JOC*Note*

A General Method for the Synthesis of 3,5-Diarylcyclopentenones via Friedel−Crafts Acylation of Vinyl Chlorides

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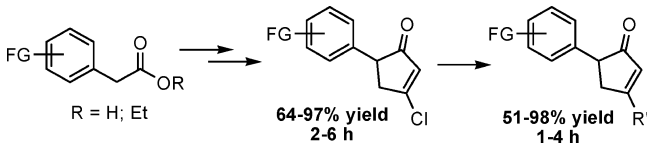

A general approach for the synthesis of 3,5-diarylcyclopentenones was developed. Key aspects of this approach are the intramolecular Friedel−Crafts-type cyclization of vinyl chlorides and subsequent Pd-catalyzed cross-coupling reactions. The requisite vinyl chloride-bearing arylacetic acid precursors are readily available by straightforward alkylation of arylacetic acid esters and undergo cyclization to yield 3-chloro-5-aryl-2-cyclopentenones when treated with $AlCl_3$. The vinylogous acid chloride functionality present in these immediate products allows for further elaboration via Pd-catalyzed cross-coupling chemistry, leading to a diverse array of products.

The Friedel−Crafts (F-C) acylation reaction represents a powerful method to introduce new carbon−carbon bonds onto aromatic compounds and other unsaturated species.[1] Acylation of arenes is a thoroughly established technique for the synthesis of aromatic ketones. Intramolecular F−C reactions have also proven highly useful in the formation of various ring systems.[2] As part of a continuing effort to develop simple and efficient approaches to functionalized organic intermediates, we recently became interested in the use of alternative nucleophilic components to the commonly used arene ring. In particular, we sought to investigate the use of vinyl chlorides as the nucleophilic component in intramolecular F−C acylation reactions. Inspection of the literature revealed only a few isolated examples of vinyl chloride-based intramolecular F-C acylations,[3] indicating good potential to expand the scope of this reaction and develop more generally applicable procedures. In this Note, we disclose the results from our work in this area, which demonstrate the utility of intramolecular F-C acylations of vinyl chlorides for the synthesis of various 3,5-disubstituted cyclopentenone derivatives. These functionalized prochiral intermediates[4] have potential as versatile precursors for various types of asymmetric catalysis, such as asymmetric conjugate reduction[5] and asymmetric conjugate additions to generate quaternary stereocenters.[6]

Figure 1 depicts our general approach for the preparation of 3,5-diarylcyclopentenones. Given the ready availability of functionalized arylacetic acids, we envisaged these to be appropriate starting materials for the construction of a range of intramolecular F-C cyclization substrates. Carboxylic acid activation and cyclization under typical Lewis acid conditions was anticipated to provide 3-chlorocyclopentenone intermediates that would be amenable to further elaboration via the reactivity conferred by the vinylogous acid chloride functional group.

Synthesis of the F-C cyclization substrates was accomplished via alkylation of aryl acetic esters (**1a**) or, more directly, via alkylation of the dianion derived from arylacetic acids (**1b**)[7] (Scheme 1). As shown, treatment of a mixture of arylacetic ester and 2-chloro-3-iodopropene (**2**) in THF with KHMDS results

