Year in Review: JACS 1991

Volume 113
2096 Papers
~33 Total Syntheses, ~71 Syntheses

Most Cited Paper: High-Field FT NMR Application of Mosher’s Method. The Absolute Configurations of Marine Terpenoids 2327 Citations

Scientific Papers with 0 Citations: 2

Nobel Prize in Chemistry: Richard R. Ernst

The 1991 Nobel Prize in Chemistry has been awarded to Professor Richard R. Ernst of the ETH, Zurich, for important methodological developments within nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy has during the last twenty years developed into perhaps the most important instrumental measuring technique within chemistry. This has occurred because of a dramatic increase in both the sensitivity and the resolution of the instruments, two areas in which Ernst has contributed more than anybody else.

Event(s) of Note... That Art Did Not Just Cover

World Series – The Minnesota Twins win 4 games to 3 over the Atlanta Braves. The series MVP is Jack Morris of Minnesota

Select Isolated Natural Products

- **Neristatin 1**
  - Pettit, G. R. 6693–6695

- **Diazonamide A**
  - Fenical, W. 2303–2304

- **Hennoxazole A**
  - Scheuer, P. J. 3173–3174

- **Phomactin A**
  - Sato, A. 5463–5464

- **Octalactin A**
  - Fenical, W. 4682–4683
Syntheses Covered

- Stemedin
  Vollhardt, 4006–4008
- (-)-Norsecurinine
  Jacobi, P. A. 5384–5392
- 2-Desoxy-2-methylenebicyclomycin
  Williams, R. M., 6621–6633
- Withanolide E
  Grieco, P. A., 1057–1059
- (+)-Griseofulvin
  Pirrung, M. C. 8561–8562
- Pumiliotoxin 251D
  Gallagher, T. 2652–2656
- Calicheamicinone
  Danishefsky, S. J. 3850–3866
- Tirandamycin B
  DeShong, P. 8791–8796
- (+)-Aphanamol
  Mehta, G. 5765–5775
- (+)-Isoamijiol

New Methods Covered

- High-Field FT NMR Application of Mosher’s Method. The Absolute Configurations of Marine Terpenoids
  Kakisawa, et al.
  JACS 1991, 113, 4092–4096

- A Useful 12-1-5 Triacetoxyperidinane (the Dess-Martin Periodinane) for the Selective Oxidation of Primary or Secondary Alcohols and a Variety of Related 12-1-5 Species
  Daniel B. Dess and J. C. Martin
  JACS 1991, 7277–7287

- A Stable Carbene
  Arduengo, et al.
  JACS 1991, 113, 361–363

- Stereospecific Synthesis of Cyclobutanol Derivatives Using a 5 Minus 1 Methodology and Platinum(II)
  Jennings, et al.
  JACS 1991, 113, 7037–7039

- Directed Formation of Carbon-Bromine and Carbon-Sulfur Bonds by Tandem Radical Chain Reactions
  Breslow, et al.
One-Step Construction of the Stemodane Framework via the Cobalt–Catalyzed Cyclization of Monocyclic Enynes: A Formal Total Synthesis of Stemodin

Juris Germanas, Corinne Aubert, and K. Peter C. Vollhardt
JACS, 1991, 113, 4006

Bis-Heteroannulation. 15. Enantiospecific Syntheses of (+)- and (-)-Norsecurinine

Peter Al. Jacobi, Charles A. Blum, Robert W. Desimone, Uko E. Udodong
JACS, 1991, 113, 5384

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**One-Step Construction of the Stemodane Framework via the Cobalt–Catalyzed Cyclization of Monocyclic Enynes:**

1. **MgBr**
   - 1. **MgBr**
   - 2. **EtOCH**
   - Hg(O_2CCF_3), Et_3N
   - 3. **110 °C**

   59% Yield

2. **OTMS**
   - 1. **MgBr**
   - 2. **Et_3N, TMS-OTf**

   80% Yield

3. **via:**
   - **Me**
   - **Nu**

   **CpCo(CO)_3**

4. **1. Fe(NO_3)_3•9H_2O**
   - 2. **TsOH, 1,2-ethanediol**

   60% yield from 3

5. **30 mol % CpCo(CO)_2**

   55% yield 2:1 dr

6. **1. DMAP, pyridine**
   - 2. **DBU**

   58% yield

7. **1. Li, NH_3**
   - 2. **Li, NH_3**

   67% yield

   1.6% overall from 1

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**Bis-Heteroannulation. 15. Enantiospecific Syntheses of (+)- and (-)-Norsecurinine**

