

Tetra-N-confused Cyclohexapyrrole: The Unusual Product Formed by Condensation of 3,3'-Dipyrromethane with Tripyrrin-aldehyde

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Abstract: Novel tetra-N-confused cyclohexapyrrole is synthesized for the first time via condensation of tripyrrinone-aldehyde with bis(2,4-dimethylpyrrole-3-yl)methane in the presence of *p*-toluenesulfonic acid monohydrate. X-ray crystal analysis indicates that it adopts a nonplanar conformation with a conelike shape.

Cyclopolypyrroles, a new family of pyrrolic macrocycles larger than tetrapyrroles, could structurally be divided into (a) fully conjugated systems such as expanded porphyrins, (b) partially conjugated systems such as calixpyrins, and (c) nonconjugated systems such as calix[*n*]pyrroles. Their chemistry has recently received considerable attention due to the possibility of developing new chemistry^{1–3} and their intriguing properties^{3–7} such

as selectively binding anions, neutral small molecules, and metal ions. Structurally, the pyrrolic units in cyclopolypyrroles can be linked through the α, α' -positions by zero, one, or two carbon bridges. N-Confused cyclopolypyrroles are pyrrolic macrocycles, in which the pyrrolic units are bridged through α, β' -positions or a mixture of α, α' - and α, β' -positions. The first such compound reported in the literature, known as the penta-N-confused cyclopentapyrrole or inverted pentaphyrinogen (**I**), was synthesized by Franck⁸ in 1989 via a biomimetic condensation of *N*-benzyl-3-hydroxymethyl-2,4-dimethylpyrrole in oxygen-free glacial acetic acid with *p*-toluenesulfonic acid. This particular macrocycle is unusual because all five pyrrolic nitrogens are on the periphery of the macrocycle instead of on the interior. More recently, Furuta's group⁹ reported the synthesis and characterization of another N-confused cyclopyrrole, N-confused sapphyrin. Almost at the same time, N-confused cyclodecapyrrole **II** was synthesized by one of us via a [3 + 2 + 3 + 2] "MacDonald-type" condensation of a tripyrrane-dialdehyde with a (2,4-dimethylpyrrole-3-yl)methane under acidic conditions.¹⁰ Although the N-confused cyclopolypyrroles have been known for more than 10 years, these systems, their chemistry, and their binding ability have not yet been thoroughly investigated. In this paper we report the synthesis and the X-ray crystal structure of tetra-N-confused cyclohexapyrrole **3**, which to the best of our knowledge is the first example of the cyclohexapyrrole system containing four N-confused pyrrolic rings.

As one of our ongoing projects on N-confused porphyrinogens and related pyrrolic macrocycles, our original goal was to try to synthesize tetra-N-confused porphyrins. We were attracted to the possibility of preparing the target via MacDonald's [2 + 2] method¹¹ from the condensation of bis(5-formyl-2,4-dimethylpyrrole-3-yl)methane¹² with bis(2,4-dimethylpyrrole-3-yl)methane (**1**) or from the condensation of **1** with aromatic aldehydes. Unfortunately, both reactions afforded insoluble and intractable mixtures. Having attempted reactions with a number of aldehydes, mostly substituted benzaldehydes, we finally found the condensation of tripyrrinone-aldehyde (**2**),¹² a red pigment prepared via silver nitrate-mediated oxidation of mesobiliverdin XIII α , with bis(2,4-dimethylpyrrole-3-yl)methane (**1**)¹³ to give the blue-green pigment **3** in 51% isolated yield (Scheme 1). To our surprise, the product was not the expected macrocycle **4** but the cyclohexapyrrole **3** (Scheme 1). Among many acidic catalysts, *p*-toluenesulfonic acid monohydrate was

