Heart Cut

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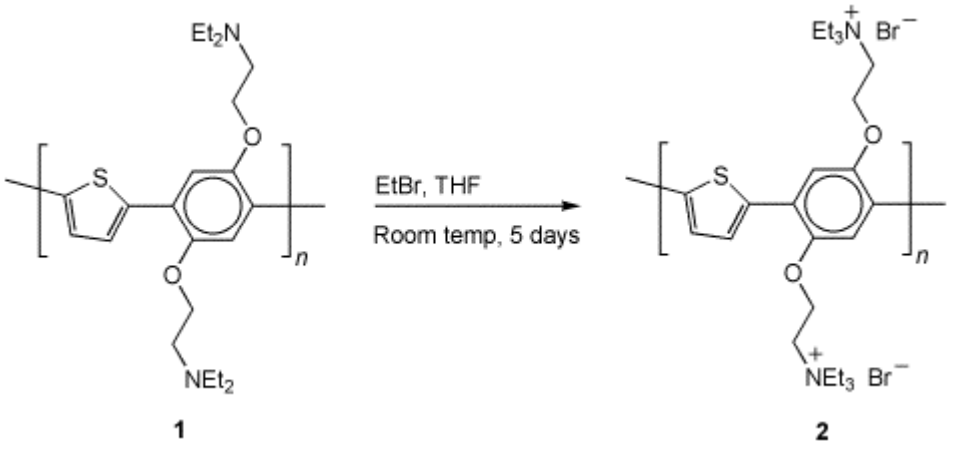
Amplified fluorescence quenching makes this p -conjugated polyelectrolyte sensitive to anionic analytes. Fluorescent, water-soluble p -conjugated polyelectrolytes (CPEs) provide a unique platform for developing sensitive chemo- and biosensors. Fluorescence quenching can be greatly amplified in CPEs through a combination of factors, including extended delocalization and rapid transport of the singlet exciton along the CPE backbone and the propensity of oppositely charged excited-state quenchers to pair with ionic groups attached to the CPE chains. Several orders of magnitude of chemo-optical signal amplification have been achieved with CPEs, as determined by their ability to detect molecular fluorescence quenchers.



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M. B. Ramey of Appalachian State University, Boone, NC, and his coauthors at MIT and the University of Florida, Gainesville, synthesized a new water-soluble cationic poly[(*p*-phenylene)-*alt*-thiophene] (PPT-NEt_3^+, **2**) by a simple and mild quaternization of the alkylamine substituents on the neutral polymer (**1**). CPE **1** displays significant fluorescence quenching and functions as an excellent chemosensor toward numerous anionic analytes. It exhibits quenching constants $>10^6\ M^{-1}$, and 25% quenching of its fluorescence can be achieved at a quencher concentration as low as 500 nM. (*Macromolecules* **2005**, *38*, 234 − 243; Ben Zhong Tang) Go to top

How do you overcome viral clearance problems when using an animal-derived enzyme for synthesizing a pharmaceutical ingredient? B. J. Gaede* and C. A. Nardelli of Abbott Laboratories report that using pig liver esterase (PLE) during the synthesis of the antiviral drug emtricitabine presented some clearance problems. There is very little regulatory guidance available for dealing with potential viral contamination of an active chemical pharmaceutical ingredient, particularly when compared with the contamination of biological products.

The authors developed a five-step protocol:

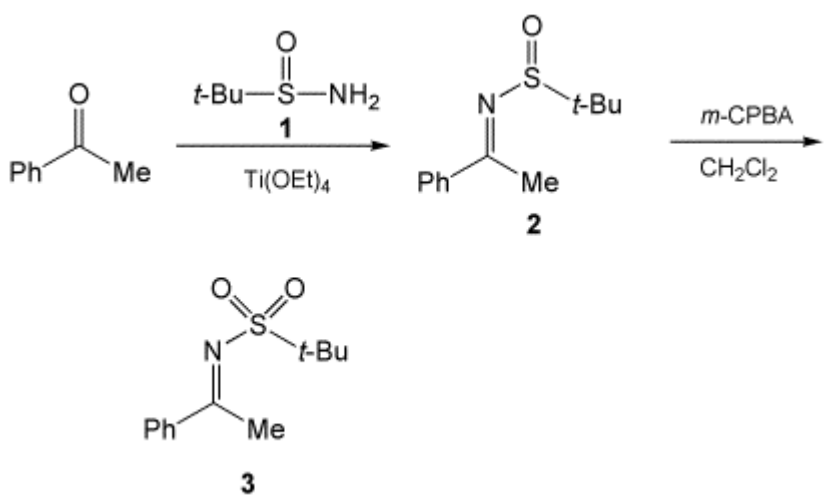
- determine the potential viral load by testing representative lots of enzyme,
- develop and validate a scaled-down laboratory process,
- develop and approve a viral clearance protocol,

- assess the viral clearance potential of a unit operation, and
- assess the viral risk.

