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Base Induced Chiral Substituted Furans and Imidazoles from Carbohydrate-Derived 2-Haloenones

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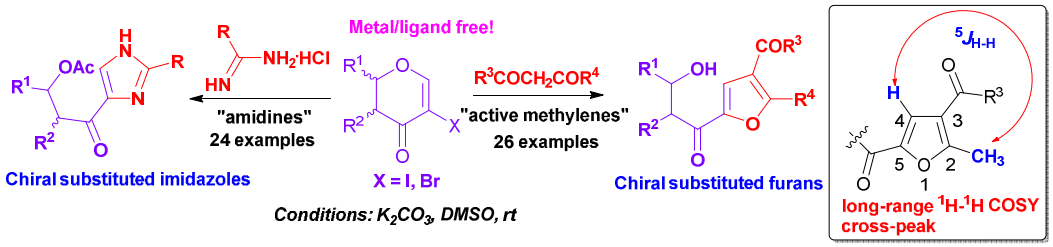


Abstract: Chiral substituted furans and imidazoles are key intermediates to access biologically important molecules. We describe herein a catalyst/ligand free cascade Michael-type addition/intramolecular cyclization/carbohydrate-ring opening of 2-haloenones with 1,3-dicarbonyl compounds or amidines utilizing K_2CO_3/DMSO at ambient temperature, that provides a straightforward approach to a variety of optically active (poly)hydroxy furans and imidazoles containing multiple stereocentres with good yield and excellent regioselectivity. The furan intermediates provide efficient access to synthetically valuable substituted α-benzyloxyvinyl ketones. The NMR spectrum of the substituted 2-methylfurans shows an unusual long-range ($^5J_{H-H}$) ^{1}H-^{1}H COSY cross-peak between C_2-CH_3 and C_4-H signals.

INTRODUCTION

Substituted furans, constituting the core structural unit in numerous biologically active natural products, pharmaceuticals and significant synthetic intermediates, are highly sought-after in heterocyclic chemistry.[1a-f] In particular, trisubstituted furans bearing an ester or keto-group at C-3 are extremely useful intermediates and promising building blocks in synthetic

processes (Figure 1).[1g-h] Chiral substituted furanyl α-ketones too form prominent structural motifs present in value-added compounds.[2a] More significantly, the ketones after reduction to furanyl α-carbinols can be easily transformed under Achmatowicz reaction conditions to versatile synthetic intermediates,[2b] which can be further transformed to modified higher-carbon sugars and aza sugars.[2a] Like Substituted furans, substituted imidazoles/optically active (poly)hydroxy-substituted imidazoles are also commonly found in many biologically relevant natural products (Figure 1), with applications in target-oriented synthesis, N-heterocyclic carbene precursors, and ionic liquids.[3]

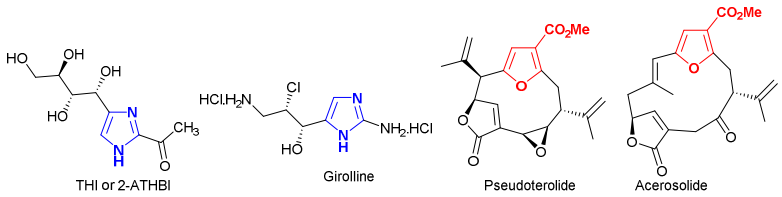


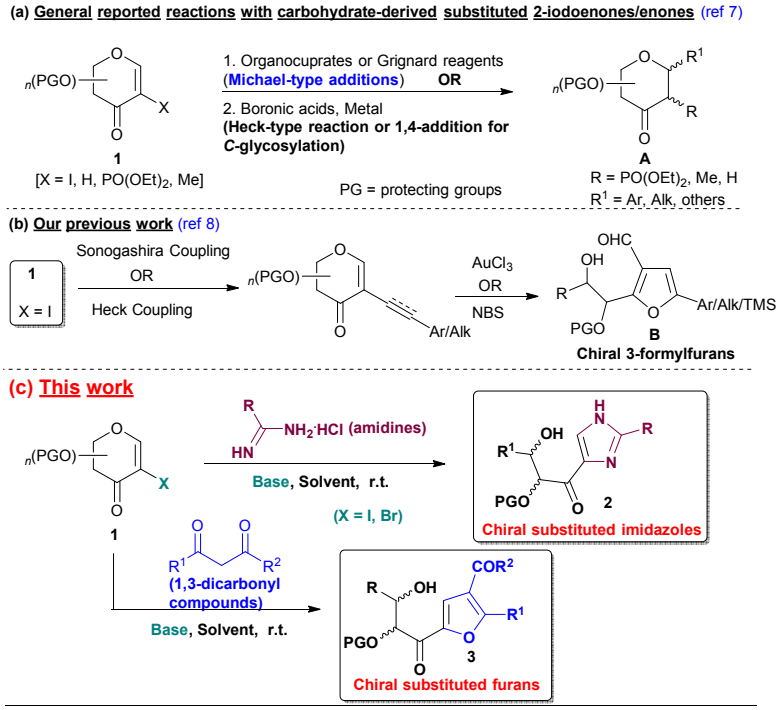
Figure 1. Pharmacologically active and naturally occurring compounds containing chiral substituted imidazoles and furan-3-carboxylic acid esters.

The chiral furanyl α-ketones/α-carbinols are prepared either by using asymmetric Friedel-Crafts reaction or chiral pool precursors, or by enzymatic as well as kinetic resolutions of racemic mixtures.[4] There are also sporadic reports on efficient synthetic strategies for optically active (poly)hydroxy-substituted imidazoles,[5] In spite of these, the development of efficient and regioselective routes to these essential scaffolds utilizing operationally simple processes under mild reaction conditions is still in great demand.

Carbohydrates have been recognized as one of the most potential sources of chirality in target oriented synthesis of complex molecules.[6] In particular, 2-iodoenones/enones **1** derived from carbohydrates are important synthetic intermediates for diverse reactions such as Diels-Alder reaction, Michael-type addition and Heck-type reaction/1,4-addition for *C*-glycosylation [**A**, Scheme 1, (a)].[7] Recently, we have described the synthesis of substituted chiral 3-formylfurans from these 2-iodoenones **1** [**B**, Scheme 1, (b)].[8] This finding prompted

us to investigate whether the combination of such haloenones **1** with bidentate nucleophiles such as amidines or with active methylene compounds could constitute an unprecendented cascade annulation process to afford the optically active substituted imidazoles **2** and furans **3**. Herein, we report the successful execution of this hypothesis by utilizing amidines and active methylene compounds through Michael-type addition followed by substitution and rearrangement.

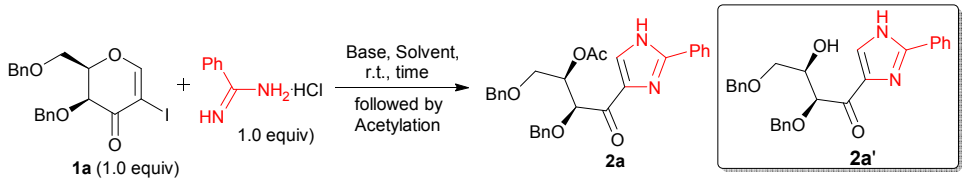
Scheme 1. Previous Work from 1 and Our Hypothesis for Accessing Chiral Substituted Imidazoles and Furans



RESULTS AND DISCUSSION

To optimize the reaction conditions for chiral imidazole derivatives, we initiated screening studies by utilizing **1a** as the substrate and benzamidine hydrochloride as the 1,3-dinucleophilic species in the presence of different bases and solvents. Pleasantly, use of K_2CO_3 (3 equiv) as a base in DMSO led to the formation of a product which from preliminary spectroscopic analysis appeared to be **2a'** (Table 1). Due to the unusual signal

Table 1. Optimization of Reaction Conditions[a]



Entry	Base	Equiv	Solvent	time	Yield (%)
1	**K_2CO_3**	**3**	**DMSO**	**75 min**	**84**
2	KO^{t}Bu	3	DMSO	15 min	38
3	Na_2CO_3	3	DMSO	1.5 h	76
4	Cs_2CO_3	3	DMSO	45 min	80
5	Ag_2CO_3	3	DMSO	3.0 h	53
6	Li_2CO_3	3	DMSO	14 h	62
7	KOH	3	DMSO	2.5 h	61
8	DBU	3	DMSO	45 min	40
9	Et_3N	3	DMSO	1 h	62
10	K_2CO_3	2	DMSO	1.5 h	78
11	K_2CO_3	1	DMSO	6 h	69
12	K_2CO_3	3	DMF	16 h	77
13	K_2CO_3	3	THF	22 h	47
14	K_2CO_3	3	1,4-Dioxane	16 h	60
15	K_2CO_3	3	CH_3CN	22 h	62
16[b]	-	-	DMSO	24 h	n.d.

[a]All reactions were carried out with **1a** (0.03 g, 0.067 mmol, 1.0 equiv), benzamidine hydrochloride (0.01 g, 0.067 mmol, 1.0 equiv), base (equiv/mmol), and solvent (1.0 mL/equiv) in open air at rt. The product obtained was acetylated with Ac_2O, py, DMAP at 0 °C for 1 h. Yields are of isolated products in two-step. [b]Not detected; starting materials isolated.

broadening in ^{13}C NMR and difficulty in purification by column chromatography, this was acetylated with Ac_2O to isolate **2a**, which could be easily spectrally analysed, in 84% overall yield (Table 1, entry 1). As demonstrtated in Table 1, different bases such as KO^{t}Bu, Na_2CO_3, Cs_2CO_3, Ag_2CO_3, Li_2CO_3, KOH, DBU, or Et_3N could all initiate this transformation, but the product **2a** was formed either in lower yields or it was necessary to conduct the reaction for a longer period (entries 2-9, Table 1). Furthermore, employing K_2CO_3 in lower ratios (2.0 equiv)/(1.0 equiv) only reduced the yields (entries 10-11, Table 1), while the reaction did not proceed at all in absence of a base (entry 16). The use of other solvents (DMF, THF, 1,4-dioxane, and CH_3CN; entries 12−15, Table 1) also failed to deliver the required products in good yields. More importantly, despite the use of basic reaction conditions (K_2CO_3), no racemization was observed in the stereogenic centre next to the

carbonyl group. Thus, we concluded that the combination of K_2CO_3 (3.0 equiv) and DMSO at room temperature (entry 1, Table 1) constitutes the optimum reaction conditions.

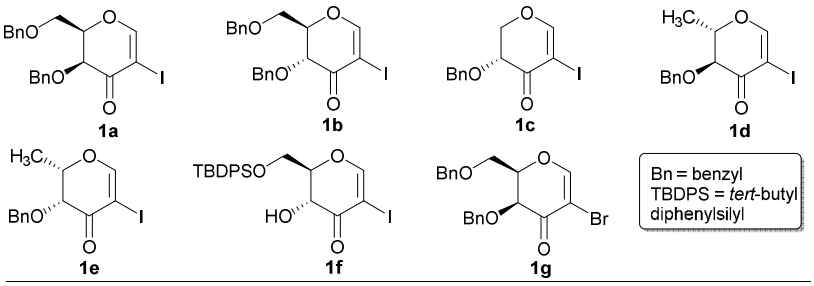
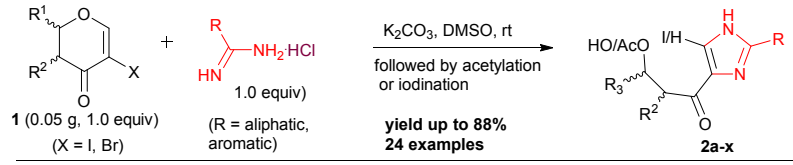


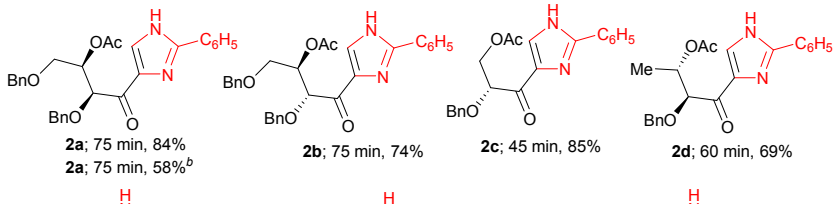
Figure 2. Substituted 2-haloenones **1a-g** derived from glycals used in this study.

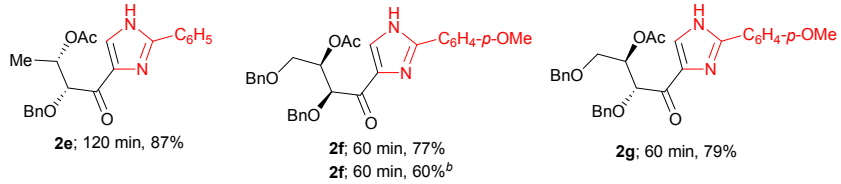
We next examined the substrate scope and generality of the approach using various 2-haloenones **1** (Figure 2)[7c,8-9] and aromatic/aliphatic amidines (Table 2). It is noteworthy that the electronic nature and location of the substituents on the aromatic/aliphatic ring of amidines or substitution/protection at carbohydrate components **1** did not influence the outcome of the reactions significantly (Table 2). In general, 2-iodoenones **1a-e** reacted with aromatic amidines containing an electron-neutral, electron-donating, or electron-deficient substituents on the aromatic ring or with aliphatic amidines such as *tert*-butylcarboxamidine hydrochloride or cyclopropylcarboxamidine hydrochloride to give chiral 2-substituted-imidazoles with (poly)hydroxylated side chains in moderate to excellent yields (**2a-v**, Table 2). 2-bromoenone (**1g**) also underwent similar conversion (to **2a**, **2f**, and **2n**, Table 2) under standard conditions, but the yields were 58-60%. The drop in yield with bromoenone compared to iodoenones may be due to the poor leaving character of bromide. To demonstrate the versatility of our developed approach, the same sequence of reactions was carried out with **1a** or **1b**, and the product obtained was iodinated (rather than acetylation) to produce optically active 5-iodoimidazoles **2w** and **2x** (Table 2).

