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TETRAHEDRON

Cobalt-Mediated Cycloisomerization of δ-Substituted ε-Acetylenic β-Ketoesters Construction of Angular Triquinane by a Sequence Ene/Pauson-Khand Reactions

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Abstract: The preparation of δ-substituted ε-acetylenic β-ketoesters is fully described. Their cobalt-mediated Conia-ene reactions led to variously functionalized methylenecyclopentanes in high yields and with a moderate control of the 1,4 diastereoselectivity. A sequence involving the cobalt-mediated ene and Pauson-Khand reactions is presented and allowed the construction of the angular triquinane framework.

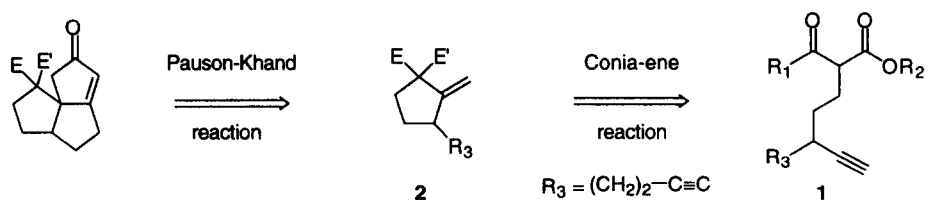
Keywords : Cobalt and compounds ; ene reaction ; 1,4 diastereoselection ; Pauson-Khand reaction

INTRODUCTION

Transition metal-mediated cyclizations of substrates containing multiple unsaturations are particularly important tools for the efficient construction of complex molecular structures.[1] Toward this aim, the catalytic cobalt-mediated ene reaction of ε-acetylenic β-ketoesters has provided a useful new method for the stereoselective preparation of highly functionalized methylenecyclopentanes[2] or bicyclic [n.3.0] derivatives.[3] The investigations into the mechanism of this new cyclization and the observed selectivities supported a process of an enol-yne cycloisomerization.[4] We also demonstrated that this cycloisomerization controlled the relative stereochemistry of 1,2[3,5] or 1,3[6] stereogenic centers with moderate to high level of diastereoselectivity.

In connection with our program devoted to the synthetic development of transition metal-mediated cyclizations, we have investigated stereoselective routes to the basic skeletons of natural tetracyclic diterpenes.

For these purposes, we already reported stereoselective approaches to phyllocladane[4,7] and kaurane[6] families *via* a cascade of cyclizations. Towards the synthesis of complex natural compounds, we were interested in the quest for a rapid and efficient access to angular triquinanes by using a combination of the ene-type and Pauson Khand[8] reactions (Scheme 1).



Scheme 1

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In relation with the diastereoselective entry into the angular triquinane,[9] the extension of the ene-type reaction to δ-substitued ε-acetylenic β-ketoesters appeared very attractive for the stereocontrol of the newly formed 1,4 stereogenic centers in the intermediate methylenecyclopentane. To our knowledge, no examples of such a control for the cycloisomerizations has been reported in the literature.

Here we present the full details of the preparation of the ω-acetylenic β-ketoesters substitued at the δ–position and their cobalt (I)-mediated cyclizations. We report especially the factors allowing to gain a better 1,4 stereocontrol in this ene-reaction.

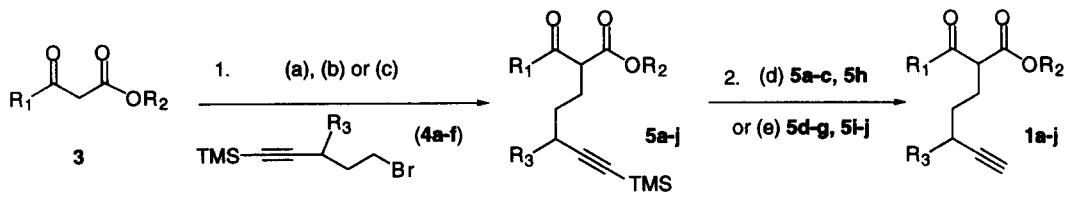
RESULTS AND DISCUSSION

A-Preparation of δ-substituted ε-acetylenic β-ketoesters 1.

The δ-substituted ε-acetylenic β-ketoesters **1** were prepared in two steps in high yields (Table 1). The alkylation of the β-ketoesters **3** (R_1 = Me, Ph ; R_2 = Me, *t*-Bu) sodium enolate with 5-bromo-4-substituted-1-trimethylsilylpentyne **4**, according to an usual procedure,[10] led to the compounds **5**. Then, the removal of the trimethylsilyl group with potassium fluoride in DMSO/H_2O or tetrabutylammonium fluoride[11] in THF afforded **1** (Scheme 2).

Table 1. Preparation of **1**.

Entry	R_1	R_2	R_3	**5** Yield (%)	**1** Yield (%)
a	Me	Me	CH_2-C≡CH	73	83
b	Me	Me	$(CH_2)_2$-C≡CH	75	90
c	Me	Me	$(CH_2)_3$-C≡CH	74	90
d	Me	Me	CH_2-Ph	51	83
e	Me	Me	$(CH_2)_2$-Ph	73	83
f	Me	Me	*n*-Pr	83	83
g	Ph	Me	*n*-Pr	87	97
h	Me	*t*-Bu	$(CH_2)_3$-C≡CH	80	90
i	Me	*t*-Bu	CH_2-Ph	71	94
j	Me	*t*-Bu	*n*-Pr	71	quant

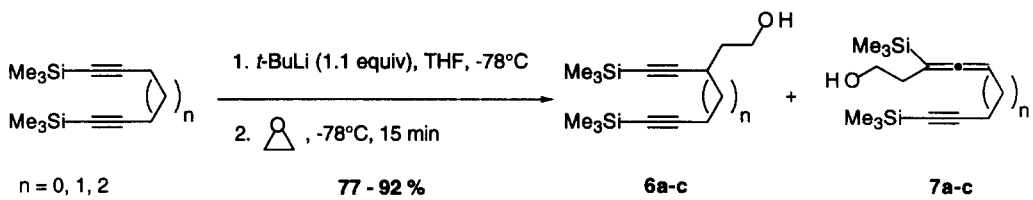


1. (a) **3** (2 equiv), NaH (1.5 equiv), THF, 0°C to r. t. ; (b) with **3** (R_2 = Me) : **4a-f** (1 equiv), HMPA (1.5 equiv) , Δ ; (c) with **3** (R_2 = *t*-Bu) : **4c-d, 4h** (1 equiv), NaI (1 equiv), HMPA (1.5 equiv), r. t. ; (d) *n*-Bu_4NF (2.2 equiv), THF, -10°C then r. t. ; (e) KF (3 equiv), DMSO (H_2O)

Scheme 2

The bromides **4a-f** were obtained from the corresponding alcohols **6a-f** which were prepared in all cases by the alkylation of the requisite propargyllithium anions with ethylene oxide. Depending on the nature of the substituent R_3, the alkyne moiety was prepared by different pathways.

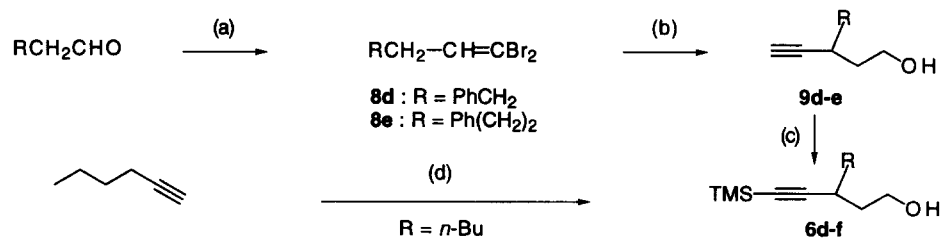
1,5-Hexa-, 1,6-hepta- and 1,7-octadiyne were quantitatively converted into the corresponding bis (trimethylsilyl)diynes.[12] Alkylation of their lithio derivatives generated with *t*-BuLi in THF with ethylene oxide provided the alcohols **6a-c** (Scheme 3).



Scheme 3

In these conditions, we observed the formation of the allenic compounds **7a-c** resulting from the alkylation of the corresponding allenyllithiums[13] as side products (10-25%). We noticed that the regioselectivity in favor of the propargylic alkylation decreased with an increasing length of the diyne.

The alcohols **6d-f** were prepared by the Brandsma procedure[14] or modified in our hands (Scheme 4).



(a) CBr_4 (2 equiv), PPh_3 (4 equiv), 0°C, CH_2Cl_2, **8d** : 95% ; **8e** : 98%. (b) (i) *n*-BuLi (3 equiv), THF, -78°C to r. t. ; (ii) C_2H_4O (5 equiv), - 40° to 10°C, **9d** : 57% ; **9e** : 53%. (c) (i) EtMgBr (3 equiv), THF, TMSCl (2 equiv), Δ ; (ii)1.4 M H_2SO_4, r. t., **6d** : quant. ; **6e** : 83%. (d) (i) *n*-BuLi (2 equiv), THF, -40°C to r. t. ; (ii) C_2H_4O (5 equiv), -40° to 10°C ; (iii) TMSCl (2.5 equiv), Δ, overnight ; (iv) 1.4 M H_2SO_4, r. t., **6f** : 52%

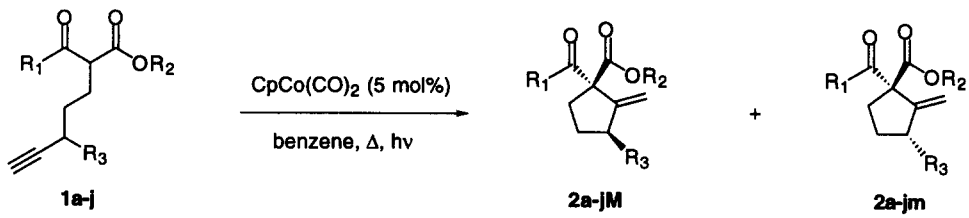
Scheme 4

Chain extension of 3-phenylpropionaldehyde and 4-phenylbutyraldehyde[15] by Corey procedure[16] furnished the dibromoalkenes **8d** and **8e** in 95 % and 98 % yield respectively. Reaction of these latter with 3 equivalents of butyllithium and consecutive alkylation with ethylene oxide led to the alcohols **9d** and **9e** in moderate yields. Subsequent protection of the alkyne by usual procedure[17] gave quantitatively or in 83 % yield the alcohols **6d** and **6e**. The alcohol **6f** was obtained in 52 % overall yield *in situ* from the reaction of the dilithio derivative of 1-hexyne with ethylene oxide followed by consecutive disilylation and deprotection of the hydroxyl group. Finally, the alcohols **6a-f** were converted consecutively into their corresponding tosylates and the bromides **4a-f** by tosylate-bromide exchange.

