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Lewis acid-catalyzed reactions of donor–acceptor cyclopropanes with furan derivatives

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ABSTRACT

Lewis acid-catalyzed reactions of dialkyl 2-arylcyclopropane-1,1-dicarboxylates with 2,5-dimethylfuran were found to give products of [3+2]-cycloaddition to C(2)–C(3) bond, which contain reactive vinyl ether moiety. These adducts can be further transformed into various products depending on the Lewis acid, the nucleophilicity of aryl group in starting cyclopropane and the ratio of reagents. The vinyl ether moiety can attack the appropriate nucleophilic center in intramolecular or intermolecular mode or can undergo cycloaddition to the second equivalent of donor–acceptor cyclopropane. Alternatively, 2,5-diphenylfuran formed Friedel–Crafts products only when reacted with donor–acceptor cyclopropanes.

1. Introduction

During the last two decades, donor–acceptor cyclopropanes have attracted significant attention from organic chemists due to the broad scope of their reactivity.[1] Indeed, the presence of electron-releasing groups increases the cyclopropane reactivity toward electrophiles.[2] On the other hand, electron-withdrawing groups activate cyclopropanes to attack by nucleophiles (homo-Michael addition).[3] Moreover, donor–acceptor cyclopropanes have been demonstrated to form [3+2]-cycloadducts with various compounds bearing C=C,[4] C=O,[5] C=N,[6] N=N,[7] C≡C,[8] or C≡N[9] bonds via either a concerted or a stepwise mechanism (path *a* on Scheme 1). [3+3]-Cycloadditions of nitrones,[10] azomethine imines,[11] and isoquinoline-*N*-oxides[12] to the donor–acceptor cyclopropanes have also been described (path *b* on Scheme 1). A broad scope of polyfunctionalized five- and six-membered carbocycles and heterocycles can be synthesized via these reactions. They have also been applied toward the total synthesis of some bioactive natural compounds[13] as well as for the construction of complex polycyclic cores of some others.[4b,14] In all these processes, cyclopropanes react with a nucleophilic counterpart via the carbon atom bearing the cation-stabilizing group and with the electrophile via the carbon connected to the electron-withdrawing substituent(s). Thus, the donor–acceptor cyclopropanes can be considered as synthon of 1,3-dipole of **A**-type (Scheme 1).

Recently we have demonstrated, for the first time, the possibility of Lewis acid-mediated [4+3]-cycloaddition of the donor–acceptor cyclopropanes (**1**) to 1,3-diphenylisobenzofuran (path *c* on Scheme 1).[15] In this transformation, **1** reacted as three-carbon dienophile, isobenzofuran being a typical 1,3-diene. The related [4+3]-cycloaddition was realized earlier for allyl cations.[16,17] Furans were shown to react as 4π-units with some other dienes leading to [4+4] cycloadducts.[18] However, the most studied process wherein furans show diene behavior is the Diels–Alder reaction. Both intra- and intermolecular modes of this process which lead to 7-oxanorbornene derivatives (or products of their further transformations) have been widely applied.[19] At the same time, furans participate in cycloaddition processes as a 2π-component too. This mode of interaction is impossible for 1,3-diphenylisobenzofuran but can be realized for furan itself and its various 2- or 2,5-substituted derivatives. Indeed, examples of [1+2]-,[20] [2+2]-,[21] [3+2]-,[22] and [4+2]-cycloadditions[23] to the C(2)–C(3) furan bond as well as formation of some bis-adducts were described. Therefore, we decided to carefully investigate reactions between different furan derivatives and cyclopropanes **1** aiming to determine the preferable mode of their interactions depending on the nature of substituents in furans and cyclopropanes as well as on the Lewis acid applied.

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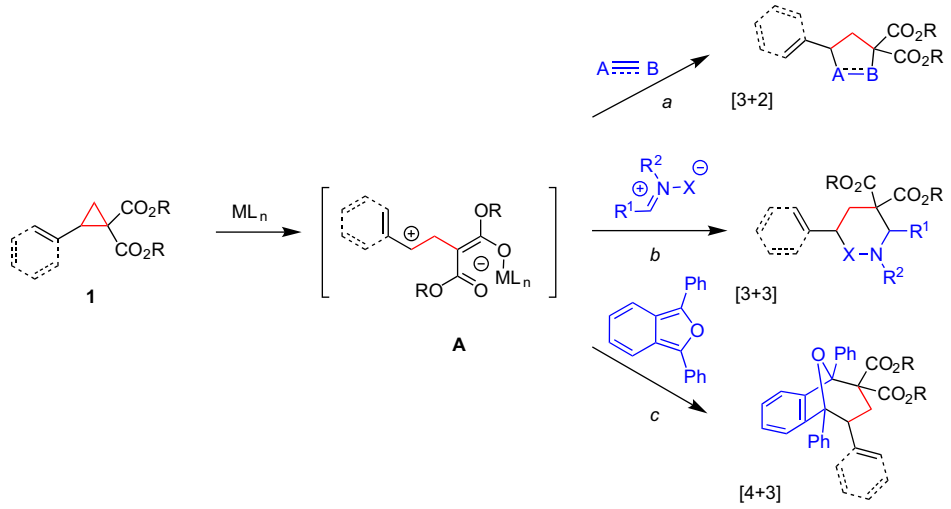


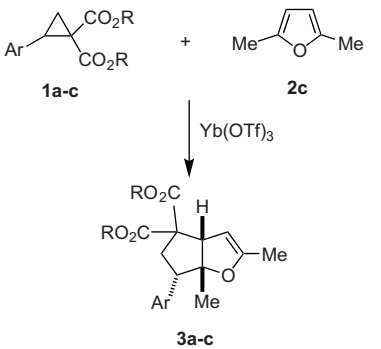
Scheme 1. Various cycloaddition reactions of donor–acceptor cyclopropanes.

2. Results and discussion

2.1. [3+2]-Cycloaddition reactions of donor–acceptor cyclopropanes with furans

We first examined the effect of substituents in the furan ring on its reactivity toward diethyl 2-(2-thienyl)cyclopropane-1,1-dicarboxylate (**1a**). This compound was selected as a model donor–acceptor cyclopropane as it was shown earlier to be effective in both [3+2]- and [4+3]-cycloaddition reactions in the presence of $Yb(OTf)_3$. However, we failed to isolate any cycloaddition products from the reaction of **1a** with unsubstituted furan (**2a**) under the same reaction conditions; only furan polymerization products were formed in this case. 2,5-Diarylfurans are known to be much more stable to acids than furan itself. So, we tried to introduce 2,5-diphenylfuran (**2b**) into reaction with **1a**. Indeed, we found no polymerization of this substrate, however, **2b** showed no reactivity toward cyclopropane **1a** either.

