Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

How an Early or Late Transition State Impacts the Stereoselectivity of Tetrahydropyran Formation by Intramolecular oxa-Michael Addition

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Supporting information I: full literature survey

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Literature survey of base- and acid-catalysed oxa-Michael cyclisation and its analysis

General information

Before we embark on the computational investigation of *oxa*-Michael reaction, we intended to examine other available examples in the literature. The thorough search for examples was carried out by parallel using SciFinder and Reaxys that have the most comprehensive database for the chemical literature. After an exhaustive review of the precedents, we came to realise that the following classification aided us to recognise certain trends in selectivity as well as to systematize the reactions. Thus, four arbitrary-categories are introduced (Figure 1),which formed the basis of the brief literature review.

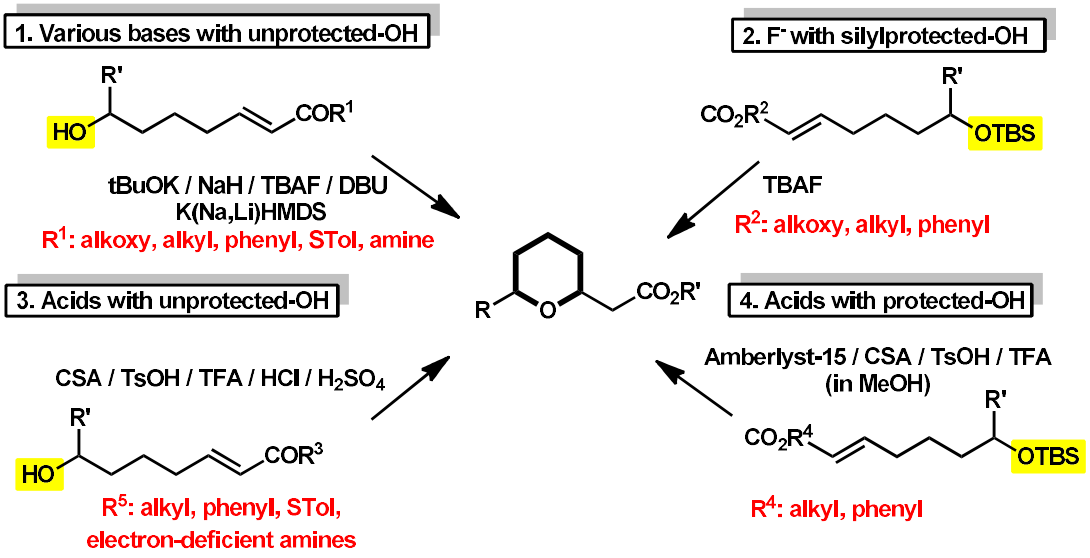


Figure 1

We intended to computationally investigate a simplified model system so that a general idea of selectivity-governing factor(s) can be extended to further similar substrates. Therefore, the substrate scope examined herein is limited to α,β -unsaturated molecules in which the geometry of double is (*E*) and which do not have fused polycyclic ring system.

The compilation of selectivities (Figure 2, 3, 4, 5) was aimed at demonstrating selectivity patterns. Since the stereochemical outcome of the *oxa*-Michael cyclisation is dependent on the temperature the selectivities are arranged according to the temperature at which the reaction was conducted. Furthermore, only the major isomer, as well as the applied base, is shown. The majority of the examined selectivities are originated from total synthesis related studies. The reference can be found in superscript after the name of the corresponding author.

Comments on categories and their brief analysis

[1.] Various bases with unprotected-OH:

The category involves the cases in which the cyclisation occurs by deprotonating the unprotected hydroxyl group. In general, the base triggering the cyclisation can be either strong inorganic base (e.g. tBuOK, NaH, F^-(relatively strong)) or mild organic base (DBU).

There are several examples for 2,6-*trans* selectivity at -78 ºC (Figure 2 blue frame), even if the molecule is highly substituted (Scope 1). All these reactions were effected by using strong bases (tBuOK, NaH) and quenched at -78 ºC so as to avoid any isomerisation reaction. On the basis of this observation, it seems reasonable to assume that the '2,6-*trans* phenomenon' is resistant to substitution pattern on the carbon chain.

Secondly, there is a temperature range (-35 ºC – RT(Figure 2 red frame)), within which the isomerisation reaction resulting in the formation of the more stable 2,6-*cis* isomer is likely to occur. This is also rather astonishing given the fact that the tendency to adopt 2,6-*cis* arrangement at a relatively elevated temperature is exclusive regardless of other substituents (Scope 2, 3). There a few exceptions (Figure 2 highlighted in bright blue). The cyclisation reactions were effected at -78 ºC and allowed to warm to RT furnishing 2,6-*trans* tetrahydropyran as a major isomer. The *trans* selectivity obtained by gradually increasing the temperature stands in contrast to the experimentally observed thermodynamic isomerisation in other cases.

Despite the reaction conditions indicated in the article, it appeared necessary to inspect the supporting information. In the cases of *Rapamycin* by *P. Arya*, *Herboxidiene* by *T. R. Webb*, *C2–C16 fragment of phorboxazole A* by *J.S. Yadav*, the exact reaction conditions differed from that in the article. Namely, the reaction was conducted at -78 ºC, but it was quenched by adding water then allowed to warm to RT. However, the resultant hydroxide is likely to induce isomerisation reaction at RT as similar cases have shown. Thus, these reaction conditions were modified according to the lowest temperature when strong base was present.

