# Copper(II)-Mediated Oxidative Coupling of 2-Aminonaphthalene Homologues. Competition between the Straight Dimerization and the Formation of Carbazoles◊

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*Received October 20, 2000*

Whereas the Cu(II)-mediated oxidative coupling of 2-aminonaphthalenes **7a** and **7b** results in the clean formation of 1,1′-binaphthyls **13a** and **13b**, respectively, their higher homologues and congeners **8**−**12** have been found to exhibit a different reaction pattern. Thus, 2-aminoanthracene (**8**) gave a ∼1:1 mixture of the expected bianthryl derivative **15** and the carbazole **16**, whereas the 9-aminophenanthrene (**10**), 3-phenyl-1-aminonaphthalene (**11**), and 2-aminochrysene (**12**) produced almost exclusively the corresponding carbazoles **19**, **20**, and **21**, respectively. By contrast, the isomeric 3-aminophenanthrene (**9**) gave rise to the azo compound **17** as a result of the preferential oxidation on the nitrogen. The carbazoles have been shown to arise directly from the coupling reactions rather than from the primarily formed binaphthyls. Alternatively, carbazole **19** can also be prepared from **1b** on reaction with hydrazine. On the other hand, treatment of **3a** with hydrazine resulted in the formation of a ∼2:7 mixture of amine **11** and arylhydrazine **22**. 2,2′-Diamino-1,1′-bianthryl (**15**) has been resolved into enantiomers via cocrystallization with (−)-*N*-benzylcinchonidinium chloride and shown to have (*R*)-(−)-**15** configuration by X-ray crystallography.

## Introduction

Both the symmetrically and nonsymmetrically 2,2′-disubstituted-1,1′-binaphthyls are widely used as chiral ligands in asymmetric synthesis.[1] In particular, BINOL,[1] BINAP,[1] MOP,[2] NOBIN,[3−5] and 2,2′-diamino-1,1′-binaphthyl (**13a**)[1] have been shown to exhibit good to excellent enantioselectivities in a number of asymmetric reactions. Thus, for example, diamine **13a** and its derivatives have been employed as ligands for the enantioselective reduction of ketones,[6a] hydrogenation of α-acylaminoacrylic acids,[6b] and other transformations.[1,6c−i]

The classical approach to the binaphthyl skeleton (Scheme 1) largely relies on the oxidative coupling of 2-naphthol (**1a**) to give BINOL (**4a**). A number of mild oxidants have been reported to facilitate this reaction, in particular, Cu(II), Fe(III), and Mn(III) salts.[3,7] Other methods involve melting the reactant[8] or its ball-milling in the presence of $FeCl_3 \cdot 6H_2O$.[9] Oxidative coupling of

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◊ Dedicated to Dr. Želimír Procházka on the occasion of his 80th birthday.

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(1) For recent reviews on binaphthyls, see: (a) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503. (b) Putala, M. *Enantiomer* **1999**, *4*, 243. See also: (c) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley & Sons: New York, 1994. (d) Ojima, I. *Catalytic Asymmetric Synthesis*, 2nd ed.; J. Wiley and Sons: New York, 2000.

(2) For a review, see: (c) Hayashi, T. *Acta Chem. Scand.* **1996**, *50*, 259.

(3) Smrčina, M.; Lorenc, M.; Hanuš, V.; Kočovský, P. *Synlett* **1991**, 231. (b) Smrčina, M.; Lorenc, M.; Hanuš, V.; Sedmera, P.; Kočovský, P. *J. Org. Chem.* **1992**, *57*, 1917. (c) Smrčina, M.; Poláková, J.; Vyskočil, Š.; Kočovský, P. *J. Org. Chem.* **1993**, *58*, 4543. (d) Smrčina, M.; Vyskočil, Š.; Polívková, J.; Poláková, J.; Kočovský, P. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1, 1520. (e) Smrčina, M.; Vyskočil, Š.; Hanuš, V.; Polášek, M.; Langer, V.; Zax, D. B.; Chew, B. G. M.; Verrier, H.; Harper, K.; Claxton, T. A.; Kočovský, P. *J. Am. Chem. Soc.* **1996**, *118*, 4878. (f) Smrčina, M.; Vyskočil, Š.; Polívková, J.; Poláková, J.; Sejbal, J.; Hanuš, V.; Polášek, M.; Verrier, H.; Kočovský, P. *Tetrahedron: Asymmetry* **1997**, *8*, 537. (g) Vyskočil, Š.; Smrčina, M.; Kočovský, P. *Collect. Czech. Chem. Commun.* **1998**, *63*, 515. (h) Vyskočil, Š.; Smrčina, M.; Lorenc, M.; Hanuš, V.; Polášek, M.; Kočovský, P. *Chem. Commun.* **1998**, 585.

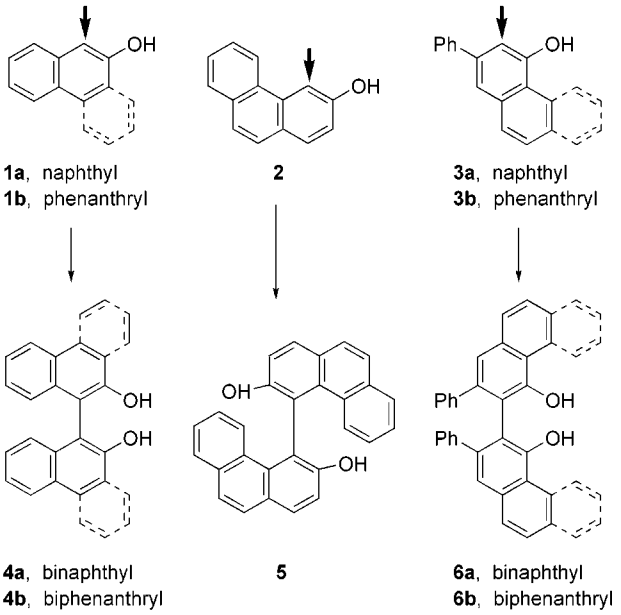
(4) (a) Mahmoud, H.; Han, Y.; Segal, B. M.; Cai, L. *Tetrahedron: Asymmetry* **1998**, *9*, 2035. (b) Wang, Y.; Guo, H.; Ding, K. L. *Tetrahedron: Asymmetry* **2000**, *11*, 4153.

(5) Carreira, E. M.; Singer, R. A.; Wheeseong, L. *J. Am. Chem. Soc.* **1994**, *116*, 8837. (b) Carreira, E. M.; Wheeseong, L.; Singer, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 3649. (c) Singer, R. A.; Carreira, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12360. (d) Knölker, H.-J.; Hermann, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 341. (e) Belokon, Yu. N.; Kochetkov, K. A.; Churkina, T. D.; Ikonnikov, N. S.; Vyskočil, Š.; Kagan, H. B. *Tetrahedron: Asymmetry* **1999**, *10*, 1723. (f) Belokon, Yu. N.; Kochetkov, K. A.; Churkina, T. D.; Ikonnikov, N. S.; Chesnokov, A. A.; Larionov, O. V.; Singh, I.; Parmar, V. S.; Vyskočil, Š.; Kagan, H. B. *J. Org. Chem.* **2000**, *65*, 7041.

