ChemPubSoc Europe

DOI: 10.1002/chem.201402286

CHEMISTRY
A European Journal
Full Paper

Chiral Furans

Gold(III) Chloride Catalyzed Synthesis of Chiral Substituted 3-Formyl Furans from Carbohydrates: Application in the Synthesis of 1,5-Dicarbonyl Derivatives and Furo[3,2-*c*]pyridine

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Abstract: This report describes a gold(III)-catalyzed efficient general route to densely substituted chiral 3-formyl furans under extremely mild conditions from suitably protected 5-(1-alkynyl)-2,3-dihydropyran-4-one using H_2O as a nucleophile. The reaction proceeds through the initial formation of an activated alkyne–gold(III) complex intermediate, followed by either a domino nucleophilic attack/*anti-endo-dig* cyclization, or the formation of a cyclic oxonium ion with subsequent attack by H_2O. To confirm the proposed mechanistic pathway, we employed MeOH as a nucleophile instead of H_2O to result in a substituted furo[3,2-*c*]pyran derivative, as anticipated. The similar furo[3,2-*c*]pyran skeleton with a hybrid carbohydrate–furan derivative has also been achieved through pyridinium dichromate (PDC) oxidation of a substituted chiral 3-formyl furan. The corresponding protected 5-(1-alkynyl)-2,3-dihydropyran-4-one can be synthesized from the monosaccharides (both hexoses and pentose) following oxidation, iodination, and Sonogashira coupling sequences. Furthermore, to demonstrate the potentiality of chiral 3-formyl furan derivatives, a $TiBr_4$-catalyzed reaction of these derivatives has been shown to offer efficient access to 1,5-dicarbonyl compounds, which on treatment with NH_4OAc in slightly acidic conditions afforded substituted furo[3,2-*c*]pyridine.

Introduction

Diversely substituted furans form an important structural motif prevalent in a biologically indispensable natural products, several pharmaceuticals, agrochemicals, as well as flavoring and aroma compounds.[1] They are also useful building blocks found in synthetic organic chemistry, materials chemistry, and self-healing macromolecular materials.[2] Moreover, the functionalized furan core has attracted tremendous attention for the design of numerous intermediates and as versatile starting materials for the synthesis of heterocyclic as well as acyclic compounds.[2a,3] Importantly, substituted chiral furans find widespread applications as versatile synthetic intermediates and are commonly found in many bioactive natural products (Figure 1).[2f,4]

Despite the development of numerous methods for the synthesis of highly substituted furans in the past few years, including transition-metal-mediated cyclization and cycloisomerization methods,[2–5] devising efficient access to substituted chiral furans from common precursors remains a challenging task. Among the many methods developed so far, the reaction of metalated furans with the carbonyl group or various other electrophiles,[6] a Grignard-type addition reaction of furan carbaldehyde with a variety of nucleophiles,[7] and Lewis acid catalyzed Friedel–Crafts-type reactions of various carbonyl compounds with furan derivatives are more common.[8] Chiral products may be accessed by the use of chiral pool precursors such as carbohydrates,[9] by enzymatic resolution of racemic mixtures,[10] or by kinetic resolution of starting materials.[11] In addition to the Garcia Gonzalez reaction,[12] addition/oxidative rearrangement of 3-furfurals with *N*-bromosuccinimide (NBS)[13] and tandem Suzuki–Miyaura coupling followed by acid-catalyzed cyclization[14] also offer new ways to obtain polyhydroxylated furans.

Furthermore, substituted 3-formyl furan derivatives have found widespread applications as synthetic intermediates for the synthesis of bioactive natural products.[15] However, there is a lack of general methods to synthesize them;[16] the few methods available mainly involve the metalation of furan rings

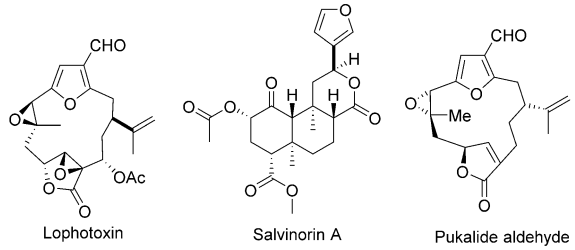

Figure 1. Examples of bioactive chiral furan-containing natural products.

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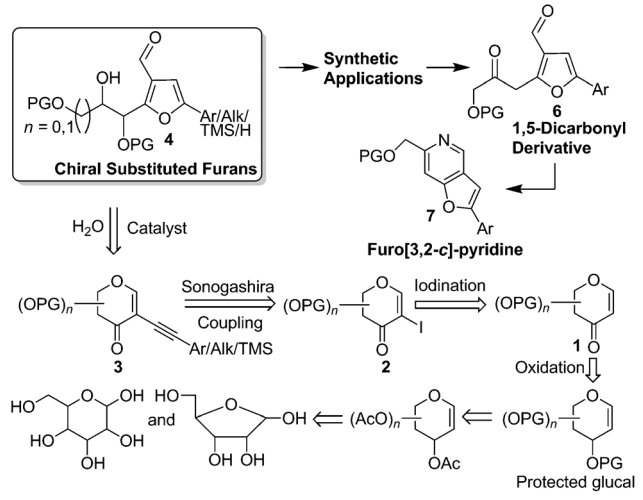
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201402286.

followed by formylation.[6b,17] This approach is somewhat restricted, because after metalation the addition of electrophiles to furan rings occurs preferentially at the C-2 and C-5 positions, and there is always a great deal of difficulty separating them from the unwanted regioisomers. The corresponding chiral products are also potentially important synthetic intermediates; however, their utility is very much underexplored owing to the lack of general methods to synthesize them.[13] As a consequence, establishing more efficient routes to highly substituted chiral 3-formyl furans from easily accessible starting materials continues to captivate synthetic chemists.

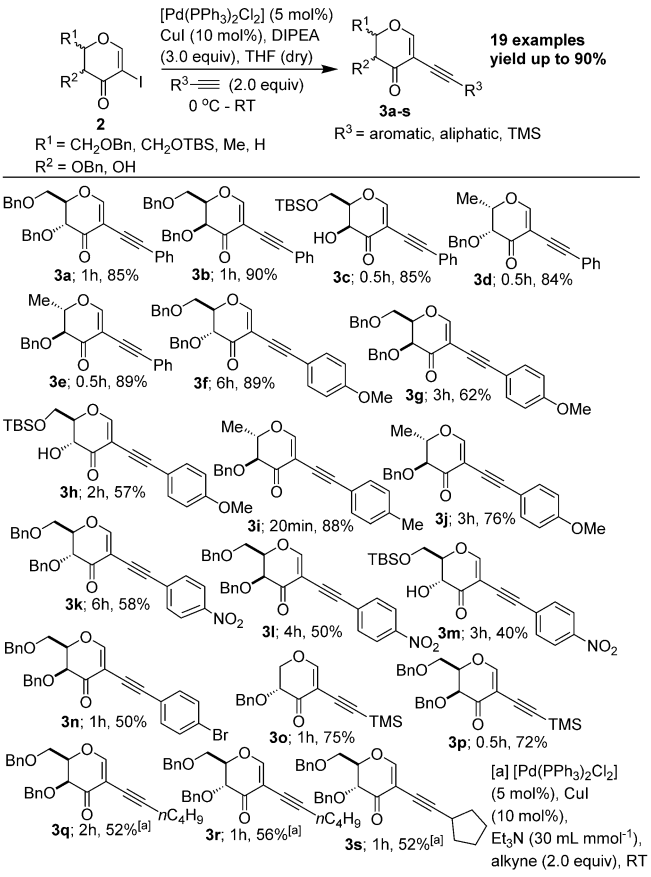
Herein, we report a gold(III)-catalyzed efficient route to highly substituted chiral 3-formyl furans under extremely mild conditions using H_2O as a nucleophile from a suitably protected 5-(1-alkynyl)-2,3-dihydropyran-4-one. The latter can be prepared from the corresponding appropriately functionalized monosaccharides or commercially available glycals in a few steps following oxidation, iodination, and Sonogashira coupling sequences. To confirm the proposed mechanistic pathway in the gold-catalyzed reaction, we employ MeOH as a nucleophile instead of H_2O to result in a substituted furo[3,2-*c*]pyran derivative. The synthesis of a similar skeleton with a hybrid carbohydrate–furan derivative was also carried out with pyridinium dichromate (PDC) oxidation of chiral 3-formyl furan. Furthermore, the substituted 3-formyl furans could then be smoothly subjected to a $TiBr_4$-catalyzed process to produce 1,5-dicarbonyl compounds, which on treatment with NH_4OAc under slightly acidic conditions afforded furo[3,2-*c*]pyridine.

Results and Discussion

A detailed retrosynthetic strategy towards substituted chiral furans from suitably substituted 2-iodoglycals as starting material is depicted in Scheme 1. 2-Iodoglycals (**2**) can easily be synthesized from the corresponding appropriately functionalized monosaccharides or commercially available glycals in a few steps by following a well-documented literature procedure (see the Supporting Information for details).[18] To obtain the carbohydrate congeners, we used different hexoses such as D-glucose, D-galactose, L-rhamnose, and L-fucose as well as the pentose sugar D-xylose.[18,19] Common protecting groups such as $-COCH_3$ (acetyl), $-CH_2Ph$ (benzyl), and –TBDMS (*tert*-butyldimethylsilyl) were used for hydroxyl-group protection in monosaccharides. 2-Alkynylated sugars (**3a**–**p**) were synthesized by the $[Pd(PPh_3)_2Cl_2]$/CuI-catalyzed standard Sonogashira coupling reaction (Scheme 2).[16c,20]



Scheme 1. Retrosynthetic analysis and synthetic applications of polyhydroxylated chiral substituted 3-formyl furans from monosaccharides (both hexoses and pentoses). PG = protecting group.



Scheme 2. Synthesis of 5-(1-alkynyl)-2,3-dihydropyran-4-ones from substituted 2-iodoglycals by Sonogashira coupling.

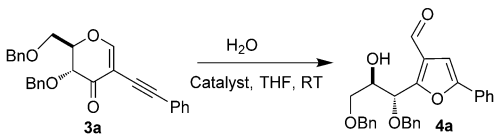
We used a variety of different aromatic, aliphatic, and TMS-protected commercially available terminal alkynes as coupling partners. It was found that the alkynes with electron-neutral (**3a**–**e**) or electron-donating substituents (**3f**–**j**) on the aromatic ring resulted in 2-alkynylated carbohydrates in good to excellent yields (57–90%; Scheme 2). However, the yields were moderate (40–58%; Scheme 2) when substrates with electron-withdrawing substituents (**3k**–**n**) on the aromatic ring were employed.

Importantly, trimethylsilyl acetylene was also found to be amenable to the reaction conditions that afforded the corresponding 2-alkynylated products (**3o**–**p**, Scheme 2) in greater than 70% yields. However, the coupling reaction with alkylace-

tylene did not produce the desired product by following the general procedure (Scheme 2). After several attempts, the coupling reaction with alkylacetylenes was successfully achieved with $[Pd(PPh_3)_2Cl_2]/CuI/Et_3N$ in moderate yields (**3q–s**, 52–56%; Scheme 2) by following the literature procedure.[20b,c]

During our initial investigations, we occasionally found that a solution of **3a** in EtOAc showed a marked propensity to undergo cyclization upon exposure to open air to result in **4a** in 50% yield after 48 h. A systematic study of this transformation (to shorten the time period and to achieve higher yields) showed that treating **3a** in THF with H_2O (0.2 mL) as a nucleophile at room temperature furnished **4a** in 55% yield (Table 1, entry 1). Interestingly, treatment with Brønsted acids such as methanesulfonic acid ($MeSO_3H$), HCl, and HBr failed to improve the yield (32–51%) even after 12–26 h (Table 1, entries 2–4). Other metal catalysts such as CuI, CuBr, $AgNO_3$, PPh_3AuCl, and AuCl also catalyzed this transformation, but resulted in moderate to lower yields (Table 1, entries 5–9). However, the more reactive cationic Au^I catalysts $Ph_3PAuNTf_2$ and $PPh_3AuCl + AgOTf$ (10 mol%) accelerated the transformations with excellent yields, and the reaction proceeded to completion within 10 to 15 min (Table 1, entries 10 and 13; 90%); whereas 1 mol% of $Ph_3PAuNTf_2$ also catalyzed this transformation, but it was necessary to conduct the reaction for a longer reaction time (Table 1, entry 11; 20 h, 89%). Inspired by these cationic Au^I catalyst results, we also explored the scope of this cyclization reaction with $Ph_3PAuCl + AgBF_4$. We observed that 10 mol% of this catalyst was not as effective as other gold(I) catalysts (Table 1, entry 12; 87%). Interestingly, a catalytic amount of $AuCl_3$ (0.5, 0.7, and 1 mol%) was also found to be equally effective (Table 1, entries 14–16; 90–91% yield), but once again longer reaction times were necessary. The use of 5 mol% $AuCl_3$ accelerated the transformation (Table 1, entry 17), and the reaction proceeded to completion within 10 min (Table 1). The yield was improved further with 10 mol% of $AuCl_3$ (Table 1, entry 18; 96% yield). $AuBr_3$ was also found to be almost equally effective (Table 1, entry 19). However, the use of other solvents (CH_3CN and CH_2Cl_2) failed to improve the yield (Table 1, entries 20 and 21). Thus, we concluded that the use of 10 mol% $AuCl_3$ in THF at room temperature constitutes the optimized reaction conditions.

