CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000369

3rd EuCheMS Chemistry Congress

Efficient Synthesis of Biologically Interesting 3,4-Diaryl-Substituted Succinimides and Maleimides: Application of Iron-Catalyzed Carbonylations

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Dedicated to Professor Uwe Rosenthal on the occasion of his 60th birthday

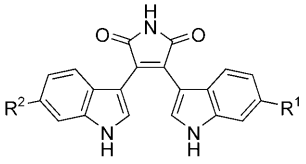
Abstract: A straightforward two-step synthesis of *trans*-3,4-disubstituted succinimides through a palladium-catalyzed Sonogashira reaction and an iron-catalyzed double carbonylation is described. In situ oxidative dehydrogenation gave the corresponding 3,4-diarylmaleimides. By starting from readily available aryl and heteroaryl halides, a variety of new analogues and derivatives of bioactive 3,4-bisindolylmaleimides are obtained in good yield and selectivity.

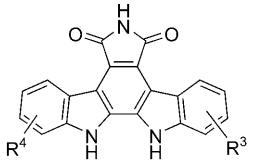
Keywords: carbonylation · iron · maleimides · Sonogashira reaction · succinimides

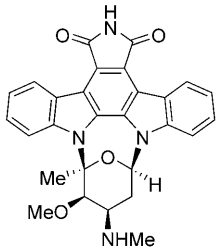
Introduction

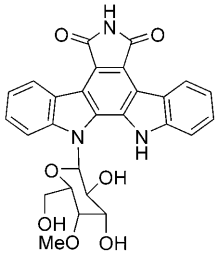
Indolocarbazole alkaloids and biosynthetically related 3,4-bisindolylmaleimides represent interesting lead structures for the pharmaceutical industry due to their broad biological activities.[1] Among these compounds, arcyriarubins, isolated from the fruiting bodies of the slime mold *Arcyria denundata*,[2] represent the simplest members of naturally occurring 3,4-bisindolylmaleimides. They are also structurally related to arcyriaflavins, the aglycon of the known protein kinase C (PKC) inhibitor staurosporine,[3] and the tumor growth inhibitor rebeccamycin.[4]

Synthetic analogues of these and related natural products possess a wide spectrum of antibacterial, antiviral, antimicrobial, and antigenic activities.[5] Furthermore, they are promising agents for autoimmune diseases[6] and also valuable inhibitors of different kinases,[7] especially PKC, which plays an important role in signal transduction pathways. Therefore, it is not surprising that several derivatives are currently being evaluated in human clinical trials as anti-









cancer drugs.[8] Beside their pharmaceutical importance, 3,4-bisindolylmaleimides have also found applications in material science as components in red light-emitting diodes (LEDs) due to their intense color.[9] The emerging interest in these compounds is clearly seen in a number of patent applications in recent years.[10]

Based on our interest in the development of transition-metal-catalyzed syntheses of indoles[11] and on our recent work on iron-catalyzed carbonylations of alkynes,[12] we started to explore the synthesis of novel 3-aryl-4-heteroaryl-

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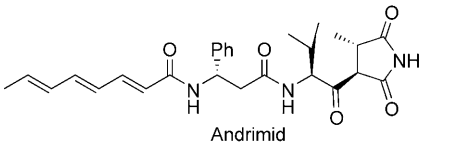
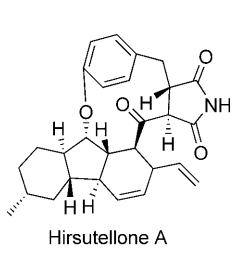
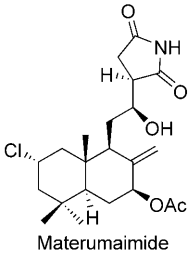
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000369.

maleimides and their corresponding succinimides. At this point it should be also noted that mono- and disubstituted succinimides are also of pharmacological interest. For example, andrimid, hirsutellone A, and haterumaimide are known natural products that possess significant bioactivities.[13]



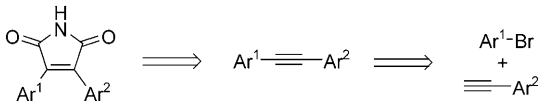




In addition, N-substituted succinimides and N-substituted 2-phenylsuccinimides were found to be active in suppressing electrically and metrazol-induced convulsions and proved to be useful in the treatment of petit mal epilepsy.[14]

Due to their attractive properties, several research groups have synthesized 3-indolo-substituted maleimides.[15] The most widely used synthetic approaches were developed by the groups of Steglich[16] and Faul[17] (Schemes 1 and 2). According to the Steglich procedure, indolyl magnesium bromide is reacted with 3,4-dibromomaleimide to give mono- or disubstituted products depending on the ratio of the starting materials. Notably, the outcome of the electrophilic arylation is also strongly dependent on the solvent. In THF the mono-substituted product is favored, but in toluene the 3,4-bisindolyl compound is obtained. The latter procedure of Faul et al. involves the construction of the central maleimide part by condensation of substituted 2-indolyl-acetamides with 2-aryl- or 2-indolyl-glyoxyl esters in the presence of a strong base.

