Selective Cross-Coupling of 2-Naphthol and 2-Naphthylamine Derivatives. A Facile Synthesis of 2,2′,3-Trisubstituted and 2,2′,3,3′-Tetrasubstituted 1,1′-Binaphthyls

Martin Smrčina,*[†,‡] Štěpán Vyskočil,[†] Bohumil Máca,[†] Miroslav Polášek,[§] Thomas A. Claxton,[⊥]
Andrew P. Abbott,[⊥] and Pavel Kočovský*[,⊥]

Department of Organic Chemistry, Charles University, 128 40 Prague 2, Czech Republic, The J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic, and Department of Chemistry, University of Leicester, Leicester LE1 7RH, England

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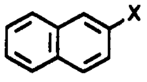
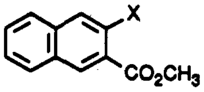
The novel 1,1′-binaphthyls with OH and/or NHR (R = H or Ph) groups in the 2,2′-positions and with additional methoxycarbonyl group(s) in the 3- or 3,3′-positions (**13**–**18**) have been synthesized from their respective precursors **1**–**5** by the $CuCl_2/t\text{-}BuNH_2$-mediated oxidative cross-coupling. In most cases, the chemoselectivity was good, and the cross-coupled products **11**–**18** were obtained in fair to excellent yields. Binaphthyls **6**–**10**, resulting from the self-coupling, and carbazoles **19**–**23** have been identified as byproducts. *Ab initio* calculations and electrochemical measurements have been employed to account for the observed selectivity.

Introduction

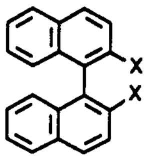
Oxidative coupling of 2-naphthol and its derivatives is a simple and efficient method for the preparation of symmetrically substituted binaphthyls as documented by numerous examples in the literature.[1] Thus, for instance, two molecules of 2-naphthol (**1**) can be coupled by means of Cu(II)[2–4] or other mild oxidants[5–7] to produce binaphthol (**6**) in high yield. Similarly, 2-naphthylamine (**2**) gives diamine **7**[8] while **4** affords **9**.[2] By contrast, selective cross-coupling of two different molecules is rare:[8–10] among the handful of examples is the Cu(II)-mediated coupling **1** + **2** producing **11**[8] and **1** + **4** furnishing **12**.[10]



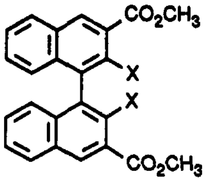
1, X = OH
2, X = NH_2
3, X = NHPh



4, X = OH
5, X = NH_2



6, X = OH
7, X = NH_2
8, X = NHPh



9, X = OH
10, X = NH_2

The symmetrically 2,2′-disubstituted 1,1′-binaphthyls, such as **6** and **7**,[11] have been extremely successful as C_2-symmetric chiral ligands in asymmetric synthesis, with >90% ee achieved being more the rule rather than the exception. Additional substituents at positions 3 and 3′ have been recognized to impose further steric interactions, an effect which often results in the remarkable increase of asymmetric induction.[12] In contrast to the wide use of

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[†] Charles University.

[‡] Current address: Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853.

[§] The J. Heyrovský Institute.

[⊥] University of Leicester.

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(5) Other metals have also been explored by other investigators, namely Fe(III)[6] and Mn(III),[7] but to date, Cu(II) has been the most successful oxidant.[2–4]

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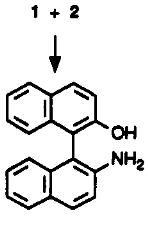
Table 1. Copper(II)-Mediated Oxidative Coupling of Naphthyl Derivatives 1–5

entry	substrates	time (h)	cross-coupling product (yield, %)[a]	self-coupling product (yield, %)	carbazole (yield, %)
1	**1** + **2**	48	**11** (85)[b]	**6** (6),[c] **7** (2)[c]	**19** (~1)[c]
2	**1** + **4**	3	**12** (81)[d]	**6** (4),[c] **9** (7)[c]	
3	**1** + **5**	48	**13** (32)	**6** (27),[a] **10** (16)[a]	**21** (12)[a]
4	**2** + **4**	36	**14** (71)[e]	**7** (11),[c] **9** (13)[c]	**19** (~1)[c]
5	**2** + **5**	48	**15** (13)	**7** (20),[a] **10** (11)[a]	**21** (10),[a,f] **22** (9)[a]
6	**3** + **4**	72	**16** (40)[g]	**8** (11),[a] **9** (28)[a]	**20** (~1)[a]
7	**3** + **5**	72	**17** (9)	**8** (15),[a] **10** (20)[a]	**21** (18),[a] **22** (~5)[a,h]
8	**4** + **5**	72	**18** (50)	**9** (18),[a] **10** (9)[a]	**21** (8)[a]
9	**3** + **3**	72		**8** (45)[a]	**20** (3)[a,i]
10	**5** + **5**	72		**10** (26)[a,e]	**21** (21)[a]

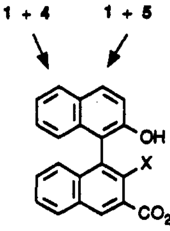
[a] Isolated by chromatography. [b] Yields obtained with $CuCl_2/PhCH(NH_2)CH_3$ (see ref 8); with $CuCl_2/t\text{-}BuNH_2$ the yields were as follows: **11** (65%), **6** (2%), **7** (5%), and **19** (~1%). [c] GC yield. [d] See ref 10. [e] Can be isolated from the mixture by crystallization from toluene. [f] Formation of **19** (~1%) was detected by GC. [g] From the crude reaction mixture, **16** can be isolated by single crystallization from acetone as a yellow clathrate (see also ref 30). [h] Formation of carbazoles **20** (2%) and **23** (<1%) has also been detected. [i] See ref 18.

these ligands, there have only been a handful of reports[13] on their congeners with two different functional groups at positions 2 and 2′, while their derivatives further substituted in the 3- or 3,3′-positions are almost unknown.[13m] Herein, we report on the synthesis of a new class of 1,1′-binaphthyls unsymmetrically substituted at the 2,2′,3- and 2,2′,3,3′-positions (**13**–**18**) employing the Cu(II)-mediated cross-coupling.[14,15]

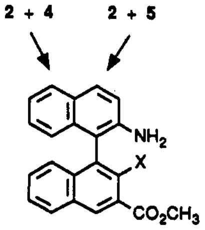
Our initial experiments aimed at the construction of the 2,2′-nonsymmetrically substituted binaphthyls, via the oxidative cross-coupling, were encouraging[8] and so were the reports by Yamamoto[9] and Hovorka et al.[10] Thus, for example, we have shown that 2-naphthol (**1**) can be cross-coupled with 2-naphthylamine (**2**) to afford the amino alcohol **11** in a remarkably high isolated yield (Table 1, entry 1).[8] Similarly, high selectivity for the cross-coupling has been observed for the pair 2-naphthol (**1**) and 3-(methoxycarbonyl)-2-naphthol (**4**) which gave the binaphthyl derivative **12** (entry 2).[10] In both cases, the self-coupling processes were largely suppressed. We have also shown that carrying out these cross-couplings with chiral complexes of Cu(II) results in the formation of enantiomerically enriched products, with ~40–100% ee.[8]



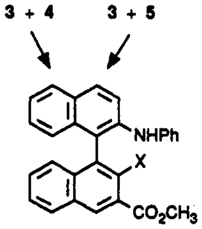
11



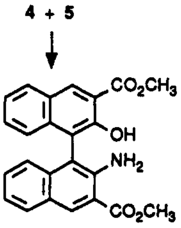
12, X = OH
13, X = NH_2



14, X = OH
15, X = NH_2

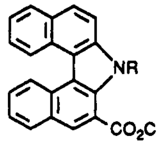


16, X = OH
17, X = NH_2



18

19, Y = H, R = H
20, Y = H, R = Ph
21, Y = CO_2CH_3, R = H



22, R = H
23, R = Ph

Since the initial experiments seemed highly successful, it was desirable to establish the scope of this methodology. We have therefore set out to investigate a series of naphthalene derivatives **1**–**5** in order to find suitable

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(14) While **11** and **12** have recently been synthesized both in racemic and enantiomerically pure forms,[8–10] the rest of the cross-coupled products are new compounds.

