

La lettre du bureau de la Division de Chimie Organique

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LE MOT DU PRÉSIDENT

Chers Sociétaires,

Après une année 2019 particulièrement riche, l'année 2020 s'annonce tout aussi pleine d'évènements et de nouveautés pour la DCO.

Nous sommes tout d'abord heureux de vous annoncer la création de deux nouveaux Groupes Thématiques de la SCF affiliés à la DCO : le Groupe de Chimie Supramoléculaire et le Groupe Français de Chémobiologie. Ces groupes auront leurs activités propres mais ils participeront aussi à l'animation de la DCO, en participant au bureau, par exemple.

Nous allons également vivre un moment exceptionnel à l'occasion de la venue de Frances Arnold, prix Nobel de Chimie, pour la Journée de Printemps, que nous organisons en partenariat avec Sanofi et Sorbonne Université et qui se déroulera dans l'enceinte historique de la Sorbonne. Ce sera l'occasion pour une partie des récipiendaires des prix DCO de montrer leur science à un public nombreux et prestigieux.

Si vous voulez également avoir cette chance, postulez au nombreux prix de la DCO.

Notre but est de promouvoir la science faite par nos sociétaires !

Très cordialement,

Matthieu SOLLOGOUB, Président de la DCO



LA JOURNÉE DCO-Frances ARNOLD @Sorbonne



La prochaine journée de printemps organisée par la DCO sera exceptionnelle à plus d'un titre. Elle aura lieu le **jeudi 9 avril 2020** dans le prestigieux **amphithéâtre RICHELIEU** de Sorbonne Université (17 rue de la Sorbonne, 75005 Paris).



Le programme comprendra :

- 3 conférenciers invités :
 - Prof. Frances ARNOLD (California Institute of Technology, EU) **Prix NOBEL de Chimie 2018**
 - Prof. Thomas CARRELL (LMU Munich, Allemagne)
 - Prof. Jonathan CLAYDEN (Université de Bristol, GB) **Prix Franco-Britannique de la SCF 2018**
- 4 lauréats des prix de la DCO 2019 :
 - **Prix DCO** : Dr. Jean-François NIERENGARTEN (LCMM, Strasbourg)
 - **Prix jeune enseignant chercheur Jean NORMANT** : Dr. Xavier BUGAUT (iS2M, Marseille)
 - **Prix émergence Marc JULIA** : Dr. Ludovic FAVEREAU (ISCR, Rennes)
 - **Prix Thèse Dina SURDIN** : Dr. Lucie JARRIGE (ICSN, Gif-sur-Yvette)
- 2 communications orales invitées :
 - Dr. Clémence ALLAIN (ENS Paris Saclay)
 - Dr. Cornelia MEINERT (ICN, Nice)

L'inscription à cette journée est gratuite obligatoire. <https://dco-su-spring20.sciencesconf.org>

Pour les non-adhérents, elle constitue une occasion pour rejoindre la SCF.

http://www.societechimiquedefrance.fr/IMG/pdf/notice_nouveautes_pour_les_adhesions_scf.pdf

Seuls les participants inscrits pourront avoir accès à la salle de conférences. Les participants inscrits devront être porteurs de leur pièce d'identité pour ne pas se voir refuser l'accès au bâtiment.

Il n'y aura pas de pauses café lors de cette journée en raison de la réglementation en vigueur à la Sorbonne.

A PPEL D'OFFRE POUR LES PRIX DE LA DCO 2020

Date limite de candidature : le **mardi 16 mars 2020 à midi**.

La Division de Chimie Organique attribuera en 2020 :

- Deux prix de thèse Dina Surdin et Henri Kagan (**candidature par Nomination**)
- Prix Emergence Marc Julia (**candidature directe**)
- Deux prix jeunes chercheur et enseignant-chercheur Jean-Pierre Sauvage et Jean Normant (**candidature directe**)
- Un prix chercheur enseignant-chercheur avancé Jean-Marie Lehn (**candidature directe**)
- Un prix industriel Yves Chauvin (**candidature par Nomination**)
- Le prix de la DCO (**candidature par Nomination**)

Quelques généralités avant le détail prix par prix.

- Les candidats pour tous ces prix doivent être membres de la SCF affiliés à la DCO.
- Pour les dossiers présentés par nomination (*cf. ci-dessous au cas par cas*), la personne qui présente et propose le candidat doit également être membre de la SCF.
- Pour les candidatures par nomination (*cf. ci-dessous en fonction des prix*), les candidats nommés devront, après avoir été informés, envoyer eux-mêmes leur dossier.
- L'ensemble des pièces demandées doit être envoyé en version électronique aux personnes indiquées (*cf. ci-dessous*).
- Les lauréats seront invités à présenter leurs travaux lors des manifestations de la DCO.

Prix de thèse Dina SURDIN et Henri KAGAN

La division de Chimie organique de la SCF attribuera 2 prix de thèse : le prix de thèse Henri Kagan et le prix Dina Surdin. Sont éligibles, les thèses soutenues pendant l'année civile précédant l'année du prix (2019).

Les doctorants encadrés ou co-encadrés par les membres du bureau de la DCO ne sont pas éligibles.

Les dossiers de candidature devront être adressés à **Xavier Guinchard** **uniquement** par mail (xavier.guinchard@cnrs.fr) avant le **16 mars 2020 à midi** et comporter :

- CV du candidat
- Avis du responsable de l'encadrement et/ou du directeur d'équipe et/ou du directeur du laboratoire.
- Résumé du manuscrit de thèse (3 pages max.) sous format pdf
- La copie des publications (format pdf).

Les candidatures se feront par nomination, c'est-à-dire que le dossier devra être présenté par exemple par les sections régionales de la SCF, les directeurs de Laboratoire, d'équipes ou de groupes ou encore les directeurs de thèse.

Prix Emergence Marc JULIA (*moins de 6 ans de métier de la recherche après la thèse*)

La Division de Chimie Organique attribue un prix à un docteur, membre de la SCF-DCO, ayant soutenu sa thèse après le 1er mars 2014.⁽¹⁾

Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, 1 à 3 diapositives résumant les faits marquants des travaux, des tirés à part des 5 publications jugées les plus significatives par le candidat (format pdf), et être envoyées avant le **16 mars 2020 à midi** à **Olivier Baslé** (olivier.basle@lcc-toulouse.fr).

Le principe retenu pour le dépôt de dossier est celui de la candidature spontanée.

⁽¹⁾ Pour les femmes, la limite est reculée d'un an par enfant à charge né pendant cette période.

Prix Jeune Enseignant-Chercheur Jean NORMANT (*moins de 8 ans de carrière*)

La Division de Chimie Organique attribue un prix à un jeune enseignant-chercheur en poste au plus tôt depuis la rentrée universitaire 2012-2013,⁽¹⁾ effectuant ses travaux en France, et membre de la SCF-DCO depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, 1 à 3 diapositives résumant les faits marquants des travaux, des tirés à part des 5 publications jugées les plus significatives par le candidat (format pdf), et être envoyées avant le **16 mars 2020 à midi** à **Muriel Durandetti** (muriel.durandetti@univ-rouen.fr).

Le principe retenu pour le dépôt de dossier est celui de la candidature spontanée.

Prix Jeune Chercheur Jean-Pierre SAUVAGE (*moins de 8 ans de carrière*)

La Division de Chimie Organique attribue un prix à un jeune chercheur en poste au plus tôt depuis la rentrée universitaire 2012-2013,⁽¹⁾ effectuant ses travaux en France, et membre de la SCF-DCO depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, 1 à 3 diapositives résumant les faits marquants des travaux, des tirés à part des 5 publications jugées les plus significatives par le candidat (format pdf), et être envoyées avant le **16 mars 2020 à midi** à **David Gueyrard** (david.gueyrard@univ-lyon1.fr).

Le principe retenu pour le dépôt de dossier est celui de la candidature spontanée.

