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Synthesis of Hexahelicene and 1-Methoxyhexahelicene via Cycloisomerization of Biphenylyl-Naphthalene Derivatives

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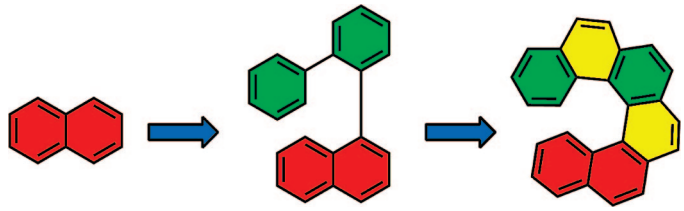

The new approach provides nonphotochemical syntheses of helicenes based on the easy, convergent, and modular assembly of key biphenylyl-naphthalenes and their platinum-catalyzed double cycloisomerization. This sequence of reactions provides a synthetic route to helicenes in two steps from simply accessible building blocks. Furthermore, the method enables the introduction of substituents into the hexahelicene skeleton. The strategy developed is exemplified by the synthesis of 6,10-dimethylhexahelicene and 1-methoxy-6,10-dimethylhexahelicene.

Introduction

The helicenes were long considered academic curiosities because of their twisted shape as a result of the steric repulsive interaction between terminal aromatic rings.[1] Their promising optical[2] and electronic[3] properties have renewed a 50 year old interest in helicene chemistry in the past decade. They are considered potentially useful for asymmetric catalysis,[4] asymmetric molecular recognition,[5] liquid crystal molecules,[6] and even in molecular machinery.[7] Their intriguing semiconductivity and conductivity was foreseen depending on the radius and the width of the helical aromatic ribbon.[8] For a specific structure, which is still far from any practical synthesis, even metallic conductivity might be expected. Their ability to bind to specific DNA structures has been demonstrated.[9] Besides photocyclization reactions,[10] new methodologies, including Diels−Alder

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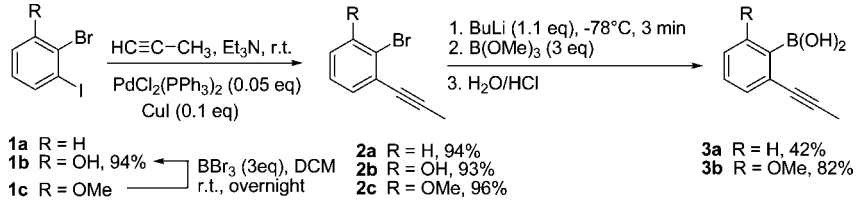
SCHEME 1



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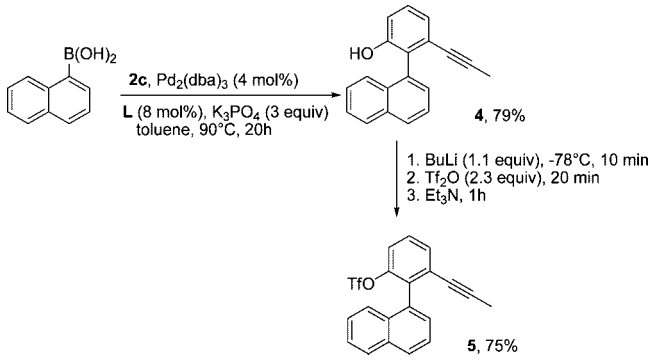

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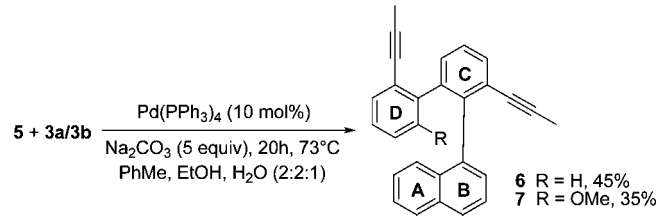

cycloadition,[11] [2 + 2 + 2] cycloisomerization,[12] carbenoid coupling,[13] radical tandem cyclization,[14] domino Friedel−Crafts-type cyclization,[15] Pd-mediated techniques,[16] and olefin metathesis,[17] have been developed.

