

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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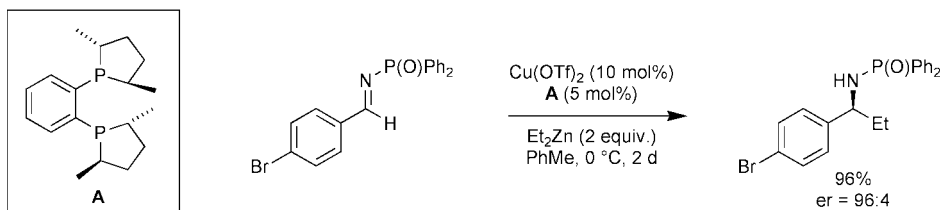
Synthesis 2003, No. 11, 05 08 2003. Article Identifier: 1437-210X,E;2003,0,11,1744,1751,ftx,en;X01103SS.pdf.
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The journals regularly covered by the abstractors are:

Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical Society
Journal of Organic Chemistry
Organic Letters
Organic and Biomolecular Chemistry
Organometallics
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Enantioselective Cu-catalyzed addition of dialkylzincs to *N*-diphenylphosphinoylimines.
Boezio, A. A.; Charette, A. B. *J. Am. Chem. Soc.* **2003**, *125*, 1692.

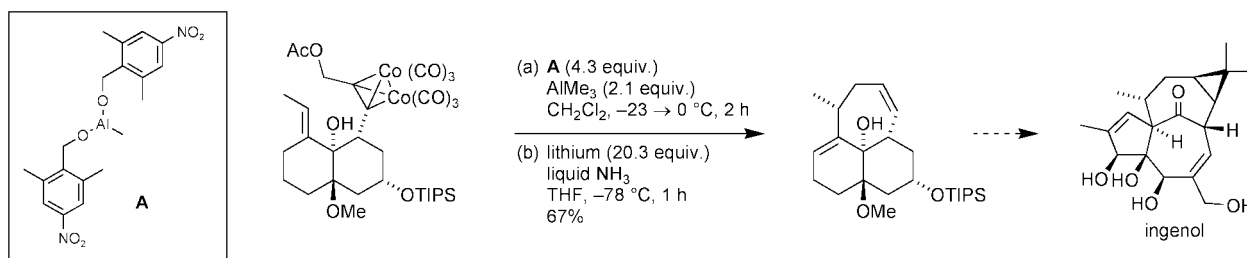
1,2-Addition



13 examples (yields 51-98%, %ee 85-96%).

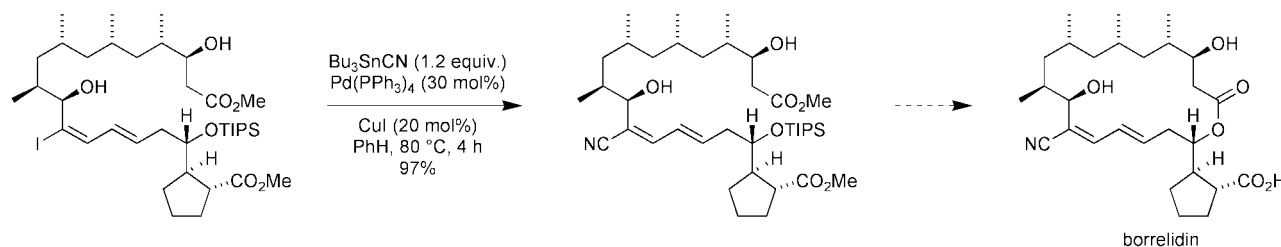
Total synthesis of Ingenol.
Tanino, K.; Onuki, K.; Asano, K.; Miyashita, M.; Nakamura, T.; Takahashi, Y.; Kuwajima, I.
J. Am. Chem. Soc. **2003**, *125*, 1498.

Annulation



Total synthesis of Borrelidin.
Duffey, M. O.; LeTiran, A.; Morken, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 1458.

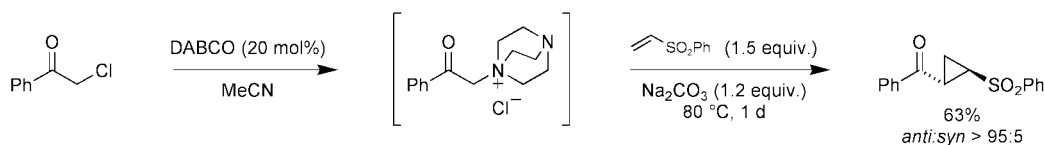
sp²-sp Coupling



Organocatalyzed cyclopropanation reaction.