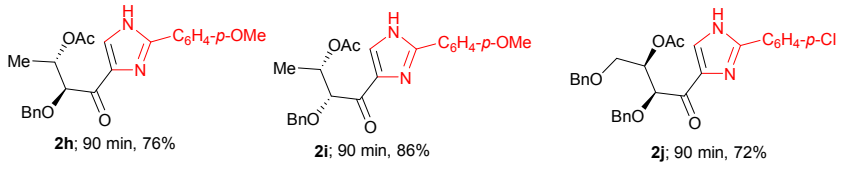
We next turned our attention to explore the substrate scope and generality of the reaction

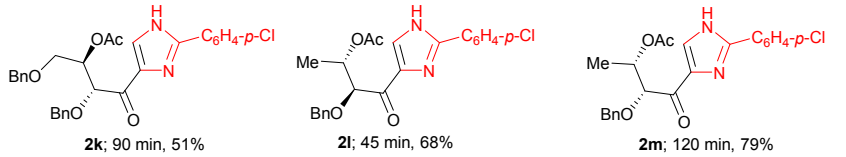
Table 2. Substrate Scope for Chiral Substituted Imidazoles[a]

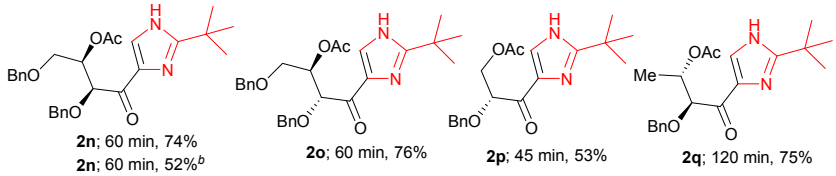


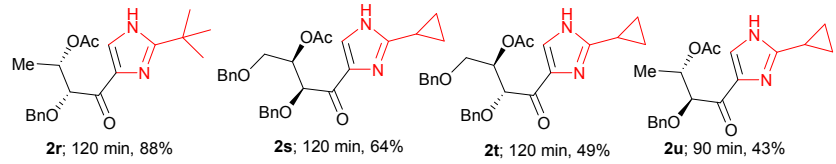


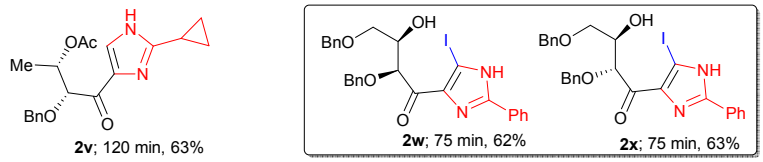








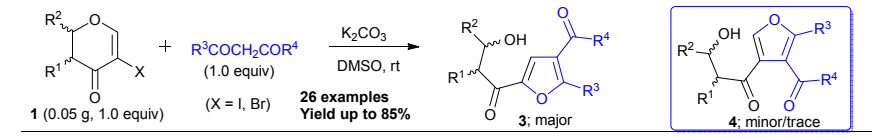


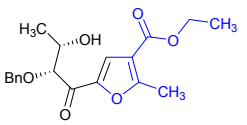


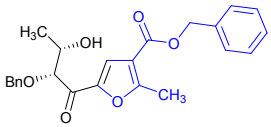
[a]Isolated yields of **2** in two-step utilizing 2-iodoenones as substrates. [b]Isolated yields of **2a**, **2f**, and **2n** from 2-bromoenone **1g**.

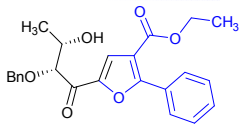
using various 2-haloenones **1** and 1,3-dicarbonyl compounds under similar reaction conditions. As shown in Table 3, the reaction is tolerant of variation in substituents in the substituted haloenones and active methylenes, which were smoothly converted into the

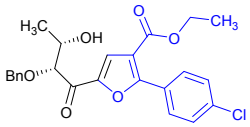
Table 3. Substrate scope for chiral substituted furans[a]

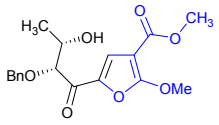


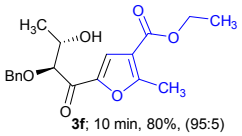

3a; 15 min, 78%, single

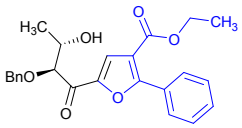

3b; 15 min, 73%, (95:5)

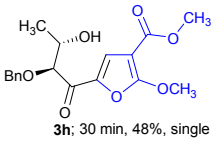

3c; 20 min, 67%, (90:10)

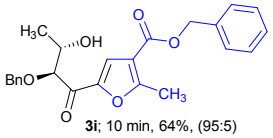

3d; 60 min, 40%, single

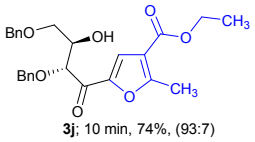

3e; 40 min, 40%, single

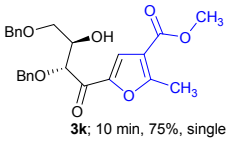

3f; 10 min, 80%, (95:5)

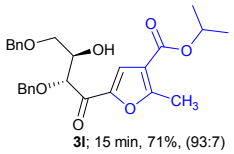

3g; 20 min, 64%, single

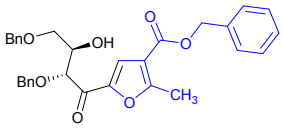

3h; 30 min, 48%, single

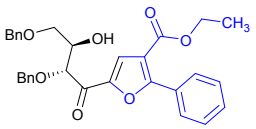

3i; 10 min, 64%, (95:5)

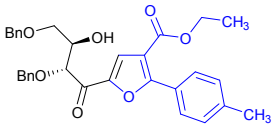

3j; 10 min, 74%, (93:7)

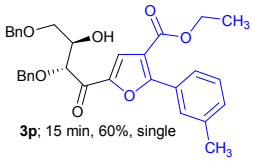

3k; 10 min, 75%, single

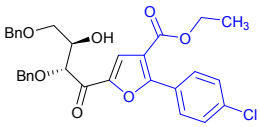

3l; 15 min, 71%, (93:7)

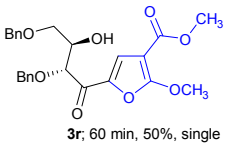

3m; 10 min, 85%, (94:6)

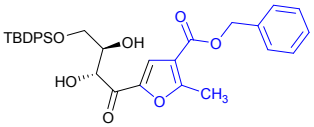

3n; 10 min, 56%, single

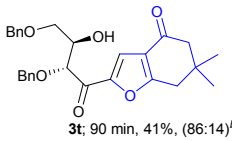

3o; 10 min, 61%, (95:5)

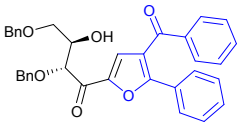

3p; 15 min, 60%, single

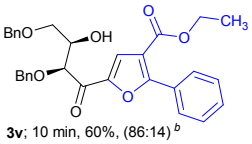

3q; 20 min, 61%, single

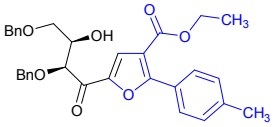

3r; 60 min, 50%, single

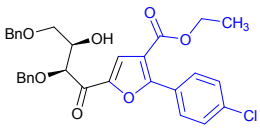

3s; 20 min, 44%, single

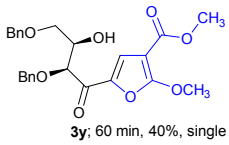

3t; 90 min, 41%, (86:14)[b]

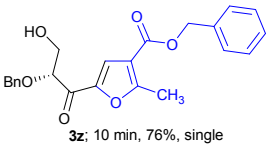

3u; 120 min, 16%, (88:12)


3v; 10 min, 60%, (86:14)[b]
3v; 20 min, 45%, (86:14)[b,c]


3w; 15 min, 56%, (90:10)


3x; 60 min, 43%, (88:12)[b]


3y; 60 min, 40%, single


3z; 10 min, 76%, single

[a]Isolated yields of **3** utilizing 2-iodoenones as substrates. The ratio of furan **3** and its regioisomer **4** was measured based on ^{1}H NMR analysis of the crude reaction mixture. The minor or trace products **4** proved inseparable by chromatography. [b]Inseparable mixtures. [c]Isolated yield of **3v** from 2-bromoenone **1g**.

corresponding optically active substituted furanyl-α-ketones in moderate to good yields and with an excellent level of regioselectivity (**3a-z**, Table 3). The drop in yield with a TBDPS group instead of benzyl group might be due to the hydrolysis of the primary silyl protection under strongly basic conditions (**3s**, Table 3). The reaction did not work well with β-diketones (**3t-u**, Table 3) compared to the other active methylene compounds, although the exact reason is not very clear at this moment.

The structures of selected optically active substituted imidazoles (**2a**, **2g**, **2i**, **2q**) and furans (**3a**, **3c**, **3f**, **3k**, **3r**, **3y)** were established by extensive 1D and 2D NMR analyses, while those of other products **2** and **3** were assigned by comparison of the 1D NMR chemical shift values for the characteristic resonances (Figure 3 and the Supporting Information for details). In addition, the single-crystal X-ray analysis of the α-benzyloxyvinyl ketone **5a** was carried out to confirm the proposed structure (see Scheme 4, *vide infra*). It must be mentioned here that though we indicate the formation of only one imidazole tautomer (Table 2), a perusal of the literature reveals that extremely fast proton transfers, depending upon solvent polarity and temperature, occur in solution between two tautomers of imidazole derivatives and these are indistinguishable by NMR technique.[5c,10] Therefore, the chiral imidazoles **2** might also exist in equilibrium between two tautomers and which are too fast in the NMR timescale.

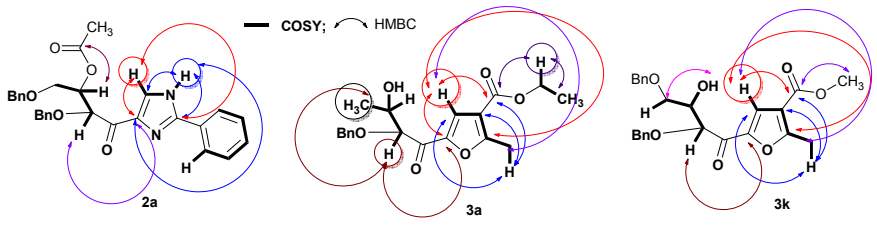


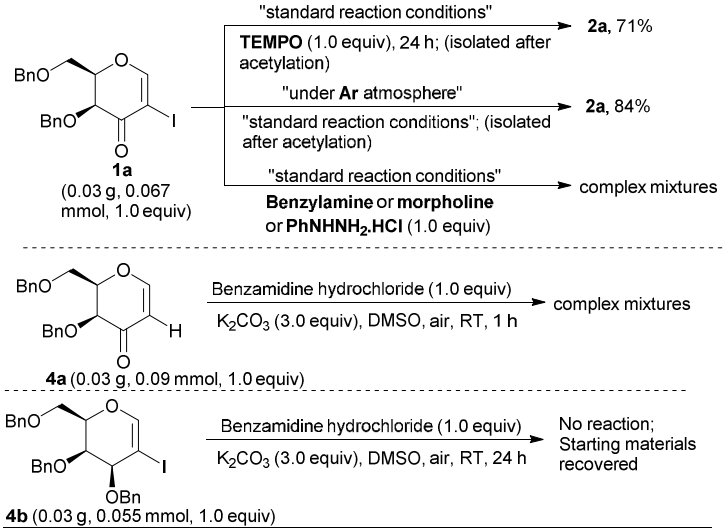
Figure 3. Key COSY and HMBC correlations observed with **2a**, **3a**, **3k** (stereochemistry omitted for clarity).

Interestingly, during the analyses of the ^{1}H-^{1}H COSY NMR experiments (2D) for substituted furans, we are surprised to observe the long-range ($^{5}J_{H\text{-}H}$) cross-peak between C_2-

CH_3 and C_4-H signal for all the tested substituted 2-methyl furans (**3a**, **3f**, **3k**, **5a**), which is quite unexpected and extremely rare in the literature (see the Supporting Information).[11] The zig-zag pathway (W-type coupling) between the concerned protons may account for this unusual correlation.

