

The ISHC Bulletin

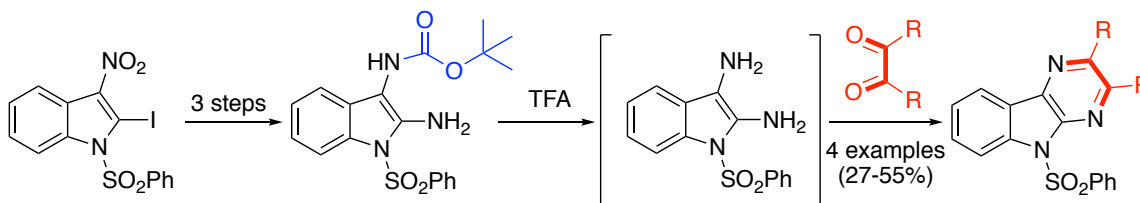
Recent Publications of ISHC Members

Issue 11; April 2017

Synthesis of a Masked 2,3-Diaminoindole

Philip Z. Mannes, Evans O. Onyango, and Gordon W. Gribble
J. Org. Chem. **2016**, *81*, 12478–12481.

DOI: 10.1021/acs.joc.6b02318

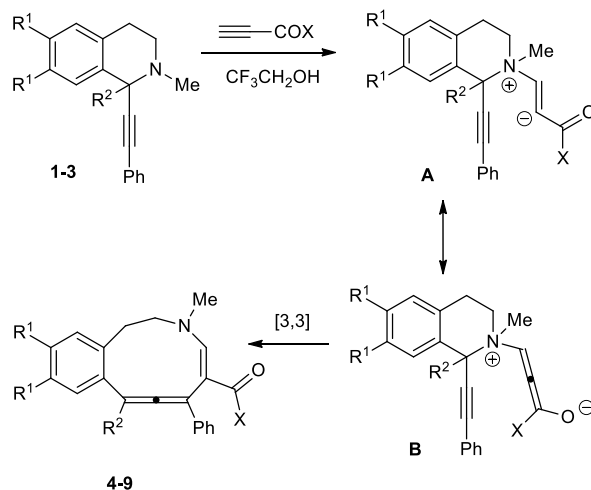


Abstract: Abstract: In an extension of our study of the synthesis and chemistry of 3- and 2-nitroindoles, we now describe a 3-step the synthesis of a masked *N*-protected 2,3-diaminoindole that can serve, for example, as a precursor to 5*H*-pyrazino[2,3-*b*]indoles, imidazo[4,5-*b*]indoles, 6*H*-indolo[2,3-*b*]quinoxalines, and similarly fused indoles that exhibit cytotoxicity, anti-viral, antibacterial, and other biological activities.

First Synthesis of Heterocyclic Allenes – Benzazecine Derivatives

Leonid G. Voskressensky, Alexander A. Titov, Maksad S. Dzhankaziev, Tatiana N. Borisova, Maxim S. Kobzev, Pavel V. Dorovatovskii, Victor N. Khrustalev, Alexander V. Aksenov, and Alexey V. Varlamov
New J. Chem. **2017**, *41*, 1902–1904.

DOI: 10.1039/c6nj03403a



1,2 R¹ = OMe; 3 R¹ = H; 4,5,8,9 R² = Me; 6,7 R² = Bn

4 R² = Me, X = OMe (84%); 5 R² = Me, X = Me (90 %);

6 R² = Bn, X = OMe (85%); 7 R² = Bn, X = Me (80%);

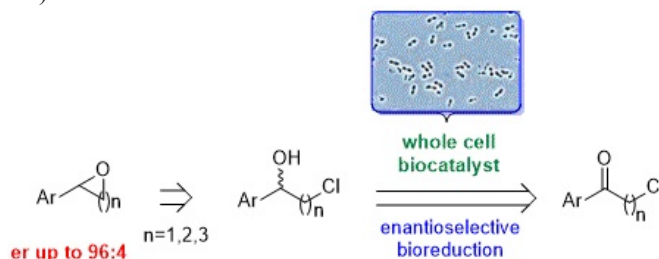
8 R² = Me, X = OMe (72%); 9 R² = Me, X = Me (84 %)

Abstract: Benzazecines with an allene fragment were prepared for the first time and in high yields via tandem reaction of 1-phenylethynyl-1- methyl(benzyl)-1,2,3,4-tetrahydroisoquinolines with activated alkynes in trifluoroethanol.