The reactions with TBAF and DBU afforded the 2,6-*cis* isomer at reflux in all cases.

It stands out from the review that hexamethyldisilazane-type (HMDS) bases did not give consistent results in terms of selectivity.

[2.] F^- with silylprotected-OH:

This category consists of the cyclisation reactions which are not directly effected by deprotonation with the basic fluoride anion. The fluoride anion cleaves the silicon-oxygen bond generating the nucleophilic alkoxide anion. As can be seen in Figure 3, there is no clear tendency as to the preferred stereochemistry in the reactions performed at RT.

[3.] Acids with unprotected-OH:

This group involves the reactions which were effected by using acid, and the precursors were unprotected alcohols. An exclusive 2,6-*cis* selectivity can be observed (

Figure 4).The summary also shows that superiority of *cis* selectivity is irrespective of the substituent pattern (Scope 3 – only exclusively 2,6-cases are depicted), the applied acid and the temperature.

[4.] Acids with protected-OH:

The fourth category showcases the reactions between the precursors with protected-OH and various acids (

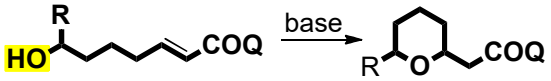
Figure 5). In the course of these reactions, free OH-group is formed *in situ* by deprotection. In principle, the acid protonates the oxygen, thereby enabling the cleavage of Si-O bond with the present methanol in a catalytic manner. For the HF-catalysed reactions, the cleavage is done by the fluoride anion to liberate the oxygen atom followed by its protonation. The second role of the acid is activation of the carbonyl group to initiate the cyclisation. Similar to the latter group of reactions, the *cis* selectivity is exclusive. No example for 2,6-*trans* selectivity was found.

Miscellaneous reactions:

This extra group (Figure 6) with two subgroups (a. Lewis acid catalysed oxa-Michael cyclisation, b. base-induced oxa-Michael cyclisation with ester protected-OH precursors) comprises the reactions which fall outside our category system.

Figure 2

Summary of base catalysed *oxa*-Michael cyclisation with unprotected-OH precursors (from (*E*)-α,β -unsaturated substrate, not fused polycyclic ring system)



cis-trans geometry with respect to 2,6-substituents (major isomer shown)

- 50°C
- 35°C
- 20°C
20°C
66°C
100°C
135°C
- 78°C
- 40°C
- 30°C
- 10°C
0°C
R.T.
60°C
95°C

Phorboxazole A — G. Pattenden(2003)[14] — NHMDS — *cis*

C1–C15 Segment of Spirastrellolide A — M. Shibasaki(2017)[15] — LHMDS *n*-BuLi — *cis* — (48h)

Phorboxazole A — C. J. Forsyth(2011)[16] — *t*BuOK — *trans*

(-)-Clavosolide A and B — D. H. Lee(2010)[17] — *t*BuOK — *trans*

Lituarine — J. Robertson(2004)[18] — LHMDS (- 78°C→) — *cis*

Spirastrellolide — A. B. Smith III (2007)[19] — *t*BuOK — *cis*

Spirastrellolide A — K. D. Brabander(2006)[20] — *t*BuOK — *cis*

SCH 351448 — K. D. Brabander(2002)[5] — *t*BuOK — *cis*

Lasonolide A — S. H. Kang(2004)[23] — NaH — *cis*

Spirastrellolide A — I. Paterson(2012)[24] — *t*BuOK — *cis* (1h)

Decytospolides — B. Das(2015)[25] — *t*BuOK — *cis* (1h)

Miyakolide — D. A. Evans(1999)[26] — *t*BuOK — *trans* (10 min)

Polycavernoside A — A. Fürstner(2013)[27] — *t*BuOK — *trans* (5 min)

Zampanolide — J. Uenishi(2009)[52] — LHMDS (TMEDA) — *cis*

Madeirolide A — I. Paterson(2013)[53] — *t*BuOK (- 78°C →) — *trans*

bis(THP)spiroacetal fragment of Lituarines — J. Robertson(2011)[54] — KHMDS (- 78°C→) — *trans*

Bistramide A analogues — O. Piva (2008)[55] — NaH (- 78°C→) — *trans*

C10-C17 segment of Pederin — M. R.Hoffmann(2002)[56] — *t*BuOK (- 78°C→) — NaH (- 78°C→) — *trans*

