

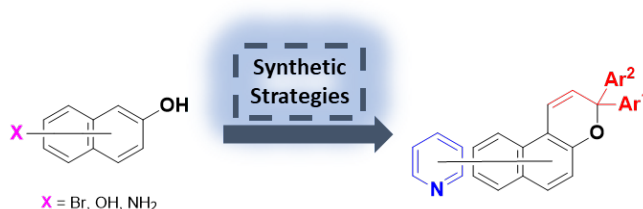
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Synthesis and Photochromism of Novel Pyridyl-Substituted Naphthopyrans

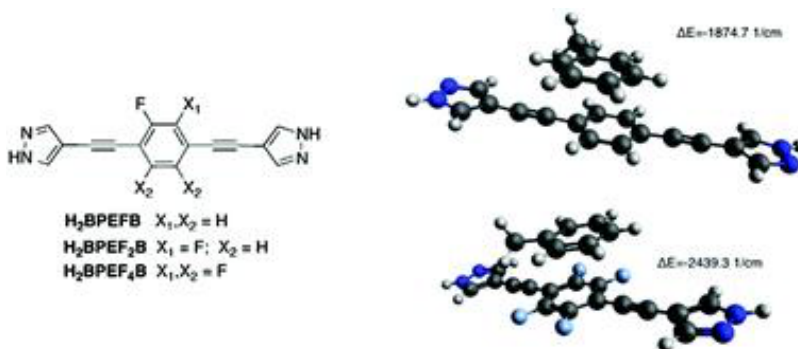
Orlando D. C. C. de Azevedo,* Paul I. P. Elliott, Christopher D. Gabbutt, B. Mark Heron,* Kyle J. Lord, and Christopher Pullen (orlando.deazevedo@hud.ac.uk or m.heron@hud.ac.uk)
J. Org. Chem. **2020**, *85*, 10772–10796. DOI: 10.1021/acs.joc.0c01296



Abstract: Multitarget synthetic strategies to access novel photochromic 3*H*-naphtho[2,1-*b*]pyrans decorated with pyridyl units are described. The new pyridyl-substituted 3*H*-naphtho[2,1-*b*]pyrans display good photochromic properties with reversible generation of photomerocyanines, which exhibit mainly orange/red hues. Photochromic parameters including photocolability and persistence of color vary tremendously on structural modification of the naphthopyran core.

Synthesis, Crystal Structure, and Optical Properties of Fluorinated Poly(pyrazole) Ligands and *in silico* Assessment of Their Affinity for Volatile Organic Compounds

Alessandro Pedrini, Angelo Maspero,* Silvia Bracco, Angelina Comotti, Simona Galli, Luciano Marchiò, Luca Nardo, Andrea Penoni, Luca Scapinello, Piero Sozzani, Guglielmo Vesco, and Massimo Mella (angelo.maspero@uninsubria.it)
New J. Chem. **2020**, *44*, 6443–6455. DOI: 10.1039/d0nj00259c



