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The Nazarov cyclization of β-carbonyl-β′-furyl-divinyl ketones and related compounds as induced by perchloric acid

A. Fernández Mateos,* E. M. Martín de la Nava and R. Rubio González

Departamento de Química Orgánica, Facultad de C. Químicas, Universidad de Salamanca, Plaza de los Caídos 1-5, 37008 Salamanca, Spain

In respectful memory of the late Professor J. de Pascual Teresa

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Abstract—Diluted solutions of perchloric acid and acetic anhydride are introduced as a new catalyst for cationic cyclizations. The influence of the strong acid concentration and the nature of the anhydride have been studied in four types of Nazarov substrates.

Over the past few years we have developed a procedure aimed at the synthesis of model limonoid insect antifeedants,[1] based on D ring construction by cationic electrocyclization, called the Nazarov reaction (Fig. 1).[2]

The approach reported by our group would gain further relevance if it could be successfully applied to the synthesis of bioactive limonoids such as those corresponding to the CDE structural fragments represented by **A** (anthotecol), **B** (amoorastatin), **C** (sendanin and trichilin), **D** (sendanal epoxide), one of whose most relevant characteristics are the oxygenated functions on the C-11/C-12 carbon atoms in the C ring, and also the oxirane ring between C-14 and C-15 in the D ring (Fig. 2).[3]

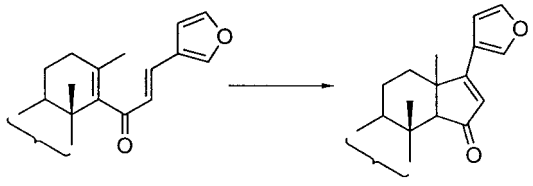

Figure 1.

These highly oxygenated limonoids show a wide range of biological activities, including insect antifeedant and inhibition of a type of lymphocytic leukemia. Moreover, limonoids with the structure represented by **D** are considered to be biosynthetic precursors of limonoids with the C-ring opened (C-*seco* limonoids), such as nimbolidin, salannin and azadirachtin, which are the most potent insect antifeedants of the limonoid family.[3] The above relevant characteristics make the group of limonoids represented by partial structures **A**–**D** an interesting target, although one for which to date no general method of synthesis has been developed.

In this work we describe our approach to the synthesis of the limonoid group represented in Fig. 1, based on the Nazarov reaction.

Electrocyclization studies were carried out with the divinyl ketone models **5a**, **6a** and **7a**. The aim of the cyclizations in

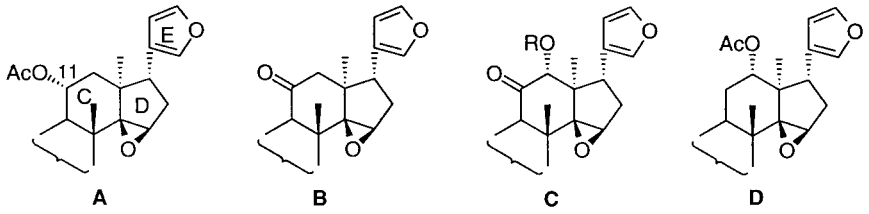

Figure 2.

Keywords: Nazarov reaction; perchloric acid; antifeedant; limonoids.
* Corresponding author. Fax: +923-294574; e-mail: afmateos@gugu.usal.es

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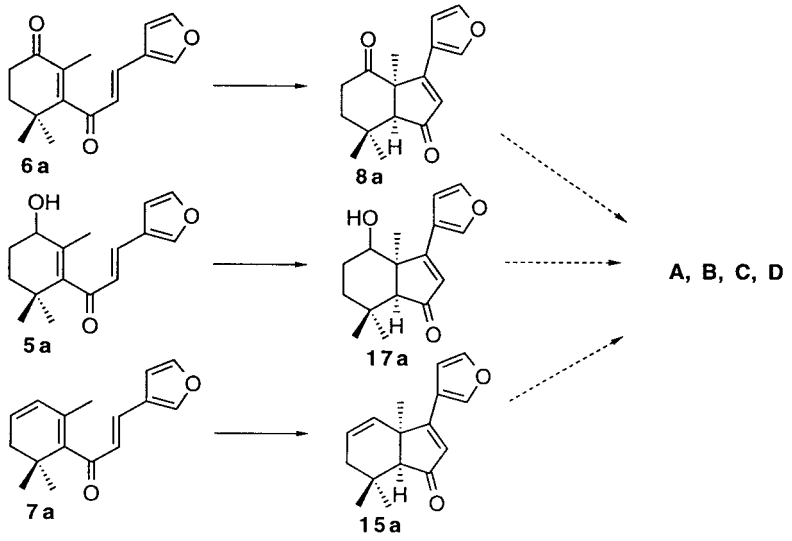


Scheme 1.

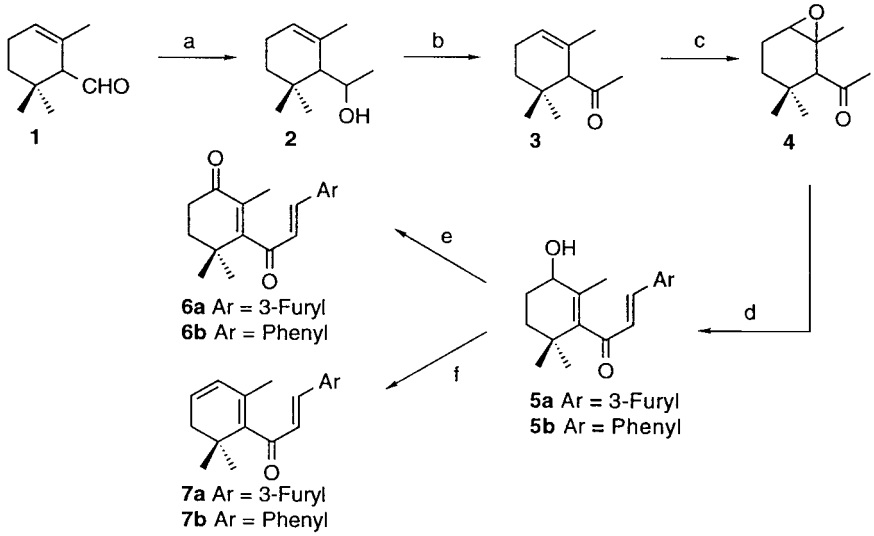
Scheme 1 was to obtain the indenones **8a**, **17a** and **15a**, which would be excellent intermediates in the synthesis of limonoid models with the functionalization shown by **A**, **B**, **C** and **D** (Fig. 2) through appropriate and selective reactions.

The Nazarov substrates were obtained from α-cyclocitral **1** by the procedure represented in Scheme 2.[4]

We have not found any reported examples of the Nazarov cyclization for the substrates represented by the structures **E** and **F** (Fig. 3). There are not many examples of the trienone model **G** cyclization, and in most of them the conjugated diene is part of an aromatic ring.[2]

Our first target was the cyclization of the diketones **6a** and **6b**. Cyclization of **6a** was tested with several protonic acids such as sulfuric, phosphoric, formic, methanesulfonic, *p*-toluensulfonic and mixtures of acids such as sulfuric/acetic, phosphoric/formic, methanesulfonic/phosphoric and a temperature range between 25 and 100°C, but without success. Only a complex mixture and starting material were recovered. At first sight we attributed the failure in cyclization to the extreme sensitivity of the furan ring of compound **6a** to acids, but with the phenyl analog **6b** we were also unable to obtain a cyclization product and only the starting material was recovered. Attempts with trimethylsilyl trifluoracetate also failed.[5] The same behaviour was found for **5a**, **5b**, **7a** and **7b**.