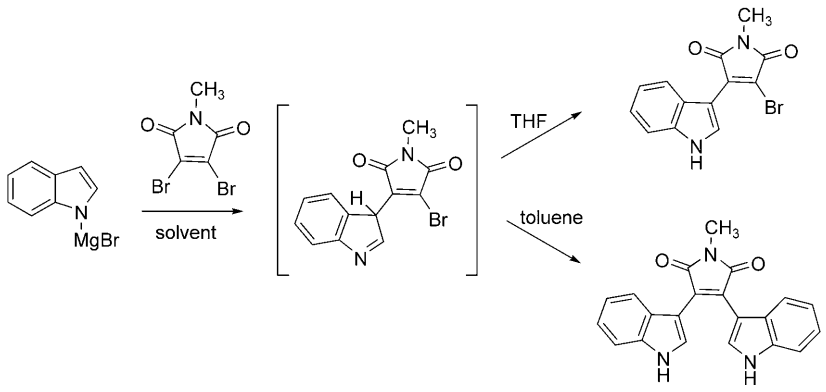
Herein, we report a new approach for the synthesis of all kinds of 3-heteroaryl-4-arylsuccinimides and -maleimides. As depicted in Scheme 3, the desired products should be obtained by an iron-catalyzed carbonylation of internal alkynes. These starting materials can be easily prepared by a palladium-catalyzed Sonogashira reaction.[18] The key step of our synthetic protocol is based on a selective double aminocarbonylation of internal alkynes in the presence of catalytic amounts of inexpensive and readily available iron–carbonyl complexes.[19]



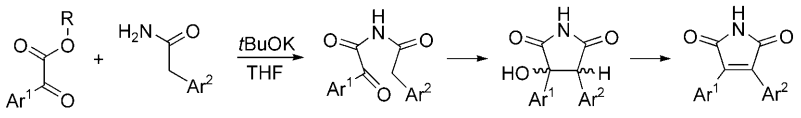
Scheme 3. A new retrosynthetic analysis of 3,4-diaryl-substituted maleimides.

So far, iron-catalyzed carbonylations of alkynes with ammonia or amines have been demonstrated only with structurally simple alkynes, such as phenylacetylene or diphenylacetylene.[12] To the best of our knowledge, there have been no investigations of this type of reaction with unsymmetrical 1,2-diarylalkynes or heteroaryl-substituted alkynes, which represent more challenging substrates.

Due to its manifold advantages, the application of iron has become a hot topic in organometallic catalysis.[20,21,22] However, iron-catalyzed processes are still considerably under-represented in the field of organic synthesis due to the poor functional group tolerance and limited substrate scope of the known methodologies.



Scheme 1. Synthesis of 3,4-bisindolylmaleimides according to Steglich et al.[16]



Scheme 2. Synthesis of 3,4-bisarylmaleimides according to Faul et al.[17]

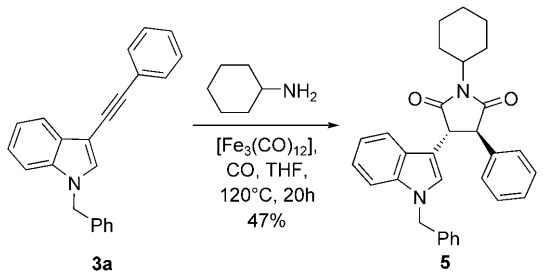
Results and Discussion

For some years we have been interested in the development of palladium catalysts that should be applicable for coupling reactions on both a laboratory and an industrial scale. Most recently we have developed 2-phosphino-*N*-arylin-

