



Silica gel enables Achmatowicz rearrangement with KBr/oxone under “anhydrous” condition for one-pot functionalization



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ABSTRACT

Silica gel was found to effectively promote Achmatowicz rearrangement (AchR) using KBr/oxone under near **anhydrous** condition. This new protocol allows direct functionalization of AchR products in a one-pot manner, effectively reducing the cost, time, and environmental impacts derived from the conventional stop-and-go approach using separate reaction vessels. These advantages were demonstrated in four types of sequential one-pot reactions: i) AchR-Kishi reduction (and AchR-Ferrier allylation); ii) AchR-acylation-O-glycosylation; iii) AchR-acylation-[5 + 2]-cycloaddition; and iv) AchR-TEMPO oxidation.

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1. Introduction

Achmatowicz rearrangement (AchR) [1] is a powerful oxidative transformation widely used for the construction of versatile dihydropyranone acetals from easily available furfuryl alcohols. The synthetic utility of dihydropyranone acetals derived from AchR has been manifested in a variety of C-C, C-O, C-H bond-forming reactions, including Kishi reduction [2], O-glycosylation [3], [5 + 2]-cycloaddition [4], Ferrier allylation [5], and arylation [6], and in the total synthesis of natural products (Fig. 1) [7–10]. Not surprisingly, many oxidants [11–19] such as Br₂/MeOH, dimethyldioxirane (DMDO), magnesium monoperoxyphthalate, metal-base oxidant (PCC, VO(acac)₂/TBHP, titanium(IV) silicalite/H₂O₂), phenyl-iodine(III) diacetate (PIDA), molecular oxygen (O₂/hν), NBS [20] and *m*-CPBA [21], have been identified and developed for AchR. Among them, NBS and *m*-CPBA represent the most efficient oxidants with the broadest substrate scope. However, the major drawback of using these two oxidants for AchR is the generation of stoichiometric organic byproducts (*m*-chlorobenzoic acid or succinimide) (Fig. 2), which usually need to be removed immediately by column chromatography. In order to address this problem, we previously

developed a new catalytic protocol using inorganic catalytic and oxidant (oxone/KBr, THF/H₂O) [22–24]. Although our new green catalytic protocol was highly efficient and tolerant of a variety of functional groups, we recognized that the use of THF/H₂O (v/v: 4/1) miscible solvents precluded any attempts of direct functionalization of the AchR products in a one-pot manner because many such classical functionalization reactions (e.g., acylation and Kishi reduction) were performed in non-protic anhydrous solvent. It should be noted that all previous oxidation methods did not allow for such one-pot functionalization due to the byproducts and/or aqueous solvent. This challenge calls for the development of a new oxidation method/condition for AchR. Herein, we describe the identification of chromatographic silica gel that enables AchR to occur with KBr/oxone under near anhydrous condition, which for the first time allows direct one-pot functionalization of the AchR products.

2. Results and discussion

It is not unprecedented in the literature that chromatographic silica gel has been used as a reaction medium in combination with organic solvents [25]. We were particularly attracted by Asensio's report [26] using silica gel deposited with oxone for Baeyer-Villiger oxidation under anhydrous CH₂Cl₂ condition. This inspired us to propose a similar silica gel-mediated AchR: KBr and oxone-deposited on silica gel. To test our hypothesis, we chose furfuryl

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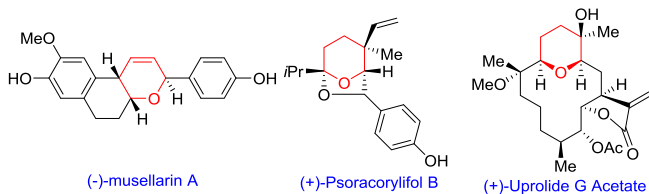


Fig. 1. Representative natural products synthesized in our lab using AchR [6–8].

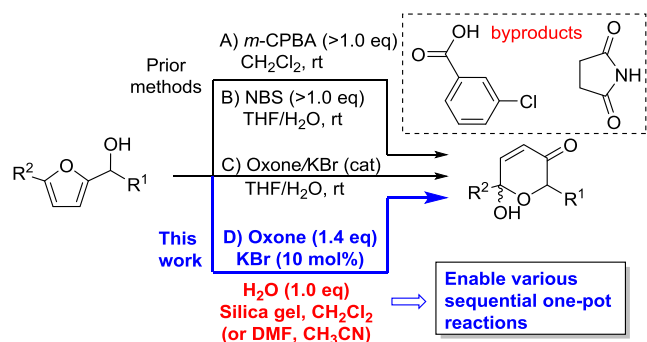
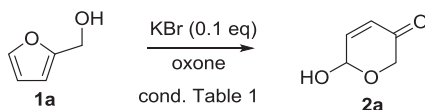


Fig. 2. AchR under classical conditions and our silica gel-mediated catalytic protocol.

alcohol (**1a**) as the model substrate for AchR (Table 1). To our delight, 76% yield of AchR product **2a** was obtained within 2 h (entry 1) when silica gel (20 mg, 200 mg/mmol) was added to the THF suspension of **1a** (0.1 mmol, 1.0 eq), KBr (0.1 eq), oxone (2.4 eq), NaHCO₃ (1.0 eq), and H₂O (1.0 eq). Without silica gel (entry 2), the otherwise identical condition gave only 10% yield of **2a** after 12 h. It should be noted that stoichiometric conversion of **1a** to **2a** requires 1.0 equivalent of H₂O with loss of 2 electrons. This was the reason we added 1.0 equivalent of H₂O and 2.4 equivalent of oxone. If water was not added (entry 3), the reaction proceeded slowly with

