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Manganese-Catalyzed Achmatowicz Rearrangement Using Green Oxidant H_2O_2

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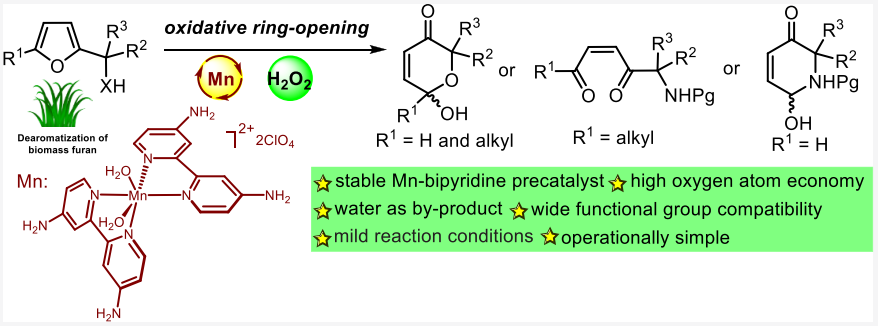

ABSTRACT: Oxidation reactions have been extensively studied in the context of the transformations of biomass-derived furans. However, in contrast to the vast literature on utilizing the stoichiometric oxidants, such as *m*-CPBA and NBS, catalytic methods for the oxidative furan-recyclizations remain scarcely investigated. Given this, we report a means of manganese-catalyzed oxidations of furan with low loading, achieving the Achmatowicz rearrangement in the presence of hydrogen peroxide as an environmentally benign oxidant under mild conditions with wide functional group compatibility.

INTRODUCTION

Biomass-derived furans, a family of the most promising sustainable raw materials, have extensively been studied for the synthesis of simple chemicals via a dearomatization reaction,[1] such as alkenes, enol ethers,[2] 1,4-diketones,[3] and carboxylic acids.[4] Moreover, furan also can easily undergo recyclization reactions to form carbocycles.[5−7] An important branch in the area of furan chemistry is selective oxidation. Achmatowicz rearrangement dominates a unique status in oxidative furan ring-opening,[8] because it efficiently converts α-heterofunctionalized furan into the densely decorated pyran as well as piperidine derivatives (Figure 1a). These much more structurally valuable scaffolds can undergo further transformations to construct diverse libraries,[9] carbohydrates,[10] and core structures of a variety of natural products.[11] Herein, we reported a Mn-catalyzed furan oxidation strategy in combination with environmentally benign H_2O_2 as the terminal oxidant, realizing the highly practicable and sustainable Achmatowicz rearrangement (Figure 1b). The protocol is suitable not only for simple furfuryl carbinols and carbinamines but likewise for a series of substrates carrying synthetically versatile functional groups.

Because of the importance of the Achmatowicz rearrangement, tremendous efforts have been devoted to developing highly efficient and selective oxidation conditions.[3,12] Regrettably, the classical known protocols require the use of toxic reagents or expensive stoichiometric oxidants, such as Br_2,[8a,b] *N*-bromosuccinimide (NBS),[13] pyridinium chlorochromate (PCC),[14] iodobenzenediacetate (IBDA),[15] and dimethyldioxirane (DMDO),[16] which produce quantitative amounts of the organic byproduct. Singlet oxygen can react with the furan via a Diels−Alder-type reaction to form a trioxolane intermediate, followed by quenching with stoichiometric triphenylphosphine or dimethyl sulfide to produce the Achmatowicz rearrangement product.[17] Although $Ti(OiPr)_4$/*t*-BuOOH,[18] VO(acac)$_2$/*t*-BuOOH,[19a,b] or $MeReO_3$/urea-H_2O_2[19c] are suitable catalytic oxidizing agents for this conversion, the oxygen atom economy of the conditions is still lower than using O_2 and H_2O_2. Recently, Tong realized a Fenton chemistry method for this conversion with H_2O_2.[22c] While several catalytic methods have been reported, including enzymatic,[20] electrochemical and photochemical oxidation,[21] KBr/oxone,[22] titanium silicate catalysts,[23] and cyclic diacyl peroxides,[24] some of them suffer from either harsh reaction conditions or long reaction times, which limits substrate diversity.

Catalytic oxidative reactions are fundamentally important in modern green and sustainable chemistry.[25] Low waste

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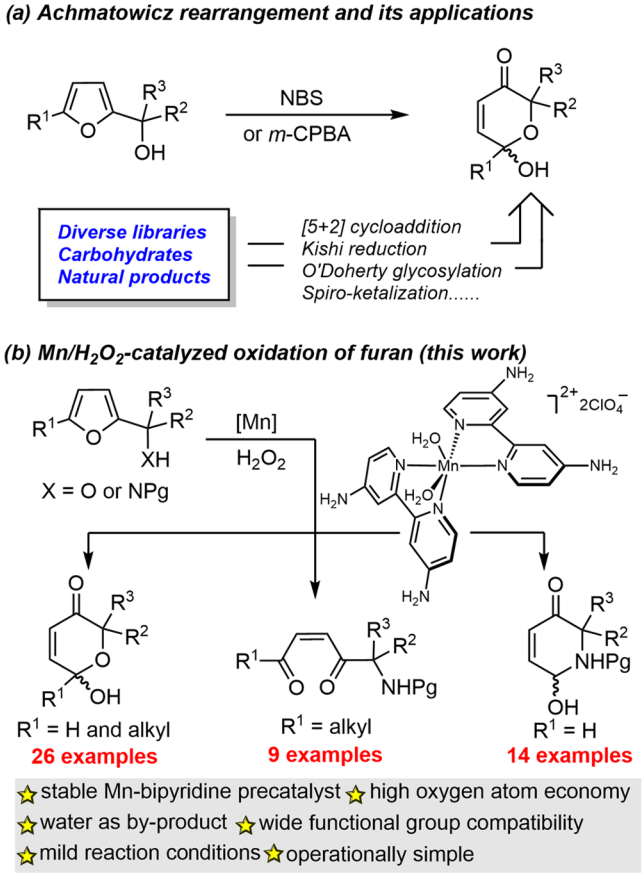


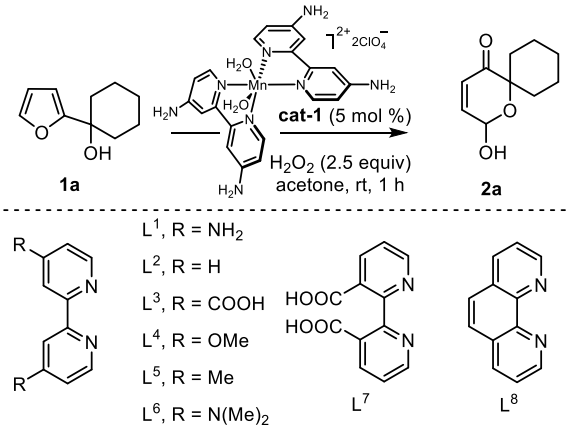
Figure 1. Achmatowicz rearrangement and Mn/H_2O_2-catalyzed furan oxidation in this work.

production and energy consumption as well as high atom economy and environmental friendliness are urgently required.[26] As the third most abundant transition metal in the earth's crust, less-toxic manganese plays a crucial role in enzymatic reactions in nature, which also has been demonstrated to be a vital strategy to perform oxidation reactions.[27] Not surprisingly, a great advance has been achieved recently in manganese-catalyzed oxidation of C=C,[28] alcohols,[29] and C(sp^3)—H bonds[30] with aqueous H_2O_2, such that the proposed active oxidants are high-valent metal–oxo intermediates. To the best of our knowledge, oxidation of aromatic heterocycles using a manganese catalyst and H_2O_2 as the terminal oxidant has never been explored. Recently, Li and Xiao reported that a manganese complex bearing the electron-rich bipyridine ligand is an efficient catalyst in the selective oxidation of organosilanes into silanols by aqueous H_2O_2 under neutral conditions.[31a] Inspired by this work and also as part of our ongoing interest in developing furan-based conversions,[32] we hypothesized that Li's manganese complex could be used in the catalytic oxidation of furan with low aromaticity, which delivers the oxygen-transfer from H_2O_2 to the π-bond of the furan ring to lead to ring-opening and further Achmatowicz rearrangement.

RESULTS AND DISCUSSION

To commence our studies, the conversion of furfuryl alcohol **1a** to dihydropyranone **2a** was selected as the model system (Table 1). After extensive optimization, it was found that a catalytic system composed of the well-defined bench-stable Mn

Table 1. Selected Optimization Data on Mn-Catalyzed Achmatowicz Rearrangement



entry[a]	variation from standard conditions	yield[b] (%)
1	none	84
2	$Mn(ClO_4)_2·6H_2O/L^1$	81
3	$Mn(OTf)_2/L^1$	77
4	cat-1 (2 mol %)	45
5	H_2O_2 (1 equiv)	36
6	EtOH instead of acetone	31
7	MeOH instead of acetone	12
8	THF instead of acetone	trace
9	DMF instead of acetone	trace
10	CH_3CN instead of acetone	78
11	$Mn(ClO_4)_2·6H_2O/L^2$	n.d.[c]
12	$Mn(ClO_4)_2·6H_2O/L^3$	trace
13	$Mn(ClO_4)_2·6H_2O/L^4$	7
14	$Mn(ClO_4)_2·6H_2O/L^5$	trace
15	$Mn(ClO_4)_2·6H_2O/L^6$	80
16	$Mn(ClO_4)_2·6H_2O/L^7$	n.d.
17	$Mn(ClO_4)_2·6H_2O/L^8$	n.d.
18	cat-1 (0 mol %)	n.d.

[a]Conditions: **1a** (0.2 mmol), H_2O_2 (0.5 mmol, 30% in H_2O), solvent (1 mL). [b]Isolated yield of **2a** after purification by flash column chromatography. [c]n.d., not detected.

bipyridine precatalyst cat-1 (5 mol %)[31a] and H_2O_2 (2.5 equiv) as the terminal oxidant in acetone at room temperature for 1 h gave **2a** in 84% isolated yield (entry 1) under an air atmosphere. The one-pot combination of $Mn(ClO_4)_2·6H_2O$ and 4,4′-diamino bipyridines generated the desired product **2a** in 81% yield (entry 2). When the manganese salt was changed into $Mn(OTf)_2$ in the same catalyst loading, the yield was slightly reduced (entry 3). Lower loading of cat-1 (2 mol %) led to a 45% yield (entry 4). A reaction using 1 equiv of H_2O_2 induced **2a** in just 36% yield (entry 5). The reaction was found to be sensitive to the organic solvent, such that the unsatisfied yields were obtained by substitution of acetone with EtOH, MeOH, THF, or DMF (entries 6–9). To our delight, using CH_3CN also provided the expected product in superior yield (entry 10). Next, the effects of varying ligands were also investigated, and it was found that the efficiency of the desired transformation dramatically decreased when 4,4′-dicarboxyl, dimethoxyl, and dimethyl bipyridines were used as ligands (entries 12–14). Further study identified the electron-rich L^6 as a superior ligand for the formation of the desired Achmatowicz rearrangement product (entry 15). Ligands L^2, L^7, and L^8 were ineffective. An amount of **1a** can be recovered

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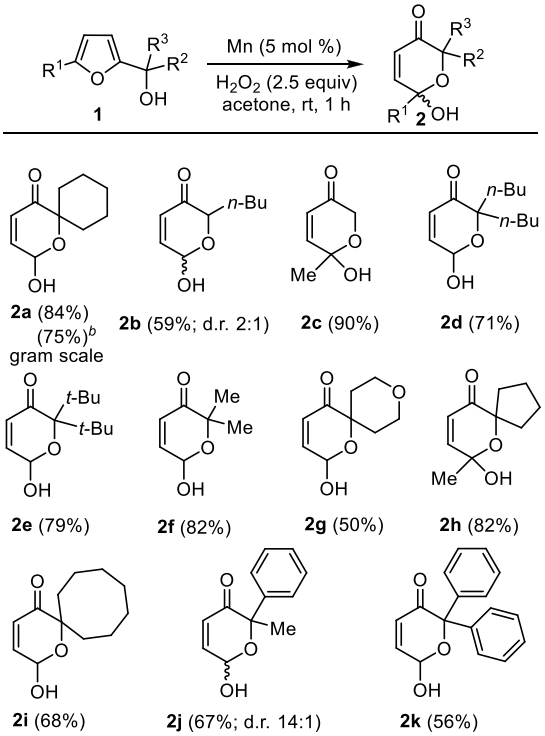
in the above-mentioned low-yield reactions. **2a** as the unique product was observed, and no side reactions were taking place, demonstrating that the catalytic systems are mild enough and perform with high oxidation specificity to **1a**. DMDO might be generated by oxidation of acetone with H_2O_2.[36] For eliminating the possibility of H_2O_2 or DMDO or related species catalyzing the reaction, a reaction in the absence of the catalyst was performed, such that the desired product was not detectable (entry 18).

With optimized reaction conditions in hand (Table 1, entry 1), the scope of the Achmatowicz rearrangement of furfuryl alcohol **1** to dihydropyranone **2** was explored (Scheme 1).

Scheme 1. Dihydropyranones Constructed in the Oxidation of α-Furfuryl Carbinols[a]

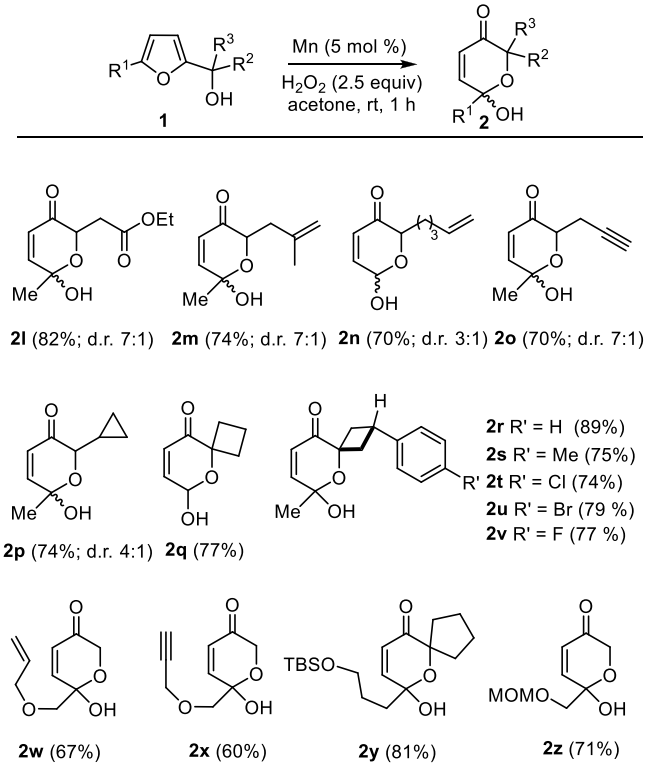


[a]Conditions: **1** (0.2 mmol), cat-1 (0.01 mmol), acetone (1 mL); H_2O_2 (0.5 mmol, 30% in H_2O) was added to the solution dropwise over 1 h using a syringe pump. Isolated yields are reported with flash column chromatography. Diastereomeric ratios were identified on the basis of ^{1}H NMR spectroscopy. [b]1.2 g of **1a** was used as the substrate for realizing the gram-scale synthesis of **2a**.

Secondary *n*-butyl and primary 5-methyl furfuryl alcohols underwent the cascade ring-opening/hemiacetalization, offering dihydropyranones **2b** and **2c** in 59% and 90% yields, respectively. The former exists as a mixture of two epimers, and the diastereomeric ratio is 2:1 in favor of the *cis* isomer. The tertiary alcohols with more steric hindrance, such as the dual *n*-butyl, *t*-butyl, and methyl, performed well and afforded (**2d**−**2f**) in 71−82% yields. The reaction of furfuryl carbinols containing tetrahydropyran, cyclopentane, and cyclooctane proceeded smoothly under the standard conditions to offer the corresponding [6, 6], [6, 5], and [6, 8] spiro bicycles **2g**−**2i** in moderate to good yields. The phenyl methyl substrate can be used to carry out the reaction, giving the Achmatowicz product **2j** in 67% yield and 14:1 d.r. The biphenyl furfuryl alcohol, which could easily generate a cation even in weak acidic conditions, was also compatible with the transformation that gave **2k** in 56% yield. Next, the gram-scale reaction using **1a** as the substrate was carried out, providing **2a** in 75% yield.

Furthermore, the compatibility of the reaction was investigated, which was found to be exceedingly mild for various functional groups (Scheme 2). It was found that ethyl

Scheme 2. Compatibility Investigation of the Functional Group in the Achmatowicz Reaction[a]



[a]Conditions: **1** (0.2 mmol), cat-1 (0.01 mmol), acetone (1 mL); H_2O_2 (0.5 mmol, 30% in H_2O) was added to the solution dropwise over 1 h using a syringe pump. Isolated yields are reported with flash column chromatography. Diastereomeric ratios (*cis*/*trans*) were identified on the basis of ^{1}H NMR spectroscopy.

ester was tolerated, giving an 82% yield of **2l**. Encouragingly, alkene and alkynyl groups did not induce any side reaction or interfere with the catalytic reactivity, despite their sensitivity to epoxidative reagents. The corresponding products **2m**−**2o** were obtained in 70−74% yields. The decent chemical specificity is the major merit of the oxidation condition by comparing with the traditional conditions, such as NBS and *m*-CPBA, which usually can oxidize π electron-rich alkene and alkyne via bromination or epoxidation. Cyclopropanyl with more strain was perfectly compatible, and **2p** was obtained in 74% yield. Generally, the conversions of 5-methyl substituted substrates were found to be more diastereoselective than C5 unsubstituted ones. Cyclobutyl with various substituted phenyl substrates performed effectively, and the corresponding spiro bicyclo products **2r**−**2v** were generated in 74−89% yields. Less stable allylic and propargyl ethers were examined next, and the desired rearrangements were slightly retarded, delivering **2w** and **2x** in 67% and 60% yields. Gratifyingly, acid-sensitive silica ether (TBS) and acetal (MOM) groups survived during the reactions, affording **2y** and **2z** in good yields.

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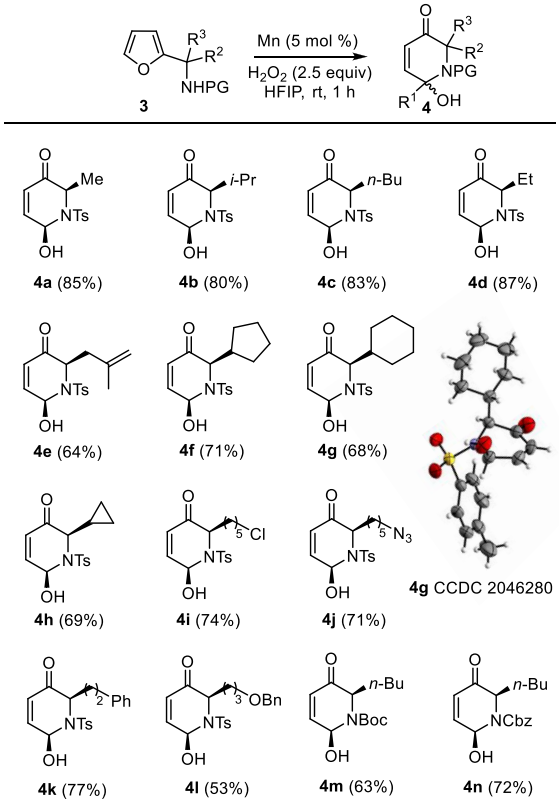
Next, we evaluated whether aza-Achmatowicz rearrangement could be achieved by using α-amino-containing furans (Scheme 3).[33] We began by optimizing reactions of the

Scheme 3. Mn/H_2O_2-Catalyzed Aza-Achmatowicz Rearrangement[a]

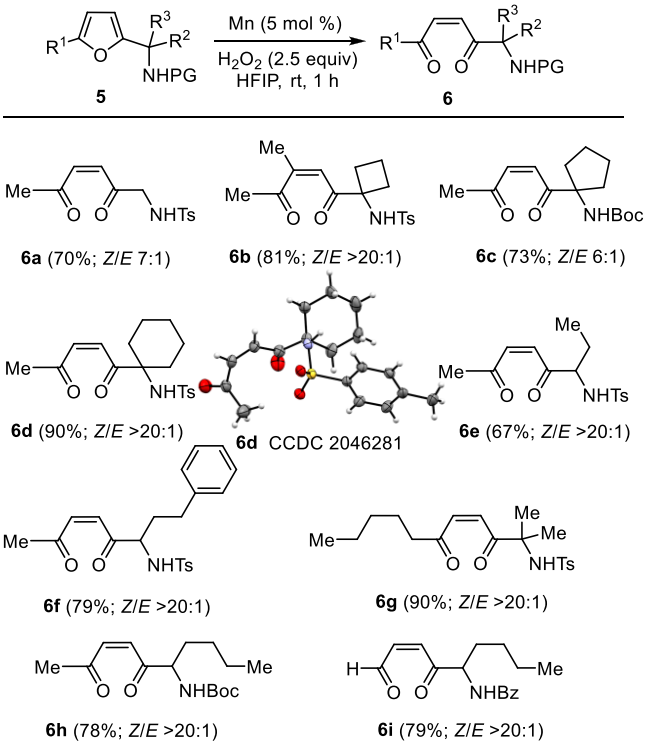


[a]Conditions: **3** (0.2 mmol), cat-1 (0.01 mmol), HFIP (1 mL); H_2O_2 (0.5 mmol, 30% in H_2O) was added to the solution dropwise over 1 h using a syringe pump. Isolated yields are reported with flash column chromatography. The *cis* isomer was observed exclusively via ^{1}H NMR spectroscopy.

analogous tosylamine and found that cat-1 (5 mol %) in HFIP instead of acetone as the solvent efficiently catalyzed intramolecular rearrangement to afford the corresponding dihydropiperidinone. Alkyl substituted *N*-tosylated α-furanyl-amines, including those bearing methyl, *i*-propyl, *n*-butyl, and ethyl substrates, were smoothly converted to products **4a**−**4d**. The olefin group also did not interrupt the cyclization and gave **4e** in 64% yield. Similarly, several cyclic products, particularly **4f**−**4h**, were constructed in synthetically useful yields. Single-crystal X-ray diffraction confirmed the structure of **4g**. Chloro, azido, phenyl, and benzyl ether-derived products **4i**−**4l** were synthesized in 53−74% yields. Boc and Cbz protecting groups for amine were also compatible, offering **4m** and **4n** in satisfactory yields, elucidating the power of this protocol in the oxidative rearrangement of furan. Remarkably, the *cis* isomer was observed exclusively in all of these cases.

