



Université de Montréal, Montréal, QC, Canada

THIRD INTERNATIONAL SYMPOSIUM
ON C-H ACTIVATION

May 30 – June 2, 2016

POSTER SESSION 2

Tuesday, May 31, 2016 from 1:30 pm to 2:30 pm

PO-36	DIRECT AMINOMETHYLATION FOR AN <i>ORTHO</i>-C-H BOND OF <i>N</i>-HETEROAROMATIC COMPOUNDS CATALYZED BY TRIAMIDO COMPLEXES OF GROUP 3 METALS Abhinanda Kundu, Osaka University
PO-37	GENERAL C-H FUNCTIONALIZATION STRATEGY FOR THE SYNTHESIS OF FULL-COLOR-TUNABLE HIGH STOKES SHIFT BENZO[<i>a</i>]IMIDAZO[2,1,5-<i>c,d</i>]INDOLIZINES FLUOROPHORES Éric Lévesque, Université de Montréal
PO-38	SCOPE OF SUCCESSIVE C-H FUNCTIONALIZATIONS IN ARYLPYRIDINES: UTILIZING METHYL GROUP AS LATENT CARBONYL FUNCTIONALITY Krupal P. Jethava, National Institute of Pharmaceutical Education and Research
PO-39	SYNTHESIS AND REACTIVITY OF STABLE GOLD(III)-FLUORIDES Roopender Kumar, University of Zurich
PO-40	SILVER CATALYZED AEROBIC OXIDATION OF ALDEHYDE IN WATER Mingxin Liu, McGill University
PO-41	DEVELOPMENT OF HETEROGENEOUS AND HOMOGENEOUS CATALYSTS FOR DIRECTED C-H HALOGENATION REACTIONS Magnus J Johansson, AstraZeneca R&D
PO-42	RHODIUM (III)-CATALYZED C-H AMIDATION FOR THE SYNTHESIS OF <i>N</i>-SULFONYLAMIDATED AND AMIDATED AZOBENZENES Taejoo Jeong, Sungkyunkwan University
PO-43	RH(III)-CATALYZED FACILE AND EFFICIENT CONSTRUCTION OF C2-AMIDATED INDOLES Taejoo Jeong, Sungkyunkwan University
PO-44	PALLADIUM(II)-CATALYZED DIRECT TRIFLUOROMETHYLTHIOLATION OF UNACTIVATED C(sp³)-H BONDS Maxime Manneveau, Normandie Université
PO-45	COOPERATIVE LEWIS ACID/Cp*Co^{III} CATALYZED C-H BOND ACTIVATION FOR THE SYNTHESIS OF ISOQUINOLIN-3-ONES Steffen GreBies, Westfälische Wilhelms-Universität Münster
PO-46	A REDOX NEUTRAL AND pH NEUTRAL TRANSITION METAL-FREE PROTOCOL TO SYNTHESIZE BENZOFURAN Wenbo Liu, McGill University
PO-47	SYNTHESIS OF ARYNE PRECURSORS VIA CATALYTIC C-H Silylation Karthik Devaraj, Uppsala University



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PO-48	MECHANISTIC INSIGHT INTO THE COPPER-CATALYZED AEROBIC OXYGENATION OF PHENOLS Yuxuan Li, Concordia University
PO-49	RH(III)-CATALYZED ALKYLATION AND INDOLE FORMATION OF ANILINES WITH DIAZO COMPOUNDS VIA C–H BOND ACTIVATION Neeraj Kumar Mishra, Sungkyunkwan University
PO-50	EXPLORING LIGAND EFFECTS IN THE COPPER-CATALYZED AEROBIC <i>ORTHO</i>-OXYGENATION OF PHENOLS Ohhyeon Kwon, McGill University
PO-51	SITE-SELECTIVE C-7 ACYLATION OF INDOLINES WITH ALDEHYDES UNDER Pd(II) CATALYSIS Jihye Park, Sungkyunkwan University
PO-52	C–H FUNCTIONALIZATION OF 2-ARYLBENZOTHAZOLES WITH α-DIAZO COMPOUNDS Jihye Park, Sungkyunkwan University
PO-53	PALLADIUM CATALYZED DIRECT TRIFLUOROETHYLATION OF AROMATIC UREAS WITH THE UTILIZATION OF HYPERVALENT IODONIUM SALT: SYNTHETIC APPLICATIONS AND MECHANISTIC STUDIES Szabolcs Kovács, Eötvös University
PO-54	EXPANSION OF THE CONCEPT OF NONLINEAR EFFECTS IN CATALYTIC REACTIONS BEYOND ASYMMETRIC CATALYSIS Michael Schnürch, Technische Universität Wien
PO-55	MICROWAVE-ASSISTED SYNTHESIS OF MAGNETICALLY RECOVERABLE SILVER-IRON OXIDE (Ag-Fe₃O₄@CMC) NANOCATALYSTS FOR CARBONYL COMPOUNDS HYDROGENATION Alain Y. Li, McGill University
PO-56	SELECTIVE C–H FUNCTIONALIZATION OF INDOLINES AND INDOLES WITH EASILY ACCESSIBLE CYANO SOURCE USING Rh(III) CATALYST Sang Hoon Han, Sungkyunkwan University
PO-57	CHELATION-ASSISTED NICKEL-CATALYZED OXIDATIVE ANNULATION VIA DOUBLE C–H BOND ACTIVATION/ALKYNE INSERTION REACTION Luis C. Misal Castro, Osaka University
PO-58	COBALT-CATALYZED REDUCTIVE CROSS-COUPPLING INVOLVING BENZYL CHLORIDES Corinne Gosmini, École Polytechnique – Université Paris-Sarclay
PO-59	AN IRIIDIUM-CATALYZED <i>ORTHO</i> SELECTIVE C–H BORYLATION OF TERTIARY BENZAMIDES Sahaj Gupta, Queen's University



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PO-60	AN EFFICIENT SOLAR-POWERED SYSTEM FOR REVERSIBLE HYDROGEN STORAGE BASED ON ORGANIC HYDROCARBONS Lu Li, McGill University
PO-61	SYNTHESIS OF A PROMISING ANTITUMOR INDOLOBENZAZOCIN-8-ONE USING PALLADIUM-CATALYZED INTRAMOLECULAR C-H ACTIVATION Nopporn Thasana, Chulabhorn Research Institute
PO-62	A PALLADIUM CATALYZED CARBOXYLATIVE C-H FUNCTIONALIZATION OF ARENES R. Garrison Kinney, McGill University
PO-63	Pd(OAc) ₂ CATALYZED C-H BOND ARYLATION OF DIAMONDIDS Radim Hrdina, Justus-Liebig University
PO-64	C-S BOND CLEAVAGE IN BENZOTHAZOLE AND S-S BOND FORMATION M'hamed Boudraa, Université Mentouri de Constantine
PO-65	C-H FUNCTIONALIZATION ON <i>ORTHO</i> -QUINONE AND ITS APPLICATIONS ON SYNTHESIS Zheng Huang, McGill University
PO-66	CROSS-DEHYDROGENATIVE COUPLING OF THIOLS WITH INDOLES USING A Cp*Co(III)-CATALYST-CU/LEWIS-ACID COOPERATIVE SYSTEM Felix Klauck, Westfälische Wilhelms-Universität Münster
PO-67	NICKEL-MEDIATED CYCLOMETALLATION OF ARYL-PHOSPHINITES AND SUBSEQUENT C-H FUNCTIONALIZATION: EXPLORATION OF THE KINETICS AND REGIOSELECTIVITY OF C-H NICKELATION Davit Zargarian, Université de Montréal
PO-68	BORYL (HETERO)ARYNE PRECURSORS: SYNTHESIS VIA C-H ACTIVATION AND ORTHOGONAL REACTIVITY Lukasz T. Pilarski, Uppsala University
PO-69	C-H ALKENYLATIONS WITH ALKENYL ACETATES, PHOSPHATES, CARBONATES AND CARBAMATES BY VERSATILE COBALT CATALYSIS AT 23 °C Marc Moselage, Georg-August Universität
PO-70	EXPEDIENT SYNTHESIS OF 3-AMINOIMIDAZO[1,2- <i>a</i>]PYRIDINES FROM α -AMINOPYRIDYL AMIDES Sophie Régnier, Université de Montréal



PO36 – Direct Aminomethylation for an *ortho*-C–H Bond of *N*-Heteroaromatic Compounds Catalyzed by Triamido Complexes of Group 3 Metals

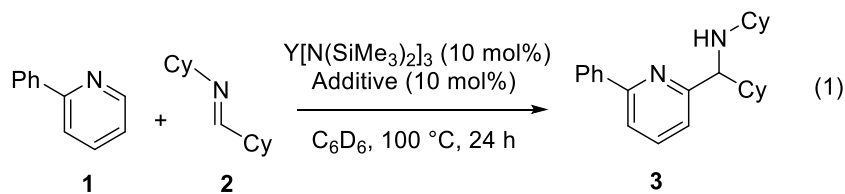
Abhinanda Kundu, Haruki Nagae, Yu Shibata, Hayato Tsurugi* and Kazushi Mashima*

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

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Metal-catalyzed direct C–H bond functionalization is an atom economical and cost effective straightforward synthetic protocols to introduce various functional groups on the aromatic compounds including *N*-heteroaromatic compounds. Alkyl and hydride complexes of early transition metals are known to react with *ortho*-C–H bond of *N*-heteroaromatic compounds via σ -bond metathesis, and newly formed $C(sp^2)$ -M bond subsequently reacted with non-polar C=C and C \equiv C functionalities to catalytically give the corresponding alkyl- and alkenylpyridine compounds.¹ In sharp contrast, insertion of polar C=E (E = N, O) into the $C(sp^2)$ -M bond resulted in the formation of unreactive M-E bonds, whose catalytic transformation is regarded as a difficult task.²

Recently, we reported that amide complexes of group 3 metals became catalyst for *ortho*-C–H bond addition of *N*-heteroaromatic compounds to a polar C=N bond of imines, regioselectively (eq. 1).³ We found additive effects of HNBn₂ to accelerate reaction rate. Thus we prepared and characterized a heteroleptic yttrium-amido complex [(Me₃Si)₂N]₂Y(NBn₂)(THF) (**4**), whose kinetic studies led to a plausible reaction mechanism involving penta-coordinated species as a key step.



