

# POSTERS

Abstracts



6<sup>th</sup> Edition of International Conference and Exhibition on

# Organic Chemistry

August 16-17, 2018 | Dublin, Ireland

August 16-17, 2018  
Dublin, IrelandChristopher Harris, J Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

# MULTIVARIATE ANALYSIS OF A NUCLEOPHILIC AROMATIC SUBSTITUTION BY REAL-TIME ON-LINE FLOW REACTION MONITORING USING MINIATURIZED MASS SPECTROMETRY

**Christopher Harris**

Microsaic Systems PLC, UK

**T**he use of automated flow systems combined with on-line MS analysis enables rapid screening and efficient optimization for process development and is fully scalable from laboratory, pilot plant to manufacturing plant. This produces a massive saving in the time and materials required if compared to common approaches. To demonstrate this, we have investigated the optimization of the nucleophilic aromatic substitution of 2,4-difluoro-nitrobenzene with morpholine over a wide variety of stoichiometric ratios, residence times and temperatures to demonstrate all the benefits of using on-line flow reaction monitoring.

**Biography**

Christopher Harris received his PhD in Chemistry from Nottingham University, UK studying the mass spectrometry and electrostatics of molecular cluster. He is an Application Specialist at Microsaic Systems PLC, developers of point-of-need mass spectrometers that serve a range of applications. His key application areas include reaction monitoring and mass directed purification. He is mainly interested in mass spectrometry.

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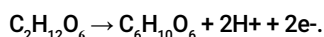
August 16-17, 2018  
Dublin, IrelandShigeki Matsunaga, J Org Inorg Chem 2018, Volume 4  
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# SIMULATION STUDY ON AQUEOUS SOLUTIONS OF BIO-MOLECULES USED IN BIOFUEL CELLS

**Shigeki Matsunaga**

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Recent years much attention has been paid to the biofuel cells, which are expected as the next generation portable, clean, and safe chemical batteries that can be used even in a human body. Glucose is one of the most promising energy resources of biomass component used in a biofuel cell, because it is most abundantly found monosaccharide in the field. Based on the recent report, the enzymatic fuel cell has achieved ten times the energy storage of lithium ion batteries. Meanwhile, in recent years the biodegradable polymers are frequently used in the broad area, especially in the medical treatment, e.g. surgical suture, cartilage support, and capsules carrying drugs to the affected part. Poly Lactic acid (L-acid) and Poly Glycolic acid (G-acid) are typical examples, which resolute to L-acid and G-acid in a human body, respectively. According to the recent literatures, the biofuel cells using L-acid and G-acid have been constructed, which are expected to work in a human body and/or on a human skin. In the cathode of biofuel cells, e.g. glucose is oxidized to produce gluconolactone, as:



Therefore, the glucose aqueous solution in the cathode of the biofuel cell contains many constituents including buffer solute. There are many molecular dynamics (MD) studies on glucose, L-acid, and G-acid aqueous solution, however, few MD studies have treated multi-component bio-molecule aqueous solutions. Recent years, we have been engaged in many MD studies on multi-component aqueous solutions including carbon dioxide, nitrate, sulfate, and amino acid ion etc. In this study, as a serial work, we wish to perform a simulation study on bio-molecule aqueous solutions as a model of a cathode of biofuel cell. In the simulation study, firstly, the structure and atomic charges of the constituents of the solution, i.e. glucose etc., are optimized using Gaussian09 on the basis of the density functional theory (DFT). Vibrational modes of ions will be discussed based on the structure difference. The transport properties, and thermodynamic properties of the solution will be examined by MD. The dielectric properties of solutions in various concentration of solutes will also be discussed.

## Recent Publications

1. S Matsunaga (2017) Molecular dynamics study on carbon dioxide absorbed potassium glycinate aqueous solution. *Journal of Solution Chemistry*. 46(12):2268-2280.
2. S Matsunaga (2018) Structure and transport properties of AgI-AgCl-CsCl glasses: molecular dynamics study. *Ionics*. 24(5):1371-1376.
3. S Matsunaga (2017) Effect of sulfate anion on the structure and transport properties of seawater: A molecular simulation study. *Journal of Molecular Liquids*. 226:90-95.
4. S Matsunaga (2015) Effect of greenhouse gases dissolved in seawater. *International Journal of Molecular Sciences*. 17(1):45.
5. S Mastunaga (2014) Anomalous electrical properties in superionic (Ag<sub>x</sub>Cu<sub>1-x</sub>)Br (x=0.5): ab initio study. *Ionics*. 21(1):161-166.

