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NH_4HF_2 as a Selective TBS-Removal Reagent for the Synthesis of Highly Functionalized Spiroketal via Tandem Deprotection/Spiroketalization Procedure

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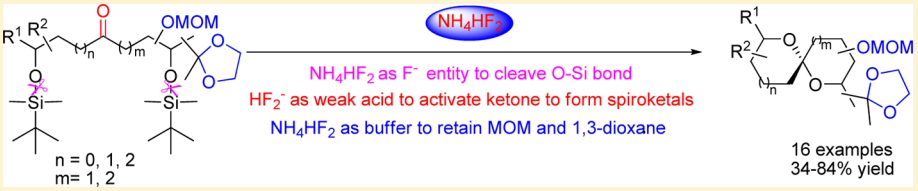
Supporting Information



ABSTRACT: NH_4HF_2 has been used for the first time to selectively remove the TBS protecting groups from diol ketone precursors in the synthesis of highly functionalized spiroketals. This method allows the synthesis of [5,6], [6,6], and [6,7] spiroketal skeletons, as well as benzannulated spiroketal with retention of acid-sensitive groups. In this way, spiroketals can be synthesized with diverse substituent groups in the skeleton or on side chains. To demonstrate the utility of this methodology, the diverse transformations of highly functionalized spiroketal **3f** were also investigated.

INTRODUCTION

Spiroketals are present as a structural motif in many bioactive natural products, pharmaceuticals, and pesticides,[1−7] and they have been used as ligands in transition-metal-catalyzed transformations.[8−10] Spiroketals show impressive structural diversity, from the simplest spiroketal, Olean (**1a**) to the sophisticated spiroketal spongistatin (**1e**) (Figure 1). The rigid structure has proven useful for configurational analysis[11] and stereocontrolled synthesis.[12] Additionally, spiroketal has been widely applied in protecting-group chemistry.[13]

Several methods have been developed to synthesize this core structure, including acid-promoted cyclization of protected diol and/or ketone precursors, in which nitro or triple bond, enol ester, and *N*,*N*-dimethylhydrazone serve as ketone equivalents;[14] addition or substitution reactions involving cyclic ether, lactone or its equivalent, followed by intermolecular cyclization;[15] hetero-Diels−Alder reaction;[16] multicomponent cascade reaction;[17,18] and radical-mediated reaction.[19] Among these methods, acid-promoted cyclization of protected diol and/or ketone precursors (or their equivalents) is a classical and efficient way to obtain thermodynamically stable spiroketals.[1,3] Typically this method involves the strategic, selective protection of hydroxyl and/or ketone groups, the subsequent removal of these protecting groups under acidic conditions, and finally cyclization to generate the desired spiroketal product. TBS-ether is often used in this procedure because it is easily installed and removed, and it does not react with numerous organic reagents.[13] However, some acid-sensitive groups are removed when TBS-ether is used, necessitating additional steps to reprotect the exposed groups. This problem highlights the need to find suitable reagents that remove the TBS-ether but not other acid-sensitive protecting groups in the same molecular skeleton, particularly when the synthetic target molecule contains multiple hydroxyl groups.

In our efforts to synthesize the polyester didemnaketal A (**1d**), we showed that NH_4HF_2 promotes selective removal of the TBS group and subsequent cyclization, allowing us to synthesize spiroketal skeletons with retention of other acid-sensitive groups such as MOM or 1,3-dioxolane.[20] NH_4HF_2 is an environmentally friendly and relatively safe reagent, which was first proposed by Pauling[21] and verified by McDonald using X-ray diffraction analysis,[22] and now it is used in diverse fields of chemistry.[23−27] In organic chemistry, it provides F^- for the preparation of fluorosilanes from chlorosilanes[28] or silylsulfates[29] and for the halofluorination of alkenes.[30] It catalyzes condensation during pyrimidine synthesis[31] and desilylates acid-sensitive substrates.[32,33]

Despite the widespread use of NH_4HF_2, few studies have examined its ability to show multifunctionality, particularly in processes where it serves as a source of F^- that cleaves O−Si bonds.[34] Therefore, we explored the use of NH_4HF_2 to generate highly functionalized spiroketal bearing acid-sensitive groups and thereby developed a more general method that would improve the long reaction time and low yield of NH_4HF_2-promoted spirocyclization in our synthesis of didemnaketal A.[20]

RESULTS AND DISCUSSION

Optimization of Reaction Conditions. As a model substrate, the compound **2a** was synthesized from the known

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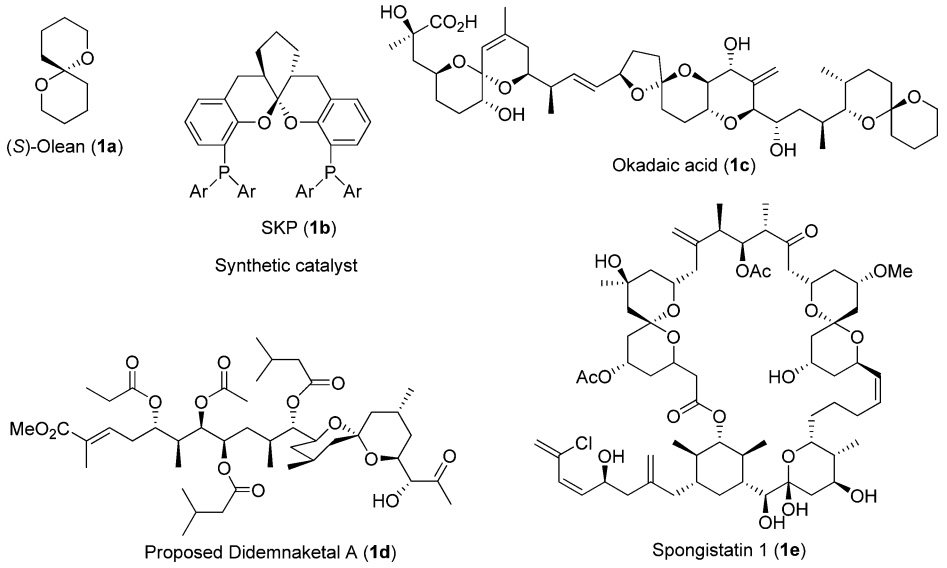
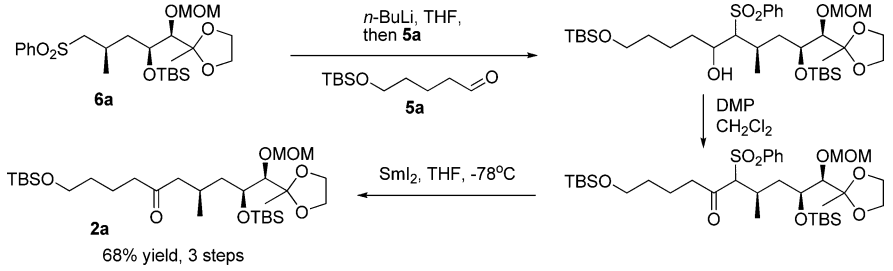


Figure 1. Representative spiroketal compounds.

Scheme 1. Synthesis of Substrate 2a



aldehyde **5a**[35] and sulfone **6a**[20] in three steps with 68% yield (Scheme 1).

Compound **2a** bears two TBS-ether groups, one MOM group, and one 1,3-dioxolane group along the main chain. In order to retain the acid-sensitive MOM and dioxolane groups, we avoided the use of strong acid and investigated various mild conditions (Table 1). First, TBAF/THF[36] (usually used as a desilyl reagent) was tested, and only the primary TBS-ether was removed (entry 1). The previously described reaction conditions, $NH_4F/CH_3OH/60$ °C[13] and $CsF/CH_3CN/80$ °C,[13] did not give the desired product and only starting material was recovered (entries 2 and 3). Various Lewis and protic acids were tested for their ability to promote this straightforward transformation. Both $BF_3{\cdot}Et_2O$[37] and TMSOTf[38] were inefficient, giving undesired complex mixtures (entries 4 and 5). PPTS did not promote the current reaction, and only starting material was recovered (entry 6). PTS, however, removed all protecting groups, generating the undesired spirocylization product (entry 7). The mixture of 5% HF in CH_3CN[39] afforded product **3a** in 38% yield (entry 8), whereas the $THF/HCO_2H/H_2O$ (6/3/1) system[40] generated only minor products (entry 9). CSA[41] and TFA[42] led to the desired product in 29% and 35% yield, respectively (entries 10 and 11). Although *t*-BuOK has been shown to remove the TBS protecting group efficiently under basic conditions to allow spiroketal synthesis,[6] it turned out to be inefficient for the current transformation (entry 12). Similarly, ceric ammonium nitrate,[13] which is broadly used for removing TBS while retaining dioxolane, was inefficient for this reaction (entry 13). TBAF/AcOH, previously shown to be effective at removing TBS,[43] generated only trace amounts of desired product (entry 14). HF·pyridine[44] gave the desired product in 47% yield (entry 15), but $HF{\cdot}Et_3N$[45] was inefficient even after 2 days of reaction (entry 16). NH_4HF_2/methanol/reflux gave the desired product in 52% isolated yield (entry 17). Since NH_4HF_2 is poorly soluble in methanol, we further optimized the reaction solvent and found DMF/NMP (3:1)[33] to give the best results (entries 18−24), and carrying out the reaction at 100 °C allowed us to shorten the reaction time to 11 h with 80% yield (entry 24). Decreasing the amount of NH_4HF_2 decreased the yield (entries 24−27), and the bifluoride ions $NaHF_2$ and KHF_2 generated the desired product with 53% and 43% yield, respectively (entries 28 and 29). Therefore, we selected NH_4HF_2 (100 equiv)/DMF−NMP (3:1)/100 °C as the optimal conditions.

Scope of Substrates. After optimizing the reaction conditions, we sought to exploit a method to synthesize a broad range of spiroketals with different stereochemistries and functional groups on the skeleton and side chains. In order to generate highly functionalized substrates to test in our spiroketal synthesis, we first had to prepare the appropriate aldehyde and sulfone starting materials.

Preparation of Aldehyde Starting Materials. The aldehydes **5a**,[35] **5b**,[46] **5c**,[47] **5d**,[48] **5f**,[20] **5h**,[49] and **5m**[50] were prepared according to the reported methods, while aldehydes **5e**, **5n**, **5o**, and **5p** were prepared as shown in Schemes 2−4.

Starting from known compound **7e**, we obtained the aldehyde **5e** by following a synthetic route similar to the one

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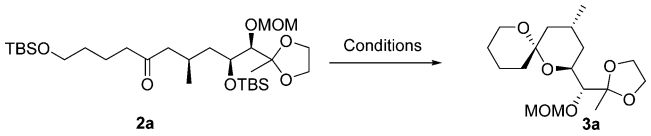
Table 1. Optimization of Reaction Conditions[a]



2a 3a

entry	reagent	solvent	temp (°C)	time	yield[b] (%)
1	TBAF	THF	rt	20 h	*d*
2	NH_4F	CH_3OH	60	20 h	*c*
3	CsF	CH_3CN/H_2O	80	4 h	*c*
4	$BF_3{\cdot}Et_2O$	$CHCl_3$	0	5 min	*e*
5	TMSOTf	CH_2Cl_2	0	5 min	*e*
6	PPTS	C_2H_5OH	rt	72 h	*c*
7	PTS	CH_3OH	0 to rt	36 h	*d*
8	5% HF	CH_3CN	0 to rt	24 h	38
9	HCO_2H	THF/H_2O	rt	48 h	15
10	CSA	CH_3OH/CH_2Cl_2	0 to rt	30 h	29
11	TFA	CH_2Cl_2/H_2O	rt	10 h	35
12	*t*-BuOK	THF	rt	44 h	*c*
13	CAN	CH_3OH	rt	4 h	*d*
14	TBAF/AcOH	DMF	rt	20 h	<5
15	HF·pyridine	THF/pyridine	rt	48 h	47
16	$HF{\cdot}Et_3N$	THF/Et_3N	rt	48 h	*d*
17	NH_4HF_2 (100 equiv)	CH_3OH	50	44 h	52
18	NH_4HF_2 (100 equiv)	NMP	50	44 h	50
19	NH_4HF_2 (100 equiv)	DMF	50	44 h	39
20	NH_4HF_2 (100 equiv)	CF_3CH_2OH	50	44 h	35
21	NH_4HF_2 (100 equiv)	NMP	100	13 h	56
22	NH_4HF_2 (100 equiv)	DMF	100	13 h	49
23	NH_4HF_2 (100 equiv)	CF_3CH_2OH	reflux	13 h	38
24	NH_4HF_2 (100 equiv)	DMF/NMP	100	11 h	80
25	NH_4HF_2 (70 equiv)	DMF/NMP	100	17 h	65
26	NH_4HF_2 (40 equiv)	DMF/NMP	100	44 h	64
27	NH_4HF_2 (10 equiv)	DMF/NMP	100	48 h	51
28	$NaHF_2$ (100 equiv)	DMF/NMP	100	11 h	53
29	KHF_2 (100 equiv)	DMF/NMP	100	11 h	43

[a]Performed on a 10 mg substrate scale. [b]Isolated yield. [c]No reaction. [d]The starting material **2a** disappeared, but the desired product **3a** was not obtained. [e]The starting material decomposed.

we had reported.[20] The process involved five straightforward manipulations: Sharpless asymmetric dihydroxylation, selective protection of two secondary hydroxyl groups, elimination of a tertiary hydroxyl group, selective removal of a TBDPS protecting group, and finally oxidation.

The aryl-containing aldehyde **5n** was prepared by converting aldehyde **7n**[51] to α,β-unsaturated ester **8n** (Scheme 3). Two subsequent reduction steps, the first using DIBAL-H and the second using $Pd(OH)_2$, provided the alcohol **10n** which was oxidized by Dess–Martin reagent to give aldehyde **5n**.

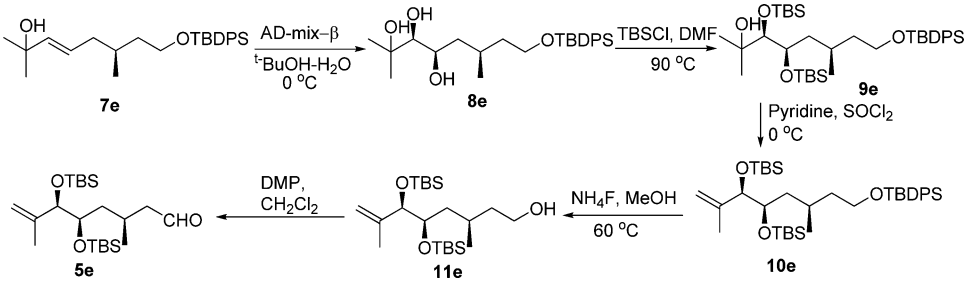
The aldehyde **5o** was prepared from the previously described aldehyde **7o**[52] (Scheme 4), which after Wittig olefination and hydroboration of the resulting double bonds afforded the alcohol **9o**. Oxidation of this alcohol furnished the aldehyde **5o**. A similar route was followed to synthesize aldehyde **5p** from the aldehyde **7p**[53] (Scheme 4).

Preparation of Sulfone Segments. After synthesizing these various aldehyde segments, we turned our attention to synthesizing the necessary sulfone segments. Sulfone **6a** was prepared using our previously published approach,[20] and sulfone **6b** was prepared from the known compound **12**.[20] Selective protection of diol groups and then selective removal of TBDPS-ether delivered the alcohol **16**. Iodination of this alcohol and sulfination of the resulting iodide intermediate **18** provided the desired sulfone **6b** (Scheme 5). Similar manipulations were used to prepare sulfone **6c** (Scheme 5).

