DOI: 10.1002/chem.200800145

Organocatalytic Multicomponent α-Methylenation/Diels–Alder Reactions: A Versatile Route to Substituted Cyclohexenecarbaldehyde Derivatives

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Abstract: This article describes the design and optimization of an effective organocatalytic three-component domino α-methylenation/Diels–Alder reaction to produce vinyl-substituted cyclohexenecarboxaldehydes in a highly regioselective fashion. In these one-pot transformations, 2-formyl-1,3-butadienes (**4**) were prepared in situ from α,β-unsaturated aldehydes and formalin and were subsequently trapped with a variety of buta-1,3-dienes. The outcomes of the reactions were dependent on the electronic properties of the dienes. 1-Vinylcyclohexenecarbaldehydes **6** were formed by use of acyclic electron-rich dienes, while the initially formed cycloadducts of **4** with cyclopentadiene underwent Cope rearrangements, leading to the formation of tetrahydro-3*H*-indene-5-carbaldehyde compounds **7**. The mechanisms involved in these reactions were deduced from experimental findings. Furthermore, the method was also extended to one-pot domino methylenation/Diels–Alder reactions of dihydrofurans and dihydropyrans to yield spirocyclic lactols **22**. In these reactions, the unstable intermediate hydroxyethyl and hydroxypropyl acroleins behaved as dienophiles, undergoing cycloaddition reactions with dienes with good yields and selectivities. The wide variety of functionalized 1-vinylcyclohex-3-enecarbaldehydes **6**, 4-vinylcyclohex-1-enecarbaldehydes **7**, and spiro lactols **22** generated through the use of these organocatalytic domino processes as a diversity-oriented synthesis provided useful intermediates for the construction of novel odorants.

Keywords: domino reactions · fragrances · multicomponent reactions · organocatalysis

Introduction

The quest for novel stereoselective multicomponent reactions (MCRs) with metal-free organic molecules as catalysts is a continuing challenge at the forefront of synthetic chemistry.[1] Organocatalytic reactions are currently very much en vogue, as the term implies a connotation of ecologically benign, green chemistry. In addition, impressive new results have been achieved over the past few years, which has triggered a dramatic increase in publications.[2] Related to this topic is the catalysis of synthetic transformations by hydrogen-bond donors and organic Brønsted acids.[3] Organocatalytic domino processes are appealing because the purification of intermediates can be avoided.[4] Today, MCRs represent ideal strategies for the preparation of complex structures from unstable and inseparable reaction intermediates and are particularly attractive for both natural product and diversity-oriented syntheses (DOS).[5] However, to date there are only a few reports of organocatalytic multicomponent Diels–Alder reactions for the synthesis of stereochemically complex compounds and of spirocyclic derivatives with quaternary carbon centers in a stereocontrolled manner.

In our search for "green" odorants of the perilla aldehyde family,[6] we were interested in the development of multicomponent reactions to provide cyclohexenecarbaldehyde derivatives, in particular those bearing unsaturated substituents in their 4-positions, which are found in several natural terpenoid products of biological and olfactory interest (Figure 1).[7]

It has been known for a long time that simple aldehydes can be methylenated with formaldehyde in the presence of variable amounts of dialkylammonium salts to afford 2-substituted acroleins.[8,9] Mannich-type α-methylenation/Diels–Alder domino processes with simple aldehydes have been

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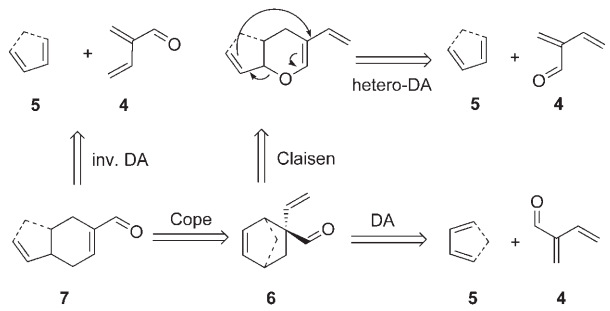


Scheme 1. Possible routes to 4-vinylcyclohexenecarbaldehyde derivatives.

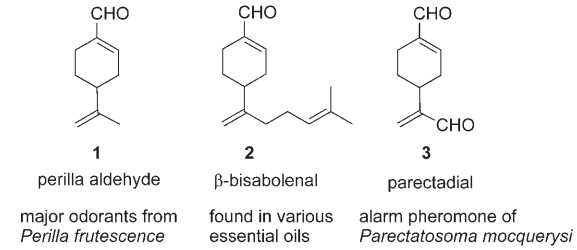


Figure 1. Selected examples of natural products containing 4-vinylcyclohex-1-enecarbaldehyde units.

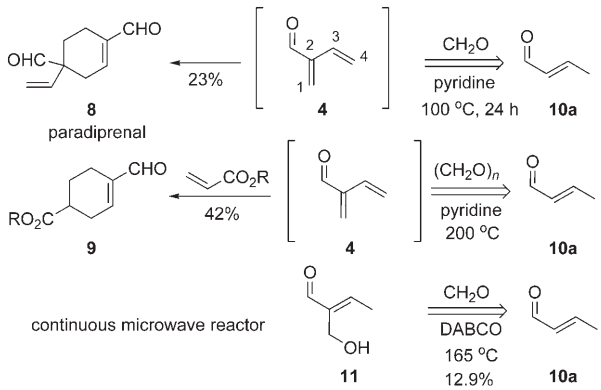
reported.[10a] In recent years, several interesting domino reactions that incorporate Knoevenagel-type α-methylenation and Diels–Alder reaction sequences have been developed.[10b–d] Yamamoto and co-workers reported elegant α-methylenation/Diels–Alder domino reactions of ketones, promoted by ammonium salts generated in situ from diamines and alkoxymethyl chlorides.[10d]

Here we present a detailed account of the design and development of large-scale one-pot organocatalytic multicomponent α-methylenation/Diels–Alder reactions to provide 2- and 4-vinylcyclohexenecarbaldehyde derivatives, which are difficult to obtain by other methods. The protocol allows the facile one-pot synthesis of perilla aldehyde (**1**) and β-bisabolenal (**2**). As an extension of our work, we also describe the domino hydrolyses, α-methylenations, and stereoselective Diels–Alder reactions of 2,3-dihydrofurans and 3,4-dihydropyrans for the synthesis of spirofurans and spiropyrans.

Results and Discussion

According to the retrosynthetic analysis of 4-vinylcyclohexenecarbaldehydes **7**, 2-formylbuta-1,3-diene (**4**) is the key intermediate for the transformation (Scheme 1). Pummerer et al. had previously described the in situ preparation and rapid dimerization of formyl butadiene **4** in the synthesis of *para*-diprenal (**8**) (Scheme 2).[11a] Treatment of formyl butadiene **4** with electron-poor methyl acrylate to afford **9** had also been reported.[11b] In both cases, the unstable 2-formylbuta-1,3-diene **4** was generated by base-catalyzed (sodium hydroxide or pyridine) cross-condensation of α,β-unsaturated aldehydes **10** and aqueous formalin solution or paraformaldehyde. The reactions may proceed through an aldol-Mannich- or a Baylis–Hillman-like[12] condensation processes for which the isolation of hydroxy aldehyde **11** from a continuous microwave process provides evidence.[12c]

We reckoned that Diels–Alder reactions of **4** prepared in this way with dienes **5** should result in 1-vinylcyclohex-3-enecarbaldehydes **6**, which might then undergo Cope rearrangements to afford 4-vinylcyclohex-1-enecarbaldehydes **7**.[13] It was also anticipated that the domino reaction might be carried out as an organocatalytic multicomponent reaction with a secondary amine as a catalyst. This assumption was based on the premise that the cross-condensations of



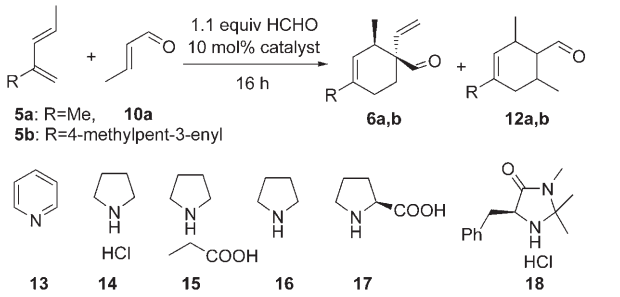
Scheme 2. Reaction behavior of unstable 2-formyl-1,3-butadiene (**4**).

α,β-unsaturated aldehydes **10** and formaldehyde to give **4**, followed by their Diels–Alder reactions with **5**, are believed to proceed more rapidly than the competitive Diels–Alder reactions between **10** and dienes **5**: to a first approximation, alkyl substitution increases the energy of the $LUMO_{dienophile}$. Since this effect is more pronounced for a substituent in the β-position of a dienophile than for one in the α-position, vinyl-acrolein **4** should react more rapidly than crotonaldehyde (**10a**) if the reaction is controlled by the dominant $HOMO_{diene}$–$LUMO_{dienophile}$ orbital interaction of normal Diels–Alder cycloadditions.[14] Furthermore, Spino and Dory have shown that electron-poor dienes react with electron-rich dienes in cross-Diels–Alder reactions to form exclusively the normal Diels–Alder cycloadducts. Well-developed C2=C3 π bonds in the butadiene parts of the transition states of related Diels–Alder reactions have been said to be the reason for the high reactivities of electron-poor dienes.[15]

Our organocatalytic domino strategy was first evaluated with crotonaldehyde (**10a**), 2-methylpenta-1,3-diene (**5a**), formalin, and pyridine, together with a series of amines and ammonium salts **13**–**18** as catalysts (Table 1). The domino reaction was unsuccessful when pyridine (pK_a of the conjugated acid 5.2) was used at 100 °C, and the predominant formation of the normal Diels–Alder adducts **12a** was observed (entry 1). As the speed of a Mannich reaction depends both on the presence of a free amine and on the formation of iminium salts as precursors for the Mannich base formation, the less acidic ammonium salts formed from sec-

ondary amines should better meet these requirements and catalyze the α-methylenation of **10** with aqueous formaldehyde at lower temperature. However, hydrochloride **14** (pK_a 11.3) proved similarly ineffective in generating **6a** (entry 4), but use of the less dissociated ammonium salt **15** finally produced compound **6a** with full conversion in 55% isolated yield (entry 7). Likewise, homomyrcene (**5b**) reacted to afford adduct **6b** in 49% isolated yield (entry 10); the distal double bond was not attacked under these mildly acidic conditions. In the absence of an acidic co-catalyst, the reaction mixture polymerized without any formation of the desired product (entry 8). Importantly, the mode of addition of the substrates is quite significant: while **10a** exothermally polymerized in the presence of catalyst **15**, the addition of **15** to a mixture of **10a** and aq. formalin led to no such decomposition, and the exclusive formation of domino process product **6a** commenced even at room temperature, although with low levels of conversion (entry 3).