(6) (a) Kabuto, K.; Yoshida, T.; Yamaguchi, S.; Miyano, S.; Hashimoto, H. *J. Org. Chem.* **1985**, *50*, 3013. (b) Miyano, S.; Nawa, M.; Mori, A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2171. (c) Kawakami, Y.; Hiratake, J.; Yamamoto, Y.; Oda, J. *J. Chem. Soc., Chem. Commun.* **1984**, 779. (d) Rosini, C.; Franzini, L.; Iuliano, A.; Pini, D.; Salvadori, P. *Tetrahedron: Asymmetry* **1991**, *2*, 363. (e) Nishida, A.; Yamanaka, M.; Nakagawa M. *Tetrahedron Lett.* **1999**, *40*, 1555. (f) Denmark, S. E.; Su, X.; Nishigaichi, Y.; Coe, D. M.; Wong, K.-T.; Winter, S. B. D.; Choi, J. Y. *J. Org. Chem.* **1999**, *64*, 1958. (g) Jamieson, J. Y.; Schrock, R. R.; Davis, W. M.; Bonitatebus, P. J.; Zhu, S. S.; Hoveyda, A. *Organometallics* **2000**, *19*, 925. (h) Reetz, M. T.; Haderlein, G.; Angermund, K. *J. Am. Chem. Soc.* **2000**, *122*, 996. (i) Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2000**, *122*, 12021.

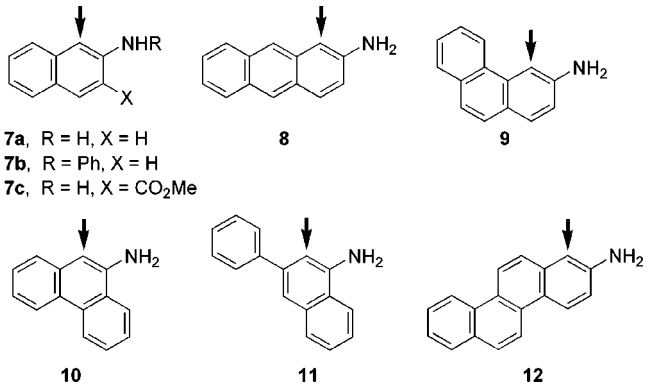
10.1021/jo005691w CCC: $20.00 © 2001 American Chemical Society
Published on Web 01/31/2001

**Scheme 1**




2-naphthol homologues has also been reported, such as that of 9-phenanthrol (**1b**), furnishing 10,10′-dihydroxy-9,9′-biphenanthryl (**4b**),[3c,10] and the dimerization of 3-phenanthrol (**2**), producing 4,4′-dihydroxy-3,3′-biphenanthryl (**5**).[11,12] The synthesis of "vaulted" biaryls **6a** and **6b** has been effected by melting the corresponding phenolic derivatives **3a** and **3b**, respectively.[8] In all these cases, the chiral axis was constructed in the position vicinal to the hydroxyl group (marked by bold arrow in Scheme 1). Herein, we report on the analogous coupling of arylamines **8**−**12** (Chart 1) and demonstrate the wider

**Chart 1**




**Scheme 2**

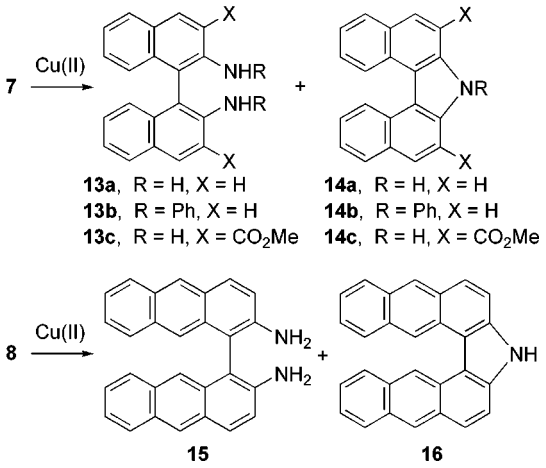



**Table 1. Copper(II)-Mediated Oxidative Coupling of Amines 7−12**

| entry | substrate | diamine (%)[a] | carbazole (%)[a] | other (%)[a] |
|---|---|---|---|---|
| 1 | **7a** | **13a** (58)[b] | **14a** (∼1)[c] | − |
| 2 | **7b** | **13b** (45)[b] | **14b** (3) | − |
| 3 | **7c** | **13c** (26)[b] | **14c** (21) | − |
| 4 | **8** | **15** (43) | **16** (39) | − |
| 5 | **9** | − | − | **17** (87) |
| 6 | **10** | **18** (2) | **19** (78)[d] | − |
| 7 | **11** | − | **20** (25) | − |
| 8 | **12** | − | **21** (85) | − |

[a] Isolated by chromatography. [b] See ref 13. [c] GC yield. [d] Starting material was recovered (10%).

variability of the reaction course that contrasts with the uniform behavior of their phenolic counterparts.

## Results and Discussion

**Coupling of Aminonaphthalenes.** By analogy to the naphthols, arylamines **7**−**12** can also be anticipated to undergo a preferential coupling in the electron-rich[13] position marked by a bold arrow (Chart 1). Indeed, we have recently reported on the Cu(II)-mediated oxidative coupling reactions of 2-aminonaphthalenes **7a**−**c** to produce, as predicted, the binaphthyls **13a**−**c** (Scheme 2) in good yields (Table 1, entries 1−3).[3,13] While **7c** gave a substantial amount of the corresponding carbazole **14c** as a byproduct (entry 3), **7a** and **7b** reacted more selectively, with only minute amounts of the carbazoles **14a** and **14b** detected (entries 1 and 2).[3,13]

(7) **Cu(II):** (a) Ferringa, B.; Wynberg, H. *Tetrahedron Lett.* **1977**, 4447. (b) Ferringa, B.; Wynberg, H. *Bioorg. Chem.* **1978**, *7*, 397. (c) Kushioka, K. *J. Org. Chem.* **1983**, *48*, 4948. (d) Yamamoto, K.; Fukushima, H.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1490. (e) Brussee, J.; Groenendijk, J. L. G.; te Koppele, J. M. Jansen, A. C. A. *Tetrahedron* **1985**, *41*, 3313. (f) Sakamoto, T.; Yonehara, H.; Pac, C. *J. Org. Chem.* **1994**, *59*, 6859. **Cu(II)/$O_2$:** (g) Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 7983. (h) Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S.; Noji, M.; Koga, K. *J. Org. Chem.* **1999**, *64*, 2264. (i) Lipshutz, B. H.; James, B.; Vance, S.; Carrico, I. *Tetrahedron Lett.* **1997**, *38*, 753. **Fe(III)**: ref 3h and the following: (j) Pummerer, R.; Rieche, A. *Chem. Ber.* **1926**, 59. (k) Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007 and references therein. (l) Ding, K.; Wang, Y.; Zhang, L.; Wu, Y.; Matsuura, Y. *Tetrahedron* **1996**, *52*, 1005. (m) Ding, K.; Xu, Q.; Wang, Y.; Liu, J.; Yu, Z.; Du, B.; Wu, Y.; Koshima, H.; Matsuura, T. *Chem. Commun.* **1997**, 693. **Mn(III)**: (n) Dewar, M. J. S.; Nakaya, T. *J. Am. Chem. Soc.* **1968**, *90*, 7134. (o) Yamamoto, K.; Fukushima, H.; Okamoto, Y.; Hatada, K.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1111. (p) Diederich, F.; Hester, M. R.; Uyeki, M. *Angew. Chem., Int. Ed. Engl.* **1988**, ***27***, 1705.

(8) Bao, J.; Wulff, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 3814. (b) Bao, J.; Wulff, W. D.; Dominy, J. B.; Fumo, M. J.; Grant, E. B.; Rob, A. C.; Whitcomb, M. C.; Yeung, S. M.; Ostrander, R. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 3392. (c) Antilla, J. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 5099. (d) Antilla, J. C.; Wulff, W. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 4581.

(9) Rasmussen, M. O.; Axelson, O.; Tanner, D. *Synth. Commun.* **1997**, *27*, 4027.