When the approach was applied for the C5 substituted furan precursors, it was found that the ring-closing products cannot be observed (Scheme 4). A series of 1,4-diketoalkenes **6a**−**6h** fixed with a tosyl- or Boc-protected amine were synthesized in satisfactory yields and excellent *Z*/*E* selectivities. Thus, it was proved that the steric hindrance of C5 substituents is extremely

Scheme 4. 1,4-Diketoalkene Generation via the Mn/H_2O_2-Catalyzed Oxidation[a]



[a]Conditions: **5** (0.2 mmol), cat-1 (0.01 mmol), HFIP (1 mL); H_2O_2 (0.5 mmol, 30% in H_2O) was added to the solution dropwise over 1 h using a syringe pump. Isolated yields are reported with flash column chromatography. The configuration of the double bond (*Z*/*E*) was identified via ^{1}H NMR spectroscopy.

temperamental for the aza-Achmatowicz rearrangement under our standard conditions. Interestingly, the benzamide adduct also gave the acyclic aldehyde **6i** in 79% yield, although it possesses a C5 unsubstituted furan. This might be caused by the low nucleophilicity of the benzene conjugated amide. These multifunctionalized chain skeletons have shown considerable structural diversity, which could be employed as useful synthons or key scaffolds in syntheses of natural products and drug libraries.

With the importance of the dihydropyranones as the bioactive scaffolds and the versatile synthons, the oxidative rearrangement products afford great potential for their further derivatizations (Scheme 5). For example, the intramolecular [5 + 2] cycloaddition of **7a** between its acetyl hemiacetal group with the terminal olefin was effective using DBU as the base, affording O-bridged cyclic product **8**. Subjecting **7b** to Lewis acid-mediated Kishi reduction provided **9** in 65% yield. Allylation of **2f** was facile, giving **10** in 58% yield. Pd-catalyzed *O*-glycosylation of Boc-protected substrate **7c** with cholesterol was successfully carried out, furnishing natural-product-derived glycoside **11** in moderate yield.

To gain mechanistic insights into the Achmatowicz rearrangement catalyzed by manganese catalyst and H_2O_2, we first conducted the oxidation of **1a** under conditions of the urea·$H_2{}^{16}O_2$ complex and $H_2{}^{18}O$. In this reaction, **2a** was obtained in 76% yield, but no ^{18}O-labeled hemiacetal product was detected by ESI-HRMS analysis. Further, when the catalytic oxidation of **1a** was carried out under an O_2 atmosphere without oxidant H_2O_2, a trace amount of **2a** was

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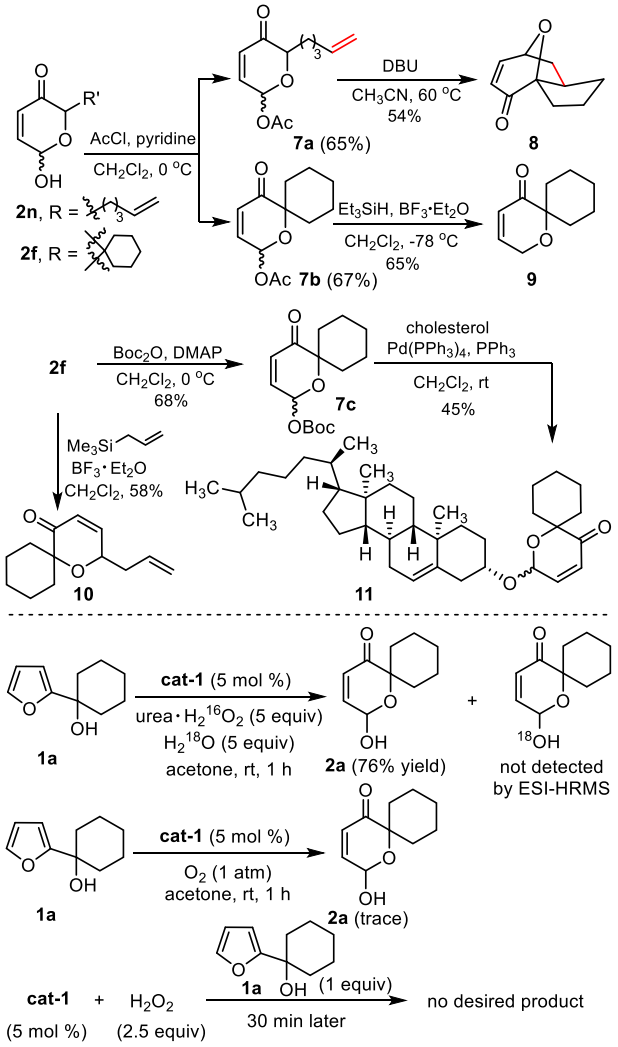
Scheme 5. Further Transformations of Dihydropyranones and Control Experiments



generated. These results indicate that neither water nor molecular oxygen is the oxygen source of the oxidative reaction. Next, the additive sequence was altered. No desired **3a** was offered when adding **2a** into the reaction mixture of cat-1 and H_2O_2. This suggests that the oxidation of furan with the metal-oxo intermediate, which was formed from cat-1 and H_2O_2, is much faster than its decomposing and loss of reactivity.

Combining with the results discussed above and those reported previously,[27−31] a possible reaction mechanism was proposed for the oxidative rearrangement of furfuryl alcohols or amines catalyzed by Mn catalysts and H_2O_2 (Figure 2). Catalyst activation occurs via substitution of one H_2O on the precatalyst species by H_2O_2 to provide entry into the catalytic cycle at species **A**. Despite the fact that a putative Mn(V)-oxo species **E** could be generated via H_2O-assisted O−O bond heterolysis of a Mn(III)-OOH, the lack of the ^{18}O label from $H_2{}^{18}O$ mentioned above implied that **E** is not involved in the oxidation. Next, the displacement of a second H_2O by binding of **1** or **3** then occurs, leading to the formation of complex **B**. Complex **B** undergoes O−O bond cleavage and dehydration to afford highly active Mn(V)-oxo **C**. Further intramolecular oxygen-transfer from Mn(V)-oxo to furan gives **D**, which is in analogy to the heteroatom-directed epoxidation of allylic

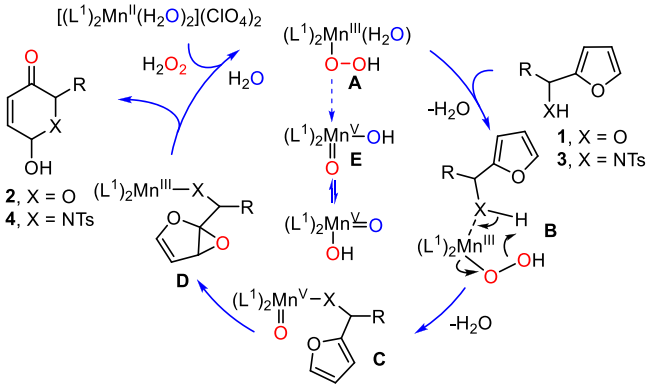


Figure 2. Proposed mechanistic cycle.

alcohols of amines. The intermediate **D** finally undergoes dissociation of Mn(III), followed by furan ring-opening/hemiacetalation to afford desired dihydropyranone or dihydropiperidinone products. The reason why the electron-rich bipyridine ligand is capable of giving a satisfied yield is unclear yet. The use of manganese with electron-rich pyridines (4-NMe_2 and 4-NH_2) as especially active catalysts in epoxidation reactions of olefin with H_2O_2 was also described by Costas[31b] and Bryliakov.[31c]

CONCLUSION

We have developed a Mn-catalyzed Achmatowicz rearrangement of furfuryl alcohols and amines using H_2O_2 as an environmentally benign oxidant, achieving the efficient construction of highly functionalized pyran and piperidine derivatives. The oxidation can be also applied to prepare chain *cis*-1,4-diketoalkenes, when C5 substituted furfuryl amines were utilized as substrates. A series of synthetic applications of the resulting dihydropyranone have been described for the production of valuable derivatives. Further studies directed at a deeper understanding of this catalytic method will be reported in due course.

EXPERIMENTAL SECTION

General Information. Dichloromethane was refluxed with CaH_2 and freshly distilled prior to use. THF was refluxed with Na and freshly distilled prior to use. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200−300 meshes) was used for column chromatography, and the distillation range of petroleum ether was 60−90 °C. High-resolution mass spectra (HRMS) were obtained on a Bruker MAXIS instrument and are reported as *m*/*z* (relative intensity). Accurate masses are reported for the molecular ion $[M + Na]^+$. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-600 MHz, Bruker AM-400 MHz, and JEOL JNM-ECZ-400 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as the internal standard. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, etc., br = broad), coupling constant (Hz), and integration. All ^{13}C NMR spectra are reported in ppm. Crystals were collected on a Bruker APEX-II CCD instrument.

Procedure for the Preparation of the Manganese Catalyst. The Mn cat-1 was synthesized according to Li's report:[31a] Under a nitrogen atmosphere, $Mn(ClO_4)_2{\cdot}6H_2O$ (181 mg, 0.5 mmol) and 4,4′-diamino-2,2′-bipyridine (186.2 mg, 1.0 mmol) were dissolved in 2 mL of CH_3CN or acetone, and the resulting mixture was stirred overnight. The resulting precipitate was collected by filtration through

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Celite in the glovebox and dried using an oil pump to give a brown solid (367.2 mg).

General Syntheses of 1a, 1d−1k, and 1q. Under an argon atmosphere, 2.2 mL of *n*-BuLi (2.5 M in hexane, 1.1 equiv) was added into the furan derivative solution (6.0 mmol, 1.2 equiv) in dry THF (15 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. Then, a solution of carbonyl compound (5.0 mmol, 1.0 equiv) in THF (3 mL) was added into the reaction mixture dropwise at 0 °C. After stirring for 4 h, the reaction was quenched by water. The resulting solution was extracted three times with ethyl acetate (25 mL). The organic layer was dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give furfuryl alcohols.

*1-(Furan-2-yl)cyclohexan-1-ol (**1a**).*[21] Isolation by column chromatography over silica gel (eluent, 25:1 petroleum ether/ethyl acetate) afforded **1a** as a yellowish oil (705.9 mg, 85% yield, 6.0 mmol of furan and 5.0 mmol of cyclohexanone as the starting material was used). R_f = 0.37 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, J = 1.7, 0.7 Hz, 1H), 6.32 (dd, J = 3.2, 1.8 Hz, 1H), 6.21 (dd, J = 3.2, 0.7 Hz, 1H), 2.02−1.94 (m, 2H), 1.88−1.79 (m, 2H), 1.78−1.66 (m, 3H), 1.55−1.44 (m, 3H), 1.41−1.33 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.9, 141.4, 110.0, 104.4, 70.1, 36.6, 25.5, 22.2.

*5-(Furan-2-yl)nonan-5-ol (**1d**).*[21] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **1d** as a yellowish oil (851.1 mg, 81% yield, 6.0 mmol of furan and 5.0 mmol of nonan-5-one as the starting material were used). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1H), 6.31 (dd, J = 3.1, 1.8 Hz, 1H), 6.17 (d, J = 3.2 Hz, 1H), 1.94 (s, 1H), 1.84−1.76 (m, 4H), 1.32−1.15 (m, 8H), 0.88 (t, J = 7.1 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 141.2, 109.9, 105.0, 74.4, 39.6, 25.7, 23.0, 14.0.

*3-(Furan-2-yl)-2,2,4,4-tetramethylpentan-3-ol (**1e**).* Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **1e** as a yellowish oil (746.1 mg, 71% yield, 6 mmol of furan and 5.0 mmol of 2,2,4,4-tetramethylpentan-3-one as the starting material were used). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, J = 1.7, 0.9 Hz, 1H), 6.32 (dd, J = 3.2, 1.8 Hz, 1H), 6.20 (dd, J = 3.2, 0.8 Hz, 1H), 2.07 (s, 1H), 1.06 (s, 18H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.8, 109.6, 106.8, 82.4, 41.5, 28.7. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{13}H_{22}O_2Na$, 233.1512; found, 233.1510.

*2-(Furan-2-yl)propan-2-ol (**1f**).*[20b,21] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **1f** as a clear oil (491.1 mg, 78% yield, 6.0 mmol of furan and 5.0 mmol of acetone as the starting material were used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, J = 1.7, 0.7 Hz, 1H), 6.29 (dd, J = 3.2, 1.8 Hz, 1H), 6.17 (dd, J = 3.2, 0.6 Hz, 1H), 2.24 (s, 1H), 1.57 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.2, 141.4, 109.9, 103.5, 68.7, 28.6.

*4-(Furan-2-yl)tetrahydro-2H-pyran-4-ol (**1g**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **1g** as a yellowish oil (529.4 mg, 63% yield, 6.0 mmol of furan and 5.0 mmol of tetrahydro-4H-pyran-4-one as the starting material were used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 1.3 Hz, 1H), 6.35 (dd, J = 3.2, 1.8 Hz, 1H), 6.23 (dd, J = 3.2, 0.5 Hz, 1H), 3.95−3.86 (m, 2H), 3.77−3.67 (m, 2H), 2.21−2.10 (m, 2H), 2.02 (s, 1H), 1.93−1.84 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.7, 141.7, 110.1, 104.6, 67.3, 63.7, 36.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{12}O_3Na$, 191.0679; found, 191.0682.

*1-(5-Methylfuran-2-yl)cyclopentan-1-ol (**1h**).*[20b] Isolation by column chromatography over silica gel (eluent, 25:1 petroleum ether/ethyl acetate) afforded **1h** as a yellowish oil (539.8 mg, 65% yield, 6.0 mmol of 5-methyl furan and 5.0 mmol of cyclopentanone as the starting material were used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (d, J = 3.0 Hz, 1H), 5.88 (dd, J = 2.2, 0.8 Hz, 1H), 2.28 (s, 3H), 2.08−2.00 (m, 2H), 1.97−1.89 (m, 4H), 1.81 (s, 1H), 1.78−1.70 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.4, 151.3, 105.8, 104.8, 79.4, 39.5, 23.5, 13.6.

*1-(Furan-2-yl)cyclooctan-1-ol (**1i**).*[33b] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **1i** as a colorless oil (805.6 mg, 83% yield, 6.0 mmol of furan and 5.0 mmol of cyclooctanone as the starting material were used). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, J = 1.8, 0.8 Hz, 1H), 6.30 (dd, J = 3.2, 1.8 Hz, 1H), 6.19 (dd, J = 5.9, 2.8 Hz, 1H), 2.11−2.03 (m, 4H), 1.95 (s, 1H), 1.71−1.61 (m, 5H), 1.54−1.43 (m, 5H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.9, 141.4, 109.9, 104.8, 73.7, 34.8, 28.1, 24.6, 21.8.

*1-(Furan-2-yl)-1-phenylethan-1-ol (**1j**).*[34a] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **1j** as a yellowish oil (658.3 mg, 70% yield, 6.0 mmol of furan and 5.0 mmol of acetophenone as the starting material were used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.36 (m, 2H), 7.34−7.29 (m, 3H), 7.28−7.18 (m, 1H), 6.32 (dd, J = 3.3, 1.8 Hz, 1H), 6.23 (d, J = 3.1 Hz, 1H), 2.62 (s, 1H), 1.85 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.9, 145.7, 142.1, 128.1, 127.2, 125.2, 110.0, 106.2, 72.9, 29.2.

*Furan-2-yldiphenylmethanol (**1k**).*[21] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **1k** as a colorless oil (750.3 mg, 60% yield, 6.0 mmol of furan and 5.0 mmol of benzophenone as the starting material were used). mp 91.0−92.5 °C. R_f = 0.2 (20:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 1.6 Hz, 1H), 7.35−7.27 (m, 10H), 6.32 (dd, J = 3.2, 1.9 Hz, 1H), 5.92 (d, J = 3.2 Hz, 1H), 3.09 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.8, 144.6, 142.6, 128.0, 127.6, 127.2, 110.0, 109.6, 78.0.

*1-(Furan-2-yl)cyclobutan-1-ol (**1q**).*[33b] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **1q** as a colorless oil (579.9 mg, 84% yield, 6.0 mmol of furan and 5.0 mmol of cyclobutanone as the starting material were used). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, J = 1.6, 0.8 Hz, 1H), 6.35−6.32 (m, 1H), 6.29 (dd, J = 3.1, 1.0 Hz, 1H), 2.56−2.44 (m, 3H), 2.38−2.26 (m, 2H), 1.94−1.80 (m, 1H), 1.74−1.56 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.1, 142.1, 110.0, 104.8, 72.2, 35.6, 12.6.

Synthesis of 1b. To a solution of furfural (960.8 mg, 10.0 mmol, 1.1 equiv) in dry THF (15 mL) at −78 °C under N_2 was added *n*-BuLi (3.6 mL, 9.1 mmol, 1.0 equiv, 2.5 M solution in hexanes). The reaction mixture was stirred further for 1.5 h at −78 °C. After 1.5 h, the reaction mixture was quenched with NH_4Cl (50 mL) and extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over with Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by silica gel column chromatography (ethyl acetate/petroleum ether) which afforded **1b**.

*1-(Furan-2-yl)pentan-1-ol (**1b**).*[12b] Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded **1b** as a yellowish oil (995.6 mg, 71% yield). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, J = 1.7, 0.7 Hz, 1H), 6.32 (dd, J = 3.2, 1.8 Hz, 1H), 6.22 (d, J = 3.2 Hz, 1H), 4.66 (t, J = 6.8 Hz, 1H), 2.05 (s, 1H), 1.88−1.81 (m, 2H), 1.44−1.28 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.9, 141.8, 110.1, 105.7, 67.8, 35.2, 27.7, 22.4, 13.9.

Synthesis of 1c. 5-Methylfurfural (550.6 mg 5.0 mmol, 1.0 equiv) was dissolved in methanol (10 mL) and cooled to 0 °C. Sodium borohydride (105.9 mg, 2.8 mmol, 0.55 equiv) was then added slowly, in portions, and the mixture was stirred at room temperature for 1 h. The solvent was then removed in vacuo, and the residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give **1c**.

*(5-Methylfuran-2-yl)methanol (**1c**).*[12b] Isolation by column chromatography over silica gel (eluent, 25:1 petroleum ether/ethyl acetate) afforded **1c** as a yellowish oil (504.2 mg, 90% yield). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (d, J = 3.0 Hz, 1H), 5.89 (d, J = 2.6 Hz, 1H), 4.47 (s, 2H), 2.97

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(s, 1H), 2.26 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.18, 152.07, 108.50, 106.04, 56.99, 13.34.

Synthesis of 1l. TMSCl (108.6 mg, 1.0 mmol, 0.2 equiv) was added to a suspension of Zn dust (523.1 mg, 8.0 mmol, 1.6 equiv) in Et_2O (15 mL) at room temperature (rt). The resulting mixture was stirred for 15 min and then heated to reflux in an oil bath while a mixture of 5-methylfurfural (550.6 mg, 5.0 mmol, 1.0 equiv) and ethyl bromoacetate (3.34 g, 10.0 mmol, 2.0 equiv) was added at such a rate to maintain a gentle reflux (~20 min). The reaction mixture was heated at reflux for 1 h and then allowed to cool to room temperature, before quenching carefully with hydrochloric acid (2 M). The resulting solution was extracted three times with Et_2O (25 mL). The combined organic extracts were washed with H_2O and then dried (Na_2SO_4). The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give **1l**.

Ethyl-3-Hydroxy-3-(5-methylfuran-2-yl)propanoate (1l).[34b] Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded **1l** as a yellowish oil (742.9 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (d, J = 3.1 Hz, 1H), 5.98−5.84 (m, 1H), 5.08 (dd, J = 11.0, 6.6 Hz, 1H), 4.23−4.15 (m, 2H), 3.22 (d, J = 4.9 Hz, 1H), 2.89 (dd, J = 16.4, 8.7 Hz, 1H), 2.80 (dd, J = 16.4, 4.1 Hz, 1H), 2.27 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.9, 152.8, 152.0, 107.1, 106.0, 64.1, 60.8, 39.8, 14.1, 13.4.

Synthesis of 1m. To a solution of 5-methylfurfural (550.6 mg, 5.0 mmol, 1.0 equiv) in anhydrous THF (10 mL) at 0 °C under a nitrogen atmosphere was added dropwise a 10 mL solution of (2-methylallyl)magnesium chloride (10.0 mL, 10.0 mmol, 2.0 equiv, 1.0 M in THF). The resulting solution was then stirred for 30 min at 0 °C and then quenched with saturated NH_4Cl (10 mL). The mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product **1m**.

3-Methyl-1-(5-methylfuran-2-yl)but-3-en-1-ol (1m).[34c] Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded **1m** as a yellowish oil (556.4 mg, 67% yield). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (d, J = 3.1 Hz, 1H), 5.96−5.80 (m, 1H), 4.92−4.89 (m, 1H), 4.85 (d, J = 0.9 Hz, 1H), 4.80−4.75 (m, 1H), 2.63−2.50 (m, 2H), 2.28 (s, 3H), 2.10 (d, J = 3.4 Hz, 1H), 1.76 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 151.7, 141.8, 114.0, 106.8, 106.0, 65.2, 44.0, 22.3, 13.5.

Synthesis of 1n. A solution of 5-bromo-1-pentene (1117.7 mg, 7.5 mmol, 1.5 equiv) in diethyl ether (5 mL) was added dropwise to a suspension of activated magnesium (240.3 mg, 10.0 mmol, 2.0 equiv) in diethyl ether (15 mL) under nitrogen. After the completion of the addition, the gray mixture was heated at reflux in an oil bath for 1 h. A solution of furfural (480.4 mg, 5.0 mmol, 1.0 equiv) in diethyl ether (5 mL) was added slowly, and the mixture was heated at reflux for a further 3 h. The mixture was cooled in an ice bath and quenched with NH_4Cl until effervescence stopped. The mixture was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product **1n**.

1-(Furan-2-yl)hex-5-en-1-ol (1n).[34d] Isolation by column chromatography over silica gel (eluent, 25:1 petroleum ether/ethyl acetate) afforded **1n** as a yellowish oil (639.4 mg, 77% yield). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 1H), 6.34 (dd, J = 2.7, 1.9 Hz, 1H), 6.24 (d, J = 3.1 Hz, 1H), 5.86−5.74 (m, 1H), 5.02 (dd, J = 17.0, 1.2 Hz, 1H), 4.98−4.94 (m, 1H), 4.67 (t, J = 6.9 Hz, 1H), 2.17 (s, 1H), 2.09 (q, J = 7.2 Hz, 2H), 1.89−1.83 (m, 2H), 1.60−1.48 (m, 1H), 1.45−1.35 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.5, 141.9, 138.4, 114.8, 110.1, 105.9, 67.5, 34.7, 33.4, 24.7.

General Synthesis of 1o. Propargyl bromide (713.8 mg, 6.0 mmol, 2.0 equiv) was added to a solution of activated Zn (392.3 mg, 6.0 mmol, 2.0 equiv) in THF/NH_4Cl (4:1, 15 mL) at 0 °C. Then, 5-methylfurfural (330.3 mg, 3.0 mmol, 1.0 equiv) was added dropwise to the solution and stirred at 0 °C for 3 h. The reaction mixture was quenched with saturated $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product **1o**.

1-(5-Methylfuran-2-yl)but-3-yn-1-ol (1o).[34e] Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded **1o** as a yellowish oil (292.6 mg, 65% yield). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.20 (d, J = 3.1 Hz, 1H), 5.93−5.90 (m, 1H), 4.81 (dd, J = 11.0, 6.0 Hz, 1H), 2.76 (dd, J = 2.8, 0.7 Hz, 1H), 2.74 (d, J = 2.7 Hz, 1H), 2.28 (s, 3H), 2.07 (t, J = 2.7 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.7, 152.0, 107.4, 106.1, 80.1, 71.0, 66.0, 25.9, 13.5.

