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Efficient Synthesis of Benzofurans Utilizing [3,3]-Sigmatropic Rearrangement Triggered by *N*-Trifluoroacetylation of Oxime Ethers: Short Synthesis of Natural 2-Arylbenzofurans

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Keywords: Benzofuran / Sigmatropic rearrangement / Total synthesis / Trifluoroacetic anhydride / Trifluoroacetyl triflate

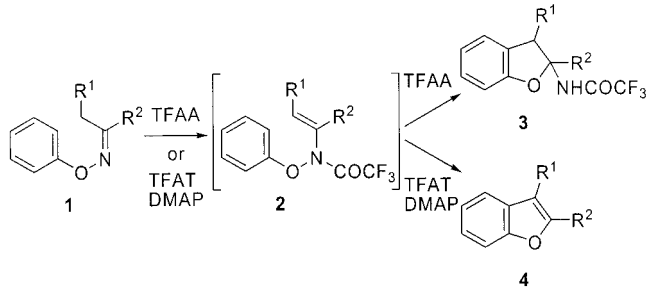
A new synthetic method for the preparation of benzofurans has been developed. The key step of this method is the [3,3]-sigmatropic rearrangement of *N*-trifluoroacetyl-ene-hydroxylamines, which was triggered by acylation of oxime ethers. TFAA has been proved to be the best reagent to induce [3,3]-sigmatropic rearrangement for the synthesis of cyclic or acyclic dihydrobenzofurans. On the other hand, the TFAT-DMAP system is found to be the most effective for constructing various benzofurans. Synthetic utility of this reaction is demonstrated by the short synthesis of natural benzofurans without protection of the hydroxy group. The synthesis of Stemofuran A was accomplished via condensation of ketones with aryloxyamine and subsequent reaction with TFAT-DMAP in a four-step synthesis with 72 % overall yield. Similarly, Eupomatenoid 6 and Coumestan were synthesized through the reaction of oxime ether with TFAT-DMAP.

Introduction

Benzofurans and dihydrobenzofuran (coumaran) have attracted widespread interest in view of their presence in natural products, and their biological and pharmacological activities.[1] The benzofuran nucleus is a central component of a diverse class of heterocyclic natural and synthetic products that possess a broad range of biological activities.[2]

However, known synthetic methods of benzofuran utilizing [3,3]-sigmatropic rearrangement[3] exhibit some disadvantages: (i) acid catalysts, such as H_2SO_4 and HCl, and high temperature are generally required for the successful reaction, (ii) these harsh conditions cannot be applied to acid-sensitive substrates, (iii) in most cases, the desired benzofurans were obtained in only moderate yields, and (iv) a synthetic method for dihydrobenzofurans has not yet been well established.

From the background described above, we have recently reported effective synthetic methods for the dihydrobenzofurans **3** and benzofurans **4** involving acylation, rearrangement, and intramolecular cyclization reactions of the oxime ethers **1** (Scheme 1).[4] In this paper, we describe the full details of the synthesis of the dihydrobenzofurans **3** and benzofurans **4** by optimizing reaction conditions. Furthermore, we have also applied a newly found efficient procedure to a short synthesis of natural products, namely Stemofuran A,[5] Eupomatenoid 6[6] and Coumestan,[7] without protection of the phenolic hydroxy group. To the best of our knowledge, there has been no report on reagent-controlled synthesis of dihydrobenzofurans **3** and benzofurans **4** by highly efficient [3,3]-sigmatropic rearrangement under mild conditions.



Scheme 1. General reaction of the oxime ethers **1** with TFAA or TFAT-DMAP.

Results and Discussion

Benzofuran and Dihydrobenzofuran Synthesis by [3,3]-Sigmatropic Rearrangement of *N*-Trifluoroacetyl-ene-hydroxylamines Generated in Situ

A series of requisite oxime ethers **7** were prepared by the reaction of *O*-arylhydroxylamine **5** with the corresponding ketones **6** in good to high yields (Table 1). Compound **5** was prepared from commercially available arylboronic acid in two steps according to the literature procedures.[8] The oxime ethers **7Ie**,**7Je**, and **7Ke** carrying either an *o*-, *m*-, or a *p*-nitro group were easily prepared from acetophenone oxime and nitrofluorobenzenes **8A**–**C** (Table 2).

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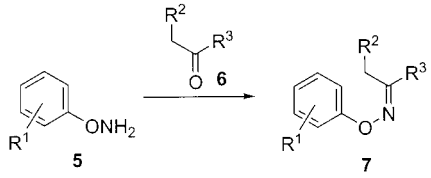
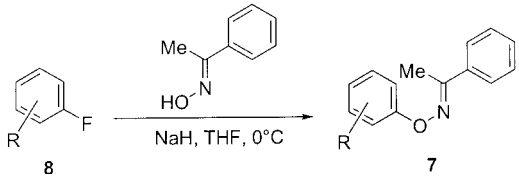
Table 1. Preparation of oxime ethers **7Aa**–**7He**.



Entry	Substrate	R^1	Ketone	R^2	R^3	Product[a]	% Yield
1	**5A**	H	**6a**	$-(CH_2)_3-$		**7Aa**	98
2	**5A**	H	**6b**	$-(CH_2)_4-$		**7Ab**	91
3	**5A**	H	**6c**	Me	Et	**7Ac**	89
4	**5A**	H	**6d**	H	Me	**7Ad**	79
5	**5A**	H	**6e**	H	Ph	**7Ae**	86
6	**5A**	H	**6f**	H	*p*-BrC_6H_4	**7Af**	91
7	**5A**	H	**6g**	H	*p*-$NO_2C_6H_4$	**7Ag**	91
8	**5A**	H	**6h**	H	*p*-OHC_6H_4	**7Ah**	98
9	**5A**	H	**6i**	H	*p*-$OMeC_6H_4$	**7Ai**	96
10	**5A**	H	**6j**	Me	Ph	**7Aj**	90[b]
11	**5A**	H	**6k**	Me	*p*-BrC_6H_4	**7Ak**	93[b]
12	**5A**	H	**6l**	Me	*p*-OHC_6H_4	**7Al**	96[b]
13	**5A**	H	**6m**	Me	*p*-$OMeC_6H_4$	**7Am**	88[b]
14	**5A**	H	**6n**	H	*m*-BrC_6H_4	**7An**	97
15	**5A**	H	**6o**	H	*m*-$NO_2C_6H_4$	**7Ao**	91
16	**5A**	H	**6p**	H	*m*-OHC_6H_4	**7Ap**	90
17	**5A**	H	**6q**	H	*m*-$OMeC_6H_4$	**7Aq**	93
18	**5A**	H	**6r**	H	*o*-BrC_6H_4	**7Ar**	89[c]
19	**5A**	H	**6s**	H	*o*-$NO_2C_6H_4$	**7As**	78[d]
20	**5A**	H	**6t**	H	*o*-OHC_6H_4	**7At**	84
21	**5A**	H	**6u**	H	*o*-$OMeC_6H_4$	**7Au**	95[b]
22	**5B**	*p*-Br	**6e**	H	Ph	**7Be**	97
23	**5C**	*p*-Me	**6e**	H	Ph	**7Ce**	99
24	**5D**	*m*-Br	**6e**	H	Ph	**7De**	94
25	**5E**	*m*-Me	**6e**	H	Ph	**7Ee**	99
26	**5F**	*m*-OMe	**6e**	H	Ph	**7Fe**	81
27	**5G**	*o*-Br	**6e**	H	Ph	**7Ge**	97
28	**5H**	*o*-Me	**6e**	H	Ph	**7He**	99

[a] **7Aa**–**7Ad** were carried out in MeOH at room temperature (Entries 1–4). **7Ae**–**7He** were carried out in EtOH and concd. aqueous HCl (cat.) at room temperature (Entries 5–28). [b] *E*:*Z* = 10:1. [c] *E*:*Z* = 4:1. [d] Stereostructures of *E* and *Z* isomers (4.5:1) have not been established.

Table 2. Preparation of oxime ethers **7Ie**–**Ke**.



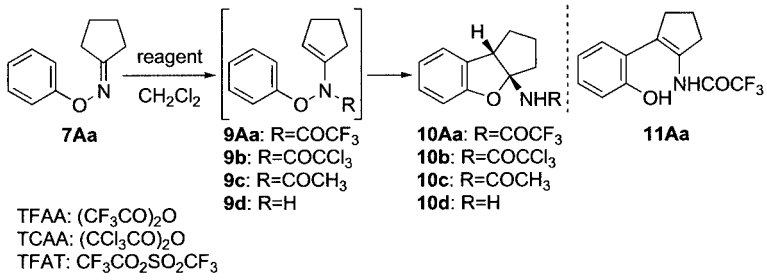
Entry	Substrate	R	Product	% Yield
1	**8A**	*p*-NO_2	**7Ie**	97
2	**8B**	*m*-NO_2	**7Je**[a]	87
3	**8C**	*o*-NO_2	**7Ke**	90

[a] **8B** and acetophenone oxime were mixed with *t*BuOK in DMF and then the reaction mixture was heated at 80 °C.

Under the reaction conditions employed in our related work involving a hydrazone system,[9] we first examined trifluoroacetylation of the oxime ether **7Aa** (Table 3). Treatment of the oxime ether **7Aa** with trifluoroacetic anhydride (TFAA) (1 equiv.) and Et_3N (1.5 equiv.) in CH_2Cl_2 at 0 °C gave the rearranged product **11Aa** in 8% yield along with the unreacted starting material **7Aa** (Entry 1).

Upon treatment with trifluoroacetic acid (TFA), the phenol **11Aa** could be readily converted to the dihydrobenzofuran **10Aa**. This result suggests strongly that **11Aa** could be formed by acylation of the oxime ether **7Aa** with TFAA followed by [3,3]-sigmatropic rearrangement of the resulting *N*-trifluoroacetyl-ene-hydroxylamine **9Aa**. Additionally, TFA was found to be essential for the cyclization reaction of the rearranged product **11Aa** as a possible intermediate. Therefore, we expected that the reaction of the oxime ether **7Aa** with TFAA in the absence of a base would proceed to afford the desired dihydrobenzofuran **10Aa**. In fact, trifluoroacetylation, [3,3]-sigmatropic rearrangement, and cyclization of **7Aa** proceeded smoothly in the presence of TFAA (1 equiv.) without a base to afford the corresponding *cis*-dihydrobenzofuran **10Aa** in excellent yield at even below room temperature (Entry 2). In the reaction at room temperature, the desired **10Aa** was formed after being stirred

Table 3. Reaction of oxime ether **7Aa** with acid anhydride.



Entry	Reagent (equiv.)	R	*T*/°C	*t*/h	% Yield **10Aa**
1	TFAA (1), Et_3N (1.5)	$COCF_3$	0	4	–[a]
2	TFAA (1)	$COCF_3$	0	3	99
3	TFAA (1)	$COCF_3$	room temp.	1	99
4	TFA (1)	H	room temp.	20	–[b]
5	TCAA (1)	$COCCl_3$	40	5	–[c]
6	Ac_2O (1)	$COCH_3$	40	8	–[d]
7	TFAT (1)	$COCF_3$	0	2	58 (9)[e]
8	TFAT (1), Et_3N (1.5)	$COCF_3$	0	0.5	24 (67)[e]
9	TFAT (1), Et_3N (5)	$COCF_3$	0	2	–[d]
10	TFAT (2), Et_3N (1)	$COCF_3$	0	0.5	80
11	TFAT (2), pyridine (1)	$COCF_3$	0	0.5	30 (39)[e]
12	TFAT (2), pyridine (1), DMAP (0.1)	$COCF_3$	0	0.5	84
13	TFAT (2), DMAP (0.1)	$COCF_3$	0	0.5	69 (16)[e]
14	TFAT (2), DMAP(1)	$COCF_3$	0	0.5	89

[a] **11Aa** was obtained in 8% yield and **7Aa** was recovered. [b] **10d** was obtained in 16% yield. [c] **10b** was obtained in 94% yield. [d] **7Aa** was recovered. [e] Yields in parentheses are for the recovered **7Aa**.

for 1 h (Entry 3). This is the first example of the formation of dihydrobenzofuran **10Aa** which was formed only by acylation conditions. The *cis*-dihydrobenzofuran **10Aa** was unambiguously characterized by ^1H NMR, ^{13}C NMR, COSY, and NOESY spectroscopic analyses.

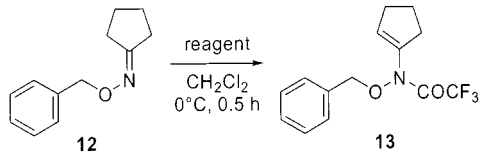
In order to check the possibility that TFA itself might facilitate the [3,3]-sigmatropic rearrangement by protonation at the nitrogen atom, we examined the reaction of oxime ether **7Aa** with only TFA and found that the 3a-aminodihydrobenzofuran **10d** was isolated in 16% yield (Entry 4). Therefore, it is apparent that the acylation reaction of **7Aa** for the formation of acyl-ene-hydroxylamine is the main and crucial step for [3,3]-sigmatropic rearrangement.

Next, we investigated systematically the acylation by changing four types of acylating reagents. When trichloroacetic anhydride (TCAA) was used as an acylating reagent, the reaction proceeded in refluxing CH_2Cl_2 to give dihydrobenzofuran **10b** in good yield (Entry 5). In contrast to TFAA and TCAA, Ac_2O did not give satisfactory results, and the starting material was completely recovered (Entry 6). The reaction of **7Aa** with trifluoroacetyl triflate (TFAT),[10] which is a stronger acylating reagent than TFAA, gave **10Aa** in lower 58% yield (Entry 7). However, treatment of **7Aa** with a mixture of TFAT (1 equiv.) and Et_3N (1.5 equiv.) gave the dihydrobenzofuran **10Aa** in 24% yield along with 67% yield of the starting material **7Aa** (Entry 8). The presence of excess Et_3N retarded the reaction (Entry 9). Reaction of **7Aa** with TFAT (2 equiv.) and Et_3N (1 equiv.) proceeded smoothly to give the desired dihydrofuran **10Aa** in 80% yield (Entry 10). Replacement of Et_3N by pyridine as a base led to lower chemical yield (30%) (Entry 11). However, the yield of dihydrobenzofuran **10Aa** was improved by the addition of a catalytic amount of DMAP (Entry 12). Though the reaction with TFAT (1 equiv.) in the presence of DMAP (0.1 equiv.) as a base proceeded effectively to give **10Aa** in moderate yield (Entry 13), reaction with a combination of TFAT (2 equiv.) and DMAP (1 equiv.) gave the desired dihydrobenzofuran **10Aa** in 89% yield (Entry 14). Thus, our reaction involving acylation, [3,3]-sigmatropic rearrangement, and cyclization was found to be accelerated when oxime ether was acylated with a stronger reagent bearing an electron-withdrawing group such as the trifluoroacetyl group. We choose TFAA in the formation of dihydrobenzofuran.

In order to establish intermediary *N*-trifluoroacetyl-ene-hydroxylamine **9Aa** which would be possibly formed by acylating oxime ether **7Aa**, we examined acylation of *O*-benzyl oxime ether **12**[11] (Table 4). Oxime ether **12** was prepared by condensation of cyclopentanone with *O*-benzylhydroxylamine and then subjected to acylation with TFAA or TFAT in the presence of DMAP. The product was expected *N*-trifluoroacetyl-ene-hydroxylamine **13** which was obtained in moderate to good yield (Entries 1 and 2). Thus, formation of the intermediate **9Aa** is proposed in our reaction though the isolation was not achieved yet.

We next investigated the reaction of the oxime ether **7Ab** derived from cyclohexanone (Table 5). Reaction of **7Ab** with TFAA at room temperature suffered from the competing formations of the dihydrobenzofuran **10Ab**, the benzo-

Table 4. Reaction of oxime ether **12** with TFAA or TFAT-DMAP.



12 13

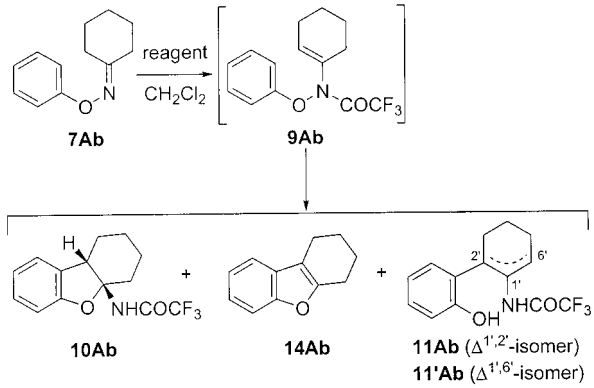
Entry	Reagent (equiv.)	Base (equiv.)	% Yield
1	TFAA (1)	–	81
2	TFAT (2)	DMAP (1)	63

furan **14Ab**, and the rearranged products **11Ab**, **11′Ab** (Entries 1, 2). The ratio of benzofuran **14Ab** to dihydrobenzofuran **10Ab** obtained was found to be influenced by the temperature used. Lower temperature (0 °C) favored the formation of dihydrobenzofuran **10Ab**. When the reaction was carried out in dichloromethane with TFAA at 0 °C, the desired dihydrobenzofuran **10Ab** was obtained as the sole product (Entry 3). On the contrary, treatment of **7Ab** with TFAT and DMAP produced exclusively the benzofuran **14Ab** in 83% yield (Entry 4). When the reaction was carried out in CH_2Cl_2 with TFAT (5 equiv.) and DMAP (3 equiv.) as a base, a highest yield of 92% was achieved for benzofuran **14Ab** (Entry 6). It is worthy to note that the selective synthesis of either dihydrobenzofuran **10Ab** or benzofuran **14Ab** was achieved only by changing the reaction conditions such as the TFAA or TFAT-DMAP system.

