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Are Terminal Aryl Butadiynes Stable? Synthesis and X-ray Crystal Structures of a Series of Aryl- and Heteroaryl-butadiynes ($Ar-C\equiv C-C\equiv C-H$)

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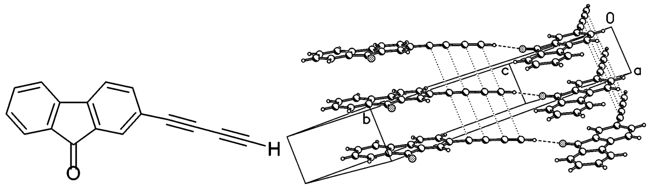
Received July 28, 2006



The synthesis and isolation are reported of a range of terminal aryl- and heteroaryl-butadiynes ($ArC\equiv C-C\equiv CH$) **4a−h** from 2-methyl-6-(aryl/heteroaryl)hexa-3,5-diyn-2-ol precursors. The stability of **4a−h** in solution is concentration dependent: many of the derivatives can be stored as dilute solutions for several days or even weeks. The X-ray crystal structures have been obtained for five $ArC\equiv C-C\equiv CH$ derivatives [Ar = 2-(9-fluorenonyl), 4-biphenyl, 2-pyridyl, 4-pyridyl, and 2-pyrazyl].

Introduction

Within contemporary acetylene chemistry,[1] there is great interest in the synthesis of conjugated diyne and oligoyne molecules. They are fundamentally important carbon-rich building blocks[2] for molecular rods and cyclic frameworks;[3] they are active components in optoelectronic devices (wires, switches and nonlinear optics, etc.),[4] and the extent of intramolecular π-conjugation within the diyne is a topic of experimental and theoretical debate.[5] Although remarkable oligoyne systems $[R-(C\equiv C)_n-R]$ of nanoscale lengths end-capped with organometallic[6] or silyl substituents[7] have been synthesized, simple terminal aryl butadiynes, $ArC\equiv C-C\equiv CH$, remain very elusive targets, which can serve as convenient synthetic reagents for both symmetric and unsymmetric homologues. They have been generated by desilylation of trialkylsilylated precursors ($ArC\equiv C-C\equiv CSiR_3$)[8] or by dehydrohalogenation of haloeneyne ($R-C\equiv C-CH=CHCl$)[9] or ene-haloyne ($R-CH=CH-C\equiv CCl$) derivatives.[10] The $ArC\equiv C-C\equiv CH$ species have generally been used in situ, and it has been frequently stated that they are unstable to isolation due to their rapid decomposition or polymerization.[8c,11] There are, however, a few exceptions. Ferrocenylbutadiyne "can be stored as a solid in a refrigerator under air for several months. However, it does decompose slowly in solutions."[11e] Crystals of 4-tBu-$C_6H_4-C\equiv C-C\equiv CH$ are "stable", and the authors state that "this result was surprising given the reported instability problems of other phenylbutadiyne derivatives."[11f] A terminal butadiyne functionalized with a

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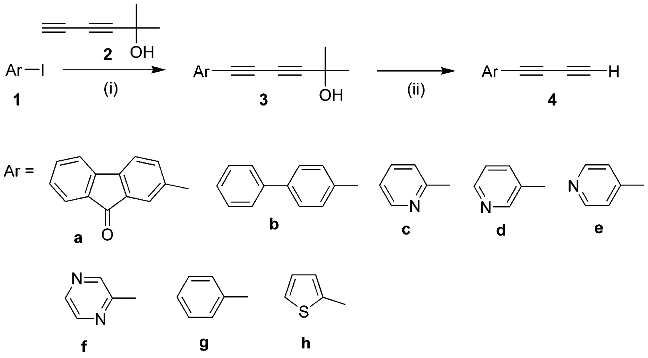
10.1021/jo0615697 CCC: $33.50 © 2006 American Chemical Society
Published on Web 10/05/2006

SCHEME 1[a]



[a] Reagents and conditions: (i) $Pd(PPh_3)_2Cl_2$, CuI, triethylamine, THF, 20 °C; (ii) NaOH, toluene, reflux.

