Total Synthesis of Astellatol: A Three-Decade Synthetic Puzzle

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Key transformations:
1) A TMS group dominated facial selective hydrogenation
2) An intramolecular Pauson–Khand reaction formed the hydrindane scaffold
3) An unprecedented SmI₂-mediated reductive radical 1,6-addition forged the cyclobutane
4) A strategic oxidation/reduction unravelled extremely challenging late-stage trans-hydrindane synthesis

The Direct Pd-Catalyzed β-C(sp³)–H Activation of Carboxylic Acids

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- R = H, Alkyl, NR₂, access to unnatural amino acids
- Non-quaternary acids
- Direct β C(sp³)–H Activation of aliphatic carboxylic acids

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Proline-Catalyzed Asymmetric α-Amination in the Synthesis of Bioactive Molecules

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Guanidines as Reagents in Proton-Coupled Electron-Transfer Reactions and Redox Catalysts

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Synthesis of Polycyclic Frameworks through Iron-Catalyzed Intramolecular [5+2] Cycloaddition

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Exploration of the Role of Double Schiff Bases as Catalytic Intermediates in the Knoevenagel Reaction of Furanic Aldehydes: Mechanistic Considerations

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L. A. Canalle  
D. Molendijk  
J. Meuldijk  
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Efficient Preparation of Cyclic α-Alkylidene β-Oxo Imides by Using a Flow Microreactor System

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A. Nagaki  
H. Shimoda  
M. Uwamori  
J.-i. Yoshida  
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Photophysical and Electrochemical Properties and Anticancer Activities of Porphyrin-Cored Fluorenodendrimers Synthesized by Click Chemistry

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A ‘Turn-on’ Fluorescence Glycosyl Dithiocarbamate Probe for Selective Fluoride Sensing in Aqueous Medium

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Chiral VAPOL Imidodiphosphoric Acid-Catalyzed Asymmetric Vinylogous Mannich Reaction for the Synthesis of Butenolides

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G. Liu
X. Guan
D. An
S. Zhang*
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A Synthesis of Novel Perinaphthenones from Acetylenic Esters and Acenaphthoquinone–Malononitrile Adduct in the Presence of Triphenylphosphine

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The Acceleration of the Rearrangement of α-Hydroxy Aldimines by Lewis or Brønsted Acids

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A Convenient Synthesis of Functionalized 2,3-Diazaspiro[4.4]nona-1,6,8-trienes

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Rhodium(III)-Catalyzed C–H Activation/Alkylation of Diazabicyclic Olefins with Aryl Ketones: Facile Synthesis of Functionalized Cyclopentenes

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Synthesis of Thiophosphates by Coupling of Phosphates with Bunte Salts under Mild Conditions

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R. Zhang
Q. Liu
S. Lin*
Z. Yan*
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R_1S=SO_3Na + \text{NaBr (10 mol%)} \rightarrow R_1S=SO_3R_2

\text{R}_1 = \text{Aryl, Alkyl} \quad \text{R}_2 = \text{Alkoxy, Aryl}

H_2O_2 (2.0 equiv)
CH_3CN (1 mL)
HOOAc (2.0 equiv)

19 examples (40–92%)
mild conditions
metal-free catalysis
H_2O_2 as a green oxidant

Synthesis of Unnatural Arundines Using a Magnetically Reusable Copper Ferrite Catalyst

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O. T. K. Nguyen
K. D. Huynh
T. T. Nguyen
N. T. S. Phan*
HCMC University of Technology, Vietnam

\text{CuFe}_2\text{O}_4 (15 mol%)

\text{R} = \text{Me, halide, MeO, TMS, Bpin, pyrazoles}
\text{R}_1 = \text{H, Me, allyl, Bin, Ar}
\text{R}_2 = \text{H, Me, Ph}

17 examples
38–88%

* reusable heterogeneous catalyst

New Cyano-Group-Containing 1,3-Oxaselenoles: Nucleophilic Substitution of a Cyano Group with Rearrangement

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A. V. Zamaraev
A. V. Gerasimenko
K. V. Maslov
O. Yu. Slabko
V. A. Kaminskii
Far Eastern Federal University, Russian Federation

