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Construction of quaternary centres for natural polycycles: The Pauson–Khand approach

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ABSTRACT

Construction of quaternary carbons is a challenge in PK chemistry, with few precedents in the literature. Starting from suitable functionalized enynes including an aromatic ring that templates the reaction, polycyclic ketones are obtained with a quaternary carbon. Special reaction conditions are necessary including the use of molecular sieves and co-catalysis with rhodium complexes jointly with cobalt carbonyl. The products obtained are intermediates in the synthesis of various natural products like the Hamigeran family and the steroidic alkaloid Conessine.

1. Introduction

The intramolecular Pauson–Khand reaction (PKR) is a powerful transformation of enynes into polycyclic cyclopentenones [1]. One of its main limitations is that, in general, substituted double bonds at the internal position react poorly. Among the exceptions we can find exocyclic double bonds, and conformationally constrained enynes in which a reactive conformation is forced by any means. Thus, Ishizaki described the use of exocyclic cyclohexenes in the PKR and used this methodology for the synthesis of several natural products [2]. Cyclopropyl tethered methylenecyclopropanes can give the expected PK products or rearranged hydroindenones in which neither of the two carbon atoms of the alkyne form part of the cyclopentenone ring in the final product [3]. Kerr used methylene cyclohexanes for the synthesis of Cedrene [4], and methylenepyranes also gave successfully the PK cyclization [5]. Other substituted alkenes, included in a cyclohexane were used by Zard in the synthesis of Dendrobine [6]. We have shown a positive effect of molecular sieves in PKRs that allow the reaction of some substituted alkenes [7]. Our conditions were used by Winkler for the synthesis of Ingenol from an exocyclic cycloheptene [8]. On the other hand, enynes connected through an aromatic ring are interesting substrates that have been used by us [9] and other groups [10] in Pauson–Khand chemistry. We have used homoaromatic and indole-based enynes to construct complex polycycles. As an extension of our work we present herein the synthesis structures related to Hamigerans-A and B via a PKR/elimination reaction and precursors of the steroidic alkaloid Connessine, both from aromatic enynes bearing substituted alkenes.

Hamigerans are a family of metabolites isolated from the poecilosclerid sponge *Hamigera tarangaensis*. Among them, Hamigeran-B has interesting biological activity as it exhibits 100% virus inhibition against both herpes and polio viruses with little cytotoxicity [11]. The tricyclic structural framework comprising an aromatic ring, has received synthetic attention from several groups. Thus, after the first asymmetric synthesis by Nicolaou based on an asymmetric Diels–Alder reaction [12], Clive used radical cyclization to build the five membered ring performing both a racemic and asymmetric synthesis [13]. More recently Trost used an asymmetric allylic alkylation as the origin of asymmetry in a new synthesis of Hamigeran-B [14], and Wright reported the synthesis of Hamigeran skeleton using an efficient electro-oxidative coupling reaction [15]. The tricyclic structure of Hamigeran has been constructed recently via PKR by Lovely [16]. In this case the cyclization, only took place when the olefin-containing moiety was tethered to the aromatic framework to reduce its conformational mobility; using a silylene protecting group. Our approach uses an intramolecular Pauson–Khand reaction strategy that would shorten the synthesis of an elaborated framework that could serve for the preparation of derivatives, an important aim in view of the biological activity of this compound.

Conessine is a steroidic alkaloid that belongs to *Holarrhena* class of Kurchi alkaloids. It was isolated from the bark of *Holarrhena antidysenterica*, and possesses significant biological activity against dysentery [17]. Several total syntheses can be found in

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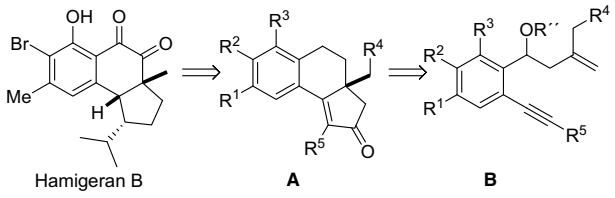
the literature. Thus, Stork [18], Nagata [19], and Johnson [20], disclosed racemic approaches to Conessine in early times. Stork used intermediate **C**, that can be obtained from precursor **D**. We envisioned the possibility of synthesizing **D** using a PKR from enyne **E**. More recently, Meyers described a non-racemic synthesis of Conessine in which polycyclic enone **G** was used to reach intermediate **F** [21]. Ketone **C** could be obtained by transformation of **D**. A highly diastereoselective method for the construction of the compact tetracycle of Conessine was accomplished recently from an elaborated enyne. The chiral tetracyclic framework was created by a Pauson–Khand reaction [22].

In this paper we describe the use of functionalized aromatic enynes to perform a Pauson–Khand reaction giving intermediates for the synthesis of Hamigerans-A and B and Conessine (Schemes 1,2).

