

Synthesis Alerts is a monthly feature to help readers of *Synthesis* keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also covered if they are used in novel and useful reactions. In each abstract, a specific example of a transformation is given in a concise format designed to aid visual retrieval of information.

Synthesis Alerts is a personal selection by:

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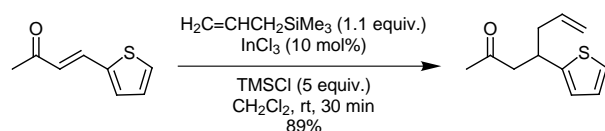
The journals regularly covered by the abstractors are:

Angewandte Chemie
Chemical Communications
Chemistry-A European Journal
Collection of Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Journal of Organic Chemistry
Journal of the American Chemical Society
Organic Letters
Organometallics
Perkin Transactions 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry
Tetrahedron Letters

Catalytic Sakurai reaction.

Lee, P. H.; Lee, K.; Sung, S.; Chang, S. *J. Org. Chem.* **2001**, 66, 8646.

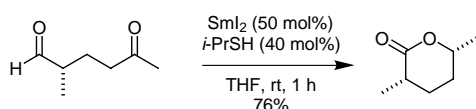
1,4-Addition



15 examples (yields 62-89%).

One pot sequential acetalisation, Tishchenko reaction and lactonisation, catalysed by Sm(II) and a mercaptan.
Hsu, J. -L.; Fang, J. -M. *J. Org. Chem.* **2001**, 66, 8573.

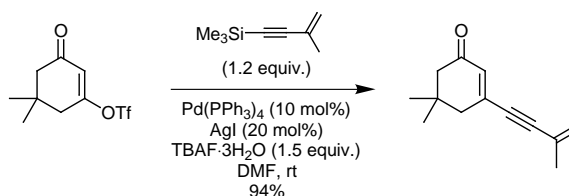
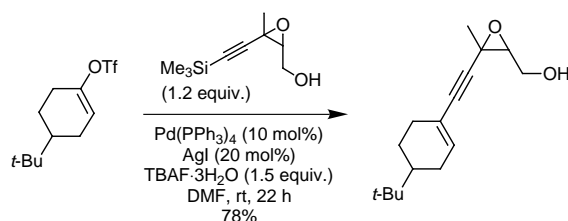
δ -Lactonisation



16 examples (yields 70-100%). Synthesis of 5-oxoalkanal starting materials (14 examples), the use of disulfides (6 examples, yields 67-100%), chiral alcohols (6 examples, yields 58-77%, %ee 21-84%) and chiral mercaptans (33 examples, yields 37-99%, %ee 10-74%) are also reported.

Pd/Ag-catalysed coupling of vinyl triflates with 1-trimethylsilyl alkynes.
Bertus, P.; Halbes, U.; Pale, P. *Eur. J. Org. Chem.* **2001**, 4391.

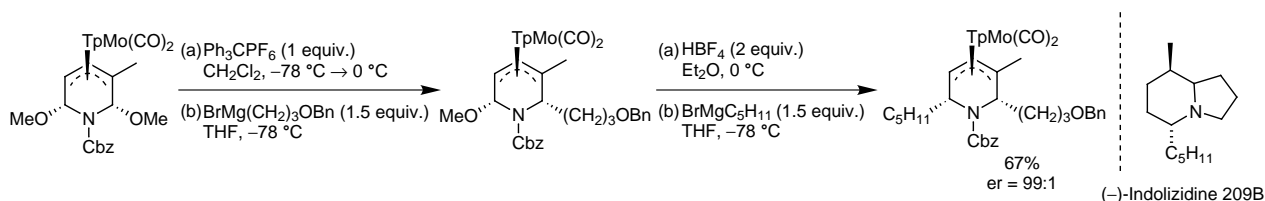
sp^2 - sp Coupling



6 examples (yields 61-99%). Coupling of the corresponding free acetylenes in the presence of DIPEA, Pd(PPh₃)₄ and AgI (4 examples, yields 55-90%) is also reported.

Use of (η^3 -dihydropyridinyl)molybdenum complexes in the synthesis of (–)-Indolizidine 209B.
Shu, C.; Alcudia, A.; Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, 123, 12477.

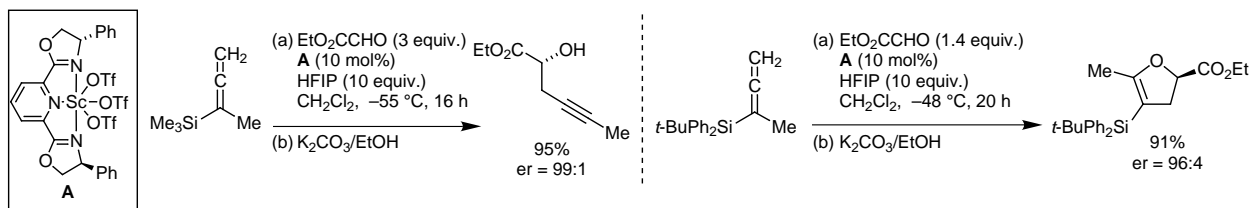
Asymmetric Allylation



5 Examples using the racemic substrate (yields 61-85%).

Enantioselective syntheses of homopropargylic alcohols and dihydrofurans.
Evans, D. A.; Sweeney, Z. K.; Rovis, T.; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, 123, 12095.

