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Synthesis of of sterically encumbered biaryls based on a 'copper(I)-catalyzed arylation/[3+3] cyclocondensation' strategy

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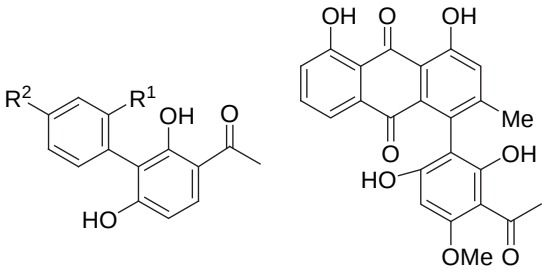
ABSTRACT

Sterically encumbered biaryls are prepared in two steps by combination of the CuI–proline-catalyzed arylation of acetylacetone with formal [3+3] cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-dienes. In addition, the synthesis of 4,6- and 5,6-diarylsalicylates based on [3+3] cyclizations is reported.

1. Introduction

Sterically encumbered and functionalized biaryls are of considerable pharmacological relevance and are present in various natural products.[1] Examples include simple structures, such as the anti-cancer agent cynandione A (Scheme 1).



Scheme 1. Structure of cynandion A and knipholone.

The substructure of hydroxylated biaryls is also present in naturally occurring flavones (e.g., 2,3-dihydroamentoflavone, bartramiaflavone, robustaflavone, dichamanetin), dibenzofurans (e.g., anastatin A), 3-alkyl-4-arylnaphth-1-ols (e.g., picropodophyllone), naphthalene-type isoquinolines, flavidines, anthraquinones (e.g., knipholone, 6′-*O*-methylknipholone or (+)-asphodelin), and bixanthenes (e.g., secalonic acid A or globulixanthone E).

A classic approach to sterically encumbered biaryls is based on reactions of diazonium salts. However, this method is not generally applicable.[2] Biaryls have been widely prepared by palladium(0)-catalyzed cross-coupling reactions.[3] Despite their great synthetic utility, the application of these methods to the synthesis of sterically encumbered and functionalized products can be a difficult task. Early methods required the use of toxic reagents, such as Tl compounds.[4] In recent years, a number of new ligands and reaction conditions have been developed, which allow to prepare sterically encumbered biaryls, such as 2,6-di-, 2,2′,6-tri- and 2,2′,6,6′-tetra-substituted biaryls. This includes Suzuki–Miyaura and Stille reactions.[5] Recently, efficient methods for CH activation have also been reported.[6] While the palladium-catalyzed C–C coupling reactions nowadays proceed in good and under relatively mild conditions, the most important limitation is related to the synthesis of the required starting materials. In fact, the synthesis of highly

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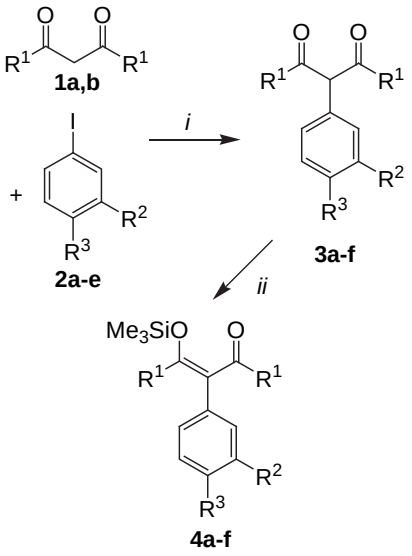
substituted and functionalized aryl halides, aryl triflates, stannanes, and boronic acids can be a difficult and time-consuming task.

An alternative approach to sterically encumbered and highly functionalized arenes relies on the application of a building block strategy. A number of applications have been reported.[7] In recent years, we have studied, based on work of Chan et al.,[8] the synthesis of various arenes by formal [3+3] cyclizations[9] of 1,3-bis-(trimethylsilyloxy)-1,3-dienes.[10] Recently, we have reported the synthesis of 3-arylsalicylates based on cyclization reactions of 4-aryl-1,3-bis(silyloxy)-1,3-butadienes with various 1,3-dielectrophiles.[11] We have also reported preliminary findings related to the synthesis of sterically encumbered 5-arylsalicylates by combination of a CuI–proline-catalyzed arylation with [3+3] cyclizations.[12] Herein, we report a comprehensive account related to the scope of this methodology. The sterically encumbered and functionalized biaryls reported herein, 5-arylsalicylates and 4,6-diarylsalicylates, have, to the best of our knowledge, not been previously prepared. Their synthesis by direct palladium-catalyzed coupling reactions would be extremely difficult, because the required salicylate-derived aryl halides or triflates are not readily available.

2. Results and discussion

The CuI–proline-catalyzed arylation[13] of 1,3-diketones **1a**,**b** with aryl iodides **2a**–**e**, following conditions reported by He et al.,[14] afforded the 2-aryl-1,3-diketones **3a**–**f** in 65–83% yield (Scheme 2, Table 1). The silylation of **3a**–**f** afforded the 3-silyloxy-2-en-1-ones **4a**–**f**.



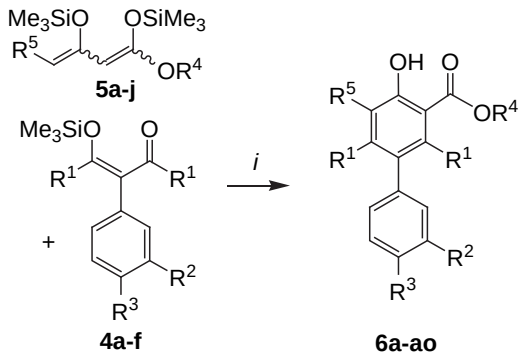
Scheme 2. Synthesis of **4a**–**f**: (i) K_2CO_3, CuI 10 mol %, L-proline 20 mol %, DMSO, 90 °C, 6–12 h; (ii) Me_3SiCl, NEt_3, C_6H_6, 20 °C, 72 h.

Table 1
Synthesis of **4a**–**f**

1	2	3,4	R^1	R^2	R^3	% (**3**)[a]	% (**4**)[a]
a	**a**	**a**	Me	H	H	76	90
b	**a**	**b**	Et	H	H	74	90
a	**b**	**c**	Me	H	Me	82	88
a	**c**	**d**	Me	H	*n*-Bu	83	85
a	**d**	**e**	Me	H	CO_2Et	72	80
a	**e**	**f**	Me	CF_3	H	65	86

[a] Yields of isolated products.

The $TiCl_4$-mediated formal [3+3] cyclocondensation of 2-aryl-3-silyloxy-2-en-1-ones **4a**–**f** with 1,3-bis(silyloxy)-1,3-dienes **5a**–**j**, readily available in two steps from the corresponding β-ketoesters,[10] afforded the biaryls **6a**–**ao** (Scheme 3, Table 2). During the optimization, it proved to be important to carry out the reactions in a highly concentrated solution. The reaction of **4a** with 1,3-bis-(silyloxy)-1,3-butadienes derived from 1,3-diketones (e.g., acetylacetone or benzoylacetone) proved to be unsuccessful. This can be explained by the lower reactivity of dienes derived from 1,3-diketones compared to those derived from β-ketoesters. The Cu-catalyzed arylation of $Ph(CO)CH_2(CO)CF_3$, $Ph(CO)CH_2(CO)CH_3$, $Ph(CO)CH_2(CO)CH_3$, $Ph(CO)CH_2(CO)Ph$, and $CF_3(CO)CH_2(CO)CH_3$ failed.



Scheme 3. Synthesis of **6a**–**s**: (i) $TiCl_4$, CH_2Cl_2, −78 °C→20 °C, 20 h.

Table 2
Synthesis of biaryls **6a**–**ao**

4	5	6	R^1	R^2	R^3	R^4	R^5	% (**6**)[a]
a	**a**	**a**	Me	H	H	Me	H	61
a	**b**	**b**	Me	H	H	Et	H	40
a	**c**	**c**	Me	H	H	CH_2Ph	H	35
a	**d**	**d**	Me	H	H	Me	Me	48
a	**e**	**e**	Me	H	H	Me	Et	53
a	**f**	**f**	Me	H	H	Me	$(CH_2)_2Ph$	38
a	**g**	**g**	Me	H	H	Me	*n*-Pent	50
a	**h**	**h**	Me	H	H	Me	*n*-Hex	46
a	**i**	**i**	Me	H	H	Me	$(CH_2)_2$ $CH{=}CH_2$	48
a	**j**	**j**	Me	H	H	Me	Cl	37
b	**a**	**k**	Et	H	H	Me	H	55
b	**b**	**l**	Et	H	H	Et	H	43
b	**c**	**m**	Et	H	H	CH_2Ph	H	36
c	**a**	**n**	Me	H	Me	Me	H	54
c	**b**	**o**	Me	H	Me	Et	H	40
c	**d**	**p**	Me	H	Me	Me	Me	41
c	**e**	**q**	Me	H	Me	Me	Et	46
c	**f**	**r**	Me	H	Me	Me	$(CH_2)_2Ph$	36
c	**h**	**s**	Me	H	Me	Me	*n*-Hex	42
d	**a**	**t**	Me	H	*n*-Bu	Me	H	52
d	**b**	**u**	Me	H	*n*-Bu	Et	H	45
d	**c**	**v**	Me	H	*n*-Bu	CH_2Ph	H	38
d	**d**	**w**	Me	H	*n*-Bu	Me	Me	58
d	**e**	**x**	Me	H	*n*-Bu	Me	Et	55
d	**f**	**y**	Me	H	*n*-Bu	Me	$(CH_2)_2Ph$	37
d	**h**	**z**	Me	H	*n*-Bu	Me	nHex	48
d	**k**	**aa**	Me	H	*n*-Bu	Me	*n*-Non	42
d	**l**	**ab**	Me	H	*n*-Bu	Me	Allyl	55
d	**i**	**ac**	Me	H	*n*-Bu	Me	$(CH_2)_2$ $CH{=}CH_2$	53
d	**j**	**ad**	Me	H	*n*-Bu	Me	Cl	35
e	**a**	**ae**	Me	H	CO_2Et	Me	H	60
e	**b**	**af**	Me	H	CO_2Et	Et	H	45
e	**d**	**ag**	Me	H	CO_2Et	Me	Me	43
e	**f**	**ah**	Me	H	CO_2Et	Me	$(CH_2)_2Ph$	35
f	**a**	**ai**	Me	CF_3	H	Me	H	43
f	**b**	**aj**	Me	CF_3	H	Et	H	35
f	**m**	**ak**	Me	CF_3	H	Et	Me	37
f	**e**	**al**	Me	CF_3	H	Me	Et	47
f	**h**	**am**	Me	CF_3	H	Me	*n*-Hex	43
f	**i**	**an**	Me	CF_3	H	Me	$(CH_2)_2$ $CH{=}CH_2$	44
f	**j**	**ao**	Me	CF_3	H	Me	Cl	32

[a] Isolated yields.

The nature of the aryl group of enones **4** has a small influence on the yield of the cyclization reactions. Relatively low yields were obtained for reactions of trifluoromethyl-substituted enone **4f**. The reactions proved to be successful for enones containing both electron-donating and electron-withdrawing substituents located at the aryl group. The application of the methodology to the synthesis of 2,2′,6-tri- and 2,2′,6,6′-tetra-substituted biaryls could not be realized because of the failure of the synthesis of the required enones **3**.

The substitution pattern of dienes **5** has a strong influence on the yields. The best yields were obtained for products derived from non-substituted diene **5a**, which is derived from methyl acetoacetate. In contrast, the yields of the products prepared from **5c**, which is derived from benzyl acetoacetate, were relatively low. This might be explained by cleavage of the benzyl ester moiety by $TiCl_4$. Surprisingly, the yields of the products derived from **5b**, derived from ethyl acetoacetate, were generally lower than the yields of the products derived from **5a**. Since both dienes are structurally closely related, this result indicates that the individual quality of the diene and reagents employed also have a strong influence. The dienes electrophiles must be pure (best results were obtained with distilled material). No polymeric impurities or mono-silyl enol ether must be contained in fractions of the dienes employed. The $TiCl_4$ employed must not be old. In addition, practical problems during the chromatographic purification play an important role. The yields of the products derived from 4-substituted dienes are often slightly lower than the yields of the products derived from **5a**. However, no clear trend is observed.

The structures of **6y** and **6ai** were independently confirmed by X-ray crystal structure analyses (Figs. 1 and 2).[15] The two aryl moieties are twisted out of plane. An intramolecular hydrogen bond O–H···O is present in all structures.

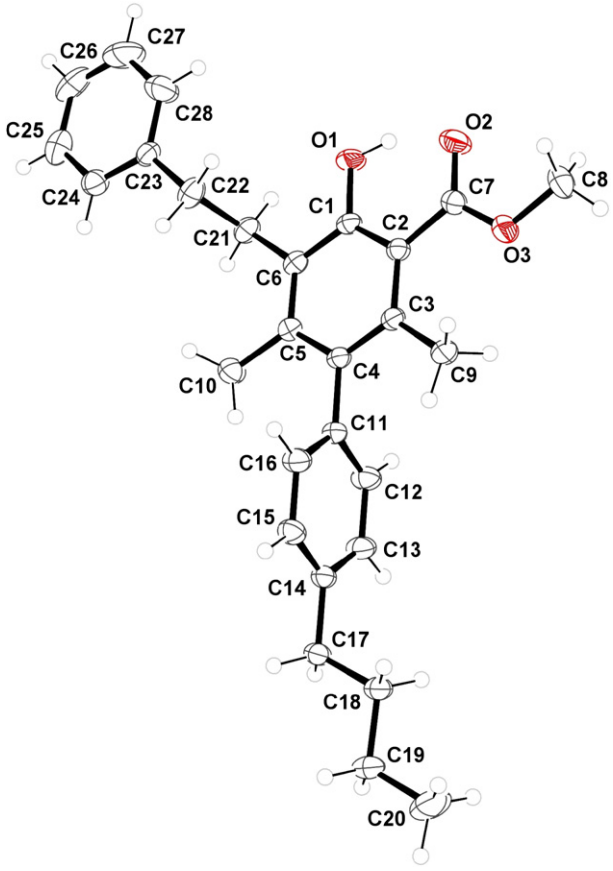


Figure 1. Ortep plot of **6y** (50% probability level).

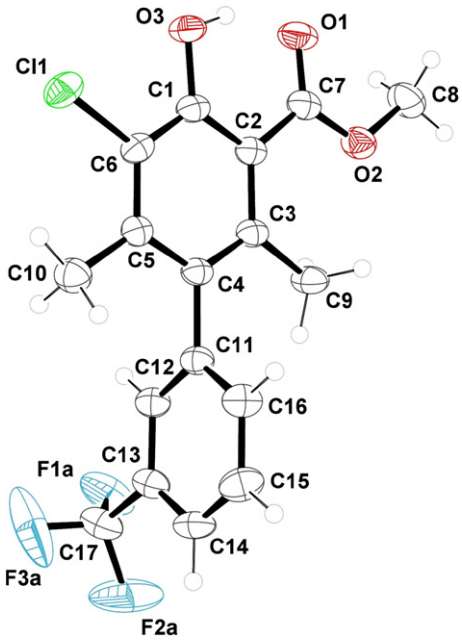
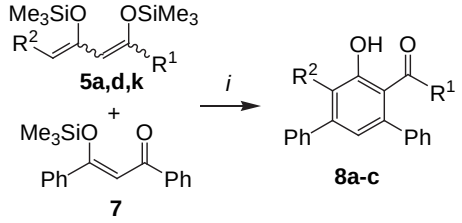


Figure 2. Ortep plot of **6ai** (50% probability level).

