**FULL PAPER**

# Route Scouting towards a Methyl Jasmonate Precursor[1])

by **Christian Chapuis***, **Eric Walther**, **Fabrice Robvieux**, **Claude-Alain Richard**, **Laurent Goumaz**, and **Jean-Yves de Saint Laumer**

*Firmenich SA*, Corporate R&D Division, Synthesis Department, P.O. Box 239, CH-1211 Geneva 8 (phone: +41-22-7803610; fax: +41-22-7803334; e-mail: christian.chapuis@firmenich.com)

Dedicated to Dr. *F. Naef* on the occasion of his 75th birthday

For the synthesis of methyl jasmonate (**1**), *via* the strategic intermediates **3**, **4**, and **6a**, we constructed a synthetic network *via* the diverse intermediates **7** – **10**, **13**, **14**, **17**, and **18**. This allowed us to compare the efficiency of more than 20 novel routes. The most productive pathway with a total yield of 38% is represented by the sequence → **5a** → **5m** → **13b** → **13a** → **6a** → **4** and proceeds *via* sequential bromination, basic elimination, decarbomethoxylation, isomerization, and finally *Lindlar* hydrogenation. The shortest selective way, **2a** → [(*E*,*E*)-**12b**] → **3** → **4**, is a two-pot sequence using a modification of *Naef*'s method, based on an aldol condensation between inexpensive cyclopentanone (**2a**) and crotonaldehyde, with *in situ Corey–Chaykovsky* cyclopropanation under phase transfer conditions. The key intermediate **3** was then simply pyrolyzed to afford **4** in 27% total yield. The alternative isomerization method *via* the six-step deviation → **5a** → **5c** → **8c** → **13a** → **6a** → **4** was longer, although more efficient, with a total yield of 32%. Alternatively, a yield of 34% was obtained *via* the five-step sequence → **5a** → **5c** → **2h** → **2i** → **4**. Another favored six-step pathway, → **5a** → **5c** → **2h** → **17a** → **14a** → **4** afforded the target compound in 35% total yield.

**Introduction.** – On the occasion of the 50th anniversary of the publication of methyl jasmonate (**1**; see the *Scheme*), we have recently presented a particularly short three-step synthesis [1] as well as a review of selected synthetic approaches towards this ubiquitous natural product, which is particularly appreciated by perfumers for its radiant, deep, and sweet floral jasmine scent [2][2]). Several outstanding, industrially feasible approaches have been discussed, such as those of *Büchi* and *Egger* [3], *Naef* and *Decorzant* [4][3]), *Tsuji et al.* [6j][4]), *Lem et al.* [8][5]), *Pauson et al.* [7i][6]), and an optically active version by *Fehr et al.* [6s][6t][12][7]). All these approaches make use of either enone **4** or **6a** as key intermediate. With respect to our own interest in this subject [13], we tried to apply the industrial

[1]) Work presented by *C. C.* at the '6ème Journée Arômes et Parfums 2015' (June 19th, 2015, Nice, France).

[2]) For its bioactivities, as well as those of its epi-stereoisomer and enantiomers, see [2a][2b]. For former reviews, see [2c][2d].

[3]) This elegant approach is based on a double alkylation of cyclopentanone (**2a**) using piperylene dibromide to afford (*E*)-**3** [5], as key intermediate for a thermal homodienyl 1,5-H shift, leading stereoselectively to **4** [3 – 6], after *in situ* equilibration of the diastereomeric mixture to the more favored and reactive *trans* cyclopropane.

[4]) Starting from either diallyl adipate or the commercially available keto ester **2c**, alkylation was performed to generate either **2g** or **5b** as key intermediates for catalytic $Pd^{2+}$-assisted intramolecular decarboxylative dehydrogenation, leading directly to either **4** or **6a** [3][6f][6j][6t][7], resp. For semi-hydrogenation of **6a** to **4** ($H_2$, *Lindlar* catalyst, BuOH, 95%), see [6j].

[5]) For a modified version, based on cascade *Baylis–Hillman*/*Claisen* rearrangement, see [9]. For a more recent application of our method, see [10].

[6]) For the first truly catalytic version of the *Pauson–Khand* reaction, applied to the analogous saturated *Hedione*® (methyl (3-oxo-2-pentylcyclopentyl)-acetate), see [11].

[7]) For a more academic approach based on asymmetric *Michael* addition to **6a**, see [7j]. When **4** was treated in analogy to [7l] (30 mol-equiv. dimethyl malonate, 0.15 mol-equiv. $K_2CO_3$, 0.10 mol-equiv. 1-(anthracen-9-ylmethyl)-9-hydroxycinchonan-1-ium chloride, 0°, 24 h, 88% (52% ee)), the intermediate dimethyl {(1*R*,2*S*)-3-oxo-2-[(2*Z*)-pent-2-en-1-yl]cyclopentyl}propanedioate exhibited the following analytical data [6g][6j]. $[\alpha]_D^{20} = 17.9$ ($c = 1.0$, $CHCl_3$). $^{13}$C-NMR: 218.3 (*s*); 168.8 (*s*); 168.4 (*s*); 134.5 (*d*); 124.4 (*d*); 53.8 (*d*); 52.6 (*q*); 52.5 (*q*); 51.6 (*d*); 40.3 (*d*); 37.5 (*t*); 26.0 (*t*); 24.1 (*t*); 20.6 (*t*); 14.1 (*q*). MS: 282 (2, $M^+$), 219 (8), 193 (7), 191 (8), 154 (10), 150 (83), 135 (20), 133 (100), 121 (32), 117 (11), 109 (18), 107 (15), 101 (22), 95 (20), 93 (20), 91 (20), 83 (31), 79 (30), 77 (17), 69 (14), 67 (18), 59 (20), 55 (22), 53 (14), 41 (26). Further demethoxycarbonylation ($H_2O$, NMP, 160°) quantitatively afforded (+)-**1** as (*E*)/(*Z*) 95:5 mixture. Dimethyl {(1*S*,2*R*)-3-oxo-2-[(2*Z*)-pent-2-en-1-yl]cyclopentyl}propanedioate ($[\alpha]_D^{20} = -26.2$ ($c = 2.2$, $CHCl_3$)) was obtained in 97% yield and 75% ee using *N*-(anthracen-9-ylmethyl)quinidinium chloride. Similarly, under the latter conditions, **6a** afforded the intermediate dimethyl [(1*S*,2*R*)-3-oxo-2-(pent-2-yn-1-yl)cyclopentyl]propanedioate. Yield: 84% (48% ee). $[\alpha]_D^{20} = -28.5$ ($c = 1.5$, $CHCl_3$). $^{13}$C-NMR: 216.8 (*s*); 168.9 (*s*); 168.5 (*s*); 84.0 (*s*); 75.4 (*s*); 53.7 (*d*); 52.6 (*q*); 52.4 (*q*); 50.6 (*d*); 40.2 (*d*); 37.5 (*t*); 24.3 (*t*); 18.0 (*t*); 14.1 (*q*); 12.4 (*t*) [3a][3c][7f][7h]. Demethoxycarbonylation towards methyl [(1*R*,2*R*)-3-oxo-2-(pent-2-yn-1-yl)cyclopentyl]acetate ($[\alpha]_D^{20} = -67.0$ ($c = 1.0$, $CHCl_3$)), followed by monohydrogenation afforded (−)-**1** as (*E*)/(*Z*) 93:7 mixture in 88% total yield. The ee values were determined either on **1** or after perhydrogenation by chiral GC (*Chirasil-DEX*; 25 m × 250 μm × 0.25 μm) [9]. As earlier reported, $K_2CO_3$ may be replaced by KOH. Thus, for example, 2-(2,2-dimethoxyethyl)cyclopent-2-en-1-one (10 mol-equiv. dimethyl malonate, 0.14 mol-equiv. KOH, 0.10 mol-equiv. *N*-(anthracen-9-ylmethyl)quinidinium chloride, toluene, 0°, 20 h, 78% (58% ee). $^{13}$C-NMR: 209.6 (*s*); 160.1 (*d*); 141.2 (*s*); 102.4 (*d*); 53.0 (2*q*); 34.2 (*t*); 28.4 (*t*); 26.8 (*t*)) also gave the opposite enantiomer dimethyl [(1*R*,2*S*)-2-(2,2-dimethoxyethyl)-3-oxocyclopentyl]propanedioate in 82% yield and 57% ee (MS: 302 (1, $M^+$), 270 (5), 207 (8), 175 (7), 155 (19), 139 (80), 138 (100), 123 (11), 109 (18), 107 (10), 101 (24), 95 (27), 89 (25), 79 (14), 75 (59), 59 (19).), using *N*-(anthracen-9-ylmethyl)quininium chloride [8]. We are indebted to Ms. *J. Quintaine* for chiral GC analyses.

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method reported for dehydrohedione by *Crawford et al.* [14] to generate the cyclopentenone functionality *via* cascade epoxidation/rearrangement of an enol derivative. Indeed, since a C≡C bond is relatively stable under mild peracidic conditions, we envisaged, starting from the commercially available methyl keto ester **2b**[8]) and *via* the known intermediates **5a**[9]) [20] and **5c**[10]) [6j][6t][7c][12][19][21a][23] the generation of the known enol acetate **7a** [7c] ($Ac_2O$, TsOH, 74% (81:19 mixture of **7a**/**8a**))[11]). Unfortunately, under acidic conditions ($H_2SO_4$ (cat.), MeOH), the 81:19 mixture of unreported epoxides **9a**/**10** (AcOOH, $NaHCO_3$, $CH_2Cl_2$, 35°, 95%) did not undergo rearrangement to form the endocyclic enone **6a**, but instead eliminated AcOH by abstraction of a more acidic H-atom, to afford the known conjugated ynenone **11a** [6j][7b][7c][12]), contaminated by *ca.* 19% of enone **13a**[13]). An identical result was observed when the intermediate 81:19 mixture of enol acetates **7a**/**8a** was used as starting material for the intermolecular *Tsuji* dehydrogenation (0.07 mol-equiv. $(AcO)_2Pd$, $MeOC(O)OCH_2$-$CH{=}CH_2$, MeCN, 82°, 65%). Finally, when a 7:3 mixture of trimethylsilyl enol ethers **7c**/**8c** ($Me_3SiCl$, $Et_3N$, DMF, 130°, 49% from **5c**)[14]) was treated with *N*-bromosuccinimide (NBS) in THF/$H_2O$ at 6°, the crude intermediate was dehydrohalogenated to afford a 73:27 mixture of **11a**/**6a** ($Li_2CO_3$, pyridine, 100°, 78% [17c]). Alternatively, **5c** was also directly treated successively in the same pot with either $CuCl_2 \cdot 2\,H_2O$, LiCl, DMF, 80°, then $Li_2CO_3$, LiBr, DMF, 80° (54% total yield) [17a] or either $CuCl_2 \cdot 2\,H_2O$ or $FeCl_3 \cdot 6\,H_2O$, EtOH, $H_2O$, 80° (35% total yield) [17d] to afford a 70:30 mixture of **11a**/**6a**. Herein, we describe our attempts to circumvent this drawback.

**Results and Discussion.** – Either the presence or absence, in our reaction mixtures, of enone **13a** reminded us that such monosubstituted cyclopentenones undergo isomerization, under either acidic or basic conditions, to the thermodynamically more stable trisubstituted compounds [27][15]). Thus, our aim was to regioselectively generate an enol derivative at the alternative $\alpha'$-position, as compared to **7**. We studied three possible options. First of all, we generated this regioisomer under kinetic rather than thermodynamic conditions. Alternatively, we also decided to take advantage of the blocked $\alpha$-position offered by intermediate **5a**. Finally, we also considered the possible activation of the $\alpha'$-position by starting from **5d** [22d], readily available from **5a** *via* a thermodynamically driven retro-*Claisen*/*Claisen* cascade reaction (MeONa, xylene, 145°, 94%), *via* the known dimethyl 2-(pent-2-yn-1-yl)hexanedioate intermediate[16]) [23a].

With respect to the first option, the enolate of **5c** (lithium diisopropylamide (LDA), THF, −78°, then either AcCl or $Me_3SiCl$) afforded either **8a** (13%)[17]) or **8c** (71%), respectively. Subsequent *Tsuji* dehydrogenation (0.07 mol-equiv. $(AcO)_2Pd$, $MeOC(O)OCH_2CH{=}CH_2$, MeCN, 82°) afforded enone **13a** in 65 and 56% yield, respectively. This regioisomer was then treated with 0.2 mol-equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene under reflux to afford the desired enone **6a** in 90% yield[18]). This approach was preferred to the alternative treatment of **8c**

[8]) The corresponding ethyl ester is also commercially available.

[9]) Instead of alkylating **2b** using 1-chloropent-2-yne ($K_2CO_3$, acetone, 90%), we preferred a slightly modified version ($K_2CO_3$, acetone, 98%) using pent-2-yn-1-yl methanesulfonate [15], readily obtained in quantitative yield from the corresponding commercially available pent-2-yn-1-ol ($MeSO_2Cl$, $Et_3N$, $CH_2Cl_2$). Attempted alkylation of **2e** [16a][16b], using either $NaNH_2$, THF, EtBr, 20°, or BuLi, THF, tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-one (DMPU), EtBr, −40°, or LDA, THF, DMPU, EtI, −78°, failed [16f]. Neither *Sonogashira* nor *Fu* method, nor an alternative coupling of EtBr with either the already reported **2j** [17b] or its corresponding analogous 2-(prop-2-yn-1-yl)cyclopent-2-en-1-one [6f][18c], or 2-(prop-2-yn-1-yl)cyclohexane-1,3-dione precursor [18] were attempted. In our case, **2j** was obtained *via* decarbomethoxylation of **2e** (LiOH, THF, $H_2O$, 96%). Hydrogenation of **5a** with *Lindlar* catalyst in cyclohexane afforded **2f** in 95% yield. For the ethyl ester analog of **2e**, see [16c–16e]. For ethyl and *tert*-butyl ester analogs of **5a**, see [19].

[10]) Readily obtained by decarbomethoxylation of either **5a** (LiOH, THF, $H_2O$, 20°, 95%) or **5d** (either LiOH, THF, $H_2O$, 20°, 94% or $H_2O$, 150°, 84%). The previously reported hydrogenation of **5c** with *Lindlar* catalyst in cyclohexane afforded the (*Z*)-substituted cyclopentanone **2h** in 95% yield [6j][21]. Furthermore, **5c** is an important synthetic intermediate, earlier used by *Demole* and *Winter*, for a regioselective *Baeyer–Villiger* oxidation directed towards (*Z*)-*δ*-jasmolactone [21a][22]. This capricious reaction was later optimized and exploited by *Nippon Zeon, Ltd.* [22c] and *Firmenich SA*.

[11]) The formation of the corresponding propanoyl analog ($((EtC(O))_2O$, TsOH, 59% (80:20 mixture of regioisomers **7b**/**8b**)) was less efficient.

[12]) Its hydrogenation with *Lindlar* catalyst in cyclohexane afforded stereoisomer (*E*,*Z*)-**12a** in 96% yield. For its stereoisomer (*E*,*E*)-**12a**, see [24a][24b]. The $pK_a$ values of allylic and propargylic H-atoms are estimated to be *ca.* 43 and 36, respectively, on *F. G. Bordwell*'s scale in DMSO [24c][24d].

[13]) *Lindlar* hydrogenation of **13a** in cyclohexane afforded **14a** in 95% yield. For the corresponding (*E*) stereoisomer, see [25]. During the syntheses of **9a**/**10**, the isomerized $\alpha$-acetoylketones **5j**/**5i** were isolated for analytical purpose. Their thermal elimination was not attempted [26], but they were eventually hydrolyzed to their corresponding hydroxy ketones **5h**/**5g**, resp. (LiOH, THF, $H_2O$, >94%). Epoxide **9b** was analogously obtained from **7b** (aq. AcOOH, $NaHCO_3$, toluene, 48%).

[14]) The same ratio of regioisomers was obtained with $Me_3SiCl$, NaI, pyridine, MeCN, 75°, but the conversion was much slower and incomplete.

[15]) For the inspiring preliminary work of *Snowden* (*Firmenich SA*, unpublished results, 1992), see reference 39a in [2a]. For an even more favorable isomerization of analogous $\alpha,\beta$-disubstituted cyclopentenones to the tetrasubstituted compounds, see [28]. The enthalpies of our diverse isomers are as follows: **13a** (5.00 kcal mol$^{-1}$) is less stable than **6a** (1.43 kcal mol$^{-1}$) and (*Z*)-**11a** (3.34 kcal mol$^{-1}$) is less stable than the most favorable (*E*)-**11a** (0.00 kcal mol$^{-1}$). Similarly, **14a** (8.32 kcal mol$^{-1}$) is less stable than **4** (4.55 kcal mol$^{-1}$) and (*Z*,*Z*)-**12a** (2.94 kcal mol$^{-1}$) is less stable than either (*E*,*Z*)-**12a** (1.57 kcal mol$^{-1}$) or the most favorable (*E*,*E*)-**12a** (0.00 kcal mol$^{-1}$). These energies do not take into account the entropic factor, advantaging the less rigid structures.

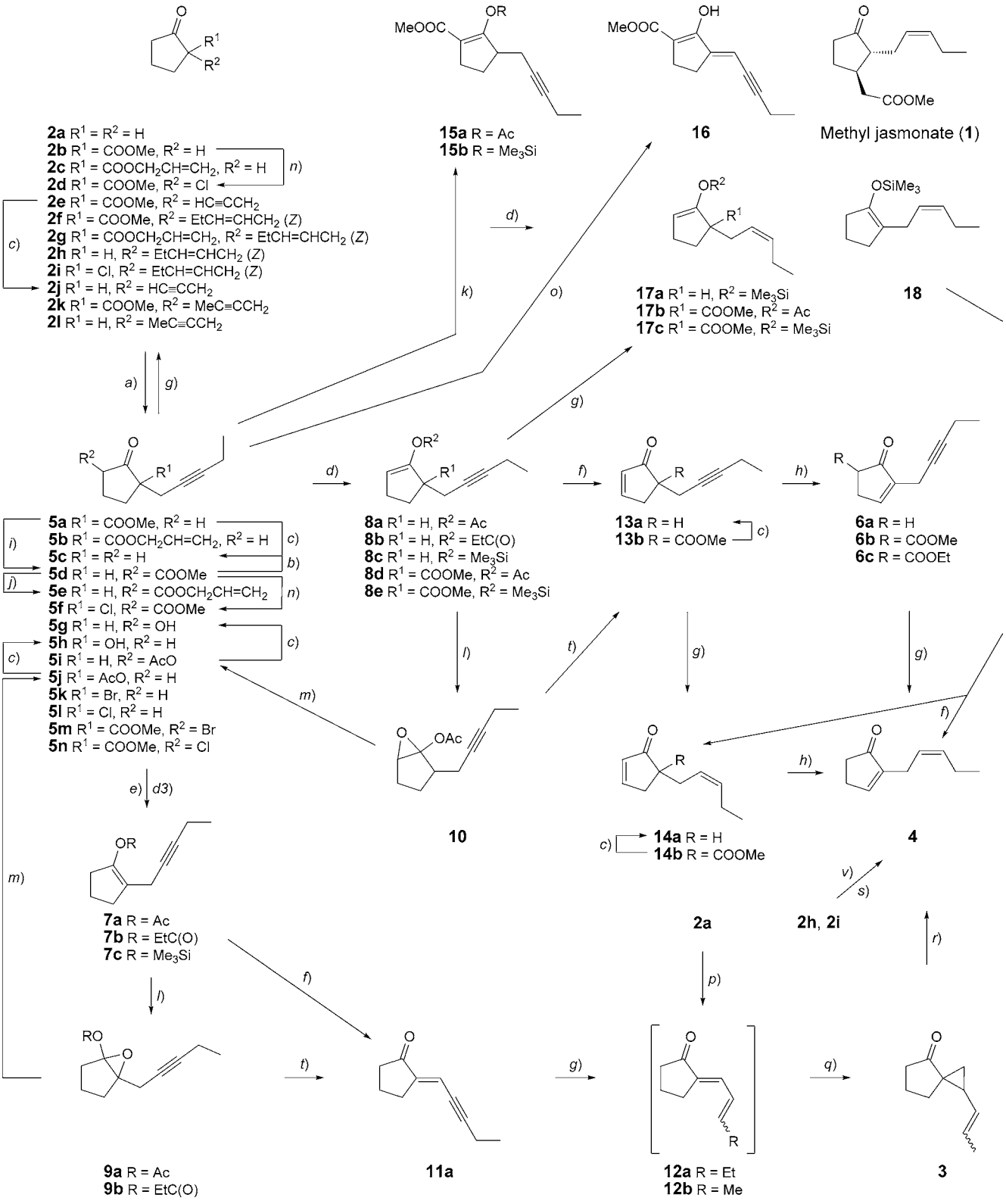
[16]) This intermediate exhibited the following NMR data: $^1$H-NMR: 3.70 (*s*, 3 H); 3.67 (*s*, 3 H); 2.54 (*m*, 1 H); 2.49–2.42 (*m*, 1 H); 2.39–2.33 (*m*, 1 H); 2.32 (br. *t*, *J* = 6.8, 2 H); 2.13 (*tq*, *J* = 7.4, 2.4, 2 H); 1.73–1.60 (*m*, 4 H); 1.09 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 175.0 (*s*); 173.6 (*s*); 83.6 (*s*); 76.0 (*s*); 51.7 (*q*); 51.5 (*q*); 44.8 (*d*); 33.8 (*t*); 30.6 (*t*); 22.5 (*t*); 21.6 (*t*); 14.2 (*q*); 12.4 (*t*).