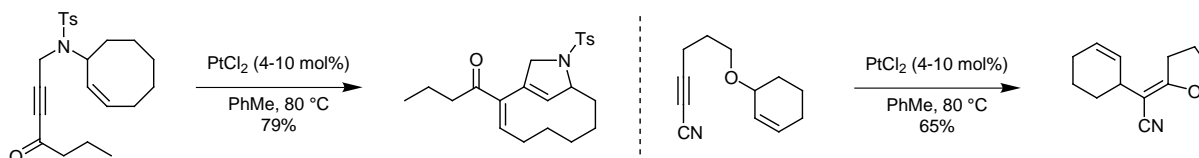
1,2-Addition/Annulation



7 Examples (yields 63-96%, %ee 84-98%) of addition reactions, 9 examples (yields 32-91%, %ee 85-94%) of annulation reactions.

Pt-catalyzed cycloisomerization reactions of enynes.
Fürstner, A.; Stelzer, F.; Szilatt, H. *J. Am. Chem. Soc.* **2001**, 123, 11863.

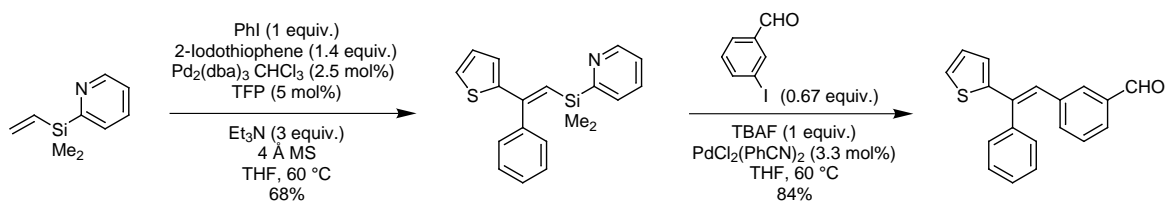
Metathesis



11 Examples (yields 54-96%) of enyne metathesis reactions, 12 examples (yields 39-87%) of formation of cyclopropane derivatives and 11 examples (yields 56-86%) of O → C allyl shift reactions.

Synthesis of olefins through sequential Pd-catalyzed cross-coupling reactions.

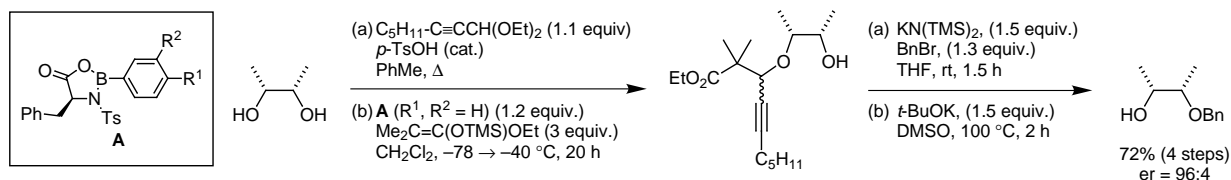
Itami, K.; Nokami, T.; Ishimura, Y.; Mitsudo, K.; Kamei, T.; Yoshida, J.-i. *J. Am. Chem. Soc.* **2001**, 123, 11577.

sp²-sp² coupling

5 Examples (yields 75-100%), 13 Examples (28-100%) involving one-pot double Heck coupling reactions and 9 examples (57-100%) of a sequential Heck/Hiyama coupling reactions.

Asymmetric desymmetrisation of *meso*-1,2-diols.
Harada, T.; Yamanaka, H.; Oku, A. *Synlett* **2001**, 61.

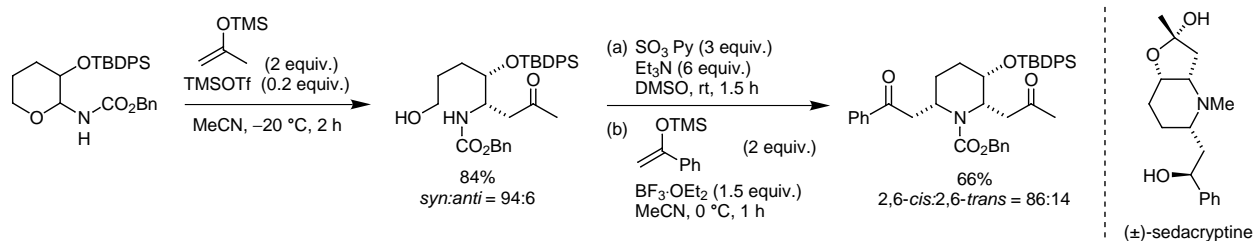
Desymmetrisation



4 examples (yields 46-72%, %ee 89-92%).

Lewis acid-catalyzed ring-opening reaction of a cyclic *N,O*-acetal: application to piperidine alkaloid synthesis. Sugiura, M.; Hagio, H.; Hirabayashi, R.; Kobayashi, S. *J. Am. Chem. Soc.* **2001**, 123, 12510.