## Biography

Shigeki Matsunaga pursued his Master's Degree from Graduate School, Division of Natural Science, Niigata University in 1983; PhD Degree on the experimental and theoretical studies on compound forming liquid alloys at the same university, graduated from the Faculty of Science, Saitama University in 1981. He is a Professor of Physics at the National Institute of Technology, Nagaoka College. He is a Member of The Physical Society of Japan, The Japanese Society for Neutron Science, The Molecular Simulation Society of Japan, The Japan Association of Solution Chemistry, and The Physics Education Society of Japan. He received Grant-in-Aid for Scientific Research (C) from The Japan Society for the Promotion of Science: Project Year: Apr 2015 - Mar 2019, Apr 2010 - Mar 2013, and Apr 2005 - Mar 2009. His research interests include: structure and transport properties of the aqueous solutions of bio-molecules mainly used in a biofuel cell. Many MD studies on the structure, transport properties, and electric properties of the multi-component solid electrolytes, molten salts, and liquid metal alloys have also been performed.

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Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
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## NOVEL ASYMMETRIC SYNTHESIS OF (S)-KETAMINE ANESTHETIC DRUG USING THE CHIRAL TERT-BUTANESULFINAMIDE

**Abdollah Javidan**

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**2**-(2-chlorophenyl)-2-(methylamino)-cyclohexanone (Ketamine), has been widely used as an anesthetic and analgesic drug. In this research work, at first the 2-(N-piperidino methyl)-1-phenyl cyclohexyl amine starting material (1), was prepared from cyclohexanone piperidine by Mannich reaction. Then, the sulfinylimin (2) was synthesized by condensation of tert-butanefulfonamide (tBS) with aminoketone (1) in presence

of  $\text{Ti}(\text{OEt})_4$  in 85% yield. The new chiral center was induced in (2) using Grignard reagent as nucleophile at  $-78^\circ\text{C}$  and 75% yield. after multi step reaction including methylation of (3) and Hoffman elimination of (4) and deprotection of (5), finally, the (S)-ketamine was synthesized under ozonolize reaction of alken (6) in good yield and enantioselectivity (95% yield and %85 ee).

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## GREEN SYNTHESIS OF THIOBENZAMIDE DERIVATIVES BY WILLGERODT KINDLER REACTIONS IN ACIDIC CATALYSIS WITH MONTMORILLONITE K-10

**Agnimonhan Finagnon Hyacinthe**

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The development of synthetic approaches that meet the principles of green chemistry for the synthesis of molecules biological interests is one of the current quests. Among these molecules, we have the thioamides. The Willgerodt-Kindler (WK) reaction is one of the most widely used synthetic methods for accessing thioamides. The purpose of our work is to study this reaction in acid heterogeneous catalysis with montmorillonite K-10 under microwave activation for the synthesis of phenyl derivatives (morpholino) methanethiones. Our work shows that the mixture (aldehyde, sulfur, morpholine and K-10) is not only suitable, but optimizes the reaction. K-10 was easily separated from the reaction mixture and was recycled at least two times without any loss of activity. Operational simplicity, short reaction

times, excellent yields and benign environmental conditions are also the advantages of this protocol, thus respecting the principles of green chemistry. In summary the synthesis of thiobenzamides in heterogeneous acid catalysis with the K-10 of the Willgerodt-Kindler reaction for carbonyl compounds is a simple, efficient protocol that respects the principles of green chemistry. The structures of thioamides synthesized were characterized and confirmed by high-resolution mass spectrometry (HRMS) and nuclear magnetic resonance (NMR) 1D and 2D (COSY, HSQC, HMBC).

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## STILLE REACTION OF $\beta$ -NITRO AND $\beta$ -TOSYL SUBSTITUTED STYRYL BROMIDES

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University of Guayaquil, Ecuador