[17]) Even under these kinetic conditions an 80:20 mixture of **7a**/**8a** was isolated in 66% yield. Alternatively, a 45:55 mixture of **7a**/**8a** was obtained when **5a** was treated under the following conditions: prop-1-en-2-yl acetate, TsOH (cat.), 100°, >97%.

[18]) Alternatively, isomerization of **13a** was also performed with 30% isolated yield, by treatment with 0.056 mol-equiv. of $RhCl_3 \cdot 3\,H_2O$ and 1.0 mol-equiv. of $K_2CO_3$ in EtOH/$H_2O$ 9:1 under reflux for 24 h, while this isomerization failed in KOH/MeOH at 65°. Carbomethoxylation of **6a** (NaH, THF, dimethylcarbonate) also failed.

*Scheme*



Scheme (*cont*). *a*) **2b** to **5a**: $K_2CO_3$, acetone, pent-2-yn-1-yl methanesulfonate, 95%. *b*) $H_2O$, 150°, 84%. *c*) LiOH, THF, $H_2O$, 20°, 93 – 95%. *d1*) **5a** to **8d** (72%); **5c** to a 45 : 55 mixture of **8a**/**7a** (98%): prop-1-en-2-yl acetate, 0.01 mol-equiv. TsOH, 100°. *d2*) **5c** to **8c** (71%); **2h** to **17a** (78%): LDA, THF, $Me_3SiCl$, −78 – 20°. *d3*) **5a** to **8e** (82%); **5c** to **7c** (49%); **2h** to **18** (19%): $Me_3SiCl$, NaI, $Et_3N$, MeCN, 75°. *e1*) **5c** to a 19 : 81 mixture of **8a**/**7a**: $Ac_2O$, TsOH, 170°, 74%. *e2*) **5c** to a 20 : 80 mixture of **8b**/**7b**: $(EtC(O))_2O$, 0.01 mol-equiv. TsOH, 170°, 50%. *f*) **8a** to **13a** (65%); **8c** to **13a** (56%); **8e** to **13b** (23%); **7a** to **11a** (65%); **17a** to **14a** (56%): 0.07 mol-equiv. $(AcO)_2Pd$, $MeOC(O)OCH_2CH{=}CH_2$, MeCN, 82°. *g*) $H_2$, cyclohexane, quinoline, *Lindlar* catalyst. *h*) **13a** to **6a** (90%); **14a** to **4** (91%): 0.2 mol-equiv. DBU, toluene, 110°. *i*) MeONa, MeOH, xylene, 110 – 145°, 81 – 94%. *j*) **5d** to **5e**: 0.03 mol-equiv. $(Oct)_2SnO$, prop-2-en-1-ol, cyclohexane, 81°, 72%. *k1*) **5d** to **15a**: AcCl, $Et_3N$, DMAP, $CH_2Cl_2$, 20°, 54%. *k2*) **5d** to **15b**: TMSOTf, $EtN(^iPr)_2$, $CH_2Cl_2$, 20°, 59%. *l*) **8a** to **10** (45%); **7a** to **9a** (95%): $AcOOH/H_2O$, $NaHCO_3$, toluene, 35°. *m*) **10** to **5i**: AcOOH/AcOH, $NaHCO_3$, toluene, 35°, >95%. *n*) **2b** to **2d** (97%); **5d** to **5f** (94%): $SO_2Cl_2$, $CH_2Cl_2$, 20°. *o*) **5f** to **16**: LiCl, DMF, 100°, 9%. *p*) **2a** to **12b**: 4% aq. NaOH, crotonaldehyde, 60%. *q*) **12b** to **3**: 50% aq. NaOH, $Me_3S(O)I$, 0.167 mol-equiv. $Bu_4NBr$, $CH_2Cl_2$, 40°, 51%. *r*) 240 – 350°, 89%. *s*) 1) $CuCl_2 \cdot 2\,H_2O$, LiCl, DMF, 80°; 2) LiBr, DMF, 80°, 34%. *t*) **9a**/**10** to **11a**/**13a**: $H_2SO_4$, MeOH, 80%. *u*) 1) NBS, THF, $H_2O$; 2) $Li_2CO_3$, pyridine, 100°. *v*) LiBr, DMF, 80°.

with NBS in THF/$H_2O$ at 6°, followed by dehydrohalogenation ($Li_2CO_3$, pyridine, 100°, 77% total yield), which afforded a 27 : 37 : 36 mixture of **6a**/**11a**/**13a**. These basic conditions are obviously too drastic and lead to excessive isomerization. Although our strategy was successful, the regioselective formation of this kinetic enolate at low temperature is not acceptable from an economical and industrial point of view. We thus repeated this sequence by generating the appropriate trimethylsilyl enol ether **8c** at a more practicable temperature of either −20 or 0° without any erosion of either regioselectivity or efficiency. Only then did we turn our attention to the second option.

The advantage of this option is the absence of regioisomers, which simplifies both halogenation and formation of the enol derivative. Starting from keto ester **5a**, we thus readily obtained enol acetate **8d** (prop-1-en-2-yl acetate, 0.01 mol-equiv. TsOH, 72%), as well as the trimethylsilyl enol ether **8e** ($Me_3SiCl$, NaI, $Et_3N$, MeCN, 75° (82%) or $Me_3SiOSO_2CF_3$ (TMSOTf), $EtN(^iPr)_2$, $CH_2Cl_2$, 20° (46%)). *Tsuji* Dehydrogenation of the latter compound (0.07 mol-equiv. $(AcO)_2Pd$, $MeOC(O)OCH_2$-$CH{=}CH_2$, MeCN, 82°, 23%) was sluggish, probably due to significant steric crowding. Similarly, when **8d** was used as starting material, *Tsuji* conditions also afforded **13b** in 39% yield. Alternatively, **8d** was sequentially treated with NBS (THF/$H_2O$, 6°, 97%) and then **5m** was dehydrohalogenated with either LiBr/$Li_2CO_3$ in DMF at 80° or DBU in toluene under reflux, to afford **13b** in 23 – 53% yield, respectively[19]). The total yield was 31% when **8e** was treated under the same conditions. The carefully monitored monohydro-

[19]) Alternatively, **5n** was obtained in 98% yield from **8d** using *N*-chlorosuccinimide (NCS) under the same conditions. Further elimination was conducted in toluene under reflux with 1.1 mol-equiv. of DBU to afford **13b** in 32% yield. Attempted epoxidation of **8d** (AcOOH, $NaHCO_3$, $CH_2Cl_2$) afforded, after purification by column chromatography (CC; $SiO_2$), methyl 3-(acetyloxy)-2-oxo-1-(pent-2-yn-1-yl)cyclopentanecarboxylate in 27% yield as 5 : 1 mixture of diastereoisomers. Major diastereoisomer: IR: 2976, 2955, 2919, 1766, 1734, 1434, 1372, 1322, 1225, 1207, 1162, 1120, 1063, 1009, 962, 945, 886, 832, 800. $^1$H-NMR: 5.43 (*dd*, *J* = 11, 8.7, 1 H); 3.72 (*s*, 3 H); 2.79 (*dt*, *J* = 16.6, 2.3, 1 H); 2.69 (*dt*, *J* = 16.6, 2.3, 1 H); 2.52 – 2.37 (*m*, 4 H); 2.15 (*s*, 3 H); 2.13 (*tq*, *J* = 7.4, 2.3, 2 H); 1.09 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 206.7 (*s*); 170.3 (*s*); 170.0 (*s*); 84.3 (*s*); 75.3 (*d*); 74.1 (*s*); 56.1 (*s*); 53.2 (*q*); 27.6 (*t*); 25.4 (*t*); 23.9 (*t*); 20.7 (*q*); 13.9 (*q*); 12.3 (*t*). MS: 266 ($M^+$), 224 (12), 207 (22), 178 (28), 165 (13), 152 (30), 147 (9), 139 (13), 137 (12), 135 (13), 121 (13), 109 (16), 93 (30), 91 (27), 79 (17), 77 (20), 65 (10), 59 (10), 55 (11), 43 (100), 41 (12). Minor diastereoisomer: $^1$H-NMR: 5.20 (*dd*, *J* = 11.8, 8.6, 1 H); 3.74 (*s*, 3 H); 2.83 (*dt*, *J* = 16.7, 2.3, 1 H); 2.60 (*dt*, *J* = 16.7, 2.3, 1 H); 2.52 – 2.37 (*m*, 4 H); 2.15 (*s*, 3 H); 2.00 (*tq*, *J* = 7.4, 2.3, 2 H); 1.10 (*t*, *J* = 7.3, 3 H). $^{13}$C-NMR: 207.6 (*s*); 170.4 (*s*), 170.1 (*s*); 85.5 (*s*); 75.9 (*d*); 74.0 (*s*); 56.9 (*s*); 53.0 (*q*); 26.9 (*t*); 26.3 (*t*); 24.6 (*t*); 20.7 (*q*); 14.1 (*q*); 12.3 (*t*). Further thermal elimination was not attempted [26]. Under identical epoxidation conditions, **8e** afforded, after purification by CC ($SiO_2$), methyl 3-oxo-1-(pent-2-yn-1-yl)-2-[(trimethylsilyl)oxy]cyclopentanecarboxylate in 10% yield. $^1$H-NMR: 4.34 (*s*, 1 H); 3.76 (*s*, 3 H); 2.75 (*dt*, *J* = 16.6, 2.4, 1 H); 2.39 – 2.36 (*m*, 4 H); 2.22 (*dt*, *J* = 16.6, 2.4, 1 H); 2.11 (*tq*, *J* = 7.4, 2.4, 2 H); 1.08 (*t*, *J* = 7.4, 3 H); 0.13 (*s*, 9 H). $^{13}$C-NMR: 212.9 (*s*); 174.7 (*s*); 84.4 (*s*); 80.2 (*d*); 75.3 (*s*); 53.6 (*s*); 52.4 (*q*); 31.8 (*t*); 25.1 (*t*); 19.9 (*t*); 14.0 (*q*); 12.4 (*t*); 0.0 (3*q*). MS: 296 (0, $M^+$), 281 (100), 240 (12), 237 (11), 229 (17), 225 (78), 221 (83), 213 (42), 209 (10), 197 (20), 195 (10), 187 (10), 181 (15), 147 (12), 136 (25), 129 (14), 121 (12), 108 (10), 101 (11), 91 (13), 89 (15), 75 (28), 73 (94), 59 (18), 45 (14).

[20]) The intermediate methyl 3-bromo-2-oxo-1-[(2*Z*)-pent-2-en-1-yl]cyclopentanecarboxylate (55 : 45 mixture of diastereoisomers) exhibited the following data. IR: 2956, 2875, 1759, 1728, 1434, 1315, 1282, 1237, 1206, 1159, 1132, 1071, 977, 837. $^1$H-NMR (major diastereoisomer): 5.59 – 5.53 (*m*, 1 H); 5.28 – 5.24 (*m*, 1 H); 4.43 (*dd*, *J* = 5.9, 3.5, 1 H); 3.71 (*s*, 3 H); 2.85 – 2.45 (*m*, 4 H); 2.33 – 1.95 (*m*, 4 H); 0.98 (*t*, *J* = 7.5, 3 H). $^1$H-NMR (minor diastereoisomer): 5.59 – 5.53 (*m*, 1 H); 5.18 – 5.14 (*m*, 1 H); 4.26 (*t*, *J* = 7.4, 1 H); 3.76 (*s*, 3 H); 2.85 – 2.45 (*m*, 4 H); 2.33 – 1.95 (*m*, 4 H); 0.95 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR (major diastereoisomer): 206.9 (*s*); 170.6 (*s*); 136.1 (*d*); 122.3 (*d*); 59.3 (*s*); 52.9 (*q*); 47.4 (*d*); 33.0 (*t*); 31.3 (*t*); 30.0 (*t*); 20.7 (*t*); 14.1 (*q*). $^{13}$C-NMR (minor diastereoisomer): 206.7 (*s*); 170.4 (*s*); 136.7 (*d*); 121.8 (*d*); 58.3 (*s*); 53.0 (*q*); 47.1 (*d*); 32.0 (*t*); 30.8 (*t*); 29.4 (*t*); 20.7 (t); 14.0 (*q*). MS (major diastereoisomer): 289 (0, $M^+$), 231 (17), 229 (24), 222 (23), 220 (25), 209 (23), 207 (56), 191 (16), 189 (10), 179 (20), 177 (35), 175 (28), 152 (31), 149 (100), 147 (42), 142 (42), 133 (23), 121 (77), 119 (32), 109 (89), 107 (27), 105 (34), 95 (24), 93 (46), 91 (82), 81 (30), 79 (62), 77 (54), 67 (40), 65 (29), 59 (28), 55 (71), 53 (31), 41 (49), 39 (32), 28 (81). MS (minor diastereoisomer): 289 (0, $M^+$), 231 (17), 229 (17), 222 (24), 220 (23), 209 (23), 191 (16), 189 (7), 179 (10), 177 (40), 153 (9), 151 (23), 149 (87), 142 (60), 133 (10), 125 (23), 121 (88), 119 (14), 109 (100), 107 (26), 105 (16), 95 (25), 93 (38), 91 (30), 81 (27), 79 (53), 77 (30), 68 (58), 67 (44), 65 (16), 59 (22), 55 (67), 53 (28), 41 (52), 39 (32), 28 (79). When **2f** was treated with AcOH, $H_2SO_4$, $KBrO_3$, and KBr, we isolated a 1 : 1 mixture of 3-(1-bromopropyl)-2-oxaspiro[4.4]nonane-1,6-dione diastereoisomers in 41% yield, which was separated in analytical amounts by CC ($SiO_2$; cyclohexane/AcOEt 8 : 2). Less polar diastereoisomer: IR: 2970, 2879, 1770, 1731, 1446, 1403, 1338, 1318, 1186, 1166, 1128, 1095, 1020, 929, 913, 845, 802, 731. $^1$H-NMR: 4.82 (*ddd*, *J* = 8.7, 7.3, 3.1, 1 H); 3.96 (*ddd*, *J* = 8.7, 4.7, 3.1, 1 H); 2.65 (*quint.*, *J* = 6.2, 1 H); 2.57 (*dd*, *J* = 13.1, 7.0, 1 H); 2.53 – 2.48 (*m*, 1 H); 2.40 – 2.33 (*m*, 2 H); 2.15 (*dd*, *J* = 12.9, 8.7, 1 H); 2.04 – 1.93 (*m*, 4 H); 1.11 (*t*, *J* = 7.3, 3 H). $^{13}$C-NMR: 214.1 (*s*); 174.0 (*s*); 78.6 (*d*); 58.9 (*d*); 58.0 (*s*); 37.4 (*t*); 36.5 (*t*); 34.0 (*t*); 28.4 (*t*); 19.7 (*t*); 12.5 (*q*). MS: 276 (8, $M^+$), 274 (9), 221 (21), 219 (20), 195 (74), 177 (100), 166 (9), 153 (26), 149 (23), 139 (63), 127 (15), 125 (28), 121 (18), 111 (23), 109 (16), 97 (24), 95 (27), 93 (81), 81 (11), 79 (22), 77 (14), 67 (29), 55 (29), 53 (14), 41 (37), 39 (23). More polar diastereoisomer: IR: 2970, 2941, 2880, 2831, 1769, 1734, 1447, 1402, 1336, 1317, 1193, 1163, 1123, 1086, 1022, 960, 937, 869, 841, 802, 732. $^1$H-NMR: 4.67 (*dt*, *J* = 9.1, 6.2, 1 H); 4.07 (*ddd*, *J* = 9.4, 5.6, 3.3, 1 H); 2.68 (*dd*, *J* = 13.3, 9.4, 1 H); 2.63 – 2.52 (*m*, 2 H); 2.37 – 2.30 (*m*, 2 H); 2.13 (*dd*, *J* = 13.3, 6.6, 1 H); 2.06 – 1.95 (*m*, 3 H); 1.88 – 1.80 (*m*, 1 H); 1.12 (*t*, *J* = 7.2, 3 H). $^{13}$C-NMR: 213.0 (*s*); 174.4 (*s*); 79.7 (*d*); 57.3 (*s*); 56.6 (*d*); 37.4 (*t*); 35.2 (*t*); 35.1 (*t*); 26.3 (*t*); 19.3 (*t*); 12.0 (*q*). MS: 276 (6, $M^+$), 274 (7), 221 (18), 219 (19), 195 (72), 177 (100), 166 (8), 153 (45), 149 (27), 139 (57), 127 (16), 125 (36), 121 (20), 111 (23), 109 (16), 97 (24), 95 (27), 93 (78), 81 (12), 79 (24), 77 (16), 67 (27), 55 (29), 53 (14), 41 (38), 39 (26).

genation of **13b** ($H_2$, *Lindlar* catalyst, cyclohexane, 87%) afforded **14b**. Finally, decarbomethoxylation of either **13b** or **14b** (LiOH, THF, $H_2O$, 20°, 93 – 95%) gave either **13a** or **14a**, respectively. A promising abridgement, consisting in treating either **5a** or **2f** under conditions described by *Ohta et al.* (either trichloroisocyanuric acid, AcOH, $BF_3 \cdot Et_2O$, 20°, then 6M aq. HCl/AcOH, 100° [27a] or NBS, $ClCH_2CH_2Cl$, 83°, then 6M aq. HCl/AcOH, 100° [28j]) to directly afford either **6a** or **4** was not attempted, in view of the alternative eliminative mechanism, concomitant to the decarbomethoxylation, suggested by these authors. We rather proceeded stepwise by direct bromination ($Me_3PhN^+Br_3^-$, THF, 0° (59%) or AcOH, $H_2SO_4$, $KBrO_3$, KBr, 20° (63%) [29a], or $CuBr_2$, MeOH, 65° (90%) [29c]), leading to either **5m** or its semi-hydrogenated analog ($CuBr_2$, MeOH, 65°, 60%)[20]), followed by basic elimination (LiBr, $Li_2CO_3$, DMF, 80°) to give **13b** (31%) or **14b** (42%), with a subsequent independent decarbomethoxylation (*vide supra*). In complement to these encouraging results, we also quickly explored the third strategy.