Synthesis of Substrates for Preparation of Spiroketal. With these aldehyde and sulfone segments in hand, we synthesized the necessary substrates bearing acid-sensitive groups. Our approach was based on that used to prepare substrate **2a**: the appropriate aldehyde and sulfone were coupled under Julia conditions, and subsequent oxidation and desulfonation furnished the desired products **2b–p** (Scheme 6).

Finally, we subjected these structurally diverse substrates to the optimized conditions for the synthesis of highly functionalized spiroketals in order to investigate the scope of this transformation (Figure 2). The process generated spiroketal products of various sizes in good yield,[54] including 1,7-dioxaspiro[5.5]undecane (**3a**), 1,6-dioxaspiro[4.5]decane (**3b**), 1,7-dioxaspiro[5.6]dodecane (**3c**), 1,6-dioxaspiro[4.5]decane (**3d**), which bears a methyl substitution on the tetrahydrofuran ring; and 1,7-dioxaspiro[5.5]undecane (**3e**), bearing OH and C=C moieties as side chain substitutions. Our optimized reaction conditions generated 1,7-dioxaspiro[4.5]dodecane (**3f**) in 84% yield in a single step, much better than the 86% yield we previously obtained only by repeating the reaction three times.[20] A substrate carrying three TBS protecting groups worked well, giving the desired product **3g** in 74% yield. A substrate containing a PMB group also reacted well to produce

Scheme 2. Preparation of Aldehyde 5e



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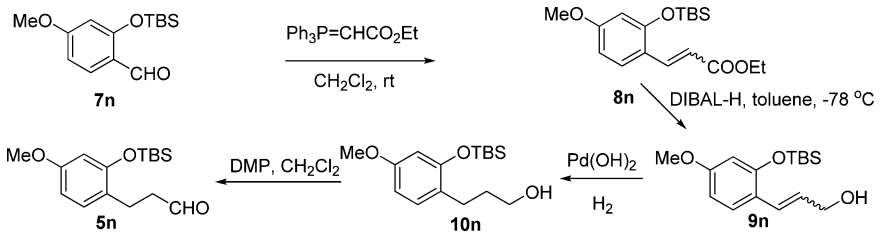
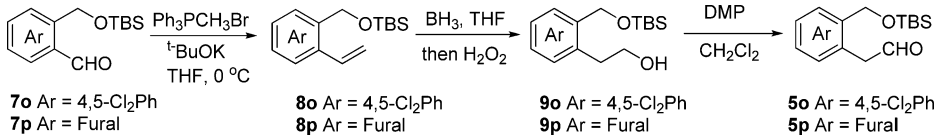
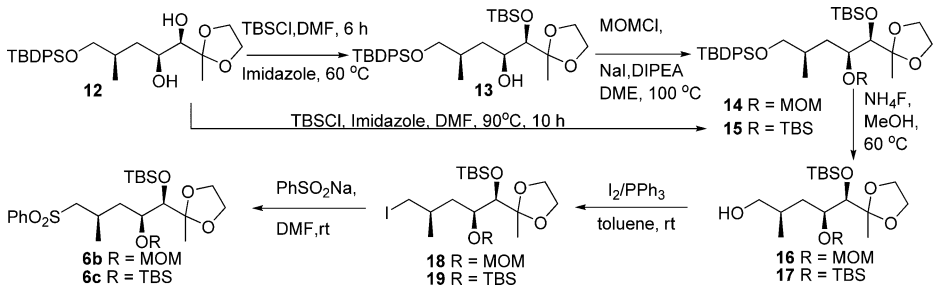
Scheme 3. Preparation of the Aldehyde 5n



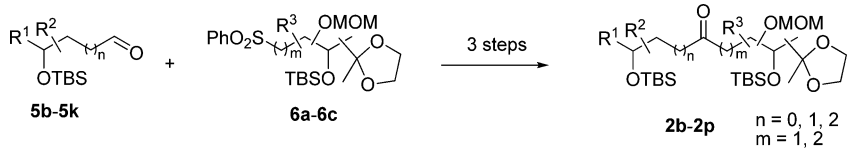
Scheme 4. Preparation of the Aldehydes 5o and 5p



Scheme 5. Preparation of Sulfones 6b and 6c



Scheme 6. Preparation of Substrates 2b–p



3h (47% yield). Furthermore, the method was effective for constructing spiroketals with a substituted hexahydrooxepin ring. For example, four spiroketal compounds (**3i–l**) featuring a common hexahydrooxepin ring bearing MOM, methyl, and 1,3-dioxolane groups were generated in good yield, most notably the highly functionalized [6,7]spiroketal compound **3l**.

A spiroketal core fused to an aromatic ring is not only a common motif in bioactive natural products,[55] it also efficiently catalyzes asymmetric reactions.[8−10] Therefore another series of substrates were subjected to our optimized NH_4HF_2/DMF–NMP procedure (Figure 3). Substrates carrying phenolic TBS-silyl ether protecting groups worked well, and both compound **3m** and MeO-substituted benzannulated spiroketal **3n** were obtained in good yield, although with poor diastereoselectivity. Importantly, isochroman-type spiroketal **3o** and the furan-fused product **3p** were synthesized.[54]

Diverse Transformations of Spiroketal 3f. The broad range of spiroketal bioactivities depends on their structural diversity, so chemical biology screening requires a diverse library of molecules. To examine the ability of our synthetic spiroketals to generate such diversity, we investigated various reactions starting from the same scaffold compound **3f** (Scheme 7). Protecting the free hydroxyl group with a TBDPS or Bn group gave **4a** and **4b**, respectively, in good yield; these compounds can be further transformed under various neutral or basic conditions. Epoxidation of the allylic alcohol in **3f** furnished epoxy compound **4c**, which reacts with numerous nucleophiles. Oxidation of **3f** with Dess–Martin reagent gave α,β-unsaturated ketone **4d**, which served as an intermediate in several synthetically important transformations. Ozanolysis of the terminal double bond in **3f** furnished the α-hydroxyl ketone **4e**. Finally, selective removal of the 1,3-dioxolane group from **3f** produced the MOM-protected the α-hydroxyl ketone **4f**. These transformations clearly demonstrate the power of **3f** as a synthetic scaffold for generating diverse spiroketals for bioactivity evaluation and for use as intermediates to synthesize other natural products.

■ CONCLUSION

In summary, we provide the first description of NH_4HF_2 for synthesizing highly functionalized spiroketal motifs. The procedure allows the retention of certain acid-sensitive groups on the spiroketal skeleton and side chains. Also, this approach may be useful for achieving the total synthesis of complex multihydroxyl natural products.

■ EXPERIMENTAL SECTION

General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded with TMS as an internal standard in $CDCl_3$ by a spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR

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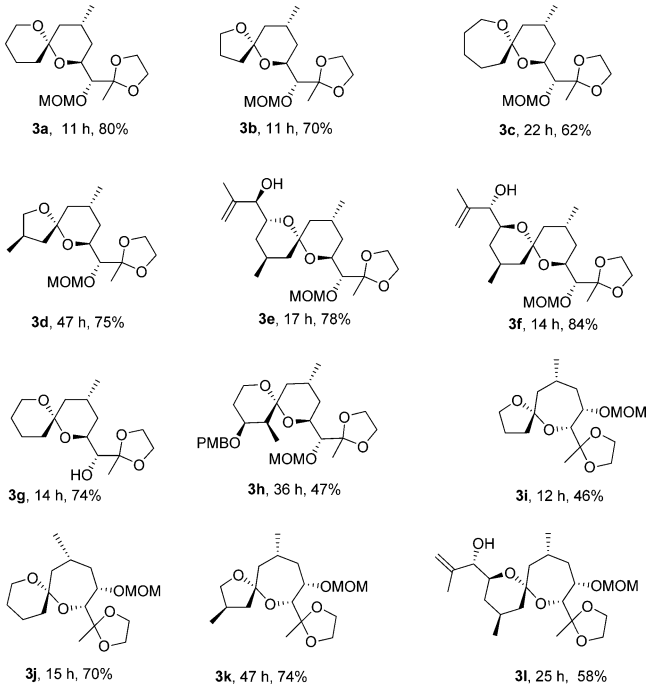

Figure 2. Spiroketal compounds synthesized using the NH_4HF_2/DMF−NMP procedure.

spectra) or a spectrometer (600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR spectra). The EI-MS spectra were recorded on GC−MS. The high-resolution mass spectra were recorded by means of the ESI technique on Fourier transform ion cyclotron resonance mass analyzer. The optical rotations were measured using a 0.1-mL cell with a 1-cm path length. Silica gel (200−300 mesh) for column chromatography and silica GF_{254} for TLC were used. Solvents for reaction were distilled prior to use, and all air- or moisture-sensitive reactions were conducted under an argon atmosphere. Aldehydes **5a**,[35] **5b**,[46] **5c**,[47] **5d**,[48] **5f**,[20] **5h**,[49] and **5m**,[50] sulfone **6a**,[20] and substrate **2f**[20] were prepared according to the literature.

Synthesis of Aldehyde 5e. *Triol 8e.* To a solution of **7e** (175 mg, 0.43 mmol) in mixed solvent (5.0 mL, *tert*-butyl alcohol/H_2O = 1:1) was added AD-mix-β (598 mg) and $MeSO_2NH_2$ (41 mg, 0.43 mmol) at 0 °C. The mixture was stirred for 48 h at this temperature until the starting material disappeared completely. The reaction was quenched by addition of sodium sulfite at 0 °C and then warmed to room temperature and stirred for another 1 h. The reaction mixture was extracted with ethyl acetate (3 × 10 mL) and then washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (EtOAc/hexane = 6:1) yielding the pure triol **8e** (165 mg, 87%). R_f = 0.20 (petroleum/EtOAc = 2:1). $[\alpha]^{20}_D$ = +1.3 (*c* = 24.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70−7.68 (m, 4 H), 7.46−7.38 (m, 6 H), 4.10 (d, *J* = 6.4 Hz, 1 H), 3.81−3.69 (m, 2 H), 3.10 (s, 1 H), 1.83−1.68 (m, 2 H), 1.61−1.47 (m, 2 H), 1.44−1.35 (m, 1 H), 1.30 (s, 3 H), 1.29 (s, 3 H), 1.08 (s, 9 H), 0.92 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.5, 133.8, 129.6, 127.6, 76.5, 74.1, 69.1, 62.2, 41.5, 39.1, 27.2, 26.8, 26.2, 20.4, 19.1. MS (EI) *m*/*z*: 59 (100), 99 (48), 139 (42), 199 (95), 267 (15), 297 (53). HRMS for $C_{26}H_{41}O_4Si$ ($M + H^+$) calcd 445.2769, found 445.2767.

Tertiary Alcohol 9e. To a solution of **8e** (533 mg, 1.20 mmol) in DMF (1.0 mL) were added imidazole (734 mg, 10.8 mmol) and TBSCl (450 mg, 3.0 mmol) at room temperature under an argon atmosphere, and the reaction mixture was warmed to 90 °C for 24 h. The mixture was cooled to room temperature and then quenched with brine (5 mL). The aqueous layer was extracted with Et_2O (3 × 50 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum/EtOAc 30:1) yielding compound **9e** (573 mg, 71%). R_f = 0.70 (petroleum/EtOAc = 8:1). $[\alpha]^{20}_D$ = +12.5 (*c* = 20.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70−7.68 (m, 4 H), 7.46−7.37 (m, 6 H), 3.89−3.86 (m, 1 H), 3.78−3.63 (m, 2 H), 3.55 (d, *J* = 4.0 Hz, 1 H), 3.30 (brs, 1 H), 1.84−1.77 (m, 1 H), 1.74−1.68 (m, 3 H), 1.57−1.53 (m, 1 H), 1.28 (s, 3 H), 1.23 (s, 3 H), 1.07 (s, 9 H), 0.95 (s, 9 H), 0.90 (s, 9 H), 0.90 (d, *J* = 6.4 Hz, 3 H), 0.17 (s, 3 H), 0.14 (s, 3 H), 0.13 (s, 3 H), 0.07 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.6, 134.1, 129.5, 127.6, 78.6, 74.6, 73.8, 62.4, 40.6, 39.1, 28.4, 28.2, 26.9, 26.8, 26.0, 25.9, 22.7, 20.9, 19.2, 18.1, 17.9, −3.4, −3.5, −4.6, −4.7. MS (EI) *m*/*z*: 73 (100), 135 (38), 147 (14), 199 (18), 267 (3), 469 (3). HRMS for $C_{38}H_{68}O_4Si_3Na$ ($M + Na^+$): calcd 695.4318, found 695.4321.

Ether 10e. To a solution of compound **9e** (107 mg, 0.16 mmol) in dried CH_2Cl_2 (5 mL) was added pyridine (48 μL) at 0 °C, and the mixture was stirred for another 10 min at this temperature. The solution was then treated with $SOCl_2$ (30 μL, 0.40 mmol) at 0 °C. After the reaction was completed (about 3 min), the mixture was poured into a stirred suspension solution of ice, water, and Et_2O. The organic phase was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (petroleum/EtOAc = 70:1) gave compound **10e** (93 mg, 89%). R_f = 0.28 (petroleum/EtOAc = 50:1). $[\alpha]^{21}_D$ = +27.5 (*c* = 4.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.69−7.67 (m, 4 H), 7.44−7.36 (m, 6 H), 4.98 (s, 1 H), 4.86 (s, 1 H), 4.04 (d, *J* = 3.2 Hz, 1 H), 3.75−3.62 (m, 3 H), 1.77 (s, 3 H), 1.75−1.69 (m, 2 H), 1.52−1.46 (m, 1 H), 1.27−1.21 (m, 1 H), 1.09−1.03 (m, 1 H), 1.05 (s, 9 H), 0.91 (s, 9 H), 0.88 (s, 9 H), 0.85 (d, *J* = 6.4 Hz, 3 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.04 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.9, 135.6, 134.2, 129.4, 127.6, 111.7, 77.8, 73.8, 62.5, 40.5, 39.6, 26.9, 26.1, 25.93, 25.88, 21.2, 20.7, 19.2, 18.2, 18.0, −3.8, −4.7, −4.9, −5.0. MS (EI) *m*/*z*: 73 (100), 135 (37), 185 (18), 243 (8), 367 (10), 469 (3). HRMS for $C_{38}H_{66}O_3Si_3Na$ ($M + Na^+$): calcd 677.4212, found 677.4208.

Alcohol 11e. To a solution of compound **10e** (320 mg, 0.49 mmol) in methanol (5.0 mL) was added $NH_4F{\cdot}3H_2O$ (544 mg, 14.7 mmol) under an argon atmosphere. The mixture was refluxed for 12 h, and then the solvent was removed. The residue was dissolved in Et_2O and then washed successively with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum/EtOAc = 3:1) to afford compound **11e** (173 mg, 85%) as an oil. R_f = 0.20 (petroleum/EtOAc = 6:1). $[\alpha]^{27}_D$ = +24.7 (*c* = 17.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.00 (s, 1 H), 4.89 (s, 1 H), 4.06 (d, *J* = 3.2 Hz, 1 H), 3.78−3.59 (m, 3 H), 1.78 (s, 3 H), 1.75−1.70 (m, 1 H), 1.65−1.51 (m, 2 H), 1.44−1.26 (m, 2 H), 1.12−1.05 (m, 1 H), 0.93 (d, *J* = 6.8

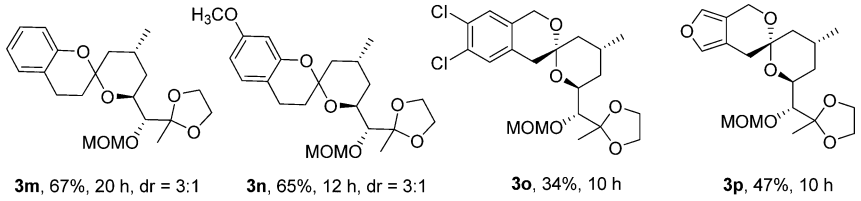

Figure 3. Benzannulated spiroketal synthesized using the NH_4HF_2/DMF−NMP procedure.