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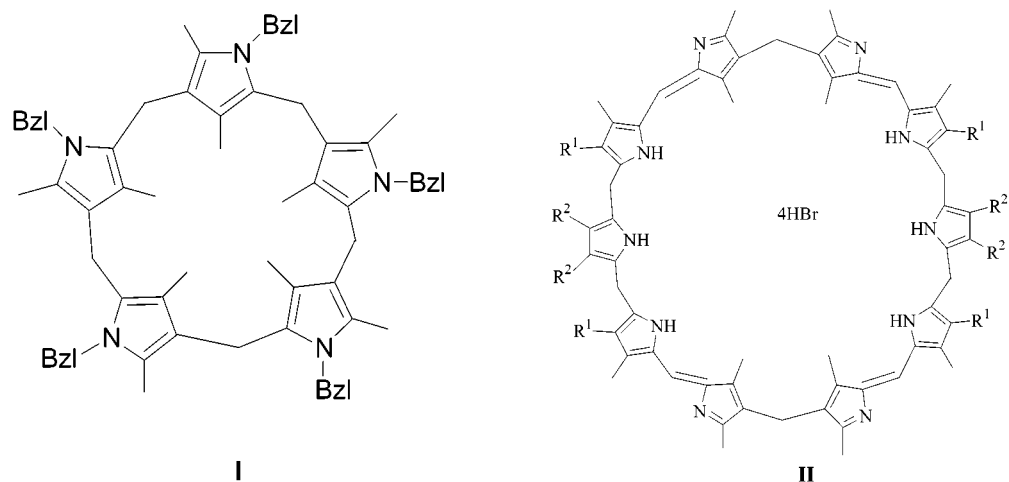
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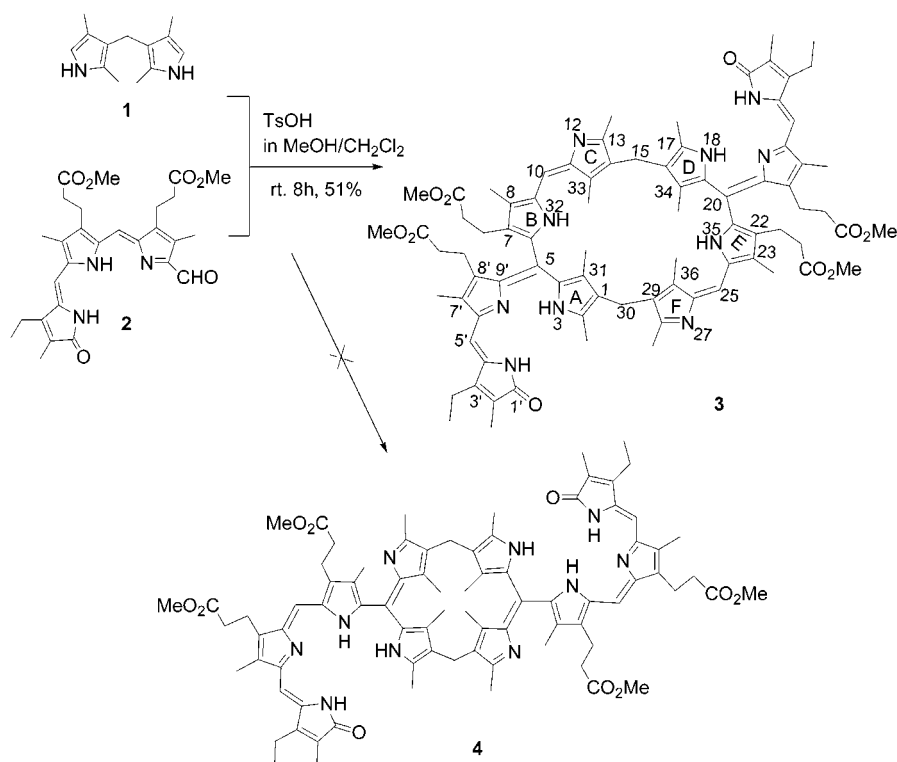
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SCHEME 1



found to be the best. This reaction does not provide the expected cyclotetrapyrrole compound **4** because the four methyl groups in the central core are too crowded to be held by the relatively small cyclotetrapyrrole ring. Unlike the tetra-*N*-confused cyclodecapyrrole systems,¹⁰ which are only stable as HBr salts, **3** is stable in the free base form.

