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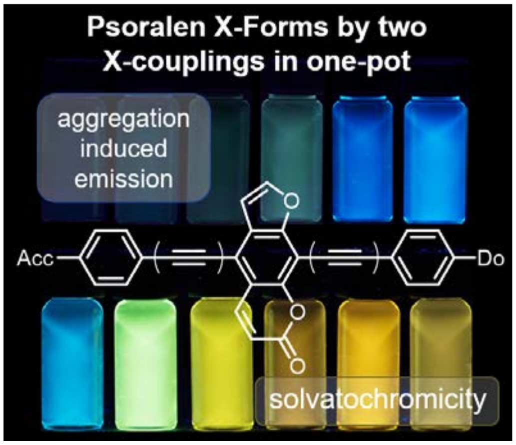
Fluorescent Donor-Acceptor-Psoralen Cruciforms by Consecutive Suzuki–Suzuki and Sonogashira–Sonogashira One-Pot Synthesis

Sarah R. Geenen, Torben Schumann, and Thomas J. J. Müller*(thomasjj.mueller@hhu.de)

J. Org. Chem. **2020**, *85*, 9737–9750. **DOI:** 10.1021/acs.joc.0c01059



Abstract: Two novel donor–acceptor cruciform topologies are efficiently synthesized by site-selective Suzuki–Suzuki and Sonogashira–Sonogashira multicomponent reactions starting from a bromo-triflate-functionalized psoralen scafford. In addition to tunability of photophysical properties, such as absorption and emission, many derivatives possess partially high relative fluorescence quantum yields in solution and fluoresce strongly in the solid state. Additionally, the promising compounds show solvatochromism and acidochromic effects. In addition, 8-*p*-anisyl-5-*p*-cyanophenyl-substituted psoralen exhibits aggregation-induced emission properties. Experimentally (applying the Lippert–Mataga model) and computationally (TD-DFT calculations), the pronounced charge transfer character of the longest wavelength absorption band was confirmed

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Studies of the Enantiocontrolled Synthesis of the C(10)–C(25) Subunit of Amphidinolide C

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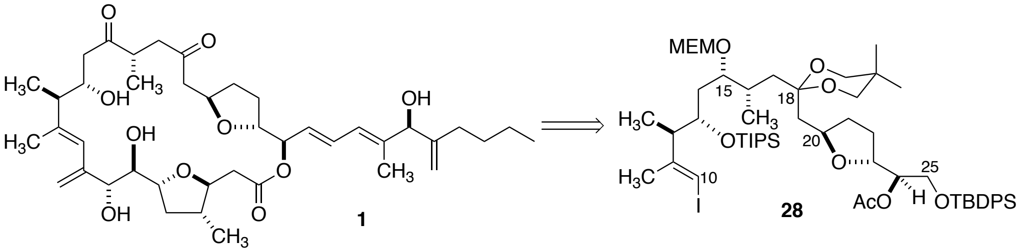
Org. Lett. **2020**, *22*, 4118–4122. **DOI:** 10.1021/acs.orglett.0c01177



Abstract: A stereocontrolled synthesis of **28**, the C(10)–C(25) component of amphidinolide C (**1**), has been efficiently achieved. Reaction of the dithiane component **21** with nonracemic bis(epoxide) **19** directly affords functionalized 2,5-*trans*-disubstituted tetrahydrofuran **22**. Propargylation is highly diastereoselective for the formation of the desired C(12)–C13 *anti* stereochemistry, and the resulting terminal alkyne **25** is utilized for a regioselective *syn*-silylstannylation. A general strategy is illustrated for sequential replacement of stannyl and silyl substituents of the trisubstituted alkene to yield (*E*)-alkenyl iodide **28**.

