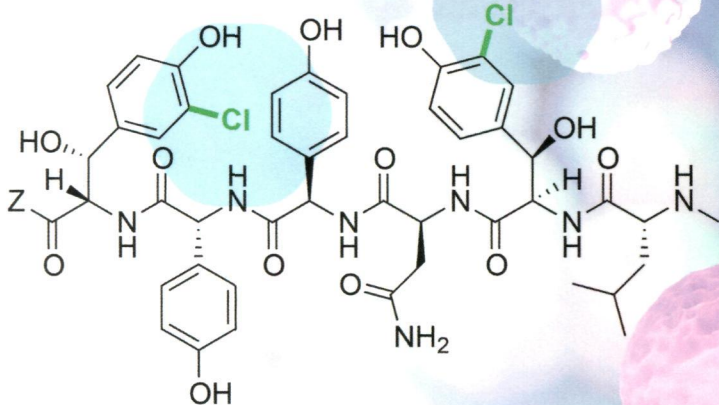


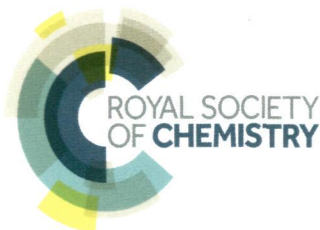
174  
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# Organic & Biomolecular Chemistry

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ISSN 1477-0520



COMMUNICATION

John A. Robinson *et al.*  
Bis-chlorination of a hexapeptide-PCP conjugate by the halogenase involved in vancomycin biosynthesis

# Organic & Biomolecular Chemistry

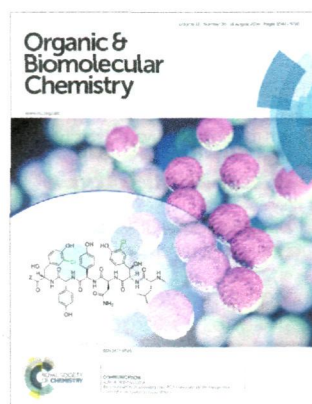
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## IN THIS ISSUE

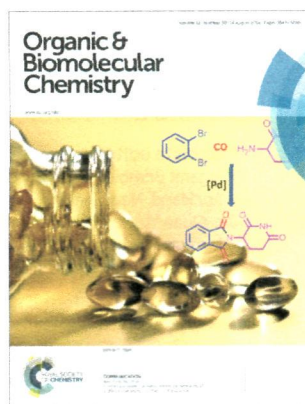
ISSN 1477-0520 CODEN OBCRAK 12(30) 5547-5790 (2014)



### Cover

See John A. Robinson et al., pp. 5574–5577.

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### Inside cover

See Xiao-Feng Wu et al., pp. 5578–5581.

Image reproduced by permission of Xiao-Feng Wu from *Org. Biomol. Chem.*, 2014, **12**, 5578.

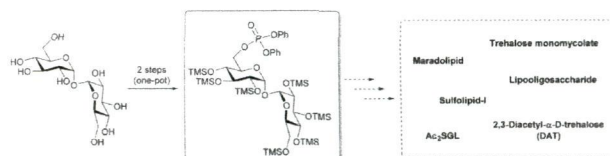
## PERSPECTIVE

5558

### Strategies for desymmetrising trehalose to synthesise trehalose glycolipids

Chia-Hui Wu and Cheng-Chung Wang\*

The desymmetrisation and regioselective protection of trehalose are major challenges in the chemical synthesis of biologically essential trehalose glycolipids.



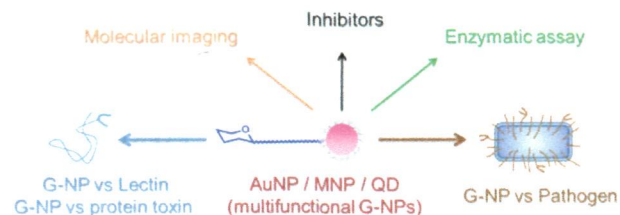
## REVIEW

5563

### Multivalent glycosylated nanoparticles for studying carbohydrate–protein interactions

Avijit K. Adak, Hong-Jyune Lin and Chun-Cheng Lin\*

Glyconanoparticles decorated with multiple copies of various biologically relevant carbohydrates serve as scaffolds for protein binding assay, molecular imaging, targeted therapy, and bacterium detection.



