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g-C_3N_4-Singlet Oxygen Made Easy for Organic Synthesis: Scope and Limitations

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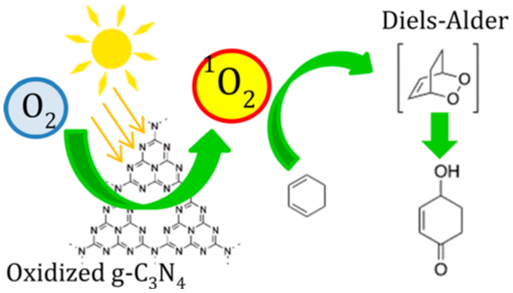
ACS Sustainable Chem. Eng. **2019**, *7*, 8176–8182. **DOI:** 10.1021/acssuschemeng.8b06164

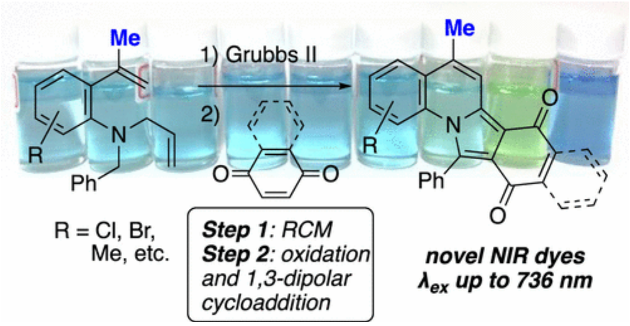


Abstract: Oxidized g-C_3N_4 displays very good catalytic performances in the generation of $^1O_2$ under photochemical conditions. The hetero-Diels–Alder and ene reactions were conducted on a variety of dienes and alkenes showing a general ability of oxidized g-C_3N_4 to promote chemoselective and unselective oxidative processes in strong dependence from the substrates. The results offer a good panorama of the ability of this type of catalysts to be employed in organic reactions to prepare valuable synthons that can be used in several value-added preparations. A fine-tuning of the oxidative properties through further investigations on the synthesis of suitably modified g-C_3N_4 will be of great importance in determining a sustainable change in the approach to $^1O_2$ generation methods, allowing for greener ways to perform organic reactions.

Metal-Free Nitrogen-Containing Polyheterocyclic Near-Infrared (NIR) Absorption Dyes: Synthesis, Absorption Properties, and Theoretical Calculation of Substituted 5-Methylisoindolo[2,1-*a*]quinolines

Yuki Fujii, Yukinori Suwa, Yuki Wada, Tsunayoshi Takehara, Takeyuki Suzuki, Yusuke Kawashima, Norihito Kawashita, Tatsuya Takagi, Hiromichi Fujioka, and Mitsuhiro Arisawa* (arisaw@phs.osaka-u.ac.jp)

ACS Omega **2019**, *4*, 5064–5075. **DOI:** 10.1021/acsomega.9b00315



Abstract: We have synthesized and theoretically calculated 5-methylisoindolo[2,1-*a*]quinoline derivatives as novel near-infrared absorption dyes via a ruthenium-catalyzed one-pot metathesis/oxidation/1,3-dipolar cycloaddition protocol. The reactivity in 1,3-dipolar cycloaddition was governed by the electronic effect of aromatic ring substituents. Substrates with an electron-withdrawing group on the aromatic ring afforded higher yields. The maximal absorption wavelength of 3,5-dimethyl-11-phenylisoindolo[2,1-*a*]quinoline-7,10-dione and 11-(4-methoxyphenyl)-5-methylisoindolo[2,1-*a*]quinoline-7,10-dione in MeOH increased to 736 and 737 nm, although that of **3a** was 727 nm.

Reassignments and Corroborations of Oxo-Bridged Natural Products Directed by OSE and DU8+ NMR Computation

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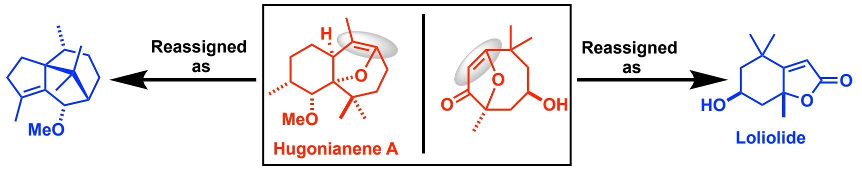
Angew. Chem. Int. Ed. **2019**, *58*, 7107–7112. **DOI:** 10.1002/anie.201902777



