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Selective Functionalization of Achmatowicz Rearrangement Products by Reactions with Potassium Organotrifluoroborates under Transition-Metal-Free Conditions

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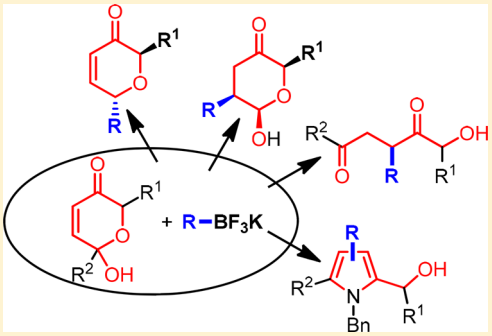
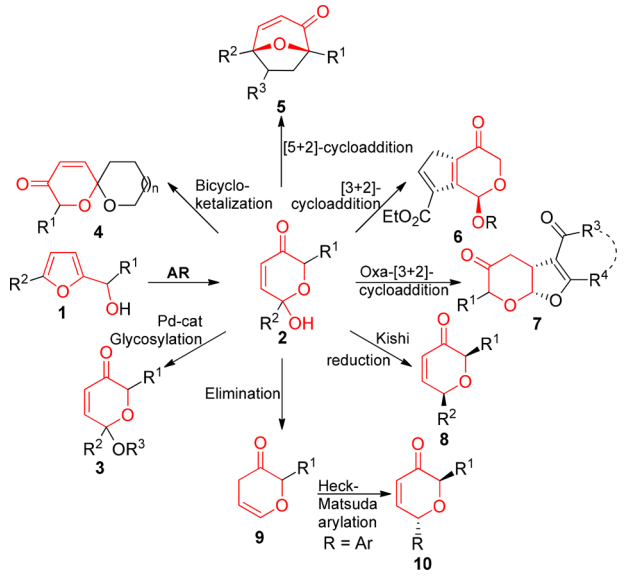
Supporting Information

ABSTRACT: The repertoire of synthetic transformations of the products of the Achmatowicz rearrangement has been expanded by exploring their reactivity with potassium organotrifluoroborates in the absence of transition metals. Depending on the reaction conditions and the substitution pattern of the starting material, the reaction may lead to the stereoselective synthesis of dihydropyranones (2,6-*trans*), tetrahydropyranones (2,3-*cis*-2,6-*cis*) or functionalized 1,4-dicarbonyl compounds. The method has also been adapted for the one-pot synthesis of functionalized pyrroles.



The Achmatowicz rearrangement (AR) consists of an oxidative ring-expansion rearrangement of readily available 2-furfuryl alcohols **1** to 6-hydroxy-3-pyranones **2** (also known as pyranuloses) (Scheme 1).[1,2] Due to their dense functionalization, the AR products **2** constitute useful starting materials for the preparation of an ample variety of molecules with dihydropyran or tetrahydropyran core, such as dihydropyranones, oxidopyryliums, δ-lactones, or pyranoses.[3]

Scheme 1. Previous Work: Synthesis and Transformations of AR Products



Thus, for example, AR products participate as glycosyl donors in Pd-catalyzed glycosylation reactions (**2** → **3**, Feringa−O'Doherty *O*-glycosylation),[4] in bicycloketalization reactions (**2** → **4**),[5] as 1,3-dipoles in [5 + 2]-cycloadditions with alkenes under basic conditions (**2** → **5**),[6] as 2π components in phosphine-catalyzed [3 + 2]-cycloaddition reactions with allenoates (**2** → **6**),[7] as 2π components in Pd-catalyzed oxa-[3 + 2]-cycloaddition reactions with 1,3-dicarbonyl compounds (**2** → **7**),[8] or in the Kishi reduction, which leads to *cis*-2,6-dihydropyranones **8**.[9] Additionally, by means of a two-step sequence consisting of elimination (**2** → **9**) followed by Heck−Matsuda arylation (Pd-catalyzed coupling with aryldiazonium salts), they may also give rise to *trans*-2,6-dihydropyranones **10**.[10] Many of these transformations have been used in the synthesis of natural products, bioactive carbohydrates, and advanced pharmaceutical ingredients.

However, taking into consideration the simultaneous presence of the hemiacetal and α,β-unsaturated ketone moieties, the synthetic potential of these densely functionalized compounds as pluripotent molecular platforms for diversity oriented synthesis (DOS) is still poorly developed.[11] In this context, we were interested in finding new transformations of the AR products **2** using aryl, alkenyl and alkynyl potassium organotrifluoroborates **11** as reagents. The interest of these reagents in synthesis is due to the fact that they are bench-stable reagents that can be used without the need for protection from humidity, and are compatible with unpro-

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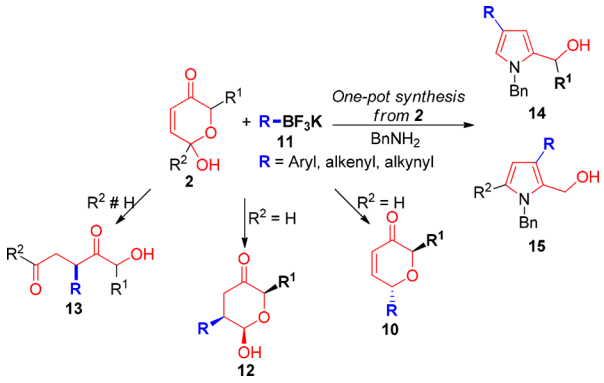
tected functional groups, such as OH.[12] In particular, we have focused our attention on finding selective reaction conditions for the stereoselective replacement of the γC−O bond in **2** by a γC−C bond, and on stereoselective conjugate addition reactions to OH-unprotected **2**, both of them under transition-metal-free conditions (Scheme 2).[13,14] Depending on the

Scheme 2. Reactions of AR Products with Organotrifluoroborates under Transition-Metal-Free Conditions



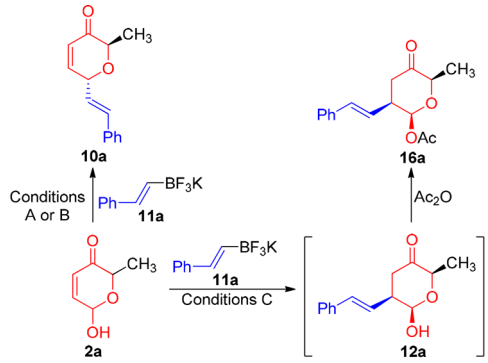
reactants and reaction conditions, these transformations will lead selectively to dihydropyranones **10**, tetrahydropyranones **12**,[1,3] or 1,4-dicarbonyl compounds **13**.[15] In addition, we will consider the application of these findings to the one-pot synthesis of highly functionalized pyrroles (**14**, **15**).[16]

With regard to literature precedents for the replacement of the γC−O bond in AR products **2** with a γC−C(sp) bond, alkynylation reactions have only been carried out in connection with the synthesis of spirocyclic pyrans and macrocyclic lactones by the Lewis-acid catalyzed addition of alkynylsilanes.[17] Concerning γC−C(sp^2) bonds, the direct arylation has been reported as a low-yielding process, and the synthesis of **10** has only been previously achieved by a sequence of elimination—Heck−Matsuda reaction.[10] To the best of our knowledge, the direct vinylation reaction is unprecedented.

With respect to literature precedents for conjugate addition reactions to AR products **2**, the addition of alkyl groups using organometallic nucleophiles[18] or radicals[19] has only been carried out on *O*-protected derivatives of the AR products **2**, and is amply precedented. However, the addition of vinyl or aryl groups is underdeveloped, and has only been carried out on *O*-protected AR products **2**.[20,21] To the best of our knowledge, the conjugate addition of C(sp)-nucleophiles has not been previously reported.

We started our investigations by considering the selective replacement of the γC−O bond in *O*-unprotected **2** with a γC−C(sp^2) bond (Scheme 3) toward the synthesis of **10**.[22] The first challenge of this transformation was finding reaction conditions devoid of competence with conjugate addition to the α,β-unsaturated ketone moiety of the AR starting materials **2**, which would lead to **12**.[23] In addition, we were concerned about the sterochemical outcome of the transformation, which could lead to the dihydropyranones **10** either in 2,6-*cis* or 2,6-*trans* relative configuration. In particular, the diastereoselective obtention of 2,6-*trans*-dihydropyranones is challenging.[10] After some experimentation using **2a** as starting material, we were pleased to find that the reaction with potassium (*E*)-phenylvinyl trifluoroborate **11a** gave rise to the selective

Scheme 3. Reactions of 2a with 11a



Conditions A: **11a** (1.2 equiv), TFAA (1.0 equiv), CH_2Cl_2, -15 °C to rt, 1 h, **10a** (90%)
Conditions B: **11a** (1.5 equiv), HBF_4OEt_2 (1.5 equiv), CH_3CN, 0 °C, 15 min, **10a** (75%)
Conditions C: i) **11a** (1.5 equiv), Bu_4NHSO_4 (0.5 equiv), CH_2Cl_2, rt, 24 h; ii) Ac_2O
16a, *dr* = 90:10, 82%

formation of **10a** either when promoted by trifluoroacetic anhydride (TFAA, Scheme 3, conditions A) or by HBF_4 (Scheme 3, conditions B). Under both reaction conditions, **10a** was obtained as a single 2,6-*trans* diastereomer.[24]

Complementarily, we looked for reaction conditions that could selectively afford the conjugate addition products **12** without formation of **10**. Again using **2a** as starting material, we found that the reaction with (*E*)-phenylvinyl potassium trifluoroborate **11a** promoted by Bu_4NHSO_4 (Scheme 3, conditions C) produced selectively the conjugate addition product **12a**. However, since **12a** was unstable to purification by silica gel chromatography, the crude reaction product was acetylated in situ to **16a**. Under both reaction conditions, **16a** was obtained with high 2,3-*cis*-2,6-*cis* diastereoselectivity.[24,25]

Under the optimum reaction conditions for the formation of **10a** (TFAA promotion, −15 °C to rt), we extended our observations to other AR products **2** for the synthesis of various 2,6-*trans*-dihydropyranones **10** (Scheme 4).[24,26] We found that the additions of arylvinyltrifluoroborates and alkylvinyltrifluoroborates to **2a** took place smoothly to give the corresponding dihydropyranones **10b**−**10e** in good yields and with *trans*:*cis dr* >98:02. Similar results were obtained for the reactions of **2a** with potassium aryltrifluoroborates (**10f**−**10h**). However, an erosion of the diastereoselectivity was observed in the addition of potassium alkynyltrifluoroborates (**10i**, **10j**). In these cases, we observed that lowering the reaction temperature to −40 °C afforded compounds **10i** and **10j** with increased *trans*:*cis dr*. Good yields and *trans*:*cis dr* >98:02 were also obtained when starting from the AR products **2b** and **2c** (synthesis of **10k**−**10n**). We were also glad to observe that the vinylation and arylation reactions of compound **2d**, with a quaternary carbon center, also took place in good yield and full 2,6-*trans* diastereoselectivity (synthesis of **10o**, **10p**), although the alkynylation reaction (synthesis of **10q**), as well as the reactions of **2e** (synthesis of **10r**, **10s**), were less stereoselective. In these cases, we were not able to improve the diastereoselectivity by diminishing the reaction temperature.