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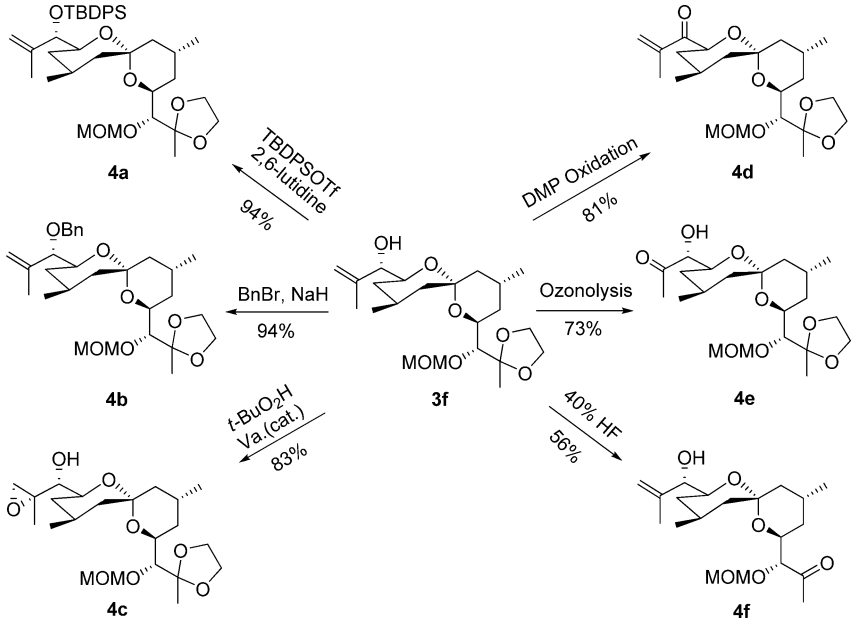
Scheme 7. Synthetic Diversity Generated from the Common Scaffold 3f



Hz, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.06 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.0, 111.7, 77.9, 73.7, 61.1, 39.9, 39.5, 25.88, 25.85, 25.8, 21.3, 20.9, 18.2, 18.0, −3.8, −4.8, −4.9, −5.0. MS (EI) *m*/*z*: 57 (18), 73 (48), 99 (100), 113 (6), 147 (7), 243 (4). HRMS for $C_{22}H_{48}O_3Si_2Na$ (M + Na^+): calcd 439.3034, found 439.3032.

*Aldehyde **5e**.* To a stirred solution of **11e** (240 mg, 0.58 mmol) in CH_2Cl_2 (3.0 mL) under an argon atomosphere were added $NaHCO_3$ (194 mg, 2.30 mmol) and then Dess−Martin reagent (294 mg, 0.69 mmol) at 0 °C. After the addition was complete, the cooling bath was removed, and the reaction mixture was warmed to room temperature. After the starting material disappeared, the mixture was diluted with Et_2O and poured into a 1:1 mixture of saturated aqueous $NaHCO_3$ and $Na_2S_2O_3$. The mixture was extracted with Et_2O, and the combined organic phase was washed successively with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 10:1) to afford compound **5e** (205 mg, 86%). R_f = 0.65 (petroleum/EtOAc = 3:1). $[\alpha]^{23}_D$ = +27.8 (*c* = 1.8, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.74 (dd, *J* = 2.8 Hz, 1.6 Hz, 1 H), 5.00 (s, 1 H), 4.90 (s, 1 H), 4.07 (d, *J* = 3.2 Hz, 1 H), 3.74−3.70 (m, 1 H), 2.39 (ddd, *J* = 15.6 Hz, 4.0 Hz, 1.6 Hz, 1 H), 2.33−2.21 (m, 1 H), 2.11 (ddd, *J* = 15.6 Hz, 8.8 Hz, 2.8 Hz, 1 H), 1.78 (s, 3 H), 1.57−1.50 (m, 1 H), 1.24−1.14 (m, 1 H), 0.99 (d, *J* = 6.8 Hz, 3 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.03 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 202.9, 144.6, 112.0, 77.6, 73.6, 50.5, 39.5, 25.9, 25.8, 24.6, 21.3, 21.2, 18.2, 18.0, −3.8, −4.8, −4.9, −5.0. MS (EI) *m*/*z*: 73 (92), 87 (100), 113 (60), 185 (17), 245 (26), 341 (6). HRMS for $C_{22}H_{46}O_3Si_2Na$ (M + Na^+): calcd 437.2878, found 437.2877.

Synthesis of Aldehyde 5n. *Ester **8n**.* To a solution of 2-((*tert*-butyldimethylsilyl)oxy)-4-methoxybenzaldehyde **7n** (988 mg, 3.71 mmol) in CH_2Cl_2 (5.0 mL) was added ethyl-2-(triphenylphosphoranylidene)acetate (1.68 g, 4.82 mmol) in CH_2Cl_2 (2.0 mL), and the reaction mixture was stirred for 2 h at rt. The solvent was evaporated in vacuo, and the crude product was purified by column chromatography to give **8n** (1.12 g, 90%). R_f = 0.60 (petroleum/EtOAc = 4:1). Major, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.02 (d, *J* = 16.4 Hz, 1 H), 7.47 (d, *J* = 8.8 Hz, 1 H), 6.53 (dd, *J* = 7.6 Hz, 2.4 Hz, 1 H), 6.37 (d, *J* = 2.4 Hz, 1 H), 6.26 (d, *J* = 16.0 Hz, 1 H), 4.23 (q, *J* = 6.8 Hz, 2 H), 3.78 (s, 3 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.05 (s, 9 H), 0.24 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.4, 162.2, 155.9, 139.5, 128.2, 118.9, 115.1, 107.5, 105.6, 60.0, 55.2, 25.7, 25.6, 18.2, 14.2, −4.4. MS (EI) *m*/*z*: 75 (74), 148 (16), 191 (34), 251 (53), 279 (64), 291 (8). HRMS for $C_{18}H_{29}O_4Si$ (M + H^+): calcd 337.1830, found 337.1834.

*Allylic Alcohol **9n**.* To a stirred solution of **8n** (1.024 g, 3.04 mmol) in toluene (5.0 mL) at −78 °C was added DIBAL-H (6.1 mL, 1.0 mol/L). The resulting mixture was stirred for 0.5 h. It was diluted with EtOAc (60 mL) and then quenched by saturated sodium potassium tartrate solution. The organic phase was separated, and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 10:1) to afford **9n** (823 mg, 92%) as a colorless oil. R_f = 0.50 (petroleum/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (d, *J* = 8.4 Hz, 1 H), 7.04 (d, *J* = 8.8 Hz, 0.1 H), 6.85 (d, *J* = 16.0 Hz, 1 H), 6.62 (d, *J* = 11.6 Hz, 0.1 H), 6.51 (dd, *J* = 8.4 Hz, 2.4 Hz, 1 H), 6.40 (d, *J* = 2.8 Hz, 0.1 H), 6.37 (d, *J* = 2.4 Hz, 1 H), 6.19 (dt, *J* = 16.0 Hz, 6.0 Hz, 1 H), 5.80 (dt, *J* = 15.6 Hz, 6.0 Hz, 0.1 H), 4.34 (dd, *J* = 6.4 Hz, 1.2 Hz, 0.2 H), 4.28 (dd, *J* = 6.4 Hz, 1.2 Hz, 2 H), 3.77 (s, 3 H), 1.96 (brs, 1 H), 1.03 (s, 8 H), 1.01 (s, 1 H), 0.23 (s, 5 H), 0.21 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.03, 159.95, 153.9, 130.7, 129.1, 127.3, 127.0, 126.5, 126.1, 121.0, 107.0, 106.0, 105.9, 105.7, 64.4, 59.9, 55.2, 25.8, 25.7, 18.3, −4.2, −4.3. MS (EI) *m*/*z*: 75 (86), 115 (41), 145 (28), 161 (26), 189 (40), 207 (28), 219 (100), 237 (70), 294 (M, 38). HRMS for $C_{16}H_{27}O_3Si$ (M + H^+): calcd 295.1724, found 295.1726.

*Alcohol **10n**.* To a solution of **9n** (300 mg, 0.10 mmol) in EtOH (3.0 mL) was added $Pd(OH)_2$/C (20%, 205 mg), and the suspension was stirred overnight under H_2 at room temperature. After the catalyst was removed by filtration, the filter cake was washed with EtOH. The solution was concentrated, and the crude product was purified by flash column chromatography to afford **10n** (300 mg, 99%) as a colorless oil. R_f = 0.60 (petroleum/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.04 (d, *J* = 8.4 Hz, 1 H), 6.48 (dd, *J* = 8.0 Hz, 2.4 Hz, 1 H), 6.40 (d, *J* = 2.4 Hz, 1 H), 3.77 (s, 3 H), 3.62 (t, *J* = 6.4 Hz, 2 H), 2.63 (t, *J* = 7.2 Hz, 2 H), 1.87−1.77 (m, 2 H), 1.64 (brs, 1 H), 1.02 (s, 9 H), 0.26 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.6, 154.2, 130.4, 124.5, 105.9, 105.5, 62.3, 55.2, 33.2, 25.82, 25.78, 18.2, −4.2. MS (EI) *m*/*z*: 75 (48), 193 (20), 211 (26), 221 (100), 239 (49), 296 (M, 10). HRMS for $C_{16}H_{29}O_3Si$ (M + H^+): calcd 297.1880, found 297.1884.

*Aldehyde **5n**.* Prepared according to the same procedure with **5e** from **10n** to afford **5n** as a colorless oil in 92% yield. R_f = 0.75 (petroleum/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.81

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(t, J = 1.6 Hz, 1 H), 7.04 (d, J = 8.4 Hz, 1 H), 6.46 (dd, J = 8.4 Hz, 2.4 Hz, 1 H), 6.40 (d, J = 2.4 Hz, 1 H), 3.76 (s, 3 H), 2.88−2.84 (m, 2 H), 2.72−2.68 (m, 2 H), 1.02 (s, 9 H), 0.26 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 202.3, 159.1, 154.3, 130.3, 123.2, 105.7, 105.5, 55.2, 44.3, 25.7, 22.9, 18.2, −4.2. MS (EI) m/z: 75 (63), 219 (100), 237 (52), 294 (M, 15). HRMS for $C_{16}H_{27}O_3Si$ (M + H^+): calcd 295.1724, found 295.1727.

Synthesis of Aldehyde 5o. *Substituted Styrene 8o.* To a stirred solution of methyltriphenylphosphonium bromide (560 mg, 1.57 mmol) in THF (3.0 mL) at 0 °C was added potassium *tert*-butoxide (175 mg, 1.56 mmol), and the mixture was stirred for another 1 h. 2-(((*tert*-Butyldimethylsilyl)oxy)methyl)-4,5-dichlorobenzaldehyde **7o** (238 mg, 0.75 mmol) in THF (2.0 mL) was added, and the reaction mixture was warmed to room temperature. After 2 h, water was added, the aqueous layer was extracted with EtOAc (3 × 50 mL), and the combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 100:1) to afford **8o** (177 mg, 75%) as a colorless oil. R_f = 0.75 (petroleum/EtOAc = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (s, 1 H), 7.53 (s, 1 H), 6.77 (dd, J = 17.2 Hz, 10.8 Hz, 1 H), 5.66 (d, J = 17.2 Hz, 1 H), 5.38 (d, J = 10.8 Hz, 1 H), 4.72 (s, 2 H), 0.96 (s, 9 H), 0.13 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.3, 135.3, 131.8, 131.4, 130.9, 128.6, 127.3, 117.5, 62.0, 25.9, 18.4, −5.3. MS (EI) m/z: 73 (100), 115 (8), 147 (31), 211 (5), 315 (15). HRMS for $C_{15}H_{23}Cl_2OSi$ (M + H^+): calcd 317.0890, found 317.0905.

Alcohol 9o. To a stirred solution of **8o** (122 mg, 0.38 mmol) in THF (2.0 mL) under an argon atmosphere at 0 °C was added BH_3·THF (0.39 mL, 1.0 mol/L), and the mixture was stirred for 1.5 h. Then saturated $NaHCO_3$ aqueous solution (0.6 mL) and H_2O_2 (0.3 mL) were added successively at 0 °C. The reaction mixture was stirred for another 3 h and then extracted with EtOAc (3 × 30 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 10:1) to afford **9o** (66 mg, 51%) as a light yellow oil. R_f = 0.50 (petroleum/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.49 (d, J = 5.2 Hz, 1 H), 7.29 (d, J = 9.6 Hz, 1 H), 4.69 (s, 2 H), 3.84 (dd, J = 10.6 Hz, 6.0 Hz, 2 H), 2.83 (t, J = 6.4 Hz, 2 H), 1.96 (brs, 1 H), 0.95 (s, 9 H), 0.14 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.5, 136.5, 131.4, 131.1, 130.4, 129.5, 62.7, 62.4, 34.5, 25.9, 18.4, −5.3. MS (EI) m/z: 75 (100), 115 (28), 149 (23), 185 (57), 247 (89), 277 (58). HRMS for $C_{15}H_{25}Cl_2O_2Si$ (M + H^+): calcd 335.0995, found 335.0993.

Aldehyde 5o. Prepared according to the same procedure with **5e** from **9o** to afford **5o** as a colorless oil with 86% yield. R_f = 0.65 (petroleum/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.71 (t, J = 1.6 Hz, 1 H), 7.50 (s, 1 H), 7.27 (s, 1 H), 4.59 (s, 2 H), 3.71 (d, J = 1.2 Hz, 2 H), 0.92 (s, 9 H), 0.10 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.8, 140.0, 132.5, 131.6, 131.3, 130.2, 129.8, 62.7, 46.7, 25.8, 18.3, −5.4. MS (EI) m/z: 57 (40), 73 (75), 75 (100), 149 (5), 201 (2), 275 (3). HRMS for $C_{15}H_{23}Cl_2O_2Si$ (M + H^+): calcd 333.0839, found 333.0842.

Synthesis of Aldehyde 5p. *Compound 8p.* Prepared according to the same procedure with **8o** from 4-(((*tert*-butyldimethylsilyl)oxy)-methyl)furan-3-carbaldehyde to afford **8p** as a colorless oil with 71% yield. R_f = 0.85 (petroleum/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45 (s, 1 H), 7.34 (d, J = 0.4 Hz, 1 H), 6.56 (dd, J = 18.0 Hz, 11.2 Hz, 1 H), 5.51 (dd, J = 18.0 Hz, 1.2 Hz, 1 H), 5.20 (dd, J = 11.2 Hz, 1.2 Hz, 1 H), 4.70 (d, J = 0.4 Hz, 2 H), 0.96 (s, 9 H), 0.12 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 141.3, 141.0, 126.5, 124.3, 123.6, 114.7, 57.0, 25.8, 18.3, −5.3. MS (EI) m/z: 57 (100), 85 (21), 139 (12), 193 (20), 221 (52). HRMS for $C_{13}H_{22}O_2SiNa$ (M + Na^+): calcd 261.1281, found 261.1277.