Synthesis of 1p. A solution of bromocyclopropane (907.4 mg, 7.5 mmol, 1.5 equiv) in diethyl ether (5 mL) was added dropwise to a suspension of activated magnesium (240.3 mg, 10.0 mmol, 2.0 equiv) in diethyl ether (15 mL) under nitrogen. After the completion of the addition, the gray mixture was heated at reflux in an oil bath for 1 h. A solution of 5-methylfurfural (550.6 mg, 5.0 mmol, 1.0 equiv) in diethyl ether (5 mL) was added slowly, and the mixture was heated at reflux for a further 3 h. The mixture was cooled in an ice bath and quenched with NH_4Cl until effervescence stopped. The mixture was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product **1p**.

Cyclopropyl(5-methylfuran-2-yl)methanol (1p).[34f] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **1p** as a yellow oil (539.9 mg, 71% yield). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17 (d, J = 3.0 Hz, 1H), 5.91 (dd, J = 3.1, 0.7 Hz, 1H), 3.96 (d, J = 8.4 Hz, 1H), 2.29 (s, 3H), 2.21 (s, 1H), 1.36−1.27 (m, 1H), 0.67−0.55 (m, 2H), 0.47−0.41 (m, 1H), 0.37−0.29 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.3, 151.7, 106.7, 105.9, 71.9, 15.9, 13.5, 3.2, 2.5.

General Syntheses of 1r−1v. To a 100 mL three-necked flask under nitrogen were added styrene (1.04 g, 10.0 mmol, 1.0 equiv), zinc−copper couple (1.60 g, 25.0 mmol, 2.5 equiv), and anhydrous ether (0.5 M). To this was added a solution of trichloroacetyl chloride (3.64 g, 20.0 mmol, 2.0 equiv) and phosphorus oxychloride (3.07 g, 20.0 mmol, 2.0 equiv) in ether (0.5 M) over 1 h through an addition funnel. The suspension was stirred overnight at reflux in an oil bath. The resulting mixture was filtered through a pad of Celite and was washed with ether (20 mL). The organic solution was successively washed with water (30 mL), a saturated aqueous solution of $NaHCO_3$ (30 mL), and brine (30 mL) and dried over Na_2SO_4. Then the solution was filtered, concentrated to afford 2,2-dichloro-3-phenylcyclobutan-1-one, and used in the next step without further purification.

A mixture of 2,2-dichloro-3-phenylcyclobutan-1-one (6.0 mmol, 1.0 equiv) and zinc dust (24.0 mmol, 4.0 equiv) in acetic acid (15 mL) was stirred at room temperature for 2 h and then heated in an oil bath at 70 °C for 4 h. The resulting mixture was allowed to cool to room temperature; then, the solution was diluted with water (30 mL) and extracted with ether (3 × 20 mL). The organic phase was washed successively with a saturated solution of aqueous $NaHCO_3$ (3 × 30 mL), water (30 mL), and brine (30 mL) and then dried over Na_2SO_4 and concentrated in vacuum. The crude material was then purified by flash chromatography with a mixture of petroleum ether and ethyl acetate to afford 3-phenylcyclobutan-1-one.

Under an argon atmosphere, 1,8 mL of *n*-BuLi (2.5 M in hexane, 4.4 mmol, 1.1 equiv) was added into the solution of 2-methylfuran

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(4.8 mmol, 1.2 equiv) in dry THF (15 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. Then, a solution of 3-phenylcyclobutan-1-one (4.0 mmol, 1.0 equiv) in THF (3 mL) was added into the reaction mixture dropwise at 0 °C. After stirring for 4 h, the reaction was quenched by water. The resulting solution was extracted three times with ethyl acetate (25 mL). The organic layer was dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give **1r**.

3-Phenylcyclobutan-1-one. Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded 3-phenylcyclobutan-1-one as a colorless oil (774.2 mg, 53% yield for two steps). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.22 (m, 5H), 3.73−3.58 (m, 1H), 3.53−3.42 (m, 2H), 3.28−3.17 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 206.7, 143.5, 128.6, 126.5, 126.4, 54.6, 28.3. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{10}ONa$, 169.0624; found, 169.0621.

3-(p-Tolyl)cyclobutan-1-one. Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded 3-(*p*-tolyl)cyclobutan-1-one as a yellow oil (800.5 mg, 50% yield for two steps, 10 mmol of 1-methyl-4-vinylbenzene as the starting material was used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22−7.13 (m, 4H), 3.69−3.58 (m, 1H), 3.52−3.40 (m, 2H), 3.27−3.15 (m, 2H), 2.34 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 207.0, 140.5, 136.2, 129.3, 126.3, 54.7, 28.0, 20.9. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{11}H_{12}ONa$, 183.0780; found, 183.0781.

3-(4-Chlorophenyl)cyclobutan-1-one. Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded 3-(4-chlorophenyl)cyclobutan-1-one as a yellow oil (846.1 mg, 47% yield for two steps, 10 mmol of 1-chloro-4-vinylbenzene as the starting material was used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.29 (m, 2H), 7.25−7.20 (m, 2H), 3.71−3.61 (m, 1H), 3.54−3.44 (m, 2H), 3.24−3.15 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 205.9, 141.9, 132.2, 128.6, 127.8, 54.6, 27.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$, [M+2+Na]$^+$ calcd for $C_{10}H_9ClONa$, 203.0234, 205.0205; found, 203.0233, 205.0213.

3-(4-Bromophenyl)cyclobutan-1-one. Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded 3-(4-bromophenyl)cyclobutan-1-one as a yellow oil (1.05 g, 47% yield for two steps, 10 mmol of 1-bromo-4-vinylbenzene as the starting material was used). mp 50.0−50.5 °C. R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.46 (m, 2H), 7.20−7.16 (m, 2H), 3.69−3.60 (m, 1H), 3.56−3.46 (m, 2H), 3.26−3.16 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 206.0, 142.5, 131.7, 128.3, 120.4, 54.7, 28.0. HRMS (ESI-TOF) m/z: [M + Na]$^+$ [M+2+Na]$^+$ calcd for $C_{10}H_9OBrNa$, 246.9729, 248.9709; found, 246.9722, 248.9722.

3-(4-Fluorophenyl)cyclobutan-1-one. Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded 3-(4-fluorophenyl)cyclobutan-1-one as a yellow oil (656.2 mg, 40% yield for two steps, 10 mmol of 1-fluoro-4-vinylbenzene as the starting material was used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.22 (m, 2H), 7.08−6.99 (m, 2H), 3.73−3.61 (m, 1H), 3.55−3.44 (m, 2H), 3.26−3.16 (m, 2H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 206.3, 161.5 (d, J = 245.0 Hz), 139.2 (d, J = 3.1 Hz), 128.0 (d, J = 8.0 Hz), 115.4 (d, J = 21.3 Hz), 54.8, 27.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_9OFNa$, 187.0530; found, 187.0529.

*1-(5-Methylfuran-2-yl)-3-phenylcyclobutan-1-ol (**1r**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **1r** as a yellow oil (693.4 mg, 76% yield). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.33−7.17 (m, 5H), 6.27 (d, J = 3.1 Hz, 1H), 5.95 (dd, J = 3.1, 0.9 Hz, 1H), 3.14−3.03 (m, 1H), 2.97−2.90 (m, 2H), 2.67 (d, J = 9.0 Hz, 1H), 2.46 (m, J = 4.9, 2.7 Hz, 2H), 2.31 (s, 3H). Minor isomer: δ 7.33−7.17 (m, 5H), 6.07 (d, J = 3.0 Hz, 1H), 5.88 (dd, J = 2.9, 1.0 Hz, 1H), 3.95−3.83 (m, 1H), 2.97−2.90 (m, 2H), 2.67 (d, J = 9.0 Hz, 1H), 2.46 (m, J = 4.9, 2.7 Hz, 2H), 2.27 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 155.8, 152.2, 144.4, 128.3, 126.6, 126.0, 106.4, 106.0, 67.9, 43.2, 30.5, 13.6. Minor isomer: δ 156.7, 151.5, 145.0, 128.4, 126.7, 126.1, 106.4, 105.0, 70.8, 42.4, 33.2, 13.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{16}O_2Na$, 251.1043; found, 251.1041.

*1-(5-Methylfuran-2-yl)-3-(p-tolyl)cyclobutan-1-ol (**1s**).* Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded **1s** as a yellow oil (678.0 mg, 70% yield, 4.0 mmol of 3-(*p*-tolyl)cyclobutan-1-one and 4.8 mmol of 2-methylfuran as the starting material were used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.18−7.10 (m, 4H), 6.27 (d, J = 3.1 Hz, 1H), 5.95 (dd, J = 3.1, 0.9 Hz, 1H), 3.11−3.00 (m, 1H), 2.96−2.88 (m, 2H), 2.65 (d, J = 9.0 Hz, 1H), 2.48−2.40 (m, 2H), 2.32 (s, 6H). Minor isomer: δ 7.18−7.10 (m, 4H), 6.07 (d, J = 3.1 Hz, 1H), 5.89 (dd, J = 3.1, 0.9 Hz, 1H), 3.92−3.76 (m, 1H), 2.96−2.88 (m, 2H), 2.65 (d, J = 9.0 Hz, 1H), 2.48−2.40 (m, 2H), 2.32 (s, 3H), 2.28 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 155.9, 152.3, 141.4, 135.6, 129.0, 126.6, 106.4, 106.0, 67.9, 43.3, 30.2, 21.0, 13.6. Minor isomer: δ 156.8, 151.5, 142.0, 135.5, 129.0, 126.4, 106.0, 105.0, 70.9, 42.6, 32.9, 21.0, 13.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{18}NaO_2$, 265.1199; found, 265.1199.

*3-(4-Chlorophenyl)-1-(5-methylfuran-2-yl)cyclobutan-1-ol (**1t**).* Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded **1t** as a yellow oil (754.8 mg, 72% yield, 4.0 mmol of 3-(4-chlorophenyl)cyclobutan-1-one and 4.8 mmol of 2-methylfuran as the starting material were used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.29−7.24 (m, 2H), 7.20−7.15 (m, 2H), 6.27 (d, J = 3.1 Hz, 1H), 5.96 (dd, J = 3.0, 1.0 Hz, 1H), 3.12−3.02 (m, 1H), 2.98−2.91 (m, 2H), 2.71−2.59 (m, 1H), 2.46−2.38 (m, 2H), 2.32 (d, J = 0.7 Hz, 3H). Minor isomer: δ 7.29−7.24 (m, 2H), 7.20−7.15 (m, 2H), 6.08 (d, J = 3.0 Hz, 1H), 5.89 (dd, J = 3.1, 0.9 Hz, 1H), 3.92−3.80 (m, 1H), 2.71−2.59 (m, 3H), 2.46−2.38 (m, 2H), 2.28 (d, J = 0.7 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 155.6, 152.4, 142.9, 131.8, 128.4, 128.0, 106.5, 106.0, 67.8, 43.2, 30.0, 13.6. Minor isomer: δ 155.6, 151.7, 143.4, 131.6, 128.4, 127.9, 106.1, 105.1, 70.8, 42.5, 32.6, 13.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$, [M +2+Na]$^+$calcd for $C_{15}H_{15}O_2ClNa$, 285.0653, 287.0623; found, 285.0650, 287.0624.

*3-(4-Bromophenyl)-1-(5-methylfuran-2-yl)cyclobutan-1-ol (**1u**).* Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded **1u** as a yellow oil (918.1 mg, 75% yield, 4 mmol of 3-(4-bromophenyl)cyclobutan-1-one and 4.8 mmol of 2-methylfuran as the starting material were used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.44−7.39 (m, 2H), 7.15−7.09 (m, 2H), 6.27 (d, J = 2.9 Hz, 1H), 5.95 (dd, J = 1.9, 0.9 Hz, 1H), 3.11−3.00 (m, 1H), 2.98−2.90 (m, 2H), 2.71−2.59 (m, 1H), 2.45−2.38 (m, 2H), 2.32 (d, J = 0.7 Hz, 3H). Minor isomer: δ 7.44−7.39 (m, 2H), 7.15−7.09 (m, 2H), 6.07 (d, J = 3.0 Hz, 1H), 5.89 (dd, J = 3.1, 0.9 Hz, 1H), 3.88−3.77 (m, 1H), 2.71−2.59 (m, 1H), 2.45−2.38 (m, 4H), 2.28 (d, J = 0.6 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 155.5, 152.4, 143.4, 131.4, 128.4, 119.8, 106.5, 106.0, 67.8, 43.1, 30.1, 13.6. Minor isomer: δ 156.5, 151.7, 143.9, 131.3, 128.3, 119.7, 106.1, 105.1, 70.8, 42.4, 32.7, 13.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$, [M + 2 + Na]$^+$ calcd for $C_{15}H_{15}O_2BrNa$, 329.0148, 331.0128; found, 329.0150, 331.0142.

*3-(4-Fluorophenyl)-1-(5-methylfuran-2-yl)cyclobutan-1-ol (**1v**).* Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded **1v** as a yellow oil (620.2 mg, 63% yield, 4.0 mmol of 3-(4-fluorophenyl)cyclobutan-1-one and 4.8 mmol of 2-methylfuran as the starting material were used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.22−7.15 (m, 2H), 7.03−6.93 (m, 2H), 6.26 (d, J = 3.1 Hz, 1H), 5.97−5.94 (m, 1H), 3.12−3.02 (m, 1H), 2.97−2.90 (m, 2H), 2.70−2.59 (m, 1H), 2.45−2.37 (m, 2H), 2.31 (d, J = 0.7 Hz, 3H). Minor isomer: δ 7.22−7.15 (m, 2H), 7.03−6.93 (m, 2H), 6.07 (d, J = 3.1 Hz, 1H), 5.91−5.86 (m, 1H), 3.91−3.79 (m, 1H), 2.97−

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2.90 (m, 2H), 2.70−2.59 (m, 1H), 2.45−2.37 (m, 2H), 2.28 (d, J = 0.7 Hz, 3H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$) Major isomer: δ 161.3 (d, J = 244.0 Hz), 155.6, 152.3, 140.1 (d, J = 2.9 Hz), 128.0 (d, J = 7.8 Hz), 115.0 (d, J = 21.2 Hz), 106.4, 106.0, 67.8, 43.3, 29.9, 13.6. Minor isomer: δ 161.2 (d, J = 243.9 Hz), 156.6, 151.6, 140.6 (d, J = 2.8 Hz), 127.9 (d, J = 7.9 Hz), 115.0 (d, J = 21.1 Hz), 106.0, 105.0, 70.7, 42.6, 32.5, 13.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{15}O_2FNa$, 269.0948; found, 269.0949.

Synthesis of 1w. To a stirring solution of 5-hydroxymethylfurfural (1.26 g, 10.0 mmol, 1.0 equiv) in CH_3CN (20 mL) was added finely ground sodium hydroxide (600.3 mg, 15.0 mmol, 1.5 equiv) at 0 °C. Subsequently, allyl bromide (1.78 g, 15.0 mmol, 1.5 equiv) was added dropwise. The reaction mixture was stirred for 24 h while the temperature was allowed to rise slowly to rt. The reaction mixture was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product 5-((allyloxy)methyl)furan-2-carbaldehyde.

5-((allyloxy)methyl)furan-2-carbaldehyde (664.2 mg, 4.0 mmol, 1.0 equiv) was dissolved in methanol (10 mL) and cooled to 0 °C. Sodium borohydride (83.2 mg, 2.2 mmol, 0.55 equiv) was then added slowly, in portions, and the mixture was stirred at room temperature for 1 h. The solvent was then removed in vacuo, and the residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give **1w**.

5-((Allyloxy)methyl)furan-2-carbaldehyde.[34g] Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded 5-((allyloxy)methyl)furan-2-carbaldehyde as a colorless oil (415.1 mg, 23% yield). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 7.22 (d, J = 3.5 Hz, 1H), 6.53 (d, J = 3.5 Hz, 1H), 5.92 (ddd, J = 22.9, 10.9, 5.7 Hz, 1H), 5.35−5.29 (m, 1H), 5.24 (dd, J = 10.4, 0.5 Hz, 1H), 4.55 (s, 2H), 4.08 (d, J = 5.7 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 177.7, 158.4, 152.6, 133.8, 121.9, 118.0, 111.1, 71.8, 64.0.

*(5-((Allyloxy)methyl)furan-2-yl)methanol (**1w**).*[34g] Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **1w** as a colorless oil (537.8 mg, 80% yield). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.26 (d, J = 3.2 Hz, 1H), 6.23 (d, J = 3.1 Hz, 1H), 5.98−5.86 (m, 1H), 5.33−5.26 (m, 1H), 5.24−5.18 (m, 1H), 4.57 (s, 2H), 4.43 (s, 2H), 4.04−4.01 (m, 2H), 2.27 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 151.5, 134.2, 117.7, 110.1, 108.3, 71.0, 63.8, 57.4.

Synthesis of 1x. To a solution of 5-hydroxymethylfurfural (1.26 g, 10.0 mmol, 1.0 equiv) dissolved in toluene/water (4:1, 15 mL) were added potassium hydroxide (673.3 mg, 12.0 mmol, 1.2 equiv) and propargyl bromide (2.38 g, 20.0 mmol, 2.0 equiv). Then, the reaction mixture was refluxed in an oil bath for 3 h. After cooling to ambient temperature, the mixture was extracted with diethyl ether; the combined organic layers were dried over Na_2SO_4, and the solvent was removed in vacuo, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product 5-((prop-2-yn-1-yloxy)methyl)furan-2-carbaldehyde.

5-((Prop-2-yn-1-yloxy)methyl)furan-2-carbaldehyde.[35g] Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded 5-((prop-2-yn-1-yloxy)methyl)furan-2-carbaldehyde as a colorless oil (935.0 mg, 57% yield). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.25 (d, J = 3.5 Hz, 1H), 6.59 (d, J = 3.6 Hz, 1H), 4.66 (s, 2H), 4.24 (d, J = 2.4 Hz, 2H), 2.55 (t, J = 2.5 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 177.7, 157.2, 152.5, 121.9, 111.8, 78.5, 75.5, 63.1, 57.6.

*(5-((Prop-2-yn-1-yloxy)methyl)furan-2-yl)methanol (**1x**).*[34h] Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded **1x** as a colorless oil (511.5 mg, 77% yield, 5 mmol of 5-((prop-2-yn-1-yloxy)methyl)furan-2-carbaldehyde as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.32 (d, J = 3.2 Hz, 1H), 6.25 (d, J = 3.2 Hz, 1H), 4.58 (s, 2H), 4.54 (s, 2H), 4.17 (d, J = 2.3 Hz, 2H), 2.48 (t, J = 2.3 Hz, 1H), 2.06 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.7, 150.6, 110.9, 108.4, 79.2, 74.9, 63.1, 57.4, 56.8.

Synthesis of 1z. To a stirred solution of 5-hydroxymethylfurfural (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) at 0 °C were added MOMCl (6.0 mmol, 1.2 equiv) and DIPEA (7.5 mmol, 1.5 equiv). The mixture was stirred at rt for 10 h and then washed with water (15 mL), saturated aqueous NH_4Cl (15 mL), and brine (15 mL). The organic layer was dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give 5-((methoxymethoxy)methyl)furan-2-carbaldehyde.

5-((Methoxymethoxy)methyl)furan-2-carbaldehyde. Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded 5-((methoxymethoxy)methyl)furan-2-carbaldehyde as a colorless oil (595.2 g, 70% yield). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.22 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 3.6 Hz, 1H), 4.71 (s, 2H), 4.63 (s, 2H), 3.41 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 177.7, 158.0, 152.7, 121.7, 111.2, 95.9, 61.1, 55.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_8H_{10}NaO_4$, 193.0471; found, 193.0475.

*(5-((Methoxymethoxy)methyl)furan-2-yl)methanol (**1z**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **1z** as a colorless oil (428.5 mg, 83% yield, 3.0 mmol of 5-((methoxymethoxy)methyl)furan-2-carbaldehyde as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (d, J = 3.1 Hz, 1H), 6.24 (d, J = 3.1 Hz, 1H), 4.67 (s, 2H), 4.57 (s, 2H), 4.51 (s, 2H), 3.39 (s, 3H), 2.46 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.6, 151.1, 110.2, 108.3, 95.1, 60.8, 57.3, 55.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_8H_{12}NaO_4$, 195.0628; found, 195.0631.

Synthesis of 1y. To a suspension of lithium aluminum hydride (607.2 mg, 16.0 mmol, 2.0 equiv) in Et_2O (20 mL) at −78 °C was added a solution of ethyl 3-(furan-2-yl)propionate (1.35 g, 8.0 mmol, 1.0 equiv) in Et_2O (3 mL) dropwise. The resulting mixture was stirred at −78 °C for 10 min, at 0 °C for 60 min, and then at room temperature for 60 min. When the TLC indicated that the starting material was completely consumed, the reaction mixture was cooled to 0 °C and quenched by the slow addition of 2.3 mL of H_2O. After stirring for 20 min, 2.3 mL of 15% aqueous NaOH and 7 mL of H_2O were slowly added to the reaction mixture successively. The resulting suspension was stirred vigorously for 5 h, and anhydrous Na_2SO_4 was added. After filtration, the mixture was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product 3-(furan-2-yl)propan-1-ol.

An oven-dried flask was charged with the 3-(furan-2-yl)propan-1-ol (883.1 mg, 7.0 mmol, 1.0 equiv), DMF (15 mL), imidazole (571.9 mg, 8.4 mmol, 1.2 equiv), and *tert*-butyldimethylsilyl chloride (1.16 g, 7.7 mmol, 1.1 equiv). The reaction mixture was stirred overnight at rt. The reaction mixture was diluted with hexane (20 mL) and quenched with water (20 mL). The resulting solution was extracted three times with Et_2O (25 mL). The combined organic extracts were washed with H_2O and then dried over Na_2SO_4. The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give *tert*-butyl(3-(furan-2-yl)propoxy)dimethylsilane.

To a solution of *tert*-butyl(3-(furan-2-yl)propoxy)dimethylsilane (1.44 g, 6.0 mmol, 1.2 equiv) in dry THF (10 mL) was added 2.2 mL of *n*-BuLi (2.5 M in hexane, 1.1 equiv) dropwise at −78 °C. The reaction mixture was allowed to warm to 0 °C over 2 h, and then cooled to −78 °C. The cyclopentanone (420.6 mg, 5.0 mmol, 1.0 equiv) was added dropwise −78 °C, and the resulting reaction mixture was allowed to warm to rt and stirred overnight. The reaction was quenched by the addition of sat. aqueous NH_4Cl (10 mL). The

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mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product **1y**.

