Cu/Graphene/Clay Nanohybrid: A Highly Efficient Heterogeneous Nano Catalyst for Synthesis of Novel Carboacyclic Nucleosides by Huisgen 1,3-Dipolar Cycloaddition

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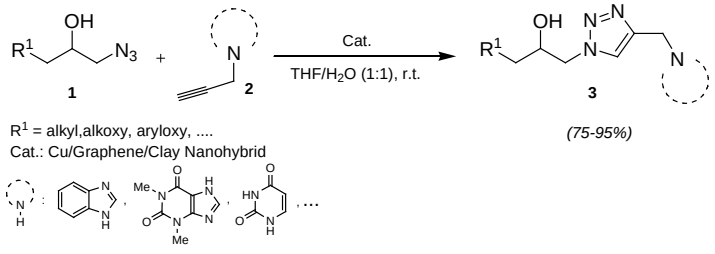
The 1*H*-1,2,3-triazoles are an important class of *N*-heterocyclic compounds with a wide range of applications in organic and medicinal chemistry.[1] The most common route for accessing 1,2,3-triazoles involves Huisgen 1,3-dipolar azide-alkyne cycloaddition.[2] However, the major limitations of this non-catalyzed process are the requirement of high temperature and poor regioselectivity giving a mixture of 1,4- and 1,5-disubstituted triazoles. The synthetic utility and selectivity of the Huisgen 1,3-dipolar cycloaddition between azides and alkynes was dramatically improved when Cu^+ salts were used.[3] Active copper (I) as the catalytic species can be *in situ* prepared by reduction of copper(II) salts, copper(II)/copper(0) comproportionation or oxidation of copper(0) and copper(I) salts. To improve reusability and recovery, copper species have been immobilized onto various supports such as activated carbon, zeolites, melamine-formaldehyde resin and etc.[4] However, the immobilized catalysts on solid supports frequently suffer from leakage of catalysts, high reaction temperatures, low activity, and requiring additives. Herein we reported the application of Cu/graphene/clay nanohybrid as a novel and efficient heterogeneous catalyst for synthesis of new carboacyclic nucleosides having 1*H*-1,2,3-triazole cores (**3**) via 1,3-dipolar cycloaddition of β-azido alcohols (**1**) and alkynes (**2**) at room temperature (Scheme 1). To prepare this catalyst, aminoclay nanostructures were first allowed to form over the surface of GO sheets and then this support was soaked in $CuSO_4$-hydrazine solution. Afterward, the catalyst was precipitated from EtOH. The catalyst was used to prepare novel purine, pyrimidine and azole carboacyclic nucleosides analogues having 1*H*-1,2,3-triazole cores (**3**) in excellent yields (75-95%).



Scheme 1. Synthesis of 1,4-disubstituted 1,2,3-triazoles using Cu/graphene/clay nanohybrid

Keywords Alkyne; β-Azido alcohol; Cu/graphene/clay nanohybrid; Triazole

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A Highly Efficient Procedure for the Synthesis of 3,5-Disubstituted Isoxazoles using Cu/Graphene/Clay Nanohybrid

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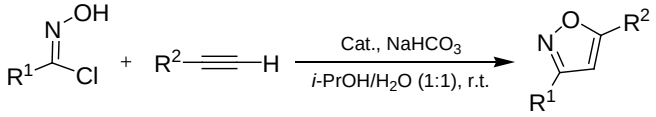
Isoxazoles are versatile substrates in medicinal and organic chemistry. Isoxazole derivatives display diverse pharmacological activities. In addition, isoxazole is a key structural motif found in many drug scaffolds having different chemotherapeutic activities.[1] Up to now, numerous general methods have been developed to access 3,5-disubstituted isoxazoles.[2] The traditional strategy for the synthesis of 3,5-disubstituted isoxazoles involves the thermal 1,3-dipolar cycloaddition reaction between alkynes and *in situ* generated nitrile oxides.[3] However, this non-catalyzed process is neither chemo- nor regioselective, which restricts the applicability of this protocol. Recently, Sharpless[4] and Fokin[5] have reported the regioselective and efficient synthesis of unsymmetrical 3,5-disubstituted isoxazoles via copper(I) catalyzed 1,3-dipolar cycloaddition reaction between alkynes and nitrile oxides. Active copper(I) as the catalytic species normally is CuI or it can be *in situ* generated by reduction of copper(II) salts. In recent years, there has been a growing interest for application of heterogeneous catalysts in organic reactions. However, there have been a few reports on the application of heterogeneous copper catalysts for cycloaddition reaction between alkynes and nitrile oxides. [2] In this context, we disclose here the application of Cu/graphene/clay nanohybrid as a novel and efficient heterogeneous catalyst for 1,3-dipolar cycloaddition of alkynes and *in situ* generated nitrile oxides at room temperature (Scheme 1). To prepare this catalyst, aminoclay nanostructures were first allowed to form over the surface of GO sheets and then this support was soaked in $CuSO_4$-hydrazine solution. Afterward, the catalyst was precipitated from EtOH. This method is suitable for various structurally diverse aliphatic and aromatic imidoyl chlorides and alkynes, and also tolerates a wide spectrum of electron-donating and electron-withdrawing functional groups in both alkynes and imidoyl chlorides. The corresponding isoxazoles were obtained in 80-92% yields.



Cat.: Cu/graphene/clay nanohybrid

R^1, R^2= aryl, alkyl, CH_2OH, CH_2OAr, ...

Scheme1. Synthesis of 3,5-disubstituted isoxazoles using Cu/graphene/clay nanohybrid

Keywords Alkyne; Cu/graphene/clay nanohybrid; 3,5-Disubstituted isoxazoles; Nitrile oxide

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Synthesis of Coumarin Derivatives and Their Antifungal Activities against Plant Pathogenic Fungi

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The aim of this study was to synthesize the coumarin derivatives and investigate their antifungal activity. All derivatives were synthesized *via* Pechmann condensation reaction, followed by *O*-alkylation. The synthesis of coumarins (7-hydroxy-4-methylcoumarin, 5,7-dihydroxy-4-methylcoumarin and 7,8-dihydroxy-4-methylcoumarin) and seven derivatives were characterized by IR and ^{1}H NMR spectra. All of these coumarin derivatives were screened for antifungal activity against *Pythium aphanidermatum*, *Rhizoctonia solani* in rice, *Rhizoctonia* sp. in lemon, *Lasiodiplodia theobromae* and *Fusarium oxysporum* by Poisoned food techniques. 10,000 mg/L concentrations of all synthesized compounds were prepared to determine for its antifungal activity and carbendazim was used as standard fungicide to be compared. Coumarin derivatives showed the highest antifungal effect against *Pythium aphanidermatum* and *Rhizoctonia* sp. in lemon (100% inhibition) except for 5,7-dihydroxy-4-methylcoumarin and 7,8-diethoxy-4-methylcoumarin, while all coumarin derivatives showed high inhibition mycelial growth of *Rhizoctonia solani* in rice (100% inhibition). The inhibition of 7-butoxy-4-methylcoumarin, 7,8-dihydroxy-4-methylcoumarin and 7,8-diethoxy-4-methylcoumarin showed the highest effect on *Lasiodiplodia theobromae*. In addition, 7,8-dihydroxy-4-methylcoumarin and 7,8-diethoxy-4-methylcoumarin showed the most effective activity on *Fusarium oxysporum* (100% inhibition). Hence, coumarin derivatives can act as potential antifungal agents and the development coumarin compounds was planned to be used as a new nano-carriers system for pesticide or plant hormones delivery.