References

1. (a) Tsurugi, H.; Koji, Y.; Nagae, H.; Kaneko, H.; Mashima, K. *Dalton Trans.* **2014**, 43, 2331. (b) Waterman, R. *Organometallics* **2013**, 32, 7249.
2. Zhang, X.-S.; Chen, K.; Shi, Z.-J. *Chem. Sci.* **2014**, 5, 2146.
3. Nagae, H.; Shibata, Y.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.* **2015**, 137, 640.



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PO37 – General C–H Functionalization Strategy for the Synthesis of Full-Color-Tunable High Stokes Shift Benzo[*a*]imidazo[2,1,5-*cd*]indolizines Fluorophores

Éric Lévesque, Léa Constantineau-Forget, William S. Bechara, Guillaume Pelletier, Natalie Rachel, Joëlle Pelletier and André B. Charette*

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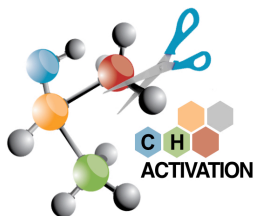
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Visible light-emitting fluorescent organic compounds are extensively used tools in microscopy for the precise tracking of specific molecules in biological systems.¹ Unfortunately, most of the commonly employed fluorescent cores suffer from a narrow variability of the absorption and emission wavelengths, and the effect of substituents on these wavelengths are often difficult to predict. This presentation reports the discovery of a previously unknown tetracyclic structure with interesting photochemical properties. These benzo[*a*]imidazo[2,1,5-*cd*]indolizines are synthesized via a previously unreported C–H activation procedure.² They are readily functionalized in a divergent synthetic pathway to yield a library of fluorescent probes with emission wavelengths covering the entire visible spectrum. DFT calculations are able to rationalize and predict these compounds' photochemical properties, allowing the precise tuning of these properties by selecting the building blocks used in the synthesis. Various reactive functional groups can be attached to the core without affecting photochemical properties, enabling the tethering of the fluorophore to biomolecules. Two different proteins were tagged as a proof of concept. Their unusually high Stokes shift makes them attractive for experiments using multiple fluorescent tags.



References

1. Kim, H. M.; Cho, B. R. *Chem. Rev.* **2015**, *115*, 5014-5055.
2. Pelletier, G.; Charette, A. B. *Org. Lett.* **2013**, *15*, 2290-2293.



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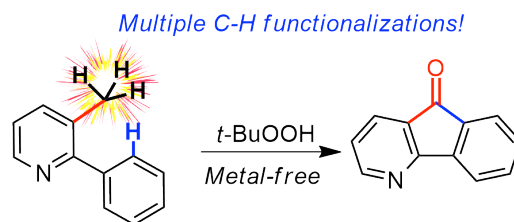
**PO38 – Scope of Successive C–H Functionalizations in Arylpyridines:
Utilizing Methyl Group as Latent Carbonyl Functionality**

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Carbon-carbon (C–C) bond formation between two C–H bonds using oxidative coupling, has received great attention over transition-metal-catalyzed cross-coupling reaction, utilizing unfunctionalized substrates, featuring high atom economy and efficiency. In particular, transition-metal-free reaction is a method of choice that often reduces generation of harmful by-products and empowers environmental compatibility. In this direction, we will present a transition-metal-free, *t*-BuOOH mediated intramolecular carbonylation of arenes in 2-aryl-3-picolines via oxidative C–H functionalizations of the methyl group, providing an expedient synthesis of 4-azafluorenones.¹ In contrast to the recent literature wherein methylarenes have been used as acylating agents, our protocol demonstrates the use of methyl group on pyridine ring which was transformed into 4-azafluorenone via rapid intramolecular acylation. This study manifest the first example of intramolecular carbonylation of arenes utilizing a methyl group as latent carbonyl functionality. Furthermore, we are currently investigating the scope of sp^3 C–H functionalizations on pyridine/arene ring via transition-metal-free oxidative C–H functionalizations of different functional groups present on arenes. These study would provide a novel feasible access to the synthesis of azafluorenones and fluorenones.



- Methyl group on pyridine
- C-H functionalization of **arenes**

Reference

1. Laha, J. K., Jethava, K. P., Patel, S., *Org. Lett.*, **2015**, *17*, 5890–5893.



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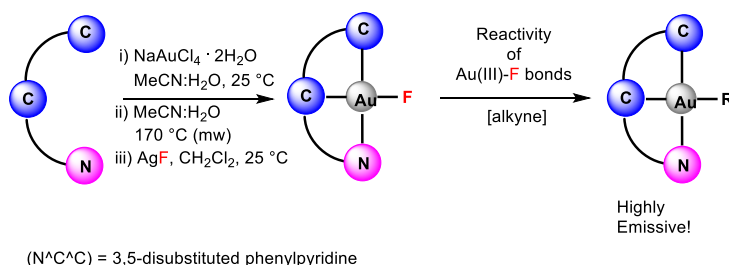
PO39 – Synthesis and Reactivity of Stable Gold(III)-Fluorides

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Late-transition metal fluorides play a pivotal role as intermediates in C–C and C–X bond forming transformations. Although Pd^{II} and Pd^{IV}-fluorides¹ have been synthesized and fully studied in order to gain a better mechanistic understanding of such transformations, the study of Au^{III}-fluorides is very limited. In fact, Csp² and Csp³-Au^{III}-fluorides have been proposed as intermediates in Au^I/Au^{III} redox catalytic cycles but the evidence of these species are scarce due to their high instability.^{2,3} Therefore we were interested to synthesize stable Au^{III}-fluorides in order to study their true chemical behavior. Here we report the synthesis of monomeric, easy to handle, bench-stable Csp²-Au^{III}-F complexes.⁴ Key for the success is the formation of stable (N[^]C[^]C)Au-Cl complexes via two sequential C-H activations of N[^]C[^]C ligand followed by a facile Cl/F ligand-exchange reaction. Devoid of oxidative conditions or stoichiometric use of toxic Hg salts, our method was applied to the preparation of multiple Csp²-Au^{III}-F complexes. These Au^{III}-fluorides provided a great platform to study their reactivity, especially with alkynes, resulting in alkynylgold(III) complexes with high luminescent properties.



References

1. a) Ball, N. D.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 3796–3797; b) Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; García-Fortanet, J.; Kinzel, T.; Buchwald, S. L. *Science* **2009**, *325*, 1661-1664.
2. Hopkinson, M. N.; Gee, A. D.; Gouverneur, V. *Isr. J. Chem.* **2010**, 675.
3. Mankad, N. P.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 12859-12861.
4. Kumar, R.; Linden, A.; Nevado, C. *Angew. Chem. Int. Ed.* **2015**, *54*, 14287-14290.



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PO40 – Silver Catalyzed Aerobic Oxidation of Aldehyde in Water

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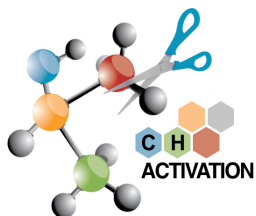
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Oxidation and reduction are the two most widely and fundamental reactions in chemistry. Enormous amount of chemical products being manufactured every year by using these reactions. However, many of the classical oxidation and reductions are far from green due to the use of stoichiometric reagent such as NaBH_4 , LiAlH_4 , H_2CrO_4 , and KMnO_4 (often dangerous and hazardous), and harsh conditions. There is a great need for developin greener alternative for oxidations and reductions. Our research at McGill is to develop unprecedented catalytic oxidation and reduction reactions in water with simple and safe reagents. A wide choice of different reductant/oxidant was investigated and the result shows a universal scope of substrate. Chromatography is completely unnecessary for certain cases. Gram scale reaction also shows promising and inspiring result.



Reference

1. Liu, M.; Wang, H.; Zeng, H.; Li, C.-J. *Sci. Adv.* **2015**, *1*, e1500020.



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**PO41 – Development of Heterogeneous and Homogeneous Catalysts
for Directed C–H Halogenation Reactions**

Magnus J. Johansson,*^a Belen Martin-Matute,^b Vlad Pascanu,^b Fabian Carson,^b Marta Vico Solano,^b Jie Su,^c Xiaodong Zou,^c Susanne Berglund,^d Pavol Zlatoidsky^d

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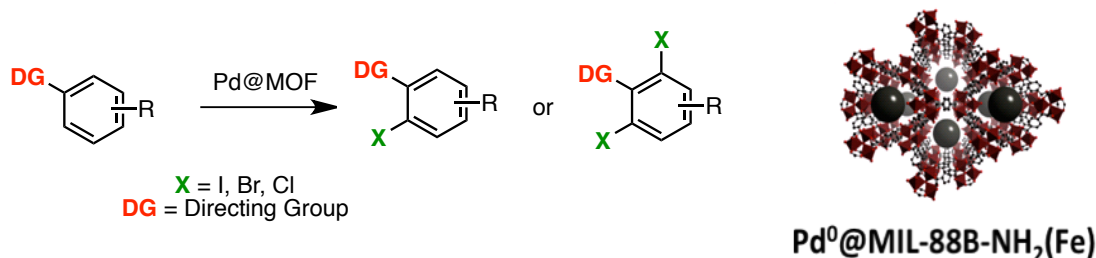
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Until today most catalytic systems described in C–H activations are based on homogeneous metal catalysts, while their heterogeneous counterparts are far less developed.¹ Herein, a directed heterogeneous C–H activation/halogenation reaction catalyzed by readily synthesized Pd@MOF nanocatalysts is reported.² The heterogeneous Pd catalysts used were a novel and environmentally benign Fe-based metal-organic framework (MOF) (Pd@MIL-88BNH₂(Fe)) and the previously developed Pd@MIL-101-NH₂(Cr). Very high conversions and selectivities were achieved under mild reaction conditions and in short reaction times. A wide variety of directing groups, halogen sources, and substitution patterns were well tolerated, and valuable mono and/or polyhalogenated compounds were synthesized in a controlled manner. In addition, directed C–H arylations using symmetrical and non-symmetrical iodonium salts were evaluated using the same catalysts.



