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Efficient Synthesis of Furan-2-ylacetates, 7-(Alkoxycarbonyl)benzofurans, and 7-(Alkoxycarbonyl)-2,3-dihydrobenzofurans Based on Cyclization Reactions of Free and Masked Dianions: A "Cyclization/Dehydrogenation" Strategy

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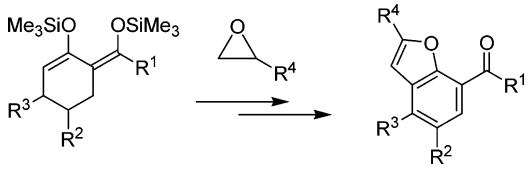

A variety of furan-2-ylacetates have been prepared by dehydrogenation of monocyclic 2-alkylidenetetrahydrofurans, which are readily available by cyclizations of open-chained 1,3-dicarbonyl dianions with 1-bromo-2-chloroethane. 5′*H*-[2,3′]Bifuranyl-2′-ones are available based on sequential "cyclization/dehydrogenation" reactions of α-acetyl-γ-butyrolactones. A variety of 7-(alkoxycarbonyl)-benzofurans and 7-(alkoxycarbonyl)-2,3-dihydrobenzofurans were prepared by a cyclization/dehydrogenation strategy. These reactions rely on cyclizations of 2-oxocycloalkane-1-carboxylate-derived 1,3-dicarbonyl dianions ("free dianions") or 1,3-bis-silyl enol ethers ("masked dianions") with various 1,2-dielectrophiles.

Introduction

Functionalized furans occur in a variety of pharmacologically relevant natural products.[1,2] Furan-2-ylacetates are present, for example, in the cytotoxic glanvillic acids

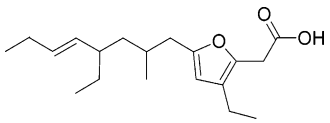

FIGURE 1. Glanvillic acid A.

A and B (Figure 1) or in the plakorsins A−C.[3] They also represent versatile synthetic building blocks and have been used, for example, during the synthesis of bis(2,6-dioxopiperazine) derivatives (Figure 2); the latter represent antineoplastic agents exhibiting a high antitumor activity (e.g. against P388-leucaemia).[4] Natural and nonnatural *benzo*furans are of equal pharmacological relevance.[5] For example, synthetic amiodarone represents a potent antiarrythmic and antianginal drug.[6] 7-Alkanoylbenzofurans and 7-alkanoyl-2,3-dihydrobenzofurans occur in a number of natural products, such as

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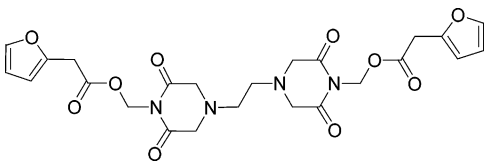

FIGURE 2. Antitumor agent.

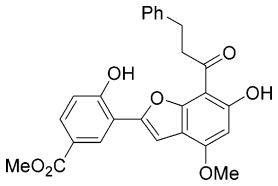

FIGURE 3. Longicaudatin.

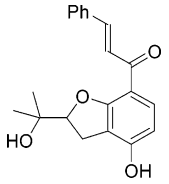

FIGURE 4. Flemistricin E.

longicaudatin (Figure 3),[7] the sessiliflorols A and B, flemistrictin E (Figure 4), tovophenone C, vismiaguianone C, and piperaduncin B.[8]

Furan and benzofuran syntheses have been known for a long time;[1,2,5] however, the development of alternative and efficient strategies for the synthesis of these important heterocyclic systems is of considerable interest. So far, dehydrogenation reactions have been rarely used for the synthesis of furans and benzofurans. For example, 2,3-dihydrobenzofurans have been transformed into benzofurans by dehydrogenation.[9] The dehydrogenation of tetrahydrofurans and 2,3,4,5,6,7-hexahydrobenzofurans has been reported to give furans and benzofurans, respectively.[10] Recently, annulated furans have been prepared on the basis of electrochemical reactions.[11] In recent years, a number of one-pot syntheses of 2-alkylidenetetrahydrofurans, based on regioselective C,O-cyclizations of 1,3-dicarbonyl dianions ("free dianions") and 1,3-bis-silyl enol ethers ("masked dianions"), have been developed.[12] Herein, we report a convenient approach to furan-2-ylacetates, 7-(alkoxycarbonyl)benzofurans, and 7-(alkoxycarbonyl)-2,3-dihydrobenzofurans based on a "cyclization/dehydrogenation" strategy. With regard to our preliminary communication in this field,[13] the preparative scope of this methodology has been considerably extended.

Results and Discussion

Synthesis of Furan-2-ylacetates Based on Cyclizations of Dianions with 1-Bromo-2-Chloroethane. Some years ago, we reported the synthesis of *monocyclic* 2-alkylidenetetrahydrofurans by cyclization of *open-chained* 1,3-dicarbonyl dianions with 1-bromo-2-chloroethane.[14] Following this procedure, 2-alkylidenetetrahydrofurans **2a,b** were prepared by cyclization of dilithiated methyl and ethyl acetoacetate (**1a,b**) with 1-bromo-2-chloroethane (Scheme 1). Treatment of **2a,b** with 2,3-dichloro-5,6-dicyano-1,4-quinone (DDQ) afforded the known[15a] furan-2-ylacetates **3a,b**. The formation of **3a,b** can be explained by dehydrogenation and subsequent aromatization by migration of the exocyclic double bond.[16]

Optimal yields were obtained when (a) an excess of DDQ (2.0 equiv) was used, (b) 1,4-dioxane was employed as solvent, and (c) the solution was heated under reflux

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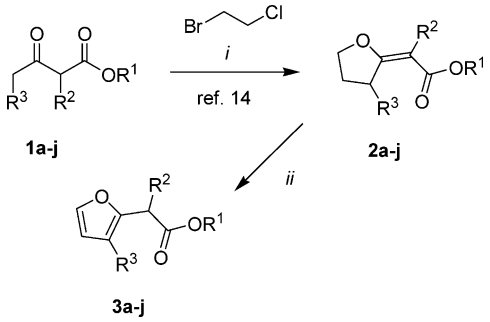
SCHEME 1. Synthesis of Furan-2-ylacetates 3a−j[a]



[a] Reagents and conditions: (i) (1) LDA (2.3 equiv), THF, 0 °C, 1 h, (2) $BrCH_2CH_2Cl$, −78 °C → 20 °C, 14 h, (3) reflux, 12 h; (ii) DDQ (see Table 2), 1,4-dioxane, reflux, 48 h.

TABLE 1. Optimization of the Synthesis of 3b

solvent	*t* (h)	conditions	%[a]	solvent	*t* (h)	conditions	%[a]
CH_3CN	24	reflux	0	dioxane	48	reflux	75
THF	24	reflux	17	toluene	24	reflux	12
dioxane	24	20 °C	0	CH_2Cl_2	24	reflux	5
dioxane	24	reflux	34				

[a] Conversion (by ^1H NMR of the crude product).

TABLE 2. Products and Yields

2, **3**	R^1	R^2	R^3	% **2**[a]	% **3**[a]	DDQ (equiv)
a	Me	H	H	86[b]	57[c]	2.0
b	Et	H	H	79[b]	59[c]	2.0
c	*i*Pr	H	H	77	52[c]	1.2
d	*t*Bu	H	H	77[b]	55	2.0
e	Me	H	Me	72[b]	41[c]	1.2
f	Et	H	Et	82[b]	53[c]	1.2
g	*t*Bu	H	$(CH_2)_2CHMe_2$	48[b]	54	2.0
h	*t*Bu	H	$(CH_2)_6Cl$	91[b]	67	2.0
i	Et	Me	H	64[b]	52	2.0
j	Et	Et	H	63[b]	55	2.0

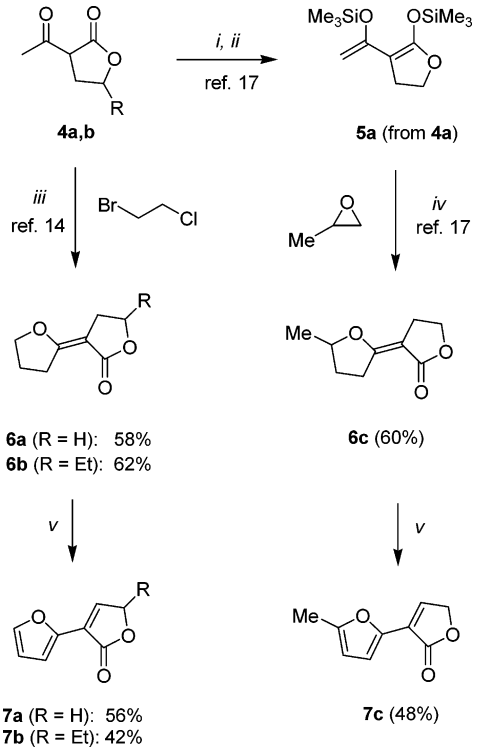
[a] Isolated yields. [b] Known compounds (ref 14). [c] Known compounds (ref 15a).

for 48 h. The employment of other solvents and oxidizing agents proved less effective in terms of yield (Table 1). No complete conversion was observed when shorter reaction times were employed; no conversion at all was obtained when the reaction was carried out at 20 °C.

The isopropyl and *tert*-butyl furan-2-ylacetates **3c,d** were prepared from 2-alkylidenetetrahydrofurans **2c,d**, respectively (Table 2). The DDQ-mediated dehydrogenation of 2-alkylidenetetrahydrofurans **2e**−**g**, again prepared by cyclization of the corresponding 1,3-dicarbonyl dianions with 1-bromo-2-chloroethane,[14] afforded the (3-methyl-, (3-ethyl-, and (3-isopentylfuran-2-yl)acetates **3e**−**g**. The dehydrogenation of chloro-substituted 2-alkylidenetetrahydrofuran **2h**, prepared from *tert*-butyl 10-chloro-3-oxodecanoate (**1h**),[14] gave the [3-(6′-chlorohexyl)-furan-2-yl]acetate **3h**. The dehydrogenation of 2-alkylidenetetrahydrofurans **2i,j**, prepared from ethyl 2-methylacetoacetate and ethyl 2-ethylacetoacetate,[14] afforded the 2-furan-2′-ylpropionate **3i** and 2-furan-2′-ylbutanoate **3j**, respectively.

Synthesis of 5′*H*-[2,3′]Bifuranyl-2′-ones. The known 2,3′-bifuranylidenes **6a,b** were prepared by cyclization of dilithiated α-acetyl-γ-butyrolactones **4a,b** with 1-bromo-2-chloroethane (Scheme 2).[14] The 2,3′-bifuranylidene **6c**

SCHEME 2. Synthesis of 5′*H*-[2,3′]Bifuranyl-2′-ones 7a−c[a]



[a] Reagents and conditions: (i) (1) NEt_3, benzene, 20 °C, 1 h, (2) Me_3SiCl, 0 °C → 20 °C, 1 d; (ii) (1) LDA, THF, −78 °C, 1 h, 2) Me_3SiCl, −78 °C → 0 °C, 2 h; (iii) (1) LDA (2.3 equiv), THF, 0 °C, 1 h, (2) $BrCH_2CH_2Cl$, −78 °C → 20 °C, 14 h, (3) reflux, 12 h; (iv) propenoxide, $TiCl_4$ (2.0 equiv), 4 Å molecular sieves, CH_2Cl_2, −78 °C → 20 °C, 14 h, 20 °C, 2 h; (v) DDQ (2.2 equiv), 1,4-dioxane, reflux, 48 h.

was prepared, following a recently reported method, by $TiCl_4$-mediated reaction of 1,3-bis-silyl enol ether **5a**, readily available from **4a**, with propenoxide.[17] Treatment of **6a**−**c** with DDQ afforded the 5′*H*-[2,3′]bifuranyl-2′-ones **7a**−**c**. The formation of **7a**−**c** can be explained by oxidation of both the tetrahydrofuran and the lactone moiety. The employment of only 1 equiv (rather than 2) of DDQ gave a complex mixture.

Synthesis of Benzofurans, 2,3-Dihydrobenzofurans, and Annulated Furans Based on Cyclizations of Dianions with 1-Bromo-2-chloroethane. Our initial attempts to prepare *bicyclic* 2-alkylidenetetrahydrofurans by cyclization of *cyclic* 1,3-dicarbonyl dianions with 1-bromo-2-chloroethane, following our original procedure,[14] were unsuccessful. Eventually, careful tuning of reaction time and temperature allowed the synthesis of the desired products [conditions: (1) −78 → −20 °C, 6 h; (2) −20 °C, 12 h; (3) −20 → 20 °C, 12 h; (4) 20 °C, 12 h]: at low temperature (−78 → −20 °C) the terminal carbon atom of the dianion chemo- and regioselectively attacked the alkyl bromide function of 1-bromo-2-chloroethane. This step was completed by stirring of the reaction mixture at −20 °C for 12 h. To induce the cyclization step, which proceeded regioselectively via the oxygen atom, the reaction mixture was slowly warmed

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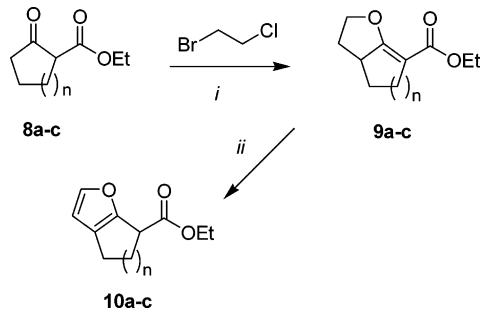
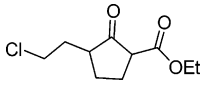
SCHEME 3. Synthesis of Bicyclic 2-Alkylidenetetrahydrofurans 9a−c and Furan 10c[a]



[a] Reagents and conditions: (i) (1) LDA (2.3 equiv), THF, 0 °C, 1 h, (2) $BrCH_2CH_2Cl$, −78 → −20 °C, 6 h, (3) −20 °C, 12 h, (4) −20 → 20 °C, 12 h, (5) 20 °C, 12 h; (ii) DDQ (2.0 equiv), 1,4-dioxane, reflux, 48 h.

TABLE 3. Products and Yields



9a'

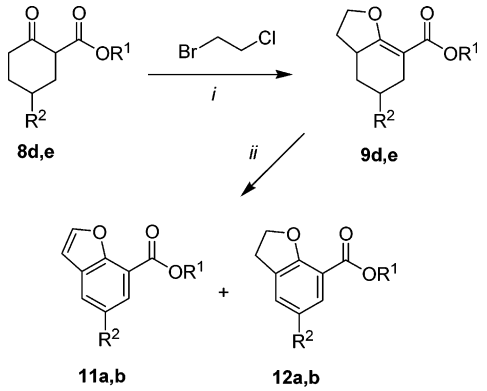
9, **10**	*n*	% **9**[a]	% **10**[a]
a	1	67[b]	0
b	4	43	0
c	8	90	80

[a] Isolated yields. [b] Yield over two steps (via **9a′**).

to 20 °C and stirred at this temperature for 12 h. Application of the reaction conditions as reported for the synthesis of monocyclic derivatives [conditions: (1) −78 → 20 °C, (2) reflux] resulted in the formation of a more complex reaction mixture and a decrease in yield. The reaction of the dianion of ethyl 2-oxocyclopentane-1-carboxylate (**8a**) with 1-bromo-2-chloroethane gave ethyl 2-oxo-3-(2′-chloroethyl)cyclopentane-1-carboxylate (**9a′**); treatment of the latter with DBU afforded the 5,5-bicyclic 2-alkylidenetetrahydrofuran **9a** (Scheme 3, Table 3). The 5,8-bicyclic 2-alkylidenetetrahydrofuran **9b** was prepared in one step by cyclization of dilithiated ethyl 2-oxocyclooctane-1-carboxylate (**8b**) with 1-bromo-2-chloroethane. The cyclization of the dianion of ethyl 2-oxocyclododecane-1-carboxylate (**8c**) with 1-bromo-2-chloroethane afforded the 5,12-bicyclic 2-alkylidenetetrahydrofuran **9c**. The requirement to carry out the synthesis of **9a** in two steps can be explained by the strain present in the 5,5-bicyclic system of **9a** compared to higher ring systems. The reaction of **9a,b** with DDQ resulted, under several conditions, in the formation of complex mixtures rather than the desired furans **10a,b**. This result can be explained on the basis of the oxidation of the cyclopentane and cyclooctane moiety and formation of complex mixtures. In contrast, **9c** was successfully transformed into the 5,12-bicyclic furan **10c** by DDQ-mediated dehydrogenation. Notably, the bicyclic furans **10b,c** have been previously prepared on the basis of a "cyclization/elimination" approach.[15a]

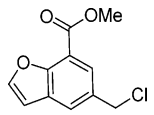
Cyclization reactions of dilithiated 2-oxocyclohexane-1-carboxylates **8d,e** with 1-bromo-2-chloroethane were next studied; they were carried out following our optimized protocol (see above). The reaction of 1-bromo-2-chloroethane with the dianions of ethyl 2-oxocyclohexane-1-carboxylate (**8d**) and methyl 2-oxo-5-methylcyclohexane-1-carboxylate (**8e**) afforded the 2,3,3a,4,5,6-hexahydrobenzofurans **9d** and **9e**, respectively (Scheme 4, Table 4). Treatment of **9d** with DDQ afforded 2,3-dihydrobenzofuran **12a** by selective dehydrogenation of the six-membered ring. The employment of an excess of DDQ (3.0 equiv) did *not* result in complete dehydrogenation and formation of benzofuran **11a**. Treatment of **9e** with DDQ (5.0 equiv) afforded 5-methylbenzofuran **11b**; in addition, a significant amount of 5-(chloromethyl)benzofuran **11b′** was formed by DDQ-mediated chlorination of the methyl group. The yield of **11b** could *not* be improved using a decreased amount of DDQ.

SCHEME 4. Synthesis of Benzofurans 11a,b and 2,3-Dihydrobenzofurans 12a,b[a]



[a] Reagents and conditions: (i) (1) LDA (2.3 equiv), THF, 0 °C, 1 h, (2) $BrCH_2CH_2Cl$, −78 → −20 °C, 6 h, (3) −20 °C, 12 h, (4) −20 → 20 °C, 12 h, (5) 20 °C, 12 h; (ii) DDQ (see Table 4), 1,4-dioxane, reflux, 48 h.

TABLE 4. Products and Yields



11b'

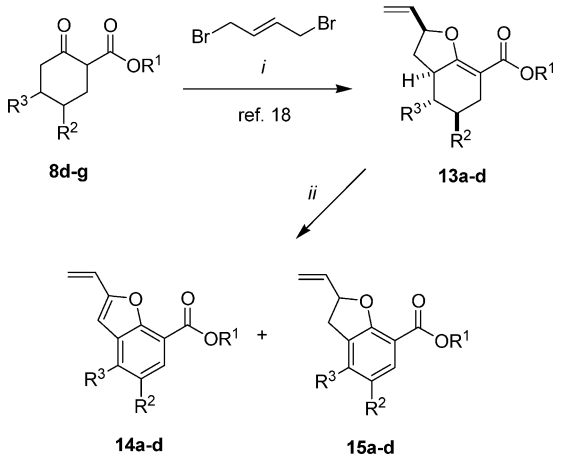
9	**11**, **12**	R^1	R^2	% **9**[a]	% **11**[a]	% **12**[a]	DDQ (equiv)
d	**a**	Et	H	42	0	57	3.0
e	**b**	Me	Me	47[b]	30[c]	0	5.0

[a] Isolated yields. [b] dr = 5:2. [c] **11b′** was isolated as a side product in 26% yield.

Synthesis of 2-Vinylbenzofurans and 2-Vinyl-2,3-dihydrobenzofurans Based on Cyclizations of Dianions with 1,4-Dibromobut-2-ene. The cyclization of dilithiated 2-oxocyclohexane-1-carboxylates with 1,4-dibromobut-2-ene were carried out according to the protocol as given for the synthesis of **9a−c** (vide supra). The cyclization of the dianions of **8d−g** with 1,4-dibromobut-2-ene afforded the known[18] 2-vinyl-2,3,3a,4,5,6-hexahydrobenzofurans **13a−d** (Scheme 5, Table 5). The DDQ-mediated dehydrogenation of **13a** gave 2-vinylbenzofuran **14a** and 2-vinyl-2,3-dihydrobenzofuran **15a**, and a small amount of ethyl 8,9-dicyanodibenzofuran-4-carboxylate **14a′** was isolated; its formation can be

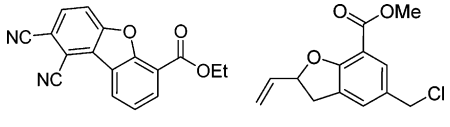
(18) Langer, P.; Holtz, E.; Saleh, N. N. R. *Chem. Eur. J.* **2002**, *8*, 917.