Table 1

Optimization of the silica gel-mediated AchR of **1a**.



| entry ^a | silica gel (mg) ^{b,c} | H ₂ O (eq) ^{c,d} | oxone (eq) ^d | solvent | time | yield (2a, %) ^e |
|--------------------|--------------------------------|--------------------------------------|-------------------------|-------------------------|----------|----------------------------|
| 1 | 20 | 1 | 2.4 | THF | 2 | 76 |
| 2 | 0 | 1 | 2.4 | THF | 12 | 10 |
| 3 | 20 | 0 | 2.4 | THF | 12 | 17 |
| 4 | 10 | 1 | 2.4 | THF | 2 | 76 |
| 5 | 5 | 1 | 2.4 | THF | 2 | 53 |
| 6 | 10 | 1 | 1.4 | THF | 2 | 74 |
| 7 | 10 | 1 | 1.4 | DCM | 1 | 90 |
| 8 | 10 | 1 | 1.4 | CHCl₃ | 1 | 91 |
| 9 | 10 | 1 | 1.4 | DMF | 1 | 94 |
| 10 | 10 | 1 | 1.4 | CH₃CN | 1 | 83 |
| 11 | 10 | 1 | 1.4 | Toluene | 1 | 61 |
| 12 | 10 | 1 | 1.4 | DMSO | 1 | 0 |
| 13 | 10 | 1 | 1.4 | Et ₂ O | 1 | 52 |

Bold means these conditions are optimal with the best yields.

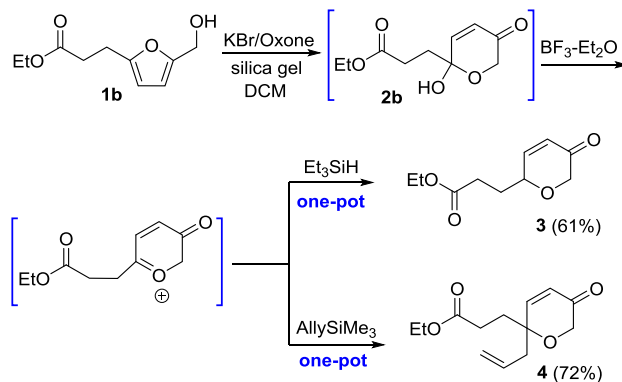
^a The reaction was carried out at rt, and only filtration was needed for the work up: **1a** (0.1 mmol) was dissolved in different solvent (0.5 mL) and stirred vigorously with silica gel, H₂O, oxone, KBr (1.2 mg, 0.1 eq) and NaHCO₃ (8.4 mg, 1 eq).

^b Silica gel was activated at 120 °C for 48 h.

^c Silica gel and H₂O were mixed and shaken to be uniform before the addition.

^d The equivalent of different material to **1a**.

^e Yield was determined by NMR of the crude reaction mixture.



Scheme 1. Representative one-pot AchR/Kishi reduction and AchR/Ferrier allylation.

poor 17% yield. Further experiments (entries 4–13) led us to identify the several optimal conditions for AchR (entries 7–10) with high yield (83–94%).

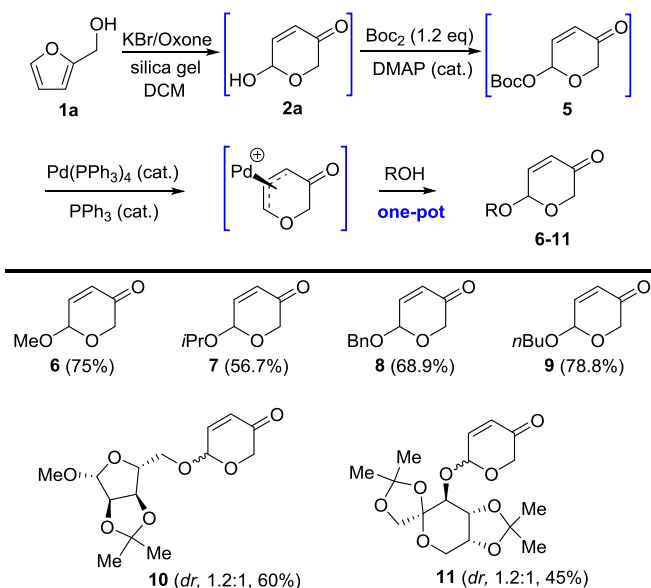
Given the fact that only stoichiometric amount of H₂O was used and converted to the product, our new reaction system was anhydrous, which may offer an invaluable opportunity for direct one-pot functionalization of AchR products. To verify our hypothesis, we first elected Kishi reduction [2] of AchR product in one pot (Scheme 1) because i) it represents one of the most classical functionalizations of AchR products to provide the dihydropyranones (tetrahydropyrans) and ii) it was unattainable using known AchR methods followed by conventional Kishi reduction (TFA/Et₃SiH or BF₃-Et₂O/Et₃SiH). In particular, the Kishi condition of BF₃-Et₂O/Et₃SiH is extremely sensitive to moisture and the resulting oxonium ion is a super electrophile. Fortunately, we were able to effect the one-pot Kishi reduction and isolate dihydropyranone **3** in 61% overall yield (2 steps, one pot) when 4.0 equivalent of BF₃-Et₂O was used. Analogously, trapping the oxonium ion with allyl silane in the same reaction vessel of AchR gave the Ferrier-type allylation [5] product **4**

in 72% yield (two steps). These two examples clearly demonstrated that our new protocol for AchR could be coupled with functionalization promoted by Lewis acid under anhydrous CH_2Cl_2 condition.

