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2*H*-Pyran-2-ones from *Trichoderma viride* and *Trichoderma asperellum*

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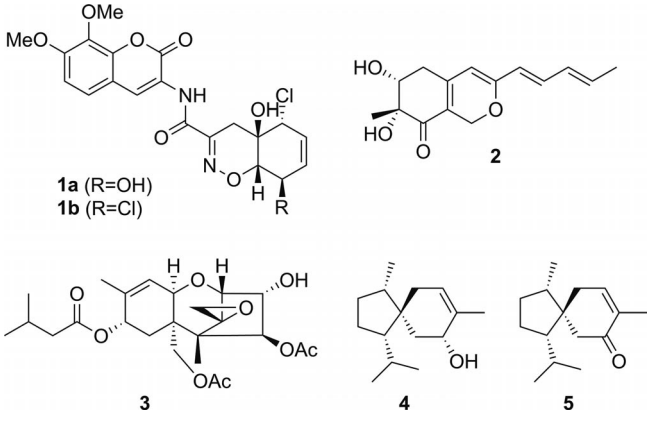
Volatiles emitted by the soil fungi *Trichoderma viride* 272 and *Trichoderma asperellum* 328 were collected by using the closed loop stripping analysis (CLSA) headspace technique, and the obtained extracts were analysed by GC/MS. Several alkyl- and alkenyl-2*H*-pyran-2-ones, including known compounds 6-pentyl-2*H*-pyran-2-one and (*E*)-6-(pent-1-en-1-yl)-2*H*-pyran-2-one, and the new derivatives (*E*)-6-(pent-2-en-1-yl)-2*H*-pyran-2-one, 6-propyl-2*H*-pyran-2-one, and 6-heptyl-2*H*-pyran-2-one were found. The alkenyl derivative (*E*)-6-(hept-1-en-1-yl)-2*H*-pyran-2-one, previously tentatively identified from a marine *Botrytis* by MS analysis, was also detected. All alkenyl pyrones were synthesised by using a reported Stille coupling followed by lactonisation, whereas the alkylated pyrones were obtained through a reported synthetic approach by radical bromination of 5-alkylpent-2-en-5-olides and dehydrobromination. Because the yields in both cases were not satisfactory and fell a long way short of the yields reported for similar compounds, all compounds were synthesised again using a gold-catalysed coupling of terminal alkynes with propiolic acid recently developed by Schreiber and co-workers, giving high yields in all cases. A comparison of the synthetic methods is given.

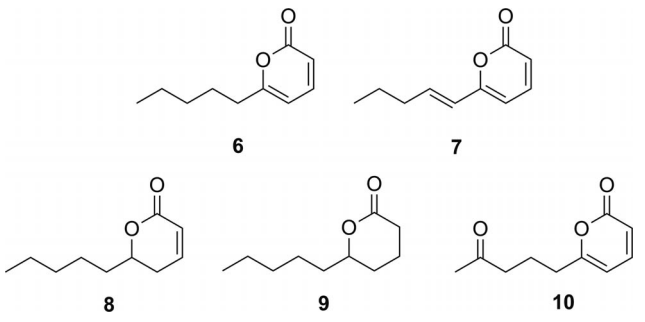
Introduction

Fungi of the genus *Trichoderma* occur on cellulose material, in soil, and root or foliar systems of plants. They are known to promote plant growth and development and are used in agriculture as biocontrol agents, taking advantage of their activity against phytopathogenic microorganisms.[1,2] The fungi exhibit cytotoxicity towards plant pathogens either by the excretion of hydrolytic cell-wall degrading enzymes such as chitinases[3] or release of a wide range of secondary metabolites with antibiotic properties,[4] exemplified by the structures of the cytotoxic compounds trichodermamides A (**1a**) and B (**1b**) from *Trichoderma virens* (Scheme 1).[5] The heptaketide harziphilone (**2**) also exhibits cytotoxic activity and was isolated from *Trichoderma harzianum*,[6] whereas the terpenoid T-2 toxine (**3**) from *Trichoderma lignorum* is a representative of the large family of trichothecenes.[7] Upon intoxication, these compounds cause symptoms such as nausea, bloody vomiting, and diarrhea, similar to acute radiation symptoms.[8]

Although these and other examples[4] demonstrate that the diverse secondary metabolism of *Trichoderma* has been intensively explored, little is known about volatiles from *Trichoderma* and fungi in general. Early investigations resulted in the identification of the spirocyclic sesquiterpenes tricho-acorenol (**4**) and acorenone (**5**) in *Trichoderma koningii*.[9] A complex pattern of volatile compounds including alcohols, ketones, lactones, terpenes, and pyrones was recently described from *Trichoderma atroviride*.[10] Pyrones are also known from *Trichoderma*, with 6-pentyl-2*H*-pyran-2-one (**6**) as the first described representative of this class (Scheme 2),[11] followed by the isolation of (*E*)-6-(pent-1-en-



Scheme 1. A selection of secondary metabolites from *Trichoderma*.



Scheme 2. 6-Pentyl-2*H*-pyran-2-one and related compounds from *Trichoderma*.

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1-yl)-2*H*-pyran-2-one (**7**).[12,13] Further known derivatives from *Trichoderma* include the saturated variants massoialactone (**8**) and δ-decanolactone (**9**),[4] and the oxygenated compound 6-(4-oxopent-1-yl)-2*H*-pyran-2-one (viridepyronone, **10**).[14] All these lactones possess inhibitory activity against plant pathogenic fungi such as *Aspergillus*, *Botrytis*, *Rhizoctonia*, *Sclerotinia*, and *Pyrenochaeta*,[13–15] or bacteria such as *Staphylococcus aureus*.[15] Interestingly, **7** is also a known component of the pheromone blend from the red fire ant *Solenopsis invicta*.[16]

Here we report on the volatiles released by two strains of *Trichoderma viride* and *Trichoderma asperellum*. The headspace extracts were mainly composed of pyrones. In addition to a few known compounds, several new derivatives were identified and their structures were unambiguously assigned by comparison to synthetic standards.

Results and Discussion

The volatiles emitted by two strains of *Trichoderma* were trapped on charcoal by using the closed loop stripping analysis (CLSA) technique,[17] and the obtained extracts were analysed by GC/MS. The results of these analyses are summarised in Table S1 of the Supporting Information. Representative gas chromatograms are illustrated in Figure 1, and the identified compounds are shown in Scheme 3. The main component **6** of *T. viride* was readily identified from its mass spectrum (Figure 2, a) and direct comparison to a commercially available standard. Furthermore, trace amounts of the terpenoid geranyl acetone (**16**), the sesquiterpenes (*E*)-β-farnesene, *trans*-α-bergamotene, (*E*)-nerolidol, and zingiberenol, the phenylpropanoid 3,4-dimethoxystyrene (**15**), and the typical fungal compounds oct-1-en-3-ol and octan-3-one were found. Two trace compounds with similar mass spectra to that of **6** were present. The first compound exhibited a molecular ion of *m*/*z* 138 (Figure 2, b), whereas the second volatile was characterised by a molecular ion at *m*/*z* 194 (Figure 2, c). Due to the mass differences of minus and plus 28 atomic mass units compared with **6**, the unknown volatiles were suggested to