In a similar fashion, under the optimum reaction conditions for the formation of **16a** (promotion with Bu_4NHSO_4, rt), we extended our observations to other representative examples of potassium organotrifluoroborates **11** in their reactions with **2a** for the synthesis of various tetrahydropyranones **16** (Scheme 5). The new compounds **16b**−**e** have been also obtained with high 2,3-*cis*-2,6-*cis* diastereoselectivity.

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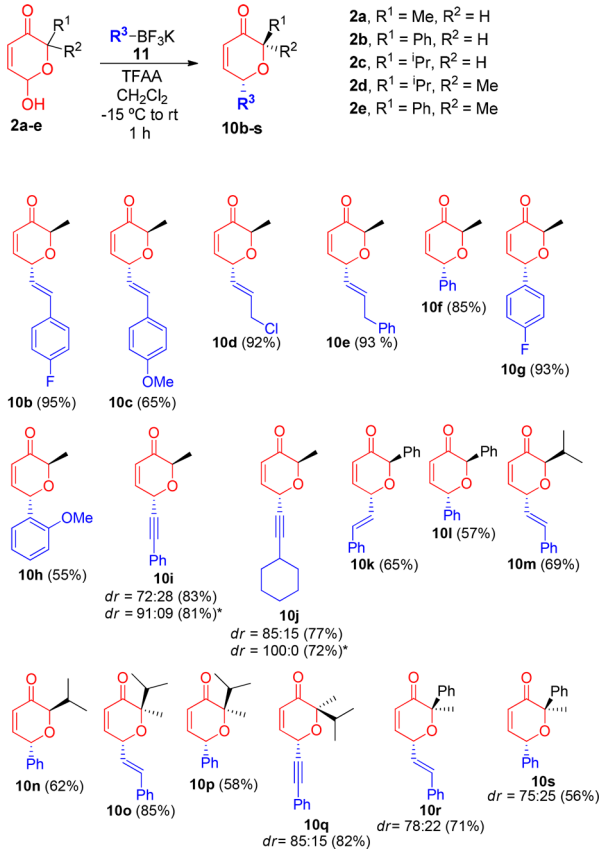
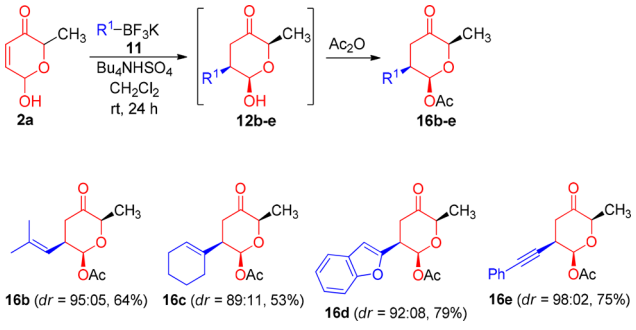
Scheme 4. Diastereoselective Synthesis of Dihydropyranones 10b–s



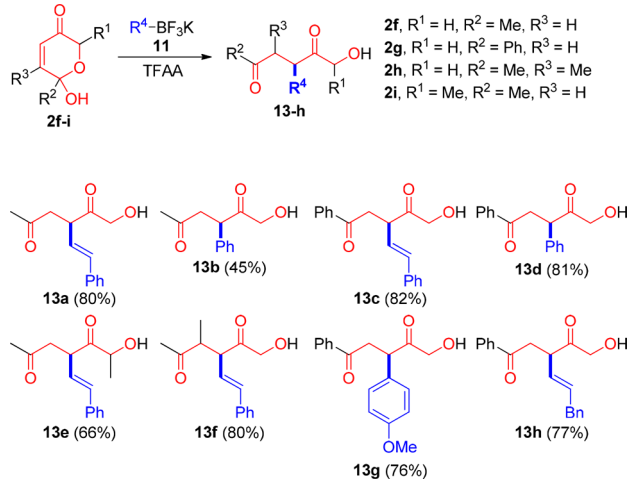
Scheme 5. Diastereoselective Synthesis of Tetrahydropyranones 16b–e



However, when the γ-carbon of the AR product **2** was fully substituted (Scheme 6, **2f** – **2i**, $R^2 \neq H$), the outcome of the reaction with potassium organotrifluoroborates **11** changed drastically. Instead of the expected dihydropyranones **10** or tetrahydropyranones **12**, the reaction gave rise to the 1,4-dicarbonyl compounds **13**.[15] The reaction was selective for α-functionalization adjacent to the hydroxymethylcarbonyl group. As observed for **13a**, this result was independent of the method of activation (**13a**: TFAA, 80%; HBF_4, 62%; Bu_4NHSO_4, 75%). Under the best conditions found for **13a** (TFAA activation) the reaction was extended to several other examples (Scheme 6).

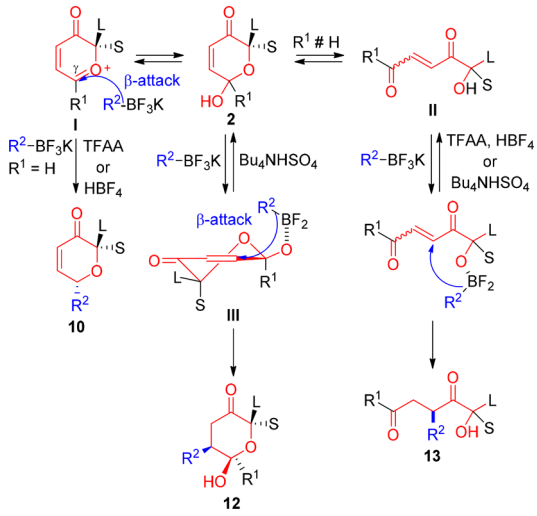
The reactions of potassium organotrifluoroborates **11** with the AR products **2** can be understood (Scheme 7) by considering the direct conjugate addition to the enone moiety

Scheme 6. Regioselective Synthesis of 1,4-Dicarbonyl Compounds 13a–h



versus addition to the oxonium **I** that results from dehydroxylation.[22]

Scheme 7. Proposed Reaction Course



In the presence of TFAA or HBF_4, formation of the oxonium **I** is expected to be easy. Direct addition of **11** to the electrophilic γ-carbon in **I** accounts for the formation of dihydropyranones **10**.[27] The relative stereochemistry of the final products **10** is governed by *trans* addition to the most bulky group (L) on the starting material. This type of reaction would be hindered for $R^1 \neq H$. On the other hand, organotrifluoroborates are known to be in equilibrium with organodifluoroboranes under a variety of circumstances.[28,29] Thus, under reaction conditions that do not favor formation of **I** (Bu_4NHSO_4), coordination of a trivalent boron species to the OH group in **2** may trigger the conjugate addition reaction that leads to tetrahydropyranones **12**. This type of addition is presumed to take place from the β-face on a reactive conformation with the most bulky group (L) at a pseudoequatorial position.[30] The formation of the 1,4-dicarbonyl compounds **13** can be understood by an OH-triggered conjugate addition to the open chain intermediates **II**, which may be in equilibrium with **2** ($R^1 \neq H$).[31]

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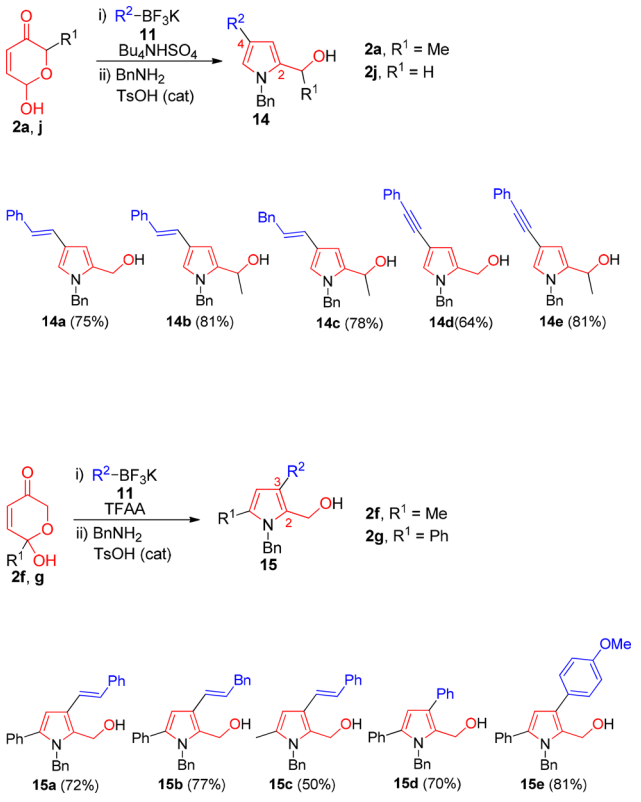
Finally, we have considered the application of this methodology to the one-pot synthesis of highly functionalized pyrroles (Scheme 8).[16] Thus, reaction of **2a** or **2j** with

Scheme 8. Synthesis of Pyrroles 14 and 15



compounds **11** in the presence of Bu_4NHSO_4 followed by the addition of benzylamine gave rise to pyrroles **14**, whereas reaction of **2f** or **2g** with compounds **11** in the presence of TFAA followed by the addition of benzylamine gave rise to pyrroles **15** in good yields. Both types of transformations were tolerant with the presence of a free OH group. It is worth mentioning the complementary relative disposition of the β-substituent and the α-hydroxyalkyl chain in pyrroles **14** (2,4-relative disposition) and **15** (2,3-relative disposition).

