

## The ISHC Bulletin

### Recent Publications of ISHC Members

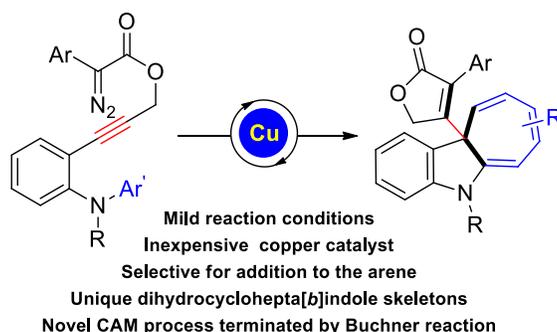
Issue 30; April 2019

#### Copper-Catalyzed Carbene/Alkyne Metathesis Terminated with the Buchner Reaction: Synthesis of Dihydrocyclohepta[b]indoles

Qian Zeng, Kuiyong Dong, Jingjing Huang, Lihua Qiu\*, and Xinfang Xu\*  
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*Org. Biomol. Chem.* **2019**, *17*, 2326–2330.

DOI: 10.1039/C9OB00113A



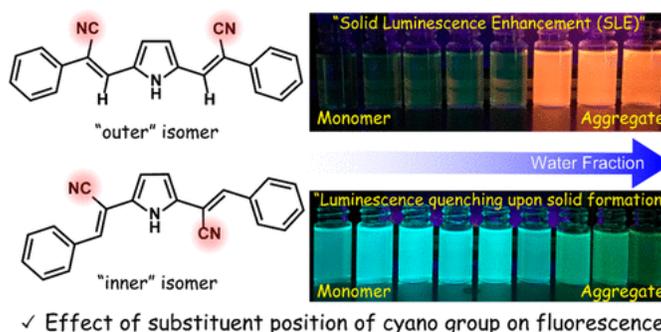
**Abstract:** A copper-catalyzed selective cascade reaction of alkyne-tethered diazo compounds is reported for the direct and efficient construction of dihydrocyclohepta[b]indole skeletons under mild reaction conditions. A vinyl copper carbene is the key intermediate, which is generated *in situ* via carbene/alkyne metathesis (CAM) and terminated with the Buchner reaction.

#### Fluorescence Behavior of Bis(cyanostyryl)pyrrole Derivatives Depending on the Substituent Position of Cyano Groups in Solution and in Solid State

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*J. Org. Chem.* **2019**, *84*, 1192–1200.

DOI: 10.1021/acs.joc8b02517



**Abstract:** We synthesized a novel fluorophore of distyrylpyrrole derivatives possessing cyano groups at different positions on olefin. Their fluorescence properties in solution and solid state were investigated by photoluminescence quantum yield and lifetime measurements, which provided a radiative decay constant ( $k_f$ ) and nonradiative decay constant ( $k_{nr}$ ). The derivative with cyano groups at the inner position of the molecule, inner isomer, shows a high fluorescence quantum yield ( $\Phi_f = 0.43$ ) in solution, while another derivative with a cyano group at the outer position, outer isomer, hardly shows fluorescence ( $\Phi_f < 0.01$ ) due to the large nonradiative decay ( $k_{nr} > 10 \text{ ns}^{-1}$ ). Upon formation of a single crystal or nanoparticles, these differences were inverted; the quantum yield of the outer and inner isomer was enhanced and diminished, respectively. We explained these differences between in solution and solid state by means of analysis of a single X-ray structure and computation study.

