Natural Product Synthesis

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Enantioselective Total Syntheses of Three Cladiellins (Eunicellins): A General Approach to the Entire Family of Natural Products**

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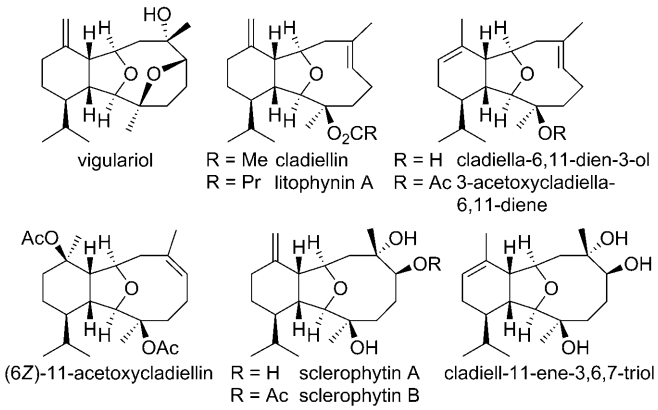
The cladiellins (eunicellins) are ether-bridged diterpenes that form part of a larger family of marine natural products along with the briarellins, asbestinins, and sarcodictyins.[1] The cladiellins have various biological activities and many of them possess significant cytotoxicity. The unusual structural features of the cladiellins, coupled with their potential anticancer activity, make them attractive synthetic targets. In recent years, several research groups have developed synthetic strategies to construct the bridged-ether core and some of this work has culminated in the total syntheses of individual members of this family of natural products.[2,3]

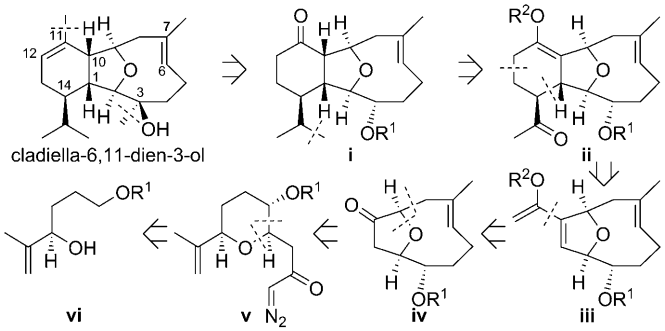
We recently reported an efficient total synthesis of (±)-vigulariol involving a late-stage intermediate bearing a *Z* alkene at the 6-position.[4] With one exception,[2k] other research groups have targeted cladiellins that contain a *Z* alkene embedded in the medium ring, or those that lack an alkene at this position. Although some cladiellins have a 6*Z* configuration [for example, (6*Z*)-11-acetoxycladiellin], the vast majority of them have the 6*E* configuration or contain an *anti*-1,2-diol at the C-6 and C-7 positions that would result from dihydroxylation of a 6*E* alkene (Scheme 1). To date, only Kim and co-workers have devised a general approach to the synthesis of cladiellins that possess the more-common 6*E* configuration.[2k] Consequently, we sought to develop a completely general strategy for the synthesis of any of the cladiellins and, in particular, those possessing the 6*E* configuration.

Cladiella-6,11-dien-3-ol, 3-acetoxycladiella-6,11-diene, and cladiell-11-ene-3,6,7-triol were selected as synthetic targets.[5–7] The isolation of cladiella-6,11-dien-3-ol from a Pacific soft coral was first reported by Hochlowski and Faulkner[5] in 1980, and Shin and co-workers reported the isolation of 3-acetoxycladiella-6,11-diene from gorgonians of the genus *Muricella* in 1997;[6] both compounds showed high activity in brine-shrimp lethality assays. The related natural product cladiell-11-ene-3,6,7-triol was isolated (*Cladiella* sp.) and characterized by Uchio and co-workers, but bioassay data was not reported for this compound.[7]



Scheme 1. Representative cladiellin (eunicellin) natural products.

Retrosynthetic analysis of cladiella-6,11-dien-3-ol commenced with disconnection of the C-3 and C-11 methyl groups to give the ketone (**i**, Scheme 2). Replacement of a methyl group on the isopropyl side chain with a carbonyl group and conversion of the C-11 carbonyl group into an enol ether (C-10–C-11) produced the methyl ketone (**ii**). Diels–Alder disconnection then revealed the diene (**iii**) and scission of the diene led to the *E*-configured oxabicyclo[6.2.1]undecenone (**iv**). Further disconnection of this intermediate, by recognition of an oxonium ylide rearrangement reaction in the forward direction, led to the diazo ketone (**v**) which could be disconnected to give the alcohol (**vi**) as the starting material.