(10) Yamamoto, K.; Fukushima, H.; Okamoto Y.; Hatada K.; Nakazaki M. *J. Chem. Soc., Chem. Commun.* **1984**, 1111. (b) Yamamoto, K.; Fukushima, H.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1490.

(11) Yamamoto, K.; Noda, K.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 1065.

(12) Interestingly, the originally proposed configuration for **5**[11] has been corrected to (*R*)-(−): (a) Koike, N.; Hatori, T.; Miyano, S. *Tetrahedron: Asymmetry* **1994**, *5*, 1899. (b) Hayashi, T.; Iwamura, H.; Uozumi, M.; Matsumoto, Y.; Ozawa, T. *Synthesis* **1994**, 526. (c) Dore, A.; Fabbri, D.; Gladiali, S. *Tetrahedron: Asymmetry* **1995**, *6*, 779.

(13) Smrčina, M.; Vyskočil Š.; Máca, B.; Polášek, M.; Claxton, T. A.; Abbott, A. P.; Kočovský, P. *J. Org. Chem.* **1994**, *59*, 2156.

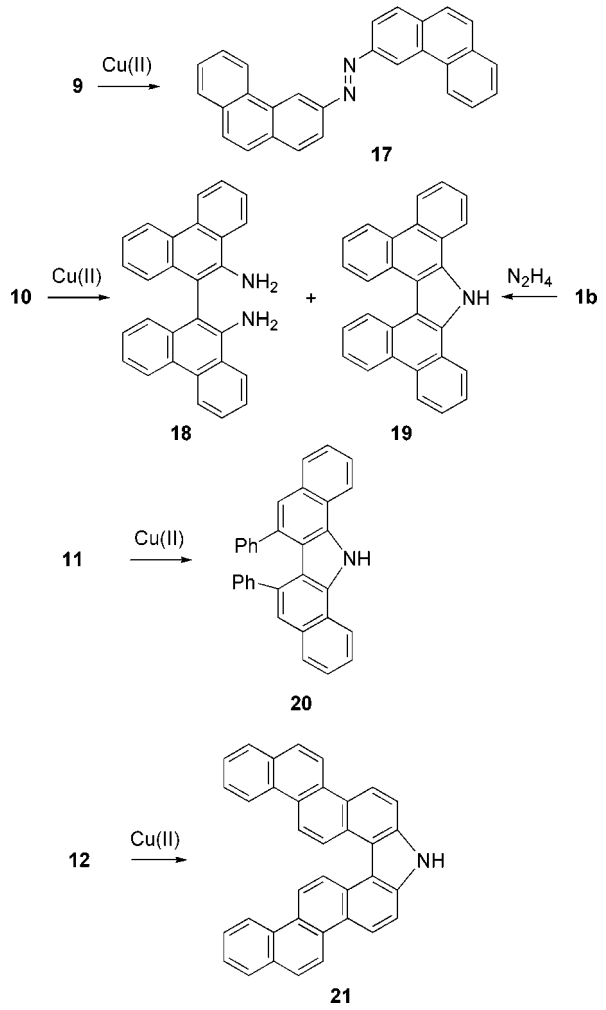
**Coupling of Aminonaphthalene Homologues.** Although the coupling procedures developed for 2-aminonaphthalenes **7** were successful,[3,13] analogous processes have not been studied for homologous aromatic amines. To explore the scope of this methodology, we set out to investigate the coupling reactions of arylamines **8**−**12** using a complex of $CuCl_2$ and benzylamine, which proved to be the reagent of choice in our previous studies.[3] While the ultimate environment of the candidate positions for coupling in **8**, **10**, and **12** resembles that of **7a** (Chart 1), more steric hindrance can be anticipated for **11** and, in particular, for **9**. Differences can also be identified in the steric hindrance of individual amino groups. Thus, in **8**, **9**, and **12**, the $NH_2$ seems to be as free as that in **7a**, whereas in the case of **7c**, **10**, and **11** it is hindered by neighboring groups (the ester functionality and the *peri*-substituents, respectively). Although the corresponding hydroxy derivatives **1** and **2** exhibited little influence of the steric congestion on the efficiency of the coupling reactions, we envisaged that the same picture may not necessarily be obtained with the amines.

The reaction of 2-aminoanthracene (**8**) with $CuCl_2$−$PhCH_2NH_2$ (MeOH, rt, 24 h; Scheme 2) afforded a mixture of diamine **15** (43%)[14] and carbazole **16** (39%, entry 4),[15] a result similar to that obtained for **7c** (entry 3).[13] The couplings of 9-aminophenanthrene (**10**), 3-phenyl-1-aminonaphthalene (**11**),[16] and 2-aminochrysene (**12**) turned out to give mainly the carbazoles **19**,[17] **20**, and **21** (Scheme 3), respectively (entries 6−8); the corresponding diamines were either formed in minute quantities (2% of **18**;[18] entry 6), or not at all (entries 7 and 8). The structure of carbazole **20** has been confirmed by single-crystal X-ray crystallography. In contrast to these reactions, the attempted self-coupling of 3-aminophenanthrene (**9**) gave the azo compound **17**[19] as the main product (entry 5).

Apparently, increasing the steric hindrance around the amino group is detrimental to the formation of the diamines but not to the biaryl coupling itself: while **7a** and **7b** give the corresponding diamines **13a** and **13b** in high yields, a ∼1:1 mixture of the diamine and the carbazole is formed in the case of **7c**, and a practically exclusive formation of the carbazole was found for **10** and **11**. However, electronic factors must also play a role, since **8**, having a similar steric environment to that in **7a**, afforded a ∼1:1 mixture, and the chrysene homologue **12** produced the carbazole exclusively. Steric hindrance at the expected coupling position, as in **9** or **11**, led to a low yield of the expected carbazole (15% yield in **11** → **20**), or even precluded the coupling and, instead, promoted oxidation on the nitrogen (**9** → **17**).

The actual mechanism for the formation of the carbazoles is not clear. Control experiments revealed that the diamines (e.g., **13c** or **15**) are inert to prolonged treatment (24 h) under the conditions of the coupling reaction. Hence, the carbazoles must arise directly from the starting amines in a competing reaction rather than via a secondary transformation of the diamines.[20]

**Scheme 3**




(14) The preparation of **15** has also been reported from the corresponding 2,2′-dicarboxylic acid via the Curtius rearrangement: (a) Lauer, K.; Oda, R.; Miyawaki, M. *J. Prakt. Chem.* **1937**, *148*, 310. (b) Bell F.; Waring D. H. *J. Chem. Soc.* **1949**, 1579. For the chiroptical properties of this material, and a tentative assignment of absolute configuration for **15**, see: (c) Fitts, D. D.; Siegel, M.; Mislow, K. *J. Am. Chem. Soc.* **1958**, *80*, 480. (d) Our synthetic procedure resulted in the formation of a compound that has a distinctly different mp and somewhat lower $[\alpha]_D$ compared to the literature data[14a,b] (see the Experimental Section for details). Furthermore, one report[14b] described the alleged **15** as "white crystals" whereas according to the other report[14a] it formed a "red-yellow solution in benzene or chloroform with green fluorescence". The latter description is certainly closer to our own observation (a yellow material). The single-crystal X-ray analysis (vide infra) proved the structure **15** for our product and also established the absolute configuration (both from the Flack factor and through the relation to the cinchonidine derivative in the crystal); chiral HPLC demonstrated its enantiopurity. We have no explanation for the discrepancy in data except that, perhaps, the other authors mixed up the appearance of the free amine with that of its hydrochloride and the melting point for the enantiomerically pure compound with that of the racemate.

(15) For an alternative preparation of carbazole **16**, see: (a) Zander, M.; Franke, W. H. *Chem. Ber.* **1966**, *99*, 2449. (b) Brandt, J.; Fauth, G.; Franke, W. H.; Zander, M. *Chem. Ber.* **1971**, *104*, 519.