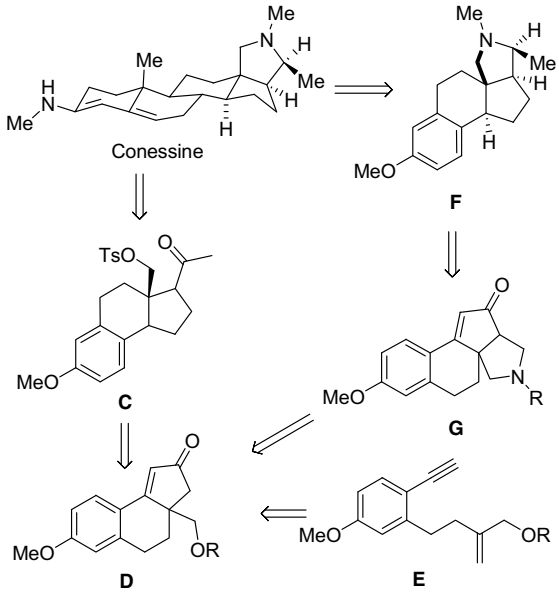
2. Results and discussion

2.1. Synthesis of the Hamigeran's skeleton

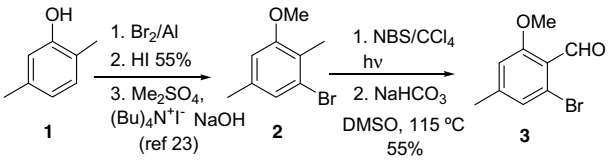
Starting with the synthesis of the Hamigeran's skeleton, the synthesis of enyne starting material was accomplished from inexpensive commercial 2,5-dimethylphenol **1**. This product was transformed into 2-bromo-6-methoxy-4-methylbenzaldehyde by a procedure described in the literature [23]. After formation of intermediate **2** we modified the method towards **3**, and we performed a bromination followed by an oxidation step which gave **3** in 55% yield (Scheme 3).



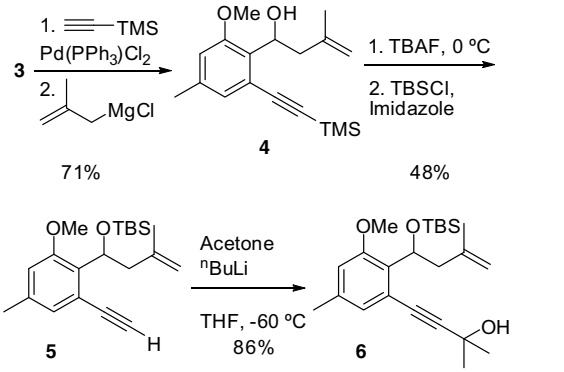
Scheme 1. Retrosynthetic approach to Hamigeran-B.



Scheme 2. Retrosynthetic outline towards Conessine.



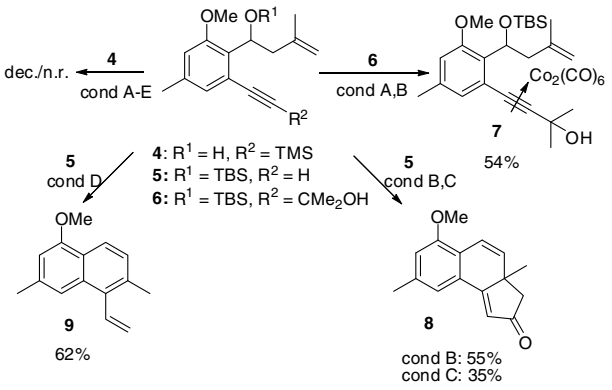
Scheme 3. Synthesis of aldehyde **3**.



Scheme 4. Synthesis of precursors for the PKR.

From compound **3**, the desired enyne was readily prepared using Sonogashira coupling and nucleophilic attack with a Grignard reagent. In addition, from enyne **4**, several derivatives were obtained to test them in the PKR. In particular, compound **6** bears the three carbon moiety present in the Hamigerans. This compound was obtained from protected derivative **5** by nucleophilic attack of the corresponding anion to acetone (Scheme 4).

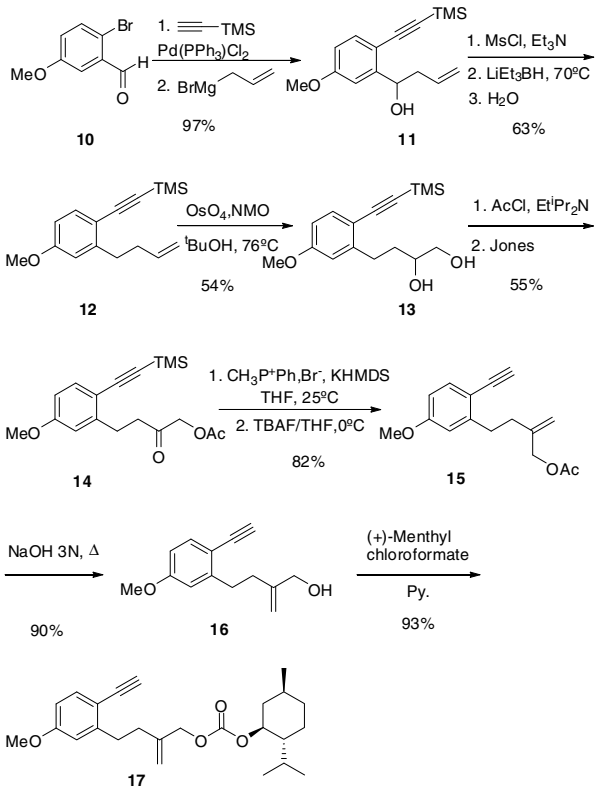
The enynes were submitted to a set of conditions for the PKR (Scheme 5). Starting with enyne **4**, we observed partial or total decomposition of starting material in the whole set of conditions tested. These included the use of $Co_2(CO)_8$ with promotion of amine *N*-oxides (Cond. A) or molecular sieves (Cond B.) [9b], and catalysis with $Co_2(CO)_8$/mol. sieves (Cond. C) [24], $[Rh(CO)_2Cl]_2$ (Cond. D) [25], or $[Ir(cod)Cl]_2$ (Cond. E) [26]. Substrate **6** was complexed to cobalt and under conditions A–B, the resulting complex **7**, did not evolve to the desired PK product. Catalytic conditions produced no reaction products with this compound. Finally, substrate **5** gave much more interesting results. In the reaction with cobalt this compound gave the PK cyclization with elimination of the OTBS group, forming an additional double bond. The best result was achieved under stoichiometric conditions B (55% yield of com-



Scheme 5. PKR of enynes **4**–**6**.

pound **8**), although under catalytic conditions we obtained a 35% yield of **8**. This result is remarkable as very few PKR give quaternary carbons.