\text{Ar} = \text{Ph, 4-MeOC_6H_4}

2\text{SeO}_2 \cdot \text{A} \rightarrow 2\text{H}_2\text{O} \rightarrow \text{HCN}

\text{R} = \text{H, NH}_2, \text{CH}_2\text{Ph}, 4-\text{Tol, 4-MeOC_6H_4}

77–81%
2 examples
37–61%
10 examples
**An Efficient Direct Access to Carbamates from Alcohols and TosMIC Mediated by Iodine in DMSO**

N. Pogaku
P. R. Krishna
Y. L. Prapurna*
CSIR-Indian Institute of Chemical Technology, India

![Chemical diagram](image)

- **R** = alkyl, aryl, heteroaryl, etc.
- **TosMIC**
- **DMSO, rt**
- **I₂ (0.6 equiv)**
- **15–20 min**

**Carbamates**
- **37 examples**
- **78–94% yield**

**Mild reaction conditions**
- **Easily available starting materials**
- **Shorter reaction times**

**Letters**

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**Length Matters: One Additional Methylene Group in a Reactant is Able to Affect the Reactivity Pattern and Significantly Increase the Product Yield**

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N. M. Podvalnyy
P. I. Abpronina
L. O. Kononov*
N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, Russian Federation

![Chemical diagram](image)

- **SnCl₄**
- **CH₂Cl₂**
- **–25 °C**
- **n = 2**
- **85%**
- **n oligomers (m ≥ 2)**

**Letters**

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**A Domino Process for the Sustainable Synthesis of Quinazolin-4(3H)-ones with Direct Chemo- and Regioselective Bromination**

E. Sheikh*
M. Adib*
R. Yazzaf
M. Jahani
M. Ghavidel
University of Tehran, Iran

![Chemical diagram](image)

- **8 examples**
- **75–95%**
- **R = Bn, CH₂-2-ClC₆H₄, 4-Tol, 4-EtC₆H₄, i-Pr, Bu, (CH₂)₄Me**

**Letters**

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Chloramine Salt Mediated Oxidative Halogenation of Terminal Alkynes with KI or NaBr: Practical Synthesis of 1-Bromoalkynes and 1-Iodoalkynes

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R — H
chloramine salt
KL, MeCN
or NaBr, MeCN/H₂O

R — X
X = I, Br
27 examples
up to 98% yield

• Practical approach
• Simple operation
• Gram-scale synthesis
• General access to 1-bromoalkynes and 1-iodoalkynes

Ligand-Free CuI-Catalyzed Chemoselective S-Arylation of 2-Mercaptobenzimidazole with Aryl Iodides

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Y.-C. Teo
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R₁ = NH₂, NO₂,
OMe, OEt etc.
R₂ = F, Cl, Br,
OMe, CF₃, NO₂,
acetyl etc.

K₃PO₄ (1.5 equiv)
DMSO (0.2 mL)
100 °C, 24 h

32 examples
up to 92% yield

Nitrile Hydration Reaction Using Copper Iodide/Cesium Carbonate/DBU in Nitromethane–Water

J. Kuwabara
Y. Sawada
M. Yoshimatsu
Gifu University, Japan

ArH⁻C≡N
CulMeNO₂–H₂O
(CuI (5 mol%), K₂PO₄ (1.5 equiv))

ArH⁻C—N
C₃H₆O₂DBU
(0.5 equiv/2 equiv)

total 30 examples
up to 90% yield, 9 examples
70–89% yield, 8 examples
selective amide formation
scalable up to 1.0 g (10 mmol)
useful for nitrile hydration
of the ester or carbamate
groups
**A De Novo Synthetic Route to 1,2,3,4-Tetrahydroisoquinoline Derivatives**

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S. Fuster
F. Fülöp*
L. Kiss*

University of Szeged, Hungary

**Cu-Catalyzed Conjugate Addition of Grignard Reagents to Thiochromones: An Enantioselective Pathway for Accessing 2-Alkylthiochromanones**

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L. Meng
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J. (J.) Wang*

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Guizhou Normal University, P. R. of China

**Transition-Metal-Free Synthesis of Thiosulfonates through Radical Coupling Reaction**

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X.-D. Xu
G.-P. Chen
W.-T. Wei*
Z. Guo*

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