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(4) For selected synthesis of substituted 2-cyclopentenone see: (a) Shi, X.; Gorin, D. J.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 5802. (b) Zhang, L.; Wang, S. *J. Am. Chem. Soc.* **2006**, *128*, 1442. (c) Arcadi, A.; Marinelli, F.; Pini, E.; Rossi, E. *Tetrahedron Lett.* **1996**, *37*, 3387. (d) Prempree, P.; Siwapinyoyos, T.; Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron Lett.* **1980**, *21*, 1169. (e) Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5881. Through [4+1] annulation see: (f) Moser, W. H.; Feltes, L. A.; Sun, L.; Giese, M. W.; Farrell, R. W. *J. Org. Chem.* **2006**, *71*, 6542. (g) Davie, C. P.; Danheiser, R. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 5867. (h) Kurahashi, T.; Wu, Y.-T.; Meindl, K.; Rühl, S.; Meijere, A. *Synlett.* **2005**, *5*, 805. For zirconium-catalyzed see: (i) Takahashi, T.; Huo, S.; Hara, R.; Noguchi, Y.; Nakajima, K; Sun, W. *J. Am. Chem. Soc.* **1999**, *121*, 1094. (j) Xi, Z.; Fan, H.; Mito, S.; Takahashi, T. *J. Organomet. Chem.* **2003**, *682*, 108. (k) Yuki, T.; Hashimoto, M.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1993**, *58*, 4497. For Pd-catalyzed see: (l) Tsukada, N.; Sugawara, S.; Okuzawa, T.; Inoue, Y. *Synthesis* **2006**, *18*, 3003. For rhodium(I)-catalyzed see: (m) Murakami, M.; Takahashi, K.; Amii, H.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 9307. (n) Matsuda, I.; Ishibashi, H.; Ii, N. *Tetrahedron Lett.* **1995**, *36*, 241. (o) Matsuda, I.; Fukuta, Y.; Tsuchihashi, T.; Nagashima, H.; Itoh, K. *Organometallics* **1997**, *16*, 4327. Through iron complex see: (p) Stokes, H. L.; Ni, L. M.; Belot, J. A.; Welker, M. E. *J. Organomet. Chem.* **1995**, *487*, 95. (q) Ni, L.; Belot, J. A.; Welker, M. E. *Tetraohedron Lett.* **1992**, *33*, 177. For Cobalt-catalyzed syntheses see: (r) Krafft, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 968. (s) Rao, M. L. N.; Periasamy, M. *Organomettallics* **1996**, *15*, 442. (t) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans 1* **1973**, 977.

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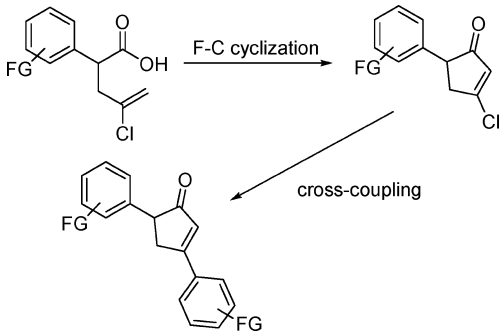
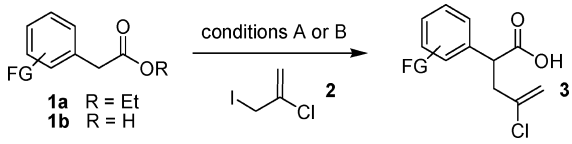


FIGURE 1. Access to 3,5-diarylcyclopentenones via intramolecular F−C acylation of vinyl chlorides and subsequent cross-coupling of the derived vinylogous acid chloride.

SCHEME 1. Synthesis of Chloroallyl F-C Cyclization Substrates[a]



[a] Conditions A for ester substrates (**1a**): direct α-alkylation followed by hydrolysis of the ester. Conditions B for free acid substrates (**1b**): direct α-alkylation via dianion chemistry.

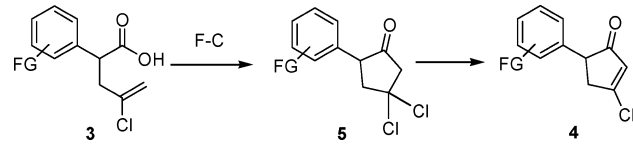
in alkylation of the α-position. In most cases some over-reaction to yield the dialkylated product was observed, although this could be suppressed (<10%) by slow addition of KHMDS at − 10 °C. Direct basic hydrolysis of the mixture of crude alkylated products was selective, leaving the sterically congested dialkylated esters intact and allowing for straightforward purification of the desired acid via standard extractive techniques. An alternative method used for preparation of certain substrates involved treatment of aryl acetic acids with 2 equiv of *n*-BuLi at − 60 °C followed by addition of 2-chloro-3-iodopropene (**2**) at −10 °C to obtain the required carboxylic acids directly in a single step[8] (conditions B).

