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Diversity-oriented syntheses of functional π-systems by multicomponent and domino reactions*,**

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Abstract: Functional π-electron systems can be synthesized in a diversity-oriented fashion by applying multicomponent and domino reactions. Based upon alkyne activation by Sonogashira coupling, reactive triple or double bonds become the key functionality for sequential and consecutive synthesis of heterocycles, such as β-amino vinyl nitrothiophenes, δ-amino propenylidene indolones, indolizines, furans, pyrroles, annelated 2-amino pyridines, and spirocyclic benzofuranones and indolones. All these chromophores and fluorophores possess peculiar properties such as nonlinear optical (NLO) activity, pH-sensitivity, distinct solid-state fluorescence, or large Stokes shifts.

Keywords: catalysis; CC-coupling; chromophores; domino reactions; multicomponent reactions.

INTRODUCTION

Functional molecules possess peculiar properties, and their facile preparation is one of the most challenging goals for synthetic chemistry. However, addressing issues such as simplicity, safety, brevity, selectivity, yield, environmental demands, availability of starting materials, and diversity all at the same time in the sense of an ideal synthesis [1] is an endeavor almost like squaring the circle (Fig. 1). Consequently, synthetic chemists have sought and devised fruitful strategies that inevitably tackle the very fundamental principles of efficiency and efficacy. Besides the criteria of selectivity (i.e., chemo-, regio- and stereoselectivity), they encompass also, and with increasing importance, economical and ecological aspects. Concise, elegant, and conceptually novel syntheses have become an inspiring and steadily accelerating driving force both in academia and industry.

In the past decade, the productive concepts of multicomponent processes, domino reactions, and sequential transformations have considerably stimulated the synthetic scientific community [2,3]. In particular, a combination of diversity and creation of functionality has merged into the field of diversity-oriented syntheses [4] that have found broad application in the discovery and development of pharmaceutical lead structures. With respect to functional π-electron systems, such as chromophores, fluorophores, and electrophores, this approach is quite novel and still pristine [5]. Therefore, modular syntheses of tailor-made functional chromophores and fluorophores are challenges for synthetic effi-

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ciency and reaction design. From a practical point of view, combinatorial chemistry [6] also offers manifold opportunities for directing diversity-oriented syntheses of π-systems [7]. Even more sophisticated than combinatorial liquid- and solid-phase syntheses are multicomponent and domino reactions where an inherent reactivity profile can be exploited in a most favorable way for the construction of complex molecular frameworks in a one-pot fashion.

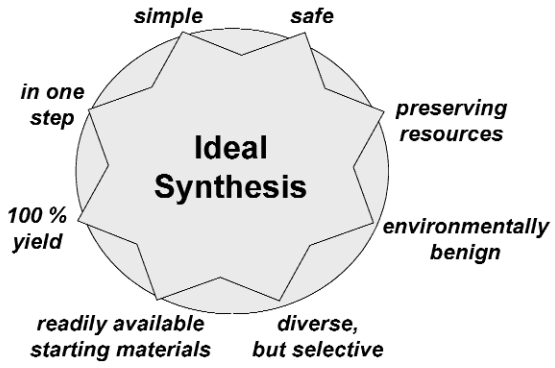


Fig. 1 The ideal synthesis—squaring the circle?

Generally, domino reactions [8] are regarded as sequences of uni- or bimolecular elementary reactions that proceed without intermediate isolation or workup as a consequence of the reactive functionality that has been formed in the previous step (Fig. 2). Besides uni- and bimolecular domino reactions that are generally referred to as "domino reactions", the third class is called multimolecular domino reactions or multicomponent reactions (MCRs).

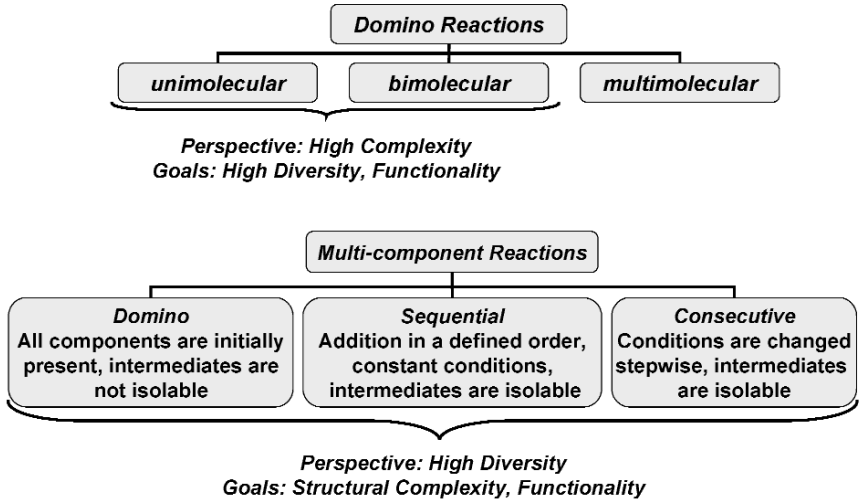


Fig. 2 Multicomponent and domino reactions—enhancing synthetic efficiency.