The constitutional structure of tetra-*N*-confused macrocycle **3** was characterized by ¹H NMR, ¹³C NMR, and MS. Its MALDI-TOF-MS, *m/z* 1379, suggests a molecular formula of C₈₂H₉₄N₁₀O₁₀, which corresponds to a condensation product of **2** and **1** with a ratio of 2:2. The structure was further confirmed by X-ray crystallographic analysis

(Figure 1). The macrocycle displays a nonplanar conformation with a conelike shape (Figure 1b), in which there are two endo pyrrolic rings (B, E), four exo or *N*-confused pyrrolic rings (A, C, D, F), and two CH₂ bridges in the macrocycles. It has marked kinks enforced by its β,β'-sp³-hybridized bridging elements and bulky groups (dipyrinones) at the meso positions. However, the molecule also displays regions of local planarity corresponding to meso-unsubstituted dipyrromethene (ring B–C, ring E–F) or dipyrinone moieties. Thus, this molecule, like calixphyrins,^{4d} is a hybrid molecule that resembles both the aromatic porphyrins and its nonplanar, fully non-conjugated calixpyrrole analogues.⁵ Two dipyrinone and dipyrromethene moieties, like bile pigments and porphyrins, respectively, adopt the common stable *Z*-configuration and are oriented in different directions. Due to the

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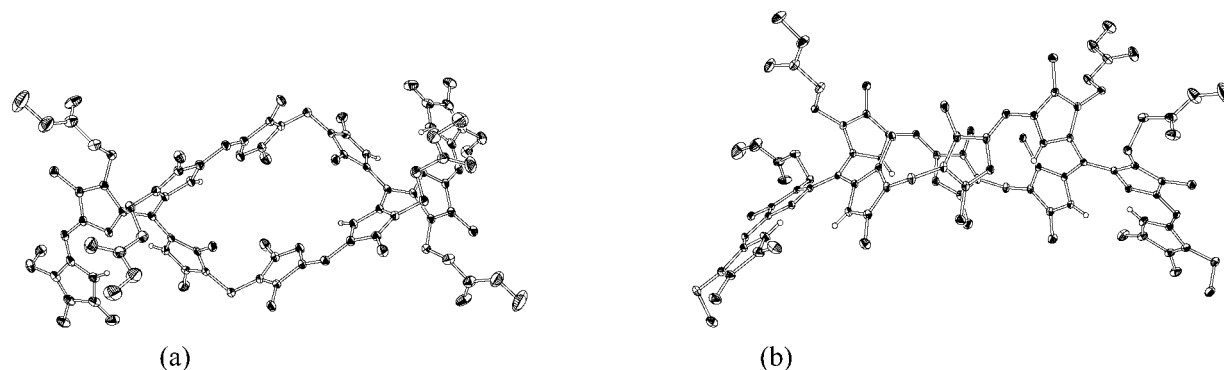


FIGURE 1. ORTEP diagrams showing the molecular structure of **3**: (a) top view; (b) side view, solvent molecules and nonacidic hydrogen atoms have been omitted for clarity. Thermal ellipsoids are scaled to 30%.

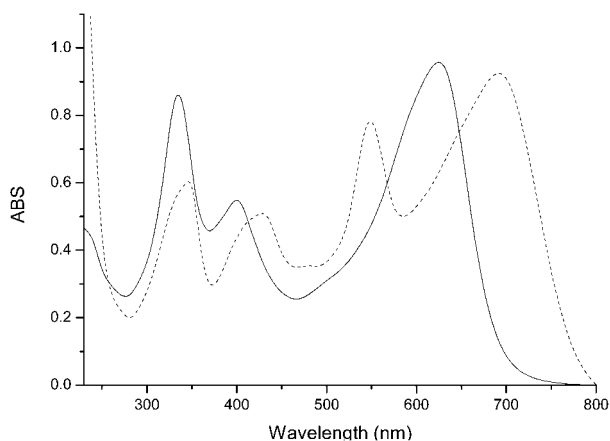


FIGURE 2. UV-vis spectra of **3**: (solid line) in dichloromethane; (broken line) in dichloromethane plus a drop of TFA.

bulky dipyrinone group at the meso position, pyrrolic ring A and ring D are twisted and oriented in different directions relative to their neighbors. Molecular modeling suggests that **3** is likely to be relatively rigid, which is confirmed by the single conformer observed in the X-ray structure of **3**. The UV-vis study of **3** in chloroform and dimethyl sulfoxide supported this conclusion; regardless of the solvent, **3** displays very similar spectra regarding the patterns, locations, and peak intensities. Its UV-vis spectra in dichloromethane and dichloromethane-TFA are shown in Figure 2.