References

1. Ackermann *et al*, Green Chem., 2016, Accepted Manuscript.
2. V. Pascanu, F. Carson, M. V. Solano, J. Su, X. Zou, M. J. Johansson, B. Martín-Matute, *Chem. Eur. J.* **2016**, 22, 3729



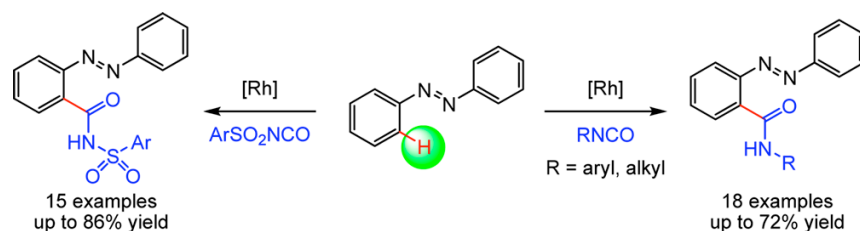
PO42 – Rhodium (III)-Catalyzed C–H Amidation for the synthesis of *N*-Sulfonylamidated and Amidated Azobenzenes

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In last decades, a great effort has been made towards the transition-metal-catalyzed direct functionalization of inactive C–H bonds with various coupling partners. In particular, the direct addition of C–H bonds to unsaturated C–N multiple bonds represents a valuable pursuit with profound synthetic potentials for the establishment of nitrogen-based functional groups into molecules. Thus, the direct insertion of C–H bonds into polar C–N π -bond of isocyanates is highly envious for providing synthetically valuable amide moieties. As amide moieties not only represent key structural motif found in many natural products, pharmaceuticals, polymers, and biological systems,¹ but they also find application as crucial intermediates for the preparation of various useful compounds.² Amidated compounds have established significant attention due to their various biological activities as precursors of therapeutic agents for Alzheimer's disease, as anti-proliferative agents, and etc. Inspired by our previous works with the Rh(III)-catalyzed addition of C(sp²)-H bonds to polarized π -bonds, we herein present the first examples of *N*-sulfonyl amidation via the Rh(III)-catalyzed direct C–H of azobenzenes with arylsulfonyl isocyanates along with amidation of azobenzenes with aryl and alkyl isocyanates.



References

- Noda, H.; Erős, G.; Bode, J. W. *J. Am. Chem. Soc.* **2014**, *136*, 5611.
- Valeur, E.; Bradley, M. *Chem. Soc. Rev.* **2009**, *38*, 606.
- Han, S.; Mishra, N. K.; Sharma, S.; Park, J.; Choi, M.; Lee, S.-Y.; Oh, J. S.; Jung, Y. H.; Kim, I. S. *J. Org. Chem.* **2015**, *80*, 8026.



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PO43 – Rh(III)-Catalyzed Facile and Efficient Construction
of C2-Amidated Indoles

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Indoles and pyrroles are among the most interesting heterocycles in nature and have been recognized as privileged structural motifs in drug discovery.¹ Consequently, there are many powerful methods for the synthesis and functionalization of these scaffolds.² In particular, C2-amidated indoles pyrroles are known to have diverse biological profiles, including androgen receptor inhibition, protein kinase inhibition, DPP-4 inhibition, allosteric modulation of cannabinoid receptor, and selective inhibition of β -amyloid. The synthetic methods for the formation of C2-amidated indoles rely on traditional approaches. However, these protocols have inherent limitations, including the preparation of prefunctionalized indoles, stoichiometric use of metallic reagents, harsh reaction conditions, and the use of hazardous CO gas. Recently, various directing groups can facilitate the arylation of the polar C–N π -bond of isocyanates. In this area, acetanilides, phenylpyridines, oximes, and benzoic acid derivatives were efficiently coupled with isocyanates to afford the corresponding ortho-amidated products under Rh, Ru, and Re catalysis. Inspired by our recent study on the site-selective functionalization of heterocycles and in consideration of the biological importance of C2-amidated indoles and pyrroles, we herein present the Rh(III)-catalyzed direct C2 addition of indoles and pyrroles to isocyanates via C–H bond activation.³



References

1. Sundberg, R. J. Indoles; *Academic Press: San Diego, CA*, 1996.
2. Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873.
3. Jeong, T.; Han, S.; Mishra, N. K.; Sharma, S.; Lee, S.-Y.; Oh, J. S.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *J. Org. Chem.* **2015**, *80*, 7243.



PO44 – Palladium(II)-Catalyzed Direct Trifluoromethylthiolation of Unactivated C(sp³)-H Bonds

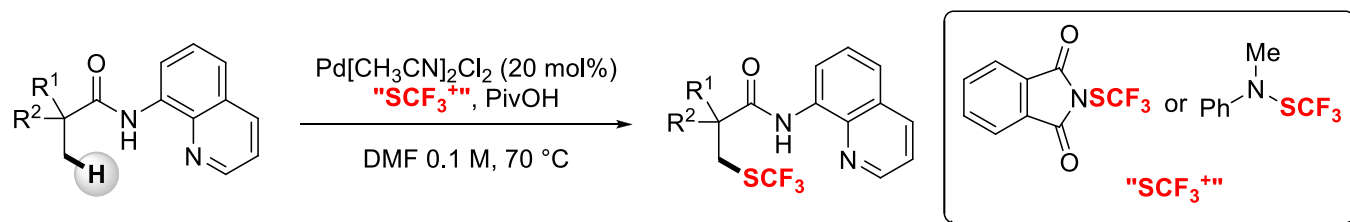
Maxime Manneveau,^a Heng-Ying Xiong,^a Xavier Pannecoucke,^a Lebel Hélène^b and Tatiana Besset*^a

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The SCF₃ moiety has attracted a special interest from the scientific community because of its remarkable properties, in particular the strong electron withdrawing effect and high lipophilicity.¹ Therefore, the direct introduction of such residue by metal catalyzed C–H bond functionalization is highly desirable. We describe herein an innovative methodology for the unprecedented Pd-catalyzed trifluoromethylthiolation of primary and secondary C-(sp³)-H bond on aliphatic acid derivatives.² Using a bidentate directing group, the direct and selective introduction of a SCF₃ moiety was possible on a range of amides with remarkable selectivity for C(sp³) centers with an electrophilic SCF₃ source and pivalic acid as additive. This novel approach offered a new disconnection for the preparation of SCF₃-containing molecules. A complementary approach using flow chemistry is currently under study in collaboration with the Prof. Lebel to improve the efficiency of the overall transformation.



References

1. Toulgoat, F.; Alazet, S.; Billard, T. *Chem. Eur. J.* **2014**, *12*, 2415.
2. Xiong, H.-Y.; Besset, T.; Cahard, D.; Pannecoucke, X. *J. Org. Chem.* **2015**, *80*, 4204.



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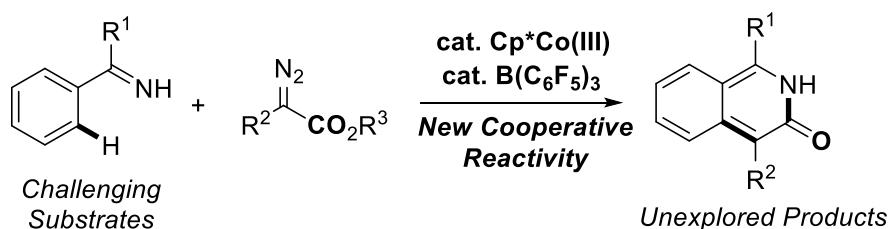
**PO45 – Cooperative Lewis Acid/Cp*Co^{III} Catalyzed C–H Bond Activation
for the Synthesis of Isoquinolin-3-ones**

Steffen Greßies, Ju Hyun Kim, Frank Glorius*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

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A facile route toward the synthesis of isoquinolin-3-ones through a cooperative B(C₆F₅)₃- and Cp*Co^{III}-catalyzed C–H bond activation of imines with diazo compounds is presented. The inclusion of catalytic amount of B(C₆F₅)₃ results in a highly efficient reaction, thus enabling unstable NH imines to serve as substrates.



Reference

1. Kim, J. H.; Greßies, S.; Glorius, F. *Angew. Chem. Int. Ed.* **2016**, *55*, ASAP (DOI: 10.1002/anie.201601003).



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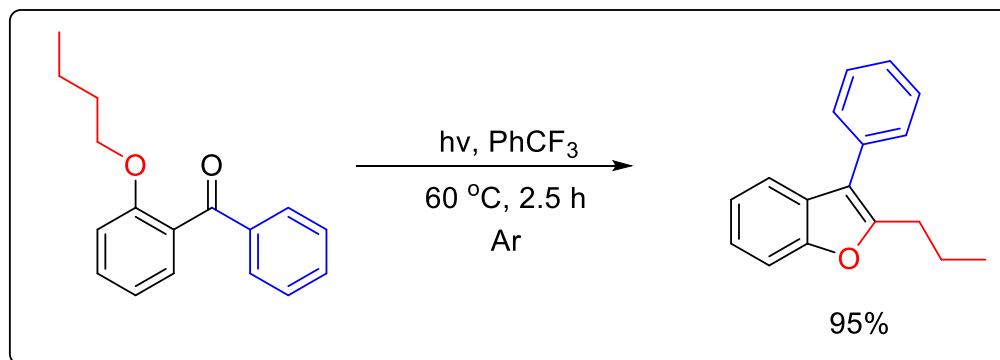
**PO46 – A Redox Neutral and pH Neutral Transition Metal-Free Protocol
to Synthesize Benzofuran**

Wenbo Liu and Chao-Jun Li*

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Benzofuran structural motifs are ubiquitous in nature products, drug candidates etc. and many methods have been developed to synthesize the benzofuran. However, these methods require either the expensive transition metals, or the strong bases or acids as the catalysts, which not only increase the overall cost but also limit the substrate scope. Methods to synthesize benzofuran in absence of transition metals and bases and acids with broad functional group tolerance would be desirable. Herein, we would like to describe such a protocol (redox neutral and pH neutral) by employing ultra-violet as the energy input.