3-(Furan-2-yl)propan-1-ol.[34i] Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded 3-(furan-2-yl)propan-1-ol as a colorless oil (857.3 mg, 85% yield). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, J = 1.8, 0.7 Hz, 1H), 6.28 (dd, J = 3.1, 1.9 Hz, 1H), 6.01 (d, J = 3.2 Hz, 1H), 3.68 (t, J = 6.3 Hz, 2H), 2.73 (t, J = 7.4 Hz, 2H), 1.93−1.85 (m, 2H), 1.76 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.5, 140.9, 110.1, 105.0, 62.0, 30.9, 24.2.

tert-Butyl(3-(furan-2-yl)propoxy)dimethylsilane.[34i] Isolation by column chromatography over silica gel (eluent, 50:1 petroleum ether/ethyl acetate) afforded *tert*-butyl(3-(furan-2-yl)propoxy)-dimethylsilane as a colorless oil (1.50 g, 89% yield). R_f = 0.5 (20:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, J = 1.8, 0.8 Hz, 1H), 6.27 (dd, J = 3.1, 1.9 Hz, 1H), 5.98 (dd, J = 3.1, 0.9 Hz, 1H), 3.65 (t, J = 6.3 Hz, 2H), 2.69 (t, J = 7.6 Hz, 2H), 1.97−1.76 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.0, 140.7, 110.0, 104.8, 62.2, 31.1, 25.9, 24.3, 18.3, −5.3.

*1-(5-(3-((tert-Butyldimethylsilyl)oxy)propyl)furan-2-yl)-cyclopentan-1-ol (**1y**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **1y** as a yellowish oil (1.09 g, 67% yield). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (d, J = 3.1 Hz, 1H), 5.89 (d, J = 3.1 Hz, 1H), 3.65 (t, J = 6.3 Hz, 2H), 2.67 (t, J = 7.5 Hz, 2H), 2.09−1.99 (m, 2H), 1.96−1.81 (m, 7H), 1.78−1.69 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.4, 155.2, 105.1, 104.5, 79.5, 62.2, 39.5, 31.0, 25.9, 24.4, 23.6, 18.3, −5.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{18}H_{32}O_3SiNa$, 347.2013; found, 347.2017.

General Syntheses of 3a, 3b, and 3d−3h. To a stirred solution of 2-furfural (960.8 mg, 10.0 mmol, 1.0 equiv) in toluene (15 mL) were added *p*-toluenesulfonamide (1.71 g, 10.0 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (86.1 mg, 0.5 mmol, 0.05 equiv). The mixture was placed in a round-bottom flask with a Dean−Stark trap and heated at reflux in an oil bath for 20 h. After the mixture cooled to room temperature, the solvent was removed under reduced pressure to give *N*-1-furan-2-ylmethylene-4-methylbenezenesulfonamide as a brown solid. It could be used directly in the next step without further purification.

To a stirred solution of *N*-1-furan-2-ylmethylene-4-methylbenezenesulfonamide (747.2, 3.0 mmol, 1.0 equiv) in THF (8 mL) was added RMgBr (6 mL, 1.0 M in THF, 6.0 mmol, 2.0 equiv) at 0 °C. The mixture was stirred at room temperature. When the reaction was completed as determined by TLC, the mixture was quenched with a saturated aqueous NH_4Cl solution (15 mL) and then extracted with ethyl acetate (3 × 20 mL). The organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue by column chromatography gave the product.

*N-(1-(Furan-2-yl)ethyl)-4-methylbenzenesulfonamide (**3a**).*[35a] Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **3a** as a white solid (485.1 mg, 61% yield for two steps). mp 71.5−72.3 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74−7.64 (m, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.17 (dd, J = 1.8, 0.6 Hz, 1H), 6.16 (dd, J = 3.2, 1.9 Hz, 1H), 5.98 (d, J = 3.3 Hz, 1H), 4.91 (d, J = 8.1 Hz, 1H), 4.60−4.44 (m, 1H), 2.40 (s, 3H), 1.45 (d, J = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.9, 143.1, 141. 9, 137. 6, 129.4, 127.0, 110.0, 106.1, 47.3, 21.5, 20.9.

*N-(1-(Furan-2-yl)-2-methylpropyl)-4-methylbenzenesulfonamide (**3b**).*[35b] Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **3b** as a white solid (483.6 mg, 55% yield for two steps, 3.0 mmol of *N*-1-furan-2-ylmethylene-4-methylbenezenesulfonamide and 6.0 mmol of isopropylmagnesium bromide as the starting materials were used). mp 75.7−77.1 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61−7.56 (m, 2H), 7.14 (d, J = 8.3 Hz, 2H), 7.11 (dd, J = 1.8, 0.8 Hz, 1H), 6.05 (dd, J = 3.2, 1.9 Hz, 1H), 5.80 (d, J = 3.2 Hz, 1H), 5.29 (d, J = 9.5 Hz, 1H), 4.13 (dd, J = 9.5, 7.0 Hz, 1H), 2.35 (s, 3H), 2.08−1.98 (m, 1H), 0.94 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 152.4, 142.8, 141.4, 137.6, 129.2, 126.9, 109.7, 107.2, 57.5, 32.9, 21.4, 18.8, 18.7.

*N-(1-(Furan-2-yl)propyl)-4-methylbenzenesulfonamide (**3d**).*[35a] Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **3d** as a white solid (586.1 mg, 70% yield, 3.0 mmol of *N*-1-furan-2-ylmethylene-4-methylbenezenesulfonamide and 6.0 mmol of ethylmagnesium bromide as the starting materials were used). mp 92.0−93.1 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.13 (dd, J = 1.7, 0.7 Hz, 1H), 6.10 (dd, J = 3.2, 1.8 Hz, 1H), 5.90 (d, J = 3.2 Hz, 1H), 5.16 (d, J = 8.7 Hz, 1H), 4.31 (dd, J = 15.8, 7.2 Hz, 1H), 2.37 (s, 3H), 1.80 (p, J = 7.4 Hz, 2H), 0.83 (t, J = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 152.9, 142.9, 141.7, 137.7, 129.3, 126.9, 109.8, 106.8, 53.1, 28.1, 21.4, 10.1.

*N-(1-(Furan-2-yl)-3-methylbut-3-en-1-yl)-4-methylbenzenesulfonamide (**3e**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **3e** as a white solid (558.3 mg, 61% yield, 3.0 mmol of *N*-1-furan-2-ylmethylene-4-methylbenezenesulfonamide and 6.0 mmol of (2-methylallyl) magnesium bromide as the starting materials were used). mp 61.9−63.3 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.58 (m, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.15−7.14 (m, 1H), 6.12 (dd, J = 3.2, 1.8 Hz, 1H), 5.99 (d, J = 3.2 Hz, 1H), 4.92 (d, J = 7.2 Hz, 1H), 4.81−4.78 (m, 1H), 4.70 (d, J = 0.7 Hz, 1H), 4.55 (dd, J = 14.7, 7.3 Hz, 1H), 2.54−2.41 (m, 2H), 2.38 (s, 3H), 1.54 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.7, 143.0, 141.7, 140.5, 137.5, 129.3, 127.0, 115.0, 110.0, 107.1, 49.7, 43.1, 21.6, 21.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{19}NO_3SNa$, 328.0978; found, 328.0987.

*N-(Cyclopentyl(furan-2-yl)methyl)-4-methylbenzenesulfonamide (**3f**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **3f** as a white solid (469.1 mg, 49% yield for two steps, 3 mmol of *N*-1-furan-2-ylmethylene-4-methylbenezenesulfonamide and 6 mmol of cyclopentylmagnesium bromide as the starting materials were used). mp 105.8−107.5 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57−7.52 (m, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.10−7.06 (m, 1H), 6.04 (dd, J = 3.2, 1.8 Hz, 1H), 5.80 (d, J = 3.2 Hz, 1H), 4.98 (d, J = 9.1 Hz, 1H), 4.17 (t, J = 9.0 Hz, 1H), 2.36 (s, 3H), 2.30−2.23 (m, 1H), 1.87−1.77 (m, 1H), 1.60−1.39 (m, 6H), 1.21−1.11 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.9, 142.8, 141.4, 137.6, 129.2, 126.9, 109.7, 107.0, 55.9, 44.2, 29.7, 29.3, 25.2, 25.2, 21.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{21}NO_3SNa$, 342.1134; found, 342.1127.

*N-(Cyclohexyl(furan-2-yl)methyl)-4-methylbenzenesulfonamide (**3g**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **3g** as a white solid (449.7 mg, 45% yield for two steps, 3 mmol of *N*-1-furan-2-ylmethylene-4-methylbenezenesulfonamide and 6 mmol of cyclohexylmagnesium bromide as the starting materials were used). mp 97.0−98.0 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.53 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.11 (dd, J = 1.8, 0.8 Hz, 1H), 6.05 (dd, J = 3.2, 1.8 Hz, 1H), 5.76 (d, J = 3.2 Hz, 1H), 5.07 (d, J = 9.5 Hz, 1H), 4.14 (dd, J = 9.5, 7.7 Hz, 1H), 2.35 (s, 3H), 1.91 (d, J = 12.9 Hz, 1H), 1.75−1.60 (m, 4H), 1.35 (d, J = 13.0 Hz, 1H), 1.22−1.06 (m, 3H), 1.00−0.87 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.2, 142.8, 141.4, 137.6, 129.2, 126.8, 109.7, 107.3, 56.8, 42.1, 29.3, 26.1, 25.8, 21.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{18}H_{23}NO_3SNa$, 356.1291; found, 356.1280.

*N-(Cyclopropyl(furan-2-yl)methyl)-4-methylbenzenesulfonamide (**3h**).*[17] Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **3h** as a yellow viscous oil (497.8 mg, 57% yield for two steps, 3 mmol of *N*-1-furan-

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2-ylmethylene-4-methylbenezenesulfonamide and 6 mmol of cyclopropylmagnesium bromide as the starting materials were used). mp 96.0−97.2 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.59 (m, 2H), 7.22−7.17 (m, 2H), 7.14 (dd, J = 1.8, 0.7 Hz, 1H), 6.15 (dd, J = 3.3, 1.9 Hz, 1H), 6.00 (d, J = 3.2 Hz, 1H), 5.08 (d, J = 7.5 Hz, 1H), 3.91 (t, J = 7.9 Hz, 1H), 2.39 (s, 3H), 1.24−1.16 (m, 1H), 0.53−0.47 (m, 2H), 0.35−0.30 (m, 1H), 0.29−0.22 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.6, 143.0, 141.9, 137.7, 129.3, 127.0, 109.9, 106.9, 55.6, 21.5, 15.8, 3.8, 3.5.

Synthesis of 3k. Under an argon atmosphere, 2.2 mL of *n*-BuLi (2.5 M in hexane, 1.1 equiv) was added into the solution of furan (816.8 mg, 12.0 mmol, 1.2 equiv) in dry THF (10 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. Then, a solution of phenylpropyl aldehyde (1.34 g, 10.0 mmol, 1.0 equiv) in THF (3 mL) was added into the reaction mixture dropwise at 0 °C. After stirring for 4 h, the reaction was quenched by water. The resulting solution was extracted three times with ethyl acetate (25 mL). The organic layer was dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give 1-(furan-2-yl)-3-phenylpropan-1-ol.

Lukewarm water (5.0 mL) was added to sodium azide (1.37 g, 21.0 mmol, 3.0 equiv), and the resultant suspension was stirred for 15 min. Benzene (15 mL) was added, and the biphasic suspension was cooled to 0 °C. Concentrated H_2SO_4 (0.8 mL) was added dropwise, and the mixture was allowed to stir at 0 °C for 20 min. The organic phase was then carefully syringed into a dry flask at 0 °C, and 1-(furan-2-yl)-3-phenylpropan-1-ol (1.42 g, 7.0 mmol, 1.0 equiv) was added followed by H_2SO_4 (0.1 mL). The resulting mixture was stirred for 5 min at 0 °C and was then quenched with ice-cold ammonium hydroxide solution (25 mL). The reaction mixture was extracted with EtOAc (3 × 25 mL). The combined organic phases were washed with saturated aqueous NH_4Cl (25 mL), dried over Na_2SO_4, and concentrated under a vacuum. The crude material was purified by silica gel column chromatography (petroleum ether/ethyl acetate) affording 2-(1-azido-3-phenylpropyl)furan.

A solution of 2-(1-azido-3-phenylpropyl)furan (1.14 g, 5.0 mmol) in EtOAc (10 mL) was treated with 10% Pd/C (56.0 mg) and placed under a H_2 atmosphere. Hydrogen was bubbled through the solution for 5 at 10 min intervals for a total of 1 h. The reaction mixture was then filtered through Celite and concentrated under a vacuum affording 1-(furan-2-yl)-3-phenylpropan-1-amine, which was used without further purification.

A solution of 1-(furan-2-yl)-3-phenylpropan-1-amine (603.3 mg, 3.0 mmol, 1.0equiv) in anhydrous dichloromethane (10 mL) was treated with triethylamine (333.9 mg, 3.3 mmol, 1.1 equiv) and cooled to 0 °C. The mixture was then treated with *p*-toluenesulfonyl chloride (629.1 mg, 3.3 mmol, 1.1 equiv), allowed to warm up to room temperature, and stirred overnight. The reaction was then diluted with dichloromethane (10 mL) and washed sequentially with saturated aqueous sodium hydrogen carbonate (15 mL) and brine (15 mL). The mixture was extracted with EtOAc (3 × 15 mL); the combined organic layers were dried over Na_2SO_4, and the solvent was removed in vacuo, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product *N*-(1-(furan-2-yl)-3-phenylpropyl)-4-methylbenzenesulfonamide **3k**.

1-(Furan-2-yl)-3-phenylpropan-1-ol. Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded 1-(furan-2-yl)-3-phenylpropan-1-ol as a colorless oil (1.66 g, 82% yield). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (dd, J = 1.8, 0.8 Hz, 1H), 7.28−7.22 (m, 2H), 7.18−7.13 (m, 3H), 6.28 (dd, J = 3.3, 1.8 Hz, 1H), 6.18 (d, J = 3.2 Hz, 1H), 4.61 (t, J = 6.8 Hz, 1H), 2.75−2.59 (m, 2H), 2.56 (s, 1H), 2.12 (dd, J = 14.7, 7.8 Hz, 2H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 156.5, 141.8, 141.4, 128.4, 128.3, 125.8, 110.0, 105.9, 66.7, 36.8, 31.6.

2-(1-Azido-3-phenylpropyl)furan. Isolation by column chromatography over silica gel (eluent, 100:1 petroleum ether/ethyl acetate) afforded 2-(1-azido-3-phenylpropyl)furan as a colorless oil (1.13 g, 71% yield). R_f = 0.5 (50:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 1.7 Hz, 1H), 7.33−7.27 (m, 2H), 7.24−7.16 (m, 3H), 6.36 (dd, J = 3.2, 1.8 Hz, 1H), 6.31 (d, J = 3.2 Hz, 1H), 4.36 (t, J = 7.4 Hz, 1H), 2.78−2.64 (m, 2H), 2.19 (q, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.2, 142.9, 140.6, 128.5, 128.5, 126.2, 110.2, 107.9, 57.9, 34.1, 32.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{13}N_3ONa$, 250.0951; found, 250.0950.

N-(1-(Furan-2-yl)-3-phenylpropyl)-4-methylbenzenesulfonamide (3k).[35a] Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **3k** as a yellow solid (596.6 mg, 56% yield for two steps). mp 87.6−88.7 °C. R_f = 0.5 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.57 (m, 2H), 7.26−7.20 (m, 2H), 7.18−7.15 (m, 2H), 7.14 (s, 1H), 7.12 (d, J = 1.7 Hz, 1H), 7.08−7.04 (m, 2H), 6.09 (dd, J = 3.3, 1.9 Hz, 1H), 5.90 (d, J = 3.3 Hz, 1H), 5.42 (d, J = 8.8 Hz, 1H), 4.40 (dd, J = 15.9, 7.3 Hz, 1H), 2.60−2.50 (m, 2H), 2.35 (s, 3H), 2.11−2.02 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.7, 142.9, 141.8, 140.7, 137.6, 129.3, 128.3, 128.3, 126.9, 125.9, 109.9, 107.0, 51.2, 36.3, 31.7, 21.4.

General Syntheses of 3i, 3j, and 3l. To a solution of the corresponding 6-chlorohexan-1-ol (1.37 g, 10.0 mmol, 1.0 equiv) in CH_2Cl_2 was added Dess−Martin periodinane (4.67 g, 11.0 mmol, 1.1 equiv). After stirring for 1 h, the reaction mixture was diluted with an aqueous mixture of saturated $Na_2S_2O_3$ and $NaHCO_3$ and then extracted with CH_2Cl_2 (3 × 20). The organic layers were combined, dried (Na_2SO_4), filtered, and concentrated under reduced pressure in an ice bath. The crude product 6-chlorohexanal was used directly in the next step.

To a solution of 6-chlorohexanol (1.37 g, 10.0 mmol, 1.0 equiv) in DMF (15 mL) was slowly added the NaN_3 (1.30 g, 20.0 mmol, 2.0 equiv), and the reaction mixture was heated in an oil bath at 80 °C for 12 h. After cooling, the water (20 mL) was added. The mixture was extracted with DCM (4 × 20 mL). The combined organic layers were washed with water (3 × 20 mL) and dried over anhydrous Na_2SO_4. Concentration by vacuum decompression gave the crude product of 6-azidohexan-1-ol. The crude product 6-azidohexan-1-ol was used directly in the next step. Next, the synthetic method of 6-azidohexanal is the same as that of 6-chlorohexanal.

To a suspension of NaH (440.0 mg, 60 wt %, 11.0 mmol, 1.1 equiv) in THF (15 mL) was added 1,4-butanediol (900.7 mg, 10.0 mmol, 1.0 equiv) at 0 °C. After the complete addition, the mixture was stirred for 30 min, and benzyl bromide (1.71 g, 10.0 mmol, 1.0 equiv) was added dropwise. Then, a catalytic amount of tetrabutylammonium iodide was added, and the reaction mixture was allowed to warm to room temperature and was stirred for 3 h. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with DCM (3 × 10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product 4-(benzyloxy)butan-1-ol.

To a stirred CH_2Cl_2 (50 mL) solution of dimethyl sulfoxide (1.09 g, 14.0 mmol, 2.8 equiv) was dropped oxalyl chloride (1.32 g, 10.4 mmol, 2.2 equiv) at −78 °C. After the mixture was stirred for 2 h, a CH_2Cl_2 (5 mL) solution of the 4-(benzyloxy)butan-1-ol s38 (900.6 mg, 5.0 mmol, 1.0 equiv) was added slowly. After the mixture was stirred for 1 h, triethylamine (2.43 g, 24.0 mmol, 4.8 equiv) was added slowly. The mixture was gradually warmed up to room temperature and then stirred for 1 h. The reaction was quenched with pH = 7 phosphate buffer, and the organic phase was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine and dried over Na_2SO_4. Concentration by vacuum decompression gave the crude product of 4-(benzyloxy)butanal. The crude product was used directly in the next step.

A mixture of aldehyde (5.0 mmol, 1.0 equiv), *p*-toluenesulfonamide (856.1 mg, 5.0 mmol, 1.0 equiv), and sodium benzenesulfinate (902.9 mg, 5.5 mmol, 1.1 equiv) in formic acid and H_2O (1.0:1.0, 10 mL) was stirred at room temperature overnight. The resulting white precipitate was filtered off and washed with H_2O (3 × 15 mL) and hexanes (3 × 15 mL).

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The white solid was dissolved in CH_2Cl_2 and treated with saturated $NaHCO_3$(aq) for 1 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was used directly in the next step.

Under an argon atmosphere, 1.1 mL of *n*-BuLi (2.5 M in hexane, 1.1 equiv) was added into the solution of furan (204.2 mg, 3.0 mmol, 1.2 equiv) in dry THF (10 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. Then, a solution of imine (2.5 mmol, 1.0 equiv) in THF (3 mL) was added into the reaction mixture dropwise at 0 °C. After stirring for 1 h, the reaction was quenched by water. The resulting solution was extracted three times with ethyl acetate (25 mL). The organic layer was dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give **3i**, **3j**, and **3l**.

4-(Benzyloxy)butan-1-ol. Isolation by column chromatography over silica gel (eluent, 4:1 petroleum ether/ethyl acetate) afforded s38 as a colorless oil (1.53 g, 85% yield). R_f = 0.4 (2:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.30 (m, 4H), 7.29−7.24 (m, 1H), 4.50 (s, 2H), 3.59 (t, J = 6.0 Hz, 2H), 3.50 (t, J = 5.9 Hz, 2H), 2.81 (s, 1H), 1.74−1.59 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.0, 128.3, 127.6, 127.5, 72.9, 70.2, 62.4, 29.8, 26.5.

N-(6-Chloro-1-(furan-2-yl)hexyl)-4-methylbenzenesulfonamide (3i). Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **3i** as a yellow solid (497.1 mg, 56% yield). mp 64.5−65.0 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.55 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 1.7 Hz, 1H), 6.11 (dd, J = 3.2, 1.9 Hz, 1H), 5.88 (d, J = 3.2 Hz, 1H), 4.94 (d, J = 8.8 Hz, 1H), 4.38 (dd, J = 16.0, 7.4 Hz, 1H), 3.47 (t, J = 6.7 Hz, 2H), 2.39 (s, 3H), 1.78 (dd, J = 15.1, 7.4 Hz, 2H), 1.73−1.64 (m, 2H), 1.42−1.31 (m, 2H), 1.28−1.14 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.8, 143.1, 141.8, 137.6, 129.3, 126.9, 109.9, 106.8, 51.6, 44.8, 34.7, 32.3, 26.2, 24.8, 21.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$, $[M + 2 + Na]^+$ calcd for $C_{17}H_{22}NO_3ClSNa$, 378.0901, 380.0872; found, 378.0895, 380.0869.

N-(6-Azido-1-(furan-2-yl)hexyl)-4-methylbenzenesulfonamide (3j). Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **3j** as a white solid (516.0 mg, 57% yield, 2.5 mmol of (*E*)-*N*-(6-azidohexylidene)-4-methylbenzenesulfonamide and 3.0 mmol of furan as the starting material were used). mp 50.0−52.5 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 8.5, 1.9 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 1.5 Hz, 1H), 6.09 (dd, J = 3.2, 1.8 Hz, 1H), 5.88 (d, J = 3.2 Hz, 1H), 5.26 (d, J = 8.8 Hz, 1H), 4.37 (dd, J = 16.0, 7.3 Hz, 1H), 3.19 (t, J = 6.9 Hz, 2H), 2.38 (s, 3H), 1.77 (q, J = 7.3 Hz, 2H), 1.54−1.47 (m, 2H), 1.35−1.25 (m, 3H), 1.22−1.15 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.8, 142.9, 141.7, 137.6, 129.3, 126.8, 109.9, 106.7, 51.5, 51.1, 34.6, 28.5, 26.0, 25.0, 21.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{22}N_4O_3SNa$, 385.1305; found, 385.1294.