In analogy with the *Tsuji* intramolecular reaction, we initially *trans*-esterified methyl ester **5d**[21]) to the unreported allyl ester **5e** ($HOCH_2CH{=}CH_2$, 0.03 mol-equiv. $(Oct)_2SnO$, cyclohexane, 81°, 72%), but the latter gave the desired enone **13a** in poor 19% yield (0.07 mol-equiv. $(AcO)_2Pd$, MeCN, 75°). We then regioselectively prepared both enol acetate **15a** (AcCl, $Et_3N$, 4-(dimethylamino)pyridine (DMAP), $CH_2Cl_2$, 20°, 54%)[22]), and trimethylsilyl enol ether **15b** (TMSOTf, $EtN(^iPr)_2$, $CH_2Cl_2$, 20°, 59%), but their epoxidation also proved to be more sluggish, due to an electronic deactivation (either AcOOH, $NaHCO_3$, toluene or *m*-chloroperoxybenzoic acid, $CH_2Cl_2$)[23]). Dehydrogenation of **15b** (0.07 mol-equiv. $(AcO)_2Pd$, $MeOC(O)OCH_2CH{=}CH_2$, MeCN, 75°) also failed, possibly due to the low temperature. We then treated **5d** with $SO_2Cl_2$ in $CH_2Cl_2$ at 20°, anticipating chlorination at the $\alpha'$-position, in between the ketone and ester functionalities. Here again, we were surprised by the result, since a 3 : 2 mixture of diastereoisomers **5f**[24]) was isolated in 94% yield, eventually as a result of a double enolization of both ester and ketone moieties, which furnished **16** under eliminating conditions (LiCl, DMF, 100°) in a fully conjugated enolic form, albeit in poor 9% yield of isolated product[25]). An alternative method to activate either **2h** or **5c**, consisted in treatment with diethyl ethanedioate (EtONa, EtOH, > 94% [27c][32])[26])[27]). Unfortunately, further chlorination

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[21]) Direct oxidation of **5d** ($HIO_3$, DMSO, 65° [9] (and references cited therein)) failed, as did treatment of **5a** with $H_2C{=}CHCH_2ONa$ in xylene under reflux. Treatment of dimethyl (3-oxo-2-pentylcyclopentyl)propanedioate with $HIO_3$ in DMSO at 65° afforded dimethyl (3-oxo-2-pentylcyclopent-1-en-1-yl)propanedioate in 7% yield. $^1$H-NMR: 4.78 (*s*, 1 H); 3.80 (*s*, 6 H); 2.73 (*t*, *J* = 4.5, 2 H); 2.43 (*dt*, *J* = 4.7, 2.6, 2 H); 2.19 (*t*, *J* = 7.5, 2 H); 1.40 – 1.20 (*m*, 6 H); 0.87 (*t*, *J* = 7.0, 3 H). $^{13}$C-NMR: 208.8 (*s*); 166.7 (2*s*); 160.6 (*s*); 145.1 (*s*); 53.1 (2*q*); 53.0 (*d*); 34.3 (*t*); 31.7 (*t*); 27.9 (*t*); 27.2 (*t*); 23.4 (*t*); 22.4 (*t*); 14.0 (*q*). MS: 282 (1, $M^+$), 223 (8), 218 (5), 194 (20), 175 (10), 167 (20), 165 (17), 162 (28), 151 (100), 137 (15), 135 (20), 133 (29), 121 (12), 107 (12), 105 (10), 91 (13), 79 (15), 77 (18), 59 (18), 55 (10), 41 (14), 29 (14). This intermediate is readily prone to quantitative demethoxycarbonylation (AcOH, $H_2O$, 20°) according to [14b].

[22]) The conditions isopropenyl acetate and TsOH at 100° afforded a 1 : 1 inseparable mixture of regioisomers in 98% yield.

[23]) Treatment of **15b** with $Pd(OH)_2$, $^t$BuOOH, and $Na_2HPO_4$ failed, and we did not prepare the corresponding triisopropylsilyl enol ether [29b].

[24]) MS Analysis of **5f** is reminiscent to that of **11a**.

[25]) No traces of **6b** were detected. For the ethyl ester analog of **6c**, see [7g]. Decarboxylative saponification of **16** with LiOH, THF, and $H_2O$ afforded mainly **11a**, whose isomerization was not attempted in view of its thermodynamic stability. Alkylation of the known chloro keto ester **2d** [30] with 1-chloropent-2-yne (either LDA, THF, – 78° or $^t$BuOK, $^t$BuOH, or KH, THF) was unsuccessful. Furthermore, either direct oxidation of **2b** ($HIO_3$, DMSO, 65° [9] (and references cited therein)) or elimination of **2d** (either DBU, toluene 110° or DMF, 100°, or NMP, 140°) failed to give the reported unstable methyl 5-oxocyclopent-1-ene-1-carboxylate [31] as a suitable substrate for *Michael* addition and cascade *in situ* alkylation. Hydrogenation of neat **5d** with 1 wt-% of *Lindlar* catalyst furnished methyl 2-oxo-3-[(2*Z*)-pent-2-en-1-yl]cyclopentanecarboxylate in 92% yield as 55 : 45 mixture of diastereoisomers. Major diastereoisomer tentatively deduced from the mixture: IR: 2957, 2930, 2872, 1753, 1725, 1662, 1621, 1435, 1341, 1297, 1245, 1199, 1177, 1130, 1037, 970, 881, 798, 726. $^1$H-NMR: 5.51 – 5.43 (*m*, 1 H); 5.31 – 5.24 (*m*, 1 H); 3.75 (*s*, 3 H); 3.13 (*dd*, *J* = 11.0, 8.2, 1 H); 2.53 – 2.10 (*m*, 6 H); 2.05 (*quint.*, *J* = 7.3, 2 H); 1.9 – 1.5 (*m*, 1 H); 0.96 (*t*, *J* = 7.3, 3 H). $^{13}$C-NMR: 212.7 (*s*); 169.9 (*s*); 134.0 (*d*); 125.2 (*d*); 55.2 (*d*); 52.7 (*q*); 49.6 (*d*); 26.9 (*t*); 26.7 (*t*); 25.1 (*t*); 20.6 (*t*); 14.3 (*q*). MS: 210 (16, $M^+$), 192 (15), 179 (16), 150 (18), 142 (100), 133 (36), 123 (15), 121 (19), 110 (88), 107 (17), 95 (30), 93 (14), 87 (27), 81 (38), 69 (20), 67 (33), 55 (73), 54 (20), 41 (40), 39 (19), 28 (25). The latter was either readily decarboxymethylated (LiOH, THF/$H_2O$, 93%) to afford **2h**, or *trans*-esterified ($HOCH_2CH{=}CH_2$, 0.03 mol-equiv. $(Oct)_2SnO$, cyclohexane, 81°, 51%) to afford the corresponding allyl ester with the following data, tentatively deduced from a 66:34 mixture of diastereoisomers. IR: 3009, 2963, 2934, 2874, 1752, 1724, 1453, 1366, 1328, 1298, 1239, 1182, 1128, 1027, 980, 930, 797, 724. $^1$H-NMR: 5.95 – 5.88 (*m*, 1 H); 5.49 – 5.44 (*m*, 1 H); 5.37 – 5.33 (*m*, 1 H); 5.29 – 5.24 (*m*, 2 H); 4.69 – 4.60 (*m*, 2 H); 3.31 (*dd*, *J* = 8.7, 5.5, 0.34 H); 3.15 (*dd*, *J* = 10.2, 7.9, 0.66 H); 2.52 – 2.41 (*m*, 1 H); 2.37 – 2.10 (*m*, 5 H); 2.04 (*quint.*, *J* = 7.1, 2 H); 1.90 – 1.83 (*m*, 0.34 H); 1.56 – 1.49 (*m*, 0.66 H); 0.96 (*t*, *J* = 7.1, 3 H). $^{13}$C-NMR (major diastereoisomer): 212.4 (*s*); 169.2 (*s*); 134.0 (*d*); 131.8 (*d*); 125.1 (*d*); 118.5 (*t*); 65.9 (*t*); 55.1 (*d*); 49.4 (*d*); 26.9 (*t*); 26.7 (*t*); 25.1 (*t*); 20.6 (*t*); 14.2 (*q*). $^{13}$C-NMR (minor diastereoisomer): 213.0 (*s*); 169.0 (*s*); 133.9 (*d*); 131.7 (*d*); 125.3 (*d*); 118.5 (*t*); 65.9 (*t*); 54.2 (*d*); 48.9 (*d*); 27.3 (*t*); 27.0 (*t*); 25.1 (*t*); 20.6 (*t*); 14.2 (*q*). MS: 236 (0, $M^+$), 152 (26), 123 (26), 95 (22), 84 (100), 83 (40), 81 (20), 79 (17), 69 (10), 67 (28), 55 (22), 41 (27), 39 (17), 32 (24), 28 (87). Further dehydrogenation (0.07 mol-equiv. $(AcO)_2Pd$, MeCN, 82°, 53%) furnished **14a**.

[26]) Ethyl (2*Z*)-hydroxy{2-oxo-3-[(2*Z*)-pent-2-en-1-yl]cyclopentylidene}acetate. IR: 2964, 2934, 2873, 1727, 1667, 1605, 1462, 1443, 1394, 1370, 1352, 1328, 1302, 1280, 1228, 1167, 1112, 1093, 1019, 966, 902, 863, 791, 728, 702, 679. $^1$H-NMR: 12.9 (br. *s*, OH); 5.52 – 5.41 (*m*, 1 H); 5.35 – 5.26 (*m*, 1 H); 4.35 (*q*, *J* = 7.0, 2 H); 3.11 – 2.97 (*m*, 1 H); 2.82 – 2.72 (*m*, 1 H); 2.61 – 2.46 (*m*, 2 H); 2.44 – 2.25 (*m*, 2 H); 2.25 – 1.98 (*m*, 2 H); 1.88 – 1.54 (*m*, 1 H); 1.38 (*t*, *J* = 7.2, 3 H); 0.96 (*t*, *J* = 7.2, 3 H). $^{13}$C-NMR: 214.9 (*s*); 162.8 (*s*); 152.7 (*s*); 134.0 (*d*); 125.1 (*d*); 116.9 (*s*); 62.0 (*t*); 49.0 (*d*); 27.4 (*t*); 26.8 (*t*); 25.6 (*t*); 20.6 (*t*); 14.2 (*q*); 14.1 (*q*). MS: 252 (11, $M^+$), 184 (54), 179 (100), 177 (47), 151 (10), 149 (10), 133 (11), 123 (29), 110 (74), 109 (49), 107 (12), 105 (10), 95 (21), 93 (14), 91 (13), 81 (39), 79 (18), 77 (13), 69 (38), 67 (28), 55 (58), 53 (18), 41 (38), 39 (15), 29 (20).

[27]) Ethyl (2*Z*)-hydroxy[2-oxo-3-(pent-2-yn-1-yl)cyclopentylidene]acetate. IR: 2977, 2937, 2915, 2878, 1726, 1661, 1600, 1473, 1459, 1437, 1396, 1377, 1359, 1338, 1280, 1259, 1224, 1182, 1164, 1136, 1088, 1036, 1016, 976, 952, 894, 867, 828, 805, 787. $^1$H-NMR: 12.82 (br. *s*, OH); 4.36 (*q*, *J* = 7.1, 2 H); 3.07 (*ddd*, *J* = 17.7, 8.4, 2.6, 1 H); 2.77 (*ddd*, *J* = 17.7, 9.2, 8.4, 1 H); 2.68 – 2.62 (*m*, 1 H); 2.62 – 2.54 (*m*, 1 H); 2.44 – 2.37 (*m*, 1 H); 2.33 – 2.25 (*m*, 1 H); 2.13 (*tq*, *J* = 7.4, 2.4, 1 H); 1.91 – 1.80 (*m*, 2 H); 1.38 (*t*, *J* = 7.1, 3 H); 1.09 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 213.4 (*s*); 162.8 (*s*); 152.8 (*s*); 116.9 (*s*); 83.5 (*s*); 75.8 (*s*); 62.1 (*t*); 48.0 (*d*); 26.6 (*t*); 25.6 (*t*); 19.3 (*t*); 14.2 (*q*); 14.1 (*q*); 12.4 (*t*). MS: 250 (2, $M^+$), 222 (13), 217 (11), 177 (100), 149 (10), 123 (12), 121 (18), 109 (24), 107 (15), 105 (10), 93 (21), 91 (20), 81 (15), 79 (27), 77 (14), 69 (11), 67 (22), 55 (41), 53 (11), 41 (15), 39 (11), 29 (12).

 

(either $SO_2Cl_2$, toluene or $CuCl_2 \cdot 2\ H_2O$, DMF, 80°) failed, and only minor side products corresponding to heterobicyclic materials[28])[29]) could be isolated in mediocre 12 and 8% yield, respectively. Alternatively, the reported product of condensation between cyclopentanone (**2a**) and diethyl ethanedioate (EtONa, 80%)[30]) [33] could be alkylated with pentynyl chloride ($K_2CO_3$, acetone) to directly afford **5c**, albeit in very poor 8% yield.

At this stage, in view of the detour inherent in this strategy, we decided to take a short-cut. We discovered that treatment of the kinetic trimethylsilyl enol ether **17a** (LDA, $Me_3SiCl$, THF, −78°, 78% from **2h**) under *Tsuji*'s dehydrogenative conditions (0.07 mol-equiv. $(AcO)_2Pd$, $MeOC(O)OCH_2CH{=}CH_2$, MeCN, 82°, 56%) afforded enone **14a**, which was then isomerized to **4** (0.2 mol-equiv. DBU, toluene, 110°, 91%). Moreover, the direct treatment of **2h** with $CuCl_2 \cdot 2\ H_2O$/LiCl in DMF at 80°, furnished quantitatively a 80:20 mixture of **4**/(*E*,*E*)-**12a**, allowing us to isolate pure **4** in 34% yield after chromatography[31]). With the end of the story in view, we revisited the beginning of our synthesis by treating either **2h** or **5c** with either $SO_2Cl_2$, toluene, 20° (6–43%) [35a–35c] or trichloroisocyanuric acid, AcOH, $BF_3 \cdot Et_2O$, 20° (32–27%) [35f], or NCS, *Amberlyst 15*, AcOEt, 20° (24–16%) [35g] to afford either **2i** or **5l**, respectively. The latter compound was sluggishly monohydrogenated to give the key intermediate **2i** ($H_2$, *Lindlar* catalyst, cyclohexane, 83%), which was heated at 80° in DMF in the presence of LiCl to afford a 72:9:19 mixture of **4**/(*E*,*Z*)-**12a**/(*E*,*E*)-**12a** in 74% yield. When **5l**[32]) was dehydrohalogenated with LiBr in DMF at 80° for 5 h, a 70:30 mixture of **6a**/**11a** was obtained in 82% yield[31]). Purification by CC ($SiO_2$) furnished pure **6a** in 36% yield. Alternatively, a 15:85 mixture of regioisomers **17a**/**18** ($Me_3SiCl$, NaI, $Et_3N$, MeCN, 75°, 57%) was purified by CC ($SiO_2$) to afford pure **18** in 19% yield. This latter compound was treated with NBS in THF/$H_2O$ at 6° to afford, after dehydrohalogenation (LiBr, DMF, 80°, 61% total yield), a 79:21 mixture of **4**/(*E*,*E*)-**12a**[33]).

Finally, reconsidering the approach designed by *Naef* and *Decorzant*, *via* pyrolysis of (*E*)-**3** (240–350°, 89% [4]), we envisaged, in order to avoid the bromination of piperylene[34]), to perform an aldol condensation between cyclopentanone (**2a**) and crotonaldehyde (4% aq. NaOH, 60% [24b]), thus affording the conjugated dienone (*E*,*E*)-**12b** [36]. Further cyclopropanation under phase transfer *Corey–Chaykovsky* conditions (50% aq. NaOH, $Me_3S(O)I$, 0.17 mol-equiv. $Bu_4NBr$, $CH_2Cl_2$, 40°, 51% [37]) afforded regioselectively (*E*)-**3**. Since the base is the same in both steps, we performed the sequential aldol condensation and cyclopropanation in a single-pot version with a total yield of 31%. The observed regioselectivity may eventually be rationalized by the higher reactivity of the trisubstituted C=C bond. Indeed, in this case, and by definition, two of the substituents are in the sterically strained (*Z*) disposition, as compared to the (*E*) configuration of the disubstituted C=C bond. For the sake of completeness, we also envisaged to take advantage of the conjugative exocyclic elimination under basic conditions. Thus, the reported norketone **2l** [38] was considered as potential starting material, but finally, the halogenation/

[28]) Ethyl (2*Z*)-(3-chloro-2-ethyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-ylidene)(hydroxy)acetate. IR: 3027, 2955, 2927, 2858, 1706, 1603, 1495, 1453, 1376, 1203, 1071, 1029, 746, 699. $^1$H-NMR: 5.50 (*dt*, *J* = 9.8, 4.3, 1 H); 5.31 (*s*, OH); 4.33 (*dq*, *J* = 9.8, 6.6, 2 H); 3.96 (*dt*, *J* = 4.3, 1 H); 3.19–3.12 (*m*, 1 H); 2.94 (*dd*, *J* = 14.8, 7.2, 1 H); 2.60 (*dd*, *J* = 13.9, 4.9, 1 H); 2.45–2.35 (*m*, 2 H); 2.19–2.11 (*m*, 1 H); 2.07–1.78 (*m*, 2 H); 1.37 (*t*, *J* = 7.2, 3 H); 1.12 (*t*, *J* = 7.1, 3 H). $^{13}$C-NMR: 181.9 (*s*); 174.4 (*s*); 164.5 (*s*); 104.6 (*s*); 95.3 (*d*); 82.1 (*s*); 63.6 (*d*); 62.1 (*t*); 42.5 (*t*); 37.6 (*t*); 31.5 (*t*); 27.8 (*t*); 14.1 (*q*); 11.2 (*q*). MS: 286 (3, $M^+$), 284 (3), 249 (27), 247 (43), 213 (33), 211 (74), 175 (100), 147 (21), 123 (10), 121 (10), 119 (14), 107 (27), 105 (13), 91 (28), 79 (17), 77 (22), 67 (14), 65 (13), 55 (18), 53 (15), 41 (13), 29 (18).

[29]) Ethyl 2-ethyl-4-hydroxy-6,7-dihydro-1-benzofuran-7a(5*H*)-carboxylate. IR: 3450, 2976, 2938, 2876, 1726, 1445, 1369, 1240, 1171, 1139, 1094, 1017, 964, 940, 899, 858, 810, 757. $^1$H-NMR: 5.82 (*s*, 1 H); 4.26 (*dq*, *J* = 11.2, 6.9, 2 H); 3.5 (br. *s*, OH); 2.67–2.54 (*m*, 2 H); 2.58 (*q*, *J* = 7.4, 2 H); 2.14–1.87 (*m*, 4 H); 1.27 (*t*, *J* = 7.4, 3 H); 1.19 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 176.0 (*s*); 156.6 (*s*); 151.6 (*s*); 118.6 (*s*); 101.8 (*d*); 71.9 (*s*); 62.1 (*t*); 35.0 (*t*); 22.7 (*t*); 21.4 (*t*); 19.5 (*t*); 14.2 (*q*); 12.1 (*q*). MS: 238 (5, $M^+$), 220 (90), 218 (21), 205 (55), 203 (10), 177 (20), 175 (28), 173 (27), 165 (100), 147 (72), 145 (18), 131 (31), 119 (13), 115 (11), 91 (96), 79 (10), 77 (19), 57 (16), 55 (15), 29 (13).