B- Cobalt(I)-mediated cyclizations of 1

Exposure of the β-ketoesters **1** to 5 mol % of $CpCo(CO)_2$ in refluxing benzene under irradiation for 2 hours furnished the methylenecyclopentanes **2** in good yields and with moderate level of diastereoselectivity as described in table 2.

Table 2 : Formation of **2** through the cyclization of **1** catalyzed by $CpCo(CO)_2$.

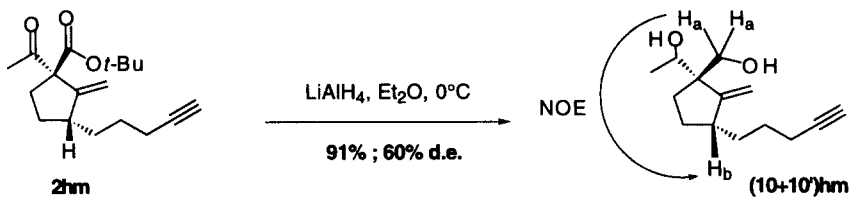


1a-j **2a-jM** **2a-jm**

Entry	2 Yield (%)[a]	d.e. (%)[b]
a	83	30
b	87	40
c	84	20
d	87	22
e	65	20
f	75	7
g	77	16
h	63	30
i	73	25
j	96	28

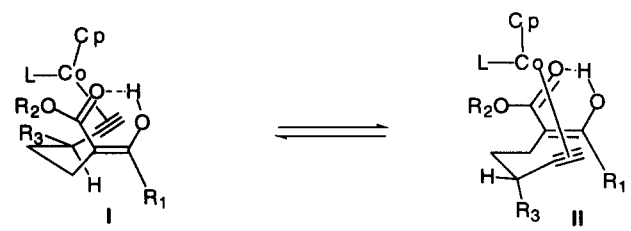
(a) For **2a-e** : isolated yield as a mixture of **2a-e(M+m)** ; for **2h-j** : isolated yield as pure cycloadducts **2h-jM** and **2h-jm**. (b) Ratio calculated by ^{1}H-NMR based on the integration of the CH_3 of the ester group or the protons of the double bond.

The relative configuration of the enecycloadduct was assigned from NOE measurements on the diol **(10+10')hm**, obtained by a $LiAlH_4$ reduction of **2hm** (Scheme 5). Significant NOE effects between H_a and H_b established a *cis* relationship between H_b and the substituent CH_2OH.



Scheme 5

Regarding our previous finding on the 1,2 diastereoselectivity, the enecycloadducts exhibit the same stereochemical behavior. However, on the contrary of this study but as it could be expected the control of the newly formed 1,4 stereogenic centers is in all cases quite moderate. Indeed, in the mechanism of the enol-yne cycloisomerization that we proposed,[5] when a substituent is present at the δ position no allylic 1,3 strain are really involved in any of the rotamers **I** and **II** thus meaning that **I** and **II** are equally present (Scheme 6).



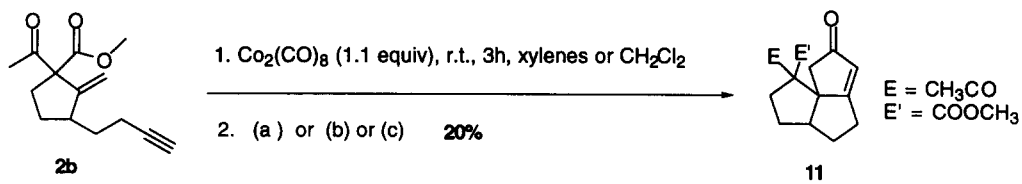
Scheme 6

Thus, the diastereoselectivities observed could be explained by fine destabilizing interactions. But in view of these results, it is quite difficult to rationalize the factors governing this 1,4 diastereoselectivity. We noticed that the steric hindrance of the esters drives slightly the diastereoselectivity of the cyclization (entries f and g ; c and h). The length of the alkynyl chain appears to influence the diastereomeric excesses (d.e.) as well : we got the best result when $R_3 = (CH_2)_2\text{-}C{\equiv}CH$ (40% d.e.). We supposed that this substituent should have the right size for a chelation with cobalt during the process of the complexation. However, when the reaction was carried out with **1e** which has an identical length and is able to develop π-stacking interaction between the aromatic ring and the metal, the d.e. was lower (20%). In order to maximize the intramolecular interactions, the cyclization of **1b** was run in cyclohexane instead of benzene but the d.e. remained unchanged. Thus, these destabilizing interactions which are developed during this cycloisomerization and which are perhaps antagonist are quite difficult to estimate and furthermore to overcome. Fortunately, the best result was obtained with the β-ketoester **2b** which is at the origin of this study. Therefore, we subjected the methylenecyclopentane adduct **2b** to a Pauson-Khand reaction.[8]

C- Pauson-Khand reaction with ***1b***

The thermal[18] and amine-oxide[19] promoted Pauson-Khand reactions of a dicobalthexacarbonyl complexed enynes have been employed for the stereocontrolled synthesis of angular fused triquinanes either in racemic[20] or enantiomeric[21] form.

First, exposure of **2b** to 1.05 equivalents of dicobalt octacarbonyl in xylenes at room temperature led after 3 hours to the corresponding complex. Refluxing of the solution of this intermediate over 1h furnished the angular triquinane **11** in 20% yield (Scheme 7). We attempted to improve the yield of the reaction by using N-oxide process. Exposure of the cobalt complexed enyne (prepared by the same procedure as before) in CH_2Cl_2 to 7 equivalents of N-methylmorpholine oxide for 24h gave the triquinane **11** but disappointingly in the same yield as the thermal conditions. Surprisingly, we noticed that in absence of molecular oxygen (when the reaction was carried out in degassed dichloromethane), the complexed enyne remained unchanged ; in contrast to the literature we did not detect the compound resulting from the interrupted Pauson-Khand reaction.[22] In the same way, when the Pauson-Khand reaction was carried out in 1,2-dichloroethane at 83°C in presence of 3.5 equivalents of cyclohexylamine,[23] the rate of the reaction was enhanced but the yield did not improve.



(a) in xylenes, Δ, 1h. (b) in CH_2Cl_2 , NMO (7 equiv), r.t., 24 h. (c) CH_2Cl_2, cyclohexylamine (3.5 equiv), 83°C, 1h

Scheme 7

Although the yield is quite moderate, the Pauson-Khand reaction remains interesting because it allowed the formation of an angular triquinane bearing two contiguous quaternary centers.

CONCLUSION

In this work, we have synthesized several δ-substituted ε-acetylenic β-ketoesters whose cycloisomerization under the procedure discovered in our laboratory led to variously substituted methylenecyclopentanes in high yields and with moderate diastereomeric excesses. Nevertheless in the case of **1b**, a sequence involving the cobalt-mediated ene cyclization and Pauson-Khand reactions allowed the construction of the angular triquinane framework.

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EXPERIMENTAL SECTION

^{1}H-NMR and ^{13}C-NMR spectra were taken on 200 MHz Bruker AC 200, 400 MHz Bruker ARX 400 spectrometers. Chemical shifts are reported in ppm referenced to the residual proton resonances of the solvants. Infrared (IR) spectra were recorded by using a Perkin Elmer 1420 spectrometer. Mass spectra (MS) were obtained on GC-MS Hewlett-Packard HP 5971 apparatus. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F 254. Silica gel Merck Geduran SI (40-63 μm) was used for flash column chromatography using the Still method.[24] PE and EE mean petroleum ether and diethyl ether.

A- Preparation of δ-substituted ε-acetylenic β-ketoesters 1

General procedure for the preparation of diynol ***6a-c***. To a cooled (-78°C) THF (18 mL) solution of diyne (15.82 mmol) was slowly added *tert*-butyllithium (1.7 M in pentane, 10.2 mL, 17.4 mmol). After being warmed to 0°C over 2h, the reaction mixture was cooled to -78°C and then a solution of ethylene oxide (3.9 mL, 79.1 mmol) in THF (5 mL) was added dropwise. After 15 min at this temperature, the solution was allowed to warm to 0°C over the period of 1h. The reaction mixture was quenched with a saturated solution of NH_4Cl, diluted with ether, washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (PE/EtOAc=85/15) to afford the diynol and alleneynol.

6-(trimethylsilyl)-3-(2'-trimethylsilyl-ethynyl)-5-hexyn-1-ol (6a) 83 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.80 (t, *J* = 6.1 Hz, 2H), 2.72 (m, 1H), 2.49 (m, 2H), 1.90 (ddt, *J* = 7.1, 6.1, 1.7 Hz, 1H), 1.70 (ddt, *J* = 1.7, 6.1, 9.4 Hz, 1H), 0.13 (s, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 108.2, 104.1, 87.3, 86.9, 61.2, 36.7, 29.4, 26.4, 0.0 (6C) ; IR (neat) 3320, 2940, 2160, 1245, 1040, 835 cm^{-1} ; Anal. Calcd for $C_{14}H_{26}OSi_2$: C, 63.10 ; H, 9.83. Found : C, 63.19 ; H, 9.84.