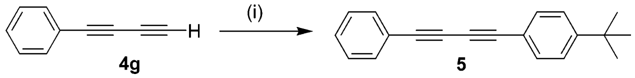
dithiafulvene unit was reported to be "quite stable", although it was not characterized and was homocoupled in situ.[12] Our unexpected finding that crystals of 2-(4-*tert*-butylphenyl)-5-(4-butadiynylphenyl)-1,3,4-oxadiazole were stable to storage at room temperature for at least 2 years[13] prompted us to explore the synthesis of simpler aryl- and heteroaryl-butadiynes.

We now report that a range of $ArC\equiv C-C\equiv CH$ derivatives can be purified under routine conditions and their solutions can be stored for weeks or even months without significant decomposition (NMR evidence). The X-ray crystal structures have been obtained for five $ArC\equiv C-C\equiv CH$ derivatives [Ar = 2-(9-fluorenonyl), 4-biphenyl, 2-pyridyl, 4-pyridyl, and 2-pyrazyl].

Results and Discussion

Synthesis. Our protocol (Scheme 1) is basically different from those used in most other laboratories for arylbutadiyne synthesis,[7−10] although phenylbutadiyne has been prepared previously by a similar method (although not using **2** as a building block) and used in situ.[14] Reaction of the aryl/heteroaryl iodides **1a**−**h** with 2-methyl-3,5-hexadiyn-2-ol **2**[15] under standard Sonogashira conditions[16] [triethylamine, CuI, $Pd(PPh_3)_2Cl_2$, THF, 20 °C] gave precursors **3a**−**h** (75−97% yields), which were deprotected with loss of acetone[17] using a catalytic amount of NaOH in refluxing toluene. Products **4a**−**h** were thereby obtained in 60−91% yields after column chromatography. The survival of **4a**−**h** in this reaction mixture at 110 °C is remarkable. Phenyl- and 2-thienyl-derivatives **4g** and **4h** were the least stable in the series. Nonetheless, NMR analysis of a solution of **4g** (25 mg) in $CDCl_3$ (0.6 mL) stored on the bench in the daylight at 20 ± 2 °C without exclusion of air revealed very little decomposition during at least 2 weeks (see Supporting Information). Refluxing a 5×10^{-2} M solution of biphenyl derivative **4b** in either toluene, cyclohexane, or 1,4-dioxane in daylight for 10 min resulted in a slight darkening of the solution and recovery of 60−70% of unchanged **4b** (NMR evidence; see Supporting Information).

SCHEME 2[a]



[a] Reagents and conditions: (i) 4-*tert*-butyliodobenzene, $Pd(PPh_3)_2Cl_2$, CuI, triethylamine, 45 °C.

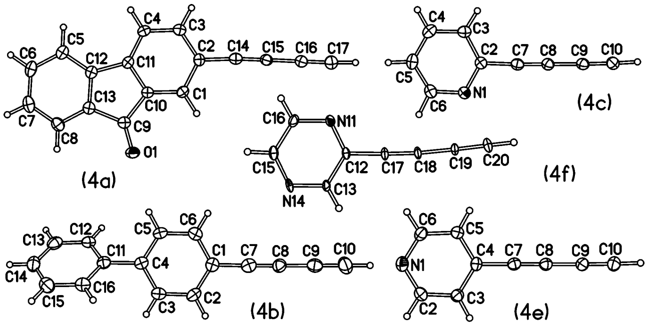


FIGURE 1. X-ray molecular structures at 120 K (50% thermal ellipsoids) of **4a**, **b** (independent molecule A), **c**, **e**, and **f** (the ordered molecule).

The stability of **4a**−**h** in solution is concentration dependent: a general trend is that stability increases with increasing dilution, as noted by other workers for arylbutadiyne species.[11c,f] Amorphous solids of most of the diynes are less stable to storage at ambient conditions, darkening in color within 24 h at 20 °C, although their crystalline forms are sufficiently stable for routine X-ray analysis within a few days of their isolation.