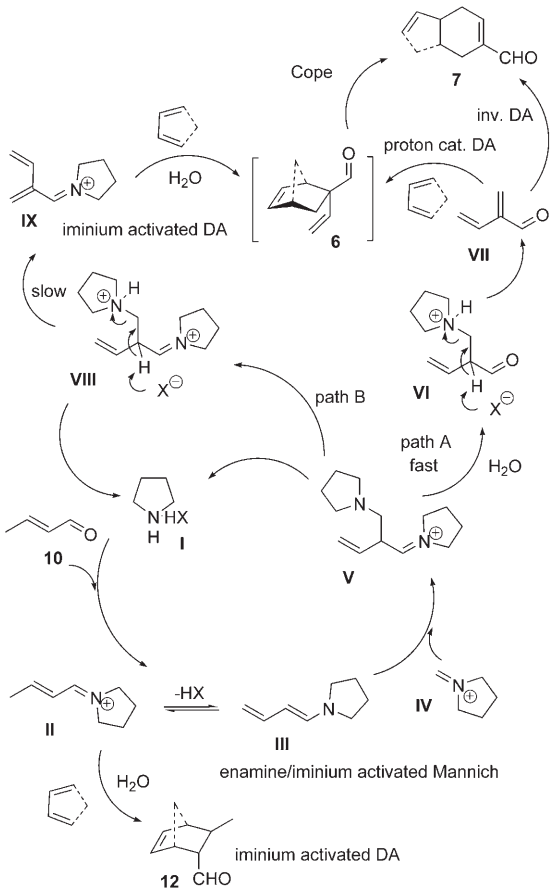
Table 1. Organocatalytic domino α-methylenation/Diels–Alder reactions of **5a–b**, **10a**, and formaldehyde.[a]



Entry	Diene	Catalyst	T [°C]	Product ratio[b]		Conv. [%][b]	Yield [%][c]
				6	**12**		
1	**5a**	**13**	100	7	93	6	–
2	**5a**	**17**	25	100	0	10	8[d]
3	**5a**	**15**	25	100	0	5	–
4	**5a**	**14**	25	0	100	17	–
5	**5a**	**17**	80	48	52	11	–
6	**5a**	**15**	80	95	5	57	–
7	**5a**	**15**	100	90	10	100	55[e]
8	**5a**	**16**	100	–	–	–	–[f]
9	**5a**	**15+18**	60	83	17	19	10[d]
10	**5b**	**15**	100	92	8	100	49[g]

[a] Experimental conditions: a mixture of **5a**/**5b** (2.5 mmol), **10a** (2.0 mmol), formaldehyde (40% aq., 2.2 mmol), and a catalyst (0.2 mmol) in a sealed tube was stirred for 16 h at the temperature displayed in the table. [b] The degree of conversion and the product ratio were determined from the 300 MHz ^{1}H NMR spectrum of the crude reaction mixture. [c] Isolated yield of **6a**/**6b** after bulb-to-bulb distillation. [d] 0% *ee*. [e] *endo*/*exo* 78:22. [f] Polymerized. [g] *endo*/*exo* 80:20.

As might be expected, use both of L-proline (**17**, entry 2) and of MacMillan's catalyst (**18**, entry 9) led to the formation of **6a** without any optical induction.[17] Pihko and coworkers have recently systematically optimized the organocatalytic α-methylenation of simple aldehydes with aqueous formaldehyde.[9a,b] Kinetic experiments indicated that the reactions are of second order in the catalyst concentration, which implies a mechanism of double activation of the aldehyde components by intermediate enamine/iminium species. We assume that in the present case (Scheme 3), the hydrolytic pathway from intermediate iminium species **V** to **VII** (path A) is faster than the pyrrolidine elimination to **IX** (path B). For this reason, relatively high temperatures are necessary to promote the Diels–Alder reaction of **VII**. This reasoning also offers an explanation for the formation of *rac*-**6a** in the case when L-proline is used as catalyst: the Diels–Alder reaction occurs only after the corresponding enantioselectivity-inducing L-proline iminium species has been hydrolyzed to **VI**.



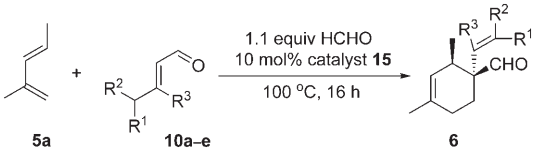
Scheme 3. Proposed catalytic cycle for the organocatalytic triple enamine/iminium/iminium activation of aldehydes in domino α-methylenation/Diels–Alder reaction sequences in one pot.

It soon turned out that this multicomponent protocol could be widely extended to different unsaturated aldehydes and dienes. The outcomes of the reactions largely depended both on the structures of the starting materials and on the reaction parameters. From the experimental findings, the reactions may be classified according to the electronic properties of the dienes, as detailed below.

Domino reactions with electron-rich acyclic dienes: In order to investigate the scope and limitations of these reactions,

the electron-rich diene **5a** was treated with α,β-unsaturated aldehydes **10a–e** under standard reaction conditions. All reactions proceeded with moderate to good yields and high *endo* selectivities to give exclusively products **6** without detection of any Cope rearrangement products **7** (Scheme 1).[18] Notably, sorbic aldehyde **10e** also yielded cyclohexenecarbaldehyde product **6f** with diene substitution (Table 2).

Table 2. Catalytic domino α-methylenation/Diels–Alder reactions of α,β-unsaturated aldehydes with electron-rich dienes.[a]



5a **10a–e** **6**

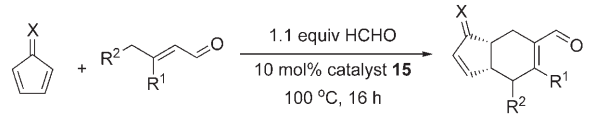
Entry		R^1	R^2	R^3	Product	*endo*/*exo*[b]	Yield [%][c]
1	**10a**	H	H	H	**6a**	78:22	55
2	**10b**	H	H	Me	**6c**	75:25	62
3	**10c**	Et	H	H	**6d**	77:23	71
4	**10d**	Me	Me	H	**6e**	88:12	52
5	**10e**	CH_3CH=		H	**6f**[d]	76:24	42

[a] Experimental conditions: a mixture of **5a** (2.5 mol), **10a–e** (2 mol), formaldehyde (40 % aq., 2.2 mol), and a catalyst (0.2 mol) without an additional solvent in an autoclave was stirred at 100 °C for 16 h. [b] The ratio of *endo*/*exo* isomers was determined by GC and NOESY ^{1}H NMR spectra. [c] Isolated yield after distillation. [d] R^2 = vinyl.

Domino reactions with electron-rich cyclic 1,3-dienes: To explore the reactivities of 2-formylbuta-1,3-dienes further, their DA reactions with cyclopentadienes were examined. Cyclopentadienes are also regarded as electron-rich dienes, and the sequences proceeded with even better regio- and face selectivities. Several α,β-unsaturated aldehydes were treated with formaldehyde in the presence of cyclopentadienes (Table 3) to generate the corresponding (±)-tetrahydro-3*H*-indene-5-carbaldehyde derivatives **7g–j** in acceptable yields. The marked difference from the reactions with noncyclic dienes is the facile Cope rearrangements of the initially formed *exo*-DA adducts **6** (Scheme 1) into aldehydes **7**. Crotonaldehyde (**10a**), for instance, reacted cleanly in a multicomponent methylenation/Diels–Alder/Cope cascade to afford aldehyde **7g** in 43 % isolated yield after simple distillation. Cope rearrangements of similar vinylbicycloheptene systems have been reported to proceed under mild conditions,[19] and we never detected the normal-electron-demand Diels–Alder products **6** as intermediates in the formation of **7**. Although we believe that these Cope rearrangements occur at temperatures around 30 °C,[20] the possibility of the alternative inverse Diels–Alder pathway (Scheme 1) between **4** and cyclopentadiene cannot be excluded (see below). The products **7g–j** display interesting powerful green, melon, and almond-type odors.[21]

Domino reactions with electron-poor dienes: While the domino processes resulted in the formation of either **6** or **7** with exclusive regioselectivities when electron-rich dienes were used, less substituted, electron-poor dienes gave rise to mixtures of **6** and **7** (Table 4).[13] Notably, when isoprene was treated with crotonaldehyde, perilla aldehyde (**1**)[7b] was isolated in low yield (entry 3). Treatment of crotonaldehyde with myrcene produced β-bisabolenal (**2**, entry 5), a constituent of various precious essential oils.[7c–e] This natural product had previously been synthesized in a 22-step sequence[7a] and is now easily available from inexpensive starting materials by this one-pot protocol.

Table 3. Catalytic domino α-methylenation/Diels–Alder reactions of compounds **5**, **10**, and formaldehyde.[a]

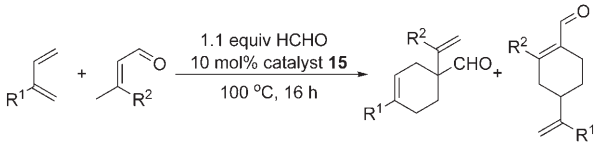


5c–d **10a–c** **7g–j**

Entry		R^1	R^2		X	Product	Yield [%][b]
1	**10a**	H	H	**5c**	2H	**7g**	43
2	**10a**	H	H	**5d**	$C(CH_3)_2$	**7h**	42
3	**10b**	Me	H	**5c**	2H	**7i**	35
4	**10c**	H	Et	**5c**	2H	**7j**	42

[a] Experimental conditions: a mixture of **5c**/**5d** (2.5 mol), **10a–c** (2 mol), formaldehyde (40 % aq., 2.2 mol), and catalyst **15** (0.2 mol), without any additional solvent, was stirred in an autoclave at 100 °C for 16 h. [b] Isolated yield after distillation or column chromatography.

