AIMS AND SCOPE

While total synthesis reached extraordinary levels of sophistication in the last century, the development of practical and efficient synthetic methodologies is still in its infancy. The goal of achieving chemical reactions that are economical, safe, environmentally benign, resource- and energy-saving will demand the highest level of scientific creativity, insight and understanding in a combined effort by academic and industrial chemists.

Advanced Synthesis & Catalysis is designed to stimulate and advance that process by focusing on the development and application of efficient synthetic methodologies and strategies in organic, bioorganic, pharmaceutical, natural product, macromolecular and materials chemistry. The targets of synthetic studies can range from natural products and pharmaceuticals to macromolecules and organic materials. While catalytic methods based on metal complexes or enzymes play an ever increasing role in achieving synthetic efficiency, all areas of interest to the practical synthetic chemist fall within the purview of Advanced Synthesis & Catalysis, including synthesis design, reaction techniques, separation science and process development.

Contributions from industrial and governmental laboratories are highly encouraged. It is the goal of the journal to help initiate a new era of chemical science, based on the efforts of synthetic chemists and on interdisciplinary collaboration, so that chemistry will make an even greater contribution to the quality of life than it does now.



succeeding Journal für praktische Chemie (founded in 1828)

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2005, 347, 11 – 13, **Pages 1457 – 1710**

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COVER PICTURE

The cover picture shows a typical industrial reaction, hydroformylation of terminal alkenes, made possible in a test tube with ambient pressure and room temperature with high regioselectivities. For more details, see the Communication by Wolfgang Seiche, Alexander Schuschkowski, and Bernhard Breit on pages 1488–1494.



COMMENTARY

Catalytic C-C Bond Formation

Eric N. Jacobsen, Andreas Pfaltz, Masakatsu Shibasaki

1471



REVIEW

1473 Stereoselective Construction of Quaternary Stereocenters

Adv. Synth. Catal. 2005, 347, 1473-1482

Jens Christoffers,* Angelika Baro

COMMUNICATIONS

1483 Highly Enantio- and Diastereoselective Construction of 1,2-Disubstituted Cyclopentane Compounds by Dirhodium(II) Tetrakis[*N*-phthaloyl-(*S*)-*tert*-leucinate]-Catalyzed C–H Insertion Reactions of α-Diazo Esters

Adv. Synth. Catal. 2005, 347, 1483-1487

Kazushi Minami, Hiroaki Saito, Hideyuki Tsutsui, Hisanori Nambu, Masahiro Anada, Shunichi Hashimoto* CO₂Me Rh₂(S-PTTL)₄ (1 mol %) (

Bidentate Ligands by Self-Assembly through Hydrogen Bonding: A General Room Temperature/Ambient Pressure Regioselective Hydroformylation of Terminal Alkenes

Adv. Synth. Catal. 2005, 347, 1488-1494

Wolfgang Seiche, Alexander Schuschkowski, Bernhard Breit*

high regioselectivity, yield and functional group compatibility

1495 Application of Rhodium Complexes of Chiral Diphenylphosphino-Functionalized N-Heterocyclic Carbenes as Catalysts in Enantioselective Conjugate Additions of Arylboronic Acids

Adv. Synth. Catal. 2005, 347, 1495-1498

Jean-Michel Becht, Erhard Bappert, Günter Helmchen*

1499 Cross – Coupling Reactions of Allylic Alcohols in Water

Adv. Synth. Catal. 2005, 347, 1499-1503

Kei Manabe, Kenji Nakada, Naohiro Aoyama, Shū Kobayashi*

1488

Enantioselective Construction of All-Carbon Quaternary Stereocenters Using Palladium-Catalyzed Asymmetric Allylic Alkylation of $\gamma\text{-Acetoxy-}\alpha,\!\beta\text{-unsaturated Carbonyl}$ Compounds

Pd cat. (2 mol %) $(S,R_p)\text{-}2\text{-Np-DIAPHOX}$ (4 mol %) $R^1 = O\text{-}t\text{-Bu or Ph}$ $R^1 = O\text{-}t\text{-Bu or Ph}$ $R^2 = O\text{-}t\text{-Bu or Ph}$ $R^2 = O\text{-}t\text{-Bu or Ph}$ $R^3 = O\text{-}t\text{-Bu or Ph}$ $R^4 = O\text{-}t\text{-Bu or Ph}$ $R^5 = O\text{-}t\text{-Bu or Ph}$ $R^6 = O\text{-$