Scheme 2. Retrosynthetic analysis of cladiella-6,11-dien-3-ol.

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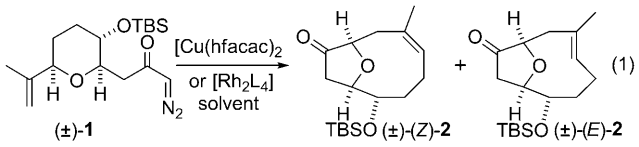
The route implied by the retrosynthetic analysis required the formation of the *E* alkene (**iv**) from the diazo ketone (**v**). In our previous work, we had shown that the copper-catalyzed reaction of a substrate [diazo ketone **1**, see reaction in Table 1] corresponding to the diazo ketone (**v**) provided the *Z* isomer as the major product with good selectivity (> 5:1, *Z*/*E*).[4] Thus, the challenge was to bias the rearrangement reaction to give the less-stable *E* isomer as the major product.

Exploratory reactions were performed with the aim of obtaining the bicyclic alkene (*E*)-**2** as the major product from rearrangement of the free or metal-bound oxonium ylide that was produced by reaction of the ether with the metal carbenoid, itself generated from diazo ketone **1**.[4,8] The reaction of the diazo ketone (±)-**1**, promoted by copper(II) hexafluoroacetylacetonate [Cu(hfacac)$_2$] or various rhodium(II) complexes, was investigated in several solvents (Table 1). The results of these studies were intriguing and

Table 1: Variation in yield and ratio of *Z*/*E* isomers with catalyst and reaction conditions.



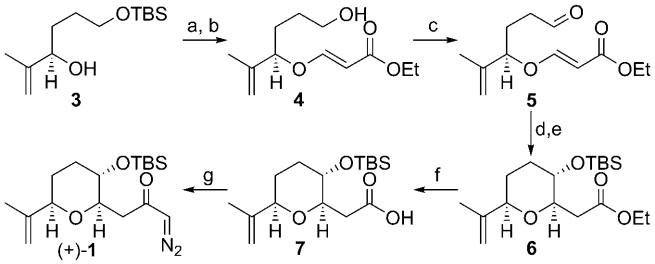
Entry	Catalyst[a]	Solvent	*T* [°C]	Yield [%][b]	*Z*/*E* ratio[c]
1	[Cu(hfacac)$_2$]	CH_2Cl_2	reflux	95	5.0:1
2	[Cu(hfacac)$_2$]	CH_2Cl_2	RT	94	5.9:1
3	[Cu(hfacac)$_2$]	CH_2Cl_2	0	96	5.5:1
4	[Cu(hfacac)$_2$]	THF	reflux	74	6.9:1
5	[Cu(hfacac)$_2$]	C_6H_6	reflux	94	4.8:1
6	[Cu(hfacac)$_2$]	DCE	reflux	85	3.9:1
7	[Cu(hfacac)$_2$]	Et_2O	reflux	93	3.1:1
8	[Cu(hfacac)$_2$]	MeCN	reflux	78	1.3:1
9	[$Rh_2(O_2CMe)_4$]	CH_2Cl_2	reflux	52	1.2:1
10	[$Rh_2(O_2CCF_3)_4$]	CH_2Cl_2	reflux	90	1.7:1
11	[$Rh_2(HNCOCF_3)_4$]	CH_2Cl_2	reflux	63	1:1.2
12	[$Rh_2(O_2CC_3F_7)_4$]	CH_2Cl_2	reflux	71	1:2.7
13	[$Rh_2(O_2CCPh_3)_4$]	CH_2Cl_2	reflux	63	1:4.3
14	[$Rh_2(O_2CCPh_3)_4$]	DCE	reflux	56	1:6.3

[a] Catalyst loading 5 mol%. [b] Combined yield of isolated (*Z*)-**2** and (*E*)-**2**. [c] Ratio of isolated products. DCE = 1,2-dichloroethane.

revealed that in the case of the [Cu(hfacac)$_2$]-catalyzed reactions, both the yield and ratio of *Z*/*E* isomers were influenced by the solvent (Table 1, entries 1–8); however, temperature had little effect on the yield or ratio of isomers when the copper-catalyzed reactions were performed in dichloromethane (Table 1, entries 1–3). The reaction that delivered the highest ratio of *Z*/*E* isomers was performed in tetrahydrofuran at reflux (Table 1, entry 4). When reactions were performed at reflux in diethyl ether, benzene, 1,2-dichloroethane, or acetonitrile (Table 1, entries 5–8), a higher proportion of the *E* isomer was obtained than from reactions performed in dichloromethane. When the reaction was performed in acetonitrile at reflux (Table 1, entry 8), almost equivalent amounts of the bicyclic ethers (*E*)-**2** and (*Z*)-**2** were obtained.