Papageorgiou, C. D.; Ley, S. V.; Gaunt, M. J. *Angew. Chem. Int. Ed.* **2003**, *42*, 828.

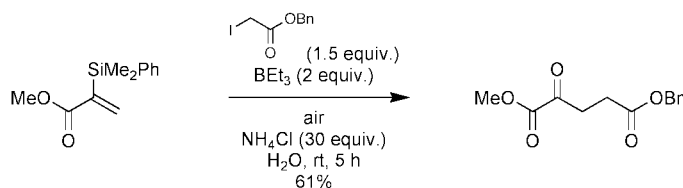
Cyclopropanation

3 examples (yields 63-82%, *anti:syn* > 95:5). 9 stoichiometric examples (yields 40-96%, 2.3:1 ≤ *anti:syn* ≤ 95:5). The use of chiral amines is also reported.

Synthesis of ketones from alkenylsilanes.

Kondo, J.; Shinokubo, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 825.

Oxidation

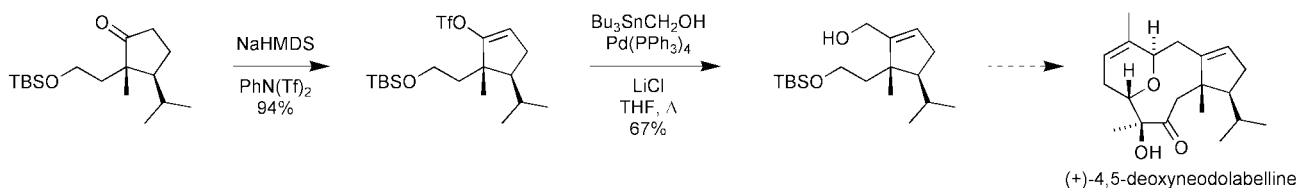


11 examples (yields 40-84%).

Total synthesis of (+)-4,5-Deoxyneodolabelline.

Williams, D. R.; Heidebrecht, R. W. *J. Am. Chem. Soc.* **2003**, *125*, 1843.

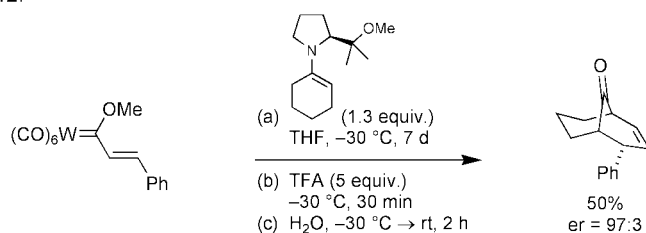
Hydroxymethylation



Annulation reactions of cyclic enamines with Fischer carbene complexes.

Bariuenga, J.; Ballesteros, A.; Bernardo de la Rúa, R.; Santamaría, J.; Rubio, E.; Tomás, M. *J. Am. Chem. Soc.* **2003**, *125*, 1712.

Annulation

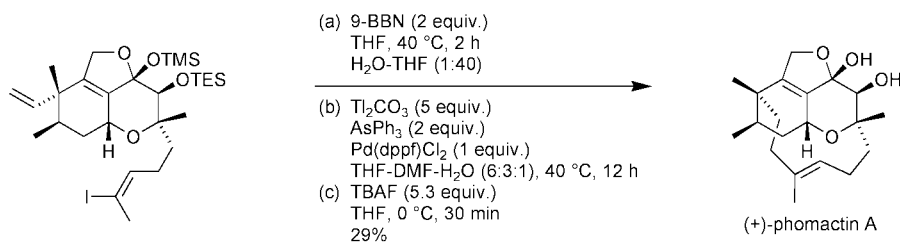


6 examples (yields 50-91%).

Total synthesis of (+)-Phomactin A.

