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# Synthesis and Structures of Diindeno-Fused 1,12-Diphenylbenzo[*c*]phenanthrene and 1,14-Diphenyl[5]helicene Bearing Severe Helical Twists

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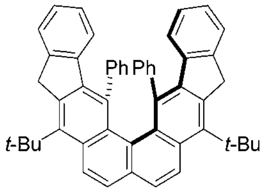
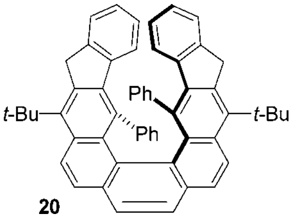
## ABSTRACT



**15**



**20**

**Diindeno-fused 1,12-diphenylbenzo[*c*]phenanthrene 15 and 1,14-diphenyl[5]helicene 20 were prepared in a four-step synthetic sequence from 2,7-naphthalenedicarboxylic acid and 3,6-phenanthrenedicarboxylic acid, respectively. The X-ray structures of 15 and 20 show that the fused ring systems possess severe helical twists. The rotational barriers of the phenyl substituents were determined by the analysis of temperature-dependent $^1$H NMR spectra.**

The sterically congested 1,12-dimethylbenzo[*c*]phenanthrene (**1a**) (Figure 1) was first synthesized by Newman and Wolf in 1952.[1] The X-ray crystallographic structure of **1a** exhibited out-of-plane deformation.[2] The resolution of an acetic acid derivative, 1,12-dimethylbenzo[*c*]phenanthrene-5-acetic acid (**1b**), provided the initial evidence of the helical shape of the molecule.[3] The corresponding methyl ester was found to be of high configurational stability, undergoing only slow racemization even at 250 °C. The stability of the structure and the ready availability of optically pure 5,8-disubstituted 1,12-dimethylbenzo[*c*]phenanthrenes (**1c**) make them excellent chiral building blocks for a variety of derivatives.[4] The synthesis of an interesting 1,12-bis(2-pyridyl) derivative was also reported.[5]

A computational study of substituted dibenzo[*c*,*g*]phenanthrenes ([5]helicenes) also showed that 1,14-dimethyl[5]helicene (**2a**) has a high racemization barrier.[6] While the

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(1) Newman, M. S.; Wolf, M. *J. Am. Chem. Soc.* **1952**, *74*, 3225−3228.

(2) Hirshfeld, F. L.; Sandler, S.; Schmidt, G. M. J. *J. Chem. Soc.* **1963**, 2108−2125.

(3) Newman, M. S.; Wise, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 450−454.

(4) (a) Yamaguchi, M.; Okubo, H.; Hirama, M. *Chem. Commun.* **1996**, 1771−1772. (b) Cheung, J.; Field, L. D.; Hambley, T. W.; Sternhell, S. *J. Org. Chem.* **1997**, *62*, 62−66. (c) Okubo, H.; Yamaguchi, M.; Kabuto, C. *J. Org. Chem.* **1998**, *63*, 9500−9509. (d) Okubo, H.; Nakano, D.; Anzai, S.; Yamaguchi, M. *J. Org. Chem.* **2001**, *66*, 557−563. (e) Saiki, Y.; Nakamura, K.; Nigorikawa, Y.; Yamaguchi, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5190−5192. (f) Sugiura, H.; Nigorikawa, Y.; Saiki, Y.; Nakamura, K.; Yamaguchi, M. *J. Am. Chem. Soc.* **2004**, *126*, 14858−14864. (g) Sugiura, H.; Takahira, Y.; Yamaguchi, M. *J. Org. Chem.* **2005**, *70*, 5698−5708. (h) Nakano, D.; Hirano, R.; Yamaguchi, M.; Kabuto, C. *Tetrahedron Lett.* **2003**, *44*, 3683−3686 and references therein.

(5) Fields, D. L.; Regan, T. H. *J. Heterocycl. Chem.* **1973**, *10*, 195−199.

