ChemPubSoc Europe

DOI: 10.1002/chem.201600432

CHEMISTRY A European Journal Communication

Synthetic Methods

Brønsted Acid-Mediated Hydrative Arylation of Unactivated Alkynes

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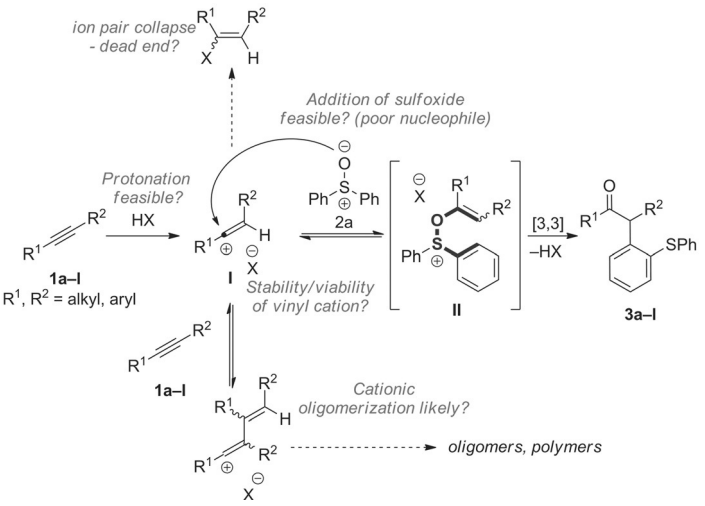
This manuscript is dedicated with respect and admiration to Prof. István E. Markó on the occasion of his 60th birthday

Abstract: The Brønsted acid-mediated reaction of unactivated alkynes with aryl sulfoxides leads to simultaneous hydration and intermolecular C–C bond formation. This solvent- and metal-free transformation directly delivers α-arylated carbonyl compounds as the products of a formal hydrative arylation in an atom-economical manner. The products bear useful synthetic handles for further functionalization.

The addition of water to an alkyne, affording a ketone, is a textbook organic transformation first discovered by Kucherov in 1881.[1] Numerous reports on the hydration of alkynes have appeared since that time,[2] and continuous developments employing water or Brønsted acids,[3,4] as well as mercury,[1,5] iron,[6] copper,[7] platinum,[8] iridium,[9] palladium,[10] and gold catalysts,[11] leading to the formation of the Markovnikov product, have been reported. Conversely, tungsten[12] and ruthenium catalyze the anti-Markovnikov hydration of alkynes,[13] whereas titanium is able to selectively yield both products.[14] This reaction forms a critical link between alkyne and carbonyl chemistries.[15] Formation of ketones by the hydration of alkynes with concomitant carbon–carbon bond formation at their α-position has been previously explored.[16,17] Examples include the gold- and mercury-catalyzed addition of sulfoxides or *N*-oxides to alkynes as well as iridium catalysis.[18,19]

Herein we describe the synthesis of α-arylated ketones by an atom-economical, Brønsted acid-catalyzed hydrative arylation of alkynes using sulfoxides. Inspired by our prior work on ynamides,[20a] we speculated that the protonation of unactivated alkynes **1a–l** could transiently furnish highly reactive vinyl cations **I** (Scheme 1).[21] The interception of these species with aryl sulfoxides, such as **2a**, would then conceivably lead to the formation of an intermediate **II**, poised to undergo charge-accelerated [3,3]-sigmatropic rearrangement to yield α-arylated ketones **3a–l**.

However, from the outset we were well aware of the potential drawbacks in this proposal (Scheme 1). For one, the poor basicity of unactivated alkynes for the formation of vinyl cations through protonation poses a challenge. Additionally, the low nucleophilicity of the sulfoxide oxygen implies that competitive addition of the counterion X^- (leading to a covalent collapse of the ion pair and possibly a "dead-end" addition product) or cationic oligomerization (or polymerization) of the alkyne partner could become serious issues.



Scheme 1. Proposed hydrative α-arylation of unactivated alkynes and possible complications.