Table 4. Catalytic domino α-methylenation/Diels–Alder reactions of α,β-unsaturated aldehydes with electron-poor dienes.[a]



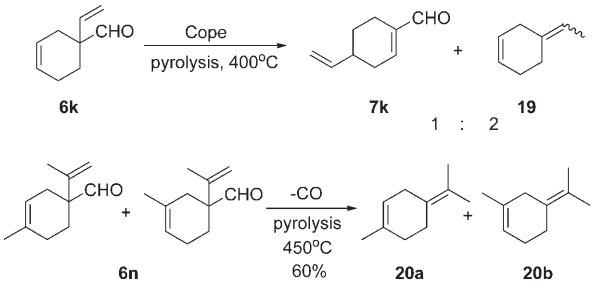
5e–g **10a–b** **6k–o** **7k–o**

Entry		R^1		R^2	Product		Ratio **6**/**7**	Yield [%][b]
1	**5e**	H	**10a**	H	**6k**	**7k**	60:40	43
2	**5e**	H	**10b**	Me	**6l**	**7l**	65:35	54
3	**5f**	Me	**10a**	H	**6m**	**1**	80:20	31
4	**5f**	Me	**10b**	Me	**6n**	**7n**	92:8	46
5	**5g**	MP[c]	**10a**	H	**6o**	**2**	80:20	45

[a] Experimental conditions: a mixture of **5e–g** (2.5 mol), **10a**/**10b** (2 mol), formaldehyde (40 % aq., 2.2 mol) and catalyst **15** (0.2 mol) was stirred in an autoclave at 100 °C for 16 h. [b] Isolated yields of **6** and **7** after distillation. [c] MP = 4-methylpent-3-enyl.

In order to increase the proportions of α,β-unsaturated products **7** and to clarify the mechanism of their formation, efforts were made to convert 1-vinylcyclohex-3-enecarbaldehydes **6** by Cope rearrangement. Unfortunately, both thermal and transition-metal-catalyzed Cope rearrangements of **6** in solution failed due to decomposition of the starting materials. However, the gas-phase pyrolysis of **6k** at 400 °C resulted in rearrangement to **7k**, but only to a minor extent

(Scheme 4). The major product was hydrocarbon **19**, which had regioselectively formed by cheletropic decarbonylation.[22] In general, sterically more hindered aldehydes **6** un-



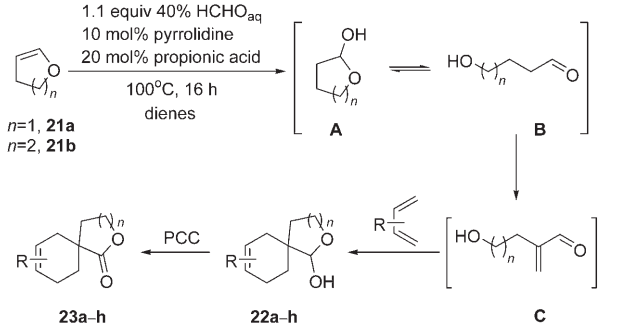
Scheme 4. Cope rearrangement and pyrolysis of **6k** and **6n**.

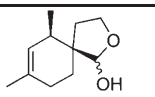
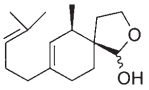
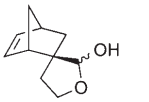
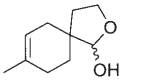
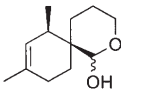
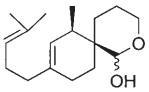
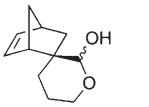
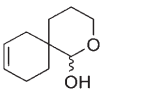
derwent this preparatively useful decarbonylation reaction. For instance, pyrolysis of **6n** led to a mixture of terpinolene (**20a**) and isosylveterpinolene (**20b**) in 60% yield; the latter compound was recently identified as an important constituent of the top note of black pepper oil.[23] From these findings it can be concluded that, in contrast with the facile Cope rearrangements of intermediate bicyclic carbaldehydes (Table 3), the formation of monocyclic cyclohexenes **7** is rather brought about by inverse-DA reactions.

Domino reactions with dihydrofurans and dihydropyrans: With this indication of inverse-DA reactions being the underlying mechanism, a one-pot reaction between **4** and ethyl vinyl ether was attempted. This, however, generated 4-ethoxycyclohex-1-enecarbaldehyde only in small amounts.[24] Treatment of **4** with dihydrofuran **21a** and dihydropyran **21b** also failed to induce inverse-electron-demand Diels–Alder reactions.[25] In situ hydrolysis of these vinyl ethers to hydroxyalkyl acroleins under the standard reaction conditions may be responsible for the observed decomposition. α-Hydroxyethyl- and -hydroxypropylacroleins (Table 5; compounds **C**) are instable α,β-unsaturated aldehydes and have never been isolated in pure form.[9b] Firstly, they are difficult to extract from aqueous solutions, and secondly, they easily form aldol and polymerization products.

Consequently, they have hardly ever been used in synthetic chemistry. In contrast, the Baylis–Hillman reaction makes shorter hydroxymethyl acroleins and derivatives available for wide use in organic chemistry.[12] We hoped to extend the in situ methylenation/DA reactions of hydroxyethyl and hydroxypropyl acroleins to spirocyclic compounds. Indeed, both 2,3-dihydrofuran (**21a**) and 3,4-dihydro-2*H*-pyran (**21b**) underwent domino hydrolysis/methylenation/DA reactions smoothly to form spirolactols **22a–h** with moderate to good yields according to the conditions described in Table 5. The domino hydrolysis/methylenation/DA reactions were also tolerant to different dienes. The *endo*/*exo* selectivities of the lactols were determined by GC and from the NMR spectra of spirolactones **23**, which were conveniently prepared by PCC oxidation. As anticipated, reactive electron-

Table 5. Catalytic domino hydrolysis/α-methylenation/Diels–Alder reactions of 2,3-dihydrofuran (**21a**) and 3,4-dihydro-2*H*-pyran (**21b**) with dienes.[a]



Entry		Diene	Product		*endo*/*exo*[b]	Yield [%][c]
1	**21a**	**5a**		**22a**	92:8	83
2	**21a**	**5b**		**22b**	88:12	79
3	**21a**	**5c**		**22c**	22:78	71
4	**21a**	**5f**		**22d**	73:27[d]	43
5	**21b**	**5a**		**22e**	90:10	78
6	**21b**	**5b**		**22f**	91:9	76
7	**21b**	**5c**		**22g**	18:82	69
8	**21b**	**5e**		**22h**	–	61

[a] Experimental conditions: a mixture of **5a–f** (2.5 mol), **21a** or **21b** (2 mol), formaldehyde (40% aq., 2.2 mol), pyrrolidine (0.2 mol), and propionic acid (0.4 mol) was stirred at 100 °C in a 2.5 L autoclave for 16 h. [b] *endo*/*exo* ratios were determined by GC and ^{1}H NMR spectroscopic data for the corresponding spirolactone. [c] Isolated yield after distillation or column chromatography. [d] Ratio of *para* and *meta* regioisomers.

rich dienes gave the best yields and selectivities both with the 2,3-dihydrofuran (entries 1–3) and with 3,4-dihydro-2*H*-pyran (entries 6–8). Formation of the *endo* adducts was preferred with electron-rich acyclic dienes (entries 1, 2, 5, 6), whereas *exo* selectivities were observed with cyclopentadienes (entries 3, 7). For less activated dienes such as isoprene, the spirolactol products were also formed in moderate yields with *para* regioselectivity (entry 4). Although products **22a–h** display weak green and floral odors, their corresponding lactones such as **23e** display interesting long-lasting earthy, woody, patchouli-like, balsamic type odors,

whereas spirolactone **23a** was also claimed recently for its fresh, green odor.[26]

Conclusion

In summary, we have described a general organocatalytic multi-component α-methylenation/Diels–Alder reaction sequence with which to obtain substituted cyclohexenecarbaldehydes in a highly selective fashion and in one-pot manner from α,β-unsaturated aldehydes, butadienes, and formaldehydes. We have also demonstrated a three-component organocatalytic domino hydrolysis/α-methylenation/Diels–Alder reaction sequence using a similar protocol to access spirolactols. The *endo*/*exo* selectivities of the spirolactols were determined by the stereochemical analysis of their PCC oxidation products. Such a one-pot spirolactol formation process provides a practical tool with which to gain access to spirofurans and spiropyrans in good yields. Overall, the domino methylenation/DA process is quite general and can be performed on large scales. It tolerates the use of a wide variety of aldehydes and dienes with different electronic characteristics. This organocatalytic MCR is particularly well adapted for applications in diversity-oriented synthesis of vinylcyclohexenecarboxaldehyde derivatives and 2-oxaspiro[4.5]dec-7-ene and 2-oxaspiro[5.5]undec-8-ene derivatives as novel odorants in the green and fruity olfactory family.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded with Bruker AW 300, DPX 400, or Avance 500 instruments in $CDCl_3$ or C_6D_6. Chemical shifts in $CDCl_3$ or [D_6]benzene are reported in δ (ppm) relative to tetramethylsilane (TMS), chloroform, or benzene as internal reference unless otherwise stated. In the ^{13}C NMR spectra, the natures of the carbons (C, CH, CH_2, or CH_3) were determined by recording of DEPT 90 and DEPT 135 experiments, and are given in parentheses. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, brs = broad singlet, sept = septet. Solvents for extraction and chromatography were technical grade and were used without further purification. Flash chromatography was performed with Tsingdao Haiyang Chemical silica gel (200–300 mesh). Unless otherwise noted, a hexane/MTBE mixture (50:1) was used as eluent. IR spectra were recorded with a Bruker Tensor 27 instrument. High-resolution MS were obtained with a Finnigan MAT 95 machine. GC/MS spectral data were obtained with Agilent 6890 N and MSD 5975 instruments and use of a HP-5 MS column (30 m, 0.25 mm, 0.25 μm). All reactions were carried out in 100 mL or 2.5 L autoclaves unless otherwise stated. The enantiomeric excess (*ee*) of **6a** was determined by GC in relation to the corresponding racemic samples with the aid of an MN Lipodex-E column (25 m × 0.25 mm, program 80 °C to 150 °C, 2 °C min^{-1}, helium carrier pressure 13.2 psi, FID detection (250 °C).

