce the MBH type adduct **D** via the six-membered transition state **K**.

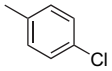
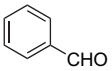
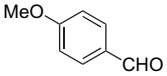
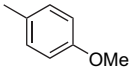
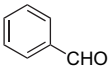
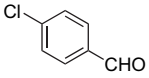
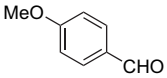
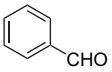
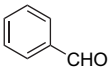
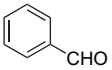
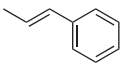
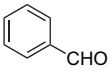
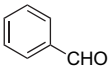
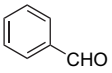
To prove whether *t*-BuOH generated in the first stage would be regenerated to *t*-BuO anion and KO*t*-Bu would work as a catalyst, the siloxypropyne **71** deuterated at the propargylic position reacted with benzaldehyde (**2a**) in the presence of 10 mol % of KO*t*-Bu with or without *t*-BuOH, as shown in Scheme 12. The MBH type adduct **72** obtained was found to be deuterated in either case. This result clearly indicates that *t*-BuO anion is not regenerated and recycled. Thus KO*t*-Bu proved to be an initiator but not a catalyst in the reaction, and the proton transfer would occur between the allenyl anion **70** and the (starting) siloxypropyne **C**.

The reactivity of the siloxyallene was confirmed by mixing the isolated crude siloxyallene **25** with benzaldehyde (**2a**) to give the MBH type adduct **3** in DMF. However, the reaction did not proceed in THF. As already described, the reaction with cinnamaldehyde (**2q**) afforded the MBH type adduct **38** as a sole isolable product but not 1,4-addition product (see Table 5). This result would suggest the formation of the six-membered transition state **K**,[17] and the aldehyde **2** would approach from the site of the hydrogen atom in the siloxyallene **A** to furnish the (*Z*)-isomer with superior stereoselectivity (Scheme 11).

The reaction of the siloxypropyne **24** with the aldehyde **2a** did not proceed well when LiO*t*-Bu or BuLi was used as already described (Table 4). This will suggest the influence of the cationic species. Furthermore, Reich and co-workers reported stabilized propargyl anions, which were not easy to isomerize to the allenyl anions.[1d] These interests led us to investigate the siloxyallene formation by use of the siloxypropyne **73** having the *tert*-butyldimethylsilyl function instead of the trimethylsilyl one, because the anion generated would attack the silicon atom of the latter as a Lewis base and decomposition would occur. As shown in Table 8, KO*t*-Bu was effective for isomerization to form the siloxyallene **74** while BuLi was not effective. Quenching the reaction using BuLi with D_2O afforded the deuterated siloxyallene accompanied with the recovered starting siloxypropyne, which was not deuterated. Thus, the reaction with BuLi would stop at the allenyl anion stage in Scheme 11, and **73** would not form the stabilized propargyl anion. The siloxyallene **74** thus obtained was easily converted to (*Z*)-chalcone by column chromatography on silica gel. The different reactivity between KO*t*-Bu and BuLi would be due to the strength of the

Table 7. Synthesis of β-substituted Morita–Baylis–Hillman type adducts **D** from the siloxypropynes **C** and various aldehydes **2**



Ar^1	Ar^2	C	Ar^3CHO	**2**	Method	**D**	Yield (%)[a]
		**52**		**2a**	A	**60**	74
				**2c**	A	**61**	71
		**53**		**2a**	A	**62**	83
				**2e**	A	**63**	83
				**2c**	A	**9**	79
		**54**		**2a**	A	**64**	80
		**55**		**2a**	A	**65**	76
		**56**		**2a**	A B	**66**	40 78
		**57**		**2a**	A B	**67**	28 50
n-C_4H_9		**58**		**2a**	A[b]	**68**	23
	n-C_4H_9	**59**		**2a**	A	—	—

Method A: To a mixture of **C** and Ar^3CHO **2** in DMF was added KO*t*-Bu at −20 °C. After being stirred at −20 °C for 1 h, the mixture was quenched with 1 N aq HCl.
Method B: To a solution of **C** in THF was added KO*t*-Bu at −78 °C. After 10 min, Ar^3CHO **2** was added at −78 °C. The mixture was warmed to 0 °C during 0.5 h, stirred at 0 °C for 1 h, and quenched with 1 N aq HCl.
[a] Isolated yield.
[b] KO*t*-Bu (20 mol %) was used.

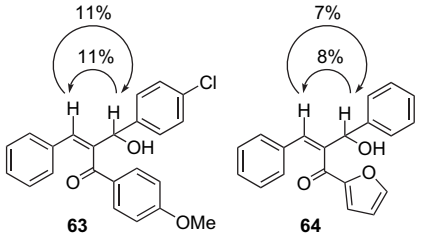


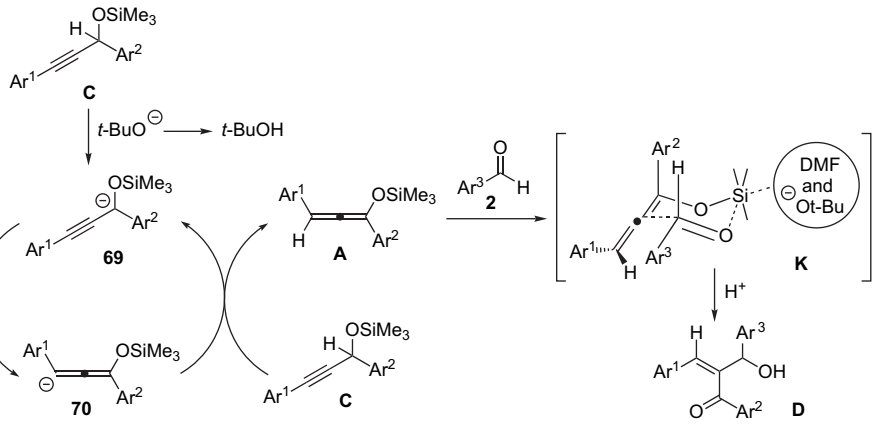
Figure 1.

coordination to the anionic species, and higher coordination of the lithium atom would stabilize the allenyl anion and the reaction would not proceed further.

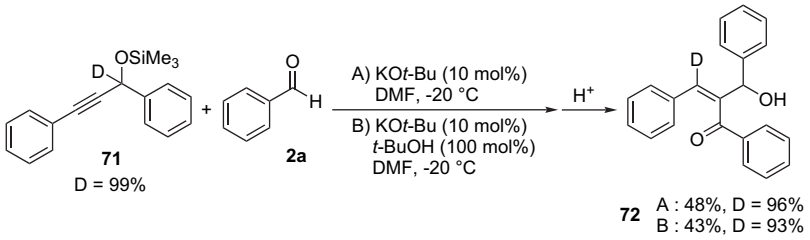
Such difference of the cationic species was also observed in the MBH type adduct synthesis utilizing the quaternary ammonium fluorides, **5a**–**c**, described in Section 2.1 (Table 1), in which the free hydroxyl function influenced the reaction. Interestingly, choline fluoride also catalyzed the reaction of the silylacetylene **1** with benzaldehyde (**2a**) in DMF to give **6a** as the MBH type adduct **3** in 59% yield while **4** was obtained in 8% yield after acid treatment. This result is contrary to that using TBAF and will suggest the importance of the presence of the β-hydroxyl function in the cinchoninium salt.

2.3. Attempts for the enantioselective reaction

The enantioselectivity for the synthesis of the MBH type adduct **3** was less than 10% ee by use of the cinchoninium fluoride **5**, as already described in Section 2.1 (Table 1). We already reported an enantioselective synthesis of optically

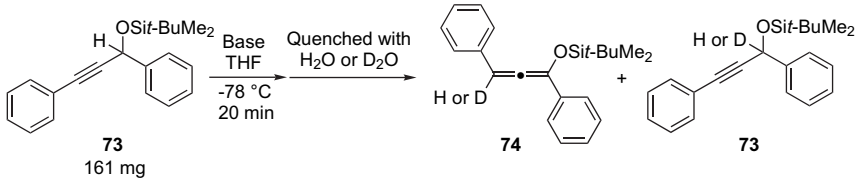


Scheme 11.



Scheme 12.

Table 8. Deuteration results using the siloxypropyne **73**



Base	Quench	Recovery (mg)	**74**:**73**
KO*t*-BU (10 mol %)	H_2O	151	100:0
n-BuLi (20 mol %)	H_2O	157	22:78
n-BuLi (20 mol %)	D_2O	158	22:78[a]

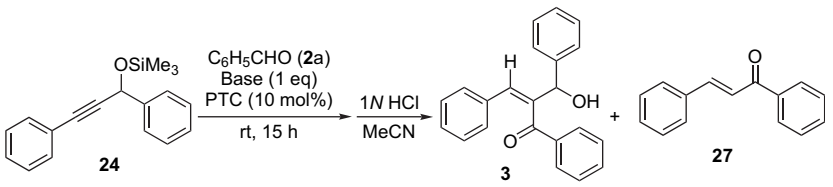
[a] D content of **74** was 78%, but no deuteride was observed in **73**.

active allenes from 1,3-biarylpropynes by a combination of base (KOH) and a chiral PTC derived from cinchonine.[18] These facts led us to investigate to change the racemic synthesis of the MBH type adduct utilizing KO*t*-Bu to an enantioselective one. Thus, a combination of chiral quaternary ammonium salts and various bases was applied to the reaction of the siloxypropyne **24** with benzaldehyde (**2a**). The results are shown in Table 9. Although most of the reaction proceeded as expected, no increase of enantioselectivity was observed at all.

Furthermore, the reaction utilizing the optically active siloxypropyne **24**[19] and benzaldehyde (**2a**) afforded the MBH type adduct **3**, but a great loss of enantiomeric purity was observed in the MBH type adduct, as shown in Scheme 13. Further investigation will be necessary to determine which step, the siloxyallene formation or reaction with the aldehyde, will induce racemization.

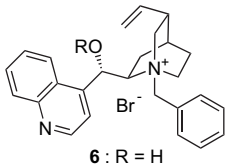
2.3.1. Synthesis of (*Z*)-chalcone derivatives. As described earlier, the crude siloxyallene **25** formed from the siloxypropyne **24** by the action of KO*t*-Bu was transformed to (*Z*)-chalcone by column chromatography on silica gel. In addition, (*Z*)-chalcone was obtained as the major product when acetic acid was used instead of benzaldehyde (**2a**) in the two-step conversion of the siloxypropyne **25** to the MBH type adduct using KO*t*-Bu. Although many (*E*)-and (*Z*)-chalcone derivatives are biologically active[20a] as well as substrates for the evaluation of various organic reactions,[20b,c] their preparative methods have been mainly concerned with thermodynamically stable (*E*)-isomers because of their easy preparation, and very few reports have been concerned with the synthesis of (*Z*)-isomers.[20] In general, photoisomerization of (*E*)-chalcones will be the choice of method for the (*Z*)-isomer synthesis. However, it takes time and a special apparatus for photochemical reactions.[21]

Table 9. Attempted asymmetric synthesis of Morita–Baylis–Hillman type adduct **3**

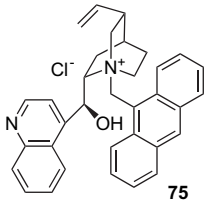


Entry	Base	Solvent	PTC	Yield (%)[a] (ee%)[b]		
				3	**27**	**24**
1	K_3PO_4	THF	—	—	—	Quant.
2	K_3PO_4	THF	TBAB	56	28	—
3[c]	K_3PO_4	THF	**6**	72 (9)	24	—
4[d]	K_3PO_4	THF	**7**	30 (3)	35	26
5[e]	K_3PO_4	THF	**75**	57 (3)	39	—
6	Cs_2CO_3	THF	—	—	—	Quant.
7	Cs_2CO_3	THF	TBAB	56	28	—
8[f]	Cs_2CO_3	THF	**6**	72 (9)	22	—
9[d]	Cs_2CO_3	THF	**7**	37 (2)	42	19
10	K_2CO_3	THF	**6**	—	—	Quant.
11	K_3PO_4	CH_2Cl_2	TBAB	3	3	80
12	K_3PO_4	CH_2Cl_2	**6**	57 (3)	31	14
13	K_3PO_4	Toluene	TBAB	49	19	28
14	K_3PO_4	Toluene	**6**	—	—	Quant.

TBAB
n-$Bu_4N^+Br^-$

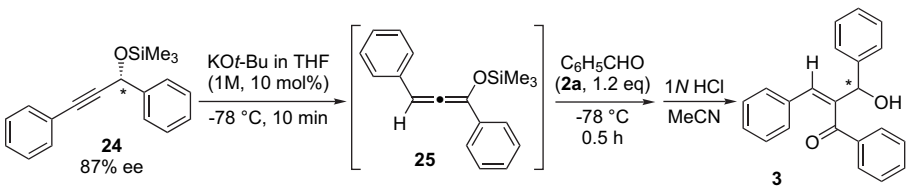


6 : R = H
7 : R = Bn



75

[a] Yields of **3** were assayed by HPLC analysis using YMC Pro C 18 (4.6 mm×150 mm) column (UV 254 nm; flow rate, 1.0 mL/min; eluent, MeCN/H_2O/70% aq $HClO_4$=600:400:1 (v/v/v)).
[b] ee% was determined by DAICEL CHIRALCEL OD (4.6 mm×150 mm) column (UV 254 nm; flow rate, 1 mL/min; eluent *n*-hexane/*i*-PrOH=9:1 (v/v)).
[c] Reacted for 6 h.
[d] Reacted for 20 h.
[e] Reacted for 4 h.
[f] Reacted for 2 h.



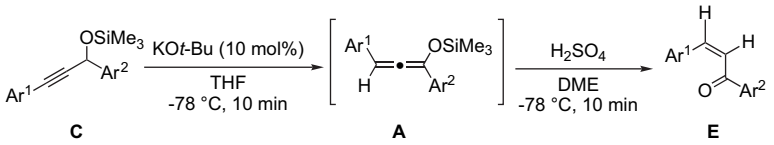
Reaction Solvent, Yield of **3** (% ee) : THF, 83% (29% ee); MeO*t*-Bu 34% (26% ee); CH_2Cl_2, 66% (12% ee)

Scheme 13.

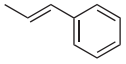
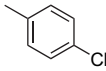
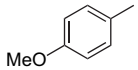
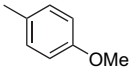
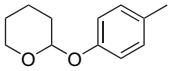
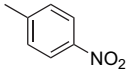
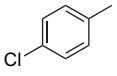
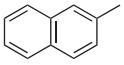
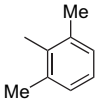
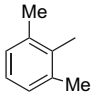
Our experimental results together with consideration of the above situation led us to explore a general synthetic method for (*Z*)-chalcone derivatives.[4] Preliminary survey of the reaction conditions suggested that addition of concd sulfuric acid in 1,2-dimethoxyethane (DME) would give a better result after the formation of the siloxyallene **25** from the siloxypropyne **24** by the action of KO*t*-Bu in THF. The results of the (*Z*)-chalcone synthesis under this preferred reaction conditions are summarized in Table 10. Most of the (*Z*)-chalcone derivatives **E** have been conveniently synthesized at −78 °C as the major product. However, in the case of the 4-nitro substrate **76**, the isomerization from the siloxypropyne to the siloxyallene did not proceed even at 0 °C. The reaction of siloxypropyne **77** having the sterically hindered 2′,6′-dimethylphenyl group at the Ar^2 position did not proceed at all, while another 2,6-dimethylphenyl analog **95** was obtained though in moderate yield. In the latter case, isomerization of the siloxypropyne **83** to the siloxyallene was not complete and **83** remained after the reaction. Thus the steric influence will be quite significant in the reaction. Exceptionally, the siloxypropyne **78** having the 4-methoxyphenyl function at the vinyl position afforded the (*E*)-isomer **90** only though the crude product was a mixture of (*Z*)- and (*E*)-isomers in a ratio of 25:75. Some of the products were isomerized during the reaction and/or purification on a silica column. Isomerization during purification could be prevented if a suitable workup for each product was devised.