With ready access to the requisite cyclization substrates, study of the planned F-C reactions was initiated. Following an established procedure, treatment of the carboxylic acids (**3**) with $(COCl)_2$ and a catalytic amount of DMF at room temperature afforded the corresponding acid chlorides. Next, in situ treatment with $AlCl_3$ served to promote the desired intramolecular F-C acylation process. In most cases, both 3-chloro-2-cyclopentenone (**4**) and 3,3-dichlorocyclopentanone (**5**) were observed (by reversed-phase HPLC) when the reaction mixture was sampled directly. However, standard aqueous workup involving treatment with sat. $NaHCO_3$ solution under biphasic conditions led to facile elimination of HCl from **5** and conversion to **4**. As shown in Table 1 there is reasonable substrate scope and a variety of vinyl chlorides (**3**) undergo smooth cyclization to deliver cyclopentenones (**4**) in 64−97% yields. The 3-chloro-2-cyclopentenones (**4**) are stable toward silica gel chromatography and were generally isolated in good yields (Table 1).

(7) (a) Chen, C.; Frey, L. F.; Shultz, S.; Wallace, D. J.; Marcantonio, K.; Payack, J. F.; Vazquez, E.; Springfield, S. A.; Zhou, G.; Liu, P.; Kieczykowski, G. R.; Chen, A. M.; Phenix, B. D.; Singh, U.; Strine, J.; Izzo, B.; Krska, S. W. *Org. Proc. Res. Dev.* **2007**, *11*, 616. (b) Rosen, J. D.; Nelson, T. D.; Huffman, M. A.; McNamara, J. M. *Tetrahedron Lett.* **2003**, *44*, 365. (c) Chen, C.; Dagneau, P.; Grabowski, E. J. J.; Oballa, R.; O'Shea, P.; Prasit, P.; Robichaud, J.; Tillyer, R.; Wang, X. *J. Org. Chem.* **2003**, *68*, 2633.

(8) Direct alkylation on free acids with *n*BuLi (conditions B) gave lower isolated yield than conditions A.

TABLE 1. Synthesis of 3-Chloro-5-arylcyclopentenones (4)[a,b]

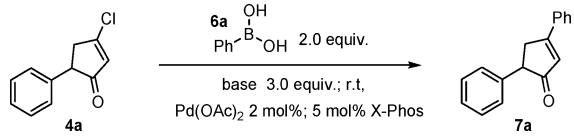


entry	substrate	chlorocyclopentenone	yield
1	**3a**	**4a**	87%
2	**3b**	**4b**	75%
3	**3c**	**4c**	93%
4	**3d**	**4d**	71%
5	**3e**	**4e**	97%
6	**3f**	**4f**	64%[c]
7	**3g**	**4g**	89%
8	**3h**	**4h**	81%

[a] The reactions were carried out at room temperature with 1.2 equiv of $(COCl)_2$ in CH_2Cl_2. Reactions were monitored by LC and upon full conversion, 1.1 equiv of $AlCl_3$ was added. A basic workup was conducted upon complete conversion of the acid chloride intermediates monitored by LC. [b] Yields of pure, isolated products (characterized by ^1H, ^{13}C NMR, and HR-MS). [c] Conducted with additional stirring at room temperature with sat. $NaHCO_3$ added before workup.

Having secured a series of 3-chlorocyclopentenones, we sought to exploit the vinylogous acid chloride reactivity displayed by these intermediates in the preparation of 3,5-disubstituted cyclopentenones. Given the ready commercial availability of functionalized arylboronic acids, the Pd-catalyzed Suzuki cross-coupling was an attractive option for increasing the flexibility of this approach. On the other hand, to our knowledge there is only one previous report describing a Suzuki cross-coupling between 3-chlorocyclopentenone and an arylboronic acid.[9] Furthermore, an additional complication inherent to the present substrates was created by the aryl group at the 5-position of the 3-chlorocyclopent-2-enones. The methine proton at the 5-position is rendered more acidic by virtue of being both benzylic and adjacent to the carbonyl group.