On the other hand, compound **5** gave, under rhodium catalysis (conditions D), a product which was identified as **9**. This product is probably the result of an enyne reorganization process, similar to enyne metathesis, and aromatization of the resulting dihydronaphthalene via elimination of the OTBS group. The product was obtained in good yield (62%). Compound **5** did not react under conditions E.



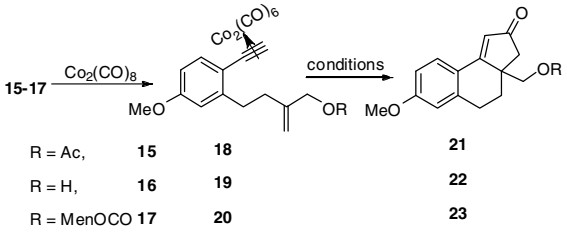
Scheme 6. Synthesis of enynes **15**–**17**.

2.2. Intermediates for the synthesis of conessine

The synthesis started from aldehyde **10**, easily obtained in four steps from commercial 4-bromo-3-methylanisol [27]. Aldehyde **10** was submitted to Sonogashira conditions, with ethynyltrimethylsilane and subsequent reaction with allylmagnesium bromide giving **11**, with 97% yield (Scheme 6). Then, hydroxyl group in **11** was reduced with superhydride giving **12**. This compound was osmylated into **13**, which was obtained in 54% yield. The primary hydroxyl was then acetylated using a bulky base (72%), and the resulting product was oxidized, obtaining **14**. The oxidation only proceeded in good yield (75%) with Jones' reagent. The other conditions tested (PCC, PDC and Swern) gave poor conversions into ketone **14**. The next step was the synthesis of enyne **15**, which was accomplished with a Wittig reaction and deprotection of the alkyne. Global yield of this enyne from starting commercial material was 14% after 12 steps. In addition, the acetyl group was changed to a chiral auxiliary, via alcohol **16**. The menthyl group was selected and thus, **17** was obtained by reaction of **16** with (+)-menthylchloroformate in pyridine (Scheme 6).

Enynes **15**–**17** were submitted to several PK reaction conditions (Table 1). Compound **15** under stoichiometric reaction at −10 °C did not react and at 70 °C, using as promoters trimethylamine *N*-oxide (TMANO) and molecular sieves, gave 45% of the desired compound **22** (entries 1 and 2). When applying catalytic conditions with 0.1 equiv. of $Co_2(CO)_8$, molecular sieves and CO atm., we only detected traces of the final product in the reaction crude residue. Enyne **16**, with less steric demand was also reacted under the latter conditions but did not gave any cyclization product (entry 4). Thus, we prepared the cobalt hexacarbonyl complex **18**, and purified it in an attempt to improve the yields. When this complex was reacted at 70 °C in the presence of molecular sieves it gave a 30% of the

Table 1
PKR conditions for the synthesis of **21** and **23**



No.	Subs.	R	Promoters	CO	*T* (°C)	(Co)	Other catalysts[a]	Yield (%)
1	**15**	Ac	TMANO/MS 4 Å		−10	1.1		
2	**15**	Ac	TMANO/MS 4 Å		70	1.1		45
3	**15**	Ac	MS 4 Å	1 atm	70	0.1		>5
4	**15**	Ac	MS 4 Å	1 atm	110	3	$Rh(PPh_3)_2ClCO$	20
5	**16**	H	MS 4 Å	1 atm	70	0.1		
6	**18**	Ac	MS 4 Å		70			30
7	**18**	Ac	MS 4 Å		70		$Rh(PPh_3)_2ClCO$	60
8	**18**	Ac	MS 4 Å		70		$[RhClCO(dppp)]_2$	40
9	**19**	H	MS 4 Å		70		$Rh(PPh_3)_2ClCO$	<5
10	**20**	R*	MS 4 Å		70		$Rh(PPh_3)_2ClCO$	45[b]

[a] When used, a 5 mol% of rhodium co-catalyst was added.
[b] Obtained as a 1:1 mixture of diastereomers.

final product (entry 6). We decided to use a rhodium co-catalyst in the reaction of complex **18**. With these novel conditions, we reached the best yields, in particular with $Rh(PPh_3)_2ClCO$ (entry 7), which gave better results than $[RhClCO(dppp)]_2$ (entry 8). These conditions were used with cobalt complexes **19**–**20**. Complex **19** decomposed to a myriad of unidentified products (entry 9), whereas **20** gave a 1:1 mixture of the diastereomeric final products **23** in 45% yield (entry 10).

2.3. Conclusions

In conclusion we show here a new approach to Hamigerans-A and B skeletons using an intramolecular PK reaction. A metathesis/elimination reaction with rhodium catalysis has been observed. The synthesis of tricyclic cyclopentenones related to intermediates in the synthesis of Conessine is achieved using a PKR. For the construction of the quaternary carbon the participation of a rhodium co-catalyst reacting with a preformed cobalt hexacarbonyl complex is necessary to reach good yields. Syntheses of natural products using this methodology are currently underway.

3. Experimental

3.1. Synthesis of 2-bromo-6-methoxy-4-methylbenzaldehyde, *3* [23]

To a solution of **2** (9.79 g, 45.54 mmol) in 334 mL of degassed CCl_4 8.11 g (45.54 mmol) of *N*-bromosuccinimide were added. The mixture was irradiated with a 150 W lamp for 16 h at 0 °C and filtered. The filtrate was washed with water (200 mL), dried over $MgSO_4$, and concentrated, obtaining 1-bromo-2-(bromomethyl)-3-methoxy-5-methylbenzene which was used without purification. This product was solved in DMSO (212 mL) and 66.22 g (728.70 mmol) of $NaHCO_3$ were added to the mixture which was heated to 115 °C and stirred for 16 h. Then, the reaction mixture was poured into an ice-water mixture (200 mL) and extracted with Et_2O (3 × 100 mL). The organic layers were washed with water (200 mL), dried over $MgSO_4$, and concentrated. The crude residue was purified by column chromatography using hexane/EtOAc (9:1) as eluent. 5.74 g (55% from **2**), of **3** are obtained as an oil that solidifies in the fridge. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 3.91 (s, 3H), 6.75 (s, 1H), 7.09 (s, 1H), 10.38 (s, 1H) ppm.