Prix Chercheur Enseignant-Chercheur Avancé Jean-Marie LEHN (*8-15 ans de carrière*)

La Division de Chimie Organique attribue un prix à un chercheur ou enseignant-chercheur avancé ayant pris ses fonctions entre les rentrées universitaires 2005-2006 et 2011-2012,⁽¹⁾ effectuant ses travaux en France, et membre de la SCF-DCO depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, 1 à 3 diapositives résumant les faits marquants des travaux, des tirés à part des 5 publications jugées les plus significatives par le candidat (format pdf), et être envoyées avant le **16 mars 2020 à midi** à **Jean-Marc Campagne** (jean-marc.campagne@enscm.fr).

Le principe retenu pour le dépôt de dossier est celui de la candidature spontanée.

Prix Industriel Yves CHAUVIN

La Division de Chimie Organique attribue un prix à un chimiste développant ses travaux en milieu industriel. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, et être envoyées avant le **16 mars 2020 à midi** à **Vincent Ferey** (vincent.ferey@sanofi.com).

Le principe retenu pour le dépôt de dossier est celui de la candidature par nomination (par une entité de la SCF, ou un responsable scientifique académique ou industriel).

Prix de la DCO

Le Prix de la Division Chimie Organique est attribué à un chimiste confirmé ayant effectué des travaux de recherche reconnus au niveau national et international, et membre de la SCF-DCO depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, et être envoyées avant le **16 mars 2020 à midi** à **Matthieu Sollogoub** (matthieu.sollogoub@sorbonne-universite.fr).

Le principe retenu pour le dépôt de dossier est celui de la candidature par nomination (par une entité de la SCF, ou un responsable scientifique académique ou industriel).

⁽¹⁾ Pour les femmes, la limite est reculée d'un an par enfant à charge né pendant cette période.

PRIX GUY OURISSON – SCF DCO 2019

Le Prix Guy OURISSON qui récompense le meilleur impromptu présenté au Groupe d'Etudes en Chimie Organique (GECO), a été attribué à l'occasion du GECO 60 (organisé à Obernai du 25 au 30 août 2019), à David LEBOEUF (ICMMO, Orsay) pour ses travaux sur la « photo-oxygénation de 2-propargylfuranes pour l'accès à une large gamme de cycles azotés à 5 chaînons substitués ».



MANIFESTATIONS SOUTENUES PAR LA DCO EN 2020

4th International Green Catalysis Symposium (GreenCat 2020, Rennes, 30 mars-2 avril 2020)
<https://igcs2020.sciencesconf.org>

Semaine d'Etudes en Chimie Organique (SECO 57, Dax, 10-15 mai 2020)
<http://www.congres-seco.fr>

Journée en hommage à François COUTY (Versailles, 19 mai 2020)
<https://francoiscouty.sciencesconf.org>

3^{ème} Colloque Français de Chimie du Fluor (CFCF 2020, Forges-les-Eaux, 25-28 mai 2020)
<http://www.lab-cobra.fr/cfcf2020/>

10^{ème} Symposium Francophone de Synthèse Totale (SFST 10, Marseille, 11-12 juin 2020)
<http://www.lab-cobra.fr/cfcf2020/>

Groupe d'Etudes en Chimie Organique (GECO 61, Cap d'Agde, 23-28 août 2020)
<https://geco61.sciencesconf.org>

LES HIGHLIGHTS DE LA CHIMIE DE LA DCO

Le bureau de la Division de Chimie Organique souhaite mettre en valeur chaque semestre, les articles les plus significatifs signés par les membres de notre division.

Vous trouverez dans les pages suivantes un choix d'articles publiés dans la deuxième moitié d'année 2019 dans les journaux suivants :

- *Science*,
- *Nature Chemistry*,
- *Nature Catalysis*,
- *Angewandte Chemie International Edition*,
- *Journal of the American Chemical Society*,
- *Chemical Science*.

Nous avons conscience que ce choix d'articles est arbitraire.

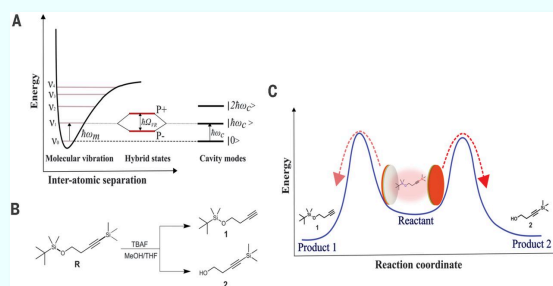
N'hésitez pas à nous faire part de vos remarques, et, éventuellement, à nous soumettre des propositions de travaux à « highlighter ».

Tilting a ground-state reactivity landscape by vibrational strong coupling

Science **2019**, 363, 615

A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Chervy, A. Shalabney, E. Devaux, C. Genet, J. Moran, T. W. Ebbesen

<https://doi.org/10.1126/science.aau7742>



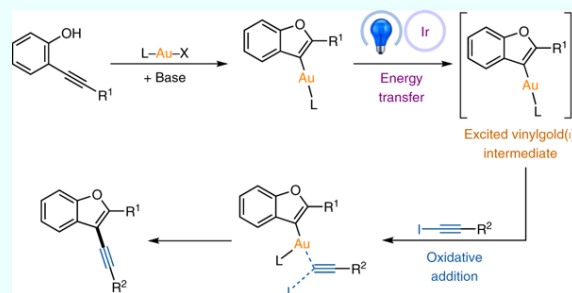
We explored a new approach to site selectivity using vibrational strong coupling (VSC) between a reactant and the vacuum field of a microfluidic optical cavity. Specifically, we studied the reactivity of a compound bearing two possible silyl bond cleavage sites—Si–C and Si–O, respectively—as a function of VSC of three distinct vibrational modes in the dark. The results show that VSC can indeed tilt the reactivity landscape to favor one product over the other. Thermodynamic parameters reveal the presence of a large activation barrier and substantial changes to the activation entropy, confirming the modified chemical landscape under strong coupling.

Photosensitized oxidative addition to gold(I) enables alkynylative cyclization of o-alkynylphenols with iodoalkynes

Nat. Chem **2019**, 11, 797

Z. Xia, V. Corcé, F. Zhao, C. Przybylski, A. Espagne, L. Jullien, T. Le Saux, Y. Gimbert, H. Dossmann, V. Mouriès-Mansuy, C. Ollivier, L. Fensterbank

<https://doi.org/10.1038/s41557-019-0295-9>



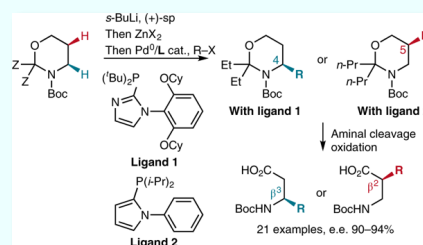
Gold(I) complexes have shown some reluctance to undergo oxidative addition unless special sets of ligands on gold(I), reagents or reaction conditions are used. Here we show that under visible-light irradiation, an iridium photocatalyst triggers—via triplet sensitization—the oxidative addition of an alkynyl iodide onto a vinylgold(I) intermediate to deliver C(sp)²–C(sp) coupling products after reductive elimination. Mechanistic and modelling studies support that an energy-transfer event takes place, rather than a redox pathway. This particular mode of activation in gold homogenous catalysis was applied in several dual catalytic processes. Alkynylbenzofuran derivatives were obtained from o-alkynylphenols and iodoalkynes in the presence of catalytic gold(I) and iridium(III) complexes under blue light-emitting diode irradiation.

