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PAPER

Environmentally benign syntheses of hexahydro-cyclopenta(*b*)furan and 2-oxabicyclo[3.2.1]octane derivatives

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Convenient and green synthesis of hexahydro-cyclopenta(*b*)furan derivatives has been achieved by the cyclization of substituted campholenic alcohols in the presence of Amberlyst-15® at ambient condition. In this reaction condition minor amount (<10%) of 2-oxabicyclo [3.2.1]octane is formed. The yield of the latter compound can be increased by modifying the reaction condition. Both heterocycles display excellent perfumery value. The catalyst can be recovered by simple filtration and reused.

Introduction

The 2-oxabicyclo[3.2.1]octane and 2-oxabicyclo[2.2.1]heptane skeletons are the basic framework of some natural compounds.[1,2] N-[2-oxa-hexahydrocyclopenta(*b*)furan-3a-yl]-acrylamide derivatives display cysteinyl protease inhibition activity.[3] The synthesis of functionalized bicyclo[3.2.1]octanes has been well evaluated.[4a] Similarly the preparation of 8-oxabicyclo[3.2.1]octane derivatives *via* asymmetric [3+2]-cycloaddition has been studied.[4b] In contrast, the synthetic strategies for the construction of 2-oxabicyclo[3.2.1]octane and hexahydrocyclopenta(*b*)furan derivatives include mainly the cyclization reactions involving either the acid catalyzed cyclization or the hydroxymercuration reactions.[5]

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Electronic supplementary information (ESI) available

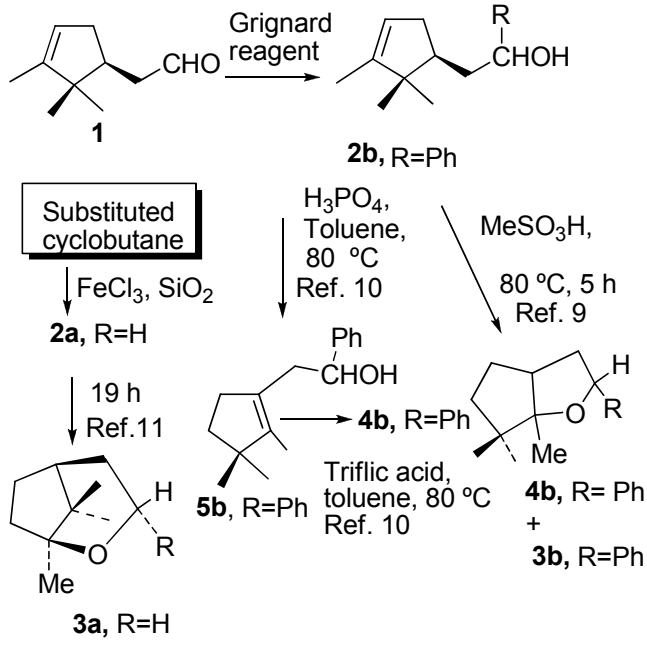
In recent years, the heterogeneous catalysts such as ion exchange resins, clay, solid acids, zeolites etc, are widely used in different areas of organic syntheses, because of their simplicity in operation, environmental compatibility, reusability, greater selectivity, non-corrosiveness and cheap availability.[6] Amberlyst-15® resin with sulfonic acid functionality is strongly acidic and can be handled easily and removed from the reaction mixture by simple filtration. Owing to the numerous advantages associated with this inexpensive catalyst. Amberlyst-15® has been explored for various organic reactions.[7] It has been recently observed that Amberlyst-15® is very effective and efficient catalyst for the synthesis of substituted tetrahydro-(2*H*)-pyran, dihydro-(2*H*)-pyran and oxepane derivatives.[8]