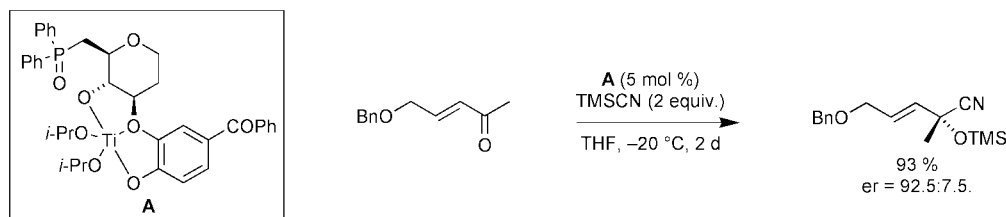
Mohr, P. J.; Halcomb, R. L. *J. Am. Chem. Soc.* **2003**, *125*, 1712.

Suzuki Macrocyclization



Total synthesis of Fostriecin *via* enantioselective Ti-catalyzed cyanosilylation.
Fujii, K.; Maki, K.; Kanai, M.; Shibasaki, M. *Org. Lett.* **2003**, *5*, 733.

1,2-Addition

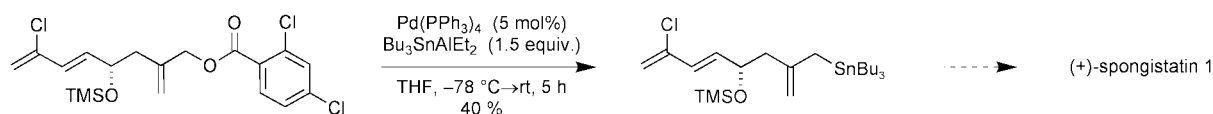


Application to the formal synthesis of fostriecin.

Total synthesis of (+)-Spongistatin 1.

Smith, A. B. III; Zhu, W.; Shirakami, S.; Sfougatakis, C.; Doughty, V. A.; Bennett, C. S.; Sakamoto, Y. *Org. Lett.* **2003**, *5*, 761.

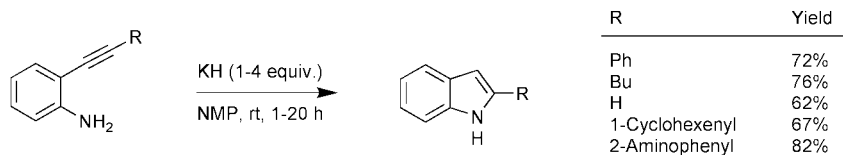
Stannylation



Synthesis of polyfunctionalized indoles.

Koradin, C.; Dohle, W.; Rodriguez, A. L.; Schmid, B.; Knochel, P. *Tetrahedron*, **2003**, *59*, 1571.

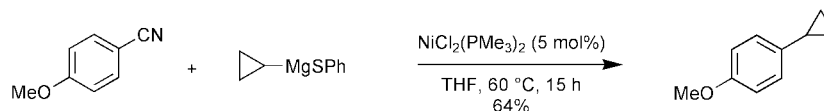
5-endo-dig Cyclization



26 examples (yields 71-94%).

Ni-catalyzed cross-coupling of modified Grignard reagents with aryl nitriles.

Miller, J. A.; Dankwardt, J. W. *Tetrahedron Lett.* **2003**, *44*, 1907.

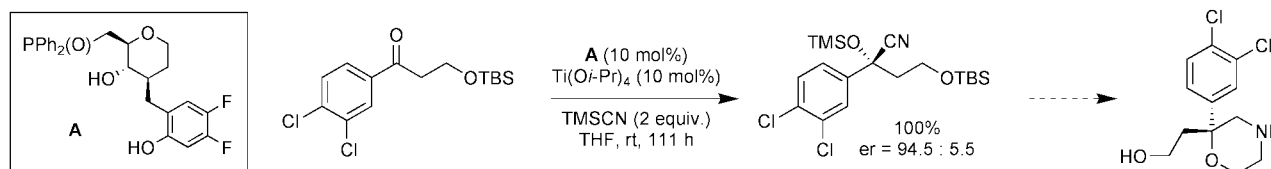
sp²-sp³ Coupling

18 examples (yields 33-80%).

Synthesis of a key intermediate of Neurokinin receptor antagonists *via* asymmetric cyanosilylation.

Takamura, M.; Yabu, K.; Nishi, T.; Yanagisawa, H.; Kanai, M.; Shibasaki, M. *Synlett*, **2003**, 353.