In the example described, the viral load could be substantially reduced by solvent and heat treatment. (*Org. Process Res. Dev*. **2005**, *9*, 23 − 29; Will Watson) Go to top

Carbon nanotubes with multivalent carbohydrate ligands capture pathogens from solution. Y.-P. Sun and co-workers at Clemson University, SC, use single-walled carbon nanotubes (SWCNTs) as high surface area platforms to bind pathogens. The authors used a carbodiimide to link carboxylic acid groups on the SWCNTs with 2´-aminoethyl-ß-D-galactopyranoside. The resulting galactosylated nanotubes were soluble in water and were highly efficient in capturing *Escherichia coli* from physiological solutions. The authors propose that other pathogens bearing galactose receptors could be similarly controlled using a modified SWCNT, and that the strategy of biological functionalization of nanotubes for clinical applications could be extended. (*Chem. Commun*. **2005**, 874 − 876; David A. Schiraldi) Go to top

Here ' s a simple preparation of *N*-sulfonylimines. J. L. García Ruano and co-workers at the Autonomous University of Madrid report a general method for converting carbonyl compounds to *N*-sulfonylaldimines and -ketimines. In this procedure, the carbonyl substrates were first treated with a sulfinylamide (**1**) to form the intermediate *N*-sulfinylimines (**2**) in high yields. Reactant **1** was readily available in two steps from a disulfide. Oxidation of **2** with *m*-chloroperbenzoic acid (*m*-CPBA) then provided the desired *N*-sulfonylimines (**3**)