Materials: All solvents and commercially available chemicals were used as received. Diene **5c** was freshly cracked from the corresponding dimer. Diene **5d**[27] and MacMillan catalyst **18**[28] were prepared by literature procedures.

Typical experimental procedure for the catalyst screening: A mixture of α,β-unsaturated aldehyde **10a** (0.18 g, 2.5 mmol), 2-methylpenta-1,3-diene (**5a**, 0.16 g, 2.0 mmol), formaldehyde (40 % aq., 2.4 mmol), and a catalyst (0.2 mmol) was stirred in a sealed tube without an additional solvent for 16 h at the temperature displayed in the table. Conversion into **6a** was monitored by ^{1}H NMR, through integration of the aldehyde CHO peaks (δ = 9.48, 9.52 ppm for **10a**, 9.50 ppm for **6a**).

Typical experimental procedure for organocatalytic domino methylenation/DA reactions: A mixture of pyrrolidine (16.0 g, 0.22 mol) and propionic acid (17.0 g, 0.23 mol) was added to a mixture of α,β-unsaturated aldehyde **10** (2.36 mol), diene **5** (4.41 mol), and formalin (40 % in water, 200 g, 2.46 mol). The mixture was placed in an autoclave and heated at 100 °C for 16 h, and was then allowed to cool to room temperature, diluted with sat. $NaHCO_3$, and extracted three times with MTBE (200 mL). The combined organic layers were washed with brine (200 mL), dried ($MgSO_4$), and evaporated in vacuo. The residue was purified by distillation or column chromatography on silica gel, eluent: hexane/MTBE (50:1). The regioselectivities and *endo*/*exo* ratios were determined by 2D NMR measurements.

Typical experimental procedure for pyrolysis: A solution of 1-(prop-1-en-2-yl)cyclohex-3-enecarbaldehyde (**6n**; 5 g) in toluene (20 mL) was transferred dropwise over 30 min into a quartz tube heated to 400–450 °C by a tube oven. A gentle stream of argon was applied to prevent oxidation and reflux of the reaction mixture. The pyrolysate was collected in a cold trap at −78 °C and concentrated. The residue was distilled bulb to bulb to give a mixture of **20a** and **20b** (3 g).

General experimental procedure for organocatalytic domino hydrolysis/methylenation/DA reactions: A mixture of pyrrolidine (16.0 g, 0.22 mol) and propionic acid (34.0 g, 0.44 mol) was added to a mixture of 2,3-dihydrofuran (**21a**) or 3,4-dihydro-2*H*-pyran (**21b**) (2.36 mol), diene **5** (4.41 mol), and formalin (40 % in water, 200 g, 2.46 mol). The mixture was placed in an autoclave and heated to 100 °C for 16 h. The reaction mixture was allowed to cool to room temperature, diluted with sat. $NaHCO_3$, and extracted three times with MTBE (200 mL). The combined organic layers were washed with brine (200 mL), dried ($MgSO_4$), and evaporated in vacuo. The residue was purified by distillation or column chromatography (silica gel, mixture of hexane and MTBE).

General experimental procedure for oxidation of spirolactols: PCC (0.06 mol) was added in four portions over 1 h to a solution of a spirolactol **22a–h** (0.03 mol) in CH_2Cl_2 (50 mL). The mixture was vigorously stirred for 2 h until completion of the reaction. Hexane (50 mL) was then added, the precipitate was filtered off, and the filtrate was concentrated under reduced pressure. The crude spirolactone product was purified by bulb-to-bulb distillation.

2,4-Dimethyl-1-vinylcyclohex-3-enecarbaldehyde (6a): This compound was purified by distillation under reduced pressure to yield **6a** (213 g, 55 %) as a colorless liquid. Odor description: green, fresh, camphoraceous. B.p. 50–53 °C/0.15 mbar; *endo*/*exo* 78:22; *endo* isomer: ^{1}H NMR (400 MHz, C_6D_6): δ = 9.39 (s, 1H; CHO), 5.61 (dd, J = 10.9, 17.7 Hz, 1H; C*H*=CH$_2$), 5.20–5.18 (m, 1H; 3-H), 5.07 (d, J = 10.9 Hz, 1H; CH=C*H$_c$*H$_t$), 5.96 (d, J = 17.7 Hz, 1H; CH=CH$_c$*H$_t$*), 2.26–2.18 (m, 1H; 2-H), 1.91–1.56 (m, 4H), 1.49 (brs, 3H; 4-CH$_3$), 0.87 ppm (d, J = 7.1 Hz, 3H; 2-CH$_3$); ^{13}C NMR (100 MHz, C_6D_6): δ = 200.9 (d; CHO), 138.7 (d; *C*H=CH$_2$), 133.5 (s; C-4), 124.9 (d; C-3), 116.9 (t; CH=*C*H$_2$), 54.0 (s; C-1), 34.8 (d; C-2), 27.0 (t; C-5), 25.1 (t; C-6), 23.0 (q; 4-CH$_3$), 16.8 ppm (q; 2-CH$_3$); IR (neat): $\tilde{\nu}$ = 2965, 2933, 2729, 1722, 1631, 1451, 921 cm^{-1}; GC/MS (EI), major *endo* isomer: 164 [M]$^+$ (11), 149 (10), 135 (22), 107 (51), 93 (38), 82 (100), 67 (86), 55 (24), 41 (26); HRMS (EI): m/z: calcd for $C_{11}H_{16}O$: 164.1201; found: 164.1192.

2-Methyl-4-(4-methylpent-3-enyl)-1-vinylcyclohex-3-enecarbaldehyde (6b): This compound was purified by distillation under reduced pressure to yield a colorless liquid (268 g, 49 %). Odor description: muguet, fruity. B.p. 122–125 °C/0.075 mbar; *endo*/*exo* 80:20; *endo* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.49 (s, 1H), 5.76 (dd, J = 17.7, 10.9 Hz, 1H), 5.37–5.33 (m, 2H), 5.27 (d, J = 10.9 Hz, 1H), 5.08 (d, J = 17.7 Hz, 1H), 2.55–2.43 (m, 1H), 2.09–2.65 (m, 8H), 1.67 (s, 3H), 1.58 (s, 3H), 1.00 ppm (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.0 (d), 138.3 (d), 137.5 (s), 131.4 (s), 124.4 (d), 124.0 (d), 117.4 (t), 54.3 (s), 37.3 (t), 34.7 (d), 26.4 (t), 25.7 (q), 25.3 (t), 25.0 (t), 17.7 (q), 17.2 ppm (q); IR (neat): $\tilde{\nu}$ = 2964, 2925, 1734, 1450, 1377, 1105, 922, 835, 724 cm^{-1}; GC/MS (EI): m/z (%): 232 [M]$^+$ (5), 217 (6), 203 (14), 189 (12), 171 (6), 150 (22), 135 (20), 119 (23), 107 (100), 91 (35), 79 (30), 69 (92), 55 (28), 41 (68); HRMS (EI): m/z: calcd for $C_{16}H_{24}O$: 232.1827; found: 232.1833.

2,4-Dimethyl-1-(prop-1-en-2-yl)cyclohex-3-enecarbaldehyde (6c): This compound was purified by distillation under reduced pressure to yield a colorless liquid (260 g, 62%). Odor description: floral, woody, earthy. B.p. 62–65 °C/0.15 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.40 (s, 1H), 5.35–5.32 (m, 1H), 5.15 (s, 1H), 4.89 (s, 1H), 2.75–2.63 (m, 1H), 2.07–1.70 (m, 4H), 1.70 (s, 3H), 1.60 (s, 3H), 1.00 ppm (d, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.8 (d; CHO), 141.8 (s; CH_2=CCH_3), 133.5 (s; 4-C), 124.9 (d; 3-C), 116.0 (t; CH_2=CCH_3), 57.6 (s; 1-C), 32.0 (d; 2-C), 27.2 (t; 5-C), 23.2 (q; 4-CH_3), 22.8 (t; 6-C), 20.0 (q; CH_2=CCH_3), 17.3 ppm (q; 2-CH_3); IR (neat): $\tilde{\nu}$ = 2966, 2693, 1721, 1636, 1447, 1378, 900 cm^{-1}; GC/MS (EI): m/z (%): 178 $[M]^+$ (54), 163 (28), 149 (74), 136 (35), 121 (58), 107 (60), 91 (53), 82 (100), 67 (84), 55 (15), 41 (33); HRMS (EI): m/z: calcd for $C_{12}H_{18}O$: 178.1358; found: 178.1372.

1-(But-1-enyl)-2,4-dimethylcyclohex-3-enecarbaldehyde (6d): This compound was purified by distillation under reduced pressure to yield a colorless liquid (322 g, 71%). Odor description: fruity, apple-like, floral. Four isomers in a ratio of 5:2:7:1. B.p. 112–115 °C/0.12 mbar. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.62, 9.53, 9.45, 9.36 (4s, 1H), 5.60–5.14 (m, 3H), 2.63–2.33 (m, 1H), 2.13–1.61 (m, 9H), 1.01–0.90 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): major isomer: δ = 203.3 (d), 137.3 (d), 134.6 (s), 129.0 (d), 124.1 (d), 53.3 (s), 36.6 (d), 27.3 (t), 27.1 (t), 23.3 (q), 22.7 (t), 17.2 (q), 14.1 ppm (q); IR (neat): $\tilde{\nu}$ = 1964, 2874, 2711, 1721, 1451 cm^{-1}; GC/MS (EI): m/z (%): 192 $[M]^+$ (20), 163 (20), 135 (13), 121 (16), 107 (35), 93 (24), 82 (100), 67 (46), 55 (18), 41 (20); HRMS (EI): m/z: calcd for $C_{13}H_{20}O$: 192.1514; found: 192.1526.

