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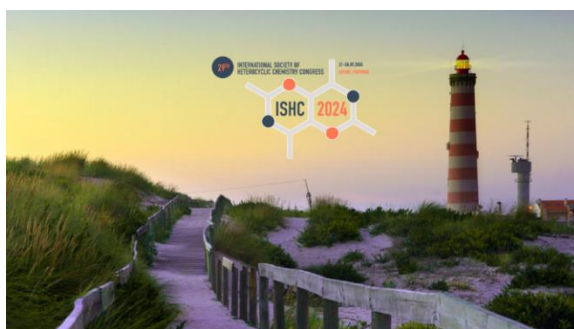
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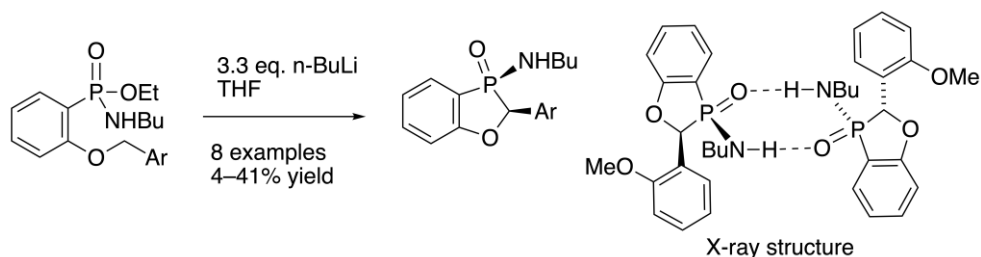


**Synthesis and Butyllithium-Induced Cyclisation of 2-Benzyloxyphenylphosphonamidates Giving 2,3-Dihydrobenzo[*d*][1,3]oxaphospholes**

R. Alan Aitken \*, Khadija Ait Moulay, David B. Cordes, Ryan A. Inwood, Fraser G. Jamieson, Alexander J. B. Nelson and Aidan P. McKay

*Organics* **2024**, 5, 12–31.

DOI: 10.3390/org5010002



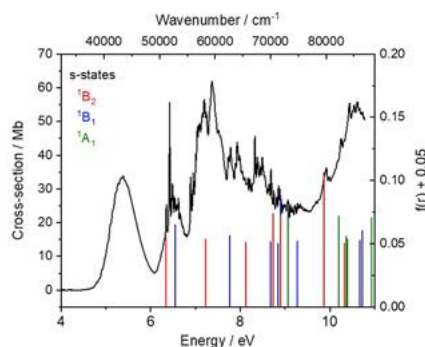
A series of fourteen *O*-ethyl-*N*-butylphenylphosphonamidates with benzyl ether substituents at the *ortho* position was prepared and fully characterised. Upon treatment with *n*-butyllithium in THF at RT, they underwent cyclisation in eight cases to give the novel 2,3-dihydrobenzo[*d*][1,3]oxaphospholes in moderate to low yield as a single diastereomer, for which the relative configuration was determined by X-ray diffraction in one case.

## The ultraviolet and vacuum ultraviolet absorption spectrum of gamma-pyrone; the singlet states studied by configuration interaction and density functional calculations

Michael H. Palmer \*, Søren Vrønning Hoffmann, Nykola C. Jones, Marcello Coreno, Monica de Simone, Cesare Grazioli, R. Alan Aitken, Loëlia Perrault and Iain L. J. Patterson

*Journal of Chemical Physics* **2024**, *160*, 054305 (13pp).