Treatment of the *tert*-butyldimethylsilyl ether **96** with 10 mol % of KO*t*-Bu afforded the siloxyallene **97**, which was converted to the crude (*Z*)-chalcone (**84**, *Z*/*E*=92:8) (Scheme 14). Purification by one recrystallization from hexane gave pure (*Z*)-chalcone (**84**, *Z*/*E*=>99:1) in 74% yield. The (*Z*)-geometry preference of the chalcone derivatives **E** will be explained by the preference of the protonation in

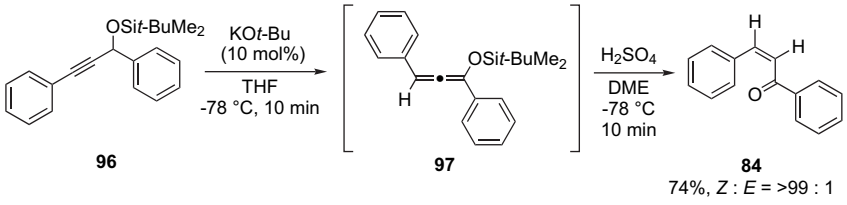
Table 10. Synthesis of (*Z*)-chalcones



C **A** **E**

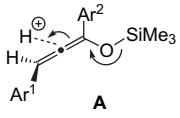
Ar^1	Ar^2	C	E	Yield (%)[a]	*Z*/*E*[b]	Ar^1	Ar^2	C	E	Yield (%)[a]	*Z*/*E*[b]
		**24**	**84**	82	93:7			**57**	**89**	75	80:20 (84:16)
		**52**	**85**	73	88:12			**78**	**90**	76	*E* only (25:75)
		**53**	**86**	66	97:3			**79**	**91**	54	85:15 (89:11)
		**76**		—	—			**80**	**92**	71	90:10
		**54**	**87**	83	93:7			**81**	**93**	85	80:20 (95:5)
		**55**	**88**	76	95:5			**82**	**94**	82	97:3
		**77**		—	—			**83**	**95**	54	70:30

[a] Isolated yield.
[b] *Z*/*E* ratio was determined by ^{1}H NMR analysis. Parentheses are *Z*/*E* ratio of crude product. No parenthesis depicts no isomerization during the purification step.



96 **97** **84**
74%, *Z* : *E* = >99 : 1

Scheme 14.



A

Figure 2.

which the reaction mainly occurs from the less hindered site of the siloxyallene **A**, as shown in Figure 2.

3. Conclusion

In conclusion, siloxyallenes well proved to be a useful functional intermediate in organic synthesis. The reaction of silylacetylenes with aromatic aldehydes was catalyzed with the quaternary ammonium fluoride derived from cinchonine, giving the β-branched MBH type adducts in moderate to good yields via the siloxypropyne and siloxyallene intermediates. Treatment of the siloxypropyne with a small amount of KO*t*-Bu afforded the siloxyallene, which reacted with aldehydes to give the MBH type adducts. Furthermore, the siloxyallene intermediates afforded (*Z*)-chalcone derivatives with sulfuric acid.

Further application of the siloxyallenes to organic synthesis will be waited.

4. Experimental

4.1. General

Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-1000 digital polarimeter. IR spectra were measured with a Perkin–Elmer 1600 FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JNM-ALPHA 400 or JNM-AL 400 spectrometer with tetramethylsilane, chloroform or dimethyl sulfoxide as an internal standard. High-resolution MS spectra were measured

on a JEOL MS-700 or HX-100 spectrometer. HPLC analysis was performed on a Shimadzu LC-10AVP high-performance liquid chromatograph. TLC was done on precoated (0.25 mm) Merck silica gel F_{254} plates. Silica gel (Merck Silica gel 60 of 0.040–0.063 mm for column chromatography) was used for column chromatography.

4.1.1. *N*-Benzylcinchoninium fluoride (5a).[5] Amberlyst A-26 resin (chloride ion form, 10 mL) swollen in water overnight was packed in a column and converted to its hydroxide ion form by passing 1 N aqueous sodium hydroxide (150 mL) until no turbidity was observed with aqueous silver nitrate in the eluate acidified with 10% aqueous nitric acid. The resin was washed with water (200 mL) until the eluate became neutral and then with methanol (200 mL). *N*-Benzylcinchoninium chloride (842 mg, 2.0 mmol) in methanol (20 mL) was slowly passed through the resin, and the resin was washed with methanol (10 mL×2). The eluate was neutralized with 1 mmol/g aqueous hydrofluoric acid (ca. 2 g, 2.0 mmol) until pH of the eluate became ca. 7, and concentrated in vacuo. The residue was co-evaporated with toluene/acetonitrile (1:1) a few times and dried in vacuo overnight. The fluoride **5a** was quantitatively obtained as a pale brown amorphous solid (848 mg) and used for the next step without further purification: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.79–0.88 (m, 1H), 1.42–1.52 (m, 3H), 2.24–2.30 (m, 1H), 2.52–2.59 (m, 1H), 2.94 (dd, J=9.2, 20.2 Hz, 1H), 3.14 (t, J=11.1 Hz, 1H), 3.71 (t, J=9.3 Hz, 1H), 3.76 (t, J=10.5 Hz, 1H), 4.50 (br s, 1H), 4.88 (d, J=11.7 Hz, 1H), 5.03 (s, 1H), 5.20 (d, J=8.3 Hz, 1H), 5.55 (d, J=7.3 Hz, 1H), 5.96–6.05 (m, 1H), 6.33 (s, 1H), 7.47–7.53 (m, 3H), 7.63–7.78 (m, 4H), 7.84 (d, J=4.4 Hz, 1H), 8.04 (d, J=8.3 Hz, 1H), 8.20 (d, J=8.3 Hz, 1H), 8.87 (d, J=4.4 Hz, 1H).

4.1.2. *N*,*O*-Dibenzylcinchoninium fluoride (5b).[9b] *N*,*O*-Dibenzylcinchoninium bromide (1.11 g, 2.0 mmol) was treated as described for the synthesis of **5a**. The fluoride **5b** was quantitatively obtained as a pale brown amorphous solid (1.02 g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.15–1.25 (m, 1H), 1.50–1.54 (m, 1H), 1.70–1.77 (m, 1H), 1.93 (br s, 1H), 1.97–2.05 (m, 1H), 2.35–2.43 (m, 2H), 2.72 (dd, J=9.5, 21.0 Hz, 1H), 3.38 (t, J=11.5 Hz, 1H), 4.07 (d, J=11.7 Hz, 1H), 4.40 (d, J=11.5 Hz, 1H), 4.60–4.75 (m, 2H), 4.83 (t, J=11.5 Hz, 1H), 5.09 (d, J=10.0 Hz, 1H), 5.25 (d, J=10.5 Hz, 1H), 5.82–5.92 (m, 2H), 6.32 (br s, 1H), 7.28–7.52 (m, 10H), 7.68 (br s, 1H), 7.81 (t, J=7.5 Hz, 1H), 7.93 (br s, 1H), 8.17 (d, J=8.5 Hz, 1H), 8.70 (d, J=8.1 Hz, 1H), 9.01 (d, J=4.4 Hz, 1H).

4.1.3. *O*-Allyl-*N*-benzylcinchoninium fluoride (5c).[22] As described for the synthesis of **5a**, *O*-allyl-*N*-benzylcinchoninium bromide (1.01 g, 2.0 mmol) was treated. The fluoride **5c** was quantitatively obtained as a pale brown amorphous solid (0.88 g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.10–1.15 (m, 1H), 1.75–1.80 (m, 1H), 1.95–2.05 (m, 2H), 2.25–2.35 (m, 1H), 2.45–2.50 (m, 1H), 2.80 (dd, J=9.8, 21.0 Hz, 1H), 3.56 (t, J=11.5 Hz, 1H), 4.01 (dd, J=6.4, 12.7 Hz, 1H), 4.17–4.25 (m, 2H), 4.45 (d, J=11.9 Hz, 1H), 4.65 (t, J=8.8 Hz, 1H), 4.72 (t, J=11.4 Hz, 1H), 5.22 (d, J=17.3 Hz, 1H), 5.31 (d, J=10.5 Hz, 1H), 5.39 (d, J=10.2 Hz, 1H), 5.43 (d, J=16.9 Hz, 1H), 5.87–5.95 (m, 1H), 6.07–6.13 (m, 2H), 6.26 (br s, 1H), 7.49–7.51 (m, 3H), 7.55–7.63 (m, 1H), 7.68–7.73 (m, 2H), 7.77–7.81 (m, 1H), 7.89 (br s, 1H), 8.15 (d, J=8.5 Hz, 1H), 8.70 (d, J=8.3 Hz, 1H), 8.96 (d, J=6.3 Hz, 1H).

4.1.4. (2*Z*)-2-[Hydroxy(phenyl)methyl]-1,3-diphenylprop-2-en-1-one (3).[8] **Typical procedure.** To a solution of the catalyst **5a** (40 mg, 0.1 mmol) and benzaldehyde (**2a**, 0.153 mL, 1.5 mmol) in CH_2Cl_2 (2 mL) was added 1-phenyl-2-(trimethylsilyl)acetylene (**1**, 0.197 mL, 1.0 mmol) at −20 °C under Ar, and then the mixture was immediately warmed to 0 °C. After 1 h, 1 N aq HCl (1 mL) and methanol (4 mL) were added, and the mixture was stirred for only a few minutes at 0 °C. Water, brine, and EtOAc were added, and the separated organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 10:1) to give **3** (219 mg, 92%) as a white solid and **4**[19b] (15 mg, 7%).

Compound **3**: mp 77 °C; IR (neat) ν 3373, 3060, 1634, 1591, 1447, 1372, 1236, 1020, 965, 757, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.14 (d, J=4.9 Hz, 1H), 5.73 (d, J=4.9 Hz, 1H), 6.97 (s, 1H), 7.03–7.09 (m, 5H), 7.13–7.16 (m, 2H), 7.20–7.24 (m, 1H), 7.29–7.32 (m, 3H), 7.44 (d, J=7.6 Hz, 2H), 7.63 (d, J=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.7, 126.2, 127.6, 127.8, 127.8, 128.1, 128.7, 129.1, 131.9, 132.8, 134.6, 135.7, 140.5, 141.5, 199.9; Anal. calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.20; H, 5.81.

Compound **4**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (m, 1H), 5.69 (d, J=6.3 Hz, 1H), 7.31–7.38 (m, 4H), 7.39–7.44 (m, 2H), 7.47–7.49 (m, 2H), 7.61–7.64 (m, 2H). The enantiomeric excess was determined by HPLC analysis: DAICEL CHIRALCEL OD (4.6 mm i.d.×250 mm), UV 254 nm, flow rate 1.0 mL/min, hexane/2-propanol=9:1, retention time **3**: 12.3 min, 14.1 min; **4**: 13.1 min, 19.8 min.

4.1.5. Preparation of (2*Z*)-2-[hydroxy(phenyl)methyl]-1,3-diphenylprop-2-en-1-one (3) using catalytic amount of quaternary ammonium bromide and CsF. To a solution of the catalyst **6** (47 mg, 0.1 mmol) and CsF (15 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) was added benzaldehyde (**2a**, 0.153 mL, 1.5 mmol) followed by 1-phenyl-2-(trimethylsilyl)acetylene (**1**, 0.197 mL, 1.0 mmol) at −20 °C under Ar, and then the mixture was immediately warmed to 0 °C. After 1 h, workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave **3** (169 mg, 72%) as a white solid and **4** (40 mg, 19%).

4.1.6. (2*Z*)-2-[Hydroxy(4-methylphenyl)methyl]-1-(4-methylphenyl)-3-phenylprop-2-en-1-one (8). As described for the synthesis of **3**, 1-phenyl-2-(trimethylsilyl)acetylene (**1**, 0.197 mL, 1.0 mmol) and 4-methylbenzaldehyde (**2b**, 0.177 mL, 1.5 mmol) were treated with the catalyst **5a** (40 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at −20 °C for 1 h. Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **8** (223 mg, 87%) as a white solid: mp 100 °C; IR (neat) ν 3393, 3026, 1635, 1602, 1446, 1362, 1240, 1179, 1027, 936, 812, 755, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H), 2.30 (s, 3H), 3.02–3.05 (m, 1H), 5.67 (d, J=4.6 Hz, 1H), 6.90 (d, J=1.2 Hz, 1H), 6.96 (d, J=7.8 Hz, 2H), 7.03–7.12

(m, 7H), 7.31 (d, J=8.0 Hz, 2H), 7.58 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 21.6, 76.6, 126.2, 127.6, 127.7, 128.6, 128.7, 128.8, 129.3, 131.2, 133.3, 134.7, 137.2, 137.6, 141.7, 143.7, 199.5; Anal. calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.04; H, 6.52.

4.1.7. (2*Z*)-2-[Hydroxy(4-methoxyphenyl)methyl]-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (9). As described for the synthesis of **3**, 1-phenyl-2-(trimethylsilyl)-acetylene (**1**, 0.197 mL, 1.0 mmol) and 4-methoxybenzaldehyde (**2c**, 0.183 mL, 1.5 mmol) were treated with the catalyst **5a** (40 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at −20 °C for 1 h. Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **9** (96 mg, 37%) as a white foam, **13**[23] (13 mg, 5%), and methyl ether of **13** (118 mg, 47%).

Compound **9**: IR (neat) ν 3415, 2969, 1645, 1592, 1509, 1462, 1364, 1240, 1164, 1026, 955, 831, 756, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.10 (d, J=4.6 Hz, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 5.65 (d, J=4.6 Hz, 1H), 6.64 (d, J=8.8 Hz, 2H), 6.83 (d, J=8.5 Hz, 2H), 6.89 (s, 1H), 7.06–7.14 (m, 5H), 7.34 (d, J=8.8 Hz, 2H), 7.65 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.1, 55.2, 76.4, 113.2, 113.5, 127.5, 127.6, 127.8, 128.6, 128.8, 130.6, 131.6, 132.8, 134.7, 141.8, 158.8, 163.2, 198.4; Anal. calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.81; H, 6.05.

Compound **13**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18–2.31 (m, 1H), 5.65 (d, J=6.1 Hz, 1H), 6.93 (dd, J=2.1, 6.8 Hz, 2H), 7.30–7.34 (m, 3H), 7.46–7.48 (m, 2H), 7.55 (dd, J=2.1, 6.6 Hz, 2H).

Methyl ether of **13**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.46 (s, 3H), 3.82 (s, 3H), 5.26 (s, 1H), 6.91 (d, J=8.8 Hz, 2H), 7.30–7.32 (m, 3H), 7.46–7.50 (m, 4H).

4.1.8. (2*Z*)-1-(4-Fluorophenyl)-2-[(4-fluorophenyl)-(hydroxy)methyl]-3-phenylprop-2-en-1-one (10). As described for the synthesis of **3**, 1-phenyl-2-(trimethylsilyl)-acetylene (**1**, 0.197 mL, 1.0 mmol) and 4-methoxybenzaldehyde (**2d**, 0.161 mL, 1.5 mmol) were treated with the catalyst **5a** (40 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at −20 °C for 1 h. Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave **10** (235 mg, 89%) as a white solid: mp 113 °C; IR (neat) ν 3453, 1665, 1597, 1503, 1408, 1222, 1150, 1034, 973, 827, 754, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.11 (d, J=4.9 Hz, 1H), 5.70 (d, J=4.9 Hz, 1H), 6.99 (s, 1H), 7.06–7.09 (m, 5H), 7.12 (d, J=8.8 Hz, 2H), 7.28 (d, J=8.6 Hz, 2H), 7.37 (d, J=8.3 Hz, 2H), 7.55 (d, J=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.0, 115.10 (d, J=19.9 Hz), 115.11 (d, J=21.6 Hz), 127.8 (d, J=8.3 Hz), 127.9, 128.1, 128.6, 131.7 (d, J=9.1 Hz), 131.9, 132.1 (d, J=2.4 Hz), 134.3, 136.3 (d, J=3.3 Hz), 141.1, 161.9 (d, J=244.7 Hz), 165.3 (d, J=253.8 Hz), 198.1; Anal. calcd for $C_{22}H_{16}F_2O_2$: C, 75.42; H, 4.60. Found: C, 75.25; H, 4.70.

4.1.9. (2*Z*)-1-(4-Chlorophenyl)-2-[(4-chlorophenyl)-(hydroxy)methyl]-3-phenylprop-2-en-1-one (11). As described for the synthesis of **3**, 1-phenyl-2-(trimethylsilyl)-acetylene (**1**, 0.197 mL, 1.0 mmol) and 4-chlorobenzaldehyde (**2e**, 211 mg, 1.5 mmol) were treated with the catalyst **5a** (40 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at −20 °C for 1 h. Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave **11** (257 mg, 89%) as a white solid: mp 151 °C; IR (neat) ν 3466, 1664, 1587, 1492, 1365, 1228, 1084, 974, 823, 755, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.11 (d, J=4.9 Hz, 1H), 5.70 (d, J=4.9 Hz, 1H), 6.99 (s, 1H), 7.06–7.09 (m, 5H), 7.12 (d, J=8.8 Hz, 2H), 7.28 (d, J=8.6 Hz, 2H), 7.37 (d, J=8.3 Hz, 2H), 7.55 (d, J=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.0, 127.5, 127.9, 128.2, 128.3, 128.4, 128.6, 130.3, 132.5, 133.4, 134.0, 134.2, 139.0, 139.4, 140.6, 198.4; Anal. calcd for $C_{22}H_{16}Cl_2O_2$: C, 68.94; H, 4.21. Found: C, 68.94; H, 4.26.

