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Annulative Synthesis of Benzofurans from General Alkenyl Sulfoxides and Phenols via Pummerer/Sigmatropic Cascade

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Abstract

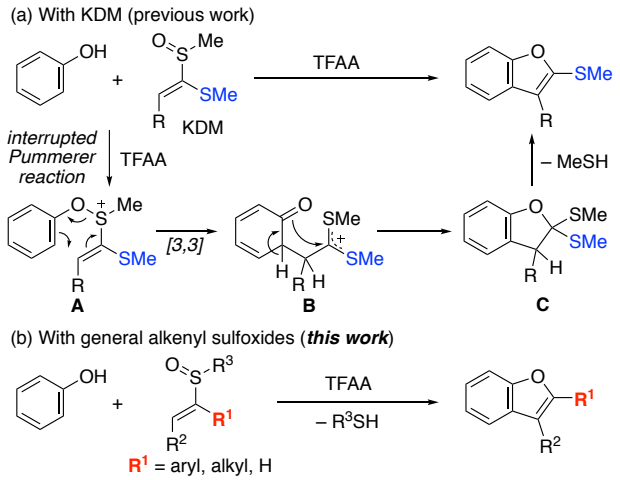
In addition to ketene dithioacetal monoxides that were specially designed and have been used so far, general alkenyl sulfoxides of moderate reactivity have now become applicable as substrates in the trifluoroacetic anhydride-mediated annulation with phenols for the shorter-step and transition-metal-free synthesis of benzofurans having diverse substituents. The improved method enabled concise formation of furan-fused complex polycyclic skeletons, which culminates in the two-step synthesis of dioxa[8]helicene. The modest reactivity of alkenyl sulfoxides has allowed isolation of dihydrobenzofurans as intermediates, which unveiled two interesting phenomena: (i) the initial cyclization reflects the stereochemistry and steric environment of alkenyl sulfoxides and (ii) the aromatization by the departure of alkanethiol is the rate-determining step.

Keywords: Pummerer/sigmatropic cascade, alkenyl sulfoxide, benzofuran

Introduction

Sulfoxides are ubiquitous organosulfur compounds, and widely utilized in organic synthesis as synthetic intermediates, chiral auxiliary, ligands, and so on.[1] Among sulfoxide-based organic synthesis, extended Pummerer reactions are emerging as valuable methods for C–H functionalizations of aryl and alkenyl sulfoxides without the use of any metal catalysts.[2]

As a part of our investigations about the development of Pummerer-based transformations,[2g,2h,3,4] we developed the annulative synthesis of benzofurans from ketene dithioacetal monoxides (KDM) and phenols by means of trifluoroacetic anhydride (TFAA) (Scheme 1a).[5] First, KDM and phenol undergo TFAA-mediated interrupted Pummerer reaction to form S–O-bonded sulfonium **A**. Via cation-accelerated [3,3] sigmatropic rearrangement,[6,7] a C–C bond is constructed to generate cationic species **B**. Subsequent cyclization and departure of methanethiol from **C** furnish benzofuran.



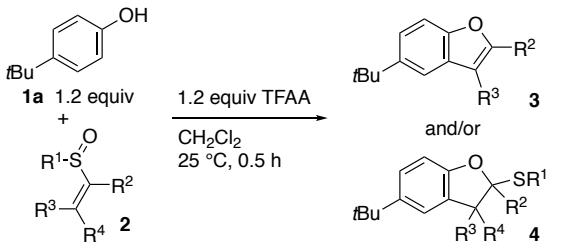
Scheme 1. Pummerer annulation for synthesis of benzofurans

Although the interrupted Pummerer/sigmatropic cascade is an instructive method for the construction of a benzofuran scaffold, a methylsulfanyl group intrinsically remains at the 2 position and further manipulations are required to remove or transform this unit. To further extend the utility and versatility of this cascade, expansion of applicable alkenyl sulfoxides should be required. Although Hendrickson tried the annulation with cyclohexenyl sulfoxides, the yields of the products were generally less than 50%.[4a] According to these considerations, we decided to apply general alkenyl sulfoxides to the interrupted Pummerer/sigmatropic cascade (Scheme 1b).

Results and Discussion

In view of the reaction mechanism, the α-sulfanyl group of KDM would stabilize cationic intermediate **B** by resonance effect. We thus envisioned that an aryl ring at the α position in place of sulfanyl group would make a similar stabilization effect. As expected, 1,2-diphenylvinyl sulfoxide **2a** smoothly underwent the reaction with 4-*tert*-butylphenol (**1a**) to afford benzofuran **3aa** in 86% yield under similar conditions of the previous report (Table 1, entry 1). With this encouraging result, we further tested various alkenyl sulfoxides **2**.[8] *β*-Unsubstituted alkenyl sulfoxide **2b** also underwent the reaction (entry 2). Chloro and ethoxycarbonyl groups at the *β* positions were compatible with the reaction albeit in moderate yields of products **3ac** and **3ad** (entries 3 and 4). In contrast, an ethoxycarbonyl group at the α position totally suppressed the reaction: a trace amount of benzofuran **3ae** was obtained from sulfoxide **2e** (entry 5). This result demonstrates the necessity of stabilization on the α position. Gratifyingly, alkyl substituents were found to be sufficient for the stabilization of the cationic charge, and benzofurans **3af**–**ah** were obtained in high yields from the corresponding 1-alkyl-2-phenylvinyl sulfoxides **2f**–**h** (entries 6–8). Acyclic as well as cyclic 1,2-dialkylvinyl sulfoxides **2i** and **2j** were also applicable to furnish **3ai** and **3aj** in 86% and 89% yields, respectively (entries 9 and 10). Instead of alkyl chains, phenyl substituent on the sulfur atom of **2j'** did not retard the reaction resulting in the formation of **3aj** (entry 11). When α-unsubstituted alkenyl sulfoxide **2k** was employed, the corresponding 2-sulfanyl-2,3-dihydrobenzofuran **4ak** was obtained in an *anti*-selective manner (entry 12, *vide infra* for mechanistic discussion). As described in Scheme 4, departure of dodecanethiol uneventfully proceeded by simply heating with TsOH. The reaction of phenyl vinyl sulfoxide (**2l**) also provided 2,3-dihydrobenzofuran **4al** selectively (entry 13). The absence of the α substituent would destabilize the intermediary oxonium cation, and the departure of thiols would be retarded. Predictably, trisubstituted vinyl sulfoxide **2m** was converted to the corresponding 2-sulfanyl-2,3-dihydrobenzofuran **4am** (entry 14).

Table 1. Scope of alkenyl sulfoxides **2**



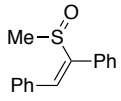
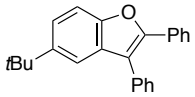
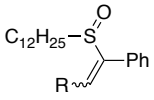
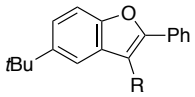
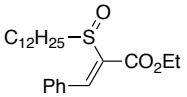
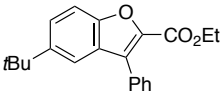
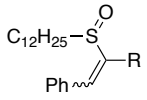
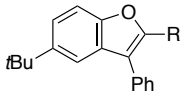
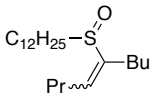
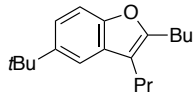
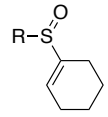
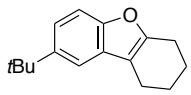
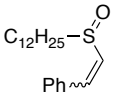
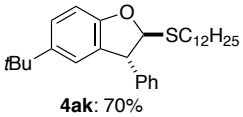
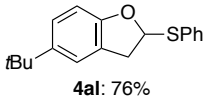
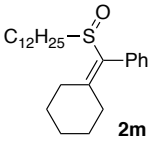
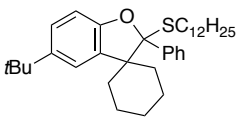
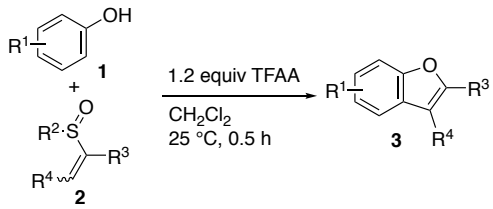
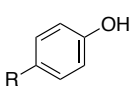
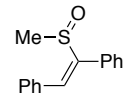
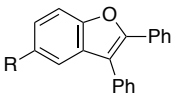
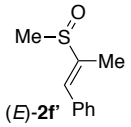
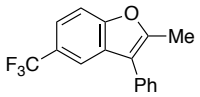
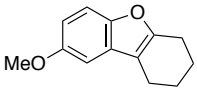
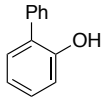
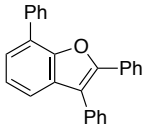
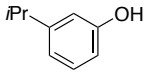
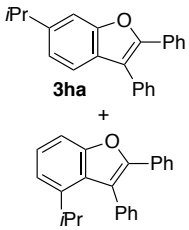
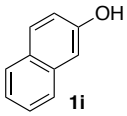
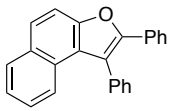
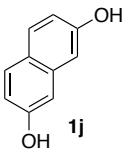
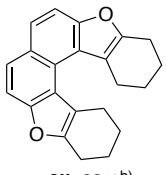
entry	sulfoxide **2**	product (%)
1	 (*Z*)-**2a**	 **3aa**: 86%
		
2	**2b** (R = H)	**3ab**: 65%
3	**2c** (R = Cl, *E*)	**3ac**: 46%
4	**2d** (R = CO_2Et, *E*/*Z* = 17/83)	**3ad**: 50%
5	 (*Z*)-**2e**	 **3ae**: trace
		
6	**2f** (R = Me, *Z*)	**3af**: 81%
7	**2g** (R = Bu, *Z*)	**3ag**: 83%
8	**2h** (R = CH_2Ph, *E*/*Z* = 30/70)	**3ah**: 84%
9	 **2i** (isomeric ratio = 42/58)	 **3ai**: 72%
		