We have earlier reported the synthesis of 6-arylsalicylates by cyclization of 1,3-bis(silyloxy)-1,3-butadienes with 1-aryl-1-silyloxy-alk-1-en-3-ones.[9] 3-Silyloxy-2-en-1-one **7** was prepared by silylation of commercially available dibenzoylmethane. The $TiCl_4$-mediated cyclization of **7** with **5a**,**d**,**k** afforded the novel 4,6-diarylsalicylates **8a**–**c** (Scheme 4, Table 3).

The reaction of **9** with triethyl chloroformiate afforded enone **10** (Scheme 5).

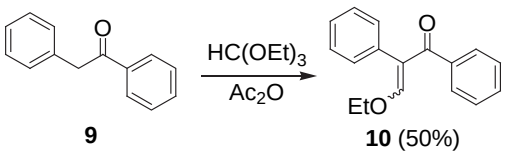


Scheme 4. Synthesis of **8a**–**c**: (i) (1) $TiCl_4$, CH_2Cl_2, −78 °C→20 °C, 20 h; (2) 10% HCl, H_2O.

Table 3
Synthesis of **8a**–**c**

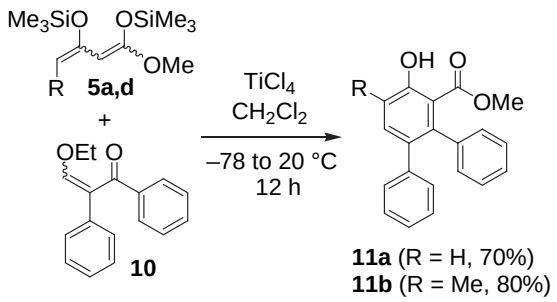
5	8	R^1	R^2	% (**8**)[a]
a	**a**	MeO	H	40
k	**b**	Me	H	41
d	**c**	MeO	Me	37

[a] Yields of isolated products.



Scheme 5. Synthesis of **10**.

The $TiCl_4$-mediated cyclization of **10** with 1,3-bis(silyloxy)-1,3-butadienes **5a**,**d** afforded the novel 5,6-diarylsalicylates **11a**,**b** (Scheme 6). The structure of **11b** was independently confirmed by X-ray crystal structure analysis (Fig. 3).



Scheme 6. Synthesis of **11a**,**b**.

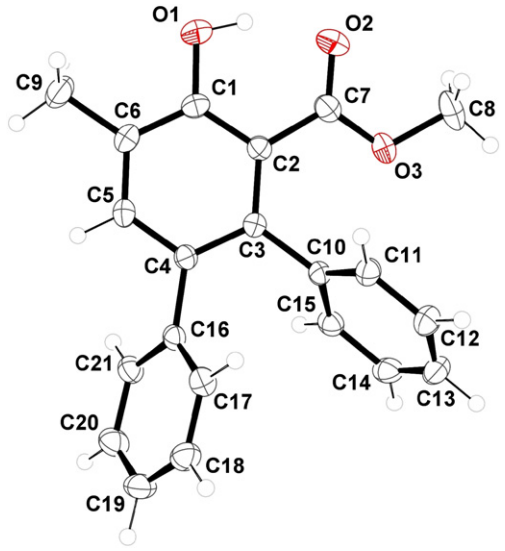


Figure 3. Ortep plot of **11b** (50% probability level).

In conclusion, a variety of functionalized and sterically encumbered biaryls were prepared by combination of CuI–proline-catalyzed arylations of 1,3-diketones and formal [3+3] cyclization reactions. In addition, we have reported the synthesis of 4,6- and 5,6-diarylsalicylates based on [3+3] cyclizations. The products are not readily available by other methods.

3. Experimental section

3.1. General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative scale chromatography silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used. The melting points given are uncorrected.

3.2. Typical procedure for the synthesis of 2-aryl-1,3-diones (3a–f)

A DMSO solution (2 mL) of **1a**,**b** (1.5 mmol), **2a**–**e** (0.5 mmol), K_2CO_3 (2.0 mmol), CuI (0.05 mmol), L-proline (1.0 mmol) was stirred at 90–120 °C under argon atmosphere for 6–12 h. The cooled solution was poured into 1.0 M HCl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography (silica gel, heptanes/EtOAc) to afford **3a**–**f**. All products mainly reside in their enol tautomeric form.

*3.2.1. 3-Phenylpentane-2,4-dione (**3a**).* Starting with **1a** (7.7 mL, 75.0 mmol), **2a** (2.7 mL, 25.0 mmol), K_2CO_3 (13.8 g, 100.0 mmol), CuI (0.47 g, 10 mol %), L-proline (0.57 g, 20 mol %), and 100 mL of DMSO (heating for 6 h at 90 °C), **3a** was obtained as a pale yellow oil (3.18 g, 76%). ^{1}H NMR (300 MHz, $CDCl_3$, enol): δ=1.93 (s, 6H, CH_3), 6.99 (br d, 2H, J=6.8 Hz, H_{Ar}), 7.23–7.34 (m, 3H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.3 (CH_3), 114.3 (C, enol form), 125.5 (CH_{Ph}), 127.3 ($2CH_{Ph}$), 128.8 ($2CH_{Ph}$), 134.2 (C_{Ar}), 190.8 (C=O).

*3.2.2. 4-Phenylheptane-3,5-dione (**3b**).* Starting with **1b** (1.25 mL, 11.25 mmol), **2a** (4.58 mL, 23.81 mmol), K_2CO_3 (6.23 g, 45.08 mmol), CuI (0.257 g, 12 mol %), L-proline (0.324 g, 25 mol %) in 45 mL of DMSO (heating for 8 h at 100 °C), **3b** was obtained as a slightly brownish oil (1.70 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$, enol): δ=1.01 (t, 6H, J=7.3 Hz, CH_3), 2.11 (q, 4H, J=7.3 Hz, CH_2), 7.16–7.32 (m, 5H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=9.6 (CH_3), 29.9 (CH_2), 113.9 (C, enol form), 127.4 (CH_{Ar}), 128.8 ($2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 136.5 (C_{Ar}), 194.1 (C=O).

*3.2.3. 3-p-Tolylpentane-2,4-dione (**3c**).* Starting with **1a** (7.7 mL, 75.0 mmol), **2b** (5.4 g, 25.0 mmol), K_2CO_3 (13.8 g, 100.0 mmol), CuI (0.47 g, 10 mol %), L-proline (0.57 g, 20 mol %) in 100 mL of DMSO (heating for 9 h at 90 °C), **3c** was obtained as a colorless solid (3.86 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$, enol): δ=1.99 (s, 6H, CH_3), 7.08 (br d, 2H, J=7.7 Hz, H_{Ar}), 7.17 (br d, 2H, J=7.7 Hz, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.7, 24.2 (CH_3), 114.7 (C, enol form), 129.2 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 135.1, 136.2 (C_{Ar}), 191.4 (C=O).

*3.2.4. 3-(4-Butylphenyl)pentane-2,4-dione (**3d**).* Starting with **1a** (9.4 mL, 92.22 mmol), **2c** (5.1 mL, 30.75 mmol), K_2CO_3 (17.04 g, 123.03 mmol), CuI (0.585 g, 10 mol %), L-proline (0.708 g, 20 mol %) in 123 mL of DMSO (heating for 10 h at 120 °C), **3d** was obtained as a viscous yellowish oil (5.93 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$, enol): δ=0.88 (t, 3H, J=7.1 Hz, CH_3), 1.31 (sextet, 2H, J=7.2 Hz, CH_2), 1.58 (quintet, 2H, J=7.8 Hz, CH_2), 1.91 (s, 6H, CH_3), 2.58 (t, 2H, J=7.6 Hz, CH_2), 6.85 (d, 2H, J=8.2 Hz, H_{Ar}), 7.11 (d, 2H, J=8.2 Hz, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9 (CH_3), 22.4 (CH_2), 24.1 (CH_3), 33.5, 35.3 (CH_2), 115.0 (C, enol form), 128.7 ($2CH_{Ar}$), 130.8 ($2CH_{Ar}$), 134.0, 142.1 (C_{Ar}), 191.0 (C=O).

*3.2.5. Ethyl 4-(2,4-dioxopentan-3-yl)benzoate (**3e**).* Starting with **1a** (3.9 mL, 38.0 mmol), **2d** (2.1 mL, 12.6 mmol), K_2CO_3 (7.0 g, 50.5 mmol), CuI (0.24 g, 10 mol %), L-proline (0.29 g, 20 mol %) in 50 mL of DMSO heating for 12 h at 120 °C, **3e** was obtained as a white solid (2.26 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.41 (t, 3H, J=7.1 Hz, CH_3), 1.89 (s, 6H, CH_3), 4.38 (q, 2H, J=7.1 Hz, OCH_2), 7.26 (d, 2H, J=8.4 Hz, H_{Ar}), 8.12 (d, 2H, J=8.4 Hz, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.3, 24.1 (CH_3), 61.1 (OCH_2), 114.5 (C, enol form), 129.8 (C_{Ar}), 130.0 ($2CH_{Ar}$), 131.2 ($2CH_{Ar}$), 141.7 (C_{Ar}), 166.2, 190.6 (C=O).

*3.2.6. 3-(3-(Trifluoromethyl)phenyl)pentane-2,4-dione (**3f**).* Starting with **1a** (7.7 mL, 75.0 mmol), **2e** (3.6 mL, 25.0 mmol), K_2CO_3 (13.8 g, 100.0 mmol), CuI (0.47 g, 10 mol %), L-proline (0.57 g, 20 mol %) in 100 mL of DMSO (heating for 10 h at 90 °C), **3f** was obtained as a brown viscous oil (3.96 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.93 (s, 6H, CH_3), 7.20 (br d, 1H, J=6.7 Hz, H_{Ar}), 7.28 (br s, 1H, H_{Ar}), 7.44 (br t, 1H, J=6.7, 7.2 Hz, H_{Ar}), 7.55 (br d, 1H, J=7.2 Hz, H_{Ar}); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.1 (CH_3), 114.5 (C, enol form), 123.0 ($J_{C,F}$=271 Hz, C_{CF3}), 123.4 ($J_{C,F}$=3.6 Hz, CH_{Ar}), 126.8 ($J_{C,F}$=3.8 Hz), 128.4 (CH_{Ar}), 130.3 ($J_{C,F}$=31.7 Hz, C_{Ar}), 133.5 ($J_{C,F}$=1.6 Hz, CH_{Ar}), 135.5 (C_{Ar}), 190.4 (C=O).

3.3. General procedure for the synthesis of silyl enol ethers (4a–f)

To a stirred benzene solution (2.5 mL per 1.0 mmol of **3a**–**f**) of **3a**–**f** (1.0 equiv) was added triethylamine (1.6 equiv). After stirring

for 2 h, trimethylchlorosilane (1.8 equiv) was added. The solution was stirred for 72 h and, subsequently, the solvent was removed in vacuo and hexane (1.5 mL per 1.0 mmol of starting material) was added to the residue to give a suspension. The latter was filtered under argon atmosphere. The filtrate was concentrated in vacuo to give silyl enol ethers **4a**–**f**, which were used without further purification. Due to the unstable nature of the products, MS and analytical data could not be obtained. All products were obtained as mixtures of *E*/*Z*-isomers.

*3.3.1. 3-Phenyl-4-(trimethylsilyloxy)pent-3-en-2-one (**4a**).* Starting with benzene (42.5 mL), **3a** (3.0 g, 17.02 mmol), triethylamine (3.2 mL, 27.2 mmol), and trimethylchlorosilane (4.5 mL, 30.6 mmol), **4a** was isolated as a yellowish oil (3.80 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.21 (s, 9H, Si[CH_3]$_3$), 2.00 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 6.99 (br d, 2H, ^3J=6.8 Hz, H_{Ar}), 7.23–7.34 (m, 3H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.4 (Si[CH_3]$_3$), 21.7, 23.7 (CH_3), 114.6 (=C), 125.5 (CH_{Ph}), 127.3 (2CH_{Ph}), 128.8 (2CH_{Ph}), 134.2 (C_{Ar}), 186.1 (COSi), 191.2 (C=O).

*3.3.2. 4-Phenyl-5-(trimethylsilyloxy)hept-4-en-3-one (**4b**).* Starting with benzene (18 mL), **3b** (1.46 g, 7.2 mmol), triethylamine (1.36 mL, 11.4 mmol), and trimethylchlorosilane (1.92 mL, 12.9 mmol), **4b** was isolated as a brownish oil (1.78 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.18 (s, 9H, Si[CH_3]$_3$), 1.06 (t, 3H, J=7.4 Hz, CH_3), 1.11 (t, 3H, J=7.3 Hz, CH_3), 2.14 (q, 2H, J=7.4 Hz, CH_2), 2.56 (q, 2H, J=7.3 Hz, CH_2), 7.16–7.32 (m, 5H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3 (Si[CH_3]$_3$), 9.6, 9.8 (CH_3), 29.2, 30.2 (CH_2), 113.3 (=C), 127.5 (CH_{Ph}), 128.8 (2CH_{Ph}), 129.4 (2CH_{Ph}), 136.6 (C_{Ar}), 186.8 (COSi), 193.8 (C=O).

*3.3.3. 3-p-Tolyl-4-(trimethylsilyloxy)pent-3-en-2-one (**4c**).* Starting with benzene (31.5 mL), **3c** (2.4 g, 12.6 mmol), triethylamine (2.4 mL, 20.1 mmol), and trimethylchlorosilane (3.38 mL, 22.7 mmol), **4c** was isolated as a slight yellowish oil (2.9 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.21 (s, 9H, Si[CH_3]$_3$), 1.93 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 7.08 (br d, 2H, J=7.7 Hz, H_{Ar}), 7.17 (br d, 2H, J=7.7 Hz, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.4 (Si[CH_3]$_3$), 21.5, 23.8, 24.1 (CH_3), 114.7 (=C), 129.2 (2CH_{Ar}), 129.5 (2CH_{Ar}), 136.3 (C_{Ar}), 186.3 (COSi), 191.0 (C=O).

*3.3.4. 3-(4-Butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one (**4d**).* Starting with benzene (50 mL), **3d** (4.4 g, 18.9 mmol), triethylamine (3.5 mL, 30.2 mmol), and trimethylchlorosilane (5.0 mL, 34.2 mmol), **4d** was isolated as a yellowish oil (4.8 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.21 (s, 9H, Si[CH_3]$_3$), 0.88 (t, 3H, J=7.1 Hz, CH_3), 1.31 (sextet, 2H, J=7.2 Hz, CH_2), 1.58 (quintet, 2H, J=7.8 Hz, CH_2), 1.87 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.58 (t, 2H, J=7.6 Hz, CH_2), 6.85 (d, 2H, J=8.2 Hz, H_{Ar}), 7.11 (d, 2H, J=8.2 Hz, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.4 (Si[CH_3]$_3$), 13.9 (CH_3), 22.4 (CH_2), 23.9, 24.2 (CH_3), 33.5, 35.3 (CH_2), 114.8 (=C), 128.7 (2CH_{Ar}), 130.8 (2CH_{Ar}), 134.0, 142.2 (C_{Ar}), 186.4 (COSi), 191.0 (C=O).