In pursuit of our previous investigations in this field,[18] we describe an alternative approach to [6]helicene synthesis based on a $PtCl_2$-catalyzed double carbocyclization reaction of alkynylated biphenylyl-naphthalene derivatives. The potential of platinum chloride and related salts to induce highly selective skeletal rearrangements of polyunsaturated compounds was recognized only recently.[19] $PtCl_x$ ($x = 2, 4$) is able to catalyze an amazingly broad spectrum of C−C bond formations that allow one to convert enynes and related substrates into a myriad of carbo- and heterocyclic products. A new pathway into highly substituted phenanthrenes and related polycyclic arenes based on the cycloisomerization process catalyzed by $PtCl_2$ was developed by Fürstner.[20] Our modular method for 1-substituted and unsubstituted 6,10-dimethylhexahelicene synthesis is based on assembling the target from functionalized building blocks with a final atom economic transformation.

Results and Discussion

Synthesis of Building Blocks. 2-Bromo-1-iodo-3-methoxybenzene[21] **1c**, whose methoxy group appears as a useful functionality in a desired position at the [6]helicene scaffold, and 1-bromo-2-iodobenzene **1a** were reacted with propyne under Sonogashira coupling conditions to obtain alkynylated products **2a** and **2c** (Scheme 1).

2-Bromo-3-iodophenol **1b** prepared from **1c** or according to the literature procedure[22] was converted into **2b** in the same manner. Boronic acids **3a** and **3b** were prepared from **2** by lithiation and subsequent reaction with $B(OMe)_3$. The synthesis of the naphthalene building block (Scheme 2) starts from naphthalene boronic acid, which was subjected to a Suzuki reaction with bromophenol **2b** under palladium/2-(2′,6′-dimethoxybiphenyl)dicyclohexylphosphine **L** catalysis[23] to give hydroxy compound **4**. Conversion to a lithium phenolate and subsequent reaction with triflic anhydride gave triflate **5**.

Construction of Hexahelicene. Having prepared the suitable building blocks, we could approach assembling the hexahelicene scaffold. Suzuki coupling of building blocks **5** and **3a** or **3b** led to the biphenylyl-naphthalenes **6** or **7** (Scheme 3). Introduction of two chiral axes (naphthyl−phenyl and phenyl−phenyl

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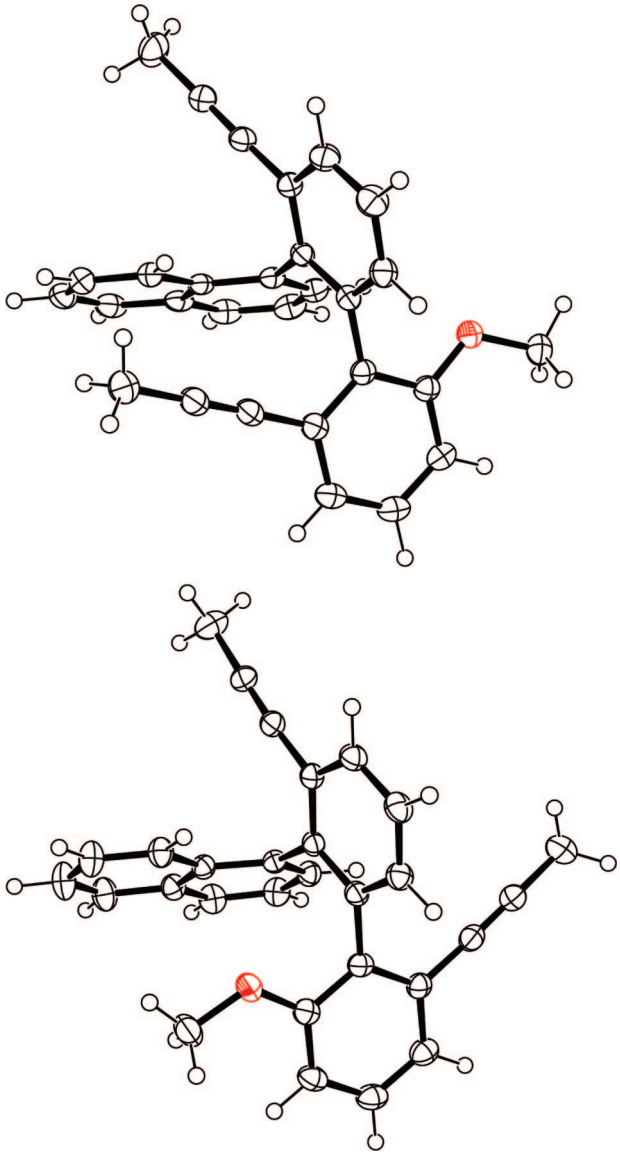
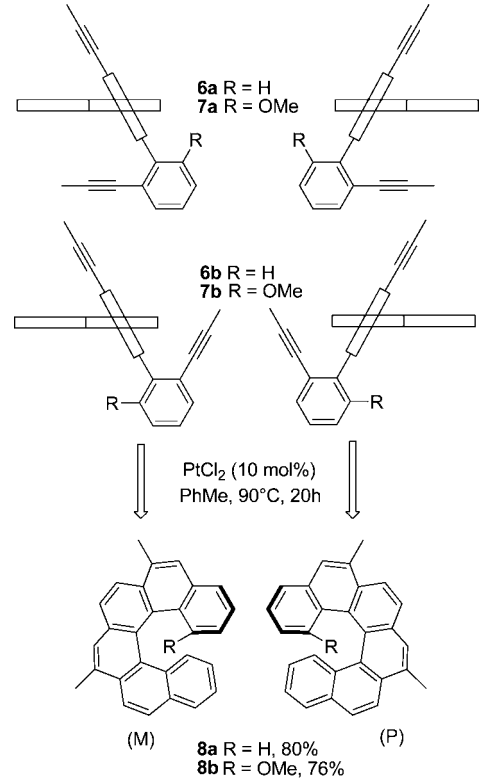