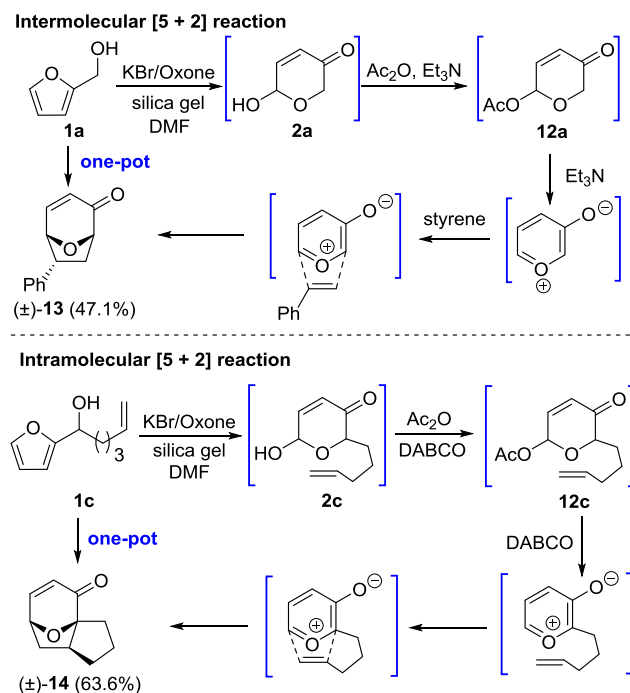
Next, we turned our attention to direct acylation of the AchR products for subsequent O-glycosylation [3] (Scheme 2) and [5 + 2] cycloaddition [4] (Scheme 3). Pd-catalyzed O-glycosylation of Boc-protected AchR product was developed by O'Doherty [27,28] and Feringa [29,30] and has constituted as a key strategic method in O'Doherty lab for *de novo* synthesis of natural and unnatural glycosides [31]. One-pot acylation of AchR product **1a** with $(\text{Boc})_2\text{O}$ in the presence of catalytic DMAP proceeded cleanly to provide quantitative Boc-protected AchR product **5** (judged by TLC, not isolated). Remarkably, addition of catalytic $\text{Pd}(\text{PPh}_3)_4$, PPh_3 and glycosyl donors (alcohols) to the crude **5** (without workup) in the same flask furnished glycosides (**6–11**) in good overall yields (45–79%, three steps). The plenty OH groups on the silica gel surface did not erode the effectiveness of Pd-catalyzed O-glycosylation. It should be noted that this three-step sequence could not be achieved by using all previous protocols for AchR due to intolerance of byproducts derived from oxidants (*m*-CPBA, NBS, *tert*-BuOOH, Br_2/MeOH etc) and/or aqueous (or protic) reaction medium in the subsequent acylation and O-glycosylation.

The success of one-pot acylation of AchR products under our new protocol prompted us to further explore the possibility of one-pot AchR-acetylation-[5 + 2]-cycloaddition (Scheme 3). AchR coupled with [5 + 2]-cycloaddition of alkenes has evolved to be a classical tactic for the synthesis of seven-membered carbocycles in organic synthesis. Conventional practice involves isolation of AchR (**2a**) and acetylation product (**12a**) and carrying out the base-promoted [5 + 2]-cycloaddition in a separate flask. Our attempt on this one-pot, three-step sequence proved fruitful. It was found that the optimal solvent was not CH_2Cl_2 but DMF. Both inter- and intramolecular [5 + 2]-cycloaddition could be carried out in the same flask used for AchR and acetylation to provide the cycloaddition adducts **13** and **14**, respectively, in good yield (47–64%) over three steps.

Finally, we were very interested in one-pot oxidation of AchR products for the synthesis of 5-hydroxy-2-pyrones, which have found wide applications (e.g., Diels-Alder [32]) in organic synthesis. Prior method for the synthesis of 5-hydroxy-2-pyrones involved



Scheme 2. One-pot AchR/acylation/Pd-catalyzed O-glycosylation.

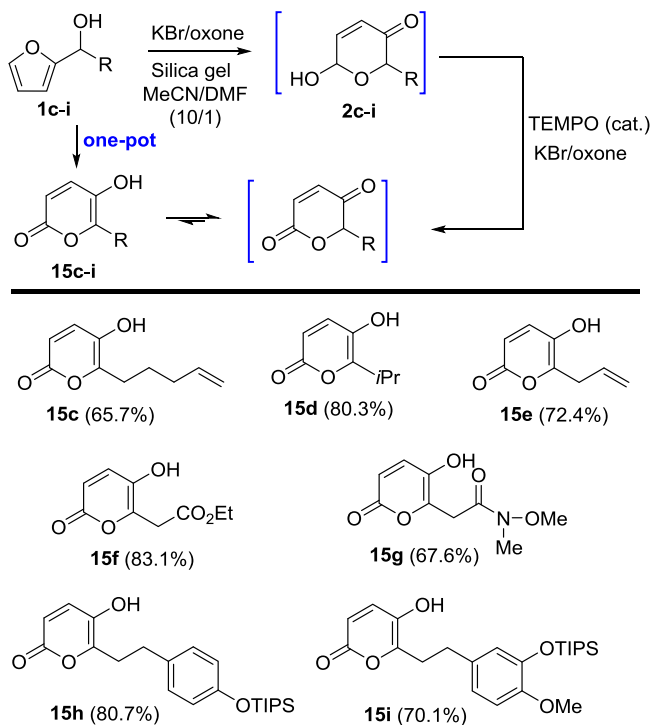


Scheme 3. Representative one-pot AchR/acetylation/[5 + 2] reaction.