3,8-bis(trimethylsilyl)-3,4-octadien-7-yn-1-ol (7a) 9 %, ^{1}H-NMR (400 MHz,$CDCl_3$) δ 4.85 (m, 2x1H), 3.70 (m, 2x2H), 2.90 (d, *J* = 5.2 Hz, 2x2H), 2.19 (m, 2x2H), 0.10 (s, 2x9H), 0.08 (s, 2x9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.2 (2C), 107.0 (2C), 93.5 (2C), 85.2 (2C), 84.7 (2C), 65.8 (2C), (31.0, 30.8), 15.2 (2C), 0.1 (6C), -0.14 (6C) ; IR (neat) 3360, 2940, 2160, 1935, 1240, 1030, 835 cm^{-1}.

7-(trimethylsilyl)-3-(2'-trimethylsilyl-ethynyl)-6-heptyn-1-ol (6b) 62%, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.77 (t, *J* = 5.6 Hz, 2H), 2.66-2.61 (m, 1H), 2.45-2.41 (m, 1H), 2.39-2.25 (m, 1H), 1.77-1.59 (m, 4H), 0.11 (s, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 108.7, 106.6, 87.1, 84.8, 61.1, 37.2, 34.0, 29.0, 17.8, 0.1 (6C) ; IR (neat) 3320, 2940, 2150, 1240, 1040, 835 cm^{-1}.

3,9-bis(trimethylsilyl)-3,4-nonadien-8-yn-1-ol (7b) 15 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.94 (tt, *J* = 6.1, 3.0 Hz, 2x1H), 3.77 (t, *J* = 5.6 Hz, 2x2H), 2.66-2.61 (m, 2x1H), 2.45-2.41 (m, 2x2H), 2.39-2.25 (m, 2x1H), 1.77-1.59 (m, 2x2H), 0.11 (s, 2x18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.9 (2C), (108.6, 106.6), 94.6 (2C), (84.8, 84.2), (68.9, 68.8), (62.3, 61.1), (37.4, 37.1), (34.1, 34.0), 32.4 (2C), 0.1 (2x3C), -1.5 (2x3C) ; IR (neat) 3300, 2950, 2160, 1935, 1245, 1040, 840, 755 cm^{-1}.

8-trimethylsilyl-3-(2'-trimethylsilyl-ethynyl)-7-octyn-1-ol (6c) 42 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.8 (t, *J* = 7.1 Hz, 2H), 2.6-2.5 (m, 1H), 2.2 (t, *J* = 7.1 Hz, 2H), 1.8-1.5 (m, 6H), 0.15 (s, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 109.6, 107.1, 86.7, 84.7, 61.2, 37.5, 34.0, 29.2, 26.1, 19.6, 0.1 (6C) ; IR (neat) 3540, 2960, 2170, 1250, 910, 845, 735, 650 cm^{-1}.

3,10-bis(trimethylsilyl)-3,4-decadien-9-yn-1-ol (7c) 25 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.76 (tt, *J* = 6.6, 3.0 Hz, 2x1H), 3.64 (td, *J* = 6.4, 2.0 Hz, 2x2H), 2.17 (t, *J* = 7.1 Hz, 2x2H), 2.12 (td, *J* = 6.6, 3.0 Hz, 2x2H), 1.98 (q, *J* = 7.1 Hz, 2x2H), 1.49 (quint., *J* = 7.1 Hz, 2x2H), 0.04 (s, 2x9H), 0.00 (s, 2x9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.2 (2C), 107.0 (2C), 93.5 (2C), 85.2 (2C), 84.7 (2C), 62.2 (2C), 32.3 (2C), 28.5 (2C), 27.5 (2C),

19.3 (2C), 0.1 (2x3C), -1.7 (2x3C) ; IR (neat) : 3340, 2950, 2900, 2170, 1930, 1245, 1040, 835, 755, 690, 635 cm^{-1}.

General procedure for the preparation of dibromoolefines ***8d-e***. To a cooled (0°C) CH_2Cl_2 (50 mL) solution of triphenyl phosphine (21.0 g, 80 mmol) was added a solution of carbone tetrabromide (13.3 g, 40 mmol) in CH_2Cl_2 (50 mL). After being stirred for 15 min at this temperature, a solution of aldehyde (20 mmol) in CH_2Cl_2 (50 mL) was added. The reaction mixture was then allowed to warm to room temperature and stirred until the completion by TLC. The mixture was concentrated and purified by flash chromatography (PE/EE = 80/20).

1,1-dibromo-4-phenyl-butene (8d) 95%, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 3H), 7.28 (m, 2H), 6.48 (t, *J* = 7.1 Hz, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.49 (td, *J* = 7.6, 7.1 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) 140.4, 137.6, 128.5 (2C), 128.3 (2C), 126.2, 89.5, 34.6, 33.8 ; IR (neat) : 3060, 3020, 2920, 2850, 1620, 1600, 1490, 1450, 1430, 1190, 1145, 1080, 1025, 905, 800, 745, 695 cm^{-1}.

1,1-dibromo-5-phenyl-pentene (8e) 98 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.26-7.22 (m, 3H), 6.46 (t, *J* = 7.4 Hz, 1H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.18 (q, *J* = 7.4 Hz, 2H), 1.81 (quint., *J* = 7.4 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.5, 138.3, 128.3 (4C), 125.9, 89.0, 35.2, 32.5, 29.4 ; IR (neat) : 3060, 3040, 3000, 2920, 2850, 1600, 1490, 1450, 905, 780, 730, 695 cm^{-1}.

General procedure for the preparation of alcohols ***9d-e***. To a cooled (-78°C) THF (6 mL) solution of dibromoolefine (5 mmol) was added *n*-butyllithium (2.0 M in hexane, 8.7 mL, 17.5 mmol). After being stirred at this temperature for 30 min, the reaction mixture was warmed to room temperature and was stirred for 2h. Then the reaction mixture was cooled to -40°C and a solution of ethylene oxide (1.25 mL, 25 mmol) in THF (1 mL) was quickly added dropwise. The reaction mixture was allowed to warm to 10°C, quenched by a saturated solution of NH_4Cl, diluted with ether, washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (PE/EE = 60/40).

3-phenylmethyl-pent-4-yn-1-ol (9d) 57 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 3H), 7.27 (m, 2H), 3.87 (t, *J* = 6.1 Hz, 2H), 2.91-2.80 (m, 3H), 2.14 (d, *J* = 1.5 Hz, 1H), 1.85-1.64 (m, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.9, 129.2 (2C), 128.2 (2C), 126.4, 86.5, 70.8, 60.8, 41.2, 36.8, 30.2 ; IR (neat) : 3350, 3295, 3020, 2920, 2840, 2100, 1600, 1490, 1450, 1045, 730, 695 cm^{-1}.

3-(2'-phenylethyl)-pent-4-yn-1ol (9e) 53 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (2H, m), 7.24-7.20 (3H, m), 3.82 (t, *J* = 6.1 Hz, 2H), 2.93-2.86 (m, 1H), 2.79-2.71 (m, 1H), 2.60-2.53 (m, 1H), 2.20 (d, *J* = 2.6 Hz, 1H), 1.85-1.70 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.6, 128.3 (4C), 125.8, 86.7, 70.5, 60.7, 37.4, 36.7, 33.3, 27.7 ; IR ($CDCl_3$) : 3610, 3450, 3300, 3050, 3020, 2930, 2880, 2100, 1600, 1490, 1445, 1420, 1380, 1340, 1255, 1060, 1045, 690, 630 cm^{-1}.

General procedure for the preparation of the alcohols ***6d-e***. To a cooled (0°C) THF (10 mL) solution of ethylmagnesium bromide (22 mmol) was added a solution of alcohol **9d-e** (7 mmol) in THF (3 mL). The suspension was stirred overnight at room temperature. The resulting solution was cooled to 0°C and trimethylsilyl chloride (1.7 mL, 14 mmol) was added dropwise. After complete addition, the mixture was heated to reflux for 2h. After being cooled to 20°C, 1.4 M H_2SO_4 (0.6 mL) was cautiously added to the suspension. After stirring for 10 min, the reaction mixture was partitionned between ether and a saturated solution of $NaHCO_3$. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (PE/EE = 70/30) to afford the alcohols **6d** and **6e**.

3-phenylmethyl-5-trimethylsilyl-pent-4-yn-1-ol (6d) quantitative, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 3.82 (t, *J* = 6.1 Hz, 2H), 2.89-2.76 (m, 3H), 1.82-1.74 (m, 1H), 1.70-1.58 (m, 1H), 0.15 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.0, 129.4 (2C), 128.1 (2C), 126.3, 109.3, 87.4, 61.2, 41.3, 36.7, 31.7, 0.00 (3C) ; IR (neat) : 3350, 3100, 2950, 2920, 2160, 1245, 1050, 835, 755, 695 cm^{-1}.

3-(2'-phenylethyl)-5-trimethylsilyl-pent-4-yn-1ol (6e) 83 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.25-7.20 (m, 3H), 3.83 (t, *J* = 6.1 Hz, 2H), 2.89 (ddd, *J* = 6.1, 8.4, 13.9 Hz, 1H), 2.76 (td, *J* = 8.4, 13.9 Hz, 1H), 2.57 (m, 1H), 1.84-1.67 (m, 4H), 0.20 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.8, 128.4 (2C), 128.3 (2C), 125.8, 109.6, 87.0, 61.1, 37.5, 36.9, 33.4, 29.1, 0.1 (3C) ; IR (neat) : 3340, 3080, 3050, 3020, 2920, 2850, 2160, 1600, 1490, 1450, 1375, 1245, 1045, 840, 740, 695 cm^{-1}.

Preparation of 3-propyl-5-trimethylsilyl-pent-4-yn-1-ol 6f. To a cooled (-40°C) ether (2 mL) solution of hexyne (1.15 mL, 10 mmol) was added *n*-butyllithium (2.2 M in hexane, 9.1 mL, 20 mmol). The mixture was heated at reflux for 2h, then cooled to -40°C. A solution of ethylene oxide (2 mL, 40 mmol) in ether (1 mL) was rapidly added dropwise at this temperature. The reaction mixture was allowed to warm to room temperature, cooled to 0°C and then TMSCl (3.2 mL, 25 mmol) was added. The solution was refluxed overnight, cooled to room temperature, treated with 10 % HCl (6 mL) and stirred for 30 min. The reaction mixture was extracted with ether, washed with saturated solution of $NaHCO_3$, brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (PE/EE = 70/30).

