Acid-catalyzed intramolecular oxa-Michael addition reactions under solvent-free and microwave irradiation conditions

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Abstract

The acid-catalyzed intramolecular oxa-Michael addition of (*E*)-1-aryl-4-hydroxy-4-methyl--pent-1-en-3-ones under solvent-free and microwave irradiation conditions has been investigated. The results showed that Bronsted acids are more efficient than Lewis acids in this reaction. Up to 90% conversion and 81% yield were obtained using trifluoromethanesulfonic acid (triflic acid) as the catalyst, with short reaction times and an environmentally benign procedure.

Keywords: Microwave, oxa-Michael addition, solvent-free, trifluoromethanesulfonic acid, (*E*)-1-aryl-4-hydroxy-4-methylpent-1-en-3-ones

Introduction

Organic chemists are constantly challenged to develop environmentally benign routes for preparing desired target compounds. Microwave irradiation has emerged as a convenient and powerful method for promoting organic reactions, owing to its uniform heating effect.[1-3] Another green chemistry principle – solvent-free organic synthesis – has also received much attention from organic chemists. The combination of solvent-free and microwave irradiation can lead to large reductions in reaction times, or enhancements in conversions, and will make synthesis more environmentally benign.[4-6]

Michael and hetero-Michael additions are effective for the formation of carbon-carbon and carbon- hetero-atom bonds, and have been utilized widely in inter- and intra- molecular reactions to obtain various products, which include important building blocks for many biologically active molecules.[7,8] Recently, the conjugate addition of oxygen nucleophiles to α,β-unsaturated carbonyl compounds (the oxa-Michael addition) has attracted much attention.[9] Various catalysts have been reported for intermolecular oxa-Michael additions, such as pro-azaphosphatranes

($P(RNCH_2CH_2)_3N$),[10] trimethylphosphine, tributylphosphine,[11] 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),[12] $[Rh(COD)(OMe)]_2$,[13] $(CH_3CN)_2PdCl_2$,[14] (1,3-bis-(2,6-di-isopropylphenyl)imidazol-2-yliden)Cu(OEt), (1,3-bis-(2,6-di-isopropylphenyl)imidazol-2-yliden)Cu(OPh), (1,3-bis-(2,6-di-isopropylphenyl)imidazolin-2-ylidene)Cu(OEt),[15] KF/Al_2O_3,[16] $(CF_3SO_2)_2NH$,[17] $BF_3{\cdot}Et_2O$,[18] $La(NO_3)_3{\cdot}6H_2O$,[19] pyrrolidine/CH_3SO_3H[20] and biphenyldiamine-based organocatalyst.[21] The use of ionic liquid as solvent for toluenesulfonic acid-catalyzed oxa-Michael addition has also been reported.[22] For intramolecular oxa-Michael addition, cinchona alkaloids,[23] thiourea derivatives,[24] quinine,[25] guanidine,[26] $[Pd(MeCN_4)](BF_4)_2$,[27] N,N-dioxide nickel(II) complex,[28] CF_3COOH[29] and toluenesulfonic acid (TsOH)[30,31] have been utilized as the catalysts. It was reported that the intramolecular oxa-Michael addition of (*E*)-1-aryl-4-hydroxy-4-methylpent-1-en-3-ones in the presence of TsOH should be carried out by refluxing in dichloroethane for 24 h, while the products were hard to purify due to the impurities.[31]

In continuation of our work on "green" chemistry,[32] we report herein an efficient acid-catalyzed intramolecular oxa-Michael addition reaction of (*E*)-1-aryl-4-hydroxy-4-methylpent-1-en-3-ones **1** under solvent-free and microwave irradiation conditions.

Results and Discussion

Effect of catalysts. In order to find the most efficient catalyst, we studied first the intramolecular oxa-Michael addition of (*E*)-4-hydroxy-4-methyl-1-phenylpent-1-en-3-one **1a** under solvent-free and microwave irradiation conditions. The results are given in Table 1.