(15) The self-coupled binaphthyls **6**,[16] **7**,[17] **8**,[18] and **9**[2,19] have also been prepared before.

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combinations which would prefer the oxidative cross-coupling over the self-coupling.

Results

The two examples of highly efficient, $CuCl_2/RNH_2$-mediated[20] cross-coupling of 2-naphthol (**1** + **2** and **1** + **4**; Table 1, entries 1 and 2) prompted us to further explore the reactivity of 2-naphthol with other reaction partners, namely with **3** (a phenylated analogue of **2**) and **5** (a 3-substituted congener of **2**). In the attempted **1** + **3** reaction, we have only been able to detect the product of self-coupling of **1**, unreacted **3**, and several unidentified byproducts. Apparently, **3** is not as reactive as its nonphenylated congener **2**. In the **1** + **5** case, the cross-coupled product **13** slightly prevailed, and its yield was approximately equal to the sum of the two possible products of self-coupling, **6** and **10** (entry 3); dibenzocarbazole **21** was isolated as the minor product. Hence, further substitution in the 2-naphthylamine molecule (with either Ph at nitrogen or CO_2Me group at position 3) has a detrimental effect on its propensity to cross-couple with 2-naphthol. In the instance of the 3-CO_2Me substitution, the reaction outcome appears to be critically dependent on the substrate: while the hydroxy derivative **4** highly favors the cross-coupling (81%; entry 2), this tendency is dramatically decreased when OH is replaced by NH_2, as in **5**. This is in sharp contrast with the behavior of the pair of the parent naphthalene derivatives **1** and **2**, where the cross-coupling dominates (entry 1).

The reactivity of 2-naphthylamine (**2**) exhibits an even more diverse pattern. Thus, we have found that the **2** + **4** coupling was almost as successful as in the case of 2-naphthol (i.e., **1** + **4**), giving the cross-coupled product **14** in a very good isolated yield (71%; entry 4); the total of the self-coupled products **7** and **9** did not exceed 25%. In sharp contrast to this high selectivity is the outcome of the reaction of the two amino derivatives **2** + **5**, which turned out to result in a nonselective coupling, giving all the expected products of cross- and self-coupling **15**, **7**, and **10** and dibenzocarbazoles **21** and **22** (entry 5).

The *N*-phenyl-substituted derivative **3** still showed some preference for coupling with **4** affording the cross-coupled product **16** in 40% isolated yield and about the same amount of the sum of the self-coupled products **8** and **9** (entry 6). However, the selectivity is considerably reduced as compared with the **2** + **4** coupling. The **3** + **5** coupling (entry 7) turned out to be as nonselective as in the case of **2** + **5** reaction.

Finally, an acceptably high tendency to cross-coupling has been observed for the **4** + **5** reaction (entry 8) in which **18** was identified as the main product (50% isolated yield).

For the sake of identification of some of the above products, the self-coupling reactions **3** + **3** and **5** + **5** have also been carried out. The respective products **8** and **10** and the corresponding dibenzocarbazoles **20** and **21** were isolated and characterized.

Discussion

The mechanism of the $CuCl_2$-mediated oxidative coupling is not clear, and essentially three possible routes have been proposed in the literature:[10] (1) homolytic coupling of two radicals ($X^\bullet + Y^\bullet$), (2) ionic reaction ($X^+ + Y$), and (3) radical insertion of one of the aryls into the C–H bond of another aryl molecule ($X^\bullet + Y$). While the recombination of two radical species is generally unlikely due to their low concentration, there is some belief, supported by experimental evidence, in the latter mechanism, i.e., that a radical, initially generated by one-electron transfer to Cu(II), attacks another neutral molecule or the corresponding anion of the substrate to give 1,1′-binaphthyl. However, Hovorka and Závada have shown that if dimeric complexes $(ArOCuL)_2$ are considered as intermediates, the coupling would occur as an intramolecular process and the differentiation between pathways 1, 2, and 3 would be "meaningless".[10d]

In a coupling reaction with two potential partners **A** and **B** present in the reaction mixture, both of them being capable of generating a radical, three possible products can be expected, namely **A–A**, **B–B**, and **A–B**. Assuming that the coupling proceeds as an orbital-controlled process, the choice of the reacting partner for the initially formed radical, e.g., $\mathbf{A}^\bullet$ (which may be coordinated to copper), will be determined by the energy difference between the SOMO of $\mathbf{A}^\bullet$ and the HOMOs and LUMOs of **A** and **B**. The high-energy SOMO (a nucleophilic radical) is likely to interact with the LUMO of the reaction partner, while the low-energy SOMO (an electrophilic radical) should prefer to mix with the HOMO.[21] If the stabilization is greater from the interaction between A_{SOMO} and $B_{HOMO/LUMO}$ than from that with $A_{HOMO/LUMO}$, then preferential formation of the cross-coupled product **A–B** can be anticipated. Conversely, a self-coupled product **A–A** would result if greater stabilization is achieved by the interaction of A_{SOMO} with $A_{HOMO/LUMO}$. Finally, mixtures of products can be expected if the energy differences between the frontier orbitals of **A** and **B** are marginal. Similar patterns can be used to assess the reactivity of the radical $\mathbf{B}^\bullet$. The overall outcome of the reaction will thus be dictated by two factors: (1) the ease of generating the radical $\mathbf{A}^\bullet$ as compared to $\mathbf{B}^\bullet$ and (2) the most stabilizing interaction between the preferred radical and the frontier orbitals of **A** and **B**. In those instances where the formation of radical $\mathbf{A}^\bullet$ is highly favored and the best stabilization is expected from the interaction between $\mathbf{A}^\bullet$ and frontier orbital(s) of **B**, a highly selective cross-coupling (affording **A–B** as the main product) will result. When no such preference for the formation of one of the radicals is expected, both $\mathbf{A}^\bullet$ and $\mathbf{B}^\bullet$ may be present in the reaction mixture (being formed at comparable rates) and compete in selecting a suitable reaction partner (**A** or **B**). This scenario will result in the formation of a mixture of products.

Ab initio calculations using the standard 3-21G basis sets have been employed to establish the energies of the frontier orbitals of **X**, $\mathbf{X}^\bullet$, and $\mathbf{X}^-$ for each of the molecules **1**, **2**, **4**, and **5**.[22-24] For the sake of simplification of the

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[20] t-$BuNH_2$ has now been used rather than the previously employed[8a] $PhCH_2NH_2$ in order to prevent ester aminolysis.

[21] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; J. Wiley & Sons: Chichester, 1976.

[22] Calculation of **3** has not been carried out because of the additional complication caused by the Ph substituent.

[23] All geometries were optimized[24] using either the RHF or ROHF method, depending on the spin multiplicity (see the supplementary material).

[24] Gaussian 92, Revision B: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresma, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

Table 2. Frontier Orbitals for Naphthalene Derivatives 1, 2, 4, and 5

	energy of frontier orbitals (in hartree)^{a}		
compd	neutral molecule	radical	anion
1	0.100 52^{b}	0.090 85^{b}	0.261 73^{b}
	−0.291 14^{c}	−0.126 92^{d}	−0.067 52^{c}
2	0.110 31^{b}	0.098 46^{b}	0.268 67^{b}
	−0.264 69^{c}	−0.094 28^{d}	−0.046 24^{c}
4^{e}	0.071 34^{b}	0.058 50^{b}	0.220 88^{b}
	−0.299 19^{c}	−0.104 36^{d}	−0.086 08^{c}
5^{e}	0.075 84^{b}	0.072 08^{b}	0.226 08^{b}
	−0.269 84^{c}	−0.098 21^{d}	−0.064 59^{c}

^{a} *Ab initio* calculation at the 3-21G basis. ^{b} LUMO. ^{c} HOMO. ^{d} SOMO. ^{e} The CO_2Me group was approximated as a nondissociable CO_2H.