stepwise reactions: AchR (NBS, $\text{THF}/\text{H}_2\text{O}$), Jones oxidation, and Et_3N -mediated tautomerization. We believed that these three reactions could be performed in a single flask if our new protocol for AchR was used. Additionally, Jones oxidation (CrO_3 , aq H_2SO_4 , acetone), classical for oxidation of cyclic acetals into lactones, uses very toxic chromium (VI) as the stoichiometric oxidant under a strong acidic condition, which posed significant environmental impacts and restricted its applications. An alternative oxidation was needed to couple with AchR. Inspired by Bolm's report [33] on using $\text{TEMPO}(\text{cat})/\text{oxone}/n\text{-Bu}_4\text{NBr}(\text{cat})$ for oxidation of alcohols to aldehydes and ketones, we proposed the one-pot AchR-TEMPO oxidation for the synthesis of 5-hydroxy-2-pyrones (see Scheme 4). One obvious advantage of integrating these two processes in a single flask was that they shared the same oxidant (oxone) and bromide catalyst (Br^-), which could be added in the first reaction (AchR) and the second reaction could be initiated by the addition of TEMPO catalyst. To our delight, mixed solvents (MeCN/DMF , 10/1) were found to enable these two reactions to occur efficiently and sequentially in the same flask, providing the 5-hydroxy-2-pyrones (**15c–i**) in good yields (66–83%, two steps). Notably, additional base was not required for tautomerization. Thus, a three-step sequence was refined to a formally one-step reaction.

3. Conclusions

In summary, we identified chromatographic silica gel as an efficient promoter/support for Achmatowicz rearrangement using KBr/oxone under anhydrous condition. In light of the insolubility of KBr and oxone in organic solvent (e.g., CH_2Cl_2), it is believed that the reaction might occur on the surface of silica gel, which absorbs furfuryl alcohol, KBr , and oxone. However, the detailed role of silica gel remains unclear. This new **anhydrous** system without organic byproducts allows for the first time direct functionalization of AchR products in a one-pot manner, which is a green chemistry approach to significantly reduce the cost, time, and environmental impacts. With the demonstrated four types of one-pot, sequential reactions,



Scheme 4. Substrate scope for one-pot AchR/oxidation.

we expect that this new protocol will be widely used for AchR in organic synthesis.

4. Experimental section

4.1. General information

Reagents were obtained commercially and used without further purification unless otherwise stated. CH_2Cl_2 , CH_3CN and DMF were all freshly distilled before use from calcium hydride (CaH_2). Flash column chromatography was performed on silica gel (200–300 mesh). All the reactions were monitored by thin layer chromatography (TLC) using GF254 plates. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer in CDCl_3 and MeOD. HRMS spectrometry was detected by CI-TOF. Infrared spectrometry was recorded on ALPHA FTIR (Bruker).

4.2. Synthesis of substrates 1b–1i

Substrates **1b–1i** were synthesized according to the published literature [6,19,34–39], and the characterization data were in agreement with those reported.

4.3. Synthesis of compound 2a

An oven-dried 5 mL flask was charged with dry CH_2Cl_2 (0.5 mL), pre-hydrated silica gel (10 mg + 1.8 mg H_2O), furfuryl alcohol (9.8 mg, 0.1 mmol, 1.0 eq), KBr (1.2 mg, 0.01 mmol, 0.1 eq), oxone (43 mg, 0.14 mmol, 1.4 eq) and NaHCO_3 (8.4 mg, 0.1 mmol, 1.0 eq). Then, the reaction mixture was stirred vigorously at rt for 1 h. Upon completion (monitored by TLC), the residue was poured onto silica gel and purified by flash chromatography (EtOAc/hexane = 1:1).

6-Hydroxy-2H-pyran-3(6H)-one (**2a**). [40] Colorless oil, yield 90%. ^1H NMR (400 MHz, CDCl_3) δ : 6.95 (dd, J = 10.4, 3.0 Hz, 1H), 6.16 (d, J = 10.4 Hz, 1H), 5.63 (dd, J = 5.6, 3.0 Hz, 1H), 4.57 (d, J = 16.9 Hz, 1H), 4.14 (d, J = 17.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 194.7,

145.8, 128.1, 88.4, 66.8.

4.4. General procedure for the synthesis of compounds 3 and 4

An oven-dried 10 mL flask was charged with dry CH_2Cl_2 (1 mL), pre-hydrated silica gel (20 mg + 3.6 mg H_2O), furfuryl alcohol (39.6 mg, 0.2 mmol, 1 eq), KBr (2.4 mg, 0.02 mmol, 0.1 eq), Oxone (86.1 mg, 0.28 mmol, 1.4 eq) and NaHCO_3 (16.8 mg, 0.2 mmol, 1.0 eq). And the reaction mixture was stirred vigorously at rt for 2 h. Upon completion (monitored by TLC), the reaction was cooled to -78°C , followed by the addition of Et_3SiH (319 μL , 2.0 mmol, 10.0 eq) or allyltrimethylsilane (318 μL , 2.0 mmol, 10.0 eq) and $\text{BF}_3\text{-Et}_2\text{O}$ (98.7 μL , 0.8 mmol, 4.0 eq) successively, and the resulting mixture was stirred for another 1 h. The mixture was quenched by addition of saturated aqueous NaHCO_3 solution, and the aqueous phase was extracted with CH_2Cl_2 . The combined organic fractions were washed with saturated aqueous NH_4Cl solution and brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc/hexane = 1:5) to provide the title compound.

