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# Toward the synthesis of macrolide aspergillide D

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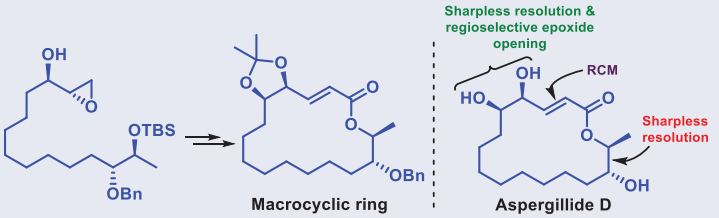
**ABSTRACT**

Stereoselective synthesis of 16-membered macrocyclic core of marine natural product, Aspergillide D is described using linear strategy. The salient features of this synthetic study include the Sharpless asymmetric kinetic resolution followed by regioselective ring-opening reaction of corresponding epoxide to establish the stereo centers and ring-closing metathesis (RCM) by Grubbs'-II catalyst for the construction of macrocyclic ring.

**GRAPHICAL ABSTRACT**

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**KEYWORDS**
Macrolide; natural product; regioselective ring-opening reaction; ring-closing metathesis (RCM); sharpless kinetic resolution

## Introduction

Fourteen- and sixteen-membered macrolides have received a lot of attention from researchers due to their prominent antibiotic activity,[1,2] and most of them were isolated from fungi and diverse species of Streptomyces. Aspergillide D (**1**) is a 16-membered marine macrolide (Figure 1), isolated by Qi et al.[3] from the extract of the gorgonian allied fungal strain *Aspergillus sp.* SCSGAF 0076 and the structure was established by $^{1}H$, $^{13}C$ NMR, NOESY, DEPT and HRMS analysis. In 2017, Mohapatra group[4] described the first total synthesis of aspergillide D. Very recently Narsaiah et al.[5] reported a formal synthesis of aspergillide D.

In continuation of our research interest in the total synthesis of macrolides,[6] herein we disclose our efforts toward the total synthesis of aspergillide D in which, ring-closing metathesis (RCM) as the key step to accumulate the macrolactone core and Sharpless

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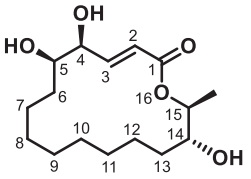
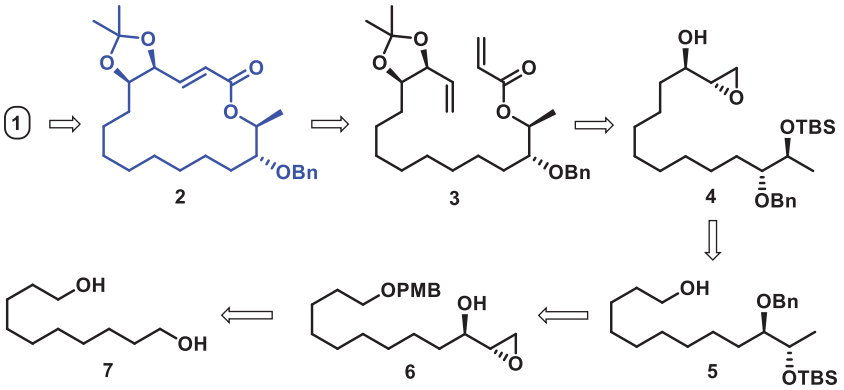



**Figure 1.** Structure of Aspergillide D (**1**).



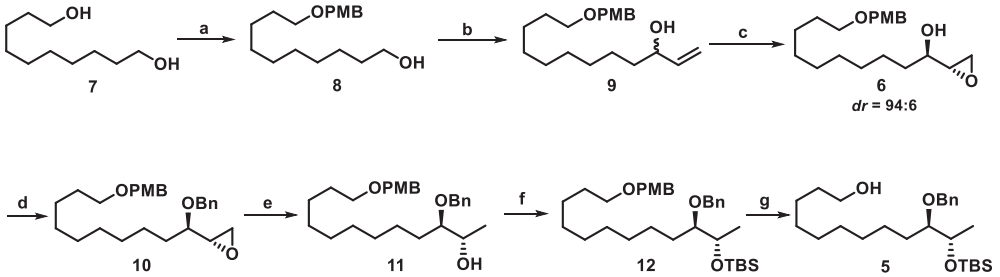

**Scheme 1.** Retrosynthetic analysis of Aspergillide D.

kinetic resolution followed by regioselective ring-opening reaction of the resultant epoxide to generate the required stereo centers.