3-propyl-5-trimethylsilyl-pent-4-yn-1-ol (6f) 52 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.81 (t, *J* = 6.0 Hz, 2H), 2.54 (m, 1H), 1.78-1.60 (m, 2H), 1.55-1.35 (m, 4H), 0.95 (t, *J* = 6.8 Hz, 3H), 0.20 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 110.2, 86.2, 61.3, 37.5, 37.2, 29.4, 20.3, 13.8, 0.1 (3C) ; IR (neat) : 3450, 2930, 2880, 2160, 1450, 1410, 1380, 1355, 1250, 1100, 850, 750, 695, 630 cm^{-1}.

General procedure for the bromides 4a-f. (a)To a CH_2Cl_2 (20 mL) solution of alcohol **6a-f** (5 mmol) was added 4-DMAP (122 mg, 1 mmol), triethylamine (0.91 mL, 6.5 mmol) and tosyl chloride (1.144 g, 6 mmol) at room temperature. The reaction mixture was stirred until the completion by TLC. The reaction mixture was then diluted with ether, washed with a saturated solution of NH_4Cl, brine, dried over Na_2SO_4 and concentrated. The crude product was used in the next step without purification. (b) To a DMF (20 mL) solution of the crude product was added lithium bromide (2.17 g, 25 mmol) at room temperature. After being stirred overnight, the reaction mixture was diluted with pentane, washed with a saturated solution of NH_4Cl, brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (PE).

1-bromo-6-(trimethylsilyl)-3-(2'-trimethylsilyl-ethynyl)-hex-5-yne (4a) 73 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.61-3.50 (m, 1H), 3.45-3.35 (m, 1H), 2.66-2.61 (m, 1H), 2.39-2.21 (ABX, *J* = 6.0 Hz, 2H), 2.04-1.65 (m, 2H), 0.00 (s, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 106.3, 103.3, 87.3, 87.0, 42.6, 36.7, 29.6, 25.7, 0.0 (3C), -0.3 (3C) ; IR (neat) 2960, 2930, 2170, 1250, 1030, 850, 760, 740, 700 cm^{-1}.

1-bromo-7-(trimethylsilyl)-3-(2'-trimethylsilyl-ethynyl)-hept-6-yne (4b) quantitative, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.59-3.50 (ABX, *J* = 8.0 Hz, 2H), 2.77 (quint., *J* = 8.0 Hz, 1H), 2.50-2.27 (m, 2H), 2.04 (q, *J* = 8.0 Hz, 2H), 1.88 (q, *J* = 8.0 Hz, 2H), 0.00 (s, 18H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 107.1, 106.3, 87.3, 85.0, 42.6, 37.5, 33.5, 29.6, 17.8, 0.0 (6C) ; IR (neat) 2960, 2930, 2170, 1250, 1030, 850, 760, 740, 700 cm^{-1}.

1-bromo-8-(trimethylsilyl)-3-(2'-trimethylsilyl-ethynyl)-oct-7-yne (4c) 84 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.53 (m, 1H), 3.40 (m, 1H), 2.49 (m, 1H), 2.11 (t, *J* = 6.6 Hz, 2H), 1.81 (q, *J* = 7.5 Hz, 1H), 1.72 (q, *J* = 6.6 Hz, 1H), 1.63-1.32 (m, 4H), 0.00 (s, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 108.1, 106.9, 86.9, 84.8, 42.8, 37.7, 33.5, 29.7, 26.1, 19.5, 0.1 (6C) ; IR (neat) 2960, 2930, 2170, 1250, 1030, 850, 760, 740, 700 cm^{-1}.

1-bromo-3-phenylmethyl-5-trimethylsilyl-pent-4-yne (4d) 73 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17-7.07 (m, 5H), 3.44-3.34 (m, 2H), 2.72-2.61 (m, 3H), 1.82-1.72 (m, 2H), 0.02 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.6, 129.3 (2C), 128.1 (2C), 126.4, 107.6, 87.6, 40.9, 37.0, 33.4, 31.3, 0.0 (3C) ; IR (neat) 3100, 2950, 2920, 2160, 1245, 835, 755, 695 cm^{-1}.

1-bromo-3-(2'-phenylethyl)-5-trimethylsilyl-pent-4-yne (4e) 84 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.28-7.23 (m, 3H), 3.65-3.53 (m, 2H), 2.90 (td, J = 7.1, 13.7 Hz, 1H), 2.77 (dt, *J* = 13.7, 8.4 Hz,

1H), 2.66 (quint., J = 6.1 Hz, 1H), 2.06-2.00 (m, 2H), 1.81 (AB, J = 8.4 Hz, 2H), 0.24 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.6, 128.4 (2C), 128.3 (2C), 125.9, 107.9, 87.3, 52.6, 37.8, 36.4, 33.4, 31.2, 0.2 (3C) ; IR (neat) 2920, 2840, 2160, 1455, 1370, 1245, 840, 695 cm^{-1}.

General procedure for the alkylation of the β-ketoesters 3. To a cooled (-10°C), stirred suspension of sodium hydride (60% in oil, 300 mg, 7.5 mmol) in THF (20 mL) was added dropwise the β-ketoester **3** (1.08 mL, 10 mmol). After being stirred for 1h at room temperature, (i) for **3** (R_2 = Me), a solution of bromoalkyne **4a-f** (5 mmol) in THF (5 mL) and HMPA (1.30 mL, 7.5 mmol) were added and the resulting mixture was heated at 50°C for 12h, cooled at room temperature and diluted with ether or (ii) for **3** (R_2 = *t*-Bu), a solution of bromoalkyne **4c-d, 4f** (5 mmol) in THF (5 mL), sodium iodide (749 mg, 5 mmol) and HMPA (1.30 mL, 7.5 mmol) were added and the resulting mixture was stirred at room temperature for 72h and diluted with ether. The organic layer was washed successively with a saturated solution of NH_4Cl, brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (PE/EE = 90/10 for **5a-g** ; 95/5 for **5h-j**).

Methyl 2-acetyl-8-trimethylsilyl-5-(2'-trimethylsilyl-ethynyl)-oct-7-ynoate (5a) 73 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 2x3H), 3.34 (ABX, J = 8.1 Hz, 2x1H), 2.80-2.75 (m, 1H), 2.46-2.38 (m, 1H), 2.33-2.17 (m, 4H), 2.10 (s, 3H), 2.09 (s, 3H), 2.01-1.89 (m, 2H), 1.87-1.78 (m, 2H), 1.54-1.42 (m, 2H), 1.38-1.23 (m, 2H), 0.01 (s, 18H), 0.00 (s, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.8 (2C), 170.0 (2C), 107.5 (2C), 103.7 (2C), 87.0 (2C), 86.6 (2C), (59.4, 59.0), (52.6, 52.5), (31.9, 31.6), (31.2, 31.1), (29.6, 29.7), (28.7, 28.4), (25.8, 25.5), 0.0 (6C) , -0.1 (6C) ; IR (neat) 2950, 2920, 2840, 2170, 1740, 1715, 1245, 840, 705, 695 cm^{-1}.

Methyl 2-acetyl-9-trimethylsilyl-5-(2'-trimethylsilyl-ethynyl)-non-8-ynoate (5b) 75 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.60 (s, 3H), 3.33 (ABX, J = 8.1 Hz, 2x1H), 2.36-2.13 (m, 2x3H), 2.09 (s, 2x3H), 1.97-1.79 (m, 2x2H), 1.55-1.47 (m, 2x2H), 1.34-1.26 (m, 2x2H), 0.00 (s, 2x18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.9 (2C), (170.1, 170.0), (108.3, 108.2), 106.5 (2C), (87.0, 86.9), 84.7 (2C), (59.4, 59.1), 52.3 (2C), (33.8, 33.7), (32.2, 31.9), (31.7, 31.4), (28.8, 28.6), (26.0, 25.7), 17.8 (2C), 0.0 (2x6C) ; IR (neat) 2950, 2920, 2840, 2170, 1740, 1715, 1245, 840, 705, 695 cm^{-1}.

Methyl 2-acetyl-10-trimethylsilyl-5-(2'-trimethylsilyl-ethynyl)-deca-9-ynoate (5c) 74 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.60 (s, 3H), 3.34 (t, J = 7.4 Hz, 1H), 3.31 (t, J = 7.6 Hz, 1H), 2.28-2.17 (m, 2x1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (t, J = 6.6 Hz, 2x2H), 1.97-1.77 (m, 2x2H), 1.61-1.50 (m, 2x1H), 1.46-1.25 (m, 2x5H), 0.00 (s, 2x18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ203.0 (2C), (170.2, 170.1), (109.2, 109.1), 107.0 (2C), 86.4 (2C), 84.7 (2C), (59.5, 59.2), 52.2 (2C), 33.8 (2C), (32.6, 32.2), (32.1, 31.9), 29.7 (2C), (28.8, 28.5), (26.1, 25.8), 19.6 (2C), 0.0 (12C); IR (neat) 2920, 2860, 2160, 1740, 1710, 1430, 1355, 1245, 1145, 900, 730 cm^{-1}.

Methyl 2-acetyl-5-phenylmethyl-7-trimethylsilyl-hepta-6-ynoate (5d) 51 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17-7.13 (m, 4H), 7.10-7.07 (m, 6H), 3.58 (s, 3H), 3.57 (s, 3H), 3.33 (AB, J = 7.8 Hz, 2H), 2.70-2.56 (m, 4H), 2.53-2.44 (m, 2H), 2.09 (s, 3H), 2.08 (s, 3H), 2.02-1.93 (m, 2H), 1.88-1.78 (m, 2H), 1.39-1.22 (m, 4H), 0.00 (s, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.9 (2C), (170.1, 170.0), 139.0 (2C), 129.3 (4C), 128.0 (4C), 126.3 (2C), (108.9, 108.8), (87.2, 87.1), (59.4, 59.0), 52.3 (2C), (41.1, 41.0), (34.5, 34.2), (31.7, 31.3), (28.8, 28.5), (26.0, 25.6), 0.00 (6C) ; IR (neat) 3040, 3020, 2990, 2940, 2920, 2860, 2160, 1740, 1710, 1640, 1600, 1490, 1450, 1430, 1355, 1145, 740, 700 cm^{-1}.