In view of high perfumery value of 2-oxabicyclo[3.2.1]octane and hexahydrocyclopenta(*b*)furan derivatives,[9,10] several attempts of the cyclization of campholenic alcohols to obtain these heterocycles have been reported (Scheme 1). The synthesis of 2-oxabicyclo[3.2.1]octane skeleton has also been achieved *via* the

rearrangement of substituted cyclobutane derivative to give (±)-campholenic alcohol **2a** (R=H), which was cyclized to 2-oxabicyclo[3.2.1]octane skeleton **3a** (R=H), in the presence of $FeCl_3$-SiO_2 at RT (19 h).[11] The reaction of campholenic aldehyde **1** with phenyl magnesium bromide gave substituted alcohol **2b** (R=Ph)**,** which on heating with methane-sulfonic acid at 80 ºC gave cyclized 2-oxabicyclo[3.2.1]octane derivative **3b** as well as the rearranged 2-phenyl-6,6,6a-trimethyl-hexahydro-cyclopenta(*b*)furan **4b** (R = Ph).[9]

The reaction of the alcohol **2b** with phosphoric acid in toluene at 80 ºC gave heterocycle **4b** and rearranged alcohol **5b**.[10] The latter compound was cyclized by the treatment with triflic acid to give the compound **4b.**[10] The synthesis of **4c** (R= -$C(Me)_2COMe$) has been achieved through cyclization in the presence of H_2SO_4 in MeOH.[12] Similarly, the synthesis of 2-oxabicyclo[3.3.1]nonane and 1,3,5,5-tetramethyl-2-oxabicyclo[2.2.2]octane have been achieved through the cyclization of the corresponding substituted alcohols with silver(I)triflate[13] and H_2SO_4 respectively.[14] On the other hand, the treatment of campholenic alcohol **2b** (R= Ph) with $BF_3.OEt_2$ resulted in dehydration and cyclization to afford norbornane derivatives.[9]

In the present study, we have evaluated the cyclization of campholenic alcohols (**6-12,** (Scheme 2) in the presence of Amberlyst-15® under ambient condition, which yielded mainly 2-substituted-6,6,6a-trimethyl-hexahydrocyclopenta(*b*)furan derivatives, with minor amount (<10%) of 1,3,8,8-tetramethyl-bicyclo[3.2.1]octane skeleton The latter compound can be obtained with yield ~50%, when the reaction mixture is diluted with toluene and heated at 80 °C (Scheme 3)..

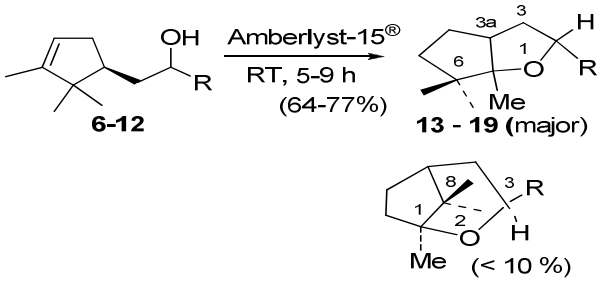


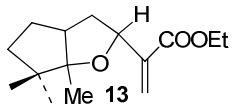
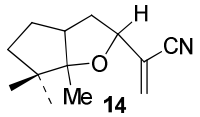
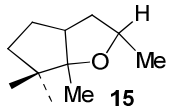
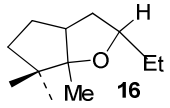
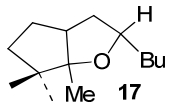
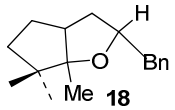
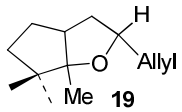
Schem1. Reported methods of cyclization of substituted campholenic alcohols

Results and Discussion

The required campholenic alcohols **6** and **7** were prepared by the Baylis-Hillman reaction[15] of (1'*S*)-campholenic aldehyde (**1)** with ethyl acrylate and acrylonitrile respectively, in the presence of catalytic amount of DABCO at room temperature for 4 d (Scheme 2). Alcohols **8-12** were obtained by the Grignard reaction of (1'*S*)-campholenic aldehyde (**1**) with the corresponding Grignard reagents (Scheme 2) and spectral values of alcohols **8-12** are in agreement with the literature values.[10] The cyclization of compounds **6-12** (0.06 mol) was achieved on stirring with Amberlyst-15® (1 g) in toluene (25 mL) at room temperature, which yielded the 2-substituted-6,6,6a-trimethyl-hexahydrocyclopenta(*b*)furan derivatives **13-19** in good yields (54-77%) (Table 1). In these