Table 3. Oxidation Potentials and HOMO Energies of Naphthalene Derivatives 1, 2, 4, and 5

	E_p vs SCE	HOMO
compd	in V	in hartree
1	1.15	−0.291 14
2	0.78^{a}	−0.264 69
3	0.66	
4	1.55	−0.299 19
5	0.88	−0.269 84

^{a} Another two maxima have been identified: 0.81 and 0.98 (see ref 25).

calculations and to save computer time, the ester group (CO_2Me) in 4 and 5 was approximated as a nondissociable carboxyl (CO_2H). The results are listed in Table 2.

The energies required for oxidation of the naphthyl derivatives to the corresponding radicals are reflected in their oxidation potentials (E_p), which were determined experimentally for 1–5 (Table 3). The E_p values agree acceptably well with the energies of the HOMO orbitals of the neutral molecules of the parent molecules (Table 3): derivatives with low lying HOMOs (1 and 4) have higher oxidation potentials (more energy is needed to abstract an electron) than those with high-energy HOMOs (2 and 5). Hence, the latter compounds are likely to undergo one-electron oxidation (to form radicals) more easily than the former.[25]

Correlation diagrams have been constructed for each of the combinations (Figures 1–6) in order to assess the possible competing pathways. Thus, for instance, in the mixture of 1 and 2 (Figure 1), all three combinations (1 + 1, 1 + 2, and 2 + 2) are considered. The energy levels for all possible species derived from each particular compound (i.e., HOMOs and LUMOs for a neutral molecule, radical, and anion) are plotted vertically. It is obvious that the LUMOs for the anions are too high in energy (Table 2) to be considered for interactions and have been omitted from the figures. The electrochemical data, as well as the HOMO energies for 1 and 2 (Table 3), suggest that 2 will form radicals in preference to 1. Hence, the reaction will be governed mostly by the reactivity of $2^{\bullet}$. Figure 1 indicates that maximum orbital stabilization can be obtained from the interaction of $2^{\bullet}$ with 1^{-} (the energy difference between the two orbitals is only 0.02676 hartree). The other two interactions, $2^{\bullet} + 2^{-}$ or $1^{\bullet} + 1^{-}$, would lead to less stabilization, as the energy differences 2^{-} vs $2^{\bullet}$ and 1^{-} vs $1^{\bullet}$ are higher (0.048 04 and 0.059 40 hartree, respectively). The reaction between two radical species is unlikely and has not been considered; other interactions, although *a priori* possible, would not offer any substantial stabilization or, at least, not comparable to those discussed. This simple analysis predicts the cross-coupling 1 + 2 → 11 to be the dominant process, which is in excellent agreement with the experimental observation (Table 1, entry 1).

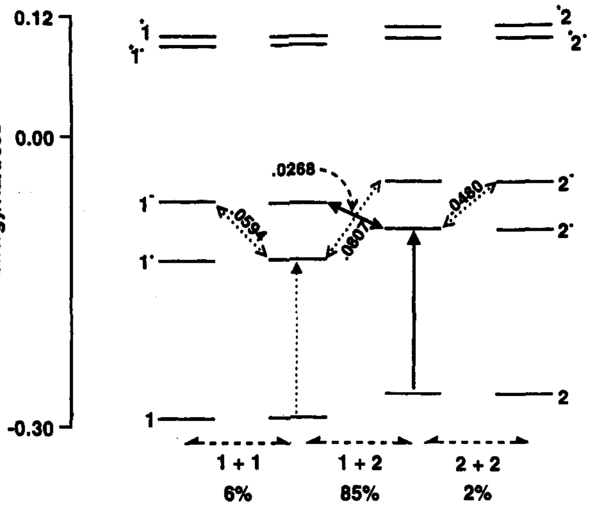

Figure 1. Orbital interactions in the 1 + 2 reaction.

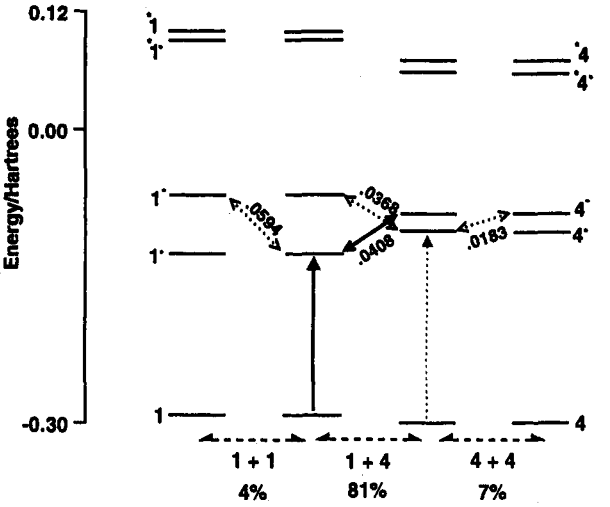

Figure 2. Orbital interactions in the 1 + 4 reaction.

For the 1 + 4 combination (Figure 2), the calculation and electrochemical data (Table 3) clearly show that it will be much easier to generate a radical from 1 as compared to 4. The radical $1^{\bullet}$ will prefer to interact with 4^{-} (the difference of the corresponding energy levels is 0.040 84). The other possibility is less likely since the difference in the orbital energy $1^{\bullet}$ vs 1^{-} is higher (0.05940). The energy of the HOMO of 4^{-} is lower than that of 1^{-} due to the electron-withdrawing effect of the CO_2Me group. This

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(25) While each of the cyclic voltamograms of 1 and 3–5 shows a single maximum (Table 3), the behavior of 2 is more complex: three maxima have been identified in this instance, which indicates the occurrence of several consecutive processes (e.g., oxidation of the NH_2 group[26] as the first step). The latter processes are apparently suppressed in the case of other amines (3 and 5), presumably owing to the effect of the substituents (Ph or CO_2Me), which renders the nitrogen less prone to oxidation. Hence, the electrochemical behavior of 2 may not be used directly as an argument in connection with the binaphthyl coupling. However, all three maxima observed on the voltamogram of 2 are below the values for 1 and 4. Moreover, the comparison of the E_p values for 1 and 4 suggests that had the same reaction occurred for 2 as for the other members of the series, the corresponding E_p value for that process would be unlikely to be higher than that for 5. Hence, generally, lower oxidation potentials can be assumed for all the amines 2, 3, and 5 as compared with those for the naphthols 1 and 4.

(26) Weinberg, N. L. *Technique of Electroorganic Synthesis*; J. Wiley and Sons: New York, 1974.

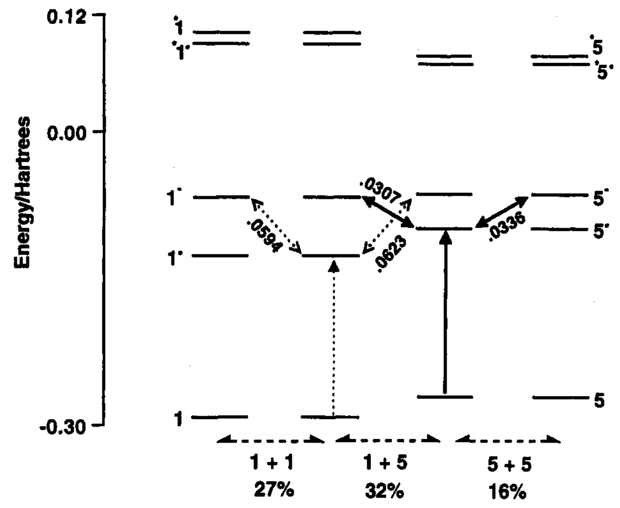

Figure 3. Orbital interactions in the 1 + 5 reaction.

effect of CO_2Me also renders 4 more acidic than 1 so that the former compound will tend to form anion (4^-) in preference to the latter (1^-). Thus, 1 will prefer to be converted to the corresponding electrophilic radical while 4 will have a higher tendency to serve as a nucleophilic receptor. Since the preferred interaction will be between $1^\bullet$ and 4^-, it can be predicted that the cross-coupling 1 + 4 → 12 will be favored which, again, is in excellent agreement with the experiment (entry 2).