4.4.1. Ethyl 3-(3-oxo-3,6-dihydro-2H-pyran-6-yl)acetate (**3**)

Colorless oil, yield 61% for 2 steps. FTIR: 2981.3, 2935.5, 2820.4, 1728.4, 1695.0, 1382.4, 1325.7, 1264.7, 1176.3, 1100.9, 1031.5, 754.4 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 6.95 (dd, J = 10.5, 1.9 Hz, 1H), 6.15 (dd, J = 10.5, 2.3 Hz, 1H), 4.39 (ddd, J = 8.5, 4.2, 2.1 Hz, 1H), 4.26 (d, J = 16.3 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 4.08 (dd, J = 16.3, 1.8 Hz, 1H), 2.53–2.43 (m, 2H), 2.12–1.91 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.8, 173.2, 151.2, 127.4, 72.6, 71.3, 60.7, 29.8, 29.2, 14.4; HRMS (CI-TOF) m/z calcd. for $\text{C}_{10}\text{H}_{13}\text{O}_4$ $[\text{M}+\text{H}]^+$ 197.0808, found 197.0819.

4.4.2. Ethyl 3-(6-allyl-3-oxo-3,6-dihydro-2H-pyran-6-yl)acetate (**4**)

Colorless oil, yield 72% for 2 steps. FTIR: 2980.1, 2936.1, 1729.9, 1693.5, 1438.7, 1391.9, 1266.1, 1181.3, 1094.4, 756.0 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 6.87 (d, J = 10.6 Hz, 1H), 6.10 (d, J = 10.6 Hz, 1H), 5.85–5.75 (m, 1H), 5.19–5.14 (m, 2H), 4.31–4.16 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.52–2.31 (m, 4H), 2.09–1.98 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 194.3, 173.4, 154.0, 132.0, 126.5, 119.6, 75.8, 67.3, 60.7, 40.8, 31.8, 28.8, 14.3; HRMS (CI-TOF) m/z calcd. for $\text{C}_{13}\text{H}_{19}\text{O}_4$ $[\text{M}+\text{H}]^+$ 239.1278, found 239.1280.

4.5. General procedure for the synthesis of compounds 6–11

An oven-dried 10 mL flask was charged with dry CH_2Cl_2 (1.0 mL), pre-hydrated silica gel (20 mg + 3.6 mg H_2O), furfuryl alcohol (0.2 mmol, 1.0 eq), KBr (2.4 mg, 0.02 mmol, 0.1 eq), oxone (86.1 mg, 0.28 mmol, 1.4 eq) and NaHCO_3 (33.6 mg, 0.4 mmol, 2.0 eq). The resulting mixture was stirred vigorously at rt. Upon completion (monitored by TLC), DMAP (2.4 mg, 0.02 mmol, 0.1 eq) and Boc_2O (55.1 μL , 0.24 mmol, 1.2 eq) were added, and the mixture was stirred for another 0.5 h. Then, to the above residue were added molecular sieve (4 Å, 40 mg), alcohol or protected monose (0.8 mmol, 4.0 eq), PPh_3 (15.7 mg, 0.06 mmol, 0.3 eq) and $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 0.01 mmol, 0.05 eq). The solution was stirred at rt for 1 h, poured onto silica gel and purified by flash chromatography (EtOAc/hexane = 1:1) to provide the title compound.

4.5.1. 6-Methoxy-2H-pyran-3(6H)-one (**6**). [29]

Colorless oil, yield 75% for 3 steps. ^1H NMR (400 MHz, CDCl_3) δ : 6.89 (dd, J = 10.4, 3.4 Hz, 1H), 6.14 (d, J = 10.3 Hz, 1H), 5.11 (d, J = 3.4 Hz, 1H), 4.45 (d, J = 16.9 Hz, 1H), 4.11 (d, J = 16.9 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 194.8, 144.3, 128.0, 94.3, 66.3, 56.8.

4.5.2. 6-Isopropoxy-2H-pyran-3(6H)-one (7). [29]

Colorless oil, yield 56.7% for 3 steps. ^1H NMR (400 MHz, CDCl_3) δ 6.86 (dd, $J = 10.3, 3.4$ Hz, 1H), 6.12 (d, $J = 10.3$ Hz, 1H), 5.30 (d, $J = 3.4$ Hz, 1H), 4.48 (d, $J = 16.8$ Hz, 1H), 4.12–3.99 (m, 2H), 1.27 (d, $J = 6.3$ Hz, 3H), 1.22 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.1, 145.1, 127.8, 91.5, 71.2, 66.3, 23.4, 21.9.

4.5.3. 6-Benzyloxy-2H-pyran-3(6H)-one (8). [30]

Colorless oil, yield 68.9% for 3 steps. ^1H NMR (400 MHz, CDCl_3) δ 7.43–7.29 (m, 5H), 6.90 (dd, $J = 10.3, 3.4$ Hz, 1H), 6.15 (d, $J = 10.3$ Hz, 1H), 5.29 (d, $J = 3.4$ Hz, 1H), 4.86 (d, $J = 11.7$ Hz, 1H), 4.67 (d, $J = 11.7$ Hz, 1H), 4.49 (d, $J = 16.9$ Hz, 1H), 4.12 (d, $J = 16.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.7, 144.4, 137.0, 128.8, 128.3, 128.3, 128.1, 92.2, 70.9, 66.5.

