Gold-Catalyzed Reactions of Enynals/Enynones with Norbornenes: Generation and Trapping of Cyclic *o*-Quinodimethanes (*o*-QDMs)

Shifa Zhu,* Zhicai Zhang, Xiaobing Huang, Huanfeng Jiang,* and Zhengjiang Guo^[a]

o-Quinodimethane (*o*-QDM), a transient short-lived and highly reactive species, has attracted great curiosity from chemists over the past 40 years, both from theoretical and synthetic points of view.^[1] As *cis*-dienes, *o*-QDMs are much more reactive than the related 'classical dienes' (such as butadiene and cyclopentadiene) in Diels–Alder reactions (DA) with olefins. They can be classified as two main types based on their structures: acyclic *o*-QDMs and cyclic *o*-QDMs (Scheme 1). During the past decades, the acyclic *o*-QDM



Scheme 1. DA reactions involving o-QDMs.

has been used as a versatile building block in the synthesis of lignans, terpenes, anthracyclines alkaloids, steroids, and other natural products by inter- or intramolecular DA reactions (Scheme 1A).^[2] Similarly, trapping of the latter would allow rapid access to the rigid fan-like structures (Scheme 1B). These interesting skeletons, which were generally difficult to acquire by conventional methods, have been extensively utilized as rigid building blocks for molecular tweezers and clips,^[3] rigid cavitands,^[4] and molecular self-as-

[a]	Prof. Dr. S. Zhu, Z. Zhang, X. Huang, Prof. Dr. H. Jiang, Z. Guo
	School of Chemistry and Chemical Engineering
	South China University of Technology
	Guangzhou 510640 (P.R. China)
	E-mail: zhusf@scut.edu.cn
	jianghf@scut.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300232.

sembly.^[5] However, the generation and trapping of the cyclic o-QDM was reported to be much scarcer than the acyclic one due to its higher reactivity and greater steric hindrance.^[6,7] For example, 2,3-dihydronaphthalene (2,3-DHN), a simple cyclic o-QDM, was typically generated by the irradiation of o-divinyl benzene (o-DVB; Scheme 1B, path a).^[6] But the resulting cyclic o-QDM would rearrange to 1,2-DHN quickly by a [1,5]-H-shift before being trapped by the dienophiles (Scheme 1B).^[6] Furthermore, the photolysis reaction is highly limited because the reaction conditions are not applicable for irradiation-sensitive groups or substrates.^[6,7] Therefore, the efficient generation and trapping of the cyclic o-QDM with dienophiles still remained a challenge in organic synthesis. In past decades, transition metals have shown exceptional efficiency in catalyzing a variety of chemical transformations.^[8] We were curious about the possibility of generating the cyclic o-QDM from an easily available starting material through a transition-metal-catalyzed pathway, with the ultimate aim of synthesizing the fan-like structures by trapping such highly reactive species (Scheme 1B, path b).

Recently, we developed an efficient silver-catalyzed method to generate the highly reactive hydroxy-*o*-QDM, which was trapped by the alkenes to form polysubstituted tetrahydronaphthols (Scheme 2).^[9] It was the first example of transition-metal-catalyzed generation of acyclic hydroxyl-*o*-QDM species. Owing to the greater challenge to generate



Scheme 2. Transition-metal-catalyzed generation of o-QDMs.

Chem. Eur. J. 2013, 19, 4695-4700

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY CONLINE LIBRARY

- 4695

the highly reactive and sterically-hindered cyclic *o*-QDM, also as part of our continuing efforts to develop *o*-QDM chemistry, we then decided to set out to search for an efficient, practical, and transition-metal-catalyzed method to generate and trap the cyclic *o*-QDM.

Enynal has been used as a versatile synthon in the Lewis acid catalyzed benzannulation in the past decade.^[10] We noticed that in the Lewis acid catalyzed benzannulation of enynal with alkene, a well-accepted intermediate **B**, which came from the pyrylium **A**, was frequently proposed.^[10] It eventually led to the formation of 1,2-DHN, which was often believed to proceed through β -H elimination (Scheme 2, path a). However, we envisioned that path b, in which a cyclic *o*-QDM intermediate was generated, would also be possible. The product 1,2-DHN could also be formed from the cyclic *o*-QDM by a [1,5]-H-shift process, or at least in part. If this was the case, we anticipated the cyclic *o*-QDM could be trapped by the dienophiles to form different fan-like molecules through DA reactions. Herein, we would like to report the results of our investigations.