1504

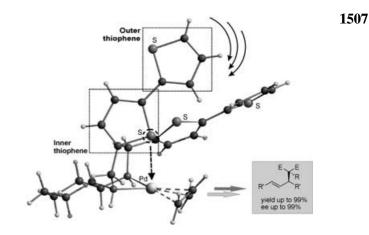
Adv. Synth. Catal. 2005, 347, 1504-1506

Tetsuhiro Nemoto, Tomoaki Fukuda, Takayoshi Matsumoto, Tsukasa Hitomi, Yasumasa Hamada*

Novel Chiral Diamino-Oligothiophenes as Valuable Ligands in Pd-Catalyzed Allylic Alkylations.
On the "Primary" Role of "Secondary" Interactions in Asymmetric Catalysis

Adv. Synth. Catal. 2005, 347, 1507-1513

Vincenzo Giulio Albano, Marco Bandini,* Manuela Melucci, Magda Monari, Fabio Piccinelli, Simona Tommasi, Achille Umani-Ronchi*



Anionic Reactions of *N*-(*trans*-2,3-Diphenylaziridin-1-yl)imines and Their Use as 1,1-Dipoles in Anionic Cyclizations

Adv. Synth. Catal. 2005, 347, 1513-1516

Jung-ll Hwang, Young-Taek Hong, Sunggak Kim*

Mannich-Type Reaction Using Alkenyl Trichloroacetates Catalyzed by Dibutyltin Dimethoxide

Adv. Synth. Catal. 2005, 347, 1517-1522

Akira Yanagisawa,* Hironao Saito, Masanori Harada, Takayoshi Arai

Enantioselective Mannich-Type Reaction Catalyzed by a Chiral Brønsted Acid Derived from TADDOL

Adv. Synth. Catal. 2005, 347, 1523-1526

Takahiko Akiyama,* Youichi Saitoh, Hisashi Morita, Kohei Fuchibe

1527 Asymmetric Catalysis of Intramolecular Cyclopropanation of 5-Aryl-1-diazo-1-mesitylsulfonyl-5-hexen-2-ones

Adv. Synth. Catal. 2005, 347, 1527-1532

Takashi Sawada, Masahisa Nakada*

- [CuOTf]₂C₆H₆ (5 mol %) ligand 1 (15 mol %) SO₂Mes SO₂Mes toluene, 50 °C 1a: R1 = Me, R2 = Bn R = H. OMe. OCH₂O, **1b**: $R^1 = Me$, $R^2 = i$ -Pr OTBS, OBz **1c**: $R^1 = Me$, $R^2 = t$ -Bu **1d**: $R^1 = Et$, $R^2 = i$ -Pr 0 - 96% ee 1e: R1 = Bn, R2 = i-Pr
- **1533** Asymmetric Catalytic Reductive Coupling of 1,3-Enynes and Aromatic Aldehydes

Adv. Synth. Catal. 2005, 347, 1533-1536

Karen M. Miller, Elizabeth A. Colby, Katrina S. Woodin, Timothy F. Jamison*

1537 Cationic Nickel Complexes with Weakly Coordinating Counterions and Their Application in the Asymmetric Cycloisomerisation of 1,6-Dienes

Adv. Synth. Catal. 2005, 347, 1537-1541

Christian Böing, Giancarlo Franciò, Walter Leitner*

 $X = C(CO_2Et)_2 \text{ or } N-Ts$ $Y^- = [AI\{OC(CF_3)_3\}_4]^- \text{ or } [AI\{OC(CF_3)_2Ph\}_4]^-$ TOF up to 158 h⁻¹ regioselectivity up to 99% ee up to 73%

1542 A New Method for the Generation of Titanium(III) Complexes and its Application in Pinacol Coupling Reactions

Adv. Synth. Catal. 2005, 347, 1542-1546

Christoph Alexander Knoop, Armido Studer*

1547 Rhodium-Catalyzed Asymmetric Intramolecular Cyclopropanation of Substituted Allylic Cyanodiazoacetates

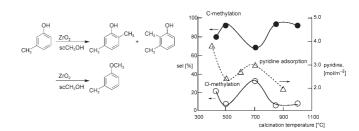
Adv. Synth. Catal. 2005, 347, 1547-1552

☐ Wei Lin, André B. Charette*

1553 Continuous Chemoselective Methylation of *m*-Cresol and Phenol with Supercritical Methanol over Solid Acid and Base Metal Oxide Catalysts

Adv. Synth. Catal. 2005, 347, 1553-1557

Tomoharu Oku, Yoshitaka Arita, Takao Ikariya*



Practical Synthesis of (E)- α , β -Unsaturated Esters from Aldehydes

1558 DMAP (10 mol %) DMF, 10 - 25 °C R1 = aliphatic 5 - 48 h 87 - 99% yield $R^2 = Et$, Bn, t-Bu aromatic E:Z ≥ 95:5

Adv. Synth. Catal. 2005, 347, 1558-1560

Benjamin List,* Arno Doehring, Maria T. Hechavarria Fonseca, Kathrin Wobser, Hendrik van Thienen, Ramon Rios Torres, Pedro Llamas Galilea