[30]) Ethyl (2*Z*)-hydroxy(2-oxocyclopentylidene)acetate. IR: 2979, 2906, 1727, 1668, 1605, 1465, 1444, 1395, 1369, 1346, 1307, 1281, 1231, 1189, 1094, 1017, 911, 861, 824, 791. MS: 184 (10, $M^+$), 111 (100), 55 (13).

[31]) In contrast to the procedure reported by *Tolstikov et al.* for an (*E*) homolog, it was neither necessary nor appropriate to perform the dehydrohalogenation with $Li_2CO_3$/LiBr in DMF under reflux [34]. This difference of behavior as compared to **5l** (see footnote 11 for estimated p$K_a$ values and the *Introduction* section for comparison) may eventually find its origin in the absence of $Li_2CO_3$ and the more acidic propargylic position, as compared to the corresponding allylic position in the case of **2i**. Alternatively, steric considerations for either accessibility to **2i**/**5l**, or stability of **11a**/**12a** may also be invoked, since the elimination is conducted under neutral conditions.

[32]) The corresponding bromides, such as **5k**, could not be obtained using either $KBrO_3$, KBr, AcOH, $H_2SO_4$ or NBS, $AcONH_4$, $Et_2O$, 20° in analogy to [29a] and [35e].

[33]) When a 85:15 mixture of trimethylsilyl enol ethers **18**/**17a** was treated under *Tsuji*'s conditions ($MeOC(O)OCH_2CH{=}CH_2$, 0.07 mol-equiv. $(AcO)_2Pd$, MeCN, 82°, 75%), a 32:56:12 mixture of **14a**/**4**/(*E*,*E*)-**12a** was isolated. This unexpected ratio may eventually result from isomerization of either the initial or the final mixture with $Pd^{2+}$, although no (*Z*)/(*E*) isomerization was observed in the side chain of either **4** or **14a**. Further isomerization (DBU, toluene, 110°, 90%) furnished a 87:13 mixture of **4**/(*E*,*E*)-**12a**. When **2h** was treated with TMSOTf and $Et_3N$ in $CH_2Cl_2$ at 0°, a 50:50 mixture of kinetic/thermodynamic trimethylsilyl enol ethers **17a**/**18** was quantitatively obtained. Alternatively, when the kinetic trimethylsilyl enol ether **17a** (LDA, THF, −78°, then $Et_3N$, $Me_3SiCl$, 78%) was treated with NBS in THF/$H_2O$ at 6°, the resulting intermediate bromoketone afforded quantitatively a 62:10:28 mixture of **4**/(*E*,*Z*)-**12a**/(*E*,*E*)-**12a** after elimination under basic conditions ($Li_2CO_3$, pyridine, 100°). Monohydrogenation of either **5**, **7**–**9**, or **10** was not systematically attempted. Indeed, only **8d** was hydrogenated to **17b** ($H_2$, *Lindlar* catalyst, cyclohexane, 18%). The analogous trimethylsilyl enol ether **17c** was more efficiently obtained from **2f** (TMSOTf, $Et_3N$, $CH_2Cl_2$, 61%). As for **8d**, we did not immediately recognize that during the hydrogenation of **8e**, the starting material, as well as both **17c** and its perhydrogenated side chain analog (MS: 284 (12, $M^+$), 269 (63), 225 (48), 214 (11), 199 (42), 142 (12), 115 (80), 73 (100), 55 (11)), exhibit the same $t_R$ values on an apolar column during GC analysis.

[34]) See footnote 27 in [2a] for our reluctance in using $Br_2$.

 

dehydrohalogenation, followed by either *Corey–Chaykovsky* reaction and *Lindlar* hydrogenation or *vice versa*, towards (*Z*)-**3** was not attempted[35]).

**Conclusions.** – We have constructed a synthetic network comprising several new intermediates, **7** – **10**, **13**, **14**, **17**, and **18**, allowing access to the desired enone **4**, precursor of methyl jasmonate (**1**), *via* more than 20 different routes. Using the isomerization strategy, most of these routes necessitated six steps. The sequences → **5a** → either **8d** or **8e** → **13b** → **13a** → **6a** → **4** are the longest and amongst the less efficient ones, with a total yield of *ca.* 22%. The alternative sequences → **5a** → **5c** → either **8a** or **8c** → **13a** → **6a** → **4** allow to increase the total yield (*ca.* 32%), whilst the most efficient sequences are either → **5a** → **5c** or **2f** → **2h** → **17a** → **14a** → **4**, or → **5a** → **5m** → **13b** → **13a** → **6a** → **4** with 35 – 38% total yields, respectively. Furthermore, this method does not need to be regioselective, since mixtures of regioisomers can be used, and intermediate purifications can be avoided until the ultimate isomerization. It is noteworthy that this method may also be performed on **14a**, by reversing the isomerization/monohydrogenation sequence[36]). Formation of the conjugated enones **11a** and **12a** is minimized under neutral $\alpha$-dehydrohalogenation conditions. A four- to five-step version *via* → **5a** → either **2f** or **5c** → **2h** → either **4**, or **14a** → **4**, or **2i** → **4** is comparatively less productive with 31 – 34% total yield, while the approach *via* inexpensive **2a** → [(*E*,*E*)-**12b**] → **3** → **4**, with a total yield of 27% is the shortest one. Indeed, it necessitates only a three-step/two-pot procedure, including a linear continuous thermal reactor.

## Experimental Part

*General.* See [42a]. Calculations were performed at the B3LYP/6-31G** level of theory [42b].

*Methyl 2-Oxo-1-[(2Z)-pent-2-en-1-yl]cyclopentanecarboxylate* (**2f**). Obtained by hydrogenation of **5a** with *Lindlar* catalyst, as described for **12a**. Yield: >95%. Jasmine, *Hedione*®, minty[37]). IR: 2962, 2877, 1748, 1722, 1451, 1434, 1405, 1316, 1224, 1208, 1149, 1093, 1006, 972, 920, 838, 797, 723. $^1$H-NMR: 5.56 – 5.48 (*m*, 1 H); 5.24 – 5.16 (*m*, 1 H); 3.71 (*s*, 3 H); 2.67 (*dd*, *J* = 15, 7.5, 1 H); 2.51 – 2.37 (*m*, 3 H); 2.33 – 2.20 (*m*, 1 H); 2.09 – 1.90 (*m*, 5 H); 0.96 (*t*, *J* = 7.5, 3 H). $^{13}$C-NMR: 214.7 (*s*); 171.6 (*s*); 135.9 (*d*); 122.8 (*d*); 60.3 (*s*); 52.7 (*q*); 38.2 (*t*); 32.3 (*t*); 31.3 (*t*); 20.8 (*t*); 19.6 (*t*); 14.1 (*q*). MS: 210 (5, $M^+$), 179 (9), 153 (13), 151 (30), 142 (58), 127 (10), 121 (100), 110 (46), 108 (12), 95 (20), 93 (19), 91 (11), 81 (15), 79 (25), 77 (13), 67 (25), 59 (10), 55 (28), 53 (14), 41 (31), 39 (13).

*2-[(2Z)-Pent-2-en-1-yl]cyclopentanone* (**2h**)[38]). Obtained by hydrogenation of **5c** with *Lindlar* catalyst according to [21a]. Yield: > 95%. Also obtained by saponification of methyl 2-oxo-3-[(2*Z*)-pent-2-en-1-yl]cyclopentanecarboxylate according to the LiOH procedure used for **5c**. Yield: 93%. Fruity, veloutone, peach, melon, ylang, green, violet leaf, nice[39]). B.p. 90°/12 mbar. IR: 3007, 2962, 2934, 2874, 1735, 1453, 1406, 1335, 1300, 1270, 1153, 1069, 1025, 1003, 923, 814, 750. $^1$H-NMR: 5.49 – 5.41 (*m*, 1 H); 5.32 – 5.26 (*m*, 1 H); 2.51 – 2.43 (*m*, 1 H); 2.35 – 2.27 (*m*, 1 H); 2.22 – 2.16 (*m*, 1 H); 2.15 – 1.96 (*m*, 6 H); 1.84 – 1.72 (*m*, 1 H); 1.61 – 1.52 (*m*, 1 H); 0.96 (*t*, *J* = 7.0, 3 H). $^{13}$C-NMR: 220.9 (*s*); 133.5 (*d*); 125.8 (*d*); 49.2 (*d*); 38.2 (*t*); 29.0 (*t*); 27.0 (*t*); 20.7 (*t*); 20.6 (*t*); 14.2 (*q*). MS: 152 (30, $M^+$), 123 (27), 97 (12), 95 (21), 84 (100), 83 (37), 81 (18), 79 (12), 69 (10), 67 (22), 56 (18), 41 (24), 39 (12).

*2-Chloro-2-[(2Z)-pent-2-en-1-yl]cyclopentanone* (**2i**). A soln. of **5l** (350 mg, 1.78 mmol) in cyclohexane (10 ml) was hydrogenated with *Lindlar* catalyst (35 mg). After 1 h and 50% of conversion according to MS analyses, the mixture was filtered and conversion completed under the same conditions with fresh *Lindlar* catalyst to afford **2i**. Yield: 83%. IR: 3016, 2960, 2924, 2853, 1750, 1462, 1404, 1196, 1161, 1023, 975, 925, 893, 861, 796, 720. $^1$H-NMR: 5.62 – 5.57 (*m*, 1 H); 5.37 – 5.31 (*m*, 1 H); 2.78 (*dd*, *J* = 14.5, 7.6, 1 H); 2.62 – 2.56 (*m*, 2 H); 2.52 (*dd*, *J* = 14.8, 7.3, 1 H); 2.31 – 2.27 (*m*, 2 H); 2.16 – 1.94 (*m*, 4 H); 0.98 (*t*, *J* = 7.6, 3 H). $^{13}$C-NMR: 211.0 (*s*); 136.2 (*d*); 121.7 (*d*); 71.7 (*s*); 37.4 (*t*); 35.3 (*t*); 34.1 (*t*); 20.8 (*t*); 18.3 (*t*); 14.0 (*q*). MS: 186 (1, $M^+$), 151 (34), 121 (25), 120 (32), 118 (100), 95 (11), 91 (10), 83 (13), 81 (10), 79 (17), 77 (12), 69 (16), 67 (16), 55 (20), 41 (17), 39 (11).

*Methyl 1-(But-2-yn-1-yl)-2-oxocyclopentanecarboxylate* (**2k**). Obtained from **2b** and the corresponding mesylate [38], as described for **5a**. Yield: 74%. IR: 2956, 2921, 1751, 1725, 1434, 1404, 1324, 1227, 1188, 1152, 1137, 1106, 1042, 1008, 928, 873, 849, 835, 809, 786, 768, 654, 619. $^1$H-NMR: 3.71 (*s*, 3 H); 2.66 (*q*, *J* = 2.5, 2 H); 2.50 – 2.44 (*m*, 2 H); 2.32 – 2.25 (*m*, 2 H); 2.10 – 2.00 (*m*, 2 H); 1.75 (*t*, *J* = 2.5, 3 H). $^{13}$C-NMR: 214.2 (*s*); 171.1 (*s*); 78.2 (*s*); 74.3 (*s*); 59.1 (*s*); 52.7 (*q*); 38.4 (*t*); 32.6 (*t*); 23.6 (*t*); 19.8 (*t*); 3.5 (*q*). MS: 194 (6, $M^+$), 166 (12), 163 (14), 138 (38), 135 (100), 109 (12), 107 (25), 105 (13), 93 (16), 92 (23), 91 (48), 79 (42), 77 (32), 74 (15), 59 (10), 55 (12), 53 (15), 39 (10).

*2-(But-2-yn-1-yl)cyclopentanone* (**2l**). Obtained from **2k** using LiOH in THF/$H_2O$, as described for **5c**. Yield: 12%. Alternatively, obtained from 1-(cyclopent-1-en-1-yl)pyrrolidine, in analogy to the procedure reported in [21a]. Yield: 27%. IR: 2960, 2920, 2875, 1739, 1452, 1433, 1405, 1343, 1271, 1157, 1117, 1071, 1032, 1008, 922, 808. $^1$H-NMR: 2.51 – 2.46 (*m*, 1 H); 2.35 – 2.26 (*m*, 3 H); 2.23 – 2.19 (*m*, 1 H); 2.14 – 2.03 (*m*, 2 H); 1.88 – 1.77 (*m*, 2 H); 1.76 (*t*, *J* = 2.5, 3 H). $^{13}$C-NMR: 219.5 (*s*); 76.8 (*s*); 76.3 (*s*); 48.1 (*d*); 38.2 (*t*); 28.8 (*t*); 20.5 (*t*); 18.9 (*t*); 3.5 (*q*). MS: 136 (2, $M^+$), 121 (6), 108 (75), 93 (8), 91 (94), 79 (37), 77 (18), 55 (8), 53 (8), 51 (7), 41 (6), 39 (13), 32 (24), 28 (100).

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[35]) Mesylation of but-2-yn-1-ol ($MeSO_2Cl$, $Et_3N$, $CH_2Cl_2$, 72% [39]: $^{13}$C-NMR: 86.6 (*s*); 71.5 (*s*); 58.5 (*t*); 39.0 (*q*); 3.7 (*q*). MS: 148 (0, $M^+$), 133 (14), 80 (17), 79 (21), 69 (57), 65 (14), 63 (12), 53 (100), 52 (26), 51 (18), 50 (12), 43 (44), 41 (16), 39 (23), 27 (16) allowed, after alkylation of **2b** [35d] ($K_2CO_3$, acetone, 74%), isolation of **2k**. For the corresponding ethyl ester, see [40a – 40c]. Further decarbomethoxylation afforded **2l** (LiOH, THF, $H_2O$, 12%). Alternatively, the latter compound was preferably obtained in 27% yield from the same mesylate by alkylation of 1-(cyclopent-1-en-1-yl)pyrrolidine, in analogy to the procedure reported in [21a]. An attempted transesterification of **2k** with $HOCH_2CH{=}CH_2$ and $(Oct)_2SnO$ at 90° failed. We were asked to interrupt our project at this point, as a result, chemical yields or failed experiments were neither optimized nor repeated. Related transformations were not studied and, as in a former case [40d], basic ideas and new intermediates were rendered public rather than patented (see footnote 1).

[36]) For the syntheses of such enones based on a retro-*Diels–Alder* method, see [41].

[37]) First delivered to our perfumers by Dr. *C. Fehr* (*Firmenich SA*, unpublished work, 2000).

[38]) Its commercially available (*E*)-stereoisomer (celery, milky odor) exhibits the following analytical data: IR: 2961, 2934, 2874, 1736, 1453, 1438, 1406, 1270, 1152, 967, 923, 822. $^1$H-NMR: 5.50 (*dtt*, *J* = 15.2, 6.8, 1.1, 1 H); 5.34 (*dtt*, *J* = 15.2, 6.8, 1.1, 1 H); 2.45 – 2.39 (*m*, 1 H); 2.34 – 2.25 (*m*, 2 H); 2.20 – 2.15 (*m*, 2 H); 2.14 – 2.07 (*m*, 1 H); 2.04 – 1.95 (*m*, 3 H); 1.83 – 1.72 (*m*, 1 H); 1.62 – 1.53 (*m*, 1 H); 0.96 (*t*, *J* = 6.8, 3 H). $^{13}$C-NMR: 220.9 (*s*); 134.3 (*d*); 126.0 (*d*); 49.1 (*d*); 38.3 (*t*); 32.7 (*t*); 28.9 (*t*); 25.6 (*t*); 20.7 (*t*); 13.9 (*q*). MS: 152 (28, $M^+$), 123 (27), 97 (12), 95 (22), 84 (100), 83 (36), 81 (22), 79 (14), 69 (13), 67 (28), 55 (23), 41 (30), 39 (15)

[39]) First delivered to our perfumers by Dr. *F. Naef* (*Firmenich SA*, unpublished work, 1978).

 

*1-[(1E)-Prop-1-en-1-yl]spiro[2.4]heptan-4-one* ((*E*)-**3**). A mixture of **12b** (0.5 g, 3.55 mmol), $Me_3S(O)I$ (0.781 g, 3.55 mmol), and $Bu_4NBr$ (0.191 g, 0.592 mmol) in $CH_2Cl_2$ (30 ml) was heated under reflux for 72 h in the presence of aq. NaOH (50%, 0.284 g, 3.55 mmol) under vigorous stirring. The cold org. phase was concentrated, and the residue was diluted in AcOEt (20 ml). The suspension was filtered over *Celite*®, concentrated, and then purified by CC ($SiO_2$; cyclohexane/AcOEt 95 : 5) to afford (*E*)-**3**. Yield: 51%. Alternatively, a soln. of aq. NaOH (1.0M, 2 ml, 2 mmol) was added dropwise to cyclopentanone (**2a**; 5.0 g, 59.4 mmol) at $< 20°$, then crotonaldehyde (4.17 g, 59.4 mmol) was added dropwise at $< 10°$. After 1 h, $CH_2Cl_2$ (100 ml) was added, then $Me_3S(O)I$ (13.08 g, 59.4 mmol) and $Bu_4NBr$ (3.19 g, 9.91 mmol), followed by solid NaOH (2.3 g, 57.5 mmol). The well-stirred mixture was heated under reflux for 18 h, than aq. NaOH (50%, 2 ml, 25 mmol) was added, and after further 18 h under reflux, the cold org. phase was concentrated. The residue was diluted in AcOEt (20 ml), filtered, concentrated, and then purified by CC ($SiO_2$; $CH_2Cl_2$) to afford pure (*E*)-**3**. Yield: 31%. Fruity, lactonic, fatty, not interesting[39]). IR: 2963, 2933, 2875, 1698, 1629, 1442, 1404, 1375, 1351, 1241, 1171, 1109, 1050, 1001, 937, 789, 738, 675. $^1$H-NMR: 5.62 (*dq*, *J* = 15, 6.5, 1 H); 5.07 (*ddq*, *J* = 15, 8.5, 1.6, 1 H); 2.32 (*t*, *J* = 7, 2 H); 2.06 – 1.90 (*m*, 5 H); 1.70 (*dd*, *J* = 6.5, 1.6, 3 H); 1.48 (*dd*, *J* = 8.5, 3.6, 1 H); 0.86 (*dd*, *J* = 6.5, 3.6, 1 H). $^{13}$C-NMR: 218.6 (*s*); 128.4 (*d*); 128.1 (*d*); 38.7 (*t*); 35.9 (*s*); 31.8 (*d*); 27.7 (*t*); 23.0 (*t*); 21.0 (*t*); 18.1 (*q*). MS: 150 (52, $M^+$), 135 (25), 121 (98), 107 (20), 94 (42), 91 (31), 79 (100), 77 (30), 67 (17), 55 (11), 39 (11).