4.5.4. 6-Butoxy-2H-pyran-3(6H)-one (9)

Colorless oil, yield 78.8% for 3 steps. FTIR: 2957.5, 2930.5, 2874.8, 1702.3, 1463.1, 1386.6, 1264.3, 1158.0, 1103.4, 1047.9, 851.9, 756.4 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.89 (dd, $J = 10.4, 3.3$ Hz, 1H), 6.12 (d, $J = 10.3$ Hz, 1H), 5.19 (dd, $J = 3.3, 0.8$ Hz, 1H), 4.45 (d, $J = 16.8$ Hz, 1H), 4.09 (d, $J = 16.8$ Hz, 1H), 3.84 (dt, $J = 9.5, 6.7$ Hz, 1H), 3.57 (dt, $J = 9.5, 6.5$ Hz, 1H), 1.69–1.55 (m, 2H), 1.48–1.34 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.9, 144.7, 127.8, 93.3, 69.4, 66.4, 31.8, 19.4, 13.9; HRMS (CI-TOF) m/z calcd. for $\text{C}_9\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$ 171.1016, found 171.1029.

4.5.5. 1-O-Methyl-2,3-O-isopropylidene-5-O-[3-oxo-3,6-dihydro-2H-pyran-6-yl]- β -D-ribofuranose (10)

dr 1.2:1, colorless oil, yield 60% for 3 steps. FTIR: 2985.4, 2938.2, 2837.4, 1701.6, 1461.2, 1379.2, 1266.3, 1206.4, 1160.5, 1099.0, 1046.6, 866.1 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.89 (ddd, $J = 10.3, 3.3, 1.4$ Hz, 1H), 6.14 (d, $J = 10.3$ Hz, 1H), 5.25 (d, $J = 3.4$ Hz, 0.45H), 5.22 (d, $J = 3.3$ Hz, 0.55H), 4.98 (s, 1H), 4.69 (d, $J = 6.0$ Hz, 0.55H), 4.65 (d, $J = 6.0$ Hz, 0.45H), 4.59 (dd, $J = 6.0, 3.9$ Hz, 1H), 4.49 (d, $J = 3.6$ Hz, 0.45H), 4.45 (d, $J = 3.7$ Hz, 0.55H), 4.41–4.30 (m, 1H), 4.13 (d, $J = 3.0$ Hz, 0.55H), 4.09 (d, $J = 3.0$ Hz, 0.45H), 3.87 (dd, $J = 10.2, 5.8$ Hz, 0.55H), 3.79 (dd, $J = 10.1, 8.1$ Hz, 0.45H), 3.62 (ddd, $J = 21.6, 10.1, 7.3$ Hz, 1H), 3.33 (s, 3H), 1.48 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.6, 144.1, 144.1, 128.1, 112.7, 112.7, 109.6, 109.5, 93.8, 93.5, 85.3, 85.2, 85.2, 82.1, 82.1, 70.3, 70.1, 66.5, 66.5, 55.2, 55.1, 26.6, 26.6, 25.2, 25.1. HRMS (CI-TOF) m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{NO}_7$ $[\text{M}+\text{NH}_4]^+$ 318.1547, found 318.1548.

4.5.6. 1,2:4,5-di-O-isopropylidene-3-O-[3-oxo-3,6-dihydro-2H-pyran-6-yl]- β -D-fructopyranose (11)

dr 1.2:1, colorless oil, yield 45% for 3 steps. FTIR: 2987.2, 2936.0, 2888.2, 1700.2, 1456.3, 1326.3, 1251.5, 1110.5, 1068.4, 996.3 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.96 (dd, $J = 10.4, 3.3$ Hz, 0.55H), 6.91 (dd, $J = 10.3, 3.4$ Hz, 0.45H), 6.18–6.08 (m, 1H), 5.75 (dd, $J = 3.3, 1.0$ Hz, 0.55H), 5.36 (dd, $J = 3.4, 0.8$ Hz, 0.45H), 4.77 (d, $J = 17.2$ Hz, 0.45H), 4.47 (d, $J = 16.8$ Hz, 0.55H), 4.35–4.28 (m, 1H), 4.24–4.19 (m, 1H), 4.19–4.13 (m, 1H), 4.14–4.05 (m, 2H), 4.05–3.96 (m, 2H), 3.89 (t, $J = 7.1$ Hz, 1H), 1.55 (d, $J = 8.6$ Hz, 3H), 1.49 (d, $J = 9.1$ Hz, 3H), 1.41–1.33 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.0, 194.5, 144.8, 143.6, 128.1, 127.6, 112.5, 112.0, 109.5, 109.4, 104.4, 104.3, 93.6, 93.5, 77.8, 75.9, 75.8, 75.5, 74.1, 73.8, 72.3, 72.2, 66.9, 66.8, 60.9, 60.4, 28.3, 27.8, 26.6, 26.6, 26.5, 26.3, 26.3, 26.2. HRMS (CI-TOF) m/z calcd. for $\text{C}_{17}\text{H}_{28}\text{NO}_8$ $[\text{M}+\text{NH}_4]^+$ 374.1809, found 374.1818.

4.6. Synthesis of compound (13)

An oven-dried 10 mL flask was charged with dry DMF (1.0 mL), pre-hydrated silica gel (20 mg + 3.6 mg H_2O), furyl alcohol (19.6 mg, 0.2 mmol, 1.0 eq), KBr (2.4 mg, 0.02 mmol, 0.1 eq), oxone (86.1 mg, 0.28 mmol, 1.4 eq) and NaHCO_3 (33.6 mg, 0.4 mmol, 2.0

eq). The reaction mixture was stirred vigorously at rt for 1 h. Upon completion (monitored by TLC), Ac_2O (28.4 μL , 0.3 mmol, 1.5 eq), Et_3N (223 μL , 1.6 mmol, 8.0 eq) and styrene (229 μL , 2.0 mmol, 10.0 eq) were added, and the resulting mixture was stirred overnight. The mixture was quenched by addition of water, and the aqueous phase was extracted with EtOAc. The combined organic fractions were washed with saturated aqueous NH_4Cl solution and brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc/hexane = 1:5) to provide the title compound.