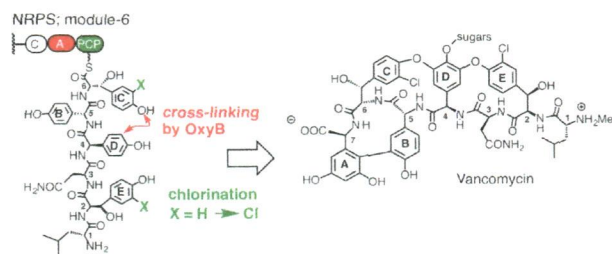
Федеральное государственное  
бюджетное учреждение науки  
Центральная научная библиотека  
Уральского отделения  
Российской академии наук (ЦНБ УрО РАН)

5574

### Bis-chlorination of a hexapeptide–PCP conjugate by the halogenase involved in vancomycin biosynthesis

Patrick C. Schmartz, Katja Zerbe, Khaled Abou-Hadeed and John A. Robinson\*

The vancomycin biosynthetic halogenase can bis-chlorinate both  $\beta$ -hydroxytyrosine residues-2 and -6 in a model substrate comprising a PCP-linked hexapeptide.



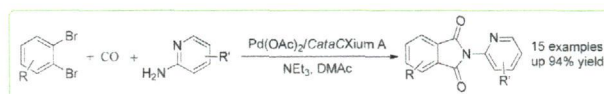
5578

### Efficient palladium-catalyzed double carbonylation of *o*-dibromobenzenes: synthesis of thalidomide

Jianbin Chen, Kishore Natte, Anke Spannenberg, Helfried Neumann, Matthias Beller and Xiao-Feng Wu\*

A convenient and mild procedure for double carbonylation of *o*-dibromobenzene with various 2-amino pyridines and naturally occurring amines has been developed.

*N*-Substituted phthalimides were produced in good to excellent yields. Furthermore, thalidomide was produced in excellent yield under these conditions.

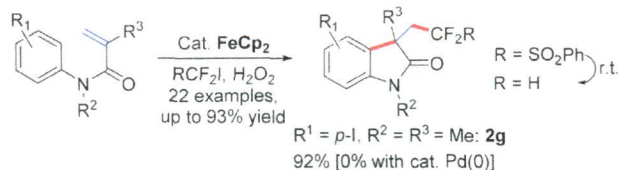


5582

### Iron-catalyzed aryldifluoromethylation of activated alkenes to difluoromethylated oxindoles

Jian-Yong Wang, Xin Zhang, Yan Bao, Yue-Ming Xu, Xiu-Fen Cheng and Xi-Sheng Wang\*

An iron-catalyzed aryldifluoromethylation of activated alkenes has been developed, which is a rare example where a cosolvent is used to improve the yield along with Fenton's reagent.

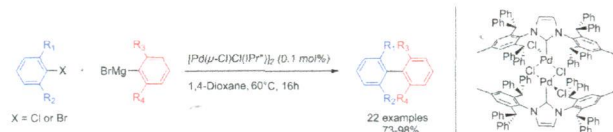


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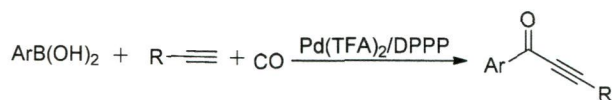
### $[\text{Pd}(\mu\text{-Cl})\text{Cl}(\text{IPr}^*)]_2$ : a highly hindered pre-catalyst for the synthesis of tetra-*ortho*-substituted biaryls via Grignard reagent cross-coupling

Mathieu Lesieur, Alexandra M. Z. Slawin and Catherine S. J. Cazin\*

The new well-defined catalyst  $[\text{Pd}(\mu\text{-Cl})\text{Cl}(\text{IPr}^*)]_2$  enables the efficient Grignard reagent cross-coupling for the synthesis of tetra-*ortho*-substituted biaryls.