The ^{13}C NMR spectrum of **3** in CDCl_3 reveals a total of 16 sp^3 carbon signals and 24 sp^2 carbon signals, which indicates that the whole molecule is C_2 symmetric. Although the proposed symmetric structure requires 25 sp^2 carbon signals, the missing carbon signal could easily be found at 173.27 ppm, which is assigned to C=O groups of methylcarbonyl ethyl fragments at C8', C7, and C22 that are double the height and intensity of other sp^2 carbon signals. The number of sp^3 carbon signals suggests that $-\text{CH}_2-$ at C15 and $-\text{CH}_2-$ at C30 are identical, which is confirmed by its APT spectrum in CDCl_3 , which exhibits six $-\text{CH}_2-$ groups. The ^{13}C NMR spectrum of **3** in pyridine- d_5 is found to be essentially identical with that in CDCl_3 regarding the signal patterns, intensities, and locations.

The ^1H NMR of **3** in pyridine- d_5 displays a singlet $-\text{CH}=\text{}$ proton of C5' at 6.06 ppm, and another singlet $-\text{CH}=\text{}$ proton of C10/C25 at 6.91 ppm. These chemical shifts (C5' and C16) reportedly point to *Z*-configurations at the two exocyclic double bonds. The two CH_2 protons of C15/C30 display doublet-doublet splits at 3.22–3.32 ppm (AB system, $J = 18$ Hz). These assignments are confirmed by HMQC experiments.

Compound **3** is noticeably blue, whereas the tripyr- rone precursor is red, as shown in Figure 2. The long wavelength band is observed at 624 nm in dichloromethane and is thus hypsochromically shifted with respect to biliverdin (640 nm),¹⁴ a fully conjugated linear tetrapyrrole bile pigment. As had been discussed for the *b*-homoverdin,¹⁵ this hypsochromic shift could be correlated to considerable twisting of the pyrrolic ring in the cyclohexapyrrolic core. Upon protonation, the long wavelength band shifted to 720 nm, which is reversible upon addition of base. This UV-vis shift behavior is similar to that found in *b*-homoverdin.^{15,16} It is ascribed to a stretching and planarization of the chromophore, especially the pyrrole ring of the cyclohexapyrrole core.

With respect to the reaction mechanism, we suggest that the condensation of **1** with **2** under acidic conditions in methanol first yields the linear pentapyrrolic derivative **3a** (Scheme 2). The intermediate **3a** could then undergo acid-catalyzed self-condensation to yield the corresponding cyclohexapyrrole intermediate **3b**. Upon further reaction with oxygen in the air, a common oxidant in porphyrin synthesis, **3b** could lose four hydrogens to result in the expected macrocycle **3**.

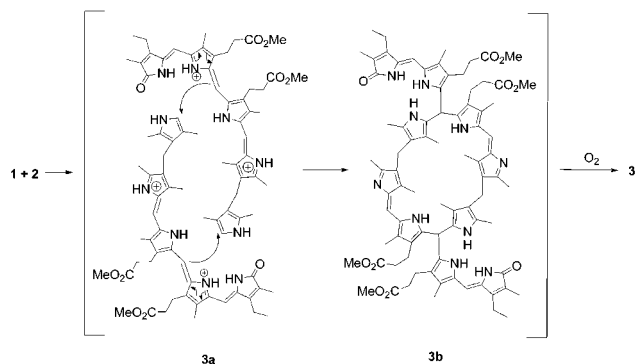
In summary, we have successfully synthesized the first tetra-*N*-confused cyclohexapyrrole and have shown that this molecule is stable and adopts a nonplanar conformation with a conelike shape. This is probably the first example of condensation between the meso position of dipyrromethene and the unsubstituted α -position of pyrrole. Binding ability experiments are currently in progress.

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SCHEME 2



Experimental Section

2,2',4,4'-Tetramethyl-3,3'-dipyrrromethane (**1**)¹³ and Meso-biliverdin XIII α dimethyl ester¹⁷ were prepared according to the literature procedures.