Stereoselective Chemoenzymatic Synthesis of Optically Active Aryl-Substituted Oxygen-Containing Heterocycles

Paola Vitale, Antonia Digeo, Filippo Maria Perna, Gennaro Agrimi, Antonio Salomone, Antonia Scilimati, Cosimo Cardellicchio, and Vito Capriati
Catalysts **2017**, 7, 37 (1–13).

DOI: 10.3390/catal7020037

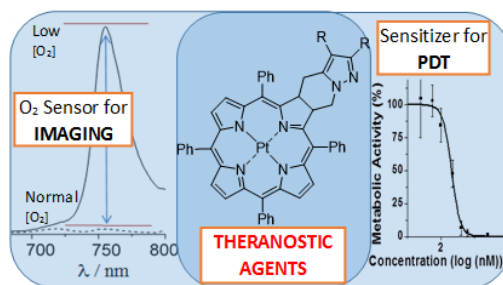


Abstract: A two-step stereoselective chemoenzymatic synthesis of optically active α -aryl-substituted oxygen heterocycles was developed, exploiting a whole-cell mediated asymmetric reduction of α -, β -, and γ -chloroalkyl arylketones followed by a stereospecific cyclization of the corresponding chlorohydrins into the target heterocycles. Among the various whole cells screened (baker's yeast, *Kluyveromyces marxianus* CBS 6556, *Saccharomyces cerevisiae* CBS 7336, *Lactobacillus reuteri* DSM 20016), baker's yeast was the one providing the best yields and the highest enantiomeric ratios (up to 95:5 er) in the bioreduction of the above ketones. The obtained optically active chlorohydrins could be almost quantitatively cyclized in a basic medium into the corresponding α -aryl-substituted cyclic ethers without any erosion of their enantiomeric integrity. In this respect, valuable, chiral non-racemic functionalized oxygen containing heterocycles (e.g., (*S*)-styrene oxide, (*S*)-2-phenyloxetane, (*S*)-2-phenyltetrahydrofuran), amenable to be further elaborated on, can be smoothly and successfully generated from their prochiral precursors.

Platinum(II) Ring-Fused Chlorins as Near-Infrared Emitting Oxygen Sensors and Photodynamic Agents

Nelson A. M. Pereira, Mafalda Laranjo, João Casalta-Lopes, Arménio C. Serra, Marta Piñeiro, João Pina, J. Sérgio Seixas de Melo, Mathias O. Senge, M. Filomena Botelho, Liliana Martelo, Hugh D. Burrows, and Teresa M. V. D. Pinho e Melo
ACS Med. Chem. Lett. **2017**, 8, 310–315.

DOI: 10.1021/acsmchemlett.6b00476



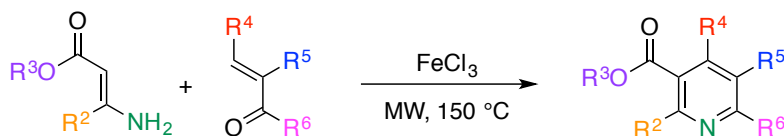
Abstract: Novel near-infrared luminescent compounds based on platinum(II) 4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine-fused chlorins are described. These compounds, have high photostability, and display light emission, in particular simultaneous fluorescence and phosphorescence emission in solution at room temperature, in the biologically relevant 700–850 nm red and near-infrared (NIR) spectral region, making them excellent materials for biological imaging. The simultaneous presence of fluorescence and phosphorescence emission at room temperature, with the phosphorescence strongly quenched by oxygen whereas fluorescence remains unaffected, allows these compounds to be used as ratiometric oxygen sensors in chemical and biological media. Both steady-state (fluorescence vs phosphorescence intensities) and dynamic (dependence of phosphorescence lifetimes upon oxygen concentration) luminescence approaches can be used. Photocytotoxicity studies against human melanocytic melanoma cells (A375) indicate that these compounds display potential as photosensitizers in photodynamic therapy.