TABLE 2. Studies of Base Effect in the Suzuki Coupling[a]



entry	base	solvent (8 mL/g)	conv at 1 h, %	AY at 2.5 h, %
1	KF	dioxane	>50	87
2	$NaHCO_3$	dioxane	≪50	2
3	K_2CO_3	dioxane	∼50	49
4	$K2CO_3$	$PhCH_3/H_2O$ (5:3)	100	86
5	$NaHCO_3$	$PhCH_3/H_2O$ (5:3)	≫50	85
6	KF	$PhCH_3/H_2O$ (5:3)	100	87

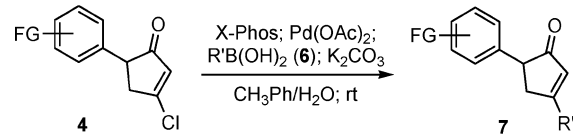
[a] The reactions were carried out in either dioxane or toluene/water mixture. Conversions at 1 h and yields (AY: assay yield) at 2.5 h were obtained by LC assay.

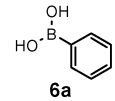
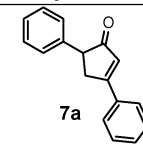
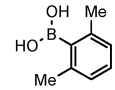
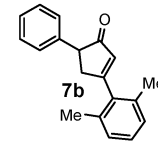
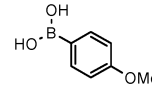
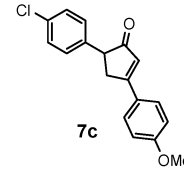
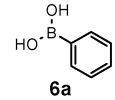
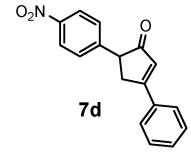
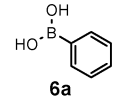
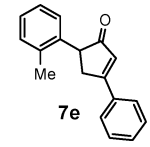
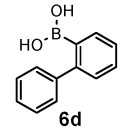
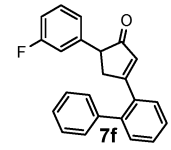
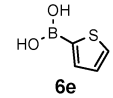
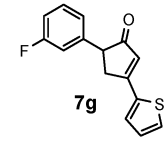
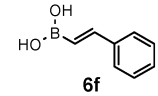
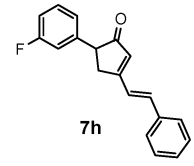
Deprotonation at this site would presumably generate a cyclopentadiene species that could undergo undesirable side reactions. Indeed, early attempts to derivatize the 3-chloro-5-arylcyclopentenones as vinylogous esters with K_2CO_3/MeOH led to dark reaction mixtures in which extensive degradation had occurred. With this in mind, it was clear that very mild conditions would be a prerequisite if the planned Suzuki cross-coupling process was to be realized. Ligand screening revealed that several of Buchwald's biarylphosphines were effective, with the highly active X-Phos showing particular promise.[10] The coupling in a biphasic solvent system with water proceeded faster than those in just organic solvents. With X-Phos as ligand, coupling proceeded very fast in a toluene/water solvent system, when K_2CO_3 or KF was used as base (Table 2).

Following some optimization, conditions for the room temperature Suzuki cross-coupling with arylboronic acids (**6**) were developed and applied to the preparation of various 3,5-diarylcyclopentenones (**7**), as shown in Table 3. Most reactions went to completion within 1 to 2 h at room temperature. Cross-coupling with more sterically hindered boronic acids required increased reaction times to achieve full conversion and the yield was slightly lower (62% for **7b**; 74% yield for **7f**, entries 2 and 6, respectively, Table 3). Cross-coupling with electron-rich boronic acids delivered desired products in excellent yields (95% yield for **7c**, entry 3; 91% for **7h**, entry 8, Table 3). An interesting observation was made when attempting to prepare 3,5-diarylcyclopentenones that were electron deficient. It was found that the initial products were prone to oxidation at the 5-position, producing a quaternary center bearing a hydroxyl group. Presumably this is related to increased ease of deprotonation at the 5-position and reaction of the resulting enolate with adventitious oxygen.[11] For example, substrate **4d** bearing a nitro group had a relatively lower yield for this coupling (51% yield for **7d**, entry 4, Table 3), with a significant portion of the mass balance found in the oxidation product. Although generation of these oxidized products could potentially be of interest, further investigation of this process was outside the scope of the current work.