We examined the reductive deamination of the dihydrobenzofuran **10Ab** for the synthesis of the 2,3-dihydrobenzofuran (coumaran) **15**.[12] Though reductive deamination of **10Ab** with sodium cyanoborohydride in acetic acid did not occur at all, the reaction of **10Ab** with the same reagent in TFA proceeded to give the desired 2,3-dihydrobenzofuran **15** in moderate yield. In order to determine the reaction pathway, we investigated the conversion of the dihydrobenzofuran **10Ab** to the benzofuran **14Ab** (Table 6). Through extensive screening of the reaction conditions, we found that treatment of the dihydrobenzofuran **10Ab** with trifluoromethanesulfonic acid (TfOH) gave the benzofuran **14Ab** effectively as a result of elimination of the trifluoroacetamido group, while the treatment with TFA required a longer reaction time (Entries 1 and 2). Treatment of **10Ab** with either DMAP or its salt **16**[13] resulted in the recovery of the starting compound only (Entries 3 and 4). In the reaction with TFAT, it was clearly indicated that the dihydrobenzofuran **10Ab** was converted to the benzofuran **14Ab** by treatment with TfOH, which was unavoidably generated as a byproduct in the trifluoroacetylation of the oxime ether **7Ab**.

From the above results, we can propose plausible reaction pathways to dihydrobenzofuran **10Ab** and benzofuran **14Ab** (Scheme 2). First, acylation on the nitrogen atom of the oxime ether **1** leads to the formation of *N*-trifluoroacetyl-ene-hydroxylamine **2**, and then the [3,3]-sigmatropic rearrangement smoothly follows to form the acylimine **17**. Formation of the dihydrobenzofuran **3** would proceed by intramolecular cyclization of **17**. When TFAT was used as an acylating agent, the benzofuran **4** was formed through oxonium ion **18**, which was generated by elimination of the trifluoroacetamido group in the presence of TfOH. The overall pathway would be very similar to that of Fischer indolization, which involves analogous three-step key reactions of hydrazones. However, it is generally difficult to isolate dihydrobenzofurans under Fischer indolization conditions. To the best of our knowledge, there has been only

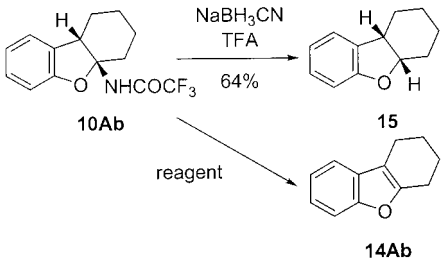
Table 5. Reaction of oxime ether **7Ab** with TFAA or TFAT-DMAP.

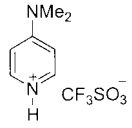


Entry	Reagent (equiv.)	*T*/°C	*t*/h	% Yield **10Ab**	**14Ab**	**11Ab+11′Ab**[a]
1	TFAA (1)	room temp.	23	37	19	23
2	TFAA (2)	room temp.	23	53	10	19
3	TFAA (4)	0	23	94	–	–
4	TFAT (2), DMAP (1)	0	0.5	–	83	–
5	TFAT (5), DMAP (3)	0	0.5	–	90	–
6	TFAT (5), DMAP (3)	room temp.	0.5	–	92	–

[a] Combined yields of two regioisomers.

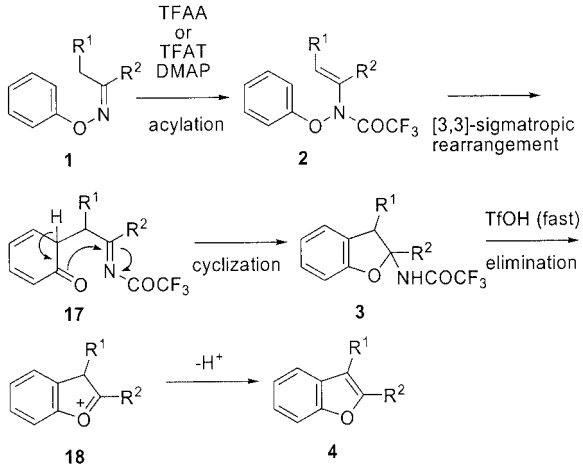
Table 6. Conversion of **10Ab** to 2,3-dihydrobenzofuran **15** and benzofuran **14Ab**.



Entry	Reagent (equiv.)	*t*	% Yield **14Ab**
1	TfOH (1)	1 min	84
2	TFA (1)	6 h	80
3	DMAP (1)	24 h	–[a]
4	 **16** (2)	24 h	–[a]
5	TFAT (5), DMAP (3)	0.5 h	94

[a] **10Ab** was recovered.

one paper pertaining to the isolation of dihydrobenzofurans which were synthesized from the oxime ethers bearing α,α′-disubstituted cyclopentane ring.[3h]



Scheme 2. Possible reaction pathway.

The different structures of the two products in the reaction with TFAT-DMAP (dihydrobenzofuran **10Aa** from cyclopentanone oxime ether **7Aa** and benzofuran **14Ab** from cyclohexanone oxime ether **7Ab**) could be explained as follows. The benzofuran double bond is not readily accommodated in a fused system such as 2,3-dihydro-1*H*-cyclopenta[*b*]benzofuran in which two rings are five-membered and rather rigid. On the other hand, it is clear that no comparable difficulty exists in the elimination of the trifluoroacetamido group when a more flexible six-membered cyclohexane ring is present.

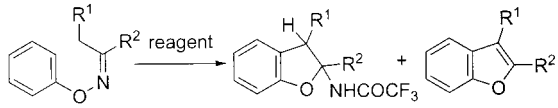
In order to disclose the role of DMAP, we examined the preparation of *N*-trifluoroacetylaniline[14] by acylation with commercially available TFAT which gave the desired amide in not quantitative yield but 63% yield. It suggests that TFAT itself is not so pure and contains a small amount of TFA and TfOH.

As shown in Entry 4 of Table 3, the reaction of **7Aa** with only TFA gave the dihydrobenzofuran **10d** in 16% yield, suggesting that the rearrangement step of the protonated intermediate is less effective than that under acylating conditions. Furthermore, reaction with commercially available TFAT gave the dihydrobenzofuran **10Aa** in 58% yield, but the product yield increased to 89% when DMAP was added (Entries 7 and 14).

Although the precise reason for the effect of DMAP on the reaction with TFAT is unclear, DMAP would accelerate the first acylation step. DMAP traps a small amount of TFA and TfOH which are contaminated with commercially available TFAT.[15] Thus, in the presence of DMAP (in the absence of a proton source such as TFA and TfOH), the acylation reaction of the oxime ether **1** (**1**→**2**) would effectively proceed to effect the subsequent rearrangement step (**2**→**17**) (Scheme 2).

To investigate the scope and limitations of the TFAA or TFAT-DMAP system utilized for benzofuran synthesis, we next tried to use a series of acyclic oxime ethers **7Ac**,**d** as substrate (Table 7). Reaction of oxime ether **7Ac**,**d** with TFAA gave the dihydrobenzofuran **10Ac**,**d** in good yield (Entries 2 and 4). On the contrary, the reaction with a combination of TFAT and DMAP gave exclusively the benzofuran **14Ac**,**d** (Entries 3, 5 and 6). These results clearly demonstrate the utility of [3,3]-sigmatropic rearrangement as a novel method for the synthesis of complex benzofurans. The remarkable result obtained in the reaction of oxime ethers **7Aa**–**d** prompted us to extend our procedure to the synthesis of various types of 2-arylbenzofurans.

Table 7. Reaction of oxime ethers **7Ac**,**d** with TFAA or TFAT-DMAP.



Entry	Substrate	Reagent (equiv.)	Solvent	*T*/°C	*t*/h	% Yield **10Ac,d**	**14Ac,d**
1	**7Ac**	TFAA (6)	CH_2Cl_2	40	9	21	–
2	**7Ac**	TFAA (6)	MeCN	80	5	64	–
3	**7Ac**	TFAT (5), DMAP (3)	CH_2Cl_2	0	2	–	89
4	**7Ad**	TFAA (6)	MeCN	80	4	94	–
5	**7Ad**	TFAT (5), DMAP (3)	CH_2Cl_2	0	2	–	43
6	**7Ad**	TFAT (5), DMAP (3)	CH_2Cl_2	room temp.	0.5	–	65

The Substituent Effect on the Benzene Ring of the Arylimine Part; Synthesis of 2-Arylbenzofurans 14Ae–u

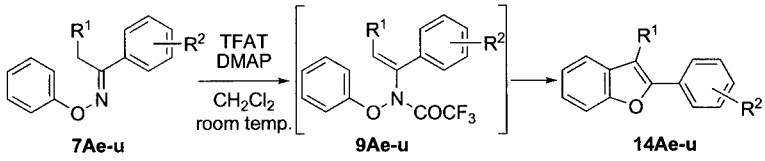
To test the scope of this novel method for the synthesis of benzofurans, we next examined the substituent effects on the aromatic ring in the reaction of the oxime ethers **7Ae–u** with the TFAT-DMAP system (Table 8).[16] Among benzofurans, 2-arylbenzofurans are inhibitors of cell proliferation and platelet activating factor and some of them show other interesting activities.[17] Thus, we started to investigate the substituent effect of our reaction and its application to the synthesis of 2-arylbenzofurans.

Treatment of the unsubstituted oxime ether **7Ae** with TFAT and DMAP gave the desired 2-phenylbenzofuran **14Ae** quantitatively. We could not isolate the proposed intermediate **9Ae** which underwent the [3,3]-sigmatropic rearrangement to afford the final benzofuran **14Ae** (Entry 1). Similarly, reaction of the oxime ether **7Af**,**g** bearing an electron-withdrawing substituent such as a bromo or nitro group at the *p* position proceeded smoothly to give the 2-arylbenzofuran **14Af**,**g** in good yields (Entries 2 and 3). To our delight, when the oxime ether **7Ah** bearing a free hydroxy group was treated with TFAT-DMAP, the hydroxybenzofuran **14Ah** was directly obtained after chromatography using silica gel (Entry 4). We succeeded in the isolation of the *p*-trifluoroacetyloxybenzofuran **14Av** by only recrystallization (not chromatography) of the crude product obtained from the oxime ether **7Ah** (Entry 5). Unfortunately, the reaction of **7Ai** with the *p*-methoxy group afforded the desired benzofuran **14Ai** (15%) along with the starting material (12%) and the 3-trifluoroacetylbenzofuran **14′Ai** (21%) (Entry 6). Compound **14′Ai** would be formed through trifluoroacetylation at the 3-position of the benzofuran **14Ai** formed under the reaction conditions.

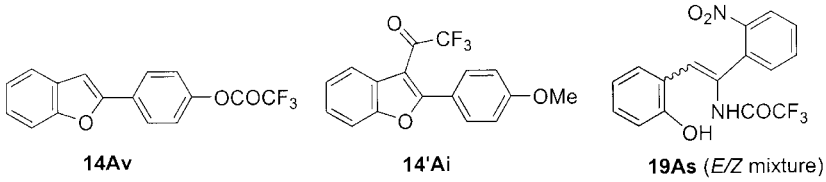
Oxime ethers bearing an additional carbon **7Aj–l** underwent effective reaction under the same reaction conditions to afford the corresponding 2-aryl-3-methylbenzofurans **14Aj–l** in excellent yields (Entries 7–9). However, the oxime ether **7Am** with the *p*-methoxy group gave the desired benzofuran **14Am** but in low yield though the reason is not clear (Entry 10). Substituents at the *m* position had no marked influence on the reaction, giving the expected benzofurans **14An–q** in excellent yields (Entries 11–14).

The next substrates of choice were the oxime ethers **7Ar–u** with an *ortho*-substituted phenyl group. *o*-Bromo, *o*-hydroxy, and *o*-methoxy-oxime ethers **7Ar**,**t**,**u** were employed

Table 8. Reaction of oxime ethers **7Ae–u** with TFAT-DMAP.



Entry	Substrate	R^1	R^2	*t*/h	Product	% Yield
1	**7Ae**	H	H	1	**14Ae**	99
2	**7Af**	H	*p*-Br	1.5	**14Af**	96
3	**7Ag**	H	*p*-NO_2	5	**14Ag**	85 (9)[a]
4	**7Ah**	H	*p*-OH	2	**14Ah**	84
5	**7Ah**	H	*p*-OH	2	**14Av**	92
6	**7Ai**	H	*p*-OMe	2	**14Ai**	15 (12)[a][b]
7	**7Aj**	Me	H	2	**14Aj**	82
8	**7Ak**	Me	*p*-Br	2	**14Ak**	91
9	**7Al**	Me	*p*-OH	2	**14Al**	86
10	**7Am**	Me	*p*-OMe	2	**14Am**	26 (13)[a]
11	**7An**	H	*m*-Br	2	**14An**	94
12	**7Ao**	H	*m*-NO_2	5	**14Ao**	95
13	**7Ap**	H	*m*-OH	2	**14Ap**	86
14	**7Aq**	H	*m*-OMe	1.5	**14Aq**	93
15	**7Ar**	H	*o*-Br	2	**14Ar**	76
16	**7As**	H	*o*-NO_2	2	**19As**	78[c]
17	**7At**	H	*o*-OH	2	**14At**	82
18	**7Au**	H	*o*-OMe	2	**14Au**	80



[a] Yields in parentheses are for the recovered starting materials. [b] **14′Ai** was obtained in 21% yield. [c] **19As** was obtained instead of **14As**.

under the same conditions to give the desired benzofurans **14Ar**,**t**,**u** in good yields (Entries 15, 17, and 18). When the *o*-nitro oxime ether **7At** was treated with TFAT-DMAP, benzofuran was not obtained, but the rearranged product **19As** was isolated (Entry 16).

In the case of the oxime ether **7Ah** with the hydroxy group, acylation would proceed at both the arylimine part and the hydroxy group to form a diacylated ene-hydroxylamine, which then rearranged to afford the acylated 2-arylbenzofuran **14Av**. This labile benzofuran **14Av** was readily hydrolyzed during column chromatography using silica gel to give the phenolic benzofuran **14Ah**. Similarly, the oxime ethers **7Al**, **7Ap** and **7At**, all of which have the hydroxy group, would give the desired 2-arylbenzofurans **14Al**, **14Ap** and **14At** via the corresponding diacylated intermediates.

As mentioned above, the series of reactions leading to the formation of 2-arylbenzofurans proceeded smoothly except for oxime ethers having a *p*-methoxy group (**7Ai** and **7Am**) (Figure 1). The electron-donating methoxy group lowers the reactivity of the intermediates **A** and **B** formed from **7Ai** and **7Am** toward nucleophilic attack of the carbonyl oxygen. In contrast, reaction of the oxime ether **7Au** bearing an *o*-methoxy group under the same conditions gave the desired 2-arylbenzofuran **14Au** in good yield. This result would be explained as follows. Steric hindrance between the *o*-methoxy group and the imine part would make the intermediate **C** nonplanar, and the resonance effect between the benzene ring and the acyl imine part would therefore not be very strong. Thus, the electrophilic reactivity of the acyl imine part is not as low as that of the *p*-methoxy substrate.

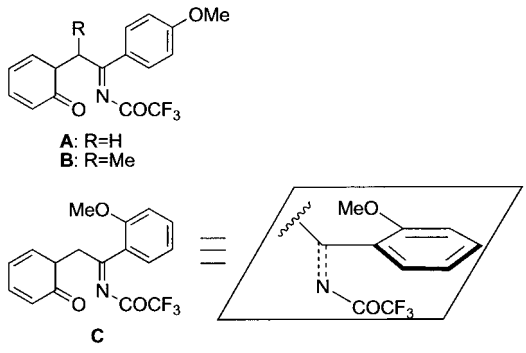
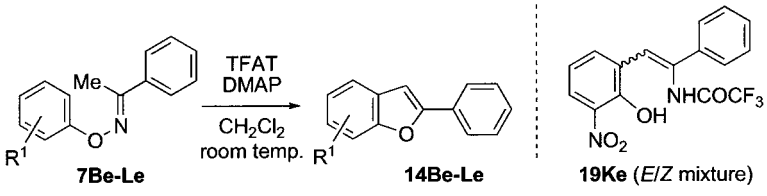


Figure 1. Acylimines **A**, **B**, and **C** with a methoxy group as intermediates.