Cyclisation

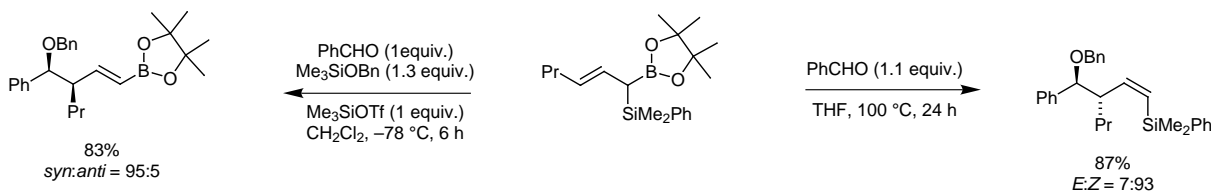


Synthesis of (+)-isofebugine is also reported.

1-Silyl-1-boryl-2-alkenes as reagents for stereodivergent allylation.

Shimizu, M.; Kitigawa, H.; Kurahashi, T.; Hiyama, T. *Angew. Chem. Int. Ed.* **2001**, 40, 4283.

Stereodivergent Allylation

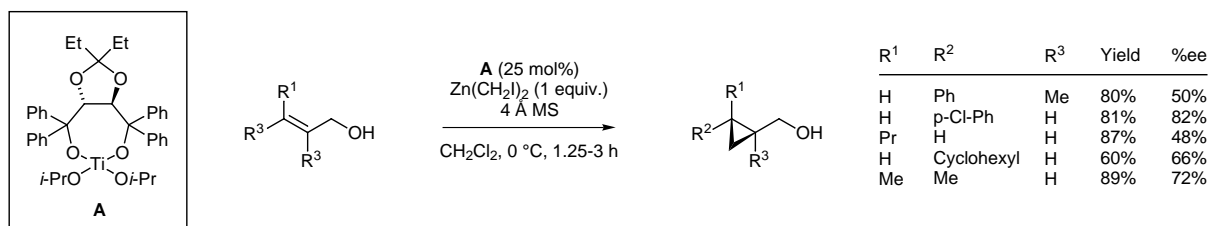


7 examples of formation of 1-silyl-boryl-2-alkenes (yields 72-86%). 12 examples of giving 4-oxy-(*E*)-1-boronates from acetals and aldehydes (yields 62-94%) & 4 examples giving 4-oxy-(*Z*)-1-alkenylsilanes (yields 46-89%).

Catalytic asymmetric cyclopropanation of allylic alcohols with Titanium-TADDOLate.

Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, 123, 12168.

Asymmetric Cyclopropanation

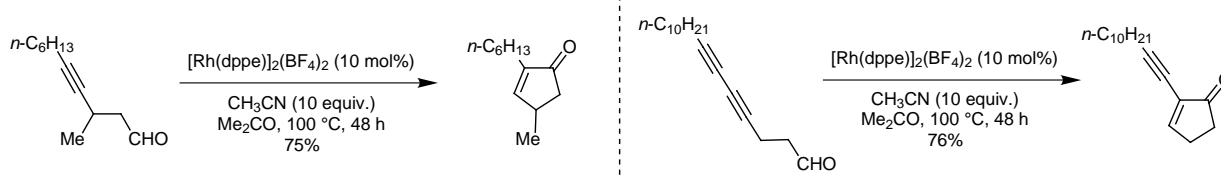


19 examples (yields 56-90%, %ee 48-92%). Development of the catalyst structure and optimization of the reaction conditions is also reported.

Synthesis of cyclopentenones via rhodium-catalyzed intramolecular *trans* hydroacylation of an alkyne.

Tanaka, K.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, 123, 11492.

Annulation

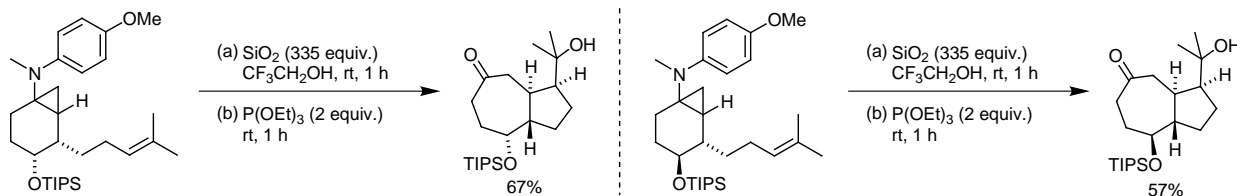


7 Examples (yields 67-88%).

Radical cation-mediated annulation by aerobic oxidation of cyclopropylamines.

Lee, H. B.; Sung, M. J.; Blackstock, S. C.; Cha, J. K. *J. Am. Chem. Soc.* **2001**, 123, 11322.

Annulation

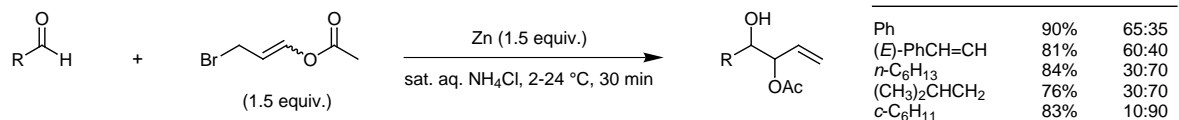


6 Examples (yields 57-68%).

Zinc-promoted acetoxyallation of aldehydes.

Lombardo, M.; Girotti, R.; Morganti, S.; Trombini, C. *Chem. Commun.* **2001**, 2310.