Nevertheless, we succeeded in performing the reaction of cyclopropane **1a** with 2,5-dimethylfuran (**2c**) in methylene chloride in the presence of $Yb(OTf)_3$. This process was found to be regio- and stereoselective leading to a single 1:1 adduct **3a** in 76% NMR yield. Analysis of NMR data allowed us to identify **3a** as the product of [3+2]-cycloaddition of cyclopropane **1a** to C(2)–C(3) bond of furan **2c** (Scheme 2). Thus, the ^1H NMR spectrum of **3a** contains



1a, 3a: R=Et, Ar=Th, 76%, d.r. > 95 : 5
1b, 3b: R=Me, Ar=Th, 53%, d.r. 90 : 10
1c, 3c: R=Et, Ar=Ph, 60%, d.r. > 95 : 5

Scheme 2.

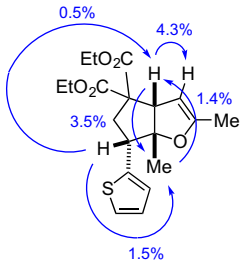


Figure 1. Some NOE data for compound **3a**.

characteristic signals at δ_H 2.99, 3.30, and 3.53 ppm, which correspond to the AMX system of the CH_2–CH fragment (^2J 13.1 Hz, ^3J 14.4 and 5.3 Hz). A significant upfield shift of the methyl group signal in comparison with that for the starting compound **2c** (δ_H 1.48 vs 2.23 ppm) is obviously caused by the loss of furan aromaticity. The relative configuration of **3a** was determined by NOE experiments (Fig. 1). It was found that the methine protons at the C(3a) and C(6) atoms as well as the methyl group at the C(6a) atom of cyclopenta[*b*]furan **3a** have a cis,cis-orientation. The further chemical transformations of **3a** confirm also its structure. The presence of the vinyl ether moiety in **3a** is in accordance with its lability during purification on silica too.

In comparison to the results observed with **1a**, dimethyl ester **1b** reacted with **2c** yielding *syn*-cycloaddition product **3b** as a mixture of two diastereomers in a 9:1 ratio (Fig. 2). We estimated the relative stability of major and minor diastereomers of **3b** using quantum chemical calculations at HF/6-31G basis set (Fig. 2).[24] We

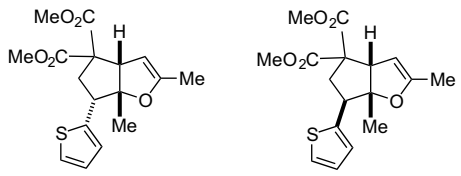


Figure 2. Two possible diastereomers of **3b**.

found that the minor diastereomer of **3b** is 2.2 kcal/mol more stable than major one. However, on the basis of all experimental data we believe that stereoselectivity of this reaction is a result of kinetic but not thermodynamic control, i.e., the major isomer of **3b** has the same relative stereochemistry as **3a**.

Unfortunately, the corresponding reactions with 2-methylfuran (**2d**) gave complex reaction mixtures containing both simple cycloadducts to C(2)–C(3) and C(4)–C(5) furan **2d** bonds and some oligomerization products.

The less reactive dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**1c**) failed to interact with **2c** under the same reaction conditions. Earlier we found that $SnCl_4$ is more efficient than $Yb(OTf)_3$ for initiation of the reaction of donor–acceptor cyclopropanes with anthracenes.[25] Similarly, **1c** reacted with **2c** in the presence of $SnCl_4$. A single set of product signals was found in ^1H and ^{13}C NMR spectra of the formed reaction mixture. These signals are very similar to those for **3a**. Therefore, the structure of product was assigned as **3c** (Scheme 2).

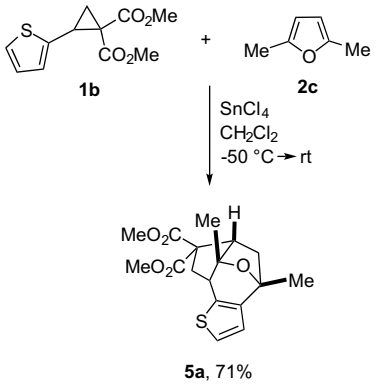
2.2. Friedel–Crafts reaction of 2,5-diphenylfuran (2b) with donor–acceptor cyclopropanes

The previous results showed that $SnCl_4$ has higher catalytic activity in reactions of donor–acceptor cyclopropanes in comparison with $Yb(OTf)_3$. As 2,5-diphenylfuran did not react with **1** under $Yb(OTf)_3$ catalysis, we tried to perform reaction of the donor–acceptor cyclopropanes with **2b** in the presence of $SnCl_4$. We found that **2b** interacted with **1d** under these reaction conditions but no cycloaddition products were identified in the reaction mixture. The Friedel–Crafts alkylation product **4** was a single isolated compound in this case (Scheme 3). In the ^1H NMR spectrum, the characteristic signals at δ_H 2.60, 2.76, 3.43, and 4.32 ppm correspond to CH–CH_2–CH fragment of substituent's open chain.

These results are similar to those for reactions of **1** with anthracenes when both cycloaddition and Friedel–Crafts products were formed depending on the substituents in the aromatic counterpart.[25]

2.3. Tandem [3+2]-cycloaddition/intramolecular electrophilic aromatic substitution of donor–acceptor cyclopropanes with furans

Encouraged by the results obtained with $SnCl_4$ as a catalyst, we decided to re-investigate reactions of donor–acceptor cyclopropanes with furan **2c** using this Lewis acid with the primary goal to optimize the reaction conditions. However, we found that instead of simple adduct **3b** its isomer **5a** was formed in 71% yield from **1b** and **2c** in the presence of $SnCl_4$ (Scheme 4). On the contrary to **3b**, **5a** was obtained as a single diastereomer. Thus, the ^1H NMR



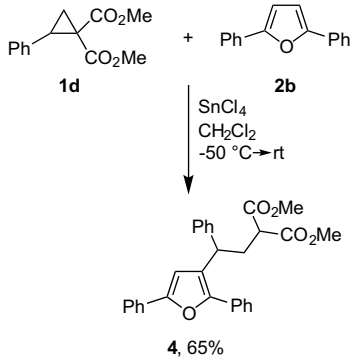
Scheme 4.

spectrum of **5a** reveals two AMX systems at δ_H 1.61, 2.24, and 3.37 ppm (^2J 13.1 Hz, ^3J 12.1 and 2.9 Hz) and δ_H 2.29, 2.93, and 3.39 (^2J 14.4 Hz, ^3J 7.0 Hz, and $^3J \leq 0.3$ Hz). These signals correspond to the protons of two isolated CH_2–CH fragments. Other characteristic signals at δ_H 6.71 and 7.13 ppm form an AX system corresponding to the 2,3-disubstituted thiophene moiety. The value of ^3J coupling constant for these signals (5.1 Hz) is typical for protons at C(2) and C(3) carbon atoms of thiophene ring. The relative stereochemistry of tetracycle **5a** was deduced from NOE experiments.