SCHEME 5. Synthesis of 2-Vinylbenzofurans 14a–d and 2-Vinyl-2,3-dihydrobenzofurans 15a–d[a]



[a] Reagents and conditions: (i) (1) LDA (2.3 equiv), THF, 0 °C, 1 h, (2) $BrCH_2CH{=}CHCH_2Br$, −78 → −20 °C, 6 h, (3) −20 °C, 12 h, (4) −20 → 20 °C, 12 h, (5) 20 °C, 12 h; (ii) DDQ (3.0 equiv), 1,4-dioxane, reflux, 48 h.

TABLE 5. Products and Yields



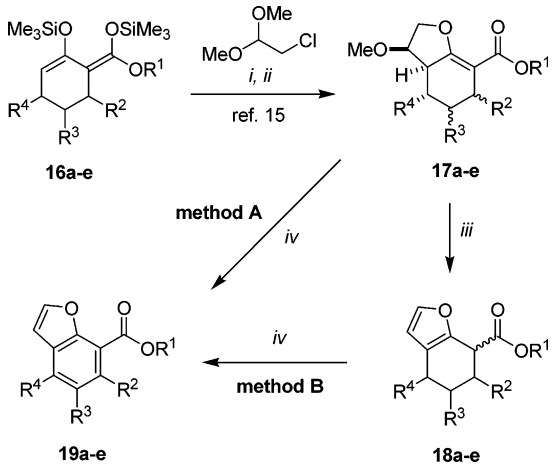
13–15	R^1	R^2	R^3	% 13[a,b]	% 14[a]	% 15[a]
a	Et	H	H	81	18[c]	63
b	Me	Me	H	63	–	36[d]
c	Me	Ph	H	65	18	43
d	Et	H	Me	74	22	50

[a] Isolated yields. [b] **13a–d** were isolated a single diastereomer; see ref 18. [c] **14a′** was isolated as a side product in 4% yield. [d] **15b′** was isolated as a side product in 18% yield.

explained by [4 + 2]-cycloaddition of **14a** with DDQ and subsequent fragmentation. The dehydrogenation of **13b** afforded the 2,3-dihydrobenzofurans **15b** and **15b′**; the latter was formed by chlorination of the methyl group. The DDQ-mediated dehydrogenation of **13c** gave benzofuran **14c** and 2,3-dihydrobenzofuran **15c**. Treatment of **13d** with DDQ afforded benzofuran **14d** and 2,3-dihydrobenzofuran **15d**. The yield of 2-vinylbenzofurans could *not* be improved by using a higher amount of DDQ or by extension of the reaction time. Thus, the strategy outlined in this paragraph is more suitable for the synthesis of 2-vinyl-2,3-dihydrobenzofurans than for 2-vinylbenzofurans.

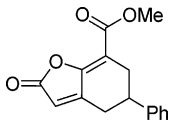
Synthesis of Benzofurans Based on Cyclizations of 1,3-Bis-silyl Enol Ethers with 1-Chloro-2,2-dimethoxyethane. The 3-methoxy-2,3,3a,4,5,6-hexahydrobenzofurans **17a–e** were prepared, following our recently reported procedure,[15] by condensation of 1,3-bis-silyl enol ethers **16a–e** with 1-chloro-2,2-dimethoxyethane and subsequent DBU-mediated cyclization (Scheme 6, Table 6). Treatment of **17a,c–e** with DDQ (1,4-dioxane, reflux, 48 h) directly afforded the 2,3-unsubstituted benzofurans **19a,c–e** by thermal elimination of methanol and subsequent dehydrogenation (method A). This transformation was also successfully carried out in two steps (method B): heating of a 1,4-dioxane solution

SCHEME 6. Synthesis of 2,3-Unsubstituted Benzofurans 19a–e[a]



[a] Reagents and conditions: (i) $ClCH_2CH(OMe)_2$, Me_3SiOTf (0.5 equiv), CH_2Cl_2, −78 °C → 20 °C; (ii) DBU (2.0 equiv), THF, 20 °C; (iii) 1,4-dioxane, reflux, 6 h; (iv) DDQ (see Table 6), 1,4-dioxane, reflux, 24 h.

TABLE 6. Products and Yields



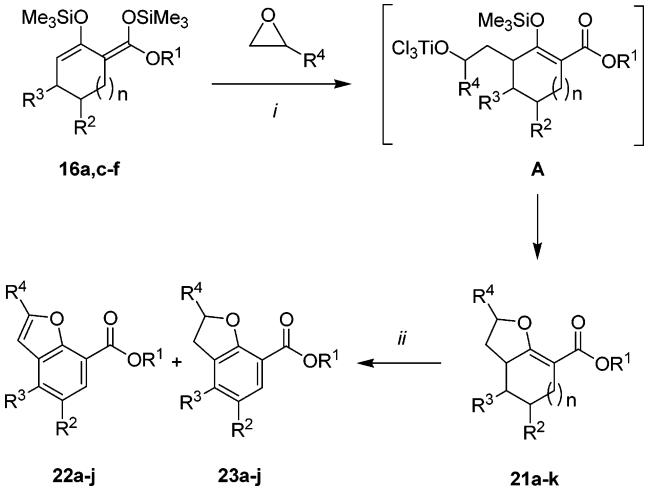
17–19	R^1	R^2	R^3	R^4	% 17[a,b]	% 18[a,d]	% 19[a]	method	DDQ (equiv)
a	Et	H	H	H	38[c]	100[c]	53	A	5.0
							53	B	4.0
b	Et	Me	H	H	71	100	–[g]	A	–[g]
							75	B	3.0
c	Me	H	Me	H	90	97	53	A	5.0
							–[g]	B	–[g]
d	Me	H	Ph	H	85[c]	100[c]	46[e]	A	4.0
							66[f]	B	3.0
e	Et	H	H	Me	60[c]	100[c]	62	A	5.0
							–[g]	B	–[g]

[a] Isolated yields. [b] Yields over two steps; **17a,e** were isolated as a single diastereomer; **17b–d** were isolated as separable mixtures of diastereomers (the yields refer to the combined yield of the separated diastereomers). [c] See ref 15a. [d] **18b–d** were isolated as a 1:1 mixture of diastereomers. [e] **20** was isolated as a side product (30%). [f] **20** was isolated as a side product (7%). [g] Experiment was not carried out.

of **17a,b,d** (in the *absence* of DDQ) afforded the 4,5,6,7-tetrahydrobenzofurans **18a,b,d**,[15a] which were isolated and subsequently transformed into benzofurans **19a,b,d** by treatment with DDQ. The direct oxidation of **17d** (method A) afforded, besides the desired product **19d** (46%), the butenolide **20** in 30% yield. The DDQ-mediated dehydrogenation of **18d**, available from **17d** in quantitative yield (method B), afforded **19d** in better yield (66%); side product **20** was formed in only 7% yield. In conclusion, method B seems to be superior to method A for the synthesis of benzofurans **19**.

Synthesis of 2-Alkylbenzofurans and 2-Alkyl-2,3-dihydrobenzofurans Based on Cyclizations of 1,3-Bis-silyl Enol Ethers with Epoxides. Some years ago, we reported the synthesis of *monocyclic* 2-alkylidenetetrahydrofurans by $TiCl_4$-mediated cyclization of *open-chained* 1,3-bis-silyl enol ethers with epoxides.[17] Our

SCHEME 7. Synthesis of 5,6- and 5,7-Bicyclic 2-Alkylidenetetrahydrofurans 21a–k, 2-Alkylbenzofurans 22a–j, and 2-Alkyl-2,3-dihydrobenzofurans 23a–j[a]



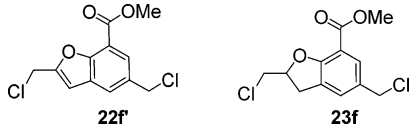
[a] Reagents and conditions: (i) (1) epoxide, $TiCl_4$ (2.0 equiv), 4 Å molecular sieves, CH_2Cl_2, −78 °C, 4 h, (2) −78 → 20 °C, 14 h, (3) 20 °C, 3 h; (ii) DDQ (see Table 7), 1,4-dioxane, reflux, 24 h.

initial attempts to prepare *bicyclic* 2-alkylidenetetrahydrofurans **21** by cyclization of *cyclic* 1,3-bis-silyl enol ethers **16** with epoxides, according to the original protocol,[17] failed. The synthesis of the desired products was eventually accomplished by thorough optimization of concentration, temperature, and reaction time. During the optimization, it proved to be important to keep the temperature at −78 °C for 4 h and to subsequently elevate the temperature very slowly [conditions: (1) −78 °C, 4 h; (2) −78 → 20 °C, 14 h; (3) 20 °C, 3 h]. This can be explained by the fact that the first attack of the bis-silyl enol ether onto the epoxide occurs at low temperature, and the cyclization occurred by warming of the reaction mixture. Notably, the reactions had to be carried out in significantly higher concentration (4 mL/mmol) than previously reported (17 mL/mmol).[17] A high quality of all starting materials proved to be mandatory. The yields of 2-alkyl-2,3,3a,4,5,6-hexahydrobenzofurans **21a–j** and of **21k** are relatively low, due to the formation of open-chained side products derived from intermediate **A** (Scheme 7, Table 7). In addition, a $TiCl_4$-mediated oxidation of the 1,3-bis-silyl enol ethers cannot be excluded.

The $TiCl_4$-mediated cyclization of 1,3-bis-silyl enol ether **16a** with propenoxide, epichlorohydrin, and epibromohydrin afforded the 2-alkyl-2,3,3a,4,5,6-hexahydrobenzofurans **21a–c** (Scheme 7, Table 7). The dehydrogenation of **21a–c** by DDQ afforded the 2-methyl-, 2-(chloromethyl)-, and 2-(bromomethyl)benzofurans **22a–c** and 2,3-dihydrobenzofurans **23b,c**. Hexahydrobenzofurans **21d–j** were prepared by cyclization of 1,3-bis-silyl enol ethers **16c–e**, available from methyl- and phenyl-substituted 2-oxocyclohexane-1-carboxylates, with various epoxides. The DDQ-mediated dehydrogenation of **21d,g–i** gave the 2,5-dialkylbenzofurans **22d,g–i** and 2,3-dihydrobenzofurans **23h,i**. The reaction of 2-(chloromethyl)-5-methyl-2,3,3a,4,5,6-hexahydrobenzofuran **21f** with DDQ gave 2-(chloromethyl)-5-methylbenzofuran **22f**, 2,5-bis(chloromethyl)benzofuran **22f′**, and 2,5-bis-(chloromethyl)-2,3-dihydrobenzofuran **23f**. The formation of **22f′** and **23f** can be explained by DDQ-mediated chlorination of the methyl group (vide supra). The reaction of DDQ with **21j** afforded 2-(chloromethyl)-4-methylbenzofuran **22j** and 2,3-dihydrobenzofuran **23j**. Notably, employment of an excess of DDQ and extension of the reaction time did *not* improve the yield of 2-alkylbenzofurans **22**. The 5,7-bicyclic 2-alkylidenetetrahydrofuran **21k** was prepared by cyclization of 1,3-bis-silyl enol ether **16f** with epichlorohydrin. The reaction of **21k** with DDQ gave complex mixtures under several conditions, due to oxidation of the cycloheptane moiety. Unfortunately, the use of an excess of DDQ did not result in complete oxidation of **21k**.

Interestingly, the oxidation of *monocyclic* 2-alkylidenetetrahydrofurans containing a substituent at carbon atom C-5 failed (Scheme 8). For example, no conversion was obtained in the reaction of DDQ with the known 2-alkylidenetetrahydrofurans **25a,b**,which are available by cyclization of 1,3-bis-silyl enol ether **24** with epoxides.[17] On the basis of this observation, the formation of significant amounts of 2,3-dihydrobenzofurans **23** during the oxidation of **21** can be rationalized. In fact, the

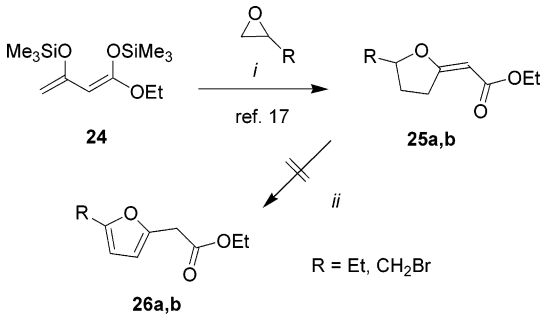
TABLE 7. Products and Yields



21–23	*n*	R^1	R^2	R^3	R^4	% **21**[a,b]	% **22**[a]	% **23**[a]	DDQ (equiv)
a	1	Et	H	H	Me	28	60	0	5.0
b	1	Et	H	H	CH_2Cl	46	30	52	5.0
c	1	Et	H	H	CH_2Br	42	18	42	3.0
d	1	Me	Me	H	Me	30	65	0	5.0
e	1	Me	Me	H	Et	21	—[c]	—[c]	—[c]
f	1	Me	Me	H	CH_2Cl	40	20[d]	20[e]	5.0
g	1	Me	Ph	H	Me	32	63	0	5.0
h	1	Me	Ph	H	CH_2Cl	42	15	80	3.0
i	1	Me	Ph	H	CH_2Br	37	31	40	5.0
j	1	Et	H	Me	CH_2Cl	57	20	38	3.0
k	2	Me	H	H	CH_2Cl	51	0[f]	0[f]	3.0

[a] Isolated yields. [b] Yields of **21a–e,g,i–k** refer to a mixture of inseparable diastereomers (see Experimental Section); yields of **21f,h** refer to combined yields of separated diastereomers (see Experimental Section). [c] Experiment not carried out. [d] **22f′** was isolated as a side product (10%). [e] The structure of **23f** is given. [f] Decomposition.

SCHEME 8. Attempted Oxidation of 2-Alkylidenetetrahydrofurans 25a,b[a]



[a] Reagents and conditions: (i) (1) epoxide, $TiCl_4$ (2.0 equiv), 4 Å molecular sieves, CH_2Cl_2, −78 °C, 4 h, (2) −78 → 20 °C, 14 h, (3) 20 °C, 3 h; (ii) DDQ (2 equiv), 1,4-dioxane, reflux, 24 h.

presence of a substituent located at carbon atom C-5 appears to be disfavorable for a clean oxidation to occur, presumably due to steric hindrance during the attack of DDQ onto carbon atom C-5.

In conclusion, a variety of furan-2-ylacetates were prepared by dehydrogenation of monocyclic 2-alkylidenetetrahydrofurans, which are readily available by cyclizations of open-chained 1,3-dicarbonyl dianions with 1-bromo-2-chloroethane. 5′*H*-[2,3′]Bifuranyl-2′-ones are available by sequential cyclization/dehydrogenation reactions of α-acetyl-γ-butyrolactones. A variety of 7-(alkoxycarbonyl)benzofurans and 7-(alkoxycarbonyl)-2,3-dihydrobenzofurans were prepared on the basis of a cyclization/dehydrogenation strategy. These reactions rely on cyclizations of 2-oxocycloalkane-1-carboxylate-derived 1,3-dicarbonyl dianions (free dianions) or 1,3-bis-silyl enol ethers (masked dianions) with various 1,2-dielectrophiles. In several cases, the reactions reported herein give better results for the synthesis of 2,3-dihydrobenzofurans than for benzofurans.

Experimental Section

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, H_2O), or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60−200 mesh) was used. Melting points are uncorrected.

General Procedure for the Cyclization of 1,3-Dicarbonyl Dianions with 1-Bromo-2-chloroethane and *trans*-1,4-Dibromo-2-butene. A THF solution of LDA was prepared by addition of *n*BuLi (2.5 equiv) to a THF solution (10 mL/mmol) of diisopropylamine (2.5 equiv) at 0 °C. To the LDA solution was added the 1,3-dicarbonyl compound (1.0 equiv) at 0 °C and the solution was stirred at 0 °C for 2 h. To the solution was added 1-bromo-2-chloroethane (or *trans*-1,4-dibromo-2-butene) (1.2 equiv) at −78 °C. The temperature was allowed to rise to −20 °C during 6 h, and the solution was stirred at −20 °C for 12 h. Subsequently, the temperature was allowed to rise to 20 °C during 10 h and the solution was stirred at 20 °C for 12 h. To the reaction mixture was added an aqueous solution of HCl (10%, 10 mL/mmol), and the mixture was extracted with diethyl ether (4 × 10 mL/mmol). The combined organic extracts were dried (Na_2SO_4) and filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc) to give 2-alkylidenetetrahydrofurans **2**. The syntheses of **2a,b**, **2d**−**j**[14] and **13a**−**d**[18] have been previously reported.

Isopropyl (Dihydrofuran-2(3*H*)-ylidene)acetate (2c). Starting with isopropyl acetoacetate (**1c**) (7.28 mL, 50.0 mmol), diisopropylamine (17.5 mL, 125.0 mmol), *n*BuLi (78.5 mL, 125.0 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (4.97 mL, 60.0 mmol) in THF (300 mL), ***E*-2c** (5.447 g, 64%) and ***Z*-2c** (1.091 g, 13%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish oils (combined yield: 77%). ***E*-2c**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (d, J = 6.3 Hz, 6 H, 2 × CH_3), 2.09 (quint, J = 7.5 Hz, 2 H, CH_2), 3.10 (dt, J = 1.9, 7.8 Hz, 2 H, CH_2), 4.21 (t, J = 6.9 Hz, 2 H, OCH_2), 5.02 (sept, J = 6.3 Hz, 1 H, OCH), 5.27 (t, J = 1.8 Hz, 1 H, CH=C). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 20.9 (2C), 29.4, 35.7, 65.1, 70.9, 89.0, 164.5, 175.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2981 (s), 2941 (m), 2889 (w), 1733 (s), 1712 (s), 1641 (s), 1459 (w), 1416 (w), 1376 (m), 1311 (m), 1245 (m), 1175 (m), 1107 (s), 1041 (s), 963 (w), 826 (w). ***Z*-2c**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (d, J = 6.3 Hz, 6 H, 2 × CH_3), 2.04 (quint, J = 7.5 Hz, 2 H, CH_2), 2.69 (dt, J = 1.2, 7.8 Hz, 2 H, CH_2), 4.44 (t, J = 6.9 Hz, 2 H, OCH_2), 4.89 (t, J = 1.1 Hz, 1 H, CH=C), 5.03 (sept, J = 6.3 Hz, 1 H, OCH).

Ethyl 3-(2′-Chloroethyl)-2-oxocyclopentanecarboxylate (9a′). Starting with ethyl 2-oxocyclopentane-1-carboxylate (**8a**) (1.48 mL, 10.0 mmol), diisopropylamine (3.51 mL, 25.0 mmol), *n*BuLi (15.7 mL, 25.0 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.91 mL, 11.0 mmol) in THF (70 mL), **9a′** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (0.994 g, 46%, an inseparable 3:1 mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz, major diastereomer): δ = 1.29 (t, J = 7.2 Hz, 3 H, CH_3), 1.43−1.57 (m, 1 H, CH_2), 1.71−1.95 (m, 2 H, CH_2), 2.08−2.17 (m, 1 H, CH_2), 2.18−2.39 (m, 2 H, CH_2), 2.41−2.55 (m, 1 H, CH), 3.12−3.20 (m, 1 H, CH), 3.55 − 3.75 (m, 2 H, CH_2Cl), 4.19 (q, J = 7.2 Hz, 2 H, OCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, major diastereomer): δ_C = 14.0, 24.9, 26.9, 32.3, 42.7, 46.6, 54.5, 61.2, 169.1, 212.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2980 (m), 1752 (s), 1724 (s), 1453 (w), 1370 (m), 1337 (m), 1299 (m), 1252 (m), 1193 (s), 1153 (m), 1134 (m), 1114 (m), 1023 (w). MS (EI, 70 eV): *m/z* (%) = 221 (M^+ [^{37}Cl], 1), 219 (M^+ [^{35}Cl], 10), 173 (21), 156 (100), 145 (7), 128 (16), 110 (91), 81 (45). Anal. Calcd for $C_{10}H_{15}ClO_3$ (218.680): C 54.93, H 6.91. Found: C 54.91, H 7.02.