5590

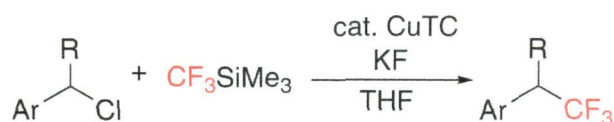


### Palladium-catalyzed oxidative carbonylative coupling of arylboronic acids with terminal alkynes to alkynes

Kishore Natte, Jianbin Chen, Helfried Neumann, Matthias Beller and Xiao-Feng Wu\*

The first example of palladium-catalyzed oxidative carbonylation of arylboronic acids with terminal alkynes has been developed. By an appropriate combination of a palladium salt, a ligand, and an oxidant, the desired alkynes were isolated in moderate to good yields.

5594



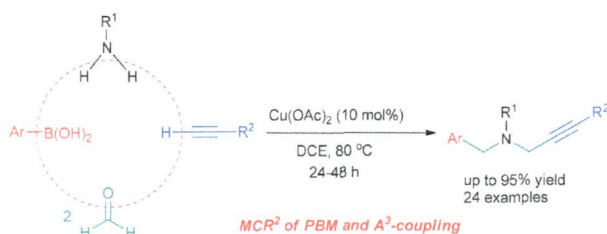
CuTC: copper(I) thiophene-2-carboxylate

### Copper-catalyzed nucleophilic trifluoromethylation of benzylic chlorides

Yoshihiro Miyake, Shin-ichi Ota, Masashi Shibata, Kazunari Nakajima and Yoshiaki Nishibayashi\*

The reactions of primary and secondary benzylic chlorides with trifluoromethyltrimethylsilane in the presence of a catalytic amount of copper(I) thiophene-2-carboxylate (CuTC) have been found to give the corresponding benzylic trifluoromethylated products in good to high yields.

5597



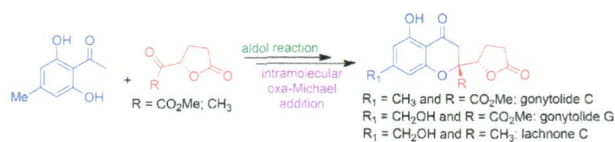
### Synthesis of tertiary propargylamines via a rationally designed multicomponent reaction of primary amines, formaldehyde, arylboronic acids and alkynes

Jiayi Wang, Qiaoying Shen, Pinzhen Li, Yanqing Peng and Gonghua Song\*

A novel approach for the synthesis of tertiary propargylamines is achieved through a  $\text{Cu(OAc)}_2$ -catalyzed multicomponent reaction of primary amines, formaldehyde, arylboronic acids and alkynes.

## PAPERS

5601



### Total synthesis of gonytolides C and G, lachnone C, and formal synthesis of blennolide C and diversanol

Gangarajula Sudhakar,\* Shruthi Bayya, Vilas D. Kadam and Jagadeesh Babu Nanubolu

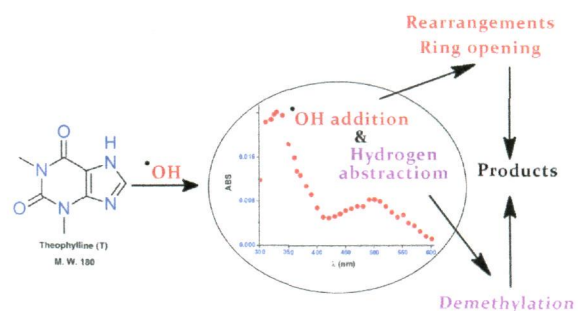
The total syntheses of gonytolide C and related compounds have been accomplished from the aldol reaction between acetophenone derived from orcinol and butyrolactone containing ketone, followed by the diastereoselective intramolecular cyclization.

5611

### Hydroxyl radical induced oxidation of theophylline in water: a kinetic and mechanistic study

M. M. Sunil Paul, U. K. Aravind, G. Pramod, A. Saha and C. T. Aravindakumar\*

Evidence is reported for the addition and hydrogen abstraction reactions of hydroxyl radicals with an important pharmaceutically active compound, theophylline.