In order to gain insights into the mechanistic pathway, several control experiments were carried out (Scheme 2). When the reaction of **1a** and benzamidine hydrochloride was conducted with TEMPO (1.0 equiv) under optimized conditions, exclusive formation of **2a** in 71% yield occurred, ruling out the possibility of any radical reaction pathway (Scheme 2). To determine whether atmospheric oxygen (open air) has any effect in this cascade, the reaction was conducted under Ar atmosphere. This afforded **2a** in 84% yield, thus suggesting no role for atmospheric oxygen in the proposed mechanism. Moreover, when **1a** was subjected to the standard conditions with benzylamine, morpholine, or phenyl hydrazine hydrochloride, only degradation of the starting materials took place, may be due to the lack of 1,3-dinucleophilic species. This experiment also supports the formation of intermediate **IV** as a carbohydrate-imidazolium-based intermediate as described in Scheme 3. Furthermore, to confirm whether

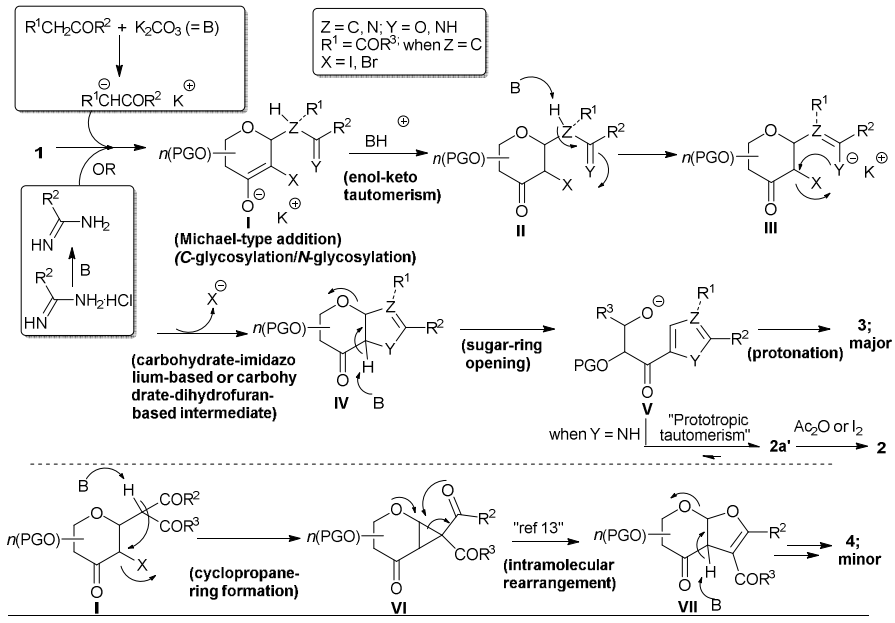
Scheme 2. Control Experiments



the substrates with a conjugated α,β-unsaturated α-iodocarbonyl are necessary, we performed two parallel experiments with **4a** and **4b**[12] under optimized reaction conditions (Scheme 2). However, no expected product was ever observed even upon heating the reaction mixture for several hours, thus suggesting that the formation of optically active imidazoles **2** may proceed through 1,4-addition (Michael-type addition) followed by intramolecular nucleophilic ring closure.

Based on the experimental results given in Table 2 and Table 3, the control experiments described in Scheme 2, and literature reports for Michael-type additions to carbohydrate-derived enones,[7b-d,f] a plausible mechanism for this novel cascade reaction is outlined in Scheme 3. We presume that initial base-induced Michael-type addition reaction of amidines or 1,3-dicarbonyl compounds to the haloenone **1** could lead to haloenolate **I**, which undergoes immediate proton transfer to generate intermediate **II** through enol-keto tautomerism. Intermediate **II** could form another enolate **III** and subsequent intramolecular

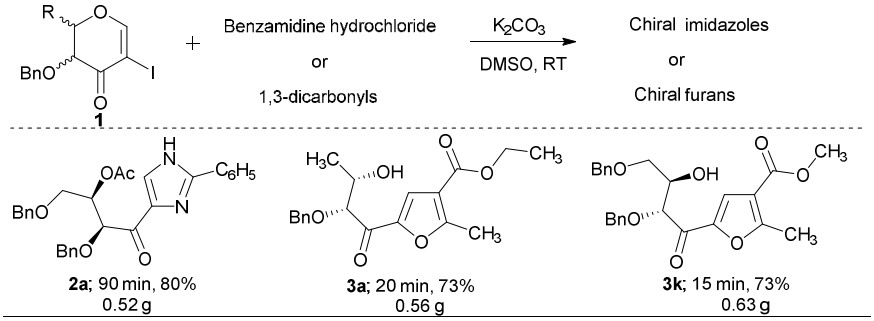
Scheme 3. Proposed Reaction Mechanism



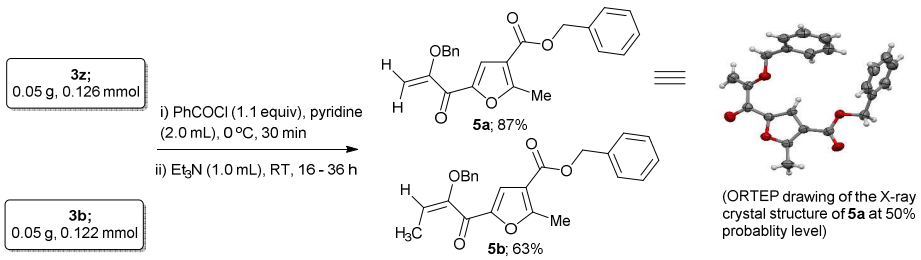
nucleophilic attack by nitrogen (for imidazoles) or oxygen (for furans) to eliminate the halogen produces the corresponding intermediate **IV**. This would then collapse by base-catalyzed sugar-ring opening via alkoxide elimination, leading to the formation of **3** via protonation of intermediate **V**. For imidazole derivatives, **V** could undergo a prototropic tautomerism to produce **2a'**. Unfortunately, attempts to isolate any of the proposed intermediates were unsuccessful. On the other hand, the formation of the minor/trace product **4** could be explained by base-mediated formation of an activated 1,2-cyclopropanated sugar **VI**, which undergoes intramolecular rearrangement to produce intermediate **VII**, as described in the literature.[13] This intermediate could then follow the pathway as described earlier for **3** in the proposed reaction mechanism (Scheme 3).

The efficacy of these developed procedures was demonstrated by accessing **2a**, **3a**, and **3k** on a large scale without any significant diminution in the yield (Table 4). Furthermore, to highlight the potentiality of these intermediates, the conversion of substituted furans **3z** and **3b** to synthetically valuable α-benzyloxyvinyl ketones **5a**-**b** was achieved in two steps (Scheme 4). The structure of **5a** was unambiguously established by single-crystal X-ray diffraction analysis (Scheme 4).[14]

Table 4. Scale-up Batches for Chiral Derivatives



Scheme 4. Synthetic Transformations to Furan-Derived α-Benzyloxyvinyl Ketones



CONCLUSION

In conclusion, we have developed a general and catalyst/ligand free cascade for the construction of chiral substituted imidazoles and furans under basic conditions at ambient temperature, utilizing readily available and inexpensive carbohydrates and amidines/1,3-dicarbonyls as starting materials. This cascade annulations process provides a straightforward access to these valuable scaffolds with good yields and excellent regioselectivity. The furan intermediates provide efficient access to synthetically valuable substituted α-benzyloxyvinyl ketones. The substituted 2-methylfurans show an intense long-range ($^5J_{H\text{-}H}$) cross-peak between C_2-CH_3 and C_4-H in ^{1}H-^{1}H COSY NMR experiments, which is rare in the literature. Further applications of these carbohydrate-derived 2-haloenones as potentially important synthetic precursors are being explored 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 vanillin charring solution. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solvent using TMS as the internal standard. HRMS (*m/z*) were measured using EI (magnetic sector,

positive ion) and ESI (Q-TOF, positive ion) techniques. Infrared (IR) spectra were recorded on Fourier transform infrared spectroscopy, only intense peaks were reported.

Experimental Section:

General Procedure for the synthesis of 1a-g. To a well-stirred solution of corresponding carbohydrate-derived enones (0.1 g, 1 equiv) in CCl_4/pyridine (1:1, 4 mL) at 0 ^oC, iodine or bromine (2.1 equiv) dissolved in CCl_4/pyridine (1:1, 4 mL) was added dropwise into it. Resulting reaction mixture was stirred for 2 h at ambient temperature (for iodination) or 0 ^oC for 1 h (for bromination). After completion of the reaction (TLC), the reaction mixture was extracted with DCM (20 mL), and washed successively with H_2O (10 mL), 1 N HCl (2 x 10 mL), and 20% aqueous $Na_2S_2O_3$ (10 mL) solution. The combined organic layer was dried over anhyd Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified by silica gel column chromatography [230-400; eluent: ethyl acetate/*n*-hexane] to obtain **1a-g**. The analytical data of compounds **1a**, **1b**, **1c**, **1d**, **1e** was exactly matched with those of the reported values.[7c,8b,9]

General Procedure for the Synthesis of 2. 2-Iodoenones/2-bromoenones **1** (0.05 g, 1.0 equiv), corresponding amidine salt (1.0 equiv), K_2CO_3 (3.0 equiv), and DMSO (1.0 mL) were added successively to a round bottom flask under open air at room temperature, and the mixture was stirred at the same temperature employing time as mentioned. After completion of the reaction (TLC), saturated ammonium chloride solution was added, and the product was extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a short pad of silica gel column [230-400; eluent: ethyl acetate/ *n*-hexane] to obtain a residue. The residue was acetylated with Ac_2O (2.0 equiv), DMAP (catalytic), py (0.5 mL) at 0 ^oC for 1 h. After completion of the reaction (TLC), saturated sodium bicarbonate solution was added at the same temperature, 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 over silica gel column chromatography [230-400; eluent: ethyl acetate/ *n*-hexane] to obtain **2**.

General procedure for the synthesis of 2w-x. 1a or **1b** (0.05 g, 1.0 equiv), corresponding amidine salt (1.0 equiv), K_2CO_3 (3.0 equiv), and DMSO (1.0 mL) was added successively in a round bottom flask under open air at room temperature, and the mixtures were stirred at the same temperature employing time as mentioned. After completion of the reaction (TLC), saturated ammonium chloride 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 passed through a short pad of silica gel column [230-400; eluent: ethyl acetate/ *n*-hexane] to obtain a residue. The residue was treated with I_2 (2.0 equiv), K_2CO_3 (2.0 equiv), DMSO (1.0 mL) at room temperature for 1 h. After completion of the reaction (TLC), saturated sodium thiosulfate solution was added into it. The product was extracted with EtOAc, and the organic layer was washed with 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 residue. The crude residue was purified over silica gel column chromatography [230-400; eluent: ethyl acetate/*n*-hexane] to obtain **2w-x**.

General Procedure for the synthesis of 3. 2-Iodoenones/2-bromoenones **1** (0.05 g, 1.0 equiv), K_2CO_3 (3.0 equiv), DMSO (1.0 mL), and the corresponding 1,3-dicarbonyls **2** (1.0 equiv) were added successively to a round bottom flask at ambient temperature under argon atmosphere, and the mixture was stirred at the same temperature employing time as mentioned. After completion of the reaction (TLC), saturated ammonium chloride solution was added, and the product was extracted with EtOAc. The combined organic layer was 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 over silica gel column chromatography [230-400; eluent: ethyl acetate/*n*-hexane] to obtain **3**.

General procedure for the synthesis of 5a-b. To a well-stirred solution of **3z** or **3b** (0.05 g, 1 equiv) in dry pyridine (1.5 mL) at 0 ^oC, benzoyl chloride (1.1 equiv/mmol) dissolved in pyridine (0.5 mL) and was added dropwise into it. The resulting reaction mixture was stirred at the same temperature for 30 min. After completion of the reaction (TLC), saturated sodium bicarbonate solution was added, and the product was extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a short pad of silica gel column [230-400; eluent: ethyl acetate/*n*-hexane] to obtain a residue. The residue was treated with Et_3N (1.0 mL, neat) at room temperature for 16-36 h. After completion of the reaction (TLC), saturated ammonium chloride 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 over silica gel column chromatography [230-400; eluent: ethyl acetate/*n*-hexane] to obtain **5a-b**.

(2*R*,3*R*)-2-(((*tert*-butyldiphenylsilyl)oxy)methyl)-3-hydroxy-5-iodo-2,3-dihydro-4*H*-pyran-4-one 1f. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (10%); isolated yield = 0.105 g, 76%; $[\alpha]_D^{20}$ = +88 (*c* = 0.11 in MeOH); colorless gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.79 (s, 1 H), 7.69 - 7.72 (m, 4 H), 7.44 - 7.47 (m, 2 H), 7.40 - 7.42 (m, 4 H), 4.66 (dd, *J* = 1.8, 13.2 Hz, 1 H), 4.30 (dt, *J* = 2.4, 13.2 Hz, 1 H), 4.10 (dd, *J* = 1.8, 12.0 Hz, 1 H), 4.07 (dd, *J* = 3.0, 12.0 Hz, 1 H), 3.45 (d, *J* = 1.8 Hz, 1 H), 1.08 ppm (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.3, 167.0, 135.6 (4 CH), 132.9, 132.8, 129.8, 127.8 (3 CH), 127.7 (2 CH), 83.8, 70.1, 67.6, 61.9 (CH_2), 26.7 (3

CH_3), 19.4 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2930, 2857, 1686, 1569, 1427, 1142, 1093, 1035, 968, 787, 742, 703, 610, 506 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{25}IO_4SiNa$ $[M + Na]^+$: 531.0465; found: 531.0456.

(2*R*,3*S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-5-bromo-2,3-dihydro-4*H*-pyran-4-one 1g. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (10%); isolated yield = 0.045 g, 72%; $[\alpha]_D^{20}$ = +4 (*c* = 0.14 in MeOH); white solid; mp 127 - 130 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71 (s, 1 H), 7.34 - 7.37 (m, 3 H), 7.31 - 7.33 (m, 3 H), 7.28 - 7.30 (m, 4 H), 4.72 (d, *J* = 12.0 Hz, 1 H), 4.56 - 4.58 (m, 2 H), 4.50 (d, *J* =12.0 Hz, 1 H), 4.48 (d, *J* = 12.0 Hz, 1 H), 3.94 (d, *J* = 2.4 Hz, 1 H), 3.90 (dd, *J* = 7.2, 10.8 Hz, 1 H), 3.76 ppm (dd, *J* = 6.0, 10.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 182.6, 161.5, 137.2, 136.5, 128.5 (2 CH), 128.5 (2 CH), 128.4 (2 CH), 128.2, 128.0, 127.8 (2 CH), 100.7, 81.4, 74.2, 73.7 (CH_2), 72.3 (CH_2), 67.1 (CH_2) ppm; IR (KBr): $\tilde{\nu}_{max}$ = 3039, 2876, 1684, 1574, 1364, 1272, 1089, 1032, 743, 697, 570 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{19}BrO_4Na$ $[M + Na]^+$: 425.0365; found: 425.0369.