Accordingly, initial experiments employing phenylacetylene (**1a**) with varying amounts of Brønsted acids in the presence of diphenyl sulfoxide (**2a**) led only to the formation of traces of **3a** (Scheme 2a).[22] Suspecting an important concentration effect with respect to the sulfoxide (given the multitude of competing processes possible; cf. Scheme 1), we turned to running the reaction under solvent-free conditions in the presence of an excess of **2a** at 80 °C. Pleasingly, these changes enabled the formation of α-arylated ketone **3a** (Scheme 2b) in a high yield with either triflic acid or bis(trifluoromethane)sulfonamide (not shown). The target compound was isolated in

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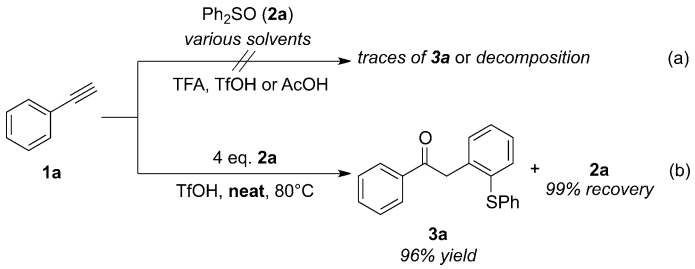
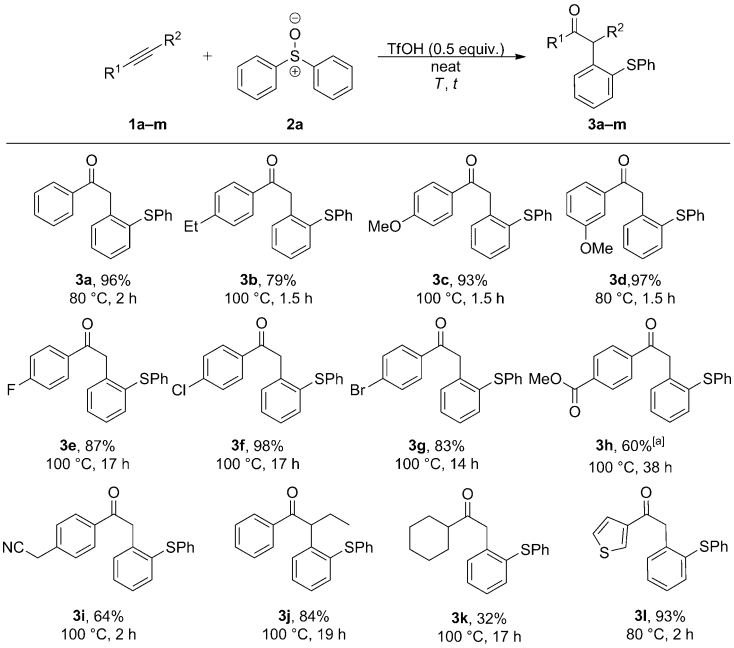
Supporting information for this article can be found under http://dx.doi.org/10.1002/chem.201600432.



Scheme 2. Screening of conditions for successful metal-free arylative coupling of phenylacetylene (**1a**) and diphenyl sulfoxide (**2a**).

96% yield, alongside a virtually complete recovery (99%) of the excess unreacted **2a**.

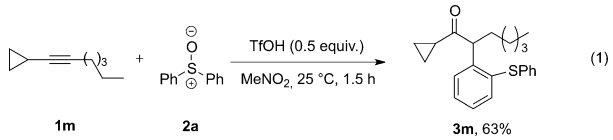
With suitable reaction conditions in hand, we explored the applicability of this transformation to various alkynes **1a–l** (Scheme 3). Both electron-rich and -poor substrates afforded high yields, generating **3a–g**. Esters and nitriles were also well-tolerated to afford **3h** and **3i**, respectively, in good yields. Importantly, **3j**, derived from an internal alkyne, was isolated in very good yield. Aliphatic substitution in the alkyne (to form **3k**) is also possible. Additionally, heteroaryl ketone **3l** was smoothly furnished in excellent yield.



Scheme 3. Hydrative arylation of alkynes with **2a**. [a] 1.0 Equiv of TfOH was used. All reactions were carried out with 4 equiv of **2a** and 0.5 equiv of TfOH. See the Supporting Information for details.

The connectivity of the final α-arylketone product depends on the selective formation of a vinyl cation. Nevertheless, certain dialkyl-substituted alkynes enable very high levels of regioselectivity [Eq. (1)]. As depicted, the use of cyclopropyl pentyl acetylene (**1m**) enables the preparation of cyclopropyl-ketone **3m** in good yield without any trace of the other regioisomer.