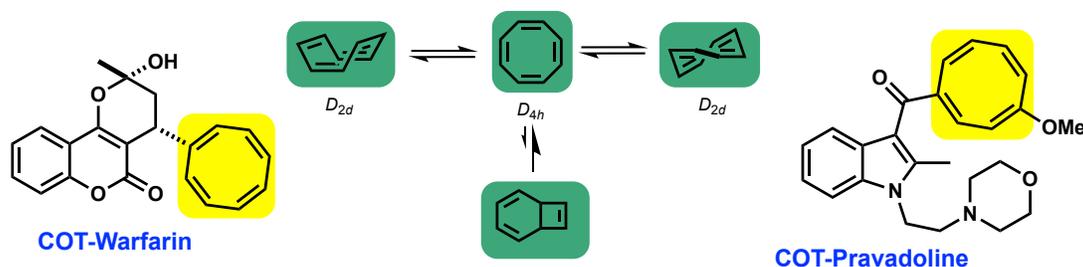
## Cyclooctatetraene: A Bioactive Cubane Paradigm Complement

Hui Xing, Sevan D. Houston, Xuejie Chen, Sussan Ghassabian, Tyler Fahrenhorst-Jones, Andy Kuo, Cody-Ellen P. Murray, Kyna-Anne Conn, Kara N. Jaeschke, Da-Yun Jin, Cielo Pasay, Paul V. Bernhardt, Jed M. Burns, John Tsanaktsidis, G. Paul Savage, Glen M. Boyle, James J. De Voss, James McCarthy, Gimme H. Walter, Thomas H. J. Burne, Maree T. Smith, Jian-Ke Tie, and Craig M. Williams\*

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*Chem. Eur. J.* **2019**, *25*, 2729–2734.

DOI: 10.1002/chem.201806277



**Abstract:** Our group recently validated cubane as a phenyl ring (bio)isostere (*ACIE*, **2016**, *55*, 3580; DOI: 10.1002/anie.201510675). However, a drawback of deploying cubane in certain biological environments is the lack of  $\pi$  character within the highly strained caged carbocyclic framework. This deficiency in electronic rich character was addressed with cubane's valence isomer cyclooctatetraene (COT). Utilising known pharmaceutical and agrochemical compound templates it was observed that COT either outperformed or matched cubane in a number of cases. The results reported in our article suggest that COT is a versatile biomotif that complements cubane for enhanced bioactive molecule discovery. Furthermore, we reported methodology to access the COT ring system in one step from cubane, see *Chem. Eur. J.* **2019**, *25*, 2735; DOI : 10.1002/chem.201805124.

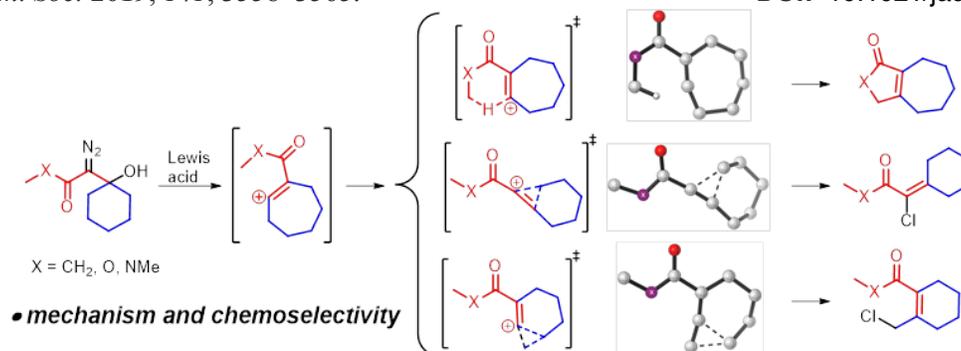
## Reactivity Profiles of Diazo Amides, Esters, and Ketones in Transition-Metal-Free C–H Insertion Reactions

Sarah E. Cleary, Xin Li, Li-Cheng Yang, K. N. Houk, Xin Hong,\* and Matthias Brewer\*

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*J. Am. Chem. Soc.* **2019**, *141*, 3558–3565.