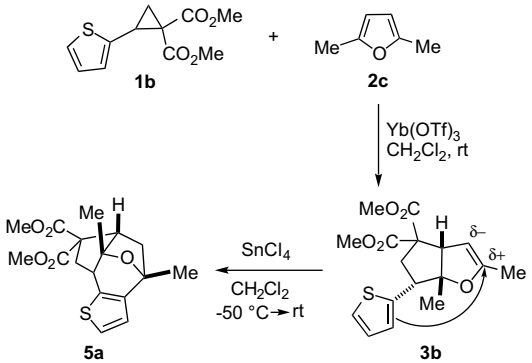
The formation of **5a** is two-step process. The [3+2]-cycloadduct **3b** was formed in the first step of this reaction. On the contrary to the softer Lewis acid $Yb(OTf)_3$, $SnCl_4$ catalyzed the further intramolecular cyclization of **3b** through an electrophilic attack of the vinyl ether moiety of **3b** onto the C(3) atom of thiophene affording **5a**. Both inter- and intramolecular analogues of this reaction are known.[26] To prove this mechanism, we treated [3+2]-cycloadduct **3b** with $SnCl_4$ and found that it was isomerized under these conditions into compound **5a** (Scheme 5).

Cyclopropane **1d** failed to form the analogous tetracyclic adduct even under more harsh reaction conditions. It means that not only the catalyst but also the nucleophilicity of the aromatic substituent in the starting cyclopropane influences the possibility of further transformations of the initial cycloadduct. The thiophene ring is more nucleophilic than the phenyl moiety and undergoes electrophilic attack. To prove this supposition, we performed the $SnCl_4$-catalyzed reaction of **2c** with cyclopropane **1e**, which has highly nucleophilic trimethoxyphenyl substituent. Indeed, we obtained the product **5b** in high yield as a single stereoisomer (Scheme 6).

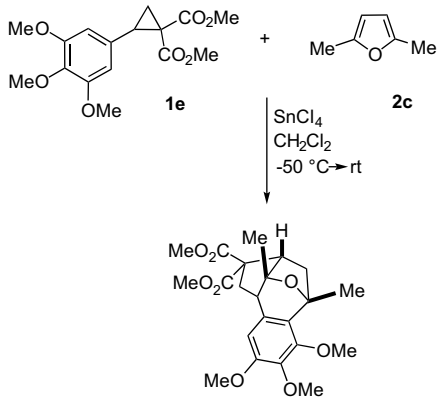
The NMR data for the saturated tricyclic moiety of compound **5b** are rather similar to those for compound **5a**. Thus, the ^1H spectrum of **5b** has two AMX type groups of signals corresponding to two isolated CH_2–CH fragments: at δ_H 1.66, 2.27, and 3.29 ppm (^2J



Scheme 3.

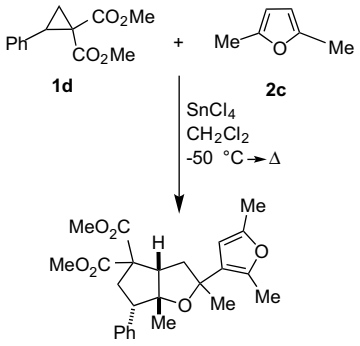


Scheme 5.



5b, 76%

Scheme 6.



6, 69%, d.r. 4:1

Scheme 7.

13.4 Hz, ^3J 12.1 and 3.0 Hz) and at δ_H 2.39, 2.78, and 3.21 ppm (^2J 14.4 Hz, ^3J 7.5 and 0.7 Hz). In accordance with the molecular structure of **5b**, the ^{1}H and ^{13}C NMR spectra have only one signal of aromatic CH group at rather high field (δ_H 6.45 ppm, δ_C 107.8 ppm) due to strong shielding effects of substituents. The NOE measurements also show that **5a** and **5b** have the same relative configurations (Fig. 3).

2.4. Tandem [3+2]-cycloaddition/intermolecular electrophilic aromatic substitution of donor–acceptor cyclopropane with furans

The formation of tetracyclic products **5** is a result of double bond activation in the monoadduct **3** by $SnCl_4$, which leads to intramolecular attack onto the nucleophilic aryl group. If the nucleophilicity of the aryl group in the starting cyclopropane **1** is small enough for participation in this process, the corresponding intermolecular process can be realized. Cyclopropane **1d** failed to give any cyclization product of type **5**. So instead, we studied its reaction with an excess of 2,5-dimethylfuran (**2c**). We found that in the presence of $SnCl_4$, this interaction led to compound **6**, which is the product of addition of the second furan molecule to the double bond of the intermediate monoadduct of [3+2]-cycloaddition **3c**. Compound **6** was isolated as a mixture of two diastereomers in a 4:1 ratio (Scheme 7).

In the ^{1}H NMR spectrum of the major diastereomer of **6** two AMX systems are present at δ_H 1.60, 2.60, and 3.37 ppm (^2J 12.9 Hz, ^3J 9.4 and 8.6 Hz) and δ_H 2.34, 2.63, and 2.90 ppm (^2J 5.6 Hz, ^3J 14.4 and 12.9 Hz). These signals correspond to two CH_2–CH fragments of saturated cyclopenta[*b*]furan moiety. Hydrogen atoms of the methyl groups connected to tetrahydrofuran ring give resonance signals at higher field (δ_H 1.21 and 1.44 ppm) in comparison with methyl groups at C(2) and C(5) carbon atoms of dimethylfuran (δ_H 2.11 and 2.19 ppm, respectively). Oppositely, in the ^{13}C NMR spectrum, the CH_3 groups of the furan moiety are more shielded (δ_C 13.2 and 13.4 ppm) versus those of saturated cycle (δ_C 25.7 and 30.1 ppm). Further, the singlet at δ_H 5.73 ppm for the isolated proton of the CH group with δ_C 106.1 ppm is a quite characteristic pattern corresponding to the trisubstituted furan ring. The structure of product **6** is in agreement with the formation of [3+2] cycloadduct **3c** during reaction between **1c** and **2c** in a ratio of 1:1. Moreover, the isolation of **6** as a mixture of two isomers is in full accordance with the formation of single isomer of **3c** in the cycloaddition process.

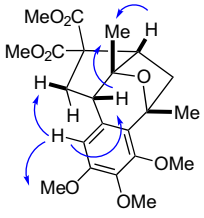
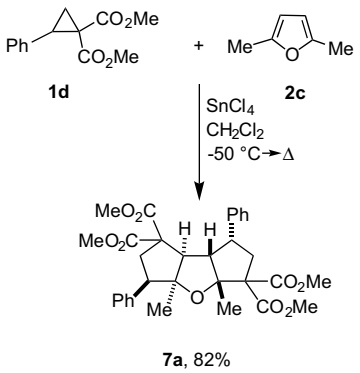


Figure 3. Some NOE responses for compound **5b**.

