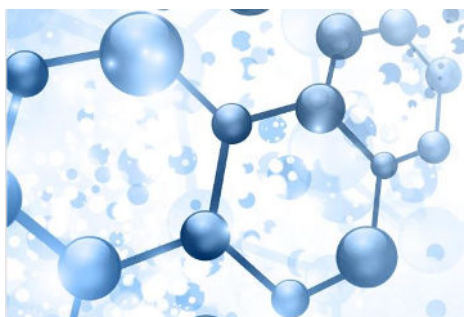


La lettre du bureau de la Division de Chimie Organique

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LE MOT DE LA PRÉSIDENTE

Chères et chers sociétaires,

Au nom de tout le bureau de la Division de Chimie Organique, je vous souhaite le meilleur pour la nouvelle année ; qu'elle vous apporte une excellente santé, de petits et grands bonheurs à partager, et la réussite dans vos entreprises personnelles et professionnelles.

Comme vous le savez, le congrès **SCF 23** est organisé cette année, fin juin à Nantes. Vous retrouverez toutes les informations qui le concernent dans ce numéro Echo-DCO ; huit sessions de deux heures y seront animées par la DCO, avec la possibilité de donner des communications orales. Il s'agit également d'une opportunité unique d'enrichissement par l'écoute de conférences et d'échanges avec les membres des autres entités de notre société savante. Le calendrier tourne, soyez attentifs aux dates limites qui approchent pour y participer activement par le dépôt d'un résumé.

Ce numéro sonne également le début de notre appel à candidature pour la distribution des prix de la DCO. Ces distinctions sont destinées à mettre en avant nos collègues, à tous les stades de leur carrière ; l'une d'entre elle doit vous correspondre ou vous inciter à nommer l'une de vos connaissances. Nous attendons avec impatience vos candidatures et nominations pour promouvoir l'excellence de la chimie organique, en France et à l'International. Nous regrettons, chaque année, de ne recevoir que très peu de candidatures féminines.

La journée de Printemps cette année sera fondue avec l'organisation du congrès SCF23, où nous vous espérons nombreux ! Nous nous retrouverons à Paris en fin d'année pour la journée d'automne 2023.

D'ici là, bonne reprise dans toutes vos activités ; nous restons à votre écoute pour toute action qui nous permette de rendre plus visible, encore, notre belle communauté de chimistes organiciens.

Très cordialement

Emmanuelle Schulz, Présidente de la DCO, pour le bureau



A ppel à candidature pour les prix de la DCO 2022

Date limite de candidature : le **lundi 13 mars 2023** à midi.

La Division de Chimie Organique attribuera en 2023 :

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

Quelques généralités avant le détail prix par prix.

- Les candidats et candidates 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 propose et présente une candidature doit également être membre de la SCF.
- L'ensemble des pièces demandées doit être envoyé en version électronique aux personnes indiquées (*cf ci-dessous*).
- Les lauréats et lauréates 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 Henri Kagan et le prix Dina Surdin. Sont éligibles, les thèses soutenues pendant l'année civile précédant l'année du prix (2022).

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 Stéphanie Norsikian uniquement par mail (stephanie.norsikian@cnsr.fr) avant le 13 mars 2023 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. Il doit être envoyé par le directeur de thèse de préférence.

Prix Emergence Marc JULIA (*moins de 4 ans de carrière*)

La Division de Chimie Organique attribue un prix à un(e) jeune chercheur ou enseignant-chercheur en poste au plus tôt depuis la rentrée universitaire 2019-2020,⁽¹⁾ effectuant ses travaux en France, et membre de la SCF-DCO **à la date de candidature**.

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 (format pdf), et être envoyées avant le 13 mars 2023 à midi à Anis Tlili (anis.tlili@univ-lyon1.fr).

Le principe retenu pour le dépôt de dossier est celui de la **candidature spontanée ou de la nomination**. En cas de candidature par nomination, le dossier de candidature sera accompagné de la lettre de nomination.

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

La Division de Chimie Organique attribue un prix à un(e) jeune enseignant-chercheur en poste au plus tôt depuis la rentrée universitaire 2015-2016,⁽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 (format pdf), et être envoyées avant le 13 mars 2023 à midi à Cyril Ollivier (cyril.ollivier@sorbonne-universite.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(e) jeune chercheur en poste au plus tôt depuis la rentrée universitaire 2015-2016,⁽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 (format pdf), et être envoyées avant le 13 mars 2023 à midi à Samir Messaoudi (samir.messaoudi@universite-paris-saclay.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(e) chercheur ou enseignant-chercheur avancé ayant pris ses fonctions entre les rentrées universitaires 2008-2009 et 2014-2015,⁽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 (format pdf), et être envoyées avant le 13 mars 2023 à midi à Sébastien Vidal (sebastien.vidal@cnrs.fr).

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

Prix Industriel Yves CHAUVIN

Ce prix vise à récompenser un(e) chimiste de moins de 50 ans évoluant dans le milieu industriel, ayant une carrière d'au moins 10 ans à un poste non académique et de nationalité française ou travaillant en France. Il/elle doit avoir fait preuve d'une excellence scientifique (jugée par la production de publications et/ou de brevets et potentiellement de conférences) mais également d'une volonté affichée de collaborations avec des partenaires académiques et/ou d'une forte implication pour la communauté des chimistes (société savante, olympiade, congrès, promotion de la chimie organique grand public, etc...). Le candidat doit être membre de la SCF-DCO **à la date de candidature**.

Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, et être envoyées avant le 13 mars 2023 à midi à Morgan Donnard (donnard@unistra.fr).

Le principe retenu pour le dépôt de dossier est celui de la **candidature spontanée ou 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(e) chimiste confirmé(e) ayant effectué des travaux de recherche reconnus au niveau national et international, et membre de la SCF-DCO **depuis au moins trois ans**.

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). La lettre de nomination doit être accompagnée d'un CV détaillé, d'un document de titres et travaux, et être envoyées avant le 13 mars 2023 à midi à Emmanuelle Schulz (emmanuelle.schulz@universite-paris-saclay.fr).

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

A VOS AGENDAS : SCF 2023

La Société Chimique de France organise son grand congrès triennal **SCF 2023** à la Cité des Congrès à Nantes du **26 au 28 juin 2023**. Vous trouverez toutes les informations sur le site web de l'événement <http://scf2023.fr/>



La Division Chimie Organique est bien sûr associée à cet événement et sera présente lors de ces trois jours. Huit sessions seront animées par la DCO, avec l'ensemble des thèmes qui lui sont chers, parmi lesquels la catalyse, la synthèse organique, la chimie supramoléculaire, la chimie durable ou encore la chémobioologie.

A cette occasion, la DCO a invité les conférencier(e)s suivant(e)s :

Dario Basani	ISM, Université de Bordeaux	
Corinna Schindler	Université du Michigan	
Svetlana Tsogoeva	Université d'Erlangen-Nuremberg	
Alain Wagner	MicroOmiX SAS, Strasbourg	
Etienne Brachet	CiTCoM, Université Paris-cité	Prix Jean Normant 2022
Rafael Gramage-Doria	ISCR, Université de Rennes	Prix Jean-Pierre Sauvage 2022
Jennifer Morvan	ENSCR, Université de Rennes	Prix de thèse Henri Kagan 2022
Julien Vantourout	ICBMS, Université de Lyon	Prix Marc Julia 2022

Les récipiendaires des prix de la DCO recevront leurs prix à cette occasion.

Nous sommes heureux d'annoncer également les conférences d'**Angela Marinetti** (ICSN) et de **Lutz Ackermann** (Université de Göttingen). Ils recevront respectivement les prestigieux prix Achille Le Bel et Franco-Allemand 2022 décernés par l'ensemble de la SCF.

Le programme présentant l'ensemble des conférenciers et conférencières invités est accessible sur le site du congrès.