The palladium-catalyzed coupling of organostannanes with organic electrophiles (Stille reaction) have become an important synthetic tool in organic chemistry. In this work, we have examined the Stille reaction of  $\beta$ -nitro and  $\beta$ -tosyl ( $\beta$ -(*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>) substituted styryl bromides. The  $\beta$ -bromo- $\beta$ -nitro-styrenes 1 and 2 reacted with a variety of organostannanes using bis(acetonitrile)dichloropalladium(II) as catalyst and N-methylpyrrolidinone (NMP) as solvent at room temperature. Good yields of 2-nitro-1,3-dienes were obtained as a mixture of isomers. The Stille reaction of  $\beta$ -bromo- $\beta$ -tosyl-styrenes 3 and 4 was also investigated. In this case, the best yields of coupling products were obtained using an excess of organotin compound (1.5

equivalents), a mixture of bis(acetonitrile)dichloropalladium(II) (5% molar) and copper iodide (10% molar) as catalysts and NMP as solvent at room temperature. Again, good yields of products, as a mixture of isomers, were obtained. The Stille reactions of  $\beta$ -nitro and  $\beta$ -tosyl substituted styryl bromides reported here constitute a useful synthetic tool towards the preparation of functionalized 1,3-dienes. These unsaturated molecules are among the most versatile organic compounds which participate in a wide variety of applications, including fine chemicals synthesis and polymer chemistry.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

# SYNTHESIS OF 2-ACYLBENZONITRILES AND REACTIVITY IN ORGANOCATALYTIC TANDEM REACTION: EASY ACCESS TO HETEROCYCLES WITH TETRASUBSTITUTED CARBON

**Antonio Massa**

University of Salerno, Italy

The interest of the chemical community towards “one-pot” reactions increased rapidly over the past two decades. These processes, which also include tandem reactions, are characterized by a high level of atom and step economy. Tandem reactions are often used to prepare heterocycles of high biopharmacological value. To facilitate the reaction design, the utilization of bifunctional building blocks in tandem reactions has emerged as an important research area of organic chemistry. However, most of the bifunctional compounds are not easy to synthesize due to the difficulty of installing two or more reactive sites into one molecule. Many 2-substituted benzaldehydes belong to this class and have been widely used in tandem reactions for the synthesis

of heterocyclic compounds. In this context, even though ketones are less electrophilic than aldehydes, the investigation of the reactivity of 2-acylbenzotrioles and related ketones appears to be of high interest because of the possibility to obtaining derivatives with tetrasubstituted stereocenters in a single pot process. Thus, in the present communication, the scope and the great potentialities of bifunctional aromatic ketones as electrophiles in asymmetric reactions will be discussed. In addition, a convenient synthesis of 2-acylbenzotrioles starting from readily available materials is proposed.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## GREEN CHEMISTRY AND ALTERNATIVES TECHNIQUES: HIKING AROUND GLYCEROL

**Christophe Len**

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**T**he design of environmentally friendly methodologies has been the driving force of scientists in recent years. In particular, the use of biomass-derived materials, green solvents and alternatives techniques has been investigated. In this regards, glycerol has the potential to be both an excellent renewable solvent in modern chemical processes and a versatile building block in biorefineries. In this conference, several green chemistry approaches that target advanced synthesis and processes using glycerol will be

presented. Few approaches will be described: (i) green synthesis of quinoline and phenanthroline derivatives in sole water using microwave irradiation and high temperature/pressure in batch and in continuous flow; (ii) production of oligomer of glycerol for polymerization in batch and in continuous flow. Conception, synthesis and physico-chemical properties will be detailed.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## ORGANIC PHOTOVOLTAIC CELL: A PROMISING INDOOR LIGHT HARVESTER FOR SELF-SUSTAINABLE ELECTRONICS

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Photovoltaic cells are attracting significant interest for harvesting indoor light for low power consumption wireless electronics such as those required for smart homes and offices, and the rapidly-growing Internet of Things. Here, we explore the potential of solution processable, small molecule photovoltaic cells as indoor power sources. By optimizing solvent vapour annealing (SVA) time to the photovoltaic layer, a balance between its crystallization and phase separation is obtained, resulting in a record power conversion efficiency of over 28% under fluorescent lamps of 1000 lux, generating a maximum power density of 78.2  $\mu\text{W}/\text{cm}^2$  (>10% efficiency under AM1.5G). This high indoor performance surpasses silicon based photovoltaic cells, and is similar to gallium arsenide photovoltaic cells. Besides, the ratios

of the voltage at maximum power point to the open circuit voltage are similar from indoor lighting to one sun condition, which is unique and allows a less power consuming method to track the maximum power point for a broad range of light intensities (potentially attractive for wearable PV). New insight on the effect of SVA to the indoor and one sun performance is provided by advanced optoelectronic characterization techniques, which shows that the mobility-lifetime products as a function of charge carrier density can be correlated well to the performance at different light levels. Our results suggest that organic photovoltaic cell could be promising as indoor power source for self-sustainable electronics.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