Keywords Coumarin derivatives; Pechmann condensation; *O*-Alkylation; Antifungal activity; Plant pathogenic fungi

Iron-Catalyzed Synthesis of 4-Substituted Coumarins

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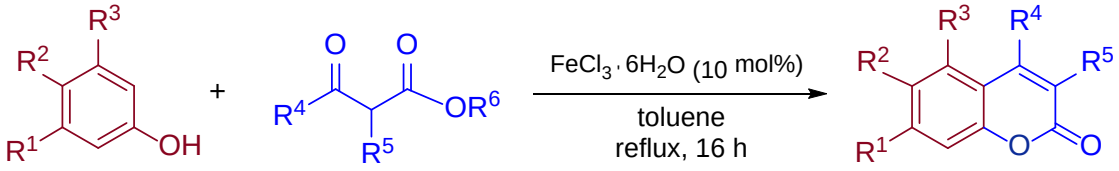
Coumarins are considered to be interesting compounds in organic synthesis and pharmaceuticals. They have displayed a wide spectrum of biological and pharmacological activities including antioxidant, anti-inflammatory, anticancer and anti-HIV. Moreover, they are widely used as additives in food and cosmetics. The Pechmann reaction is considered to be one of the most valuable methods for the synthesis of coumarins as it proceeds from simple starting materials, a phenol and a β-keto ester in the presence of an acid catalyst. A variety of synthetic protocols using several acid condensing agents have been investigated and reported in the literature. However, the development of practical, efficient and environmentally benign synthetic protocols for the synthesis of coumarins is greatly desirable. Among the transition metal catalysts, iron is an ideal transition metal catalyst owing to its ready available, low price and environmentally friendly character. Recently, $FeCl_3$-catalyzed Pechmann reaction has received considerable attention. Herein, we report a practical and inexpensive synthesis of coumarins employing a variety of phenols and *β*-keto esters in the presence of 10 mol% of $FeCl_3 \cdot 6H_2O$ as acid catalyst. Under the optimized conditions, the corresponding 4-substituted coumarin derivatives coumarins were synthesized in moderate to excellent yields in refluxing toluene for 16 h.



Keywords Pechmann reaction; Coumarins; Iron; Phenols; β-Keto esters

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Cross Metathesis/Tandem *N*-Acyliminium Ion Cyclization Approach toward the Synthesis of Grandisine A

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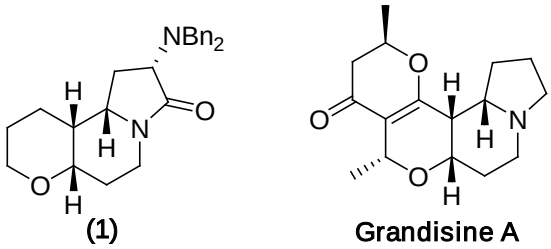
Model studies for the synthesis of grandisine A[1] were carried out featuring cross metathesis and tandem *N*-acyliminium ion cyclization.[2] Cross metathesis of TBS ether of 4-penten-1-ol and an imide derived from 3-butenylamine and L-aspartic acid, and subsequent carbonyl reduction resulted in the corresponding tethered hydroxyalkene-hydroxyl-γ-lactam, which is the precursor for tandem *N*-acyliminium ion cyclization. Treatment of this lactam with TMSOTf resulted in a diastereoselective cyclization to afford the tricyclic product (**1**) with a pyranoindolizidine ring system of grandisine A. The stereogenic center bearing the protected amino group derived from L-aspartic acid served as the stereocontrol element and gave the diastereomeric products in non-racemic form.



Keywords Tandem *N*-acyliminium ion cyclization ; Cross metathesis; Grandisine A

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Total Synthesis of Dihydrotetrabenazine Methyl Ether

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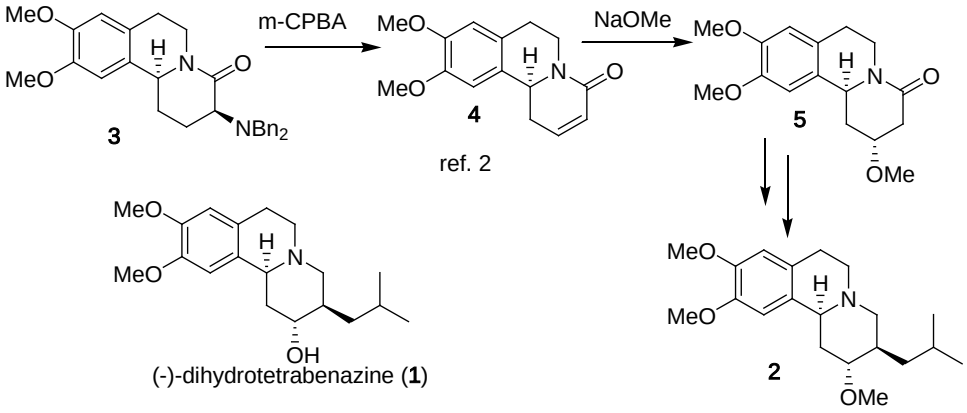
Tetrabenazine is a chiral synthetic drug used for treatment of motor dysfunction associated with the Huntington's disease. Tetrabenazine is a pro-drug that is metabolized to the active drug dihydrotetrabenazine (**1**).[1] Herein, we report a total synthesis of dihydrotetrabenazine methyl ether (**2**). From our previous work, we have synthesized benzoquinolizidinone **3** from homoveratrylamine and L-glutamic acid, using *N*-acyliminium ion cyclization. This compound was converted to tricyclic enamide **4** by Cope elimination.[2] The enamide functionality is susceptible for further reactions such as Michael, hetero-Michael, and Diels-Alder reactions. In this synthesis, tricyclic enamide **4** underwent hetero-Michael addition to give methyl ether-lactam **5** as a single diastereomer. The remaining steps are straight-forward alkylation of the α-carbon of the lactam and reduction of the lactam carbonyl group.