14-Formyl-2,7,13-trimethyl-3-ethyl-8,12-bis(methoxycarbonyl)ethyl-tripyrinone-1 (2) was prepared from AgNO₃ oxidation of mesobiliverdin XIII α dimethyl ester using an improved procedure based on our previous report.¹⁶ A solution of aqueous silver nitrate (0.1 M, 30 mL, 3 mmol, 60 equiv) was added with stirring to a solution of **3** (30 mg, 0.05 mmol) and sodium bicarbonate (5 mg) in THF (30 mL). The mixture was then stirred at room temperature and monitored frequently by TLC (EtOAc/CH₂Cl₂/CCl₄, v/v/v, 2/2/1) and UV-vis. The solution first turned blue-green, and then blue, purple, and finally dark red. After 20–40 min the reaction was completed and the mixture was partitioned by dichloromethane (100 mL) and water (200 mL). The organic phase was separated, and aqueous phase was extracted with dichloromethane (30 mL \times 3). The organic phase and combined extracts were washed successively with aqueous saturated sodium bicarbonate (50 mL) and brine (50 mL), dried over sodium sulfate, filtered, and evaporated under reduced pressure. The resulting dark-red solid was purified by column chromatography (EtOAc/CH₂Cl₂/CCl₄, v/v/v, 2/2/1) on silica gel and crystallization from chloroform–hexane to give 20 mg of **2** with a yield of 78%: mp 156–157 °C; UV-vis λ_{max} (CHCl₃, nm) 545 (ϵ 23 500), 507 (ϵ 24 200), 321 (ϵ 61 000); EIMS (m/z) 507 (M⁺), 475, 434, 360, 302; IR (KBr) 3422, 1736, 1704, 1648, 1602 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.20 (t, J = 13.8 Hz, 3H, CH₂CH₃), 1.97 (s, 3H, CH₃), 2.09 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 2.48–2.60 (m, 6H, CH₂CH₃, 2CH₂CH₂COO), 2.90–2.98 (m, 4H, 2CH₂CH₂COO), 3.65 (s, 3H, COOCH₃), 3.67 (s, 3H, COOCH₃), 5.88 (s, 1H, –CH= at C5), 6.81 (s, 1H, –CH= at C10), 9.38 (s, 1H, lactam NH), 9.82 (s, 1H, CHO), 11.30 (br, 1H, pyrrole NH); ¹³C NMR (100 Hz, CDCl₃) δ 8.51, 9.83, 14.31, 17.65, 19.15, 19.73, 34.88, 51.68, 95.16, 113.86, 128.56, 129.95, 130.32, 133.11, 134.94, 143.26, 145.27, 146.07, 153.20, 169.18, 171.68, 172.86, 172.95, 177.87. Anal. Calcd for C₂₈H₃₃N₃O₆: C, 66.26; H, 6.55; N, 8.28. Found: C, 66.02; H, 6.32; N, 8.01.

Tetra-N-confused Cyclohexapyrrole (3). To a solution of **2** (200 mg, 0.39 mmol) and **1** (80 mg, 0.39 mmol) in dichloromethane was added a solution of *p*-toluenesulfonic acid

