

EVOLVING STRATEGIES TOWARD THE SYNTHESIS OF CURCUSONE C

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To my family

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ABSTRACT

Curcusone C is a tricyclic diterpenoid natural product possessing potent anti-cancer activities as well as a structurally unusual 2,3,7,8-tetrahydroazulene-1,4-dione skeleton. Herein, we report our evolving synthetic efforts toward the divergent total syntheses of *ent*-curcusone C and several structural congeners, which commenced with a Suzuki coupling of the peripheral carbon-based rings. Whereas the boronate partner was constructed from cyclopentenone, the halide partner could be elaborated from (S)-perillaldehyde. The alcohol coupling product was next esterified, then subjected to diazo transfer and cyclopropanation to produce a lactone. The resulting vinyl cyclopropane moiety was exposed to Kauffmann olefination conditions in order to form a divinylcyclopropane, which upon reductive lactone opening smoothly underwent a Cope rearrangement to establish the essential tricyclic core embedded in the curcusones.

Due to ongoing issues of scalability as well as unsatisfactory yields for the key cyclopropanation step, this route was ultimately abandoned, and an alternative strategy was devised which instead relied on a cross-electrophile coupling to join the peripheral rings. We further found that a central ring could be constructed via either Stetter annulation or ring-closing metathesis (RCM), accessing the tricyclic core of the curcusones in only 9 steps. Potential end-game strategies are further described.

We additionally report our experimental research into the acyl-amination of *in situ*-generated arynes using symmetrical imides. The difunctionalized aryl products could be further derivatized to synthetically useful indoles and quinolones via McMurray coupling and Camps cyclization, respectively.

PUBLISHED CONTENT AND CONTRIBUTIONS

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LIST OF ABBREVIATIONS

Å	Ångstrom
$[\alpha]_D$	specific rotation at wavelength of sodium D line
[H]	reduction
[O]	oxidation
Ac	acetyl
acac	acetylacetone
Anal.	combustion elemental analysis
APCI	atmospheric pressure chemical ionization
app	apparent
aq	aqueous
AIBN	2,2'-azobisisobutyronitrile
Ar	aryl
atm	atmosphere
Bn	benzyl
BOX	bisoxazoline
bp	boiling point
br	broad
Bu	butyl
<i>i</i> -Bu	<i>iso</i> -butyl
<i>n</i> -Bu	butyl
<i>t</i> -Bu	<i>tert</i> -butyl

Bz	benzoyl
<i>c</i>	concentration for specific rotation measurements
°C	degrees Celsius
ca.	circa
calc'd	calculated
CAN	ceric ammonium nitrate
cat	catalytic
Cbz	carbobenzyloxy
CI	chemical ionization
cm ⁻¹	wavenumber(s)
Cp	cyclopentadienyl
Cy	cyclohexyl
d	doublet
D	deuterium
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	<i>N,N'</i> -dicyclohexylcarbodiimide
DCE	dichloroethane
DCM	dichloromethane
decomp	decomposition
DIBAL	diisobutylaluminum hydride
DMAP	4-dimethylaminopyridine
dmdba	bis(3,5-dimethoxybenzylidene)acetone

DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
dr	diastereomeric ratio
ee	enantiomeric excess
EI	electron impact
e.g.	exempli gratia
equiv	equivalent
ESI	electrospray ionization
exp	experimental
FAB	fast atom bombardment
FID	flame ionization detector
g	gram(s)
GC	gas chromatography
gCOSY	gradient-selected correlation spectroscopy
h	hour(s)
HMDS	1,1,1,3,3,3-hexamethyldisilazane
HMPA	hexamethylphosphoramide
HPLC	high-performance liquid chromatography
HSQC	heteronuclear single quantum coherence
<i>hν</i>	light
Hz	hertz
IBX	2-iodobenzoic acid
IC ₅₀	median inhibition concentration (50%)

i.e.	id est
<i>i</i> -Pr	<i>iso</i> -propyl
IR	infrared (spectroscopy)
<i>J</i>	coupling constant
JohnPhos	(2-Biphenyl)di- <i>tert</i> -butylphosphine
kcal	kilocalorie
KHMDS	potassium hexamethyldisilazide
1	wavelength
L	liter, ligand
LDA	lithium hexamethyldisilazide
lit.	literature value
m	multiplet; milli
<i>m</i>	<i>meta</i>
<i>m/z</i>	mass to charge ratio
M	metal; molar; molecular ion
<i>m</i> -CPBA	<i>meta</i> -chloroperbenzoic acid
Me	methyl
MHz	megahertz
min	minute(s)
μ	micro
MM	mixed method
mol	mole(s)
MOM	methoxymethyl

mp	melting point
Ms	methanesulfonyl (mesyl)
MS	molecular sieves
n	nano
nbd	norbornadiene
NBS	<i>N</i> -bromosuccinimide
NMO	<i>N</i> -methylmorpholine <i>N</i> -oxide
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser enhancement spectroscopy
Nu	nucleophile
<i>o</i>	<i>ortho</i>
<i>p</i>	<i>para</i>
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
Ph	phenyl
pH	hydrogen ion concentration in aqueous solution
PhH	benzene
PhMe	toluene
Pin	pinacol
pKa	p <i>K</i> for association of an acid
PMB	<i>p</i> -methoxybenzyl
ppm	parts per million

PPTS	pyridinium <i>p</i> -toluenesulfonate
Pr	propyl
Py	pyridine
q	quartet
ref	reference
R	generic for any atom or functional group
rt	room temperature
s	singlet or strong or selectivity factor
sat.	saturated
S _N 2	second-order nucleophilic substitution
sp.	species
t	triplet
TBAF	tetrabutylammonium fluoride
TBHP	<i>tert</i> -butyl hydroperoxide
TBS	<i>tert</i> -butyldimethylsilyl
TBSal	(6Z)-6-[(<i>tert</i> -butylamino)methylidene]cyclohexa-2,4-dien-1-one
TES	triethylsilyl
Tf	trifluoromethanesulfonyl (triflyl)
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin-layer chromatography
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine

TMS	trimethylsilyl
TOF	time-of-flight
Tol	tolyl
Ts	<i>p</i> -toluenesulfonyl (tosyl)
UV	ultraviolet
<i>v/v</i>	volume to volume
w	weak
X	anionic ligand or halide
Xyl	xylyl