Keywords *N*-Acyliminium ion cyclization; Dihydrotetrabenazine; Tetrabenazine

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A Highly Diastereoselective Route toward Dibenzylaminobenzoindolizidinones and Different Reactivity of Their *N*-Oxides; Cope Elimination vs Meisenheimer Rearrangement

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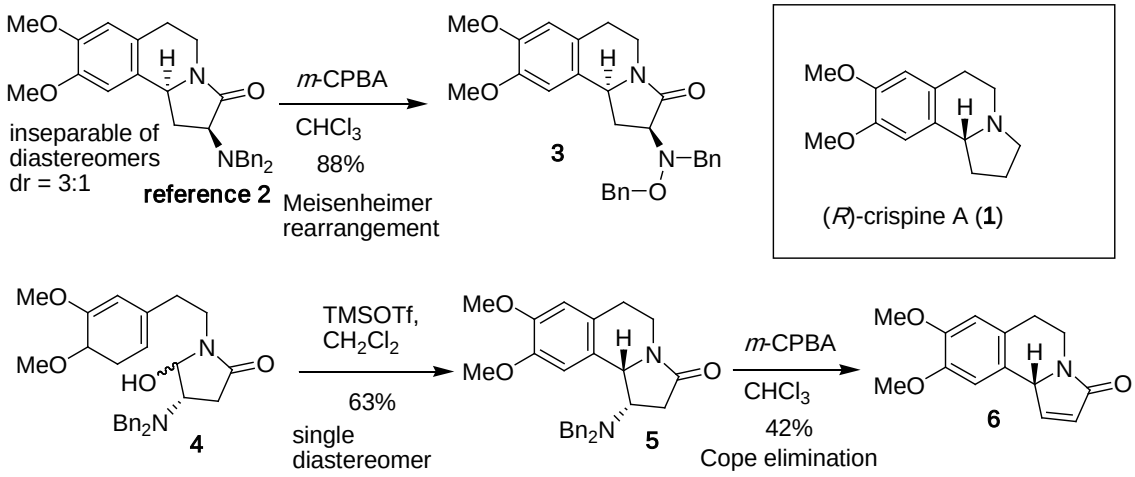
In our previous work on synthetic studies of cytotoxic crispine A (**1**), we have synthesized benzoindolizidinone **2** as mixture of 2 diastereomers from homoveratrylamine and L-aspartic acid using *N*-acyliminium ion cyclization as the key reaction[2]. Herein we report its subsequent treatment with *m*-CPBA that gave undesired *N*,*O*-dibenzylamino derivative **3** from Meisenheimer rearrangement of the corresponding *N*-oxide. A new and highly diastereoselective route that gave regioisomeric benzoindolizidinone **5** via *N*-acyliminium ion cyclization of γ-hydroxy-γ-lactam **4** was developed. The single diastereomer **5** underwent Cope elimination upon treatment of *m*-CPBA to give tricyclic enamide **6** as an advanced synthetic precursor of (*R*)-crispine A.



Keywords *N*-Acyliminium ion cyclization; Dibenzylaminobenzoindolizidinones; Crispine A

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Oxidation of Thiol into Disulfide using Polystyrene-supported (Diacetoxyiodo)benzene

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Disulfides are important compounds in biological and chemical processes which can be prepared by the oxidation of thiols. For this work, we have developed a new preparative method for the disulfide using inexpensive, recyclable, and relatively non-toxic polymer-supported(diacetoxyiodo)benzene (PS-DIB) as the oxidant under mild conditions. PS-DIB, a yellow powder, was prepared from iodination of commercially available polystryrene (MW=35,000) followed by oxidation with either $NaBO_3 \cdot 4H_2O$ or Ac_2O/H_2O_2 in 43% and 70% yield, respectively. The structure of the prepared PS-DIB was confirmed by FTIR which exhibited two strong bands at 1639 and 1712 cm^{-1} corresponding to the carbonyl group. The loading of the (diacetoxyiodo)phenyl group on polystyrene was determined by iodometric titration and calculated to be 1.39 mmol/g. The reaction conditions were optimized for solvent, time and equivalent of PS-DIB using 4-chlorothiophenol as substrate and the yields were determined using HPLC. We discovered that, under the optimized condition (*i*-PrOH as solvent, 1 equivalent of PS-DIB, open air, 1 h, room temperature) for 4-chlorothiophenol, the corresponding disulfide product was obtained in 79% yield following chromatography. This methodology could be extended to a variety of aromatic thiols, giving the disulfides in 69-79% yields.

Keywords PS-DIB; Disulfides; Hypervalent iodine(III); Polystyrene

Chemoselective Reductions of Nitrobenzene using Chitosan-Coated Metal as a Catalyst

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A micellar technology for chemoselective reductions has been developed using chitosan-coated metal as a catalyst. The chitosan-coated metal bead nanoparticles were prepared and characterized by XRD and TEM. TEM results showed that the average size of nanoparticles was about 8 nm. Our works focus, in part, on the design of nonionic surfactants that enable transition-metal-catalyzed reactions to be performed in water at room temperature (rt), rather than in traditional organic solvents. Several applications of micellar technology to an array of valued organic transformations have already been developed. To further expand the scope of these micellar surfactant conditions, zinc mediated reductions of nitrobenzene offer 100% conversion within 2 hours at room temperature.

Keywords Reduction; Micellar technology; Nanoparticles

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Alpha-Bromination of Ketone using Hexabromoacetone

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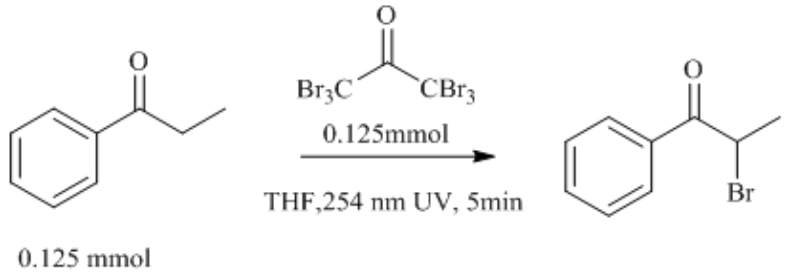
An efficient method for the preparation of α-bromoketone has been disclosed. Propiophenone, a model substrate was treated with hexabromoacetone (HBA) with the ratio of substrate to HBA (1:1) in THF at RT for 5 min with UV (254 nm) irradiation. 2-Bromopropiophenone was obtained as a sole product in high yield under optimum conditions. Various parameters including reaction time, solvent and ratio of substrate: HBA were scrutinized. This developed protocol could be successfully utilized for other ketones yielding the corresponding α-bromoketones in good to excellent yield.