1,2-Addition

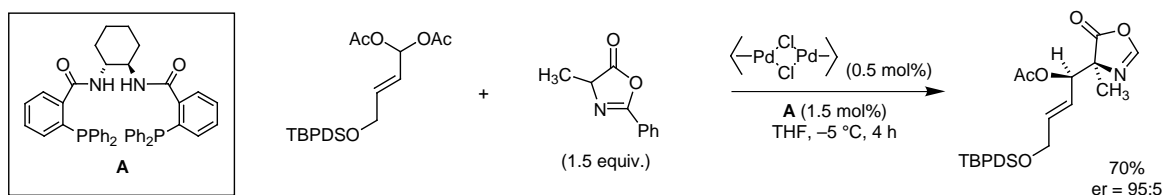


10 examples (yields 42-90%, 1:9 ≤ syn:anti ≤ 8:2).

gem-Diacetates as carbonyl surrogates.

Trost, B. M.; Lee, C. *J. Am. Chem. Soc.* **2001**, 123, 12191.

Asymmetric Addition

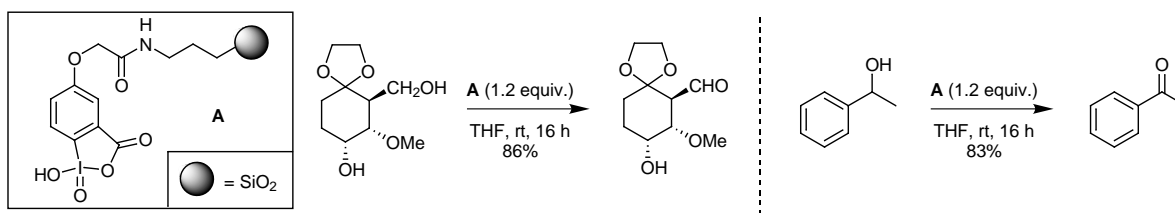


2 examples as the key steps in the total syntheses of the sphingofungins E and F.

Synthesis and oxidative properties of polymer-supported IBX (1-hydroxy-1,2-benziodoxol-3(1H)-one-1-oxide).

Mulbauer, M.; Giannis, A. *Angew. Chem. Int. Ed.* **2001**, 23, 4393.

Oxidation

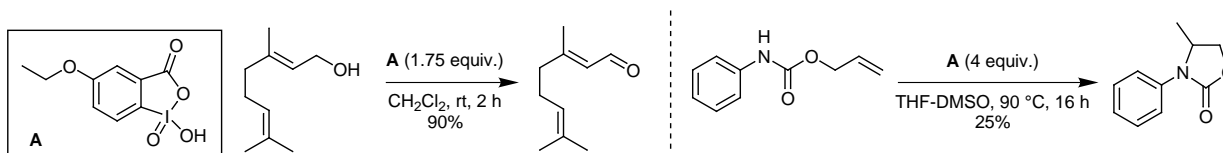


11 examples of oxidations to aldehydes and ketones (yields 80-97%). A can be regenerated by oxidation with oxone.

Polymer supported periodinane reagent for the conversion of alcohols, carbonyl compounds and unsaturated carbamates.

Sorg, G.; Mengel, A.; Jung, G.; Rademann, J. *Angew. Chem. Int. Ed.* **2001**, 23, 4395.

Oxidation

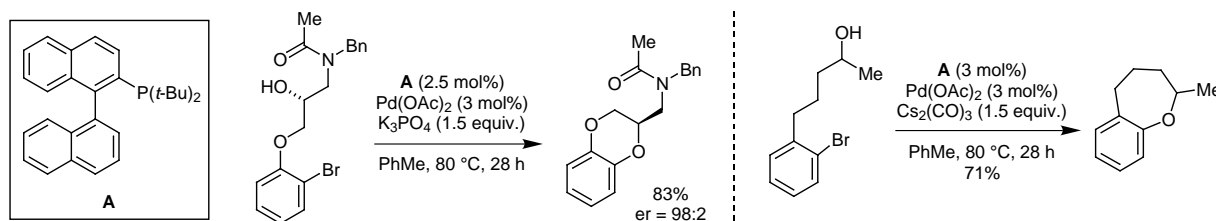


18 examples of oxidation of alcohols to aldehydes or ketones (yields 26-95%). 1 example of the α,β-desaturation of a carbonyl compound and 1 example of a radical cyclisation of an unsaturated carbamate.

Palladium-catalyzed intramolecular C-O bond formation.

Kuwabe, S.; Torracca, K. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, 123, 12202.

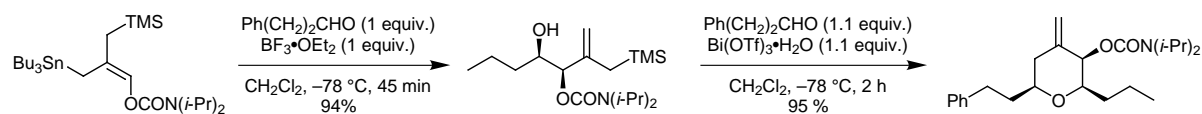
C-O Bond Formation



13 examples of cyclic aryl ethers from aryl chlorides or bromides (yields 65-85%), 17 examples of chiral and non-chiral benzoxanones and benzoxazines using various ligands (yields 67-95%, %ee 95-99%). The methodology was also applied to the synthesis of the antidepressant MKC-242.

Allylstannylation/Bi(III)-promoted Sakurai cyclisation.
Leroy, B.; Markó, I. E. *Tetrahedron Lett.* **2001**, 42, 8685.