4.1.10. (2*Z*)-1-(3,4-Dimethoxyphenyl)-2-[(3,4-dimethoxyphenyl)(hydroxy)methyl]-3-phenylprop-2-en-1-one (12). To a solution of the catalyst **5a** (40 mg, 0.1 mmol) and 2,3-dimethoxybenzaldehyde (**2g**, 0.153 mL, 1.5 mmol) in CH_2Cl_2 (2 mL) was added 1-phenyl-2-(trimethylsilyl)acetylene (**1**, 0.197 mL, 1.0 mmol) at −20 °C under Ar, and then the mixture was immediately warmed to 0 °C. After 1 h, 1 N aq HCl (1 mL) and acetonitrile (10 mL) were added, and the mixture was stirred for only a few minutes. Water, brine, and EtOAc were added, and the separated organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 2:1) to give **12** (74 mg, 23%) as a white foam and **14** (71 mg, 26%) as a white solid.

Compound **12**: IR (neat) ν 3492, 2935, 1642, 1579, 1510, 1462, 1417, 1260, 1134, 1020, 761, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.13 (d, J=4.6 Hz, 1H), 3.77 (s, 3H), 3.81 (s, 3H), 3.82 (s, 3H), 3.84 (s, 3H), 5.65 (d, J=4.4 Hz, 1H), 6.57 (d, J=8.6 Hz, 1H), 6.79 (d, J=8.8 Hz, 1H), 6.92 (s, 1H), 6.96–6.98 (m, 2H), 7.07–7.10 (m, 5H), 7.28–7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.65, 55.72, 55.75, 55.77, 77.0, 109.4, 109.57, 109.64, 118.6, 124.8, 127.8, 127.9, 128.6, 128.8, 130.6, 133.3, 134.7, 141.6, 148.3, 148.6, 153.1, 198.3; Anal. calcd for $C_{26}H_{26}O_6$: C, 71.87; H, 6.03. Found: C, 71.54; H, 6.19.

Compound **14**: mp 87 °C; IR (neat) ν 3274, 2934, 1592, 1518, 1416, 1237, 1133, 1022, 984, 755, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21 (d, J=6.1 Hz, 1H), 3.90 (s, 3H), 3.93 (s, 3H), 5.65 (d, J=6.1 Hz, 1H), 6.88 (d, J=8.8 Hz, 1H), 7.16–7.18 (m, 2H), 7.31–7.33 (m, 3H), 7.46–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.78, 55.84, 77.0, 86.3, 88.5, 109.7, 110.7, 118.8, 122.1, 128.0, 128.3, 131.3, 131.4, 148.75, 148.82; Anal. calcd for $C_{26}H_{26}O_6$: C, 76.10; H, 6.01. Found: C, 76.00; H, 6.10.

4.1.11. (2*Z*)-1-(1,3-Benzodioxol-5-yl)-2-[1,3-benzodioxol-5-yl(hydroxy)methyl]-3-phenylprop-2-en-1-one (15). As described for the synthesis of **3**, 1-phenyl-2-(trimethylsilyl)-acetylene **1** (0.197 mL, 1.0 mmol) and piperonal (**2h**, 225 mg, 1.5 mmol) were treated with the catalyst (**5a**, 40 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at −20 °C for 1 h. Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **15** (262 mg, 87%) as a white solid: mp 133 °C; IR (neat) ν 3352, 1619, 1590, 1486, 1441, 1365, 1248, 1035, 928, 807, 759, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.05

(br s, 1H), 5.60 (d, J=4.6 Hz, 1H), 5.92 (d, J=2.4 Hz, 4H), 6.53 (d, J=8.6 Hz, 1H), 6.72 (d, J=8.1 Hz, 1H), 6.86 (d, J=8.0 Hz, 1H), 6.88 (s, 1H), 7.08–7.12 (m, 5H), 7.22–7.25 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 100.8, 101.5, 106.8, 107.4, 107.8, 108.1, 119.8, 126.6, 127.7, 127.8, 128.6, 130.6, 130.8, 134.60, 134.61, 141.5, 146.8, 147.4, 147.5, 151.6, 197.7; Anal. calcd for $C_{24}H_{18}O_6$: C, 71.64; H, 4.51. Found: C, 71.19; H, 4.66.

4.1.12. (2*Z*)-2-[Hydroxy(2-naphthyl)methyl]-1-(2-naphthyl)-3-phenylprop-2-en-1-one (16). As described for the synthesis of **3**, 1-phenyl-2-(trimethylsilyl)acetylene (**1**, 0.197 mL, 1.0 mmol) and 2-naphthaldehyde (**2i**, 234 mg, 1.5 mmol) were treated with the catalyst **5a** (40 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at −20 °C for 1 h. Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **16** (265 mg, 85%) as a white solid: mp 142–143 °C; IR (neat) ν 3399, 1618, 1358, 1230, 1128, 1060, 938, 817, 787, 742, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.27 (d, J=4.6 Hz, 1H), 5.95 (d, J=4.6 Hz, 1H), 6.95–7.01 (m, 3H), 7.06 (s, 1H), 7.13 (d, J=7.8 Hz, 2H), 7.35–7.48 (m, 4H), 7.60–7.69 (m, 4H), 7.75–7.81 (m, 4H), 7.94 (s, 1H), 8.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.8, 124.1, 124.2, 125.3, 125.7, 125.8, 126.1, 127.2, 127.3, 127.75, 127.79, 127.81, 128.0, 128.1, 128.6, 129.3, 131.8, 131.9, 132.3, 132.7, 132.9, 133.1, 134.6, 135.2, 138.0, 141.6, 199.7; Anal. calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.51; H, 5.36.

4.1.13. (2*Z*)-1-(2-Furyl)-2-[2-furyl(hydroxy)methyl]-3-phenylprop-2-en-1-one (17). As described for the synthesis of **3**, 1-phenyl-2-(trimethylsilyl)acetylene (**1**, 0.197 mL, 1.0 mmol) and 2-furaldehyde (**2j**, 0.124 mL, 1.5 mmol) were treated with the catalyst **5a** (40 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at −20 °C for 1 h. Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **17** (119 mg, 54%) as a pale yellow oil: IR (neat) ν 3410, 1627, 1561, 1460, 1269, 1163, 1012, 853, 754, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.14 (d, J=6.6 Hz, 1H), 5.70 (d, J=6.3 Hz, 1H), 6.22 (dd, J=1.4, 3.4 Hz, 1H), 6.28 (dd, J=2.0, 3.2 Hz, 1H), 6.34 (d, J=2.9 Hz, 1H), 6.80 (d, J=3.4 Hz, 1H), 7.12 (s, 1H), 7.14–7.19 (m, 5H), 7.35 (dd, J=1.5, 15.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.7, 107.6, 110.2, 111.9, 120.7, 127.96, 128.00, 128.5, 133.7, 134.7, 138.3, 142.1, 146.9, 151.5, 153.0, 185.5; Anal. calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.45; H, 4.89.

4.1.14. (*E*)-2,3-Dihydro-3-hydroxy-2-(phenylmethylene)-1*H*-inden-1-one (*E*-18). As described for the synthesis of **3**, 1-phenyl-2-(trimethylsilyl)acetylene (**1**, 0.197 mL, 1.0 mmol) and 2-phthalaldehyde (**2m**, 101 mg, 1.5 mmol) were treated with the catalyst **5a** (40 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at −20 °C for 1 h. Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave *E*-**18** (86 mg, 49%) as a pale yellow solid and **19** (68 mg, 27%) as a pale yellow oil.

Compound *E*-**18**: mp 188 °C; IR (neat) ν 3380, 1682, 1617, 1422, 1335, 1262, 1024, 955, 751, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21 (d, J=9.5 Hz, 1H), 5.96 (d, J=9.5 Hz, 1H), 7.42–7.54 (m, 4H), 7.70–7.74 (m, 2H), 7.81 (d, J=7.4 Hz, 1H), 7.85–7.89 (m, 1H), 7.94–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 68.7, 123.5, 125.7, 128.7, 129.5, 130.2, 131.5, 133.5, 135.1, 136.7, 136.9, 137.4, 151.0, 191.9; Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 80.95; H, 5.18.

Compound **19**: IR (neat) ν 2932, 1490, 1370, 1326, 1192, 1086, 964, 748, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.41 (s, 1.5H), 3.53 (s, 1.5H), 6.04 (s, 0.5H), 6.24 (d, J=6.1 Hz, 0.5H), 6.27 (d, J=1.6 Hz, 0.5H), 6.30 (s, 0.5H), 7.27–7.31 (m, 3H), 7.40–7.47 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 53.1, 55.3, 72.5, 72.7, 85.9, 86.0, 86.1, 86.8, 106.6, 107.0, 121.6, 121.7, 121.9, 122.2, 122.6, 122.7, 122.8, 127.86, 127.90, 128.2, 128.31, 128.34, 129.3, 129.5, 131.5, 131.6, 136.3, 137.0, 140.0, 140.1; HRMS (EI) calcd for $C_{20}H_{16}O_2S$ (M^+) 250.0994, Found 250.0985.

4.1.15. (*Z*)-2,3-Dihydro-3-hydroxy-2-(phenylmethylene)-1*H*-inden-1-one (*Z*-18). A solution of *E*-**18** (210 mg, 0.89 mmol) in acetonitrile (25 mL) was exposed to UV (365 nm) light for 10 h at rt. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/ether, 2:1) to give *Z*-**18** (42 mg, 20%) as yellow crystals: mp 77 °C; IR (neat) ν 3356, 2973, 1686, 1613, 1385, 1240, 1185, 1072, 1019, 970, 739, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27 (d, J=10.0 Hz, 1H), 5.60 (d, J=9.5 Hz, 1H), 7.30 (d, J=1.2 Hz, 1H), 7.41–7.44 (m, 3H), 7.48–7.51 (m, 1H), 7.68 (dt, J=1.0, 7.6 Hz, 1H), 7.74 (dd, J=1.0, 7.6 Hz, 1H), 7.81 (d, J=7.8 Hz, 1H), 8.13–8.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 72.0, 123.4, 125.3, 127.9, 129.4, 130.1, 131.1, 133.8, 134.7, 138.6, 138.7, 141.4, 149.6, 189.7; Anal. calcd for $C_{26}H_{26}O_6$: C, 71.34; H, 5.12. Found: C, 71.16; H, 5.16.

4.1.16. 3-(4-Fluorophenyl)-1-phenylprop-2-yn-1-ol (20). To a solution of 4-fluorophenylacetylene (360 mg, 3 mmol) in THF (5 mL) was added *n*-BuLi in hexane (1.58 M, 2 mL, 3.15 mmol) at −78 °C under N_2. After 5 min, a solution of benzaldehyde (**2a**, 318 mg, 3 mmol) in THF (2.5 mL) was added to the mixture, and then the mixture was immediately warmed to rt. After 21 h, the reaction mixture was quenched with water, followed by addition of EtOAc. The separated organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 5:1) to give **20** (603 mg, 89%) as a colorless oil: IR (neat) ν 3323, 3064, 1601, 1505, 1219, 1155, 1014, 960, 833, 747, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.23–2.26 (m, 1H), 5.68 (d, J=6.1 Hz, 1H), 7.01 (t, J=8.5 Hz, 2H), 7.35–7.46 (m, 5H), 7.50 (d, J=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 64.9, 85.4, 88.2, 115.3 (d, J=22.4 Hz), 118.2 (d, J=4.4 Hz), 126.4, 128.2, 128.4, 133.3 (d, J=8.3 Hz), 140.2, 162.3 (d, J=248.4 Hz); Anal. calcd for $C_{26}H_{26}O_6$: C, 79.63; H, 4.90. Found: C, 79.71; H, 4.91.

4.1.17. A mixture of (2*Z*)-1-(4-fluorophenyl)-2-[(4-fluorophenyl)(hydroxy)methyl]-3-phenylprop-2-en-1-one (10) and (2*Z*)-1,3-bis(4-fluorophenyl)-2-[hydroxy(phenyl)-methyl]prop-2-en-1-one (21). A mixture of **20** (136 mg, 0.6 mmol), 4-fluorobenzaldehyde (**2d**, 0.054 mL, 0.5 mmol), and $VO(OSiPh_3)_3$ (22 mg, 0.025 mmol) in 1,2-dichloroethane (0.3 mL) was stirred at 80 °C for 20 h under Ar. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc,

5:1) to give a mixture of **10** and **21** (3:2, 32 mg, 18%) as a colorless oil: IR (neat) ν 3414, 2975, 1652, 1594, 1506, 1227, 1152, 1013, 956, 835, 756, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.04 (d, J=4.5 Hz, 0.4H), 3.16 (d, J=4.5 Hz, 0.6H), 5.71 (d, J=4.2 Hz, 0.6H), 5.72 (d, J=3.7 Hz, 0.4H), 6.74–6.85 (m, 2.8H), 6.91 (s, 0.4H), 6.96–7.09 (m, 5.4H), 7.21–7.25 (m, 0.4H), 7.28–7.32 (m, 1H), 7.38–7.42 (m, 1H), 7.62–7.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.0, 115.0 (d, J=17.4 Hz), 115.2 (d, J=17.4 Hz), 126.1, 127.7, 128.2, 130.2, 130.3 (d, J=8.3 Hz), 130.6 (d, J=3.3 Hz), 140.4, 141.5, 162.0 (d, J=247.2 Hz), 165.3 (d, J=254.6 Hz), 198.07; HRMS (EI) calcd for $C_{20}H_{16}O_2S$ (M^+) 350.1118, Found 350.1107. The ratio of **10** and **21** was determined by ^1H NMR analysis.

4.1.18. 1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-ol (22).[19b] To a solution of phenylacetylene (**27**, 0.33 mL, 3 mmol) in THF (5 mL) was added *n*-BuLi in hexane (1.58 M, 2 mL, 3.15 mmol) at −78 °C under N_2. After 5 min, to the mixture was added a solution of 4-fluorobenzaldehyde (**2d**, 0.32 mL, 3 mmol) in THF (2.5 mL), and then the mixture was immediately warmed to rt. After 21 h, the reaction mixture was quenched with water, followed by addition of EtOAc. The separated organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 5:1) to give **22** (550 mg, 81%) as a colorless oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 2.26 (d, J=6.1 Hz, 1H), 5.68 (d, J=5.9 Hz, 1H), 7.08 (t, J=8.6 Hz, 2H), 7.30–7.35 (m, 3H), 7.46–7.48 (m, 2H), 7.59 (dd, J=2.1, 5.4 Hz, 2H).

4.1.19. (2*Z*)-3-(4-Fluorophenyl)-2-[(4-fluorophenyl)-(hydroxy)methyl]-1-phenylprop-2-en-1-one (23). A mixture of **22** (136 mg, 0.6 mmol), 4-fluorobenzaldehyde (**2d**, 0.054 mL, 0.5 mmol), and $VO(OSiPh_3)_3$ (22 mg, 0.025 mmol) in 1,2-dichloroethane (0.3 mL) was stirred at 80 °C for 20 h under Ar. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 5:1) to give **23** (41 mg, 23%) as a white solid: mp 77–78 °C; IR (neat) ν 3429, 3064, 1645, 1601, 1221, 1157, 1013, 954, 829, 729, 686 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.13 (d, J=4.9 Hz, 1H), 5.71 (d, J=4.4 Hz, 1H), 6.75 (t, J=8.6 Hz, 2H), 6.93 (s, 1H), 6.97–7.07 (m, 4H), 7.17–7.21 (m, 2H), 7.34–7.43 (m, 3H), 7.61–7.63 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.0, 114.9 (d, J=21.6 Hz), 115.1 (d, J=20.7 Hz), 127.9 (d, J=8.3 Hz), 128.0, 129.0, 130.4 (d, J=8.3 Hz), 130.58, 130.62, 131.9, 133.1, 135.5, 136.3 (d, J=3.3 Hz), 141.3, 161.95 (d, J=244.7 Hz), 161.96 (d, J=248.0 Hz), 199.6; Anal. calcd for $C_{22}H_{16}F_2O_2$: C, 75.42; H, 4.60. Found: C, 75.30; H, 4.62.

