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Chemical & Engineering News

Cover Story

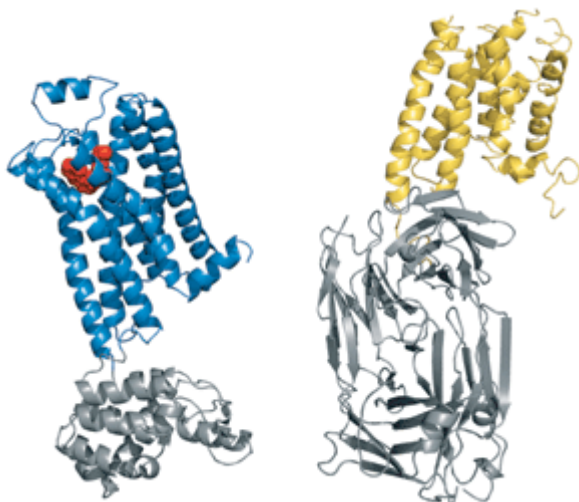
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2007 Chemistry Highlights

This year's selections include numerous advances in structural analysis

Stu Borman

EACH YEAR the editors of C&EN select some of the most important research advances from among the stories we've reported throughout the year and highlight them in a year-end issue. This year we've selected about two dozen examples of chemistry-based research at its best.



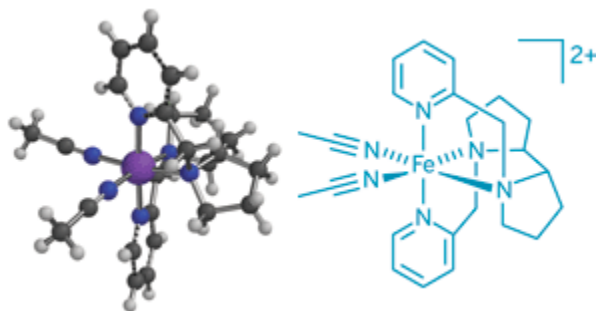
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Two Approaches Similar structures (one gold and one blue and red) of the membrane receptor β 2AR were obtained by stabilizing the receptor with T4 lysozyme (gray, left) or an antibody fragment (gray, right). β 2AR is only the second G-protein-coupled receptor ever analyzed structurally.

Of the various chemically related subdisciplines spanned by our selections, structural analysis stands out as the most prolific. Highlighted breakthroughs include structures of a G-protein-coupled receptor, a type of protein that's been nearly impossible to analyze; and a new technique that made it possible to obtain the first detailed structure of one of the largest biomolecular complexes in cells.

Other selections this year range from advances in neurochemistry and molecular biology to key discoveries in organic synthesis, nanotechnology, molecular imaging, and environmental chemistry. They include a possible cure for a mental retardation disorder, a surprising finding about a common

innovative way. And they synthesized welwitindolinone A by an eight-step protection-free sequence that is 17 steps shorter than another approach reported last year.



M. Christina White

Oxidizing Catalyst This catalyst (shown in molecular model and line structure representations) enables oxidation of the unreactive aliphatic C–H bonds at tertiary carbons in complex molecules without the need for directing or activating groups.

A new catalyst developed by M. Christina White and Mark S. Chen at the University of Illinois, Urbana-Champaign, simplifies the synthesis of highly complex organic molecules in an environmentally friendly way. The iron-based catalyst makes it possible to oxidize the unreactive aliphatic C–H bonds at tertiary carbons in complex molecules without the need for directing or activating groups (*Science* **2007**, *318*, 783). It uses hydrogen peroxide to oxidize C–H to C–OH bonds. Given a choice of C–H bonds in a complex molecule, it preferentially targets sterically accessible, electron-rich bonds at tertiary carbons. The researchers used the catalyst to oxidize the antimalarial natural product (+)-artemisinin primarily at only one of its five tertiary C–H bonds. The reaction not only eliminates the need for wasteful protecting groups but also produces water as the only catalytic by-product.

Also this year, White and Kenneth J. Fraunhofer developed the first method to carry out aminations by catalytically converting allylic C–H bonds directly to C–N bonds. Chemists had long sought a direct catalytic form of the reaction, skipping a preceding oxygenation that was formerly necessary. The direct reaction has become possible with White and Fraunhofer's Pd(II)/sulfoxide catalyst (*J. Am. Chem. Soc.* **2007**, *129*, 7274).



Amide Route Coupling reaction generates amide catalytically from alcohol and amine.

In another organic synthesis advance, chemists in Israel developed a new ruthenium catalyst that can make amides simply by coupling alcohols and amines (*Science* **2007**, *317*, 790). Routes to amides usually require toxic reagents like thionyl chloride and corrosive acidic or basic conditions, and they often generate unwanted by-products. The catalytic reaction developed by David Milstein and coworkers Chidambaram Gunanathan and Yehoshoa Ben-David of Weizmann Institute couples alcohols and amines under neutral conditions. It is both clean and selective, sidestepping the need for harsh reagents and conditions and creating H₂ gas as the only by-product. The rationally designed ruthenium catalyst works by a unique mechanism involving metal-ligand cooperation. Potential applications include the synthesis of industrially important amides and polyamides.