*3.3.5. Ethyl 4-(4-oxo-2-(trimethylsilyloxy)pent-2-en-3-yl)-benzoate (**4e**).* Starting with benzene (21.1 mL), **3e** (2.1 g, 8.45 mmol), triethylamine (1.6 mL, 13.5 mmol), and trimethylchlorosilane (2.2 mL, 15.21 mmol), **4e** was isolated as a colorless oil (2.16 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.21 (s, 9H, Si[CH_3]$_3$), 1.40 (t, 3H, J=7.1 Hz, CH_3), 1.88 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 4.36 (q, 2H, J=7.1 Hz, OCH_2), 7.26 (d, 2H, J=8.4 Hz, H_{Ar}), 8.12 (d, 2H, J=8.4 Hz, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.4 (Si[CH_3]$_3$), 14.3, 23.8, 24.2 (CH_3), 61.1 (OCH_2), 114.7 (=C), 129.8 (C_{Ar}), 130.0 (2CH_{Ar}), 131.2 (2CH_{Ar}), 141.8 (C_{Ar}), 166.3 (C=O), 185.9 (COSi), 190.5 (C=O).

*3.3.6. 3-(3-(Trifluoromethyl)phenyl)-4-(trimethylsilyloxy)-pent-3-en-2-one (**4f**).* Starting with benzene (32.5 mL), **3f** (3.2 g, 13.1 mmol), triethylamine (2.4 mL, 20.9 mmol), and trimethylchlorosilane (3.5 mL, 23.5 mmol), **4f** was isolated as a slight dark brown oil (3.5 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.21 (s, 9H, Si[CH_3]$_3$), 1.93 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 7.21 (br d, 1H, $J_{H,H}$=6.7 Hz, H_{Ar}), 7.29 (br s, 1H, H_{Ar}), 7.45 (br t, 1H, $J_{H,H}$=6.7, 7.2 Hz, H_{Ar}), 7.54 (br d, 1H, $J_{H,H}$=7.2 Hz, H_{Ar}); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.4 (Si[CH_3]$_3$), 21.4, 23.6 (CH_3), 114.3 (=C), 122.9 ($J_{C,F}$=270 Hz, C_{CF3}), 123.4 ($J_{C,F}$=3.6 Hz, CH_{Ar}), 126.8 ($J_{C,F}$=3.8 Hz), 128.5 (CH_{Ar}), 130.4 ($J_{C,F}$=31.8 Hz, C_{Ar}), 133.6 ($J_{C,F}$=1.6 Hz, CH_{Ar}), 135.3 (C_{Ar}), 186.5 (COSi), 191.1 (C=O).

3.4. General procedure for the synthesis of 4-hydroxybiphenyl-3-carboxylates (6a–ao)

To a CH_2Cl_2 solution (2 mL/1.0 mmol of **5**) of **5** (1.0 equiv) was added **4** (1.0 equiv) and subsequently $TiCl_4$ (1.0 equiv) at −78 °C. The temperature of the solution was allowed to warm to 20 °C for 14 h with stirring. To the solution was added a saturated aqueous solution of sodium bicarbonate (10 mL) and the organic and the aqueous layers were separated. The latter was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc) to give product **6**.

*3.4.1. Methyl 4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6a**).* Starting with 1,3-bis(silyl enol ether) **5a** (600 mg, 2.30 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (571 mg, 2.30 mmol), and $TiCl_4$ (0.25 mL, 2.30 mmol), **6a** was obtained as a light yellow solid (360 mg, 61%), mp=80–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.93 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 6.76 (s, 1H, H_{Ar}), 7.05 (br d, 2H, ^3J=7.0 Hz, H_{Ar}), 7.31–7.41 (m, 3H, H_{Ar}), 11.01 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.8, 21.9 (CH_3), 52.1 (OCH_3), 110.8 (C_{Ar}), 116.2 (CH_{Ar}), 126.8 (CH_{Ph}), 128.6 (2CHPh), 129.7 (2CH_{Ph}), 135.2, 138.5, 140.9, 144.0, 161.1 (C_{Ar}), 172.3 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3060, 3004, 2953, 2852 (w), 1655, 1597 (m), 1441 (s), 1356 (m), 1318, 1228 (s), 1092 (m), 990 (w), 881, 810 (m), 701 (s); MS (EI, 70 eV): *m*/*z* (%)=256 (M^+, 77), 225 (61), 224 (100), 196 (40), 181 (10), 167 (18), 165 (14), 153 (17), 152 (22); HRMS (EI): calcd for $C_{16}H_{16}O_3$ $[M]^+$: 256.10940; found: 256.10877.

*3.4.2. Ethyl 4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6b**).* Starting with 1,3-bis(silyl enol ether) **5b** (600 mg, 2.18 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (542 mg, 2.18 mmol), and $TiCl_4$ (0.24 mL, 2.18 mmol), **6b** was obtained as a colorless solid (236 mg, 40%), mp=78–79 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.34 (t, 3H, ^3J=7.0 Hz, CH_3), 1.90 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 4.36 (q, 2H, ^3J=7.0 Hz, OCH_2), 6.73 (s, 1H, H_{Ar}), 7.03 (br d, 2H, ^3J=6.9 Hz, H_{Ar}), 7.28–7.37 (m, 3H, H_{Ar}), 11.06 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.2 (CH_3), 20.9, 21.9 (CH_3), 61.5 (OCH_2), 111.0 (C_{Ar}), 116.2 (CH_{Ar}), 126.8 (CH_{Ph}), 128.6 (2CH_{Ph}), 129.8 (2CH_{Ph}), 135.1, 138.6, 140.9, 143.8, 161.1 (C_{Ar}), 171.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3057, 3005, 2983, 2873 (w), 1648 (s), 1597, 1462, 1371, 1315 (m), 1224, 1091 (s), 1008, 857, 802 (m), 707 (s); MS (EI, 70 eV): *m*/*z* (%)=270 (M^+, 84), 225 (79), 224 (100), 196 (43), 181 (12), 167 (20), 165 (18), 153 (21), 152 (24); HRMS (EI): calcd for $C_{17}H_{18}O_3$ $[M]^+$: 270.12505; found: 270.12507.

*3.4.3. Benzyl 4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6c**).* Starting with 1,3-bis(silyl enol ether) **5c** (600 mg, 1.78 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (442 mg, 1.78 mmol), and $TiCl_4$ (0.19 mL, 1.78 mmol), **6c** was obtained as a light yellow solid (207 mg, 35%), mp=59–60 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.87 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 5.32 (s, 2H, OCH_2), 6.71 (s, 1H, H_{Ar}), 6.98–7.34 (m, 10H, 2Ph), 10.97 (s, 1H, OH); ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.2, 21.9 (CH_3), 67.3 (OCH_2), 110.8 (C_{Ar}), 116.2 (CH_{Ar}), 126.8 (CH_{Ph}), 128.5 (2CH_{Ph}), 128.6 (3CH_{Ph}), 128.7 (2CH_{Ph}), 129.8 (2CH_{Ph}),

135.2, 137.0, 138.7, 140.8, 144.1, 161.2 (C_{Ar}), 171.6 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3059, 2964, 1950, 1879, 1726 (w), 1649 (s), 1595, 1495, 1449 (m), 1375, 1311, 1221 (s), 1153 (m), 1089 (s), 1026, 985, 934, 884, 802 (m), 751, 694 (s), 639, 576 (m); MS (EI, 70 eV): *m*/*z* (%)=332 (M^+, 25), 314 (4), 225 (11), 224 (55), 223 (5), 165 (5), 152 (6), 91 (100), 65 (5); HRMS (EI): calcd for $C_{22}H_{20}O_3$ $[M]^+$: 332.14070; found: 332.14053.

*3.4.4. Methyl 4-hydroxy-2,5,6-trimethylbiphenyl-3-carboxylate (**6d**).* Starting with 1,3-bis(silyl enol ether) **5d** (500 mg, 1.82 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (452 mg, 1.82 mmol), and $TiCl_4$ (0.20 mL, 1.82 mmol), **6d** was obtained as a colorless solid (236 mg, 48%), mp=99–101 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.85 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.98 (br d, 2H, ^3J=6.9 Hz, H_{Ar}), 7.23–7.35 (m, 3H, H_{Ar}), 11.20 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.0, 18.8, 20.9 (CH_3), 52.0 (OCH_3), 110.2 (C_{Ar}), 126.6 (CH_{Ph}), 127.5 (C_{Ar}), 128.5 ($2CH_{Ph}$), 129.9 ($2CH_{Ph}$), 135.1, 136.9, 141.9, 142.2, 159.0 (C_{Ar}), 172.9 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3074, 3020, 2926, 2857 (w), 1652, 1600, 1537, 1403 (m), 1326, 1223 (s), 1141, 1068, 983 (m), 911 (w), 806, 765 (m), 702 (s), 609, 556 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=271 (8), 270 (M^+, 46), 239 (25), 238 (100), 237 (27), 210 (31), 196 (11), 195 (55), 165 (30), 152 (15), 77 (5); HRMS (EI): calcd for $C_{17}H_{18}O_3$ $[M]^+$: 270.12505; found: 270.12488.

*3.4.5. Methyl 5-ethyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6e**).* Starting with 1,3-bis(silyl enol ether) **5e** (600 mg, 2.07 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (514 mg, 2.07 mmol), and $TiCl_4$ (0.22 mL, 2.07 mmol), **6e** was obtained as a colorless solid (312 mg, 53%), mp=125–126 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.07 (t, 3H, ^3J=7.4 Hz, CH_3), 1.87 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.67 (q, 2H, ^3J=7.4 Hz, CH_2), 3.86 (s, 3H, OCH_3), 6.99 (br d, 2H, ^3J=6.8 Hz, H_{Ar}), 7.22–7.34 (m, 3H, H_{Ar}), 11.18 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.2, 16.9 (CH_3), 18.8 (CH_2), 19.8 (CH_3), 50.9 (OCH_3), 109.4 (C_{Ar}), 125.5 (CH_{Ph}), 127.3 (C_{Ar}), 127.4 ($2CH_{Ph}$), 128.8 ($2CH_{Ph}$), 134.0, 134.2, 140.4, 140.9, 157.8 (C_{Ar}), 171.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3072(w), 2971, 2876, 1650, 1599 (m), 1493 (w), 1435, 1364, 1321 (m), 1221 (s), 1142, 1067, 1001, 952 (m), 853 (w), 808, 705 (s), 650, 580 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=284 (M^+, 73), 253 (30), 252 (100), 251 (69), 224 (96), 209 (43), 196 (10), 195 (40), 178 (12), 166 (21), 165 (47), 152 (13); HRMS (EI): calcd for $C_{18}H_{20}O_3$ $[M]^+$: 284.14070; found: 284.140870.

*3.4.6. Methyl 4-hydroxy-2,6-dimethyl-5-phenethylbiphenyl-3-carboxylate (**6f**).* Starting with 1,3-bis(silyl enol ether) **5f** (500 mg, 1.37 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (340 mg, 1.37 mmol), and $TiCl_4$ (0.15 mL, 1.37 mmol), **6f** was obtained as a colorless solid (187 mg, 38%), mp=109–111 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.64 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.63 (t, 2H, ^3J=5.0 Hz, CH_2), 2.78 (t, 2H, ^3J=5.0 Hz, CH_2), 3.78 (s, 3H, OCH_3), 6.84 (br d, 2H, ^3J=6.8 Hz, H_{Ar}), 7.03–7.23 (m, 8H, H_{Ar}), 11.17 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.3, 22.1 (CH_3), 30.3, 36.3 (CH_2), 53.2 (OCH_3), 111.7 (C_{Ar}), 127.0 (CH_{Ph}), 127.2 (C_{Ar}), 127.8 (CH_{Ph}), 129.4 ($2CH_{Ph}$), 129.7 ($2CH_{Ph}$), 129.8 ($2CH_{Ph}$), 131.0 ($2CH_{Ph}$), 136.3, 136.8, 143.0, 143.1, 143.7, 160.4 (C_{Ar}), 174.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3081, 3025, 2950, 2865 (w), 1650, 1596, 1494, 1438 (m), 1325, 1219 (s), 1163, 1082, 1033, 987, 912, 804 (m), 700 (s); MS (EI, 70 eV): *m*/*z* (%)=360 (M^+, 28), 328 (5), 270 (6), 269 (39), 238 (24), 237 (100), 166 (7), 165 (11); HRMS (EI): calcd for $C_{24}H_{24}O_3$ $[M]^+$: 360.17200; found: 360.17109.

*3.4.7. Methyl 4-hydroxy-2,6-dimethyl-5-pentylbiphenyl-3-carboxylate (**6g**).* Starting with 1,3-bis(silyl enol ether) **5g** (700 mg, 2.11 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (524 mg, 2.11 mmol), and $TiCl_4$ (0.23 mL, 2.11 mmol), **6g** was obtained as a light yellow solid (345 mg, 50%), mp=102–104 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.71 (t, 3H, ^3J=7.6 Hz, CH_3), 1.09–1.31 (m, 6H, $3CH_2$), 1.75 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.52 (t, 2H, ^3J=7.4 Hz, CH_2), 3.75 (s, 3H, OCH_3), 6.89 (br d, 2H, ^3J=6.8 Hz, H_{Ar}), 7.13–7.24 (m, 3H, Ph), 11.05 (s, 1H, OH); ^{13}C NMR (62 MHz, $CDCl_3$): δ=15.2, 19.3, 22.0 (CH_3), 23.8, 27.8, 29.9, 33.4 (CH_2), 53.1 (OCH_3), 111.6 (C_{Ar}), 127.7 (CH_{Ph}), 128.4 (C_{Ar}), 129.7 ($2CH_{Ph}$), 131.0 ($2CH_{Ph}$), 136.2, 136.3, 142.8, 143.2, 160.2 (C_{Ar}), 174.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2953(m), 2857, 1933 (w), 1702, 1655, 1595, 1438, 1377, 1326 (m), 1213 (s), 1142, 1048, 1003 (m), 903 (w), 839 (s), 772 (m), 702 (s), 627, 579 (w); GC–MS (EI, 70 eV): *m*/*z* (%)=326 (M^+, 76), 294 (33), 277 (63), 265 (25), 251 (22), 239 (19), 238 (100), 237 (81), 210 (30), 195 (24), 166 (25), 165 (54), 152 (10); HRMS (EI): calcd for $C_{21}H_{26}O_3$ $[M]^+$: 326.18765; found: 326.18798.

*3.4.8. Methyl 5-hexyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6h**).* Starting with 1,3-bis(silyl enol ether) **5h** (500 mg, 1.45 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (360 mg, 1.45 mmol), and $TiCl_4$ (0.16 mL, 1.45 mmol), **6h** was obtained as a light yellowish solid (227 mg, 46%), mp=105–107 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.71 (t, 3H, ^3J=7.1 Hz, CH_3), 1.09–1.34 (m, 8H, $4CH_2$), 1.75 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.52 (t, 2H, ^3J=7.2 Hz, CH_2), 3.75 (s, 3H, OCH_3), 6.89 (br d, 2H, ^3J=6.8 Hz, H_{Ar}), 7.12–7.25 (m, 3H, Ph), 11.06 (s, 1H, OH); ^{13}C NMR (62 MHz, $CDCl_3$): δ=15.3, 19.3, 22.0 (CH_3), 23.8, 27.8, 30.2, 30.9, 32.9 (CH_2), 53.1 (OCH_3), 111.5 (C_{Ar}), 127.7 (CH_{Ph}), 128.4 (C_{Ar}), 129.6 ($2CH_{Ph}$), 131.0 ($2CH_{Ph}$), 136.2, 136.3, 142.7, 143.2, 160.2 (C_{Ar}), 174.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2955(m), 2852 (w), 1652, 1597, 1537, 1405 (m), 1328, 1217 (s), 1141, 1065 (m), 983 (m), 903 (w), 835 (s), 770 (m), 702 (s), 609, 556 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=340 (M^+, 65), 308 (30), 293 (43), 291 (53), 279 (33), 265 (25), 251 (20), 239 (20), 238 (100), 237 (76), 210 (26), 195 (21), 165 (43), 152 (9); HRMS (EI): calcd for $C_{22}H_{28}O_3$ $[M]^+$: 340.20330; found: 340.20341.