1. **MeNHOMe**
   - 2. **NaBH_4 / ClCO_2Et**

   30% yield

2. **Li**

   76% yield

3. **Available in 4 steps from D-proline**

   50% yield

4. **1. NaBH_4**
   - 2. **Martin Sulfurane**

   53% yield

   60% yield

5. **1. Bu_4NF**
   - 2. **NaI, TiCl_4**

   (−)-Norsecurinine

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**Stemodin**

**Corey et al.**
J. Am. Chem. Soc. 1980, 102, 7612-7613
Novel Ring Contractions via [2,3] Wittig Type Rearrangements: Synthesis of 2-Deoxy-2-methylenebicyclomycin
Robert M. Williams, Mark R. Sabol, Hee-doo Kim, Andrzej Kwast
JACS 1991, 113, 6621–6633

Total Synthesis of (+)-Griseoflavin
Michael C. Pirrung, William L. Brown, Sushil Rege, and Pierre Laughton
JACS 1991, 113, 8562–8564
Synthesis of the Highly Oxygenated Ergostane Type Steroid (+)-Withanolide E
Arturo Perez-Medrano and Paul A. Grieco*
JACS 1991, 113, 1057-1059

A Total Synthesis of (A)-Tirandamycin B
Stephen J. Shimshock, Robert E. Waltermire, Philip DeShong
JACS 1991, 113, 8791-8796
Enantioselective Synthesis of Pumiliotoxin 251D. A Strategy Employing an Allene-Based Electrophile-Mediated Cyclization

David N. A. Fox, David Lathbury, Mary F. Mahon, Kieran C. Molloy, and Timothy Gallagher

JACS 1991, 113, 2652–2656

Total Synthesis of Calicheamicinone: New Arrangements for Actuation of the Reductive Cycloaromatization of Aglycone Congeners

John N. Haseltine, Maria Paz Cabal, Nathan B. Mantlo, Nobuharu Iwasawa, Dennis S. Yamashita, Robert S. Coleman, Samuel J. Danishefsky,* and Gayle K. Schulte

JACS, 1991, 113, 3850–3866

Pumiliotoxin 251D

Gallagher, T. 2652–2656

Calicheamicinone

Danishefsky, S. J. 3850–3866
Terpenoids to Terpenoids: Enantioselective Construction of 5,6-, 5,7-, and 5,8-Fused Bicyclic Systems. Application to the Total Synthesis of Isoauacane Sesquiterpenes and Dolastane Diterpenes

Goverdhan Mehta, Nacharaju Krishnamurthy, and Srinivas Rao Karra
JACS 1991, 113, 5765–5775
Year in Review: JACS 1991

Stereospecific Synthesis of Cyclobutanol Derivatives Using a 5 Minus 1 Methodology and Platinum(II)
Jennings, et al.
JACS 1991, 113, 7037–7039

1. \( \text{NH}_2\text{CHCO}_2\text{Et}, \text{Rh(OAc)}_2 \)
2. LAH
3. Pt(II)
4. \( \text{H}^+ \)
5. Pt(OMe)_3
6. \( \Delta \)

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High-Field FT NMR Application of Mosher’s Method. The Absolute Configurations of Marine Terpenoids
Kakisawa, et al.
JACS 1991, 113, 4092–4096

\( \Delta \delta > 0 \)

Thus, probability of the correct prediction made by the \( ^{19}\text{F} \) method is less than 50%! This finding indicates that the absolute configurations of the natural products in the literature determined by \( ^{19}\text{F} \) NMR spectra of MTPA esters ought to be all reexamined.

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Directed Formation of Carbon-Bromine and Carbon-Sulfur Bonds by Tandem Radical Chain Reactions
Breslow, et al.

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A Useful 12-1-5 Triacetoxyperipidinane (the Dess-Martin Periodinane) for the Selective Oxidation of Primary or Secondary Alcohols and a Variety of Related 12-1-5 Species
Daniel B. Dess and J. C. Martin
JACS 1991, 7277–7287

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A Stable Carbene
Arduengo, et al.
JACS 1991, 113, 361–363

"Until now there have not been any 'bottle-able' carbenes, and we hope that the production of these stable nucleophilic carbenes will allow for convenient study of this class of compounds".
Select Syntheses Not Covered Today

(-)-Quadrone
Smith III, A.B. 3533–3542

dehydrotubifoline
Overman, L. 5085–5087

(+)-7,8-Epoxy-2-basmen-6-one
Paquette, L. A. 2610–2621

Deoxoapodine
1-Acetylaspidoabidine
Overman, L. 2598–2610

Erythromycin A
Mulzer, J. 910–923

Illudol
Vollhardt, K. P. C. 381–382

(+)-(15,16,19,20,23,24)-hexepi-Uvaricin
Hoye, T. R. 9369–9371

Deoxybouvardin
Boger, D. L. 1427–1429