Compound **4g** was cross-coupled in situ with 4-*tert*-butyliodobenzene to afford the expected product **5** in 75% yield based on **3g** (Scheme 2).

X-ray Molecular Structures. X-ray crystal structures were obtained for derivatives **4a**, **b**, **c**, **e**, and **f** (Figure 1) and precursors **3a** and **c** (see Supporting Information).

The packing motifs of **4a**, **c**, **e**, and **f** are basically similar. Molecules are linked by $\equiv C-H\cdots O$ (**4a**; Figure 2) or $\equiv C-H\cdots N$ (**4c**, **e**, **f**) (Figure 3 for **4c**) hydrogen bonds into infinite chains zigzagging along the *y* axis (**4a**, **c**) or running parallel to the $(10\bar{1})$ line (**4e**, **f**), while in the perpendicular direction they form slanted stacks of aryl moieties, as well as arrays of parallel diyne rods, related by the lattice translation *a* (Figure 4 for **4e**). Structure **4f** contains two independent molecules, one of them disordered equally between two positions differing by

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(11) For statements on the instability of simple $ArC\equiv CC\equiv CH$ species, see: (a) Morisaki, Y.; Luu, T.; Tykwinski, R. R. *Org. Lett.* **2006**, *8*, 689−692. This paper states that "aryl butadiynes are unstable to isolation." (b) Heuft, M. A.; Collins, S. K.; Yap, G. P. A.; Fallis, A. G. *Org. Lett.* **2001**, *3*, 2883−2886. (c) Haley, M. M.; Bell, M. L.; English, J. J.; Johnson, C. A.; Weakely, T. J. R. *J. Am. Chem. Soc.* **1997**, *119*, 2956−2957. (d) Graham, E. M.; Miskowski, V. M.; Perry, J. W.; Coulter, D. R.; Stiegman, A. E.; Schaefer, W. P.; Marsh, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 8771−8779. (e) Yuan, Z.; Stringer, G.; Jobe, I. R.; Kreller, D.; Scott, K.; Koch, L.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1993**, *452*, 115−120. (f) Wan, W. B.; Haley, M. M. *J. Org. Chem.* **2001**, *66*, 3893−3901 and references therein. (g) Brandsma, L. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 2004; p 360 describes $PhC\equiv CC\equiv CH$ as "extremely unstable".

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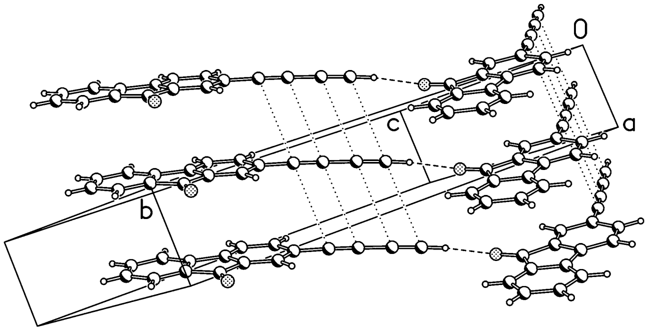

FIGURE 2. Crystal packing of **4a**, showing hydrogen bonds (dashed lines). The repeat vectors of the diyne array (dotted lines) equal the lattice vector **a** (3.79 Å) and form an angle of ca. 68.5° with the diyne rod.

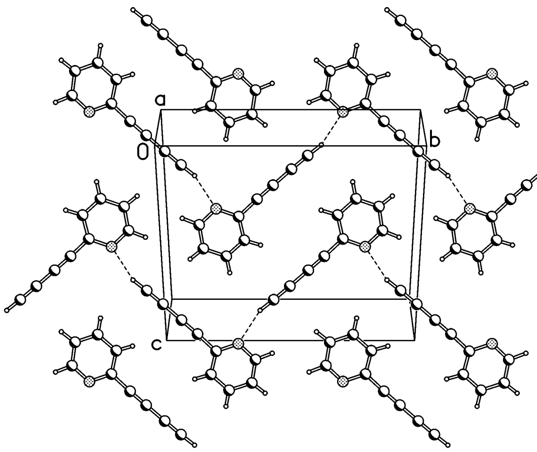

FIGURE 3. Hydrogen bonding (dashed lines) in the crystal of **4c**. Projection on the (101) plane.

