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# Heart Cut

February 20, 2006

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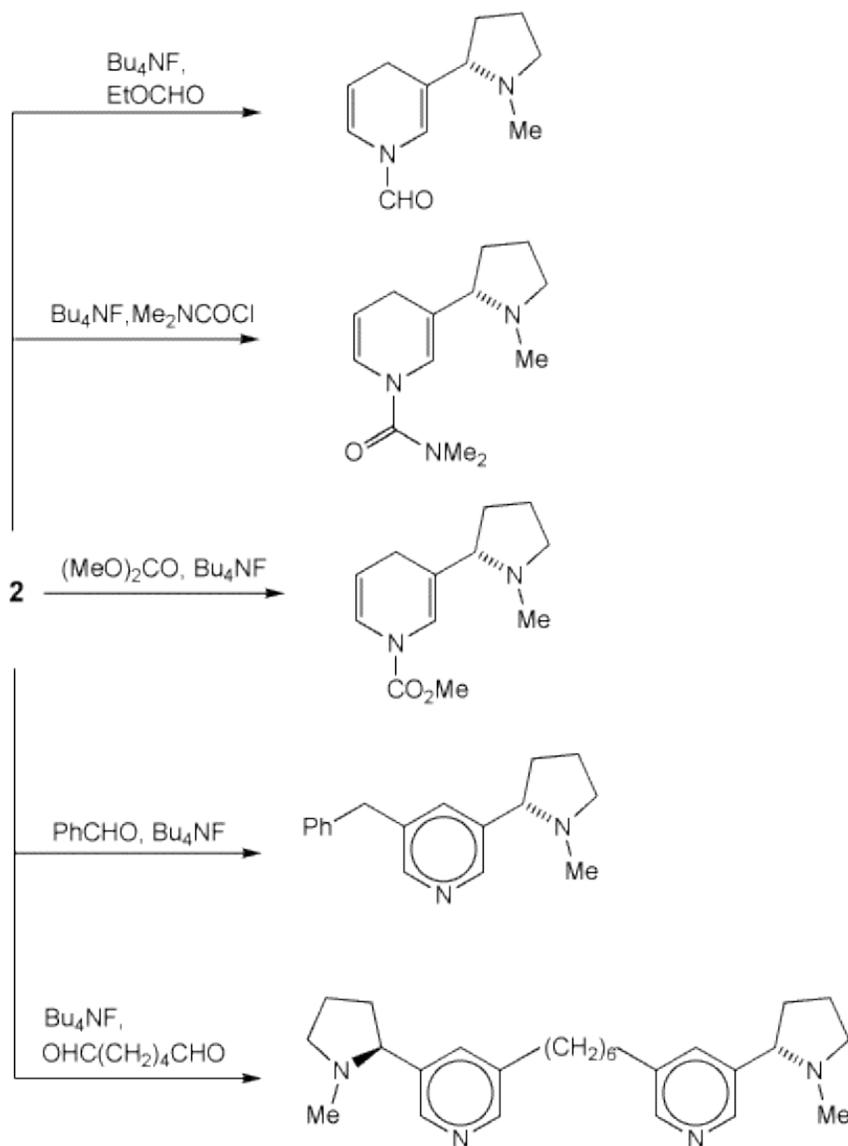
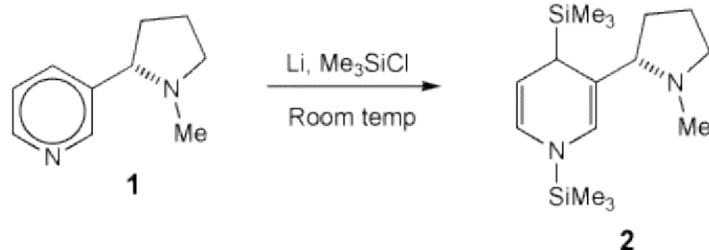
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**Reductive desilylation provides synthesis routes to (S)-nicotine derivatives.** (S)-Nicotine (**1**) has wide-ranging pharmacological properties, including benefits to patients with Parkinson's disease, schizophrenia, Alzheimer's disease, and ulcerative colitis. However, these benefits come with detrimental side effects that limit its use as a therapeutic agent.