FIGURE 1. ORTEP projection of the crystal structure **7a** (top) and **7b** (bottom).

bond) gives rise to four isomers of **6** and **7** (Scheme 3). Free rotation in **6** around the phenyl−phenyl bond (ring **C** and **D**) at ambient temperature makes it impossible to separate the two diastereomers.

The ^{1}H NMR spectra show broad signals of the aromatic protons in rings **C** and **D**. On the other hand, presence of the methoxy group in **7** hinders rotation at ambient temperature, and two diastereomers **7a** and **7b** can be separated using

SCHEME 4



reversed phase chromatographic conditions, and their ^{1}H NMR spectra can be acquired via LC-NMR technique. The on-flow LC-NMR experiment showed both isomers of **7** in an approximate ratio of 30:70 (**7a**/**7b**) in acetonitrile/deuterium oxide solvent mixture (Figure S8, Supporting Information). Semi-preparative HPLC led to isolation of pure compounds **7a** and **7b**. The full assignment was performed on the basis of classic 1D and 2D NMR experiments in $CDCl_3$. The NOE experiment on **7a** revealed strong interaction between the methoxy group and naphthyl ring **B** and weak interaction of propynyl group and ring **A**. At the same time, only interactions between the methoxy group and naphthyl ring **A** were found in **7b**. The results of NOE experiments indicate the opposite orientation of the methoxy(propynyl)phenyl ring **D** around the phenyl−phenyl bond in both isomers. The sharp signals of the methyl groups indicate that no dynamic behavior takes place. The methoxy(propynyl)phenyl group can stop even the rotation of the (propynyl)phenyl group **C** around naphthyl−phenyl bond, and thus the conformation is fixed in both isomers. Furthermore, suitable single crystals were grown from the chloroform/acetonitrile mixture, and both structures were proven by X-ray crystallography (Figure 1).

7a and **7b** crystallize in the space group $P\bar{1}$, thus the crystals contain also the opposite enantiomers. To achieve the desired cycloisomerization and, accordingly, to build up the helix, biphenylyl-naphthalenes **6** and **7** were exposed to $PtCl_2$ (Scheme 4).

The desired double cycloisomerization took place following a 6-*endo* pathway, and racemic unsubstituted and 1-substituted 6,10-dimethylhexahelicenes **8a** and **8b** were formed in good yields. The enantiomers of **7a** and **7b** undergo double cycloisomerization, yielding hexahelicene **8b**. Regardless of which diastereomeric form of **7** (or a mixture of both) was taken into the reaction, the same product (i.e., two enantiomeric forms of

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the helix; Scheme 4), was built. Thus, the final product always contains a racemic mixture of the hexahelicenes. The X-ray crystallography has revealed both enantiomers of **8b** in the crystal lattice (Figure S9, Supporting Information).

Experimental Section

For general procedure, see Supporting Information.

2-Bromo-1-methoxy-3-(propyn-1-yl)benzene (2c): 1c (6.3 g, 20 mmol) was used according to general procedure. Yield 4.3 g (96%) of slightly yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (m, 1H), 7.05 (dd, J = 1.4, 7.7 Hz, 1H), 6.80 (dd, J = 1.4, 8.2 Hz, 1H), 2.11 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8 (s), 127.2 (d), 127.1 (s), 125.1 (d), 114.5, (s), 110.6 (d), 90.7 (s), 77.1 (s), 56.0 (q), 4.2 (q); MS (EI) *m*/*z* 224 (100% M^+), 210, 182, 145, 130, 115, 102, 75. Anal. Calcd for $C_{10}H_9BrO$: C, 53.36; H, 4.03. Found: C, 53.25; H, 4.17.