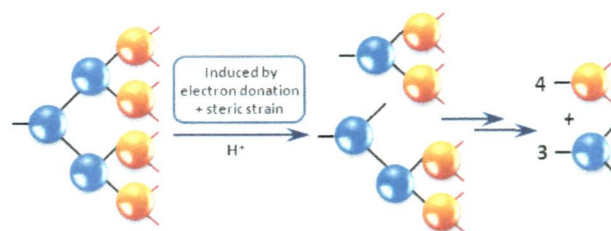


5621

### Elucidating factors leading to acidolytic degradation of sterically strained oligoether dendrons

J. Karabline-Kuks, A. Fallek and M. Portnoy\*

Monitoring of the disassembly of third-generation sterically crowded oligoether dendrons in acidic solution reveals their exact degradation sequence, synergistically induced by electron donation and steric strain.

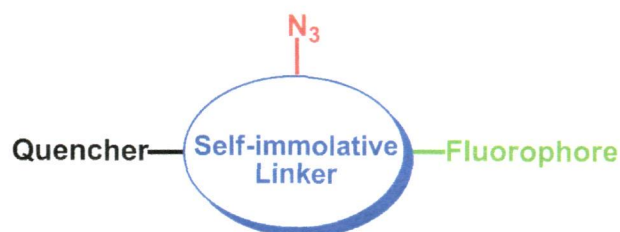


5629

### Chemoselective reduction and self-immolation based FRET probes for detecting hydrogen sulfide in solution and in cells

Bifeng Chen, Peng Wang, Qingqing Jin and Xinjing Tang\*

A general approach in designing H<sub>2</sub>S fluorescent probes based on FRET and self-immolative linkers.

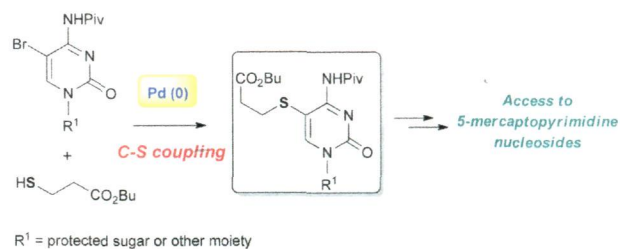


5634

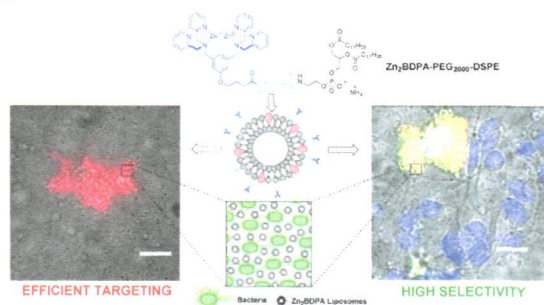
### A general approach to the synthesis of 5-S-functionalized pyrimidine nucleosides and their analogues

Dzmitry G. Kananovich, Alli Reino, Kaja Ilmarinen, Marko Rõõmusoks, Mati Karelson and Margus Lopp\*

A palladium-catalyzed C–S coupling reaction has been used as a key step for the introduction of S-functionality at the C-5 position of the cytosine and uracil nucleosides and their analogues.



5645

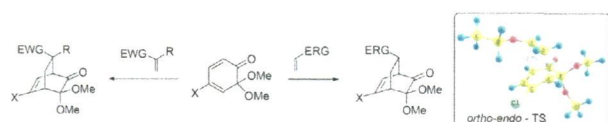


### Selective recognition of anionic cell membranes using targeted liposomes coated with zinc(II)-bis(dipicolylamine) affinity units

Serhan Turkyilmaz, Douglas R. Rice, Rachael Palumbo and Bradley D. Smith\*

Liposomes containing phospholipid-PEG conjugates with terminal zinc(II)-bis(dipicolylamine) affinity units selectively target anionic membrane surfaces including the exterior of bacterial and dead/dying mammalian cells.