Enantioselective Addition of Organozinc Reagents to Aldehydes Catalyzed by 3,3'-Bis(diphenylphosphinoyl)-BINOL

Adv. Synth. Catal. 2005, 347, 1561-1568

Manabu Hatano, Takashi Miyamoto, Kazuaki Ishihara*

FULL PAPERS

Enantioselective Heck-Type Reaction Catalyzed by tropos-Pd(II) Complex with Chiraphos Ligand

Adv. Synth. Catal. 2005, 347, 1569-1575

Katsuhiro Akiyama, Kazuki Wakabayashi, Koichi Mikami*

Catalytic Enantioselective Michael Reaction of 1,3-Dicarbonyl Compounds via Formation of Chiral Palladium Enolate

Adv. Synth. Catal. 2005, 347, 1576-1586

Yoshitaka Hamashima, Daido Hotta, Natsuko Umebayashi, Yasunori Tsuchiya, Takeyuki Suzuki, Mikiko Sodeoka*

Thiophenol-Mediated 1,5-Hydrogen Atom Abstraction: Easy Access to Mono- and Bicyclic Compounds

Adv. Synth. Catal. 2005, 347, 1587-1594

Florent Beaufils, Fabrice Dénès, Barbara Becattini, Philippe Renaud,* Kurt Schenk

1595 The Direct, Enantioselective, One-Pot, Three-Component, Cross-Mannich Reaction of Aldehydes: The Reason for the Higher Reactivity of Aldimine *versus* Aldehyde in Proline-Mediated Mannich and Aldol Reactions

Yujiro Hayashi,* Tatsuya Urushima, Mitsuru Shoji, Tadafumi Uchimaru, Isamu Shiina

1605 Imine Additions of Internal Alkynes for the Synthesis of Trisubstituted (*E*)-Alkene and Cyclopropane Peptide Isosteres

Peter Wipf,* Jingbo Xiao, Steven J. Geib

Bu₃Sn

OTBDPS

$$R_{i+2}$$

OTBDPS

 R_{i+1}

O

 R_{i+1}

O

 R_{i+1}

O

 R_{i+2}

1614 Synthesis of *N*-Aryl-2-allylpyrrolidines *via* Palladium-Catalyzed Carboamination Reactions of γ -(*N*-Arylamino)alkenes with Vinyl Bromides

Joshua E. Ney, Michael B. Hay, Qifei Yang, John P. Wolfe*

1621 Diastereoselective Synthesis of Enantioenriched, Annulated Tetrahydrofurans by Simultaneous Formation of the O-1–C-5 and the C-5–C-4 Bonds

Seda Ünaldi, Mustafa Özlügedik, Roland Fröhlich, Dieter Hoppe*

1627 Synthesis of Enantioenriched *trans*-Fused Bicyclo[4.4.0]-dec-3-enes and Bicyclo[4.3.0]non-3-enes Bearing a 1,5-Lactone Bridge

Mustafa Özlügedik, Seda Ünaldi, Birgit Wibbeling, Dieter Hoppe*

$$\begin{array}{c} OCb \\ R \end{array} + H_2C = CH - CH = O \\ \hline \\ R \\ \hline \\ R \\ \end{array}$$

Stereoselective Synthesis of 3-Alkylideneoxindoles using Tandem Indium-Mediated Carbometallation and Palladium-Catalyzed Cross-Coupling Reactions

Adv. Synth. Catal. 2005, 347, 1632-1642

Reiko Yanada, Shingo Obika, Yusuke Kobayashi, Tsubasa Inokuma, Munetaka Oyama, Kazuo Yanada, Yoshiji Takemoto*

$$\begin{bmatrix} R^2 \\ In \\ Br_2 \\ N \\ O \end{bmatrix}$$

$$\begin{bmatrix} R^2 \\ R^3 \\ N \\ R^1 \end{bmatrix}$$

$$\begin{bmatrix} R^2 \\ R^3 \\ N \\ R^1 \end{bmatrix}$$

$$\begin{bmatrix} NHPI \\ Co(OAc)_2 \\ Mn(OAc)_2 \\ Mn(OAc)_2 \end{bmatrix}$$

$$\begin{bmatrix} R^1 = Bn \\ R^2 \\ R^3 \end{bmatrix}$$

1632

Guanidine-Thiourea Bifunctional Organocatalyst for the Asymmetric Henry (Nitroaldol) Reaction