Alcohol 9p. Prepared according to the same procedure with **9o** from **8p** to afford **9p** as a colorless oil with 65% yield. R_f = 0.60 (petroleum/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33 (s, 1 H), 7.26 (s, 1 H), 4.56 (s, 2 H), 3.78 (t, J = 6.0 Hz, 2 H), 2.70 (t, J = 6.0 Hz, 2 H), 2.41 (brs, 1 H), 0.92 (s, 9 H), 0.10 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.81, 140.76, 124.9, 121.3, 62.5, 56.1, 27.1, 25.9, 18.3, −5.3. MS (EI) m/z: 57 (40), 75 (100), 79 (22), 107 (14), 169 (28), 221 (21), 239 (10). HRMS for $C_{13}H_{25}O_3Si$ (M + H^+): calcd 257.1567, found 257.1564.

Aldehyde 5p. Prepared according to the same procedure with **5e** from **9p** to afford **5p** as a colorless oil with 90% yield. R_f = 0.75 (petroleum/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.73 (t, J = 2.0 Hz, 1 H), 7.37 (s, 1 H), 7.36 (s, 1 H), 4.54 (s, 2 H), 3.56 (d, J = 0.8 Hz, 2 H), 0.90 (s, 9 H), 0.08 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.9, 141.7, 140.4, 125.1, 115.4, 56.3, 38.6, 25.9, 18.3, −5.4. MS (EI) m/z: 75 (100), 95 (14), 123 (10), 139 (6), 183 (8), 197 (12). HRMS for $C_{13}H_{23}O_3Si$ (M + H^+): calcd 255.1411, found 255.1412.

Synthesis of Sulfone 6b. *Alcohol 13.* To a stirred solution of **12** (1.13 g, 2.47 mmol) in DMF (6.0 mL) were added imidazole (503 mg, 7.4 mmol) and *tert*-butyldimethylsilyl chloride (557 mg, 3.71 mmol), and the mixture was stirred for 6 h at 60 °C. The reaction mixture was poured into water and extracted with EtOAc, and the organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 6:1) to afford **13** (817 mg, 65%) as a colorless oil. R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{26}_D$ = +4.6 (c = 19.5, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.72−7.70 (m, 4 H), 7.46−7.38 (m, 6 H), 4.03−3.97 (m, 1 H), 3.94−3.83 (m, 4 H), 3.58 (d, J = 5.6 Hz, 2 H), 3.37 (s, 1 H), 2.50 (brs, 1 H), 1.94−1.86 (m, 1 H), 1.64−1.58 (m, 1 H), 1.46−1.40 (m, 1 H), 1.37 (s, 3 H), 1.09 (s, 9 H), 1.05 (d, J = 6.8 Hz, 3 H), 0.95 (s, 9 H), 0.18 (s, 3 H), 0.11 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.6, 134.0, 129.5, 127.6, 110.5, 76.7, 68.4, 68.3, 64.8, 64.5, 39.7, 32.6, 26.9, 26.1, 20.0, 19.3, 18.4, 17.7, −4.2, −4.9. MS (EI) m/z: 87 (82), 199 (47), 283 (100), 341 (14), 411 (18). HRMS for $C_{32}H_{52}O_5Si_2Na$ (M + Na^+): calcd 595.3245, found 595.3242.

Ether 14. To a solution of NaI (750 mg, 5.0 mmol) in DME (3.0 mL) under an argon atmosphere at room temperature was added MOMCl (0.38 mL, 5.0 mmol), and the mixture was stirred for 0.5 h. Then a solution of compounds **13** (286 mg, 0.5 mmol) and DIPEA (1.04 mL, 6.0 mmol) in DME (2.0 mL) was added, and the mixture was stirred for 1 h at room temperature. The solution was heated for 12 h at 100 °C before it was quenched with the saturated aqueous $NaHCO_3$ at room temperature. The aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were washed successively with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 10:1) to afford **14** as an oil (308 mg, 71%). R_f = 0.45 (petroleum/EtOAc = 8:1). $[\alpha]^{26}_D$ = −2.4 (c = 12.8, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.75−7.69 (m, 4 H), 7.45−7.37 (m, 6 H), 4.73 (d, J = 6.8 Hz, 1 H), 4.61 (d, J = 6.8 Hz, 1 H), 3.98−3.94 (m, 1 H), 3.91−3.81 (m, 3 H), 3.74−3.70 (m, 1 H), 3.65 (dd, J = 9.6 Hz, 4.0 Hz, 1 H), 3.53 (d, J = 3.6 Hz, 1 H), 3.46 (dd, J = 9.6 Hz, 7.2 Hz, 1 H), 3.36 (s, 3 H), 1.91−1.85 (m, 1 H), 1.80−1.73 (m, 1 H), 1.50−1.43 (m, 1 H), 1.37 (s, 3 H), 1.10 (s, 9 H), 1.07 (d, J = 7.6 Hz, 3 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.05 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.6, 134.1, 129.4, 127.6, 110.7, 96.9, 76.8, 68.6, 64.7, 55.8, 35.6, 32.7, 26.9, 26.0, 21.1, 19.3, 18.2, 18.1, −4.6, −4.9. MS (EI) m/z: 87 (100), 159 (18), 199 (10), 245 (10), 283 (6), 411 (4), 453 (2). HRMS for $C_{34}H_{56}O_6Si_2Na$ (M + Na^+): calcd 639.3508, found 639.3518.

Alcohol 16. To a solution of **14** (846 mg, 1.37 mmol) in methanol (5.0 mL) under an argon atmosphere was added NH_4F (1.063 g, 27.47 mmol), and the mixture was refluxed for 24 h. After the solvent was removed, the residue was dissolved in EtOAc (200 mL), and the organic phase was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum/EtOAc = 3:1) to afford compound **16** (369 mg, 71%) as an oil. R_f = 0.25 (petroleum/EtOAc = 3:1). $[\alpha]^{26}_D$ = −33.6 (c = 33.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.74 (d, J = 6.8 Hz, 1 H), 4.59 (d, J = 6.8 Hz, 1 H), 3.94−3.82 (m, 4 H), 3.77−3.73 (m, 1 H), 3.53−3.43 (m, 3 H), 3.36 (s, 3 H), 2.50 (brs, 1 H), 1.88−1.84 (m, 1 H), 1.71−1.64 (m, 1 H), 1.56−1.49 (m, 1 H), 1.32 (s, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 0.88 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.6, 97.2, 76.9, 76.6, 67.7, 64.7, 64.6, 55.7, 36.9, 32.2, 25.9, 20.6,

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18.1, 18.0, −4.7, −4.8. MS (EI) *m/z*: 87 (100), 131 (16), 159 (8), 259 (6), 317 (1). HRMS for $C_{18}H_{38}O_6SiNa$ (M + Na^+): calcd 401.2330, found 401.2340.

Iodine ***18***. To a solution of **16** (1.618g, 4.28 mmol) in toluene (10.0 mL) under argon atmosphere wer added successively Ph_3P (1.458 g, 5.56 mmol), imidazole (407 mg, 5.99 mmol), and I_2 (1.522 g, 5.99 mmol), and the mixture was stirred at rt for 10 min. After being quenched by the addition of the saturated aqueous $Na_2S_2O_3$ at 0 °C, the organic phase was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layers were washed successively with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 50:1) to afford compound **18** (1.931g, 92%) as an oil, which was immediately used in the next step. R_f = 0.70 (petroleum/EtOAc = 4:1). $[\alpha]^{27}_D$ = −40.0 (*c* = 1.3, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.78 (d, *J* = 6.8 Hz, 1 H), 4.59 (d, *J* = 6.8 Hz, 1 H), 4.00−3.88 (m, 4 H), 3.69−3.65 (m, 1 H), 3.51 (d, *J* = 4.4 Hz, 1 H), 3.39 (s, 3 H), 3.38−3.37 (m, 1 H), 3.21 (dd, *J* = 9.6 Hz, 6.4 Hz, 1 H), 1.67−1.53 (m, 3 H), 1.36 (s, 3 H), 1.03 (d, *J* = 6.4 Hz, 3 H), 0.92 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.5, 97.0, 75.8, 64.83, 64.79, 56.0, 39.2, 31.0, 26.0, 22.0, 21.1, 18.2, 17.5, −4.6, −4.7. MS (EI) *m/z*: 85 (46), 87 (100), 131 (18), 281 (18), 303 (5). HRMS for $C_{18}H_{37}IO_5SiNa$ (M + Na^+): calcd 511.1347, found 511.1341.

Sulfone ***6b***. To a solution of **18** (482 mg, 0.988 mmol) in DMF (6.0 mL) was added $PhSO_2Na$ (324 mg, 1.975 mmol), and the mixture was stirred for 2 days at room temperature. The solution was diluted with ether (150 mL) and then washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 8:1) to afford compound **6b** (402 mg, 81%) as an oil. R_f = 0.50 (petroleum/EtOAc = 3:1). $[\alpha]^{27}_D$ = −16.0 (*c* = 2.5, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.93 (d, *J* = 7.2 Hz, 2 H), 7.67−7.63 (m, 1 H), 7.59−7.55 (m, 2 H), 4.64 (d, *J* = 6.8 Hz, 1 H), 4.51 (d, *J* = 6.8 Hz, 1 H), 3.95−3.83 (m, 4 H), 3.56−3.52 (m, 2 H), 3.35 (s, 3 H), 3.29 (dd, *J* = 14.0 Hz, 2.8 Hz, 1 H), 2.91 (dd, *J* = 14.0 Hz, 9.6 Hz, 1 H), 2.32 (brs, 1 H), 1.74−1.68 (m, 1 H), 1.62−1.57 (m, 1 H), 1.31 (s, 3 H), 1.19 (d, *J* = 6.4 Hz, 3 H), 0.87 (s, 9 H), 0.08 (s, 3 H), 0.06 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.6, 133.4, 129.2, 127.8, 110.4, 97.4, 65.1, 64.7, 62.1, 56.0, 39.4, 26.0, 25.7, 21.4, 20.7, 18.1, −4.7, −4.8. MS (EI) *m/z*: 87 (100), 131 (13), 225 (10), 271 (6), 297 (7), 339 (3). HRMS for $C_{24}H_{46}O_7NSSi$ (M + NH_4^+): calcd 520.2759, found 520.2754.

Synthesis of Sulfone 6c. *Ether* ***15***. Prepared according to the same procedurte with **9e** from **12** to afford **15** as a colorless oil in 30% yield. R_f = 0.62 (petroleum/EtOAc = 8:1). $[\alpha]^{21}_D$ = −4.6 (*c* = 4.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.69−7.66 (m, 4 H), 7.44−7.35 (m, 6 H), 3.98−3.81 (m, 5 H), 3.61 (dd, *J* = 9.6 Hz, 4.0 Hz, 1 H), 3.50 (d, *J* = 2.4 Hz, 1 H), 3.30 (dd, *J* = 9.6 Hz, 8.0 Hz, 1 H), 1.84−1.73 (m, 2 H), 1.36 (s, 3 H), 1.34−1.27 (m, 1 H), 1.06 (s, 9 H), 1.06 (d, *J* = 6.0 Hz, 3 H), 0.89 (s, 9 H), 0.82 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.06 (s, 3 H), −0.03 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.6, 134.1, 134.0, 129.4, 127.5, 110.8, 71.9, 69.3, 65.6, 64.4, 36.8, 32.6, 26.9, 25.9, 22.5, 19.3, 18.1, 18.0, 17.9, −3.8, −4.4, −4.5, −5.0. MS (EI) *m/z*: 57 (16), 87 (100), 147 (4), 199 (30), 289 (7), 413 (6). HRMS for $C_{38}H_{66}O_5Si_3Na$ (M + Na^+): calcd 709.4110, found 709.4106.

Alcohol ***17***. To a solution of **15** (800 mg, 1.30 mmol) in methanol (5.0 mL) under an argon atmosphere was added NH_4F (962 mg, 26 mmol), and the mixture was refluxed for 24 h. After the solvent was removed, the residue was dissolved in EtOAc (150 mL), and the organic phase was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum/EtOAc = 3:1) to afford compound **17** (368 mg, 75%) as an oil. R_f = 0.35 (petroleum/EtOAc = 3:1). $[\alpha]^{21}_D$ = −0.9 (*c* = 11.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.02−3.84 (m, 5 H), 3.65 (d, *J* = 2.8 Hz, 1 H), 3.42 (d, *J* = 6.0 Hz, 2 H), 2.05−1.90 (m, 2 H), 1.81 (brs, 1 H), 1.38 (s, 3 H), 1.25 (dt, *J* = 13.6 Hz, 7.2 Hz, 1 H), 0.96 (d, *J* = 6.8 Hz, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.093 (s, 6 H), 0.088 (s, 3 H), 0.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.8, 78.1, 72.2, 68.3, 66.1, 64.1, 37.3, 31.9, 25.9, 25.8, 23.0, 18.1, 17.9, 17.7, −4.0, −4.6, −4.8. MS (EI) *m/z*: 85 (63), 87 (100), 159 (10), 217 (4), 289 (3). HRMS for $C_{22}H_{48}O_5Si_2Na$ (M + Na^+): calcd 471.2932, found 471.2927.

Iodine ***19***. To a solution of **17** (467 mg, 1.04 mmol) in toluene (5.0 mL) under an argon atmosphere were added successively Ph_3P (354 mg, 1.35 mmol), imidazole (99 mg, 1.46 mmol), and I_2 (371 mg, 1.46 mmol), and the mixture was stirred at rt for 10 min. After being quenched by the addition of the saturated aqueous $Na_2S_2O_3$ at 0 °C, the organic phase was separated and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layers were washed successively with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 50:1) to afford compound **19** (360 mg, 98%) as an oil, which was immediately used in the next step. R_f = 0.85 (petroleum/EtOAc = 8:1). $[\alpha]^{22}_D$ = −7.4 (*c* = 23.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.00−3.77 (m, 5 H), 3.59 (d, *J* = 2.8 Hz, 1 H), 3.29 (dd, *J* = 9.6 Hz, 3.2 Hz, 1 H), 2.99 (dd, *J* = 9.2 Hz, 7.6 Hz, 1 H), 1.85−1.78 (m, 1 H), 1.74−1.70 (m, 1 H), 1.49−1.43 (m, 1 H), 1.35 (s, 3 H), 1.04 (d, *J* = 6.4 Hz, 3 H), 0.91 (s, 9 H), 0.89 (s, 9 H), 0.10 (s, 9 H), 0.09 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.5, 77.6, 72.3, 66.1, 64.2, 39.8, 31.5, 26.0, 25.9, 23.1, 21.7, 18.1, 18.0, 17.2, −3.7, −4.6, −4.8. MS (EI) *m/z*: 115 (4), 131 (6), 159 (3), 289 (5), 327 (9), 401 (1). HRMS for $C_{22}H_{47}IO_4Si_2Na$ (M + Na^+): calcd 581.1950, found 581.1944.