5656

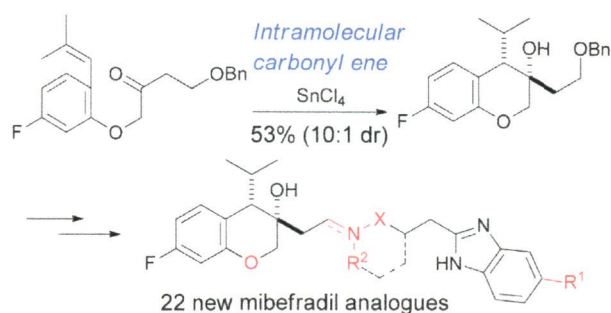


### Diels-Alder reactions of 4-halo masked o-benzoquinones. Experimental and theoretical investigations

Seshi Reddy Surasani, Santosh Kumar Reddy Parumala and Rama Krishna Peddinti\*

The title reactions afforded densely substituted bicyclo-[2.2.2]octenones in high yields and high selectivities. The transition-state energies and global electronic indexes computed at the B3LYP/6-31G\*\* theory level supported the observed selectivities of the reaction.

5669

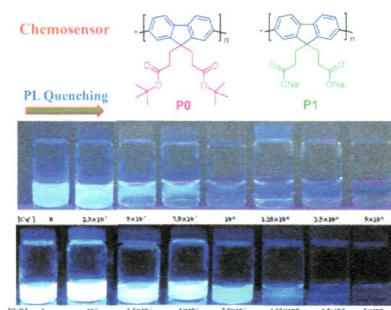


### Efficient synthesis of mibefradil analogues: an insight into *in vitro* stability

Ji Eun Lee, Tae Hui Kwon, Su Jin Gu, Duck-Hyung Lee, B. Moon Kim, Jae Yeol Lee, Jae Kyun Lee, Seon Hee Seo, Ae Nim Pae, Gyochang Keum, Yong Seo Cho\* and Sun-Joon Min\*

New mibefradil analogues were synthesized by a diastereoselective intramolecular carbonyl-ene reaction as a key transformation. The structural modification of mibefradil significantly reduced CYP inhibition and microsomal degradation.

5682



### Synthesis and chemosensory application of water-soluble polyfluorenes containing carboxylated groups

Chia-Shing Wu, Hsiao-Chu Su and Yun Chen\*

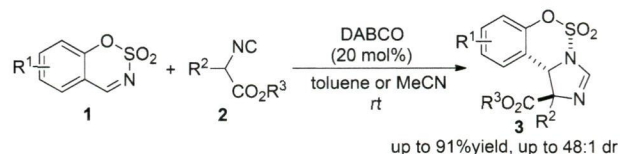
A water-soluble polyfluorene containing carboxylated groups (**P1**), prepared via the hydrolysis of poly[9,9'-bis(*tert*-butyl-3'-propanoate)fluorene-2,7-yl] (**P0**), shows high selectivity and sensitivity toward Cu<sup>+</sup> and Cu<sup>2+</sup>, with the Stern-Volmer constants ( $K_{sv}$ ) being  $3.5 \times 10^6$  and  $5.78 \times 10^6 \text{ M}^{-1}$ , respectively.

5691

### DABCO-catalyzed [3 + 2] annulation of sulfamate-derived cyclic imines with isocyanacetates: synthesis of sulfamate-fused 2-imidazoline

Zhenzhen Gao, Lei Zhang, Zhanhu Sun, Hao Yu, Yumei Xiao\* and Hongchao Guo\*

A novel DABCO-catalyzed [3 + 2] annulation of sulfamate-derived cyclic imines with isocyanacetates.

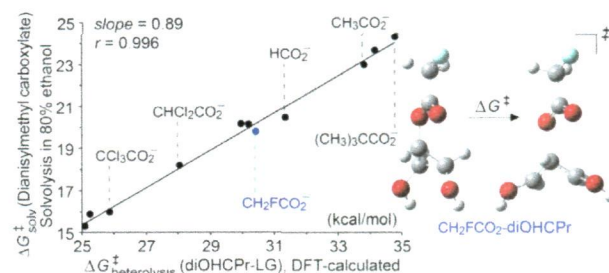


5698

### A DFT-based model for calculating solvolytic reactivity. The nucleofugality of aliphatic carboxylates in terms of $N_f$ parameters

Bernard Denegri,\* Mirela Matic and Olga Kronja

The proposed model reaction affords heterolytic reactivities of carboxylates that correlate well with the corresponding experimental data, enabling the use of DFT methods in estimating solvolytic reactivities of carboxylates.