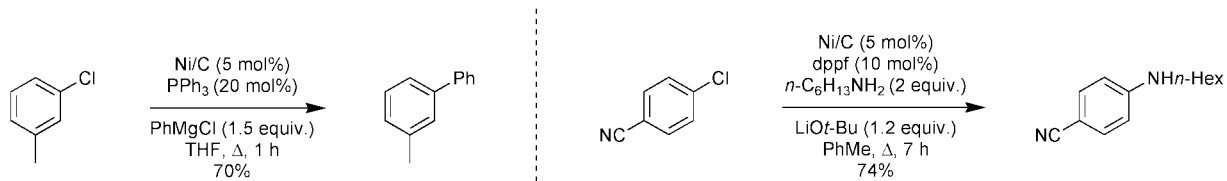
1,2-Addition



7 examples (yields 67-100%, %ee 75-89%).

Ni-catalyzed aromatic aminations and Kumada couplings.
Tasler, S.; Lipshutz, B. H. *J. Org. Chem.* **2003**, *68*, 1177, 1190.

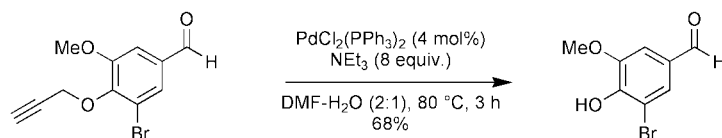
C-C/C-N Bond Formation



47 examples of aromatic aminations (yields 0-88%) and 37 examples of Kumada couplings (20-87%).

Pd-catalyzed cleavage of O/N-propargyl protecting groups in aqueous media under copper free conditions.
Pal, M.; Parasuraman, K.; Yeleswarapu, K. R. *Org. Lett.* **2003**, *5*, 349.

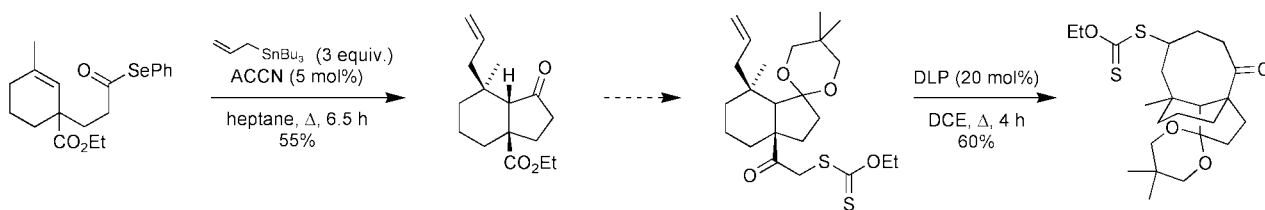
Deprotection



16 examples (yields 45-78%).

Synthesis of the tricyclic skeleton of Pleuromutilin.
Bacqué, E.; Pautrat, F.; Zard, S. Z. *Org. Lett.* **2003**, *5*, 325.

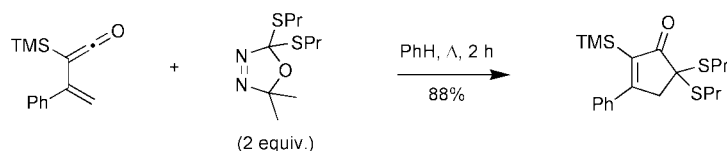
Radical Annulation



ACCN = 1,1'-azobis(cyclohexanecarbonitrile). DLP = lauroyl peroxide

Synthesis of substituted cyclopentenones *via* the [4+1] cycloaddition of nucleophilic carbenes and vinyl ketenes.
Rigby, J. H.; Wang, Z. *Org. Lett.* **2003**, *5*, 263.

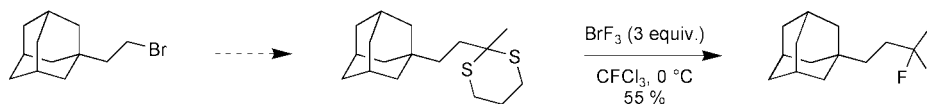
[4+1] Cycloaddition



11 examples (yields 55-96%).

Novel method for incorporating CHF₂ into organic molecules using BrF₃.
Sasson, R.; Hagooly, A.; Rozen S. *Org. Lett.* **2003**, *5*, 769.

Difluoromethylation

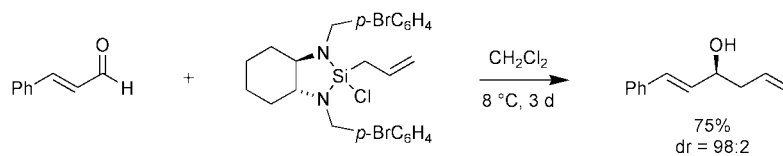


8 examples (yields 55-75%).