DOI: 10.1063/5.0186919

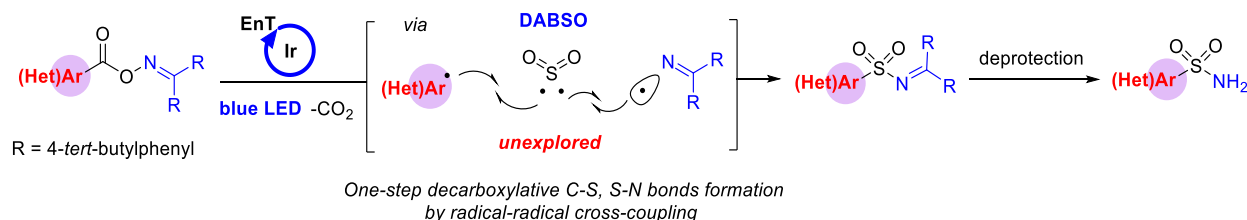


A synchrotron based vacuum ultraviolet absorption spectrum for  $\gamma$ -pyrone has been interpreted in terms of singlet excited electronic states using a variety of coupled cluster, configuration interaction, and density functional calculations. The extremely weak spectral onset at 3.557 eV shows eight vibrational peaks, which following previous analyses, are attributed to a forbidden  $^1A_2$  state. A contrasting broad peak with a maximum at 5.381 eV has a relatively high cross-section of 30 Mb; this arises from three overlapping states, where a  $^1A_1$  state dominates over progressively weaker  $^1B_2$  and  $^1B_1$  states. After fitting the second band to a polynomial Gaussian function and plotting the regular residuals over 20 vibrational peaks, we have had limited success in analyzing this fine structure. However, the small separation between these three states clearly shows that their vibrational satellites must overlap. Singlet valence and Rydberg state vibrational profiles were determined by configuration interaction using the CAM-B3LYP density functional. Vibrational analysis using both the Franck–Condon and Herzberg–Teller procedures showed that both procedures contributed to the profiles. Theoretical Rydberg states were evaluated by a highly focused CI procedure. The superposition of the lowest photoelectron spectral band on the vacuum ultraviolet spectrum near 6.4 eV shows that the 3s and 3p Rydberg states based on the  $^2B_2$  ionic state are present; those based on the other low-lying ionic state ( $X^2B_1$ ) are destroyed by broadening; this is a dramatic extension of the broadening previously witnessed in our studies of halogenobenzenes.

## Visible-Light-Induced Decarboxylative Aminosulfonylation of (Hetero)Aryl Carboxylic Oxime Esters

Zhen Zhuang, Yuting Sun, Yuanchen Zhong, Qian He, Xiaofei Zhang\*, and Chunhao Yang\*.

*Org. Lett.* **2024**, *26*, 713–718. DOI: 10.1021/acs.orglett.3c04142



- Mild conditons
- Diverse scope (40 examples)
- High efficiency (up to 94% yield)
- Late-stage modification

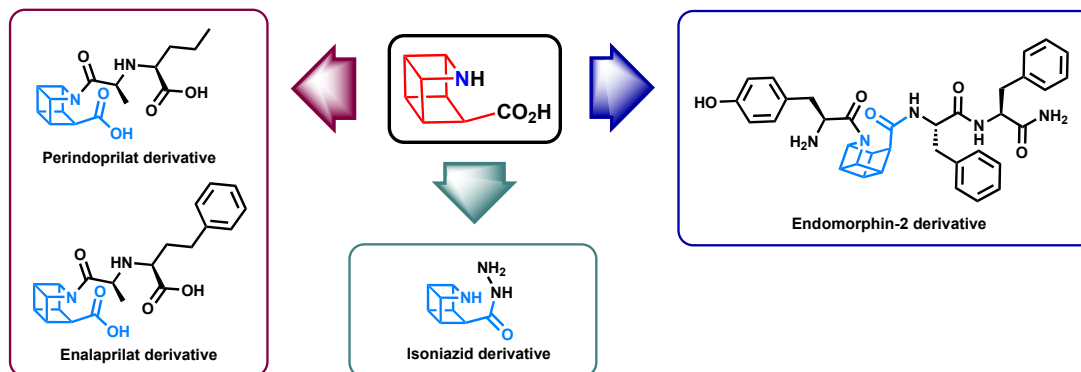
Sulfonamides are important structures in pharmaceuticals, agrochemicals and organocatalysts, yet the rapid and benign synthesis of these compounds is still a great challenge. Herein we report a photo-induced method for synthesizing sulfonamides from (hetero)aryl carboxylic acid oxime esters. This reaction proceeds *via* one-pot cascade radical-radical cross-coupling by energy-transfer-mediated photocatalysis. Wide substrate scope including aryl, heteroaryl substrates and late-stage modification of pharmaceutical molecular entities reveal its generality.