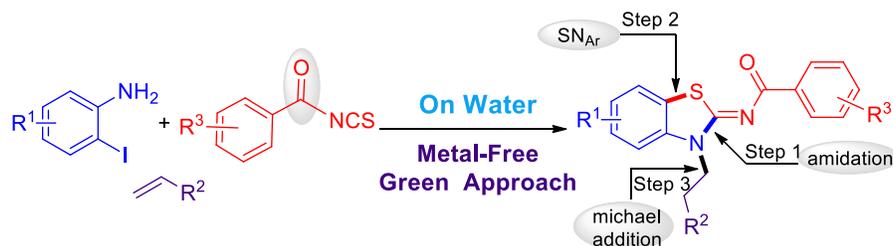
DOI: 10.1021/jacs.8b12420



**Abstract:** Vinyl cations derived from diazo ketones participate in transition-metal-free C–H insertion reactions, but the corresponding amide and ester analog exhibit divergent reactivity profiles. Whereas cations formed from diazo ketones undergo a rearrangement and C–H insertion sequence, those from diazo amides do so less efficiently and tend to be competitively trapped before the insertion step occurs. Diazo esters undergo several rearrangement steps and fail to insert. DFT calculations reveal that this disparity stems from two factors: differing levels of electrostatic stabilization of the initially formed vinyl cation by the adjacent carbonyl oxygen and predistortion of the ketone and amide systems toward C–H insertion. The computational data is in strong agreement with experimental results, and this study explains how structural and electronic factors determine the outcome of reactions of diazo carbonyl-derived vinyl cations.

## On Water: Metal-Free Synthesis of Highly Functionalized Benzothiazolidene from *ortho*-Haloanilines

Kapil Mohan Saini, Rakesh K. Saunthwal, Shiv Kumar, and Akhilesh K. Verma\* ([averma@acbr.du.ac.in](mailto:averma@acbr.du.ac.in))  
*J. Org. Chem.* **2019**, *84*, 2689–2698. DOI: 10.1021/acs.joc.8b03107

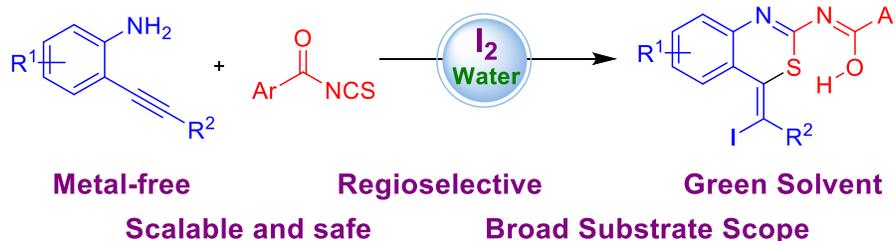


**Metal-Free    Mild Condition    Green Solvent    Broad Substrate Scope**

**Abstract:** An environmentally benign, transition-metal-free organic base promoted one-pot cascade synthesis of highly functionalized benzo[*d*]thiazol-2(3H)-ylidene benzamide in the presence of water has been accomplished by three-component reaction of *ortho*-iodoanilines, acrylates, and aroyl isothiocyanates. The protocol involves the *in situ* generation of thiourea intermediate followed by triethylamine induced intramolecular  $S_NAr$  displacement reaction and subsequent Michael addition onto acrylate leads to the formation of benzo[*d*]thiazol-2(3H)-ylidene benzamide. Benzo[*b*]thiazole is also generated in good yields using amidation and intramolecular aromatic nucleophilic substitution chemistry. The control experiments support the proposed mechanistic pathway. Further X-ray crystallographic studies confirm the assigned structures of the fused benzamide.

## On Water: Iodine-Mediated Direct Construction of 1,3-Benzothiazines from *ortho*-alkynylanilines by Regioselective 6-*exo-dig* Cyclization

Kapil Mohan Saini, Rakesh K. Saunthwal, Shiv Kumar, and Akhilesh K. Verma\* ([averma@acbr.du.ac.in](mailto:averma@acbr.du.ac.in))  
*Org. Biomol. Chem.* **2019**, *17*, 2657–2662. DOI: 10.1039/C9OB00128J