10	**2j** (R = $C_{12}H_{25}$)	**3aj**: 89%
11	**2j'** (R = Ph)	**3aj**: 89%
12	 **2k** (*E*/*Z* = 9/91)	 **4ak**: 70% (*syn*/*anti* = 1/18)
13	 **2l**	 **4al**: 76%
14	 **2m**	 **4am**: 73%

Table 2. Scope of phenols **1**



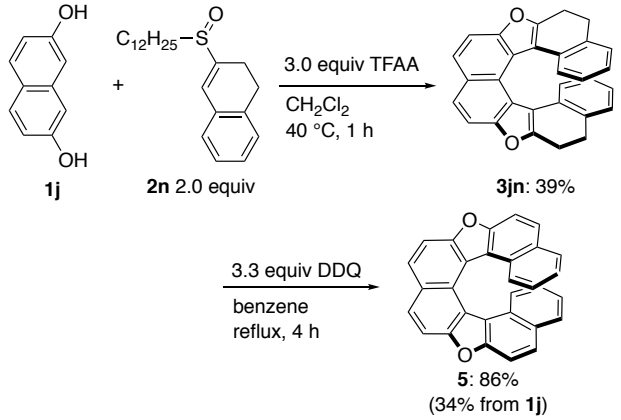
entry	phenol **1**	sulfoxide **2**	product (%)
			
1	**1b** (R = Cl)	(*Z*)-**2a**	**3ba**: 64%
2	**1c** (R = Br)	(*Z*)-**2a**	**3ca**: 80%
3	**1d** (R = I)	(*Z*)-**2a**	**3da**: 73%
4	**1e** (R = CF_3)	 (*E*)-**2f'**	 **3ef**: 41%[a]
5	**1f** (R = OMe)	**2j**	 **3fj**: 86%
6	 **1g**	(*Z*)-**2a**	 **3ga**: 76%
7	 **1h**	(*Z*)-**2a**	 **3ha** + **3ha'** **3ha**+**3ha'**: 87% (11/1)
8	 **1i**	(*Z*)-**2a**	 **3ia**: 89%
9	 **1j**	**2j**	 **3jj**: 63%[b]

a) at 40 °C for 2.5 h. b) 3 equiv of **2j** and 3 equiv of TFAA.

We then checked the scope with respect to phenols (Table 2). Owing to the absence of transition metal catalysts, chloro, bromo, and iodo substituents were intact during the reaction and benzofurans **3ba**–**da** were obtained in moderate to good yields (entries 1–3). The reaction of electron-deficient 4-trifluoromethylphenol (**1e**) was not efficient, and the coupling products, **3ef** and 2-sulfanyl-2,3-dihydrobenzofuran **4ef**, were obtained in 24% and 28% NMR yields, respectively. Increasing the reaction temperature to 40 °C promoted the departure of methanethiol to provide **3ef** albeit in moderate yield (entry 4).

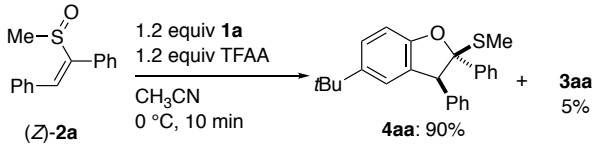
On the other hand, electron-rich 4-methoxyphenol (**1f**) uneventfully reacted with **2j** to furnish **3fj** in 86% yield (entry 5). An *ortho*-substituent did not hamper the reaction: 2-phenylphenol (**1g**) underwent the reaction with **2a** to yield **3ga** (entry 6). The reaction of 3-isopropylphenol (**1h**) proceeded in a regioselective fashion to provide 6-isopropylbenzofuran **3ha** as a major product (entry 7). 2-Naphthol (**1i**) was also smoothly converted to naphthofuran **3ia** in high yield (entry 8). Gratifyingly, 2,7-dihydroxynaphthalene (**1j**) underwent the annulation with alkenyl sulfoxide **2j** twice, affording **3jj** in one pot (entry 9). Such cyclohexane-fused product is difficult to synthesize by the previous method using KDM, which clearly demonstrates the advantage of the present protocol.

This concise construction of polycyclic skeletons culminates in the two-step synthesis of dioxa[8]helicene (Scheme 2). Treatment of naphthalenediol **1j** with 2 equivalents of alkenyl sulfoxide **2n** derived from β-tetralone provided tetrahydro-7,12-dioxa[8]helicene **3jn** in 39% yield. Following oxidation with DDQ furnished desired 7,12-dioxa[8]helicene (**5**)[3h] in 34% yield over two steps.



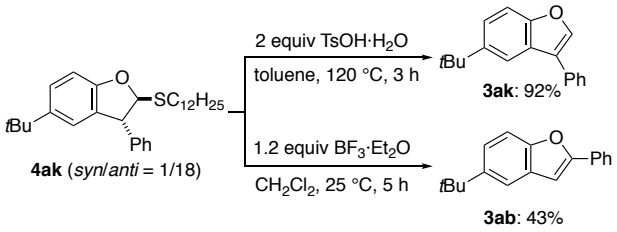
Scheme 2. Synthesis of 7,12-dioxa[8]helicene **5**.

During the course of the investigation, we found that acetonitrile as the solvent suppressed the departure of alkanethiols. Treatment of **1a** and (*Z*)-**2a** with TFAA in acetonitrile stereoselectively furnished *syn*-**4aa** in 64% yield accompanied by a 16% yield of **3aa**. The lower reaction temperature (0 °C) and the shorter reaction time (10 min) were found to be effective for the formation of **4aa**; the product was obtained in 90% yield (Scheme 3). Acetonitrile might decrease the acidity of the reaction system and disturb protonation of the sulfanyl group.



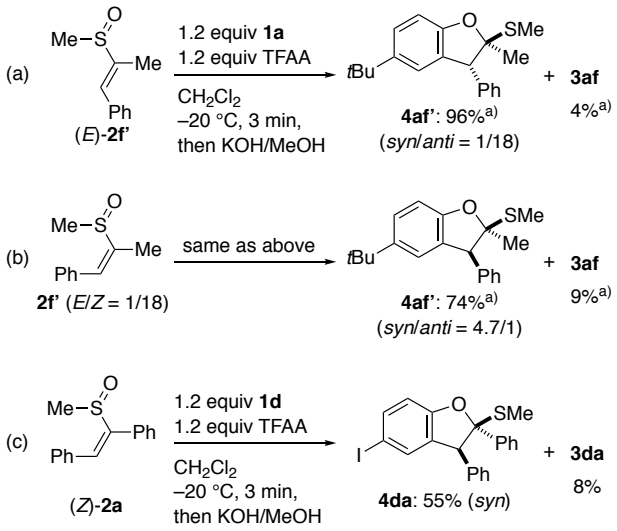
Scheme 3. Synthesis of 2-sulfanyl-2,3-dihydrobenzofuran **4aa** in CH_3CN.

2-Sulfanyl-2,3-dihydrobenzofuran **4ak** obtained from α-unsubstituted alkenyl sulfoxide **2k** (Table 1, entry 12) could be converted to the corresponding benzofuran **3ak** with the aid of TsOH in hot toluene (Scheme 4).[9] Interestingly, when **4ak** was treated with Lewis acidic $BF_3{\cdot}Et_2O$ instead of TsOH in CH_2Cl_2 at 25 °C, 1,2-phenyl shift proceeded concomitantly with the departure of dodecanethiol to furnish 2-phenylbenzofuran **3ab** albeit in moderate yield. Similar 1,2-aryl shifts on cyclic *O*,*S*-acetals induced by $BF_3{\cdot}Et_2O$ were reported by Procter.[4g]



Scheme 4. Departure of dodecanethiol from **4ak** with or without 1,2-phenyl shift

To gain insight into the reaction mechanism, especially the deprotonative cyclization process, we tried to identify reaction intermediates. A mixture of **1a** and (*E*)-**2f'** reacted with TFAA at –20 °C, and the reaction was quenched by methanolic KOH in 3 min. As a result, a 96% yield of 2-sulfanyl-2,3-dihydrobenzofuran **4af'** was obtained accompanied by a 4% yield of benzofuran **3af** (Scheme 5a). This implies that the departure of alkanethiol would be the rate-determining step of the present annulation. The sluggish departure would stem from the milder reactivity of alkenyl sulfoxides than KDM. Indeed, the use of KDM invoked facile departure of methanethiol even when the instant quench was applied. The electron donation of the α-methylsulfanyl group on KDM would facilitate the departure event.

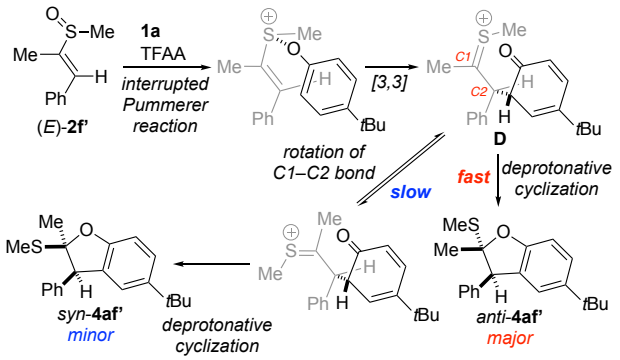


Scheme 5. Stereospecific synthesis of 2-sulfanyl-2,3-dihydrobenzofurans **4**. a) NMR yield.

It is noteworthy that the formation of **4af'** proceeded in a diastereoselective fashion, and the *anti*-form was obtained preferentially (Scheme 5a). In contrast, under the same conditions, the use of (*Z*)-**2f'** afforded *syn*-**4af'** as the major product (Scheme 5b). A similar trend was observed with the reaction of (*Z*)-**2a** with **1d**, and *syn*-**4da** was obtained in a diastereoselective manner (Scheme 5c). The configuration of *syn*-**4da** was confirmed by X-ray crystallographic analysis[10] as well as NMR analyses.