Methyl 2-acetyl-5-(2'-phenyl-ethyl)-7-trimethylsilyl-hepta-6-ynoate (5e) 73 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.13-7.08 (m, 4H), 7.03-6.99 (m, 6H), 3.55 (s, 3H), 3.54 (s, 3H), 3.28 (AB, J = 7.9 Hz, 2H), 2.64 (td, J = 13.7, 7.0 Hz, 2H), 2.51 (td, J = 13.7, 8.1 Hz, 2H), 2.23-2.14 (m, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 1.92-1.84 (m, 2H), 1.81-1.71 (m, 2H), 1.58-1.52 (m, 4H), 1.30-1.20 (m, 4H), 0.00 (s, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.0 (2C), (170.2, 170.1), 141.8 (2C), 128.5 (4C), 128.3 (4C), 125.8 (2C), (109.2, 109.1), 86.8 (2C), (59.5, 59.1), 52.3 (2C), (36.6, 36.5), 33.4 (2C), (32.4, 32.1), (32.0, 31.7), (28.8, 28.5), (26.1, 25.7), 0.2 (6C) ; IR ($CHCl_3$) 3050, 3020, 2940, 2850, 2160, 1740, 1710, 1640, 1600, 1490, 1450, 1430, 1355, 1245, 840, 690 cm^{-1}.

Methyl 2-acetyl-5-propyl-7-trimethylsilyl-hepta-6-ynoate (5f) 83 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.66 (s, 3H), 3.46-3.40 (ABX, *J* = 7.6 Hz, 2x1H), 2.37-2.28 (m, 2x1H), 2.21 (s, 3H), 2.20 (s, 3H), 2.10-2.01 (m, 2x1H), 1.98-1.76 (m, 2x1H), 1.53-1.31 (m, 2x4H), 1.28-1.20 (m, 2x2H), 0.88 (t, 2x3H, *J* = 7.1Hz), 0.00 (s, 2x9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.3 (2C), (170.1, 170.4), (110.0, 109.9), (59.8, 59.6), (52.7, 52.6), (37.3, 37.2), (32.9, 32.8), (31.5, 31.3), (29.2, 29.1), (26.4, 26.2), 20.7 (2C), (14.4, 14.2) ; IR (neat) 2940, 2920, 2860, 2160, 1740, 1720, 1450, 1430, 1350, 1250, 1205, 1150, 730, 840, 625 cm^{-1}.

Methyl 2-phenylacetyl-5-propyl-7-trimethylsilyl-hepta-6-ynoate (5g) 87 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2x2H), 7.61 (t, *J* = 7.6 Hz, 2x1H), 7.50 (t, *J* = 7.6 Hz, 2x2H), 4.41 (dd, *J* = 7.6, 8.1 Hz, 2x1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.47-2.34 (m, 2x1H), 2.29-2.08 (m, 2x3H), 1.57-1.34 (m, 2x5H), 0.91 (m, 2x3H), 0.13 (s, 2x9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.1 (2C), (170.4, 170.3), (136.1, 136.0), 133.5 (2C), 128.8 (2x2C), 128.6 (2x2C), (110.0, 109.9), 85.9 (2C), (53.9, 53.6), 36.9 (2C), (32.8, 32.5), (32.3, 32.0), 29.8 (2C), (27.1, 26.8), (20.4, 20.3) 13.9 (2C), 0.2 (6C) ; IR (neat) 2940, 2920, 2860, 2150, 1740, 1680, 1590, 1570, 1440, 1240, 860, 835, 750, 685, 630 cm^{-1}.

***tert*-butyl 2-acetyl-10-trimethylsilyl-5-(2'-trimethylsilyl-ethynyl)-deca-9-ynoate (5h)** 80 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.76 (s, 1H_{enol}), 3.19 (ABX, *J* = 7.9 Hz, 2x1H), 2.28-2.16 (m, 2x1H), 2.08 (s, 3H), 2.07 (s, 3H), 2.11-2.00 (m, 2x2H), 1.93-1.70 (m, 2x2H), 1.58-1.51 (m, 2x1H), 1.48-1.20 (m, 2x5H), 1.32 (s, 2x9H), 0.00 (s, 2x18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.3 (2C), 168.8 (2C), (109.4, 109.3), 107.0 (2C), (86.3, 86.2), 84.6 (2C), 81.8 (2C), (60.8, 60.5), 33.8 (2C), (32.4, 32.2), (32.1, 31.8), (28.6, 28.3), 27.9 (6C), 26.2 (2C), (25.9, 25.7), 19.6 (2C), 0.2 (6C), 0.1 (6C) ; IR (neat) 2940, 2860, 2160, 1730, 1710, 1450, 1390, 1360, 1240, 1135, 835, 755, 690, 630 cm^{-1}.

***tert*-butyl 2-acetyl-5-phenylmethyl-7-trimethylsilyl-hepta-6-ynoate (5i)** 71 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16-7.13 (m, 2x2H), 7.09-7.08 (m, 2x3H), 3.22-3.16 (m, 2x1H), 2.71-2.65 (m, 2x1H), 2.62-2.57 (m, 2x1H), 2.56-2.47 (m, 2x1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.97-1.87 (m, 2x2H), 1.84-1.73 (m, 2x2H), 1.30 (s, 2x9H), 0.00 (s, 2x9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (203.4, 203.3), (168.9, 168.8), 139.1 (2C), 129.3 (4C), 128.1 (4C), 126.3 (2C), (109.1, 108.9), (87.1, 86.9), 81.9 (2C), (60.7, 60.4), 41.1 (2C), (34.6, 34.3), (31.6, 31.3), (28.6, 28.3), 27.8 (6C), (25.9, 25.6), 0.1 (6C) ; IR ($CHCl_3$) 2160, 1730, 1710, 1320, 1245, 910, 850, 830, 730, 695, 640 cm^{-1}.

***tert*-butyl 2-acetyl-5-propyl-7-trimethylsilyl-hepta-6-ynoate (5j)** 71%, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.58 (t, *J* = 6.4 Hz, 1H), 3.56 (t, *J* = 7.8 Hz, 1H), 2.45-2.32 (m, 2x1H), 2.21 (s, 3H), 2.20 (s, 3H), 2.07-1.95 (m, 2x1H), 1.93-1.85 (m, 2x1H), 1.50 (s, 2x9H), 1.49-1.35 (m, 2x6H), 0.96 (t, *J* = 7.4 Hz, 2x3H), 0.20 (s, 2x9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.5 (2C), 168.9 (2C), (110.0, 109.8), (85.8, 85.7), 81.8 (2C), (60.8, 60.5), 36.9 (2C), 32.4 (2C), (32.2, 31.9), (28.6, 28.3), 27.9 (2x3C), (25.7, 25.6), 20.3 (2C), 13.9 (2C), 0.2 (2x3C) ; IR (neat) 2930, 2860, 2160, 1750, 1715, 1370, 1245, 830, 695, 640 cm^{-1}.

*General procedure for the preparation of **1a-i**.* I-Deprotection of compounds **5a-c, 5h**: To a cooled (-10°C) solution of **5a-c, 5h** (2 mmol) in THF (50 mL) was added dropwise a THF solution of tetrabutylammonium fluoride (1M in THF, 4.4 mL, 4.4 mmol). After being stirred for 30 min at -10 °C and an additionnal 3h at room temperature, the reaction mixture was extracted with ether, washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash chromatography (PE/EE = 90/10 for **1a-c** ; 95/5 for **1h**).

Methyl 2-acetyl-5-ethynyl-octa-7-ynoate (1a) 83 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 2x3H), 3.35 (t, *J* = 8.1 Hz, 1H), 3.33 (t, *J* = 8.1 Hz, 1H), 2.56-2.46 (m, 2x1H), 2.42-2.26 (ABXY, *J* = 2.0, 7.6 Hz, 2x2H), 2.18 (s, 3H), 2.17 (s, 3H), 2.10 (d, *J* = 2.6 Hz, 2x1H), 2.06-2.00 (m, 2x1H), 1.99 (t, *J* = 2.6 Hz, 2x1H), 1.94-1.83 (m, 2x1H), 1.62-1;51 (m, 2x1H), 1.50-1.39 (m, 2x1H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.6 (2C), (170.0, 169.9), (84.9, 84.8), 81.0 (2C), (70.9, 70.8), 70.3 (2C), (59.2, 59.0), 52.4 (2C), (31.6, 31.4), (31.1, 30.9), (29.3, 29.1), (26.0, 25.9), 24.9 (2C) ; IR (neat) 3300, 2950, 2920, 2100, 1740, 1710, 1430, 1355, 1145, 680, 645 cm^{-1}.

Methyl 2-acetyl-5-ethynyl-nona-8-ynoate (1b) 90 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.66 (s, 1H_{enol}), 3.74 (s, 3H_{enol}), 3.73 (s, 3H), 3.72 (s, 3H), 3.34 (t, *J* = 8.1 Hz, 1H), 3.32 (t, *J* = 7.6 Hz, 1H), 2.53-2.49 (m, 2x1H), 2.38-2.31 (m, 2x2H), 2.22 (s, 2x3H), 2.10 (d, *J* = 2.0 Hz, 2x1H), 2.08-2.04 (m, 2x1H), 1.95 (t, *J* = 2.5 Hz, 2x1H), 1.98-

1.89 (m, 2x1H), 1.69-1.61 (m, 2x2H), 1.51-1.36 (m, 2x2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.7 (2C), (170.0, 169.9), (85.5, 85.4), 83.4 (2C), (70.7, 70.2), (68.8, 68.6), (59.2, 59.0), (52.3, 51.4), (33.4, 33.3), (32.1, 31.9), (30.4, 30.1), (28.8, 28.7), (25.8, 25.6), 16.2 (2C), enol form : 172.5, 135.0, 99.5, 85.5 ; IR (neat) 3330, 2920, 2860, 2100, 1740, 1710, 1430, 1355, 1245, 1220, 1145, 900, 730, 645 cm^{-1}.