4.1.20. [(1,3-Diphenyl-2-propynyl)oxy]-trimethylsilane (24).[24] To a solution of phenylacetylene (**26**, 2.97 mL, 27 mmol) in THF (25 mL) was added *n*-BuLi in hexane (1.58 M, 16.5 mL, 26 mmol) at −78 °C under N_2. After 10 min, benzaldehyde (**2a**, 2.54 mL, 25 mmol) in THF (10 mL) was added, and then the mixture was immediately warmed to rt. After 1 h, water was added to the reaction mixture, followed by addition of ether, and the separated organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, 1,3-diphenylprop-2-yn-1-ol (**4**, 5.12 g, 98%) was obtained as a pale yellow oil and used for the next step without further purification. To a solution of **4** (2.50 g, 12 mmol) and triethylamine (2.17 mL, 15.6 mmol) in THF (50 mL) was added chlorotrimethylsilane (1.83 mL, 14.4 mmol) at 0 °C, and then the mixture was immediately warmed to rt. After 30 min, the insoluble ammonium salt was filtered off and washed with hexane. After removal of the solvent of the filtrate in vacuo, the residue was passed through a short silica gel column chromatography (hexane/EtOAc, 10:1) to give **24** (3.29 g, 98%) as a pale yellow oil.

Compound **4**: ^1H NMR ($CDCl_3$, 400 MHz) δ 2.29 (m, 1H), 5.69 (d, J=6.3 Hz, 1H), 7.31–7.38 (m, 4H), 7.39–7.44 (m, 2H), 7.47–7.49 (m, 2H), 7.61–7.64 (m, 2H).

Compound **24**: ^1H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 9H), 5.71 (s, 1H), 7.29–7.32 (m, 4H), 7.36–7.39 (m, 2H), 7.43–7.46 (m, 2H), 7.56–7.57 (m, 2H).

4.1.21. [(1,3-Diphenyl-1,2-propadienyl)oxy]-trimethylsilane (25). To a solution of **24** (140 mg, 0.5 mmol) in THF (1 mL) was added 1 M KO*t*-Bu in THF (0.05 mL, 0.05 mmol) at −78 °C under Ar. After 10 min, water and *tert*-butyl methyl ether were added, and the separated organic layer was washed with water and brine and dried over $MgSO_4$. After removal of the solvent in vacuo, crude **25** (127 mg) was obtained as a yellow oil: IR (neat) ν 2958, 1928, 1665, 1597, 1492, 1447, 1251, 1201, 1073, 1019, 867, 747, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 9H), 6.94 (s, 1H), 7.21–7.40 (m, 8H), 7.53 (d, J=5.9 Hz, 2H).

4.1.22. Preparation of (2*Z*)-2-[hydroxy(phenyl)methyl]-1,3-diphenylprop-2-en-1-one (3) from 1 and 2a using catalytic amount of KO*t*-Bu. To a solution of **1** (0.197 mL, 1.0 mmol) and benzaldehyde (**2a**, 0.152 mL, 1.5 mmol) in DMF (2 mL) was added KO*t*-Bu (11 mg, 0.1 mmol) at −20 °C under Ar. After 1 h, 1 N aq HCl (1 mL) and acetonitrile (2 mL) were added, and the yield (33%) of **3** was assayed by HPLC analysis of the diluted mixture. HPLC analysis for determination of the yield of **3**: YMC Pro C18 (4.6 mm i.d.×150 mm), UV 254 nm, flow rate 1.0 mL/min, MeCN/H_2O/70% aq $HClO_4$=600:400:1 (v/v/v), retention time **3**: 7.4 min.

4.1.23. (2*Z*)-2-[Hydroxy(phenyl)methyl]-1,3-diphenylprop-2-en-1-one (3) from 24. Typical procedure. *Method A*: To a solution of **24** (280 mg, 1.0 mmol) and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) in DMF (2 mL) was added KO*t*-Bu (11 mg, 0.1 mmol) at −20 °C under Ar. After 1 h, 1 N aq HCl (1 mL) and acetonitrile (2 mL) were added, and the mixture was stirred at rt for a few minutes. Water and EtOAc were added, and the separated organic layer was washed with water and brine, and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 10:1) to give **3** (258 mg, 82%) as a white solid.

Method B: To a solution of **24** (280 mg, 1.0 mmol) in THF (2 mL) was added 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol) at −78 °C under Ar. After 10 min, benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) was added, and then the mixture was warmed to 0 °C in 30 min. After 1 h, 1 N aq HCl (1 mL) and acetonitrile (2 mL) were added, and the mixture

was stirred at rt for a few minutes. Water and EtOAc were added, and the separated organic layer was washed with brine, and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 10:1) to give **3** (267 mg, 85%) as a white solid.

4.1.24. (2*Z*)-2-[(4-Chlorophenyl)(hydroxy)methyl]-1,3-diphenylprop-2-en-1-one (29). As described for the synthesis of **3** by Method A, **24** (0.280 mg, 1.0 mmol) and 4-chlorobenzaldehyde (**2e**, 0.169 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave **29** (265 mg, 76%) as a white solid: mp 121 °C; IR (neat) ν 3362, 1634, 1592, 1447, 1369, 1237, 1082, 1031, 959, 828, 757, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.30 (m, 1H), 5.70 (d, J=4.9 Hz, 1H), 6.99 (d, J=1.2 Hz, 1H), 7.05–7.09 (m, 5H), 7.15–7.19 (m, 2H), 7.27–7.35 (m, 3H), 7.38 (d, J=8.5 Hz, 2H), 7.63 (dd, J=1.2, 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.1, 127.5, 127.8, 127.9, 128.0, 128.3, 128.7, 129.0, 132.4, 133.0, 133.3, 134.3, 135.6, 139.1, 140.9, 199.7; Anal. calcd for $C_{22}H_{17}ClO_2$: C, 75.75; H, 4.91. Found: C, 75.49; H, 5.03.

4.1.25. (2*Z*)-2-[Hydroxy(4-methoxyphenyl)methyl]-1,3-diphenylprop-2-en-1-one (30). As described for the synthesis of **3** by Method A, **24** (0.280 mg, 1.0 mmol) and 4-methoxybenzaldehyde (**2c**, 0.146 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave **30** (246 mg, 72%) as a white solid: mp 92–93 °C; IR (neat) ν 3367, 1637, 1592, 1510, 1447, 1368, 1236, 1172, 1033, 828, 753, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.01 (d, J=4.6 Hz, 1H), 3.77 (s, 3H), 5.70 (d, J=3.9 Hz, 1H), 6.85 (dd, J=2.2, 6.6 Hz, 2H), 6.96 (d, J=1.2 Hz, 1H), 7.04–7.10 (m, 5H), 7.15–7.19 (m, 2H), 7.30–7.38 (m, 3H), 7.67 (dd, J=1.2, 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 76.7, 114.1, 128.0, 128.2, 128.2, 128.3, 129.2, 129.6, 131.9, 133.2, 133.3, 135.1, 136.3, 142.3, 159.3, 200.4; Anal. calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.14; H, 5.98.

4.1.26. (2*Z*)-2-{[4-(Dimethylamino)phenyl](hydroxy)methyl}-1,3-diphenylprop-2-en-1-one (31). As described for the synthesis of **3** by Method A, **24** (0.280 mg, 1.0 mmol) and 4-dimethylaminobenzaldehyde (**2l**, 179 mg, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). After the reaction mixture was quenched with 1 N aq HCl (1 mL) and acetonitrile (2 mL), water and EtOAc were added, and the separated organic layer was washed with water, saturated aq $NaHCO_3$, and brine. After the solution was dried over $MgSO_4$ followed by removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 2:1) that gave **31** (123 mg, 35%) as a yellow foam.

As described for the synthesis of **3** by Method B, **24** (280 mg, 1.0 mmol) in THF (2 mL) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with a THF (0.5 mL) solution of 4-dimethylaminobenzaldehyde (**2l**, 179 mg, 1.2 mmol). Workup as described in Method A followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **31** (264 mg, 74%) as a yellow foam: IR (neat) ν 3414, 2885, 1650, 1612, 1520, 1446, 1351, 1227, 1163, 1032, 946, 818, 754, 693 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.85 (d, J=4.2 Hz, 1H), 2.90 (s, 6H), 5.65 (d, J=2.2 Hz, 1H), 6.67 (dd, J=2.0, 6.6 Hz, 2H), 6.93 (s, 1H), 7.02–7.10 (m, 5H), 7.15–7.19 (m, 2H), 7.29–7.33 (m, 3H), 7.70–7.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 76.3, 112.2, 127.4, 127.5, 127.7, 127.8, 128.3, 128.6, 129.1, 130.9, 132.6, 134.9, 136.0, 142.4, 150.0, 199.9; Anal. calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.38; H, 6.64; N, 3.71.

4.1.27. Methyl 4-[(2*Z*)-2-benzoyl-1-hydroxy-3-phenylprop-2-en-1-yl]benzoate (32). As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with a THF (1 mL) solution of methyl 4-formylbenzoate (**2n**, 197 mg, 1.2 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave **32** (310 mg, 83%) as a white solid: mp 116 °C; IR (neat) ν 3359, 2952, 1722, 1634, 1592, 1446, 1278, 1113, 1032, 958, 872, 758, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.18 (d, J=4.9 Hz, 1H), 5.71 (d, J=4.6 Hz, 1H), 6.73 (dd, J=3.9, 4.9 Hz, 1H), 6.93 (s, 1H), 7.10–7.14 (m, 3H), 7.16–7.20 (m, 3H), 7.20–7.25 (m, 1H), 7.28–7.32 (m, 2H), 7.41–7.45 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 51.9, 76.4, 126.1, 127.8, 127.9, 128.0, 128.7, 129.0, 129.2, 129.4, 132.7, 133.0, 134.3, 135.5, 140.7, 145.8, 166.4, 199.6; Anal. calcd for $C_{26}H_{26}O_6$: C, 77.40; H, 5.41. Found: C, 77.47; H, 5.54.

4.1.28. (2*Z*)-2-[Hydroxy(4-nitrophenyl)methyl]-1,3-diphenylprop-2-en-1-one (33). As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with a THF (1 mL) solution of 2-nitrobenzaldehyde (**2f**, 181 mg, 1.2 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **33** (241 mg, 67%) as a pale yellow solid: mp 174 °C; IR (neat) ν 3337, 1634, 1592, 1447, 1351, 1238, 1032, 956, 872, 761, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.60 (d, J=5.4 Hz, 1H), 5.80 (d, J=5.1 Hz, 1H), 7.07–7.09 (m, 6H), 7.13–7.17 (m, 2H), 7.33 (t, J=7.3 Hz, 1H), 7.59–7.64 (m, 4H), 8.16 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.3, 123.3, 126.9, 127.9, 128.0, 128.3, 128.8, 129.0, 133.3, 133.8, 134.0, 135.3, 139.7, 147.1, 148.0, 199.3; Anal. calcd for $C_{22}H_{17}NO_4$: C, 73.53; H, 4.77; N, 3.90. Found: C, 73.41; H, 4.87; N, 3.88.

4.1.29. (2*Z*)-2-[(2,6-Dimethylphenyl)(hydroxy)methyl]-1,3-diphenylprop-2-en-1-one (34). As described for the synthesis of **3** by Method A, **24** (0.280 mg, 1.0 mmol) and 2,6-dimethylbenzaldehyde (**2o**, 161 mg, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **34** (234 mg, 68%) as a white solid: mp 97 °C; IR (neat) ν 3443, 2966, 1639, 1594, 1447, 1378, 1232, 1172, 1046, 950, 756, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 6H), 2.52 (d, J=4.4 Hz, 1H), 6.32 (dd, J=2.2, 4.4 Hz,

1H), 6.54 (d, J=2.2 Hz, 1H), 7.02–7.13 (m, 8H), 7.24–7.28 (m, 2H), 7.37–7.41 (m, 1H), 7.83 (dd, J=1.3, 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 72.5, 127.6, 127.6, 127.8, 128.0, 128.5, 128.9, 129.0, 129.9, 132.8, 134.7, 135.7, 136.1, 137.0, 140.6, 199.8; Anal. calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.03; H, 6.57.

4.1.30. (2*Z*)-2-[2-Furyl(hydroxy)methyl]-1,3-diphenylprop-2-en-1-one (35). As described for the synthesis of **3** by Method A, **24** (0.280 mg, 1.0 mmol) and 2-furaldehyde (**2j**, 0.099 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **35** (288 mg, 95%) as a pale yellow oil: IR (neat) ν 3414, 3059, 1643, 1594, 1447, 1365, 1230, 1072, 1009, 954, 723, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.41 (d, J=6.6 Hz, 1H), 5.70 (d, J=6.6 Hz, 1H), 6.25 (dd, J=1.8, 3.4 Hz, 1H), 6.32 (d, J=3.4 Hz, 1H), 7.06–7.08 (m, 3H), 7.10–7.14 (m, 3H), 7.17–7.21 (m, 2H), 7.30 (dd, J=0.8, 1.7 Hz, 1H), 7.33 (t, J=7.4 Hz, 1H), 7.71–7.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 71.2, 107.4, 110.1, 127.8, 127.8, 127.9, 128.7, 129.1, 132.9, 133.0, 134.4, 135.5, 138.6, 142.0, 153.2, 199.4; HRMS (EI) calcd for $C_{20}H_{16}O_3$ (M^+) 304.1099, Found 304.1092.

4.1.31. (2*Z*)-2-[Hydroxy(2-thienyl)methyl]-1,3-diphenylprop-2-en-1-one (36). As described for the synthesis of **3** by Method A, **24** (0.280 mg, 1.0 mmol) and 2-thiophenecarboxaldehyde (**2p**, 0.112 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave **36** (264 mg, 83%) as a colorless oil: IR (neat) ν 3413, 3058, 1646, 1594, 1447, 1364, 1229, 1022, 946, 853, 757, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.52 (d, J=4.4 Hz, 1H), 5.97 (d, J=2.2 Hz, 1H), 6.90 (dd, J=3.6, 5.1 Hz, 1H), 7.02–7.11 (m, 6H), 7.15–7.22 (m, 4H), 7.30–7.34 (m, 1H), 7.70 (d, J=7.8, Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 73.5, 125.3, 125.6, 127.1, 128.4, 128.5, 128.6, 129.5, 129.4, 133.3, 133.6, 135.1, 136.5, 141.2, 145.6, 200.5; HRMS (EI) calcd for $C_{20}H_{16}O_2S$ (M^+) 320.0871, Found 320.0877.

4.1.32. (2*Z*)-2-[Hydroxy(pyridin-2-yl)methyl]-1,3-diphenylprop-2-en-1-one (37). As described for the synthesis of **3** by Method A, **24** (0.140 mg, 0.5 mmol) and 2-pyridinecarboxaldehyde (**2q**, 0.057 mL, 0.6 mmol) were treated with KO*t*-Bu (6 mg, 0.05 mmol) in DMF (1 mL). After the reaction mixture was quenched with 1 N aq HCl (1 mL) and acetonitrile (2 mL), water and EtOAc were added, and the separated organic layer was washed with water, saturated aq $NaHCO_3$, and brine. After the solution was dried over $MgSO_4$ followed by removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 2:1) that gave **37** (55 mg, 35%) as a yellow oil.

As described for the synthesis of **3** by Method B, THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with 2-pyridinecarboxaldehyde (**2q**, 0.114 mL, 1.2 mmol). Workup as described in Method A followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **37** (171 mg, 54%) as a yellow oil: IR (neat) ν 3057, 1651, 1593, 1447, 1375, 1229, 1043, 956, 752, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.16 (d, J=5.6 Hz, 1H), 5.67 (d, J=5.1 Hz, 1H), 7.06–7.08 (m, 3H), 7.11–7.14 (m, 3H), 7.17–7.21 (m, 3H), 7.33 (t, J=7.5 Hz, 1H), 7.41 (d, J=7.8 Hz, 2H), 7.63 (dt, J=1.7, 7.6 Hz, 1H), 7.74–7.76 (m, 2H), 8.52 (d, J=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.1, 121.1, 122.4, 127.8, 128.7, 129.1, 132.1, 132.7, 134.5, 136.1, 136.4, 141.1, 147.6, 158.4, 199.1; HRMS (EI) calcd for $C_{21}H_{17}NO_2$ (M^+) 315.1259, Found 315.1273.

4.1.33. (2*Z*,4*E*)-2-Benzylidene-3-hydroxy-1,5-diphenylpent-4-en-1-one (38). As described for the synthesis of **3** by Method A, **24** (0.280 mg, 1.0 mmol) and cinnamaldehyde (**2r**, 0.151 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **38** (176 mg, 52%) as a yellow solid.