doles, -pyrroles,[23] and -imidazoles[24] and demonstrated their applicability in cross-coupling reactions of aryl chlorides and bromides. Indeed, coupling of *N*-benzyl-3-bromoindole **1a**[25] with phenylacetylene **2a** in the presence of $K_2[PdCl_4]$/CuI/2-(di-*tert*-butylphosphino)-*N*-phenylindole as the catalytic system proceeded smoothly in *N,N,N′,N′*-tetramethylethane-1,2-diamine (TMEDA) at 80 °C. By using different palladium sources ($K_2[PdCl_4]$, $Pd(OAc)_2$, and $Na_2[PdCl_4]$) at comparably low catalyst loading (0.5 mol %), the Sonogashira product is obtained in high yield (80–86 %). Next, this procedure was applied to the Sonogashira reaction of six different aryl and heteroaryl bromides with five different terminal arylalkynes (Table 1). In all cases, desired 1,2-diarylalkynes **3** were obtained in good to excellent yields (78–99 %; Table 1). Electronic effects of substituents on the aryl and heteroaryl bromides did not seem to be important for the reaction. Thus, electron-rich indole, naphthalene, and benzo[*b*]thiophene derivatives were successfully coupled with aromatic alkynes (Table 1, entries 1–4, 16–20). Similarly, the desired products were obtained in excellent yields in the presence of electron-deficient pyridines and pyrimidine derivatives (Table 1, entries 5–15). Additionally, substituents appeared to have no effect on this reaction for phenylacetylene derivatives. On the other hand, the position of the substituent slightly influenced the reaction outcome; generally, *ortho*-substituted arylalkynes gave slightly lower yields of the 1,2-diarylalkyne (Table 1, entries 5, 6 and 8, 9).

Next, 1,2-diarylalkynes **3** were subjected to the iron-catalyzed carbonylation with ammonia to generate the corresponding 3,4-diarylsuccinimides **4**. After some optimization, the double-carbonylation reactions were carried out in THF at 120 °C for 20 h in the presence of excess ammonia and 10 mol % $[Fe_3(CO)_{12}]$ under CO (20 bar). When 3-alkynylindoles **3a–d** were employed, desired succinimides **4a–d** were obtained in moderate to good yields (48–75 %; Table 1, entries 1–4). It is worth noting that in case of *N*-benzyl-3-[(2-methoxyphenyl)ethynyl]-indole (**3b**), the mono-carbonylation product (*E*)-2-(1-benzyl-1*H*-indol-3-yl)-3-(2-methoxyphenyl)acrylamide was isolated as a by-product in 21 % yield (Table 1, entry 2); 2- and 3-alkynylpyridines **3e–k** and 3-alkynylbenzo[*b*]thiophenes **3q–t** gave the corresponding succinimides in good yield without problems (Table 1, entries 5–11, 17–20). When 2-alkynyl-6-methoxynaphthalene **3p** was employed, the carbonylation gave succinimide **4p** in 76 % yield along with a trace of the monocarbonylation product, which was detected by GC–MS (Table 1, entry 16). The carbonylation of 5-alkynylpyrimidines **3l–o** gave biologically interesting succinimides **4l–o** (Table 1, entries 12–15).

In general, the substituent pattern of the phenyl ring of the initially employed alkyne has an influence on the product yield. For example, 4-fluorophenyl-substituted alkynes led to lower yields compared with electron-rich 1,2-diarylalkynes, except in the case of **3k** (Table 1, entries 11). In the double-carbonylation reaction of more sterically crowded 1,2-diaryl- or 1-aryl-2-heteroarylalkynes with, for example, *ortho* substituents on the aryl moiety, the selectivity of the carbonylation reaction is affected and affords not only the desired succinimides but also minor amounts of the monocarbonylation products (Table 1, entries 2, 16). This monocarbonylation reaction is more pronounced if primary amines are used as the nucleophile instead of ammonia, due to the increased steric bulk of the amine. For example, treatment of 3-alkynylindole **3a** with cyclohexylamine gave desired product **5** in 47 % yield, but treatment with ammonia gave the corresponding product **4a** in 70 % yield. In addition to **5**, the monocarbonylation product (*E*)-2-(1-benzyl-1*H*-indol-3-yl)-*N*-cyclohexyl-3-phenylacrylamide is obtained in 47 % yield (Scheme 4).



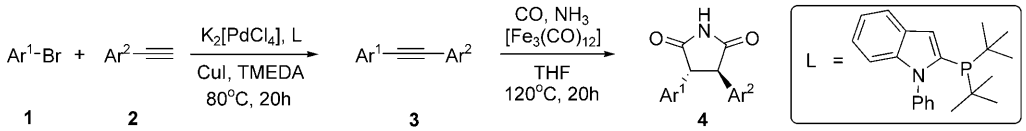
3a **5**

Scheme 4. Fe-catalyzed carbonylation with cyclohexylamine.