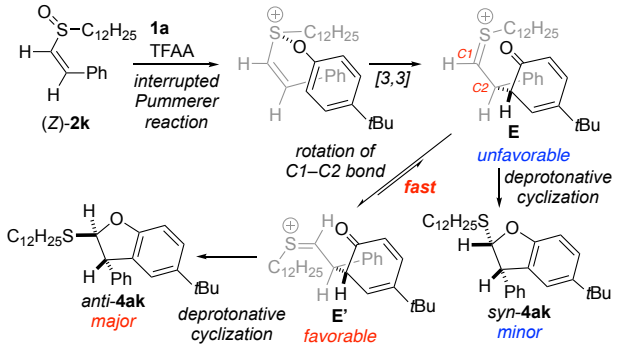
A description on these cyclization processes is depicted in Scheme 6 with (*E*)-**2f'** as a model substrate. Interrupted Pummerer reaction and subsequent [3,3] sigmatropic rearrangement would proceed with retention of the stereochemistry affording intermediate **D**. Although the C1–C2 bond of **D** is potentially rotative, deprotonative cyclization would occur faster to afford *anti*-**4af'** selectively. Through a

similar fast deprotonative cyclization, (*Z*)-**2f'** would be converted to *syn*-**4af'** reflecting the (*Z*)-configuration of the alkenyl sulfoxide.



Scheme 6. Description on stereospecific formation of **4af'**

On the other hand, (*Z*)-rich sulfoxide **2k** preferably provided the *anti*-form of 2-sulfanyl-2,3-dihydrofuran **4ak** (Table 1, entry 12). The absence of the α substituent would facilitate rotation of the C1–C2 bond of intermediate **E** (Scheme 7). The fast bond rotation leads **E** to **E'** to relieve the steric repulsion between the thionium unit and the phenyl ring, *anti*-**4ak** was thus obtained as the major product even from (*Z*)-rich sulfoxide **2k**.



Scheme 7. Description on favorable formation of *anti*-**4ak**

Conclusion

We succeeded in applying general alkenyl sulfoxides to the annulative synthesis of benzofurans via interrupted Pumemrer/sigmatropic cascade. The improved method enabled concise formation of furan-fused complex polycyclic skeletons, which culminates in the two-step synthesis of 7,12-dioxa[8]helicene. The milder reactivity of alkenyl sulfoxides than KDM has allowed isolation of 2-sulfanyl-2,3-dihydrobenzofurans, which unveiled the aromatization by the departure of alkanethiol is the rate-determining step. The stereochemistry of 2-sulfanyl-2,3-dihydrobenzofurans proved that the deprotonative cyclization reflects the configuration of the C–C double bond and steric environment of alkenyl sulfoxides.

Experimental

Instrumentation and Chemicals. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were taken on a JEOL ECA-600 or JEOL ECZ-600 spectrometer. Chemical shifts (δ) are reported in parts per million in $CDCl_3$ relative to residual $CHCl_3$ at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.16 ppm for ^{13}C, and in dichloromethane-d_2 relative to $CDHCl_2$ at 5.32 ppm for ^{1}H and relative to CD_2Cl_2 at 53.84 ppm for ^{13}C. Mass spectra were determined on a Bruker micrOTOF II spectrometer. Melting points were determined on a Stanford Research Systems MPA100 melting point apparatus. PTLC analyses were performed on commercial aluminium sheets bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Purification was done by column chromatography using silica gel (Wakosil® C-300) and preparative TLC using silica gel (Merck $60PF_{254}$).

All reactions were performed under nitrogen atmosphere. Dehydrated acetonitrile, benzene, toluene and DMSO were purchased from Wako Pure Chemical Industries, Ltd. and stored under nitrogen atmosphere. Dehydrated CH_2Cl_2 were purchased from KANTO CHEMICAL CO., INC. and stored under nitrogen atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Alkenyl sulfoxides **2j'**[14a] and **2l**[11] were prepared according to the literature.

General Procedure for Oxidation of Alkenyl Sulfides to Alkenyl Sulfoxides (GP1): *m*-Chloroperbenzoic acid (contains ca. 30% H_2O, 1.0 equiv) was added to a solution of an alkenyl sulfide in CH_2Cl_2 (0.10 M) portionwise at 0 °C. The resulting solution was stirred and gradually warmed to room temperature. Progress of the oxidation was checked by TLC. After completion of the reaction, saturated aqueous $NaHCO_3$ was added to the reaction mixture and the resulting solution was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated under a reduced pressure. The residue was purified by silica gel chromatography with an eluent (hexane/EtOAc = 1/1) to give the corresponding alkenyl sulfoxide.

Procedure for Preparation of Alkenyl Sulfoxides 2a and 2f': Procedures described in the previous report[12] were used with some modifications. The synthesis of **2a** is representative. A 200-mL Schlenk tube was charged with TEMPO (0.31 g, 2.0 mmol, 0.10 equiv), methyl mercaptan sodium salt (ca. 15% in water, 11 mL, 24 mmol, 1.2 equiv) and DMSO (100 mL). Diphenylacetylene (3.4 g, 20 mmol) was then added and the resulting mixture was stirred at 85 °C for 2.5 h. After cooling the mixture, water (100 mL) was added and the resulting biphasic solution was extracted with a mixture of hexane/AcOEt (v/v = 40/1, 100 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under a reduced pressure to give (*Z*)-1,2-diphenylvinyl methyl sulfide with some impurities. Subsequent oxidation in accordance with **GP1** provided (*Z*)-**2a** (3.3 g, 14 mmol, 70%) as a white solid. With the same procedures, (*Z*)-rich alkenyl sulfoxide **2f'** was prepared.

General Procedure for Synthesis of Benzofurans (GP2): The synthesis of **3aa** is representative. A 10-mL Schlenk flask was charged with 4-*tert*-butylphenol (**1a**, 36 mg, 0.24 mmol), **2a** (49 mg, 0.20 mmol), and CH_2Cl_2 (2 mL). TFAA (34 μL, 0.24 mmol) was added at 25 °C, and the resulting mixture was stirred for 30 min. The mixture was filtered through a pad of alumina and concentrated under reduced pressure. Purification by preparative TLC (hexane/CH_2Cl_2 = 5/1) provided **3aa** (56 mg, 0.17 mmol, 86%) as a white solid.

Synthesis of 7,12-dioxa[8]helicene 5 (Scheme 2): According to **GP2**, 5,6,13,14-tetrahydro-7,12-dioxa[8]helicene (**3jn**, 32 mg, 0.078 mmol, 39%) was synthesized from **1j** (32 mg, 0.20 mmol) and **2n** (0.14 g, 0.40 mmol, 2.0 equiv). A solution of **3jn** (39 mg, 0.095 mmol) and DDQ (70 mg, 0.31 mmol) in benzene (10 mL) was refluxed for 4 h. After cooling the reaction mixture to room temperature, the mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was washed with hexane (30 mL) to give **5** (34 mg, 0.082 mmol, 86%) as a white solid.

Procedure for Synthesis of 2-Methylsulfanyl-2,3-dihydrobenzofuran 4aa in CH_3CN Solvent (Scheme 3): A 10-mL Schlenk flask was charged with **1a** (36 mg, 0.24 mmol), **2a** (48 mg, 0.20 mmol), and acetonitrile (2 mL). Trifluoroacetic anhydride (34 μL, 0.24 mmol) was added at 0 °C, and the resulting mixture was stirred for 10 min. The mixture was filtered through a pad of alumina and concentrated under reduced pressure. Purification by preparative TLC (hexane/CH_2Cl_2 = 20/1) provided **4aa** (67 mg, 0.18 mmol, 90%) as colorless oil.

Conversion of 2-Sulfanyl-2,3-dihydrobenzofuran 4ak to Benzofuran 3ak by TsOH (Scheme 4): To a solution of **4ak** (88 mg, 0.19 mmol) in toluene (2 mL), TsOH·H_2O (76 mg, 0.40 mmol) was added. The mixture was heated in an oil bath at 120 °C for 3 h, and then was allowed to cool to room temperature. The mixture was filtered through a pad of alumina and concentrated under reduced pressure. Purification by preparative TLC (hexane/CH_2Cl_2= 20/1) provided **3ak** (45 mg, 0.18 mmol, 92%) as pale yellow oil.

Conversion of Dihydrobenzofuran 4ak to Benzofuran 3ab by BF_3·Et_2O via 1,2-phenyl shift (Scheme 4): To a solution of **4ak** (91 mg, 0.20 mmol) in CH_2Cl_2 (2 mL), BF_3·Et_2O (30 μL, 0.24 mmol) was added. The mixture was stirred at 25 °C for 5 h. After the reaction, saturated aqueous $NaHCO_3$ (10 mL) was added and the resulting mixture was extracted with AcOEt (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by preparative TLC (hexane/CH_2Cl_2 = 20/1) provided **3ab** (22 mg, 0.086 mmol, 43%) as a white solid.

Procedure for Short-Time Reaction (Scheme 5): The synthesis of **4da** (Scheme 5c) is representative. A solution of 4-iodophenol (53 mg, 0.24 mmol) and **2a** (48 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) was placed in a flask. TFAA (34 μL, 0.24 mmol) was then added at –20 °C. After 3 min, a KOH solution in MeOH (0.5 M, 4 mL) was added at –20 °C with stirring. Water (15 mL) was then added and the resulting biphasic solution was extracted with EtOAc (15 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by preparative TLC (hexane/CH_2Cl_2 = 10/1) provided **4da** (49 mg, 0.11 mmol, 55%) as a white solid.

Characterization Data

(*Z*)-1,2-Diphenylvinyl methyl sulfoxide (2a): White solid. m.p. = 90.5–94.3 °C. ^{1}H NMR ($CDCl_3$) δ 7.59–7.61 (m, 2H), 7.37–7.45 (m, 8H), 7.19 (s, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 144.83, 139.07, 134.43, 134.05, 130.01, 129.45, 129.02, 128.99, 128.55, 128.51, 37.92. HRMS (APCI-MS, positive): *m/z* = 243.0845. Calcd for $C_{15}H_{15}OS$: 243.0838 $[M+H]^+$.