# SYNTHESIS AND EVALUATION OF ANTIBACTERIAL AND ANTIOXIDANT ACTIVITY OF NEW DERIVATIVE PYRIDO [1,2-B] [1,2,4] TRIAZEPINE DERIVATIVES

**Houda Serrar**

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Pyridine derivatives are an important class of azaheterocycles found in many natural products, active pharmaceuticals and functional materials. Whereas pyridine-derived pharmaceuticals include Atazanavir (Reyataz®) and Imatinib mesylate (Gleevec®), respectively prescribed for human immunodeficiency virus (HIV) and chronic myelogenous leukemia. In particular, some pyridotriazepines derivatives possess diverse bioactivities, such as analgesic, anti-inflammatory, anticancer, antihelminthic, fungicide, and antagonistic activity towards several receptor. In this work, and as part of our ongoing research focusing on developing synthetic routes to heterocyclic derivatives with potential biological activities, we herein report a safe, facile, fast, one-pot reaction and ecofriendly synthesis of a novel substituted 4,8-dioxo-pyrido[1,2-b] [1,2,4] triazepines (3a-l) from epoxides 2. The new proposed synthetic routes seem to be of interest, since they have been compared with existing methods. The synthesized pyridotriazepines are characterized using spectral methods (IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS), then they were screened at first for

their antioxidant activities using DPPH, FRAP and ABTS methods. The results show that the antioxidant properties don't follow the same tendency in all assays, due to the nature of the scavenged radicals and the reaction mechanism. Also, the present study revealed that the nature of the substituent on the phenyl ring is crucial for the exhibited antioxidant activities, and that the increased activities follow systematically the order CH<sub>3</sub>>Cl>H. Furthermore the synthesized compounds were also evaluated for their antibacterial activity against four pathogenic bacteria which are *Staphylococcus* sp, *Escherichia coli* sp, *Bacillus* sp and *Enterobacterium* sp. The antibacterial effect was determined using the Muller-Hinton agar diffusion method for bacterial strains. The results shows that these compounds have good inhibitory activity towards the studied pathogenic strains. The minimum inhibitory concentrations are also determined for the samples that were displayed the best antibacterial power.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## DISCOVERY OF NEW SYNTHETIC REACTIVITIES OF THE ENAMINE CHEMISTRY

**Jiang Yaojia**

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**E**namines and their derivatives are useful synthetic building blocks since they can function as stable enolates to react with a wide variety of electrophiles under neutral conditions. Furthermore, they can also function as latent amino groups since they can easily be obtained via reduction of the unsaturated double bond. Therefore, it has attracted widely attention to employing enamines as synthons in organic transformations in past decades. In our group, we are focused on discovering new synthetic

reactivities of the enamine chemistry. Recently, we developed efficient methods for regioselective C-H bond functionalization of the enamines and constructed new C-S, C-O and C-C bonds. These obtained results offer the potential applications in complex molecule synthesis and better understanding of reactivities of the enamines.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## QUALITY ASSESSMENT OF SEWAGE POLLUTION AND WASTEWATER EFFLUENT: A CASE STUDY OF ACCRA METROPOLIS, GHANA

**Emmanuel Oduro Sarkodie**

Ghana Co-Operative Credit Unions Association (CUA) Ltd, Ghana

Effluent samples were collected from main manholes comprising raw wastewater from domestic, central business area (CBA), industrial and the outfall point at sea, Osu beach. The environmental effects of sewage pollution and wastewater effluent quality management in the Accra Metropolis, Ghana was assessed over a three month period. The physico-chemical and bacteriological analysis were determined using standard methods. The results of the physico-chemical parameters values were; pH 7.3- 8.2; EC 1277 –56828  $\mu\text{S}/\text{cm}$ ; TDS 613-28413 mg/l; BOD 3.8-53 mg/l; and the nutrients  $\text{NO}_3\text{-N}$  ranged from 1.5- 13.5 mg/l;  $\text{NH}_3\text{-N}$ , 0.2-3.8 mg/l;  $\text{PO}_4\text{-P}$  0.6-6.4 mg/l. The bacteriological analysis also recorded TC 6.6-5761 cfu/100ml; FC 0.6-139 cfu/100ml and *E.coli* 0.3-34 cfu/1m respectively. The level of compliance of effluent with the physico-chemical and bacteriological parameters were all below the Ghana Environmental Protection Agency (EPA) permissible standards for wastewater discharge at the outfall point at the Sakumono