Scheme1. α-Bromination of propiophenone using HBA

Keywords α-Bromoketone; Hexabromoacetone (HBA)

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Synthesis towards N-Heteroaromatic THENA Derivative: Investigation on [4+2]-Cycloaddition of Highly Reactive Pyridyne

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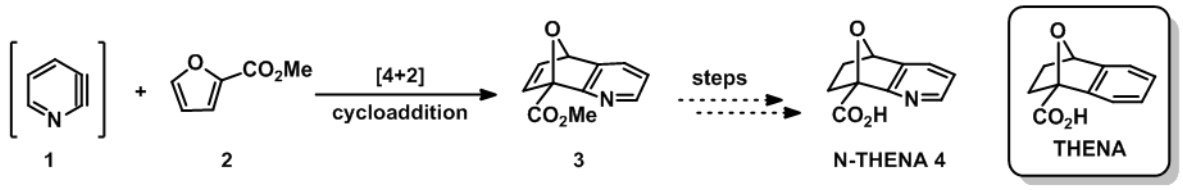
Analogous to 1,2,3,4-tetrahydro-1,4-epoxynaphthalene-1-carboxylic acid (THENA), a novel chiral derivatizing agent (N-THENA **4**) bearing a pyridine moiety as an anisotropic group was first designed and synthesized. The second objective is to study the anisotropic effect of heteroaromatic compound in the absolute configuration analysis. The key synthetic step is the formation of intermediate **3** which could be directly synthesized from [4+2]-cycloaddition reaction of a highly reactive 2,3-pyridyne intermediate **1** and an electron deficient methyl furan-2-carboxylate **2**. A variety of conditions to generate 2,3-pyridyne intermediate from 3-(trimethylsilyl)pyridin-2-yl triflate were investigated and the bicyclic compound **3** could be obtained in 5% yield under the optimal condition.



Keywords Chiral derivatizing agent; 2,3-Pyridyne; [4+2]-Cycloaddition

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Cyclic Alkyl Sulfide Diether Derivative as an Electron Donor for Ziegler-Natta Catalyst in Olefin Polymerization

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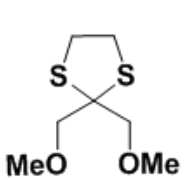
Lewis base or electron donor is one of the key components in propylene polymerization using Ziegler-Natta catalyst. In this research, novel electron donor **1** based on 1,3-diether grafted with cyclic alkyl sulfide framework was designed and synthesized. In optimal conditions, the sulfur derivative **1** was obtained in satisfactory yield. Model compound **1** was then introduced to the polymerization reaction of propylene in a lab scale to synthesize polypropylene (PP). The resulting PPs were characterized and compared to the systems without electron donor and with commercial electron donor, 2,2-diisobutyl-1,3-dimethoxypropane (DIBDMP). By using DIBDMP as a benchmark, isotacticity of PP from sulfur donor **1** is quite similar with 92% of *mmmm* characterized by ^{13}C-NMR analysis and 91% of I.I. determined from the weight of insoluble polymers with polymer melting point (T_m) of 158 °C. The M_n, M_w, and MWD are 2.89×10^4, 4.63×10^5, and 16.02, respectively. These numbers are inferior as compared to the commercial donor but similar to the PP from the system without donor. The activity of the catalyst donor **1** is 1943 $g_{PP}/g_{Ti}h$.



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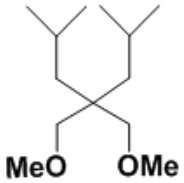

DIBDMP

Keywords 1,3-Diether electron donor; Ziegler-Natta catalyst; Propylene polymerization

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Tetrabutylammonium Silica Sulfate as a Novel and Efficient Heterogeneous Catalyst for the Chemoselective Ring Opening of Epoxides with Acefylline

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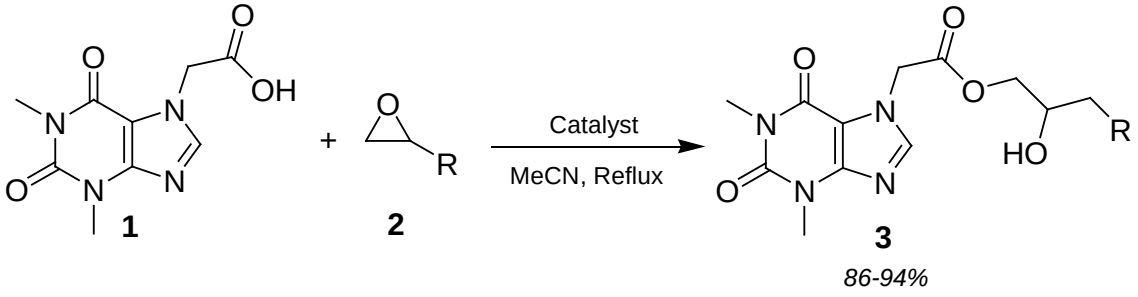
The reaction of carboxylic acids with epoxides provides a suitable and attractive strategy for the protection of 1,2-diols, which in turn leads to the formation of 1,2-diol mono-esters as precursors for many organic syntheses.[1] The reaction is generally carried out using various protic/Lewis acids and bases.[2] Indeed, there are only rare reports on the selective ring opening of epoxides with carboxylic acids in neutral condition.[2,3] Acefylline (**1**) is a stimulant drug which acts as cardiotic, diuretic, antispasmodic, and bronchodilator.[4] Therefore, the β-hydroxy esters of acefylline (**3**) seem to be attractive prodrugs in medicinal chemistry. We hereby report a simple and highly efficient protocol for the regio- and chemoselective synthesis of β-hydroxy ester of acefylline via ring opening of terminal epoxides **2** with acefylline using tetrabutylammonium silica sulfate as a novel and highly efficient catalyst in neutral condition (Scheme 1). Using this method, a variety of β-hydroxy esters of acefylline **3** were obtained in 86-94% yields. To prepare this catalyst, silica sulfuric acid (SSA) was primarily synthesized by the method described in the literature.[5] Then, SSA was neutralized by tetrabutylammonium hydroxide in methanol to afford a white precipitate. The catalyst has been fully characterized by means of different microscopic, spectroscopic and physical techniques, including scanning electron microscopy (SEM), transmission inductively coupled plasma (ICP) analysis, thermogravimetric analysis (TGA) and FT-IR.