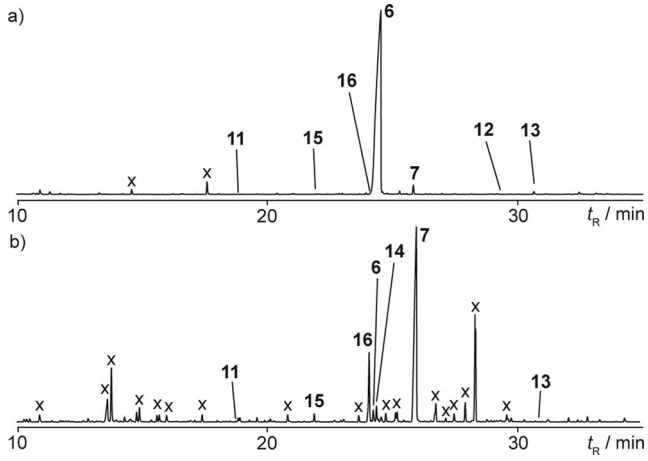
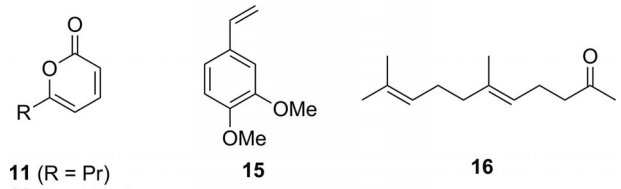


Figure 1. Total ion chromatograms of the headspace extracts obtained from (a) *T. viride*, and (b) *T. asperellum*. Peaks marked by × indicate unidentified compounds or compounds originating from the medium.



11 (R = Pr)
12 (R = Hept)
13 (R = (*E*)-hept-1-enyl)
14 (R = pent-2-enyl)

15 **16**

Scheme 3. Volatiles identified in the headspace extracts from *Trichoderma*.

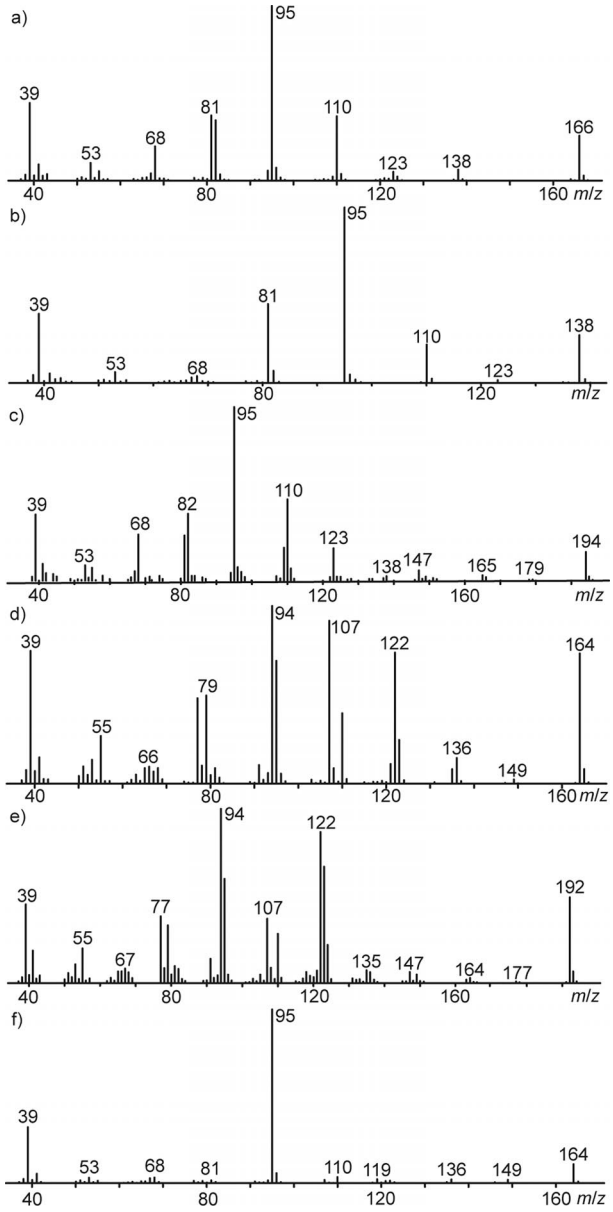


Figure 2. EI mass spectra of (a) 6-pentyl-2*H*-pyran-2-one (**6**), (b) 6-propyl-2*H*-pyran-2-one (**11**), (c) 6-heptyl-2*H*-pyran-2-one (**12**), (d) (*E*)-6-(pent-1-en-1-yl)-2*H*-pyran-2-one (**7**), (e) (*E*)-6-(hept-1-en-1-yl)-2*H*-pyran-2-one (**13**), and (f) tentatively identified (*E*)-6-(pent-2-en-1-yl)-2*H*-pyran-2-one (**14**).

be the two carbon truncated and elongated homologues 6-propyl-2*H*-pyran-2-one (**11**) and 6-heptyl-2*H*-pyran-2-one (**12**), respectively. A synthesis of reference compounds was carried out as described below, which established their identity.

Another trace compound from *T. viride* eluted slightly later (I = 1533) than the main compound **6** (I = 1464) and showed a molecular ion of *m*/*z* 164 in its mass spectrum (Figure 2, d). This compound was assumed to be an unsaturated analogue of **6**. Due to its increased retention index compared with **6**, the structure of (*E*)-6-(pent-1-en-1-yl)-2*H*-pyran-2-one (**7**) was suggested, in agreement with other examples for which extended π systems result in increased GC retention times.[18] The previous identification of this compound from *Trichoderma* lent further support to this idea.[12,13] Another volatile with a similar mass spectrum and a molecular ion of *m*/*z* 192 (Figure 2, e) was assumed to be the previously unreported (*E*)-6-(hept-1-en-1-yl)-2*H*-pyran-2-one (**13**). A synthesis of **7** and **13** was carried out as described below, which confirmed the suggested structures.

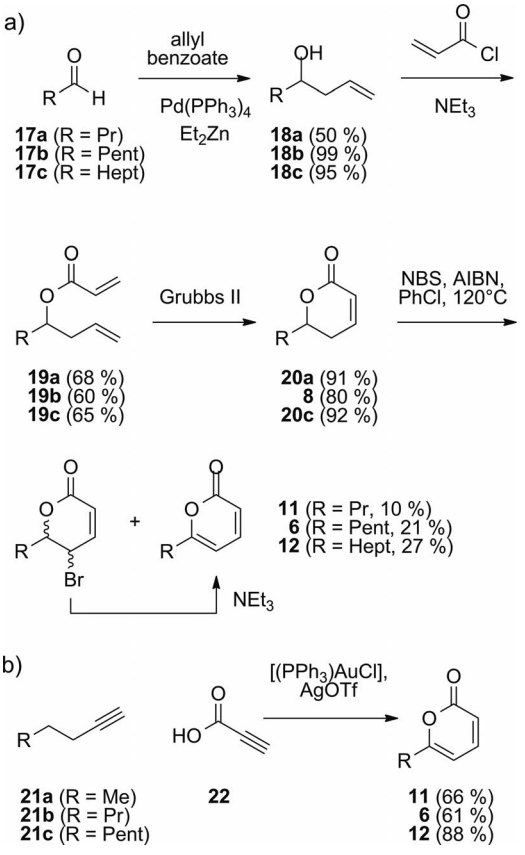
The same analytical method used for the identification of volatiles from *T. viride* was also applied for *T. asperellum*. The gas chromatogram of a representative headspace extract from a *T. asperellum* agar plate culture obtained after four days of growth is shown in Figure 1 (b). The main component emitted by *T. asperellum* was readily identified as **7** by comparison to the synthetic standard. Further pyrone derivatives were represented by two compounds with saturated side chains, **11** and **6**. Geranylacetone (**16**) was also found in large amounts, in addition to traces of **15**.