Annulation

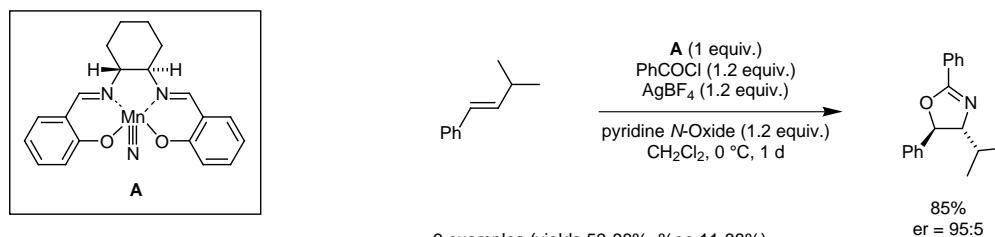


5 examples (yields 84-98%).

Asymmetric synthesis of oxazolines from olefins.

Minakata, S.; Nishimura, M.; Takahashi, T.; Oderaotoshi, Y.; Komatsu, M. *Tetrahedron Lett.* **2001**, 42, 9019.

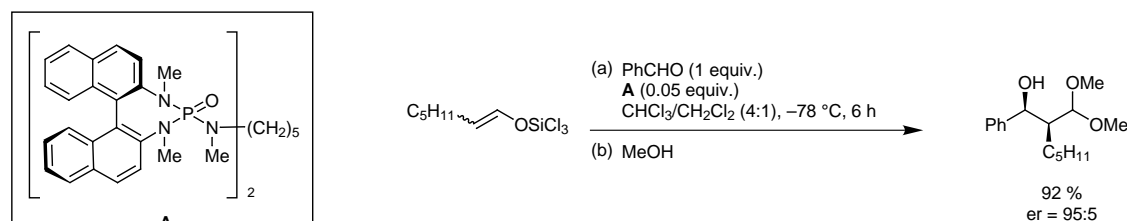
Asymmetric Heteroannulation



9 examples (yields 53-88%, %ee 11-88%).

Catalytic diastereo- and enantioselective crossed Aldol reactions of aldehydes.
Denmark, S. E.; Ghosh, S. K. *Angew. Chem. Int. Ed.* **2001**, 40, 4759.

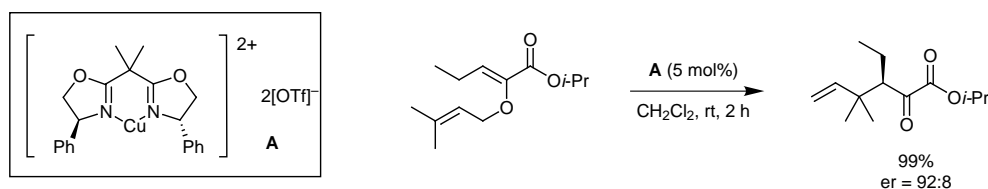
Asymmetric Aldol Reaction



20 examples (yields 42-99%, %ee 5-90%)

Catalytic, enantioselective Claisen rearrangement of an allyl vinyl ether.
Abraham, L.; Czerwonka, R.; Hiersmann, M.; *Angew. Chem. Int. Ed.* **2001**, 40, 4700.

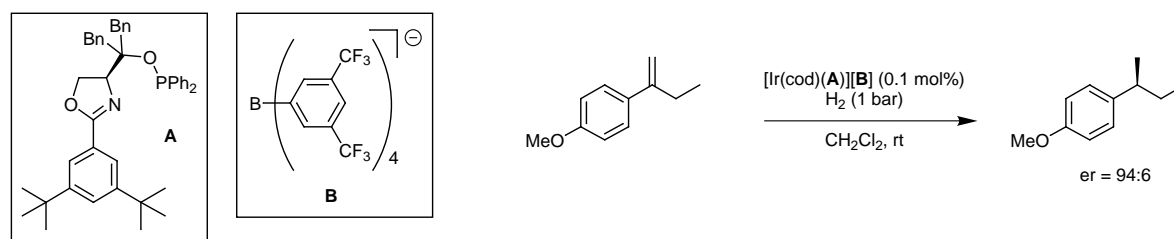
Asymmetric [3,3]-Sigmatropic Rearrangement



17 examples (yields 96-100%, %ee 72-88%).

Enantioselective hydrogenation of alkenes using iridium-phosphinooxazoline complexes.
Blankenstein, J.; Pfaltz, A. *Angew. Chem. Int. Ed.* **2001**, 40, 4445.

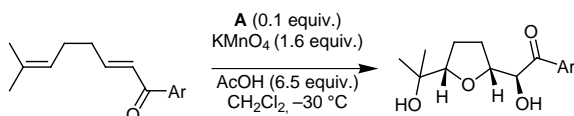
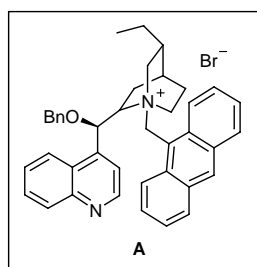
Asymmetric Hydrogenation



6 examples (%ee 62-98%). The use of 4 other ligand analogues is also reported.

Asymmetric permanganate-promoted oxidative cyclization of 1,5-dienes using chiral phase-transfer catalysis. Brown, R. C. D.; Kiely, J. F. *Angew. Chem. Int. Ed.* **2001**, 40, 4496.