3.2. Synthesis of 1-(2-methoxy-4-methyl-6-((trimethylsilyl)ethynyl)phenyl)-3-methylbut-3-en-1-ol, *4*

To a solution of **3** (1.45 g, 6.3. mmol) in distilled triethylamine (30.0 mL), were added 1.8 mL (12.7 mmol) of ethynyltrimethylsilane, 0.09 g (0.13 mmol) of $Pd(PPh_3)_2Cl_2$ and 0.006 g (0.03 mmol) of CuI. The mixture was stirred at 80 °C for 4 h, concentrated, redissolved in toluene and filtered through Celite. The crude residue was concentrated and purified by column chromatography using hexane/EtOAc (9:1) as eluent. 1.25 g (81%) of 2-methoxy-4-methyl-6-((trimethylsilyl)ethynyl) benzaldehyde were obtained as a yellow solid (m.p. 75–78 °C). To a solution of this aldehyde (0.66 g, 2.7 mmol) in anhydrous THF (20 mL) at −78 °C, 3.0 mmol of 2-methylallylmagnesium chloride were added dropwise. The mixture was stirred for 2 h and then, 20 mL of saturated NH_4Cl were added. The crude residue was extracted with EtOAc (2 × 15 mL), washed with water (20 mL) and with brine (20 mL). The organic layer was dried over $MgSO_4$ filtered and concentrated. Purification was carried out by column chromatography using hexane/EtOAc (9:1) as eluent. Compound **4** was obtained (0.71 g, 88%; 71% from **3**) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.21 (s, 9H), 1.82 (s, 3H), 2.27 (s, 3H), 2.41 (dd, 1H, J_1 = 13.2 Hz, J_2 = 5.0 Hz), 2.63 (dd, 1H, J_1 = 13.7 Hz, J_2 = 9.4 Hz), 3.57 (d, 1H, J = 11.5 Hz), 3.84 (s, 3H), 4.71 (s, 1H), 4.79 (s, 1H), 5.32–5.40 (m, 1H), 6.67 (s, 1H), 6.89 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.2, 21.1, 22.3, 46.6, 55.4, 70.2, 98.6, 103.0, 112.7, 112.7, 121.7, 125.9, 130.9, 137.7, 142.9, 156.9 ppm. IR (film): ν = 3550, 2140, 1650, 1610 cm^{-1}. Calc. for $C_{18}H_{26}O_2Si$ (302.48): C, 71.47; H, 8.66. Found: C, 71.30; H, 8.81%.

3.3. Synthesis of tert-butyl(1-(2-ethynyl-6-methoxy-4-methylphenyl)-3-methylbut-3-enyloxy)dimethylsilane, *5*

To a solution of **4** (0.13 g, 0.43 mmol) in THF (2.0 mL) at 0 °C, 0.65 mL of TBAF (1 M) were added. The mixture was stirred at 0 °C for 1 h and 1 mL of water, 1 mL of hexane and 1 mL of ether were added. The organic layer was separated, washed with brine (1.0 mL), dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography using hexane/EtOAc (4:1) as eluent. Sixty-four milligrams (65%) of 1-(2-ethynyl-6-methoxy-4-methylphenyl)-3-methylbut-3-en-1-ol as a yellow oil. A solution of this compound (0.18 g, 0.78 mmol) in DMF (4 mL), 0.14 g (2.05 mmol) of imidazole, and 0.25 g (1.64 mmol) of *tert*-butylchlorodimethylsilane stirred at rt for 15 h. Then, an ice-water mixture (5 mL) was added. The reaction mixture was extracted with Et_2O (3 × 2 mL), dried over $MgSO_4$ and concentrated. Upon chromatography (hexane/EtOAc 49:1) 0.20 g (74%) of **5** were obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.23 (s, 3H), 0.00 (s, 3H), 0.83 (s, 9H), 1.76 (s, 3H), 2.29 (s, 3H), 2.54 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.1 Hz), 2.75–2.82 (m, 1H), 3.23 (s, 1H), 3.80 (s, 3H), 4.67 (s, 1H), 4.70 (s, 1H), 5.47 (dd, 1H, J_1 = 7.7 Hz, J_2 = 6.1 Hz), 6.67 (s, 1H), 6.91 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.9, 18.2, 21.2, 22.8, 25.8, 44.8, 55.5, 71.5, 81.0, 82.8, 112.3, 113.9, 121.5, 125.3, 127.9, 137.7, 143.3, 157.0 ppm. IR (film): ν = 3300, 3060, 2940, 2920, 2840, 2100, 1650, 1600 cm^{-1}. Calc. for $C_{21}H_{32}O_2Si$ (344.56): C, 73.20; H, 9.36. Found: C, 73.30; H, 9.44%.

