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Access to Wieland−Miescher Diketone-Derived Building Blocks by Stereoselective Construction of the C-9 Quaternary Carbon Center Using the Mukaiyama Aldol Reaction

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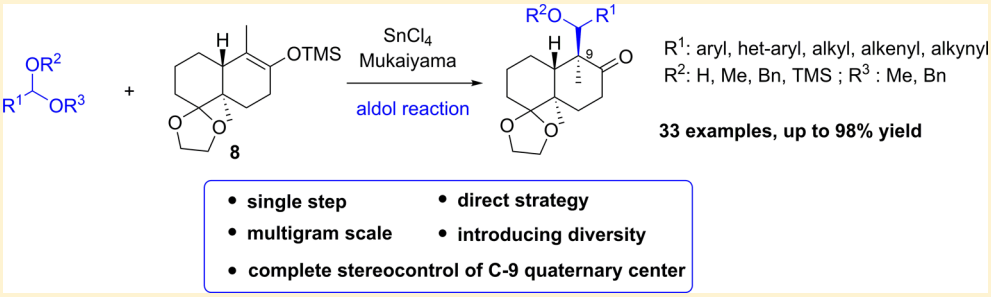
Supporting Information

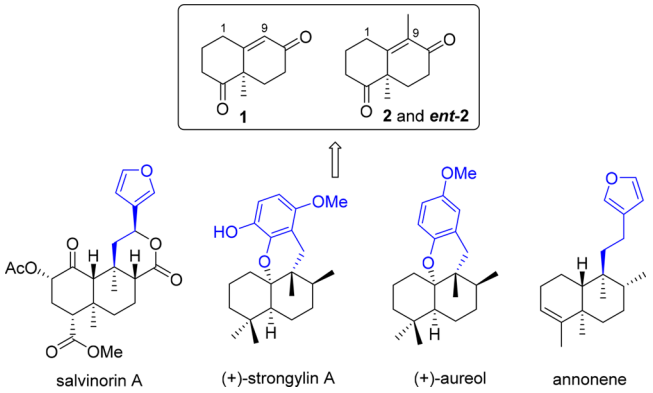


ABSTRACT: The Mukaiyama aldol reaction has been used to efficiently install a lateral chain at the C-9 position of the Wieland−Miescher ketone derivative **3** within two steps, representing a shortcut compared to that of the classical sequences. The treatment of the silylated enol ether **8** with a wide range of acetals in the presence of tin tetrachloride led to a the diastereoselective construction of the C-9 quaternary center of 33 new building blocks derived from the Wieland−Miescher ketone derivative **3**.

INTRODUCTION

The Wieland−Miesch diketone **1** and its C-9 methylated analogues **2** or ***ent*-2** are well-known building blocks for the total synthesis of natural products (Scheme 1).[1] These easily accessible synthons are often employed for the versatility of their functionalization. Thus, several terpenoids, such as the extensively studied neoclerodane diterpenoid salvinorin A, which is the first nonalcaloid agonist of κ-opioid receptor (KOR), have been synthesized from **2** by Hagiwara et al.[2] Marine natural sesquiterpenoids, such as (+)-aureol and (+)-strongylin A, have also been synthesized from diketone **2** or its enantiomer ***ent*-2**.[3]

Scheme 1. Natural Clerodane Diterpenoids and Their Common Building Blocks



A common structural feature of these terpenoids is a lateral chain, such as 2-(aryl/hetaryl)ethyl or a benzyl moiety substituted or not with an oxygen-atom and positioned at a quaternary center. The general and direct introduction of the benzyl chain on the protected ketone **3** by Birch reductive alkylation, using the corresponding halogenated electrophile,[4] cannot be efficiently applied in the case of an 2-(aryl/hetaryl)ethyl moiety according to the predominant elimination of the halogen rather than alkylation reaction (Scheme 2a).[5] Therefore, installation of such chains requires lengthy sequences starting from the monoprotected ketone **3.** The aldehydes **4** (route 1) are prepared using Birch reductive alkylation of **3**, either with ethyl 2-iodoacetate followed by sequential reduction and oxidation of the resulting ester[2c] or with allyl bromide followed by an oxidative cleavage−oxidation sequence of the resulting allyl group.[2a] The aldehydes **6** (route 2) are obtained from **3** in three steps using a Birch reductive *O*-silylation followed by a Mukaiyama-type aldol reaction of the resulting silyl enol ether with formaldehyde and subsequent oxidation.[3d,6] The construction of the side chain ends with the addition of aryl lithium or titanium species on aldehydes **4** or **6**,

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Scheme 2. General Strategy for C-9 Functionalization and Comparison with Previous Literature

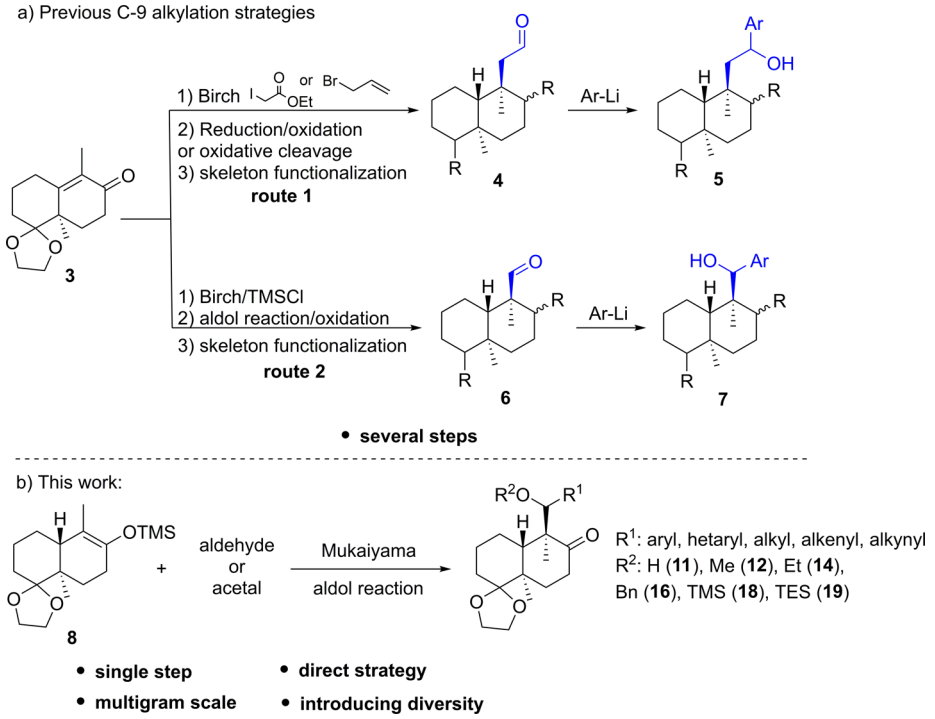
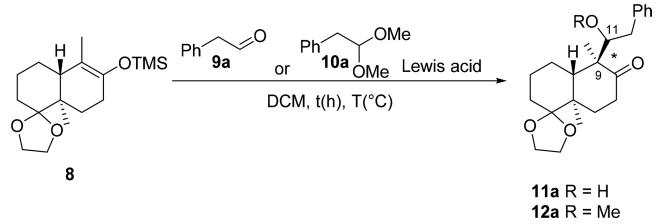


Table 1. Optimization of Mukaiyama Aldol Reaction of Aldehyde 9a and Its Corresponding Dimethyl Acetal 10a with Silyl Enol Ether 8



entry	E^+	Lewis acid/base (equiv)	time (h)	temp (°C)	11a/12a	yield[c] (%)
method A[a]						
1	**9a**/**10a**	$FeCl_3 \cdot 6H_2O$ (0.1)	3	0	**11a**/**12a**	
2[d]	**9a**	$Sc(OTf)_3$ (0.1)	3.5	r.t.	**11a**	[d]
3	**9a**	$TMSNTf_2$ (1)	5	−78	**11a**	
4	**9a**	$B(C_6F_5)_3$ (1)	5	−78	**11a**	
5	**9a**	$SnCl_4$ (1)	5	−78	**11a**	16
6	**10a**	$SnCl_4$ (1)	5	−78	**12a**	25
7	**10a**	$SnCl_4$ (1)	5	−30	**12a**	22
method B[b]						
8	**9a**	$SnCl_4$ (1)	5	−78	**11a**	24
9	**10a**	$SnCl_4$ (1)	5	−78	**12a**	75
10	**10a**	$TiCl_4$ (1)	5	−78	**12a**	
11	**10a**	$ZnCl_2$ (1)	4	−78	**12a**	
12	**10a**	$TrBF_4$ (1)	5	−78	**12a**	
13	**10a**	TBAF (1)	5	−78	**12a**	
14	**10a**	TMSOTf (1)	5	−78	**12a**	
15	**10a**	$BF_3 \bullet OEt_2$ (1)	5	−78	**12a**	25[e]
16	**10a**	$SnCl_4$ (1)	2	−78	**12a**	73
17	**10a**	$SnCl_4$ (0.5)	2	−78	**12a**	20
18	**10a**	$SnCl_4$ (0.1)	2	−78	**12a**	

[a]Method A: **9a** or **10a** (1.1 equiv), **8** (1 equiv), and then Lewis acid (0.1−1 equiv). [b]Method B: **9a** or **10a** (1.1 equiv), Lewis acid (0.1−1 equiv), and then **8** (1 equiv) in DCM. [c]Isolated yield. [d]**9a** (3 equiv), reaction in THF/H_2O. [e]^1H NMR yield using triphenylmethane as internal standard.

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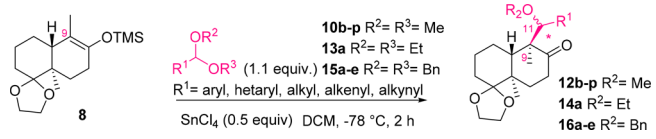
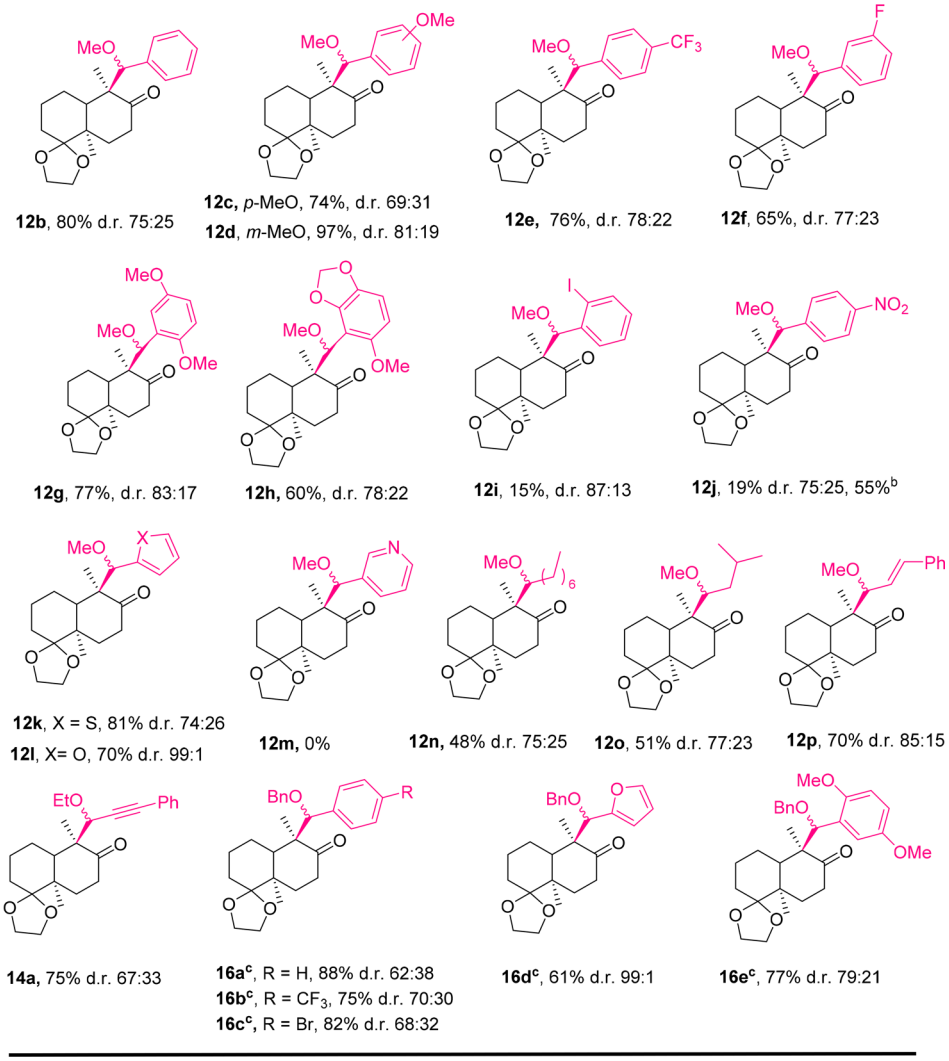
Table 2. Substrate Scope for the Stereoselective Mukaiyama Aldol Reaction of Silyl Enol Ether 8 with Dimethyl, Diethyl, and Dibenzyl Acetals 10b−p, 13a, 15a−e





[a]d.r. was measured by ^{1}H NMR of the crude material. d.r. determination method is examplified at the end of the SI by the crude NMR spectra analysis of compound 12a, 12b and 16b. [b]1 equiv of $SnCl_4$ was used. [c]Racemic compounds obtained from (±)-**8**.

followed by the deoxygenation of the resulting alcohols **5** or **7**, if needed.[3b,d,7]

To the best of our knowledge, no work reporting on the stereoselective introduction of functionalized benzylic or 2-(aryl/hetaryl)ethyl chains at C-9 position of the enantiopure Wieland−Miescher ketone derivatives **2** or **3** has been described so far. Having in mind the successful condensation of formaldehyde on the enolate resulting from the Birch reduction of the derivative **3**, we envisaged that the use of more complex aldehydes would be possible.