In conclusion, the results presented in this paper put forward new valorizations of Achmatowicz rearrangement products **2** using potassium organotrifluoroborates **11** as reagents in the absence of transition metals. The substitution pattern at position γ of the starting material **2** is crucial in determining the course of the reaction. When the γ-carbon is fully substituted, the reaction leads to 1,4-dicarbonyl compounds **13** independently of the reaction conditions. Compounds **13** show the particular feature of functionalization in α-position to the carbonyl group of a hydroxymethylcarbonyl group. When the γ-carbon of **2** is tertiary, the reaction can be controlled to obtain selectively the dihydropyranones **10** (TFAA-promotion, 2,6-*trans*) or the tetrahydropyranones **12** (Bu_4NHSO_4-promotion, 2,3-*cis*-2,6-*cis*). Compounds **10**, **12** and **13** are useful intermediates for the synthesis of an ample diversity of products. As an example, crude **12** and **13** have been transformed into functionalized pyrroles **14** and **15** bearing α-hydroxyalkyl chains in a one-pot operation.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all starting materials acids were commercially available research-grade chemicals and were used without further purification. Silica gel 60 F254 was used for TLC, and the spots were detected with UV light (254 and/or 366 nm) and/or vanillin solution. Flash column chromatography was carried out on silica gel 60. ^{1}H NMR spectra were recorded at 300 or 500 MHz, ^{13}C NMR spectra were recorded at 75 or 125 MHz, and ^{19}F NMR spectra were recorded at 282 MHz, all of them in $CDCl_3$, or acetone-d_6 solution.

Synthesis of 1a–g, 1i and 1j. 1-(Furan-2-yl)ethanol (**1a**),[32] furan-2-yl(phenyl)methanol (**1b**),[33] 1-(furan-2-yl)-2-methylpropan-1-ol (**1c**),[34] 2-(furan-2-yl)-3-methylbutan-2-ol (**1d**),[35] 1-(furan-2-yl)-1-phenylethanol (**1e**),[36] (5-methylfuran-2-yl)methanol (**1f**),[37] (5-phenylfuran-2-yl)methanol (**1g**),[34] 1-(5-methylfuran-2-yl)ethanol (**1i**),[38] and furan-2-ylmethanol (**1j**)[39] were synthesized following previous literature procedures.

*(4,5-Dimethylfuran-2-yl)methanol (**1h**).* 4,5-Dimethylfurfural (300 mg, 2.2 mmol) was dissolved in anhydrous methanol (1.3 mL) and sodium borohydride (163.4 mg, 4.5 mmol) was added at 0 °C. The mixture was stirred for 1 h at room temperature, water was then added, and the aqueous phase was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was evaporated and the crude product was purified via flash column chromatography on silica gel eluting with hexane:AcOEt 8:2 (260.6 mg, 94% yield). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (S, 1H), 4.50 (S, 2H), 2.19 (s, 3H), 1.91 (s, 3H), 1.76 (bs, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 147.7, 114.8, 111.4, 57.7, 11.5, 9.91 ppm. Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.69; H, 7.98.

Synthesis of 2a–c, 2f, 2g, 2i, and 2j. 6-Hydroxy-2-methyl-2*H*-pyran-3(6*H*)-one (**2a**),[40] 6-hydroxy-2-phenyl-2*H*-pyran-3(6*H*)-one (**2b**),[41] 6-hydroxy-2-isopropyl-2*H*-pyran-3(6*H*)-one (**2c**),[41] 6-hydroxy-6-methyl-2*H*-pyran-3(6*H*)-one (**2f**),[31] 6-hydroxy-6-phenyl-2*H*-pyran-3(6*H*)-one (**2g**),[41] 6-hydroxy-2,6-dimethyl-2H-pyran-3(6*H*)-one (**2i**),[42] and 6-hydroxy-2H-pyran-3(6*H*)-one (**2j**)[43] were synthesized following previous literature procedures.

General Procedure for the Synthesis of 2d, 2e, and 2h. To a stirred solution of the furfuryl alcohol **1** (1 mmol) in DCM (8 mL) was added *m*-chloroperbenzoic acid (*m*CPBA, 1.5 mmol) at 0 °C. After completion of the addition, the reaction was allowed to stir at 0 °C for 1 h. Evaporation of the solvent gave the crude product which was purified via flash column chromatography on silica gel.

*6-Hydroxy-2-isopropyl-2-methyl-2H-pyran-3(6H)-one (**2d**).* Colorless oil. Major diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (d, J = 10.3 Hz, 1H), 6.05 (d, J = 10.3 Hz, 1H), 5.70–5.69 (m, 1H), 4.55 (bs, 1H), 2.15–2.06 (m, 1H), 1.34 (s, 3H), 0.90–0.83 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 145.3, 126.9, 87.6, 84.3, 33.5, 21.9, 17.3, 16.3 ppm. Minor diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (d, J = 10.3 Hz, 1H), 6.03 (d, J = 10.3 Hz, 1H), 5.68–5.67 (m, 1H), 4.55 (bs, 1H), 2.28–2.21 (m, 1H), 1.25 (s, 3H), 0.90–0.83 (m, 6H) ppm ^{13}C NMR (75 MHz, CDCl3) δ 200.1, 146.7, 127.4, 87.7, 83.8, 34.5, 18.9, 17.2, 16.1 ppm. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.58; H, 8.30.

*6-Hydroxy-2-methyl-2-phenyl-2H-pyran-3(6H)-one (**2e**).* White solid (mp 77–79 °C). Major diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.33 (m, 5H), 6.79 (d, J = 10.3 Hz, J = 1.3 Hz, 1H), 6.20 (d, J = 10.3 Hz, J = 1.7 Hz, 1H), 5.42 (s, 1H), 3.24 (bs, 1H), 1.67 (s, 3H) ppm. ^{13}C NMR (750 MHz, $CDCl_3$) δ 196.2, 147.4, 138.5, 128.9 (2C), 128.5, 128.4, 125.5 (2C), 88.6, 83.6, 27.8 ppm. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.61; H, 5.92.

*6-Hydroxy-5,6-dimethyl-2H-pyran-3(6H)-one (**2h**).* Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (s, 1H), 4.48 (d, J = 16.9 Hz, 1H), 4.08 (d, J = 16.9 Hz, 1H), 3.51 (bs, 1H), 2.04–2.03 (m, 3H), 1.61 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 161.0, 124.4, 95.4, 66.6, 25.9, 19.9 ppm. Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.08; H, 7.08.

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General Procedure for the Synthesis of Compounds 10 and 13, Conditions A. A stirred solution of compound **2** (0.23 mmol, 1.0 equiv) and the corresponding potassium trifluoroborate **11** (0.28 mmol, 1.2 equiv) in DCM (1.4 mL, 6 mL/mmol) was cooled to −15 °C. After stirring for 5 min, TFAA (0.23−0.52 mmol, 1.0−2.2 equiv) was added and the reaction mixture was allowed to warm to rt. Then, the solvent was removed in vacuo and the crude product was purified by flash column chromatography on silica gel.

General Procedure for the Synthesis of Compounds 10, Conditions B. A stirred solution of compound **2** (0.23 mmol, 1.0 equiv) and the corresponding potassium *trans*-styryltrifluoroborate **11** (0.35 mmol, 1.5 equiv) in MeCN (2.3 mL, 10 mL/mmol) was cooled to 0 °C. After stirring for 5 min, $HBF_4{\cdot}OEt_2$ (0.35 mmol, 1.5 equiv) was added, and the solution was stirred at 0 °C for 15 min. The reaction was quenched with water (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried with $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel.

General Procedure for the Synthesis of Compounds 16, Conditions C. A solution of compound **2** (0.23 mmol, 1.0 equiv), the corresponding potassium trifluoroborate **11** (0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (0.12 mmol, 0.5 equiv) in DCM (4.6 mL, 20 mL/mmol) was allowed to stir at rt for 24−48 h. After reaction completion as determined by TLC analysis, the crude mixture was cooled to 0 °C, and Ac_2O (0.23 mmol, 1.0 equiv), DMAP (0.012 mmol, 5% mol) and Et_3N (0.47 mmol, 2.0 equiv) were added, and the reaction mixture was stirred at 0 °C for 1 h. Then, the mixture was concentrated and purified via flash column chromatography on silica gel.

General Procedure for the One-Pot Synthesis of Pyrroles 14. A solution of compound **2** (0.23 mmol, 1.0 equiv), the corresponding potassium trifluoroborate **11** (0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL, 20 mL/mmol) was allowed to stir at rt for 24−48 h. After reaction completion as determined by TLC analysis, the solvent was removed in vacuo and the residue was redissolved in toluene (1.1 mL, 5 mL/mmol). Benzylamine (0.23 mmol, 1 equiv) and *p*-toluenesulfonic acid (0.023 mmol, 0.1 equiv) were added and the mixture was stirred at rt. Then, the mixture was concentrated and purified via flash column chromatography on silica gel.

General Procedure for the One-Pot Synthesis of Pyrroles 15. A stirred solution of compound **2** (0.23 mmol, 1.0 equiv) and the corresponding potassium trifluoroborate **11** (0.28 mmol, 1.2 equiv) in DCM (1.4 mL, 6 mL/mmol) was cooled to −15 °C. After stirring for 5 min, TFAA (0.23−0.52 mmol, 1.0−2.2 equiv) was added and the reaction mixture was allowed to warm to rt. Then, the solvent was removed in vacuo and the residue was redissolved in toluene (1.1 mL, 5 mL/mmol). Benzylamine (0.23 mmol, 1 equiv) and *p*-toluenesulfonic acid (0.023 mmol, 0.1 equiv) were added and the mixture was stirred at rt. Then, the mixture was concentrated and purified via flash column chromatography on silica gel.