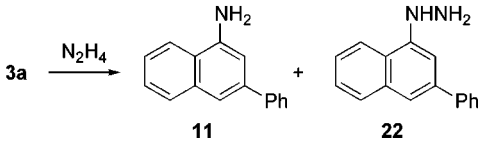
(16) Prepared from **3a**[8] via Bucherer reaction in 56% yield: Selvaraj, S.; Ramakrishnan, P. S.; Arumugam, N. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 36.

(17) Carbazole **19** has been prepared previously by the iodine-mediated oxidation of **10** at 260 °C or by photolysis of the aziridine derived from phenanthrene: Weitzberg M.; Avnir D.; Aizenshtat Z.; Blum J. *J. Heterocycl. Chem.* **1983**, *20*, 1019.

(18) Diamine **18** also has been synthesized by the Zn−KOH reduction of the corresponding dinitro derivative, which, in turn, was obtained via the Cu-mediated dimerization of 9-nitro-10-bromophenanthrene: Hughes, A. N.; Prankprakma, V. *Tetrahedron* **1966**, *22*, 2053.

(19) (a) This reaction involves two oxidation steps (the C−C coupling itself and the N−N bond oxidation). The standard procedure using 1 equiv of Cu(II) lead to an inseparable mixture of **17** and the corresponding hydrazo derivative, as revealed by GCMS. Therefore, to run the reaction to completion, 2 equiv of $CuCl_2$ were employed. (b) The azo derivative **17** is assumed to be a *trans*-isomer in view of the generally higher stability of *trans*-azo compounds. Thus, for instance, *cis*-azo-2,2′-naphthalene has been reported to isomerize to the *trans*-isomer with $\tau_{1/2} = 150$ min at 29 °C: Frankel, M.; Wolovsky, R.; Fischer, E. *J. Chem. Soc.* **1955**, 3441.

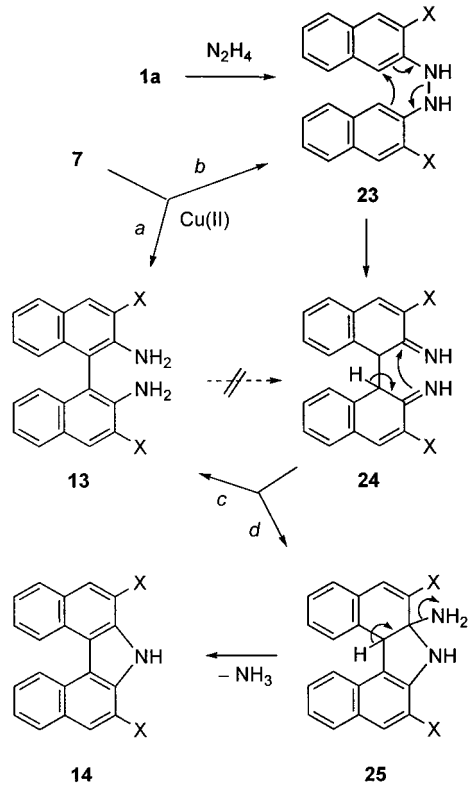
**Scheme 4**




Since the preparation of the diamines from **10** and **11** failed, another approach was attempted, based on the analogy with 2-naphthol (**1a**), which can be readily converted into the diamine **13a** on heating with hydrazine hydrate in an autoclave.[21,22] However, under the same conditions (190 °C, 48 h), **1b** afforded, again, the carbazole **19** (58%) rather than the expected diamine. This experiment shows that the carbazole formation is not associated with the presence of the oxidizing agent but, rather, with the nature of the skeleton. Interestingly, **3a** produced, under the same conditions (Scheme 4), a mixture of amine **11** (9%), identical with the compound prepared from **3a** via Bucherer reaction,[16] and hydrazine derivative **22** (30%).

Comparison of the reactivity of the phenolic substrates **1**−**3** with that of the amines **7**−**12** shows that there must be a fundamental difference in the mechanism of the dimerization. Whereas **1**−**3** readily afford the corresponding diols (Scheme 1), the amines exhibit greater variability, affording diamines, carbazoles, or even the product of *N*,*N*-dimerization (Schemes 2 and 3). We believe that the mechanistic rationale can be found in the oxidation of **9**, which differs most dramatically from the coupling of its oxygen analogue **2**. An exclusive formation of the azo derivative **17** on the oxidation of **9** suggests that the oxidative *N*,*N*-dimerization represents a competing pathway for the amines. Under normal circumstances, the C−C coupling prevails but if the candidate position is more hindered (as in **9**), the alternative reaction becomes relatively less costly in energy and the azo derivative **17** is formed, presumably via the corresponding hydrazo intermediate.[19a,23] Note that this pathway is not available for the phenolic derivatives (e.g., **2**), as it would generate an unstable peroxide intermediate. Hence, assuming the two competing pathways *a* and *b* (Scheme 5) for the Cu(II)-facilitated reaction of amines, exemplified by **7**, path *a* would lead directly to the diamine **13**, whereas path *b* would generate the hydrazo species **23**, which is also believed to be the intermediate in the reaction of, e.g., 2-naphthol (**1a**) with hydrazine.[21,22,24] Rearrangement of **23** would then generate **24**, which can either be stabilized by tautomerization to produce diamine **13** (path *c*) or undergo an intramolecular attack on one of the imino groups (path *d*); elimination of ammonia from the intermediate **25** thus

**Scheme 5**[a]




[a] X = H or $CO_2Me$.

formed would then give rise to the carbazole **14**. The latter mechanism is further supported by the reaction of **1b** with hydrazine, which gives carbazole **19** (vide supra), showing that for the carbazole formation from **23**, Cu(II) is not required. The competition between pathways *c* and *d* is apparently influenced by steric and electronic factors; control experiments have demonstrated that path *c* is irreversible under the reaction conditions.[20,25] The sterically congested hydrazo intermediate (analogous to **23**), arising from **9**, is further oxidized to produce **17** in preference to the C−C bond-forming rearrangement.

**Resolution and Absolute Configuration of 2,2′-Diamino-1,1′-bianthryl (15).** Diamine (±)-**15** was resolved via the method developed by Toda[26] and further improved by the Merck group[27] for the resolution of BINOL:[27,28] Racemic **15** was cocrystallized with (−)-*N*-benzylcinchonidinium chloride (−)-**26** from acetonitrile to produce a 1:1 inclusion complex (or molecular crystal[28])

(20) On the other hand, pyrolysis of the hydrochloride of **13a** or refluxing **13a** in 2 N $H_2SO_4$ are known to produce carbazole **14a**, apparently owing to the conversion of the $NH_2$ into a good leaving group by protonation: (a) Meisenheimer, J.; Witte, K. *Chem. Ber.* **1903**, *36*, 4153. (b) Banthorpe, D. V. *J. Chem. Soc.* **1962**, 2407 and 2413. (c) Bridger, R. F.; Law, D. A.; Bowman, D. F.; Middleton, B. S.; Ingold, K. U. *J. Org. Chem.* **1968**, *33*, 4329.

(21) Miyano, S.; Nawa, M.; Mori, A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2171.

(22) Shine, H. J.; Gruszecka, E.; Subotkowski, W.; Brownawell, M.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 3218.

(23) Traces of the corresponding hydrazo compound could be detected by EI MS (direct inlet) analysis of the reaction mixture.

(24) Shine, H. J.; Trisler, J. C. *J. Am. Chem. Soc.* **1960**, *82*, 4054. (b) Shine, H. J.; Huang, F.-T.; Snell, R. L. *J. Org. Chem.* **1961**, *26*, 380. (c) Banthorpe, D. V.; Hughes, E. D.; Ingold, C. *J. Chem. Soc.* **1962**, 2418 and refs cited therein.