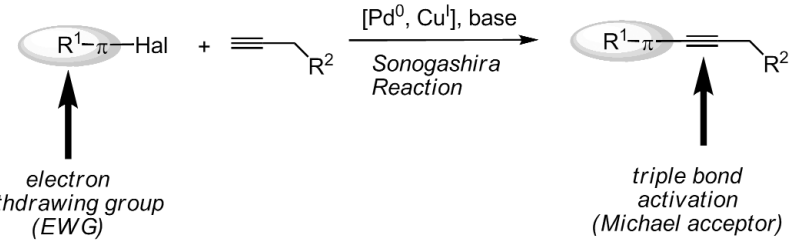
Whereas uni- and bimolecular domino reactions inevitably cause a significant increase in the degree of molecular complexity, MCRs inherently lead to an increase in molecular diversity. Therefore, MCRs bear some significant advantages over uni- and bimolecular domino reactions. Besides the facile accessibility and high diversity of starting materials, multicomponent syntheses promise high conver-

gence and enormous exploratory potential. In addition to a purist standpoint, where all ingredients of MCRs have to be present from the very beginning of the process (MCRs in a domino fashion), nowadays sequential (subsequent addition of reagents in a well-defined order without changing the conditions) and consecutive (subsequent addition of reagents with changing the conditions) one-pot reactions are counted as well in the class of MCRs [2,3b,g]. Although MCR technology has considerably fertilized pharmaceutically relevant lead finding, surprisingly, it is still in its infancy with respect to the application to functional π-electron systems. This contribution gives a brief overview on our endeavors in diversity-oriented synthesis of chromophores and fluorophores, applying one-pot processes, namely, MCRs and examples of domino sequences.

MULTICOMPONENT SYNTHESES OF CHROMOPHORES AND FLUOROPHORES BY COUPLING-ADDITION SEQUENCES

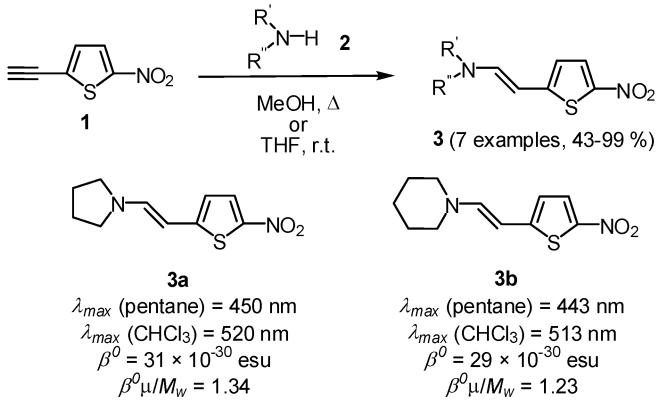
Transition-metal-catalyzed cross-coupling reactions [9] have notably revolutionized the conceptual construction of carbon framework and have also had a significant impact on the synthesis of π-electron systems with extended conjugation [10]. For devising consecutive MCRs, most advantageously cross-coupling methodologies offer an excellent compatibility with numerous polar functional groups as a consequence of the mild reaction conditions. In turn, polar functionality can be easily applied for subsequent transformations, most favorably within a one-pot sequence. For sequentially palladium-catalyzed processes [11] and heterocycle synthesis [12], this principle has been established.

Taking into account the excellent compatibility of polar functional groups that often dispense with tedious protection–deprotection steps, the Sonogashira coupling [13], a straightforward alkyne-to-alkyne transformation, is a highly favorable tool for devising novel synthetic strategies to functional π-electron systems. Conceptually, the installation of a reactive functional group such as an alkyne with an electron-withdrawing substituent predictably could result in an in situ activation of alkynes toward Michael-type addition, i.e., an entry to a coupling-addition sequence (Scheme 1).



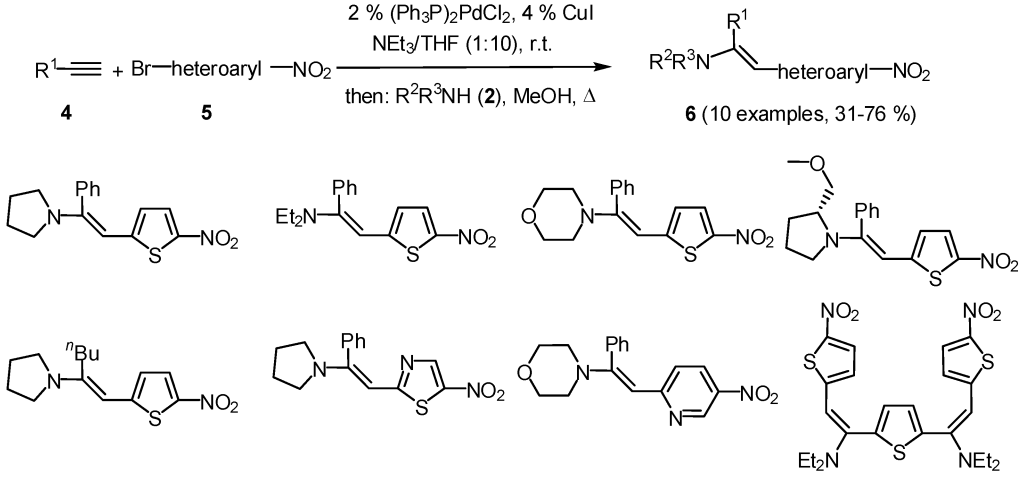
Scheme 1 Alkyne activation by Sonogashira coupling of an electron-poor halide as an entry to coupling-Michael addition sequences.