Regiodivergent enantioselective C–H functionalization of Boc-1,3-oxazinanones for the synthesis of β²- and β³-amino acids

Nature Catal. **2019**, 2, 882

W. Lin, K.-F. Zhang, O. Baudoin

<https://doi.org/10.1038/s41929-019-0336-1>



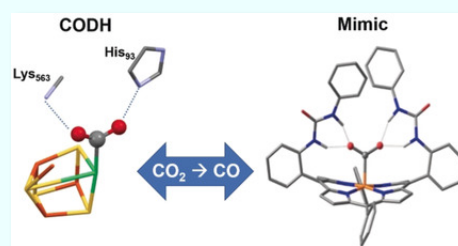
We report a straightforward regio- and enantiodivergent access to β²- and β³-amino acids using a one-pot reaction composed of sparteine-mediated enantioselective lithiation of a Boc-1,3-oxazinanone, transmetalation to zinc and direct or migratory Negishi coupling with an organic electrophile. The regioselectivity of the Negishi coupling was highly ligand-controlled and switch-able to obtain the C4- or the C5-functionalized product exclusively. High enantioselectivities were achieved on a broad range of examples, and a catalytic version in chiral diamine was developed using the (+)-sparteine surrogate. Selected C4- and C5-functionalized

Second-Sphere Biomimetic Multipoint Hydrogen-Bonding Patterns to Boost CO₂ Reduction of Iron Porphyrins

Angew. Chem. Int. Ed. **2019**, *58*, 4504

P. Gotico, B. Boitrel, R. Guillot, M. Sircoglou, A. Quaranta, Z. Halime, W. Leibl, A. Aukauloo

<https://doi.org/10.1002/anie.201814339>



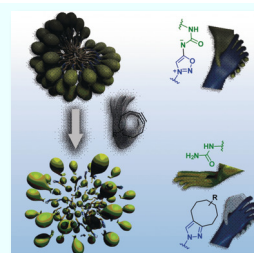
Like CODH: Urea groups at an iron porphyrin catalyst give multipoint hydrogen-bonding stabilization resembling that found in the CO₂ adduct of carbon monoxide dehydrogenase (CODH). The catalyst gave improved CO₂ reduction to CO. Entrapped water molecules within the molecular clefts were found to be the source of protons for the CO₂ reduction.

Controlled Release of a Micelle Payload via Sequential Enzymatic and Bioorthogonal Reactions in Living Systems

Angew. Chem. Int. Ed. **2019**, *58*, 6366

K. Porte, B. Renoux, E. Péraudeau, J. Clarhaut, B. Eddhif, P. Pointot, E. Gravel, E. Doris, A. Wijkhuisen, D. Audisio, S. Papot, F. Taran

<https://doi.org/10.1002/anie.201902137>



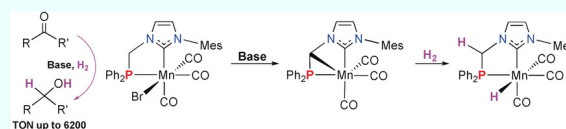
Bioorthogonal nano-explosion: Nanoparticles designed with bioorthogonal iminosydnone cleavable linkers can be destroyed on demand to release their content upon reaction with cyclooctynes. This approach of controlled release was successfully used in living cells as well as in mice.

Phosphine-NHC Manganese Hydrogenation Catalyst Exhibiting a Non-Classical Metal-Ligand Cooperative H₂ Activation Mode

Angew. Chem. Int. Ed. **2019**, *58*, 6727

R. Buhaibeh, O. A. Filippov, A. Bruneau-Voisine, J. Willot, C. Duhayon, D. A. Valyaev, N. Lukan, Y. Canac, J.-B. Sortais

<https://doi.org/10.1002/anie.201901169>



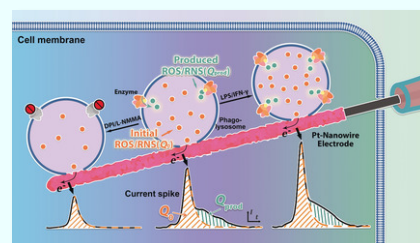
A NHC-phosphine manganese complex in the presence of base is transformed into a NHC-phosphinomethanide derivative able to easily activate dihydrogen via a non-classical metal-ligand cooperative mode. This process is relevant for catalysis, providing one of the most efficient Mn-based systems for ketone hydrogenation.

Electrochemical Monitoring of ROS/RNS Homeostasis Within Individual Phagolysosomes Inside Single Macrophages

Angew. Chem. Int. Ed. **2019**, *58*, 7753

X.-W. Zhang, A. Oleinick, H. Jiang, Q.-L. Liao, Q.-F. Qiu, I. Svir, Y.-L. Liu, C. Amatore, W.-H. Huang

<https://doi.org/10.1002/anie.201902734>



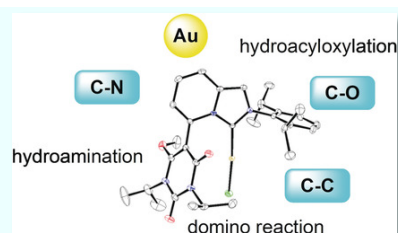
Single nanowire electrode amperometry was used to establish that the consumption of ROS/RNS in a phagolysosome leads to a ROS/RNS production. This validates the long-sought ROS/RNS homeostatic mechanism that was hypothesized to regulate the ROS/RNS intravesicular content during pathogens digestion.

An Original L-shape, Tunable N-Heterocyclic Carbene Platform for Efficient Gold(I) Catalysis

Angew. Chem. Int. Ed. **2019**, *58*, 7977

Y. Tang, I. Benaissa, M. Huynh, L. Vendier, N. Lugan, S. Bastin, P. Belmont, V. César, V. Michelet

<https://doi.org/10.1002/anie.201901090>



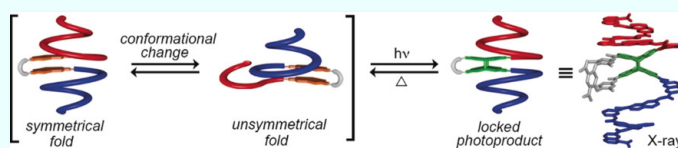
Broadband ligands: The synthesis and characterization of original NHC ligands based on a imidazo[1,5-a]pyridin-3-ylidene (IPy) scaffold functionalized with a flanking barbituric heterocycle is described as well as their use as tunable ligands. High and unprecedented efficiency for gold-catalyzed C–N, C–O, and C–C bond formations is disclosed.

Light-Controlled Conformational Switch of an Aromatic Oligoamide Foldamer

Angew. Chem. Int. Ed. **2019**, *58*, 8063

B. Gole, B. Kauffmann, V. Maurizot, I. Huc, Y. Ferrand

<https://doi.org/10.1002/anie.201902378>



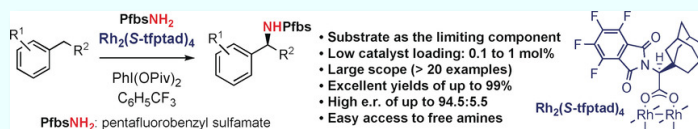
A **helical conformational switch** can be locked upon photoirradiation. The oligomers adopt two distinct conformations: a canonical symmetrical conformation and an unanticipated unsymmetrical conformation. Photoirradiation of the foldamer leads to the quantitative and thermally reversible formation of a single photoproduct resulting from the [4+4] cycloaddition of two diazaanthracenes.

Catalytic Enantioselective Intermolecular Benzylic C(sp³)–H Amination

Angew. Chem. Int. Ed. **2019**, *58*, 8192

A. Nasrallah, V. Boquet, A. Hecker, P. Retailleau, B. Darses, P. Dauban

<https://doi.org/10.1002/anie.201902882>



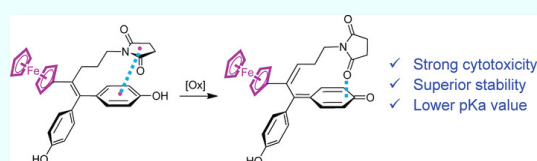
Benz to benz: A practical method for asymmetric intermolecular benzylic C(sp³)–H amination is reported. The latter is based on the combination of the pentafluorobenzyl sulfamate PfbzNH₂ with the chiral rhodium(II) catalyst Rh₂(S-tfptad)₄. Various substrates are converted to benzylic amines with excellent yields and high levels of enantioselectivity. The Pfbz group can be removed under mild conditions to afford the free-NH benzylic amines.