Furthermore, an unknown compound was present in the headspace extract with a mass spectrum showing a molecular ion at *m*/*z* 164 and a base peak at *m*/*z* 95 (Figure 2, f) that was also seen in the mass spectrum of **6**. This compound was suggested to be an analogue of **6** with an unsaturated side chain and an isomer of the main compound **7** with a different double bond position in the side chain. An attempt to synthesise (*E*)-6-(pent-2-en-1-yl)-2*H*-pyran-2-one (**14**) failed (see below), because this compound was highly sensitive towards isomerisation to **7**. However, immediate GC analysis of the crude reaction product after workup showed the presence of two compounds, one of which was the main product **7**, accompanied by traces of **14**. Comparison of the mass spectrum and retention index to those of the natural product confirmed the identity of the two compounds, but because we were not able to obtain NMR spectroscopic data from the minor synthetic product, the structure assignment of the volatile as (*E*)-6-(pent-2-en-1-yl)-2*H*-pyran-2-one (**14**) remains tentative.

Analysis of the volatiles released by *T. viride* and *T. asperellum* resulted in the identification of a pattern of several alkylated and alkenylated 2*H*-pyran-2-ones with different lengths of the side chains and positions of olefinic double bonds. Compounds **6** and **7** were detected in both headspace extracts, with **6** being the main volatile from *T. viride*, and *T. asperellum* mainly producing **7**. These compounds have been described previously from other *Trichoderma* strains. The high potential of the CLSA headspace method was demonstrated in the identification of some previously unknown 2*H*-pyran-2-one derivatives including **11**–**14**. The aromatic compound 3,4-dimethoxystyrene (**15**) was described previously from liverworts[19] and is a constituent of roasted coffee,[20] but has never been identified from a fungus.

Usually for the identification of natural products large volumes of cultures are extracted, followed by laborious purification steps using chromatographic methods. During such procedures trace compounds are frequently overlooked, especially in the case of volatiles, because they are easily lost during concentration steps. Application of the CLSA headspace method and analysis of the obtained headspace extracts avoids fractioning and, consequently, the danger of losing trace compounds is eliminated. However, unambiguous structural assignment is often only possible by comparison to reference compounds that can be obtained by synthesis.

Known synthetic approaches to 6-pentyl-2*H*-pyran-2-one include a formylation of 3-heptanone to the corresponding hydroxy methylene ketone, followed by Knoevenagel condensation with malonic acid to the keto acid. Treatment with acetic anhydride yields 6-pentyl-2*H*-pyran-2-one.[21] For the synthesis of 6-alkyl-2*H*-pyran-2-ones **6**, **11**, and **12**, a route was developed using a radical bromination of 5-alkylpent-2-en-5-olides followed by dehydrobromination as key steps (Scheme 4, a). These reactions have been described for a successful synthesis of the 2*H*-pyran-2-one



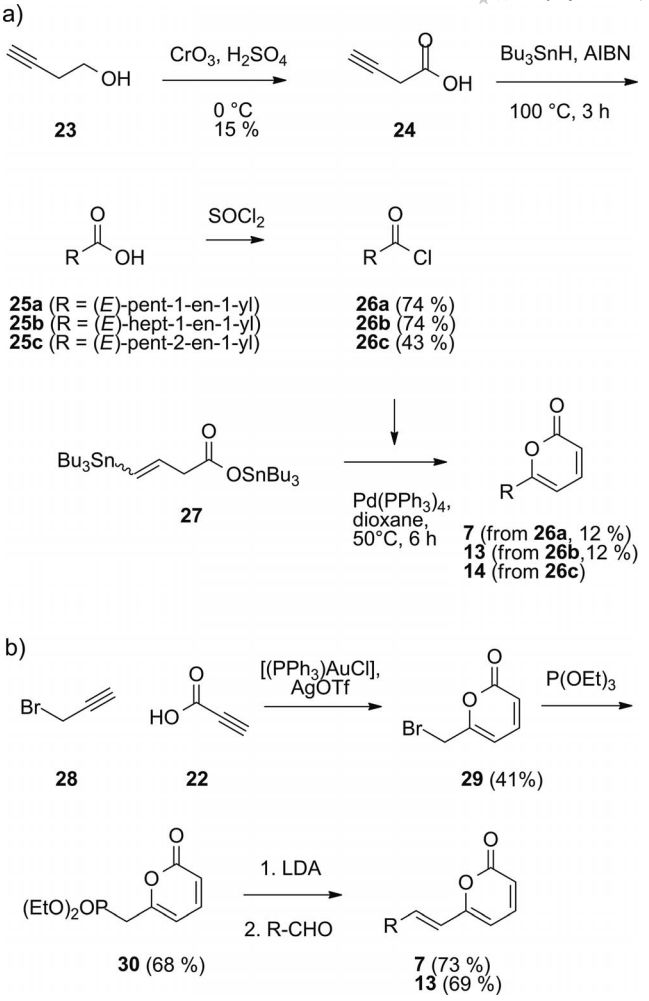
Scheme 4. Synthesis of 6-alkyl-2*H*-pyran-2-ones.

system from pent-2-en-5-olide (R = H).[22] Aldehydes **17a**–**c** were transformed into homoallyl alcohols **18a**–**c** with allyl benzoate, diethylzinc, and $[Pd(PPh_3)_4]$.[23] Treatment with acryloyl chloride in triethylamine gave acrylate esters **19a**–**c**, which were converted into the α,β-unsaturated lactones **20a**, massoialactone (**8**), and **20c** by subsequent ring closing metathesis using the second-generation Grubbs' catalyst.[24] Subsequent radical bromination with *N*-bromosuccinimide (NBS)/ azobisisobutyronitrile (AIBN) in chlorobenzene (120 °C) gave complex mixtures containing two diastereoisomeric bromination products and the desired 6-alkyl-2*H*-pyran-2-ones. Treatment with triethylamine resulted in conversion of the bromo derivatives into the respective 6-alkyl-2*H*-pyran-2-ones **6**, **11**, and **12**, which were subsequently isolated by repeated column chromatography.

After the syntheses of the 6-alkyl-2*H*-pyran-2-ones through the bromination-dehydrobromination methodology had been performed in our laboratory, Schreiber and co-workers published a gold-catalysed coupling reaction of terminal alkynes with propiolic acids to pyrones.[25] Because the yields obtained with the bromination–dehydrobromination approach were unsatisfactory and much lower than reported for the stem system (reported yield 70%), the synthesis of **11**, **6**, and **12** was repeated by using gold-catalysed coupling of propiolic acid with 1-pentyne, 1-heptyne, and 1-nonyne, respectively (Scheme 4, b), resulting in yields of 61–88%, in agreement with published data (65% for **6**).