*2-[(2Z)-Pent-2-en-1-yl]cyclopent-2-en-1-one* (**4**). A 85 : 15 mixture of thermodynamic/kinetic trimethylsilyl enol ethers **18**/**17a** (80 mg, 0.356 mmol) was treated as described for **13b** to afford a 32 : 56 : 12 mixture of **14a**/**4**/(*E*,*E*)-**12a** in 75% yield, further isomerized with DBU as described for **6a** to afford a 87 : 13 mixture of **4**/(*E*,*E*)-**12a** in 90% yield. This mixture was also obtained from pure **14a** with 0.2 mol-equiv. of DBU as described for **6a**. Yield: 91%. Alternatively, a soln. of **2h** (120 mg, 0.788 mmol) in DMF (2 ml) was added dropwise to a suspension of $CuCl_2 \cdot 2\,H_2O$ (660 mg, 3.87 mmol) and LiCl (66 mg, 1.56 mmol) in DMF (8 ml) at 80°. After 6 h, the cold mixture was poured into $H_2O$ (40 ml) and extracted with hexane. The org. phase was washed with brine and dried ($Na_2SO_4$) to afford quantitatively a 80 : 20 mixture of **4**/(*E*,*E*)-**12a**. Purification by CC ($SiO_2$; cyclohexane/AcOEt 96 : 4) afforded pure **4**. Yield: 34%. For analyses, see [3][6r].

*Methyl 2-Oxo-1-(pent-2-yn-1-yl)cyclopentanecarboxylate* (**5a**). In a 2-l *Schmizo* reactor, a suspension of $K_2CO_3$ (280 g, 2.03 mol), **2b** (200 g, 1.35 mol), and pent-2-yn-1-yl methanesulfonate [15][40]) (219 g, 1.35 mol) in acetone (1000 g) was heated at 60° for 20 h. Acetone was then distilled off under 400 mbar and the mixture was finally cooled to 25°. Toluene (250 g) and $H_2O$ (800 g) were added. The org. phase was washed with $H_2O$ (2 × 300 g), concentrated, and then purified by distillation to afford pure **5a**. Yield: 95%. Jasmine, *Hedione*®, green, paper[37]). For $^1$H- and $^{13}$C-NMR analyses, see [20]. B.p. 120°/0.06 hPa. IR: 2974, 2955, 2919, 1753, 1727, 1434, 1404, 1321, 1244, 1227, 1189, 1151, 1137, 1106, 1008, 925, 835, 783, 688, 620. MS: 208 (3, $M^+$), 193 (12), 180 (10), 177 (12), 165 (8), 152 (47), 149 (100), 147 (32), 137 (14), 121 (14), 109 (15), 105 (21), 93 (27), 91 (51), 79 (22), 77 (28), 65 (10), 55 (13), 41 (12), 39 (11).

*2-(Pent-2-yn-1-yl)cyclopentanone* (**5c**). To a 2-l *Schmizo* reactor containing *Marlotherm SH* (125 g) and **5d** (25 g, 120.2 mmol) at 150°, **5d** (225 g, 1082 mmol) and $H_2O$ (24 g, 1333 mmol) were simultaneously added within 3 h, with the aid of an immersed long needle. After further 0.5 h, the mixture was cooled to 25°, and the crude material was distilled to furnish pure **5c**. Yield: 84%. Alternatively, a mixture of **5a** (120 mg, 0.576 mmol) and LiOH (179 mg, 7.49 mmol) in THF (5 ml) and $H_2O$ (1 ml) was stirred at 20° for 2 h. The mixture was acidified with 1N aq. HCl and extracted with $Et_2O$. The org. phase was dried ($Na_2SO_4$) and then concentrated to afford pure **5c**. Yield: 95%. Alternatively, **5d** afforded **5c** when submitted to the latter conditions. Yield: 94%. Chemical odor[37]). B.p. 52 – 58°/1 hPa. For IR and $^1$H-NMR analyses, see [6j][19a]. $^{13}$C-NMR: 216.4 (*s*); 82.9 (*s*); 77.4 (*s*); 48.0 (*d*); 37.8 (*t*); 28.8 (*t*); 20.5 (*t*); 19.3 (*t*); 14.5 (*q*); 12.7 (*t*). MS: 150 (4, $M^+$), 135 (19), 122 (100), 107 (44), 93 (12), 91 (22), 79 (49), 77 (22), 67 (9), 65 (10), 55 (12), 41 (11), 39 (12).

*Methyl 2-Oxo-3-(pent-2-yn-1-yl)cyclopentanecarboxylate* (**5d**). In a 2-l *Schmizo* reactor, MeONa (30% in MeOH, 225 g, 1249 mmol) in xylene (800 ml) was heated from 110 to 145° to distill the MeOH off. The temp. was adjusted to 70° and *N*-methylpyrrolidone (66 g) was added, followed by addition of dimethyl adipate (200 g, 1149 mmol) within 0.5 h, the mixture was heated for 3 h from 100 to 145° to distill the formed MeOH off, then 1-chloropent-2-yne (113 g, 1102 mmol) was added at 100° within 0.5 h, and the mixture was further stirred at 100° for 17 h. MeONa (30% in MeOH, 214 g, 1188 mmol) was added within 0.5 h at 70°, and the mixture was heated at 110° to distill off MeOH. After 2 h, the dark brown soln. was cooled down to 25° and AcOH (162 g) was added, followed by $H_2O$ (380 g). The aq. phase was removed, and the org. phase was washed with $H_2O$ (2 × 150 g). The org. phase was concentrated and then distilled to afford **5d** as 2 : 1 mixture of diastereoisomers. Yield: 94%. Alternatively, in a 2-l *Schmizo* reactor, MeONa (30% in MeOH, 225 g, 1249 mmol) and **5a** (239 g, 1150 mmol) in xylene (800 ml) were heated from 110 to 145° to distill the MeOH off. After 2 h the dark brown soln. was cooled down to 25° and AcOH (162 g) was added, followed by $H_2O$ (380 g). The aq. phase was removed and the org. phase was washed with $H_2O$ (2 × 150 g). The org. phase was concentrated and then distilled to afford **5d** as 2 : 1 mixture of diastereoisomers. Yield: 81%. IR: 2974, 2952, 2925, 2878, 2850, 1754, 1726, 1448, 1435, 1346, 1335, 1321, 1298, 1254, 1199, 1177, 1136, 1111, 1044, 980, 964, 880, 786. $^1$H-NMR (major diastereoisomer): 3.74 (*s*, 3 H); 3.14 (*dd*, *J* = 11.2, 8.3, 1 H); 2.49 – 2.46 (*m*, 1 H); 2.44 – 2.30 (*m*, 4 H); 2.22 – 2.16 (*m*, 1 H); 2.12 (*tq*, *J* = 7.4, 2.5, 2 H); 1.85 – 1.75 (*m*, 1 H); 1.09 (*t*, *J* = 7.4, 3 H). $^1$H-NMR (minor diastereoisomer): 3.72 (*s*, 3 H); 3.32 (*dd*, *J* = 8.3, 5.4, 1 H); 2.53 – 2.50 (*m*, 1 H); 2.44 – 2.30 (*m*, 4 H); 2.25 – 2.16 (*m*, 3 H); 1.85 – 1.75 (*m*, 1 H); 1.09 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 211.8 (*s*); 169.2 (*s*); 83.2 (*s*); 76.1 (*s*); 54.0 (*d*); 52.4 (*q*); 48.0 (*d*); 27.0 (*t*); 24.8 (*t*); 19.3 (*t*); 14.2 (*q*); 12.4 (*t*). MS (major diastereoisomer): 208 (0, $M^+$), 135 (19), 122 (100), 107 (50), 93 (14), 91 (29), 79 (53), 77 (28), 65 (10), 55 (13), 41 (11), 39 (15). MS (minor diastereoisomer): 208 (0, $M^+$), 135 (19), 122 (100), 107 (46), 93 (14), 91 (29), 79 (53), 77 (29), 67 10), 65 (10), 55 (12), 41 (12), 39 (16).

*Prop-2-en-1-yl 2-Oxo-3-(pent-2-yn-1-yl)cyclopentanecarboxylate* (**5e**). A mixture of **5d** (558 mg, 2.68 mmol), prop-2-en-1-ol (156 mg, 2.68 mmol) and $(Oct)_2SnO$ (29 mg, 0.081 mmol) in cyclohexane (5 ml) was heated under reflux for 1 h, and MeOH was distilled off. The cold mixture was concentrated and then purified by CC ($SiO_2$; cyclohexane/AcOEt 9 : 1) to afford **5e**. Yield: 72%. IR: 2974, 2938, 2878, 1753, 1725, 1663, 1452, 1366, 1321, 1296, 1238, 1182, 1134, 1111, 978, 931, 785. $^1$H-NMR (major diastereoisomer): 5.97 – 5.86 (*m*, 1 H); 5.35 (*dq*, *J* = 17, 1.5, 1 H); 5.24 (*dq*, *J* = 10.2, 1.3, 1 H); 4.70 – 4.58 (*m*, 1 H); 3.16 (*dd*, *J* = 11.2, 8.4, 1 H); 2.56 – 2.47 (*m*, 1 H); 2.45 – 2.07 (*m*, 8 H); 1.86 – 1.75 (*m*, 1 H); 1.09 (*t*, *J* = 7.4, 3 H). $^1$H-NMR (minor diastereoisomer): 5.97 – 5.86 (*m*, 1 H); 5.33 (*dq*, *J* = 17.1, 1.5, 1 H); 5.24 (*dq*, *J* = 10.2, 1.3, 1 H); 4.70 – 4.58 (*m*, 1 H); 3.33 (*dd*, *J* = 8.2, 5.3, 1 H); 2.56 – 2.47 (*m*, 1 H); 2.45 – 2.07 (*m*, 8 H); 1.86 – 1.75 (*m*, 1 H); 1.10 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR (major diastereoisomer): 211.2 (*s*); 169.0 (*s*); 131.8 (*d*); 118.5 (*t*); 83.5 (*s*); 75.8 (*s*); 65.9 (*t*); 55.2 (*d*); 48.2 (*d*); 26.2 (*t*); 25.0 (*t*) 18.9 (*t*); 14.2 (*q*); 12.3 (*t*). $^{13}$C-NMR (minor diastereoisomer): 211.6 (*s*); 168.5 (*s*); 131.7 (*d*); 118.4 (*t*); 83.2 (*s*); 76.1 (*s*); 65.9 (*t*); 54.1 (*d*); 48.1 (*d*); 27.0 (*t*); 24.8 (*t*); 19.3 (*t*); 14.2 (*q*); 12.4 (*t*). MS: 234 (0, $M^+$), 135 (18), 122 (100), 107 (47), 93 (13), 91 (23), 79 (52), 77 (22), 55 (11), 41 (10), 39 (12).

[40]) This reagent exhibits the following analytical data: $^{13}$C-NMR: 92.3 (*s*); 71.7 (*s*); 58.6 (*t*); 39.0 (*q*); 13.3 (*q*); 12.4 (*t*). MS: 162 (0, $M^+$), 147 (20), 97 (17), 83 (49), 79 (41), 67 (94), 66 (74), 65 (84), 63 (15), 57 (100), 55 (45), 53 (22), 51 (20), 41 (58), 39 (50).

 

*Methyl 3-Chloro-2-oxo-3-(pent-2-yn-1-yl)cyclopentanecarboxylate* (**5f**). A soln. of $SO_2Cl_2$ (0.561 g, 4.16 mmol) in $CH_2Cl_2$ (5 ml) was added to a soln. of **5d** (0.866 g, 4.16 mmol) in $CH_2Cl_2$ (20 ml) at 20°. After 2 h, the mixture was poured into $H_2O$, washed with sat. aq. $NaHCO_3$ and brine, dried ($Na_2SO_4$), and concentrated to afford crude **5f** as 3:2 mixture of major diastereoisomers. Yield: 94%. The main diastereoisomer deduced from the mixture showed the following analytical data. IR: 2976, 2953, 2938, 2877, 1734, 1671, 1630, 1446, 1321, 1233, 1211, 1197, 1148, 1031, 979, 880, 853, 780, 735, 700, 668. $^1$H-NMR: 3.80 (*s*, 3 H); 2.91 (*t*, *J* = 2.2, 1 H); 2.62 – 2.29 (*m*, 6 H); 2.17 – 2.11 (*m*, 2 H); 1.09 (*t*, *J* = 7.2, 3 H). $^{13}$C-NMR: 202.7 (*s*); 170.4 (*s*); 85.0 (*s*); 75.0 (*s*); 73.7 (*s*); 52.8 (*d*); 51.6 (*q*); 36.0 (*t*); 30.5 (*t*); 24.4 (*t*); 14.0 (*q*); 12.4 (*t*). MS: 242 (0, $M^+$), 148 (92), 147 (83), 105 (31), 91 (100), 79 (12), 77 (16), 65 (12), 51 (12).

*2-Hydroxy-5-(pent-2-yn-1-yl)cyclopentanone* (**5g**). A 55:(23:22) mixture of **5j**/**5i** (1.2 g, 5.759 mmol) and LiOH (0.538 g, 22.47 mmol) in THF (10 ml) and $H_2O$ (2 ml) was stirred for 4 h at 20°. The mixture was diluted with $H_2O$ (10 ml) and extracted with $Et_2O$. The org. phase was washed with brine, dried ($Na_2SO_4$), and then concentrated to afford quantitatively a 55:(23:22) mixture of **5h**/**5g**. Purification by CC ($SiO_2$; cyclohexane/AcOEt 8:2) afforded pure **5g**. Yield: 1.6% (9:1 mixture of diastereoisomers). $^1$H-NMR: 3.94 (*dd*, *J* = 11.2, 1.7, 1 H); 2.77 (br. *s*, OH); 2.55 – 2.42 (*m*, 3 H); 2.37 – 2.29 (*m*, 1 H); 2.25 – 1.98 (*m*, 4 H); 1.81 – 1.75 (*m*, 1 H); 1.13 (*t*, *J* = 7.5, 3 H). $^{13}$C-NMR: 217.2 (*s*); 84.7 (*s*); 79.0 (*d*); 75.3 (*s*); 42.3 (*d*); 33.7 (*t*); 21.5 (*t*); 21.4 (*t*); 14.3 (*q*); 12.4 (*t*). MS (major diastereoisomer): 166 (2, $M^+$), 137 (24), 123 (14), 110 (64), 107 (14), 105 (15), 99 (80), 95 (100), 93 (10), 91 (29), 81 (62), 79 (63), 77 (29), 67 (48), 65 (14), 57 (27), 55 (22), 53 (20), 51 (11), 43 (14), 41 (30), 39 (27), 29 (12), 27 (11). MS (minor diastereoisomer): 166 (2, $M^+$), 137 (19), 123 (12), 110 (32), 107 (13), 105 (16), 99 (83), 95 (52), 93 (17), 91 (33), 81 (34), 79 (100), 77 (50), 67 (41), 65 (14), 57 (13), 55 (25), 53 (14), 51 (10), 43 (13), 41 (27), 39 (22), 29 (9), 27 (13).

*2-Hydroxy-2-(pent-2-yn-1-yl)cyclopentanone* (**5h**). See above, pure **5h** was isolated during the chromatographic purification of **5g**. Yield: 5%. $^1$H-NMR: 2.80 (br. *s*, OH); 2.45 (*dt*, *J* = 2.4, 1.6, 2 H); 2.38 – 2.34 (*m*, 2 H); 2.28 – 2.23 (*m*, 1 H); 2.17 (*tq*, *J* = 7.5, 2.3, 2 H); 2.04 – 1.96 (*m*, 2 H); 1.93 – 1.85 (*m*, 1 H); 1.12 (*t*, *J* = 7.5, 3 H). $^{13}$C-NMR: 218.1 (*s*); 85.1 (*s*); 77.6 (*s*); 73.2 (*s*); 35.4 (*t*); 34.8 (*t*); 27.1 (*t*); 17.4 (*t*); 14.1 (*q*); 12.4 (*t*). MS: 166 (41, $M^+$), 138 (32), 122 (12), 110 (26), 98 (14), 95 (25), 91 (14), 81 (100), 71 (32), 67 (42), 57 (21), 55 (14), 53 (28), 43 (22), 42 (20), 41 (18), 39 (17).

*2-Oxo-3-(pent-2-yn-1-yl)cyclopentyl Acetate* (**5i**). AcOOH (39% in AcOH, 2.62 g, 13.42 mmol) was added dropwise within 3 h to a 45:55 mixture of **8a**/**7a** (2.0 g, 10.4 mmol) and $NaHCO_3$ (1.31 g, 15.6 mmol) in toluene (15 ml) at 35°. The cold mixture was washed with $H_2O$ and then sat. aq. $NaHCO_3$, dried ($Na_2SO_4$), and concentrated to afford quantitatively a 55:(23:22) mixture of **5j**/**5i** as a *ca.* 1:1 mixture for the latter. MS (1st diastereoisomer): 208 (1, $M^+$), 165 (14), 148 (89), 137 (10), 133 (13), 130 (17), 109 (22), 105 (11), 95 (13), 93 (14), 91 (28), 86 (10), 79 (29), 77 (20), 67 (17), 55 (13), 43 (100), 41 (13), 39 (11). MS (2nd diastereoisomer): 208 (1, $M^+$), 165 (23), 148 (54), 137 (9), 133 (11), 130 (35), 109 (22), 105 (11), 95 (12), 93 (13), 91 (28), 86 (10), 79 (28), 77 (19), 67 (17), 55 (13), 43 (100), 41 (13), 39 (10).

*2-Oxo-1-(pent-2-yn-1-yl)cyclopentyl Acetate* (**5j**). See **5i**. Obtained pure after CC ($SiO_2$; cyclohexane/AcOEt 99:1 to 9:1). Yield: 9%. $^1$H-NMR: 2.76 (*dt*, *J* = 7.2, 3, 1 H); 2.67 (*quint.*, *J* = 9.3, 2 H); 2.52 (*dt*, *J* = 8.2, 2.5, 2 H); 2.46 – 2.23 (*m*, 2 H); 2.16 (*tq*, *J* = 7.5, 2.3, 2 H), 2.04 (*s*, 3 H); 1.98 – 1.88 (*m*, 1 H); 1.12 (*t*, *J* = 7.5, 3 H). $^{13}$C-NMR: 214.4 (*s*); 169.8 (*s*); 84.8 (*s*); 82.7 (*s*); 72.8 (*s*); 36.3 (*t*); 32.2 (*t*); 26.3 (*t*); 20.7 (*q*); 18.2 (*t*); 14.0 (*q*); 12.4 (*t*). MS: 208 (0.5, $M^+$), 148 (100), 147 (54), 137 (10), 105 (18), 95 (18), 91 (47), 81 (16), 77 (10), 67 (11), 43 (45).

*2-Bromo-2-(pent-2-yn-1-yl)cyclopentanone* (**5k**). Compound **5** was obtained and used crude when a 7:3 mixture of **7c**/**8c** was treated with NBS in THF/$H_2O$ at 6°. The following analytical data were tentatively deduced from the crude mixture. $^1$H-NMR: 3.05 – 3.02 (*m*, 2 H); 2.94 – 1.70 (*m*, 8 H); 1.09 (*t*, *J* = 7.1, 3 H). $^{13}$C-NMR: 209.9 (*s*); 85.8 (*s*); 74.4 (*s*); 64.9 (*s*); 36.9 (*t*); 35.0 (*t*); 29.0 (*t*); 15.7 (*t*); 14.3 (*q*); 12.9 (*t*). MS: 229 (2, $M^+$), 227 (2), 167 (11), 140 (29), 137 (12), 125 (11), 109 (14), 97 (12), 84 (34), 81 (12), 79 (10), 57 (79), 55 (22), 41 (11), 39 (10), 32 (33), 28 (100).