We have illustrated this concept as an entry to intensely colored, highly solvochromic β-amino vinyl nitrothiophenes (Scheme 2) [14]. Independently, Lin [15] has also discovered that 2-alkynyl 5-nitrothiophenes **1** react very smoothly with secondary amines **2** to furnish β-amino vinyl nitrothiophenes **3**. We have closely investigated these novel types of push–pull chromophores with respect to their nonlinear optical (NLO) and thermal properties [14]. Hyper Rayleigh scattering (HRS) measurements at a fundamental of 1500 nm have revealed that β-values are surprisingly large for such short dipoles (**3a**: = 31×10^{-30} esu; **3b**: = 29×10^{-30} esu). With respect to the relatively low molecular mass, these chromophores display a rather favorable molecular figure of merit, $\beta^0\mu/M_w$, where M_w is the molar mass. Furthermore, selected push–pull chromophores **3** were investigated by differential scanning calorimetry (DSC), revealing relatively low T_g (i.e., glass transitions), a favorable property for composites in photo-refractive materials.



Scheme 2 Michael-type addition of secondary amines to nitrothienyl-substituted alkynes and NLO data of selected β-amino vinyl nitrothiophenes **3**.

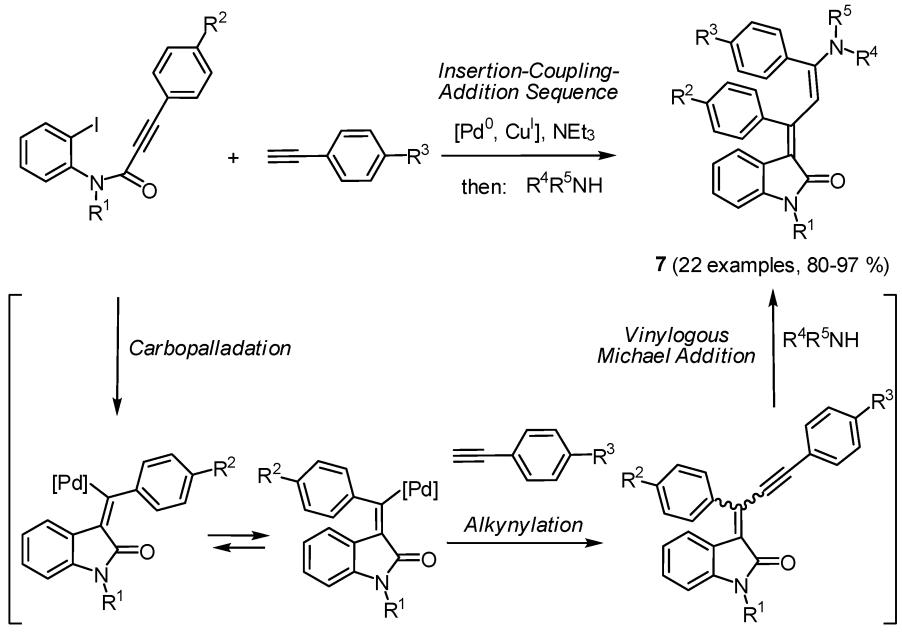
Based upon the peculiar reactivity of nitrothienyl-substituted alkynes, we have developed a one-pot three-component coupling-aminovinylation sequence to push–pull chromophores [16]. Terminal alkynes **4** and sufficiently electron-deficient heteroaryl halides **5** were transformed under Sonogashira conditions into the expected coupling products, which were subsequently reacted with secondary amines **2** to furnish the push–pull systems **6** in good yields (Scheme 3). The critical step in this consecutive reaction is the addition of the amine to the intermediate internal acceptor-substituted alkyne. According to semi-empirical and density functional theory (DFT) calculations, the crucial parameters for the success of the amine addition are the relative lowest unoccupied molecular orbital (LUMO) energies and the charge distribution at the β-alkynyl carbon atom.



Scheme 3 A coupling-aminovinylation sequence to β-amino vinyl hetero arenes **6**.