N-(4-(Benzyloxy)-1-(furan-2-yl)butyl)-4-methylbenzenesulfonamide (3l). Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **3l** as a white solid (608.7 mg, 61% yield, 2.5 mmol of (*E*)-*N*-(4-(benzyloxy)butylidene)-4-methylbenzenesulfonamide and 3.0 mmol of furan as the starting material were used). mp 65.0−66.5 °C. R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.3 Hz, 2H), 7.34 (dd, J = 6.3, 5.0 Hz, 1H), 7.32 (d, J = 3.9 Hz, 2H), 7.30−7.25 (m, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.12−7.11 (m, 1H), 6.09 (dd, J = 3.2, 1.9 Hz, 1H), 5.88 (d, J = 3.2 Hz, 1H), 5.25 (d, J = 8.5 Hz, 1H), 4.46 (s, 2H), 4.42 (dd, J = 15.6, 7.3 Hz, 1H), 3.41 (t, J = 6.1 Hz, 2H), 2.36 (s, 3H), 1.88 (q, J = 7.4 Hz, 1H), 1.66−1.57 (m, 1H), 1.55−1.48 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.9, 142.9, 141.7, 138.2, 137.6, 129.3, 128.3, 127.6, 127.5, 126.9, 109.9, 106.8, 72.8, 69.4, 51.5, 31.8, 25.7, 21.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{25}NO_4SNa$, 422.1397; found, 422.1382.

General Syntheses of 3c, 3m, 3n, and 3o. Lukewarm water (5.0 mL) was added to sodium azide (1.56 g, 24.0 mmol, 3.0 equiv), and the resultant suspension was stirred for 15 min. Benzene (15 mL) was added, and the biphasic suspension was cooled to 0 °C. Concentrated H_2SO_4 (0.8 mL) was added dropwise, and the mixture was allowed to stir at 0 °C for 20 min. The organic phase was then carefully syringed into a dry flask at 0 °C, and 1-(furan-2-yl)pentan-1-ol **1b** (1.23 g, 8.0 mmol, 1.0 equiv) was added followed by concentrated H_2SO_4 (0.1 mL). The resulting mixture was stirred for 5 min at 0 °C and was then quenched with ice-cold ammonium hydroxide solution (25 mL). The reaction mixture was extracted with EtOAc (3 × 25 mL). The combined organic phases were washed with saturated aqueous NH_4Cl (25 mL), dried over Na_2SO_4, and concentrated under a vacuum. The crude material was purified by silica gel column chromatography (petroleum ether/ethyl acetate) affording 2-(1-azidopentyl)furan.

A solution of 2-(1-azidopentyl)furan (895.5 mg, 5.0 mmol) in EtOAc (10 mL) was treated with 10% Pd/C (56.0 mg) and placed under a H_2 atmosphere. Hydrogen was bubbled through the solution for 5 at 10 min intervals for a total of 1 h. The reaction mixture was then filtered through Celite and concentrated under a vacuum affording 1-(furan-2-yl)pentan-1-amine, which was used without further purification.

A solution of 1-(furan-2-yl)pentan-1-amine (459.4 mg, 3.0 mmol, 1.0 equiv) in anhydrous dichloromethane (10 mL) was treated with triethylamine (333.9 mg, 3.3 mmol, 1.1 equiv) and cooled to 0 °C. The mixture was then treated with *p*-toluenesulfonyl chloride (629.1 mg, 3.3 mmol, 1.1 equiv), allowed to warm up to room temperature, and stirred overnight. The reaction was then diluted with dichloromethane (10 mL) and washed sequentially with sodium bicarbonate (20 mL) and brine (20 mL). The mixture was extracted with EtOAc (3 × 20 mL); the combined organic layers were dried over Na_2SO_4, and the solvent was removed in vacuo, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product **3c**.

1-(Furan-2-yl)pentan-1-amine (459.4 mg, 3.0 mmol, 1.0 equiv) and Boc_2O (785.7 mg, 3.6 mmol, 1.2 equiv) were added to THF (10 mL) and heated in an oil bath under nitrogen at 40 °C for 2 h at which point gas evolution ceased. The mixture was quenched with water and imidazole and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo to give *tert*-butyl (1-(furan-2-yl)pentyl)-carbamate quantitatively, **3m**.

A solution of 1-(furan-2-yl)pentan-1-amine (459.4 mg, 3.0 mmol, 1.0 equiv) and triethylamine (455.4 mg, 4.5 mmol, 1.5 equiv) in DCM (5 mL) was added dropwise to a solution of benzyl chloroformate (665.3 mg, 3.9 mmol, 1.3 equiv) in DCM (5 mL) at 0 °C. The solution was warmed to room temperature and stirred overnight. Then, the reaction was quenched by water (10 mL). The organic layer was separated and extracted with a saturated $NaHCO_3$ solution (3 × 15 mL) and then dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the corresponding product **3n**.

2-(1-Azidopentyl)furan.[18] Isolation by column chromatography over silica gel (eluent, 100:1 petroleum ether/ethyl acetate) afforded 2-(1-azidopentyl)furan as a colorless oil (1.15 g, 80% yield). R_f = 0.6 (50:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, J = 1.8, 0.6 Hz, 1H), 6.35 (dd, J = 3.2, 1.8 Hz, 1H), 6.29 (d, J = 3.2 Hz, 1H), 4.36 (t, J = 7.4 Hz, 1H), 1.95−1.81 (m, 2H), 1.46−1.25 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.5, 142.6, 110.1, 107.5, 58.8, 32.2, 28.2, 22.2, 13.9.

N-(1-(Furan-2-yl)pentyl)-4-methylbenzenesulfonamide (3c).[35b] Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **3c** as a yellow viscous oil (589.6 mg, 65% yield for two steps). R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.59 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.13 (s, 1H), 6.10 (dd, J = 3.1, 1.7 Hz, 1H), 5.88 (d, J = 3.2 Hz, 1H), 4.94 (s, 1H), 4.38 (q, J = 7.5 Hz, 1H), 2.38

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(s, 3H), 1.76 (q, J = 7.3 Hz, 2H), 1.28−1.20 (m, 3H), 1.18−1.09 (m, 1H), 0.82 (t, J = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.1, 142.9, 141.7, 137.7, 129.3, 126.9, 109.9, 106.7, 51.7, 34.7, 27.7, 22.1, 21.4, 13.8.

*tert-Butyl(1-(furan-2-yl)pentyl)carbamate (**3m**).* Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **3m** as a colorless oil (531.7 mg, 70% yield for two steps). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, J = 1.8, 0.8 Hz, 1H), 6.29 (dd, J = 3.2, 1.8 Hz, 1H), 6.14 (d, J = 3.0 Hz, 1H), 4.83−4.70 (m, 1H), 4.56 (s, 1H), 1.87−1.77 (m, 1H), 1.76−1.68 (m, 1H), 1.44 (s, 9H), 1.37−1.23 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.2, 141.5, 110.0, 105.6, 79.5, 48.7, 34.1, 28.4, 28.0, 22.3, 13.9. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{23}NO_3Na$, 276.1570; found, 276.1565.

*Benzyl(1-(furan-2-yl)pentyl)carbamate (**3n**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **3n** as a yellow solid (559.9 mg, 65% yield). mp 55.0−55.5 °C. R_f = 0.5 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.28 (m, 6H), 6.29 (dd, J = 3.2, 1.9 Hz, 1H), 6.17 (d, J = 2.9 Hz, 1H), 5.17−5.02 (m, 3H), 4.81 (dd, J = 16.0, 7.6 Hz, 1H), 1.89−1.72 (m, 2H), 1.38−1.22 (m, 4H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.6, 154.6, 141.7, 136.3, 128.4, 128.1, 110.0, 105.9, 66.7, 49.1, 33.8, 27.9, 22.3, 13.9. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{21}NO_3Na$, 310.1414; found, 310.1408.

Synthesis of 5a. 5-Methyl furfural (550.6 mg, 5.0 mmol, 1.0 equiv), tosylamide (1.71 g, 10.0 mmol, 2.0 equiv), and triethylamine (2.53 g, 25.0 mmol, 5.0 equiv) were dissolved in dichloromethane (30 mL) and cooled to 0 °C. $TiCl_4$ (2.5 mL, 2.5 mmol, 0.5 equiv, 1.0 M in CH_2Cl_2) in dichloromethane was added at that temperature; then, the ice-bath was removed, and stirring was continued for 30 min (monitoring by TLC). The mixture was hydrolyzed with saturated $NaHCO_3$ solution; the phases were separated, and the aqueous phase was extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with water (20 mL). After drying over Na_2SO_4 and filtration, the crude product (*Z*)-4-methyl-*N*-((5-methylfuran-2-yl)methylene)benzenesulfonamide can be used in the next step directly.

To the crude product (1.05 g, 4.0 mmol, 1.0 equiv) in MeOH (10 mL), $NaBH_4$ (151.3 mg, 4.0 mmol, 1.0 equiv) was added in small portions at room temperature; then, the solution was stirred overnight. The reaction was quenched by water. The resulting solution was extracted three times with ethyl acetate (25 mL). The organic layer was dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give **5a**.

*4-Methyl-N-((5-methylfuran-2-yl)methyl)benzenesulfonamide (**5a**).*[35e] Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **5a** as a white solid (526 mg, 50% yield for two steps). mp 82.1−83.0 °C. R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 5.95 (d, J = 2.9 Hz, 1H), 5.77 (d, J = 2.4 Hz, 1H), 4.84 (t, J = 5.6 Hz, 1H), 4.10 (d, J = 6.0 Hz, 2H), 2.41 (s, 3H), 2.12 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)δ 152.2, 147.6, 143.3, 137.0, 129.5, 127.1, 109.1, 106.1, 40.2, 21.4, 13.3.

General Syntheses of 5b−5i. Refer to the synthetic procedures of **3k** and **3m**.

A solution of BzCl (421.7 mg, 3.0 mmol, 1.0 equiv) in DCM (5 mL) was added dropwise to a solution of 1-(furan-2-yl)pentan-1-amine (551.2 mg, 3.6 mmol, 1.2 equiv) and Et_3N (394.6 mg, 3.9 mmol, 1.3 equiv) in DCM (5 mL) at 0 °C. The reaction mixture was stirred for 5 h at room temperature and then was diluted with dichloromethane (15 mL). The solution was transferred to a separation funnel and was washed with 1 M HCl (20 mL). The mixture was extracted with EtOAc (3 × 5 mL); the combined organic layers were dried over Na_2SO_4, and the solvent was removed in vacuo, which was purified by using flash column chromatography with petroleum ether/ethyl acetate as the eluent to afford the product **5i**.

1-(4,5-Dimethylfuran-2-yl)cyclobutan-1-ol. Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded 1-(4,5-dimethylfuran-2-yl)cyclobutan-1-ol as a colorless oil (1.36 g, 82% yield, 12 mmol of 2,3-dimethylfuran and 10 mmol of cyclobutanone as the starting material were used). R_f = 0.4 (15:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (s, 1H), 2.50−2.41 (m, 3H), 2.33−2.25 (m, 2H), 2.19 (s, 3H), 1.92 (s, 3H), 1.87−1.77 (m, 1H), 1.67−1.57 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.8, 147.0, 114.2, 108.2, 71.9, 35.5, 12.6, 11.3, 9.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{14}O_2Na$, 189.0886; found, 189.0884.

1-(5-Methylfuran-2-yl)cyclohexan-1-ol. Isolation by column chromatography over silica gel (eluent, 25:1 petroleum ether/ethyl acetate) afforded 1-(5-methylfuran-2-yl)cyclohexan-1-ol as a colorless oil (1.53 g, 85% yield, 12 mmol of 2-methylfuran and 10 mmol of cyclohexanone as the starting material were used). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (d, J = 2.6 Hz, 1H), 5.87 (s, 1H), 2.25 (s, 3H), 2.11 (s, 1H), 1.99−1.88 (m, 2H), 1.80 (d, J = 12.9 Hz, 2H), 1.74−1.65 (m, 2H), 1.48 (s, 3H), 1.41−1.28 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.1, 150.7, 105.7, 105.0, 69.8, 36.4, 25.4, 22.1, 13.3.

5-(1-Azidocyclobutyl)-2,3-dimethylfuran. Isolation by column chromatography over silica gel (eluent, 100:1 petroleum ether/ethyl acetate) afforded 5-(1-azidocyclobutyl)-2,3-dimethylfuran as a colorless oil (1.15 g, 75% yield, 8 mmol of 1-(4,5-dimethylfuran-2-yl)cyclobutan-1-ol as the starting material was used). R_f = 0.6 (50:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (s, 1H), 2.54−2.47 (m, 2H), 2.43−2.34 (m, 2H), 2.20 (s, 3H), 2.00−1.94 (m, 1H), 1.93 (s, 3H), 1.86−1.77 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.4, 147.8, 114.3, 109.9, 62.29, 32.7, 14.5, 11.4, 9.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{13}N_3ONa$, 214.0951; found, 214.0955.

2-(1-Azidocyclopentyl)-5-methylfuran. Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded 2-(1-azidocyclopentyl)-5-methylfuran as a colorless oil (1.17 g, 77% yield, 8 mmol of **1h** as the starting material was used). R_f = 0.4 (15:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (d, J = 3.1 Hz, 1H), 5.91 (d, J = 2.4 Hz, 1H), 2.29 (s, 3H), 2.08−2.03 (m, 4H), 1.89−1.82 (m, 2H), 1.81−1.73 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.4, 152.2, 107.0, 105.9, 70.7, 36.5, 23.3, 13.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{13}N_3ONa$, 214.0951; found, 214.0943.

2-(1-Azidocyclohexyl)-5-methylfuran. Isolation by column chromatography over silica gel (eluent, 100:1 petroleum ether/ethyl acetate) afforded 2-(1-azidocyclohexyl)-5-methylfuran as a colorless oil (1.11 g, 68% yield, 8 mmol of 2-methylfuran as the starting material was used). R_f = 0.6 (50:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (d, J = 3.1 Hz, 1H), 5.92 (dd, J = 2.0, 0.9 Hz, 1H), 2.28 (s, 3H), 2.00−1.91 (m, 4H), 1.71−1.61 (m, 2H), 1.58−1.46 (m, 3H), 1.42−1.32 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.8, 151.9, 107.0, 105.9, 62.8, 33.7, 25.2, 22.1, 13.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{11}H_{15}N_3ONa$, 228.1107; found, 228.1112.

*N-(1-(4,5-Dimethylfuran-2-yl)cyclobutyl)-4-methylbenzenesulfonamide (**5b**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **5b** as a white solid (1.10 g, 69% yield for two steps, 5 mmol of 5-(1-azidocyclobutyl)-2,3-dimethylfuran as the starting material was used). mp 114.1−116.0 °C. R_f = 0.4 (15:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.39 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.95 (s, 1H), 5.23 (s, 1H), 2.51 (ddd, J = 19.0, 9.4, 2.5 Hz, 2H), 2.41−2.37 (m, 2H), 2.36 (s, 3H), 1.96−1.87 (m, 1H), 1.84−1.80 (m, 1H), 1.79 (s, 3H), 1.76 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.8, 146.8, 142.2, 138.0, 128.5, 127.1, 113.7, 111.1, 56.0, 34.0, 21.3, 15.6, 10.8, 9.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{21}NO_3SNa$, 342.1134; found, 342.1140.

*tert-Butyl(1-(5-methylfuran-2-yl)cyclopentyl)carbamate (**5c**).* Isolation by column chromatography over silica gel (eluent, 15:1 petroleum ether/ethyl acetate) afforded **5c** as a colorless oil (861.8 mg, 65% yield for two steps, 5 mmol of 2-(1-azidocyclopentyl)-5-

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methylfuran as the starting material was used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.01 (d, J = 2.4 Hz, 1H), 5.85 (dd, J = 2.7, 0.7 Hz, 1H), 4.81 (s, 1H), 2.24 (s, 3H), 2.10 (d, J = 4.8 Hz, 4H), 1.83−1.75 (m, 2H), 1.74−1.67 (m, 2H), 1.39 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.0, 150.4, 105.9, 105.5, 62.2, 37.9, 28.3, 23.3, 13.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{23}NO_3Na$, 288.1570; found, 288.1576.

*4-Methyl-N-(1-(5-methylfuran-2-yl)cyclohexyl)-benzenesulfonamide (**5d**).* Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded **5d** as a yellow solid (812.9 mg, 61% yield for two steps, 4 mmol of 2-(1-azidocyclohexyl)-5-methylfuran as the starting material was used). mp 115.1−117.0 °C. R_f = 0.4 (15:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.41 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.94 (d, J = 3.1 Hz, 1H), 5.55 (dd, J = 3.1, 0.9 Hz, 1H), 5.05 (d, J = 15.1 Hz, 1H), 2.35 (s, 3H), 2.11−2.04 (m, 2H), 1.98 (dd, J = 11.1, 7.9 Hz, 2H), 1.83 (d, J = 0.7 Hz, 3H), 1.72−1.66 (m, 2H), 1.49−1.33 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.7, 150.7, 141.9, 138.4, 128.6, 126.9, 108.6, 105.3, 56.7, 35.7, 25.3, 21.7, 21.3, 12.9. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{18}H_{23}NO_3SNa$, 356.1291; found, 356.1299.

1-(5-Methylfuran-2-yl)propan-1-ol. Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded 1-(5-methylfuran-2-yl)propan-1-ol as a colorless oil (980 mg, 70% yield, 10 mmol of 5-methylfurfural and 15 mmol of ethylmagnesium chloride as the starting material were used). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (d, J = 3.1 Hz, 1H), 5.88 (d, J = 2.3 Hz, 1H), 4.48 (t, J = 6.8 Hz, 1H), 2.44 (s, 1H), 2.26 (s, 3H), 1.90−1.74 (m, 2H), 0.93 (t, J = 7.5 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.9, 151.3, 106.5, 105.8, 69.0, 28.4, 13.3, 9.9.

2-(1-Azidopropyl)-5-methylfuran. Isolation by column chromatography over silica gel (eluent, 100:1 petroleum ether/ethyl acetate) afforded 2-(1-azidopropyl)-5-methylfuran as a colorless oil (785 mg, 68% yield, 7 mmol of 2-methylfuran as the starting material was used). R_f = 0.6 (50:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17 (d, J = 3.1 Hz, 1H), 5.92 (dd, J = 3.0, 1.0 Hz, 1H), 4.23 (t, J = 7.3 Hz, 1H), 2.28 (d, J = 0.6 Hz, 3H), 1.94−1.81 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.4, 150.3, 108.5, 106.0, 60.6, 25.9, 13.5, 10.7. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_8H_{11}N_3ONa$, 188.0794; found, 188.0797.

*4-Methyl-N-(1-(5-methylfuran-2-yl)propyl)benzenesulfonamide (**5e**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **5e** as a white solid (1.13 g, 77% yield for two steps, 5 mmol of 2-(1-azidopropyl)-5-methylfuran as the starting material was used). mp 70.1−72.5 °C. R_f = 0.4 (15:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 5.8, 4.4 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 5.79 (d, J = 3.0 Hz, 1H), 5.67 (dd, J = 3.1, 0.9 Hz, 1H), 4.75 (d, J = 8.5 Hz, 1H), 4.24 (dd, J = 15.6, 7.4 Hz, 1H), 2.39 (s, 3H), 2.05 (s, 3H), 1.86−1.71 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.4, 150.8, 142.8, 137.8, 129.2, 127.0, 107.8, 105.7, 53.3, 28.1, 21.4, 13.2, 10.3. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{19}NO_3SNa$, 316.0978; found, 316.0981.

1-(5-Methylfuran-2-yl)-3-phenylpropan-1-ol. Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded 1-(5-methylfuran-2-yl)-3-phenylpropan-1-ol as a colorless oil (1.47 g, 68% yield, 12 mmol of 2-methylfuran and 10 mmol of phenylpropyl aldehyde as the starting material were used). R_f = 0.4 (15:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.25 (m, 2H), 7.22−7.15 (m, 3H), 6.10 (d, J = 3.1 Hz, 1H), 5.89 (dd, J = 3.1, 0.9 Hz, 1H), 4.59 (dd, J = 11.7, 6.7 Hz, 1H), 2.81−2.63 (m, 2H), 2.27 (d, J = 0.5 Hz, 3H), 2.18−2.10 (m, 2H), 2.00 (d, J = 4.9 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.6, 151.7, 141.6, 128.5, 128.3, 125.8, 106.8, 106.0, 66.9, 36.8, 31.8, 13.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{16}O_2Na$, 239.1043; found, 239.1035.

2-(1-Azido-3-phenylpropyl)-5-methylfuran. Isolation by column chromatography over silica gel (eluent, 100:1 petroleum ether/ethyl acetate) afforded 2-(1-azido-3-phenylpropyl)-5-methylfuran as a colorless oil (1.21 g, 72% yield, 7 mmol of 1-(5-methylfuran-2-yl)-3-phenylpropan-1-ol as the starting material was used). R_f = 0.6 (50:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.25 (m, 2H), 7.24−7.17 (m, 3H), 6.18 (d, J = 3.1 Hz, 1H), 5.93 (dd, J = 3.1, 0.8 Hz, 1H), 4.29 (t, J = 7.4 Hz, 1H), 2.79−2.63 (m, 2H), 2.28 (d, J = 0.6 Hz, 3H), 2.17 (q, J = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.7, 150.1, 140.7, 128.5, 126.1, 108.8, 106.1, 58.2, 34.1, 32.2, 13.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{15}N_3ONa$, 264.1107; found, 264.1111.

*4-Methyl-N-(1-(5-methylfuran-2-yl)-3-phenylpropyl)-benzenesulfonamide (**5f**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **5f** as a yellow solid (1.12 g, 65% yield for two steps, 5 mmol of 2-(1-azido-3-phenylpropyl)-5-methylfuran as the starting material was used). mp 89.1−89.8 °C. R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, J = 8.5, 1.8 Hz, 2H), 7.29−7.22 (m, 2H), 7.21−7.16 (m, 3H), 7.11 (d, J = 7.0 Hz, 2H), 5.79 (d, J = 3.0 Hz, 1H), 5.67 (dd, J = 2.9, 1.0 Hz, 1H), 4.87 (d, J = 8.6 Hz, 1H), 4.34 (dd, J = 15.8, 7.3 Hz, 1H), 2.68−2.52 (m, 2H), 2.38 (s, 3H), 2.11−2.05 (m, 2H), 2.05 (d, J = 0.8 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.5, 150.6, 142.9, 140.9, 137.6, 129.2, 128.4, 127.0, 126.0, 107.9, 105.8, 51.4, 36.4, 31.9, 21.4, 13.2. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{21}H_{23}NO_3SNa$, 392.1291; found, 392.1296.

2-(5-Ethylfuran-2-yl)propan-2-ol. Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded 2-(5-ethylfuran-2-yl)propan-2-ol as a colorless oil (1.26 g, 82% yield, 12 mmol of 5-*n*-pentyl furan and 10 mmol of acetone as the starting material were used). R_f = 0.4 (15:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (d, J = 3.1 Hz, 1H), 5.87 (dd, J = 3.2, 0.8 Hz, 1H), 2.59 (t, J = 7.8 Hz, 2H), 2.06 (s, 1H), 1.67−1.59 (m, 2H), 1.56 (s, 6H), 1.37−1.29 (m, 4H), 0.93−0.87 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.1, 155.7, 104.8, 104.0, 68.7, 31.4, 28.5, 28.0, 27.6, 22.4, 14.0. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{12}H_{20}O_2Na$, 219.1356; found, 219.1358.