Herein, we present a Mukaiyama aldol reaction[8,9] between the Wieland−Miescher ketone-derived silyl enol ether **8** and various 2-(aryl/hetaryl)ethyl- or benzyl-derived aldehydes or their corresponding acetals as a straightforward diastereoselective construction of the C-9 quaternary center (Scheme 2b).

RESULTS AND DISCUSSION

We first focused on enolizable aldehydes, which are rarely employed due to their low reactivity toward silyl enol ethers or their degradation to self-polymerized products under aldolization conditions.[10] The most common method to prevent enolization is the use of the corresponding acetals, which are more stable toward acidic or basic media.[11,12] We started with the conditions of Rodríguez-Gimeno et al.,[13] using phenylacetaldehyde **9a** and its corresponding dimethyl acetal **10a** as electrophiles and silyl enol ether **8** as a nucleophile in the presence of a weak Lewis acid, namely $FeCl_3{\cdot}6H_2O$ (Table 1).

Under these reaction conditions consisting of a dropwise addition of the Lewis acid to the solution of silyl enol ether **8** and the electrophile **9a** or **10a** at 0 °C (method A), no aldol product was obtained (Table 1, entry 1). Indeed, a trans-

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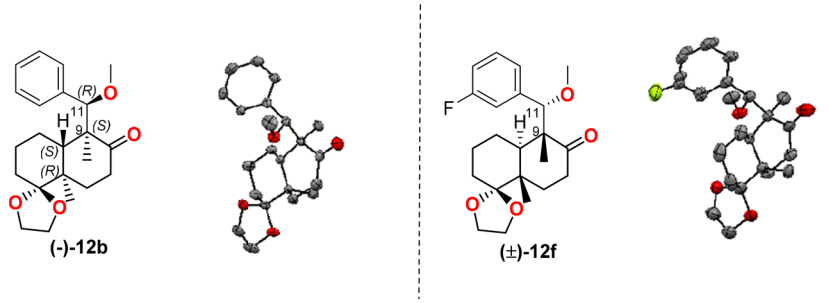
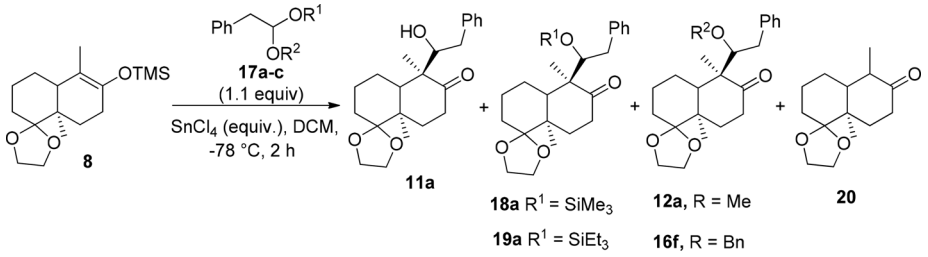
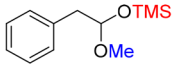
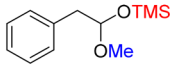
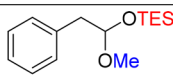
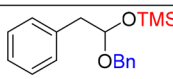


Figure 1. X-ray diffraction crystallography structures of major diastereomers (−)-**12b** and (±)-**12f** obtained by crystallization from EtOH.

Table 3. Optimization of the Mukaiyama Aldol Reaction with Mixed Acetals 17a−c



Entry	Mixed acetals **17a-c**	$SnCl_4$ (equiv)	**Products**[a], Yield[b,c] (conversion) (%)			
			11a	**18a/19a**	**12a/16f**	**20**
1	 **17a**	0.5	-	- (**18a**)	- (**12a**)	99
2	 **17a**	1	39 (53)	19 (29) (**18a**)	- (**12a**)	26 (18)
3	 **17b**	1	27 (41)	18 (28) (**19a**)	- (**12a**)	31 (31)
4	 **17c**	1	26 (38)	13 (17) (**18a**)	17 (24) (**16f**)	25 (21)

[a]All reactions were carried out in the presence of silyl enol ether **8** (1 equiv), mixed acetals **17a−c** (1.1 equiv), and $SnCl_4$ (0.5 or 1 equiv) in DCM. [b]Isolated yield. [c]Conversion is indicated in brackets and determined by ^1H NMR of the crude.

acetalization was observed between the dioxolane moiety of **8** and phenylacetaldehyde **9a**.[14] Decreasing to lower temperature (between −78 °C and −20 °C) prevented deprotection of **8** but no formation of the product was observed. Then, Smith's conditions,[5] using $Sc(OTf)_3$ as a Lewis acid, were also unfruitful (entry 2), as well as the use of other Lewis acids, such as TMSNTf (entry 3),[15] $B(C_6F_5)_3$ (entry 4),[16] TMSOTf, and $BF_3{\cdot}OEt_2$. Finally, Barlow et al.'s conditions, using a stoichiometric amount of $SnCl_4$, were more successful since 16% of **11a** and 25% of **12a** were isolated (entries 5 and 6).[17] In the latter case, increasing the temperature to −30 °C did not improve the formation of **12a** (entry 7). Further optimization of the reaction resulted in the change of the addition order of reactants, leading to a significant increase of yield: the Lewis acid was added to the electrophiles **9a**/**10a** to form the oxocarbenium species before the subsequent dropwise addition of the silyl enol ether **8** solution (method B). In sharp contrast to method A, the nature of the substrate is important. Indeed, whereas the yield did not increase in the case of aldehyde **9a** (entry 8), compound **12a** was obtained with a total conversion and 75% of the isolated yield from acetal **10a** (entry 9), even after only 2 h of reaction (entry 16). Again, changes of a Lewis acid for $TiCl_4$, $ZnCl_2$, TMSOTf, and even $TrBF_4$ using these new addition conditions with acetal **10a** were unsuccessful (entries 10, 11, 12 and 14), except for $BF_3{\cdot}OEt_2$, which provided **12a** with a modest 25% NMR yield (entry 15). However, a decrease in the amount of $SnCl_4$ to 0.5 equiv provided only 20% yield (entry 17), and a further decrease to 0.1 equiv afforded no conversion (entry 18). Finally, switching to a Lewis base catalysis[18] was totally ineffective (entry 13). It has to be noted, that compounds **11a** and **12a** are obtained with a total diastereoselectivity at C-9 and a 7/3 mixture of diastereoisomers at C-11 (vide infra).

With the optimized conditions in hand (1 equiv of $SnCl_4$ at −78 °C in DCM), we explored the reaction on a wide range of substrates. We began by introducing shorter alkyl chains, such as benzylic acetals **10b−m**,[19] for which we rapidly observed that the use of 1 equiv of a Lewis acid was not mandatory, and that the completion of the reaction occurred using only 0.5 equiv of catalyst (Table 2). Once more, we noticed that the use of the corresponding aldehydes led to a significantly lower conversion (10−30%).

Thus, a simple phenyl ring (**12b**), electron-rich aromatics (**12c,d,g,h**), and electron-poor aromatics (**12e,f**) afforded good to excellent yields (65−97%), providing substitutions in various positions. Although a limitation was observed with acetals that

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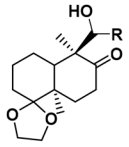
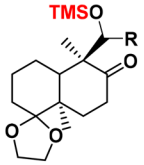
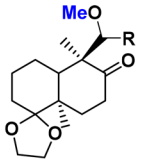
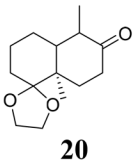
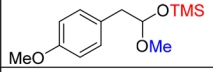
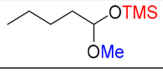
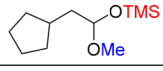
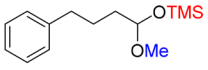
Table 4. Scope of the Mukaiyama Aldol Reaction of 8 with Mixed Acetals 17d−g

Entry	Mixed acetals **17d-g**	Products,[a] Yield[b] (%)			
		 **11b-e**	 **18b-e**	 **12q-t**	 **20**
1	 **17d**	13 (**11b**)	45 (**18b**)	- (**12q**)	28
2	 **17e**	29 (**11c**)	14 (**18c**)	22 (**12r**)	11
3	 **17f**	12 (**11d**)	15 (**18d**)	43 (**12s**)	30
4	 **17g**	34 (**11e**)	7(**18e**)	30 (**12t**)	22

[a]All reactions were carried out in the presence of silyl enol ether **8** (1 equiv), mixed acetals **17d−g** (1.1 equiv), and $SnCl_4$ (1 equiv) in DCM. [b]Isolated yield.

are sterically hindered in the *ortho* position (**12i**, 15%),[20] we were pleased to obtain the potential synthesis precursors of (+)-aureol **12g** and (+)-strongylin A **12h** (Scheme 1) with, respectively, 77 and 60% yield. Accessing heterocyclic aldol products was also possible under the reaction conditions, since **12k** and **12l** were isolated with 81 and 70% yield. Little reactivity was observed with acetals presenting moieties, which can also coordinate tin salts, such as the nitro group (**12j**, 19%)[19] or the 3-pyridyl one (**12m**, 0%). Nevertheless, the yield of **12j** can be improved to 55% using 1 equiv of $SnCl_4$, whereas in the case of 3-pyridine, no conversion was observed even when using 2 equiv of $SnCl_4$. Aliphatic chains coming from acetals of enolizable aliphatic aldehydes were also efficiently introduced at the C-9 position (**12n,o**). Longer ω-(aryl)alkyl chains can also be introduced via this methodology (*vide infra*), and double or triple bonds were tolerated (**12p**, **14a**). It is important to note that other kinds of acetals (diethyl acetal **13a** and dibenzyl acetals[21] **15a−e**) were also reactive, leading to the formation of products **14a** and **16a−e**, and that reaction could be scaled up to a 5 mmol scale.

In each case, ω-(aryl)alkyl chains were introduced with a total diastereoselectively at C-9, *trans* to the angular methyl group in C-5 position. This stereoselectivity is easily explained by the 1,3-diaxial interaction between the Me group at C-5 and the substituent at C-9, leading to the introduction of the larger substituent in the *trans* position. This has been verified by NOESY experiments and confirmed by X-ray diffraction crystallographic structures of enantiopure (−)-**12b** and racemic (±)-**12f** (Figure 1).

The C-11 stereochemistry of the major diastereomer (*syn* relationship between C-11 and C-9) is in accordance with the Noyori stereoselectivity model.[22] If benzyl ether deprotection of adducts **16a−e** leading to the corresponding synthetically useful alcohols could be envisioned by hydrogenation over Pd/C or use of DDQ,[23] chemoselective cleavage of methyl ethers **12a−p** might be an issue, even though demethylation methodologies have been developed.[24] To circumvent such problems, we decided to apply our reaction conditions (Table 3) to silylated mixed acetals. Acetals **17a−c** bearing different alkoxy and silyloxy groups were prepared by DIBAL-H reduction of the corresponding esters in pyridine and quenching of the reaction mixture by R_3SiOTf.[25]

As expected from our preliminary results (Table 1), the use of 0.5 equiv of a Lewis acid in the reaction of monosilyl methoxy acetal **17a** led to an incomplete reaction (Table 3, entry 1), and a total conversion of silyl enol ether **8** was linked to the addition of a stoichiometric amount of $SnCl_4$ (entry 2). The obtained crude product showed the major presence of alcohol **11a** (53%) and silyl ether **18a** (29%), while 18% of ketone **20** was detected, probably due to a partial decomposition of **the unreacted 8** in the presence of the Lewis acid. Each compound could be isolated from the crude material by chromatography, leading to 39, 19, and 26% isolated yields. The increasing amount of ketone **20** after chromatography is probably due to a partial retroaldolization of alcohol **11a** on silica gel. Alternatively, acidic treatment (50% PPTS, overnight) of the crude mixture (**11a** and **18a**) led after the hydrolysis of the silyl ether **18a** to **11a** with a 60% yield. It has to be noted that the TBAF treatment of the crude mixture provided mainly retroaldol product **20**.[6] Employing the more stable TES-mixed acetal **17b** did not improve the overall efficiency in the formation of the alcohol **11a** after acidic treatment of the crude product (entry 3). The reaction of the mixed acetal **17c** led to the formation of the benzyl ether **16f** along with the alcohol **11a** and silyl ether **18a**, showing a putative competition between the two leaving groups of the acetal in this case (entry 4).[26]

The reaction of **17d**, bearing a *p*-methoxybenzyl substituent (Table 4, entry 1), afforded a distribution of products **11b**, **18b**, and **12q**, similar to that obtained with **17a**. Methyl ethers **12r−t** were detected in the crude mixture when the alkyl-derived mixed acetals **17e−g** were used as reagents (entries 2, 3, and 4). Nevertheless, as mentioned above, the corresponding free alcohols **11b−e** were obtained in an interesting yield up to 60% after acidic treatment of products **18b−e** (PPTS, overnight) and chromatography of the reaction mixture.

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CONCLUSIONS

In summary, we have developed a stereoselective homologation of the Wieland−Miescher diketone analog **3** with benzylic or 2-(aryl/hetaryl)ethyl chains, which was achieved in only two steps by means of a $SnCl_4$-catalyzed Mukaiyama aldol reaction. Even though the direct use of aldehydes was not possible, the corresponding dimethyl, dibenzyl, or alkyl/silyl-mixed acetals reacted on silyl enol ether **8** in the presence of $SnCl_4$ with relatively good yields, which proved to be a novel alternative pathway to prepare useful terpenoid precursors. The corresponding aldols might be obtained by selective cleavage of methyl ethers,[24] benzyl ether, or silyl ethers leading to synthetically useful intermediates. Moreover, this method is highly diastereoselective and has been proven robust by an easy scale-up to afford adducts **12g**, **12h**, and **16e** as enantiomeric precursors for the total syntheses of (+)-aureol and (+)-strongylin A, which are currently under investigation from ***ent*-3** in our laboratory and will be published in due course.

EXPERIMENTAL SECTION

General Information. Reactions were conducted under air atmosphere unless otherwise noted. Appropriate flamed glassware was used for reactions conducted under an argon atmosphere. Liquids and solutions were transferred with syringes. All commercially available reagents were used without further purification unless otherwise noted. Air- and moisture-sensitive materials were stored protected and handled under an atmosphere of argon with appropriate glassware. Dry dichloromethane and toluene were purchased in sealed bottles under argon from Sigma-Aldrich. Dry THF was freshly prepared by distillation from sodium and benzophenone. Technical grade solvents for extraction and chromatography (cyclohexane, dichloromethane, and ethyl acetate) were used without purification. All reagents were purchased from standard suppliers (Sigma-Aldrich, Alfa-Aesar, Acros, and Fluorochem) and used as such, unless otherwise noted. $SnCl_4$ and dry pyridine were purchased from Sigma-Aldrich in a sealed bottle (Sure/Seal packaging). *t*-BuOH was distilled before use and kept under argon in the fridge. TMSCl was distilled over CaH_2 and kept in a Schlenk tube under argon over molecular sieves. Et_3N was distilled over KOH and stored over KOH under argon in the fridge.

Reactions were monitored either by thin-layer chromatography, ^1H NMR, or GC-MS analysis. Analytical thin-layer chromatography (TLC) was carried out on 0.25 mm Merck silica gel (60-F254) with UV and $KMnO_4$ solution revealing.

Column chromatography was performed manually on silica gel 60 (40−63 μm, 230−400 mesh, ASTM) by Merck using the indicated solvents. Usually the silica gel was prepared with the less polar solvent, and the gradient was performed from 95/5, V/V, to 7/3 or 5/5, V/V. The column was always flushed with the more polar solvent.

NMR analysis was recorded in $CDCl_3$, unless otherwise noted. ^1H and ^{13}C spectra were either recorded on Bruker AV 400 (^1H: 400 MHz, ^{13}C: 100 MHz), Bruker AV 300 (^1H: 300 MHz, ^{13}C: 75 MHz), or Bruker AV 500 (^1H: 500 MHz, ^{13}C: 125 MHz) instruments. ^{19}F spectra were recorded on a Bruker AV 400 (^{19}F: 376 MHz) instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (chloroform: δ [^1H] = 7.267 and accordingly δ [^{13}C] = 77.16 ppm). Data are reported as follows: chemical shift (multiplicity, integration, attribution, and coupling constant (in Hz)). The spectra were processed with the NMR Notebook program (Version 2.70, NMRtech). Diastereomeric ratio of aldols **12a−p** was determined on the crude ^1H NMR spectra according to the integration of the signals of the C−H present at the bottom of the methoxy aldol or considering the methoxy aldol signals. Diastereomeric ratio of aldol **14a** was determined on the crude ^1H NMR spectra according to the integration of the two different signals of C−H bearing the ethoxy aldol. Diastereomeric ratio of aldols **16a−e** was determined on the crude ^1H NMR spectra according to the integrations of the AB signals of the benzylic group (OBn). For the aldols **18b−e** and **12q−t** obtained using mixed acetals **17d−g**, the diastereomeric ratios were not determined because of the complexity of the crude ^1H NMR.

Melting points (mp) were determined for crystalline or solid diastereopure compounds with a Büchi melting point apparatus M-560 and are not corrected.

Optical rotations were measured with an Anton Paar polarimeter MCP 200 (L = 1 dm).

Chiral HPLC measurements were performed on a Shimadzu system with a quaternary low-pressure LC-20AD pump, an automatic SIL-20A HT injector, a CTO-10 AS oven, and a SPD-M20 A diode array detector (DAD). Hexane and *i*-propanol were used as eluents. The injection volume was 1 μL, the temperature of the oven was set to 35 °C, the flow was 0.5 mL/min, and the concentration of the sample was around 1 g/L in hexane/*i*-PrOH (80/20).

Infrared spectra were recorded on a PerkinElmer Spectrum UATR two equipped with a diamond detection and an ATR unit.

High-resolution mass spectrometry (HRMS, measurement accuracy ≤15 ppm) analysis and elemental analysis were performed by the analytical facility at the University of Strasbourg.

Crystal X-ray diffraction analyses were carried out by the Radiocrystallography Service of the University of Strasbourg.

The preparation of the enone **2** was realized using the procedure described by Hanquet.[27] The preparation of the silyl enol ether **8** was realized using the procedure described by Smith.[28]

The compound **3** is a known compound but the described method was adapted to this compound.[29]

5,8a-Dimethyl-3,4,8,8a-tetrahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(7H)-one ***3***. To a solution of diketone **2** (1 equiv, 7.37 g, 38.3 mmol) in anhydrous toluene (85 mL), anhydrous ethylene glycol (3.98 equiv, 8.5 mL, 152 mmol) and camphorsulfonic acid (0.102 equiv, 0.906 g, 3.9 mmol) were added under argon. Triethyl orthoformate (1 equiv, 6.4 mL, 38.4 mmol) was added dropwise, and the reaction mixture was stirred at r.t. for 7 h. Saturated $NaHCO_3$ solution was added, and the aqueous layer was extracted 3 times with EtOAc. The organic layers were combined, washed with distilled water and brine, dried over Na_2SO_4, filtered, and evaporated to dryness to afford a dark brown oil (9.155 g). The dark crude oil was filtered on silica (elution 8/2 to pure EA) to give a white solid (8.95 g, 99%). ^1H NMR (400 MHz, $CDCl_3$, δ): 4.00−3.90 (m, 4H), 2.77−2.68 (m, 1H), 2,51−2.35 (m, 2H), 2.27−2.09 (m, 2H), 1.93−1.60 (m, 5H), 1.78 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 198.8, 160.2, 130.3, 112.9, 65.5, 65.2, 45.4, 33.8, 29.8, 2*26.6, 21.5, 21.0, 11.6. mp: 58−60 °C. IR (cm^{-1}): 2948, 2878, 1660, 1608, 1020. Specific rotation: $[\alpha]_D^{20}$ = −106 (MeOH, c = 0.5).

General Procedure for the Preparation of Dimethyl Acetals 10b−p from the Corresponding Aldehydes.[30] Aldehyde (1 equiv) was dissolved in cyclohexane (3.7 equiv, 2.5 M) and dry MeOH (3.4 equiv, 2.3M) in a tube. $ZnCl_2$ (0.1 equiv) and trimethylorthoformate (2 equiv) were added to the tube. The tube was sealed, and the heterogeneous reaction mixture was stirred at reflux for 16 h. The reaction mixture was then cooled down to r.t., filtered over Celite, and evaporated with carefulness (some acetals can be volatile) to give a pure acetal, which was used without purification.

*2-(Dimethoxymethyl)-1,4-dimethoxybenzene (**10g**).* **10g** was obtained from 2,5-dimethoxybenzaldehyde (286 mg, 1.72 mmol) as a yellow oil (358 mg, 98%). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.12−7.11 (m, 1H, C*H*), 6.84 (m, 2H, C*H*), 5.64 (s, 1H, C*H*$(OMe)_2$), 3.81, 3.79 (2s, 2 × 3H, COCH_3), 3.38 (s, 6H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 153.6 (CArOMe), 151.5 (CArOMe), 127.3 (*C*), 115.0 (CHAr), 112.8 (CHAr), 112.3 (CHAr), 99.1 (CH$(OMe)_2$), 56.5, 55.9 (2×ArOCH_3), 53.8 ($(OCH_3)_2$). HRMS (ESI-TOF) (*m*/*z*): $[M + Na]^+$ Calcd for $C_{11}H_{16}O_4Na$, 235.0941; found, 235.0951.

*4-(Dimethoxymethyl)-5-methoxybenzo[d][1,3]dioxole (**10h**).* **10h** was obtained from 5-methoxy-2H-1,3-benzodioxole-4-carbaldehyde (100 mg, 0.56 mmol) as an uncolored oil (119 mg, 95%). ^1H NMR (400 MHz, $CDCl_3$, δ): 6.51 (AB, 2H, C*H*, J_{AB} = 8.4 Hz, $\Delta\nu$ = 163 Hz), 5.98 (s, 2H, C*H*), 5.68 (s, 1H, C*H*$(OMe)_2$), 3.79 (s, 3H, COCH_3), 3.45 (s, 6H, 2×OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ):

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152.7 (C^{IV}Ar), 146.3 (C^{IV}Ar), 142.4 (C^{IV}Ar), 110.5 (*C*), 107.8 (CH), 102.7 (CH), 101.7 (CH_2), 99.8 (CH), 56.7 ($ArOCH_3$), 54.8 ($(OCH_3)_2$). HRMS (ESI-TOF) (*m*/*z*): $[M + Na]^+$ Calcd for $C_{11}H_{14}O_5Na$, 249.0733; found, 249.0743.

General Procedure for the Preparation of Dibenzyl acetals 15 from the Corresponding Aldehydes. Aldehyde (1 equiv) was dissolved in cyclohexane (3.7 equiv, 2.5 M) and BnOH (2 or 4 equiv) in a tube. $ZnCl_2$ (0.1 equiv) and trimethylorthoformate (0.1 equiv) were added to the tube. The tube was sealed, and the heterogeneous reaction mixture was stirred at reflux for 16 h. The reaction mixture was then cooled down to r.t., filtered over Celite, and evaporated under reduced pressure. The crude product was purified by silica gel chromatography using a cyclohexane/ethyl acetate gradient.

*(2,5-Dimethoxyphenyl)methylene)bis(oxy))bis(methylene))-dibenzene (**15e**).* Cyclohexane (1 mL), benzyl alcohol (1 mL), and calcium hydride (1.5 equiv, 189 mg, 4.50 mmol) were mixed in a sealed tube. After 5 min, 2,5-dimethoxybenzaldehyde (1 equiv, 500 mg, 3.01 mmol) and $ZnCl_2$ (0.12 equiv, 49 mg, 0.36 mmol) were added. The reaction mixture was stirred at 70 °C over 2 days (weekend). The reaction mixture was filtered over a pad of silica gel (elution DCM and Et_2O) and evaporated to get a slightly colored oil. The crude product was purified by silica gel chromatography using cyclohexane to give rise to the desired compound as an uncolored oil (503 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38−7.26 (m, 11H, *CH*Bn, C*H*), 6.88−6.82 (m, 2H, C*H*, C*H*), 5.99 (s, 1H, C*H*$(OBn)_2$), 4.63 (s, 4H, 2×OCH_2Bn), 3.80, 3.77 (2s, 2 × 3H, COCH_3, COCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 153.7 (C^{IV}ArOMe), 151.7 (C^{IV}ArOMe), 138.3 (C^{IV}Bn), 128.4 (CHBn), 128.0 (CHBn), 127.7 (*C*), 127.6 (CHBn), 114.8 (CHAr), 113.5 (CHAr), 112.2 (CHAr), 96.6 (CH$(OBn)_2$), 68.2 (OCH_2Bn), 56.3, 56.0 (2×OMe). HRMS (ESI-TOF) (*m*/*z*): $[M + K]^+$ Calcd for $C_{23}H_{24}O_4K$, 403.1306; found, 403.1308.

General Procedure for the Preparation of Mixed Acetals 17 from the Corresponding Esters.[31] Ester (1 equiv) was dissolved in dry DCM (77 equiv, 0.2 M) under an argon atmosphere and cooled to −78 °C. DIBAL-H (1.1 equiv, 1 M in toluene) was added dropwise, and the reaction mixture became thick white. After 2 h at −78 °C, dry pyridine (6 equiv) was added followed by TMSOTf (or TESOTf) (1.1 equiv) dropwise. The reaction mixture remained thick white. It was stirred at −78 °C for 3 h.

Aqueous saturated potassium and sodium tartrate solution were added at −78 °C, and then the cold bath was removed. The mixture was stirred for 15 min, and DCM was added to the reaction mixture with saturated $NaHCO_3$ solution. The aqueous layer was extracted with DCM. The organic layers were combined, washed 2 times with $CuSO_4$ solution and once with water, dried over Na_2SO_4, filtered, and evaporated with carefulness (some acetals are volatile).

Mixed TMS acetals are not stable on silicagel (cleaved to give the corresponding aldehyde) and cannot be purified.

*(1-Methoxy-2-phenylethoxy)trimethylsilane (**17a**).* **17a** was obtained from methyl phenylacetate (1.07 g, 7.11 mmol) as an uncolored oil (1.30 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32−7.20 (m, 5H), 4.81 (ABX, 1H, *J* = 5.6, *J* = 5.2 Hz), 3.33 (s, 3H, OMe), 2.90 (ABX, 4H, CH_2, J_{AB} = 13.6, J_{AX} = 5.6, J_{BX} = 5.2 Hz, $\Delta\nu$ = 62 Hz), 0.04 (s, 9H, OSi$(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 137.2 (*C*), 130.0 (CHAr), 128.3 (CHAr), 128.4 (CHAr), 126.5 (CHAr), 100.1 54.6, 44.4, 0.32 (OSi$(CH_3)_3$).

*Triethyl(1-methoxy-2-phenylethoxy)silane (**17b**).* **17b** was obtained from methyl phenylacetate (309 mg, 2.06 mmol). The crude product was purified by silica gel chromatography using a cyclohexane/ethyl acetate gradient to give rise to **17b** as an uncolored oil (292 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31−7.19 (m, 5H, *CH*Ph), 4.86 (ABX, 1H, C*H*, *J* = 6.0, *J* = 4.8 Hz), 3.33 (s, 3H, OMe), 2.90 (ABX, 2H, CH_2, J_{AB} = 13.6, J_{AX} = 6.0, J_{BX} = 4.8 Hz, $\Delta\nu$ = 45 Hz), 0.94 (t, 9H, CH_3CH_2SiO, *J* = 7.6 Hz), 0.62−0.54 (m, 6H, CH_3CH_2SiO). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 137.4 (*C*), 129.9 (CHPh), 128.3 (CHPh), 126.5 (CHPh), 99.9 (CH), 53.9 (OMe), 44.2 (CH_2), 6.9 ($(CH_3CH_2)_3SiO$), 5.1 ($(CH_3CH_2)_3SiO$). IR (cm^{-1}): 2954, 2877, 1455, 1129, 1060, 1002, 727, 698. HRMS (ESI-TOF) (*m*/*z*): $[M + Na]^+$ Calcd for $C_{15}H_{26}O_2SiNa$, 289.1594; found, 289.1597.

*(1-(Benzyloxy)-2-phenylethoxy)trimethylsilane (**17c**).* **17c** was obtained from benzyl 2-phenylacetate (502 mg, 2.22 mmol) as an uncolored oil (604 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34−7.21 (m, 10H, C*H*Ph, C*H*Bn), 4.86 (ABX, 1H, C*H*, *J* = 5.6, *J* = 5.2 Hz), 4.59 (ABX, 2H, CH_2Bn, *J* = 12.0 Hz, $\Delta\nu$ = 119 Hz), 2.98 (ABX, 2H, CH_2, J_{AB} = 13.4, J_{AX} = 5.6, J_{BX} = 5.2 Hz, $\Delta\nu$ = 62 Hz), 0.07 (s, 9H, $(CH_3)_3SiO$). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 138.3 (*C*), 137.2 (*C*), 130.1 (CH), 128.4 (CH), 128.3 (CH), 127.6 (CH), 127.5 (CH), 126.5 (CH), 98.6 (C^1H), 68.8 (CH_2Bn), 44.7 (CH_2), 0.5 ($(CH_3)_3SiO$). HRMS (ESI-TOF) (*m*/*z*): $[M + Na]^+$ Calcd for $C_{18}H_{24}O_2SiNa$, 323.1438; found, 323.1467.

*(1-Methoxy-2-(4-methoxyphenyl)ethoxy)trimethylsilane (**17d**).* **17d** was obtained from methyl 4-methoxyphenylacetate (410 mg, 2.28 mmol) as an uncolored oil (447 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.99 (A_2X_2, 4H, C*H*, C*H*, J_{AX} = 8.8 Hz, $\Delta\nu$ = 120 Hz), 4.76 (ABX, 1H, C*H*, *J* = 5.6, *J* = 5.2 Hz), 3.80 (s, 3H, ArOMe), 3.33 (s, 3H, OMe), 2.83 (ABX, 4H, CH_2, J_{AB} = 14.0, J_{AX} = 5.6, J_{BX} = 5.2 Hz, $\Delta\nu$ = 58 Hz), 0.06 (s, 9H, OSi$(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.3, 130.9, 129.3, 113.8, 100.2, 55.3, 55.6, 53.4, 0.4. HRMS (ESI-TOF) (*m*/*z*): $[M + Na]^+$ Calcd for $C_{13}H_{22}O_3SiNa$, 277.1230; found, 277.1227.

*((1-Methoxypentyl)oxy)trimethylsilane (**17e**).* **17e** was obtained from methyl pentanoate (500 mg, 4.30 mmol) as a pale yellow oil (67%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.65 (dd, 1H, *J* = 5.6, *J* = 5.2 Hz), 3.32 (s, 3H), 1.66−1.50 (m, 2H), 1.40−1.29 (m, 4H), 0.94−0.88 (m, 3H), 0.17 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 99.6, 54.2, 37.5, 26.7, 22.7, 14.2, 0.6. IR (cm^{-1}): 2962, 2925, 2852, 1460, 741, 697. HRMS (ESI-TOF) (*m*/*z*): $[M + Na]^+$ Calcd for $C_9H_{22}O_2SiNa$, 213.1281; found, 213.1271.

*(2-Cyclopentyl-1-methoxyethoxy)trimethylsilane (**17f**).* **17f** was obtained from methyl 2-cyclopentylacetate (561 mg, 3.94 mmol) as an uncolored oil (435 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.68 (ABX, 1H, C^1*H*, *J* = 6.4, *J* = 4.8 Hz), 3.32 (s, 3H, OMe), 1.92−1.47 (m, 9H), 1.15−1.04 (m, 2H), 0.17 (s, 9H, OSi$(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 98.7 (CH), 53.5 (OMe), 43.1 (CH_2), 35.4 (CH), 32.4, 32.3, 24.4, 24.4 (CH_2), 0.0 (OSi$(CH_3)_3$). IR (cm^{-1}): 2950, 2871, 1250, 1135, 1052, 1031, 838. HRMS (ESI-TOF) (*m*/*z*): $[M + Na]^+$ Calcd for $C_{11}H_{24}O_2SiNa$, 239.1438; found, 239.1426.

*(1-Methoxy-4-phenylbutoxy)trimethylsilane (**17g**).* **17g** was obtained from methyl 4-phenylbutanoate (404 mg, 2.27 mmol) as an uncolored oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): (ppm) = 7.29, 7.14 (m, 5H, C*H*Ph), 4.67−4.64 (m, 1H, C*H*), 3.29 (br s, 3H, OMe), 2.63−2.59 (m, 2H, alkyl chain), 1.17−1.54 (m, 4H, alkyl chain), 0.14 (s, 9H, $(CH_3)_3SiO$). ^{13}C NMR (126 MHz, $CDCl_3$, δ): (ppm) = 141.8, 128.0, 127.8, 125.2, 98.8, 53.6, 36.5, 25.2, 25.7, 0.0. HRMS (ESI-TOF) (*m*/*z*): $[M + Na]^+$ Calcd for $C_{14}H_{24}O_2SiNa$, 275.1438; found, 275.1433.

General Experimental Procedure for the Mukaiyama Aldol Reaction of 8 and Aldehydes 9 or (Mixed) Acetals 10, 13, 15, and 17. Method A: To a solution of {5′,8′a-dimethyl-3′,4′,4′a,7′,8′,8′a-hexahydro-2′H-spiro[1,3-dioxolane-2,1′-naphthalene]-6′-yloxy}trimethylsilane **8** (1 equiv) in dry DCM (422 equiv, 0.04 M) at −78 °C, were sequentially added aldehyde or acetal (1.1 equiv) and $SnCl_4$ (1 M in DCM, 1 equiv) under an argon atmosphere. The reaction mixture was stirred for 5 h at −78 °C. Saturated $NaHCO_3$ solution was rapidly introduced at −78 °C, and the cold bath was removed. The aqueous layer was extracted with DCM (3×), and the organic layers were combined, dried over Na_2SO_4, filtered, and evaporated to dryness to give the crude product. The crude product was purified by silica gel chromatography using a cyclohexane/EtOAc gradient of eluent.

Method B: To a solution of acetal (1.1 equiv, 0.35 mmol) in dry DCM (1 mL) at −78 °C, $SnCl_4$ (1 M in DCM, 1 to 0.5 equiv) was added dropwise under an argon atmosphere. {5′,8′a-Dimethyl-3′,4′,4′a,7′,8′,8′a-hexahydro-2′H-spiro[1,3-dioxolane-2,1′-naphthalene]-6′-yloxy}trimethylsilane **8** (1 equiv, 100 mg, 0.32 mmol) in dry DCM (1.4 mL) was directly added dropwise. The reaction mixture was stirred for 2 h at −78 °C. The saturated $NaHCO_3$ solution was introduced rapidly at −78 °C, and the cold bath was removed. The aqueous layer was extracted with DCM (3×), and the organic layers

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were combined, dried over Na_2SO_4, filtered, and evaporated to dryness to give the crude product. The crude product was purified by silica gel chromatography using a cyclohexane/EtOAc gradient of eluent.

*(4aS,5S,8aR)-5-((R)-1-Hydroxy-2-phenylethyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**11a**).* **11a** was obtained from aldehyde **9a** as a yellowish oil (25%, d.r. 71:29) (method B). The major diastereomer was partially separated by column chromatography. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.33−7.19 (m, 5H, C*H*Ph), 4.03−3.87 (m, 4H, 2CH_2), 3.67−3.60 (m, 1H, C*H*), 2.97 (dd, 1H, CH_2, J = 14 Hz, J = 2.0 Hz), 2.73−2.71 (d, 1H, OH), 2.75−2.35 (m, 4H, 2CH_2), 2.06 (td, 1H, CH_2, J = 13.2, J = 6.4 Hz), 1.77−1.41 (m, 7H, CH_2), 1.26 (s, 3H, CH_3), 1.18 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 220.0 (O═*C*), 139.6 (C^{IV}Ph), 129.4 (2*CH, Ph), 128.6 (2*CH, Ph), 126.4 (CH, Ph), 112.8 (*C*), 79.9 (CH), 65.4, 65.2 (CH_2), 54.1 (*C*), 43.1 (CH), 42.6 (*C*), 39.9 (CH_2), 36.1 (CH_2), 30.5 (CH_2), 27.4 (CH_2), 23.2, 23.0 (CH_2), 19.0 (CH_3), 15.7 (CH_3).

*(4aS,5S,8aR)-5-((R)-1-Methoxy-2-phenylethyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12a**).* **12a** was obtained from acetal **10a** as a white solid (75%, d.r. 67:33) (method B). The major diastereomer was partially separated by column chromatography. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30−7.18 (m, 5H, C*H*Ph), 4.06−3.86 (m, 4H, 2CH_2), 3.42 (dd, 1H, C*H*, J = 10.4, J = 2.4 Hz), 2.84 (m, 1H, CH_2), 2.76 (s, 3H, CH_3O), 2.66−2.60 (m, 2H, CH_2), 2.40−2.36 (m, 2H, CH_2), 2.18−2.10 (m, 1H, CH_2), 1.79−1.41 (m, 7H, 4CH_2), 1.13 (s, 3H, CH_3), 1.01 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 218.5 (O═*C*), 140.0 (C^{IV}Ph), 129.6 (2*CH, Ph), 128.5 (2*CH, Ph), 126.3 (CH, Ph), 112.8 (*C*), 93.2 (CH), 65.4 (CH_2), 65.1 (CH_2), 60.7 (CH_3O), 54.7 (*C*), 42.4 (*C*), 42.2 (CH), 38.1 (CH_2), 36.0 (CH_2), 30.5 (CH_2), 26.2 (CH_2), 25.6 (CH_2), 23.1 (CH_2), 18.9 (CH_3), 15.4 (CH_3). IR (cm^{-1}): 2948, 2884, 1693, 1455, 1181, 1091, 1081, 914, 732, 699. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{23}H_{32}O_4Na$, 395.2193; found, 395.2167.

*(4aS,5S,8aR)-5-((R)-Methoxy(phenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12b**).* **12b** was obtained from acetal **10b** as a white solid (92 mg, 80%, d.r. 75:25) (method B). The major diastereomer was partially separated by recrystallization from ethanol. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39−7.29 (m, 5H, C*H*Ph), 4.20 (s, 1H, C*H*), 4.05−3.90 (m, 4H, 2CH_2), 3.13 (s, 3H, CH_3O), 2.67 (dd, 1H, C*H*, J = 12.8, J = 2.8 Hz), 2.58−2.35 (m, 2H, CH_2), 2.22−2.14 (m, 1H, CH_2), 1.65−1.46 (m, 3H, 2CH_2), 1.31−1.17 (m, 2H, CH_2), 1.01 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 0.92−0.80 (m, 1H, CH_2), 0-(−0.08) (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 218.1 (O═*C*), 138.0 (C^{IV}Ph), 127.9 (CHPh), 127.8 (2*CHPh), 112.9 (*C*), 91.3 (CH), 65.4 (CH_2), 65.1 (CH_2), 57.3 (CH_3O), 54.7 (*C*), 42.3 (*C*), 40.3 (CH), 36.2 (CH_2), 30.5 (CH_2), 25.9 (CH_2), 24.3 (CH_2), 22.4 (CH_2), 20.0 (CH_3), 15.3 (CH_3). mp: 181.0−182.5 °C. $[\alpha]_D^{20}$ = −140 ($CHCl_3$, c = 0.31). IR (cm^{-1}): 2981, 2942, 2872, 1692, 1452, 1179, 1089, 1055, 916, 747, 708. Elementary analysis: $C_{22}H_{30}O_4$: calcd (%), C 73.71, H 8.44; found, C 73.76, H 8.40.

*(4aS,5S,8aR)-5-((R)-Methoxy(4-methoxyphenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12c**).* **12c** was obtained from **10c** as a white solid (93 mg, 74%, d.r. 69:31) (method B). The major diastereomer was partially separated by recrystallization from ethanol. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.08 (A_2X_2, 4H, 2C*H*Ar, J_{AX} = 8.4 Hz, $\Delta\nu$ = 168 Hz), 4.14 (s, 1H, C*H*), 4.05−3.88 (m, 4H, 2CH_2), 3.82 (s, 3H, ArOCH_3), 3.10 (s, 3H, CH_3O), 2.65 (dd, 1H, C*H*, J = 12.8, J = 3.2 Hz), 2.57−2.32 (m, 2H, CH_2), 2.21−2.12 (m, 1H, CH_2), 1.65−1.44 (m, 3H, C*H*, CH_2), 1.34−1.18 (m, 2H, CH_2), 0.98 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 0.92−0.82 (m, 1H, CH_2), 0.10−0.06 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 218.3 (O═*C*), 159.4 (C^{IV}ArOCH_3), 130.0 (C^{IV}Ar), 128.9 (2*CH, Ar), 113.3 (2*CH, Ar), 112.9 (*C*), 91.0 (CH), 65.4 (CH_2), 65.1 (CH_2), 57.1 (CH_3OC), 55,3 (CH_3OAr), 54.8 (*C*), 42.2 (*C*), 40.3 (CH), 36.1 (CH_2), 30.5 (CH_2), 25.9 (CH_2), 24.3 (CH_2), 22.6 (CH_2), 19.9 (CH_3), 15.3 (CH_3). mp: 159.1−159.7 °C. IR (cm^{-1}): 2930, 2882, 1697, 1511, 1240, 1179, 1088, 1049, 1024, 820. Elementary analysis: $C_{23}H_{32}O_5$: calcd (%), C 71.11, H 8.30; found, C 70.78, H 8.24.

*(4aS,5S,8aR)-5-((R)-Methoxy(3-methoxyphenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12d**).* **12d** was obtained from **10d** as an uncolored oil (121 mg, 97%, d.r. 81:19) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): −7.24 (t, 1H, J = 7.6 Hz), 6.99−6.92 (m, 2H), 6.86−6.83 (m, 1H), 4.17 (s, 1H), 4.02−3.90 (m, 4H), 3.83 (s, 3H), 3.13 (s, 3H), 2,68 (dd, 1H, J = 12.8, J = 3.2 Hz), 2.57−2.39 (m, 2H), 2.20−2.12 (m, 1H), 1.65−1.43 (m, 3H), 1.34−1.16 (m, 2H), 1.02 (s, 3H), 0.96 (s, 3H), 0.92−0.87 (m, 1H), 0.1−0.03 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 218.0, 159.5, 139.9, 128.9, 120.4, 113.6, 112.8, 91.2, 65.4, 65.1, 57.3, 55.4, 54.8, 42.2, 40.3, 36.1, 30.5, 25.9, 24.3, 22.6, 20.0, 15.3. IR (cm^{-1}): 2946, 2882, 1694, 1259, 1180, 1094, 1048, 913. HRMS (ESI-TOF) (m/z): [M]$^+$ Calcd for $C_{23}H_{33}O_5$, 389.2323; found, 389.2342.

*(4aS,5S,8aR)-5-((R)-Methoxy(4-(trifluoromethyl)phenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12e**).* **12e** was obtained from **10e** as a white solid (104 mg, 76%, d.r. 78:22) (method B). The major diastereomer was partially separated by recrystallization from ethanol. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.56 (A_2X_2, 4H, 2C*H*Ar, J_{AX} = 8.0 Hz, $\Delta\nu$ = 35 Hz), 4.27 (s, 1H, C*H*), 4.06−3.89 (m, 4H, CH_2), 3.12 (s, 3H, CH_3O), 2.64 (dd, 1H, C*H*, J = 12.0, J = 2.0 Hz), 2.58−2.36 (m, 2H, CH_2), 2.20−2.12 (m, 1H, CH_2), 1.67−1.49 (m, 3H, C*H*, CH_2), 1.32−1.11 (m, 2H, CH_2), 1.02 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 0.95−0.81 (m, 1H, CH_2), −0.05-(−0.13) (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.4 (O═*C*), 142.5 (CAr), 130.2 (q, *C*, J = 33 Hz), 128.2 (CH), 124.9 (q, CH, J = 3.7 Hz), 112.7 (*C*), 90.7 (CH), 65.4, (CH_2), 65.1 (CH_2), 57.5 (CH_3OC), 54,7 (CH_3OAr), 54.7 (*C*), 42.2 (*C*), 40.3 (CH), 36.1 (CH_2), 30.4 (CH_2), 25.8 (CH_2), 24.4 (CH_2), 22.4 (CH_2), 19.9 (CH_3), 15.3 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, δ): −62.40 (m, 1F, ArCF_3). Specific rotation: $[\alpha]_D^{20}$ = −125 ($CHCl_3$, c = 0.14). IR (cm^{-1}): 2981, 2952, 1695, 1324, 1124, 1086, 1066. Elementary analysis: $C_{23}H_{29}F_3O_4$: calcd (%), C 64.78, H 6.85; found, C 65.05, H 7.10.

*(4aS,5S,8aR)-5-((R)-(3-Fluorophenyl)(methoxy)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12f**).* **12f** was obtained from acetal **10f** as a white solid (79 mg, 65%, d.r. 77:23.) (method B). The major diastereomer was partially separated by recrystallization from ethanol. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.33−7.27 (m, 1H, C*H*Ar), 7.16−7.12 (m, 2H, C*H*Ar), 7.02−6.97 (m, 1H, C*H*Ar), 4.20 (s, 1H, C*H*), 4.05−3.89 (m, 4H, 2CH_2), 3.13 (s, 3H, CH_3O), 2.64 (dd, 1H, C*H*, J = 12.8, J = 3.2 Hz), 2.57−2.35 (m, 2H, CH_2), 2.20−2.11 (m, 1H, CH_2), 1.66−1.48 (m, 3H, C*H*, CH_2), 1.34−1.15 (m, 2H, CH_2), 1.02 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 0.93−0.80 (m, 1H, CH_2), 0-(−0.04) (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.6 (O═*C*), 162.9 (d, C^{IV}Ar−F, J = 244 Hz), 141.1 (d, C^{IV}Ar, J = 6.6 Hz), 129.4 (d, CHAr, J = 8.8 Hz), 123,6 (d, CHAr, J = 2.2 Hz), 114.8 (d, CHAr,, J = 21.1 Hz), 114.6 (d, CHAr, J = 21.1 Hz), 112.8 (*C*), 90.6 (CH), 65.4 (CH_2), 65.1 (CH_2), 57.4 (CH_3O), 54.7 (*C*), 42.2 (*C*), 40.2 (CH), 36.1 (CH_2), 30.5 (CH_2), 25.8 (CH_2), 24.4 (CH_2), 22.4 (CH_2), 19.9 (CH_3), 15.3 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, δ): −113.58 (m, 1F, Ar*F*). mp: 201.3−202.7 °C. IR (cm^{-1}): 2929, 2892, 1694, 1589, 1178, 1089, 1056, 1020, 915, 799. HRMS (ESI-TOF) (m/z): [M + K]$^+$ Calcd for $C_{22}H_{29}FO_4K$, 415.1681; found, 415.1692.

*(4aS,5S,8aR)-5-((R)-(2,5-Dimethoxyphenyl)(methoxy)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12g**).* **12g** was obtained from acetal **10g** as a white solid (104 mg, 77%, d.r. 83:17) (method B). The major diastereomer was partially separated by recrystallization from ethanol. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.11 (m, 1H, C*H*Ar), 6.82−6.78 (m, 2H, C*H*Ar), 4.78 (s, 1H, C*H*), 4.03−3.89 (m, 4H, CH_2), 3.81 (s, 3H, ArCH_3O), 3.74 (s, 3H, ArCH_3O), 3.08 (s, 3H, CH_3O), 2.72 (dd, 1H, C*H*, J = 12.8, J = 2.8 Hz), 2.59−2.32 (m, 2H, CH_2), 2.19−2.11 (m, 1H, CH_2), 1.62−1.48 (m, 3H, C*H*, CH_2), 1.42−1.25 (m, 2H, CH_2), 1.07−0.97 (m, 1H, CH_2), 0.98 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 0.59−0.46 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.9 (O═*C*), 153.9 (C^{IV}ArOMe), 152.7 (C^{IV}ArOMe), 127.8

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(C^{IV}Ar), 114.3 (CHAr), 113.7 (CHAr), 111.6 (CHAr), 113.0 (*C*), 83.9 (CH), 65.5 (CH_2), 65.2 (CH_2), 57.3 (CH_3OC), −56.2 (CH_3OAr), 55.9 (*C*), 55.8 (CH_3OAr), 42.4 (*C*), 41.1 (CH), 36.2 (CH_2), 30.6 (CH_2), 26.3 (CH_2), 24.6 (CH_2), 22.8 (CH_2), 19.0 (CH_3), 15.6 (CH_3). mp: 181.2−182.5 °C. IR (cm^{-1}): 2946, 2887, 1689, 1493, 1214, 1179, 1076, 1048, 1023. Elementary analysis: $C_{24}H_{34}O_6$: calcd (%), C 68.88, H 8.19; found, C 68.57, H 8.06.

(4aS,5S,8aR)-5-((R)-Methoxy(5-methoxybenzo[d][1,3]dioxol-4-yl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***12h***). **12h** was obtained from acetal **10h** as a white solid (60%, d.r. 78:22) (method B). The major diastereomer was partially separated by recrystallization from ethanol. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.69 (d, 1H, CHAr, J = 8.4 Hz), 6.29 (d, 1H, CHAr, J = 8.4 Hz), 6.00−5.91 (m, 2H, CH_2 dioxole), 4.83 (s, 1H, CH), 4.00−3.87 (m, 4H, CH_2), 3.73 (s, 3H, ArCH_3O), 3.17 (s, 3H, CH_3O), 3.08 (broad dd, 1H, CH, J = 13.2, J = 3.6 Hz), 2.64−2.34 (m, 2H, CH_2), 2.25−2.17 (m, 1H, CH_2), 1.63−1.34 (m, 3H, CH, CH_2), 1.27−1.16 (m, 1H, CH_2), 1.01−0.95 (m, 1H, CH_2), 1,02 (s, 3H, CH_3), 0.99 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.7 (O═*C*), 154.0 (C^{IV}ArOR), 146.8 (C^{IV}ArOR), 141,9 (C^{IV}ArOR), 112.8 (*C*), 111.0 (C^{IV}Ar), 107.1 (CHAr), 102.3 (CHAr), 101.3 (CH_2 dioxole), 84.6 (CH), 65.4 (CH_2), 65.0 (CH_2), 58.0 (CH_3OC), 56.5 (*C*),56.0 (CH_3OAr), 42.4 (*C*), 41.5 (CH), 36.1 (CH_2), 30.5 (CH_2), 26.4 (CH_2), 24.9 (CH_2), 23.0 (CH_2), 18.5 (CH_3), 15.5 (CH_3). mp: 177.9−179.0 °C. IR (cm^{-1}): 2946, 2997, 1686, 1456, 1238, 1077, 1051, 915, 795. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{24}H_{32}O_7Na$, 455.2040; found, 455.2053.

(4aS,5S,8aR)-5-((S)-(2-Iodophenyl)(methoxy)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***12i***). **12i** was obtained from acetal **10i** as a white solid (24 mg, 15%, d.r. 87:13) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.86 (dd, 1H, J = 8.0, J = 1.2 Hz), 7.62 (dd, 1H, J = 7.6, J = 1.2 Hz), 7.34 (m, 1H), 7.02−6.98 (m, 1H), 4.67 (s, 1H), 4.05−3.90 (m, 4H), 3.05 (s, 3H), 2.79 (dd, 1H, J = 13.2, J = 3.2 Hz), 2.59−2.40 (m, 2H), 2.16−2.08 (m, 1H), 1.65−1.50 (m, 3H), 1.40−1.24 (m, 2H), 1.16 (s, 3H), 0.97 (s, 3H), 1.08−0.97 (m, 1H), 0.43−0.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 216.9, 140.6, 139.9, 129.8, 129.0, 127.8, 112.8, 92.1, 65.3, 65.0, 56.9, 56.7, 42.2, 39.9, 36.0, 30.4, 25.8, 24.4, 22.3, 20.5, 15.1. IR (cm^{-1}): 2991, 2940, 2882, 1698, 1461, 1083, 1050, 914, 764. HRMS (ESI-TOF) (m/z): [M + K]$^+$ Calcd for $C_{22}H_{29}IO_4K$, 523.0742; found, 523.0754.

(4aS,5S,8aR)-5-((R)-Methoxy(4-nitrophenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***12j***). **12j** was obtained from **10j** as white solid (72 mg, 55%, d.r. 75:25 (1 equiv. $SnCl_4$)) (method B). The major diastereomer was partially separated by recrystallization from ethanol. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.90 (A_2X_2, 4H, J_{AX} = 8.8 Hz, $\Delta\nu$ = 255 Hz), 4.33 (s, 1H), 4.05−3.91 (m, 4H), 3.14 (s, 3H), 2.62 (dd, 1H, J = 12.8, J = 3.2 Hz), 2.58−2.38 (m, 2H), 2.19−2.11 (m, 1H), 1.68−1.51 (m, 3H), 1.32−1.11 (m, 2H), 1.03 (s, 3H), 0.98 (s, 3H), 0.94−0.81 (m, 1H), −0.1-(−0.14) (m, 1H), ^{13}C NMR (125 MHz, $CDCl_3$, δ): 216.8, 147.9, 146.3, 128.6, 123.2, 112.6, 90.4, 65.4, 65.2, 57.7, 54.9, 42.2, 40.3, 36.0, 30.4, 25.8, 24.5, 22.4, 19.9, 15.3. mp: 176.8−178.4 °C. IR (cm^{-1}): 2931, 2877, 1696, 1519, 1341, 1181, 1089, 1053. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{22}H_{29}NO_6Na$, 426.1887; found, 426.1881.

(4aS,5S,8aR)-5-((S)-Methoxy(thiophen-2-yl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***12k***). **12k** was obtained from acetal **10k** as a beige solid (95 mg, 81%, d.r. 74:26) (method B). The major diastereomer was partially separated by recrystallization from ethanol. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.29−7.28 (dd, 1H, J = 5.2, J = 1.2 Hz, CHAr), 7.00−6.96 (m, 2H, CHAr), 4.42 (s, 1H, CH), 4.04−3.89 (m, 4H, $2CH_2$), 3.21 (s, 3H, CH_3O), 2.67 (dd, 1H, CH, J = 12.8, J = 3.2 Hz), 2.55−2.34 (m, 2H, CH_2), 2.20−2.12 (m, 1H, CH_2), 1.66−1.49 (m, 3H, $2CH_2$), 1.39−1.28 (m, 2H, CH_2), 1.06 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.04−0.93 (m, 1H, CH_2), 0.22−0.16 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.6 (O═*C*), 142.5 (C^{IV}Ph), 126.5 (CHAr), 125.9 (CHAr), 125.3 (CHAr), 112.8 (*C*), 88.3 (CH), 65.4 (CH_2), 65.1 (CH_2), 57.8 (CH_3O), 54.5 (*C*), 42.2 (*C*), 40.9 (CH), 36.1 (CH_2), 30.5 (CH_2), 25.8 (CH_2), 24.5 (CH_2), 22.6 (CH_2), 19.6 (CH_3), 15.3 (CH_3). mp: 173.3−174.6 °C. IR (cm^{-1}): 2981, 2942, 2872, 1692, 1452, 1179, 1090, 1056, 916, 708. Elementary analysis: $C_{20}H_{28}O_4S$: calcd (%), C 65.90, H 7.74; found, C 65.62, H 7.74.

(4aS,5S,8aR)-5-((S)-Furan-2-yl(methoxy)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***12l***). **12l** was obtained from acetal **10l** as an orange solid (79 mg, 70%, d.r. 99:1) (method B). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42−7.41 (m, 1H, CHFuryl), 6.37−6.36 (m, 1H, CHFuryl), 6.32−6.31 (m, 1H, CHFuryl), 4.20 (s, 1H, CH), 4.04−3.87 (m, 4H, CH_2), 3.17 (s, 3H, CH_3O), 2.70 (dd, 1H, CH, J = 12.8, J = 3.2 Hz), 2.55−2.33 (m, 2H, CH_2), 2.18−2.10 (m, 1H, CH_2), 1.67−1.25 (m, 6H, $3CH_2$), 1.03 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.04−0.97 (m, 1H, CH_2), 0.22−0.15 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.2 (O═*C*), 152.0 (C^{IV}Furyl), 142.3 (CHFuryl), 112.8 (*C*), 110.4 (CHFuryl), 109.3 (CHFuryl), 85.3 (CH), 65.4 (CH_2), 65.1 (CH_2), 57.8 (CH_3O), 54.6 (*C*), 42.2 (*C*), 41.1 (CH), 36.0 (CH_2), 30.6 (CH_2), 25.9 (CH_2), 24.0 (CH_2), 22.9 (CH_2), 19.2 (CH_3), 15.2 (CH_3). mp: 101.4−102.0 °C. $[\alpha]_D^{20}$ = −104 ($CHCl_3$, c = 1.33). IR (cm^{-1}): 2949, 2884, 1694, 1182, 1087, 1054, 952, 914, 740. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{20}H_{28}O_5Na$, 371.1829; found, 371.1837.

(4aS,5S,8aR)-5-((R)-1-Methoxyoctyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***12n***). **12n** was obtained from **10n** as an uncolored oil (59 mg, 48%, d.r. 75:25) (method B). Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.00−3.90 (m, 4H), 3.28 (s, 3H), 3.17−3.14 (m, 1H), 2.46 (dd, 1H, J = 13.0, J = 3.5 Hz), 2.40−2.36 (m, 2H), 2.14−2.07 (m, 1H), 1.74−1.23 (m, 19H), 1.01 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 219.1, 112.8, 91.9, 65.4, 65.1, 60.9, 54.5, 42.4, 42.2, 36.1, 32.1, 32.0, 30.4, 30.1, 29.5, 27.6, 26.1, 25.6, 23.0, 22.8, 18.8, 15.3, 14.2. IR (cm^{-1}): 2926, 2857, 1694, 1461, 1182, 1092, 1056, 949, 914. Elementary analysis: $C_{23}H_{40}O_4$: calcd (%), C 72.59, H 10.59; found, C 72.41, H 10.83.

(4aS,5S,8aR)-5-((R)-1-Methoxy-3-methylbutyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***12o***). **12o** was obtained from acetal **10o** as an uncolored oil (56 mg, 51%, d.r. 77:23) (method B). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.00−3.86 (m, 4H, $2CH_2$), 3.47 (s, 3H, CH_3O), 3.34 (dd, 1H, CH, J = 10.0, J = 2.4 Hz), 2.51−2.34 (m, 2H, CH, CH_2), 2.10−2.02 (m, 1H, CH_2), 1.76−1.23 (m, 10H, $6CH_2$, 1.11−1.01 (m, 1H, CH_2), 1.09 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 0.92 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 216.7 (O═*C*), 112.9 (*C*), 87.0 (CH), 65.3 (CH_2), 65.0 (CH_2), 62.0 (CH_3O), 55.5 (*C*), 43.0 (CH), 42.4 (*C*), 41.9 (CH_2), 36.3 (CH_2), 30.4 (CH_2), 27.7 (CH_2), 25.6, 24.3 (2*CH_3), 23.5, 23.0 (CH_2, CH_2), 21.9 (CH), 19.1 (CH_3), 16.5 (CH_3). Specific rotation: Minor diastereomer: $[\alpha]_D^{20}$ = −21 ($CHCl_3$, c = 1.30). IR (cm^{-1}): 2951, 2871, 1692, 1467, 1182, 1087, 1056, 914. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{20}H_{34}O_4Na$, 361.2349; found, 361.2362.

(4aS,5S,8aR)-5-((R,E)-1-Methoxy-3-phenylallyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***12p***). **12p** was obtained from acetal **10p** as an uncolored oil (87 mg, 70%, d.r. 85:15) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.46−7.24 (m, 5H, CHPh), 6.57 (d, 1H, CH, J_{trans} = 16.0 Hz), 6.08 (dd, 1H, CH, J_{trans} = 16.0, J = 8.4 Hz), 4.06−3.85 (m, 4H, $2CH_2$), 3.70 (d, 1H, CH, J = 8.4 Hz), 3.18 (s, 1H, CH_3O), 2.64 (dd, 1H, CH, J = 12.4, J = 3.6 Hz), 2.53−2.33 (m, 2H, CH_2), 2.18−2.09 (m, 1H, CH_2), 1.80−1.25 (m, 7H, $4CH_2$), 1.03 (s, 3H, CH_3), 1.00 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.9 (O═*C*), 136.6 (C^{IV}Ar), 133.9 (CH), 128.8 (CHPh), 128.0 (CHPh), 126.6 (CHPh), 126.5 (CH), 112.8 (*C*), 91.7 (CH), 65.4, (CH_2), 65.1 (CH_2), 57.1 (CH_3O), 54.6 (*C*), 42.4 (*C*), 41.6 (CH), 36.2 (CH_2), 30.6 (CH_2), 26.0 (CH_2), 25.6 (CH_2), 22.9 (CH_2), 19.4 (CH_3), 15.3 (CH_3). IR (cm^{-1}): 2944, 2881, 1694, 1181, 1084, 1057, 913, 747, 692. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{24}H_{32}O_4Na$, 407.2193; found, 407.2187.

(4aS,5S,8aR)-5-((R)-1-Ethoxy-3-phenylprop-2-yn-1-yl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (***14a***). **14a** was obtained from acetal **13a** as a uncolored oil (96 mg, 75%, d.r. 67:33) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.72−4.40 (m, 2H), 7.34−7.30 (m, 3H), 4.22 (s, 1H), 4.05−3.90 (m, 4H), 3.84−3.78 (m, 1H), 3.36−3.30 (m, 1H),

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2.80 (dd, 1H, J = 12.8, J = 3.2 Hz), 2.55−2.34 (m, 2H), 2.22−2.10 (m, 2H), 1.75−1.57 (m, 5H), 1.46−1.32 (m, 1H), 1.20 (s, 3H), 1.16 (t, 3H, J = 6.8 Hz), 1.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 216.6, 131.8, 128.5, 128.3, 122.9, 112.9, 87.1, 86.9, 78.3, 65.4, 65.1, 65.1, 54.3, 42.5, 42.3, 36.2, 30.5, 26.0, 24.8, 23.0, 19.0, 15.4, 14.9. IR (cm^{-1}): 2981, 2949, 2878, 1697, 1181, 1085, 1051, 757, 691. HRMS (ESI-TOF) (m/z): $[M + K]^+$ Calcd for $C_{25}H_{32}O_4K$, 435.1932; found, 435.1960.

*(4aS,5S,8aR)-5-((R)-(Benzyloxy)(phenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**16a**).* **16a** was obtained from acetal **15a** as a white oil (123 mg, 88%, d.r. 62:38) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.46−7.21 (m, 10H), 4,49 (s, 1H), 4.30 (AB, 2H, J = 11.8 Hz, $\Delta\nu$ = 85 Hz), 4.05−3.86 (m, 4H), 2.83 (dd, 1H, J = 12.8, J = 3.2 Hz), 2.51−2.28 (m, 2H), 2.23−2.13 (m, 1H), 1.63−1.19 (m, 5H), 1.04 (s, 3H), 0.97 (s, 3H), 0.92−0.81 (m, 1H), 0.024-(−0.13) (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.9, 138.7, 138.0, 128.9−127.3, 112.9, 89.5, 71.0, 65.4, 65.2, 54.8, 42.3, 40.3, 36.2, 30.6, 25.8, 24.3, 22.5, 20.0, 15.3. IR (cm^{-1}): 2948, 2867, 1694, 1452, 1179, 1057, 915, 700. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{28}H_{34}O_4Na$, 457.2349; found, 457.2345.

*(4aS,5S,8aR)-5-((R)-(Benzyloxy)(4-(trifluoromethyl)phenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**16b**).* **16b** was obtained from acetal **15b** as a yellow oil (103 mg, 75%, d.r. 70:30) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.62−7.25 (m, 9H), 4.55 (s, 1H), 4.34 (AB, 2H, J = 11.6 Hz, $\Delta\nu$ = 57 Hz), 4.03−3.86 (m, 4H), 2.79 (dd, 1H, J = 13.2, J = 3.2 Hz), 2.55−2.28 (m, 2H), 2.21−2.13 (m, 1H), 1.67−1.42 (m, 3H), 1.38−1.13 (m, 2H), 1.03 (s, 3H), 0.97 (s, 3H), 0.95−0.84 (m, 1H), −0.005-(−0.09) (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 217.2, 142.5, 138.1, 130.4 (q, J = 32 Hz), 129.2−127.4, 125,0 (m), 124.7 (q, J = 270 Hz), 112.7, 88.8, 71.3, 65.4, 65.2, 54.7, 42.3, 40.3, 36.1, 30.4, 25.8, 24.4, 22.4, 19.9, 15.3. ^{19}F NMR (376 MHz, $CDCl_3$, δ): −62.41 (m, 3F). IR (cm^{-1}): 2948, 2868, 1695, 1323, 1163, 1122, 1056, 1017, 699. HRMS (ESI-TOF) (m/z): $[M]^+$ Calcd for $C_{29}H_{34}F_3O_4$, 503.2404; found, 503.2411.

*(4aS,5S,8aR)-5-((R)-(Benzyloxy)(4-bromophenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**16c**).* **16c** was obtained from acetal **15c** as a yellow oil (136 mg, 82%, d.r. 68:32) (method B). The two diastereomers were partially separated by silica gel column chromatography. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.45−7.29 (m, 9H, 4C*H*Ar, 5C*H*Bn), 4.44 (s, 1H, C*H*), 4.28 (AB, 2H, CH_2Bn, J_{AB} = 11.6 Hz, $\Delta\nu$ = 67 Hz), 4.04−3.89 (m, 4H, 2CH_2), 2.77 (dd, 1H, C*H*, J = 12.8, J = 3.2 Hz), 2.54−2.34 (m, 2H, CH_2), 2.20−2.12 (m, 1H, CH_2), 1.64−1.48 (m, 3H, 2CH_2), 1.38−1.15 (m, 2H, CH_2), 1.01 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 0.95−0.79 (m, 1H, CH_2), 0.11−0.05 (m, 1H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 217.5 (O═*C*), 138.3, 137.3 (C^{IV}Ar, C^{IV}Bn), 129.6 (2*C*HAr), 130.6 (2*C*HAr), 128.4 (2*C*HBn), 127.5 (2*C*HBn), 127.3 (*C*HBn), 127.8 (2*C*HBn), 122.2 (C^{IV}Ar), 112.8 (*C*), 88.9 (CH), 71,1 (CH$_2$Bn), 65.4, (CH$_2$), 65.2 (CH$_2$), 54.6 (*C*), 42.3 (*C*), 40.3 (CH), 36.1 (CH$_2$), 30.5 (CH$_2$), 25.8 (CH$_2$), 24.5 (CH$_2$), 22.5 (CH$_2$), 19.9 (CH$_3$), 15.3 (CH$_3$). mp: 131.3−132.2 °C. IR (cm^{-1}): 2949, 2877, 1693, 1057, 1010, 751, 697. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{28}H_{33}BrO_4Na$, 535.1454; found, 535.1465.

*(4aS,5S,8aR)-5-((S)-(Benzyloxy)(furan-2-yl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**16d**).* **16d** was obtained from acetal **15d** as a white solid (83 mg, 61%, d.r. 99:1) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.44−7.43 (m, 1H, C*H*Fur), 7.34−7.25 (m, 5H, C*H*Bn), 6.38−6.34 (m, 2H, 2*C*HFuryl), 4.45 (s, 3H, C*H*), 4.34 (AB, 2H, CH_2Bn, J = 11.4 Hz, $\Delta\nu$ = 101 Hz), 4.05−3.86 (m, 4H, 2CH_2), 2,85 (dd, 1H, C*H*, J = 12.8, J = 3.2 Hz), 2.53−2.32 (m, 2H, CH_2), 2.19−2.11 (m, 1H, CH_2), 1.66−1.26 (m, 6H, 3CH_2), 1.05 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.10−1.03 (m, 1H, CH_2), 0.27−0.20 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.1 (O═*C*), 152.8 (C^{IV}Furyl), 142.4 (*C*HFur), 138.3 (C^{IV}Bn), 128.3, 127.5 (*C*HBn), 112.8 (*C*), 110.5 (*C*HFuryl), 109.4 (*C*HFuryl), 88.4 (CH), 71.3 (CH$_2$Bn), 65.4 (CH$_2$), 65.2 (CH$_2$), 54.6 (*C*), 42.3 (*C*), 41.2 (CH), 36.1 (CH$_2$), 30.6 (CH$_2$), 25.8 (CH$_2$), 24.0 (CH$_2$), 22.9 (CH$_2$), 19.2 (CH$_3$), 15.2 (CH$_3$). mp: 84.4−85.7 °C. IR (cm^{-1}): 2981, 2941, 2872, 1698, 1055, 747, 696. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{26}H_{32}O_5Na$, 447.2142; found, 447.2157.

*(4aS,5S,8aR)-5-((R)-(Benzyloxy)(2,5-dimethoxyphenyl)methyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**16e**).* **16e** was obtained from acetal **15e** as a fluorescent yellow sticky oil (123 mg, 77%, d.r. 79:21) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34−7.19 (m, 5H), 7.21 (s, 1H), 6.84−6.80 (m, 2H), 5.08 (s, 1H), 4.25 (AB, 2H, J = 11.6 Hz, $\Delta\nu$ = 55 Hz), 4.05−3.87 (m, 4H, 2CH_2), 3.77 (s, 3H), 3.76 (s, 3H), 2.87 (dd, 1H, J = 12.8, J = 2.8 Hz), 2.58−2.31 (m, 2H, CH_2), 2.22−2.13 (m, 1H, CH_2), 1.63−1.48 (m, 3H, C*H*, CH_2), 1.43−1.18 (m, 2H, CH_2), 1.07−1.02 (m, 1H, CH_2), 1.00 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 0.62−0.55 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.6, 153.8, 152.5, 138.9, 128.3, 127.6, 127.4, 127.3, 114.2, 113.8, 112.9, 111.5, 82.1, 71,0, 65.3, 65.1, 56,0, 55.8, 55.7, 42.4, 41.2, 36.1, 30.5, 26.2, 24.6, 22.7, 18.8, 15.5. IR (cm^{-1}): 2928, 2868, 1694, 1497, 1216, 1049. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{30}H_{38}O_6Na$, 517.2561; found, 517.2571.

*(4aS,5S,8aR)-5,8a-Dimethyl-5-((R)-2-phenyl-1-((trimethylsilyl)oxy)ethyl)hexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**18a**).* **18a** was obtained from **17a** as an uncolored oil (26 mg, 19%, d.r. n.d.) (method B). The two diastereomers were partially separated by column chromatography. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38−7.11 (m, 5H, C*H*Ph), 4.06−3.91 (m, 5H, CH_2, C*H*), 2.84−2.80 (m, 1H, CH_2), 2.62−2.37 (m, 4H, 2CH_2, C*H*), 2.17−2.09 (m, 1H, CH_2), 1.77−1.41 (m, 7H, 4CH_2), 1.13 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), −0.23 (s, 9H, (CH_3)$_3$Si). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.2 (O═*C*), 140.3 (C^{IV}Ph), 130.0 (2*CHPh), 128.3 (2*CHPh), 126.3 (CHPh), 113.1 (*C*), 81.8 (CH), 65.2 (CH$_2$), 65.1 (CH$_2$), 55.2 (*C*), 42.6 (CH), 42.4 (*C*), 40.1 (CH$_2$), 36.7 (CH$_2$), 30.4 (CH$_2$), 27.6 (CH$_2$), 23.4 (CH$_2$), 22.9 (CH$_2$), 19.8 (CH$_3$), 16.7 (CH$_3$), 0.29 ((CH$_3$)$_3$Si). IR (cm^{-1}): 2952, 2882, 1696, 1250, 1081, 840. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{25}H_{38}O_4SiNa$, 453.2432; found, 453.2417.

*(4aS,5S,8aR)-5,8a-Dimethyl-5-((R)-2-phenyl-1-((triethylsilyl)oxy)ethyl)hexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**19a**).* **19a** was obtained from acetal **17b** as an uncolored oil (27 mg, 18%, d.r. n.d.) (method B). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32−7.19 (m, 5H), 4.20 (ABX, 1H, J = 8.4, J = 2.4 Hz), 4.07−3.90 (m, 4H), 2.89−2.85 (m, 1H), 2.66−2.38 (m, 4H), 2.19−2.05 (m, 1H), 1.86−1.40 (m, 7H), 1.13 (2s, 6H), 0.87−0.82 (m, 9H), 0.38−0.24 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.1, 140.2, 129.8, 128.2, 126.3, 113.1, 81.6, 65.3, 65.1, 55.5, 42.6, 42.5, 41.0, 36.5, 30.5, 27.5, 23.4, 22.9, 20.1, 16.5, 7.2, 5.1. IR (cm^{-1}): 2951, 2876, 1695, 1455, 1081, 736, 699. HRMS (ESI-TOF) (m/z): $[M]^+$ Calcd for $C_{28}H_{45}O_4Si$, 473.3082; found, 473.3099.

*(4aS,5S,8aR)-5-((R)-1-(Benzyloxy)-2-phenylethyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**16f**).* **16f** was obtained from acetal **17c** as an uncolored oil (27 mg, 17%, d.r. n.d.) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): (ppm) = 7.32−7.05 (m, 10H), 3.95−3.64 (*AB*, 2H, J = 10.8 Hz, $\Delta\nu$ = 110.8 Hz), 4.05−3.89 (m, 4H), 3.78−3.74 (m, 1H), 2.93−2.64 (m, 3H), 2.35−2.28 (m, 2H), 2.15−2.04 (m, 1H), 1.83−1.34 (m, 7H), 1.01 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): (ppm) = 216.6, 139.8, 138.6, 129.8−126.2, 112.8, 91.2, 74.5, 65.4, 65.1, 55.6, 42.5, 42.3, 38.2, 36.0, 30.5, 26.0, 25.6, 23.0, 19.0, 15.4. IR (cm^{-1}): 2949, 2882, 1693, 1454, 1180, 1058, 1028, 748, 698. HRMS (ESI-TOF) (m/z): $[M + K]^+$ Calcd for $C_{29}H_{36}O_4K$, 487.2245; found, 487.2225.

*(4aS,5S,8aR)-5-((R)-1-Hydroxy-2-(4-methoxyphenyl)ethyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**11b**).* **11b** was obtained from mixed acetals **17d** as a pale white oil (16 mg, 13%, d.r. n.d.) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.99 (A_2X_2, 4H, J_{AX} = 8.8 Hz, $\Delta\nu$ = 121 Hz), 4.02−3.90 (m, 4H), 3.79 (s, 3H), 3.58 (m, 1H), 2.91 (dd, 1H, J = 14,0, J = 2.0 Hz), 2.65 (d, 1H, O*H*, J = 8.0 Hz), 2.56−2.36 (m, 4H), 2.06 (td, 1H, J = 13.2, J = 6.4 Hz), 1.77−1.44 (m, 7H), 1.25 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 220.0, 158.3, 131.5, 130.4, 114.1, 112.8, 80.2, 65.4, 65.2, 55.4, 54.0, 43.0, 42.6, 38.9, 36.1, 30.5, 27.4, 23.3, 23.0, 19.0, 15.7. IR (cm^{-1}): 3498, 2933, 2884, 1690,

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1511, 1244, 1178, 1035, 754. HRMS (ESI-TOF) (m/z): $[M]^+$ Calcd for $C_{23}H_{33}O_5$, 389.2323; found, 389.2317.

*(4aS,5S,8aR)-5-((R)-1-Hydroxypentyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**11c**).* **11c** was obtained from mixed acetal **17e** as an uncolored oil. (31 mg, 29%, d.r. n.d) (method B). Only one diastereomer was obtained from purification. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.00−3.85 (m, 4H, 2CH_2), 3.32 (t, 1H, CH, J = 8.6 Hz), 2.85 (d, 1H, OH, J = 9.6 Hz), 2.54−2.29 (m, 2H, CH_2), 2.20−2.16 (m, 1H, CH), 2.00−1.91 (m, 1H, CH_2), 1.78−1.24 (m, 13H, 7CH_2), 1.21 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 0.90 (t, 3H, CH_3, J = 6.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 220.7 (O=C), 112.7 (C), 78.1 (CH), 65.4 (CH_2), 65.1 (CH_2), 54.0 (C), 43.3 (CH), 42.5 (C), 36.1 (CH_2), 32.8 (CH_2), 30.4 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 23.0 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 19.2 (CH_3), 15.8 (CH_3), 14.2 (CH_3). IR (cm^{-1}): 3495, 2950, 2872, 1691, 1460, 1182, 1055, 1016, 914. HRMS (ESI-TOF) (m/z): $[M]^+$ Calcd for $C_{19}H_{33}O_4$, 325.2373; found, 325.2373.

*(4aS,5S,8aR)-5-((R)-2-Cyclopentyl-1-hydroxyethyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**11d**).* **11d** was obtained from acetal **17f** as an uncolored oil (14 mg, 12%, d.r. n.d.) (method B). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.00−3.86 (m, 4H), 3.38 (m, 1H), 2.82 (d, 1H, OH, J = 10 Hz), 2.55−2.29 (m, 2H), 2.20−2.17 (m, 1H), 2.10−1.25 (m, 19H), 1.22 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 220.7, 112.7, 77.4, 65.4, 65.1, 53.9, 43.3, 42.5, 39.6, 37.6, 36.1, 33.7, 32.1, 30.5, 27.7, 25.2, 25.1, 23.0, 22.5, 19.2, 15.8. IR (cm^{-1}): 3491, 2927, 2862, 1689, 1454, 1182, 1056, 1019, 950, 915. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{21}H_{34}O_4Na$, 373.2349; found, 373.2362.

*4aS,5S,8aR)-5-((R)-1-Hydroxy-4-phenylbutyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**11e**).* **11e** was obtained from acetal **17g** as an uncolored oil (43 mg, 34%, d.r. n.d.) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32−7.16 (m, 5H), 4.02−3.85 (m, 4H), 3.38 (t, 1H, J = 10.4 Hz), 2.92 (d, 1H, OH, J = 10.0 Hz), 2.72−1.31 (m, 17H), 1.24 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 220.7, 142.6, 128.5, 128.4, 125.8, 112.7, 77.8, 65.4, 65.1, 54.0, 43.3, 42.6, 36.4, 35.7, 32.7, 30.4, 28.8, 27.7, 23.0, 22.4, 19.3, 15.8. IR (cm^{-1}): 3491, 2945, 2877, 1709, 1694, 1453, 1182, 1058, 949, 914, 699. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{24}H_{34}O_4Na$, 409.2349; found, 409.2364.

*(4aS,5S,8aR)-5-((R)-2-(4-Methoxyphenyl)-1-((trimethylsilyl)oxy)-ethyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]-dioxolan]-6(5H)-one (**18b**).* **18b** was obtained from **17d** as an uncolored oil (67 mg, 45%, d.r. n.d.) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.09−7.07 (m, 2H), 6.83−6.80 (m, 2H), 4.07 (dd, 1H, J = 10.0, J = 2.0 Hz), 4.05−3.89 (m, 4H), 3.79 (s, 3H), 2.85−2.80 (m, 1H), 2.67 (dd, 1H, J = 13.2, J = 3.2 Hz), 2.57−2.36 (m, 3H), 2.15−2.02 (m, 1H), 1.79−1.36 (m, 7H), 1.09 (s, 3H), 1.04 (s, 3H), −0.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.3, 158.3, 131.8, 130.8, 113.9, 113.0, 83.8, 65.4, 65.2, 55.9, 55.5, 41.9, 42.4, 38.9, 36.1, 30.5, 25.9, 23.4, 22.9, 19.0, 15.7, 0.4. IR (cm^{-1}): 2951, 2882, 1694, 1512, 1245, 838. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{26}H_{40}O_5SiNa$, 483.2537; found, 483.2541.

*(4aS,5S,8aR)-5,8a-Dimethyl-5-((R)-1-((trimethylsilyl)oxy)pentyl)-hexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**18c**).* **18c** was obtained from **17e** as an uncolored oil (18 mg, 14%, d.r. n.d.) (method B). Only one diastereomer was obtained after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.01−3.88 (m, 4H, 2CH_2), 3.61−3.59 (m, 1H, CH), 2.56−2.50 (m, 1H, CH), 2.54−2.30 (m, 2H, CH_2), 2.16−2.07 (m, 1H, CH_2), 1.77−1.25 (m, 13H, 7CH_2), 1.03, 1.02 (2s, 6H, 2CH_3), 0.88 (t, 3H, CH_3,, J = 7.2 Hz), 0.15 (s, 9H, OSiCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.3 (O=C), 113.0 (C), 80.3 (CH), 65.2 (CH_2), 65.0 (CH_2), 55.0 (C), 42.6 (CH), 42.3 (C), 36.8 (CH_2), 32.9 (CH_2), 30.3 (CH_2), 30.0 (CH_2), 27.5 (CH_2), 23.5 (CH_2), 22.9 (CH_2), 22.9 (CH_2) 19.3 (CH_3), 16.7 (CH_3), 14.2 (CH_3), 0.93 (OSiCH_3).. IR (cm^{-1}): 2953, 2932, 2872, 1695, 1250, 1054, 838. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ Calcd for $C_{22}H_{40}O_4SiNa$, 419.2588; found, 419.2604.

*(4aS,5S,8aR)-5-((R)-2-Cyclopentyl-1-((trimethylsilyl)oxy)ethyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]-dioxolan]-6(5H)-one (**18d**).* **18d** was obtained from **17f** as an uncolored oil (21 mg, 15%, d.r. n.d.) (method B). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.02−3.88 (m, 4H), 3.65 (ABX, 1H, J = 9.6, J = 2.0 Hz), 2.57−2.47 (m, 2H), 2.38−2.29 (m, 1H), 2.18−2.07 (m, 1H), 1.90−1.46 (m, 18H), 1.03, 1.02 (2s, 6H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.2, 113.1, 79.3, 65.2, 65.0, 54.9, 42.4, 42.3, 39.6, 36.9, 36.8, 33.7, 31.8, 30.3, 27.5, 25.3, 25.1, 23.5, 22.9, 19.4, 16.8, 0.91. IR (cm^{-1}): 2946, 2927, 2867, 1699, 1457, 1251, 1073, 838. HRMS (ESI-TOF) (m/z): $[M]^+$ Calcd for $C_{24}H_{43}O_4$, 423.2925; found, 423.2934.

*(4aS,5S,8aR)-5,8a-Dimethyl-5-((R)-4-phenyl-1-((trimethylsilyl)-oxy)butyl)hexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**18e**).* **18e** was obtained from acetal **17g** as an uncolored oil (10 mg, 7%, d.r. n.d.) (method B). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32−7.15 (m, 5H, 5CH), 4.02−3.89 (m, 4H, 2CH_2), 3.67−3.63 (m, 1H, CH), 2.60−2.30 (m, 5H, 2CH_2, CH), 2.14−2.06 (m, 1H, CH_2), 1.79−1.23 (m, 11H, 6CH_2), 1.03 (s, 6H, 2CH_3), 0.14 (OSi(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 217.2 (O=C), 142.7 (C^{IV}), 128.5 (CH), 128.4 (CH), 125.8 (CH), 113.0 (C), 80.1 (CH), 65.2 (CH_2), 65.0 (CH2), 55.0 (C), 42.7 (CH), 42.3 (C), 36.7 (CH_2), 36.3 (CH_2), 33.1 (CH_2), 30.3 (CH_2), 29.6 (CH_2), 27.4 (CH_2), 23.5 (CH_2), 22.9 (CH_2), 19.3 (CH_3), 16.7 (CH_3), 0.94 (OSi(CH_3)$_3$). IR (cm^{-1}): 2950, 2861, 1694, 1250, 1180, 1087, 837. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{27}H_{42}O_4Na$, 481.2745; found, 481.2746.

*(4aS,5S,8aR)-5-((R)-1-Methoxypentyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12r**).* **12r** was obtained from **17e** as an uncolored oil (24 mg, 22%, d.r. n.d.) (method B). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.00−3.88 (m, 4H, 2CH_2), 3.29 (s, 3H, OMe), 3.17−3.14 (m, 1H, CH), 2.46 (dd, 1H, CH, J = 12.4, J = 3.2 Hz), 2.40−2.35 (m, 2H, CH_2), 2.15−2.06 (m, 1H, CH_2), 1.71−1.26 (m, 13H, 7CH_2), 1.00 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 0.91 (t, 3H, CH_3, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 219.1 (O=C), 112.8 (C), 91.9 (CH), 65.4 (CH_2), 65.1 (CH_2), 60.9 (OMe), 54.5 (C), 42.4 (C), 42.2 (CH), 36.1 (CH_2), 31.8 (CH_2), 30.5 (CH_2), 29.7 (CH_2), 26.1 (CH_2), 25.6 (CH_2), 23.2 (CH_2), 23.0 (CH_2), 18.8 (CH_3), 15.3 (CH_3), 14.2 (CH_3). IR (cm^{-1}): 2956, 2930, 2872, 1694, 1460, 1181, 1088, 1055, 914. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{20}H_{34}O_4Na$, 361.2349; found, 361.2358.

*(4aS,5S,8aR)-5-((R)-2-Cyclopentyl-1-methoxyethyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12s**).* **12s** was obtained from **17f** as an uncolored oil (51 mg, 43%, d.r. n.d.) (method B). The two diastereomers were partially separated by column chromatography. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.00−3.87 (m, 4H), 3.30 (s, 3H), 3.22 (ABX, 1H, J = 9.6, J = 2.0 Hz), 2.47 (dd, 1H, J = 12.8, J = 3.6 Hz) 2.41-2.35 (m, 2H), 2.14−2.07 (m, 1H), 2.03−1.92 (m, 1H), 1.93−1.30 (m, 17H), 1.00 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 219.2.6, 112.8, 90.8.3, 65.3, 65.1, 60.8, 54.4 42.4, 42.2, 38.9, 37.0, 36.1, 34.2, 32.1, 30.3, 26.1, 25.6, 25.4, 23.0, 18.7, 15.3 IR (cm^{-1}): 2923, 2854, 1697, 1461, 1182, 1108. HRMS (ESI-TOF) (m/z): $[M]^+$ Calcd for $C_{22}H_{37}O_4$, 365.2686; found, 423.2686.

*(4aS,5S,8aR)-5-((R)-1-Methoxy-4-phenylbutyl)-5,8a-dimethylhexahydro-2H-spiro[naphthalene-1,2′-[1,3]dioxolan]-6(5H)-one (**12t**).* **12t** was obtained from acetal **17g** as an uncolored oil (38 mg, 30%, d.r. n.d.) (method B). The two diastereomers were partially separated by column chromatography. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30−7.16 (m, 5H, CH), 4.01−3.86 (m, 4H, 2CH_2), 3.27 (s, 3H, OMe), 3.21−3.18 (m, 1H, CH), 2.62 (t, 2H, CH_2, J = 7.6 Hz), 2.48−2.35 (m, 3H, CH, CH_2), 2.13−2.02 (m, 1H, CH_2), 1.95−1.22 (m, 11H, 6CH_2), 1.00 (s, 3H, CH_3), 0.97 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 218.9 (O=C), 142.4 (C^{IV}Ph), 128.5 (CHPh), 128.5 (CHPh), 125.9 (CHPh), 112.7 (C), 91.7 (CH), 65.4 (CH_2), 65.1 (CH_2), 60.9 (OMe), 54.4 (C), 42.4 (C), 42.2 (CH), 36.4 (CH_2), 36.1 (CH_2), 31.8, (CH_2), 30.4 (CH_2), 29.5 (CH_2), 26.1 (CH_2), 25.6 (CH_2), 23.0 (CH_2), 18.9 (CH_3), 15.3 (CH_3). IR (cm^{-1}): 2930, 2877, 1694, 1453, 1182, 1105, 1045, 949, 911, 748, 699. HRMS (ESI-TOF) (m/z): [M + Na]$^+$ Calcd for $C_{25}H_{36}O_4Na$, 423.2506; found, 423.2519.

■ ASSOCIATED CONTENT

Supporting Information

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X-ray crystallographic data for compound **12b** (CIF)
X-ray crystallographic data for compound **12f** (CIF)
Complementary experimental details; characterizations and ^{1}H, ^{13}C, and ^{19}F spectra of new compounds; and X-ray data for **12b** and **12f** (ZIP)

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Notes

The authors declare no competing financial interest.

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