3.4. Synthesis of 4-(2-(1-(tert-butyldimethylsilyloxy)-3-methylbut-3-enyl)-3-methoxy-5-methylphenyl)-2-methylbut-3-yn-2-ol, *6*

To a solution of **5** (0.15 g, 0.44 mmol) in 3 mL of anhydrous THF, 0.14 mL (0.92 mmol) of TMEDA were added. The mixture was cooled at −60 °C and 0.5 mL (0.92 mmol) of ^{n}BuLi (1.6 M) were added, stirring the mixture for 1 h. Then, 0.32 mL (4.4 mmol) of dry acetone were added and the resulting mixture was stirred for 3 h, when 2 mL of saturated solution of NH_4Cl, were added. The reaction mixture was extracted with EtOAc (3 × 1 mL), dried over $MgSO_4$ and concentrated. Upon column chromatography (hexane/EtOAc, 49:1 to 20:1) 0.15 g (86%) of **6** were obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.21 (br s, 3H), −0.02 (br s, 3H), 0.83 (s, 9H), 1.62 (s, 6H), 1.77 (s, 3H), 2.28 (s, 3H), 2.42–2.59 (m, 1H), 2.70–2.95 (m, 1H), 3.80 (s, 3H), 4.69 (s, 1H), 4.71 (s, 1H), 5.54 (br s, 1H), 6.62 (br s, 1H), 6.86 (br s, 1H) ppm. IR (film): ν = 3380, 3060, 2940, 2840, 1650, 1600 cm^{-1}. Calc. for $C_{24}H_{38}O_3Si$ (402.64): C, 71.59; H, 9.51. Found: C, 71.66; H, 9.62%.

3.5. Synthesis of 4-(2-(1-(tert-butyldimethylsilyloxy)-3-methylbut-3-enyl)-3-methoxy-5-methylphenyl)-2-methylbut-3-yn-2-ol-dicobalt hexacarbonyl, *7*

To a solution of **6** (0.11 g, 0.28 mmol) in 5 mL of anhydrous Et_2O, 0.13 g (0.37 mmol) of dicobalt octacarbonyl were added. The mixture was stirred at rt for 3 h and filtered through Celite. Upon column chromatography (hexane/EtOAc 49:1) 0.10 g (54%) of **7** were obtained as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 3H), 0.20 (s, 3H), 0.88 (s, 9H), 1.37(s, 3H), 1.57 (s, 3H), 1.68 (s, 3H), 2.35 (s, 3H), 2.76–2.84 (m, 1H), 3.08–3.15 (m, 1H), 3.85 (s, 3H), 4.32 (s, 1H), 4.71 (s, 1H), 4.76 (s, 1H), 5.45 (br s, 1H),

6.68 (s, 1H), 7.02 (s, 1H) ppm. IR (film): ν = 3400, 3060, 2960, 2840, 2080, 2040, 2020, 1640, 1600 cm^{-1}.

3.6. Synthesis of 6-methoxy-3a,8-dimethyl-3,3a-dihydro-2H-cyclopenta[a] naphthalen-2-one, **8**

To a solution of enyne **5** (0.20 g, 0.58 mmol) in anhydrous toluene (12 mL), 1.6 g of molecular sieves, and 0.24 g (0.70 mmol) of $Co_2(CO)_8$ were added. The resulting mixture was stirred under Ar at rt until total complexation of the enyne (t.l.c.). Then, the reaction mixture was refluxed for 2 days. After filtration through Celite and solvent elimination, the residue was purified by column chromatography (hexane/EtOAc 49:1), giving **8** (76 mg, 55%) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3H), 2.40 (s, 3H), 2.48 (d, 1H, J = 17.1 Hz), 2.70 (d, 1H, J = 17.1 Hz), 3.86 (s, 3H), 6.15 (s, 1H), 6.16 (d, 1H, J = 9,9 Hz), 6.77 (s, 1H), 6.79 (d, 1H, J = 9,9 Hz), 7.01 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 29.8, 44.9, 49.2, 55.6, 114.2, 118.8, 119.0, 119.4, 124.2, 128.8, 135.5, 138.9, 155.1, 181.2, 199.8 ppm. IR (film): ν = 2890, 1680, 1580, 1540 cm^{-1}. Calc. for $C_{16}H_{16}O_2$ (240.30): C, 79.97; H, 6.71. Found: C, 80.14; H, 6.82%.

3.7. Synthesis of 5-methoxy-2,7-dimethyl-1-vinylnaphthalene, **9**

Seven milligrams (0.01 mmol) of $[Rh(CO)_2Cl]_2$ were solved in anhydrous toluene (4 mL) under Ar, and the mixture was cannulated to a flask containing 120 mg (0.35 mmol) of **5**. Then the mixture was put under CO atmosphere and refluxed for 24 h. After cooling, the reaction mixture was filtered through Celite and concentrated. Forty-six milligrams (62%) of **9** were obtained as a yellow oil after column chromatography (hexane/EtOAc 20:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 2.50 (s, 3H), 4.00 (s, 3H), 5.41 (dd, 1H, J_1 = 17.6 Hz, J_2 = 2.2 Hz), 5.75 (dd, 1H, J_1 = 11.0 Hz, J_2 = 2.2 Hz), 6.63 (s, 1H), 7.02 (dd, 1H, J_1 = 18.1 Hz, J_2 = 11.5 Hz), 7.27 (d, 1H, J = 8.8 Hz), 7.46 (s, 1H), 8.06 (d, 1H, J = 8.2 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 22.6, 55.4, 105.1, 116.6, 120.6, 120.6, 122.4, 127.2, 132.9, 133.3, 133.5, 134.7, 135.5, 155.4 ppm. IR (film): ν = 2920, 1660, 1590, 1520 cm^{-1}. Calc. for $C_{15}H_{16}O$ (212.29): C, 84.87; H, 7.60. Found: C, 84.94; H, 7.72%.