Table 1 Synthesis of 2-substituted-6,6,6a-trimethyl-hexahydrocyclopenta(*b*)furan derivatives **13-19**

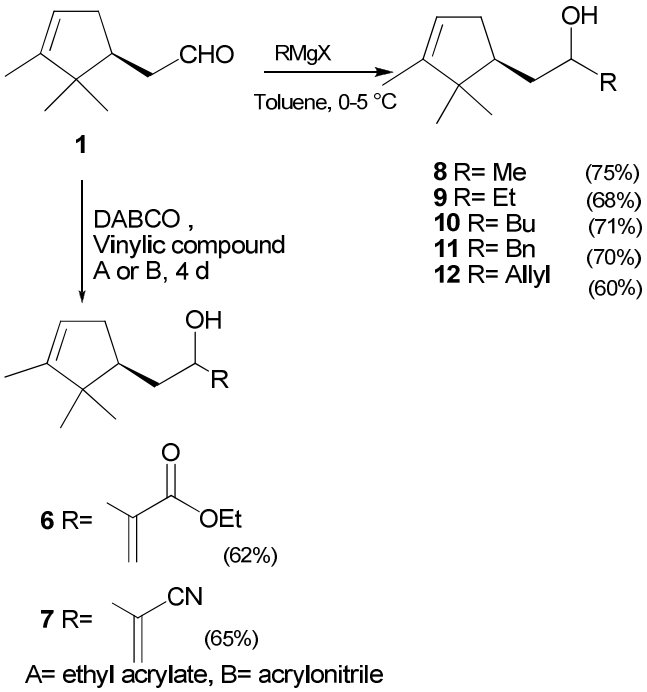


Entry	Comp.	Product*	Time (h)	Yield (%)
1	**6**		5	77
2	**7**		5	72
3	**8**		6	75
4	**9**		6	68
5	**10**		6	67
6	**11**		9	60
7	**12**		5	54

* Minor amount of formation of 3-substituted-1,8,8-trimethyl-2-oxabicyclo[3.2.1]octane (<10%) has been observed

cyclization reactions minor amount of formation of 3-substituted-1,8,8-trimethyl-2-oxabicyclo[3.2.1]octane (<10%) has been observed.

The formation of 2-substituted-6,6,6a-trimethyl-hexahydrocyclopenta(*b*)furan derivatives **13-19** was indicated by ^{1}H NMR spectra, which showed the absence of a olefinic proton at δ ~5.3 (1H, t) and the presence of a band δ ~ 4.3 (1H, dd or m) due to a proton next to etherial oxygen atom of tetrahydrofuran and the shift of a olefinic methyl protons from δ 1.7 (3H, s) to 1.3 (3H, s) indicating cyclization. In the ^{13}C spectra of these compounds, the ethereal carbons C_{6a} and C_2 of tetrahydrofuran moiety appeared at δ 94-97 and 73-80 respectively. Thus, 2-substituted 6,6,6a-trimethyl-hexahydro-cyclopenta(*b*)furan derivatives **13-19** have been synthesized at ambient condition in 60-77% yield.



Scheme 2. Synthesis of campholenic alcohol and derivatives

It is interesting to observe that the hydroxyl groups in compounds **6** and **7** with adjacent vinyl group (Table 1, entries 1 and 2); compounds **8**-**10** with adjacent alkyl groups (Table 1, entries 3-5), compound **11**with adjacent benzyl group (Table 1, entry 6) and compound **12** with adjacent allyl group (Table 1, entry 7) do not undergo dehydration and cyclization to 2-substituted-6,6,6a-trimethyl-hexahydro-cyclopenta(*b*)furan derivatives is the major reaction.

The cyclization of alcohol **8** with dried Amberlyst-15® was also studied by heating at 80 ºC for 5 h, which yielded a mixture of 1,3,8,8-tetramethyl-2-oxabicyclo[3.2.1]octane (**20**) and 2,6,6,6a-Tetramethyl-hexahydrocyclopenta(b)furan (**15**) (1:1), Scheme 3).[13]C NMR of compound **20** showed the etherial carbons of tetrahydropyran ring at C_1 and C_3 at δ 86.2 and 70.9 respectively.