<http://scf2023.fr/speakers2023/>

La DCO co-organise 8 sessions de 2 h au cours du congrès ; nous aurons le plaisir de proposer à cette occasion une quarantaine de créneaux dédiés à des **communications orales**. Nous vous invitons chaleureusement à vous inscrire et à nous proposer vos travaux. 8 communications orales parmi les candidatures seront labellisées "**communications orales invitées par la DCO**" (ce qui impliquera une prise en charge des frais d'inscription par la DCO). Ne pourront être labellisées que des communications orales proposées par des membres de la SCF ; il n'y a pas de limitation d'âge pour soumettre un résumé de communication orale. Il est bien sûr possible, et très encouragé, de présenter également un poster.

Les inscriptions sont ouvertes sur le site <http://scf2023.fr/> jusqu'à fin février.

Plus encore qu'un « simple congrès scientifique », SCF 2023 organise des actions en faveur du grand public, des table-rondes, des discussions concernant les carrières, l'industrie et beaucoup d'autres activités encore. Il s'agit d'un événement riche qui va célébrer la chimie en France, organisé par votre société savante. Les tarifs sont attractifs pour les sociétaires de la SCF, en

particulier pour les plus jeunes de nos laboratoires ! Venez nombreux et offrez aux étudiants l'opportunité de vivre cette expérience riche !

CONGRES A VENIR SOUTENUS PAR LA DCO

- La **Semaine d'Études en Chimie Organique (SECO)** est un événement annuel destiné aux doctorants, qui permet une semaine d'échanges entre scientifiques. La SECO60 se tiendra à Arêches-Beaufort du 21 au 26 mai 2023.

Retrouvez toutes les informations sur <http://www.congres-seco.fr/>



- Le groupe thématique de **Chimie Supramoléculaire** de la Société Chimique de France organisera la prochaine édition des Journées de Chimie Supramoléculaire (JCS) du 1er juin au 2 juin 2023 à Montpellier. Cette 2^{de} édition sera l'occasion pour la communauté de Chimie Supramoléculaire française de se retrouver et de partager ses résultats dans une atmosphère stimulante et conviviale. 14 créneaux pour des communications orales (en anglais) et 1 session de présentations de posters sont prévus.

Le programme inclut 3 conférences plénières :

Dr Anne-Marie Caminade, LCC

Pr Thomas Hermans, Université de Strasbourg

Dr. Mihail D. Barboiu, Université de Montpellier

Retrouvez toutes les informations sur <https://jcs2023.sciencesconf.org/>



- Le **Groupe d'Étude en Chimie Organique (GECO63)** se tiendra à Kerjouanno du 27 août au 1^{er} septembre 2023. Les inscriptions sont ouvertes jusqu'au 1^{er} juin 2023.

Le programme du GECO 63 inclut 12 conférencier(e)s nationaux et internationaux et issus du monde académique et industriel.

Dr. Xavier Bantreil, IBMMS (France)

Dr Olivier Baslé, LCC (France)

Prof. Marine Desage-El Murr, Univ. Strasbourg (France)

Dr Laure Haberkorn, Servier (France)

Prof. Véronique Michelet, Univ. Nice (France)

Prof. Sarah O'connor, Max Planck Institute (Allemagne)

Dr Gregory Pieters, CEA Saclay (France)

Dr Adrien Quintard, DCM (France)

Prof. Joost Reek, Amsterdam University (Pays-Bas)

Prof. Peter Seeberger, Max Planck Institute (Allemagne)

Dr Emmanuelle Schulz, ICMMO (France)

Prof. Mariola Tortosa, Université Autonome de Madrid (Espagne)

Retrouvez toutes les informations sur <https://geco63.sciencesconf.org/>



LES HIGHLIGHTS DE LA CHIMIE DE LA DCO

Le bureau de la Division de Chimie Organique se propose de mettre en valeur chaque semestre les articles les plus significatifs dont les auteurs correspondants sont membres de notre division.

Vous trouverez dans les pages suivantes un choix d'articles publiés sur la période juillet 2021-décembre 2022 dans les journaux suivants :

- *Science*
- *Chem*
- *J. Am. Chem. Soc.*
- *Chem. Sci.*
- *Angew. Chem. Int. Ed.*

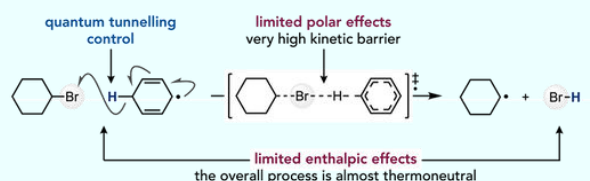
Nous avons conscience que ce choix d'articles est arbitraire. N'hésitez pas à nous faire part de vos remarques, et, éventuellement, à nous soumettre des propositions de travaux à « mettre en lumière ».

Halogen-atom and group transfer reactivity enabled by hydrogen tunneling

Timothee Constantin, Bartosz Gorski, Michael J. Tilby, Saloua Chelli, Fabio Juliá, Josep Llaveria, Kevin J. Gillen, Hendrik Zipse, Sami Lakhdar,* and Daniele Leonori* *Science* **2022**, *377*, 1323-1328

<https://dx.doi.org/10.1126/science.abq8663>

The generation of carbon radicals by halogen-atom and group transfer reactions is generally achieved using tin and silicon reagents that maximize the interplay of enthalpic (thermodynamic) and polar (kinetic) effects. In this work, we demonstrate a distinct reactivity mode enabled by quantum mechanical tunneling that uses the cyclohexadiene derivative γ -terpinene as the abstractor under mild photochemical conditions. This protocol activates alkyl and aryl halides as well as several alcohol and thiol derivatives. Experimental and computational studies unveiled a noncanonical pathway whereby a cyclohexadienyl radical undergoes concerted aromatization and halogen-atom or group abstraction through the reactivity of an effective H atom. This activation mechanism is seemingly thermodynamically and kinetically unfavorable but is rendered feasible through quantum tunneling

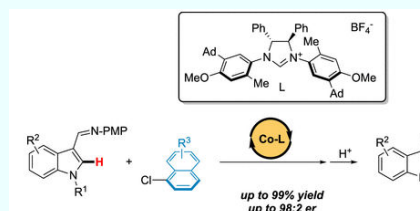


Cobalt-Catalyzed Enantioselective C–H Arylation of Indoles

Nicolas Jacob, Yassir Zaid, João C. A. Oliveira, Lutz Ackermann*, and Joanna Wencel-Delord* *J. Am. Chem. Soc.* **2022**, *144*, 798–806

<https://dx.doi.org/10.1021/jacs.1c09889>

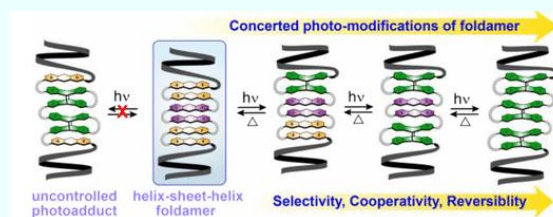
Atropisomeric (hetero)biaryls are scaffolds with increasing importance in the pharmaceutical and agrochemical industries. Although it is the most obvious disconnection to construct such compounds, the direct enantioselective C–H arylation through the concomitant induction of the chiral information remains extremely challenging and uncommon. Herein, the unprecedented earth-abundant 3d-metal-catalyzed atroposelective direct arylation is reported, furnishing rare atropisomeric C2-arylated indoles. Kinetic studies and DFT computation revealed an uncommon mechanism for this asymmetric transformation, with the oxidative addition being the rate- and enantio-determining step. Excellent stereoselectivities were reached (up to 96% ee), while using an unusual N-heterocyclic carbene ligand bearing an essential remote substituent. Attractive dispersion interactions along with positive C–H \cdots π interactions exerted by the ligand were identified as key factors to guarantee the excellent enantioselection.