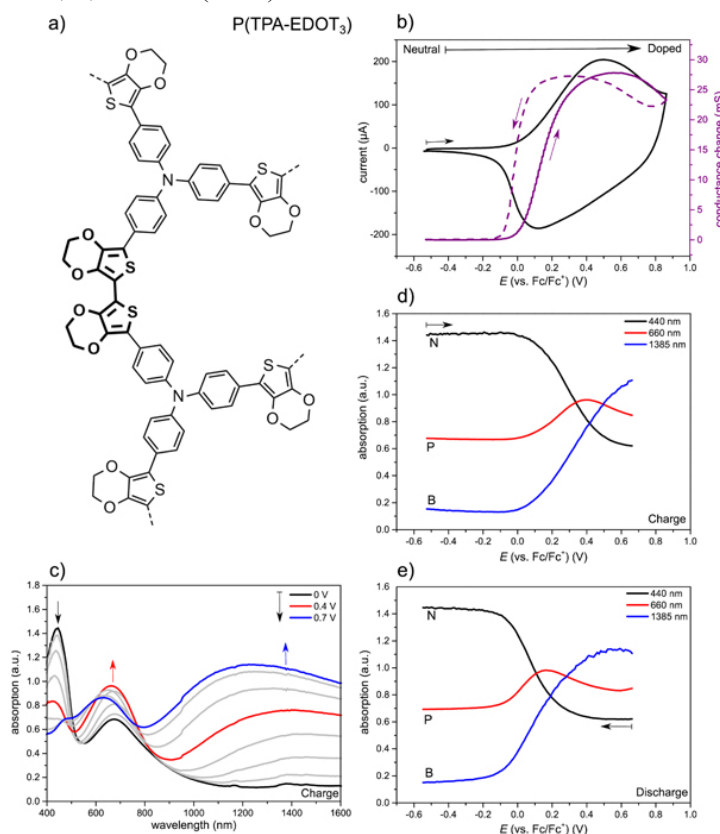
Abstract: Three new fluorinated bis(pyrazoles), namely: 1,4-bis(1*H*-pyrazol-4-ylethynyl)-2-fluorobenzene (**H₂BPEFB**), 1,4-bis(1*H*-pyrazol-4-ylethynyl)-2,3-difluorobenzene (**H₂BPEF₂B**) and 1,4-bis(1*H*-pyrazol-4-ylethynyl)-tetrafluorobenzene (**H₂BPEF₄B**), have been synthesized taking advantage of Sonogashira coupling reactions, and characterized as per their crystal and molecular structure, spectroscopic and dielectric properties, and hydrophobicity. In the crystal structures, the three molecules, whose deviation from planarity increases on increasing the fluorination degree, interact by means of hydrogen bonds, forming 2D supramolecular layers. Notably, the absorption and fluorescence emission properties are only slightly affected by the fluorination degree in both the solid state and solution. Furthermore, the spectral line-shapes are weakly dependent on the environment when dissolved in a number of solvents of different polarity and hydrogen-bonding affinity. On the other hand, the dielectric constant monotonically increases on increasing the number of fluorine atoms. *In silico* molecular modeling with time-dependent density functional theory has offered a valuable means to rationalize the above-mentioned behaviors and has shed some light on the ligand affinity towards representative gases – H₂O and CO₂ – and organic solvents – toluene.

Conductance and Spectroscopic Mapping of EDOT Polymer Films Upon Electrochemical Doping

Matthias Wieland, Claudia Malacrida Qiulin Yu, Claire Schlewitz, Luca Scapinello, Andrea Penoni, and Sabine Ludwigs* (sabine.ludwigs@ipoc.uni-stuttgart.de)

Flex. Print. Electron. **2020**, 5, 014016 (1–12).

DOI: 10.1088/2058-8585/ab76e0



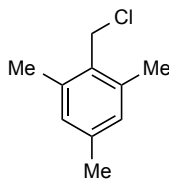
Abstract: This paper deals with the electrochemical doping of different poly(ethylenedioxythiophene) (PEDOT)-based active layers performed in an organic electrochemical transistor configuration through the mapping of *in situ* conductance trends during electrochemical doping and dedoping. The experiments are complemented by UV/Vis/NIR *in situ* spectroelectrochemistry in the wavelength range from 400 to 1600 nm, which allow monitoring of the development of the neutral and charged redox species. Both electropolymerized EDOT-based layers and solution-processed chemically synthesized PEDOT films are characterized. In addition to pure electropolymerized PEDOT (e-PEDOT), tris(4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)phenyl) (TPA-EDOT₃) is electrodeposited to generate highly branched networks of P(TPA-EDOT₃). The solution-deposited PEDOT films contain poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) with ratios of 1:2.5 and 1:6. Overall, we find that e-PEDOT and PEDOT:PSS(1:2.5) behave like classical conjugated polymers with a plateau-like conductance over a wide potential region. In contrast, PEDOT:PSS(1:6) and P(TPA-EDOT₃) show rather bell-shaped conductance profiles. The mixed-valence conductivity model is used to interpret the experimental results in terms of the number of accessible redox states. We suggest that the bell-shaped conductance in the case of PEDOT:PSS(1:6) is caused by a high amount of PSS insulator that limits the inter-chain interaction between PEDOT moieties and in the case of P(TPA-EDOT₃) by its distorted molecular architecture.

2,4,6-Trimethylbenzyl Chloride (α^2 -Chloroisodurene)

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Molbank **2020**, M1156, (1–4).

DOI: 10.3390/M1156



X-ray structure

Abstract: The X-ray structure of the title compound has been determined and it is compared with those of other substituted benzyl chlorides reported previously. It has an atypically long CH₂–Cl bond.