The retrosynthetic analysis of Aspergillide D (**1**) is illustrated in Scheme 1, the macrocyclic core **2** could be constructed from the diene compound **3** *via* Ring closing metathesis using Grubbs'-II catalyst. The diene compound **3** could be synthesized from epoxy alcohol **4** through one carbon homologation of compound **4** by regioselective epoxide ring opening using $Me_3SI$ (trimethylsufonium iodide), TBS-deprotection followed by acrylation. The epoxy alcohol **4** could be obtained from alcohol **5** *via* oxidation on 1° alcohol and the resultant aldehyde could be coupled with vinylmagnesium bromide, which would be accessed racemic allylic alcohol, followed by Sharpless kinetic resolution. The compound **5** would be prepared from epoxy alcohol **6** by benzylation of 2° alcohol and epoxide ring opening with LAH, followed by deprotection of PMB group with DDQ. Further, the epoxy alcohol **6** could be derived from commercially available 1,10-decanediol (**7**) through Sharpless asymmetric kinetic resolution.

## Results and discussion

We initiated the synthesis of required alcohol intermediate **5** (Scheme 2) with commercially available 1,10-decanediol (**7**). Mono-PMB protection of diol **7** with 4-methoxybenzyl alcohol using Amberlyst-15 in $CH_2Cl_2$ reflux conditions[7] provided PMB ether **8** in 90% yield. The primary alcohol **8** was oxidized by PCC (Pyridinium Chlorochromate)[8] in $CH_2Cl_2$ to get the resultant aldehyde, which was subjected to Grignard reaction with vinylmagnesium bromide (1 M solution in THF) at −78 °C to give the racemic allylic alcohol **9** in 75% yield over two steps. Then, the allylic alcohol **9** was converted to the chiral epoxy alcohol **6** in 44% yield under Sharpless kinetic resolution conditions[9] by

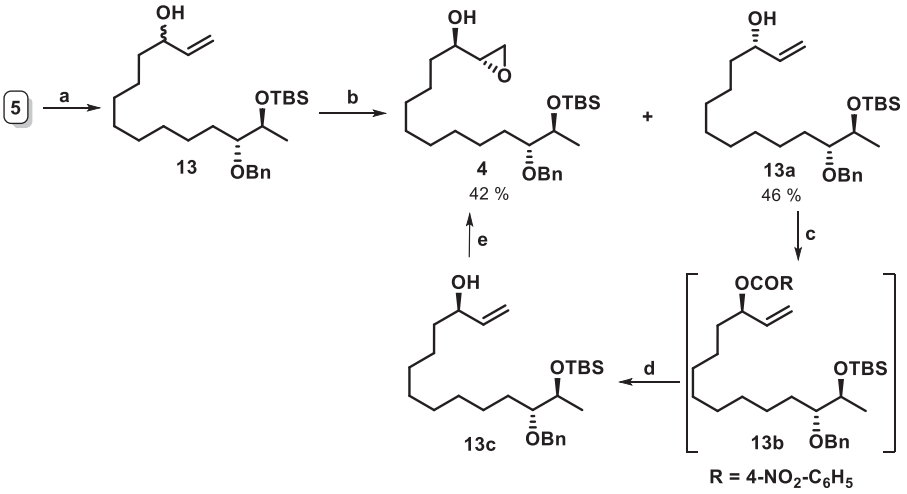



**Scheme 2.** Reagents and conditions: (a) PMB-OH, Amberlyst-15, $CH_2Cl_2$, reflux, 12 h, 90%; (b) 1) PCC, $CH_2Cl_2$, rt, 1–2 h, 2) VinylMgBr, THF, −20 °C, 2 h, 75% yield, over two steps; (c) (-)-DIPT, $Ti(O^iPr)_4$, TBHP, MS (4 A°), $CH_2Cl_2$, −25 °C, 12 h, 44%; (d) NaH, BnBr, DMF, 0 °C-rt, 4–5 h, 94%; (e) $LiAlH_4$, THF, 0 °C-rt, 2–3 h, 90%; (f) TBSCl, Im, $CH_2Cl_2$, 0 °C-rt, 2 h, 95%; (g) DDQ, $CH_2Cl_2$:$H_2O$ (19:1), pH = 7 buffer, rt, 1 h, 86%.