Methyl 2-acetyl-5-ethynyl-deca-9-ynoate (1c) 90 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 2x3H), 3.46 (ABX, 2x1H), 2.41-2.33 (m, 2x1H), 2.25 (s, 3H), 2.24 (s, 3H), 2.22 (td, *J* = 7.1, 2.5 Hz, 2x2H), 2.09 (AB, 2x2H), 1.96 (t, *J* = 2.5 Hz, 2x1H), 2.00-1.91 (m, 2x1H), 1.81-1.70 (m, 2x1H), 1.67-1.42 (m, 2x5H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.8 (2C), (170.1, 170.0), (86.3, 86.2), 84.0 (2C), (70.4, 70.3), 68.6 (2C), (59.4, 59.1), (52.6, 52.4), 33.6 (2C), (32.5, 32.3), (31.0, 30.8), (28.9, 28.6), (25.9, 25.7), 25.9 (2C), 18.1 (2C) ; IR (neat) 3330, 2920, 2860, 2240, 1740, 1710, 1430, 1355, 1245, 1220, 1145, 900, 730, 645 cm^{-1}.

***tert*-butyl 2-acetyl-5-ethynyl-deca-9-ynoate (1h)** 90 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.34 (t, *J* = 6.4 Hz, 1H), 3.32 (t, *J* = 6.4 Hz, 1H), 2.42-2.34 (m, 2x2H), 2.21 (s, 3H), 2.20 (s, 3H), 2.20 (td, *J* = 7.4, 2.5 Hz, 2x2H), 2.07 (d, *J* = 2.1 Hz, 2x1H), 2.04-1.97 (m, 2x1H), 1.94 (t, *J* = 2.5 Hz, 2x1H), 1.91-1.83 (m, 2x1H), 1.78-1.69 (m, 2x1H), 1.65-1.48 (m, 2x4H), 1.45 (s, 2x9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.2 (2C), (168.8, 168.7), (86.4, 86.3), 83.9 (2C), 81.8 (2C), (70.2, 70.1), 68.5 (2C), (60.6, 60.4), (33.6, 33.5), (32.4, 32.2), (31.0, 30.7), (28.6, 28.4), 27.8 (2x3C), 25.9 (2C), (25.7, 25.5), 18.1 (2C) ; IR (neat) 3330, 2920, 2860, 2240, 1740, 1710, 1430, 1355, 1245, 1220, 1145, 900, 730, 645 cm^{-1}.

II-Deprotection of compounds **5d-g,5i-j**: To a solution of potassium fluoride (876 mg ; 15 mmol) in DMSO (40 mL) and some drops of water was added a solution of the preceding compound in DMSO (10 mL). After being stirred at room temperature for 3h, the reaction mixture was diluted with ethyl acetate (100 mL). The organic layer was washed with brine (3x40 mL), dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by flash chromatography (PE/EE = 90/10 for **1d-g** ; 95/5 for **1i-j**).

Methyl 2-acetyl-5-phenylmethyl-hepta-6-ynoate (1d) 83 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 1.5, 6.1 Hz, 2x2H), 7.16 (m, 2x3H), 3.63 (s, 3H), 3.62 (s, 3H), 3.36 (ABX, *J* = 7.4 Hz, 2x1H), 2.77-2.63 (m, 2x2H), 2.57-2.52 (m, 2x1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.09-2.01 (m, 2x1H), 2.03 (d, *J* = 2.6 Hz, 1H), 2.02 (d, *J* = 2.0 Hz, 1H), 1.96-1.83 (m, 2x1H), 1.46-1.32 (m, 2x2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.8 (2C), (170.0, 169.9), 138.8 (2C), 129.1 (4C), 128.2 (4C), 126.4 (2C), (86.1, 86.0), (70.9, 70.8), (59.3, 59.0), (52.5, 52.3), 40.9 (2C), (33.3, 33.0), (31.7, 31.4), (28.8, 28.6), (25.8, 25.6) ; IR (neat) 3280, 3040, 3020, 2990, 2940, 2920, 2860, 2100, 1740, 1710, 1640, 1600, 1490, 1450, 1430, 1355, 1145, 740, 700 cm^{-1}.

Methyl 2-acetyl-5-(2'-phenyl-ethyl)-hepta-6-ynoate (1e) 83 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15-7.10 (m, 2x2H), 7.06-7.01 (m, 2x3H), 3.58 (s, 2x3H), 3.28 (ABX, *J* = 7.6 Hz, 2x1H), 2.72-2.65 (m, 2x1H), 2.55 (dt, *J* = 13.9, 8.1 Hz, 2x1H), 2.23-2.13 (m, 2x1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.00 (d, *J* = 2.5 Hz, 2x1H), 1.96-1.89 (m, 2x1H), 1.83-1.73 (m, 2x1H), 1.64-1.54 (m, 2x2H), 1.33-1.25 (m, 2x2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.9 (2C), 170.1 (2C), 141.6 (2C), 128.5 (4C), 128.4 (4C), 125.9 (2C), (86.5, 86.4), 70.6 (2C), (59.4, 59.2), (52.6, 52.4), 36.5 (2C), 33.3 (2C), (32.5, 32.3), (30.9, 30.7), (28.9, 28.7), (25.9, 25.7) ; IR ($CHCl_3$) 3275, 3050, 3010, 2920, 2850, 2100, 1740, 1710, 1600, 1490, 1445, 1350, 740, 690 cm^{-1} ; Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50 ; H, 7.74. Found : C, 75.60 ; H, 7.90.

Methyl 2-acetyl-5-propyl-hepta-6-ynoate (1f) 83 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.66 (s, 3H), 3.38 (t, *J* = 8.4 Hz, 1H), 3.45 (t, *J* = 8.4 Hz, 1H), 2.37-2.28 (m, 2x1H), 2.21 (s, 3H), 2.20 (s, 3H), 2.05 (d, *J* = 2.0 Hz, 2x1H), 2.10-2.01 (m, 2x1H), 1.98-1.76 (m, 2x1H), 1.53-1.31 (m, 2x4H), 1.28-1.20 (m, 2x2H), 0.88 (t, *J* = 7.1Hz, 2x3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.3 (2C), (170.1, 170.4), (87.3, 87.2), (70.3, 70.2), (59.8, 59.6), (52.7, 52.6), (37.3, 37.2), (32.9, 32.8), (31.5, 31.3), (29.2, 29.1), (26.4, 26.2), 20.7 (2C), (14.4, 14.2) ; IR (neat) 3280, 2940, 2920, 2860, 2100, 1740, 1720, 1450, 1430, 1350, 1250, 1205, 1150, 730, 625 cm^{-1}.

Methyl 2-phenylacetyl-5-propyl-hepta-6-ynoate (1g) 97%, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 3.6, 7.4 Hz, 2x2H), 7.60 (t, *J* = 7.4 Hz, 2x1H), 7.49 (t, *J* = 7.4 Hz, 2x2H), 4.39 (t, *J* = 7.1 Hz, 1H), 4.36 (t, *J* = 6.6 Hz, 1H), 3.69 (s, 2x3C), 2.45-2.32 (m, 2x1H), 2.30-2.20 (m, 2x1H), 2.19-2.09 (m, 2x1H), 2.06 (d, *J* = 2.0 Hz, 2x1H),

1.60-1.36 (m, 2x6H), 0.91 (dd, J =6.6, 10.2 Hz, 3H), 0.90 (dd, J =7.1, 3.6 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.9 (2C), 170.3 2C), 136.0 (2C), 133.5 (2C), 128.7(2x2C), 128.6 (2x2C), 87.0 (2C), (69.8, 69.7), (53.8, 53.6), 52.4 (2C), (36.9, 36.8), (32.6, 32.5), (31.1, 30.9), (26.8, 26.7), 20.3 (2C), 13.8 (2C) ; IR (neat) 3300, 2940, 2920, 2860, 2100, 1740, 1680, 1590, 1570, 1440, 1240, 750, 685, 630 cm^{-1}.

***tert*-butyl 2-acetyl-5-phenylmethyl-hepta-6-ynoate (1i)** 94 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16-7.13 (m, 2x2H), 7.09-7.08 (m, 2x3H), 3.20 (dd, J = 6.4, 8.4 Hz, 1H), 3.17 (t, J = 7.6 Hz, 1H), 2.75-2.65 (m, 2x1H), 2.62-2.57 (m, 2x1H), 2.56-2.47 (m, 2x1H), 2.08 (s, 3H), 2.07 (s, 3H), 2.05 (d, J = 2.0 Hz, 2x1H), 1.97-1.87 (m, 2x2H), 1.84-1.73 (m, 2x2H), 1.30 (s, 2x9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (203.4, 203.3), (168.9, 168.8), 139.1 (2C), 129.3 (4C), 128.1 (4C), 126.3 (2C), (87.1, 86.9), 81.9 (2C), (70.4, 70.3), (60.7, 60.4), 41.1 (2C), (34.6, 34.3), (31.6, 31.3), (28.6, 28.3), 27.8 (6C), (25.9, 25.6) ; IR ($CHCl_3$) 2100, 1730, 1710, 1320, 1245, 910, 850, 830, 730, 695, 640 cm^{-1} ; Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40 ; H, 8.33. Found : C, 76.26 ; H, 8.20.

***tert*-butyl 2-acetyl-5-propyl-hepta-6-ynoate (1j)** quantitative, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.30 (ABX, J = 6.9 Hz, 2x1H), 2.37-2.29 (m, 2x1H), 2.21 (s, 3H), 2.20 (s, 3H), 2.05 (d, J = 2.0 Hz, 2x1H,), 2.04-1.92 (m, 2x1H), 1.91-1.85 (m, 2x1H), 1.45 (s, 2x9H), 1.42-1.38 (m, 2x6H), 0.89 (t, J = 7.1 Hz, 2x3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.3 (2C), (168.8, 168.7), (87.0, 86.9), 81.8 (2C), (69.7, 69.6), (60.7, 60.5), 36.8 (2C), (32.4, 32.1), (31.1, 30.9), (28.6, 28.4), 27.8 (6C), (25.8, 25.6), 20.2 (2C), 13.8 (2C) ; IR ($CHCl_3$) 2100, 1730, 1710, 1320, 1245, 910, 850, 830, 730, 695, 640 cm^{-1} ; Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14 ; H, 9.84. Found : C, 72.10 ; H, 9.90.