### ***seco*-1-Azacubane-2-carboxylic Acid: Derivative Scope and Comparative Biological Evaluation**

Dehui Kong, Tyler Fahrenhorst-Jones, Andy Kuo, Jacinta L. Simmons, Lendl Tan, Jed M. Burns, Gregory K. Pierens, Rui Li, Nicholas P. West, Glen M. Boyle, Maree T. Smith, G. Paul Savage, and Craig M. Williams\* ([c.williams3@uq.edu.au](mailto:c.williams3@uq.edu.au))

*J. Org. Chem.* **2024**, 89, 1, 798-803

DOI: 10.1021/acs.joc.3c02333



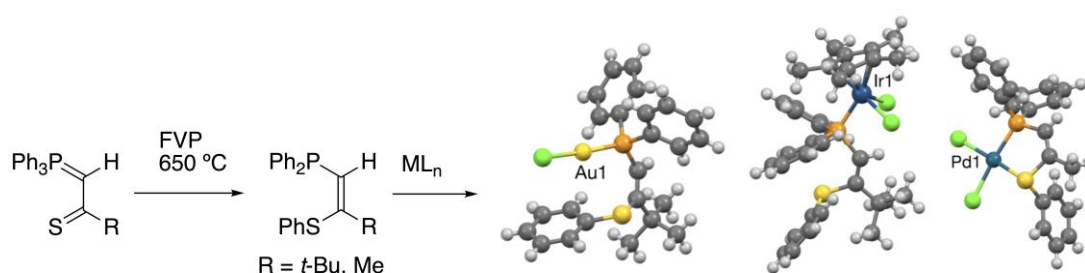
With the previous discovery that the unusual and sterically congested non-natural amino acid, *seco*-1-azacubane-2-carboxylic acid, could be synthetically manipulated, a further scope investigation was undertaken to unearth potential attributes conducive of bioisostere, scaffold or bio-motif features. A range of drug templates were investigated, including the ACE inhibitors, enalaprilat and perindoprilat, the opioid peptide endomorphin-2, and the anti-tuberculosis drug isoniazid. It was observed that the endomorphin-2 derivative expressed increased  $\delta$  opioid receptor agonism, and partially decreased  $\mu$  opioid receptor agonism. Loss of activity was observed in the other cases.

### **Thermal Rearrangement of Thiocarbonyl-Stabilised Triphenylphosphonium Ylides Leading to (*Z*)-1-Diphenylphosphino-2-(phenylsulfenyl)alkenes and Their Coordination Chemistry**

R. Alan Aitken, Graham Dawson, Neil S. Keddie, Helmut Kraus, Heather L. Milton, Alexandra M. Z. Slawin, Joanne Wheatley and J. Derek Woollins

*Molecules* **2024**, 29, 221 (1–13).

