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Amine-Catalyzed Coupling of Aldehydes and Ketenes Derived from Fischer Carbene Complexes: Formation of β-Lactones and Enol Ethers

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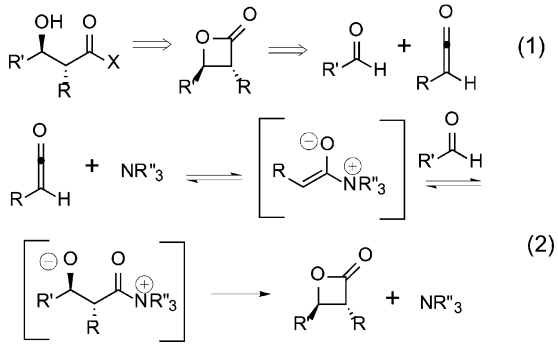
Abstract: Aldehydes react with ketenes generated from photolysis of Fischer chromium carbene complexes to generate either β-lactones or enol ethers resulting from decarboxylation of β-lactones. The reaction is catalyzed by tertiary amines and can occur with diastereoselectivity greater than 20:1 with DMAP as the catalyst.

Considerable effort has recently been directed toward the diastereo- and enantioselective synthesis of β-lactones (2-oxetanones).[1,2] This is due in part to their presence in biologically active natural products,[3] but more importantly, the 2-oxetanone moiety displays a rich pattern of reactivity. Apart from more common ester-type reactivity, these species undergo several interesting reactions that are atypical of esters and lactones.[1] Also, β-lactones contain a "masked aldol" connectivity. Therefore, diastereoselective β-lactone synthesis effectively constitutes a means for producing either syn or anti aldol products while at the same time obviating the necessity for enolate or enol ether formation that is required in many current selective aldol reactions.[4] Despite their synthetic utility, few effective diastereoselective methods exist for formation of β-lactones, and even fewer of these are enantioselective.[1b,2]

The most versatile route to β-lactones is the [2 + 2] cycloaddition between ketenes and carbonyl compounds, which has been known for more than 90 years (eq 1).[5] However, ketenes are usually not reactive enough to trap efficiently most carbonyl compounds. Hence, a Lewis acid catalyst is typically required to enhance the reactivity of the carbonyl partner.[6] Intriguingly, Lewis base catalysts can also be utilized and, in pioneering work by Wynberg,[7] the cinchona alkaloid quinine and its pseudoenantiomer quinidine catalyzed enantioselective reactions between ketene and aldehydes or ketones. This method utilizes the enhanced nucleophilicity of the enolate-like ketene−amine adduct to promote reaction with the carbonyl partner (eq 2). However, additional activation of the carbonyl reactant was found to be extremely important since multiple electron withdrawing groups, as in trichloroacetaldehyde, were required at the α-position for productive reaction. Romo and co-workers recently investigated intramolecular ketene-aldehyde cyclizations in the hope that minimization of the entropic barriers might aid the reaction.[8] Using cinchona alkaloid derived amines, chiral β-lactones were prepared with enantiomeric excesses near or above 90%, but with modest yields. In general, limitations on the carbonyl reaction partner make this Lewis base methodology less attractive than the Lewis acid-catalyzed versions.



Fischer chromium carbene complexes are extremely useful in organic synthesis owing to their versatile reactivity.[9] A particularly useful reactivity pattern is direct insertion of a chromium-bound CO ligand into the carbene moiety yielding a chromium-bound ketene species (eq 3).[10] Hegedus employed this reactivity advantageously in β-lactam syntheses via the photoreaction of Fischer chromium carbene complexes and imines.[11] Hegedus also reported that β-lactones can be prepared via photolysis of Fischer carbene complexes and aldehydes in the presence of a Lewis acid catalyst.[12] The yields obtained in the intermolecular reactions were low (<30%),

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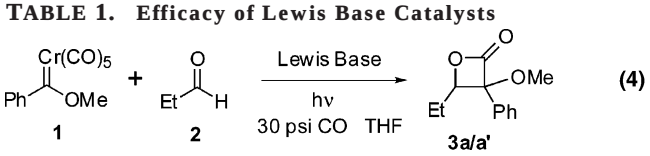
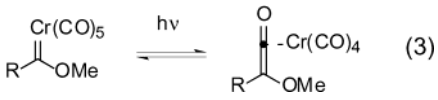
TABLE 1. Efficacy of Lewis Base Catalysts



(4)

Lewis base	yield (%)	dr (**3a**/**3a′**)
none	0	
PBu_3	0	
cinchonidine	0	
pyridine	<5	1/1
DBU	15	1.6/1
DABCO	40	2/1
DMAP	53	15/1

and the diastereoselectivity was less than 3:1 in all cases. We reinvestigated this coupling of aldehydes and photogenerated ketenes and report herein our results of an amine base-catalyzed version of this reaction that can be highly stereoselective.