*2-Chloro-2-(pent-2-yn-1-yl)cyclopentanone* (**5l**). A soln. of $SO_2Cl_2$ (4.94 g, 2.97 ml, 36.6 mmol) in toluene (5 ml) was added dropwise to a soln. of **5c** (5.0 g, 33.3 mmol) in toluene (15 ml) at < 30°. After 2.5 h at 20°, $H_2O$ was added at 0°. The mixture was washed with sat. aq. $NaHCO_3$ and brine, dried ($Na_2SO_4$), and concentrated to afford **5l** after bulb-to-bulb distillation. Yield: 43%. B.p. 100°/0.05 mbar. IR: 2976, 2938, 2917, 1751, 1614, 1461, 1438, 1422, 1402, 1374, 1323, 1259, 1242, 1198, 1160, 1147, 1112, 1005, 937, 924, 894, 799, 776, 716, 661. $^1$H-NMR: 2.81 (*t*, *J* = 2.5, 2 H); 2.62 – 2.11 (*m*, 8 H); 1.10 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 210.0 (*s*); 85.2 (*s*); 73.7 (*s*); 69.4 (*s*); 37.2 (*t*); 35.6 (*t*); 27.5 (*t*); 18.3 (*t*); 14.0 (*q*); 12.3 (*t*). MS: 184 (2, $M^+$), 149 (100), 105 (17), 93 (16), 91 (38), 79 (16), 77 (25).

*Methyl 3-Bromo-2-oxo-1-(pent-2-yn-1-yl)cyclopentanecarboxylate* (**5m**). NBS (1.47 g, 8.28 mmol) was added in five portions to a soln. of **8d** (1172 mg, 6.84 mmol) in THF (10 ml) and $H_2O$ (0.9 ml) at 6° in the dark. After 1 h the mixture was poured into brine and extracted with $CH_2Cl_2$. The org. phase was washed with $H_2O$, dried ($Na_2SO_4$), and then concentrated to afford crude **5m**. Yield: 97% (4:1 mixture of diastereoisomers). Alternatively, $H_2SO_4$ (210 mg, 2.16 mmol) was added dropwise to a soln. of **5a** (150 mg, 0.72 mmol) in AcOH (3 ml) at 20°. A mixture of KBr (214 mg, 1.8 mmol) and $KBrO_3$ (60 mg, 0.36 mmol) was then added portionwise. After 18 h at 20°, the mixture was filtered and diluted with $CH_2Cl_2$. Extraction with $H_2O$, 15% aq. $NaHCO_3$, and then addition of $H_2O$ until neutrality, afforded pure **5m**. Yield: 63% (3:1 mixture of diastereoisomers). IR (major diastereoisomer): 2976, 2954, 2879, 1759, 1722, 1434, 1367, 1320, 1241, 1206, 1176, 1159, 1138, 1112, 1062, 1004, 977, 933, 917, 871, 833, 795, 768, 747, 661, 631. $^1$H-NMR: 4.50 (*dd*, *J* = 7.1, 5.3, 1 H); 3.72 (*s*, 3 H); 2.78 (*tq*, *J* = 16.9, 2.4, 2 H); 2.70 – 2.60 (*m*, 1 H); 2.56 – 2.45 (*m*, 2 H); 2.36 – 2.28 (*m*, 1 H); 2.16 – 2.10 (*m*, 2 H); 1.10 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR (major diastereoisomer): 206.1 (*s*); 170.1 (*s*); 85.0 (*s*); 74.0 (*s*); 58.7 (*s*); 53.1 (*q*); 47.2 (*d*); 31.3 (*t*); 30.5 (*t*); 24.9 (*t*); 13.9 (*q*); 12.4 (*t*). $^{13}$C-NMR (minor diastereoisomer deduced from the mixture): 206.2 (*s*); 170.0 (*s*); 85.3 (*s*); 68.0 (*s*); 57.2 (*s*); 53.1 (*q*); 47.5 (*d*); 31.1 (*t*); 29.6 (*t*); 24.5 (*t*); 14.1 (*q*); 12.3 (*t*). MS: 287 (0, $M^+$), 229 (17), 227 (16), 207 (100), 179 (18), 175 (40), 152 (35), 148 (32), 147 (43), 137 (16), 133 (14), 119 (26), 109 (21), 105 (24), 93 (13), 91 (53), 79 (14), 77 (27), 65 (14), 59 (10), 55 (20), 41 (13), 39 (12).

*Methyl 3-Chloro-2-oxo-1-(pent-2-yn-1-yl)cyclopentanecarboxylate* (**5n**). NCS (913 mg, 6.84 mmol) was added portionwise to a soln. of **8d** (2000 mg, 6.84 mmol) in THF (10 ml) and $H_2O$ (0.86 ml) at 6° in absence of light. After 1 h at 6°, the mixture was poured onto ice and then extracted with $CH_2Cl_2$. The org. phase was dried ($Na_2SO_4$) and then concentrated to afford quantitatively crude **5n**, used as such for the next step. For anal. purpose, CC ($SiO_2$; cyclohexane/AcOEt 93:7) afforded pure **5n**. Yield: 50%. IR: 2976, 2954, 2920, 2879, 2848, 1766, 1732, 1434, 1319, 1217, 1162, 1136, 1113, 1073, 1007, 980, 919, 872, 841, 799, 787. $^1$H-NMR: 4.42 (*t*, *J* = 8.1, 1 H); 3.72 (*s*, 3 H); 2.77 (*tq*, *J* = 14.5, 2.3, 2 H); 2.59 (*dq*, *J* = 13.8, 6.6, 1 H); 2.48 (*t*, *J* = 6.6, 2 H); 2.22 (*dq*, *J* = 15.3, 7.9, 1 H); 2.13 (*tq*, *J* = 7.6, 2.6, 2 H); 1.09 (*t*, *J* = 7.6, 3 H). $^{13}$C-NMR: 205.7 (*s*); 170.3 (*s*); 84.8 (*s*); 73.9 (*s*); 58.4 (*d*); 57.8 (*s*); 53.1 (*q*); 30.6 (*t*); 29.7 (*t*); 24.4 (*t*); 13.9 (*q*); 12.3 (*t*). MS: 242 (1, $M^+$), 211 (7), 207 (6), 185 (23), 183 (58), 179 (42), 152 (100), 149 (13), 147 (47), 137 (28), 119 (21), 109 (26), 105 (16), 93 (18), 91 (58), 79 (18), 77 (34), 65 (19), 59 (13), 55 (13), 53 (11), 51 (12), 41 (17), 39 (16), 28 (14).

*2-(Pent-2-yn-1-yl)cyclopent-2-en-1-one* (**6a**). A mixture of **13a** (150 mg, 0.977 mmol) and DBU (30 mg, 0.195 mmol) in toluene was heated under reflux for 2 h. The cold mixture was concentrated and then purified by CC ($SiO_2$; cyclohexane/AcOEt 97:3) to afford pure **6a**. Yield: 90%. Compound **6a** was also obtained after CC ($SiO_2$) purification of a 70:30 mixture of **6a**/**11a** obtained by dehydrohalogenating **5l** with LiBr in DMF at 80°. Yield: 36%. For analyses, see [3][6j][7a][7d][7e][7i]. Jasmine absolute, osmanthus, violet leaf[37]).

 

*2-(Pent-2-yn-1-yl)cyclopent-1-en-1-yl Acetate* (**7a**). $Ac_2O$ (50 g, 0.5 mol) was added dropwise to a mixture of **5c** (35 g, 0.2 mol) and TsOH (0.35 g, 0.002 mol) at 150°, and AcOH was distilled off using a *Vigreux* column. After 20 h, another portion of $Ac_2O$ (45 g, 0.44 mol) was added dropwise and distillation was carried out under 800 mbar. After a total of 26 h, the residue was distilled under reduced pressure to afford a 81:19 mixture of **7a**/**8a**. Yield: 74%. B.p. 50°/0.2 mbar. IR: 2973, 2937, 2853, 1750, 1433, 1369, 1201, 1183, 1029, 886. $^1$H-NMR: 2.88 (br. *s*, 2 H); 2.53 – 2.47 (*m*, 2 H); 2.45 – 2.39 (*m*, 2 H); 2.18 – 2.11 (*m*, 2 H); 2.15 (*s*, 3 H); 1.93 (*quint.*, $J$ = 7.5, 2 H); 1.11 (*t*, $J$ = 7.2, 3 H). $^{13}$C-NMR: 168.7 (*s*); 144.4 (*s*); 122.1 (*s*); 82.0 (*s*); 75.4 (*s*); 31.2 (*t*); 31.1 (*t*); 20.8 (*q*); 19.5 (*t*); 16.7 (*t*); 14.2 (*q*); 12.4 (*t*). MS: 192 (3, $M^+$), 150 (25), 135 (18), 122 (30), 107 (10), 95 (9), 83 (100), 55 (19), 43 (30).

*2-(Pent-2-yn-1-yl)cyclopent-1-en-1-yl Propanoate* (**7b**)[41]). Propanoic anhydride (65 g, 0.5 mol) was added dropwise to a mixture of **5c** (25 g, 0.2 mol) and TsOH (0.3 g, 0.001 mol) at 160°, and propanoic acid was distilled off using a *Vigreux* column. After a total of 8 h, the residue was distilled under reduced pressure to afford a 4:1 mixture of **7b**/**8b** in 33% yield, as well as pure **7b** in 26% yield. B.p. 90 – 97°/0.2 mbar. IR: 2974, 2938, 2878, 2854, 1757, 1701, 1461, 1421, 1352, 1334, 1321, 1300, 1268, 1182, 1145, 1077, 1063, 1026, 973, 869, 805. $^1$H-NMR: 2.88 (br. *s*, 2 H); 2.53 – 2.46 (*m*, 2 H); 2.45 – 2.39 (*m*, 2 H); 2.37 – 2.27 (*m*, 2 H); 2.18 – 2.10 (*m*, 2 H); 1.93 (*quint.*, $J$ = 7.2, 2 H); 1.18 (*t*, $J$ = 7.6, 3 H); 1.10 (*t*, $J$ = 7.3, 3 H). $^{13}$C-NMR: 172.0 (*s*); 144.5 (*s*); 121.8 (*s*); 82.0 (*s*); 75.5 (*s*); 31.3 (*t*); 31.1 (*t*); 27.5 (*t*); 19.6 (*t*); 16.7 (*t*); 14.2 (*q*); 12.4 (*t*); 9.1 (*q*). MS: 206 (5, $M^+$), 150 (100), 149 (45), 135 (31), 132 (22), 122 (80), 121 (64), 107 (30), 91 (21), 79 (19), 57 (53), 25 (17).

*Trimethyl{[2-(pent-2-yn-1-yl)cyclopent-1-en-1-yl]oxy}silane* (**7c**). $Me_3SiCl$ (3.98 g, 36.6 mmol) was added dropwise to a soln. of **5c** (5.0 g, 33.3 mmol) and $Et_3N$ (6.74 g, 66.6 mmol) in DMF (30 ml) at 20°. After 18 h at 130°, the cold mixture was diluted with $Et_2O$ (50 ml), extracted with 10% aq. HCl (2 × 20 ml), washed with sat. aq. $NaHCO_3$ and brine, dried ($Na_2SO_4$), and concentrated to afford a 7:3 mixture of **7c**/**8c** in 74% yield, still contaminated by 10% of **5c**. Purification by CC ($SiO_2$; cyclohexane/AcOEt 98:2) afforded a 7:3 mixture of **7c**/**8c**. Yield: 49%. The following anal. data were deduced from this mixture. IR: 2957, 2937, 1686, 1448, 1341, 1312, 1251, 1207, 1045, 1033, 885, 867, 839, 751. $^1$H-NMR: 2.89 (br. *s*, 2 H); 2.34 – 2.27 (*m*, 4 H); 2.14 (*tq*, $J$ = 7.5, 2.5, 2 H); 1.82 (*quint.*, $J$ = 7.5, 2 H); 1.10 (*t*, $J$ = 7.4, 3 H); 0.18 (*s*, 9 H). $^{13}$C-NMR: 147.0 (*s*); 112.5 (*s*); 81.1 (*s*); 77.1 (*s*); 33.8 (*t*); 30.7 (*t*); 19.5 (*t*); 16.3 (*t*); 14.4 (*q*); 12.5 (*t*); 0.63 (3*q*). MS: 222 (68, $M^+$), 207 (25), 193 (20), 179 (27), 155 (14), 111 (11), 91 (10), 75 (30), 73 (100), 45 (13).

*5-(Pent-2-yn-1-yl)cyclopent-1-en-1-yl Acetate* (**8a**). A mixture of **5c** (10 g, 66.6 mmol), prop-1-en-2-yl acetate (13.2 g, 132 mmol), and TsOH (0.115 g, 0.666 mmol) was heated to 100°, while acetone was slowly distilled off using a *Vigreux* column within 20 h. The cold mixture was washed with sat. aq. $NaHCO_3$. The aq. phase was extracted with $Et_2O$, and the org. phase was washed with $H_2O$, dried ($Na_2SO_4$), and concentrated to afford quantitatively a 45:55 chromatographically inseparable mixture of **8a**/**7a**. For analytical purposes, pure **8a** was obtained by *Fischer* distillation. Yield: 6%. B.p. 100 – 135°/0.1 mbar. IR: 2973, 2937, 2855, 1753, 1432, 1368, 1194, 1166, 1030, 1012, 905, 883, 819. $^1$H-NMR: 5.51 (*q*, $J$ = 2, 1 H); 2.98 – 2.91 (*m*, 1 H); 2.50 – 2.31 (*m*, 4 H); 2.21 – 2.12 (*m*, 3 H); 2.10 (*s*, 3 H); 1.80 – 1.73 (*m*, 1 H); 1.11 (*t*, $J$ = 7.3, 3 H). $^{13}$C-NMR: 168.7 (*s*); 151.6 (*s*); 114.0 (*d*); 82.4 (*s*); 77.2 (*s*); 42.7 (*d*); 27.2 (2*t*); 22.6 (*t*); 21.1 (*q*); 14.3 (*q*); 12.5 (*t*). MS: 192 (4, $M^+$), 150 (100), 149 (40), 135 (27), 122 (70), 121 (66), 107 (38), 93 (11), 91 (28), 79 (30), 77 (20), 55 (10), 43 (30).

*Trimethyl{[5-(pent-2-yn-1-yl)cyclopent-1-en-1-yl]oxy}silane* (**8c**). A soln. of BuLi (1.6M, 35.7 ml, 57.2 mmol) was added to a soln. of $HN(^iPr)_2$ (5.78 g, 57.2 mmol) in THF (80 ml) at −78°. After 30 min, a soln. of **5c** (2.7 g, 17.97 mmol) in THF (20 ml) followed, after 45 min, by $Me_3SiCl$ (5.62 g, 51.8 mmol) were added. The temp. was adjusted to 20° and after 0.5 h, the mixture was washed with sat. aq. $NaHCO_3$. The aq. phase was washed with $Et_2O$ (2 × 25 ml), and the org. phase was dried ($Na_2SO_4$), concentrated, and then purified by CC ($SiO_2$; cyclohexane/AcOEt 9:1) to afford pure **8c** after bulb-to-bulb distillation. Yield: 71%. B.p. 100°/1.1 mbar. IR: 2957, 2849, 1644, 1450, 1341, 1264, 1251, 1207, 1134, 1045, 1033, 885, 867, 839, 751, 691, 626. $^1$H-NMR: 4.62 (*q*, $J$ = 1.9, 1 H); 2.64 – 2.56 (*m*, 1 H); 2.39 (*dquint.*, $J$ = 16.3, 2.3, 1 H); 2.29 – 2.04 (*m*, 6 H); 1.76 – 1.67 (*m*, 1 H); 1.11 (*t*, $J$ = 7.3, 3 H); 0.21 (*s*, 9 H). $^{13}$C-NMR: 155.9 (*s*); 102.0 (*d*); 82.0 (*s*); 78.0 (*s*); 44.5 (*d*); 27.2 (*t*); 27.0 (*t*); 22.5 (*t*); 14.4 (*q*); 12.5 (*t*); 0.0 (3*q*). MS: 222 (9, $M^+$), 207 (13), 194 (52), 165 (17), 155 (32), 75 (14), 73 (100), 45 (7).

*Methyl 2-(Acetyloxy)-1-(pent-2-yn-1-yl)cyclopent-2-ene-1-carboxylate* (**8d**). A mixture of **5a** (0.7 g, 3.06 mmol), prop-1-en-2-yl acetate (1.53 g, 15.3 mmol), and TsOH (15 mg, 0.087 mmol) was heated at 90° and acetone was slowly distilled off within 18 h. The reaction volume was maintained by adding prop-1-en-2-yl acetate (1.53 g, 15.3 mmol). The cold mixture was washed with sat. aq. $NaHCO_3$. The aq. phase was extracted with $Et_2O$ (3 × 10 ml). The org. phase was then washed with brine, dried ($Na_2SO_4$), concentrated, and purified by CC ($SiO_2$; cyclohexane/AcOEt 96:4 to 9:1) to afford pure **8d** in 52% yield, besides recovered **5a** (21%). When this reaction was repeated with a reaction time of 7 d, complete conversion was obtained and **8d** was isolated in 72% yield after distillation. B.p. 115°/0.08 mbar. IR: 2975, 2938, 2857, 1763, 1731, 1434, 1369, 1320, 1250, 1196, 1179, 1066, 1050, 1007, 878, 802, 715. $^1$H-NMR: 5.78 (*t*, $J$ = 2.5, 1 H); 3.70 (*s*, 3 H); 2.68 (*dt*, $J$ = 16.6, 2.5, 1 H); 2.55 (*dt*, $J$ = 16.6, 2.5, 1 H); 2.52 – 2.37 (*m*, 2 H); 2.16 – 2.09 (*m*, 4 H); 2.14 (*s*, 3 H); 1.08 (*t*, $J$ = 7.4, 3 H). $^{13}$C-NMR: 174.0 (*s*); 168.2 (*s*); 147.6 (*s*); 116.9 (*d*); 83.7 (*s*); 75.0 (*s*); 57.7 (*s*); 52.4 (*q*); 31.4 (*t*); 27.2 (*t*); 25.2 (*t*); 21.1 (*q*); 14.2 (*q*); 12.4 (*t*). MS: 250 (4, $M^+$), 208 (20), 191 (33), 180 (64), 153 (16), 149 (58), 148 (54), 147 (23), 141 (20), 133 (13), 131 (10), 121 (18), 109 (100), 105 (13), 93 (12), 91 (29), 79 (11), 77 (16), 55 (22), 43 (43).

*Methyl 1-(Pent-2-yn-1-yl)-2-[(trimethylsilyl)oxy]cyclopent-2-ene-1-carboxylate* (**8e**). $Me_3SiCl$ (2.035 g, 18.73 mmol) was added to a suspension of NaI (4.32 g, 28.8 mmol) in MeCN (6 ml) at 0°. After 0.15 h, $Et_3N$ (2.92 g, 28.8 mmol) followed by a soln. of **5a** (3.0 g, 14.41 mmol) in MeCN (4 ml) were added dropwise. After 0.5 h at 75°, the mixture was poured into sat. aq. $NaHCO_3$ and then extracted with $Et_2O$ (3 × 20 ml). The org. phase was dried ($Na_2SO_4$), concentrated, and purified by bulb-to-bulb distillation to afford pure **8e**. Yield: 82%. B.p. 120°/0.4 mbar. IR: 2951, 2912, 2859, 1732, 1650, 1434, 1320, 1251, 1239, 1218, 1167, 1071, 1057, 842, 780, 753. $^1$H-NMR: 4.75 (*t*, $J$ = 2.1, 1 H); 3.69 (*s*, 3 H); 2.68 (*dt*, $J$ = 16.6, 2.4, 1 H); 2.48 (*dt*, $J$ = 16.6, 2.4, 1 H); 2.40 – 2.26 (*m*, 3 H); 2.15 – 2.06 (*m*, 3 H); 1.09 (*t*, $J$ = 7.5, 3 H); 0.19 (*s*, 9 H). $^{13}$C-NMR: 175.0 (*s*); 153.1 (*s*); 103.9 (*d*); 82.9 (*s*); 76.1 (*s*); 58.3 (*s*); 52.0 (*q*); 31.6 (*t*); 26.7 (*t*); 24.6 (*t*); 14.3 (*q*); 12.5 (*t*); −0.1 (3*q*). MS: 280 (25, $M^+$), 265 (22), 252 (28), 237 (92), 221 (34), 213 (13), 197 (31), 181 (21), 109 (100), 107 (11), 89 (10), 75 (10), 73 (77), 45 (9).