After all these unsuccessful experiments, we decided to introduce as a cyclization promoter a very strong acid, such as perchloric acid, which has been used successfully in the preparation of enol acetates from ketones.[6] We found that diluted solutions of perchloric acid in a mixture of acetic anhydride and ethyl acetate (10^{-3} or 10^{-2} M $HClO_4$/1 M Ac_2O/ethyl acetate) promoted the Nazarov cyclization of type **E** diketones at room temperature. Treatment of the diketone **6b** with the 10^{-3} M $HClO_4$ solution afforded the bicyclic ketone **9b** in 62% yield after 160 h at



Scheme 2. (a) MeLi, ether, −10°C, 90%; (b) PCC, CH_2Cl_2, 92%; (c) mCPBA, CH_2Cl_2, 86%; (d) NaOH, ArCHO, EtOH, 61% Ar=3-Furyl, 96% Ar=Phenyl; (e) PCC, CH_2Cl_2, 86% Ar=3-Furyl, 93% Ar=Phenyl; (f) HCO_2H, 70°C, 48% Ar=3-Furyl, 78% Ar=Phenyl.

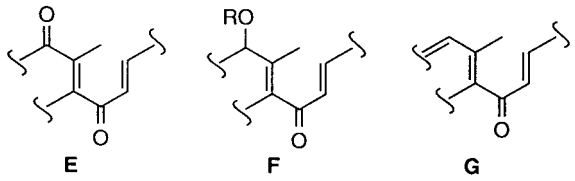


Figure 3.

room temperature, while most of the starting material was recovered (Table 1). A 10^{-2} M $HClO_4$ solution afforded **9b** in 75% yield in only 9 h at room temperature with total consumption of diketone **6b**.

The reaction of **6a** with the 10^{-3} M $HClO_4$ solution was very slow (Table 2). These kinetics afforded sufficient time for degradation of the furane. Furan acylation also occurred. A more complicated reaction took place with the diketone **6a** and the 10^{-2} M $HClO_4$ solution. After 24 h at room temperature, a mixture of five products in 53% yield was obtained.

The more nucleophilic character of the furan ring in **6a** as compared to the phenyl ring in **6b** is responsible for the difference in the behaviour of both compounds; the acylation competes with the electrocyclization in **6a** and does not occur in **6b**. Another interesting observation was that enol acetylation only occurred in cyclized products. We did not find enol acetates from compounds **6a**, **6b**, **10** or **12**. This could mean that these enol acetates are transient intermediates that cyclize immediately. The acylated diketones **10** and **12** are less prone to cyclization than the non-acylated **6a**. Thus, treatment of **10** or **12** with the 10^{-2} M perchloric acid solution afforded 50% conversion in **11** or **13** after 65 h at room temperature.

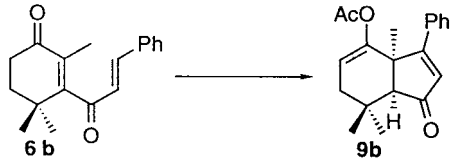
To avoid the undesired acylation of furan in the cyclization of **6a** we tried a more diluted solution in acetic anhydride (10^{-2} M $HClO_4$/0.5 M Ac_2O/ethyl acetate). However, under these conditions conversion was very low (30% after 26 h) and the products consisted of a 1:1 mixture of **9a** and **10**. A more concentrated solution in perchloric acid and diluted in acetic anhydride (10^{-1} M $HClO_4$/0.5 M Ac_2O/ethyl acetate) did not induce the cyclization of **6a** at all after 17 h.

To determine the influence of the anhydride component in the cyclization we replaced the acetic anhydride by propionic, isobutyric and pivalic anhydride. The aim of these changes was also to suppress furan acylation by increasing steric hindrance around the anhydride carbonyl group. In all three cases the concentration of perchloric solution was 10^{-2} M $HClO_4$, 1 M anhydride. No new results were obtained with propionic anhydride with respect to acetic anhydride. For the isobutyric anhydride solution the major product was that corresponding to **9a**, although a minor furan acylated product corresponding to **13** was detected by NMR analysis. With the pivalic anhydride solution a short study was carried out by tuning the concentration of the acid and the anhydride (Table 3). Fortunately, to our interest no furan acylated products were found. An increase in the concentration of the anhydride caused a decrease in the reaction time, but did not improve the yield. For 1 M anhydride solutions, the one most concentrated in perchloric acid, gave better yields in cyclization products and a lower proportion of enolic esters.

Our next targets were the hydroxy ketones **5a** and **5b**. Treatment of the furyl derivative **5a** with 10^{-2} and 10^{-3} M perchloric acid and 1 M acetic anhydride solutions afforded a Nazarov cyclization product **15a**, but in dehydrated form (Table 4). The yield of **15a** increased with the reaction time, while that of the acetylated product **16a** decreased.

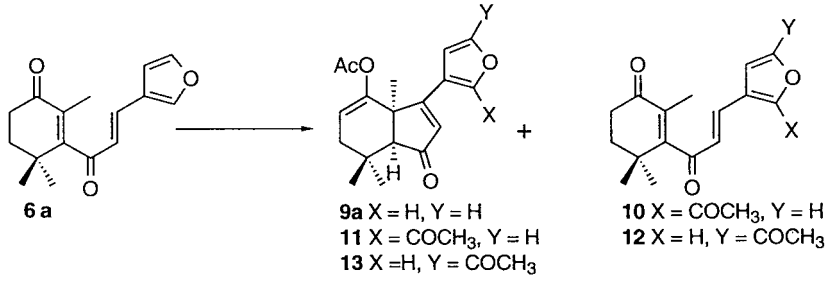
This relationship could be interpreted in terms of acetate **16a** being the precursor of **15a**. Treatment of **16a** with a

Table 1.



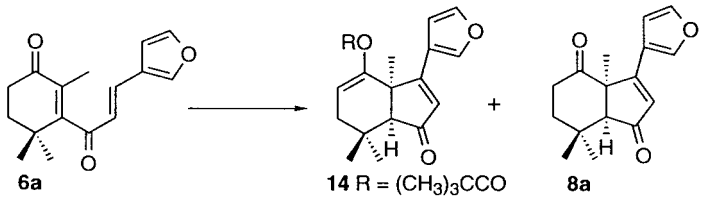
$HClO_4$ (M)	Time (h)	Conversion (%)	Yield (%)
10^{-3}	160	22	62
10^{-2}	9	100	75

Table 2.