(3)

We began by exploring the reaction of phenyl-methoxy Fischer chromium carbene complex **1** and propionaldehyde (Table 1). Photolysis of **1** in THF with propionaldehyde under CO pressure did not yield the desired β-lactone. In the presence of catalytic DABCO (12%), the results proved encouraging as the reaction produced the desired β-lactone in 40% yield, albeit as a 2:1 mixture of diastereomers. Screening of other potential bases initially failed to discover another that was as effective. Especially disappointing was that cinchonidine was ineffective, since cinchona alkaloids catalyze coupling with highly activated aldehydes and often with excellent enantioselectivity.[7,13] Finally, we found that DMAP catalyzed the reaction, yielding **3a/a′** in 53% yield. Even more impressive was that DMAP afforded excellent selectivity, yielding a 15:1 diastereomeric ratio. THF and toluene were both effective solvents as the yield and selectivity were not appreciably different between the two. However, reactions in either acetonitrile or methylene chloride were not productive.

The DMAP-catalyzed reaction of **1** with benzaldehyde also yielded excellent 15:1 diastereoselectivity (Table 2). Acetaldehyde, *n*-butyraldehyde, and isobutyraldehyde all reacted diastereoselectively with complex **1** to yield β-lactones **3b/b′**, **3c/c′**, and **3d/d′**. The yields were consistently modest while the diastereoselectivities were good to excellent. The reaction with isobutyraldehyde also produced some of the dimerized ketene (vide infra).

Since typical Wynberg lactonization[7] requires electron-deficient aldehydes, we sought to determine if such aldehydes were better substrates. However, bromal and *p*-chlorobenzaldehyde were ineffective, and methyl 4-formylbenzoate gave a low yield. Perplexed by this failure of electrophilic aldehydes to participate, more electron-rich aldehydes were examined. Surprisingly, a coupling reaction proceeded smoothly with 2-furfural, but product characterization revealed it to be the olefin resulting from decarboxylation. The olefin was a 3:1 mixture of isomers

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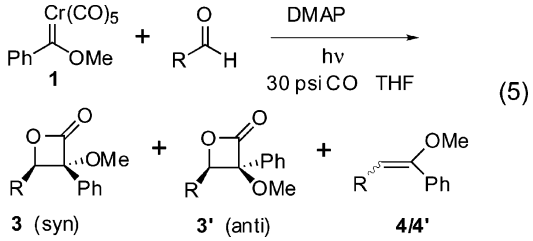
TABLE 2. Results of Ketene−Aldehyde Coupling



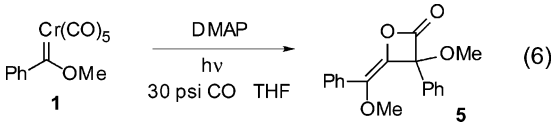
(5)

aldehyde	product	yield of **3** (%) (syn/anti)	yield of **4** (%) (*E*/*Z*)
propionaldehyde	**3a/3a′**	53 (15/1)	0
acetaldehyde	**3b/b′**	55 (8/1)	0
n-butyraldehyde	**3c/c′**	43 (23/1)	0
isobutyraldehyde	**3d/d′**	35 (4/1)	0
benzaldehyde	**3e/e′**	33 (15/1)	0
2-furfural	**4f/f′**	0	52 (3/1)
p-anisaldehyde	**4g/g′**	0	61 (3/1)
3-methyl-2-butenal	**4h/h′**	0	43 (1/1)
methyl 4-formylbenzoate	**0**	<5	0
bromal (Br_3CCHO)	**0**	0	0

4f and **4f′** favoring the *Z* isomer as determined by a NOESY spectrum. The 3:1 mixture of olefin isomers was at first alarming; however, the enol ether product, like stilbene,[14] is likely to isomerize under photochemical conditions leading to a mixture of olefin isomers that is not necessarily representative of the initial β-lactone isomeric ratio. Reaction with *p*-anisaldehyde again yielded the olefin product resulting from decarboxylation. As with the furfural reaction, the ratio of olefin isomers **4g** and **4g′** was 3:1 in favor of the *Z* olefin and the yield exceeded 60%. 3-Methyl-2-butenal gave similar results.