At this juncture, the scope of our study was extended to include the use of rhodium catalysts. Although the yields of rearrangement products obtained when copper(II) complexes are used for carbenoid generation are usually higher than those obtained from the corresponding rhodium(II)-catalyzed reactions,[9] rhodium(II) complexes were investigated because there would be additional opportunities to tune the reaction to deliver the *E* isomer by varying the steric or electronic characteristics of the ligand. Preliminary experiments performed using rhodium(II) acetate and rhodium(II) trifluoroacetate were encouraging (Table 1, entries 9 and 10). Subsequent reactions catalyzed by rhodium(II) trifluoroacetamide, rhodium(II) perfluorobutyrate, or rhodium(II) triphenylacetate increased the proportion of the ketone (*E*)-**2**. The highest *E*/*Z* ratio was obtained using rhodium(II) triphenylacetate in 1,2-dichloroethane at reflux (Table 1, entry 14).

It was now possible to obtain significant quantities of the bridged bicyclic alkene (*E*)-**2** and so the synthesis of cladiella-6,11-dien-3-ol was undertaken. Diazo ketone (+)-**1**, which was required for the key cyclization reaction, was prepared in seven steps from the known allylic alcohol **3**[10] (Scheme 3).



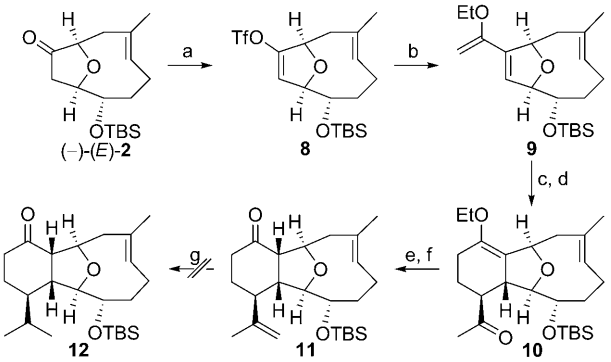
Scheme 3. Synthesis of the cyclization precursor (+)-**1**. a) $HCCCO_2Et$, *N*-methylmorpholine, CH_2Cl_2, RT, 94%; b) 10-camphorsulfonic acid, MeOH, RT, 86%; c) $(COCl)_2$, Me_2SO, CH_2Cl_2, −78 °C then Et_3N, RT, 97%; d) SmI_2, MeOH, THF, RT, 86%; e) TBSCl, imidazole, Me_2NCHO, RT, 96%; f) LiOH, EtOH–H_2O, RT, 89%; g) *i*BuO_2CCl, Et_3N, Et_2O, RT, then CH_2N_2, Et_2O, 0 °C → RT, 88%. THF = tetrahydrofuran, TBS = *tert*-butyldimethylsilyl.

Large quantities of the starting material **3** (high *ee*) were required and so two routes were explored. In the first route, the alcohol was prepared by enantioselective reduction of the corresponding enone using the Corey–Bakshi–Shibata (CBS) catalyst.[11] Although alcohol **3** was obtained in 87% yield and with 96% *ee*, scale-up was expensive and the quality of commercially available CBS catalyst was variable. Consequently, a literature procedure,[10] involving the Sharpless asymmetric epoxidation reaction, was used to give the alcohol **3** (94% *ee*) in batches of 30 grams.

Treatment of alcohol **3** with ethyl propiolate and *N*-methylmorpholine followed by O-deprotection gave the vinylogous carbonate **4** (Scheme 3). Swern oxidation afforded the aldehyde **5** and reaction with SmI_2 followed by *tert*-butyldimethylsilyl protection of the intermediate alcohol afforded the tetrahydropyran **6**.[4,12] Ester hydrolysis provided the carboxylic acid **7** and sequential treatment of the acid with

isobutyl chloroformate and diazomethane gave the diazo ketone (+)-**1**.