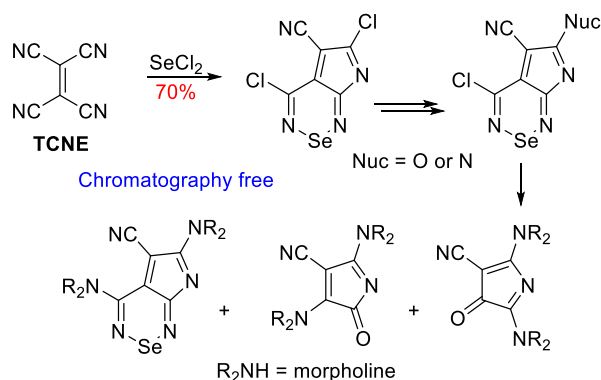
DOI: 10.3390/molecules29010221



While thiocarbonyl-stabilised phosphonium ylides generally react upon flash vacuum pyrolysis by the extrusion of Ph<sub>3</sub>PS to give alkynes in an analogous way to their carbonyl-stabilised analogues, two examples with a hydrogen atom on the ylidic carbon are found to undergo a quite different process. The net transfer of a phenyl group from P to S gives (*Z*)-configured 1-diphenylphosphino-2-(phenylsulfenyl)alkenes in a novel isomerisation process via intermediate  $\lambda^5$ -1,2-thiaphosphetes. These prove to be versatile hemilabile ligands with a total of seven complexes prepared involving five different transition metals. Four of these are characterised by X-ray diffraction with two involving the bidentate ligand forming a five-membered ring metallacycle and two with the ligand coordinating to the metal only through phosphorus.

## Reaction of tetracyanoethylene with diselenium dichloride: a route to pyrrolo[2,3-c][1,2,6]selenadiazines

Cory Laurent, Andreas Kourtellaris and Panayiotis A. Koutentis  
*New J. Chem.*, 2024, 48, 1206-1211 DOI: 10.1039/d3nj04876d



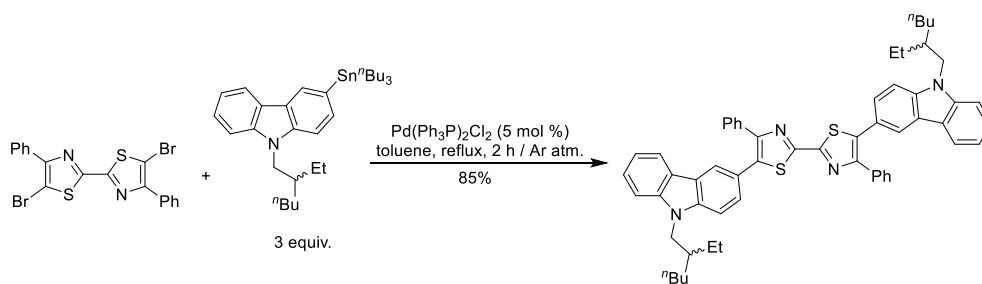
Tetracyanoethylene reacts with Se<sub>2</sub>Cl<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub> and catalytic BnEt<sub>3</sub>NCl in 1,2-dichloroethane heated at *ca.* 70 °C for 40 h to give 4,6-dichloropyrrolo[2,3-c][1,2,6]selenadiazine-5-carbonitrile (42%) and 4-chloro-6-oxo-6,7-dihydropyrrolo[2,3-c][1,2,6]selenadiazine-5-carbonitrile (30%). A chromatography free procedure allows isolation of 4,6-dichloropyrrolo[2,3-c][1,2,6]selenadiazine-5-carbonitrile in 70% yield. Regioselective displacement of the 6-chloro by O- and N-nucleophiles is demonstrated. Treatment of 4-chloro-6-morpholinopyrrolo[2,3-c][1,2,6]selenadiazine-5-carbonitrile with morpholine gives a low yield of the 4,6-dimorpholinopyrrolo[2,3-c][1,2,6]selenadiazine-5-carbonitrile (8%) together with 2,5-dimorpholino-3-oxo-3H-pyrrole-4-carbonitrile (13%) and 3,5-dimorpholino-2-oxo-2H-pyrrole-4-carbonitrile (55%).