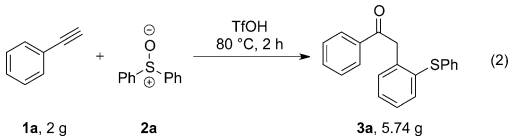
Subsequently, the scope of aryl sulfoxides in this reaction was investigated (Scheme 4). Products **4ab–ad** were easily prepared from **1a** and diaryl sulfoxides **2b–d**. Additionally, alkyl aryl sulfoxides could be employed to provide **4ae–cl**, containing an alkyl sulfide moiety as a handle for further functionalization (vide infra), in moderate to excellent yields. Importantly, all sulfoxides employed in Scheme 4 were either commercially available or readily prepared in a single step.[22]

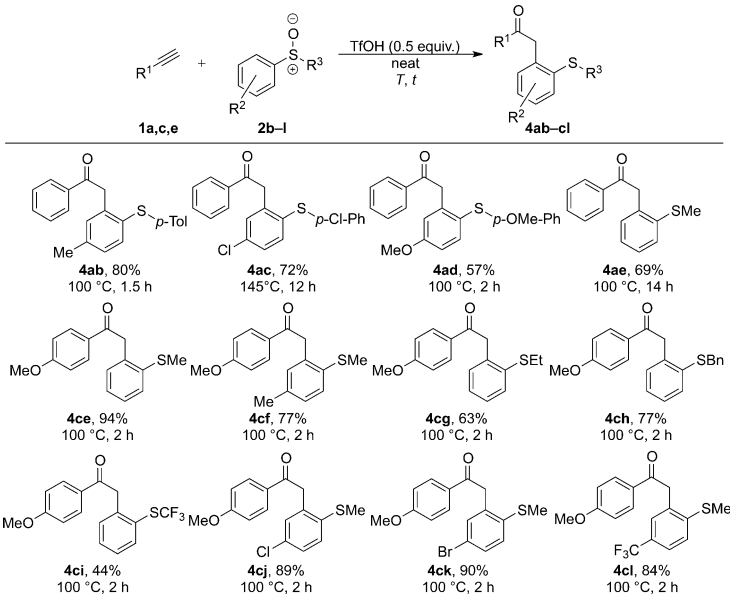


Control experiments were conducted in order to gain more insight into the reaction (Scheme 5). The reaction of **1a** with equimolar amounts of **2b** and **2c** led to the formation of a 70:30 mixture of **4ab** and **4ac**, showing a clear bias towards the sulfoxide bearing the more electron-rich aryl moieties (Scheme 5a). Furthermore, addition of **2a** to equimolar amounts of alkynes **1c** and **1e** gave rise to the formation of **3c** and **3e** in a ratio of 79:21 (Scheme 5b). This result confirms the expected preferential protonation of the more electron-rich alkyne.

The simple solvent-free conditions, under which the atom-economical reaction takes place, enable a straightforward scaling up. Thus, treating **1a** (2 g, 19.7 mmol) with triflic acid and **2a** afforded 5.74 g of the corresponding α-arylated ketone **3a** [Eq (2)]. A rapid filtration over silica allows easy isolation of the product and near quantitative recovery of the unreacted sulfoxide.

DFT calculations were used to investigate a mechanism of the reaction, using phenylacetylene (**1a**) and either diphenyl sulfoxide (**2a**) or methyl phenyl sulfoxide (**2e**) as reactants.[23] The free energy profile obtained for the reaction with **2a** is represented in Scheme 6 (For the reaction with **2e**, see the Supporting Information). The first step, **A**→**B**, corresponds to the protonation of the acetylene by triflic acid. This step has a barrier of 10.1 kcal mol^{-1} and is endergonic ($\Delta G = 5.6$ kcal mol^{-1}), reflecting the instability of the vinyl cation intermediate. The reaction proceeds with O-nucleophilic attack of the sulfoxide on the carbocation, **B**→**D**, producing an intermediate