2-Methoxy-6-(propyn-1-yl)phenylboronic acid (3b): 2c (11.55 g, 51.3 mmol) was used according to general procedure. Yield 8.0 g (82%) of slightly yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (dd, J = 0.7, 7.7 Hz, 1H), 6.92 (m, 1H), 5.33−4.58 (br s, 2H), 7.36 (m, 1H), 3.92 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5 (s), 131.7 (d), 129.5 (s), 126.0 (d), 110.6 (d), 91.8 (s), 80.4 (s), 55.9 (q), 4.4 (q); MS (EI) *m*/*z* 146 (100%, M^+ − BOOH), 131, 115, 103, 77. Anal. Calcd for $C_{10}H_{11}BO_3$: C, 63.21; H, 5.84. Found: C, 63.11; H, 5.53.

2-(Naphthalen-1-yl)-3-(propyn-1-yl)phenol (4): The Schlenk tube was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (612 mg, 0.59 mmol, 3 mol %), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (485 mg, 1.18 mmol, 6 mol %), anhydrous K_3PO_4 (12.55 g, 59.1 mmol, 3 equiv), and naphthaleneboronic acid (8.45 g, 49.1 mmol, 2.5 equiv). The Schlenk tube was then evacuated and backfilled with argon (this sequence was repeated three times). Dry toluene (170 mL) was added, and the resulting mixture was stirred at room temperature for ∼2 min. Then **2c** (4.13 g, 19.6 mmol) was added, and the reaction mixture was heated at 90 °C with stirring for 20 h. The reaction mixture was then allowed to cool to room temperature, diluted with diethyl ether (50 mL), filtered through a thin pad of silica gel (eluting with diethyl ether), and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel (hexane/ethyl acetate, 3:1) to provide 4.0 g (79%) of **4** as a slightly yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96−7.89 (m, 2H), 7.64−7.39 (m, 5H), 7.28 (m, 1H), 7.16 (dd, J = 1.2, 7.7 Hz, 1H), 7.00 (dd, J = 1.2, 8.1 Hz, 1H), 4.72 (s, 1H), 1.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3 (s), 134.3 (s), 133.9 (s), 132.2 (s), 132.0 (s), 129.1 (d), 129.0 (d), 128.9 (d), 128.4 (d), 128.3 (d), 126.6 (d), 126.3 (d), 125.7 (d), 125.6 (d), 124.7 (d), 115.0 (d), 89.1 (s), 78.5 (s), 4.1 (q); MS (EI) *m*/*z* 258 (100%, M^+), 241, 231, 226, 213, 202, 189, 119, 113, 106, 101. Anal. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.22; H, 5.61.

2-(Naphthalen-1-yl)-3-(propyn-1-yl)phenyl trifluoromethanesulfonate (5): *n*-Butyllithium (2.5 M in hexanes, 6.8 mL, 17.0 mmol, 1.1 equiv) was added dropwise to phenol **4** (4.0 g, 15.5 mmol) in THF (80 mL) under an atmosphere of argon, and the mixture was stirred at −78 °C for 10 min. Triflic anhydride (6.0 mL, 35.7 mmol, 2.3 equiv) was added dropwise, and the reaction mixture was stirred at −78 °C for 20 min. To prevent decomposition of the product, triethylamine (3.2 mL, 23.0 mmol, 1.5 equiv) was added, and the reaction mixture was allowed to reach rt. The solvents were removed in vacuo, and the residue was chromatographed on silica gel (hexane/acetone, 4:1) to obtain triflate **5** (4.5 g, 75%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95−7.88 (m, 2H), 7.61−7.34 (m, 8H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0 (s), 136.4 (s), 133.6 (s), 132.4 (d), 131.9 (s), 131.8 (s), 129.2 (s), 129.1 (d), 128.7 (d), 128.4 (d), 126.4 (d), 126.0 (d), 125.6 (d), 125.2 (d), 120.9 (d), 92.0 (s), 77.5 (s), 4.3 (q); MS (EI) *m*/*z* 390 (80% M^+), 257, 242, 226, 202. Anal. Calcd for $C_{20}H_{13}F_3O_3S$: C, 61.53; H, 3.36. Found: C, 61.43; H, 3.49.