Enantioselective allylation of aldehydes.

Kubota, K.; Leighton, J. L. *Angew. Chem. Int. Ed.* **2003**, *42*, 946.

1,2-Addition

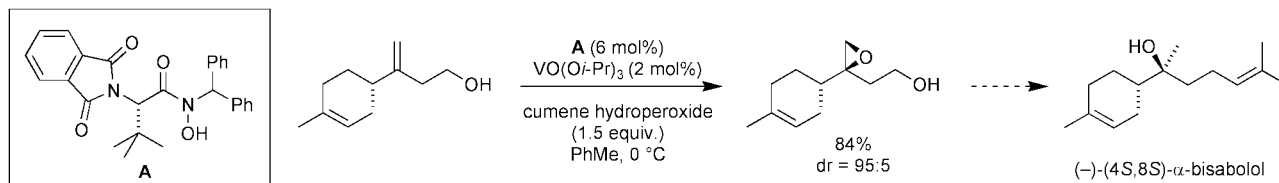


16 examples (yields 61-93%, %ee 94-98%). Various diamine auxiliaries employed.

Asymmetric epoxidation of homoallylic alcohols.

Makita, N.; Hoshino, Y.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 941.

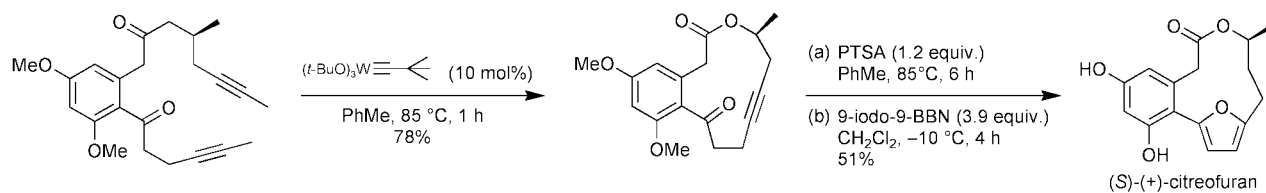
Epoxidation

Application to the total synthesis of (-)-(4S,8R)-*epi*- α -Bisabolol is also reported.

Total synthesis of (S)-(+)-Citreofofan by ring closing metathesis.

Fürstner, A.; Castanet, A.-S.; Lehmann, C. W. *J. Org. Chem.* **2003**, *68*, 1521.

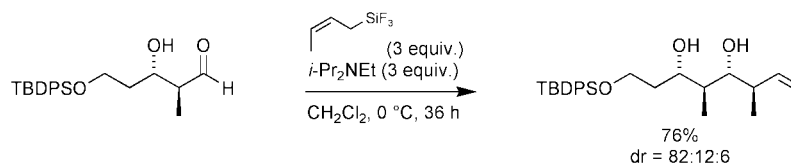
Ring Closing Alkyne Metathesis



Allylation and crotylation of aldehydes with allyl and crotyltrifluorosilanes.

Chemler, S. R.; Roush, W. R. *J. Org. Chem.* **2003**, *68*, 1319.

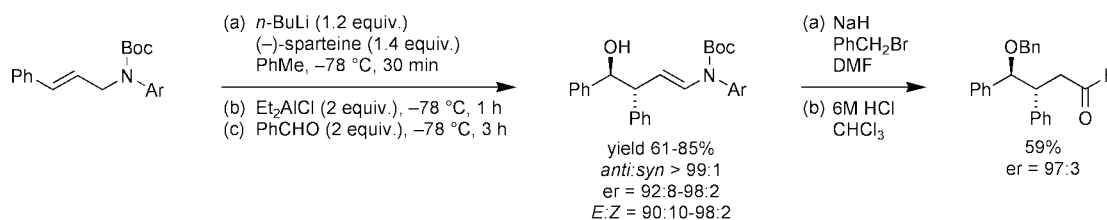
1,2-Addition



19 examples (yields 24-80%).

Lithiated *N*-Boc allylic amines as asymmetric homoenolate equivalents.Whisler, M. C.; Beak, P. J. *Org. Chem.* **2003**, *68*, 1207.