*3.4.9. Methyl5-(but-3-enyl)-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6i**).* Starting with 1,3-bis(silyl enol ether) **5i** (600 mg, 1.90 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (472 mg, 1.90 mmol), and $TiCl_4$ (0.20 mL, 1.90 mmol), **6i** was obtained as a light yellowish solid (283 mg, 48%), mp=112–114 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.76 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.07–2.13 (m, 2H, CH_2), 2.63 (t, 2H, ^3J=7.8 Hz, CH_2), 3.78 (s, 3H, OCH_3), 4.77–4.92 (m, 2H, $=CH_2$), 5.69–5.83 (m, 1H, =CH), 6.89 (d, 2H, ^3J=6.8 Hz, H_{Ar}), 7.11–7.25 (m, 3H, Ph), 11.09 (s, 1H, OH); ^{13}C NMR (62 MHz, $CDCl_3$): δ=19.4, 22.0 (CH_3), 27.4, 34.2 (CH_2), 53.2 (OCH_3), 111.6 (C_{Ar}), 115.6 ($=CH_2$), 127.7 (CH_{Ph}), 128.6 (C_{Ar}), 129.7 ($2CH_{Ph}$), 131.0 ($2CH_{Ph}$), 136.3, 136.7 (C_{Ar}), 139.9 (=CH), 142.9, 143.1, 160.2 (C_{Ar}), 174.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3057, 2952 (w), 1708, 1651, 1597, 1493, 1404, 1325 (m), 1215 (s), 1142, 1071, 1000, 908, 763, 763 (m), 701 (s), 609, 555 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=310 (M^+, 11), 270 (5), 269 (24), 238 (17), 237 (100), 166 (9), 165 (18), 152 (3); HRMS (EI): calcd for $C_{20}H_{22}O_3$ $[M]^+$: 310.15635; found: 310.15668.

*3.4.10. Methyl 5-chloro-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6j**).* Starting with 1,3-bis(silyl enol ether) **5j** (600 mg, 2.03 mmol), 3-phenyl-4-(trimethylsilyloxy)pent-3-en-2-one **4a** (504 mg, 2.03 mmol), and $TiCl_4$ (0.22 mL, 2.03 mmol), **6j** was obtained as a colorless solid (218 mg, 37%), mp=98–99 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=2.07 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 3.97 (s, 3H, OCH_3), 7.06 (d, 2H, ^3J=6.9 Hz, H_{Ar}), 7.32–7.43 (m, 3H, H_{Ar}), 11.40 (s, 1H, OH); ^{13}C NMR (62 MHz, $CDCl_3$): δ=19.4, 20.7 (CH_3), 52.5 (OCH_3), 115.2 (C_{Ar}), 127.4 (CH_{Ph}), 128.7 (C_{Ar}), 129.6 ($2CH_{Ph}$), 131.0 ($2CH_{Ph}$), 136.4, 136.9, 140.6, 141.4, 156.1 (C_{Ar}), 171.9 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3023(m), 2958, 2851, 1731 (w), 1657 (s), 1595, 1493, 1437 (m), 1363 (s), 1285 (m), 1225 (s), 1072, 995 (m), 910 (w), 804 (s), 736 (m), 702 (s), 602, 558 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=292 (M^+, ^{37}Cl, 8), 290 (M^+, ^{35}Cl, 22), 260 (36), 259 (25), 258 (100), 167 (9), 166 (7), 165

(17), 152 (13); HRMS (EI): calcd for $C_{16}H_{15}ClO_3$ $[M]^+$: 290.07042; found: 290.07071.

*3.4.11. Methyl 2,6-diethyl-4-hydroxybiphenyl-3-carboxylate (**6k**).* Starting with 1,3-bis(silyl enol ether) **5a** (500 mg, 1.91 mmol), 4-phenyl-5-(trimethylsilyloxy)hept-4-en-3-one **4b** (528 mg, 1.91 mmol), and $TiCl_4$ (0.21 mL, 1.91 mmol), **6k** was obtained as a colorless crystalline solid (298 mg, 55%), mp=88–90 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.84 (t, 3H, ^3J=7.4 Hz, CH_3), 0.93 (t, 3H, ^3J=7.5 Hz, CH_3), 2.13 (q, 2H, ^3J=7.5 Hz, CH_2), 2.57 (q, 2H, ^3J=7.4 Hz, CH_2), 4.36 (s, 3H, OCH_3), 6.74 (s, 1H, H_{Ar}), 7.05 (d, 2H, ^3J=7.8 Hz, H_{Ar}), 7.27–7.35 (m, 3H, H_{Ar}), 10.92 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.4, 15.8 (CH_3), 25.7, 27.9 (CH_2), 52.1 (OCH_3), 109.9 (C_{Ar}), 114.7 (CH_{Ar}), 126.7 (CH_{Ph}), 128.1 ($2CH_{Ph}$), 130.1 ($2CH_{Ph}$), 134.3, 140.1, 144.8, 150.1, 161.5 (C_{Ar}), 172.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3058(w), 2975 (m), 2874 (w), 1650, 1596 (m), 1487 (w), 1430, 1369, 1315, 1245 (m), 1214 (s), 1174, 1088, 1035, 967, 883, 810, 766 (m), 705 (s), 643, 574 (m); EIMS (EI, 70 eV): *m*/*z* (%)=284 (M^+, 27), 253 (21), 252 (100), 209 (18), 195 (4), 181 (5), 166 (8), 165 (14), 152 (7); HRMS (EI): calcd for $C_{18}H_{20}O_3$ $[M]^+$: 284.14070; found: 284.14064.

*3.4.12. Ethyl 2,6-diethyl-4-hydroxybiphenyl-3-carboxylate (**6l**).* Starting with 1,3-bis(silyl enol ether) **5b** (600 mg, 2.18 mmol), 4-phenyl-5-(trimethylsilyloxy)hept-4-en-3-one **4b** (603 mg, 2.18 mmol), and $TiCl_4$ (0.24 mL, 2.18 mmol), **6l** was obtained as a colorless crystalline solid (280 mg, 43%), mp=102–103 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.86 (t, 3H, ^3J=7.4 Hz, CH_3), 0.93 (t, 3H, ^3J=7.5 Hz, CH_3), 1.33 (t, 3H, ^3J=7.2 Hz, CH_3), 2.12 (q, 2H, ^3J=7.5 Hz, CH_2), 2.60 (q, 2H, ^3J=7.4 Hz, CH_2), 4.36 (q, 2H, ^3J=7.2 Hz, OCH_2), 6.73 (s, 1H, H_{Ar}), 7.05 (d, 2H, ^3J=7.8 Hz, H_{Ar}), 7.24–7.35 (m, 3H, H_{Ar}), 11.04 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 14.5, 15.9 (CH_3), 25.7, 27.5 (CH_2), 61.5 (OCH_2), 110.0 (C_{Ar}), 114.7 (CH_{Ar}), 126.7 (CH_{Ph}), 128.1 ($2CH_{Ph}$), 130.1 ($2CH_{Ph}$), 134.2, 140.1, 144.8, 150.0, 161.6 (C_{Ar}), 171.6 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055(w), 2974, 2873, 1644, 1594 (m), 1488 (w), 1439, 1371, 1311 (m), 1215 (s), 1088, 1012, 956, 874, 808 (m), 708 (s), 651, 573 (m); MS (EI, 70 eV): *m*/*z* (%)=298 (M^+, 24), 253 (22), 252 (100), 209 (15), 195 (4), 166 (7), 165 (13),152 (6); HRMS (EI): calcd for $C_{19}H_{22}O_3$ $[M]^+$: 298.15635; found: 298.15641.

*3.4.13. Benzyl 2,6-diethyl-4-hydroxybiphenyl-3-carboxylate (**6m**).* Starting with 1,3-bis(silyl enol ether) **5c** (600 mg, 1.78 mmol), 4-phenyl-5-(trimethylsilyloxy)hept-4-en-3-one **4b** (492 mg, 1.78 mmol), and $TiCl_4$ (0.19 mL, 1.78 mmol), **6m** was obtained as a colorless crystalline solid (231 mg, 36%), mp=65–66 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.72 (t, 3H, ^3J=7.4 Hz, CH_3), 0.89 (t, 3H, ^3J=7.5 Hz, CH_3), 2.09 (q, 2H, ^3J=7.5 Hz, CH_2), 2.54 (q, 2H, ^3J=7.4 Hz, CH_2), 5.29 (s, 2H, OCH_2), 6.72 (s, 1H, H_{Ar}), 6.99–7.31 (m, 10H, 2Ph), 10.93 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.5, 16.0 (CH_3), 25.6, 27.5 (CH_2), 67.6 (OCH_2), 109.9 (C_{Ar}), 114.7 (CH_{Ar}), 126.7 (CH_{Ph}), 128.1 ($2CH_{Ph}$), 128.6 ($2CH_{Ph}$), 128.7 (CH_{Ph}), 128.8 ($2CH_{Ph}$), 130.1 ($2CH_{Ph}$), 134.3, 134.9, 140.1, 144.9, 150.2, 161.7 (C_{Ar}), 171.4 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3027(w), 2965, 2878 (m), 1705 (w), 1644 (s), 1594, 1494, 1439, 1378 (m), 1311 (s), 1254 (m), 1212 (s), 1174, 1087, 1035, 959, 880, 807 (m), 748, 705 (s), 654, 573 (m); MS (EI, 70 eV): *m*/*z* (%)=361 (10), 360 (M^+, 46), 342 (11), 269 (22), 253 (26), 252 (100), 251 (31), 165 (6), 152 (4), 91 (82), 29 (5); HRMS (EI): calcd for $C_{24}H_{22}O_3$ $[M]^+$: 360.17200; found: 360.17292.

*3.4.14. Methyl 4-hydroxy-2,4′,6-trimethylbiphenyl-3-carboxylate (**6n**).* Starting with 1,3-bis(silyl enol ether) **5a** (600 mg, 2.30 mmol), 3-*p*-tolyl-4-(trimethylsilyloxy)pent-3-en-2-one **4c** (603 mg, 2.30 mmol), and $TiCl_4$ (0.25 mL, 2.30 mmol), **6n** was obtained as white solid (335 mg, 54%), mp=112–114 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.98 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.96 (s, 3H, OCH_3), 6.79 (s, 1H, H_{Ar}), 6.97 (br d, 2H, ^3J=8.1 Hz, H_{Ar}), 7.21 (br d, 2H, ^3J=8.1 Hz, H_{Ar}), 11.01 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.8, 21.2, 21.9 (CH_3), 52.0 (OCH_3), 110.7 (C_{Ar}), 116.1 (CH_{Ar}), 129.2 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 135.1, 136.2, 137.7, 138.6, 144.2, 160.9 (C_{Ar}), 172.2 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3048, 2952, 1808 (w), 1708, 1664, 1605, 1512, 1438, 1351, 1319 (m), 1222 (s), 1156 (s), 1090 (m), 994, 899, 805, 733, 654, 564 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=270 (M^+, 36), 239 (23), 238 (100), 210 (12), 209 (5), 165 (14), 152 (9); HRMS (EI): calcd for $C_{17}H_{18}O_3$ $[M]^+$: 270.12505; found: 270.12516.

*3.4.15. Ethyl 4-hydroxy-2,4′,6-trimethylbiphenyl-3-carboxylate (**6o**).* Starting with 1,3-bis(silyl enol ether) **5b** (600 mg, 2.18 mmol), 3-*p*-tolyl-4-(trimethylsilyloxy)pent-3-en-2-one **4c** (572 mg, 2.18 mmol), and $TiCl_4$ (0.24 mL, 2.18 mmol), **6o** was obtained as a white solid (248 mg, 40%), mp=117–119 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.38 (t, 3H, ^3J=7.1 Hz, CH_3), 1.95 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 4.40 (q, 2H, ^3J=7.1 Hz, OCH_2), 6.76 (s, 1H, H_{Ar}), 6.95 (br d, 2H, ^3J=8.0 Hz, H_{Ar}), 7.18 (br d, 2H, ^3J=8.0 Hz, H_{Ar}), 11.07 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.2, 20.9, 21.2, 21.9 (CH_3), 61.4 (OCH_2), 111.0 (C_{Ar}), 116.2 (CH_{Ar}), 129.2 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 135.1, 136.2, 137.9, 138.7, 144.0, 161.0 (C_{Ar}), 171.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3049, 2919, 2860 (w), 1645, 1595, 1514, 1463, 1392 (m), 1314 (s), 1224 (m), 1103 (w), 1061, 994, 920 (m), 813 (s), 723, 653, 551 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=284 (M^+, 30), 239 (24), 238 (100), 210 (13), 195 (6), 165 (14), 152 (8); HRMS (EI): calcd for $C_{18}H_{20}O_3$ $[M]^+$: 284.14070; found: 284.14118.

*3.4.16. Methyl 4-hydroxy-2,4′,5,6-tetramethylbiphenyl-3-carboxylate (**6p**).* Starting with 1,3-bis(silyl enol ether), **5d** (600 mg, 2.18 mmol), 3-*p*-tolyl-4-(trimethylsilyloxy)pent-3-en-2-one **4c** (572 mg, 2.18 mmol), and $TiCl_4$ (0.24 mL, 2.18 mmol), **6p** was obtained as a white solid (254 mg, 41%), mp=143–145 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.89 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.93 (s, 3H, OCH_3), 6.92 (br d, 2H, ^3J=7.9 Hz, H_{Ar}), 7.21 (br d, 2H, ^3J=7.9 Hz, H_{Ar}), 11.28 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.0, 18.8, 20.9, 21.2 (CH_3), 52.0 (OCH_3), 110.2, 122.2 (C_{Ar}), 129.2 ($2CH_{Ar}$), 129.7 ($2CH_{Ar}$), 134.8, 135.2, 136.1, 138.8, 142.4, 158.9 (C_{Ar}), 172.9 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3012, 2953, 2864, 1711 (w), 1651, 1597, 1514, 1404 (m), 1327 (s), 1294 (m), 1222 (s), 1141, 1060, 987, 919, 857 (m), 804 (s), 736, 698, 551 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=284 (M^+, 42), 253 (23), 252 (100), 251 (16), 237 (15), 224 (22), 210 (9), 209 (43), 181 (13), 166 (13), 165 (25), 152 (5), 126 (7); HRMS (EI): calcd for $C_{18}H_{20}O_3$ $[M]^+$: 284.14070; found: 284.14063.