Ethyl 3,3a,4,5-Tetrahydro-2*H*-cyclopenta[*b*]furan-6-carboxylate (9a). Starting with **9a′** (0.400 g, 1.83 mmol) and DBU (0.55 mL, 3.66 mmol) in THF (10 mL), **9a** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 50:1 → 1:1) as a yellowish oil (0.207 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.30 (t, J = 7.2 Hz, 3 H, CH_3), 1.50−1.63 (m, 1 H, CH_2), 1.68−1.82 (m, 1 H, CH_2), 2.06−2.19 (m, 1 H, CH_2), 2.80−2.87 (m, 2 H, CH_2), 3.28−3.40 (m, 1 H, CH), 4.15−4.26 (m, 2 H, OCH_2CH_3), 4.60−4.68 (m, 1 H, OCH_2), 4.85 (t, J = 8.45 Hz, 1 H, OCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.1, 28.4, 30.1, 34.1, 49.4, 59.0, 80.8, 94.6, 164.4, 175.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2980 (s), 2940 (m), 2905 (m), 2866 (m), 1732 (s), 1688 (s), 1660 (s), 1464 (m), 1447 (m), 1412 (s), 1386 (m), 1366 (m), 1329 (s), 1295 (s), 1281 (s), 1263 (s), 1204 (s), 1187 (s), 1169 (m), 1158 (m), 1125 (s), 1095 (m), 1072 (m), 1045 (s), 1027 (m), 977 (w), 966 (w), 948 (w), 916 (m), 839 (w), 772 (w). MS (EI, 70 eV): *m/z* (%) = 182 (M^+, 68), 167 (1), 153 (45), 137 (100), 109 (60). The exact molecular mass *m/z* = 182.0943 ± 2 ppm [M^+] for $C_{10}H_{14}O_3$ was confirmed by HRMS (EI, 70 eV).

Ethyl 2,3,3a,4,5,6,7,8-Octahydrocycloocta[*b*]furan-9-carboxylate (9b). Starting with 2-oxocyclooctane-1-carboxylate (**8b**) (1.983 g, 10.0 mmol), diisopropylamine (3.51 mL, 25.0 mmol), *n*BuLi (15.7 mL, 25.0 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.92 mL, 11.0 mmol) in THF (100 mL), **9b** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (0.961 g, 43%, an inseparable 1:1 mixture of *E*/*Z* diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.24−1.30 (dt, J = 7.2 Hz, 3 H, CH_3), 1.33−1.63 (m, 4 H, 2 × CH_2), 1.64−1.83 (m, 4 H, 2 × CH_2), 2.01−2.13 (m, 1 H, CH_2), 2.19−2.37 (m, 2 H, CH_2), 2.68−2.98 (m, 1 H, CH_2), 3.05−3.19 (m, 1 H, CH), 4.09−4.22 (m, 2 H, OCH_2CH_3), 4.30−4.58 (m, 2 H, OCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, both diastereomers): δ_C = 14.0, 14.3, 24.9, 25.0, 25.6, 26.0, 26.2, 26.3, 28.8, 29.1, 31.0, 31.5, 35.6 (2C), 42.9, 43.7, 59.2, 60.1, 71.3, 72.2, 83.4, 98.4, 166.8, 171.1, 173.7, 176.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2927 (s), 2854 (s), 1739 (s), 1707 (s), 1677 (s), 1622 (s), 1586 (s), 1450 (s), 1386 (s), 1327 (m), 1302 (s), 1273 (m), 1195 (s), 1167 (s), 1139 (s), 1117 (s), 1095 (s), 1054 (s), 1026 (m), 986 (m), 878 (w), 749 (w). MS (EI, 70 eV): *m/z* (%) = 224 (M^+, 14), 179 (100), 150 (17). Anal. Calcd for $C_{13}H_{20}O_3$ (224.299): C 69.61, H 8.99. Found: C 69.46, H 8.46.

Ethyl 2,3,3a,4,5,6,7,8,9,10,11,12-Dodecahydrocyclododeca[*b*]furan-13-carboxylate (9c). Starting with 2-oxocyclododecane-1-carboxylate (**8c**) (1.272 g, 5.0 mmol), diisopropylamine (1.80 mL, 12.5 mmol), *n*BuLi (79 mL, 12.5 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.46 mL, 5.5 mmol) in THF (50 mL), **9c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 50:1 → 1:1) as a yellowish solid (0.793 g, 57%). Mp = 80 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ =

1.28 (t, J = 7.2 Hz, 3 H, CH_3), 1.30−1.58 (m, 14 H, 7 × CH_2), 1.62−1.80 (m, 4 H, 2 × CH_2), 2.05−2.28 (m, 2 H, CH_2), 3.08−3.16 (m, 1 H, CH), 4.11−4.26 (m, 2 H, OCH_2CH$_3$), 4.27−4.36 (m, 1 H, OCH_2). 4.44 (dt, J = 0.9, 9.0 Hz, 1 H, OCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 21.8, 23.2, 25.3, 26.2, 26.7, 27.2, 27.6, 27.7, 29.3, 31.5, 40.6, 59.5, 71.2, 101.4, 167.3, 170.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2975 (m), 2928 (s), 2905 (s), 2858 (m), 1670 (s), 1628 (s), 1467 (w), 1445 (w), 1394 (w), 1376 (m), 1332 (w), 1308 (m), 1291 (w), 1195 (m), 1165 (s), 1136 (s), 1117(w), 1099 (w), 1032 (m), 868 (w). MS (EI, 70 eV): m/z (%) = 280 (M^+, 100), 235 (91), 207 (22). Anal. Calcd for $C_{17}H_{28}O_3$ (280.406): C 72.82, H 10.06. Found: C 72.57, H 10.24.

Ethyl 2,3,3a,4,5,6-Hexahydrobenzofuran-7-carboxylate (9d). Starting with ethyl 2-oxocyclohexane-1-carboxylate (**8d**) (1.400 g, 8.23 mmol), diisopropylamine (5.3 mL, 37.5 mmol), nBuLi (23.6 mL, 37.5 mmol, 15% in n-hexane), and 1-bromo-2-chloroethane (0.87 mL, 10.5 mmol) in THF (50 mL), **9d** was isolated after chromatography (silica gel, n-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (0.683 g, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (t, J = 7.2 Hz, 3 H, CH_3), 1.38−1.55 (m, 1 H, CH_2), 1.57−1.77 (m, 1 H, CH_2), 1.90−1.99 (m, 1 H, CH_2), 2.07−2.15 (m, 1 H, CH_2), 2.17−2.34 (m, 2 H, CH_2), 2.36−2.44 (m, 1 H, CH_2), 2.55−2.67 (m, 1 H, CH_2), 4.11−4.27 (m, 2 H, OCH_2), 4.17 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 4.45 (t, J = 8.4 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.2, 22.1, 23.7, 27.3, 30.5, 40.9, 59.2, 71.0, 96.7, 166.8, 168.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2979 (w), 2937 (m), 2904 (w), 2862 (w), 1738 (m), 1711 (s), 1681 (s), 1651 (s), 1449 (w), 1398 (w), 1381 (w), 1303 (m), 1297 (m), 1270 (m), 1245 (m), 1223 (w), 1197 (s), 1180 (m), 1163 (m), 1145 (s), 1108 (m), 1075 (s), 1045 (w), 1024 (w), 996 (w), 909 (w). MS (EI, 70 eV): m/z (%) = 196 (M^+, 49), 168 (97), 150 (82), 122 (100). Anal. Calcd for $C_{11}H_{16}O_3$ (196.246): C 67.32, H 8.22. Found: C 66.96, H 8.38.

Methyl 5-Methyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (9e). Starting with methyl 5-methyl-2-oxocyclohexane-1-carboxylate (**8e**) (5.106 g, 30.0 mmol), diisopropylamine (11 mL, 75.0 mmol), nBuLi (30 mL, 75.0 mmol, 2.5 M solution in n-hexane), and 1-bromo-2-chloroethane (3 mL, 36.0 mmol) in THF (200 mL), **9e** was isolated after chromatography (silica gel, n-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish oil (2.751 g, 47%, an inseparable 1:1 mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (dd, J = 6.6, 1.5 Hz, 3 H, CH_3), 1.42−1.56 (m, 1 H, CH), 1.60−1.76 (m, 2 H, CH_2), 1.77−1.92 (m, 1 H, CH_2), 1.97−2.03 (m, 1 H, CH_2), 2.18−2.26 (m, 1 H, CH_2), 2.35−2.48 (m, 1 H, CH_2), 2.65−2.80 (m, 1 H, CH), 3.70 (s, 3 H, OCH_3), 4.11−4.21 (m, 1 H, OCH_2), 4.44 (t, J = 8.4 Hz, 1 H, OCH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 21.1, 27.8, 29.4, 32.5, 35.2, 41.1, 50.2, 71.1, 95.6, 166.6, 167.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2953 (m), 2927 (m), 2876 (w), 2850 (w), 1745 (m), 1712 (s), 1685 (s), 1656 (s), 1440 (s), 1386 (m), 1386 (m), 1355 (w), 1325 (m), 1274 (s), 1252 (s), 1207 (s), 1147 (s), 1120 (m), 1088 (w), 1051 (w), 1022 (w), 989 (w), 931 (w), 775 (w). MS (EI, 70 eV): m/z (%) = 196 (M^+, 2), 168 (9), 165 (3), 154 (16), 137 (4), 108 (6), 96 (4), 87 (100), 81 (20). HRMS (ESI): calcd for $C_{11}H_{16}O_3$ ([M + 1]$^+$) 197.11777, found 197.11703.

Methyl 5-Methyl-2-vinyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (13b). Starting with 5-methyl-2-oxocyclohexane-1-carboxylate (**8e**) (3.404 g, 20.0 mmol), diisopropylamine (7.03 mL, 50.0 mmol), nBuLi (50.0 mmol, 2.5 M solution in n-hexane, 20 mL), and *trans*-1,4-dibromo-2-butene (5.134 g, 24.0 mmol) in THF (200 mL), **13b** was isolated after chromatography (silica gel, n-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (2.820 g, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.05 (d, J = 6.6 Hz, 3 H, CH_3), 1.36−1.48 (m, 1 H, CH), 1.68−1.81 (m, 2 H, CH_2), 1.85−2.03 (m, 2 H, CH_2), 2.27−2.35 (m, 1 H, CH_2), 2.43−2.52 (m, 1 H, CH_2), 2.75−2.82 (m, 1 H, CH), 3.73 (s, 3 H, OCH_3), 4.78−4.85 (m, 1 H, OCH), 5.24 (dt, J = 10.5, 1.2 Hz, 1 H, CH_2=CH), 5.40 (dt, J = 17.4, 1.2 Hz, CH_2=CH), 5.87−5.96 (m, 1 H, CH=CH$_2$). ^{13}C NMR $CDCl_3$, 75 MHz): δ_C = 21.4, 28.8, 32.8, 35.5, 36.8, 42.0, 50.3, 83.6, 95.7, 116.9, 136.0, 166.6, 167.2. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2951 (m), 2925 (m), 2873 (w), 1712 (m), 1685 (s), 1653 (s), 1585 (w), 1437 (m), 1378 (m), 1336 (m), 1303 (m), 1271 (s), 1243 (m), 1193 (s), 1143 (s), 1104 (m), 1037 (m), 990 (m), 931 (m), 858 (w), 775 (w), 733 (w). MS (EI, 70 eV): m/z (%) = 222 (M^+, 61), 191 (17), 170 (55), 161 (19), 139 (46), 106 (31), 93 (31), 81 (100). Anal. Calcd for $C_{13}H_{18}O_3$ (222.283): C 70.25, H 8.16. Found: C 70.04, H 8.12.

General Procedure for the Synthesis of Benzofurans Based on Sequential Cyclization/Elimination Reactions of 1,3-Bis-silyl Enol Ethers with 1-Chloro-2,2-dimethoxyethane. To a CH_2Cl_2 solution (4 mL/mmol) of 1,3-bis-silyl enol ether **16** (1.0 equiv) and 1-chloro-2,2-dimethoxyethane (1.2 equiv) was added Me_3SiOTf (0.5 equiv) at −78 °C, and the solution was stirred for 2 h at −78 °C. The temperature was allowed to rise to 20 °C during 14 h and the solution was stirred for 3 h at 20 °C. To the solution was added a saturated aqueous solution of $NaHCO_3$, the organic layer was separated, and the aqueous layer was repeatedly extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo to give the open-chained intermediate. The latter was dissolved in THF (3 mL/mmol) and to the solution was added DBU (2.0 equiv). The reaction mixture was stirred for 12 h at 20 °C. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, n-hexane/EtOAc) to give **17**. The synthesis of **17a,d,e** has been previously reported.[15]

Ethyl 3-Methoxy-6-methyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (17b). Starting with 1,3-bis-silyl enol ether **16b** (3.286 g, 10.0 mmol), 1-chloro-2,2-dimethoxyethane (1.4 mL, 12.0 mmol), and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), the open-chained intermediate was isolated without further purification as a brownish oil. Starting with the intermediate (2.758 g, 10.0 mmol) and DBU (3.0 mL, 20.0 mmol) in THF (30 mL), **17b** was isolated by chromatography (silica gel, n-hexane/EtOAc = 100:1 → 1:1) in the form of fraction **17b$_1$** (0.642 g, 27% over two steps, an inseparable 2:1 mixture of diastereomers) and fraction **17b$_2$** (1.051 g, 44% over two steps, an inseparable 2:1 mixture of diastereomers) as yellowish and brownish oils, respectively (combined yield: 71% over two steps).

17b$_1$: ^{1}H NMR ($CDCl_3$, 300 MHz, major diastereomer): δ = 1.06 (d, J = 6.9 Hz, 3 H, CH_3), 1.28 (t, J = 7.2 Hz, 3 H, CH_3), 1.51−1.69 (m, 2 H, CH_2), 1.88−2.08 (m, 2 H, CH_2), 2.59−2.69 (m, 1 H, CH), 2.78−2.84 (m, 1 H, CH), 3.44 (s, 3 H, OCH_3), 3.80 (dd, J = 9.6, 6.6 Hz, 1 H, OCH_2), 3.90 (t, J = 8.4 Hz, 1 H, OCH_2), 4.20 (q, J = 7.2 Hz, 2 H, OCH_2), 4.54 (dd, J = 8.4, 6.9 Hz, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz, major diastereomer): δ_C = 14.2, 21.5, 22.0, 27.6, 29.4, 46.9, 58.5, 59.4, 73.2, 82.1, 104.1, 166.0, 166.2. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2930 (m), 2869 (w), 1736 (m), 1706 (s), 1683 (s), 1648 (s), 1576 (w), 1552 (w), 1453 (s), 1399 (m), 1374 (m), 1346 (w), 1322 (w), 1277 (m), 1259 (m), 1227 (m), 1199 (m), 1142 (s), 1095 (s), 1073 (m), 1031 (m), 987 (w), 792 (w). MS (EI, 70 eV): m/z (%) = 240 (M^+, 17), 225 (100), 195 (23), 181 (31), 167 (24), 147 (13), 135 (33), 85 (22). HRMS (ESI): calcd for $C_{13}H_{20}O_4$ ([M + 1]$^+$) 241.14398, found 241.14341. Anal. Calcd for $C_{13}H_{20}O_4$ (240.299): C 64.98, H 8.39. Found C 64.46, H 8.35.

17b$_2$: ^{1}H NMR ($CDCl_3$, 300 MHz): (major diastereomer) δ = 1.05 (d, J = 6.9 Hz, 3 H, CH_3), 1.26 (t, J = 7.2 Hz, 3 H, CH_3), 1.60−1.74 (m, 2 H, CH_2), 1.80−1.89 (m, 1 H, CH), 1.93−2.04 (m, 1 H, CH), 2.63−2.69 (m, 2 H, CH_2), 3.33 (s, 3 H, OCH_3), 3.87−3.90 (m, 1 H, OCH_2), 4.13−4.25 (m, 3 H, 2 × OCH_2), 4.43 (d, J = 10.5 Hz, 1 H, OCH); (minor diastereomer) δ = 1.10 (d, J = 6.9 Hz, 3 H, CH_3), 1.26 (t, J = 7.2 Hz, 3 H, CH_3), 1.60−1.74 (m, 2 H, CH_2), 1.80−1.89 (m, 1 H, CH), 1.93−2.04 (m, 1 H, CH), 2.69−2.80 (m, 2 H, CH_2), 3.34 (s, 3 H, OCH_3), 3.87−3.90 (m, 1 H, OCH_2), 4.13−4.25 (m, 3 H, 2 × OCH_2), 4.51 (d, J = 10.2 Hz, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz): (major diastereomer) δ_C = 14.3, 21.0, 21.6, 29.8, 31.8, 45.2, 57.0, 59.4, 74.1, 79.2, 104.4, 165.4, 166.8; (minor diastereomer) δ_C = 14.3, 16.8, 22.0, 28.0, 29.77, 46.5, 56.9, 59.3, 74.5, 78.9, 103.3, 166.5, 166.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2979 (m),

2938 (s), 2874 (m), 2831 (w), 1705 (s), 1682 (s), 1646 (s), 1460 (m), 1390 (m), 1375 (m), 1327 (w), 1294 (m), 1267 (s), 1232 (m), 1200 (s), 1158 (s), 1121 (s), 1071 (s), 1031 (s), 963 (w), 938 (w), 900 (w), 851 (w), 785 (w), 756 (w). MS (EI, 70 eV): *m/z* (%) = 240 (M^+, 18), 225 (100), 195 (31), 182 (31), 179 (7), 167 (32), 146 (6), 135 (29), 85 (36). Anal. Calcd for $C_{13}H_{20}O_4$ (240.299): C 64.98, H 8.39. Found: C 64.87, H 7.98.

Methyl 3-Methoxy-5-methyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (17c). Starting with **16c** (3.146 g, 10.0 mmol), 1-chloro-2,2-dimethoxyethane (1.4 mL, 12.0 mmol), and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), the open-chained intermediate was isolated without further purification as a brownish oil. Starting with the intermediate (2.617 g, 10.0 mmol) and DBU (3.0 mL, 20.0 mmol) in THF (30 mL), **17c$_1$** (0.758 g, 34% over two steps, dr > 98:2) and **17c$_2$** (1.268 g, 56% over two steps, dr > 98:2) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil and brownish solid, respectively (combined yield: 90% over two steps).

Diastereomer 17c$_1$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (d, J = 6.5 Hz, 3 H, CH_3), 1.63−1.78 (m, 2 H, CH_2), 1.82−1.92 (m, 1 H, CH), 2.08−2.15 (m, 1 H, CH_2), 2.41−2.49 (m, 1 H, CH_2), 2.69−2.80 (m, 1 H, CH), 3.44 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.74−3.80 (m, 1 H, OCH_2), 3.95 (t, J = 8.6 Hz, 1 H, OCH_2), 4.53 (dd, J = 8.5, 6.9 Hz, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 21.2, 28.4, 32.3, 34.2, 46.5, 50.5, 58.1, 73.1, 81.6, 97.6, 165.9, 166.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2951 (s), 2898 (m), 2847 (w), 1709 (s), 1687 (s), 1657 (s), 1439 (m), 1395 (m), 1358 (m), 1311 (m), 1267 (s), 1201 (s), 1140 (s), 1109 (s), 1050 (m), 1018 (m), 977 (m), 777 (w). MS (EI, 70 eV): *m/z* (%) = 226 (M^+, 44), 195 (24), 168 (76), 53 (100), 136 (29), 121 (16), 93 (30). Anal. Calcd for $C_{12}H_{18}O_4$ (226.272): C 63.70, H 8.02. Found: C 63.64, H 8.00.