The Effects of Substituents on the Phenoxy Ring; Synthesis of 2-Phenylbenzofurans 14Be–Le Functionalized at the 4–7 Positions

In order to explore the wide generality of our benzofuran synthesis, we have newly investigated the substituent effects in [3,3]-sigmatropic rearrangement of *O*-aryl-ene-hydroxylamines **9Be**–**Le**, which were generated in situ by acylation of the substituted oxime ethers **7Be**–**Le** (Table 9). Treatment of the oxime ethers **7Be**, **7Ie**, **7Ce** carrying *p*-bromo, *p*-nitro, *p*-methyl groups with TFAT-DMAP afforded, as expected, the functionalized 2-phenylbenzofurans **14Be**, **14Ie**, **14Ce** in good to excellent yields (Entries 1–3). A similar trend was observed in the reaction of the oxime ethers **7Ge**, **7Ke**, **7He** with the *o*-substituted group such as bromo, nitro, and methyl groups. *o*-Bromo and *o*-methyl oxime ethers **7Ge** and **7He** gave the corresponding 7-substituted 2-phenylbenzofurans **14Ge** and **14He** in good yields though reaction times are different (Entries 9 and 11). Reaction of the oxime ether **7Ke** having the *o*-nitro group proceeded to give a sepa-

Table 9. Reaction of oxime ethers **7Be**–**Le** with TFAT-DMAP.



7Be-Le **14Be-Le** **19Ke** (*E*/*Z* mixture)

Entry	Substrate	R^1	*t*/h	Product	% Yield	Ratio[g] **14**:**14′**
1	**7Be**	*p*-Br	2	**14Be**[a]	81	
2	**7Ie**	*p*-NO_2	22	**14Ie**[a]	84	
3	**7Ce**	*p*-Me	2	**14Ce**[a]	73[h]	
4	**7De**	*m*-Br	3	**14De**[b]+**14′De**[c]	92	1:1
5	**7Je**	*m*-NO_2	22	**14Je**[b]+**14′Je**[c]	84	2:1
6	**7Ee**	*m*-Me	2	**14Ee**[b]+**14′Ee**[c]	94	1:1.5
7	**7Le**[e]	*m*-OH	2.5	**14Le**[b]+**14′Le**[c]	85	1:1.5
8	**7Fe**	*m*-OMe	3	**14Fe**[b]+**14′Fe**[c]	78	1:4
9	**7Ge**	*o*-Br	22	**14Ge**[d]	80	
10	**7Ke**	*o*-NO_2	22	**14Ke**[d]	41[f]	
11	**7He**	*o*-Me	4	**14He**[d]	89	

[a] **14Be**,**Ie**,**Ce** were 5-substituted benzofurans. [b] **14De**,**Je**,**Ee**,**Le**,**Fe** were 4-substituted benzofurans. [c] **14′De**,**Je**,**Ee**,**Le**,**Fe** were 6-substituted benzofurans. [d] **14Ge**,**Ke**,**He** were 7-substituted benzofurans. [e] **7Le** was prepared by treatment of **7Fe** with BBr_3. [f] **19Ke** was obtained in 24% yield and **7Ke** was recovered in 16% yield. [g] The ratios of regioisomers were determined by ^1H NMR analysis. [h] Reaction was carried out at 0 °C.

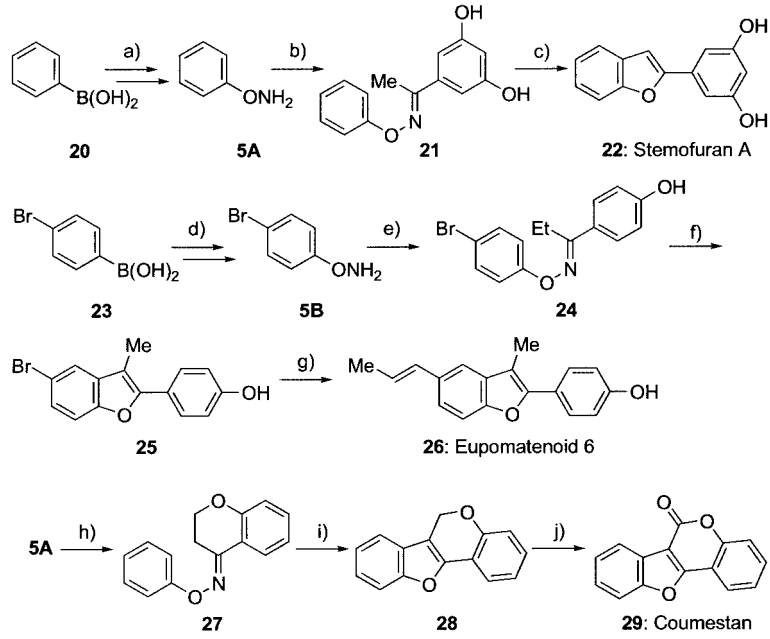
rable mixture of the 7-substituted 2-phenylbenzofurans **14Ke** and rearranged product **19Ke** (Entry 10). Reaction of oxime ether **7De**, **7Je**, **7Ee**, **7Le**, **7Fe** bearing a bromo, nitro, methyl, hydroxy or methoxy group at the *m* position proceeded smoothly to give the desired 2-phenylbenzofuran **14De**, **14Je**, **14Ee**, **14Le**, **14Fe** and **14′De**, **14′Je**, **14′Ee**, **14′Le**, **14′Fe** in good yields (Entries 4–8). The *m*-substituted oxime ethers **7De**, **7Je**, **7Ee**, **7Le**, **7Fe**, however, gave two types of benzofurans with low regioselectivity in all cases.

Effective and Short Syntheses of Stemofuran A, Eupomatenoid 6 and Coumestan

As mentioned above, our novel synthetic method for benzofurans is an efficient and practical method because protection of the phenolic hydroxy groups is not required in the synthesis of hydroxylated 2-arylbenzofurans. This finding prompts us to explore a new efficient procedure for the synthesis of biologically active natural benzofurans. Thus, we started to synthesize natural and biologically active benzofuran products such as Stemofuran A (**22**)[5] Eupomatenoid 6 (**26**),[6] and Coumestan (**29**),[7] the latter of which does not have a hydroxy group. Our short synthesis of these products has been accomplished without protection of the phenolic hydroxy groups (Scheme 3).

At first, we examined the synthesis of Stemofuran A (**22**), recently isolated from *Stemona collinsae*.[5] The known synthesis of Stemofuran A reported by Pasturel et al.[18] involved many steps including the protection/deprotection of the hydroxy group. *O*-Phenylhydroxylamine (**5A**), readily prepared from **20**, was condensed with dihydroxyacetophenone to afford the oxime ether **21** in good yield. When the oxime ether **21** was treated with TFAT in the presence of DMAP at room temperature, the desired benzofuran was isolated in excellent yield and found to be identical with Stemofuran A (**22**) upon comparison of their spectroscopic data with those reported in the literature.[5] Thus, short synthesis of Stemofuran A (**22**) was accomplished in four steps with 72% overall yield.

Secondly, we chose Eupomatenoid 6 (**26**)[6] as our synthetic target which has shown antifungal, insecticidal, and antioxidant activities. Although Bach's[19] and Stevenson's[20] groups synthesized Eupomatenoid 6, the syntheses include many transformations involving protection and deprotection of the hydroxy group. To introduce the (*E*)-propenyl group of Eupomatenoid 6 at the last stage of our synthesis, we constructed the benzofuran part as the first step. Condensation of *O*-phenylhydroxylamine (**5B**) carrying the *p*-bromo group with *p*-hydroxypropiophenone gave the oxime ether **24** which was subjected to our reaction conditions to afford the 5-bromobenzofuran **25** in 95% yield. Finally, the benzofuran **25** was subjected to the Suzuki coupling reaction with (*E*)-propenyl boronic acid to afford Eupomatenoid 6 (**26**) in excellent yield. Thus, we succeeded in the total synthesis of Eupomatenoid 6 in 52% overall yield from **23** in five steps. Physical and spectral properties of our prepared benzofuran **26** were identical with those of natural Eupomatenoid 6 reported in the literature.[6] Our synthesis is superior to those reported by Bach's and Stevenson's groups in both yield and number of steps.



Scheme 3. Short syntheses of Stemofuran A, Eupomatenoid 6, and Coumestan. Reaction conditions: a) 2 steps, 83%, ref.[8]; b) 3,5-dihydroxyacetophenone, concd. aqueous HCl, EtOH, room temp., 3 h, 92%; c) TFAT, DMAP, CH_2Cl_2, room temp., 26 h, 95%; d) 2 steps, 62%, ref.[8]; e) 4-hydroxypropiophenone, concd. aqueous HCl, EtOH, room temp., 2 h, 92%; f) TFAT, DMAP, CH_2Cl_2, room temp., 8.5 h, 95%; g) *trans*-propenylboronic acid, $Pd(PPh_3)_4$, CsF, DME, 100 °C, 7 h, 97%; h) 4-chromanone, concd. aqueous HCl, EtOH, room temp., 2 h, 93%; i) TFAT, DMAP, CH_2Cl_2, room temp., 4 h, 78%; j) PCC, CH_2Cl_2, 40 °C, 4 h, 76%.

The third target of our synthesis is Coumestan (**29**),[7] which is a basic pharmacophore containing Coumestanes such as Coumestrol[21] which shows estrogenic activity. Due to its unique structure and biological activities, Coumestan (**29**) had been synthesized by many organic chemists using independent approaches.[22] Known synthetic methods involved the preparation of the benzofuran part at the last stage while we constructed the benzofuran part of Coumestan as the first step. Condensation of a common *O*-phenylhydroxylamine (**5A**) with 4-chromanone followed by sequential acylation and rearrangement of the resulting oxime ether **27** furnished the desired tricyclic benzofuran **28** in 73% yield via two steps. Finally, introduction of the carbonyl group was achieved by treatment of tricyclic benzofuran **28** with PCC to give Coumestan (**29**) in 76% yield. The spectroscopic data of the product are identical with those of Coumestan **29** reported in the literature.[7a] Thus, we succeeded in effective and short total synthesis of Stemofuran A (**22**), Eupomatenoid 6 (**26**), and Coumestan (**29**) without protection of the phenolic hydroxy groups in the former two cases.

Conclusions

In conclusion, we have established a highly efficient and general synthetic method for dihydrobenzofurans and benzofurans by sequential acylation, rearrangement and cyclization of oxime ethers under mild conditions. We found that the [3,3]-sigmatropic rearrangement took place smoothly during the course of trifluoroacetylation of *O*-aryloxime ether at lower temperature to give the dihydrobenzofuran or benzofuran as a result of concomitant cyclization. Additionally the [3,3]-sigmatropic rearrangement process promoted by the trifluoroacetyl group would represent a general strategy that may be of great use in the synthesis of more complex heterocycles. Further studies including the synthesis of biologically active compounds via our methodology are now in progress in our laboratory.

Experimental Section

The melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 200, 300, or 500 MHz and at 50, 75, 125 MHz, respectively. IR spectra were recorded using FTIR apparatus. Mass spectra were obtained by EI method. Flash column chromatography (FCC) was performed using E. Merck Kieselgel 60 (230–400 mesh). Medium-pressure column chromatography (MCC) was performed using Lober Größe B (E. Merck 310–25, LiChroprep Si60). Preparative TLC separations were carried out on precoated silica gel plates (E. Merck, 60F254). TFAA was obtained from Wako Pure Chemical Industries (Wako). TFAT was obtained from Tokyo Chemical industry (TCI).

General Procedure for Preparation of *N*-(Aryloxy)phthalimides: According to the literature procedure,[8] to a suspension of *N*-hydroxyphthalimide (1.63 g, 10 mmol) and CuCl (0.99 g, 10 mmol) in 1,2-dichloroethane (50 mL) were added freshly activated 4-Å molecular sieves (2.4 g) and arylboronic acid (20 mmol) at room temperature. Then pyridine (0.83 mL, 11 mmol) was added to the reaction mixture resulting in a light brown suspension. Reaction flask was open to the atmosphere. After being stirred at the same temperature for 48 h, the reaction mixture became green as the reaction proceeded. The reaction mixture was adsorbed to SiO_2 (50 g) by removing the solvent under reduced pressure in the presence of silica gel. Purification of the residue by flash column chromatography (*n*-hexane/AcOEt) afforded *N*-aryloxyphthalimides. Note: The use of not freshly activated 4-Å molecular sieves gave poor yield.

N-Phenoxyphthalimide, *N*-(4-bromophenoxy)phthalimide, *N*-(4-methylphenoxy)phthalimide, *N*-(3-methoxyphenoxy)phthalimide, *N*-(3-methylphenoxy)phthalimide, *N*-(2-methylphenoxy)phthalimide were prepared according to the literature procedure.[8]

***N*-(3-Bromophenoxy)phthalimide:** Yield 42%; colorless crystals. M.p. 138–139 °C (MeOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.96–7.90 (m, 2 H), 7.86–7.80 (m, 2 H), 7.32 (br. t, J = 1.5 Hz, 1 H), 7.29 (br. dd, J = 8, 2 Hz, 1 H), 7.22 (t, J = 8 Hz, 1 H), 7.13 (br. ddd, J = 8, 2, 1.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.7, 159.3, 135.0, 130.9, 128.7, 127.8, 124.1, 122.9, 117.8, 113.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1797 and 1745 cm^{-1} (CONCO). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_8{}^{79}BrNO_3$ (M^+) 316.9688, found 316.9692. $C_{14}H_8BrNO_3$: calcd. C 52.86, H 2.53, N 4.27; found C 53.02, H 2.40, N 4.27.

***N*-(3-Methylphenoxy)phthalimide:** Yield 74%; colorless crystals. M.p. 145.5–147 °C (MeOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.95–7.89 (m, 2 H), 7.84–7.78 (m, 2 H), 7.21 (br. t, J = 8 Hz, 1 H), 6.99–6.93 (m, 3 H), 2.34 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 163.0, 158.8, 140.1, 134.8, 129.4, 128.8, 125.4, 123.9, 114.9, 111.3, 21.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1795 and 1741 cm^{-1} (CONCO). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{11}NO_3$ (M^+) 253.0738, found 253.0741. $C_{15}H_{11}NO_3$: calcd. C 71.14, H 4.38, N 5.53; found C 71.19, H 4.15, N 5.49.

***N*-(2-Bromophenoxy)phthalimide:** Yield 25%; colorless crystals. M.p. 174.5–175.5 °C (MeOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.93–7.89 (m, 2 H), 7.86–7.81 (m, 2 H), 7.59 (br. d, J = 8 Hz, 1 H), 7.27–7.20 (m, 1 H), 7.04–6.98 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 162.5, 155.0, 135.0, 133.9, 128.7, 128.6, 125.4, 124.0, 113.6, 109.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1798 and 1744 cm^{-1} (CONCO). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_8{}^{79}BrNO_3$ (M^+) 316.9688, found 316.9698. $C_{14}H_8BrNO_3$: calcd. C 52.86, H 2.53, N 4.40; found C 53.05, H 2.79, N 4.40.

General Procedure for Preparation of *O*-Arylhydroxylamines 5: To a solution of *N*-aryloxyphthalimide (7 mmol) in MeOH/$CHCl_3$ (v/v, 1:9) (160 mL) was added hydrazine monohydrate (1.02 mL, 21 mmol) under nitrogen at room temperature, resulting in a colorless solution. White precipitate appeared in a colorless solution as the reaction proceeded. After being stirred at the same temperature for 24 h, the reaction mixture was filtered and washed by $CHCl_3$. Then the filtrate was concentrated at reduced pressure. Purification of the residue by flash column chromatography (*n*-hexane/AcOEt) afforded *O*-arylhydroxylamines **5A**–**H**.

***O*-(4-Bromophenyl)hydroxylamine (5B):**[23] Yield 85%; colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36 (br. d, J = 8 Hz, 2 H), 7.03 (br. d, J = 8 Hz, 2 H), 5.86 (br. s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 160.4, 131.9, 115.0, 113.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3334 cm^{-1} (NH_2). HRMS (EI, *m*/*z*) calcd. for $C_6H_6{}^{79}BrNO$ (M^+) 186.9632, found 186.9630.

***O*-(4-Methylphenyl)hydroxylamine (5C):**[24] Yield 99%; colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.04 (br. d, J = 8 Hz, 2 H), 6.99 (br. d, J = 8 Hz, 2 H), 5.65 (br. s, 2 H), 2.26 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.1, 130.1, 129.5, 112.9, 20.3 ppm.

IR ($CHCl_3$): $\tilde{\nu}$ = 3332 cm^{-1} (NH_2). HRMS (EI, *m*/*z*) calcd. for C_7H_9NO (M^+) 123.0684, found 123.0692.

***O*-(3-Bromophenyl)hydroxylamine (5D):** Yield 73%; colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.38 (t, *J* = 2 Hz, 1 H), 7.12 (t, *J* = 8 Hz, 1 H), 7.06 (br. dt, *J* = 8, 2 Hz, 1 H), 7.02 (br. dt, *J* = 8, 2 Hz, 1 H), 5.82 (br. s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.0, 130.3, 124.1, 122.7, 116.5, 112.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3333 cm^{-1} (NH_2). HRMS (EI, *m*/*z*) calcd. for $C_6H_6{}^{79}BrNO$ (M^+) 186.9632, found 186.9648.

