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Stereoselective Olefination of Unfunctionalized Ketones via Ynolates

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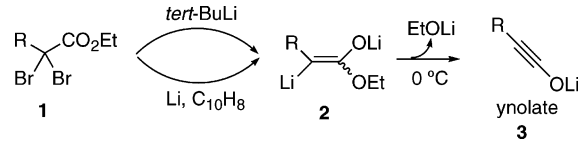
Ynolates react with ketones at room temperature to afford α,*β*,*β*-trisubstituted acrylates (tetrasubstituted olefins) with 2:1−8:1 geometrical selectivities. This can be regarded as a new olefination reaction of ketones giving tetrasubstituted olefins in good yield, even in the case of sterically hindered substrates. The reaction mechanism involves cycloaddition of ynolates with a carbonyl group and subsequent thermal electrocyclic ring-opening of the resulting *β*-lactone enolates. The stereoselectivity is determined in the ring-opening, which is regulated by torquoselectivity. In this paper, we describe the scope and limitations of olefination of ketones via ynolates and discuss the stereocontrol mechanism.

Introduction

Olefination of carbonyl compounds is a fundamental carbon−carbon bond-forming reaction in synthetic organic chemistry.[1] Although conventional olefinations, such as the Wittig[2] and the Horner−Wadsworth−Emmons reactions,[3] are generally effective in providing di- and trisubstituted olefins from aldehydes, the low reactivity and/or stereoselectivity of these methods make them less desirable in the olefination of ketones to furnish tetrasubstituted olefins,[4] which serve as important synthetic intermediates and useful units in medicinal chemistry[5] and material science.[6] Considering how difficult it is to achieve high stereoselectivity in the olefination of ketones using phosphorus reagents, development of a novel reaction with a new mechanism would be extremely useful.[7]

We have reported a novel methodology for the generation of ynolate anions **3** via cleavage of ester dianions **2** derived from α,α-dibromo esters **1**[8] (Scheme 1).[9] Since ynolate anions are ketene anion equivalents, they are expected to act as multifunctional reactive species.[10] We have already demonstrated the synthetic utility of the unique anions, including tandem reactions providing polysubstituted carbocycles,[11] cycloaddition with aldimines giving *β*-lactams,[12] and 1,3-dipolar cycloadditions with nitrones leading to *β*-amino acids.[13]

SCHEME 1



In a previous paper, we reported an olefination of aldehydes using the ynolate anions **3**,[14] via ring-opening of the *β*-lactone enolates **4** derived from the cycloaddition

(1) Kelly, S. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon: Oxford, 1991; Vol. 1, pp 729−817.

(2) For a representative review of the Wittig olefination, see: Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, 89, 863.

(3) For a representative review for Horner−Wadsworth−Emmons reaction, see: Wadsworth, W. S. *Org. React.* **1977**, *25*, 73−253.

(4) For recent examples of olefination of ketones leading to tetrasubstituted olefins, see: (b) Sano, S.; Yokoyama, K.; Teranishi, R.; Shiro, M.; Nagao, Y. *Tetrahedron Lett.* **2002**, *43*, 281−284. (c) Sano, S.; Takehisa, T.; Ogawa, S.; Yokoyama, K.; Nagao, Y. *Chem. Pharm. Bull.* **2002**, *50*, 1300−1302. (d) Mantani, T.; Shiomi, K.; Konno, T.; Ishihara, T.; Yamanaka, H. *J. Org. Chem.* **2001**, *66*, 3442−3448.

(5) For an example, see: Levenson, A. S.; Jordan, V. C. *Eur. J. Cancer* **1999**, *35*, 1628−1639.

(6) For recent examples, see: (a) Valliant, J. F.; Schaffer, P.; Stephenson, K. A.; Britten, J. F. *J. Org. Chem.* **2002**, *67*, 383−387. (b) Rathore, R.; Deselnicu, M. I.; Burns, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 14832−14833. (c) Harada, N.; Saito, A.; Koumura, N.; Uda, H.; de Lange, B.; Jager, W. F.; Wynberg, H.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7241−7248.