The concept of alkyne activation by Sonogashira coupling was successfully extended to the in situ generation of alkynones, highly reactive and versatile synthetic equivalents of 1,3-dicarbonyl compounds. Hence, the consecutive one-pot reaction principle of the coupling-addition sequence led to a synthetic and methodological extension in enaminone [17] and heterocycle synthesis [18].

In a sequence of carbopalladation and Sonogashira coupling followed by Michael addition of a secondary amine, we could successfully develop a three-component synthesis of amino propenylidene indolones **7**, which are conjugated δ-amino diene carboxamides (Scheme 4) [19]. Due to their push–pull nature, all representatives of **7** show positive solvochromicity and absorb between 446 and 488 nm. However, the pronounced orange–red solid-state fluorescence of δ-amino propenylidene indolones **7** with large Stokes shifts (Fig. 3) is quite remarkable, in particular since the chromophores do not fluoresce in solution.



Scheme 4 A CI-aminovinylation sequence to δ-amino propenylidene indolones **7**.

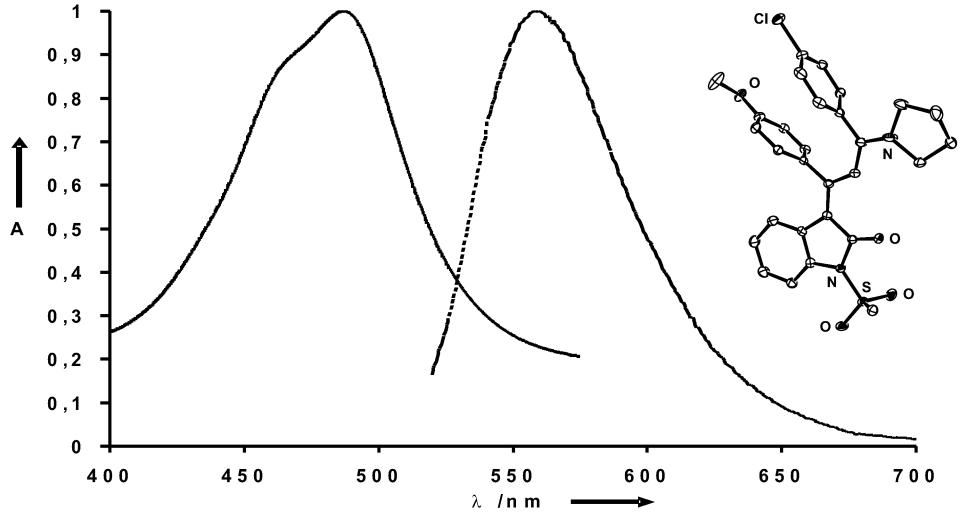
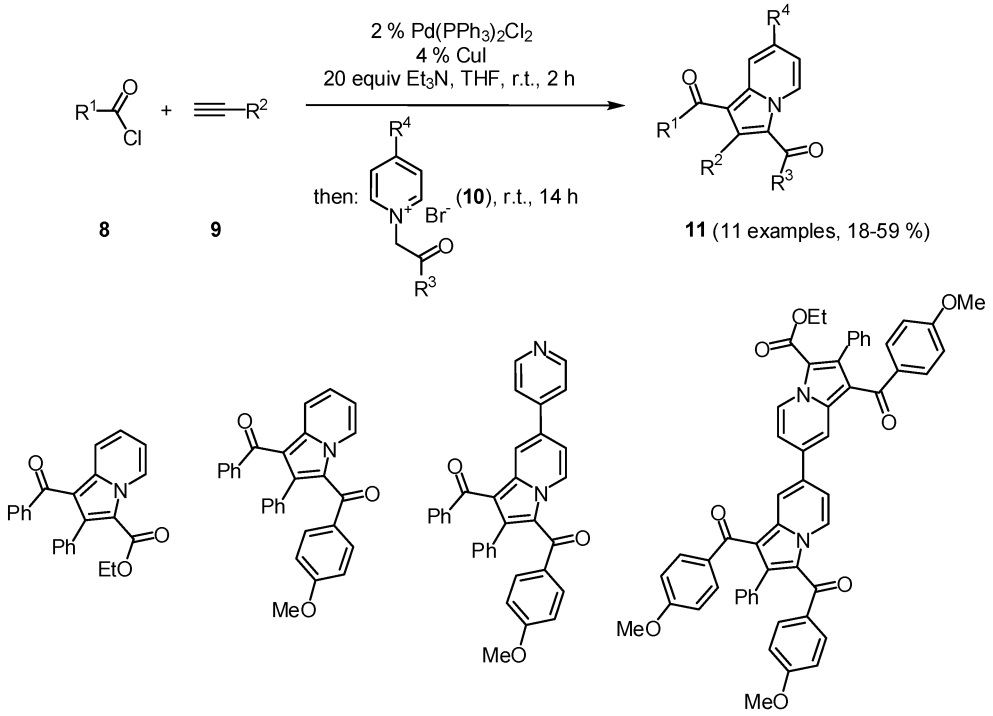