(6) Janke, R. H.; Haufe, G.; Würthwein, E.-U.; Borkent, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 6031−6035.

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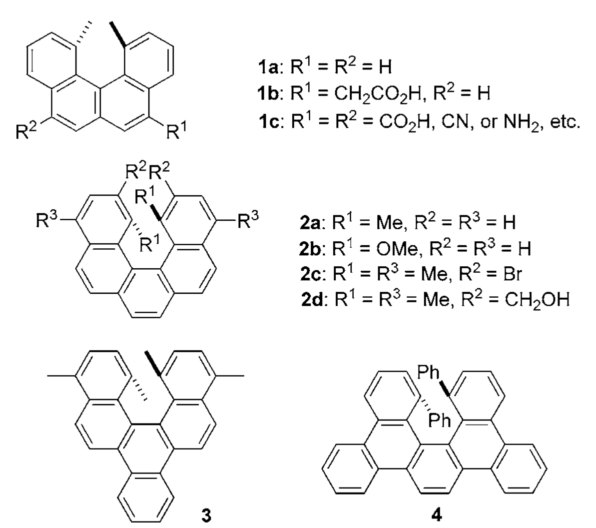


**Figure 1.** 1,12-Dimethylbenzo[*c*]phenanthrenes **1**, 1,14-disubstituted-[5]helicenes **2**, and related compounds **3** and **4**.

synthesis of **2a** has not been reported, photodehydrocyclization of a stilbene-like derivative produced 1,14-dimethoxy-[5]helicene (**2b**) in 61% yield.[7] Other closely related compounds, including **2c**,**d** and **3**, have also been synthesized by photodehydrocyclization or by the Diels–Alder reaction.[8,9] For 14,15-diphenyldibenzo[*f*,*j*]picene (**4**) with the two phenyl substituents at the most sterically hindered positions, the use of the photodehydrocyclization method gave only very low yield (<1%).[10]

We recently reported the use of *p*-dipivalobenzene in a three-step synthetic sequence for the preparation of the diindeno-fused 4,5-diphenylphenanthrene **5** (Figure 2) in 38% overall yield.[11] The X-ray structure of **5** shows a severe helical twist of the fused ring system. Similarly, **6** bearing four congested phenyl substituents and possessing a severe helical twist of the fused ring system was likewise synthesized from *p*-dipivalobenzene in 18% overall yield.[12] The structure of **6** resembles that of a segment of a spiral staircase with the four phenyl groups mimicking the four parallel steps. We now have successfully extended this three-step reaction sequence to the synthesis of a diindeno-fused 1,12-diphenylbenzo[*c*]phenanthrene and 1,14-diphenyl[5]helicene bearing severe helical twists.

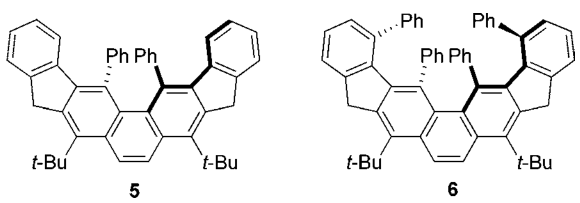
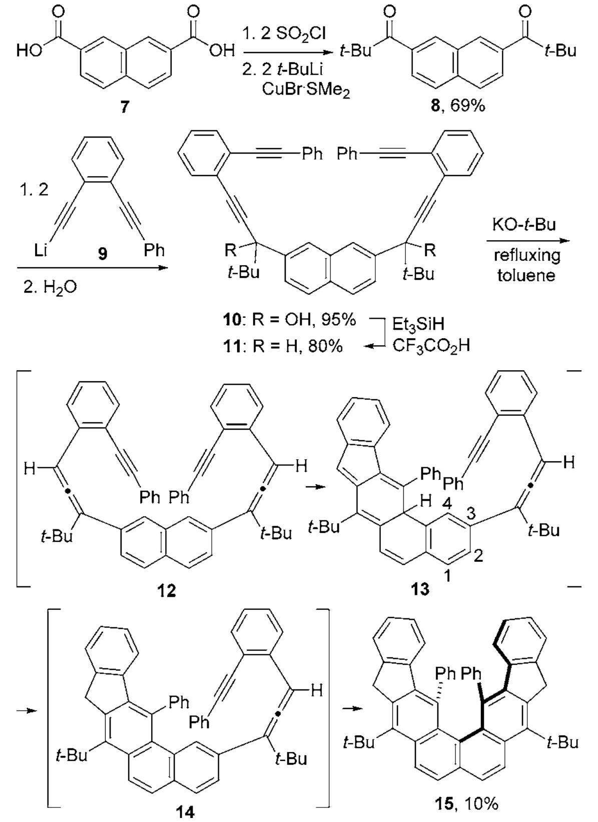