For substrate **4b**, which contains a 5-(*p*-bromophenyl) group, the Suzuki cross-coupling with phenylboronic acid (**6a**) under

TABLE 3. 3,5-Diarylcyclopentenones via Suzuki Coupling[a,b]



entry	substrate	$R'B(OH)_2$	product	yield
1	**4a**	 **6a**	 **7a**	85%
2	**4a**	 **6b**	 **7b**	62%
3	**4h**	 **6c**	 **7c**	95%
4	**4d**	 **6a**	 **7d**	51%
5	**4e**	 **6a**	 **7e**	98%
6	**4c**	 **6d**	 **7f**	74%
7	**4c**	 **6e**	 **7g**	57%
8	**4c**	 **6f**	 **7h**	91%

[a] The reactions were carried out at room temperature with 2 mol % of $Pd(OAc)_2$, 5 mol % of X-Phos, 2 equiv of boronic acids (**6**), and 3 equiv of K_2CO_3 in a mixture of toluene and water. [b] Yields of pure, isolated products (characterized by ^1H, ^{13}C NMR, and HR-MS).

(9) (a) Murray, A.; Hansen, J. B.; Christensen, B. V. *Tetrahedron* **2001**, *57*, 7383. For Pd-mediated coupling of 3-chlorocyclopentenone derivative (Stille coupling) see: (b) Araki, K.; Saito, K.; Arimoto, H.; Uemura, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 81. For selective examples of cross-coupling reactions between 3-bromo or 3-iodo cyclopentenones and aryl or vinyl boronic acids see: (c) Marson, C. M.; Farrand, L. D.; Dunmur, D. A. *Tetrahedron* **2003**, *59*, 4377. (d) Genêt, J. P.; Linquist, A.; Blart, E.; Mouriès, V.; Savignac, M.; Vaultier, M. *Tetrahedron Lett.* **1995**, *36*, 1443. (e) Conchon, E.; Anizon, F.; Aboab, B.; Prudhomme, M. *J. Med. Chem.* **2007**, *50*, 4669. (f) Okamoto, K.; Akiyama, R.; Kobayashi, S. *Org. Lett.* **2004**, *6*, 1987.

(10) X-phos, 2-dicyclohexyldiphenylphosphine, cyclohexyldiphenylphosphine, and dppb (5 mol % each) were evaluated with 2.0 equiv of phenylboronic acid (**6a**), 3.0 equiv of K_2CO_3, 2 mol % of $Pd(OAc)_2$, in dioxane or dioxane/water at 70 °C. X-phos and 2-dicyclohexyldiphenylphosphine gave faster reactions and higher assay yields, where X-phos gave highest assay yield in dioxane.

(11) The solvents used in these experiments were not degassed.

the developed standard conditions led to unselective reaction at both the halogen-bearing carbon atoms. In contrast, the aryl chloride group in substrate **4h** was unreactive under the standard conditions and allowed for clean cross-coupling at the vinylogous acid chloride (95% for **7c**, entry 3, Table 3).

In summary, the developed chemistry represents a general method that employs simple procedures and readily available starting materials for the synthesis of 3,5-diarylcyclopentenones. Previously under utilized as a synthetic method, the key intramolecular F-C acylation of easily accessible vinyl chloride-bearing compounds was shown to deliver 3-chloro-5-arylcyclopentenone intermediates in good yields across a range of substrates. As a demonstration of the utility of these vinylogous acid chloride intermediates, Pd-catalyzed Suzuki-type cross-coupling reactions were applied in the synthesis of a series of 3,5-diarylcyclopentenones. These prochiral compounds are potential substrates for a variety of asymmetric transformations, which will be the focus of future investigations in these laboratories.