(2R,6R)-2-Methyl-6-((E)-styryl)-2H-pyran-3(6H)-one ***(10a)***. Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (30.1 mg, 0.23 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (59.0 mg, 0.28 mmol, 1.2 equiv) and TFAA (33 μL, 0.23 mmol, 1.0 equiv) in DCM anh. (1.4 mL) for 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (45.1 mg, 90% yield). Following general procedure for the synthesis of compounds **10**, Conditions B, starting from **2a** (30.3 mg, 0.23 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (73.8 mg, 0.35 mmol, 1.5 equiv) and $HBF_4{\cdot}OEt_2$ (48 μL, 0.35 mmol, 1.5 equiv) in MeCN anh. (2.3 mL). The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (37.6 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17−7.39 (m, 5H), 7.00 (dd, *J* = 10.4 Hz, *J* = 3.5 Hz, 1H), 7.60 (d, *J* = 16.1 Hz, 1H), 6.24 (dd, *J* = 16.1 Hz, *J* = 6.2 Hz, 1H), 6.10 (dd, *J* = 10.4 Hz, *J* = 1.7 Hz, 1H), 5.01−5.08 (m, 1H), 4.34 (c. *J* = 6.8 Hz, 1H), 1.34 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 148.9, 135.9, 134.6, 128.9, 128.6, 126.8, 126.3, 124.0, 72.8, 71.6, 15.6 ppm. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.55; H, 6.58.

(2R,6R)-6-((E)-4-Fluorostyryl)-2-methyl-2H-pyran-3(6H)-one ***(10b)***. Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (29.7 mg, 0.23 mmol, 1.0 equiv), potassium 2-(4-fluorophenyl)vinyltrifluoroborate **11b** (64.1 mg, 0.28 mmol, 1.2 equiv) and TFAA (33 μL, 0.23 mmol, 1.0 equiv) in DCM anh. (1.4 mL) for 2 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a yellow oil (51.6 mg, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.42 (m, 2H), 6.97−7.09 (m, 3H), 6.63 (d, *J* = 16.1 Hz, 1H), 6.23 (dd, *J* = 16.1 Hz, *J* = 6.0 Hz, 1H), 6.16 (dd, *J* = 10.4 Hz, *J* = 1.8 Hz, 1H), 5.06−5.13 (m, 1H), 4.40 (c. *J* = 6.8 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 164.6, 161.3, 148.8, 133.4, 132.1, 132.0, 128.5, 128.4, 126.3, 123.8, 123.7, 116.0, 115.7, 72.9, 71.5, 15.6 ppm. Anal. Calcd for $C_{14}H_{13}FO_2$: C, 72.40; H, 5.64. Found: C, 72.49; H, 5.62.

(2R,6R)-6-((E)-4-Methoxystyryl)-2-methyl-2H-pyran-3(6H)-one ***(10c)***. Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (29.7 mg, 0.23 mmol, 1.0 equiv), potassium 2-(4-methoxyphenyl)vinyltrifluoroborate **11c** (67.4 mg, 0.28 mmol, 1.2 equiv) and TFAA (33 μL, 0.23 mmol, 1.0 equiv) in DCM anh. (1.4 mL) for 2 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a yellow oil (37.2 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.7 Hz, 2H), 7.06 (dd, *J* = 10.8 Hz, *J* = 4.3 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.14−6.20 (m, 2H), 5.06−5.11 (m, 1H), 4.40 (c. *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 160.0, 149.2, 134.3, 128.7, 128.1, 126.2, 121.6, 114.3, 72.7, 71.8, 55.5, 15.6 ppm. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.64; H, 6.58.

(2R,6S)-6-((E)-3-Chloroprop-1-en-1-yl)-2-methyl-2H-pyran-3(6H)-one ***(10d)***. Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (30.1 mg, 0.23 mmol, 1.0 equiv), potassium *trans*-2-chloromethylvinyltrifluoroborate **11d** (51.2 mg, 0.28 mmol, 1.2 equiv) and TFAA (39 μL, 0.28 mmol, 1.2 equiv) in DCM anh. (1.4 mL) for 2 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (40.2 mg, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 10.4 Hz, *J* = 3.4 Hz, 1H), 6.12 (dd, *J* = 10.4 Hz, *J* = 1.7 Hz, 1H), 5.86−6.01 (m, 2H), 4.93−5.00 (m, 1H), 4.32 (c. *J* = 6.8 Hz, 1H), 4.00−4.16 (m, 2H), 1.38 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 148.1, 130.7, 129.4, 126.3, 73.0, 70.4, 43.8, 15.4 ppm. Anal. Calcd for $C_9H_{11}ClO_2$: C, 57.92; H, 5.94. Found: C, 57.99; H, 5.92.

(2R,6R)-2-Methyl-6-((E)-3-phenylprop-1-en-1-yl)-2H-pyran-3(6H)-one ***(10e)***. Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (30.0 mg, 0.23 mmol, 1.0 equiv), potassium *trans*-3-phenyl-1-propen-1-yltrifluoroborate **11e** (63.0 mg, 0.28 mmol, 1.2 equiv) and TFAA (39 μL, 0.28 mmol, 1.2 equiv) in DCM anh. (1.4 mL) for 2 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (49.7 mg, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05−7.31 (m, 5H), 6.89 (dd, *J* = 10.2 Hz, *J* = 3.4 Hz, 1H), 6.00 (dd, *J* = 10.2 Hz, *J* = 1.3 Hz, 1H), 5.87 (dt, *J* = 15.5 Hz, *J* = 16.7 Hz, 1H), 5.59 (dd, *J* = 15.5 Hz, *J* = 6.7 Hz, 1H), 4.82−4.90 (m, 1H), 4.26 (c. *J* = 6.8 Hz, 1H), 3.37 (d, *J* = 6.7 Hz, 2H), 1.31 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 149.4, 139.3, 135.3, 128.7, 128.6, 126.5, 126.2, 125.9, 72.7, 71.3, 38.9, 15.5 ppm. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.90; H, 7.07.

(2R,6S)-2-Methyl-6-phenyl-2H-pyran-3(6H)-one ***(10f)***. Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (29.5 mg, 0.23 mmol, 1.0 equiv), potassium phenyltrifluoroborate **11f** (51.7 mg, 0.28 mmol, 1.2 equiv) and TFAA (39 μL, 0.28 mmol, 1.2 equiv) in DCM anh. (1.4 mL) for 2 h. Then, a second equivalent of TFAA (33 μL, 0.23 mmol, 1.0 equiv) was added and the reaction mixture was allowed to warm to room temperature for 4 h. The crude product was purified by flash column

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chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (37.4 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.43 (m, 5H), 7.16 (dd, J = 10.4 Hz, J = 3.1 Hz, 1H), 6.23 (dd, J = 10.4 Hz, J = 1.9 Hz, 1H), 5.48−5.54 (m, 1H), 4.26 (c. J = 6.9 Hz, 1H), 1.40 (d, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 149.3, 136.9, 129.0, 128.9, 128.2, 126.2, 73.3, 72.8, 15.4 ppm. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.62; H, 6.42.

(2R,6S)-6-(4-Fluorophenyl)-2-methyl-2H-pyran-3(6H)-one (**10g**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (29.9 mg, 0.23 mmol, 1.0 equiv), potassium 4-fluorophenyltrifluoroborate **11g** (56.8 mg, 0.28 mmol, 1.2 equiv) and TFAA (39 μL, 0.28 mmol, 1.2 equiv) in DCM anh. (1.4 mL) for 2 h. Then, the mixture was cooled at 0 °C and a second equivalent of TFAA (33 μL, 0.23 mmol, 1.0 equiv) was added and the reaction mixture was allowed to warm to room temperature for 4 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (44.9 mg, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.44 (m, 2H), 7.04−7.17 (m, 3H), 6.23 (dd, J = 10.4 Hz, J = 1.9 Hz, 1H), 5.46−5.50 (m, 1H), 4.23 (c. J = 6.8 Hz, 1H), 1.40 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 164.7, 161.4, 148.9, 132.9, 132.8, 130.0, 129.9, 126.3, 116.0, 115.8, 73.3, 72.0, 15.4 ppm. Anal. Calcd for $C_{12}H_{11}FO_2$: C, 69.89; H, 5.38. Found: C, 69.85; H, 5.37.

(2R,6S)-6-(2-Methoxyphenyl)-2-methyl-2H-pyran-3(6H)-one (**10h**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (30.1 mg, 0.23 mmol, 1.0 equiv), potassium 2-mehtoxyphenyltrifluoroborate **11h** (60.1 mg, 0.28 mmol, 1.2 equiv) and TFAA (33 μL, 0.23 mmol, 1.0 equiv) in DCM anh. (1.4 mL) for 3 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a yellow oil (28.1 mg, 55% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.40 (m, 2H), 7.08 (dd, J = 10.3 Hz, J = 2.8 Hz, 1H), 6.92−7.01 (m, 2H), 6.17 (dd, J = 10.4 Hz, J = 2.2 Hz, 1H), 5.88−5.94 (m, 1H), 4.38 (c. J = 7.0 Hz, 1H), 3.89 (s, 3H), 1.43 (d, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 157.1, 150.2, 130.0, 128.3, 125.5, 125.2, 120.7, 111.1, 74.1, 66.8, 55.8, 15.4 ppm. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.61; H, 6.45.

(2R,6S)-2-Methyl-6-(phenylethynyl)-2H-pyran-3(6H)-one (**10i**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (30.1 mg, 0.23 mmol, 1.0 equiv), potassium phenylethylnyltrifluoroborate **11i** (58.5 mg, 0.28 mmol, 1.2 equiv) and TFAA (33 μL, 0.23 mmol, 1.0 equiv) in DCM anh. (1.4 mL) at −40 °C for 3 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (40.2 mg, 81% yield, *dr* 91:09). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.50 (m, 2H), 7.32−7.38 (m, 3H), 7.03 (dd, J = 10.2 Hz, J = 4.2 Hz, 1H), 6.11 (dd, J = 10.2 Hz, J = 1.5 Hz, 1H), 5.37 (dd, J = 4.2 Hz, J = 1.5 Hz, 1H), 4.67 (c. J = 6.7 Hz, 1H), 1.44 (d, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 146.3, 132.1, 129.2, 128.5, 125.8, 121.8, 87.9, 81.8, 73.3, 63.4, 15.4 ppm. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.29; H, 5.69.