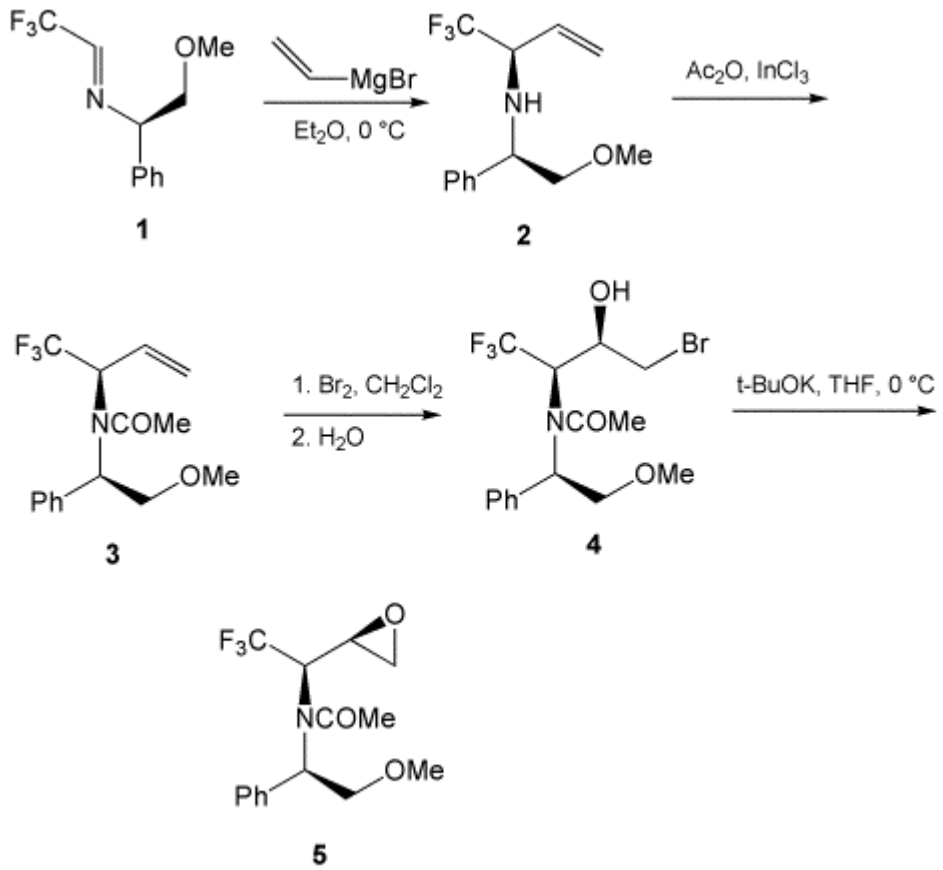


The method is applicable to aromatic and aliphatic carbonyl substrates, even those having enolizable protons. Importantly, this synthesis proceeds without a-epimerization at the stereogenic center, so that chiral substrates are oxidized with complete regioselectivity. In addition, the reaction sequence does not affect C=N or C=C bonds, indicating the high chemoselectivity of *m*-CPBA toward sulfur. The authors point out that sulfonylimines are useful substrates for aza Diels − Alder reactions, aziridine synthesis, and nucleophilic additions. (*Org. Lett*. **2005**, *7*, 179 − 182; W. Jerry Patterson) Go to top

Uranium-based nanotubes have zeolite-like pores. Many inorganic systems have been converted into nanotubes, but until now actinide-based nanotubes have been elusive. S. V. Krivovichev and coauthors of St. Petersburg State University, Russia, the University of Innsbruck, Austria, and the Russian Academy of Sciences, Moscow, prepared and characterized templated uranyl selenate nanotubes. They obtained transparent yellow crystals of the nanotubes from the room temperature reaction of $UO_2(NO_3)_2$, *n*-$BuNH_2$, and H_2SeO_4.

The product, whose composition was determined to be $(n\text{-}C_4H_9N)_{14}[(UO_2)_{10}(SeO_4)_{17}(H_2O)]$, consisted of elliptical nanometer-scale tubular $[(UO_2)_{10}(SeO_4)_{17}(H_2O)]$ units organized in a hexagonally packed structure. The crystallographic diameter of 12.6 Å was similar to that of some zeolites. No applications of these highly electropositive structures have been investigated to date. (*J. Am. Chem. Soc*. **2005**, *127*, 1072 − 1073; David A. Schiraldi) Go to top

Synthesize trifluoromethyl amino epoxides from aldimines. These epoxides are analogues of key precursors of various HIV protease inhibitors, yet classical methods used for preparing nonfluorinated amino epoxides could not be applied to the trifluoromethyl compounds. D. Bonnet-Delpon and co-workers at the Center of Pharmaceutical Studies, Châtenay-Malabry, France, have remedied this situation by developing a highly efficient chiral synthesis of trifluoromethyl ß-amino epoxides (**5**) starting from chiral trifluoromethyl aldimines (**1**).