The stereochemistry of **4b** and **5** was unambiguously determined by single-crystal X-ray crystallographic analysis, which showed that the relative stereochemistry at C3 and C4 is *trans* (Figure 1). Based on this observation, the stereochemistry of the other succinimides was established by using NMR spectroscopy. In general, the vicinal coupling constants between the succinimide methine protons were observed in the range of 5.8–8.6 Hz. This is in agreement with the NMR spectroscopic data of other reported *trans*-disubstituted succinimides.[13b,26]

Concerning the mechanism of the iron-catalyzed double-aminocarbonylation reaction we propose the initial formation of an iron(carbonyl)–alkyne complex, although the details are not yet fully understood. According to Periasamy et al., who studied stoichiometric reactions of alkynes with $[Fe_3(CO)_{12}]$ in the presence of primary amines in detail, an amine $Fe(CO)_4$ and a $Fe_2(CO)_8$ species were formed, which on further reaction led to complexes **A** and **B**.[27] Nucleophilic attack of ammonia on one of the carbonyl groups in **B** gives **C**. Subsequent intramolecular amidation and reduction forms the cyclic imide (Scheme 5). Under catalytic conditions, the involvement of bi- or trimetallic complexes cannot yet be excluded. Notably, if the amine is added before the alkyne to the catalyst solution, the product yield is increased by about 10 %. To prepare 3,4-diarylmaleimides **E** from corresponding succinimides **C** and **D**, we envisioned an oxidative dehydrogenation reaction. Indeed, in the presence of one equivalent of the known dehydrogenating reagent 2,3-dichloro-5,6-dicyano-1,4 benzoquinone (DDQ), seven selected succinimides were oxidatively transformed into **6a–g** under mild conditions.[30] As shown in Table 2, 3-aryl-4-indolylsuccinimides **5**, **4b**, **4d**, and 3-aryl-4-naphthylsuccinimide

Table 1. Sequential synthesis of 1,2-diarylalkynes and *trans*-3,4-diarylsuccinimides.[a]



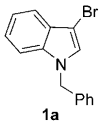
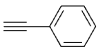
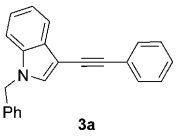
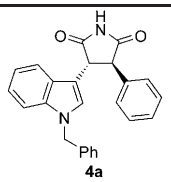
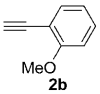
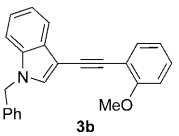
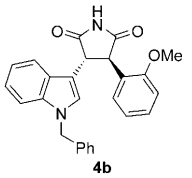
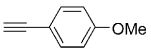
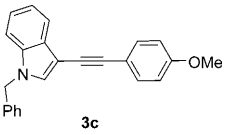
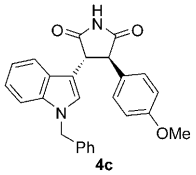
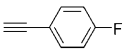
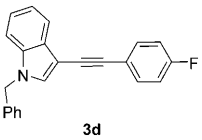
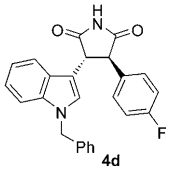
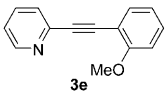
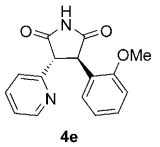
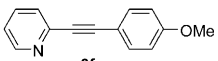
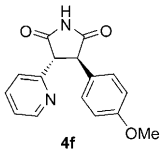
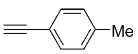
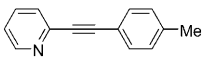
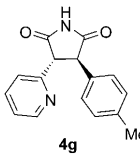
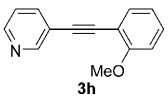
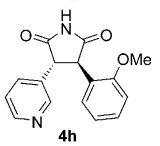
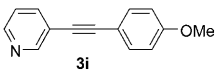
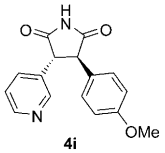
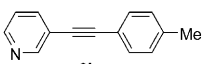
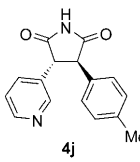
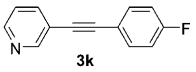
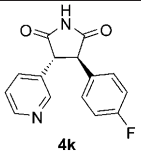
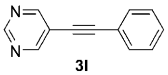
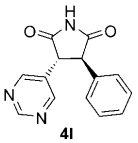
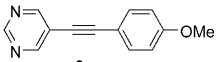
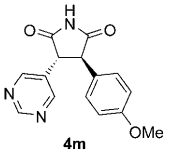
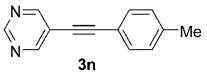
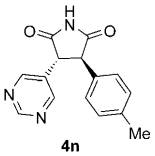
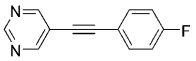
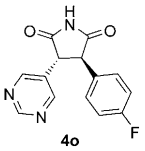
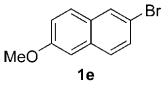
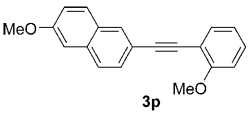
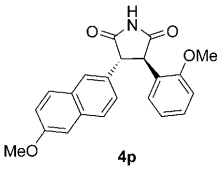
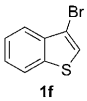
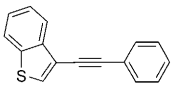
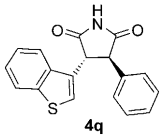
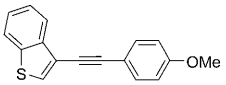
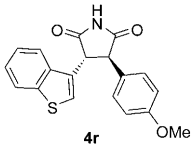
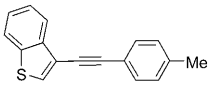
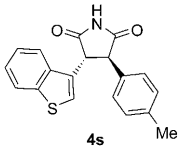
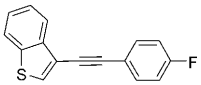
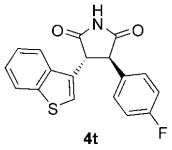
Entry	Aryl bromide	Alkyne	Product **3**	Yield[b] [%]	Product **4**	Yield[b] [%]
1	 **1a**	 **2a**	 **3a**	86	 **4a**	70
2	**1a**	 **2b**	 **3b**	90	 **4b**	48[c]
3	**1a**	 **2c**	 **3c**	82	 **4c**	75
4	**1a**	 **2d**	 **3d**	90	 **4d**	59
5	 **1b**	**2b**	 **3e**	78	 **4e**	83
6	**1b**	**2c**	 **3f**	99	 **4f**	80
7	**1b**	 **2e**	 **3g**	98	 **4g**	74
8	 **1c**	**2b**	 **3h**	92	 **4h**	70
9	**1c**	**2c**	 **3i**	99	 **4i**	62
10	**1c**	**2e**	 **3j**	99	 **4j**	85