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PO47 – Synthesis of Aryne Precursors via Catalytic C–H Silylation

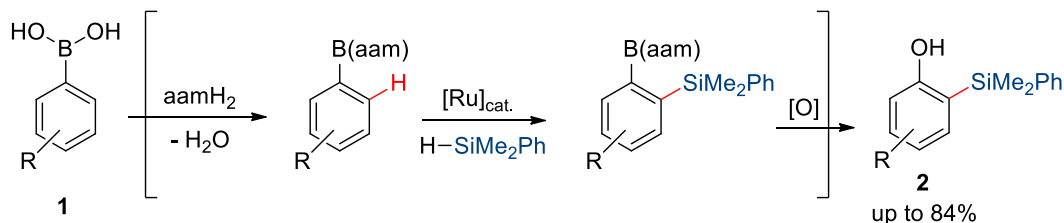
Karthik Devaraj, Carina Sollert, Alèria Garcia-Roca and Lukasz T. Pilarski*

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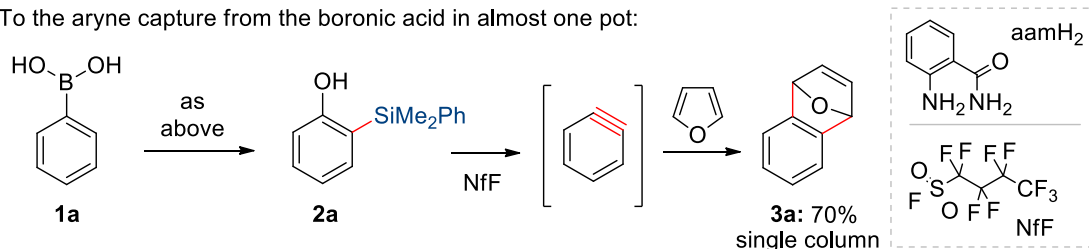
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An approach based on Ru-catalyzed C–H silylation¹ has been used to access new aryne precursors in an expedient way. A wide variety of commercially available arylboronic acids can be converted to the corresponding *ortho*-silyl phenols in a process involving only a single chromatographic purification. This approach increases the options for including diverse substituents on the aryne. The *ortho*-silyl phenols can be converted to the corresponding triflates or nanoflates, or activated directly using NfF.² A sequence starting with phenylboronic acid **1a** and ending with the 4+2 cycloaddition product **3a** proceeds in 70% yield (over 4 steps).³

The general approach:



To the aryne capture from the boronic acid in almost one pot:



References

- (a) For a recent review on C-H silylation, see: C. Cheng, J. F. Hartwig, *Chem. Rev.* **2015**, *115*, 8946; (b) For C–H silylation directed by -B(aam) boronates, see: H. Ihara, M. Koyanagi, M. Sugimoto, *Org. Lett.* **2011**, *13*, 2662.
- T. Ikawa, T. Nishiyama, T. Nosaki, A. Takagi, S. Akai, *Org. Lett.* **2011**, *13*, 1730.
- Pelletier, G.; Bechara, W. S.; Charette, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 12817.



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PO48 – Mechanistic Insight into the Copper-Catalyzed
Aerobic Oxygenation of Phenols

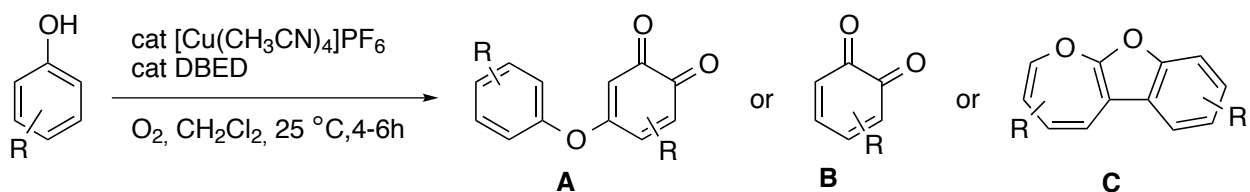
Yuxuan Li,^a Ohhyeon Kwon,^b Jean-Philip Lumb*^b and Xavier Ottenwaelder*^a

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The copper-catalyzed aerobic oxygenation of phenols is an attractive green method for the preparation of reactive and synthetically useful *ortho*-quinones. The Lumb group has developed fully catalytic conditions to perform this reaction with unsurpassed simplicity and efficiency.¹ This reaction employs catalytic amounts of copper(I) and *N,N'*-di-*tert*-butylethylenediamine (DBED) as the supporting ligand. Our mechanistic study of this reaction on 4-*tert*-butylphenol revealed the intermediacy of a copper(II)-semiquinone intermediate during the reaction towards **A**.² However, not all substrates behave equivalently under these or similar reaction conditions. For example, 3,5-di-*tert*-butylphenol gets oxygenated readily to a **B**-type species, whereas the isomeric 2,4-di-*tert*-butylphenol undergoes radical-based coupling reactions to **C** type.³ We here present mechanistic studies on the oxidation/oxygenation reactions, including characterization of reaction intermediates and kinetic studies. The goal is to gain control over the nature and efficiency of the oxidative pathways in order to develop a C-H oxygenation protocol that is general for synthetic applications.



References

1. Esguerra, K. V. N.; Fall, Y.; Lumb, J. P. *Angew. Chem. Int. Ed.* **2014**, 53, 5987.
2. Askari, M. S.; Esguerra, K. V. N.; Lumb, J.-P.; Ottenwaelder, X. *Inorg. Chem.* **2015**, 54, 8665.
3. Esguerra, K. V. N.; Fall, Y.; Petitjean, L. Lumb, J.-P. *J. Am. Chem. Soc.* **2014**, 136, 7662.



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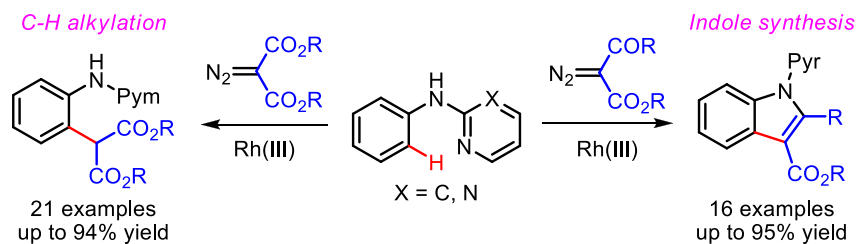
**PO49 – Rh(III)-Catalyzed Alkylation and Indole Formation of Anilines
with Diazo Compounds via C–H Bond Activation**

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The indole nucleus is a privileged structural motif in natural bioactive products, drugs, and other functional molecules.¹ The prevalence of indoles in bioactive molecules has led to lots of efforts for the development of many useful methods for their preparation. Recently, direct synthesis of indoles based on the catalytic C–H bond activation has attracted much attention owing to its remarkable potential for atom economy and environmental sustainability.² In addition, progress has been made on the catalytic carbenoid insertion reaction as a new approach toward C–H bond functionalization. We herein present the Rh(III)-catalyzed *ortho*-C–H alkylation of anilines with α -diazo esters. Additionally, the synthesis of indoles derived from anilines and alkyl α -diazo acetoacetates is also described. Furthermore, the formed indole adducts were subsequently used in the sequential C–H functionalization process to give C7-alkylated, cyanated, and amidated indoles.³



References

1. Joule J. A.; Mills, K.; *Heterocyclic Chemistry*, Blackwell Science Ltd, Oxford, 2000.
2. Guo, T.; Huang, F.; Yu, L.; Yu, Z. *Tetrahedron Lett.* **2015**, *56*, 296.
3. Mishra, N. K.; Choi, M.; Jo, H.; Oh, Y.; Sharma, S.; Han, S. H.; Jeong, T.; Han, S.; Lee, S.-Y.; Kim, I. S. *Chem. Commun.* **2015**, *51*, 17229.



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PO50 – Exploring Ligand Effects in the Copper-Catalyzed Aerobic *ortho*-Oxygenation of Phenols

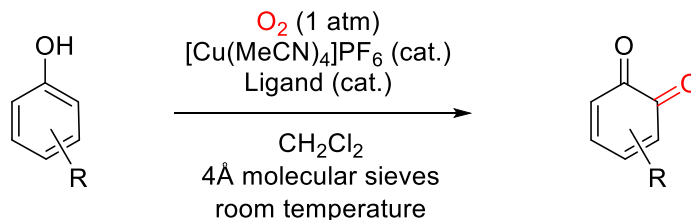
Ohhyeon Kwon,^a Laura Andrea Rodríguez Solano,^b Kenneth Virgel N. Esguerra,^a
Xavier Ottenwaelder*^b and Jean-Philip Lumb*^a

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There is significant literature precedent on the stoichiometric activation of molecular oxygen with biomimetic copper-amine complexes. These studies have provided important insights into the coordination chemistry and reactivity of Cu and O₂, but few have examined oxygen atom transfer (OAT) from the Cu/O₂ core to an organic substrate under catalytic conditions. Recent work from the Lumb group has demonstrated efficient catalysis in the aerobic *ortho*-oxygenation of phenols utilizing Cu(I) and *N,N'*-di-*tert*-butylethylenediamine (DBED).^{1,2} Mechanistic studies in collaboration with Ottenwaelder's group, support an inner-sphere mechanism for OAT under the conditions of catalysis,³ providing an important framework for future reaction design. The current work examines ligand effects on the efficiency of OAT, and provides the first correlation between the structure of L_nCu_m-O₂ complexes, which are generally determined at low-temperatures under stoichiometric conditions, to catalytic efficiency at room temperature. These studies set the stage for our ultimate goal of developing ligand-directed C–H oxygenation reactions where O₂ is employed as the atom transfer agent.



References

1. Esguerra, K. V. N.; Fall, Y.; Lumb, J. P. *Angew. Chem. Int. Ed.* **2014**, *53*, 5987.
2. Esguerra, K. V. N.; Fall, Y.; Petitjean, L. Lumb, J.-P. *J. Am. Chem. Soc.* **2014**, *136*, 7662.
3. Askari, M. S.; Esguerra, K. V. N.; Lumb, J.-P.; Ottenwaelder, X. *Inorg. Chem.* **2015**, *54*, 8665.