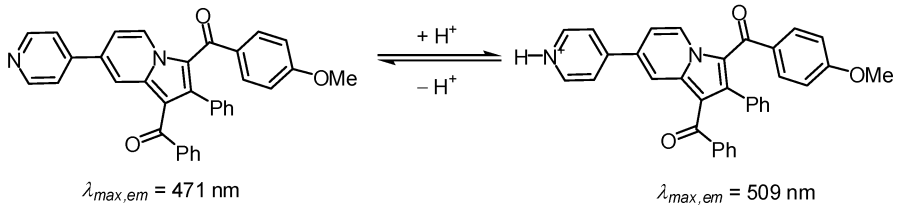
Fig. 3 Absorption (solid line, $\lambda_{max,abs}$ = 486 nm) and solid-state emission spectra (dotted line, $\lambda_{max,em}$ = 558 nm) of a δ-amino propenylidene indolone **7** (R^1 = $MeSO_2$, R^2 = OMe, R^3 = Cl, R^4,R^5 = $(CH_2)_4$.

Alkynones can also be reaction partners in cycloadditions. In particular, the 1,3-dipolar cycloaddition promises rapid access to many classes of conjugated and annelated five-membered heterocycles [20]. In the sense of a coupling-1,3-dipolar cycloaddition sequence, we have disclosed a consecutive one-pot three-component process to indolizines [21]. Starting from (hetero)aroyl chlorides **8** and terminal alkynes **9** under Sonogashira conditions, the expected alkynones were formed (Scheme 5). Under the amine basic conditions, the subsequently added 1-(2-oxoethyl) pyridinium bromide derivatives **10** are transformed in situ into pyridinium ylides that undergo a (2+3)-cycloaddition with the alkynone dipolarophiles present in the reaction mixture. The initial cycloadducts instantaneously aromatize to give rise to the isolation of highly fluorescent indolizine derivatives **11**.



Scheme 5 One-pot three-component coupling-1,3-dipolar cycloaddition synthesis of indolizines **11**.

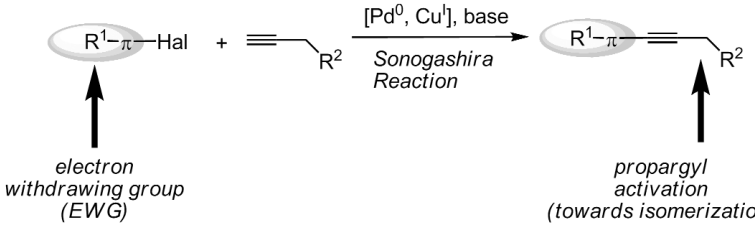
Fluorescence studies with pyridyl-substituted representatives not only show that indolizines are highly interesting fluorescent dyes but that their emission color can also be reversibly switched upon altering the pH of the medium (Scheme 6).



Scheme 6 Protonation equilibrium of a pyridyl indolizine **11** at pH 6.0.

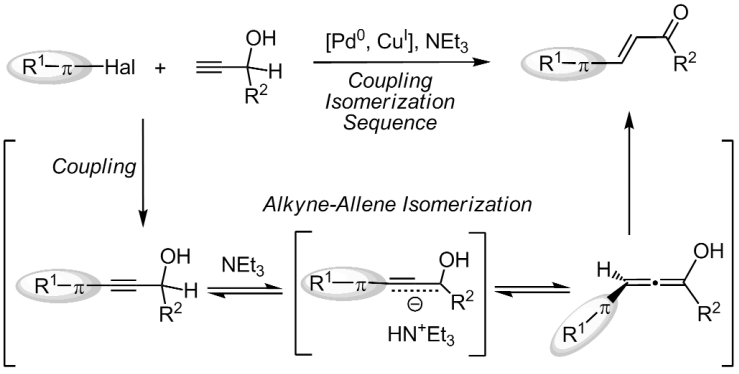
MULTICOMPONENT AND DOMINO SYNTHESES OF FLUOROPHORES INITIATED BY COUPLING-ISOMERIZATION

Besides activating the triple bond toward Michael addition, the electron-withdrawing group introduced by Sonogashira coupling can also exert an activation of the remote propargyl position (Scheme 7). This propargyl activation could, for instance, trigger an alkyne-allene isomerization, over the complete sequence a coupling-isomerization (CI) reaction would be the consequence.