beach. Although, the nutrient levels were not too high, yet may have the potential to cause eutrophication especially in the water bodies that sewage overflow into such as Korle, Lavender Hill and Odor lagoon and deplete the oxygen levels which will affect the aquatic life. The results of the social survey analysis observed some challenges with respect to the management of wastewater in the Accra Metropolis. Eighty percent admitted environmental, social and public health effects such as water borne diseases such as malaria, typhoid, diarrhea, dysentery among others. To prevent or reduce environmental effects and health risk associated with wastewater and sewage pollution, adoption and utilization of decentralized wastewater technologies that are most economically useful and efficient for the tropics such as waste stabilization ponds to safeguard public health and prevent negative environmental effects.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012**C→N COORDINATION BONDS IN (NL<sub>2</sub>)<sup>+</sup> COMPLEXES****Neha Patel**

NIPER, India

**N**-heterocyclic carbenes (NHCs) are known to form coordination complexes with transition metals, also their coordination chemistry with main group elements is well established. In the recent past, the nitrogen cation centre was proven to be an efficient electron accepting centre. The unique bonding nature of electron donating ligands (NHC/Carbocyclic carbene) and nitrogen cation centre inspired us to design several complexes having (L→N←L)<sup>+</sup>

species and explore their applicability. In this work, the quantum chemical design, synthesis and X-ray diffraction analysis of the same are presented. Quantum chemical analysis established the divalent NI character at the central nitrogen, X-ray diffraction studies validated the structural features.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## BIOCATALYTIC APPROACHES TOWARDS ENANTIOSELECTIVE SYNTHESIS OF 1,2-AMINO ALCOHOLS AND OTHER USEFUL PRECURSORS OF BIOACTIVE MOLECULES

**Pankaj Gupta**

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Despite tremendous advances accomplished through developing cheaper and more versatile chemical catalysts and optimizing the reaction media, the global needs for clean manufacturing technologies, management of hazardous chemicals and waste present new research challenges to both chemistry and biotechnology. Recent advances in biocatalysis, fueled by either protein engineering or screening, greatly improved the number of synthetic opportunities from small chiral polyfunctional molecules to highly complex analogs. Chiral 1,2-amino alcohols, 1,3-diols and carboxylic acids are the vital structural components of a large number of biologically active molecules with potential pharmaceutical relevance

and in chiral auxiliaries. The development of new protocols utilizing biocatalysts/chemocatalysts for the stereoselective synthesis of these molecules continue to be of great interest in organic chemistry. The present work involves the biocatalytic approaches towards the synthesis of these molecules by panel of microorganisms bearing lipases/oxidoreductases belonging to IIM-Jammu, SMVDU-Katra repositories as well as those procured from commercial sources. The immobilization of the substrate on a solid inert support as well as immobilization of enzymes significantly improved the enantioselectivity factor (E). The effect of acyl substituents and co-solvents were also studied.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## SYNTHESIS OF NOVEL QUINOLINE HYBRIDS VIA MOLECULAR HYBRIDIZATION AND THEIR PHARMACO-POTENTIAL EVALUATION

**Paul Awolade**

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The global threat of pathogenic resistance to available therapeutic agents has become a menace to clinical practice, public health and man's existence in consequential. This has therefore led to an exigency in the development of new molecular scaffolds with profound activity profiles. In this vein, a versatile synthetic tool for accessing new molecules by incorporating two or more pharmacophores into a single entity with the unique ability to be recognized by multiple receptors hence leading to an improved bioactivity, known as molecular hybridization, has been explored with tremendous success. Accordingly, aware of the similarity in pharmacological activity spectrum of quinoline and 1,2,3-triazole pharmacophores such as; anti-Alzheimer, anticancer, anti-HIV, antimalarial and antimicrobial to mention but

a few, the present study sets out to synthesize novel hybrids of quinoline and 1,2,3-triazole. The new hybrids were accessed via click chemistry using copper catalysed azide-alkyne 1,3-dipolar cycloaddition reaction. All synthesized compounds were evaluated for their pharmaco-potential in an antimicrobial assay out of which the 3-OH derivative emerged as the most active with MIC value of 4 µg/mL against *Creptococcus neoformans*; a value superior to standard Fluconazole and comparable to Amphotericin B. Structures of synthesized hybrids were elucidated using appropriate spectroscopic techniques (1H, 13C and 2D NMR, FT-IR and HRMS).