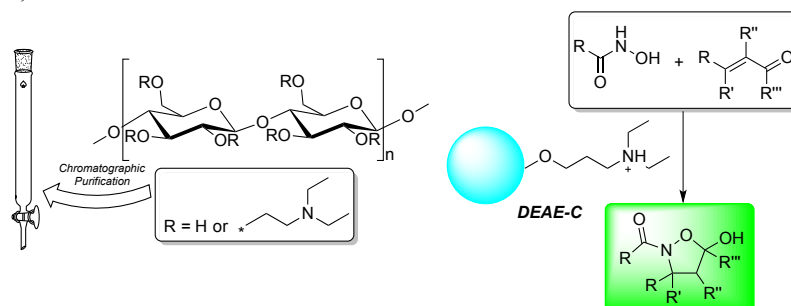
Diethylaminoethyl Cellulose (DEAE-C): Applications in Chromatography and Organic Synthesis

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Arkivoc **2020**, part i, 153–179.

DOI: 10.24820/ark.5550190.p011.310



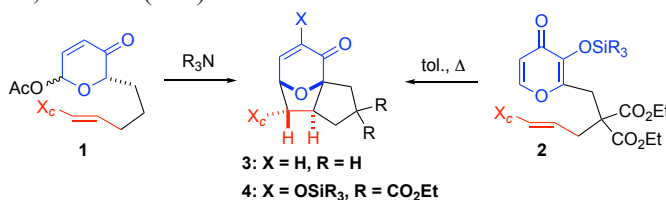
Abstract: The aim of this review is to point out the attention of the reader to the use of DEAE-C in organic reactions, possibly not only devoted to the preparation of heterocycles but potentially extending to other classes of organic compounds. Being DEAE-C an ammonium salt commonly used in chromatographic applications, it can be considered as a potential mild acid catalyst or a proton donor and these features can in theory catalyze standard acid-catalyzed organic reactions. In addition, the resin nature of DEAE-C could suggest the way to perform organic reactions in the solid state.

Intramolecular Asymmetric Oxidopyrylium-Based [5 + 2] Cycloadditions

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Tetrahedron Lett. **2020**, 61, 152377 (1–5).

DOI: 10.1016/j.tetlet.2020.152377



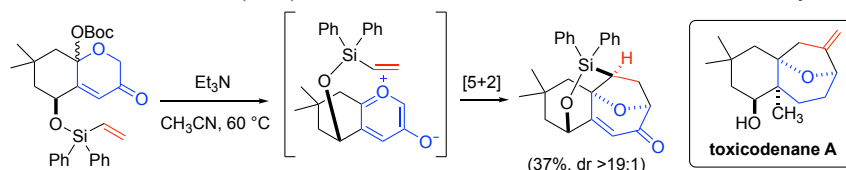
Abstract: Intramolecular oxidopyrylium-based [5 + 2] cycloadditions utilizing chiral auxiliaries were investigated. Both acetoxypyranones and silyloxypyranones were employed and sulfinimines, oxazolidinones, hydrazones, and chiral enamines were explored. Carbonyl-based auxiliaries gave low selectivity, but enamines afforded excellent diastereoselectivity. Overall, facial selectivity varied significantly providing insight regarding the scope and limitation of chiral auxiliary-based oxidopyrylium-alkene [5 + 2] cycloadditions.

Efforts Toward the Total Synthesis of (±)-Toxicodenane A Utilizing an Oxidopyrylium-Based [5 + 2] Cycloaddition of a Silicon-Tethered BOC-Pyranone

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Tetrahedron Lett. **2020**, *61*, 152324 (1–3)

DOI: 10.1016/j.tetlet.2020.152324



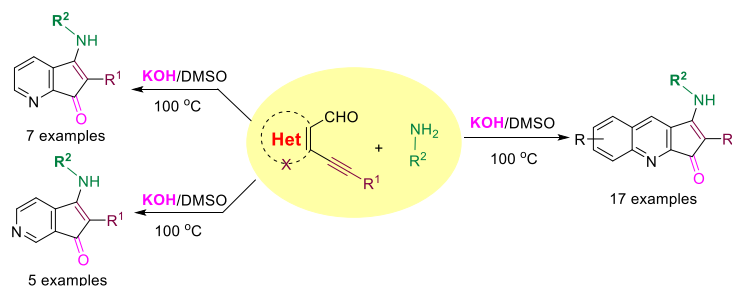
Abstract: Synthetic efforts toward the tricyclic core of (±)-toxicodenane A are reported. This strategy takes advantage of the Feist–Benary furan annulation, Achmatowicz oxidative rearrangement, and oxidopyrylium-based [5 + 2] cycloaddition to access a key tetracyclic intermediate. This work provides a foundation that can be utilized toward the total synthesis of the natural product.