*3.4.17. Methyl 5-ethyl-4-hydroxy-2,4′,6-trimethylbiphenyl-3-carboxylate (**6q**).* Starting with 1,3-bis(silyl enol ether) **5e** (600 mg, 2.07 mmol), 3-*p*-tolyl-4-(trimethylsilyloxy)pent-3-en-2-one **4c** (543 mg, 2.07 mmol), and $TiCl_4$ (0.22 mL, 2.07 mmol), **6q** was obtained as a white solid (284 mg, 46%), mp=137–138 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.96 (t, 3H, ^3J=7.4 Hz, CH_3), 1.77 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.56 (q, 2H, ^3J=7.4 Hz, CH_2), 3.75 (s, 3H, OCH_3), 6.78 (br d, 2H, ^3J=7.8 Hz, H_{Ar}), 7.03 (br d, 2H, ^3J=7.8 Hz, H_{Ar}), 11.05 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.2, 17.9 (CH_3), 19.8 (CH_2), 20.8, 21.2 (CH_3), 51.9 (OCH_3), 110.4, 128.2 (C_{Ar}), 129.1 ($2CH_{Ar}$), 129.7 ($2CH_{Ar}$), 135.0, 135.3, 136.0, 138.8, 141.6, 158.7 (C_{Ar}), 172.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3009(w), 2953 (m), 2873 (w), 1650, 1597, 1514, 1434, 1358, 1290 (m), 1221 (s), 1141, 1066, 987 (m), 855 (w), 807 (s), 695 (m), 590 (w), 529 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=298 (M^+, 87), 267 (30), 266 (100), 265 (55), 251 (85), 238 (80), 223 (44), 209 (42), 195 (11), 179 (22), 165 (34); HRMS (EI): calcd for $C_{19}H_{22}O_3$ $[M]^+$: 298.15635; found: 298.15990.

*3.4.18. Methyl 4-hydroxy-2,4′,6-trimethyl-5-phenethylbiphenyl-3-carboxylate (**6r**).* Starting with 1,3-bis(silyl enol ether) **5f** (600 mg, 1.64 mmol), 3-*p*-tolyl-4-(trimethylsilyloxy)pent-3-en-2-one **4c** (430 mg, 1.64 mmol), and $TiCl_4$ (0.18 mL, 1.64 mmol), **6r** was obtained as a white solid (221 mg, 36%), mp=122–124 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.72 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.66 (t, 2H, ^3J=5.0 Hz, CH_2), 2.79 (t, 2H, ^3J=5.0 Hz, CH_2), 3.76 (s, 3H, OCH_3), 6.79 (br d, 2H, ^3J=7.9 Hz, H_{Ar}), 7.04 (br d, 2H, ^3J=7.9 Hz, H_{Ar}), 11.16 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.3, 22.1, 22.4 (CH_3), 30.4, 36.3 (CH_2), 53.2 (OCH_3), 111.6 (C_{Ar}), 127.0 (CH_{Ar}), 127.1

(C_{Ar}), 129.4 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 129.7 ($2CH_{Ar}$), 130.4 ($2CH_{Ar}$), 136.2, 137.0, 137.3, 140.0, 143.2, 143.8, 160.2 (C_{Ar}), 174.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3025, 2947, 2862, 1699 (w), 1650, 1600, 1513, 1440, 1406 (m), 1325, 1225 (s), 1145, 1085, 990, 920, 872 (m), 807 (s), 753, 698 (m), 632 (w), 549 (m); MS (EI, 70 eV): *m*/*z* (%)=374 (M^+, 29), 342 (5), 283 (28), 252 (22), 251 (100), 180 (5), 165 (9), 91 (4); HRMS (EI): calcd for $C_{25}H_{26}O_3$ $[M]^+$: 374.18765; found: 374.18782.

*3.4.19. Methyl 5-hexyl-4-hydroxy-2,4′,6-trimethylbiphenyl-3-carboxylate (**6s**).* Starting with 1,3-bis(silyl enol ether) **5h** (600 mg, 1.74 mmol), 3-*p*-tolyl-4-(trimethylsilyloxy)pent-3-en-2-one **4c** (457 mg, 1.74 mmol), and $TiCl_4$ (0.19 mL, 1.74 mmol), **6s** was obtained as white solid (259 mg, 42%), mp=105–107 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.71 (t, 3H, ^3J=7.2 Hz, CH_3), 1.09–1.34 (m, 8H, $4CH_2$), 1.76 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.51 (t, 2H, ^3J=7.1 Hz, CH_2), 3.75 (s, 3H, OCH_3), 6.77 (br d, 2H, ^3J=7.8 Hz, H_{Ar}), 7.03 (br d, 2H, ^3J=7.8 Hz, H_{Ar}), 11.03 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.3, 19.4, 22.0, 22.5 (CH_3), 23.8, 27.9, 30.2, 30.9, 32.9 (CH_2), 51.1 (OCH_3), 111.5, 128.3 (C_{Ar}), 130.6 ($2CH_{Ar}$), 132.1 ($2CH_{Ar}$), 136.1, 136.5, 138.3, 140.1, 143.0, 160.0 (C_{Ar}), 174.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2953, 2855, 1933 (w), 1702, 1655, 1593 (m), 1513 (w), 1437, 1378, 1325 (m), 1216 (s), 1141 (m), 1051, 987 (m), 902 (w), 841 (s), 765, 696 (m), 628, 557 (w); GC–MS (EI, 70 eV): *m*/*z* (%)=354 (M^+, 45), 322 (19), 307 (53), 305 (37), 293 (24), 279 (21), 253 (26), 252 (100), 251 (61), 224 (19), 209 (31), 207 (56), 165 (11); HRMS (EI): calcd for $C_{23}H_{30}O_3$ $[M]^+$: 354.21895; found: 354.21973.

*3.4.20. Methyl 4′-butyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6t**).* Starting with 1,3-bis(silyl enol ether) **5a** (600 mg, 2.30 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (700 mg, 2.30 mmol), and $TiCl_4$ (0.25 mL, 2.30 mmol), **6t** was obtained as a colorless solid (373 mg, 52%), mp=66–68 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.87 (t, 3H, ^3J=7.3 Hz, CH_3), 1.32 (sextet, 2H, ^3J=7.3 Hz, CH_2), 1.57 (quintet, 2H, ^3J=7.7 Hz, CH_2), 1.88 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.58 (t, 2H, ^3J=7.6 Hz, CH_2), 3.86 (s, 3H, OCH_3), 6.69 (s, 1H, H_{Ar}), 6.88 (d, 2H, ^3J=8.1 Hz, H_{Ar}), 7.14 (d, 2H, ^3J=8.1 Hz, H_{Ar}), 10.91 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0, 20.8, 21.9 (CH_3), 22.4, 33.5, 35.4 (CH_2), 52.0 (OCH_3), 110.7 (C_{Ar}), 116.1 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 135.2, 137.9, 138.7, 141.3, 144.3, 160.9 (C_{Ar}), 172.3 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2953, 2856, 1730 (w), 1657 (s), 1599, 1512, 1437, 1376, 1318 (m), 1220 (s), 1113, 1061, 993, 858, 803, 736 (m), 653 (w), 575 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=312 (M^+, 24), 281 (25), 280 (100), 237 (12), 209 (11), 166 (5), 165 (12), 152 (3); HRMS (EI): calcd for $C_{20}H_{24}O_3$ $[M]^+$: 312.17200; found: 312.17167.

*3.4.21. Ethyl 4′-butyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6u**).* Starting with 1,3-bis(silyl enol ether) **5b** (600 mg, 2.18 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (664 mg, 2.18 mmol), and $TiCl_4$ (0.24 mL, 2.18 mmol), **6u** was obtained as a colorless solid (320 mg, 45%), mp=73–75 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.88–0.98 (m, 6H, $2CH_3$), 1.34 (sextet, 2H, ^3J=7.2 Hz, CH_2), 1.58 (quintet, 2H, ^3J=7.3 Hz, CH_2), 1.89 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.59 (t, 2H, ^3J=7.6 Hz, CH_2), 4.41 (q, 2H, ^3J=7.2 Hz, OCH_2), 6.71 (s, 1H, H_{Ar}), 6.90 (d, 2H, ^3J=8.0 Hz, H_{Ar}), 7.14 (d, 2H, ^3J=8.0 Hz, H_{Ar}), 11.01 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 14.1, 20.9, 21.9 (CH_3), 22.4, 33.5, 35.3 (CH_2), 61.4 (OCH_2), 110.9 (C_{Ar}), 116.0 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 135.1, 138.7, 141.2, 142.1, 144.1, 160.9 (C_{Ar}), 171.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2956, 2858, 1809 (w), 1708 (m), 1654 (s), 1574 (m), 1510 (w), 1462, 1395 (m), 1314, 1221 (s), 1178, 1091, 1012 (m), 931 (w), 859, 802, 737, 653, 573 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=326 (M^+, 24), 281 (26), 280 (100), 252 (4), 237 (10), 209 (10), 166 (4), 165 (9), 152 (3); HRMS (EI): calcd for $C_{21}H_{26}O_3$ $[M]^+$: 326.18765; found: 326.18752.

*3.4.22. Benzyl 4′-butyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6v**).* Starting with 1,3-bis(silyl enol ether) **5c** (500 mg, 1.45 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (442 mg, 1.45 mmol), and $TiCl_4$ (0.16 mL, 1.45 mmol), **6v** was obtained as a yellowish solid (215 mg, 38%), mp=64–66 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, 3H, ^3J=7.3 Hz, CH_3), 1.31 (sextet, 2H, ^3J=7.3 Hz, CH_2), 1.57 (quintet, 2H, ^3J=7.8 Hz, CH_2), 1.89 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.57 (t, 2H, ^3J=7.5 Hz, CH_2), 5.33 (s, 2H, OCH_2), 6.70 (s, 1H, H_{Ar}), 6.91–7.33 (m, 9H, H_{Ar}), 10.93 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 21.2, 21.9 (CH_3), 22.4, 33.5, 35.3 (CH_2), 67.3 (OCH_2), 110.6 (C_{Ar}), 116.1 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 128.7 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 135.2, 137.8, 138.8, 141.3, 142.1, 144.4, 161.0 (C_{Ar}), 171.6 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3032, 2955, 2857, 1760 (w), 1709 (m), 1655 (s), 1573 (m), 1498 (w), 1416, 1344,1289 (m), 1216, 1156 (s), 1088, 1028, 947, 835, 737, 653, 570 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=388 (M^+, 54), 346 (25), 282 (41), 281 (28), 280 (100), 254 (18), 237 (13), 208 (68), 165 (16), 133 (35); HRMS (EI): calcd for $C_{26}H_{27}O_3$ $[M-H]^+$: 387.19657; found: 387.19655.

*3.4.23. Methyl 4′-butyl-4-hydroxy-2,5,6-trimethylbiphenyl-3-carboxylate (**6w**).* Starting with 1,3-bis(silyl enol ether) **5d** (500 mg, 1.82 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (554 mg, 1.82 mmol), and $TiCl_4$ (0.20 mL, 1.82 mmol), **6w** was obtained as a colorless solid (344 mg, 58%), mp=68–70 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, 3H, ^3J=7.5 Hz, CH_3), 1.32 (sextet, 2H, ^3J=7.4 Hz, CH_2), 1.58 (quintet, 2H, ^3J=7.8 Hz, CH_2), 1.84 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.58 (t, 2H, ^3J=7.6 Hz, CH_2), 3.85 (s, 2H, OCH_3), 6.87 (d, 2H, ^3J=8.2 Hz, H_{Ar}), 7.13 (d, 2H, ^3J=8.2 Hz, H_{Ar}), 11.21 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.0, 13.9, 18.7, 20.8 (CH_3), 22.4, 33.6, 35.3 (CH_2), 52.0 (OCH_3), 110.2, 122.1 (C_{Ar}), 128.4 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 134.9, 135.2, 138.9, 141.1, 142.2, 159.8 (C_{Ar}), 172.9 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3038(w), 2955 (m), 2860, 1689 (w), 1649, 1597, 1511, 1431 (m), 1326, 1219 (s), 1141, 1097, 1029 (m), 940 (w), 860 (m), 805 (s), 748, 708, 653, 594, 547 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=326 (M^+, 31), 295 (25), 294 (100), 293 (8), 266 (6), 251 (21), 237 (14), 223 (10), 209 (10), 179 (7), 165 (13), 152 (2); HRMS (EI): calcd for $C_{21}H_{26}O_3$ $[M]^+$: 326.18765; found: 326.18774.

*3.4.24. Methyl 4′-butyl-5-ethyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6x**).* Starting with 1,3-bis(silyl enol ether) **5e** (600 mg, 2.07 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (630 mg, 2.07 mmol), and $TiCl_4$ (0.22 mL, 2.07 mmol), **6x** was obtained as a colorless solid (387 mg, 55%), mp=81–83 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, 3H, ^3J=7.3 Hz, CH_3), 1.05 (t, 3H, ^3J=7.5 Hz, CH_3), 1.31 (sextet, 2H, ^3J=7.4 Hz, CH_2), 1.58 (quintet, 2H, ^3J=7.8 Hz, CH_2), 1.87 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.58 (t, 2H, ^3J=7.6 Hz, CH_2), 2.66 (q, 2H, ^3J=7.5 Hz, CH_2), 3.85 (s, 1H, OCH_3), 6.88 (d, 2H, ^3J=8.2 Hz, H_{Ar}), 7.12 (d, 2H, ^3J=8.2 Hz, H_{Ar}), 11.15 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.2, 13.9, 18.0 (CH_3), 19.8 (CH_2), 20.9 (CH_3), 22.4, 33.5, 35.4 (CH_2), 51.9 (OCH_3), 110.4, 128.2 (C_{Ar}), 128.4 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 135.1, 135.4, 139.0, 141.0, 141.7, 158.7 (C_{Ar}), 172.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2955(m), 2871, 1730 (w), 1653 (s), 1593 (m), 1512 (w), 1438, 1376, 1320 (m), 1212 (s), 1141, 1065, 987, 808, 756, 705, 649, 578 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=340 (M^+, 54), 309 (30), 308 (74), 307 (17), 281 (10), 280 (40), 265 (28), 252 (17), 251 (100), 237 (15), 179 (16), 165 (16); HRMS (EI): calcd for $C_{22}H_{28}O_3$ $[M]^+$: 340.20330; found: 340.20332.

*3.4.25. Methyl 4′-butyl-4-hydroxy-2,6-dimethyl-5-phenethylbiphenyl-3-carboxylate (**6y**).* Starting with 1,3-bis(silyl enol ether) **5f** (500 mg, 1.37 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (417 mg, 1.37 mmol), and $TiCl_4$ (0.15 mL, 1.37 mmol), **6y** was obtained as a colorless solid (211 mg, 37%), mp=69–71 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.87 (t, 3H, ^3J=7.2 Hz, CH_3), 1.32 (sextet, 2H, ^3J=7.4 Hz, CH_2), 1.58 (quintet, 2H, ^3J=7.8. Hz, CH_2), 1.78 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.58 (t, 2H, ^3J=7.5 Hz, CH_2), 2.74 (t, 2H, ^3J=4.8 Hz,

CH_2), 2.92 (t, 2H, ^3J=4.8 Hz, CH_2), 3.87 (s, 3H, OCH_3), 6.86 (d, 2H, ^3J=7.9 Hz, H_{Ar}), 7.11–7.23 (m, 7H, H_{Ar}), 11.24 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0, 18.1, 20.9 (CH_3), 22.4, 29.1, 33.6, 35.1, 35.3 (CH_2), 52.0 (OCH_3), 110.4 (C_{Ar}), 125.7 (CH_{Ar}), 125.9 (C_{Ar}), 128.2 ($2CH_{Ar}$), 128.4 ($2CH_{Ar}$), 128.7 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 135.1, 135.8, 138.9, 141.1, 142.0, 142.6, 159.0 (C_{Ar}), 172.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3024(w), 2951 (m), 2859 (w), 1707, 1650, 1599, 1512, 1452, 1405, 1354,1293 (m), 1220 (s), 1160, 1083, 1029, 949, 870, 804, 743 (m), 696 (s), 614, 567 (m); EIMS (EI, 70 eV): *m*/*z* (%)=416 (M^+, 24), 385 (16), 325 (42), 283 (28), 252 (35), 251 (100), 237 (10), 180 (19), 165 (11), 152 (12), 91 (8); HRMS (EI): calcd for $C_{28}H_{33}O_3$ $[M+H]^+$: 417.24242; found: 417.24261.