Diastereomer 17c$_2$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.08 (d, J = 6.4 Hz, 3 H, CH_3), 1.73−1.96 (m, 2 H, CH_2), 2.07−2.21 (m, 1 H, CH), 2.42−2 54 (m, 2 H, CH_2), 2.76−2.83 (m, 1 H, CH), 3.34 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.89 (dd, J = 4.7, 2.8 Hz, 1 H, OCH_2), 4.19 (dd, J = 10.5, 2.8 Hz, 1 H, OCH_2), 4.52 (d, J = 10.5 Hz, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 20.9, 28.2, 28.9, 32.1, 45.5, 49.7, 56.0, 74.1, 78.1, 95.9, 165.9, 166.1. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2950 (m), 2897 (w), 1710 (s), 1687 (w,), 1642 (s), 1436 (w), 1267 (m), 1204 (s), 1153 (m), 1122 (s), 1092 (w), 1066 (m), 1029 (w). MS (EI, 70 eV): *m/z* (%) = 226 (M^+, 36), 195 (31), 168 (100), 153 (80), 136 (42), 121 (13). Anal. Calcd for $C_{12}H_{18}O_4$ (226.272): C 63.70, H 8.02. Found: C 63.39, H 8.05.

General Procedure for the Cyclization of Cyclic 1,3-Bis-silyl Enol Ethers with Epoxides. To a CH_2Cl_2 solution (4 mL/mmol) of 1,3-bis-silyl enol ethers **16** (1.0 equiv) and the epoxide (1.2 equiv), in the presence of molecular sieves (4 Å), was added $TiCl_4$ (2.0 equiv) at −78 °C. The solution was stirred for 4 h at −78 °C; subsequently, the temperature was allowed to rise to 20 °C during 14 h and the solution was stirred for 3 h at 20 °C. The molecular sieves were filtered off and washed with CH_2Cl_2. To the solution was added a saturated aqueous solution of $NaHCO_3$, the organic layer was separated, and the aqueous layer was repeatedly extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc) to give the 2-alkyl 2,3,3a,4,5,6-hexahydrobenzofurans **21**.

Ethyl 2-Methyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21a). Starting with 1,3-bis-silyl enol ether **16a** (3.146 g, 10.0 mmol), propenoxide (0.704 g, 12.0 mmol), and $TiCl_4$ (2.2 mL, 20.0 mmol) in CH_2Cl_2 (100 mL), **21a** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (0.590 g, 28%, an inseparable mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.27−1.34 (m, 3 H, CH_3), 1.48 (dd, J = 22.5, 6.6 Hz, 3 H, CH_3), 1.69−1.79 (m, 2 H, CH_2), 1.94−2.13 (m, 2 H, CH_2), 2.22−2.45 (m, 2 H, CH_2), 2.97−3.21 (m, 1 H, CH_2), 3.38−3.48 (m, 1 H, CH_2), 3.61−3.77 (m, 1 H, CH), 4.11−4.24 (m, 2 H, OCH_2), 4.42−4.53 (m, 1 H, OCH). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2976 (w), 2937 (m), 2866 (w), 1737 (s), 1711 (s), 1645 (s), 1449 (m), 1398 (m), 1376 (m), 1305 (m), 1249 (m), 1224 (m), 1199 (m), 1179 (m), 1148 (m), 1094 (m), 1049 (m), 1025 (m), 972 (w), 851 (w). MS (EI, 70 eV): *m/z* (%) = 210 (M^+, 42), 181 (11), 168 (100), 165 (62), 137 (30), 122 (88), 95 (35), 81 (10). HRMS (ESI): calcd for $C_{12}H_{18}O_3$ ($[M + 1]^+$) 211.13342, found 211.13284.

Ethyl 2-(Chloromethyl)-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21b). Starting with 1,3-bis-silyl enol ether **16a** (1.573 g, 5.0 mmol), epichlorohydrin (0.47 mL, 6.0 mmol), and $TiCl_4$ (1.1 mL, 10.0 mmol) in CH_2Cl_2 (100 mL), **21b** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a colorless solid (0.550 g, 46%, an inseparable 10:1 mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz, major diastereomer): δ = 1.28 (t, J = 7.2 Hz, 3 H, CH_3), 1.42−1.54 (m, 2 H, CH_2), 1.68−1.80 (m, 1 H, CH_2), 1.90−1.98 (m, 1 H, CH_2), 2.05−2.12 (m, 1 H, CH_2), 2.21−2.33 (m, 1 H, CH_2), 2.35−2.44 (m, 2 H, CH_2), 2.65−2.79 (m, 1 H, CH), 3.63 (dd, J = 11.4, 6.6 Hz, 1 H, CH_2Cl), 3.80 (dd, J = 11.4, 4.8 Hz, 1 H, CH_2Cl), 4.09−4.26 (m, 2 H, OCH_2), 4.56−4.66 (m, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz, major diastereomer): δ_C = 14.3, 22.0, 23.8, 27.4, 34.7, 41.2, 45.3, 59.4, 81.4, 97.6, 166.6, 166.7. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2977 (m), 2939 (s), 28.63 (m), 1738 (s), 1688 (s), 1451 (m), 1376 (m), 1339 (w), 1297 (s), 1251 (s), 1203 (s), 1174 (m), 1147 (s), 1082 (s), 1031 (s), 968 (w), 909 (w), 774 (w), 747 (w). MS (EI, 70 eV): *m/z* (%) = 246 (M^+ [^{37}Cl], 7), 244 (M^+ [^{35}Cl], 28), 215 (3), 209 (39), 201 (14), 199 (48), 171 (18), 168 (100), 163 (32), 122 (58), 107 (11), 95 (17). Anal. Calcd for $C_{12}H_{17}ClO_3$ (244.718): C 58.90, H 7.00. Found: C 58.39, H 6.92.

Ethyl 2-(Bromomethyl)-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21c). Starting with 1,3-bis-silyl enol ether **16a** (3.146 g, 10.0 mmol), epibromohydrin (1.0 mL, 12.0 mmol), and $TiCl_4$ (2.2 mL, 20.0 mmol) in CH_2Cl_2 (100 mL), **21c** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish oil (1.204 g, 42%, an inseparable 4:1 mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz, major diastereomer): δ = 1.29 (t, J = 7.2 Hz, 3 H, CH_3), 1.37−1.51 (m, 2 H, CH_2), 1.67−1 77 (m, 1 H, CH_2), 1.89−1.99 (m, 1 H, CH_2), 2.05−2.13 (m, 1 H, CH_2), 2.21−2.33 (m, 1 H, CH_2), 2.35−2.40 (m, 1 H, CH_2), 2.42−2.50 (m, 1 H, CH_2), 2.67−2.78 (m, 1 H, CH), 3.45 (dd, J = 10.2, 7.2 Hz, 1 H, CH_2-Br), 3.67 (dd, J = 10.2, 4.8 Hz, 1 H, CH_2Br), 4.11−4.27 (m, 2 H, OCH_2), 4.61 (m, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz, major diastereomer): δ_C = 14.4, 22.1, 23.9, 27.5, 33.3, 36.0, 41.4, 59.6, 81.3, 97.8, 166.7, 166.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2977 (m), 2938 (s), 2861 (m), 1736 (m), 1706 (s), 1677 (s), 1653 (s), 1579 (w), 1574 (w), 1449 (m), 1425 (w), 1706 (s), 1677 (s), 1653 (s), 1579 (w), 1574 (w), 1449 (m), 1425 (w), 1399 (m), 1374 (m), 1342 (w), 1326 (w), 1299 (s), 1257 (s), 1200 (s), 1172 (s), 1147 (s), 1101 (s), 1074 (s), 1022 (s), 908 (w), 888 (w), 858 (w), 823 (w), 774 (w), 721 (w), 650 (w). MS (EI, 70 eV): *m/z* (%) = 300 (M^+ [^{81}Br], 5), 288 (M^+ [^{79}Br], 6), 245 (16), 215 (5), 209 (79), 182 (3), 163 (100), 149 (14), 135 (14), 122 (13), 107 (17), 95 826), 79 (27). HRMS (ESI): calcd for $C_{12}H_{17}BrO_3$ ($[M + 1]^+$) 291.04188 (^{81}Br), 289.04393 (^{79}Br), found 291.04155 (^{81}Br), 289.04354 (^{79}Br).

Methyl 2,5-Dimethyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21d). Starting with 1,3-bis-silyl enol ether **16c** (3.146 g, 10.0 mmol), propenoxide (0.704 g, 12.0 mmol), and $TiCl_4$ (2.2 mL, 20.0 mmol) in CH_2Cl_2 (100 mL), **21d** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish oil (0.634 g, 30%, an inseparable mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.7 (d, J = 6.6 Hz, 3 H, CH_3), 1.21 (d, J = 6.3 Hz, 3 H, CH_3), 1.57−1.65 (m, 1 H, CH), 1.68−1.80 (m, 1 H, CH_2), 1.84−2−01 (m, 2 H, CH_2), 2.09−2.29 (m, 1 H, CH_2), 2.38−2.51 (m, 2 H, CH_2), 2.71−2.88 (m, 1 H, CH), 3.71, 3.72, 3.73 (ts, 3 H, OCH_3), 4.29−4.58 (m, 1 H, OCH). IR (neat, cm^{-1}):

$\tilde{\nu}$ = 2953 (s), 2928 (s), 2875 (m), 1741 (s), 1711 (s), 1687 (s), 1652 (s), 1573 (w), 1442 (s), 1382 (m), 1350 (w), 1271 (s), 1250 (m), 1196 (s), 1148 (s), 1094 (m), 1030 (w), 992 (w), 973 (w), 915 (w). MS (EI, 70 eV): *m/z* (%) = 210 (M^+, 25), 179 (27), 168 (100), 152 (47), 136 (53), 121 (29). HRMS (ESI): calcd for $C_{12}H_{18}O_3$ ([M + 1]$^+$) 211.13342, found 211.13289.

Methyl 2-Ethyl-5-methyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21e). Starting with 1,3-bis-silyl enol ether **16c** (3.146 g, 10.0 mmol), 1,2-butenoxide (1.03 mL, 12.0 mmol), and $TiCl_4$ (2.2 mL, 20.0 mmol) in CH_2Cl_2 (100 mL), **21e** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (0.476 g, 21%, an inseparable mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.97−1.07 (m, 6 H, 2 × CH_3), 1.42−1.51 (m, 1 H, CH), 1.57−1.78 (m, 2 H, CH_2), 1.82−2.05 (m, 2 H, CH_2), 2.10−2.26 (m, 1 H, CH_2), 2.29−2.49 (m, 1 H, CH_2), 2.52−2.70 (m, 1 H, CH), 3.68, 3.73, 3.77 (ts, 3 H, OCH_3), 4.22−4.54 (m, 1 H, OCH). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2954 (s), 2927 (s), 2871 (m), 1742 (s), 1713 (s), 1652 (s), 1620 (m), 1440 (s), 1376 (m), 1265 (s), 1225 (s), 1201 (s), 1149 (s), 1116 (m), 1045 (m), 1018 (m), 972 (w), 946 (w), 848 (w). MS (EI, 70 eV): *m/z* (%) = 224 (M^+, 16), 193 (15), 182 (4), 168 (37), 165 (7), 152 (1009, 136 (23), 121 (15), 93 (20). HRMS (ESI): calcd for $C_{13}H_{20}O_3$ ([M + 1]$^+$) 225.14907, found 225.14882.

Methyl 2-(Chloromethyl)-5-methyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21f). Starting with 1,3-bis-silyl enol ether **16c** (3.146 g, 10.0 mmol), epichlorohydrin (0.94 mL, 12.0 mmol), and $TiCl_4$ (2.2 mL, 20.0 mmol) in CH_2Cl_2 (100 mL), the diastereomers **21f$_1$** (0.506 g, 21%) and **21f$_2$** (0.464 g, 19%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish oils (combined yield: 40%).

Diastereomer 21f$_1$ (containing a small amount of diastereomer **21f$_2$**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.05 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.35−1.51 (m, 1 H, CH), 1.65−1.80 (m, 2 H, CH_2), 1.82−1.92 (m, 1 H, CH_2), 1.94−2.05 (m, 1 H, CH_2), 2.28−2.37 (m, 1 H, CH_2), 2.42−2.54 (m, 1 H, CH_2), 2.78−2.93 (m, 1 H, CH), 3.50−3.58 (m, 1 H, CH_2Cl), 3.68−3.79 (m, 1 H, CH_2Cl), 3.72 (s, 3 H, OCH_3), 4.75−4.82 (m, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 21.3, 29.0, 31.5, 32.6, 35.6, 38.9, 44.1, 50.6, 81.5, 97.1, 166.6, 167.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2954 (s), 2927 (m), 2887 (w), 2871 (w), 1741 (m), 1711 (s), 1691 (s), 1656 (s), 1439 (m), 1377 (m), 1346 (w), 1304 (m), 1273 (s), 1198 (s), 1145 (s), 1110 (m), 1039 (m), 972 (w), 771 (w). MS (EI, 70 eV): *m/z* (%) = 246 (M^+ [^{37}Cl], 6), 244 (M^+ [^{35}Cl], 28), 213 (36), 209 (21), 204 (18), 202 (64), 185 (16), 177 (32), 168 (100), 152 (26), 136 (48), 121 (20), 112 (63), 93 (32). HRMS (ESI): calcd for $C_{12}H_{17}ClO_3$ ([M + 1]$^+$) 247.09150 (^{37}Cl), 245.09445 (^{35}Cl), found 247.09086 (^{37}Cl), 245.09375 (^{35}Cl).

Diastereomer 21f$_2$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.05 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.44−1.55 (m, 1 H, CH), 1.67−1.81 (m, 1 H, CH_2), 1.88 (dd, *J* = 10.8, 3.3 Hz, 1 H, CH_2), 1.94 (dd, *J* = 10.8, 3.3 Hz, 1 H, CH_2), 1.96−2.01 (m, 1 H, CH_2), 2.35−2.51 (m, 2 H, CH_2), 2.77−2.89 (m, 1 H, CH), 3.63 (dd, *J* = 11.4, 6.6 Hz, 1 H, CH_2Cl), 3.72 (s, 3 H, OCH_3), 3.82 (dd, *J* = 11.4, 4.5 Hz, 1 H, CH_2Cl), 4.58−4.68 (m, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 21.5, 29.0, 32.8, 34.4, 35.6, 41.8, 45.2, 50.8, 81.8, 96.9, 166.8, 166.9. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2953 (m), 2925 (m), 2873 (w), 1741 (m), 1712 (s), 1685 (s), 1656 (s), 1574 (w), 1515 (w), 1438 (m), 1379 (m), 1339 (w), 1311 (w), 1271 (s), 1193 (s), 1145 (s), 1105 (m), 1030 (m), 998 (w), 994 (w), 987 (w), 940 (w), 900 (w), 876 (w), 849 (w), 775 (w), 729 (w). MS (EI, 70 eV): *m/z* (%) = 246 (M^+ [^{37}Cl], 5), 244 (M^+ [^{35}Cl], 23), 213 (32), 209 (20), 202 (45), 185 (15), 177 (39), 168 (100), 152 (25), 136 (53), 121 (22), 112 (53), 93 (32). HRMS (ESI): calcd for $C_{12}H_{17}ClO_3$ ([M + 1]$^+$): 247.09150 (^{37}Cl), 245.09445 (^{35}Cl), found 247.09086 (^{37}Cl), 245.09375 (^{35}Cl).

Methyl 2-Methyl-5-phenyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21g). Starting with 1,3-bis-silyl enol ether **16d** (1.889 g, 5.0 mmol), propylene oxide (0.352 g, 6.0 mmol), and $TiCl_4$ (1.1 mL, 10.0 mmol) in CH_2Cl_2 (70 mL), **21g** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish solid (0.441 g, 32%, an inseparable mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.21 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.98−2.55 (m, 5 H, 2 × CH_2, CH), 2.66−2.79 (m, 2 H, CH_2), 2.89−3.09 (m, 1 H, CH), 3.71, 3.78 (ds, 3 H, OCH_3), 4.37−4.59 (m, 1 H, OCH). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2948 (m), 2933 (m), 2867 (w), 1737 (s), 1685 (m), 1655 (s), 1494 (w), 1375 (m), 1321 (w), 1260 (s), 1236 (s), 1202 (m), 1174 (m), 1148 (m), 1115 (m), 1077 (m), 1034 (w), 762 (w), 702 (m). MS (EI, 70 eV): *m/z* (%) = 272 (M^+, 32), 241 (3), 168 (100), 153 (46), 121 (10), 104 (59), 91 (50), 77 (19). HRMS (ESI): calcd for $C_{17}H_{20}O_3$ ([M + 1]$^+$) 273.14907, found 273.14838.

Methyl 2-(Chloromethyl)-5-phenyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21h). Starting with 1,3-bis-silyl enol ether **16d** (1.889 g, 5.0 mmol), epichlorohydrin (0.47 mL, 6.0 mmol), and $TiCl_4$ (1.1 mL, 10.0 mmol) in CH_2Cl_2 (70 mL), the diastereomers **21h$_1$** (0.162 g, 11%), **21h$_2$** (0.280 g, 18%), and **21h$_3$** (0.204 g, 13%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as brownish oils (combined yield: 42%).

Diastereomer 21h$_1$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.49−1.61 (m, 1 H, CH_2), 1.68−1.77 (m, 1 H, CH_2), 2.12−2.27 (m, 2 H, CH_2), 2.37−2.49 (m, 1 H, CH), 2.73−2.77 (m, 2 H, CH_2), 3.36−3.41 (m, 1 H, CH), 3.63−3.86 (m, 2 H, CH_2Cl), 3.79 (s, 3 H, OCH_3), 4.49−4.58 (m, 1 H, CH), 7.17−7.31 (m, 5 H, 5 × CH of Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 28.0, 34.0, 34.1, 36.0, 36.3, 45.2, 51.1, 81.6, 96.7, 126.1, 127.0 (2C), 128.5 (2C), 144.9, 166.9, 167.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 3027 (w), 2947 (m), 2932 (m), 2861 (m), 1741 (s), 1713 (s), 1683 (s), 1654 (s), 1494 (m), 1448 (s), 1439 (s), 1377 (m), 1302 (m), 1260 (s), 1230 (m), 1197 (s), 1147 (s), 1114 (m), 1084 (m), 1034 (m), 977 (w), 919 (w), 903 (w), 848 (w), 758 (m), 740 (m), 703 (m). MS (EI, 70 eV): *m/z* (%) = 308 (M^+ [^{37}Cl], 8), 306 (M^+ [^{35}Cl], 28), 275 (9), 230 (5), 204 (31), 202 (100), 167 (15), 153 (14), 121 (15), 114 (19), 112 (31), 104 (17), 93 (15), 91 (21), 77 (11). The exact molecular mass *m/z* = 306.1023 ± 2 ppm [M^+] for $C_{17}H_{19}ClO_3$ was confirmed by HRMS (EI, 70 eV).

Diastereomer 21h$_2$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.58−1.73 (m, 1 H, CH_2), 1.79−1.98 (m, 1 H, CH_2), 2.12−2.24 (m, 2 H, CH_2), 2.32−2.53 (m, 2 H, CH_2), 2.73−2.76 (m, 1 H, CH), 3.32−3.41 (m, 1 H, CH), 3.59−3.79 (m, 2 H, CH_2Cl), 3.78 (s, 3 H, OCH_3), 4.74−4.89 (m, 1 H, CH), 7.18−7.32 (m, 5 H, 5 × CH of Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 31.4, 31.7, 32.8, 33.1, 39.4, 44.0, 51.0, 81.4, 96.9, 126.0, 126.5 (2C), 128.1 (2C), 144.9, 166.8, 167.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3028 (w), 2975 (m), 2945 (m), 2931 (m), 2901 (w), 2863 (m), 1739 (m), 1713 (s), 1686 (s), 1658 (s), 1606 (w), 1580 (w), 1494 (w), 1438 (m), 1277 (m), 1343 (w), 1259 (s), 1229 (m), 1193 (s), 1146 (s), 1116 (m), 1077 (m), 1027 (m), 976 (w), 908 (w), 848 (w), 765 (m), 702 (m). MS (EI, 70 eV): *m/z* (%) = 308 (M^+ [^{37}Cl], 2), 306 (M^+ [^{35}Cl], 14), 275 (2), 256 (6), 204 (21), 202 (71), 167 (7), 153 (13), 136 (16), 121 (100), 114 (13), 112 (19), 104 (9), 91 (22), 77 (15). The exact molecular mass *m/z* = 306.1023 ± 2 ppm [M^+] for $C_{17}H_{19}ClO_3$ was confirmed by HRMS (EI, 70 eV).