(2R,6S)-6-(Cyclohexylethynyl)-2-methyl-2H-pyran-3(6H)-one (**10j**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2a** (30.4 mg, 0.23 mmol, 1.0 equiv), potassium cyclohexylethylnyltrifluoroborate **11j** (60.1 mg, 0.28 mmol, 1.2 equiv) and TFAA (33 μL, 0.23 mmol, 1.0 equiv) in DCM anh. (1.4 mL) at −40 °C for 3 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (37.3 mg, 72% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (dd, J = 10.1 Hz, J = 4.2 Hz, 1H), 6.00 (dd, J = 10.1 Hz, J = 1.4 Hz, 1H), 5.09−5.17 (m, 1H), 4.56 (c. J = 6.7 Hz, 1H), 2.36−2.47 (m, 1H), 1.40 (d, J = 6.7 Hz, 3H), 1.18−1.84 (m, 10H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 147.4, 125.1, 93.2, 72.9, 63.1, 32.5, 32.4, 29.2, 25.9, 24.9, 15.3 ppm. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.00; H, 8.25.

(2S,6S)-2-Phenyl-6-((E)-styryl)-2H-pyran-3(6H)-one (**10k**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2b** (30.0 mg, 0.16 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (39.9 mg, 0.19 mmol, 1.2 equiv) and TFAA (23 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (28.7 mg, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.31 (m, 10H), 7.07 (dd, J = 10.4 Hz, J = 2.8 Hz, 1H), 6.73 (d, J = 16.0 Hz, 1H), 6.28−6.36 (m, 2H), 5.34 (s, 1H), 5.04−5.06 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.4, 149.5, 136.0, 134.8, 134.4, 128.9 (2C), 128.7 (3C), 128.6, 127.7 (2C), 127.0, 126.9 (2C), 124.6, 79.4, 71.1 ppm. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.51; H, 5.86.

(2S,6R)-2,6-Diphenyl-2H-pyran-3(6H)-one (**10l**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2b** (30.0 mg, 0.16 mmol, 1.0 equiv), potassium phenyltrifluoroborate **11f** (35.0 mg, 0.19 mmol, 1.2 equiv) and TFAA (23 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 24 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (22.8 mg, 57% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.39 (m, 10H), 7.10 (dd, J = 10.4 Hz, J = 2.4 Hz, 1H), 6.37 (dd, J = 10.4 Hz, J = 2.4 Hz, 1H), 5.35 (t, J = 2.4 Hz, 1H), 5.31 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 150.3, 137.8, 134.4, 129.1 (2C), 129.0, 128.8 (2C), 128.7, 127.9 (2C), 127.6 (2C), 126.8, 79.9, 72.3 ppm. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.55; H, 5.71.

(2S,6S)-2-Isopropyl-6-((E)-styryl)-2H-pyran-3(6H)-one (**10m**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2c** (29.4 mg, 0.19 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (47.5 mg, 0.23 mmol, 1.2 equiv) and TFAA (26 μL, 0.19 mmol, 1.0 equiv) in DCM anh. (1.1 mL) for 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (31.7 mg, 69% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.28 (m, 5H), 7.03 (dd, J = 10.4 Hz, J = 3.4 Hz, 1H), 6.66 (d, J = 16.2 Hz, 1H), 6.26 (dd, J = 16.2 Hz, J = 6.0 Hz, 1H), 6.14 (dd, J = 10.4 Hz, J = 1.9 Hz, 1H), 5.10−5.12 (m, 1H), 4.00 (d, J = 5.3 Hz, 1H), 2.41−2.30 (m, 1H), 1.01 (d, J = 6.9 Hz, 3H), 1.00 (d, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 148.6, 136.0, 134.2, 128.8 (2C), 128.5, 126.9, 126.8 (2C), 124.5, 81.4, 71.5, 28.4, 19.0, 17.7 ppm. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.20; H, 7.37.

(2S,6R)-2-Isopropyl-6-phenyl-2H-pyran-3(6H)-one (**10n**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2c** (29.1 mg, 0.19 mmol, 1.0 equiv), potassium phenyltrifluoroborate **11f** (41.2 mg, 0.22 mmol, 1.2 equiv) and TFAA (26 μL, 0.19 mmol, 1.0 equiv) in DCM anh. (1.1 mL) for 24 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (25.5 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.39 (m, 5H), 7.13 (dd, J = 10.4 Hz, J = 3.1 Hz, 1H), 6.20 (dd, J = 10.4 Hz, J = 2.1 Hz, 1H), 5.51−5.49 (m, 1H), 3.80 (d, J = 6.4 Hz, 1H), 2.38−2.27 (m, 1H), 1.03 (d, J = 6.7 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 149.0, 137.6, 128.9 (2C), 128.8, 128.0 (2C), 126.7, 82.1, 72.6, 28.1, 18.8, 18.2 ppm. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.73; H, 7.58.

(2S,6S)-2-Isopropyl-2-methyl-6-((E)-styryl)-2H-pyran-3(6H)-one (**10o**). Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2d** (29.9 mg, 0.18 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (44.3 mg, 0.21 mmol, 1.2 equiv) and TFAA (25 μL, 0.18 mmol, 1.0 equiv) in DCM anh. (1.1 mL) for 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (39.2 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.28 (m, 5H), 6.84 (dd, J = 10.3 Hz, J = 1.5 Hz, 1H), 6.72 (d, J = 15.9 Hz, 1H), 6.20 (dd, J = 15.9 Hz, J = 7.0 Hz, 1H), 6.00 (dd, J = 10.3 Hz, J = 2.5 Hz, 1H), 5.03−5.06 (m, 1H), 2.32−2.23 (m, 1H), 1.26 (s, 3H), 1.07 (d, J = 6.9 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 148.2, 136.2, 133.1, 128.7 (2C), 128.3, 126.8 (3C), 124.7, 83.6, 70.1, 29.4, 17.3, 17.0, 16.3 ppm. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.74; H, 7.76.

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*(2S,6R)-2-Isopropyl-2-methyl-6-phenyl-2H-pyran-3(6H)-one (**10p**).* Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2d** (29.5 mg, 0.17 mmol, 1.0 equiv), potassium phenyltrifluoroborate **11f** (38.3 mg, 0.21 mmol, 1.2 equiv) and TFAA (24 μL, 0.17 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 24 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (22.7 mg, 58% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.36 (m, 5H), 6.87 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 6.04 (dd, *J* = 10.3 Hz, *J* = 2.6 Hz, 1H), 5.40−5.42 (m, 1H), 2.42−2.32 (m, 1H), 1.25 (s, 3H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 149.2, 139.5, 129.0 (2C), 128.7, 127.5 (2C), 124.3, 84.0, 71.6, 29.2, 17.4, 17.0, 16.0 ppm. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.15; H, 7.93.

*(2S,6R)-2-Isopropyl-2-methyl-6-(phenylethynyl)-2H-pyran-3(6H)-one (**10q**).* Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2d** (30.1 mg, 0.18 mmol, 1.0 equiv), potassium phenylethylnyltrifluoroborate **11i** (44.2 mg, 0.28 mmol, 1.2 equiv) and TFAA (25 μL, 0.18 mmol, 1.0 equiv) in DCM anh. (1.1 mL) at −40 °C for 3 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (37.5 mg, 82% yield, *dr* = 85:15). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.46 (m, 2H), 7.33−7.31 (m, 3H), 6.93 (dd, *J* = 10.2 Hz, *J* = 2.4 Hz, 1H), 6.05 (dd, *J* = 10.2 Hz, *J* = 2.5 Hz, 1H), 5.45 (t, *J* = 2.5 Hz, 1H), 2.22 (heptet, *J* = 6.8 Hz, 1H), 1.37 (s, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 145.7, 132.0 (2C), 129.0, 128.4 (2C), 125.1, 122.1, 86.4, 85.0, 84.4, 60.6, 30.6, 17.9, 17.2, 16.8 ppm. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.30; H, 7.24.

*(2S,6S)-2-Methyl-2-phenyl-6-((E)-styryl)-2H-pyran-3(6H)-one (**10r**).* Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2e** (30.0 mg, 0.15 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (37.1 mg, 0.18 mmol, 1.2 equiv) and TFAA (21 μL, 0.15 mmol, 1.0 equiv) in DCM anh. (0.9 mL) for 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford the desired compound as a separable mixture of diastereomers (30.9 mg, 72% yield, *dr* = 78:22).

(2*S*,6*S*)-2-Methyl-2-phenyl-6-((*E*)-styryl)-2*H*-pyran-3(6*H*)-one. Major diastereomer. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.30 (m, 10H), 6.80−6.71 (m, 2H), 6.28−6.17 (m, 2H), 4.80−4.77 (m, 1H), 1.66 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 149.4, 138.6, 136.2, 133.3, 128.8 (2C), 128.7 (2C), 128.4, 128.3, 126.8 (2C), 126.2, 126.0, 125.8 (2C), 83.1, 71.0, 27.5 ppm. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.86; H, 6.18.

(2*R*,6*S*)-2-Methyl-2-phenyl-6-((*E*)-styryl)-2*H*-pyran-3(6*H*)-one. Minor diastereomer. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.38−7.29 (m, 8H), 7.00 (dd, *J* = 10.3 Hz, *J* = 1.9 Hz, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.21−6.10 (m, 2H), 5.25 (d, *J* = 7.1 Hz, 1H), 1.80 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 148.9, 141.7, 136.2, 133.3, 128.7 (2C), 128.3, 128.1 (2C), 127.9, 126.8 (2C), 126.6 (2C), 126.4, 125.6, 81.9, 71.2, 22.5 ppm. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.80; H, 6.17.

*(2S,6R)-2-Methyl-2,6-diphenyl-2H-pyran-3(6H)-one (**10s**).* Following general procedure for the synthesis of compounds **10**, Conditions A, starting from **2e** (30.0 mg, 0.15 mmol, 1.0 equiv), potassium phenyltrifluoroborate **11f** (33.1 mg, 0.18 mmol, 1.2 equiv) and TFAA (21 μL, 0.15 mmol, 1.0 equiv) in DCM anh. (0.9 mL) for 24 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford the desired compound as a separable mixture of diastereomers (22.2 mg, 56% yield, *dr* = 75:25).

