Correction to “A Concise Construction of the Chlorahololide Heptacyclic Core”

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Supporting Information

The relevant intermediate compounds **27** and **28** in Scheme 5 in this paper are incorrect. The corrections are detailed below:

Scheme 5 is corrected as follows:

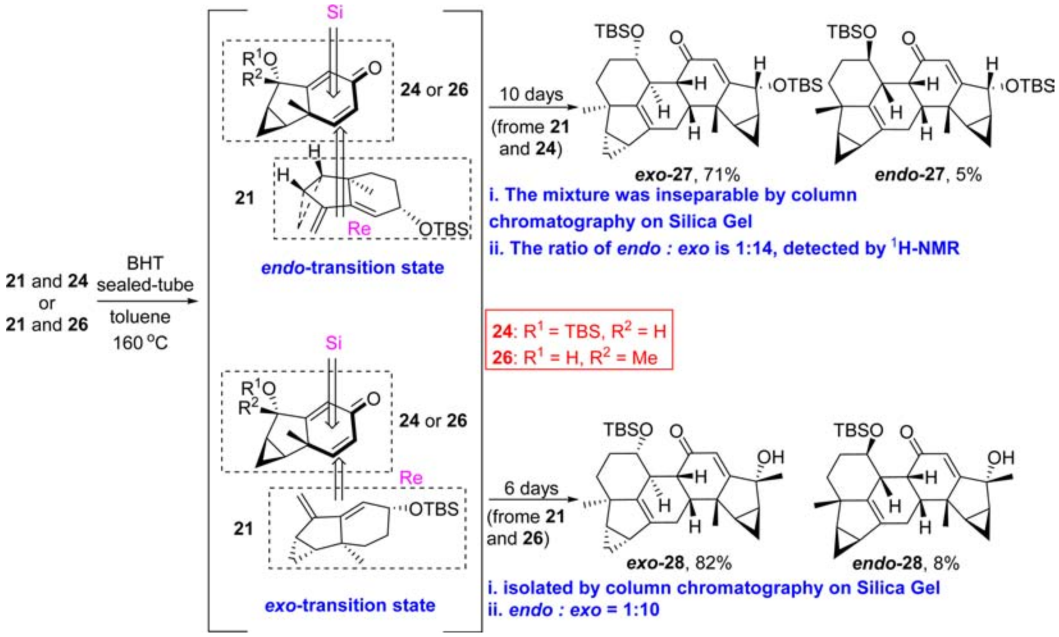
Figure 2 title is corrected as follows: “X-ray-derived ORTEP drawing of alcohol *exo*-**28**.”

The last three paragraphs in the original text are revised as follows:

“With the desired diene **21** and dienophile **24** secured, the construction of the linking six-membered ring was pursued (Scheme 5). After considerable experiments to carry out the Diels−Alder cycloaddition reaction between diene **21** and dienophile **24**,[23] it was found that treatment of diene **21** (2.25 equiv) and dienophile **24** (1.0 equiv) with butylated hydroxytoluene (BHT)[24] in reflux toluene (160 °C, sealed tube) furnished the inseparable Diels−Alder cyclization products *endo*-**27** and *exo*-**27** in 76% yield (92% yield on BRSM) with the *endo*/*exo* diastereoselectivity of 1:14 (detected by ^{1}H NMR spectrum). Presumably, the angular methyl and cyclopropyl groups in **24** served to preferablely direct the Diels−Alder addition to the less hindered *Si* face, as indicated in Scheme 5. The stereochemistry of the major heptacyclic core *exo*-**27** in the inseparable mixture (*endo*-**27** and *exo*- **27**) was assigned to be *exo*-isomer by NMR spectroscopic analysis (HMBC, NOESY correlations, see the Supporting Information).

Encouraged by the expected success in the preparation of the minor heptacyclic core *endo*-**27** via an expected *endo*-Diels−Alder cycloaddition, conversion of diene **21** (2.5 equiv) and dienophile **26** (1.0 equiv) under similar aforementioned conditions also smoothly afforded the separable Diels−Alder cyclization products *endo*-**28** and *exo*-**28** with the direction of the angular methyl and cyclopropyl groups in 8% and 82% yields, respectively. The *endo*/*exo* diastereoselectivity was detected to be 1:10 by isolated yields of *endo*-**28** and *exo*-**28**. The stereochemistry of the major heptacyclic *exo*-**28** was unambiguously confirmed by its X-ray crystallographic analysis (Figure 2). The stereochemistry of the heptacyclic core *endo*-**28** was assigned by the comparable NMR spectroscopic analysis with that of *exo*-**28** (see the Supporting Information).

Scheme 5. Synthesis of the Heptacyclic Cores via Diels-Alder Cycloaddition



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In summary, we have illustrated a concise and efficient strategy for the construction of the either *endo*- or *exo*- heptacyclic core of the chloranthaceae family, together with the acceptable stereoselective generation of the three contiguous stereocenters, via a biomimetic Diels–Alder cycloaddition as the pivotal step. The crucial precursors **27** and **28** were prepared in only 12 linear steps from commercially available Wieland–Miescher ketone (**11**), and the strategy developed here is directly amenable to an asymmetric synthesis starting from the commercially available enantiopure Wieland-Miescher ketone (**11**). Application of the disclosed strategy here to the total synthesizes of chlorahololide A (**2**) and shizukaol A (**1**) from the desried core *endo*-**28** are underway and will be reported in due course."

A revised Supporting Information file is included that includes the following changes: p S16, a new scheme; pp S17 and S18, experimental details for the preparation of the inseparable heptacyclic key cores *exo*-**27** and *endo*-**27** and the heptacyclic key cores *exo*-**28** and *endo*-**28**; pp S51–S62 and S64, revised relevant structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02786.

Revised file containing a new scheme, experimental details, and revised structures (PDF)