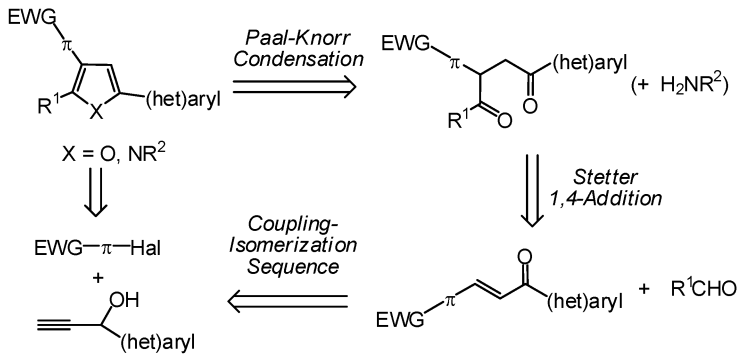
Scheme 7 Propargyl activation by Sonogashira coupling of an electron-poor halide as an entry to CI sequences.

Driven by a concluding tautomerization, the CI reaction of electron-deficient (hetero)aryl halides and 1-(hetero)aryl propargyl alcohols gives rise to the formation of 1,3-di(hetero)aryl propenones (Scheme 8) [22], i.e., chalcones that are as Michael acceptors suitable starting points for consecutive multicomponent syntheses of heterocycles in a one-pot fashion [12].



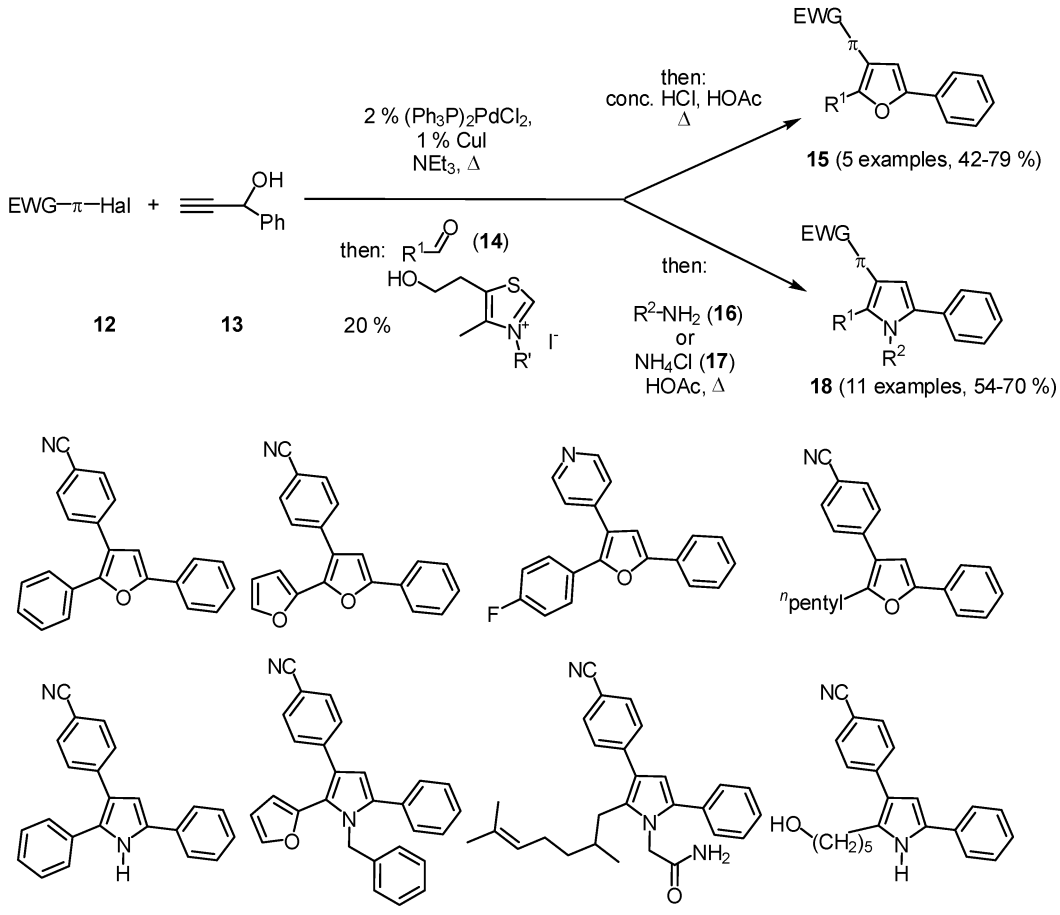
Scheme 8 The CI reaction—a catalytic access to enones.

The CI reaction is exceptionally well suited as an entry to multicomponent syntheses of polysubstituted aromatic heterocycles, and on this basis a CI–Stetter–Paal–Knorr sequence was designed as an diversity-oriented approach to highly substituted furans and pyrroles (Scheme 9) [23].



Scheme 9 Retrosynthetic concept for a three-component furan and four-component pyrrole synthesis.