Selective and Cooperative Photocycloadditions within Multistranded Aromatic Sheets

Bappaditya Gole, Brice Kauffmann, Brice Kauffmann, Arnaud Tron, Victor Maurizot, Nathan McClenaghan, Ivan Huc*, and Yann Ferrand* *J. Am. Chem. Soc.* **2022**, *144*, 6894–6906

<https://dx.doi.org/10.1021/jacs.2c01269>

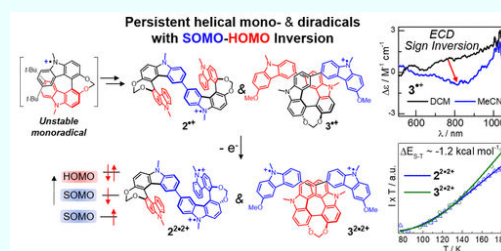


A series of aromatic helix-sheet-helix oligoamide foldamers composed of several different photosensitive diazaanthracene units have been designed and synthesized. Molecular objects up to 7 kDa were straightforwardly produced on a 100 mg scale. Nuclear magnetic resonance and crystallographic investigations revealed that helix-sheet-helix architectures can adopt one or two distinct conformations. Sequences composed of an even number of turn units were found to fold in a canonical symmetrical conformation with two helices of identical handedness stacked above and below the sheet segment. Sequences composed of an odd number of turns revealed a coexistence between a canonical fold with helices of opposite handedness and an alternate fold with a twist within the sheet and two helices of identical handedness. The proportions between these species could be manipulated, in some cases quantitatively, being dependent on solvent, temperature, and absolute control of helix handedness. Diazaanthracene units were shown to display distinct reactivity toward [4 + 4] photocycloadditions according to the substituent in position 9. Their organization within the sequences was programmed to allow photoreactions to take place in a specific order. Reaction pathways and kinetics were deciphered and product characterized, demonstrating the possibility to orchestrate successive photoreactions so as to avoid orphan units or to deliberately produce orphan units at precise locations. Strong cooperative effects were observed in which the photoreaction rate was influenced by the presence (or absence) of photoadducts in the structure. Multiple photoreactions within the aromatic sheet eventually lead to structure lengthening and stiffening, locking conformational equilibria. Photoproducts could be thermally reverted.

Carbazole Isomerism in Helical Radical Cations: Spin Delocalization and SOMO–HOMO Level Inversion in the Diradical State

Sitthichok Kasemthaveechok, Laura Abella, Marion Jean, Marie Cordier, Nicolas Vanthuyne, Thierry Guizouarn, Olivier Cadot, Jochen Autschbach*, Jeanne Crassous, and Ludovic Favereau* *J. Am. Chem. Soc.* **2022**, *144*, 7253–7263

<https://dx.doi.org/10.1021/jacs.2c00331>

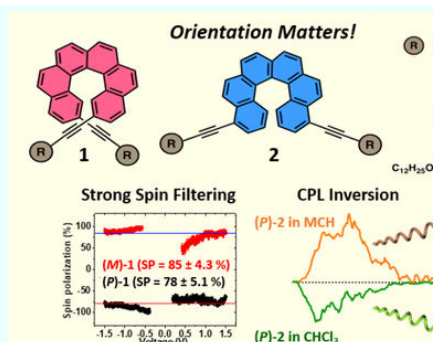


We report a new molecular design to afford persistent chiral organic open-shell systems with configurational stability and an inversion in energy of the singly occupied molecular orbital (SOMO) and the highest doubly occupied molecular orbital (HOMO) for both mono- and diradical states. The unpaired electron delocalization within the designed extended helical π -conjugated systems is a crucial factor to reach chemical stabilities, which is not obtained using the classical steric protection approach. The unique features of the obtained helical monoradicals allow an exploration of the chiral intramolecular electron transfer (IET) process in solvents of different polarity by means of optical and chiroptical spectroscopies, resulting in an unprecedented electronic circular dichroism (ECD) sign inversion for the radical transitions. We also characterized the corresponding helical diradicals, which show near-infrared electronic circular dichroism at wavelengths up to 1100 nm and an antiferromagnetic coupling between the spins, with an estimated singlet–triplet gap (ΔE_{ST}) of about $-1.2 \text{ kcal mol}^{-1}$. The study also revealed an intriguing double SOMO–HOMO inversion (SHI) electronic configuration for these diradicals, providing new insight regarding the peculiar energetic ordering of radical orbitals and the impact on the corresponding (chiral) optoelectronic properties.

Mutual Monomer Orientation To Bias the Supramolecular Polymerization of [6]Helicenes and the Resulting Circularly Polarized Light and Spin Filtering Properties

Rafael Rodríguez, Cristina Naranjo, Anil Kumar, Paola Matozzo, Tapan Kumar Das, Qirong Zhu, Nicolas Vanthuyne, Rafael Gómez, Ron Naaman*, Luis Sánchez*, and Jeanne Crassous* *J. Am. Chem. Soc.* **2022**, *144*, 7709-7719

<https://dx.doi.org/10.1021/jacs.2c00556>

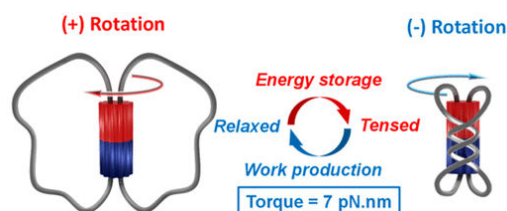


We report on the synthesis and self-assembly of 2,15- and 4,13-disubstituted carbo[6]helicenes **1** and **2** bearing 3,4,5-tridodecyloxybenzamide groups. The self-assembly of these [6]helicenes is strongly influenced by the substitution pattern in the helicene core that affects the mutual orientation of the monomeric units in the aggregated form. Thus, the 2,15-substituted derivative **1** undergoes an isodesmic supramolecular polymerization forming globular nanoparticles that maintain circularly polarized light (CPL) with glum values as high as 2×10^{-2} . Unlike carbo[6]helicene **1**, the 4,13-substituted derivative **2** follows a cooperative mechanism generating helical one-dimensional fibers. As a result of this helical organization, [6]helicene **2** exhibits a unique modification in its ECD spectral pattern showing sign inversion at low energy, accompanied by a sign change of the CPL with glum values of 1.2×10^{-3} , thus unveiling an example of CPL inversion upon supramolecular polymerization. These helical supramolecular structures with high chiroptical activity, when deposited on conductive surfaces, revealed highly efficient electron-spin filtering abilities, with electron spin polarizations up to 80% for **1** and 60% for **2**, as measured by magnetic conducting atomic force microscopy.

Light-Driven Molecular Whirligig

Chuan Gao, Andreas Vargas Jentzsch, Emilie Moulin, and Nicolas Giuseppone* *J. Am. Chem. Soc.* **2022**, *144*, 9845-9852

<https://dx.doi.org/10.1021/jacs.2c02547>

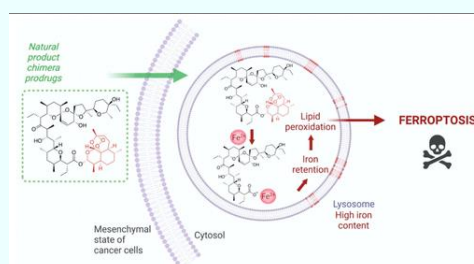


A unidirectional light-driven rotary motor was looped in a figure-of-eight molecule by linking two polymer chains between its stator and rotor parts. By properly tuning the size of these linkers, clockwise rotation of the motor under UV light was shown to create conformationally strained twists between the polymer chains, and in this tensed conformation, the energy stored in the molecular object was sufficient to trigger the reverse rotation of the motor back to its fully relaxed state. The functioning principle of this motorized molecular device appears very similar to that of macroscopic whirligig crafts used by children for fun. In addition, we found that in its out-of-equilibrium tensed state, the fluorescence emission of the molecular motor increased by 500% due to the mechanical constraints imposed by the polymer chains on its conjugated core. Finally, by calculating the apparent thermal energies of activation for the backward rotations at different levels of twisting, we quantitatively determined a lower estimate of the work generated by this rotary motor, from which a torque and a force were extracted, thus answering a long-term open question in this field of research.