1-(2′-Methoxy-3,6′-di(propyn-1-yl)biphenyl-2-yl)naphthalene (7): 3b (0.68 g, 3.6 mmol, 2 equiv) was used according to general procedure. Purification by column chromatography on silica gel 60 RP-C18 (acetonitrile/water, 70:30 to 80:20) gave **7** (0.24 g, 35%) as a white solid. **7a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70−7.67 (m, 2H), 7.64−7.61 (m, 1H), 7.57 (dd, J = 1.3, 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.36 (dd, J = 1.3, 7.1 Hz, 1H), 7.34−7.25 (m, 4H), 6.87 (t, J = 7.8 Hz, 1H), 6.68 (dd, J = 0.9, 7.7 Hz, 1H), 6.53 (dd, J = 0.8, 8.3 Hz, 1H), 3.62 (s, 3H), 1.85 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (125.69 MHz, $CDCl_3$) δ 156.3 (s), 142.5 (s), 138.0 (s), 137.8 (s), 132.8 (s), 132.4 (s), 132.0 (s), 131.3 (d), 130.4 (d), 127.8 (d), 127.5 (d), 127.4 (d), 127.1 (d), 127.0 (d), 126.9 (d), 124.9 (d), 124.8 (s), 124.6 (s), 124.3 (d), 124.2 (d), 124.1 (d), 109.3 (d), 89.0 (s), 88.9 (s), 79.3 (s), 79.1 (s), 55.1 (q), 4.4 (q), 4.0 (q); MS (EI) *m*/*z* 386 (100%, M^+), 371, 356, 340, 313, 168, 156. Anal. Calcd for $C_{29}H_{22}O$: C, 90.12; H, 5.74. Found: C, 90.28; H, 5.80. **7b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80−7.76 (m, 1H), 7.75−7.71 (m, 1H), 7.62−7.59 (m, 1H), 7.55 (dd, J = 1.5, 7.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.38−7.34 (m, 3H), 7.20−7.16 (m, 1H), 7.14 (dd, J = 1.3, 7.1 Hz, 1H), 6.96−6.90 (m, 2H), 6.26 (dd, J = 1.9, 7.4 Hz, 1H), 2.77 (s, 3H), 1.90 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (125.69 MHz, $CDCl_3$) δ 156.0 (s), 142.5 (s), 138.0 (s), 137.8 (s), 132.9 (s), 132.6 (s), 132.0 (s), 131.0 (d), 130.7 (d), 127.8 (d), 127.6 (d), 127.4 (d), 127.1 (d), 126.9 (d), 126.8 (d), 125.4 (s), 124.7 (d), 124.6 (s), 124.5 (d), 124.4 (d), 123.8 (d), 109.2 (d), 89.4 (s), 89.1 (s), 79.5 (s), 79.2 (s), 54.4 (q), 4.4 (q), 4.0 (q); MS (EI) *m*/*z* 386 (100%, M^+), 371, 356, 340, 313, 168, 156. Anal. Calcd for $C_{29}H_{22}O$: C, 90.12; H, 5.74. Found: C, 90.26; H, 5.82.

1-Methoxy-6,10-dimethylhexahelicene (8b): 7 (0.5 g, 1.3 mmol) was used according to general procedure. Purification by column chromatography on silica gel (hexane/chloroform, 3:1) gave 0.38 g (76%) of **8b** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 8.3 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.84 (s, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.72 (s, 1H), 7.42 (d, J = 7.9 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 6.51 (t, J = 8.2 Hz, 1H), 6.03 (d, J = 7.8 Hz, 1H), 2.93 (s, 3H), 2.91 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (125.69 MHz, $CDCl_3$) δ 154.9 (s), 133.2 (s), 132.6 (s), 132.4 (s), 131.4 (s), 131.3 (s), 131.2 (s), 130.9 (s), 128.4 (s), 128.3 (s), 127.4 (d), 127.0 (d), 126.6 (d), 126.3 (d), 126.2 (d), 126.2 (d), 126.1 (d), 124.9 (s), 124.4 (s), 123.2 (d), 122.2 (d), 122.1 (d), 121.2 (s), 119.2 (d), 104.5 (d), 89.8 (d), 53.7 (q), 20.2 (q), 20.0 (q); MS (EI) *m*/*z* 386 (100%, M^+), 369, 356, 178, 156. Anal. Calcd for $C_{29}H_{22}O$: C, 90.12; H, 5.74. Found: C, 90.20; H, 5.82.

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Supporting Information Available: Experimental procedures and spectroscopic details for compounds **1b**, **2a**, **2b**, **3a**, **6**, **8a**; and a copy of ^{1}H NMR spectra for all compounds; and X-ray diffraction data for **7a**, **7b**, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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