Dodecyl 1-phenylvinyl sulfoxide (2b): Dodecyl 1-phenylvinyl sulfide was synthesized via procedures similar in the previous report[13] and was oxidized into **2b** according to **GP1**. Orange oil. ^{1}H NMR ($CDCl_3$) δ 7.35–7.41 (m, 5H), 6.02 (s, 1H), 5.99 (s, 1H), 2.61 (ddd, *J* = 12.8, 10.2, 6.0 Hz, 1H), 2.36 (ddd, *J* = 12.8, 10.2, 6.0 Hz, 1H), 1.71–1.77 (m, 1H), 1.55–1.61 (m, 1H), 1.21–1.36 (m, 18H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 152.57, 134.33, 129.40, 129.22, 126.74, 117.25, 51.81, 32.03, 29.71 (2C), 29.61, 29.44 (2C), 29.25, 28.63, 22.80, 21.59, 14.23. HRMS (APCI-MS, positive): *m/z* = 321.2249. Calcd for $C_{20}H_{33}OS$: 321.2247 $[M+H]^+$.

(*E*)-2-Chloro-1-phenylvinyl dodecyl sulfoxide (2c): Via procedures similar in the previous report,[14] (*E*)-2-chloro-1-phenylvinyl dodecyl sulfide was synthesized, and oxidized into **2c** according to **GP1**. Yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.41–7.47 (m, 3H), 7.36 (dd, *J* = 7.9, 1.7 Hz, 2H), 6.83 (s, 1H), 2.57 (ddd, *J* = 13.2, 10.2, 6.0 Hz, 1H), 2.40 (ddd, *J* = 13.2, 10.2, 6.0 Hz, 1H), 1.69–1.75 (m, 1H), 1.56–1.63 (m, 1H), 1.22–1.36 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 144.79, 129.98, 129.73, 129.22, 128.62, 122.47, 51.77, 32.04, 29.72 (2C), 29.62, 29.47, 29.43, 29.25, 28.61, 22.83, 21.38, 14.25. HRMS (APCI-MS, positive): *m/z* = 355.1861. Calcd for $C_{20}H_{32}{}^{35}ClOS$: 355.1857 $[M+H]^+$.

2-Ethoxycarbonyl-1-phenylvinyl dodecyl sulfoxide (2d, *E*/*Z* = 17:83): 2-Ethoxycarbonyl-1-phenylvinyl dodecyl sulfide was synthesized via procedures similar in the previous report[15] and was oxidized into **2d** according to **GP1**. Orange oil. The configuration of the olefin moiety was determined by NOESY analysis. ^{1}H NMR ($CDCl_3$) δ 7.40–7.46 (m, 5H), 6.61 (s, 0.17 × 1H), 6.31 (s, 0.83 × 1H), 4.26 (q, *J* = 7.2 Hz, 0.83 × 2H), 4.07–4.14 (m, 0.17 × 2H), 2.90–2.99 (m, 0.83 × 2H), 2.55 (ddd, *J* = 14.6, 8.7, 4.6 Hz, 0.17 × 1H), 2.34 (ddd, *J* = 14.6, 8.7, 4.6 Hz, 0.17 × 1H), 1.74–1.86 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 0.83 × 3H), 1.21–1.52 (m, 18H), 1.15 (t, *J* = 7.2 Hz, 0.17 × 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) for the major isomer δ 164.52, 131.83, 130.01, 129.52, 128.88, 128.33, 122.89, 61.55, 54.96, 32.05, 29.75 (2C), 29.69, 29.50, 29.48, 29.39, 28.78, 23.70, 22.83, 14.34, 14.25. HRMS (APCI-MS, positive): *m/z* = 393.2462. Calcd for $C_{23}H_{37}O_3S$: 393.2458 $[M+H]^+$.

(*Z*)-1-Ethoxycarbonyl-2-phenylvinyl dodecyl sulfoxide (2e): Via procedures similar in the previous report,[15] (*Z*)-1-ethoxycarbonyl-2-phenylvinyl dodecyl sulfide was synthesized, and oxidized into **2e** according to **GP1**. Yellow solid. m.p. = 52.5–54.3 °C. ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 1H), 7.49–7.51 (m, 2H), 7.40–7.44 (m, 3H), 4.35–4.44 (m, 2H), 3.58 (ddd, *J* = 12.6, 9.6, 5.4 Hz, 1H), 3.12 (ddd, *J* = 12.6, 7.2, 9.6 Hz, 1H), 1.67–1.77 (m, 2H), 1.43 (t, *J* = 7.8 Hz, 3H), 1.24–1.47 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 163.29, 148.62, 135.41, 132.48, 131.24, 130.83, 128.68, 62.15, 52.51, 32.04, 29.74 (2C), 29.66, 29.50 (2C), 29.31, 28.95, 23.87, 22.83, 14.41, 14.25. HRMS (APCI-MS, positive): *m/z* = 393.2462. Calcd for $C_{23}H_{37}O_3S$: 393.2458 $[M+H]^+$.

Dodecyl (*Z*)-1-methyl-2-phenylvinyl sulfoxide (2f): Via procedures similar in the previous report,[12] dodecyl (*Z*)-1-methyl-2-phenylvinyl sulfide was synthesized, and oxidized into **2f** according to **GP1**. White solid. m.p. = 51.8–53.0 °C. ^{1}H NMR ($CDCl_3$) δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.25–7.30 (m, 3H), 6.92 (s, 1H), 2.89 (dt, J_d = 13.2, J_t = 7.2 Hz, 1H), 2.62 (dt, J_d = 13.2, J_t = 7.2 Hz, 1H), 2.20 (s, 3H), 1.62–1.68 (m, 2H), 1.23–1.41 (m, 18H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 142.01, 135.20, 134.59, 129.45, 128.50, 128.24, 51.77, 32.04, 29.73 (2C), 29.65, 29.47 (2C), 29.29, 28.89, 23.26, 22.82, 14.24, 13.76. HRMS (APCI-MS, positive): *m/z* = 335.2411. Calcd for $C_{21}H_{35}OS$: 335.2403 $[M+H]^+$.

1-Methyl-2-phenylvinyl methyl sulfoxide (2f', *E*/*Z* = 26:74): (For *E* isomer): Yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.38–7.40 (m, 4H), 7.31–7.34 (m, 1H), 7.14 (d, *J* = 1.4 Hz, 1H), 2.62 (s, 3H), 2.15 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 141.31, 134.82, 130.42, 129.36, 128.72, 128.47, 39.12, 11.26. HRMS (APCI-MS, positive): *m/z* = 181.0688. Calcd for $C_{10}H_{13}OS$: 181.0682 $[M+H]^+$. (For *Z* isomer): Yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.34–7.37 (m, 2H), 7.29–7.32 (m, 1H), 7.22 (d, *J* = 7.1 Hz, 2H), 6.91 (s, 1H), 2.62 (s, 3H), 2.24 (d, *J* = 1.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 142.91, 134.67, 134.42, 129.43, 128.54, 128.37, 37.69, 13.05. HRMS (APCI-MS, positive): *m/z* = 181.0691. Calcd for $C_{10}H_{13}OS$: 181.0682 $[M+H]^+$.

(*Z*)-1-Butyl-2-phenylvinyl dodecyl sulfoxide (2g): Via procedures similar in the previous report,[12] (*Z*)-1-butyl-2-phenylvinyl dodecyl sulfide was synthesized, and oxidized into **2g** according to **GP1**. Colorless oil. The configuration of the olefin moiety was confirmed by NOESY

analysis. ^{1}H NMR ($CDCl_3$) δ 7.34 (t, J = 7.2 Hz, 2H), 7.25–7.29 (m, 3H), 6.86 (s, 1H), 2.84 (dt, J_d = 12.8, J_t = 7.2 Hz, 1H), 2.68–2.69 (m, 1H), 2.58 (dt, J_d = 12.8, J_t = 7.2 Hz, 1H), 2.39–2.46 (m, 1H), 1.62–1.69 (m, 4H), 1.46–1.50 (m, 2H), 1.22–1.37 (m, 18H), 0.98 (t, J = 7.5 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 146.65, 134.83, 133.42, 129.46, 128.51, 128.11, 52.55, 32.05, 31.60, 29.74 (2C), 29.66, 29.48 (2C), 29.28, 28.82, 25.93, 23.36, 22.83, 22.69, 14.25, 14.12. HRMS (APCI-MS, positive): *m/z* = 377.2876. Calcd for $C_{24}H_{41}OS$: 377.2873 $[M+H]^+$.

1-Benzyl-2-phenylvinyl dodecyl sulfoxide (2h, *E*/*Z* = 30:70): Via procedures similar in the previous report,[16] (*Z*)-rich 1-benzyl-2-phenylvinyl dodecyl sulfide was synthesized and oxidized into **2h** according to **GP1**. Yellow solid. The configuration of the olefin moiety was confirmed by NOESY analysis. ^{1}H NMR ($CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 0.30 × 2H), 7.39 (s, 0.30 × 1H), 7.29–7.37 (m, 6H), 7.28 (d, J = 7.8 Hz, 0.70 × 2H), 7.23 (d, J = 7.8 Hz, 0.30 × 2H), 7.20 (d, J = 7.2 Hz, 0.70 × 2H), 6.65 (s, 0.70 × 1H), 4.06 (d, J = 16.8 Hz, 0.30 × 1H), 4.00 (d, J = 16.5 Hz, 0.70 × 1H), 3.84 (d, J = 16.8 Hz, 0.30 × 1H), 3.82 (dd, J = 16.5, 1.8 Hz, 0.70 × 1H), 2.82 (ddd, J = 13.2, 7.2 Hz, 6.6 Hz, 0.70 × 1H), 2.64 (ddd, J = 13.2, 10.5, 6.0 Hz, 0.30 × 1H), 2.59 (dt, J_d = 13.2, J_t = 7.8 Hz, 0.70 × 1H), 2.46 (ddd, J = 13.2, 9.6, 4.8 Hz, 0.30 × 1H), 1.62–1.76 (m, 2H), 1.22–1.34 (m, 18H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) for the major isomer δ 145.85, 138.30, 136.06, 134.51, 129.86, 129.48, 128.90, 128.49, 128.35, 126.91, 52.60, 32.31, 32.06, 29.75 (2C), 29.66, 29.49 (2C), 29.26, 28.79, 23.40, 22.84, 14.26. HRMS (APCI-MS, positive): *m/z* = 411.2720. Calcd for $C_{27}H_{39}OS$: 411.2716 $[M+H]^+$.