2-(2-Azidopropan-2-yl)-5-ethylfuran. Isolation by column chromatography over silica gel (eluent, 100:1 petroleum ether/ethyl acetate) afforded 2-(2-azidopropan-2-yl)-5-ethylfuran as a colorless oil (984.5 g, 82% yield, 8 mmol of 2-(5-ethylfuran-2-yl)propan-2-ol as the starting material was used). R_f = 0.6 (50:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (d, J = 3.1 Hz, 1H), 5.92−5.88 (m, 1H), 2.60 (t, J = 7.6 Hz, 2H), 1.68−1.60 (m, 2H), 1.58 (s, 6H), 1.36−1.25 (m, 4H), 0.93−0.82 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.6, 154.3, 106.2, 105.0, 59.8, 31.3, 28.0, 27.4, 25.7, 22.4, 14.0. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{12}H_{19}N_3ONa$, 244.1420; found, 244.1430.

*N-(2-(5-Ethylfuran-2-yl)propan-2-yl)-4-methylbenzenesulfonamide (**5g**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **5g** as a yellow oil (792.5 mg, 57% yield for two steps, 5 mmol of 2-(2-azidopropan-2-yl)-5-ethylfuran as the starting material was used). R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.46 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 5.91 (d, J = 3.1 Hz, 1H), 5.64 (d, J = 3.1 Hz, 1H), 4.98 (s, 1H), 2.36 (s, 3H), 2.27−2.22 (m, 2H), 1.59 (s, 6H), 1.51−1.42 (m, 2H), 1.35−1.25 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.7, 154.0, 142.3, 138.6, 129.0, 127.0, 106.5, 104.4, 77.3, 77.0, 76.7, 54.4, 31.5, 27.8, 27.6, 27.2, 22.4, 21.4, 14.0. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{19}H_{27}NO_3SNa$, 372.1604; found, 372.1614.

1-(5-Methylfuran-2-yl)pentan-1-ol. Isolation by column chromatography over silica gel (eluent, 30:1 petroleum ether/ethyl acetate) afforded 1-(5-methylfuran-2-yl)pentan-1-ol as a colorless oil (1.29 g, 77% yield, 10 mmol of 5-methylfurfural and 8 mmol of *n*-BuLi as the starting material were used). R_f = 0.4 (15:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06 (d, J = 3.1 Hz, 1H), 5.87 (dd, J = 3.1, 0.9 Hz, 1H), 4.54 (dd, J = 11.3, 6.8 Hz, 1H), 2.62 (d, J = 4.5 Hz, 1H), 2.26 (s, 3H), 1.85−1.72 (m, 2H), 1.42−1.23 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.0, 151.2, 106.4, 105.7, 67.5, 34.9, 27.7, 22.3, 13.9, 13.4.

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2-(1-Azidopentyl)-5-methylfuran. Isolation by column chromatography over silica gel (eluent, 100:1 petroleum ether/ethyl acetate) afforded 2-(1-azidopentyl)-5-methylfuran as a colorless oil (905.1 mg, 67% yield, 7 mmol of 1-(5-methylfuran-2-yl)pentan-1-ol as the starting material was used). R_f = 0.6 (50:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.16 (d, J = 3.1 Hz, 1H), 5.92 (dd, J = 3.1, 0.9 Hz, 1H), 4.29 (t, J = 7.4 Hz, 1H), 2.28 (s, 3H), 1.89−1.79 (m, 2H), 1.43−1.27 (m, 3H), 0.91 (t, J = 7.0 Hz, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.4, 150.5, 108.4, 106.0, 59.1, 32.2, 28.3, 22.2, 13.9, 13.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{15}N_3ONa$, 216.1107; found, 216.1117.

*tert-Butyl(1-(5-methylfuran-2-yl)pentyl)carbamate (**5h**).* Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **5h** as a colorless oil (780.2 mg, 73% yield for two steps, 4 mmol of 2-(1-azidopentyl)-5-methylfuran as the starting material was used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00 (d, J = 2.7 Hz, 1H), 5.85 (dd, J = 2.8, 0.9 Hz, 1H), 4.81 (d, J = 6.9 Hz, 1H), 4.65 (d, J = 7.3 Hz, 1H), 2.25 (d, J = 0.6 Hz, 3H), 1.83−1.74 (m, 1H), 1.74−1.62 (m, 1H), 1.44 (s, 9H), 1.37−1.20 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 153.3, 151.1, 106.3, 105.8, 79.3, 48.7, 34.2, 28.3, 28.0, 22.3, 13.9, 13.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{25}NO_3Na$, 290.1727; found, 290.1735.

*N-(1-(Furan-2-yl)pentyl)benzamide (**5i**).*[35f] Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **5i** as a yellow oil (493.6 mg, 64% yield for two steps, 3 mmol of 2-(1-azidopentyl)furan as the starting material was used). R_f = 0.5 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79−7.75 (m, 2H), 7.50−7.45 (m, 1H), 7.39 (dd, J = 10.4, 4.6 Hz, 2H), 7.35−7.34 (m, 1H), 6.54 (d, J = 8.5 Hz, 1H), 6.30 (dd, J = 3.1, 1.9 Hz, 1H), 6.22 (d, J = 3.2 Hz, 1H), 5.30 (dd, J = 15.9, 7.5 Hz, 1H), 1.98−1.83 (m, 1H), 1.41−1.27 (m, 4H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.5, 154.4, 141.7, 134.3, 131.4, 128.4, 126.9, 110.1, 106.2, 47.6, 33.7, 28.0, 22.3, 13.9.

Typical Procedure for Mn-Catalyzed Achmatowicz Rearrangement. To a mixture of Mn cat-1 (0.01 mmol) and 1-(furan-2-yl)cyclohexan-1-ol **1a** (0.2 mmol) in acetone (1.0 mL) was added 30% H_2O_2 (0.5 mmol) in 0.5 mL acetone via a syringe pump within 1 h at rt, with further stirring for 1 h. After completion of the reaction, the resulting mixture was quenched with a saturated aqueous solution of Na_2SO_3, and the mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over Na_2SO_4, and the crude product was purified by silica column chromatography affording the product **2a**.

*2-Hydroxy-1-oxaspiro[5.5]undec-3-en-5-one (**2a**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2a** as a colorless oil (31 mg, 84% yield, 0.2 mmol of **1a** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, J = 10.3 Hz, 1H), 6.06 (d, J = 10.2 Hz, 1H), 5.71 (d, J = 5.6 Hz, 1H), 3.51 (d, J = 6.7 Hz, 1H), 1.92 (d, J = 12.0 Hz, 1H), 1.87−1.76 (m, 2H), 1.72−1.56 (m, 6H), 1.33−1.24 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.4, 145.6, 126.7, 87.5, 80.6, 33.4, 31.0, 25.1, 20.9, 20.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{14}O_3Na$, 205.0835; found, 205.0842.

Gram-Scale Reaction of 1a to Synthesize 2a. To a mixture of Mn cat-1 (0.36 mmol) and 1-(furan-2-yl)cyclohexan-1-ol **1a** (1.2 g, 7.2 mmol) in acetone (50.0 mL) was added 30% H_2O_2 (2.04 mL, 18.0 mmol) in 8.0 mL of acetone via a syringe pump within 2 h at rt, which was further stirred for 1 h. After completion of the reaction, the resulting mixture was quenched with a saturated aqueous solution of Na_2SO_3, and the mixture was extracted with ethyl acetate (3 × 50 mL). The organic layer was dried over Na_2SO_4, and the crude product was purified by silica column chromatography affording the product **2a** (0.98 g, 75% yield).

*2-Butyl-6-hydroxy-2H-pyran-3(6H)-one (**2b**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2b** as a colorless oil (21 mg, 59% yield, 0.2 mmol of **1b** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.90 (dd, J = 10.2, 3.4 Hz, 1H), 6.11 (d, J = 10.2 Hz, 1H), 5.65 (s, J = 3.1 Hz, 1H), 4.56 (dd, J = 8.0, 3.9 Hz, 1H), 3.70 (s, 1H), 1.98−1.88 (m, 1H), 1.81−1.65 (m, 1H), 1.47−1.29 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H). Minor isomer: δ 6.94 (dd, J = 10.3, 1.5 Hz, 1H), 6.15 (dd, J = 10.3, 1.5 Hz, 1H), 5.65 (s, 1H), 4.08 (dd, J = 7.8, 3.5 Hz, 1H), 3.98 (s, 1H), 1.98−1.88 (m, 1H), 1.81−1.65 (m, 1H), 1.47−1.29 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 196.9, 144.6, 127.5, 87.6, 74.2, 29.3, 27.1, 22.4, 13.9. Minor isomer: δ 196.5, 147.9, 128.7, 90.8, 78.9, 30.3, 27.2, 22.4, 13.9. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{14}O_3Na$, 193.0835; found, 193.0842.

*6-Hydroxy-6-methyl-2H-pyran-3(6H)-one (**2c**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2c** as a colorless oil (23 mg, 90% yield, 0.2 mmol of **1c** as the starting material was used). R_f = 0.2 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, J = 10.3 Hz, 1H), 6.06 (d, J = 10.3 Hz, 1H), 4.56 (d, J = 17.0 Hz, 1H), 4.12 (d, J = 17.0 Hz, 1H), 3.48 (s, 1H), 1.64 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 195.1, 149.1, 126.3, 92.8, 66.5, 27.7. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_6H_8O_3Na$, 151.0366; found, 151.0366.

*2,2-Dibutyl-6-hydroxy-2H-pyran-3(6H)-one (**2d**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2d** as a colorless oil (32 mg, 71% yield, 0.2 mmol of **1d** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (dd, J = 10.3, 2.1 Hz, 1H), 6.07 (dd, J = 10.3, 1.2 Hz, 1H), 5.77−5.71 (m, 1H), 3.70 (d, J = 6.9 Hz, 1H), 1.94−1.55 (m, 4H), 1.43−1.22 (m, 8H), 0.91−0.86 (m, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.3, 145.5, 127.2, 87.6, 84.6, 37.1, 35.1, 25.5, 25.3, 23.0, 13.9, 13.9. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for calcd. for $C_{13}H_{22}O_3Na$, 249.1461; found, 249.1457.

*2,2-Di-tert-butyl-6-hydroxy-2H-pyran-3(6H)-one (**2e**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2e** as a yellow solid (36 mg, 79% yield, 0.2 mmol of **1e** as the starting material was used). mp 89.1−92.0 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (dd, J = 10.4, 2.0 Hz, 1H), 6.09 (dd, J = 10.5, 1.3 Hz, 1H), 5.93−5.89 (m, 1H), 3.12 (d, J = 6.8 Hz, 1H), 1.14 (s, 9H), 1.10 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 198.1, 142.4, 130.5, 91.1, 88.6, 42.8, 42.0, 29.1, 29.1. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{13}H_{22}O_3Na$, 249.1461; found, 249.1467.

*6-Hydroxy-2,2-dimethyl-2H-pyran-3(6H)-one (**2f**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2f** as a colorless oil (24 mg, 82% yield, 0.2 mmol of **1f** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (dd, J = 10.3, 2.2 Hz, 1H), 6.09 (dd, J = 10.3, 1.1 Hz, 1H), 5.71 (d, J = 6.3 Hz, 1H), 3.89 (d, J = 6.7 Hz, 1H), 1.50 (s, 3H), 1.40 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.0, 145.9, 126.4, 87.8, 79.4, 26.5, 23.7. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_7H_{10}O_3Na$, 165.0522; found, 165.0529.

*2-Hydroxy-1,9-dioxaspiro[5.5]undec-3-en-5-one (**2g**).* Isolation by column chromatography over silica gel (eluent, 7:1 petroleum ether/ethyl acetate) afforded **2g** as a colorless oil (19 mg, 50% yield, 0.2 mmol of **1g** as the starting material was used). R_f = 0.3 (4:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (dd, J = 10.3, 2.4 Hz, 1H), 6.10 (dd, J = 10.2, 0.8 Hz, 1H), 5.74 (s, 1H), 3.89−3.80 (m, 5H), 2.09−1.94 (m, 3H), 1.70−1.64 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.5, 145.2, 126.3, 87.6, 77.5, 62.8, 62.8, 34.2, 31.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{12}O_4Na$, 207.0628; found, 207.0636.

*7-Hydroxy-7-methyl-6-oxaspiro[4.5]dec-8-en-10-one (**2h**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2h** as a yellow solid (30 mg, 82% yield, 0.2 mmol of **1h** as the starting material was used). mp 57.4−59.2 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (d, J = 10.2 Hz, 1H), 6.07 (d, J = 10.2 Hz, 1H), 2.79 (s, 1H), 2.37−2.21 (m, 2H), 1.92−1.67 (m, 6H), 1.60 (s,

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3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 199.3, 147.5, 125.6, 92.8, 88.7, 40.5, 37.8, 30.2, 25.1, 24.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_{14}O_3Na$, 205.0835; found, 205.0834.

*2-Hydroxy-1-oxaspiro[5.7]tridec-3-en-5-one (**2i**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2i** as a colorless oil (29 mg, 68% yield, 0.2 mmol of **1i** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ 6.84 (dd, J = 10.3, 2.0 Hz, 1H), 6.02 (dd, J = 10.2, 1.4 Hz, 1H), 5.70−5.67 (m, 1H), 3.60 (d, J = 7.1 Hz, 1H), 2.15−2.07 (m, 1H), 1.98−1.85 (m, 3H), 1.79−1.69 (m, 2H), 1.63−1.51 (m, 8H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 199.4, 145.3, 126.5, 87.6, 83.2, 33.0, 29.8, 28.0, 27.6, 24.3, 21.0, 20.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{18}O_3Na$, 233.1148; found, 233.1158.

*6-Hydroxy-2-methyl-2-phenyl-2H-pyran-3(6H)-one (**2j**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2j** as a colorless oil (27 mg, 67% yield, 0.2 mmol of **1j** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.39−7.29 (m, 5H), 6.80 (dd, J = 10.2, 1.3 Hz, 1H), 6.21 (dd, J = 10.2, 1.8 Hz, 1H), 5.43 (s, 1H), 3.86 (s, 1H), 1.66 (s, 3H). Minor isomer: δ 7.39−7.29 (m, 5H), 6.90 (dd, J = 10.3, 2.5 Hz, 1H), 6.21 (dd, J = 10.2, 1.8 Hz, 1H), 5.77 (s, 1H), 3.86 (s, 1H), 1.71 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 196.3, 147.6, 128.7, 128.3, 128.2, 125.3, 88.4, 83.4, 27.6, 26.0. Minor isomer: δ 196.3, 145.7, 138.2, 128.3, 128.0, 126.8, 125.7, 88.3, 81.8, 26.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{12}O_3Na$, 227.0679; found, 227.0687.

*6-Hydroxy-2,2-diphenyl-2H-pyran-3(6H)-one (**2k**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2k** as a colorless oil (30 mg, 56% yield, 0.2 mmol of **1k** as the starting material was used). R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ 7.39−7.26 (m, 10H), 6.89 (dd, J = 10.2, 1.4 Hz, 1H), 6.30 (dd, J = 10.3, 1.6 Hz, 1H), 5.49 (d, J = 4.3 Hz, 1H), 3.23 (d, J = 7.0 Hz, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 194.2, 147.3, 141.3, 137.4, 129.0, 128.6, 128.6, 127.9, 127.7, 127.6, 127.5, 88.9, 86.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{14}O_3Na$, 289.0835; found, 289.0842.

*Ethyl-2-(6-hydroxy-6-methyl-3-oxo-3,6-dihydro-2H-pyran-2-yl)-acetate (**2l**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2l** as a yellowish oil (35 mg, 82% yield, 0.2 mmol of **1l** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.84 (d, J = 10.2 Hz, 1H), 6.05 (d, J = 10.2 Hz, 1H), 4.97 (dd, J = 7.6, 4.0 Hz, 1H), 4.19−4.12 (m, 2H), 3.80 (s, 1H), 2.99 (dd, J = 16.8, 4.0 Hz, 1H), 2.70 (dd, J = 16.8, 7.6 Hz, 1H), 1.62 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). Minor isomer: δ 6.91 (d, J = 10.3 Hz, 1H), 6.09 (d, J = 10.3 Hz, 1H), 4.61 (dd, J = 6.5, 5.0 Hz, 1H), 4.19−4.12 (m, 2H), 4.04 (s, 1H), 2.92 (d, J = 0.9 Hz, 1H), 2.91 (d, J = 2.8 Hz, 1H), 1.62 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 195.2, 171.0, 148.3, 125.9, 93.0, 71.2, 60.9, 35.2, 28.5, 14.1. Minor isomer: δ195.2, 171.0, 150.9, 125.8, 94.5, 74.4, 61.1, 37.0, 24.4, 14.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_{14}O_5Na$, 237.0733; found, 237.0732.

*6-Hydroxy-6-methyl-2-(2-methylallyl)-2H-pyran-3(6H)-one (**2m**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2m** as a colorless oil (27 mg, 74% yield, 0.2 mmol of **1m** as the starting material was used). R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.82 (d, J = 10.1 Hz, 1H), 6.03 (d, J = 10.1 Hz, 1H), 4.82 (dd, J = 2.5, 1.0 Hz, 2H), 4.70 (dd, J = 9.2, 3.2 Hz, 1H), 3.18 (s, 1H), 2.78−2.72 (m, 1H), 2.35−2.27 (m, 1H), 1.77 (s, 3H), 1.63 (s, 3H). Minor isomer: δ 6.88 (d, J = 10.2 Hz, 1H), 6.06 (d, J = 10.2 Hz, 1H), 4.87 (s, 2H), 4.38 (dd, J = 9.9, 3.8 Hz, 1H), 3.25 (s, 1H), 2.64 (d, J = 3.7 Hz, 1H), 2.53 (dd, J = 15.1, 10.2 Hz, 1H), 1.78 (s, 3H), 1.61 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 196.4, 147.9, 141.7, 126.3, 112.4, 92.8, 73.0, 37.0, 28.8, 22.9. Minor isomer: δ 196.1, 150.1, 141.7, 125.9, 113.1, 94.1, 76.4, 39.6, 25.3, 22.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_{14}O_3Na$, 205.0835; found, 205.0833.

*2-Allyl-6-hydroxy-2H-pyran-3(6H)-one (**2n**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2n** as a white solid (26 mg, 70% yield, 0.2 mmol of **1n** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.91 (dd, J = 10.2, 3.5 Hz, 1H), 6.11 (d, J = 10.0 Hz, 1H), 5.86−5.75 (m, 1H), 5.65 (s, 1H), 5.02 (ddd, J = 17.1, 3.5, 1.7 Hz, 1H), 4.99−4.94 (m, 1H), 4.58 (dd, J = 8.0, 3.9 Hz, 1H), 3.51 (d, J = 4.5 Hz, 1H), 2.13−2.04 (m, 2H), 1.99−1.90 (m, 2H), 1.84−1.68 (m, 1H), 1.59−1.48 (m, 1H). Minor isomer: δ 6.94 (dd, J = 10.1, 1.4 Hz, 1H), 6.15 (dd, J = 10.2, 1.6 Hz, 1H), 5.86−5.75 (m, 1H), 5.65 (s, 1H), 5.02 (ddd, J = 17.1, 3.5, 1.7 Hz, 1H), 4.99−4.94 (m, 1H), 4.09 (ddd, J = 8.3, 3.9, 1.1 Hz, 1H), 3.79 (d, J = 7.2 Hz, 1H), 2.13−2.04 (m, 2H), 1.99−1.90 (m, 2H), 1.84−1.68 (m, 1H), 1.59−1.48 (m, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 196.7, 144.5, 138.3, 127.5, 114.8, 87.6, 74.0, 33.4, 29.0, 24.1. Minor isomer: δ 196.3, 147.9, 138.2, 128.7, 114.8, 90.8, 78.7, 33.4, 30.0, 24.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_{14}O_3Na$, 205.0835; found, 205.0837.

*6-Hydroxy-6-methyl-2-(prop-2-yn-1-yl)-2H-pyran-3(6H)-one (**2o**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2o** as a colorless oil (23 mg, 70% yield, 0.2 mmol of **1o** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.86 (d, J = 10.3 Hz, 1H), 6.06 (d, J = 10.2 Hz, 1H), 4.69 (dd, J = 7.5, 3.8 Hz, 1H), 3.19 (s, 1H), 2.86 (ddd, J = 17.3, 3.7, 2.8 Hz, 1H), 2.61 (ddd, J = 17.3, 7.6, 2.7 Hz, 1H), 2.01 (t, J = 2.6 Hz, 1H), 1.69 (s, 3H). Minor isomer: δ 6.92 (d, J = 10.4 Hz, 1H), 6.09 (d, J = 10.3 Hz, 1H), 4.38 (dd, J = 6.9, 4.7 Hz, 1H), 3.58 (s, 1H), 2.86 (ddd, J = 17.3, 3.7, 2.8 Hz, 1H), 2.83−2.79 (m, 1H), 2.11 (t, J = 2.7 Hz, 1H), 1.65 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 194.7, 148.4, 126.1, 93.2, 80.4, 72.8, 69.7, 28.8, 20.1. Minor isomer: δ 194.3, 150.5, 125.8, 94.0, 80.3, 76.1, 71.0, 25.6, 22.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_{10}O_3Na$, 189.0522; found, 189.0522.

*2-Cyclopropyl-6-hydroxy-6-methyl-2H-pyran-3(6H)-one (**2p**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2p** as a yellowish oil (25 mg, 74% yield, 0.2 mmol of **1p** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.82 (d, J = 10.1 Hz, 1H), 6.03 (d, J = 10.1 Hz, 1H), 3.98 (d, J = 7.6 Hz, 1H), 3.70 (s, 1H), 1.64 (s, 3H), 1.21−1.14 (m, 1H), 0.74−0.67 (m, 1H), 0.55−0.44 (m, 2H), 0.39−0.33 (m, 1H). Minor isomer: δ 6.89 (d, J = 10.4 Hz, 1H), 6.06 (d, J = 10.3 Hz, 1H), 3.70 (s, 1H), 3.51 (d, J = 8.4 Hz, 1H), 1.60 (s, 3H), 1.21−1.14 (m, 1H), 0.74−0.67 (m, 1H), 0.61−0.57 (m, 1H), 0.55−0.44 (m, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 196.7, 148.1, 126.2, 92.9, 77.2, 28.7, 10.9, 2.7, 1.1. Minor isomer: δ195.9, 149.9, 125.7, 93.8, 81.7, 28.6, 13.8, 3.5, 2.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_{12}O_3Na$, 191.0679; found, 191.0681.

*6-Hydroxy-5-oxaspiro[3.5]non-7-en-9-one (**2q**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **2q** as a yellowish oil (24 mg, 77% yield, 0.2 mmol of **1q** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ 6.89 (dd, J = 10.2, 2.4 Hz, 1H), 6.11 (dd, J = 10.2, 1.0 Hz, 1H), 5.66 (d, J = 3.8 Hz, 1H), 4.01 (d, J = 6.5 Hz, 1H), 2.60−2.52 (m, 1H), 2.48−2.40 (m, 1H), 2.40−2.22 (m, 2H), 1.95−1.86 (m, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 197.2, 145.6, 126.7, 88.1, 80.1, 34.1, 31.0, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_8H_{10}O_3Na$, 177.0522; found, 177.0526.