Table 1. Effect of catalysts in the intramolecular oxa-Michael addition of **1a**[a]

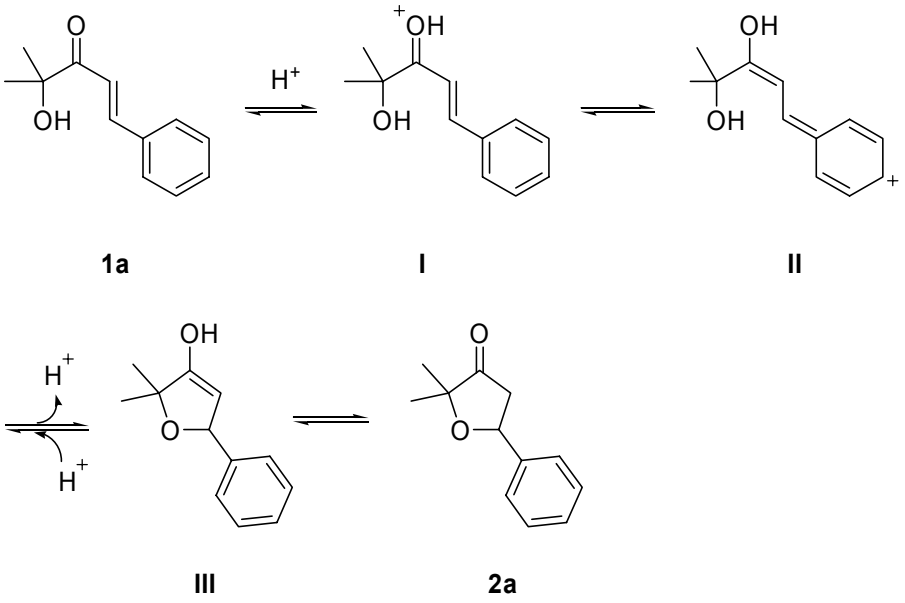
Entry	Catalyst	T_{final} (°C)	Conversion (%)[b]	Selectivity (%)[b]	Yield (%)[c]
1	$Zn(OTf)_2$	141	32	83	20
2	$Cu(OTf)_2$	143	59	87	46
3	$TsOH{\cdot}H_2O$	118	69	91	57
4	CH_3SO_3H	115	64	97	58
5	TfOH	117	88	94	78
6	DBU	116	0	-	-
7	DABCO	116	0	-	-
8	$(CH_3CN)_2PdCl_2$	165	96	16	-

[a] Reaction conditions: **1a** (0.5 mmol), catalyst (0.05 mmol), 650 W microwave power, 9 min total reaction time, with alternation between 9 s of irradiating time and 21 s of cooling time.
[b] Conversion of **1a** and selectivity to **2a** were measured on the reaction mixture by gas chromatography. [c] Isolated yield.

When the Lewis acid zinc trifluoromethanesulfonate ($Zn(OTf)_2$) was used as catalyst, the conversion of **1a** and the selectivity to 2,2-dimethyl-5-phenyl-dihydrofuran-3(2*H*)-one **2a** were 32 and 83%, respectively, and the isolated yield of **2a** was only 20% (entry 1). The other Lewis acid, copper trifluoromethanesulfonate ($Cu(OTf)_2$) showed higher activity, and a 59% conversion with 87% selectivity was obtained (entry 2). However, it was found that Bronsted acids are more efficient than Lewis acids in this reaction (entries 3-5). Among the tested Bronsted acids trifluoromethanesulfonic acid (triflic acid, TfOH), TsOH, and CH_3SO_3H, the TfOH gave the best result, with up to 88% conversion and 94% selectivity (entry 5). Organic bases, such as DBU and 1,4-diazabicyclo[2.2.2]octane (DABCO), were also examined but showed no activity in this intramolecular oxa-Michael addition (entries 6 and 7), although they have been employed as catalysts in some intermolecular oxa-Michael additions.[12,33] The highest conversion (96%) of **1a** was observed in the presence of $(CH_3CN)_2PdCl_2$, but many unidentified by-products were observed and the selectivity to **2a** was only 16% (entry 8).

Comparison of plausible reaction mechanism in the presence of Bronsted acids and Lewis acid