Abstract: Structure elucidation, especially when it concerns complex natural products, has become a sophisticated science given the process nominally involves the interpretation of a series of high-powered spectroscopic techniques. This often arduous task can result in structural misassignments, which unfortunately continue to appear in the literature. Errors of this nature generate phantom chemical entities, which intrigue biologists and synthetic chemists alike – albeit falsely. Consequently, developing methods, and theoretical concepts, to help prevent structural misassignments is of paramount importance. Utilising the concept of olefin strain energy (OSE), first developed by Schleyer for predicting anti-Bredt compounds, and combining it with NMR chemical shifts and coupling constants (DU8+) calculations, enabled the reassignment of oxo-bridgehead double bond containing natural products. This approach provides a further tool for the community to correctly elucidate natural product chemical structures.

Efficient *N*-Arylation of Azole Compounds Utilizing Selective Aryl-Transfer TMP-Iodonium(III) Reagents

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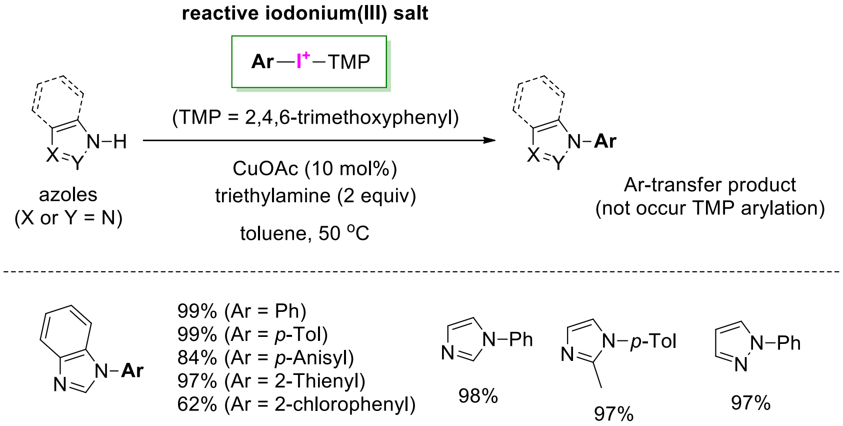
Tetrahedron Lett. **2019**, *60*, 1281–1286. **DOI:** 10.1016/j.tetlet.2019.04.012



Abstract: It was determined that diaryliodonium(III) triflates bearing a trimethoxybenzene (TMP) auxiliary are more reactive than the reported selective aryl-transfer iodonium salts in the *N*-arylation of benzimidazoles and other types of azole compounds under catalytic conditions. The TMP-iodonium(III) salts can thus effectively facilitate the reaction at 50 °C or below, producing the corresponding *N*-arylated biaryls without the formation of TMP-derived coupling byproducts. Utilization of this TMP reagent under mild conditions would prevent the underlying problem of participation of the auxiliary group in the coupling reactions, which is observed while using the iodonium(III) salts that require elevated temperatures.

ortho-Alkylation of Pyridine *N*-Oxides with Alkynes by Photocatalysis: Pyridine *N*-Oxide as a Redox Auxiliary

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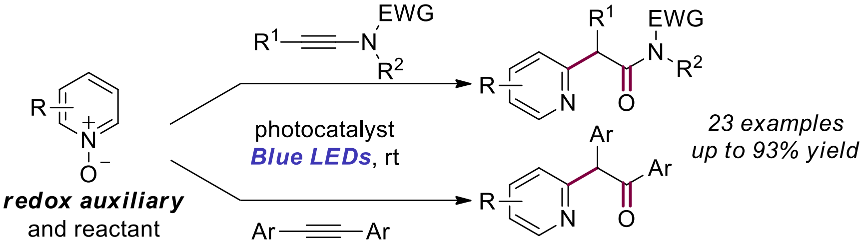
(yongming.deng@wku.edu)