Tailor-Made Synthesis of Fully Alkylated/Arylated Nicotinates by FeCl₃-Mediated Condensation of Enamino Esters with Enones

Sho Hirai, Yurie Horikawa, Haruyasu Asahara, and Nagatoshi Nishiwaki

Chem. Commun. **2017**, 53, 2390–2393

DOI: 10.1039/c7cc00051k



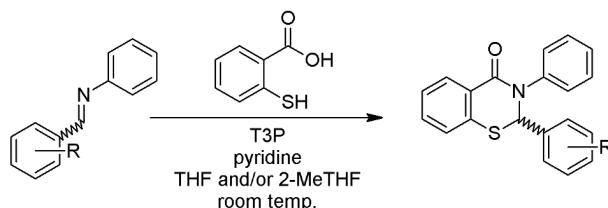
Abstract: A new method for synthesizing polyalkylated/arylated nicotinates is established using a condensation of enamino esters with enones in the presence of FeCl₃. This method facilitates the introduction of alkyl or aryl groups at any position on demand, which has not been achieved by other procedures.

Synthesis and Spectroscopic Properties of a Series of Novel 2-Aryl-3-phenyl-2,3-dihydro-4H-1,3-benzothiazin-4-ones

Lee J. Silverberg, Carlos Pacheco, Anthony Lagalante, John Tierney, Joshua T. Bachert, J. Austin Bayliff, Ryan V. Bendinsky, Aaron S. Cali, Liuxi Chen, Avril D. Cooper, Michael J. Minehan, Caitlin R. Mroz, Duncan J. Noble, Alexander K. Weisbeck, Yiwen Xie, and Ziwei Yang

ARKIVOC **2016**, vi 122–143.

DOI: <http://dx.doi.org/10.3998/ark.5550190.p009.875>



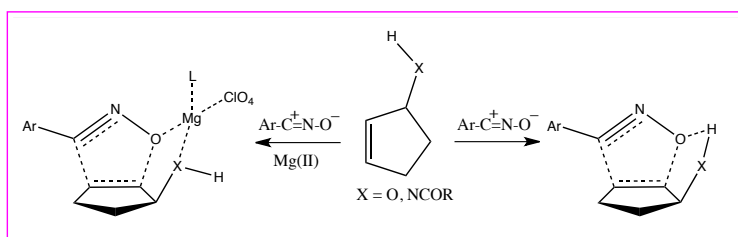
Abstract: A series of thirteen novel 2-aryl-3-phenyl-2,3-dihydro-4H-1,3-benzothiazin-4-ones was prepared at room temperature by T3P-mediated cyclization of *N*-phenyl-*C*-aryl imines with thiosalicylic acid. The spectral and physical properties are reported and discussed. ¹H-¹⁹F and ¹³C-¹⁹F couplings were observed in the NMR spectra of fluorinated compounds. Through-space interactions were observed in the ¹H and ¹³C NMR spectra of the *ortho*-nitro compound. Trends were observed in the IR and UV absorptions of the *ortho*/*meta*/*para*-nitro series.

The Hydrogen Bond Directing Effect in Nitrile Oxide Cycloadditions to Allylic Substituted Cyclopentenes

Anna Maria Cardarelli, Vera Fassardi, Misal Giuseppe Memeo, Paolo Quadrelli

Tetrahedron **2017**, 73, 2602–2613.

DOI: <http://dx.doi.org/10.1016/j.tet.2017.03.042>



Abstract: A quantitative evaluation of the H-bond directing effect on the stereoselectivity in the cycloaddition of nitrile oxides to 2-cyclopenten-1-ol and allylic cyclopentenyl amides is reported. In apolar solvents the H-bond directing effect promotes a high *syn* stereoselectivity while H-bond acceptor solvents divert the reactions to the *anti* face of the dipolarophile. Taft's β parameter gives a good description of the solvent effect on the H-bond directing effect. The persistence of some *syn* stereoselectivity even in good H-bond acceptor solvents points out the existence of some residual hydrogen bond direction. The *syn* stereoselectivity in the presence of M(II) salts was also investigated and the results discussed in the light of the potential application of these scaffolds in nucleoside synthesis.