Total Syntheses of (+)- and (-)-Tetrapetalones A and C

Heemal H. Dhanjee, Yutaka Kobayashi, Jonas F. Buergler, Travis C. McMahon, Matthew W. Haley, Jennifer M. Howell, Koichi Fujiwara, and John L. Wood *J. Am. Chem. Soc.* **2017**, *139*, 14901-14904

- Was first isolated by Hirota and co-workers from Streptomyces sp. USF-4727 in 2003 in their pursuit of novel lipoxygenase inhibitors.
- Contains a stereogenic p-quinol, four contiguous stereocenters, and a trisubstituted olefin lies in the fused azepine.
- Has a β-linked rhodinose moiety.

Tetrapetalone A

Tetrapetalone A





Previous Work and retro-synthesis

1. Et
$$CO_2Me$$

Br $DMF, 60^{\circ}C$

2. i TIPSCI, imid, CH_2CI_2
 ii $DMAP$ (cat)

OTIPS

OTIPS

OTIPS

9

Ph ATPH

$$\begin{bmatrix}
-C = C - CH = O + AI \\
Ph ATPH

\end{bmatrix}$$

$$\begin{bmatrix}
-C = C - CH = O + AI \\
Ph ATPH

\end{bmatrix}$$

$$\begin{bmatrix}
AI(OAr)_3AI \\
AI(OAr)_3
\end{bmatrix}$$

$$\begin{bmatrix}
AI(OAr)_3AI \\
O = Et \\
O = O \\
O$$

 $CIO_2 + H_2PO_4^- = HCIO_2 + HPO_4^{2-}$

Br O (COCI)₂, DMF (cat) then HFIP, mw then DBU, TIPSCI OTIPS

To
$$CO_2Et$$
 CO_2Et CO_2ET

TFÁ

concerted

C-H activation

`R

 $\text{CF}_3\text{SO}_3^{\bigcirc}$

6