Iron-Sensitive Prodrugs That Trigger Active Ferroptosis in Drug-Tolerant Pancreatic Cancer Cells

Michał Antoszczak, Sebastian Müller, Tatiana Cañeque, Ludovic Colombeau, Nelson Dusetti, Patricia Santofimia-Castaño, Christine Gaillet, Alain Puisieux, Juan Lucio Iovanna, and Raphaël Rodriguez* *J. Am. Chem. Soc.* **2022**, *144*, 11536-11545

<https://dx.doi.org/10.1021/jacs.2c03973>



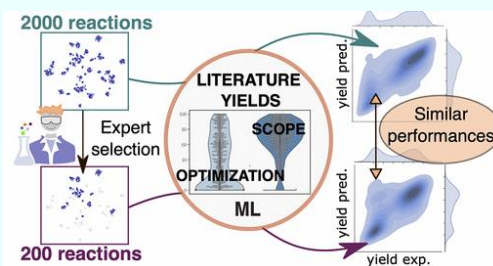
Persist cancer cells represent rare populations of cells resistant to therapy. Cancer cells can exploit epithelial-mesenchymal plasticity to adopt a drug-tolerant state that does not depend on genetic alterations. Small molecules that can interfere with cell plasticity or kill cells in a cell state-dependent manner are highly sought after. Salinomycin has been shown to kill cancer cells in the mesenchymal state by sequestering iron in lysosomes, taking advantage of the iron addiction of this cell state. Here, we report the chemo- and stereoselective synthesis of a series of structurally complex small molecule chimeras of salinomycin derivatives and the iron-reactive dihydroartemisinin. We show that these chimeras accumulate in lysosomes and can react with iron to release bioactive species, thereby inducing ferroptosis in drug-tolerant pancreatic cancer cells and biopsy-derived organoids of pancreatic ductal adenocarcinoma. This work paves the way toward the development of new cancer medicines acting through active ferroptosis.

Machine Learning Yield Prediction from NiCOLit, a Small-Size Literature Data Set of Nickel Catalyzed C–O Couplings

Jules Schleinitz*, Maxime Langevin*, Yanis Smail, Benjamin Wehnert, Laurence Grimaud*, and Rodolphe Vuilleumier* *J. Am. Chem. Soc.* **2022**, *144*, 14722–14730

<https://dx.doi.org/10.1021/jacs.2c05302>

Synthetic yield prediction using machine learning is intensively studied. Previous work has focused on two categories of data sets: high-throughput experimentation data, as an ideal case study, and data sets extracted from proprietary databases, which are known to have a strong reporting bias toward high yields. However, predicting yields using published reaction data remains elusive. To fill the gap, we built a data set on nickel-catalyzed cross-couplings extracted from organic reaction publications, including scope and optimization information. We demonstrate the importance of including optimization data as a source of failed experiments and emphasize how publication constraints shape the exploration of the chemical space by the synthetic community. While machine learning models still fail to perform out-of-sample predictions, this work shows that adding chemical knowledge enables fair predictions in a low-data regime. Eventually, we hope that this unique public database will foster further improvements of machine learning methods for reaction yield prediction in a more realistic context.

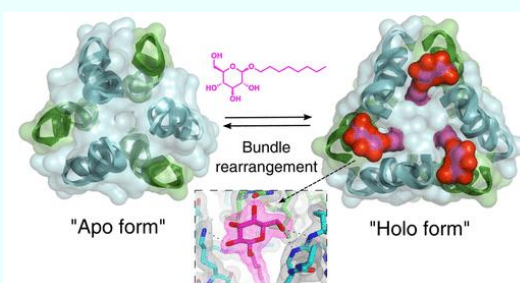


Adaptive Binding of Alkyl Glycosides by Nonpeptidic Helix Bundles in Water: Toward Artificial Glycolipid Binding Proteins

Sung Hyun Yoo, Jérémie Buratto, Arup Roy, Estelle Morvan, Morgane Pasco, Karolina Pulka-Ziach, Caterina M. Lombardo, Frédéric Rosu, Valérie Gabelica, Cameron D. Mackereth, Gavin W. Collie, and Gilles Guichard* *J. Am. Chem. Soc.* **2022**, *144*, 15988–15998

<https://dx.doi.org/10.1021/jacs.2c05234>

Amphipathic water-soluble helices formed from synthetic peptides or foldamers are promising building blocks for the creation of self-assembled architectures with non-natural shapes and functions. While rationally designed artificial quaternary structures such as helix bundles have been shown to contain preformed cavities suitable for guest binding, there are no examples of adaptive binding of guest molecules by such assemblies in aqueous conditions. We have previously reported a foldamer 6-helix bundle that contains an internal nonpolar cavity able to bind primary alcohols as guest molecules. Here, we show that this 6-helix bundle can also interact with larger, more complex guests such as n-alkyl glycosides. X-ray diffraction analysis of co-crystals using a diverse set of guests together with solution and gas-phase studies reveals an adaptive binding mode whereby the apo form of the 6-helix bundle undergoes substantial conformational change to accommodate the hydrocarbon chain in a manner reminiscent of glycolipid transfer proteins in which the cavity forms upon lipid uptake. The dynamic nature of the self-assembling and molecular recognition processes reported here marks a step forward in the design of functional proteomimetic molecular assemblies.

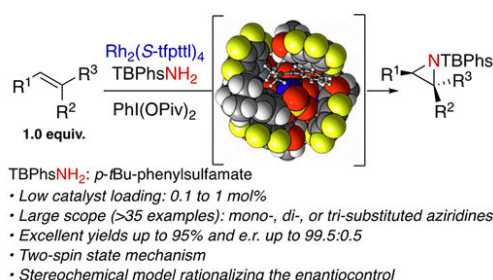


Rhodium(II)-Catalyzed Enantioselective Intermolecular Aziridination of Alkenes

Vincent Boquet, Ali Nasrallah, Alejandro L. Dana, Erwan Brunard, Pablo H. Di Chenna, Fernando J. Duran, Pascal Retailleau, Benjamin Darses*, Marie Sircoglou*, and Philippe Dauban* *J. Am. Chem. Soc.* **2022**, *144*, 17156–17164

<https://dx.doi.org/10.1021/jacs.2c07337>

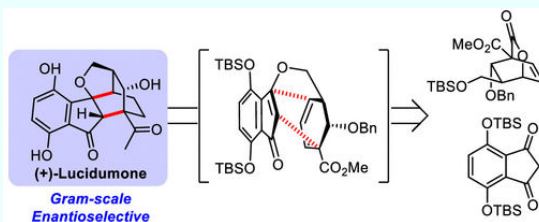
C4-Symmetrical dirhodium(II) tetracarboxylates are highly efficient catalysts for the asymmetric intermolecular aziridination of substituted alkenes with sulfamates. The reaction proceeds with high levels of efficiency and chemoselectivity to afford aziridines with excellent yields of up to 95% and enantiomeric excesses of up to 99%. The scope of the alkene aziridination includes mono-, di-, and trisubstituted olefins as well as the late-stage functionalization of complex substrates. The reaction can be performed on a gram-scale with a catalyst loading of 0.1 mol %. Our DFT study led us to propose a two-spin-state mechanism, involving a triplet Rh–nitrene species as key intermediate to drive the stereocontrolled approach and activation of the substrate.



Gram-Scale Enantioselective Synthesis of (+)-Lucidumone

Guanghao Huang, Cyrille Kouklovsky, and Aurélien de la Torre*
J. Am. Chem. Soc. **2022**, *144*, 17803-17807

<https://dx.doi.org/10.1021/jacs.2c08760>



The first enantioselective total synthesis of (+)-lucidumone is described through a 13-step synthetic pathway (longest linear sequence). The key steps involve the formation of a bridged bicyclic lactone by an enantioselective inverse-electron-demand Diels–Alder cycloaddition, C–O bond formation to assemble two fragments, and a one-pot retro-[4 + 2]/[4 + 2] cycloaddition cascade. The synthesis is scalable, and more than one gram of natural product was synthesized in one batch.