*3.4.26. Methyl 4′-butyl-5-hexyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6z**).* Starting with 1,3-bis(silyl enol ether) **5h** (600 mg, 1.74 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (530 mg, 1.74 mmol), and $TiCl_4$ (0.19 mL, 1.74 mmol), **6z** was obtained as a yellowish solid (331 mg, 48%), mp=84–85 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.71 (t, 3H, ^3J=7.2 Hz, CH_3), 0.78 (t, 3H, ^3J=7.3 Hz, CH_3), 1.09–1.59 (m, 12H, $6CH_2$), 1.76 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.47–2.52 (m, 4H, $2CH_2$), 3.75 (s, 3H, OCH_3), 6.78 (d, 2H, ^3J=7.9 Hz, H_{Ar}), 7.02 (d, 2H, ^3J=7.9 Hz, H_{Ar}), 11.04 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.2, 15.3, 19.4, 22.1 (CH_3), 23.6, 23.8, 27.9, 30.2, 30.9, 32.9, 34.7, 36.5 (CH_2), 53.0 (OCH_3), 111.5, 128.3 (C_{Ar}), 129.6 ($2CH_{Ar}$), 130.8 ($2CH_{Ar}$), 135.2, 136.3, 140.3, 142.2, 143.0, 160.0 (C_{Ar}), 174.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2953, 2855 (m), 1933 (w), 1703 (m), 1654 (s), 1593 (m), 1512 (w), 1438, 1377, 1325 (m), 1213 (s), 1141, 1057, 987 (m), 901 (w), 840, 752, 696, 651, 578 (m); MS (EI, 70 eV): *m*/*z* (%)=396 (M^+, 42), 365 (25), 335 (35), 294 (100), 293 (54), 251 (18), 237 (29), 209 (19), 165 (11); HRMS (EI): calcd for $C_{26}H_{37}O_3$ $[M+H]^+$: 397.27372; found: 397.27411.

*3.4.27. Methyl 4′-butyl-4-hydroxy-2,6-dimethyl-5-nonylbiphenyl-3-carboxylate (**6aa**).* Starting with 1,3-bis(silyl enol ether) **5k** (600 mg, 1.55 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (472 mg, 1.55 mmol), and $TiCl_4$ (0.17 mL, 1.55 mmol), **6aa** was obtained as a yellowish solid (285 mg, 42%), mp=66–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.69 (t, 3H, ^3J=6.7 Hz, CH_3), 0.78 (t, 3H, ^3J=7.2 Hz, CH_3), 1.09–1.58 (m, 18H, $9CH_2$), 1.76 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.45–2.53 (m, 4H, $2CH_2$), 3.75 (s, 3H, OCH_3), 6.78 (d, 2H, ^3J=8.0 Hz, H_{Ar}), 7.03 (d, 2H, ^3J=8.0 Hz, H_{Ar}), 11.03 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.2, 15.3, 19.4, 22.1 (CH_3), 22.8, 23.6, 23.7, 27.8, 30.2, 30.5, 30.7, 30.8, 31.1, 34.8, 36.6 (CH_2), 53.1 (OCH_3), 111.5, 128.2 (C_{Ar}), 129.6 ($2CH_{Ar}$), 130.8 ($2CH_{Ar}$), 136.2, 136.5, 140.2, 142.2, 143.0, 160.0 (C_{Ar}), 174.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2953, 2853 (m), 1731 (w), 1654 (s), 1593 (m), 1512 (w), 1438 (m), 1325, 1212 (s), 1140, 1058, 987 (m), 887 (w), 807, 752, 651, 578 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=438 (M^+, 38), 406 (22), 391 (30), 389 (32), 349 (56), 335 (51), 295 (20), 294 (100), 293 (50), 251 (14), 237 (22), 209 (15), 165 (15); HRMS (EI): calcd for $C_{29}H_{42}O_3$ $[M]^+$: 438.64583; found: 438.64927.

*3.4.28. Methyl 5-allyl-4′-butyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6ab**).* Starting with 1,3-bis(silyl enol ether) **5l** (600 mg, 1.99 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (606 mg, 1.99 mmol), and $TiCl_4$ (0.21 mL, 1.99 mmol), **6ab** was obtained as a yellowish solid (386 mg, 55%), mp=74–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.78 (t, 3H, ^3J=7.2 Hz, CH_3), 1.18 (sextet, 2H, ^3J=7.3 Hz, CH_2), 1.45 (quintet, 2H, ^3J=7.6 Hz, CH_2), 1.75 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.47 (t, 2H, ^3J=7.4 Hz, CH_2), 3.32 (d, 2H, ^3J=5.7 Hz, CH_2), 3.75 (s, 3H, OCH_3), 4.76–4.98 (m, 2H, =CH_2), 5.72–5.85 (m, 1H, =CH), 6.78 (d, 2H, ^3J=8.1 Hz, H_{Ar}), 7.03 (d, 2H, ^3J=8.1 Hz, H_{Ar}), 11.09 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.1, 19.4, 22.1 (CH_3), 23.5, 30.8, 34.7, 36.5 (CH_2), 53.2 (OCH_3), 111.7 (C_{Ar}), 115.7 (=CH_2), 124.8 (C_{Ar}), 129.6 ($2CH_{Ar}$), 130.8 ($2CH_{Ar}$), 135.2, 136.4 (C_{Ar}), 137.0 (=CH), 140.0, 142.3, 143.8, 159.9 (C_{Ar}), 173.9 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2955, 2926 (m), 2856 (w), 1656, 1595 (m), 1512 (w), 1438, 1325, 1287 (m), 1219 (s), 1139, 1059, 993, 911, 833, 750, 654, 565 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=353 (19), 352 (M^+, 88), 320 (88), 305 (65), 292 (100), 263 (48), 249 (61), 235 (35), 203 (32), 179 (25), 165 (10), 152 (11), 129 (31); HRMS (EI): calcd for $C_{23}H_{28}O_3$ $[M]^+$: 352.20330; found: 352.20362.

*3.4.29. Methyl 5-(but-3-enyl)-4′-butyl-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6ac**).* Starting with 1,3-bis(silyl enol ether) **5i** (500 mg, 1.58 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (481 mg, 1.58 mmol), and $TiCl_4$ (0.17 mL, 1.58 mmol), **6ac** was obtained as a yellowish solid (306 mg, 53%), mp=76–78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.79 (t, 3H, ^3J=7.2 Hz, CH_3), 1.20 (sextet, 2H, ^3J=7.3 Hz, CH_2), 1.44 (quintet, 2H, ^3J=7.6 Hz, CH_2), 1.76 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.10–2.13 (m, 2H, CH_2), 2.46 (t, 2H, ^3J=7.4 Hz, CH_2), 2.62 (t, 2H, ^3J=7.6 Hz, CH_2), 3.75 (s, 3H, OCH_3), 4.77–4.92 (m, 2H, =CH_2), 5.69–5.83 (m, 1H, =CH), 6.78 (d, 2H, ^3J=8.0 Hz, H_{Ar}), 7.02 (d, 2H, ^3J=8.0 Hz, H_{Ar}), 11.07 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 18.3, 20.9 (CH_3), 22.4, 26.2, 33.0, 33.6, 35.3 (CH_2), 52.0 (OCH_3), 110.4 (C_{Ar}), 114.4 (=CH_2), 126.0 (C_{Ar}), 128.4 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 135.1, 135.7 (C_{Ar}), 138.8 (=CH), 139.0, 141.1, 142.1, 158.9 (C_{Ar}), 172.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2954(m), 2858, 2667, 1786 (w), 1710, 1655, 1606 (m), 1511 (w), 1438, 1377, 1324, 1286 (m), 1216 (s), 1157, 1058, 991, 906, 807 (m), 751, 700 (s), 634 (w), 576 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=367 (33), 366 (M^+, 100), 335 (25), 333 (12), 305 (9), 293 (24), 277 (11), 249 (11), 235 (29), 203 (10), 179 (9), 165 (9), 152 (6), 115 (9); HRMS (EI): calcd for $C_{24}H_{30}O_3$ $[M]^+$: 366.21895; found: 366.21880.

*3.4.30. Methyl 4′-butyl-5-chloro-4-hydroxy-2,6-dimethylbiphenyl-3-carboxylate (**6ad**).* Starting with 1,3-bis(silyl enol ether) **5j** (600 mg, 2.06 mmol), 3-(4-butylphenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4d** (627 mg, 2.06 mmol), and $TiCl_4$ (0.22 mL, 2.06 mmol), **6ad** was obtained as a light yellowish solid (250 mg, 35%), mp=71–73 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.96 (t, 3H, ^3J=7.2 Hz, CH_3), 1.40 (sextet, 2H, ^3J=7.3 Hz, CH_2), 1.64 (quintet, 2H, ^3J=7.5 Hz, CH_2), 2.09 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.65 (t, 2H, ^3J=7.4 Hz, CH_2), 3.98 (s, 1H, OCH_3), 6.97 (d, 2H, ^3J=7.8 Hz, H_{Ar}), 7.24 (d, 2H, ^3J=7.8 Hz, H_{Ar}), 11.37 (s, 1H, OH); ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.9, 19.6, 20.7 (CH_3), 22.4, 33.5, 35.3 (CH_2), 52.4 (OCH_3), 112.1, 120.2 (C_{Ar}), 128.4 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 135.6, 139.5, 137.7, 141.6, 142.1, 156.0 (C_{Ar}), 172.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3412(w), 2955 (m), 2858, 2671, 2551, 1807 (w), 1706, 1666, 1605 (m), 1553 (w), 1416, 1353, 1285 (m), 1217 (s), 1157, 1102, 1001, 899, 805, 750, 697, 571 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=348 (M^+, ^{37}Cl, 7), 346 (M^+, ^{35}Cl, 23), 316 (38), 315 (24), 314 (100), 271 (17), 243 (6), 237 (10), 166 (3), 165 (9), 152 (3); HRMS (EI): calcd for $C_{20}H_{23}ClO_3$ $[M]^+$: 346.13302; found: 346.13295.

*3.4.31. 4′-Ethyl 3-methyl 4-hydroxy-2,6-dimethylbiphenyl-3,4′-dicarboxylate (**6ae**).* Starting with 1,3-bis(silyl enol ether) **5a** (500 mg, 1.91 mmol), ethyl 4-(4-oxo-2-(trimethylsilyloxy)pent-2-en-3-yl)benzoate **4e** (612 mg, 1.91 mmol), and $TiCl_4$ (0.21 mL, 1.91 mmol), **6ae** was obtained as colorless solid (376 mg, 60%), mp=86–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.42 (t, 3H, ^3J=7.0 Hz, CH_3), 1.93 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.95 (s, 3H, OCH_3), 4.41 (q, 2H, ^3J=7.0 Hz, OCH_2), 6.78 (s, 1H, H_{Ar}), 7.18 (d, 2H, ^3J=8.5 Hz, H_{Ar}), 8.12 (d, 2H, ^3J=8.5 Hz, H_{Ar}), 11.05 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.3, 20.7, 21.7 (CH_3), 52.0 (OCH_3), 61.0 (OCH_2), 110.9 (C_{Ar}), 116.4 (CH_{Ar}), 129.1 (C_{Ar}), 129.7 ($2CH_{Ar}$), 129.8 ($2CH_{Ar}$), 134.0, 138.1, 143.3, 145.8, 161.2 (C_{Ar}), 166.4, 172.0 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2981, 2954, 1712 (w), 1659, 1607, 1440, 1351, 1321 (m), 1269 (s), 1175 (m), 1099 (s), 993, 907, 804 (m), 727 (s), 647 (m), 564 (w); GC–MS (EI, 70 eV): *m*/*z* (%)=328 (M^+, 25), 297 (23), 296 (100), 268 (11), 165 (11), 152 (11); HRMS (EI): calcd for $C_{19}H_{20}O_5$ $[M]^+$: 328.13053; found: 328.13047.

*3.4.32. Diethyl 4-hydroxy-2,6-dimethylbiphenyl-3,4′-dicarboxylate (**6af**).* Starting with 1,3-bis(silyl enol ether) **5b** (500 mg, 1.82 mmol),

ethyl 4-(4-oxo-2-(trimethylsilyloxy)pent-2-en-3-yl)benzoate **4e** (583 mg, 1.82 mmol), and $TiCl_4$ (0.20 mL, 1.82 mmol), **6af** was obtained as colorless solid (280 mg, 45%), mp=87–88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.38 (t, 3H, ^3J=7.1 Hz, CH_3), 1.43 (t, 3H, ^3J=7.1 Hz, CH_3), 1.93 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 4.38 (q, 2H, ^3J=7.1 Hz, OCH_2), 4.44 (q, 2H, ^3J=7.1 Hz, OCH_2), 6.78 (s, 1H, H_{Ar}), 7.17 (d, 2H, ^3J=8.4 Hz, H_{Ar}), 8.12 (d, 2H, ^3J=8.4 Hz, H_{Ar}), 11.11 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0, 14.2, 20.7, 21.6 (CH_3), 60.8, 61.4 (OCH_2), 110.9 (C_{Ar}), 116.2 (CH_{Ar}), 128.9 (C_{Ar}), 129.7 ($2CH_{Ar}$), 129.8 ($2CH_{Ar}$), 133.9, 138.0, 143.0, 145.7, 161.2 (C_{Ar}), 166.3, 171.5 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2987, 2937, 1717 (w), 1651, 1598 (m), 1513 (w), 1443, 1371, 1313, 1271 (m), 1226 (s), 1178 (m), 1091 (s), 1019 (m), 964 (w), 856, 801 (m), 711 (s), 647, 597, 561 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=342 (M^+, 23), 297 (29), 296 (100), 268 (10), 165 (9), 152 (9); HRMS (EI): calcd for $C_{20}H_{22}O_5$ $[M]^+$: 342.14618; found: 342.14621.