3.8. Synthesis of 1-(5-methoxy-2-((trimethylsilyl)ethynyl)phenyl)but-3-en-1-ol, **11**

To a suspension of **10** (1.07 g, 5.0 mmol) in dry triethylamine (15 mL), ethynyltrimethylsilane (0.85 mL, 6.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol) and CuI (0.004 g, 0.02 mmol) were successively added. The mixture was stirred at 60 °C for 5 h, concentrated, redissolved in toluene and filtered through Celite. The crude residue was concentrated and purified by column chromatography using hexane/EtOAc (20:1) as eluent. 1.16 g (100%) of 5-methoxy-2-((trimethylsilyl)ethynyl) benzaldehyde were obtained as a yellow oil. To a solution of this aldehyde (2.44 g, 10.5 mmol) in anhydrous THF (100 mL) at −78 °C, 12.6 mL (12.6 mmol) of allylmagnesium bromide (1.0 M) were added dropwise. The mixture was stirred for 1.5 h and then, 100 mL of saturated NH_4Cl were added. The crude residue was extracted with EtOAc (2 × 40 mL), washed with water (100 mL) and with brine (100 mL). The organic layer was dried over $MgSO_4$ filtered and concentrated. Purification was carried out by column chromatography using hexane/EtOAc (9:1) as eluent. Compound **11** was obtained (2.80 g, 97% from **10**) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 9H), 2.27 (d, 1H, J = 3.8 Hz), 2.36–2.46 (m, 1H), 2.65–2.73 (m, 1H), 3.84 (s, 3H), 5.12–5.23 (m, 3H), 5.82–5.95 (m, 1H), 6.74 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 7.06 (d, 1H, J = 2.2 Hz), 7.38 (d, 1H, J = 8.2 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.1, 42.5, 55.2, 71.2, 97.9, 102.9, 110.4, 112.2, 160.0, 148.4, 134.7, 133.7, 118.0, 112.7, IR (film): ν = 3460, 3080, 2260, 2160, 1730, 1640, 1610 cm^{-1}. Calc. for $C_{16}H_{22}O_2Si$ (274.43): C, 70.03; H, 8.08. Found: C, 69.91; H, 8.23%.

3.9. Synthesis of ((2-(but-3-enyl)-4-methoxyphenyl)ethynyl)trimethylsilane, **12**

To a solution of **11** (2.05 g, 7.5 mmol) in anhydrous THF (60 mL) triethylamine (4.3 mL, 30.2 mmol) was added. After cooling to 0 °C mesyl chloride was added dropwise (1.17 mL, 15.1 mmol). The reaction mixture was stirred at rt for 2 h, filtered and concentrated. Then, EtOAc (20 mL) and water (20 mL) were added to the residue and the organic layer was washed with saturated $NaHCO_3$ (20 mL), dried over $MgSO_4$ and concentrated. Then, 37.2 mL (37.2 mmol) of lithium triethylborohydride 1 M was added over a solution of the crude residue mesyl derivative in anhydrous THF (110 mL). The reaction mixture was stirred at 60 °C for 18 h and cooled to 0 °C. In this point, H_2O (30 mL), 3 N NaOH (2.2 mL) and 35% H_2O_2 (0.6 mL, 6.5 mmol) were successively added, and the resulting mixture was refluxed during 1 h. After cooling, the reaction mixture was extracted with hexane, dried over $MgSO_4$ and concentrated. Purification was carried out by column chromatography using hexane/EtOAc (9:1) as eluent. **12** was obtained (1.22 g, 63%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (q, 2H, J = 7.7 Hz), 2.87 (t, 2H, J = 7.7 Hz), 3.19 (s, 1H), 3.82 (s, 3H), 5.00 (d, 1H, J = 9.9 Hz), 5.07 (dd, 1H, J_1 = 17.3 Hz, J_2 = 1.9 Hz), 5.83–5.96 (m, 1H), 6.71 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.7 Hz), 6.75 (d, 1H, J = 2.2 Hz), 7.42 (d, 1H, J = 8.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.1, 34.4, 55.2, 79.3, 82.3, 111.3, 113.7, 114.5, 114.9, 134.2, 138.0, 146.3, 159.8 ppm. IR (film): ν = 3300, 3080, 2150, 2100, 1640, 1600 cm^{-1}. Calc. for $C_{16}H_{22}OSi$ (258.43): C, 74.36; H, 8.58. Found: C, 74.29; H, 8.82%.

3.10. Synthesis of 4-(5-methoxy-2-((trimethylsilyl)ethynyl)phenyl)butane-1,2-diol, **13**

To a solution of **12** (3.70 g, 14.4 mmol) in *tert*-butanol (130 mL), 11.80 g (100.0 mmol) of NMO and 0.36 mL (0.03 mmol) of OsO_4 (2.5% in *tert*-butanol) were added. The mixture was stirred at 76 °C for 5 h, $NaHSO_3$ was added and solvent was eliminated under vacuo. The crude residue was suspended in brine (50 mL), extracted with EtOAc (3 × 25 mL), washed with water (2 × 50 mL) and brine (2 × 50 mL), dried over $MgSO_4$, filtered and concentrated. Purification was carried out by column chromatography using hexane/EtOAc (1:1) as eluent. Compound **13** was obtained (2.28 g, 54%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.21 (s, 9H), 1.69–1.71 (m, 2H), 2.84 (t, 2H, J = 7.7 Hz), 3.43 (dd, 1H, J_1 = 11.5 Hz, J_2 = 7.7 Hz), 3.59 (dd, 1H, J_1 = 11.5 Hz, J_2 = 2.2 Hz), 3.65 (m, 1H), 3.73 (s, 3H), 6.63 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.2 Hz), 6.70 (d, 1H, J = 2.2 Hz), 7.33 (d, 1H, J = 8.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.0, 30.5, 33.6, 55.1, 66.6, 71.3, 96.1, 104.1, 111.4, 114.5, 114.6, 133.9, 145.9, 159.8 ppm. IR (film): ν = 3350, 2950, 2140, 1610 cm^{-1}. Calc. for $C_{16}H_{24}O_3Si$ (292.45): C, 65.71; H, 8.27. Found: C, 65.59; H, 8.16%.