(7) For recent examples of stereoselective construction of tetrasubstituted olefins via carbometalation of alkynes, see: (a) Itami, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2003**, *125*, 14670−14671. (b) Zhou, C.; Emrich, D. E.; Larock. R. C. *Org. Lett.* **2003**, *5*, 1579−1582. (c) Zhu, N.; Hall. D. G. *J. Org. Chem.* **2003**, *68*, 6066−6069. (d) Tessier, P. E.; Penwell, A. J.; Souza, F. E. S.; Fallis, A. G. *Org. Lett.* **2003**, *5*, 2989−2992. (e) Tietze, L. F.; Kahle, K.; Raschke, T. *Chem. Eur. J.* **2002**, *8*, 401−407. (f) Marino, J. P.; Nguyen, H. N. *J. Org. Chem.* **2002**, *67*, 6291−6296. (g) Hojo, M.; Murakami, Y.; Aihara, H.; Sakuragi, R.; Baba, Y.; Hosomi, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 621−623. For other approaches, see: (h) Maciagiewicz, I.; Dybowski, P.; Skowronska, A. *Tetrahedron* **2003**, *59*, 6057−6066. (i) Shimizu, M.; Fujimoto, T.; Minezaki, H.; Hata, T.; Hiyama, T. *J. Am. Chem. Soc.* **2001**, *123*, 6947−6948. (j) Kakiya, H.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2001**, *57*, 10063−10069. (k) Ide, M.; Nakata, M. *Synlett* **2001**, 1511−1515.

(8) Shindo, M.; Sato, Y.; Koretsune, R.; Yoshikawa, T,; Matsumoto, K.; Itoh, K.; Shishido, K. *Chem. Pharm. Bull.* **2003**, *51*, 477−478.

(9) (a) Shindo, M. *Tetrahedron Lett.* **1997**, *38*, 4433−4436. (b) Shindo, M.; Sato, Y.; Shishido, K. *Tetrahedron* **1998**, *54*, 2411−2422. (c) Shindo, M.; Koretsune, R.; Yokota, W.; Itoh, K.; Shishido, K. *Tetrahedron Lett.* **2001**, *42*, 8357−8360.

(10) For reviews, see: (a) Shindo, M. *Synthesis* **2003**, 2275−2288. (b) Shindo, M. *J. Synth. Org. Chem. Jpn.* **2000**, *58*, 1155−1166. (c) Shindo, M. *Yakugaku Zasshi* **2000**, *120*, 1233−1246. (d) Shindo, M. *Chem. Soc. Rev.* **1998**, *27*, 367−374.

(11) (a) Shindo, M.; Sato, Y.; Shishido, K. *J. Am. Chem. Soc.* **1999**, *121*, 1, 6507−6508. (b) Shindo, M.; Matsumoto, K.; Sato, Y.; Shishido, K. *Org. Lett.* **2001**, *3*, 2029−2031. (c) Shindo, M.; Sato, Y.; Shishido, K. *J. Org. Chem.* **2001**, *66*, 7818−7824.

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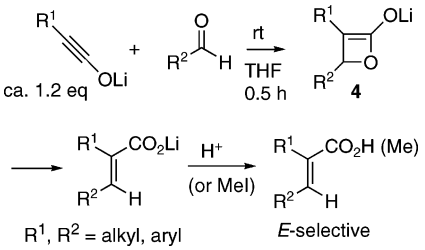
SCHEME 2



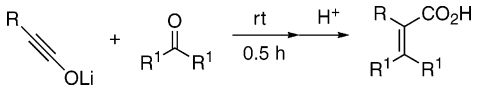
of aldehydes with ynolates, with excellent *E* selectivity (Scheme 2), and briefly mentioned the preliminary results of olefination of ketones.[15] In the next paper, we presented a stereoelectronic effect on the *E*/*Z* selectivity in the olefination of acetophenone and benzophenone.[16] Although we have achieved high *Z*-selectivity in the olefination of acylsilanes to give vinylsilanes,[17] the generality including the mechanistic considerations in the olefination of unfunctionalized ketones have not been known. The development of general methods for the efficient olefination of ketones is, therefore, still a challenge. In this paper, we describe the scope and limitations of the olefination of unfunctionalized ketones via ynolates with mechanistic considerations on the stereocontrol.