2,4-Dimethyl-1-(2-methylprop-1-enyl)cyclohex-3-enecarbaldehyde (6e): This compound was purified by distillation under reduced pressure to yield a colorless liquid (235 g, 52%). Odor description: fruity, apple, rose-petal, watery. B.p. 88–92 °C/0.12 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.42 (s, 1H), 5.29–5.27 (m, 1H), 4.95 (s, 1H), 2.34–2.24 (m, 1H), 1.90–1.70 (m, 4H), 1.71 (s, 3H), 1.61 (s, 3H), 1.49 (s, 3H), 0.85 ppm (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.3 (d), 137.6 (s), 134.6 (s), 124.8 (d), 124.1 (d), 52.9 (s), 36.9 (d), 27.4 (t), 27.1 (q), 23.3 (q), 21.9 (t), 18.6 (q), 17.3 ppm (q); IR (neat): $\tilde{\nu}$ = 2912, 2712, 1721, 1449, 1378, 821 cm^{-1}; GC/MS (EI): m/z (%): 192 $[M]^+$ (63), 177 (21), 163 (31), 135 (19), 121 (27), 107 (69), 95 (35), 82 (100), 67 (46), 55 (14), 41 (23); HRMS (EI): m/z: calcd for $C_{13}H_{20}O$: 192.1514; found: 192.1508.

1-(Buta-1,3-dienyl)-2,4-dimethylcyclohex-3-enecarbaldehyde (6f): This compound was purified by column chromatography to yield a yellowish liquid (188 g, 42%). Odor description: fruity, apple, mild floral. Four isomers in a ratio of 9:5:2:1. ^{1}H NMR (300 MHz, CDCl3): δ = 9.62, 9.52, 9.48, 9.39 (4s, 1H), 6.44–6.01 (m, 2H), 5.63–5.05 (m, 4H), 2.62–2.40 (m, 1H), 1.95–1.60 (m, 7H), 0.99, 0.98, 0.92, 0.91 ppm (4d, J = 7.1 Hz, 3H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.1 (d), 136.7 (d), 134.1 (s), 134.0 (d), 133.3 (d), 124.6 (d), 117.4 (t), 53.6 (s), 35.2 (d), 27.1 (t), 25.0 (t), 23.3 (q), 17.16 ppm (q); IR (neat): $\tilde{\nu}$ = 2963, 2710, 1718, 1449, 1378, 1006, 907 cm^{-1}; GC/MS (EI): m/z (%): 190 $[M]^+$ (37), 175 (5), 161 (16), 147 (12), 133 (12), 119 (27), 105 (40), 91 (45), 82 (100), 67 (65), 55 (13), 41 (20); HRMS (EI): m/z: calcd for $C_{13}H_{18}O$: 190.1358; found: 190.1368.

***rac*-3a,4,7,7a-Tetrahydro-1*H*-indene-6-carbaldehyde (7g)**: This compound was purified by distillation under reduced pressure to yield a yellowish liquid (150 g, 43%). Odor description: green, melon, cucumber, apple, marine, floral. B.p. 65–70 °C/0.054 mbar; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.44 (s, 1H), 6.97 (dd, J = 4.9, 4.9 Hz, 1H), 5.69–5.56 (m, 2H), 2.99–2.97 (m, 1H), 2.61–2.39 (m, 4H), 2.23–2.19 (m, 1H), 2.09–1.95 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6 (d), 152.2 (d), 142.6 (s), 134.8 (d), 130.3 (d), 42.9 (d), 39.8 (t), 34.6 (d), 29.2 (t), 24.2 ppm (t); IR (neat): $\tilde{\nu}$ = 3050, 2924, 2717, 1678, 1171 cm^{-1}; GC/MS (EI): m/z (%): 148 $[M]^+$ (26), 133 (6), 120 (10), 105 (6), 91 (18), 77 (13), 66 (100), 55 (6), 39 (12); HRMS (EI): m/z: calcd for $C_{10}H_{12}O$: 148.0888; found: 148.0884.

***rac*-1-(Propan-2-ylidene)-3a,4,7,7a-tetrahydro-1*H*-indene-6-carbaldehyde (7h)**: A total of 290 g crude product was obtained. The crude product (5 g) was purified by column chromatography to yield a yellowish liquid (3.2 g, 42%). The product easily decomposed at RT. Odor description: fruity, green, woody. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.44 (s, 1H; C*H*O), 6.95 (ddd, J = 5.9, 4.5, 1.5 Hz, 1H; 5-H), 6.34 (dd, J = 5.7, 2.3 Hz, 1H; 2-H), 5.70 (br d, J = 5.7 Hz, 1H; 3-H), 3.24–3.17 (m, 1H; 3a-H), 2.92 (ddd, J = 7.5, 7.5, 7.5 Hz, 1H; 7a-H), 2.72–2.62 (m, 2H; 4-H_a, 7-H_a), 2.27–2.17 (dddd, J = 16.6, 6.1, 4.5, 1.5 Hz, 1H; 4-H_b), 1.91 (dd, J = 15.5, 8.3 Hz, 1H; 7-H_b), 1.79 (s, 3H; (CH_3)$_a$), 1.74 ppm (s, H, CH_3)$_b$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.1 (d; *C*HO), 151.8 (d; C-5), 143.7 (s, C-6), 142.9 (s, C-1), 136.7 (d; C-3), 131.4 (d; C-2), 122.6 (s, $C(CH_3)_2$), 43.4 (d; C-3a), 39.4 (d; C-7a), 29.3 (t, C-4), 23.8 (t, C-7), 21.1 (q, (CH_3)$_a$), 21.0 ppm (q, (CH_3)$_b$); IR (neat): $\tilde{\nu}$ = 2910, 2716, 1681, 1443, 1374 cm^{-1}; GC/MS (EI): m/z (%): 188 $[M]^+$ (30), 173 (4), 159 (2), 145 (5), 128 (6), 115 (7), 106 (100), 91 (40), 77 (7), 65 (6), 53 (4), 39 (5); HRMS (EI): m/z: calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1199.

5-Methyl-3a,4,7,7a-tetrahydro-1*H*-indene-6-carbaldehyde (7i): This compound was purified by distillation under reduced pressure to yield a yellowish liquid (134 g, 35%). Odor description: green, fruity, melon. ^{1}H NMR (400 MHz, C_6D_6): δ = 10.07 (s, 1H), 5.51–5.49 (m, 1H), 5.29–5.25 (m, 1H), 2.71–2.64 (m, 1H), 2.44–2.18 (m, 4H), 1.88–1.78 (m, 2H), 1.62 (s, 3H), 1.61–1.45 ppm (m, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ = 187.3 (d), 157.1 (s), 134.9 (s), 133.3 (d), 130.8 (d), 44.2 (d), 40.0 (t), 37.1 (t), 34.5 (d), 25.7 (t), 18.0 ppm (q); GC/MS (EI): m/z (%): 162 $[M]^+$ (46), 147 (22), 131 (10), 115 (6), 105 (9), 91 (20), 77 (14), 66 (100), 51 (6), 39 (12); IR (neat): $\tilde{\nu}$ = 3048, 2925, 2848, 1665, 1632, 1434, 1377 cm^{-1}; HRMS (EI): m/z: calcd for $C_{11}H_{14}O$: 162.1045; found: 162.1041.

4-Ethyl-3a,4,7,7a-tetrahydro-1*H*-indene-6-carbaldehyde (7j): This compound was purified by distillation under reduced pressure to yield a yellowish liquid 177 g (42%). Odor description: green, fruity, weak. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.42, 9.40 (2s, 1H), 6.84–6.83, 6.74–6.72 (2m, 1H), 5.74–5.53 (m, 2H), 3.26–3.13 (m, 1H), 2.87–2.75 (m, 1H), 2.66–1.46 (m, 7H), 1.06, 1.02 ppm (2t, J = 7.5 Hz, 3H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.7 (d), 157.3 (d), 142.4 (s), 132.5 (d), 130.3 (d), 49.1 (d), 41.2 (d), 41.0 (t), 34.4 (d), 25.1 (t), 24.9 (t), 12.44 ppm (q); GC/MS (EI): m/z (%): 176 $[M]^+$ (28), 147 (23), 117 (13), 105 (8), 91 (21), 77 (14), 66 (100), 41 (10); minor isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.7 (d), 156.3 (d), 142.5 (s), 133.9 (d), 130.2 (d), 49.4 (d), 41.9 (d), 39.4 (t), 35.5 (d), 27.1 (t), 24.7 (t), 11.63 ppm (q); IR (neat): $\tilde{\nu}$ = 3054, 2961, 2929, 1683, 1447 cm^{-1}; HRMS (EI): m/z: calcd for $C_{12}H_{16}O$: 176.1201; found: 176.1198.

1-Vinylcyclohex-3-enecarbaldehyde (6k): This compound was purified by column chromatography to yield a colorless liquid. Odor description of the mixture: green, fruity, apple, melon, floral, violet. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.37 (s, 1H), 5.77–5.63 (m, 3H), 5.29 (d, J = 10.6 Hz, 1H), 5.16 (d, J = 17.7 Hz, 1H), 2.53–1.67 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.8 (d), 137.9 (d), 127.1 (d), 123.9 (d), 117.0 (t), 51.7 (s), 29.4 (t), 26.9 (t), 22.0 ppm (t); IR (neat): $\tilde{\nu}$ = 3027, 2921, 2840, 1725, 1439, 922, 717, 665 cm^{-1}; GC/MS (EI): m/z (%): 136 $[M]^+$ (5), 118 (17), 107 (28), 91 (46), 79 (100), 67 (9), 53 (14), 39 (23); HRMS (EI): m/z: calcd for $C_9H_{12}O$: 136.0888; found: 136.0880.

4-Vinylcyclohex-1-enecarbaldehyde (7k): This compound was purified by column chromatography to yield a colorless liquid. Odor description of the mixture: green, fruity, apple, melon ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.44 (s, 1H), 6.82–6.80 (m, 1H), 5.81 (ddd, J = 17.0, 10.2, 6.6 Hz, 1H), 5.04 (d, J = 17.0 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 2.55–2.05 (m, 5H), 1.91–1.83 (m, 1H), 1.44–1.30 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.9 (d), 149.9 (d), 142.1 (d), 141.3 (s), 113.5 (t), 37.1 (d), 32.0 (t), 27.2 (t), 20.8 ppm (t); IR (neat): $\tilde{\nu}$ = 2928, 1686, 1643, 1420, 1178, 916 cm^{-1}; GC/MS (EI): m/z (%): 136 $[M]^+$ (21), 121 (14), 107 (60), 91 (41), 79 (88), 67 (27), 54 (100), 39 (49); HRMS (EI): m/z: calcd for $C_9H_{12}O$: 136.0888; found: 136.0883.