## 5,5'-Bis[9-(2-ethylhexyl)-9H-carbazol-3-yl]-4,4'-diphenyl-2,2'-bithiazole

Andreas S. Kalogirou and Panayiotis A. Koutentis

*Molbank* 2024, 2024(1), M1761;

<https://doi.org/10.3390/M1761>

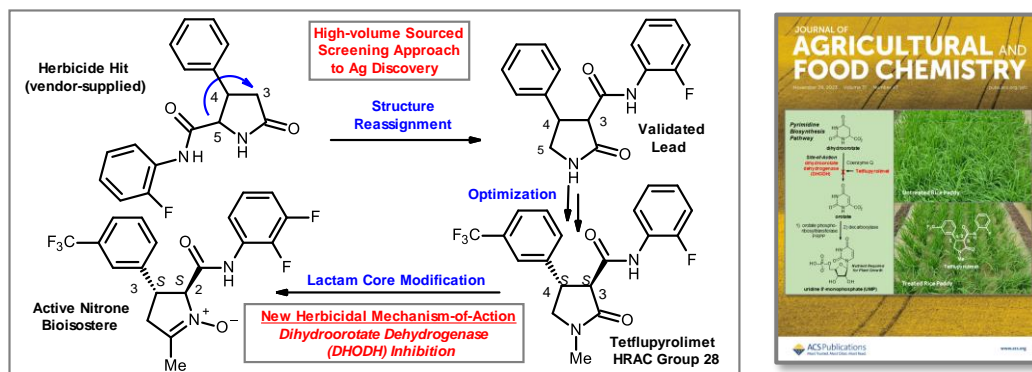


Stille coupling between 5,5'-dibromo-4,4'-diphenyl-2,2'-bithiazole and 9-(2-ethylhexyl)-3-(tributylstannyl)-9H-carbazole in the presence of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in toluene, heated at reflux for 2 h, gave 5,5'-bis[9-(2-ethylhexyl)-9H-carbazol-3-yl]-4,4'-diphenyl-2,2'-bithiazole in 85% yield.

## Bioisosteric Tactics in the Discovery of Tetflupyrolimet: A New Mode-of-Action Herbicide

Thomas P. Selby\*, Andrew D. Satterfield, Atul Puri, Thomas M. Stevenson, D. Andrew Travis, Matthew J. Campbell, Andrew E. Taggi, Kenneth A. Hughes and James Berezna

*Journal of Agricultural and Food Chemistry*, **2023**, 71 (47) 18197-18204. (doi.org/10.1021/acs.jafc.3c01634)

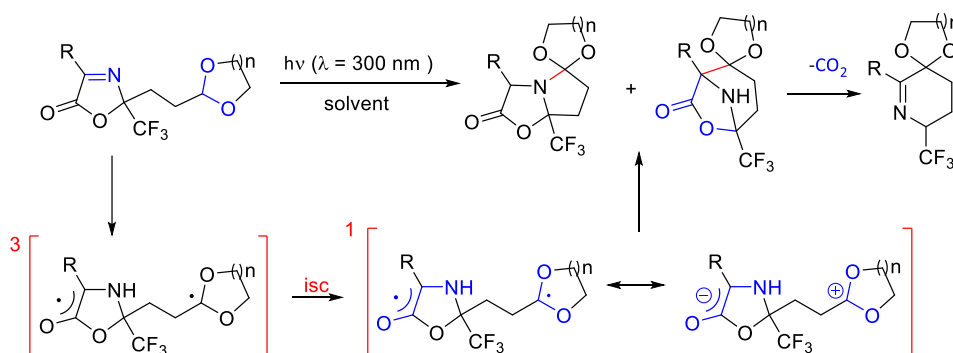


The last new herbicidal modes-of-action with commercial significance were introduced to the marketplace multiple decades ago. Serious weed resistance to most herbicidal classes have since emerged with widespread use. Aryl pyrrolidinone anilides represent an entirely new mode-of-action class of herbicides that interferes with *de novo* pyrimidine biosynthesis in plants via inhibition of dihydroorotate dehydrogenase. The chemical lead for this new herbicide class discovery was identified from high-volume sourced greenhouse screening that required structural reassignment of the hit molecule followed by an extensive synthetic optimization effort. With excellent grass weed control and pronounced safety on rice, the selected commercial development candidate has a proposed common name of tetflupyrolimet and represents the first member of the new HRAC (Herbicide Resistance Action Committee) Group 28. This paper describes the discovery path to tetflupyrolimet with an added focus on the bioisosteric modifications pursued in optimization, including replacements of the lactam core itself.