Figure 3 illustrates the situation when 1 + 5 coupling is attempted. Less energy is required to generate a radical species $5^\bullet$, whereas there is only a marginal difference in the HOMO energy levels of 1^- and 5^-. Hence, there will be no preference for the radical $5^\bullet$ in selecting a suitable partner. As a result, one statistically predicts the formation of the cross- and self-coupled products which is in consonance with experiment (entry 3).[27]

The 2 + 4 combination is shown in Figure 4. In this case, the radical $2^\bullet$ is more likely to be generated in preference to $4^\bullet$ (Table 3). The most stabilizing interaction will originate from mixing the SOMO of $2^\bullet$ and HOMO of 4^- so that a high proportion of cross-coupling can be expected. This is, again, in a very good agreement with the experimental observation (entry 4).

The overall picture of the 2 + 5 combination (Figure 5) is partly distorted by the high proportion of carbazoles being formed as byproducts. The orbital energies and E_p values (Table 3) suggest that both radicals $2^\bullet$ and $5^\bullet$ will require approximately the same energy for their formation. While $2^\bullet$ should favor cross-coupling, $5^\bullet$ will prefer self-coupling. This seems to be partly in conflict with the experimental observation (entry 5) which suggests that self-coupling of 2 is the main reaction pathway. However, if the two carbazoles are taken into account (21 arising from self-coupling of 5 and 22 being formed by cross-coupling), we obtain ca. a 1:1:1 ratio of the three processes which is in a reasonable agreement with the prediction.

Finally, when 4 and 5 are combined (Figure 6), the HOMO and E_p values (Table 3) suggest that $5^\bullet$ will be generated preferentially and will reach best stabilization by interacting with 4^-. Comparing this analysis with the experiment (entry 8) shows, again, an excellent agreement, the cross-coupled binaphthyl 18 being the main product.

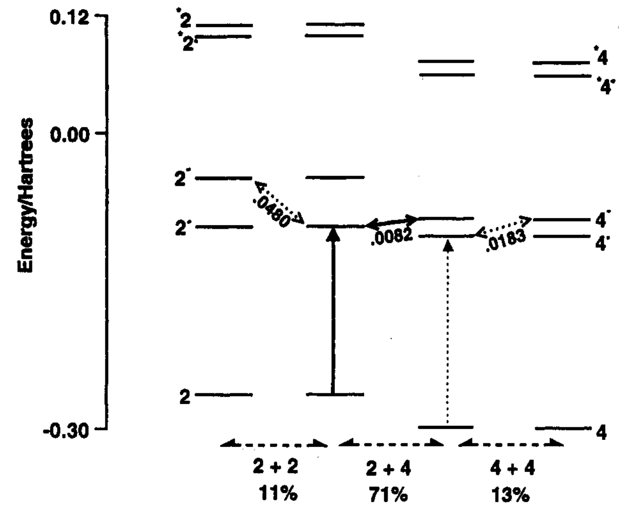

Figure 4. Orbital interactions in the 2 + 4 reaction.

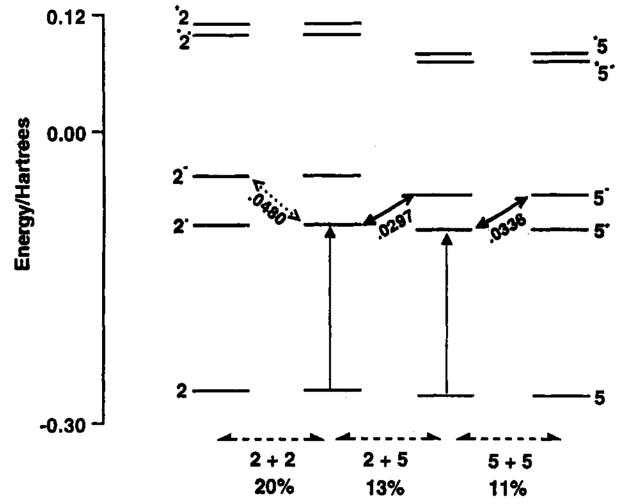

Figure 5. Orbital interactions in the 2 + 5 reaction.

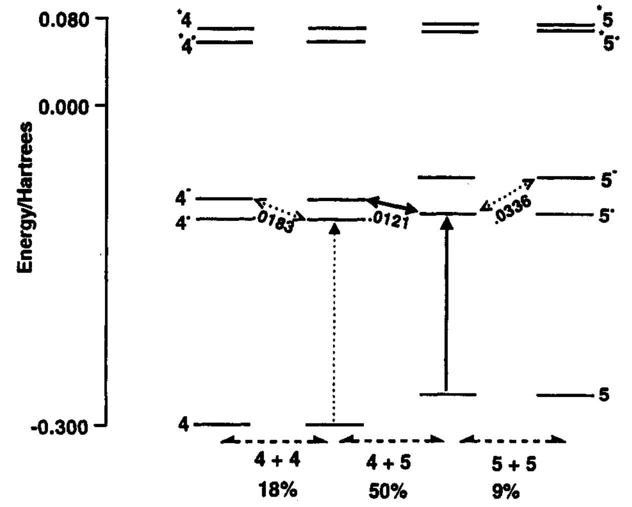

Figure 6. Orbital interactions in the 4 + 5 reaction.

In summary, the analysis of orbital energies and electrochemical data predicts a high proportion of cross-coupled products for the following combinations: 1 + 2, 1 + 4, 2 + 4, and 4 + 5. By contrast, little selectivity can be expected for 1 + 5 and 2 + 5 couplings. Although this analysis has to be considered with caution since the data have been obtained for processes not identical to the Cu-

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[27] Since the carbazole 21 (12%) also arises from the 5 + 5 coupling, the total of the self-coupling of 5 amounts to 28%, which is roughly equal to the extent of cross-coupling (32%).

Table 4. HOMO Coefficients at the Naphthalene Nucleus of 1, $1^{\bullet}$, 1^{-}, 2, $2^{\bullet}$, and 2^{-}

	species					
position	1	$1^{\bullet}$	1^{-}	2	$2^{\bullet}$	2^{-}
1	−0.30	−0.16	−0.40	−0.31	−0.18	−0.40
2	−0.20	−0.06	−0.04	−0.21	−0.05	0.01
3	0.06	−0.09	−0.19	−0.04	−0.10	−0.18
4	0.20	−0.03	0.06	0.16	0.09	0.01
5	−0.22	−0.01	−0.03	−0.16	−0.01	−0.01
6	−0.24	−0.05	−0.27	−0.24	−0.06	−0.27
7	0.09	0.00	−0.01	0.04	−0.01	0.00
8	0.24	0.05	0.20	0.21	0.05	0.21
9	0.09	0.03	0.02	0.10	0.03	0.01
10	0.10	0.07	0.27	0.18	0.09	0.27
X[a]	0.19	0.58	0.33	0.32	0.60	0.38

[a] Key: 1, X = OH; $1^{\bullet}$, X = $O^{\bullet}$; 1^{-}, X = O^{-}; 2, X = NH_2; $2^{\bullet}$, X = $^{\bullet}NH$; 2^{-}, X = ^{-}NH.

(II)-mediated coupling, the experimental results are in remarkably good agreement with the predictions.