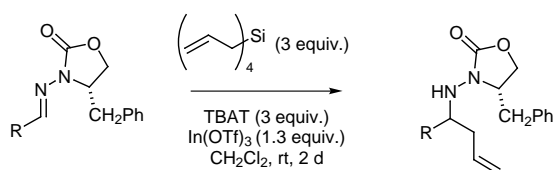
Asymmetric Oxidation



Ar	Yield	%ee
Ph	47%	58%
<i>p</i> -C ₆ H ₄ F	50%	72%
<i>p</i> -C ₆ H ₄ Br	26%	75%

Stereoselective addition of allylsilanes to chiral *N*-acylhydrazones activation by fluoride and In(OTf)₃. Friestad, G. K.; Ding, H. *Angew. Chem. Int. Ed.* **2001**, 40, 4491.

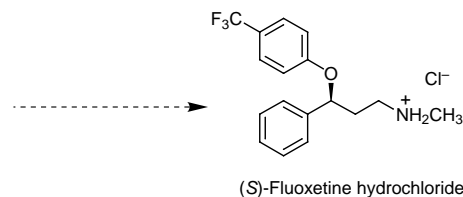
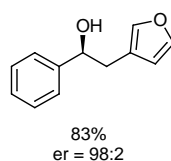
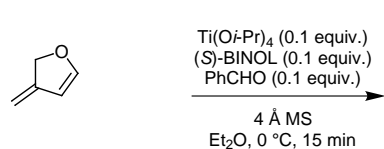
Asymmetric 1,2-Addition



R	Yield	dr
Ph	78%	99:1
<i>p</i> -tolyl	94%	98:2
<i>m</i> -nitrophenyl	71%	99:1
2-naphthyl	82%	98:2
2-furyl	58%	96:4
(<i>E</i>)-CH=CHPh	60%	95:5
CH ₂ CH ₃	51%	82:18

Ti(O-*i*-Pr)₄ and BINOL-catalysed enantioselective synthesis of (*S*)- and (*R*)-fluoxetine hydrochloride. Miles, W. H.; Fialcowitz, E. J.; Halstead, E. S. *Tetrahedron* **2001**, 57, 9925.

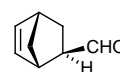
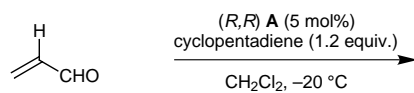
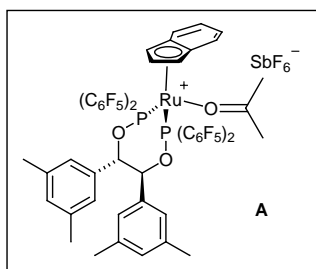
Asymmetric Ene Reaction



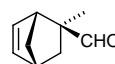
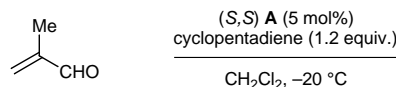
Total synthesis of (*S*)-fluoxetine (yields 56%, %ee 97%) has been reported.

Lewis acid catalyst control of diene and dienophile facial selectivity in Diels–Alder reaction. Kündig, E. P.; Saudan, C. M.; Alezra, V.; Viton, F.; Bernardinelli, G. *Angew. Chem. Int. Ed.* **2001**, 40, 4481.

Asymmetric [4+2] Cycloaddition



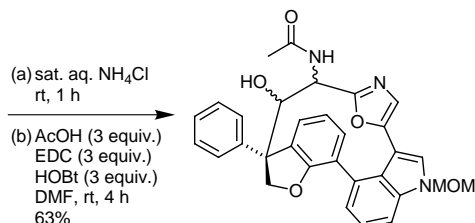
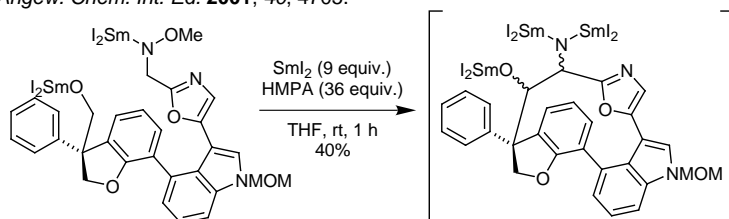
84%
er = 93:7
exo:endo = 71:29



80%
er = 98:2
exo:endo = 99.8:0.2

Hetero-pinacol macrocyclization cascade reaction: application to Diazonamide A. Nicolaou, K. C.; Huang, X.; Giuseppone, N.; Bheema Rao, P.; Bella, M.; Reddy, M. V.; Snyder, S. A. *Angew. Chem. Int. Ed.* **2001**, 40, 4705.

Hetero-Pinacol

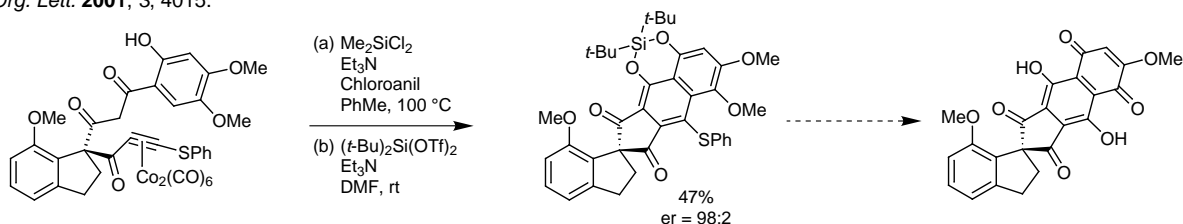


Key cascade step proceeded in 25% overall yield.