Table 1. Reaction optimization for substituted chiral 3-formyl furans from 3-benzyloxy-2-benzyloxymethyl-5-phenylethynyl-2,3-dihydropyran-4-one.[a]



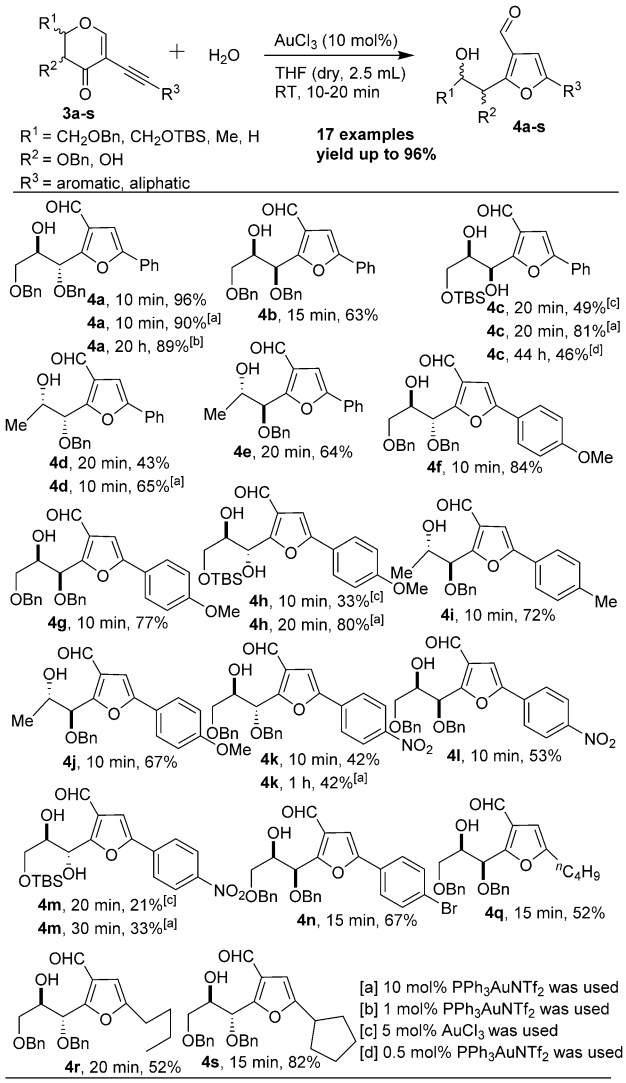
Entry	Catalyst	Mol [%]	*t*	Yield[b] [%]
1	no catalyst	–	48 h	55
2	$MeSO_3H$	20	12 h	32
3	HCl	10	24 h	51
4	HBr/AcOH	10	26 h	50
5	CuI	10	12 h	52
6[c]	CuBr	10	10 h	42
7	$AgNO_3$	10	12 h	73
8	PPh_3AuCl	10	12 h	65
9	AuCl	10	10 min	71
10	PPh_3AuNTf_2	10	10 min	90
11	PPh_3AuNTf_2	1	20 h	89
12	$PPh_3AuCl + AgBF_4$	10	15 h	87
13	$PPh_3AuCl + AgOTf$	10	15 min	90
14	$AuCl_3$	1	5 h	91
15	$AuCl_3$	0.7	18 h	90
16	$AuCl_3$	0.5	26 h	90
17	$AuCl_3$	5	10 min	92
18	$AuCl_3$	10	10 min	96
19	$AuBr_3$	10	10 min	90
20[d]	$AuCl_3$	10	10 min	42
21[e]	$AuCl_3$	10	10 min	77

[a] By stirring a mixture of **3a** (0.03 g, 0.071 mmol, 1.0 equiv) and catalyst (mol%) in dry THF (2 mL) under an Ar atmosphere at room temperature (20–25 °C), employing time as noted, followed by quenching with H_2O. [b] Yields are of isolated products. [c] Reaction was performed at 50 °C. [d] Reaction was carried out in acetonitrile. [e] Reaction was carried out in dichloromethane; Tf = trifluoromethane sulfonyl.

Having established the optimized protocol, we next investigated the substrate scope and generality for this transformation with H_2O as a nucleophile. Scheme 3 summarizes the results. In general, the reaction is tolerant to variation in substitution/protection at both the alkyne and the 4- and 6-positions of the hexopyranose ring. It is interesting to note that the electronic nature of the aromatic substituents on the alkyne moiety and the substitution/protection in carbohydrate congeners played a significant role in the yield of the reaction. With benzyl as a protecting group for the hexopyranose OH groups, substrates that contain electron-neutral (**4a,b,d,e**) or electron-donating (**4f,g,i,j**) substituents on the terminal alkyne resulted in chiral substituted 3-formyl furans in moderate to excellent yields (Scheme 3; 43–96%). However, substrates that contain electron-withdrawing substituents delivered the corresponding chiral furans (**4k,l,n**) only in moderate yields (Scheme 3; 42–67%). Furthermore, replacement of the aryl group with an alkyl group in the terminal alkyne was also found to be compatible under the reaction conditions and delivered the corresponding chiral furans (**4q–s**) in moderate to good yields (Scheme 3; 52–82%).

When we replaced the benzyl protection for OH groups with a TBDMS group, it lowered the yield dramatically (**4c,h,m**, Scheme 3; 21–49%). This might be attributed to the acid hydrolysis of the primary TBDMS group during the course of the reaction, which results from the mild acidic property of $AuCl_3$ in H_2O, as it is well-documented in the literature that a secondary benzylic hydroxyl group protected by TBDMS substitution is stable under gold catalysis.[21] However, the purported products remained to be isolated by silica-gel column chromatography. Thus, the possibility of competing intermolecular Reppe-type vinylation that results from the C-4 hydroxyl group of the hexopyranose ring might play an important role in the low yields with the TBDMS group.[21b,22a]

To achieve higher yields for the entries with lower than 50% yields (Scheme 3), the more reactive cationic gold(I) catalyst was examined.[22b,c] To our surprise, when we treated **3c** with $Ph_3PAuNTf_2$ (10 mol%)/THF/H_2O at room temperature, the corresponding **4c** was isolated in 81% yield, and the reaction pro-

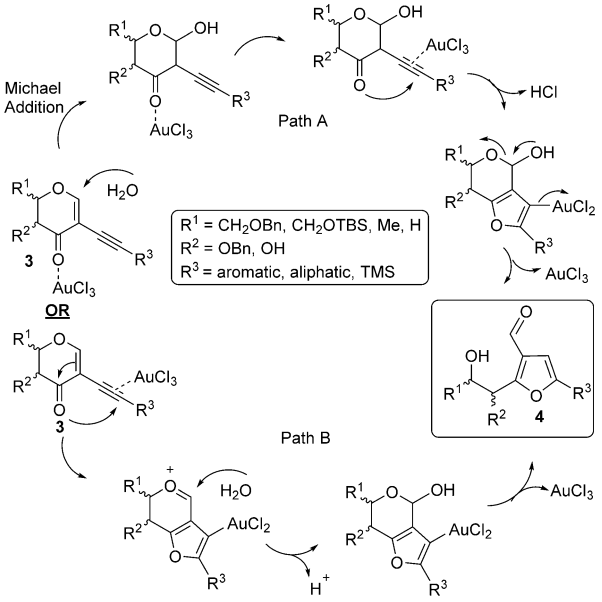


Scheme 3. $AuCl_3$- and $Ph_3PAuNTf_2$-catalyzed synthesis of substituted chiral 3-formyl furans from protected 5-(1-alkynyl)-2,3-dihydropyran-4-ones.

ceeded to completion within 20 min. However, we observed that use of 0.5 mol% $Ph_3PAuNTf_2$ was not effective to catalyze this transformation (46% yields), even after 44 h. Similarly, under these remarkably mild reaction conditions, the other 2-alknylated glycals (**3d** and **3h**) were converted to their respective furans (**4d** and **4h**) in moderate to good yields relative to the $AuCl_3$-catalyzed reaction (Scheme 3). Unfortunately, **3k** and **3m** did not produce the corresponding **4k** and **4m** in satisfactory yields under the same conditions, ostensibly owing to the presence of a strong electron-withdrawing (–NO_2) group on the aromatic ring (Scheme 3).

All the above reactions in Scheme 3 proceeded to full conversion to the product irrespective of the starting materials used, as monitored by TLC. For some of the entries, the drop in yield was due to the inherent reactivity of these systems as well as degradation of some of the products during column chromatography (with both silica gel and neutral or basic alumina). Otherwise, most of the substituted chiral furan aldehydes were stable, and we did not find any difficulty in purification or storing them for a long time. The structures of 3-formyl furan products were assigned by 2D NMR spectroscopy (see the Supporting Information).

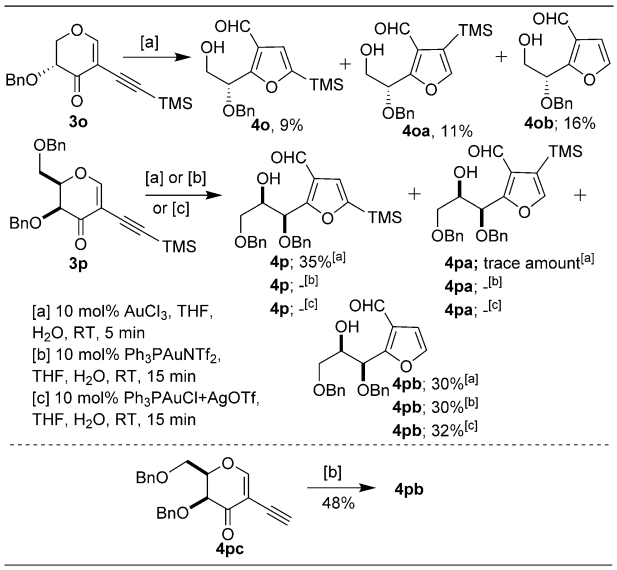
The probable mechanism of the reaction may be explained on the basis of that proposed for the chromones system.[23] After the initial formation of an activated alkyne–gold intermediate in the presence of $AuCl_3$, it would undergo either a domino nucleophilic attack by H_2O followed by *anti-endo-dig* cyclization (Scheme 4, path A) or the formation of a cyclic oxonium ion with subsequent attack by H_2O (Scheme 4, path B).



Scheme 4. A plausible mechanism for the formation of chiral substituted furan.

Inspired by the above findings, and to further exploit the potential of $AuCl_3$ as a catalyst for chiral substituted furan synthesis, the TMS-protected 2-alkynylated glycal derivatives (**3o** and **3p**) were treated under the standard reaction conditions.[23a] The results are shown in Scheme 5. To our delight, **3o** also underwent $AuCl_3$-catalyzed cyclization, and the corresponding furan derivative **4o** was obtained in only 9% yield. In addition, products **4oa** and **4ob** were also isolated in 11 and 16% yields, respectively (Scheme 5). Formation of **4ob** could be explained on the basis of removal of the TMS group either prior to or soon after cyclization under slightly acidic reaction conditions ($AuCl_3/H_2O$), whereas **4oa** resulted from a 1,2-Si migration from C-5 to the carbenoid center generated at C-4.