Initial efforts were made to systematically investigate various catalytic reaction conditions for the reaction of enynal 1a and alkenes 2. By following the conditions reported in our previous work,^[9] different alkenes were then tested. Disappointedly, both the styrene derivatives and aliphatic olefins, which were good substrates in our previous work, did not afford the desired products 3 (Table 1, entry 1). Even when norbornene (NB), a naked and more reactive alkene, was used as the substrate, no desired product 3 was detected either (entry 2). Other metal salts (Cu, Pd, Pt, Rh, Hg), which are traditionally used to activate the $C \equiv C$ triple bond, were also proven ineffective. In the past decade, gold catalysis has emerged as a powerful method for activating alkynes toward nucleophiles.^[11,12] The reduced oxophilicity of gold relative to other transition metals allowed for high functional-group tolerance and presented an ideal platform for selective functionalization of alkynes. Therefore, we then turned to different inorganic and organic gold sources as the catalysts. To our delight, when NaAuCl₄·2H₂O or KAuCl₄·2H₂O were applied as the catalyst, both afforded the desired product 3a in 21% yield (entries 3, 4). Additionally, 2-picolinic acid and N-heterocyclic carbene (NHC)-supported gold(III) complexes could catalyze the reactions as well (entries 5, 6). Among them, $[AuCl_3(IMes)]$ (IMes = N,N'-bis[2,4,6-(trimethyl)phenyl]imidazol-2-ylidene) afforded the product 3a in 34% yield (entry 6). Trying to improve the reaction efficiency by adding a silver salt to scavenge the chloride atoms of [AuCl₃(IMes)] failed (entry 7). The analogues Au^I complex, [AuCl(IMes)], with or without silver salts, could catalyze the reaction as well (entries 8, 9). But the yields were lower than the corresponding Au^{III} complexes. With the fact that Au^{III} was a better catalyst to promote this transformation than the others being tested, we then focused our attention to find better Au^{III} sources. Recently, Selectfluor was extensively used as a mild organic oxidant in the reactions to oxidize the transition metals, especially in the conversion of Au^I to Au^{III}.^[12] Inspired by these

Table 1. Optimization of reaction conditions.[a]



Entry	Catalyst	Additive	Alkene	Yield 3	Yield 4
	•			[%]	[%]
1	AgSbF ₆	-	styrene	n.d.	n.d.
2	AgSbF ₆	-	norbornene	n.d.	n.d.
3	NaAuCl ₄ •2H ₂ O	-	norbornene	21	n.d.
4	KAuCl ₄ •2H ₂ O	-	norbornene	21	n.d.
5	[AuCl ₂ (Pic)] ^[b]	-	norbornene	15	n.d.
6	[AuCl ₃ (IMes)]	_	norbornene	34	n.d.
7 ^[c]	[AuCl ₃ (IMes)]	AgSbF ₆	norbornene	n.d.	n.d.
8	[AuCl(IMes)]	-	norbornene	20	n.d.
9 ^[d]	[AuCl(IMes)]	AgSbF ₆	norbornene	21	n.d.
10	[AuCl(IMes)]	Selectfluor	norbornene	47	25
11	[AuCl(SIMes)] ^[e]	Selectfluor	norbornene	37	17
12	[AuCl(IPr)] ^[f]	Selectfluor	norbornene	35	3
13	SIPr-AuCl	Selectfluor	norbornene	52	14
14 ^[g]	[AuCl(IMes)]	Selectfluor	norbornene	58	33
15 ^[g,h]	[AuCl(IMes)]	Selectfluor	norbornene	60 ^[i]	29 ^[i]
16 ^[h]	-	Selectfluor	norbornene	n.d.	n.d.