2.5. Tandem [3+2]/[3+2]-cycloadditions of donor–acceptor cyclopropane with furans

In the reactions discussed in Sections 2.3 and 2.4 the intermediate monoadducts **3** were further transformed with the participation of the double bond of the enol ether moiety formed. However, this double bond can also react with another donor–acceptor cyclopropane similarly to many other examples of this cycloaddition.[4] Therefore, we supposed that it is possible to perform reaction of furans with 2 equiv of cyclopropanes with formation of products of double cycloaddition. Indeed, we found that moderate heating of furan **2c** with an excess of cyclopropane **1d** afforded bis-adduct **7a** as a single isomer in high yield (Scheme 8).

The two singlets of the methyl groups in the upfield region of ^{1}H NMR spectrum of **7a** (δ_H 1.30 and 1.85 ppm) showed that these groups connect to the C(2) and C(5) atoms of tetrahydrofuran moiety. The spectrum of the cyclic skeleton protons reveals superposition of signals of C^2H_2–C^3H and C^6H_2–C^7H–$C^{7a}H$–$C^{7b}H$



7a, 82%

Scheme 8.

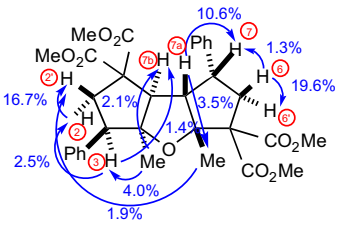


Figure 4. Some NOE data for compound **7a**.

fragments (see Experimental part and Fig. 4). Weak long-range spin–spin coupling exists between H^{2b} and H^{7b} protons of two fragments (^4J 1.0 Hz). Note that the vicinal spin–spin coupling constant for protons H^{7a} and H^{7b}, which belong to the tetrahydrofuran ring has also a rather small value (^3J 1.8 Hz). Stereochemical assignment was established using the results of NOE experiments, which are represented in Figure 4.

The determined structure of compound **7a** was unambiguously proven by single-crystal X-ray analysis (Fig. 5). The central tetrahydrofuran ring of **7a** is almost flat compared to the cyclopentane rings, which have the typical envelope conformations where C(6) and C(2) atoms (numeration on Fig. 5) are out of the ring planes and directed to the central five-membered ring. It is interesting that C(4a)–C(5) bond in **7a** is rather long (1.58 Å). Another bond between carbon atom bearing two methoxycarbonyl groups and tetrahydrofuran ring [C(1)–C(7b)] is also slightly elongated (bond length is 1.56 Å).

The formation of asymmetric product **7a** in this reaction is in accordance with the different polarization of C=C bonds in the starting furan **2c** and in vinyl ether moiety of the intermediate monoadduct **3c**. The electrophilic center of activated cyclopropane **1d** attacks the α-carbon atom of furan **2c** but the β-carbon atom of vinyl ether **3c**.

The analogous compound **7b** was formed in a high yield in the reaction of furan **2c** with dimethyl 2-(2-thienyl)cyclopropane-1,1-dicarboxylate (**1b**) in the presence of 10 mol % of $Yb(OTf)_3$ (Scheme 9). However, this product was isolated as a mixture of two diastereomers in a ratio of 2:1. A comparison of the spectral data for compounds **7a** and **7b** revealed that chemical shifts and coupling constants, which correspond to tricyclic framework of major isomer of **7b** have the similar values with those for **7a**. Thus, we

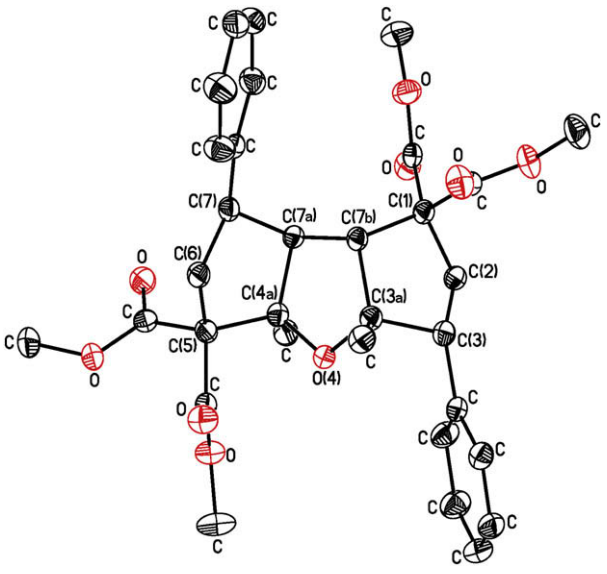
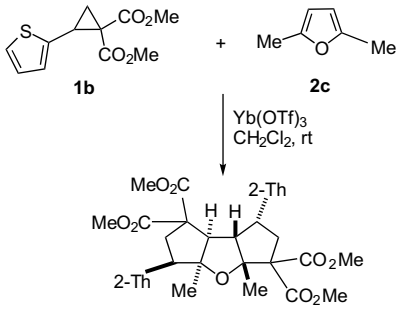


Figure 5. Single-crystal X-ray structure of **7a**.



7b, 94%, d.r. 66:34

Scheme 9.

concluded that the major isomer of **7b** has the same relative configuration as **7a**.

3. Conclusions

Contrary to our previous results concerning the [4+3]-cycloaddition of donor–acceptor cyclopropanes to 1,3-diphenylisobenzofuran,[15] 2,5-dimethylfuran reacts with these cyclopropanes through [3+2]-cycloaddition to the C(2)–C(3) bond. Due to the presence of the reactive vinyl ether moiety, under more harsh reaction conditions these cycloadducts can be further transformed into different products depending on the ratio of reagents and the nature of substituents in the starting cyclopropanes. When the cyclopropane/furan ratio was 2:1, products of double [3+2]-cycloaddition were isolated in good yields independent of the nature of the aryl group. Oppositely, when an excess of furan was used, the initial product of the reaction between 2,5-dimethylfuran and 2-phenylcyclopropane-1,1-diester interacted with the second furan molecule by Lewis acid-induced Friedel–Crafts alkylation. However, if the cyclopropane contained more nucleophilic aryl groups, the products of intramolecular alkylation were formed. 2,5-Diphenylfuran failed to give any cycloaddition product in the reactions with 2-phenylcyclopropane-1,1-diesters but yielded the product of Friedel–Crafts alkylation on the β-carbon atom. Reactions of donor–acceptor cyclopropanes with 3- and 3,4-substituted furans as well as with furans containing electron-withdrawing groups are under investigation now.