A synthetic route to (*E*)-6-(pent-1-en-1-yl)-2*H*-pyran-2-ones was developed by Rocca et al. that starts with condensation of (*E*)-but-2-enoyl chloride and trichloroacetyl chloride in triethylamine to yield 6-trichloromethyl-2*H*-pyran-2-one. The trichloromethyl group is subsequently converted into the corresponding carboxylic acid, then into the acid chloride and Rosenmund reduction to the aldehyde; a final Wittig reaction yields **7**.[16] Another method for the preparation of (*E*)-6-(alk-1-en-1-yl)-2*H*-pyran-2-ones reported by Thibonet et al.[26] proceeds through Stille reaction of tributylstannyl 4-(tributylstannyl)but-3-enoate (**27**), which is readily available from homopropargyl alcohol (**23**) by Jones oxidation to but-3-ynoic acid (**24**) and radical stannylation, with an acid chloride (**26**) and subsequent lactonisation (Scheme 5, a). This method was successfully applied in the synthesis of **7** and **13**, albeit in much lower than the reported yield of 52% for **7**, whereas the synthesis of **14** proved to be difficult due to the rapid isomerisation of the product to **7**. However, as discussed above, GC/MS analysis of the crude product gave mass spectroscopic data of the desired compound that served in the tentative identification of **14** in the headspace extract from *T. asperellum*.

Because the syntheses of **7** and **13** were performed using highly toxic tin compounds and the obtained yields were low, another route to these compounds using Schreiber's efficient gold-catalysed method[25] was developed (Scheme 5, b). Compound **29** was obtained by gold-catalysed coupling of propargyl bromide (**28**) with **22** and subsequently converted with $P(OEt)_3$ into diethyl phosphonate **30**. A Horner–Wadsworth–Emmons reaction with butyraldehyde or hexanal yielded **7** and **13** in acceptable yields.



Scheme 5. Synthesis of (*E*)-6-(alken-1-yl)-2*H*-pyran-2-ones.

Conclusions

In summary, the volatiles emitted by the soil fungi *T. viride* and *T. asperellum* were collected using the CLSA technique. GC/MS analyses showed a pattern of structurally related 2*H*-pyran-2-ones released by both fungi. The principle components of *T. viride*, **6**, and of *T. asperellum*, **7**, have previously been reported from other strains of the *Trichoderma* genus. In addition to these known compounds, three novel 2*H*-pyran-2-ones **11**–**13** were detected. Structural proposals were based on their mass spectra and corroborated by the synthesis of reference materials. For the synthesis of the 6-alkyl-2*H*-pyran-2-ones, a method involving radical bromination of α,β-unsaturated δ-lactones and subsequent elimination of hydrogen bromide was developed, whereas the 6-alkenyl-2*H*-pyran-2-ones were prepared by a reported Stille coupling and lactonisation approach.[26] However, the best method for the synthesis of these compounds proved to be the gold-catalysed coupling of propiolic acid with terminal alkynes.[25] Future experiments in our laboratory will include the analysis of further fungal strains for the production of novel volatile compounds.

Experimental Section

Strains, Media, and Growth Conditions: *Trichoderma viride* 272 and *Trichoderma asperellum* 328 were obtained from Gabriele König (University of Bonn, Germany) and cultured in BM medium (biomalt, 20 g L^{-1}). Mycelia were maintained at 28 °C and 200 rpm in liquid medium. After 5 d of growth, agar plates containing BM agar were inoculated with three pieces of mycelium and incubated at 28 °C for 3 d prior to headspace analysis.

Sampling of Volatiles: The volatile organic compounds released by the agar plate cultures were collected by using the CLSA headspace technique.[12] In a closed apparatus containing the agar plates, a circulating air stream was passed through a charcoal filter (Chromtech GmbH, Idstein, Germany, Precision Charcoal Filter, 5 mg) for 24 h. The adsorbed volatiles were eluted with 30 μL of analytically pure dichloromethane. The obtained extracts were analysed by GC/MS and stored at –80 °C.

GC/MS: GC/MS analyses were carried out with an Agilent 7890A gas chromatograph fitted with a HP-5 fused silica capillary column (30 m, 0.25 mm i. d., 0.25 μm film) connected to an Agilent 5975C inert mass selective detector. Conditions were as follows, inlet pressure: 77.1 kPa, He 23.3 mL min^{-1}; injection volume: 2 μL; transfer line: 300 °C; electron energy: 70 eV. The GC was programmed as follows: 5 min at 50 °C, 5 °C min^{-1} to 320 °C, and operated in splitless mode (60 s valve time). The carrier gas was He at 1 mL^{-1}. Retention indices *I* were determined from a homologous series of *n*-alkanes (C_8–C_{32}). Identification of compounds was performed by comparison of mass spectra to library spectra, of retention indices to tabulated data from the literature, and by direct comparison to synthetic standards.

General Synthetic Methods: Chemicals were purchased from Acros Organics (Thermo Fisher Scientific Schwerte, Germany) or Sigma Aldrich GmbH (Steinheim, Germany) and used without further purification. Solvents were purified by distillation and dried according to standard methods. Reactions were performed in flame-dried glassware under nitrogen atmosphere. Thin-layer chromatography was carried out using 0.2 mm precoated plastic sheets Polygram Sil G/UV_{254} (Machery–Nagel). Column chromatography was performed with Merck silica gel 60 (70–200 mesh) and the same solvent mixtures used for the determination of R_f values in TLC. ^{1}H and ^{13}C NMR spectra were determined with a Bruker AMX400 spectrometer (chemical shifts are given in ppm, and *J* values are given in Hz). UV spectra were obtained with a Varian Cary 100 Bio spectrometer and IR spectra were recorded with a Bruker Tensor 27 ATR spectrometer.

Preparation of Homoallyl Alcohols: To a solution of [$Pd(PPh_3)_4$] (0.58 g, 0.5 mmol) in anhydrous THF (30 mL) was added allyl benzoate (1.94 g, 12 mmol), aldehyde **17a–c** (10 mmol), and diethylzinc (1 M in hexane, 24 mmol, 24 mL).[19] The resulting pale-yellow solution was stirred at room temp. for 4 h. The reaction mixture was diluted with ethyl acetate, washed with 2 N HCl, and aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and concentrated. Column chromatography on silica gel yielded the homoallyl alcohols **18** as colourless oils.

Hept-1-en-4-ol (18a): Yield 0.57 g (5.0 mmol, 50%). R_f = 0.43 (hexane/ethyl acetate, 4:1). GC (BPX5): *I* = 873. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 231 (125) nm. IR (ATR): $\tilde{\nu}$ = 3353 (br), 3077 (w), 2959 (w), 2931 (w), 2873 (w), 1641 (w), 1463 (w), 1226 (w), 1122 (w), 1084 (w), 1066 (w), 1015 (w), 995 (s), 957 (w), 911 (s), 868 (w), 844 (w), 744 (w), 640 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 5.88–5.78 (m, 1 H, CH), 5.16–5.14 (m, 1 H, CH_2), 5.13–5.11 (m, 1 H, CH_2), 3.69–3.63 (m, 1 H, CH), 2.34–2.27 (m, 1 H, CH_2), 2.14 (dtt, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.1 Hz, 1 H, CH_2), 1.87 (br. s, 1 H, OH), 1.52–1.30 (m, 4 H, 2× CH_2), 0.94 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9 (CH), 118.0 (CH_2), 70.4 (CH), 41.9 (CH_2), 39.0 (CH_2), 18.8 (CH_2), 14.1 (CH_3) ppm. MS (EI, 70 eV): *m/z* (%) = 114 (1) [M^+], 96 (1), 73 (53), 69 (4), 55 (100).

