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# Nitrene Transfer Reactions Catalyzed by Gold Complexes

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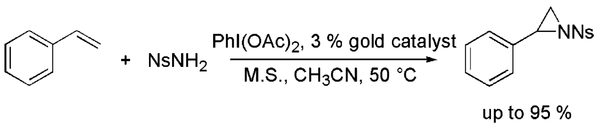

We report here the first gold-catalyzed nitrene transfer reaction. A gold(I) compound, supported by 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine ($t$Bu$_3$tpy) as the ligand, efficiently catalyzes olefin aziridination with the use of the commercially available oxidant PhI(OAc)$_2$ and sulfonamides. This system also mediates carbene insertion into benzene.

## Introduction

Metal-catalyzed nitrene transfers to unsaturated and saturated organic substrates are important tools in synthetic chemistry.[1] Various transition metal complexes such as those of rhodium, copper, ruthenium, cobalt, iron, manganese, and nickel have been shown to catalyze these transformations.[2] Our laboratory also discovered a unique disilver(I)-based catalyst, with 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2′′terpyridine ($t$Bu$_3$tpy) as the ligand, which mediates efficient olefin aziridination and intramolecular amidation of saturated C−H groups.[3] This success prompted us to explore nitrene transfer reactions that could be catalyzed by similar complexes of the other two coinage metals, gold and copper. Reported herein is the first homogeneous gold-catalyzed olefin aziridination that proceeds with the use of commercially available oxidant PhI(OAc)$_2$ and different sulfonamides. This process avoids the use of the sulfonyliminoiodinane-type nitrenoids such as PhI═NTs,[4] which are commonly employed in olefin aziridination reactions and have to be synthesized beforehand in unsatisfying yields.[1c,5] Further study of the new activity reported here may lead to a better understanding of the redox chemistry of gold and development of other gold-mediated oxidation reactions.

Gold-based catalysis has recently attracted intensive interest from the chemistry community.[6] Especially in the past few years, numerous reactions catalyzed by gold(I) and gold(III) complexes have been reported. In most cases, the metal ions act as Lewis acids that activate alkyne or alkene substrates.[7] Gold(III) is also

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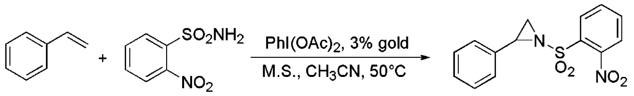
**TABLE 1. Effect of Selected Gold-based Precatalysts on an Olefin Aziridination Reaction**[a]



| entry | precatalyst | conversion (%)[b] |
|---|---|---|
| 1 | AuCl | 0 |
| 2 | AuCl + AgOTf | 0 |
| 3 | Au(PPh$_3$)Cl | 0 |
| 4 | Au(PPh$_3$)Cl + AgOTf | 7 |
| 5 | Au(P*t*-Bu$_3$)Cl | 0 |
| 6 | AuCl + 4,4′-di-*tert*-butyl-2,2′-bipyridine | 18[c] |
| 7 | AuCl + 2,2′:6′,2″-terpyridine | 50[c] |
| 8 | AuCl + 4,4′,4″-tri-*tert*-butyl-2,2′: 6′,2″-terpyridine | 56[c] |
| 9 | [Au(4,4′-di-*tert*-butyl-2,2′-bipyridine)]OTf | 60[d] |
| 10 | [Au(2,2′:6′,2″-terpyridine)]OTf | 70[d] |
| 11 | [Au(4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine)]OTf | 83 (75)[d,e,f] |
| 12 | [Au(4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine)]OTf | >95 (88)[d,e,g] |
| 13 | [Au(bathophenanthroline)]OTf | 55[h] |
| 14 | [Au(bathophenanthroline)]OTf | 80 (70)[d,e,g] |