## Photochemically Induced Hydrogen Atom Transfer and Intramolecular Radical Cyclization Reactions with Oxazolones

Mohammed Latrache, Corentin Lefebvre, Manabu Abe and Norbert Hoffmann\*

*J. Org. Chem.* **2023**, 88, 16435-16455. <https://doi.org/10.1021/acs.joc.3c01951>



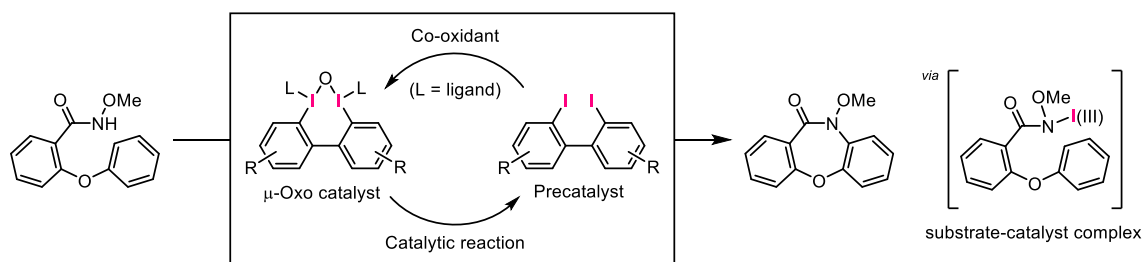
Photochemically induced intramolecular hydrogen atom transfer in oxazolones is reported. An acetal or thioacetal function at the side chain acts as a hydrogen donor while the photochemical excited oxazolone is the acceptor. A one-step process—the electron and the proton are simultaneously transferred—is productive, while electron transfer followed by proton transfer is inefficient. Radical combination then takes place, leading to the formation of a C–C or C–N bond. The regioselectivity of the reaction is explained by the diradical/zwitterion dichotomy of radical intermediates at the singlet state. In the present case, the zwitterion structure plays a central role, and intramolecular electron transfer favors spin–orbit coupling and thus the intersystem crossing to the singlet state. The reaction of corresponding thioacetal derivatives is less efficient. In this case, photochemical electron transfer

is competitive. The photoproducts resulting from C–C bond formation easily undergo stepwise thermal decarboxylation in which zwitterionic and polar transition states are involved. A computational study of this step has also been performed.

## Efficient Metal-Free Oxidative C–H Amination for Accessing Dibenzoxazepinones via $\mu$ -Oxo Hypervalent Iodine Catalysis

Hiroataka Sasa, Syotaro Hamatani, Mayu Hirashima, Naoko Takenaga, Tomonori Hanasaki,\* and Toshifumi Dohi\*