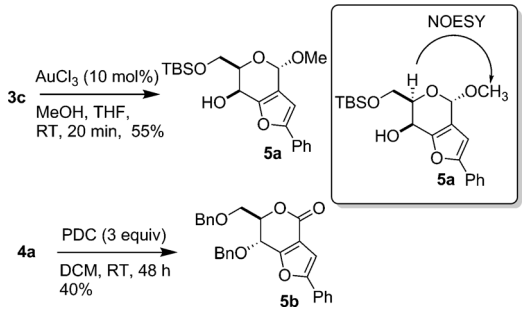
This unique 1,2-Si migration is particularly attractive as it allows the synthesis of hitherto inaccessible unsymmetrical 2,3-disubstituted C-4 silylated chiral furans.[16a] Further work is in progress to increase the yield of the desired product. A perusal of the literature also revealed that the 1,2-Si migration is kinetically favored over 1,2-H migration in the case of an Au–carbene intermediate.[2a,24] Switching to the galacto substrate **3p** also revealed the same situation (furan derivative **4p**, 35%,



Scheme 5. Scope for the gold-catalyzed synthesis of polyhydroxylated chiral furans from TMS-protected 2-alkynylated glycals.

and desilylated product **4pb**, 30%), except that the 1,2-Si migration product **4pa** was isolated only in trace amount (Scheme 5). To achieve higher yields for the unsymmetrical 2,3-disubstituted C-4 silylated chiral furans, the more reactive cationic gold(I) catalysts were examined. To our great disappointment, when we treated **3p** with 10 mol% $Ph_3PAuNTf_2$ and $PPh_3AuCl + AgOTf$, respectively, only the corresponding **4pb** (Scheme 5; 30–32%) was isolated, devoid of any **4p** and **4pa**. In addition, product **4pc**, which resulted from the desilylation of **3p** before cyclization, was also obtained in 34 and 18% yields, respectively (see the Supporting Information). Subsequently, we successfully performed the PPh_3AuNTf_2-catalyzed cyclization reaction of **4pc** to yield **4pb** (Scheme 5; 48%).

Interestingly, when MeOH was used as a nucleophile instead of H_2O in the $AuCl_3$-catalyzed cyclization, the corresponding substituted 4-methoxy-2-phenyl-6,7-dihydro-4*H*-furo[3,2-*c*]pyran **5a** was isolated from **3c** in moderate yield (Scheme 6; 55%),[25] which might be considered a hybrid carbohydrate–furan derivative, and also confirmed the mechanistic pathway described in Scheme 4. The stereochemistry of MeOH addition was assigned on the basis of NOESY experiments (see the Supporting Information). Furthermore, synthesis of substituted

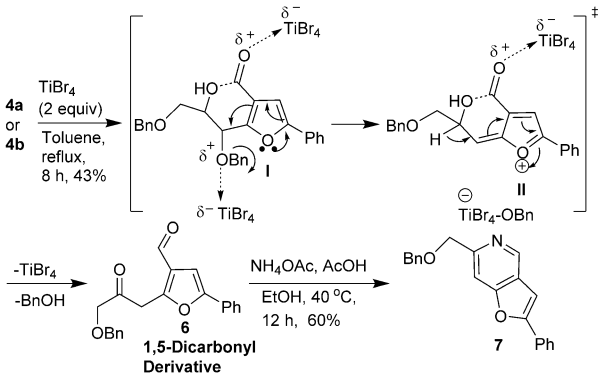


Scheme 6. Synthesis of substituted furo[3,2-*c*]pyran derivatives.

furo[3,2-*c*]pyran-4-one (**5b**) could be possible upon PDC oxidation of chiral substituted furan **4a** (Scheme 6; 40%).[26]

To demonstrate the potential utility of the highly substituted polyhydroxylated furan derivatives, we undertook a synthesis of 2-phenyl-substituted furo[3,2-*c*]pyridine. Substituted furo[3,2-*c*]pyridines form a key structural unit in drugs and biologically active natural products and exhibit a wide range of pharmaceutical activities.[27] Owing to their potential applications, a number of synthetically useful routes have been developed for their synthesis.[28] Furthermore, a literature survey revealed that treatment of α,β-unsaturated 1,5-dicarbonyl derivatives with NH_4OAc under mild acidic conditions delivered the corresponding substituted pyridine in good to excellent yield.[29]

We therefore became interested in the synthesis of the key intermediate α,β-unsaturated 1,5-dicarbonyl derivatives from our synthesized furan products. When we treated **4a** or **4b** with $TiBr_4$ (2 equiv) in toluene under reflux conditions, the corresponding 1,5-dicarbonyl derivative **6** was isolated in 43% yield (Scheme 7).



Scheme 7. Synthesis of substituted 2-phenylfuro[3,2-*c*]pyridine through 1,5-dicarbonyl derivative.

The mechanism of the reaction might be explained on the basis of generation of the oxonium cationic species (II) through $TiBr_4$-mediated formation of complex (I) with secondary –OBn group, as described in Scheme 7.[30] Rearomatization of the furanoid ring and subsequent tautomerization afforded α,β-unsaturated 1,5-dicarbonyl derivative **6**. With the α,β-unsaturated 1,5-dicarbonyl precursor in hand, we next turned our attention to the synthesis of substituted furo[3,2-*c*]pyridine following the literature procedure.[29] The treatment of **6** with EtOH/NH_4OAc under mild acidic conditions at 40 °C indeed delivered the corresponding 2-phenyl-substituted furo[3,2-*c*]pyridine **7** in 60% yield (Scheme 7).

Conclusion

In conclusion, we have successfully developed an efficient general route to densely functionalized chiral 3-formyl furans from suitably protected 5-(1-alkynyl)-2,3-dihydropyran-4-ones using catalytic $AuCl_3$ and water as a nucleophile. The reactions pro-

ceeded under mild conditions and resulted in moderate to excellent yields. The protected 5-(1-alkynyl)-2,3-dihydropyran-4-ones have been prepared from the corresponding monosaccharides following oxidation, iodination, and Sonogashira coupling sequences. The potential of this approach has been described by the preparation of a substituted furo[3,2-*c*]pyridine derivative by following two-step reaction sequences: a $TiBr_4$-catalyzed reaction of the 3-formyl furan derivatives resulted in the 1,5-dicarbonyl compound, which on treatment with NH_4OAc under slightly acidic conditions afforded substituted furo[3,2-*c*]pyridine. The scope and limitations of these new densely functionalized chiral furans towards synthesis of biologically active heterocycles are currently under study in our laboratory.

Experimental Section

General information

Melting points were determined in open-end capillary tubes and are uncorrected. TLC was performed on silica gel plates (Merck silica gel 60, f_{254}), and the spots were visualized with UV light (254 and 365 nm) or by charring the plate dipped in 5% H_2SO_4/MeOH or 5% H_2SO_4/vanillin/EtOH solution. ^1H (300 and 600 MHz) and ^{13}C (75 and 150 MHz) NMR spectra were recorded in $CDCl_3$ solvent using TMS as the internal standard. HRMS (*m/z*) was measured using EI and ESI techniques. Infrared (IR) spectra were recorded using Fourier transform infrared spectroscopy; only intense peaks are reported. Optical rotations were recorded at 589 nm.

A. General procedure for the synthesis of 3 a–p

Corresponding iodo compounds (**2 a**–**g**, 1.0 equiv) in dry THF (10 mL mmol^{-1}) were placed separately into a flame-dried, two-necked, round-bottomed flask equipped with a magnetic stir bar and rubber septa. $[PdCl_2(PPh_3)_2]$ (0.05 equiv), terminal alkyne (2.0 equiv), and CuI (0.1 equiv) were added into the flask at 0 °C and then *N*,*N*-diisopropylethylamine (DIPEA; 3.0 equiv) was added dropwise to the resulting mixtures and allowed to stir at room temperature for the required times. After completion of the reaction (TLC), saturated NH_4Cl solution was added, and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The crude residue was purified by using silica gel column chromatography (230–400 mesh particle size; eluent: ethyl acetate/*n*-hexane) to obtain **3 a**–**p**. These compounds should not be either stored in solution or exposed to open air for a long time, as they showed a marked propensity to undergo cyclization to result in mixtures of **3 a**–**p** and **4 a**–**p**. Owing to this tendency for cyclization, HRMS for some of these derivatives were not matched exactly.

B. General procedure for the synthesis of 3 q–s

Corresponding iodo compounds (**2 a**,**b**, 1.0 equiv) and the respective aliphatic terminal alkyne (2.0 equiv) were dissolved separately in NEt_3 (30 mL mmol^{-1}) in a flame-dried, two-necked, round-bottomed flask equipped with a magnetic stir bar and rubber septa. $[PdCl_2(PPh_3)_2]$ (5 mol%) and CuI (10 mol%) were subsequently added into the flask, and the resulting mixtures were allowed to stir at room temperature for the required times. After completion of the reaction (TLC), saturated NH_4Cl solution was added, and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The crude residue was purified by using silica gel column chromatography (230–400 mesh particle size; eluent: ethyl acetate/*n*-hexane) to obtain **3 q**–**s**.

3-Benzyloxy-2-benzyloxymethyl-5-phenylethynyl-2,3-dihydropyran-4-one (3 a)

Compound **2 a** (0.1 g, 0.222 mmol) was converted to **3 a** (0.08 g, 85%) by following general procedure A: eluent, EtOAc/*n*-hexane (8%); $[\alpha]_D^{20} = +147$ (*c* = 0.1 in MeOH); yellow gum. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.74$ (s, 1H), 7.47–7.50 (m, 2H), 7.30–7.38 (m, 13H), 5.08 (d, *J* = 11.1 Hz, 1H), 4.62 (d, *J* = 10.8 Hz, 1H), 4.51–4.64 (m, 3H), 4.29 (d, *J* = 10.8 Hz, 1H), 3.82 ppm (d, *J* = 3.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 190.3$, 165.3, 137.3, 137.1, 131.6 (2CH), 128.5 (4CH), 128.4 (2CH), 128.2 (3CH), 128.1, 127.9, 127.8 (2CH), 122.9, 103.7, 92.3, 81.6, 79.3, 74.5 (CH_2), 73.7, 73.6 (CH_2), 67.7 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max} = 2217$, 1694, 1604, 1588, 1247, 1149, 1102 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1573; found: 447.1943.

3-Benzyloxy-2-benzyloxymethyl-5-phenylethynyl-2,3-dihydropyran-4-one (3 b)

Compound **2 b** (0.1 g, 0.222 mmol) was converted to **3 b** (0.085 g, 90%) by following general procedure A: eluent, EtOAc/*n*-hexane (10%); $[\alpha]_D^{20} = +66$ (*c* = 0.1 in MeOH); yellow gum. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.79$ (s, 1H), 7.48–7.51 (m, 2H), 7.30–7.37 (m, 13H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.47–4.60 (m, 4H), 3.93 (dd, *J* = 6.9, 10.2 Hz, 1H), 3.82 (d, *J* = 2.1 Hz, 1H), 3.78 ppm (dd, *J* = 5.4, 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 186.4$, 165.7, 137.2, 136.6, 131.5 (2CH), 128.4 (2CH), 128.4 (2CH), 128.3 (2CH), 128.2, 128.2 (2CH), 128.0, 127.9, 127.7 (2CH), 122.9, 103.5, 92.4, 81.1, 79.8, 73.6 (CH_2), 73.4, 72.0 (CH_2), 67.2 ppm (CH_2); IR (neat): $\tilde{\nu}_{max} = 2218$, 1683, 1588, 1367, 1256 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1573; found: 447.3194.

2-(*tert*-Butyldimethylsilanyloxymethyl)-3-hydroxy-5-phenylethynyl-2,3-dihydropyran-4-one (3 c)

Compound **2 c** (0.1 g, 0.26 mmol) was converted to **3 c** (0.079 g, 85%) by following general procedure A: eluent, EtOAc/*n*-hexane (10%); $[\alpha]_D^{20} = +89$ (*c* = 0.1 in MeOH); brown gum. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.68$ (s, 1H), 7.44–7.46 (m, 2H), 7.29–7.31 (m, 3H), 4.73–4.76 (m, 1H), 4.61 (d, *J* = 6.6 Hz, 1H), 4.09 (dd, *J* = 3.6, 11.4 Hz, 1H), 3.95 (dd, *J* = 2.4, 11.4 Hz, 1H), 3.66 (br s, 1H), 0.87 (s, 9H), 0.05 ppm (d, *J* = 9.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 189.6, 165.9, 131.6 (2CH), 128.2 (2CH), 128.2, 123.1, 102.1, 92.0, 82.5, 79.2, 68.5, 61.3 (CH_2), 25.7 (3CH_3), 18.2, −5.7, −5.8 ppm; IR (KBr): $\tilde{\nu}_{max} = 2214$, 1691, 1602, 1588, 1253, 1140 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{26}O_4SiNa$ $[M+Na]^+$: 381.1498; found: 381.1515.