Diastereomer 21h$_3$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.55−1.71 (m, 1 H, CH_2), 2.21−2.22 (m, 1 H, CH_2), 2.23−2.26 (m, 1 H, CH_2), 2.33−2.50 (m, 2 H, CH_2), 2.66−2.74 (m, 1 H, CH_2), 2.82−2.94 (m, 1 H, CH), 2.97−3.07 (m, 1 H, CH), 3.65−3.88 (m, 2 H, CH_2Cl), 3.71 (s, 3 H, OCH_3), 4.66−4.76 (m, 1 H, CH), 7.20−7.35 (m, 5 H, 5 × CH of Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 33.0, 34.0, 34.5, 40.4, 42.2, 45.2, 51.0, 82.1, 97.3, 126.4, 126.7 (2C), 128.5 (2C), 145.1, 166.6, 166.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3061 (w), 3027 (w), 2975 (m), 2947 (m), 2860 (m), 1738 (s), 1713 (s), 1687 (s), 1656 (s), 1608 (m), 1494 (m), 1439 (m), 1376 (m), 1302 (m), 1260 (s), 1235 (s)1193 (s), 1144 (s), 1112 (m), 1080 (m), 1047 (m), 1013 (m), 952 (w), 913 (w), 843 (w), 762 (m), 737 (w), 703 (m). MS (EI, 70 eV): *m/z* (%) = 308 (M^+ [^{37}Cl], 7), 307 (3), 306 (M^+ [^{35}Cl], 29), 275 (9), 202 (100), 167 (13), 153 (16), 121 (43), 114 (20), 112 (23), 104 (19), 91 (26), 77 (15). The exact molecular mass *m/z* = 306.1023 ± 2 ppm [M^+] for $C_{17}H_{19}ClO_3$ was confirmed by HRMS (EI, 70 eV).

Methyl 2-(Bromomethyl)-5-phenyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21i). Starting with 1,3-bis-silyl enol ether **16d** (1.889 g, 5.0 mmol), epibromohydrin (0.50 mL, 6.0 mmol), and $TiCl_4$ (1.1 mL, 10.0 mmol) in CH_2Cl_2 (70 mL), **21i** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a brownish solid (0.646 g, 37%, an inseparable mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.55−1.78 (m, 1 H, CH_2), 2.02−2.28 (m, 1 H, CH_2), 2.33−2.49 (m, 1 H, C*H*−Ph), 2.51−2.88 (m, 4 H, 2 × CH), 3.03−3.28 (m, 1 H, CH), 3.72 (s, 3 H, OCH_3), 3.90−3.93 (m, 1 H, CH_2Br), 3.98−4.03 (m, 1 H, CH_2Br), 4.19−4.31 (m, 1 H, OCH), 7.20−7.36 (m, 5 H, 5 × CH of Ph). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2946 (m), 1737 (s), 1717 (s), 1657 (s), 1612 (m), 1495 (w), 1444 (s), 1364 (m), 1337 (m), 1328 (m), 1261 (s), 1229 (s), 1205 (s), 1149 (m), 1111 (w), 1075 (w), 1027 (w), 761 (m), 702 (s). MS (EI, 70 eV): *m/z* (%) = 352 (M^+ [^{81}Br], 3), 350 (M^+ [^{79}Br], 4), 248 (49), 246 (42), 232 (2), 197 (6), 184 (100), 171 (11), 135 (12), 117 (15), 104 (55), 91 (31). HRMS (ESI): calcd for $C_{17}H_{19}BrO_3$ ([M + 1]$^+$) 353.05753 (^{81}Br), 351.05958 (^{79}Br), found 353.05708 (^{81}Br), 351.05903 (^{79}Br).

Ethyl 2-(Chloromethyl)-4-methyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (21j). Starting with 1,3-bis-silyl enol ether **16e** (3.286 g, 10.0 mmol), epichlorohydrin (0.94 mL, 12.0 mmol), and $TiCl_4$ (2.2 mL, 20.0 mmol) in CH_2Cl_2 (100 mL), **21j** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil (1.475 g, 57%, an inseparable mixture of two diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.05 (d, J = 6.6 Hz, 3 H, CH_3), 1.28 (t, J = 7.2 Hz, 3 H, CH_3), 1.39−1.51 (m, 1 H, CH_2), 1.55−1.73 (m, 1 H, CH_2), 1.76−1.89 (m, 1 H, CH), 1.91−2.10 (m, 1 H, CH_2), 2.26−2.41 (m, 3 H, 2 × CH_2), 3.46−3.53 (m, 1 H, CH), 3.66−3.83 (m, 2 H, CH_2Cl), 4.14−4.25 (m, 2 H, OCH_2), 4.58−4.82 (dm, 1 H, OCH). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (m), 2930 (s), 2872 (m), 1739 (s), 1710 (s), 1657 (s), 1453 (m), 1376 (m), 1307 (m), 1268 (m), 1204 (s), 1176 (m), 1151 (s), 1098 (m), 1035 (m), 975 (w), 908 (w), 884 (w), 857 (w), 769 (w), 746 (w). MS (EI, 70 eV): *m/z* (%) = 260 (M^+ [^{37}Cl], 8), 258 (M^+ [^{35}Cl], 28), 243 (17), 229 (14), 223 (34), 213 (54), 209 (11), 197 (8), 185 (55), 182 (100), 167 (80), 150 (9), 136 (56), 123 (17), 108 (22), 93 (20). Anal. Calcd for $C_{13}H_{19}ClO_3$ (258.744): C 60.35, H 7.49. Found: C 60.40; H 7.19.

Methyl 2-(Chloromethyl)-3,3a,4,5,6,7-hexahydro-2*H*-cyclohepta[*b*]furan-8-carboxylate (21k). Starting with 1,3-bis-silyl enol ether **16f** (3.146 g, 10.0 mmol), epichlorohydrin (0.94 mL, 12.0 mmol), and $TiCl_4$ (2.2 mL, 20.0 mmol) in CH_2Cl_2 (100 mL), **21k** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish oil (1.250 g, 51%, an inseparable 1:1 mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz, both diastereomers): δ = 1.19−1.40 (m, 4 H, 2 × CH_2), 1.48−1.68 (m, 4 H, 2 × CH_2), 1.71−1.96 (m, 4 H, 2 × CH_2), 1.98−2.11 (m, 4 H, 2 × CH_2), 2.24−2.33 (m, 1 H, CH), 2.46−2.56 (m, 1 H, CH), 2.82−2.90 (m, 2 H, CH_2), 3.06−3.23 (m, 2 H, CH_2), 3.54−3.80 (m, 4 H, 2 × CH_2-Cl), 3.72 (s, 6 H, 2 × OCH_3), 4.52−4.60 (m, 1 H, OCH), 4.78−4.86 (m, 1 H, OCH). ^{13}C NMR ($CDCl_3$, 75 MHz, both diastereomers): δ_C = 26.5, 26.8, 27.1, 27.2, 30.4, 31.1, 32.7, 33.2, 34.8, 35.4, 44.0, 44.2, 45.6, 45.8, 51.1 (2C), 81.8, 82.0, 102.7, 102.8, 167.9, 168.0, 171.8, 172.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2922 (s), 2852 (m), 1704 (s), 1681 (s), 1636 (s), 1439 (s), 1370 (m), 1329 (w), 1300 (s), 1264 (m), 1182 (s), 1147 (s), 1095 (w), 1048 (s), 1020 (m), 941 (w), 915 (w), 872 (w), 854 (w), 824 (w), 780 (w), 744 (w), 711 (w). MS (EI, 70 eV): *m/z* (%) = 246 (M^+ [^{37}Cl], 8), 244 (M^+ [^{35}Cl], 23), 229 (2), 215 (10), 213 (33), 209 (9), 185 (10), 177 (16), 168 (56), 148 (6), 136 (100), 121 (6), 107 (13), 93 (18), 79 (38). Anal. Calcd for $C_{12}H_{17}ClO_3$ (244.718): C 58.90, H 7.00. Found: C 58.71, H 7.68.

General Procedure for the Synthesis of 4,5,6,7-Tetrahydrobenzofurans (18). A CH_2Cl_2 (or 1,4-dioxane) solution (10 mL/mmol) of **17** (1.0 equiv) was heated under reflux for 6 h. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc) to give **18**. The synthesis of **18a,d** has been previously reported.[15]

Ethyl 6-Methyl-4,5,6,7-tetrahydrobenzofuran-7-carboxylate (18b). Starting with **17b$_2$** (0.300 g, 1.25 mmol) in CH_2Cl_2 (13 mL), **18b** was isolated without further purification as a slightly yellowish oil (0.260 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.09 (d, J = 6.9 Hz, 3 H, CH_3), 1.29 (t, J = 7.2 Hz, 3 H, CH_3), 1.47−1.54 (m, 1 H, CH_2), 1.84−1.93 (m, 1 H, CH_2), 2.24−2.31 (m, 1 H, CH), 2.44−2.53 (m, 2 H, CH_2), 3.32 (d, J = 7.8 Hz, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH_2), 6.20 (d, J = 1 H, CH), 7.27 (d, J = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 19.6, 20.6, 29.9, 33.5, 48.6, 61.0, 110.2, 118.3, 141.6, 146.7, 172.6. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2962 (m), 2930 (m), 2878 (w), 2856 (w), 1735 (s), 1691 (w), 1639 (w), 1503 (w), 1456 (m), 1374 (w), 1309 (w), 1253 (m), 1217 (m), 1185 (s), 1160 (s), 1102 (w), 1030 (m), 737 (m). MS (EI, 70 eV): *m/z* (%) = 208 (M^+, 66), 163 (1), 135 (100), 120 (2), 107 (4), 93 (2), 79 (6), 66 (2). HRMS (ESI): calcd for $C_{12}H_{16}O_3$ ([M + 1]$^+$) 209.11777, found 209.11721.

Methyl 5-Methyl-4,5,6,7-tetrahydrobenzofuran-7-carboxylate (18c). Starting with **17c$_2$** (0.100 g, 0.44 mmol) in 1,4-dioxane (5 mL), **18c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 5:1) as a colorless oil (0.083 g, 97%, an inseparable 1:1 mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz, both diastereomers): δ = 1.06 (d, J = 6.3 Hz, 3 H, CH_3), 1.09 (d, J = 6.5 Hz, 3 H, CH_3), 1.61−1.78 (m, 4 H, 2 × CH_2), 1.80−1.93 (m, 2 H, 2 × CH), 1.98−2.09 (m, 2 H, CH_2), 2.12−2.23 (m, 2 H, CH_2), 2.47−2.61 (m, 2 H, 2 × CH), 3.72 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 6.19 (d, J = 1.9 Hz, 1 H, CH), 6.20 (d, J = 1.9 Hz, 1 H, CH), 7.29 (dd, J = 1.9, 0.9 Hz, 1 H, CH), 7.31 (d, J = 1.9 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz, both diastereomers): δ_C = 21.0, 21.4, 26.8, 29.6, 30.2, 30.3, 34.6, 35.8, 39.3, 41.4, 52.2 (2C), 110.2, 110.3, 119.2, 119.3, 141.75, 141.82, 146.0, 146.4, 173.1, 173.2. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2955 (m), 2926 (m), 2873 (w), 2852 (w), 1741 (s), 1619 (w), 1503 (w), 1452 (m), 1441 (m), 1376 (w), 1340 (w), 1317 (w), 1277 (s), 1250 (m), 1213 (m), 1202 (m), 1169 (s), 1111 (w), 1037 (w), 1000 (w), 736 (m). MS (EI, 70 eV): *m/z* (%) = 194 (M^+, 15), 135 (100). Anal. Calcd for $C_{11}H_{14}O_3$ (194.230): C 68.02, H 7.27. Found: C 67.61, H 7.26.

General Procedure for DDQ-Mediated Dehydrogenation Reactions. To a 1,4-dioxane solution (7 mL/mmol) of the substrate (1.0 equiv) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (1.0−5.0 equiv, depending on the substrate) under argon atmosphere at 20 °C. The mixture was heated under reflux for 48 h and, after cooling to 20 °C, the solvent was removed in vacuo. To the residue was added ether to give a precipitate that was filtered off. The filtrate was concentrated in vacuo and the residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc) to give the products. Notably, the furan derivatives were not UV active (neither at short nor at long wavelength); to detect the products on TLC, the following mixture was used as a dying agent: MeOH/AcOH/anisaldehyde = 85:14:1.

Methyl Furan-2-ylacetate (3a). Starting with **2a** (0.100 g, 0.70 mmol) and DDQ (0.319 g, 1.4 mmol) in 1,4-dioxane (7 mL), **3a** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1→ 50:1) as a colorless oil (0.056 g, 57%). The spectroscopic data were identical with those reported.[15a]

Ethyl Furan-2-ylacetate (3b). Starting with **2b** (0.100 g, 0.64 mmol) and DDQ (0.291 g, 1.3 mmol) in 1,4-dioxane (7 mL), **3b** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1→ 75:1) as a slightly yellowish oil (0.058 g, 59%). The spectroscopic data were identical with those reported.[15a]

Isopropyl Furan-2-ylacetate (3c). Starting with **2c** (0.100 g, 0.59 mmol) and DDQ (0.161 g, 0.71 mmol) in 1,4-dioxane (5 mL), **3c** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 50:1) as a slightly yellowish oil (0.052 g, 52%). The spectroscopic data were identical with those reported.[15a]

***tert*-Butyl Furan-2-ylacetate (3d).** Starting with **2d** (0.100 g, 0.54 mmol) and DDQ (0.246 g, 1.09 mmol) in 1,4-dioxane (10 mL), **3d** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 50:1) as a slightly yellowish oil (0.054 g, 55%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.46 (s, 9 H, O*t*Bu), 3.59 (s, 2 H, CH_2), 6.19−6.21 (m, 1 H, CH), 6.32−6.33 (m, 1 H, CH), 7.35−7.36 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 28.2 (3C), 35.5, 81.5, 107.9, 110.6, 142.1, 148.6, 168.9. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2980 (w), 1739 (s), 1394 (w), 1370 (m), 1340 (w), 1279 (w), 1255 (w), 1234 (m), 1152 (s), 1096 (w), 1013 (w), 734 (w). MS (EI, 70 eV): *m/z* (%) = 183 (M^+, 13), 123 (20), 116 (100), 108 (8), 101 (48), 81 (65). The exact molecular mass *m/z* = 182.0943 ± 2 ppm [M^+] for $C_{10}H_{14}O_3$ was confirmed by HRMS (EI, 70 eV).

Methyl (3-Methylfuran-2-yl)acetate (3e). Starting with **2e** (0.500 g, 3.20 mmol) and DDQ (0.87 g, 3.84 mmol) in 1,4-dioxane (15 mL), **3e** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 50:1) as a colorless oil (0.202 g, 41%). The spectroscopic data were identical with those reported.[15a]

Ethyl (3-Ethylfuran-2-yl)acetate (3f). Starting with **2f** (0.500 g, 2.71 mmol) and DDQ (0.739 g, 3.26 mmol) in 1,4-dioxane (15 mL), **3f** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 50:1) as a colorless oil (0.260 g, 53%). The spectroscopic data were identical with those reported.[15a]

***tert*-Butyl [3-(3′-Methylbutyl)furan-2-yl]acetate (3g).** Starting with **2g** (0.250 g, 0.98 mmol) and DDQ (0.446 g, 1.97 mmol) in 1,4-dioxane (10 mL), **3g** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 75:1) as a yellowish oil (0.133 g, 54%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.91 (d, *J* = 6.6 Hz, 6 H, 2 × CH_3), 1.44 (s, 9 H, O*t*Bu), 1.36−1.48 (m, 2 H, CH_2), 1.51−1.57 (m, 1 H, CH), 2.34 (t, *J* = 7.8 Hz, 2 H, CH_2), 3.52 (s, 2 H, CH_2), 6.23 (d, *J* = 1.8 Hz, 1 H, CH), 7.27 (d, *J* = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 22.61 (2C), 22.62, 27.7, 28.1 (3C), 33.7, 39.6, 81.2, 111.7, 122.0, 141.1, 143.7, 169.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2959 (s), 2932 (s), 2871 (m), 1737 (s), 1640 (m), 1510 (w), 1461 (m), 1392 (m), 1368 (m), 1335 (m), 1257 (m), 1219 (m), 1151 (s), 1107 (m), 1051 (m), 1034 (m), 949 (w), 894 (w), 855 (w), 804 (w), 760 (w), 735 (w). MS (EI, 70 eV): *m/z* (%) = 252 (M^+, 13), 221 (2), 196 (4), 181 (2), 150 (19), 107 (4), 95 (100), 57 (97). HRMS (ESI): calcd for $C_{15}H_{24}O_3$ ([M + 1]$^+$) 253.18036, found 253.18075.

***tert*-Butyl [3-(6′-Chlorohexyl)furan-2-yl]acetate (3h).** Starting with **2h** (0.500 g, 1.65 mmol) and DDQ (0.749 g, 3.30 mmol) in 1,4-dioxane (10 mL), **3h** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 75:1) as a yellowish oil (0.330 g, 67%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.38 (s, 9 H, O*t*Bu), 1.40−1.58 (m, 6 H, 3 × CH_2), 1.78 (quint, *J* = 7.5 Hz, 2 H, CH_2), 2.38 (t, *J* = 7.5 Hz, 2 H, CH_2), 3.51 (s, 2 H, CH_2), 3.53 (t, *J* = 6.6 Hz, 2 H, CH_2Cl), 6.19 (d, *J* = 1.8 Hz, 1 H, CH), 7.22 (d, *J* = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 16.2, 24.9, 27.0, 28.2 (3C), 28.9, 29.9, 32.8, 45.3, 80.9, 111.7, 122.8, 140.7, 148.5, 172.6. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2976 (w), 2934 (m), 2960 (w), 1719 (s), 1686 (w), 1456 (w), 1394 (w), 1368 (w), 1307 (m), 1254 (w), 1201 (w), 1158 (s), 1098 (m), 1036 (w), 846 (w), 746 (w), 739 (w). MS (EI, 70 eV): *m/z* (%) = 302 (M^+ [^{37}Cl], 1), 300 (M^+ [^{35}Cl], 5), 270 (6), 225 (2), 199 (21), 179 (2), 165 (4), 150 (2), 121 (6), 95 (42), 57 (100). Anal. Calcd for $C_{16}H_{25}ClO_3$ (300.825): C 63.88, H 8.38. Found: C 64.57, H 8.35.

Ethyl 2-Furan-2′-ylpropionate (3i). Starting with **2i** (0.100 g, 0.59 mmol) and DDQ (0.267 g, 1.2 mmol) in 1,4-dioxane (5 mL), **3i** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 10:1) as a colorless oil (0.052 g, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.52 (d, *J* = 7.3 Hz, 3 H, CH_3), 3.81 (q, *J* = 7.3 Hz, 1 H, CH), 4.13 (q, *J* = 7.2 Hz, 2 H, OCH_2), 6.17 (dt, *J* = 3.2, 0.8 Hz, 1 H, CH), 6.32 (dd, *J* = 3.2, 1.8 Hz, 1 H, CH), 7.34 (dd, *J* = 1.8, 0.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.1, 15.8, 39.5, 61.0, 105.9, 110.2. 141.7, 153.4, 172.6. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2986 (m), 2937 (w), 1738 (s), 1648 (w), 1505 (w), 1457 (m), 1376 (w), 1322 (m), 1255 (m), 1203 (s), 1169 (s), 1096 (m), 1070 (m), 1017 (m), 927 (w), 793 (w), 738 (s). MS (EI, 70 eV): *m/z* (%) = 168 (M^+, 13), 121 (2), 105 (2), 95 (100), 81 (2), 68 (13). HRMS (ESI): calcd for $C_9H_{12}O_3$ ([M + 1]$^+$) 169.08647, found 169.08574.