*Chemistry* **2023**, *5*, 2155-2165. <https://doi.org/10.3390/chemistry5040145>

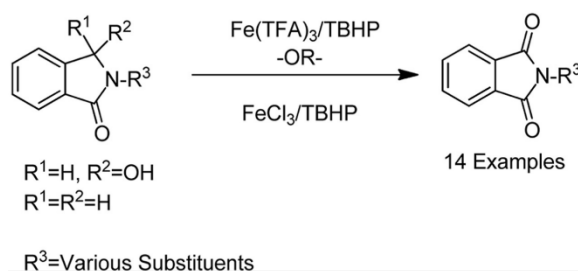


Dibenzoxazepinones exhibit unique biological activities and serve as building blocks for synthesizing pharmaceutical compounds. Despite remarkable advancements in organic chemistry and recent developments in synthetic approaches to dibenzoxazepinone motifs, there is a strong demand for more streamlined synthesis methods. The application of catalytic C–H amination strategy, which enables direct transformation of inert aromatic C–H bonds into C–N bonds, offers a rapid route to access dibenzoxazepinone frameworks. Hypervalent-iodine-catalyzed oxidative C–H amination should become one of the effective approaches for synthesizing dibenzoxazepinones. In this study, we present our method of employing  $\mu$ -oxo hypervalent iodine catalysis for intramolecular oxidative C–H amination of *O*-aryl salicylamides, facilitating the synthesis of target dibenzoxazepinone derivatives bearing various functional groups in a highly efficient manner.

## Iron-catalyzed oxidation of phthalimide-derived hydroxylactams and isoindolinones

Bernard L. Adjei, Frederick A. Luzzio

*Tetrahedron* **149** (2023) 133739. <https://doi.org/10.1016/j.tet.2023.133739>

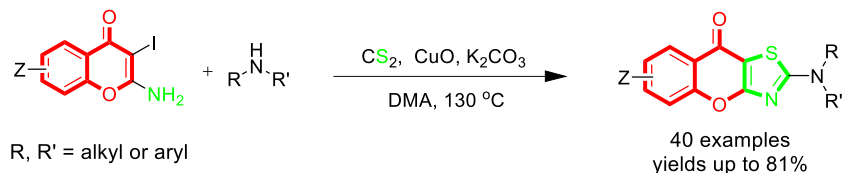


The oxidation of both N-substituted hydroxylactams and isoindolinones to the corresponding phthalimides using catalytic iron/tert-butylhydroperoxide (TBHP) reagent systems is detailed. The 2-substituted-3-hydroxyisoindolin-1-one (hydroxylactam) to imide oxidation constitutes a rather straightforward hydroxyl  $\rightarrow$  carbonyl group conversion while the latter process is a methylene  $\rightarrow$  carbonyl transformation. The iron oxidant  $\text{Fe(TFA)}_3$  (10 mol%), prepared by the treatment of iron (III) chloride with trifluoroacetic acid, is used in conjunction with TBHP (one equivalent). For the hydroxylactam substrates, the oxidation system was effective in providing the corresponding phthalimides in isolated yields ranging from 41 to 88% within a reaction time of 24 h. For the N-substituted isoindolinone to phthalimide conversions, the imide products were obtained in isolated yields of 53–96% while using the same catalyst/oxidant system. For comparison, oxidations were run with catalytic iron (III) chloride (10 mol%) and TBHP and the yields were comparable to the reactions using the trifluoroacetate-based reagent.

## Synthesis of 2-amino-9*H*-chromeno[2,3-*d*]thiazol-9-ones with Anti-inflammatory Activity via Cascade Reactions of 2-amino-3-iodochromones with Amines and Carbon Disulfide.

Jiangtao Tan, Yifan He, Yu Lin, Yuanchen Zhong, Shijun He,\* Jianping Zuo and Chunhao Yang\*. ([heshijun@shutcm.edu.cn](mailto:heshijun@shutcm.edu.cn) or [chyang@simm.ac.cn](mailto:chyang@simm.ac.cn))

*RSC Adv.*, 2024, 14, 3158–3162. DOI: 10.1039/d3ra07209f



A simple and efficient synthetic approach to 2-amino-9*H*-chromeno[2,3-*d*]thiazol-9-ones via copper promoted cascade reactions was developed. The reaction employed easily available 2-amino-3-iodochromones and amines as substrates and the targeting tricyclic compounds could be obtained with moderate to good yields. Even more important, several synthesized compounds exhibited potent anti-inflammatory activities, which suggested that this protocol may provide valuable hits for drug development in the future.