[a] All reactions were carried out under nitrogen in predried solvent with 3% gold catalyst and 0.5 mmol amide (styrene:amide:PhI(OAc)$_2$ = 2:1:1.2). [b] NMR yield with 1,3,5-trimethoxybenzene as an internal standard. [c] AuCl and the ligand were mixed first and the formed precipitate was filtered off before the reaction was conducted. [d] Homogeneous gold complex was used (see the Supporting Information for the preparation procedure). [e] Isolated yield in parentheses. [f] Cl$^-$, NO$_3$$^-$, and ClO$_4$$^-$ have been tested as counteranions which gave 35−65% conversion. [g] *p*-Nitrosulfonamide was used. [h] Other phenanthroline-type ligands gave lower conversions.

known to readily metalate arenes[8] and this activity has been utilized in hydroarylation reactions.[9] Despite this progress, homogeneous gold-catalyzed redox transformations are still rare. Very recently, Corma and co-workers reported a homo-coupling of boronic acid with nano-CeO$_2$-supported gold(I);[10] Ito, Sawamura, and co-workers reported an interesting dehydrogenative coupling of silane and alcohol with Au(xantphos)Cl;[11] Nolan and Peréz reported a gold(I)−NHC complex that mediates carbene insertions to benzene, O−H, and N−H bonds;[12] and Shi and co-workers reported an interesting alcohol oxidation chemistry catalyzed by gold(I).[13] These examples showed that the redox potential gap between gold(I)/gold(III)[14] could possibly be tuned by employing ligands or in crystalline states, which could result in unique redox properties.

## Results and Discussion

In our initial investigation, we employed *o*-nitrosulfonamide (0.5 mmol) as the nitrene source, PhI(OAc)$_2$ (0.6 mmol) as the oxidant, and styrene (1 mmol) as the olefin substrate. The reaction was run in acetonitrile at 50 °C with 3 mol % of gold catalyst. As indicated in Table 1, simple gold(I) complexes did not exhibit any significant activity (Table 1, entries 1−5). Mixing AuCl with ligands such as pyridine, dipyridine, and terpyridine typically led to precipitations in common organic solvents, which complicates the characterization of the catalyst and the reaction (for selected examples see Table 1, entries 6−8). However, with ligands bearing *tert*-butyl or phenyl substitutions, we could prepare gold complexes[15] that have good solubilities in either CH$_2$Cl$_2$ or CH$_3$CN. Some of these compounds serve as excellent catalysts in mediating styrene aziridination (Table 1). Most noticeable is the gold(I) complex of 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2′′terpyridine, denoted as [Au(*t*Bu$_3$tpy)](OTf), which gave 83% conversion and 75% isolated yield of the aziridine product in an overnight reaction at 50 °C (Table 1, entry 11). The reaction also proceeded at room temperature; however, only about 40% conversion was observed overnight. Thus, our standard reaction conditions are set at 50 °C overnight. Counteranions did affect the product yield to a certain extent as OTf$^-$ is superior to Cl$^-$, NO$_3$$^-$, and ClO$_4$$^-$ (Table 1). Furthermore, a more reactive *p*-nitrosulfonamide was tested as the nitrenoid, which led to an almost quantitative conversion of styrene to the corresponding aziridine (Table 1, entry 12).[16]

Then *p*-nitrosulfonamide (NsNH$_2$) was employed to react with different olefins. The scope of the reaction was studied as shown in Table 2. The use of styrenes bearing different functional groups led to excellent yields of the corresponding aziridines. Norbornene and cyclooctene, as well as a substrate for an

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[7] For selected examples, see: (a) Hashmi, A. S. K.; Rudolph, M.; Weyrauch, J. P.; Woelfle, M.; Frey, W.; Bats, J. W. *Angew. Chem., Int. Ed.* **2005**, *44*, 2798. (b) Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2005**, *127*, 6966. (c) Staben, S. T.; Kennedy-Smith, J. J.; Toste, F. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 5350. (d) Zhang, L. M.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 11806. (e) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2003**, *125*, 9584. (f) Mizushima, E. S.; Sato, K.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4563. (g) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11553. (h) Yao, X.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 6884. (i) Hashmi, A. S. K.; Weyrauch, J. P.; Rudolph, M.; Kurpejovic, E. *Angew. Chem., Int. Ed.* **2004**, *43*, 6545. (j) Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 15978. (k) Nieto-Oberhuber, C.; Munoz, M. P.; Bunuel, E.; Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402. (l) Sromek, A. W.; Gevorgyan, M. R. V. *J. Am. Chem. Soc.* **2005**, *127*, 10500.