1-(Prop-1-en-2-yl)cyclohex-3-enecarbaldehyde (6l): This compound was purified by column chromatography to yield a colorless liquid. Odor description: fresh, green, camphoraceous, perilla aldehyde-like. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.23 (s, 1H), 5.72–5.60 (m, 2H), 5.07 (s, 1H), 4.91 (s, 1H), 2.54–2.44 (m, 1H), 2.18–2.71 (m, 5H), 1.68 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.4 (d), 143.0 (s), 126.8 (d), 124.4 (d), 114.4 (t), 54.4 (s), 29.0 (t), 25.5 (t), 22.4 (t), 19.5 ppm (q); IR (neat): $\tilde{\nu}$ = 3028, 2923, 2698, 1725, 1668, 1634, 1440, 1377, 901 cm^{-1}; GC/MS (EI): m/z (%): 150 $[M]^+$ (9), 135 (17), 121 (36), 107 (21), 93 (73), 79 (100), 67 (21), 55 (24), 41 (27); HRMS (EI): m/z: calcd for $C_{10}H_{14}O$: 150.1045; found: 150.1041.

2-Methyl-4-vinylcyclohex-1-ene carbaldehyde (7l): This compound was purified by column chromatography to yield a colorless liquid. Odor description: green, fruity, cinnamon. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.15$ (s, 1H), 5.79 (ddd, $J = 17.0$, 10.2, 6.1 Hz, 1H), 5.06–4.95 (m, 2H), 2.48–1.22 (m, 7H), 2.14 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 190.7$ (d), 154.7 (s), 142.2 (d), 133.3 (s), 113.3 (t), 39.7 (t), 37.0 (d), 27.5 (t), 21.9 (t), 18.2 ppm (q); IR (neat): $\tilde{\nu} = 2921$, 1714, 1666, 1440, 1379, 1244, 914 cm^{-1}; GC/MS (EI): m/z (%): 150 $[M]^+$ (42), 135 (45), 121 (47), 107 (55), 93 (87), 79 (100), 67 (94), 54 (57), 41 (54); HRMS (EI):m/z: calcd for $C_{10}H_{14}O$: 150.1045; found: 150.1016.

4-Methyl-1-vinylcyclohex-3-enecarbaldehyde[29a] **and 3-methyl-1-vinylcyclohex-3-ene-carbaldehyde (6m)**:[29b] Purification by column chromatography yielded a colorless liquid. Odor description of the mixture: powerful, fresh green, fruity, spicy. IR (neat): $\tilde{\nu} = 2917$, 2854, 2707, 1726, 1632, 1439, 921 cm^{-1}.

4-Methyl-1-vinylcyclohex-3-enecarbaldehyde: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.35$ (s, 1H), 5.69 (dd, $J = 17.7$, 10.7 Hz, 1H), 5.41–5.39 (m, 1H), 5.26 (d, $J = 10.7$ Hz, 1H), 5.13 (d, $J = 17.7$ Hz, 1H), 2.44–2.31 (m, 1H), 2.10–1.64 (m, 5H), 1.63 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 202.0$ (d), 138 (d), 134.4 (s), 118.0 (d), 116.9 (t), 51.4 (s), 29.8 (t), 27.3 (t), 26.9 (t), 22.0 ppm (q); GC/MS (EI): m/z (%): 150 $[M]^+$ (23), 135 (24), 121 (45), 107 (33), 93 (100), 79 (98), 67 (54), 55 (37), 39 (38).

3-Methyl-1-vinylcyclohex-3-enecarbaldehyde: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.36$ (s, 1H), 5.71 (dd, $J = 10.7$, 17.7 Hz, 1H), 5.38–5.36 (m, 1H), 5.27 (d, $J = 10.7$ Hz, 1H), 5.12 (d, $J = 17.7$ Hz, 1H), 2.37–2.33 (m, 1H), 2.10–1.64 (m, 5H), 1.72 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 201.7$ (d), 137.9 (d), 131.2 (s), 120.9 (d), 116.8 (t), 52.2 (s), 34.1 (t), 26.7 (t), 23.6 (q), 22.2 ppm (t); GC/MS (EI): m/z (%): 150 $[M]^+$ (10), 135 (16), 121 (78), 107 (29), 93 (100), 79 (88), 67 (32), 55 (31), 39 (32).

***rac*-Perillaldehyde (1)**:[7b] This compound was purified by column chromatography to yield a slightly yellow liquid. Odor description: powerful, fresh, green. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.43$ (s, 1H), 6.83 (m, 1H), 4.78 (br s, 1H), 4.74 (br s, 1H), 2.45 (m, 2H), 2.25 (m, 2H), 2.15 (m, 1H), 1.91 (m, 1H), 1.77 (s, 3H), 1.46 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 193.9$ (d), 150.6 (d), 148.3 (s), 141.3 (s), 109.5 (t), 40.7 (d), 31.7 (t), 26.3 (t), 21.6 (t), 20.7 ppm (t); IR (neat): $\nu = 3038$, 2932, 2814, 2719, 1686, 1645, 1453, 1377, 1211, 1167, 891, 816, 771, 692 cm^{-1}; GC/MS (EI): m/z (%): 150 $[M]^+$ (26), 135 (39), 122 (41), 93 (43), 79 (90), 68 (100), 53 (44), 39 (36).

4-Methyl-1-(prop-1-en-2-yl)cyclohex-3-enecarbaldehyde and 3-methyl-1-(prop-1-en-2-yl)cyclohex-3-enecarbaldehyde (6n): Purification by distillation under reduced pressure yielded a colorless liquid. Mixture of isomers in a ratio of 6:4. Odor description: green, fruity, mango, damascone, plum. B.p. 65–71 °C/0.06 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.22$, 9.21 (2 s, 1H), 5.04–4.83 (m, 3H), 2.51–2.33 (m, 2H), 2.17–1.72 (m, 5H), 1.70, 1.68, 1.67, 1.60 ppm (4 s, 6H); IR (neat): $\tilde{\nu} = 2967$, 2921, 1726, 1635, 1441, 1377, 899 cm^{-1}; HRMS (EI): m/z: calcd for $C_{11}H_{16}O$: 164.1201; found: 164.1210.

4-Methyl-1-(prop-1-en-2-yl)cyclohex-3-enecarbaldehyde: ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 201.7$ (d), 143.0 (s), 134.0 (s), 118.4 (d), 114.4 (t), 54.2 (s), 29.3 (t), 27.2 (t), 26.0 (t), 23.2 (q), 19.6 ppm (q); GC/MS (EI): m/z (%): 164 $[M]^+$ (20), 149 (31), 135 (68), 121 (35), 107 (71), 93 (100), 79 (64), 67 (40), 55 (28), 41 (38).

3-Methyl-1-(prop-1-en-2-yl)cyclohex-3-enecarbaldehyde: ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 201.5$ (d), 143.0 (s), 131.6 (s), 120.6 (d), 114.3 (t), 55.0 (s), 33.7 (t), 25.4 (t), 23.6 (q), 22.4 (t), 19.6 ppm (q); GC/MS (EI): m/z (%): 164 $[M]^+$ (18), 149 (32), 135 (68), 121 (34), 107 (72), 93 (100), 79 (64), 67 (41), 55 (27), 41 (38)

4-(4-Methylpent-3-enyl)-1-vinylcyclohex-3-enecarbaldehyde and 3-(4-methylpent-3-enyl)-1-vinylcyclohex-3-enecarbaldehyde (6o): Purification by column chromatography yielded a colorless liquid. Odor description: green, fruity, weak. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.36$ (s, 1H), 5.70 (m, 1H), 5.40 (m, 1H), 5.25 (m, 1H), 5.10–5.08 (m, 2H), 2.40 (m, 2H), 2.10–1.90 (m, 8H), 1.68 (s, 3H), 1.58 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 202.1$ (d), 137.9 (d), 134.9 (s), 131.5 (s), 120.7 (d), 117.7 (d), 116.9 (t), 52.2 (s), 37.4 (t), 29.7 (t), 27.4 (t), 26.3 (t), 25.7 (q), 25.2 (t), 17.7 ppm (q); IR (neat): $\tilde{\nu} = 2966$, 2921, 2852, 1726, 1439, 921 cm^{-1}; HRMS (EI): m/z: calcd for $C_{15}H_{22}O$: 218.1671; found: 218.1662.

***rac*-β-Bisabolenal (2)**:[7c] This compound was purified by column chromatography to yield a yellowish liquid. Odor description: green, fruity, fatty. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.44$ (s, 1H), 6.84 (m, 1H), 5.08 (m, 1H), 4.82 (s, 1H), 4.79 (s, 1H), 2.48 (m, 1H), 2.22 (m, 2H), 2.20–2.04 (m, 5H), 1.97–1.85 (m, 2H), 1.69 (s, 3H), 1.62 (s, 3H), 1.50 ppm (m, 1H); ^{13}C NMR (100 MHz, d_6-acetone): $\delta = 192.5$ (d), 152.7 (s), 148.9 (d), 141.4 (s), 131.5 (s), 124.6 (d), 108.3 (t), 39.7 (d), 35.0 (t), 32.2 (t), 27.1 (t), 27.0 (t), 25.8 (q), 22.1 (t), 17.7 ppm (q); IR (neat): $\tilde{\nu} = 2923$, 1686, 1645, 1435, 1166 cm^{-1}; GC/MS (EI): m/z (%): 218 $[M]^+$ (5), 175 (22), 109 (37), 91 (14), 79 (18), 69 (100), 53 (10), 41 (52); HRMS (EI): m/z: calcd for $C_{15}H_{22}O$: 218.1671; found: 218.1673.

4-Isopropylidene-1-methylcyclohexene (20a) and 5-isopropylidene-1-methylcyclohexene (20b):[23] Purification by distillation under reduced pressure yielded a colorless liquid. Odor description: spicy, peppery. B.p. 62–65 °C/8.7 mbar; IR (neat): $\tilde{\nu} = 2912$, 1445, 1375, 899, 790 cm^{-1}.

Compound 20a: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.40$ (m, 1H), 2.76 (br, 2H), 2.36 (t, $J = 6.3$ Hz, 2H), 2.05 (t, $J = 6.3$ Hz, 2H), 1.71 (s, 3H), 1.70 (s, 3H), 1.68 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 134.0$ (s), 127.6 (s), 121.6 (s), 120.8 (d), 31.5 (t), 29.5 (t), 26.6 (t), 23.4 (q), 19.8 (q), 19.7 ppm (s); GC/MS (EI): m/z (%): 136 $[M]^+$ (90), 121 (100), 105 (27), 93 (98), 79 (41), 67 (11), 53 (12), 41 (17).