Chem. Eur. J. **2019**, *25*, 6638–6644. **DOI:** 10.1002/chem.201901065

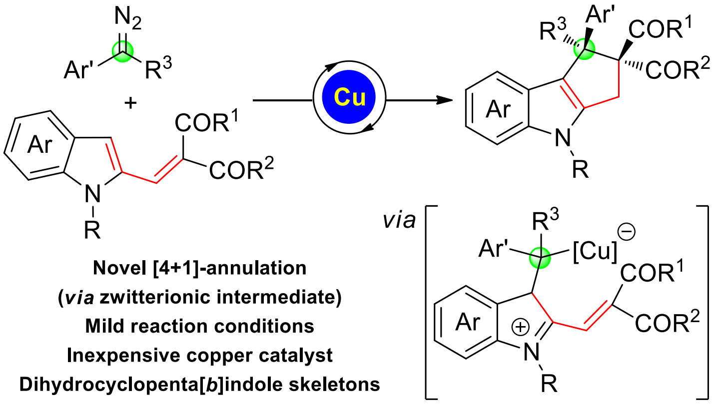


Abstract: A photocatalyzed *ortho*-alkylation of pyridine *N*-oxide with ynamides and arylacetylenes has been developed, yielding a series of α-(2-pyridinyl) benzyl amides/ketones. Mechanistic studies, including electrochemical studies, radical-trapping experiments, and Stern–Volmer fluorescence quenching studies demonstrate pyridine *N*-oxide serves as both a redox auxiliary and radical acceptor to achieve the mild photocatalytic single-electron oxidation of carbon-carbon triple bonds with the generation of cationic vinyl radical intermediate.

Copper-Catalyzed [4+1]-Annulation of 2-Alkenylindoles with Diazoacetates: A Facile Access to Dihydrocyclopenta[*b*]indoles

Kuiyong Dong, Chao Pei, Qian Zeng, Lihua Qiu, Wenhao Hu, Yu Qian,* and Xinfang Xu*
(qianyu5@mail.sysu.edu.cn or xinfangxu@suda.edu.cn)

Chem. Commun. **2019**, *55*, 6393–6396. **DOI:** 10.1039/c9cc02257k



Abstract: A copper-catalyzed [4+1]-annulation of 2-vinylindoles with diazoacetates has been developed that provides a straightforward access to the dihydrocyclopenta[b]indoles bearing two contiguous all-carbon quaternary centers in good yields. Mechanistic studies indicate that the reaction goes through a concerted and asynchronous annulation process via the key zwitterionic intermediate.

Pd-Catalyzed Migratory Cycloisomerization of *N*-Allyl-*o*-allenylaniline Derivatives

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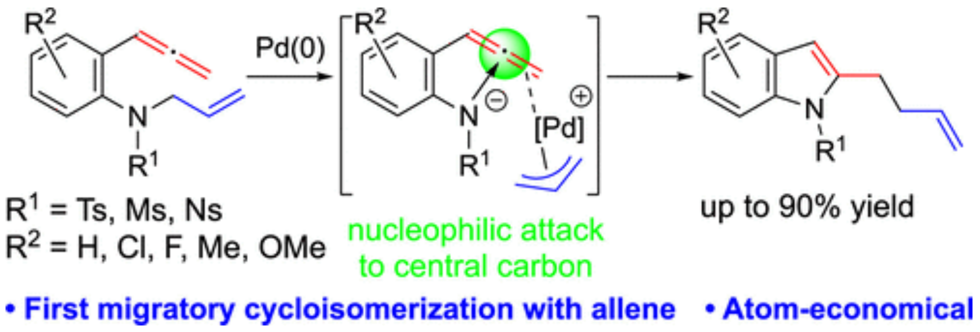
Org. Lett. **2019**, *21*, 3501–3504. **DOI:** 10.1021/acs.orglett.9b00676



Abstract: The Pd-catalyzed migratory cycloisomerization of *N*-allyl-*o*-allenyl aniline derivatives is first reported to give indoles having a substituent at the 2-position.

Lipase/Oxovanadium Co-Catalyzed Dynamic Kinetic Resolution of Propargyl Alcohols: Competition between Racemization and Rearrangement

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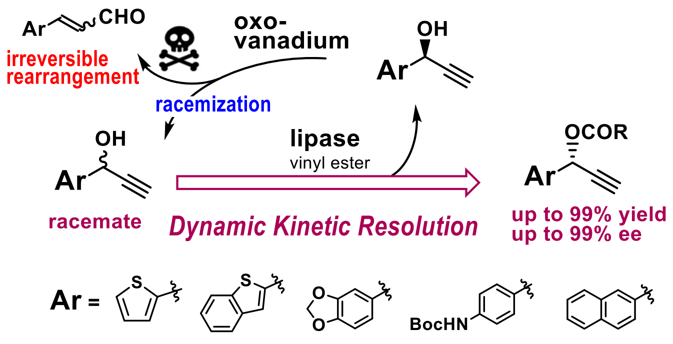
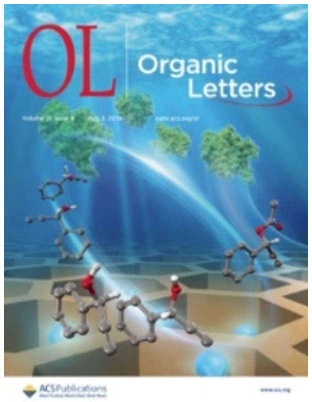
Org. Lett. **2019**, *21*, 2978–2982. **DOI:** 10.1021/acs.orglett.9b00334