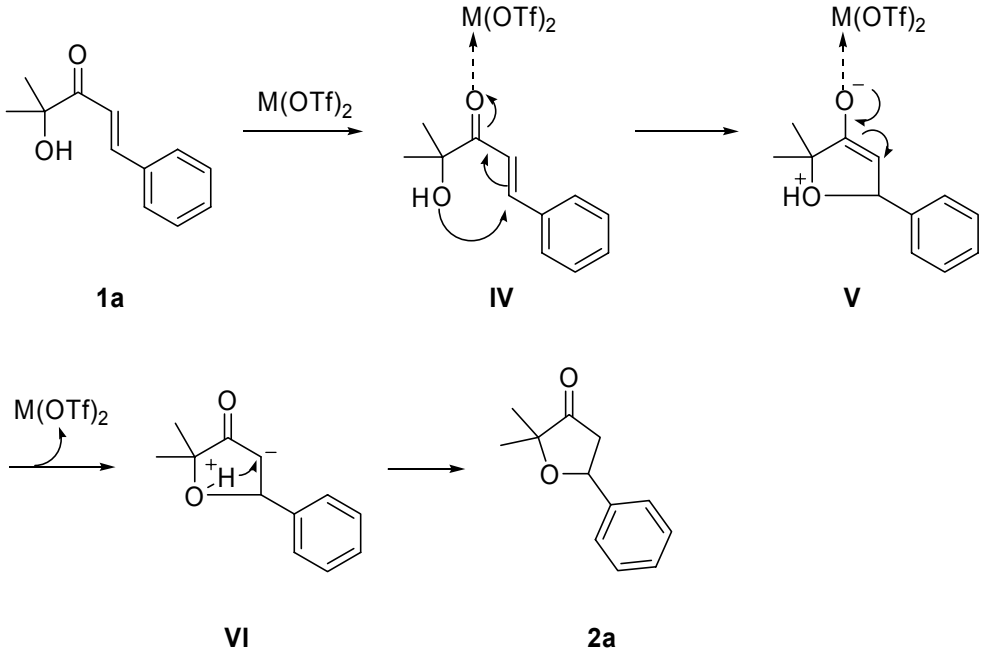
A plausible reaction mechanism for the intramolecular oxa-Michael addition of **1a**, promoted with Bronsted acid, as given by Johnson's group, is outlined in Scheme 1.[31,34] The carbonyl oxygen of **1a** accepts one proton from the Bronsted acid to give the protonated form **I** and canonical form **II**, and undergoes ring closure to give the enol form **III** of **2a**.



Scheme 1. Plausible reaction mechanism in the presence of Bronsted acids.

It is presumed that in the presence of Bronsted acid, there exists an equilibrium between **1a** and **2a**.[31] When a mixture of **2a** (0.5 mmol) and TfOH (0.05 mmol) was irradiated at 650 W for 9 min, it was found that 13% of **2a** did convert into **1a**.

Spencer and colleagues have reported that protons generated through *in situ* hydrolysis of metal salts were the active catalysts in some Lewis acid mediated hetero-Michael additions.[35] In order to ascertain whether protons are the actual catalysts in this intramolecular oxa-Michael addition in the presence of Lewis acids, $Zn(OTf)_2$ and $Cu(OTf)_2$, the above experiment was repeated using $Zn(OTf)_2$ in place of TfOH. The experiments showed that no **2a** was converted into **1a** after irradiating for 9 min, while our previous experiments showed both Lewis acids and Bronsted acids could catalyze this intramolecular oxa-Michael reaction (Table 1, entries 1 and 2 versus 3-5). These results suggest that protons were not the active catalysts in this Lewis acid-catalyzed oxa-Michael addition. Based on our experimental results we propose a plausible reaction mechanism shown in Scheme 2. $Zn(OTf)_2$ and $Cu(OTf)_2$ are highly oxophilic, and could form a carbonyl– metal-ion complex **IV** with **1a**, which would initiate the formation of a C-O bond to generate the intermediate **V**. This could regenerate the catalyst and give the intermediate **VI**. After the intramolecular proton transfer step, **2a** was obtained.

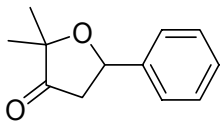


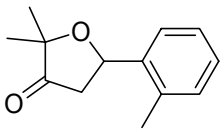
Scheme 2. Plausible reaction mechanism in the presence of $M(OTf)_2$.

Intramolecular oxa-Michael addition of (*E*)-1-aryl-4-hydroxy-4-methylpent-1-en-3-ones

To evaluate the scope of the intramolecular oxa-Michael addition, substrates with different steric property and electron property have been investigated using TfOH as the catalyst under the microwave-assisted process. As shown in Table 2, most of the reactions proceeded efficiently, high conversions of (*E*)-1-aryl-4-hydroxy-4-methylpent-1-en-3-ones **1** and selectivities to the

desired products 5-aryl-2,2-dimethyl-dihydrofuran-3(2*H*)-ones **2** were obtained within several minutes.