Functionalized Magnetic PAMAM Dendrimer as an Efficient Nanocatalyst for a New Synthetic Strategy of Xanthene Pigments

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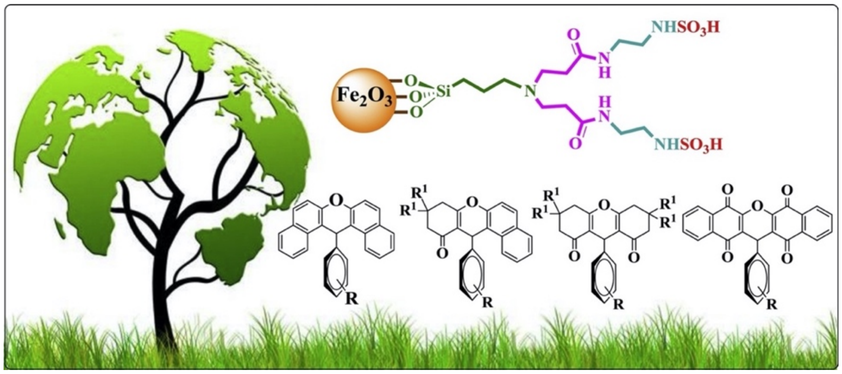
J. Hazard. Mater. **2020**, *400*, 122985 (1–23). **DOI:** 10.1016/j.jhazmat.2020.122985



Abstract: A green protocol has been developed for preparation of the wide variety of colored xanthene derivatives using a new efficient magnetic solid acid catalyst bearing polyamidoamine dendrimer moiety as a nanoscopic compound. Dendrimers, highly symmetric molecules around a core and 3D spherical morphology, show interesting traits based on their functionalized groups on the branched surface. They can be designed to provide water soluble structures or pseudo-active sites of biomolecules. The catalyst was assembled *via* a polyamidoamine dendrimer immobilized on the surface of γ-Fe_2O_3 followed by the sulfonylation of the amine groups by chlorosulfonic acid resulting in γ-Fe_2O_3@PAMAM-SO_3H. Herein, PAMAM dendrimer with repeating amine/amide branches as catchable sites of sulfonic acid groups was introduced as transformer of homogeneous to heterogeneous acidic catalysts. The physicochemical properties of synthesized catalyst were studied using by FT-IR, FE-SEM, XRD, VSM, EDS, TGA/DTG, and TEM. Finally, the catalytic activity of γ-Fe_2O_3@PAMAM-SO_3H was evaluated for the preparation of xanthene derivatives *via* a one-pot, three components reaction of aromatic aldehydes with *i)* β-naphthol, *ii)* cyclic 1,3-dicarbonyl, *iii)* β-naphthol and cyclic 1,3-dicarbonyl compounds, *iv)* 2-hydroxy-1,4-naphthoquinone, leading to the eco-friendly preparation of the target compounds in good to excellent yields. The catalyst could be easily recycled for at least five consecutive runs without significant loss in its catalytic activity.

Comparison of Substituting Ability of Nitronate versus Enolate for Direct Substitution of a Nitro Group

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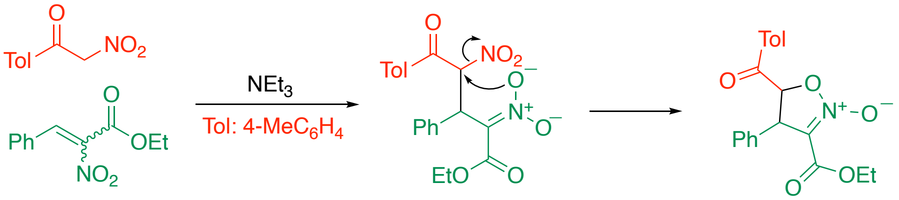
Molecules **2020**, *25*, 2048 (1–9). **DOI:** 10.3390/molecules25092048



Abstract: α-Nitrocinnamate underwent the conjugate addition of an active methylene compound such as nitroacetate, 1,3-dicarbonyl compound, or α-nitroketone, and the following ring closure afforded functionalized heterocyclic frameworks. The reaction of cinnamate with nitroacetate occurs via nucleophilic substitution of a nitro group by the *O*-attack of the nitronate, which results in isoxazoline *N*-oxide. This protocol was applicable to 1,3-dicarbonyl compounds to afford dihydrofuran derivatives, including those derived from direct substitution of a nitro group caused by *O*-attack of enolate. It was found the reactivity was lowered by an electron-withdrawing group on the carbonyl moiety. When α-nitroketone was employed as a substrate, three kinds of products were possibly formed; of these, only isoxazoline *N*-oxide was identified. This result indicates that the substituting ability of nitronate is higher than that of enolate for the direct S_N2 substitution of a nitro group.