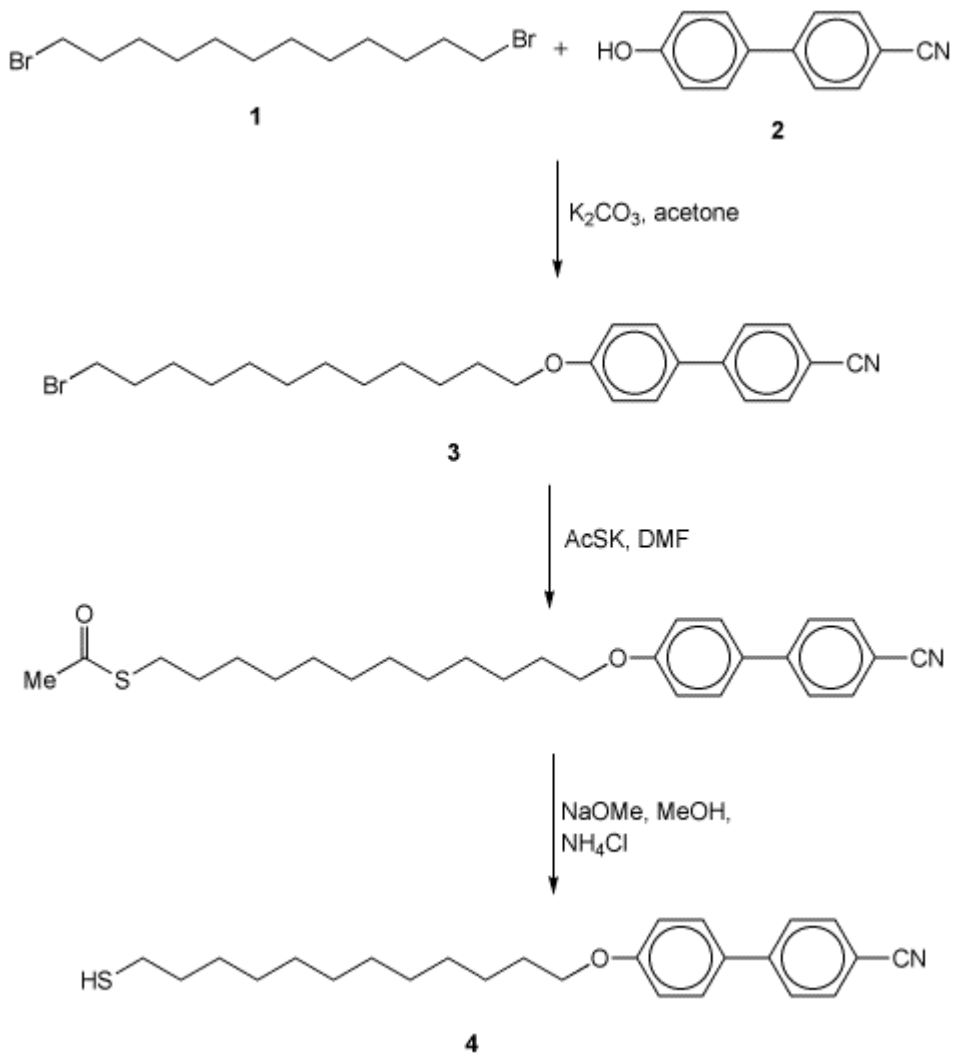
Directly adding vinylmagnesium bromide to **1** provided the allylamine (**2**) in almost optically pure form (de = 98%). The allylamine nitrogen was protected by converting it to the *N*-acylamine (**3**), followed by formation of the bromohydrin (**4**) and subsequent cyclization to give the target epoxide **5**, also with very high diastereoselectivity (de = 98%). The indirect formation of the epoxide by ring-closing the bromohydrin was a key to this synthesis because the double bond of the allylic amine was completely unreactive toward epoxidation using *m*-chloroperbenzoic acid.

The authors quantitatively converted **5** by simple reflux in *i*-PrOH into the azetidinol, which was obtained as a single diastereomer. Subsequent X-ray diffraction analysis allowed them to assign **5** a syn *R*,*R* configuration. (*J. Org. Chem.* **2005**, *70*, 699 − 702; W. Jerry Patterson) Go to top

These 3-D metal − organic rotaxane frameworks have lanthanide-ion nodes, bipyridylium *N*-oxide axles, and crown-ether wheels. D. J. Hoffart and R. J. Loeb* of the University of Windsor, ON, prepared metal − organic rotaxane frameworks (MORFs) in MeCN at room temperature using dibenzo [24]crown-8 ether as a wheel, $[M(OTf)_3]$ (M is Sm, Eu, Gd, or Tb; OTf is trifluoromethanesulfonate [triflate]) as a framework, and a bis(bipyridylium *N*-oxide triflate) as an axle.

The structural unit comprised eight-coordinated metal centers with square antiprismatic geometry that contained six rotaxane ligands, one water molecule, and one coordinated triflate ion. The 3-D MORFs had cavity volumes of ~10 nm^3 and thermal stabilities up to 240 °C. (*Angew. Chem., Int. Ed*. **2005**, *44*, 901 − 904; George Xiu Song Zhao) Go to top

Gold nanoparticles and liquid crystalline thiol ligands organize themselves into 1-D arrays. S. Y. Kim and co-workers at the Korea Advanced Institute of Science and Technology, Daejeon, report that liquid crystalline (LC) thiol ligands spontaneously arrange themselves around spherical gold nanoparticles. 1,12-Dibromododecane (**1**) and 4-hydroxy-4′-cyanobiphenyl (**2**) reacted to produce the 12-bromoalkoxycyanobiphenyl **3**. Treatment with thioacetate followed by methanolic saponification produced the LC thiol ligands **4**.



Gold nanoparticles were produced by reducing $HAuCl_4$ with $NaBH_4$. When the gold particles and LC thiols were combined, the free ligand nematic transition between 50 and 66 ºC was replaced by a 110 − 130 ºC mesophase and a 130 ºC melting peak. After forming the mesophase, the Au − LC particles organized into 13 − 60 nm long linear double rows of gold particles. These structures contained mesogen chains that pointed toward one another in a manner reminiscent of micelles. (*Chem. Comm*. **2005**, 800 − 801; David A. Schiraldi) Go to top

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