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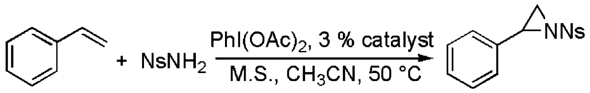
[13] Guan, B.; Xing, D.; Cai, G.; Wan, X.; Yu, N.; Fang, Z.; Yang, L.; Shi, Z. *J. Am. Chem. Soc.* **2005**, *127*, 18004.

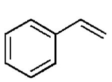
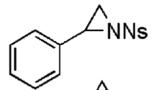
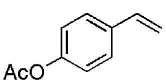
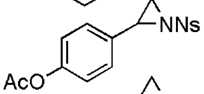
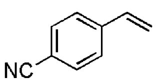
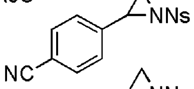
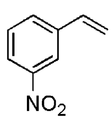
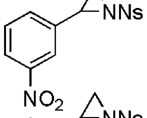
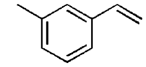
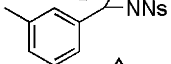
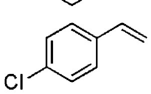
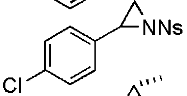
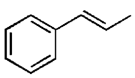
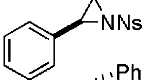
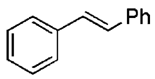
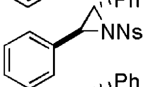
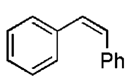
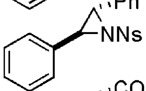
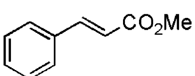
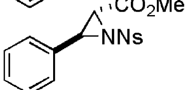
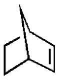
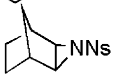
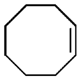
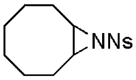
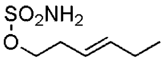
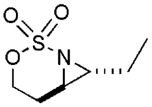
[14] Rao, B. V. *Anal. Chim. Acta* **1992**, *258*, 167.

[15] Please see the Supporting Information for procedures.

[16] For the reactivity comparison of different sulfonamides, see: Leung, S. K.-Y.; Tsui, W.-M.; Huang, J.-S.; Che, C.-M.; Liang, J.-L.; Zhu, N. *J. Am. Chem. Soc.* **2005**, *127*, 16629.

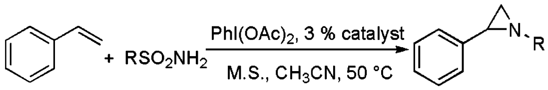
**TABLE 2. Aziridination of Olefins by [Au(*t*Bu$_3$Tpy)](OTf)[a]**

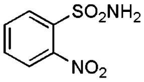
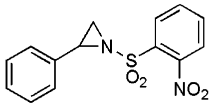
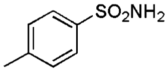
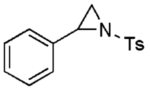
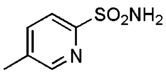
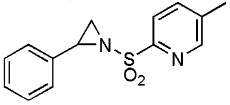
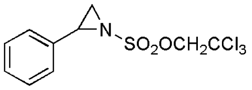


| Entry | Olefin | Product | yield(%)[b] |
|---|---|---|---|
| 1 |  |  | 88 |
| 2 |  |  | 68 |
| 3 |  |  | 53 |
| 4 |  |  | 49 |
| 5 |  |  | 80 |
| 6 |  |  | 95 |
| 7 |  |  | 94[c] |
| 8 |  |  | 66[c] |
| 9 |  |  | 80[c] |
| 10 |  |  | 25[c] |
| 11 |  |  | 79[d] |
| 12 |  |  | 37 |
| 13 |  |  | 55[e] |

[a] All reactions were carried out overnight at 50 °C. [b] Isolated yield. [c] Only the trans isomer was detected. [d] Exo product. [e] NMR yield.