As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with cinnamaldehyde (**2r**, 0.151 mL, 1.2 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave **38** (225 mg, 66%) as a yellow solid: mp 118 °C; IR (neat) ν 3343, 3027, 1643, 1592, 1447, 1362, 1237, 1088, 1022, 968, 739, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.81 (m, 1H), 5.27 (t, J=5.7 Hz, 1H), 6.34 (dd, J=6.6, 15.9 Hz, 1H), 6.72 (d, J=15.9 Hz, 1H), 7.07–7.14 (m, 6H), 7.20–7.33 (m, 7H), 7.38 (t, J=7.3 Hz, 1H), 7.83 (d, J=3.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 75.6, 126.3, 127.5, 127.8, 128.0, 128.2, 128.5, 128.6, 129.2, 131.6, 133.0, 134.6, 135.9, 136.0, 140.6, 199.7; Anal. calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.35; H, 5.99.

4.1.34. (2*Z*)-2-Benzylidene-3-hydroxy-4,4-dimethyl-1-phenylpentan-1-one (39). As described for the synthesis of **3** by Method A, **24** (0.280 mg, 1.0 mmol) and pivalaldehyde (**2s**, 0.130 mL, 1.5 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave **39** (198 mg, 67%) as a pale yellow solid: mp 96 °C; IR (neat) ν 3468, 2955, 1637, 1595, 1445, 1350, 1235, 1178, 1077, 954, 756, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.96 (s, 9H), 3.36 (d, J=5.9 Hz, 1H), 4.37 (d, J=5.8 Hz, 1H), 7.03–7.07 (m, 5H), 7.17 (s, 1H), 7.21 (t, J=7.8 Hz, 2H), 7.35 (t, J=7.3 Hz, 1H), 7.77–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.3, 36.8, 84.4, 127.7, 127.9, 128.3, 129.5, 132.7, 135.1, 135.4, 136.2, 139.7, 199.6; Anal. calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.59; H, 7.59.

4.1.35. (2*Z*)-2-Benzylidene-3-hydroxy-4-methyl-1-phenylpentan-1-one (40). As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with isobutyraldehyde (**2t**, 0.137 mL, 1.5 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave **40** (192 mg, 69%) as a pale yellow solid: mp 104 °C; IR (neat) ν 3495, 2960, 1645, 1593, 1448, 1371, 1234, 1031, 912, 858, 735, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.01 (d, J=6.6 Hz, 3H), 1.03 (d, J=6.6 Hz, 3H), 1.90 (dq, J=6.6, 6.8 Hz, 1H), 2.51 (d, J=6.1 Hz, 1H),

4.24 (m, 1H), 7.04 (s, 1H), 7.06–7.13 (m, 5H), 7.23–7.27 (m, 2H), 7.39 (t, J=7.3 Hz, 1H), 7.82–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.4, 19.8, 32.5, 81.1, 127.6, 127.8, 128.0, 128.6, 129.2, 132.3, 132.9, 134.9, 135.7, 141.1, 199.7; Anal. calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.09; H, 7.21.

4.1.36. (2*Z*)-2-Benzylidene-3-hydroxy-1-phenylheptan-1-one (41). As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with valeraldehyde (**2u**, 0.160 mL, 1.5 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave **41** (198 mg, 67%) as a pale yellow oil: IR (neat) ν 3413, 2956, 1650, 1595, 1447, 1377, 1229, 1070, 1001, 950, 720, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, J=7.3 Hz, 3H), 1.27–1.58 (m, 4H), 1.60–1.72 (m, 2H), 2.45 (d, J=5.9 Hz, 1H), 4.52 (dd, J=5.4, 13.2 Hz, 1H), 7.02 (s, 1H), 7.06–7.12 (m, 5H), 7.26 (t, J=7.8 Hz, 2H), 7.40 (t, J=7.3 Hz, 1H), 7.81–7.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 22.4, 28.0, 36.0, 75.3, 127.6, 127.8, 128.1, 128.6, 129.1, 130.7, 133.0, 134.8, 135.9, 142.2, 200.0; HRMS (EI) calcd for $C_{20}H_{22}O_2$ (M^+) 294.1620, Found 294.1602.

4.1.37. (2*Z*)-2-Benzylidene-4,4,4-trifluoro-3-trimethylsiloxy-1,3-diphenylbutan-1-one (48). As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with trifluoroacetophenone (**45**, 0.225 mL, 1.5 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave **48** (356 mg, 78%) as a white solid: mp 70 °C; IR (neat) ν 2957, 1656, 1593, 1449, 1254, 1201, 1153, 983, 894, 841, 757, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.12 (s, 9H), 7.08–7.10 (m, 3H), 7.12 (s, 1H), 7.14–7.16 (m, 2H), 7.23–7.27 (m, 2H), 7.36–7.41 (m, 4H), 7.61–7.63 (m, 2H), 7.78–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.1, 127.4 (q, J=2.5 Hz), 127.75, 127.81, 127.9, 128.0, 128.3, 128.7, 129.0, 132.5, 133.51, 133.53, 134.2, 136.4, 138.5, 139.1, 196.2; Anal. calcd for $C_{26}H_{25}F_3O_2Si$: C, 68.70; H, 5.54. Found: C, 69.03; H, 5.59.

4.1.38. Methyl (3*Z*)-3-benzoyl-2-hydroxy-2-methyl-4-phenylbut-3-enoate (49). As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with methyl pyruvate (**46**, 0.109 mL, 1.2 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave **49** (35 mg, 11%) as a colorless oil: IR (neat) ν 3484, 2952, 1732, 1655, 1595, 1448, 1362, 1253, 1133, 947, 758, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.79 (s, 3H), 3.68 (s, 3H), 3.90 (s, 1H), 7.06–7.09 (m, 3H), 7.10–7.14 (m, 2H), 7.21–7.26 (m, 3H), 7.34–7.38 (m, 1H), 7.77 (d, J=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.8, 53.0, 76.1, 127.8, 127.90, 127.92, 128.7, 128.9, 130.7, 132.8, 134.3, 136.0, 140.7, 174.8, 198.7; Anal. calcd for $C_{26}H_{26}O_6$: C, 73.53; H, 5.85. Found: C, 73.35; H, 5.86.

4.1.39. Methyl (3*Z*)-3-benzoyl-2-trimethylsiloxy-2,4-diphenylbut-3-enoate (50). As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **24** (280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with methyl benzoylformate (**47**, 0.171 mL, 1.2 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave **50** (265 mg, 60%) as a colorless oil: IR (neat) ν 2952, 1749, 1660, 1594, 1448, 1247, 1137, 1011, 837, 757, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.12 (s, 9H), 3.88 (s, 3H), 6.48 (s, 1H), 7.01–7.03 (m, 5H), 7.23–7.27 (m, 3H), 7.35–7.45 (m, 4H), 7.57–7.60 (m, 2H), 7.80–7.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.6, 52.5, 85.4, 127.3, 127.66, 127.68, 127.9, 128.1, 128.7, 128.8, 132.3, 132.5, 134.5, 137.1, 140.9, 143.3, 171.9, 198.5; Anal. calcd for $C_{26}H_{26}O_6$: C, 72.94; H, 6.35. Found: C, 72.73; H, 6.40.

4.1.40. [[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]oxy]-trimethylsilane (52). As described for the synthesis of **24**, a THF (25 mL) solution of phenylacetylene (**26**, 2.97 mL, 27 mmol) was treated with *n*-BuLi in hexane (1.58 M, 16.5 mL, 26 mmol), followed by reaction with a THF (10 mL) solution of 4-chlorobenzaldehyde (**2e**, 3.51 g, 25 mmol). Workup as described previously gave 1-(4-chlorophenyl)-3-phenylprop-2-yn-1-ol (6.28 g, quant.) as a pale yellow oil and used for the next step without further purification. A THF (50 mL) solution of 1-(4-chlorophenyl)-3-phenylprop-2-yn-1-ol (2.91 g, 12 mmol) and triethylamine (2.17 mL, 15.6 mmol) was treated with chlorotrimethysilane (1.83 mL, 14.4 mmol). Workup as described previously gave **52** (3.49 g, 92%) as a pale yellow oil.

1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-ol:[19a] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (dd, J=0.5, 6.1 Hz, 1H), 5.67 (d, J=6.1 Hz, 1H), 7.32–7.39 (m, 3H), 7.38 (dd, J=2.0, 6.6 Hz, 2H), 7.46–7.48 (m, 2H), 7.56 (dd, J=2.2, 6.1 Hz, 2H).

Compound **52**: IR (neat) ν 2957, 1489, 1250, 1068, 979, 873, 837, 752, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.25 (s, 9H), 5.67 (s, 1H), 7.30–7.36 (m, 5H), 7.42–7.45 (m, 2H), 7.49 (dd, J=1.7, 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.3, 64.3, 86.0, 89.0, 122.3, 127.5, 128.0, 128.2, 128.2, 131.3, 133.3, 139.7; HRMS (EI) calcd for $C_{18}H_{19}ClOSi$ (M^+) 314.0894, Found 314.0877.

4.1.41. [[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]-oxy]-trimethylsilane (53). As described for the synthesis of **24**, a THF (25 mL) solution of phenylacetylene (**26**, 2.97 mL, 27 mmol) was treated with *n*-BuLi in hexane (1.58 M, 16.5 mL, 26 mmol), followed by reaction with a THF (10 mL) solution of 4-methoxybenzaldehyde (**2c**, 3.04 mL, 25 mmol). Workup as described previously gave 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**13**, 5.98 g, quant.) as a pale yellow oil and used for the next step without further purification. A THF (50 mL) solution of **13** (2.91 g, 12 mmol) and triethylamine (2.17 mL, 15.6 mmol) was treated with chlorotrimethylsilane (1.83 mL, 14.4 mmol). Workup as described previously gave **53** (3.49 g, 92%) as a pale yellow oil.

Compound **13**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18–2.31 (m, 1H), 3.81 (s, 3H), 5.65 (d, J=6.1 Hz, 1H), 6.93 (dd, J=2.1, 6.8 Hz, 2H), 7.30–7.34 (m, 3H), 7.46–7.48 (m, 2H), 7.55 (dd, J=2.1, 6.6 Hz, 2H).

Compound **53**: IR (neat) ν 2956, 1509, 1246, 1171, 1034, 979, 873, 836, 753, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 9H), 3.81 (s, 3H), 5.66 (s, 1H), 6.90 (dd, J=2.1, 6.8 Hz, 2H), 7.29–7.32 (m, 3H), 7.43–7.46 (m, 2H), 6.90 (dd, J=2.0, 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.4, 55.2, 64.7, 85.6, 89.7, 113.5, 122.6, 127.6, 127.9, 128.0, 131.3, 133.4, 158.9; HRMS (EI) calcd for $C_{19}H_{22}O_2Si$ (M^+) 310.1389, Found 310.1401.

4.1.42. [[1-(2-Furyl)-3-phenyl-2-propynyl]oxy]-trimethylsilane (54). As described for the synthesis of **24**, a THF (13 mL) solution of phenylacetylene (**26**, 1.48 mL, 13.5 mmol) was treated with *n*-BuLi in hexane (1.6 M, 8.1 mL, 13 mmol), followed by reaction with a THF (5 mL) solution of 2-furaldehyde (**2j**, 1.03 mL, 12.5 mmol). Workup as described previously gave 1-(2-furyl)-3-phenylprop-2-yn-1-ol (2.59 g, quant.) as a pale yellow oil and used for the next step without further purification. A THF (25 mL) solution of 1-(2-furyl)-3-phenylprop-2-yn-1-ol (1.19 g, 6 mmol) and triethylamine (1.09 mL, 7.8 mmol) was treated with chlorotrimethylsilane (0.91 mL, 7.2 mmol). Workup as described previously gave **54** (1.48 g, 91%) as a pale yellow oil.

1-(2-Furyl)-3-phenylprop-2-yn-1-ol:[25] ^1H NMR ($CDCl_3$, 400 MHz) δ 2.39–2.43 (m, 1H), 5.69 (d, J=6.5 Hz, 1H), 6.38 (dd, J=1.7, 3.2 Hz, 1H), 6.53 (d, J=3.4 Hz, 1H), 7.30–7.35 (m, 3H), 7.45 (dd, J=0.9, 1.7 Hz, 1H), 7.47–7.50 (m, 2H).

Compound **54**: IR (neat) ν 2958, 1490, 1251, 1143, 1055, 867, 839, 753, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.22 (s, 9H), 5.72 (s, 1H), 6.36 (dd, J=1.8, 3.4 Hz, 1H), 6.48 (dd, J=0.7, 3.9 Hz, 1H), 7.31–7.33 (m, 3H), 7.42 (dd, J=0.9, 2.0 Hz, 1H), 7.46–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.2, 58.9, 64.7, 85.0, 86.8, 107.3, 110.1, 122.2, 127.9, 128.2, 131.4, 142.3, 152.9; HRMS (EI) calcd for $C_{16}H_{18}O_2Si$ (M^+) 270.1076, Found 270.1064.

4.1.43. [[1-(2-Thienyl)-3-phenyl-2-propynyl]oxy]-trimethylsilane (55). As described for the synthesis of **24**, a THF (12 mL) solution of phenylacetylene (**26**, 1.54 mL, 14 mmol) was treated with *n*-BuLi in hexane (1.6 M, 8.1 mL, 13 mmol), followed by reaction with a THF (6 mL) solution of 2-thiophenecarboxaldehyde (**2p**, 1.12 mL, 12 mmol). Workup as described previously gave 3-phenyl-1-(2-thienyl)prop-2-yn-1-ol (2.60 g, quant.) as a pale yellow oil and used for the next step without further purification. A THF (30 mL) solution of 3-phenyl-1-(2-thienyl)prop-2-yn-1-ol (1.50 g, 7 mmol) and triethylamine (1.27 mL, 9.1 mmol) was treated with chlorotrimethylsilane (1.07 mL, 8.4 mmol). Workup as described previously gave **55** (2.01 g, quant.) as a colorless oil.

3-Phenyl-1-(2-thienyl)prop-2-yn-1-ol:[26] ^1H NMR ($CDCl_3$, 400 MHz) δ 2.49 (br, 1H), 5.89 (d, J=7.0 Hz, 1H), 7.00 (dd, J=3.7, 5.1 Hz, 1H), 7.24–7.26 (m, 1H), 7.31–7.35 (m, 4H), 7.47–7.50 (m, 2H).

Compound **55**: IR (neat) ν 2957, 1490, 1250, 1060, 962, 868, 837, 753, 688 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.25 (s, 9H), 5.92 (s, 1H), 6.96 (dd, J=3.7, 5.1 Hz, 1H), 7.15–7.17 (m, 1H), 7.27 (dd, J=3.6, 4.9 Hz, 1H), 7.30–7.32 (m, 3H), 7.45–7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.3, 61.0, 85.4, 88.6, 122.2, 124.5, 125.2, 126.2, 128.0, 128.2, 131.3, 145.4; HRMS (EI) calcd for $C_{16}H_{18}OSSi$ (M^+) 286.0848, Found 286.0832.

4.1.44. [[3-Phenyl-1-(pyridin-2-yl)-2-propynyl]oxy]-trimethylsilane (56). To phenylacetylene (**26**, 0.88 mL, 8 mmol) in THF (8 mL) was added *n*-BuLi in hexane (1.6 M, 5.0 mL, 8 mmol) at −78 °C under N_2. After 10 min, the mixture was warmed to 0 °C and added dropwise to a THF (10 mL) solution of 2-pyridinecarboxaldehyde (**2q**, 0.95 mL, 10 mmol) at −8 °C for 30 min. After 20 min, the reaction mixture was poured into water, followed by addition of *tert*-butyl methyl ether, and the separated organic layer was washed with water and brine, and then dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 2:1) to give 3-phenyl-1-pyridin-2-ylprop-2-yn-1-ol (1.09 g, 52%) as a yellow oil. As described for the synthesis of **24**, a THF (17 mL) solution of 3-phenyl-1-pyridin-2-ylprop-2-yn-1-ol (897 mg, 4.2 mmol) and triethylamine (0.76 mL, 5.46 mmol) was treated with chlorotrimethylsilane (0.64 mL, 5.04 mmol). Workup as described previously followed by short silica gel column chromatography (hexane/EtOAc, 4:1) gave **56** (1.03 g, 87%) as a yellow oil.

3-Phenyl-1-pyridin-2-ylprop-2-yn-1-ol: IR (neat) ν 3056, 1670, 1594, 1489, 1315, 1033, 969, 751, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.85 (br, 1H), 5.73 (s, 1H), 7.26–7.31 (m, 4H), 7.44–7.46 (m, 2H), 7.60 (d, J=7.8 Hz, 1H), 7.76 (dt, J=1.6, 7.8 Hz, 1H), 8.58 (d, J=4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 63.8, 85.4, 88.1, 120.7, 122.1, 122.9, 127.9, 128.2, 131.5, 137.0, 147.8, 157.5; HRMS (EI) calcd for $C_{14}H_{11}NO$ (M^+) 209.0841, Found 209.0835.