3-Benzyloxy-2-methyl-5-phenylethynyl-2,3-dihydropyran-4-one (3 d)

Compound **2 d** (0.1 g, 0.29 mmol) was converted to **3 d** (0.077 g, 84%) by following general procedure A: eluent, EtOAc/*n*-hexane (8%); $[\alpha]_D^{20} = -159$ (*c* = 0.1 in MeOH); brown solid; m.p. 90 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$ (s, 1H), 7.47–7.52 (m, 2H), 7.30–7.41 (m, 8H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.52–4.56 (m, 2H), 3.62 (d, *J* = 2.4 Hz, 1H), 1.50 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 187.5$, 166.3, 136.9, 131.6 (2CH), 128.4 (2CH), 128.4

(2CH), 128.2 (3CH), 128.1, 123.0, 102.9, 92.3, 80.0, 79.0, 75.8, 71.9 (CH_2), 15.0 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2220, 1674, 1581, 1255 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{18}O_3Na$ $[M+Na]^+$: 341.1154; found: 341.2915.

3-Benzyloxy-2-methyl-5-phenylethynyl-2,3-dihydropyran-4-one (3e)

Compound **2e** (0.1 g, 0.29 mmol) was converted to **3e** (0.082 g, 89%) by following general procedure A: eluent, EtOAc/*n*-hexane (5%); $[\alpha]_D^{20} = -186$ (*c* = 0.1 in MeOH); brown solid; m.p. 96 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.69 (s, 1H), 7.48–7.49 (m, 2H), 7.29–7.40 (m, 8H), 5.03 (d, *J* = 11.4 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.60 (dq, *J* = 6.6, 9.0 Hz, 1H), 3.78 (d, *J* = 9.0 Hz, 1H), 1.45 ppm (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.7, 165.2, 137.0, 131.6 (2CH), 128.5 (2CH), 128.5 (2CH), 128.2 (3CH), 128.1, 123.0, 103.4, 92.2, 79.5, 79.4, 77.9, 73.7 (CH_2), 17.0 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2217, 1688, 1604, 1588, 1252, 1143 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{18}O_3Na$ $[M+Na]^+$: 341.1154; found: 341.1152.

3-Benzyloxy-2-benzyloxymethyl-5-(4-methoxyphenylethynyl)-2,3-dihydropyran-4-one (3f)

Compound **2a** (0.1 g, 0.222 mmol) was converted to **3f** (0.089 g, 89%) by following general procedure A: eluent, EtOAc/*n*-hexane (15%); $[\alpha]_D^{20} = +146$ (*c* = 0.1 in MeOH); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.42–7.44 (m, 2H), 7.29–7.37 (m, 10H), 6.83–6.86 (m, 2H), 5.08 (d, *J* = 11.4 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.51–4.55 (m, 2H), 4.29 (d, *J* = 11.4 Hz, 1H), 3.82 (m, 2H), 3.82 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.5, 164.9, 159.6, 137.3, 137.2, 133.1 (2CH), 128.5 (4CH), 128.4 (2CH), 128.1, 128.0, 127.8 (2CH), 115.1, 113.9 (2CH), 104.0, 92.3, 81.5, 77.8, 74.5 (CH_2), 73.7, 73.6 (CH_2), 67.7 (CH_2), 55.3 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2183, 1607, 1509, 1248 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{27}O_5$ $[M+H]^+$: 455.1858; found: 455.1334.

3-Benzyloxy-2-benzyloxymethyl-5-(4-methoxyphenylethynyl)-2,3-dihydropyran-4-one (3g)

Compound **2b** (0.1 g, 0.222 mmol) was converted to **3g** (0.063 g, 62%) by following general procedure A: eluent, EtOAc/*n*-hexane (15%); $[\alpha]_D^{20} = +39$ (*c* = 0.1 in MeOH); brown solid; m.p. 84 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 7.43 (dt, *J* = 2.4, 9.6 Hz, 2H), 7.28–7.37 (m, 10H), 6.84 (dt, *J* = 2.4, 9.6 Hz, 2H), 4.74 (d, *J* = 11.4 Hz, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.53–4.55 (m, 1H), 4.49 (dd, *J* = 6.6, 12.0 Hz, 2H), 3.93 (dd, *J* = 6.6, 9.6 Hz, 1H), 3.81 (s, 3H), 3.80–3.81 (m, 1H), 3.77 ppm (dd, *J* = 6.0, 10.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.6, 165.4, 159.6, 137.3, 136.7, 133.1 (2CH), 128.5 (2CH), 128.4 (2CH), 128.4, 128.3, 128.1, 128.0, 127.8 (2CH), 115.0, 113.8 (2CH), 103.8, 92.4, 81.1, 78.3, 73.7 (CH_2), 73.5, 72.0 (CH_2), 67.3 (CH_2), 55.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2212, 1699, 1605, 1510, 1259, 1099 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{26}O_5Na$ $[M+Na]^+$: 477.1678; found: 477.2356.

2-(*tert*-Butyldimethylsilanyloxymethyl)-3-hydroxy-5-(4-methoxyphenylethynyl)-2,3-dihydropyran-4-one (3h)

Compound **2f** (0.1 g, 0.26 mmol) was converted to **3h** (0.058 g, 57%) by following general procedure A: eluent, EtOAc/*n*-hexane (15%); $[\alpha]_D^{20} = +171$ (*c* = 0.1 in MeOH); white solid; m.p. 104 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.46 (d, *J* = 12.9 Hz, 1H), 4.22 (d, *J* = 13.5 Hz, 1H), 4.13 (dd, *J* = 3.6, 12.0 Hz, 1H), 4.05 (dd, *J* = 3.6, 12.0 Hz, 1H), 3.83 (s, 3H), 3.56 (br s, 1H), 0.95 (s, 9H), 0.14 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.3, 167.0, 159.7, 133.1 (2CH), 114.8, 113.9 (2CH), 102.3, 92.2, 83.9, 77.2, 67.0, 61.6 (CH_2), 55.3, 25.8 ($3CH_3$), 18.4, −5.3, −5.4 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2207, 1677, 1607, 1512, 1251, 1240, 1140 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{21}H_{28}O_5Si$ $[M]^+$: 388.1706; found: 388.1704.

3-Benzyloxy-2-methyl-5-*p*-tolylethynyl-2,3-dihydropyran-4-one (3i)

Compound **2e** (0.1 g, 0.29 mmol) was converted to **3i** (0.085 g, 88%) by following general procedure A: eluent, EtOAc/*n*-hexane (5%); $[\alpha]_D^{20} = -164$ (*c* = 0.1 in MeOH); white solid; m.p. 54 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68 (s, 1H), 7.29–7.39 (m, 7H), 7.11 (d, *J* = 7.8 Hz, 2H), 5.03 (d, *J* = 11.4 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.58 (dd, *J* = 6.6, 9.3 Hz, 1H), 3.77 (d, *J* = 9.3 Hz, 1H), 2.34 (s, 3H), 1.45 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.8, 165.0, 138.3, 137.0, 131.4 (2CH), 129.0 (2CH), 128.5 (2CH), 128.4 (2CH), 128.1, 119.9, 103.6, 92.4, 79.3, 78.7, 77.9, 73.7 (CH_2), 21.5, 17.0 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2216, 1689, 1593, 1246, 1148 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}O_3$ $[M+H]^+$: 333.1490; found: 333.1439.

3-Benzyloxy-5-(4-methoxyphenylethynyl)-2-methyl-2,3-dihydropyran-4-one (3j)

Compound **2e** (0.1 g, 0.29 mmol) was converted to **3j** (0.077 g, 76%) by following general procedure A: eluent, EtOAc/*n*-hexane (15%); $[\alpha]_D^{20} = -194$ (*c* = 0.1 in MeOH); yellow gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.67 (s, 1H), 7.31–7.44 (m, 7H), 6.83–6.86 (m, 2H), 5.04 (d, *J* = 11.4 Hz, 1H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.57–4.61 (m, 1H), 3.82 (s, 3H), 3.78 (d, *J* = 9.6 Hz, 1H), 1.45 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.9, 164.9, 159.6, 137.1, 133.1 (2CH), 128.5 (2CH), 128.5 (2CH), 128.1, 115.1, 113.9 (2CH), 103.7, 92.2, 79.3, 78.0, 77.9, 73.7 (CH_2), 55.3, 17.0 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 1694, 1609, 1594, 1509, 1245 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}O_5Na$ $[M+Na+H_2O]^+$: 389.1366; found: 389.1379.

3-Benzyloxy-2-benzyloxymethyl-5-(4-nitrophenylethynyl)-2,3-dihydropyran-4-one (3k)

Compound **2a** (0.1 g, 0.222 mmol) was converted to **3k** (0.06 g, 58%) by following general procedure A: eluent, EtOAc/*n*-hexane (15%); $[\alpha]_D^{20} = +197$ (*c* = 0.1 in MeOH); yellow solid; m.p. 70 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.7 Hz, 2H), 7.80 (s, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.31–7.38 (m, 10H), 5.06 (d, *J* = 11.1 Hz, 1H), 4.62 (d, *J* = 11.1 Hz, 1H), 4.51–4.59 (m, 3H), 4.31 (d, *J* = 10.8 Hz, 1H), 3.83 ppm (d, *J* = 3.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.8, 166.3, 146.9, 137.2, 137.0, 132.1 (2CH), 130.0, 128.5 (4CH), 128.5, 128.2, 128.0, 127.8 (2CH), 123.6 (3CH), 103.0, 90.8, 85.3, 82.0, 74.5 (CH_2), 73.7 (CH_2), 73.6, 67.6 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max}$ 2213, 1681, 1594, 1581, 1522, 1345, 1252 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{23}NO_6Na$ $[M+Na]^+$ 492.1423; found: 492.1452.

3-Benzyloxy-2-benzyloxymethyl-5-(4-nitrophenylethynyl)-2,3-dihydropyran-4-one (3l)

Compound **2b** (0.1 g, 0.222 mmol) was converted to **3l** (0.052 g, 50%) by following general procedure A: eluent, EtOAc/*n*-hexane (15%); $[\alpha]_D^{20} = +116$ (*c* = 0.2 in MeOH); red gum. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.7 Hz, 2H), 7.84 (s, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.28–7.38 (m, 10H), 4.71–4.77 (m, 1H), 4.48–4.60 (m, 4H), 3.95 (dd, *J* = 6.9, 10.2 Hz, 1H), 3.85 (d, *J* = 2.4 Hz, 1H), 3.78 ppm (dd, *J* = 5.4, 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.0, 166.7, 146.9, 137.2, 136.5, 132.1 (2CH), 129.9, 128.5 (2CH), 128.5 (2CH), 128.3 (2CH), 128.2, 128.0, 127.8 (2CH), 123.5 (2CH), 102.8, 90.9, 85.6,

81.5, 73.7 (CH_2), 73.3, 72.1 (CH_2), 67.2 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max}$ = 2216, 1582, 1516, 1341 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{23}NO_6Na$ $[M+Na]^+$ 492.1423; found: 492.1390.

2-(*tert*-Butyldimethylsilanyloxymethyl)-3-hydroxy-5-(4-nitrophenylethynyl)-2,3-dihydropyran-4-one (3 m)

Compound **2 f** (0.1 g, 0.26 mmol) was converted to **3 m** (0.042 g, 40%) by following general procedure A: eluent, EtOAc/*n*-hexane (15%); $[\alpha]_D^{20} = +135$ (*c* = 0.1 in MeOH); yellow solid; m.p. 128 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.7 Hz, 2H), 7.91 (s, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 4.50 (d, *J* = 13.2 Hz, 1H), 4.28 (d, *J* = 13.2 Hz, 1H), 4.15 (dd, *J* = 3.3, 12.0 Hz, 1H), 4.06 (dd, *J* = 3.3, 12.0 Hz, 1H), 3.53 (brs, 1H), 0.95 (s, 9H), 0.15 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.8, 168.3, 147.0, 132.2 (2CH), 129.7, 123.6 (2CH), 101.4, 90.7, 84.4, 84.2, 67.0, 61.4 (CH_2), 25.8 ($3CH_3$), 18.4, −5.4 ppm ($2CH_3$); IR (KBr): $\tilde{\nu}_{max}$ = 2213, 1676, 1583, 1517, 1340, 1250 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{25}NO_6SiNa$ $[M+Na]^+$: 426.1349; found: 426.1346.