Synthesis of Cyclopentaquinolinone and Cyclopentapyridinone from *ortho*-Alkynyl-*N*-Arylaldehyde *via* Superbase-Promoted C–N, C–O and C–C Bond Formation

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Org. Biomol. Chem. **2020**, *18*, 5594–5601.

DOI: 10.1039/d0ob01281e



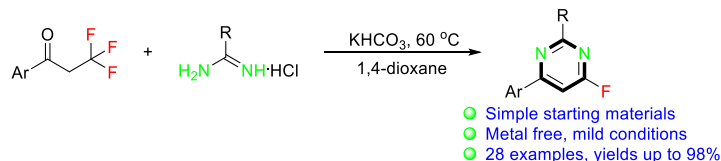
Abstract: An environmentally benign, transition metal-free, superbase-mediated intramolecular annulation of *o*-alkynylaldehydes with primary amines forms highly functionalized amino-substituted cyclopentaquinolinones and cyclopentapyridinones via C–N, C–C, and C=O bond formation. Contrary to the traditional approaches of ring closures, a different mode of annulation is disclosed. The protocol involves the *in situ* generations of imine intermediate followed by potassium hydroxide-promoted intramolecular cyclization and subsequent dimethyl sulfoxide induced dehydrogenation leads to the formation of *N*-heterocycles. X-ray crystallographic studies support the assigned structures of the amino-fused *N*-heterocycles.

A Concise and Efficient Approach to 2,6-Disubstituted 4-Fluoro-pyrimidines from α -CF₃ Aryl Ketones

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Synthesis **2020**, *52*, 273–280.

DOI: 10.1055/s003901690248



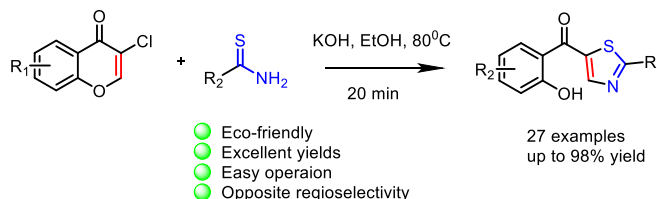
Abstract: Herein, a concise and efficient protocol to synthesize a series of 2,6-disubstituted 4-fluoropyrimidines as universal and useful building blocks in medicinal chemistry is reported. From readily accessible α -CF₃ aryl ketones and different amidine hydrochlorides, this method provides a very practical approach to this kind of compound under mild conditions with good to excellent yields.

Regioselective Synthesis of Substituted Thiazoles *via* Cascade Reactions from 3-Chlorochromones and Thioamides

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Org. Biomol. Chem. **2020**, *18*, 6162–6170.

DOI: 10.1039/d0ob01019g



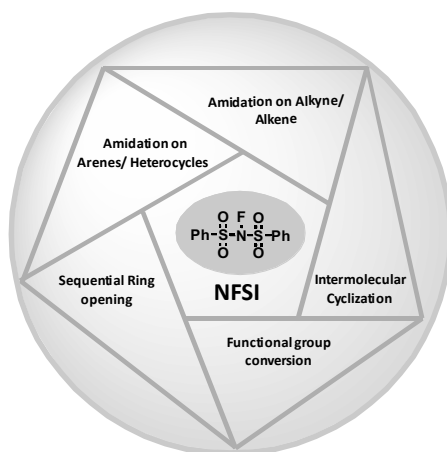
Abstract: A facile and efficient strategy to synthesize substituted thiazoles *via* a cascade reaction from chromone derivatives and thioamides in an environmentally benign medium was developed. This cascade reaction involves a Michael addition/intramolecular cyclization process and a broad scope of reversed regioselectivity products were prepared in a short reaction time with excellent yields. The reversed regioselectivity was also explained by DFT calculations.

Exploring the Behavior of the NFSI Reagent as a Nitrogen Source

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Org. Biomol. Chem. **2020**, *18*, 7056–7073.