Atypical Lone Pair–π Interaction with Quinone Methides in a Series of Imido-Ferrociphenol Anticancer Drug Candidates

Angew. Chem. Int. Ed. **2019**, *58*, 8421

Y. Wang, P. Pigeon, S. Top, J. S. García, C. Troufflard, I. Ciofini, M. J. McGlinchey, G. Jaouen

<https://doi.org/10.1002/anie.201902456>



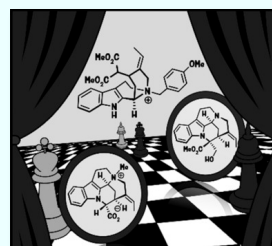
Heterocycle-substituted ferrociphenols display strong anticancer activity through the generation of active metabolites such as quinone methides (QMs). The specific lone pair–π interaction between an imide carbonyl group and the quinone motif is crucial for the cytotoxic behaviour of their imido-ferrociphenol precursors as it markedly enhances the stability of the QMs and lowers the pK_a values of the corresponding phenolates.

Bioinspired Oxidative Cyclization of the Geissoschizine Skeleton for Enantioselective Total Synthesis of Mavacuran Alkaloids

Angew. Chem. Int. Ed. **2019**, *58*, 9861

M. Jarret, V. Turpin, A. Tap, J.-F. Gallard, C. Kouklovsky, E. Poupon, G. Vincent, L. Evanno

<https://doi.org/10.1002/anie.201905227>



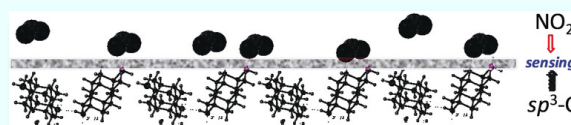
Skeleton assembly: The long-standing problem of effecting the bioinspired oxidative cyclization of geissoschizine to the mavacuran skeleton has been resolved. The key N1–C16 bond was formed by locking in the cis conformation through quaternization of the aliphatic nitrogen atom, and allowed the total syntheses of (+)-taberdivarine H, (+)-16-hydroxymethyl-pleiocarpamine, and (+)-16-epi-pleiocarpamine, and their postulated biosynthetic precursor 16-formyl-pleiocarpamine.

Diamondoid Nanostructures as sp^3 -Carbon-Based Gas Sensors

Angew. Chem. Int. Ed. **2019**, *58*, 9933

O. Moncea, J. Casanova-Chafer, D. Poinso, L. Ochmann, C. D. Mboyi, H. Nasrallah, E. Llobet, I. Makni, M. El Atrous, S. Brandès, Y. Rousselin, B. Domenichini, N. Nuns, A. A. Fokin, P. R. Schreiner, J.-C. Hierso

<https://doi.org/10.1002/anie.201903089>



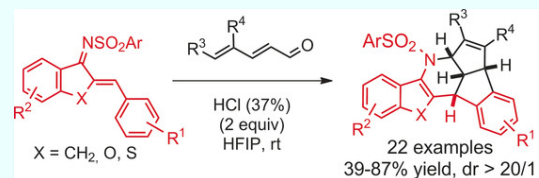
A nanodiamond-based chemical nose: sp^3 -C-based diamondoid nanostructures, either Pd-coated or pristine, detect NO_2 and NH_3 at ppb to ppm levels at low operating temperatures.

A Fused Hexacyclic Ring System: Diastereoselective Polycyclization of 2,4-Dienals through an Interrupted iso-Nazarov Reaction

Angew. Chem. Int. Ed. **2019**, *58*, 9969

A.-S. Marques, T. Duhail, J. Marrot, I. Chataigner, V. Coeffard, G. Vincent, X. Moreau

<https://doi.org/10.1002/anie.201903860>



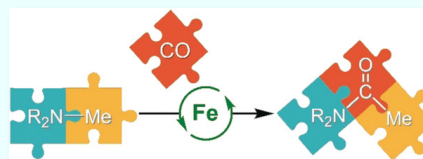
Ring, ring, ring: An unprecedented domino polycyclization from readily available 2,4-dienals and cyclic α,β -unsaturated imines, initiated by an iso-Nazarov reaction, is reported. This Brønsted acid promoted transformation affords original polycyclic scaffolds and enables the formation of three new cycles, four new bonds, and four contiguous stereocenters in a single operation and in a highly diastereoselective manner.

Carbonylation of C–N Bonds in Tertiary Amines Catalyzed by Low-Valent Iron Catalysts

Angew. Chem. Int. Ed. **2019**, *58*, 10884

T. Nasr Allah, S. Savourey, J.-C. Berthet, E. Nicolas, T. Cantat

<https://doi.org/10.1002/anie.201903740>



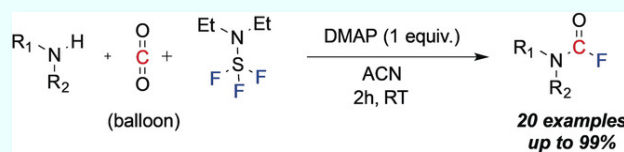
No pressure: Low-valent iron complexes, such as $\text{K}_2[\text{Fe}(\text{CO})_4]$, efficiently catalyze the carbonylation of C–N bonds in amines by CO insertion. Lewis acids such as AlCl_3 and $\text{Nd}(\text{OTf})_3$ have a positive influence on the catalytic activity and enable the carbonylation at a low pressure of CO.

Direct Synthesis of Carbamoyl Fluorides by CO₂ Deoxyfluorination

Angew. Chem. Int. Ed. **2019**, *58*, 12545

K. Onida, A. Tlili

<https://doi.org/10.1002/anie.201907354>



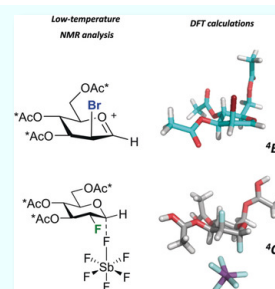
CO₂ deoxyfluorination: The reductive fluorination of CO₂ enables the synthesis of carbamoyl fluorides. The reactions are easily scalable, and the concept was exploited for the synthesis of ¹³C-labeled carbamoyl compounds.

Structural and Computational Analysis of 2-Halogeno-Glycosyl Cations in the Presence of a Superacid: An Expansive Platform

Angew. Chem. Int. Ed. **2019**, *58*, 13758

L. Lebedel, A. Ardá, A. Martin, J. Désiré, A. Mingot, M. Auferio, N. Aiguabella Font, R. Gilmour, J. Jiménez-Barbero, Y. Blériot, S. Thibaudeau

<https://doi.org/10.1002/anie.201907001>



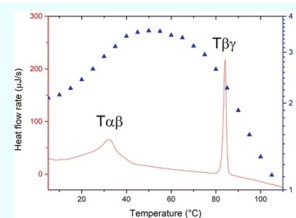
Influential halogens: Halogen substitution effects on the conformation of superacid-generated glucosyl, galactosyl, and mannosyl cations are described. The 2-bromo derivatives display intramolecular stabilization of the glycosyl cations. Introducing an electron-withdrawing fluorine atom at C2 influences the oxocarbenium ion reactivity in a superacid, with quenching by weakly coordinating SbF₆⁻ anions.

A Competing Hydrogen Bonding Pattern to Yield a Thermo-Thickening Supramolecular Polymer

Angew. Chem. Int. Ed. **2019**, *58*, 13849

V. Ayzac, Q. Sallembien, M. Raynal, B. Isare, J. Jestin, L. Bouteiller

<https://doi.org/10.1002/anie.201908954>



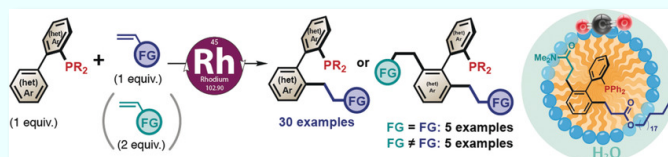
An ester-bis-urea self-assembles into three competing rod-like structures in non-polar solvents. At high T, isotropic dispersions of rods are stabilized by the classical urea-urea hydrogen bonding pattern. At low T, the ester groups interfere in the hydrogen bond network and trigger a mesoscopic alignment of the rods. The transition from low to high T structure is reversible and accompanied by a viscosity increase.