1,2-Addition/Hydrolysis

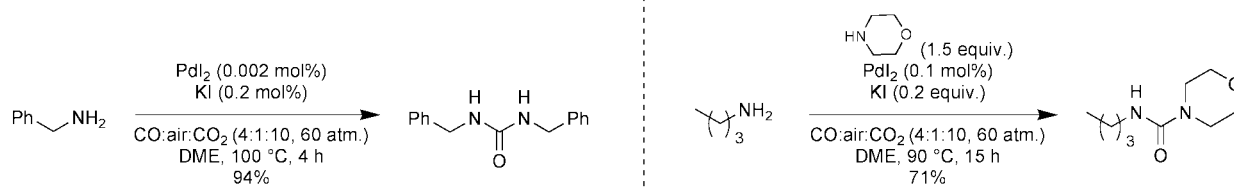


5 examples (yields 53-77%).

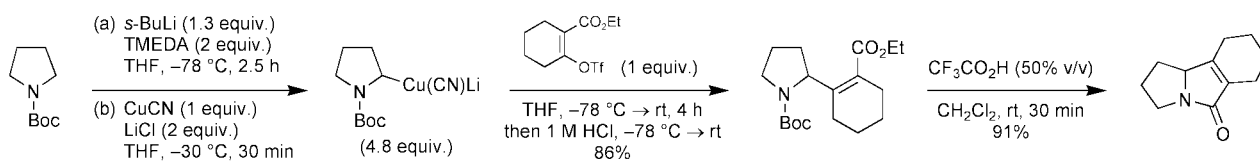
Pd-catalyzed oxidative carbonylation of amines.

Gabriele, B.; Mancuso, R.; Salerno, G.; Costa, M. *Chem. Commun.* **2003**, 486.

Carbonylation



5 examples of symmetrical ureas (yields 87-98%), 2 examples of unsymmetrical ureas (yields 71-75%).

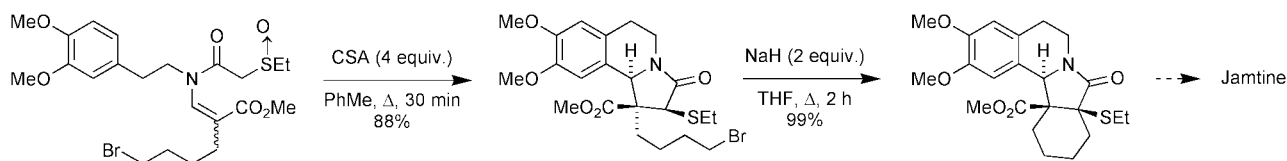
Coupling of α -(*N*-carbamoyl)alkylcuprates with enol triflates derived from cyclic β -keto esters.Li, S.; Dieter, R. K. *J. Org. Chem.* **2003**, *68*, 969. sp^2 - sp^3 Coupling

7 examples (yields 56-93%).

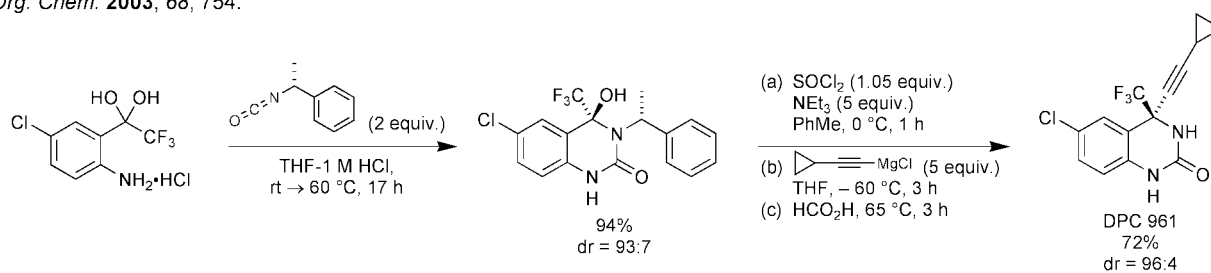
Synthesis of Jamtine via a tandem Pummerer/Mannich cyclization sequence.

Padwa, A.; Danca, M. D.; Hardcastle, K. I.; McClure, M. S. *J. Org. Chem.* **2003**, *68*, 929.