Intramolecular [4+2] cycloaddition.

Akai, S.; Tsujino, T.; Fukuda, N.; Iio, K.; Takeda, Y.; Kawaguchi, K.; Naka, T.; Higuchi, K.; Kita, Y. *Org. Lett.* **2001**, 3, 4015.

[4+2]-Cycloaddition

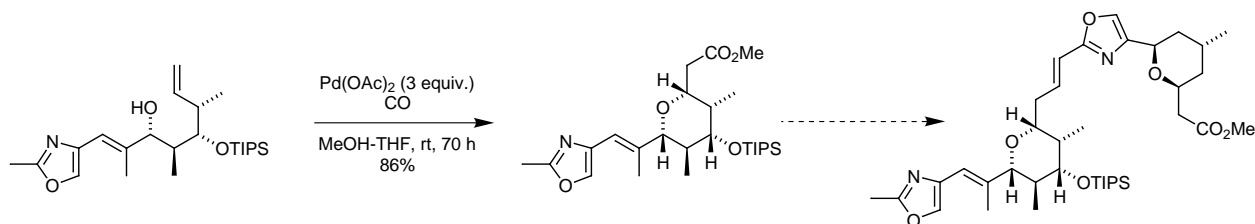


2 examples (yields 45-86%) towards the synthesis of both enantiomers the ABCDE-ring analogue of Fredericamycin A.

Intramolecular palladium(II)-mediated alkoxy carbonylation.

White, J. D.; Kranemann, C. L.; Kuntiyong, P. *Org. Lett.* **2001**, 3, 4003.

Carbonylation

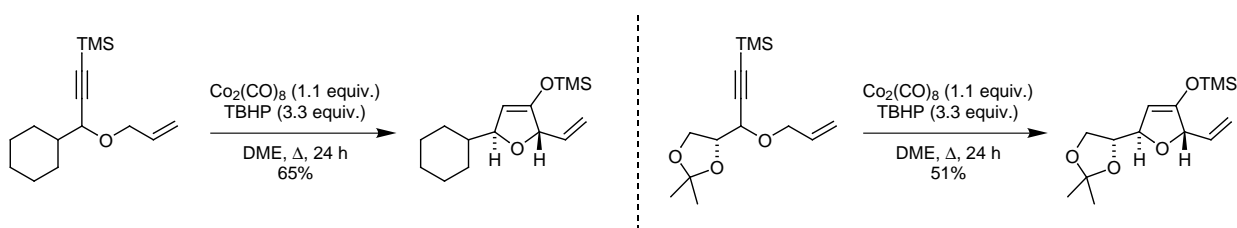


2 examples (yields 45-86%) are reported towards the synthesis of the C9-C32 segment of Phorboxazole A.

Cobalt-mediated cycloisomerisation of allyl propargyl ethers.

Marshall, J. A.; Chobanian, H. R.; Yanik, M. M. *Org. Lett.* **2001**, 3, 4161.

Cycloisomerisation

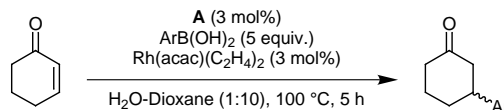
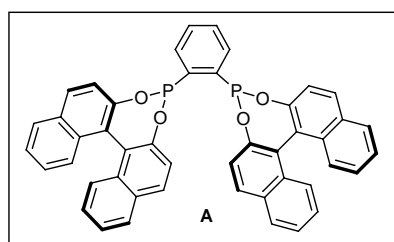


8 examples (yields 40-65%).

Asymmetric Rh-catalysed conjugate addition of arylboronic acids.

Reetz, M. T.; Moulin, D.; Gosberg, A. *Org. Lett.* **2001**, 3, 4083.

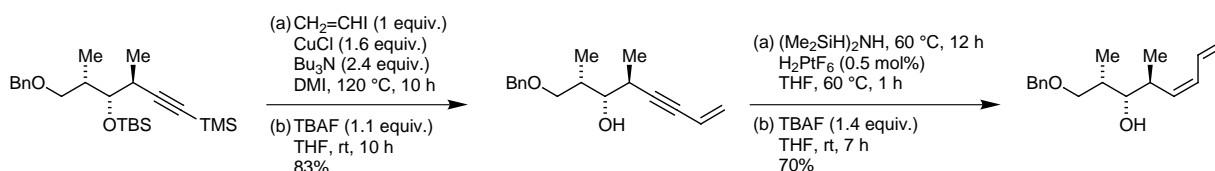
Asymmetric Conjugate Addition



Ar	%conv.	%ee
Ph	100%	99%
2-MePh	96%	93%
4-MePh	100%	94%
4-MeOPh	87%	95%
4-MeCOPh	88%	94%
4-ClPh	75%	91%
4-CF ₃ Ph	93%	89%

11 examples (%conv. 58-100%, %ee 85-99%).