To check the reusability of catalyst, the cyclization reaction of alcohol **12** (0.06 mol) was repeated three times with recovered Amberlyst-15® in toluene (25 mL) at RT which yielded 2-Allyl-6,6,6a-trimethyl-hexahydro-cyclopenta(b)furan **19** and the results are shown in Table 2.

Table 2 Reusability of recovered catalyst for cyclization of alcohol **12**

Entry	Reusability	Time (h)	Yield (%)
1	1st	9	62
2	2nd	13	59
3	3rd	17	58

In the first reuse of recovered Amberlyst-15® required 9 h for completion of reaction The 2nd and 3rd reuse of catalyst for the cyclization required 13 h and 17 h with yields 59% and 58% respectively.

The cyclization of alcohol **12** (0.06 mol) in the presence of Amberlyst-15® (1 g) was also studied in different solvents and at different temperatures, which yielded mainly 2-allyl-6,6,6a-trimethyl-hexahydrocyclopenta(*b*)furan **19** and the results are summarised in Table 3 and Table 4 respectively. The cyclization of alcohol **12** in methyl-cyclohexane, chloroform and hexane was studied, which yielded almost similar yields and the reaction time as compared to that of alcohol **12** in toluene. The alcohol **12**, on cyclization at 80 °C gave a (3:1) mixture of compound **19** and the 3-allyl-1,8,8-trimethyl-2-oxabicyclo[3.2.1]octane, which could not be separated on column chromatography over silica gel.

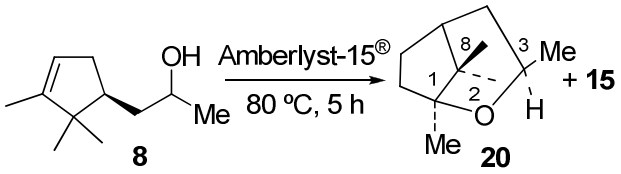
Table 3 Cyclization of alcohol **12** in different solvents

Entry	Solvent	Temp.	Time (h)	Yield (%)
1	Methyl cyclohexane	RT	6	65
2	$CHCl_3$	RT	7	64
3	Hexane	RT	7	65

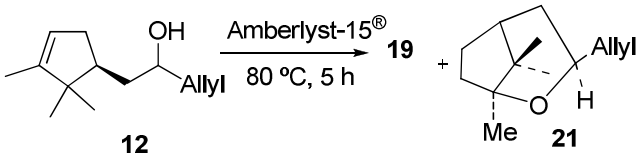
Table 4 Cyclization of alcohol **12** at different temperatures

Entry	Temp/ (°C)	Time (h)	Yield (%)
1	40	5	**19** (65)
2	60	5	**19** (64)
3	80	5	**19** + **21** (67)

- Inseparable (3:1) mixture of **19** and the corresponding 2-oxabicyclo[3.2.1]octane. **21**



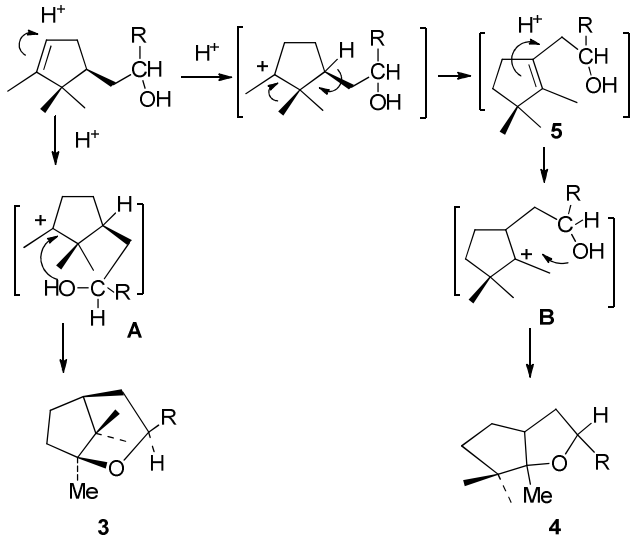
Scheme 3 Synthesis of 1,3,8,8-tetramethyl-2-oxabicyclo[3.2.1]octane