**TABLE 3. Effect of Different Nitrene Sources[a]**



| Entry | Amide | Product | Yield(%)[b] |
|---|---|---|---|
| 1 |  |  | 75 |
| 2 |  |  | 40 |
| 3 |  |  | 54 |
| 4 | $CCl_3CH_2OSO_2NH_2$ |  | 25 |

[a] All reactions were carried out overnight at 50 °C. [b] Isolated yield.

intramolecular example, also worked for this reaction. The aziridination of simple aliphatic olefins could not be mediated by our gold catalyst, except for activated ones and intramolecular reactions (Table 2, entries 11−13).

In entry 9 of Table 2, we did observe total conversion of the cis-olefin substrate to the trans aziridine product, which may suggest a stepwise mechanism instead of a concerted one. Che and co-workers used isolated Ru−nitrene complexes to react with cis-olefins.[21] In their experiments mixed products were detected and several different mechanisms were proposed to explain the result. Interestingly, some metal−porphyrin complexes also gave *trans*-aziridine product from cis-olefins in aziridination reactions,[2j] and in most cases, the stereoselectivity largely depended on reaction temperatures (for example −20 vs 0 °C).[2] In our case, we cannot completely rule out the possibility that gold(I) acts as a Lewis acid; however, as shown in Table 1, all commonly used cationic gold(I) Lewis acids did not show catalytic activity, which seems to argue strongly against the Lewis acid mechanism.

Other types of sulfonamides can be employed in this system (Table 3), albeit with lower product yields in some cases. It should be noted that the reactions with 5-methylpyridine-2-sulfonamide and trichloroethylsulfamate ester as the nitrene sources did not work for the disilver(I)-based catalytic system we reported previously,[3] which indicates reactivity difference between the two systems (Scheme 1). This reaction has a limitation that the aziridination of unactivated olefins could not be catalyzed so far. More research is required to obtain a more active gold-based catalyst in the future.

Electron-spray mass spectrometry (ESI-MS) was used to characterize the precatalyst [Au(*t*Bu$_3$tpy)](OTf). The molecular peak at ~598.2 bearing a 2+ charge was observed (Figure 1), indicating a molecular formula of $[Au_2(t\text{Bu}_3\text{tPy})_2]^{2+}$ (calculated *m*/*z* 598), which is in agreement with the elemental analysis of the complex.[17] This result suggests that the gold(I) precatalyst is in a dimeric $[Au_2(t\text{Bu}_3\text{tPy})_2](OTf)_2$ form in solution, which may resemble the disilver(I) structure we reported previously.[3]

The [Au(*t*Bu$_3$tpy)](OTf) system exhibits other interesting reactivities as well. It can mediate a carbene insertion to neat benzene with ethyl diazoacetate (EDA). A 57% conversion was obtained overnight at 80 °C with diethyl fumarate and diethyl maleate produced as side products in an almost identical ratio (Scheme 2).[18] When the reaction temperature was lowered to 50 °C, only 28% of the benzene insertion product was generated with the remaining EDA untouched. The [Au(bathophenanthroline)](OTf) complex exhibits similar activity, as shown in Scheme 2. Recently, Nolan and Pérez reported a NHC−gold complex that can mediate the carbene insertion.[12] They detected the carbene insertion into the aromatic C−H bond, instead of the aromatic ring. In our case we did not detect any C−H insertion product; the result may suggest that gold can mediate