B- *Ene type reactions. General procedure.*

Cyclopentadienyldicarbonylcobalt (I) (6 μL ; 0.05 mmol) was added to a boiling solution of the ω-acetylenic β–ketoester (1 mmol) in benzene (15 mL) degassed by three freeze-pump-thaw cycles and the resulting solution was irradiated (light from a projector lamp ; ELW, 300W, 50% of its power). The reaction was monitored by TLC and after completion the solvent was removed *in vacuo*. The residue was purified by flash chromatography to afford the enecycloadducts either as a mixture or as pure compounds. **M** and **m** mean Major and minor.

2a(M+m) 83 %, d.e. 30 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.38 (d, J = 2.5 Hz, $1H_M$+ $1H_m$), 5.37 (d, J = 2.5 Hz, $1H_M$), 5.35 (d, J = 2.0 Hz, $1H_m$), 3.77 (s, $3H_m$), 3.76 (s, $3H_M$), 2.80-2.75 (m, $1H_m$), 2.74-2.65 (m, $1H_M$), 2.53-2.44 (m, 2x2H), 2.39-2.2.23 (m, 2x2H), 2.25 (s, $3H_m$), 2.22 (s, $3H_M$), 2.09-2.00 (m, 2x2H), 1.98-1.94 (m, 2x1H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (203.1, 203.0), (171.5, 171.4), 150.1 (2C), (113.3, 112.8), 82.4 (2C), 71.0 (2C), (69.4, 69.3), 52.7 (2C), (43.6, 43.5), (32.4, 32.3), (30.2, 29.7), (26.8, 26.5), (23.0, 22.8) ; IR (neat) 3295, 2940, 2920, 2860, 2105, 1740, 1710, 1640, 1430, 1350, 1250, 1140, 910, 730, 645 cm^{-1}.

2b(M+m) 87 %, d.e. 40 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.32 (d, J = 2.6 Hz, $1H_M$+$1H_m$), 5.30 (d, J = 2.0 Hz, $1H_M$), 5.27 (d, J = 2.0 Hz, $1H_m$), 3.76 (s, $3H_M$), 3.75 (s, $3H_m$), 2.77-2.67 (m, 2x1H), 2.32-2.27 (m, 2x3H), 2.26-2.15 (m, 2x1H), 2.22 (s, 2x3H), 2.01 (sext, J = 6.3 Hz, 2x1H), 1.97 (t, J = 1.9 Hz, 2x1H), 1.86 (sext, J = 6.3 Hz, 2x1H), 1.54-1.47 (m, 2x1H), 1.37-1.31 (m, 2x2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.1, 171.8, 151.5, 112.5, 83.9, 70.9 (2C), 68.8, 52.7, 43.7, 32.9, 29.8, 26.8, 16.6 ; IR (CH_2Cl_2) 3300, 2950, 2920, 2250, 1740, 1710, 1640, 1450, 1380, 1350, 1260, 900, 735, 650 cm^{-1}.

2c(M+m) 84 %, d.e. 20 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.28 (d, J = 2.5 Hz, $1H_m$), 5.27 (d, J = 2.5 Hz, $1H_M$), 5.26 (d, J = 2.5 Hz, $1H_m$), 5.24 (d, J = 2.5 Hz, $1H_M$),3.74 (s, $3H_M$), 3.73 (s, $3H_m$), 2.56-2.41 (m, 2x1H), 2.36-2.22 (m, 2x1H), 2.21-2.18 (m, 2x2H), 2.20 (s, $3H_m$), 2.19 (s, $3H_M$), 2.03-1.89 (m, 2x2H), 1.96 (t, J = 2.0 Hz, $1H_m$), 1.94 (dd, J = 2.5, 1.0 Hz, $1H_M$), 1.83-1.70 (m, 2x1H), 1.64-1.47 (m, 2x2H), 1.46-1.29(m, 2x2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (203.4, 203.1), (171.8, 171.6), (151.9, 151.7), (112.0, 111.7), 84.1 (2C), 70.8 (2C), 68.4 (2C), 52.6 (2C), 44.3 (2C), (33.2,32.6), (32.5, 32.4), (30.2, 30.0), (26.7, 26.4), 26.3 (2C), (18.5, 18.4) ; IR (neat) 3280, 2940, 2860, 2110, 1740, 1710, 1640, 1430, 1350, 1250, 1130, 1080, 900 cm^{-1}.

2d(M+m) 87 %, d.e. 22 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 2x2H), 7.21 (m, 2x3H), 5.36 (d, J = 2.5 Hz, $1H_M$), 5.34 (d, J = 2.6Hz, $1H_m$), 5.31 (d, J = 2.0 Hz, $1H_M$), 5.29 (d, J = 2.0 Hz, $1H_m$), 3.78 (s, $3H_M$), 3.77 (s, $3H_m$), 3.06 (ABX, J = 5.1 Hz, $1H_M$), 3.01 (ABX, J = 5.1 Hz, $1H_m$), 2.88-2.83 (m, $1H_m$), 2.83-2.74 (m, $1H_M$), 2.55-2.46 (m, 2x1H), 2.33-2.21 (m, 1H), 2.25 (s, $3H_m$), 2.23 (s, $3H_M$), 2.02-1.94 (m, 2x1H), 1.84-1.71 (m, 2x1H), 1.54-1.46 (m, 2x1H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (203.3, 203.1), (171.7, 171.6), 151.3 (2C), (140.3, 140.2), 128.8 (4C), 128.2 (4C), 126.0 (2C), (112.4, 112.1), 71.0 (2C), 52.6 (2C), (46.6, 46.5), (40.4, 40.0), (32.4, 32.3), (30.3, 30.0), (26.7, 26.4) ; IR (neat) 3100, 2940, 2920, 2840, 1740, 1705, 1640, 1595, 1490, 1445, 1425, 1350, 1250, 1130, 900, 740, 695 cm^{-1} ; Anal. Calcd for $C_{16}H_{26}O_3$: C, 76.40 ; H, 8.33. Found : C, 76.52 ; H, 8.56.

2e(M+m) 65 %, d.e. 20 %, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2x2H), 7.22-7.20 (m, 2x3H), 5.32 (d, J = 2.6 Hz, $1H_m$), 5.31 (d, J = 2.6 Hz, $1H_M$), 5.29 (d, J = 2.6 Hz, $1H_m$), 5.27 (d, J = 2.6 Hz, $1H_M$), 3.77 (s, 2x3H), 2.78-2.70 (m, $1H_M$), 2.69-2.47 (m, $1H_M$ and $2H_m$), 2.40-2.27 (m, 2x1H), 2.25 (s, $3H_m$), 2.22 (s, $3H_M$), 2.10-1.95 (m, 2x3H), 1.65-1.55 (m, 2x1H), 1.54-1.47 (m, 1H), 1.45-1.36 (m, 1H), 0.92-0.89 (2x1H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (203.6, 203.5), (171.8, 171.7), (152.0, 151.9), 142.1 (2C), 128.4 (4C), 128.3 (4C), (112.1, 111.8), 70.0 (2C), 52.7 (2C), 44.4 (2C), (36.2, 35.5), 33.8 (2C), (32.8, 32.7), (30.4, 30.1), (26.6, 26.5) ; IR (neat) 3080, 3050, 3020, 2920, 2850, 1740, 1710, 1640, 1600, 1490, 1450, 1350, 1250, 900, 740, 695 cm^{-1}.

2f(M+m) %, d.e. 7%, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.25 (d, J = 2.6 Hz, $1H_m$), 5.24 (d, J = 2.6 Hz, $1H_m$), 5.23 (d, J = 2.5 Hz, $1H_M$), 5.21 (d, J = 2.5 Hz, $1H_M$), 3.74 (s, $3H_m$), 3.73 (s, $3H_M$), 2.55-2.49 (m, $1H_m$), 2.48-2.40 (m, $1H_M$), 2.33-2.23 (m, 2x1H), 2.21 (s, $3H_m$), 2.20 (s, $3H_M$), 2.00-1.97 (m, 2x1H), 1.65-1.55 (m, 2x1H), 1.40-1.20 (m, 2x6H), 0.90 (td, J = 7.1, 1.5 Hz, $3H_M$), 0.86 (t; J = 7.3 Hz, $3H_m$) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (203.6, 203.3), (171.9, 171.6), (152.5, 152.3), (111.7, 111.3), 71.0 (2C), (52.5, 52.2), 44.6 (2C), (36.5, 35.7), (32.7, 32.6), (30.3, 30.0), (26.5, 26.4), 20.6 (2C), (14.1, 14.0) ; IR (neat) 2950, 2920, 2860, 1730, 1710, 1640, 1450, 1430, 1350, 1250, 1155, 905, 730, 645 cm^{-1}.

2g(M+m) 77%, d.e. 16%, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.1, 1.5 Hz, 2x2H), 7.55-7.51 (m, 2x1H), 7.43 (t, J = 7.1 Hz, 2x2H), 5.30 (d, J = 2.0 Hz, $1H_m$), 5.29 (d, J = 2.5 Hz, $1H_M$), 5.26 (d, J = 2.5 Hz, $1H_M$), 5.25 (d, J = 2.0 Hz, $1H_m$), 3.66 (s, $3H_M$), 3.65 (s, $3H_m$), 2.90-2.73 (m, 2x1H), 2.62-2.48 (m, 2x1H), 2.30-2.00 (m, 2x1H), 2.05-1.88 (m, 2x1H), 1.83-1.60 (m, 2x1H), 1.40-1.20 (m, 2x4H), 0;95 (t, J = 7.1 Hz, 2x3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (195.2, 195.1), (172.6, 172.4), (152.8, 152.7), 135.2 (2C), (132.7, 132.6), 128.8 (2C), (128.7, 128.4), (110.9, 110.6), (68.1, 67.9), 52.6 (2C), (44.7, 44.6), (36.0, 35.4), (34.6, 34.4), (30.8, 30.2), (20.8, 20.7), (14.2, 14.1); IR (neat) 3080, 3040, 2950, 2920, 2860, 1730, 1680, 1640, 1590, 1575, 1440, 1250, 1165, 1125, 905, 790, 730, 700 cm^{-1}.