Ni-Centered Coordination-Induced Spin-State Switching Triggered by Electrical Stimulation

Shaymaa Al Shehimi, Orsola Baydoun, Sandrine Denis-Quanquin, Jean-Christophe Mulatier, Lhoussain Khrouz, Denis Frath, Élise Dumont, Muralee Murugesu, Floris Chevallier*, and Christophe Bucher* *J. Am. Chem. Soc.* **2022**, *144*, 17955-17965

<https://dx.doi.org/10.1021/jacs.2c07196>

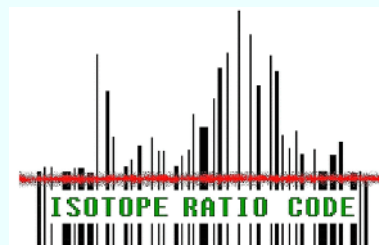


We herein report the synthesis and magnetic properties of a Ni(II)-porphyrin tethered to an imidazole ligand through a flexible electron-responsive mechanical hinge. The latter is capable of undergoing a large amplitude and fully reversible folding motion under the effect of electrical stimulation. This redox-triggered movement is exploited to force the axial coordination of the appended imidazole ligand onto the square-planar Ni(II) center, resulting in a change in its spin state from low spin ($S = 0$) to high spin ($S = 1$) proceeding with an 80% switching efficiency. The driving force of this reversible folding motion is the π -dimerization between two electrogenerated viologen cation radicals. The folding motion and the associated spin state switching are demonstrated on the grounds of NMR, (spectro)electrochemical, and magnetic data supported by quantum calculations.

Isotope Ratio Encoding of Sequence-Defined Oligomers

Márton Zwillinger, Lucile Fischer, Gergő Sályi, Soma Szabó, Márton Csékei, Ivan Huc*, and András Kotschy* *J. Am. Chem. Soc.* **2022**, *144*, 19078-19088

<https://dx.doi.org/10.1021/jacs.2c08135>

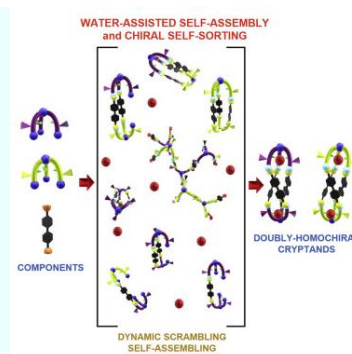


Information storage at the molecular level commonly entails encoding in the form of ordered sequences of different monomers and subsequent fragmentation and tandem mass spectrometry analysis to read this information. Recent approaches also include the use of mixtures of distinct molecules noncovalently bonded to one another. Here, we present an alternate isotope ratio encoding approach utilizing deuterium-labeled monomers to produce hundreds of oligomers endowed with unique isotope distribution patterns. Mass spectrometric recognition of these patterns then allowed us to directly readout encoded information with high fidelity. Specifically, we show that all 256 tetramers composed of four different monomers of identical constitution can be distinguished by their mass fingerprint using mono-, di-, tri-, and tetradeuterated building blocks. The method is robust to experimental errors and does not require the most sophisticated mass spectrometry instrumentation. Such isotope ratio-encoded oligomers may serve as tags that carry information, but the method mainly opens up the capability to write information, for example, about molecular identity, directly into a pure compound via its isotopologue distribution obviating the need for additional tagging and avoiding the use of mixtures of different molecules.

Doubly chiral pseudopeptidic macrobicyclic molecular cages: Water-assisted dynamic covalent self-assembly and chiral self-sorting

Ferran Esteve, Belén Altava, Eduardo García-Verdugo, Santiago V. Luis, Jean-Marie Lehn* *Chem* **2022**, *8*, 2023-2042

<https://dx.doi.org/10.1016/j.chempr.2022.04.007>

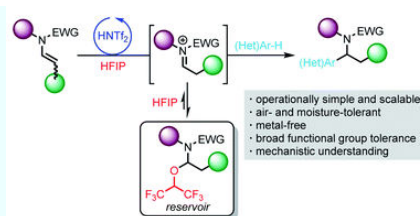


Taking advantage of the dynamic covalent chemistry approach, four different cages were synthesized by condensation of tripodal pseudopeptides with 4,4'-biphenyldicarboxaldehyde. Whereas undesired products of polymeric nature were obtained in polar solvents, the [3+2] cryptand-type macrobicyclic architectures were obtained in excellent yields using chloroform as solvent, even at relatively high concentrations. The presence of two encapsulated water molecules may provide a positive template effect in the low polarity medium. The final macrobicycles display a combination of two types of chirality: d,l chirality due to the asymmetric α -C centers and P,M helical chirality. The homochiral helicity found for all the enantiomerically pure molecular cages indicates strong chirality induction by the asymmetric α -C. Besides, the self-sorting properties of the different chiral pseudopeptides have been studied, resulting in high-fidelity homo-self-sorting. DFT calculations point out that the self-sorting outcome may also be a direct result of the encapsulation of two water molecules within the cavity.

Hydroarylation of enamides enabled by HFIP via a hexafluoroisopropyl ether as iminium reservoir

Nicolas Zeidan, Sergiu Bicic, Robert J. Mayer, David Leboeuf* and Joseph Moran* *Chem. Sci.* **2022**, *13*, 8436-8443

<https://dx.doi.org/10.1039/D2SC02012B>

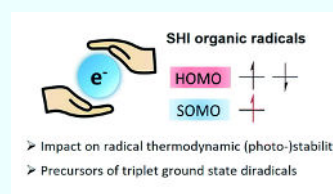


Here we describe that HFIP greatly expands the scope with respect to both reaction partners of the Brønsted acid-catalyzed hydroarylation of enamides. The reaction is fast and practical and can be performed on the gram scale. A hexafluoroisopropyl ether intermediate was isolated from the reaction mixture and was shown to convert to the product when resubmitted to the reaction conditions. Extensive kinetic studies and computations reveal that the hexafluoroisopropyl ether is formed rapidly and serves as a slow-release reservoir for the key cationic intermediate, preventing the oligomerization of the substrate under the reaction conditions. Given the relatively low electrophilicity of the cationic intermediates in the present study, it seems likely that HFIP also actively participates in other reactions involving more electrophilic carbocations.

Organic radicals with inversion of SOMO and HOMO energies and potential applications in optoelectronics

Sitthichok Kasemthaveechok, Laura Abella, Jeanne Crassous, Jochen Autschbach* and Ludovic Favereau* *Chem. Sci.* **2022**, *13*, 9833-9847

<https://dx.doi.org/10.1039/D2SC02480B>



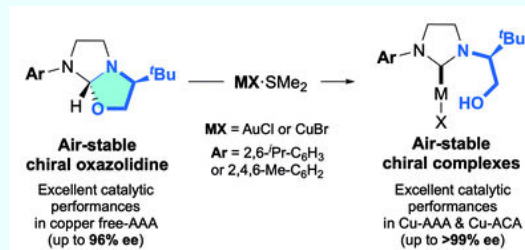
Organic radicals possessing an electronic configuration in which the energy of the singly occupied molecular orbital (SOMO) is below the highest doubly occupied molecular orbital (HOMO) level have recently attracted significant interest, both theoretically and experimentally. The peculiar orbital energetics of these SOMO–HOMO inversion (SHI) organic radicals set their electronic properties apart from the more common situation where the SOMO is the highest occupied orbital of the system. This review gives a general perspective on SHI, with key fundamental aspects regarding the electronic and structural factors that govern this particular electronic configuration in organic radicals. Selected examples of reported compounds with SHI are highlighted to establish molecular guidelines for designing this type of radical, and to showcase the potential of SHI radicals in organic spintronics as well as for the development of more stable luminescent radicals for OLED applications.