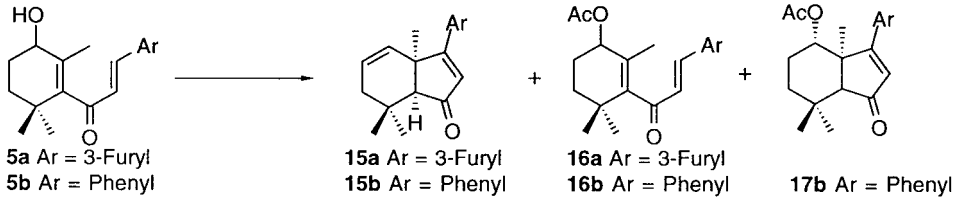
$HClO_4$ (M)	Time (h)	Yield (%)				
		9a	**10**	**11**	**12**	**13**
10^{-3}	48	–	6	–	6	6
10^{-2}	24	13	9	6	7	18

Table 3.



$HClO_4$ (M)	$(CH_3)_3CCO)_2O$ (M)	Time (h)	Conversion (%)	**14** (%)	**8a** (%)
10^{-2}	0.5	20	70	54	11
10^{-2}	1	15	94	57	5
10^{-2}	2	9	100	53	–
10^{-1}	0.5	46	30	27	28
10^{-1}	1	16	100	24	35

Table 4.



Substrate	$HClO_4$ (M)	Time	Yield (%)		
			15a/b	**16a/b**	**17b**
5a	10^{-3}	1 h	14	36	–
5a	10^{-3}	2 h 30 min	26	10	–
5a	10^{-3}	6 h 30 min	32	7	–
5a	10^{-2}	30 min	45	11	–
5a	10^{-2}	1 h	42	3	–
5b	10^{-3}	30 h	43	13	5
5b	10^{-2}	45 min	64	–	16

10^{-2} M perchloric acid solution gave the ketone **15a** quantitatively in 1 h 30 min. The time required for cyclization was longer for the acetate **16a** than for alcohols **5a** and **5b**, implying the existence of other intermediates that would be the dehydration products arising from the alcohols **5a** and **5b**, i.e. the trienones **7a** and **7b**, respectively. Our suspicion was confirmed when we observed that the trienones **7a** and **7b** instantaneously gave cyclization with 10^{-2} M $HClO_4$ reagent to afford **15a** and **15b** in quantitative yield (Schemes 1 and 3).

This result is in agreement with the absence of enol acetates of compounds **6a**, **6b**, **10** or **12** among the products from the treatment of diketones **6a** and **6b** with perchloric acid. In other words, compounds of the **G** type (Fig. 3) are excellent

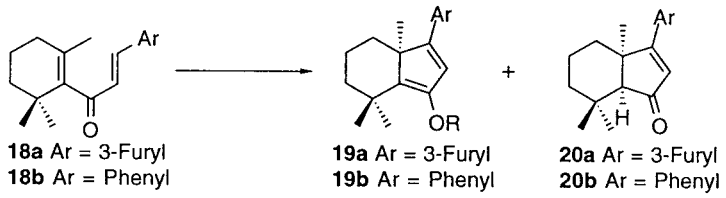
Scheme 3.

substrates for the Nazarov reaction if diluted solutions of perchloric acid are used as the catalyst. We also observed that the presence of an anhydride of the type shown before is absolutely essential for the success of the cyclization. Phthalic anhydride does not work at all.

After these experiments, we were interested in comparing the catalytic power of the perchloric acid solutions with the classic acids employed in the Nazarov reaction. The selected substrate employed was the divinyl ketone **18a**. As described, cyclization of this ketone with a formic/phosphoric acid mixture required 1/2 h at 70°C (70% yield).[2] With the 10^{-2} M perchloric acid solution, the reaction was instantaneous at room temperature, affording a 7:3 mixture of the enone **20a** and the enol acetate **19a** in 70% yield (Table 5). Substitution of 3-furyl group by the phenyl group afforded similar results.

We carried out three experiments with **18b** and a solution of 10^{-2} M $HClO_4$, 1 M anhydride in ethyl acetate. For propionic and isobutyric anhydride the result was identical to that obtained for acetic anhydride. For pivalic anhydride the product was exclusively the enone **20b**. A qualitatively similar result was obtained with a solution of 10^{-1} M $HClO_4$, 0.5 M acetic anhydride.

Table 5.



Substrate	$HClO_4$ (M)	Anhydride	Yield (%)	
			19a/b	**20a/b**
18a	10^{-2}	1 M acetic	21 (R=Ac)	49
18b	10^{-2}	1 M acetic	32 (R=Ac)	54
18b	10^{-2}	1 M propionic	17 (R=Prop)	66
18b	10^{-2}	1 M isobutyric	16 (R=^{i}But)	70
18b	10^{-2}	1 M pivalic	–	83
18b	10^{-1}	0.5 M acetic	–	85

1. Experimental

1.1. General methods

Commercial reagents were used as received. Dichloromethane was distilled under argon over calcium hydride. Diethyl ether was distilled under argon from sodium. Hexane, ethyl acetate and ethanol were distilled before use. Melting points were determined with a Büchi 500 apparatus and are not corrected. IR spectra were obtained on a Bomem FT MB-100 as thin films. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker WP 200 SY (200 and 50 MHz, respectively) or on a Bruker Advance DRX 400 (400 and 100 MHz, respectively). Mass spectra were obtained on a Shimadzu 17A GC/QP 5000 MS at 70 eV (EI). High-resolution mass spectra were measured on a VG-TS 250 at 70 eV (EI). Elemental analyses were obtained on a LECO CHNS-932 instrument. All reactions were carried out under argon atmosphere in glassware dried overnight and cooled under argon. Reactions were monitored by TLC. Flash column chromatographies were carried out using silica gel 60 (0.040–0.063 mm Merck). Organic extracts were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure with the aid of a rotary evaporator.

1.1.1. Solution of 10^{-3} M $HClO_4$/1 M acetic anhydride (50 mL). To 50 mL of absolute ethyl acetate was added 0.05 ml of 72% perchloric acid (0.58 mmol). Then 5 mL of this solution was added to 30 mL of absolute ethyl acetate and 4.8 mL (51 mmol) of acetic anhydride. The solution was filled up to 50 mL with ethyl acetate.

1.1.2. Solution of 10^{-2} M $HClO_4$/1 M acetic anhydride (50 mL). To 40 mL of absolute ethyl acetate was added 0.05 mL of 72% perchloric acid (0.58 mmol) and 4.8 mL (51 mmol) of acetic anhydride. The solution was filled up to 50 mL with ethyl acetate.

1.1.3. Solution of 10^{-1} M $HClO_4$/1 M pivalic anhydride (50 mL). To 30 mL of absolute ethyl acetate was added 0.5 mL of 72% perchloric acid (5.8 mmol) and 10 mL (49 mmol) of pivalic anhydride. The solution was filled up to 50 mL with ethyl acetate.