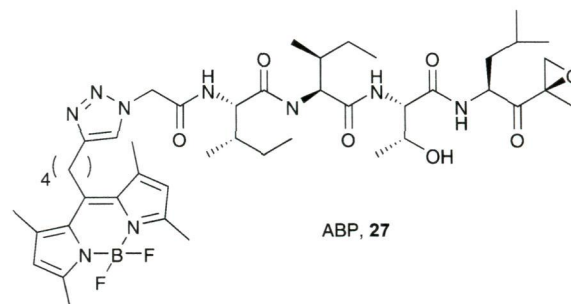


5710

### Exploring dual electrophiles in peptide-based proteasome inhibitors: carbonyls and epoxides

Bo-Tao Xin, Gerjan de Bruin, Martijn Verdoes, Dmitri V. Filippov, Gijs A. van der Marel and Herman S. Overkleeft\*

Peptide epoxyketones are potent and selective proteasome inhibitors.

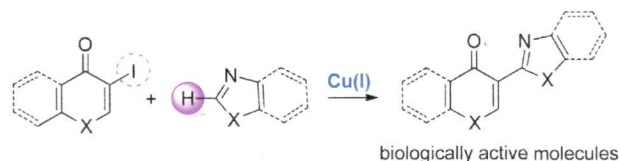


5719

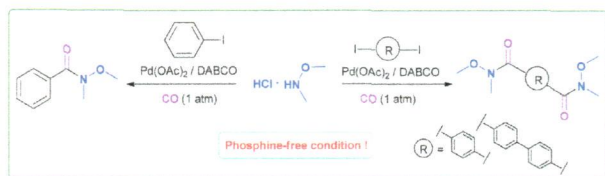
### A copper-mediated cross-coupling approach for the synthesis of 3-heteroaryl quinolone and related analogues

Sanghye Shin, Yechan Kim, Kiho Kim and Sungwoo Hong\*

An efficient and practical method for the direct cross-coupling between quinolones and a range of azoles was developed via copper-mediated C–H functionalization.



5727

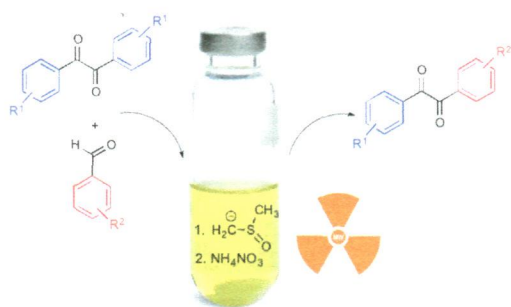


### **Pd(OAc)<sub>2</sub>/DABCO as an efficient and phosphine-free catalytic system for the synthesis of single and double Weinreb amides by the aminocarbonylation of aryl iodides**

Sandip T. Gadge and Bhalchandra M. Bhanage\*

Single and double Weinreb amides were synthesized using a Pd(OAc)<sub>2</sub> catalyst and DABCO as an inexpensive and stable ligand using carbonylation methodology under phosphine-free conditions.

5733

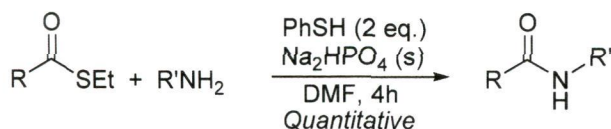


### **One-pot, two-step desymmetrization of symmetrical benzils catalyzed by the methylsulfinyl (dimsyl) anion**

Daniele Ragno, Olga Bortolini,\* Pier Paolo Giovannini, Alessandro Massi,\* Salvatore Pacifico and Anna Zaghi

Symmetrical-to-unsymmetrical benzil conversion is realized by a one-pot two-step procedure involving a chemoselective cross-benzoin reaction followed by microwave-assisted oxidation of the benzoylated benzoin intermediate.

5745



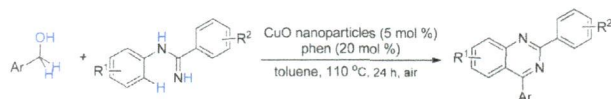
R, R' = alkyl e.g. side-chain protected peptide sequence

### **Mechanistic insight into benzenethiol catalyzed amide bond formations from thioesters and primary amines**

Nicolai Stühr-Hansen, Nicolai Bork\* and Kristian Strømgaard

Thiophenol catalysed formations of amides from alkyl thioesters and primary amines in DMF were studied experimentally and theoretically.