Non-1-en-4-ol (18b): Yield 1.41 g (9.9 mmol, 99%). R_f = 0.53 (hexane/ethyl acetate, 4:1). GC (BPX5): *I* = 1070. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 230 (213) nm. IR (ATR): $\tilde{\nu}$ = 3351 (w, br), 3077 (w), 2958 (w), 2930 (s), 2862 (w), 1714 (w), 1641 (w), 1463 (w), 1438 (w), 1379 (w), 1271 (w), 1124 (w), 1025 (w), 996 (w), 969 (w), 911 (s), 857 (w), 788 (w), 733 (w), 640 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 5.89–5.78 (m, 1 H, CH), 5.17–5.14 (m, 1 H, CH_2), 5.13–5.11 (m, 1 H, CH_2), 3.68–3.62 (m, 1 H, CH), 2.34–2.28 (m, 1 H, CH_2), 2.19–2.09 (m, 1 H, CH_2), 1.58 (br. s, 1 H, OH), 1.49–1.26 (m, 8 H, 4× CH_2), 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9 (CH), 118.0 (CH_2), 70.7 (CH), 41.9 (CH_2), 37.3 (CH_2), 31.9 (CH_2), 25.3 (CH_2), 22.6 (CH_2), 14.0 (CH_3) ppm. MS (EI, 70 eV): *m/z* (%) = 101 (19) [M^+ – vinyl], 83 (56), 71 (7), 55 (87), 41 (100).

Undec-1-en-4-ol (18c): Yield 1.62 g (9.5 mmol, 95%). R_f = 0.53 (hexane/ethyl acetate, 5:1). GC (BPX5): *I* = 1278. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 230 (122) nm. IR (ATR): $\tilde{\nu}$ = 3349 (w, br), 3077 (w), 2956 (w), 2925 (vs), 2855 (vs), 1641 (w), 1464 (w), 1126 (w), 1043 (w), 994 (w), 912 (vs), 722 (w), 641 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 5.89–5.78 (m, 1 H, CH), 5.17–5.14 (m, 1 H, CH_2), 5.12–5.11 (m, 1 H, CH_2), 3.66–3.61 (m, 1 H, CH), 2.34–2.27 (m, 1 H, CH_2), 2.18–2.10 (m, 1 H, CH_2), 1.64 (br. s, 1 H, OH), 1.50–1.24 (m, 12 H, 6× CH_2), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9 (CH), 118.0 (CH_2), 70.7 (CH), 41.9 (CH_2), 36.8 (CH_2), 31.8 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 25.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3) ppm. MS (EI, 70 eV): *m/z* (%) = 170 (1) [M^+], 129 (17), 111 (19), 83 (6), 69 (100), 55 (39), 41 (54).

Preparation of Homoallyl Acrylates: To an ice-cold solution of homoallyl alcohol **18a–c** (5.00 mmol) in anhydrous CH_2Cl_2 (50 mL) and triethylamine (40 mmol, 4.0 g) was added dropwise acryloyl chloride (32 mmol, 2.88 g).[20] The reaction mixture was stirred overnight and warmed to room temperature. The excess of acryloyl chloride was quenched by the addition of satd. $NaHCO_3$ solution. The resulting mixture was extracted three times with Et_2O. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel to yield the esters **24** as colourless liquids.

Hept-1-en-4-yl Acrylate (19a): Yield 571 mg (3.40 mmol, 68%). R_f = 0.37 (pentane/diethyl ether, 20:1). GC (BPX5): *I* = 1088. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 228 (242) nm. IR (ATR): $\tilde{\nu}$ = 3080 (w), 2961 (w), 2937 (w), 2875 (w), 1722 (vs), 1640 (w), 1405 (s), 1295 (s), 1270 (s), 1190 (vs), 1128 (w), 1046 (s), 985 (s), 964 (s), 915 (s), 809 (s), 674 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.39 (dd, $^3J_{H,H}$ = 17.3, $^2J_{H,H}$ = 1.6 Hz, 1 H, CH_2), 6.39 (dd, $^3J_{H,H}$ = 17.3, $^2J_{H,H}$ = 1.6 Hz, 1 H, CH_2), 6.11 (dd, $^3J_{H,H}$ = 17.3, 10.3 Hz, 1 H, CH), 5.80 (dd, $^3J_{H,H}$ = 10.4, $^2J_{H,H}$ = 1.6 Hz, 1 H, CH_2), 5.76 (ddt, $^3J_{H,H}$ = 17.1, 10.1, 7.1 Hz, 1 H, CH), 5.12–4.97 (m, 3 H, CH, CH_2), 2.35 (m, 2 H, CH_2), 1.62–1.50 (m, 2 H, CH_2), 1.44–1.25 (m, 2 H, CH_2), 0.91 (t, $^3J_{H,H}$ = 7.3, $^1J_{C,H}$ = 124.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9 (C), 133.7 (CH), 130.3 (CH_2), 128.9 (CH), 117.6 (CH_2), 73.3 (CH), 38.6 (CH_2), 35.7 (CH_2), 18.5 (CH_2), 13.9 (CH_3) ppm. MS (EI, 70 eV): *m/z* (%) = 127 (22) [M^+ – allyl], 96 (4), 81 (5), 67 (4), 55 (100), 41 (19).

Non-1-en-4-yl Acrylate (19b): Yield 592 mg (3.02 mmol, 60%). R_f = 0.59 (hexane/ethyl acetate, 10:1). GC (BPX5): I = 1262. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 228 (397) nm. IR (ATR): $\tilde{\nu}$ = 3079 (w), 2956 (w), 2931 (w), 2861 (w), 1722 (vs), 1640 (s), 1620 (w), 1464 (w), 1405 (s), 1295 (s), 1270 (s), 1190 (vs), 1128 (w), 1046 (s), 985 (s), 965 (s), 916 (s), 809 (s), 728 (w), 650 (w), 552 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.39 (dd, $^2J_{H,H}$ = 1.6, $^3J_{H,H}$ = 17.3 Hz, 1 H, CH_2), 6.11 (dd, $^3J_{H,H}$ = 10.3, 17.3 Hz, 1 H, CH), 5.80 (dd, $^2J_{H,H}$ = 1.6, $^3J_{H,H}$ = 10.3 Hz, 1 H, CH_2), 5.76 (ddt, $^3J_{H,H}$ = 17.1, 10.1, 7.0 Hz, 1 H, CH), 5.10–5.03 (m, 2 H, CH_2), 5.00 (quint, $^3J_{H,H}$ = 6.1 Hz, 1 H, CH), 2.38–2.32 (m, 2 H, CH_2), 1.64–1.53 (m, 2 H, CH_2), 1.38–1.23 (m, 6 H, 3× CH_2), 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9 (C), 133.7 (CH), 130.3 (CH_2), 128.9 (CH), 117.6 (CH_2), 73.6 (CH), 38.6 (CH_2), 33.5 (CH_2), 31.6 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 155 (58) [M$^+$ – allyl], 124 (12), 96 (9), 83 (56), 73 (10), 67 (30), 55 (100), 41 (96).