It can be argued that anionic species (as partners for the radicals) will be rare in the reaction mixture, particularly in the case of amines. However, the coupling presumably occurs in the coordination sphere of copper, which may modify the character of the reactants. The present analysis suggests that the behavior of the reacting partners (coordinated to Cu) may be approximated by that of a radical and of an anion; the HOMO energies of X^- apparently reflect the capability of the molecules to serve as nucleophilic acceptors.[28] Although a detailed calculation at the level of Cu complexes cannot be carried out at present, we believe that our simple analysis has been done at the level sufficient for qualitative predicting which pairs of substrates will be suitable for cross-coupling and for which combinations low selectivity can be anticipated.

In cases when the less reactive amino derivatives 3 or 5 were used as partners for coupling, substantial amounts of dibenzocarbazoles (both symmetric and nonsymmetric) have been identified as byproducts (Table 1, entries 3, 5, 7, and 10). Although the mechanism of their formation is not quite clear, blank experiments showed that the carbazoles are not produced by secondary reactions from the binaphthyls. It appears that the corresponding radicals generated from 3 or 5 tend to couple differently as compared with the radicals derived from other naphthalene derivatives.[29] As a result, two different reaction pathways can be discerned for aminonaphthalene derivatives 3 and 5: one leading to binaphthyls and another that produces carbazoles. These two pathways may have a common intermediate, but further investigation is needed before a more detailed mechanism can be proposed.

The orbital coefficients for the carbons of the aromatic nucleus of 1, 2, 4, and 5 (Tables 4 and 5) reach the highest (absolute) values at C(1); other positions have considerably lower values. This is in agreement with the remarkably high C(1) regioselectivity of the coupling observed throughout this series and with other naphthalene derivatives.

Conclusions

The 1,1′-binaphthyls with OH and/or NHR (R = H or Ph) groups in the 2,2′-positions with additional methoxycarbonyl group(s) in the 3- or 3,3′-positions (**13–18**) have been synthesized from their respective precursors **1–5** by the $CuCl_2/t\text{-}BuNH_2$-mediated oxidative cross-coupling. Carbazoles **19–23** have been identified as byproducts. The tendency for selective cross-coupling is highest for the following combinations: **1** + **2** → **11** (85%), **1** + **4** → **12** (81%), **2** + **4** → **14** (71%), and **4** + **5** → **18** (50%). A lower proportion of the cross-coupled product has been observed for the **3** + **4** → **16** (40%) reaction,[30] whereas the **1** + **5**, **2** + **5**, and **3** + **5** mixtures exhibit no preference for the cross-coupling. The ready availability of the cross-coupled products **11**, **12**, **14**, **16**, and **18** has the promise that this series may be employed as a novel class of ligands for a variety of metal-mediated synthetic reactions.

Table 5. HOMO Coefficients at the Naphthalene Nucleus of 4, $4^{\bullet}$, 4^{-}, 5, $5^{\bullet}$, and 5^{-}

	species					
position	4	$4^{\bullet}$	4^{-}	5	$5^{\bullet}$	5^{-}
1	−0.30	−0.55	−0.38	−0.32	−0.18	−0.38
2	−0.19	−0.02	−0.01	−0.18	−0.04	−0.05
3	0.05	−0.06	−0.23	−0.06	−0.10	−0.24
4	0.17	0.06	0.12	0.17	0.03	0.08
5	−0.21	−0.04	−0.06	−0.16	−0.01	−0.04
6	−0.24	−0.14	−0.26	−0.24	−0.06	−0.26
7	0.09	0.01	0.05	0.05	0.00	0.04
8	0.21	0.16	0.19	0.21	0.05	0.19
9	0.09	0.05	−0.02	0.07	0.02	−0.04
10	0.11	0.16	0.28	0.18	0.08	0.29
X[a]	0.19	0.27	0.30	0.32	0.57	0.35

[a] Key: 4, X = OH; $4^{\bullet}$, X = $O^{\bullet}$; 4^{-}, X = O^{-}; 5, X = NH_2; $5^{\bullet}$, X = $^{\bullet}NH$; 5^{-}, X = ^{-}NH.

Frontier orbital theory and electrochemical measurements have been employed to account for the observed selectivity. It has been suggested that **4** acts as an acceptor molecule on reaction with radicals generated from the more readily oxidized molecules **1**, **2**, **3**, and **5**. The lower propensity of **4** to generate a radical species can be attributed to the higher oxidation potential (as compared to other reaction partners) due to the electron-withdrawing effect of the CO_2Me group. By contrast, **1** serves as a source of a radical in reaction with **4** and as an acceptor molecule for a radical generated from **2**. A marginal difference in the energy required to generate a radical from **2** and **5** results in approximately equal population of all competing processes in this coupling reaction. These findings appear to have a predictive value for the cross-coupling reactions: in summary, to obtain a high proportion of cross-coupling, one partner must be relatively easily oxidized to an electrophilic radical (e.g., **2**) while the acceptor molecule should be capable of electron donation (preferably in an anionic form, e.g., 4^-) with the HOMO close in energy to the SOMO of the radical. Although the mechanism is more complex and the coupling probably occurs in the coordination sphere of copper, it seems that the basic properties of the reaction partners can be approximated by the frontier orbital theory assuming interactions between electrophilic radicals and anionic acceptors.

Experimental Section

Materials and Equipment. Melting points (uncorrected) were obtained on a Boetius microapparatus. ^1H NMR spectra were recorded on Bruker 400 AT (FT mode) instrument for $CDCl_3$

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(28) Moreover, 4 is the most acidic derivative of our series. Thus, at least with 4 (and 1 as well) existence of the corresponding anion as an acceptor of the more readily formed (electrophilic) radical is not unreasonable.

(29) If a similar reaction operated for hydroxynaphthalenes, formation of the corresponding dinaphthofuranes should be observed which, however, was not the case.

(30) Although the isolated yield in this case is relatively low, the crystallinity of 16 allows an extremely easy isolation so that even this compound can be prepared in a satisfactory way.

solutions at 25 °C with TMS as internal reference. The high-resolution mass spectra were measured on a JEOL JMS D-100 double-focusing spectrometer (70 eV, 3 kV) using direct inlet and the lowest temperature enabling evaporation; the accuracy of m/z measurements was ≤5 ppm. GCMS spectra were recorded on INCOS 50, Finnigan MAT (70 eV) coupled with GC Varian 3400; injection temperature was 250 °C; column temperature 150 °C/1 min, gradient 150 → 300 °C at 10 °C/min, then 300 °C isothermal; capillary column DB-5, J&W (methylphenylsilicon, 30 m × 0.32 mm, film thickness 0.25 μm) with He as a carrier gas. The IR spectra were recorded in chloroform on a Perkin-Elmer 490 instrument. UV spectra were measured in ethanol on Specord 80. All the solvents used for the coupling reactions or for crystallization experiments were degassed by purging with argon (20 min; 60 mL of Ar/min). Light petroleum refers to the fraction boiling in the range 40–60 °C. Yields are given in mg of isolated product showing one spot on a chromatographic plate and no impurities detectable in the NMR spectrum. Methyl 3-hydroxy-2-naphthoate (**4**) was prepared by esterification of the corresponding acid[19] (Fluka), and methyl 3-amino-2-naphthoate (**5**) was prepared from 3-hydroxy-2-naphthoic acid via Bucherer transformation[31] followed by diazomethane esterification;[32] **1** and **2** were purchased from Lachema. The oxidation potentials of the naphthalene derivatives **1**, **2**, **4**, and **5** on platinum electrode were obtained using cyclic voltametry. The oxidation processes listed in Table 3 were all totally irreversible, and thus, the values for the peak potential E_p are given. The experiments were run at 25 °C at 5 mM concentrations in 0.1 M Me_4NBF_4 methanolic solutions, which were deoxygenated by purging with nitrogen for 20 min prior to use. The potentials were applied using an EG&G Model 173 potentiostat, which was controlled by an EG&G program controller. The potential sweep rate was 10 mV s^{-1}.