3-Benzyloxy-2-benzyloxymethyl-5-(4-bromophenylethynyl)-2,3-dihydropyran-4-one (3 n)

Compound **2 b** (0.1 g, 0.222 mmol) was converted to **3 n** (0.056 g, 50%) by following general procedure A: eluent, EtOAc/*n*-hexane (10%); $[\alpha]_D^{20} = +88$ (*c* = 0.1 in MeOH); white solid; m.p. 80 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.44–7.46 (m, 2H), 7.29–7.37 (m, 12H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.56–4.59 (m, 2H), 4.50 (dd, *J* = 8.4, 11.4 Hz, 2H), 3.94 (dd, *J* = 7.2, 10.2 Hz, 1H), 3.82 (d, *J* = 3.0 Hz, 1H), 3.78 ppm (dd, *J* = 5.4, 10.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.3, 165.9, 137.3, 136.6, 133.0 (2CH), 131.5 (2CH), 128.5 (2CH), 128.5 (2CH), 128.4 (2CH), 128.2, 128.0, 127.8 (2CH), 122.5, 121.9, 103.3, 91.5, 81.3, 81.0, 73.7 (CH_2), 73.4, 72.1 (CH_2), 67.3 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max}$ = 2220, 1684, 1595, 1580, 1485, 1368, 1261, 1171, 1101, 1070 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{23}BrO_4Na$ $[M+Na]^+$: 525.0678; found: 525.1106.

3-Benzyloxy-5-trimethylsilanylethynyl-2,3-dihydropyran-4-one (3 o)

Compound **2 g** (0.1 g, 0.30 mmol) was converted to **3 o** (0.068 g, 75%) by following general procedure A: eluent, EtOAc/*n*-hexane (15%); $[\alpha]_D^{20} = -24$ (*c* = 0.1 in MeOH); yellowish white solid; m.p. 70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.31–7.37 (m, 5H), 4.85 (d, *J* = 11.7 Hz, 1H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.55 (dd, *J* = 5.7, 12.6 Hz, 1H), 4.40 (dd, *J* = 3.6, 12.6 Hz, 1H), 3.83–3.86 (m, 1H), 0.23 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.1, 167.0, 136.8, 128.5 (2CH), 128.2 (2CH), 128.1, 103.8, 97.7, 95.0, 72.7, 72.4 (CH_2), 71.9 (CH_2), −0.08 ppm ($3CH_3$); IR (KBr): $\tilde{\nu}_{max}$ = 2158, 1676, 1587, 1192 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{20}O_3SiNa$ $[M+Na]^+$: 323.1080; found: 322.6480.

3-Benzyloxy-2-benzyloxymethyl-5-trimethylsilanylethynyl-2,3-dihydropyran-4-one (3 p)

Compound **2 b** (0.1 g, 0.222 mmol) was converted to **3 p** (0.067 g, 72%) by following general procedure A: eluent, EtOAc/*n*-hexane (8%); $[\alpha]_D^{20} = +70$ (*c* = 0.1 in MeOH); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73 (s, 1H), 7.26–7.37 (m, 10H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 4.46–4.50 (m, 3H), 3.90 (dd, *J* = 6.6, 9.6 Hz, 1H), 3.77 (d, *J* = 2.4 Hz, 1H), 3.75 (dd, *J* = 5.4, 10.2 Hz, 1H), 0.23 ppm (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.4, 166.7, 137.3, 136.7, 128.5 (2CH), 128.4 (2CH), 128.3 (2CH), 128.1, 128.0, 127.8 (2CH), 103.6, 97.9, 95.2, 81.2, 73.7 (CH_2), 73.3, 72.0 (CH_2), 67.3 (CH_2), −0.04 ppm ($3CH_3$); IR (KBr): $\tilde{\nu}_{max}$ = 2158, 1687, 1589, 1250, 1203, 1104 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{29}O_4Si$ $[M+H]^+$: 421.1835; found: 421.2083.

3-Benzyloxy-2-benzyloxymethyl-5-hex-1-ynyl-2,3-dihydropyran-4-one (3 q)

Compound **2 b** (0.1 g, 0.222 mmol) was converted to **3 q** (0.0467 g, 52%) by following general procedure B: eluent, EtOAc/*n*-hexane (6%); $[\alpha]_D^{20} = +50$ (*c* = 0.1 in MeOH); yellow solid; m.p. 55 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (s, 1H), 7.29–7.37 (m, 10H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 11.7 Hz, 1H), 4.44–4.50 (m, 3H), 3.90 (dd, *J* = 6.9, 9.9 Hz, 1H), 3.72–3.77 (m, 2H), 2.38 (t, *J* = 6.9 Hz, 2H), 1.51–1.58 (m, 2H), 1.39–1.47 (m, 2H), 0.92 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.1, 165.2, 137.4, 136.8, 128.5 (2CH), 128.4 (2CH), 128.4 (2CH), 128.1, 128.0, 127.8 (2CH), 103.9, 93.6, 81.0, 73.7 (CH_2), 73.5, 72.0 (CH_2), 70.4, 67.4 (CH_2), 30.8 (CH_2), 22.0 (CH_2), 19.2 (CH_2), 13.6 ppm (CH_3); IR (KBr): $\tilde{\nu}_{max}$ = 2363, 1673, 1583, 1221 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{28}O_4$ $[M+Na]^+$: 427.1886; found: 427.2039; HRMS (ESI): *m/z* calcd for $C_{26}H_{28}O_4$ $[M+Na+H_2O]^+$: 445.1992; found: 445.1985.

3-Benzyloxy-2-benzyloxymethyl-5-hex-1-ynyl-2,3-dihydropyran-4-one (3 r)

Compound **2 a** (0.1 g, 0.222 mmol) was converted to **3 r** (0.05 g, 56%) by following general procedure B: eluent, EtOAc/*n*-hexane (6%); $[\alpha]_D^{20} = +114$ (*c* = 0.1 in MeOH); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 (s, 1H), 7.28–7.34 (m, 10H), 5.06 (d, *J* = 10.8 Hz, 1H), 4.59 (d, *J* = 10.8 Hz, 1H), 4.49–4.57 (m, 2H), 4.45 (dt, *J* = 3.0, 11.4 Hz, 1H), 4.23 (d, *J* = 10.8 Hz, 1H), 3.78 (d, *J* = 3.0 Hz, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.52–1.57 (m, 2H), 1.40–1.47 (m, 2H), 0.92 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.0, 165.7, 138.4, 138.2, 129.5 (4CH), 129.4 (2CH), 129.1, 128.9, 128.8 (2CH), 105.1, 94.5, 82.3, 75.4 (CH_2), 74.6 (CH_2), 74.6, 70.9, 68.7 (CH_2), 31.8 (CH_2), 23.0 (CH_2), 20.2 (CH_2), 14.6 ppm (CH_3); IR (neat): $\tilde{\nu}_{max}$ = 2363, 1695, 1598, 1207 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{28}O_4$ $[M+Na+H_2O]^+$: 445.1992; found: 445.1560.

3-Benzyloxy-2-benzyloxymethyl-5-cyclopentylethynyl-2,3-dihydropyran-4-one (3 s)

Compound **2 a** (0.1 g, 0.222 mmol) was converted to **3 s** (0.048 g, 52%) by following general procedure B: eluent, EtOAc/*n*-hexane (7.5%); $[\alpha]_D^{20} = +25$ (*c* = 0.1 in MeOH); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 (s, 1H), 7.27–7.36 (m, 10H), 5.06 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 10.8 Hz, 1H), 4.50–4.57 (m, 2H), 4.44 (dt, *J* = 3.0, 11.4 Hz, 1H), 4.23 (d, *J* = 11.4 Hz, 1H), 3.78 (d, *J* = 3.0 Hz, 2H), 2.78 (quin, *J* = 7.2 Hz, 1H), 1.94–1.99 (m, 2H), 1.71–1.77 (m, 2H), 1.63–1.68 (m, 2H), 1.53–1.60 ppm (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.0, 165.6, 138.4, 138.2, 129.5 (4CH), 129.4 (2CH), 129.1, 128.9, 128.8 (2CH), 105.1, 98.6, 82.3, 75.4 (CH_2), 74.7, 74.6 (CH_2), 70.4, 68.7 (CH_2), 34.8 ($2CH_2$), 31.8, 26.0 ppm ($2CH_2$); IR (neat): $\tilde{\nu}_{max}$ = 2363, 1694, 1598, 1210 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{28}O_4$ $[M+Na+H_2O]^+$: 457.1992; found: 457.1516.

General procedure for the synthesis of 4 a–s

In a 25 mL flame-dried, two-necked, round-bottomed flask equipped with a magnetic stir bar the corresponding substituted ethynyl-2,3-dihydro-pyran-4-one (**3 a–s**) was dissolved in dry THF (2.5 mL) at room temperature under an argon atmosphere. $AuCl_3$ [mol%] or PPh_3AuNTf_2 [mol%] or $PPh_3AuCl + AgOTf$ [mol%] was added to the reaction mixtures and stirred for the required times.

The resulting reaction mixtures were quenched with H_2O, saturated NH_4Cl solution was added, and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified by using silica gel column chromatography (230–400; EtOAc/*n*-hexane) to afford **4a**–**s**.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-phenylfuran-3-carbaldehyde (4a)

Compound **3a** (0.05 g, 0.117 mmol) was converted to **4a** (0.05 g, 96%) by following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = +59$ ($c = 0.1$ in MeOH); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 10.01$ (s, 1H), 7.68–7.69 (m, 2H), 7.40–7.43 (m, 2H), 7.29–7.36 (m, 9H), 7.23–7.24 (m, 2H), 6.99 (s, 1H), 4.93 (d, $J = 7.8$ Hz, 1H), 4.61 (d, $J = 11.4$ Hz, 1H), 4.56 (d, $J = 12.0$ Hz, 1H), 4.52 (d, $J = 11.4$ Hz, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 4.31 (dt, $J = 4.2$, 7.2 Hz, 1H), 3.74 (dd, $J = 4.8$, 9.6 Hz, 1H), 3.70 (dd, $J = 3.6$, 9.0 Hz, 1H), 2.57 ppm (brs, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 185.2$ (d, 1C), 159.5, 154.9, 137.6, 136.8, 129.3, 128.8 (2CH), 128.5 (2CH), 128.5, 128.5 (2CH), 128.3, 128.2, 128.1 (2CH), 127.9, 127.8 (2CH), 124.3 (2CH), 102.6, 73.8, 73.6 (CH_2), 71.8 (CH_2), 71.7, 70.2 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max} = 1678$ cm^{-1}; HRMS (EI): *m/z* calcd for $C_{28}H_{26}O_5$ $[M]^+$: 442.1780; found: 442.1777.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-phenylfuran-3-carbaldehyde (4b)

Compound **3b** (0.05 g, 0.117 mmol) was converted to **4b** (0.033 g, 63%) by following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = -2$ ($c = 0.1$ in MeOH); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.0$ (s, 1H), 7.65–7.68 (m, 2H), 7.19–7.45 (m, 13H), 6.95 (s, 1H), 5.03 (d, $J = 6.9$ Hz, 1H), 4.66 (d, $J = 11.4$ Hz, 1H), 4.51 (d, $J = 11.7$ Hz, 1H), 4.44–4.45 (m, 2H), 4.24–4.27 (m, 1H), 3.60 (dd, $J = 3.9$, 10.2 Hz, 1H), 3.36 (dd, $J = 4.8$, 10.2 Hz, 1H), 2.89 ppm (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 185.0$, 158.7, 155.0, 137.4, 136.7, 129.1, 128.8 (2CH), 128.6 (2CH), 128.6 (2CH), 128.3 (2CH), 128.2 (2CH), 128.1 (2CH), 127.9, 127.8, 124.2 (2CH), 102.5, 74.7, 73.6 (CH_2), 72.5, 72.1 (CH_2), 69.9 ppm (CH_2); IR (neat): $\tilde{\nu}_{max} = 1678$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{26}O_5Na$ $[M+Na]^+$: 465.1678; found: 465.1669.

2-[3-(*tert*-Butyldimethylsilanyloxy)-1,2-dihydroxypropyl]-5-phenylfuran-3-carbaldehyde (4c)

Compound **3c** (0.05 g, 0.14 mmol) was converted to **4c** (0.026 g, 49%) by following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = -1$ ($c = 0.1$ in MeOH); brown gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.14$ (s, 1H), 7.65–7.68 (m, 2H), 7.29–7.44 (m, 3H), 6.99 (s, 1H), 5.16–5.19 (m, 1H), 4.03–4.05 (m, 2H), 3.82 (dd, $J = 4.2$, 10.5 Hz, 1H), 3.73 (dd, $J = 4.5$, 10.5 Hz, 1H), 2.82 (d, $J = 5.4$ Hz, 1H), 0.91 (s, 9H), 0.09 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 186.7$, 160.7, 154.2, 129.2, 128.8 (2CH), 128.5, 126.4, 124.2 (2CH), 103.5, 73.2, 69.5, 64.0 (CH_2), 25.8 ($3CH_3$), 18.2, −5.5 ppm ($2CH_3$); IR (KBr): $\tilde{\nu}_{max} = 1673$, 1121 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{28}O_5SiNa$ $[M+Na]^+$: 399.1604; found: 399.1870.