Compound **56**: IR (neat) ν 2957, 1588, 1435, 1250, 1102, 1068, 838, 749, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.26 (s, 9H), 5.76 (s, 1H), 7.22 (t, J=6.0 Hz, 1H), 7.27–7.28 (m, 3H), 7.42–7.44 (m, 2H), 7.69–7.76 (m, 2H), 8.57 (d, J=4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.3, 66.7, 85.7, 89.0, 120.3, 122.4, 122.5, 127.8, 128.0, 131.4, 136.7, 148.5, 160.1; HRMS (EI) calcd for $C_{17}H_{19}NOSi$ (M^+) 281.1236, Found 281.1225.

4.1.45. (2*E*)-[[3-Phenyl-1-(phenylethynyl)-2-propenyl]oxy]-trimethylsilane (57). To phenylacetylene (**26**, 1.21 mL, 11 mmol) in THF (5 mL) was added *n*-BuLi in hexane (1.58 M, 6.3 mL, 10 mmol) at −78 °C under N_2. After 10 min, the mixture was warmed to 0 °C and added to a THF (10 mL) solution of cinnamaldehyde (**2r**, 1.26 mL, 10 mmol) at −78 °C. After 1 h, water was added to the reaction mixture, followed by addition of EtOAc, and the separated organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, (1*E*)-1,5-diphenylpent-1-en-4-yn-3-ol (2.28 g, 97%) was obtained as a pale yellow oil and used for the next step without further purification. As described for the synthesis of **24**, a THF (40 mL) solution of (1*E*)-1,5-diphenylpent-1-en-4-yn-3-ol (2.28 g, 9.73 mmol) and triethylamine (1.73 mL, 12.7 mmol) was treated with chlorotrimethylsilane (1.48 mL, 11.7 mmol). Workup as described previously gave **57** (3.12 g, quant.) as a white solid.

(1*E*)-1,5-Diphenylpent-1-en-4-yn-3-ol:[27] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.14 (d, J=6.1 Hz, 1H), 5.29 (dt, J=1.5, 6.1 Hz, 1H), 6.39 (dd, J=6.1, 15.8 Hz, 1H), 6.84 (d, J=15.9 Hz, 1H), 7.27–7.30 (m, 1H), 7.31–7.36 (m, 5H), 7.42–7.45 (m, 2H), 7.46–7.49 (m, 2H).

Compound **57**: mp 47–48 °C; IR (neat) ν 2957, 1489, 1315, 1251, 1099, 1056, 961, 871, 834, 754, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.27 (s, 9H), 5.29 (dd, J=1.4, 5.9 Hz, 1H), 6.34 (dd, J=5.9, 15.6 Hz, 1H), 6.75 (dd, J=1.0, 15.6 Hz, 1H), 7.25–7.27 (m, 1H), 7.31–7.35 (m, 5H), 7.41–7.47 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.3, 63.5, 85.5, 88.2, 122.3, 126.3, 127.3, 127.8, 127.9, 128.0, 128.5, 130.3, 131.1, 135.9; Anal. calcd for $C_{20}H_{22}OSi$: C, 78.38; H, 7.24. Found: C, 78.27; H, 7.29.

4.1.46. [(1-Phenyl-2-heptynl)oxy]-trimethylsilane (58). As described for the synthesis of **24**, a THF (15 mL) solution of 1-hexyne (1.95 mL, 17 mmol) was treated with *n*-BuLi in hexane (1.58 M, 10.1 mL, 16 mmol) at −78 °C for 30 min, followed by reaction with the THF (5 mL) solution of benzaldehyde (**2a**, 1.52 mL, 15 mmol) for 3 h at rt. Workup as described previously gave 1-phenylhept-2-yn-1-ol (2.71 g, 96%) as a colorless oil and used for the next step without further purification. A THF (16 mL) solution of 1-phenylhept-2-yn-1-ol (753 mg, 4 mmol) and triethylamine (0.725 mL, 5.2 mmol) was treated with chlorotrimethylsilane (0.609 mL, 4.8 mmol). Workup as described previously gave **58** (997 mg, 96%) as a colorless oil.

1-Phenylhept-2-yn-1-ol:[28] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (t, J=7.3 Hz, 3H), 1.38–1.47 (m, 2H), 1.50–1.57 (m, 2H), 2.09 (d, J=6.1 Hz, 1H), 2.28 (dt, J=2.0, 7.0 Hz, 2H), 5.45 (d, J=6.1 Hz, 1H), 7.29–7.33 (m, 1H), 7.35–7.39 (m, 2H), 7.53–7.55 (m, 2H).

Compound **58**: IR (neat) ν 2958, 1452, 1250, 1137, 1057, 874, 838, 750, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.19 (s, 9H), 0.90 (t, J=7.2 Hz, 3H), 1.36–1.45 (m, 2H), 1.47–1.54 (m, 2H), 2.24 (dt, J=2.2, 7.1 Hz, 2H), 5.47 (s, 1H), 7.24–7.28 (m, 2H), 7.31–7.35 (m, 2H), 7.48 (d, J=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.3, 13.6, 18.5, 22.0, 30.6, 64.7, 80.5, 86.6, 126.0, 127.3, 127.9, 141.8; HRMS (EI) calcd for $C_{16}H_{24}OSi$ (M^+) 260.1596, Found 260.1593.

4.1.47. [[1-(Phenylethynyl)pentyl]oxy]-trimethylsilane (59).[29] As described for the synthesis of **24**, a THF (15 mL) solution of phenylacetylene (**26**, 1.89 mL, 17 mmol) was treated with *n*-BuLi in hexane (1.58 M, 10.1 mL, 16 mmol), followed by reaction with a THF (5 mL) solution of valeraldehyde (**2u**, 1.60 mL, 15 mmol) for 3 h at rt. Workup as described previously gave 1-phenylhept-1-yn-3-ol (2.73 g, 97%) as a colorless oil and used for the next step without further purification. A THF (16 mL) solution of 1-phenylhept-1-yn-3-ol (753 mg, 4 mmol) and triethylamine (0.725 mL, 5.2 mmol) was treated with chlorotrimethylsilane (0.609 mL, 4.8 mmol). Workup as described previously gave **59** (902 mg, 87%) as a colorless oil.

1-Phenylhept-1-yn-3-ol:[27] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.94 (t, J=7.1 Hz, 3H), 1.35–1.44 (m, 2H), 1.46–1.53 (m, 2H), 1.77–1.86 (m, 3H), 4.59 (d, J=2.6, 12.2 Hz, 1H), 7.29–7.32 (m, 3H), 7.41–7.44 (m, 2H).

Compound **59**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.21 (s, 9H), 0.93 (t, J=7.1 Hz, 3H), 1.32–1.50 (m, 4H), 1.74–1.79 (m, 2H), 4.55 (d, J=6.6 Hz, 1H), 7.28–7.30 (m, 3H), 7.40–7.42 (m, 2H).

4.1.48. (2*Z*)-1-(4-Chlorophenyl)-2-[hydroxy(phenyl)-methyl]-3-phenylprop-2-en-1-one (60). As described for the synthesis of **3** by Method A, **52** (315 mg, 1.0 mmol) and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) was treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **60** (258 mg, 74%) as a colorless oil: IR (neat) ν 3421, 3028, 1651, 1585, 1400, 1227, 1089, 1013, 956, 843, 741, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.07 (m, 1H), 5.74 (d, J=4.9 Hz, 1H), 6.99 (d, J=1.2 Hz, 1H), 7.07–7.08 (m, 5H), 7.11 (d, J=8.8 Hz, 2H), 7.22–7.25 (m, 1H), 7.29–7.33 (m, 2H), 7.41–7.44 (m, 2H), 7.55 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.5, 126.1, 127.7, 127.9, 128.0, 128.1, 128.2, 128.6, 130.3, 131.7, 134.2, 134.4, 139.1, 140.4, 141.3, 198.6; HRMS (EI) calcd for $C_{22}H_{17}ClO_2$ (M^+) 348.0917, Found 348.0941.

4.1.49. (2*Z*)-1-(4-Chlorophenyl)-2-[hydroxy(4-methoxy-phenyl)methyl]-3-phenylprop-2-en-1-one (61). As described for the synthesis of **3** by Method A, **52** (315 mg, 1.0 mmol) and 4-methoxybenzaldehyde (**2c**, 0.146 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **61** (269 mg, 71%) as a colorless oil: IR (neat) ν 3438, 2967, 1652, 1584, 1509, 1400, 1242, 1170, 1089, 1031, 956, 830, 747, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.91 (dd, J=1.5, 4.6 Hz, 1H), 3.77 (s, 3H), 5.69 (d, J=4.6 Hz, 1H), 6.84 (d, J=8.8 Hz, 2H), 6.98 (d, J=5.2 Hz, 1H), 7.05–7.09 (m, 5H), 7.12 (d, J=8.8 Hz, 2H), 7.34 (d, J=4.3 Hz, 2H), 7.58 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.3, 76.3, 113.8, 127.7, 128.0, 128.1, 128.3, 128.8, 130.6, 131.5, 132.8, 134.4, 134.6, 139.3, 141.8, 159.1, 198.8; HRMS (EI) calcd for $C_{23}H_{19}ClO_3$ (M^+) 378.1023, Found 378.1006.

4.1.50. (2*Z*)-2-[Hydroxy(phenyl)methyl]-1-(4-methoxy-phenyl)-3-phenylprop-2-en-1-one (62). As described for the synthesis of **3** by Method A, **53** (310 mg, 1.0 mmol) and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **62** (287 mg, 83%) as a white solid: mp 106–107 °C; IR (neat) ν 3388, 3024, 1625, 1595, 1423, 1353, 1245, 1167, 1106, 1021, 942, 753, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.30 (d, J=4.9 Hz, 1H), 3.73 (s, 3H), 5.69 (d, J=4.9 Hz, 1H), 6.63 (d, J=9.0 Hz, 2H), 6.90 (d, J=1.0 Hz, 1H), 7.06–7.12 (m, 5H), 7.20–7.24 (m, 1H), 7.28–7.32 (m, 2H), 7.42–7.44 (m, 2H), 7.63 (d, J=9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.2, 76.9, 113.1, 126.1, 127.5, 127.7, 127.8, 128.1, 128.6, 128.7, 130.9, 131.5, 134.6, 130.6, 141.5, 163.2, 198.3; Anal. calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 79.87; H, 6.00.

4.1.51. (2*Z*)-2-[(4-Chlorophenyl)(hydroxy)methyl]-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (63). As described for the synthesis of **3** by Method A, **53** (310 mg, 1.0 mmol) and 4-chlorobenzaldehyde (**2e**, 0.169 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **63** (313 mg, 83%) as a colorless oil: IR (neat) ν 3414, 2972, 1643, 1591, 1489, 1365, 1242, 1164, 1027, 956, 831, 756, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.40–3.44 (m, 1H), 3.74 (s, 3H), 5.65 (d, J=4.9 Hz, 1H), 6.64 (d, J=9.0 Hz, 2H), 6.91 (d, J=1.0 Hz, 1H), 7.07–7.11 (m, 5H), 7.25–7.28 (m, 3H), 7.35–7.39 (m, 2H), 7.62 (d, J=9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.2, 76.3, 113.3, 127.5, 127.8, 127.9, 128.2, 128.5, 128.7, 131.4, 131.6, 133.1, 134.4, 139.2, 140.9, 163.3, 198.1; HRMS (EI) calcd for $C_{23}H_{19}ClO_3$ (M^+) 378.1023, Found 378.0992.

4.1.52. (2*Z*)-2-[Hydroxy(4-methoxyphenyl)methyl]-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (9). As described for the synthesis of **3** by Method A, **53** (310 mg, 1.0 mmol) and 4-methoxybenzaldehyde (**2c**, 0.169 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **9** (296 mg, 79%) as a colorless oil.

4.1.53. (2*Z*)-1-(2-Furyl)-2-[hydroxy(phenyl)methyl]-3-phenylprop-2-en-1-one (64). As described for the synthesis of **3** by Method A, **54** (270 mg, 1.0 mmol) and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **64** (242 mg, 80%) as a colorless oil: IR (neat) ν 3412, 3028, 1625, 2560, 1459, 1394, 1266, 1017, 955, 855, 754, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.44 (d, J=5.4 Hz, 1H), 5.68 (d, J=5.1 Hz, 1H), 6.34 (d, J=16.1 Hz, 1H), 7.08 (s, 1H), 7.11 (d, J=7.1 Hz, 2H), 7.21–7.29 (m, 11H), 7.31–7.35 (m, 2H), 7.44 (d, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.3, 111.9, 120.6, 126.2, 127.6, 127.8, 127.9, 128.1, 128.4, 132.7, 134.9, 140.5, 141.2, 146.8, 151.7, 186.2; HRMS (EI) calcd for $C_{20}H_{16}O_3$ (M^+) 304.1099, Found 304.1092.

4.1.54. (2*Z*)-2-[Hydroxy(phenyl)methyl]-3-phenyl-1-(2-thienyl)prop-2-en-1-one (65). As described for the synthesis of **3** by Method A, **55** (286 mg, 1.0 mmol) and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **65** (243 mg, 76%) as a colorless oil: IR (neat) ν 3413, 3027, 1619, 1514, 1408, 1240, 1033, 924, 839, 722, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.18 (d, J=4.9 Hz, 1H), 5.71 (d, J=4.6 Hz, 1H), 6.73 (dd, J=3.9, 4.9 Hz, 1H), 6.93 (s, 1H), 7.10–7.14 (m, 3H), 7.16–7.20 (m, 3H), 7.20–7.25 (m, 1H), 7.28–7.32 (m, 2H), 7.41–7.45 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.5, 126.2, 127.5, 127.6, 127.8, 127.9, 128.1, 128.6, 131.4, 134.5, 134.7, 140.4, 142.0, 143.2, 191.5; HRMS (EI) calcd for $C_{20}H_{16}O_2S$ (M^+) 320.0871, Found 320.0895.

4.1.55. (2*Z*)-2-[Hydroxy(phenyl)methyl]-3-phenyl-1-pyridin-2-ylprop-2-en-1-one (66). As described for the synthesis of **3** by Method A, **56** (281 mg, 1.0 mmol) and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). After the reaction mixture was quenched, 1 N aq HCl (1 mL), acetonitrile (2 mL), water, and EtOAc were added, and the separated organic layer was washed with water, saturated aq $NaHCO_3$, and brine. After the solution was dried over $MgSO_4$ followed by removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 2:1) that gave **66** (127 mg, 40%) as a yellow oil.

As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **56** (281 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with benzaldehyde (**2a**, 0.122 mL, 1.2 mmol). Workup as described in Method A followed by silica gel column chromatography (hexane/EtOAc, 2:1) gave **66** (246 mg, 78%) as a yellow oil: IR (neat) ν 3333, 3058, 1675, 1582, 1449, 1364, 1227, 1023, 964, 866, 750, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.54 (br s, 1H), 5.70 (s, 1H), 6.91 (s, 1H), 7.10–7.12 (m, 5H), 7.21–7.24 (m, 1H), 7.29–7.32 (m, 2H), 7.39–7.45 (m, 3H), 7.77 (dt, J=1.7, 7.8 Hz, 1H), 7.90 (d, J=7.8 Hz, 1H), 8.61 (d, J=3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 75.6, 123.1, 126.1, 126.8, 127.1, 127.7, 127.86, 127.89, 128.4, 134.4, 134.8, 137.2, 140.9, 144.0, 148.2, 153.4, 197.9; HRMS (EI) calcd for $C_{21}H_{17}NO_2$ (M^+) 315.1259, Found 315.1249.

4.1.56. (1*Z*,4*E*)-2-[Hydroxy(phenyl)methyl]-1,5-diphenylpenta-1,4-dien-3-one (67). As described for the synthesis of **3** by Method A, **57** (306 mg, 1.0 mmol) and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) were treated with KO*t*-Bu (11 mg, 0.1 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **67** (94 mg, 28%) as a yellow oil.