[a] Unless otherwise noted, the reactions were performed in DCE at 80 °C for 24 h by using 5 mol% cat. and 10 mol% add. under N₂, 1/2=1:5, [1]=0.05 M. The yield was determined by ¹H NMR spectroscopy (n.d.=not determined). [b] Pic=2-picolinate. [c] 15 mol% AgSbF₆. [d] 5 mol% AgSbF₆. [e] SIMes=1,3-dimesityl-4,5-dihydroimidazol-2-ylidene. [f] IPr=1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. [g] 1/2=1:10. [h] 15 mol% add. [i] The isolated yields were 58 and 28%, respectively.

facts, we then tried to produce the NHC-Au^{III} in situ through the reaction of NHC-Au^I and Selectfluor. Interestingly, a significant positive effect was observed when the combination of [AuCl(IMes)]/Selectfluor was applied; the yield of **3** was improved to 47% (entry 10). Additionally, a side product 4 was also isolated in 25% yield. The product 4 was formed presumably through the tandem 1,3-dipolar addition/cyclopropanation of gold carbene species. Among four different [AuCl(NHC)] complexes being tested, [AuCl-(IMes)]/Selectfluor and [AuCl(SIPr)] (SIPr = N,N'-bis(2,6diisopropylphenyl)dihydroimidazol-2-ylidene)/Selectfluor functioned better than the other two (entries 10-13). Although the yield of [AuCl(SIPr)]/Selectfluor was slightly higher than [AuCl(IMes)]/Selectfluor, however, the latter one had better reproducibility. Increasing the amount of NB or Selectfluor could improve the yields of 3 and 4 further (entries 14, 15). For example, the overall yield of 3 and 4 was up to 91% when 10.0 equivalents of NB was applied (entry 14). The best results were obtained when the reaction was conducted in 1,2-dichloroethane (DCE) at 80°C for 24 h by using 5 mol% [AuCl(IMes)] as the catalyst and 15 mol % Selectfluor as an additive under N2, and the molar ratio of 1/2 = 1:10 (entry 15). Under the optimized reaction conditions, the yields of 3 and 4 climbed to 60 and 29%, respectively. Additionally, the reaction did not occur without catalyst (entry 16).

COMMUNICATION

Table 2. Substrate scope of enynals/enynones and norbornene.^[a]



[a] The reactions were carried out under N_2 with a molar ratio of 1/2 = 1:10, [1] = 0.05 m. The yield refers to the isolated yield.

With the optimized reaction conditions (Table 1, entry 15) in hand, the substrate scope was then examined. As summarized in Table 2, the catalytic process could be successfully applied to a variety of enynals **1** when NB was used as the substrate. For example, when different aromatic alkynyl-substituted benzaldehydes were used as the substrates

(Table 2, entries 1–6), the reactions occurred smoothly with high conversion (54–100%). The conversions for those substrates substituted with electron-withdrawing groups were higher than the electron-donor ones (entries 2–5). For example, NO₂-substituted enynal **1e** gave quantitative reaction conversion (entry 5), whereas the MeO-substituted **1b** gave only 55% (entry 2). Notably, the reaction could proceed smoothly even for the pyridine-containing substrate **1f**, albeit with a slightly lower yield (entry 6). The fan-like molecules **3** dominated in all these cases. Moreover, the reactions have excellent diastereoselectivities. Only one isomer was formed in all cases, the stereochemistry of which was determined by the X-ray diffraction analysis of the single crystals **3a** and **4e** (Figure 1).



Figure 1. X-ray diffraction analysis of A) 3a and B) 4e.

It is interesting to note both norbornanyl substructures in compounds **3a** adopted the *exo*-configuration; such a configuration would efficiently reduce the steric repulsion between the perpendicular phenyl group and diethylene groups (Figure 1).