2-(1-Benzyloxy-2-hydroxypropyl)-5-phenylfuran-3-carbaldehyde (4d)

Compound **3d** (0.05 g, 0.157 mmol) was converted to **4d** (0.023 g, 43%) by following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = +27$ ($c = 0.1$ in MeOH); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.05$ (s, 1H), 7.68–7.71 (m, 2H), 7.30–7.46 (m, 8H), 6.98 (s, 1H), 4.66 (d, $J = 11.4$ Hz, 1H), 4.62 (d, $J = 7.8$ Hz, 1H), 4.51 (d, $J = 11.4$ Hz, 1H), 4.21–4.25 (m, 1H), 2.89 (m, 1H), 1.11 ppm (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 184.8$, 159.0, 155.1, 136.6, 129.1, 128.9 (2CH), 128.7, 128.7 (2CH), 128.3, 128.1 (2CH), 127.9, 124.3 (2CH), 102.7, 79.3, 72.1 (CH_2), 69.8, 18.0 ppm; IR (KBr): $\tilde{\nu}_{max} = 1679$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{20}O_4Na$ $[M+Na]^+$: 359.1260; found: 359.1257.

2-(1-Benzyloxy-2-hydroxypropyl)-5-phenylfuran-3-carbaldehyde (4e)

Compound **3e** (0.05 g, 0.157 mmol) was converted to compound **4e** (0.034 g, 64%) by following the general procedure: eluent, EtOAc/*n*-hexane (20%); $[\alpha]_D^{20} = -3$ ($c = 0.1$ in MeOH); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 10.06$ (s, 1H), 7.69 (d, $J = 7.2$ Hz, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.29–7.36 (m, 6H), 7.01 (s, 1H), 4.75 (d, $J = 4.8$ Hz, 1H), 4.69 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 11.4$ Hz, 1H), 4.27–4.31 (m, 1H), 2.20 (brs, 1H), 1.24 ppm (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 185.7$, 159.0, 154.9, 136.8, 129.3, 128.9 (2CH), 128.6 (2CH), 128.6, 128.3, 128.2, 128.1 (2CH), 124.2 (2CH), 102.8, 78.4, 72.0 (CH_2), 69.3, 18.7 ppm (CH_3); IR (KBr): $\tilde{\nu}_{max} = 1678$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{20}O_4Na$ $[M+Na]^+$: 359.1260; found: 359.1257.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-(4-methoxyphenyl)furan-3-carbaldehyde (4f)

Compound **3f** (0.05 g, 0.11 mmol) was converted to **4f** (0.044 g, 84%) by following the general procedure: eluent, EtOAc/*n*-hexane (30%); $[\alpha]_D^{20} = +75$ ($c = 0.1$ in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 9.99$ (s, 1H), 7.61–7.62 (m, 2H), 7.28–7.36 (m, 8H), 7.23–7.24 (m, 2H), 6.93–6.95 (m, 2H), 6.85 (s, 1H), 4.92 (d, $J = 7.2$ Hz, 1H), 4.61 (d, $J = 11.4$ Hz, 1H), 4.56 (d, $J = 12.0$ Hz, 1H), 4.52 (d, $J = 11.4$ Hz, 1H), 4.42 (d, $J = 11.4$ Hz, 1H), 4.31 (m, 1H), 3.85 (s, 3H), 3.74 (dd, $J = 4.8$, 9.6 Hz, 1H), 3.70 (dd, $J = 4.2$, 9.6 Hz, 1H), 2.55 ppm (brs, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 185.2$ (d, 1C), 159.9, 158.9, 155.1, 137.6, 136.9, 128.5 (2CH), 128.5 (2CH), 128.5, 128.2, 128.1 (2CH), 127.9, 127.9 (2CH), 125.8 (2CH), 122.3, 114.2 (2CH), 100.9, 73.8, 73.6 (CH_2), 71.7, 71.7 (CH_2), 70.2 (CH_2), 55.4 ppm; IR (KBr): $\tilde{\nu}_{max} = 1677$, 1502 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{29}H_{28}O_6$ $[M]^+$: 472.1886; found: 472.1895.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-(4-methoxyphenyl)furan-3-carbaldehyde (4g)

Compound **3g** (0.05 g, 0.11 mmol) was converted to **4g** (0.040 g, 77%) by following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = -89$ ($c = 0.1$ in MeOH); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.98$ (s, 1H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.20–7.31 (m, 10H), 6.95 (d, $J = 8.7$ Hz, 2H), 6.81 (s, 1H), 5.01 (d, $J = 6.9$ Hz, 1H), 4.66 (d, $J = 11.4$ Hz, 1H), 4.51 (d, $J = 11.4$ Hz, 1H), 4.40–4.45 (m, 2H), 4.24–4.28 (m, 1H), 3.86 (s, 3H), 3.59 (dd, $J = 3.6$, 9.9 Hz, 1H), 3.36 (dd, $J = 4.5$, 10.2 Hz, 1H), 2.87 ppm (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 185.0$, 160.0, 158.1, 155.2, 137.4, 136.7, 128.6 (2CH), 128.4 (2CH), 128.3 (2CH), 128.2 (2CH), 128.1, 127.8 (2CH), 125.8 (2CH), 122.1, 114.3 (2CH), 100.8, 74.6, 73.6 (CH_2), 72.6, 72.1 (CH_2), 69.9 (CH_2), 55.4 ppm; IR (KBr): $\tilde{\nu}_{max} = 1676$, 1501, 1252 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{28}O_6Na$ $[M+Na]^+$: 495.1784; found: 495.1786.

2-[3-(*tert*-Butyldimethylsilanyloxy)-1,2-dihydroxypropyl]-5-(4-methoxyphenyl)-furan-3-carbaldehyde (4h)

Compound **3h** (0.05 g, 0.128 mmol) was converted to **4h** (0.018 g, 33%) by following the general procedure: eluent, EtOAc/*n*-hexane (30%); $[\alpha]_D^{20} = -0.1$ ($c = 0.05$ in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 10.04$ (s, 1H), 7.58 (d, $J = 8.4$ Hz, 2H), 6.93 (d, $J = 9.0$ Hz, 2H), 6.84 (s, 1H), 5.06 (m, 1H), 4.17 (d, $J = 6.6$ Hz, 1H), 4.00 (brs, 1H), 3.89 (dd, $J = 4.2$, 10.2 Hz, 1H), 3.84 (s, 3H), 3.82 (dd, $J = 4.2$, 10.2 Hz, 1H), 2.74 (brs, 1H), 0.90 (s, 9H), 0.09 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 187.0$ (d, 1C), 160.9, 159.9, 154.3, 125.7 (2CH), 125.7, 122.1, 114.2 (2CH), 102.2, 72.7, 69.8, 63.8 (CH_2), 55.3, 25.8 (3CH_3), 18.2, −5.5 ppm (2CH_3); IR (KBr): $\tilde{\nu}_{max} = 1671$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{30}O_6SiNa$ $[M+Na]^+$: 429.1710; found: 429.0250.

2-(1-Benzyloxy-2-hydroxypropyl)-5-*p*-tolylfuran-3-carbaldehyde (4i)

Compound **3i** (0.05 g, 0.15 mmol) was converted to **4i** (0.037 g, 72%) by following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = -124$ ($c = 0.1$ in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.05$ (s, 1H), 7.57 (d, $J = 8.1$ Hz, 2H), 7.21–7.38 (m, 7H), 6.94 (s, 1H), 4.74 (d, $J = 5.1$ Hz, 1H), 4.68 (d, $J = 11.7$ Hz, 1H), 4.48 (d, $J = 11.7$ Hz, 1H), 4.25–4.30 (m, 1H), 2.38 (s, 3H), 2.19 (d, $J = 4.8$ Hz, 1H), 1.24 ppm (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 185.8$, 158.9, 155.1, 138.6, 136.9, 129.5 (2CH), 128.6 (2CH), 128.2 (2CH), 128.1 (2CH), 126.6, 124.2 (2CH), 102.0, 78.4, 71.9 (CH_2), 69.2, 21.3, 18.8 ppm (CH_3); IR (KBr): $\tilde{\nu}_{max} = 1676$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}O_4Na$ $[M+Na]^+$: 373.1416; found: 373.1413.

2-(1-Benzyloxy-2-hydroxypropyl)-5-(4-methoxyphenyl)furan-3-carbaldehyde (4j)

Compound **3j** (0.05 g, 0.143 mmol) was converted to **4j** (0.035 g, 67%) by following the general procedure: eluent, EtOAc/*n*-hexane (30%); $[\alpha]_D^{20} = -120$ ($c = 0.1$ in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.04$ (s, 1H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.31–7.37 (m, 5H), 6.95 (d, $J = 8.7$ Hz, 2H), 6.87 (s, 1H), 4.73 (d, $J = 4.8$ Hz, 1H), 4.68 (d, $J = 11.7$ Hz, 1H), 4.48 (d, $J = 11.7$ Hz, 1H), 4.27–4.29 (m, 1H), 3.85 (s, 3H), 2.17 (d, $J = 4.8$ Hz, 1H), 1.24 ppm (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 185.7$, 159.9, 158.5, 155.0, 136.9, 128.6 (2CH), 128.3, 128.2, 128.1 (2CH), 125.8 (2CH), 122.2, 114.3 (2CH), 101.1, 78.3, 71.9 (CH_2), 69.3, 55.4, 18.8 ppm (CH_3); IR (KBr): $\tilde{\nu}_{max} = 1676$, 1502, 1252 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{22}H_{22}O_5$ $[M]^+$: 366.1467; found: 366.1466.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-(4-nitrophenyl)furan-3-carbaldehyde (4k)

Compound **3k** (0.05 g, 0.106 mmol) was converted to **4k** (0.022 g, 42%) by following the general procedure: eluent, EtOAc/*n*-hexane (30%); $[\alpha]_D^{20} = -40$ ($c = 0.05$ in MeOH); reddish gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 10.02$ (s, 1H), 8.28 (d, $J = 9.0$ Hz, 2H), 7.81 (d, $J = 9.0$ Hz, 2H), 7.29–7.37 (m, 8H), 7.22 (d, $J = 6.6$ Hz, 2H), 7.19 (s, 1H), 4.95 (d, $J = 7.2$ Hz, 1H), 4.60 (d, $J = 11.4$ Hz, 1H), 4.57 (d, $J = 11.4$, 1H), 4.53 (d, $J = 11.4$ Hz, 1H), 4.46 (d, $J = 11.4$ Hz, 1H), 4.27–4.30 (m, 1H), 3.76 (dd, $J = 4.8$, 9.6 Hz, 1H), 3.70 (dd, $J = 4.2$, 9.6 Hz, 1H), 2.56 ppm (brs, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 184.8$ (d, 1C), 161.3, 152.4, 147.2, 137.4, 136.6, 135.0, 128.6 (2CH), 128.5 (2CH), 128.4, 128.3, 128.1 (2CH), 128.0, 127.9 (2CH), 124.6 (2CH), 124.4 (2CH), 106.5, 73.9, 73.6 (CH_2), 72.1 (CH_2), 71.7, 70.0 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max}$ 1680, 1602, 1516, 1343 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{25}NO_7Na$ $[M+Na]^+$: 510.1529; found: 510.1526.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-(4-nitrophenyl)furan-3-carbaldehyde (4l)

Compound **3l** (0.05 g, 0.106 mmol) was converted to **4l** (0.027 g, 53%) following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = -1$ ($c = 0.1$ in MeOH); yellow gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.02$ (s, 1H), 8.28 (d, $J = 8.7$ Hz, 2H), 7.77 (d, $J = 9.0$ Hz, 2H), 7.19–7.36 (m, 10H), 7.14 (s, 1H), 5.04 (d, $J = 6.3$ Hz, 1H), 4.67 (d, $J = 11.4$ Hz, 1H), 4.55 (d, $J = 11.4$ Hz, 1H), 4.45 (m, 2H), 4.22–4.24 (m, 1H), 3.62 (dd, $J = 4.5$, 10.2 Hz, 1H), 3.42 ppm (dd, $J = 4.5$, 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 184.7$, 160.5, 152.4, 147.3, 137.3, 136.5, 134.8, 128.7 (2CH), 128.4 (2CH), 128.2 (2CH), 128.0, 127.9 (2CH), 127.8 (2CH), 124.6 (2CH), 124.4 (2CH), 106.4, 74.9, 73.7 (CH_2), 72.6 (CH_2), 72.4, 69.9 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max} =$ 1598, 1516, 1339 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{25}NO_7Na$ $[M+Na]^+$: 510.1529; found: 510.1527.