General Procedure for the Coupling. Into a stirred solution of $CuCl_2\cdot 4H_2O$ (600 mg, 3 mmol) in degassed methanol (5 mL) was added a solution of *tert*-butylamine (876 mg, 12 mmol) in methanol (5 mL). After 10 min, a solution of the two edducts (1 mmol each) in methanol (10 mL) was added, and the reaction mixture was stirred at room temperature under an argon atmosphere for 48 h (or longer; see Table 1). The mixture was first acidified with concd HCl (5 mL) and stirred for 5 min and then treated with concd ammonia (10 mL) for another 5 min and finally diluted with water (100 mL). The resulting suspension was extracted with $CHCl_3$ (three 20-mL portions), and the organic extract was dried with Na_2SO_4 and evaporated. The residue was analyzed by GC and chromatographed on silica (50 g) using toluene as eluent. The yields are given in Table 1.

2,2′-Bis(*N*-phenylamino)-1,1′-binaphthyl (8): mp 167–168 °C (benzene) (lit.[18b] mp 167.5–168 °C); ^{1}H NMR δ 5.59 (s, 2 H, two NH), 6.91 (t, $J_{3''\text{-H},4''\text{-H}}$ = 7.4 Hz, 2 H, 4″- and 4‴-H), 6.94 (br dd, $J_{7\text{-H},8\text{-H}}$ = 8.3 Hz, $J_{6\text{-H},8\text{-H}}$ = 1.1 Hz, 2 H, 8-H and 8′-H), 6.94 (d, $J_{2''\text{-H},3''\text{-H}}$ = 8.4 Hz, 4 H, 2″-H, 6″-H, 2‴-H, and 6‴-H), 7.15 (br dd, $J_{2''\text{-H},3''\text{-H}}$ = 8.4 Hz, $J_{3''\text{-H},4''\text{-H}}$ = 7.4 Hz, 4 H, 3″-H, 5″-H, 3‴-H, and 5‴-H), 7.23 (ddd, $J_{6\text{-H},7\text{-H}}$ = 7.0 Hz, $J_{7\text{-H},8\text{-H}}$ = 8.3, $J_{5\text{-H},7\text{-H}}$ = 1.3 Hz, 2 H, 7-H and 7′-H), 7.30 (ddd, $J_{5\text{-H},6\text{-H}}$ = 7.9 Hz, $J_{6\text{-H},7\text{-H}}$ = 7.0 Hz, $J_{6\text{-H},8\text{-H}}$ = 1.1 Hz, 2 H, 6-H and 6′-H), 7.67 and 7.87 (two d, $J_{3\text{-H},4\text{-H}}$ = 9.0 Hz, 2 × 2 H, 3-H, 3′-H, 4-H, and 4′-H), 7.83 (br dd, $J_{5\text{-H},6\text{-H}}$ = 7.9 Hz, $J_{5\text{-H},7\text{-H}}$ = 1.3 Hz, 2 H, 5-H and 5′-H); IR 1595 and 1619 (C═C arom.), 3399 (NH) cm^{-1}; UV λ (ε) 223 (78 900), 248 (37 000), 275 (48 000), 305 (38 900) nm; HRMS m/z 436 (100, $C_{32}H_{24}N_2$), 344 (78, $C_{26}H_{18}N$), 343 (42, $C_{26}H_{17}N$), 267 (19), 266 (13), 239 (6) 218 (13), 179 (8). Anal. Calcd for $C_{32}H_{24}N_2$: C, 88.07; H, 5.50; N, 6.42. Found: C, 88.19; H, 5.62; N, 6.33.

3,3′-Bis(methoxycarbonyl)-2,2′-diamino-1,1′-binaphthyl (10): mp 233–236 °C (toluene); ^{1}H NMR δ 3.99 (s, 6 H, two OCH_3), 5.60 (bs, 4 H, two NH_2), 6.95 (dd, $J_{7\text{-H},8\text{-H}}$ = 7.8 Hz, $J_{6\text{-H},8\text{-H}}$ = 1.6 Hz, 2 H, 8-H and 8′-H), 7.17–7.27 (m, 4 H, 6-H, 6′-H, 7-H, and 7′-H), 7.83 (dd, $J_{5\text{-H},6\text{-H}}$ = 8.2 Hz, $J_{5\text{-H},7\text{-H}}$ = 1.2 Hz, 2 H, 5-H and 5′-H), 8.70 (s, 2 H, 4-H and 4′-H); IR 1597 and 1621 (C═C arom), 1696 (C═O), 3378 and 3491 (NH_2) cm^{-1}; UV λ (ε) 228 (52 000), 254 (91 500), 282 (11 800), 292 (11 200), 410 (7000) nm; HRMS m/z 400 (100, $C_{24}H_{20}N_2O_4$), 383 (20, $C_{24}H_{17}NO_4$), 351 (11, $C_{23}H_{13}NO_3$), 340 (8, $C_{22}H_{16}N_2O_2$), 308 (19, $C_{21}H_{12}N_2O$), 293 (11), 280 (21, $C_{20}H_{12}N_2$), 279 (31, $C_{20}H_{11}N_2$), 264 (15, $C_{20}H_{10}N$), 140 (31, $C_{20}H_{12}N_2^{2+}$), 126 (13, $C_{19}H_{10}N^{2+}$), 113 (16). Anal. Calcd for $C_{24}H_{20}N_2O_4$: C, 72.00; H, 5.00; N, 7.00. Found: C, 71.86; H, 5.14; N, 6.91.

2-Amino-3-(methoxycarbonyl)-2′-hydroxy-1,1′-binaphthyl (13): mp 168–170 °C (*n*-heptane); ^{1}H NMR δ 3.97 (s, 3 H, OCH_3), 5.14 (s, 1 H, OH), 5.61 (bs, 2 H, NH_2), 6.95 (dd, $J_{7\text{-H},8\text{-H}}$ = 8.0 Hz, $J_{6\text{-H},8\text{-H}}$ = 2.0 Hz, 1 H, 8-H), 7.13 (dd, $J_{7'\text{-H},8'\text{-H}}$ = 8.0 Hz, $J_{6'\text{-H},8'\text{-H}}$ = 2.0 Hz, 1 H, 8′-H), 7.22 (ddd, $J_{5\text{-H},6\text{-H}}$ = 8.0 Hz, $J_{6\text{-H},7\text{-H}}$ = 6.7 Hz, $J_{6\text{-H},8\text{-H}}$ = 2.0 Hz, 1 H, 6-H), 7.24–7.30 (m, 2 H, 7-H and 6′-H), 7.35 (ddd, $J_{5'\text{-H},7'\text{-H}}$ = 1.0 Hz, $J_{6'\text{-H},7'\text{-H}}$ = 6.7 Hz, $J_{7'\text{-H},8'\text{-H}}$ = 8.0 Hz, 1 H, 7′-H), 7.39 and 7.94 (two d, $J_{3'\text{-H},4'\text{-H}}$ = 8.9 Hz, 2 × 1 H, 3′-H and 4′-H), 7.84 (dd, $J_{5\text{-H},6\text{-H}}$ = 8.0 Hz, $J_{5\text{-H},7\text{-H}}$ = 1.0 Hz, 1 H, 5-H), 7.88 (dd, $J_{5'\text{-H},6'\text{-H}}$ = 8.0 Hz, $J_{5'\text{-H},7'\text{-H}}$ = 1.0 Hz, 1 H, 5′-H) 8.73 (s, 1 H, 4-H); IR 1599 and 1622 (C═C arom), 1699 (C═O), 3381 and 3503 (NH_2), 3518 (OH) cm^{-1}; UV λ (ε) 228 (95 000), 256 (53 200), 286 (10 600), 334 (3400), 402 (3800) nm; HRMS m/z 343 (100, $C_{22}H_{17}NO_3$), 326 (13, $C_{22}H_{14}O_3$), 311 (10, $C_{21}H_{13}NO_2$), 283 (44, $C_{20}H_{13}NO$), 270 (21, $C_{19}H_{12}NO$), 268 (27, $C_{20}H_{12}O$), 254 (21, $C_{19}H_{12}N$), 239 (13, $C_{19}H_{11}$), 226 (9, $C_{18}H_{10}$), 127 (19, $C_{19}H_{12}N^{2+}$), 113 (23, $C_{18}H_{10}^{2+}$). Anal. Calcd for $C_{22}H_{17}NO_3$: C, 76.97; H, 4.96; N, 4.08. Found: C, 76.71, H, 4.96; N, 3.88.