1.1.4. 1-(2,6,6-Trimethyl-cyclohex-2-enyl)-ethan-1-ol (2). To a stirred solution of α-cyclocitral (4.30 g, 28.3 mmol) in diethyl ether (138 mL) at −10°C under argon, was added a solution of MeLi 1.6 M in diethyl ether (17.7 mL, 28.3 mmol). The reaction mixture was stirred at −10°C for 10 min, then warmed to 0°C and saturated NH_4Cl was added. The organic layer was separated and the aqueous phase was extracted with diethyl ether. The combined organic extracts were washed with brine and then dried. Distillation of the solvent with a Vigreux column afforded an epimeric mixture of alcohols **2** as an orange oil, which was purified by flash chromatography. The major alcohol (95/5 hexane/diethyl ether) was obtained as a colourless oil (3.04 g, 18.1 mmol, 64%): IR ν 3430, 2928 cm^{-1}, ^{1}H NMR δ 0.85 (3H, s), 0.97 (3H, s), 1.28 (3H, d, J=6.6 Hz), 1.80 (3H, s), 4.00 (1H, m), 5.65 (1H, m) ppm; ^{13}C NMR δ 23.3, 25.7, 27.6, 28.1, 28.5, 30.5, 32.5, 56.6, 65.6, 125.0, 132.1 ppm; MS *m/z* (relative intensity) 168 (M^+, 20), 153 (24), 150 (29), 135 (99), 123 (57), 107 (92), 103 (100), 79 (84), 67 (63), 55 (89). The minor alcohol (90/10 hexane/diethyl ether) was obtained as a colourless oil (1.24 g, 7.36 mmol, 26%): IR ν 3430, 2928 cm^{-1}, ^{1}H NMR δ 0.87 (3H, s), 0.99 (3H, s), 1.14 (3H, d, J=6.5 Hz), 1.80 (3H, s), 4.11 (1H, m), 5.48 (1H, m) ppm; ^{13}C NMR δ 21.4, 22.9, 25.8, 28.6 (2C), 31.3, 32.0, 56.5, 68.6, 122.5, 133.2 ppm.

1.1.5. 1-(2,6,6-Trimethyl-cyclohex-2-enyl)-ethanone (3).[7] To a stirred suspension of pyridinium chlorochromate (8.11 g, 37.6 mmol) and silica (8.11 g) in CH_2Cl_2 (198 mL), was added dropwise a solution of alcohols **2** (4.20 g, 25.0 mmol) in CH_2Cl_2 (51 mL). The reaction mixture was vigorously stirred at room temperature under argon atmosphere for 2 h. The resulting dark brown slurry was filtered through a short column of silica and eluted with CH_2Cl_2. Removal of the solvent with a Vigreux column afforded **3** (3.82 g, 23.0 mmol, 92%) as a pale yellow oil: IR ν 2922, 1711 cm^{-1}; ^{1}H NMR δ 0.89 (3H, s), 0.90 (3H, s), 1.15 (1H, m), 1.56 (3H, s), 1.70 (1H, m), 2.07 (2H, m), 2.15 (3H, s), 2.71 (1H, s), 5.56 (1H, s) ppm; ^{13}C NMR δ 22.5,

23.0, 27.5, 27.7, 30.9, 31.7, 31.9, 64.4, 123.3, 130.2, 210.9 ppm; MS *m/z* (relative intensity) 166 (M^+, 31), 123 (94), 109 (19), 91 (39), 81 (100), 67 (32), 53 (28).

1.1.6. 1-(1,3,3-Trimethyl-7-oxa-bicyclo[4.1.0]hept-2-yl)-ethanone (4). To a stirred solution of ketone **3** (3.70 g, 22.3 mmol) in CH_2Cl_2 (136 mL) was added *m*-chloroperbenzoic acid (3.85 g, 22.3 mmol). The reaction mixture was stirred under argon atmosphere at room temperature for 1 h. A solution of Na_2SO_3 (5%) was added and the resulting heterogeneous mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried. Removal of the solvent under reduced pressure afforded **4** (3.49 g, 19.2 mmol, 86%) as a colourless oil: IR ν 2963, 1719 cm^{-1}; ^1H NMR δ 0.89 (3H, s), 0.90 (3H, s), 1.02 (1H, m), 1.35 (3H, s), 1.70 (1H, m), 1.95 (2H, m), 2.26 (3H, s), 2.47 (1H, s), 2.99 (1H, m) ppm; ^{13}C NMR δ 21.4, 24.5, 25.7, 29.1, 29.9, 30.8, 31.2, 56.2, 58.5, 61.9, 207.6 ppm; MS *m/z* (relative intensity) 182 (0.41, M^+), 167 (0.85), 111 (29), 107 (100), 91 (30), 84 (56), 69 (59), 55 (76).

1.2. Condensation of 4 with 3-furaldehyde and benzaldehyde

1.2.1. General procedure. To a stirred solution of epoxide ketone **4** (1.82 g, 10.0 mmol) in EtOH (45 mL) were added gradually the aldehyde (10.0 mmol) and NaOH (800 mg, 20.0 mmol). The reaction mixture was stirred at room temperature under argon atmosphere for 12 h and then concentrated under vacuo to afford a residue, which was dissolved in water and extracted with diethyl ether. The combined organic extracts were washed with brine and then dried. Removal of the solvent under reduced pressure afforded the hydroxy ketone, which was purified by flash chromatography (65/35 hexane/ethyl acetate).

1.2.2. (*E*)-3-(Furan-3-yl)-1-(3-hydroxy-2,6,6-trimethylcyclohex-1-enyl)-prop-2-en-1-one (5a). According to the general procedure, reaction of **4** (2.40 g, 13.2 mmol) with 3-furaldehyde (1.14 mL, 1.27 g, 13.2 mmol) afforded **5a** (2.09 g, 8.05 mmol, 61%) as a pale yellow solid: mp 70–72°C; IR ν 3404, 2926, 1626 cm^{-1}; ^1H NMR δ 1.05 (6H, s), 1.45 (1H, m), 1.60–1.85 (2H, m), 1.66 (3H, s), 1.97 (1H, m), 4.02 (1H, t, J=4.8 Hz), 6.47 (1H, d, J=16 Hz), 6.61 (1H, m), 7.34 (1H, d, J=16 Hz), 7.43 (1H, m), 7.69 (1H, s) ppm; ^{13}C NMR δ 17.8, 27.7, 28.7 (2C), 34.1, 34.7, 68.9, 107.5, 123.0, 128.4, 131.4, 135.5, 143.6, 144.5, 145.1, 200.6 ppm; MS *m/z* (relative intensity) 260 (M^+, 17), 245 (14), 242 (11), 139 (43), 121 (100), 93 (48), 67 (18), 65 (80), 55 (33). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.8; H, 7.7. Found: C, 73.7; H, 7.8.

1.2.3. *E*-1-(3-Hydroxy-2,6,6-trimethylcyclohex-1-enyl)-3-phenylprop-2-en-1-one (5b). According to the general procedure, reaction of **4** (1.00 g, 5.49 mmol) with benzaldehyde (0.55 mL, 0.58 g, 5.5 mmol) afforded **5b** (1.42 g, 5.27 mmol, 96%) as a white solid: mp 94–96°C; IR ν 3412, 2936, 1624, 760 cm^{-1}; ^1H NMR δ 1.09 (6H, s), 1.49 (1H, m), 1.70 (3H, s), 1.70–1.90 (2H, m), 2.00 (1H, m), 4.05 (1H, t, J=5.4 Hz), 6.76 (1H, d, J=16 Hz), 7.47 (1H, d, J=16 Hz), 7.37–7.60 (5H, m) ppm; ^{13}C NMR δ 17.7, 27.6, 28.5, 28.6, 34.0, 34.7, 66.6, 128.1, 128.2 (2C), 128.7 (2C), 130.4, 131.5, 134.5, 143.4, 145.4, 200.7 ppm; MS *m/z* (relative intensity) 270 (M^+, 7), 252 (8), 237 (4), 139 (42), 131 (91), 103 (82), 77 (100), 55 (25). Anal. Calcd for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2. Found: C, 79.7; H, 8.2.