Ethyl 2-Furan-2′-ylbutyrate (3j). Starting with **2j** (0.100 g, 0.54 mmol) and DDQ (0.245 g, 1.1 mmol) in 1,4-dioxane (5 mL), **3j** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 30:1) as a colorless oil (0.054 g, 55%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.94 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.25 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.87−2.08 (m, 2 H, CH_2), 3.60 (t, *J* = 7.8 Hz, 1 H, CH), 4.17 (dq, *J* = 7.2, 1.0 Hz, 2 H, OCH_2), 6.19 (dt, *J* = 3.2, 0.8 Hz, 1 H, CH), 6.32 (dd, *J* = 3.0, 1.8 Hz, 1 H, CH), 7.34 (dd, *J* = 1.8, 0.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 11.9, 14.2, 24.4, 47.1, 60.9, 106.6, 110.3, 141.7, 152.4, 172.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2972 (w), 2934 (w), 1738 (s), 1650 (w), 1503 (w), 1459 (m), 1392 (w), 1376 (w), 1337 (w), 1296 (w), 1257 (m), 1231 (w), 1197 (m), 1160 (s), 1092 (w), 1018 (m), 737 (m). MS (EI, 70 eV): *m/z* (%) = 182 (M^+, 100), 168 (7), 153 (58), 139 (53), 125 (12), 108 (42), 91 (8), 80 (19). Anal. Calcd for $C_{10}H_{14}O_3$ (182.219): C 65.92, H 7.74. Found: C 66.03, H 7.12.

***5′H*-[2,3′]Bifuranyl-2′-one (7a).** Starting with **6a** (0.100 g, 0.65 mmol) and DDQ (0.325 g, 1.43 mmol) in 1,4-dioxane (10 mL), **7a** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 50:1 → 1:1) as a colorless solid (0.050 g, 56%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 4.96 (m, 2 H, OCH_2), 6.48 (m, 1 H, CH), 7.15 (m, 1 H, CH), 7.48 (m, 1 H, CH), 7.52 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 70.4, 111.0, 111.7, 123.2, 139.3, 143.6, 145.3, 169.3. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3148 (w), 3117 (w), 2931 (w), 1750 (s), 1657 (w), 1552 (w), 1442 (w), 1351 (w), 1324 (w), 1127 (m), 1053 (s), 1020 (m), 998 (w), 973 (w), 897 (w), 812 (m), 753 (m), 726 (w). MS (EI, 70 eV): *m/z* (%) = 150 (M^+, 53), 122 (66), 93 (100), 65 (29), 51 (11). The exact molecular mass *m/z* = 150.0317 ± 2 ppm [M^+] for $C_8H_6O_3$ was confirmed by HRMS (EI, 70 eV).

5′-Ethyl-*5′H*-[2,3′]bifuranyl-2′-one (7b). Starting with **6b** (0.120 g, 0.66 mmol) and DDQ (0.330 g, 1.45 mmol) in 1,4-dioxane (10 mL), **7b** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 50:1 → 1:1) as a colorless solid (0.050 g, 42%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.06 (t, *J* = 7.0 Hz, 3 H, CH_3), 2.84 (m, 2 H, CH_2), 5.05 (t, *J* = 5.0 Hz, 1 H, CH), 6.49 (m, 1 H, CH), 7.14 (m, 1 H, CH), 7.43 (m, 1 H, CH), 7.48 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 15.5, 26.8, 82.6, 111.1, 111.7, 123.4, 142.8, 143.5, 145.3, 171.6. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3439 (m), 2970 (w), 2926 (w), 2855 (w), 2361 (w), 1745 (s), 1649 (m), 1454 (m), 1125 (m), 1093 (m), 1045 (m), 1022 (m). MS (EI, 70 eV): *m/z* (%) = 178 (M^+, 100), 149 (19), 121 (29), 93 (62), 57 (13). The exact molecular mass *m/z* = 178.0629 ± 2 ppm [M^+] for $C_{10}H_{10}O_3$ was confirmed by HRMS (EI, 70 eV).

5-Methyl-*5′H*-[2,3′]bifuranyl-2′-one (7c). Starting with **6c** (0.080 g, 0.46 mmol) and DDQ (0.230 g, 1.01 mmol) in 1,4-dioxane (7 mL), **7c** was isolated y chromatography (silica gel, *n*-hexane/EtOAc = 50:1 → 1:1) as a reddish solid (0.040 g, 48%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.36 (s, 3 H, CH_3), 4.93 (m, 2 H, OCH_2), 6.08 (m, 1 H, CH), 7.03 (m, 1 H, CH), 7.41 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 13.7, 65.9, 70.3, 107.9, 112.1, 123.2, 137.4, 153.9, 170.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2962 (w), 2927 (w), 1751 (s), 1657 (m), 1588 (m), 1447 (w), 1350 (m), 1318 (w), 1261 (w), 1135 (s), 1098 (m), 1052 (s), 1023 (s), 955 (w), 814 (s), 792 (s). UV−vis (CH_3CN, nm): λ_{max} (log ϵ) = 293 (3.9). MS (EI, 70 eV): *m/z* (%) = 164 (M^+, 100), 136 (62), 107 (93), 77 (5). The exact molecular mass *m/z* = 164.0473 ± 2 ppm [M^+] for $C_9H_8O_3$ was confirmed by HRMS (EI, 70 eV).

Ethyl 4,5,6,7,8,9,10,11,12,13-Decahydrocyclododeca[*b*]-furan-13-carboxylate (10c). Starting with **9c** (0.150 g, 0.53 mmol) and DDQ (0.243 g, 1.07 mmol) in 1,4-dioxane (10 mL), **10c** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 50:1) as a yellowish oil (0.118 g, 80%). The spectroscopic data were identical with those reported.[15a]

Methyl 5-Methylbenzofuran-7-carboxylate (11b) and Methyl 5-(Chloromethyl)benzofuran-7-carboxylate (11b′). Starting with **9e** (0.200 g, 1.02 mmol) and DDQ (1.157 g, 5.10 mmol) in 1,4-dioxane (20 mL), **11b** (0.058 g, 30%) and **11b′** (0.059 g, 26%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 10:1) as slightly yellowish solids.

Compound 11b. Mp = 60−61 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.47 (s, 3 H, CH_3), 4.01 (s, 3 H, OCH_3), 6.75 (d, J = 2.2 Hz, 1 H, CH), 7.59 (m, 1 H, CH), 7.72 (d, J = 2.2 Hz, 1 H, CH), 7.79 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 20.8, 52.0, 106.0, 114.2, 126.2, 127.7, 129.1, 131.9, 145.8, 151.6, 165.4. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3130 (w), 2955 (w), 2922 (w), 1715 (s), 1606 (m), 1544 (w), 1441 (s), 1352 (m), 1330 (w), 1297 (s), 1257 (s), 1220 (m), 1194 (s), 1127 (s), 087 (w), 909 (w), 872 (m), 771 (s). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 228 (4.2), 266 (4.0), 301 (3.7). MS (EI, 70 eV): *m/z* (%) = 190 (M^+, 68), 175 (1), 159 (100), 131 (26). Anal. Calcd for $C_{11}H_{10}O_3$ (190.198): C 69.47, H 5.30. Found: C 69.36, H 5.46.

Compound 11b′. Mp = 90 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.02 (s, 3 H, OCH_3), 4.72 (s, 2 H, CH_2Cl), 6.83 (d, J = 2.4 Hz, 1 H, CH), 7.79 (d, J = 2.4 Hz, 1 H, CH), 7.84 (d, J = 1.8 Hz, 1 H, CH), 8.01 (d, J = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 45.9, 52.4, 106.5, 115.3, 126.4, 127.6, 129.8, 132.3, 146.9, 153.1, 165.0. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2958 (w), 2927 (w), 1711 (s), 1679 (m), 1609 (w), 1446 (m), 1343 (w), 1307 (m), 1269 (s), 1215 (m), 1198 (s), 1128 (m), 1030 (w), 794 (w), 767 (w), 737 (w), 701 (w). MS (EI, 70 eV): *m/z* (%) = 226 (M^+ [^{37}Cl], 7), 225 (2), 224 (M^+ [^{35}Cl], 20), 193 (14), 189 (100), 167 (2), 165 (6), 130 (7).

Ethyl 2,3-dihydrobenzofuran-7-carboxylate (12a). Starting with **9d** (0.200 g, 1.02 mmol) and DDQ (0.694 g, 3.06 mmol) in 1,4-dioxane (10 mL), **12a** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a slightly yellowish oil (0.111 g, 57%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.38 (t, J = 7.2 Hz, 3 H, CH_3), 3.23 (t, J = 8.7 Hz, 2 H, CH_2), 4.37 (q, J = 7.2 Hz, 2 H, OCH_2), 4.72 (t, J = 8.7 Hz, 2 H, OCH_2), 6.87 (t, J = 7.5 Hz, 1 H, CH), 7.36 (dd, J = 7.2, 1.2 Hz, 1 H, CH), 7.72 (dd, J = 7.5, 1.2 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 29.0, 60.7, 72.2, 113.4, 120.0, 129.2, 129.3, 129.6, 160.7, 165.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2981 (m), 2935 (m), 2904 (w), 2864 (w), 1721 (s), 1673 (m), 1605 (s), 1541 (w), 1476 (m), 1444 (s), 1396 (m), 1370 (m), 1294 (s), 1268 (s), 1207 (s), 1168 (m), 1135 (s), 1100 (m), 1062 (m), 1026 (m), 994 (m), 930 (m), 890 (w), 866 (w), 843 (w), 800 (w), 758 (s). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 228 (3.8), 319 (3.4). MS (EI, 70 eV): *m/z* (%) = 192 (M^+, 38), 177 (4), 163 (12), 147 (100), 119 (4), 91 (20). HRMS (ESI): calcd for $C_{11}H_{12}O_3$ ([M + Na]$^+$) 215.06841, found 215.74301.

Ethyl 2-Vinylbenzofuran-7-carboxylate (14a), Ethyl 2-Vinyl-2,3-dihydrobenzofuran-7-carboxylate (15a), and Ethyl 8,9-Dicyanodibenzofuran-4-carboxylate (14a′). Starting with **13a** (0.100 g, 0.45 mmol) and DDQ (0.306 g, 1.35 mmol) in 1,4-dioxane (7 mL), **14a** (0.017 g, 18%), **15a** (0.062 g, 63%), and **14a′** (0.005 g, 4%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish oils and as a yellowish solid, respectively.

Compound 14a. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1,42 (t, J = 7.2 Hz, 3 H, CH_3), 4.40 (q, J = 7.2 Hz, 2 H, OCH_2), 5.39 (dd, J = 11.2, 1.2 Hz, 1 H, CH_2=CH), 6.00 (dd, J = 17.4, 0.9 Hz, 1 H, CH_2=CH), 6.56 (s, 1 H, CH), 6.60 (dd, J = 17.4, 11.2, 1 H, CH=CH_2), 7.18 (dd, J = 15.4, 2.4 Hz, 1 H, CH), 7.63 (dd, J = 7.7, 1.2 Hz, 1 H, CH), 7.86 (dd, J = 7.7, 1.2 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 61.1, 104.1, 115.1, 116.9, 122.6, 124.9, 125.8, 127.0, 130.6, 153.3, 155.8, 165.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2961 (s), 2926 (s), 2858 (w), 1725 (s), 1674 (m), 1609 (w), 1456 (m), 1426 (m), 1392 (w), 1375 (m), 1286 (s), 1263 (s), 1221 (w), 1180 (m), 1116 (s), 1095 (s), 1024 (s), 867 (w), 780 (s), 756 (m). MS (EI, 70 eV): *m/z* (%) = 216 (M^+, 94), 188 (40), 173 (31), 171 (100), 143 (9), 114 (50).

Compound 15a. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.38 (t, J = 7.2 Hz, 3 H, CH_3), 3.00 (dd, J = 15.7, 7.3 Hz, 1 H, CH_2), 3.39 (dd, J = 15.7, 9.4 Hz, 1 H, CH_2), 433−4.41 (m, 2 H, OCH_2), 5.24 (dt, J = 10.5, 1.3 Hz, 1 H, CH_2=CH), 5.32−5.37 (m, 1 H, OCH), 5.42 (dt, J = 17.0, 1.3 Hz, 1 H, CH_2=CH), 5.98−6.09 (m,1 H, CH=CH_2), 6.86 (dd, J = 7.8, 7.3 Hz, 1 H, CH), 7.30 (dd, J = 7.3, 1.3 Hz, 1 H, CH), 7.72 (dm, J = 7.3 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.3, 34.9, 60.6, 84.2, 113.4, 116.8, 120.0, 128.7, 129.0, 129.6, 136.8, 159.9, 165.2. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2984 (w), 1716 (s), 1609 (w), 1448 (s), 1291 (s), 1263 (s), 1207 (m), 1171 (w), 1138 (s), 1062 (w), 1031 (w), 985 (w), 933 (w), 757 (m). MS (EI, 70 eV): *m/z* (%) = 218 (M^+, 100), 203 (3), 190 (2), 173 (52), 144 (98), 133 (5), 114 (65). HRMS (ESI): calcd for $C_{13}H_{14}O_3$ [M^+] 218.09430, found 218.09608.

Compound 14a′. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.50 (t, J = 7.2 Hz, 3 H, CH_3), 4.54 (q, J = 7.2 Hz, 2 H, OCH_2), 7.63 (t, J = 7.8 Hz, 1 H, CH), 7.93 (d, J = 8.6 Hz, 1 H, CH), 8.05 (d, J = 8.6 Hz, 1 H, CH), 8.34 (dd, J = 7.8, 1.3 Hz, 1 H, CH), 8.66 (dd, J = 7.8, 1.3 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 61.8, 108.6, 111.1, 114.0, 115.6, 116.8, 117.2, 122.1, 124.6, 126.6, 126.8, 132.0, 132.8, 156.1, 157.7, 163.6. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (w), 2925 (m), 2854 (w), 1715 (s), 1671 (s), 1615 (m), 1447 (s), 1374 (m), 1291 (s), 1275 (s), 1206 (m), 1179 (s), 1145 (s), 1098 (m), 1023 (m), 929 (w), 756 (w). MS (EI, 70 eV): *m/z* (%) = 290 (M^+, 19), 264 (38), 261 (31), 249 (83), 244 (65), 217 (14), 193 (19), 188 (49), 161 (13), 148 (41), 142 (14), 129 (20), 115 (53), 102 (13), 101 (46), 87 (100), 74 (43).

Methyl 5-(Chloromethyl)-2-vinyl-2,3-dihydrobenzofuran-7-carboxylate (15b′) and Methyl 5-Methyl-2-vinyl-2,3-dihydrobenzofuran-7-carboxylate (15b). Starting with **13b** (0.100 g, 0.45 mmol) and DDQ (0.306 g, 1.35 mmol) in 1,4-dioxane (7 mL), **15b′** (0.020 g, 18%) and **15b** (0.035 g, 36%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as yellowish and slightly yellowish oils, respectively.

Compound 15b′. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.02 (dd, J = 15.6, 7.2 Hz, 1 H, CH_2), 3.37 (dd, J = 15.6, 9.6 Hz, 1 H, CH_2), 3.91 (s, 3 H, OCH_3), 4.55 (s, 2 H, CH_2Cl), 5.26 (dt, J = 10.5, 1.2 Hz, 1 H, CH_2=CH), 5.37−5.41 (m, 1 H, OCH), 5.43 (dt, J = 17.1, 1.2 Hz, 1 H, CH_2=CH), 5.97−6.08 (m, 1 H, CH=CH_2), 7.37 (d, J = 1.8 Hz, 1 H, CH), 7.75 (d, J = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 34.8, 46.0, 52.1, 85.0, 112.8, 117.5, 129.6, 129.8, 130.0, 130.5, 136.5, 160.1, 165.4. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2951 (w), 2927 (w), 1713 (s), 1616 (w), 1445 (m), 1317 (w), 1274 (s), 1242 (m), 1204 (s), 1123 (w), 1009 (w), 959 (w), 935 (w). MS (EI, 70 eV): *m/z* (%) = 254 (M^+ [^{37}Cl], 7), 252 (M^+ [^{35}Cl], 30), 221 (12), 217 (95), 192 (10), 185 (100), 171 (18), 157 (43), 128 (39), 105 (29). HRMS (ESI): calcd for $C_{13}H_{13}ClO_3$ [M^+] 254.05237 (^{37}Cl), 252.05533 (^{35}Cl), found 254.05228 (^{37}Cl), 252.05554 (^{35}Cl).

Compound 15b. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.29 (s, 3 H, CH_3), 2.96 (dd, J = 15.6, 7.2 Hz, 1 H, CH_2), 3.36 (dd, J = 15.6, 9.3 Hz, 1 H, CH_2), 3.90 (s, 3 H, OCH_3), 5.23 (dt, J = 10.5, 1.2 Hz, 1 H, CH_2=CH), 5.31−5.34 (m, 1 H, OCH), 5.40 (dt, J = 17.1, 1.2 Hz, 1 H, CH_2=CH), 5.97−6.08 (m, 1 H, CH=CH_2), 7.13 (s, 1 H, CH), 7.53 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 20.5, 35.1, 51.9, 84.4, 112.4, 117.1, 128.9, 129.6, 129.7, 130.3, 136.9, 157.9, 166.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2953 (w), 2925 (s), 2856 (w), 1715 (s), 1679 (s), 1611 (w), 1465 (s), 1441 (s), 1376 (w), 1349 (m), 1272 (s), 1237 (s), 1201 (s), 1120 (m), 1088 (w), 1027 (w), 990 (w), 937 (w), 790 (w). MS (EI, 70 eV): *m/z* (%) = 218 (M^+, 85), 203 (5), 187 (28), 171 (6), 158 (100), 147 (18), 130 (52), 119 (10), 114 (55), 91 (21).

Methyl 5-Phenyl-2-vinylbenzofuran-7-carboxylate (14c) and Methyl 5-Phenyl-2-vinyl-2,3-dihydrobenzofuran-7-carboxylate (15c). Starting with methyl 5-phenyl-2-vinyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (**13c**) (0.150 g, 0.53 mmol) and DDQ (0.359 g, 1.6 mmol) in 1,4-dioxane (10 mL), **14c** (0.027 g, 18%) and **15c** (0.064 g, 43%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a yellowish oil and solid, respectively.

Compound 14c. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.04 (s, 3 H, OCH_3), 5.48 (dd, J = 11.1, 1.2 Hz, 1 H, CH_2=CH), 6.11 (dd, J = 17.4, 1.2 Hz, 1 H, CH_2=CH), 6.69 (s, 1 H, CH), 6.70 (dd, J = 17.4, 11.1 Hz, 1 H, CH=CH_2), 7.37−7.66 (m, 5 H, 5 ×

CH of Ph), 7.91 (d, J = 1.8 Hz, 1 H, CH), 8.17 (d, J = 1.8 Hz, 1 H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 52.3, 104.2, 114.7, 117.3, 124.1, 124.8, 126.4, 126.7, 127.4 (2C), 128.9 (2C), 130.9, 131.2, 136.3, 140.4, 156.5, 165.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (m), 2927 (m), 2856 (w), 1724 (s), 1680 (m), 1604 (w), 1442 (s), 1418 (w), 1382 (w), 1351 (w), 1282 (s), 1256 (s), 1164 (w), 1144 (m), 1076 (w), 1036 (m), 881 (w), 843 (m), 802 (m), 763 (m), 699 (m). MS (EI, 70 eV): *m/z* (%) = 278 (M^+, 71), 260 (12), 246 (8), 218 (8), 204 (50), 202 (51), 188 (31), 146 (15), 142 (10), 132 (7), 129 (26), 116 (4), 114 (7), 102 (2), 87 (9), 73 (100).

Compound 15c. Mp = 90 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.07 (dd, J = 15.6, 7.4 Hz, 1 H, CH_2), 3.46 (dd, J = 15.6, 9.3 Hz, 1 H, CH_2), 3.93 (s, 3 H, OCH_3), 5.27 (dt, J = 10.4, 1.2 Hz, 1 H, CH_2=CH), 5.40−5.43 (m, 1 H, OCH), 5.45 (dt, J = 17.1, 1.2 Hz, 1 H, CH_2=CH), 6.01−6.12 (m, 1 H, CH=CH_2), 7.29−7.34 (m, 1 H, CH), 7.39−7.45 (m, 2 H, 2 × CH), 7.53−7.56 (m, 3 H, 3 × CH), 7.98 (d, J = 0.9 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 35.1, 52.0, 84.8, 113.0, 117.3, 126.7 (2C), 127.0, 128.0, 128.6, 128.8 (2C), 129.6, 133.8, 136.7, 140.2, 159.4, 165.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2951 (w), 2928 (w), 1707 (s), 1613 (w), 1458 (s), 1431 (m), 1359 (w), 1322 (w), 1266 (s), 1253 (s), 1210 (s), 1137 (m), 1005 (w), 963 (w), 929 (m), 838 (w), 793 (w), 767 (m), 701 (w). MS (EI, 70 eV): *m/z* (%) = 280 (M^+, 100), 249 (24), 220 (39), 203 (10), 193 (3), 189 (9), 173 (6), 165 (26), 151 (5), 144 (17), 105 (5), 91 (6). HRMS (ESI): calcd for $C_{18}H_{16}O_3$ [M^+] 280.10995, found 280.10973.