Compound 20b: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.49$ (m, 1H), 2.68 (br, 2H), 2.28 (t, $J = 6.3$ Hz, 2H), 2.05 (t, $J = 6.3$ Hz, 2H), 1.71 (s, 3H), 1.70 (s, 3H), 1.68 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 134.2$ (s), 128.2 (s), 121.7 (s), 121.3 (d), 34.5 (t), 26.5 (t), 26.3 (t), 23.5(q), 20.2 (s), 20.1 ppm (s); GC/MS (EI): m/z (%): 136 $[M]^+$ (80), 121 (68), 105 (24), 93 (100), 79 (38), 67 (16), 53 (12), 41 (18).

6,8-Dimethyl-2-oxaspiro[4.5]dec-7-en-1-ol (22a): This compound was purified by distillation under reduced pressure to yield a colorless liquid that crystallized on standing. M.p. 62–65 °C; b.p. 85–89 °C/0.09 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.42$, 5.22 (2 s, 1H), 5.17, 4.91 (2 s, 1H), 4.15–4.00 (m, 1H), 3.93–3.85 (m, 1H), 3.40 (br, 1H), 2.20–2.05 (m, 1H), 2.11–1.50 (m, 9H), 1.05, 0.85 ppm (2 d, $J = 6.9$ Hz, 3H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 131.2$ (s), 126.3 (d), 102.8 (d), 66.6 (t), 48.4 (s), 35.6 (d), 31.4 (t), 27.3 (t), 23.3 (q), 22.6 (t), 17.9 ppm (q); IR (neat): $\tilde{\nu} = 3424$, 2967, 1453, 1365, 1032, 903 cm^{-1}; GC/MS (EI): m/z (%): 182 $[M]^+$ (2), 164 (48), 149 (23), 136 (20), 121 (54), 108 (64), 93 (100), 82 (80), 67 (41), 55 (16), 41 (24); HRMS (EI): m/z: calcd for $C_{11}H_{18}O_2$: 182.1307; found: 182.1303.

6-Methyl-8-(4-methylpent-3-enyl)-2-oxaspiro[4.5]dec-7-en-1-ol (22b): This compound was purified by distillation under reduced pressure to yield a colorless liquid. B.p. 135–140 °C/0.09 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.44$–5.23 (m, 1H), 5.17–4.92 (m, 2H), 4.11–4.06 (m, 1H), 3.92–3.88 (m, 1H), 3.20 (br, 1H), 2.18–1.61 (m, 17H), 1.07, 0.94 ppm (2 d, $J = 6.9$ Hz, 3H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 134.7$ (s), 131.4 (s), 127.2 (d), 124.3 (d), 102.8 (d), 66.6 (t), 48.5 (s), 37.3 (t), 36.6 (d), 31.4 (t), 26.5 (t), 25.7 (q), 25.4 (t), 18.0 (q), 17.7 ppm (q); IR (neat): $\tilde{\nu} = 3404$, 2916, 1438, 1027, 905 cm^{-1}; GC/MS (EI): m/z (%): 250 $[M]^+$ (1), 232 (53), 217 (16), 204 (10), 189 (26), 163 (29), 147 (24), 135 (29), 119 (41), 107 (100), 93 (81), 79 (51), 69 (94), 55 (28), 41 (83); HRMS (EI): m/z: calcd for $C_{16}H_{26}O_2$: 250.1933; found: 250.1913.

4′,5′-Dihydro-2′*H*-spiro[bicyclo[2.2.1]hept-5-ene-2,3′-furan]-2′-ol (22c): This compound was purified by distillation under reduced pressure to yield a colorless liquid. B.p. 95–99 °C/0.11 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.25$–6.06 (m, 2H), 5.07–4.60 (4 s, 1H), 4.07–3.74 (m, 3H), 2.93–2.53 (m, 2H), 2.32–1.77 (m, 2H), 1.67–1.58 (m, 1H), 1.54–0.93 ppm (m, 3H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.0$ (d), 138.3 (d), 104.3 (d), 67.1 (t), 54.5 (s), 48.0 (t), 45.7 (d), 42.9 (d), 40.0 (t), 34.6 ppm (t); IR (neat): $\tilde{\nu} = 3416$, 3059, 2970, 1447, 1333, 1012, 905, 723 cm^{-1}; GC/MS (EI): m/z (%): 166 $[M]^+$ (0.5), 148 (8), 105 (7), 83 (33), 66 (100), 55 (4), 39 (11); HRMS (EI): m/z: calcd for $C_{10}H_{14}O_2$: 166.0994; found: 166.0987.

8-Methyl-2-oxaspiro[4.5]dec-7-en-1-ol (22d): This compound was purified by distillation under reduced pressure to yield a colorless liquid. B.p. 102–106 °C/0.13 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.45$–5.25 (m,

1H), 5.05–4.95 (m, 1H), 4.14–4.02 (m, 1H), 3.95–3.83 (m, 1H), 2.40–1.40 ppm (m, 12H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.4 (s), 118.7 (d), 102.2 (d), 66.1 (t), 45.2 (s), 39.1 (t), 29.4 (t), 28.3 (t), 27.7 (t), 23.4 ppm (q); IR (neat): $\tilde{\nu}$ = 3404, 2913, 1438, 1118, 1018, 903, 805 cm^{-1}; GC/MS (EI): *m/z* (%): 168 $[M]^+$ (1), 150 (94), 135 (38), 120 (25), 107 (47), 93 (68), 79 (100), 67 (28), 53 (18), 41 (22); HRMS (EI): *m/z*: calcd for $C_{10}H_{16}O_2$: 168.1150; found: 168.1151.

7,9-Dimethyl-2-oxaspiro[5.5]undec-8-en-1-ol (22e): This compound was purified by distillation under reduced pressure to yield a colorless liquid that crystallized on standing. M.p. 88–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.25–5.24 (m, 1H), 4.67 (s, 1H), 3.98–3.54 (br m, 3H), 1.93–1.31 (m, 12H), 0.95–0.91 (m, 3H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.7 (s), 126.3 (d), 96.9(d), 69.3 (t), 37.7 (d), 36.5 (s), 26.6 (t), 24.5 (t), 23.2 (q), 21.7 (t), 21.6 (t), 15.8 ppm (q); IR (neat): $\tilde{\nu}$ = 3370, 2925, 1454, 1377, 1036, 965, 930, 877, 843 cm^{-1}; GC/MS (EI): *m/z* (%): 196 $[M]^+$ (4), 178 (20), 163 (9), 150 (8), 134 (73), 122 (39), 107 (98), 93 (50), 82 (100), 67 (70), 55 (22), 41 (35); HRMS (EI): *m/z*: calcd for $C_{12}H_{20}O_2$: 196.1463; found: 196.1460.

7-Methyl-9-(4-methylpent-3-enyl)-2-oxaspiro[5.5]undec-8-en-1-ol (22f): This compound was purified by distillation under reduced pressure to yield a colorless liquid. B.p. 150–156 °C/0.09 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.40–5.20 (m, 1H), 5.09–5.05 (m, 1H), 4.69 (s, 1H), 4.03–3.96 (m, 1H), 3.61–3.56 (m, 1H), 3.48 (br, 1H), 2.09–1.31 (m, 19H), 0.97–0.85 ppm (2d, J = 6.9 Hz, 3H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.9 (s), 134.3 (s), 126.1 (d), 124.4 (d), 96.9 (d), 59.4 (t), 37.7 (d), 37.4 (t), 36.7 (s), 26.5 (t), 25.7 (q), 24.8 (t), 24.6 (t), 24.4 (t), 21.6 (t), 17.7 (q), 15.9 ppm (q); IR (neat): $\tilde{\nu}$ = 3394, 2918, 1454, 1376, 1026, 967 cm^{-1}; GC/MS (EI): *m/z* (%): 264 $[M]^+$ (8), 246 (18), 231 (6), 221 (8), 202 (41), 190 (14), 177 (11), 159 (18), 147 (18), 133 (53), 121 (41), 107 (100), 91 (45), 79 (45), 69 (88), 55 (23), 41 (73); HRMS (EI): *m/z*: calcd for $C_{17}H_{28}O_2$: 264.2089; found: 264.2083.

2′,4′,5′,6′-Tetrahydrospiro[bicyclo[2.2.1]hept-5-ene-2,3′-pyran]-2′-ol (22g): This compound was purified by distillation under reduced pressure to yield a colorless liquid. B.p. 114–117 °C/0.10 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.13–6.01 (m, 2H), 4.89–4.87 (m, 1H), 4.30 (br, 1H), 3.98–3.84 (m, 1H), 3.57–3.43 (m, 1H), 2.93–2.71 (m, 2H), 1.82–1.18 ppm (m, 7H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.9 (s), 134.3 (s), 126.1 (d), 124.4 (d), 96.9 (d), 59.4 (t), 37.7 (d), 37.4 (t), 36.7 (s), 26.5 (t), 25.7 (q), 24.8 (t), 24.6 (t), 24.4 (t), 21.6 (t), 17.7 (q), 15.9 ppm (q); IR (neat): $\tilde{\nu}$ = 3382, 3058, 2947, 1448, 1333, 1189, 1084, 1049, 722 cm^{-1}; GC/MS (EI): *m/z* (%): 180 $[M]^+$ (1), 162 (7), 113 (10), 97 (28), 66 (100), 39 (9); HRMS (EI): *m/z*: calcd for $C_{11}H_{16}O_2$: 180.1150; found: 180.1157.

2-Oxaspiro[5.5]undec-8-en-1-ol (22h): This compound was purified by distillation under reduced pressure to yield a colorless liquid. B.p. 110–115 °C/0.12 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.60 (m, 2H), 4.71, 4.53 (2s, 1H), 3.95 (m, 1H), 3.50 (m, 1H), 2.35–1.90 (m, 3H), 1.85–1.65 (m, 3H), 1.65–1.55 (m, 2H), 1.50–1.30 ppm (m, 2H); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.6 (d), 124.9 (d), 96.4 (d), 60.8 (t), 34.9 (s), 32.8 (t), 29.6 (t), 28.2 (t), 21.6 (t), 21.2 ppm (t); IR (neat): $\tilde{\nu}$ = 3380, 3021, 2918, 1437, 1086, 1022, 937, 658 cm^{-1}; GC/MS (EI): *m/z* (%): 168 $[M]^+$ (1), 150 (25), 106 (27), 94 (33), 79 (100), 67 (16); HRMS (EI): *m/z*: calcd for $C_{10}H_{16}O_2$: 168.1150; found: 168.1153.