(2*R*,3*S*)-1,3-bis(benzyloxy)-4-oxo-4-(2-phenyl-1*H*-imidazol-4-yl)butan-2-yl acetate 2a. Prepared according to the general procedure discussed above: eluent, R_f = 0.30; EtOAc/*n*-hexane (35%); isolated yield = 0.045 g, 84%; $[\alpha]_D^{20}$ = −2 (*c* = 0.065 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.08 (br. s., 1 H), 8.13 (s, 1 H), 8.01 - 8.02 (m, 2 H), 7.40 - 7.46 (m, 3 H), 7.22 - 7.33 (m, 10 H), 5.45 - 5.47 (m, 1 H), 4.74 (d, *J* = 12.0 Hz, 1 H), 4.59 (d, *J* = 4.2 Hz, 1 H), 4.49 (d, *J* = 11.4 Hz, 1 H), 4.46 (d, *J* = 6.0 Hz, 2 H), 3.73 (dd, *J* = 6.6, 9.6 Hz, 1 H), 3.62 (dd, *J* = 5.4, 10.2 Hz, 1 H), 1.92 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.2, 170.1, 151.2, 140.0, 137.4, 136.5, 131.2, 130.3, 129.0 (2 CH), 128.5 (2 CH), 128.4, 128.3 (4 CH), 128.2 (2 CH), 127.7, 127.6 (2 CH), 126.4, 81.6, 73.4 (CH_2), 73.2 (CH_2), 72.2, 67.4 (CH_2), 20.7 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2867, 1745, 1662, 1525, 1457,

1374, 1232, 1101, 1050, 745, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{28}N_2O_5Na$ [*M* + Na]$^+$: 507.1896; found: 507.1896.

(2*R*,3*R*)-1,3-bis(benzyloxy)-4-oxo-4-(2-phenyl-1*H*-imidazol-4-yl)butan-2-yl acetate 2b. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (35%); isolated yield = 0.039 g, 74%; $[\alpha]_D^{20}$ = +3 (*c* = 0.12 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.49 (br. s., 1 H), 8.11 (s, 1 H), 7.89 - 7.92 (m, 2 H), 7.47 - 7.49 (m, 3 H), 7.34 (m, 4 H), 7.25 - 7.28 (m, 6 H), 5.45 (q, *J* = 4.8 Hz, 1 H), 4.76 (d, *J* = 11.7 Hz, 1 H), 4.65 (d, *J* = 4.5 Hz, 1 H), 4.56 (d, *J* = 11.4 Hz, 1 H), 4.49 (m, 2 H), 3.80 (d, *J* = 4.5 Hz, 2 H), 2.01 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.7, 170.4, 150.6, 139.3, 137.6, 136.6, 131.0, 130.3, 129.0 (2 CH), 128.5 (2 CH), 128.5, 128.3 (2 CH), 128.2, 128.2 (2 CH), 127.6, 127.6 (2 CH), 126.2 (2 CH), 81.0, 73.3, 73.2 (CH_2), 73.1 (CH_2), 67.4 (CH_2), 20.9 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2924, 1742, 1659, 1458, 1373, 1234, 1097, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{28}N_2O_5Na$ [*M* + Na]$^+$: 507.1896; found: 507.1884.

(*R*)-2-(benzyloxy)-3-oxo-3-(2-phenyl-1*H*-imidazol-4-yl)propyl acetate 2c. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.047 g, 85%; $[\alpha]_D^{20}$ = +3 (*c* = 0.17 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.11 (br. s., 1 H), 8.15 (s, 1 H), 7.99 - 8.01 (m, 2 H), 7.44 - 7.45 (m, 3 H), 7.32 - 7.35 (m, 5 H), 4.75 (d, *J* = 11.4 Hz, 1 H), 4.62 (d, *J* = 11.4 Hz, 1 H), 4.53 - 4.57 (m, 2 H), 4.41 - 4.45 (m, 1 H), 2.01 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.3, 171.7, 152.1, 140.9, 137.5, 131.8, 131.5, 130.1 (2 CH), 129.7 (2 CH), 129.4, 129.3, 129.2 (2 CH), 127.3 (2 CH), 82.1, 73.8 (CH_2), 65.3 (CH_2), 21.8 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2924, 1743, 1663, 1525, 1457, 1379, 1231, 1118, 1044, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{20}N_2O_4Na$ [*M* + Na]$^+$: 387.1321; found: 387.1317.

(2*S*,3*S*)-3-(benzyloxy)-4-oxo-4-(2-phenyl-1*H*-imidazol-4-yl)butan-2-yl acetate 2d. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-

hexane (30%); isolated yield = 0.038 g, 69%; $[\alpha]_D^{20}$ = −24 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.65 (br. s., 1 H), 8.13 (s, 1 H), 7.92 - 7.95 (m, 2 H), 7.46 - 7.51 (m, 3 H), 7.35 (m, 5 H), 5.27 - 5.35 (m, 1 H), 4.78 (d, *J* = 12.0 Hz, 1 H), 4.55 (d, *J* = 11.7 Hz, 1 H), 4.47 (d, *J* = 3.6 Hz, 1 H), 1.99 (s, 3 H), 1.33 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.4, 170.5, 151.1, 139.8, 136.8, 131.1, 130.4, 129.1 (2 CH), 128.6 (3 CH), 128.2, 128.1 (2 CH), 126.4 (2 CH), 83.8, 72.9 (CH_2), 71.4, 21.1, 15.3 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2927, 1738, 1659, 1458, 1374, 1238, 1074, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}N_2O_4Na$ $[M + Na]^+$: 401.1478; found: 401.1491.

(2*S*,3*R*)-3-(benzyloxy)-4-oxo-4-(2-phenyl-1*H*-imidazol-4-yl)butan-2-yl acetate 2e. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (35%); isolated yield = 0.048 g, 87%; $[\alpha]_D^{20}$ = +18 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.74 (br. s., 1 H), 8.14 (s, 1 H), 7.96 - 7.97 (m, 2 H), 7.46 - 7.48 (m, 3 H), 7.33 (m, 5 H), 5.34 (quin, *J* = 6.0 Hz, 1 H), 4.77 (d, *J* = 11.7 Hz, 1 H), 4.50 (d, *J* = 11.7 Hz, 1 H), 4.22 (d, *J* = 4.8 Hz, 1 H), 1.94 (s, 3 H), 1.32 ppm (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.4, 170.3, 151.1, 140.0, 136.5, 131.2, 130.4, 129.0 (2 CH), 128.5 (3 CH), 128.2 (3 CH), 126.4 (2 CH), 85.1, 73.2 (CH_2), 70.4, 21.0, 16.5 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2928, 1740, 1660, 1525, 1457, 1375, 1238, 1069, 751, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}N_2O_4Na$ $[M + Na]^+$: 401.1478; found: 401.1496.

(2*R*,3*S*)-1,3-bis(benzyloxy)-4-(2-(4-methoxyphenyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2f. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.044 g, 77%; $[\alpha]_D^{20}$ = −5 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.33 (br. s., 1 H), 8.06 (s, 1 H), 7.86 (d, *J* = 9.0 Hz, 2 H), 7.22 - 7.30 (m, 10 H), 6.98 (d, *J* = 8.7 Hz, 2 H), 5.41 - 5.47 (m, 1 H), 4.73 (d, *J* = 11.4 Hz, 1 H), 4.53 (d, *J* = 3.9 Hz, 1 H), 4.46 - 4.50 (m, 3 H), 3.85 (s, 3 H), 3.71 (dd, *J* = 6.3, 9.6 Hz, 1 H), 3.61 (dd, *J* = 5.7, 9.9 Hz, 1 H), 1.94 ppm (s, 3 H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 188.8, 170.1, 161.4, 151.6, 140.3, 137.5, 136.6, 131.1, 128.5 (2 CH), 128.4 (2 CH), 128.2 (2 CH), 128.2 (2 CH), 128.2, 127.7, 127.6 (2 CH), 121.1, 114.5 (2 CH), 81.4, 73.3 (CH_2), 73.3 (CH_2), 72.3, 67.5 (CH_2), 55.3, 20.8 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2926, 1744, 1656, 1614, 1496, 1374, 1254, 1093, 1030, 839, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{30}N_2O_6Na$ $[M + Na]^+$: 537.2002; found: 537.2015.

(2*R*,3*R*)-1,3-bis(benzyloxy)-4-(2-(4-methoxyphenyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2g. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.045 g, 79%; $[\alpha]_D^{20}$ = +6 (*c* = 0.11 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.85 (br. s., 1 H), 8.10 (s, 1 H), 7.94 (d, *J* = 9.0 Hz, 2 H), 7.29 - 7.34 (m, 5 H), 7.24 - 7.25 (m, 2 H), 7.20 - 7.22 (m, 3 H), 6.96 (d, *J* = 9.0 Hz, 2 H), 5.42 (q, *J* = 4.8 Hz, 1 H), 4.74 (d, *J* = 12.0 Hz, 1 H), 4.68 (d, *J* = 4.8 Hz, 1 H), 4.51 (d, *J* = 11.4 Hz, 1 H), 4.47 (d, *J* = 12.0 Hz, 1 H), 4.43 (d, *J* = 12.0 Hz, 1 H), 3.83 (s, 3 H), 3.80 (dd, *J* = 5.4, 10.2 Hz, 1 H), 3.76 (dd, *J* = 4.2, 10.8 Hz, 1 H), 1.97 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.4, 170.4, 161.3, 151.0, 139.5, 137.6, 136.7, 130.8, 128.5 (2 CH), 128.3 (2 CH), 128.2, 128.1 (2 CH), 127.9 (2 CH), 127.6, 127.6 (2 CH), 121.2, 114.4 (2 CH), 80.9, 73.4, 73.2 (CH_2), 73.0 (CH_2), 67.5 (CH_2), 55.4, 20.9 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2927, 1742, 1654, 1614, 1496, 1476, 1374, 1254, 1092, 1029, 838, 741, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{30}N_2O_6Na$ $[M + Na]^+$: 537.2002; found: 537.2010.

(2*S*,3*S*)-3-(benzyloxy)-4-(2-(4-methoxyphenyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2h. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.045 g, 76%; $[\alpha]_D^{20}$ = −7 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.55 (br. s., 1 H), 8.13 (s, 1 H), 7.91 (d, *J* = 8.7 Hz, 2 H), 7.36 (m, 5 H), 7.00 (d, *J* = 9.0 Hz, 2 H), 5.28 - 5.36 (m, 1 H), 4.80 (d, *J* = 11.7 Hz, 1 H), 4.55 (d, *J* = 11.7 Hz, 1 H), 4.48 (d, *J* = 3.6 Hz, 1 H), 3.88 (s, 3 H), 2.01 (s, 3 H), 1.35 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.1, 170.4, 161.4, 151.5,

140.2, 136.9, 130.9, 128.5 (2 CH), 128.2 (2 CH), 128.1 (3 CH), 121.2, 114.4 (2 CH), 83.6, 72.8 (CH_2), 71.4, 55.3, 21.1, 15.3 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2933, 1740, 1656, 1615, 1497, 1375, 1252, 1181, 1070, 1028, 840, 744, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{24}N_2O_5Na$ [*M* + Na]$^+$: 431.1583; found: 431.1567.

(2*S*,3*R*)-3-(benzyloxy)-4-(2-(4-methoxyphenyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2i. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.051 g, 86%; $[\alpha]_D^{20}$ = +1 (*c* = 0.11 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.28 (br. s., 1 H), 8.14 (s, 1 H), 8.03 (d, *J* = 8.4 Hz, 2 H), 7.29 - 7.34 (m, 5 H), 6.96 (d, *J* = 9.0 Hz, 2 H), 5.34 - 5.38 (m, 1 H), 4.77 (d, *J* = 12.0 Hz, 1 H), 4.49 (d, *J* = 12.0 Hz, 1 H), 4.28 (d, *J* = 4.8 Hz, 1 H), 3.84 (s, 3 H), 1.94 (s, 3 H), 1.31 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.0, 170.3, 161.4, 151.4, 140.2, 136.6, 131.0, 128.5 (2 CH), 128.2, 128.1 (2 CH), 128.1 (2 CH), 121.1, 114.4 (2 CH), 84.8, 73.1 (CH_2), 70.4, 55.3, 21.0, 16.5 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2932, 1738, 1654, 1614, 1497, 1477, 1374, 1252, 1181, 1078, 1030, 838, 744, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{24}N_2O_5Na$ [*M* + Na]$^+$: 431.1583; found: 431.1573.

(2*R*,3*S*)-1,3-bis(benzyloxy)-4-(2-(4-chlorophenyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2j. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (35%); isolated yield = 0.041 g, 72%; $[\alpha]_D^{20}$ = −4 (*c* = 0.13 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.84 (br. s., 1 H), 8.10 (s, 1 H), 7.91 (d, *J* = 8.1 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.28 - 7.32 (m, 10 H), 5.42 - 5.47 (m, 1 H), 4.73 (d, *J* = 11.7 Hz, 1 H), 4.57 (d, *J* = 3.9 Hz, 1 H), 4.49 - 4.53 (m, 3 H), 3.73 (dd, *J* = 7.2, 9.6 Hz, 1 H), 3.63 (dd, *J* = 5.7, 9.9 Hz, 1 H), 1.95 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.5, 170.1, 150.3, 140.1, 137.4, 136.5, 136.4, 131.4, 129.3 (2 CH), 128.6 (2 CH), 128.4 (4 CH), 128.3 (2 CH), 127.8 (2 CH), 127.7 (2 CH), 127.0, 81.5, 73.5 (CH_2), 73.3 (CH_2), 72.3, 67.3 (CH_2), 20.8 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2866, 1745, 1662, 1480, 1425, 1373, 1231, 1095,

1050, 738, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{27}ClN_2O_5Na$ $[M + Na]^+$: 541.1506; found: 541.1506.