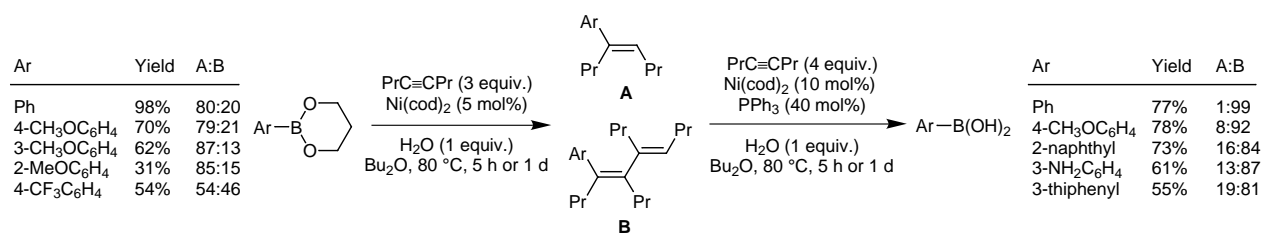
An efficient route to 1,3-dienes.

Marshall, J. A.; Chobanian, H. R.; Yanik, M. M. *Org. Lett.* **2001**, 3, 4107.sp-sp² Coupling

2 examples (yields 50-58%, over 4 steps).

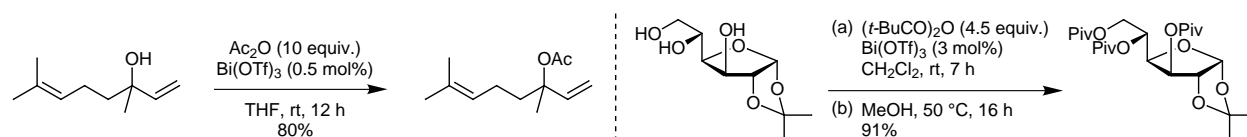
Nickel-catalyzed hydroarylation of alkynes using arylboron compounds.
Shirakawa, E.; Takahashi, G.; Tsuchimoto, T.; Kawakami, Y. *Chem. Commun.* **2001**, 2688.

Hydroarylation



Acylation of alcohols with acid anhydride catalyzed by Bi(OTf)₃.
Orita, A.; Tanahashi, C.; Kakuda, A.; Otera, J. *J. Org. Chem.* **2001**, 66, 8926.

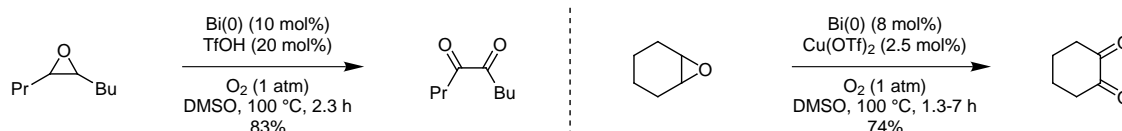
Acylation



28 examples of acetylation (72-99%), 8 examples of benzooylation (yields 0-99%) and 11 examples of pivaloylation (yields 0-98%) are reported. Acid sensitive functionalities (e.g. THP- and TBS- protected alcohols) are tolerated.

Catalytic oxidation of internal epoxides to α -diketones.
Antonietti, S.; Duñach, E. *Chem. Commun.* **2001**, 2566.

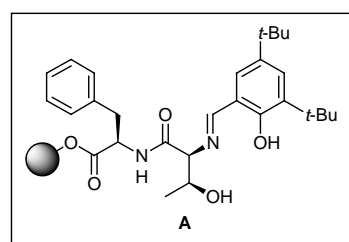
Epoxide Oxidation



6 examples (yields 48-83%).

Solid phase sulfur oxidation catalyst.
Green, S. D.; Monti, C.; Jackson, R. F. W.; Anson, M. S.; Macdonald, S. J. F. *Chem. Commun.* **2001**, 2594.

Sulfur Oxidation

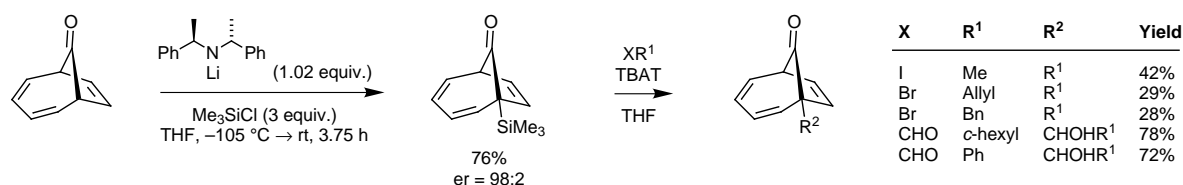


Ar	R	Yield	%ee
Ph	Me	100%	64%
Ph	Et	96%	64%
Ph	Pr	90%	57%
4-CH ₃ OC ₆ H ₄	Me	85%	63%
4-ClC ₆ H ₄	Me	90%	58%
4-BrC ₆ H ₄	Me	70%	53%
4-NO ₂ C ₆ H ₄	Me	61%	64%
4-NCC ₆ H ₄	Me	90%	45%
2-Naphthyl	Me	87%	72%

Over-oxidation to the sulfone in most cases occurred in less than 5% yield.

Enantioselective generation of bridgehead enolates.
Blake, A. J.; Giblin, G. M. P.; Kirk, D. T.; Simpkins, N. S.; Wilson, C. *Chem. Commun.* **2001**, 2668.

Bridgehead Deprotonation



TBAT = tetrabutylammonium triphenyldifluorosilicate