2-[3-(*tert*-Butyldimethylsilanyloxy)-1,2-dihydroxypropyl]-5-(4-nitrophenyl)furan-3-carbaldehyde (4m)

Compound **3m** (0.05 g, 0.124 mmol) was converted to **4m** (0.011 g, 21%) by following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = -60$ ($c = 0.1$ in MeOH); reddish solid; m.p. 72 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 10.09$ (s, 1H), 8.29 (d, $J = 9.0$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.23 (s, 1H), 5.09 (d, $J = 6.6$ Hz, 1H), 4.14 (brs, 1H), 4.01–4.03 (m, 1H), 3.91 (dd, $J = 3.6$, 10.2 Hz, 1H), 3.84 (dd, $J = 4.2$, 10.8 Hz, 1H), 2.74 (brs, 1H), 0.92 (s, 9H), 0.11 ppm (d, $J = 1.2$ Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 186.5$ (d, 1C), 163.3, 151.7, 147.2, 134.9, 125.9, 124.5 (2CH), 124.4 (2CH), 107.8, 72.6, 69.8, 63.6 (CH_2), 25.8 (3CH_3), 18.2, −5.5 ppm (2CH_3); IR (KBr): $\tilde{\nu}_{max} = 1685$, 1673, 1524, 1345 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{27}NO_7SiNa$ $[M+Na]^+$: 444.1455; found: 444.1710.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-(4-bromophenyl)-furan-3-carbaldehyde (4n)

Compound **3n** (0.05 g, 0.099 mmol) was converted to **4n** (0.034 g, 67%) by following the general procedure: eluent, EtOAc/*n*-hexane (25%); $[\alpha]_D^{20} = -30$ ($c = 0.1$ in MeOH); white solid; m.p. 95 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 10.0$ (s, 1H), 7.50–7.56 (m, 4H), 7.20–7.34 (m, 10H), 6.94 (s, 1H), 5.02 (d, $J = 7.2$ Hz, 1H), 4.65 (d, $J = 11.4$ Hz, 1H), 4.52 (d, $J = 11.4$ Hz, 1H), 4.46 (d, $J = 12.0$, Hz, 1H), 4.43 (d, $J = 11.4$ Hz, 1H), 4.23 (dt, $J = 4.2$, 6.6 Hz, 1H), 3.60 (dd, $J = 4.2$, 10.2 Hz, 1H), 3.38 (dd, $J = 4.2$, 10.2 Hz, 1H), 2.83 ppm (brs, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 184.9$ (d, 1C), 159.0, 153.9, 137.4, 136.6, 132.1 (2CH), 128.6 (2CH), 128.4 (2CH), 128.3, 128.2 (2CH), 128.1, 127.9, 127.8, 127.8 (2CH), 125.7 (2CH), 122.6, 103.1, 74.7, 73.6 (CH_2), 72.5, 72.3 (CH_2), 69.8 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max} = 1642$, 1546, 1496, 1478, 1452 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{25}O_5BrNa$ $[M+Na]^+$: 543.0783; found: 543.0782.

2-(1-Benzyloxy-2-hydroxyethyl)-5-trimethylsilanylfuran-3-carbaldehyde (4o), 2-(1-benzyloxy-2-hydroxyethyl)-4-trimethylsilanylfuran-3-carbaldehyde (4oa), and 2-(1-benzyloxy-2-hydroxyethyl)furan-3-carbaldehyde (4ob)

Compound **3o** (0.05 g, 0.166 mmol) was converted to **4o** (0.005 g, 9%), **4oa** (0.006 g, 11%), and **4ob** (0.0065 g, 16%) by following the general procedure. Compound **4o**: eluent, EtOAc/*n*-hexane (20%); $[\alpha]_D^{20} = -1$ ($c = 0.11$ in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 10.06$ (s, 1H), 7.27–7.35 (m, 5H), 6.95 (s, 1H),

4.97 (dd, $J=4.2$, 7.8 Hz, 1H), 4.62 (d, $J=12.0$ Hz, 1H), 4.49 (d, $J=11.4$ Hz, 1H), 3.99 (dd, $J=7.8$, 12.0 Hz, 1H), 3.86 (dd, $J=4.2$, 12.0 Hz, 1H), 2.24 (br s, 1H), 0.29 ppm (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=185.4$ (d, 1C), 163.4, 162.5, 136.9, 128.6 (2CH), 128.2, 128.1 (2CH), 125.9, 117.9, 75.5, 72.0 (CH_2), 64.7 (CH_2), −1.9 ppm ($3CH_3$); IR (KBr): $\tilde{\nu}_{max}=1678$, 1251 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{22}O_4SiNa$ $[M+Na]^+$: 341.1185; found: 341.1183. Compound **4oa**: eluent, EtOAc/*n*-hexane (20%); $[\alpha]_D^{20}=+24$ ($c=0.1$ in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=10.07$ (s, 1H), 7.25–7.35 (m, 6H), 4.96 (dd, $J=3.6$, 7.2 Hz, 1H), 4.62 (d, $J=12.0$ Hz, 1H), 4.48 (d, $J=11.4$ Hz, 1H), 3.99 (dd, $J=7.8$, 12.0 Hz, 1H), 3.84 (dd, $J=4.2$, 12.0 Hz, 1H), 2.20 (br s, 1H), 0.26 ppm (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=185.4$ (d, 1C), 161.4, 148.6, 136.8, 129.1, 128.6 (2CH), 128.2, 128.0 (2CH), 119.0, 74.7, 71.9 (CH_2), 64.6 (CH_2), −1.1 ppm ($3CH_3$); IR (KBr): $\tilde{\nu}_{max}=1679$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{22}O_4SiNa$ $[M+Na]^+$: 341.1185; found: 341.1182. Compound **4ob**: eluent, EtOAc/*n*-hexane (30%); $[\alpha]_D^{20}=+35.2$ ($c=0.5$ in MeOH); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=10.05$ (s, 1H), 7.43 (d, $J=1.8$ Hz, 1H), 7.28–7.36 (m, 5H), 6.78 (d, $J=1.8$ Hz, 1H), 4.96 (dd, $J=4.2$, 7.2 Hz, 1H), 4.63 (d, $J=11.4$ Hz, 1H), 4.48 (d, $J=11.4$ Hz, 1H), 3.99 (dd, $J=7.2$, 11.4 Hz, 1H), 3.86 (dd, $J=4.2$, 12.0 Hz, 1H), 2.20 ppm (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=185.1$ (d, 1C), 159.5, 143.6, 136.7, 128.7 (2CH), 128.3, 128.1 (2CH), 125.8, 108.5, 74.8, 71.9 (CH_2), 64.5 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max}=1679$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}O_4Na$ $[M+Na]^+$: 269.0790; found: 269.0792.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-trimethylsilanylfuran-3-carbaldehyde (4p) and 2-(1,3-bis(benzyloxy)-2-hydroxypropyl)furan-3-carbaldehyde (4pb)

Compound **3p** (0.05 g, 0.118 mmol) was converted to **4p** (0.018 g, 35%) and **4pb** (0.013 g, 30%) by following the general procedure with $AuCl_3$ as catalyst. Compound **4p**: eluent, EtOAc/*n*-hexane (20%); $[\alpha]_D^{20}=-1$ ($c=0.1$ in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=10.0$ (s, 1H), 7.24–7.30 (m, 10H), 6.92 (s, 1H), 4.97 (d, $J=6.6$ Hz, 1H), 4.58 (d, $J=11.4$ Hz, 1H), 4.43–4.48 (m, 3H), 4.18–4.19 (m, 1H), 3.54 (dd, $J=4.2$, 10.2 Hz, 1H), 3.27 (dd, $J=4.8$, 10.2 Hz, 1H), 2.82 (d, $J=3.6$ Hz, 1H), 0.26 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=185.3$, 163.4, 162.5, 137.5, 136.8, 128.6 (2CH), 128.4 (2CH), 128.2 (2CH), 128.1 (2CH), 127.8 (2CH), 126.3, 117.7, 75.1, 73.6 (CH_2), 72.6, 72.2 (CH_2), 69.9 (CH_2), −1.9 ppm ($3CH_3$); IR (neat): $\tilde{\nu}_{max}=1680$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{30}O_5SiNa$ $[M+Na]^+$: 461.1761; found: 461.1762. Compound **4pb**: eluent, EtOAc/*n*-hexane (30%); $[\alpha]_D^{20}=-116$ ($c=0.1$ in MeOH); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=9.98$ (s, 1H), 7.40 (d, $J=1.8$ Hz, 1H), 7.22–7.34 (m, 10H), 6.75 (d, $J=2.4$ Hz, 1H), 4.99 (d, $J=6.6$ Hz, 1H), 4.60 (d, $J=12.0$ Hz, 1H), 4.44–4.47 (m, 2H), 4.42 (d, $J=11.4$ Hz, 1H), 4.18 (dt, $J=4.2$, 7.2 Hz, 1H), 3.54 (dd, $J=4.2$, 10.2 Hz, 1H), 3.29 (dd, $J=4.8$, 10.8 Hz, 1H), 2.83 ppm (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=184.9$ (d, 1C), 159.5, 143.6, 137.4, 136.7, 128.6 (2CH), 128.4 (2CH), 128.3, 128.1 (2CH), 127.9 (2CH), 127.8, 126.2, 108.2, 74.4, 73.6 (CH_2), 72.5, 72.1 (CH_2), 69.8 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max}=1680$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}O_5Na$ $[M+Na]^+$: 389.1365; found: 389.1364.

3-Benzyloxy-2-benzyloxymethyl-5-ethynyl-2,3-dihydropyran-4-one (4pc)

Compound **3p** (0.05 g, 0.118 mmol) was converted to **4pb** (0.013 g, 30%) and **4pc** (0.014 g, 34%) by following the general procedure with PPh_3AuNTf_2 as catalyst. Similarly, **3p** (0.05 g, 0.118 mmol) was converted to **4pb** (0.014 g, 32%) and **4pc** (0.0075 g, 18%) by following the general procedure with $PPh_3AuCl+AgOTf$ as catalyst. The analytical data of **4pb** were consistent with the experimental details discussed above. Compound **4pc**: eluent, EtOAc/*n*-hexane (12%); $[\alpha]_D^{20}=+14$ ($c=0.1$ in MeOH); white solid; m.p. 132 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.75$ (s, 1H), 7.27–7.36 (m, 10H), 4.71 (d, $J=12.0$ Hz, 1H), 4.56 (d, $J=11.4$ Hz, 1H), 4.52–4.54 (m, 1H), 4.49 (d, $J=11.4$ Hz, 1H), 4.46 (d, $J=12.0$ Hz, 1H), 3.91 (dd, $J=6.6$, 10.2 Hz, 1H), 3.79 (d, $J=1.8$ Hz, 1H), 3.76 (dd, $J=5.4$, 10.2 Hz, 1H), 3.07 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=186.5$, 166.8, 137.3, 136.6, 128.5 (3CH), 128.4 (2CH), 128.4, 128.1, 128.0, 127.8 (2CH), 102.4, 81.3, 80.7, 74.4, 73.7 (CH_2), 73.3, 72.1 (CH_2), 67.2 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max}=3265$, 1693, 1586, 1198, 1102 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{20}O_4Na$ $[M+Na]^+$: 371.1260; found: 371.1254.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)furan-3-carbaldehyde (4pb)

Compound **4pc** (0.05 g, 0.143 mmol) was converted to **4pb** (0.025 g, 48%) by following the general procedure with PPh_3AuNTf_2 as catalyst. The analytical data of **4pb** were consistent with the experimental details discussed above: eluent, EtOAc/*n*-hexane (30%).