Chiral oxazolidines acting as transient hydroxyalkyl-functionalized N-heterocyclic carbenes: an efficient route to air stable copper and gold complexes for asymmetric catalysis

Delphine Pichon-Barré, Ziyun Zhang, Aël Cador, Thomas Vives, Thierry Roisnel, Olivier Baslé, Lucie Jarrige, Luigi Cavallo,* Laura Falivene* and Marc Mauduit* *Chem. Sci.* **2022**, *13*, 8773-8780

<https://dx.doi.org/10.1039/D2SC02908A>

Optically pure oxazolidines were synthesized in nearly quantitative yields from chiral hydroxyalkyl-functionalized imidazolium salts. Acting as transient chiral diamino N-heterocyclic carbenes (NHCs), these oxazolidines allowed the efficient formation of well-defined copper(I) and gold(I) hydroxyalkyl-NHC complexes, which could be isolated, for the first time, as air stable complexes after silica gel chromatography. Interestingly, X-ray analysis of gold complexes revealed that the hydroxyl-function is not chelated to the metal. Computational studies suggested that both cyclisation to produce oxazolidine and O–H bond elimination to form the transient carbene (prior to coordination) occur through a concerted mechanism. The novel chiral copper-catalysts, as well as oxazolidines alone (copper free), demonstrated excellent performances in asymmetric conjugate addition and allylic alkylation with high regio- and enantioselectivities (up to 99% ee).

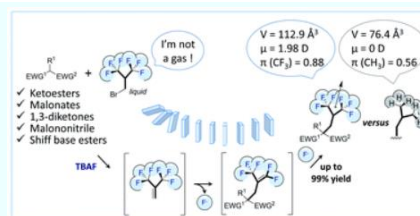


Hexafluoroisobutylation of enolates through a tandem elimination/allylic shift/hydrofluorination reaction

Aline Delamare, Guillaume Naulet, Brice Kauffmann, Gilles Guichard* and Guillaume Compain* *Chem. Sci.* **2022**, *13*, 9507-9514

<https://dx.doi.org/10.1039/D2SC02871A>

The isobutyl side chain is a highly prevalent hydrophobic group in drugs, and it notably constitutes the side chain of leucine. Its replacement by a hexafluorinated version containing two CF₃ groups may endow the target compound with new and advantageous properties, yet this modification remains overlooked due to the absence of a general and practical synthetic methodology. Herein, we report the first general method to introduce the hexafluoroisobutyl group into ketoesters, malonates, 1,3-diketones, Schiff base esters and malononitrile. We demonstrated that the reaction occurs through an elimination/allylic shift/hydrofluorination cascade process which efficiently overcomes the usual fluoride β-elimination observed with α-CF₃-vinyl groups. We showed that with alkali metal bases, a pentafluorinated alkene is obtained predominantly, whereas the use of tetrabutylammonium fluoride (TBAF) allows hydrofluorination to occur. This tandem process represents a conceptually new pathway to synthesize bis-trifluoromethylated compounds. This methodology was applied to the multigram-scale synthesis of enantiopure (S)-5,5,5,5',5'-hexafluoroisobutyl leucine.

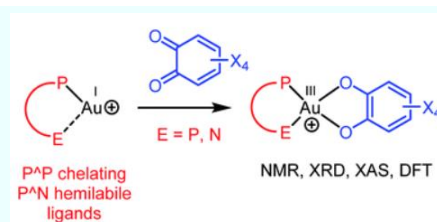


Ligand-enabled oxidation of gold(I) complexes with o-quinones

György Szalóki, Julien Babinot, Vlad Martin-Diaconescu, Sonia Mallet-Ladeira, Yago García-Rodeja, Karinne Miqueu and Didier Bourissou* *Chem. Sci.* **2022**, *13*, 10499-10505

<https://dx.doi.org/10.1039/D2SC03724F>

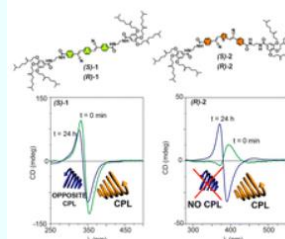
Chelating P^P and hemilabile P^N ligands were found to trigger the oxidation of Au(I) complexes by o-benzoquinones. The ensuing Au(III) catecholate complexes have been characterized by NMR spectroscopy, single crystal X-ray diffraction and X-ray absorption spectroscopy. They adopt tetracoordinate square-planar structures. Reactivity studies substantiate the reversibility of the transformation. In particular, the addition of competing ligands such as chloride and alkenes gives back Au(I) complexes with concomitant release of the o-quinone. DFT calculations provide insight about the structure and relative stability of the Au(I) o-quinone and Au(III) catecholate forms, and shed light on the 2-electron transfer from gold to the o-quinone.



Stereomutation and chiroptical bias in the kinetically controlled supramolecular polymerization of cyanoluminogens

Lucía López-Gandul, Cristina Naranjo, Cecilia Sánchez, Rafael Rodríguez, Rafael Gómez, Jeanne Crassous* and Luis Sánchez* *Chem. Sci.* **2022**, *13*, 11577-11584

<https://dx.doi.org/10.1039/D2SC03449B>

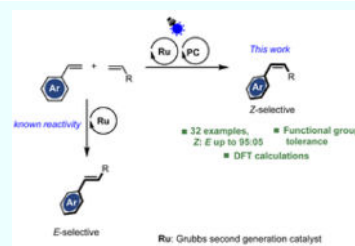


The synthesis of two pairs of enantiomeric cyano-luminogens **1** and **2**, in which the central chromophore is a p-phenylene or a 2,5-dithienylbenzene moiety, respectively, is described and their supramolecular polymerization under kinetic and thermodynamic control investigated. Compounds **1** and **2** form supramolecular polymers by quadruple H-bonding arrays between the amide groups and the π -stacking of the central aromatic moieties. In addition, the peripheral benzamide units are able to form intramolecularly H-bonded pseudocycles that behave as metastable monomer M^* thus affording kinetically and thermodynamically controlled aggregated species AggI and AggII. The chiroptical and emissive features of compounds **1** and **2** strongly depend on the aggregation state and the nature of the central aromatic unit. Compounds **1** exhibit a bisignated dichroic response of different intensity but with similar sign for both AggI and AggII species, which suggests the formation of helical aggregates. In fact, these helical supramolecular polymers can be visualized by AFM imaging. Furthermore, both AggI and AggII species formed by the self-assembly of compounds **1** show CPL (circularly polarized light) activity of opposite sign depending on the aggregation state. Thienyl-derivatives **2** display dissimilar chiroptical, morphological and emissive characteristics for the corresponding kinetically and thermodynamically controlled aggregated species AggI and AggII in comparison to those registered for compounds **1**. Thus, a stereomutation phenomenon is observed in the AggI2 \rightarrow AggII2 conversion. In addition, AggI2 is arranged into nanoparticles that evolve to helical aggregates to afford AggII2. The dissimilar chiroptical and morphological features of AggI2 and AggII2 are also appreciated in the emissive properties. Thus, whilst AggI2 experiences a clear AIE (aggregation induced emission) process and CPL activity, the thermodynamically controlled AggII2 undergoes an ACQ (aggregation caused quenching) process in which the CPL activity is cancelled.

Merging Grubbs second-generation catalyst with photocatalysis enables Z-selective metathesis of olefins: scope, limitations, and mechanism

Saïf Eddine Chérif, Avisek Ghosh, Saloua Chelli, Isabelle M. Dixon,* Jamil Kraiemb and Sami Lakhdar* *Chem. Sci.* **2022**, *13*, 12065-12070

<https://dx.doi.org/10.1039/D2SC03961C>

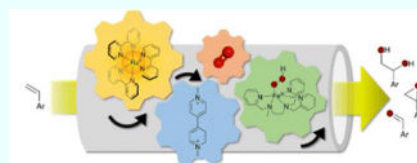


Olefin cross-metathesis is a cornerstone reaction in organic synthesis where stereoselectivity is typically governed by the structure of the catalyst. In this work, we show that merging Grubbs second generation catalyst, a classical E-selective catalyst, with a readily available photocatalyst, enables the exclusive formation of the contra-thermodynamic Z-isomer. The scope and limitations of this unprecedented approach are discussed based on both computational and experimental mechanistic data.