E. D. Smith, F. C. Fevrier, and D. L. Comins\* at North Carolina State University (Raleigh) have devised a simple procedure for preparing derivatives of **1** that may have beneficial properties with lower toxicity. They carried out the reductive desilylation of **1** with lithium powder and Me<sub>3</sub>SiCl to give dihydropyridine derivative **2** in 95% yield. This versatile intermediate led to a variety of (S)-nicotine derivatives.

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The authors isolated **2** in high yields by running the reaction at room temperature and using high vacuum to distill the product. Fluoride catalysis using  $\text{Bu}_4\text{NF}$  appeared to be a key to forming derivatives from **2**. These methods provide nicotine derivatives regiospecifically with good to high enantiomeric purity. (*Org. Lett.* **2006**, *8*, 179–182; [W. Jerry Patterson](#)) [Go to top](#)

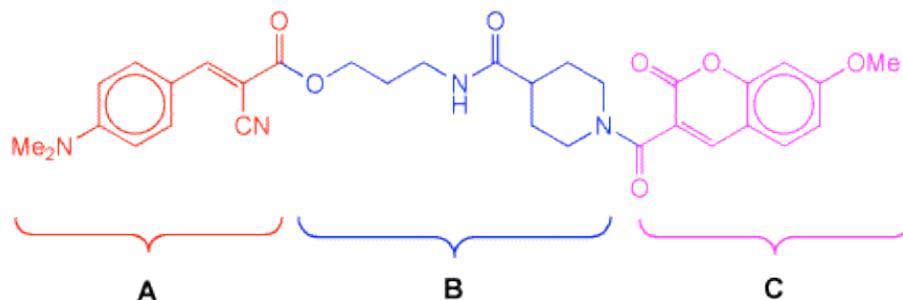
**In these "plastic supermolecules", functional group interactions determine molecular geometry.** Supramolecular systems are becoming increasingly important and demonstrate that there are means other than covalent bonds for designing new materials. J. L. Serrano and coauthors at the University of Zaragoza (Spain) and the Strasbourg Institute of Chemistry and Physics of Materials (France) report that when a dendrimeric core is functionalized with mesogenic units, it reorganizes into supramolecular columns. The exact geometry of the columns depends on the diameter of the core (number of dendritic generations) as well as the geometry of the mesogens.

The authors propose that as the volume of the mesogenic groups increases, the dendritic core distorts from spherical to columnar geometry to accommodate the peripheral units. They present simulated and

measured morphologies and show that strong interactions between the mesogens bind the structures together. (*Chem. Mater.* **2006**, *18*, 249–254; [David A. Schiraldi](#)) [Go to top](#)

**Detect variations in fluid viscosity ratiometrically.** Variations in the viscosity of body fluids are linked to a variety of dysfunctions at the cell and organism levels. Monitoring biofluid viscosity may provide information for diagnosing diseases.

Mechanical devices for measuring viscosity clearly cannot meet the spatial and temporal resolutions required for the bioassay. But M. A. Haidekker of University of Missouri–Columbia, E. A. Theodorakis of the University of California, San Diego, and coauthors have developed a photonic viscosity sensor based on a dual fluorescent probe.