Pummerer/Mannich Cyclization

Synthesis of DPC 961 via a diastereoselective 1,4-addition to a 2(3*H*)-quinazolinone.Magnus, N. A.; Confalone, P. N.; Storase, L.; Patel, M.; Wood, C. C.; Davis, W. P.; Parsons, R. L. *J. Org. Chem.* **2003**, *68*, 754.

1,4-Addition



Osmium tetroxide-catalyzed oxidative cyclization of 1,5-dienes.

Donohoe, T. J.; Butterworth, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 948.

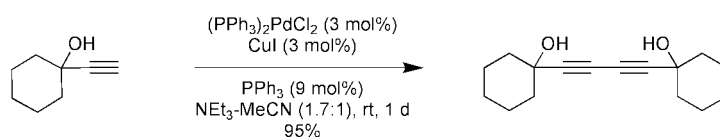
Oxidative Cyclization



7 examples (yields 60-95%). Application towards the synthesis of D-chitaric acid.

Synthesis of diynes via Pd-catalyzed cross-coupling in the absence of a stoichiometric additive.
Fairlamb, I. J. S.; Bauerlein, P. S.; Marrison, L. R.; Dickinson, J. M. *Chem. Commun.* **2003**, 632.

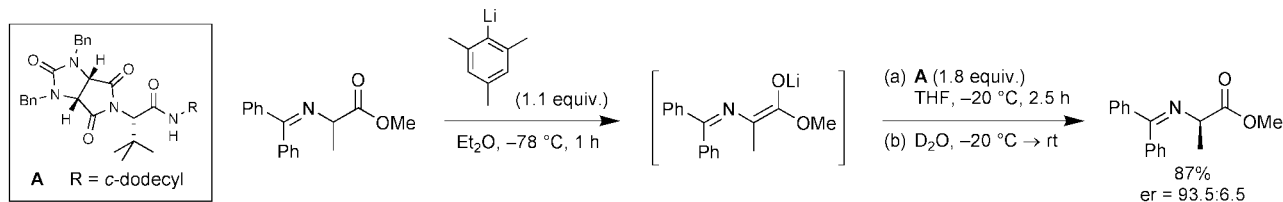
sp-sp Coupling



14 examples (yields 0-99%). Optimization of the reaction conditions is also reported.

Asymmetric protonation of lithium enolates of α -amino-acid derivatives with chiral amides.
Futatsugi, K.; Yanagisawa, A.; Yamamoto, H. *Chem. Commun.* **2003**, 566.

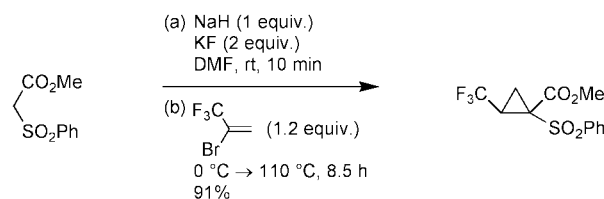
Asymmetric Protonation



7 examples (yields 27-89%, %ee 23-87%). Optimization studies towards chiral amide **A** are also reported.

One-pot synthesis of trifluoromethyl-substituted polyfunctionalized cyclopropanes.
Jiang, B.; Zhang, F.; Xiong, W. *Chem. Commun.* **2003**, 536.

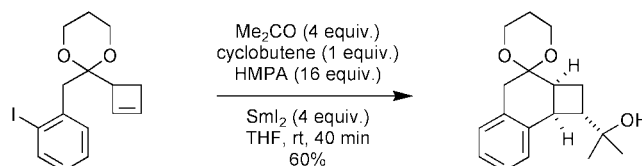
Cyclopropanation



6 examples (yields 60-91%). The synthesis of (\pm)-*trans*-trifluoronorcoronamic acid is also reported.

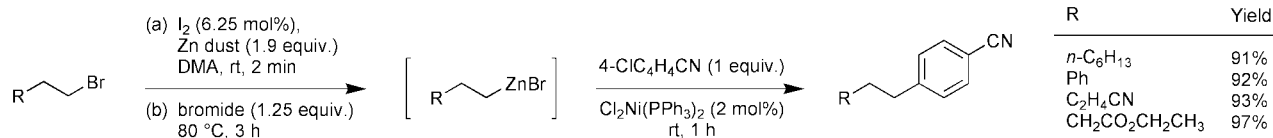
Samarium (II) iodide-mediated radical/polar crossover reactions of cyclobutenes.
Rivkin, A.; Nagashima, T.; Curran, D. P. *Org. Lett.* **2003**, *4*, 419.

