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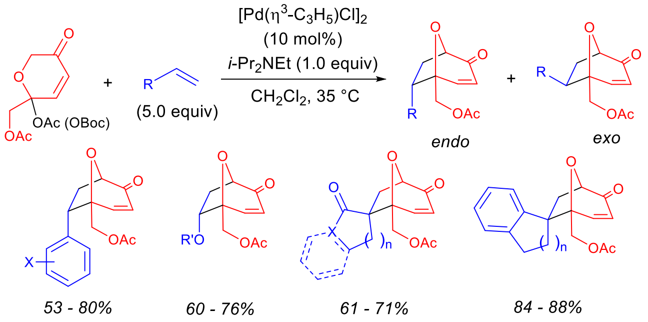
Efficient Generation of an Oxidopyrylium Ylide Using a Pd Catalyst and its [5+2] Cycloadditions with Several Dipolarophiles

Hiroyuki Suga, Taichi Iwai, Masahiro Shimizu, Kie Takahashi, and Yasunori Toda

Chem. Commun. **2018**, *54*, 1109–1112. **DOI:** 10.1039/c7cc09552j

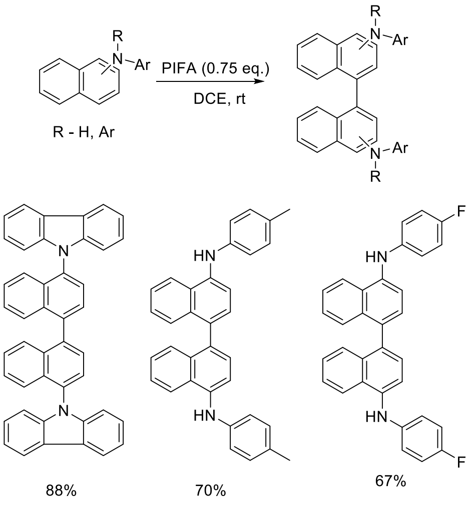


Abstract: An efficient method for the generation of an oxidopyrylium ylide from 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one using a Pd catalyst and [5+2] cycloadditions of the resulting ylide are described. Among substituted styrene derivatives as dipolarophiles, electron-rich styrenes showed higher yield (up to 80%). The [5+2] cycloaddition reactions can also be applied to *exo*-methylene cyclic compounds, and an improved method for the synthesis of polygalolide intermediate has been demonstrated.

Oxidative Biaryl Coupling of *N*-Aryl Anilines by Using a Hypervalent Iodine(III) Reagent

Koji Morimoto, Daichi Koseki, Toshifumi Dohi, and Yasuyuki Kita

Synlett **2017**, *28*, 2941–2945. **DOI:** 10.1055/s-0036-1590875

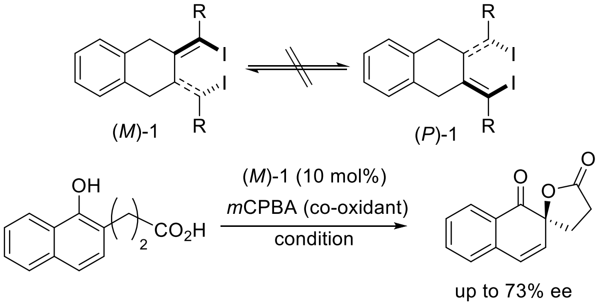


Abstract: The biaryl diamines are important building blocks in organic synthesis. Thus, it is desirable to develop a general and mild synthetic approach to diverse biaryl diamines. The oxidative coupling is an efficient and promising strategy to synthesize these targets. We have developed the direct formations of biaryl diamines by an oxidative coupling using the hypervalent(III) iodine reagent.

Atropisomeric Chiral Diiododienes (*Z*,*Z*)-2,3-Di(1-iodoalkylidene)tetralins: Synthesis, Enantiomeric Resolution, and Application in Asymmetric Catalysis

Masamichi Ogasawara, Hirotaka Sasa, Hao Hu, Yuta Amano, Hikaru Nakajima, Naoko Takenaga, Kiyohiko Nakajima, Yasuyuki Kita, Tamotsu Takahashi, and Toshifumi Dohi

Org. Lett. **2017**, *19*, 4102–4105. **DOI:** 10.1021/acs.orglett.7b01876

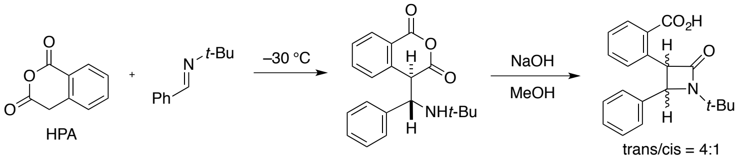


Abstract: The C_2-symmetric tetralin-fused 1,4-diiodo-1,3-butadiene derivatives, (*Z*,*Z*)-2,3-di(1-iodoalkylidene)tetralin, are atropisomeric and can be resolved into the two persistent axially chiral enantiomers by HPLC on a chiral stationary phase. The enantiomerically pure compounds can serve as chiral organocatalysts for dearomatizing spirolactonization to show good performance in up to 73% ee.