(2*R*,3*R*)-1,3-bis(benzyloxy)-4-(2-(4-chlorophenyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2k. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (%); isolated yield = 0.029 g, 51%; $[\alpha]_D^{20}$ = +3 (*c* = 0.13 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.73 (br. s., 1 H), 8.11 (s, 1 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.1 Hz, 2 H), 7.23 - 7.34 (m, 10 H), 5.40 - 5.45 (m, 1 H), 4.76 (d, *J* = 11.4 Hz, 1 H), 4.66 (d, *J* = 4.2 Hz, 1 H), 4.55 (d, *J* = 11.7 Hz, 1 H), 4.48 (s, 2 H), 3.80 (d, *J* = 5.4 Hz, 2 H), 2.01 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.0, 170.4, 149.9, 139.6, 137.5, 136.5, 136.4, 131.2, 129.3 (2 CH), 128.6 (2 CH), 128.3 (4 CH), 128.2 (2 CH), 127.7 (2 CH), 127.6 (2 CH), 127.0, 80.9, 73.4, 73.3 (CH_2), 73.2 (CH_2), 67.4 (CH_2), 20.9 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2925, 1742, 1659, 1462, 1372, 1234, 1094, 837, 738, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{27}ClN_2O_5Na$ $[M + Na]^+$: 541.1506; found: 541.1504.

(2*S*,3*S*)-3-(benzyloxy)-4-(2-(4-chlorophenyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2l. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (30%); isolated yield = 0.040 g, 68%; $[\alpha]_D^{20}$ = −8 (*c* = 0.11 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.00 (br. s., 1 H), 8.14 (s, 1 H), 7.94 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.34 (m, 5 H), 5.26 - 5.34 (m, 1 H), 4.77 (d, *J* = 11.7 Hz, 1 H), 4.54 (d, *J* = 11.7 Hz, 1 H), 4.50 (d, *J* = 4.2 Hz, 1 H), 1.99 (s, 3 H), 1.33 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.1, 170.1, 149.9, 139.6, 136.3, 136.1, 130.9, 128.9 (2 CH), 128.2 (2 CH), 127.9, 127.8 (2 CH), 127.4 (2 CH), 126.7, 83.2, 72.6 (CH_2), 71.0, 20.7, 14.8 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2927, 1738, 1658, 1478, 1464, 1373, 1238, 1089, 836, 737, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}ClN_2O_4Na$ $[M + Na]^+$: 435.1088; found: 435.1080.

(2*S*,3*R*)-3-(benzyloxy)-4-(2-(4-chlorophenyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2m. Prepared according to the general procedure discussed above: R_f = 0.30; eluent,

EtOAc/*n*-hexane (35%); isolated yield = 0.047 g, 79%; $[\alpha]_D^{20}$ = +1 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.71 (br. s., 1 H), 8.11 (s, 1 H), 7.89 (d, *J* = 8.7 Hz, 2 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 7.32 - 7.33 (m, 5 H), 5.29 - 5.37 (m, 1 H), 4.75 (d, *J* = 11.7 Hz, 1 H), 4.51 (d, *J* = 11.7 Hz, 1 H), 4.20 (d, *J* = 5.1 Hz, 1 H), 1.94 (s, 3 H), 1.32 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.6, 170.4, 150.4, 140.1, 136.6, 136.4, 131.4, 129.3 (2 CH), 128.6 (2 CH), 128.4, 128.2 (2 CH), 127.9 (2 CH), 127.0, 84.8, 73.3 (CH_2), 70.4, 21.0, 16.6 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2927, 1741, 1660, 1481, 1425, 1374, 1237, 1090, 1070, 838, 738, 697 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}ClN_2O_4Na$ $[M+Na]^+$: 435.1088; found: 435.1090.

(2*R*,3*S*)-1,3-bis(benzyloxy)-4-(2-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2n. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.038 g, 74%; $[\alpha]_D^{20}$ = −4 (*c* = 0.13 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.74 (br. s., 1 H), 7.92 (s, 1 H), 7.23 - 7.32 (m, 10 H), 5.37 - 5.43 (m, 1 H), 4.70 (d, *J* = 11.7 Hz, 1 H), 4.43 - 4.49 (m, 4 H), 3.68 (dd, *J* = 6.3, 9.9 Hz, 1 H), 3.59 (dd, *J* = 5.7, 9.6 Hz, 1 H), 1.94 (s, 3 H), 1.37 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.6, 170.1, 161.1, 138.3, 137.6, 136.6, 129.7, 128.5 (2 CH), 128.3 (2 CH), 128.1 (CH), 128.1 (2 CH), 127.7, 127.6 (2 CH), 81.5, 73.3 (CH_2), 73.2 (CH_2), 72.0, 67.4 (CH_2), 33.1, 29.0 (3 CH_3), 20.8 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2966, 2927, 2870, 1745, 1660, 1532, 1371, 1231, 1106, 1051, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{32}N_2O_5Na$ $[M + Na]^+$: 487.2209; found: 487.2203.

(2*R*,3*R*)-1,3-bis(benzyloxy)-4-(2-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2o. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (35%); isolated yield = 0.039 g, 76%; $[\alpha]_D^{20}$ = +1 (*c* = 0.15 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.79 (br. s., 1 H), 7.95 (s, 1 H), 7.28 - 7.32 (m, 10 H), 5.42 (br. s., 1 H), 4.72 (d, *J* = 11.1 Hz, 1 H), 4.60 (br. s., 1 H), 4.49 - 4.53 (m, 3 H), 3.77 (br. s., 2

H), 1.99 (s, 3 H), 1.38 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.5, 170.2, 161.1, 138.0, 137.8, 136.7, 129.7, 128.5 (2 CH), 128.3 (2 CH), 128.1, 128.1 (2 CH), 127.6, 127.5 (2 CH), 80.9, 73.2 (1 CH & 1 CH_2), 73.0 (CH_2), 67.6 (CH_2), 33.1, 29.1 (3 CH_3), 20.9 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2965, 2928, 2870, 1743, 1662, 1532, 1457, 1370, 1234, 1110, 741, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{32}N_2O_5Na$ $[M + Na]^+$: 487.2209; found: 487.2213.

(*R*)-2-(benzyloxy)-3-(2-(*tert*-butyl)-1*H*-imidazol-4-yl)-3-oxopropyl acetate 2p. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.028 g, 53%; $[\alpha]_D^{20}$ = +1 (*c* = 0.12 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.93 (br. s., 1 H), 7.96 (s, 1 H), 7.31 - 7.36 (m, 5 H), 4.72 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* = 11.4 Hz, 1 H), 4.46 - 4.49 (m, 2 H), 4.35 - 4.39 (m, 1 H), 2.01 (s, 3 H), 1.39 ppm (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.0, 171.6, 162.4, 139.5, 137.6, 130.4, 129.6 (2 CH), 129.3, 129.1 (2 CH), 82.0, 73.7 (CH_2), 65.3 (CH_2), 34.2, 30.1 (3 CH_3), 21.8 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2965, 2928, 1744, 1661, 1533, 1458, 1372, 1228, 1111, 1045, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{24}N_2O_4Na$ $[M + Na]^+$: 367.1634; found: 367.1637.

(2*S*,3*S*)-3-(benzyloxy)-4-(2-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2q. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.039 g, 75%; $[\alpha]_D^{20}$ = −7 (*c* = 0.11 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.09 (br. s., 1 H), 7.98 (s, 1 H), 7.29 - 7.36 (m, 5 H), 5.24 - 5.28 (m, 1 H), 4.75 (d, *J* = 12.0 Hz, 1 H), 4.50 (d, *J* = 11.4 Hz, 1 H), 4.42 (d, *J* = 4.2 Hz, 1 H), 1.97 (s, 3 H), 1.40 (s, 9 H), 1.31 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.0, 170.3, 161.2, 138.4, 136.8, 129.7, 128.5 (2 CH), 128.1, 128.0 (2 CH), 83.7, 72.8 (CH_2), 71.3, 33.1, 29.1 (3 CH_3), 21.1, 15.1 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2969, 1739, 1661, 1532, 1371, 1240, 1072, 748 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{26}N_2O_4Na$ $[M + Na]^+$: 381.1791; found: 381.1778.

(2*S*,3*R*)-3-(benzyloxy)-4-(2-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2r. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.046 g, 88%; $[\alpha]_D^{20}$ = +1 (*c* = 0.11 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.84 (br. s., 1 H), 7.96 (s, 1 H), 7.29 - 7.38 (m, 5 H), 5.29 (quin, *J* = 6.0 Hz, 1 H), 4.73 (d, *J* = 11.7 Hz, 1 H), 4.46 (d, *J* = 11.7 Hz, 1 H), 4.15 (d, *J* = 4.8 Hz, 1 H), 1.94 (s, 3 H), 1.39 (s, 9 H), 1.28 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.0, 170.2, 161.3, 138.5, 136.6, 129.8, 128.5 (2 CH), 128.1, 128.0 (2 CH), 85.3, 73.1 (CH_2), 70.3, 33.2, 29.1 (3 CH_3), 21.0, 16.5 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2968, 2931, 1741, 1658, 1532, 1372, 1238, 1070, 742, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{26}N_2O_4Na$ $[M+Na]^+$: 381.1791; found: 381.1800.

(2*R*,3*S*)-1,3-bis(benzyloxy)-4-(2-cyclopropyl-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2s. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.032 g, 64%; $[\alpha]_D^{20}$ = −6 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.49 (br. s., 1 H), 7.90 (s, 1 H), 7.29 - 7.32 (m, 4 H), 7.26 - 7.28 (m, 4 H), 7.22 (d, *J* = 7.2 Hz, 2 H), 5.39 - 5.41 (m, 1 H), 4.71 (d, *J* = 12.0 Hz, 1 H), 4.49 (d, *J* = 3.6 Hz, 1 H), 4.42 - 4.47 (m, 3 H), 3.68 (dd, *J* = 6.6, 10.2 Hz, 1 H), 3.58 (dd, *J* = 6.0, 9.6 Hz, 1 H), 1.97 - 2.00 (m, 1 H), 1.94 (s, 3 H), 1.08 (m, 2 H), 1.03 - 1.06 ppm (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.1, 171.2, 157.2, 140.1, 138.6, 137.6, 131.0, 129.5 (2 CH), 129.4 (2 CH), 129.2, 129.2 (2 CH), 128.7, 128.6 (2 CH), 82.4, 74.2 (CH_2), 74.2 (CH_2), 73.1, 68.6 (CH_2), 21.8, 10.3, 10.0 ppm (2 CH_2); IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2868, 1744, 1657, 1526, 1372, 1232, 1105, 1054, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{28}N_2O_5Na$ $[M + Na]^+$: 471.1896; found: 471.1902.

(2*R*,3*R*)-1,3-bis(benzyloxy)-4-(2-cyclopropyl-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2t. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.024 g, 49%; $[\alpha]_D^{20}$ = +1 (*c* = 0.1 in MeOH); colorless gum.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.01 (br. s., 1 H), 7.89 (s, 1 H), 7.28 - 7.32 (m, 10 H), 5.40 (m, 1 H), 4.72 (d, J = 11.1 Hz, 1 H), 4.57 (m, 1 H), 4.48 (m, 3 H), 3.77 (m, 2 H), 1.99 (s, 3 H), 1.93 - 1.95 (m, 1 H), 1.08 ppm (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.0, 170.2, 156.0, 138.8, 137.7, 136.8, 129.9, 128.5 (2 CH), 128.3 (2 CH), 128.1, 128.0 (2 CH), 127.6, 127.5 (2 CH), 80.7, 73.2, 73.2 (CH_2) 73.0 (CH_2), 67.6 (CH_2), 20.9, 9.3, 8.9 ppm (2 CH_2); IR (KBr): $\tilde{\nu}_{max}$ = 2924, 1742, 1657, 1522, 1371, 1234, 1107, 740, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{28}N_2O_5Na$ $[M + Na]^+$: 471.1896; found: 471.1887.

(2*S*,3*S*)-3-(benzyloxy)-4-(2-cyclopropyl-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2u. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (43%); isolated yield = 0.021 g, 43%; $[\alpha]_D^{20}$ = −8 (*c* = 0.11 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.73 (br. s., 1 H), 7.94 (s, 1 H), 7.29 - 7.36 (m, 5 H), 5.22 - 5.29 (m, 1 H), 4.74 (d, J = 12.0 Hz, 1 H), 4.47 (d, J = 12.0 Hz, 1 H), 4.40 (br. s., 1 H), 1.98 - 2.06 (m, 1 H), 1.96 (s, 3 H), 1.29 (d, J = 6.6 Hz, 3 H), 1.04 - 1.10 ppm (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.6, 171.3, 157.2, 140.1, 137.9, 130.9, 129.5 (2 CH), 129.1, 128.9 (2 CH), 84.7, 73.8 (CH_2), 72.4, 22.1, 16.2, 10.3, 9.9 (2 CH_2) ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2926, 1738, 1656, 1523, 1239, 1070 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{22}N_2O_4Na$ $[M + Na]^+$: 365.1478; found: 365.1470.