Decytospolides A, B — P. R. Krishna(2012)[57] — DBU — *cis*

RQN-18690A — Y. Matsumoto & Y. Hayashi(2016)[58] — TBAF — *cis*

Herboxidiene — F. Urpí(2011)[60] — DBU — *cis*

Neopeltolide — H. Fuwa(2010)[61] — DBU — *cis*

Polycavernoside A — A. Fürstner(2013)[27] — DBU — *cis*

Aspergillide A — H. Fuwa(2013)[59] — DBU — *cis*

Spongistatin — W. R. Roush(2000)[62] — DBU — *cis*

Spirastrellolide A — I. Paterson(2005)[21] — *t*BuOK(-78°C→) — *cis*

Rapamycin — P. Arya(2015)[22] — *t*BuOK — *cis*

Pyranicin and Pyragonicin — T. Rein(2006)[28] — *t*BuOK — *cis*

Core of Leucascandrolide A — J. Cossy(2008)[29] — *t*BuOK — *cis*

Leucascandrolide A — M. T. Crimmins(2003)[30] — *t*BuOK — *cis*

Leucascandrolide A — E. M. Carreira(2002)[31] — *t*BuOK — *cis*

Halichondrin — Y. Kishi(1997)[32] — *t*BuOK — *cis*

SCH 351448 — K. D. Brabander(2002)[5] — *t*BuOK — *cis*

Herboxidiene — T. R. Webb(2014)[33] — *t*BuOK — *cis*

Cis-2,6-Disubstituted THP Acetic Acid Derivatives — A.J.F. Edmunds(1997)[34] — NaH NaOMe/MeOH — *cis*

Montanacin — S. Takahashi(2008)[35] — *t*BuOK — *trans* (5 min) *cis* (3h)

Lasonolide A — S. H. Kang(2003)[23] — NaH (-78°C→) — *cis*

pyran synthesis via hydroformylation–Wittig — L. Zhou & B. Breit(2014)[36] — *t*BuOK — *cis*

Bryostatins — E. J. Thomas(2017)[37] — *t*BuOK — *cis*

synthesis of cyclic ethers — A. F. Parsons(2004)[38] — *t*BuOK — *cis*

Civet — J.-H. Xie & Q.-L. Zhou(2014)[39] — *t*BuOK — *cis*

THP ring of Clavosolide — R. W. Bates(2010)[40] — *t*BuOK — *cis*

Herboxidiene A — N.D. Smith(1996)[41] — *t*BuOK — *cis*

Isocladosorpin — B. V. S. Reddy(2013)[42] — NaH — *cis*

Lasonolide A — B. M. Trost(2016)[43] — NaH(0°C→) — *cis*

Goniothalesdiol A — N. W. Fadnavis(2009)[44] — NaH (- 78°C →) — *cis*

Clavosolide A — D. H. Lee(2006)[45] — NaH — *cis*

C2–C16 fragment of phorboxazole A — J.S. Yadav(2005)[46] — NaH — *cis*

Herboxidiene/GEX 1A — F. Urpí(2017)[47] — *t*BuOK — *cis*

Norhalichondrins — G. Sabitha(2012)[49] — TBAF — *cis*

stereodivergent formation of THPs — P. A. Clarke(2007)[50] — TBAF (AcOH) — *trans*

core THP of Pederin, Psymberin, Onnamides — D. C. Harrowven(2013)[51] — DBU — *cis* — DBU (DMF) — *trans*

Macrolactin — P. R. Krishna(2014)[1] — *t*BuOK — *trans*

Bistramide A — P. G. Goekjian(2012)[2] — *t*BuOK — *trans*

Synthesis of 2,6-substituted tetrahydropyrans — H. Fuwa(2011)[3] — *t*BuOK — *trans*

Aspergillides A and B — H. Fuwa(2010)[4] — *t*BuOK — *trans*

SCH 351448 — K. D. Brabander(2002)[5] — *t*BuOK — *trans*

THP of Bistramide D analogue — R. W. Bates(2008)[6] — NaH — *trans*

2,6-disubstituted tetrahydropyrans — M. G. Banwell(1996)[7] — *t*BuOK — *trans*

THP of Bistramide A — O. Piva(2010)[8] — *t*BuOK — *trans*

Cryptopyranmoscatone A1 — G. Sabitha(2011)[9] — *t*BuOK — *trans*

Stereodivergent Synthesis of Highly Substituted Tetrahydropyrans — C. Schneider (2000)[10] — *t*BuOK — *trans*

THP of Bistramide D — R. W. Bates(2014)[11] — *t*BuOK — *trans*

Cryptopyranmoscatone A3, Cryptopyranmoscatone B4 — G. Sabitha(2018)[12] — *t*BuOK — *trans*

Polyketide Scaffolds via Vinylogous Mukaiyama Aldol Reactions — M. Kalesse(2001)[13] — *t*BuOK — *trans* — no detail for condition

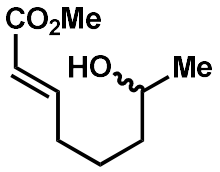
C1–C13 Fragment of Bistramide A — P. G. Goekjian(2012)[2] — *t*BuOK (toluene–*t*BuOH) — *trans* (5 mins)