Effect of Reaction Media on Photosensitized [2+2]-Cycloaddition of Cinnamates

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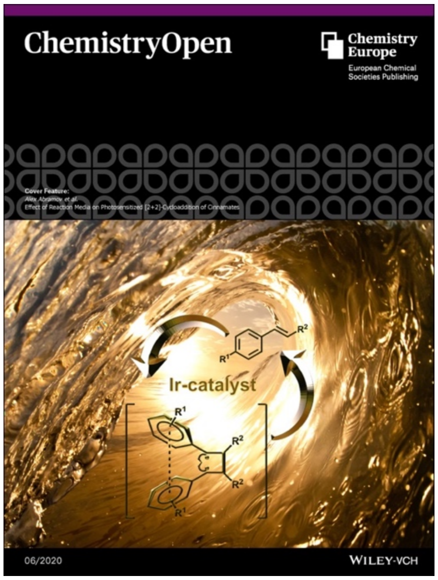
ChemistryOpen **2020**, *9*, 649–656. **DOI:** 10.1002/open.202000092



Abstract: The outcome of photosensitized [2+2]-cycloaddition reactions of various cinnamates has been compared in different reaction media, including homogeneous organic solutions under inert conditions, degassed water, and aerated physical gels. The reactions were performed under LED blue light (λ_{max}=455 nm) irradiation and $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1.0 mol%) as photocatalyst. The processes were optimized taking into consideration solvent, gelator, and substrate. Comparative kinetics analyses, as well as the effect of the reaction media on the diastereoselectivity of the process, were evaluated during this investigation. In a number of cases, carrying out the reaction in a less polar solvent, like toluene or highly polar solvent, like water had a tremendous impact on the diastereoselectivity of the process, pointing towards an effect on the stabilization of the putative diradical intermediate in this medium. Moreover, while for reactions run in homogeneous solution oxygen needs to be excluded, no erosion in yield is observed when the photoadditions were run in aerated gel media.

N-Heterocyclic Carbene Based Catalytic Platform for Hauser–Kraus Annulations

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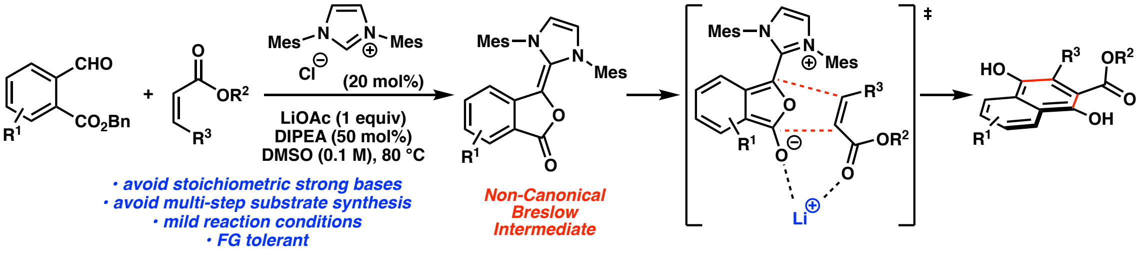
Chem. Sci. **2020**, *11*, 7239–7243. **DOI:** 10.1039/d0sc03116j



Abstract: The venerable Hauser–Kraus annulation is an effective and convergent method for generating oxygenated polycyclic aromatic compounds. Despite its application in complex molecule synthesis, the harsh and strongly basic conditions can limit its utility in more functionalized molecular settings. We have developed the first catalytic Hauser–Kraus annulation based on *N*-heterocyclic carbene catalysis that proceeds under milder conditions. We demonstrate the scope of the transformation in the presence of several functional groups. We also propose a concerted mechanism for the annulation that proceeds through a non-canonical Breslow intermediate.