It was surprising that decarboxylation took place with electron-rich aryl or unsaturated aldehydes. Substitution at the C3 position in β-lactones is extremely important to the rate of thermal decarboxylation.[15] Substituents that donate electron density increase the rate of decarboxylation, since they are better able to stabilize emerging carbocation character at C3. Nevertheless, similar compounds are known to be stable at room temperature, so two other factors can be considered.[16] First, chromium(III) salts are Lewis acidic, which could increase the rate of decarboxylation if some decomposition occurred during the reaction. Second, it is also possible that the decarboxylation is facilitated by the photolytic conditions with these unsaturated systems.

A competing reaction is dimerization of the chromium-bound ketene in the absence of aldehyde (eq 6). The yield is modest (19%), but the product is a single olefin isomer. The low yield is expected due to the low concentration of photogenerated ketene complex. This result is interesting in that Hegedus reported that chromium carbene-derived ketenes do not dimerize under photolytic conditions, even in the presence of a strong Lewis acid catalyst.[10]



(6)

Understanding the diastereoselectivity required establishing the relative stereochemistry at C2 and C3. NOESY spectroscopy experiments showed only correlations between the phenyl and methoxy protons and

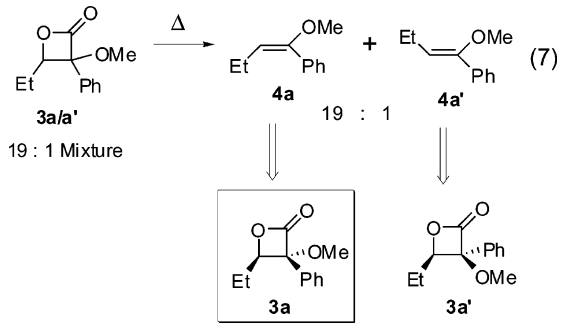
TABLE 3. ^{1}H NMR Shifts for β-Lactones

β-lactones	δ OMe (maj,min) $\Delta\delta$	δ H-C3 (maj,min) $\Delta\delta$	other H	(maj,min) $\Delta\delta$
3a/**a′**	3.37, 3.33, +**0.04**	4.60, 4.36, +**0.24**	C4 methylene	(1.28, 1.18)[a] 1.99, −**0.76**[b]
3b/**b′**	3.36, 3.35, +**0.01**	4.87, 4.63, +**0.24**	C4 methyl	1.04, 1.18, −**0.14**
3c/**c′**	3.38, 3.35, +**0.03**	4.70, 4.45, +**0.25**		
3d/**d′**	3.45, 3.37, +**0.08**	4.27, 3.99, +**0.28**	C4 methine	1.42, 2.34, −**0.92**
3e/**e′**	3.44, 3.19, +**0.25**	5.76, 5.53, +**0.23**		

[a] Shifts of diastereotopic protons. [b] Calculated from the mean value of the diastereotopic protons.