Dodecyl 4-nonen-5-yl sulfoxide (2i, isomeric ratio = 42:58): Dodecyl 4-nonen-5-yl sulfide was synthesized via procedures similar in the previous report[4a] and was oxidized into **2i** according to **GP1**. Colorless oil. ^{1}H NMR ($CDCl_3$) δ 6.13 (t, J = 7.5 Hz, 0.42 × 1H), 5.83 (t, J = 7.5 Hz, 0.58 × 1H), 2.84 (ddd, J = 13.9, 8.1, 4.6 Hz, 0.58 × 1H), 2.68 (ddd, J = 14.6, 8.4, 5.0 Hz, 0.42 × 1H), 2.45–2.56 (m, 0.42 × 1H, 0.58 × 2H), 2.33–2.39 (m, 1H), 2.17–2.24 (m, 0.42 × 2H, 0.58 × 1H), 2.04–2.14 (m, 1H), 1.25–1.70 (m, 26H), 0.90–0.95 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) mixture of isomers δ 143.28, 142.26, 135.51, 133.72, 52.38, 52.24, 32.05, 31.83, 31.26, 30.26, 30.19, 29.74, 29.68, 29.51, 29.48, 29.40, 29.36, 29.00, 28.92, 25.32, 24.98, 23.27, 22.90, 22.84, 22.83, 22.63, 22.42, 22.38, 14.25, 14.09, 13.98, 13.91, 13.79 (nine of the aliphatic signals contain overlapping). HRMS (APCI-MS, positive): *m/z* = 343.3028. Calcd for $C_{21}H_{43}OS$: 343.3029 $[M+H]^+$.

1-Cyclohexenyl dodecyl sulfoxide (2j): 1-Cyclohexenyl dodecyl sulfide was synthesized via procedures similar in the previous report[4a] and was oxidized into **2j** according to **GP1**. Colorless oil. ^{1}H NMR ($CDCl_3$) δ 6.41–6.42 (m, 1H), 2.62–2.70 (m, 2H), 2.26–2.30 (m, 1H), 2.20–2.24 (m, 2H), 2.03–2.08 (m, 1H), 1.68–1.81 (m, 3H), 1.60–1.67 (m, 3H), 1.25–1.46 (m, 18H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 140.91, 132.70, 51.10, 32.03, 29.73 (2C), 29.66, 29.50, 29.46, 29.35, 28.92, 25.67, 22.81, 22.47, 22.36, 22.16, 20.58, 14.23. HRMS (APCI-MS, positive): *m/z* = 299.2403. Calcd for $C_{18}H_{35}OS$: 299.2403 $[M+H]^+$.

Dodecyl 2-phenylvinyl sulfoxide (2k, *E*/*Z* = 9:91): Via procedures similar in the previous report,[12] (*Z*)-rich dodecyl 2-phenylvinyl sulfide was synthesized, and oxidized into **2k** according to **GP1**. White solid. ^{1}H NMR ($CDCl_3$) δ 7.47 (d, J = 6.9 Hz, 0.09 × 2H), 7.35–7.42 (m, 0.91 × 5H, 0.09 × 3H), 7.24 (d, J = 15.1 Hz, 0.09 × 1H), 7.08 (d, J = 10.6 Hz, 0.91 × 1H), 6.83 (d, J = 15.1 Hz, 0.09 × 1H), 6.41 (d, J = 10.6 Hz, 0.91 × 1H), 2.92 (ddd, J = 13.9, 7.4, 5.7 Hz, 0.91 × 1H), 2.78–2.85 (m, 0.09 × 2H), 2.75 (ddd, J = 13.9, 7.4, 5.7 Hz, 0.91 × 1H), 1.72–1.80 (m, 2H), 1.25–1.49 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) for major isomer δ 139.19, 135.82, 134.12, 129.84, 129.48, 128.76, 54.45, 32.03, 29.73 (2C), 29.66, 29.47 (2C), 29.33, 28.95, 22.82, 22.65, 14.24. HRMS (APCI-MS, positive): *m/z* = 321.2241. Calcd for $C_{20}H_{33}OS$: 321.2247 $[M+H]^+$.

Cyclohexylidene(phenyl)methyl dodecyl sulfoxide (2m): Cyclohexylidene(phenyl)methyl dodecyl sulfide was synthesized via procedures similar in the previous report[4a] and was oxidized into **2m** according to **GP1**. White solid. m.p. = 66.7–68.0 °C. ^{1}H NMR (CD_2Cl_2) δ 7.36–7.40 (m, 3H), 7.16–7.28 (brs, 2H), 2.65–2.71 (m, 2H), 2.43 (ddd, J = 12.6, 9.0, 6.0 Hz, 1H), 2.29 (ddd, J = 12.6, 9.0, 6.0 Hz, 1H), 1.99–2.12 (m, 2H), 1.77–1.82 (m, 1H), 1.45–1.62 (m, 7H), 1.26–1.36 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (CD_2Cl_2) δ 152.41, 135.71, 132.27, 131.53, 128.27, 128.20, 51.68, 34.03, 32.34, 31.10, 30.03 (2C), 29.94, 29.78, 29.76, 29.64, 29.27, 28.76, 28.69, 26.77, 23.39, 23.11, 14.28. HRMS (APCI-MS, positive): *m/z* = 389.2878. Calcd for $C_{25}H_{41}OS$: 389.2873 $[M+H]^+$.

3,4-Dihydronaphthalen-2-yl dodecyl sulfoxide (2n): 3,4-Dihydronaphthalen-2-yl dodecyl sulfide was synthesized via procedures similar in the previous report[4a] and was oxidized into **2n** according to **GP1**. Yellow solid. m.p. = 43.3–44.0 °C. ^{1}H NMR ($CDCl_3$) δ 7.21–7.25 (m, 2H), 7.16–7.18 (m, 2H), 7.06 (s, 1H), 2.92–3.01 (m, 2H), 2.69–2.79 (m, 2H), 2.54–2.59 (m, 1H), 2.37–2.42 (m, 1H), 1.64–1.77 (m, 2H), 1.25–1.47 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 141.73, 135.63, 132.12, 129.77, 129.13, 127.85, 127.64, 127.21, 51.53, 32.04, 29.73 (2C), 29.66, 29.51, 29.47, 29.35, 28.93, 28.01, 22.83, 22.23, 20.33, 14.25. HRMS (APCI-MS, positive): *m/z* = 347.2403. Calcd for $C_{22}H_{35}OS$: 347.2403 $[M+H]^+$.

5-*tert*-Butyl-2,3-diphenylbenzofuran (3aa): White solid (56 mg, 0.17 mmol, 86%). m.p. = 136.2–137.7 °C. ^{1}H NMR ($CDCl_3$) δ 7.66 (d, J = 7.1 Hz, 2H), 7.50–7.55 (m, 6H), 7.44 (t, J = 7.1 Hz, 2H), 7.30–7.34 (m, 3H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.40, 150.91, 146.26, 133.22, 131.00, 129.98, 129.93, 129.15, 128.52, 128.33, 127.69, 127.13, 122.85, 117.86, 116.10, 110.58, 34.95, 32.01. HRMS (APCI-MS, positive): *m/z* = 326.1669. Calcd for $C_{24}H_{22}O$: 326.1665 $[M]^+$.

5-*tert*-Butyl-2-phenylbenzofuran (3ab): White solid (33 mg, 0.13 mmol, 65%). m.p. = 102.5–105.1 °C. ^{1}H NMR ($CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2H), 7.59 (s, 1H), 7.43–7.46 (m, 3H), 7.35–7.37 (m, 2H), 7.00 (s, 1H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$) δ156.18, 153.29, 146.13, 130.85, 129.04, 128.90, 128.51, 125.00, 122.40, 117.23, 110.58, 101.64, 34.87, 32.00. HRMS (APCI-MS, positive): *m/z* = 250.1359. Calcd for $C_{18}H_{18}O$: 250.1352 $[M]^+$. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[17]

5-*tert*-Butyl-3-chloro-2-phenylbenzofuran (3ac): Colorless oil (26 mg, 0.092 mmol, 46%). ^{1}H NMR ($CDCl_3$) δ 8.14 (d, J = 7.5 Hz, 2H), 7.59 (s, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.43–7.43 (m, 2H), 7.40 (t, J = 7.5 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 151.11, 149.14, 146.89, 129.63, 128.88, 128.76, 127.80, 126.34, 123.76, 115.12, 110.92, 108.27, 35.03, 31.94. HRMS (APCI-MS, positive): *m/z* = 284.0976. Calcd for $C_{18}H_{17}{}^{35}ClO$: 284.0962 $[M]^+$.

5-*tert*-Butyl-3-ethoxycarbonyl-2-phenylbenzofuran (3ad): Pale yellow oil (32 mg, 0.10 mmol, 50%). ^{1}H NMR ($CDCl_3$) δ 8.13 (s, 1H), 8.02 (d, J = 7.5 Hz, 2H), 7.43–7.51 (m, 5H), 4.42 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 164.30, 161.00, 152.22, 147.24, 130.24, 129.95, 129.61, 128.16, 126.91, 123.32, 118.91, 110.57, 109.11, 60.68, 35.05, 31.94, 14.34. HRMS (APCI-MS, positive): *m/z* = 322.1567. Calcd for $C_{21}H_{22}O_3$: 322.1563 $[M]^+$.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[18]

5-*tert*-Butyl-2-methyl-3-phenylbenzofuran (3af): Pale yellow oil (42 mg, 0.16 mmol, 81%). ^{1}H NMR ($CDCl_3$) δ 7.62 (d, *J* = 1.7 Hz, 1H), 7.53–7.57 (m, 4H), 7.40–7.44 (m, 2H), 7.38 (dd, *J* = 8.6, 1.7 Hz, 1H), 2.56 (s, 3H), 1.41 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.38, 151.62, 145.88, 133.26, 129.14, 128.93, 128.47, 127.01, 121.53, 117.16, 115.56, 110.18, 34.91, 32.07, 12.97. HRMS (APCI-MS, positive): *m/z* =264.1519. Calcd for $C_{19}H_{20}O$: 264.1509 $[M]^+$.