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## KINETIC REGULARITIES OF PHOTOCHEMICAL PROCESSES IN AIR-METHANE GAS PHASE SYSTEM

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**M**ethane is the most important representative of organic substances in the atmosphere. Its concentration significantly exceeds the concentration of the remaining organic compounds. In the last decade, the amount of methane in the atmosphere has increased at a rate of 1% per year. The main sources of methane emissions are energy, automobile and aviation transport, ferrous and non-ferrous metallurgy, chemical, petrochemical and coal industries. Methane ranks second after carbon dioxide in the efficiency of absorbing thermal radiation of the earth. The contribution of methane to the creation of the greenhouse effect is approximately 30% of the value adopted for carbon dioxide. As the content of methane increases, chemical processes in the atmosphere change, which can lead to a deterioration of the ecological situation on earth. The question naturally arises of the management of the chemical and physical processes in which

methane takes part. The experiment was carried out under the following conditions: the range of variation of the composition of the mixture [CH<sub>4</sub>-air]=0-100%, the reaction time of the reaction is up to 6 hours and at the wavelength of vacuum ultraviolet radiation (VUV -radiation)-  $\lambda=123$  nm. In the experiment, the initial partial pressure of methane was: P1=0.13 kPa and P2=22.5 kPa. In this case, the partial pressure of air containing 2% of water vapor varied from 0.13 kPa to 99.8 kPa. The working pressure range is chosen in connection with the fact that it is at 0.13 kPa to 99.8 kPa that methane absorption is almost completely observed. Thus, the VUV (Vacuum ultraviolet) photolysis of a complex mixture of N<sub>2</sub>-CH<sub>4</sub>-O<sub>2</sub>-H<sub>2</sub>O was studied in the component ratio range air / CH<sub>4</sub> = 0.750. The flux of the VUV- radiation is I=4.4 • 10<sup>15</sup> quant/s.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## ELECTROSYNTHESIS AS AN INVESTIGATION TOOL

**Victor Mairanovsky**

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**E**lectrolysis is one of the classic preparative methods of organic chemistry. At the same time, substances produced by electrolysis (electro-generated species, EGS) - primary generally unstable particles and final electrolysis-products, can be used for subsequent investigations. Respectively, two options (a) without isolation and (b) with isolation of the EGS are considered. The former includes various electrochemical techniques - cyclic voltammetry, voltammetry with rotating ring-disc electrode, etc., and combined electrochemical (EC-) methods, such as EC- ESR, EC- NMR, EC- stop flow, etc. These allow to receive valuable information on the structure of the primary EGSSs, kinetics and laws of their transformations. The latter case, (b) refers to study of properties and effects of pre-electrode medium, comparing results of a usual electrolysis, i.e. heterogeneous (EHET), and

homogeneous electro-catalytic processes (EHOM). Taking this idea a step further, a method with expansion of the reaction zone from the electrode surface to the bulk of the solution by a gradual increase in the contribution of EHOM - method. Pre-electrode tomography (PELTO) is developed. First results of using the PELTO included detection of differences in the structure of the EHOM- and EHET- products, determination of the effective orientation of the substrate particle at the electrode surface, estimate of transition time to the equilibrium orientation - evaluation of the "orientation memory", "Superviscosity"-hypothesis for the pre-electrode medium, etc. Further applications of the PELTO- method are discussed.

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August 16-17, 2018  
Dublin, IrelandJ Org Inorg Chem 2018, Volume 4  
DOI: 10.21767/2472-1123-C4-012

## CARBON ELECTRODE-MOLECULE JUNCTIONS: A RELIABLE PLATFORM FOR MOLECULAR ELECTRONICS

**Xuefeng Guo**

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This talk will exemplify our on-going interest and great effort in developing efficient lithographic methodologies capable of creating molecular electronic devices through the combination of top-down micro/nanofabrication with bottom-up molecular assembly. These devices use nanogapped carbon nanomaterials (such as single-walled carbon nanotubes (SWCNTs) and graphene) as point contacts formed by electron beam lithography and precise oxygen plasma etching. Through robust amide linkages, functional molecular bridges terminated with diamine moieties are covalently wired into the carboxylic acid-functionalized nanogaps

to form stable carbon electrode-molecule junctions with desired functionalities. We have used these approaches to reveal the dependence of the charge transport of individual metallo-DNA duplexes on  $\pi$ -stacking integrity, and fabricate molecular devices capable of realizing label-free, real-time electrical detection of biological interactions at the single-event level, or switching their molecular conductance upon exposure to external stimuli, such as ion, pH and light.

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