2,8′-Disubstituted-1,1′-Binaphthyls: A New Pattern in Chiral Ligands

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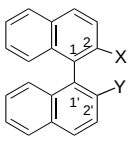
Dedicated to the memory of Professor Otakar Červinka

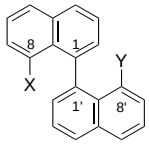
Abstract: The title binaphthyls **19** and **26**, which are the positional isomers of 2-methoxy-2′-(diphenylphosphino)-1,1′-binaphthyl (MOP, **19**) and 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN, **26**), have been synthesized by Suzuki coupling as the key step (**10** + **15** → **18**), followed by functional group transformations, involving C–P and C–N bond formation (**18** → **19** and **18** → **23**). Racemic intermediate **22** was resolved by co-crystallization with *N*-benzylcinchonidinium chloride and the absolute configuration determined by X-ray crystallography. These novel binaphthyls are configurationally stable and, as such, potentially usable as chiral ligands in asymmetric reactions. Michael addition of the glycine-derived enolate **40** to methyl acrylate, carried out in the presence of (*R*)-(−)-**27** as the chiral phase-transfer catalyst, afforded L-glutamic acid (*S*)-(+)-**43** of 92 % *ee* (after hydrolysis of the primary product).

Keywords: amination · binaphthyls · chirality · chiral resolution · Suzuki coupling

Introduction

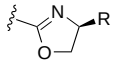
2,2′-Substituted 1,1′-binaphthyls (**1**)[1] have played a major role in the development of chiral catalysts for asymmetric synthesis. Whilst the classical first generation possessed identical substituents X and Y [e.g., 2,2′-dihydroxy-1,1′-binaphthyl (BINOL),[2] 2,2′-diamino-1,1′-binaphthyl (BINAM),[3] and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP);[4] **1a**–**1c**], new development is characterized by non-identical groups [e.g., 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN),[5, 6] 2-methoxy-2′-(diphenylphosphino)-1,1′-binaphthyl (MOP),[7] and 2-(*N*,*N*-dimethylamino)-2′-(diphenylphosphino)-1,1′-binaphthyl (MAP);[5m, 8] **1d**–**1f**].





1a, X = Y = OH
1b, X = Y = NH_2
1c, X = Y = PPh_2
1d, X = OH, Y = NH_2
1e, X = OMe, Y = PPh_2
1f, X = NMe_2, Y = PPh_2
1g, X = Y = H
1h, X = OH, Y = H
1i, X = OH, Y = NHCOMe

2a, X = Y = OH
2b, X = Y = OXZ
2c, X = Y = COOH
2d, X = Y = Me
2e, X = OMe, Y = PPh_2
2f, X = COOH, Y = H

OXZ = 

Further locations in the binaphthyl skeleton, available to accommodate the ligating groups, would be the 8,8′- and 2,8′-positions.[9] While the former pattern (**2**) has been synthesized[10] and shown to give high levels of asymmetric induction in selected cases,[11] the latter series (**3**; Scheme 1) remains

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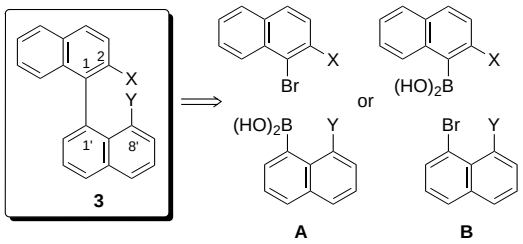
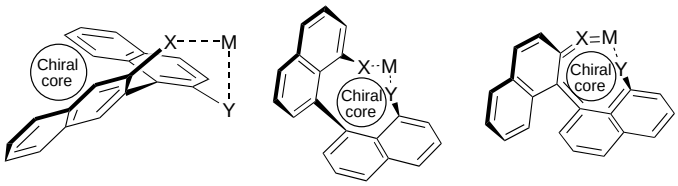


Scheme 1. Retrosynthetic analysis of **3**.

unexplored. Yet another molecular architecture encompasses a shift of the classical 1,1′-chiral axis into the 2,2′-position.[12] Although these VAPOL-type ligands (e.g. 2,2′-diphenyl-(3,3′-biphenanthrene)-4,4′-diol) require further substituents to prevent rotation about the chiral axis, this complication is compensated by excellent enantioselectivities attained in selected asymmetric reactions.[12]

The common feature of 1,1′-binaphthyls is the chiral axis between C-1 and C-1′, which creates a chiral cavity. However, when the coordinating atoms are located in the 2,2′-position, this molecular architecture fails to offer a chiral environment in the immediate vicinity of the reaction center (**1**/M), so that the high degree of enantioselection reported for these ligands has to be attributed to additional effects. Thus, for instance, in



Complex **1**/M Complex **2**/M Complex **3**/M

the case of BINAP (**1c**), the binaphthyl moiety serves merely as a chiral scaffold, which dictates the orientation of the Ph groups adjacent to the phosphorus atoms.[13] It is this relayed effect, which then controls the enantioselection of the catalytic reactions.[13] With these systems, the chiral environment at the reaction center can be further enhanced by additional, bulky groups in 3,3′-positions;[1, 14] however, this increases the synthetic complexity of the ligands. By contrast, binaphthyl complexes with ligating groups located at 8,8′- or 2,8′-positions (**2**/M[10, 11] or **3**/M) appear to offer a chiral environment directly created by the binaphthyl skeleton so that the binaphthyl moiety itself can be expected to exercise asymmetric control, which may have interesting implications in the level of asymmetric induction. The 8,8′-system (**2**/M) has recently been shown to behave along these lines,[10, 11] but the practicality of these ligands is somewhat hampered by their low configurational stability (as compared to the 2,2′-substituted binaphthyls).[11, 15] