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Mild Approach to 2-Acylfurans via Intercepted Meyer–Schuster Rearrangement of 6-Hydroxyhex-2-en-4-ynals†

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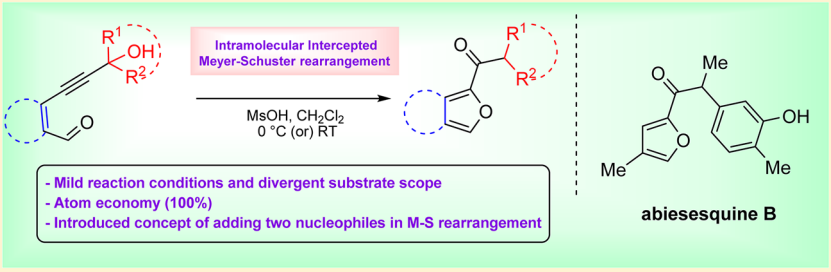
Supporting Information



ABSTRACT: We have developed a mild, intramolecular intercepted Meyer–Schuster (M-S) rearrangement for the synthesis of 2-acylfurans from corresponding *cis*-6-hydroxyhex-2-en-4-ynals. This reaction was found to be very general, and the starting materials are easily accessible. By this methodology the first synthesis of deoxy-*nor*-abiesesquine B, a sesquiterpene, was also achieved in three steps. The concept of adding two nucleophiles during the M-S rearrangement was introduced.

INTRODUCTION

Propargylic alcohols have been found to be very useful structural units, with two functional groups (alkyne and hydroxyl) available to synthetic organic chemists. They have been well utilized in exploring many new synthetic methodologies.[1] The acid (Brønsted or Lewis)-catalyzed 1,3-transposition of propargylic alcohols **1** to the corresponding α,β-unsaturated ketones/aldehydes **2** via the allenic carbocation **3b**, known as the Meyer–Schuster (M-S) rearrangement[2] (Scheme 1), has recently attracted the synthetic community.[3] In recent times trapping (interception) of this carbocation **3b** in either intra- or intermolecular fashion with various nucleophiles was also developed (Scheme 1, interrupted M-S).[4] This particular variation of the M-S rearrangement has been very useful in organic synthesis to generate interesting heterocyclic as well as carbocyclic systems.

Acyl furans are valuable structural units that can be transformed into many other functional groups in synthetic organic chemistry.[5] Additionally, these structures are ubiquitous in many bioactive natural products[6] and pharmaceutical molecules[7] (Figure 1). Accordingly, several methods exist for the synthesis of this class of compounds.[8] Nonetheless, the development of mild and efficient methods to synthesize these structures from readily available or easily accessible starting materials is still necessary.

Herein we report a new method, which involves for the first time employing the intramolecular intercepted Meyer–Schuster rearrangement of 6-hydroxyhex-2-en-4-ynals for the generation of 2-acylfuran framework. In this work, we introduce the concept of adding two nucleophiles (intramolecular followed by intermolecular) to an allenic carbocation (the M-S intermediate) rather than a nucleophile (intra- or intermolecular) followed by an electrophile (intermolecular), as in known intercepted M-S rearrangements.

According to our designed strategy, *cis*-6-hydroxyhex-2-en-4-ynals **4**, in the presence of acid, can generate the oxonium ion **5** via an intramolecular interception of an allenic carbocation such as **3b**, by the nicely positioned aldehyde carbonyl as the nucleophile. This conjugated oxonium ion **5** can be further trapped by the second nucleophile, i.e. water (H_2O), in an intermolecular fashion by 1,6-addition to give the 2-acylfuran **6**.

RESULTS AND DISCUSSION

To test our designed hypothesis, we took the seven-membered 6-hydroxyhex-2-en-4-ynal **7a** in dichloromethane (CH_2Cl_2), at ice-cold temperature and added 1.3 equiv of *p*-toluenesulfonic acid (*p*-TSA). After complete consumption of the alcohol **7a**, in ca. 48 h, we isolated a 3.4/1 inseparable mixture of the expected 2-acylfuran derivative **8a** and the byproduct olefin **9a** (via dehydration), in 53% combined yield after chromatographic purification (Table 1, entry 1). Since a mixture of products was observed and the reaction was took a longer time with *p*-TSA, we next used a stronger acid: i.e., methanesulfonic acid (MsOH). In this case, to our delight, we observed the exclusive formation of the 2-acylfuran **8a**, in 77% isolated yield, in 1 h of reaction time (Table 1, entry 2). The structure of the 2-acylfuran **8a** was extensively characterized by NMR spectroscopy and mass spectrometry.

We next carried out a screening study for more acids, solvents, and temperature, to determine more general, efficient,

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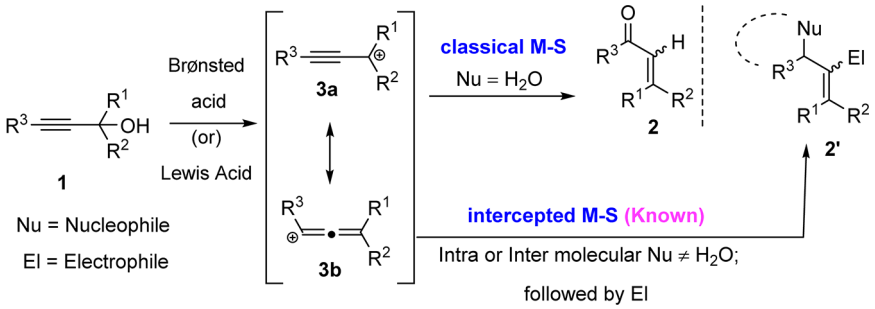
Scheme 1. Classical and Known Intercepted Meyer−Schuster Rearrangements



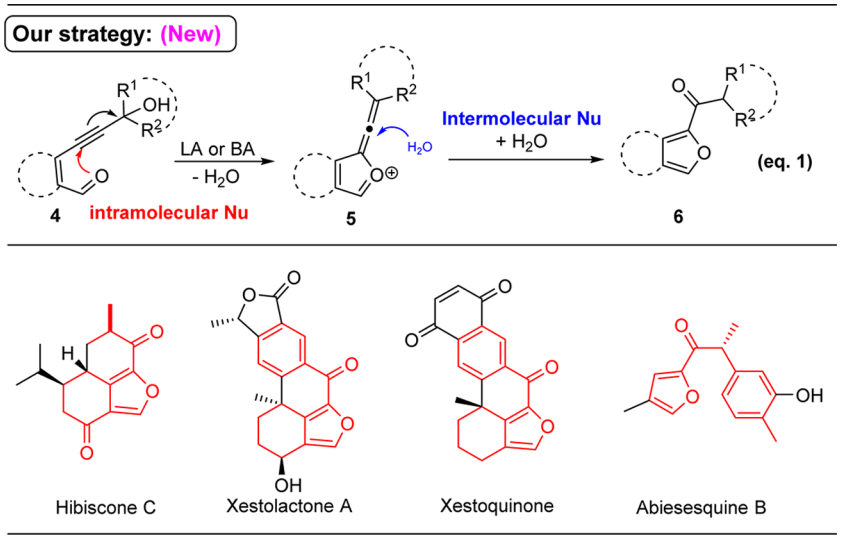


Figure 1. Our designed strategy for synthesis of the 2-acylfuran framework and selected natural products.

and mild reaction conditions. When the very strong acid trifluoromethanesulfonic acid (TfOH) was used in CH_2Cl_2, at 0 °C, the 2-acylfuran **8a** was exclusively formed in 54% yield (entry 3). The mild acid camphorsulfonic acid afforded an inseparable (3.4/1) mixture of **8a** and **9a**, respectively, after 48 h. Then we turned to screening a few Lewis acids (entries 4 and 5). With $AlCl_3$, an inseparable 2.5/1 mixture of **8a** and **9a** was obtained, in 75% yield. In the case of $TiCl_4$, alcohol **7a** was consumed completely in 1 h, generating exclusively an unexpected product, 2-(1-chlorovinyl)furan **10**, in 72% yield (Table 1, entry 5). None of the 2-acylfuran **8a** was isolated. The vinyl chloride **10** was extensively characterized by NMR spectroscopy and mass spectrometry. The formation of **10** can be explained via trapping of the intermediate **5** (Figure 1, eq 1) with the chloride ion from $TiCl_4$.[9] After finding MsOH to be the best acid, we focused on studying this transformation under catalytic conditions: i.e., acid amounts from 1.3 equiv to less than 1 equiv (Table 1, entries 6−8). As we decreased the amount of the acid MsOH below 1 equiv, i.e., making the acid a catalyst, it was found that (a) the reaction (consumption of alcohol) became very slow (1−36 h; compare entries 6−8 with entry 2, Table 1), (b) the selectivity for 2-acylfuran **8a** was poor, i.e. the amount of olefin **9a** increased from 0 (entry 2) to 10% (entry 6), and (c) the yields dropped from 77% (only **8a**, entry 2) to 35% (**8a** and **9a**, entry 8). In the case of an increase in the acid load we observed faster reaction times but a decrease in yields; e.g., with 2.2 equiv of acid (entry 9, Table 1), the reaction was complete in 50 min and the yield was 47% of only 2-acylfuran **8a**, whereas 3.2 equiv of acid (entry 10, Table 1) took 35 min for reaction completion but the yield decreased to 41% (compare with entry 2, Table 1). Since TfOH is a stronger acid, we expected that it would be suitable for use in catalytic amounts, without altering the selectivity and efficiency (entries 11 and 12, Table 1). However, quite surprisingly, 0.25 equiv of TfOH gave a 9/1 mixture of **8a** and **9a**, whereas 0.5 equiv resulted in a 14:1 mixture. Hence, 1.3 equiv of MsOH stood out as the best condition to give the best yield of 2-acylfuran **8a** in a short reaction time.

We then screened several solvents (Table 1, entries 13−17) by using 1.3 equiv of MsOH at 0 °C. 1,2-DCB gave a 72% combined yield of 32/1 mixture of **8a** and **9a**. On the other hand, 1,2-DCE and CCl_4 were very selective to give 2-acylfuran **8a** in 70% and 68% yields, respectively, along with ∼10% of vinyl chloride **10** via trapping with chloride ion, possibly from the solvents.[9] Both THF and acetonitrile (entry 16) did not afford any better outcome. When we used ethyl acetate as the solvent, **8a** was the major product (34%), along with the formation of the interesting vinyl acetate **11** in 6% yield. The formation of **11** is possible via trapping of intermediate **5** (Figure 1, eq 1) by EtOAc.[10] Thus, among the various solvents screened, CH_2Cl_2 was found to be the solvent of choice to obtain the 2-acylfuran derivatives selectively and efficiently. We also studied this transformation at different temperatures varying from −15 °C to room temperature (30 °C), using MsOH (1.3 equiv), and 1,2-DCB as solvent. From Table 1, entries 18 and 19, it is clear that as the temperature increases from −15 to 0 °C to room temperature, the preference for the 2-acylfuran **8a** increases within the same time period (1 h, time

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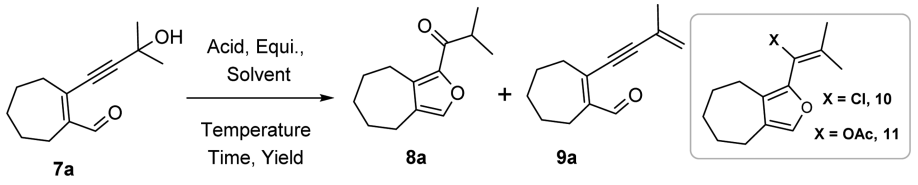
Table 1. Screening of Reaction Conditions for Synthesis of 2-Acylfuran 8a via Designed Intercepted Meyer–Schuster Rearrangement[a]

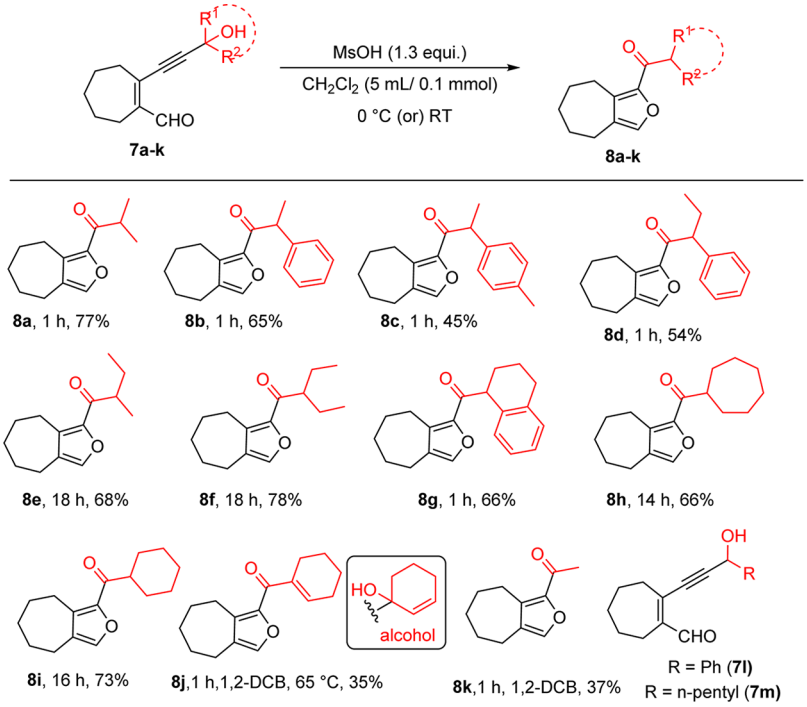


7a 8a 9a

entry	acid	amt of acid (equiv)	solvent	temp (°C)	time[d]	yield (%)[g]	8a:9a[h]
1	*p*-TSA	1.3	CH_2Cl_2	0	48 h	53[b]	3.4:1
2	CH_3SO_3H	1.3	CH_2Cl_2	0	1 h	77	1:0
3	CF_3SO_3H	1.3	CH_2Cl_2	0	1 h	54	1:0
4	$AlCl_3$	1.3	CH_2Cl_2	0	1 h	75[b]	2.5:1
5	$TiCl_4$	1.3	CH_2Cl_2	0	1 h	[e]	
6	CH_3SO_3H	0.25	CH_2Cl_2	0	36 h	35[b,f]	10:1
7	CH_3SO_3H	0.50	CH_2Cl_2	0	17 h	57[b]	25:1
8	CH_3SO_3H	0.75	CH_2Cl_2	0	2 h	63[b]	44:1
9	CH_3SO_3H	2.2	CH_2Cl_2	0	50 min	47	1:0
10	CH_3SO_3H	3.2	CH_2Cl_2	0	35 min	41	1:0
11	CF_3SO_3H	0.25	CH_2Cl_2	0	24 h	48[b]	9:1
12	CF_3SO_3H	0.50	CH_2Cl_2	0	2.5 h	52[b]	14:1
13	CH_3SO_3H	1.3	1,2-DCB	0	1 h	72[b]	32:1
14	CH_3SO_3H	1.3	1,2-DCE[e]	0	1 h	70	1:0
15	CH_3SO_3H	1.3	CCl_4[e]	0	1 h	68	1:0
16	CH_3SO_3H	1.3	CH_3CN	0	1 h	60[b]	36:1
17	CH_3SO_3H	1.3	EtOAc	0	15 h	34[i]	1:0
18	CH_3SO_3H	1.3	1,2-DCB	−15	50 min	60[b]	10:1
19	CH_3SO_3H	1.3	1,2-DCB	room temp[c]	1 h	70	1:0

[a]Typical conditions: alcohol **7a** (1 mmol), solvent (5 mL/0.2 mmol). Abbreviations: 1,2-DCB, 1,2-dichlorobenzene; 1,2-DCE, 1,2-dichloroethane. [b]Combined yield of **8a** and **9a**. [c]Room temperature, 30 °C. [d]In all cases, the time reflects complete consumption of **7a**. [e]Vinyl chloride **10** was isolated (see text). [f]~25% of SM was recovered. [g]Isolated yields after column chromatography. [h]Determined by ^{1}H NMR of mixture. [i]6% of **11** was also isolated.

Table 2. Scope for Structurally Divergent Alcohols with Fused Cycloheptane



for consumption of **7a**). At room temperature (30 °C), only **8a** was observed with no drop in efficiency: i.e., 70% yield. At elevated temperatures such as 70, 100, and 150 °C there was no definable change in the reaction outcome, as the reactions all

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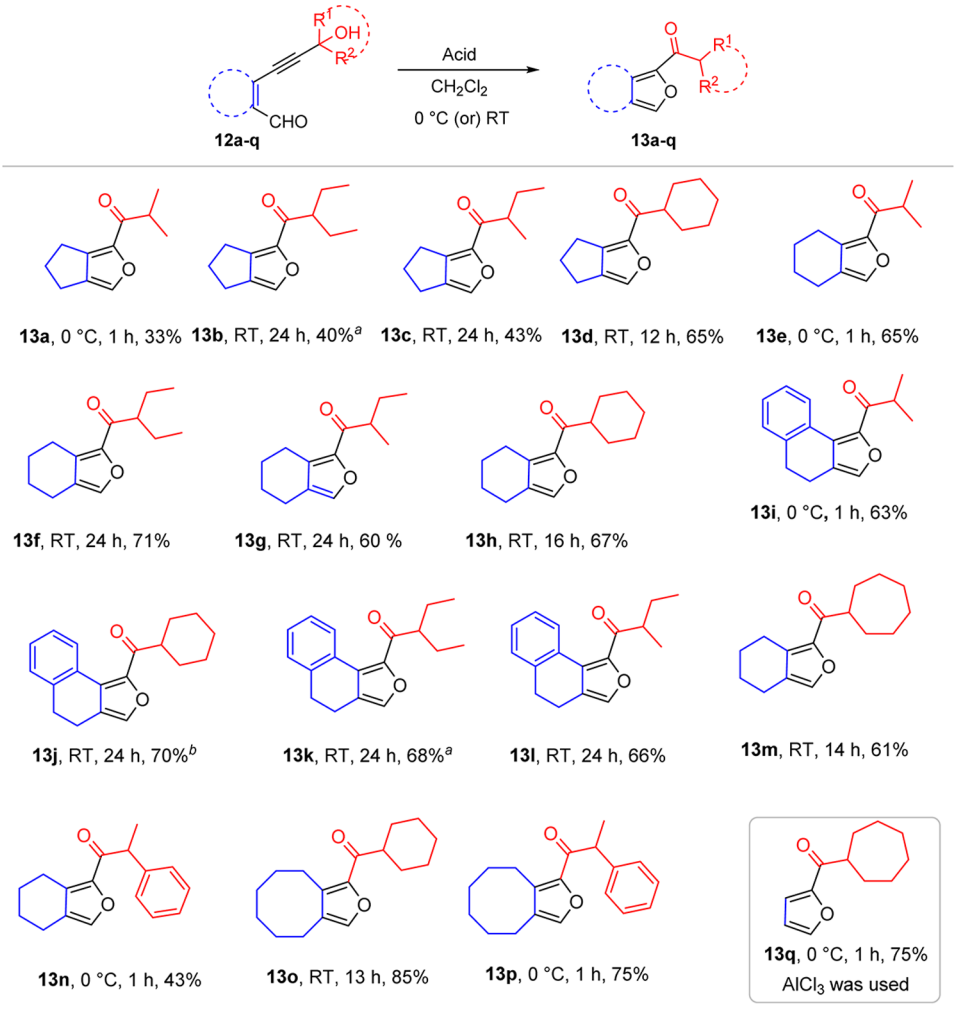
Table 3. Scope for Various Tethers for Structurally Interesting 2-Acylfurans[c]



[a]Olefin **13b′** was also observed (see Experimental Section). [b]Olefin **13j′** was also isolated (see Experimental Section). [c]Standard conditions: CH_3SO_3H (1.3 equiv), CH_2Cl_2 (5 mL/0.1 mmol), 0 °C or room temperature.

gave exclusively **8a**. This clearly suggests that the 2-acylfuran product is thermodynamically controlled, whereas the olefin product is kinetically controlled.

After having the best conditions, i.e. 1.3 equiv of CH_3SO_3H and CH_2Cl_2 and 0 °C or 1,2-DCB and room temperature, in hand for the synthesis of 2-acylfurans selectively and efficiently, we then focused on the screening of various structurally interesting substrates. The results are presented in Tables 2 and 3. This transformation was found to be very general in the nature of substituents on tertiary alcohols as well as the tethering unit. Initially, we studied many different types of alcohols **7a−k**, as shown in Table 2. Symmetrical and unsymmetrical propargylic alcohols were efficiently converted to the corresponding 2-acylfurans. Even the cyclic alcohols **7g−j** underwent the cyclization very smoothly and gave 2-acylfurans **8g−j** in good yields. In the case of **7j**, the double bond in the cyclohexenol migrated in the product **8j**, as expected.

The aryl tertiary alkyl propargylic alcohols **7b−d** were also employed, and the corresponding 2-acylfurans **8b−d** asynthesized re bicyclic derivatives of the natural product abiesesquine B (Figure 1). When we used the primary alcohol **7k**,[11] the corresponding 2-acetylfuran derivative **8k** was isolated, but in relatively low yield (37%). This may be due to the poorer stability of the 1°-carbocation intermediate.

The reaction scope expansion to include substrates bearing several cyclic tethers against different alcohols was also investigated (Table 3). In all cases we could isolate the corresponding 2-acylfurans in good yields. For all of the substrates, we performed the experiments at at either 0 °C or room temperature and varied the reaction time from 1 to 24 h. For the substrates with five-membered tethers **13a−d**, we always observed a drop in 2-acylfuran yield and a minor amount (~5%) of olefin formation in comparison with their six-, seven-, and eight-membered counterparts.

In addition to spectroscopic characterization, the structure of the 2-acylfuran **13h** was unambiguously assigned on the basis of single-crystal X-ray diffraction analysis,[12] and its ORTEP diagram is presented in Figure 2.

To identify the possibility for reversible conversion of olefin **9a** to 2-acylfuran **8a** and also to get evidence for the mechanism, we took the pure olefin **9a** and subjected it to the standard reaction conditions in the presence of 2 equiv of external water (Scheme 2B).[13] After 24 h, there was no evidence for the formation of 2-acylfuran **8a**; instead, olefin **9a** decomposed completely. This clearly ruled out the possibility for interconversion between olefins and 2-acylfurans under the reaction conditions.

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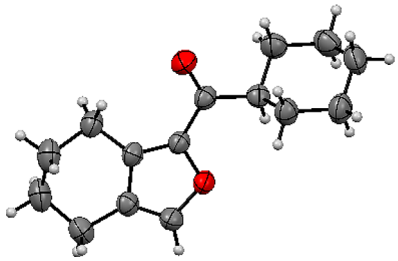


Figure 2. ORTEP diagram of **13h**. The ellipsoid contours are set at 50% probability.

As our designed strategy shows (Figure 1, eq 1), in the second step water adds as a nucleophile. Hence, we have performed this reaction by adding the external water as well as by trapping the water generated during the first step and studied the outcome. In the case of addition of external water (10 equiv) there was no reaction observed and ~100% starting alcohol **7a** was recovered after 13 h (entry 1, Scheme 2B). On the other hand, in the presence of molecular sieves (MS-4Å, 1 g), the reaction was found to be very slow; even after 13 h, formation of only 7% of the 2-acylfuran **8a** was observed (entry 2, Scheme 2B). We have also performed this experiment in the presence of anhydrous $MgSO_4$ (1 g). In this case after 13 h, ~50% of the conversion to **8a** was seen (entry 3, Scheme 2). It is worth noting here that, in both of these cases, there no formation of olefin **9a** was observed. On the basis of these observations we have proposed a possible mechanism in Scheme 3.

Initial protonation of the hydroxyl group in **7a** followed by the elimination of water gives the propargylic carbocation **14**, which can also be represented as its corresponding resonance structure **15**: i.e. an allenic carbocation, the Meyer–Schuster intermediate. An intramolecular interception of **15** by aldehyde as nucleophile generates the cyclic oxonium ion **16** (Scheme 3, path b). The intermediates **14** and **15** are interconvertible (resonance structures). In the next step, a 1,6-addition of water (intermolecular nucleophile) to the oxonium ion **16** gives the furan-enol **17**, which then isomerizes to the 2-acylfuran **8a**. On the other hand, olefin **9a** can be generated from **14** via deprotonation (Scheme 3, path a).

Finally, we have shown the strength of this methodology by extending it to the first synthesis of deoxy-*nor*-abiesesquine B (**18**), an analogue of the sesquiterpene abiesesquine B, as shown in Scheme 4. The Sonogashira coupling[14] of the iodo alcohol[15] **19** and *tert*-propargyl alcohol[16] **20** gave the diol **21** in excellent yield. The primary alcohol in **21** was oxidized in the presence of IBX[17] to yield corresponding the 6-hydroxyhex-2-en-4-ynal **22**. This hydroxyl aldehyde **22** upon treatment with MsOH in CH_2Cl_2 at 0 °C afforded the expected product deoxy-*nor*-abiesesquine B (**18**) in only 23% yield. To improve the efficiency of the formation of **18**, the hydroxyl aldehyde **22** was treated with $AlCl_3$ in CH_2Cl_2 at 0 °C. To our delight, **18** was formed in good yield (57%).

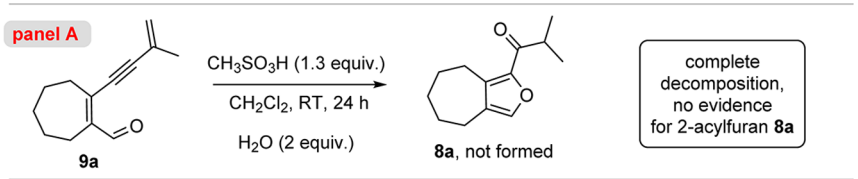
CONCLUSIONS

In conclusion, we have developed a mild method for the synthesis of 2-acylfurans from easily accessible 6-hydroxyhex-2-en-4-ynals. This is the first time an intramolecular intercepted Meyer–Schuster rearrangement has been employed to prepare 2-acylfurans. We have shown a very broad scope in terms of structural variations at both the alcohol side and the tethering unit side. Here, we have also introduced the new concept that two nucleophiles can be added, rather than a nucleophile and an electrophile, during the M-S rearrangement. Finally we have shown that this method can be well utilized for the total synthesis of 2-acylfuran natural products, by synthesizing deoxy-*nor*-abiesesquine B (**18**). Further developments and application of this methodology to more natural product syntheses are in progress.

EXPERIMENTAL SECTION

General Methods. Reactions were monitored by thin-layer chromatography (TLC) carried out on Merck silica plates using UV light and anisaldehyde or potassium permanganate stains for visualization. Column chromatography was performed on silica gel (60–120 mesh) using hexanes and ethyl acetate as eluents unless otherwise specified. Evaporation of solvents was conducted under reduced pressure at temperatures less than 45 °C using a rotary evaporator. NMR data were recorded on 400 and 500 MHz

Scheme 2. Control Experiments



entry	additive	amount	8a	9a	7a
1	H_2O	10 eq.	0	0	1
2	MS (4A°)	1 g	1	0	14
3	$MgSO_4$	1 g	1	0	1.2

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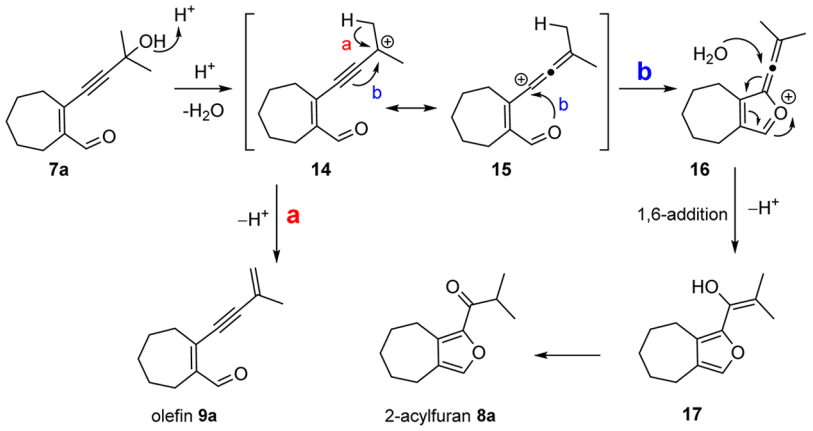
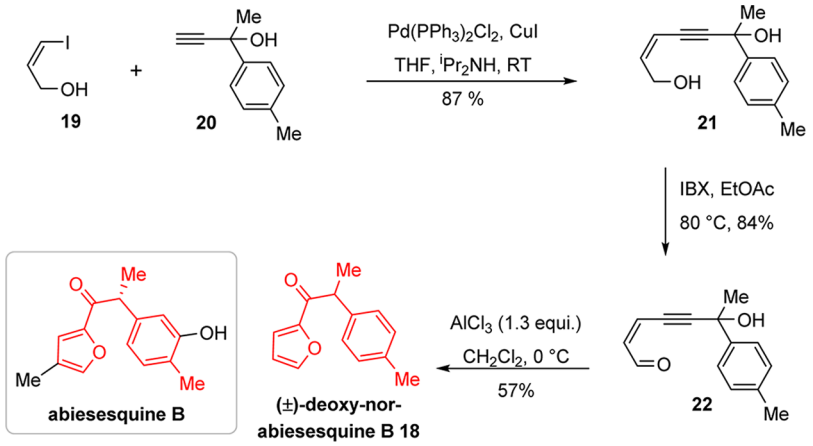
Scheme 3. Possible Mechanism for the Formation of 2-Acylfurans and Olefins



Scheme 4. Application to the First Synthesis of Deoxy-*nor*-abiesesquine B (18)



spectrometers. ^{13}C and ^{1}H chemical shifts in NMR spectra were referenced relative to signals of $CDCl_3$ (δ 7.263 ppm for ^{1}H and 77.16 ppm for ^{13}C). HRMS were recorded by the electron spray ionization (ESI) method on a Q-TOF Micro instrument with lock spray source. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz), respectively. All reactions were carried out using reaction tubes. Known compound data have been compared with the reported data, and references are given appropriately. Characterization data for new compounds is given below, and ^{1}H and ^{13}C NMR spectra for all new compounds are given in the Supporting Information.

General Procedure A: Synthesis of (*Z*)-6-Hydroxy-6-methylhept-2-en-4-ynals 7a–k and 12a–q via Sonogashira Coupling Reaction. The bromo aldehyde (1 equiv) and propargylic alcohol (1.2 equiv) were placed in a clean and anhydrous round-bottom flask equipped with a stir bar, then anhydrous THF and $^{i}Pr_2NH$ were added under a nitrogen atmosphere, and the flask was cooled to 0 °C. Subsequently, CuI (0.15 equiv) and $Pd(PPh_3)_2Cl_2$ (1 mol %) were placed in the reaction flask; then after 30 min at 0 °C, the reaction mixture was warmed to room temperature and the stirring was continued at the same temperature for 14–18 h. Reaction progress was monitored by thin-layer chromatography (TLC) analysis. After complete consumption of the bromo aldehyde, the reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried ($MgSO_4$), and concentrated. The crude material was typically purified by flash chromatography using a hexane/ethyl acetate mixture as eluent to yield the (*Z*)-6-hydroxy-6-methylhept-2-en-4-ynal derivatives **7a–k** and **12a–k**.

*2-(3-Hydroxy-3-methylbut-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**7a**).* The hydroxyl aldehyde **7a** was prepared following the general procedure A from bromo aldehyde[18] (340 mg, 1.68 mmol), propargyl alcohol (169 mg, 2.0 mmol), anhydrous THF (13 mL), anhydrous $^{i}Pr_2NH$ (3 mL), CuI (48 mg, 0.25 mmol), and $Pd(PPh_3)_2Cl_2$ (12 mg, 0.016 mmol), by stirring for 16 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7a** (330 mg, 1.60 mmol, 95%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (1 H, s), 2.60–2.56 (2 H, m), 2.51–2.46 (2 H, m), 2.04 (1 H, br s) 1.83–1.75 (2 H, m), 1.66–1.61 (2 H, m), 1.58 (6 H, s), and 1.47–1.41 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 148.7, 145.5, 104.9, 80.6, 65.9, 37.5, 32.3, 31.4, 25.7, and 24.3 ppm. IR (neat): 3423 (OH), 2979, 2926, 2853, 2750 (H–CO), 1665 (C=O), 1591, 1447, 1366, 1231, 1164, and 961 cm^{-1}. HR ESI-MS: $[C_{13}H_{19}O_2]^+ = [M + H]^+$ requires 207.1380; found 207.1392. TLC: R_f = 0.35 (4/1, Hex/EtOAc).

*2-(3-Hydroxy-3-phenylbut-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**7b**).* The hydroxyl aldehyde **7b** was prepared following the general procedure A from bromo aldehyde (202 mg, 1 mmol), propargyl alcohol (160 mg, 1.1 mmol), anhydrous THF (12 mL), anhydrous $^{i}Pr_2NH$ (2 mL), CuI (28 mg, 0.15 mmol), and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), by stirring for 19 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7b** (245 mg, 0.92 mmol, 92%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (1 H, s), 7.65–7.61 (2 H, m), 7.42–7.36 (2 H, m), 7.34–7.31 (1 H, m), 2.66–2.62 (2 H, m), 2.57 (1 H, br s) 2.53–2.52 (2 H, m), 1.84 (3 H, s), 1.83–1.77 (2 H, m), 1.69–1.62 (2 H, m), and 1.49–1.42 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 149.1, 145.1, 128.7, 128.1, 124.9, 103.6, 83.2, 70.7, 37.5, 33.2, 32.3, 25.8, 25.7, and 24.4 ppm. IR (neat): 3442 (OH), 2926, 2853, 2835 (H–CO), 2362, 1667 (C=O), 1596, 1447, 1361,

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1184, 763, and 699 cm^{-1}. HR ESI-MS: $[C_{18}H_{21}O_2]^+ = [M + H]^+$ requires 269.1536; found 269.1553. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Hydroxy-3-p-tolylbut-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**7c**).* The hydroxyl aldehyde **7c** was prepared following the general procedure A from bromo aldehyde (202 mg, 1.0 mmol), propargyl alcohol[19] (165 mg, 1.1 mmol), anhydrous THF (10 mL), anhydrous $^iPr_2NH$ (2 mL), CuI (28 mg, 0.15 mmol), and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), by stirring for 19 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7c** (185 mg, 0.65 mmol, 66%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ 10.29 (1 H, s), 7.66−7.63 (2 H, m), 7.32 (2 H, d, J = 7.9 Hz), 2.77 (2 H, t, J = 5.4 Hz), 2.63 (2H, t, J = 5.5 Hz), 2.49 (3 H, s), 1.96 (3 H, s), 1.95−1.91 (2 H, m), 1.81−1.75 (2 H, m), and 1.61−1.55 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 148.8, 145.4, 142.3, 137.8, 129.2, 124.8, 104.1, 82.8, 70.3, 37.5, 33.0, 32.2, 25.7, 25.6, 24.3, and 21.1 ppm. IR (neat): 3438 (OH), 2930, 2858, 2751 (*H*-CO), 1670 (C═O), 1599, 1447, 1363, 1164, 758, and 731 cm^{-1}. HR ESI-MS: $[C_{19}H_{23}O_2]^+ = [M + H]^+$ requires 283.1693; found 283.1700. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Hydroxy-3-phenylpent-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**7d**).* The hydroxyl aldehyde **7d** was prepared following the general procedure A from bromo aldehyde (227 mg, 1.12 mmol), propargyl alcohol[20] (150 mg, 0.94 mmol), anhydrous THF (10 mL), anhydrous $^iPr_2NH$ (2 mL), CuI (28 mg, 0.15 mmol), and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), by stirring for 17 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7d** (180 mg, 0.64 mmol, 71%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ 10.10 (1 H, s), 7.51−7.47 (2 H, m), 7.30−7.24 (2 H, m), 7.22−7.17 (1 H, m), 3.15 (1 H, br s), 2.55 (2 H, t, J = 5.4 Hz), 2.40 (2 H, t, J = 5.4 Hz), 2.00−1.83 (2 H, m), 1.75−1.64 (2 H, m), 1.59−1.52 (2 H, m), 1.39−1.32 (2 H, m), and 0.87 (3 H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 148.8, 145.5, 143.9, 128.3, 127.8, 125.4, 102.9, 84.0, 74.4, 38.3, 37.6, 32.1, 25.6, 24.2, and 9.2 ppm. IR (neat): 3436 (OH), 2927, 2853, 2754 (H−CO), 1665 (C═O), 1594, 1448, 1366, 1184, 759, and 697 cm^{-1}. HR ESI-MS: $[C_{19}H_{22}NaO_2]^+ = [M + Na]^+$ requires 305.1512; found 305.1516. TLC: R_f = 0.4 (5/1, Hex/EtOAc).

*2-(3-Hydroxy-3-methylpent-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**7e**).* The hydroxyl aldehyde **7e** was prepared following the general procedure A from bromo aldehyde (88 mg, 0.43 mmol), propargyl alcohol[21] (36 mg, 0.36 mmol), anhydrous THF (7 mL), anhydrous $^iPr_2NH$ (1.5 mL), CuI (10 mg, 0.054 mmol), and $Pd(PPh_3)_2Cl_2$ (2.54 mg, 0.0036 mmol), by stirring for 13 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7e** (48 mg, 0.22 mmol, 80%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ 10.11 (1 H, s), 2.60−2.55 (2 H, m), 2.50−2.46 (2 H, m), 1.81−1.76 (4 H, m), 1.66−1.58 (2 H, m), 1.52 (3 H, s), and 1.04 (3 H, t, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 148.5, 145.5, 104.1, 81.7, 69.4, 37.7, 36.6, 32.3, 29.2, 25.7, 24.3, and 9.2 ppm. IR (neat): 3424 (OH), 2927, 2855, 2745 (H−CO), 1665 (C═O), 1596, 1449, and 1368 cm^{-1}. HR ESI-MS: $[C_{14}H_{20}O_2Na]^+ = [M + Na]^+$ requires 243.1356; found 243.1353. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Ethyl-3-hydroxypent-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**7f**).* The hydroxyl aldehyde **7f** was prepared following the general procedure A from bromo aldehyde (247 mg, 1.22 mmol), propargyl alcohol[22] (115 mg, 1.02 mmol), anhydrous THF (10 mL), anhydrous $^iPr_2NH$ (3 mL), CuI (29 mg, 0.153 mmol), and $Pd(PPh_3)_2Cl_2$ (8 mg, 0.01 mmol), by stirring for 13 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7f** (200 mg, 0.85 mmol, 85%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ 10.12 (1 H, s), 2.61−2.56 (2 H, m), 2.50−2.46 (2 H, m), 1.83−1.68 (6 H, m), 1.66−1.59 (2 H, m), 1.46−1.40 (2 H, m), and 1.04 (6 H, t, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 148.5, 145.5, 103.3, 82.8, 72.9, 37.8, 34.5, 32.3, 25.7, 24.3, and 8.8 ppm. IR (neat): 3439 (OH), 2927, 2855, 2750 (*H*-CO), 1666 (C═O), 1595, 1453, 1370, 1265, 1196, 1147, and 959 cm^{-1}. HR ESI-MS: $[C_{15}H_{22}NaO_2]^+ = [M + Na]^+$ requires 257.1512; found 257.1518. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-[(1-Hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethynyl]-cyclohept-1-ene-1-carbaldehyde (**7g**).* The hydroxyl aldehyde **7g** was prepared following the general procedure A from bromo aldehyde (352 mg, 1.74 mmol), propargyl alcohol[23] (250 mg, 1.45 mmol), anhydrous THF (13 mL), anhydrous $^iPr_2NH$ (4 mL), CuI (50 mg, 0.26 mmol), and $Pd(PPh_3)_2Cl_2$ (12 mg, 0.0174 mmol), by stirring for 17 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7g** (400 mg, 1.36 mmol, 78%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ 10.10 (1 H, s), 7.73−7.68 (1 H, m), 7.27−7.19 (2 H, m), 7.12−7.08 (1 H, m), 2.89−2.85 (2 H, m), 2.61−2.57 (2 H, m), 2.49−2.45 (2 H, m), 2.27−2.22 (2 H, m), 2.09−1.87 (2 H, m), 1.82−1.74 (2 H, m), 1.65−1.58 (2 H, m), and 1.46−1.39 (2 H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 148.8, 145.4, 138.7, 136.1, 129.4, 128.5, 127.8, 126.8, 104.6, 82.6, 68.6, 39.0, 37.5, 32.2, 29.3, 25.7, 25.6, 24.3, and 19.3 ppm. IR (neat): 3422 (OH), 2927, 2854, 2748 (H−C═O), 1664 (C═O), 1593, 1447, 1196, and 962 cm^{-1}. HR ESI-MS: $[C_{20}H_{22}O_2Na]^+ = [M + Na]^+$ requires 317.1512; found 317.1510. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-[(1-Hydroxycycloheptyl)ethynyl]cyclohept-1-ene-1-carbaldehyde (**7h**).* The hydroxyl aldehyde **7h** was prepared following the general procedure A from bromo aldehyde (380 mg, 1.88 mmol), propargyl alcohol[22] (200 mg, 1.45 mmol), anhydrous THF (13 mL), anhydrous $^iPr_2NH$ (3 mL), CuI (42 mg, 0.23 mmol), and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.015 mmol), by stirring for 16 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7h** (307 mg, 1.18 mmol, 81%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ 10.11 (1 H, s), 2.66−2.55 (2 H, m), 2.50−2.45 (2 H, m), 2.09−2.01 (2 H, m), 1.80−1.71 (2 H, m), 1.66−1.53 (10 H, m), and 1.45−1.38 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 148.1, 145.9, 105.6, 81.7, 72.3, 43.0, 37.6, 32.1, 28.0, 25.6, 24.1, and 22.3 ppm. IR (neat): 3404 (OH), 2927, 2743 (H−CO), 1668 (C═O), 1593, 1451, 1202, 1028, and 735 cm^{-1}. HR ESI-MS: $[C_{17}H_{24}O_2Na]^+ = [M + Na]^+$ requires 283.1669; found 283.1682. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-[(1-Hydroxycyclohexyl)ethynyl]cyclohept-1-ene-1-carbaldehyde (**7i**).* The hydroxyl aldehyde **7i** was prepared following the general procedure A from bromo aldehyde (250 mg, 1.23 mmol), propargyl alcohol (200 mg, 1.6 mmol), anhydrous THF (13 mL), anhydrous $^iPr_2NH$ (2.5 mL), CuI (35 mg, 0.19 mmol), and $Pd(PPh_3)_2Cl_2$ (8.7 mg, 0.012 mmol) by stirring at room temperature for 14 h. Purification by flash chromatography (hexane/EtOAc, 4/1) gave the hydroxy aldehyde **7i** (282 mg, 1.39 mmol, 93%) as a pale yellow oil.

^1H NMR (500 MHz, $CDCl_3$): δ 10.11 (1 H, s), 2.60−2.55 (2 H, m), 2.48−2.42 (2 H, m), 1.98−1.91 (2 H, m), 1.80−1.68 (4 H, m), 1.64−1.56 (4 H, m), 1.53−1.46 (2 H, m), 1.44−1.37 (2 H, m), and 1.32−1.20 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 148.3, 145.9, 104.4, 82.5, 69.3, 39.8, 37.7, 32.2, 25.6, 25.2, 24.2, and 23.4 ppm. IR (neat): 3405 (OH), 2930, 2854, 2828 (H−CO), 1665 (C═O), 1592, 1447, 1262, 1186, 1069, and 962 cm^{-1}. HR ESI-MS: $[C_{16}H_{23}O_2]^+ = [M + H]^+$ requires 247.1693; found 247.1691. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-[(1-Hydroxycyclohex-2-enyl)ethynyl]cyclohept-1-ene-1-carbaldehyde (**7j**).* The hydroxyl aldehyde **7j** was prepared following the general procedure A from bromo aldehyde (363 mg, 1.5 mmol), propargyl alcohol[24] (183 mg, 1.5 mmol), anhydrous THF (13 mL), anhydrous $^iPr_2NH$ (3 mL), CuI (42 mg, 0.23 mmol), and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.015 mmol), by stirring for 17 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7j** (220 mg, 0.9 mmol, 60%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ 10.09 (1 H, s), 5.87−5.82 (1H, tt, J = 10.0 and 3.6 Hz), 5.78−5.73 (1 H, tt, J = 10.0 and 2.4 Hz), 2.59−2.55 (2 H, m), 2.48−2.43 (2 H, m), 2.10−1.90 (4 H, m), 1.85−1.70 (4 H, m), 1.60−1.55 (2 H, m), and 1.44−1.37 (2 H, m). ^{13}C NMR (125

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MHz, $CDCl_3$): δ 192.6, 148.5, 145.7, 130.2, 129.9, 104.0, 81.9, 65.8, 37.7, 37.4, 32.2, 25.6, 24.7, 24.2, and 19.2 ppm. IR (neat): 3412 (OH), 3031, 2927, 2853, 2738 (*H*-CO), 1664 (C═O), 1594, 1446, 1366, 1262, 1198, 1059, 963, and 735 cm^{-1}. HR ESI-MS: $[C_{16}H_{21}O_2]^+$ = [M + H]$^+$ requires 245.1536; found 245.1542. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Hydroxyprop-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**7k**).* The hydroxyl aldehyde **7k** was prepared following the general procedure A from bromo aldehyde (404 mg, 2 mmol), propargyl alcohol (145 mg, 2.6 mmol), anhydrous THF (13 mL), anhydrous $^iPr_2NH$ (4 mL), CuI (57 mg, 0.3 mmol), and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), by stirring for 12 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **7k** (230 mg, 1.29 mmol, 65%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (1 H, s), 4.47 (1 H, d, *J* = 9.6 Hz), 2.57 (2 H, bt, *J* = 6.0 Hz), 2.45 (2 H, bt, *J* = 6.0 Hz), 1.78−1.75 (2 H, m), 1.61−1.58 (2 H, m), and 1.41−1.38 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.7, 148.7, 145.7, 98.9, 83.7, 51.5, 37.4, 32.2, 25.6, and 24.2 ppm. IR (neat): 3428 (OH), 2923, 2858, 2753 (H−CO), 1670 (C═O), 1600, 1538, 1438, 1322, 1245, 1111, and 856 cm^{-1}. HR ESI-MS: $[C_{11}H_{15}O_2]^+$ = [M + H]$^+$ requires 179.1067; found 179.1058. TLC: R_f = 0.4 (3/1, Hex/EtOAc).

*2-(3-Hydroxy-3-methylbut-1-ynyl)cyclopent-1-ene-1-carbaldehyde (**12a**).* The hydroxyl aldehyde **12a** was prepared following the general procedure A from bromo aldehyde[25] (348 mg, 2.0 mmol), propargyl alcohol (201 mg, 2.4 mmol), anhydrous THF (15 mL), anhydrous $^iPr_2NH$ (4 mL), CuI (57 mg, 0.3 mmol), and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), by stirring for 17 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12a** (295 mg, 1.66 mmol, 83%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (1 H, s), 3.0 (1 H, br s), 2.68−2.61 (2 H, m), 2.58−2.51 (2 H, m), 1.95−1.85 (2 H, m), and 1.54 (6 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 147.9, 143.5, 105.9, 75.9, 65.5, 38.9, 31.2, 29.5, and 22.1 ppm. IR (neat): 3414 (OH), 2976, 2929, 2851, 2829 (*H*-C═O), 1664 (C═O), 1595, 1360, 1239, 1166, and 956 cm^{-1}. HR ESI-MS: $[C_{11}H_{15}O_2]^+$ = [M + H]$^+$ requires 179.1067; found 179.1074. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Ethyl-3-hydroxypent-1-ynyl)cyclopent-1-ene-1-carbaldehyde (**12b**).* The hydroxyl aldehyde **12b** was prepared following the general procedure A from bromo aldehyde (234 mg, 1.35 mmol), propargyl alcohol (181 mg, 1.62 mmol), anhydrous THF (13 mL), anhydrous $^iPr_2NH$ (3 mL), CuI (38 mg, 0.20 mmol), and $Pd(PPh_3)_2Cl_2$ (9.5 mg, 0.013 mmol), by stirring for 16 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12b** (170 mg, 0.83 mmol, 61%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (1 H, s), 2.71 (2 H, tt, *J* = 2.2 and 7.5 Hz), 2.61 (2 H, tt, *J* = 2.2 and 7.6 Hz), 2.01−1.92 (2 H, m), 1.79−1.66 (4 H, m), 1.62 (1 H, br s), and 1.05 (6 H, t, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 148.3, 143.0, 103.8, 78.5, 73.0, 309.2, 34.5, 29.7, 22.2, and 8.7 ppm. IR (neat): 3434 (OH), 2969, 2937, 2882, 2735 (H−CO), 1664 (C═O), 1594, 1458, 1385, 1354, 1222, 1144, and 962 cm^{-1}. HR ESI-MS: $[C_{13}H_{18}NaO_2]^+$ = [M + Na]$^+$ requires 229.1199; found 229.1214. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Hydroxy-3-methylpent-1-ynyl)cyclopent-1-ene-1-carbaldehyde (**12c**).* The hydroxyl aldehyde **12c** was prepared following the general procedure A from bromo aldehyde (348 mg, 2.0 mmol), propargyl alcohol (254 mg, 2.6 mmol), anhydrous THF (10 mL), anhydrous $^iPr_2NH$ (4 mL), CuI (57 mg, 0.3 mmol), and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), by stirring for 17 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12c** (260 mg, 1.35 mmol, 68%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (1 H, s), 2.69 (2 H, tt, *J* = 2.4, and 7.4 Hz), 2.60 (2 H, tt, *J* = 2.3 and 7.8 Hz), 2.16 (1 H, br s), 1.95 (2 H, quintet, *J* = 7.6), 1.81−1.72 (2 H, m), 1.54 (3 H, s), and 1.06 (3 H, t, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 148.3, 143.0, 104.6, 77.4, 69.4, 39.1, 36.6, 29.6, 29.2, 22.2, and 9.2 ppm. IR (neat): 3429 (OH), 2972, 2933, 2876, 2750 (*H*-CO), 1670 (C═O), 1595, 1459, 1352, 1228, 1130, 915, and 705 cm^{-1}. HR ESI-MS: $[C_{12}H_{17}O_2]^+$ = [M + H]$^+$ requires 193.1223; found 193.1235. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-[(1-Hydroxycyclohexyl)ethynyl]cyclopent-1-ene-1-carbaldehyde (**12d**).* The hydroxy aldehyde **12d** was prepared following the general procedure A from bromo aldehyde (348 mg, 2.0 mmol), alcohol (297 mg, 2.4 mmol), anhydrous THF (15 mL), anhydrous $^iPr_2NH$ (5 mL), CuI (57 mg, 0.3 mmol), and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol) by stirring at room temperature for 16 h. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12d** (390 mg, 1.79 mmol, 89%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.0 (1 H, s), 2.70 (2 H, tt, *J* = 7.6 and 1.6 Hz), 2.57 (2 H, tt, *J* = 7.6 and 2.0 Hz), 2.00−1.87 (4 H, m), 1.75−1.43 (6 H, m), and 1.25−1.20 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 147.9, 143.5, 105.1, 78.2, 69.2, 39.8, 39.1, 29.5, 25.1, 23.4, and 22.1 ppm. IR (neat): 3400 (OH), 2937, 2857, 2744 (*H*-CO), 1665 (C═O), 1594, 1071, and 966 cm^{-1}. HR ESI-MS: $[C_{14}H_{18}O_2Na]^+$ = [M + Na]$^+$ requires 241.1199; found 241.1195. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Hydroxy-3-methylbut-1-ynyl)cyclohex-1-ene-1-carbaldehyde (**12e**).* The hydroxyl aldehyde **12e** was prepared following the general procedure A from bromo aldehyde[26] (564 mg, 3 mmol), propargyl alcohol (327 mg, 3.9 mmol), anhydrous THF (18 mL), anhydrous $^iPr_2NH$ (6 mL), CuI (86 mg, 0.45 mmol), and $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol), by stirring for 17 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12e** (500 mg, 2.6 mmol, 87%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (1 H, s), 2.40−2.37 (2 H, m), 2.26−2.23 (2 H, m), 1.69−1.65 (2 H, m), and 1.58 (6 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.1, 142.8, 139.8, 103.5, 79.2, 65.7, 32.4, 31.4, 22.1, 21.9, and 21.1 ppm. IR (neat): 3418 (OH), 2966, 2920, 2853, 2753 (H−CO), 1666 (C═O), 1589, 1350, 1233, 1163, and 947 cm^{-1}. HR ESI-MS: $[C_{12}H_{17}O_2]^+$ = [M + H]$^+$ requires 193.1223; found 193.1215. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Ethyl-3-hydroxypent-1-ynyl)cyclohex-1-ene-1-carbaldehyde (**12f**).* The hydroxyl aldehyde **12f** was prepared following the general procedure A from bromo aldehyde (470 mg, 2.5 mmol), propargyl alcohol (364 mg, 3.25 mmol), anhydrous THF (15 mL), anhydrous $^iPr_2NH$ (5 mL), CuI (71 mg, 0.38 mmol), and $Pd(PPh_3)_2Cl_2$ (18 mg, 0.025 mmol), by stirring for 16 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12f** (350 mg, 1.86 mmol, 67%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (1 H, s), 2.42−2.38 (2 H, m), 2.27−2.24 (2 H, m), 2.00 (1 H, br s), 1.78−1.62 (8 H, m), and 1.05 (6 H, t, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 142.9, 139.8, 101.6, 81.6, 72.9, 34.5, 32.7, 22.1, 22.0, 21.2, and 8.8 ppm. IR (neat): 3437 (OH), 2967, 2872, 2730 (*H*-CO), 1668 (C═O), 1601, 1457, 1369, 1229, 1204, 1143, 962, and 755 cm^{-1}. HR ESI-MS: $[C_{14}H_{20}NaO_2]^+$ = [M + Na]$^+$ requires 243.1356; found 243.1368. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Hydroxy-3-methylpent-1-ynyl)cyclohex-1-ene-1-carbaldehyde (**12g**).* The hydroxyl aldehyde **12g** was prepared following the general procedure A from bromo aldehyde (376 mg, 2.0 mmol), propargyl alcohol (254 mg, 2.6 mmol), anhydrous THF (10 mL), anhydrous $^iPr_2NH$ (4 mL), CuI (57 mg, 0.3 mmol), and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), by stirring for 17 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12g** (300 mg, 1.46 mmol, 73%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.16 (1 H, s), 2.41−2.37 (2 H, m), 2.27−2.23 (2 H, m), 2.08 (1 H, br s), 1.79−1.72 (2 H, m), 1.70−1.61 (2 H, m), 1.53 (3 H, s), and 1.05 (3 H, t, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9, 142.9, 139.7, 102.4, 80.5, 69.4, 36.6, 32.6, 29.3, 22.1, 22.0, 21.1, and 10.0 ppm. IR (neat): 3426 (OH), 2972, 2938, 2660, 2725 (H−CO), 1675 (C═O), 1600, 1459, 1364, 1233, 1213, 1162, 996, and 924 cm^{-1}. HR ESI-MS: $[C_{13}H_{19}O_2]^+$ = [M + H]$^+$ requires 207.1380; found 207.1378. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-[(1-Hydroxycyclohexyl)ethynyl]cyclohex-1-ene-1-carbaldehyde (**12h**).* The hydroxyl aldehyde **12h** was prepared following the general procedure A from bromo aldehyde (372 mg, 2 mmol), propargyl alcohol (297 mg, 2.4 mmol), anhydrous THF (15 mL), anhydrous

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$^{i}Pr_2NH$ (4 mL), CuI (57 mg, 0.3 mmol), and $Pd(PPh_3)_2Cl_2$ (14.4 mg, 0.02 mmol) by stirring at room temperature for 14 h. Purification by flash chromatography (hexane/EtOAc 4/1) gave the hydroxyl aldehyde **12h** (394 mg, 1.7 mmol, 85%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.16 (1 H, s), 2.42−2.36 (2 H, m), 2.26−2.21 (2 H, m), 1.98−1.91 (2 H, m), 1.75−1.46 (10 H, m), and 1.30−1.18 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.0, 142.4, 140.2, 102.8, 81.1, 69.1, 39.8, 32.5, 25.1, 23.4, 22.0, 21.8, and 21.0 ppm. IR (neat): 3409 (OH), 2934, 2858, 2734 (*H*-CO), 1669 (C═O), 1601, 1232, 1069, and 965 cm^{-1}. HR ESI-MS: $[C_{15}H_{21}O_2]^+ = [M + H]^+$ requires 233.1536; found 233.1541. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*1-(3-Hydroxy-3-methylbut-1-ynyl)-3,4-dihydronaphthalene-2-carbaldehyde (**12i**).* The hydroxyl aldehyde **12i** was prepared following the general procedure A from bromo aldehyde[27] (100 mg, 0.42 mmol), propargyl alcohol (84 mg, 0.5 mmol), anhydrous THF (7 mL), anhydrous $^{i}Pr_2NH$ (1 mL), CuI (12 mg, 0.063 mmol), and $Pd(PPh_3)_2Cl_2$ (3 mg, 0.042 mmol), by stirring for 15 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12i** (89 mg, 0.37 mmol, 86%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (1 H, s), 7.79−7.76 (1 H, m), 7.35−7.26 (2 H, m), 7.19−7.15 (1 H, m), 2.78 (2 H, t, J = 8.4 Hz), 2.57 (2 H, t, J = 8.4 Hz), and 1.69 (6 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.6, 140.5, 137.7, 135.9, 132.2, 127.9, 127.3, 127.1, 106.2, 75.8, 65.9, 31.4, 26.8, and 19.9 ppm. IR (neat): 3422 (OH), 2955, 2925, 2853, 2730 (*H*-CO), 1665 (C═O), 1579, 1462, 1378, 1261, 1017, and 764 cm^{-1}. HR ESI-MS: $[C_{16}H_{16}O_2Na]^+ = [M + Na]^+$ requires 263.1043; found 263.1046. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*1-[(1-Hydroxycyclohexyl)ethynyl]-3,4-dihydronaphthalene-2-carbaldehyde (**12j**).* The hydroxyl aldehyde **12j** was prepared following the general procedure A from bromo aldehyde (236 mg, 1.5 mmol), propargyl alcohol (124 mg, 1.93 mmol), anhydrous THF (10 mL), anhydrous $^{i}Pr_2NH$ (3 mL), CuI (42 mg, 0.22 mmol), and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol), by stirring for 15 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12j** (310 mg, 1.11 mmol, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.39 (1 H, s), 7.82−7.80 (1 H, m), 7.37−7.28 (2 H, m), 7.19−7.17 (1 H, m), 2.79 (2 H, t, J = 8.4 Hz), 2.58 (2 H, t, J = 7.5 Hz), 2.09−2.06 (2 H, m), 1.83−1.55 (6 H, m), and 1.29−1.23 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 140.6, 137.7, 135.9, 132.3, 130.9, 127.9, 127.3, 127.1, 105.5, 69.5 (*C*−OH), 39.9, 26.8, 25.2, 23.5, and 19.9 ppm. IR (neat): 3412 (OH), 2934, 2855, 2735 (H−CO), 1657 (C═O), 1597, 1554, 1445, 1371, 1300, 1182, 1069, 965, and 736 cm^{-1}. HR ESI-MS: $[C_{19}H_{20}O_2Na]^+ = [M + Na]^+$ requires 303.1356; found 303.1355. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*1-(3-Ethyl-3-hydroxypent-1-ynyl)-3,4-dihydronaphthalene-2-carbaldehyde (**12k**).* The hydroxyl aldehyde **12k** was prepared following the general procedure A from bromo aldehyde (236 mg, 2.5 mmol), propargyl alcohol (364 mg, 3.25 mmol), anhydrous THF (15 mL), anhydrous $^{i}Pr_2NH$ (5 mL), CuI (71 mg, 0.38 mmol), and $Pd(PPh_3)_2Cl_2$ (17.5 mg, 0.025 mmol), by stirring for 16 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12k** (500 mg, 1.86 mmol, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.38 (1 H, s), 7.81−7.78 (1 H, m), 7.37−7.29 (2 H, m), 7.21−7.19 (1 H, m), 2.83 (2 H, t, J = 7.8 Hz), 2.60 (2 H, t, J = 7.8 Hz), 2.10 (1 H, br s), 1.90−1.78 (4 H, m), and 1.14 (6 H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 140.8, 137.8, 135.8, 132.4, 130.9, 128.0, 127.3, 127.1, 104.4, 78.0, 73.1, 34.6, 26.8, 20.0, and 8.9 ppm. IR (neat): 3445 (OH), 2968, 2935, 2880, 2841 (H−CO), 1661 (C═O), 1597, 1555, 1455, 1366, 1295, 1189, and 962 cm^{-1}. HR ESI-MS: $[C_{18}H_{21}O_2]^+ = [M + H]^+$ requires 269.1536; found 269.1538. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*1-(3-Hydroxy-3-methylpent-1-ynyl)-3,4-dihydronaphthalene-2-carbaldehyde (**12l**).* The hydroxyl aldehyde **12l** was prepared following the general procedure A from bromo-aldehyde (472 mg, 2 mmol), propargyl alcohol (254 mg, 2.6 mmol), anhydrous THF (10 mL), anhydrous $^{i}Pr_2NH$ (4 mL), CuI (57 mg, 0.3 mmol), and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), by stirring for 16 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12l** (410 mg, 1.61 mmol, 81%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.37 (1 H, s), 7.80−7.78 (1 H, m), 7.36−7.29 (2 H, m), 7.21−7.19 (1 H, m), 2.82 (2 H, t, J = 8.4 Hz), 2.60 (2 H, t, J = 7.5 Hz), 2.16 (1 H, br s), 1.90−1.84 (2 H, m), 1.65 (3 H, s), and 1.14 (3 H, t, J = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 140.8, 137.8, 135.7, 132.3, 130.9, 128.0, 127.3, 127.1, 105.1, 77.1, 69.6, 36.7, 29.4, 26.9, 20.0, and 9.3 ppm. IR (neat): 3425 (OH), 2972, 2934, 2888, 2745 (*H*-CO), 1658 (C═O), 1600, 1556, 1365, 1303, 1158, 996, and 771 cm^{-1}. HR ESI-MS: $[C_{17}H_{19}O_2]^+ = [M + H]^+$ requires 255.1380; found 255.1379. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-[(1-Hydroxycycloheptyl)ethynyl]cyclohex-1-ene-1-carbaldehyde (**12m**).* The hydroxyl aldehyde **12m** was prepared following the general procedure A from bromo aldehyde (354 mg, 1.45 mmol), propargyl alcohol (200 mg, 1.5 mmol), anhydrous THF (10 mL), anhydrous $^{i}Pr_2NH$ (3 mL), CuI (42 mg, 0.23 mmol), and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.015 mmol), by stirring for 16 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12m** (294 mg, 1.20 mmol, 80%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (1 H, s), 2.43−2.37 (2 H, m), 2.27−2.22 (2 H, m), 1.93−1.84 (2 H, m), and 1.72−1.53 (12 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.0, 142.5, 140.2, 103.9, 80.4, 72.2, 43.0, 32.5, 28.0, 22.3, 22.0, 21.8, and 21.1 ppm. IR (neat): 3425 (OH), 2923, 2859, 2753 (*H*-CO), 1670 (C═O), 1600, 1227, 1030, and 736 cm^{-1}. HR ESI-MS: $[C_{16}H_{22}O_2Na]^+ = [M + Na]^+$ requires 269.1512; found 269.1521. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Hydroxy-3-phenylbut-1-ynyl)cyclohex-1-ene-1-carbaldehyde (**12n**).* The hydroxyl aldehyde **12n** was prepared following the general procedure A from bromo aldehyde (225 mg, 1.2 mmol), propargyl alcohol (146 mg, 1 mmol), anhydrous THF (12 mL), anhydrous $^{i}Pr_2NH$ (2 mL), CuI (28 mg, 0.15 mmol), and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), by stirring for 19 h at room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12n** (170 mg, 0.67 mmol, 67%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.20 (1 H, s), 7.64−7.61 (2 H, m), 7.40−7.36 (2 H, m), 7.34−7.29 (1 H, m), 2.64 (1 H, br s), 2.46−2.43 (2 H, m), 2.29−2.25 (2 H, m), 1.83 (3 H, s), and 1.72−1.63 (4 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9, 145.1, 143.1, 139.7, 128.5, 127.9, 124.8, 102.2, 81.6, 70.4, 33.2, 32.4, 22.1, 21.8, and 21.0 ppm. IR (neat): 3423 (OH), 2985, 2931, 2860, 2748 (*H*-CO), 1674 (C═O), 1599, 1491, 1363, 1275, 1192, 1173, 1128, 1027, 937, and 735 cm^{-1}. HR ESI-MS: $[C_{17}H_{19}O_2]^+ = [M + H]^+$ requires 255.1385; found 255.1381. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-[(1-Hydroxycyclohexyl)ethynyl]cyclooct-1-ene-1-carbaldehyde (**12o**).* The hydroxyl aldehyde **12o** was prepared following the general procedure A from bromo aldehyde[26] (216 mg, 1 mmol), propargyl alcohol (124 mg, 1.2 mmol), dry THF (8 mL), dry $^{i}Pr_2NH$ (2 mL), CuI (29 mg, 0.15 mmol), and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), stirred for 18 h at 0 °C to room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave the hydroxy aldehyde **12o** (220 mg, 0.85 mmol, 85%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (1 H, s), 2.59−2.56 (2 H, bt, J = 6.0 Hz), 2.46−2.43 (2 H, bt, J = 6.0 Hz), 2.04 (1 H, s), 1.99−1.95 (2 H, m), 1.76−1.72 (4 H, m), 1.67−1.59 (2 H, m), 1.56−1.49 (4 H, m), 1.47−1.45 (4 H, m), and 1.32−1.22 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.6, 146.1, 142.8, 103.0, 81.9, 69.5, 40.1, 34.4, 29.9, 29.0, 26.6, 26.1, 25.3, 23.7, and 23.6 ppm. IR (neat): 3413 (OH), 2930, 2855, 2741 (*H*-CO), 2363, 1669 (C═O), 1592, 1448, 1261, 1211, 1070, and 966 cm^{-1}. HR ESI-MS: $[C_{17}H_{24}NaO_2]^+ = [M+ Na]^+$ requires 283.1669; found 283.1665. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*2-(3-Hydroxy-3-phenylbut-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**12p**).* The hydroxyl aldehyde **12p** was prepared following the general procedure A from bromo aldehyde (216 mg, 1 mmol), alcohol (175 mg, 1.2 mmol), dry THF (8 mL), dry $^{i}Pr_2NH$ (2 mL), CuI (28

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mg, 0.15 mmol), and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), stirred for 12 h at 0 °C to room temperature. Purification by flash chromatography (4/1 hexane/EtOAc) gave aldehyde **12p** (260 mg, 0.92 mmol, 92%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.20 (1 H, s), 7.64−7.61 (2 H, m), 7.39−7.36 (2 H, m), 7.34−7.28 (1 H, m), 2.83 (1 H, m), 2.60 (2 H, bt, J = 6.0 Hz), 2.46 (2 H, bt, J = 6.0 Hz), 1.83 (3 H, s), 1.81−1.75 (2 H, m), 1.57−1.50 (2 H, m), and 1.46−1.44 (4 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 146.6, 145.2, 142.5, 128.6, 128.0, 124.9, 102.6, 82.2, 70.6, 34.2, 33.2, 29.8, 29.0, 26.6, 26.0, and 23.6 ppm. IR (neat): 3436 (OH), 2929, 2856, 2735 (H−CO), 2361, 1666 (C═O), 1593, 1449, 1364, 1228, 1094, 910, and 733 cm^{-1}. HR ESI-MS: $[C_{19}H_{23}O_2]^+ = [M + H]^+$ requires 283.1693; found 283.1685. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*(Z)-1-(5-Hydroxypent-3-en-1-ynyl)cycloheptanol (**12q′**).* The diol **12q′** was prepared following the general procedure A from iodo alcohol **19** (130 mg, 0.7 mmol), propargyl alcohol (138 mg, 0.78 mmol), dry THF (7 mL), dry DIPA (2 mL), CuI (20 mg, 0.1 mmol), and Pd(II) $(PPh_3)_2Cl_2$ (5 mg, 0.007 mmol), stirred for 18 h at 0 °C to room temperature. Purification by flash chromatography (3/1 hexane/EtOAc) gave diol **12q′** (105 mg, 0.55 mmol, 77%) as a color less oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10−6.04 (1 H, m), 5.63−5.61 (1 H, m), 4.39 (2 H, m, J = 6.2 Hz), 2.05−2.00 (2 H, m), 1.89−1.83 (2 H, m), and 1.71−1.50 (8 H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 110.5, 100.3, 79.2, 72.4, 61.0, 43.2, 28.1, and 22.4 ppm. IR (neat): 3337 (OH), 2926, 2857, 2358, 1619, 1454, 1193, 1024, 973, and 911 cm^{-1}. HR ESI-MS: $[C_{12}H_{18}NaO_2]^+ = [M + Na]^+$ requires 217.1199; found 217.1200. TLC: R_f = 0.4 (3/1, Hex/EtOAc).

*(Z)-5-(1-Hydroxycycloheptyl)pent-2-en-4-ynal (**12q**).* The diol **12q′** (55 mg, 0.28 mmol) and IBX (160 mg, 0.57 mmol) were taken up in dry EtOAc (6 mL) and refluxed for 2 h at 80 °C. Filtration through a silica gel plug using EtOAc (25 mL) gave the crude mixture. Purification of the crude reaction mixture by flash chromatography (4/1 hexane/EtOAc) gave aldehyde **12q** (51 mg, 0.26 mmol, 93%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (1 H, d, J = 8.2 Hz), 6.68 (1 H, d, J = 10.8 Hz), 6.68 (1 H, d, J = 10.8 Hz), 2.17−2.04 (2 H, m), 1.94−1.89 (2 H, m), 1.74−1.67 (2 H, m), 1.63−1.60 (4 H, m), and 1.57−1.54 (2 H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 137.9, 128.7, 106.7, 78.2, 72.5, 43.0, 28.2, and 22.3 ppm. IR (neat): 3417 (OH), 2930, 2857, 2815 (H−CO), 2206, 1677 (C═O), 1582, 1458, 1213, 1124, 1029, and 737 cm^{-1}. HR ESI-MS: $[C_{12}H_{16}NaO_2]^+ = [M + Na]^+$ requires 215.1043; found 215.1049. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

*(Z)-6-p-Tolylhept-2-en-4-yne-1,6-diol (**21**).* The diol **21** was prepared following the general procedure A from the iodo alcohol **19** (120 mg, 0.65 mmol), propargyl alcohol **20** (115 mg, 0.72 mmol), dry ^{i}Pr$_2$NH (2 mL), CuI (19 mg, 0.09 mmol), and $Pd^{II}(PPh_3)_2Cl_2$ (5 mg, 0.007 mmol), stirred for 12 h at 0 °C to room temperature. Purification by flash chromatography (3/1 hexane/EtOAc) gave the diol **21** (120 mg, 0.56 mmol, 86%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (2 H, d, J = 8.2 Hz), 7.16 (2 H, d, J = 8.0 Hz), 6.10−6.04 (1 H, m), 5.65 (1 H, d, J = 10.9 Hz), 4.36 (2 H, d, J = 6.2 Hz), 2.35 (3 H, s), and 1.77 (3 H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 141.9, 137.5, 129.1, 124.9, 110.3, 98.9, 80.4, 70.2, 60.8, 33.2, and 21.2 ppm. IR (neat): 3340 (OH), 2923, 2857, 2360, 1693, 1513, 1408, 1369, 1233, 1175, 1026, 818, and 729 cm^{-1}. HR ESI-MS: $[C_{14}H_{17}O_2]^+ = [M + H]^+$ requires 217.1223; found 217.1230. TLC: R_f = 0.4 (3/1, Hex/EtOAc).

*(Z)-6-Hydroxy-6-p-tolylhept-2-en-4-ynal (**22**).* The diol **21** (100 mg, 0.462 mmol) and IBX (260 mg, 0.93 mmol) were taken up in dry EtOAc (7 mL) and refluxed for 2 h at 80 °C. Filtration through a silica gel plug using EtOAc (25 mL) gave the crude mixture. Purification of the crude reaction mixture by flash chromatography (4/1 hexane/EtOAc) gave the aldehyde **22** (92 mg, 0.43 mmol, 92%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (1 H, d, J = 8.2 Hz), 7.49 (2 H, d, J = 8.2 Hz), 7.18 (2 H, d, J = 8.0 Hz), 6.71 (1 H, d, J = 10.8 Hz), 6.29 (1 H, dd, J = 8.2 and 10.8 Hz), 2.36 (3 H, s), and 1.83 (3 H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 141.8, 138.2, 138.0, 129.3, 128.4, 124.8, 105.2, 79.1, 70.4, 32.7, and 21.1 ppm. IR (neat): 3409 (OH), 2984, 2924, 2854, 2753 (H−CO), 1676 (C═O), 1583, 1510, 1407, 1358, 1225, 1172, 1095, 916, and 732 cm^{-1}. HR ESI-MS: $[C_{14}H_{14}NaO_2]^+ = [M + Na]^+$ requires 237.0886; found 237.0887. TLC: R_f = 0.4 (4/1, Hex/EtOAc).