Stereochemistry and Reactivity of the HPA-imine Mannich Intermediate

Daniel Polyak, Ngan Phung, Jian Liu, Robert Barrows, Thomas J. Emge, and Spencer Knapp

Tetrahedron Lett. **2017**, *58*, 3879–3883. **DOI:** 10.1016/j.tetlet.2017.08.070

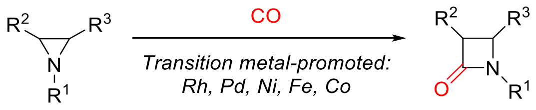


Abstract: Homophthalic anhydride (HPA) typically reacts rapidly with benzalimines to afford the formal [4+2] adduct, a 1,2,3,4-tetrahydroisoquinolin-1-one-4-carboxylic acid. The stereochemical outcome of this reaction is consistent with an open transition state comprising an iminium species and enolized HPA, leading to a short-lived amino-anhydride intermediate. In the case of *N-tert*-butylbenzalimine, this Mannich-type intermediate, which would normally cyclize at low temperature to a single isomer of the *delta*-lactam, is intercepted by base treatment to afford *beta*-lactam products. A pathway featuring ketene formation followed by ring closure is implicated.

Carbonylation of Aziridines as a Powerful Tool for the Synthesis of Functionalized β-lactams

Nicola Piens and Matthias D'hooghe

Eur. J. Org. Chem. **2017**, 5943–5960. **DOI:** 10.1002/ejoc.201700698

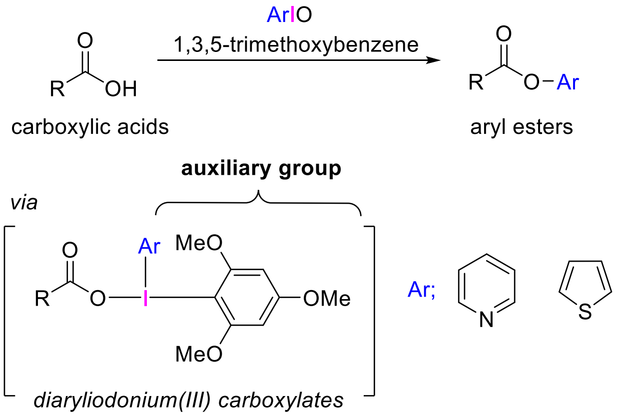


Abstract: In light of the emerging interest in the preparation of azetidin-2-ones via carbonylative methods as a green alternative for the conventional methodologies, a comprehensive overview of different transition metal-promoted aziridine-to-azetidin-2-one carbonylations is provided in this microreview.

Metal-Free *O*-Arylation of Carboxylic Acid by Active Diaryliodonium(III) Intermediates Generated *in situ* from Iodosoarenes

Toshifumi Dohi, Daichi Koseki, Kohei Sumida, Kana Okada, Serina Mizuno, Asami Kato, Koji Morimoto, and Yasuyuki Kita

Adv. Synth. Catal. **2017**, *359*, 3503–3508. **DOI:** 10.1002/adsc.201700843

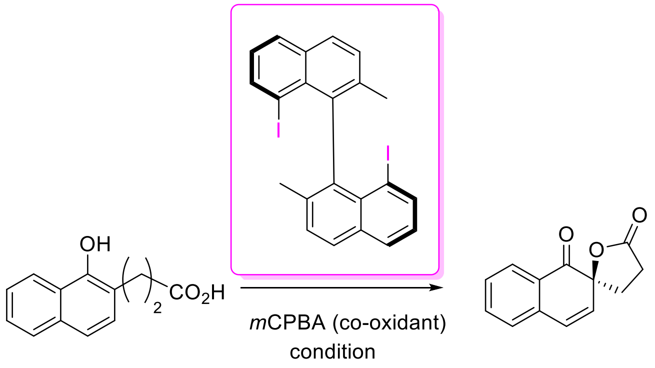


Abstract: The metal-free arylative coupling of carboxylic acids using iodosoarenes without the use of a catalyst and base, which is applicable to even a highly-polar molecule bearing multiple alcohol groups, is reported. The *in situ* preparation of the reactive diaryliodonium(III) carboxylates is the important key to this approach, and the introduction of the trimethoxybenzene auxiliary enables both the smooth salt formations and the selective aryl transfer events during the couplings.