Acyltetronic acid ionophore tetronasin — S.V. Ley(1998)[48] — KHMDS — *cis*

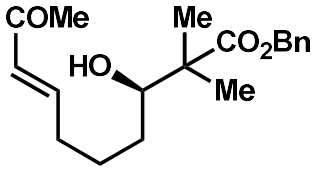
Scope 1

Substrates that follow the *trans* selectivity rule at -78°C

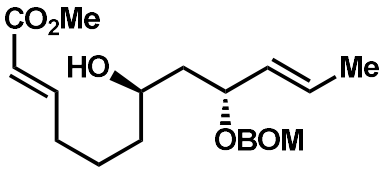
exclusively 2,6-2,6-disubstituted



2,6-disubstituted tetrahydropyrans
M. G. Banwell(1996)
*t*BuOK
trans

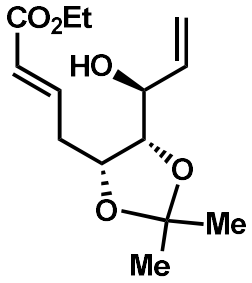


SCH 351448
K. D. Brabander(2002)
*t*BuOK
trans

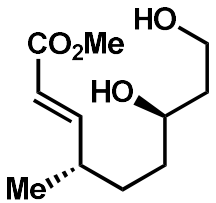


THP of Bistramide D analogue
R. W. Bates(2008)
NaH
trans

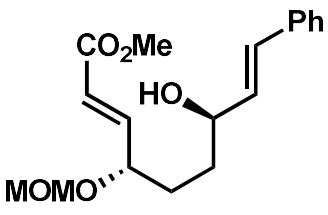
polysubstituted



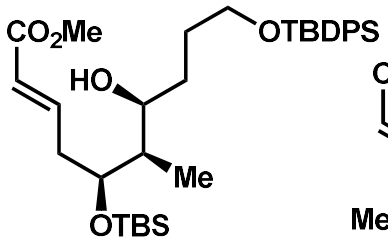
Macrolactin
P. R. Krishna(2014)
*t*BuOK
trans



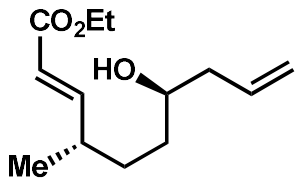
Bistramide A
P. G. Goekjian(2012)
*t*BuOK
trans



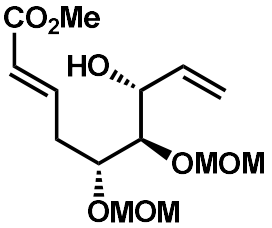
Aspergillides A and B
H. Fuwa(2010)
*t*BuOK
trans



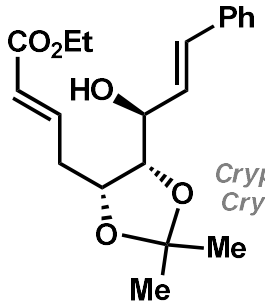
Synthesis of 2,6-substituted THPs
H. Fuwa(2011)
*t*BuOK
trans



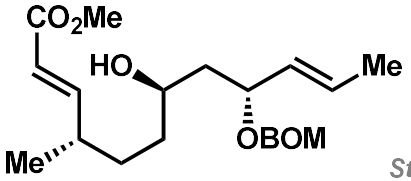
THP of Bistramide D
O. Piva(2010)
*t*BuOK
trans



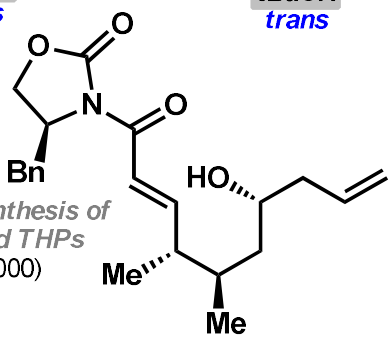
Cryptopyranmoscatone A1
G. Sabitha(2011)
*t*BuOK
trans



Cryptopyranmoscatone A3,
Cryptopyranmoscatone B4
G. Sabitha(2018)
*t*BuOK
trans



THP of Bistramide D
R. W. Bates(2014)
*t*BuOK
trans

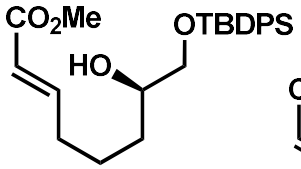


Stereodivergent Synthesis of
Highly Substituted THPs
C. Schneider (2000)
*t*BuOK
trans

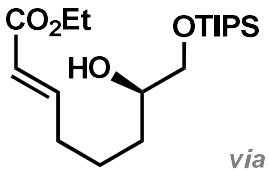
Scope 2

Substrates that follow the *cis* selectivity rule above 0°C

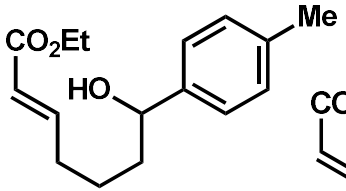
exclusively 2,6-disubstituted



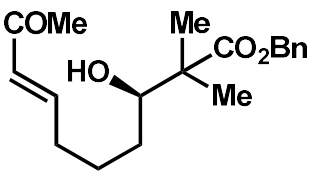
Cis-2,6-Disubstituted THP Acetic Acid Derivatives
A.J.F. Edmunds(1997)
NaH NaOMe/MeOH
cis



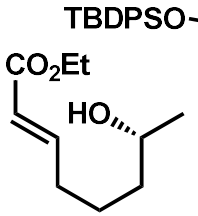
Montanacin
S. Takahashi(2008)
*t*BuOK
cis (3h)



pyran synthesis via hydroformylation–Wittig
L. Zhou & B. Breit(2014)
*t*BuOK
cis
(more examples in paper)