Scheme1. Ring opening of epoxides with acefylline using tetrabutylammonium silica sulfate

Keywords Acefylline; Epoxide; β-Hydroxy ester; Tetrabutylammonium silica sulfate

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Synthesis and Characterization of Isoindigo Derivatives as Molecular Donors for Organic Photovoltaics

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Isoindigo, a typical industrial pigment chromophores with high optical density, has demonstrated its valuable utility as a building block for used in constructing donor molecules due to its facile synthesis from low-cost starting materials, strong electron affinity that enables lower frontier energy levels and ease of structural modification that allows for tailored optoelectronic properties. In this work, we design new high performance isoindigo-containing donor molecules employing a novel molecular architecture with two isoindigo chromophores in the conjugated backbone (Figure 1). Three isoindigo derivatives containing aromatic cores were synthesized using a combination of aldol condensation, alkylation and Suzuki-Miyaura cross coupling reactions. The different core moieties, anthracene, benzothiadiazole and fluorene, were used in order to increase molar absorptivity of desired molecules. In order to increase the solubility of synthesized compound, the branch alkyll chain were introduced as the *N*-substituent. They were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and mass spectrometry. The optical property was study as dichloromethane solution. The desired compounds exhibited wide absorption spectra in UV-visible region (300-600 nm) with high molar extinction coefficient. The result suggests that the synthesized compounds can be used as donor molecules in organic photovoltaic devices.

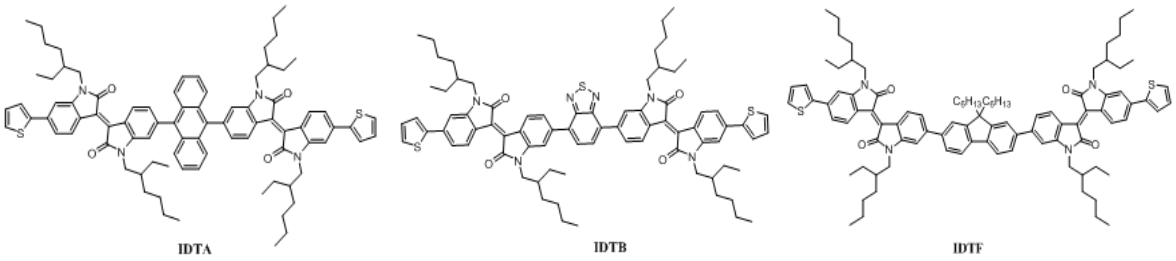

Figure 1. Structure of Target molecules

Keywords Organic photovoltaic; Molecular donor; Isoindigo

Synthesis and Characterization of Star-shaped Pyrenyl Triazatruxenes

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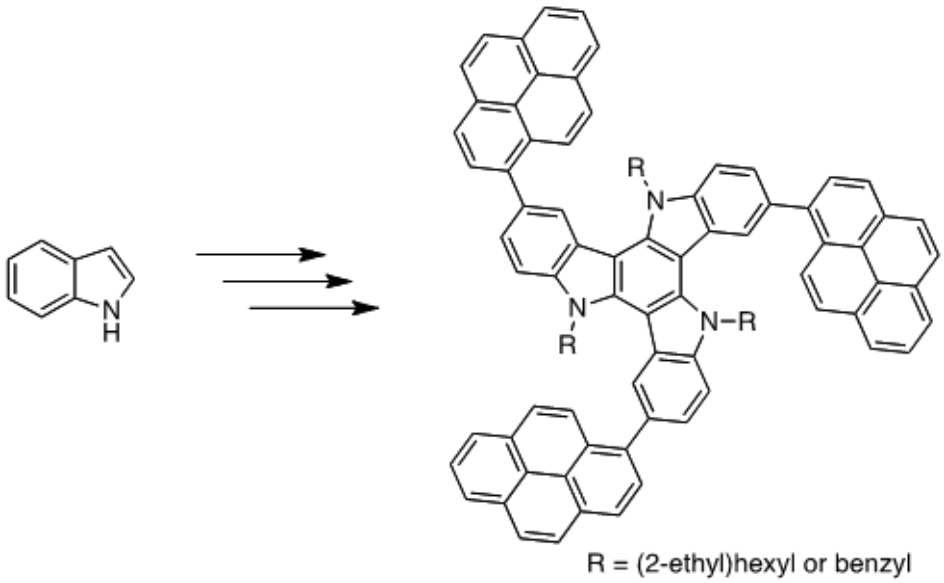
Triazatruxene derivatives have received much attention in the research field of organic light-emitting diode (OLED) due to their unique optical properties and excellent thermal stabilities. In this research project, we designed and synthesized two symmetrical triazatruxene derivatives containing 2-ethyl hexyl or benzyl groups. The triazatruxene has been synthesized from the Br_2-catalyzed cyclotrimerization of indole. A sequential debromination-bromination thus provides a tribromo triazatruxene core with a complete regioselectivity. Alkylation of the N-H group and Suzuki cross-coupling with pyrene-1-boronic acid give rise to the target compounds in good yields. After the characterization by ^{1}H NMR, ^{13}C NMR, IR, and mass spectrometry, their photophysical properties are investigated by UV-Vis and fluorescence spectrophotometry.



Keywords Triazatruxene; OLED; Electroluminescent; Pyrene; Cyclotrimerization

Melamine Fluorescent Sensors from Cyanuric Acid Substituted 1,8-Naphthalimide

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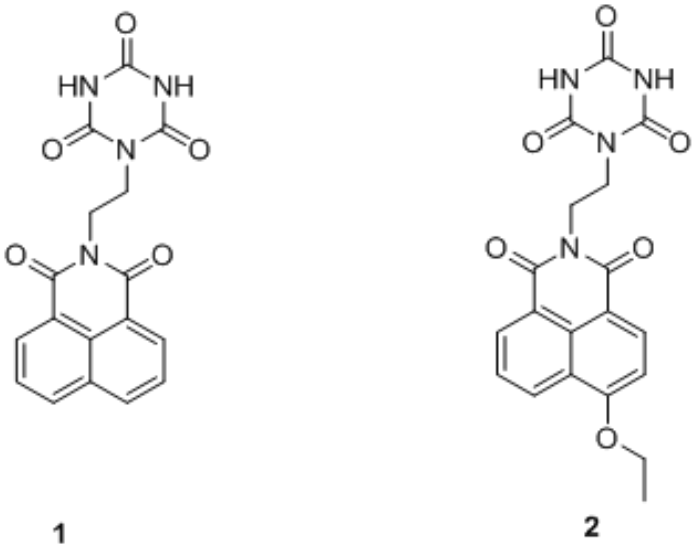
Two novel fluorescent sensors (**1** and **2**) for melamine detection containing 1,8-naphthalimide as fluorophore and cyanuric acid as melamine receptor are successfully synthesized. The synthesis involves an imidation of 1,8-naphthalic anhydride with ethanolamine, transformation of the hydroxyl group to a bromo group, and *N*-alkylation of isocyanuric acid by the bromo group. The target compounds are characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis. The photophysical properties are investigated by UV-Vis and fluorescence spectroscopy. The selectivity towards melamine is studied using solutions of these compounds in organic solvent with various water contents. The difference in substitution at the 4-position of the naphthalimide moiety is expected to play an important effect on the emission wavelengths, fluorescence efficiencies, and sensitivity for melamine sensors. Progress on the optimization of a sensing system will be presented.