2a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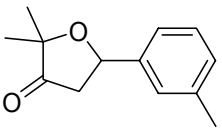
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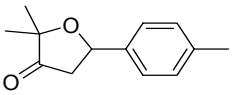
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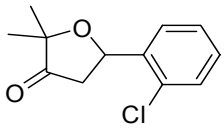
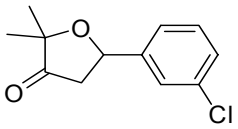
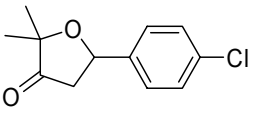

2e


2f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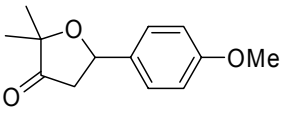
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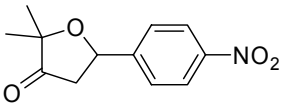
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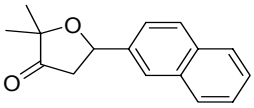
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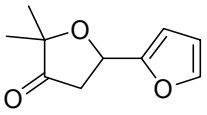
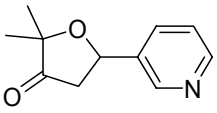
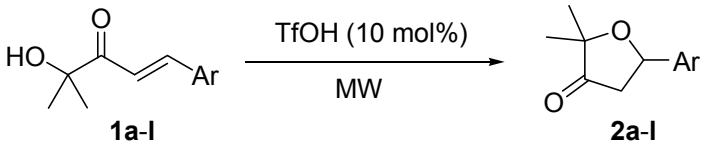

2k


2l

It was observed that the position of substituents on the benzene ring had little effect on the conversions and selectivities (entries 2-4, methyl as substituent; entries 5-6, chlorine as substituent). Also, the electronic properties of substituents on the benzene ring showed marginal effects on the conversions and selectivities (entry 4, *p*-Me; entry 7, *p*-Cl; entry 8, *p*-OCH_3), even with a strongly electron-withdrawing group (entry 9, *p*-NO_2). A similar result was obtained when a naphthalene ring replaced a benzene ring, the conversion of **1j** and selectivity to **2j** were 84 and 95%, respectively (entry 10). When (*E*)-1-(furan-2-yl)-4-hydroxy-4-methylpent-1-en-3-one **1k** was used as the substrate, the irradiating period and reaction time must be shortened. Otherwise, the selectivity to **2k** would drastically decrease, which may be due to the polymerization of **2k**. Under our conditions, 17% conversion of **1k** and 8% isolated yield of **2k** were obtained (entry 11). The intramolecular oxa-Michael addition of (*E*)-4-hydroxy-4-methyl-1-(pyridin-3-yl)--pent-1-en-3-one **1l** could not occur under microwave irradiation or refluxing conditions because the proton of Bronsted acid would be captured by the N- atom of the pyridinyl group.

Table 2. Intramolecular oxa-Michael addition of (*E*)-1-aryl-4-hydroxy-4-methylpent-1-en-3-ones under solvent-free and microwave conditions[a]



1a-l **2a-l**

Entry	Product	T_{final} (°C)	Conversion (%)	Selectivity (%)	Yield (%) [b]
1	**2a**	117	88	94	78
2	**2b**	116	85	94	62
3	**2c**	116	83	93	60
4	**2d**	117	81	95	63
5	**2e**	115	90	97	80
6	**2f**	116	90	98	81
7	**2g**	116	90	96	80
8[c]	**2h**	97	80	92	65
9	**2i**	117	81	85	55
10	**2j**	116	84	95	71
11[d]	**2k**	30	17	94	8
12	**2l**	-	0	-	-

[a] Reaction conditions: **1** (0.5 mmol), TfOH (0.05 mmol), 650 W (microwave power), 9 min (total reaction time, with an alternation between 9 s of irradiating time and 21 s of cooling time).
[b] Isolated yield. [c] With an alternation between 6 s of irradiating time and 24 s of cooling time. [d] Total reaction time 3 min, with an alternation between 3 s of irradiating time and 27 s of cooling time.

Conclusions

The acid-catalyzed intramolecular oxa-Michael addition of (*E*)-1-aryl-4-hydroxy-4-methylpent--1-en-3-ones could be performed under solvent-free and microwave irradiation conditions, providing an environmentally benign method for preparing 5-aryl-2,2-dimethyl-dihydrofuran-3(2*H*)-ones. It was found that Bronsted acids are more efficient than Lewis acids in this reaction. Unlike traditional reactions, the solvent-free and microwave-assisted reactions could be finished within several minutes to give high conversions and selectivities.