Photocatalytic generation of a non-heme Fe(III)-hydroperoxo species with O₂ in water for the oxygen atom transfer reaction

Eva Pugliese, Nhat Tam Vo, Alain Boussac, Frédéric Banse, Yasmina Mekmouche, Jalila Simaan, Thierry Tron, Philipp Gotico, Marie Sircoglou, Zakaria Halime, Winfried Leibl* and Ally Aukauloo * *Chem. Sci.* **2022**, *13*, 12332-12339

<https://dx.doi.org/10.1039/D2SC03129A>

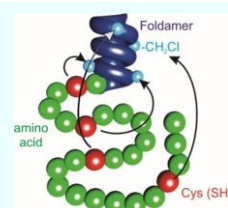


Coupling a photoredox module and a bio-inspired non-heme model to activate O₂ for the oxygen atom transfer (OAT) reaction requires a vigorous investigation to shed light on the multiple competing electron transfer steps, charge accumulation and annihilation processes, and the activation of O₂ at the catalytic unit. We found that the efficient oxidative quenching mechanism between a [Ru(bpy)₃]²⁺ chromophore and a reversible electron mediator, methyl viologen (MV²⁺), to form the reducing species methyl viologen radical (MV^{•+}) can convey an electron to O₂ to form the superoxide radical and reset an Fe(III) species in a catalytic cycle to the Fe(II) state in an aqueous solution. The formation of the Fe(III)-hydroperoxo (Fe(III)-OOH) intermediate can evolve to a highly oxidized iron-oxo species to perform the OAT reaction to an alkene substrate. Such a strategy allows us to bypass the challenging task of charge accumulation at the molecular catalytic unit for the two-electron activation of O₂. The Fe(III)-OOH catalytic precursor was trapped and characterized by EPR spectroscopy pertaining to a metal assisted catalysis. Importantly, we found that the substrate itself can act as an electron donor to reset the photooxidized chromophore in the initial state closing the photocatalytic loop and hence excluding the use of a sacrificial electron donor. Laser Flash Photolysis (LFP) studies and spectroscopic monitoring during photocatalysis lend credence to the proposed catalytic cycle.

Differential Peptide Multi-Macrocyclizations at the Surface of a Helical Foldamer Template

Sebastian Dengler, Céline Douat, Ivan Huc * *Angew. Chem. Int. Ed.* **2022**, *61*, e202211138

<https://onlinelibrary.wiley.com/doi/10.1002/anie.202211138>



The selective formation of different macrocycles can be implemented using Cys residues within a peptide and chloroacetamides at the surface of a foldamer helix by placing the latter at precise locations. Helix rigidity and faster formation of smaller macrocycles make the favored product largely predictable.

Regioselective Magnesiations of Fluorinated Arenes and Heteroarenes Using Magnesium-bis-Diisopropylamide (MBDA) in Hydrocarbons

Andreas Hess, Nurtalya Alandini, Yusuf C. Guersoy, Paul Knochel*
Angew. Chem. Int. Ed. **2022**, *61*, e202206176

<https://onlinelibrary.wiley.com/doi/10.1002/anie.202206176>

Various fluoro-substituted aromatics and heterocycles were magnesiated with the hydrocarbon-soluble organomagnesium amide ($(i\text{Pr}_2\text{N})_2\text{Mg}$ (magnesium-*bis*-diisopropylamide; MBDA) at non-cryogenic temperatures providing thermally stable arylmagnesium amides (or diheteroarylmagnesium amides in the case of heterocyclic substrates). Trapping reactions with typical electrophiles furnished polyfunctional fluoro-substituted building blocks.

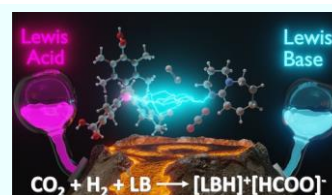


Design of Frustrated Lewis Pair Catalysts for Direct Hydrogenation of CO₂

Shubhajit Das, Roland C. Turnell-Ritson, Paul J. Dyson,* Clémence Corminboeuf
Angew. Chem. Int. Ed. **2022**, *61*, e202208987

<https://onlinelibrary.wiley.com/doi/10.1002/anie.202208987>

The direct dearomative addition of arenes to the C3 position of unprotected indoles is reported under operationally simple conditions, using triflic acid at room temperature. The present regioselective hydroarylation is a straightforward manner to generate an electrophilic indole at the C3 position from unbiased indoles in sharp contrast to previous strategies. This atom-economical method delivers biologically relevant 3-arylindolines and 3,3-spiroindolines in high yields and regioselectivities from both intra- and intermolecular processes. DFT computations suggest the stabilization of cationic or dicationic intermediates with H-bonded (TfOH)_(n) clusters.

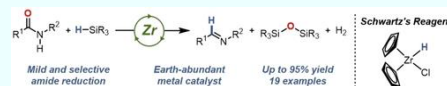


Selective Reduction of Secondary Amides to Imines Catalysed by Schwartz's Reagent

Liam J. Donnelly,* Jean-Claude Berthet, Thibault Cantat* *Angew. Chem. Int. Ed.* **2022**, *61*, e202206170

<https://onlinelibrary.wiley.com/doi/10.1002/anie.202206170>

The mild and selective catalytic reduction of secondary amides to imines was achieved using the classical organometallic reagent Cp₂Zr(H)Cl (Schwartz's reagent) as a catalyst. This approach avoids overreduction of the imines to amines and utilises hydrosilanes to enable catalyst turnover and control the reactivity.

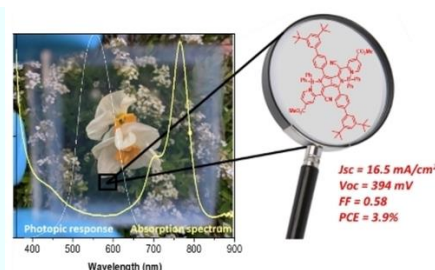


Transparent and Colorless Dye-Sensitized Solar Cells Based on Pyrrolopyrrole Cyanine Sensitizers

Thibaut Baron, Waad Naim, Ilias Nikolinakos, Baptiste Andrin, Yann Pellegrin, Denis Jacquemin,* Stefan Haacke,* Frédéric Sauvage,* Fabrice Odobel* *Angew. Chem. Int. Ed.* **2022**, *61*, e202207459

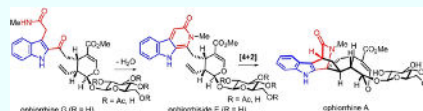
<https://onlinelibrary.wiley.com/doi/10.1002/anie.202207459>

Transparent photovoltaics is a disruptive technology which widens the deployment of photovoltaics into new sectors such as for windows beyond the classical use of opaque panels. The great potential of pyrrolopyrrole cyanine dyes as NIR-sensitizers for the development of fully transparent and colorless dye sensitized solar cells is demonstrated.



Total Synthesis of Ophiorrhine A, G and Ophiorrhiside E Featuring a Bioinspired Intramolecular Diels–Alder Cycloaddition

Wei Cao, Yingchao Dou, Cyrille Kouklovsky, Guillaume Vincent* *Angew. Chem. Int. Ed.* **2022**, *61*, e202209135

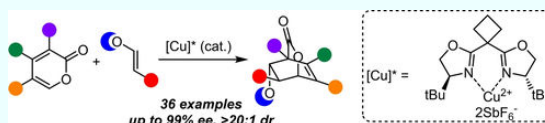


<https://onlinelibrary.wiley.com/doi/10.1002/anie.202209135>

A late stage bioinspired intramolecular Diels–Alder cycloaddition of the indolopyridone of ophiorrhiside E was deployed to access the spirocyclic azabicyclic[2.2.2]octanone ring system of ophiorrhine A and achieve its total synthesis. The indolopyridone of ophiorrhiside E was synthesized by the cyclodehydration of ophiorrhine G which was formed by the acylation of N-methyl indolylacetamide by a secologanin derivative.