Scheme 4. Cyclization of alcohol **12** at 80° C

The probable mechanism of acid catalyzed rearrangement and cyclization of campholenic alcohol **2** with the formation of 2-substituted-6,6,6a-trimethyl- hexahydro-cyclopenta(*b*)furan and 3-substituted-1,8,8-trimethyl-2-oxabicyclo[3.2.1]octane is shown in Scheme 3. The double bond of campholenic alcohol **2** is protonated to give carbonium ion **A** followed by methyl migration and adjacent proton loss leads to the \isomerized alcohol **5.** The protonation of double bond of isomeric alcohol **5** leads carbocation **B.** The cyclization through carbonium ion **A** yields 2-oxabicyclo[3.2.1]octane skeleton, whereas the cyclization through the carbonium ion **B** leads to 6,6,6a-trimethyl-hexahydro-cyclopenta(*b*)furan.

The advantages of present cyclization method are as follows: (a) the products are isolated by simple filtration and purified by column chromatography, (b) catalyst can be reused, (c) the cyclization takes place under mild condition, (d) campholenic alcohols tolerate adjacent vinyl, benzyl or allyl groups during cyclization and no dehydration has been observed.



Scheme 5. Probable mechanism of formation of hexahydro-cyclopenta(*b*)furan and 2-oxabicyclo[3.2.1]octane skeletons from campholenic alcohols

Conclusions

In conclusion, we have reported a mild, simple and environmentally benign procedure for synthesis of hexahydro-cyclopenta(*b*)furan and 2-oxabicyclo[3.2.1]octane skeletons from campholenic alcohols in the presence of Amberlyst-15®. This one pot- green method is superior to the existing procedures and offers

several advantages including the use of green catalyst, cleaner reaction condition, easy recovery and reusability of catalyst. The probable mechanism for the formation of both heterocycles has been proposed. These derivatives have high olfactory value and we hope that our present method will be widely beneficial to both academic and industrial processes.

Experiment

General procedures

The reaction progress was also monitored by GC analysis. GC-MS analysis was carried on instrument, where GC-6890 was coupled with mass spectrometer MS-5973 N with quadrupole mass detector, using 5% phenyl methyl siloxane column. Electrospray ionization and a TOF mass analyser were used for HRMS measurements. The compounds **13-20** showed the required m/z: (M^+) values. IR spectra (Neat) were recorded on FT-IR spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on spectrometers at 300 or 400 MHz and ^{13}C at 75 or 100 MHz at ambient temperature. Multiplicities is reported as follows: s = singlet, d = doublet, dd = doublets of doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet.

Materials

Amberlyst-15® and pre-coated silica gel 254 plates were obtained from Fluka and Merck respectively. The monitoring of reaction and checking of purity of the products were done using pre-coated silica gel 254 plates (Merck) and visualization using anisaldehyde-sulfuric acid reagent. Silica gel used for column chromatography was activated by heating at 200 °C for 4 h. The dried Amberlyst-15® was prepared by heating at 200 °C for 1 h. Toluene was distilled and dried over Na.

Synthesis of ethyl 3-hydroxy-2-methylene-4-(2,2,3-trimethylcyclopent-3-en-1-yl)butanoate (6) and 3-hydroxy-2-methylene-4-(2,2,3-trimethylcyclopent-3-en-1-yl)butanenitrile (7). A mixture of (1'*S*)-campholenic aldehyde **1** (32 mmol), activated vinyl compound namely ethyl acrylate or acrylonitrile (60 mmol) and DABCO (0.5 wt eqv) was stirred at room temperature for 4 d. The reaction mixture was diluted with dichloromethane (20 ml); the organic layer was washed with 2N HCl and water and was dried over anhydrous Na_2SO_4. Solvent was evaporated and the residue was purified by silica gel column chromatography, the elution with hexane-ethyl acetate (8:2) provided the corresponding Baylis−Hillman adducts **6 -7** (Scheme 2).