Rh^I-Catalyzed P^{III}-Directed C-H Bond Alkylation: Design of Multifunctional Phosphines for Carboxylation of Aryl Bromides with Carbon Dioxide

Angew. Chem. Int. Ed. **2019**, *58*, 14110

Z. Zhang, T. Roisnel, P. H. Dixneuf, J.-F. Soulé

<https://doi.org/10.1002/anie.201906913>

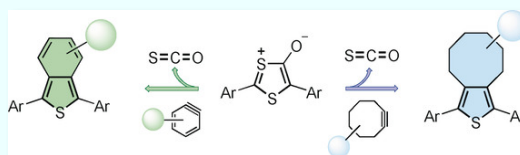


Multifunctional phosphines bearing flexible pendant groups, such as ester, amide, pyridine, aryl, or cyano groups, were synthesized through Rh^I-catalyzed C-H alkylation of biarylphosphines with functionalized alkenes (40 examples). An unprecedented CO₂-responsive surfactant was prepared that exhibits high catalytic activity in the Pd-catalyzed carboxylation of aryl bromides in aqueous media.

Strain-Promoted 1,3-Dithiolium-4-olates–Alkyne Cycloaddition

Angew. Chem. Int. Ed. **2019**, *58*, 14544

R. A. Kumar, M. R. Pattanayak, E. Yen-Pon, J. Eliyan, K. Porte, S. Bernard, M. Riomet, P. Thuéry, D. Audisio, F. Taran
<https://doi.org/10.1002/anie.201908052>

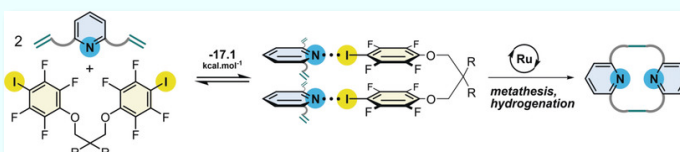


Under strain: 1,3-dithiolium-4-olates reacted with strained alkynes, affording polyaromatic thiophene structures in high yields. Their use for ligation applications has also been investigated with cyclooctynes, offering a new orthogonal reaction to the strain-promoted azide–alkyne reaction.

Halogen-Bond Donor Catalyst for Templated Macrocyclization

Angew. Chem. Int. Ed. **2019**, *58*, 14940

K. Guillier, E. Caytan, V. Dorcet, F. Mongin, É. Dumont, F. Chevallier
<https://doi.org/10.1002/anie.201908317>

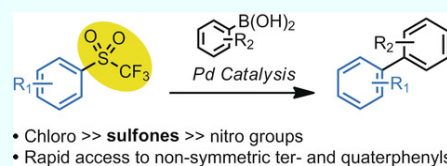


Iodoperfluorophenyl ethers were used as exotemplates in a substoichiometric amount to perform a halogen-bond templated 1:1 macrocyclization of pyridine derivatives through a tandem olefin metathesis/transfer hydrogenation.

Suzuki–Miyaura Coupling of (Hetero)Aryl Sulfones: Complementary Reactivity Enables Iterative Polyaryl Synthesis

Angew. Chem. Int. Ed. **2019**, *58*, 14959

P. Chatelain, A. Sau, C. N. Rowley, J. Moran
<https://doi.org/10.1002/anie.201908336>

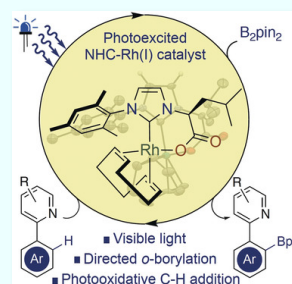


Complementary reactivity: Aryl sulfones undergo Suzuki–Miyaura coupling with intermediate reactivity between aryl halides and nitroarenes, enabling the iterative synthesis of non-symmetric polyaromatics.

Visible Light Induced Rhodium(I)-Catalyzed C–H Borylation

Angew. Chem. Int. Ed. **2019**, *58*, 15244

J. Thongpaen, R. Manguin, V. Dorcet, T. Vives, C. Duhayon, M. Mauduit, O. Baslé
<https://doi.org/10.1002/anie.201905924>



Double agent: An efficient visible light induced rhodium(I)-catalyzed regioselective borylation of aromatic C–H bonds is reported. The photocatalytic system is based on a single NHC–Rh^I complex capable of both harvesting visible light and enabling the bond breaking/forming at room temperature. The bidentate structure of the NHC ligand was shown to be critical both for the stability and the reactivity of the Rh^I complex.

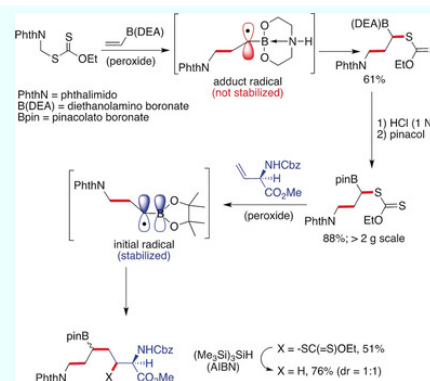
Alternating Radical Stabilities: A Convergent Route to Terminal and Internal Boronates

Angew. Chem. Int. Ed. **2019**, *58*, 16936

Q. Huang, J. Michalland, S. Z. Zard

<https://doi.org/10.1002/anie.201906497>

To stabilize or not to stabilize: Alternating the relative stabilities of intermediate radicals by switching the hybridization of the adjacent boron atom from sp^2 to sp^3 and vice versa provides a convenient method to control successive intermolecular radical additions, leading to complex, highly functionalized boronates.

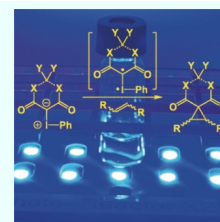


Blue LED Irradiation of Iodonium Ylides Gives Diradical Intermediates for Efficient Metal-free Cyclopropanation with Alkenes

Angew. Chem. Int. Ed. **2019**, *58*, 16959

Tristan Chidley, Islam Jameel, Shafa Rizwan, Philippe A. Peixoto, Laurent Pouységu, Stéphane Quideau, W. Scott Hopkins, Graham K. Murphy

<https://doi.org/10.1002/anie.201908994>



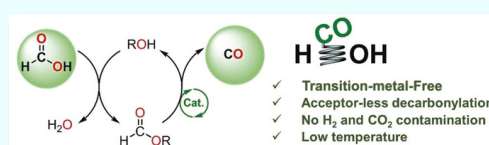
Doubly activated cyclopropanes are generated upon irradiating alkenes and β -dicarbonyl-derived iodonium ylides with visible light from blue LEDs. This metal-free cyclopropane synthesis works with cyclic and acyclic ylides, and with electronically-diverse alkenes, in yields up to 96%. Computational analysis supports a mechanism based on exclusive HOMO to LUMO excitation, instead of free carbene generation.

Transition-Metal-Free Acceptorless Decarbonylation of Formic Acid Enabled by a Liquid Chemical-Looping Strategy

Angew. Chem. Int. Ed. **2019**, *58*, 17215

A. Imberdis, G. Lefèvre, T. Cantat

<https://doi.org/10.1002/anie.201909039>



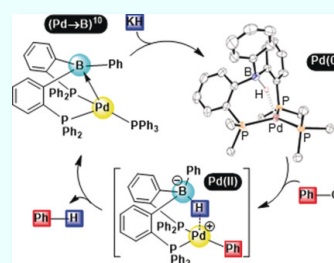
In the loop: Selective and acceptorless decarbonylation of formic acid was achieved for the first time under transition-metal-free conditions. The approach, inspired by chemical-looping strategies, shuts down the thermodynamically favored dehydrogenation of formic acid, yielding a pure stream of CO without H₂ or CO₂ contamination.