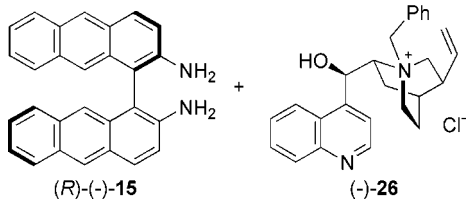
(25) Note that while 2-naphthol readily reacts with hydrazine, BINOL is inert, which demonstrates that the keto form is not available in the latter case. Similarly, generating the imino form **23** from amine **13** can be regarded as unlikely, lending further credence to our mechanistic argument.

(26) Tanaka, K.; Okada, T.; Toda, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1147. (b) Toda, F.; Tanaka, K.; Stein, Z.; Goldberg, I. *J. Org. Chem.* **1994**, *59*, 5748.

(27) The original Toda's method suffered from lower enantioselectivity. A simple switching of the solvent employed for crystallization from methanol to acetonitrile dramatically improved the resolution of BINOL: (a) Cai, D.; Hughes, D. L.; Verhoeven. T. R.; Reider, P. J. *Tetrahedron Lett.* **1995**, *36*, 7991. For other recent applications of this method, see: (b) Reeder, J.; Castro, P. P.; Knobler, C. B.; Martinborough, E.; Owens, L.; Diederich, F. *J. Org. Chem.* **1994**, *59*, 3151. (c) Wipf, P.; Jung, J.-K. *J. Org. Chem.* **2000**, *65*, 6319. (d) Wang, Y.; Sun, J.; Ding, K. L. *Tetrahedron* **2000**, *56*, 4447.

(28) This method has recently been applied to the resolution of NOBIN with acetone as the preferred solvent: Ding, K.; Wang, Y.; Yun, H.; Liu, J.; Wu, Y.; Terada, M.; Okubo, Y.; Mikami, K. *Chem. Eur. J.* **1999**, *5*, 1734.

**Chart 2**




that was diastereoisomerically enriched by 73% (de) as shown by chiral HPLC (Chart 2). A single crystallization of the latter complex from a dichloromethane−diethyl ether mixture furnished a diastereoisomerically pure species (i.e., **15** of ∼100% ee). This material was characterized by single-crystal X-ray crystallography (Figure 1) that revealed not only the (*R*)-configuration of **15** but also an interesting fit of the molecule of (*R*)-**15** into the cleft created by the quinoline nucleus and the vinyl group of the alkaloid on one side and the insertion of the benzyl group of (−)-**26** into the cleft of another molecule of (*R*)-**15**.[29] Another interesting structural feature is the formation of an infinite 3D-network of hydrogen bonds with the chloride ion as their acceptor; both amino groups of **15** and the hydroxy group of **25** are involved. Together with three other contacts (C3A of **15** and C8C and C11C of **26**), a distorted square bipyramid of hydrogen contacts around the $Cl^-$ ion is thus formed.

Dissolving the crystal in dichloromethane, followed by a chromatographic separation of the desired product from benzylcinchonidinium chloride, afforded a laevorotatory material. Therefore, 2,2′-diamino-1,1′-bianthryl can be assigned the (*R*)-(−)-**15** configuration.[30]

## Conclusion

We have prepared the bianthryl diamine (*R*)-(−)-**15** as a potential new ligand for asymmetric synthesis.[31] Further investigation has led to defining the scope of the oxidative coupling of aromatic amines, in particular, of the extent of the formation of carbazoles and other byproducts. In the case of **10, 11**, and **12**, this protocol can be used as a reliable synthetic route to the corresponding carbazoles **19**, **20**, and **21**. Two competing mechanisms have been proposed for the coupling of amines (Scheme 5), one leading directly to the C−C bond formation (**7** → **13**), the other to the *N*−*N* coupling (**7** → **23**); the latter pathway can branch either to diamine (**13**), carbazole (**14**), or azo-derivative (**17**) as the product.

## Experimental Section

**Materials and Equipment.** Optical rotations were measured with an error of < ± 0.1; the $[\alpha]_D$ values are given in $10^{-1}$ deg cm$^2$ g$^{-1}$. $^1$H NMR spectra were recorded on a 400 or 250 MHz instrument (FT mode) for $CDCl_3$ solutions at 25 °C with TMS as internal reference. The $^{13}$C NMR spectra were recorded at 101 MHz (FT mode) for $CDCl_3$ or acetone-$d_6$ solutions at 25 °C. 2D NMR techniques (COSY, HSQC, and HMBC) and DEPT were used for signal assignment. The IR spectra were measured in chloroform. The high-resolution mass spectra were measured on a double focusing spectrometer (70 eV, 3 kV) using a direct inlet and the lowest temperature enabling evaporation; the accuracy was ≤5 ppm. All the solvents used for the reactions or for crystallization experiments were degassed by purging with argon (20 min; 60 mL Ar/min). Petroleum ether refers to the fraction boiling in the range 40−60 °C. Yields are given in milligrams of isolated product showing one spot on a chromatographic plate and no impurities detectable in the NMR spectra. Crystal data for carbazole **20**: $C_{32}H_{21}N$, $M = 419.52$. Crystals (pale yellow) were obtained from a $CH_2Cl_2$ solution into which hexane slowly diffused at ∼0 °C over a period of 2 weeks; they are orthorhombic of space group *Pcab*, $a = 13.6545(3)$ Å, $b = 15.2033(3)$ Å, $c = 20.1647(5)$ Å. Data were collected at 150 K on a Nonius KappaCCD diffractometer, running under Nonius-Collect software, and using graphite monochromated X-radiation ($\lambda = 0.71073$ Å). Precise unit cell dimensions were determined by refinement of the setting angles of 5221 reflections. Lorentz-polarization corrections were then applied to the reflection data. The data were averaged using SORTAV and an empirical absorption correction was applied.[32] The structure was solved by direct methods (SHELXS-97[33]). All non-H atoms were allowed anisotropic thermal motion. Aromatic C−H hydrogen atoms were included at calculated positions, with C−H = 0.96 Å, and were refined with a riding model and with $U_{iso}$ set to 1.2 times that of the attached C-atom. The H atom of nitrogen was found from a difference map and was refined without constraints. Refinement (SHELXL97−2[33]) was performed by full-matrix least-squares on $F^2$, using all the unique data and the weighting scheme $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$ where $P = [F_o^2/3 + 2F_c^2/3]$ and $A = 0.0644$ $B = 0.0$. Neutral atom scattering factors, coefficients of anomalous dispersion, and absorption coefficients were obtained from ref 34. Calculations using PLATON[35] indicated that there were no voids in the lattice capable of containing any solvent molecules. Thermal ellipsoid plots were obtained using the program ORTEP-3 for Windows.[36] All calculations were carried out using the WinGX package[37] of crystallographic programs. The estimated error in the bond distances is 0.002 Å. Crystal data for the molecular crystal (*R*)-(−)-**15**·(−)-**26**: $C_{27}H_{29}ClN_4O$, $M = 805.44$. Crystals

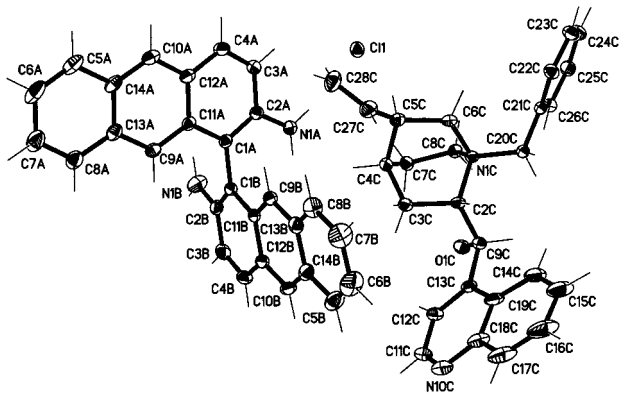



**Figure 1.** ORTEP diagram of the inclusion complex (*R*)-(−)-**15**·(−)-**26** showing the atom labeling scheme. Displacement parameters are shown at the 30% probability level. H atoms are omitted for clarity and their positions are indicated by thin lines.