Sulfone ***6c***. To a solution of **19** (349 mg, 0.72 mmol) in DMF (5.0 mL) was added $PhSO_2Na$ (236 mg, 1.44 mmol), and the mixture was stirred for 2 days at room temperature. The solution was diluted with ether (150 mL), washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 8:1) to afford compound **6c** (294 mg, 82%) as an oil. R_f = 0.30 (petroleum/EtOAc = 4:1). $[\alpha]^{22}_D$ = −6.3 (*c* = 23.7, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.89−7.87 (m, 2 H), 7.63−7.59 (m, 1 H), 7.55−7.51 (m, 2 H), 3.89−3.69 (m, 5 H), 3.55 (d, *J* = 2.8 Hz, 1 H), 3.08 (dd, *J* = 13.6, 2.4 Hz, 1 H), 2.86 (dd, *J* = 14.0 Hz, 10.8 Hz, 1 H), 2.35−2.32 (m, 1 H), 1.87−1.80 (m, 1 H), 1.36 (dt, *J* = 13.6 Hz, 6.8 Hz, 1 H), 1.29 (s, 3 H), 1.18 (d, *J* = 6.4 Hz, 3 H), 0.84 (s, 9 H), 0.81 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 6 H), 0.02 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.6, 133.3, 129.2, 127.7, 110.3, 77.5, 71.9, 66.0, 64.1, 63.2, 41.0, 25.8, 25.7, 25.7, 25.5, 23.1, 20.3, 17.9, 17.8, −3.9, −4.7, −4.9, −5.0. MS (EI) *m/z*: 87 (100), 135 (9), 289 (30), 341 (52), 415 (1). HRMS for $C_{28}H_{53}O_6SSi_2$ (M + H^+): calcd 573.3096, found 573.3104.

General Procedure for Synthesis of Substrates. To a solution of sulfone (0.24 mmol) in dried THF (2.0 mL) under an argon atmosphere was added *n*-BuLi (0.26 mmol, 1.6 M in hexane) at −78 °C. The mixture was stirred for 30 min at 0 °C. Then a solution of the corresponding aldehyde (0.38 mmol) in dried THF (2.0 mL) was added dropwise to the mixture at −78 °C. The reaction was stirred until the starting material disappeared (monitored by TLC), and then it was quenched with aqueous NH_4Cl solution. The aqueous layer was extracted with Et_2O (3 × 30 mL), and the combined organic phase was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified (petroleum/EtOAc = 10:1) to afford a mixture of compounds. To a stirred solution of the mixture in CH_2Cl_2 (10.0 mL) under an argon atomosphere were added $NaHCO_3$ (1.02 mmol) and Dess−Martin reagent (0.29 mmol) at 0 °C. After the addition was complete, the cooling bath was removed, and the reaction mixture was warmed to room temperature. After 0.5 h of stirring at rt, the mixture was diluted with Et_2O and poured into a 1:1 mixture of saturated aqueous $NaHCO_3$ and $Na_2S_2O_3$. The mixture was extracted with Et_2O and washed successively with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 10:1) to afford the mixture of products as an oil. To a solution of this product mixtures in dried THF (2.0 mL) under an argon atmosphere was added SmI_2 (9.6 mL, 0.1 M in THF) at −78 °C. The reaction was stirred for 10 min until the starting material disappeared. The reaction was quenched with saturated aqueous NH_4Cl solution. The aqueous layer was extracted with Et_2O (3 × 10

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mL), and the combined organic phase was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified on silica gel (petroleum/EtOAc = 10:1) to afford the corresponding substates **2a**–**p**.

Compound **2a**: colorless oil, 68% yield (three steps). R_f = 0.70 (petroleum/EtOAc = 3:1). $[\alpha]^{26}_D$ = +30.7 (*c* = 1.6, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.80 (d, *J* = 6.8 Hz, 1 H), 4.68 (d, *J* = 6.4 Hz, 1 H), 4.03–3.96 (m, 2 H), 3.92–3.89 (m, 3 H), 3.60 (t, *J* = 6.4 Hz, 2 H), 3.53 (d, *J* = 3.2 Hz, 1 H), 3.41 (s, 3 H), 2.46–2.38 (m, 3 H), 2.18–2.15 (m, 2 H), 1.72–1.58 (m, 3 H), 1.53–1.45 (m, 2 H), 1.43–1.42 (m, 1 H), 1.39 (s, 3 H), 0.92 (d, *J* = 6.0 Hz, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.04 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.7, 110.8, 97.8, 81.4, 70.9, 65.5, 64.6, 62.8, 55.8, 50.0, 43.2, 41.1, 32.3, 26.1, 25.94, 25.88, 22.6, 20.8, 20.2, 18.3, 18.0, −3.9, −4.7, −5.3. MS (EI) *m*/*z*: 131 (17), 169 (16), 199 (10), 283 (5), 413 (3). HRMS for $C_{29}H_{60}O_7Si_2Na$ (M + Na^+): calcd 599.3770, found 599.3774.

Compound **2b**: colorless oil, 61% yield (three steps). R_f = 0.65 (petroleum/EtOAc = 3:1). $[\alpha]^{19}_D$ = +15.0 (*c* = 2.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.81 (d, *J* = 6.4 Hz, 1 H), 4.69 (d, *J* = 6.4 Hz, 1 H), 4.03–3.97 (m, 2 H), 3.94–3.90 (m, 3 H), 3.61 (t, *J* = 6.0 Hz, 2 H), 3.53 (d, *J* = 3.6 Hz, 1 H), 3.41 (s, 3 H), 2.53–2.42 (m, 3 H), 2.22–2.15 (m, 2 H), 1.81–1.68 (m, 3 H), 1.46–1.42 (m, 1 H), 1.40 (s, 3 H), 0.93 (d, *J* = 6.0 Hz, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.04 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.6, 110.7, 97.8, 81.5, 70.9, 65.5, 64.6, 62.1, 55.9, 50.1, 41.2, 39.7, 26.7, 25.98, 25.96, 25.92, 22.6, 20.7, 18.3, 18.0, −3.9, −4.7, −5.4. MS (EI) *m*/*z*: 131 (11), 185 (22), 269 (6), 381 (3), 443 (1). HRMS for $C_{28}H_{58}O_7Si_2Na$ (M + Na^+): calcd 585.3613, found 585.3608.

Compound **2c**, colorless oil, 58% yield (three steps). R_f = 0.70 (petroleum/EtOAc = 3:1). $[\alpha]^{22}_D$ = +16.0 (*c* = 2.5, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.81 (d, *J* = 6.8 Hz, 1 H), 4.69 (d, *J* = 6.4 Hz, 1 H), 4.03–3.94 (m, 2 H), 3.93–3.90 (m, 3 H), 3.62–3.58 (m, 2 H), 3.53 (d, *J* = 3.6 Hz, 1 H), 3.41 (s, 3 H), 2.46–2.36 (m, 3 H), 2.18–2.16 (m, 2 H), 1.73–1.69 (m, 1 H), 1.62–1.42 (m, 5 H), 1.40 (s, 3 H), 1.36–1.30 (m, 2 H), 0.93 (d, *J* = 6.0 Hz, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.05 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.7, 110.8, 97.9, 81.5, 70.9, 65.5, 64.6, 63.0, 62.9, 55.9, 50.1, 43.5, 41.2, 32.7, 26.00, 25.96, 25.5, 23.6, 22.6, 20.7, 18.3, 18.1, −3.9, −4.7, −5.3. MS (EI) *m*/*z*: 131 (15), 185 (8), 213 (13), 371 (2), 427 (3). HRMS for $C_{30}H_{62}O_7Si_2Na$ (M + Na^+): calcd 613.3926, found 613.3933.

Compound **2d**: colorless oil, 52% yield (three steps). R_f = 0.75 (petroleum/EtOAc = 3:1). $[\alpha]^{27}_D$ = +40.0 (*c* = 2.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.80 (d, *J* = 6.4 Hz, 1 H), 4.68 (d, *J* = 6.4 Hz, 1 H), 4.03–3.96 (m, 2 H), 3.92–3.89 (m, 3 H), 3.54 (d, *J* = 3.6 Hz, 1 H), 3.46 (dd, *J* = 9.6 Hz, 4.8 Hz, 1 H), 3.41 (s, 3 H), 3.37 (dd, *J* = 9.6 Hz, 6.0 Hz, 1 H), 2.62–2.55 (m, 1 H), 2.48–2.42 (m, 1 H), 2.18–2.11 (m, 4 H), 1.73–1.67 (m, 1 H), 1.44–1.38 (m, 1 H), 1.40 (s, 3 H), 0.92 (d, *J* = 6.0 Hz, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.88 (d, *J* = 6.0 Hz, 3 H), 0.11 (s, 3 H), 0.08 (s, 3 H), 0.033 (s, 3 H), 0.027 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.4, 110.8, 97.8, 81.5, 70.9, 67.4, 65.5, 64.6, 55.8, 50.5, 47.0, 41.2, 31.8, 26.0, 25.9, 22.6, 20.7, 18.3, 18.0, 16.7, −3.9, −4.7, −5.4, −5.5. MS (EI) *m*/*z*: 87 (100), 131 (12), 213 (10), 243 (8), 343 (1). HRMS for $C_{29}H_{60}O_7Si_2Na$ (M + Na^+): calcd 599.3770, found 599.3762.

Compound **2e**: colorless oil, 73% yield (three steps). R_f = 0.65 (petroleum/EtOAc = 3:1). $[\alpha]^{23}_D$ = +21.3 (*c* = 30.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.98 (s, 1H), 4.87 (s, 1 H), 4.80 (d, *J* = 6.4 Hz, 1 H), 4.67 (d, *J* = 6.4 Hz, 1 H), 4.04 (d, *J* = 4.4 Hz, 1 H), 4.01–3.95 (m, 2 H), 3.92–3.88 (m, 3 H), 3.65 (dt, *J* = 8.0 Hz, 4.0 Hz, 1 H), 3.52 (d, *J* = 3.6 Hz, 1 H), 3.39 (s, 3 H), 2.44–2.33 (m, 2 H), 2.16–2.02 (m, 4 H), 1.71 (s, 3 H), 1.69–1.67 (m, 1 H), 1.46–1.40 (m, 2 H), 1.38 (s, 3 H), 1.14–1.09 (m, 1 H), 0.91 (d, *J* = 6.0 Hz, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.88 (d, *J* = 5.2 Hz, 3 H), 0.88 (s, 9H), 0.09 (s, 3 H), 0.08 (s, 3 H), 0.06 (s, 3 H), 0.05 (s, 3 H), 0.04 (s, 3 H), 0.01 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.1, 144.7, 111.9, 110.7, 97.8, 81.3, 77.5, 73.7, 70.8, 65.4, 64.6, 55.8, 50.6, 50.5, 41.0, 40.0, 26.0, 25.9, 25.8, 25.61, 25.58, 22.52, 21.2, 21.1, 20.7, 18.1, 18.01, 17.96, −3.8, −3.9, −4.7, −4.9, −5.1. MS (EI) *m*/*z*: 87 (100), 131 (10), 185 (40), 295 (8), 427 (9), 295 (8), 557 (3). HRMS for $C_{40}H_{82}O_8Si_3Na$ (M + Na^+): calcd 797.5210, found 797.5202.

Compound **2g**: colorless oil, 51% yield (three steps). R_f = 0.75 (petroleum/EtOAc = 3:1). $[\alpha]^{26}_D$ = +1.6 (*c* = 6.3, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.00–3.90 (m, 3 H), 3.87–3.83 (m, 1 H), 3.80–3.76 (m, 1 H), 3.62–3.59 (m, 3 H), 2.41–2.37 (m, 3 H), 2.15–2.07 (m, 2 H), 1.78–1.71 (m, 1 H), 1.65–1.58 (m, 2 H), 1.53–1.46 (m, 2 H), 1.40–1.32 (m, 1 H), 1.36 (s, 3 H), 0.91 (d, *J* = 4.4 Hz, 3 H), 0.90 (s, 9 H), 0.888 (s, 9 H), 0.885 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.04 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 210.6, 110.7, 77.3, 72.0, 65.9, 64.3, 62.8, 50.0, 43.1, 40.3, 32.3, 26.0, 25.91, 25.85, 23.0, 20.7, 20.2, 18.3, 18.1, 18.0, −3.7, −4.5, −4.7, −5.0, −5.3. MS (EI) *m*/*z*: 131 (15), 185 (8), 213 (13), 371 (2), 427 (3). HRMS for $C_{33}H_{70}O_6Si_3Na$ (M + Na^+): calcd 669.4372, found 669.4366.

Compound **2h**: colorless oil, 48% yield (three steps). R_f = 0.75 (petroleum/EtOAc = 3:1). $[\alpha]^{23}_D$ = +15.0 (*c* = 2.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 4.80 (d, *J* = 6.8 Hz, 1 H), 4.68 (d, *J* = 6.8 Hz, 1 H), 4.44–4.37 (m, 2 H), 4.02–3.97 (m, 2 H), 3.92–3.85 (m, 4 H), 3.80 (s, 3 H), 3.73–3.70 (m, 2 H), 3.52 (d, *J* = 3.2 Hz, 1 H), 3.38 (s, 3 H), 2.90–2.81 (m, 1 H), 2.54 (dd, *J* = 16.8 Hz, 3.2 Hz, 1 H), 2.27 (dd, *J* = 16.8 Hz, 9.6 Hz, 1 H), 2.18 (s, 3 H), 1.72–1.57 (m, 2 H), 1.40 (s, 3 H), 1.01 (d, *J* = 6.8 Hz, 3 H), 0.91 (d, *J* = 7.6 Hz, 3 H), 0.90 (s, 9 H), 0.88 (s, 9H), 0.10 (s, 3 H), 0.07 (s, 3 H), 0.052 (s, 3 H), 0.049 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 212.9, 130.7, 129.4, 113.7, 110.8, 97.8, 81.3, 77.6, 77.3, 72.0, 71.0, 65.4, 64.7, 59.1, 55.8, 55.3, 50.7, 49.9, 41.2, 34.2, 26.00, 25.95, 25.1, 22.5, 21.0, 18.3, 18.1, 12.2, −3.9, −4.7, −5.3, −5.4. MS (EI) *m*/*z*: 121 (100), 185 (5), 219 (2), 377 (1), 563 (1). HRMS for $C_{38}H_{70}O_9Si_2Na$ (M + Na^+): calcd 749.4451, found 749.4442.

Compound **2i**: colorless oil, 65% yield (three steps). R_f = 0.70 (petroleum/EtOAc = 3:1). $[\alpha]^{21}_D$ = −30.0 (*c* = 5.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.76 (d, *J* = 6.8 Hz, 1 H), 4.60 (d, *J* = 6.8 Hz, 1 H), 4.00–3.86 (m, 4 H), 3.68–3.64 (m, 1 H), 3.61 (t, *J* = 6.0 Hz, 2 H), 3.55 (d, *J* = 4.0 Hz, 1 H), 3.39 (s, 3 H), 2.55 (d, *J* = 12.4 Hz, 1 H), 2.50–2.41 (m, 2 H), 2.19–2.11 (m, 2 H), 1.81–1.74 (m, 2 H), 1.64–1.49 (m, 2 H), 1.36 (s, 3 H), 0.93 (d, *J* = 6.0 Hz, 3 H), 0.91 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.04 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.8, 110.6, 96.9, 76.6, 76.1, 64.9, 64.8, 62.2, 56.0, 49.4, 39.6, 39.4, 26.7, 26.0, 25.9, 21.2, 20.7, 18.3, 18.2, −4.7, −4.8, −5.4. MS (EI) *m*/*z*: 137 (12), 185 (7), 211 (3), 241 (10), 331 (2). HRMS for $C_{28}H_{58}O_7Si_2Na$ (M + Na^+): calcd 585.3613, found 585.3605.