Palladium–Borane Cooperation: Evidence for an Anionic Pathway and Its Application to Catalytic Hydro-/Deutero-dechlorination

Angew. Chem. Int. Ed. **2019**, *58*, 18783

H. Kameo, J. Yamamoto, A. Asada, H. Nakazawa, H. Matsuzaka, D. Bourissou

<https://doi.org/10.1002/anie.201909675>

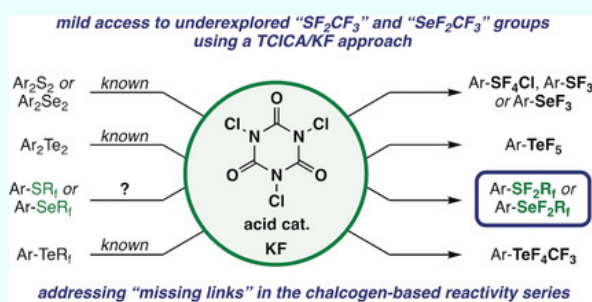


A palladium–borane dance: An anionic reaction pathway involving hydride insertion into a Pd→B bond, C–Cl bond activation by an anionic Pd⁰ species, and B-assisted C–H bond formation has been discovered and leveraged into catalysis of hydro-/deutero-dechlorination. The boron acts as an acceptor towards Pd via the Pd→B interaction (see figure), but as a donor in the Pd⁰ borohydride thanks to B–H–Pd bridging.

Difluoro(aryl)(perfluoroalkyl)- λ^4 -sulfanes and Selanes: Missing Links of Trichloroisocyanuric Acid/Potassium Fluoride Chemistry

Angew. Chem. Int. Ed. **2019**, *58*, 18937

F. Brüning, C. Ross Pitts, J. Kalim, D. Bornemann, C. Ghiazza, J. de Montmollin, N. Trapp, T. Billard, A. Togni
<https://doi.org/10.1002/anie.201910594>

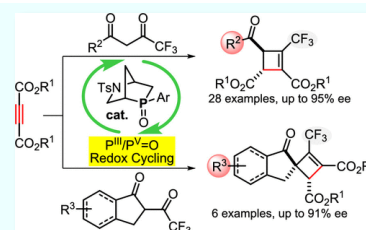


The TCICA/KF approach to oxidative fluorination of heteroatoms has emerged as a surprisingly simple, safe, and versatile surrogate to classically challenging fluorination reactions. The mild syntheses of metastable difluoro(aryl)(perfluoroalkyl)- λ^4 -sulfanes and selanes is reported and preliminary evidence is provided that difluoro(aryl)(trifluoro-methyl)- λ^4 -sulfanes may act as fluorinating reagents.

Catalytic and Asymmetric Process via $\text{P}^{\text{III}}/\text{P}^{\text{V}}=\text{O}$ Redox Cycling: Access to (Trifluoromethyl)cyclobutenes via a Michael Addition/Wittig Olefination Reaction

J. Am. Chem. Soc. **2019**, *141*, 10142

C. Lorton, T. Castanheiro, A. Voituriez
<https://doi.org/10.1021/jacs.9b02539>

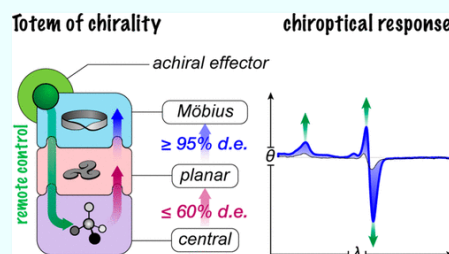


In the present study, we report the first enantioselective and highly efficient phosphine-catalyzed process via a chemoselective in situ phosphine oxide reduction. Starting with 4,4,4-trifluorobutane-1,3-dione and dialkyl acetylenedicarboxylate substrates, highly functionalized fluorinated cyclobutenes were obtained in excellent yields and enantioselectivities. Using the same methodology, CF_3 -spirocyclobutene derivatives were also synthesized (34 examples, up to 95% ee).

Orchestrating Communications in a Three-Type Chirality Totem: Remote Control of the Chiroptical Response of a Möbius Aromatic System

J. Am. Chem. Soc. **2019**, *141*, 11583

R. Benchouaia, N. Cissé, B. Boitrel, M. Sollogoub, St. Le Gac, M. Menand
<https://doi.org/10.1021/jacs.9b04074>



We report herein the first example of a Möbius aromatic ring capped by a cavity, consisting of a Möbius [28]hexaphyrin doubly linked to an α -cyclodextrin. This unique design affords a "totem" of three different chirality elements arising from the cyclodextrin (fix central chirality), the bridging pattern (dynamic planar chirality), and the hexaphyrin (dynamic topological chirality). Chirality transfers (as shown in the TOC graphic) are characterized by a stereospecific planar-to-topological communication (diastereomeric excess >95%; the highest asymmetric selectivity reported to date for a Möbius ring) combined to a stereoselective central-to-planar communication (up to 60% diastereomeric excess). The stereoselectivity is remotely controlled by coordination of an achiral effector to the hexaphyrin, increasing up to 5 times the chiroptical response of the Möbius aromatic π -system.

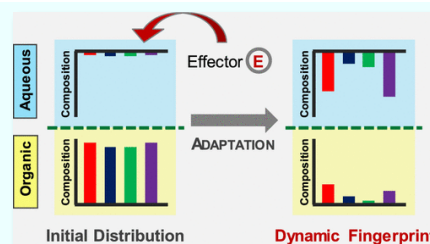
Pattern Generation and Information Transfer through a Liquid/Liquid Interface in 3D Constitutional Dynamic Networks of Imine Ligands in Response to Metal Cation Effectors

J. Am. Chem. Soc. **2019**, *141*, 12724

A. Osypenko, S. Dhers, J.-M. Lehn

<https://doi.org/10.1021/jacs.9b05438>

We report the generation of distributional signals by the action of particular effectors (metal cations), on dynamic covalent libraries (DCLs) of receptor molecules, (ligands for metal cations). Different effectors are discriminated by the formation of different constitutional distributions, which result from the adaptation of the DCL to the action of a particular cation effector through the selection and exchange of components. Compartmentalization by operation in a system of immiscible solvents (water and chloroform) results in a 3D constitutional dynamic network (CDN), effecting distributional signal and information transfer between two domains, through the interface from the “writing” input phase (the IN-phase) and the “reading” output phase (the OUT-phase). The pattern recognition techniques were successfully applied to analyze the output generated by the action of different effectors on the higher order [5 × 5] DCL.



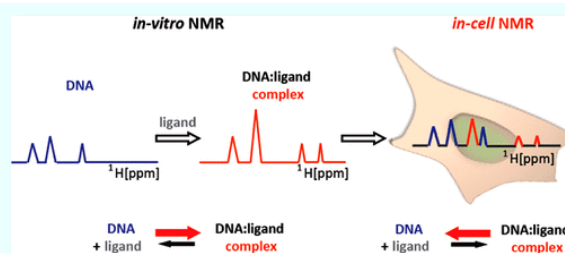
Monitoring DNA–Ligand Interactions in Living Human Cells Using NMR Spectroscopy

J. Am. Chem. Soc. **2019**, *141*, 13281

M. Krafcikova, S. Dzatko, C. Caron, A. Granzhan, R. Fiala, T. Loja, M.-P. Teulade-Fichou, T. Fessl, R. Hänsel-Hertsch, J.-L. Mergny, S. Foldynova-Trantirkova, L. Trantirek

<https://doi.org/10.1021/jacs.9b03031>

We developed an in-cell NMR-based approach for monitoring DNA–ligand interactions inside the nuclei of living human cells. Our method relies on the acquisition of NMR data from cells electroporated with preformed DNA–ligand complexes. The impact of the intracellular environment on the integrity of the complexes is assessed based on in-cell NMR signals from unbound and ligand-bound forms of a given DNA target. This technique was tested on complexes of two model DNA fragments and four ligands, namely, a representative DNA minor-groove binder (netropsin) and ligands binding DNA base-pairing defects (naphthalenophanes).