Chiral Atropisomeric 8,8′- Diiodobinaphthalene for Asymmetric Dearomatizing Spirolactonizations in Hypervalent Iodine Oxidations

Toshifumi Dohi, Hirotaka Sasa, Keitaro Miyazaki, Mihoyo Fujitake, Naoko Takenaga, and Yasuyuki Kita

J. Org. Chem. **2017**, *82*, 11954–11960. **DOI:** 10.1021/acs.joc.7b02037

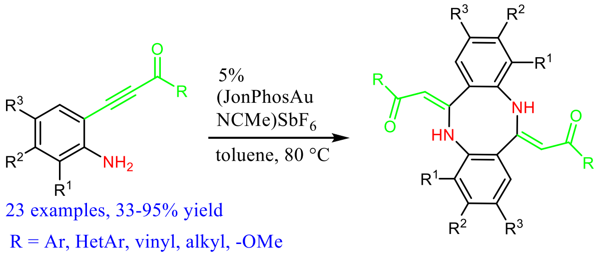


Abstract: A new type of binaphthyl-based chiral iodide functionalized at positions 8 and 8′ of the naphthalene rings has been found as a promising structural motif for the asymmetric hypervalent iodine(III) oxidations, specifically, for the dearomatizing spirocyclization of naphthol carboxylic acids showing expectedly better enantioselectivities versus other atropisomeric biaryls, i.e., a conventionally used binaphthalene having the diiodides in the minor groove.

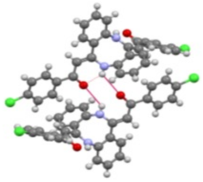
Gold-Catalyzed Synthesis of Dibenzo[1,5]diazocines from β-(2-Aminophenyl)-α,β-ynones

Navnath D. Rode, Antonio Arcadi, Marco Chiarini, Fabio Marinelli, and Gustavo Portalone

Adv. Synth. Catal. **2017**, *359*, 3371–3377. **DOI:** 10.1002/adsc.201700694



x-ray structure:

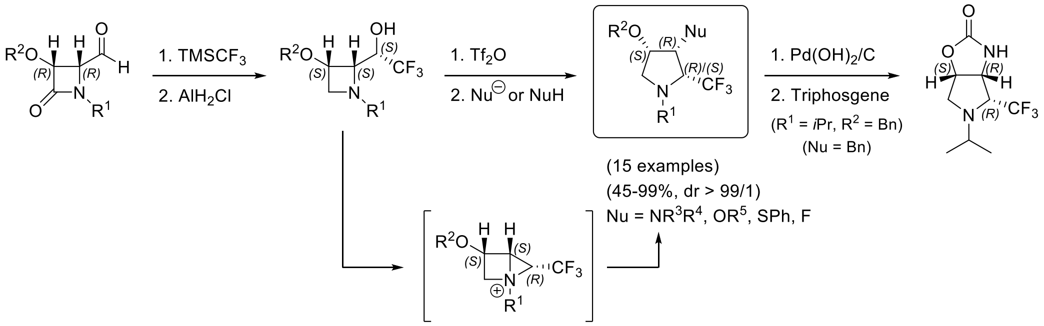


Abstract: β-(2-Aminophenyl)-α,β-ynones afforded exclusively challenging dibenzo [1,5]diazocines by means of (JonPhosAuNCMe)SbF$_6$ catalysis. In contrast with the known Au-catalyzed reaction path of 2-alkynylanilines that leads to indoles, ynones underwent an auto intermolecular hydroamination. This process resulted finally in the formation of an eight-membered ring, likely through a selective *8-exo-dig* intramolecular hydroamination that prevailed over the possible cyclocondensation reaction (that would result in the formation of 4-aminoquinoline derivatives). The easy availability of β-(2-aminophenyl)-α,β-ynones and the simple cyclization procedure make this approach suitable for the preparation of a wide range of useful dibenzodiazocines . The methodology can be extended to the use of β-(2-aminophenyl)-α,β-ynoates as substrates.

Asymmetric Synthesis of 3,4-Disbustituted 2-(Trifluoromethyl)pyrrolidines through Rearrangement of Chiral 2-(2,2,2-Trifluoro-1-hydroxyethyl)azetidines

Jeroen Dolfen, Esma Birsen Boydas, Veronique Van Speybroeck, Saron Catak, Kristof Van Hecke, and Matthias D'hooghe