Results

Olefination of ketones providing tetrasubstituted olefins was investigated under the conditions used in olefination of aldehydes. Table 1 shows the olefination of symmetrical ketones. As expected, the tetrasubstituted olefins were synthesized in good yields. The sterically hindered ynolate **3d**, aromatic ynolate **3e**, and trimethylsilyl-substituted ynolate **3g** afforded the tetrasubstituted olefins in good yields. It was also demonstrated that not only the lithium−halogen exchange method (method A) but also the reductive lithiation method (method B) for the generation of the ynolates were applicable to the olefination.[9c]

Next, we examined the stereoselective olefination of unsymmetrical ketones. As shown in Table 2, the reactions of methyl-, butyl-, cyclohexyl-, and phenyl-substituted ynolates with aryl alkyl ketones gave the desired olefins in good yield and in unprecedented *E*-selectivities (entries 1−4, 6−10) except for indanone, which afforded the *Z*-olefin preferentially (entry 11).[18] These results indicate that aryl groups and alkyl groups of ketones were recognized efficiently in the olefination. Olefination of acetophenone with the trimethylsilyl-substituted ynolate was unsuccessful (entry 5), probably due to enolization of the ketone by the sterically hindered ynolate. Olefination of chalcone preferred the (*E*,*E*)-diene, where the aryl group is cis to the carboxylate (entry 12). The stereochemical preference for olefination of pinacolone (*tert*-butyl methyl ketone) is the production of the *Z*-olefin (entry 13). Since the *E*-selectivity using 2-methylcyclohexanone was poor, the recognition between the secondary and tertiary carbons on sp^3 carbons is not very good (entry 14). Table 2 also demonstrates that the one-pot methyl esterification can be applicable to this olefination of ketones.

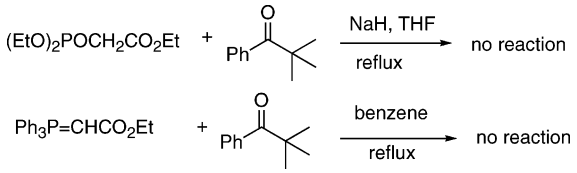
TABLE 1. Olefination of Symmetrical Ketones via Ynolates



entry	ynolate (R)	ketone (R^1)	conditions[a]	product	yield (%)
1	**3a** (Bu)	Ph	A	**5**	82
2	**3a** (Bu)	Me	A	**6**	51
3	**3a** (Bu)	$-(CH_2)_5-$	A	**7**	68
4	**3b** (Me)	Ph	A	**8**	>99
5	**3e** (Ph)	Ph	B	**9**	94
6	**3f** (*i*-Pr)	Ph	B	**10**	99
7	**3d** (*t*-Bu)	Ph	B	**11**	85
8	**3f** ($PhCH_2CH_2$)	Ph	B	**12**	94
9	**3g** (Me_3Si)	Ph	A	**13**	98[b]

[a] After ketones were added to a THF solution of Ynolates at room temperature, the mixture was stirred for 0.5 h. Condition A: Ynolates were prepared with *t*-BuLi. Condition B: ynolates were prepared with naphthalene-catalyzed lithiation. [b] Isolated as methyl ester.

SCHEME 3



For comparison, olefination of *tert*-butyl phenyl ketone via the Wittig and Horner−Wadsworth−Emmons reactions was attempted, but no reaction occurred (Scheme 3). It can be seen from these results that ynolates turn out to be much better reagents than conventional reagents for the olefination of ketones, especially sterically hindered ones.

During the course of this research, we also observed a stereoelectronic effect, which has already been reported.[16] The elucidation of this effect, as well as that of the stereoselectivity, requires theoretical calculations and will be published elsewhere.