5-*tert*-Butyl-2-butyl-3-phenylbenzofuran (3ag): Colorless oil (51 mg, 0.17 mmol, 83%). ^{1}H NMR ($CDCl_3$) δ 7.54 (s, 1H), 7.50–7.50 (m, 4H), 7.39–7.41 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 2.84 (t, *J* = 7.7 Hz, 2H), 1.72–1.77 (m, 2H), 1.37–1.40 (m, 2H), 1.37 (s, 9H), 0.91 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 155.69, 152.34, 145.83, 133.28, 129.29, 128.89, 128.58, 127.03, 121.51, 117.03, 115.64, 110.25, 34.91, 32.06, 30.71, 26.65, 22.57, 13.94. HRMS (APCI-MS, positive): *m/z* =306.1976. Calcd for $C_{22}H_{26}O$: 306.1978 $[M]^+$.

2-Benzyl-5-*tert*-butyl-3-phenylbenzofuran (3ah): Yellow oil (57 mg, 0.17 mmol, 84%). ^{1}H NMR ($CDCl_3$) δ 7.58 (d, *J* = 1.4 Hz, 1H), 7.49–7.54 (m, 4H), 7.39–7.41 (m, 2H), 7.36 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.28–7.31 (m, 2H), 7.21–7.26 (m, 3H), 4.20 (s, 2H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.92, 152.72, 146.04, 138.19, 132.90, 129.28, 129.02, 128.72, 128.63, 128.40, 127.37, 126.66, 122.00, 118.60, 115.93, 110.58, 34.94, 33.05, 32.05. HRMS (APCI-MS, positive): *m/z* =340.1822. Calcd for $C_{25}H_{24}O$: 340.1822 $[M]^+$.

5-*tert*-Butyl-2-butyl-3-propylbenzofuran (3ai): Colorless oil (39 mg, 0.14 mmol, 72%). ^{1}H NMR ($CDCl_3$) δ 7.43 (s, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.65–1.69 (m, 4H), 1.35–1.41 (m, 2H), 1.38 (s, 9H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 154.99, 152.23, 144.98, 129.54, 120.80, 115.19, 114.33, 109.99, 34.80, 32.10, 30.73, 26.25, 25.74, 23.26, 22.53, 14.28, 14.02. HRMS (APCI-MS, positive): *m/z* =272.2129. Calcd for $C_{19}H_{28}O$: 272.2135 $[M]^+$.

8-*tert*-Butyl-1,2,3,4-tetrahydrodibenzo[*b*,*d*]furan (3aj): White solid (40 mg, 0.18 mmol, 89%). m.p. = 53.9–55.4 °C. ^{1}H NMR ($CDCl_3$) δ 7.43 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 2.74–2.76 (m, 2H), 2.65–2.67 (m, 2H), 1.94–1.98 (m, 2H), 1.85–1.89 (m, 2H), 1.41 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 154.27, 152.62, 145.30, 128.57, 120.82, 114.67, 113.00, 110.14, 34.82, 32.08, 23.62, 23.15, 22.88, 20.66. HRMS (APCI-MS, positive): *m/z* =228.1512. Calcd for $C_{16}H_{20}O$: 228.1509 $[M]^+$. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[19]

5-*tert*-Butyl-3-phenylbenzofuran (3ak): Pale yellow oil (45 mg, 0.18 mmol, 92%). ^{1}H NMR ($CDCl_3$) δ 7.84 (d, *J* = 2.1 Hz, 1H), 7.77 (s, 1H), 7.67 (d, *J* = 6.9 Hz, 2H), 7.52 (t, *J* = 6.9 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.45 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.41 (t, *J* = 6.9 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 154.19, 146.28, 141.68, 132.49, 129.15, 127.75, 127.51, 126.24, 122.68, 122.57, 116.46, 111.20, 34.99, 32.06. HRMS (APCI-MS, positive): *m/z* =251.1422. Calcd for $C_{18}H_{19}O$: 251.1430 $[M+H]^+$.

5-Chloro-2,3-diphenylbenzofuran (3ba): White solid (39 mg, 0.13 mmol, 64%). m.p. = 116.0–118.1 °C. ^{1}H NMR ($CDCl_3$) δ 7.63–7.66 (m, 2H), 7.41–7.50 (m, 7H), 7.31–7.34 (m, 3H), 7.27–7.30 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 152.49, 152.06, 132.28, 131.82, 130.31, 129.79, 129.27, 128.89, 128.76, 128.64, 128.08, 127.19, 124.97, 119.78, 117.25, 112.25. HRMS (APCI-MS, positive): *m/z* =304.0654. Calcd for $C_{20}H_{13}{}^{35}ClO$: 304.0649 $[M]^+$.

5-Bromo-2,3-diphenylbenzofuran (3ca): White solid (56 mg, 0.16 mmol, 80%). m.p. = 131.3–134.5 °C. ^{1}H NMR ($CDCl_3$) δ 7.65–7.67 (m, 2H), 7.62 (t, *J* = 1.2 Hz, 1H), 7.48–7.51 (m, 4H), 7.43–7.46 (m, 3H), 7.32–7.35 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 152.85, 151.89, 132.41, 132.23, 130.24, 129.79, 129.27, 128.89, 128.63, 128.09, 127.66, 127.19, 122.80, 117.10, 116.24, 112.73. HRMS (APCI-MS, positive): *m/z* =348.0144. Calcd for $C_{20}H_{13}{}^{79}BrO$: 348.0144 $[M]^+$.

5-Iodo-2,3-diphenylbenzofuran (3da): White solid (55 mg, 0.14 mmol, 73%). m.p. = 162.2–164.8 °C. ^{1}H NMR ($CDCl_3$) δ 7.80 (d, *J* = 1.4 Hz, 1H), 7.63–7.65 (m, 2H), 7.60 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.42–7.50 (m, 5H), 7.31–7.34 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 153.47, 151.47, 133.35, 133.07, 132.23, 130.19, 129.82, 129.28, 128.95, 128.88, 128.64, 128.09, 127.19, 116.77, 113.29, 86.61. HRMS (APCI-MS, positive): *m/z* = 396.0007. Calcd for $C_{20}H_{13}IO$: 396.0006 $[M]^+$.

2-Methyl-3-phenyl-5-(trifluoromethyl)benzofuran (3ef): Pale yellow oil (23 mg, 0.082 mmol, 41%). ^{1}H NMR ($CDCl_3$) δ 7.84 (s, 1H), 7.48–7.54 (m, 6H), 7.41 (t, *J* = 7.3 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 155.51, 153.38, 131.88, 129.07, 128.98, 127.56, 125.46 (q, *J* = 31.9 Hz), 124.85 (q, *J* = 272.0 Hz), 120.84 (q, *J* = 4.4 Hz), 117.35, 117.08 (q, *J* = 4.4 Hz), 111.36, 111.17, 12.91. HRMS (APCI-MS, positive): *m/z* = 276.0753. Calcd for $C_{16}H_{11}F_3O$: 276.0757 $[M]^+$.

8-Methoxy-1,2,3,4-tetrahydrodibenzo[*b*,*d*]furan (3fj): Orange oil (35 mg, 0.17 mmol, 86%). ^{1}H NMR ($CDCl_3$) δ 7.28 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 2.7 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.7 Hz, 1H), 3.84 (s, 3H), 2.72 (tt, *J* = 6.0, 2.1 Hz, 2H), 2.60 (tt, *J* = 6.0, 2.1 Hz, 2H), 1.91–1.95 (m, 2H), 1.82–1.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 155.80, 155.14, 149.35, 129.55, 113.11, 111.20, 111.09, 101.73, 56.13, 23.70, 23.08, 22.83, 20.64. HRMS (APCI-MS, positive): *m/z* = 202.0993. Calcd for $C_{13}H_{14}O_2$: 202.0988 $[M]^+$. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[19]

2,3,7-Triphenylbenzofuran (3ga): White solid (53 mg, 0.15 mmol, 76%). m.p. = 156.9–158.3 °C. ^{1}H NMR ($CDCl_3$) δ 7.99 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.67 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.54–7.57 (m, 4H), 7.49–7.52 (m, 3H), 7.47 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.44 (td, *J* = 7.4, 1.0 Hz, 2H), 7.28–7.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 151.26, 150.79, 136.69, 133.00, 131.28, 130.75, 129.99, 129.16, 128.81, 128.58, 128.51, 127.86, 127.78, 127.13, 125.39, 124.41, 123.68, 119.37, 117.80, (one of these aromatic signals contains overlapping). HRMS (APCI-MS, positive): *m/z* = 347.1428. Calcd for $C_{26}H_{19}O$: 347.1430 $[M+H]^+$.

6-Isopropyl-2,3-diphenylbenzofuran / 4-isopropyl-2,3-diphenylbenzofuran (3ha/3ha' = 11/1): Colorless oil (53 mg, 0.17 mmol, 87%). ^{1}H NMR ($CDCl_3$) for major isomer δ 7.65 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.51 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.47 (t, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 1.0 Hz, 1H), 7.40–7.43 (m, 2H), 7.28–7.33 (m, 3H), 7.15 (dd, *J* = 8.2, 1.0 Hz, 1H), 3.07 (sep, *J* = 6.8 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$) for major isomer δ 154.56, 150.28, 146.67, 133.23, 131.03, 129.88, 129.07, 128.53, 128.32, 128.26, 127.67, 127.01, 122.17, 119.79, 117.59, 108.71, 34.55, 24.52. HRMS (APCI-MS, positive): *m/z* = 312.1510. Calcd for $C_{23}H_{20}O$: 312.1509 $[M]^+$.