4. Experimental

4.1. General remarks

NMR spectra were recorded on a 'Bruker Avance-400' (400 MHz for ^1H and 100 MHz for ^{13}C NMR) spectrometer at room temperature; the chemical shifts δ were measured in parts per million with respect to the solvent ($CDCl_3$, ^1H: δ_H=7.26 ppm, ^{13}C: δ_C=77.13 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet. Coupling constants (J) are in hertz. The structures of all compounds were elucidated with the aid of 1D NMR (^1H, ^{13}C, DEPT-90 and 135) and 2D NMR (^1H, ^1H COSY and ^{13}C, ^1H XHCORR) spectroscopy. MS were recorded on the MALDI-TOF mass-spectrometer 'Bruker Ultraflex' in positive mode, dithranol was used as a matrix. Melting points (mp): Electrothermal 9100 capillary melting point apparatus, the values are uncorrected. Column chromatography was performed on silica gel 60 (230–400 mesh, Merck). $TiCl_4$, $SnCl_4$, $Yb(OTf)_3$, and all studied furans are available commercially. 2-Aryl-1,1-cyclopropane diesters **1** were prepared by published

procedures.[27] All the reactions were carried out using freshly distilled and dry solvents.

4.2. General procedure for $Yb(OTf)_3$ catalyzed reactions of donor–acceptor cyclopropanes with furans

The solution of cyclopropane **1**, furan **2**, and $Yb(OTf)_3$ (5 mol % to **1**) in CH_2Cl_2 or PhCl was stirred under an Ar atmosphere in the presence of 4 Å molecular sieves under the conditions specified. The reaction progress was monitored by TLC and ^1H NMR. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

4.3. General procedure for $SnCl_4$-catalyzed reactions of donor–acceptor cyclopropanes with furans

A solution of $SnCl_4$ in CH_2Cl_2 was added dropwise to a vigorously stirred solution of cyclopropane **1** and furan **2** in CH_2Cl_2 at −50→−60 °C under an Ar atmosphere. The reaction mixture was allowed to warm to room temperature, stirred under conditions specified, and poured into 10 mL of saturated aqueous $NaHCO_3$. After extraction with CH_2Cl_2 (3×10 mL), combined organic layers were washed with Trilon B solution (3×10 mL) then with water (2×10 mL), dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel.

4.4. [3+2]-Cycloaddition of donor–acceptor cyclopropanes to 2,5-dimethylfuran

*4.4.1. Diethyl (3aSR,6RS,6aSR)-2,6a-Dimethyl-6-(thiophen-2-yl)-6,6a-dihydro-3aH-cyclopenta[b]-furan-4,4(5H)-dicarboxylate (**3a**)*

Compound **1a** (200 mg, 0.75 mmol), **2c** (200 mg, 2.1 mmol), and $Yb(OTf)_3$ (24 mg, 0.037 mmol) in 8 mL of CH_2Cl_2 was stirred at room temperature for 24 h. Petroleum ether–chloroform (1:1) mixture was used as an eluent. Compound **3a** was isolated in 76% yield (210 mg) as crude compound, which can not be fully purified due to partial decomposition during column chromatography; slight yellow oil; R_f 0.26 ($CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.27 (t, ^3J=7.2 Hz, 3H, CH_3), 1.29 (t, ^3J=7.2 Hz, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 2.37 (dd, ^2J=13.1 Hz, ^3J=5.3 Hz, 1H, CH_2), 2.75 (dd, ^2J=13.1 Hz, ^3J=14.4 Hz, 1H, CH_2), 3.29 (dd, ^3J=5.3, 14.4 Hz, 1H, CH), 3.83 (br s, 1H, CH), 3.61–3.73 (m, 4H, 2×CH_2O), 4.33 (br s, 1H, CH=), 6.91 (br d, ^3J=3.4 Hz, 1H, Th), 6.98 (dd, ^3J=3.4, 5.0 Hz, 1H, Th), 7.23 (br d, ^3J=5.0 Hz, 1H, Th); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.8 (CH_3), 14.1 (CH_3), 14.2 (CH_3), 23.6 (CH_3), 38.6 (CH_2), 48.9 ($^1J_{CH}$=121 Hz, *C*HTh), 58.4 ($^1J_{CH}$=147 Hz, CH), 61.2 (CH_2O), 61.7 (CH_2O), 63.9 (C), 93.0 ($^1J_{CH}$=173 Hz, CH=), 93.3 (C), 124.6 (CH, Th), 125.8 (CH, Th), 126.2 (CH, Th), 140.7 (C, Th), 157.2 (C), 169.3 (*C*O_2Et), 171.7 (*C*O_2Et). HRMS MALDI-TOF: m/z=364.1338 $[M]^+$ (364.1344 calcd for $C_{19}H_{24}O_5S$).

*4.4.2. (3aSR,6RS,6aSR)-Dimethyl 2,6a-dimethyl-6-(thiophen-2-yl)-6,6a-dihydro-3aH-cyclopenta[b]-furan-4,4(5H)-dicarboxylate (**3b**)*

Compound **1b** (200 mg, 0.83 mmol), **2c** (200 mg, 2.1 mmol), and $Yb(OTf)_3$ (27 mg, 0.042 mmol) in 8 mL of CH_2Cl_2 was stirred at room temperature for 24 h. Petroleum ether–chloroform (1:1) mixture was used as an eluent. Yield of crude **3b** 150 mg (53%) as a 9:1 mixture of diastereomers; slight yellow oil; R_f 0.26 ($CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ for major isomer 1.45 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 2.99 (dd, ^2J=14.0 Hz, ^3J=5.7 Hz, 1H, CH_2), 3.30 (dd, ^2J=14.0 Hz, ^3J=5.3 Hz, 1H, CH_2), 3.53 (m, 1H, CH), 3.63 (m, 1H, CH), 3.72 (s, 3H, CH_3O), 3.74 (s, 3H, CH_3O), 4.34 (br s, 1H, CH=), 6.84 (br d, ^3J=3.4 Hz, 1H, Th), 6.94 (dd, ^3J=3.4, 5.0 Hz, 1H, Th), 7.18 (br d, ^3J=5.0 Hz, 1H, Th); ^{13}C NMR ($CDCl_3$, 100 MHz): δ for major isomer 13.7 (CH_3), 23.6 (CH_3), 38.7 (CH_2), 48.9 (*C*HTh), 52.8 (CH_3O), 53.0 (CH_3O), 58.6 (CH), 63.8 (C), 93.0 (CH=), 93.9 (C), 124.6 (CH, Th), 125.9 (CH, Th), 126.2 (CH, Th), 141.2 (C, Th), 157.3 (C), 169.5 (*C*O_2Me), 172.0 (*C*O_2Me). MS MALDI-TOF: m/z=336 $[M]^+$. HRMS MALDI-TOF: m/z=336.1024 $[M]^+$ (336.1031 calcd for $C_{17}H_{20}O_5S$).