Therefore, the CI–Stetter–Paal–Knorr synthesis of furans and pyrroles begins with the CI reaction starting from electron-deficient (hetero)aryl halides **12** and 1-phenylpropyn-1-ol (**13**) (Scheme 10). Upon addition of aromatic or aliphatic aldehydes **14** and a thiazolium salt catalyst, the intermediate chalcones are subsequently transformed by a Stetter reaction into 1,4-diketones. Without isolation, the

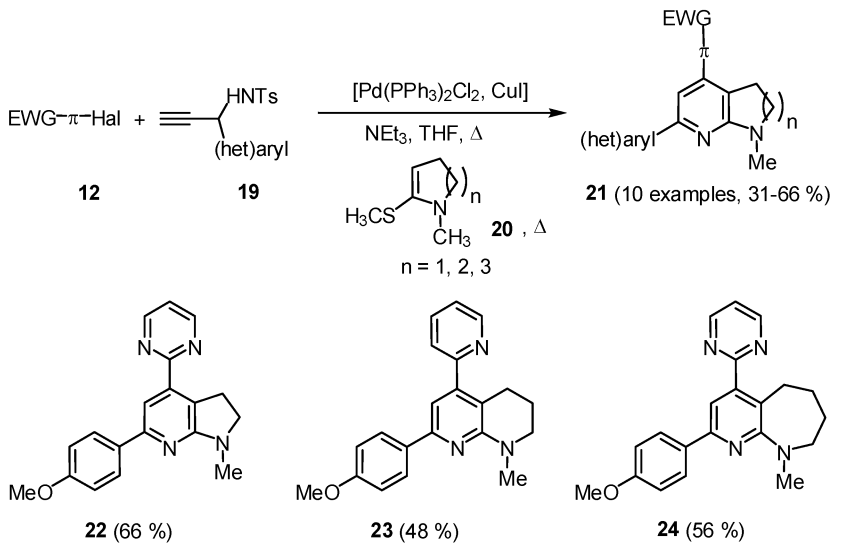


Scheme 10 CI-Stetter–Paal–Knorr synthesis of furans **15** and pyrroles **18**.

1,4-dicarbonyl compounds are reacted with concentrated hydrochloric acid and acetic acid in the same vessel to give rise to 2,3,5-trisubstituted furans **15**, or, upon subsequent addition of primary amines **16** or ammonium chloride (**17**) and acetic acid, 2,3,5-trisubstituted and 1,2,3,5-tetrasubstituted pyrroles **18** were obtained in good overall yields.

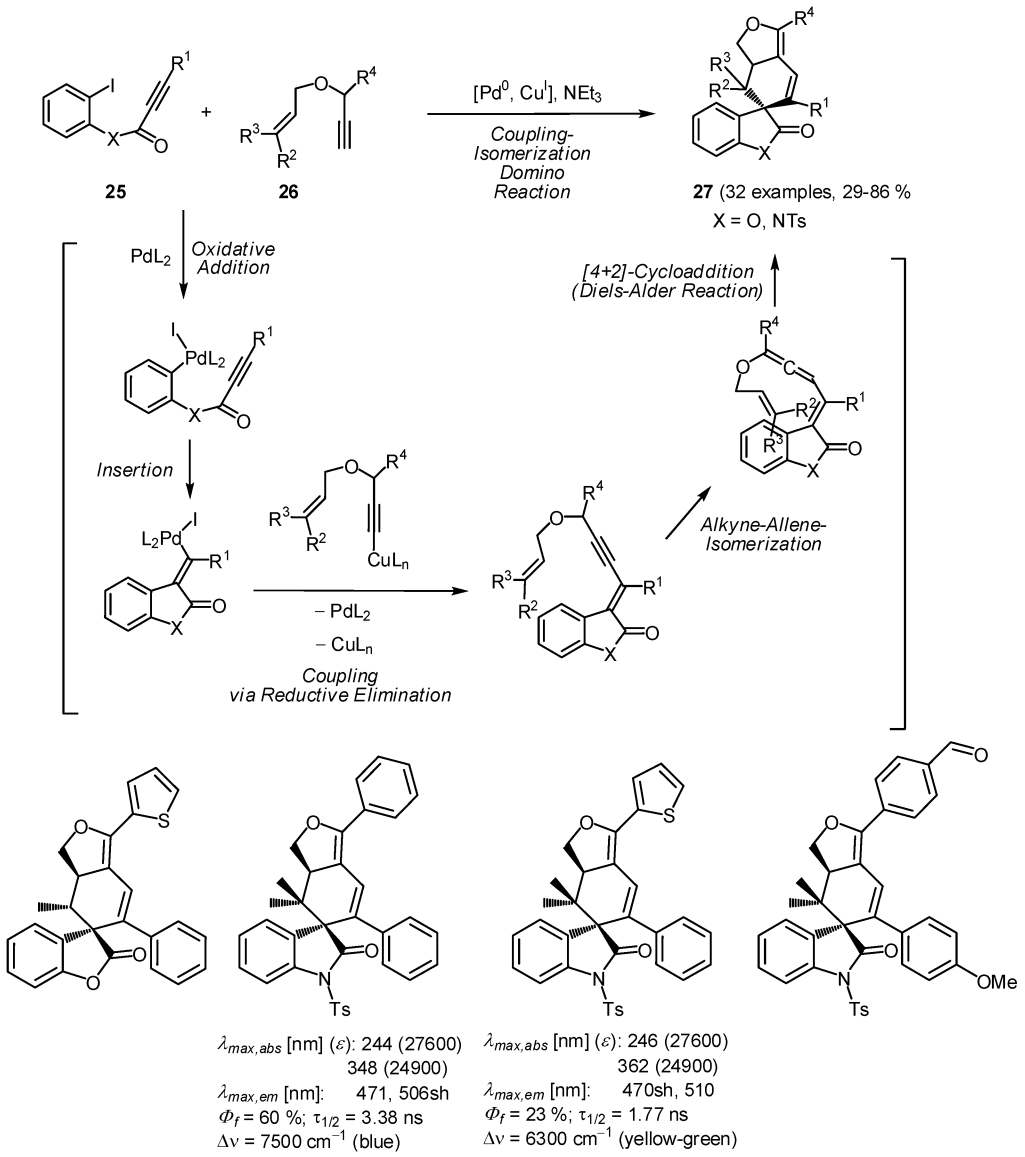
All novel furans **15** and pyrroles **18** exhibit a strong blue fluorescence with considerable Stokes shifts. The absorption maxima are found in a range of $\lambda_{max,abs}$ = 312–327 nm and the emission occurs at $\lambda_{max,em}$ = 401–451 nm. Hence, this multicomponent approach to fluorophores can be exploited for combinatorial optimization of emission properties.