2,3-Diphenylnaphtho[2,1-*b*]furan (3ia): White solid (57 mg, 0.18 mmol, 89%). m.p. = 103.3–106.1 °C. ^{1}H NMR ($CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.76 (q, *J* = 8.7 Hz, 2H), 7.55–7.58 (m, 8H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.25–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 151.56, 150.24, 134.87, 131.08, 131.03, 130.73, 129.54, 129.09, 128.55, 128.50, 128.35, 127.93, 126.36, 126.12, 124.40, 123.79, 123.22, 119.71, 112.35 (one of these aromatic signals contains overlapping). HRMS (APCI-MS, positive): *m/z* = 320.1192. Calcd for $C_{24}H_{16}O$: 320.1196 $[M]^+$. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent

with the reported values.[20]

Compound 3jj: White solid (40 mg, 0.13 mmol, 63%). m.p. > 190 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 7.66 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 3.09 (t, J = 6.6 Hz, 4H), 2.87 (t, J = 6.6 Hz, 4H), 2.00–2.04 (m, 4H), 1.63–1.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 154.22, 152.90, 128.45, 125.11, 123.14, 122.58, 116.37, 110.63, 25.66, 24.26, 24.10, 22.86. HRMS (APCI-MS, positive): *m/z* = 317.1539. Calcd for $C_{22}H_{21}O_2$: 317.1536 $[M+H]^+$.

5,6,13,14-Tetrahydro-7,12-dioxa[8]helicene (3jn): White solid. m.p. > 270 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 7.89 (d, J = 8.9 Hz, 2H), 7.73 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 7.5 Hz, 2H), 6.88 (t, J = 7.5 Hz, 2H), 6.84 (d, J = 7.5 Hz, 2H), 6.76 (t, J = 7.5 Hz, 2H), 3.03–3.09 (m, 4H), 2.80–2.88 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 157.01, 154.15, 133.25, 132.74, 128.94, 126.59, 125.41, 124.99, 124.86, 123.90, 122.01, 119.55, 119.47, 110.82, 30.09, 23.32. HRMS (APCI-MS, positive): *m/z* = 412.1448. Calcd for $C_{30}H_{20}O_2$: 412.1458 $[M]^+$.

(2*R,3*S**)-5-*tert*-Butyl-2-methylsulfanyl-2,3-diphenyl-2,3-dihydrobenzofuran (4aa):** Colorless oil. The stereochemistry was determined by the analogy with that of **4da**. The stereochemistry was supported by NMR analysis: no correlation was observed between the two hydrogen atoms on C2 and C3 positions in NOESY analysis after reduction[21] to the corresponding 2,3-diphenyl-2,3-dihydrobenzofuran. ^{1}H NMR ($CDCl_3$) δ 7.68 (d, J = 7.5 Hz, 2H), 7.36–7.41 (m, 5H), 7.30–7.34 (m, 2H), 7.26–7.28 (m, 2H), 7.04 (s, 1H), 6.98 (d, J = 8.9 Hz, 1H), 4.86 (s, 1H), 1.77 (s, 3H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 156.16, 144.81, 143.08, 136.48, 130.74, 129.64, 128.51, 128.24, 128.19, 127.84, 126.88, 125.78, 122.48, 109.81, 103.91, 62.81, 34.62, 31.85, 11.86. HRMS (APCI-MS, positive): *m/z* = 375.1771. Calcd for $C_{25}H_{27}OS$: 375.1777 $[M+H]^+$.

(2*S,3*S**)-5-*tert*-Butyl-2-methyl-2-methylsulfanyl-3-phenyl-2,3-dihydrobenzofuran (*syn*-4af'):** White solid. m.p. = 93.8–97.7 °C. The stereochemistry was determined by NOESY analysis. ^{1}H NMR ($CDCl_3$) δ 7.38 (brs, 5H), 7.26 (d, J = 8.2 Hz, 1H), 7.14 (s, 1H), 6.82 (d, J = 8.2 Hz, 1H), 4.73 (s, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 156.12, 144.54, 136.29, 130.00, 129.54, 128.39, 128.19, 125.61, 122.61, 109.77, 99.34, 60.72, 34.61, 31.86, 27.00, 11.19. HRMS (APCI-MS, positive): *m/z* = 313.1624. Calcd for $C_{20}H_{25}OS$: 313.1621 $[M+H]^+$.

(2*S,3*R**)-5-*tert*-Butyl-2-methyl-2-methylsulfanyl-3-phenyl-2,3-dihydrobenzofuran (*anti*-4af'):** Colorless oil. The stereochemistry was determined by NOESY analysis. ^{1}H NMR ($CDCl_3$) δ 7.24–7.33 (m, 4H), 7.11 (d, J = 1.4 Hz, 1H), 7.05 (d, J = 6.8 Hz, 2H), 6.82 (d, J = 8.2 Hz, 1H), 4.55 (s, 1H), 2.24 (s, 3H), 1.32 (s, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 156.03, 144.72, 139.44, 130.13, 129.28, 128.56, 127.49, 125.78, 122.88, 109.41, 98.31, 58.98, 34.56, 31.85, 24.25, 11.97. HRMS (APCI-MS, positive): *m/z* = 313.1628. Calcd for $C_{20}H_{25}OS$: 313.1621 $[M+H]^+$.

(2*S,3*R**)-5-*tert*-Butyl-2-dodecylsulfanyl-3-phenyl-2,3-dihydrobenzofuran (4ak):** White solid (1.6 g, 3.5 mmol, 70%). m.p. = 41.6–42.9 °C. The stereochemistry was determined by the vicinal coupling constant between the two hydrogen atoms on C2 and C3 positions. ^{1}H NMR ($CDCl_3$) δ 7.33 (t, J = 7.5 Hz, 2H), 7.26–7.29 (m, 1H), 7.23 (dd, J = 8.2, 2.1 Hz, 1H), 7.19 (d, J = 7.5 Hz, 2H), 7.05 (d, J = 2.1 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 5.63 (d, J = 5.5 Hz, 1H), 4.42 (d, J = 5.5 Hz, 1H), 2.69–2.79 (m, 2H), 1.61–1.66 (m, 2H), 1.22–1.37 (m, 18H), 1.26 (s, 9H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 156.56, 144.64, 142.04, 129.20, 128.96, 127.91, 127.45, 125.90, 122.31, 109.55, 95.71, 55.89, 34.55, 32.07, 31.84, 31.60, 29.97, 29.80, 29.78, 29.73, 29.65, 29.50, 29.32, 29.03, 22.84, 14.27. HRMS (APCI-MS, positive): *m/z* = 452.3112. Calcd for $C_{30}H_{45}OS$: 452.3107 $[M+H]^+$.

5-*tert*-Butyl-2-phenylsulfanyl-2,3-dihydrobenzofuran (4al): Colorless oil (43 mg, 0.15 mmol, 76%). ^{1}H NMR ($CDCl_3$) δ 7.57–7.58 (m, 2H), 7.32–7.35 (m, 2H), 7.27–7.30 (m, 1H), 7.23 (s, 1H), 7.18–7.19 (m, 1H), 6.79 (d, J = 8.2 Hz, 1H), 6.19 (dd, J = 8.9, 5.5 Hz, 1H), 3.67 (dd, J = 16.5, 8.9 Hz, 1H), 3.19 (dd, J = 16.5, 5.5 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 155.97, 144.42, 134.25, 131.89, 129.10, 127.66, 125.56, 125.29, 121.77, 109.60, 89.47, 37.15, 34.49, 31.85. HRMS (APCI-MS, positive): *m/z* = 284.1223. Calcd for $C_{18}H_{20}OS$: 284.1229 $[M]^+$.

5-*tert*-Butyl-2-dodecylsulfanyl-2-phenyl-2*H*-spiro[benzofuran-3,1'-cyclohexane] (4am): Colorless oil (75 mg, 0.15 mmol, 73%). ^{1}H NMR ($CDCl_3$) δ 7.79 (brs, 2H), 7.54 (d, J = 2.1 Hz, 1H), 7.40 (brs, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.23 (dd, J = 8.2, 2.1 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 2.37–2.42 (m, 2H), 2.11 (ddd, J = 12.3, 8.4, 6.6 Hz, 1H), 1.98–2.02 (m, 1H), 1.81–1.86 (m, 2H), 1.69 (d, J = 13.0 Hz, 1H), 1.34 (s, 9H), 1.04–1.38 (m, 24H), 0.88 (t, J = 7.2 Hz, 3H), 0.63 (td, J_t = 13.0, J_d = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 154.18, 143.63, 139.91, 136.94, 128.00, 127.80, 124.53, 122.84, 110.17, 109.45, 53.91, 35.91, 34.58, 32.07, 31.98, 29.97, 29.77, 29.72, 29.57, 29.50, 29.26, 29.24, 29.11, 29.09, 25.50, 23.47, 22.84, 21.17, 14.27 (two of these signals contains overlapping). HRMS (APCI-MS, positive): *m/z* = 521.3814. Calcd for $C_{35}H_{53}OS$: 521.3812 $[M+H]^+$.

(2*R,3*S**)-5-Iodo-2-methylsulfanyl-2,3-diphenyl-2,3-dihydrobenzofuran (4da):** White solid (49 mg, 0.11 mmol, 55%). m.p. = 166.6–169.8 °C. The stereochemistry was determined by X-ray crystallographic analysis (Figure S1). ^{1}H NMR ($CDCl_3$) δ 7.61–7.63 (m, 2H), 7.57 (dd, J = 7.5, 2.1 Hz, 1H), 7.36–7.42 (m, 5H), 7.32–7.35 (m, 1H), 7.29 (d, J = 2.1 Hz, 1H), 7.24–7.25 (m, 2H), 6.85 (d, J = 9.3 Hz, 1H), 4.84 (s, 1H), 1.76 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 158.34, 142.57, 137.91, 135.71, 134.14, 133.29, 130.59, 128.65, 128.54, 128.36, 128.07, 126.62, 112.99, 104.34, 83.25, 62.26, 11.99. HRMS (APCI-MS, positive): *m/z* = 445.0114. Calcd for $C_{21}H_{18}IOS$: 445.0118 $[M+H]^+$.