*3.4.33. 4′-Ethyl 3-methyl 4-hydroxy-2,5,6-trimethylbiphenyl-3,4′-dicarboxylate (**6ag**).* Starting with 1,3-bis(silyl enol ether) **5d** (600 mg, 2.18 mmol), ethyl 4-(4-oxo-2-(trimethylsilyloxy)pent-2-en-3-yl)benzoate **4e** (698 mg, 2.18 mmol), and $TiCl_4$ (0.24 mL, 2.18 mmol), **6ag** was obtained as colorless solid (320 mg, 43%), mp=98–100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.42 (t, 3H, ^3J=7.1 Hz, CH_3), 1.89 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.94 (s, 3H, OCH_3), 4.41 (q, 2H, ^3J=7.1 Hz, OCH_2), 7.16 (d, 2H, ^3J=8.5 Hz, H_{Ar}), 8.09 (d, 2H, ^3J=8.5 Hz, H_{Ar}), 11.36 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.0, 14.4, 18.7, 20.8 (CH_3), 52.1 (OCH_3), 61.0 (OCH_2), 110.3, 122.5, 129.0 (C_{Ar}), 129.8 ($2CH_{Ar}$), 130.1 ($2CH_{Ar}$), 133.8, 134.7, 141.6, 147.0, 159.3 (C_{Ar}), 166.6, 172.7 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2954, 2871 (w), 1714 (s), 1650, 1608 (m), 1565, 1504 (w), 1435, 1358, 1307, 1258 (m), 1220 (s), 1142 (m), 1096 (s), 1026, 968, 871 (m), 802, 714 (s), 644, 580 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=342 (M^+, 23), 311 (29), 310 (100), 309 (10), 265 (10), 267 (21), 237 (13), 209 (17), 195 (10), 166 (10), 165 (21), 152 (6), 132 (9); HRMS (EI): calcd for $C_{20}H_{22}O_5$ $[M]^+$: 342.14618; found: 342.14631.

*3.4.34. 4′-Ethyl 3-methyl 4-hydroxy-2,6-dimethyl-5-phenethylbiphenyl-3,4′-dicarboxylate (**6ah**).* Starting with 1,3-bis(silyl enol ether) **5f** (500 mg, 1.37 mmol), ethyl 4-(4-oxo-2-(trimethylsilyloxy)pent-2-en-3-yl)benzoate **4e** (439 mg, 1.37 mmol), and $TiCl_4$ (0.15 mL, 1.37 mmol), **6ah** was obtained as colorless solid (207 mg, 35%), mp=100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.42 (t, 3H, ^3J=7.1 Hz, CH_3), 1.80 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.83 (t, 2H, ^3J=5.0 Hz, CH_2), 3.00 (t, 2H, ^3J=5.0 Hz, CH_2), 3.95 (s, 3H, OCH_3), 4.40 (q, 2H, ^3J=7.1 Hz, OCH_2), 7.17–7.30 (m, 7H, H_{Ar}), 8.09 (d, 2H, ^3J=8.5 Hz, H_{Ar}), 11.39 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.4, 18.1, 20.9 (CH_3), 29.1, 35.1 (CH_2), 52.2 (OCH_3), 61.0 (OCH_2), 110.5 (C_{Ar}), 125.8 (CH_{Ph}), 126.2 (C_{Ar}), 128.3 (C_{Ar}), 128.5 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 129.9 ($2CH_{Ar}$), 130.0 ($2CH_{Ar}$), 134.1, 135.3, 141.4, 142.4, 147.0, 159.5 (C_{Ar}), 166.6, 172.7 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3054, 2952, 2871 (w), 1711, 1645 (m), 1562 (w), 1495, 1437, 1363, 1268 (m), 1219 (s), 1143 (m), 1093 (s), 1022, 969, 877, 807, 753 (m), 699 (s), 628, 566 (m); MS (EI, 70 eV): *m*/*z* (%)=432 (M^+, 8), 385 (19), 384 (31), 383 (100), 355 (15), 309 (42), 266 (26), 251 (49), 207 (31), 179 (18), 178 (19), 165 (23), 91 (56), 29 (35); HRMS (ESI-TOF): calcd for $C_{27}H_{29}O_5$ $[M+H]^+$: 433.20095; found: 433.20142.

*3.4.35. Methyl 4-hydroxy-2,6-dimethyl-3′-(trifluoromethyl)-biphenyl-3-carboxylate (**6ai**).* Starting with 1,3-bis(silyl enol ether) **5a** (600 mg, 2.30 mmol), 3-(3-(trifluoromethyl)phenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4f** (727 mg, 2.30 mmol), and $TiCl_4$ (0.25 mL, 2.30 mmol), **6ai** was obtained as white solid (320 mg, 43%), mp=104–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.93 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.95 (s, 3H, OCH_3), 6.79 (s, 1H, H_{Ar}), 7.29 (br d, 1H, $^3J_{H,H}$=7.5 Hz, H_{Ar}), 7.37 (br s, 1H, H_{Ar}), 7.55 (br t, 1H, $^3J_{H,H}$=7.5, 7.8 Hz, H_{Ar}), 7.62 (br d, 1H, $^3J_{H,H}$=7.8 Hz, H_{Ar}), 11.06 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.9, 21.9 (CH_3), 52.2 (OCH_3), 110.9 (C_{Ar}), 116.6, 123.7 ($^3J_{C,F}$=3.4 Hz) (CH_{Ar}), 124.1 ($^1J_{C,F}$=271.3 Hz, C_{CF3}), 126.5 ($^3J_{C,F}$=3.8 Hz), 129.1 (CH_{Ar}), 130.6 ($^2J_{C,F}$=31.6 Hz, C_{Ar}), 133.4 ($^4J_{C,F}$=1.6 Hz, CH_{Ar}), 133.5, 138.5, 141.7, 143.7, 161.4 (C_{Ar}), 172.2 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3013, 2955 (w), 1651, 1597, 1444, 1357 (m), 1306 (s), 1229 (m), 1157 (s), 1108 (m), 1072 (s), 1008, 944, 860 (m), 804, 708 (s), 656, 578 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=324 (M^+, 28), 293 (24), 292 (100), 264 (18), 167 (7), 165 (11), 152 (7); HRMS (EI): calcd for $C_{17}H_{16}F_3O_3$ $[M+H]^+$: 325.10461; found: 325.10479.

*3.4.36. Ethyl 4-hydroxy-2,6-dimethyl-3′-(trifluoromethyl)-biphenyl-3-carboxylate (**6aj**).* Starting with 1,3-bis(silyl enol ether) **5b** (500 mg, 1.82 mmol), 3-(3-(trifluoromethyl)phenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4f** (576 mg, 1.82 mmol), and $TiCl_4$ (0.20 mL, 1.82 mmol), **6aj** was obtained as white solid (215 mg, 35%), mp=88–89 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.40 (t, 3H, ^3J=7.1 Hz, CH_3), 1.93 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 4.43 (q, 2H, ^3J=7.1 Hz, OCH_2), 6.79 (s, 1H, H_{Ar}), 7.28 (br d, 1H, $^3J_{H,H}$=7.5 Hz, H_{Ar}), 7.36 (br s, 1H, H_{Ar}), 7.53 (br t, 1H, $^3J_{H,H}$=7.5, 7.8 Hz, H_{Ar}), 7.60 (br d, 1H, $^3J_{H,H}$=7.8 Hz, H_{Ar}), 11.14 (s, 1H, OH): ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1, 20.9, 21.9 (CH_3), 61.7 (OCH_2), 111.1 (C_{Ar}), 116.6, 123.7 ($^3J_{C,F}$=3.6 Hz) (CH_{Ar}), 124.1 ($^1J_{C,F}$=271.8 Hz, C_{CF3}), 126.6 ($^3J_{C,F}$=3.6 Hz), 129.7 (CH_{Ar}), 130.6 ($^2J_{C,F}$=32.4 Hz, C_{Ar}), 133.3 ($^4J_{C,F}$=1.5 Hz, CH_{Ar}), 133.5, 138.6, 141.7, 143.5, 161.5 (C_{Ar}), 171.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3071, 2985, 2872 (w), 1650, 1595, 1467, 1400, 1349 (m), 1304, 1228, 1166, 1114 (s), 1065, 1007, 928, 874 (m), 804 (s), 761 (m), 709 (s), 655, 578 (m); MS (EI, 70 eV): *m*/*z* (%)=338 (M^+, 26), 293 (26), 292 (100), 264 (14), 263 (5), 167 (5), 165 (8), 152 (4); HRMS (EI): calcd for $C_{18}H_{17}F_3O_3$ $[M]^+$: 338.11243; found: 338.11236.

*3.4.37. Methyl ethyl 4-hydroxy-2,5,6-trimethyl-3′-(trifluoromethyl)-biphenyl-3-carboxylate (**6ak**).* Starting with 1,3-bis(silyl enol ether) **5m** (600 mg, 2.07 mmol), 3-(3-(trifluoromethyl)phenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4f** (655 mg, 2.07 mmol), and $TiCl_4$ (0.22 mL, 2.07 mmol), **6ak** was obtained as white solid (270 mg, 37%), mp=100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.32 (t, 3H, ^3J=7.2 Hz, CH_3), 1.82 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 4.35 (q, 2H, ^3J=7.2 Hz, OCH_2), 7.20 (br d, 1H, $^3J_{H,H}$=7.4 Hz, H_{Ar}), 7.29 (br s, 1H, H_{Ar}), 7.45 (br t, 1H, $^3J_{H,H}$=7.4, 7.7 Hz, H_{Ar}), 7.53 (br d, 1H, $^3J_{H,H}$=7.7 Hz, H_{Ar}), 11.33 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.9, 14.1, 18.7, 20.9 (CH_3), 61.6 (OCH_2), 110.6, 122.6 (C_{Ar}), 123.5 ($^3J_{C,F}$=3.5 Hz, CH_{Ar}), 124.1 ($^1J_{C,F}$=270.7 Hz, C_{CF3}), 126.7 ($^3J_{C,F}$=4.0 Hz), 129.0 (CH_{Ar}), 130.9 ($^2J_{C,F}$=31.9 Hz), 133.2 (C_{Ar}), 133.4 ($^4J_{C,F}$=1.6 Hz, CH_{Ar}), 135.0, 141.6, 142.7, 159.4 (C_{Ar}), 172.2 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3018, 2925, 2854 (w), 1642, 1596, 1492, 1435, 1379, 1332, 1220, 1160 (m), 1114, 1074 (s), 1030, 928, 869 (m), 802, 710 (s), 648, 580 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=352 (M^+, 31), 307 (29), 306 (100), 305 (61), 278 (26), 264 (9), 263 (34), 235 (9), 209 (5), 166 (7), 165 (11), 152 (3); HRMS (EI): calcd for $C_{19}H_{19}F_3O_3$ $[M]^+$: 352.12808; found: 352.12847.

*3.4.38. Methyl 5-ethyl-4-hydroxy-2,6-dimethyl-3′-(trifluoromethyl)-biphenyl-3-carboxylate (**6al**).* Starting with 1,3-bis(silyl enol ether) **5e** (500 mg, 1.73 mmol), 3-(3-(trifluoromethyl)phenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4f** (547 mg, 1.73 mmol), and $TiCl_4$ (0.19 mL, 1.73 mmol), **6al** was obtained as white solid (286 mg, 47%), mp=113–115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.06 (t, 3H, ^3J=7.5 Hz, CH_3), 1.84 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.67 (q, 2H, ^3J=7.5 Hz, CH_2), 3.87 (s, 1H, OCH_3), 7.21 (br d, 1H, $^3J_{H,H}$=7.6 Hz, H_{Ar}), 7.29 (br s, 1H, H_{Ar}), 7.46 (br t, 1H, $^3J_{H,H}$=7.9, 7.6 Hz, H_{Ar}), 7.53 (br d, 1H, $^3J_{H,H}$=7.9 Hz, H_{Ar}), 11.22 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.2, 17.9 (CH_3), 19.7 (CH_2), 20.8 (CH_3), 52.1 (OCH_3), 110.1, 123.5 ($^3J_{C,F}$=4.0 Hz, CH_{Ar}), 124.1 ($^1J_{C,F}$=270.6 Hz, C_{CF3}), 126.6 ($^3J_{C,F}$=3.3 Hz), 128.7 (C_{Ar}), 129.0 (CH_{Ar}), 130.9 ($^2J_{C,F}$=32.1 Hz), 133.3 (C_{Ar}), 133.4 ($^4J_{C,F}$=1.1 Hz, CH_{Ar}), 135.1,

141.0, 142.7, 159.3 (C_{Ar}), 172.6 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3064(w), 2954 (m), 2852 (w), 1650, 1596 (m), 1490 (w), 1439, 1360 (m), 1308, 1220 (s), 1159 (m), 1108 (s), 1036, 965 (m), 855 (w), 806 (s), 710, 651, 577 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=353 (9), 352 (M^+, 42), 321 (26), 320 (100), 293 (10), 292 (59), 277 (29), 263 (10), 179 (6),178 (6), 165 (14), 152 (4); HRMS (EI): calcd for $C_{19}H_{19}F_3O_3$ $[M]^+$: 352.12808; found: 352.12838.

*3.4.39. Methyl 4-hydroxy-2,6-dimethyl-5-phenethylbiphenyl-3-carboxylate (**6am**).* Starting with 1,3-bis(silyl enol ether) **5h** (500 mg, 1.45 mmol), 3-(3-(trifluoromethyl)phenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4f** (458 mg, 1.45 mmol), and $TiCl_4$ (0.16 mL, 1.45 mmol), **6am** was obtained as a light yellowish solid (254 mg, 43%), mp=96–97 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.71 (t, 3H, ^3J=7.0 Hz, CH_3), 1.08–1.33 (m, 8H, $4CH_2$), 1.73 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 2.52 (t, 2H, ^3J=6.9 Hz, CH_2), 3.76 (s, 1H, OCH_3), 7.21 (br d, 1H, $^3J_{H,H}$=7.5 Hz, H_{Ar}), 7.29 (br s, 1H, H_{Ar}), 7.46 (br t, 1H, $^3J_{H,H}$=7.8, 7.5 Hz, H_{Ar}), 7.54 (br d, 1H, $^3J_{H,H}$=7.8 Hz, H_{Ar}), 11.10 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (62 MHz, $CDCl_3$): δ=15.3, 19.4, 22.1 (CH_3), 23.8, 27.8, 30.2, 30.9, 33.0 (CH_2), 53.0 (OCH_3), 111.7 (C_{Ar}), 124.7 ($^3J_{C,F}$=3.8 Hz, CH_{Ar}), 125.6 ($^1J_{C,F}$=270.8 Hz, C_{CF3}), 127.8 ($^3J_{C,F}$=3.8 Hz, CH_{Ar}), 128.8 (C_{Ar}), 130.2 (CH_{Ar}), 132.5 ($^2J_{C,F}$=32.3 Hz), 134.5 (C_{Ar}), 134.6 ($^4J_{C,F}$=1.5 Hz, CH_{Ar}), 136.3, 142.4, 144.0, 160.6 (C_{Ar}), 173.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2955, 2857, 1933 (w), 1703, 1656, 1592, 1490, 1437, 1317, 1215 (m), 1123, 1071 (s), 1002, 958, 903, 805 (m), 704 (s), 652, 579 (m); MS (EI, 70 eV): *m*/*z* (%)=409 (11), 408 (M^+, 48), 376 (18), 361 (45), 359 (41), 347 (24), 333 (20), 319 (20), 306 (100), 305 (94), 278 (16), 263 (14), 165 (11); HRMS (EI): calcd for $C_{23}H_{27}F_3O_3$ $[M]^+$: 408.19068; found: 408.19096.