6-endo-6-phenyl-8-oxabicyclo[3.2.1]oct-3-en-2-one (13). [41] Colorless oil, yield 47.1% for 3 steps. ^1H NMR (400 MHz, CDCl_3) δ 7.45–7.12 (m, 5H), 6.82 (dd, $J = 9.9, 4.4$ Hz, 1H), 6.12 (dd, $J = 9.9, 1.4$ Hz, 1H), 4.93 (dd, $J = 6.6, 4.4$ Hz, 1H), 4.68 (dt, $J = 8.7, 1.7$ Hz, 1H), 3.87 (dt, $J = 10.1, 6.9$ Hz, 1H), 2.85 (ddd, $J = 13.6, 10.0, 8.6$ Hz, 1H), 2.01 (ddd, $J = 13.6, 7.1, 1.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 151.7, 137.2, 128.7, 128.4, 127.5, 127.4, 82.0, 47.9, 31.1.

4.7. Synthesis of compound 14

An oven-dried 10 mL flask was charged with dry DMF (1 mL), pre-hydrated silica gel (20 mg + 3.6 mg H_2O), furyl alcohol (33.2 mg, 0.2 mmol, 1 eq), KBr (2.4 mg, 0.02 mmol, 0.1 eq), oxone (86.1 mg, 0.28 mmol, 1.4 eq) and NaHCO_3 (33.6 mg, 0.4 mmol, 2.0 eq). And the reaction mixture was stirred vigorously at rt for 6 h. Upon completion (monitored by TLC), Ac_2O (37.8 μL , 0.4 mmol, 2.0 eq) and DABCO (179 mg, 1.6 mmol, 8.0 eq) were added, and the resulting mixture was stirred for another 5 h. The mixture was quenched by addition of water, and the aqueous phase was extracted with EtOAc. The combined organic fractions were washed with saturated aqueous NH_4Cl solution and brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc/hexane = 1:5) to provide the title compound.

(3aS,7R,8aS)-2,3,8,8a-tetrahydro-1H-3a,7-epoxyazulen-4(7H)-one and (3aR,7S,8aR)-2,3,8,8a-tetrahydro-1H-3a,7-epoxyazulen-4(7H)-one (14) [42]. Colorless oil, yield 63.6% for 3 steps. ^1H NMR (400 MHz, CDCl_3) δ 7.13 (dd, $J = 9.7, 4.3$ Hz, 1H), 5.97 (d, $J = 9.7$ Hz, 1H), 4.88 (dd, $J = 6.6, 4.3$ Hz, 1H), 2.44–2.38 (m, 1H), 2.35–2.27 (m, 1H), 2.16 (dd, $J = 12.0, 8.9$ Hz, 1H), 1.99–1.65 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 151.9, 126.2, 98.1, 76.1, 44.5, 36.7, 32.4, 30.0, 26.1.

4.8. General procedure for the synthesis of compounds 15c–15i

An oven-dried 10 mL flask was charged with dry CH_3CN (1 mL) and DMF (0.1 mL), pre-hydrated silica gel (20 mg + 3.6 mg H_2O), furfuryl alcohol (0.2 mmol, 1.0 eq), KBr (9.52 mg, 0.08 mmol, 0.4 eq), oxone (332 mg, 1.08 mmol, 5.4 eq) and NaHCO_3 (45.3 mg, 0.54 mmol, 2.7 eq). Then, the reaction mixture was stirred vigorously at rt. Upon completion (monitored by TLC), TEMPO (9.4 mg, 0.06 mmol, 0.3 eq) was added, and the resulting mixture was stirred for another 1–3 h. Then the residue was diluted by hexane and poured onto silica gel and purified by flash chromatography (EtOAc/hexane = 1:1 to EtOAc) to provide the title compound.

4.8.1. 5-Hydroxy-6-(4-penten-1-yl)-2H-pyran-2-one (15c)

Colorless oil, yield 65.7% for 2 steps. FTIR: 3377.6, 2934.0, 2875.2, 1771.9, 1722.7, 1629.5, 1446.0, 1389.2, 1173.2, 1081.3, 1015.6, 911.8 cm^{-1} ; ^1H NMR (400 MHz, MeOD) δ 7.39 (d, $J = 9.7$ Hz, 1H), 6.13 (d, $J = 9.7$ Hz, 1H), 5.83 (ddt, $J = 17.0, 10.2, 6.7$ Hz, 1H), 5.08–4.92 (m, 2H), 2.60 (t, $J = 7.5$ Hz, 2H), 2.11 (q, $J = 7.1$ Hz, 2H), 1.73 (p, $J = 7.4$ Hz, 2H). ^{13}C NMR (100 MHz, MeOD) δ 164.8, 151.4, 143.6, 139.1, 137.6, 115.6, 113.6, 34.2, 28.4, 27.3. HRMS (CI-TOF) m/z calcd. for $\text{C}_{10}\text{H}_{11}\text{O}_3$ $[\text{M}-\text{H}]^+$ 179.0703, found 179.0710.