**Figure 2.** Structures of 4,5-diphenylphenanthrenes **5** and **6**.

The requisite 2,7-dipivalonaphthalene (**8**) was prepared by converting 2,7-naphthalenedicarboxylic acid (**7**)[13] to the corresponding acid chloride followed by treatment with *tert*-butylcopper, prepared from *tert*-butyllithium and CuBr•$SMe_2$ (Scheme 1). Condensation between **8** and 2 equiv of lithium acetylide **9** furnished the benzannulated enediynyl alcohol **10** as an essentially 1:1 mixture of two diastereomers. Treatment of **10** with triethylsilane in the presence of trifluoroacetic acid at room temperature for 10 min produced the benzannulated enediyne **11** also as an essentially 1:1 mixture of two diastereomers. On exposure to potassium *tert*-

**Scheme 1**



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[7] Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769–3775.

[8] (a) Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 271–276. (b) Nakazaki, M.; Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 787–788. (c) Minuti, L.; Taticchi, A.; Marrocchi, A.; Gacs-Baitz, E.; Galeazzi, R. *Eur. J. Org. Chem.* **1999**, 3155–3163.

[9] Sudhakar, A.; Katz, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 179–181.

[10] Laarhoven, W. H.; Boumans, P. G. F. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 114–118.

[11] Li, H.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 7804–7810.

[12] Dai, W.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2004**, *6*, 4355–4357.

[13] (a) Honzawa, S.; Okubo, H.; Nakamura, K.; Anzai, S.; Yamaguchi, M.; Kabuto, C. *Tetrahedron: Asymmetry* **2002**, *13*, 1043–1052. (b) Katz, T. J.; Liu, L.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S.; Nuckolls, C.; Rickman, B. H. *J. Am. Chem. Soc.* **1997**, *119*, 10054–10063.

butoxide in refluxing toluene for 3 h, **11** was transformed to the diindeno-fused 1,12-diphenylbenzo[*c*]phenanthrene **15** in a single operation in 10% yield. While the yield of the reaction is not high, it is significantly better than the yield of less than 1% of **4** by the photodehydrocyclization method.

The transformation from **11** to **15** likely involved initial prototropic rearrangements to form the benzannulated enyne−allene **12** as described previously for **5** and **6**. An intramolecular Diels−Alder reaction, presumably proceeding through a Schmittel cyclization reaction[14] to generate the corresponding biradical followed by an intramolecular radical−radical coupling involving a sterically more hindered α-carbon of the naphthyl ring, then produced **13**. The higher reactivity of the α-position than the *β*-position of the naphthyl ring in the homolytic addition reaction was reported previously.[15] A subsequent prototropic rearrangement to regain aromaticity then led to **14**. A similar cascade sequence of the second benzannulated enyne-allene unit then furnished **15**. The preferential attack of the sterically more hindered C4 position of the phenanthryl ring in **14** was also observed previously.[16] It is worth noting that without a prior prototropic rearrangement of **13** to form **14**, the C4 carbon of **13** could only be regarded as a member of a benzene ring. Consequently, it could be anticipated that the sterically less hindered C2 position of **13** would have been attached preferentially.