Table 1. (Continued)

Entry	Aryl bromide	Alkyne	Product **3**	Yield[b] [%]	Product **4**	Yield[b] [%]
11	**1c**	**2d**	 **3k**	98	 **4k**	72
12	 **1d**	**2a**	 **3l**	83	 **4l**	33
13	**1d**	**2c**	 **3m**	99	 **4m**	56
14	**1d**	**2e**	 **3n**	99	 **4n**	38
15	**1d**	**2d**	 **3o**	98	 **4o**	35
16	 **1e**	**2b**	 **3p**	98	 **4p**	76[d]
17	 **1f**	**2a**	 **3q**	94	 **4q**	52
18	**1f**	**2c**	 **3r**	98	 **4r**	58
19	**1f**	**2e**	 **3s**	99	 **4s**	51
20	**1f**	**2d**	 **3t**	99	 **4t**	43

[a] Sonogashira conditions: aryl bromide (1 equiv), alkyne (1.2 equiv), $K_2[PdCl_4]$ (0.5 mol%), CuI (1 mol%), L (1 mol%), 1M TMEDA, 80°C, 20 h. Carbonylation conditions: $[Fe_3(CO)_{12}]$ (10 mol% of Fe), **1** (1.5–3 mmol), NH_3 (5 g), CO (20 bar), THF (20 mL), 120°C, 20 h. [b] Yield of isolated product. [c] Cinnamamide derivative was isolated as a minor product in 21% yield. [d] Cinnamamide derivative was detected by GC–MS.