4.8.2. 5-Hydroxy-6-isopropyl-2H-pyran-2-one (**15d**)

Colorless oil, yield 80.3% for 2 steps. FTIR: 3376.7, 2975.7, 2936.2, 2881.3, 1710.4, 1620.0, 1548.2, 1461.5, 1328.5, 1137.9, 754.8 cm^{-1} ; ^1H NMR (400 MHz, MeOD) δ : 7.40 (d, $J = 9.7$ Hz, 1H), 6.12 (d, $J = 9.7$ Hz, 1H), 3.24 (p, $J = 7.0$ Hz, 1H), 1.20 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, MeOD) δ : 164.8, 155.4, 143.9, 136.0, 113.4, 28.1, 19.9; HRMS (CI-TOF) m/z calcd. for $\text{C}_8\text{H}_{10}\text{O}_3$ $[\text{M}]^+$ 154.0624, found 154.0636.

4.8.3. 5-Hydroxy-6-allyl-2H-pyran-2-one (**15e**)

Colorless oil, yield 72.4% for 2 steps. FTIR: 3380.5, 2926.4, 2860.7, 1765.3, 1730.7, 1633.2, 1424.4, 1378.1, 1226.4, 1080.0, 1023.8, 917.6 cm^{-1} ; ^1H NMR (400 MHz, MeOD) δ 7.41 (d, $J = 9.7$ Hz, 1H), 6.16 (d, $J = 9.8$ Hz, 1H), 5.89 (ddt, $J = 16.7, 10.1, 6.5$ Hz, 1H), 5.21–5.07 (m, 2H), 3.39–3.26 (m, 2H). ^{13}C NMR (100 MHz, MeOD) δ 164.5, 148.8, 143.6, 137.5, 133.4, 118.0, 114.2, 33.4; HRMS (CI-TOF) m/z calcd. for $\text{C}_8\text{H}_9\text{O}_3$ $[\text{M}+\text{H}]^+$ 153.0546, found 153.0556.

4.8.4. Ethyl 2-(5-hydroxy-2-oxo-2H-pyran-6-yl)acetate (**15f**)

Colorless oil, yield 83.1% for 2 steps. FTIR: 3387.3, 2979.1, 2926.1, 2859.5, 1731.2, 1635.7, 1381.9, 1299.3, 1162.0, 1087.2, 1022.3, 921.3 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 9.8$ Hz, 1H), 6.22 (d, $J = 9.8$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 3.68 (s, 2H), 1.30 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.06, 161.90, 142.27, 140.27, 137.91, 115.48, 62.82, 36.36, 14.12. HRMS (CI-TOF) m/z calcd. for $\text{C}_9\text{H}_{11}\text{O}_5$ $[\text{M}+\text{H}]^+$ 199.0601, found 199.0602.

4.8.5. 2-[5-hydroxy-2-oxo-2H-pyran-6-yl]-N-methoxy-N-methylacetamide (**15g**)

Colorless oil, yield 67.6% for 2 steps. FTIR: 3239.3, 2927.1, 2858.0, 1716.1, 1638.4, 1556.3, 1436.5, 1385.8, 1251.1, 1182.6, 1121.0, 876.7 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 9.8$ Hz, 1H), 6.21 (d, $J = 9.8$ Hz, 1H), 3.88 (s, 2H), 3.80 (s, 3H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 161.8, 142.5, 139.2, 139.1, 115.4, 62.4, 34.1, 32.4. HRMS (CI-TOF) m/z calcd. for $\text{C}_9\text{H}_{12}\text{NO}_5$ $[\text{M}+\text{H}]^+$ 214.0710, found 214.0723.

4.8.6. 5-Hydroxy-6-(4-((triisopropylsilyloxy)phenethyl)-2H-pyran-2-one (**15h**)

Colorless oil, yield 80.7% for 2 steps. FTIR: 3378.6, 2942.6, 2865.4, 1772.1, 1731.0, 1609.5, 1509.3, 1461.1, 1392.2, 1261.8, 1074.4, 1002.2, 911.9 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.17 (d, $J = 9.7$ Hz, 1H), 7.01 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.5$ Hz, 2H), 6.09 (d, $J = 9.7$ Hz, 1H), 2.94–2.78 (m, 4H), 1.29–1.15 (m, 3H), 1.07–1.08 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.8, 154.9, 150.1, 141.7, 135.6, 132.8, 129.4, 120.3, 113.6, 32.4, 31.1, 18.0, 12.8. HRMS (CI-TOF) m/z calcd. for $\text{C}_{22}\text{H}_{32}\text{O}_4\text{Si}$ $[\text{M}]^+$ 388.2064, found 388.2057.

4.8.7. 5-Hydroxy-6-(4-methoxy-3-((triisopropylsilyloxy)phenethyl)-2H-pyran-2-one (**15i**)

Colorless oil, yield 70.1% for 2 steps. FTIR: 2943.4, 2866.6, 1773.1, 1732.8, 1512.0, 1456.3, 1277.4, 1229.3, 1140.5, 1076.5, 988.2 cm^{-1} ; ^1H NMR (400 MHz, MeOD) δ 7.33 (d, $J = 9.8$ Hz, 1H), 6.85–6.67 (m, 3H), 6.10 (d, $J = 9.8$ Hz, 1H), 3.75 (s, 3H), 2.84 (s, 4H), 1.29–1.13 (m, 3H), 1.15–1.02 (m, 18H). ^{13}C NMR (101 MHz, MeOD) δ 164.8, 150.8, 150.5, 146.6, 143.6, 138.1, 134.5, 122.6, 121.8, 113.8, 113.5, 56.1, 33.0, 31.2, 18.6, 14.2; HRMS (CI-TOF) m/z calcd. for $\text{C}_{23}\text{H}_{33}\text{O}_5\text{Si}$ $[\text{M}-\text{H}]^+$ 417.2092, found 417.2100.

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Appendix A. Supplementary data

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