Similarly, by starting from 3,6-phenanthrenedicarboxylic acid (**16**) (Figure 3),[17] 3,6-dipivalophenanthrene (**17**) was obtained in 43% yield and then was used for condensation with 2 equiv of **9** to produce the benzannulated enediynyl alcohol **18** in 91% yield. Subsequent reduction with triethylsilane in the presence of trifluoroacetic acid gave **19** in 83% yield. On treatment of **19** with potassium *tert*-butoxide in refluxing toluene for 3 h, the diindeno-fused 1,14-diphenyl[5]helicene **20** was produced in 47% yield.

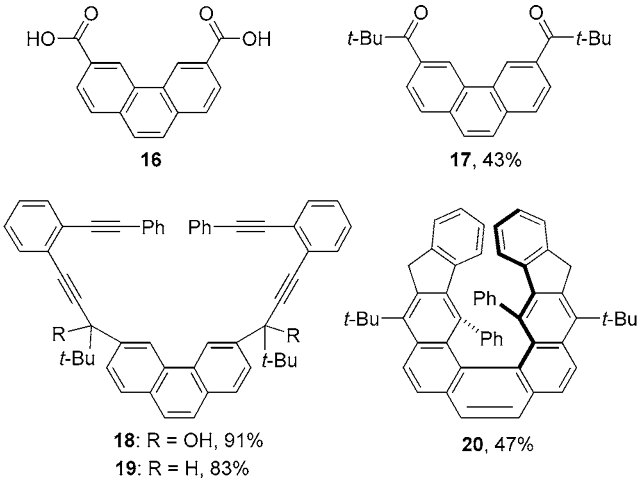

**Figure 3.** 3,6-Phenanthrenedicarboxylic acid (**16**), 3,6-dipivalophenanthrene (**17**), benzannulated enediynyl alcohol **18**, benzannulated enediyne **19**, and 1,14-diphenyl[5]helicene **20**.