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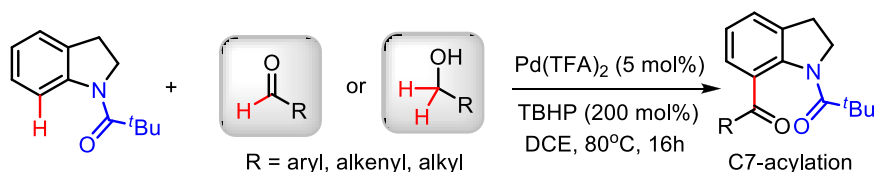
**PO51 – Site-Selective C-7 Acylation of Indolines with Aldehydes
under Pd(II) Catalysis**

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The C7-acylated indoles are known as heterocyclic compounds found in a number of natural products and bioactive synthetic molecules.¹ The 2-acylated indoles can be generated from the direct addition of acyl equivalents into 2-lithioindoles² or the Pd-catalyzed tandem cyclization reactions.³ However, to the best of our knowledge, there has been no previous report on catalytic C–H acylation at the C7-position of indoles with aldehydes or alcohols. Transition-metal-catalyzed C–H acylation of indolines using acyl surrogates is a promising synthetic strategy for C7-acylated indolines, which can be readily converted to C7-acylated indoles under oxidative conditions. We herein disclose the palladium-catalyzed oxidative C7-acylation of indolines with aldehydes or alcohols via C–H bond activation.⁴



References

1. (a) J. E. Saxton, *Nat. Prod. Rep.* **1992**, *9*, 393; (b) D. R. Beukes, M. T. Davies-Coleman, M. Kelly-Borges, M. K. Harper, D. J. Faulkner, *J. Nat. Prod.* **1998**, *61*, 699.
2. (a) M. Saulnier, G. Gribble, *J. Org. Chem.* **1982**, *47*, 757; (b) A. R. Katritzky, K. Akutagawa, *Tetrahedron Lett.* **1985**, *26*, 5935.
3. (a) M. Ishikura, M. Terashima, *J. Org. Chem.* **1994**, *59*, 2634; (b) R. Soley, F. Albericio, M. Alvarez, *Synthesis* **2007**, 559.
4. Shin, Y. Sharma, S. Mishra, N. K. Han, S. Park, J. Oh, H. Ha, J. Yoo, H. Jung, Y. H. Kim, I. S. *Adv. Synth. Catal.* **2015**, *357*, 594.



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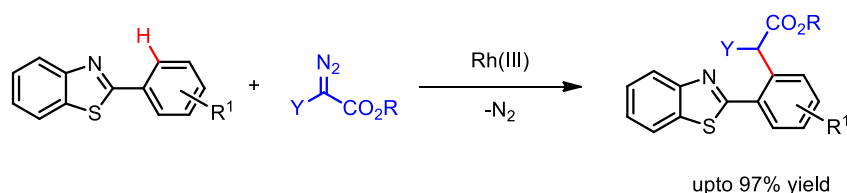
PO52 – C–H Functionalization of 2-Arylbenzothiazoles with α -Diazo Compounds

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2-Arylbenzothiazoles have shown potential as important structural motifs in organic and medicinal chemistry due to their remarkable pharmacological functions including antitumour activity, antibacterial activity, potassium channel activation, neurotransmission blockage, and neuroprotective activity. Moreover, 2-arylbenzo[d]thiazole derivatives are known as very crucial constituents found in organic light-emitting diodes (OLEDs), chemosensors, and photosensitizers. Therefore, the development of efficient strategies for the formation and functionalization of these heterocyclic architectures is an area of great interest in organic synthesis.¹ Recently, the catalytic C–H functionalization of 2-arylbenzothiazoles and 2-arylbenzoxazoles with various coupling partners has been explored, such as the palladium-catalyzed arylation, acetoxylation, acylation, hydroxylation, and halogenations.² In addition, direct olefination and amination of 2-arylbenzothiazoles under ruthenium catalysis were also examined. We herein present the Rh(III)-catalyzed direct coupling reaction of 2-arylbenzothiazoles and α -diazo esters to afford ortho-alkylated 2-arylbenzothiazoles via C–H bond activation.³



References

1. R. S. Keri, M. R. Patil, S. A. Patil, and S. Budagumpi *Eur. J. Med. Chem.* **2015**, *89*, 207.
2. Z. Chen, B. Wang, J. Zhang, W. Yu, Z. Liu, Y. Zhang *Org. Chem. Front.* **2015**, *2*, 1107.
3. Choi, M. Park, J. Mishra, N. K. Lee, S.-Y. Kim, J. H. Jeong, K. M. Lee, J. Jung, Y. H. Kim, I. S. *Tetrahedron Lett.* **2015**, *56*, 4678.



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**PO53 – Palladium Catalyzed Direct Trifluoroethylation of Aromatic Ureas
with the Utilization of Hypervalent Iodonium Salt:
Synthetic Applications and Mechanistic Studies**

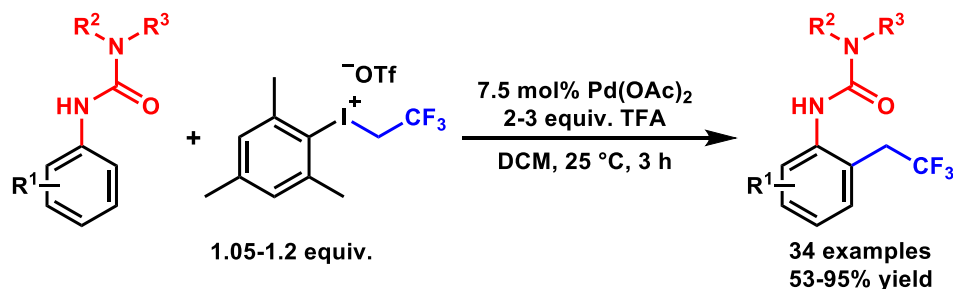
Szabolcs Kovács,^a Balázs L. Tóth,^a Gábor Borsik,^a Tamás Bihari,^b András Stirling^b and Zoltán Novák^{a*}

^aMTA-ELTE „Lendület” Catalysis and Organic Synthesis Research Group, Eötvös University, Institute of Chemistry, Pázmány Péter stny. 1/a, Budapest, H-1117, Hungary

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Activation of C-H bond using directing groups has become an important tool for the functionalization of aromatic compounds. Besides various groups, the urea function serves as excellent *ortho* directing functional group and it was utilized in several *ortho* functionalization even under mild reaction conditions. Interestingly, the direct alkylation of aromatic ureas is unprecedented, considering not only the modern transition metal mediated C-H activation reactions, but the classic organic synthetic tools.



We have developed a novel procedure for the trifluoroethylation of aromatic ureas via palladium catalyzed C-H activation with the application of mesityltrifluoroethylidonium salt as an excellent fluoroalkylating agent, developed in our laboratory.^{1,2} This methodology enables the simple, late stage alkylation of urea derivatives for the first time with high efficiency and functional group tolerance under mild reaction conditions. Beyond the synthetic developments, theoretical calculations were also investigated to reveal the reaction mechanism and the intermediates.

References

1. Tolnai, G. L.; Székely, A.; Makó, Z.; Gáti, T.; Daru, J.; Bihari, T.; Stirling, A. Novák, Z. *Chem. Commun.* **2015**, 51, 4488.
2. Tóth, B. L.; Kovács, Sz.; Sályi, G.; Novák, Z. *Angew. Chem. Int. Ed.* **2016**, 55, 1988.



PO54 – Expansion of the Concept of Nonlinear Effects in Catalytic Reactions Beyond Asymmetric Catalysis

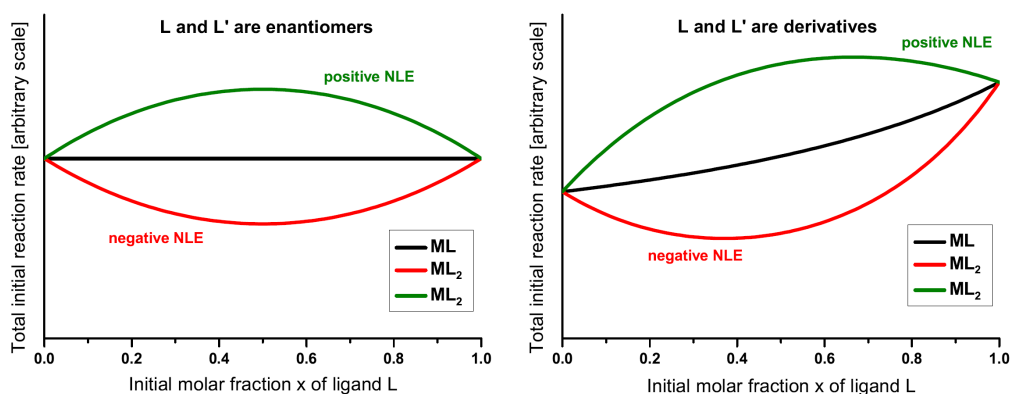
Michael Schnürch* and Robert Pollice

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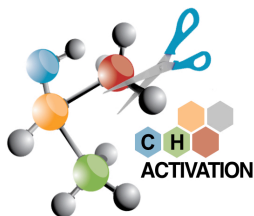
The concept of nonlinear effects^{1,2} is expanded from asymmetric catalysis to catalytic reactions in general by investigating reaction rates instead of enantiomeric purity and using derivatives instead of enantiomers.

The observation and investigation of nonlinear effects in catalytic reactions provides valuable mechanistic insight. However, the applicability of this method was, until now, limited to molecules possessing chirality and therefore to asymmetric synthesis. Within this contribution, the concept of nonlinear effects is expanded to catalytic reactions beyond asymmetric catalysis by using derivatives instead of enantiomers and by considering rates instead of enantiomeric excess.³ Additionally, its systematic application to investigate the mechanism of catalytic reactions is presented. By exceeding the limitation to asymmetric reactions, the study of nonlinear effects can become a general tool to elucidate reaction mechanisms.



References

1. Puchot, C. Samuel, O. Dunach, E. Zhao, S. Agami, C. Kagan, H. *J. Am. Chem. Soc.* **1986**, *108*, 2353.
2. Blackmond, D. G. *Acc. Chem. Res.* **2000**, *33*, 402.
3. Pollice, R. Schnürch, M. *Chem. Eur. J.* **2016**, *22*, 5637.