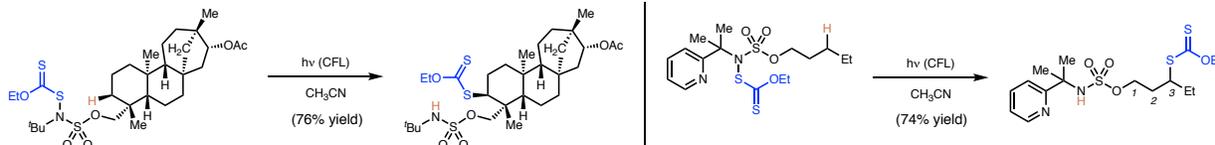


**Abstract:** Herein, we report the 6-*exo-dig* ring closure of *ortho*-alkynylanilines with readily available aroylisothiocyanate. An environmentally benign, metal- and base-free, iodine promoted cascade synthesis of highly functionalized (benzo[1,3]thiazin-2-yl)benzimidic acids has been accomplished via *in situ* generated *ortho*-alkynylthiourea. The established methodology employs the abundant chemical feed stocks of *ortho*-alkynylanilines and aroylisothiocyanates and could be applied in the late-stage synthesis of pharmaceutically active 1,3-benzothiazine containing molecules. Furthermore, the discovered protocol exclusively delivers the bis (benzo[1,3]thiazin-2-yl)dibenzimidic acid products and preserves the iodo-olefin substitution pattern which can be exploited by further derivatization.

## Sulfamate Esters Guide C(3)-Selective Xanthylation of Alkanes

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*J. Org. Chem.* **2019**, *84*, 3508–3525.

DOI: 10.1021/acs.joc.9b00105

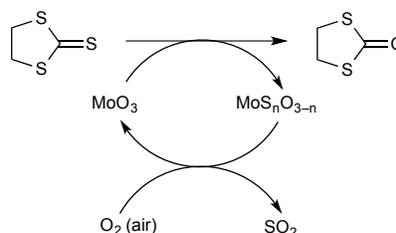


**Abstract:** Given the prevalence of alcohols in natural products, alcohol derivatives are promising directing groups. Herein, alcohol-derived sulfamate esters direct the light-initiated, diastereoselective xanthate-transfer to C(sp<sup>3</sup>)-H centers. This technology enables formal C(3)-selective guided deuteration, azidation, thiolation, and vinylation processes.

## Gas-Phase Conversion of 1,3-Dithiolane-2-Thione Into 1,3-Dithiolan-2-One Over Molybdenum Trioxide

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*Front. Chem.* **2019**, *7*, 204 (1–5).

DOI: 10.3389/fchem.2019.00204

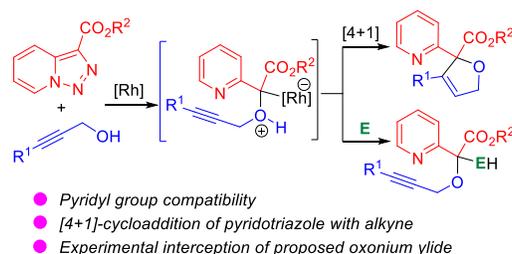


**Abstract:** Gas-phase reaction of 1,3-dithiolane-2-thione over molybdenum trioxide supported on pumice stone results in efficient conversion into 1,3-dithiolan-2-one. The solid reagent is regenerated on exposure to air and thus acts as a catalyst for the overall conversion of the thione and oxygen from the air into the ketone and sulfur dioxide. The process can be carried out under either dynamic vacuum or atmospheric pressure flow conditions and using a solid reagent prepared either by physical mixing of MoO<sub>3</sub> with the support or by solution impregnation, with an isolated yield of up to 67% obtained.

## Rhodium(II)-Catalyzed Formal [4+1]-Cycloaddition of Pyridotriazoles and Propargyl Alcohols: Synthesis of 2,5-Dihydrofurans

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(huwh9@mail.sysu.edu.cn)  
*Adv. Synth. Catal.* **2019**, *361*, 1265–1270.