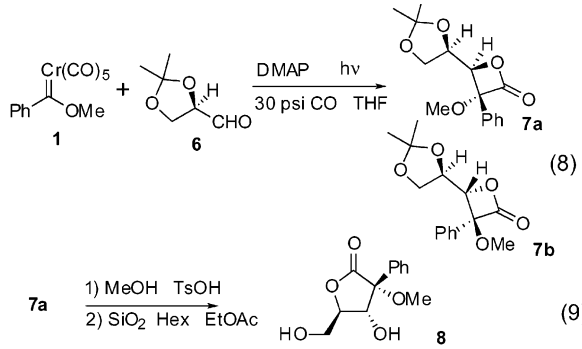
between the methine proton and the ethyl substituent. There is a literature report[17] that the relative stereochemistry of 3-methoxy-4-phenyl β-lactams can be elucidated by observing the chemical shift of the methoxy singlets. When the two groups are syn, the methoxy singlet is shifted upfield to ~3.0 ppm (instead of the usual ~3.3 ppm) due to the methoxy group residing in the phenyl ring shielding cone. The methoxy singlet of the major diastereomer in benzaldehyde adduct **3e** occurs at 3.44 ppm in the ^{1}H NMR spectrum, while the analogous signal in the minor diastereomer occurs at 3.19 ppm, suggesting that the two phenyl groups are syn in the major isomer. Since the β-lactones described herein have a phenyl substituent at the C2 position, it is logical that a similar result might be seen for alkyl substituents syn at C3. Table 3 lists the proton chemical shift values and differences between diagnostic protons for several β-lactones and the stereochemical assignments. The data suggest that the methoxy singlet is an excellent marker for determining the relative stereochemistry of β-lactones formed from aromatic aldehydes. However, for those derived from aliphatic aldehydes the methine proton at C3 has greater utility. In all cases, the methine proton is shifted downfield by approximately 0.25 ppm in the major isomer. Also useful are the signals for protons at C4 (originating from the aldehyde α-position). Though the magnitudes of the shift differences for these protons are not as consistent as those of the C3 methine protons, in all cases the C4 protons are shifted upfield for the major isomer. Further support for a syn relationship between the phenyl and alkyl substituents is the observation that the diastereotopic methylene protons in major diastereomer **3a** and the diastereotopic methyl groups in major diastereomer **3d** show quite different chemical shifts, whereas in the minor diastereomers they appear as essentially one signal.

Conclusive chemical evidence was sought to confirm these spectral assignments. The stereochemistry of **3a** was thus investigated by examining the geometry of the enol ether resulting from thermal decarboxylation.[18] Passing a 19:1 mixture of **3a** and **3a′** (in benzene) through a quartz tube packed with glass beads at 420 °C under reduced pressure (100 mmHg) gave quantitative decarboxylation. Satisfyingly, the resulting enol ethers (**4a** and **4a′**) had the same 19:1 ratio of alkene isomers indicating that no isomerization took place during the conversion (eq 7). Compounds **4a** and **4a′** are known in the literature,[19] and identification of the major isomer **4a** was confirmed by comparing the chemical shifts of the vinyl protons.[20] That **4a** was indeed the *Z*-enol ether was satisfying, as it confirmed the analysis of the β-lactone NMR data. The stereochemistries of the remaining C3 alkyl substituted β-lactones were assigned in analogy to **3a** and **3a′** due to the similarities in chemical shifts described above.



(7)

Having defined the reaction to be diastereoselective for carbon substituents cis on the β-lactone ring and most efficient with aliphatic aldehydes, we turned to the question of diastereoselection with a chiral aldehyde. Reaction with (*R*)-glyceraldehyde acetonide led to a 1.3:1 mixture of cis diastereomers **7a/b** in a 65% yield (eq 8). Surpassing all the previous examples, there was less than 1% of the trans diastereomers detected by ^{1}H NMR using the trends delineated above. The identity of the major diastereomer **7a** was established by conversion to γ-lactone **8** via cleavage of the acetonide group in acidic methanol and trans-lactonization promoted by silica gel (eq 9). The stereochemistry of **8** was established by analysis of coupling constants and a NOESY spectrum. Aldol-type additions to (*R*)-glyceraldehyde often occur with high levels of substrate control,[21] so the lack of Felkin−Anh diastereoselectivity for this β-lactone formation is unusual, but the level of cis diastereoselectivity was remarkable nonetheless.