1 **2**

Keywords Fluorescent sensor; 1,8-Naphthalimide; Cyanuric acid; Melamine

Synthesis and Effect of Eugenol Derivatives on HepG2 Cells

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The aim of this study is to modify structure of eugenol and examine cytotoxicity against the Human liver hepatocellular carcinoma cell line (HepG2 cells). The synthetic methodology was started from alkylation of commercially available eugenol using 2-methyloxirane/K_2CO_3 to provide 1-(4-allyl-2-methoxyphenoxy)propan-2-ol in 73% yield. For 5-allyl-1,3-diisopropyl-2-methoxybenzene, it can be synthesized in one step by electrophilic aromatic substitution reaction of 4-allyl anisole with 2-bromopropane in 73% yield. 2-(4-Allyl-2-methoxyphenoxy)ethanol was synthesized from eugenol by alkylation with *tert*-butyl chloroacetate to get *tert*-butyl 2-(4-allyl-2-methoxyphenoxy)acetate and then reduced with $LiAlH_4$ to get the desired product in 15% yield. Next, the cytotoxic effect of 15 eugenol derivatives from our previous work including the 3 new compounds was tested on HepG2 cells using MTT assay. The results revealed that all of compounds had no cytotoxic effect on HepG2 cells at 1 – 250 μM. All eugenol derivatives will be further investigated for antioxidant activities by DPPH assay.

Keywords Eugenol; Cytotoxicity; MTT assay

Oxidation of Cycloheptatriene Derivatives and Synthesis of New Tropolone Derivatives

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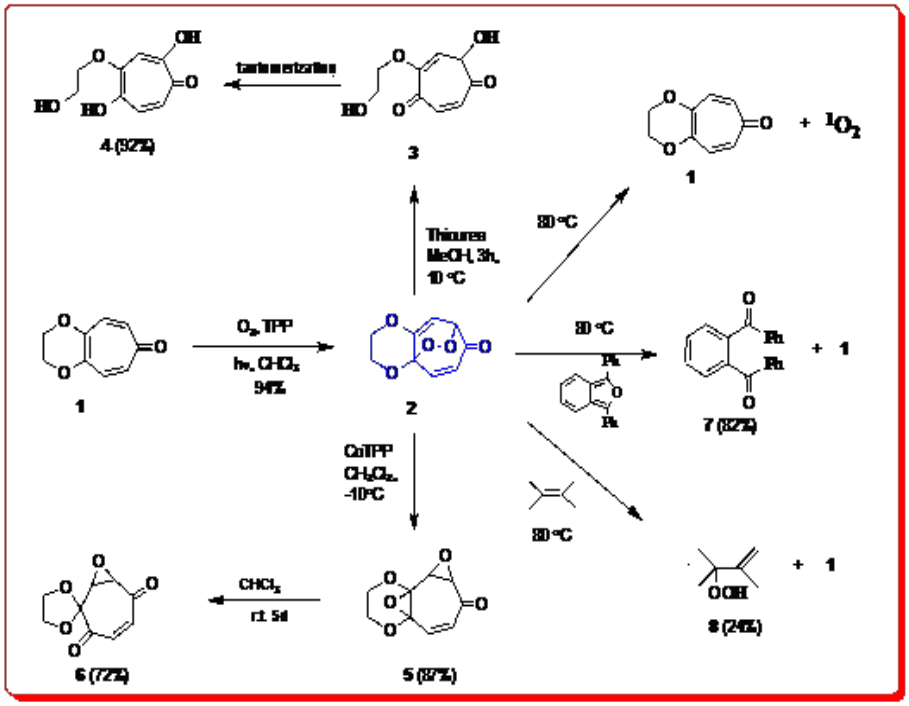
A large number and variety of tropone and tropolone derivatives are found in nature.[1] In addition to this, tropone and tropolone derivatives have drawn considerable interest because of their biological activities.[1,2] Despite the considerable theoretical, biological and synthetic interest in troponoids, development of general and flexible synthetic routes to these compounds remains a challenging problem. Although the tropones can be oxidized to the tropolones, this approach suffers from problem of regiochemical control when the substituted tropones are used as starting materials.[3] In connection with the development of a new synthetic strategy to tropolones, we have studied the applicability of bicyclic endoperoxides like **2**. Short, selective and efficient synthesis for some tropolone derivatives such as **4** was performed.[4] The tricyclic endoperoxide **2** obtained by the photooxygenation of **1** showed an unprecedented behavior and produced singlet oxygen and the parent tropone **1** upon thermolysis. To the best of our knowledge it is the first report where a *non*-benzonoid system generates singlet oxygen.



Keywords Tropone; Tropolone; Oxidation; Singlet oxygen

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Friedel–Crafts Benzylation of Toluene using $NdCl_3$ Impregnated on Aluminium Pillared Montmorillonite

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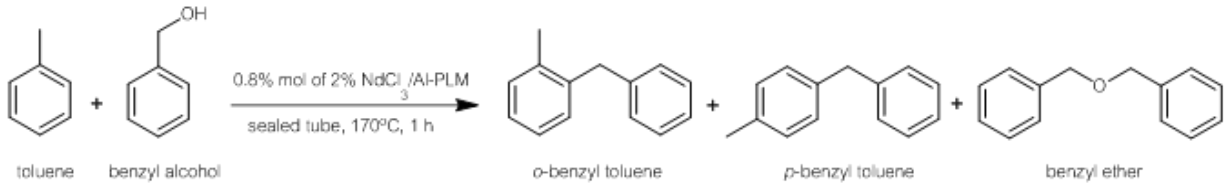
2% $NdCl_3$ impregnated on aluminium pillared montmorillonite (2% $NdCl_3$/Al-PLM) was prepared as a catalyst for the Friedel–Crafts benzylation of toluene with benzyl alcohol. The appropriate amount of 2% $NdCl_3$/Al-PLM was investigated. Its basal spacing was characterized by XRD technique. The reaction was performed by using 0.8 mol% of 2% $NdCl_3$/Al-PLM at 170 °C within 1 h and with 8:1 molar ratios of toluene and benzyl alcohol. This acid catalyst showed 100% yield of benzyl toluene with *ortho*:*para* ratio = 1.52. In addition, this clay catalyst could be easily separated from the reaction and reuse for 5 times without losing catalytic activity.