General Procedure B: Acid-Catalyzed, Intercepted Meyer−Schuster Rearrangement for the Synthesis of 2-Acylfurans 8a−k and 13a−p. To a solution of the (*Z*)-6-hydroxy-6-methylhept-2-en-4-ynals **7a−k** and **12a−p** (1 equiv) and dichloromethane (5 mL/0.2 mmol, 0.04 M) at 0 °C, under a nitrogen atmosphere in an oven-dried reaction tube (25 mL) equipped with a stir bar, was added an acid (1.3 equiv, 1.4 M in CH_2Cl_2) with a syringe. The contents of the reaction tube were stirred at 0 °C for 1 h or at room temperature for 12−24 h. After completion of the reaction (by TLC analysis), saturated $NaHCO_3$ and CH_2Cl_2 were added to the reaction mixture, which was then extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried ($MgSO_4$), and concentrated. The crude material was typically purified by flash chromatography using a hexane/ethyl acetate mixture as eluent to yield the 2-acylfuran derivatives **8a−k** and **13a−q**.

*2-Methyl-1-(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)-propan-1-one (**8a**).* The 2-acylfuran **8a** was prepared following the general procedure B from propargyl alcohol **7a** (50 mg, 0.24 mmol), CH_2Cl_2 (6 mL), and CH_3SO_3H (28 mg, 0.29 mmol, 0.2 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8a** (39 mg, 0.19 mmol, 77%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (1 H, s), 3.46−3.35 (1 H, m), 3.12−3.06 (2 H, m), 2.55−2.50 (2 H, m), 1.85−1.77 (2 H, m), 1.65−1.57 (4 H, m), and 1.16 (6 H, d, J = 6.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.6, 147.1, 140.1, 137.3, 130.9, 36.5, 32.8, 29.1, 28.6, 25.9, 25.7, and 18.6 ppm. IR (neat): 2924, 2854, 1666 (C═O), 1527, 1657, and 1270 cm^{-1}. HR ESI-MS: $[C_{13}H_{19}O_2]^+ = [M + H]^+$ requires 207.1380; found 207.1387. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*2-(3-Methylbut-3-en-1-ynyl)cyclohept-1-ene-1-carbaldehyde (**9a**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.16 (1 H, s), 5.40−5.39 (1 H, m), 5.35−5.34 (1 H, m), 2.62 (2 H, t, J = 5.5 Hz), 2.51 (2 H, t, J = 5.6 Hz), 1.95 (3 H, t, J = 1.2 Hz), 1.83−1.76 (2 H, m), 1.67−1.62 (2 H, m), and 1.48−1.42 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 148.3, 145.8, 126.5, 123.6, 101.5, 86.6, 37.6, 32.3, 29.8, 25.8, 24.4, and 23.3 ppm. IR (neat): 2923, 2852, 2360, 2183, 1671 (C═O), 1587, 1447, 1365, 1250, 1159, and 896 cm^{-1}. HR ESI-MS: $[C_{13}H_{17}O]^+ = [M + H]^+$ requires 189.1274; found 189.1283. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*2-Phenyl-1-(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)-propan-1-one (**8b**).* The 2-acylfuran **8b** was prepared following the general procedure B from propargyl alcohol **7b** (42 mg, 0.16 mmol), CH_2Cl_2 (4 mL), and CH_3SO_3H (18 mg, 0.18 mmol, 0.13 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8b** (27 mg, 0.11, 65%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.40−7.35 (2 H, m), 7.32−7.24 (2 H, m), 7.26−7.22 (1 H, m), 7.14 (1 H, s), 4.66 (1 H, q, J = 7.2 Hz), 3.22−2.98 (2 H, m), 2.55−2.43 (2 H, m), 1.85−1.73 (2 H, m), 1.65−1.57 (4 H, m), and 1.50 (3 H, d, J = 6.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.3, 147.1, 141.3, 140.5, 138.2, 131.1, 128.6, 126.8, 47.6, 32.7, 28.9, 28.4, 25.9, 25.6, and 18.2 ppm. IR (neat): 2923, 2849, 1666 (C═O), 1597, 1524, 1447, 1402, 1271, and 896 cm^{-1}. HR ESI-MS: $[C_{18}H_{21}O_2]^+ = [M + H]^+$ requires 269.1536; found 269.1552. TLC: R_f = 0.4 (19/1, Hex/EtOAc).

*1-(5,6,7,8-Tetrahydro-4H-cyclohepta[c]furan-1-yl)-2-p-tolylpropan-1-one (**8c**).* The 2-acylfuran **8c** was prepared following the general procedure B from propargyl alcohol **7c** (30 mg, 0.11 mmol), CH_2Cl_2 (3 mL), and CH_3SO_3H (14 mg, 0.14 mmol, 0.1 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8c** (14 mg, 0.048 mmol, 45%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.26−7.23 (2 H, m), 7.13−7.08 (3 H, m), 4.60 (1 H, q, J = 7.0 Hz), 3.15−2.97 (2 H, m), 2.52−2.44 (2 H, m), 2.29 (3 H, s), 1.79−1.76 (2 H, m), 1.60−1.55 (4 H, m), and 1.46

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(3 H, d, J = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.9, 152.2, 148.1, 140.5, 136.7, 131.1, 124.1, 123.6, 116.1, 32.7, 31.8, 29.8, 29.1, 28.5, 27.3, 25.9, and 25.6 ppm. IR (neat): 2921, 2851, 1672 (C═O), 1603, 1530, 1438, 1360, 1294, 1123, and 910 cm^{-1}. HR ESI-MS: $[C_{19}H_{23}O_2]^+ = [M + H]^+$ requires 283.1698; found 283.1710. TLC: R_f = 0.4 (19/1, Hex/EtOAc).

*2-Phenyl-1-(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)-butan-1-one (**8d**).* The 2-acylfuran **8d** was prepared following the general procedure B from propargyl alcohol **7d** (50 mg, 0.18 mmol), CH_2Cl_2 (5 mL), and CH_3SO_3H (20 mg, 0.212 mmol, 0.15 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8d** (27 mg, 0.095 mmol, 54%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.26 (2 H, m), 7.23−7.18 (2 H, m), 7.14−7.10 (1 H, m), 7.06 (1 H, s), 4.34 (1 H, t, J = 7.5 Hz), 3.07−2.89 (2 H, m), 2.42−2.38 (2 H, q, J = 4.6 Hz), 2.11−2.02 (2 H, m) 1.79−1.67 (4 H, m), 1.55−1.45 (2 H, m), and 0.8 (3 H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 147.5, 140.5, 139.8, 137.8, 131.1, 128.8, 126.8, 55.4, 32.7, 28.9, 28.4, 26.1, 25.9, 25.6, and 12.5 ppm. IR (neat): 2959, 2924, 2851, 1662 (C═O), 1601, 1525, 1450, 1403, and 1286 cm^{-1}. HR ESI-MS: $[C_{19}H_{23}O_2]^+ = [M + H]^+$ requires 283.1693; found 283.1697. TLC: R_f = 0.4 (9/1 Hex/EtOAc).

*2-Methyl-1-(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)-butan-1-one (**8e**).* The 2-acylfuran **8e** was prepared following the general procedure B from propargyl alcohol **7e** (40 mg, 0.18 mmol), CH_2Cl_2 (4 mL), and CH_3SO_3H (23 mg, 0.24 mmol, 0.17 mL of 1.4 M in CH_2Cl_2), by stirring for 18 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8e** (27 mg, 0.122 mmol, 68%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (1 H, s), 3.30−3.22 (1 H, m), 3.11−3.04 (2 H, m), 2.55−2.50 (2 H, m), 1.85−1.76 (2 H, m), 1.67−1.58 (4 H, m), 1.51−1.33 (2 H, m), 1.28 (3 H, d, J = 7.2 Hz), and 0.89 (3 H, t, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 147.6, 140.2, 137.3, 131.1, 43.3, 32.9, 29.2, 28.7, 26.5, 26.0, 25.8, 16.4, and 12.1 ppm. IR (neat): 2925, 2854, 2366, 1664 (C═O), 1525, 1450, 1408, 1118, 1087, 1054, and 905 cm^{-1}. HR ESI-MS: $[C_{14}H_{21}O_2]^+ = [M + H]^+$ requires 221.1536; found 221.1545. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*2-Ethyl-1-(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)butan-1-one (**8f**).* The 2-acylfuran **8f** was prepared following the general procedure B from propargyl alcohol **7f** (70 mg, 0.29 mmol), CH_2Cl_2 (7 mL), and CH_3SO_3H (36 mg, 0.36 mmol, 0.26 mL of 1.4 M in CH_2Cl_2), by stirring for 18 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8f** (55 mg, 0.24 mmol, 78%) as a pale yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.15 (1 H, s), 3.21−3.14 (1 H, m), 3.12−3.04 (2 H, m), 2.55−2.50 (2 H, m), 1.85−1.77 (2 H, m), 1.76−1.68 (2 H, m), 1.66−1.58 (4 H, m) 1.55−1.43 (2 H, m), and 0.86 (6 H, t, J = 7.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5, 148.3, 140.1, 136.9, 130.9, 50.2, 32.7, 29.1, 28.6, 25.9, 25.7, 24.6, and 12.0 ppm. IR (neat): 2925, 2855, 2367, 1664 (C═O), 1600, 1525, 1449, 1407, and 827 cm^{-1}. HR ESI-MS: $[C_{15}H_{23}O_2]^+ = [M + H]^+$ requires 235.1693; found 235.1701. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*(5,6,7,8-Tetrahydro-4H-cyclohepta[c]furan-1-yl) (1,2,3,4-tetrahydronaphthalen-1-yl)methanone (**8g**).* The 2-acylfuran **8g** was prepared following the general procedure B from propargyl alcohol **7g** (60 mg, 0.2 mmol), CH_2Cl_2 (6 mL), and CH_3SO_3H (19.5 mg, 0.20 mmol, 0.2 mL of 1.4 M in CH_2Cl_2), by stirring for 11 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave the ketone **8g** (38 mg, 0.13 mmol, 66%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (1 H, s), 7.18−7.09 (3 H, m), 7.00−6.96 (1 H, m), 4.79 (1 H, t, J = 6.8 Hz), 3.20−3.07 (2 H, m), 2.96−2.76 (2 H, m), 2.62−2.58 (2 H, m), 2.20−1.96 (4 H, m), 1.89−1.81 (2 H, m), and 1.71−1.64 (4 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 147.4, 140.5, 138.2, 134.9, 131.3, 129.5, 129.4, 126.5, 125.8, 47.6, 32.7, 29.5, 29.1, 28.5, 27.0, 26.0, 25.7, and 20.8 ppm. IR (neat): 2926, 2853, 1664 (C═O), 1600, 1522, 1442, 1402, 894, and 741 cm^{-1}. HR ESI-MS: $[C_{20}H_{22}O_2]^+ = [M + H]^+$ requires 295.1693; found 295.1695. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Cycloheptyl(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)-methanone (**8h**).* The 2-acylfuran **8h** was prepared following the general procedure B from propargyl alcohol **7h** (60 mg, 0.23 mmol), CH_2Cl_2 (6 mL), and CH_3SO_3H (29 mg, 0.3 mmol, 0.21 mL of 1.4 M in CH_2Cl_2), by stirring for 14 h at 0 °C to room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8h** (40 mg, 0.153 mmol, 66%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.15 (1 H, s), 3.34−3.23 (1 H, tt, J = 4.0 and 9.6 Hz), 3.10−3.04 (2 H, m), 2.54−2.50 (2 H, m), 1.93−1.85 (2 H, m), 1.83−1.74 (4 H, m), and 1.65−1.53 (12 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 147.0, 140.1, 137.3, 131.0, 47.7, 32.8, 30.4, 29.1, 28.6, 27.0, 25.9, and 25.7 ppm. IR (neat): 2923, 2853, 1665 (C═O), 1525, 1448, and 894 cm^{-1}. HR ESI-MS: $[C_{17}H_{25}O_2]^+ = [M + H]^+$ requires 261.1849; found 261.1862. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Cyclohexyl(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)-methanone (**8i**).* The 2-acylfuran **8i** was prepared following the general procedure B from propargyl alcohol **7i** (90 mg, 0.36 mmol), CH_2Cl_2 (8 mL), and CH_3SO_3H (42 mg, 0.44 mmol, 0.31 mL of 1.4 M in CH_2Cl_2), by stirring for 16 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8i** (66 mg, 0.27 mmol, 73%) as a viscous, pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (1 H, s), 3.14 (1 H, tt, J = 11.2 and 3.2 Hz), 3.07 (2 H, br t, J = 6.0 Hz), 2.52 (2 H, t, J = 6.0 Hz), 1.91−1.80 (6 H, m), 1.67−1.59 (4 H, m), and 1.20−1.50 (6 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 147.4, 140.1, 137.3, 131.1, 46.6, 32.9, 29.2, 28.9, 28.5, 26.2, 26.1, 26.0, and 25.8 ppm. IR (neat): 2935, 2867, 1663 (C═O), 1609, 1515, 1445, 1403, 1332, 1279, 918, and 792 cm^{-1}. HR ESI-MS: $[C_{16}H_{23}O_2]^+ = [M + H]^+$ requires 247.1693; found 247.1688. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Cyclohexenyl(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)-methanone (**8j**).* The 2-acylfuran **8j** was prepared following the general procedure B from propargyl alcohol **7j** (100 mg, 0.41 mmol), 1,2-DCB (8 mL), and CH_3SO_3H (51 mg, 0.53 mmol, 0.4 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 65 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **8j** (35 mg, 0.143 mmol, 35%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (1 H, s), 7.24 (1 H, m), 3.36−3.32 (2 H, m), 2.92−2.87 (2 H, m), 2.76−2.71 (2 H, m), 2.67−2.61 (2 H, m), 2.21−2.15 (2 H, m), and 2.09−1.97 (8 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 147.8, 141.1, 139.9, 138.8, 137.2, 130.4, 32.8, 32.8, 29.8, 29.2, 28.7, 26.3, 26.2, 25.6, 24.2, 22.3, and 21.8 ppm. IR (neat): 2925, 2853, 1627 (C═O), 1602, 1523, 1447, 1404, 1290, 964, 872, 820, and 738 cm^{-1}. HR ESI-MS: $[C_{16}H_{21}O_2]^+ = [M + H]^+$ requires 245.1536; found 245.1528. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*2-Methyl-1-(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)-propan-1-one (**8k**).* The 2-acylfuran **8k** was prepared following the general procedure B from propargyl alcohol **7k** (24 mg, 0.14 mmol), CH_2Cl_2 (3 mL), and CH_3SO_3H (17 mg, 0.18 mmol, 0.12 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave the ketone **8k** (9 mg, 0.052 mmol, 37%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (1 H, s), 3.007 (2 H, t, J = 5.6 Hz), 2.53 (2 H, t, J = 5.5 Hz), 2.44 (3 H, s), 1.84−1.79 (2 H, m), and 1.68−1.58 (4 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.9, 148.1, 140.5, 136.7, 131.1, 32.7, 29.1, 28.5, 27.3, 25.9, and 25.7 ppm. IR (neat): 2924, 2853, 1739, 1688 (C═O), 1598, 1523, 1457, 1400, 1269, 1118, and 896 cm^{-1}. HR ESI-MS: $[C_{11}H_{15}O_2]^+ = [M + H]^+$ requires 179.1072; found 179.1077. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*1-(1-Chloro-2-methylprop-1-enyl)-4,5,6,7-tetrahydroisobenzofuran (**10**).* The vinyl chloride **10** was prepared following the general procedure B from propargyl alcohol **7a** (20 mg, 0.09 mmol), CH_2Cl_2 (2.5 mL), and $TiCl_4$ (13 mg, 0.13 mmol, 0.13 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (99/1 hexanes/EtOAc) gave vinyl chloride **10** (15 mg, 0.07 mmol, 74%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.11 (1 H, s), 2.51−2.48 (2 H, m), 2.42−2.39 (2 H, m), 1.99 (3 H, s), 1.81−1.76 (2 H, m), 1.74 (3 H,

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s), and 1.65−1.57 (4 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 136.7, 128.1, 126.3, 116.1, 114.2, 32.9, 29.9, 29.1, 26.5, 26.1, 22.2, and 21.8 ppm. IR (neat): 2922, 2853, 1764, 1445, 1371, 1269, 1070, 999, and 870 cm^{-1}. HR ESI-MS: $[C_{13}H_{17}ClNaO]^+$ = [M + Na]$^+$ requires 247.0860; found 247.0872. TLC: R_f = 0.4 (Hex).