Experimental Section

General. ^{1}H- and ^{13}C- NMR spectra were obtained on a Bruker Avance III (500 MHz) spectrometer. $CDCl_3$ was used as the solvent with tetramethylsilane (TMS) as the internal standard. Low and high resolution mass spectra were recorded in the EI mode on a Waters GCT Premier mass spectrometer. Melting points were measured using CRC-1 melting point instrument and are uncorrected. Microwave experiments were performed at a LWMC-201 microwave reactor. The reaction temperature was determined by an IR thermometer (SUN-GUN SG-20). Reactions were monitored by gas chromatography (GC-6890) with an HP-5 capillary column (30m x 0.25mm). All reagents were obtained from commercial sources and used as received. (*E*)-1-Aryl-4-hydroxy-4-methylpent-1-en-3-ones were prepared as previously described.[30,36]

General procedure for the synthesis of 5-aryl-2,2-dimethyl-dihydrofuran-3(2*H*)-ones (2a-k) To an open glass tube, were added (*E*)-1-aryl-4-hydroxy-4-methylpent-1-en-3-one (0.5 mmol) and triflic acid (0.05 mmol). The tube was positioned in the centre of the microwave cavity, and irradiated (650 W) for 9 min (total reaction time, with alternation of 9s irradiating time and 21s of cooling time). After the last period of irradiating, the temperature (on the surface of the tube) was determined by an IR thermometer. After cooling, the reaction mixture was diluted with CH_2Cl_2 and purified through a column of silica gel to obtain the pure products **2a-k**.

2,2-Dimethyl-5-phenyl-dihydrofuran-3(2*H*)-one (2a). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3H, -CH_3), 1.41 (s, 3H, -CH_3), 2.56 (dd, *J* = 10.5 Hz; *J* = 18 Hz, 1H, H-4a), 2.87 (dd, *J* = 6 Hz; *J* = 18.5 Hz, 1H, H-4b), 5.21 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 7.30-7.34 (m, 1H, phenyl-H), 7.37-7.42 (m, 4H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.70 (-CH_3), 24.47 (-CH_3), 44.24 (C-4), 74.51 (C-5), 81.51 (C-2), 126.13 (phenyl-C), 128.32 (phenyl-C), 128.78 (phenyl-C), 140.69 (phenyl-C), 217.35 (O=C). MS (EI), *m/z* (%) 190.1 (M^+, 2), 104.1 (100).

2,2-Dimethyl-5-*o*-tolyl-dihydrofuran-3(2*H*)-one (2b). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3H, -CH_3), 1.43 (s, 3H, -CH_3), 2.34 (s, 3H, phenyl-CH_3), 2.46 (dd, *J* = 10.5 Hz; *J* = 18 Hz, 1H, H-4a), 2.90 (dd, *J* = 6 Hz; *J* = 18 Hz, 1H, H-4b), 5.38 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 7.17 (d, *J* = 7.5 Hz, 1H, phenyl-H), 7.20-7.26 (m, 2H, phenyl-H), 7.56 (d, 1H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 19.19 (phenyl-CH_3), 21.60 (-CH_3), 24.31 (-CH_3), 42.82 (C-4), 71.44 (C-5), 81.11 (C-2), 124.77 (phenyl-C), 126.52 (phenyl-C), 127.80 (phenyl-C), 130.41 (phenyl-C), 134.80 (phenyl-C), 138.79 (phenyl-C), 217.46 (O=C). MS (EI), *m/z* (%) 204.1 (M^+, 3), 118.1(100). HRMS Calcd. for $C_{13}H_{16}O_2$ 204.1150, found 204.1158.

2,2-Dimethyl-5-*m*-tolyl-dihydrofuran-3(2*H*)-one (2c). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H, -CH_3), 1.41 (s, 3H, -CH_3), 2.37 (s, 3H, phenyl-CH_3), 2.57 (dd, *J* = 10.5 Hz; *J* = 18 Hz, 1H, H-4a), 2.86 (dd, *J* = 6 Hz; *J* = 18 Hz, 1H, H-4b), 5.18 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 7.14 (d, *J* = 7.5 Hz, 1H, phenyl-H), 7.20 (d, *J* = 8 Hz, 1H, phenyl-H), 7.23 (s, 1H, phenyl-H), 7.27 (t, *J* = 8 Hz, 1H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.47 (phenyl-CH_3), 21.60 (-CH_3), 24.39 (-CH_3), 44.13 (C-4), 74.47 (C-5), 81.43 (C-2), 123.16 (phenyl-C), 126.66 (phenyl-C), 128.58 (phenyl-C), 129.00

(phenyl-C), 138.44 (phenyl-C), 140.44 (phenyl-C), 217.42 (O=C). MS (EI), *m/z* (%) 204.1 (M^+, 3), 118.1 (100).