2-Amino-2′-hydroxy-3′-(methoxycarbonyl)-1,1′-binaphthyl (14): mp 216–218 °C (toluene), corresponds to the product of thermal rearrangement;[33] ^{1}H NMR δ 3.30 (bs, 2 H, NH_2), 4.06 (s, 3 H, OCH_3), 6.95–7.03 (m, 1 H, 8-H), 7.10–7.26 (m, 4 H, 3-H, 6-H, 7-H, and 8′-H), 7.32–7.38 (m, 2 H, 6′-H and 7′-H), 7.76–7.85 (m, 2 H, 4-H and 5-H), 7.88–7.96 (m, 1 H, 5′-H), 8.69 (s, 1 H, 4′-H), 10.70 (bs, 1 H, OH); IR 1611 and 1622 (C═C arom), 1681 (C═O), 3228 (OH), 3393 and 3452 (NH) cm^{-1}; UV λ (ε) 240 (101 200), 286 (12 500), 364 (4900) nm; HRMS (corresponding to the thermally rearranged product[33]) m/z 343 (100, $C_{22}H_{17}NO_3$), 297 (43, $C_{21}H_{15}NO$), 280 (34, $C_{21}H_{14}N$), 268 (80, $C_{20}H_{14}N$), 254 (22, $C_{19}H_{12}N$), 239 (20, $C_{19}H_{11}$), 226 (15), 113 (27, $C_{18}H_{10}^{2+}$). Anal. Calcd for $C_{22}H_{17}NO_3$: C, 76.97; H, 4.96; N, 4.08. Found: C, 76.75; H, 5.00; N, 3.88.

2,2′-Diamino-3-(methoxycarbonyl)-1,1′-binaphthyl (15): mp 187–190 °C (toluene); ^{1}H NMR δ 3.70 (bs, 2 H, NH_2'), 5.50 (bs, 2 H, NH_2), 3.98 (s, 3 H, OCH_3), 6.95–7.10 (m, 2 H, 8-H and 8′-H), 7.15–7.30 (m, 4 H, 6-H, 6′-H, 7-H, and 7′-H), 7.15 and 7.82 (two d, $J_{3'\text{-H},4'\text{-H}}$ = 8.6 Hz, 2 × 1 H, 3′-H and 4′-H), 7.75–7.85 (m, 2 H, 5-H and 5′-H), 8.68 (s, 1 H, 4-H); IR 1597 and 1621 (C═C arom), 1697 (C═O), 3382 and 3488 (NH) cm^{-1}; UV λ (ε) 242 (82 700), 282 (13 400), 292 (10 900), 346 (3300), 404 (3900) nm; HRMS m/z 342 (100, $C_{22}H_{18}N_2O_2$), 325 (6), 293 (14, $C_{11}H_{11}NO$), 282 (39, $C_{20}H_{14}N_2$), 281 (19), 266 (18), 265 (19), 264 (23, $C_{20}H_{10}N$), 140 (29), 132 (17). Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.99; H, 5.46; N, 8.24.

2-Hydroxy-3-(methoxycarbonyl)-2′-(*N*-phenylamino)-1,1′-binaphthyl (16): mp 188–191 °C (toluene); ^{1}H NMR δ 4.07 (s, 3 H, OCH_3), 5.50 (s, 1 H, NH), 6.89 (t, $J_{3''\text{-H},4''\text{-H}}$ = 7.4 Hz, 1 H, 4″-H), 7.00 (d, $J_{2''\text{-H},3''\text{-H}}$ = 8.4 Hz, 2 H, 2″-H and 6″-H), 7.02 (br dd, $J_{7'\text{-H},8'\text{-H}}$ = 8.2 Hz, $J_{6'\text{-H},8'\text{-H}}$ = 1.2 Hz; 1 H, 8′-H), 7.19 (dd, $J_{2''\text{-H},3''\text{-H}}$ = 8.4 Hz, $J_{3''\text{-H},4''\text{-H}}$ = 7.4 Hz, 2 H, 3″-H and 5″-H), 7.20 (ddd, $J_{7'\text{-H},8'\text{-H}}$ = 8.2 Hz, $J_{6'\text{-H},7'\text{-H}}$ = 6.9 Hz, $J_{5'\text{-H},7'\text{-H}}$ = 1.3 Hz, 1 H, 7′-H), 7.24 (m, 1 H, 8-H), 7.28 (ddd, $J_{5'\text{-H},6'\text{-H}}$ = 7.9 Hz, $J_{6'\text{-H},7'\text{-H}}$ = 6.9 Hz, $J_{6'\text{-H},8'\text{-H}}$ = 1.2 Hz, 1 H, 6′-H), 7.34 (m, 2 H, 6-H and 7-H), 7.69 and 7.87 (two d, $J_{3'\text{-H},4'\text{-H}}$ = 9.0 Hz, 2 × 1 H, 3′-H and 4′-H), 7.83 (dd, $J_{5'\text{-H},6'\text{-H}}$ = 7.9 Hz, $J_{5'\text{-H},7'\text{-H}}$ = 1.3 Hz, 1 H, 5′-H), 7.92 (m, 1 H, 5-H), 8.69 (s, 1 H, 4-H), 10.73 (s, 1 H, OH); IR 1595 and 1621 (C═C arom), 1682 (C═O), 3224 (OH), 3411 (NH) cm^{-1}; UV λ (ε) 223 (70 400), 243 (73 000), 275 (29 300), 291 (sh), 302 (24 300), 310 (sh), 357 (6700) nm; HRMS m/z 419 (100, $C_{28}H_{21}NO_3$), 387

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(31) Allen, C. F. H.; Bell, A. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 78.

(32) Obtained in good yield by stirring a suspension of 3-amino-2-naphthoic acid in ether with CH_2N_2 at rt for 1 h followed by chromatography on silica using petroleum ether–ether mixture (1:1) as eluent.

(33) The MS behavior revealed that, on heating, crystalline **14** is gradually rearranged to the isomeric 2-hydroxy-3-carboxy-2′-(methylamino)-1,1′-binaphthyl before it melts (heating at 150–160 °C for 1 h gives a quantitative conversion). Thus, both the mp and MS spectrum observed correspond to the rearranged product and not to **14**. This rearrangement has only been observed in the crystal of racemic **14** (in contrast, **14** is stable in refluxing xylene for 2 h) and occurs as a transfer of the methyl group between the two molecules of **14** due to the favorable arrangement in the crystalline lattice: Smrčina, M., Hanuš, V. et al., to be published.

(4), 370 (9, $C_{27}H_{16}NO$), 360 (11), 359 (34, $C_{26}H_{17}NO$), 358 (18), 343 (24, $C_{26}H_{17}N$), 330 (16, $C_{25}H_{16}N$), 267 (15), 239 (14). Anal. Calcd for $C_{28}H_{21}NO_3$: C, 80.20; H, 5.01; N, 3.34. Found: C, 80.31; H, 5.11; N, 3.20.