(29) The importance of the vinyl group for the resolution process is further demonstrated by our failure to resolve (±)-**15** with benzylcinchoninium chloride, a diastereoisomer of benzylcinchonidinium chloride, where the vinyl group is not available in the right position.

(30) This assignment confirms that made tentatively by Mislow.[14c] However, see the comments on the reported structure (ref 14d).

(31) The cost of **8** as starting material for **15** might be viewed as a deterrent (5 g at £ 33.40 according to the latest Aldrich catalogue). However, **8** can be readily prepared on a large scale in an economically viable way by reduction of 2-aminoanthraquinone (500 g at £ 22.40) with zinc in aqueous NaOH solution: Ruggli, P.; Henzi, E. *Helv. Chim. Acta* **1930**, *13*, 409.

(32) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(33) SHELX-97 Programs for crystal structure analysis: Sheldrick, G. M. University of Göttingen, Germany, 1997, Release 97-2.

(34) Tables 4.2.4.2, 4.2.6.8, 6.1.1.4 from *International Tables for Crystallography, Volume C Mathematical, Physical and Chemical Tables*; Kluwer: Dordrecht, 1995.

(35) PLATON: Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(36) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(37) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

were obtained by a slow crystallization from acetonitrile solution; they are monoclinic, of space group $P2_1$, $a = 13.4647(6)$ Å, $b = 10.5784(4)$ Å, $c = 15.5742(6)$ Å, $\beta = 101.796(1)$. Data were collected at −85 °C on a Siemens SMART CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and $\omega$ scan mode at four different $\phi$ orientations, covering thus the entire reciprocal sphere up to 0.73 Å resolution. A total of 28054 reflections were measured, from which 11610 were unique ($R_{int} = 0.0388$), with 8382 observed data having $I > 2\sigma_I$. All reflections were used in the structure refinement based on $F^2$ by full-matrix least-squares technique with hydrogen atoms calculated into theoretical positions, riding during refinement on the respective pivot atom (592 parameters). Final $R$-factors: $R_1 = 0.0455$ for the observed data and 0.0768 for all data; $wR_2 = 0.0998$, $S = 1.010$. Flack $x$ parameter = −0.0447 with esd 0.0432; expected values are 0 (within 3 esd's) for the correct and +1 for inverted absolute structure and thus there is no doubt about the absolute structure determination. The estimated error in the bond distances is in the interval 0.002 to 0.004 Å. All calculations were performed using SHELXTL software [SHELXTL (version 5.10), Structure Determination Software Programs, Bruker AXS Inc., Madison, WI, 1997].

**General Procedure for the Coupling.** A solution of benzylamine (4.28 g; 40 mmol) in degassed methanol (50 mL) was added to a stirred solution of $CuCl_2 \cdot 2H_2O$ (1.7 g; 10 mmol) in degassed methanol (150 mL). The solution was purged with argon for 5 min, a solution of the arylamine (10 mmol) in degassed anisole (50 mL) was added, and the mixture was stirred at room temperature for 24 h under argon. The reaction mixture was then first acidified with concd HCl (50 mL), stirred for 5 min, and then treated with concd ammonia (100 mL) for another 5 min and finally diluted with water (1 L). The resulting suspension was extracted with $CHCl_3$ (3 × 100 mL), and the organic extract was dried with $Na_2SO_4$ and evaporated.

**3-Phenyl-1-aminonaphthalene (11). Method A.** A mixture of **3a**[8b,38] (855 mg; 3,87 mmol), $NaHSO_3$ (5 g), 30% aqueous ammonia (40 mL), and water (10 mL) was heated in a sealed tube at 200 °C for 48 h. The mixture was then cooled, treated with 10% aqueous KOH (40 mL), and extracted with ether. Gaseous HCl was then passed through this ethereal solution, and the solid hydrochloride was collected by filtration. The hydrochloride was dissolved in water (50 mL), the solution was alkalized with a 10% aqueous NaOH, and the free base was extracted with ether. Evaporation of the ethereal solution followed by crystallization from petroleum ether afforded solid **11** (358 mg; 42%), which decomposed at ≥100 °C before melting; hydrochloride **11**·HCl had mp 124−6 °C (methanol−dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.26 (br s, 2 H, $NH_2$), 7.05 (d, $J = 1.7$ Hz, 1 H, 2-H), 7.35 (tt, $J = 7.8$ and 1.5 Hz, 1 H, 4′-H), 7.44 (m, 1 H, 7-H), 7.45 (m, 2 H, 3′-H and 5′-H), 7.47 (m, 1 H, 6-H), 7.52 (br s, 1 H, 4-H), 7.67−7.71 (m, 2 H, 2′-H and 6′-H), 7.82 (m, 1 H, 8-H), 7.84 (m, 1 H, 5-H); $^{13}$C NMR $\delta$ 109.19 (d, C-2), 117.06 (d, C-4), 120.67 (d, C-8), 122.88 (s, C-9), 124.84 (d, C-7), 126.23 (d, C-6), 127.19 (d, C-4′), 127.26 (2 × d, C-2′ and C-6′), 128.65 (2 × d, C-3′ and C-5′), 128.80 (d, C-5), 134.63 (s, C-10), 139.09 (s, C-3), 141.36 (s, C-1′), 142.45 (s, C-1); IR ($CHCl_3$) $\nu$ 3481 and 3397 (NH), 1626 and 1596 (C=C arom) cm$^{-1}$; MS $m/z$ (%) 219 ([M]$^{+\bullet}$, 100), 217 (9.8), 202 (2.5), 191 (6.3), 165 (3.3), 140 (2.2), 115 (2.6), 109 (5.5).

**Method B.** A mixture of 3-phenyl-1-naphthol **3a**[8b,38] (220 mg, 1 mmol) and a 100% hydrazine hydrate (250 mg, 5 mmol) was heated in a sealed tube at 200 °C for 24 h. The reaction mixture was poured in water (10 mL) and extracted with $Et_2O$ (3 × 10 mL). The organic phase was dried with anhydrous $MgSO_4$ and filtered. A solution of HCl in THF (2 mL of 1 M solution) was then added, and the precipitate that contained hydrochlorides of **11** and **22** was filtered off. The etheric phase, containing mainly the unreacted naphthol **3a**, was discarded. The mixture of hydrochlorides was treated with satd ammonia in $Et_2O$ (10 mL) and evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (20 g) with a 1:1 mixture of hexane and ethyl acetate to elute amine **11** (20 mg; 9%) followed by the hydrazine derivative **22** (70 mg, 30%). Amine **11** was identical with the product obtained from the Bucherer reaction (method A).

**Oxidative Coupling of 8.** The oxidative coupling was carried out as described in the general procedure, using **8** (1.93 g). After workup, the residue was chromatographed on silica (300 g) using toluene as eluent to give diamine **15** (820 mg, 43%) and carbazole **16** (710 mg, 39%).