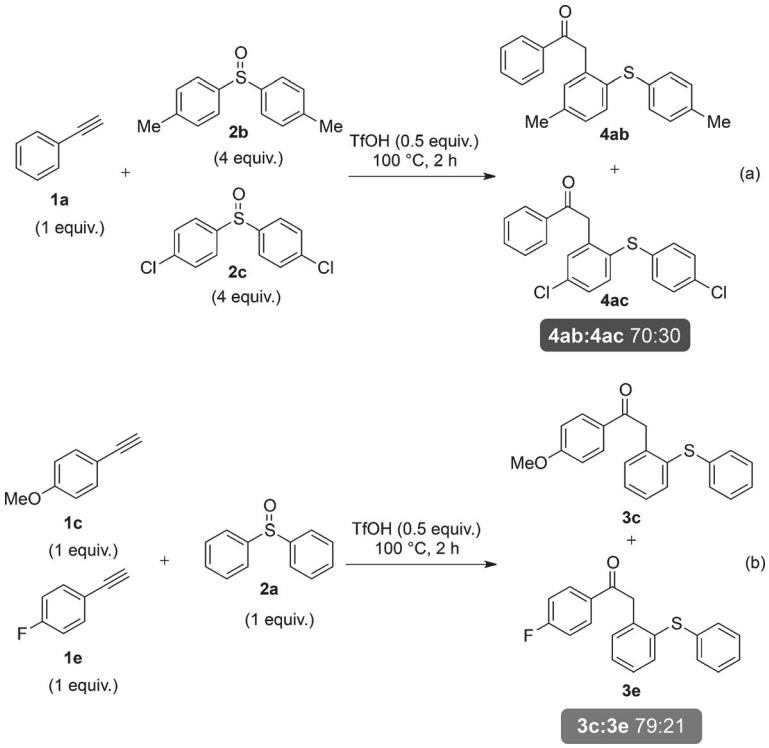


Scheme 4. Hydrative arylation of alkynes with various aryl sulfoxides. All reactions were carried out with 4 equiv of sulfoxide and 0.5 equiv of TfOH. See the Supporting Information for details.

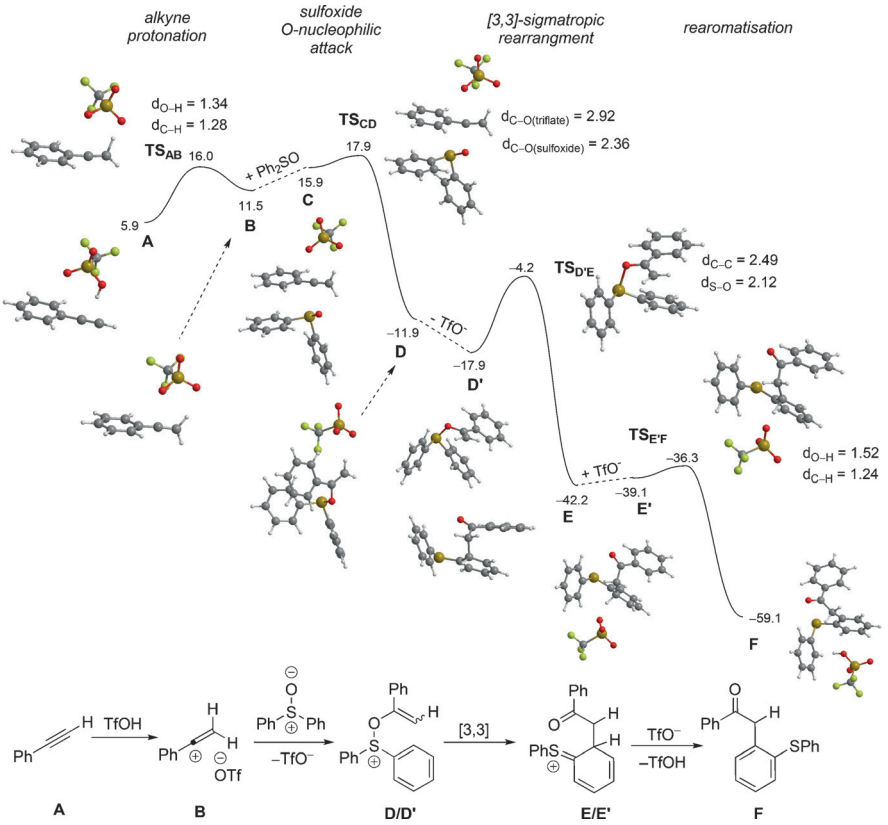
with the O–C bond fully established and a formally positive S-atom. This is a fairly easy step, with a barrier of only 2.0 kcal mol^{-1}, being also clearly exergonic ($\Delta G = -27.8$ kcal mol^{-1}). The reaction is completed with a [3,3]-sigmatropic shift, followed by facile rearomatization (**D**→**E**→**F**) with triflate acting as base, and regenerating triflic acid. The barrier associated with the [3,3] shift has a value of $\Delta G^{\ddagger} = 13.7$ kcal mol^{-1}, suggesting a facile step, under the reaction conditions (see Scheme 2 and 3). The two final steps are both exergonic, as is the entire reaction with an overall free energy balance of $\Delta G = -65.0$ kcal mol^{-1}, indicating a thermodynamically favorable process.

