Total Syntheses of (+)- and (-)-Tetrapetalalones 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.

Presented by Yuanzhe Zhang, Liu group.
Previous Work and retro-synthesis

Frontier, 2014

Porco, 2005

Sarpong, 2010

glycosylation

crotylation

glycosylation

this work (-)-1 phenolic oxidation
(COCl)₂, DMF (cat) then HFIP, mwa then DBU, TIPSCI

\[ \text{dr} = 2.8 : 1 \] column separation, pure

OCOCl + DMF

RCOCI + DMF

Pd(TFA)₂, PIFA, DCE, 80°C, then SiO₂

OTIPS 17

Pd(TFA)₂, ligand assisted concerted C-H activation

F₃C\text{O} \rightarrow \text{HOh}
Obtained from the another enantiomer

(-)-tetrapetalone A

(-)-tetrapetalone C

Obtained from the another enantiomer

R

| TIPS | R

| TBAF | OAc

| Phenol | OAc

| Phl | HO'O'Bu

| hydrolysis |

| CO₂Et | LiOMe

| +Me | Me

| then H₂O | -CO₂

| DMDO | OH

| OH | OH