DOI: 10.1039/d0obo01429j



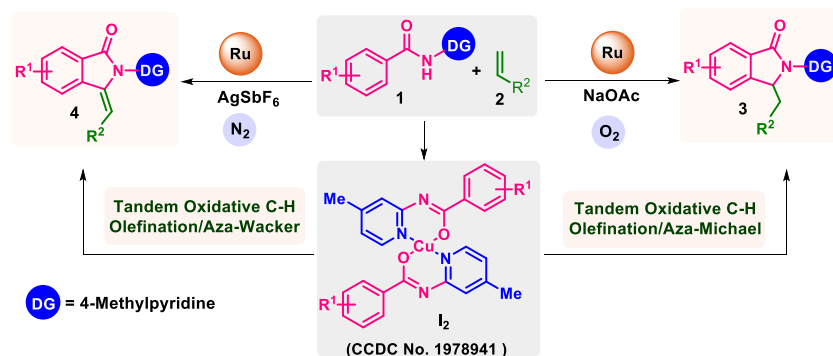
Abstract: The diverse biological activities of nitrogen-containing compounds make the construction of the C–N bond of great importance. As *N*-fluorobenzenesulfonimide, one of the most abundant chemical feedstock, has a dual behaviour, i.e. as an electrophilic fluorination and amidation source, it attracts the attention of synthetic chemists for exploitation. This review comprehensively summarizes the significant progress of the efficient and mild amidation reactions, with an emphasis on approaches for the generation of nitrogen-centered intermediates, related mechanisms and new synthetic chemistry methods that offer opportunities to overcome obstacles in pharmaceutical applications. In this perspective, we discuss the developments in the amidation reaction using NFSI in the past decade. We discuss the recent progress, challenges and future outcomes in the area of the amidation chemistry using commercially available NFSI.

Ru(II)-Catalyzed Oxidative Olefination of Benzamides: Switchable Aza-Michael and Aza-Wacker Reaction for Synthesis of Isoindolinones

Manoj Kumar, Shalini Verma, and Akhilesh K. Verma* (averma@acbr.du.ac.in)

Org. Lett. **2020**, 22, 4620–4626.

DOI: 10.1021/acs.orglett.0c01237



• Detection of intermediates via mass-spectrometry • Late-stage modification of active molecules

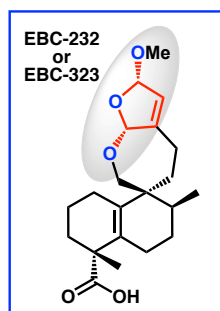
Abstract: Selective tandem oxidative C–H olefination–aza-Michael/aza-Wacker reaction of *N*-arylbenzamides is achieved by fine-tuning between base and additive to access valuable 3-oxoisindolinyls and 3-oxoisindolinylidenes, respectively. Careful optimization and control experiments provides a guiding principle in the design of a proposed catalytic cycle. The copper–iminium complex acting as a precursor for the binding of Ru catalyst was isolated and confirmed by X-ray diffraction. The versatility of this catalytic system has been demonstrated by the synthesis of biologically relevant molecules.

EBC-232 and 323: A Structural Conundrum Necessitating Unification of Five *in silico* Prediction and Elucidation Methods (EBC = EcoBiotics Compound)

Lidia A. Maslovskaya, Andrei I. Savchenko, Elizabeth H. Krenske, Sharon Chow, Tina Holt, Victoria A. Gordon, Paul W. Reddell, Carly J. Pierce, Peter G. Parsons, Glen M. Boyle, Andrei G. Kutateladze, and Craig M. Williams* (c.williams3@uq.edu.au)

Chem. Eur. J. **2020**, 26, 11862–11867.

DOI: 10.1002/chem.202001884



Abstract: Novel halimanes EBC-232 and EBC-323, isolated from *Croton insularis*, an Australian rainforest plant, were found to be extremely difficult to fully elucidate. These two diterpene diastereomers, contained a rare dihydrofuran fused to a oxo-6,7-spiro ring system. To differentiate the two diastereomers no less than five *in silico* NMR elucidation and prediction methods [i.e., ACDLabs, olefin strain energy (OSE), DP4, DU8+ and TD DFT CD] were required to fully appreciate and solve the structure. Elucidation examples such as these are pivotal for empowering future AI learning in computer aided chemical structure elucidation.