Definitive explanations for the reaction stereoselectivity and high reactivity with electron-rich aldehydes re-

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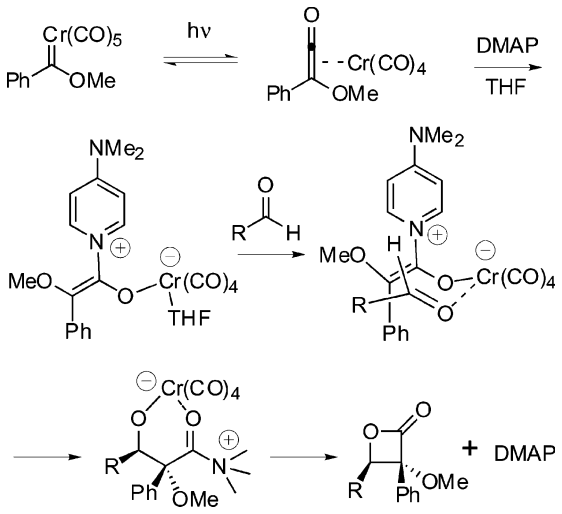
SCHEME 1



main elusive. The diastereoselectivity is dependent on the detailed geometry of reaction with the aldehyde. However, the reactivity patterns of the aldehyde partner suggest there are additional aspects of the reaction beyond the simplistic mechanism outlined in eq 2. One possible rationale that contains several unique aspects is illustrated in Scheme 1. First, the chromium tetracarbonyl moiety may remain coordinated to the ketene unit after addition of DMAP. Second, addition leads to the adduct with the methoxy group cis to the ammonium group due to favorable electronic interactions. Third, only electron-rich aldehydes displace solvent to coordinate to the weakly Lewis acidic chromium. Fourth, only aldehydes within the coordination sphere of the chromium react with the bound enolate that is expected to be otherwise fairly unreactive. Finally, reaction via a geometry that places the aldehyde substituent in a sterically favorable position leads to the correct final observed stereochemistry.

In conclusion, we have discovered an amine-catalyzed reaction between in situ formed chromium-bound ketenes and aldehydes. This reaction is particularly interesting since it can be highly diastereoselective and electron-rich aldehydes are required as the reaction partner. This heretofore unreported reactivity suggests that this reaction may be viewed as a complementary extension to the Wynberg β-lactone synthesis.

Experimental Section

***cis*- and *trans*-4-Ethyl-3-methoxy-3-phenyloxetan-2-one (3a, 3a′). General Photolysis Procedure.** Propionaldehyde (1.2 mL, 16.0 mmol) and DMAP (60 mg, 0.5 mmol) were added to a solution of pentacarbonyl[(methoxy)(phenyl) methylene]-chromium(0) (1.25 g, 4.10 mmol) in THF (35 mL) in a Pyrex pressure tube. The tube was pressurized and purged with carbon monoxide (5 cycles) and then pressurized (30 psi). The tube was irradiated with a 450 W medium-pressure Hg lamp water cooled in a quartz immersion well for 20 h. The crude reaction mixture was then concentrated and chromatographed on silica gel (99:1 hexanes/EtOAc) to yield 435 mg (53%) of 4-ethyl-3-methoxy-3-phenyloxetan-2-one as a colorless oil as a 15:1 mixture of diastereomers as evidenced by methoxy resonances at 3.37 and 3.33 ppm in the ^{1}H NMR spectrum. ^{1}H NMR (major diastereomer, 400 MHz): δ 7.42−7.33 (m, 5H), 4.62 (dd, 1H, J = 9.4, 4.7 Hz), 3.37 (s, 3H), 1.29−1.17 (m, 2H), 0.84 (t, 3H, J = 7.4 Hz). ^{13}C NMR (major diastereomer, 100 MHz): δ 169.0, 131.5, 129.5, 128.8, 127.5, 94.4, 86.3, 54.0, 24.4, 9.3. IR (neat): 3063, 2972, 2835, 1822, 1495, 1450, 1068, 858 cm^{-1}. MS (CI): 162.1 (M − CO_2)$^+$, 147.1 (45), 129.1 (15), 121.1 (41), 111.1 (27), 105.0 (100). HRMS: mass calcd for $C_{11}H_{14}O$ (M − CO_2)$^+$ 162.1045, found 162.1049. Partial data for minor isomer. ^{1}H NMR (minor diastereomer, 400 MHz): δ 7.42−7.33 (m, 5H), 4.36 (t, 1H, J = 6.7 Hz), 3.33 (s, 3H), 2.0−1.97 (m, 2H), 1.06 (t, 3H, J = 7.4 Hz).