(2*S*,6*R*)-2-Methyl-2,6-diphenyl-2*H*-pyran-3(6*H*)-one. Colorless oil. Major diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.38 (m, 10H), 6.82 (dd, *J* = 10.3 Hz, *J* = 1.6 Hz, 1H), 6.22 (dd, *J* = 10.4 Hz, *J* = 2.7 Hz, 1H), 5.14−5.13 (m, 1H), 1.67 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 150.3, 139.1, 138.6, 129.0 (2C), 128.8 (2C), 128.7, 128.3, 127.5 (2C), 125.9 (2C), 125.8, 83.4, 72.9, 27.6 ppm. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.64; H, 6.02.

(2*R*,6*R*)-2-Methyl-2,6-diphenyl-2*H*-pyran-3(6*H*)-one. Colorless oil. Minor diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.49−7.29 (m, 8H), 7.03 (dd, *J* = 10.3 Hz, *J* = 1.6 Hz, 1H), 6.20 (dd, *J* = 10.3 Hz, *J* = 2.4 Hz, 1H), 5.65 (s, 1H), 1.87 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 149.9, 141.3, 139.3, 129.1 (2C), 128.7, 128.1 (2C), 127.8, 127.5 (2C), 126.7 (2C), 125.4, 82.2, 72.2, 21.5 ppm. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.85; H, 6.00.

*(E)-1-Hydroxy-3-styrylhexane-2,5-dione (**13a**).* Following general procedure for the synthesis of compounds **13**, Conditions A, starting from **2f** (30.0 mg, 0.23 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (59.1 mg, 0.28 mmol, 1.2 equiv) and TFAA (32 μL, 0.23 mmol, 1.0 equiv) in DCM anh. (1.4 mL) for 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (42.7 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.27 (m, 5H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8 Hz, *J* = 9.3 Hz, 1H), 4.48 (s, 2H), 3.75 (td, *J* = 9.5 Hz, *J* = 3.8 Hz, 1H), 3.29 (dd, *J* = 18.3 Hz, *J* = 9.8 Hz, 1H), 2.92 (bs, 1H), 2.74 (dd, *J* = 18.3 Hz, *J* = 3.8 Hz, 1H), 2.17 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5, 206.3, 136.1, 134.7, 128.8 (2C), 128.4, 126.5 (2C), 124.7, 67.6, 47.4, 45.5, 29.8 ppm. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.33; H, 6.80.

*1-Hydroxy-3-phenylhexane-2,5-dione (**13b**).* Following general procedure for the synthesis of compounds **13**, Conditions A, starting from **2f** (30.0 mg, 0.23 mmol, 1.0 equiv), potassium phenyltrifluoroborate **11f** (51.5 mg, 0.28 mmol, 1.2 equiv) and TFAA (32 μL, 0.23 mmol, 1.0 equiv) in DCM anh. (1.4 mL) for 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (21.3 mg, 45% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.28 (m, 3H), 7.21−7.18 (m 2H), 4.42 (d, *J* = 18.9 Hz, 1H), 4.23 (d, *J* = 18.9 Hz, 1H), 4.17 (dd, *J* = 10.7 Hz, *J* = 3.6 Hz, 1H), 3.55 (dd, *J* = 18.3 Hz, *J* = 10.7 Hz, 1H), 2.86 (bs, 1H), 2.74 (dd, *J* = 18.3 Hz, *J* = 3.6 Hz, 1H), 2.17 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 206.6, 136.7, 129.4 (2C), 128.2 (2C), 128.1, 67.4, 49.3, 46.9, 29.8 ppm. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.99; H, 6.95.

*(E)-5-Hydroxy-1-phenyl-3-styrylpentane-1,4-dione (**13c**).* Following general procedure for the synthesis of compounds **13**, Conditions A, starting from **2g** (29.7 mg, 0.16 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (39.4 mg, 0.19 mmol, 1.2 equiv) and TFAA (22 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (38.6 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.36−7.28 (m, 5H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.8 Hz, *J* = 9.0 Hz, 1H), 4.59 (q, *J* = 19.0 Hz, 2H), 3.95 (td, *J* = 9.5 Hz, *J* = 3.4 Hz, 1H), 3.86 (dd, *J* = 17.8 Hz, *J* = 9.5 Hz, 1H), 3.31 (dd, *J* = 17.8 Hz, *J* = 3.4 Hz, 1H), 3.00 (bs, 1H), ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 197.7, 136.2, 136.1 134.7, 133.7, 128.9 (4C), 128.4, 128.3 (2C); 126.6 (2C); 125.1, 67.7, 47.5, 41.3 ppm. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.67; H, 6.02.

*5-Hydroxy-1,3-diphenylpentane-1,4-dione (**13d**).* Following general procedure for the synthesis of compounds **13**, Conditions A, starting from **2g** (29.9 mg, 0.16 mmol, 1.0 equiv), potassium phenyltrifluoroborate **11f** (34.8 mg, 0.19 mmol, 1.2 equiv) and TFAA (22 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (34.7 mg, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.36−7.27 (m, 5H), 4.58 (d, *J* = 18.8 Hz, 1H), 4.40−4.30 (m, 2H), 4.11 (dd, *J* = 18.0 Hz, *J* = 10.6 Hz, 1H), 3.32 (dd, *J* = 18.0 Hz, *J* = 3.4 Hz, 1H), 3.17 (bs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.0, 197.9, 136.9, 136.1, 133.7, 129.5 (2C), 128.8 (2C), 128.3 (2C), 128.2 (2C); 128.1, 67.5, 49.4, 42.8 ppm. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.93; H, 5.86.

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*(E)-6-Hydroxy-4-styrylheptane-2,5-dione (**13e**).* Following general procedure for the synthesis of compounds **13**, Conditions A, starting from **2i** (29.8 mg, 0.21 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (52.9 mg, 0.25 mmol, 1.2 equiv) and TFAA (29 μL, 0.21 mmol, 1.0 equiv) in DCM anh. (1.3 mL) for 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford the desired compound as a mixture of diastereomers (66:33 mixture, 34.1 mg, 66% yield). Major diastereomer. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.28 (m, 5H), 6.56 (d, J = 15.9 Hz, 1H), 5.98 (dd, J = 15.9 Hz, J = 9.4 Hz, 1H), 4.50 (q, J = 7.1, 1H), 3.75 (td, J = 9.7 Hz, J = 4.0 Hz, 1H), 3.40 (bs, 1H), 3.30 (dd, J = 18.3 Hz, J = 10.0 Hz, 1H), 2.66 (dd, J = 18.3 Hz, J = 3.8 Hz, 1H), 2.18 (s, 3H), 1.50 (d, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.3, 206.6, 136.1, 134.7, 128.8 (2C), 128.3, 126.5 (2C), 125.2, 71.8, 45.9, 45.3, 29.9, 20.3 ppm. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.22; H, 7.39.

*(E)-1-Hydroxy-4-methyl-3-styrylhexane-2,5-dione (**13f**).* Following general procedure for the synthesis of compounds **13**, Conditions A, starting from **2h** (30.0 mg, 0.21 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (53.3 mg, 0.25 mmol, 1.2 equiv) and TFAA (29 μL, 0.21 mmol, 1.0 equiv) in DCM anh. (1.3 mL) 1 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford the desired compound as a mixture of diastereomers (90:10 mixture, 41.3 mg, 80% yield). Major diastereomer. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.29 (m, 5H), 6.60 (d, J = 15.7 Hz, 1H), 6.00 (dd, J = 15.7 Hz, J = 10.0 Hz, 1H), 4.43 (s, 2H), 3.52 (t, J = 10.0 Hz, 1H), 3.28−3.17 (m, 1H), 2.86 (bs, 1H), 2.22 (s, 3H), 1.16 (d, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.4, 210.2, 136.2, 136.1, 128.9 (2C), 128.4, 126.6 (2C), 124.4, 67.5, 54.9, 48.5, 28.7, 14.9 ppm. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.19; H, 7.21.

*5-Hydroxy-3-(4-methoxyphenyl)-1-phenylpentane-1,4-dione (**13g**).* Following general procedure for the synthesis of compounds **13**, Conditions A, starting from **2g** (30.1 mg, 0.16 mmol, 1.0 equiv), potassium 4-mehtoxyphenyltrifluoroborate **11m** (40.7 mg, 0.19 mmol, 1.2 equiv) and TFAA (22 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 3 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (36.3 mg, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96−7.93 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.55 (d, J = 18.7 Hz, 1H), 4.36−4.29 (m, 2H), 4.07 (dd, J = 18.2 Hz, J = 10.5 Hz, 1H), 3.80 (s, 3H), 3.28 (dd, J = 18.2 Hz, J = 3.5 Hz, 1H), 2.86 (bs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.2, 198.0, 159.5, 136.2, 133.6, 129.4 (2C), 128.8 (3C), 128.2 (2C), 114.8, 67.3, 55.5, 48.5, 42.8 ppm. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.61; H, 6.20.

*(E)-5-Hydroxy-1-phenyl-3-(3-phenylprop-1-en-1-yl)pentane-1,4-dione (**13h**).* Following general procedure for the synthesis of compounds **13**, Conditions A, starting from **2g** (29.8 mg, 0.16 mmol, 1.0 equiv), potassium *trans*-3-Phenyl-1-propen-1-yltrifluoroborate **11e** (42.6 mg, 0.19 mmol, 1.2 equiv) and TFAA (22 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 3 h. The crude product was purified by flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (38.0 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H),7.32−7.21 (m, 3H), 7.14 (d, J = 7.4 Hz, 2H), 5.94−5.84 (m, 1H), 5.46 (dd, J = 15.3 Hz, J = 7.8 Hz, 1H), 4.59 (s, 2H), 3.81−3.70 (m, 2H), 3.37 (d, J = 6.6 Hz, 2H), 3.25−3.16 (m, 1H), 2.98 (bs, 1H), ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.8, 197.8, 139.4, 136.2, 134.9, 133.7, 128.8 (2C), 128.7 (2C), 128.6 (2C), 128.2 (2C), 127.0, 126.5, 67.5, 47.2, 41.1, 39.0 ppm. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 78.03; H, 6.49.