1.3. Oxidation of 5a and 5b

1.3.1. General procedure. To a stirred suspension of pyridinium chlorochromate (1.62 g, 7.50 mmol) and silica (1.62 g) in CH_2Cl_2 (40 mL) was added dropwise a solution of the hydroxy ketone (5.00 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was vigorously stirred at room temperature under argon atmosphere for 1 h. The resulting dark brown slurry was filtered through a short column of silica and eluted with CH_2Cl_2. Removal of the solvent under reduced pressure afforded the diketone.

1.3.2. *E*-3-(3-Furan-3-yl-acryloyl)-2,4,4-trimethylcyclohex-2-enone (6a). According to the general procedure, reaction of **5a** (1.30 g, 5.00 mmol) afforded **6a** (1.11 g, 4.3 mmol, 86%) as a colourless solid: mp 112–114°C; IR ν 2924, 1669, 1620 cm^{-1}; ^1H NMR δ 1.22 (6H, s), 1.66 (3H, s), 1.96 (2H, t, J=6.6 Hz), 2.60 (2H, t, J=6.6 Hz), 6.48 (1H, d, J=16 Hz), 6.63 (1H, m), 7.29 (1H, d, J=16 Hz), 7.49 (1H, m), 7.72 (1H, s) ppm; ^{13}C NMR δ 12.9, 27.3 (2C), 34.2, 34.8, 38.1, 107.4, 122.8, 127.0, 129.6, 138.5, 144.8, 145.5, 160.7, 197.2, 198.6 ppm; MS *m/z* (relative intensity) 258 (M^+, 37), 243 (6), 121 (100), 93 (29), 67 (14), 65 (50), 55(19). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.4; H, 7.0. Found: C, 74.4; H, 7.0.

1.3.3. *E*-2,4,4-Trimethyl-3-(3-phenyl-acryloyl)-cyclohex-2-enone (6b). According to the general procedure, reaction of **5b** (500 mg, 1.85 mmol) afforded **6b** (461 mg, 1.72 mmol, 93%) as a colourless solid: mp 94–96°C; IR ν 2930, 1678, 760, 700 cm^{-1}; ^1H NMR δ 1.23 (6H, s), 1.68 (3H, s), 1.98 (2H, t, J=6.8 Hz), 2.62 (2H, t, J=6.8 Hz), 6.78 (1H, d, J=16 Hz), 7.38 (1H, d, J=16 Hz), 7.40–7.60 (5H, m) ppm; ^{13}C NMR δ 13.0, 27.3 (2C), 34.2, 34.8, 38.0, 126.9, 128.6 (2C), 129.0 (2C), 129.5, 131.1, 134.2, 146.7, 160.7, 197.4, 198.3 ppm; MS *m/z* (relative intensity) 268 (M^+, 25), 253 (6), 131 (100), 103 (45), 91 (19), 77 (43), 67 (15), 55 (15). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found: C, 80.5; H, 7.5.

1.4. Dehydratation of 5a and 5b

1.4.1. General procedure. To a solution of the hydroxy divinyl ketone (0.50 mmol) in toluene (0.5 mL) was added 90% HCO_2H (0.25 mL). The reaction mixture was stirred at 70°C under argon atmosphere for 3 h. After cooling to room temperature the mixture was poured onto water and extracted with diethyl ether. The combined organic extracts were washed with NaOH (2%), brine and then dried. Removal of the solvent under reduced pressure followed by flash chromatography (90/10 hexane/diethyl ether) afforded the trienone.

1.4.2. *E*-3-(3-Furyl)-1-(2,6,6-trimethylcyclohex-1,3-dienyl)-prop-2-en-1-one (7a). According to the general procedure, reaction of **5a** (110 mg, 0.42 mmol) afforded **7a** (49 mg, 0.20 mmol, 48%) as a yellow oil: IR ν 2964, 1627 cm^{-1}; ^1H NMR δ 1.07 (6H, s), 1.67 (3H, s), 2.14 (2H, d,

J=3.0 Hz), 5.85 (2H, m), 6.51 (1H, d, J=16 Hz), 6.62 (1H, m), 7.40 (1H, d, J=16 Hz), 7.45 (1H, m), 7.68 (1H, m) ppm.

1.4.3. *E*-3-Phenyl-1-(2,6,6-trimethylcyclohex-1,3-dienyl)-prop-2-en-1-one (7b). According to the general procedure, reaction of **5b** (104 mg, 0.38 mmol) afforded **7b** (75 mg, 0.30 mmol, 78%) as a yellow oil: IR ν 2959, 1630, 782, 691 cm^{-1}; ^1H NMR δ 1.10 (6H, s), 1.71 (3H, s), 2.18 (2H, d, J=3.0 Hz), 5.88 (2H, m), 6.81 (1H, d, J=16 Hz), 7.45 (1H, d, J=16 Hz), 7.40–7.60 (5H, m) ppm.

1.5. Nazarov cyclizations with $HClO_4$/anhydride/ethyl acetate

1.5.1. General procedure. The substrate (1.00 g) was dissolved in 100 mL of $HClO_4$/anhydride/ethyl acetate reagent. The solution was allowed to stand at room temperature under argon atmosphere. Saturated $NaHCO_3$ was added to quench the reaction. The organic layer was separated and the aqueous phase was extracted with diethyl ether. The combined organic extracts were washed with Na_2CO_3 (5%), with brine and then dried. Removal of the solvent under reduced pressure afforded a residue, which was purified by flash chromatography.

1.5.2. Reaction of 6b with 10^{-2} M $HClO_4$/1 M acetic anhydride. According to the general procedure, reaction of **6b** (100 mg, 0.37 mmol) after 9 h, followed by flash chromatography (90/10 hexane/ethyl acetate) afforded acetic acid *(3aRS,7aSR)-3a,7,7-trimethyl-1-oxo-3-phenyl-3a,6,7,7a-tetrahydro-1H-inden-4-yl ester* ***9b*** (87 mg, 0.28 mmol, 75%) as a colourless solid: mp 66–68°C; IR ν 2959, 1761, 1697, 700 cm^{-1}; ^1H NMR δ 1.01 (3H, s), 1.20 (3H, s), 1.43 (3H, s), 1.56 (3H, s), 1.93 (1H, dd, J_1=4.0 Hz, J_2=17 Hz), 2.09 (1H, dd, J_1=5.6 Hz, J_2=17 Hz), 2.25 (1H, s), 5.35 (1H, dd, J_1=4.0 Hz, J_2=5.6 Hz), 5.88 (1H, s), 7.20–7.33 (5H, m) ppm; ^{13}C NMR δ 20.1, 24.3, 27.4, 28.6, 34.1, 38.2, 50.4, 65.3, 114.8, 127.1 (2C), 127.7 (2C), 128.0, 131.9, 136.7, 146.6, 166.3, 178.1, 207.2 ppm; MS *m/z* (relative intensity) 310 (M^+, 8), 267 (12), 250 (21), 172 (100), 77 (16), 55 (46). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.4; H, 7.1. Found: C, 77.2; H, 7.2.