*(2s,4s)-6-Hydroxy-6-methyl-2-phenyl-5-oxaspiro[3.5]non-7-en-9-one (**2r**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2r** as a white solid (43 mg, 89% yield, 0.2 mmol of **1r** as the starting material was used). mp 98.1−98.9 °C. R_f = 0.3 (4:1 petroleum ether/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.32−7.17 (m, 5H), 6.84 (dd, J = 10.2, 2.9 Hz, 1H), 6.07 (dd, J = 10.2, 5.0 Hz, 1H), 3.51−3.39 (m, 1H), 3.19 (s, 1H), 3.06−2.97 (m, 1H), 2.93−2.83 (m, 1H), 2.62−2.53 (m, 1H), 2.34−2.26 (m, 1H), 1.61 (s, 3H).

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Minor isomer: δ 7.32−7.17 (m, 5H), 6.84 (dd, J = 10.2, 2.9 Hz, 1H), 6.07 (dd, J = 10.2, 5.0 Hz, 1H), 3.80 (p, J = 9.3 Hz, 1H), 3.19 (s, 1H), 3.06−2.97 (m, 1H), 2.93−2.83 (m, 1H), 2.62−2.53 (m, 1H), 2.34−2.26 (m, 1H), 1.68 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 198.0, 148.3, 144.5, 128.3, 126.5, 126.2, 125.1, 93.4, 75.6, 44.2, 40.3, 31.8, 28.9. Minor isomer: δ 196.8, 148.3, 144.3, 128.3, 126.7, 126.2, 125.2, 93.6, 79.0, 43.0, 38.2, 32.6, 29.6. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{16}O_3Na$, 267.0992; found, 267.0995.

*(2s,4s)-6-Hydroxy-6-methyl-2-(p-tolyl)-5-oxaspiro[3.5]non-7-en-9-one (**2s**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2s** as a white solid (39 mg, 75% yield, 0.2 mmol of **1s** as the starting material was used). mp 90.1−93.0 °C. R_f = 0.3 (4:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.21−7.08 (m, 4H), 6.84 (dd, J = 10.2, 2.8 Hz, 1H), 6.06 (dd, J = 10.2, 4.6 Hz, 1H), 3.46−3.35 (m, 1H), 3.19 (s, 1H), 3.04−2.95 (m, 1H), 2.89−2.82 (m, 1H), 2.54 (m, 1H), 2.31 (s, 3H), 2.30−2.24 (m, 1H), 1.61 (s, 3H). Minor isomer: δ 7.21−7.08 (m, 4H), 6.84 (dd, J = 10.2, 2.8 Hz, 1H), 6.06 (dd, J = 10.2, 4.6 Hz, 1H), 3.81−3.70 (m, 1H), 3.29 (s, 1H), 3.04−2.95 (m, 1H), 2.89−2.82 (m, 1H), 2.54 (m, 1H), 2.31 (s, 3H), 2.30−2.24 (m, 1H), 1.68 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 198.1, 148.3, 141.5, 135.7, 129.0, 126.4, 125.1, 93.4, 75.6, 44.3, 40.5, 31.5, 28.9, 20.9. Minor isomer: δ 196.8, 148.3, 141.3, 135.7, 129.5, 126.6, 125.2, 93.6, 79.1, 43.2, 38.3, 32.3, 29.6, 23.8. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{18}O_3Na$, 281.1148; found, 281.1152.

*(2s,4s)-2-(4-Chlorophenyl)-6-hydroxy-6-methyl-5-oxaspiro[3.5]non-7-en-9-one (**2t**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2t** as a white solid (41 mg, 74% yield, 0.2 mmol of **1t** as the starting material was used). mp 114.4−117.0 °C. R_f = 0.3 (4:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.28−7.24 (m, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.86 (dd, J = 10.2, 2.9 Hz, 1H), 6.07 (dd, J = 10.2, 5.1 Hz, 1H), 3.48−3.37 (m, 1H), 3.11 (s, 1H), 3.04−2.98 (m, 1H), 2.91−2.84 (m, 1H), 2.52 (dd, J = 15.1, 6.7 Hz, 1H), 2.23 (dd, J = 14.8, 6.4 Hz, 1H), 1.62 (s, 3H). Minor isomer: δ 7.28−7.24 (m, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.86 (dd, J = 10.2, 2.9 Hz, 1H), 6.07 (dd, J = 10.2, 5.1 Hz, 1H), 3.81−3.70 (m, 1H), 3.11 (s, 1H), 3.04−2.98 (m, 1H), 2.91−2.84 (m, 1H), 2.52 (dd, J = 15.1, 6.7 Hz, 1H), 2.23 (dd, J = 14.8, 6.4 Hz, 1H), 1.69 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 197.8, 148.33, 143.0, 131.8, 128.4, 127.9, 125.1, 93.4, 75.4, 44.3, 40.3, 31.3, 28.9. Minor isomer: δ 196.7, 150.8, 142.6, 131.8, 128.4, 128.1, 125.2, 93.6, 78.8, 43.0, 38.2, 32.0, 29.6. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$, $[M + 2 + Na]^+$ calcd for $C_{15}H_{15}O_3ClNa$, 301.0602, 303.0572; found, 301.0607, 303.0579.

*(2s,4s)-2-(4-Bromophenyl)-6-hydroxy-6-methyl-5-oxaspiro[3.5]non-7-en-9-one (**2u**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2u** as a yellow solid (51 mg, 79% yield, 0.2 mmol of **1u** as the starting material was used). mp 99.4−102.2 °C. R_f = 0.3 (4:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.45−7.41 (m, 2H), 7.15−7.11 (m, 2H), 6.86 (dd, J = 10.2, 2.7 Hz, 1H), 6.09 (d, J = 10.1 Hz, 1H), 3.48−3.35 (m, 1H), 3.08−2.98 (m, 1H), 2.93−2.84 (m, 1H), 2.59 (s, 1H), 2.55−2.48 (m, 1H), 2.28−2.20 (m, 1H), 1.63 (s, 3H). Minor isomer: δ 7.45−7.41 (m, 2H), 7.15−7.11 (m, 2H), 6.86 (dd, J = 10.2, 2.7 Hz, 1H), 6.09 (d, J = 10.1 Hz, 1H), 3.75 (t, J = 9.1 Hz, 1H), 3.08−2.98 (m, 1H), 2.93−2.84 (m, 1H), 2.67 (s, 1H), 2.55−2.48 (m, 1H), 2.28−2.20 (m, 1H), 1.70 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 197.9, 148.4, 143.5, 131.3, 128.3, 125.1, 119.9, 93.4, 75.4, 44.2, 40.2, 31.4, 28.9. Minor isomer: δ 196.7, 148.4, 143.4, 131.3, 128.5, 125.2, 119.9, 93.6, 78.8, 42.9, 38.2, 32.0, 29.6. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$, $[M + 2 + Na]^+$ calcd for $C_{15}H_{15}O_3BrNa$, 345.0098, 347.0058; found, 345.0100, 347.0070.

*(2s,4s)-2-(4-Fluorophenyl)-6-hydroxy-6-methyl-5-oxaspiro[3.5]non-7-en-9-one (**2v**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2v** as a yellow solid (40 mg, 77% yield, 0.2 mmol of **1v** as the starting material was used). mp 97.1−98.1 °C. R_f = 0.3 (4:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.46−7.41 (m, 2H), 7.15−7.11 (m, 2H), 6.86 (d, J = 10.1 Hz, 1H), 6.09 (d, J = 10.1 Hz, 1H), 3.47−3.37 (m, 1H), 3.08−2.97 (m, 1H), 2.93−2.84 (m, 1H), 2.59 (s, 1H), 2.55−2.48 (m, 1H), 2.29−2.20 (m, 1H), 1.63 (s, 3H). Minor isomer: δ 7.46−7.41 (m, 2H), 7.20−7.17 (m, 2H), 6.86 (d, J = 10.1 Hz, 1H), 6.09 (d, J = 10.1 Hz, 1H), 3.82−3.69 (m, 1H), 3.08−2.97 (m, 1H), 2.93−2.84 (m, 1H), 2.67 (s, 1H), 2.55−2.48 (m, 1H), 2.29−2.20 (m, 1H), 1.70 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) Major isomer: δ 198.0, 161.3 (d, J = 244.1 Hz), 148.4, 140.2 (d, J = 2.9 Hz), 128.0 (d, J = 8.0 Hz), 125.1, 115.0 (d, J = 21.2 Hz), 93.4, 75.4, 44.5, 40.5, 31.2, 28.9. Minor isomer: δ 196.8, 161.3 (d, J = 244.1 Hz), 148.4, 140.2 (d, J = 2.9 Hz), 128.2 (d, J = 7.8 Hz), 125.2, 115.0 (d, J = 21.2 Hz), 93.6, 78.8, 43.2, 38.5, 31.9, 29.6. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{15}O_3FNa$, 285.0897; found, 285.0903.

*6-((Allyloxy)methyl)-6-hydroxy-2H-pyran-3(6H)-one (**2w**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2w** as a colorless oil (25 mg, 67% yield, 0.2 mmol of **1w** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, J = 10.3 Hz, 1H), 6.17 (d, J = 10.3 Hz, 1H), 5.99−5.86 (m, 1H), 5.32 (dd, J = 17.3, 1.4 Hz, 1H), 5.28−5.24 (m, 1H), 4.62 (d, J = 17.0 Hz, 1H), 4.22−4.10 (m, 3H), 3.78 (s, 1H), 3.65 (d, J = 10.0 Hz, 1H), 3.57 (d, J = 10.0 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.8, 145.5, 133.6, 128.4, 118.3, 92.5, 73.8, 73.0, 66.5. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_9H_{12}O_4Na$, 207.0628; found, 207.0633.

*6-Hydroxy-6-((prop-2-yn-1-yloxy)methyl)-2H-pyran-3(6H)-one (**2x**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2x** as a colorless oil (22 mg, 60% yield, 0.2 mmol of **1x** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (d, J = 10.3 Hz, 1H), 6.17 (d, J = 10.4 Hz, 1H), 4.61 (d, J = 17.0 Hz, 1H), 4.32 (dd, J = 4.6, 2.4 Hz, 2H), 4.18 (d, J = 17.0 Hz, 1H), 3.94 (s, 1H), 3.76 (d, J = 10.0 Hz, 1H), 3.69 (d, J = 10.0 Hz, 1H), 2.54 (t, J = 2.4 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.77, 145.57, 128.20, 92.46, 78.53, 75.67, 73.32, 66.39, 58.99. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_9H_{10}O_4Na$, 205.0471; found, 205.0473.

*7-(3-((tert-Butyldimethylsilyl)oxy)propyl)-7-hydroxy-6-oxaspiro[4.5]dec-8-en-10-one (**2y**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2y** as a colorless oil (55 mg, 81% yield, 0.2 mmol of **1y** as the starting material was used). R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, J = 10.2 Hz, 1H), 6.05 (d, J = 10.2 Hz, 1H), 5.25 (s, 1H), 3.83−3.75 (m, 1H), 3.67−3.59 (m, 1H), 2.53−2.40 (m, 1H), 2.31−2.17 (m, 1H), 2.08−1.93 (m, 2H), 1.85−1.75 (m, 4H), 1.73−1.58 (m, 4H), 0.92 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 200.1, 148.7, 125.6, 92.5, 88.6, 63.7, 40.5, 40.4, 37.9, 25.8, 25.7, 25.1, 24.4, 18.3, −5.5, −5.5. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{32}O_4SiNa$, 363.1962; found, 363.1962.

*6-Hydroxy-6-((methoxymethoxy)methyl)-2H-pyran-3(6H)-one (**2z**).* Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **2z** as a colorless oil (27 mg, 71% yield, 0.2 mmol of **1z** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, J = 10.4 Hz, 1H), 6.17 (d, J = 10.4 Hz, 1H), 4.75 (s, 2H), 4.62 (d, J = 17.0 Hz, 1H), 4.35 (s, 1H), 4.18 (d, J = 17.0 Hz, 1H), 3.80 (d, J = 10.8 Hz, 1H), 3.67 (d, J = 10.8 Hz, 1H), 3.43 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.9, 145.7, 128.1, 97.2, 92.2, 72.6, 66.4, 55.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_8H_{12}O_5Na$, 211.0577; found, 211.0581.

Typical Procedure for Mn-Catalyzed Aza-Achmatowicz Rearrangement. To a mixture of Mn cat-1 (0.01 mol) and furfuramine **3a** (0.2 mmol) in HFIP (1.0 mL) was added 30% H_2O_2 (0.5 mmol dissolved in 0.5 mL of HFIP) via a syringe pump within 1 h at rt, which then further reacted for 1 h. After completion of the reaction, the resulting mixture was quenched with a saturated aqueous solution of Na_2SO_3, and the mixture was extracted with ethyl acetate

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(3 × 10 mL). The organic layer was dried over Na_2SO_4, and the crude product was purified by silica column chromatography affording the product **4a**.

*6-Hydroxy-2-methyl-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4a**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4a** as a white solid (48 mg, 85% yield, 0.2 mmol of **3a** as the starting material was used). mp 85.1−88.0 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.55 (m, 2H), 7.28 (d, J = 8.3 Hz, 2H), 6.88 (dd, J = 10.4, 4.6 Hz, 1H), 5.99 (dd, J = 10.3, 1.1 Hz, 1H), 5.91 (t, J = 3.3 Hz, 1H), 4.38 (q, J = 7.2 Hz, 1H), 3.74 (d, J = 4.1 Hz, 1H), 2.41 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 195.2, 144.3, 143.4, 136.5, 130.0, 126.6, 126.3, 73.4, 57.0, 22.2, 21.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{13}H_{15}NO_4SNa$, 304.0614; found, 304.0621.

*6-Hydroxy-2-isopropyl-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4b**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4b** as a white solid (49 mg, 80% yield, 0.2 mmol of **3b** as the starting material was used). mp 128.2−130.2 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.55 (m, 2H), 7.25 (d, J = 8.1 Hz, 2H), 6.69 (dd, J = 10.3, 4.0 Hz, 1H), 5.88 (dd, J = 10.3, 1.3 Hz, 1H), 5.76 (td, J = 4.2, 1.6 Hz, 1H), 3.96 (d, J = 9.8 Hz, 1H), 3.69 (d, J = 4.4 Hz, 1H), 2.39 (s, 3H), 2.28−2.11 (m, 1H), 1.22 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.3, 144.1, 142.2, 136.4, 130.0, 127.0, 126.4, 73.8, 67.0, 32.5, 21.5, 20.0, 19.0. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{19}NO_4SNa$, 332.0927; found, 332.0937.

*2-Butyl-6-hydrocy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4c**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4c** as a colorless oil (54 mg, 83% yield, 0.2 mmol of **3c** as the starting material was used). mp 91.2−93.1 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 6.78 (dd, J = 10.3, 4.4 Hz, 1H), 5.90 (d, J = 10.3 Hz, 1H), 5.87 (d, J = 4.3 Hz, 1H), 4.29 (dd, J = 8.3, 7.0 Hz, 1H), 3.89 (d, J = 4.1 Hz, 1H), 2.39 (s, 3H), 2.05−1.94 (m, 1H), 1.87−1.77 (m, 1H), 1.58−1.48 (m, 1H), 1.46−1.40 (m, 1H), 1.38−1.31 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.8, 144.1, 142.8, 136.5, 130.0, 126.5, 126.4, 73.6, 61.3, 35.2, 27.8, 22.1, 21.4, 13.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{21}NO_4SNa$, 346.1083; found, 346.1087.

*2-Ethyl-6-hydroxy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4d**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4d** as a white solid (51 mg, 87% yield, 0.2 mmol of **3d** as the starting material was used). mp 65.7−67.2 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.56 (m, 2H), 7.26 (d, J = 8.7 Hz, 2H), 6.78 (dd, J = 10.3, 4.4 Hz, 1H), 5.91 (dd, J = 10.3, 1.2 Hz, 1H), 5.86 (d, J = 3.8 Hz, 1H), 4.22 (dd, J = 8.5, 6.9 Hz, 1H), 3.88 (s, 1H), 2.39 (s, 3H), 2.06−1.98 (m, 1H), 1.96−1.84 (m, 1H), 1.08 (t, J = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.7, 144.1, 142.9, 136.4, 130.0, 126.5, 73.5, 62.7, 28.8, 21.5, 10.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{17}NO_4SNa$, 318.0770; found, 318.0781.

*6-Hydroxy-2-(2-methylallyl)-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4e**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4e** as a colorless oil (41 mg, 64% yield, 0.2 mmol of **3e** as the starting material was used). R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 6.9 Hz, 2H), 6.77 (dd, J = 10.3, 4.2 Hz, 1H), 5.92 (d, J = 10.3 Hz, 1H), 5.80 (s, 1H), 4.90 (s, 1H), 4.78 (s, 1H), 4.52 (t, J = 7.7 Hz, 1H), 3.33 (d, J = 3.9 Hz, 1H), 2.77 (dd, J = 13.5, 8.1 Hz, 1H), 2.57 (dd, J = 13.5, 7.3 Hz, 1H), 2.40 (s, 3H), 1.85 (s, 3H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.7, 144.3, 142.5, 140.4, 136.5, 130.1, 126.6, 126.6, 115.4, 73.7, 59.7, 44.4, 21.5, 21.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{19}NO_4SNa$, 344.0927; found, 344.0935.

*2-Cyclopentyl-6-hydroxy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4f**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4f** as a yellow solid (48 mg, 71% yield, 0.2 mmol of **3f** as the starting material was used). mp 132.4−135.3 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.70 (dd, J = 10.3, 4.1 Hz, 1H), 5.86 (d, J = 10.3 Hz, 1H), 5.79−5.75 (m, 1H), 4.08 (d, J = 10.6 Hz, 1H), 3.65 (s, 1H), 2.47−2.40 (m, 1H), 2.38 (s, 3H), 2.03−1.96 (m, 1H), 1.78−1.67 (m, 3H), 1.60−1.49 (m, 3H), 1.36−1.29 (m, 1H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 194.4, 144.1, 142.2, 136.5, 130.0, 126.8, 126.4, 73.8, 65.1, 44.2, 30.4, 29.3, 25.4, 24.5, 21.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{21}NO_4SNa$, 358.1083; found, 358.1088.

*2-Cyclohexyl-6-hydroxy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4g**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4g** as a white solid (46 mg, 68% yield, 0.2 mmol of **3g** as the starting material was used). mp 143.6−145.1 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.50 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.65 (dd, J = 10.4, 4.0 Hz, 1H), 5.83 (dd, J = 10.3, 1.3 Hz, 1H), 5.73 (d, J = 2.7 Hz, 1H), 3.99 (d, J = 9.9 Hz, 1H), 3.95 (s, 1H), 2.34 (s, 3H), 2.21 (dd, J = 14.8, 4.3 Hz, 1H), 1.90−1.76 (m, 2H), 1.72−1.65 (m, 1H), 1.61 (s, 1H), 1.54−1.47 (m, 1H), 1.19−1.08 (m, 4H), 1.01−0.91 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.1, 144.0, 142.3, 136.4, 130.0, 126.9, 126.4, 73.7, 66.1, 41.0, 29.9, 29.4, 26.0, 25.8, 25.6, 21.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{18}H_{23}NO_4SNa$, 372.1240; found, 372.1245.

*2-Cyclopropyl-6-hydroxy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4h**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4h** as a white solid (42 mg, 69% yield, 0.2 mmol of **3h** as the starting material was used). mp 97.7−101.1 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62−7.57 (m, 2H), 7.26 (d, J = 7.3 Hz, 2H), 6.81 (dd, J = 10.4, 4.3 Hz, 1H), 6.00 (dd, J = 10.3, 0.9 Hz, 1H), 5.79 (d, J = 3.6 Hz, 1H), 3.63 (d, J = 9.3 Hz, 1H), 3.57 (s, 1H), 2.39 (s, 3H), 1.51−1.40 (m, 1H), 0.79−0.71 (m, 1H), 0.69−0.53 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.1, 144.2, 142.7, 136.6, 130.0, 127.1, 126.6, 73.6, 65.2, 21.5, 17.0, 5.1, 4.9. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{17}NO_4SNa$, 330.0770; found, 330.0776.

*2-(Chloromethyl)-6-hydroxy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4i**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4i** as a white solid (47 mg, 74% yield, 0.2 mmol of **3i** as the starting material was used). mp 73.2.1−76.0 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69−7.54 (m, 2H), 7.33−7.23 (m, 2H), 6.78 (dd, J = 10.3, 4.3 Hz, 1H), 5.91 (d, J = 10.3 Hz, 1H), 5.86 (s, 1H), 4.29 (t, J = 7.6 Hz, 1H), 3.80 (s, 1H), 3.53 (t, J = 6.7 Hz, 2H), 2.40 (s, 3H), 2.08−1.95 (m, 1H), 1.87−1.82 (m, 1H), 1.80−1.76 (m, 2H), 1.62−1.56 (m, 1H), 1.51−1.44 (m, 3H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 194.6, 144.2, 142.9, 136.4, 130.1, 126.5, 126.5, 73.6, 61.1, 44.9, 35.2, 32.2, 26.2, 25.0, 21.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$, [M + 2 + Na]$^+$ calcd for $C_{17}H_{22}ClNO_4SNa$, 394.0850, 396.0822; found, 394.0859, 396.0833.

*2-(Azidomethyl)-6-hydroxy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4j**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4j** as a colorless viscous oil (46 mg, 71% yield, 0.2 mmol of **3j** as the starting material was used). mp 71.0−75.4 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61−7.55 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.78 (dd, J = 10.3, 4.3 Hz, 1H), 5.92 (dd, J = 10.4, 1.2 Hz, 1H), 5.86−5.79 (m, 1H), 4.30 (dd, J = 8.6, 6.6 Hz, 1H), 3.58 (d, J = 4.4 Hz, 1H), 3.27 (t, J = 6.9 Hz, 2H), 2.40 (s, 3H), 2.07−1.97 (m, 1H), 1.88−1.78 (m, 1H), 1.66−1.57 (m, 2H), 1.57−1.47 (m, 2H), 1.47−1.38 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.6, 144.3, 142.7, 136.4, 130.1, 126.6, 126.5, 73.6, 61.1, 51.3, 35.3, 28.5, 26.1, 25.2, 21.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{22}N_4O_4SNa$, 401.1254; found, 401.1248.

*2-Benzyl-6-hydroxy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4k**).* Isolation by column chromatography over silica gel (eluent, 4:1 petroleum ether/ethyl acetate) afforded **4k** as a white solid (58 mg, 77% yield, 0.2 mmol of **3k** as the starting material was used). mp

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138.9−142.5 °C. R_f = 0.4 (2:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59−7.55 (m, 2H), 7.29−7.26 (m, 1H), 7.26−7.25 (m, 2H), 7.24−7.16 (m, 4H), 6.78 (dd, *J* = 10.2, 4.5 Hz, 1H), 5.94−5.87 (m, 2H), 4.37 (dd, *J* = 8.5, 6.7 Hz, 1H), 3.82 (d, *J* = 4.5 Hz, 1H), 2.91 (ddd, *J* = 13.9, 11.0, 5.7 Hz, 1H), 2.75 (ddd, *J* = 13.9, 11.0, 5.3 Hz, 1H), 2.39 (s, 3H), 2.35−2.25 (m, 1H), 2.17−2.07 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.4, 144.2, 142.9, 140.8, 136.3, 130.1, 128.5, 128.4, 126.6, 126.5, 126.0, 73.6, 60.9, 37.1, 32.1, 21.5. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{20}H_{21}NO_4SNa$, 394.1083; found, 394.1088.