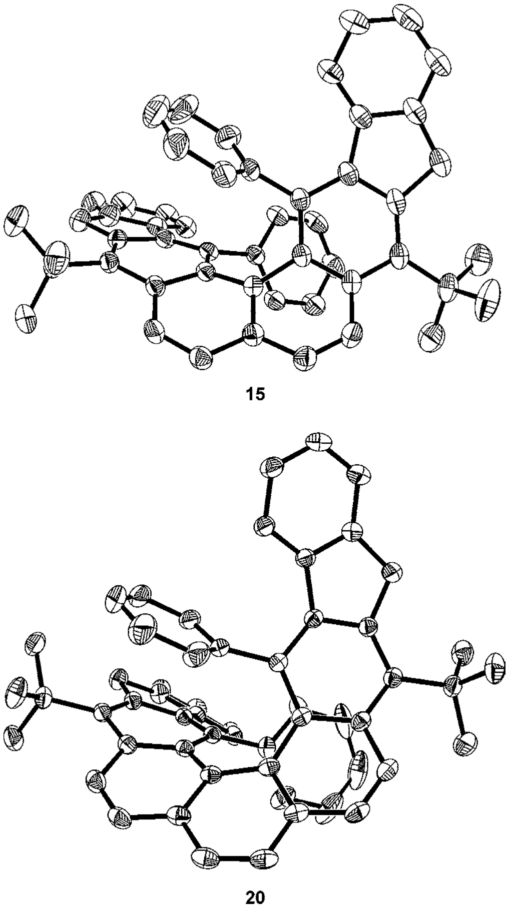

**Figure 4.** ORTEP drawings of the crystal structures of **15** and **20** with hydrogen atoms omitted for clarity.

As in the cases of **5** and **6**, the structures of **15** and **20** were established by X-ray structure analyses (Figure 4). The X-ray structure of **5** showed a helical twist of the phenanthrene ring system with a 46.1° acute dihedral angle between the mean planes of the two outer benzene rings bearing the phenyl substituents. A more pronounced 59.2° twist angle was observed for **6**. The X-ray structure of **15** also showed a severe helical twist of the benzo[*c*]phenanthrene ring system with a 59.9° acute dihedral angle between the mean planes of the two outer benzene rings bearing the phenyl substituents. The phenyl substituents are oriented in such a way that each is at a 60.8° angle from the benzene ring to

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(14) (a) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999−1002. (b) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843−1845. (c) Schmittel, M.; Vavilala, C. *J. Org. Chem.* **2005**, *70*, 4865−4868.

(15) (a) Tinnemans, A. H. A.; Laarhoven, W. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1115−1120. (b) Tinnemans, A. H. A.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1974**, *96*, 4617−4622.

(16) Yang, H.; Petersen, J. L.; Wang, K. K. *Tetrahedron* **2006**, *62*, 8133−8141.

(17) (a) Du Vernet, R. B.; Wennerström, O.; Lawson, J.; Otsubo, T.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2457−2464. (b) Khalaf, A. I.; Pitt, A. R.; Scobie, M.; Suckling, C. J.; Urwin, J.; Waigh, R. D.; Fishleigh, R. V.; Young, S. C.; Wylie, W. A. *Tetrahedron* **2000**, *56*, 5225−5239.

which it is connected but is roughly parallel to the opposite side of the twisted benzo[*c*]phenanthrene ring system with a distance of ca. 2.94 Å at the closest points, which is shorter than the usual $\pi$-system van der Waals contact distance of ca. 3.4 Å between parallel aromatic hydrocarbons in crystals.[18] For the [5]helicene ring system of **20**, the acute dihedral angle between the mean planes of the two outer benzene rings bearing the phenyl substituents is 57.8°. In comparison, the parent [5]helicene has a corresponding acute dihedral angle of only ca. 30°.[19] In addition, each of the phenyl substituents of **20** is at a 60.2° angle from the benzene ring to which it is attached, but is in roughly parallel orientation to the opposite side of the twisted[5]helicene ring system with a distance of ca. 3.00 Å at the closest points.

As observed previously in **5** and **6**, the existence of a helical twist was also manifested with a set of AB quartet $^1$H NMR signals from the diastereotopic methylene hydrogens on the five-membered rings of **15** or **20**. For **15** in $CDCl_3$, the AB quartet signals recorded on a 600 MHz NMR spectrometer appeared at $\delta$ 4.26 and 4.09 with a large geminal coupling constant of 21.0 Hz, whereas those for **20** appeared at $\delta$ 4.43 and 4.22 ($J = 21.0$ Hz). In addition, the upfield-shift aromatic signal of **15** at $\delta$ 6.31, attributable to the two hydrogens closest to the phenyl substituents on the two outermost benzene rings, also indicates that each of the phenyl substituents is oriented, to a large degree (60.8° from the X-ray structure), perpendicular to the benzene ring to which it is connected. As a result, the two neighboring hydrogens are located in shielding regions, giving an upfield-shift signal. In the case of **20**, the signal of the corresponding aromatic hydrogens appeared even more upfield at $\delta$ 5.19.