*(E)-(1-Benzyl-4-styryl-1H-pyrrol-2-yl)methanol (**14a**).* Following general procedure for the synthesis of pyrroles **14**, starting from **2j** (35.0 mg, 0.31 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (96.8 mg, 0.46 mmol, 1.5 equiv), tetrabutylammonium hydrogenosulfate (52.6 mg, 0.16 mmol, 0.5 equiv) in DCM anh. (6.2 mL) at rt for 48 h. Then, benzylamine (34 μL, 0.31 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (5.9 mg, 0.03 mmol, 0.1 equiv) in toluene (1.6 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (67.3 mg, 75% yield). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.44 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 8.1 Hz, 3H), 7.18 (d, J = 7.8 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 16.3 Hz, 1H), 6.92 (d, J = 1.8 Hz, 1H), 6.76 (d, J = 16.3 Hz, 1H), 6.36 (d, J = 1.8 Hz, 1H), 5.23 (s, 2H), 4.47 (s, 2H), 2.81 (bs, 1H) ppm. ^{13}C NMR (125 MHz, acetone-d_6) δ 139.8, 139.6, 135.2, 129.4 (2C), 129.3 (2C), 128.1, 127.8 (2C), 127.0, 126.4 (2C), 124.1, 123.7, 123.4, 122.6, 106.5, 56.7, 50.9 ppm. Anal. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62. Found: C, 82.90; H, 6.74.

*(E)-1-(1-Benzyl-4-styryl-1H-pyrrol-2-yl)ethanol (**14b**).* Following general procedure for the synthesis of pyrroles **14**, starting from **2a** (29.7 mg, 0.23 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (73.8 mg, 0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (39.7 mg, 0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL) at rt for 48 h. Then, benzyl amine (26 μL, 0.23 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (4.4 mg, 0.02 mmol, 0.1 equiv) in toluene (1.2 mL) at rt for 1 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a yellow oil (57.5 mg, 81% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.42−7.47 (m, 2H), 7.22−7.37 (m, 6H), 7.12−7.18 (m, 2H), 7.06 (d, J = 16.2 Hz, 1H), 6.88 (d, J = 1.7 Hz, 1H), 6.77 (d, J = 16.2 Hz, 1H), 6.40 (d, J = 1.7 Hz, 1H), 5.36 (d, J = 16.0 Hz, 1H), 5.20 (d, J = 16.0 Hz, 1H), 4.70 (q. J = 6.3 Hz, 1H), 3.91 (d, J = 6.3 Hz, 1H), 1.48 (d, J = 6.3 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 139.6, 139.0, 129.4, 129.3, 128.0, 127.7, 126.9, 126.3, 124.0, 123.8, 123.2, 122.3, 103.6, 62.2, 50.9, 22.9 ppm. Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98. Found: C, 83.09; H, 6.99.

*(E)-1-(1-Benzyl-4-(3-phenylprop-1-en-1-yl)-1H-pyrrol-2-yl)-ethanol (**14c**).* Following general procedure for the synthesis of pyrroles **14**, starting from **2a** (30.3 mg, 0.23 mmol, 1.0 equiv), *trans*-3-phenyl-1-propen-1-yltrifluoroborate **11e** (78.5 mg, 0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (39.7 mg, 0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL) rt for 48 h. Then, benzyl amine (26 μL, 0.23 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (4.4 mg, 0.02 mmol, 0.1 equiv) in toluene (1.2 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a yellow oil (57.9 mg, 78% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.06−7.38 (m, 10H), 6.69 (d, J = 1.9 Hz, 1H), 6.30 (d, J = 15.5 Hz, 1H), 6.21 (d, J = 1.9 Hz, 1H), 5.94 (dt, J = 15.5 Hz, J = 7.1 Hz, 1H), 5.32 (d, J = 16.1 Hz, 1H), 5.14 (d, J = 16.1 Hz, 1H), 4.68 (q. J = 6.5 Hz, 1H), 3.83 (d, J = 6.8 Hz, 1H), 3.44 (d, J = 6.8 Hz, 2H),1.43 (d, J = 6.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 140.2, 138.5, 129.4, 129.2, 128.0, 127.7, 126.7, 125.6, 124.3, 122.2, 121.8, 103.6, 62.3, 50.8, 40.0, 23.0 ppm. Anal. Calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30. Found: C, 83.31; H, 7.28.

*(1-Benzyl-4-(phenylethynyl)-1H-pyrrol-2-yl)methanol (**14d**).* Following general procedure for the synthesis of pyrroles **14**, starting from **2j** (36.0 mg, 0.31 mmol, 1.0 equiv), potassium phenylethynyltrifluoroborate **11i** (95.7 mg, 0.46 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (52.6 mg, 0.16 mmol, 0.5 equiv) in DCM anh. (6.2 mL) at rt for 48 h. Then, benzylamine (34 μL, 0.31 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (5.9 mg, 0.03 mmol, 0.1 equiv) in toluene (1.6 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (57.0 mg, 64% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.45−7.29 (m, 8H), 7.20 (d, J = 7.5 Hz, 2H), 7.09 (d, J = 1.8 Hz, 1H), 6.22 (d, J = 1.8 Hz, 1H), 5.28 (s, 2H), 4.48−4.47 (m, 2H), 4.08 (bs, 1H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 139.2, 134.4, 131.7 (2C), 129.4 (2C), 129.2 (2C), 128.3, 128.2, 127.8 (2C), 127.5, 125.4, 112.2, 103.6, 87.9, 86.5, 56.3, 51.0 ppm. Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96. Found: C, 83.76; H, 6.08.

*1-(1-Benzyl-4-(phenylethynyl)-1H-pyrrol-2-yl)ethanol (**14e**).* Following general procedure for the synthesis of pyrroles **14**, starting from **2a** (30.3 mg, 0.23 mmol, 1.0 equiv), potassium phenylethynyltrifluoroborate **11i** (73.1 mg, 0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (39.7 mg, 0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL) at rt for 48 h. Then, benzyl amine (26

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μL, 0.23 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (4.4 mg, 0.02 mmol, 0.1 equiv) in toluene (1.2 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a yellow oil (57.2 mg, 81% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.25−7.46 (m, 8H), 7.17 (d, J = 7.4 Hz, 2H), 7.05 (d, J = 1.7 Hz, 1H), 6.23 (d, J = 1.0 Hz, 1H), 5.41 (d, J = 15.8 Hz, 1H), 5.25 (d, J = 15.8 Hz, 1H), 4.73 (q. J = 6.5 Hz, 1H), 4.04 (d, J = 6.5 Hz, 1H), 1.43 (d, J = 6.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 138.2, 131.7, 129.4, 129.3, 128.2, 128.1, 127.7, 127.2, 125.4, 109.6, 103.4, 87.9, 86.6, 62.0, 51.1.22.8 ppm. Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35. Found: C, 83.60; H, 6.34.

*(E)-(1-Benzyl-5-phenyl-3-styryl-1H-pyrrol-2-yl)methanol (**15a**).* Following general procedure for the synthesis of pyrroles **15**, starting from **2g** (29.7 mg, 0.16 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (39.4 mg, 0.19 mmol, 1.2 equiv) and TFAA (22 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 1 h. Then, benzylamine (17 μL, 0.16 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (3.0 mg, 0.02 mmol, 0.1 equiv) in toluene (0.8 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (42.1 mg, 72% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.55−7.53 (m, 2H), 7.35−7.26 (m, 12H), 6.98−6.96 (m, 3H), 6.61 (s, 1H), 5.41 (s, 2H), 4.62 (s, 2H), 4.07 (bs, 1H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 140.3, 139.6, 137.1, 134.0, 133.7, 129.6 (2C), 129.5 (2C), 129.4 (2C), 129.3 (2C), 128.2, 127.8, 127.2, 126.6 (2C), 126.4 (2C), 125.4, 122.2, 122.0, 106.1, 53.8, 48.2 ppm. Anal. Calcd for $C_{26}H_{23}NO$: C, 85.45; H, 6.34. Found: C, 85.35; H, 6.48.

*(E)-(1-Benzyl-5-phenyl-3-(3-phenylprop-1-en-1-yl)-1H-pyrrol-2-yl)methanol (**15b**).* Following general procedure for the synthesis of pyrroles **15**, starting from **2g** (29.8 mg, 0.16 mmol, 1.0 equiv), potassium *trans*-3-phenyl-1-propen-1-yltrifluoroborate **11e** (42.6 mg, 0.19 mmol, 1.2 equiv) and TFAA (22 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 3 h. Then, benzylamine (17 μL, 0.16 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (3.0 mg, 0.02 mmol, 0.1 equiv) in toluene (0.8 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (46.7 mg, 77% yield). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.32−7.26 (m, 11H), 7.22−7.19 (m, 2H), 6.92 (d, J = 7.3 Hz, 2H), 6.56 (d, J = 15.6 Hz, 1H), 6.40 (s, 1H), 6.11 (dt, J = 15.6, Hz, J = 7.1 Hz, 1H), 5.36 (s, 2H), 4.49 (d, J = 5.3 Hz, 2H), 3.93 (t, J = 5.3 Hz, 1H), 3.52 (d, J = 7.1 Hz, 2H) ppm. ^{13}C NMR (125 MHz, acetone-d_6) δ 142.1, 140.5, 136.6, 134.2, 132.1, 129.6 (2C), 129.5 (2C), 129.4 (2C), 129.3 (2C), 129.2 (2C), 128.0, 127.7, 126.7, 126.4 (2C), 125.9, 124.0, 122.1, 106.3, 53.9, 48.1, 40.2 ppm. Anal. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64. Found: C, 85.31; H, 6.75.

*(E)-(1-Benzyl-5-methyl-3-styryl-1H-pyrrol-2-yl)methanol (**15c**).* Following general procedure for the synthesis of pyrroles **15**, starting from **2f** (30.5 mg, 0.24 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (65.0 mg, 0.29 mmol, 1.2 equiv) and TFAA (33 μL, 0.24 mmol, 1.0 equiv) in DCM anh. (1.4 mL) for 1 h. Then, benzylamine (26 μL, 0.24 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (4.6 mg, 0.02 mmol, 0.1 equiv) in toluene (1.2 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (36.4 mg, 50% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.50 (d, J = 7.6 Hz, 2H), 7.34−7.13 (m, 8H), 7.01 (d, J = 7.5 Hz, 2H), 6.78 (d, J = 16.1 Hz, 1H), 6.23 (s, 1H), 5.28 (s, 2H), 4.62−4.61 (m, 2H), 3.92 (t, J = 5.4 Hz, 1H), 2.11 (s, 3H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 139.9, 139.8, 132.2, 131.2, 129.4 (2C), 129.3 (2C), 127.8, 126.9, 126.7 (2C), 126.4 (2C), 124.2, 122.5, 120.9, 104.0, 53.5, 47.4, 12.3 ppm. Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98. Found: C, 83.29; H, 6.90.