Compound **2j**: colorless oil, 65% yield (three steps). R_f = 0.70 (petroleum/EtOAc = 3:1). $[\alpha]^{23}_D$ = −26.0 (*c* = 10.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.75 (d, *J* = 6.8 Hz, 1 H), 4.59 (d, *J* = 6.8 Hz, 1 H), 3.99–3.86 (m, 4 H), 3.67–3.65 (m, 1 H), 3.61 (t, *J* = 6.0 Hz, 2 H), 3.55 (d, *J* = 4.0 Hz, 1 H), 3.39 (s, 3 H), 2.55–2.47 (m, 1 H), 2.46–2.34 (m, 2 H), 2.19–2.10 (m, 2 H), 1.65–1.47 (m, 6 H), 1.35 (s, 3 H), 0.92 (d, *J* = 6.8 Hz, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.04 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.8, 110.6, 96.9, 76.6, 76.1, 64.9, 64.7, 62.9, 56.0, 49.2, 43.1, 39.4, 32.3, 26.0, 25.9, 21.2, 20.8, 20.2, 18.3, 18.2, −4.7, −4.8, −5.3. MS (EI) *m*/*z*: 151 (12), 199 (6), 255 (12), 283 (6), 413 (2), 457 (0.5). HRMS for $C_{29}H_{60}O_7Si_2Na$ (M + Na^+): calcd 599.3770, found 599.3760.

Compound **2k**: colorless oil, 54% yield (three steps). R_f = 0.70 (petroleum/EtOAc = 3:1). $[\alpha]^{26}_D$ = +5.0 (*c* = 2.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.76 (d, *J* = 6.8 Hz, 1 H), 4.60 (d, *J* = 6.8 Hz, 1 H), 4.00–3.86 (m, 4 H), 3.69–3.65 (m, 1 H), 3.55 (d, *J* = 4.4 Hz, 1 H), 3.46 (dd, *J* = 10.0 Hz, 5.2 Hz, 1 H), 3.40–3.36 (m, 1 H), 3.39 (s, 3 H), 2.61–2.52 (m, 2 H), 2.19–2.10 (m, 4 H), 1.64–1.49 (m, 2 H), 1.36 (s, 3 H), 0.93 (d, *J* = 6.4 Hz, 3 H), 0.91 (s, 9 H), 0.89 (d, *J* = 4.4 Hz, 3 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.04 (s, 3 H), 0.03 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.7, 110.7, 96.9, 76.6, 67.4, 64.9, 64.8, 56.0, 49.9, 46.9, 39.4, 31.9, 26.0, 25.9, 21.2, 20.7, 18.3, 18.2, 16.7, −4.6, −4.8, −5.4, −5.5. MS (EI) *m*/*z*: 57 (100), 71 (60), 99 (22), 127 (14), 239 (8), 267 (15), 341 (17).

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HRMS for $C_{29}H_{60}O_7Si_2Na$ ($M + Na^+$): calcd 599.3770, found 599.3762.

Compound **2l**: colorless oil, 71% yield (three steps). R_f = 0.65 (petroleum/EtOAc = 3:1). $[\alpha]^{23}_D$ = −50.0 (*c* = 10.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.96 (s, 1 H), 4.85 (s, 1 H), 4.75 (d, *J* = 6.8 Hz, 1 H), 4.59 (d, *J* = 6.8 Hz, 1 H), 4.05 (d, *J* = 3.6 Hz, 1 H), 4.00−3.85 (m, 4 H), 3.72−3.62 (m, 2 H), 3.53 (d, *J* = 4.1 Hz, 1 H), 3.37 (s, 3 H), 2.53−2.42 (m, 1 H), 2.36−2.04 (m, 5 H), 1.75 (s, 3 H), 1.63−1.45 (m, 2 H), 1.35 (s, 3 H), 1.31−1.24 (m, 1 H), 1.18−1.09 (m, 1 H), 0.90 (s, 27 H), 0.90 (d, *J* = 3.6 Hz, 3 H), 0.85 (d, *J* = 6.4 Hz, 3 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.095 (s, 3 H), 0.08 (s, 3 H), 0.05 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.2, 144.6, 111.7, 110.6, 96.9, 77.1, 76.6, 76.0, 73.6, 64.81, 64.76, 56.0, 52.1, 49.6, 39.4, 38.7, 26.01, 25.95, 25.8, 25.7, 25.4, 21.3, 21.1, 20.7, 19.2, 18.2, 18.1, 18.0, −3.6, −4.6, −4.79, −4.84, −5.1. MS (EI) *m*/*z*: 185 (21), 245 (9), 313 (16), 425 (7), 557 (2). HRMS for $C_{40}H_{82}O_8Si_3Na$ ($M + Na^+$): calcd 797.5210, found 797.5197.

Compound **2m**: colorless oil, 63% yield (three steps). R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{21}_D$ = +5.0 (*c* = 2.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.13−7.06 (m, 2 H), 6.88−6.85 (m, 1 H), 6.80 (d, *J* = 7.6 Hz, 1 H), 4.80 (d, *J* = 6.4 Hz, 1 H), 4.67 (d, *J* = 6.4 Hz, 1 H), 4.03−3.95 (m, 2 H), 3.91−3.88 (m, 3 H), 3.53 (d, *J* = 3.6 Hz, 1 H), 3.39 (s, 3 H), 2.87−2.83 (m, 2 H), 2.71−2.65 (m, 2 H), 2.46−2.39 (m, 1 H), 2.20−2.15 (m, 2 H), 1.75−1.65 (m, 1 H), 1.44−1.37 (m, 1 H), 1.39 (s, 3 H), 1.01 (s, 9 H), 0.91 (d, *J* = 6.0 Hz, 3 H), 0.90 (s, 9 H), 0.24 (s, 6 H), 0.10 (s, 3 H), 0.07 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 209.9, 153.6, 131.7, 130.2, 127.1, 121.1, 118.4, 110.8, 97.8, 81.5, 70.9, 65.5, 64.6, 55.8, 50.1, 43.6, 41.1, 26.0, 25.8, 25.1, 22.6, 20.7, 18.2, 18.0, −3.9, −4.2, −4.7. MS (EI) *m*/*z*: 131 (25), 185 (12), 247 (10), 361 (4), 461 (4). HRMS for $C_{33}H_{60}O_7Si_2Na$ ($M + Na^+$): calcd 647.3770, found 647.3766.

Compound **2n**: colorless oil, 63% yield (three steps). R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{26}_D$ = +21.4 (*c* = 4.7, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.01 (d, *J* = 8.4 Hz, 1 H), 6.43 (dd, *J* = 8.4 Hz, 2.4 Hz, 1 H), 6.37 (d, *J* = 2.4 Hz, 1 H), 4.80 (d, *J* = 6.8 Hz, 1 H), 4.67 (d, *J* = 6.8 Hz, 1 H), 4.04−3.94 (m, 2 H), 3.91−3.88 (m, 3 H), 3.75 (s, 3 H), 3.52 (d, *J* = 3.6 Hz, 1 H), 3.41 (s, 3 H), 2.81−2.72 (m, 2 H), 2.71−2.58 (m, 2 H), 2.45−2.37 (m, 1 H), 2.19−2.11 (m, 2 H), 1.72−1.65 (m, 1 H), 1.43−1.39 (m, 1 H), 1.37 (s, 3 H), 1.00 (s, 9 H), 0.90 (d, *J* = 3.2 Hz, 3 H), 0.89 (s, 9 H), 0.24 (s, 6 H), 0.10 (s, 3 H), 0.06 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.1, 158.8, 154.3, 130.4, 124.0, 110.7, 105.6, 105.5, 97.8, 81.4, 70.8, 65.4, 64.6, 55.8, 55.2, 50.1, 43.8, 41.1, 26.0, 25.9, 25.8, 25.7, 24.4, 22.6, 20.7, 18.2, 18.0, −4.0, −4.2, −4.7. MS (EI) *m*/*z*: 87 (100), 131 (19), 251 (35), 341 (22), 565 (6). HRMS for $C_{34}H_{62}O_8Si_2Na$ ($M + Na^+$): calcd 677.3875, found 677.3868.

Compound **2o**: colorless oil, 35% yield (three steps). R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{28}_D$ = +20.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52 (s, 1 H), 7.20 (s, 1 H), 4.79 (d, *J* = 6.4 Hz, 1 H), 4.67 (d, *J* = 6.4 Hz, 1 H), 4.56 (s, 2 H), 4.03−3.94 (m, 2 H), 3.92−3.86 (m, 3 H), 3.68 (s, 2 H), 3.53 (d, *J* = 3.6 Hz, 1 H), 3.38 (s, 3 H), 2.50 (d, *J* = 12.4 Hz, 1 H), 2.28−2.22 (m, 2 H), 1.74−1.67 (m, 1 H), 1.46−1.43 (m, 1 H), 1.39 (s, 3 H), 0.94 (d, *J* = 6.4 Hz, 3 H), 0.93 (s, 9 H), 0.90 (s, 9 H), 0.10 (s, 3 H), 0.09 (s, 6 H), 0.05 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 206.3, 140.1, 132.1, 131.8, 131.2, 130.8, 129.2, 110.7, 97.9, 81.7, 71.0, 65.6, 64.6, 62.3, 55.8, 49.5, 46.7, 41.0, 26.0, 25.9, 22.6, 20.8, 18.3, 18.0, −4.0, −4.8, −5.3. MS (EI) *m*/*z*: 87 (100), 131 (18), 219 (4), 315 (5), 399 (1). HRMS for $C_{33}H_{58}Cl_2O_7Si_2Na$ ($M + Na^+$): calcd 715.2990, found 715.2994.

Compound **2p**: colorless oil, 30% yield (three steps). R_f = 0.55 (petroleum/EtOAc = 3:1). $[\alpha]^{28}_D$ = +30.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33 (s, 2 H), 7.31 (s, 1 H), 4.80 (d, *J* = 6.4 Hz, 1 H), 4.68 (d, *J* = 6.4 Hz, 1 H), 4.51 (s, 2 H), 4.02−3.89 (m, 5 H), 3.54−3.53 (m, 2 H), 3.39 (s, 3 H), 2.52 (dd, *J* = 16.0 Hz, 3.2 Hz, 1 H), 2.30−2.14 (m, 2 H), 1.75−1.68 (m, 1 H), 1.45−1.42 (m, 1 H), 1.40 (s, 3 H), 0.93 (d, *J* = 6.4 Hz, 3 H), 0.90 (s, 18 H), 0.10 (s, 3 H), 0.071 (s, 3 H), 0.066 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 207.2, 141.4, 140.1, 125.2, 117.1, 110.8, 97.9, 81.5, 70.9, 65.5, 64.6, 56.6, 55.8, 49.3, 41.1, 38.6, 26.0, 25.9, 22.6, 20.7, 18.3, 18.0, −4.0, −4.7, −5.3. MS (EI) *m*/*z*: 87 (100), 131 (7), 185 (4), 269 (2), 335 (1). HRMS for $C_{31}H_{58}O_8Si_2Na$ ($M + Na^+$): calcd 637.3562, found 637.3566.

General Procedure of Synthesis of Spiroketals. To a solution of substrate (10.0 mg) in 0.4 mL of DMF/NMP (3:1) in a plastic vessel was added NH_4HF_2 at rt, and the reaction was incubated at 100 °C and monitored by TLC. After the starting material disappeared, the reaction was quenched by pouring it into water. It was extracted with EtOAc, and the combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel to afford the spiroketal compound **3a**−**p**.

Spiroketal **3a**: colorless oil, 80% yield. R_f = 0.65 (petroleum/EtOAc = 3:1). $[\alpha]^{25}_D$ = +40.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.99 (d, *J* = 6.8 Hz, 1 H), 4.79 (d, *J* = 6.4 Hz, 1 H), 4.16 (dt, *J* = 12.0 Hz, 2.8 Hz, 1 H), 4.03−3.85 (m, 5 H), 3.58−3.54 (m, 1 H), 3.46 (s, 3 H), 3.40 (d, *J* = 3.6 Hz, 1 H), 2.05−2.04 (m, 1 H), 1.95−1.87 (m, 1 H), 1.85−1.77 (m, 1 H), 1.71 (d, *J* = 12.0 Hz, 1 H), 1.60 (dd, *J* = 14.0 Hz, 5.6 Hz, 2 H), 1.56 (s, 3 H), 1.53−1.40 (m, 4 H), 1.32 (d, *J* = 13.2 Hz, 1 H), 1.21 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 110.7, 97.6, 97.4, 81.0, 64.9, 64.0, 60.3, 56.4, 40.5, 35.9, 33.4, 25.1, 25.0, 21.1, 20.7, 18.8. MS (EI) *m*/*z*: 69 (7), 125 (13), 169 (12), 211 (2), 243 (2). HRMS for $C_{17}H_{30}O_6Na$ ($M + Na^+$): calcd 353.1935, found 353.1940.

Spiroketal **3b**: colorless oil, 70% yield. R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{19}_D$ = +60.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.99 (d, *J* = 6.8 Hz, 1 H), 4.72 (d, *J* = 6.8 Hz, 1 H), 4.26 (dt, *J* = 12.0 Hz, 2.4 Hz, 1 H), 4.00−3.90 (m, 6 H), 3.45 (s, 3 H), 3.37 (d, *J* = 2.4 Hz, 1 H), 2.14−2.04 (m, 2 H), 2.00−1.89 (m, 3 H), 1.86−1.79 (m, 1 H), 1.67−1.61 (m, 1 H), 1.55−1.51 (m, 1 H), 1.45 (s, 3 H), 1.28−1.25 (m, 1 H), 1.24 (d, *J* = 7.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 110.8, 106.8, 97.3, 80.6, 67.1, 65.1, 64.8, 64.1, 56.3, 38.3, 37.2, 33.2, 25.6, 22.7, 20.9, 20.3. MS (EI) *m*/*z*: 57 (100), 87 (50), 99 (13), 127 (7), 239 (10), 267 (6), 313 (10). HRMS for $C_{16}H_{28}O_6Na$ ($M + Na^+$): calcd 339.1778, found 339.1768.

Spiroketal **3c**: colorless oil, 62% yield. R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{23}_D$ = +60.0 (*c* = 0.5, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.99 (d, *J* = 6.8 Hz, 1 H), 4.80 (d, *J* = 6.8 Hz, 1 H), 4.17−4.14 (m, 1 H), 4.02 − 3.85 (m, 5 H), 3.58−3.55 (m, 1 H), 3.47 (s, 3 H), 3.40 (d, *J* = 3.2 Hz, 1 H), 2.05 (brs, 1 H), 1.96−1.88 (m, 1 H), 1.85−1.79 (m, 1 H), 1.72 (d, *J* = 11.6 Hz, 1 H), 1.63−1.60 (m, 5 H), 1.48−1.44 (m, 6 H), 1.33 (d, *J* = 13.2 Hz, 1 H), 1.22 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 110.7, 97.6, 97.4, 80.9, 64.9, 64.8, 64.0, 60.3, 56.4, 40.4, 35.9, 33.4, 30.9, 25.1, 25.0, 21.1, 20.7, 18.8. MS (EI) *m*/*z*: 71 (54), 85 (40), 129 (10), 267 (16), 299 (4), 327 (4). HRMS for $C_{18}H_{32}O_6Na$ ($M + Na^+$): calcd 367.2091, found 367.2082.