1.5.3. Reaction of 6a with 10^{-2} M $HClO_4$/1 M acetic anhydride. According to the general procedure, reaction of **6a** (210 mg, 0.81 mmol) after 24 h afforded a crude, which was purified by flash chromatography. 80/20 Hexane/ethyl acetate afforded acetic acid *(3aRS,7aSR)-3-furan-3-yl-3a,7,7-trimethyl-1-oxo-3a,6,7,7a-tetrahydro-1H-inden-4-yl ester* ***9a*** (33 mg, 0.11 mmol, 13%) as a yellow oil: IR ν 2928, 1763, 1692, 756 cm^{-1}; ^1H NMR δ 1.18 (3H, s), 1.25 (3H, s), 1.55 (3H, s), 2.01 (3H, s), 2.05 (2H, m), 2.25 (1H, s), 5.39 (1H, t, J=5.0 Hz), 6.11 (1H, s), 6.58 (1H, m), 7.45 (1H, m), 7.82 (1H, s) ppm; ^{13}C NMR δ 20.9, 25.4, 25.7, 29.3, 34.8, 37.2, 50.2, 65.7, 110.7, 116.2, 120.7, 129.6, 142.6, 143.1, 147.7, 168.6, 168.9, 206.6 ppm; MS *m/z* (relative intensity) 300 (M^+, 12), 257 (37), 174 (40), 162 (100), 91 (17), 55 (55). 75/25 hexane/ethyl acetate afforded *E-3-[3-(2-acetyl-furan-3-yl)-acryloyl]-2,4,4-trimethyl-cyclohex-2-enone* ***10*** (21 mg, 0.073 mmol, 9%) as a pale yellow solid: mp 174–176°C; IR ν 2924, 1669, 1642 cm^{-1}; ^1H NMR δ 1.24 (6H, s), 1.64 (3H, s), 2.01 (2H, t, J=7.0 Hz), 2.52 (3H, s), 2.61 (2H, t, J=7.0 Hz), 6.60 (1H, d, J=17 Hz), 6.77 (1H, d, J=2.0 Hz), 7.51 (1H, d, J=2.0 Hz), 8.09 (1H, d, J=17 Hz) ppm; ^{13}C NMR δ 13.0, 26.9, 27.3 (2C), 34.2, 34.8, 38.0, 110.2, 127.1, 130.1, 131.6, 137.6, 145.1, 149.8, 160.0, 188.9, 198.2 (2C) ppm; MS *m/z* (relative intensity) 300 (M^+, 2), 258 (4), 243 (3), 135 (100), 121 (33), 177 (15), 55 (14). Anal. Calcd for $C_{18}H_{20}O_4$: C, 72.0; H, 6.7. Found: C, 71.7; H, 6.8. 70/30 hexane/ethyl acetate afforded acetic acid *(3aRS,7aSR)-3-(2-acetyl-furan-3-yl)-3a,7,7-trimethyl-1-oxo-3a,6,7,7a-tetrahydro-1H-inden-4-yl ester* ***11*** (17 mg, 0.049 mmol, 6%) as a white solid: mp 82–84°C; IR ν 2922, 1759, 1703 cm^{-1}; ^1H NMR δ 1.17 (3H, s), 1.26 (3H, s), 1.43 (3H, s), 1.77 (3H, s), 2.04 (1H, dd, J_1=5.1 Hz, J_2=17 Hz), 2.12 (1H, dd, J_1=4.0 Hz, J_2=17 Hz), 2.31 (1H, s), 2.48 (3H, s), 5.41 (1H, dd, J_1=4.0 Hz, J_2=5.1 Hz), 6.03 (1H, s), 6.53 (1H, d, J=2.0 Hz), 7.55 (1H, d, J=2.0 Hz) ppm; ^{13}C NMR δ 20.6, 24.6, 26.5, 27.0, 29.1, 34.5, 38.1, 51.1, 64.8, 114.2, 115.1, 126.3, 133.7, 143.9, 146.9, 147.9, 168.5, 168.7, 187.1, 207.2 ppm; MS *m/z* (relative intensity) 342 (M^+, 4), 300 (14), 282 (15), 257 (100), 216 (43), 201 (45), 162 (46), 77 (26), 55 (82). Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.2; H, 6.5. Found: C, 70.2; H, 6.4. 60/40 hexane/ethyl acetate afforded a mixture of two products. The first one was identified as *E-3-[3-(5-acetyl-furan-3-yl)-acryloyl]-2,4,4-trimethyl-cyclohex-2-enone* ***12*** (17 mg, 0.057 mmol, 7%): ^1H NMR δ 1.19 (6H, s), 1.62 (3H, s), 1.95 (2H, t, J=7.0 Hz), 2.47 (3H, s), 2.60 (2H, t, J=7.0 Hz), 6.55 (1H, d, J=16 Hz), 7.25 (1H, d, J=16 Hz), 7.35 (1H, s), 7.85 (1H, s) ppm. The second product was identified as acetic acid *(3aRS,7aSR)-3-(5-acetyl-furan-3-yl)-3a,7,7-trimethyl-1-oxo-3a,6,7,7a-tetrahydro-1H-inden-4-yl ester* ***13*** (51 mg, 0.15 mmol, 18%): IR ν 2932, 1761, 1688, 1609, 756 cm^{-1}; ^1H NMR δ 1.17 (3H, s), 1.26 (3H, s), 1.55 (3H, s), 1.98 (2H, m), 2.03 (3H, s), 2.05 (2H, m), 2.28 (1H, s), 2.50 (3H, s), 5.41 (1H, t, J=5.0 Hz), 6.19 (1H, s), 7.35 (1H, m), 7.91 (1H, m) ppm; ^{13}C NMR δ 21.0, 25.6, 26.0 (2C), 29.2, 34.8, 37.3, 50.2, 65.7, 116.6 (2C), 122.9, 130.6, 145.0, 147.2, 153.2, 166.8, 168.8, 186.5, 206.2 ppm; MS *m/z* (relative intensity) 342 (M^+, 2), 300 (7), 282 (15), 257 (49), 201 (30), 162 (38), 77 (32), 55 (100); HRMS 342.1473 (M^+), Calcd for $C_{20}H_{22}O_5$ 342.1467.