Ethyl 4-Methyl-2-vinylbenzofuran-7-carboxylate (14d) and Ethyl 4-Methyl-2-vinyl-2,3-dihydrobenzofuran-7-carboxylate (15d). Starting with ethyl 4-methyl-2-vinyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylate (**13d**) (0.100 g, 0.42 mmol) and DDQ (0.288 g, 1.27 mmol) in 1,4-dioxane (7 mL), **14d** (0.021 g, 22%) and **15d** (0.049 g, 50%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish and yellowish oils, respectively.

Compound 14d. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.47 (t, J = 7.2 Hz, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 4.46 (q, J = 7.2 Hz, 2 H, OCH_2), 5.44 (dd, J = 11.1, 11.2 Hz, 1 H, CH_2=CH), 6.06 (dd, J = 17.4, 0.9 Hz, 1 H, CH_2=CH), 6.65 (s, 1 H, CH), 6.68 (dd, J = 17.4, 11.1 Hz, 1 H, CH=CH_2), 7.05 (dd, J = 7.8, 0.9 Hz, 1 H, CH), 7.84 (d, J = 7.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 19.0, 60.9, 102.8, 112.8, 116.6, 123.1, 124.9, 127.2, 128.8, 130.1, 136.8, 155.3, 165.2 8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2961 (w), 2928 (w), 1718 (s), 1614 (w), 1453 (w), 1385 (m), 1283 (s), 1217 (m), 1128 (s), 1066 (w), 1028 (w), 774 (w). MS (EI, 70 eV): *m/z* (%) = 230 (M^+, 93), 215 (5), 202 (34), 185 (100), 157 (20), 128 (33), 114 (3), 102 (5).

Compound 15d. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.37 (t, J = 7.2 Hz, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.89 (dd, J = 15.6, 7.2 Hz, 1 H, CH_2), 3.30 (dd, J = 15.6, 9.3 Hz, 1 H, CH_2), 4.3−4.39 (m, 2 H, OCH_2), 5.23 (dt, J = 10.5, 1.2 Hz, 1 H, CH_2=CH), 5.35−5.39 (m, 1 H, OCH), 5.41 (dt, J = 17.1, 1.2 Hz, 1 H, CH_2=CH), 5.98−6.10 (m, 1 H, CH=CH_2), 6.69 (dd, J = 8.1, 0.3 Hz, 1 H, CH), 6.64 (d, J = 8.1 Hz, 1 H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 19.3, 34.1, 60.5, 84.2, 111.0, 116.7, 121.4, 127.3, 129.7, 137.1, 139.9, 159.8, 165.4. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2956 (w), 2928 (w), 1716 (s), 1622 (w), 1451 (w), 1412 (w), 1282 (m), 1207 (w), 1177 (w), 1137 (m), 1066 (w), 1030 (w). MS (EI, 70 eV): *m/z* (%) = 232 (M^+, 100), 187 (57), 158 (93), 148 (91), 114 (38), 102 (41).

Ethyl Benzofuran-7-carboxylate (19a). Method A. Starting with **17a** (0.400 g, 1.77 mmol) and DDQ (2.007 g. 8.84 mmol) in 1,4-dioxane (15 mL), **19a** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1→ 1:1) as a colorless oil (0.178 g, 53%).

Method B. Starting with **18a** (0.300 g 1.55 mmol) and DDQ (1.403 g, 6.18 mmol) in 1,4-dioxane (10 mL), **19a** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as a colorless oil (0.156 g, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.45 (t, J = 7.2 Hz, 3 H, CH_3), 4.48 (q, J = 7.2 Hz, 2 H, OCH_2), 6.83 (d, J = 2.2 Hz, 1 H, CH), 7.30 (t, J = 7.5 Hz. 1 H, CH), 7.76 (d, J = 2.2 Hz, 1 H, CH), 7.80 (dd, J = 7.8, 1.3 Hz, 1 H, CH), 7.97 (dd, J = 7.8, 1.3 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.2, 60.9, 106.2, 115.3, 122.3, 126.0, 126.5, 129.0, 145.8, 153.2, 164.7. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2983 (w), 1719 (s), 1672 (w), 1612 (w), 1544 (w), 1461 (w), 1448 (w), 1425 (m), 1394 (w), 1369 (w), 1328 (w), 1291 (s), 1276 (s), 1217 (m), 1171 (m), 1141 (s), 1097 (w), 1061 (w), 1034 (s), 755 (s). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 227 (4.1), 262 (3.9), 267 (3.9), 294 (3.6). MS (EI, 70 eV): *m/z* (%) = 190 (M^+, 51), 175 (3), 162 (24), 145 (100), 117 (23), 89 (43). Anal. Calcd for $C_{11}H_{10}O_3$ (190.198): C 69.47, H 5.30. Found: C 69.41, H 5.52.

Ethyl 6-Methylbenzofuran-7-carboxylate (19b). Method B. Starting with **18b** (0.400 g, 1.92 mmol) and DDQ (1.308 g, 5.76 mmol) in 1,4-dioxane (20 mL), **19b** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 30:1) as a slightly yellowish oil (0.292 g, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.45 (t, J = 7.2 Hz, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 4.49 (q, J = 7.2 Hz, 2 H, OCH_2), 6.74 (d, J = 2.2 Hz, 1 H, CH), 7.11 (dd, J = 8.0, 0.5 Hz, 1 H, CH), 7.56 (d, J = 8.0 Hz, 1 H, CH), 7.63 (d, J = 2.2 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C = 13.9, 20.1, 60.6, 105.9, 115.9, 123.0, 125.5, 125.9, 134.4, 144.8, 152.8, 165.7. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2982 (w), 2931 (w), 1721 (s), 1649 (w), 1617 (w), 1538 (w), 1447 (m), 1418 (m), 1390 (w), 1371 (w), 1346 (w), 1316 (m) 1266 (s), 1136 (s), 1101 (w), 1033 (s), 819 (m), 790 (w), 755 (m). MS (EI, 70 eV): *m/z* (%) = 204 (M^+, 86), 189 (1), 175 (86), 159 (100), 145 (1), 131 (62), 102 (21), 91 (27). Anal. Calcd for $C_{12}H_{12}O_3$ (204.225): C 70.58, H 5.92. Found: C 70.74, H 6.43.

Methyl 5-Methylbenzofuran-7-carboxylate (19c). Method A. Starting with **17c** (0.400 g, 1.77 mmol) and DDQ (2.007 g, 8.84 mmol) in 1,4-dioxane (40 mL), **19c** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 20:1) as a slightly yellowish solid (0.179 g, 53%). Mp = 60−61 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.47 (s, 3 H, CH_3), 4.01 (s, 3 H, OCH_3), 6.75 (d, J = 2.2 Hz, 1 H, CH), 7.59 (m, 1 H, CH), 7.72 (d, J = 2.2 Hz, 1 H, CH), 7.79 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 20.8, 52.0, 106.0, 114.2, 126.2, 127.7, 129.1, 131.9, 145.8, 151.6, 165.4. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3130 (w), 2955 (w), 2922 (w), 1715 (s), 1606 (m), 1544 (w), 1441 (s), 1352 (m), 1330 (w), 1297 (s), 1257 (s), 1220 (m), 1194 (s), 1127 (s), 087 (w), 909 (w), 872 (m), 771 (s). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 228 (4.2), 266 (4.0), 301 (3.7). MS (EI, 70 eV): *m/z* (%) = 190 (M^+, 68), 175 (1), 159 (100), 131 (26). Anal. Calcd for $C_{11}H_{10}O_3$ (190.198): C 69.47, H 5.30. Found: C 69.36, H 5.46.

Methyl 5-Phenylbenzofuran-7-carboxylate (19d) and Methyl 2-Oxo-5-phenyl-2,4,5,6-tetrahydrobenzofuran-7-carboxylate (20). Method A. Starting with **17d** (0.150 g, 0.52 mmol) and DDQ (0.472 g, 2.08 mmol) in 1,4-dioxane (10 mL), **19d** (0.060 g, 46%) and **20** (0.042 g, 30%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish and orange solids, respectively.
Method B. Starting with **18d** (0.600 g, 2.34 mmol) and DDQ (1.593 g, 7.02 mmol) in 1,4-dioxane (25 mL), **19d** (0.389 g, 66%) and **20** (0.042 g, 7%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish and orange solids, respectively.

Compound 19d. Mp = 84.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.04 (s, 3 H, OCH_3), 6.88 (d, J = 2.2 Hz, 1 H, CH), 7.37−7.40 (m, 1 H, CH), 7.44−7.49 (m, 2 H, 2 × CH), 7.63−7.66 (m, 2 H, 2 × CH), 7.79 (d, J = 2.2 Hz, 1 H, CH), 7.99 (d, J = 1.9 Hz, 1 H, CH), 8.21 (d, J = 1.9 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 51.9, 106.4, 114.7, 124.2, 125.9, 127.0 (2C), 128.5 (2C), 129.5, 135.9, 140.0, 146.2, 152.5, 165.0. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2952 (w), 1716 (s), 1603 (w), 1545 (w), 1443 (s), 1472 (m), 1354 (w), 1314 (m), 1281 (m), 1257 (s), 1224 (s), 1146 (s), 1031 (m), 883 (m), 848 (w), 766 (s), 741 (w), 703 (m). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 245 (4.5), 313 (3.6). Fluorescence (CH_2Cl_2, nm): λ_{max} (λ_{Ex}) = 363 (316). MS (EI, 70 eV): *m/z* (%) = 252 (M^+, 100), 221 (80), 205 (1), 183 (8). Anal. Calcd for $C_{16}H_{12}O_3$ (252.269): C 76.18, H 4.79. Found: C 75.43, H 4.65.

Compound 20. Mp = 160 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.67 (dd, J = 17.7, 11.3 Hz, 1 H, CH_2), 2.83 (ddd, J =

17.0, 12.8, 2.2 Hz, 1 H, CH_2), 3.02 (dd, J = 4.1, 1.2 Hz, 1 H, CH_2), 3.08 (d, J = 4.0 Hz, 1 H, CH_2), 3.10−3.20 (m, 1 H, C*H*Ph), 3.86 (s, 3 H, OCH_3), 6.03 (m, 1 H, CH=C), 7.25−7.39 (m, 5 H, 5 × CH of Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 31.3, 32.3, 40.6, 52.5, 105.6, 114.5, 126.7 (2C), 127.3, 128.8 (2C), 142.3, 152.5, 156.7, 165.1, 168.6. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3095 (w), 2953 (w), 1778 (s), 1699 (s), 1653 (m), 1615 (m),1500 (w), 1436 (m), 1374 (w), 1317 (m), 1298 (m), 1260 (s), 1228 (m), 1185 (w), 1139 (m), 1107 (w), 1075 (w), 1027 (w), 873 (m), 852 (m), 760 (m), 704 (w). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 292 (4.2), 352 (4.1), 370 (4.1). Fluorescence (CH_2Cl_2, nm): λ_{max} (λ_{Ex}) = 379 (370), 400 (353). MS (EI, 70 eV): *m/z* (%) = 270 (M^+, 100), 139 (26), 210 (99), 182 (25), 154 (19), 105 (12), 91 (23), 77 (19). Anal. Calcd for $C_{16}H_{14}O_4$ (270.284): C 71.10, H 5.22. Found: C 70.45, H 4.97.

Ethyl 4-Methylbenzofuran-7-carboxylate (19e). Method A. Starting with **17e** (0.050 g, 0.208 mmol) and DDQ (0.236 g, 1.04 mmol) in 1,4-dioxane (5 mL), **19e** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 20:1) as a slightly yellowish oil (0.026 g, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.37 (t, J = 7.2 Hz, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 4.39 (q, J = 7.2 Hz, 2 H, OCH_2), 6.76 (d, J = 2.2 Hz, 1 H, CH), 7.02 (dd, J = 7.8, 0.7 Hz, 1 H, CH), 7.68 (d, J = 2.2 Hz, 1 H, CH), 7.80 (d, J = 7.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 19.0, 60.9, 105.0, 113.1, 123.0, 126.9, 128.7, 137.1, 145.4, 153.1, 165.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2960 (w), 2927 (w), 1716 (s), 1658 (w), 1616 (w), 1450 (w), 1389 (m), 1285 (s), 1264 (s), 1218 (m), 1189 (w), 1131 (s), 1097 (w), 1067 (w), 1036 (m), 760 (m). MS (EI, 70 eV): *m/z* (%) = 204 (M^+, 40), 189 (4), 176 (16), 159 (100), 131 (20), 103 (12). HRMS (ESI): calcd for $C_{12}H_{12}O_3$ ([M + 1]$^+$) 205.08647, found 205.08581.

Ethyl 2-Methylbenzofuran-7-carboxylate (22a). Starting with **21a** (0.050 g, 0.238 mmol) and DDQ (0.270 g, 1.19 mmol) in 1,4-dioxane (5 mL), **22a** was isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 10:1) as a slightly yellowish oil (0.029 g, 60%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.45 (t, J = 7.2 Hz, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 4.43 (q, J = 7.2 Hz, 2 H, OCH_2), 6.96 (t, J = 7.5 Hz, 1 H, CH), 7.31 (d, J = 7.5 Hz, 1 H, CH), 7.52 (dd, J = 7.5, 1.5 Hz, 1 H, CH), 7.71 (dd, J = 7.5, 1.5 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.2, 14.4, 61.1, 115.3, 118.6, 122.0, 124.3, 126.6, 137.4, 159.3, 165.1, 170.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2980 (w), 2932 (w), 2865 (w), 1719 (s), 1671 (s), 1610 (m), 1443 (s), 1428 (s), 1393 (w), 1374 (m), 1291 (s), 1272 (s), 1251 (m), 1217 (m), 1183 (s), 1150 (s), 1112 (s), 1065 (w), 1024 (m), 795 (w), 757 (s). MS (EI, 70 eV): *m/z* (%) = 204 (M^+, 61), 189 (3), 175 (21), 159 (100), 131 (15).

Ethyl 2-(Chloromethyl)benzofuran-7-carboxylate (22b) and Ethyl 2-(Chloromethyl)-2,3-dihydrobenzofuran-7-carboxylate (23b). Starting with **21b** (0.120 g, 0.49 mmol) and DDQ (0.557 g, 2.45 mmol) in 1,4-dioxane (10 mL), **22b** (0.035 g, 30%) and **23b** (0.061 g, 52%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as colorless solids.

Compound 22b. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.46 (t, J = 7.2 Hz, 3 H, CH_3), 4.48 (q, J = 7.2 Hz, 2 H, OCH_2), 4.76 (s, 2 H, CH_2Cl), 6.81 (s, 1 H, CH), 7.30 (t, J = 7.5 Hz, 1 H, CH), 7.74 (dd, J = 7.5, 1.2 Hz, 1 H, CH), 7.97 (dd, J = 7.5, 1.2 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 37.5, 61.2, 105.8, 115.6, 122.8, 126.1, 127.3, 129.7, 153.7, 154.0, 164.7. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2929 (w), 1719 (s), 1693 (w), 1666 (w), 1607 (w), 1426 (m), 1323 (w), 1298 (s), 1274 (s), 1223 (w), 1180 (m), 1137 (s), 1097 (w), 1063 (w), 1032 (m), 797 (w), 754 (m), 715 (w). MS (EI, 70 eV): *m/z* (%) = 240 (M^+ [^{37}Cl], 9), 238 (M^+ [^{35}Cl], 27), 203 (100), 195 (10), 193 (22), 189 (4), 175 (49), 159 (71). HRMS (ESI): calcd for $C_{12}H_{11}ClO_3$ ([M + 1]$^+$) 241.04455 (^{37}Cl), 239.04750 (^{35}Cl), found 241.04701 (^{37}Cl), 239.04688 (^{35}Cl).

Compound 23b. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.38 (t, J = 7.2 Hz, 3 H, CH_3), 3.19 (dd, J = 15.9, 6.3 Hz, 1 H, CH_2), 3.39 (dd, J = 15.9, 9.3 Hz, 1 H, CH_2), 3.69 (dd, J = 11.4, 6.9 Hz, 1 H, CH_2Cl), 3.83 (dd, J = 11.4, 5.1 Hz, 1 H, CH_2Cl), 4.36 (dq, J = 7.2, 1.2 Hz, 2 H, OCH_2), 5.10−5.21 (m, 1 H, OCH), 6.90 (t, J = 7.5 Hz, 1 H, CH), 7.33 (dd, J = 7.5, 1.2 Hz, 1 H, CH), 7.73 (dd, J = 7.5, 1.2 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.3, 32.6, 45.7, 60.7, 82.2, 113.6, 120.5, 128.0, 129.3, 129.8, 159.7, 165.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2980 (m), 2932 (w), 1719 (s), 1610 (m), 1449 (s), 1394 (w), 1368 (m), 1325 (w), 1293 (s), 1267 (s), 1209 (s), 1170 (m), 1139 (s), 1100 (m), 1064 (m), 1032 (s), 987 (w), 859 (w), 757 (s). MS (EI, 70 eV): *m/z* (%) = 242 (M^+ [^{37}Cl], 30), 241 (8), 240 (M^+ [^{35}Cl], 100), 226 (1), 212 (5), 197 (21), 195 (71), 191 (58), 159 (23), 131 (21), 119 (43), 105 (17), 103 (31), 91 (47), 77 (36). HRMS (ESI): calcd for $C_{12}H_{13}ClO_3$ ([M + 1]$^+$) 243.06020 (^{37}Cl), 241.06315 (^{35}Cl), found 243.05960 (^{37}Cl), 241.04701 (^{35}Cl).

Ethyl 2-(Bromomethyl)benzofuran-7-carboxylate (22c) and Ethyl 2-(Bromomethyl)-2,3-dihydrobenzofuran-7-carboxylate (23c). Starting with **21c** (0.058 g, 0.20 mmol) and DDQ (0.136 g, 0.60 mmol), in 1,4-dioxane (5 mL), **22c** (0.010 g, 18%) and **23c** (0.024 g, 42%) were isolated by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish solids.

Compound 22c. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.46 (t, J = 7.2 Hz, 3 H, CH_3), 4.48 (q, J = 7.2 Hz, 2 H, OCH_2), 4.65 (s, 2 H, CH_2Br), 6.81 (s, 1 H, CH), 7.31 (dd, J = 7.8, 1.2 Hz, 1 H, CH), 7.75 (dd, J = 7.2, 1.2 Hz, 1 H, CH), 7.97 (dd, J = 7.8, 1.2 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 37.5, 61.2, 105.9, 115.7, 122.9, 126.1, 127.5, 129.7, 154.1, 158.6, 164.7. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2954 (w), 2928 (m), 1719 (s), 1667 (m), 1613 (w), 1427 (m), 1395 (w), 1375 (w), 1322 (w), 1287 (s), 1274 (s), 1217 (w), 1182 (s), 1144 (s), 1103 (w), 1065 (w), 1032 (w), 756 (m). MS (EI, 70 eV): *m/z* (%) = 284 (M^+ [^{81}Br], 3), 282 (M^+ [^{79}Br], 3), 238 (17), 221 (1), 203 (100), 189 (2), 175 (38), 159 (9), 130 (14), 102 (22). HRMS (ESI): calcd for $C_{12}H_{11}BrO_3$ [M^+] 283.98711 (^{81}Br), 281.98916 (^{79}Br), found 283.98639 (^{81}Br), 281.98894 (^{79}Br).