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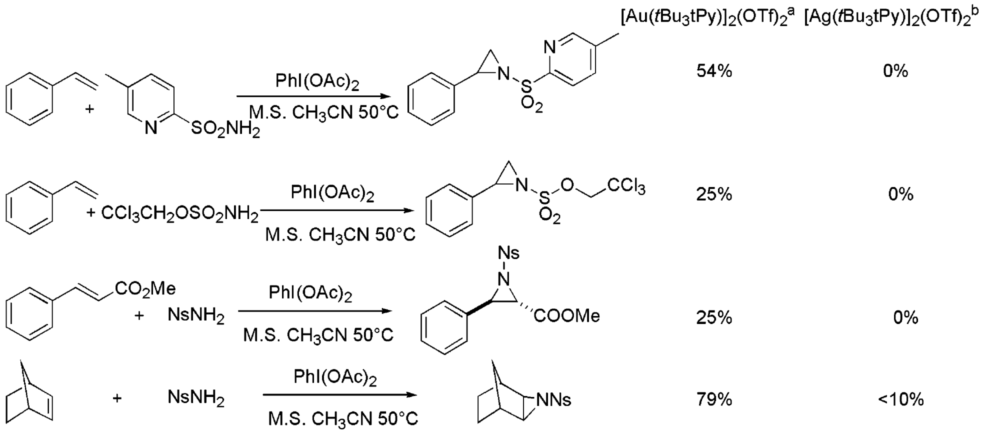
(17) Main peaks at 598.7 and 598.2 indicate a 2+ charge, which suggests a dimmer structure. Elemental analysis for $[Au t\text{Bu}_3\text{tpy}]_2(OTf)_2$, $[C_{28}H_{35}AuF_3N_3O_3S]_2$ found (%): C 45.19, H 4.66, N 5.42. Calcd: C 44.98, H 4.72, N 5.62.

(18) Please see spectra in the Supporting Information.

**SCHEME 1. Difference between Gold- and Silver-Mediated Nitrene Transfer Reactions**



[a] All are isolated yields. [b]The silver-catalyzed reactions were also repeated under different conditions; no improvement was found with the change of temperature, solvent, and reaction time.

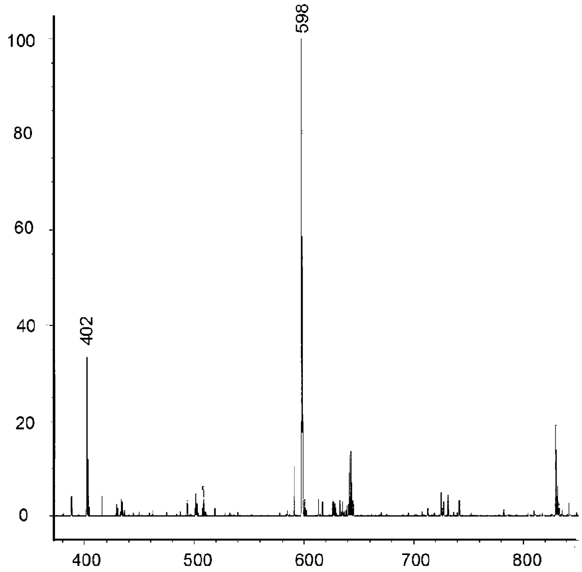
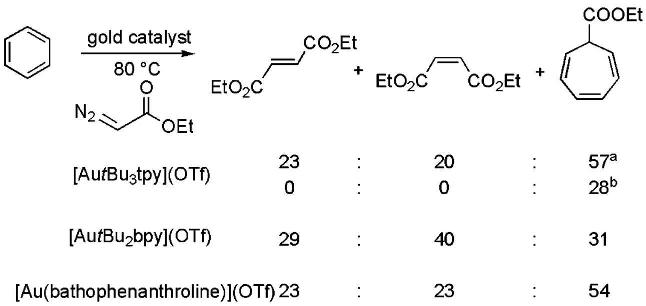


**FIGURE 1.** ESI-MS spectrum for $[Au(tBu_3tPy)]_2(OTf)_2$

**SCHEME 2. Gold-Mediated Carbene Insertion to Benzene**



[a] NMR conversions. [b]Reaction at 50 °C with 3% catalyst.

carbene insertion via different reaction pathways depending on the ligand systems employed.