*4.4.3. (3aSR,6SR,6aRS)-Diethyl 2,6a-dimethyl-6-phenyl-6,6a-dihydro-3aH-cyclopenta[b]-furan-4,4(5H)-dicarboxylate (**3c**)*

Compound **1c** (200 mg, 0.76 mmol), **2c** (200 mg, 2.1 mmol), and $Yb(OTf)_3$ (24 mg, 0.038 mmol) in 10 mL of PhCl was stirred under reflux for 6 h. Petroleum ether–chloroform (1:1) mixture was used as an eluent. Yield of crude **3c** 160 mg (60%); slight yellow oil; R_f 0.34 ($CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.27 (m, 6H, 2×CH_3), 1.52 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 2.20–2.40 (m, 2H, CH_2), 2.71–2.75 (m, 1H, CH), 3.58–3.62 (m, 1H, CH), 4.19–4.38 (m, 5H, CH=, 2×OCH_2), 7.25–7.42 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.8 (CH_3), 14.1 (2×CH_3), 23.8 (CH_3), 38.4 (CH_2), 53.1 (CH), 58.5 (CH), 61.1 (CH_2O), 61.6 (CH_2O), 63.8 (C), 93.1 (CH), 94.0 (C), 126.5 (CH, Ph), 127.9 (2×CH, Ph), 128.6 (2×CH, Ph), 137.5 (C), 157.1 (C), 169.3 (*C*O_2Et), 171.7 (*C*O_2Et). HRMS MALDI-TOF: m/z=358.1772 $[M]^+$ (358.1780 calcd for $C_{21}H_{26}O_5$).

4.5. Friedel–Crafts reaction of 2,5-diphenylfuran (3d) with donor–acceptor cyclopropanes

*4.5.1. Dimethyl 2-(2-(2,5-diphenylfuran-3-yl)-2-phenylethyl)malonate (**4**)*

A solution of $SnCl_4$ (0.12 mL, 1.0 mmol) in 1 mL of CH_2Cl_2 was added dropwise to a solution of **1d** (200 mg, 0.85 mmol) and **2b** (190 mg, 0.86 mmol) in 8 mL of CH_2Cl_2 under specified conditions and stirred at room temperature for 23 h. Petroleum ether–chloroform (4:1) mixture was used as an eluent. Yield of **4** 250 mg (65%); colorless solid; mp 107.8–108.0 °C; R_f 0.41 ($CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.60 (ddd, ^2J=13.9 Hz, ^3J=6.1, 9.9 Hz, 1H, CH_2), 2.76 (ddd, ^2J=13.9 Hz, ^3J=6.3, 9.1 Hz, 1H, CH_2), 3.43 (dd, ^3J=6.1, 9.1 Hz, 1H, CH), 3.47 (s, 3H, CH_3O), 3.72 (s, 3H, CH_3O), 4.32 (dd, ^3J=6.3, 9.9 Hz, 1H, CH), 6.89 (s, 1H, CH), 7.28–7.48 (m, 11H, Ph), 7.64–7.67 (m, 2H, Ph), 7.78–7.82 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.1 (CH_2), 39.4 (CH), 49.9 (CH), 52.3 (CH_3O), 52.6 (CH_3O), 106.6 (CH, Fu), 123.9 (2×CH, Ph), 124.0 (C), 126.5 (2×CH, Ph), 126.8 (CH, Ph), 127.6 (2×CH, Ph), 127.7 (2×CH, Ph), 128.6 (2×CH, Ph), 128.8 (2×CH, Ph), 128.9 (2×CH, Ph), 130.5 (C), 131.0 (C), 143.1 (C), 149.7 (C), 153.1 (C), 169.7 (*C*O_2Me), 169.8 (*C*O_2Me). Anal. Calcd for $C_{29}H_{26}O_5$: C, 76.63; H, 5.77. Found: C, 76.80; H, 5.64.

4.6. Tandem [3+2]-cycloaddition/intramolecular electrophilic aromatic substitution of donor–acceptor cyclopropanes with furans

*4.6.1. Dimethyl (4RS,5aSR,6SR,8aRS)-4,5a-dimethyl-5a,6,8,8a-tetrahydro-4,6-methanocyclopenta[b]thieno[2,3-d]pyran-7,7(4H)-dicarboxylate (**5a**)*

A solution of $SnCl_4$ (0.20 mL, 1.8 mmol) in 1 mL of CH_2Cl_2 was added dropwise to a solution of **1b** (200 mg, 0.83 mmol) and **2c** (200 mg, 2.1 mmol) in 8 mL of CH_2Cl_2 under specified conditions and stirred at room temperature for 23 h. Petroleum ether–chloroform (2:1) mixture was used as an eluent. Yield of **5a** 200 mg (71%); colorless solid; mp 103.0–103.2 °C; R_f 0.35 ($CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.59 (s, 3H, CH_3), 1.61 (dd, ^2J=13.1 Hz, ^3J=2.9 Hz, 1H, C(9)H_2), 1.66 (s, 3H, CH_3), 2.24 (dd, ^2J=13.1 Hz, ^3J=12.1 Hz, 1H, C(9)H_2), 2.29 (dd, ^2J=14.4 Hz, ^3J=7.0 Hz, 1H, C(8)H_2), 2.93 (br d, ^2J=14.4 Hz, 1H, C(8)H_2), 3.37 (dd, ^3J=2.9, 12.1 Hz, 1H, C(6)H), 3.39 (br d, ^3J=7.0 Hz, 1H, C(8a)H), 3.47 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 6.71 (d, ^3J=5.1 Hz, 1H, Th), 7.13 (d, ^3J=5.1 Hz, 1H, Th); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.7 (CH_3), 23.5 (CH_3), 41.2 (C(8)H_2), 46.3 (C(6)H), 48.0 (C(9)H_2), 52.3 (C(8a)H), 53.0 (2×CH_3O), 61.7 (C), 79.7 (C), 91.2 (C), 121.5 (CH, Th), 124.1 (CH, Th), 137.6 (C, Th), 144.4 (C, Th),

170.4 (CO_2Me), 173.1 (CO_2Me). Anal. Calcd for $C_{17}H_{20}O_5S$: C, 60.70; H, 5.99. Found: C, 60.61; H, 6.05.