In analogy to the chalcone formation by CI reaction, the use of *N*-tosyl propargyl amines **19** leads to the formation of *N*-tosyl enimines [24]. Likewise, this new enimine synthesis can be applied in a consecutive CI-cycloaddition-aromatization sequence with diethyl ketene acetal furnishing 2-ethoxy pyridines in moderate yields [24]. Furthermore, upon reaction of electron-poor (hetero)aryl halides **12**, terminal propargyl *N*-tosyl amines **19**, and highly reactive cyclic *N*,*S*-ketene acetals **20**, annelated 2-amino pyridines **21** such as the pyrrolo[2,3-*b*]pyridine **22**, the 1,8-naphthyridine **23**, and the pyrido[2,3-*b*]azepine **24** can be synthesized in moderate to good yields (Scheme 11) [25]. These heterocycles are highly fluorescent and, as a consequence of conformational biases, highly pH-sensitive (**24**: $\lambda_{max,em}$ = 512 nm at pH 4; $\lambda_{max,em}$ = 478 nm at pH 9).



Scheme 11 Three-component synthesis of annelated 2-amino pyridines **21** by CI-cycloaddition.

Finally, we could also demonstrate that the CI reaction can also be applied in domino reactions [26]. Inspired by mechanistic studies on the CI reaction, the elusiveness of the proposed allenol intermediate suggested that we open a pathway to the more stable allenyl ether intermediate. Thus, initiated by cyclic carbopalladation and followed by the CI reaction, the allenyl ether could be a reactive amphiphilic partner for subsequent elementary reactions in the sense of a hetero-domino reaction. Indeed, reaction of alkynoyl *ortho*-iodo phenolates or anilides **25** and propargyl allyl ethers **26** in the presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$ and CuI in a boiling mixture of toluene or butyronitrile and triethylamine gives rise to the formation of the class of spirocyclic benzofuranones or spiroindolones **27** in moderate to excellent yields (Scheme 12) [27].



Scheme 12 Insertion-CI-Diels–Alder domino reaction to spirocyclic benzofuranones and indolones **27** and selected photophysical data.

Hence, this insertion-CI-Diels–Alder sequence can be rationalized as follows: oxidative addition of the Pd catalyst and subsequent intramolecular alkyne insertion furnishes a vinyl Pd species. This intermediate undergoes alkynylation and gives rise to the formation of an electron-poor vinyl propargyl allyl ether, which isomerizes by base catalysis to give an electron-poor vinyl allene that reacts in an intramolecular (4+2)-cycloaddition through an *anti-exo* transition state to conclude the sequence by formation of the spirocycles **27**.

Interestingly, all chromophores **27** absorb between near UV and the edge to visible ($\lambda_{max,abs}$ = 327–398 nm) and fluoresce intensely with blue, green, or orange light ($\lambda_{max,em}$ = 433 to 545 nm) and with large Stokes shifts, both in solution and in the solid state.

CONCLUSION

Modern photonic applications and future molecular electronics have generated a considerable demand for tailor-made functional π-electron systems. Therefore, multicomponent and domino reactions open new avenues for a rational and rapid design of chromophores and fluorophores. In particular, catalytic cross-coupling methodologies are most favorable for inventing new sequences and reaction cascades since the reaction conditions are highly tolerable for many polar functional groups. Therefore, the search and development of new diversity-oriented syntheses and reactions will be an ongoing driving force in the search for new functional π-electron systems.

ACKNOWLEDGMENTS

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