For the enynals bearing the alkyl or alkenyl alkynes, the reactions proceed efficiently as well (Table 2, entries 7-9). For these substrates, the reactions selectively gave product 3. The reaction functioned particularly efficiently for the cyclopropyl substituted 1i, which gave the corresponding product 3 in quantitative yield (entry 9). Importantly, the reaction selectivity was completely reversed when a terminal alkyne was applied (entry 10). In this case, only the cyclopropanation product 4j was obtained in 55% yield. We also noted that the reactions could proceed efficiently as well when varying \mathbf{R}^1 groups of the enynals **1** (entries 11–13). A similar reaction trend was observed for these substrates: electron-deficient substrates had better conversions and selectivity. For example, 5-MeO-enynal 1k furnished the corresponding products 3k and 4k in almost a 1:1 ratio (entry 11), whereas the corresponding electron-deficient ones (5-F and 5-CF₃) gave 31 and 3m dominantly. In addition to the enynals, enynonoes can serve as efficient substrates as well (entries 14 and 15). For example, both the methyl ketone 1n and phenyl ketone 10 furnished the corresponding fan-like molecules 3n and 3o in 70 and 76% yields, respectively. The reactions had excellent selectivities and no cyclopropanation products 4n and 4o were detected.

www.chemeurj.org

After having established the reactions of NB with enynals and enynones as a reliable and efficient synthetic process, we then proceeded to the other NB derivatives. When 2,5norbornadiene (NBD) was subjected to the same reaction conditions, however, the desired fan-type products **5** were obtained only as minor products (Table 3). The yields of

Table 3. Substrate scope of enynals/enynones and 2,5-norbornadiene.^[a]



[a] The reactions were carried out under N_2 with a molar ratio of 1/2 = 1:10, [1] = 0.05 m. The yield refers to the isolated yield.

compounds **5** were typically lower than 20%, except in the case of **5i** (Table 3, entry 6). Compound **5** has the same skeleton as **3** but with different stereochemistry, in which one norbornenyl group took the *endo-* and another took the *exo*-configuration. This orientation may be partially attributed to the balance between steric hindrance and electronic effects.

Actually, another unexpected 1-naphthyl ketone **6** dominated the product distribution. Such ketones substituted at the 1-position of naphthalenes were typically difficult to access through traditional Friedel–Crafts acylation.^[13] The yields of **6** were ranging from 40–95%. In this reaction, a tandem DA/retro-DA reaction was proposed. The retro-DA process was accompanied by the release of one molecule of cyclopentadiene (see the mechanistic discussion for details). Therefore, the NBD here served as the acetylene (HC \equiv CH) equivalent, a gas which is not easily accessible and operationally inconvenient in common labs. Due to the excellent substrate scopes and selectivities, this reaction could be regarded as a reliable alternative method to prepare such 1-naphthyl ketones.

More importantly, this gold-catalyzed system also had excellent functional-group tolerance (Table 4). For example, in





[a] 1/2 = 1.5, [1] = 0.05 M. The yield refers to the isolated yield.

addition to the simple NB and NBD, the norbornenes substituted with a terminal or internal alkenyl group could also be used as the substrates and furnished the desired products **7a** and **7b** in 75 and 78% yields, respectively. When benzonorbornene was applied as the substrate, the corresponding product **7c** was formed in 95% yield. The structure and stereochemistry of **7c** were also confirmed by X-ray diffraction analysis (see the Supporting Information). We also noted that even the functional groups of ether, ester, and halogen atoms can also be well-tolerated; in these cases, the corresponding products (**7d–f**) could be formed in moderate yields (38–45%).

COMMUNICATION



Scheme 3. Proposed reaction mechanism.

A plausible mechanism is shown in Scheme 3. Initially, the catalytically active species, [Au^{III}ClF(NHC)]⁺ (simplified as [Au] in the catalytic cycle), was generated in situ from the oxidation of [AuCl(NHC)] with Selectfluor.^[12] The coordination of the triple bond of enynal 1 to [Au] enhanced the electrophilicity of the alkyne, and the subsequent nucleophilic attack of the carbonyl oxygen atom to the electrondeficient alkyne would form the intermediate pyrylium A, which was in equilibrium with another intermediate carbene C. Two different pathways would then be followed based on two different intermediates: 1) tandem DA/DA or DA/ retro-DA based on pyrylium A and 2) tandem 1,3-dipolar addition/cyclopropanation based on carbene C. Pyrylium A served as an electron-deficient diene that was trapped by NB or NBD to form intermediate B. Due to the instability of **B**, the cleavage of the carbon–oxygen bond, followed by the release of catalyst [Au], formed the key intermediate, o-QDM E. In the presence of NB, a second DA reaction then occurred to give product 3. While in the presence of NBD, a retro-DA reaction occurred instead to furnish naphthyl ketone 6, accompanied by the release of pentadiene. When it came to the carbene C, the 1,3-dipolar addition and cyclopropanation reactions proceed sequentially to form product 4.