Keywords $NdCl_3$; Aluminium pillared montmorillonite; Clay; Friedel-crafts benzylation

Synthesis of Oseltamivir Derivatives with Anti-Alzheimer Activity

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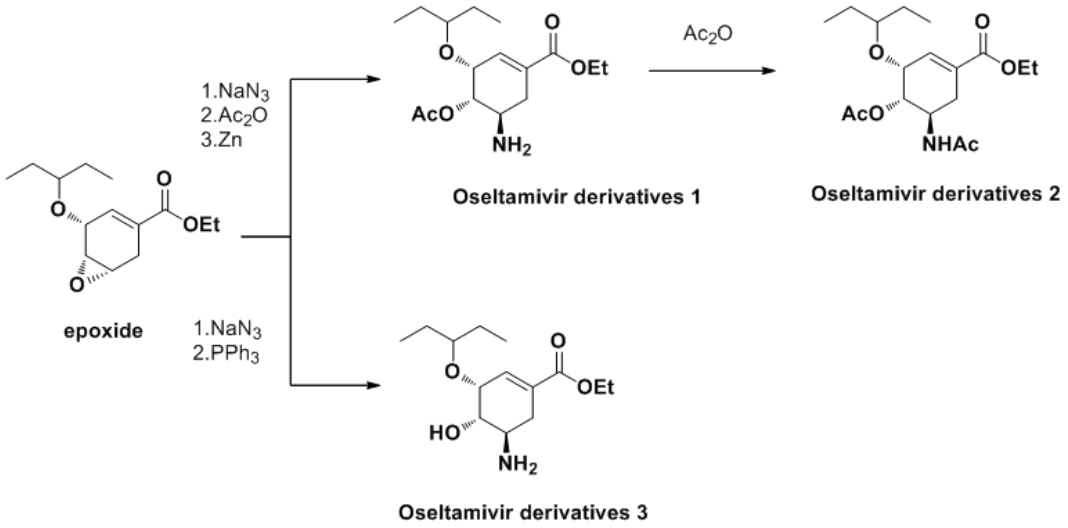
Oseltamivir phosphate or Tamiflu is an antiviral licensed to prevent or slow down the spread of influenza A and influenza B (Bird flu). To the present date many syntheses of oseltamivir phosphate have been documented. Oseltamivir derivatives, **1**-**3** were synthesized starting from the epoxide intermediate by S_N2 substitution with azide, reduction and acetylation (Scheme 1). Acetyl cholinesterase inhibition was determined by modifying the method of Ellman by using galantamine as a reference standard (IC_{50} 1.45 ± 0.04 µM). The oseltamivir derivatives **3** showed moderate anti-Alzheimer activity with IC_{50} = 91.14±2.36 µM



Scheme 1

Keywords Oseltamivir derivatives; Anti-Alzheimer activity

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ORC-PO-023

Synthesis of Substituted Phenanthrenes by Platinum-catalyzed Cyclization of Biaryl Propargyl Alcohols

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Recent research progress in transition metal-catalyzed reactions of electrophilic alkynes has provided efficient access to an *α,β*-unsaturated carbene with the concomitant formation of a ring structure. This transformation is achieved through an initial intramolecular nucleophilic attack on the π-coordinated alkyne to afford a vinyl-metal species and subsequent loss of a leaving group. A variety of functional groups can serve as the nucleophile in this reaction. However, there are only a few examples of using a carbon-centered nucleophile, despite the great potential for constructing a wide range of carbocyclic compounds. We developed a Pt-catalyzed synthesis of phenanthrene from biaryl propargyl alcohol via the intermediacy of the *α,β*-unsaturated metal carbene. $PtCl_2$ efficiently induces the desired 6-*exo-dig* cyclization and subsequent loss of a leaving group to construct the phenanthrene skeleton with carbene functionality. The resulting carbene complex rapidly undergoes 1,2-H migration to afford a vinylphenanthrene. The reaction proceeds under mild conditions and tolerates important functional groups, making it possible to obtain highly functionalized phenanthrenes. In addition, this efficient synthetic protocol has potential for the rapid synthesis of biologically intriguing phenanthrene alkaloids, as demonstrated by the concise synthesis of antofine.

Keywords Phenanthrene; Unsaturated carbene; Platinum chloride; Antofine

Synthesis and Characterization of Iridium (III) Complexes for Amine Sensing Application

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In this work, we describe the synthesis and characterization of charged iridium(III) complexes, namely, [(dimethyl 2,2'-bipyridine 3,3'dicarboxylate)-bis-(2,4-difluorophenyl pyridine)-iridium(III)] hexafluorophosphate (**SY-09**), [(dimethyl 2,2'-bipyridine 3,3'dicarboxylate)-bis-(2,4-difluorophenyl-4-trifluoromethyl pyridine)-iridium(III)] hexafluorophosphate (**SY-10**), [(dimethyl 2,2'-bipyridine 3,3'dicarboxylate)-bis-(phenyl-4-trifluoromethyl pyridine)-iridium(III)] hexafluorophosphate (**SY-11**) and [(dimethyl 2,2'-bipyridine 3,3'dicarboxylate)-bis-(phenyl-5-trifluoromethyl pyridine)-iridium(III)] hexafluorophosphate (**SY-12**) by using the esterification reaction. We investigated the individual solution absorption of **SY-09**, **SY-10**, **SY-11** and **SY-12** with n-butylamine (3 eq.) and HCl (100 eq.). It was found that the solutions of **SY-11** and **SY-12** underwent significant color change from orange-yellow to clear yellow when the acid was added after 30 and 40 min, respectively. These preliminary results suggest that the complexes could be potentially used as amine drug sensor in the future.