monohydrate (300 mg, 1.44 mmol) in methanol (15 mL). The mixture was stirred at room temperature for 8 h. Then the green solution was washed with aqueous saturated sodium bicarbonate (50 mL) and brine (50 mL). After the solution was dried over anhydrous sodium sulfate, the solvent was removed under vacuum. The resulting black solid was purified by flash chromatography (dichloromethane/methanol, 50/1), and crystallization from methanol gave the title compound **3** (140 mg, 51%): mp > 250 °C; UV-vis λ_{max} (CH₂Cl₂, nm) 624 (ϵ 74 600), 399 (ϵ 42 600), 334 (ϵ 67 000); UV-vis λ_{max} (CH₂Cl₂ plus a drop of TFA, nm) 691 (ϵ 72 000), 548 (ϵ 60 900), 429 (ϵ 39 600), 345 nm (ϵ 47 000); ¹H NMR (400 MHz, pyridine-*d*₅) δ 1.01 (t, 6H, CH₂CH₃), 1.36 (s, 6H, CH₃), 1.84 (s, 6H, CH₃), 1.93 (s, 6H, CH₃), 2.06 (s, 6H, CH₃), 2.11 (s, 6H, CH₃), 2.34 (s, 6H, CH₃), 2.37 (q, 4H, –CH₂–CH₃), 2.50–2.34 (m, 4H, –CH₂CH₂COOCH₃), 2.59 (t, 4H, –CH₂CH₂COOCH₃), 2.66 (s, 6H, CH₃), 2.77–3.00 (m, 4H, –CH₂CH₂COOCH₃), 3.00–3.14 (m, 4H, –CH₂CH₂COOCH₃), 3.22 (d, ¹ J (H,H) = 18 Hz, 2H, –CH₂–), 3.32 (d, ¹ J (H,H) = 18 Hz, 2H, –CH₂–), 3.43 (s, 6H, CH₃), 3.45 (s, 6H, CH₃), 6.07 (s, 2H, CH), 6.92 (s, 2H, CH), 10.92 (s, 2H, NH), 11.96 (s, 2H, NH); ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS) δ 1.22 (t, 6H, CH₃), 1.25 (s, 6H, CH₃), 1.76 (s, 6H, CH₃), 1.98 (s, 6H, CH₃), 2.07 (s, 6H, CH₃), 2.13 (s, 6H, CH₃), 2.18 (s, 6H, CH₃), 2.42 (s, 6H, CH₃), 2.34–2.69 (m, 20H, CH₂), 3.30–3.60 (m, 4H, –CH₂–), 3.45 (s, 6H, CH₃), 3.55 (s, 6H, CH₃), 6.01 (s, 2H, CH), 6.60 (s, 2H, CH), 9.94 (br, 2H, NH); ¹³C NMR (100 Hz, CDCl₃) δ 8.54, 9.36, 9.72, 9.83, 11.12, 12.47, 14.65, 17.35, 17.91, 19.90, 20.98, 21.33, 29.75, 34.38, 34.75, 51.29, 51.49, 97.65, 114.40, 122.94, 125.77, 128.15, 128.32, 128.50, 129.51, 132.12, 132.67, 133.22, 133.85, 135.42, 138.05, 139.57, 141.00, 145.32, 146.68, 146.80, 160.11, 166.92, 172.26, 173.27; ¹³C NMR (100 MHz, pyridine-*d*₅) δ 7.85, 8.72, 8.82, 9.07, 10.66, 11.62, 13.94, 17.11, 19.80, 20.29, 21.07, 34.07, 34.48, 50.57, 96.91, 114.19, 122.36, 126.16, 127.39, 127.80, 128.18, 129.23, 132.22, 132.32, 132.77, 133.17, 138.13, 138.55, 139.83, 140.98, 145.15, 146.11, 147.98, 159.77, 168.49, 171.48, 172.29, 172.35; MALDI-TOF-MS m/z (%) 1379 (100) [M⁺]; HR-ESI-MS calcd for C₈₂H₉₆N₁₀O₁₀ (M + 2)²⁺ 690.3650, found 690.3645.

Crystallographic Data. Crystal structure analyses were measured using graphite-monochromatized Mo K α radiation (λ = 0.71037 Å) at –113 °C: C_{82.5}H_{95.5}Cl_{0.5}N₁₀O_{10.25}; M = 1408.91; block/violet crystal (size 0.35 \times 0.2 \times 0.11 mm) grown from dichloromethane/methanol; monoclinic, space group *C2/c*, Z = 4, a = 29.0577 (8) Å, b = 13.0136 (6) Å, c = 22.3053 (9) Å, β = 112.210 (2)°, V = 7808.8 (5) Å³, ρ_{calcd} = 1.198 g/cm³, $F(000)$ = 3004. A total of 52025 reflections were measured in the range $3.46 = \theta = 27.47$ (hkl range indices $-37 \leq h \leq 37$, $-16 \leq k \leq 16$, $-28 \leq l \leq 28$), 8935 unique (R_{int} = 0.1001). The structure was refined on F^2 to R_w = 0.2398, R = 0.0908 (5377 reflections with $I > 2\sigma(I)$), and GOF = 1.058 for 498 refined parameters.

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Supporting Information Available: NMR spectra, MS spectra, and X-ray crystallographic data for compound **3** and NMR spectra for compound **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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