*4.6.2. Dimethyl (3RS,3aSR,5SR,9bRS)-6,7,8-trimethoxy-3a,5-dimethyl-3,3a,5,9b-tetrahydro-3,5-methanocyclopenta[c]-isochromene-2,2(1H)-dicarboxylate (**5b**)*

A solution of $SnCl_4$ (0.23 mL, 2.0 mmol) in 1 mL of CH_2Cl_2 was added dropwise to solution of **1e** (320 mg, 1.0 mmol) and **2c** (100 mg, 1.0 mmol) in 10 mL of CH_2Cl_2 under the specified conditions and stirred at room temperature for 18 h. Petroleum ether–chloroform (2:1) mixture was used as an eluent. Yield of **5b** 320 mg (76%); colorless solid; mp 98.0–99.0 °C; R_f 0.10 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.53 (s, 3H, CH_3), 1.66 (dd, ^2J=13.4 Hz, ^3J=3.0 Hz, 1H, C(10)H$_2$), 1.82 (s, 3H, CH_3), 2.27 (dd, ^2J=13.4 Hz, ^3J=12.1 Hz, 1H, C(10)H$_2$), 2.39 (dd, ^2J=14.4 Hz, ^3J=7.5 Hz, 1H, C(1)H$_2$); 2.78 (dd, ^2J=14.4 Hz, ^3J=0.7 Hz, 1H, C(1)H$_2$), 3.21 (dd, ^3J=0.7, 7.5 Hz, 1H, C(9b)H), 3.29 (dd, ^3J=3.0, 12.1 Hz, 1H, C(3)H), 3.71 (s, 3H, CH_3O), 3.72 (s, 3H, CH_3O), 3.74 (s, 6H, 2×CH_3O), 3.80 (s, 3H, CH_3O), 6.45 (s, 1H, CH, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.8 ($^1J_{CH}$=127 Hz, CH_3), 25.2 ($^1J_{CH}$=127 Hz, CH_3), 41.3 ($^1J_{CH}$=136 Hz, C(1)H$_2$), 47.3 ($^1J_{CH}$=132 Hz, C(10)H$_2$), 48.7 ($^1J_{CH}$=134 Hz, C(9b)H), 52.0 ($^1J_{CH}$=148 Hz, CH_3O), 52.8 ($^1J_{CH}$=148 Hz, CH_3O), 53.3 ($^1J_{CH}$=141 Hz, C(3)H), 55.8 ($^1J_{CH}$=144 Hz, CH_3O), 60.5 ($^1J_{CH}$=144 Hz, CH_3O), 60.6 ($^1J_{CH}$=144 Hz, CH_3O), 61.3 (C), 80.3 (C), 89.9 (C), 107.8 ($^1J_{CH}$=153 Hz, CH, Ar), 129.5 (C, Ar), 133.7 (C, Ar), 140.6 (C, Ar), 149.1 (C, Ar), 152.6 (C, Ar), 170.3 (CO_2Me), 172.8 (CO_2Me). Anal. Calcd for $C_{22}H_{28}O_8$: C, 62.85; H, 6.71. Found: C, 62.65; H, 6.73.

4.7. Tandem [3+2]-cycloaddition/intermolecular electrophilic aromatic substitution of donor–acceptor cyclopropanes with furans

*4.7.1. Dimethyl 2-(2,5-dimethyl-3-furyl)-2,6a-dimetyl-6-phenylhexahydro-4H-cyclopenta[b]furan-4,4-dicarboxylate (**6**)*

A solution of $SnCl_4$ (0.12 mL, 1.0 mmol) in 1 mL of CH_2Cl_2 was added dropwise to solution of **1d** (200 mg, 0.85 mmol) and **2c** (240 mg, 2.5 mmol) in 10 mL of CH_2Cl_2 under the specified conditions and stirred under reflux for 23 h. Petroleum ether–chloroform (4:1) mixture was used as an eluent. Yield **6** 250 mg (69%) as a mixture of isomers (dr 4:1); colorless oil; R_f 0.50 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ for major isomer 1.21 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.60 (dd, ^2J=12.9 Hz, ^3J=8.6 Hz, 1H, CH_2), 2.11 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.34 (dd, ^2J=12.9 Hz, ^3J=5.6 Hz, 1H, CH_2), 2.60 (dd, ^2J=12.9 Hz, ^3J=9.4 Hz, 1H, CH_2), 2.63 (dd, ^3J=5.6, 14.4 Hz, 1H, CH), 2.90 (dd, ^2J=12.9 Hz, ^3J=14.4 Hz, 1H, CH_2), 3.37 (dd, ^3J=8.6, 9.4 Hz, 1H, CH), 3.76 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 5.73 (s, 1H, CH, Fu), 7.22–7.32 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz): δ for major isomer 13.2 (CH_3), 13.4 (CH_3), 25.7 (CH_3), 30.1 (CH_3), 36.8 (CH_2), 42.7 (CH_2), 52.6 (CH_3O), 53.0 (CH), 53.4 (CH), 54.4 (CH_3O), 62.4 (C), 80.4 (C), 91.2 (C), 106.1 (CH), 126.5 (CH), 127.5 (2×CH), 129.7 (2×CH), 138.1 (C), 145.5 (C), 148.2 (2×C), 170.5 (CO_2Me), 172.2 (CO_2Me); δ for minor isomer 13.1 (CH_3), 13.4 (CH_3), 28.8 (CH_3), 29.8 (CH_3), 35.8 (CH_2), 43.3 (CH_2), 52.6 (CH_3O), 53.5 (CH), 53.7 (CH), 54.4 (CH_3O), 62.3 (C), 81.2 (C), 90.5 (C), 106.1 (CH), 126.3 (2×CH), 127.6 (CH), 129.6 (2×CH), 137.8 (C), 143.8 (C), 148.2 (2×C), 170.2 (CO_2Me), 172.0 (CO_2Me). Anal. Calcd for $C_{25}H_{30}O_6$: C, 70.40; H, 7.09. Found: C, 70.05; H, 6.68.

4.8. Tandem [3+2]/[3+2]-cycloadditions of donor–acceptor cyclopropanes with furans

*4.8.1. Tetramethyl (3RS,3aSR,4aRS,7RS,7aRS,7bRS)-3a,4a-dimethyl-3,7-diphenyloctahydrodicyclopenta[b,d]furan-1,1,5,5-tetracarboxylate (**7a**)*