*(1-Benzyl-3,5-diphenyl-1H-pyrrol-2-yl)methanol (**15d**).* Following general procedure for the synthesis of pyrroles **15**, starting from **2g** (30.3 mg, 0.16 mmol, 1.0 equiv), potassium phenyltrifluoroborate **11f** (34.8 mg, 0.19 mmol, 1.2 equiv) and TFAA (22 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 1 h. Then, benzylamine (17 μL, 0.16 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (3.0 mg, 0.02 mmol, 0.1 equiv) in toluene (0.8 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (38.0 mg, 70% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.62−7.58 (m, 2H), 7.42−7.22 (m, 11H), 6.98 (d, J = 7.1 Hz, 2H), 6.44 (s, 1H), 5.47 (s, 2H), 4.55−4.53 (m, 2H), 4.07 (t, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 140.4, 137.5, 136.1, 134.2, 130.8 129.6 (2C), 129.5 (2C), 129.3 (2C), 129.2 (2C), 129.0 (2C), 128.1, 127.8, 126.5, 126.4 (2C), 125.8, 109.4, 54.7, 48.3 ppm. Anal. Calcd for $C_{24}H_{21}NO$: C, 84.92; H, 6.24. Found: C, 85.11; H, 6.15.

*(1-Benzyl-3-(4-methoxyphenyl)-5-phenyl-1H-pyrrol-2-yl)-methanol (**15e**).* Following general procedure for the synthesis of pyrroles **15**, starting from **2g** (30.4 mg, 0.16 mmol, 1.0 equiv), potassium 4-mehtoxyphenyltrifluoroborate **11m** (40.7 mg, 0.19 mmol, 1.2 equiv) and TFAA (22 μL, 0.16 mmol, 1.0 equiv) in DCM anh. (1.0 mL) for 3 h. Then, benzylamine (17 μL, 0.16 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (3.0 mg, 0.02 mmol, 0.1 equiv) in toluene (0.8 mL) at rt for 12 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 (47.8 mg, 81% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.52 (d, J = 8.9 Hz, 2H), 7.37−7.22 (m, 8H), 6.99−6.96 (m, 4H), 6.39 (s, 1H), 5.44 (s, 2H), 4.51 (s, 2H), 4.06 (bs, 1H), 3.81 (s, 3H) ppm. ^{13}C NMR (75 MHz, acetone-d_6): 159.1, 140.5, 139.5, 134.3, 130.4, 130.0 (2C), 129.9, 129.6 (2C), 129.4 (2C), 129.3 (2C), 128.0, 127.8, 126.4 (2C), 125.6, 114.7 (2C), 109.3, 55.5, 54.9, 48.3 δ ppm. Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27. Found: C, 81.22; H, 6.38.

*(2S,3R,6R)-6-Methyl-5-oxo-3-((E)-styryl)tetrahydro-2H-pyran-2-yl acetate (**16a**).* Following general procedure for the synthesis of compounds **16**, Conditions C, starting from **2a** (29.4 mg, 0.23 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate **11a** (73.8 mg, 0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (39.7 mg, 0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL) at rt for 48 h. Then, Ac_2O (22 μL, 0.23 mmol, 1.0 equiv), DMAP (1.4 mg, 0.012 mmol, 5% mmol) and Et_3N (65 μL, 0.47 mmol, 2.0 equiv) at 0 °C for 1 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a yellow oil (52.6 mg, 82% yield, *dr* 90:10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14−7.34 (m, 5H), 6.42 (d, J = 15.8 Hz, 1H), 6.09 (d, J = 5.4 Hz, 1H), 6.03 (dd, J = 15.8 Hz, J = 7.7 Hz, 1H), 4.31 (q. J = 6.8 Hz, 1H), 2.93−3.06 (m, 1H), 2.51−2.69 (m, 2H), 2.08 (s, 3H), 1.27 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 169.9, 136.4, 133.0, 128.8, 128.2, 126.6, 126.5, 94.4, 73.2, 42.2, 39.5, 21.3, 15.1 ppm. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.14; H, 6.59.

*(2S,3R,6R)-6-Methyl-3-(2-methylprop-1-en-1-yl)-5-oxotetrahydro-2H-pyran-2-yl acetate (**16b**).* Following general procedure for the synthesis of compounds **16**, Conditions C, starting from **2a** (29.9 mg, 0.23 mmol, 1.0 equiv), potassium 2-methyl-1-propenyltrifluoroborate **11k** (56.9 mg, 0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (39.7 mg, 0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL) at rt for 48 h. Then, Ac_2O (22 μL, 0.23 mmol, 1.0 equiv), DMAP (1.4 mg, 0.012 mmol, 5% mmol) and Et_3N (65 μL, 0.47 mmol, 2.0 equiv) at 0 °C for 1 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (33.9 mg, 64% yield, *dr* 95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97 (d, J = 5.3 Hz, 1H), 5.02 (dt, J = 9.4 Hz, J = 1.3 Hz, 1H), 4.33 (c. J = 6.8 Hz, 1H), 3.02−3.13 (m, 1H), 2.36−2.57 (m, 2H), 2.12 (s, 3H), 1.71 (s, 3H), 1.64 (s, 3H), 1.31 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 170.0, 136.4, 121.8, 95.2, 73.0, 40.1, 37.9, 25.9, 21.4, 18.3, 15.1 ppm. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.75; H, 8.03.

*(2S,3R,6R)-3-(Cyclohex-1-en-1-yl)-6-methyl-5-oxotetrahydro-2H-pyran-2-yl acetate (**16c**).* Following general procedure for the synthesis of compounds **16**, Conditions C, starting from **2a** (29.5 mg, 0.23 mmol, 1.0 equiv), potassium cyclohexenyltrifluoroborate **11l** (66.0 mg, 0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (39.7 mg, 0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL) at rt for 18 h. Then, Ac_2O (22 μL, 0.23 mmol, 1.0 equiv), DMAP (1.4 mg, 0.012 mmol, 5% mmol) and Et_3N (65 μL, 0.47 mmol, 2.0 equiv) at 0 °C for 1 h. The crude product was purified via flash column

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chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (31.3 mg, 53% yield, *dr* 89:11). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.12 (d, J = 5.4 Hz, 1H), 5.55 (s, 1H), 4.28 (c. J = 6.6 Hz, 1H), 2.41−2.70 (m, 3H), 2.11 (s, 3H), 1.90−2.05 (m, 4H), 1.51−1.65 (m, 4H), 1.31 (d, J = 6.6 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9, 170.1, 134.4, 125.5, 94.0, 72.6, 45.6, 38.5, 26.4, 25.3, 22.8, 22.2, 21.4, 15.3 ppm. Anal. Calcd for $C_{14}H_{20}O_4$: 66.65; H, 7.99. Found: 66.59; H, 8.01.

*(2S,3R,6R)-3-(Benzofuran-2-yl)-6-methyl-5-oxotetrahydro-2H-pyran-2-yl acetate (**16d**).* Following general procedure for the synthesis of compounds **16**, Conditions C, starting from **2a** (29.4 mg, 0.23 mmol, 1.0 equiv), potassium benzofuran-2-trifluoroborate **11m** (78.7 mg, 0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (39.7 mg, 0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL) at rt for 24 h. Then, Ac_2O (22 μL, 0.23 mmol, 1.0 equiv), DMAP (1.4 mg, 0.012 mmol, 5% mmol) and Et_3N (65 μL, 0.47 mmol, 2.0 equiv) at 0 °C for 1 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a yellow oil (53.3 mg, 79% yield, *dr* 92:8). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49−7.55 (m, 1H), 7.41−7.47 (m, 1H), 7.18−7.31 (m, 2H), 6.47−6.58 (m, 2H), 4.43 (c. J = 6.6 Hz, 1H), 3.64−3.78 (m, 1H), 2.92−3.03 (m, 2H), 2.17 (s, 3H), 1.35 (d, J = 6.6 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6, 169.6, 155.0, 154.7, 128.1, 124.5, 123.1, 121.1, 111.3, 104.2, 92.5, 73.3, 39.3, 38.0, 21.2, 15.2 ppm. Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.58; H, 5.60.

*(2S,3R,6R)-6-Methyl-5-oxo-3-(phenylethynyl)tetrahydro-2H-pyran-2-yl acetate (**16e**).* Following general procedure for the synthesis of compounds **16**, Conditions C, starting from **2a** (29.8 mg, 0.23 mmol, 1.0 equiv), potassium phenylethynyltrifluoroborate **11i** (73.1 mg, 0.35 mmol, 1.5 equiv) and tetrabutylammonium hydrogenosulfate (39.7 mg, 0.12 mmol, 0.5 equiv) in DCM anh. (4.6 mL) at rt for 48 h. Then, Ac_2O (22 μL, 0.23 mmol, 1.0 equiv), DMAP (1.4 mg, 0.012 mmol, 5% mmol) and Et_3N (65 μL, 0.47 mmol, 2.0 equiv) at 0 °C for 1 h. The crude product was purified via flash column chromatography on silica gel eluting with Hexane:AcOEt 8:2 to afford a colorless oil (47.4 mg, 75% yield, *dr* 98:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23−7.46 (m, 5H), 6.36 (d, J = 4.6 Hz, 1H), 4.36 (q. J = 6.9 Hz, 1H), 3.37−3.45 (m, 1H), 2.89 (dd, J = 16.0 Hz, J = 5.4 Hz, 1H), 2.78 (dd, J = 16.0 Hz, J = 8.0 Hz, 1H), 2.18 (s, 3H), 1.38 (d, J = 6.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.9, 169.6, 131.8, 128.7, 128.4, 122.4, 93.0, 85.5, 85.1, 73.3, 39.5, 32.8, 21.3, 15.3 ppm. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.50; H, 5.93.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01643.

^{1}H NMR and ^{13}C NMR spectra, and NOE determinations (PDF)

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Notes

The authors declare no competing financial interest.

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(26) Unless otherwise stated (see text and Scheme 4), only one diastereomer (2,6-*trans*) was observed on the ^{1}H NMR ($CHCl_3$, 300 MHz) spectra of the crude reaction products.

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