As described for the synthesis of **3** by Method B, a THF (2 mL) solution of **57** (306 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mL, 0.1 mmol), followed by reaction with benzaldehyde (**2a**, 0.122 mL, 1.2 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 3:1) gave **67** (169 mg, 50%) as a yellow oil: IR (neat) ν 3402, 3027, 1622, 1593, 1448, 1365, 1228, 1193, 1068, 976, 727, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.44 (d, J=5.4 Hz, 1H), 5.68 (d, J=5.1 Hz, 1H), 6.34 (d, J=16.1 Hz, 1H), 7.08 (s, 1H), 7.11 (d, J=7.1 Hz, 2H), 7.21–7.29 (m, 11H), 7.31–7.35 (m, 2H), 7.44 (d, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.4, 126.1, 127.5, 127.9, 128.09, 128.13, 128.3, 128.9, 130.0, 133.5, 134.1, 135.0, 140.9, 143.2, 143.6, 197.5; HRMS (EI) calcd for $C_{24}H_{20}O_2$ (M^+) 340.1463, Found 340.1464.

4.1.57. (2*Z*)-2-[Hydroxy(phenyl)methyl]-1-phenylhept-2-en-1-one (68). As described for the synthesis of **3** by Method A, **58** (260 mg, 1.0 mmol) and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) were treated with KO*t*-Bu (22 mg, 0.2 mmol) in DMF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave **68** (67 mg, 23%) as a colorless oil: IR (neat) ν 3437, 2957, 1650, 1595, 1449, 1377, 1232, 1022, 956, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.74 (t, J=7.1 Hz, 3H),

1.10–1.18 (m, 2H), 1.22–1.30 (m, 2H), 1.80 (q, J=7.6 Hz, 2H), 3.14 (d, J=5.4 Hz, 1H), 5.54 (d, J=5.4 Hz, 1H), 5.91 (dt, J=1.0, 7.8 Hz, 1H), 7.19–7.23 (m, 1H), 7.27–7.31 (m, 2H), 7.35–7.38 (m, 4H), 7.50 (t, J=7.5 Hz, 1H), 7.71–7.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 22.1, 26.9, 29.4, 31.0, 126.0, 127.3, 128.0, 128.1, 128.9, 133.0, 134.8, 137.4, 140.8, 141.2, 199.6; HRMS (EI) calcd for $C_{20}H_{22}O_2$ (M^+) 294.1620, Found 294.1628.

4.1.58. Preparation of (2*Z*)-2-[hydroxy(phenyl)methyl]-1,3-diphenylprop-2-en-1-one (3) from 24 using phase transfer catalyst. Typical procedure. To a solution of **24** (280 mg, 1 mmol), the catalyst **6** (47 mg, 0.1 mmol), and benzaldehyde (**2a**, 0.122 mL, 1.2 mmol) in THF (2 mL) was added K_3PO_4 (212 mg, 1.0 mmol) at rt under Ar. After 6 h, the insoluble salts were filtered and the yields of **3**, **27** and **24** were assayed by HPLC analysis of the filtrate. After the remaining sample was treated with EtOAc and water, the separated organic layer was washed with water and brine, and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 10:1) to give **3**. HPLC analysis for determination of the yield of **3**, **27** and **24**: YMC Pro C18 (4.6 mm i.d.×150 mm), UV 254 nm, flow rate 1.0 mL/min, MeCN/H_2O/70% aq $HClO_4$=600:400:1 (v/v/v), retention time **3**: 7.4 min; **27**: 9.1 min; **24**: 5.4 min. HPLC analysis for determination of the enantiomeric excess of **3**: DAICEL CHIRALCEL OD (4.6 mm i.d.×250 mm), UV 254 nm, flow rate 1.0 mL/min, hexane/2-propanol=9:1, retention time **3**: 12.3 min, 14.1 min; **4**: 13.1 min, 19.8 min.

4.1.59. Preparation of optically active (*R*)-[(1,3-diphenyl-2-propynyl)oxy]-trimethylsilane (24).[19] To a solution of phenylacetylene (**26**, 2.31 mL, 21 mmol) in THF (20 mL) was added 1 M Et_2Zn in hexane (20 mL, 20 mmol) at rt under Ar, and then the mixture was warmed to 70 °C. After 5 h, to the mixture was added a solution of (*S*)-BINOL (285 mg, 1 mmol), phenol (100 mg, 1 mmol), and Ti(O*i*-Pr)$_4$ (0.9 mL, 3 mmol) in THF (10 mL) at 0 °C. After 40 min, benzaldehyde (**2a**, 1.02 mL, 10 mmol) was added to the mixture, and then the mixture was stirred at 0 °C for 24 h. 1 N aq HCl (100 mL) and *tert*-butyl methyl ether (50 mL) were added, and the separated organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 10:1) to give (*R*)-**4** (1.79 g, 82%) as a colorless oil.

A THF (16 mL) solution of optically active (*R*)-**4** (874 mg, 4.2 mmol) and triethylamine (0.76 mL, 5.5 mmol) was treated with chlorotrimethylsilane (0.64 mL, 5.0 mmol). Workup as described previously gave optically active (*R*)-**24** (1.15 g, 98%) as a pale yellow oil. The enantiomeric excess of **4** was determined by HPLC analysis: DAICEL CHIRALCEL OD (4.6 mm i.d.×250 mm), UV 254 nm, flow rate 1.0 mL/min, hexane/2-propanol=9:1, retention time **4**: 13.1 min (major), 19.8 min (minor).

4.1.60. [(1,3-Diphenyl-2-propynyl)oxy]-*tert*-butyldimethylsilane (73).[30] To a solution of **4** (1.67 g, 8 mmol) in THF (8 mL) was added *n*-BuLi in hexane (1.58 M, 5.57 mL, 8.8 mmol) at −78 °C under N_2, and then the mixture was immediately warmed to 0 °C. After 10 min, a solution of *tert*-butyldimethylsilylchloride (1.33 g, 8.8 mmol) in THF (4 mL) was added and the mixture was warmed to rt. After 2 h, water and *tert*-butyl methyl ether were added, and the separated organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 10:1) to give **73** (0.78 g, 30%) as a colorless oil: IR (neat) ν 2957, 1599, 1490, 1443, 1250, 1192, 1061, 977, 838, 753, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.20 (s, 3H), 0.22 (s, 3H), 0.97 (s, 9H), 5.73 (s, 1H), 7.281–7.30 (m, 4H), 7.35–7.38 (m, 2H), 7.42–7.44 (m, 2H), 7.55–7.57 (m, 2H).

4.1.61. [(1,3-Diphenyl-1,2-propadienyl)oxy]-*tert*-butyldimethylsilane (74). To a solution of **73** (161 mg, 0.5 mmol) in THF (1 mL) was added 1 M KO*t*-Bu in THF (0.05 mL, 0.05 mmol) at −78 °C under N_2. After 20 min, water and *tert*-butyl methyl ether were added, and the separated organic layer was dried over $MgSO_4$. After removal of the solvent in vacuo, crude **74** (151 mg) was obtained as a yellow oil: IR (neat) ν 2929, 1929, 1597, 1492, 1447, 1251, 1202, 1072, 1019, 834, 778, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.14 (s, 3H), 0.19 (s, 3H), 1.02 (s, 9H), 6.94 (s, 1H), 7.22–7.27 (m, 2H), 7.30–7.35 (m, 4H), 7.38–7.41 (m, 2H), 7.53–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −4.5, 18.4, 26.0, 107.3, 124.9, 127.5, 127.7, 128.1, 128.6, 129.7, 134.2, 135.0, 200.1.

4.1.62. [[3-(4-Methoxyphenyl)-1-phenyl-2-propynyl]-oxy]-trimethylsilane (78). As described for the synthesis of **24**, a THF (4 mL) solution of 2-ethynyl-4-methoxybenzene (529 mg, 4 mmol) was treated with *n*-BuLi in hexane (1.57 M, 2.55 mL, 4 mmol), followed by reaction with a THF (3 mL) solution of benzaldehyde (**2a**, 0.41 mL, 4 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol (0.83 g, 87%) as a colorless oil. A THF (10 mL) solution of 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol (596 mg, 2.5 mmol) and triethylamine (0.45 mL, 3.25 mmol) was treated with chlorotrimethylsilane (0.38 mL, 3 mmol). Workup as described previously gave **78** (0.76 g, 98%) as a colorless oil.

3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-ol:[31] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 1H), 3.80 (s, 3H), 5.67 (s, 1H), 6.83 (d, J=8.8 Hz, 2H), 7.33–7.41 (m, 5H), 7.61 (d, J=7.6 Hz, 2H).

Compound **78**: IR (neat) ν 2957, 1770, 1508, 1246, 1057, 829, 750, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 9H), 3.80 (s, 3H), 5.70 (s, 1H), 6.83 (d, J=8.8 Hz, 2H), 7.28–7.39 (m, 5H), 7.56 (d, J=7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.5, 55.3, 65.2, 85.9, 88.3, 113.8, 114.9, 126.4, 127.7, 128.2, 132.9, 141.5, 159.4; HRMS (EI) calcd for $C_{19}H_{22}O_2Si$ (M^+) 310.1389, Found 310.1304.

4.1.63. [[1-Phenyl-3-[4-(tetrahydro-2*H*-pyran-2-yloxy)-phenyl]-2-propynyl]oxy]-trimethylsilane (79). As described for the synthesis of **24**, a THF (7 mL) solution of 2-(4-ethynylphenoxy)tetrahydro-2*H*-pyran (1.42 g, 7 mmol) was treated with *n*-BuLi in hexane (2.67 M, 2.62 mL, 7 mmol), followed by reaction with a THF (3 mL) solution of benzaldehyde (**2a**, 0.71 mL, 7 mmol). Workup as

described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave 1-phenyl-3-[4-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]prop-2-yn-1-ol (2.08 g, 96%) as a pale yellow oil. A THF (25 mL) solution of 1-phenyl-3-[4-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]prop-2-yn-1-ol (1.04 g, 3.37 mmol) and triethylamine (0.61 mL, 4.38 mmol) was treated with chlorotrimethylsilane (0.51 mL, 4.05 mmol). Workup as described previously gave **79** (1.10 g, 86%) as a colorless oil.

1-Phenyl-3-[4-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]prop-2-yn-1-ol: IR (neat) ν 3390, 2946, 1770, 1604, 1506, 1384, 1239, 1020, 956, 917, 832, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.58–1.73 (m, 3H), 1.83–1.87 (m, 2H), 1.95–2.04 (m, 1H), 2.36 (br s, 1H), 3.58–3.62 (m, 1H), 3.84–3.90 (m, 1H), 5.42 (t, J=3.2 Hz, 1H), 5.67 (d, J=7.3 Hz, 1H), 6.99 (d, J=8.8 Hz, 2H), 7.32–7.41 (m, 5H), 7.62 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.8, 25.3, 30.3, 62.1, 65.1, 86.6, 87.4, 96.2, 115.2, 116.2, 126.6, 128.2, 128.5, 133.0, 140.7, 157.1; HRMS (EI) calcd for $C_{20}H_{20}O_3$ (M^+) 308.1412, Found 308.1388.

Compound **79**: IR (neat) ν 2950, 1770, 1604, 1506, 1383, 1239, 1060, 958, 918, 831, 751, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 9H), 1.56–1.70 (m, 3H), 1.83–1.86 (m, 2H), 1.95–2.05 (m, 1H), 3.57–3.61 (m, 1H), 3.83–3.90 (m, 1H), 5.41 (t, J=2.9 Hz, 1H), 5.69 (s, 1H), 6.97 (d, J=8.3 Hz, 2H), 7.27–7.38 (m, 5H), 7.55 (d, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.6, 18.8, 25.3, 30.3, 62.0, 65.2, 85.9, 88.3, 96.1, 115.7, 116.2, 126.4, 127.6, 128.2, 132.8, 141.4, 156.9; Anal. calcd for $C_{23}H_{20}O_3Si$: C, 72.59; H, 7.42. Found: C, 72.56; H, 7.95.

4.1.64. [[3-(4-Chlorophenyl)-1-phenyl-2-propynyl]oxy]-trimethylsilane (80). As described for the synthesis of **24**, a THF (4 mL) solution of 4-chloro-2-ethynylbenzene (546 mg, 4 mmol) was treated with *n*-BuLi in hexane (1.57 M, 2.55 mL, 4 mmol), followed by reaction with a THF (2 mL) solution of benzaldehyde (**2a**, 0.41 mL, 4 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave 3-(4-chlorophenyl)-1-phenylprop-2-yn-1-ol (0.89 g, 91%) as a white solid. A THF (25 mL) solution of 3-(4-chlorophenyl)-1-phenylprop-2-yn-1-ol (607 mg, 2.5 mmol) and triethylamine (0.45 mL, 3.25 mmol) was treated with chlorotrimethylsilane (0.38 mL, 3 mmol). Workup as described previously gave **79** (1.10 g, 86%) as a colorless oil.

3-(4-Chlorophenyl)-1-phenylprop-2-yn-1-ol: mp 56 °C; IR (neat) ν 3235, 2995, 1770, 1488, 1383, 1246, 1014, 824, 756, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.35 (br s, 1H), 5.67 (s, 1H), 7.27–7.30 (m, 2H), 7.32–7.42 (m, 5H), 7.59 (d, J=7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 65.1, 85.5, 89.6, 120.8, 126.5, 128.4, 128.5, 128.6, 132.8, 134.5, 140.3; Anal. calcd for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57. Found: C, 74.01; H, 4.83.

Compound **80**: IR (neat) ν 2957, 1770, 1489, 1383, 1249, 1087, 844, 734, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 9H), 5.69 (s, 1H), 7.26–7.40 (m, 7H), 7.53–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 65.1, 84.7, 90.7, 121.2, 126.3, 127.8, 128.3, 128.5, 132.7, 134.3, 141.1; HRMS (EI) calcd for $C_{18}H_{19}ClOSi$ (M^+) 314.0894, Found 314.0854.

4.1.65. [[3-(2-Naphthyl)-1-phenyl-2-propynyl]oxy]-trimethylsilane (81). As described for the synthesis of **24**, a THF (4 mL) solution of 2-ethynylnaphthalene (609 mg, 4 mmol) was treated with *n*-BuLi in hexane (1.57 M, 2.55 mL, 4 mmol), followed by reaction with a THF (2 mL) solution of benzaldehyde (**2a**, 0.41 mL, 4 mmol). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 5:1) gave 3-(2-naphthyl)-1-phenylprop-2-yn-1-ol (0.81 g, 78%) as a pale yellow solid. A THF (10 mL) solution of 3-(4-chlorophenyl)-1-phenylprop-2-yn-1-ol (646 mg, 2.5 mmol) and triethylamine (0.45 mL, 3.25 mmol) was treated with chlorotrimethylsilane (0.38 mL, 3 mmol). Workup as described previously gave **81** (0.78 g, 94%) as a pale yellow solid.

3-(2-Naphthyl)-1-phenylprop-2-yn-1-ol: mp 51 °C; IR (neat) ν 3289, 2995, 1770, 1383, 1246, 1014, 818, 744, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.43 (br s, 1H), 5.74 (s, 1H), 7.34–7.52 (m, 6H), 7.65 (d, J=7.6 Hz, 2H), 7.76–7.81 (m, 3H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 65.2, 87.0, 89.0, 199.6, 126.4, 126.6, 126.7, 127.61, 127.62, 127.8, 128.2, 128.3, 128.6, 131.6, 132.7, 132.8, 140.5; Anal. calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.22; H, 5.57.

Compound **81**: mp 41 °C; IR (neat) ν 2995, 1770, 1382, 1248, 1064, 841, 748, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.25 (s, 9H), 5.76 (s, 1H), 7.30–7.34 (m, 1H), 7.38–7.41 (m, 2H), 7.46–7.50 (m, 3H), 7.60 (d, J=7.0 Hz, 2H), 7.75–7.81 (m, 3H), 7.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.6, 65.3, 86.2, 90.0, 120.0, 126.36, 126.39, 126.5, 127.6, 127.8, 128.2, 128.3, 131.4, 132.68, 132.74, 141.3; Anal. calcd for $C_{22}H_{22}OSi$: C, 79.95; H, 6.71. Found: C, 79.77; H, 6.72.

4.1.66. [[1-Phenyl-3-(2-thienyl)-2-propynyl]oxy]-trimethylsilane (82). As described for the synthesis of **24**, a THF (2 mL) solution of 2-ethynylthiophene (0.40 g, 2.2 mmol) was treated with *n*-BuLi in hexane (1.57 M, 1.40 mL, 2.2 mmol), followed by reaction with a THF (2 mL) solution of benzaldehyde (**2a**, 0.41 mL, 4 mmol). Workup as described previously gave 1-phenyl-3-(2-thienyl)prop-2-yn-1-ol (0.55 g, quant.) as a pale yellow oil and used for the next step without further purification. A THF (8 mL) solution of 1-phenyl-3-(2-thienyl)prop-2-yn-1-ol (0.40 g, 1.87 mmol) and triethylamine (0.34 mL, 2.43 mmol) was treated with chlorotrimethylsilane (0.28 mL, 2.24 mmol). Workup as described previously gave **82** (0.53 g, 99%) as a yellow oil.