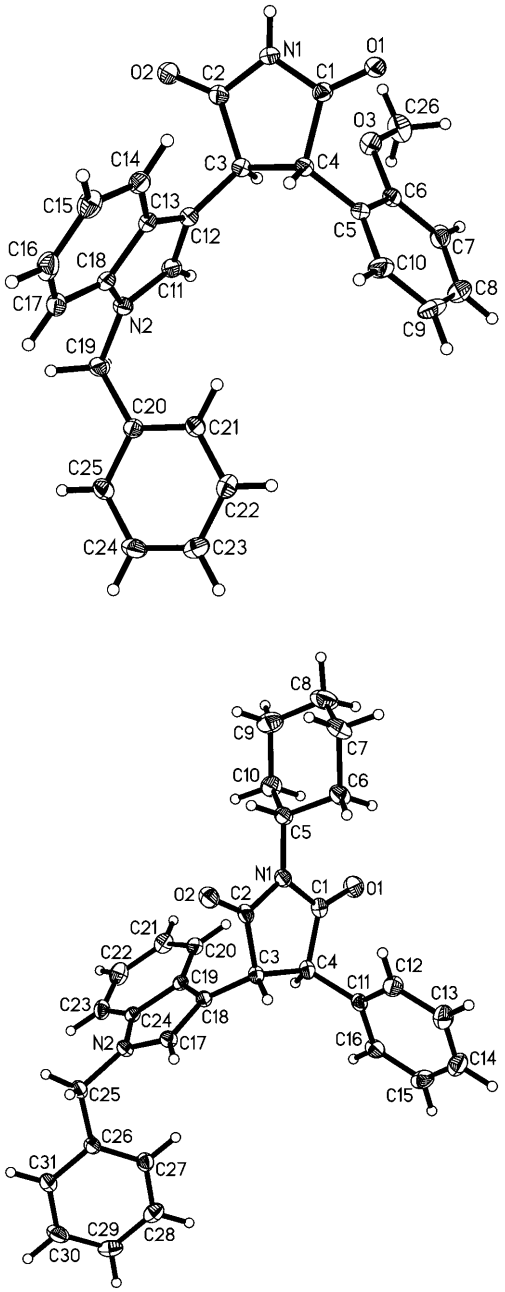
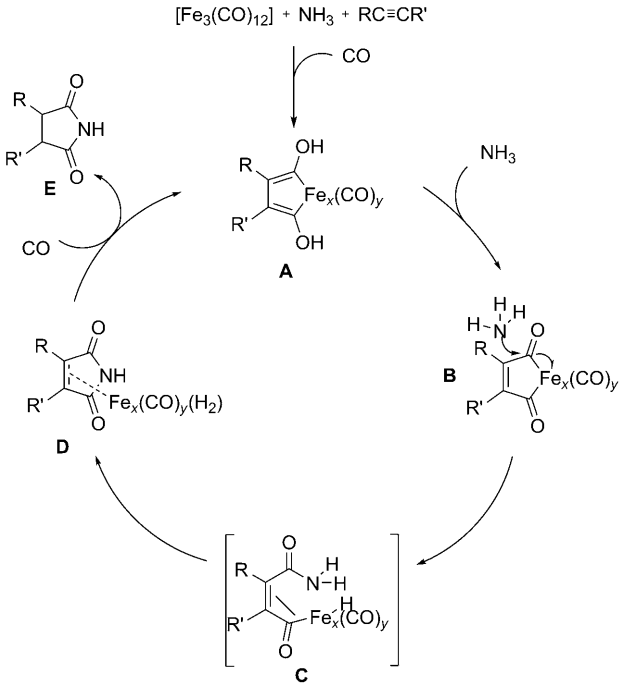


Figure 1. Molecular structures of **4b**[28] and **5**.[29] The thermal ellipsoids correspond to 30% probability.



Scheme 5. Proposed mechanism for the Fe-catalyzed carbonylation of alkynes.

4p were readily dehydrogenated within 1–1.5 h at room temperature to the corresponding maleimides in moderate to excellent yields (65–98%; Table 2, entries 1–3, 6).

A prolonged reaction time was required for the conversion of 3-aryl-4-pyridylsuccinimide **4e** and 3-aryl-4-pyrimidylsuccinimide **4n** due to their lower solubility in toluene (Table 2, entries 4, 5). The dehydrogenation of aryl benzo[*b*]thiophenylsuccinimide **4r** was the most difficult. Here, a reaction temperature of 80°C was needed to obtain **6g**. In agreement with the spectroscopic data, the structure of **6a** was confirmed by single-crystal X-ray crystallographic analysis (Figure 2).

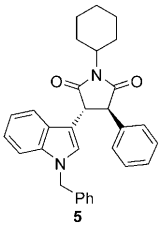
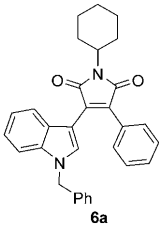
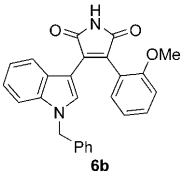
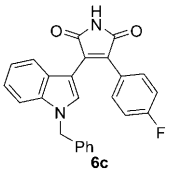
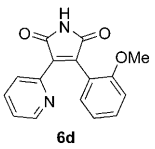
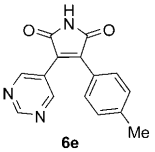
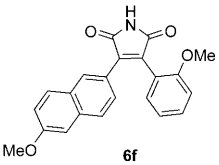
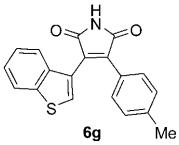
To omit purification procedures and to demonstrate a more straightforward synthesis of 3,4-bisarylmaleimides from 1,2-diarylalkynes, we performed a one-pot procedure for the synthesis of 3-(1-benzyl-1*H*-indol-3-yl)-4-phenyl-1*H*-pyrrole-2,5-dione (Scheme 6). Here, the iron catalyst was removed by a scavenger (Quadrasil™ TA) after the initial carbonylation step, and the crude product from the carbonylation reaction of **3a** was directly treated with 1.5 equivalents of DDQ in toluene at room temperature for 1 h. To our delight, maleimide **6h** was isolated in 82% yield after final purification.