Adv. Synth. Catal. 2005, 347, 1643-1648

Yoshihiro Sohtome, Yuichi Hashimoto, Kazuo Nagasawa*

$$F_{3}C \xrightarrow{H} \begin{array}{c} H \\ S \\ \hline \\ E \\ \hline \\ CF_{3} \end{array}$$

$$\begin{array}{c} Ie \\ \hline \\ CH_{3}NO_{2} (3-10 \text{ equivs.}) \\ \hline \\ Ioluene-H_{2}O (1:1) \\ \hline \\ KI (50 \text{ mol } \%), 0 \text{ °C} \end{array}$$

$$\begin{array}{c} O \\ CH_{3}NO_{2} \\ \hline \\ Up \text{ to } 92\% \text{ ee} \end{array}$$

Catalytic Asymmetric Addition of Terminal Alkynes to Aldehydes Mediated by (1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethanol

Adv. Synth. Catal. 2005, 347, 1649-1652

Mitsuaki Yamashita, Ken-ichi Yamada, Kiyoshi Tomioka*

Guanidine-Catalyzed Asymmetric Trimethylsilylcyanation of Carbonyl Compounds

Adv. Synth. Catal. 2005, 347, 1653-1658

Yukari Kitani, Takuya Kumamoto, Toshio Isobe, Keiko Fukuda, Tsutomu Ishikawa*

 R^1 = cyclohexyl, pivaloyl, 2-phenylethyl R^2 = H or Me

Synthesis of New C_2 -Symmetrical Bissulfonamide Ligands and Application in the Enantioselective Addition of Alkynylzinc to Aldehydes and Ketones

Adv. Synth. Catal. 2005, 347, 1659-1665

Ming Ni, Rui Wang,* Zhi-jian Han, Bin Mao, Chao-shan Da, Lei Liu, Chao Chen

$$R^{1} = R^{2} + Ph = \frac{7a}{\text{Ti}(O-i-Pr)_{4}, \text{ Et}_{2}\text{Zn}} + R^{1} = \text{Ph}$$

$$R^{2} = R^{2} + Ph = \frac{7a}{\text{Ti}(O-i-Pr)_{4}, \text{ Et}_{2}\text{Zn}} + R^{1} = \text{Ph}$$

$$R^{2} = R^{1} + Ph = \frac{7a}{\text{Ph}} + Ph = \frac$$

1666 Iron(III)-Catalyzed Tandem Sequential Methanol Oxidation/ Aldol Coupling

Adv. Synth. Catal. 2005, 347, 1666-1672

Vincent Lecomte, Carsten Bolm*

1673 Allylation of Aldehydes Promoted by the Cerium(III)
Chloride Heptahydrate/Sodium Iodide System: the Dependence of Regio- and Stereocontrol on the Reaction Conditions

Adv. Synth. Catal. 2005, 347, 1673-1680

G. Bartoli,* A. Giuliani, E. Marcantoni, M. Massaccesi, P. Melchiorre, S. Lanari, L. Sambri

CeCl₃7 H₂O/Nal OH
Al₂O₃ Method A

6

CeCl₃7 H₂O/Nal OH
CH₃CN
Method B

7

1681 A Modular Approach to α-Arylated Carbonyl Compounds *via* Indium Tris(bistriflylamide)-Catalyzed Regioselective Addition of β-Ketoesters to 1,3-Diynes

Adv. Synth. Catal. 2005, 347, 1681-1686

Masaharu Nakamura,* Kohei Endo, Eiichi Nakamura*

 $R^{4} = H \text{ In-catalyst (step 1)}$ $R^{2} \cap R^{3} \cap R^{4} = R^{6} \cap R^{4} \cap R^{2} \cap R^{2} \cap R^{3} \cap R^{4} \cap R^{4}$

1687 Substrate-Controlled Palladium-Catalyzed Allylic Alkylations of Chelated Enolates – Scope and Limitations

Adv. Synth. Catal. 2005, 347, 1687-1695

TBDPSQ OF Tfall Z_{nr} OTBDPS NHTfa Z_{n

Thomas Lindner, Uli Kazmaier*

1696 Ethylene-Bridged Bissulfoximines in Copper-Catalyzed Enantioselective Hetero-Diels-Alder Reactions

Adv. Synth. Catal. 2005, 347, 1696-1700

Carsten Bolm,* Marinella Verrucci, Oliver Simic, Christian P. R. Hackenberger

1701 Highly Enantioselective Aza-Baylis-Hillman Reactions Catalyzed by Chiral Thiourea Derivatives

Adv. Synth. Catal. 2005, 347, 1701-1708

Izzat T. Raheem, Eric N. Jacobsen*

Supporting information on the WWW (see article for access details).

*Author to whom correspondence should be addressed.