2-Amino-3-(methoxycarbonyl)-2′-(*N*-phenylamino)-1,1′-binaphthyl (17): mp 194–197 °C (toluene); ^1H NMR δ 3.99 (s, 3 H, OCH_3), 5.56 (s, 1 H, NH), 5.59 (bs, 2 H, NH_2), 6.94 (t, $J_{3''\text{-H},4''\text{-H}} = 7.3$ Hz, 1 H, 4″-H), 7.02 (d, $J_{2''\text{-H},3''\text{-H}} = 8.0$ Hz, 2 H, 2″-H and 6″-H), 7.02 (d, $J_{7'\text{-H},8'\text{-H}} = 8.0$ Hz, 1 H, 8′-H), 7.06 (d, $J_{7\text{-H},8\text{-H}} = 8.4$ Hz, 1 H, 8-H), 7.20 (m, $J_{6'\text{-H},7'\text{-H}} = 7.5$ Hz, $J_{7'\text{-H},8'\text{-H}} = 8.0$ Hz, 1 H, 7′-H), 7.20 (m, $J_{5\text{-H},6\text{-H}} = 8.0$ Hz, $J_{7\text{-H},8\text{-H}} = 8.4$ Hz, 2 × 1 H, 6-H and 7-H), 7.22 (m, $J_{2''\text{-H},3''\text{-H}} = 8.0$ Hz, $J_{3''\text{-H},4''\text{-H}} = 7.3$ Hz, 2 H, 3″-H and 5″-H), 7.30 (t, $J_{5'\text{-H},6'\text{-H}} = 7.5$ Hz, $J_{6'\text{-H},7'\text{-H}} = 7.5$ Hz, 1 H, 6′-H), 7.69 and 7.87 (two d, $J_{3'\text{-H},4'\text{-H}} = 9.0$ Hz, 2 × 1 H, 3′-H and 4′-H), 7.83 (two d, $J_{5\text{-H},6\text{-H}} = 8.0$ Hz, $J_{5'\text{-H},6'\text{-H}} = 7.5$ Hz, 2 × 1 H, 5-H and 5′-H), 8.70 (s, 1 H, 4-H); IR 1595 and 1620 (C═C arom), 1697 (C═O), 3380 and 3493 (NH) cm^{-1}; UV λ (ϵ) 224 (63 700), 256 (63 700), 296 (22 400), 308 (20 200) nm; HRMS *m/z* 418 (100, $C_{28}H_{22}N_2O_2$), 401 (6), 359 (10), 358 (32), 357 (10), 325 (6), 294 (12), 266 (17), 265 (12), 264 (15). Anal. Calcd for $C_{28}H_{22}N_2O_2$: C, 80.38; H, 5.26; N, 6.70. Found: C, 80.54; H, 5.45; N, 6.60.

2-Amino-2′-hydroxy-3,3′-bis(methoxycarbonyl)-1,1′-binaphthyl (18): mp 230–233 °C (toluene); ^1H NMR δ 3.98 (s, 3 H, OCH_3'), 4.06 (s, 3 H, OCH_3), 5.49 (s, 2 H, NH_2), 6.91 (dd, $J_{7'\text{-H},8'\text{-H}} = 7.7$ Hz, $J_{6'\text{-H},8'\text{-H}} = 1.5$ Hz, 1 H, 8′-H), 7.15–7.27 (m, 3 H, 6′-H, 7′-H, and 8-H), 7.33–7.40 (m, 2 H, 6-H and 7-H), 7.83 (dd, $J_{5'\text{-H},6'\text{-H}} = 8.1$ Hz, $J_{5'\text{-H},7'\text{-H}} = 0.9$ Hz, 1 H, 5′-H), 7.90–7.96 (m, 1 H, 5-H), 8.70 and 8.71 (two s, 2 × 1 H, 4-H and 4′-H), 10.70 (bs, 1 H, OH); IR 1599, 1624 (C═C arom), 1687 (C═O), 3215 (OH), 3379 and 3493 (NH) cm^{-1}; UV λ (ϵ) 224 (sh), 244 (81 000), 288 (11 800), 302 (sh), 388 (5400) nm; HRMS *m/z* 401 (100, $C_{24}H_{19}NO_5$), 383 (9, $C_{24}H_{17}NO_4$), 369 (14), 309 (15, $C_{21}H_{11}NO_2$), 295 (42, $C_{21}H_{11}O_2$), 281 (26, $C_{20}H_{11}NO$), 280 (15), 254 (17), 253 (22, $C_{19}H_{11}N$), 252 (15), 251 (14, $C_{19}H_9N$), 226 (13), 140.5 (20, $C_{20}H_{11}NO_2^{2+}$), 126 (20), 113 (40, $C_{18}H_{10}^{2+}$). Anal. Calcd for $C_{24}H_{19}NO_5$: C, 71.82; H, 4.74; N, 3.49. Found: C, 71.95; H, 4.95; N, 3.37.

Dibenzo[*c,d*]carbazole (19): mp 156–159 °C (lit.[34] gives 157 °C); HRMS *m/z* 267 (100, $C_{20}H_{13}N$).

***N*-Phenyldibenzo[*c,d*]carbazole (20):** mp 142.5–143 °C (benzene) (lit.[18b] mp 142.5–143 °C); HRMS *m/z* 343 (100, $C_{26}H_{17}N$).

1,8-Bis(methoxycarbonyl)dibenzo[*c,d*]carbazole (21): mp 255–257 °C (toluene); ^1H NMR δ 4.10 (s, 6 H, two OCH_3), 7.53 (t, $J = 7.4$ Hz, 2 H), 7.74 (t, $J = 7.3$ Hz, 2 H), 8.09 (d, $J = 8.0$ Hz, 2 H), 8.62 (s, 2 H, 4-H and 4′-H), 9.09 (d, $J = 8.5$ Hz, 2 H), 12.00 (bs, 1 H, NH); IR 1598 and 1618 (C═C arom), 1705 (C═O), 3437 (NH) cm^{-1}; UV λ (ϵ) 224 (61 700), 252 (23 400), 272 (sh), 282 (30 700), 292 (sh), 380 (12 300), 402 (14 800) nm; HRMS *m/z* 383 (100, $C_{24}H_{17}NO_4$), 351 (23), 308 (13, $C_{21}H_{10}NO_2$), 293 (29, $C_{21}H_{11}NO$), 265 (20), 264 (35, $C_{20}H_{10}N$), 160 (24, $C_{22}H_{10}NO_2^{2+}$), 132 (39, $C_{20}H_{10}N^{2+}$), 118.5 (21). Anal. Calcd for $C_{24}H_{17}NO_4$: C, 75.19; H, 4.44; N, 3.65. Found: C, 74.74; H, 4.58; N, 3.83.

1-(Methoxycarbonyl)dibenzo[*c,d*]carbazole (22): mp 176–179 °C (toluene); ^1H NMR δ 4.10 (s, 3 H, OCH_3), 7.47–7.60 (m, 2 H, 5-H and 5′-H), 7.63–7.83 (m, 2 H, 6-H and 6′-H), 7.75 and 7.91 (two d, $J = 8.5$ Hz, 2 × 1 H, 3′-H and 4′-H), 8.02–8.15 (m, 2 H, 7-H and 7′-H), 8.62 (s, 1 H, 4-H), 9.10–9.25 (2 H, 8-H and 8′-H), 10.70 (bs, 1 H, NH); IR 1618 (C═C arom), 1698 (C═O), 3437 (NH) cm^{-1}; UV λ (ϵ) 220 (64 600), 264 (33 300), 278 (39 300), 312 (sh), 368 (sh), 382 (13 500), 402 (sh) nm; HRMS *m/z* 325 (100, $C_{22}H_{15}NO_2$), 293 (66), 265 (50), 264 (78, $C_{20}H_{10}N$), 146.5 (14), 132.5 (44), 132 (14), 119 (17), 118.5 (25). Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.23; H, 4.61; N, 4.31. Found: C, 80.93; H, 4.76; N, 4.54.

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Supplementary Material Available: Frontier orbitals for the radical cations derived from **1**, **2**, **4**, and **5** (Table VI), the HOMO coefficients at the naphthalene nucleus for the radical cations derived from **1**, **2**, **4**, and **5** (Table VII), coordinates for the optimized geometries of **1**, **2**, **4**, and **5**, and cyclic voltamograms for the naphthalene derivatives **1**–**5** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(34) Meisenheimer, J.; Witte, K. *Chem. Ber.* **1903**, *36*, 4153.