Experimental Section

Typical Experimental Procedure for Friedel−Crafts Cyclization of Vinyl Chloride 3a To Afford 3-Chloro-5-arylcyclopentenone 4a (entry 1, Table 1): To a solution of alkylated acid derivative **3a** (2.00 g, 9.49 mmol) in CH_2Cl_2 (35 mL) was added a few drops of DMF followed by $(COCl)_2$ (0.984 mL, 11.4 mmol). After 1 h, LC analysis indicated complete conversion of starting material to the corresponding acid chloride. $AlCl_3$ (1.39 g, 10.4 mmol) was added and the mixture was stirred at room temperature for 1.5 h until LC analysis indicated the full conversion of the acid chloride intermediate. The mixture was cooled in an ice bath and quenched by the careful addition of water. Saturated aqueous $NaHCO_3$ (20 mL) and MTBE (50 mL) were added and the separated organic phase was washed with brine (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude product. The crude material was further purified by silica gel flash chromatography eluting with 30% EtOAc/hexanes to give the product **4a** as a light yellow solid (1.6 g, 87% yield). **4a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 (t, J = 7.4 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 7.3 Hz, 2H), 6.33 (m, 1H), 3.80 (dd, J = 7.4, 2.6 Hz, 1H), 3.40 (ddd, J = 18.9, 7.4, 1.5 Hz, 1H), 3.01 (d, J = 18.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 204.5, 170.4, 138.3, 130.7, 129.2, 127.8, 127.6, 53.7, 44.1. Exact mass calcd for $[C_{11}H_9ClO + Ag]^+$ requires m/z 298.9393, found 298.9388 (ESI+).

Typical Experimental Procedure for Suzuki Cross-Coupling of 3-Chloro-5-arylcyclopentenone 4a To Deliver 3,5-Diphenyl-2-cyclopentenone 7a (entry 1, Table 2): To a solution of 3-chlorocyclopentenone derivative **4a** (0.200 g, 1.04 mmol) in toluene/H_2O (5:3, 1.6 mL) was added X-Phos (0.025 g, 0.052 mmol), boronic acid **6a** (0.253 g, 2.08 mmol), $Pd(OAc)_2$ (0.0047 g, 0.021 mmol), and K_2CO_3 (0.430 g, 3.11 mmol). The reaction was stirred at room temperature in a sealed vial for 1 h and LC indicated complete conversion of **4a**. Brine (5 mL) and MTBE (10 mL) were added and the separated aqueous phase was extracted with a second portion of MTBE (10 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to give a crude product. The crude material was further purified by silica gel flash chromatography eluting with 30% EtOAc/hexenes to give 3,5-diphenyl-2-cyclopentenone **7a** in 85% yield (0.208 g). **7a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (dd, J = 7.4, 1.5 Hz, 2H), 7.50 (d, J = 7 Hz, 3H), 7.35 (t, J = 7.3 Hz, 2H), 7.27 (m, 1H), 7.23 (d, J = 7.6 Hz, 2H), 6.68 (m, 1H), 3.81 (dd, J = 7.3, 2.6 Hz, 1H), 3.62 (ddd, J = 18.3, 7.4, 1.6 Hz, 1H), 3.19 (ddd, J = 18.3, 2.5, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 208.4, 173.0, 140.0, 134.0, 131.7, 129.2, 129.1, 127.8, 127.2, 127.1, 126.6, 52.4, 38.6. Exact mass calcd for $[C_{17}H_{14}O + Ag]^+$ requires m/z 341.0096, found 341.0101 (ESI+).

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Supporting Information Available: Experimental procedures and analytical data for all the F−C starting materials (**3a**−**h**), products (**4a**−**h**) and Suzuki products (**7a**−**h**) with reprints of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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