**2,2′-Diamino-1,1′-bianthryl (15):** mp 160−3 °C (toluene), 165−8 °C (benzene−ethanol; lit.[14b] gives 233 °C for the compound crystallized from benzene−ethanol); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.76 (br s, 4 H, $NH_2$), 7.19−7.31 (m, 6 H), 7.53 (dd, $J = 8.4$ and 0.8 Hz, 2 H), 7.34 (s, 2 H), 7.92 (dd, $J = 8.2$ and 0.8 Hz, 2 H), 8.06 (dd, $J = 9.6$ and 0.8 Hz, 2 H), 8.40 (s, 2 H); $^{13}$C NMR $\delta$ 110.12 (s), 120.14 (d), 121.21 (d), 123.99 (d), 125.20 (d), 126.84 (d), 127.93 (d), 127.94 (d), 128.26 (s), 129.61 (s), 130.01 (d), 131.93 (s), 132.64 (s), 141.98 (s); IR ($CHCl_3$) $\nu$ 3390 and 3486 (NH) cm$^{-1}$; MS (EI) $m/z$ (%) 384 ([M]$^{+\bullet}$, 100), 383 (14), 368 (24), 367 ($C_{28}H_{17}N$, 37), 192 ($M^{2+}$, 8), 190 (8), 183.5 (13), 183 (11), 182.5 (17), 176 (10), 169.5 (14); HRMS for $C_{28}H_{20}N_2$ calcd 384.1626 found 384.1629.

**Resolution of (±)-15.** A solution of racemic **15** (384 mg, 1 mmol) and (−)-*N*-benzylcinchonidinium chloride (210 mg, 0.5 mmol) in acetonitrile (5 mL) was heated at 70 °C for 4 h. The mixture was then cooled, and the crystals formed were washed with acetonitrile (1 mL) and isolated with suction to give the inclusion complex (345 mg). Chiral chromatography on a Daicel Chiralpak AD column with a 68:22:10 hexane−methanol−2-propanol mixture as eluent (flow rate 1 mL/min, UV detection at 256 nm) showed that the crystals contained (*R*)-**15** enriched in 73% ee ($t_R = 8.6$ min, $t_S = 12.4$ min). The crystals were then dissolved in dichloromethane (1 mL), and the solution was covered with a layer of diethyl ether (5 mL) and allowed to slowly crystallize. The crystals (240 mg) thus formed contained the enantiomerically pure (*R*)-(−)-**15**, as revealed by chiral chromatography: mp 240−242 °C. Dissolving these crystals in dichloromethane followed by chromatography on silica gel with $CH_2Cl_2$ afforded pure (*R*)-(−)-**15** (132 mg, 34%): mp 253−5 °C (benzene−ethanol; lit.[14b] gives 182−4 °C from the same solvent or 174−5 °C from an unidentified solvent[14a]); $[\alpha]_D$ −302 (*c* 4, $CHCl_3$) [lit. $[\alpha]_D$ −384 (*c* 4, $CHCl_3$)[14b] or −336.7 ($CHCl_3$)[14a]]. The mother liquor from the first resolution step was evaporated under a reduced pressure to give an amorphous material (240 mg) that contained (*S*)-(+)-**15** enriched in 72% ee.

**8*H*-Dinaphtho[2,3-*c*:2′,3′-*g*]carbazole (16):** mp 274−7 °C (toluene; lit.[15] gives 264−6 °C); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.50−7.61 (m, 4 H), 7.70 (d, $J = 9.0$ Hz, 2 H), 7.99 (d, $J = 9.0$ Hz, 2 H), 8.10 (dd, $J = 9.2$ Hz, $J = 0.9$ Hz, 2 H), 8.18 (dd, $J = 9.2$ Hz, $J = 0.9$ Hz, 2 H), 8.61 (s, 2 H), 8.94 (s, 1 H), 9.94 (s, 2 H); $^{13}$C NMR $\delta$ 114.01 (d), 117.24 (s), 122.95 (d), 124.79 (d), 125.75 (d), 127.01 (d), 127.46 (d), 127.80 (s), 127.92 (d), 128.06 (d), 129.83 (s), 130.06 (s), 131.28 (s), 134.69 (s); IR ($CHCl_3$) $\nu$ 3462 (NH) cm$^{-1}$; MS (EI) $m/z$ (%) 367 ([M]$^{+\bullet}$, 100), 366(17), 364 (10), 183.5 ($M^{2+}$, 9), 182.5 (9), 181.5 (10), 169.5 (10); HRMS for $C_{28}H_{17}N$ calcd 367.1361 found 367.1363.

**Oxidative Coupling of 9.** The oxidative coupling was carried out as described in the general procedure, using **9** (1.93 g, 10 mmol) and a complex of copper(II) chloride dihydrate (3.4 g, 20 mmol) with benzylamine (5.56 g, 80 mmol); note that, in this case, 2 equiv of Cu(II) were required (one for the coupling and one for the *N*,*N*-oxidation). After workup, the residue was chromatographed on a column of silica gel (200 g) using a toluene−petroleum ether mixture (1:1) as eluent to give the azo compound **17** (1.66 g, 87%).

**Azo-3,3′-phenanthrene (17):** mp 266−9 °C (toluene); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.68 (ddd, $J = 8.0$ Hz, $J = 6.9$ Hz, $J = 1.2$ Hz, 2 H), 7.77 (ddd, $J = 8.3$ Hz, $J = 6.9$ Hz, $J = 1.4$ Hz, 2 H) 7.84 (bd, $J = 9.2$ Hz, 2 H), 7.87 (bd, $J = 9.2$ Hz, 2 H) 7.96 (dd, $J = 7.8$ Hz, $J = 1.4$ Hz, 2 H), 8.05 (d, $J = 8.6$ Hz, 2 H), 8.29 (dd, $J = 8.5$ Hz, $J = 1.8$ Hz, 2 H), 8.91 (dm, $J = 8.2$ Hz, 2 H), 9.40 (d, $J = 1.8$ Hz, 2 H); $^{13}$C NMR $\delta$ 118.34 (d),

(38) Kipping, C.; Schiffer, H.; Schönfelder, K. *J. Prakt. Chem.* **1973**, *315*, 887.

121.80 (d), 123.06 (d), 126.57 (d), 127.10 (2 × d), 128.73 (d), 128.79 (d), 129.67 (d), 130.84 (s), 130.91(s), 132.30 (s), 133.93 (s), 151.01 (s); IR ($CHCl_3$) $\nu$ 1612 and 1602 (C═C arom); MS *m*/*z* (%) 382 ($[M]^{+\bullet}$, 32), 354 (5), 352 (7), 191 (4), 177 (100), 176 (18), 151 (9); HRMS for $C_{28}H_{18}N_2$ calcd 382.1470 found 382.1476.

**Oxidative Coupling of 10.** The oxidative coupling was carried out as described in the general procedure, using **10** (1.93 g). After workup, the residue was chromatographed on a column of silica gel (50 g) using toluene as eluent to give carbazole **19** (1.43 g, 78%) and a mixture of unreacted **10** and diamine **18**. The latter mixture was separated using a semi-preparative HPLC (Magnum 9 column, Whatman) with a petroleum ether−ethyl acetate mixture (4:1) as eluent to give diamine **18** (40 mg, 2%) and unreacted **10** (190 mg, 10%).