The probe consists of three units: a primary fluorophore (**A**) in the molecule shown with viscosity-independent fluorescence, a secondary fluorophore (**C**) with viscosity-sensitive emission, and a covalent linker (**B**) of appropriate length that allows resonance-energy transfer. The dye can be excited by a single source with two emission channels, and the probe covers a wide range of viscosities (1–400 mPa·s). The emission ratio eliminates such interferences as fluctuations in refractive index and dye concentration and allows fast and accurate measurements of fluid viscosity. (*J. Am. Chem. Soc.* **2006**, *128*, 398–399; [Ben Zhong Tang](#)) [Go to top](#)

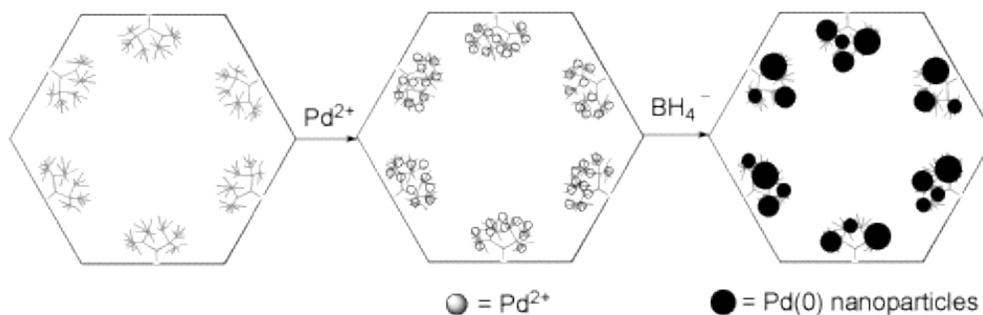
**Use buffers to separate reaction mixtures containing primary, secondary, and tertiary amines.**

The propargylation of 2-aminoheptane produces a mixture of unreacted primary amine starting material and secondary and tertiary amine products in a ratio of ~10:64:26. The secondary amine is of great interest to G. Ma of MDS Pharma Services (Montreal) and A. Jha\* of Acadia University (Wolfville, NS).

This mixture can be separated by washing the organic phase with the appropriate buffer solution to separate the three components. For example, washing with a pH 3.4 buffer (1.0 M NaH<sub>2</sub>PO<sub>4</sub>) selectively extracts the secondary amine into the aqueous layer. Subsequent washing with a pH 8.0 buffer (citric acid–sodium citrate) separated the tertiary amine. The authors describe a practical general method for separating amine mixtures. (*Org. Process Res. Dev.* **2005**, *9*, 847–852; [Will Watson](#)) [Go to top](#)

**Immobilize palladium nanoparticles on an organic–inorganic hybrid to make an efficient heterogeneous catalyst.** Polyamidoamine (PAMAM) dendrimers are highly branched, well-defined synthetic macromolecules. Dendrimer-encapsulated noble metal nanoparticles are homogeneous catalysts with unique characteristics; but they are difficult to separate from reaction mixtures and cannot be reused, which limits their applications.

Y. Jiang and Q. Gao\* of the Chinese Academy of Sciences (Beijing) describe a route to a heterogeneous palladium catalyst immobilized on SBA-15 mesoporous silica. PAMAM dendrimers up to generation 4 ( $G_n$ ,  $n = 1–4$ ) were built into the channel surfaces of amine-functionalized SBA-15 by the following procedure: The amino groups were treated with methyl acrylate in a Michael-type addition reaction to form aminopropionate esters. Subsequent amidation of the esters with ethylenediamine completed the generation. Repetition of these two reactions produced the desired number of generations of the dendrimers.



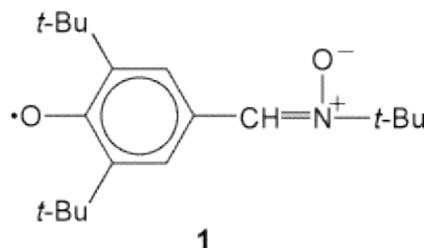
Pd<sup>2+</sup> ions were introduced into the dendrimers grafted on SBA-15 and were subsequently reduced with BH<sub>4</sub><sup>-</sup> to yield dark brown powders of Pd(0)-Gn-PAMAM-SBA-15. The Pd(0) particles were quite monodisperse in the SBA-15 channels. Hydrogenating allyl alcohol with this catalyst showed that activity and selectivity were quite sensitive to the generation of dendrimer.