5752



### **Synthesis of quinazolines via CuO nanoparticles catalyzed aerobic oxidative coupling of aromatic alcohols and amidines**

Wu Zhang,\* Fei Guo, Fei Wang, Na Zhao, Liang Liu, Jia Li and Zhenghua Wang

Quinazoline derivatives were obtained via CuO nanoparticles catalyzed reaction of *N*-arylamidines and aromatic alcohols in air.

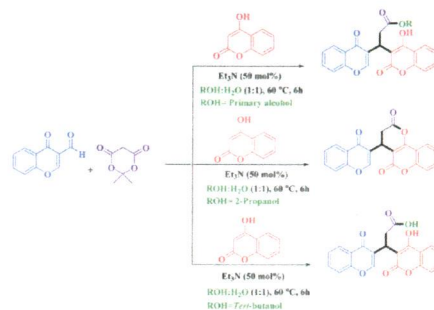


5757

### Synthesis of functionalized chromones through sequential reactions in aqueous media

Saber Mehrparvar, Saeed Balalaie,\*  
Mahnaz Rabbanizadeh, Frank Rominger and  
Elmira Ghabraie

An efficient synthesis protocol has been developed for diversity-oriented functionalized compounds *via* four-component reaction of chromone carbaldehydes, Meldrum's acid, 4-hydroxyl coumarin or 6-methyl-4-hydroxyl-pyrone and primary alcohols in aqueous media.

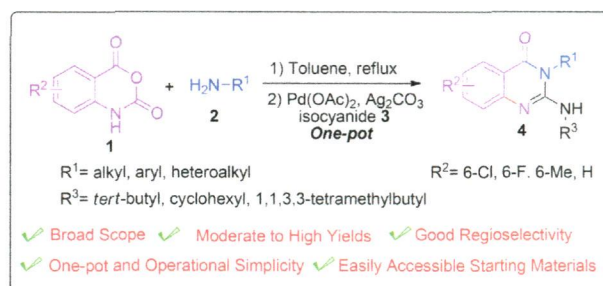


5766

### One-pot synthesis of 2-amino-4(3H)-quinazolinones *via* ring-opening of isatoic anhydride and palladium-catalyzed oxidative isocyanide-insertion

Fei Ji, Mei-Fang Lv, Wen-Bin Yi and Chun Cai\*

An efficient and practical two-step process has been developed for the synthesis of 2-amino-4(3H)-quinazolinones *via* ring-opening of isatoic anhydride and palladium-catalyzed oxidative isocyanide-insertion in one pot.

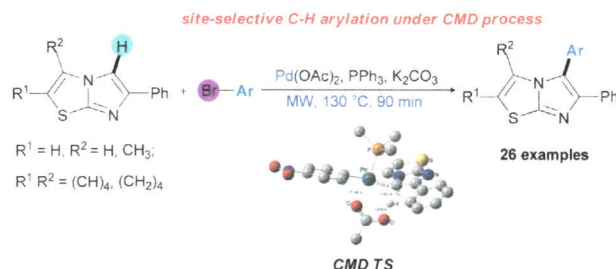


5773

### Palladium-catalyzed microwave-assisted direct arylation of imidazo[2,1-*b*]thiazoles with aryl bromides: synthesis and mechanistic study

Yi-Shuo Zhu, Benyi Shi, Ran Fang, Xiaoxuan Wang and  
Huanwang Jing\*

A palladium-catalyzed regioselective C–H arylation of imidazo[2,1-*b*]thiazoles under microwave irradiation *via* a concerted metalation–deprotonation (CMD) pathway was developed.



5781

### Electrophilicity and nucleophilicity of commonly used aldehydes

Sanjay Pratihar

The present approach for determining the electrophilicity (*E*) and nucleophilicity (*N*) of aldehydes includes a kinetic study of KMnO<sub>4</sub> oxidation and NaBH<sub>4</sub> reduction of aldehydes.