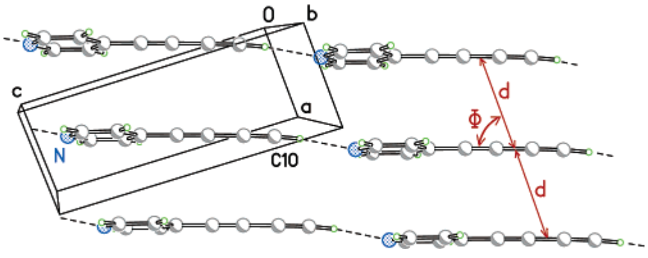

FIGURE 4. Crystal packing of **4e**, showing hydrogen bonds as dashed lines ($d = a = 3.82$ Å, $\Phi = 68.9°$).

a 0.75 Å shift along the direction of the diyne rod as well as the hydrogen-bonded chain. The average of these two positions is related to the second (ordered) molecule by a pseudo-inversion center (${}^{1}/_{2}{}^{1}/_{4}{}^{1}/_{2}$), "upgrading" the actual space group Pn to pseudo-$P2_1/n$.

The asymmetric unit of **4b** comprises two molecules, A and B, whose biphenyl moieties adopt similarly twisted conformations (dihedral angles 45.6° and 42.6°). Molecules of type A form zigzag chains through weak hydrogen bonds[18] $\equiv$C$-$H$\cdots\pi$(Ph), and molecules of type B form parallel chains through $\equiv$C$-$H$\cdots\pi$(C$\equiv$C) bonds.[19] The structure is thus a succession of herringbone layers parallel to the (010) plane (Figure 5). There are no continuous arrays of diyne groups, only isolated (A$\cdots$B) dimers with $d = 5.32$ Å and $\Phi = 63.5°$. In **4b**, the molecular "rod" is slightly bent: the angle between the C(11)$\cdots$C(14) and C(9)$-$C(10) vectors equals 3.4°, and that between the C(11′)$\cdots$C(14′) and C(9′)$-$C(10′) vectors is 9.2°. Compound **4b** is among the most stable of the series, and this increased stability can be explained by this packing mode, which will disfavor polymerization.

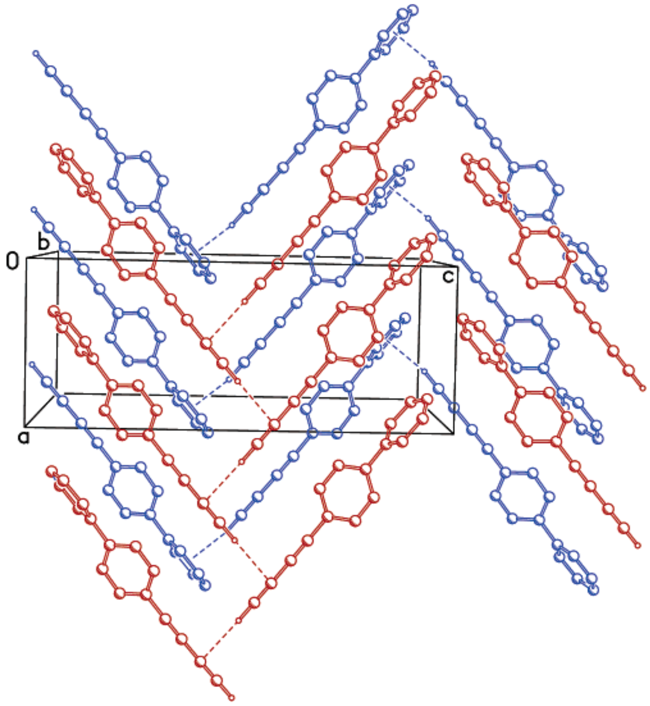

FIGURE 5. Crystal packing of **4b**, projected on the (010) plane. Molecules of type A (blue) lie at $z \approx {}^{1}/_{2}$, and those of type B (red) lie at $z \approx {}^{1}/_{4}$. Nonacetylenic H atoms are omitted.