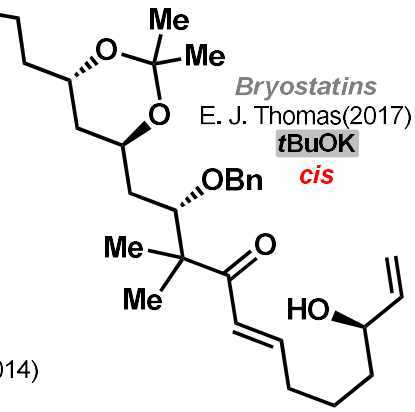


SCH 351448
K. D. Brabander(2002)
*t*BuOK
cis



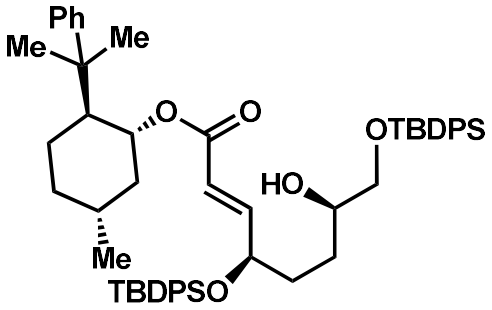
Isocladosorpin
B. V. S. Reddy(2013)
NaH
cis

Civet
J.-H. Xie & Q.-L. Zhou(2014)
*t*BuOK
cis

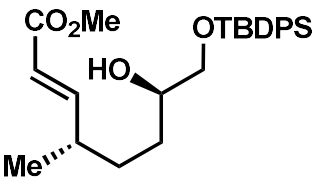


Bryostatins
E. J. Thomas(2017)
*t*BuOK
cis

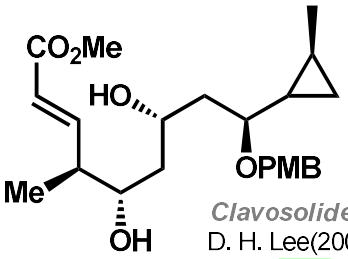
polysubstituted



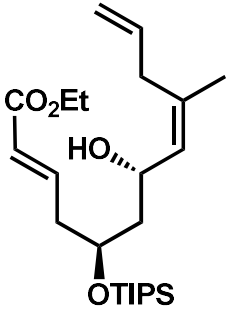
Pyranicin and Pyragonicin
T. Rein(2006)
*t*BuOK
cis



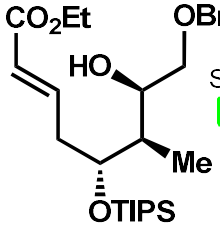
synthesis of cyclic ethers
A. F. Parsons(2004)
*t*BuOK
cis



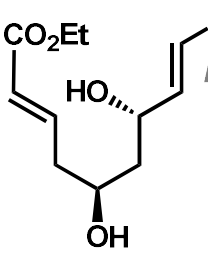
Clavosolide A
D. H. Lee(2006)
NaH
cis



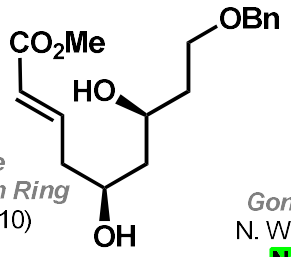
Lasonolide A
B. M. Trost(2016)
NaH(0°C→R.T.)
cis



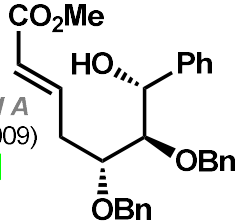
Lasonolide A
S. H. Kang(2003)
NaH(- 78°C→)
cis



Leucascandrolide A
E. M. Carreira(2002)
*t*BuOK
cis



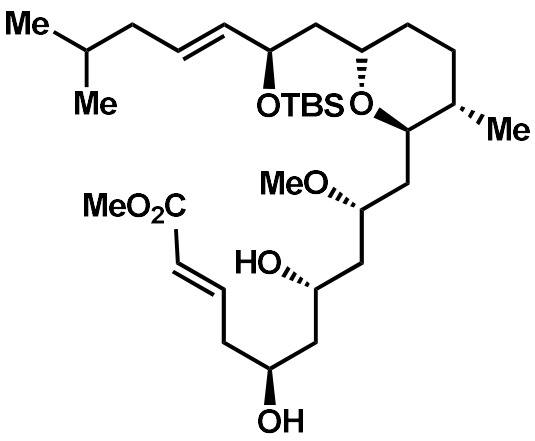
Clavosolide Tetrahydropyran Ring
R. W. Bates(2010)
*t*BuOK
cis