1.5.4. Reaction of 6a with 10^{-1} M $HClO_4$/1 M pivalic anhydride. According to the general procedure, reaction of **6a** (97 mg, 0.38 mmol) after 16 h afforded a crude which was purified by flash chromatography. 93/7 hexane/diethyl ether afforded *2,2-dimethyl-propionic acid (3aRS,7aSR)-3-furan-3-yl-3a,7,7-trimethyl-1-oxo-3a,6,7,7a-tetrahydro-1H-inden-4-yl ester* ***14*** (31 mg, 0.091 mmol, 24%) as a colourless solid: mp 83–85°C, IR ν 2969, 1748, 1694, 735 cm^{-1}; ^1H NMR δ 1.17 (9H, s), 1.25 (3H, s), 1.27 (3H, s), 1.49 (3H, s), 1.98 (2H, m), 2.25 (1H, s), 5.31 (1H, dd, J_1=3.8, J_2=6.3 Hz), 6.10 (1H, s), 6.55 (1H, m), 7.44 (1H, m), 7.83 (1H, m) ppm; ^{13}C NMR δ 24.4, 26.7, 27.0 (3C), 29.5, 35.5, 36.6, 39.1, 50.8, 66.0, 110.7, 116.4, 120.6, 129.7, 141.9, 143.1, 148.5, 169.1, 177.6, 206.8 ppm; MS *m/z* (relative intensity) 342 (M^+, 2), 327 (2), 300 (2), 285 (2), 257 (30), 240 (40), 174 (100), 77 (24). Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.7; H, 7.6. Found: C, 73.7; H, 7.6. 90/10 hexane/diethyl ether afforded *(3aRS,7aSR)-3-furan-3-yl-3a,7,7-trimethyl-3a,6,7,7a-tetrahydro-5H-indene-1,4-dione* ***8a*** (33 mg, 0.13 mmol, 35%) as a colourless solid: mp 108–110°C; IR ν 2926, 1682, 1605, 1458 cm^{-1}; ^1H NMR δ 1.09 (3H, s), 1.15 (3H, s), 1.54 (3H, s), 1.65 (1H, m), 1.97 (1H, m), 2.27 (1H, s), 2.46 (1H, m), 2.53 (1H, m), 6.38 (1H, s),

6.57 (1H, m), 7.44 (1H, m), 7.80 (1H, m) ppm; ^{13}C NMR δ 25.2, 26.2, 28.5, 33.5, 34.5, 35.4, 58.7, 67.6, 109.5, 119.3, 129.1, 143.6, 144.3, 166.7, 206.8, 213.8 ppm; MS *m/z* (relative intensity) 258 (M^+, 12), 243 (2), 174 (100), 69 (52), 55 (34). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.4; H, 7.0. Found: C, 74.4; H, 7.0.

1.5.5. Reaction of 5a with 10^{-2} M $HClO_4$/1 M acetic anhydride. According to the general procedure, reaction of **5a** (95 mg, 0.37 mmol) after 30 min afforded a crude, which was purified by flash chromatography (90/10 hexane/ethyl acetate). The first fraction was a pale yellow solid identified as *(3aRS,7aSR)-3-furan-3-yl-3a,7,7-trimethyl-3a,6,7,7a-tetrahydro-inden-1-one* ***15a*** (41 mg, 0.17 mmol, 45%): mp 48–50°C; IR ν 2961, 1688 cm^{-1}; ^{1}H NMR δ 0.85 (3H, s), 1.22 (3H, s), 1.42 (3H, s), 1.80 (1H, m), 1.96 (1H, m), 2.14 (1H, s), 5.76 (1H, m), 5.99 (1H, m), 6.09 (1H, s), 6.59 (1H, m), 7.48 (1H, m), 7.83 (1H, s) ppm; ^{13}C NMR δ 24.0, 29.2, 30.6, 34.3, 39.1, 47.8, 64.1, 110.0, 119.7, 126.7 (2C), 129.6, 142.4, 143.7, 170.3, 208.8 ppm; MS *m/z* (relative intensity) 242 (M^+, 100), 227 (89), 199 (77), 174 (99), 115 (52), 91 (80), 77 (64), 65 (49), 63 (75), 55 (45). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5. Found: C, 79.4; H, 7.4. The second fraction was a pale yellow solid identified as acetic acid *3-(3-furan-3-yl-acryloyl)-2,4,4-trimethyl-cyclohex-2-enyl ester* ***16a*** (12 mg, 0.041 mmol, 11%): mp 112–114°C; IR ν 2969, 1730, 1626 cm^{-1}; ^{1}H NMR δ 1.08 (3H, s), 1.10 (3H, s), 1.49 (1H, m), 1.55 (3H, s), 1.60–1.90 (2H, m), 2.01 (1H, m), 2.10 (3H, s), 5.27 (1H, t, J=5.0 Hz), 6.48 (1H, d, J=16 Hz), 6.62 (1H, d, J=2.0 Hz), 7.33 (1H, d, J=16 Hz), 7.46 (1H, m), 7.71 (1H, s) ppm; ^{13}C NMR δ 17.2, 20.7, 25.0, 27.2, 28.1, 33.5, 34.5, 70.6, 107.2, 122.6, 127.6, 127.8, 135.1, 144.2, 144.9, 145.4, 170.2, 199.2 ppm; MS *m/z* (relative intensity) 302 (M^+, 7), 260 (22), 227 (23), 139 (19), 121 (100), 93 (32), 65 (45). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.5; H, 7.3. Found: C, 71.5; H, 7.3.

1.5.6. Reaction of 5b with 10^{-3} M $HClO_4$/1 M acetic anhydride. According to the general procedure, reaction of **5b** (135 mg, 0.50 mmol) after 30 h afforded a crude which was purified by flash chromatography. 90/10 hexane/ethyl acetate afforded *(3aRS,7aSR)-3a,7,7-trimethyl-3-phenyl-3a,6,7,7a-tetrahydro-inden-1-one* ***15b*** (53 mg, 0.21 mmol, 43%) as a white solid: mp 100–102°C; IR ν 2924, 1690, 700 cm^{-1}; ^{1}H NMR δ 0.87 (3H, s), 1.23 (3H, s), 1.40 (3H, s), 1.81 (1H, m), 1.99 (1H, m), 2.19 (1H, s), 5.75 (1H, m), 5.85 (1H, m), 6.03 (1H, s), 7.41 (5H, s) ppm; ^{13}C NMR δ 23.8, 28.9, 31.1, 34.1, 39.3, 48.2, 64.4, 126.0, 127.7 (2C), 128.4 (2C), 129.0, 129.2 (2C), 134.8, 180.1, 209.7 ppm; MS *m/z* (relative intensity) 252 (M^+, 32), 237 (43), 184 (52), 115 (49), 102 (55), 91 (100), 77 (82), 65 (51), 55 (51), 51 (68). Anal. Calcd for $C_{18}H_{20}O$: C, 85.7; H, 8.0. Found: C, 85.7; H, 8.0. 85/15 hexane/ethyl acetate afforded acetic acid *E-2,4,4-trimethyl-3-(3-phenyl-acryloyl)-cyclohex-2-enyl ester* ***16b*** (20 mg, 0.064 mmol, 13%) as a white solid: mp 116–118°C; IR ν 2924, 1738, 1630 cm^{-1}; ^{1}H NMR δ 1.09 (3H, s), 1.11 (3H, s), 1.48 (1H, m), 1.57 (3H, s), 1.60–1.90 (2H, m), 1.99 (1H, m), 2.10 (3H, s), 5.27 (1H, t, J=5.0 Hz), 6.76 (1H, d, J=16 Hz), 7.45 (1H, d, J=16 Hz), 7.40–7.60 (5H, m) ppm; ^{13}C NMR d 17.6, 21.1, 25.4, 27.6, 28.5, 34.0, 35.0, 71.1, 128.1, 128.2, 128.3 (2C), 128.9 (2C), 130.6, 134.7, 145.4, 146.1, 170.6, 199.8 ppm; MS *m/z* (relative intensity) 312 (M^+, 30), 252 (100), 172 (88), 131 (84), 77 (97). Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.9; H, 7.7. Found: C, 76.7; H, 7.7. 80/20 hexane/ethyl acetate afforded acetic acid *(3aRS,4RS,7aSR)-3a,7,7-trimethyl-1-oxo-3-phenyl-3a,4,5,6,7,7a-hexahydro-1H-inden-4-yl ester* ***17b*** (8.0 mg, 0.025 mmol, 5%) as a colourless solid: mp 104–106°C; IR ν 2961, 1738, 1696, 698 cm^{-1}; ^{1}H NMR δ 1.00 (3H, s), 1.25 (3H, s), 1.40–1.70 (3H, m), 1.54 (3H, s), 1.57 (3H, s), 1.88 (1H, m), 2.21 (1H, s), 5.30 (1H, dd, J_1=5.0 Hz, J_2=5.5 Hz), 6.04 (1H, s), 7.30–7.42 (5H, m) ppm; ^{13}C NMR δ 20.4, 23.9, 24.3, 25.1, 32.4, 34.0, 35.0, 50.2, 64.7, 72.6, 127.2 (2C), 128.3 (2C), 128.8, 131.8, 136.1, 169.8, 180.9, 207.7 ppm; MS *m/z* (relative intensity) 312 (M^+, 7), 270 (25), 237 (20), 131 (100), 103 (61), 91 (34), 77 (58). Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.9; H, 7.7. Found: C, 76.7; H, 7.8.

