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Coupling-Isomerization-Cycloisomerization Reaction (CICIR) – An Unexpected and Efficient Domino Approach to Luminescent 2-(Hydroxymethylene)indenones

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Eur. J. Org. Chem. **2019**, 7058–7062.

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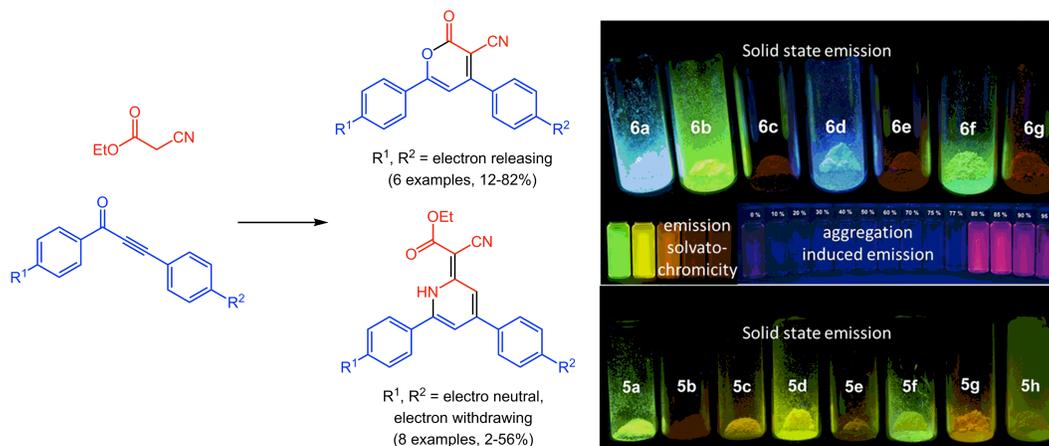
Abstract: A Pd/Cu-catalyzed base mediated domino process of *ortho*-halo (hetero)aryl carboxaldehydes and propargyl alcohols unexpectedly furnish 2-(hydroxymethylene)indenones in good to excellent yield as a result of a coupling-isomerization-cycloisomerization reaction (CICIR). In addition, the title compounds constitute an interesting class of luminophores with tunable emission solvatochromicity.

Emission Solvatochromic, Solid-State and Aggregation-Induced Emissive α -Pyrone and Emission-Tuneable 1*H*-Pyridines by Michael Addition–Cyclocondensation Sequences

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Beilstein J. Org. Chem. **2019**, 15, 2684–2703.

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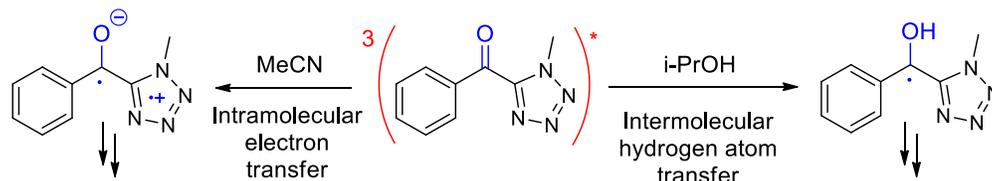
Abstract: Starting from substituted alkynones, α -pyrones and/or 1*H*-pyridines were generated in a Michael addition–cyclocondensation with ethyl cyanoacetate. The peculiar product formation depends on the reaction conditions as well as on the electronic substitution pattern of the alkynone. While electron-donating groups furnish α -pyrones as main products, electron-withdrawing groups predominantly give the corresponding 1*H*-pyridines. Both heterocycle classes fluoresce in solution and in the solid state. In particular, dimethylamino-substituted α -pyrones, as donor-acceptor systems, display remarkable photophysical properties, such as strongly red-shifted absorption and emission maxima with daylight fluorescence and fluorescence quantum yields up to 99% in solution and around 11% in the solid state, as well as pronounced emission solvatochromism. Also a donor-substituted α -pyrone shows pronounced aggregation-induced emission enhancement.