*2-Methyl-1-(5,6,7,8-tetrahydro-4H-cyclohepta[c]furan-1-yl)prop-1-en-1-yl Acetate (**11**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (1 H, s), 2.49−2.46 (2 H, m), 2.15 (3 H, s), 1.73 (6 H, d, J = 5.3 Hz), and 1.63−1.58 (6 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 143.1, 137.7, 132.7, 127.9, 127.2, 127.0, 32.8, 29.0, 26.4, 26.1, 20.7, 19.8, and 18.1 ppm. IR (neat): 2923, 2849, 2322, 1757, 1446, 1370, 1208, and 885 cm^{-1}. HR ESI-MS: $[C_{15}H_{20}NaO_3]^+$ = [M + Na]$^+$ requires 271.1305; found 271.1312. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*1-(5,6-Dihydro-4H-cyclopenta[c]furan-1-yl)-2-methylpropan-1-one (**13a**).* The 2-acylfuran **13a** was prepared following the general procedure B from propargyl alcohol **12a** (40 mg, 0.22 mmol), CH_2Cl_2 (5 mL), and CH_3SO_3H (26 mg, 0.27 mmol, 0.2 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13a** (13 mg, 0.07 mmol, 33%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (1 H, s), 3.23 (1 H, septet, J = 6.9 Hz), 2.87 (2 H, t, J = 7.2 Hz), 2.68−2.63 (2 H, m), 2.48−2.38 (2 H, m), and 1.18 (6 H, d, J = 6.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.7, 143.5, 142.8, 136.7, 135.6, 36.4, 31.9, 26.1, 23.4, and 18.7 ppm. IR (neat): 2958, 2929, 2862, 2362, 1669 (C═O), 1543, 1386, 1261, and 936 cm^{-1}. HR ESI-MS: $[C_{11}H_{15}O_2]^+$ = [M + H]$^+$ requires 179.1067; found 179.1071. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*1-(5,6-Dihydro-4H-cyclopenta[c]furan-1-yl)-2-ethylbutan-1-one (**13b**) and (E)-2-(3-Ethylpent-3-en-1-ynyl)cyclopent-1-ene-1-carbaldehyde (**13b′**).* The 2-acylfuran **13b** was prepared following the general procedure B from propargyl alcohol **12b** (100 mg, 0.48 mmol), CH_2Cl_2 (10 mL), and CH_3SO_3H (60 mg, 0.6 mmol, 0.22 mL of 1.4 M in CH_2Cl_2), by stirring for 24 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13b** (40 mg, 0.194 mmol, 40%) and the dehydration product olefin **13b′** (29 mg, 0.15 mmol, 30%) as a pale yellow oil.

*Data for 1-(5,6-Dihydro-4H-cyclopenta[c]furan-1-yl)-2-ethylbutan-1-one (**13b**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (1 H, s), 2.97(1H, tt, J = 5.5 and 8.0 Hz), 2.90 (2 H, t, J = 7.3 Hz), 2.65 (2 H, t, J = 7.7 Hz), 2.43 (2 H, quintet, J = 7.2 Hz) 1.81−1.70 (2 H, m), 1.58−1.47 (2 H, m), and 0.87 (6 H, t, J = 7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.5, 144.8, 142.7, 136.7, 135.6, 50.5, 31.9, 26.4, 24.8, 23.4, and 12.0 ppm. IR (neat): 2960, 2933, 2873, 1656 (C═O), 1613, 1539, 1459, 1215, 771, and 669 cm^{-1}. HR ESI-MS: $[C_{13}H_{19}O_2]^+$ = [M + H]$^+$ requires 207.1380; found 207.1384. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Data for (E)-2-(3-Ethylpent-3-en-1-ynyl)cyclopent-1-ene-1-carbaldehyde (**13b′**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (1 H, s), 5.94−5.88 (1H, m), 2.75 (2 H, tt, J = 7.8 and 2.2 Hz), 2.63 (2 H, tt, J = 7.8 and 2.0 Hz), 1.88−1.86 (3 H, tt, J = 6.8 and 1.0), and 1.10 (3 H, t, J = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 147.1, 144.0, 134.3, 125.2, 99.9, 88.0, 39.3, 30.0, 29.7, 22.3, 16.6, and 13.5 ppm. IR (neat): 2967, 2932, 2851, 2745 (*H*-C═O), 2361, 2254, 2183, 1662 (C═O), 1586, 1459, 1378, 1233, 910, and 736 cm^{-1}. HR ESI-MS: $[C_{13}H_{17}O]^+$ = [M + H]$^+$ requires 189.1274; found 189.1275. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*1-(5,6-Dihydro-4H-cyclopenta[c]furan-1-yl)-2-methylbutan-1-one (**13c**).* The 2-acylfuran **13c** was prepared following the general procedure B from propargyl alcohol **12c** (100 mg, 0.52 mmol), CH_2Cl_2 (10 mL), and CH_3SO_3H (65 mg, 0.66 mmol, 0.5 mL of 1.4 M in CH_2Cl_2), by stirring for 24 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13c** (43 mg, 0.22 mmol, 43%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (1 H, s), 3.07 (1 H, sextet, J = 6.8 Hz), 2.88 (2 H, t, J = 7.4 Hz), 2.66 (2 H, t, J = 7.4 Hz), 2.43 (2H, quintet, J = 7.1 Hz) 1.86−1.75 (1 H, m), 1.52−1.41 (1 H, m), 1.16 (3 H, d, J = 6.8 Hz), and 0.91 (3 H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 114.0, 142.7, 136.6, 135.6, 43.3, 31.9, 26.5, 26.2, 23.4, 16.4, and 12.0 ppm. IR (neat): 2964, 2935, 2873, 1671 (C═O), 1616, 1541, 1457, 1385, 1287, 1096, and 929 cm^{-1}. HR ESI-MS: $[C_{12}H_{17}O_2]^+$ = [M + H]$^+$ requires 193.1223; found 193.1227. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Cyclohexyl(5,6-dihydro-4H-cyclopenta[c]furan-1-yl)methanone (**13d**).* The 2-acylfuran **13d** was prepared following the general procedure B from propargyl alcohol **12d** (20 mg, 0.09 mmol), CH_2Cl_2 (5 mL), and CH_3SO_3H (10.5 mg, 0.11 mmol, 0.1 mL of 1.4 M in CH_2Cl_2), by stirring for 12 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13d** (13 mg, 0.06 mmol, 65%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (1 H, s), 2.95 (1 H, tt, J = 11.6 and 3.2 Hz), 2.87 (2 H, t, J = 7.2 Hz), 2.68−2.63 (2 H, m), 2.47−2.39 (2 H, m), 1.88−1.82 (4 H, m), 1.75−1.66 (2 H, m), and 1.55−1.32 (4 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 143.6, 142.7, 136.6, 135.5, 46.7, 31.9, 28.8, 26.2, 26.1, 26.0, and 23.4 ppm. IR (neat): 2925, 2853, 1663 (C═O), 1601, 1523, 1447, 1399, 1323, 1256, 907, and 785 cm^{-1}. HR ESI-MS: $[C_{14}H_{19}O_2]^+$ = [M + H]$^+$ requires 219.1380; found 219.1388. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*1-(5,6-Dihydro-4H-cyclopenta[c]furan-1-yl)-2-methylpropan-1-one (**13e**).* The 2-acylfuran **13e** was prepared following the general procedure B from propargyl alcohol **12e** (20 mg, 0.11 mmol), CH_2Cl_2 (2.5 mL), and CH_3SO_3H (11 mg, 0.12 mmol, 0.09 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13e** (13 mg, 0.07 mmol, 65%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.21(1 H, s), 3.37 (1 H, quintet, J = 6.7 Hz), 2.87 (2 H, t, J = 6.2 Hz), 2.54 (2 H, t, J = 5.7 Hz), 1.76−1.66 (4 H, m), and 1.17 (6 H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 145.9, 139.1, 131.9, 123.9, 35.2, 21.8, 21.7, 19.1, and 17.5 ppm. IR (neat): 2927, 2857, 1771 (C═O), 1659, 1599, 1520, 1457, 1399, 1268, 1081, 1030, 917, and 791 cm^{-1}. HR ESI-MS: $[C_{12}H_{16}NaO_2]^+$ = [M + Na]$^+$ requires 215.1043; found 215.1033. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*2-Ethyl-1-(4,5,6,7-tetrahydroisobenzofuran-1-yl)butan-1-one (**13f**).* The 2-acylfuran **13f** was prepared following the general procedure B from propargyl alcohol **12f** (50 mg, 0.23 mmol), CH_2Cl_2 (6 mL), and CH_3SO_3H (28.3 mg, 0.3 mmol, 0.2 mL of 1.4 M in CH_2Cl_2), by stirring for 24 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13f** (36 mg, 0.16 mmol, 71%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (1 H, s), 3.13 (1H, tt, J = 5.6 and 8.0 Hz), 2.54 (2 H, t, J = 5.8 Hz), 2.54 (2 H, t, J = 6.0 Hz), 1.79−1.68 (6 H, m), 1.58−1.47 (2 H, m), and 0.86 (6 H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 148.1, 140.1, 132.0, 125.0, 50.1, 24.6, 22.8, 22.7, 22.6, 20.1, and 12.0 ppm. IR (neat): 2962, 2934, 2860, 1660 (C═O), 1598, 1524, 1457, 1285, 1083, 912, and 836 cm^{-1}. HR ESI-MS: $[C_{14}H_{21}O_2]^+$ = [M + H]$^+$ requires 221.1536; found 221.1534. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*2-Methyl-1-(4,5,6,7-tetrahydroisobenzofuran-1-yl)butan-1-one (**13g**).* The 2-acylfuran **13g** was prepared following the general procedure B from propargyl alcohol **12g** (30 mg, 0.145 mmol), CH_2Cl_2 (3 mL), and CH_3SO_3H (36 mg, 0.38 mmol, 0.25 mL of 1.4 M in CH_2Cl_2), by stirring for 24 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13g** (16 mg, 0.08 mmol, 60%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (1 H, s), 3.22 (1 H, sextet, J = 6.8 Hz), 2.87 (2 H, t, J = 5.9 Hz), 2.54 (2 H, t, J = 5.6 Hz), 1.82−1.67 (5 H, m), 1.50−1.39 (1 H, m), 1.13 (3 H, d, J = 6.8 Hz), and 0.89 (3 H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 147.3, 140.1, 132.3, 124.9, 43.0, 26.3, 22.8, 22.7, 22.6, 20.1, 16.2, and 12.0 ppm. IR (neat): 2962, 2934, 2857, 1664 (C═O), 1599, 1524, 1457, 1400, 1280, 1128, 1085, 907, and 815 cm^{-1}. HR ESI-MS: $[C_{13}H_{19}O_2]^+$ = [M + H]$^+$ requires 207.1380; found 207.1381. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Cyclohexyl(4,5,6,7-tetrahydroisobenzofuran-1-yl)methanone (**13h**).* The 2-acylfuran **13h** was prepared following the general procedure B from propargyl alcohol **12h** (100 mg, 0.43 mmol), CH_2Cl_2 (10 mL), and CH_3SO_3H (49.6 mg, 0.51 mmol, 0.36 mL of 1.4 M in CH_2Cl_2), by stirring for 16 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13h** (67 mg, 0.262 mmol, 67%) as a pale yellow solid. It was recrystallized from

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2:1 mixture of CH_2Cl_2:hexane and single crystal X-ray analysis was recorded.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (1 H, s), 3.10 (1 H, tt, J = 11.6 and 3.2 Hz), 2.85 (2 H, t, J = 6.0 Hz), 2.53 (2 H, t, J = 6.0 Hz), 1.77−1.90 (4 H, m), 1.65−1.76 (4 H, m), and 1.20−1.50 (6 H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.6, 147.1, 140.1, 132.3, 125.0, 46.4, 28.8, 26.2, 26.1, 22.9, 22.7, and 20.2 ppm. IR (neat): 2930, 2857, 1661 (C═O), 1602, 1525, 1447, 1400, 1332, 1277, 914, and 790 cm^{-1}. HR ESI-MS: $[C_{15}H_{21}O_2]^+ = [M + H]^+$ requires 233.1536; found 233.1544. TLC: R_f = 0.4 (19/1 Hex/EtOAc). Mp: 66−68 °C.

*1-(4,5-Dihydronaphtho[2,1-c]furan-1-yl)-2-methylpropan-1-one (**13i**).* The 2-acylfuran **13i** was prepared following the general procedure B from propargyl alcohol **12i** (89 mg, 0.37 mmol), CH_2Cl_2 (8 mL), and CH_3SO_3H (42.5 mg, 0.44 mmol, 0.3 mL of 1.4 M in CH_2Cl_2), by stirring for1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13i** (54 mg, 0.23 mmol, 63%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.78−8.74 (1 H, m), 7.35−7.21 (4 H, m), 3.60 (1 H, m, J = 7.2 Hz), 2.87 (2 H, t, J = 7.2 Hz), 2.69 (2 H, t, J = 6.4 Hz), and 1.22 (2 H, d, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 146.4, 138.7, 138.2, 129.1, 129.0, 128.3, 127.0, 125.9, 36.8, 30.4, 19.2, and 18.8 ppm. IR (neat): 2926, 2931, 2847, 1670 (C═O), 1525, 1458, 1384, 1262, 921, and 856 cm^{-1}. HR ESI-MS: $[C_{16}H_{17}O_2]^+ = [M + H]^+$ requires 241.1223; found 241.1238. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Cyclohexyl(4,5-dihydronaphtho[2,1-c]furan-1-yl)methanone (**13j**) and 1-(Cyclohexenylethynyl)-3,4-dihydronaphthalene-2-carbaldehyde (**13j′**).* The 2-acylfuran **13j** was prepared following the general procedure B from propargyl alcohol **12j** (60 mg, 0.21 mmol), CH_2Cl_2 (5 mL), and CH_3SO_3H (27 mg, 0.27 mmol, 0.2 mL of 1.4 M in CH_2Cl_2), by stirring for 24 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13j** (42 mg, 0.15 mmol, 70%) as a pale yellow oil. Further elution yielded the olefin **13j′** (9 mg, 0.03 mmol, 15%).