*5-(Pent-2-yn-1-yl)-6-oxabicyclo[3.1.0]hex-1-yl Acetate* (**9a**). AcOOH (31.5% in $H_2O$, 20 g, 0.0825 mol) was added dropwise to a 9:1 mixture of **7a**/**8a** (10 g, 0.05 mol) and $NaHCO_3$ (6.5 g, 0.08 mol) in toluene (5 ml) at 35°. After 3 h, the cold mixture was diluted with $H_2O$ (5 ml). The org. phase was washed with sat. aq. $NaHCO_3$, 10% aq. $Na_2SO_3$, and sat. aq. $NaHCO_3$, dried ($Na_2SO_4$), concentrated, and then the *ca.* 90:5:5 mixture of diastereoisomers (95%) was used as such in the next step. For analytical purposes, an aliquot was purified by CC ($SiO_2$; cyclohexane/AcOEt 99:1 to 8:2) to afford pure **9a**. Yield: 81%. IR: 2975, 2940, 2855, 1758, 1462, 1335, 1321, 1185, 1148, 1080. $^1$H-NMR: 2.57 (*q*, $J$ = 2.2, 1 H); 2.41 (*dd*, $J$ = 13.2, 8.5, 1 H); 2.17 (*tq*, $J$ = 7.7, 2.5,

[41]) Its regioisomer, **8b**, exhibits an olefinic signal at $\delta$(H) 5.52 (*q*, $J$ = 2.2, 1 H) in the $^1$H-NMR spectrum. The following spectral analytical data were deduced from the mixture: $^{13}$C-NMR: 172.1 (*s*); 151.7 (*s*); 113.6 (*d*); 82.4 (*s*); 77.2 (*s*); 42.9 (*d*); 28.7 (*t*); 27.4 (*t*); 27.2 (*t*); 22.6 (*t*); 14.3 (*q*); 12.5 (*t*); 9.1 (*q*). MS: 206 (4, $M^+$), 177 (39), 150 (28), 149 (28), 135 (28), 122 (36), 121 (26), 107 (15), 95 (10), 91 (10), 83 (70), 79 (11), 77 (10), 57 (100), 29 (21).

 

2 H); 2.10 (*s*, 3 H); 2.08 – 1.87 (*m*, 4 H); 1.69 – 1.61 (*m*, 1 H); 1.50 – 1.37 (*m*, 1 H); 1.12 (*t*, *J* = 7.7, 3 H). $^{13}$C-NMR: 169.3 (*s*); 91.8 (*s*); 84.0 (*s*); 73.6 (*s*); 69.1 (*s*); 28.6 (*t*); 28.1 (*t*); 20.9 (*q*); 20.4 (*t*); 19.0 (*t*); 14.1 (*q*); 12.4 (*t*). MS: 208 (1, $M^+$), 165 (13), 148 (83), 133 (13), 130 (17), 109 (20), 105 (10), 95 (13), 93 (13), 91 (28), 86 (10), 79 (28), 77 (19), 67 (17), 55 (13), 43 (100), 41 (13), 39 (10).

*5-(Pent-2-yn-1-yl)-6-oxabicyclo[3.1.0]hex-1-yl Propanoate* (**9b**). Compound **9b** was obtained from **7b** according to the procedure used for **9a**. Yield: 48%. IR: 2976, 2937, 2851, 1761, 1461, 1431, 1357, 1310, 1271, 1177, 1143, 1090, 1076, 1062, 1014, 941, 805, 687, 651. $^1$H-NMR: 2.56 (*tq*, *J* = 13.0, 2.5, 1 H); 2.43 – 2.41 (*m*, 1 H); 2.39 (*q*, *J* = 7.5, 2 H); 2.18 (*tq*, *J* = 7.4, 2.5, 1 H); 2.06 – 1.97 (*m*, 2 H); 1.94 – 1.89 (*m*, 1 H); 1.69 – 1.63 (*m*, 1 H); 1.47 – 1.41 (*m*, 3 H); 1.15 (*t*, *J* = 7.5, 3 H); 1.12 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 172.8 (*s*); 91.8 (*s*); 83.9 (*s*); 73.7 (*s*); 69.1 (*s*); 28.7 (*t*); 28.1 (*t*); 27.5 (*t*); 20.5 (*t*); 19.0 (*t*); 14.1 (*q*); 12.5 (*t*); 8.8 (*q*). MS: 222 (0, $M^+$), 165 (23), 148 (68), 147 (43), 137 (20), 109 (10), 105 (17), 99 (13), 95 (26), 91 (56), 81 (9), 79 (15), 77 (15), 67 (23), 57 (100), 55 (23), 41 (17), 28 (36).

*2-(Pent-2-yn-1-yl)-6-oxabicyclo[3.1.0]hex-1-yl Acetate* (**10**). See above for **9a**, **10** was also obtained as 55 : 45 mixture of diastereoisomers. Yield: 45%. Analytical data deduced from the mixture: $^1$H-NMR: 3.76 (br. *s*, 1 H); 2.41 (*dd*, *J* = 13.2, 8.5, 1 H); 2.17 (*tq*, *J* = 7.7, 2.5, 2 H); 2.10 (*s*, 3 H); 2.08 – 1.87 (*m*, 4 H); 1.69 – 1.61 (*m*, 1 H); 1.50 – 1.37 (*m*, 1 H); 1.11 (*t*, *J* = 7.7, 3 H). $^{13}$C-NMR: 168.7 (*s*); 89.8 (*s*); 82.0 (*s*); 77.3 (*s*); 63.9 (*d*); 39.6 (*d*); 26.6 (*t*); 25.4 (*t*); 21.6 (*q*); 18.1 (*t*); 14.3 (*q*); 12.4 (*t*). MS: 208 (1, $M^+$), 165 (23), 148 (54), 133 (12), 130 (34), 109 (22), 105 (12), 95 (13), 93 (14), 91 (28), 86 (10), 79 (28), 77 (19), 67 (17), 55 (13), 43 (100), 41 (13), 39 (10).

*(2*E*)-2-(Pent-2-yn-1-ylidene)cyclopentanone* (**11a**). Pure **9a** (8.7 g, 41.82 mmol) was added dropwise during 1 h to $H_2SO_4$ (0.6 g) in MeOH (15 ml) at 65°. After 1.5 h, MeONa (30% in MeOH, 1.6 g) was added to the cold mixture, followed by toluene (25 ml). The org. phase was washed with $H_2O$ (3 × 35 ml), dried ($Na_2SO_4$), concentrated, and purified by distillation to afford **11a** in 43% yield, as well as **4** in 7% yield. Alternatively, a soln. of **5c** (1.2 g, 7.99 mmol) in DMF (10 ml) was added dropwise to a suspension of $CuCl_2 \cdot 2\ H_2O$ (2.24 g, 13.14 mmol) and LiCl (0.224 g, 5.28 mmol) in DMF at 80°. After 3 h, LiBr (0.406 g, 4.68 mmol), as well as $Li_2CO_3$ (0.59 g, 8.0 mmol) were added. After 5 h at 80°, the cold mixture was diluted with $H_2O$ (40 ml) and then extracted with hexane. The org. phase was washed with brine, dried ($Na_2SO_4$), and concentrated to afford a 70 : 30 mixture of **11a**/**6a** in 54% yield. Further purification by CC ($SiO_2$; cyclohexane/AcOEt 99 : 1 to 8 : 2) afforded pure **11a** in 35% yield, as well as an anal. quantity of the intermediate **5l**. For IR and $^1$H-NMR analyses, see [6j][7b][7c]. B.p. 120°/0.02 mbar. $^{13}$C-NMR: 206.0 (*s*); 146.5 (*s*); 113.4 (*d*); 105.0 (*s*); 78.0 (*s*); 38.6 (*t*); 28.9 (*t*); 19.4 (*t*); 13.8 (*t*); 13.8 (*q*). MS: 148 (100, $M^+$), 147 (90), 105 (30), 92 (30), 91 (95), 79 (13), 77 (13), 65 (11), 51 (11), 39 (10).

*(2*E*)-2-[(2*Z*)-Pent-2-en-1-ylidene]cyclopentanone* (**12a**). A soln. of **11a** (148 mg, 1.0 mmol) in cyclohexane (7 ml) was hydrogenated with *Lindlar* catalyst (14 mg) at atmospheric pressure in the presence of a drop of quinoline. After absorption of 1 equiv. of $H_2$, the mixture was filtered, concentrated, and bulb-to-bulb distilled to afford > 95% pure **12a**. Yield: 95%. IR: 2955, 2935, 2865, 1708, 1460, 1375, 1360, 1305, 1275, 1255, 1227, 1175, 1117, 1057, 968, 950, 940, 865. $^1$H-NMR: 7.25 (*dt*, *J* = 12, 2.5, 1 H); 6.09 (*dd*, *J* = 12, 11, 1 H); 5.98 (*dt*, *J* = 11, 7.6, 1 H); 2.70 (*dt*, *J* = 7.6, 2.5, 2 H); 2.37 (*t*, *J* = 7.6, 2 H); 2.34 (*quint.*, *J* = 7.6, 2 H); 1.97 (*quint.*, *J* = 7.6, 2 H); 1.03 (*t*, *J* = 7.6, 3 H). $^{13}$C-NMR: 208.0 (*s*); 144.4 (*d*); 136.6 (*s*); 126.2 (*d*); 124.2 (*d*); 38.7 (*t*); 27.0 (*t*); 21.6 (*t*); 19.8 (*t*); 14.0 (*q*). MS: 150 (21, $M^+$), 121 (100), 93 (7), 91 (10), 79 (23), 77 (12)[42]).

*(2*E*)-2-[(2*E*)-But-2-en-1-ylidene]cyclopentanone* (**12b**). A soln. of aq. NaOH (1.0M, 2 ml, 2 mmol) was added dropwise to cyclopentanone (**2a**; 5.0 g, 59.4 mmol) at < 20° and then, crotonaldehyde (2.08 g, 29.7 mmol) was added dropwise at < 10°. After 1 h, the mixture was extracted with $Et_2O$ (3 × 30 ml). The org. phase was washed with 1N aq. HCl, then with sat. aq. $NaHCO_3$ to neutrality, and with brine, dried ($Na_2SO_4$), and concentrated. The residual oil (80% yield) was purified by bulb-to-bulb distillation to afford pure **12b**. Yield: 60%. *Delphone®*, celery, spearmint, slightly phenolic[43])[44]). IR: 2954, 2935, 2863, 1708, 1460, 1376, 1359, 1306, 1275, 1254, 1227, 1175, 1117, 1057, 968, 950, 940, 864, 605. $^1$H-NMR: 6.89 (*dq*, *J* = 7.7, 2.6, 1 H); 6.22 – 6.18 (*m*, 2 H); 2.68 (*tq*, *J* = 7.4, 1.6, 2 H); 2.34 (*t*, *J* = 7.7, 2 H); 1.96 (*quint.*, *J* = 7.4, 2 H); 1.89 (*d*, *J* = 5.0, 3 H). $^{13}$C-NMR: 207.8 (*s*); 140.6 (*d*); 134.6 (*s*); 131.6 (*d*); 128.3 (*d*); 38.6 (*t*); 27.0 (*t*); 19.9 (*t*); 19.1 (*q*). MS: 136 (29, $M^+$), 121 (100), 93 (10), 91 (11), 80 (17), 79 (56), 77 (21), 39 (16).

*5-(Pent-2-yn-1-yl)cyclopent-2-en-1-one* (**13a**). $(AcO)_2Pd$ (25 mg, 0.112 mmol) was added to a soln. of **8c** (0.4 g, 1.60 mmol) and $MeOC(O)OCH_2CH{=}CH_2$ (0.558 g, 4.8 mmol) in MeCN (5 ml). After 1.5 h under reflux, the cold mixture was concentrated, diluted with $Et_2O$ (10 ml), filtered over *Celite®*, concentrated, and then purified by CC ($SiO_2$; cyclohexane/AcOEt 95 : 5) to afford pure **13a**. Yield: 56%. Alternatively, $(AcO)_2Pd$ (8.2 mg, 0.364 mmol) was added to a soln. of a 45 : 55 mixture of **8a**/**7a** (2.0 g, 10.4 mmol) and $MeOC(O)OCH_2CH{=}CH_2$ (1.81 g, 15.60 mmol) in MeCN (15 ml). After 1.5 h under reflux, the cold mixture was concentrated to afford quantitatively a 45 : 55 mixture of **13a**/**11a**. Purification by CC ($SiO_2$; cyclohexane/AcOEt 95 : 5) afforded pure **13a** in 26% yield, as well as pure **11a** in 29% yield. When pure **8a** was used as starting material, pure **13a** was obtained after bulb-to-bulb distillation. Yield: 65%. Alternatively, a mixture of **13b** (53 mg, 0.257 mmol) and LiOH (80 mg, 3.34 mmol) in THF (2 ml) and $H_2O$ (0.5 ml) was stirred at 20° for 2 h. The mixture was acidified with 1N aq. HCl and extracted with $Et_2O$. The org. phase was dried ($Na_2SO_4$) and then concentrated to afford pure **13a**. Yield: > 95%. Alternatively, an 8 : 2 mixture of **9a**/**10** (208 mg, 1.0 mmol) in MeOH (0.7 ml) was added dropwise to a soln. of $H_2SO_4$ (15 mg) in MeOH (1 ml) at 65° to afford a 19 : 9 : 72 mixture of **13a**/**6a**/**11a**. Yield: 80%. $^1$H-NMR: 7.73 (*dt*, *J* = 5.7, 2.4, 1 H); 6.20 (*dt*, *J* = 5.7, 2.1, 1 H); 2.89 (*ddt*, *J* = 19.3, 6.3, 2.4, 1 H); 2.64 (*dq*, *J* = 19.3, 2.3, 1 H); 2.57 (*ddt*, *J* = 15.7, 3.8, 2.4, 1 H); 2.49 – 2.42 (*m*, 1 H); 2.39 (*tt*, *J* = 7.4, 2.4, 1 H); 2.10 (*tq*, *J* = 7.4, 2.1, 2 H); 1.08 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 210.5 (*s*); 164.0 (*d*); 133.8 (*d*); 83.0 (*s*); 75.6 (*s*); 43.6 (*d*); 34.8 (*t*); 20.2 (*t*); 14.2 (*q*); 12.3 (*t*). MS: 148 (39, $M^+$), 133 (100), 119 (22), 105 (53), 103 (10), 91 (61), 82 (23), 81 (26), 79 (25), 77 (25), 68 (12), 65 (15), 53 (29), 51 (11), 41 (10), 39 (20).

[42]) Anal. traces (< 2%) of both the (*E*,*E*)-stereoisomer (*Veloutone®*, lactonic, peach, celery. IR: 2964, 2933, 2875, 1707, 1629, 1609, 1461, 1436, 1410, 1271, 1185, 968, 826, 760, 641. $^1$H-NMR: 6.91 (*dt*, *J* = 10.6, 2.2, 1 H); 6.28 – 6.13 (*m*, 2 H); 2.69 (*dt*, *J* = 7.2, 2.2, 2 H); 2.34 (*t*, *J* = 7.6, 2 H); 2.23 (*quint.*, *J* = 7.2, 2 H); 1.96 (*quint.*, *J* = 7.6, 2 H); 1.06 (*t*, *J* = 7.6, 3 H). $^{13}$C-NMR: 207.9 (*s*); 147.4 (*d*); 134.9 (*s*); 131.9 (*d*); 125.9 (*d*); 38.7 (*t*); 27.1 (*t*); 26.5 (*t*); 19.9 (*t*); 13.0 (*q*). MS: 150 (13, $M^+$), 121 (100), 93 (6), 91 (11), 79 (26), 77 (15), 39 (9), 28 (6)), as well as the (*Z*,*E*)-stereoisomer ($^1$H-NMR: 7.51 (*dd*, *J* = 13.4, 11.2, 1 H); 6.33 (br. *d*, *J* = 11.2, 1 H); 6.01 (*dt*, *J* = 15.2, 6.9, 1 H); 2.65 (*dt*, *J* = 15.2, 7.4, 2 H); 2.34 (*t*, *J* = 7.6, 2 H); 2.21 (*quint.*, *J* = 7.6, 2 H); 1.91 (*quint.*, *J* = 7.4, 2 H); 1.04 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 207.7 (*s*); 145.9 (*d*); 136.5 (*d*); 132.7 (*s*); 125.8 (*d*); 40.6 (*t*); 31.8 (*t*); 20.5 (*t*); 16.1 (*t*); 13.3 (*q*)) could also be either isolated or deduced from the mixture, after purification by CC ($SiO_2$; cyclohexane/AcOEt 95 : 5).

[43]) First delivered to our perfumers by Dr. *H. Strickler*, (*Firmenich SA*, unpublished work, 1976).

[44]) When purification was performed by CC ($SiO_2$; cyclohexane/AcOEt 99 : 1 to 9 : 1), analytical traces of (*E*,*Z*)-**12b** could be isolated in < 2% yield. $^1$H-NMR: 7.27 (*dt*, *J* = 11.3, 2.8, 1 H); 6.21 – 6.01 (*m*, 2 H); 2.70 (br. *t*, *J* = 5.7, 2 H); 2.37 (*t*, *J* = 7.5, 2 H); 1.97 (*quint.*, *J* = 7.5, 2 H); 1.91 (*d*, *J* = 7.0, 3 H). $^{13}$C-NMR: 208.0 (*s*); 137.1 (*d*); 136.5 (*s*); 126.0 (*d*); 125.8 (*d*); 38.7 (*t*); 26.9 (*t*); 19.8 (*t*); 14.1 (*q*). MS: 136 (31, $M^+$), 121 (100), 93 (11), 91 (12), 80 (13), 79 (44), 77 (15).