Photochemical Reactivity of Phenyl (Methyl-tetrazolyl) Ketone – Hydrogen Atom Transfer vs. Electron Transfer

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New J. Chem. **2019**, *43*, 17151–17158.

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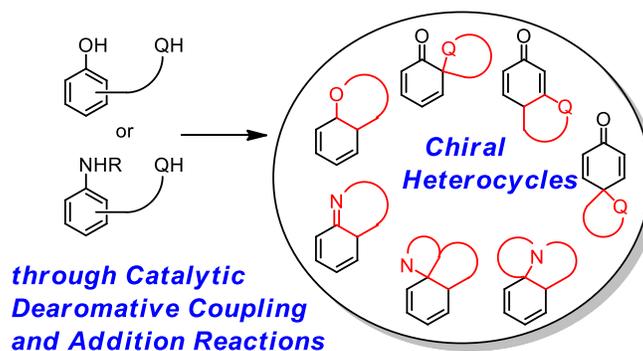
Abstract: Phenyl (methyl-tetrazolyl) ketone (**1**) is a synthesis intermediate of tetrazolyloxime fungicides and can also be generated upon their irradiation. Its photolysis is highly solvent-dependent which prompted us to investigate the reaction mechanism more deeply. The nanosecond laser flash photolysis of **1** yielded the triplet excited state ($\lambda_{\text{max}} = 390/570$ nm) immediately after the pulse. This was later converted into different secondary species that were identified using their specific reactivity as well as product studies. The ketyl radical ($\lambda_{\text{max}} = 315/475$ nm) was generated in less than $0.02 \mu\text{s}$ in a good H-donor solvent such as 2-propanol and in around $0.06 \mu\text{s}$ in cyclohexane, a medium H-donor solvent. In 2-propanol, ketyl radicals decayed by a second order reaction to yield pinacol (yield 45%); in contrast, in cyclohexane, they decayed by a second order reaction in the bulk leading to the pinacol (yield 21%) and by recombination with the cyclohexyl radical in the cage in an apparent first order reaction to generate an adduct (yield 10%). In a polar and non H-atom donor solvent such as acetonitrile, the zwitterionic diradical ($\lambda_{\text{max}} = 460$ nm) was formed in $0.6 \mu\text{s}$ with the formation of the final atypical dimer. Thus two mechanisms of hydrogen atom transfer were observed. In the polar acetonitrile solvent, a two-step-process occurred where an electron was transferred first followed by a proton. In less polar 2-propanol and non-polar cyclohexane solvents, a one-step process occurred where an electron and a proton were simultaneously transferred.

Asymmetric Construction of Heterocycles via Dearomative Coupling and Addition Reactions Phenol and Aniline Derivatives

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Heterocycles **2019**, *98*, 1489–1511.

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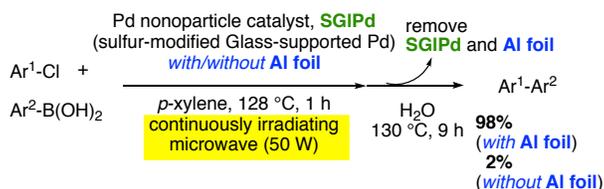


Abstract: Efficient methods for the formation of chiral heterocycles are considerably important in the synthesis of naturally-occurring compounds and pharmaceutical products. This review highlights the formation of chiral heterocycles through dearomative bond-formations as the key reactions, wherein the phenol or aniline derivatives serve as the nucleophiles. Transition-metal-catalyzed intramolecular coupling reactions in the presence of chiral ligands afford the enantioenriched multicyclic compounds bearing heterocycles. Chiral bifunctional organocatalysts induce the formation of dearomative coupling products, which could be converted to heterocycles through further transformations.

Ligand-free Suzuki–Miyaura Coupling Reaction of an Aryl Chloride Using a Continuous Irradiation Type Microwave and a Palladium Nanoparticle Catalyst: Effect of a Co-existing Solid

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Green Chem. **2019**, *21*, 4541–4549.