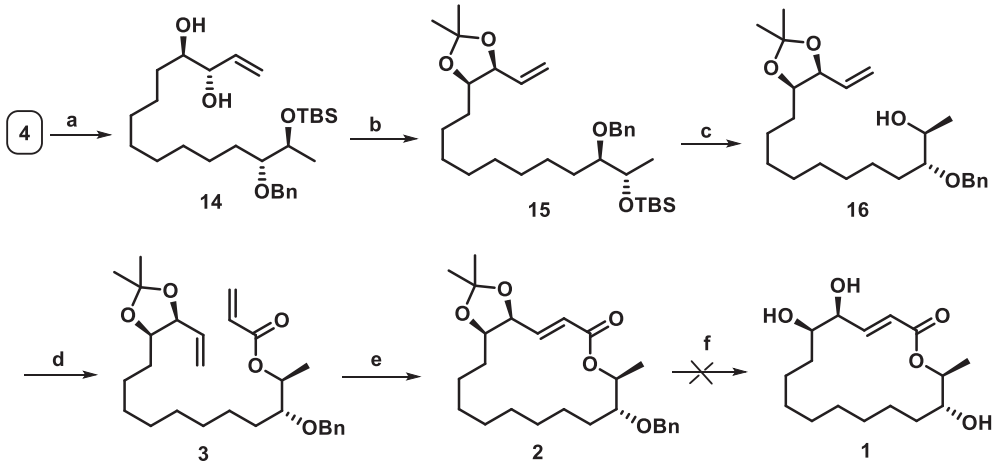
the reaction of (-)-DIPT and $Ti(O^iPr)_4$ in the presence of 0.5 equivalents of *tert*-butyl-hydroperoxide in $CH_2Cl_2$ at −25 °C. The enantiomeric purity of compound **6** was determined by LCMS analysis (*dr* = 94:6). The free 2° alcohol group in **6** was protected as its benzyl ether to produce **10** in 94% yield by treating it with Benzyl bromide and Sodium hydride (NaH) in DMF. The terminal epoxide **10** was reductively opened with $LiAlH_4$ in THF at 0 °C to achieve **11** in 90% yield. Then the corresponding 2° alcohol **11** was masked with TBS-Cl in the presence of Imidazole in $CH_2Cl_2$ to obtain compound **12** in 95% yield. The PMB group in compound **12** was oxidatively removed under neutral conditions using DDQ in $CH_2Cl_2$:$H_2O$ (19:1) in phosphate buffer solution (pH = 7) to get the desired alcohol **5** in 86% yield.[10]

Subsequently, the primary alcohol **5** was oxidized under IBX conditions[11] to obtain the corresponding aldehyde, which was coupled with vinylmagnesium bromide gave the resultant racemic allylic alcohol **13** in 70% yield over two steps. Following the similar chemistry of compound **6**, the epoxy alcohol **4** was also prepared as enantiomerically rich in 42% yield under Sharpless kinetic resolution conditions along with enantiomerically pure (*S*)-allylic alcohol (**13a**) in 46% yield.[9] At this stage to improve the yield of alcohol **4**, successively we converted the (*S*)-allylic alcohol (**13a**) into (*R*)-alcohol (**13c**) by inversion of the hydroxyl configuration using the Mitsunobu procedure in 72% yield through the corresponding ester **13 b**.[12] Then, the (*R*)-alcohol (**13c**) was transformed to the epoxy alcohol **4** by Sharpless epoxidation using (-)-DIPT/$Ti(O^iPr)_4$ in 77% yield (Scheme 3).

Consequently, one carbon homologation on the resultant epoxy alcohol **4** was carried out *via* regioselective epoxide ring opening with $Me_3SI$/*n*-BuLi[13] to obtain diol compound **14** in 75% yield (Scheme 4). The stereo chemistry of 1,2-diol **14** was determined using a modified Mosher ester analysis.[14] So that to conform the configurations at C-3 and C-4 of diol **14** was treated with *R*- or *S*-methoxy-(trifluoromethyl)phenylacetyl acid [MTPA, as chiral dervatizing agent (CDA)] and DCC (coupling reagent) in the presence of DMAP in $CH_2Cl_2$ to give the corresponding (*S,S*)- and (*R,R*)-bis-MTPA esters respectively.[15] Then, recorded the $^1$HNMR spectra of both bis-MTPA esters and calculated the $\Delta\delta^{SR}$ values as shown in Figure 2. Thus the absolute configuration of 1,2-diol (**14**) was established as 3*S*, 4*R* (See in detail results in the supporting information).