***O*-(3-Methylphenyl)hydroxylamine (5E):**[24] Yield 91%; colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.16 (t, *J* = 8 Hz, 1 H), 6.96 (br. s, 1 H), 6.94 (br. d, *J* = 8 Hz, 1 H), 6.76 (br. d, *J* = 8 Hz, 1 H), 5.58 (br. s, 2 H), 2.33 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 161.2, 139.1, 128.8, 121.7, 113.6, 110.0, 21.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3331 cm^{-1} (NH_2). HRMS (EI, *m*/*z*) calcd. for C_7H_9NO (M^+) 123.0684, found 123.0699.

***O*-(3-Methoxyphenyl)hydroxylamine (5F):**[24] Yield 95%; colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.16 (t, *J* = 8 Hz, 1 H), 6.75 (br. t, *J* = 2 Hz, 1 H), 6.71 (br. ddd, *J* = 8, 2, 1 Hz, 1 H), 6.50 (br. ddd, *J* = 8, 2, 1 Hz, 1 H), 5.37 (br. s, 2 H), 3.79 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.5, 160.7, 129.7, 106.7, 105.5, 99.1, 55.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3332 cm^{-1} (NH_2). HRMS (EI, *m*/*z*) calcd. for $C_7H_9NO_2$ (M^+) 139.0632, found 139.0647.

***O*-(2-Bromophenyl)hydroxylamine (5G):**[24] Yield 97%; colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.53 (br. dd, *J* = 8, 1.5 Hz, 1 H), 7.47 (br. dd, *J* = 8, 1.5 Hz, 1 H), 7.28 (br. td, *J* = 8, 1.5 Hz, 1 H), 6.84 (br. td, *J* = 8, 1.5 Hz, 1 H), 5.59 (br. s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 157.3, 132.8, 128.4, 122.3, 114.0, 108.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3333 cm^{-1} (NH_2). HRMS (EI, *m*/*z*) calcd. for $C_6H_6{}^{79}BrNO$ (M^+) 186.9632, found 186.9660.

***O*-(2-Methylphenyl)hydroxylamine (5H):**[24] Yield 78%; colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.35 (br. d, *J* = 8 Hz, 1 H), 7.14 (br. t, *J* = 8 Hz, 1 H), 7.05 (br. d, *J* = 8 Hz, 1 H), 6.82 (br. t, *J* = 8 Hz, 1 H), 5.72 (br. s, 2 H), 2.16 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.0, 130.3, 126.7, 123.8, 120.6, 111.3, 15.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3331 cm^{-1} (NH_2). HRMS (EI, *m*/*z*) calcd. for C_7H_9NO (M^+) 123.0684, found 123.0685.

General Procedure for Preparation of Oxime Ethers 7Aa–Ad: To a solution of *O*-phenylhydroxylamine **5A** (2 mmol) in MeOH (4 mL) was added the ketone (2.2 mmol) under nitrogen at room temperature. After being stirred at the same temperature for several hours, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt) afforded oxime ethers **7** as shown in Table 1.

Cyclopentanone *O*-Phenyloxime (7Aa): A colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (br. t, *J* = 8 Hz, 2 H), 7.15 (br. d, *J* = 8 Hz, 2 H), 6.97 (br. t, *J* = 8 Hz, 1 H), 2.65–2.60 (m, 2 H), 2.54–2.49 (m, 2 H), 1.85–1.77 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.0, 159.6, 129.0, 121.5, 114.4, 31.0, 28.2, 25.0, 24.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1659 cm^{-1} (C=N). HRMS (EI, *m*/*z*) calcd. for $C_{11}H_{13}NO$ (M^+) 175.0997, found 175.1000.

Cyclohexanone *O*-Phenyloxime (7Ab):[25] Colorless crystals. M.p. 45–46 °C (*n*-hexane) (ref.[25] 47° C). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 163.6, 159.4, 129.1, 121.5, 114.4, 32.0, 26.9, 25.8, 25.7, 25.6 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{12}H_{15}NO$ (M^+) 189.1153, found 189.1167.

3-Pentanone *O*-Phenyloxime (7Ac): A colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (br. t, *J* = 8 Hz, 2 H), 7.17 (br. d, *J* = 8 Hz, 2 H), 6.96 (br. tt, *J* = 8, 1.5 Hz, 1 H), 2.48 (br. q, *J* = 7.5 Hz, 2 H), 2.34 (br. q, *J* = 7.5 Hz, 2 H), 1.17 (br. t, *J* = 7.5 Hz, 3 H), 1.14 (br. t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 166.7, 159.6, 129.1, 121.5, 114.5, 27.2, 22.0, 10.7, 10.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1638 cm^{-1} (C=N). HRMS (EI, *m*/*z*) calcd. for $C_{11}H_{15}NO$ (M^+) 177.1153, found 177.1157.

2-Propanone *O*-Phenyloxime (7Ad):[3f] A colorless oil. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.4, 158.3, 129.1, 121.6, 114.5, 21.7, 16.0 ppm.

General Procedure for Preparation of the Oxime Ethers 7Ae–7Au, 7Be–7He: To a solution of the *O*-arylhydroxylamine **5** (2 mmol) in EtOH (4 mL) was added acetophenone or propiophenone (2 mmol) and concd. aqueous HCl (0.10 mL) under nitrogen at room temperature. After being stirred at the same temperature for several hours, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt) afforded the oxime ether **7Ae–He** as shown in Table 1.

(*E*)-1-Phenylethanone *O*-Phenyloxime (7Ae):[25] A colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.79–7.75 (m, 2 H), 7.47–7.27 (m, 7 H), 7.03 (tt, *J* = 8, 1.5 Hz, 1 H), 2.45 (br. s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.5, 157.6, 135.9, 129.6, 129.2, 128.4, 126.4, 122.1, 114.7, 13.2 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{13}NO$ (M^+) 211.0996, found 211.0990.

(*E*)-1-(4-Bromophenyl)ethanone *O*-Phenyloxime (7Af): A colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (br. d, *J* = 8.5 Hz, 2 H), 7.54 (br. d, *J* = 8.5 Hz, 2 H), 7.36–7.25 (m, 4 H), 7.04 (tt, *J* = 8, 1.5 Hz, 1 H), 2.42 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.4, 156.6, 134.8, 131.6, 129.3, 127.9, 124.0, 122.3, 114.7, 13.0 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}{}^{79}BrNO$ (M^+) 289.0102, found 289.0099.

(*E*)-1-(4-Nitrophenyl)ethanone *O*-Phenyloxime (7Ag): Colorless crystals. M.p. 78–79 °C (*n*-hexane/AcOEt). ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.25 (br. d, *J* = 8.5 Hz, 2 H), 7.94 (br. d, *J* = 8.5 Hz, 2 H), 7.39–7.27 (m, 4 H), 7.08 (br. t, *J* = 8 Hz, 1 H), 2.48 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.2, 155.7, 148.4, 141.9, 129.4, 127.2, 123.7, 122.8, 114.8, 13.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1523 and 1348 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}N_2O_3$ (M^+) 256.0847, found 256.0850. $C_{14}H_{12}N_2O_3$: calcd. C 65.62, H 4.72, N 10.93; found C 65.64, H 4.88, N 10.89.

(*E*)-1-(4-Hydroxyphenyl)ethanone *O*-Phenyloxime (7Ah): Colorless crystals. M.p. 85–86 °C (*n*-hexane/AcOEt). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.69 (br. d, *J* = 8.5 Hz, 2 H), 7.35–7.25 (m, 4 H), 7.02 (tt, *J* = 8, 1.5 Hz, 1 H), 6.86 (br. d, *J* = 8.5 Hz, 2 H), 5.04 (br. s, 1 H), 2.41 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.5, 157.9, 157.0, 129.2, 128.3, 128.1, 122.1, 115.4, 114.8, 13.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3594 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{13}NO_2$ (M^+) 227.0946, found 227.0944. $C_{14}H_{13}NO_2$: calcd. C 73.99, H 5.77, N 6.16; found C 73.97, H 5.85, N 6.13.

(*E*)-1-(4-Methoxyphenyl)ethanone *O*-Phenyloxime (7Ai): Colorless crystals. M.p. 32–34 °C (*n*-hexane/AcOEt). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.73 (br. d, *J* = 8.5 Hz, 2 H), 7.35–7.24 (m, 4 H), 7.01 (tt, *J* = 8, 1.5 Hz, 1 H), 6.92 (br. d, *J* = 8.5 Hz, 2 H), 3.83 (s, 3 H), 2.41 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 160.9, 159.6, 157.2, 129.2, 128.4, 127.8, 121.9, 114.7, 113.8, 55.3, 13.1 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO_2$ (M^+) 241.1102, found 241.1080. $C_{15}H_{15}NO_2$: calcd. C 74.67, H 6.27, N 5.81; found C 74.76, H 6.33, N 5.79.

(*E*/*Z*)-1-Phenyl-1-propanone *O*-Phenyloxime (7Aj): The oxime ethers (*E*)-**7Aj** and (*Z*)-**7Aj** were inseparable (*E*:*Z* = 10:1); colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.78–7.75 (m, 2 H), 7.45–7.39 (m, 3 H), 7.36–7.27 (m, 4 H), 7.03 (br. tt, *J* = 8, 1.5 Hz, 1 H),

2.96 (q, *J* = 7.5 Hz, 20/11 H), 2.70 (q, *J* = 7.5 Hz, 2/11 H), 1.25 (t, *J* = 7.5 Hz, 30/11 H), 1.17 (t, *J* = 7.5 Hz, 3/11 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 162.7, 159.6, 129.6, 129.2, 128.5, 128.1, 127.7, 122.0, 114.7, 20.7, 11.3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO$ (M^+) 225.1153, found 225.1165. The ^{13}C NMR spectroscopic data of only (*E*)-**7Aj** was described.

(*E*/*Z*)-1-(4-Bromophenyl)-1-propanone *O*-Phenyloxime (7Ak): The oxime ethers (*E*)-**7Ak** and (*Z*)-**7Ak** were inseparable (*E*:*Z* = 10:1); colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.64 (br. d, *J* = 8.5 Hz, 2 H), 7.54 (br. d, *J* = 8.5 Hz, 2 H), 7.33 (br. t, *J* = 8 Hz, 2 H), 7.27 (br. d, *J* = 8 Hz, 2 H), 7.04 (br. tt, *J* = 8, 1.5 Hz, 1 H), 2.92 (q, *J* = 7.5 Hz, 20/11 H), 2.67 (q, *J* = 7.5 Hz, 2/11 H), 1.23 (t, *J* = 7.5 Hz, 30/11 H), 1.16 (t, *J* = 7.5 Hz, 3/11 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 161.7, 159.5, 133.8, 131.7, 129.3, 128.2, 124.0, 122.3, 114.8, 20.4, 11.3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{14}{}^{79}BrNO$ (M^+) 303.0258, found 302.0262. The ^{13}C NMR spectroscopic data of only (*E*)-**7Ak** was described.

(*E*/*Z*)-1-(4-Hydroxyphenyl)-1-propanone *O*-Phenyloxime (7Al): The oxime ethers (*E*)-**7Al** and (*Z*)-**7Al** were inseparable (*E*:*Z* = 10:1); colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.66 (br. d, *J* = 8.5 Hz, 2 H), 7.36–7.24 (m, 4 H), 7.02 (br. tt, *J* = 8, 1.5 Hz, 1 H), 6.84 (br. d, *J* = 8.5 Hz, 2 H), 5.36 (br. s, 1 H), 2.91 (q, *J* = 7.5 Hz, 20/11 H), 2.69 (q, *J* = 7.5 Hz, 2/11 H), 1.23 (t, *J* = 7.5 Hz, 30/11 H), 1.15 (t, *J* = 7.5 Hz, 3/11 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 163.0, 159.6, 157.1, 129.2, 128.3, 127.2, 122.0, 115.5, 114.8, 20.7, 11.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3590 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO_2$ (M^+) 241.1102, found 241.1108. The ^{13}C NMR spectroscopic data of only (*E*)-**7Al** was described.

(*E*/*Z*)-1-(4-Methoxyphenyl)-1-propanone *O*-Phenyloxime (7Am): (*E*,*Z*)-**7Am** (*E*:*Z* = 10:1) as colorless crystals. M.p. 45–46 °C (AcOEt); (*E*,*Z*)-**7Am**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.72 (br. d, *J* = 8.5 Hz, 2 H), 7.35–7.26 (m, 4 H), 7.01 (br. tt, *J* = 8, 1.5 Hz, 1 H), 6.93 (br. d, *J* = 8.5 Hz, 2 H), 3.83 (s, 3 H), 2.92 (q, *J* = 7.5 Hz, 20/11 H), 2.70 (q, *J* = 7.5 Hz, 2/11 H), 1.23 (t, *J* = 7.5 Hz, 30/11 H), 1.16 (t, *J* = 7.5 Hz, 3/11 H) ppm. HRMS (EI, *m*/*z*) calcd. for $C_{16}H_{17}NO_2$ (M^+) 255.1259, found 255.1257.

(*E*)-7Am: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.72 (br. d, *J* = 8.5 Hz, 2 H), 7.36–7.26 (m, 4 H), 7.01 (br. tt, *J* = 8, 1.5 Hz, 1 H), 6.93 (br. d, *J* = 8.5 Hz, 2 H), 3.83 (s, 3 H), 2.92 (q, *J* = 7.5 Hz, 2 H), 1.23 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.3, 160.8, 159.6, 129.2, 128.0, 127.2, 121.9, 114.7, 113.9, 55.2, 20.5, 11.4 ppm. $C_{16}H_{17}NO_2$: calcd. C 75.27, H 6.71, N 5.49; found C 75.36, H 6.78, N 5.44.

(*E*)-1-(3-Bromophenyl)ethanone *O*-Phenyloxime (7An): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.93 (t, *J* = 2 Hz, 1 H), 7.69 (ddd, *J* = 8, 2, 1 Hz, 1 H), 7.54 (ddd, *J* = 8, 2, 1 Hz, 1 H), 7.37–7.25 (m, 5 H), 7.05 (tt, *J* = 8, 1.5 Hz, 1 H), 2.42 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.8, 156.7, 138.3, 133.0, 130.4, 129.8, 129.7, 125.4, 123.1, 122.8, 115.2, 13.6 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}{}^{79}BrNO$ (M^+) 289.0102, found 289.0108.

(*E*)-1-(3-Nitrophenyl)ethanone *O*-Phenyloxime (7Ao): Colorless crystals. M.p. 64–65 °C (*n*-hexane/AcOEt). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.59 (t, *J* = 2 Hz, 1 H), 8.25 (ddd, *J* = 8, 2, 1 Hz, 1 H), 7.58 (t, *J* = 8 Hz, 1 H), 7.35 (br. t, *J* = 8 Hz, 2 H), 7.29 (br. d, *J* = 8 Hz, 2 H), 7.07 (br. tt, *J* = 8, 1.5 Hz, 1 H), 2.49 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.2, 155.5, 148.4, 137.6, 132.1, 129.5, 129.4, 124.2, 122.7, 121.3, 114.8, 13.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1533 and 1353 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}N_2O_3$ (M^+) 256.0847, found 256.0845. $C_{14}H_{12}N_2O_3$: calcd. C 65.62, H 4.72, N 10.93; found C 65.62, H 4.86, N 10.88.

(*E*)-1-(3-Hydroxyphenyl)ethanone *O*-Phenyloxime (7Ap): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36–7.25 (m, 7 H), 7.03 (tt, *J* = 8, 1.5 Hz, 1 H), 6.89 (dm, *J* = 8 Hz, 1 H), 5.06 (br. s, 1 H), 2.42 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.3, 155.5, 137.2, 129.8, 129.3, 122.3, 119.1, 117.0, 114.9, 113.3, 13.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3595 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{13}NO_2$ (M^+) 227.0946, found 227.0960.

(*E*)-1-(3-Methoxyphenyl)ethanone *O*-Phenyloxime (7Aq): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36–7.27 (m, 7 H), 7.03 (tt, *J* = 8, 1.5 Hz, 1 H), 6.98–6.94 (m, 1 H), 3.85 (s, 3 H), 2.44 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.6, 159.5, 157.6, 137.3, 129.5, 129.2, 122.1, 119.0, 115.3, 114.8, 111.9, 55.3, 13.4 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO_2$ (M^+) 241.1102, found 241.1098.

(*E*/*Z*)-1-(2-Bromophenyl)ethanone *O*-Phenyloxime (7Ar): The oxime ethers (*E*)-**7Ar** and (*Z*)-**7Ar** were inseparable (*E*:*Z* = 4:1); colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.63 (br. d, *J* = 8 Hz, 1 H), 7.41–7.10 (m, 7 H), 7.03 (br. t, *J* = 8 Hz, 4/5 H), 6.98 (br. t, *J* = 8 Hz, 1/5 H), 2.44 (s, 12/5 H), 2.33 (s, 3/5 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 160.2, 159.2, 138.2, 133.1, 132.6, 130.31, 130.28, 129.8, 129.2, 129.1, 127.8, 127.4, 127.3, 122.3, 122.1, 121.6, 115.0, 114.8, 21.2, 17.3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}{}^{79}BrNO$ (M^+) 289.0102, found 289.0112.