The profile for the reaction of **1a** with methyl phenyl sulfoxide (**2e**) was also calculated (see Figure S2 in the Supporting Information). The reaction path is similar to the one obtained for **2a**, with barriers within less than 2 kcal mol^{-1} difference for both sulfoxide O-nucleophilic attack and the final acid–base step. However, the [3,3]-sigmatropic shift has a barrier 4.4 kcal mol^{-1} higher than the one calculated for the reaction with **2a**. This difference indicates an easier reaction in the case of diphenyl sulfoxide (**2a**) and is in agreement with the experimental results discussed above (see Scheme 2 and 3).[24]

Moreover, results obtained by the calculations are also in agreement with the results of the control experiments. It is shown in Scheme 5a that sulfoxide **2b**, being more electron-rich, outcompetes **2c** for nucleophilic attack (as reflected in the relative product ratios). Calculations for diphenyl sulfoxide (**2a**) and methyl phenyl sulfoxide (**2e**) show that the energy barrier for the nucleophilic attack of **2a**, the less-electron rich sulfoxide of the pair **2a**/**2e**, lies 1.6 kcal mol^{-1} higher than the corresponding barrier for **2e**, thus reflecting the experimental results. In addition, the stability of the vinyl cation is crucial for the entire process. A more electron-rich alkyne will produce



Scheme 5. Control experiments.



Scheme 6. Schematic profile calculated for the reaction of **1a** with **2a** (distances in Å). Free energy values (kcal mol^{-1}) relative to the separated reactants. See the Supporting Information for details and for a larger version of this Scheme.

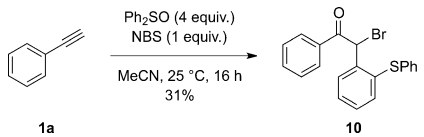
a more stable cation and therefore lead to a faster reaction, as shown by the control experiments described in Scheme 5b.

Electrospray ionization mass spectrometry is an emerging technique for monitoring of short-lived intermediates in reactions proceeding through cationic mechanisms. The application of this technique to our reaction afforded further insight into the mechanism by allowing the identification of key intermediates and expected fragments thereof (see the Supporting Information for MS spectra and further details), corroborating and consubstantiating the results obtained by DFT analysis.

Bearing a carbonyl and thioether functionality, the products of the hydrative arylation procedure lend themselves to further structural elaborations. While reduction of the aryl sulfanyl moiety has been previously reported for similar substrates,[20a] a palladium-catalyzed cross coupling of alkyl aryl sulfides with arylzinc reagents offers a possibility of increasing structural complexity in a facile manner.[25] The reaction of **4ce/ae/cf** with an arylzinc reagent and Pd-PEPPSI-SIPr afforded **5a–d** in very good yields, showing complete chemoselectivity and no competing addition of the organometallic species to the carbonyl moiety (Scheme 7a).