For the most efficient topochemical polymerization of butadiynes to occur, the guidelines are that the vector between the diyne centroids should have the length ("repeat distance", d) of 4.7$-$5.2 Å and form an angle (Φ) of ca. 45° with the diyne rod, such an arrangement bringing the C_α atom of one diyne opposite to the C_δ of the next.[20] A nonslanted array, with every diyne carbon in close contact with its counterparts, is also favorable.[20c] Structures **4a**, **c**, **e**, and **f** have $d \approx 3.8$ Å and $\Phi = 68-69°$, not far from the ideal parameters of the latter arrangement ($d = 3.4$ Å, $\Phi = 90°$) and practically the same as in the structures of $C_6F_5C{\equiv}C{-}C{\equiv}CPh$ ($d = 3.7$ Å, $\Phi = 75°$) or $PhC{\equiv}C{-}C{\equiv}CPh{\cdot}C_6F_5C{\equiv}C{-}C{\equiv}CC_6F_5$ ($d = 3.7$ Å, $\Phi = 72-82°$), both of which undergo a neat lattice-preserving polymerization.[20c] Indeed, solid-state polymerization without preservation of crystallinity can occur even with much more awkward packing. However, it has been shown that structures outside the general guidelines will not readily react and molecules that might be chemically labile are kinetically trapped and thereby stabilized in the crystal lattice.[21]

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Conclusions

In summary, we have synthesized and isolated a range of terminal aryl- and heteroaryl-butadiynes **4a**−**h**. A general trend is that stability in solution increases with increasing dilution. Many of the $ArC\equiv C-C\equiv CH$ derivatives can be stored as dilute solutions for several days or even weeks, and crystal structures can be readily obtained within a few days of their preparation. The shelf-stability of many of these $ArC\equiv C-C\equiv CH$ derivatives is notable as it is often stated that aryl butadiynes are unstable to isolation.[11] The availability of $ArC\equiv C-C\equiv CH$ species from readily available precursors should facilitate the synthesis of new acetylenic scaffolds, molecular rods and cycles, as well as transition metal complexes of conjugated di- and oligoyne species.

Experimental Section

General Procedure for the Preparation of 3a−h. A mixture of the iodoarenes **1a**−**h**, 2-methyl-3,5-hexadiyn-2-ol **2**,[15] $Pd(PPh_3)_2Cl_2$, CuI, and triethylamine (with additional THF for **3a**) was stirred at 20 or 45 °C for 5−18 h, as detailed below. The volatile liquids were removed by vacuum evaporation, and the residue was chromatographed on a silica column and/or recrystallized to afford products **3a**−**h**.

2-(5-Hydroxy-5-methylhexa-1,3-diynyl)-9-fluorenone (3a). 2-Iodofluorenone **1a** (0.35 g, 1.14 mmol), 2-methyl-3,5-hexadiyn-2-ol **2** (0.25 g, 2.31 mmol), THF (5 mL), $Pd(PPh_3)_2Cl_2$ (40 mg), CuI (15 mg), and triethylamine (30 mL) at 20 °C for 5 h gave **3a** as yellow needles (0.32 g, 97%) after column chromatography (silica, chloroform−diethyl ether 85:15 v/v) and recrystallization from an ethanol−H_2O mixture: mp 157.0−157.8 °C. The single crystal used for X-ray analysis (orange needle) was obtained by slow evaporation of its chloroform solution at room temperature. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.72 (s, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.58 (dd, $J_{12} = 7.6$ Hz, $J_{13} = 1.2$ Hz, 1H), 7.51 (s, 1H), 7.50 (d, $J = 2.2$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.32 (m, 1H), 2.05 (s, 1H), 1.59 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.6, 144.6, 143.7, 138.7, 135.0, 134.0, 134.2, 129.7, 128.0, 124.6, 122.4, 120.8, 120.3, 87.8, 77.8, 74.8, 66.9, 65.8, 31.1. MS (EI) m/z 285.9 (M^+, 87%), 270.9 ($M^+ - 15$, 100%). Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.82; H, 4.93.