*3.4.40. Methyl 5-(but-3-enyl)-4-hydroxy-2,6-dimethyl-3′-(trifluoromethyl)-biphenyl-3-carboxylate (**6an**).* Starting with 1,3-bis(silyl enol ether) **5i** (600 mg, 1.90 mmol), 3-(3-(trifluoromethyl)phenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4f** (601 mg, 1.90 mmol), and $TiCl_4$ (0.20 mL, 1.90 mmol), **6an** was obtained as light yellowish solid (316 mg, 44%), mp=86–87 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.84 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.20 (br q, 2H, ^3J=6.7 Hz, CH_2), 2.74 (t, 2H, ^3J=7.7 Hz, CH_2), 3.87 (s, 3H, OCH_3), 4.88–5.03 (m, 2H, =CH_2), 5.79–5.93 (m, 1H, =CH), 7.21 (br d, 1H, $^3J_{H,H}$=7.5 Hz, H_{Ar}), 7.29 (br s, 1H, H_{Ar}), 7.47 (br t, 1H, $^3J_{H,H}$=7.5, 7.7 Hz, H_{Ar}), 7.53 (br d, 1H, $^3J_{H,H}$=7.7 Hz, H_{Ar}), 11.24 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.3, 20.9 (CH_3), 26.2, 32.9 (CH_2), 52.1 (OCH_3), 110.6 (C_{Ar}), 114.5 (=CH_2), 123.5 ($^3J_{C,F}$=3.8 Hz, CH_{Ar}), 124.1 ($^1J_{C,F}$=271.2 Hz, C_{CF3}), 126.5 (C_{Ar}), 126.7 ($^3J_{C,F}$=3.8 Hz), 129.0 (CH_{Ar}), 131.0 ($^2J_{C,F}$=31.8 Hz), 133.4 (C_{Ar}), 133.5 ($^4J_{C,F}$=3.2 Hz, CH_{Ar}), 135.1 (C_{Ar}), 138.6 (=CH), 141.3, 142.7, 159.5 (C_{Ar}), 172.6 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3075, 3075, 2953, 1731 (w), 1655, 1591, 1439 (m), 1317 (s), 1214 (m), 1122 (s), 1071, 1001 (m), 908 (s), 849, 806, 758, 708, 652 (m), 588 (w); GC–MS (EI, 70 eV): *m*/*z* (%)=378 (M^+, 8), 338 (5), 337 (25), 307 (3), 306 (19), 305 (100), 277 (4), 234 (2), 233 (4), 209 (3), 165 (9), 152 (2); HRMS (EI): calcd for $C_{21}H_{21}F_3O_3$ $[M]^+$: 378.14373; found: 378.14378.

*3.4.41. Methyl 5-chloro-4-hydroxy-2,6-dimethyl-3′-(trifluoromethyl)-biphenyl-3-carboxylate (**6ao**).* Starting with 1,3-bis(silyl enol ether) **5j** (500 mg, 1.69 mmol), 3-(3-(trifluoromethyl)phenyl)-4-(trimethylsilyloxy)pent-3-en-2-one **4f** (535 mg, 1.69 mmol), and $TiCl_4$ (0.18 mL, 1.69 mmol), **6ao** was obtained as light yellowish crystalline solid (194 mg, 32%), mp=92–94 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=1.97 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 7.21 (br d, 1H, $^3J_{H,H}$=6.7 Hz, H_{Ar}), 7.29 (br s, 1H, H_{Ar}), 7.45 (br t, 1H, $^3J_{H,H}$=6.7, 7.2 Hz, H_{Ar}), 7.54 (br d, 1H, $^3J_{H,H}$=7.2 Hz, H_{Ar}), 11.38 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.5; ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.5, 19.7 (CH_3), 51.5 (OCH_3), 113.0 (C_{Ar}), 122.9 ($^1J_{C,F}$=271.1 Hz, C_{CF3}), 123.4 ($^3J_{C,F}$=3.6 Hz), 126.8 ($^3J_{C,F}$=3.8 Hz, CH_{Ar}), 128.3 (C_{Ar}), 128.4 (CH_{Ar}), 130.3 ($^2J_{C,F}$=31.9 Hz), 132.9 (C_{Ar}), 133.6 ($^4J_{C,F}$=1.6 Hz, CH_{Ar}), 135.3, 140.1, 140.5, 155.6 (C_{Ar}), 170.8 (C=O); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3066, 2961, 2852 (w), 1650, 1587, 1490, 1403, 1303, 1224, 1175 (m), 1120, 1069 (s),1009, 904 (m), 806, 702 (s), 649, 544 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=360 (M^+, ^{37}Cl, 6), 358 (M^+, ^{35}Cl, 25), 328 (36), 327 (27), 326 (100), 235 (6), 165 (13), 153 (4), 152 (2); HRMS (EI): calcd for $C_{17}H_{14}ClF_3O_3$ $[M]^+$:358.05781; found: 358.05738.

*3.4.42. Methyl 5′-hydroxy-[1,1′;3′,1″]terphenyl-4′-carboxylate (**8a**).* Starting with **7** (430 mg, 1.65 mmol), **5a** (444 mg, 1.5 mmol), $TiCl_4$ (0.2 mL, 1.65 mmol), and CH_2Cl_2 (9 mL), **8a** was isolated as a highly viscous colorless oil (201 mg, 40%). ^1H NMR (300 MHz, $CDCl_3$): δ=3.40 (s, 3H, OCH_3), 6.96–7.54 (m, 12H, ArH), 10.75 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.1 (OCH_3), 111.1, 115.1, 122.0, 127.3 (ArCH), 127.6, 128.0, 128.5 (2C, ArCH), 128.9 (ArCH), 129.3 (2C, ArCH), 139.7, 143.2, 145.8, 146.8, 162.3 (ArCH), 171.7 (C); IR (neat, cm^{-1}): $\tilde{\nu}$ = 3426(m), 3083 (w), 3054 (m), 3025 (m), 2947 (m), 1664 (s), 1597 (m), 1553 (m), 1491 (w), 1437 (s), 1386 (s), 1354 (m), 1319 (s), 1256 (s), 1230 (s), 1198 (m),. 1142 (s), 1014 (m), 776 (m), 767 (m), 702 (s); GC–MS (EI, 70 eV): *m*/*z* (%): 304 (40), 273 (23), 272 (M^+, 100), 245 (9), 244 (38), 216 (11), 215 (54), 213 (8), 202 (3), 189 (3), 152 (5), 139 (3), 122 (6), 113 (4), 107 (16), 94 (7); HRMS (EI): calcd for $C_{20}H_{16}O_3$ $[M^+]$: 304.10940; found 304.109762.

*3.4.43. 1-(5′-Hydroxy-[1,1′;3′,1″]terphenyl-4′-yl)-ethanone (**8b**).* Starting with **7** (403 mg, 1.65 mmol), **5k** (444 mg, 1.5 mmol), $TiCl_4$ (0.2 mL, 1.65 mmol) and CH_2Cl_2 (9 mL), **8b** was isolated as a highly viscous colorless oil (194 mg, 41%). ^1H NMR (300 MHz, $CDCl_3$): δ=1.80 (s, 3H, CH_3), 6.79–7.93 (m, 12H, ArH), 11.87 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=28.6 (CH_3), 114.1, 116.3, 118.8, 120.3, 122.4 (ArCH), 126.2 (2C, ArCH), 127.7 (ArCH), 127.9 (2C, ArCH), 131.4, 134.5, 138.2, 142.2, 144.3 145.6, 160.8, 184.7 (ArCH), 205.6 (C); IR (neat, cm^{-1}): $\tilde{\nu}$ = 3425(m), 3086 (w), 3054 (m), 3025 (m), 2946 (m), 1665 (s), 1596 (m), 1554 (m), 1492 (w), 1437 (s), 1386 (s), 1354 (m), 1319 (s),1230 (s), 1198 (m),. 1142 (s), 1014 (m), 776 (m), 767 (m), 702 (s); GC–MS (EI, 70 eV): *m*/*z* (%): 288 (M^+, 100), 245 (9), 244 (38), 216 (11), 215 (54), 213 (8), 202 (3), 189 (3), 152 (5), 139 (3), 122 (6), 113 (4), 107 (16), 94 (7); HRMS (EI): calcd for $C_{20}H_{16}O_2$ $[M^+]$: 288.10632; found 288.105768.

*3.4.44. Methyl 5′-hydroxy-6′-methyl-[1,1′;3′,1″]terphenyl-4′-carboxylate (**8c**).* Starting with **7** (453 mg, 1.65 mmol), **5d** (444 mg, 1.5 mmol), $TiCl_4$ (0.2 mL, 1.65 mmol), and CH_2Cl_2 (9 mL), **8c** was isolated as a highly viscous colorless oil (223 mg, 37%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.12 (s, 3H, CH_3), 3.39 (s, 3H, OCH_3), 6.66–7.29 (m, 11H, ArH), 11.05 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7 (CH_3), 52.1 (OCH_3), 110.4, 123.7, 124.2, 127.1, 127.6 (ArCH), 127.9, 128.0, 128.5 (2C, ArCH), 141.2, 141.9, 143.3, 145.3, 144.5, 147.5, 160.6 (ArCH), 172.3 (C); IR (neat, cm^{-1}): $\tilde{\nu}$ = 3426(m), 3087 (w), 3052 (m), 3028 (m), 2947 (m), 1664 (s), 1597 (m), 1556 (m), 1493 (w), 1437 (s), 1386 (s), 1359 (m), 1320 (s), 1256 (s), 1230 (s), 1198 (m), 1143 (s), 1014 (m), 776 (m), 767 (m), 702 (s); GC–MS (EI, 70 eV): *m*/*z* (%): 318 (M^+, 100), 300 (20), 288 (4), 276 (3), 245 (9), 244 (38), 216 (11), 215 (54), 213 (8), 202 (9), 189 (7), 152 (3), 139 (9), 122 (8), 113 (6), 107 (16), 94 (7); HRMS (EI): calcd for $C_{21}H_{18}O_3$ $[M^+]$: 318.10654; found 318.10976.

3.5. Synthesis of 3-ethoxy-1,2-diphenylprop-2-en-1-one (10)

Deoxybenzoin (2.0 g, 10.2 mmol) was added to a mixture of triethyl orthoformate (2.5 mL) and acetic anhydride (2.5 mL) and the mixture was heated under reflux for 8 h. The mixture was concentrated in vacuo and purified by chromatography (silica gel, *n*-heptane/EtOAc) to give **10** as a pale green oil (1.28 g, 50%, 92:8 mixture of geometric isomers, only NMR data of the major isomer are listed). ^1H NMR (300 MHz, $CDCl_3$): δ=1.23 (t, ^3J=7.1 Hz, 3H, CH_3), 3.97 (q, ^3J=7.2 Hz, 2H, CH_2), 7.13–7.32 (m, 10H, CH_{Ar}), 7.54–7.55 (br s, 1H, CH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=15.4 (CH_3), 70.9 (OCH_2), 121.2 (C), 127.0, 127.9, 128.1, 129.3, 130.1, 131.3 (CH_{Ar}), 133.9,

139.7 (C_{Ar}), 160.8 (CH), 195.9 (CO); IR (neat, cm^{-1}): $\tilde{\nu}$ = 3434(w), 3056 (w), 2978 (w), 2930 (w), 2895 (w), 1725 (w), 1627 (w), 1656 (m), 1614 (m), 1596 (m), 1495 (w), 1445 (m), 1381 (w), 1299 (m), 1277 (m), 1224 (s), 1175 (m), 1143 (m), 1082 (m), 1014 (m), 909 (m), 836 (m), 798 (w), 763 (m), 763 (m), 694 (s), 663 (m), 643 (m), 606 (w); GC–MS (EI, 70 eV): *m*/*z* (%)=253 (19), 252 ($[M]^+$, 100), 224 (13), 223 (61), 178 (10), 167 (13), 165 (20), 146 (12), 105 (61), 102 (10), 77 (38); HRMS (EI): calcd for $C_{17}H_{17}O_2$ ($[M+H]^+$): 253.1223; found: 253.1224.

3.6. Synthesis of 11a,b

The reactions were carried out following the procedure given for the synthesis of **6**.

*3.6.1. Methyl 5,6-diphenylsalicylate (**11a**).* Starting with **10** (0.378 g, 1.5 mmol) and **5a** (0.429 g, 1.65 mmol), **11a** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a pale yellowish solid (0.319 g, 70%), mp=119–121 °C.

^1H NMR (300 MHz, $CDCl_3$): δ=3.32 (s, 3H, OCH_3), 6.83–6.90 (m, 4H, CH_{Ar}), 7.00–7.10 (m, 7H, CH_{Ar}), 7.35 (d, ^3J=8.9 Hz, 1H, CH_{Ar}), 10.32 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=52.0 (OCH_3), 113.5 (C_{Ar}), 116.6, 126.0, 126.3, 127.1, 127.5, 129.7, 129.9 (CH_{Ar}), 134.0 (C_{Ar}), 135.9 (CH_{Ar}), 140.6, 140.9, 142.1 (C_{Ar}), 160.5 (COH), 171.7 (CO); IR (neat, cm^{-1}): $\tilde{\nu}$ = 3052(w), 2922 (w), 2851 (w), 1814 (w), 1738 (w), 1664 (s), 1590 (m), 1493 (m), 1435 (s), 1317 (s), 1259 (m), 1216 (s), 1141 (m), 1094 (m), 1073 (m), 1024 (w), 960 (m), 901 (m), 847 (m), 813 (m), 748 (s), 720 (m), 695 (s), 640 (m), 598 (m), 576 (m), 547 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=304 ($[M]^+$, 34), 273 (21), 272 (100), 244 (10), 215 (40), 107 (12); HRMS (EI): calcd for $C_{20}H_{17}O_3$ ($[M+H]^+$): 305.1172; found: 305.1175.

*3.6.2. Methyl 3-methyl-5,6-diphenylsalicylate (**11b**).* Starting with **10** (0.378 g, 1.5 mmol) and **5d** (0.453 g, 1.65 mmol), **11b** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a white solid (0.382 g, 80%), mp=150–152 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.20 (s, 3H, CH_3), 3.22 (s, 3H, OCH_3), 6.72–6.80 (m, 4H, CH_{Ar}), 6.88–6.97 (m, 6H, CH_{Ar}), 7.14 (s, 1H, CH_{Ar}), 10.47 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=15.9 (CH_3), 51.7 (OCH_3), 112.7, 125.6 (C_{Ar}), 125.9, 126.1, 127.1, 127.5, 129.7, 129.9 (CH_{Ar}), 133.3 (C_{Ar}), 136.9 (CH_{Ar}), 139.5, 140.9, 141.1 (C_{Ar}), 158.4 (COH), 172.0 (CO); IR (neat, cm^{-1}): $\tilde{\nu}$ = 3071(w), 3021 (w), 2920 (m), 2851 (w), 1665 (m), 1653 (m), 1607 (w), 1568 (w), 1492 (w), 1436 (m), 1404 (m), 1377 (m), 1338 (m), 1301 (m), 1237 (m), 1209 (m), 1156 (m), 1070 (m), 1014 (m), 984 (m), 917 (w), 902 (m), 884 (w), 842 (w), 811 (m), 772 (m), 757 (s), 698 (s), 645 (m), 613 (m), 563 (m); GC–MS (EI, 70 eV): *m*/*z* (%)=319 (9), 318 ($[M]^+$, 38), 287 (23), 286 (100), 285 (41), 257 (12), 229 (13), 228 (14), 215 (14); HRMS (EI): calcd for $C_{21}H_{19}O_3$ ($[M+H]^+$): 319.1329; found: 319.1329.

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