The authors believe that the inorganic carrier reduces the aggregation of the dendrimer-encapsulated Pd(0) nanoparticles relative to homogeneous dendrimer-encapsulated Pd(0) catalysts. In addition, the dendrimers may not only stabilize the nanoparticles but also may modify the environment of the active sites and access to these sites. These catalysts can be easily recovered, reused multiple times, and preserved for 1 month in air, maintaining high catalytic efficiencies. (*J. Am. Chem. Soc.* **2006**, *128*, [716–717](#); [George Xiu Song Zhao](#)) [Go to top](#)

**Weak noncovalent bonds can be used to assemble "tunable" thermosensitive polymers.** Much in the field of supramolecular chemistry depends upon the strong noncovalent interactions by which macromolecules are assembled. M. E. Mackay, S. J. Rowan, and coauthors at Case Western Reserve University (Cleveland) and Michigan State University (East Lansing) report that aromatic amide-protected nucleobases located at the end of poly(tetrahydrofuran) (PTHF) cores can be assembled into useful materials.

Functionalizing the nucleobases limits their ability to hydrogen bond and permits phase separation into the "soft" PTHF and the "hard" nucleobases. But the nucleotide-modified PTHF molecules described in this work self-assemble into flexible film-forming plastics with melting points in the range of 130 °C. Dynamic analysis of these supramolecular polymers reveals that the end groups and their dissociation frequencies from "hard" segments play a defining role in polymers' properties over a wide range of temperatures. The ability to tailor the end groups' association and phase-separation properties could be crucial in designing self-healing polymers of the future. (*J. Am. Chem. Soc.* **2005**, *127*, [18202–18211](#); [David A. Schiraldi](#)) [Go to top](#)

**Multifrequency electron spin resonance is a potential characterization technique for powder sample radicals.** T. Yamaji\* and coauthors at Kyoto University and Tohoku University (Sendai, Japan) show that multifrequency electron spin resonance (ESR) can characterize phenoxy radicals. Three frequencies, the X-band (9.5 GHz), the Q-band (35.86 GHz), and the W-band (93.64 GHz), were selected to study the phenoxy radical **1** derived from a new spin-trapping reagent,  $\alpha$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitron, in frozen toluene solution.



The X-band ESR could not detect the molecular structure because of insufficient signal sensitivity and a low *g* factor. With a higher frequency, the Q-band ESR spectrum revealed axially symmetric *g* factors due to the para-substituted nitrogen atom, but it could not distinguish the perpendicular components into *x* and *y* components. With the highest resolution, the W-band ESR was capable of assigning all three components, *x*, *y*, and *z*. Furthermore, these results were all consistent with computer simulations based on the experimental parameters. (*J. Phys. Chem. A* **2006**, *110*, [1196–1200](#); [Sally Peng Li](#)) [Go to top](#)

**Run Baeyer–Villiger oxidations with a supported reagent.** Potassium peroxomonosulfate triple salt

(Oxone) is an efficient reagent for Baeyer–Villiger oxidation, but it requires an aqueous reaction medium that can lead to extensive product hydrolysis. G. Asensio and co-workers at the University of Valencia (Spain) have found that anhydrous potassium peroxomonosulfate supported on silica ( $\text{SiO}_2 \cdot \text{KHSO}_5$ ) efficiently oxidizes a variety of acyclic and cyclic ketones to the corresponding esters or lactones in quantitative yield at room temperature. Oxidizing cyclic ketones gave lactones exclusively. Importantly, the method avoids hydrolysis of the reaction products.

The authors prepared this reagent by mixing a 2 M aqueous solution of the peracid with chromatographic grade silica gel. The solvent was evaporated at room temperature under vacuum, and the resulting free-flowing powder was dried under vacuum to constant weight. The peroxide content of the supported reagent (as determined by iodometric titration) was 1.0–2.2 mmol peracid/g. The reagent could be stored at 2 °C in a desiccator for several days without noticeable loss of activity, but it does decompose slowly at room temperature. (*J. Org. Chem.* **2005**, *70*, [10879–10882](#); [W. Jerry Patterson](#))

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