Keywords Iridium (III) complexes; Drug sensor; Amine sensor

Synthesis of Truxene Derivatives with Dipyrenylcarbazole Pendants

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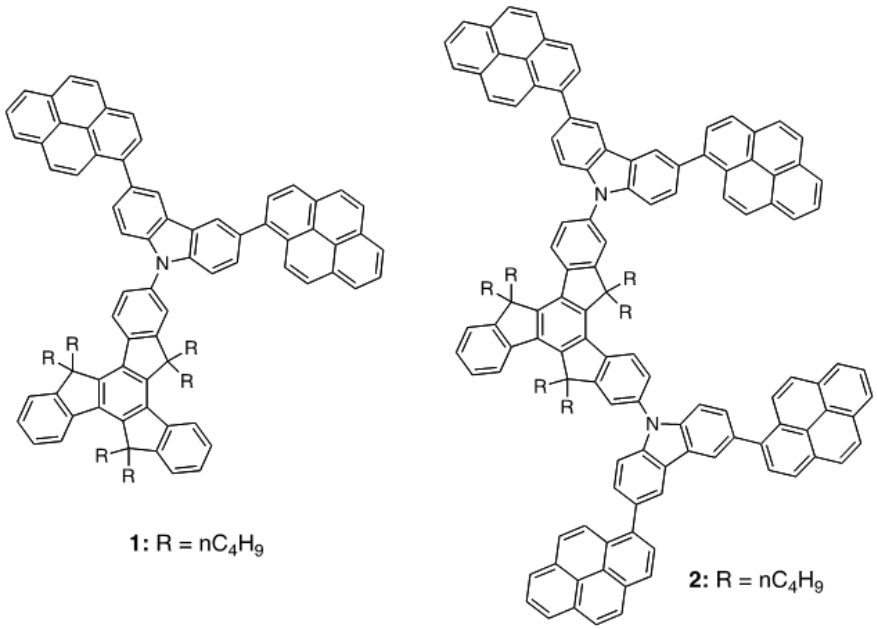
Derivatives of truxene exhibited excellent photophysical properties along with good thermal and electrochemical stabilities suitable for application in optoelectronic devices. In this paper, we report the synthesis and characterization of truxene derivatives with different numbers of dipyrenylcarbazole substituents. The truxene core is readily accessible *via* the dehydro-cyclotrimerization of hydrocinnamic acid. The solubility in organic solvent is enhanced when the methylene units of truxene are substituted by n-butyl groups. The dipyrenylcarbazole pendant is prepared from iodination of carbazole followed by a Suzuki coupling with the commercially available pyrene-1-boronic acid. The Cu-catalyzed C-N coupling between the iodinated truxene core and dipyrenylcarbazole thus provides the target **1** and **2**, which were characterized by ^{1}H NMR, ^{13}C NMR and MALDI-TOF mass spectroscopy. The photophysical properties of both compounds are examined by UV-visible and fluorescence spectrophotometry.



Keywords Truxene; Pyrene; Carbazole; Cyclotrimerization; Ullmann cross-coupling

Fluorescence Chemosensor Based on BODIPY Containing Salicylaldehyde Group for Cyanide Detection

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Boron-dipyrromethene (BODIPY) has unique advantages such as high fluorescence quantum yield, narrow emission bandwidth, greater photostability and tunable fluorescence characteristic, making the compound as great sensing material. In this contribution, we present the synthesis of a new red BODIPY containing salicylaldehyde moiety from inexpensive calcium carbide as starting material for the detection of cyanide anion. Acetophenone oxime is condensed with calcium carbide to give 2-phenylpyrrole in 65% yield. Condensation of 2-phenylpyrrole with 4-iodobenzaldehyde followed by typical three steps oxidation, complexation and Sonogashira coupling reaction with 5-ethynyl-2-hydroxybenzaldehyde as receptor gave the desired **RSB** in 71% yield. The prepared compound corresponds with NMR and mass spectra. The UV absorption maximum was found at 557 nm corresponding to the red color. The sensing properties toward the anions will be discussed during the poster presentation.

Keywords BODIPY; Fluorescence sensor; Anion sensor

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Synthesis of Pyrrolidinyl Peptide Nucleic Acid Carrying Novel Hydrophilic β-Amino Acid Spacer

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Peptide nucleic acid (PNA) is a synthetic DNA analogue carrying an uncharged peptide backbone. Recently, we introduced a new pyrrolidinyl PNA system consisting of the modified proline and a cyclic five-membered β-amino acid spacer (*acpc*PNA) that can form very stable hybrids to DNA with high specificity. This *acpc*PNA is therefore one of the most promising PNA system for many applications. However, *acpc*PNAs have some limitation regarding water solubility and non-specific interactions with non-polar substrates similar to many other uncharged DNA analogues. To address this problem, one or more hydrophilic hydroxybutyl groups were post-synthetically introduced into the *acpc*PNA backbone *via* the reductive alkylation strategy previously developed by our group. The desired hydrophilic modifier bearing a hydroxy protecting group and an aldehyde function was prepared starting from the commercially available 1,4-butanediol. One of the hydroxyl group was protected by tritylation and the other was oxidized to the corresponding aldehyde by IBX/DMSO. Reductive alkylation of this aldehyde to a *acpc*PNA decamer pre-modified with 3-aminopyrrolidine-4-carboxylic acid (APC) gave the hydroxybutyl-modifed *acpc*PNA after deprotection and cleavage from the solid support (*m/z* calcd for $M{\cdot}H^+$ 3631.8, found 3629.9). Thermal denaturation experiment with complementary DNA gave a T_m value of 54.4 ^oC. which was comparable to the unmodified *acpc*PNA. Furthermore, the T_m values with single mismatched DNA targets were decreased by 20–30 ^oC compared to the complementary DNA. This indicated that the hydroxybutyl-modified *acpc*PNA still retained excellent DNA binding properties of *acpc*PNA. Solubility and non-specific interactions will be the subject of next investigations.

Keywords Hydrophilic; Solubility; Non-specific interaction

Electron Donating Abilities of Certain Polyaromatic Amines

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Amines can be oxidized readily to radical cations. Nevertheless, to yield a stable radical cation, an aromatic amine is needed to allow electron delocalization. Furthermore, bulky groups are usually introduced to provide extra stability. Aromatic amines are therefore used extensively in many applications such as anticorrosion, radical scavengers, and redox gradient dendrimers. In this research, three polyaromatic triamines were synthesized which are N^2,N^4,N^6-triphenyl-1,3,5-triazine-2,4,6-triamine (**Ani**), N^2,N^4,N^6-tris(4-nitrophenyl)-1,3,5-triazine-2,4,6-triamine (**Nit**), and 2,4,6-tri(10*H*-phenothiazin-10-yl)-1,3,5-triazine (**Phe**). The electron donating ability of each amine was determined from (i) its oxidation potential using cyclic voltammetry technique and (ii) from the charge transfer band when it forms complex with metal. Alternatively, their relative donating abilities could be assessed from their reactions with oxidants of different oxidizing power. Experimental results show that **Phe** has the lowest oxidation potential (E_{ox} = 1.33 V *vs* Ag/AgCl), followed by **Ani** (E_{ox} = 1.40 V *vs* Ag/AgCl). **Nit** has the highest oxidation potential (E_{ox} = 1.52 V *vs* Ag/AgCl). When these polyaromatic amines were mixed with Co^{2+} in a solution, only **Ani** was able to form complex with Co^{2+} and exhibited a charge transfer band at 659 nm.

Keywords Polyaromatic amines; Oxidation potential; Charge transfer