Ethyl 3-hydroxy-2-methylene-4-((S)-2,2,3-trimethylcyclopent-3-en-1-yl)butanoate (6). (*Mixture of diasteremors).

IR (neat): 3448, 2956, 1736, 1629, 1460, 1445, 1375, 1263, 1144, 1072 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (d, *J* = 1Hz, 1H), 6.22 (d, *J* = 1Hz, 1H), 5.83 (t, *J* = 1.1Hz, 1H), 5.76 (t, *J* = 1.1 Hz, 1H), 5.23 (m, 2H), 4.45 (dd, *J* = 9.8, 2.7 Hz, 1H), 4.38 (t, *J* = 7.5 Hz, 1H), 4.26 (m, 4H), 2.37-2.43 (m, 1H), 2.28-2.33 (m, 1H), 2.05-2.12 9 m, 1H), 1.85-1.95 (m, 3H), 1.68-1.73 (m, 2H), 1.6 (m, 6H), 0.98 (s, 3H), 0.95 (s, 3H), 0.77 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.79, 166.76, 146.75, 148.56, 143.77, 142.24, 125.53, 124.44, 121.92, 121.71, 72.64, 72.62, 70.52, 70.49, 61.00, 6095, 47.52, 47.11, 46.84, 46.33, 37.16, 36.92, 35.95,. 35.20, 25.68, 25.63, 19.68, 19.78, 14.31, 12.79. *MS m/z 252 (M^+), 234, 219, 207, 191, 173, 161, 145, 129, 108, 101, 93, 83, 67, 55, 41; EI-HRMS m/z (M^+) calcd for $C_{15}H_{24}O_3$ 252.1725, found 252.1730.

3-Hydroxy-2-methylene-4-((*S*)-2,2,3-trimethylcyclopent-3-en-1-yl)butan-nitrile (7).

IR (neat): 3419, 2959, 2228, 1446, 1360, 1303, 1216, 1086, 1037 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.04 (d, *J* = 1 Hz, 1H), 5.98 (d, *J* = 1Hz, 1H), 5.23 (s, 1H), 4.28 (dd, *J* = 9.7, 6.4 Hz, 1H), 2.32-2.38 (ddd, *J* = 10.8, 9, 1.4 Hz, 1H), 2.0-2.07 (m, 1H), 1.99 (OH, 1H), 1.86-1.93 (m, 1H), 1.68-1.72 (m, 2H), 1.61 (s, 3H), 0.99 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 129.5, 127.8, 121.4, 117.3, 71.2, 46.9, 45.8, 36.5, 35.1, 25.5, 19.9, 12.7; MS m/z 205 (M^+), 190, 177, 172, 157, 145, 130, 123, 108, 95, 91, 79, 67, 53, 41; EI-HRMS m/z (M^+) calcd for $C_{13}H_{19}NO$ 205.1467, found 205.1469.

Synthesis of (1'*S*)-campholenic alcohols 8-12. (1'*S*)-campholenic aldehyde 1 was treated with the corresponding Grignard reagents according to literature procedure to obtain alcohols **8-12**.[10]

General procedure for the synthesis of 2-substituted-6, 6,6a-trimethylhexahydro-cyclopenta (*b*) furan derivatives 13-19. To a stirred solution of (1'*S*)-campholenic alcohols **6-12** (0.06 mol) in dry toluene (50 mL) Amberlyst-15® (1 g,) was added and the reaction mixture was stirred at room temperature for 5-9 h. The reaction was monitored by TLC or GC and was filtered after completion. The filtrate was evaporated *in vacuum* and the residue was purified by column chromatography (silica gel; 100-200 mesh), the elution with hexane-ethyl acetate (8:2) provided compounds **13-19** respectively (Table I).

Synthesis of 1,3,8,8-tetramethyl-2-oxabiclo[3.2.1]octane (20*). To a stirred solution of **8** (0.06 mole) in dry toluene (100 mL) dried Amberlyst-15 (1 g) was added and reaction mixture was then stirred at 80 °C for 5 h. Reaction mixture was filtered, the solvent was removed in *vacuum* and the residue was subjected to column chromatography (silica gel; 100-200 mesh), the elution with EtOAc-Hexane (1:9) gave 1,3,8,8-tetramethyl-2-oxabiclo[3.2.1]octane **20** (50%) (Scheme 3).