(*E*/*Z*)-1-(2-Nitrophenyl)ethanone *O*-Phenyloxime (7As): The oxime ethers (*E*)-**7As** and (*Z*)-**7As** were inseparable. Stereostructures of *E* and *Z* isomers (4.5:1) have not been established; colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.13 (br. d, *J* = 8 Hz, 2/11 H), 8.05 (br. d, *J* = 8 Hz, 9/11 H), 7.71 (br. t, *J* = 8 Hz, 2/11 H), 7.67 (br. t, *J* = 8 Hz, 9/11 H), 7.60–7.52 (m, 20/11 H), 7.35–7.17 (m, 42/11 H), 7.05–6.94 (m, 15/11 H), 2.43 (s, 6/11 H), 2.40 (s, 27/11 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.0, 158.7, 157.6, 155.7, 147.8, 146.6, 133.7, 133.2, 132.2, 130.54, 130.46, 129.8, 129.5, 129.1, 129.0, 128.0, 124.5, 124.1, 122.4, 122.3, 114.7, 114.6, 21.0, 16.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1531 and 1349 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}N_2O_3$ (M^+) 256.0847, found 256.0857.

(*E*)-1-(2-Hydroxyphenyl)ethanone *O*-Phenyloxime (7At): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.10 (br. s, 1 H), 7.48 (dd, *J* = 8, 1.5 Hz, 1 H), 7.38–7.28 (m, 3 H), 7.19 (br. d, *J* = 8 Hz, 2 H), 7.08 (br. t, *J* = 8 Hz, 1 H), 7.01 (br. dd, *J* = 8, 1.5 Hz, 1 H), 6.92 (br. t, *J* = 8 Hz, 1 H), 2.51 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 161.7, 158.6, 157.9, 131.6, 129.6, 128.1, 123.1, 119.3, 117.9, 117.6, 114.8, 12.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3456–2725 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{13}NO_2$ (M^+) 227.0946, found 227.0960.

(*E*/*Z*)-1-(2-Methoxyphenyl)ethanone *O*-Phenyloxime (7Au): The oxime ethers (*E*)-**7Au** and (*Z*)-**7Au** were inseparable (*E*:*Z* = 10:1); colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40 (br. td, *J* = 8, 1.5 Hz, 10/11 H), 7.35 (td, *J* = 8, 1.5 Hz, 11/11 H), 7.30–7.23 (m, 55/11 H), 7.19 (dd, *J* = 8, 1.5 Hz, 1/11 H), 7.10 (br. dd, *J* = 8, 1.5 Hz, 1/11 H), 7.02–6.92 (m, 21/11 H), 3.85 (s, 30/11 H), 3.79 (s, 3/11 H), 2.40 (s, 30/11 H), 2.30 (s, 3/11 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 160.0, 159.5, 157.5, 130.6, 129.7, 129.1, 126.3, 121.9, 120.5, 114.7, 111.0, 55.3, 16.6 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO_2$ (M^+) 241.1102, found 241.1102. The ^{13}C NMR spectroscopic data of only (*E*)-**7Au** was described.

(*E*)-1-Phenylethanone *O*-(4-Bromophenyl)oxime (7Be): Colorless crystals. M.p. 93–94 °C (*n*-hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.78–7.75 (m, 2 H), 7.45–7.40 (m, 5 H), 7.18 (br. d, *J* = 8.5 Hz, 2 H), 2.45 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 158.7, 158.3, 135.7, 132.1, 130.0, 128.5, 126.5, 116.5, 114.3, 13.4 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}{}^{79}BrNO$ (M^+) 289.0102, found 289.0101. $C_{14}H_{12}BrNO$: calcd. C 57.95, H 4.17, N 4.83; found C 58.21, H 4.17, N 4.74.

(*E*)-1-Phenylethanone *O*-(4-Methylphenyl)oxime (7Ce): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79–7.73 (m, 2 H), 7.43–7.38 (m, 3 H), 7.19–7.10 (m, 4 H), 2.43 (s, 3 H), 2.32 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 157.5, 157.3, 136.1, 131.4, 129.7, 129.6, 128.4, 126.4, 114.7, 20.6, 13,3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO$ (M^+) 225.1153, found 225.1163.

(*E*)-1-Phenylethanone *O*-(3-Bromophenyl)oxime (7De): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.78–7.75 (m, 2 H), 7.51 (br. s, 1 H), 7.45–7.15 (m, 6 H), 2.44 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 160.1, 158.5, 135.5, 130.3, 129.9, 128.5, 126.5, 125.0, 122.6, 117.9, 113.5, 13.4 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}{}^{79}BrNO$ (M^+) 289.0102, found 289.0107.

(*E*)-1-Phenylethanone *O*-(3-Methylphenyl)oxime (7Ee): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79–7.75 (m, 2 H), 7.43–7.39 (m, 3 H), 7.21 (t, *J* = 8 Hz, 1 H), 7.12 (br. s, 1 H), 7.09 (br. d, *J* = 8 Hz, 1 H), 6.84 (br. d, *J* = 8 Hz, 1 H), 2.44 (s, 3 H), 2.36 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 160.0, 157.6, 139.3, 136.0, 129.6, 129.0, 128.5, 126.5, 122.9, 115.4, 111.8, 21.5, 13.3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO$ (M^+) 225.1153, found 225.1160.

(*E*)-1-Phenylethanone *O*-(3-Methoxyphenyl)oxime (7Fe): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.81–7.75 (m, 2 H), 7.44–7.39 (m, 3 H), 7.23 (br. t, *J* = 8 Hz, 1 H), 6.90 (br. s, 1 H), 6.88 (br. dm, *J* = 8 Hz, 1 H), 6.59 (br. dm, *J* = 8 Hz, 1 H), 3.82 (s, 3 H), 2.45 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 160.7, 160.6, 157.7, 135.9, 129.7, 128.5, 126.5, 107.7, 107.1, 100.8, 55.3, 13.3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO_2$ (M^+) 241.1102, found 241.1102.

(*E*)-1-Phenylethanone *O*-(2-Bromophenyl)oxime (7Ge): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79–7.76 (m, 2 H), 7.60 (dd, *J* = 8, 1.5 Hz, 1 H), 7.54 (dd, *J* = 8, 1.5 Hz, 1 H), 7.45–7.40 (m, 3 H), 7.29 (br. td, *J* = 8, 1.5 Hz, 1 H), 6.90 (br. td, *J* = 8, 1.5 Hz, 1 H), 2.53 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.3, 155.3, 135.5, 132.9, 129.9, 128.5, 128.4, 126.6, 123.0, 115.9, 109.2, 13.8 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}{}^{79}BrNO$ (M^+) 289.0102, found 289.0100.

(*E*)-1-Phenylethanone *O*-(2-Methylphenyl)oxime (7He): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80–7.75 (m, 2 H), 7.50 (br. d, *J* = 8 Hz, 1 H), 7.43–7.39 (m, 3 H), 7.19 (br. t, *J* = 8 Hz, 1 H), 7.15 (br. d, *J* = 8 Hz, 1 H), 6.94 (br. t, *J* = 8 Hz, 1 H), 2.47 (s, 3 H), 2.32 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 157.7, 157.5, 136.0, 130.5, 129.6, 128.4, 126.9, 126.4, 124.7, 121.8, 114.2, 16.0, 13,3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{15}NO$ (M^+) 225.1153, found 225.1171.

General Procedure for Preparation of the Oxime Ethers 7Ie, Ke: To a mixture of NaH (164.5 mg, 4.11 mmol) (60% w/w dispersion in mineral oil, washed with dry *n*-hexane) in dry THF (8.5 mL) was added acetophenone oxime (500 mg, 3.70 mmol) in dry THF (3.0 mL) under nitrogen at 0 °C. After being stirred at the same temperature for 30 min, nitrofluorobenzene (**8**) (4.11 mmol) and 18-crown-6 (31.7 mg, 0.12 mmol) were added and the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was quenched with H_2O and extracted with $CHCl_3$. The organic phase was washed brine, dried with $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt) afforded the oxime ethers **7Ie**,[26] **7Ke**[26] as shown in Table 2.

(*E*)-1-Phenylethanone *O*-(4-Nitrophenyl)oxime (7Ie):[26] Yellow crystals. M.p. 122–123 °C (MeOH) (ref.[26] 122–124° C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.25 (br. d, *J* = 8 Hz, 2 H), 7.80–7.76 (m, 2 H), 7.49–7.44 (m, 3 H), 7.43–7.37 (br. d, *J* = 8 Hz, 2 H), 2.50 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 164.2, 160.2, 142.4, 135.0, 130.4, 128.7, 126.6, 125.7, 114.5, 13.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1519 and 1343 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}N_2O_3$ (M^+) 256.0847, found 256.0839.

(*E*)-1-Phenylethanone *O*-(2-Nitrophenyl)oxime (7Ke):[26] Yellow crystals. M.p. 32–33 °C (*n*-hexane/MeOH) (ref.[26] 151–152° C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.97 (dd, *J* = 8, 1.5 Hz, 1 H), 7.86 (dd, *J* = 8, 1.5 Hz, 1 H), 7.79–7.74 (m, 2 H), 7.57 (br. td, *J* = 8, 1.5 Hz, 1 H), 7.47–7.40 (m, 3 H), 7.08 (br. td, *J* = 8, 1.5 Hz, 1 H), 2.54 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 161.0, 153.2, 137.3, 135.0, 134.6, 130.4, 128.6, 126.7, 125.5, 121.4, 117.1, 14.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1525 and 1349 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}N_2O_3$ (M^+) 256.0847, found 256.0855.

(*E*)-1-Phenylethanone *O*-(3-Nitrophenyl)oxime (7Je): To a mixture of *t*BuOK (506.2 mg, 4.52 mmol) in dry DMF (4 mL) was added acetophenone oxime (500 mg, 3.70 mmol) under nitrogen at 0 °C. After being stirred at room temperature for 30 min, nitrofluorobenzene **8B** (0.44 mL, 4.11 mmol) was added and the reaction mixture was heated at 80 °C for 4 h. The reaction mixture was cooled to room temperature, quenched with H_2O and extracted with Et_2O. The organic phase was washed brine, dried with $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt) afforded the oxime ether **7Je** (913.1 mg, 87%) as a yellow oil.^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.18 (t, *J* = 2 Hz, 1 H), 7.90 (ddd, *J* = 8, 2, 1 Hz, 1 H), 7.81–7.78 (m, 2 H), 7.59 (ddd, *J* = 8, 2, 1 Hz, 1 H), 7.51–7.43 (m, 4 H), 2.49 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.9, 159.4, 149.0, 135.1, 130.2, 129.7, 128.6, 126.6, 120.9, 116.8, 109.9, 13.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1531 and 1354 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{12}N_2O_3$ (M^+) 256.0847, found 256.0847.

(*E*)-1-Phenylethanone *O*-(3-Hydroxyphenyl)oxime (7Le): To a solution of the oxime ether **7Fe** (216.2 mg, 0.90 mmol) in CH_2Cl_2 (6.8 mL) was added BBr_3 (1.35 mL, 1.35 mmol) (1.0 M in CH_2Cl_2 solution) under nitrogen at 0 °C. After being stirred at room temperature for 2 h, the reaction mixture was quenched with H_2O and extracted with $CHCl_3$. The organic phase was washed brine, dried with $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt) afforded the oxime ether **7Le** (72.4 mg, 36%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.78–7.74 (m, 2 H), 7.44–7.40 (m, 3 H), 7.17 (t, *J* = 8 Hz, 1 H), 6.87–6.82 (m, 2 H), 6.50 (ddd, *J* = 8, 2, 1 Hz, 1 H), 4.90 (br. s, 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 160.8, 158.0, 156.5, 135.9, 130.0, 129.8, 128.5, 126.5, 109.0, 107.2, 102.1, 13.4 ppm; $\tilde{\nu}$ = 3597 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{13}NO_2$ (M^+) 227.0946, found 227.0963.

2,2,2-Trifluoro-*N*-[2-(2-hydroxyphenyl)-1-cyclopenten-1-yl]acetamide (11Aa): (Table 3, Entry 1) To a solution of oxime ether **7Aa** (35.0 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) were added Et_3N (0.042 mL, 0.30 mmol) and TFAA (0.028 mL, 0.20 mmol) under nitrogen at 0 °C. After being stirred at the same temperature for 4 h, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 20:1) afforded the rearranged product **11Aa** (4.5 mg, 8%) as a colorless oil and recovered **7Aa** (30.5 mg, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.53 (br. s, 1 H), 7.26–7.17 (m, 2 H), 7.01–6.91 (m, 2 H), 6.75 (br. s, 1 H), 3.11 (br. t, *J* = 7.5 Hz, 2 H), 2.76 (br. t, *J* = 7.5 Hz, 2 H), 2.06 (br. quint, *J* = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 154.4 (q, *C*OCF_3), 150.6, 132.4, 129.02, 129.00, 124.3, 122.4, 121.5, 116.2, 115.9 (q, *C*F_3), 35.0, 33.7, 22.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3240 (OH

and NH), 1718 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{13}H_{12}F_3NO_2$ (M^+) 271.0820, found 271.0816.

2,2,2-Trifluoro-*N*-(*cis*-1,2,3,8b-tetrahydro-3a*H*-cyclopenta[*b*]benzofuran-3a-yl)acetamide (10Aa): (Table 3, Entry 2) To a solution of the oxime ether **7Aa** (40 mg, 0.23 mmol) in CH_2Cl_2 (4 mL) was added TFAA (0.033 mL, 0.23 mmol) under nitrogen at 0 °C. After being stirred at the same temperature for 3 h, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 7:1) afforded **10Aa** (61.2 mg, 99%) as colorless crystals. M.p. 78–80 °C (*n*-hexane). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.16 (br. t, J = 8 Hz, 1 H), 7.15 (br. d, J = 8 Hz, 1 H), 6.94 (br. t, J = 8 Hz, 1 H), 6.89 (br. s, 1 H), 6.78 (br. d, J = 8 Hz, 1 H), 4.00 (br. d, J = 8.5 Hz, 1 H), 2.41–2.24 (m, 3 H), 1.87–1.83 (m, 2 H), 1.63–1.58 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.3, 155.8 (q, $COCF_3$), 129.7, 128.5, 124.7, 121.8, 115.3 (q, CF_3), 108.9, 105.7, 51.4, 38.7, 34.1, 24.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3423 (NH), 1726 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{13}H_{12}F_3NO_2$ (M^+) 271.0820, found 271.0820. $C_{13}H_{12}F_3NO_2$: calcd. C 57.57, H 4.46, N 5.16; found C 57.43, H 4.32, N 5.11; NOE was observed between 8b-H (δ = 4.00 ppm) and NH (δ = 6.89 ppm) in NOESY spectroscopy.

3a-Amino-1,2,3,8b-tetrahydro-3a*H*-cyclopenta[*b*]benzofuran (10d): (Table 3, Entry 4) To a solution of the oxime ether **7Aa** (40 mg, 0.23 mmol) in CH_2Cl_2 (4 mL) was added TFA (0.018 mL, 0.23 mmol) under nitrogen at room temperature. After being stirred at the same temperature for 20 h, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 5:1) afforded dihydrobenzofuran **10d** (6.3 mg, 16%) as a colorless solid. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.51 (br. s, 2 H), 7.15 (br. t, J = 8 Hz, 1 H), 7.11 (br. d, J = 8 Hz, 1 H), 6.93 (br. t, J = 8 Hz, 1 H), 6.89 (br. d, J = 8 Hz, 1 H), 3.65 (br. t, J = 8.5 Hz, 1 H), 2.48–2.34 (m, 3 H), 2.27–2.19 (m, 2 H), 2.06–1.98 (m, 1 H) ppm. HRMS (EI, *m*/*z*) calcd. for $C_{11}H_{13}NO$ (M^+) 175.0996, found 175.0995. The stereostructures of **10d** were not determined.

2,2,2-Trichloro-*N*-(*cis*-1,2,3,8b-tetrahydro-3a*H*-cyclopenta[*b*]benzofuran-3a-yl)acetamide (10b): (Table 3 Entry 5) To a solution of the oxime ether **7Aa** (40 mg, 0.23 mmol) in CH_2Cl_2 (4 mL) was added TCAA (0.042 mL, 0.23 mmol) under nitrogen at room temperature. After being heated at reflux for 3 h, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 5:1) afforded **10b** (68.2 mg, 94%) as colorless crystals. M.p. 127–128 °C (*n*-hexane/AcOEt). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.26 (br. s, 1 H), 7.18–7.14 (m, 2 H), 6.94 (td, J = 8, 1 Hz, 1 H), 6.79 (br. d, J = 8 Hz, 1 H), 4.03 (br. d, J = 8.5 Hz, 1 H), 2.40–2.26 (m, 3 H), 1.89–1.82 (m, 2 H), 1.65–1.55 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 160.3, 158.4, 129.9, 128.3, 124.6, 121.7, 108.8, 106.4, 51.2, 38.6, 34.2, 24.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3419 (NH), 1714 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{13}H_{12}{}^{35}Cl_3NO_2$ (M^+) 318.9933, found 318.9941. $C_{13}H_{12}Cl_3NO_2$: calcd. C 48.70, H 3.77, N 4.37; found C 48.72, H 3.80, N 4.36; NOE was observed between 8b-H (δ = 4.03 ppm) and NH (δ = 7.26 ppm) in NOESY spectroscopy.