In conclusion, we have developed an efficient gold-catalyzed method to generate the highly reactive cyclic *o*-QDM species from the easily available enyals or enynones. This method allowed rapid access to a variety of structurally unique fan-like products. Meanwhile, an important retro-DA reaction was also observed when NBD was applied as the dienophile of the DA reaction. In this case, all kinds of 1-naphthyl ketones were formed in good to excellent yields. Owing to the mild reaction conditions, excellent diastereoselectivities, and high functional-group tolerance, this system holds considerable potential in the design of structurally interesting fan-like molecules, which are frequently encountered in molecular self-assembly and materials chemistry.

Experimental Section

General experimental procedure: The corresponding enynals/enynones (0.2 mmol) and norbornene (188.3 mg, 2.0 mmol) were added to a solution of the catalyst combination of [AuCl(IMes)] (5.37 mg, 0.01 mmol) and Selectfluor (10.62 mg, 0.03 mmol) in DCE (4 mL, 0.05 M). The reaction mixture was stirred under a nitrogen atmosphere at 80 °C for 24 h. After the reaction was finished, the mixture was filtered by short silica, and then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired products **3** and **4**.

Acknowledgements

We are grateful for funding from the NNSFC (20902028 and 21172077), the Program for New Century Excellent Talents in University (NCET-10–0403), Guangdong NSF (10351064101000000), the National Basic Research Program of China (973) (2011CB808600), SRF for ROCS, State Education Ministry, and the Fundamental Research Funds for the Central Universities, SCUT (2012ZZ0038).

Keywords: carbenes • diastereoselectivity • Diels-Alder reaction • gold catalysis • QDM

- For general reviews on *o*-QDMs, see: a) J. L. Segura, N. Martin, *Chem. Rev.* **1999**, *99*, 3199; b) N. Martin, C. Seoane, M. Hanack, *Org. Prep. Proced.* **1991**, *23*, 237.
- [2] a) G. Quinkert, H. Stark, Angew. Chem. 1983, 95, 651; Angew. Chem. Int. Ed. Engl. 1983, 22, 637; b) G. A. Kraus, Y. Wu, J. Org. Chem. 1992, 57, 2922; c) K. Hashimoto, M. Horikawa, H. Shirahama, Tetrahedron Lett. 1990, 31, 7047; d) W. Oppolzer, K. Keller, Angew. Chem. 1972, 84, 712; Angew. Chem. Int. Ed. Engl. 1972, 11, 728; e) G. A. Kraus, L. Chen, Synth. Commun. 1993, 23, 2041; f) N. C. Yang, C. Rivas, J. Am. Chem. Soc. 1961, 83, 2213; g) P. G. Sammes, Tetrahedron 1976, 32, 405; h) J. L. Charlton, M. M. Alauddin, Tetrahedron 1987, 43, 2873; i) F. Nerdel, W. Brodowski, Chem. Ber. 1968, 101, 1398; j) M. Pfau, S. Combrisson, J. E. Rowe, N. D. Heindel, Tetrahedron 1978, 34, 3459; k) R. Haag, J. Wirz, P. J. Wagner, Helv. Chim. Acta 1977, 60, 2595; l) T. J. Connolly, T. Durst, Tetrahedron 1997, 53, 15969.
- [3] F.-G. Klärner, B. Kahlert, Acc. Chem. Res. 2003, 36, 919.
- [4] a) M. J. Stoermer, D. N. Butler, R. N. Warrener, K. D. V. Weerasuria, D. P. Fairlie, *Chem. Eur. J.* 2003, *9*, 2068; b) D. N. Butler, R. Smits, D. A. C. Evans, K. D. V. Weerasuria, R. N. Warrener, *Tetrahedron Lett.* 1996, *37*, 2157; c) T. Mathew, J. Tonne, G. Sedelmeier, C. Grund, M. Keller, D. Hunkler, L. Knothe, H. Prinzbach, *Eur. J. Org. Chem.* 2007, 2133.
- [5] a) G. H. Clever, W. Kawamura, S. Tashiro, M. Shiro, M. Shionoya, Angew. Chem. 2012, 124, 2660; Angew. Chem. Int. Ed. 2012, 51, 2606; b) D. M. Engelhard, S. Freye, K. Grohe, M. John, G. H. Clever, Angew. Chem. 2012, 124, 4828; Angew. Chem. Int. Ed. 2012, 51, 4747; c) G. H. Clever, M. Shionoya, Chem. Eur. J. 2010, 16, 11792.
- [6] a) M. Pomerantz, G. W. Gruber, J. Am. Chem. Soc. 1971, 93, 6615;
 b) D. Vuk, Z. Marini, K. Molcanov, B. Kojic-Prodic, M. Sindler-Kulyk, *Tetrahedron* 2012, 68, 6873.