Discussion

The olefination of ketones via ynolates consists of the two steps of cycloaddition and ring-opening as shown in Scheme 2. This olefination has two notable features, the first being high reactivity toward sterically hindered ketones. Ynolates can react with phenyl *tert*-butyl ketone *at room temperature* to provide the tetrasubstituted olefin in good yield. It would be probably due to the fact that ynolates are highly nucleophilic compact nucleophiles

(12) (a) Shindo, M.; Oya, S.; Sato, Y.; Shishido, K.*Heterocycles* **1998**, *49*, 113−116. (b) Shindo, M.; Oya, S.; Murakami, R.; Sato, Y.; Shishido, K. *Tetrahedron Lett.* **2000,** *41*, 5943−5946.

(13) (a) Shindo, M.; Itoh, K.; Tsuchiya, C.; Shishido, K. *Org. Lett.* **2002,** *4*, 3119−3121. (b) Shindo, M.; Itoh, K.; Ohtsuki, K.; Tsuchiya, C.; Shishido, K. *Synthesis* **2003**, 1441−1445.

(14) Shindo, M.; Sato, Y.; Shishido, K. *Tetrahedron Lett.* **1998**, *39*, 4857−4860.

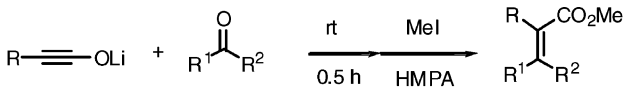
(15) For a pioneering work, see: Kowalski, C. J.; Fields, K. W. *J. Am. Chem. Soc.* **1982**, *104*, 321−323.

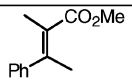
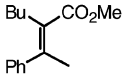
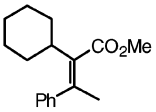
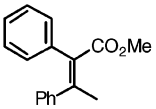
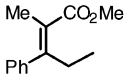
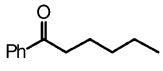
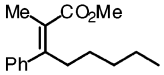
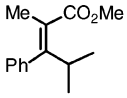
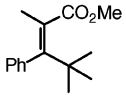
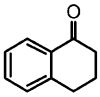
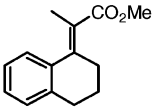
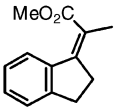
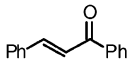
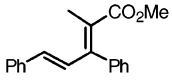
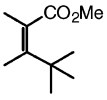
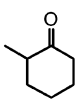
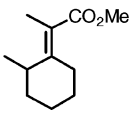
(16) Shindo, M.; Sato, Y.; Shishido, K. *J. Org. Chem.* **2000**, *65*, 5443−5445.

(17) Shindo, M.; Matsumoto, K.; Mori, S.; Shishido, K. *J. Am. Chem. Soc.* **2002**, *124*, 6840−6841.

(18) The configurations of the unknown olefins were determined by NOE experiments. The *E*/*Z* ratios were determined by ^1H NMR spectra. See the Supporting Information.

TABLE 2. Olefination of Unsymmetrical Ketones via Ynolates



entry	ynolate (R)		ketone	product		
				major isomer	yield (%)	major:minor
1	**3b**	Me			**14** >99	80 : 20
2	**3a**	Bu			**15** 82	85 : 15
3	**3c**	cyclohexyl			**16** 79	85 : 15
4	**3e**	Ph[a]			**17** 66	86 : 14
5	**3g**	Me_3Si		-	mess	-
6	**3b**	Me			**18** 89	86 : 14
7	**3b**	Me			**19** 96	83 : 17
8	**3b**	Me			**20** 86	73 : 27
9	**3b**	Me			**21** 74	85 : 15
10	**3b**	Me			**22** 96	83 : 17
11	**3b**	Me			**23** 89	75 : 25
12	**3b**	Me			**24** 66	79 : 21
13	**3b**	Me			**25** 67	81 : 19
14	**3b**	Me			**26** 80	67 : 33

[a] The ynolate was prepared via naphthalene-catalyzed lithiation.