2-(1'-Ethoxycarbonyl-ethen-1'-yl)-6,6,6a-trimethyl-hexahydrocyclopenta(b)furan (13). IR (neat): 2959, 1718, 1631, 1454, 1385, 1266, 1075,1025, 807 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (d, *J* = 2Hz, 2H), 5.99 (d, *J* = 2 Hz, 1H), 4.70 (dd, *J* = 5.4,11 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 2.42-2.49 (m, 1H), 2.2 (dd, *J* = 5.4, 12.2 Hz 1H), 1.98-2.05 (m, 1H), 1.67-1.83 (m, 2H), 1.34-1.39 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.14 (s, 3H), 1.03 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 143.3, 122.8, 95.6, 78.2, 60.4, 48.0, 46.4, 41.7, 40.1, 29.0, 25.4, 22.1, 19.9, 14.2; MS m/z 252 (M^+), 237, 222, 207, 193, 164, 148, 132, 120, 108, 95, 79, 67, 55, 41; EI-HRMS m/z (M^+) calcd for $C_{15}H_{24}O_3$ 252.1725, found 252.1732.

2-(1'-Cyano-ethen-1'-yl)-6,6,6a-trimethyl-hexahydro-cyclopenta(b)furan(14). IR (neat): 2872, 2228, 1453, 1386, 1260, 1167, 1131, 1074, 946, 867 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 5.99 (d, *J* = 2 Hz, 1H) , 5.91 (d, *J* = 2 Hz, 1H), 4.40 (dd, *J* = 5.3, 10.7 Hz, 1H), 2.49-2.55 (m, 1 H), 1.98-2.18 (m, 3H) 1.25-1.68 (m, 3H), 1.20 (s, 3H), 1.02 (s, 3H), 0.86 (s, 3H).^{13}C NMR (100 MHz,$CDCl_3$) δ 129.7, 126.1, 117.0, 97.2, 80.0, 47.5, 46.4, 40.1, 39.8., 28.8, 25.1, 21.9, 19.6;MS m/z 205 (M^+), 191, 176, 161, 149, 123, 109, 92, 82, 79, 65, 51; EI-HRMS m/z (M^+) calcd for $C_{13}H_{19}NO$ 205.1467, found 205.1473.

2,6,6,6a-Tetramethyl-hexahydrocyclopenta(b)furan (15). IR (neat) 2960, 1455, 1381, 1256, 1119, 941, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.98-4.03 (m, 1H), 2.36-2.41 (m, 1H), 2.03-1.92

(m, 1H), 1.58-1.81 (m, 3H), 1.72 (t, J = 6.5 Hz, 2H), 1.24 (d, J = 5.96 Hz, 3H), 1.12 (s, 3H), 1.01 (s, 3H), 0.82 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 95.1, 73.5, 48.2, 46.5, 42.6, 40.5, 29.5, 25.5, 22.4, 22.3, 21.0; MS m/z 168 (M^+), 153, 139, 125, 111, 97, 83, 69, 57, 43; EI-HRMS m/z (M^+) calcd for $C_{11}H_{20}O$168.1514, found 168.1521.

2-Ethyl-6,6,6a-trimethyl-hexahydro-cyclopenta(b)furan (16).IR (neat): 2957, 2868, 1464, 1369, 1313, 1260, 1116, 888, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78-3.82 (m, 1H), 2.35- 2.4 (m, 1H), 1.81-2.03 (m, 2H), 1.69-1.75 (4H), 1.42 (dd, J = 6, 7.4 Hz, 2H), 1.09 (s, 3H), 1.01 (s, 3H), 0.88 (t, J = 7.4 Hz, 3H), 0.82 (s, 3H). ^{13}C NMR (100 MHz,$CDCl_3$) δ 96.0, 81.6, 47.8, 40.5, 39.8, 29.8, 29.5, 25.5, 22.3, 20.7, 12.8, 10.2; MS m/z 182 (M^+) 167, 153, 139, 125, 109, 96, 83, 69, 56, 43; EI-HRMS m/z (M^+) calcd for $C_{12}H_{22}O$ 182.1671, found 182.1678.