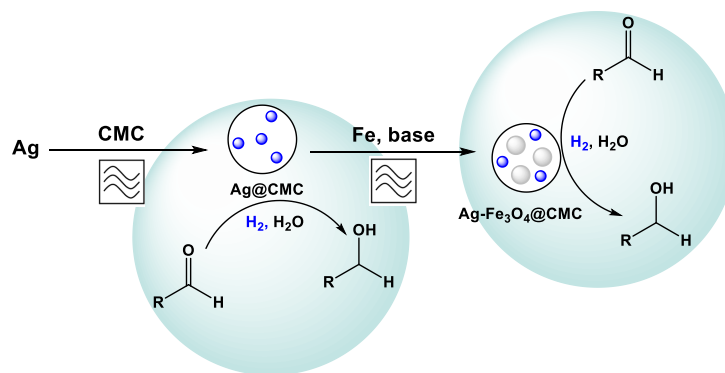
PO55 – Microwave-Assisted Synthesis of Magnetically Recoverable Silver-Iron Oxide ($\text{Ag-Fe}_3\text{O}_4@ \text{CMC}$) Nanocatalysts for Carbonyl Compounds Hydrogenation

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Iron oxide nanoparticles (NPs) have been used as magnetic supports to enable the easy recovery of catalysts.¹ By grafting metal nanoparticles catalysts on them, they can contribute to more sustainable industrial processes. The synthesis under mild conditions of a magnetically retrievable catalyst for aldehyde hydrogenation was investigated in this work. Under very short microwave irradiation conditions, silver and iron nanoparticles were grafted on carboxymethyl cellulose (CMC), as an inexpensive and bio-based polymer support.² The use of biodegradable polymers as a capping agent and reductant decreases their environmental impact while allowing a better NP size control. The catalyst was tested for the hydrogenation of aldehydes in water, showing a high activity and selectivity to C=O bonds against C=C bonds. The organic matrix and the magnetic support allowed the catalyst to be recycled up to five times with a negligible silver leaching in the reaction medium.



References

1. Hudson, R. *et al. Green Chem.* **2014**, *16*, 4493.
2. Horikoshi, S. *et al. Nanoscale* **2010**, *2*, 1441.



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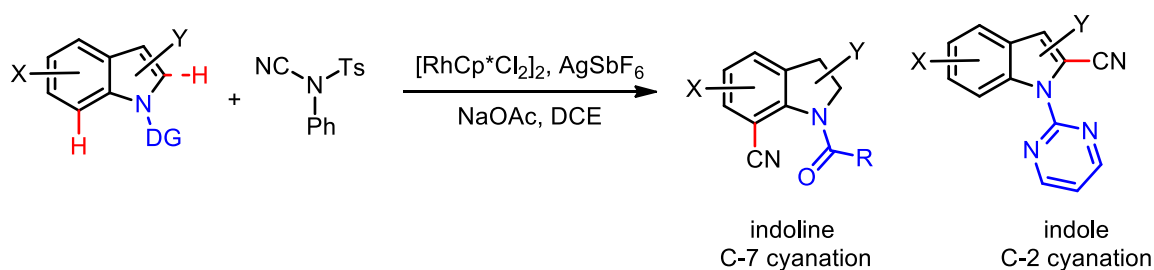
PO56 – Selective C–H Functionalization of Indolines and Indoles with Easily Accessible Cyano Source Using Rh(III) Catalyst

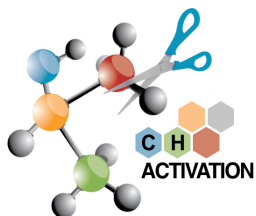
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The indoline nucleus is a ubiquitous structural core and is widely found in heterocyclic compounds with biological and medicinal applications. In particular, many pharmaceutical agents include C7-substituted indoline framework. The installation of the CN group into bioactive molecules may dramatically modify their biological properties. Recently, the directing group-assisted C7-functionalizations of indolines have been an intensive research area to override the inherent selectivity of indoles. In this area, acylation, arylation, alkenylation, alkylation, and amidation were developed. Herein, we described a facile approach for the C7-selective C–H cyanation of indolines with NCTS as the user-friendly cyanation reagent. It is noteworthy that the formed C7-cyanated indolines can be readily transformed to C7-cyanated indoles under the oxidative conditions.





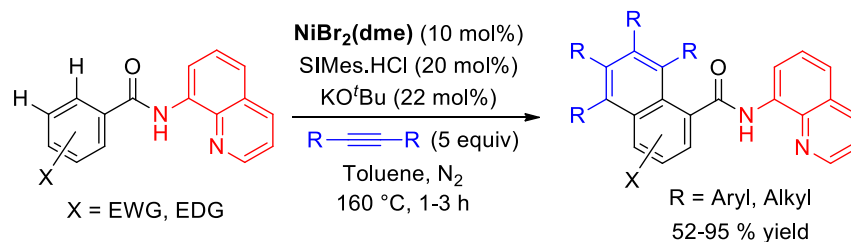
**PO57 – Chelation-Assisted Nickel-Catalyzed Oxidative Annulation via
Double C–H Bond Activation/Alkyne Insertion Reaction**

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A nickel/NHC-carbene system for regioselective oxidative annulation by double C–H bond activation and concomitant alkyne insertion has been developed. The catalytic reaction requires a bidentate directing group, such as an 8-aminoquinoline, embedded in the substrate. Various 5,6,7,8-tetrasubstituted-*N*-(quinolin-8-yl)-1-naphthamides can be prepared as well as phenanthrene and benzo[*h*]quinoline amide derivatives. Diarylalkynes, dialkylalkynes, and arylalkylalkynes can be used in the system. A Ni(0)/Ni(II) manifold is proposed as the main catalytic cycle. The alkyne plays a double role in the reaction as a coupling partner and as a hydrogen acceptor.



References

1. Misal Castro, L. C.; Obata, A.; Aihara, Y.; Chatani, N. *Chem. Eur. J.* **2016**, *22*, 1362.
2. Misal Castro, L. C.; Chatani, N. *Chem. Lett.* **2015**, *44*, 410.



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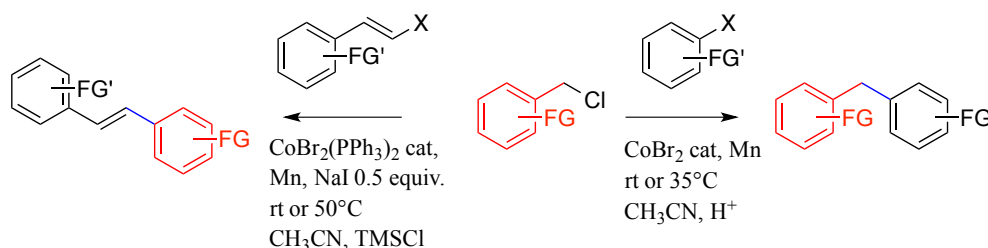
PO58 – Cobalt-Catalyzed Reductive Cross-Coupling Involving Benzyl Chlorides

Corinne Gosmini,* Yingxiao Cai, Suman Pal, Sushobhan Chowdhury and Audrey Auffrant

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Our group develops various cobalt-catalyzed reductive cross-coupling reactions in order to create C–C bonds.¹ This presentation is focused on recent developments concerning coupling of benzyl chlorides. Both aryl-benzyl² and vinyl-benzyl³ bonds were formed with these methodologies. Therefore, these different procedures allow one-pot synthesis of various functionalized molecules in mild conditions without the formation of preliminary stoichiometric organometallic compounds. Importantly all these reactions were performed with a cheap metal under “bench-friendly” conditions.



References

1. Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi von Wangelin, A. *Chem Eur. J.* **2014**, 20, 6828.
2. Pal, S.; Chowdhury, S.; Auffrant, A.; Gosmini, C. *submitted*.
3. Cai, Y.; Benischke, A. D.; Knochel, P.; Gosmini, C. *submitted*.



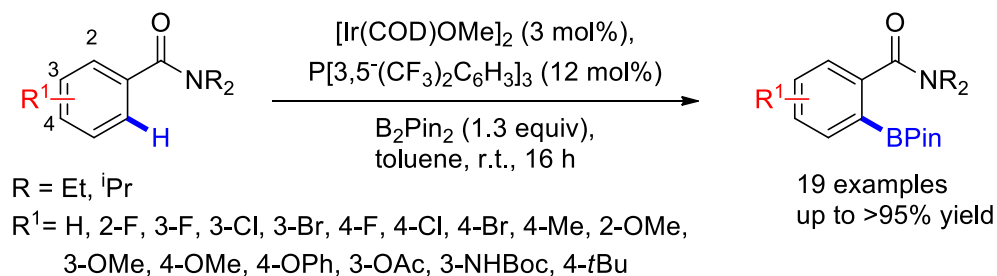
PO59 – An Iridium-Catalyzed *ortho* selective C–H Borylation of Tertiary Benzamides

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We have developed an iridium-catalyzed amide directed C–H borylation reaction of tertiary benzamides. An iridium(I) complex paired with an electron-deficient phosphine ligand allows for efficient C–H activation and borylation using bis(pinacolato)diboron (B_2pin_2). This methodology acts as a complementary method to both directed *ortho* metalation (*DoM*) and a previously developed *meta*-selective borylation. We have demonstrated the utility of these boron-containing products by further cross-coupling reactions and *DoM* chemistry.



References

1. Zhao, Y.; Snieckus, V. *J. Am. Chem. Soc.* **2014**, *136*, 11224.
2. Hurst, T. E.; Macklin, T. K.; Becker, M.; Hartmann, E.; Kügel, W.; Parisienne-LaSalle, J. C.; Batsanov, A. S.; Marder, T. B.; Snieckus, V. *Chem. Eur. J.* **2010**, *16*, 8155.



PO60 – An Efficient Solar-Powered System for Reversible Hydrogen Storage based on Organic Hydrocarbons

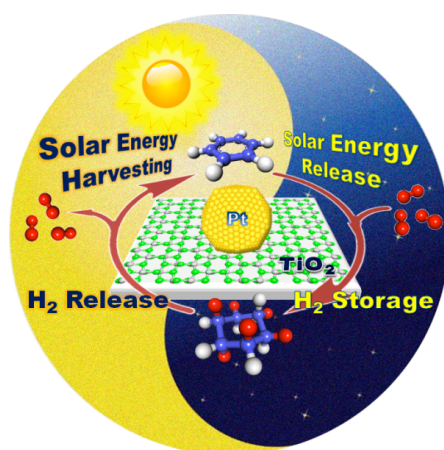
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Solar energy harvesting and hydrogen economy are the two most important green energy endeavors for the future. Currently, artificial photosynthesis has been recognized as a desirable strategy to provide clean hydrogen fuel from water by light. However, a critical scientific and practical challenge is how to safely and densely store and transfer hydrogen, a highly explosive gas. Herein, we designed a reversible hydrogen storage system based on low-cost and abundant liquid organic cyclic hydrocarbons (benzene, toluene and xylene, the so-called BTX family). A facile switch of hydrogen addition (>97% conversion) and release (>99% conversion) with superior capacity of 7.1 H₂ wt% can be quickly achieved over a rationally optimized platinum catalyst with high electron density under exceptionally mild conditions, simply regulated by dark/visible-light conditions at room temperature and atmospheric pressure.