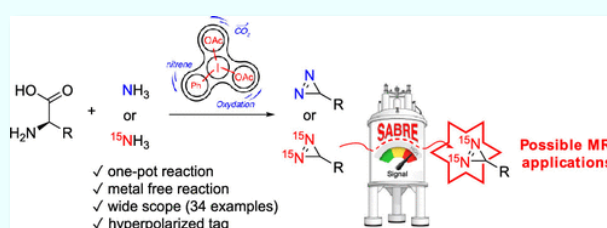
Iodonitrene in Action: Direct Transformation of Amino Acids into Terminal Diazirines and ¹⁵N₂-Diazirines and Their Application as Hyperpolarized Markers

J. Am. Chem. Soc. **2019**, *141*, 13689

T. Glachet, H. Marzag, N. Saraiva Rosa, J. F. P. Colell, G. Zhang, W. S. Warren, X. Franck, T. Theis, V. Reboul

<https://doi.org/10.1021/jacs.9b07035>

A one-pot metal-free conversion of unprotected amino acids to terminal diazirines has been developed using $\text{PhI}(\text{OAc})_2$ and NH_3 . This PIDA-mediated transformation occurs via 3 consecutive reactions and involves an iodonitrene intermediate. This method is tolerant to most functional groups found on the lateral chain of amino acids, it is operationally simple, and it can be scaled up to provide multigram quantities of diazirine. We also demonstrated that this transformation could be applied to dipeptides without racemization. $^{14}\text{N}_2$ and $^{15}\text{N}_2$ isotopomers can be obtained, emphasizing a key transimination step when using $^{15}\text{NH}_3$. In addition, we report the first experimental observation of $^{14}\text{N}/^{15}\text{N}$ isotopomers directly creating an asymmetric carbon.

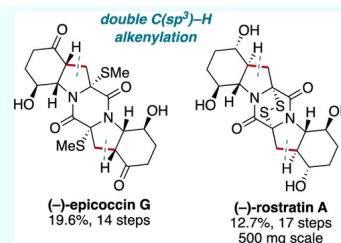


Efficient and Divergent Total Synthesis of (–)-Epicoccin G and (–)-Rostratin A Enabled by Double C(sp³)–H Activation

J. Am. Chem. Soc. **2019**, *141*, 15779

P. Thesmar, O. Baudoïn

<https://doi.org/10.1021/jacs.9b09359>



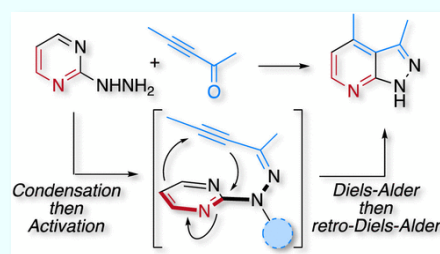
We report the enantioselective, scalable, and divergent total synthesis of 2 symmetrical pentacyclic dithiodiketopiperazines, (–)-epiccocin G and (–)-rostratin A. A common intermediate was synthesized on a multigram scale from inexpensive, commercially available starting materials using an enantioselective organocatalytic epoxidation and a double C(sp³)–H activation as key steps, with the latter allowing the efficient simultaneous construction of the two 5-membered rings. In addition to the cis,cis-fused target (–)-epiccocin G, the more challenging (–)-rostratin A, possessing two trans ring junctions, was obtained for the first time on a 500 mg scale. Both natural products were synthesized with high overall yields (13–20%).

Activating Pyrimidines by Pre-distortion for the General Synthesis of 7-Aza-indazoles from 2-Hydrazonylpyrimidines via Intramolecular Diels–Alder Reactions

J. Am. Chem. Soc. **2019**, *141*, 15901

V. Le Foulér, Y. Chen, V. Gandon, V. Bizet, C. Salomé, T. Fessard, F. Liu, K. N. Houk, N. Blanchard

<https://doi.org/10.1021/jacs.9b07037>



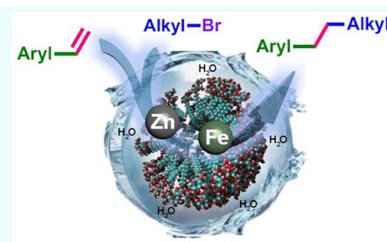
We describe how 2-hydrazonylpyrimidines, easily obtained in two steps from commercially available 2-halopyrimidines, can be exceptionally activated by trifluoroacetylation. This allows a Diels–Alder cycloaddition under very mild reaction conditions, leading to a large diversity of aza-indazoles, a ubiquitous scaffold in medicinal chemistry. This reaction is general and scalable and has an excellent functional group tolerance. A straightforward synthesis of a key intermediate of Bayer's Vericiguat illustrates the potential of this cycloaddition strategy. Quantum mechanical calculations show how the simple N-trifluoroacetylation of 2-hydrazonylpyrimidines distorts the substrate into a transition-state-like geometry that readily undergoes the intramolecular Diels–Alder cycloaddition.

Fe-Catalyzed Reductive Couplings of Terminal (Hetero)Aryl Alkenes and Alkyl Halides under Aqueous Micellar Conditions

J. Am. Chem. Soc. **2019**, *141*, 17117

H. Pang, Y. Wang, F. Gallou, B. H. Lipshutz

<https://doi.org/10.1021/jacs.9b04510>



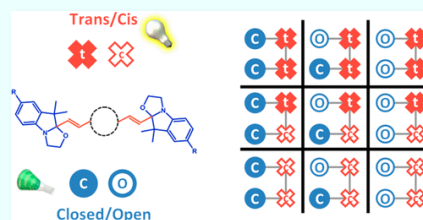
The combination of a vinyl-substituted aromatic or heteroaromatic and an alkyl bromide or iodide leads, in the presence of Zn and a catalytic amount of an Fe(II) salt, to a net reductive coupling. The new C–C bond is regioselectively formed at rt at the β-site of the alkene. The coupling only occurs in an aqueous micellar medium, where a radical process is likely, supported by several control experiments. A mechanism based on these data is proposed.

When Light and Acid Play Tic-Tac-Toe with a Nine-State Molecular Switch

J. Am. Chem. Soc. **2019**, *141*, 19151

C. Guerrin, Y. Aidibi, L. Sanguinet, P. Leriche, S. Aloise, M. Orio, S. Delbaere

<https://doi.org/10.1021/jacs.9b11048>



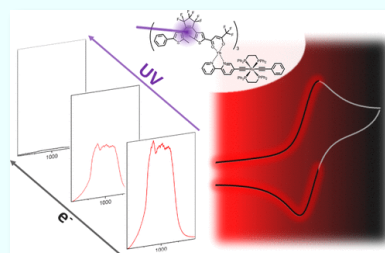
The present study reports on two molecular systems consisting of two indolino-oxazolidine (Box) moieties connected to an aromatic bridge (phenyl or bithiophene) by ethylenic junctions. Such systems, referenced as BiBox, are expected to show up multiaddressable and multiresponsive behaviors. On one hand, the oxazolidine ring opening/closure of Box moieties can be addressed by chemical stimuli, and on the other hand, the trans-to-cis isomerization of the ethylenic junctions is induced by visible light irradiation (with a thermal back conversion). NMR and UV–visible spectroscopies allowed to characterize up to nine out of the ten theoretically expected commutation states as well as to measure the kinetics of the interconversions. Also, steady state fluorescence spectroscopy measurements highlighted the strong influence of the open/closed states of the Box moieties on their emission properties.

Dual Light and Redox Control of NIR Luminescence with Complementary Photochromic and Organometallic Antennae

J. Am. Chem. Soc. **2019**, *141*, 20026

H. AlSabea, L. Norel, O. Galangau, H. Hijazi, R. Metivier, T. Roisnel, O. Maury, C. Bucher, F. Riobe, S. Rigaut

<https://doi.org/10.1021/jacs.9b11318>



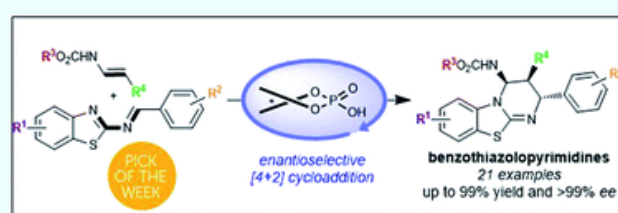
With the help of a judicious association between dithienylethene (DTE) units, an ytterbium ion, and a ruthenium carbon-rich complex, we describe (i) the efficient (on/off) switching of pure NIR luminescence with a photochromic unit absorbing in the UV range and (ii) the association of electrochemical and photochemical control of this NIR emission in a single system with nondestructive readout.