Diastereo- and Enantioselective Inverse-Electron-Demand Diels–Alder Cycloaddition between 2-Pyrones and Acyclic Enol Ethers

Guanghao Huang, Régis Guillot, Cyrille Kouklovsky, Boris Maryasin,* Aurélien de la Torre* *Angew. Chem. Int. Ed.* **2022**, *61*, e202208185

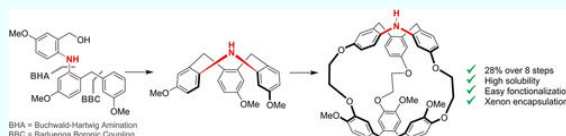


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The inverse-electron-demand Diels–Alder cycloaddition between 2-pyrones and acyclic enol ethers was investigated. Bridged bicyclic lactones were obtained diastereo- and enantioselectively and converted into synthetically relevant polysubstituted enantioenriched cyclohexene and cyclohexadiene derivatives. Mechanistic evidence as well as DFT calculations point towards a stepwise mechanism.

Synthesis and Physicochemical Properties of Cryptophazane—A Soluble and Functionalizable C₁-Symmetrical Cryptophane

Clément Vigier, Dimitri Fayolle, Hussein El Siblani, Jana Sopkova - de Oliveira Santos, Frederic Fabis, Thomas Cailly,* Emmanuelle Dubost* *Angew. Chem. Int. Ed.* **2022**, *61*, e202208580



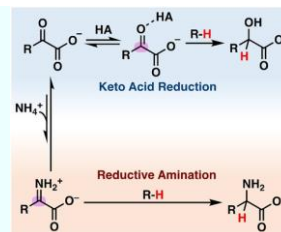
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Cryptophanes are molecular hosts of particular interest for the development of biosensors based on xenon magnetic resonance imaging as they bind xenon reversibly. To prepare such a biosensor, a reactive site on the cryptophane core, which is desirable for such applications but synthetically challenging, has now been introduced by replacing a crown methylene bridge by a nitrogen atom to form a cryptophazane.

Quantifying Reductive Amination in Nonenzymatic Amino Acid Synthesis

Robert J. Mayer, Joseph Moran* *Angew. Chem. Int. Ed.* **2022**, *61*, e202212237

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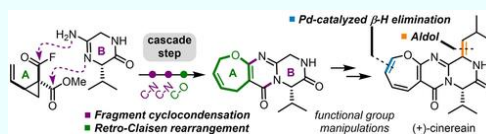
Why does biochemical amino acid synthesis proceed the way it does? Kinetic and mechanistic experiments with a model hydride donor were used to determine the intrinsic electrophilic reactivities of keto acids in reduction and reductive amination reactions. Comparing the nonenzymatic reactivity trends with those found in biology provides new insight into the structure of amino acid metabolism.

Total Synthesis of (+)-Cinereain and (-)-Janoxepin through a Fragment Coupling/Retro-Claisen Rearrangement Cascade

Quentin Ronzon, Wei Zhang, Thomas Charote, Nicolas Casaretto, Gilles Frison, Bastien Nay * *Angew. Chem. Int. Ed.* **2022**, *61*, e202212855

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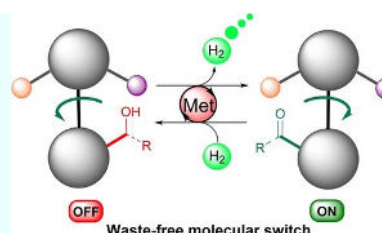
Total syntheses of (+)-cinereain and (-)-janoxepin, two fungal cyclotripeptides featuring a complex heterocyclic core and interesting phytotoxic and antimalarial activities, have been achieved in a highly convergent manner. In the key step, a one-pot cascade initiated by fragment coupling (cyclocondensation) was followed by a spontaneous retro-Claisen rearrangement to afford a 2,5-dihydrooxepin-fused heterocyclic product.



Catalytic Reversible (De)hydrogenation To Rotate a Chemically Fueled Molecular Switch

Enzo Olivieri, Na Shao, Roselyne Rosas, Jean-Valère Naubron, Adrien Quintard * *Angew. Chem. Int. Ed.* **2022**, *61*, e202214763

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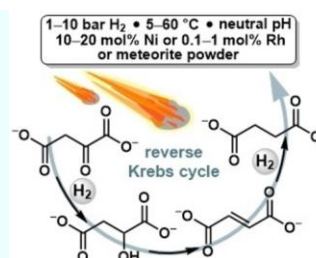


Most chemically fueled molecular switches suffer from the problem of waste accumulation inhibiting the system. Herein, we present a 180° rotating molecular switch based on reversible (de)hydrogenation avoiding waste accumulation. Catalyzed by an iridium complex, switching from a pressure of argon to a pressure of hydrogen triggers a reversible change in the system from alcohol to ketone, promoting the rotation around an alkyne axis.

Hydrogen Drives Part of the Reverse Krebs Cycle under Metal or Meteorite Catalysis

Sophia A. Rauscher, Joseph Moran* *Angew. Chem. Int. Ed.* **2022**, *61*, e202212932

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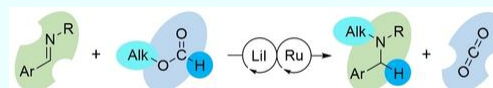


Hydrogen is a geological reducing agent that powers the metabolisms of modern organisms and potentially also powered the metabolism of the last universal common ancestor to all extant life. It is shown that catalytic amounts of transition metals or small amounts of powdered meteorites allow hydrogen to drive a key sequence of the reverse Krebs cycle under mild aqueous non-enzymatic conditions potentially relevant to the emergence of metabolic networks.

Alkyl Formates as Transfer Hydroalkylation Reagents and Their Use in the Catalytic Conversion of Imines to Alkylamines

Etienne Crochet, Lucile Anthore-Dalton, Thibault Cantat* *Angew. Chem. Int. Ed.* **2022**, *61*, e202214069

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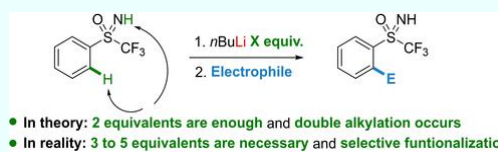
Alkyl formates can serve as a new class of bifunctional reagents for transfer hydroalkylation reactions. Using a ruthenium(II) catalyst combined with lithium iodide, they can promote the hydroalkylation of imines to amines, with the formation of CO₂ as the only by-product.

NMR and DFT Studies with a Doubly Labeled $^{15}\text{N}/^6\text{Li}$ S-Trifluoromethyl Sulfoximine Reveal Why a Directed *ortho*-Lithiation Requires an Excess of *n*-BuLi

Matthieu Hédouin, Anne-Laure Barthelemy, Nicolas Vanthuynne, Hend Besrour, Jacques Maddaluno,* Emmanuel Magnier,* Hassan Oulyadi* *Angew. Chem. Int. Ed.* **2022**, *61*, e202214106

<https://onlinelibrary.wiley.com/doi/10.1002/anie.202214106>

An NMR study was able to clearly explain why an excess of base is needed to deprotonate the aromatic ring of a S-trifluoromethylsulfoximine, thanks in particular to the identification and characterization of all the aggregates present in the medium.



Stable Luminescent $[\text{Cu}(\text{NN})(\text{PP})]^+$ Complexes Incorporating a β -Cyclodextrin-Based Diphosphane Ligand with Metal-Confining Properties

Tuan-Anh Phan, Nicola Armaroli,* Alejandra Saavedra Moncada, Dr. Elisa Bandini, Béatrice Delavaux-Nicot,* Jean-François Nierengarten,* Dominique Armpach* *Angew. Chem. Int. Ed.* **2022**, *61*, e202214638

<https://onlinelibrary.wiley.com/doi/10.1002/anie.202214638>

An unprecedented Smiles-like rearrangement of diphenyl-(2-phosphanylphenyl)phosphane gives access to a β -cyclodextrin-based diphosphane that forms stable heteroleptic $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes. Unfavorable flattening of the metal tetrahedral geometry in the excited state as a result of diimine encapsulation (bpy, phen, or mmp) is responsible for the enhanced luminescent properties.