Reference

1. Li, L.; Mu, X.; Liu, W.; Mi, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2015**, *137*, 7576.



PO61 – Synthesis of a Promising Antitumor Indolobenzazocin-8-one Using Palladium-Catalyzed Intramolecular C–H Activation

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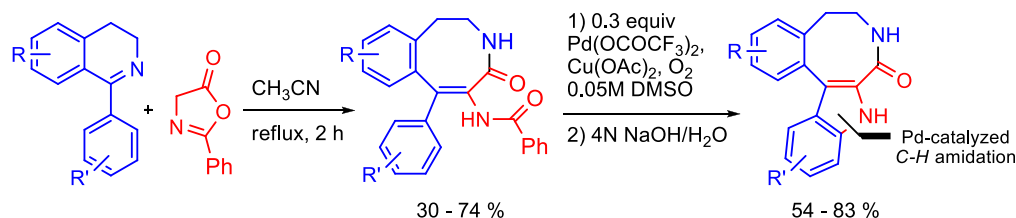
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A facile and direct synthetic entry to benzoazocin-4-ones is reported based on the ring annulations of 1-substituted dihydroisoquinolines with azlactones under neutral conditions. This protocol served as a useful template for the synthesis of eight-membered ring molecule. In addition, the benzoazocinones has been carried out using palladium-catalyzed C–H activation to form indolobenzazocinone derivatives via intramolecular amidation. The cytotoxicity against a panel of cancer cell lines was studied and will be presented.



References

1. Worayuthakarn, R.; Thasana, N.; Ruchirawat, S. *Org. Lett.* **2006**, *8*, 5845.
2. Boonya-udtayan, S.; Meredith Eno; Ruchirawat, S.; Thasana, N. *Tetrahedron* **2012**, *68*, 10293.



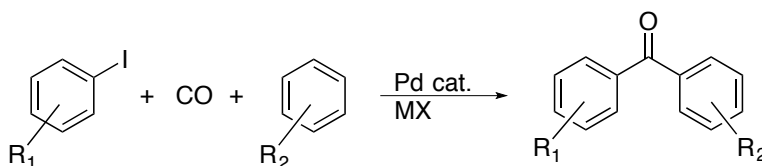
PO62 – A Palladium Catalyzed Carbonylative C–H Functionalization of Arenes

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The ability to functionalize inert hydrocarbons represents one of the most potentially useful transformations in synthetic organic chemistry. Palladium catalysis has proven to be quite fruitful in this area with the ability to activate C–H bonds and directly install useful functionality. A common platform for these transformations is through a carboxylate assisted CMD pathway, which can require directing groups, intramolecular reaction, or very specific substrates with weaker C–H bonds. An alternative approach to this widely used strategy would be to use transition metal catalysis to make highly reactive organic fragments that could be used to functionalize a C–H bond. Carbonylation chemistry, and in particular palladium catalyzed carbonylation chemistry, has seen growing use in the construction of esters, amides, ketones and other products and could thus be useful for the synthesis of potent carbonylated electrophiles. We have recently demonstrated that this approach is viable by using palladium catalysis to functionalize electron rich heteroarenes through the generation of a putative aroyl iodide intermediate. In this work, an efficient method for the carbonylative functionalization of unactivated arenes (benzene and benzene derivatives) has been developed. This reaction is thought to proceed through an unusual, highly electrophilic aroylating intermediate.





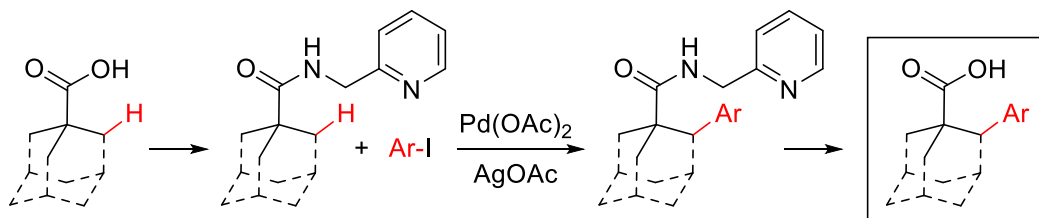
PO63 – Pd(OAc)₂ Catalyzed C–H Bond Arylation of Diamondoids

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We present an effective approach to 1,2-disubstituted diamondoids by Pd(OAc)₂ catalyzed arylation of C–H bond.¹ Selective *mono*-functionalisation of the adamantane framework was achieved using picolylamide as a directing group in yields up to 87%. Mechanistic studies of this transformation will be discussed in detail. Acidolysis of the directing group provides access to 2-aryl diamondoid carboxylic acids, which are common precursors for the synthesis of various bioactive compounds (drug candidates).²



References

1. Larrosa, M.; Heiles, S.; Becker, J.; Spengler, B.; Hrdina R. *Adv. Synth. Catal.* **2016**, accepted.
2. Wanka, L.; Iqbal, K.; Schreiner, P. R. *Chem. Rev.* **2013**, *113*, 3516-3604.



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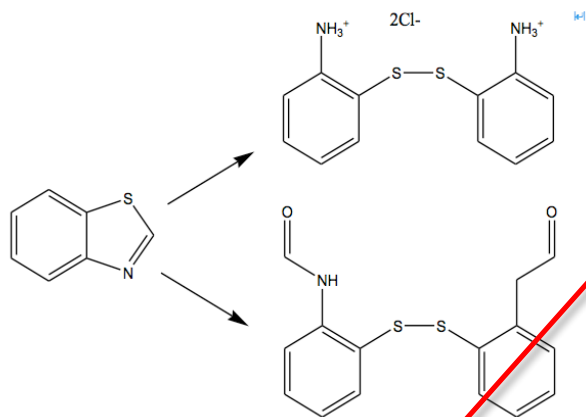
PO64 – C–S Bond Cleavage in Benzothiazole and S–S Bond Formation

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Unexpected C–S bond cleavage and S–S bond formation were observed in benzothiazole reactions that produced 2,2'-(disulfanediyl)dianilinium dichloride and 2,2'-(disulfanediyl)di-*N*-formylphenyl. The reactions were catalyzed by cerium(III) chloride and temperature. A computational studies were carried out in order to propose a rational mechanism.



References

Bouchareb, H. ; Boudraa, M. ; Bouacida, S. ; Merazig, H. *Acta Cryst.* **2013**, E69, o1078–o10792.

WITHDRAWN



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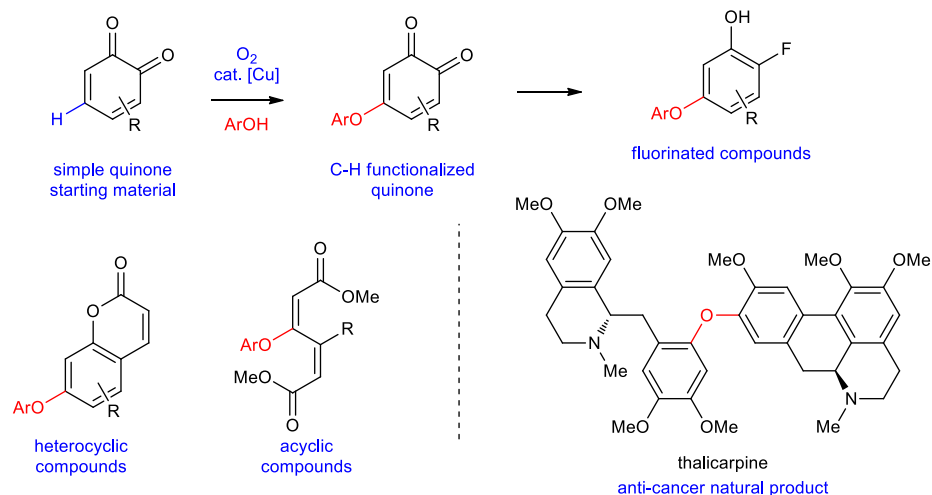
PO65 – C–H Functionalization on *ortho*-Quinone and Its Applications on Synthesis

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ortho-Quinone is under-developed in chemical synthesis, due to their low stability. We have developed mild conditions for the selective C–H functionalization of *ortho*-quinone, and oxidatively coupled with phenol to generate O-coupled quinone using oxygen as the terminal oxidant. The product O-coupled quinone can be transferred to heterocyclic compounds, fluorinated compounds and acyclic compounds via short sequences. We are now exploiting this new chemistry on the natural product synthesis.





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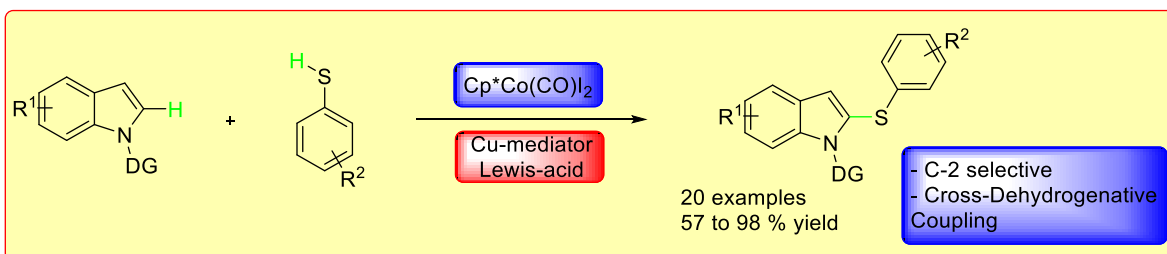
**PO66 – Cross-Dehydrogenative Coupling of Thiols with Indoles
Using a Cp*Co(III)-catalyst-Cu/Lewis-Acid Cooperative System**

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Since the seminal report of Matsunaga and Kanai,¹ Cp*Co(III)-catalysts have evolved as a comparable catalytic system to the widely used Cp*Rh(III)-catalysts. However reports on divergent reactivity of the Cp*Co(III)-fragment remain scarce.² Herein we report on the unique reactivity of the Cp*Co(III)-catalyst to promote a challenging C-2-selective Cross-Dehydrogenative Coupling of indoles with thiols. This reactivity has thus far not been observed with the Cp*Rh(III)-catalyst system and highlights the complementary reactivity of the Cp*Co(III)-complexes in C–H-activation. The resulting C-2 sulfenylated indoles were obtained in good to excellent yields employing a cooperative system of Cp*Co(III)-catalyst and Cu- as well as Lewis-acid additive.³



References

1. Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 2207.
2. Moselage, M.; Li, J.; Ackermann L. *ACS Catal.* **2016**, *6*, 498.
3. Gensch, T.,[§] Klauck, F.; Glorius F. *Manuscript submitted*.