The $^1$H NMR signals of the ortho hydrogens on the phenyl substituents of **15** in $CDCl_3$ appeared at $\delta$ 7.88 and 5.71 as doublets. The fact that two distinct signals were observed for the ortho hydrogen indicates restricted rotation of the phenyl group on the NMR time scale, causing the two ortho hydrogens on the same phenyl group to be located in very different magnetic environments. The upfield-shift signal at $\delta$ 5.71 is attributable to the two ortho hydrogens pointing in the direction of the inner benzene rings of the fused ring system, placing them in the shielding regions of the aromatic ring current. The other two ortho hydrogens, pointing away from the inner benzene rings, appear to be in the deshielding regions, giving a downfield shift signal at $\delta$ 7.88. Similarly, the signals of the meta hydrogens appeared at $\delta$ 6.96 and 6.76. In 1,1,2,2-tetrachloroethane-$d_2$ and recorded on a 270 MHz NMR spectrometer, the signals of the meta hydrogens at $\delta$ 7.01 and 6.76 coalesced at 95 °C, whereas those of the ortho hydrogens at $\delta$ 7.88 and 5.72 coalesced at ca. 125 °C, corresponding to a rotational barrier of 18.5 kcal/mol, which is significantly higher than the rotational barriers of 12.5 kcal/mol of **5**[12] and ca. 13 kcal/mol of several 1-phenylbenzo[*c*]phenanthrene derivatives reported earlier.[20] As expected, the AB quartet signals remained unaffected due to the slow rate of racemization.

In the case of **20** in $CDCl_3$ recorded on a 600 MHz NMR spectrometer, the ortho hydrogens appeared as a very broad hump at $\delta$ 6.1, barely discernible from the baseline, and the meta hydrogens also appeared as a broad peak at $\delta$ 6.79. At −30 °C, a doublet at $\delta$ 5.58 and a signal overlapping with other signals at $\delta$ 6.65, attributable to the ortho hydrogens were observed. For the meta hydrogens, an overlapping signal at $\delta$ 6.65 and an overlapping triplet at $\delta$ 6.98 could be discerned. The coalescence temperatures of the ortho and meta hydrogens were determined to be at 20 and 5 °C, respectively, corresponding to a rotational barrier of 12.9 kcal/mol. It is interesting to note that this rotational barrier is significantly lower than that of **15** and is also lower than the rotational barrier of ca. 16 kcal/mol of a 1-phenyl[5]-helicene derivative reported earlier.[20] One possible explanation for this unexpected observation is the lack of a more stable ground state that is accessible to the rotating phenyl substituents in **20**, reminiscent of a faster rate of rotation in a 1-triptycyl[4]helicene system as a molecular ratchet than that of 4-(9-triptycyl)phenanthrene reported previously.[21] In 1,1,2,2-tetrachloroethane-$d_2$ and recorded on a 270 MHz NMR spectrometer at 100 °C, a doublet at $\delta$ 6.18 from the ortho hydrogens and a triple at $\delta$ 6.83 from the meta hydrogens could be clearly discerned. The AB quartet signals also remained unaffected due to the slow rate of racemization.

In conclusion, two polycyclic aromatic hydrocarbons possessing severe helical twists were readily synthesized. The X-ray structures of these two molecules permitted direct measurements of the extents of distortion from planarity. The convergent nature of the synthetic sequence could also allow easy placement of functional groups at various positions of the aromatic ring systems for synthetic elaborations.

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**Supporting Information Available:** Experimental procedures, spectroscopic data, and $^1$H and $^{13}$C NMR spectra of **8**, **10**, **11**, **15**, and **17**−**20**; ORTEP drawings of the crystal structures of **15** and **20** in PDF format; and X-ray crystallographic data of **15** and **20** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Robertson, J. M. *Organic Crystals and Molecules*; Cornell University Press: Ithaca, NY, 1953; pp 206−214.

[19] (a) Kuroda, R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 789−794. (b) Frimer, A. A.; Kinder, J. D.; Youngs, W. J.; Meador, M. A. B. *J. Org. Chem.* **1995**, *60*, 1658−1664.

[20] Laarhoven, W. H.; Peters, W. H. M.; Tinnemans, A. H. A. *Tetrahedron* **1978**, *34*, 769−777.

[21] Kelly, T. R.; Sestelo, J. P.; Tellitu, I. *J. Org. Chem.* **1998**, *63*, 3655−3665.