Undec-1-en-4-yl Acrylate (19c): Yield 730 mg (3.26 mmol, 65%). R_f = 0.59 (hexane/ethyl acetate, 10:1). GC (BPX5): I = 1458. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 228 (437) nm. IR (ATR): $\tilde{\nu}$ = 2927 (s), 2857 (w), 1723 (s), 1640 (s), 1463 (w), 1405 (s), 1295 (w), 1269 (s), 1191 (vs), 1046 (s), 984 (s), 964 (s), 915 (s), 808 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.38 (dd, $^2J_{H,H}$ = 1.5, $^3J_{H,H}$ = 17.3 Hz, 1 H, CH_2), 6.10 (dd, $^3J_{H,H}$ = 10.4, 17.3 Hz, 1 H, CH), 5.80 (dd, $^2J_{H,H}$ = 1.5, $^3J_{H,H}$ = 10.4 Hz, 1 H, CH_2), 5.76 (ddt, $^3J_{H,H}$ = 17.2, 10.1, 7.0 Hz, 1 H, CH), 5.10–5.03 (m, 2 H, CH_2), 5.00 (quint, $^3J_{H,H}$ = 6.2 Hz, 1 H, CH), 2.37–2.32 (m, 2 H, CH_2), 1.63–1.56 (m, 2 H, CH_2), 1.43–1.19 (m, 10 H, 5× CH_2), 0.87 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9 (C), 133.7 (CH), 130.3 (CH_2), 128.9 (CH), 117.6 (CH_2), 73.6 (CH), 38.6 (CH_2), 33.6 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 25.3 (CH_2), 22.6 (CH_2), 14.0 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 183 (5) [M$^+$ – allyl], 152 (3), 111 (39), 96 (3), 81 (5), 67 (11), 55 (100), 41 (34).

Preparation of 5,6-Dihydro-2*H*-pyran-2-ones: Acrylates **19a**–**c** (2.00 mmol) were dissolved in toluene (40 mL). Grubbs' second-generation catalyst (20 mg, 0.02 mmol) was added and the reaction mixture was heated to reflux for 1.5 h. After cooling to room temperature the solvent was removed under reduced pressure. Purification of the residue by column chromatography on silica gel yielded the 5,6-dihydro-2*H*-pyran-2-ones as colourless oils.

6-Propyl-5,6-dihydro-2*H*-pyran-2-one (20a): Yield 255 mg (1.82 mmol, 91%). R_f = 0.20 (hexane/ethyl acetate, 3:1). GC (BPX5): I = 1302. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 228 (1514) nm. IR (ATR): $\tilde{\nu}$ = 2960 (w), 2935 (w), 2875 (w), 1714 (vs), 1466 (w), 1385 (s), 1243 (vs), 1159 (w), 1114 (s), 1069 (s), 1027 (s), 960 (w), 920 (w), 813 (vs), 744 (s), 662 (w), 575 (w), 553 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.91–6.87 (m, 1 H, CH), 6.03 (ddd, $^3J_{H,H}$ = 9.7, $^4J_{H,H}$ = 2.3, 1.5 Hz, 1 H, CH), 4.47–4.40 (m, 1 H, CH), 2.38–2.29 (m, 2 H, CH_2), 1.85–1.76 (m, 1 H, CH_2), 1.67–1.40 (m, 3 H, 2× CH_2), 0.96 (t, $^3J_{H,H}$ = 7.3, $^1J_{C,H}$ = 125.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5 (C), 145.0 (CH), 121.4 (CH), 77.7 (CH), 36.8 (CH_2), 29.3 (CH_2), 18.0 (CH_2), 13.7 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 140 (1) [M$^+$], 122 (2), 112 (3), 97 (99), 68 (100), 55 (6), 41 (46).

6-Pentyl-5,6-dihydro-2*H*-pyran-2-one (8): Yield 269 mg (1.60 mmol, 80%). R_f = 0.30 (hexane/ethyl acetate, 3:1). GC (BPX5): I = 1516. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 228 (1161), 355 (16) nm. IR (ATR): $\tilde{\nu}$ = 2931 (s), 2868 (w), 1715 (vs), 1464 (w), 1385 (s), 1248 (vs), 1156 (w), 1118 (s), 1058 (s), 1037 (s), 954 (s), 813 (vs), 729 (w), 662 (w), 552 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.92–6.86 (m, 1 H, CH), 6.01 (ddd, $^3J_{H,H}$ = 9.8, $^4J_{H,H}$ = 2.1, 1.6 Hz, 1 H, CH), 4.47–4.38 (m, 1 H, CH), 2.42–2.25 (m, 2 H, 2× CH_2), 1.86–1.74 (m, 1 H, CH_2), 1.70–1.37 (m, 3 H, 2× CH_2), 1.37–1.29 (m, 4 H, 2× CH_2), 0.90 (t, $^3J_{H,H}$ = 6.8, $^1J_{C,H}$ = 124.7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6 (C), 145.0 (CH), 121.3 (CH), 78.0 (CH), 34.8 (CH_2), 31.5 (CH_2), 29.3 (CH_2), 24.4 (CH_2), 22.4 (CH_2), 13.9 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 168 (1) [M$^+$], 150 (1), 139 (2), 122 (3), 108 (7), 97 (100), 68 (78), 55 (9), 41 (50).

6-Heptyl-5,6-dihydro-2*H*-pyran-2-one (20c): Yield 361 mg (1.84 mmol, 92%). R_f = 0.35 (hexane/ethyl acetate, 3:1). GC (BPX5): I = 1729. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 229 (1203) nm. IR (ATR): $\tilde{\nu}$ = 3358 (w, br), 3077 (w), 2958 (w), 2930 (s), 1641 (w), 1464 (w), 1437 (w), 1124 (w), 1124 (w), 1025 (w), 995 (w), 911 (s), 731 (w), 639 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.89 (ddd, $^3J_{H,H}$ = 9.7, 5.4, 3.2 Hz, 1 H, CH), 6.01 (ddd, $^3J_{H,H}$ = 9.7, $^4J_{H,H}$ = 2.2, 1.4 Hz, 1 H, CH), 4.42 (m, 1 H, CH), 2.40–2.26 (m, 2 H, CH_2), 1.84–1.74 (m, 1 H, CH_2), 1.71–1.60 (m, 1 H, CH_2), 1.55–1.36 (m, 2 H, CH_2), 1.36–1.28 (m, 8 H, 4× CH_2), 0.88 (t, $^3J_{H,H}$ = 6.7, $^1J_{C,H}$ = 124.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5 (C), 145.0 (CH), 121.3 (CH), 78.0 (CH), 34.8 (CH_2), 31.7 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 24.7 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 196 (1) [M$^+$], 168 (1), 150 (2), 136 (4), 125 (2), 111 (3), 97 (100), 86 (4), 81 (5), 68 (67), 55 (11).