Spiroketal **3d**: colorless oil, 75% yield. R_f = 0.55 (petroleum/EtOAc = 3:1). $[\alpha]^{23}_D$ = +50.0 (*c* = 2.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.99 (d, *J* = 6.8 Hz, 1 H), 4.72 (d, *J* = 6.8 Hz, 1 H), 4.28−4.25 (m, 1 H), 4.10 (t, *J* = 8.0 Hz, 1 H), 4.00−3.97 (m, 1 H), 3.95−3.90 (m, 3 H), 3.48−3.46 (m, 1 H), 3.45 (s, 3 H), 3.36 (d, *J* = 2.4 Hz, 1 H), 2.48 (td, *J* = 15.2 Hz, 8.0 Hz, 1 H), 2.24 (dd, *J* = 12.4 Hz, 8.0 Hz, 1 H), 2.12−2.09 (m, 1 H), 1.98−1.90 (m, 2 H), 1.52 (brs, 1 H), 1.51−1.48 (m, 1 H), 1.45 (s, 3 H), 1.31−1.26 (m, 1 H), 1.23 (d, *J* = 7.2 Hz, 3 H), 1.03 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.8, 107.6, 97.4, 80.7, 74.5, 65.1, 64.8, 64.2, 56.3, 47.4, 37.6, 33.3, 30.9, 25.6, 20.9, 20.4, 19.4. MS (EI) *m*/*z*: 71 (55), 129 (44), 239 (18), 267 (17), 313 (17), 341 (19). HRMS for $C_{17}H_{30}O_6Na$ ($M + Na^+$): calcd 353.1935, found 353.1940.

Spiroketal **3e**: colorless oil, 78% yield. R_f = 0.55 (petroleum/EtOAc = 3:1). $[\alpha]^{27}_D$ = +74.3 (*c* = 1.8, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.00 (s, 1 H), 4.94 (d, *J* = 6.8 Hz, 1 H), 4.83 (s, 1 H), 4.71 (d, *J* = 6.8 Hz, 1 H), 4.31 (brs, 1 H), 4.27 (brs, 1 H), 4.01−3.95 (m, 5 H), 3.44 (s, 3 H), 3.35 (s, 1 H), 2.14−2.05 (m, 1 H), 1.96−1.93 (m, 2 H), 1.80 (dd, *J* = 13.2 Hz, 5.2 Hz, 1 H), 1.72 (s, 3 H), 1.67−1.42 (m, 6 H), 1.40 (s, 3 H), 1.31 (d, *J* = 12.0 Hz, 1 H), 1.06 (d, *J* = 6.4 Hz, 3 H), 0.94 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.1, 111.8, 111.0, 109.9, 98.1, 82.3, 80.9, 78.5, 68.1, 64.9, 56.4, 44.2, 43.2, 41.9, 37.3, 25.4, 23.9, 21.7, 21.6, 21.3, 18.3. MS (EI) *m*/*z*: 87 (100), 113 (12), 213 (10), 243 (8), 343 (1). HRMS for $C_{22}H_{38}O_7H$ ($M + H^+$): calcd 415.2690, found 415.2694.

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Spiroketal **3f**: colorless oil, 84% yield. R_f = 0.55 (petroleum/EtOAc = 3:1). $[\alpha]^{19}_D$ = +70.6 (*c* = 4.3, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.00−4.98 (m, 2 H), 4.92 (s, 1 H), 4.74 (d, *J* = 6.4 Hz, 1 H), 4.21−4.18 (m, 1 H), 4.01−3.84 (m, 6 H), 3.45 (s, 3 H), 3.37 (d, *J* = 2.4 Hz, 1 H), 2.70 (d, *J* = 3.6 Hz, 1 H), 2.08 (brs, 1 H), 1.96 (td, *J* = 12.8 Hz, 5.4 Hz, 2 H), 1.80−1.76 (m, 1 H), 1.78 (s, 3 H), 1.67 (dd, *J* = 13.9 Hz, 5.9 Hz, 2 H), 1.52 (s, 3 H), 1.48−1.46 (m, 1 H), 1.29 (d, *J* = 13.2 Hz, 1 H), 1.21 (d, *J* = 7.2 Hz, 3 H), 0.99 (t, *J* = 12.8 Hz, 1 H), 0.87−0.78 (m, 1 H), 0.84 (d, *J* = 13.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.2, 113.7, 110.7, 98.7, 97.4, 80.8, 79.4, 70.8, 64.8, 64.7, 63.9, 56.4, 44.1, 40.3, 35.4, 33.0, 24.9, 24.8, 22.1, 21.2, 21.1, 17.6.

Spiroketal **3g**: colorless oil, 74% yield. R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{22}_D$ = −30.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.41 (s, 1 H), 4.03−3.94 (m, 4 H), 3.85 (s, 1 H), 3.66 (t, *J* = 6.0 Hz, 2 H), 2.11−2.01 (m,, 1 H), 1.82−1.75 (m, 3 H), 1.65−1.52 (m, 5 H), 1.47−1.39 (m, 1 H), 1.31 (s, 3 H), 1.27−1.21 (m, 2 H), 0.93 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 109.8, 109.5, 81.81, 81.78, 75.7, 65.3, 64.9, 62.7, 41.6, 37.4, 37.1, 32.9, 23.9, 21.6, 20.2, 19.9. MS (EI) *m*/*z*: 55 (21), 87 (100), 101 (3), 149 (2), 171 (1). HRMS for $C_{15}H_{26}O_5H$ (M + H$^+$): calcd 287.1853, found 287.1849.

Spiroketal **3h**: colorless oil, 47% yield. R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{24}_D$ = +20.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.25 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 4.78 (d, *J* = 6.8 Hz, 1 H), 4.70 (d, *J* = 6.4 Hz, 1 H), 4.46 (d, *J* = 11.6 Hz, 1 H), 4.35 (d, *J* = 11.2 Hz, 1 H), 4.04−3.92 (m, 6 H), 3.84−3.77 (m, 1 H), 3.80 (s, 3 H), 3.63 (dd, *J* = 10.8 Hz, 5.2 Hz, 1 H), 3.43 (s, 3 H), 3.37 (d, *J* = 4.4 Hz, 1 H), 2.16−2.09 (m, 2 H), 1.84 (td, *J* = 13.6 Hz, 5.6 Hz, 1 H), 1.78−1.67 (m, 1 H), 1.61−1.56 (m, 2 H), 1.52−1.49 (m, 2 H), 1.41 (s, 3 H), 1.20 (d, *J* = 7.6 Hz, 3 H), 0.95 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 159.0, 130.9, 129.1, 113.8, 110.3, 101.6, 99.4, 99.3, 97.6, 80.9, 72.3, 68.8, 65.3, 64.8, 64.0, 58.9, 56.3, 55.3, 40.2, 37.8, 33.0, 30.9, 26.0, 24.9, 21.2, 20.7, 7.3. MS (EI) *m*/*z*: 87 (100), 131 (12), 199 (16), 283 (3), 395 (2), 457 (1). HRMS for $C_{26}H_{40}O_8Na$ (M + Na$^+$): calcd 503.2615, found 503.2621.

Spiroketal **3i**: colorless oil, 46% yield. R_f = 0.55 (petroleum/EtOAc = 3:1). $[\alpha]^{27}_D$ = +40.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.74 (d, *J* = 6.8 Hz, 1 H), 4.68 (d, *J* = 6.8 Hz, 1 H), 4.19 (td, *J* = 8.4 Hz, 4.0 Hz, 1 H), 4.05−3.97 (m, 3 H), 3.95−3.84 (m, 4 H), 3.40 (s, 3 H), 2.19−2.06 (m, 3 H), 1.99−1.91 (m, 1 H), 1.89−1.84 (m, 1 H), 1.82−1.78 (m, 2 H), 1.71−1.64 (m, 1 H), 1.66−1.51 (m, 1 H), 1.47 (s, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.8, 108.0, 96.3, 76.1, 72.6, 68.2, 64.8, 63.9, 55.9, 49.5, 42.4, 26.0, 24.1, 23.8, 21.0. MS (EI) *m*/*z*: 71 (64), 113 (15), 155 (7), 239 (6), 267 (8). HRMS for $C_{16}H_{28}O_6H$ (M + H$^+$): calcd 317.1959, found 317.1965.

Spiroketal **3j**: colorless oil, 70% yield. R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{25}_D$ = +60.0 (*c* = 0.5, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.76 (d, *J* = 6.8 Hz, 1 H), 4.71 (d, *J* = 6.8 Hz, 1 H), 4.39−4.33 (m, 1 H), 4.09−4.05 (m, 1 H), 4.04−3.99 (m, 1 H), 3.98−3.89 (m, 4 H), 3.53 (d, *J* = 12.4 Hz, 1 H), 3.41 (s, 3 H), 2.10−2.04 (m, 2 H), 1.88−1.81 (m, 2 H), 1.74 (d, *J* = 14.0 Hz, 1 H), 1.66−1.62 (m, 1 H), 1.54−1.44 (m, 5 H), 1.52 (s, 3 H), 0.93 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 111.0, 97.9, 96.8, 76.2, 73.2, 64.6, 63.9, 61.0, 55.9, 52.1, 42.3, 36.5, 25.3, 24.4, 24.2, 21.2, 19.2. MS (EI) *m*/*z*: 87 (76), 149 (34), 239 (16), 267 (8), 330 (M, 3). HRMS for $C_{17}H_{30}O_6H$ (M + H$^+$): calcd 331.2115, found 331.2121.

Spiroketal **3k**: colorless oil, 74% yield. R_f = 0.55 (petroleum/EtOAc = 3:1). $[\alpha]^{23}_D$ = −40.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.74 (d, *J* = 6.8 Hz, 1 H), 4.69 (d, *J* = 6.8 Hz, 1 H), 4.05−3.90 (m, 7 H), 3.83 (t, *J* = 8.4 Hz, 1 H), 3.40 (s, 3 H), 2.38−2.28 (m, 1 H), 2.12−2.01 (m, 2 H), 1.95−1.92 (m, 1 H), 1.87 (dd, *J* = 13.2 Hz, 6.4 Hz, 1 H), 1.82−1.80 (m, 2 H), 1.55−1.51 (m, 1 H), 1.49 (s, 3 H), 1.09 (d, *J* = 6.8 Hz, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.6, 109.1, 96.4, 75.9, 74.2, 73.3, 64.7, 63.8, 55.9, 50.5, 47.6, 42.5, 32.6, 25.9, 23.9, 21.1, 18.2. MS (EI) *m*/*z*: 75 (100), 87 (44), 131 (28), 149 (8), 185 (11), 199 (10). HRMS for $C_{17}H_{30}O_6Na$ (M + Na$^+$): calcd 353.1935, found 353.1938.

Spiroketal **3l**: colorless oil, 58% yield. R_f = 0.50 (petroleum/EtOAc = 3:1). $[\alpha]^{27}_D$ = −20.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.01 (s, 1 H), 4.84 (s, 1 H), 4.74−4.70 (m, 2 H), 4.34 (s, 1 H), 4.20 (d, *J* = 5.2 Hz, 1 H), 4.02−3.92 (m, 4 H), 3.81−3.77 (m, 1 H), 3.47 (d, *J* = 2.4 Hz, 1 H), 3.42 (s, 3 H), 2.22−2.15 (m, 1 H), 2.02−1.97 (m, 1 H), 1.95−1.92 (m, 1 H), 1.90−1.81 (m, 3 H), 1.72 (s, 3 H), 1.68−1.64 (m, 1 H), 1.51 (dd, *J* = 13.6 Hz, 4.2 Hz, 2 H), 1.48−1.44 (m, 1 H), 1.37 (s, 3 H), 1.35 (s, 1 H), 1.20 (d, *J* = 7.6 Hz, 3 H), 1.07 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.1, 111.5, 110.1, 109.4, 96.7, 83.4, 76.6, 75.6, 75.0, 65.0, 64.9, 56.1, 45.7, 40.6, 38.9, 35.2, 25.3, 23.5, 22.7, 21.1, 20.4, 18.5. MS (EI) *m*/*z*: 113 (14), 213 (10), 243 (7), 275 (2). HRMS for $C_{22}H_{38}O_7Na$ (M + Na$^+$): calcd 437.2510, found 437.2515.

Spiroketal **3m**: colorless oil, 67% yield. R_f = 0.55 (petroleum/EtOAc = 3:1). dr = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.09−7.01 (m, 2 H), 6.85−6.80 (m, 2 H), 4.81 (d, *J* = 6.8 Hz, 0.80 H), 4.70−4.66 (m, 1 H), 4.61 (d, *J* = 6.8 Hz, 0.28 H), 4.51−4.48 (m, 0.37 H), 4.32 (dt, *J* = 11.6 Hz, 2.8 Hz, 1.12 H), 4.03−3.67 (m, 4 H), 3.40 (s, 2.04 H), 3.38 (s, 0.60 H), 3.32−3.16 (m, 1 H), 3.11−3.02 (m, 1 H), 2.61−2.55 (m, 1 H), 2.19−2.03 (m, 3 H), 1.85−1.72 (m, 3 H), 1.43−1.35 (m, 4 H), 1.34 (s, 1 H), 0.98 (s, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 152.6, 129.2, 128.9, 127.0, 126.8, 122.5, 120.9, 120.3, 117.2, 117.0, 110.4, 98.2, 97.8, 96.5, 83.4, 81.0, 68.0, 66.8, 65.9, 64.4, 56.3, 56.2, 39.3, 38.6, 33.3, 31.9, 31.7, 31.6, 25.7, 25.0, 21.3, 20.8, 20.7, 20.0. MS (EI) *m*/*z*: 107 (6), 173 (3), 215 (4), 289 (3), 333 (2). HRMS for $C_{21}H_{30}O_6Na$ (M + Na$^+$): calcd 401.1935, found 401.1938.

Spiroketal **3n**: white amorphous solid, 65% yield. R_f = 0.50 (petroleum/EtOAc = 3:1). dr = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.93−6.89 (m, 1 H), 6.47−6.43 (m, 1 H), 6.39−6.37 (m, 1 H), 4.82−4.60 (m, 2 H), 4.51−4.49 (m, 0.24 H), 4.33 (dt, *J* = 12.0 Hz, 2.8 Hz, 0.74 H), 4.04−3.70 (m, 7 H), 3.40 (s, 2.23 H), 3.38 (s, 0.65 H), 3.36−3.29 (m, 1 H), 3.01−2.84 (m, 1 H), 2.54−2.45 (m, 1 H), 2.18−1.99 (m, 3 H), 1.83−1.71 (m, 3 H), 1.44−1.34 (m, 4 H), 1.03 (s, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 158.8, 153.4, 129.6, 129.3, 114.7, 110.4, 107.4, 107.2, 102.1, 102.0, 98.3, 97.7, 96.5, 83.4, 81.0, 66.8, 65.9, 64.4, 63.7, 56.24, 56.15, 55.3, 39.2, 38.6, 33.3, 32.2, 31.8, 31.6, 30.9, 25.8, 25.0, 20.7, 20.6, 20.1, 20.0. MS (EI) *m*/*z*: 87 (100), 137 (15), 203 (2), 363 (3), 408 (M, 2). HRMS for $C_{22}H_{32}O_7Na$ (M + Na$^+$): calcd 431.2040, found 431.2047.

Spiroketal **3o**: white amorphous solid, 34% yield. R_f = 0.50 (petroleum/EtOAc = 3:1). $[\alpha]^{22}_D$ = +40.0 (*c* = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.14 (s, 1 H), 7.11 (s, 1 H), 5.13 (d, *J* = 15.2 Hz, 1 H), 4.77 (d, *J* = 6.4 Hz, 1 H), 4.60 (d, *J* = 6.4 Hz, 1 H), 4.58 (d, *J* = 14.8 Hz, 1 H), 4.02 (dt, *J* = 12.0 Hz, 3.2 Hz, 1 H), 3.94−3.84 (m, 4 H), 3.34 (s, 3 H), 3.28 (d, *J* = 3.6 Hz, 1 H), 2.79 (q, *J* = 16.4 Hz, 2 H), 2.36−2.21 (m, 2 H), 1.95 (dd, *J* = 14.0, 6.4 Hz, 1 H), 1.52−1.45 (m, 1 H), 1.19 (dt, *J* = 13.6, 3.2 Hz, 1 H), 1.09 (s, 3 H), 1.06 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 134.6, 132.5, 130.5, 129.4, 125.5, 110.5, 97.4, 96.9, 80.7, 69.9, 64.9, 63.9, 61.4, 56.2, 39.7, 37.6, 32.1, 21.8, 21.4, 20.2. MS (EI) *m*/*z*: 75 (21), 87 (100), 149 (14), 199 (5), 279 (3). HRMS for $C_{21}H_{28}Cl_2O_6Na$ (M + Na$^+$): calcd 469.1155, found 469.1153.