2,2-Dimethyl-5-*p*-tolyl-dihydrofuran-3(2*H*)-one (2d). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 2.36 (s, 3H, phenyl-CH_3), 2.56 (dd, *J* = 10.5 Hz; *J* = 18 Hz, 1H, H-4a), 2.85 (dd, *J* = 6 Hz; *J* = 18.5 Hz, 1H, H-4b), 5.18 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 7.19 (d, *J* = 8 Hz, 2H, phenyl-H), 7.30 (d, *J* = 8 Hz, 2H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.18 (phenyl-CH_3), 21.62 (-CH_3), 24.41 (-CH_3), 44.15 (C-4), 74.33 (C-5), 81.39 (C-2), 126.03 (phenyl-C), 129.34 (phenyl-C), 137.54 (phenyl-C), 138.02 (phenyl-C), 217.54 (O=C). MS (EI), *m/z* (%) 204.1 (M^+, 3), 118.1 (100).

5-(2-Chlorophenyl)-2,2-dimethyl-dihydrofuran-3(2*H*)-one (2e). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3H, -CH_3), 1.44 (s, 3H, -CH_3), 2.33 (dd, *J* = 10.5 Hz; *J* = 18 Hz, 1H, H-4a), 3.13 (dd, *J* = 6 Hz; *J* = 18.5 Hz, 1H, H-4b), 5.19 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 7.23-7.27 (m, 3H, phenyl-H), 7.32-7.37 (m, 1H, phenyl-H), 7.67-7.67 (m, 1H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.71 (-CH_3), 24.21 (-CH_3), 42.67 (C-4), 71.35 (C-5), 81.27 (C-2), 126.37 (phenyl-C), 127.33 (phenyl-C), 128.91 (phenyl-C), 129.36 (phenyl-C), 131.90 (phenyl-C), 138.97 (phenyl-C), 216.74 (O=C). MS (EI), *m/z* (%) 223.9 (M^+, 2), 137.6 (100). HRMS Calcd. for $C_{12}H_{13}O_2Cl$ 224.0604, found 224.0610.

5-(3-Chlorophenyl)-2,2-dimethyl-dihydrofuran-3(2*H*)-one (2f). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H, -CH_3), 1.41 (s, 3H, -CH_3), 2.50 (dd, *J* = 10.5 Hz; *J* = 18 Hz, 1H, H-4a), 2.80 (dd, *J* = 6 Hz; *J* = 18 Hz, 1H, H-4b), 5.19 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 7.26-7.33 (m, 3H, phenyl-H), 7.42 (s, 1H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.59 (-CH_3), 24.32 (-CH_3), 44.00 (C-4), 73.71 (C-5), 81.59 (C-2), 124.12 (phenyl-C), 126.09 (phenyl-C), 128.31 (phenyl-C), 129.98 (phenyl-C), 134.64 (phenyl-C), 142.79 (phenyl-C), 216.53 (O=C). MS (EI), *m/z* (%) 224.1 (M^+, 2), 138.0 (100).

5-(4-Chlorophenyl)-2,2-dimethyl-dihydrofuran-3(2*H*)-one (2g). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H, -CH_3), 1.40 (s, 3H, -CH_3), 2.49 (dd, *J* = 10 Hz; *J* = 18 Hz, 1H, H-4a), 2.87 (dd, *J* = 6 Hz; *J* = 18 Hz, 1H, H-4b), 5.19 (dd, *J* = 10 Hz; *J* = 6 Hz, 1H, -CH), 7.33-7.37 (m, 4H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.71 (-CH_3), 24.46 (-CH_3), 44.19 (C-4), 73.86 (C-5), 81.67 (C-2), 127.49 (phenyl-C), 128.97 (phenyl-C), 134.02 (phenyl-C), 139.33 (phenyl-C), 216.84 (O=C). MS (EI), *m/z* (%) 224.1 (M^+, 2), 138.0 (100).