Reaction of 7Aa with TFAT: (Table 3, Entry 7) To a solution of the oxime ether **7Aa** (35.0 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) was added TFAT (0.030 mL, 0.20 mmol) under nitrogen at 0 °C. After being stirred at the same temperature for 2 h, the reaction mixture was neutralized with the saturated aqueous $NaHCO_3$ and extracted with $CHCl_3$. The organic phase was washed with H_2O, dried with $MgSO_4$, and concentrated under reduced pressure. Purification of the residue by preparative TLC (*n*-hexane/AcOEt, 10:1) afforded **10Aa** (31.6 mg, 58%) as colorless crystals and recovered **7Aa** (3.3 mg, 9%).

Reaction of 7Aa with TFAT-DMAP: (Table 3, Entry 14) To a solution of oxime ether **7Aa** (35.0 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) were added DMAP (24.4 mg, 0.20 mmol) and TFAT (0.060 mL, 0.40 mmol) under nitrogen at 0 °C. After being stirred at the same temperature for 0.5 h, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The organic phase was washed with H_2O, dried with $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by preparative TLC (*n*-hexane/AcOEt, 10:1) afforded **10Aa** (48.0 mg, 89%) as colorless crystals.

***N*-(1-Cyclopentyl)-2,2,2-trifluoro-*N*-(phenylmethoxy)acetamide (13):** (Table 4, Entry 1) To a solution of the oxime ether **12**[11] (37.8 mg, 0.20 mmol), prepared by condensation of cyclopentanone with *O*-benzylhydroxylamine, in CH_2Cl_2 (3 mL) was added TFAA (0.028 mL, 0.20 mmol) under nitrogen at 0 °C. After being stirred at the same temperature for 30 min, the reaction mixture was concentrated at reduced pressure. Purification of the residue by preparative TLC (*n*-hexane/AcOEt, 20:1) afforded **13** (46.3 mg, 81%) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39 (br. s, 5 H), 5.88 (br. t, J = 2 Hz, 1 H), 4.92 (br. s, 2 H), 2.72 (br. s, 2 H), 2.52–2.46 (m, 2 H), 2.01 (br. quint, J = 7 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.4 (q, $COCF_3$), 137.2, 133.1, 129.23, 129.18, 128.7, 121.0, 116.1 (q, CF_3), 77.6, 31.8, 30.3, 22.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1708 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{14}F_3NO_2$ (M^+) 285.0976, found 285.0973.

Reaction of 7Ab with TFAA: (Table 5, Entry 1) To a solution of the oxime ether **7Ab** (37.8 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) was added TFAA (0.028 mL, 0.20 mmol) under nitrogen at room temperature. After being stirred at the same temperature for 23 h, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 10:1) afforded **10Ab** (21.1 mg, 37%) as colorless crystals, **14Ab** (6.6 mg, 19%) as a colorless oil, and **11Ab**, **11′Ab** (combined two isomers, 13.3 mg, 23%), respectively.

2,2,2-Trifluoro-*N*-[*cis*-1,3,4,9b-tetrahydro-4a(2*H*)-dibenzofuranyl]-acetamide (10Ab): M.p. 64–66 °C (*n*-hexane/AcOEt). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.18 (br. t, J = 8 Hz, 1 H), 7.17 (br. d, J = 8 Hz, 1 H), 6.96 (td, J = 8, 1 Hz, 1 H), 6.88 (dd, J = 8, 1 Hz, 1 H), 6.52 (br. s, 1 H), 3.76 (br. t, J = 8.5 Hz, 1 H), 2.43–2.36 (m, 1 H), 2.23 (dt, J = 14.5, 4 Hz, 1 H), 2.18–2.13 (m, 1 H), 1.75–1.71 (m, 1 H), 1.53–1.45 (m, 2 H), 1.38–1.25 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 156.7, 156.3 (q, $COCF_3$), 132.1, 128.4, 124.4, 122.2, 115.3 (q, CF_3), 110.5, 98.0, 44.8, 30.4, 30.0, 20.4, 20.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3417 (NH), 1726 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{14}F_3NO_2$ (M^+) 285.0976, found 285.0991. $C_{14}H_{14}F_3NO_2$: calcd. C 58.95, H 4.95, N 4.91; found C 58.65, H 4.97, N 4.92; NOE was observed between 8b-H (δ = 3.76 ppm) and NH (δ = 6.52 ppm) in NOESY spectroscopy.

1,2,3,4-Tetrahydrodibenzofuran (14Ab):[27] ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.41–7.37 (m, 2 H), 7.19–7.17 (m, 2 H), 2.74 (m, 2 H), 2.62 (m, 2 H), 1.97–1.80 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 154.3, 154.0, 128.8, 122.9, 122.1, 118.3, 112.8, 110.7, 23.4, 22.9, 22.7, 20.4 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{12}H_{12}O$ (M^+) 172.0887, found 172.0901.

2,2,2-Trifluoro-*N*-[2-(2-hydroxyphenyl)-1-cyclohexen-1-yl]acetamide (11Ab): A colorless oil (5.6 mg, 10%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.48 and 5.18 *ppm*(br. s, each 1 H), 7.22 (br. t, J = 8 Hz, 1 H), 7.06 (br. dd, J = 8, 1 Hz, 1 H), 6.96 (br. td, J = 8, 1 Hz, 1 H), 6.93 (br. dd, J = 8, 1 Hz, 1 H), 2.66 and 2.36 (m, each 2 H), 1.88–1.75 (m, 4 H). IR ($CHCl_3$): $\tilde{\nu}$ = 3537 (OH), 3392 (NH),

1718 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{14}F_3NO_2$ (M^+) 285.0976, found 285.0981.

2,2,2-Trifluoro-*N*-[6-(2-hydroxyphenyl)-1-cyclohexen-1-yl]acetamide (11′Ab): A colorless oil (7.5 mg,13%). ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.26–7.11 (m, 2 H), 6.97 and 5.24 (br. s, each 1 H), 6.92 (br. t, *J* = 8 Hz, 1 H), 6.80 (br. dd, *J* = 8, 1 Hz, 1 H), 6.69 (br. td, *J* = 4.5, 1.5 Hz, 1 H), 3.93–3.86 (m, 1 H), 2.33–2.25 (m, 2 H), 2.10–1.55 (m, 4 H). IR ($CHCl_3$): $\tilde{\nu}$ = 3595 (OH), 3406 (NH), 1718 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{14}F_3NO_2$ (M^+) 285.0976, found 285.0971.

Reaction of 7Ab with TFAA: (Table 5, Entry 3) To a solution of the oxime ether **7Ab** (37.8 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) was added TFAA (0.11 mL, 0.80 mmol) under nitrogen at 0 °C. After being stirred at the same temperature for 23 h, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 10:1) afforded **10Ab** (53.3 mg, 94%) as colorless crystals.

Reaction of 7Ab with TFAT-DMAP: (Table 5, Entry 6) To a solution of the oxime ether **7Ab** (37.8 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) were added DMAP (73.3 mg, 0.60 mmol) and TFAT (0.15 mL, 1.0 mmol) under nitrogen at room temperature. After being stirred at the same temperature for 0.5 h, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The organic phase was washed with H_2O, dried with $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 10:1) afforded **14Ab** (31.6 mg, 92%) as a colorless oil.

***cis*-1,2,3,4,4a,9b-Hexahydrodibenzofuran (15):**[12] To a solution of the dihydrobenzofuran **10Ab** (42.7 mg, 0.15 mmol) in TFA (1.0 mL) was added $NaBH_3CN$ (94.2 mg, 1.50 mmol) under nitrogen at 0 °C. After being stirred at room temperature for 4 h, the reaction mixture was neutralized with the saturated aqueous $NaHCO_3$ and extracted with $CHCl_3$. The organic phase was washed with H_2O, dried with $MgSO_4$, and concentrated under reduced pressure. Purification of the residue by preparative TLC (*n*-hexane/AcOEt, 10:1) afforded 2,3-dihydrobenzofuran **15** (16.8 mg, 64%) as a colorless oil.

Conversion of 10Ab to 14Ab: (Table 6, Entry 1) To a solution of the dihydrobenzofuran **10Ab** (30.9 mg, 0.11 mmol) in CH_2Cl_2 (1.8 mL) was added TfOH (0.010 mL, 0.11 mmol) under nitrogen at room temperature. After being stirred at the same temperature for 1 min, the reaction mixture was neutralized with the saturated aqueous $NaHCO_3$ and extracted with $CHCl_3$. The organic phase was washed with H_2O, dried with $MgSO_4$, and concentrated under reduced pressure. Purification of the residue by preparative TLC (*n*-hexane/AcOEt, 10:1) afforded benzofuran **14Ab** (15.7 mg, 84%).

***N*-(2-Ethyl-2,3-dihydro-3-methyl-2-benzofuranyl)-2,2,2-trifluoroacetamide (10Ac):** (Table 7, Entry 2) To a solution of the the oxime ether **7Ac** (36.8 mg, 0.21 mmol) in MeCN (3 mL) was added TFAA (0.17 mL, 1.26 mmol) under nitrogen at room temperature. After being heated at reflux for 5 h, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 10:1) afforded an inseparable mixture of **10Ac** (36.3 mg, 64%, *cis*:*trans* = 1:1) as colorless solid. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.20–7.13 (m, 4/2 H), 6.97 and 6.95 (br. t, *J* = 8 Hz, each 1/2 H), 6.84 and 6.82 (br. d, *J* = 8 Hz, each 1/2 H), 6.59 and 6.53 (br. s, each 1/2 H), 3.78 and 3.53 (br. q, *J* = 7.5 Hz, each 1/2 H), 2.53 and 2.43 (dq, *J* = 14, 7.5 Hz, each 1/2 H), 2.11 and 1.96 (dq, *J* = 14, 7.5 Hz, each 1/2 H), 1.33 and 1.30 (d, *J* = 7.5 Hz, each 3/2 H), 1.07 and 1.01 (t, *J* = 7.5 Hz, each 3/2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.83, 155.81, 155.80 (q, *C*OCF_3), 155.7 (q, *C*OCF_3), 131.7, 130.9, 128.6, 128.5, 124.6, 124.14, 122.1, 121.8, 115.5 (q, *C*F_3), 115.3 (q, *C*F_3), 110.0, 109.7, 101.5, 101.3, 45.84, 45.80, 29.9, 24.7, 16.6, 15.0, 7.3, 7.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3418 (NH), 1729 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{13}H_{14}F_3NO_2$ (M^+) 273.0975, found 273.0979.

2-Ethyl-3-methylbenzofuran (14Ac):[28] (Table 7, Entry 3) To a solution of the oxime ether **7Ac** (36.8 mg, 0.21 mmol) in CH_2Cl_2 (3 mL) were added DMAP (76.6 mg, 0.63 mmol) and TFAT (0.16 mL, 1.05 mmol) under nitrogen at 0 °C. After being stirred at the same temperature for 2 h, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The organic phase was washed with H_2O, dried with $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 10:1) afforded **14Ac** (29.8 mg, 89%) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.43–7.36 (m, 2 H), 7.22–7.16 (m, 2 H), 2.75 (br. q, *J* = 7.5 Hz, 2 H), 2.16 (s, 3 H), 1.29 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.5, 153.8, 130.5, 123.0, 121.9, 118.6, 110.5, 108.7, 19.7, 12.8, 7.8 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{11}H_{12}O$ (M^+) 160.0887, found 160.0881.

***N*-(2,3-Dihydro-2-methyl-2-benzofuranyl)-2,2,2-trifluoroacetamide (10Ad):** (Table 7, Entry 4) To a solution of the oxime ether **7Ad** (210 mg, 1.41 mmol) in MeCN (15 mL) was added TFAA (1.17 mL, 8.46 mmol) under nitrogen at room temperature. After being heated at reflux for 4 h, the reaction mixture was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 10:1) afforded **10Ad** (325.5 mg, 94%) as a colorless solid. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.19 (br. d, *J* = 8 Hz, 1 H), 7.18 (br. t, *J* = 8 Hz, 1 H), 6.94 (br. t, *J* = 8 Hz, 1 H), 6.83 (br. d, *J* = 8 Hz, 1 H), 6.79 (br. s, 1 H), 3.69 and 3.30 (br. d, *J* = 16.5 Hz, each 1 H), 1.90 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 157.2, 155.8 (q, *C*OCF_3), 128.5, 125.3, 125.1, 121.9, 115.3 (q, *C*F_3), 109.7, 96.2, 41.5, 25.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3421 (NH), 1728 cm^{-1} ($NCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{11}H_{10}F_3NO_2$ (M^+) 245.0663, found 245.0654.

2-Methylbenzofuran (14Ad):[3f] (Table 7, Entry 6) To a solution of the oxime ether **7Ad** (31.1 mg, 0.21 mmol) in CH_2Cl_2 (3 mL) were added DMAP (76.6 mg, 0.63 mmol) and TFAT (0.16 mL, 1.05 mmol) under nitrogen at room temperature. After being stirred at the same temperature for 0.5 h, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The organic phase was washed with H_2O, dried with $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 10:1) afforded **14Ad** (18.0 mg, 65%) as a colorless oil. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.4, 154.7, 129.2, 123.0, 122.4, 120.0, 110.6, 102.6, 14.1 ppm. HRMS (EI, *m*/*z*) calcd. for C_9H_8O (M^+) 132.0575, found 132.0576.

General Procedure for Synthesis of 2-Arylbenzofurans 14: To a solution of the oxime ether **7Ae**–**u** and **7Be**–**Le** (0.17 mmol) in CH_2Cl_2 (3 mL) were added DMAP (63.0 mg, 0.52 mmol) and TFAT (0.13 mL, 0.86 mmol) under nitrogen at room temperature. After being stirred at the same temperature for several hours, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The organic phase was washed with H_2O, dried with $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 20:1–5:1) afforded benzofuran **14Ae**–**u** and **14Be**–**Le** in the yield shown in Table 8 and Table 9.

2-Phenylbenzofuran (14Ae):[29] A colorless oil. M.p. 118–120 °C (*n*-hexane) (ref.[29] 118–120° C). ^{13}C NMR ($CDCl_3$, 50 MHz): δ =

155.9, 154.9, 130.5, 129.2, 128.8, 128.5, 124.9, 124.3, 122.9, 120.9, 111.2, 101.3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{10}O$ (M^+) 194.0371, found 194.0719.

2-(4-Bromophenyl)benzofuran (14Af):[29] Colorless crystals. M.p. 159–160 °C (*n*-hexane/AcOEt) (ref.[29] 159–161° C). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 154.9, 154.8, 132.0, 129.4, 129.1, 126.4, 124.6, 123.1, 122.5, 121.0, 111.2, 101.8 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9{}^{79}BrO$ (M^+) 271.9837, found 271.9828.

2-(4-Nitrophenyl)benzofuran (14Ag):[30] Colorless crystals. M.p. 184.5–185 °C (MeOH/$CHCl_3$) (ref.[30] 183.5–184.5 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.16 (br. d, *J* = 8.5 Hz, 2 H), 7.98 (br. d, *J* = 8.5 Hz, 2 H), 7.65–7.62 (dm, *J* = 8 Hz, 1 H), 7.57–7.54 (dm, *J* = 8 Hz, 1 H), 7.36 (td, *J* = 8, 1.5 Hz, 1 H), 7.27 (td, *J* = 8, 1.5 Hz, 1 H), 7.22 (d, *J* = 1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.4, 153.2, 147.2, 136.3, 128.6, 125.2, 124.3, 123.5, 121.6, 111.5, 105.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1519 and 1346 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9NO_3$ (M^+) 239.0582, found 239.0586.

4-(2-Benzofuranyl)phenol (14Ah):[31] Colorless crystals. M.p. 195–196 °C (MeOH) (ref.[31] 195–197 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.76 (br. d, *J* = 8.5 Hz, 2 H), 7.57–7.54 (dm, *J* = 8 Hz, 1 H), 7.51–7.48 (dm, *J* = 8 Hz, 1 H), 7.25 (td, *J* = 8, 1.5 Hz, 1 H), 7.21 (td, *J* = 8, 1.5 Hz, 1 H), 6.91 (br. d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 1 Hz, 1 H), 4.92 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 156.0, 154.7, 129.4, 126.7, 123.8, 123.7, 122.8, 120.6, 115.7, 111.0, 99.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3414 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{10}O_2$ (M^+) 210.0681, found 210.0682.