Direct Evidence of Visible Light-Induced Homolysis in Chlorobis(2,9-dimethyl-1,10-phenanthroline)copper(II)

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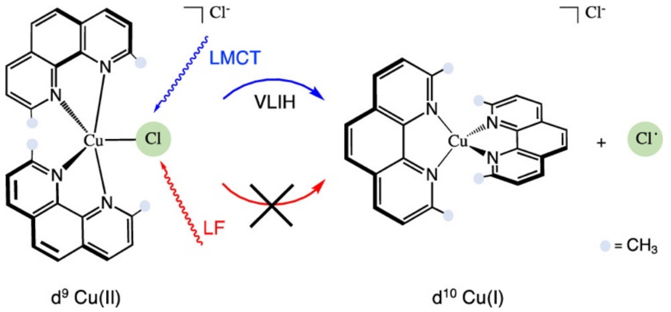
J. Phys. Chem. Lett. **2020**, *11*, 5345–5349. **DOI:** 10.1021/acs/jpclett.0c01601

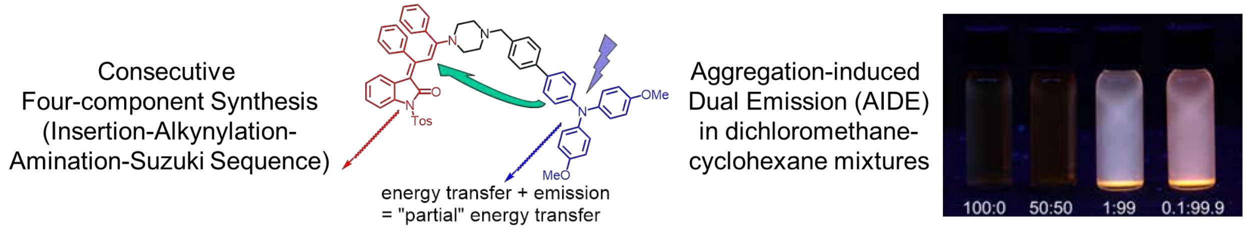


Abstract: Developments in the field of photoredox catalysis that leveraged the long-lived excited states of Ir(III) and Ru(II) photosensitizers to enable radical coupling processes paved the way for explorations of synthetic transformations that would otherwise remain unrealized. While first row transition metal photocatalysts have not been as extensively investigated, valuable synthetic transformations covering broad scopes of olefin functionalization have been recently reported featuring photoactivated chlorobis(phenanthroline) Cu(II) complexes. In this study, the photochemical processes underpinning the catalytic activity of [Cu(dmp)$_2$Cl]Cl (dmp = 2,9-dimethyl-1,10-phenanthroline) were studied. The combined results from static spectroscopic measurements and conventional photochemistry, ultrafast transient absorption, and electron paramagnetic resonance spin trapping experiments strongly support blue light (λ_{ex} = 427 or 470 nm)-induced Cu–Cl homolytic bond cleavage in [Cu(dmp)$_2$Cl]$^+$ occurring in <100 fs. On the basis of electronic structure calculations, this bond-breaking photochemistry corresponds to the Cl → Cu(II) ligand-to-metal charge transfer transition, unmasking a Cu(I) species [Cu(dmp)$_2$]$^+$ and a Cl atom, thereby serving as a departure point for both Cu(I)- or Cu(II)-based photoredox transformations. No net photochemistry was observed through direct excitation of the ligand-field transitions in the red (λ_{ex} = 785 or 800 nm), and all combined experiments indicated no evidence of Cu–Cl bond cleavage under these conditions. The underlying visible light-induced homolysis of a metal–ligand bond yielding a one-electron-reduced photosensitizer and a radical species may form the basis for novel transformations initiated by photoinduced homolysis featuring *in situ*-formed metal–substrate adducts utilizing first row transition metal complexes.