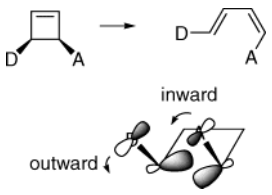


FIGURE 1. Torquoselectivity for conrotatory electrocyclic ring-opening of a *cis*-3-donor-4-acceptor-cyclobutene.

bearing linear sp-hybridized carbons at the reaction site. In addition, although it is not clear that the first step giving β-lactone enolates is the concerted cycloaddition or the stepwise addition−cyclization, the reverse reaction, which is frequently found in aldol reactions of ketones, is constrained by the spontaneous conversion of the highly labile adduct, the β-lactone enolate, into the α,β-unsaturated carboxylate at room temperature. As described above, the conventional phosphorus ylide methods, like the Wittig reaction, are sensitive to steric congestion, presumably due to the steric hindrance of the triphenylphosphorus unit and their moderate nucleophilicity.

The second feature is the stereoselectivity. The *E*/*Z* stereochemistry of the olefination products is determined in the thermal conrotatory electrocyclic ring-opening of the β-lactone enolates. Since this ring-opening would be an exothermic irreversible reaction, the transition state also should be "reactant-like". Thus, the relative energy of the transition states should take precedence over the relative thermodynamic stability of the products. The ring-opening of β-lactone enolates should be similar to that of oxetenes. It is known that cycloadditions of aldehydes or ketones with alkynyl ethers are promoted by Lewis acids to give alkoxyoxetenes, which are converted to α,β-unsaturated esters via ring-opening.[19] There have been, however, few reports on the *E*/*Z* selectivity, especially for the olefination of ketones. Thermal ring-opening of cyclobutenes giving butadienes has been well studied experimentally[20,21] and theoretically. In particular, Houk's torquoselectivity[22] provides a reasonable explanation for our results (Figure 1).

The olefination of aldehydes corresponds to the ring-opening of 3-alkyl(or 3-aryl)cyclobutenes (Figure 2). It has been reported that 3-methylcyclobutene gives only *E*-alkenes,[23] which is in good agreement with our results. In both cases, alkyl substituents rotate outward exclusively. Houk and co-workers interpret this finding, based on theoretical calculations, as a steric effect, which, in part, involves repulsion between filled orbitals of R′ and the σ-orbital of the breaking C−C bond.[24] In the case of β-lactone enolates, it can be similarly suggested that the alkyl and the aryl groups (R′) derived from aldehydes rotate outward, partially due to repulsion between filled orbitals of the alkyl (or aryl) group (R′) and the σ-orbital of the breaking C−O bond. This repulsion would be larger than the steric repulsion between the alkyl group (R′) and the substituent (R) derived from the ynolate, unless the transition state is late. This would be one reason the thermodynamically unstable (*E*)-olefins were generated exclusively.

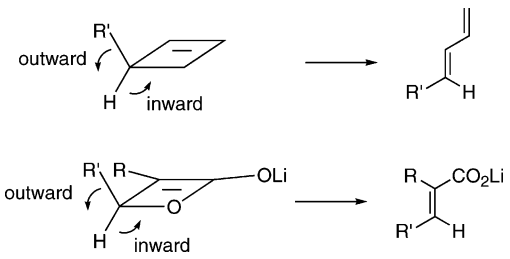


FIGURE 2. Electrocyclic ring-opening of 3-alkylcyclobutenes and β-lactone enolates derived from aldehydes.

The olefination of ketones via ynolates corresponds to the ring-opening of 3,3-dialkyl(or aryl)cyclobutenes, which was extensively studied by Stevens[20] and Houk.[25] Stevens reported that 3-*tert*-butyl-3-methylcyclobutenes preferentially gave the *E*-isomer as the major isomer, which is not in accord with our results (Figure 3). In his case, since the transition state occurs at a relatively late stage, if the *tert*-butyl group rotates inwardly, the steric repulsion between the *tert*-butyl group and the methylene group would be critical and thus the *E*-isomer would be favored. In our case, because the transition state would occur at an early stage, the steric repulsion between the *tert*-butyl and oxygen atom would be expected to be smaller than in Stevens' case. According to Houk's torquoselectivity, the electron-donating groups rotate outward and the electron-accepting substituents inward (Figure 1). In our case, although the obvious electron-accepting substituents are not present, some orbital interactions should nonetheless participate in the selectivity. Recently, the role of σ^* orbitals as acceptors has been discussed by Murakami[26] and Houk.[27] If the σ^* orbital of the C−C bond is supposed to be more electron accepting than that of the C−H bond,[28] the inward rotation of the *tert*-butyl