6,8-Dimethyl-2-oxaspiro[4.5]dec-7-en-1-one (23a):[26] This compound was purified by bulb to bulb distillation under reduced pressure to yield a colorless liquid. B.p. 110–113 °C/0.15 mbar; yield 79%; *exo*/*endo* 8:92; *endo* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.20 (d, J = 2.1 Hz, 1H), 4.20 (m, 2H), 2.25–1.65 (m, 6H), 1.60 (s, 3H), 1.44 (m, 1H), 0.95 ppm (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.8 (s), 132.6 (s), 124.3 (d), 64.9 (t), 44.2 (s), 34.6 (t), 34.4 (d), 26.9 (t), 26.5 (t), 23.3 (q), 17.4 ppm (q) ; IR (neat): $\tilde{\nu}$ = 2965, 1767, 1454, 1375, 1193, 1151, 1032 cm^{-1}; GC/MS (EI): *m/z* (%): 180 $[M]^+$ (38), 152 (62), 137 (48), 107 (55), 93 (44), 82 (100), 67 (64), 53 (13), 41 (19).

6-Methyl-8-(4-methylpent-3-enyl)-2-oxaspiro[4.5]dec-7-en-1-one (23b): This compound was purified by bulb to bulb distillation under reduced pressure to yield a colorless liquid. Yield 78%. B.p. 128–132 °C/0.09 mbar; *exo*/*endo* 12:88; *endo* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (d, J = 4.2 Hz, 1H), 5.06 (t, J = 6.3 Hz, 1H), 4.30–4.24 (m, 2H), 2.32–2.22 (m, 1H), 2.22–1.88 (m, 9H), 1.67 (s, 3H), 1.59 (s, 3H), 1.53–1.46 (m, 1H), 1.03 ppm (d, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.9 (s), 136.2 (s), 131.3 (s), 124.1 (d), 124.0 (d), 64.9 (t), 44.3 (s), 37.3 (t), 34.6 (t), 34.2 (d), 26.3 (t), 26.2 (t), 25.7 (q), 25.2 (t), 17.7 (q), 17.5 ppm (q); IR (neat): $\tilde{\nu}$ = 2925, 1767, 1450, 1375, 1169, 1031 cm^{-1}; GC/MS (EI): *m/z* (%): 248 $[M]^+$ (29), 233 (39), 205 (73), 192 (28), 180 (19), 164 (25), 152 (89), 135 (56), 107 (90), 99 (35), 91 (61), 82 (81), 69 (100), 41 (87); HRMS (EI): *m/z*: calcd for $C_{16}H_{24}O_2$: 248.1776; found: 248.1778.

4′,5′-Dihydro-2′*H*-spiro[bicyclo[2.2.1]hept-5-ene-2,3′-furan]-2′-one (23c):[30] This compound was purified by bulb to bulb distillation under reduced pressure to give a colorless liquid. Yield 85%; b.p. 82–86 °C/0.09 mbar; *exo*/*endo* 78:22; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.35–6.32 (m, 1H), 6.19–6.16 (m, 1H), 4.32–4.19 (m, 2H), 2.99 (s, 1H), 2.93 (s, 1H), 2.26–2.22 (m, 1H), 2.12–2.06 (m, 2H), 1.98–1.70 (m, 1H), 1.43 (d, J = 7.8 Hz, 1H), 1.12 ppm (dd, J_1 = 11.4 Hz, J_2 = 2.7 Hz, 1H); *exo* isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.1 (s), 133.5 (s), 117.7 (d), 65.3 (t), 41.0 (s), 33.0 (t), 32.4 (t), 28.7 (t), 26.7 (t), 23.3 ppm (q); IR (neat): $\tilde{\nu}$ = 2974, 1763, 1455, 1370, 1335, 1210, 1028, 972, 728 cm^{-1}; GC/MS (EI): *m/z* (%): 164 $[M]^+$ (7), 99 (86), 66 (100), 39 (12).

8-Methyl-2-oxaspiro[4.5]dec-7-en-1-one (23d):[26] This compound was purified by bulb to bulb distillation under reduced pressure as a colorless liquid. Yield 82%; b.p. 95–97 °C/0.11 mbar; *para*/*meta* 73:27; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.44–6.36 (m, 1H), 4.34–4.25 (m, 2H), 2.33–2.38 (m, 1H), 2.20–1.75 (m, 6H), 1.70–1.61 ppm (m, 4H); *para* isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.4 (s), 139.9 (d), 134.1 (d), 65.1 (t), 49.2 (d), 47.7 (s), 47.0 (t), 42.8 (d), 39.3 (t), 35.3 ppm (t); IR (neat): $\tilde{\nu}$ = 2914, 1767, 1448, 1374, 1199, 1177, 1151, 1026, 957 cm^{-1}; GC/MS (EI): *m/z* (%): 164 $[M]^+$ (7), 99 (86), 66 (100), 39 (12).

7,9-Dimethyl-2-oxaspiro[5.5]undec-8-en-1-one (23e): This compound was purified by distillation under reduced pressure as a colorless liquid. Yield 83%; b.p. 120–122 °C/0.10 mbar; *exo*/*endo* 10:90; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.23–5.22 (m, 1H), 4.39–4.29 (m, 2H), 2.30–2.22 (m, 2H), 2.08–1.85 (m, 5H), 1.67 (s, 3H), 1.63–1.46 (m, 2H), 0.98 ppm (d, J = 6.9 Hz); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.1 (s), 132.3 (s), 124.0 (d), 68.7 (t), 43.7 (s), 35.9 (d), 29.6 (t), 28.3 (t), 26.3 (t), 23.2 (q), 20.3 (t), 17.9 ppm (q); IR (neat): $\tilde{\nu}$ = 3408, 2957, 1734, 1448, 1397, 1262, 1153 cm^{-1}; GC/MS (EI): *m/z* (%): 194 $[M]^+$ (38), 179 (22), 165 (12), 151 (19), 113 (68), 93 (32), 82 (100), 67 (56), 53 (10), 41 (20); HRMS (EI): *m/z*: calcd for $C_{12}H_{18}O_2$: 194.1307; found: 194.1306.

7-Methyl-9-(4-methylpent-3-enyl)-2-oxaspiro[5.5]undec-8-en-1-one (23f): This compound was purified by column chromatography as a colorless liquid. B.p. 142–145 °C/0.08 mbar; *exo*/*endo* 9:91; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.25–5.22 (m, 1H), 5.12–5.05 (m, 1H), 4.40–4.29 (m, 2H), 2.38–2.29 (m, 1H), 2.22–1.86 (m, 10H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55–1.46 (m, 1H), 1.01 ppm (d, J = 7.2 Hz, 3H); *endo* isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.3 (s), 135.9 (s), 131.4 (s), 124.1 (d), 123.8 (d), 68.7 (t), 43.8 (s), 37.2 (t), 35.6 (d), 29.3 (t), 28.0 (t), 26.4 (t), 25.7 (q), 24.5 (t), 20.3 (t), 18.0 (q), 17.7 ppm (q); IR (neat): $\tilde{\nu}$ = 2962, 1731, 1448, 1261, 1135, 1100, 976 cm^{-1}; GC/MS (EI): *m/z* (%): 262 $[M]^+$ (54), 247 (26), 219 (59), 206 (20), 193 (42), 179 (16), 165 (58), 151 (51), 121 (48), 107 (100), 91 (56), 79 (38), 69 (49), 55 (12), 41 (63); HRMS (EI): *m/z*: calcd for $C_{17}H_{26}O_2$: 262.1933; found: 262.1927.

5′,6′-Dihydrospiro[bicyclo[2.2.1]hept-5-ene-2,3′-pyran]-2′(4′*H*)-one (23g):[31] This compound was purified by distillation under reduced pressure as a colorless liquid; *exo*/*endo* 82:18; b.p. 105–107 °C/0.10 mbar; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.29–6.26 (m, 1H), 6.11–6.07 (m, 1H), 4.35–4.31 (m, 2H), 3.06 (s, 1H), 2.91 (1H), 2.41–2.36 (m, 1H), 2.00–1.90 (m, 2H), 1.83–1.75 (m, 1H), 1.70–1.66 (m, 2H), 1.48–1.45 (m, 1H), 0.99 ppm (dd, J = 2.6 Hz, 11.6 Hz); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.5 (s), 139.2 (d), 133.7 (d), 69.2 (t), 50.5 (d), 48.9 (s), 48.0 (t), 42.5 (d), 38.9 (t), 31.0 (t), 21.0 ppm (t). IR (neat): $\tilde{\nu}$ = 2971, 1728, 1457, 1398, 1266, 1151, 1098, 728 cm^{-1}; GC/MS (EI): *m/z* (%): 178 $[M]^+$ (3), 113 (100), 95 (28), 66 (68), 39 (13).

Acknowledgements

We are grateful to Dr. Gerhard Brunner for multi-dimensional NMR measurements and to Dr. Peter Gygax, Dr. Samuel Derrer, Prof. Dr. Georg Fráter, and Prof. Dawei Ma for fruitful discussions and proofreading of the manuscript.

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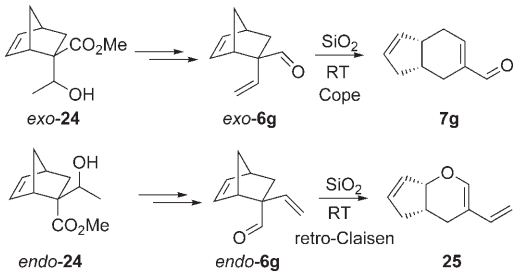

[21] Odor descriptions of compounds **6**, **7**, **19**, **20**, **22**, and **23** are given in the Experimental Section.

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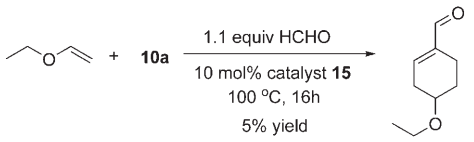

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Received: January 24, 2008
Published online: April 30, 2008