**Scheme 3.** Reagents and conditions: (a) 1) IBX, ACN, reflux, 1 h, 2) VinylMgBr, THF, −20 °C-rt, 2 h, 70% yield, over two steps; (b) (-)-DIPT, Ti($O^iPr$)$_4$, TBHP, MS (4 A°), $CH_2Cl_2$, −25 °C, 12 h, 42%; (c) DIAD, TPP, *P*-Nitrobenzoicacid, THF, 0 °C, 1 h; (d) $K_2CO_3$, MeOH, rt, 2 h, 72%; (e) (-)-DIPT, Ti($O^iPr$)$_4$, TBHP, MS (4 A°), $CH_2Cl_2$, −25 °C, 12 h, 77%.




**Scheme 4.** Reagents and conditions: (a) *n*-BuLi, $Me_3SI$, THF, −20 °C-rt, 3 h, 75%; (b) 2,2-DMP, PPTS, $CH_2Cl_2$, 0 °C-rt, 3 h 90%; (c) TBAF (1.0 M), THF, 0 °C-rt, 24 h, 84%; (d) Acryloyl Chloride, TEA, $CH_2Cl_2$, 0 °C-rt, 30 min., 76%; (e) Grubbs'-II Catalyst, $CH_2Cl_2$, reflux, 16 h, 61%; (f) $TiCl_4$, $CH_2Cl_2$, 0 °C.

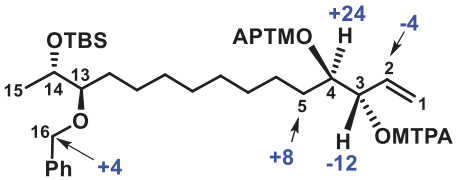



**Figure 2.** Selected $\Delta\delta$ Values of the (*S,S*)- and (*R,R*)-MTPA bis-esters of 1,2-diol (**14**) {$\Delta\delta^{SR} = \delta$ [(*S,S*)-MTPA bis-ester] - $\delta$ [(*R,R*)- MTPA bis-ester] in ppm}{$\Delta\delta^{SR}$ values (in Hz): $\Delta\delta^{SR}$ ($=\delta^S - \delta^R$) 400 MHz}.

Then, the acetonide compound **15**, achieved from **14** by treatment with 2,2-dimethoxypropane in the presence of PPTS in $CH_2Cl_2$ at room temperature in 90% yield. The compound **15** further reacted with TBAF (1.0 M) in THF to access the TBS-deprotected intermediate **16** in 84% yield, followed by acrylation in the presence of acryloyl chloride, TEA in DCM produced diene compound **3** in 76% yield. The diene ester **3**, which set the stage for the ring-closing metathesis (RCM) reaction[16] to accumulate the 16-membered macrocyclic lactone **2**. The diene ester was dissolved in degassed $CH_2Cl_2$ and refluxed with Grubbs' 2nd generation catalyst under high dilution conditions to deliver the macrolactone **2** in 61% yield. The RCM product **2** was established by $^1$H and $^{13}$C NMR spectral analysis. $^1$H NMR revealed the resonating peaks at δ 6.82 (dd, $J_1$ = 15.7 Hz, $J_2$ = 7.5 Hz, 1 H) and 6.04 (dd, $J_1$ = 15.7 Hz, $J_2$ = 1.2 Hz, 1 H) for newly generated internal double bond and coupling constant $J$ = 15.7 Hz shows its *trans*-geometry. $^{13}$C NMR also disclosed the peaks at $\delta$ 142.6 and 124.2 ppm for the double bond carbons and a peak at *m/z* 453.2615 $[M + Na]^+$ in ESI-HRMS further confirmed the formation of 16-membered macrocycle **2**.

Finally, the total deprotection of cyclic compound **2** having benzyl (Bn) and acetonide groups tried with $TiCl_4$ to achieve the synthesis of aspergillide D (**1**). Unfortunately, we could not get the final product and observed the decomposition of cyclised product **2**. At this stage, though we had a small quantity of **2**, started further investigation to complete the total synthesis of **1** as well as we thought that Bn group may create the problem in final step. Then, a selective protection of the secondary hydroxyl group also required instead of Bn group to achieve the target molecule. These efforts are under progress in our group and will be reported in due course.