Spiroketal **3p**: white amorphous solid, 47% yield. R_f = 0.50 (petroleum/EtOAc = 3:1). $[\alpha]^{22}_D$ = +40.0 (*c* = 0.5, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (s, 1 H), 7.14 (s, 1 H), 4.93 (d, *J* = 14.8 Hz, 1 H), 4.85 (d, *J* = 7.2 Hz, 1 H), 4.68 (d, *J* = 14.2 Hz, 1 H), 4.63 (d, *J* = 6.8 Hz, 1 H), 4.18 (d, *J* = 12.8 Hz, 1 H), 3.97−3.87 (m, 4 H), 3.37 (s, 3 H), 3.34 (s, 1 H), 2.77 (d, *J* = 16.0 Hz, 1 H), 2.56 (d, *J* = 16.4 Hz, 1 H), 2.14 (brs, 1 H), 1.97−1.89 (m, 1 H), 1.80 (dd, *J* = 14.0 Hz, 6.0 Hz, 1 H), 1.68 (d, *J* = 16.4 Hz, 1 H), 1.14 (d, *J* = 13.6 Hz, 1 H), 1.30 (d, *J* = 7.2 Hz, 3 H), 1.21 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 137.7, 134.2, 118.2, 116.9, 110.6, 97.4, 96.6, 80.2, 66.2, 64.9, 63.8, 56.24, 56.19, 39.4, 32.8, 31.7, 25.0, 20.5, 20.2. MS (EI) *m*/*z*: 69 (18), 87 (100), 149 (13), 285 (10), 401 (1). HRMS for $C_{19}H_{28}O_7Na$ (M + Na$^+$): calcd 391.1727, found 391.1730.

Diverse Transformation of Spiroketal 3f. *Compound 4a.* To a solution of **3f** (31 mg, 0.075 mmol) in CH_2Cl_2 (3.0 mL) under an argon atmosphere at −78 °C was added a mixed solution of TBDPSOTf (53 μL, 0.15 mmol) and 2,6-lutidine (26 μL, 0.225 mmol). The mixture was stirred for 2 h at 0 °C and then for 5 h at room temperature before quenched with saturated $NaHCO_3$ solution. The solution was extracted with ether (3 × 30 mL), and the combined

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organic layers were washed successively with saturated $NaHCO_3$ solution and brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 10:1) to afford silyl ether **4a** (46 mg, 94%) as a colorless oil. R_f = 0.35 (petroleum/EtOAc = 6:1). $[\alpha]^{25}_D$ = +30.0 (c = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.78−7.76 (m, 2 H), 7.71−7.69 (m, 2 H), 7.39−7.25 (m, 6 H), 4.95 (d, J = 6.8 Hz, 1 H), 4.79 (d, J = 6.8 Hz, 1 H), 4.68 (s, 1 H), 4.62 (s, 1 H), 4.26−4.23 (m, 1 H), 4.09 (d, J = 6.0 Hz, 1 H), 4.03−3.87 (m, 4 H), 3.83−3.80 (m, 1 H), 3.44 (s, 3 H), 3.36 (d, J = 2.8 Hz, 1 H), 1.91−1.80 (m, 3 H), 1.74 (d, J = 12.8 Hz, 1 H), 1.64−1.1.61 (m, 2 H), 1.58 (s, 3 H), 1.49 (s, 3 H), 1.41 (dd, J = 13.6 Hz, 4.8 Hz, 1 H), 1.33 (d, J = 12.0 Hz, 1 H), 1.08 (s, 9 H), 0.99 (d, J = 6.8 Hz, 3 H), 0.94−0.91 (m, 1 H), 0.77 (d, J = 6.0 Hz, 3 H), 0.69 (dd, J = 24.8 Hz, 12.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.5, 136.3, 136.2, 134.8, 134.4, 129.3, 129.1, 127.12, 127.07, 113.6, 110.6, 98.2, 97.6, 81.4, 80.3, 71.8, 65.5, 64.8, 63.9, 56.2, 44.5, 41.3, 34.9, 33.5, 27.2, 24.9, 24.8, 22.3, 21.4, 21.1, 19.6, 19.0. MS (EI) m/z: 87 (100), 281 (3), 343 (5), 417 (1), 504 (M, 0.02). HRMS for $C_{38}H_{56}O_7SiNa$ (M + Na^+): calcd 675.3688, found 675.3684.

Compound ***4b***. To a stirred solution of **3f** (10.5 mg, 0.025 mmol) in dried DMF (1.0 mL) was added sodium hydride (1.0 mg, 0.030 mmol), followed by benzyl bromide (3.7 μL, 0.030 mmol) at 0 °C. The reaction mixture was stirred for 30 min and then quenched with the addition of H_2O. The aqueous layer was extracted with Et_2O (3 × 20 mL), and the organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified on silica gel (petroleum/EtOAc = 10:1) to afford compound **4b** (12 mg, 94%). R_f = 0.65 (petroleum/EtOAc = 3:1). $[\alpha]^{25}_D$ = +35.4 (c = 4.8, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36−7.22 (m, 5 H), 5.02 (s, 1 H), 4.99 (s, 1 H), 4.93 (d, J = 6.8 Hz, 1 H), 4.75 (d, J = 6.4 Hz, 1 H), 4.49 (d, J = 11.6 Hz, 1 H), 4.35−4.31 (m, 2 H), 4.12−4.07 (m, 1 H), 3.96−3.91 (m, 1 H), 3.88−3.79 (m, 3 H), 3.67 (d, J = 7.6 Hz, 1 H), 3.44 (s, 3 H), 3.37 (d, J = 3.2 Hz, 1 H), 2.05−2.04 (m, 1 H), 1.96−1.85 (m, 2 H), 1.75−1.74 (m, 1 H), 1.72 (s, 3 H), 1.66−1.61 (m, 2 H), 1.46 (s, 3 H), 1.38 (d, J = 13.2 Hz, 1 H), 1.30 (d, J = 13.2 Hz, 1 H), 1.25 (s, 3 H), 0.99 (t, J = 12.8 Hz, 1 H), 0.84 (d, J = 6.4 Hz, 3 H), 0.77 (dd, J = 25.2 Hz, 12.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.6, 139.3, 127.9, 127.6, 126.9, 115.2, 110.6, 98.3, 97.4, 86.8, 80.8, 70.0, 69.7, 64.8, 64.7, 63.9, 56.3, 44.0, 39.9, 35.1, 33.3, 25.4, 25.2, 22.3, 21.2, 20.6, 17.7. MS (EI) m/z: 135 (15), 199 (8), 281 (4), 410 (15), 595 (1), 652 (M, 0.01). HRMS for $C_{29}H_{44}O_7Na$ (M + Na^+): calcd 527.2979, found 527.3004.

Compound ***4c***. To a stirred solution of **3f** (21 mg, 0.0507 mmol) in dried benzene (1.0 mL) was added vanadyl acetylacetonate (3.0 mg, 0.010 mmol), followed by *tert*-butyl hydroperoxide (14 μL, 0.076 mmol) at room temperature. The reaction mixture was stirred for 10 min and then quenched by the addition of H_2O. The aqueous layer was extracted with CH_2Cl_2, and the organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified on silica gel (petroleum/EtOAc = 10:1) to afford compound **4c** (18 mg, 83%). R_f = 0.15 (petroleum/EtOAc = 5:1). $[\alpha]^{25}_D$ = +64.3 (c = 1.4, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.99 (d, J = 6.4 Hz, 1 H), 4.76 (d, J = 6.8 Hz, 1 H), 4.18 (d, J = 11.6 Hz, 1 H), 4.11−4.06 (m, 1 H), 4.02−4.00 (m, 1 H), 3.97−3.88 (m, 3 H), 3.46 (s, 3 H), 3.38 (d, J = 3.2 Hz, 1 H), 3.27 (d, J = 5.6 Hz, 1 H), 2.87 (d, J = 4.8 Hz, 1 H), 2.63 (d, J = 4.8 Hz, 1 H), 2.06−1.92 (m, 3 H), 1.78 (dd, J = 13.6 Hz, 2.4 Hz, 1 H), 1.71−1.64 (m, 2 H), 1.54 (s, 3 H), 1.51 (d, J = 13.2 Hz, 1 H), 1.42 (s, 3 H), 1.30 (d, J = 13.2 Hz, 1 H), 1.19 (d, J = 7.2 Hz, 3 H), 1.10−1.00 (m, 2 H), 0.88 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.6, 98.7, 97.5, 80.8, 76.5, 69.8, 65.1, 64.7, 63.9, 56.9, 56.4, 52.1, 44.3, 40.3, 35.3, 33.0, 24.8, 24.7, 22.1, 21.2, 20.9, 17.0. MS (EI) m/z: 87 (100), 113 (3), 281 (2), 343 (2), 399 (1). HRMS for $C_{22}H_{38}O_8Na$ (M + Na^+): calcd 453.2459, found 453.2463.

Compound ***4d***. To a stirred solution of **3f** (21 mg, 0.0507 mmol) in CH_2Cl_2 (1.0 mL) under an argon atomosphere were added $NaHCO_3$ (42 mg, 0.50 mmol) and then Dess−Martin reagent (42 mg, 0.10 mmol) at 0 °C. After the addition was complete, the cooling bath was removed, and the reaction mixture was warmed to room temperature. After the starting material disappeared, the mixture was diluted with Et_2O and poured into a 1:1 mixture of saturated aqueous $NaHCO_3$ and $Na_2S_2O_3$. The mixture was extracted with Et_2O (3 × 30 mL), and the combined organic phase was washed successively with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum/EtOAc = 10:1) to afford compound **4d** (17 mg, 81%) as a colorless oil. R_f = 0.45 (petroleum/EtOAc = 5:1). $[\alpha]^{25}_D$ = +69.2 (c = 2.6, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.13 (s, 1 H), 5.79 (s, 1 H), 5.17 (dd, J = 12.0 Hz, 2.0 Hz, 1 H), 5.00 (d, J = 6.8 Hz, 1 H), 4.74 (d, J = 6.8 Hz, 1 H), 4.17−4.14 (m, 1 H), 4.02−3.97 (m, 1 H), 3.90−3.84 (m, 3 H), 3.45 (s, 3 H), 3.37 (d, J = 2.4 Hz, 1 H), 2.10−2.06 (m, 2 H), 2.00−1.93 (m, 1 H), 1.92 (s, 3 H), 1.83−1.74 (m, 2 H), 1.66−1.61 (m, 3 H), 1.56 (s, 3 H), 1.22 (d, J = 7.2 Hz, 3 H), 1.13−1.05 (m, 2 H), 0.87 (d, J = 6.4 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 200.5, 143.1, 124.5, 110.7, 99.2, 97.3, 80.7, 70.8, 65.2, 64.8, 63.9, 56.4, 43.6, 39.8, 36.3, 33.2, 29.7, 25.2, 25.0, 22.0, 21.4, 20.4, 18.2. MS (EI) m/z: 87 (100), 111 (3), 207 (2), 281 (2), 343 (4). HRMS for $C_{22}H_{36}O_7Na$ (M + Na^+): calcd 435.2353, found 435.2350.

Compound ***4e***. After a brief oxygen purge (5 min), ozone was slowly bubbled through a solution of substrate **3f** (30 mg, 0.072 mmol) in CH_2Cl_2 (3.0 mL) until the reaction was completed. After PPh_3 (29 mg, 0.11 mmol) was added to quench the reaction, it was stirred at room temperature for 3 h. Concentration of the reaction gave a colorless oil, which was purified on silica gel (petroleum/EtOAc = 3:1) to afford compound **4e** (22 mg, 73%). R_f = 0.25 (petroleum/EtOAc = 3:1). $[\alpha]^{22}_D$ = +20.0 (c = 1.0, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.96 (d, J = 6.8 Hz, 1 H), 4.76 (d, J = 6.4 Hz, 1 H), 4.31 (dt, J = 12.0 Hz, 2.8 Hz, 1 H), 4.08−3.86 (m, 6 H), 3.44 (s, 3 H), 3.34 (d, J = 3.2 Hz, 1 H), 2.36 (s, 3 H), 2.06−2.00 (m, 2 H), 1.92−1.85 (m, 1 H), 1.75−1.71 (m, 1 H), 1.62−1.57 (m, 2 H), 1.51 (s, 3 H), 1.45 (dd, J = 13.6 Hz, 1.6 Hz, 1 H), 1.29−1.25 (m, 2 H), 1.07 (d, J = 7.2 Hz, 3 H), 0.98 (t, J = 13.2 Hz, 1 H), 0.87 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 208.4, 110.6, 98.8, 97.5, 80.8, 79.3, 70.4, 65.4, 64.7, 63.8, 56.4, 43.9, 40.0, 34.5, 33.1, 26.1, 24.7, 24.6, 22.1, 21.1, 20.4. MS (EI) m/z: 75 (20), 87 (100), 199 (9), 279 (4), 341 (3). HRMS for $C_{21}H_{36}O_8Na$ (M + Na^+): calcd 439.2302, found 439.2319.

Compound ***4f***. To a stirred solution of **3f** (52 mg, 0.126 mmol) in dried THF (2.0 mL) was added 40% HF (0.5 mL, 0.252 mmol) at 0 °C. The reaction mixture was stirred for 3 h and then quenched by the addition of saturated $NaHCO_3$ solution. The aqueous layer was extracted with Et_2O, and the organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified on silica gel (petroleum/EtOAc = 10:1) to afford compound **4f** (26 mg, 56%). R_f = 0.60 (petroleum/EtOAc = 3:1). $[\alpha]^{27}_D$ = +83.0 (c = 6.8, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.98 (s, 1 H), 4.93 (s, 1 H), 4.71 (q, J = 6.8 Hz, 2 H), 4.19 (d, J = 11.6 Hz, 1 H), 3.95 (d, J = 3.2 Hz, 1 H), 3.83 (brs, 1 H), 3.47 (ddd, J = 11.6 Hz, 6.4 Hz, 2.0 Hz, 1 H), 3.41 (s, 3 H), 2.56 (d, J = 3.2 Hz, 1 H), 2.28 (s, 3 H), 2.08 (brs, 1 H), 1.96−1.88 (m, 1 H), 1.80 (s, 3 H), 1.72 (dd, J = 13.2 Hz, 2.4 Hz, 1 H), 1.65 (dd, J = 14.0 Hz, 6.0 Hz, 1 H), 1.49−1.37 (m, 3 H), 1.26 (d, J = 12.8 Hz, 1 H), 1.19 (d, J = 7.6 Hz, 3 H), 1.00−0.88 (m, 1 H), 0.84 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 210.0, 144.1, 113.3, 98.6, 97.2, 84.8, 78.6, 71.0, 66.8, 56.3, 43.9, 39.8, 35.3, 31.6, 28.1, 24.70, 24.68, 22.0, 20.9, 18.0. MS (EI) m/z: 69 (100), 113 (82), 167 (40), 237 (74), 253 (46), 299 (88), 327 (10). HRMS for $C_{20}H_{34}O_6Na$ (M + Na^+): calcd 393.2248, found 393.2251.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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