2-(4-Methoxyphenyl)benzofuran (14Ai):[29] Colorless crystals. M.p. 148–149 °C (*n*-hexane/AcOEt) (ref.[29] 146–147 °C). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 160.0, 156.1, 154.7, 129.5, 126.4, 123.7, 123.4, 122.8, 120.6, 114.3, 111.0, 99.7, 55.4 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0856.

2,2,2-Trifluoro-1-[2-(4-methoxyphenyl)-3-benzofuranyl]ethanone (14′Ai): Yellow crystals. M.p. 73–75 °C (*n*-hexane). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.94 (br. d, *J* = 8 Hz, 1 H), 7.86 (br. d, *J* = 8.5 Hz, 2 H), 7.58 (br. d, *J* = 8 Hz, 1 H), 7.43–7.38 (m, 2 H), 7.03 (br. d, *J* = 8.5 Hz, 2 H), 3.90 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$,125 MHz): δ = 177.7 (q, *C*OCF_3), 164.8, 162.1, 153.6, 131.4, 125.8, 125.3, 124.7, 121.4, 121.3, 116.2 (q, *C*F_3), 113.9, 111.4, 110.5, 55.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1698 cm^{-1} (CO). HRMS (EI, *m*/*z*) calcd. for $C_{17}H_{11}F_3O_3$ (M^+) 320.0659, found 320.0666. $C_{17}H_{11}F_3O_3$: calcd. C 63.75, H 3.46; found C 63.84, H 3.26.

4-(2-Benzofuranyl)phenyl Trifluoroacetate (14Av): The oxime ether **7Ah** (80.3 mg, 0.35 mmol) was treated with DMAP (128.3 mg, 1.05 mmol) and TFAT (0.26 mL, 1.75 mmol). Workup and recrystallization (*n*-hexane/AcOEt) afforded **14Av** (99.9 mg, 92%) as colorless crystals. M.p. 165–167 °C (*n*-hexane/AcOEt). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.94 (br. d, *J* = 8.5 Hz, 2 H), 7.62–7.59 (dm, *J* = 8 Hz, 1 H), 7.54–7.52 (dm, *J* = 8 Hz, 1 H), 7.34–7.22 (m, 4 H), 7.05 (d, *J* = 1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.8 (q, *C*OCF_3), 155.0, 154.3, 149.2, 129.8, 129.0, 126.3, 124.7, 123.2, 121.1, 121.0, 115.0 (q, *C*F_3), 111.3, 102.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1799 cm^{-1} ($OCOCF_3$). HRMS (EI, *m*/*z*) calcd. for $C_{16}H_9F_3O_3$ (M^+) 306.0503, found 306.0512. $C_{16}H_9F_3O_3 \cdot 1/2H_2O$: calcd. C 60.96, H 3.20; found C 60.96, H 3.09.

3-Methyl-2-phenylbenzofuran (14Aj):[32] A colorless oil. The spectroscopic data of **14Aj** were identical with those previously reported.[32]

2-(4-Bromophenyl)-3-methylbenzofuran (14Ak): Colorless crystals. M.p. 80–81 °C (*n*-hexane/AcOEt). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.66 (br. d, *J* = 8.5 Hz, 2 H), 7.58 (br. d, *J* = 8.5 Hz, 2 H), 7.54–7.50 (dm, *J* = 8 Hz, 1 H), 7.48–7.44 (dm, *J* = 8 Hz, 1 H), 7.30 (td, *J* = 8, 1.5 Hz, 1 H), 7.24 (td, *J* = 8, 1.5 Hz, 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 153.8, 150.0, 131.8, 131.0, 130.3, 128.0, 124.6, 122.5, 121.9, 119.4, 111.9, 111.0, 9.5 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{11}{}^{79}BrO$ (M^+) 285.9993, found 285.9998. $C_{15}H_{11}BrO$: calcd. C 62.74, H 3.86; found C 62.65, H 3.70.

4-(3-Methyl-2-benzofuranyl)phenol (14Al):[33] Colorless crystals. M.p. 85–87 °C (*n*-hexane/AcOEt). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.69 (br. d, *J* = 8.5 Hz, 2 H), 7.52–7.49 (dm, *J* = 8 Hz, 1 H), 7.47–7.44 (dm, *J* = 8 Hz, 1 H), 7.27 (td, *J* = 8, 1.5 Hz, 1 H), 7.23 (td, *J* = 8, 1.5 Hz, 1 H), 6.94 (br. d, *J* = 8.5 Hz, 2 H), 4.99 (br. s, 1 H), 2.43 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.3, 153.6, 150.7, 131.3, 128.4, 124.4, 123.9, 122.3, 119.0, 115.6, 110.8, 109.7, 9.4 ppm. IR (nujol): $\tilde{\nu}$ = 3294 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{12}O_2$ (M^+) 224.0836, found 224.0841.

2-(4-Methoxyphenyl)-3-methylbenzofuran (14Am):[19] Colorless crystals. M.p. 87–88 °C (*n*-hexane) (ref.[19] 87 °C). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.4, 153.6, 150.9, 131.3, 128.2, 124.2, 123.9, 122.3, 119.0, 114.1, 110.8, 109.7, 55.4, 9.4 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{16}H_{14}O_2$ (M^+) 238.0993, found 238.1000.

2-(3-Bromophenyl)benzofuran (14An):[34] Colorless crystals. M.p. 84–85 °C (*n*-hexane/AcOEt) (ref.[34] 85 °C). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.9, 154.2, 132.4, 131.3, 130.3, 128.9, 127.8, 124.8, 123.4, 123.1, 122.9, 121.1, 111.2, 102.4 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9{}^{79}BrO$ (M^+) 271.9837, found 271.9837.

2-(3-Nitrophenyl)benzofuran (14Ao):[35] Colorless crystals. M.p. 134–135 °C (MeOH/$CHCl_3$) (ref.[35] 129–130 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.68 (t, *J* = 2 Hz, 1 H), 8.19–8.12 (m, 2 H), 7.62 (br. d, *J* = 8 Hz, 1 H), 7.61 (br. t, *J* = 8 Hz, 1 H), 7.55 (br. d, *J* = 8 Hz, 1 H), 7.35 (td, *J* = 8, 1.5 Hz, 1 H), 7.27 (td, *J* = 8, 1.5 Hz, 1 H), 7.17 (d, *J* = 1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.1, 153.1, 148.7, 132.1, 130.2, 129.8, 128.6, 125.3, 123.4, 122.8, 121.4, 119.6, 111.4, 103.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1531 and 1353 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9NO_3$ (M^+) 239.0582, found 239.0579.

3-(2-Benzofuranyl)phenol (14Ap):[36] Colorless crystals. M.p. 133–134 °C (MeOH) (ref.[36] 131–133 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.58–7.55 (dm, *J* = 8 Hz, 1 H), 7.52–7.49 (dm, *J* = 8 Hz, 1 H), 7.44 (ddd, *J* = 8, 2, 1 Hz, 1 H), 7.35–7.19 (m, 4 H), 6.99 (d, *J* = 1 Hz, 1 H), 6.82 (ddd, *J* = 8, 2, 1 Hz, 1 H), 5.03 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.8, 155.4, 154.8, 132.0, 130.1, 129.1, 124.4, 123.0, 121.0, 117.6, 115.6, 111.7, 111.2, 101.7 ppm. IR (nujol): $\tilde{\nu}$ = 3414 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{10}O_2$ (M^+) 210.0681, found 210.0679.

2-(3-Methoxyphenyl)benzofuran (14Aq):[37] Colorless crystals. M.p. 48–49 °C (*n*-hexane/AcOEt) (ref.[37] 51 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.59–7.56 (dm, *J* = 8 Hz, 1 H), 7.54–7.50 (dm, *J* = 8 Hz, 1 H), 7.45 (dm, *J* = 8 Hz, 1 H), 7.41 (t, *J* = 2 Hz, 1 H), 7.35 (t, *J* = 8 Hz, 1 H), 7.28 (td, *J* = 8, 1.5 Hz, 1 H), 7.22 (td, *J* = 8, 1.5 Hz, 1 H), 7.01 (d, *J* = 1 Hz, 1 H), 6.90 (ddd, *J* = 8, 2, 1 Hz, 1 H), 3.88 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.9, 155.7, 154.8, 131.8, 129.8, 129.2, 124.3, 122.9, 120.9, 117.5, 114.5, 111.2, 110.1, 101.6, 55.4 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0841.

2-(2-Bromophenyl)benzofuran (14Ar):[38] Colorless crystals. M.p. 35–37 °C (*n*-hexane) (ref.[38] 36–37 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.97 (dd, *J* = 8, 1.5 Hz, 1 H), 7.71 (dd, *J* = 8, 1.5 Hz, 1 H), 7.64 (br. d, *J* = 8 Hz, 1 H), 7.54 (br. s, 1 H), 7.53 (br. d, *J* = 8 Hz, 1 H), 7.42 (td, *J* = 8, 1.5 Hz, 1 H), 7.33 (td, *J* = 8, 1.5 Hz, 1 H), 7.25 (td, *J* = 8, 1.5 Hz, 1 H), 7.20 (td, *J* = 8, 1.5 Hz, 1 H) ppm.

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 154.3, 153.1, 134.3, 131.0, 129.8, 129.4, 128.8, 127.5, 124.8, 123.0, 121.4, 120.7, 111.1, 107.0 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9{}^{79}BrO$ (M^+) 271.9837, found 271.9835.

2,2,2-Trifluoro-*N*-[2-(2-hydroxyphenyl)-1-(2-nitrophenyl)-1-ethenyl]-acetamide (19As): The rearranged products (*E*)-**19As** and (*Z*)-**19As** were inseparable. Stereostructures of *E* and *Z* isomers (1:1) have not been established; yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.60 (br. s, 1/2 H), 8.04 (br. d, *J* = 8 Hz, 2/2 H), 7.98 (br. s, 1/2 H), 7,70–7.67 (m, 2/2 H), 7,52–7.49 (m, 2/2 H), 7,38–7.35 (m, 2/2 H), 7.25 (br. t, *J* = 8 Hz, 1/2 H), 7.24 (br. d, *J* = 8 Hz, 1/2 H), 7.20 (br. s, 1/2 H), 7.03 (br. t, *J* = 8 Hz, 1/2 H), 7.01 (br. t, *J* = 8 Hz, 1/2 H), 6.92 (br. d, *J* = 8 Hz, 1/2 H), 6.70–6,61 (m, 3/2 H), 6.30 (br. s, 1/2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.5 (q, *C*OCF_3), 154.6 (q, *C*OCF_3), 153.4, 151.6, 148.1, 147.6, 134.0, 133.6, 133.5, 132.6, 132.3, 131.3, 131.0, 130.4, 130.2, 130.0, 129.63, 129.58, 125.0, 124.6, 121.7, 121.2, 120.6, 120.5, 120.4, 116.8, 115.9, 115.6 (q, CO*C*F_3) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3589 (OH), 3406 (NH), 1730 ($NCOCF_3$), 1531 and 1353 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{16}H_{11}F_3N_2O_4$ (M^+) 352.0670, found 352.0682.

2-(2-Benzofuranyl)phenol (14At):[39] Colorless crystals. M.p. 94–95 °C (*n*-hexane) (ref.[39] 93–94 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.71 (dd, *J* = 8, 1.5 Hz, 1 H), 7.60 (br. d, *J* = 8 Hz, 1 H), 7.53 (br. d, *J* = 8 Hz, 1 H), 7.34–7.24 (m, 3 H), 7.14 (br. s, 1 H), 7.09 (d, *J* = 1 Hz, 1 H), 7.03–6.97 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 154.3, 154.0, 153.3, 130.3, 128.5, 127.2, 124.4, 123.4, 121.0, 120.8, 117.4, 116.1, 111.0, 103.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3527 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{10}O_2$ (M^+) 210.0681, found 210.0689.

2-(2-Methoxyphenyl)benzofuran (14Au):[40] Colorless crystals. M.p. 78–79 °C (*n*-hexane) (ref.[40] 78.5–80 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.07 (br. dd, *J* = 8, 1.5 Hz, 1 H), 7.60–7.57 (dm, *J* = 8 Hz, 1 H), 7.52–7.549 (dm, *J* = 8 Hz, 1 H), 7.35 (br. s, 1 H), 7.35–7.18 (m, 3 H), 7.08 (br. t, *J* = 8 Hz, 1 H), 7.00 (br. d, *J* = 8 Hz, 1 H), 4.00 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.9, 153.2, 151.5, 129.1, 128.6, 126.4, 123.4, 122.0, 120.4, 120.1, 118.7, 110.4, 110.4, 110.2, 105.7, 54.8 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0851.

5-Bromo-2-phenylbenzofuran (14Be):[41] Colorless crystals. M.p. 158–159 °C (MeOH) (ref.[41] 158–159 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.85 (br. d, *J* = 8.5 Hz, 2 H), 7.71–7.70 (m, 1 H), 7.49–7.34 (m, 5 H), 6.96 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 157.3, 153.6, 131.2, 129.9, 129.0, 128.9, 127.1, 125.1, 123.5, 116.0, 112.6, 100.6 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9{}^{79}BrO$ (M^+) 271.9837, found 271.9837.

5-Nitro-2-phenylbenzofuran (14Ie):[42] Yellow crystals. M.p. 159–161 °C (MeOH) (ref.[42] 158–161 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.48 (d, *J* = 2 Hz, 1 H), 8.20 (br. dd, *J* = 8, 2 Hz, 1 H), 7.86 (br. d, *J* = 8.5 Hz, 2 H), 7.57 (br. d, *J* = 8 Hz, 1 H), 7.51–7.39 (m, 3 H), 7.10 (d, *J* = 1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.2, 157.6, 144.3, 129.7, 129.6, 129.1, 129.0, 125.2, 120.1, 117.2, 111.4, 101.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1525 and 1350 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9NO_3$ (M^+) 239.0582, found 239.0581.

5-Methyl-2-phenylbenzofuran (14Ce):[43] Colorless crystals. M.p.128–130 °C (EtOH) (ref.[43] 125–126 °C). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 156.0, 153.3, 132.3, 130.6, 129.3, 128.7, 128.4, 125.5, 124.8, 120.7, 110.6, 101.1, 21.3 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{12}O$ (M^+) 208.0888, found 208.0888.

4-Bromo-2-phenylbenzofuran (14De) and 6-Bromo-2-phenylbenzofuran (14′De):[44,45] The benzofurans **14De** and **14′De** were inseparable (**14De/14′De** = 1:1); colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.88 and 7.84 ppm (br. d, *J* = 8.5 Hz, each 2/2 H), 7.69 (br. s, 1/2 H), 7.49–7.34 (m, 10/2 H), 7.15 (br. t, *J* = 8 Hz, 1/2 H), 7.06 and 6.98 (d, *J* = 1 Hz, each 1/2 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 156.5, 156.4, 155.0, 154.4, 130.7, 129.9, 129.8, 129.2, 129.0, 128.8, 128.5, 128.2, 126.3, 125.9, 125.0, 124.9, 121.7, 117.3, 114.6, 113.8, 111.1, 110.2, 101.3, 101.0 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9{}^{79}BrO$ (M^+) 271.9837, found 271.9862.

4-Nitro-2-phenylbenzofuran (14Je) and 6-Nitro-2-phenylbenzofuran (14′Je):[46] The benzofurans **14Je** and **14′Je** were inseparable (**14Je/14′Je** = 2:1); yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.40 (br. s, 1/3 H), 8.18 (br. d, *J* = 8 Hz, 1/3 H), 8.16 (br. dd, *J* = 8 Hz, 2/3 H), 7.93 (br. d, *J* = 8.5 Hz, 4/3 H), 7.89 (br. d, *J* = 8.5 Hz, 2/3 H), 7.81 (br. d, *J* = 8 Hz, 2/3 H), 7.74 (d, *J* = 1 Hz, 2/3 H), 7.63 (d, *J* = 8 Hz, 1/3 H), 7.52–7.41 (m, 9/3 H), 7.37 (t, *J* = 8 Hz, 2/3 H), 7.09 (d, *J* = 1 Hz, 1/3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 161.3, 159.9, 155.9, 153.4, 144.7, 140.4, 135.2, 130.0, 129.1, 129.0, 125.6, 125.5, 125.3, 123.2, 120.5, 119.7, 118.9, 117.2, 107.6, 101.4, 101.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1519 and 1337 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9NO_3$ (M^+) 239.0582, found 239.0610.

4-Methyl-2-phenylbenzofuran (14Ee) and 6-Methyl-2-phenylbenzofuran (14′Ee):[47,48] The benzofurans **14Ee** and **14′Ee** were inseparable (**14Ee/14′Ee** = 1:1.5); colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.87 (br. d, *J* = 8.5 Hz, 4/5 H), 7.83 (br. d, *J* = 8.5 Hz, 6/5 H), 7.47–7.23 (m, 23/5 H), 7.18 (br. t, *J* = 8 Hz, 2/5 H), 7.06 (br. s, 3/5 H), 7.03 (d, *J* = 1 Hz, 2/5 H), 7.02 (br. d, *J* = 8 Hz, 2/5 H), 6.96 (d, *J* = 1 Hz, 3/5 H), 2.54 (s, 6/5 H), 2.48 (s, 9/5 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 155.3, 154.7, 134.5, 130.8, 130.7, 130.6, 129.0, 128.7, 128.4, 128.2, 126.7, 124.8, 124.7, 124.3, 124.2, 123.2, 120.3, 111.4, 108.6, 101.1, 100.0, 21.7, 18.6 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{12}O$ (M^+) 208.0888, found 208.0897.