2h 63%, d.e. 30% ; **2hM** : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.49 (d, J = 2.5 Hz, 1H), 5.44 (d, J = 2.5 Hz, 1H), 2.71-2.61 (m, 1H), 2.41 (s, 3H), 2.20-2.11 (m, 3H), 1.99-1.92 (m, 1H), 1.85-1.71 (m, 3H), 1.67 (s, 9H), 1.62-1.41 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.5, 170.0, 151.9, 111.2, 84.2, 81.8, 71.5, 68.4, 44.4, 32.5, 30.1, 27.7 (3C), 26.6, 26.3, 18.5. **2hm** : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.51 (d, J = 2.5 Hz, 1H), 5.46 (d, J = 2.5 Hz, 1H), 2.77-2.68 (m, 1H), 2.42 (s, 3H), 2.16 (t, J = Hz, 1H), 2.18-2.10 (m, 2H), 1.98-1.90 (m, 1H), 1.84-1.71 (m, 3H), 1.67 (s, 9H), 1.61-1.39 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.3, 170.2, 152.2, 111.6, 84.2, 81.9, 71.6, 68.4, 44.5, 33.2, 32.6, 29.9, 27.7 (3C), 26.8, 26.4, 18.5. IR (neat) 3280, 2970, 2930, 2860, 2110, 1735, 1710, 1640, 1450, 1390, 1365, 1350, 1250, 1160, 1135, 900, 840 cm^{-1} ; Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.44 ; H, 9.02. Found : C, 74.27 ; H, 9.19.

2i : 73 %, d.e. 25 % ; **2iM** : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.20 (m, 3H), 5.35 (d, J = 2.0 Hz, 1H), 5.28 (d, J = 2.5 Hz, 1H), 3.05 (AB, J = 5.1 Hz, 1H), 2.80-2.70 (m, 1H), 2.49 (AB, J = 10.2 Hz, 1H), 2.53-2.42 (m, 1H), 2.23 (s, 3H), 1.90 (dq, J = 9.0, 6.6 Hz, 1H), 1.75-1.66 (m, 1H), 1.50 (s, 9H), 1.39-1.31 (m, 1H) ; ^{13}C-NMR

(50 MHz, $CDCl_3$) δ 203.3, 170.0, 151.4, 140.4, 128.8 (2C), 128.2 (2C), 125.9, 111.3, 81.8, 71.6, 46.6, 40.0, 32.3, 30.2, 27.7 (3C), 26.6. **2im** : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.21 (m, 3H), 5.35 (d, *J* = 2.5 Hz, 1H), 5.28 (d, *J* = 2.0 Hz, 1H), 3.00 (AB, *J* = 5.6 Hz, 1H), 2.89-2.80 (m, 1H), 2.50 (ABX, *J* = 9.7 Hz, 1H), 2.25 (s, 3H), 2.23 (dt, *J* = 8.4, 5.6 Hz, 1H), 1.77 (dt, *J* = 12.6, 5.6Hz, 1H), 1.39-1.31 (m, 2H), 1.49 (s, 9H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 203.3, 170.1, 151.5, 140.5, 128.9 (2C), 128.2 (2C), 125.9, 111.9, 81.9, 71.8, 46.7, 40.5, 32.4, 29.9, 27.8 (3C), 26.9 ; IR (neat) 2970, 2920, 2880, 1730, 1710, 1640, 1450, 1365, 1250, 1160, 1130, 900, 840, 740, 695 cm^{-1}.

2j : 63 %, d.e. 30 % ; **2jM** : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.19 (d, *J* = 2.5 Hz, 1H), 5.14 (d, *J* = 2.5 Hz, 1H), 2.38-2.31 (m, 2H), 2.13 (s, 3H), 1.88-1.78 (m, 2H), 1.60-1.52 (m, 2H), 1.38 (s, 9H), 1.36-1.30 (m, 3H), 0.85 (t, *J* = 7.1 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.8, 170.2, 152.5, 110.9, 81.7, 71.6, 44.7, 35.8, 32.6, 29.7, 27.7 (3C), 26.7, 20.6, 14.2. **2jm** : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.32 (d, *J* = 2.5 Hz, 1H), 5.27 (d, *J* = 2.0 Hz, 1H), 2.58-2.53 (m, 1H), 2.30-2.20 (m, 2H), 2.24 (s, 3H), 1.96 (m, 1H), 1.69-1.56 (m, 1H), 1.50 (s, 9H), 1.30-1.22 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.5, 170.2, 152.7, 111.2, 81.7, 71.7, 44.7, 36.5, 32.6, 29.9, 27.7 (3C), 26.8, 20.7, 14.1 ; IR (neat) 2950, 2920, 2860, 1705, 1640, 1450, 1365, 1250, 1150, 905, 730, 645 cm^{-1} ; Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14 ; H, 9.84. Found : C, 72.19 ; H, 9.80.

*Preparation of the diol **10 hm***: At 0°C, a solution of **2hm** (164 mg, 0.56 mmol) in Et_2O (8 mL) was added dropwise to a suspension of $LiAlH_4$ (64 mg, 1.7 mmol) in Et_2O (3 mL). After being stirred for 10 min, the mixture was diluted in CH_2Cl_2 (15 mL) and hydrolyzed with saturated solution of Na_2SO_4 until a white suspension is formed. The mixture was filtered on Celite and concentrated. The residue was purified by flash chromatography (PE/AcOEt = 60/40) to afford the diol as a mixture of two diastereomers (**10+10'**)**hm** : 91%, d.e. 60% , ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.13 (d, *J* = 2.6 Hz, $1H_{10hm}$), 5.08 (d, *J* = 2.6 Hz, $1H_{10hm}$), 4.98 (d, *J* = 2.5 Hz, $1H_{10'hm}$), 4.79 (d, *J* = 2.5 Hz, $1H_{10'hm}$), 4.05 (q, *J* = 6.6 Hz, $1H_{10'hm}$), 4.02 (q, *J* = 6.6 Hz, $1H_{10hm}$), 3.60 (AB, 2H), 3.51 (AB, 2H), 2.49-2.40 (m, 2x1H), 2.22 (dt, *J* = 6.9, 2.6 Hz, 2x2H), 1.97 (t, *J* = 2.6 Hz, 2x1H), 1.95-1.81 (m, 2x2H), 1.79-1.70 (m, 2x1H), 1.68-1.50 (m, 2x2H), 1.46-1.25 (m, 2x3H), 1.20 (d, *J* = 6.6 Hz, $3H_{10hm}$), 1.09 (d, *J* = 6.6 Hz, $3H_{10'hm}$) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (158.4, 158.1), (107.4, 106.6), 84.3 (2C), 74.1 (2C), 68.7 (2C), (68.4, 67.9), 55.9 (2C), (44.8, 44.4), (32.9, 32.8), (29.7, 29.6), (29.3, 29.1), (26.8, 26.5), (19.0, 18.5), (18.5, 18.2) ; IR ($CHCl_3$) 3600, 3460, 3300, 3070, 2940, 2860, 2110, 1640, 1455, 1260, 1040, 635 cm^{-1} ; Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63 ; H, 9.97. Found : C, 75.81 ; H, 10.31.

*C- Preparation of the angular triquinane **11***

To a solution of **2b** (164 mg, 0.7 mmol) either in xylenes (10 mL) or CH_2Cl_2 (10 mL) or 1,2-dichloroethane (10 mL) was added $Co_2(CO)_8$ (252 mg, 0.77 mmol, 1.05 equiv) in one portion and the resulting dark-colored solution was stirred at room temperature until the formation of the hexacarbonyl dicobalt complex was complete (*c.a.* 3h) (TLC). Then, the resulting solution was subjected to one of the following procedures. (a) The solution was refluxed in xylenes for 1 h, until the complete disappearance of the complex, concentrated and directly flash chromatographed (EP/AcOEt = 80/20). (b) N-Methylmorpholine oxide (NMO, 574 mg, 7 equiv) in CH_2Cl_2 (10 mL) was added to the solution. After being stirred at room temperature for 24 h, the resulting mixture was filtered on celite and washed successively with saturated solution of NH_4Cl and brine. The organic layer was dried over $MgSO_4$, evaporated and flash chromatographed. (c) Cyclohexylamine (0.28 mL, 3.5 equiv) was to the solution and the resulting mixture was refluxed at 83°C for 1h. After cooling to room temperature, Et_2O was added and the resulting mixture was filtered on celite. The filtrate was washed successively with saturated solution of NH_4Cl, brine, dried over $MgSO_4$ and concentrated. The crude residue was purified by flash chromatography to afford **11** (37 mg, 20%) as a mixture of two diastereomers. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.23-5.19 (m, 2x1H), 3.71 (s,

3H), 3.67 (s, 3H), 2.50-2.35 (m, 2x2H), 2.35-2.17 (m, 2x2H), 2.16 (s, 3H), 2.14 (s, 3H), 2.05-1.82 (m, 2x3H), 1.77-1.58 (m, 2x1H), 1.45-1.00 (m, 2x4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.0 (2C), (203.9, 203.7), (172.3, 171.8), (144.9, 144.5),(125.9, 125.8), 53.0 (2C), (44.3, 43.2), (43.0, 42.9), 35.3 (2C), 34.2 (2C), 33.2 (2C), (32.7, 32.6), (31.9, 31.7), (27.1, 26.9) ; IR (neat) 3040, 2950, 2920, 2840, 1720, 1700, 1640, 1430, 1365, 1260, 740, 700 cm^{-1}.

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