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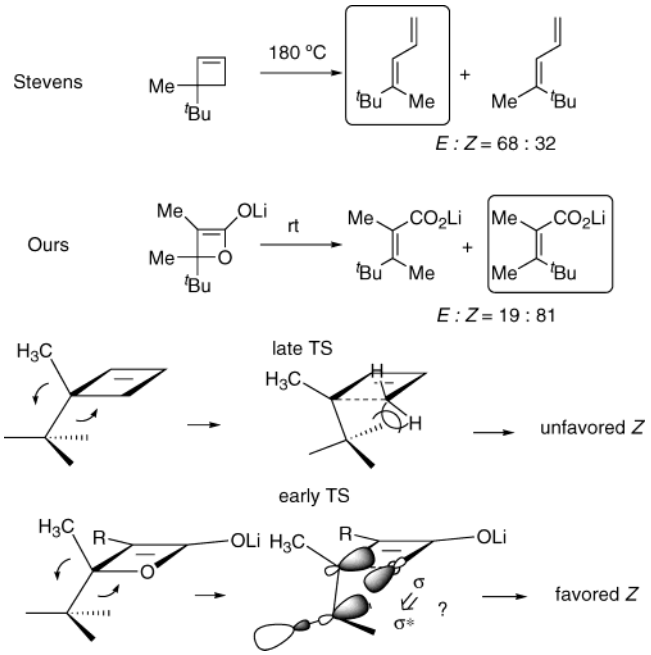

FIGURE 3. Electrocyclic ring-opening of 3-*tert*-butyl-3-methylcyclobutene and β-lactone enolate derived from pinacolone.

group might be expected. Further theoretical calculations are still needed before a more precise explanation of these results can be forthcoming.

In contrast, the results of olefination of phenyl alkyl ketones are consistent with that of 3-methyl-3-phenylcyclobutene; that is, the phenyl group rotates outward preferentially in both cases (Figure 4). In this case, since the phenyl group has an electron-rich π-orbital, it can be regarded as an electron-donating group compared with the alkyl group. The stereoelectronic factor would overcome the steric factor. Our findings are consistent with those indicating that a phenyl group bearing an electron-donating substituent at the para position rotates outward more preferentially and that the one bearing an electron-withdrawing group rotates inward.[16] In the olefination of indanone and chalcone, however, the phenyl group prefers to rotate inward. As the reason is unclear, more detailed theoretical calculations are required.

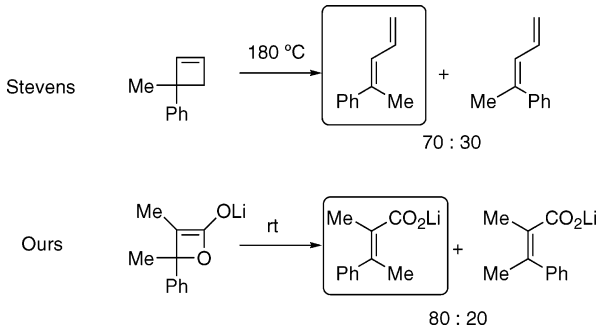

FIGURE 4. Electrocyclic ring-opening of 3-methyl-3-phenylcyclobutene and the β-lactone enolate derived from acetophenone.

In conclusion, we have developed a new olefination reaction of ketones via ynolates. The reaction mechanism, involving cycloaddition of the ynolate with a carbonyl, followed by thermal electrocyclic ring-opening of the resulting β-lactone enolates, is quite different from the conventional ylide and metal carbenoid methods. Thus, it would constitute a new category of olefination. The stereoselectivity is determined in the ring-opening, which is mainly regulated by stereoelectronic effects and torquoselectivity, which can be predicted theoretically. Since ynolates are highly reactive, even sterically hindered ketones can be olefinated under mild conditions to give tetrasubstituted olefins in good yield and in unprecedented *E*/*Z* selectivity. Although the detailed stereocontrol mechanism is still unclear, this reaction can be applied to a wide variety of organic syntheses, especially sterically congested systems.

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Supporting Information Available: General experimental procedures and spectral data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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