3.11. Synthesis of 4-(5-methoxy-2-((trimethylsilyl)ethynyl)phenyl)-2-oxobutyl acetate, **14**

Compound **13** (0.29 g, 1.0 mmol) was solved in anhydrous DCM (6 mL), Et^iPr_2N (0.52 mL, 3.0 mmol) and acetyl chloride (0.1 mL, 1.4 mmol) were added. The mixture was stirred at rt for 3 h, then, water (10 mL) was added at 0 °C and the reaction mixture was extracted with EtOAc (3 × 15 mL). The organic layer was washed with water (2 × 10 mL) and brine (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated. 0.24 g (71%) of the acetate was obtained upon purification by column chromatography (hexane/EtOAc 2:1) as a white solid (m.p. 62–65 °C). To a solution of this compound (0.57 g, 1.7 mmol) in acetone (25 mL) at 0 °C, 1.3 mL of Jones

reactive cooled to 0 °C were added. The resulting mixture was stirred during 2 h, isopropanol (3 mL) was added and the reaction mixture was extracted with EtOAc (2 × 25 mL). The organic layer was washed with water until loss of its color, and it was dried over $MgSO_4$, filtered and concentrated. Purification by column chromatography (hexane/EtOAc 4:1) gives 0.42 g (75%) of **14** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 9H), 2.09 (s, 3H), 2.73 (t, 2H, J = 7.7 Hz), 2.97 (t, 2H, J = 7.7 Hz), 3.72 (s, 3H), 4.56 (s, 2H), 6.62 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.2 Hz), 6.67 (d, 1H, J = 2.2 Hz), 7.31 (d, 1H, J = 8.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.1, 20.3, 28.4, 38.9, 55.0, 67.7, 96.7, 103.3, 111.7, 114.4, 114.5, 133.8, 144.6, 159.7, 169.9, 202.8 ppm. IR (film): ν = 2960, 2150, 1760, 1740 cm^{-1}. Calc. for $C_{18}H_{24}O_4Si$ (332.47): C, 65.03; H, 7.28. Found: C, 64.97; H, 7.19%.

3.12. Synthesis of 4-(2-ethynyl-5-methoxyphenyl)-2-methylenebutyl acetate, **15**

Methyl triphenylphosphonium chloride (0.54 g, 1.5 mmol) was suspended in anhydrous THF (8 mL) and KHMDS 0.5 M (2.6 mL, 1.3 mmol) was added dropwise. After stirring at rt for 30 min this mixture was cannulated to a flask containing a solution of **14** (0.33 g, 1.0 mmol) in anhydrous THF (4 mL). The resulting mixture was stirred for 30 min, poured onto a 1:1 mixture of water and Et_2O (20 mL), and extracted. The organic layer was washed with water (2 × 10 mL) and brine (2 × 10 mL), dried over $MgSO_4$ and concentrated. After purification by column chromatography (hexane/EtOAc 4:1), the resulting intermediate was solved in 6 mL of anhydrous THF at 0 °C, and TBAF 1.0 M (2 mL, 2.0 mmol) was added. The resulting mixture was stirred during 2 h and Et_2O (6 mL), hexane (6 mL) and water (6 mL) were added. The organic layer was washed with water (12 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (hexane/EtOAc 4:1) gives 0.21 g (82%) of **15** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 2.39 (t, 2H, J = 8.8 Hz), 2.92 (t, 2H, J = 8.8 Hz), 3.19 (s, 1H), 3.79 (s, 3H), 4.58 (s, 2H), 5.00 (s, 1H), 5.08 (s, 1H), 6.70 (dd, 1H, J_1 = 8.3 Hz, J_2 = 2.2 Hz), 6.74 (d, 1H, J = 2.2 Hz), 7.40 (d, 1H, J = 8.3 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 33.1, 33.8, 55.2, 66.8, 79.4, 82.1, 111.4, 112.9, 113.6, 114.4, 134.3, 143.2, 145.9, 159.9, 170.7 ppm. IR (film): ν = 3280, 2940, 2100, 1740, 1610 cm^{-1}. Calc. for $C_{16}H_{18}O_3$ (258.31): C, 74.39; H, 7.02. Found: C, 74.44; H, 7.10%.

3.13. Synthesis of 4-(2-ethynyl-5-methoxyphenyl)-2-methylenebutan-1-ol, **16**

To a solution of **15** (0.23 g, 0.9 mmol) in THF (5.3 mL), 12.6 mL (37.9 mmol) of 3 N NaOH were added and the resulting mixture was refluxed for 2 h. The reaction mixture was extracted with EtOAc (2 × 6 mL), washed with 0.1 N HCl (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated. Upon purification by column chromatography using hexane/EtOAc as eluent, 0.18 g (90%) of **16** were obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (t, 2H, J = 8.2 Hz), 2.90 (t, 2H, J = 8.2 Hz), 3.17 (s, 1H), 3.77 (s, 3H), 4.10 (s, 2H), 4.90 (s, 1H), 5.05 (s, 1H), 6.67 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.72 (d, 1H, J = 2.2 Hz), 7.38 (d, 1H, J = 8.2 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.3, 33.7, 55.2, 65.7, 79.3, 82.3, 109.8, 111.4, 113.6, 114.3, 134.3, 146.2, 148.3, 159.9 ppm. IR (film): ν = 3400, 3290, 2930, 2100, 1610 cm^{-1}. Calc. for $C_{14}H_{16}O_2$ (216.28): C, 77.75; H, 7.46. Found: C, 77.80; H, 7.51%.