Encouraged by the success of the synthesis of various maleimides, we turned our attention to the preparation of 3,4-bisindolylmaleimide **9**, which is an intermediate of the natural product acyriarubin. As shown in Scheme 7, the Sonogashira reaction of 3-bromoindole **1a** with trimethylsilylacetylene followed by removal of the silyl protecting group with tetra-*n*-butylammonium fluoride (TBAF) afforded 3-alkynylindole **7** in 63% yield. Another Sonogashira coupling led to bisindolylacetylene **8**, which afforded the corresponding 3,4-bisindolylmaleimide **9** without optimization upon carbonylation with ammonia and dehydrogenation with DDQ.

Conclusion

A novel synthetic strategy for the synthesis of analogues of arcyriarubin and related natural products has been reported. Combining palladium-catalyzed Sonogashira reactions with iron-catalyzed double aminocarbonylations provides effi-

Table 2. Oxidative dehydrogenation of *trans*-3,4-diaryl-substituted succinaimides with DDQ.[a],[30]

Entry	Succinimide	Product	*t* [h]	Yield[b] [%]
1			1	93
2	**4b**		1.5	98
3	**4d**		1	93
4	**4e**		12	95
5	**4n**		16	68
6	**4p**		1	65
7	**4r**		1.5[c]	28

[a] Conditions: succinimide (0.1–0.6 mmol), DDQ (1 equiv), toluene (10 mL), RT. [b] Yield of isolated product. [c] 80 °C for 1.5 h then RT for 16 h.

cient access to variety of new, potentially bioactive 3,4-diaryl-substituted succinimdes and maleimides. Notably, non-symmetrically disubstituted maleimides can be easily synthesized by using a variety of commercially available aryl and heteroaryl halides. For the first time it has been shown that iron-catalyzed carbonylations proceed smoothly in the presence of various heterocycles and that the carbonylation protocol is tolerant to different functional groups. The utility of the methodology is also shown in the synthesis of natural product intermediate **9**. Biological tests of the isolated succinimides and maleimides are currently in progress.

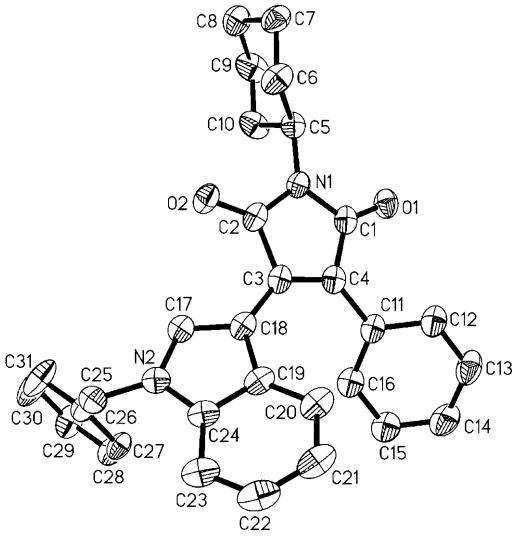
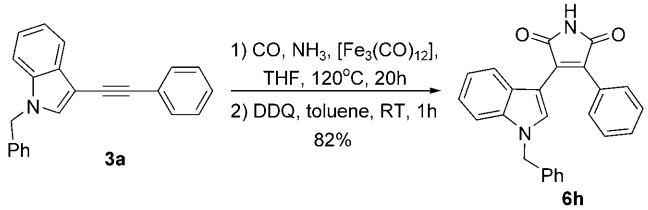
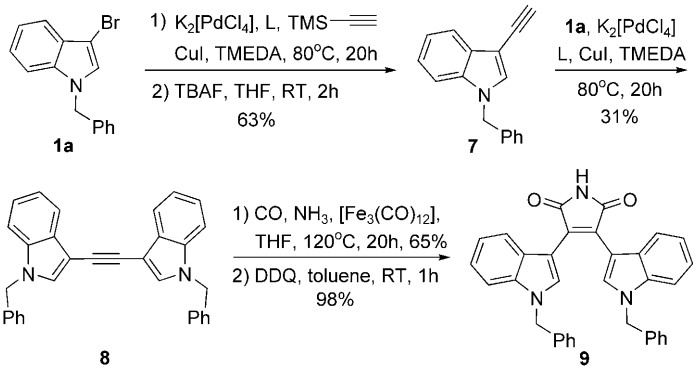


Figure 2. Molecular structure of **6a**.[31] The thermal ellipsoids correspond to 30% probability.



Scheme 6. One-pot synthesis of 3-indolyl-4-phenyl-maleimide **6h**.



Scheme 7. Short synthesis of Arcyriarubin intermediate **9**.

Experimental Section

General procedure for the Sonogashira coupling: $K_2[PdCl_4]$ (0.5 mol%), ligand (1 mol%), and CuI (1 mol%) were placed in a 25 mL Schlenk tube; if it was a solid, the heteroaryl bromide was also added at this point. Then TMEDA (1 M), liquid heteroaryl bromide (3–5 mmol), and the acetylene substrate (1.2 equiv) were successively added under an argon atmosphere. The reaction mixture was heated at 80 °C for 20 h. After cooling to RT, the mixture was quenched with H_2O (15 mL) and the aqueous phase was extracted with Et_2O (3×20 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, and concentrated

in vacuo, then the residue was purified by silica gel column chromatography (hexane/EtOAc) to give product **3** (Table 1).