DOI: 10.1002/adsc.201801497



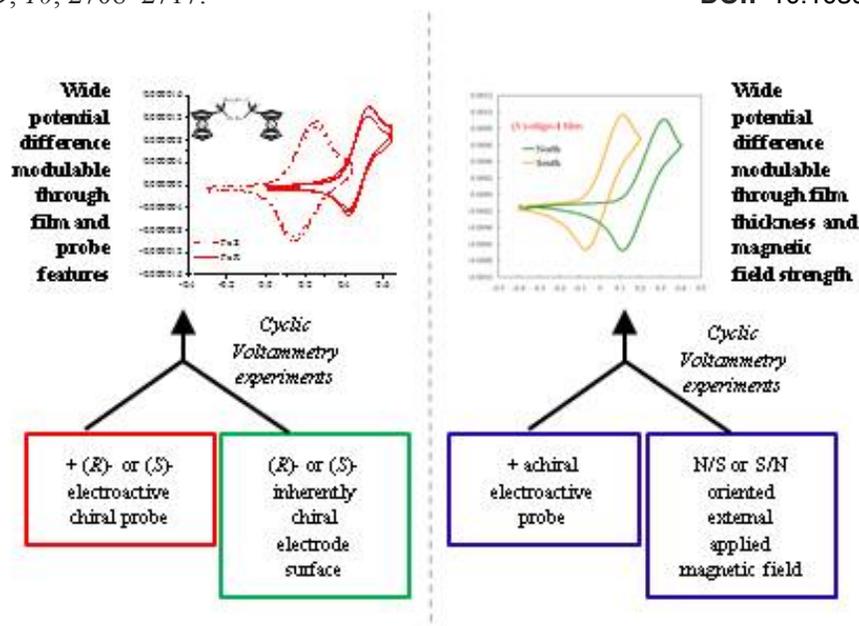
**Abstract:** A silver-catalyzed carbocyclization of azide-tethered alkynes has been developed for the synthesis of polysubstituted quinolines in good to high yields. Mechanistic studies indicate that this reaction is initiated by a silver-catalyzed 6-*endo-dig* azide-yne cyclization, followed by a formal R-X (X = Cl, Br, or I) insertion with external halide through an ylide intermediate. The salient features of this reaction include readily available materials, inexpensive silver-catalyst, mild reaction conditions, good functional group tolerance, and ease in further transformations.

## Highly Enantioselective “Inherently Chiral” Electroactive Materials Based on a 2,2'-Biindole Atropisomeric Scaffold

Serena Arnaboldi, Tiziana Benincori,\* Andrea Penoni, Luca Vaghi, Roberto Cirilli, Sergio Abbate, Giovanna Longhi, Giuseppe Mazzeo, Sara Grecchi, Monica Panigati, and Patrizia Romana Mussini\*  
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*Chem. Sci.* **2019**, *10*, 2708–2717.

DOI: 10.1039/C8SC04862B



**Abstract:** Chiral oligothiophene monomers with C<sub>2</sub> symmetry, based on 3,3'-bithiophene atropisomeric cores with high racemization barriers, have recently been shown to provide excellent chiral starting materials with high electroactivity for the easy preparation of enantiopure electroactive films endowed with powerful chirality manifestations. We now introduce an inherently chiral monomer based on a 2,2'-biindole core, as the prototype of a new inherently chiral monomer family, whose properties could be modulable through functionalization of the pyrrolic N atoms. By fast, regular electrooligomerization the new monomer yields inherently chiral films with high, reversible electroactivity and, above all, impressive enantioselectivity towards very different chiral probes, some of pharmaceutical interest, as general-scope electrode surfaces. Such results, while opening the way to a new, attractive inherently chiral selector class, nicely confirm the general validity of the inherent chirality strategy for chiral electrochemistry. Furthermore, the enantioselectivity of the new selectors not only holds with electroactive chiral probes, but also with circularly polarized light components as well as electron spins, resulting in good chiroptical and spin filter performances, which suggests fascinating correlations between the three contexts.