*Data for Cyclohexyl(4,5-dihydronaphtho[2,1-c]furan-1-yl)-methanone (**13j**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76−8.74 (1 H, m), 7.34 (1 H, s), 7.32−7.28 (1 H, m), 7.27−7.22 (2 H, m), 3.33 (1 H, tt, J = 3.2 and 1.3 Hz), 2.87 (2 H, t, J = 7.5 Hz), 2.69 (2 H, t, J = 6.3 Hz), 1.94−1.91 (2 H, m), 1.87−1.83 (2 H, m), and 1.55−1.23 (6 H, d, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 146.6, 138.6, 138.2, 129.7, 129.1, 129.0, 128.4, 128.3, 127.0, 125.9, 47.0, 30.4, 29.1, 26.2, 26.1, and 19.2 ppm. IR (neat): 2930, 2854, 1775, 1665 (C═O), 1605, 1523, 1455, 1266, 1154, 926, and 736 cm^{-1}. HR ESI-MS: $[C_{19}H_{20}NaO_2]^+ = [M + Na]^+$ requires 303.1356; found 303.1370. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Data for 1-(Cyclohexenylethynyl)-3,4-dihydronaphthalene-2-carbaldehyde (**13j′**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ= 10.39 (1 H, s), 7.84−7.82 (1 H, m), 7.35−7.28 (2 H, m), 7.20−7.18 (1 H, m), 6.39−6.36 (1 H, m), 2.82 (2 H, t, J = 8.3 Hz), 2.60 (2 H, t, J = 5.8 Hz), 2.21−2.36 (2 H, m), 2.22−2.17 (2 H, m), and 1.75−1.62 (4 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.6, 139.5, 137.9, 137.8, 136.7, 132.6, 130.7, 127.9, 127.4, 127.0, 120.5, 103.6, 88.75, 29.1, 26.9, 26.0, 22.3, 21.5, and 20.0 ppm. IR (neat): 2930, 2854, 1775, 1665 (C═O), 1605, 1523, 1455, 1266, 1154, 926, and 736 cm^{-1}. HR ESI-MS: $[C_{19}H_{18}NaO]^+ = [M + Na]^+$ requires 285.1250; found 285.1259. TLC: R_f = 0.3 (19/1 Hex/EtOAc).

*1-(4,5-Dihydronaphtho[2,1-c]furan-1-yl)-2-ethylbutan-1-one (**13k**).* The 2-acylfuran **13k** was prepared following the general procedure B from propargyl alcohol **12k** (220 mg, 0.82 mmol), CH_2Cl_2 (22 mL), and CH_3SO_3H (102 mg, 1.07 mmol, 0.75 mL of 1.4 M in CH_2Cl_2) by stirring for 24 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13k** (150 mg, 0.56 mmol, 68%). Further elution gave olefin **13k′** (30 mg, 0.11 mmol, 13%) as pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.77−8.75 (1 H, dd, J = 8.0 and 1.1 Hz), 7.34 (1 H, t, J = 7.1 Hz), 7.26−7.21 (2 H, m), 3.38 (1 H, tt, J = 7.9 and 5.6 Hz), 2.88 (2 H, t, J = 7.6 Hz), 2.69 (2 H, t, J = 7.8 Hz), 1.85−1.74 (2 H, m), 1.63−1.53 (2 H, m), and 0.09 (6 H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 147.5, 138.8, 138.2, 129.8, 129.1, 128.9, 128.4, 128.3, 127.0, 125.9, 50.6, 30.4, 24.9, 19.2, and 12.1 ppm. IR (neat): 2962, 2855, 2361, 1667 (C═O), 1601, 1522, 1458, 1383, 1112, 910, and 741 cm^{-1}. HR ESI-MS: $[C_{18}H_{21}O_2]^+ = [M + H]^+$ requires 269.1536; found 269.1552. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*1-(4,5-Dihydronaphtho[2,1-c]furan-1-yl)-2-methylbutan-1-one (**13l**).* The 2-acylfuran **13l** was prepared following the general procedure B from propargyl alcohol **12l** (120 mg, 0.472 mmol), CH_2Cl_2 (12 mL), and CH_3SO_3H (59 mg, 0.62 mmol, 0.43 mL of 1.4 M in CH_2Cl_2), by stirring for 24 h at room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13l** (79.5 mg, 0.313 mmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77−8.75 (1 H, m), 7.34−7.35 (4 H, m), 3.45 (1 H, m, J = 6.8 Hz), 2.88 (2 H, t, J = 7.6 Hz), 2.69 (2 H, t, J = 6.4 Hz), 1.90−1.79 (2 H, m), 1.56−1.45 (1 H, m), 1.56−1.56 (1 H, m), 1.20 (3 H, d, J = 6.9 Hz), and 0.94 (3 H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 146.8, 138.7, 138.2, 129.6, 129.1, 128.9, 128.3, 128.2, 127.0, 125.9, 43.5, 30.4, 26.6, 19.2, 16.5, and 12.1 ppm. IR (neat): 2965, 2933, 2876, 1670 (C═O), 1610, 1523, 1384, 1265, 1175, 1111, 1062, 835, and 773 cm^{-1}. HR ESI-MS: $[C_{17}H_{19}O_2]^+ = [M + H]^+$ requires 255.1380; found 255.1388. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*Cycloheptyl(4,5,6,7-tetrahydroisobenzofuran-1-yl)methanone (**13m**).* The 2-acylfuran **13m** was prepared following the general procedure B from propargyl alcohol **12m** (35 mg, 0.14 mmol), CH_2Cl_2 (4 mL), and CH_3SO_3H (18 mg, 0.184 mmol, 0.13 mL of 1.4 M in CH_2Cl_2), by stirring for 14 h at 0 °C to room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13m** (23 mg, 0.09 mmol, 61%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (1 H, s), 3.31−3.23 (1 H, tt, J = 4.0 and 9.7 Hz), 2.86 (2 H, t, J = 6.4 Hz), 2.54 (2 H, t, J = 6.4 Hz), 1.93−1.85 (2 H, m), and 1.76−1.54 (14 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 146, 140.0, 132.3, 124.9, 47.5, 30.3, 28.6, 28.6, 27.0, 22.8, 22.7, and 20.2 ppm. IR (neat): 2934, 2863, 2361, 2336, 1665 (C═O), 1522 and 902 cm^{-1}. HR ESI-MS: $[C_{16}H_{23}O_2]^+ = [M + H]^+$ requires 247.1693; found 247.1691. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*2-Phenyl-1-(4,5,6,7-tetrahydroisobenzofuran-1-yl)propan-1-one (**13n**).* The 2-acylfuran **13n** was prepared following the general procedure B from propargyl alcohol **12n** (30 mg, 0.12 mmol), CH_2Cl_2 (3 mL), and CH_3SO_3H (15 mg, 0.15 mmol, 0.11 mL of 1.4 M in CH_2Cl_2), by stirring for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13n** (13 mg, 0.05 mmol, 43%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.40−7.36 (2 H, m), 7.30−7.25 (2 H, m), 7.21−7.18 (1 H, m), 7.17 (1 H, s), 4.66 (1 H, q, J = 7.0 Hz), 2.86−2.82 (2 H, m), 2.56−2.46 (2 H, m), 1.72−1.63 (4 H, m), and 1.50 (3 H, d, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.9, 146.9, 141.2, 140.5, 133.3, 128.6, 128.3, 126.9, 47.4, 22.8, 22.6, 20.0, and 18.1 ppm. IR (neat): 2931, 2858, 1666 (C═O), 1598, 1399, 1334, 1273, 900, and 699 cm^{-1}. HR ESI-MS: $[C_{17}H_{19}O_2]^+ = [M + H]^+$ requires 255.1385; found 255.1388. TLC: R_f = 0.4 (19/1, Hex/EtOAc).

*Cyclohexyl(4,5,6,7,8,9-hexahydrocycloocta[c]furan-1-yl)-methanone (**13o**).* The 2-acylfuran **13o** was prepared following the general procedure B from propargyl alcohol **12o** (60 mg, 0.23 mmol), CH_2Cl_2 (6 mL), and MsOH (29 mg, 0.3 mmol, 0.26 mL of 1.4 M in CH_2Cl_2), stirred for 13 h at 0 °C to room temperature. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13o** (51 mg, 0.20 mmol, 85%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.17 (1 H, s), 3.13 (1 H, tt, J = 3.3 and 11.3 Hz), 2.91 (2 H, t, J = 6.4 Hz), 2.51 (2 H, t, J = 6.2 Hz), 1.87−1.77 (4 H, m), 1.72−1.65 (2 H, m), 1.61−1.55 (2 H, m) 1.48−1.33 (8 H, m), and 1.30−1.18 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 147.6, 140.3, 135.4, 129.4, 46.4, 31.7, 28.8, 28.7, 26.1, 26.0, 25.9, 25.5, 22.3, and 22.2 ppm. IR (neat): 2928, 2851, 1665(C═O), 1600, 1525, 1447, 1405, 1276, 913, and 806 cm^{-1}. HR ESI-MS: $[C_{17}H_{25}O_2]^+ = [M + H]^+$ requires 261.1849; found 261.1866. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*1-(4,5,6,7,8,9-Hexahydrocycloocta[c]furan-1-yl)-2-phenylpropan-1-one (**13p**).* The 2-acylfuran **13p** was prepared following the

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general procedure B from propargyl alcohol **12p** (60 mg, 0.21 mmol), CH_2Cl_2 (6 mL), and MsOH (27 mg, 0.27 mmol, 0.2 mL of 1.4 M in CH_2Cl_2), stirred for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave ketone **13p** (42 mg, 0.15 mmol, 70%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.38−7.36 (2 H, m,), 7.32−7.28 (2 H, m), 7.23−7.18 (1 H, m), 7.17 (1 H, s), 4.66 (1 H, q, J = 6.2 Hz), 3.03−2.84 (2 H, m), 2.55−2.43 (2 H, m), 1.75−1.68 (2 H, m), 1.64−1.55 (2 H, m), 1.52 (3 H, m, J = 8.4 Hz), 1.49−1.42 (2 H, m), and 1.40−1.34 (2 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.5, 147.5, 141.4, 140.8, 136.2, 129.4, 128.6, 128.2, 126.7, 47.6, 31.6, 28.7, 25.9, 25.5, 22.3, and 18.2 ppm. IR (neat): 2928, 2855, 2360, 1665, 1599, 1524, 1454, 1405, 1279, 1126, and 897 cm^{-1}. HR ESI-MS: $[C_{19}H_{22}NaO_2]^+$ = $[M + Na]^+$ requires 305.1512; found 305.1517. TLC: R_f = 0.4 (19/1, Hex/EtOAc).

*Cycloheptyl(furan-2-yl)methanone (**13q**).* The 2-acylfuran **13q** was prepared following the general procedure B from the hydroxyl aldehyde **12q** (75 mg, 0.39 mmol), CH_2Cl_2 (8 mL), and MsOH (49.3 mg, 0.51 mmol, 0.35 mL of 1.4 M in CH_2Cl_2), stirred for 1 h at 0 °C. Purification by flash chromatography (32/1 hexanes/EtOAc) gave the ketone **13q** (58 mg, 0.30 mmol, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57(1 H, dd, J = 1.6 and 0.6 Hz), 7.17 (1 H, dd, J = 4.0 and 0.7 Hz), 6.52 (1 H, dd, J = 3.5 and 1.7 Hz), 3.22 (1 H, m), 1.95−1.89 (2 H, m), 1.83−1.76 (2 H, m), 1.73−1.69 (2 H, m), and 1.63−1.51 (6 H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 152.4, 146.2, 117.0, 112.2, 47.8, 30.7, 28.5, and 27.0 ppm. IR (neat): 2926, 2856, 2360, 2333, 1673 (C═O), 1564, 1466, 1240, 1013, and 759 cm^{-1}. HR ESI-MS: $[C_{12}H_{17}O_2]^+$ = $[M + H]^+$ requires 193.1223; found 193.1237. TLC: R_f = 0.4 (19/1 Hex/EtOAc).

*1-(Furan-2-yl)-2-p-tolylpropan-1-one (**18**; Deoxy-nor-abiesesquine B).* Deoxy-*nor*-abiesesquine B (**18**) was prepared following the general procedure B from the hydroxyl aldehyde **22** (30 mg, 0.14 mmol), CH_2Cl_2 (4 mL), and $AlCl_3$ (24 mg, 0.18 mmol), stirred for 1 h at 0 °C. Purification by flash chromatography (19/1 hexanes/EtOAc) gave deoxy-*nor*-abiesesquine B **18** (17 mg, 0.08 mmol, 57%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (1 H, dd, J = 1.1 and 1.7 Hz), 7.22−7.21 (1 H, m), 7.13−7.10 (3 H, m), 6.45 (1 H, dd, J = 3.4 and 1.2 Hz), 4.45 (1 H, qt, J = 7.1 Hz) 2.30 (3 H, s), and 1.50 (3 H, d, J = 7.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 146.4, 138.0, 136.8, 129.6, 127.9, 117.9, 112.3, 47.7, 21.2, and 18.4 ppm. IR (neat): 2953, 2852, 1676 (C═O), 1566, 1511, 1466, 1263, 1015, 758, and 742 cm^{-1}. HR ESI-MS: $[C_{14}H_{14}NaO_2]^+$ = $[M + Na]^+$ requires 237.0886; found 237.0877. TLC: R_f = 0.2 (9/1 Hex/EtOAc).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01420.

Crystallographic data for **13h** (CIF)

^{1}H and ^{13}C NMR spectra of all new compounds synthesized during this study (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

†Dedicated to the memory of the late Prof. Adusumilli Srikrishna.

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(10) The compound **11** was characterized by spectroscopic data. To rule out the involvement of any trace of AcOH present in the EtOAc in the formation of **11**, we have done the experiment in CH_2Cl_2 along with 5 equiv of AcOH. The formation of **11** was not observed.
(11) We have also done experiments with secondary alcohols **7l,m** in the presence of $AlCl_3$ and MsOH. The reaction was not clean, but all the starting alcohols **7l,m** were consumed. In the ^{1}H NMR spectrum of the crude reaction mixture for **7l** we can see peaks corresponding to the acyl furan product **8l**.
(12) Crystallographic data for 2-acylfuran **13h** has been deposited with the Cambridge Crystallographic Data Centre with the file number CCDC 1054792. Further details are given in the Supporting Information.
(13) We also performed the same experiment with moist CH_2Cl_2 as solvent and observed similar decomposition.
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