 

*Methyl 2-Oxo-1-(pent-2-yn-1-yl)cyclopent-3-ene-1-carboxylate* (**13b**). $(AcO)_2Pd$ (81 mg, 0.359 mmol) was added to a soln. of **8d** (1.5 g, 5.13 mmol) and $MeOC(O)OCH_2CH=CH_2$ (1.78 g, 15.4 mmol) in MeCN (20 ml). After 1.5 h under reflux, the cold mixture was concentrated, diluted with $Et_2O$ (20 ml), filtered over *Celite*®, concentrated, and then purified by CC ($SiO_2$; cyclohexane/AcOEt 97:3) to afford pure **13b**. Yield: 39%. Alternatively, $(AcO)_2Pd$ (112 mg, 0.499 mmol) was added to a soln. of **8e** (2.0 g, 7.13 mmol), and $MeOC(O)OCH_2CH=CH_2$ (2.484 g, 21.4 mmol) in MeCN (25 ml). After 1.5 h under reflux, the cold mixture was concentrated, diluted with $Et_2O$ (20 ml), filtered over *Celite*®, concentrated, and then purified by CC ($SiO_2$; cyclohexane/AcOEt 95:5) to afford pure **13b**. Yield: 23%. Alternatively, **5m** afforded **13b** either in 23 – 31% yield after treatment with either LiBr or $Li_2CO_3$ in DMF at 80° for 5 h, or in 53% yield after treatment with 1.1 mol-equiv. of DBU in toluene under reflux for 4 h. IR: 2976, 2954, 2939, 2919, 2879, 2847, 1740, 1705, 1591, 1435, 1343, 1323, 1299, 1257, 1240, 1178, 1144, 1119, 1098, 1066, 1018, 956, 900, 867, 819, 759, 729. $^1$H-NMR: 7.83 (*dt*, *J* = 5.7, 2.7, 1 H); 6.21 (*dt*, *J* = 5.7, 2.2, 1 H); 3.71 (*s*, 3 H); 3.22 (*dt*, *J* = 19.2, 2.4, 1 H); 2.92 (*dt*, *J* = 19.2, 2.5, 1 H); 2.77 (*tq*, *J* = 16.5, 2.2, 2 H); 2.06 (*tq*, *J* = 7.5, 2.4, 2 H); 1.04 (*t*, *J* = 7.5, 3 H). $^{13}$C-NMR: 204.6 (*s*); 170.4 (*s*); 164.5 (*d*); 132.2 (*d*); 84.0 (*s*); 73.8 (*s*); 56.8 (*s*); 52.9 (*q*); 39.4 (*t*); 24.0 (*t*); 14.1 (*q*); 12.3 (*t*). MS: 206 (6, $M^+$), 147 (100), 145 (13), 117 (18), 107 (10), 91 (29), 77 (10), 39 (8).

*5-[(2Z)-Pent-2-en-1-yl]cyclopent-2-en-1-one* (**14a**). Compound **14a** was obtained by hydrogenation of **13a** with *Lindlar* catalyst, as described for **12a**. Yield: 95%. Alternatively, $(AcO)_2Pd$ (10.5 mg, 0.047 mmol) was added to a mixture of **17a** (150 mg, 0.668 mmol) and $MeOC(O)OCH_2CH=CH_2$ (233 mg, 2.0 mmol) in MeCN (5 ml). After 1.5 h at 80°, the cold mixture was concentrated, diluted with $Et_2O$, filtered, and concentrated again to afford quantitatively an 80:20 mixture of **14a**/**2h**. Purification by CC ($SiO_2$; cyclohexane/AcOEt 97:3) afforded pure **14a**. Yield: 56%. Alternatively, prop-2-en-1-yl 2-oxo-3-[(2*Z*)-pent-2-en-1-yl]cyclopentanecarboxylate (180 mg, 0.762 mmol) was treated with $(AcO)_2Pd$ (12 mg, 0.057 mmol) in MeCN under reflux for 1.5 h to afford **14a** after purification by CC ($SiO_2$). Yield: 53%. Alternatively, **14a** was obtained by saponification of **14b** with LiOH, according to the procedure used for **13a**. Yield: 93%. IR: 3008, 2962, 2930, 2874, 1701, 1588, 1462, 1431, 1344, 1205, 1171, 1092, 1069, 1026, 948, 840, 773, 742, 718, 670. $^1$H-NMR: 7.69 (*dt*, *J* = 5.8, 2.6, 1 H); 6.19 (*dt*, *J* = 5.8, 2.2, 1 H); 5.47 (*dtt*, *J* = 11.0, 7.3, 2.0, 1 H); 5.27 (*dtt*, *J* = 11.0, 7.3, 2.0, 1 H); 2.85 – 2.80 (*m*, 1 H); 2.55 – 2.50 (*m*, 1 H); 2.41 – 2.35 (*m*, 2 H); 2.22 – 2.16 (*m*, 1 H); 2.06 (br. *quint.*, *J* = 7.4, 2 H); 0.96 (*t*, *J* = 7.4, 3 H). $^{13}$C-NMR: 212.0 (*s*); 163.8 (*d*); 134.1 (*d*); 133.9 (*d*); 125.0 (*d*); 44.6 (*d*); 35.0 (*t*); 28.4 (*t*); 20.6 (*t*); 14.2 (*q*). MS: 150 (12, $M^+$), 121 (20), 95 (10), 82 (100), 81 (10), 79 (12), 77 (10), 53 (10), 41 (12), 39 (10).

*Methyl 2-Oxo-1-[(2Z)-pent-2-en-1-yl]cyclopent-3-ene-1-carboxylate* (**14b**). Compound **14b** was obtained by hydrogenation of **13b** with 3 wt-% of *Lindlar* catalyst in cyclohexane as described for **12a**. Yield: 87%. Alternatively, **17c** was treated with $(AcO)_2Pd$ and $MeOC(O)OCH_2CH=CH_2$ in MeCN as described for **13b** to afford **14b**. Yield: 52%. IR: 3011, 2960, 2933, 2874, 1741, 1705, 1592, 1434, 1373, 1343, 1291, 1246, 1176, 1095, 1065, 1046, 1027, 979, 956, 891, 860, 820, 753, 734, 676, 638. $^1$H-NMR: 7.76 (*dt*, *J* = 5.7, 2.6, 1 H); 6.17 (*dt*, *J* = 5.7, 1.8, 1 H); 5.52 – 5.47 (*m*, 1 H); 5.15 – 5.10 (*m*, 1 H); 3.71 (*s*, 3 H); 3.22 (*dt*, *J* = 19.4, 2.6, 1 H); 2.78 (*dd*, *J* = 14.1, 7.5, 1 H); 2.62 (*dt*, *J* = 19.4, 2.2, 1 H); 2.54 (*dd*, *J* = 14.1, 7.0, 1 H); 2.06 (*quint.*, *J* = 7.0, 2 H); 0.95 (*t*, *J* = 7.0, 3 H). $^{13}$C-NMR: 205.6 (*s*); 171.0 (*s*); 164.1 (*d*); 135.9 (*d*); 132.2 (*d*); 122.1 (*d*); 57.5 (*s*); 52.8 (*q*); 38.8 (*t*); 31.8 (*t*); 20.6 (*t*); 14.1 (*q*). MS: 208 (2, $M^+$), 176 (8), 149 (64), 147 (13), 140 (100), 133 (8), 119 (50), 108 (66), 107 (19), 105 (10), 93 (10), 91 (18), 80 (16), 79 (18), 77 (13), 55 (18), 41 (12), 39 (10).

*Methyl 2-(Acetyloxy)-3-(pent-2-yn-1-yl)cyclopent-1-ene-1-carboxylate* (**15a**). DMAP (0.146 g, 1.2 mmol) was added to a soln. of **5d** (6 g, 21.9 mmol), $Et_3N$ (3.32 g, 32.8 mmol), and AcCl (2.15 g, 27.4 mmol) in $CH_2Cl_2$ (100 ml) at 0°. After 2 h at 20°, the mixture was washed with brine, dried ($Na_2SO_4$), concentrated, and purified by CC ($SiO_2$; cyclohexane/AcOEt 95:5) to afford pure **15a**. Yield: 54%. IR: 2974, 2939, 2876, 1776, 1714, 1658, 1435, 1363, 1272, 1223, 1170, 1143, 1130, 1039, 1002, 877, 769. $^1$H-NMR: 3.71 (*s*, 3 H); 3.09 – 3.04 (*m*, 1 H); 2.67 – 2.54 (*m*, 2 H); 2.37 (*ddt*, *J* = 16.6, 5.5, 2.3, 1 H); 2.28 – 2.11 (*m*, 4 H); 2.24 (*s*, 3 H); 1.84 – 1.75 (*m*, 1 H); 1.10 (*t*, *J* = 7.5, 3 H). $^{13}$C-NMR: 167.7 (*s*); 164.0 (*s*); 160.3 (*s*); 118.9 (*s*); 83.0 (*s*); 76.3 (*s*); 51.4 (*q*); 44.9 (*d*); 27.9 (*t*); 25.6 (*t*); 22.0 (*t*); 20.8 (*q*); 14.2 (*q*); 12.4 (*t*). MS: 250 (1, $M^+$), 180 (68), 177 (13), 148 (24), 140 (10), 131 (13), 109 (100), 91 (14), 79 (11), 77 (10), 55 (12), 43 (42), 41 (11).

*Methyl 3-(Pent-2-yn-1-yl)-2-[(trimethylsilyl)oxy]cyclopent-1-ene-1-carboxylate* (**15b**). TMSOTf (6.93 g, 31.16 mmol) was added dropwise to a soln. of **5d** (5 g, 24.01 mmol) and $EtN(^iPr)_2$ (4.65 g, 36 mmol) in $CH_2Cl_2$ (25 ml) at 20°. After 2 h, the mixture was concentrated, diluted with pentane, filtered over *Celite*®, concentrated, and then purified by CC ($SiO_2$; cyclohexane/AcOEt 96:4) to afford pure **15b**. Yield: 59%. IR: 2952, 2867, 1709, 1621, 1436, 1376, 1249, 1225, 1192, 1151, 1134, 1055, 844, 771, 751, 690. $^1$H-NMR: 3.70 (*s*, 3 H); 2.74 – 2.66 (*m*, 1 H); 2.61 – 2.54 (*m*, 1 H); 2.48 (*ddd*, *J* = 8.8, 6.2, 1.6, 1 H); 2.41 (*ddt*, *J* = 16.6, 4.2, 2.5, 1 H); 2.23 (*ddt*, *J* = 16.6, 7.7, 2.4, 1 H); 2.14 (*tq*, *J* = 7.4, 2.4, 2 H); 2.03 (*ddq*, *J* = 13.1, 8.8, 4.7, 1 H); 1.81 – 1.72 (*m*, 1 H); 1.10 (*t*, *J* = 7.4, 3 H); 0.27 (*s*, 9 H). $^{13}$C-NMR: 166.0 (*s*); 165.6 (*s*); 109.2 (*s*); 83.1 (*s*); 76.8 (*s*); 50.6 (*q*); 46.9 (*d*); 27.6 (*t*); 24.8 (*t*); 21.7 (*t*); 14.2 (*q*); 12.5 (*t*); 0.7 (3*q*). MS: 280 (4, $M^+$), 265 (60), 249 (10), 197 (21), 109 (100), 107 (11), 89 (10), 73 (50).

*Methyl (3E)-2-Hydroxy-3-(pent-2-yn-1-ylidene)cyclopent-1-ene-1-carboxylate* (**16**). A mixture of **5f** (946 mg, 3.89 mmol) and LiCl (247 mg, 5.83 mmol) in DMF (10 ml) was heated at 100° for 0.5 h. To the cold mixture was added aq. $H_2SO_4$ (2.5%, 5 ml) and $Et_2O$ (5 ml). After 1 h at 20°, the mixture was partitioned between brine and $Et_2O$. The org. phase was washed with $H_2O$, dried ($Na_2SO_4$), concentrated, and then purified by CC ($SiO_2$; cyclohexane/AcOEt 95:5) and bulb-to-bulb distillation to afford pure **16**. Yield: 9%. B.p. 90°/0.09 mbar. IR: 3271, 2968, 2934, 2875, 2206, 1661, 1596, 1445, 1373, 1321, 1278, 1249, 1218, 1196, 1139, 1096, 998, 964, 887, 840, 817, 762, 727, 663, 627. $^1$H-NMR: 9.89 (*s*, OH); 5.90 (*quint.*, *J* = 2.4, 1 H); 3.79 (*s*, 3 H); 2.67 – 2.63 (*m*, 2 H); 2.55 – 2.53 (*m*, 2 H); 2.41 (*dq*, *J* = 7.5, 2.4, 2 H); 1.19 (*t*, *J* = 7.5, 3 H). $^{13}$C-NMR: 170.0 (*s*), 167.6 (*s*); 148.9 (*s*); 107.8 (*s*); 104.4 (*d*); 101.5 (*s*); 77.8 (*s*); 51.4 (*q*); 25.6 (*t*); 24.4 (*t*); 14.1 (*q*); 13.6 (*t*). MS: 206 (0, $M^+$), 148 (80), 147 (72), 105 (23), 92 (24), 91 (100), 79 (10), 77 (12), 65 (10), 51 (10), 39 (8).

*Trimethyl({5-[(2Z)-pent-2-en-1-yl]cyclopent-1-en-1-yl}oxy)silane* (**17a**). BuLi (1.6M, 3.92 ml, 6.27 mmol) was added dropwise to a soln. of $HN(^iPr)_2$ (634 mg, 6.27 mmol) in THF (1 ml) at −78°. After 0.5 h, a soln. of **2h** (300 mg, 1.97 mmol) in THF (1 ml) was added. After 0.75 h at −78°, $Me_3SiCl$ (617 mg, 5.68 mmol) was added. The temp. was equilibrated to 20°, and the mixture was poured into aq. sat. $NaHCO_3$. The aq. phase was washed with $Et_2O$. The org. phase was dried ($Na_2SO_4$), concentrated, and purified by CC ($SiO_2$; cyclohexane/AcOEt 99:1) to afford **17a**. Yield: 78%. IR: 3006, 2959, 2926, 2852, 1641, 1446, 1348, 1251, 1188, 1047, 957, 873, 840, 776, 755, 693. $^1$H-NMR: 5.44 – 5.38 (*m*, 1 H); 5.35 – 5.30 (*m*, 1 H); 4.59 (*q*, *J* = 2.0, 1 H); 2.51 – 2.47 (*m*, 1 H); 2.35 – 2.29 (*m*, 1 H); 2.21 – 2.16 (*m*, 2 H); 2.05 (*quint.*, *J* = 7.5, 2 H); 2.01 – 1.94 (*m*, 2 H); 1.51 – 1.45 (*m*, 1 H); 0.96 (*t*, *J* = 7.5, 3 H); 0.20 (*s*, 9 H). $^{13}$C-NMR: 157.1 (*s*); 132.5 (*d*); 127.3 (*d*); 101.4 (*d*); 44.8 (*d*); 30.3 (*t*); 27.3 (*t*); 27.0 (*t*); 20.7 (*t*); 14.4 (*q*); 0.0 (3*q*). MS: 224 (8, $M^+$), 167 (22), 156 (39), 155 (76), 154 (10), 75 (13), 73 (100), 45 (8), 41 (6).

*Methyl 2-(Acetyloxy)-1-[(2Z)-pent-2-en-1-yl]cyclopent-2-ene-1-carboxylate* (**17b**). Compound **17b** was obtained from **8d**, as described for **2i**. Yield: 18%. IR: 3012, 2959, 2934, 2858, 1763, 1731, 1654, 1434, 1369, 1245, 1197, 1179, 1065, 1046, 1006, 868, 799, 725. $^1$H-NMR: 5.72 (*t*, *J* = 2.2, 1 H); 5.53 – 5.48 (*m*, 1 H); 5.27 – 5.23 (*m*, 1 H); 3.69 (*s*, 3 H); 2.62 (*dd*, *J* = 14.4, 8.3, 1 H); 2.50 – 2.44 (*m*, 1 H); 2.40 (*dd*, *J* = 14.4, 6.6, 1 H); 2.37 – 2.30 (*m*, 2 H); 2.15 (*s*, 3 H); 2.06 (*quint.*, *J* = 7.2, 2 H); 1.90 – 1.86 (*m*, 1 H); 0.96 (*t*, *J* = 7.2, 3 H). $^{13}$C-NMR: 174.9 (*s*); 168.3 (s); 148.3 (*s*); 134.8 (*d*); 123.3 (*d*); 116.4 (*d*); 57.6 (*s*); 52.2 (*q*); 32.0 (*t*); 31.0

 

(*t*); 27.1 (*t*); 21.2 (q); 20.7 (*t*); 14.2 (*q*); 0.0 (3*q*). MS: 252 (1, $M^+$), 210 (7), 178 (7), 153 (153), 151 (18), 142 (83), 141 (33), 140 (27), 121 (9), 109 (100), 95 (11), 81 (10), 79 (12), 69 (15), 67 (12), 55 (31), 53 (13), 43 (67), 41 (28), 39 (10), 28 (27).

*Methyl 1-[(2Z)-Pent-2-en-1-yl]-2-[(trimethylsilyl)oxy]cyclopent-2-ene-1-carboxylate* (**17c**). Compound **17c** was obtained from **2f** according to the procedure used for **15b**. Yield: 61%. IR: 3012, 2960, 2906, 2858, 1731, 1647, 1433, 1264, 1251, 1238, 1216, 1164, 1067, 867, 842, 785, 753. $^1$H-NMR: 5.50 – 5.45 (*m*, 1 H); 5.30 – 5.25 (*m*, 1 H); 4.70 (*t*, *J* = 2.4, 1 H); 3.67 (*s*, 3 H); 2.60 (*dd*, *J* = 14.5, 8.0, 1 H); 2.36 (*dd*, *J* = 14.5, 6.3, 1 H); 2.34 – 2.30 (*m*, 1 H); 2.27 – 2.22 (*m*, 1 H); 2.20 – 2.15 (*m*, 1 H); 2.07 (*quint.*, *J* = 7.5, 2 H); 1.83 – 1.78 (*m*, 1 H); 0.96 (*t*, *J* = 7.5, 3 H); 0.19 (*s*, 9 H). $^{13}$C-NMR: 175.8 (*s*); 153.9 (*s*); 134.1 (*d*); 124.4 (*d*); 103.3 (*d*); 58.1 (*s*); 51.8 (*q*); 31.5 (*t*); 31.3 (*t*); 26.5 (*t*); 20.7 (*t*); 14.3 (*q*); 0.0 (3*q*). MS: 282 (7, $M^+$), 267 (8), 225 (12), 223 (21), 213 (25), 199 (21), 197 (23), 181 (11), 109 (100), 73 (49).

*Trimethyl({2-[(2Z)-pent-2-en-1-yl]cyclopent-1-en-1-yl}oxy)silane* (**18**). Compound **18** was obtained in 57% yield from **2h**, as a 15 : 85 mixture of **17a**/**18**, as described for **8e**. Alternatively, **18** was obtained quantitatively from **2h**, as a 50 : 50 mixture of **17a**/**18**, as described for **15b**. Analytically pure **18** (cyclohexane/AcOEt 99 : 1, 19% yield from the 15 : 85 mixture) exhibited the following analytical data: IR: 3009, 2958, 2927, 2872, 2848, 1683, 1462, 1340, 1304, 1251, 1204, 1045, 902, 872, 839, 751, 687, 625. $^1$H-NMR: 5.40 – 5.35 (*m*, 1 H); 5.30 – 5.25 (*m*, 1 H); 2.75 (br. *d*, *J* = 7.2, 2 H); 2.28 (br. *t*, *J* = 7.5, 2 H); 2.18 (br. *t*, *J* = 7.2, 2 H); 2.08 (*quint.*, *J* = 7.7, 2 H); 1.78 (*quint.*, *J* = 7.5, 2 H); 0.96 (*t*, *J* = 7.5, 3 H); 0.19 (*s*, 9 H). $^{13}$C-NMR: 146.2 (*s*); 131.9 (*d*); 126.6 (*d*); 115.8 (*s*); 33.7 (*t*); 30.9 (*t*); 24.5 (*t*); 20.4 (*t*); 19.7 (*t*); 14.3 (*q*); 0.6 (3*q*). MS: 224 (10, $M^+$), 209 (7), 195 (38), 167 (10), 156 (100), 155 (42), 75 (21), 73 (73), 45 (9), 32 (10), 28 (30).

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