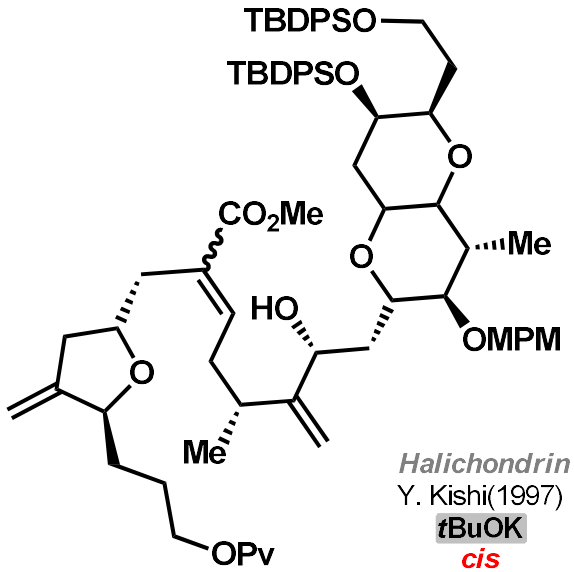
Goniothalesdiol A
N. W. Fadnavis(2009)
NaH(- 78°C→)
cis

Scope 3

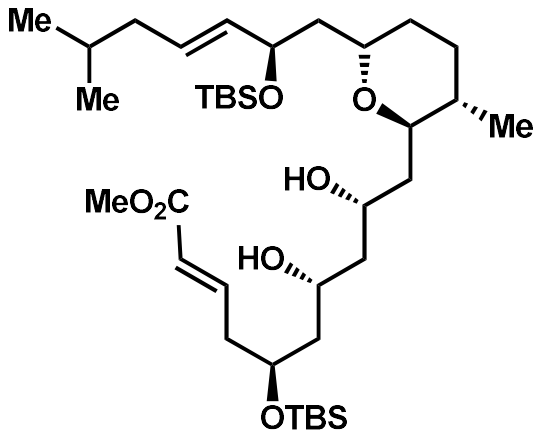
polysubstituted



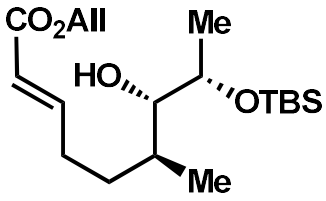
Core of Leucascandrolide A
J. Cossy(2008)
*t*BuOK
cis



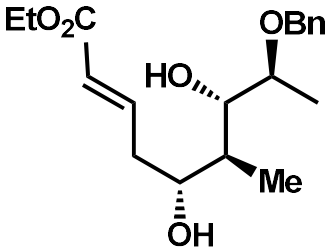
Halichondrin
Y. Kishi(1997)
*t*BuOK
cis



Leucascandrolide A
M. T. Crimmins(2003)
*t*BuOK
cis

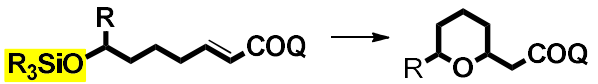


Herboxidiene A
N.D. Smith(1996)
*t*BuOK
cis

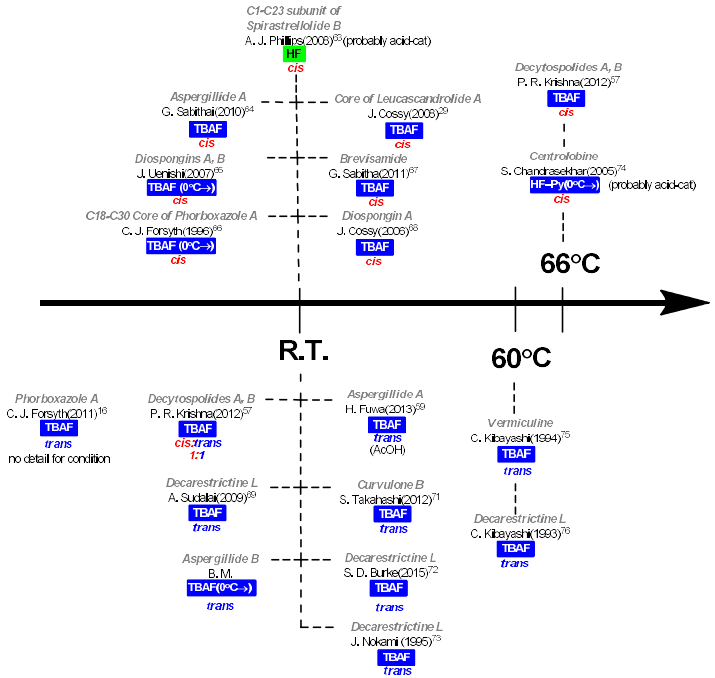


Herboxidiene/GEX 1A
F. Urpí(2017)
*t*BuOK
cis

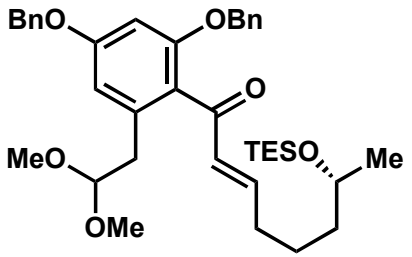
Summary of *oxa*-Michael cyclisation with sylilprotected-OH precursors with F⁻
(from (*E*)-α,β–unsaturated substrate, not fused polycyclic ring system)