3.14. Synthesis of 4-(2-ethynyl-5-methoxyphenyl)-2-methylenebutyl (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl carbonate, **17**

To a solution of **16** (0.86 g, 0.4 mmol) in anhydrous DCM (5.5 mL) at 0 °C, pyridine (0.1 mL) and (+)-2-isopropyl-5-methylcyclohexyl chlorocarbonate (0.1 g, 0.45 mmol) were added. The mixture was stirred at room temperature for 2 h. Then, water (10 mL) was added at 0 °C and the reaction mixture was extracted with DCM (3 × 10 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered and concentrated. Purification was carried out by column chromatography using hexane/EtOAc (20:1) as eluent. Compound **17** was obtained (0.15 g, 93%) as a whitish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (d, 3H, J = 6.6 Hz), 0.89–0.93 (m, 6H), 1.00–1.12 (m, 2H), 1.26–1.46 (m, 3H), 1.63–1.72 (m, 2H), 1.93–2.01 (m, 1H), 2.03–2.13 (m, 1H), 2.41 (t, 2H, J = 8,2 Hz), 2.93 (t, 2H, J = 8,2 Hz), 3.18 (s, 1H), 3.79 (s, 3H), 4.22 (td, 1H, J_1 = 10.9 Hz, J_2 = 4.4 Hz), 4.63 (s, 2H), 5.01 (s, 1H), 5.11 (s, 1H), 6.68–6.74 (m, 2H), 7.40 (d, 1H, J = 8.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.2, 20.6, 21.9, 23.2, 26.0, 31.3, 33.0, 33.6, 34.0, 40.7, 46.9, 55.1, 69.7, 78.3, 79.5, 82.1, 111.5, 113.0, 113.6, 114.3, 134.2, 142.9, 145.9, 154.8, 159.8 ppm. IR (film): ν = 2930, 2100, 1740, 1610 cm^{-1}. Calc. for $C_{25}H_{34}O_4$ (398.54): C, 75.34; H, 8.60. Found: C, 75.08; H, 8.41%.

3.15. Synthesis of (7-methoxy-2-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalen-3a-yl)methyl acetate, **21**

To a solution of **15** (0.28 g, 1.1 mmol) in 5 mL of anhydrous Et_2O, 0.13 g (0.37 mmol) of dicobalt octacarbonyl were added. The mixture was stirred at rt for 3 h and filtered through Celite. Upon column chromatography (hexane/EtOAc 49:1) 0.55 g (90%) of **18** were obtained as a brown oil. To a solution of **18** (0.55 g 1.0 mmol) in 15.0 mL of anhydrous toluene, powdered 4 Å molecular sieves (two times the mass of the enyne) and $Rh(PPh_3)_2ClCO$ (0.05 mmol) were added. The mixture was stirred at 70 °C under argon for 18 h. The crude residue was filtered through Celite, concentrated and purified by column chromatography (hexane/EtOAc 10:1), giving 0.17 g (60%) of **21** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.88 (td, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz), 2.01 (s, 3H), 2.23 (d, 1H, J = 18.1 Hz), 2.25–2.30 (m, 1H), 2.67 (d, 1H, J = 18.1 Hz), 2.87 (dd, 1H, J_1 = 17.6 Hz, J_2 = 6.0 Hz), 2.96–3.08 (m, 1H), 3.82 (s, 3H), 3.87 (d, 1H, J = 11.0 Hz), 4.22 (d, 1H, J = 11.0 Hz), 6.27 (s, 1H), 6.69 (br s, 1H), 6.81 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.7 Hz), 7.54 (d, 1H, J = 8.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 26.3, 30.3, 44.8, 47.6, 55.4, 66.8, 113.6, 113.8, 121.9, 123.3, 129.3, 139.6, 161.9, 170.8, 173.3, 206.1 ppm. IR (film): ν = 1750, 1690 cm^{-1}. Calc. for $C_{17}H_{18}O_4$ (286.32): C, 71.31; H, 6.34. Found: C, 71.58; H, 6.17%.

3.16. (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl (7-methoxy-2-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalen-3a-yl)methyl carbonate, **23**

Following the same procedure than for the synthesis of **21**, from 0.10 g of **20**, which was obtained from 0.06 g (0.15 mmol) of **17**, 0.03 g (45%) of a (1:1) mixture of diastereomers was obtained as a yellow oil. Data for the mixture: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.74 (d, 3H, J = 7.2 Hz), 0.86–0.90 (m, 6H), 0.96–1.08 (m, 1H), 1.23 (s, 2H), 1.39–1.42 (m, 1H), 1.57–1.67 (m, 4H), 1.82–1.91 (m, 1H), 1.98 (d, 1H, J = 12.1 Hz), 2.24 (d, 1H, J = 18.2 Hz), 2.34 (dd, 1H, J_1 = 13.2 Hz, J_2 = 5.5 Hz), 2.74 (d, 1H, J = 18.2 Hz), 2.88 (dd, 1H, J_1 = 17.6 Hz, J_2 = 6.0 Hz), 3.02 (dd, 1H, J_1 = 12.6 Hz, J_2 = 5.5 Hz), 3.86–3.93 (m, 1H), 4.22–4.29 (m, 1H), 4.41–4.50 (m, 1H), 6.26 (s, 1H), 6.71 (br s, 1H), 6.81 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.2 Hz), 7.53 (d, 1H, J = 8.3 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 16.3, 20.7, 21.8, 22.7, 23.3, 26.0, 26.3, 29.4, 29.5, 29.6, 29.7, 29.9, 30.9, 31.4, 32.0, 34.0, 40.6, 45.2, 46.9, 47.5, 55.4, 69.8, 78.8, 113.6, 113.8, 121.9, 123.5, 129.2, 139.7, 154.8, 161.9, 173.2, 190.0, 196.1 ppm. IR (film): ν = 1740, 1600 cm^{-1}.

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