2-((Benzyloxy)methyl)-6-hydroxy-1-tosyl-1,6-dihydropyridin-3(2H)-one (**4l**). Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **4l** as a white solid (45 mg, 53% yield, 0.2 mmol of **3l** as the starting material was used). mp 80.8−84.2 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 5.9, 4.2 Hz, 2H), 7.35−7.32 (m, 4H), 7.30−7.27 (m, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.75 (dd, *J* = 10.3, 4.4 Hz, 1H), 5.88 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.84−5.80 (m, 1H), 4.50 (d, *J* = 1.8 Hz, 2H), 4.36−4.30 (m, 1H), 3.83 (s, 1H), 3.56−3.49 (m, 2H), 2.38 (s, 3H), 2.15−2.04 (m, 1H), 2.01−1.87 (m, 2H), 1.84−1.74 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.5, 144.2, 142.9, 138.2, 136.4, 130.0, 128.3, 127.7, 127.5, 126.5, 126.5, 73.6, 72.8, 69.3, 61.1, 31.9, 25.8, 21.5. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{22}H_{25}NO_5SNa$, 438.1346; found, 438.1344.

tert-Butyl-2-butyl-6-hydroxy-3-oxo-3,6-dihydropyridine-1(2H)-carboxylate (**4m**). Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **4m** as a yellow solid (37 mg, 63% yield, 0.2 mmol of **3m** as the starting material was used). mp 87.1−90.0 °C. R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.90 (dd, *J* = 10.2, 4.0 Hz, 1H), 6.11 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.03 (s, 1H), 4.47−4.43 (m, 1H), 3.81 (d, *J* = 4.3 Hz, 1H), 1.86−1.78 (m, 1H), 1.77−1.69 (m, 1H), 1.51 (s, 9H), 1.41−1.29 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 196.2, 155.1, 144.2, 126.8, 81.9, 71.7, 60.3, 35.5, 28.2, 28.1, 22.3, 13.9. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{14}H_{23}NO_4Na$, 292.1519; found, 292.1517.

Benzyl-2-butyl-6-hydroxy-3-oxo-3,6-dihydropyridine-1(2H)-carboxylate (**4n**). Isolation by column chromatography over silica gel (eluent, 8:1 petroleum ether/ethyl acetate) afforded **4n** as a colorless oil (44 mg, 72% yield, 0.2 mmol of **3n** as the starting material was used). R_f = 0.3 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.32 (m, 5H), 6.80 (dd, *J* = 10.5, 3.0 Hz, 1H), 6.21 (dd, *J* = 10.5, 1.3 Hz, 1H), 5.91 (ddd, *J* = 4.7, 3.0, 1.3 Hz, 1H), 5.43 (s, 1H), 5.22 (dd, *J* = 28.6, 12.1 Hz, 2H), 4.53−4.46 (m, 1H), 1.78−1.66 (m, 2H), 1.26−1.10 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 195.4, 155.9, 143.8, 135.4, 128.6, 128.3, 126.9, 72.1, 68.0, 60.2, 35.4, 27.8, 22.3, 13.8. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{17}H_{21}NO_4Na$, 326.1363; found, 326.1359.

Typical Procedure for the Synthesis of 1,4-Diketoalkene. To a mixture of Mn cat-1 (0.01 mol) and furfuramine **5a** (0.2 mmol) in HFIP (1.0 mL) was added 30% H_2O_2 (0.5 mmol dissolved in 0.5 mL of HFIP) via a syringe pump within 1 h at rt, which then further reacted for 1 h. After completion of the reaction, the resulting mixture was quenched with a saturated aqueous solution of Na_2SO_3, and the mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over Na_2SO_4, and the crude product was purified by silica column chromatography affording the product **6a**.

(Z)-N-(2,5-Dioxohex-3-en-1-yl)-4-methylbenzenesulfonamide (**6a**). Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **6a** as a yellow oil (39 mg, 70% yield, 0.2 mmol of **5a** as the starting material was used). R_f = 0.4 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.76−7.72 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 11.9 Hz, 1H), 6.23 (d, *J* = 11.9 Hz, 1H), 5.31 (t, *J* = 5.0 Hz, 1H), 3.97 (d, *J* = 5.3 Hz, 2H), 2.42 (s, 3H), 2.26 (s, 3H). Minor isomer: δ 7.76−7.72 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 16.3 Hz, 1H), 6.79 (d, *J* = 16.3 Hz, 1H), 5.40 (t, *J* = 4.5 Hz, 1H), 4.10 (d, *J* = 4.9 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.7, 196.9, 143.8, 137.2, 136.3, 133.2, 129.8, 127.1, 51.5, 29.7, 21.5. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{13}H_{15}NO_4SNa$, 304.0614; found, 304.0617.

(Z)-4-Methyl-N-(1-(3-methyl-4-oxopent-2-enoyl)cyclobutyl)-benzenesulfonamide (**6b**). Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **6b** as a colorless viscous oil (54 mg, 81% yield, 0.2 mmol of **5b** as the starting material was used). R_f = 0.4 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76−7.67 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.42 (d, *J* = 1.5 Hz, 1H), 5.56 (s, 1H), 2.43 (s, 3H), 2.42−2.36 (m, 2H), 2.35 (s, 3H), 2.00 (d, *J* = 1.6 Hz, 3H), 1.97−1.87 (m, 2H), 1.74−1.62 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 207.9, 195.4, 157.3, 143.9, 138.2, 129.7, 127.2, 112.0, 63.8, 30.6, 27.9, 21.6, 20.6, 14.1. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{17}H_{21}NO_4SNa$, 358.1083; found, 358.1086.

tert-Butyl(Z)-(1-(4-oxopent-2-enoyl)cyclopentyl)carbamate (**6c**). Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **6c** as a yellow solid (41 mg, 73% yield, 0.2 mmol of **5c** as the starting material was used). mp 63.6−65.3 °C. R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.63 (d, *J* = 12.1 Hz, 1H), 6.27 (d, *J* = 12.1 Hz, 1H), 5.02 (s, 1H), 2.31 (s, 3H), 2.28−2.13 (m, 2H), 1.72 (s, 6H), 1.39 (s, 9H). Minor isomer: δ 7.31 (d, *J* = 15.9 Hz, 1H), 7.00 (d, *J* = 16.3 Hz, 1H), 5.12 (s, 1H), 2.31 (s, 3H), 2.28−2.13 (m, 2H), 1.72 (s, 6H), 1.39 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.2, 197.7, 155.0, 139.1, 133.2, 80.1, 70.7, 36.6, 29.6, 28.3, 24.6. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{15}H_{23}NO_4Na$, 304.1519; found, 304.1523.

(Z)-4-Methyl-N-(1-(4-oxopent-2-enoyl)cyclohexyl)-benzenesulfonamide (**6d**). Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **6d** as a white solid (62 mg, 90% yield, 0.2 mmol of **5d** as the starting material was used). mp 129.6−133.1 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 12.1 Hz, 1H), 6.41 (d, *J* = 12.1 Hz, 1H), 5.60 (s, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 1.82−1.69 (m, 4H), 1.47−1.34 (m, 3H), 1.20−1.04 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 203.9, 200.3, 143.5, 141.7, 139.1, 129.6, 127.7, 126.8, 65.3, 31.4, 29.3, 24.6, 21.5, 20.7. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{18}H_{23}NO_4SNa$, 372.1240; found, 372.1240.

(Z)-N-(4,7-Dioxooct-5-en-3-yl)-4-methylbenzenesulfonamide (**6e**). Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **6e** as a yellow solid (41 mg, 67% yield, 0.2 mmol of **5e** as the starting material was used). mp 54.7−57.2 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74−7.71 (m, 2H), 7.30−7.26 (m, 2H), 6.37 (d, *J* = 12.0 Hz, 1H), 6.30 (d, *J* = 12.0 Hz, 1H), 5.51 (d, *J* = 7.6 Hz, 1H), 4.06−3.98 (m, 1H), 2.41 (s, 3H), 2.19 (s, 3H), 1.93−1.84 (m, 1H), 1.67−1.55 (m, 1H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 200.8, 199.0, 143.6, 139.7, 136.9, 130.9, 129.6, 127.0, 62.3, 29.4, 25.0, 21.4, 9.0. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{15}H_{19}NO_4SNa$, 332.0927; found, 332.0933.

(Z)-N-(4,7-Dioxo-1-phenyloct-5-en-3-yl)-4-methylbenzenesulfonamide (**6f**). Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **6f** as a white solid (61 mg, 79% yield, 0.2 mmol of **5f** as the starting material was used). mp 118.7−121.5 °C. R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.25−7.15 (m, 3H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.34 (d, *J* = 11.9 Hz, 1H), 6.21 (d, *J* = 11.9 Hz, 1H), 5.54 (d, *J* = 8.0 Hz, 1H), 4.11−4.04 (m, 1H), 2.63−2.56 (m, 2H), 2.41 (s, 3H), 2.18 (s, 3H), 2.16−2.06 (m, 1H), 1.85−1.75 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 200.7, 199.1, 143.8, 140.4, 139.4, 136.9, 131.3, 129.7, 128.4, 128.4, 127.1, 126.2, 60.8, 33.5, 30.9, 29.4, 21.5. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{21}H_{23}NO_4SNa$, 408.1240; found, 408.1241.

(Z)-4-Methyl-N-(2-methyl-3,6-dioxoundec-4-en-2-yl)-benzenesulfonamide (**6g**). Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **6g** as a colorless oil (65 mg, 90% yield, 0.2 mmol of **5g** as the starting

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material was used). R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.63 (d, J = 11.4 Hz, 1H), 6.40 (d, J = 11.4 Hz, 1H), 5.68 (s, 1H), 2.49 (t, J = 7.5 Hz, 2H), 2.34 (s, 3H), 1.60−1.52 (m, 2H), 1.30 (s, 6H), 1.27−1.21 (m, 4H), 0.82 (t, J = 6.6 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 204.4, 201.9, 143.3, 139.8, 139.6, 130.4, 129.6, 126.8, 63.2, 42.1, 31.2, 24.4, 23.1, 22.4, 21.5, 13.9. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{19}H_{27}NO_4SNa$, 388.1553; found, 388.1553.

*tert-Butyl(Z)-(6,9-dioxodec-7-en-5-yl)carbamate (**6h**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **6h** as a yellow oil (44 mg, 78% yield, 0.2 mmol of **5h** as the starting material was used). R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.44 (d, J = 11.9 Hz, 1H), 6.40 (d, J = 12.0 Hz, 1H), 5.15 (d, J = 7.9 Hz, 1H), 4.42−4.34 (m, 1H), 2.31 (s, 3H), 1.97−1.87 (m, 1H), 1.61−1.53 (m, 1H), 1.44 (s, 9H), 1.37−1.28 (m, 4H), 0.93−0.87 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 201.1, 201.0, 155.5, 138.6, 132.5, 79.8, 59.0, 30.7, 29.5, 28.2, 27.3, 22.4, 13.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{25}NO_4Na$, 306.1676; found, 306.1681.

*(Z)-N-(1,4-Dioxonon-2-en-5-yl)benzamide (**6i**).* Isolation by column chromatography over silica gel (eluent, 5:1 petroleum ether/ethyl acetate) afforded **6i** as a yellow oil (43 mg, 79% yield, 0.2 mmol of **5i** as the starting material was used). R_f = 0.3 (3:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.28 (d, J = 7.0 Hz, 1H), 7.86−7.81 (m, 2H), 7.55 (dd, J = 8.4, 6.3 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H), 7.15−7.08 (m, 1H), 6.90 (d, J = 6.8 Hz, 1H), 6.34 (dd, J = 11.8, 7.0 Hz, 1H), 5.05−4.97 (m, 1H), 2.12−2.04 (m, 1H), 1.79−1.72 (m, 1H), 1.42−1.32 (m, 4H), 0.90 (t, J = 6.7 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 198.7, 192.2, 167.3, 140.2, 137.1, 133.5, 132.0, 128.7, 127.1, 58.8, 30.8, 27.2, 22.5, 13.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{19}NO_3Na$, 296.1257; found, 296.1256.

Synthesis of 8. To a solution of 6-hydroxy-2-(pent-4-en-1-yl)-2*H*-pyran-3(6*H*)-one **2n** (0.4 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (2 mL) was added pyridine (0.8 mmol, 2.0 equiv) followed by acetyl chloride (0.48 mmol, 1.2 equiv) at 0 °C. The resulting solution was allowed to warm to 23 °C and was stirred for 2 h. The solution was washed with ice-cold saturated aqueous NaCl (2 × 10 mL), dried with Na_2SO_4, filtered, and concentrated to provide crude acetoxypyranone **7a** as a mixture of diastereomers.

To an oven-dried 1 dram vial was added the appropriate acetoxypyranone (0.1 mmol, 1.0 equiv) as a stock solution in anhydrous CH_3CN (0.1 M). Next, the appropriate amine base was added (DBU, 0.4 mmol, 4.0 equiv). The vial was backfilled with Ar, capped, and stirred for 6 h. Acetic acid (0.44 mmol, 4.4 equiv) was added in order to quench the reaction. The organic layer was dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by silica gel with petroleum ether/ethyl acetate as the eluent to give **8**.

*5-Oxo-6-(pent-4-en-1-yl)-5,6-dihydro-2H-pyran-2-yl-acetate (**7a**).*[35c] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **7a** as a yellow oil (116 mg, 65% yield, 0.8 mmol of **2n** as the starting material was used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (dd, J = 10.3, 2.7 Hz, 1H), 6.55 (dd, J = 2.7, 1.3 Hz, 1H), 6.23 (dd, J = 10.4, 1.3 Hz, 1H), 5.86−5.73 (m, 1H), 5.02 (ddd, J = 17.0, 3.3, 1.5 Hz, 1H), 4.99−4.95 (m, 1H), 4.23 (dd, J = 8.3, 5.7 Hz, 1H), 2.15 (s, 3H), 2.13−2.03 (m, 2H), 1.87 (ddd, J = 12.5, 6.9, 4.2 Hz, 2H), 1.65−1.49 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 195.6, 169.3, 142.8, 138.0, 128.3, 115.0, 87.5, 79.4, 33.3, 32.3, 24.5, 21.0.

*1,2,3,7,8,8a-Hexahydro-4H-3a,7-epoxyazulen-4-one (**8**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **8** as a colorless oil (9 mg, 54% yield, 0.1 mmol of **7a** as the starting material was used). R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (dd, J = 9.7, 4.4 Hz, 1H), 5.98 (d, J = 9.8 Hz, 1H), 4.89 (dd, J = 6.5, 4.4 Hz, 1H), 2.46−2.38 (m, 1H), 2.36−2.27 (m, 1H), 2.17 (dd, J = 11.9, 8.9 Hz, 1H), 1.99−1.86 (m, 2H), 1.86−1.78 (m, 2H), 1.77−1.69 (m, 1H), 1.64−1.57 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.6, 151.9, 126.2, 98.1, 76.0, 44.5, 36.7, 32.3, 30.0, 26.1. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{12}O_2Na$, 187.0730; found, 187.0728.

Synthesis of 9. To a magnetically stirred solution of acetate **7b** (0.2 mmol, 1.0 equiv) and triethylsilane (0.4 mmol, 2.0 equiv) in CH_2Cl_2 (2 mL), $BF_3{\cdot}Et_2O$ (0.25 mmol, 1.25 equiv) was added at −78 °C; stirring was continued until the complete consumption of starting material occurred (ca. 1 h). The reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL) and then extracted with CH_2Cl_2 (3 × 10 mL), washed with brine (10 mL), and dried over anhydrous Na_2SO_4. Evaporation of CH_2Cl_2 in vacuo gave the crude product, which was subjected to silica gel column chromatography to give desired enone **9**.

*5-Oxo-1-oxaspiro[5.5]undec-3-en-2-yl-acetate (**7b**).*[35d] Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **7b** as a colorless oil (30 mg, 67% yield, 0.2 mmol of **2f** as the starting material was used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (dd, J = 10.4, 3.1 Hz, 1H), 6.60 (dd, J = 3.1, 1.1 Hz, 1H), 6.15 (dd, J = 10.3, 1.1 Hz, 1H), 2.13 (s, 3H), 2.10−2.04 (m, 1H), 1.86−1.77 (m, 1H), 1.75−1.67 (m, 2H), 1.66−1.61 (m, 2H), 1.60−1.56 (m, 3H), 1.33−1.22 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 198.3, 169.6, 141.0, 127.2, 86.5, 81.1, 34.3, 31.7, 24.9, 21.0, 20.4, 20.3.

*1-Oxaspiro[5.5]undec-3-en-5-one (**9**).* Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **9** as a colorless oil (11 mg, 65% yield, 0.1 mmol of **7b** as the starting material was used). R_f = 0.4 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (dt, J = 10.4, 2.8 Hz, 1H), 6.01 (dt, J = 10.3, 2.2 Hz, 1H), 4.39−4.37 (m, 2H), 1.82 (d, J = 11.3 Hz, 2H), 1.70−1.53 (m, 7H), 1.33−1.23 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.1, 146.7, 125.2, 79.4, 59.7, 29.6, 25.3, 21.0. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{14}O_2Na$, 189.0886; found, 189.0885.

Synthesis of 10. A solution of the 2-hydroxy-1-oxaspiro[5.5]-undec-3-en-5-one **2f** (0.6 mmol, 1.0 equiv) in dichloromethane (3 mL) was treated with allyltrimethylsilane (1.8 mmol, 3.0 equiv) under an argon atmosphere. The resulting mixture was cooled to −78 °C, and boron trifluoride-diethyl etherate complex (0.6 mmol, 1.0 equiv) was then added. The resulting reaction mixture was stirred at −78 °C until completion as indicated by TLC analysis (1 h). The reaction was then diluted with dichloromethane (5 mL) and quenched by the slow addition of aqueous saturated ammonium chloride (10 mL). The phases were separated, and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were combined, washed with saturated aqueous $NaHCO_3$ (25 mL) and brine (25 mL), dried over Na_2SO_4, filtered, and concentrated under a vacuum. Purification of the crude residue by flash column chromatography (petroleum ether/ethyl acetate) afforded **10**.

*2-Allyl-1-oxaspiro[5.5]undec-3-en-5-one (**10**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **10** as a colorless oil (24 mg, 58% yield, 0.2 mmol of **2f** as the starting material was used). R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (dd, J = 10.2, 1.4 Hz, 1H), 5.97 (dd, J = 10.3, 2.4 Hz, 1H), 5.95−5.85 (m, 1H), 5.22−5.13 (m, 2H), 4.41−4.36 (m, 1H), 2.53−2.36 (m, 2H), 2.06−1.98 (m, 1H), 1.97−1.89 (m, 1H), 1.71−1.53 (m, 6H), 1.32−1.22 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.6, 149.5, 133.6, 125.3, 118.0, 79.1, 67.5, 39.3, 31.6, 28.4, 25.4, 21.5, 20.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{13}H_{18}O_2Na$, 229.1199; found, 229.1196.

Synthesis of 11. To a solution of 2-hydroxy-1-oxaspiro[5.5]-undec-3-en-5-one **2f** (0.5 mmol, 1.0 equiv) in dry DCM (3 mL) were added Boc_2O (0.75 mmol, 1.5 equiv) and DMAP (0.025 mmol, 0.05 equiv) at −78 °C. The mixture was then stirred at −78 °C for 3.5 h, diluted with ether, and quenched with saturated aqueous $NaHCO_3$. The organic layers were separated and dried with Na_2SO_4. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) affording the desired product **7c**.

A dry DCM (3 mL) solution of **7c** (0.2 mmol, 1.0 equiv) and cholesterol (0.4 mmol, 2.0 equiv) was purged with nitrogen. Then, a

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solution of the $Pd_2(PPh)_4$ (0.01 mmol, 0.05 equiv) and PPh_3 (0.06 mmol, 0.3 equiv) in dry DCM (2 mL) was added at 0 °C under nitrogen. The reaction was stirred at rt for 3 h before it was quenched with saturated aqueous $NaHCO_3$. Then, the reaction was extracted with Et_2O (3 × 20 mL), dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate) affording the desired product **11**.

*tert-Butyl(5-oxo-1-oxaspiro[5.5]undec-3-en-2-yl) carbonate (**7c**).* Isolation by column chromatography over silica gel (eluent, 20:1 petroleum ether/ethyl acetate) afforded **7c** as a colorless oil (40 mg, 68% yield, 0.2 mmol of **2f** as the starting material was used). R_f = 0.5 (10:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (dd, J = 10.2, 3.2 Hz, 1H), 6.42−6.41 (m, 1H), 6.15 (dd, J = 10.4, 0.8 Hz, 1H), 2.11 (d, J = 6.6 Hz, 1H), 1.87−1.75 (m, 1H), 1.74−1.55 (m, 7H), 1.53 (s, 9H), 1.30−1.21 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 198.5, 152.0, 140.5, 127.4, 88.7, 83.1, 81.2, 34.4, 32.0, 27.6, 25.0, 20.4, 20.3. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{22}O_5Na$, 305.1359; found, 305.1360.

*2-(((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-1-oxaspiro[5.5]undec-3-en-5-one (**11**).* Isolation by column chromatography over silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded **11** as a colorless oil (25 mg, 45% yield, 0.1 mmol of **7c** as the starting material was used). R_f = 0.4 (5:1 petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (dd, J = 10.3, 2.1 Hz, 1H), 6.03 (dd, J = 10.3, 0.9 Hz, 1H), 5.49 (d, J = 1.2 Hz, 1H), 5.38 (d, J = 5.1 Hz, 1H), 3.81−3.68 (m, 1H), 2.48−2.20 (m, 2H), 2.05−1.95 (m, 4H), 1.90 (d, J = 13.9 Hz, 1H), 1.86−1.76 (m, 2H), 1.75−1.56 (m, 10H), 1.55−1.42 (m, 5H), 1.40−1.25 (m, 5H), 1.20−1.05 (m, 7H), 1.02 (s, 3H), 1.01−0.95 (m, 2H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 1.7 Hz, 3H), 0.86 (d, J = 1.7 Hz, 3H), 0.68 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.5, 199.5, 145.0, 144.9, 140.6, 140.4, 126.7, 126.7, 122.1, 121.9, 90.4, 90.3, 80.5, 80.4, 77.9, 77.7, 56.7, 56.1, 50.1, 50.0, 42.3, 40.0, 39.7, 39.5, 38.6, 37.4, 37.1, 36.8, 36.7, 36.1, 35.8, 33.7, 33.6, 31.9, 31.9, 31.9, 31.8, 31.6, 31.5, 29.4, 28.2, 28.0, 28.0, 25.2, 24.3, 23.8, 22.8, 22.5, 21.1, 21.1, 21.0, 21.0, 20.9, 20.8, 19.3, 18.7, 11.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{37}H_{58}O_3Na$, 573.4278; found, 573.4280.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00858.

Copies of ^{1}H and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 2046280−2046281 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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