1.5.7. Reaction of 7a with 10^{-2} M $HClO_4$/1 M acetic anhydride. According to the general procedure, reaction of **7a** (39 mg, 0.16 mmol) after 1 min, followed by flash chromatography (90/10 hexane/ethyl acetate) afforded **15a** (36 mg, 0.15 mmol, 95%).

1.5.8. Reaction of 7b with 10^{-2} M $HClO_4$/1 M acetic anhydride. According to the general procedure, reaction of **7b** (50 mg, 0.20 mmol) after 1 min, followed by flash chromatography (90/10 hexane/ethyl acetate) afforded **15b** (48 mg, 0.19 mmol, 97%).

1.5.9. Reaction of 18a with 10^{-2} M $HClO_4$/1 M acetic anhydride. According to the general procedure, reaction of **18a** (125 mg, 0.51 mmol) after 1 min afforded a crude, which was purified by flash chromatography. 96/4 hexane/diethyl ether afforded acetic acid *3-furan-3-yl-3a,7,7-trimethyl-3a,5,6,7-tetrahydro-4H-inden-1-yl ester* ***19a*** (31 mg, 0.11 mmol, 21%) as a yellow oil: IR ν 2932, 1765 cm^{-1}; ^{1}H NMR δ 1.10–2.10 (6H, m), 1.23 (3H, s), 1.29 (3H, s), 1.30 (3H, s), 2.20 (3H, s), 6.29 (1H, s), 6.51 (1H, s), 7.36 (1H, m), 7.46 (1H, s) ppm; ^{13}C NMR δ 19.4, 21.0, 23.1, 26.4, 30.9, 35.2, 36.2, 43.4, 52.3, 109.3, 120.2, 122.2, 137.9, 141.6, 142.0, 142.6, 146.4, 169.0 ppm. 90/10 hexane/diethyl ether afforded *(3aRS,7aSR)-3-furan-3-yl-3a,7,7-trimethyl-3a,4,5,6,7,7a-hexahydro-inden-1-one* ***20a*** (61 mg, 0.25 mmol, 49%) as a pale yellow solid: mp 58–59°C; IR ν 2980, 1690 cm^{-1}; ^{1}H NMR δ?0.92 (3H, s), 1.15–1.95 (6H, m), 1.23 (3H, s), 1.39 (3H, s), 1.94 (1H, s), 6.13 (1H, s), 6.58 (1H, m), 7.47 (1H, m), 7.78 (1H, m) ppm; ^{13}C NMR δ 17.0, 24.4, 28.8, 30.7, 32.6, 34.0, 35.6, 46.0, 63.6, 109.8, 119.5, 126.9, 142.5, 143.5, 173.9, 209.7 ppm; MS *m/z* (relative intensity) 244 (M^+, 16), 229 (16), 175 (25), 162 (42), 145 (20), 131 (3), 115 (51), 91 (100), 77 (75), 63 (78). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.6; H, 8.2. Found: C, 78.7; H, 8.3.

1.5.10. Reaction of 18b with 10^{-2} M $HClO_4$/1 M acetic anhydride. According to the general procedure, reaction of **18b** (120 mg, 0.47 mmol) after 1 min afforded a crude which was purified by flash chromatography (96/4 hexane/ethyl acetate). The first fraction was a yellow solid identified as acetic acid *3a,7,7-trimethyl-3-phenyl-3a,5,6,7,-tetrahydro-4H-inden-1-yl ester* ***19b*** (44 mg, 0.15 mmol, 32%): mp 124–126°C, IR ν 2930, 1755, 698 cm^{-1}; ^{1}H NMR δ 1.20–1.90 (5H, m), 1.24, (3H, s) 1.29 (3H, s), 1.32 (3H, s), 2.22 (3H, s), 2.35 (1H, m), 6.43 (1H, s), 7.22–7.49

(5H, m) ppm; ^{13}C NMR δ 19.5, 21.0, 22.3, 26.2, 31.0, 35.3, 35.7, 42.7, 53.2, 124.2, 126.8, 127.2 (2C), 128.2 (2C), 135.7, 141.5, 142.0, 154.2, 169.0 ppm. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.0; H, 8.2. Found: C, 80.9; H, 8.2. The second fraction was a yellow oil identified as *(3aRS,7aSR)-3a,7,7-trimethyl-3-phenyl-3a,4,5,6,7,7a-hexahydro-inden-1-one* ***20b*** (53 mg, 0.21 mmol, 45%): IR ν 2947, 1694, 768 cm^{-1}; ^{1}H NMR δ 0.95 (3H, s), 1.22 (3H, s), 1.30–1.70 (5H, m), 1.37 (3H, s), 1.98 (1H, m), 2.02 (1H, s), 6.07 (1H, s), 7.40 (5H, m) ppm; ^{13}C NMR δ 18.0, 25.1, 30.7, 31.4, 32.4, 34.1, 36.9, 47.1, 64.5, 127.6 (2C), 128.4 (2C), 129.2, 130.2, 135.1, 182.6, 210.1 ppm; MS *m/z* (relative intensity) 254 (24, M^+), 239 (58), 185 (60), 172 (100), 115 (30), 91 (46), 77 (44), 55 (46); HRMS 254.1676 (M^+), Calcd for $C_{18}H_{22}O$ 254.1671.

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