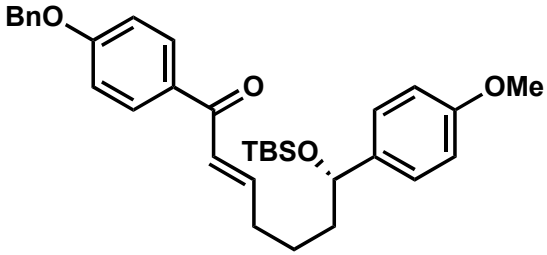
cis-*trans* *geometry with respect to 2,6-substituents (major isomer shown)*



exclusively 2,6-disubstituted



Curvulone B
S. Takahashi(2012)
TBAF
trans



Centrolobine
S. Chandrasekhar(2005)
HF–Py
cis
(probably acid-cat)

Figure 3

Summary of acid-catalysed *oxa*-Michael cyclisation with unprotected-OH precursors (from (*E*)-α,β -unsaturated substrate, not fused polycyclic ring system)

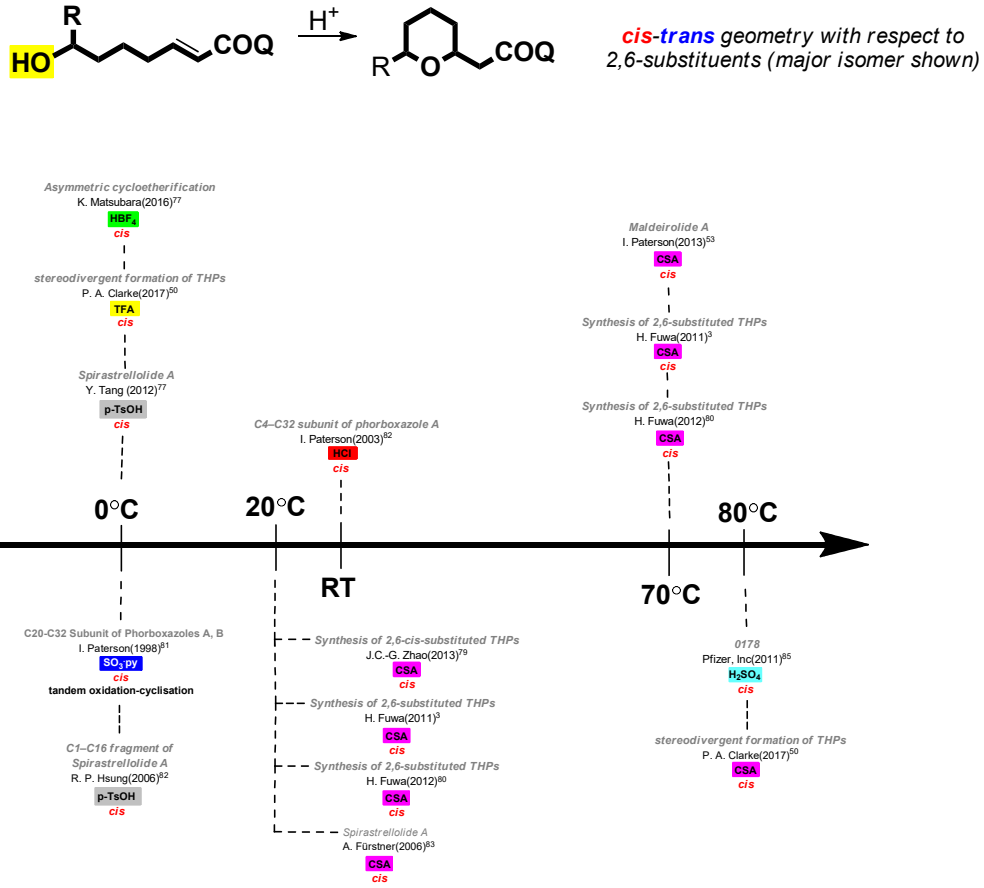
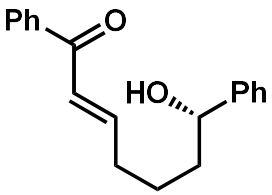