2-Phenyl-4-benzofuranol (14Le) and 2-Phenyl-6-benzofuranol (14′Le):[49] The benzofurans **14Le** and **14′Le** were inseparable (**14Le/14′Le** = 1:1.5); colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.85 (br. d, *J* = 8.5 Hz, 4/5 H), 7.81 (br. d, *J* = 8.5 Hz, 6/5 H), 7.47–7.29 (m, 20/5 H), 7.14 (br. d, *J* = 8 Hz, 2/5 H), 7.10 (br. d, *J* = 1 Hz, 2/5 H), 7.01 (br. d, *J* = 2 Hz, 3/5 H), 6.94 (br. d, *J* = 1 Hz, 3/5 H), 6.77 (br. dd, *J* = 8, 2 Hz, 3/5 H), 6.63 (br. dd, *J* = 8, 2 Hz, 2/5 H), 5.01 (br. s, 5/5 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.5, 155.8, 155.3, 154.9, 153.6, 149.1, 130.6, 130.4, 128.8, 128.7, 128.5, 128.1, 124.9, 124.8, 124.5, 122.9, 121.1, 118.5, 112.0, 108.0, 104.4, 101.1, 98.3, 98.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3597 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{10}O_2$ (M^+) 210.0681, found 210.0681.

4-Methoxy-2-phenylbenzofuran (14Fe) and 6-Methoxy-2-phenylbenzofuran (14′Fe):[50,51] The benzofurans **14Fe** and **14′Fe** were inseparable (**14Fe/14′Fe** = 1:4); colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.84 (br. d, *J* = 8.5 Hz, 2/5 H), 7.80 (br. d, *J* = 8.5 Hz, 8/5 H), 7.45–7.39 (m, 14/5 H), 7.33 (br. t, *J* = 8.5 Hz, 1/5 H), 7.31 (br. t, *J* = 8.5 Hz, 4/5 H), 7.21 (t, *J* = 8 Hz, 1/5 H), 7.15 (br. d, *J* = 8 Hz, 1/5 H), 7.12 (d, *J* = 1 Hz, 1/5 H), 7.07 (br. d, *J* = 2 Hz, 4/5 H), 6.94 (d, *J* = 1 Hz, 4/5 H), 6.87 (br. dd, *J* = 8, 2 Hz, 4/5 H), 6.66 (br. d, *J* = 8 Hz, 1/5 H), 3.96 (s, 3/5 H), 3.87 (s, 12/5 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 158.1, 156.1, 155.9, 155.1, 154.6, 153.4, 130.7, 130.5, 128.7, 128.2, 128.0, 124.9, 124.7, 124.4, 122.5, 121.0, 119.5, 111.9, 104.4, 103.3, 101.1, 98.8, 95.9, 55.7, 55.5 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0852.

7-Bromo-2-phenylbenzofuran (14Ge): A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.89 (br. d, *J* = 8.5 Hz, 2 H), 7.52–7.35 (m, 5 H), 7.10 (br. t, *J* = 8 Hz, 1 H), 7.07 (s, 1 H) ppm. ^{13}C NMR

($CDCl_3$, 50 MHz): δ = 156.7 152.0, 130.5, 129.8, 129.0, 128.8, 127.2, 125.2, 124.2, 120.0, 103.9, 101.8 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9{}^{79}BrO$ (M^+) 271.9837, found 271.9843.

7-Nitro-2-phenylbenzofuran (14Ke):[52] Yellow crystals. M.p. 118–119 °C (*n*-hexane) (ref.[52] 119–120 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.12 (br. dd, *J* = 8, 2 Hz, 1 H), 7.96 (br. d, *J* = 8 Hz, 2 H), 7.88 (dd, *J* = 8.5, 2 Hz, 1 H), 7.53–7.40 (m, 3 H), 7.35 (t, *J* = 8 Hz, 1 H), 7.13 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 158.6, 146.8, 133.8, 133.2, 129.6, 128.9, 127.4, 125.4, 122.8, 120.4, 100.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1529 and 1343 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_9NO_3$ (M^+) 239.0582, found 239.0584.

2,2,2-Trifluoro-*N*-[2-(2-hydroxy-3-nitrophenyl)-1-phenyl-1-ethenyl]-acetamide (19Ke): The rearranged products (*E*)-**19Ke** and (*Z*)-**19Ke** were inseparable. Stereostructures of *E* and *Z* isomers (2:1) have not been established; yellow solid. ^1H NMR ($CDCl_3$, 300 MHz): δ = 11.3 (br. s, 2/3 H), 10.9 (br. s, 1/3 H), 8.06 (br. d, *J* = 8 Hz, 2/3 H), 8.05 (br. s, 2/3 H), 7.85 (br. d, *J* = 8 Hz, 1/3 H), 7.58 (br. d, *J* = 8 Hz, 2/3 H), 7.57 (br. s, 1/3 H), 7.46–7.19 (m, 16/3 H), 6.99 (br. t, *J* = 8 Hz, 2/3 H), 6.93 (br. d, *J* = 8 Hz, 1/3 H), 6.73 (br. s, 2/3 H), 6.56 (br. t, *J* = 8 Hz, 1/3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.3 (q, *C*OCF_3), 154.8 (q, *C*OCF_3), 153.2, 151.9, 137.9, 137.2, 135.7, 134.7, 134.6, 134.5, 134.3, 133.8, 129.8, 129.6, 129.4, 128.94, 128.92, 126.6, 126.2, 125,0, 123.8, 120.1, 119.2, 117.4, 116.8, 115.7 (q, CO*C*F_3), 114.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3565 (OH), 3406 (NH), 1739 ($NCOCF_3$), 1540 and 1306 cm^{-1} (NO_2). HRMS (EI, *m*/*z*) calcd. for $C_{16}H_{11}F_3N_2O_4$ (M^+) 352.0670, found 352.0696.

7-Methyl-2-phenylbenzofuran (14He):[50] A colorless oil. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 173.3, 155.5, 153.9, 130.7, 128.7, 128.4, 125.2, 124.9, 123.0, 121.4, 118.3, 101.6, 15.1 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{12}O$ (M^+) 208.0888, found 208.0894.

(*E*)-1-(3,5-Dihydroxyphenyl)ethanone *O*-Phenyloxime (21): According to the procedure given for **7**, reaction of *O*-phenylhydroxylamine **5A** (218 mg, 2 mmol) with 3,5-dihydroxyacetophenone (304.3 mg, 2 mmol) and concd. aqueous HCl (0.10 mL) in EtOH (4 mL) gave the oxime ether **21** (447.1 mg, 92%) as colorless crystals. M.p. 104–106 °C (CH_2Cl_2). ^1H NMR (CD_3OD, 300 MHz): δ = 7.32 (br. t, *J* = 8 Hz, 2 H), 7.25 (br. d, *J* = 8 Hz, 2 H), 7.02 (br. t, *J* = 8 Hz, 1 H), 6.77 (d, *J* = 2 Hz, 2 H), 6.41 (t, *J* = 2 Hz, 1 H), 3.89 (br. s, 2 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (CD_3OD, 50 MHz): δ = 161.1, 159.7, 159.5, 139.2, 130.4, 123.3, 115.9, 106.3, 105.3, 13.8 ppm. IR (nujol): $\tilde{\nu}$ = 3242 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{13}NO_3$ (M^+) 243.0894, found 243.0897. $C_{14}H_{13}NO_3 \cdot 1/30CH_2Cl_2$: calcd. C 68.49, H 5.35, N 5.69; found C 68.61, H 5.48, N 5.39.

5-(2-Benzofuranyl)-1,3-benzenediol (22) (Stemofuran A): According to the procedure given for **14**, reaction of the oxime ether **21** (32.7 mg, 0.13 mmol) with DMAP (127.0 mg, 1.04 mmol) and TFAT (0.35 mL, 2.35 mmol) in CH_2Cl_2 (4 mL) gave Stemofuran A (**22**) (28.7 mg, 95%) as colorless crystals. M.p. 182–183 °C ($CHCl_3$). ^1H NMR (CD_3OD, 500 MHz): δ = 7.56 (br. dd, *J* = 8, 1.5 Hz, 1 H), 7.48 (br. dd, *J* = 8, 1.5 Hz, 1 H), 7.25 (td, *J* = 8, 1.5 Hz, 1 H), 7.20 (td, *J* = 8, 1.5 Hz, 1 H), 7.02 (br. d, *J* = 1 Hz, 1 H), 6.84 (d, *J* = 2 Hz, 2 H), 6.30 (t, *J* = 2, Hz, 1 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 160.0, 157.4, 156.0, 133.4, 130.5, 125.3, 123.9, 121.9, 111.8, 104.4, 104.1, 102.2 ppm. IR (nujol): $\tilde{\nu}$ = 3294 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{14}H_{10}O_3$ (M^+) 226.0629, found 226.0645. $C_{14}H_{10}O_3$: calcd. C 74.33, H 4.46; found C 74.31, H 4.33. The spectroscopic data of **22** were identical with those previously reported.[5]

(*E*/*Z*)-1-(4-Hydroxyphenyl)-1-propanone *O*-(4-Bromophenyl)oxime (24): According to the procedure given for **7**, reaction of *O*-(4-bromophenyl)hydroxylamine (**5B**) (376.0 mg, 2 mmol) with 4-hydroxypropiophenone (300.0 mg, 2 mmol) and concd. aqueous HCl (0.10 mL) in EtOH (4 mL) gave the oxime ether **24** (601.6 mg, 94%, *E*:*Z* = 10:1) as a colorless oil. The oxime ethers (*E*)-**24** and (*Z*)-**24** were inseparable. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (br. d, *J* = 8.5 Hz, 2 H), 7.41 (br. d, *J* = 8.5 Hz, 2 H), 7.16 (br. d, *J* = 8.5 Hz, 2 H), 6.86 (br. d, *J* = 8.5 Hz, 2 H), 5.08 (br. s, 1 H), 2.90 (q, *J* = 7.5 Hz, 20/11 H), 2.68 (q, *J* = 7.5 Hz, 2/11 H), 1.22 (t, *J* = 7.5 Hz, 30/11 H), 1.15 (t, *J* = 7.5 Hz, 3/11 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 163.3, 158.6, 157.3, 132.0, 128.3, 126.9, 116.5, 115.5, 114.0, 20.7, 11.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3592 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{14}{}^{79}BrNO_2$ (M^+) 319.0207, found 319.0210. The ^{13}C NMR spectroscopic data of only (*E*)-**24** was described.

4-(5-Bromo-3-methyl-2-benzofuranyl)phenol (25): According to the procedure given for **14**, reaction of the oxime ether **24** (37.4 mg, 0.12 mmol) with DMAP (42.8 mg, 0.35 mmol) and TFAT (0.09 mL, 0.59 mmol) in CH_2Cl_2 (4 mL) gave the benzofuran **25** (32.7 mg, 92%) as colorless crystals. M.p. 157–159 °C (*n*-hexane/Et_2O). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.67 (br. d, *J* = 8.5 Hz, 2 H), 7.60 (dd, *J* = 2, 0.5 Hz, 1 H), 7.32 (d, *J* = 2 Hz, 1 H), 7.31 (d, *J* = 0.5 Hz, 1 H), 6.94 (br. d, *J* = 8.5 Hz, 2 H), 5.12 (br. s, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.6, 152.3, 152.1, 133.3, 128.5, 126.6, 123.8, 121.8, 115.7, 115.4, 112.2, 109.3, 9.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3594 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{11}{}^{79}BrO_2$ (M^+) 301.9941, found 301.9939. $C_{15}H_{11}BrO_2$: calcd. C 59.43, H 3.66; found C 59.37, H 3.48.

4-[3-Methyl-5-(1*E*)-1-propenyl-2-benzofuranyl]phenol (26) (Eupomatenoid 6): To a stirred mixture of the bromobenzofuran **25** (46.2 mg, 0.15 mmol), powdered CsF (93.0 mg, 0.60 mmol), and *trans*-propenylboronic acid (39 mg, 0.45 mmol) in DME (0.54 mL) was added $Pd(PPh_3)_4$ (0.005 mg, 3 mol-%) at room temperature. The reaction mixture was heated at reflux for 7 h under argon. The reaction mixture was then cooled, diluted with AcOEt, and washed with brine. The organic phase was dried with $MgSO_4$ and concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 5:1) afforded Eupomatenoid 6 (**26**) (39.0 mg, 97%) as colorless crystals. M.p. 147.5–148 °C (benzene/petroleum ether) (ref.[20] 147.5–149 °C). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.68 (br. d, *J* = 8.5 Hz, 2 H), 7.43 (br. d, *J* = 2 Hz, 1 H), 7.36 (br. d, *J* = 8.5 Hz, 1 H), 7.27 (br. dd, *J* = 8.5, 2 Hz, 1 H), 6.93 (br. d, *J* = 8.5 Hz, 2 H), 6.52 (br. dd, *J* = 15.5, 2 Hz, 1 H), 6.33 (dq, *J* = 15.5, 6.5 Hz, 1 H), 4.90 (br. s, 1 H), 2.42 (s, 3 H), 1.91 (dd, *J* = 6.5, 2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 155.3, 152.9, 151.1, 132.6, 131.5, 131.3, 128.3, 124.4, 124.2, 122.2, 116.1, 115.6, 110.6, 109.8, 18.5, 9.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3596 cm^{-1} (OH). HRMS (EI, *m*/*z*) calcd. for $C_{18}H_{16}O_2$ (M^+) 264.1149, found 264.1145. The spectroscopic data of **26** were identical with those previously reported.[6b,20]

2,3-Dihydro-4*H*-1-benzopyran-4-one *O*-Phenyloxime (27): According to the procedure given for **7**, reaction of *O*-phenylhydroxylamine (**5A**) (218 mg, 2 mmol) with 4-chromanone (296.3 mg, 2 mmol) and concd. aqueous HCl (0.10 mL) in EtOH (4 mL) gave the oxime ether **27** (439.7 mg, 92%) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.06 (dd, *J* = 8, 1.5 Hz, 1 H), 7.37–7.29 (m, 5 H), 7.09–6.91 (m, 3 H), 4.28 (t, *J* = 6 Hz, 2 H), 3.15 (t, *J* = 6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.4, 157.1, 151.5, 131.7, 129.3, 124.8, 122.3, 121.5, 117.8, 114.7, 64.9, 24.7 ppm. HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{13}NO_2$ (M^+) 239.0946, found 239.0942.

6*H*-Benzofuro[3,2-*c*][1]benzopyran (28):[2i] According to the procedure given for **14**, reaction of the oxime ether **27** (186.7 mg,

0.78 mmol) with DMAP (285.0 mg, 2.34 mmol) and TFAT (0.58 mL, 3.90 mmol) in CH_2Cl_2 (12 mL) gave the benzofuran **28** (135.0 mg, 78%) as colorless crystals. M.p. 76–78 °C (EtOH) (ref.[2i] 76.0–76.9 °C). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{10}O_2$ (M^+) 221.0681, found 221.0672.

6*H*-Benzofuro[3,2-*c*][1]benzopyran-6-one (29) (Coumestan): To the solution of the benzofuran **28** (53.3 mg, 0.24 mmol) and silica gel (53.0 mg) in CH_2Cl_2 (17 mL) was added 1 equiv. of PCC (53.0 mg, 0.24 mmol) and the mixture was heated at reflux. After a few hours, two other portions of PCC (2 equiv.) were added to the mixture. After 4 h, the cooled mixture was filtered through celite, then the filtrate was concentrated at reduced pressure. Purification of the residue by medium-pressure column chromatography (*n*-hexane/AcOEt, 10:1) afforded Coumestan **29** (42.9 mg, 76%) as colorless crystals. M.p. 186.5–187.5 °C (cyclohexane) (ref.[7a] 187–188 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.16 (dd, J = 7.5, 1.5 Hz, 1 H), 8.05 (dd, J = 7.5, 1.5 Hz, 1 H), 7.68 (dd, J = 7.5, 1.5 Hz, 1 H), 7.62 (td, J = 7.5, 1.5 Hz, 1 H), 7.52 (dd, J = 7.5, 1.5 Hz, 1 H), 7.49 (td, J = 7.5, 1.5 Hz, 1 H), 7.47 (td, J = 7.5, 1.5 Hz, 1 H), 7.43 (td, J = 7.5, 1.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.0, 130.1, 127.6, 125.7, 98.8, 97.2, 96.7, 95.5, 93.90, 93.88, 89.5, 84.7, 83.8, 77.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1735 cm^{-1} (CO_2). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_8O_3$ (M^+) 236.0473, found 236.0466. The spectroscopic data of **29** were identical with those previously reported.[7a]

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