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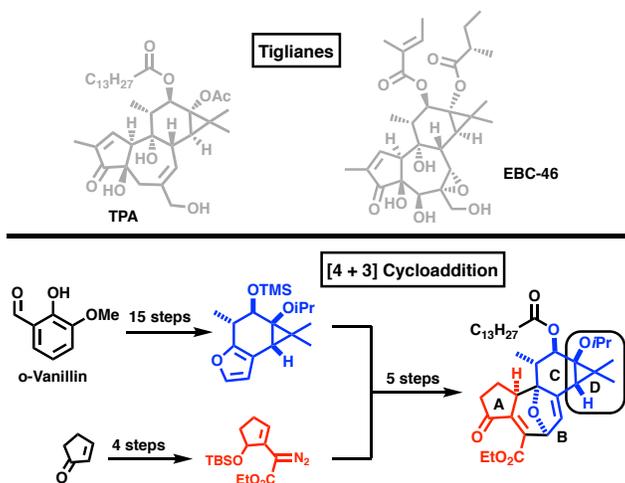
A co-existent solid, **Al foil**, plays a key role in ligand-free Suzuki–Miyaura coupling using **SGIPd** and **continuously microwave irradiation**.

Abstract: We have explored the effect of a co-existing metal in the ligand-free Suzuki–Miyaura coupling reaction of an aryl chloride, which is promoted by a “continuous irradiation type microwave” and a “palladium nanoparticle catalyst”, and found that the co-existing metal affects this reaction due to its absorption ability of microwave energy in the reaction system. We also observed that spiking occurred more frequently in the presence of a co-existing metal.

En Route to D-Ring Inverted Phorbol Esters

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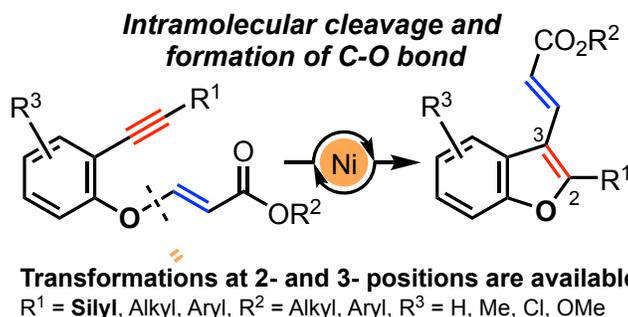


Abstract: The tiglane ring system, highlighted by phorbol esters, were long considered tumor promoters, via protein kinase C (PKC) activation (e.g. 12-*O*-tetradecanoylphorbol-13-acetate, PMA or TPA). More recently, however, highly oxidized tiglanes (e.g. tiglane tiglate, EBC-46) have paradoxically demonstrated strong anti-tumor activity. In broad consideration of the fact that, only limited synthetic investigation toward skeletal stereochemical modification has been undertaken to date, ready access to non-natural systems would provide the ability to probe PKC isoforms and gain a better understanding of the phorbol ester pharmacophore. Concise construction of a considerably advanced intermediate towards D-ring inverted phorbol esters, was recently reported, enabled by a rhodium-catalyzed [4+3] cycloaddition. A feature of the synthesis, and the key cycloaddition reaction, was the construction and utilization of a highly functionalized tetrahydrobenzofuran.

Ni-Catalyzed Cycloisomerization between 3-Phenoxy Acrylic Acid Derivatives and Alkynes via Intramolecular Cleavage and Formation of the C–O Bond to Give 2,3-Disubstituted Benzofurans

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Org. Lett. **2019**, *21*, 8400–8403.