One-Pot Synthesis of a White-Light Emissive Bichromophore Operated by Aggregation-Induced Dual Emission (AIDE) and Partial Energy Transfer

Melanie Denißen, Ricarda Hannen, Dana Itskalov, Lukas Biesen, Nithiya Nirmalananthan-Budau, Katrin Hoffmann, Guido J. Reiss, Ute Resch-Genger,* and Thomas J. J. Müller* (ute.resch@bam.de or thomasjj.mueller@hhu.de)

Chem. Commun. **2020**, *56*, 7407–7410. **DOI:** 10.1039/d0cc03451g

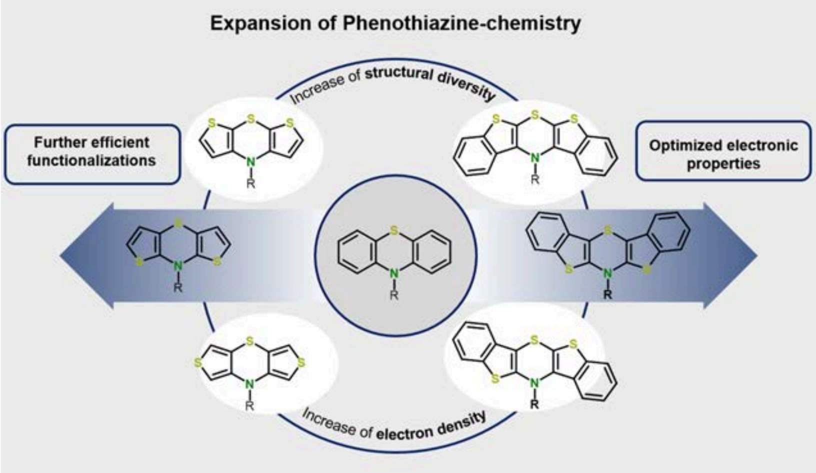


Abstract: Merocyanine-triarylamine bichromophores are readily synthesized by sequentially Pd-catalyzed insertion-alkynylation-Michael–Suzuki four-component reactions. White light emissive systems form upon aggregation in 1:99 and 0.1:99.9 vol% CH$_2$Cl$_2$-cyclohexane mixtures, ascribed to aggregation-induced dual emission (AIDE) in combination with partial energy transfer between both chromophore units as supported by spectroscopic studies.

Dithieno[1,4]thiazines and Bis[1]benzothieno[1,4]thiazines – Organometallic Synthesis and Functionalization of Electron Density Enriched Congeners of Phenothiazine

Lars May and Thomas J. J. Müller* (thomasjj.mueller@uni-duesseldorf.de)

Molecules **2020**, *25*, 2180 (1–16). **DOI:** 10.3390/molecules25092180



Abstract: This mini-review summarizes the syntheses and functionalizations of dithieno[1,4]thiazines and bis[1]benzothieno[1,4]thiazines, both electron density-enriched congeners of phenothiazines with remarkable electronic properties. Diversity-oriented, straightforward, and efficient syntheses, including versatile one-pot processes, have been developed for the anellated 1,4-thiazines as well as various functionalization for the expansion of the π-systems. Thereby, syntheses of different regioisomers depending on the (benzo)thieno-thiazine anellation are discussed, which exert a deep impact on the electronic properties. The tunable photophysical and electrochemical properties of dithieno[1,4]thiazines and bis[1]benzothiene[1,4]thiazines outscore phenothiazines on many points and promise an enormous potential in molecular electronics and applications beyond.

Solid State Emossove Aroyl-*S*,*N*-Ketene Acetals with Tunable Aggregation-Induced Emission Characteristics

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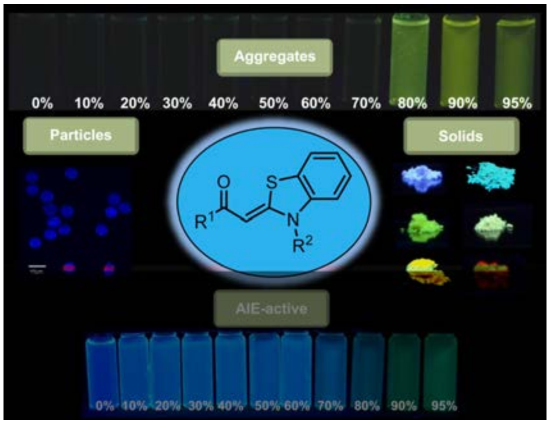
Angew. Chem. Int. Ed. **2020**, *59*, 10037–10041. **DOI:** 10.1002/anie.201916396