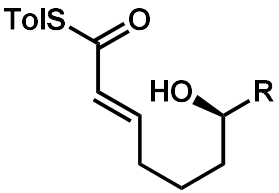
Figure 4

Scope 4

exclusively 2,6-disubstituted

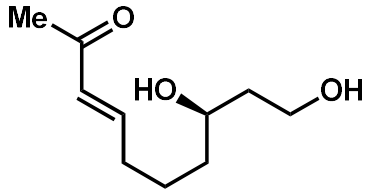


Asymmetric cycloetherification
K. Matsubara(2016)
HBF_4
cis



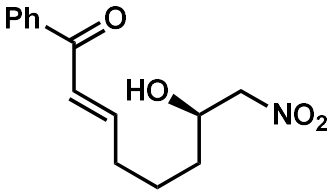
R: iPr
Ph
C_7H_{15}

stereodivergent formation of THPs
P. A. Clarke(2017)
TFA
cis

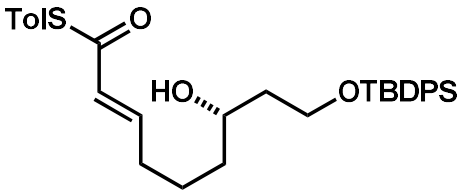


Spirastrellolide A
Y. Tang (2012)
p-TsOH
cis

C1–C16 fragment of Spirastrellolide A
R. P. Hsung(2006)
p-TsOH
cis

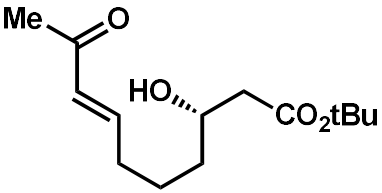


Synthesis of 2,6-cis-substituted THPs
J.C.-G. Zhao(2013)
CSA
cis



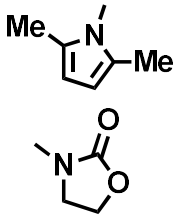
Synthesis of 2,6-substituted THPs
H. Fuwa(2011)
CSA
cis

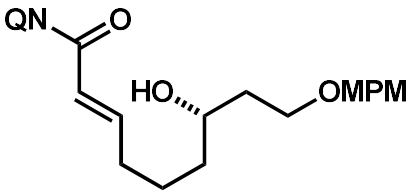
(more examples in paper)



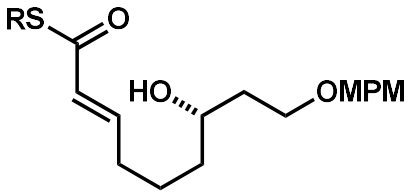
Spirastrellolide A
A. Fürstner(2006)
CSA
cis

Q:





R: Et
Ph
p-MeC6H4
p-MeOC6H4
p-NO2C6H4
1-naphthyl

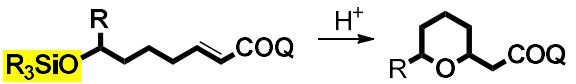


Synthesis of 2,6-substituted THPs
H. Fuwa(2012)
CSA
cis

(more examples in paper)

Figure 5

Summary of acid-catalysed *oxa*-Michael cyclisation with protected-OH precursors (from (*E*)-α,β -unsaturated substrate, not fused polycyclic ring system)



cis-trans geometry with respect to 2,6-substituents (major isomer shown)

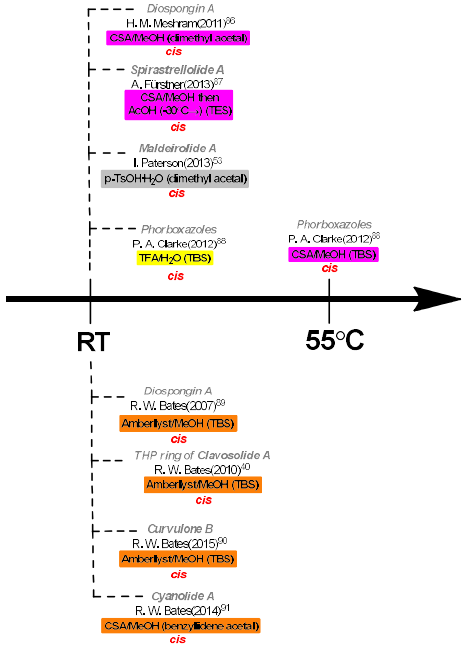


Figure 6

Miscellaneous

Lewis acid catalysed *oxa*-Michael cyclisation

Spongistatin 2
S.V. Ley(2013)[92]
$Zn(OTf)_2$
cis

cis-2,6-disubstituted tetrahydropyrans
P. A. Evans(2005)[93]
BiX_3
cis

Goniothalesdiol A
G. Sabitha(2011)[94]
TfOH
cis

base-induced *oxa*-Michael cyclisation with esterprotected-OH precursors

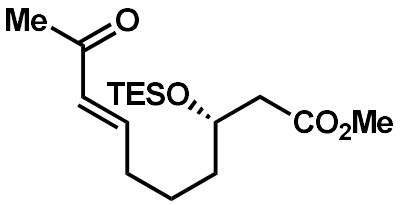
Herboxidiene
M. G. Banwell(1996)[95]
K_2CO_3/MeOH (OAc)
cis

C20-C32 Subunit of Phorboxazoles A, B
I. Paterson(1998)[81]
K_2CO_3/MeOH (OAc)
cis

Cis-2,6-Disubstituted THP Acetic Acid Derivatives
A.J.F. Edmunds(1997)[24]
NaOMe/MeOH (OCHO)
cis

Decarestrictine L
C. Kibayashi(1993)[76]
K_2CO_3
trans

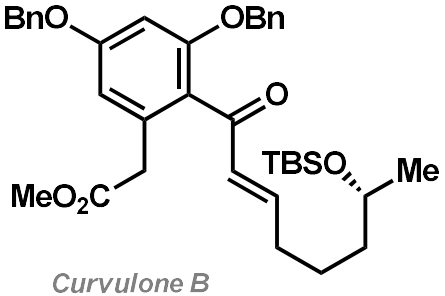
exclusively 2,6-disubstituted



Spirastrellolide A
A. Fürstner(2013)

CSA/MeOH then AcOH (-30°C→) (TES)

cis



Curvulone B
R. W.Bates (2015)

Amberlyst/MeOH (TBS)

cis

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