(2*S*,3*R*)-3-(benzyloxy)-4-(2-cyclopropyl-1*H*-imidazol-4-yl)-4-oxobutan-2-yl acetate 2v. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.031 g, 63%; $[\alpha]_D^{20}$ = +4 (*c* = 0.11 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.05 (br. s., 1 H), 7.91 (s, 1 H), 7.30 - 7.32 (m, 5 H), 5.27 (quin, J = 6.0 Hz, 1 H), 4.73 (d, J = 11.7 Hz, 1 H), 4.43 (d, J = 11.7 Hz, 1 H), 4.13 (d, J = 4.8 Hz, 1 H), 1.96 - 2.01 (m, 1 H), 1.94 (s, 3 H), 1.26 (d, J = 6.6 Hz, 3 H), 1.07 - 1.10 ppm (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.5, 170.3, 156.5, 139.4, 136.7, 130.0, 128.5 (2 CH), 128.1, 128.0 (2 CH), 84.9, 73.0 (CH_2), 70.4, 21.0, 16.5, 9.3, 9.0 (2 CH_2) ppm; IR (KBr): $\tilde{\nu}_{max}$

= 2927, 1740, 1656, 1526, 1374, 1238, 1069, 747, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{22}N_2O_4Na$ $[M + Na]^+$: 365.1478; found: 365.1460.

(2*S*,3*R*)-2,4-bis(benzyloxy)-3-hydroxy-1-(5-iodo-2-phenyl-1*H*-imidazol-4-yl)butan-1-one

2w. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (35%); isolated yield = 0.039 g, 62%; $[\alpha]_D^{20}$ = −9 (*c* = 0.12 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.15 (br. s., 1 H), 7.64 - 7.65 (m, 2 H), 7.40 - 7.43 (m, 1 H), 7.35 - 7.38 (m, 2 H), 7.27 - 7.34 (m, 8 H), 7.23 - 7.24 (m, 2 H), 4.59 (d, *J* = 10.8 Hz, 1 H), 4.56 (d, *J* = 12.0 Hz, 1 H), 4.51 - 4.55 (m, 2 H), 4.50 (d, *J* = 3.0 Hz, 1 H), 4.25 - 4.26 (m, 1 H), 3.72 (dd, *J* = 6.6, 9.6 Hz, 1 H), 3.65 (dd, *J* = 5.4, 10.2 Hz, 1 H), 2.95 ppm (d, *J* = 4.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.3, 150.7, 137.4, 136.1, 130.5, 130.4, 128.9 (2 CH), 128.7 (2 CH), 128.6, 128.5 (4 CH), 127.9, 127.8 (2 CH), 127.7, 125.9 (2 CH), 94.4, 84.1, 73.6 (2 CH_2), 71.3, 70.6 (CH_2) ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2924, 2858, 1661, 1591, 1458, 1385, 1236, 1074, 741, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{25}IN_2O_4Na$ $[M + Na]^+$: 591.0757; found: 591.0777.

(2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxy-1-(5-iodo-2-phenyl-1*H*-imidazol-4-yl)butan-1-one

2x. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (35%); isolated yield = 0.040 g, 63%; $[\alpha]_D^{20}$ = −1 (*c* = 0.12 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.16 (br. s., 1 H), 7.64 (d, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.2 Hz, 1 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 7.30 - 7.31 (m, 3 H), 7.23 - 7.29 (m, 7 H), 4.63 (d, *J* = 10.8 Hz, 2 H), 4.59 (d, *J* = 11.4 Hz, 1 H), 4.49 (s, 2 H), 4.34 (m, 1 H), 3.69 (dd, *J* = 4.2, 10.2 Hz, 1 H), 3.60 (dd, *J* = 6.6, 9.6 Hz, 1 H), 3.01 ppm (br. s., 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.8, 150.6, 137.3, 136.3, 131.0, 130.4, 128.9 (2 CH), 128.8 (2 CH), 128.5, 128.4 (2 CH), 128.4 (2 CH), 127.9, 127.8 (2 CH), 127.6, 125.9 (2 CH), 94.6, 84.4, 73.6 (CH_2), 73.4 (CH_2), 71.7, 70.0 (CH_2) ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2924, 2860, 1661, 1496, 1459,

1233, 1093, 745, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{25}IN_2O_4Na$ $[M + Na]^+$: 591.0757; found: 591.0770.

Ethyl 5-((2*R*,3*S*)-2-(benzyloxy)-3-hydroxybutanoyl)-2-methylfuran-3-carboxylate 3a. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (22%); isolated yield = 0.039 g, 78%; $[\alpha]_D^{20}$ = +8 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (s, 1 H), 7.30 - 7.36 (m, 5 H), 4.72 (d, *J* = 11.4 Hz, 1 H), 4.47 (d, *J* = 11.4 Hz, 1 H), 4.32 (q, *J* = 7.8, 14.4 Hz, 2 H), 4.14 (d, *J* = 6.0 Hz, 1 H), 4.07 - 4.12 (m, 1 H), 2.69 (s, 3 H), 2.62 (d, *J* = 4.8 Hz, 1 H), 1.36 (t, *J* = 7.2 Hz, 3 H), 1.19 ppm (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.6, 165.2, 163.7, 149.7, 137.6, 129.6 (2 CH), 129.4 (2 CH), 129.4, 122.5, 117.3, 88.2, 74.1 (CH_2), 69.9, 61.8 (CH_2), 19.7, 15.3, 15.3 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2927, 1719, 1668, 1592, 1528, 1432, 1241, 1097 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{22}O_6Na$ $[M + Na]^+$: 369.1314; found: 369.1321.

Benzyl 5-((2*R*,3*S*)-2-(benzyloxy)-3-hydroxybutanoyl)-2-methylfuran-3-carboxylate 3b. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.043 g, 73%; $[\alpha]_D^{20}$ = +4 (*c* = 0.25 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.42 (m, 5 H), 7.32 (m, 5 H), 5.32 (s, 2 H), 4.72 (d, *J* = 11.4 Hz, 1 H), 4.48 (d, *J* = 11.4 Hz, 1 H), 4.07 - 4.16 (m, 2 H), 2.71 (s, 3 H), 2.60 (d, *J* = 4.2 Hz, 1 H), 1.20 ppm (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.6, 164.4, 162.5, 148.8, 136.5, 135.5, 128.6 (2 CH), 128.5 (2 CH), 128.4, 128.3 (2 CH), 128.3 (2 CH), 128.1, 121.2, 115.9, 87.1, 73.1 (CH_2), 68.8, 66.5 (CH_2), 18.7, 14.3 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2926, 1721, 1670, 1592, 1529, 1454, 1235, 1094, 748, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{24}O_6Na$ $[M + Na]^+$: 431.1471; found: 431.1462.

Ethyl 5-((2*R*,3*S*)-2-(benzyloxy)-3-hydroxybutanoyl)-2-phenylfuran-3-carboxylate 3c. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.040 g, 67%; $[\alpha]_D^{20}$ = +1 (*c* = 0.2 in MeOH); colorless gum.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 - 8.09 (m, 2 H), 7.82 (s, 1 H), 7.46 - 7.50 (m, 3 H), 7.31 - 7.37 (m, 5 H), 4.76 (d, J = 11.4 Hz, 1 H), 4.53 (d, J = 11.4 Hz, 1 H), 4.35 (dd, J = 0.6, 7.2 Hz, 1 H), 4.33 (dd, J = 1.2, 7.2 Hz, 1 H), 4.25 (d, J = 6.6 Hz, 1 H), 4.17 (quin, J = 6.6 Hz, 1 H), 2.68 (br. s., 1 H), 1.36 (t, J = 7.2 Hz, 3 H), 1.24 ppm (d, J = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.8, 162.4, 160.8, 148.7, 136.6, 130.9, 129.1 (2 CH), 128.6 (2 CH), 128.4 (2 CH), 128.4, 128.3 (2 CH), 128.2, 122.9, 116.0, 87.2, 73.2 (CH_2), 68.8, 61.1 (CH_2), 18.8, 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2979, 2929, 1722, 1668, 1574, 1525, 1484, 1218, 1101, 763, 696 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{24}O_6Na$ $[M + Na]^+$: 431.1471; found: 431.1489.

Ethyl 5-((2*R*,3*S*)-2-(benzyloxy)-3-hydroxybutanoyl)-2-(4-chlorophenyl)furan-3-carboxylate 3d. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.026 g, 40%; $[\alpha]_D^{20}$ = −4 (c = 0.33 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.4 Hz, 2 H), 7.82 (s, 1 H), 7.46 (d, J = 8.4 Hz, 2 H), 7.33 - 7.36 (m, 5 H), 4.76 (d, J = 11.4 Hz, 1 H), 4.54 (d, J = 11.4 Hz, 1 H), 4.35 (q, J = 7.2, 14.4 Hz, 2 H), 4.22 (d, J = 6.0 Hz, 1 H), 4.15 - 4.17 (m, 1 H), 2.64 (br. s., 1 H), 1.37 (t, J = 6.6 Hz, 3 H), 1.24 ppm (d, J = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.8, 162.2, 159.5, 148.7, 137.1, 136.5, 130.4 (2 CH), 128.7 (2 CH), 128.6 (2 CH), 128.4 (2 CH), 128.4, 126.6, 122.9, 116.2, 87.3, 73.2 (CH_2), 68.8, 61.3 (CH_2), 18.7, 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2923, 2853, 1722, 1668, 1585, 1479, 1219, 1095, 838, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{23}ClO_6Na$ $[M + Na]^+$: 465.1081; found: 465.1098.

Methyl 5-((2*R*,3*S*)-2-(benzyloxy)-3-hydroxybutanoyl)-2-methoxyfuran-3-carboxylate 3e. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.020 g, 40%; $[\alpha]_D^{20}$ = +1 (c = 0.12 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (s, 1 H), 7.31 - 7.37 (m, 5 H), 4.72 (d, J = 11.4 Hz, 1 H), 4.47 (d, J = 11.4 Hz, 1 H), 4.27 (s, 3 H), 4.04 - 4.08 (m, 2 H), 3.83 (s, 3 H), 2.67 (br. s., 1 H), 1.18 ppm (d, J = 5.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 185.5, 164.2, 162.1,

141.1, 136.5, 128.6 (2 CH), 128.4 (2 CH), 128.3, 125.1, 94.4, 87.1, 73.0 (CH_2), 69.0, 58.6, 51.7, 18.6 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2928, 1718, 1657, 1597, 1544, 1409, 1243, 1100, 776 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{20}O_7Na$ $[M + Na]^+$: 371.1107; found: 371.1126.

Ethyl 5-((2*S*,3*S*)-2-(benzyloxy)-3-hydroxybutanoyl)-2-methylfuran-3-carboxylate 3f. Prepared according to the general procedure discussed above: R_f = 0.32; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.040 g, 80%; $[\alpha]_D^{20}$ = −1 (*c* = 0.12 in MeOH); colorless gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.66 (s, 1 H), 7.30 - 7.36 (m, 5 H), 4.73 (d, *J* = 11.4 Hz, 1 H), 4.47 (d, *J* = 11.4 Hz, 1 H), 4.34 (d, *J* = 4.8 Hz, 1 H), 4.31 (q, *J* = 7.2, 14.4 Hz, 2 H), 4.18 - 4.21 (m, 1 H), 2.68 (s, 3 H), 2.31 (d, *J* = 6.0 Hz, 1 H), 1.36 (t, *J* = 7.2 Hz, 3 H), 1.25 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.5, 163.9, 162.7, 148.9, 136.8, 128.5 (2 CH), 128.1 (3 CH), 121.2, 116.2, 85.8, 72.9 (CH_2), 68.8, 60.7 (CH_2), 18.9, 14.3, 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2980, 2931, 1719, 1675, 1593, 1528, 1434, 1242, 1098, 746, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{22}O_6Na$ $[M + Na]^+$: 369.1314; found: 369.1319.

Ethyl 5-((2*S*,3*S*)-2-(benzyloxy)-3-hydroxybutanoyl)-2-phenylfuran-3-carboxylate 3g. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.038 g, 64%; $[\alpha]_D^{20}$ = −1 (*c* = 0.10 in MeOH); colorless gum. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.06 - 8.09 (m, 2 H), 7.80 (s, 1 H), 7.45 - 7.49 (m, 3 H), 7.31 - 7.36 (m, 5 H), 4.78 (d, *J* = 11.4 Hz, 1 H), 4.52 (d, *J* = 11.4 Hz, 1 H), 4.45 (d, *J* = 5.1 Hz, 1 H), 4.33 (q, *J* = 7.2, 14.4 Hz, 2 H), 4.22 - 4.30 (m, 1 H), 2.20 (d, *J* = 6.9 Hz, 1 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 1.28 ppm (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.8, 162.4, 160.7, 148.9, 136.9, 130.8, 129.1 (2 CH), 128.5 (2 CH), 128.3 (3 CH), 128.2 (2 CH, C^0), 122.7, 115.9, 85.9, 72.9 (CH_2), 68.8, 61.1 (CH_2), 19.0, 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2980, 2929, 1722, 1675, 1572, 1525, 1485, 1450, 1218, 1102, 762, 695 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{24}O_6Na$ $[M + Na]^+$: 431.1471; found: 431.1484.

Methyl 5-((2*S*,3*S*)-2-(benzyloxy)-3-hydroxybutanoyl)-2-methoxyfuran-3-carboxylate 3h. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.024 g, 48%; $[\alpha]_D^{20}$ = −14 (*c* = 0.19 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (s, 1 H), 7.32 - 7.37 (m, 5 H), 4.73 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 11.4 Hz, 1 H), 4.26 (s, 3 H), 4.20 (d, *J* = 5.4 Hz, 1 H), 4.13 - 4.17 (m, 1 H), 3.82 (s, 3 H), 2.27 (d, *J* = 5.4 Hz, 1 H), 1.26 ppm (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 185.6, 164.1, 162.1, 141.3, 136.8, 128.5 (2 CH), 128.2, 128.2 (2 CH), 125.0, 94.4, 85.9, 72.9 (CH_2), 69.0, 58.6, 51.6, 19.1 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2928, 1718, 1659, 1598, 1545, 1409, 1244, 1100 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{20}O_7Na$ $[M + Na]^+$: 371.1107; found: 371.1113.