7,12-Dioxa[8]helicene (5): White solid. m.p. = 299.9–303.2 °C. ^{1}H NMR ($CDCl_3$) δ 8.14 (d, J = 8.9 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.9 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 6.91 (t, J = 7.5 Hz, 2H), 6.39 (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 155.85, 153.22, 130.02, 129.80, 128.96, 128.58, 128.27, 127.60, 125.89, 123.94, 123.92, 123.62, 121.81, 119.34, 112.16, 111.31. HRMS (APCI-MS, positive): *m/z* = 408.1155. Calcd for $C_{30}H_{16}O_2$: 408.1145 $[M]^+$. All the resonances in ^{1}H and ^{13}C spectra were consistent with the reported values.[3h]

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References

1. a) *The Chemistry of Sulphones and Sulphoxides*, ed. by S. Patai, Z. Rappoport, C. Stirling, Wiley, Chichester, **1988**. b) *An Introduction to Organosulfur Chemistry*, ed. by R. J. Cremlyn, Wiley, Hoboken, **1996**. c) *Organosulfur Chemistry I*, ed. by P. C. B. Page, Springer, Heidelberg, **1999**. d) *Organosulfur Chemistry II*, ed. by P. C. B. Page, Springer, Heidelberg, **1999**. e) *Advances in Sulfur Chemistry, Vol. 2*, ed. by C. M. Rayner, JAI Press, Greenwich, **2000**. f) *Sulfur Compounds: Advances in*

Research and Application, ed. by A. Q. Acton, Scholarly Eds., Atlanta, **2012**. g) I. Fernandez, N. Khiar, *Chem. Rev.* **2003**, *103*, 3651. h) H. Pellissier, *Tetrahedron* **2006**, *62*, 5559. i) G. Sipos, E. E. Drinkel, R. Dorta, *Chem. Soc. Rev.* **2015**, *44*, 3834.

2. a) S. K. Bur, A. Padwa, *Chem. Rev.* **2004**, *104*, 2401. b) K. S. Feldman, *Tetrahedron* **2006**, *62*, 5003. c) S. Akai, Y. Kita, *Top. Curr. Chem.* **2007**, *274*, 35. d) L. H. S. Smith, S. C. Coote, H. F. Sneddon, D. J. Procter, *Angew. Chem. Int. Ed.* **2010**, *49*, 5832. e) A. P. Pulis, D. J. Procter, *Angew. Chem. Int. Ed.* **2016**, *55*, 9842. f) A. Shafir, *Tetrahedron Lett.* **2016**, *57*, 2673. g) H. Yorimitsu, *Chem. Rec.* **2017**, *17*, 1156. h) T. Yanagi, K. Nogi, H. Yorimitsu, *Tetrahedron Lett.* **2018**, *59*, 2951.
3. Our recent review and examples: a) H. Yorimitsu, *J. Synth. Org. Chem. Jpn.* **2013**, *71*, 341. b) S. Yoshida, H. Yorimitsu, K. Oshima, *Org. Lett.* **2007**, *9*, 5573. c) S. Yoshida, H. Yorimitsu, K. Oshima, *Chem. Lett.* **2008**, *37*, 786. d) S. Yoshida, H. Yorimitsu, K. Oshima, *Org. Lett.* **2009**, *11*, 2185. e) T. Kobatake, S. Yoshida, H. Yorimitsu, K. Oshima, *Angew. Chem. Int. Ed.* **2010**, *49*, 2340. f) T. Kobatake, D. Fujino, S. Yoshida, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2010**, *132*, 11838. g) Y. Ookubo, A. Wakamiya, H. Yorimitsu, A. Osuka, *Chem. Eur. J.* **2012**, *18*, 12690. h) T. Yanagi, S. Otsuka, Y. Kasuga, K. Fujimoto, K. Murakami, K. Nogi, H. Yorimitsu, A. Osuka, *J. Am. Chem. Soc.* **2016**, *138*, 14582. i) H. Kawashima, T. Yanagi, C.-C. Wu, K. Nogi, H. Yorimitsu, *Org. Lett.* **2017**, *19*, 4552. j) K. Okamoto, M. Hori, T. Yanagi, K. Murakami, K. Nogi, H. Yorimitsu, *Angew. Chem. Int. Ed.* **2018**, *57*, 14230.
4. Functionalizations of alkenyl and aryl sulfoxides with phenols or enolizable compounds by sigmatropic rearrangement: a) J. B. Hendrickson, M. A. Walker, *Org. Lett.* **2000**, *2*, 2729. b) S. Akai, N. Kawashita, H. Satoh, Y. Wada, K. Kakiguchi, I. Kuriwaki, Y. Kita, *Org. Lett.* **2004**, *6*, 3793. c) S. Akai, N. Kawashita, Y. Wada, H. Satoh, A. H. Alinejad, K. Kakiguchi, I. Kuriwaki, Y. Kita, *Tetrahedron Lett.* **2006**, *47*, 1881. d) X. Hung, N. Maulide, *J. Am. Chem. Soc.* **2011**, *133,* 8510. e) X. Hung, M. Patil, C. Farès, W. Thiel, N. Maulide, *J. Am. Chem. Soc.* **2013**, *135*, 7312. f) H. J. Shrives, J. A. Fernández-Salas, C. Hedtke, A. P. Pulis, D. J. Procter, *Nat. Commun.* **2017**, *8*, 14801. g) Z. He, H. J. Shrives, J. A. Fernández-Salas, A. Abengózar, J. Neufeld, K. Yang, A. P. Pulis, D. J. Procter, *Angew. Chem. Int. Ed.* **2018**, *57*, 5759.
5. a) K. Murakami, H. Yorimitsu, A. Osuka, *Angew. Chem. Int. Ed.* **2014**, *53*, 7510. b) K. Murakami, H. Yorimitsu, A. Osuka, *Bull. Chem. Soc. Jpn.* **2014**, *87*, 1349.
6. A review on charge-accelerated [3,3] sigmatropic rearrangement: X. Huang, S. Klimczyk, N. Maulide, *Synthesis* **2012**, *44*, 175.
7. Selected recent reports on cation-accelerated [3,3] sigmatropic rearrangement of sulfoniums: a) B. Peng, D. Geerdink, C. Farès, N. Maulide, *Angew. Chem. Int. Ed.* **2014**, *53*, 5462. b) B. Peng, X. Huang, L.-G. Xie, N. Maulide, *Angew. Chem. Int. Ed.* **2014**, *53*, 8718. c) A. J. Eberhart, H. J. Shrives, E. Álvarez, A. Carrër, Y. Zhang, D. J. Procter, *Chem. Eur. J.* **2015**, *21*, 7428. d) J. A. Fernández-Salas, A. J. Eberhart, D. J. Procter, *J. Am. Chem. Soc.* **2016**, *138*, 790. e) A. J. Eberhart, H. Shrives, Y. Zhang, A. Carrër, A. V. S. Parry, D. J. Tate, M. L. Turner, D. J. Procter, *Chem. Sci.* **2016**, *7*, 1281. f) L. Hu, Q. Gui, X. Chen, Z. Tan, G. Zhu, *J. Org. Chem.* **2016**, *81*, 4861. g) D. Kaiser, L. F. Veiros, N. Maulide, *Chem. Eur. J.* **2016**, *22*, 4727. h) D. Kaiser, L. F. Veiros, N. Maulide, *Adv. Synth. Catal.* **2017**, *359*, 64. i) D. Kaldre, B. Maryasin, D. Kaiser, O. Gajsek, L. González, N. Maulide, *Angew. Chem. Int. Ed.* **2017**, *56*, 2212. j) L. Shang, Y. Chang, F. Luo, J.-N. He, X. Huang, L. Zhang, L. Kong, K. Li, B. Peng, *J. Am. Chem. Soc.* **2017**, *139*, 4211. k) M. Šiaučiulis, S. Sapmaz, A. P. Pulis, D. J. Procter, *Chem. Sci.* **2018**, *9*, 754. l) F. Luo, Y. Lu, M. Hu, J. Tian, L. Zhang, W. Bao, C. Yan, X. Huang, Z.-X. Wang, B. Peng, *Org. Chem. Front.* **2018**, *5*, 1756. m) D. Kaldre, I. Klose, N. Maulide, *Science* **2018**, *361*, 664. n) B. Maryasin, D. Kaldre, R. Galaverna, I. Klose, S. Ruider, M. Drescher, H. Kählig, L. González, M. N. Eberlin, I. D. Jurberg, N. Maulide, *Chem. Sci.* **2018**, *9*, 4124.
8. Some of alkenyl sulfoxides were used as a mixture of stereoisomers since the reactions proceeded successfully from both (*E*)- and (*Z*)-isomers.
9. a) M. L. Kerns, S. M. Conroy, J. S. Swenton, *Tetrahedron Lett.* **1994**, *35*, 7529. b) Y. Hu, T. Kamitanaka, Y. Mishima, T. Dohi, Y. Kita, *J. Org. Chem.* **2013**, *78*, 5530.
10. See Figure S1 in the Supporting Information.
11. I. Bassanini, E. E. Ferrandi, M. Vanoni, G. Ottolina, S. Riva, M. Crotti, E. Brenna, D. Monti, *Eur. J. Org. Chem.* **2017**, 7186.
12. A. Kondoh, K. Takami, H. Yorimitsu, K. Oshima, *J. Org. Chem.* **2005**, *70,* 6468.
13. B. Vacher, A. Samat, A. Allouche, A. Lakniflil, A. Baldyl, M. Chanon, *Tetrahedron* **1998**, *44*, 2925.
14. V. Caló, G. Scorrano, G. Modena, *J. Org. Chem.* **1969**, *34*, 2020.
15. A. F. Meindertsma, M. Pollard, B. L. Feringa, J. G. de Vries, A. J. Minnaard, *Tetrahedron: Asymmetry* **2007**, *18*, 2849.
16. B. S. Ong, *Tetrahedron Lett.* **1980**, *21*, 4225.
17. T. J. Maimone, S. L. Buchwald, *J. Am. Chem. Soc.* **2010**, *132*, 9990.
18. X. Guo, R. Yu, H. Li, Z. Li, *J. Am. Chem. Soc.* **2009**, *131*, 17387.
19. M. Yagoubi, A. C. F. Cruz, P. L. Nichols, R. L. Elliott, M. C. Willis, *Angew. Chem. Int. Ed.* **2010**, *49*, 7958.
20. M. Shimizu, H. Tsurugi, T. Satoh, M. Miura, *Chem. Asian J.* **2008**, *3*, 881.
21. T. Matsumura, T. Niwa, M. Nakada, *Tetrahedron Lett.* **2012**, *53*, 4313.