Compound 23c. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.38 (t, J = 7.2 Hz, 3 H, CH_3), 3.17 (dd, J = 16.2, 6.0 Hz, 1 H, CH_2), 3.41 (dd, J = 16.2, 9.3 Hz, 1 H, CH_2), 3.52 (dd, J = 10.2, 7.8 Hz, 1 H, CH_2Br), 3.70 (dd, J = 10.2, 4.5 Hz, 1 H, CH_2Br), 4.36 (dq, J = 7.2, 2.1 Hz, 2 H, OCH_2), 5.11−5.20 (m, 1 H, OCH), 6.90 (dd, J = 7.8, 7.5 Hz, 1 H, CH), 7.33 (dd, J = 7.2, 1.2 Hz, 1 H, CH), 7.74 (dd, J = 7.8, 1.2 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 33.7, 34.1, 60.8, 82.1, 113.6, 120.6, 128.0, 129.3, 129.9, 159.7, 165.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2979 (w), 2967 (w), 2926 (m), 2852 (w), 1717 (s), 1612 (m), 1451 (s), 1368 (m), 1322 (w), 1292 (s), 1267 (s), 1234 (w), 1208 (s), 1170 (m), 1140 (s), 1095 (w), 1062 (m), 1032 (m), 1002 (w), 756 (s). MS (EI, 70 eV): *m/z* (%) = 286 (M^+ [^{81}Br], 20), 284 (M^+ [^{79}Br], 18), 241 (6), 239 (7), 192 (37), 176 (81), 149 (18), 133 (9), 130 (61), 119 (8), 106 (9), 103 (17), 91 (100), 77 (16). HRMS (ESI): calcd for $C_{12}H_{13}BrO_3$ ([M + 1]$^+$) 287.01058 (^{81}Br), 285.01208 (^{79}Br), found 287.01084 (^{81}Br), 285.01285 (^{79}Br).

Methyl 2,5-Dimethylbenzofuran-7-carboxylate (22d). Starting with **21d** (0.050 g, 0.238 mmol) and DDQ (0.270 g, 1.19 mmol) in 1,4-dioxane (5 mL), **22d** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 10:1) as a slightly yellowish oil (0.032 g, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.24 (s, 3 H, CH_3), 2.94 (s, 3 H, CH_3), 4.00 (s, 3 H, OCH_3), 7.51 (m, 2 H, 2 × CH), 7.78 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 20.9, 21.1, 52.2, 114.3, 115.1, 124.6, 127.7, 130.9, 131.7, 142.5, 152.2, 165.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2962 (w), 2928 (w), 1717 (s), 1657 (w), 1615 (w), 1451 (w), 1390 (m), 1286 (s), 1265 (s), 1215 (m), 1130 (s), 1098 (w), 1065 (w), 1035 (w), 762 (w). MS (EI, 70 eV): *m/z* (%) = 204 (M^+, 25), 189 (5), 173 (45), 157 (23), 145 (100), 130 (17). HRMS (ESI): calcd for $C_{12}H_{12}O_3$ ([M + 1]$^+$) 205.08647, found 205.08581.

Methyl 2-(Chloromethyl)-5-methylbenzofuran-7-carboxylate (22f), Methyl 2,5-Bis(chloromethyl)benzofuran-7-carboxylate (22f′), and Methyl 2,5-Bis(chloromethyl)-2,3-dihydrobenzofuran-7-carboxylate (23f). Starting with **21f** (0.200 g, 0.82 mmol) and DDQ (0.928 g, 4.09 mmol) in 1,4-dioxane (20 mL), **22f** (0.039 g, 20%), **22f′** (0.022 g, 10%), and **23f** (0.045 g, 20%) were isolated after chromatography (silica

gel, *n*-hexane/EtOAc = 100:1 → 1:1) as colorless, colorless and slightly yellowish solids, respectively.

Compound 22f. Mp = 88 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.46 (s, 3 H, CH_3), 4.00 (s, 3 H, OCH_3), 4.74 (s, 2 H, CH_2-Cl), 6.73 (s, 1 H, CH), 7.53 (d, J = 1.8 Hz, 1 H, CH), 7.79 (d, J = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 21.1, 37.5, 52.2, 105.7, 114.6, 126.3, 128.5, 129.8, 132.5, 152.1, 154.0, 165.4. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2954 (w), 2924 (w), 1715 (s), 1440 (m), 1268 (s), 1224 (w), 1200 (m), 1122 (w), 1040 (w), 954 (w), 780 (w), 709 (w). MS (EI, 70 eV): *m/z* (%) = 240 (M^+ [^{37}Cl], 6), 239 (3), 238 (M^+ [^{35}Cl], 20), 209 (3), 207 (9), 203 (100), 189 (1), 179 (1), 173 (5), 171 (9), 144 (6), 114 (18). HRMS (ESI): calcd for $C_{12}H_{11}ClO_3$ ([M + 1]$^+$) 241.04455 (^{37}Cl), 239.04750 (^{35}Cl), found 241.04734 (^{37}Cl), 239.04716 (^{35}Cl). Anal. Calcd for $C_{12}H_{11}ClO_3$ (238.670): C 60.39, H 4.65. Found: C 60.12, H 5.48.

Compound 22f'. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.02 (s, 3 H, OCH_3), 4.70 (s, 2 H, CH_2Cl), 4.75 (s, 2 H, CH_2Cl), 6.81 (s, 1 H, CH), 7.79 (d, J = 1.8 Hz, 1 H, CH), 8.00 (d, J = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 37.3, 45.8, 52.4, 105.9, 115.4, 126.2, 128.1, 130.2, 136.6, 153.4, 155.0, 164.7. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2952 (w), 2929 (w), 1712 (s), 1604 (w), 1440 (s), 1432 (w), 1360 (w), 1331 (m), 1278 (s), 1232 (m), 1200 (s), 1185 (w), 1157 (w), 1145 (w), 1122 (m), 1029 (w), 954 (m), 899 (w), 828 (w), 786 (m), 778 (w), 707 (m), 599 (w). MS (EI, 70 eV): *m/z* (%) = 274 (M^+ [2 × ^{37}Cl], 14), 272 (M^+ [2 × ^{35}Cl], 23), 241 (6), 239 (31), 237 (100), 203 (100), 173 (3), 159 (2), 143 (5), 114 (19). HRMS (ESI): calcd for $C_{12}H_{10}Cl_2O_3$ [M^+] 275.99478 (2 × ^{37}Cl), 273.99775 (^{37}Cl ^{35}Cl), 272.00070 (2 × ^{35}Cl), found 276.00053 (2 × ^{37}Cl), 273.99714 (^{37}Cl ^{35}Cl), 272.00044 (2 × ^{35}Cl).

Compound 23f. Mp = 78 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.21 (dd, J = 16.2, 6.3 Hz, 1 H, CH_2), 3.40 (dd, J = 16.2, 9.3 Hz, 1 H, CH_2), 3.71 (dd, J = 10.2, 7.8 Hz, 1 H, CH_2Cl), 3.81 (dd, J = 10.2, 4.5 Hz, 1 H, CH_2Cl), 4.04 (s, 3 H, OCH_3), 4.55 (s, 2 H, CH_2Cl), 5.16−5.22 (m, 1 H, OCH), 7.39 (d, J = 1.8 Hz, 1 H, CH), 7.75 (d, J = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 32.4, 45.7, 45.8, 52.6, 82.7, 115.1, 128.5, 129.3, 132.8, 152.9, 153.6, 164.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2955 (w), 1721 (s), 1688 (s), 1566 (w), 1467 (w), 1439 (m), 1340 (m), 1292 (m), 1268 (s), 1236 (m), 1201 (s), 1153 (w), 1121 (m), 1036 (w), 947 (w), 846 (w), 781 (w). MS (EI, 70 eV): *m/z* (%) = 276 (M^+ [^{37}Cl ^{35}Cl], 4), 274 (M^+ [2 × ^{35}Cl], 4), 239 (34), 241 (10), 218 (54), 206 (13), 186 (100), 158 (4), 145 (1), 103 (18), 91 (2), 77 (18). HRMS (ESI): calcd for $C_{12}H_{12}Cl_2O_3$ [M^+] 276.01340 (^{37}Cl ^{35}Cl), 274.01635 (2 × ^{35}Cl), found 276.01308 (^{37}Cl ^{35}Cl), 274.01611 (2 × ^{35}Cl).

Methyl 2-Methyl-5-phenylbenzofuran-7-carboxylate (22g). Starting with **21g** (0.050 g, 0.18 mmol) and DDQ (0.208 g, 0.92 mmol) in 1,4-dioxane (5 mL), **22g** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 10:1) as a slightly yellowish solid (0.031 g, 63%). Mp = 98 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.31 (s, 3 H, CH_3), 4.03 (s, 3 H, OCH_3), 7.37 (t, J = 7.2 Hz, 1 H, CH of Ph), 7.47 (t, J = 7.2 Hz, 2 H, 2 × CH of Ph), 7.57 (d, J = 1.2 Hz, 1H, CH), 7.66 (dd, J = 7.2, 1.2 Hz, 2H, 2 × CH of Ph), 7.90 (d, J = 2.1 Hz, 1 H, CH), 8.20 (d, J = 2.1 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 7.9, 52.3, 115.0, 115.7, 122.8, 126.2, 127.3, 127.4 (2C), 128.9 (2C), 131.4, 136.0, 140.6, 143.1, 153.2, 165.5. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2952 (w), 1720 (s), 1461 (w), 1440 (s), 1351 (w), 1288 (m), 1253 (s), 1225 (s), 1182 (m), 1104 (m), 1082 (m), 753 (s), 699 (m). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 247 (4.4), 315 (3.6). MS (EI, 70 eV): *m/z* (%) = 266 (M^+, 100), 235 (87), 207 (14), 178 (30).

Methyl 2-(Chloromethyl)-5-phenylbenzofuran-7-carboxylate (22h) and Methyl 2-(Chloromethyl)-5-phenyl-2,3-dihydrobenzofuran-7-carboxylate (23h). Starting with **21h** (0.150 g, 0.49 mmol) and DDQ (0.334 g, 1.47 mmol) in 1,4-dioxane (10 mL), **22h** (0.022 g, 15%) and **23h** (0.118 g, 80%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish oil and yellowish solid, respectively.

Compound 22h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.03 (s, 3 H, OCH_3), 4.77 (s, 2 H, CH_2Cl), 6.85 (s, 1 H, CH), 7.35−7.40 (m, 1 H, CH of Ph), 7.46 (t, J = 7.5 Hz, 2 H, 2 × CH of Ph), 7.63 (d, J = 7.5 Hz, 2 H, 2 × CH of Ph), 7.93 (d, J = 2.0 Hz, 1 H, CH), 8.21 (d, J = 2.0 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 37.4, 52.4, 106.1, 115.2, 124.5, 126.9, 127.4 (2C), 127.5, 128.9 (2C), 130.3, 136.7, 140.2, 153.1, 154.6, 165.7. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2954 (w), 2927 (w), 2856 (w), 1723 (s), 1678 (w), 1605 (w), 1463 (w), 1441 (m), 1417 (w), 1379 (w), 1351 (w), 1282 (m), 1258 (s), 1231 (s), 1189 (w), 1163 (m), 1123 (s), 1077 (w), 1034 (w), 955 (w), 889 (w), 818 (w), 786 (w), 763 (m), 701 (m). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 246 (4.5), 319 (3.6). MS (EI, 70 eV): *m/z* (%) = 302 (M^+ [^{37}Cl], 10), 300 (M^+ [^{35}Cl], 64), 265 (100), 219 (15), 142 (99), 128 (51), 114 (30), 112 (42). HRMS (ESI): calcd for $C_{17}H_{13}ClO_3$ ([M + 1]$^+$) 303.06020 (^{37}Cl), 301.06315 (^{35}Cl), found 303.06017 (^{37}Cl), 301.06307 (^{35}Cl).

Compound 23h. Mp = 162−163 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.27 (dd, J = 16.2, 6.3 Hz, 1 H, CH_2), 3.46 (dd, J = 16.2, 9.3 Hz, 1 H, CH_2), 3.74 (dd, J = 11.1, 6.9 Hz, 1 H, CH_2Cl), 3.86 (dd, J = 11.1, 4.2 Hz, 1 H, CH_2Cl), 3.93 (s, 3 H, OCH_3), 5.17−5.26 (m, 1 H, OCH), 7.30−7.35 (m, 1 H, CH of Ph), 7.40−7.45 (m, 2 H, 2 × CH of Ph), 7.52−7.88 (m, 3 H, 3 × CH of Ph), 7.98 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 32.5, 45.7, 51.9, 82.5, 113.0, 126.7 (2C), 127.0, 128.0, 128.6, 128.7 (2C), 128.8, 134.2, 139.9, 159.0, 165.4. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2950 (w), 1719 (s), 1603 (w), 1466 (s), 1433 (m), 1347 (w), 1285 (m), 1267 (m), 1245 (m), 1255 (s), 1188 (m), 1140 (s), 1030 (m), 1004 (w), 890 (w), 837 (w), 763 (m), 699 (w). UV−vis (CH_2Cl_2, nm): λ_{max} (log ϵ) = 230 (4.4), 264 (4.2), 324 (3.7). Fluorescence (CH_2Cl_2, nm): λ_{max} (λ_{Ex}) = 376 (328). MS (EI, 70 eV): *m/z* (%) = 304 (M^+ [^{37}Cl], 29), 303 (14), 302 (M^+ [^{35}Cl], 100), 271 (9), 266 (1), 253 (3), 207 (6), 179 (33), 165 (15), 150 (8). Anal. Calcd for $C_{17}H_{15}ClO_3$ (302.757): C 67.44, H 4.99. Found: C 67.51, H 4.98.

Methyl 2-(Bromomethyl)-5-phenylbenzofuran-7-carboxylate (22i) and Methyl 2-(Bromomethyl)-5-phenyl-2,3-dihydrobenzofuran-7-carboxylate (23i). Starting with **21i** (0.075 g, 0.21 mmol) and DDQ (0.242 g, 1.07 mmol) in 1,4-dioxane (7 mL), **22i** (0.022 g, 31%) and **23i** (0.029 g, 40%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish solids.

Compound 22i. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.04 (s, 3 H, OCH_3), 4.78 (s, 2 H, CH_2Br), 6.86 (d, J = 1.6 Hz, 1 H, CH), 7.31−7.49 (m, 3 H, 3 × CH of Ph), 7.58−7.65 (m, 2 H, 2 × CH of Ph), 7.93 (dd, J = 4.2, 1.8 Hz, 1 H, CH), 8.21 (d, J = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 37.4, 52.4, 106.1, 115.2, 124.5, 126.8, 126.9, 127.0, 127.4 (2C), 128.9 (2C), 130.5, 136. 7, 154.6, 158.7, 165.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2972 (w), 2928, 2860 (w), 1723 (s), 1676 (m), 1604 (w), 1442 (s), 1348 (m), 1283 (s), 1256 (s), 1235 (s), 1198 (m), 1162 (m), 1121 (m), 1075 (w), 1032 (w), 954 (w), 889 (w), 762 (s), 700 (m). MS (EI, 70 eV): *m/z* (%) = 347 (M^+ [^{81}Br], 77), 345 (M^+ [^{79}Br], 100), 265 (61), 250 (19), 234 (29), 188 (15), 160 (23), 125 (28). HRMS (ESI): calcd for $C_{17}H_{13}BrO_3$ ([M − Br]$^+$) 265.08647, found 265.08711.

Compound 23i. Mp = 140 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.24 (dd, J = 16.2, 6.3 Hz, 1 H, CH_2), 3.47 (dd, J = 16.2, 9.3 Hz, 1 H, CH_2), 3.56 (dd, J = 10.5, 7.8 Hz, 1 H, CH_2Br), 3.73 (dd, J = 10.5, 4.2 Hz, 1 H, CH_2Br), 3.92 (s, 3 H, OCH_3), 5.18−5.23 (m, 1 H, OCH), 7.28−7.57 (m, 6 H, 5 × CH of Ph, CH), 7.98 (d, J = 1.8 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 33.8, 34.1, 52.1, 82.4, 113.2, 126.8 (2C), 127.1, 128.2, 128.7, 128.8 (2C), 128.9, 134.3, 140.0, 159.1, 165.5. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2950 (w), 1718 (s), 1602 (w), 1465 (s), 1452 (m), 1432 (w), 1348 (w), 1285 (w), 1272 (w), 1250 (s), 1223 (s), 1187 (w), 1139 (s), 1057 (w), 1027 (w), 992 (w), 884 (w), 786 (w), 762 (m), 698 (m). MS (EI, 70 eV): *m/z* (%) = 348 (M^+ [^{81}Br], 73), 346 (M^+ [^{79}Br], 72), 226 (3), 253 (4), 235 (100), 207 (21), 194 (9), 181 (21), 165 (34), 151 (31), 77 (9). HRMS (ESI): calcd for $C_{17}H_{15}BrO_3$ ([M + 1]$^+$) 349.02623 (^{81}Br), 347.02828 (^{79}Br), found 349.02626 (^{81}Br), 347.02840 (^{79}Br).

Ethyl 2-(Chloromethyl)-4-methylbenzofuran-7-carboxylate (22j) and Ethyl 2-(Chloromethyl)-4-methyl-2,3-dihydrobenzofuran-7-carboxylate (23j). Starting with **21j** (0.100 g, 0.39 mmol) and DDQ (0.263 g, 1.16 mmol) in 1,4-dioxane (7 mL), **22j** (0.020 g, 20%) and **23j** (0.038 g, 38%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) as slightly yellowish solids.

Compound 22j. Mp = 50 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.45 (t, J = 7.2 Hz, 3 H, CH_3), 2.54 (s, 3 H, CH_3), 4.45 (q, J = 7.2 Hz, 2 H, OCH_2), 4.77 (s, 2 H, CH_2Cl), 6.82 (s, 1 H, CH), 7.09 (dd, J = 7.8, 0.9 Hz, 1 H, CH), 7.87 (d, J = 7.8 Hz, 1 H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 19.0, 37.6, 61.0, 104.5, 113.2, 123.3, 127.5, 129.3, 137.2, 153.4, 153.5, 164.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2981 (w), 2958 (w), 2928 (w), 2861 (w), 1714 (s), 1613 (m), 1471 (w), 1450 (w), 1385 (w), 1324 (w), 1278 (s), 2117 (s), 1131 (s), 1063 (w), 1033 (w), 956 (w), 772 (m), 712 (w). MS (EI, 70 eV): *m/z* (%) = 253 (M^+ [^{37}Cl], 7), 251 (M^+ [^{35}Cl], 26), 216 (100), 206 (22), 188 (49), 171 (4), 158 (6), 148 (19), 143 (11), 114 (34), 89 (4), 72 (13). HRMS (ESI): calcd for $C_{13}H_{13}ClO_3$ [M^+] 254.05237 (^{37}Cl), 252.05533 (^{35}Cl), found 254.04970 (^{37}Cl), 252.05511 (^{35}Cl).

Compound 23j. Mp = 60 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.37 (t, J = 7.2 Hz, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 3.08 (dd, J = 15.9, 6.3 Hz, 1 H, CH_2), 3.29 (dd, J = 15.9, 9.6 Hz, 1 H, CH_2), 3.68 (dd, J = 11.1, 7.5 Hz, 1 H, CH_2Cl), 3.84 (dd, J = 11.1, 4.5 Hz, 1 H, CH_2Cl), 4.29−4.40 (m, 2 H, OCH_2), 5.11−5.20 (m, 1 H, OCH), 6.72 (d, J = 8.1 Hz, 1 H, CH), 7.65 (d, J = 8.1 Hz, 1 H, CH), ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.4, 19.3, 31.8, 45.9, 60.6, 82.2, 111.1, 121.9, 126.6, 129.9, 140.1, 159.5, 165.1. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2978 (w), 2928 (w), 1713 (s), 1620 (w), 1446 (w), 1418 (w), 1367 (w), 1280 (m), 1238 (m), 1212 (w), 1178 (m), 1138 (m), 1064 (w), 1033 (w), 1012 (w), 773 (w). MS (EI, 70 eV): *m/z* (%) = 256 (M^+ [^{37}Cl], 23), 254 (M^+ [^{35}Cl], 84), 226 (11), 211 (30) 209 (100), 205 (48), 177 (14), 159 (16), 146 (20), 133 (74), 117 (14), 105 (54), 91 (31), 77 (29). HRMS (ESI): calcd for $C_{13}H_{15}ClO_3$ [M^+] 256.06802 (^{37}Cl), 254.07097 (^{35}Cl), found 256.06743 (^{37}Cl), 254.07049 (^{35}Cl).

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Supporting Information Available: Experimental procedures, spectroscopic data, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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