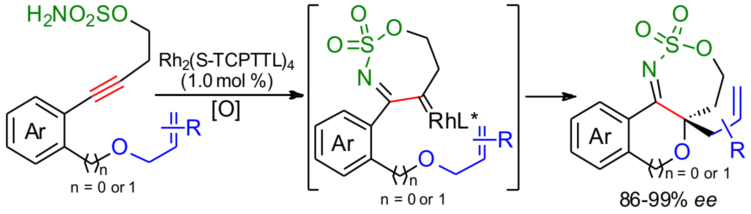


Abstract: Quantitative conversion of racemic propargyl alcohols into optically active propargyl esters with up to 99% ee has been achieved by lipase/oxovanadium co-catalyzed dynamic kinetic resolution, which combines the lipase-catalyzed enantioselective esterification of the racemic substrates and the *in situ* racemization of the remaining enantiomers. The success is owing to our discovery of a magic solvent, (trifluoromethyl)benzene, that accelerated the racemization while sufficiently suppressing the common oxovanadium-catalyzed rearrangement of propargyl alcohols to irreversibly produce enals.

Rhodium-Catalyzed Nitrene/Alkyne Metathesis: An Enantioselective Process for the Synthesis of *N*-Heterocycles

Kemiao Hong, Han Su, Chao Pei, Xinxin Lv, Wenhao Hu, Lihua Qiu,* and Xinfang Xu* (qiulihua@suda.edu.cn or xinfangxu@suda.edu.cn)

Org. Lett. **2019**, *21*, 3328–3331. **DOI:** 10.1021/acs.orglett.9b01074



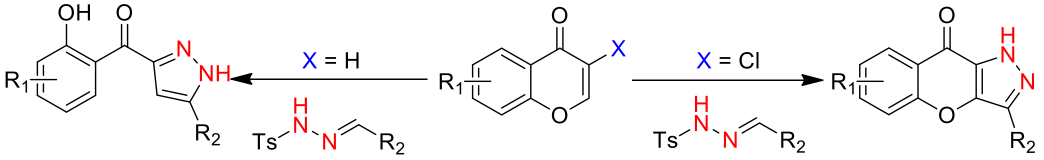
- ***Asymmetric Nitrene/Alkyne Metathesis (NAM) cascade reaction***
- ***Building C=N, C-O, and C-C bonds on the alkyne species in one-pot***
- ***Mild conditions***
- ***Good yields & excellent enantioselectivity***
- ***Broad substrate generality***
- ***Amenable to further transformations***

Abstract: A chiral dirhodium-carboxylates-catalyzed asymmetric nitrene/alkyne metathesis (NAM) cascade reaction of alkyne-tethered sulfamates has been developed, which provides a general access to the synthesis of tricyclic *N*-heterocycles in good yields and excellent enantioselectivity. The chiral dirhodium catalyst not only promotes the nitrene/alkyne metathesis (NAM) to generate the key α-imino metal carbene intermediate but is also responsible for the observed asymmetric induction in the terminating [2,3]-sigmatropic rearrangement of oxonium ylide species.

Substituent-Oriented Synthesis of Substituted Pyrazoles/Chromeno[3,2-*c*]pyrazoles via Sequential Reactions of Chromones/3-Chlorochromones and Tosylhydrazones

Tianzi Dai, Qunyi Li, Xiaofei Zhang,* and Chunhao Yang* (xiaofeizhang@simm.ac.cn or chyang@simm.ac.cn)

J. Org. Chem. **2019**, *84*, 5913–5921. **DOI:** 10.1021/acs.joc.9b00282



29 examples
up to 98% yield

14 examples
up to 94% yield

- **Substituent-oriented**
- **Metal-free**
- **High chemoselectivity**
- **Broad scope**

Abstract: A facile and efficient synthetic strategy for the chemoselective synthesis of monocyclic/tricyclic-fused pyrazoles was developed, and it was oriented by different 3-position substituents (H or Cl) on the chromones. The reaction proceeded in a one-pot sequential way with a broad substrate scope and moderate to excellent yields.