2-Ethyl-1-methoxy-1-phenylethene (4a, 4a′). A quartz tube, packed with glass beads and equipped with a cold trap of dry ice/acetone and then a vacuum pump, was heated to 420 °C under reduced pressure (100 mmHg). 4-Ethyl-3-methoxy-3-phenyloxetan-2-one 19:1 (**3a**/**3a′**) (50 mg) in benzene (1 mL) was injected through a septa into tube, and product was collected in the trap. After removal of the solvent under reduced pressure 2-ethyl-1-methoxy-1-phenylethene was isolated in 99% yield in a 19:1 mixture of olefin isomers. Assignment of the major isomer was made by correlation of the spectral data with the reported literature values.[18,19]

(*Z*)- and (*E*)-1-Methoxy-1-phenyl-2-(2-furyl)ethene (4f/4f′). 2-Furfuraldehyde (1.32 mL, 16.0 mmol), DMAP (60 mg, 0.5 mmol), and pentacarbonyl[(methoxy)(phenyl)methylene]chromium(0) (1.25 g, 4.10 mmol) in THF (35 mL) were photolyzed following the general procedure. The crude reaction mixture was then concentrated and chromatographed on silica gel (99:1 hexanes/EtOAc) to yield 282 mg (52%) of 1-methoxy-1-phenyl-2-(2-furyl)ethene as a colorless oil as a 2.6:1 mixture of *Z*/*E* isomers, as evidenced by methoxy signals at 3.81 and 3.69 ppm in the ^{1}H NMR, inseparable by chromatography. ^{1}H NMR: (*Z* isomer) δ 7.55−7.49 (m, 2H), 7.41−7.29 (m, 4H), 6.72 (d, 1H, J = 3.4 Hz), 6.45 (ddd, 1H, J = 3.33, 1.83, 0.57 Hz), 6.20 (s, 1H), 3.69 (s, 3H); (*E* isomer) 7.41−7.29 (m, 5H), 7.17 (d, 1H, J = 1.82 Hz), 6.16 (dd, 1 H, J = 3.33, 1.84 Hz), 5.70 (s, 1H), 5.52 (d, 1H, J = 3.33 Hz), 3.79 (s, 3 H). ^{13}C NMR (mixture, 125 MHz): δ 157.6, 154.5, 151.7, 151.3, 140.6, 140.0, 136.2, 135.1, 128.8, 128.7, 128.5, 128.3, 128.2, 126.2, 111.7, 110.9, 108.5, 105.2, 102.9, 92.0, 57.7, 55.6. IR (neat): mixture 3057, 2936, 2837, 1639, 1487, 1236, 1088, 1012, 773 cm^{-1}. MS (mixture, EI): 200 (M$^+$, 15), 161 (100), 134.1 (36), 115 (27), 105.0 (85). HRMS: mass calcd for $C_{12}H_{12}O_2$ 200.0837, found 200.0834.

(*E*)-3-Methoxy-4-[(methoxy)benzylidene]-3-phenyloxetan-2-one (5). DMAP (47 mg, 0.39 mmol) and pentacarbonyl-[(methoxy)(phenyl) methylene]chromium(0) (1.0 g, 3.2 mmol) in THF (35 mL) were photolyzed following the general procedure. The crude reaction mixture was then concentrated and chromatographed on silica gel (99:1 hexanes/EtOAc) to yield 90 mg (19%) of the ketene dimer as a colorless oil and a single olefin isomer. ^{1}H NMR (400 MHz): δ 7.73−7.70 (m, 4 H), 7.49−7.42 (m, 6H), 3.74 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (100 MHz): δ 168.2, 138.8, 137.9, 133.5, 131.1, 129.6, 128.8, 128.8, 128.5, 126.9, 126.2, 96.9, 59.3, 54.8. IR (neat): 3061, 2936, 2833, 1875, 1495, 1450, 1188, 993, 696 cm^{-1}. MS (EI): 296 (M$^+$, 5), 282.1 (61), 269.1 (100), 265.1 (90), 253.1 (84), 236.1 (44), 225 (70), 197 (71), 161 (39). HRMS (EI): mass calcd for $C_{18}H_{16}O_4$ 296.1049, found 296.1048.

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Supporting Information Available: Experimental procedures and spectral data for compounds **3b/b′**, **3c/c′**, **3d/d′**, **3e/e′**, **4g/g′**, **4h/h′**, **7a/b**, and **8** and copies of ^{1}H NMR spectra for compounds **3**−**5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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