Preparation of 6-Alkyl-2*H*-pyran-2-ones: To a solution of the respective 5,6-dihydro-2*H*-pyran-2-one **20a**, **8**, or **20c** (1.0 mmol) in chlorobenzene (5 mL), was added NBS (196 mg, 1.1 mmol) and a catalytic amount of AIBN (1 mg). The resulting mixture was heated to 120 °C for 8 h. After cooling to room temperature, the precipitated solids were filtered off and washed with $CHCl_3$. The combined organic portions were washed with saturated aqueous $NaSO_3$ solution and brine, dried ($MgSO_4$), and concentrated under reduced pressure. Purification by column chromatography on silica gel gave an inseparable mixture of the respective 6-alkyl-2*H*-pyran-2-one and two diastereomeric 5-bromo-6-alkyl-5,6-dihydro-2*H*-pyran-2-ones. This mixture was heated to reflux in triethylamine (5 mL) for 4 d. The precipitate was removed by filtration and washed with petane. The filtrate was diluted with pentane, washed with 2 N HCl to remove triethylamine, and extracted three times with pentane. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel yielded the desired 6-alkyl-2*H*-pyran-2-ones as pale-yellow liquids. Due to the volatility of the products, the use of solvents with low boiling points (pentane, diethyl ether) during the workup procedure and chromatographic purification is strongly recommended.

6-Propyl-2*H*-pyran-2-one (11): Yield 14 mg (0.10 mmol, 10%). R_f = 0.21 (pentane/diethyl ether, 5:1). GC (HP-5): I = 1253. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 228 (1766), 300 (2855) nm. IR (ATR): $\tilde{\nu}$ = 3402 (w), 3088 (w), 2965 (w), 2877 (w), 1699 (vs), 1629 (s), 1554 (s), 1465 (w), 1381 (w), 1208 (w), 1173 (w), 1108 (w), 1085 (w), 990 (w), 908 (w), 801 (s), 731, 554 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.26 (dd, $^3J_{H,H}$ = 9.3, 6.5 Hz, 1 H, CH), 6.16 (dd, $^3J_{H,H}$ = 9.2, $^4J_{H,H}$ = 0.5 Hz, 1 H, CH), 5.99 (dd, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 0.8 Hz, 1 H, CH), 2.47 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 1.60 (sext, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 0.97 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5 (C), 162.9 (C), 143.8 (CH), 113.1 (CH), 102.8 (CH), 35.7 (CH_2), 20.2 (CH_2), 13.4 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 138 (38) [M$^+$], 110 (27), 95 (100), 81 (47), 39 (35).

6-Pentyl-2*H*-pyran-2-one (6): Yield 35 mg (0.21 mmol, 21%). R_f = 0.22 (pentane/diethyl ether, 5:1). GC (HP-5): I = 1468. UV/Vis

(CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 229 (1544), 299 (1620) nm. IR (ATR): $\tilde{\nu}$ = 2957 (s), 2931 (s), 2871 (w), 1704 (vs), 1629 (s), 1554 (w), 1467 (w), 1406 (w), 1379 (w), 1209 (w), 1173 (w), 1092 (w), 984 (w), 937 (w), 804 (w), 729 (w), 560 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.26 (dd, $^3J_{H,H}$ = 6.5, 9.4 Hz, 1 H, CH), 6.15 (dd, $^3J_{H,H}$ = 9.3, $^4J_{H,H}$ = 0.6 Hz, 1 H, CH), 5.97 (dd, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 0.8 Hz, 1 H, CH), 2.48 (t, $^3J_{H,H}$ = 7.6, $^1J_{C,H}$ = 128.8 Hz, 2 H, CH_2), 1.72–1.63 (m, 2 H, CH_2), 1.36–1.24 (m, 4 H, 2× CH_2), 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8 (C), 162.9 (C), 143.7 (CH), 102.5 (CH), 33.8 (CH_2), 31.5 (CH_2), 26.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 166 (34) [M$^+$], 138 (8), 123 (6), 110 (39), 95 (100), 81 (36), 67 (17), 53 (7), 39 (29).

6-Heptyl-α-pyrone (12): Yield 52 mg (0.27 mmol, 27%). R_f = 0.25 (pentane/diethyl ether, 5:1). GC (HP-5): *I* = 1677. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 228 (2364), 300 (5170) nm. IR (ATR): $\tilde{\nu}$ = 2955 (w), 2926 (s), 2856 (s), 1727 (vs), 1634 (s), 1557 (s), 1463 (s), 1378 (w), 1356 (w), 1256 (w), 1211 (w), 1211 (w), 1084 (s), 979 (w), 857 (w), 797 (s), 549 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.26 (dd, $^3J_{H,H}$ = 9.3, 6.4 Hz, 1 H, CH), 6.15 (dd, $^3J_{H,H}$ = 9.3, $^4J_{H,H}$ = 0.8 Hz, 1 H, CH), 5.97 (dd, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 0.8 Hz, 1 H, CH), 2.48 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 1.70–1.62 (m, 2 H, CH_2), 1.38–1.20 (m, 8 H, 4× CH_2), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8 (C), 162.9 (C), 143.7 (CH), 113.0 (CH), 102.6 (CH), 33.8 (CH_2), 31.6 (CH_2), 28.89 (CH_2), 28.87 (CH_2), 26.8 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 194 (16) [M$^+$], 165 (5), 149 (5), 137 (5), 123 (21), 110 (32), 95 (100), 82 (50), 68 (18), 53 (19), 41 (41).

Preparation of 6-Alkyl-2*H*-pyran-2-ones and 6-(Bromomethyl)-2*H*-pyran-2-one by Gold Catalysis:[25] In a sealed tube, propiolic acid (95 mg, 1.36 mmol), the respective alkyne **21a**–**c** or **28** (6.8 mmol, 5 equiv.) and [(PPh_3)AuCl] (0.068 mmol, 0.05 equiv.) were dissolved in CH_2Cl_2 (6 mL). After addition of AgOTf (0.068 mmol, 0.05 equiv.), the tube was immediately sealed and heated to 50 °C for 8–12 h. The reaction was then stopped and the solvent was evaporated. Column chromatography of the residue on silica gel yielded the pure 2*H*-pyran-2-ones. Spectroscopic data of **6**, **11**, and **12** were the same as noted above.

6-(Bromomethyl)-2*H*-pyran-2-one (29): Yield 105 mg (0.56 mmol, 41%). R_f = 0.21 (pentane/diethyl ether, 1:2). GC (BPX5): *I* = 1437. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 300 (6788) nm. IR (ATR): $\tilde{\nu}$ = 3077 (w), 3045 (w), 2985 (w), 1717 (s), 1631 (s), 1552 (s), 1444 (w), 1408 (w), 1356 (m), 1243 (m), 1208 (m), 1178 (m), 1092 (s), 983 (m), 918 (m), 874 (m), 849 (m), 802 (s), 724 (m), 678 (m), 562 (s), 546 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.30 (dd, $^3J_{H,H}$ = 9.2, 6.8 Hz, 1 H, CH), 6.31–6.28 (m, 2 H, 2× CH), 4.17 (s, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1 (C), 159.3 (C), 142.8 (CH), 116.2 (CH), 104.8 (CH), 26.7 (CH_2) ppm. MS (EI, 70 eV): *m*/*z* (%) = 188 (1) [M$^+$], 162 (2), 146 (3), 109 (18), 95 (60), 81 (90), 79 (27), 62 (14), 53 (73), 42 (34), 39 (100).