**10,10′-Diamino-9,9′-biphenanthryl (18):**[18] $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.17 (bs, 4 H), 7.20 (dd, $J$ = 8.2 Hz, $J$ = 1.2 Hz, 2 H), 7.26−7.31 (m, 2 H), 7.42−7.47 (m, 2 H), 7.68−7.80 (m, 4 H), 8.02 (dd, $J$ = 8.2 Hz, $J$ = 1.2 Hz, 2 H), 8.71 (dd, $J$ = 8.4 Hz, $J$ = 0.4 Hz, 2 H), 8.86 (dd, $J$ = 8.4 Hz, $J$ = 0.4 Hz, 2 H); $^{13}$C NMR $\delta$ 110.91 (s), 121.77 (d), 122.64 (d), 123.43 (d), 123.53 (d), 124.78 (d), 125.05 (s), 126.35 (s), 126.57 (d), 127.01 (d), 127.43 (d), 131.26 (s), 132.29 (s), 138.84 (s); IR ($CHCl_3$) $\nu$ 3477 and 3678 (NH) cm$^{-1}$; MS (EI) *m*/*z* (%) 384 ($[M]^{+\bullet}$, 100), 368 (25), 367 (53), 366 (18), 365 (23), 190 (10), 184 (10), 183.5 (34), 183 (23), 182.5 (40), 176 (20); HRMS for $C_{28}H_{20}N_2$ calcd 384.1626 found 384.1620.

**9*H*-Tetrabenzo[*a*,*c*,*g*,*i*]carbazole (19). Method A (Oxidative Coupling):** mp 257−8 °C (toluene; lit.[17] gives 242−4 °C); $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 7.62−7.68 (m, 2 H), 7.69−7.78 (m, 6 H), 8.74 (dd, $J$ = 8 Hz, $J$ = 1.2 Hz, 2 H), 8.91 (d, $J$ = 8.4 Hz, 4 H), 9.09 (d, $J$ = 8 Hz, 2 H), 12.08 (bs, 1 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 115.33 (s), 122.58 (d), 123.34 (s), 124.15 (d), 124.61 (d), 124.67 (d), 125.18 (d), 126.37 (d), 126.42 (d), 127.46 (d), 127.69 (s), 128.98 (s), 129.34 (s), 133.38 (s); MS (EI) *m*/*z* (%) 367 ($[M]^{+\bullet}$, 100); HRMS for $C_{28}H_{17}N$ calcd 367.1361 found 367.1357.

**Method B.** A mixture of 9-phenanthrol (5.00 g) and 80% aqueous hydrazine hydrate (0.8 mL) was heated in a sealed tube at 180 °C for 24 h. The mixture was cooled and dissolved in dichloromethane, and the solution was worked up. Chromatography on silica gel (50 g) with toluene gave **19** (2.88 g, 58%), which had identical MS and NMR spectra as those obtained for the product resulting from Method A.

**Oxidative Coupling of 11.** The oxidative coupling was carried out as described in the general procedure, using **11** (2.19 g). After workup, the residue was chromatographed on a column of silica gel (50 g) using toluene as eluent to give carbazole **20** (505 mg, 25%).

**6,7-Diphenyl-13*H*-dibenzo[*a*,*i*]carbazole (20):** mp 294−6 °C (sublim); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.95−7.00 (m, 6 H), 7.15−7.20 (m, 4 H), 7.41 (s, 2 H), 7.54 (ddd, $J$ = 8.2, 7.0, and 1.2 Hz, 2 H), 7.64 (ddd, $J$ = 8.2, 7.0, and 1.4 Hz, 2 H), 7.96 (dm, $J$ = 8.1 Hz, 2 H), 8.33 (dm, $J$ = 8.2 Hz, 2 H), 9.76 (bs, 1 H, NH); $^{13}$C NMR $\delta$ 117.34 (s), 119.90 (d), 120.26 (s), 123.31 (d), 125.54 (d), 125.58 (d), 126.38 (d), 128.12 (2 × d), 128.37 (2 × d), 128.81 (d), 131.66 (s), 135.15 (s), 136.90 (s), 143.04 (s); IR ($CHCl_3$) $\nu$ 3488 (NH), 1600 (C═C arom) cm$^{-1}$; MS (EI) *m*/*z* (%) 419 ($[M]^{+\bullet}$, 100), 341 (16), 209.5 ($M^{2+}$, 4), 170.5 (30); HRMS for $C_{32}H_{21}N$ calcd 419.1674 found 419.1672.

**Oxidative Coupling of 12.** The oxidative coupling was carried out as described in the general procedure, using **12** (2.43 g). After workup, the residue was chromatographed on a column of silica gel (50 g) using toluene as eluent to give carbazole **21** (2.06 g, 85%).

**9*H*-Diphenanthro[1,2-*c*:2′,1′-*g*]carbazole (21):** mp >320 °C (dec); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.32 (ddd, $J$ = 8.3, 6.7, and 1.5 Hz, 2 H), 7.12 (ddd, $J$ = 8.0, 6.9, and 1.2 Hz, 2 H), 7.57 (d, $J$ = 8.4 Hz, 2 H), 7.77−7.86 (m, 6 H), 8.00 (d, $J$ = 8.7 Hz, 2 H), 8.52 (dd, $J$ = 8.4 and 1.6 Hz, 2 H), 8.86 (d, $J$ = 8.7 Hz, 2 H), 8.96 (dd, $J$ = 8.1 and 1.5 Hz, 2 H), 10.17 (bs, 1 H, NH); $^{13}$C NMR $\delta$ 115.94 (s), 120.41 (d), 120.75 (d), 122.02 (s), 123.33 (d), 124.35 (d), 124.53 (s), 125.06 (d), 125.73 (d), 126.09 (d), 126.29 (d), 126.61 (d), 127.07 (s), 128.63 (d), 129.60 (s), 130.61 (s), 131.19 (s), 133.28 (s); IR ($CHCl_3$) $\nu$ 3467 cm$^{-1}$; MS (ES) *m*/*z* (%) 466 ($[M]^+ - 1$, 100).

**3-Phenyl-1-hydrazinonaphthalene (22)** was obtained along with **11** on reaction of **3a** with hydrazine hydrate: mp (hydrochloride) 136−8 °C; $^1$H NMR $\delta$ 4.59 (m, 2 H, $NH_2$), 6.02 (m, 1 H, NH), 7.25 (bs, 1 H, 2-H), 7.38 (tt, $J$ = 7.5 and 1.5 Hz, 4′-H), 7.45 (m, 1 H, 7-H), 7.48 (m, 2 H, 3′-H and 5′-H), 7.49 (m, 1 H, 6-H), 7.54 (bs, 1 H, 4-H), 7.74 (m, 2 H, 2′-H and 6′-H), 7.78 (dm, $J$ = 8.1 Hz, 1 H, 8-H), 7.87 (dm, $J$ = 8.1 Hz, 1 H, 5-H); $^{13}$C NMR $\delta$ 104.19 (d, C-2), 117.44 (d, C-4), 119.50 (d, C-8), 121.81 (s, C-9), 125.16 (d, C-7), 126.41 (d, C-6), 127.31 (d, C-4′), 127.37 (2 × d, C-2′ and C-6′), 128.71 (2 × d, C-3′ and C-5′), 128.91 (d, C-5), 134.35 (s, C-10), 139.11 (s, C-3), 141.73 (s, C-1′), 146.54 (s, C-1); IR ($CHCl_3$) $\nu$ 3417, 3394 and 3343 (NH), 1628 and 1596 (C═C arom) cm$^{-1}$; MS (EI) *m*/*z* (%) 234 ($[M]^{+\bullet}$, 100), 218 ($M - NH_2$, 36.9), 204 ($M - N_2H_3$, 16.3), 191 ($M - CN_2H_3$, 56.3), 189 (16.0), 176 (2.9), 165 (8.8), 140 (3.4), 117 (3.5).

**Acknowledgment.** We thank the Grant Agency of the Czech Republic for grant No. 203/00/0601, the Grant Agency of the Charles University for grant No 18/98, the Ministry of Education of the Czech Republic for grants No. VS 96140 and LB 98233, and the EPSRC and Merck Sharp & Dohme for a CASE award (to R.D.B.).

**Supporting Information Available:** Details of the crystallographic analysis with fully labeled ORTEP diagram for **20**, atomic coordinates, selected bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

JO005691W