## Conclusion

In this report, we have accomplished a linear synthesis of macrocyclic ring of aspergillide D starting from 1,10-decanediol in 14 steps. Key steps in the synthetic sequence include Sharpless kinetic resolution followed by regioselective ring-opening reaction of corresponding epoxide to create the stereo centers and ring-closing metathesis (RCM) to assemble the macrolactone core.

## Experimental

General: All reactions were carried out using standard syringe, septa and cannula techniques under inert atmosphere. All glassware apparatus used for reactions are perfectly oven/flame dried. Anhydrous solvents were distilled prior to use: THF from Na and benzophenone; $CH_2Cl_2$ from $CaH_2$; MeOH from Mg cake. Commercial reagents were used without purification. All organic extracts were dried with anhydrous $Na_2SO_4$. Organic solutions were concentrated in a rotary evaporator under reduced pressure at a bath temperature below 35 °C. The diastereomeric ratio of the products were measured with a chiral-phase HPLC using Chiralpak AS column. Column chromatography was carried out by using silica gel (60–120 mesh) unless otherwise mentioned. Analytical thin layer chromatography (TLC) was run on silica gel 60 F254 pre-coated plates (250 μm thickness). Optical rotations $[\alpha]_D$ were measured on a polarimeter and given in

$10^{-1}$ degcm$^2$g$^{-1}$. Infrared (IR) spectra were recorded in $CHCl_3$/KBr or neat (as mentioned) and reported in wave number (cm$^{-1}$). Mass spectral data were obtained using MS (EI) ESI, HRMS mass spectrometers. High resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double focusing spectrometer. $^1$H NMR spectra were recorded at 400, 500 MHz and $^{13}$C NMR spectra at 100 MHz in $CDCl_3$ solution unless otherwise mentioned, chemical shifts are in ppm downfield from tetramethylsilane and coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

**(3a*S*,8*S*,9*R*,17a*R*,*E*)-9-(benzyloxy)-2,2,8-trimethyl-3a,8,9,10,11,12,13,14,15,16,17,17a-dodeca hydro-6*H*[4,5-*e*][1]oxacyclohexadecin-6-one (macrolactone core 2):** Grubbs'-II catalyst (0.031 g, 0.037 mmol) was added to a solution (degassed with nitrogen) of compound **3** (0.170 g, 0.371 mmol) in $CH_2Cl_2$ (150 mL) at room temperature. The resultant reaction mixture was stirred overnight at 40 °C. The solvent was evaporated under rota and the crude product was purified by column chromatography using silica gel (EtOAc:hexane = 1:9) to provide lactone **2** (0.087 g, 61% yield) as a pale-yellow oil. $[\alpha]_D^{20} = -3.81$ (*c* 0.41, $CHCl_3$); IR (neat): 2927, 2855, 1939, 1717, 1637, 1452, 1373, 1263, 1170, 1066, 979, 739, 696 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 1.20–1.56 (m, 25 H), 3.38–3.44 (m, 1 H), 3.50–3.59 (m, 1 H), 4.18–4.25 (m, 1 H), 4.55 (d, $J = 11.6$ Hz, 1 H), 4.60 (d, $J = 11.6$ Hz, 1 H), 5.03–5.10 (m, 1 H), 6.04 (dd, $J_1 = 15.7$ Hz, $J_2 = 1.2$ Hz, 1 H), 6.82 (dd, $J_1 = 15.7$ Hz, $J_2 = 7.5$ Hz, 1 H), 7.30–7.38 (m, 5 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 17.9, 22.7, 23.2, 25.7, 26.2, 26.9, 27.7, 28.4, 29.3, 29.4, 29.6, 78.5, 78.7, 79.7, 80.7, 80.9, 108.1, 124.2, 127.9(2 C), 128.3, 128.4(2 C), 139.3, 142.6, 164.7; HRMS calcd for $C_{26}H_{38}O_5Na$ 453.2617 $[M + Na]^+$, found 453.2615.

Full experimental detail, $^1$H and $^{13}$C NMR spectra can be found via the "Supplementary Content" section of this article.

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