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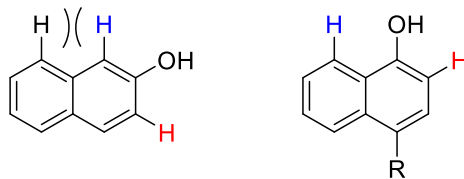
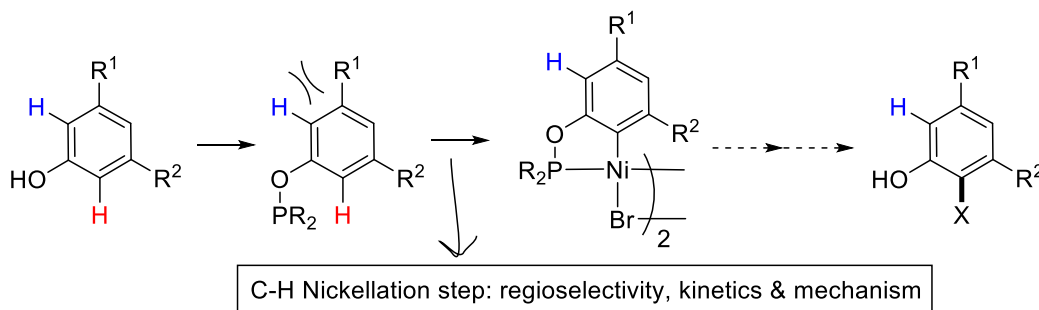
**PO67 – Nickel-mediated Cyclometallation of Aryl-phosphinites and
Subsequent C–H Functionalization:
Exploration of the Kinetics and Regioselectivity of C–H Nickelation**

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Nickelation of aromatic and aliphatic C–H bonds of pincer-type ligands has been proven very efficient for the synthesis of a wide variety of pincer-Ni complexes. Our group has also shown that a similar C_{sp^2} –H nickelation approach can be used to functionalize aryl-monophosphinites.¹ The initial results of this latter study spurred us to further explore the often very high regioselectivity of the nickelation by investigating this step using various phenyl- and naphthyl-phosphinites bearing different substituents. This poster will disclose what we have learnt so far on the regioselectivity and kinetics of C–H nickelation in our systems.



Reference

1. Vabre, B.; Deschamps, F.; Zargarian, D. *Organometallics*, **2014**, *33*, 6623.



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PO68 – Boryl (Hetero)Aryne Precursors: Synthesis via C–H Activation and Orthogonal Reactivity

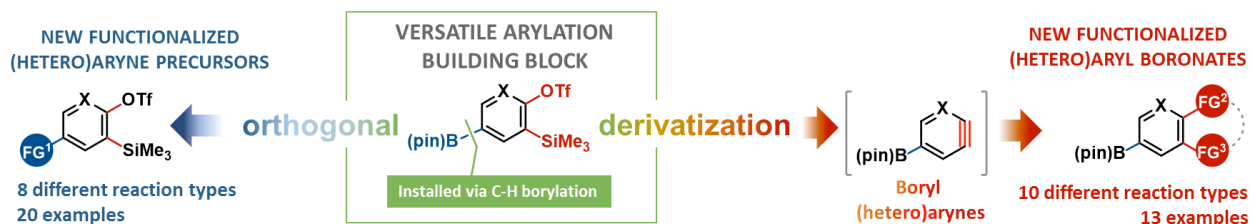
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(Hetero)aryne chemistry has undergone a considerable resurgence in recent years.¹ In large part, this is due to the recognition of Kobayashi's *ortho*-silyl aryltriflate aryne precursors as versatile and convenient starting materials.² However, the synthetic utility of aryne chemistry also depends on the ease with which diversely functionalized precursors can be prepared. We report that Ir-catalyzed C–H borylation³ can be used to prepare versatile boryl aryne precursors. These may be derivatized under orthogonal conditions by selective activation of the boronate or aryne components. Thus, from a single family of starting materials, it is possible to arrive at postfunctionalized arylboronates or *ortho*-silyl aryltriflates through a large number of transformations. This method constitutes a very flexible method to prepare many new types of building blocks for arylation.⁴



References

1. A. Bhunia, S. Reddy Yetra, A. T. Biju, *Chem. Soc. Rev.* **2012**, *41*, 3140
2. Y. Himeshima, T. Sonoda, H. Kobayashi, *Chem. Lett.* **1983**, 1211.
3. I. A. I. Mkhaliid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890.
4. E. Demory, K. Devaraj, A. Orthaber, P. J. Gates, L. T. Pilarski, *Angew. Chem. Int. Ed.* **2015**, *54*, 11765.



PO69 – C–H Alkenylations with Alkenyl Acetates, Phosphates, Carbonates and Carbamates by Versatile Cobalt Catalysis at 23 °C

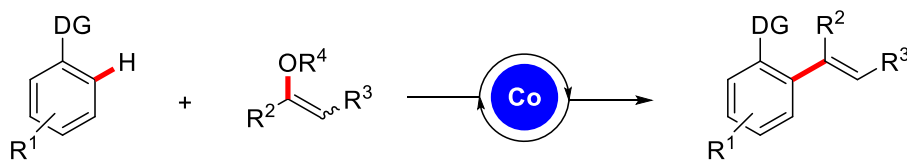
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Cobalt-catalyzed C–H activation represents a powerful tool for the sustainable synthesis of biologically active compounds and functional materials,¹ which were as of yet mostly achieved by the use of more expensive second row transition metal-complexes. In recent years, considerable success has been accomplished with the development of C–H arylations, alkylations and benzylations with organic electrophiles by low-valent cobalt catalysis.² As of yet, cobalt-catalyzed olefinations were solely accomplished by hydroarylations of alkynes.³ Despite significant advances, this method faces considerable limitations, including the restriction to the synthesis of acyclic alkenes.

Herein, we present a cobalt-catalyzed C–H olefination with easily accessible enol derivatives.⁴ Notable features of our isohypsic strategy are not limited to a predictable regio-control, challenging C–H/C–O functionalizations with unactivated alkenyl acetates, phosphates, carbonates, and carbamates in a stereoconvergent fashion, as well as oxidant-free olefinations under remarkably mild conditions at 23 °C.



References

1. a) Moselage, M.; Ji, L.; Ackermann, L. *ACS Catal.* **2016**, *6*, 498. b) Yoshikai, N.; *ChemCatChem.* **2015**, *7*, 732. c) Ackermann, L. *J. Org. Chem.* **2014**, *79*, 8948, and references cited therein.
2. a) Xu, W.; Paira, R.; Yoshikai, N. *Org. Lett.* **2015**, *17*, 4192. b) Li, J.; Ackermann, L. *Chem Eur. J.* **2015**, *20*, 5718. c) Gao, K.; Yoshikai, N. *J. Am. Chem. Soc.* **2013**, *135*, 9279. d) Punji, B.; Song, W.; Shevchenko, G. A. Ackermann, L. *Chem Eur. J.* **2013**, *19*, 10605. e) Song, W.; Ackermann, L. *Angew. Chem. Int. Ed.* **2012**, *51*, 8251.
3. For selected examples, see: a) Ikemoto, H.; Yoshino, T.; Matsunaga, S. Kanai, M. *J. Am. Chem. Soc.* **2014**, *135*, 5424. b) Ding, Z.; Yoshikai, N. *Angew. Chem. Int. Ed.* **2012**, *53*, 4698. c) Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2011**, *133*, 17283. d) Gao, K.; Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2010**, *132*, 12249. e) Halbritter, G.; Knoch, F.; Wolski, A.; Kisch, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1603.
4. Moselage, M.; Sauermann, N.; Richter, S. C.; Ackermann, L.; *Angew. Chem. Int. Ed.* **2015**, *54*, 6352.



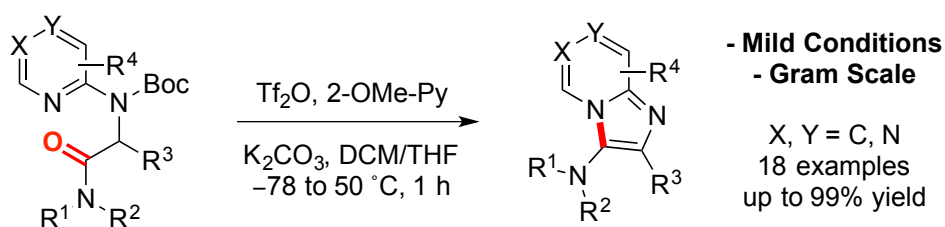
PO70 – Expedient Synthesis of 3-Aminoimidazo[1,2-*a*]pyridines from α -Aminopyridyl Amides

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3-Aminoimidazo[1,2-*a*]pyridines are rapidly synthesized via an hour-long and mild cyclodehydration/aromatization reaction starting from readily available amides. The activation/cyclodehydration step is mediated by triflic anhydride (Tf₂O) in presence of 2-methoxypyridine (2-OMe-Py) from a *N*-Boc-protected 2-aminopyridine-containing amide, and a mixture of K₂CO₃/THF provided a clean deprotection/aromatization to the desired heterocycle. A wide variety of functional groups and substitution patterns were tolerated under this optimized procedure, and good to excellent yields were obtained for the fused bicyclic 3-aza-heterocycles.¹ In addition, the reaction is found to be easily scalable to gram-scale and could be performed with unprotected acyclic amide precursors. We also found that the resulting products were valuable intermediates for diverse Pd- and Ru-catalyzed C–H arylation reactions, allowing for the formation of further functionalized building blocks.²



References

1. Pelletier, G.; Charette, A. B. *Org. Lett.* **2013**, *15*, 2290.
2. (a) Roman, D. S.; Poiret, V.; Pelletier, G. *Eur. J. Org. Chem.* **2015**, 67. (b) Shibahara, F.; Yamaguchi, E.; Murai, T. *Chem. Commun.* **2010**, 46, 2471.