Preparation of Alkenyl Pyrones: As reported by Thibonnet et al.,[26] to a solution of freshly distilled acid chloride **26a**–**c** (15 mmol) in abs. dioxane (50 mL), was added dropwise tributylstannyl 4-(tributylstannyl)but-3-enoate (6.64 g, 10 mmol), followed by the addition of tetrakis(triphenylphosphane)palladium(0) (5 mol-%, 570 mg). After stirring for 6 h at 50 °C, the mixture was hydrolysed by addition of a saturated solution of ammonium chloride, and extracted with diethyl ether. The organic layer was washed with brine, dried, and concentrated under reduced pressure. Purification by column chromatography on silica gel containing 10% potassium fluoride yielded the desired alkenyl pyrones **7** and **13** as yellow liquids. The synthesis of **14** was unsuccessful due to the rapid isomerisation of this compound to **13** under the reaction and/or workup conditions. However, the reaction product contained traces of a compound tentatively identified as **14** in addition to the main product **13**.

(*E*)-6-(Pent-1-en-1-yl)-2*H*-pyran-2-one (7): Yield 0.21 g (1.3 mmol, 12%). R_f = 0.18 (hexane/ethyl acetate, 5:1). GC (HP-5): *I* = 1533. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.29 (dd, $^3J_{H,H}$ = 6.8, 9.4 Hz, 1 H, CH), 6.70 (dt, $^3J_{H,H}$ = 7.2, 15.6 Hz, 1 H, CH), 6.17 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, CH), 6.03–5.97 (m, 2 H, 2× CH_2), 2.20 (dq, $^3J_{H,H}$ = 7.3, $^4J_{H,H}$ = 1.5 Hz, 2 H, CH_2), 1.50 (sext, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 0.94 (t, $^3J_{H,H}$ = 7.4, $^1J_{C,H}$ = 125.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0 (C), 159.7 (C), 143.8 (CH), 139.6 (CH), 113.6 (CH), 103.0 (CH), 34.8 (CH_2), 21.8 (CH_2), 13.6 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 164 (92) [M$^+$], 136 (13), 122 (83), 109 (45), 107 (97), 94 (100), 79 (44), 77 (43), 66 (8), 55 (21), 50 (7), 39 (55).

(*E*)-6-(Hept-1-en-1-yl)-2*H*-pyran-2-one (13): Yield 0.232 g (1.2 mmol, 12%). R_f = 0.24 (hexane/ethyl acetate, 8:1). GC (HP-5): *I* = 1744. UV/Vis (CH_2Cl_2): λ_{max} (ε, L mol^{-1} cm^{-1}) = 231 (5531), 325 (4210) nm. IR (ATR): $\tilde{\nu}$ = 3434 (w), 2957 (w), 2928 (s), 2858 (w), 1726 (vs), 1648 (s), 1537 (s), 1461 (w), 1095 (s), 974 (w), 908 (w), 878 (w), 796 (s), 728 (w), 549 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.29 (dd, $^3J_{H,H}$ = 9.3, 6.7 Hz, 1 H, CH), 6.71 (dt, $^3J_{H,H}$ = 15.6, 7.2 Hz, 1 H, CH), 6.17 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, CH), 5.99 (dt, $^3J_{H,H}$ = 15.6, $^4J_{H,H}$ = 1.5 Hz, 1 H, CH), 5.97 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, CH), 2.22 (dt, $^4J_{H,H}$ = 1.4, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 1.51–1.42 (m, 2 H, CH_2), 1.37–1.25 (m, 4 H, 2× CH_2), 0.92–0.87 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0 (C), 159.7 (C), 143.8 (CH), 139.9 (CH), 121.5 (CH), 113.6 (CH), 103.0 (CH), 32.7 (CH_2), 31.3 (CH_2), 28.3 (CH_2), 22.4 (CH_2), 13.9 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 192 (31) [M$^+$], 164 (2), 147 (4), 135 (8), 122 (50), 107 (35), 94 (100), 77 (57), 66 (10), 39 (75).

(*E*)-6-(Pent-2-en-1-yl)-2*H*-pyran-2-one (14): Yield <1% determined by GC analysis. GC (HP-5): *I* = 1468. MS (EI, 70 eV): *m*/*z* (%) = 164 (36) [M$^+$], 149 (1), 136 (5), 107 (17), 95 (100), 79 (8), 77 (11), 67 (3), 39 (26).

Diethyl [(2-Oxo-2*H*-pyran-6-yl)methyl]phosphonate (30): Compound **29** (357 mg, 1.9 mmol, 1 equiv.) and triethyl phosphite (316 mg, 1.9 mmol, 1 equiv.) were mixed and heated to 160 °C for 3 h. After cooling to room temperature, the product was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 10:1) to give **30** as a pale-yellow oil, yield 422 mg (1.3 mmol, 68%). R_f = 0.44 (CH_2Cl_2/MeOH, 10:1). IR (ATR): $\tilde{\nu}$ = 3084 (w), 2984 (w), 2911 (w), 1724 (s), 1635 (m), 1554 (m), 1445 (w), 1394 (w), 1356 (w), 1241 (m), 1202 (w), 1163 (w), 1087 (w), 1016 (s), 961 (s), 806 (m), 779 (m), 738 (m), 642 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.30 (dd, $^3J_{H,H}$ = 6.6, 9.4 Hz, 1 H, CH), 6.24–6.21 (m, 2 H, 2× CH), 4.21–4.11 (m, 4 H, 2× CH_2), 3.08 (d, $^2J_{P,H}$ = 22.0 Hz, 2 H, CH_2), 1.34 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2× CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 161.7 (C), 156.8 (d, $^2J_{C,P}$ = 10.0 Hz, C), 143.4 (d, $J_{C,P}$ = 3.7 Hz, CH), 114.0 (d, $J_{C,P}$ = 3.7 Hz, CH), 105.2 (d, $J_{C,P}$ = 8.2 Hz, CH), 62.7 (d, $^2J_{C,P}$ = 6.6 Hz, 2× CH_2), 32.3 (d, $^1J_{C,P}$ = 39.3 Hz, CH_2), 16.2 (d, $^3J_{C,P}$ = 6.0 Hz, 2× CH_3) ppm.

Preparation of Alkenylpyrones by Horner–Wadsworth–Emmons Reaction: To a solution of diisopropylamine (137 mg, 1.36 mmol, 1.05 equiv.) in anhydrous THF (4 mL) was added dropwise at 0 °C a solution of *n*BuLi (1.6 M in hexane, 0.85 mL, 1.36 mmol, 1.05 equiv.), and the reaction mixture was stirred for 45 min at

0 °C. After cooling to –78 °C, phosphonate **30** (0.41 g, 1.28 mmol, 1 equiv.) in anhydrous THF (2 mL) was added dropwise. The mixture was further stirred for 1 h, maintaining the temperature below –20 °C. After cooling to –78 °C, freshly distilled butyric aldehyde (121 mg, 1.68 mmol, 1.3 equiv.) or hexanal (168 mg, 1.68, 1.3 equiv.), respectively, was added. Stirring was continued overnight, while the mixture was allowed to slowly warm to room temperature. The reaction was quenched by the addition of water, followed by extraction with diethyl ether (3 × 20 mL). The combined extracts were dried with $MgSO_4$ and concentrated in vacuo. Purification by column chromatography on silica gel yielded **7** (152 mg, 0.93 mmol, 73%) and **13** (169 mg, 0.88 mmol, 69%) as pale-yellow oils. Spectroscopic data matched those reported above.

Supporting Information (see footnote on the first page of this article): Tabulated results of headspace analyses, synthetic procedures for compounds **24**, **26a**–**c**, and **27**, and copies of ^{1}H and ^{13}C NMR spectra of synthetic compounds.

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