Following the key cyclization reaction (see reaction in Table 1), ketones (−)-(*E*)-**2** and (+)-(*Z*)-**2** were separated and the *E* isomer was converted into the tricyclic ring system found in the cladiellins (Scheme 4). Conversion of the ketone

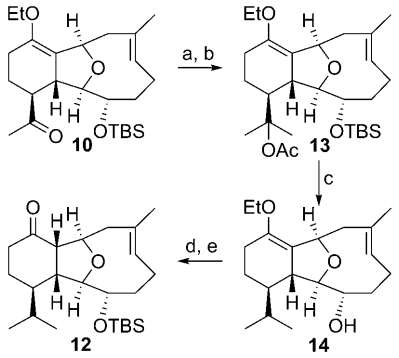


Scheme 4. Elaboration of the *E*-configured rearrangement product to give ketone **11**, which possesses the complete tricyclic cladiellin core. a) $NaN(SiMe_3)_2$, $PhN(Tf)_2$, THF, −78 °C; b) $CH_2C(OEt)SnBu_3$, [Pd-$(PPh_3)_4$], LiCl, THF, reflux; c) $CH_2CHCOMe$, PhMe, 120 °C (sealed tube), 62% over 3 steps, 1.6:1 *endo/exo*; d) K_2CO_3, MeOH, RT, 95%; e) $(Ph_3PCH_3)^+Br^-$, $NaN(SiMe_3)_2$, THF, 0 °C→RT, 80%; f) 1 M HCl, THF aq., RT, 74%; g) H_2, catalyst. Tf = trifluoromethanesulfonyl.

(−)-(*E*)-**2** into the enol triflate **8** was followed by Stille coupling of this compound with (1-ethoxyvinyl)tributylstannane to give the diene **9**.[13] A Diels–Alder reaction between the diene and methyl vinyl ketone, conducted in a sealed tube, afforded ketone **10** as a mixture of isomers (1.6:1, *endo/exo*) in 62% yield over three steps.[14] Treatment of the mixture of isomers with K_2CO_3 in methanol delivered the thermodynamically favored epimer in high yield. Ketone methylenation followed by hydrolysis of the enol ether provided ketone **11** (Scheme 4).

At this juncture, selective hydrogenation of the 1,1-disubstituted alkene was required to give an isopropyl group. Unfortunately, discrimination between the strained trisubstituted alkene and the terminal alkene was not possible; the fully saturated product and products arising from *E* to *Z* isomerization were obtained upon hydrogenation of the diene **11** (Scheme 4).

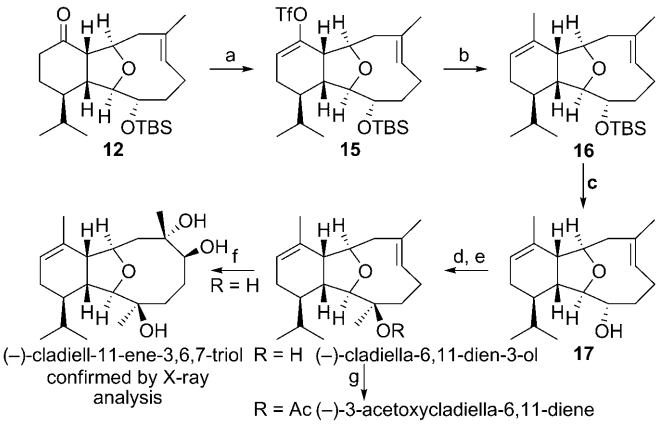
An alternative approach for the installation of the isopropyl group was required. Thus, ketone **10** was treated with methylmagnesium bromide and the resulting tertiary alcohol was acetylated to give the ester **13** (Scheme 5). Reductive removal of the acetate group was performed by treatment of ester **13** with potassium and [18]crown-6 in $tBuNH_2$ and tetrahydrofuran, as described by Barrett and co-workers for the deoxygenation of related compounds and by Kim and co-workers during their synthesis of cladiella-6,11-dien-3-ol.[2k,15] The reaction conditions employed for acetate removal led to partial or complete loss of the *tert*-butyldimethylsilyl group to give alcohol **14** and so reprotection was necessary. Hydrolysis of the enol ether under acidic conditions followed by TBS-protection of the alcohol afforded ketone **12** in high yield (Scheme 5).



Scheme 5. Introduction of the isopropyl group. a) MeMgBr, THF, 0 °C→RT, 78%; b) Ac_2O, DMAP, Et_3N, 40 °C; c) K, $tBuNH_2$, [18]crown-6, THF, RT, 65% over 2 steps; d) HCl, THF, RT, 89%; e) TBSOTf, 2,6-lutidine, CH_2Cl_2, −78 °C, 78%. DMAP = 4-dimethylaminopyridine.