Abstract: *N*-Benzyl aroyl-*S*,*N*-ketene acetals can be readily synthesized by condensation of aroyl chlorides and *N*-benzyl 2-methyl benzothiazolium salts in good to excellent yields, yielding a library of 35 chromophores with bright solid-state emission and aggregation-induced emission characteristics. Varying the substituent from electron-donating to electron-withdrawing enables the tuning of the solid-state emission color from deep blue to red.

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Recent Progress Toward the Asymmetric Synthesis of Carbon-Substituted Piperazine Pharmacophores and Oxidative Related Heterocycles

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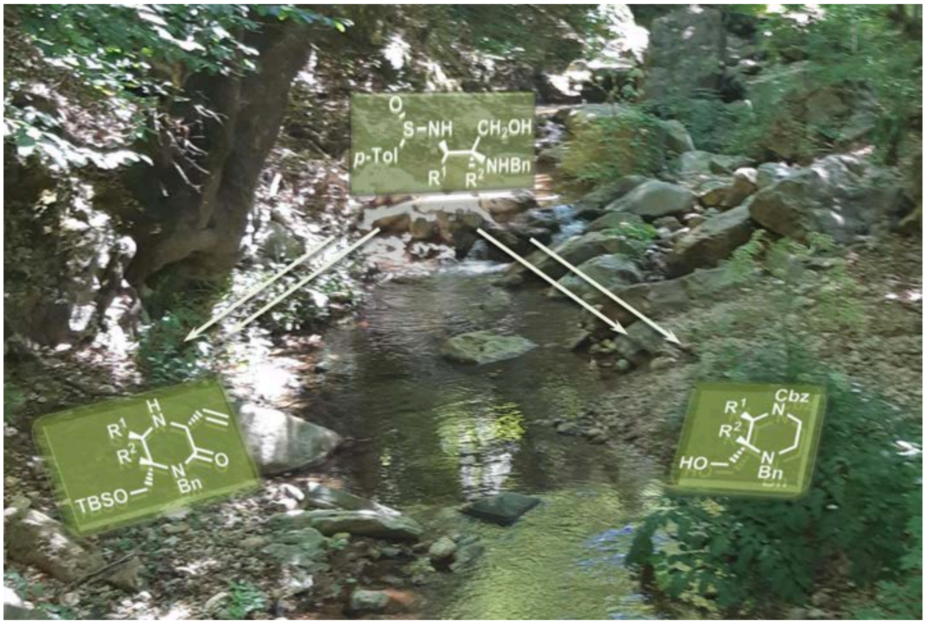
RSC Med. Chem. **2020**, *11*, 745–759. **DOI:** 10.1039/d0md00053a



Abstract: The important requirement for approval of a new drug, in case it happens to be chiral, is that both enantiomers of the drug should be studied in detail, which has led synthetic organic and medicinal chemists to focus their attention on the development of new methods for asymmetric synthesis especially of relevant saturated *N*-heterocycles. On the other hand, the piperazine ring, besides defining a major class of saturated *N*-heterocycles, has been classified as a privileged structure in medicinal chemistry, since it is more than frequently found in biologically active compounds including several marketed blockbuster drugs such as Glivec (imatinib) and Viagra (sildenafil). Indeed, 13 of the 200 best-selling small molecule drugs in 2012 contained a piperazine ring. Nevertheless, analysis of the piperazine substitution pattern reveals a lack of structural diversity, with almost every single drug in this category (83%) containing a substituent at both the N1- and N4-positions compared to a few drugs having a substituent at any other position (C2, C3, C5, and C6). Significant chemical space that is closely related to that known to be biologically relevant therefore, remains unexplored. In order to explore this chemical space, efficient and asymmetric syntheses of carbon-substituted piperazines and related heterocycles must be designed and developed. Initial, recent efforts toward the implementation of this particular target are in fact the subject of this review.