5-(4-Methoxyphenyl)-2,2-dimethyl-dihydrofuran-3(2*H*)-one (2h). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 2.56 (dd, *J* = 10.5 Hz; *J* = 18 Hz, 1H, H-4a), 2.83 (dd, *J* = 6 Hz; *J* = 18 Hz, 1H, H-4b), 3.81 (s, 3H, -OCH_3), 5.16 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 6.90-6.93 (m, 2H, phenyl-H), 7.33-7.35 (m, 2H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.59 (-CH_3), 24.42 (-CH_3), 44.13 (C-4), 55.34 (-OCH_3), 74.17 (C-5), 81.39 (C-2), 114.06 (phenyl-C), 127.47 (phenyl-C), 132.49 (phenyl-C), 159.58 (phenyl-C), 217.56 (O=C). MS (EI), *m/z* (%) 220.0 (M^+, 3), 133.8 (100).

2,2-Dimethyl-5-(4-nitrophenyl)-dihydrofuran-3(2*H*)-one (2i). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3H, -CH_3), 1.43 (s, 3H, -CH_3), 2.49 (dd, *J* = 10.5 Hz; *J* = 18 Hz, 1H, H-4a), 2.97 (dd, *J* = 6 Hz; *J* = 18 Hz, 1H, H-4b), 5.33 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 7.58-7.61 (m, 2H, phenyl-H),

8.24-8.27 (m, 2H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.61 (-CH_3), 24.28 (-CH_3), 43.78 (C-4), 73.34 (C-5), 81.79 (C-2), 123.96 (phenyl-C), 126.62 (phenyl-C), 147.65 (phenyl-C), 148.16 (phenyl-C), 215.58 (O=C). MS (EI), *m/z* (%) 235.1 (M^+, 1), 149.0 (100). HRMS Calcd. for $C_{12}H_{13}NO_2$ 235.0845, found 235.0851.

2,2-Dimethyl-5-(naphthalen-2-yl)-dihydrofuran-3(2*H*)-one (2j). Yellow solid, mp 63-64 ^oC. ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 3H, -CH_3), 1.46 (s, 3H, -CH_3), 2.66 (dd, *J* = 10.5 Hz; *J* = 18.5 Hz, 1H, H-4a), 2.95 (dd, *J* = 6 Hz; *J* = 18 Hz, 1H, H-4b), 5.39 (dd, *J* = 10.5 Hz; *J* = 6 Hz, 1H, -CH), 7.47-7.52 (m, 3H, phenyl-H), 7.84-8.89 (m, 4H, phenyl-H). ^{13}C NMR ($CDCl_3$) δ 21.73 (-CH_3), 24.44 (-CH_3), 44.11 (C-4), 74.56 (C-5), 81.55 (C-2), 123.68 (naphthyl-C), 125.03 (naphthyl-C), 126.19 (naphthyl-C), 126.38 (naphthyl-C), 127.76 (naphthyl-C), 128.00 (naphthyl-C), 128.68 (naphthyl-C), 133.22 (naphthyl-C), 137.97 (naphthyl-C), 217.18 (O=C). MS (EI), *m/z* (%) 240.0 (M^+, 5), 153.9 (100). HRMS Calcd. for $C_{16}H_{16}O_2$ 240.1150, found 240.1163.

5-(Furan-2-yl)-2,2-dimethyl-dihydrofuran-3(2*H*)-one (2k). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3H, -CH_3), 1.33 (s, 3H, -CH_3), 2.80 (dd, *J* = 7 Hz; *J* = 18 Hz, 1H, H-4a), 2.93 (dd, *J* = 9 Hz; *J* = 18 Hz, 1H, H-4b), 5.25 (dd, *J* = 9 Hz; *J* = 7 Hz, 1H, -CH), 6.37-6.40 (m, 2H, furyl-H), 7.44 (m, 1H, furyl-H). ^{13}C NMR ($CDCl_3$) δ 22.28 (-CH_3), 24.29 (-CH_3), 39.71 (C-4), 67.74 (C-5), 80.97 (C-2), 108.50 (furyl-C), 110.39 (furyl-C), 143.10 (furyl-C), 152.37 (furyl-C), 216.35 (O=C). MS (EI), *m/z* (%) 180.1 (M^+, 5), 94.0 (100). HRMS calcd. for $C_{10}H_{12}O_3$ 180.0786, found 180.0795.

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