1-Phenyl-3-(2-thienyl)prop-2-yn-1-ol:[32] ^1H NMR ($CDCl_3$, 400 MHz) δ 2.27 (br s, 1H), 5.71 (s, 1H), 6.98 (dd, J=3.7, 5.1 Hz, 1H), 7.24–7.28 (m, 2H), 7.34–7.43 (m, 3H), 7.59–7.61 (m, 2H).

Compound **82**: IR (neat) ν 2995, 1770, 1383, 1248, 1058, 839, 750, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 9H), 5.71 (s, 1H), 6.96 (dd, J=3.7, 5.1 Hz, 1H), 7.21 (dd, J=1.2, 3.7 Hz, 1H), 7.23–7.25 (m, 1H), 7.29–7.40 (m, 3H), 7.53–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.5, 65.3, 79.3, 93.5, 122.6, 126.3, 126.8, 127.0, 127.8,

128.3, 131.9, 140.9; Anal. calcd for $C_{16}H_{18}OSSi$: C, 67.08; H, 6.33. Found: C, 66.63; H, 6.36.

4.1.67. [[3-(2,6-Dimethylphenyl)-1-phenyl-2-propynyl]-oxy]-trimethylsilane (83). As described for the synthesis of **24**, a THF (6 mL) solution of 2-ethynyl-1,3-dimethylbenzene (781 mg, 6 mmol) was treated with *n*-BuLi in hexane (2.67 M, 2.25 mL, 6 mmol), followed by reaction with a THF (3 mL) solution of benzaldehyde (**2a**, 0.41 mL, 4 mmol). Workup as described previously gave 3-(2,6-dimethylphenyl)-1-phenylprop-2-yn-1-ol (1.28 g, 90%) as a pale yellow solid and used for the next step without further purification. A THF (10 mL) solution of 3-(2,6-dimethylphenyl)-1-phenylprop-2-yn-1-ol (0.64 g, 2.71 mmol) and triethylamine (0.45 mL, 3.25 mmol) was treated with chlorotrimethylsilane (0.38 mL, 3 mmol). Workup as described previously gave **83** (788 mg, 94%) as a pale yellow oil.

1-Phenyl-3-(2-thienyl)prop-2-yn-1-ol: mp 66 °C; IR (neat) ν 3297, 2995, 1770, 1466, 1381, 1246, 1019, 769, 731, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.28 (br s, 1H), 2.43 (s, 6H), 5.78 (s, 1H), 7.03 (d, J=7.8 Hz, 1H), 7.11 (dd, J=6.8, 8.3 Hz, 1H), 7.33–7.37 (m, 1H), 7.38–7.42 (m, 2H), 7.64 (d, J=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 65.5, 84.4, 97.0, 122.0, 126.55, 126.60, 127.9, 128.2, 128.5, 140.4, 140.8; Anal. calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 85.99; H, 6.98.

Compound **83**: IR (neat) ν 2995, 1770, 1468, 1377, 1248, 1058, 839, 768, 731, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.28 (br s, 1H), 2.43 (s, 6H), 5.78 (s, 1H), 7.03 (d, J=7.8 Hz, 1H), 7.11 (dd, J=6.8, 8.3 Hz, 1H), 7.33–7.37 (m, 1H), 7.38–7.42 (m, 2H), 7.64 (d, J=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.5, 21.3, 65.3, 83.6, 98.1, 122.4, 126.3, 126.5, 127.6, 127.7, 128.2, 140.4, 141.6; HRMS (EI) calcd for $C_{20}H_{24}OSi$ (M^+) 308.1596, Found 308.1550.

4.1.68. (2*Z*)-1,3-Diphenylprop-2-en-1-one (84).[33] To a solution of **24** (280 mg, 1.0 mmol) in THF (2 mL) was added 1 M KO*t*-Bu in THF (0.1 mmol) at −78 °C under Ar. After 10 min, 2 M sulfuric acid in DME (1 mL, 2.0 mmol) was added dropwise for 5 min at −78 °C. After 10 min, water and EtOAc were added, and the separated organic layer was washed with brine, and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (hexane/EtOAc, 20:1) to give a mixture of *Z*-**84** and *E*-**84** (93:7, 171 mg, 82%) as a yellow solid: ^1H NMR (DMSO-d_6, 400 MHz) δ 6.81 (d, J=13.0 Hz, 1H), 7.05 (d, J=13.0 Hz, 1H), 7.23–7.29 (m, 3H), 7.47–7.51 (m, 2H), 7.59–7.62 (m, 1H), 7.75 (d, J=15.6 Hz, 0.07H), 7.92–7.95 (m, 2H), 8.13–8.16 (m, 0.14H). The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.81 and 7.75.

4.1.69. (2*Z*)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-one (85).[34] As described for the synthesis of **84**, **52** (0.280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave a mixture of *Z*-**85** and *E*-**85** (88:12, 176 mg, 73%) as a yellow solid: ^1H NMR (DMSO-d_6, 400 MHz) δ 6.80 (d, J=12.9 Hz, 1H), 7.09 (d, J=13.0 Hz, 1H), 7.26–7.28 (m, 3H), 7.36–7.39 (m, 2H), 7.45–7.47 (m, 0.42H), 7.55 (d, J=8.6 Hz, 2H), 7.63 (d, J=8.6 Hz, 0.28H), 7.76 (d, J=15.6 Hz, 0.14H), 7.92 (d, J=8.6 Hz, 2H), 8.18 (d, J=8.5 Hz, 0.28H). The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.80 and 7.76.

4.1.70. (2*Z*)-1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one (86).[35] As described for the synthesis of **84**, **53** (0.280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave a mixture of *Z*-**86** and *E*-**86** (97:3, 157 mg, 66%) as a yellow solid: ^1H NMR (DMSO-d_6, 400 MHz) δ 3.82 (s, 3H), 3.86 (s, 0.09H), 6.75 (d, J=13.0 Hz, 1H), 6.97 (d, J=13.0 Hz, 1H), 7.01 (d, J=9.0 Hz, 2H), 7.21–7.28 (m, 3H), 7.35–7.37 (m, 2H), 7.70 (d, J=15.6 Hz, 0.03H), 7.92 (d, J=8.8 Hz, 2H), 8.15–8.18 (m, 0.06H). The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.75 and 7.70.

4.1.71. (2*Z*)-1-(2-Furyl)-3-phenylprop-2-en-1-one (87).[36] As described for the synthesis of **84**, **54** (0.280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave a mixture of *Z*-**87** and *E*-**87** (93:7, 164 mg, 83%) as a yellow solid: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.50 (dd, J=1.7, 3.7 Hz, 1H), 6.60 (dd, J=1.7, 3.7 Hz, 0.07H), 6.69 (d, J=12.7 Hz, 1H), 7.01 (d, J=12.7 Hz, 1H), 7.16–7.17 (m, 1H), 7.30–7.33 (m, 3H), 7.46 (d, J=15.9 Hz, 0.07H), 7.56–7.57 (m, 1H), 7.63–7.65 (m, 2H), 7.89 (d, J=15.9 Hz, 0.07H). The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.69 and 7.89.

4.1.72. (2*Z*)-3-Phenyl-1-(2-thienyl)prop-2-en-1-one (88).[37] As described for the synthesis of **84**, **55** (0.280 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave a mixture of *Z*-**88** and *E*-**88** (95:5, 162 mg, 76%) as a yellow solid: ^1H NMR (DMSO-d_6, 400 MHz) δ 6.89 (d, J=13.0 Hz, 1H), 7.04 (d, J=12.7 Hz, 1H), 7.21 (dd, J=3.9, 4.9 Hz, 1H), 7.29–7.34 (m, 3H), 7.45–7.47 (m, 0.15H), 7.54–7.56 (m, 2H), 7.73 (d, J=15.6 Hz, 0.05H), 7.87–7.89 (m, 1H), 8.01 (dd, J=1.0, 4.9 Hz, 1H), 8.06 (d, J=4.9 Hz, 0.05H), 8.34 (d, J=3.9 Hz, 0.05H). The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.89 and 7.73.

4.1.73. (1*Z*,4*E*)-1,5-Diphenylpenta-1,4-dien-3-one (89). As described for the synthesis of **84**, **57** (306 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 20:1) gave a mixture of *Z*-**89** and *E*-**89** (80:20,

176 mg, 75%) as a yellow oil: IR (neat) ν 2996, 1770, 1671, 1589, 1324, 1246, 1194, 1095, 980, 787, 687 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 6.46 (d, J=12.7 Hz, 1H), 6.80 (d, J=16.1 Hz, 1H), 6.93 (d, J=12.7 Hz, 1H), 7.22–7.32 (m, 7.2H), 7.36–7.38 (m, 1.2H), 7.42–7.44 (m, 2H), 7.49–7.53 (m, 3H), 7.68–7.72 (m, 1.2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 126.9, 128.0, 128.18, 128.24, 128.3, 128.7, 129.2, 130.4, 135.0, 138.9, 143.2, 192.1; HRMS (EI) calcd for $C_{17}H_{14}O$ (M^+) 234.1045, Found 234.1004. The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.46 and 7.68–7.72.

4.1.74. (2*Z*)-3-(4-Methoxyphenyl)-1-phenylprop-2-en-1-one (90).[34] As described for the synthesis of **84**, **78** (310 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave *E*-**90** (180 mg, 76%) as a yellow solid: ^1H NMR (DMSO-d_6, 400 MHz) δ 3.82 (s, 3H), 7.01 (d, J=8.8 Hz, 2H), 7.56 (m, 2H), 7.65 (m, 1H), 7.70 (d, J=15.6 Hz, 1H), 7.79 (d, J=15.6 Hz, 1H), 7.85 (d, J=8.8 Hz, 2H), 8.12 (m, 2H), 8.25–8.28 (m, 2H), 8.29–8.31 (m, 0.06H). The ratio of *Z*- and *E*-isomers of clued product was determined by ^1H NMR analysis of clear vinylic proton, δ 6.73 (d, J=13.0 Hz) and 7.70.

4.1.75. (2*Z*)-1-Phenyl-3-[4-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]prop-2-en-1-one (91). As described for the synthesis of **84**, **79** (380 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave a mixture of *Z*-**91** and *E*-**91** (85:15, 165 mg, 54%) as a yellow oil: IR (neat) ν 2946, 1770, 1659, 1596, 1506, 1372, 1241, 1110, 1035, 956, 917, 834, 724, 689 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 1.50–1.84 (m, 7.08H), 3.50–3.54 (m, 1.18H), 3.67–3.72 (m, 1.18H), 5.46 (t, J=3.4 Hz, 1H), 5.57 (s, 0.18H), 6.75 (d, J=12.9 Hz, 1H), 6.92 (d, J=8.8 Hz, 2H), 6.97 (d, J=12.9 Hz, 1H), 7.08 (d, J=8.8 Hz, 0.36H), 7.47–7.52 (m, 4H), 7.53–7.65 (m, 1.72H), 7.70 (d, J=15.6 Hz, 0.18H), 7.79 (d, J=15.8 Hz, 0.18H), 7.83 (d, J=8.8 Hz, 0.36H), 8.12 (d, J=8.3 Hz, 0.36H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 18.5, 24.6, 29.7, 61.5, 95.3, 115.7, 124.2, 128.16, 128.22, 128.5, 131.0, 133.1, 136.9, 139.0, 156.8, 193.0; Anal. calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.49; H, 6.89. The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.75 and 7.70.

4.1.76. (2*Z*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (92).[38] As described for the synthesis of **84**, **80** (315 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave a mixture of *Z*-**92** and *E*-**92** (90:10, 172 mg, 71%) as a yellow solid: ^1H NMR (DMSO-d_6, 400 MHz) δ 6.84 (d, J=12.7 Hz, 1H), 7.00 (d, J=13.0 Hz, 1H), 7.28–7.31 (m, 2H), 7.36–7.39 (m, 2H), 7.43–7.48 (m, 2H), 7.50–7.54 (m, 0.33H), 7.56–7.60 (m, 1H), 7.60–7.64 (m, 0.11H), 7.67 (d, J=15.6 Hz, 0.11H), 7.87–7.89 (m, 2H), 8.09–8.11 (m, 0.22H). The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.84 and 7.67.

4.1.77. (2*Z*)-3-(2-Naphthyl)-1-phenylprop-2-en-1-one (93). As described for the synthesis of **84**, **81** (330 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave a mixture of *Z*-**93** and *E*-**93** (80:20, 191 mg, 85%) as a yellow solid: IR (neat) ν 2995, 1770, 1659, 1588, 1383, 1246, 1057, 824, 691 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 6.92 (d, J=12.7 Hz, 1H), 7.23 (d, J=13.0 Hz, 1H), 7.46–7.51 (m, 5H), 7.56–7.61 (m, 2H), 7.65–7.70 (m, 0.5H), 7.76 (d, J=8.5 Hz, 1H), 7.82–7.84 (m, 2H), 7.88–7.93 (m, 0.25H), 7.95–8.00 (m, 4H), 8.07 (d, J=15.6 Hz, 0.25H), 8.10–8.15 (m, 0.25H), 8.18–8.20 (m, 0.5H), 8.35 (s, 0.25H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 126.0, 126.2, 126.6, 127.2, 127.3, 127.9, 128.29, 128.33, 128.6, 129.0, 130.5, 132.3, 132.4, 132.6, 133.2, 138.6, 193.6; HRMS (EI) calcd for $C_{19}H_{14}O$ (M^+) 258.1045, Found 258.0983. The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 6.92 and 8.07.

4.1.78. (2*Z*)-1-Phenyl-3-(2-thienyl)prop-2-en-1-one (94).[39] As described for the synthesis of **84**, **82** (286 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave a mixture of *Z*-**94** and *E*-**94** (97:3, 175 mg, 82%) as a yellow solid: ^1H NMR (DMSO-d_6, 400 MHz) δ 7.23 (d, J=12.4 Hz, 1H), 7.39 (dd, J=3.8, 5.1 Hz, 1H), 7.65 (d, J=12.2 Hz, 1H), 7.75–7.80 (m, 2H), 7.85–7.89 (m, 2H), 8.00 (d, J=11.4 Hz, 1H), 8.13 (d, J=15.4 Hz, 0.03H), 8.25–8.28 (m, 2H), 8.29–8.31 (m, 0.06H). The ratio of *Z*- and *E*-isomers was determined by ^1H NMR analysis of vinylic proton, δ 7.23 and 8.13.

4.1.79. (2*Z*)-3-(2,6-Dimethylphenyl)-1-phenylprop-2-en-1-one (95). As described for the synthesis of **84**, **83** (308 mg, 1.0 mmol) was treated with 1 M KO*t*-Bu in THF (0.1 mmol), and then 2 M sulfuric acid in DME (1 mL, 2.0 mmol) in THF (2 mL). Workup as described previously followed by silica gel column chromatography (hexane/EtOAc, 10:1) gave a mixture of *Z*-**95** and *E*-**95** (70:30, 128 mg, 54%) as a yellow solid. Pure *Z*-isomer was obtained as a pale yellow solid by crystallization from *n*-hexane.

Compound *Z*-**95**: mp 61 °C; IR (neat) ν 2995, 1770, 1665, 1448, 1386, 1246, 1058, 1007, 758, 689 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.10 (s, 6H), 6.94 (d, J=7.6 Hz, 2H), 7.00–7.03 (m, 1H), 7.17 (d, J=12.2 Hz, 1H), 7.26 (d, J=12.2 Hz, 1H), 7.46–7.50 (m, 2H), 7.57–7.61 (m, 1H), 7.88 (d, J=8.3 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 20.0, 126.5, 126.6, 127.3, 127.9, 128.4, 132.9, 134.1, 135.9, 136.7, 141.1, 190.5; Anal. calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.37; H, 7.02.

Compound *E*-**95**: ^1H NMR (DMSO-d_6, 400 MHz) δ 2.37 (s, 6H), 7.11–7.15 (m, 3H), 7.40 (d, J=16.1 Hz, 1H), 7.54–7.57 (m, 2H), 7.64–7.68 (m, 1H), 7.83 (d, J=16.1 Hz, 1H), 8.07 (d, J=7.3 Hz, 2H).

The ratio of *Z*- and *E*-isomers was determined by ^{1}H NMR analysis of vinylic proton, δ 7.26 and 7.40.

Acknowledgements

We thank Eisai Co., Ltd., for partial support of this research and financial support to K. Y. This work was also financially supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science. The mass spectra were measured by Prof. Osamu Hara and Dr. Daiki Furuta of Meijo University, to whom the authors' thanks are due.

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