General Procedure for the Preparation of 4a−h. Compounds **3a**−**h** were dissolved in dry toluene. NaOH powder was added, and the mixture was stirred and heated under Ar for 15−60 min with an oil-bath at 135 °C. TLC was used to monitor the end-point of the reaction. The reaction mixture was evaporated, and the residue was purified by column chromatography on silica. *Caution: Although no problems were experienced in the present work, care should be taken when handling solid samples of the terminal butadiynes. There is a history of explosions with analogous compounds in other laboratories, for example, terminal hexatriynes.*[22]

2-(Buta-1,3-diynyl)-9-fluorenone (4a). Compound **3a** (0.29 g, 1.01 mmol), NaOH (120 mg), toluene (15 mL), and heating afforded **4a** as greenish-yellow needles (0.17 g, 72%) after column chromatography (silica, chloroform) and recrystallization from a chloroform−ethanol mixture. The single crystal (a greenish-yellow needle) used for X-ray structural analysis was obtained by slow evaporation of its chloroform solution. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.77 (s, 1H), 7.68 (d, $J = 6.8$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.53 (s, 1H), 7.51 (m, 2H), 7.34 (t, $J = 7.0$ Hz, 1H), 2.54 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, 333 K): δ 192.2, 144.9, 143.7, 138.9, 134.9, 134.6, 134.5, 129.8, 128.3, 124.6, 122.1, 120.8, 120.3, 75.2, 74.5, 72.2, 68.0. MS (EI) m/z 227.9 (M^+, 100%). Anal. Calcd for $C_{17}H_8O$: C, 89.46; H, 3.53. Found: C, 88.98; H, 3.44. Upon standing on the laboratory bench at ambient conditions, crystals of **4a** gradually turned dark green. The crystals did not have a melting point at <350 °C. Upon heating the $CDCl_3$ solution (∼15 mg in 0.5 mL) at 65 °C, a multiplet ^1H NMR signal at δ ∼7.5 ppm increased gradually, indicating a structural change of the diyne group.

1-(4-*tert*-Butylphenyl)-4-phenylbutadiyne (5). Compound **3g** (0.29 g, 1.53 mmol), NaOH (0.14 g), and toluene (30 mL) afforded **4g** as a colorless oil (0.18 g, 1.45 mmol), which was purified by column chromatography (silica, hexane). Hexane was removed in vacuo, and without delay this sample of **4g**, 4-*tert*-butyliodobenzene (0.18 mL, 0.96 mmol), $Pd(PPh_3)_2Cl_2$ (34 mg), CuI (10 mg), and triethylamine (50 mL) was mixed and stirred at 45 °C for 18 h to afford **5** as a yellow solid (0.19 g, 75% from **3g**) after column chromatography (silica, dichloromethane): mp 79.7−80.5 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55−7.53 (m, Ar−H, 2H), 7.49−7.47 (m, Ar−H, 2H), 7.38−7.34 (m, Ar−H, 5H), 1.33 (s, $(CH_3)_3$, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.8, 132.6, 132.4, 129.2, 128.6, 125.6, 122.1, 118.8, 82.0, 81.3, 74.3, 73.4, 35.1, 31.2. GC−MS (EI) m/z 259.1 (M^+). Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.75; H, 6.96.

Acknowledgment. We thank EPSRC for funding this work.

Supporting Information Available: Description of the general protocols for the synthesis and characterization of **3b**−**h** and **4b**−**h**; copies of ^1H and ^{13}C NMR spectra of **4g** and **4b**; X-ray crystallographic file for **3a**, **3c**, **4a**, **4b**, **4c**, **4e**, and **4f** in CIF format; additional ORTEP drawings and discussion of their structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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