## Conclusions

In summary, we have described the first example of the gold-catalyzed nitrene transfer reaction. Styrenes bearing various functional groups could react with different sulfonamides directly to give good yields of the aziridine products. Organic reactions mediated by gold with pyridine-based ligands are rare. We hope to further explore pyridine-based ligands and study the scope, mechanism, and applications of the chemistry described here. This discovery provides opportunities for more extensive exploration of gold-mediated redox transformations. Potential intermediates may be stabilized and characterized in the future, which would significantly enhance our understanding of the gold oxidation chemistry and the metal−nitrene interaction in general.

## Experimental Section

**General Procedure To Prepare Gold Complexes.** In general, gold(I) complexes were made according to a previously reported procedure,[19] except that 0.95 equiv of silver was used to eliminate potential silver contamination. The yields were around 50% to 60% based on gold. In a typical process, a portion of $AuSMe_2Cl$ (100 mg, 0.337 mmol) was dissolved in 30 mL of $CH_2Cl_2$ at room temperature. Then 77 mg of AgOTf (0.320 mmol, 0.95 equiv) was added and the mixture was stirred vigorously in the dark for 2 h. The precipitate was filtered off, 136 mg of $t$Bu$_3$tpy (0.337 mmol, 1 equiv) was added, and the solution was stirred in the dark for an additional 2 h. The reaction solution was filtered again to remove any potential residual precipitate and evaporated to dryness. Then the residue was dissolved in $CH_2Cl_2$ and hexanes were added to precipitate the gold complex, which was dried under vacuum. This process has been repeated numerous times in different scales, and the resulting products showed the same catalytic reactivity.

**General Procedure for the Olefin Aziridination Reaction.** The gold(I) catalyst (3 mol %) was dissolved in 4 mL of $CH_3CN$ with104 mg of styrene (1 mmol), 100 mg of $NsNH_2$ (0.5 mmol), 193 mg of $PhI(OAc)_2$ (0.6 mmol), and 500 mg of 4 Å molecular sieves under nitrogen. The reaction was then stirred at 50 °C overnight. The reaction mixture was filtered through a short Celite pad, washed with $CH_2Cl_2$, and concentrated and the residue was applied to column chromatography to afford the purified product.

**Proton and Carbon NMR Data for 4-[1-(4-Nitrobenzenesulfonyl)aziridin-2-yl]benzonitrile.** IR (% T): 3105 (w), 3056 (w), 2916 (w), 2231 (m), 1652 (w), 1533 (s), 1349 (s), 1265 (s), 1167 (s), 1092 (m), 737 (s). $^1H$ NMR ($\delta$, ppm): 8.41−8.39 (dd, 2H, $J$ = 6.9,1.9 Hz), 8.20−8.18 (dd, 2H, $J$ = 6.9, 1.9 Hz), 7.63−7.61 (dd, 2H, $J$ = 6.7, 1.7 Hz), 7.37−7.35 (dd, 2H, $J$ = 6.7, 1.7 Hz), 3.96−3.93 (dd, 1H, $J$ = 7.2, 4.4 Hz), 3,15−3.13 (d, 1H, $J$ = 7.2 Hz), 2.47−2.46 (d, 1H, $J$ = 4.4 Hz). $^{13}C$ NMR ($\delta$, ppm): 150.8,

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[19] Uson, R.; Laguna, A.; Navarro, A.; Parish, R. V.; Moore, L. S. *Inorg. Chim. Acta* **1986**, *112*, 205.

143.4, 139.6, 132.6, 129.3, 127.2, 124.5, 118.2, 112.6, 40.5, 37.1. 37.1. HRMS: MW calcd 329.3305, MW found (M + 1) 330.3430.

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**Supporting Information Available:** The characterization of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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