Cyclization



6 examples (yields 40-60%).

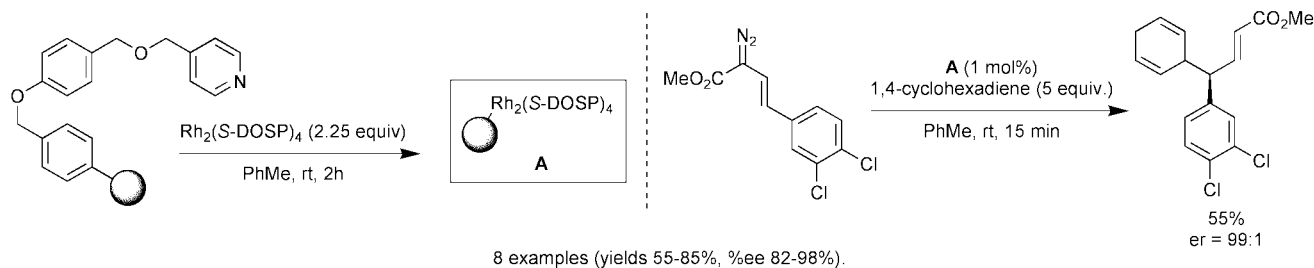
Preparation of alkylzinc reagents from unactivated alkyl bromides and chlorides.
Huo, S. *Org. Lett.* **2003**, *4*, 423.

sp²-sp³ Coupling

10 examples (yields 71-97%).

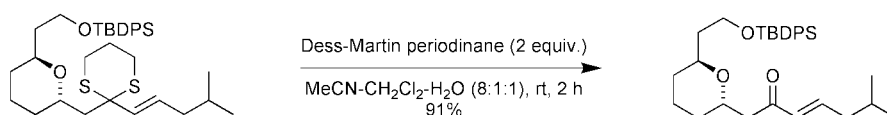
Enantioselective intermolecular C-H activation mediated by a dirhodium polymer-supported recoverable catalyst.
Davies, H. M. L.; Walji, A. M. *Org. Lett.* **2003**, *4*, 479.

C-H Insertion



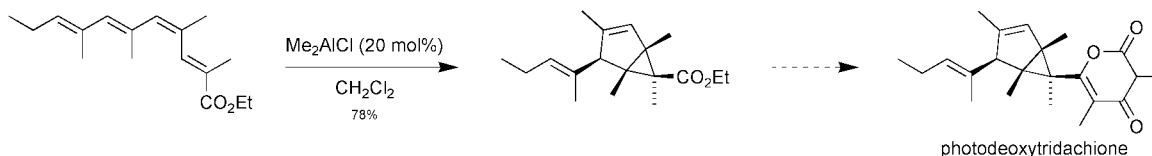
A mild chemoselective protocol for the removal of thioketals and thioacetals.
Langille, N. F.; Dakin, L. A.; Panek, J. S. *Org. Lett.* **2003**, *4*, 575.

Deprotection

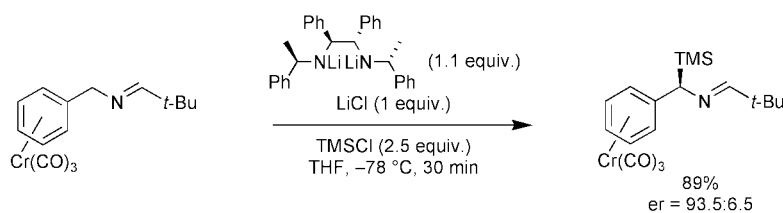


Total Synthesis of Photodeoxytridachione via Lewis acid catalyzed cyclization.
Miller, A. K.; Trauner, D. *Angew. Chem. Int. Ed.* **2003**, *5*, 549.

Annulation



Chiral base-mediated functionalization of tricarbonylchromium(0) complexes of benzylamine derivatives.
Gibson, S. E.; Smith, M. H. *Org. Biomol. Chem.* **2003**, *1*, 676.

Deprotonation/
Nucleophilic Addition

Total synthesis of the proposed structure of (+)-Jamtine using a chiral base approach.
Simpkins, N. S.; Gill, C. D. *Org. Lett.* **2003**, *4*, 535.

Enantioselective Desymmetrization