Benzyl 5-((2S,3S)-2-(benzyloxy)-3-hydroxybutanoyl)-2-methylfuran-3-carboxylate 3i: Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.038 g, 64%; $[\alpha]_D^{20}$ = −2 (*c* = 0.14 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (s, 1 H), 7.39 - 7.41 (m, 5 H), 7.31 (m, 5 H), 5.30 (s, 2 H), 4.72 (d, *J* = 11.4 Hz, 1 H), 4.45 (d, *J* = 11.4 Hz, 1 H), 4.33 (d, *J* = 5.1 Hz, 1 H), 4.16 - 4.22 (m, 1 H), 2.69 (s, 3 H), 2.12 (d, *J* = 6.9 Hz, 1 H), 1.24 ppm (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.5, 164.2, 162.5, 149.0, 136.8, 135.5, 128.6 (2 CH), 128.5 (2 CH), 128.4, 128.3 (2 CH), 128.1 (3 CH), 121.0, 115.9, 85.8, 72.9 (CH_2), 68.8, 66.5 (CH_2), 19.0, 14.4 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2927, 1720, 1673, 1591, 1529, 1429, 1235, 1094, 745, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{24}O_6Na$ $[M + Na]^+$: 431.1471; found: 431.1487.

Ethyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-methylfuran-3-carboxylate 3j. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (22%); isolated yield = 0.037 g, 74%; $[\alpha]_D^{20}$ = −1 (*c* = 0.15 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (s, 1 H), 7.28 - 7.36 (m, 10 H), 4.68 (d, *J* = 11.7 Hz, 1 H), 4.54 (d, *J* = 11.7 Hz, 1 H), 4.49 (d, *J* = 5.1 Hz, 1 H), 4.43 - 4.46 (m, 2 H), 4.33 (q, *J*

= 7.2, 14.4 Hz, 2 H), 4.16 - 4.24 (m, 1 H), 3.68 (d, *J* = 4.5 Hz, 2 H), 2.68 (s, 3 H), 2.56 (d, *J* = 7.2 Hz, 1 H), 1.37 ppm (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.0, 165.4, 164.3, 150.5, 139.1, 138.3, 130.0 (2 CH), 129.9 (2 CH), 129.7 (2 CH), 129.7, 129.3 (3 CH), 122.3, 117.6, 83.3, 74.9 (CH_2), 74.3 (CH_2), 73.1, 71.7 (CH_2), 62.2 (CH_2), 15.8 (2 CH_3) ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2926, 2864, 1720, 1676, 1592, 1530, 1453, 1236, 1093, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{28}O_7Na$ $[M + Na]^+$: 475.1733; found: 475.1742.

Methyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-methylfuran-3-carboxylate 3k. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.036 g, 75%; $[\alpha]_D^{20}$ = −1 (*c* = 0.17 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (s, 1 H), 7.25 - 7.34 (m, 10 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.51 (d, *J* = 12.0 Hz, 1 H), 4.46 (d, *J* = 10.8 Hz, 1 H), 4.42 - 4.44 (m, 2 H), 4.15 - 4.19 (m, 1 H), 3.84 (s, 3 H), 3.66 (d, *J* = 4.2 Hz, 2 H), 2.66 (s, 3 H), 2.55 - 2.58 ppm (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.4, 163.9, 163.2, 149.0, 137.6, 136.7, 128.5 (2 CH), 128.4 (2 CH), 128.2 (2 CH), 128.1, 127.8, 127.8 (2 CH), 120.7, 115.8, 81.7, 73.4 (CH_2), 72.8 (CH_2), 71.6, 70.1 (CH_2), 51.7, 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2924, 2865, 1722, 1677, 1594, 1530, 1449, 1244, 1100, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{26}O_7Na$ $[M + Na]^+$: 461.1577; found: 461.1577.

Isopropyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-methylfuran-3-carboxylate 3l. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.037 g, 71%; $[\alpha]_D^{20}$ = −1 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (s, 1 H), 7.26 - 7.33 (m, 10 H), 5.18 (dt, *J* = 6.3, 12.6 Hz, 1 H), 4.66 (d, *J* = 11.4 Hz, 1 H), 4.41 - 4.51 (m, 4 H), 4.15 - 4.22 (m, 1 H), 3.67 (d, *J* = 4.8 Hz, 2 H), 2.66 (s, 3 H), 2.53 (d, *J* = 7.2 Hz, 1 H), 1.33 ppm (d, *J* = 6.3 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.4, 163.7, 162.3, 148.9, 137.6, 136.8, 128.5 (2 CH), 128.4 (2 CH), 128.2 (2 CH), 128.1, 127.8 (3 CH), 120.9, 116.5, 81.7, 73.4 (CH_2),

72.8 (CH_2), 71.6, 70.1 (CH_2), 68.3, 21.9 (2 CH_3), 14.3 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2980, 2928, 2867, 1714, 1676, 1593, 1529, 1245, 1097, 742, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{30}O_7Na$ $[M + Na]^+$: 489.1890; found: 489.1906.

Benzyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-methylfuran-3-carboxylate 3m. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.0485 g, 85%; $[\alpha]_D^{20}$ = −1 (*c* = 0.12 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (s, 1 H), 7.41 - 7.43 (m, 5 H), 7.26 - 7.32 (m, 10 H), 5.31 (s, 2 H), 4.66 (d, *J* = 11.4 Hz, 1 H), 4.53 (d, *J* = 12.0 Hz, 1 H), 4.48 (d, *J* = 5.4 Hz, 1 H), 4.43 (d, *J* = 11.4 Hz, 2 H), 4.15 - 4.22 (m, 1 H), 3.67 (d, *J* = 4.2 Hz, 2 H), 2.68 (s, 3 H), 2.53 ppm (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.4, 164.1, 162.6, 149.0, 137.6, 136.8, 135.6, 128.6 (2 CH), 128.4 (2 CH), 128.4 (3 CH), 128.3 (2 CH), 128.2 (3 CH), 128.1, 127.8 (2 CH), 120.6, 115.8, 81.7, 73.4 (CH_2), 72.8 (CH_2), 71.5, 70.1 (CH_2), 66.4 (CH_2), 14.3 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2864, 1720, 1676, 1592, 1530, 1236, 1094, 743, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{30}O_7Na$ $[M + Na]^+$: 537.1890; found: 537.1899.

Ethyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-phenylfuran-3-carboxylate 3n. Prepared according to the general procedure discussed above: R_f = 0.31; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.032 g, 56%; $[\alpha]_D^{20}$ = −1 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 1.8, 6.9 Hz, 2 H), 7.76 (s, 1 H), 7.47 - 7.49 (m, 3 H), 7.28 - 7.33 (m, 10 H), 4.72 (d, *J* = 11.4 Hz, 1 H), 4.59 (d, *J* = 6.9 Hz, 1 H), 4.51 (t, *J* = 7.2 Hz, 3 H), 4.34 (q, *J* = 7.5, 14.4 Hz, 2 H), 4.22 - 4.29 (m, 1 H), 3.71 (d, *J* = 4.5 Hz, 2 H), 2.59 (d, *J* = 7.2 Hz, 1 H), 1.36 ppm (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.6, 162.4, 160.5, 149.0, 137.6, 136.8, 130.8, 129.1 (2 CH), 128.5 (2 CH), 128.4 (3 CH), 128.2 (4 CH), 128.2, 127.8 (3 CH), 122.2, 115.9, 81.7, 73.4 (CH_2), 72.8 (CH_2), 71.6, 70.1 (CH_2), 61.0 (CH_2), 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2926, 2865, 1722, 1677, 1576,

1526, 1485, 1217, 1102, 761, 696 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{30}O_7Na$ $[M + Na]^+$: 537.1890; found: 537.1904.

Ethyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-(*p*-tolyl)furan-3-carboxylate 3o. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.0355 g, 61%; $[\alpha]_D^{20}$ = −1 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 2 H), 7.74 (s, 1 H), 7.30 - 7.34 (m, 5 H), 7.28 - 7.30 (m, 5 H), 7.25 - 7.26 (m, 2 H), 4.70 (d, *J* = 11.4 Hz, 1 H), 4.58 (d, *J* = 6.6 Hz, 1 H), 4.53 (d, *J* = 12.0 Hz, 1 H), 4.48 (dd, *J* = 3.0, 12.0 Hz, 2 H), 4.31 (q, *J* = 7.2, 14.4 Hz, 2 H), 4.24 (quin, *J* = 4.2 Hz, 1 H), 3.68 (d, *J* = 4.2 Hz, 2 H), 2.65 (d, *J* = 7.2 Hz, 1 H), 2.42 (s, 3 H), 1.34 ppm (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.6, 163.5, 161.9, 149.8, 142.3, 138.6, 137.9, 130.1 (2 CH), 130.0 (2 CH), 129.5 (2 CH), 129.4 (2 CH), 129.3 (2 CH), 129.2 (2 CH), 128.8 (2 CH), 126.6, 123.4, 116.4, 82.7, 74.4 (CH_2), 73.8 (CH_2), 72.6, 71.2 (CH_2), 62.0 (CH_2), 22.6, 15.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2863, 1722, 1676, 1583, 1493, 1215, 1100, 1027, 742, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{32}H_{32}O_7Na$ $[M + Na]^+$: 551.2046; found: 551.2044.

Ethyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-(*m*-tolyl)furan-3-carboxylate 3p. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.035 g, 60%; $[\alpha]_D^{20}$ = +1 (*c* = 0.12 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 - 7.89 (m, 2 H), 7.76 (s, 1 H), 7.28 - 7.36 (m, 12 H), 4.72 (d, *J* = 11.7 Hz, 1 H), 4.58 (d, *J* = 6.9 Hz, 1 H), 4.51 (t, *J* = 7.8 Hz, 3 H), 4.33 (q, *J* = 6.9, 14.4 Hz, 2 H), 4.22 - 4.28 (m, 1 H), 3.71 (d, *J* = 4.2 Hz, 2 H), 2.60 (d, *J* = 7.2 Hz, 1 H), 2.43 (s, 3 H), 1.36 ppm (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.6, 162.4, 160.8, 148.9, 137.9, 137.6, 136.8, 131.6, 129.5, 128.5 (2 CH), 128.4 (2 CH), 128.2 (2 CH), 128.1, 128.1, 127.8, 127.8 (2 CH), 126.4 (CH, C), 122.3, 115.8, 81.7, 73.4 (CH_2), 72.8 (CH_2), 71.6, 70.1 (CH_2), 61.0 (CH_2), 21.4, 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2863, 1721, 1678, 1574,

1522, 1455, 1222, 1100, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{32}H_{32}O_7Na$ $[M + Na]^+$: 551.2046; found: 551.2040.

Ethyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-(4-chlorophenyl)furan-3-carboxylate 3q. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.037 g, 61%; $[\alpha]_D^{20} = -1$ (*c* = 0.30 in MeOH); colorless gum. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.7 Hz, 2 H), 7.76 (s, 1 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 7.28 - 7.33 (m, 10 H), 4.71 (d, *J* = 11.7 Hz, 1 H), 4.56 (d, *J* = 6.6 Hz, 1 H), 4.51 (t, *J* = 7.2 Hz, 3 H), 4.34 (q, *J* = 7.2, 14.4 Hz, 2 H), 4.21 - 4.29 (m, 1 H), 3.71 (d, *J* = 4.2 Hz, 2 H), 2.59 (d, *J* = 7.2 Hz, 1 H), 1.37 ppm (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.2, 163.8, 160.7, 150.6, 139.1, 138.5, 138.3, 131.9 (2 CH), 130.1 (2 CH), 130.0 (2 CH), 129.9 (2 CH), 129.8 (2 CH), 129.7, 129.4, 129.3 (2 CH), 128.3, 123.7, 117.7, 83.3, 75.0 (CH_2), 74.4 (CH_2), 73.2, 71.7 (CH_2), 62.7 (CH_2), 15.7 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2926, 2861, 1722, 1676, 1585, 1480, 1268, 1217, 1096, 1023, 838, 740, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{29}ClO_7Na$ $[M + Na]^+$: 571.1500; found: 571.1498.

Methyl 5-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-methoxyfuran-3-carboxylate 3r. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (42%); isolated yield = 0.025 g, 50%; $[\alpha]_D^{20} = -1$ (*c* = 0.16 in MeOH); colorless gum. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.25 - 7.35 (m, 10 H), 4.65 (d, *J* = 11.4 Hz, 1 H), 4.52 (d, *J* = 12.0 Hz, 1 H), 4.48 (d, *J* = 11.4 Hz, 1 H), 4.43 (d, *J* = 11.4 Hz, 1 H), 4.35 (d, *J* = 7.2 Hz, 1 H), 4.22 (s, 3 H), 4.12 - 4.16 (m, 1 H), 3.82 (s, 3 H), 3.67 (d, *J* = 4.2 Hz, 2 H), 2.59 ppm (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 185.5, 164.1, 162.2, 141.3, 137.6, 136.8, 128.5 (2 CH), 128.4 (2 CH), 128.2 (2 CH), 128.2, 127.8, 127.8 (2 CH), 124.5, 94.3, 81.4, 73.4 (CH_2), 72.7 (CH_2), 71.7, 70.2 (CH_2), 58.5, 51.6 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2866, 1719, 1663, 1598, 1545, 1409, 1245, 1099, 743, 701 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{26}O_8Na$ $[M + Na]^+$: 477.1526; found: 477.1540.