The synthesis of cladiella-6,11-dien-3-ol from ketone **12** was accomplished as shown in Scheme 6. Ketone **12** was deprotonated using NaHMDS in tetrahydrofuran at low temperature and the resulting enolate was trapped as the enol triflate **15**. The C-11 methyl substituent was then introduced by palladium(0)-mediated cross-coupling of the enol triflate **15** with methylmagnesium bromide.[16] Removal of the TBS protecting group from the resulting diene **16** provided alcohol **17** in 68% yield over three steps. Dess–Martin oxidation of this alcohol followed by addition of MeLi in the presence of $NaBF_4$ completed the synthesis of (−)-cladiella-6,11-dien-3-ol;[2k] the spectroscopic and other characterization data were identical to those reported for the natural product.[2k,5]

Two other cladiellins were prepared from synthetic (−)-cladiella-6,11-dien-3-ol (Scheme 6). Exposure to a catalytic amount of osmium tetroxide in the presence of NMO resulted in dihydroxylation of the reactive *E* alkene, as reported by Kim and co-workers.[2k] (−)-Cladiell-11-ene-3,6,7-triol was obtained as a crystalline solid in 66% yield. Spectroscopic and



Scheme 6. Completion of the total syntheses of (−)-cladiella-6,11-dien-3-ol, (−)-cladiell-11-ene-3,6,7-triol, and (−)-3-acetoxycladiella-6,11-diene. a) $NaN(SiMe_3)_2$, $PhN(Tf)_2$, THF, −78 °C; b) MeMgBr, [Pd-$(PPh_3)_4$], LiCl, THF, RT; c) $nBu_4N^+F^-$, 4 Å M.S., THF, RT 68% over 3 steps; d) Dess–Martin reagent, pyridine, CH_2Cl_2, RT; e) MeLi, $NaBF_4$, THF, −78 °C 69% over 2 steps; f) OsO_4, NMO, THF/H_2O (1:1), 0 °C→RT 66%; g) Ac_2O, DMAP, Et_3N, RT 25%.

other characterization data for this compound were identical to those reported in the literature and further confirmation of structure was provided by X-ray crystallography.[7,17] Acetylation of (−)-cladiella-6,11-dien-3-ol was extremely difficult, which suggests that this compound adopts a conformation in which the hydroxyl group is oriented towards the interior of the medium ring. However, the natural product (−)-3-acetoxycladiella-6,11-diene was obtained in modest yield by direct acylation under standard conditions. Spectroscopic data for this compound were also identical to data reported in the literature for material obtained from the natural source.[6] Kim and co-workers have shown that it is possible to convert (−)-cladiella-6,11-dien-3-ol into the natural products (+)-polyanthellin A and (−)-deacetoxyalcyonin acetate in two and five steps respectively, and so our route also constitutes a formal synthesis of these compounds.[2k]

In summary, we have shown that it is possible to vary the stereochemical outcome of the key catalytic reaction (**1**→(*E/Z*)-**2**) by selecting the appropriate catalyst and solvent. It is possible to tune the reaction to predominantly give (*E*)-**2** as the product using rhodium(II) triphenylacetate as the catalyst. The bridged bicyclic ether (−)-(*E*)-**2** can be elaborated to give (−)-cladiella-6,11-dien-3-ol and this compound can be converted into several other cladiellin natural products, including (−)-3-acetoxycladiella-6,11-diene, which has not been synthesized previously. The fact that the cyclization reaction can be tuned to give either the *E* or *Z* product means that our synthetic strategy can be applied to virtually any member of the cladiellin family of marine diterpenes and is one of only two general routes to this group of natural products.[2k]

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[14] Complete facial selectivity was observed with respect to the diene during the thermal Diels–Alder reaction (**9**→**10**, Scheme 3). Decomposition of diene **9** was observed when a Lewis acid catalyst was added to the Diels–Alder reaction.

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[17] Crystal data for cladiell-11-ene-3,6,7-triol: $C_{20}H_{34}O_4$, $M_r = 338.47$, crystal dimensions $0.30 \times 0.1 \times 0.05$ mm^3, orthorhombic, space group $P2_12_12_1$, $a = 6.9388(6)$, $b = 8.1850(10)$, $c = 33.548(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1905.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.18$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.08$ mm^{-1}, $T = 100(2)$ K.; 13485 reflections collected of which 4356 were independent, $2\theta_{max} = 55°$. Structure solved by direct methods (SHELXS-97) and refined by full-matrix least squares against F^2 (SHELXL-97), $R_1 = 0.074$, $wR_2 = 0.096$, 225 parameters. CCDC 787739 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