www.chemeurj.org

- [7] a) C. Di Valentin, M. Freccero, M. Sarzi-Amade, R. Zanaletti, *Tetra-hedron* 2000, 56, 2547; b) E. M. Cabaleiro-Lago, J. Rodriguez-Otero, A. Pena-Gallego, J. Mol. Struct. 2007, 811, 141.
- [8] a) J. F. Hartwig, Organotransition Metal Chemistry, from Bonding to Catalysis; University Science Books: New York, 2010; b) L. Yin, J. Liebscher, Chem. Rev. 2007, 107, 133; c) R. Jana, T. P. Pathak, M. S. Sigman, Chem. Rev. 2011, 111, 1417; d) A. Molnar, Chem. Rev. 2011, 111, 2251; e) N. Miyaura, A. Suzuki, Chem. Rev. 1995, 95, 2457; f) A. Roglans, A. Pla-Quintana, M. Moreno-Mañas, Chem. Rev. 2006, 106, 4622; g) B. M. Rosen, K. W. Quasdorf, D. A. Wilson, N. Zhang, A.-M. Resmerita, N. K. Garg, V. Percec, Chem. Rev. 2011, 111, 1346; h) J.-P. Corbet, G. Mignani, Chem. Rev. 2006, 106, 2651; i) G. Evano, N. Blanchard, M. Toumi, Chem. Rev. 2008, 108, 3054; j) A. Bino, M. Ardon, E. Shirman, Science 2005, 308, 234; k) H. B. Kagan, O. Riant, Chem. Rev. 1992, 92, 1007; m) K. C. Nicolaou, S. A. Snyder, T. Montagnon, G. Vassilikogiannakis, Angew. Chem. 2002, 114, 1742; Angew. Chem. Int. Ed. 2002, 41, 1668; n) J.G. Smith, "The Diels-Alder Reaction." Organic Chemistry. 3rd ed. New York, NY: McGraw-Hill, 2011, 588-589; o) A. C. Weedon, in The Chemistry of Enols, Wiley, New York, 1990, 615-621.
- [9] S. F. Zhu, R. X. Liang, H. F. Jiang, W. Q. Wu, Angew. Chem. 2012, 124, 11019; Agnew. Chem. Int. Ed. 2012, 51, 10861.
- [10] a) N. Asao, T. Nogami, S. Lee, Y. Yamamoto, J. Am. Chem. Soc. 2003, 125, 10921; b) N. Asao, H. Aikawa, J. Org. Chem. 2006, 71, 5249; c) N. Asao, K. Sato, Menggenbateer, Y. Yamamoto, J. Org. Chem. 2005, 70, 3682; d) N. Asao, H. Aikawa, Y. Yamamoto, J. Am. Chem. Soc. 2004, 126, 7458; e) L. Liu, L. Wei, J. Zhang, Adv. Synth. Catal. 2010, 352, 1920; f) Y. Chen, M. Chen, Y. Liu, Angew. Chem. 2012, 124, 6285; Angew. Chem. Int. Ed. 2012, 51, 6181.
- [11] a) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* 2008, *108*, 3351;
 b) N. Mankad, F. D. Toste, *Chem. Sci.* 2012, *3*, 72; c) C. H. Cheon, O. Kanno, F. D. Toste, *J. Am. Chem. Soc.* 2011, *133*, 13248; d) Y.-M. Wang, C. N. Kuzniewski, V. Rauniyar, C. Hoong, F. D. Toste, *J. Am. Chem. Soc.* 2011, *133*, 12972; e) C. Zhao, F. D. Toste, R. G. Berg-