Chiral phosphoric acid-catalyzed enantioselective construction of structurally diverse benzothiazolopyrimidines

Chem. Sci. **2019**, *10*, 3765

L. Jarrige, D. Glavac, G. Levitre, P. Retailleau, G. Bernadat, L. Neuville, G. Masson

<https://doi.org/10.1039/C8SC05581E>



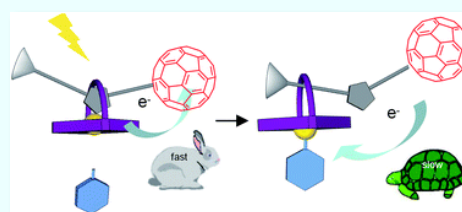
Chiral phosphoric acid catalyzed the formal [4+2]-cycloaddition of 2-benzothiazolamines with enecarbamates to provide benzothiazolopyrimidines with up to 99% yield and >99% ee.

Light triggers molecular shuttling in rotaxanes: control over proximity and charge recombination

Chem. Sci. **2019**, *10*, 3846

M. Wolf, A. Ogawa, M. Bechtold, M. Vonesch, J. A. Wytko, K. Oohora, S. Campidelli, T. Hayashi, D. M. Guldi, J. Weiss

<https://doi.org/10.1039/C8SC05328F>



The lifetime of a charge separated state is enhanced by the effects of solvent polarity and the coordination-controlled shuttling of a dumbbell in a porphyrin/fullerene rotaxane.

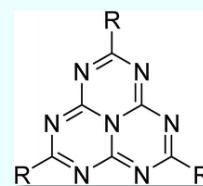
Renewing accessible heptazine chemistry: 2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine, a new highly soluble heptazine derivative with exchangeable groups, and examples of newly derived heptazines and their physical chemistry

Chem. Sci. 2019, 10, 5513

L. Galmiche, C. Allain, T. Le, R. Guillot, P. Audebert

<https://doi.org/10.1039/C9SC00665F>

We have prepared 2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine, the first highly soluble heptazine derivative possessing easily exchangeable leaving groups.



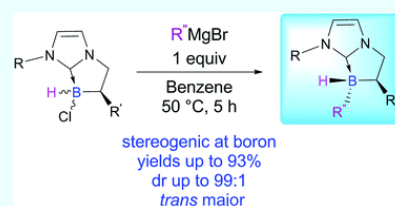
Highly diastereoselective preparation of chiral NHC-boranes stereogenic at the boron atom

Chem. Sci. 2019, 10, 6524

C. Aupic, A. A. Mohamed, C. Figliola, P. Nava, B. Tuccio,

G. Chouraqui, J.-L. Parrain, O. Chuzel

<https://doi.org/10.1039/C9SC01454C>



Stereogenic main group elements, a promising strategy for metal-free enantioselective catalysis.

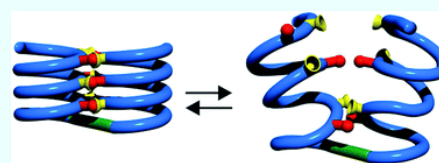
Interplay of secondary and tertiary folding in abiotic foldamers

Chem. Sci. 2019, 10, 6984

D. Mazzier, S. De, B. Wicher, V. Maurizot, I. Huc

<https://doi.org/10.1039/C9SC01322A>

Helical secondary folds are stabilized within abiotic helix–turn–helix tertiary structures in organic solvents.



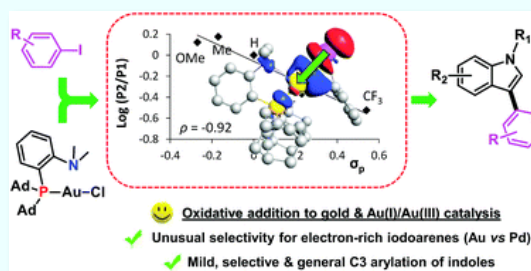
Catalytic Au(I)/Au(III) arylation with the hemilabile MeDalphos ligand: unusual selectivity for electron-rich iodoarenes and efficient application to indoles

Chem. Sci. 2019, 10, 7183

J. Rodriguez, A. Zeineddine, E. D. Sosa Carrizo, K. Miqueu, N. Saffon-Merceron, A. Amgoune, D. Bourissou

<https://doi.org/10.1039/C9SC01954E>

The ability of the MeDalphos ligand to trigger oxidative addition of iodoarenes preferentially electron-rich, to gold has been thoroughly studied and exploited to develop an efficient Au(I)/Au(III)-catalysed C3-arylation of indoles.



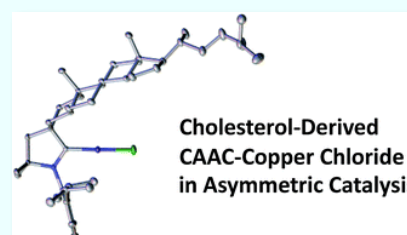
The debut of chiral cyclic (alkyl)(amino)carbenes(CAACs) in enantioselective catalysis

Chem. Sci. 2019, 10, 7807

D. Pichon, M. Soleilhavoup, J. Morvan, G. P. Junor, T. Vives, C. Crévisy, V. Lavallo, J.-M. Campagne, M. Mauduit, R. Jazza, G. Bertrand

<https://doi.org/10.1039/C9SC02810B>

Cyclic (alkyl)(amino)carbene (CAAC) metal complexes can also engage in asymmetric transformations, thereby expanding the toolbox of available chiral carbene ligands.



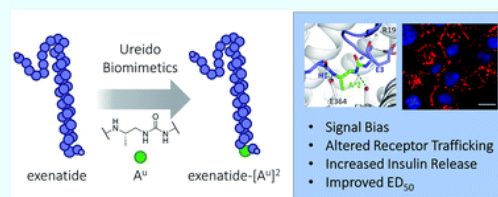
Ureidopeptide GLP-1 analogues with prolonged activity in vivo via signal bias and altered receptor trafficking

Chem. Sci. **2019**, *10*, 9872

J. Fremaux, C. Venin, L. Mauran, R. Zimmer, F. Koensgen, D. Rognan, S. Bitsi, M. A. Lucey, B. Jones, A. Tomas, G. Guichard, S. R. Goudreau

<https://doi.org/10.1039/C9SC02079A>

This study demonstrates the efficacy of single α -amino acids substitution with ureido residues to design long lasting peptides.



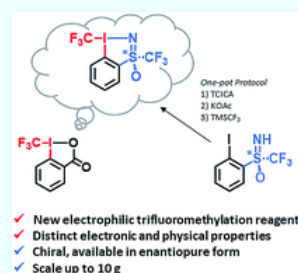
Merging hypervalent iodine and sulfoximine chemistry: a new electrophilic trifluoromethylation reagent

Chem. Sci. **2019**, *10*, 10516

J. Kalim, T. Duhail, T.-N. Le, N. Vanthuyne, E. Anselmi, A. Togni, E. Magnier

<https://doi.org/10.1039/C9SC04289J>

Two prominent trifluoromethylation reagent classes join forces in a bench stable hypervalent iodosulfoximine CF_3 transfer agent. We report its synthesis, properties and reactivity, opening up new possibilities in trifluoromethylation chemistry.



Sustainable ppm level palladium-catalyzed aminations in nanoreactors under mild, aqueous conditions

Chem. Sci. **2019**, *10*, 10556

Y. Zhang, B. S. Takale, F. Gallou, J. Reilly, B. H. Lipshutz

<https://doi.org/10.1039/C9SC03710A>

Greening-up aminations: a well-defined palladium pre-catalyst enables ppm-level Pd-catalyzed C–N cross couplings in water under very mild conditions. Comparisons using this protocol vs. traditional amination conditions for preparing key medicinal intermediates are demonstrated.