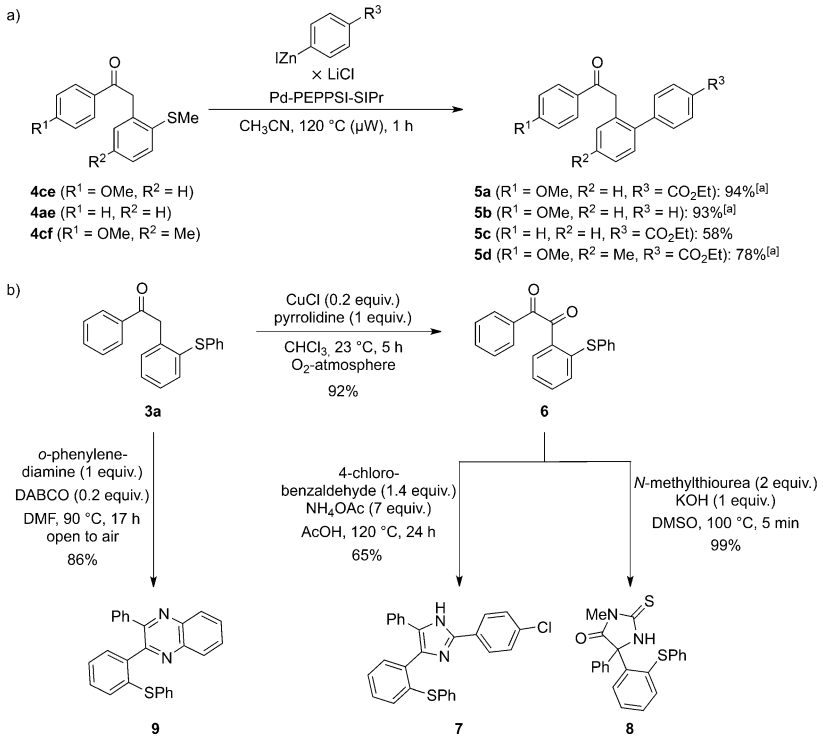
Additionally, rapid conversion of the products to drug-like aromatic heterocycles can be achieved by a simple oxidation to the corresponding 1,2-diketone (Scheme 7b). Diketone **6** is furnished in excellent yield from **3a** by a copper-catalyzed oxidation,[26] and can be smoothly converted to imidazole **7** and diaryl-thioxoimidazolidinone **8** in high yields.[27,28] Even more conveniently, aerobic oxidation of **3a** can also be conducted in situ in the presence of *o*-phenylenediamine to deliver the disubstituted quinoxaline **9** in excellent yield.[29] The overall atom economy of these sequences towards various heterocycles is testified by the fact that **9** is prepared in only two steps from phenylacetylene, diphenyl sulfoxide, *o*-phenylenediamine, air, and two simple non-metallic promoters (TfOH and DABCO). Quinoxaline cores related to **9** have been described in DNA-cleaving agents or electroluminescent materials.[30]

The activation of alkynes is not limited to the proton, the simplest electrophile. In an unoptimized experiment, combining **1a** with *N*-bromosuccinimide (NBS) and diphenyl sulfoxide (**2a**) led to the formation of α-bromo ketone **10**, in what is effectively a three-component coupling [Eq (3)].



(3)

In summary, we have developed an atom-economical, operationally simple, and metal-free hydrative arylation of alkynes. This solvent-free reaction tolerates a range of functional groups and yields valuable α-arylated ketones in good to excellent yields. The promising possibility to use electrophiles



Scheme 7. a) Palladium-catalyzed cross coupling of **4ce/ae/cf** with an arylzinc reagent. b) Facile oxidation and subsequent condensation of the products, leading to heterocycles. [a] Yield based on recovered starting material.

other than a proton hints at the generality of electrophile-driven arylation processes.

Acknowledgements

Generous support of this research by the University of Vienna is acknowledged. D.K. is a recipient of a DOC Fellowship of the Austrian Academy of Sciences. L.F.V. acknowledges Fundação para a Ciência e Tecnologia, UID/QUI/00100/2013. N.M. acknowledges the Deutsche Forschungsgemeinschaft (Grant MA 4861/4-1 and 4-2). We are indebted to Dr. I. D. Jurberg and Prof. M. Eberlin of the University of Campinas, Brazil (UNICAMP) for insightful discussions and ESI-MS in situ analysis of reaction mixtures.

Keywords: alkynes · arylation · organic chemistry · rearrangement · sulfoxides

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[24] Differences in the energy barriers of the [3,3] shift are also reflected in the geometries of the corresponding transition states. Thus, in the case of reaction with PhS(O)Me, the reactants have to move further along the reaction coordinate in order to attain the transition state, corroborating a more difficult reaction in this case. See the Supporting Information for details.
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Received: January 29, 2016
Published online on February 25, 2016