man, J. Am. Chem. Soc. 2011, 133, 10787; f) R. M. Zeldin, F. D. Toste, Chem. Sci. 2011, 2, 1706; g) M. J. Campbell, F. D. Toste, Chem. Sci. 2011, 2, 1369; h) Z. J. Wang, C. J. Casey, R. G. Bergman, K. N. Raymond, F. D. Toste, J. Am. Chem. Soc. 2011, 133, 7358; i) A. Z. González, D. Benitez, E. Thatchouk, W. A. Goddard, F. D. Toste, J. Am. Chem. Soc. 2011, 133, 5500; j) A. D. Melhado, G. W. Amarante, Z. J. Wang, M. Luparia, F. D. Toste, J. Am. Chem. Soc. 2011, 133, 3517; k) L. Zhang, J. Am. Chem. Soc. 2005, 127, 16804; l) G. Li, L. Zhang, Angew. Chem. 2007, 119, 5248; Angew. Chem. Int. Ed. 2007, 46, 5156; m) G. Zhang, Y. Peng, L. Cui, L. Zhang, Angew. Chem. 2009, 121, 3158; Angew. Chem. Int. Ed. 2009, 48, 3112; n) L. Ye, L. Cui, G. Zhang, L. Zhang, J. Am. Chem. Soc. 2010, 132, 3258; o) L. Ye, Y. Wang, D. H. Aue, L. Zhang, J. Am. Chem. Soc. 2012, 134, 31; p) A. Mukherjee, R. B. Dateer, R. Chaudhuri, S. Bhunia, S. N. Karad, R.-S. Liu, J. Am. Chem. Soc. 2011, 133, 15372; q) S. M. Abu Sohel, R.-S. Liu, Chem. Soc. Rev. 2009, 38, 2269; r) A. S. K. Hashmi, Chem. Rev. 2007, 107, 3180; s) A. Fürstner, Chem. Soc. Rev. 2009, 38, 3208; t) N. T. Patil, Y. Yamamoto, Chem. Rev. 2008, 108, 3395.

- [12] a) A. D. Melhado, W. E. Brenzovich, Jr., A. D. Lackner, F. D. Toste, J. Am. Chem. Soc. 2010, 132, 8885; b) W. E. Brenzovich Jr., D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard III, F. D. Toste, Angew. Chem. 2010, 122, 5651; Angew. Chem. Int. Ed. 2010, 49, 5519; c) G. Zhang, L. Cui, Y. Wang, L. Zhang, J. Am. Chem. Soc. 2010, 132, 1474.
- [13] a) S. Gmouh, H. Yang, M. Vaultier, Org. Lett. 2003, 5, 2219; b) M. J. Earle, U. Hakala, C. Hardacre, J. Karkkainen, B. J. McAuley, D. W. Rooney, K. R. Seddon, J. M. Thompson, K. Wähälä, Chem. Commun. 2008, 9, 1101; c) M. Gopalakrishnan, P. Sureshkumar, V. Kanagarajan, J. Thanusu, Catal. Commun. 2005, 6, 753; d) M. Al-Masum, M. C. Wai, H. Dunnenberger, Synth. Commun. 2011, 41, 2888.

Received: January 21, 2013 Published online: March 4, 2013

4700 -