A solution of $SnCl_4$ (0.28 mL, 2.4 mmol) in 1 mL of CH_2Cl_2 was added dropwise to a solution of **1d** (320 mg, 1.4 mmol) and **2c** (58 mg, 0.6 mmol) in 10 mL of CH_2Cl_2 under the specified conditions and stirred at room temperature for 2 h and under reflux for 3 h. Petroleum ether–chloroform (2:1) mixture was used as an eluent. Yield of **7a** 280 mg (82%); colorless solid; mp 145.0–147.0 °C; R_f 0.25 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.30 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.14 (dd, ^2J=13.6 Hz, ^3J=5.7 Hz, 1H, HC*H*(6)), 2.27 (ddd, ^2J=13.2 Hz, ^3J=5.7 Hz, ^4J=1.0 Hz, 1H, HC*H*(2)), 2.52 (dd, ^3J=14.7, 5.7 Hz, 1H, CH(3)), 2.61 (dd, ^3J=9.4, 1.8 Hz, 1H, CH(7a)), 2.94 (dd, ^2J=13.2 Hz, ^3J=14.7 Hz, 1H, HC*H*(2′)), 3.14 (dd, ^2J=13.6 Hz, ^3J=15.1 Hz, 1H, HC*H*(6′)), 3.18 (d, ^3J=1.8 Hz, 1H, CH(7b)), 3.43 (s, 3H, CH_3O), 3.61 (s, 3H, CH_3O), 3.69 (s, 3H, CH_3O), 3.75 (s, 3H, CH_3O), 3.95 (ddd, ^3J=5.7, 9.4, 15.1 Hz, 1H, CH(7)), 7.19–7.41 (m, 10H, CH, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.6 (J_{CH}=127 Hz, CH_3), 25.3 ($^1J_{CH}$=126 Hz, CH_3), 36.4 ($^1J_{CH}$=136 Hz, C(6)H$_2$), 37.8 $^1J_{CH}$=136 Hz, C(2)H$_2$), 44.6 ($^1J_{CH}$=128 Hz, C(7)H), 51.7 ($^1J_{CH}$=147 Hz, CH_3O), 52.4 ($^1J_{CH}$=148 Hz, CH_3O), 52.5 ($^1J_{CH}$=148 Hz, CH_3O), 52.9 ($^1J_{CH}$=148 Hz, CH_3O), 53.5 ($^1J_{CH}$=124 Hz, C(3)H), 56.7 ($^1J_{CH}$=141 Hz, C(7b)H), 59.4 ($^1J_{CH}$=135 Hz, C(7a)H), 63.7 (C), 68.4 (C), 93.9 (C), 97.4 (C), 123.5 (CH, Ph), 126.8 (CH, Ph), 127.3 (2×CH, Ph), 128.3 (2×CH, Ph), 128.4 (2×CH, Ph), 129.7 (2×CH, Ph), 137.7 (C), 139.3 (C), 169.3 (CO_2Me), 170.2 (CO_2Me), 171.7 (CO_2Me), 171.8 (CO_2Me). Anal. Calcd for $C_{32}H_{36}O_9$: C, 68.07; H, 6.43. Found: C, 68.18; H, 6.27.

*4.8.2. Tetramethyl 3a,4a-dimethyl-3,7-di-2-thienyloctahydro-dicyclopenta[b,d]furan-1,1,5,5-tetracarboxylate (**7b**)*

Compound **1b** (200 mg, 0.83 mmol), **2c** (40 mg, 0.4 mmol), and $Yb(OTf)_3$ (26 mg, 0.042 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature for 72 h. Petroleum ether–chloroform (4:1) mixture was used as an eluent. Yield of **7b** 220 mg (94%); mixture of two isomers (dr 2:1); colorless solid; mp 158.0–160.0 °C; R_f 0.33 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ for major isomer 1.36 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 2.28 (dd, ^2J=13.6 Hz, ^3J=5.9 Hz, 1H, CH_2), 2.36 (ddd, ^2J=13.2 Hz, ^3J=5.8 Hz, ^4J=1.0 Hz, 1H, CH_2), 2.52 (dd, ^3J=1.3, 9.4 Hz, 1H, CH), 2.80 (dd, ^2J=13.2 Hz, ^3J=14.4 Hz, 1H, CH_2), 2.93 (dd, ^3J=5.8, 14.4 Hz, 1H, CH), 3.07 (dd, ^2J=13.6 Hz, ^3J=14.7 Hz, 1H, CH_2), 3.34 (m, 1H, CH), 3.61 (s, 3H, CH_3O), 3.66 (s, 3H, CH_3O), 3.71 (s, 3H, CH_3O), 3.76 (s, 3H, CH_3O), 4.20 (ddd, ^3J=5.9, 9.4, 14.7 Hz 1H, CH), 6.84 (br d, ^3J=3.5 Hz, 1H, Th), 6.88–6.92 (m, 2H, Th), 7.02 (dd, ^3J=3.5, 5.1 Hz, 1H, Th), 7.17 (dd, ^3J=5.1 Hz, ^4J=0.8 Hz, 1H, Th), 7.23 (dd, ^3J=5.1 Hz, ^4J=0.8 Hz, 1H, Th); ^{13}C NMR ($CDCl_3$, 100 MHz): δ for major isomer 23.7 (CH_3), 25.2 (CH_3), 38.5 (CH_2), 40.5 (CH_2), 40.7 (CH), 49.2 (CH), 52.0 (CH_3O), 52.5 (CH_3O), 52.6 (CH_3O), 52.9 (CH_3O), 56.7 (CH), 59.8 (CH), 63.7 (C), 68.3 (C), 93.5 (C), 97.6 (C), 124.3 (CH, Th), 124.8 (CH, Th), 125.2 (CH, Th), 125.4 (CH, Th), 126.1 (CH, Th), 126.9 (CH, Th), 140.7 (C, Th), 142.8 (C, Th), 169.1 (CO_2Me), 169.9 (CO_2Me), 171.6 (CO_2Me), 171.8 (CO_2Me); δ for minor isomer 25.4 (CH_3), 26.6 (CH_3), 40.5 (CH_2), 42.4 (CH_2), 47.3 (CH), 49.8 (CH), 52.2 (OCH_3), 52.3 (OCH_3), 52.6 (OCH_3), 53.2 (OCH_3), 62.0 (CH), 65.2 (CH), 62.9 (C), 69.3 (C), 95.1 (C), 97.1 (C), 123.2 (CH, Th), 123.3 (CH, Th), 124.9 (CH, Th), 125.7 (CH, Th), 126.1 (CH, Th), 126.9 (CH, Th), 140.6 (C, Th), 147.8 (C, Th), 169.6 (CO_2Me), 169.7 (CO_2Me), 171.8 (CO_2Me), 172.2 (CO_2Me). Anal. Calcd for $C_{28}H_{32}O_9S_2$: C, 58.32; H, 5.59. Found: C, 58.33; H, 5.63.

4.9. X-ray structure determination of compound 7a

$C_{32}H_{36}O_9$, M=564.61, T=120(2) K, λ=0.71073 Å, triclinic, space group P-1, a=8.7876(6) Å, b=10.9970(8) Å, c=15.6556(11), α=85.000(5)°, β=87.032(5)°, γ=73.430(5)°, V=1443.99(18) Å^3, Z=2, d_{calcd}=1.299 Mg/m^3, μ=0.095 mm^{-1}, F(000)=600, crystal size=0.35×0.15×0.10 mm^3, reflections collected=15,989, independent reflections=7616 [R(int)=0.0250], refinement method=full-matrix least-squares on F^2, goodness-of-fit on F^2=1.001, final R indices [$I>2\sigma(I)$] R_1=0.0563, wR_2=0.1433, largest diff. peak and hole=0.369 and −0.235 e Å^{-3}.

Crystallographic data for compound **7a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 717759. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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