General procedure for the iron-catalyzed carbonylation—Synthesis of 3,4-diarylsuccinimides: Alkyne (1.5–3 mmol), amine (15 equiv), and $[Fe_3(CO)_{12}]$ (10 mol % of Fe) was dissolved in THF (20 mL) under an argon atmosphere in a 50 mL Schlenk flask before being transferred into an autoclave. If ammonia (5 g) was used instead of amine, it was condensed from a small bomb into a 100 mL Parr autoclave. The autoclave was pressurized with CO and heated to 120 °C for 20 h, then the contents were cooled to RT. The pressure was released and the reaction mixture was transferred to the 50 mL Schlenk flask. QuadraSil™ TA (0.5–1 g) was added and the reaction mixture was stirred at RT for 30 min. After filtration of QuadraSil™ TA and removal of the solvent in vacuo, the crude succinimide product was purified by column chromatography on silica gel (hexane/EtOAc) to give product **4** or **5** (Table 1).

General procedure for the synthesis of 3,4-diarylmaleimides from 3,4-diarylsuccinimides: Succinimide (0.1–0.6 mmol) was dissolved in toluene (10 mL), then DDQ (1 equiv) was added in portions and the solution was stirred at RT for the indicated period of time. The solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: heptane/EtOAc or CH_2Cl_2/MeOH) to give product **6** (Table 2).

Acknowledgements

This work has been funded by the State of Mecklenburg-Western Pomerania, the Bundesministerium für Bildung und Forschung (BMBF), the Deutsche Forschungsgemeinschaft (Graduiertenkolleg 1213 and Leibnizprice). We thank Dr. C. Fischer, S. Buchholz, S. Schareina, Dr. W. Baumann, and K. Mevius for their excellent technical and analytical support.

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[28] Compound **4b**: $C_{26}H_{22}N_2O_3$; $M_r = 410.46$; triclinic; space group $P\bar{1}$; $a = 9.4289(5)$, $b = 10.4081(6)$, $c = 10.9481(6)$ Å; $\alpha = 89.763(5)$, $\beta = 80.782(4)$, $\gamma = 80.790(5)°$; $V = 1046.61(10)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.302$ g cm^{-3}; $\mu = 0.086$ mm^{-1}; $T = 200$ K; 20152 reflections measured, 5642 independent reflections ($R_{int} = 0.0381$), 3745 reflections ob-

served [$I>2\sigma(I)$]; final R indices [$I>2\sigma(I)$]: $R_1=0.0370$, $wR_2=0.0863$; R indices (all data): $R_1=0.0619$, $wR_2=0.0909$; 285 refined parameters. CCDC-768506 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[29] Compound **5**: $C_{31}H_{30}N_2O_2$; $M_r=462.57$; triclinic; space group $P\bar{1}$; $a=10.9632(6)$, $b=11.3517(6)$, $c=11.5312(6)$ Å; $\alpha=106.660(4)$, $\beta=104.051(4)$, $\gamma=107.982(4)°$; $V=1218.19(11)$ Å^3; $Z=2$; $\rho_{calcd}=1.261$ g cm^{-3}; $\mu=0.079$ mm^{-1}; $T=200$ K; 19683 reflections measured, 5582 independent reflections ($R_{int}=0.0349$), 3801 reflections observed [$I>2\sigma(I)$]; final R indices [$I>2\sigma(I)$]: $R_1=0.0388$, $wR_2=0.0859$; R indices (all data): $R_1=0.0614$, $wR_2=0.0908$; 316 refined parameters. CCDC-768504 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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[31] Compound **6a**: $C_{31}H_{28}N_2O_2$; $M_r=460.55$; monoclinic; space group $C2/c$; $a=21.519(3)$, $b=21.451(2)$, $c=10.689(2)$ Å; $\beta=92.090(12)°$; $V=4930.7(11)$ Å^3; $Z=8$; $\rho_{calcd}=1.241$ g cm^{-3}; $\mu=0.078$ mm^{-1}; $T=200$ K; 23603 reflections measured, 5284 independent reflections ($R_{int}=0.0736$), 2604 reflections observed [$I>2\sigma(I)$]; final R indices [$I>2\sigma(I)$]: $R_1=0.0553$, $wR_2=0.1344$; R indices (all data): $R_1=0.1121$, $wR_2=0.1525$; 305 refined parameters. CCDC-768505 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Received: February 11, 2010
Published online: June 2, 2010

