What happened in 1994?

- **Top story in the US:** O. J. Simpson arrested for accused murder

- **Around the world:**
  - Nelson Mandela began his presidency in SA

- **Back in my hometown...**
  - Oriental Pearl TV Tower finished construction

In the world of sports:

1994 NBA Champion: Houston Rockets
- Rockets won the series 4-3 against Knicks
- Finals MVP: Hakeem Olajuwon
- Jordan-less Bulls lost to Knicks 3-4 in ECSF

Brazil won the 1994 FIFA World Cup

Other fun facts:
- Java™ released by Sun Microsystems
- *The Elder Scrolls: Arena* was released
- Justin Bieber was born
- *Beauty and the Beast* premiered on Broadway
- 7th place in top TV series: *Absolutely Fabulous*

ACIEE 1994 statistics:

- Total articles: 756
- Most prolific authors:
  1) Peter Jones (9)
  2) Dietmar Stalke (9)
  3) Francois Diederich (8)
  4) Hebert Roesky (7)
  5) Samuel Danishefsky (6)
  6) K. C. Nicolaou (6)
  7) Englert Ulli (6)

- Honorable mention: 12) Julius Rebek (4)

Most cited papers (not including reviews):

1) Tetra-p-tolylporphyrin with an Inverted Pyrrole Ring: A Novel Isomer of Porphyrin
   Glowiak et al. 779 (542 citations)

2) Fullerene Chemistry in Three Dimensions: Isolation of Seven Regiosomeric Bisadducts and Chiral Trisadducts of C60 and Di(ethoxy carbonyl)methylene
   Karfunkel et al. 437 (489 citations)

3) 1,3-Dialkoxycalix[4]arenecrowns-6 in 1,3-Alternate Conformation: Cesium-Selective Ligands that Exploit Cation-Arene Interactions
   Ungaro et al. 1506 (355 citations)

4) A Glucose-Selective Molecular Fluorescence Sensor
   Shinkai et al. 2207 (336 citations)

5) Self-Assembly and Structure of a 3 x 3 Inorganic Grid form Nine Silver Ions and Six Ligand Components
   Baxter et al. 2284 (329 citations)
**Methodology:**

1. **(S,S)-imide 1** (1.2 eq.)
   - 68% ee
   - (R,R)-imide 2
   - 70% ee

2. **Me**
   - 87% ee
   - **n-C11H23**
   - 96% ee

   (All yields 45%-90%, not specified)

   - **Yamamoto, H. et al., 107.**

3. **MeLi**
   - **Ph**
   - **OH**
   - **Me**
   - **Pr**

   - **94%, 94% ee**

   - **Galindro et al., 1888.**

4. **MeI**
   - **Pd(OAc)2**
   - **K2CO3, nBu4NBr**
   - **DMF, 110 °C, 3 d**

   - **75%**

   - **Meier et al., 465.**

5. **Mechanism?**

   - **Dyker, 103.**

**Example:**

- **Schaumann et al., 217**:
  - **MeS**
  - **SMe**
  - **Li**
  - **+ O**
  - **1,4-Brook**
  - **OTMS**
  - **OTs**
  - **HOAc**

   - **Schaumann et al., 217**
Why two different SM’s give the same product?

Ph N

CoOBz

– 78 °C, 72 h
endo/exo > 99:1
93:7 e.r.
(after auxiliary removal)

Yamamoto, Y. et al., 652

Waldmann et al., 683

Cowley et al., 1370

Kammermeier et al., 685

Herges et al, 993

Ireland-Claisen

Kazmaier, 998

62% - 72% yield
d.r. = 5.5 : 1 (SRRS:SSSS)
kilogram scale
HIV protease inhibitor
Activity requires C₂ sym.
Kammermeier et al., 685
**ACIEE Year in Review: 1994**

**Dongmin Xu**

**Baran Group Meeting**

11/10/18

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**AcO**

6 steps 66%

\[
\text{R-OH} \rightarrow \text{DDQ} \]

Intermediate?

**AgOTf, SnCl\(_2\), DBMP, Et\(_2\)O**

**74% single diastereomer**

**Ogawa et al., 1765**

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{Br} & \quad \text{O} \\
\text{O} & \quad \text{Bn} \\
\text{O} & \quad \text{Bn} \\
\text{O} & \quad \text{Bn}
\end{align*}
\]

1) \(t\)BuLi; CuCN; O\(_2\)

2) NBS, then KOH

86% single diastereomer

**Lipshutz et al., 1842**

\[
\begin{align*}
\text{HO}_2\text{C} & \quad \text{R} \\
\text{Me} & \quad \text{O}_2, \text{sens., } \text{hv}
\end{align*}
\]

68% – 89%

**HO\(_2\)C**

\[
\begin{align*}
\text{trans} & \quad \text{cis}
\end{align*}
\]

**Linker et al., 1971**

**Zadel et al., 454**

**Stoddart et al., 1286**

First Synthesis of "**Olympiadane**"

- 5% yield of the [5]catenane
- Topology controlled by \(\pi-\pi\) stacking
- See Yoshi GM, 2010 for more details

**H**

\[
\begin{align*}
\text{MeMgI} & \quad \text{B} = 1.2 \text{T} \\
\text{MeOH} & \quad 98\% \text{ ee}
\end{align*}
\]

**Lerner et al., 475**

gram-scale multiple cycles

**Antibody 14D9**

1 mol %

\(\text{pH} = 6.0, \text{rt, } 5 \text{ h}\)

65% yield, 86% ee

95% cat. recovery

**Stoddart et al., 1286**

"**Enantioselective Reactions in a Static Magnetic Field**"
Total Syntheses:

1) LiAlH₄, 25 d
2) Ac₂O, Et₃N

Danishefsky et al., 853
Total Syntheses Not Covered:

- **Zaragozic Acid A**
  *Nicolaou et al.*, 2184-2191

- **Cyclotheonamide B**
  *Shioiri et al.*, 1729

- **Calicheamicin γ₁**
  *Danishefsky et al.*, 858

- **(−)-Calyculin A**
  *Masamune et al.*, 673

**ACIEE Year in Review: 1994**

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MM

Me

OH

(±)-rabelomycin

TMS−TMS

MeLi

HMPT

TMS−Si−Li

Me

+

Me

Me

OH

58%

1) LDA, −78°C

2) TMSCl

76%

EtO

POEt

OEt

OEt

95%

LDA

OEt

Me

Si

2

Me

5

OTMS

33%

32%

AlCl₃

KF, H₂O₂

76%

78%

daylight, air

70%

(±)-rabelomycin

Krohn et al., 99