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-butylfuran-3-carbaldehyde (4q)

Compound **3q** (0.05 g, 0.124 mmol) was converted to **4q** (0.027 g, 52%) by following the general procedure: eluent, EtOAc/*n*-hexane (20%); $[\alpha]_D^{20}=-22$ ($c=0.1$ in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=9.91$ (s, 1H), 7.21–7.34 (m, 10H), 6.33 (s, 1H), 4.91 (d, $J=7.2$ Hz, 1H), 4.59 (d, $J=12.0$ Hz, 1H), 4.41–4.46 (m, 3H), 4.17–4.18 (m, 1H), 3.53 (dd, $J=3.6$, 10.2 Hz, 1H), 3.28 (dd, $J=4.2$, 9.6 Hz, 1H), 2.85 (br s, 1H), 2.58–2.61 (m, 2H), 1.58–1.62 (m, 2H), 1.32–1.39 (m, 2H), 0.93 ppm (t, $J=7.8$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=185.0$, 158.3, 157.9, 137.5, 136.8, 128.6 (2CH), 128.4 (2CH), 128.2, 128.1 (2CH), 127.8 (2CH), 127.8, 127.1, 102.9, 74.3, 73.6 (CH_2), 72.5, 71.9 (CH_2), 69.8 (CH_2), 29.5 (CH_2), 27.3 (CH_2), 22.1 (CH_2), 13.7 ppm (CH_3); IR (KBr): $\tilde{\nu}_{max}=1677$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{30}O_5Na$ $[M+Na]^+$: 445.1991; found: 445.1991.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-butylfuran-3-carbaldehyde (4r)

Compound **3r** (0.05 g, 0.124 mmol) was converted to **4r** (0.027 g, 52%) by following the general procedure: eluent, EtOAc/*n*-hexane (20%); $[\alpha]_D^{20}=+1$ ($c=0.1$ in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=9.91$ (s, 1H), 7.21–7.36 (m, 10H), 6.36 (s, 1H), 4.82 (d, $J=7.2$ Hz, 1H), 4.49–4.55 (m, 3H), 4.36 (d, $J=12.0$ Hz, 1H), 4.19–4.23 (m, 1H), 3.69 (dd, $J=5.4$, 9.6 Hz, 1H), 3.65 (dd, $J=3.6$, 9.6 Hz, 1H), 2.63 (t, $J=7.8$ Hz, 2H), 2.47 (d, $J=6.0$ Hz, 1H), 1.60–1.65 (m, 2H), 1.36–1.39 (m, 2H), 0.93 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=186.2$ (d, 1C), 159.7, 159.2, 138.6, 137.9, 129.5 (2CH), 129.5 (2CH), 129.1, 129.0 (2CH), 128.9, 128.8 (2CH), 128.5, 104.0, 74.5 (CH_2), 74.4 (CH_2), 72.6, 72.5 (CH_2), 71.3 (CH_2), 30.6 (CH_2), 28.4 (CH_2), 23.1 (CH_2), 14.8 ppm (CH_3); IR (KBr): $\tilde{\nu}_{max}=1675$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{30}O_5Na$ $[M+Na]^+$: 445.1991; found: 445.1987.

2-(1,3-Bis(benzyloxy)-2-hydroxypropyl)-5-cyclopentylfuran-3-carbaldehyde (4s)

Compound **3s** (0.05 g, 0.120 mmol) was converted to **4s** (0.043 g, 82%) by following the general procedure: eluent, EtOAc/*n*-hexane (20%); $[\alpha]_D^{20}=+66$ ($c=0.1$ in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=9.91$ (s, 1H), 7.20–7.37 (m, 10H), 6.36 (s, 1H),

4.82 (d, $J=7.2$ Hz, 1H), 4.48–4.56 (m, 3H), 4.37 (d, $J=11.7$ Hz, 1H), 4.22 (m, 1H), 3.62–3.71 (m, 2H), 3.08 (quin, $J=7.2$ Hz, 1H), 2.50 (d, $J=4.5$ Hz, 1H), 2.00–2.50 (m, 2H), 1.50–1.74 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=185.3$, 161.6, 158.7, 137.6, 137.0, 128.5 (2CH), 128.5 (2CH), 128.1 (2CH), 128.0, 127.9, 127.8 (2CH), 127.3, 101.6, 73.7, 73.5 (CH_2), 71.6 (CH_2), 71.6, 70.3 (CH_2), 38.3, 31.6 (CH_2), 31.5 (CH_2), 25.1 ppm (2CH_2); IR (KBr): $\tilde{\nu}_{max}=1676$ cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{30}O_5Na$ $[M+Na]^+$: 457.1991; found: 457.2024.

6-(*tert*-Butyldimethylsilanyloxymethyl)-4-methoxy-2-phenyl-6,7-dihydro-4*H*-furo[3,2-*c*]pyran-7-ol (5a)

$AuCl_3$ (0.0127 g, 10 mol%) and then methanol (0.034 mL, 2 equiv) were added to a well-stirred solution of **3c** (0.150 g, 0.418 mmol) in dry THF (2.5 mL) under an argon atmosphere. The resulting reaction mixture was stirred at room temperature for 20 min. After completion of the reaction (TLC), the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (230–400) to obtain compound **5a** (0.089 g, 55%): eluent: EtOAc/*n*-hexane (7.5%); white solid; m.p. 120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.67$ (d, $J=7.2$ Hz, 2H), 7.35–7.40 (m, 2H), 7.26–7.30 (m, 1H), 6.60 (s, 1H), 5.53 (s, 1H), 4.65 (dd, $J=1.5$, 6.9 Hz, 1H), 4.20–4.25 (m, 1H), 3.97–4.04 (m, 2H), 3.54 (s, 3H), 2.42 (d, $J=7.5$ Hz, 1H), 0.93 (s, 9H), 0.13 ppm (d, $J=2.4$ Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=154.8$, 150.3, 130.3, 128.7 (2CH), 127.9, 124.1 (2CH), 121.4, 102.5, 95.9, 71.7, 62.4 (CH_2), 61.8, 55.7, 25.9 (3CH_3), 18.2, −5.4 ppm (2CH_3); HRMS (ESI): *m/z* calcd for $C_{21}H_{30}O_5SiNa$ $[M+Na]^+$: 413.1761; found: 413.1755.

7-Benzyloxy-6-benzyloxymethyl-2-phenyl-6,7-dihydrofuro-[3,2-*c*]pyran-4-one (5b)

PDC (0.127 g, 0.339 mmol, 3 equiv) was added to a well-stirred solution of **4a** (0.05 g, 0.113 mmol) in dry dichloromethane (5 mL) under an argon atmosphere. The resulting reaction mixture was stirred at room temperature for 48 h. After completion of reaction (TLC), saturated $NaHCO_3$ solution was added, and the product was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a crude residue. The residue was purified by using silica gel column chromatography to obtain **5b** (0.020 g, 40%): eluent: EtOAc/*n*-hexane (20%); $[\alpha]_D^{20}=+48$ (*c*= 0.1 in MeOH); white solid; m.p. 74 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.67$–7.68 (m, 2H), 7.43–7.45 (m, 2H), 7.25–7.38 (m, 9H), 7.21–7.22 (m, 2H), 6.94 (s, 1H), 5.00 (d, $J=4.2$ Hz, 1H), 4.85–4.87 (m, 2H), 4.73 (d, $J=11.4$ Hz, 1H), 4.52 (d, $J=11.4$ Hz, 1H), 4.48 (d, $J=$ 12.0 Hz, 1H), 3.77 (dd, $J=4.2$, 10.2 Hz, 1H), 3.63 ppm (dd, $J=6.0$, 10.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=160.8$, 158.1, 156.4, 137.3, 136.9, 129.1, 128.9 (2CH), 128.8, 128.6 (2CH), 128.4 (2CH), 128.2, 128.1 (2CH), 127.9, 127.6 (2CH), 124.3 (2CH), 114.9, 102.5, 81.5, 73.5 (CH_2), 72.2 (CH_2), 68.5 (CH_2), 67.0 ppm; IR (KBr): $\tilde{\nu}_{max}=$ 1745 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{24}O_5Na$ $[M+Na]^+$: 463.1522; found: 463.1192.

2-(3-Benzyloxy-2-oxopropyl)-5-phenylfuran-3-carbaldehyde (6)

$TiBr_4$ (0.083 g, 0.226 mmol, 2 equiv) was added to a well-stirred solution of **4a** or **4b** (0.05 g, 0.113 mmol) in dry toluene (2.5 mL) under an argon atmosphere. The resulting reaction mixture was heated under reflux conditions for 8 h. After completion of reaction (TLC), saturated NH_4Cl solution was added, and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a crude residue. The residue was purified by using silica gel column chromatography to obtain **6** (0.016 g, 43%): eluent: EtOAc/*n*-hexane (15–20%); yellow gum. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=9.91$ (s, 1H), 7.64 (d, $J=7.2$ Hz, 2H), 7.31–7.42 (m, 8H), 6.96 (s, 1H), 4.64 (s, 2H), 4.26 (s, 2H), 4.22 ppm (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=202.1$, 185.2 (d, 1C), 154.8, 154.7, 136.7, 129.3, 128.8 (2CH), 128.6 (2CH), 128.4, 128.2, 128.0 (2CH), 125.7, 124.1 (2CH), 103.4, 74.9 (CH_2), 73.7 (CH_2), 38.4 ppm (CH_2); IR (KBr): $\tilde{\nu}_{max}=1681$, 1735 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{18}O_4Na$ $[M+Na]^+$: 357.1103; found: 357.1106.

6-Benzyloxymethyl-2-phenylfuro[3,2-*c*]pyridine (7)

1,5-Dicarbonyl derivative **6** (0.022 g, 0.066 mmol) was dissolved in a solution of NH_4OAc (50.7 mg, 0.66 mmol, 10 equiv) and acetic acid (0.04 mL, 0.66 mmol, 10 equiv) in ethanol (0.01 M with respect to **6**). The resulting mixture was heated at 40 °C for 12 h. After completion of reaction (TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate, washed with aqueous saturated $NaHCO_3$ solution, followed by brine solution. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a crude residue. The crude residue was purified by using silica gel column chromatography to obtain **7** (0.012 g, 60%); eluent: EtOAc/*n*-hexane (35%); light yellow solid; m.p. 88 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=8.84$ (s, 1H), 7.86–7.87 (m, 2H), 7.68 (s, 1H), 7.47 (t, $J=7.2$ Hz, 2H), 7.36–7.43 (m, 5H), 7.30–7.32 (m, 1H), 7.05 (s, 1H), 4.83 (s, 2H), 4.70 ppm (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=160.3$, 157.1, 153.9, 142.7, 138.0, 129.5, 129.3, 128.9 (2CH), 128.4 (2CH), 127.8 (2CH), 127.7, 125.5, 125.2 (2CH), 104.6, 99.0, 73.0 (CH_2), 72.9 ppm (CH_2); HRMS (ESI): *m/z* calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1337; found: 316.1104.

Acknowledgements

I.D. thanks DST-SERB (no. SB/FT/CS-105/2012) for financial support, and Drs. Basudeb Achari and Ramalingam Natarajan for valuable discussions. K.M. thanks the CSIR, India for a fellowship. A.S. thanks NIPER-Kolkata for a fellowship. We thank the reviewers for their valuable comments and suggestions, which helped significantly to improve the quality of the manuscript.

Keywords: carbohydrates · chirality · furans · gold · homogeneous catalysis

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Received: February 21, 2014
Published online on ■■ ■■, 0000

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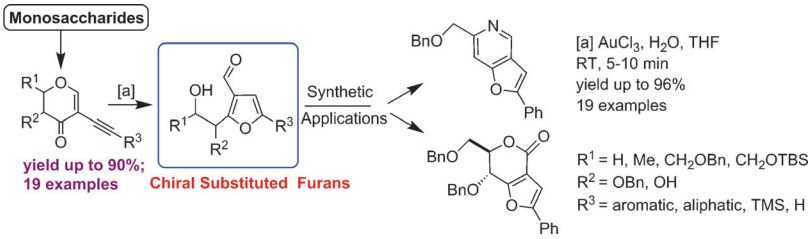

Golden energy! An efficient gold(III)-catalyzed route to substituted chiral 3-formyl furans under extremely mild conditions from suitably protected 5-(1-alkynyl)-2,3-dihydropyran-4-ones and H_2O as a nucleophile is described (see scheme, TBS = *tert*-butyldimethylsilyl). The latter can easily be synthesized from appropriately functionalized monosaccharides or commercially available glycals in a few steps.

Chiral Furans

*K. Mal, A. Sharma, I. Das**

■■ – ■■

Gold(III) Chloride Catalyzed Synthesis of Chiral Substituted 3-Formyl Furans from Carbohydrates: Application in the Synthesis of 1,5-Dicarbonyl Derivatives and Furo[3,2-*c*]pyridine