J. Org. Chem. **2017**, *82*, 10092–10109. **DOI:** 10.1021/acs.joc.7b01241

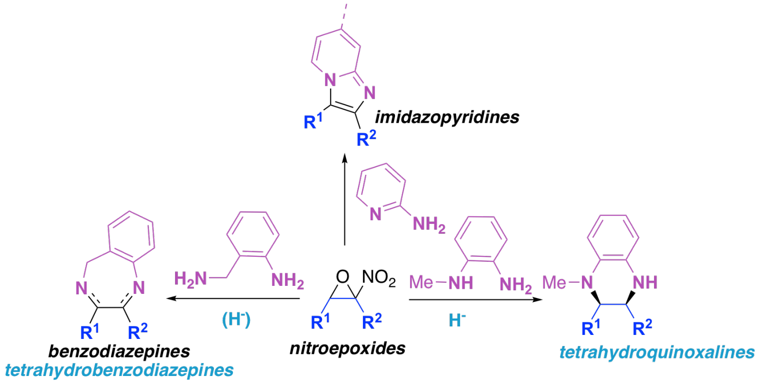


Abstract: Enantiopure 4-formyl-β-lactams were deployed as synthons for the diastereoselective formation of chiral 2-(2,2,2-trifluoro-1-hydroxyethyl)azetidines via trifluoromethylation through aldehyde modification followed by reductive removal of the β-lactam carbonyl moiety. Subsequent treatment of the (*in situ*) activated 2-trifluoroethylated azetidines with a variety of nitrogen, oxygen, sulfur and fluorine nucleophiles afforded chiral 3,4-disubstituted 2-(trifluoromethyl)pyrrolidines in good to excellent yields (45–99%) and high diastereoselectivities (dr > 99/1, ^{1}H NMR) via interception of bicyclic aziridinium intermediates. Furthermore, representative pyrrolidines were *N*,*O*-debenzylated in a selective way and used for further synthetic elaboration to produce e.g. a CF$_3$-substituted 2-oxa-4,7-diazabicyclo[3.3.0]octan-3-one system.

Regioselective Opening of Nitroepoxides with Unsymmetrical Diamines

Yazdanbakhsh L. Nosood, Azim Ziyaei Halimehjani, and Florenci V. González

J. Org. Chem. **2018**, *83*, 1252–1258. **DOI:** 10.1021/acs.joc.7b02795

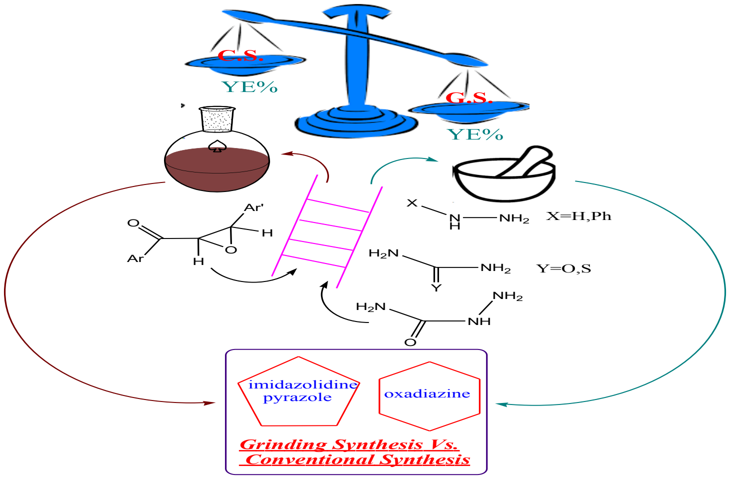


Abstract: Nitroepoxides are easily transformed into benzodiazepines, tetrahydrobenzodiazepines, imidazopyridines, and *N*-alkyl tetrahydroquinoxalines by treatment with 2-aminobenzylamines, 2-aminopyridines and *N*-alkyl 1,2-diaminobenzenes respectively. Regioselectivity is controlled through attack of the most nucleophilic nitrogen of the unsymmetrical diamine to the β-position of the epoxide. These reactions represent an efficient way to prepare privileged bioactive structures.

Synthesis of *N*-Containing Heterocycles *via* Mechanochemical Grinding and Conventional Techniques

Amin F. M. Fahmy, Amira A. El-Sayed, Magdy M. Hemdan, Aya I. Hassaballah, and Ahmed F. Mabied

Asian J. Chem. **2017**, *29*, 2679–2686. **DOI:** 10.14233/ajchem.2017.20798



Abstract: Mechano heterocyclic chemistry (MHC) is a recent, quickly growing technique that draws the attention of hetrocyclic chemists towards the use of grindstone technique in a solvent free green efficient clean synthesis of many heterocyclic systems. α,β-Epoxy ketones were used as a unique scaffold for synthesis of stable hydroxyazoles. The key advantage of grinding technique over the conventional thermal technique includes its simple, solvent-free conditions, as well as facile work up with high yield economy (YE). It is also successful in achieving three of the green chemistry objectives of a solvent free, high atom economy, save energy thus combining the features of both economic and environmental advantages.