2-Butyl-6,6,6a-trimethyl-hexahydro-cyclopenta(b)furan (17). IR (neat): 2987, 2869, 1465, 1388, 1215, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (m, 1H), 2.35-2.4 (m, 1H), 1.78-2.03 (3H), 1.66-1.76 (m, 3H), 1.57-1.64 (m, 2H), 1.25-1.36 (m, 4H) 1.1 (s, 3H), 1.01 (s, 3 H), 0.89 (t, J = 6.8 Hz, 3H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 94.5, 80.4, 47.8, 46.5, 40.5, 36.8, 29.5, 28.4,.25.5, 23.06, 22.32, 20.8, 19.4, 14.2;MS m/z 210 (M^+), 195, 167, 153, 140, 125, 109, 95, 85, 69; EI-HRMS m/z (M^+) calcd for $C_{14}H_{26}O$ 210.1984, found 210.1989.

2-Benzyl-6,6,6a-trimethyl-hexahydro-cyclopenta(b)furan (18). IR (neat) 2947, 2867, 1463, 1378, 1218, 758 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3-7.15 (m, 5H), 4.05-4.12 (m, 1H), 3.1 (dd, J = 5.4 and 13.5 Hz, 1H), 2.65 (dd, J = 5.7, 13.5 Hz, 1H), 2.3-2.4 (m, 1H), 1.5- 2.0 (m, 4H), 1.3-1.45 (m, 2H), 1.09 (s, 3H), 1.03 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 129.6, 129.4, 128.5, 128.2, 126.1, 95.3, 80.8, 47.6, 46.4, 43.4, 40.3, 40.1, 29.2, 25.4, 22.3, 20.7; MS m/z 244 (M^+), 187, 153, 135, 109, 91, 69, 56, 43; EI-HRMS m/z (M^+) calcd for $C_{17}H_{24}O$ 244.1827, found 244.1832.

2-Allyl-6,6,6a-trimethyl-hexahydrocyclopenta(b)furan (19). IR (neat) 2953, 2869, 1464, 1371, 1216, 1072, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.8 (dd, J = 17, 10 Hz, 1H), 5.07 (dd, J = 17, 1.6 Hz, 1H), 5.02 (ddd, J = 10, 1.6,1.1 Hz, 1H), 3.89-3.96 (m, 1H), 2.35-2.48 (m, 2H), 1.94-2.01 (m, 1H), 1.75 (d, J = 6.5 Hz, 2H), 1.58-1.66 (m, 1H), 1.17-1.36 (m, 3H), 1.11 (s, 3H), 1.01 (s, 3H), 0.83 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 116.6, 95.1, 79.4, 47.7, 46.5, 41.1, 40.4, 39.9, 29.4, 25.5, 22.7, 20.6. MS m/z 194 (M^+), 179, 166, 153, 137, 123, 109, 95, 79, 55, 43; EI-HRMS m/z (M^+) calcd for $C_{13}H_{22}O$194.1671, found 194.1676.

1,3,8,8-tetramethyl-2-oxabiclo[3.2.1]octane (20). IR (Neat) 2934, 1458, 1375, 1259, 1114, 1035, 869, 771 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.86-3.91 (m, 1H), 2.34-2.38 (m, 1H), 2.13-2.20 (m, 2H), 1.91-1.99 (m, 2H), 1.77-1.85 (m, 2H), 1.20 (d, J = 6.0 Hz, 3H), 1.07 (3H, s), 1.01 (3H, s)), 0.85 (s, 3H, s).^{13}C NMR (125 MHz, $CDCl_3$): δ 86.2, 70.9, 48.3, 43.9. 35.3, 35.2, 24.0, 22.5, 21.7, 18.4, 18.3; GC-MS (m/z) 168 (M^+), 153, 139, 125, 111, 97, 83, 69, 57, 43; EI-HRMS m/z (M^+) calcd for $C_{11}H_{20}O$ 168.1514, found 168.1523.

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