DOI: 10.1021/acs.orglett.9b03170



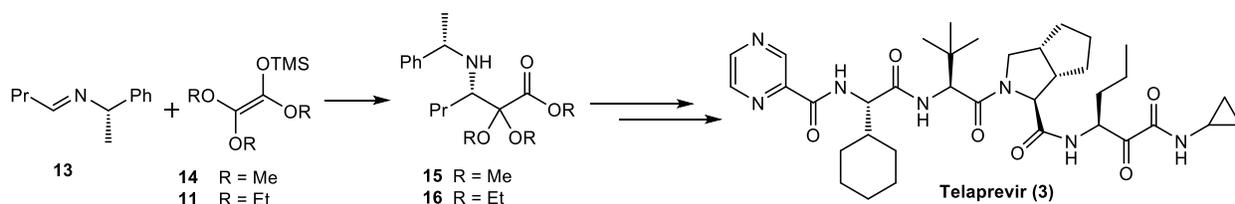
Abstract: Reactions based on transition-metal-catalyzed C–O bond cleavage have attracted much attention as a new synthetic method. Until now, several intermolecular reactions via C–O bond cleavage of aryl ethers, alkenyl ethers, esters, and others have been reported. Here we report an unprecedented C–O bond cleavage of 3-phenoxy acrylic acid derivatives, followed by intramolecular C–O bond formation with alkynes. This reaction gave 2,3-disubstituted benzofurans having useful functional groups—silyl substituents and acrylic acid derivatives—at the 2- and 3-positions, respectively. This report also described theoretical (DFT) insights into the mechanism.

Stereoselective Synthesis of β -Amino Acids by Aldol-Type Addition

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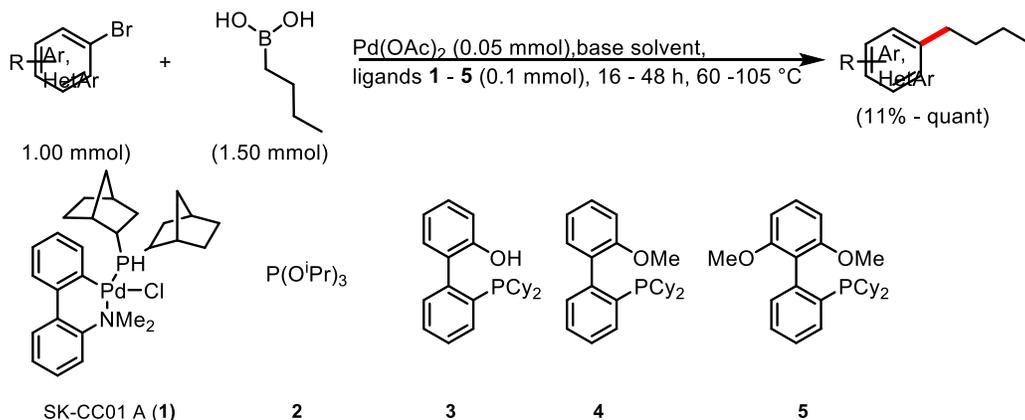
Abstract: A synthesis of α -oxygenated β -amino acid derivatives using an aldol-type addition is described. Depending on the enol equivalent different oxidation states of the oxygen substituent are accessible, while choosing a chiral imine allows to generate the aldol product in a stereoselective manner. This methodology has been applied to the synthesis of the biologically active compound Telaprevir, used in the treatment of Hepatitis C.

Ligand Assessment for the Suzuki–Miyaura Cross Coupling Reaction of Aryl and Heteroaryl Bromides with *n*-Butylboronic Acid. The Advantages of Buchwald’s *S*-Phos

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DOI: 10.3987/COM-19-S(F)54



Abstract: An investigation of biarylphosphine ligands for the Suzuki–Miyaura cross coupling reaction of aryl and heteroaryl bromides with *n*-butylboronic acids is presented. The obtained results on ligand modification and aryl as well as heteroaryl bromides variation represent a significant improvement in the state of the art of alkylboronic acid cross coupling methodology:

- Ligand **5** functions well across base/solvent combinations
- Ligands **3** and **4** are commercially available
- Non-chromatography dependent processing of reactions