Benzyl 5-((2*R*,3*R*)-4-((*tert*-butyldiphenylsilyl)oxy)-2,3-dihydroxybutanoyl)-2-methylfuran-3-carboxylate 3s. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (30%); isolated yield = 0.025 g, 44%; $[\alpha]_D^{20} = -1$ (*c* = 0.14 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57 - 7.60 (m, 5 H), 7.39 - 7.43 (m, 6 H), 7.34 - 7.38 (m, 5 H), 5.34 (d, *J* = 12.0 Hz, 1 H), 5.30 (d, *J* = 12.0 Hz, 1 H), 4.89 (t, *J* = 6.6 Hz, 1 H), 3.98 - 4.02 (m, 1 H), 3.74 - 3.79 (m, 2 H), 3.61 (d, *J* = 7.8 Hz, 1 H), 2.73 (d, *J* = 8.4 Hz, 1 H), 2.67 (s, 3 H), 1.00 ppm (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.5, 164.2, 162.4, 148.5, 135.5, 135.5 (2 CH), 135.4 (2 CH), 132.5 (2 C^0), 129.9, 129.9, 128.7 (2 CH), 128.5, 128.3 (2 CH), 127.8 (2 CH), 127.8 (2 CH), 120.5, 116.1, 74.4, 73.4, 66.6 (CH_2), 63.7 (CH_2), 26.7 (3 CH_3), 19.1, 14.4 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2928, 2857, 1721, 1674, 1594, 1533, 1427, 1236, 1109, 743, 702 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{36}O_7SiNa$ $[M + Na]^+$: 595.2128; found: 595.2106.

2-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one 3t and 3-((2*R*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one 4t. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (28%); isolated yield = 0.021 g, 41%; colorless gum; **3t**:**4t** = 86:14; inseparable mixtures. Major peaks: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (s, 1 H), 7.24 - 7.35 (m, 10 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.51 (d, *J* = 12.0 Hz, 1 H), 4.46 (d, *J* = 12.0 Hz, 1 H), 4.42 - 4.44 (m, 2 H), 4.16 (m, 1 H), 3.67 (dd, *J* = 1.2, 4.8 Hz, 2 H), 2.81 (s, 2 H), 2.54 (d, *J* = 7.2 Hz, 1 H), 2.42 (s, 2 H), 1.16 (s, 3 H), 1.15 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.3, 188.1, 169.8, 151.2, 137.6, 136.7, 128.5 (2 CH), 128.4 (2 CH), 128.2 (3 CH), 127.8, 127.8 (2 CH), 121.4, 115.8, 81.9, 73.4 (CH_2), 72.9 (CH_2), 71.6, 70.0 (CH_2), 52.0 (CH_2), 37.5 (CH_2), 35.1, 28.6, 28.5 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2958, 2928, 2869, 1677, 1584, 1525, 1452, 1208, 1118, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{28}H_{30}O_6Na$ $[M + Na]^+$: 485.1940; found: 485.1922.

(2*R*,3*R*)-1-(4-Benzoyl-5-phenylfuran-2-yl)-2,4-bis(benzyloxy)-3-hydroxybutan-1-one 3u and (2*R*,3*R*)-1-(4-Benzoyl-5-phenylfuran-3-yl)-2,4-bis(benzyloxy)-3-hydroxybutan-1-one 4u. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.010 g, 16 %; $[\alpha]_D^{20} = -1$ (*c* = 0.40 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (t, *J* = 7.2 Hz, 3 H), 7.53 - 7.56 (m, 2 H), 7.26 - 7.42 (m, 16 H), 4.71 (d, *J* = 11.4 Hz, 1 H), 4.59 (d, *J* = 6.9 Hz, 1 H), 4.46 - 4.52 (m, 3 H), 4.21 - 4.28 (m, 1 H), 3.70 (d, *J* = 3.9 Hz, 2 H), 2.60 ppm (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.5, 187.7, 158.8, 149.2, 137.6, 137.2, 136.8, 133.4, 130.5, 129.7 (2 CH), 128.6 (2 CH), 128.5 (2 CH), 128.5 (2 CH), 128.4 (2 CH), 128.3, 128.2 (2 CH), 128.2 (3 CH), 127.8, 127.7 (2 CH), 122.5, 122.2, 81.7, 73.4 (CH_2), 72.9 (CH_2), 71.6, 70.1 (CH_2) ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2924, 2858, 1660, 1565, 1480, 1450, 1389, 1265, 1075, 893, 732, 695 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{35}H_{30}O_6Na$ $[M + Na]^+$: 569.1940; found: 569.1942.

Ethyl 5-((2*S*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-phenylfuran-3-carboxylate 3v and Ethyl 4-((2*S*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-phenylfuran-3-carboxylate 4v. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.034 g, 60%; colorless gum; **3v**:**4v** = 86:14; inseparable mixtures. Major peaks: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 - 8.08 (m, 2 H), 7.76 (s, 1 H), 7.43 - 7.47 (m, 3 H), 7.24 - 7.32 (m, 10 H), 4.78 (d, *J* = 11.4 Hz, 1 H), 4.69 (d, *J* = 4.2 Hz, 1 H), 4.42 - 4.51 (m, 3 H), 4.32 (q, *J* = 6.9, 14.1 Hz, 2 H), 4.20 - 4.28 (m, 1 H), 3.60 (d, *J* = 5.4 Hz, 2 H), 2.63 (d, *J* = 6.6 Hz, 1 H), 1.34 ppm (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.2, 162.4, 160.5, 148.8, 137.6, 136.7, 130.8, 129.1 (2 CH), 128.5 (2 CH), 128.4 (2 CH), 128.3 (2 CH), 128.3 (3 CH), 127.7 (3 CH, C^0), 122.4, 115.9, 81.8, 73.4 (CH_2), 73.0 (CH_2), 71.6, 70.1 (CH_2), 61.1 (CH_2), 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2927, 2867, 1722, 1675, 1575, 1526, 1486, 1451, 1390, 1218, 1102, 760, 696 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{30}O_7Na$ $[M + Na]^+$: 537.1890; found: 537.1890.

Ethyl 5-((2*S*,3*R*)-2,4-bis(bdenzyloxy)-3-hydroxybutanoyl)-2-(*p*-tolyl)furan-3-carboxylate 3w. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.0325 g, 56%; $[\alpha]_D^{20}$ = +1 (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 2 H), 7.77 (s, 1 H), 7.23 - 7.34 (m, 12 H), 4.79 (d, *J* = 11.4 Hz, 1 H), 4.71 (d, *J* = 4.2 Hz, 1 H), 4.43 - 4.52 (m, 3 H), 4.33 (q, *J* = 7.2, 14.4 Hz, 2 H), 4.22 - 4.27 (m, 1 H), 3.62 (d, *J* = 6.0 Hz, 2 H), 2.66 (d, *J* = 6.6 Hz, 1 H), 2.43 (s, 3 H), 1.36 ppm (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.1, 162.5, 160.9, 148.5, 141.3, 137.6, 136.8, 129.0 (5 CH), 128.5 (2 CH), 128.4 (2 CH), 128.3 (2 CH), 128.2, 127.7 (2 CH), 125.5, 122.6, 115.4, 81.7, 73.4 (CH_2), 73.0 (CH_2), 71.6, 70.1 (CH_2), 61.0 (CH_2), 21.6, 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2926, 1721, 1666, 1585, 1493, 1269, 1216, 1099, 742, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{32}H_{32}O_7Na$ $[M + Na]^+$: 551.2046; found: 551.2056.

Ethyl 5-((2*S*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-(4-chlorophenyl)furan-3-carboxylate 3x and Ethyl 4-((2*S*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-(4-chlorophenyl)furan-3-carboxylate 4x. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.026 g, 43%; colorless gum; **3x**:**4x** = 88:12; inseparable mixtures. Major peaks: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.4 Hz, 2 H), 7.76 (s, 1 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.22 - 7.34 (m, 10 H), 4.78 (d, *J* = 11.4 Hz, 1 H), 4.68 (d, *J* = 4.2 Hz, 1 H), 4.43 - 4.51 (m, 3 H), 4.32 (q, *J* = 7.2, 14.4 Hz, 2 H), 4.24 (br. s., 1 H), 3.61 (d, *J* = 6.0 Hz, 2 H), 2.69 (br. s., 1 H), 1.35 ppm (t, *J* = 7.8 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.3, 162.3, 159.2, 148.8, 137.6, 137.0, 136.7, 130.3 (2 CH), 128.6 (2 CH), 128.5 (2 CH), 128.4 (2 CH), 128.4 (2 CH), 128.3, 127.8, 127.7 (2 CH), 126.7, 122.4, 116.2, 81.9, 73.4 (CH_2), 73.1 (CH_2), 71.6, 70.1 (CH_2), 61.2 (CH_2), 14.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2924, 2854, 1723, 1682, 1586, 1478, 1268, 1218, 1095,

839, 741, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{29}ClO_7Na$ $[M + Na]^+$: 571.1500; found: 571.1518.

Methyl 5-((2*S*,3*R*)-2,4-bis(benzyloxy)-3-hydroxybutanoyl)-2-methoxyfuran-3-carboxylate 3y. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (40%); isolated yield = 0.02 g, 40%; $[\alpha]_D^{20} = -1$ (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.27 - 7.35 (m, 8 H), 7.23 - 7.25 (m, 2 H), 4.73 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 4.2 Hz, 1 H), 4.42 - 4.45 (m, 3 H), 4.18 (s, 3 H), 4.12 (quin, *J* = 6.0 Hz, 1 H), 3.81 (s, 3 H), 3.56 (dd, *J* = 3.0, 5.4 Hz, 2 H), 2.66 ppm (d, *J* = 6.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 185.1, 164.1, 162.1, 141.1, 137.6, 136.7, 128.5 (2 CH), 128.4 (2 CH), 128.3 (2 CH), 128.3, 127.7 (2 CH), 127.7, 124.6, 94.4, 81.5, 73.4 (CH_2), 72.9 (CH_2), 71.8, 70.1 (CH_2), 58.5, 51.6 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2861, 1719, 1655, 1598, 1545, 1408, 1243, 1100, 744, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{26}O_8Na$ $[M + Na]^+$: 477.1526; found: 477.1508.

Benzyl (*R*)-5-(2-(benzyloxy)-3-hydroxypropanoyl)-2-methylfuran-3-carboxylate 3z. Prepared according to the general procedure discussed above: R_f = 0.40; eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.045 g, 76%; $[\alpha]_D^{20} = -1$ (*c* = 0.10 in MeOH); colorless gum. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (s, 1 H), 7.36 - 7.43 (m, 5 H), 7.31 - 7.34 (m, 5 H), 5.32 (d, *J* = 12.0 Hz, 1 H), 5.29 (d, *J* = 12.6 Hz, 1 H), 4.75 (d, *J* = 11.4 Hz, 1 H), 4.55 (dd, *J* = 3.6, 6.0 Hz, 1 H), 4.52 (d, *J* = 11.4 Hz, 1 H), 3.95 (ddd, *J* = 4.2, 7.8, 12.0 Hz, 1 H), 3.90 (dt, *J* = 6.0, 12.0 Hz, 1 H), 2.69 (s, 3 H), 2.22 ppm (t, *J* = 6.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.7, 164.3, 162.5, 148.5, 136.7, 135.5, 128.7 (2 CH), 128.6 (2 CH), 128.4, 128.3 (3 CH), 128.2 (2 CH), 121.0, 115.9, 82.8, 72.8 (CH_2), 66.5 (CH_2), 63.6 (CH_2), 14.4 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2927, 1720, 1675, 1592, 1530, 1429, 1236, 1096, 744, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{22}O_6Na$ $[M + Na]^+$: 417.1314; found: 417.1304.

Benzyl 5-(2-(benzyloxy)acryloyl)-2-methylfuran-3-carboxylate 5a. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (10%); isolated yield = 0.041 g, 87%; white solid, mp 122 - 124 °C; solvent of crystallization, acetone. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (s, 1 H), 7.38 - 7.44 (m, 7 H), 7.33 - 7.34 (m, 3 H), 5.47 (d, J = 3.0 Hz, 1 H), 5.28 (s, 2 H), 4.98 (s, 2 H), 4.74 (d, J = 3.0 Hz, 1 H), 2.71 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.5, 164.6, 162.8, 157.3, 148.4, 135.7, 135.6, 128.7 (2 CH), 128.7 (2 CH), 128.4, 128.4, 128.3 (2 CH), 127.7 (2 CH), 122.9, 115.7, 94.1 (CH_2), 70.7 (CH_2), 66.4 (CH_2), 14.4 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 3140, 2951, 1707, 1656, 1605, 1411, 1329, 1278, 1227, 1136, 1086, 1020, 954, 867, 753, 699 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{20}O_5Na$ $[M + Na]^+$: 399.1209; found: 399.1219.

Benzyl (*E*)-5-(2-(benzyloxy)but-2-enoyl)-2-methylfuran-3-carboxylate 5b. Prepared according to the general procedure discussed above: R_f = 0.30; eluent, EtOAc/*n*-hexane (10%); isolated yield = 0.03 g, 63%; colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (s, 1 H), 7.31 - 7.43 (m, 10 H), 6.28 (q, J = 7.2 Hz, 1 H), 5.31 (s, 2 H), 4.84 (s, 2 H), 2.71 (s, 3 H), 1.80 ppm (d, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.6, 164.2, 162.7, 152.2, 149.0, 136.5, 135.7, 128.6 (2 CH), 128.6 (2 CH), 128.5 (2 CH), 128.4, 128.3, 128.3 (2 CH), 125.0, 121.1, 115.5, 73.7 (CH_2), 66.4 (CH_2), 14.4, 11.5 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 3033, 2927, 1721, 1644, 1528, 1430, 1308, 1238, 1135, 1077, 876, 757, 697 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{22}O_5Na$ $[M + Na]^+$: 413.1365; found: 413.1357.

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

Copies of 1D and 2D NMR spectra, and X-ray crystal structure of **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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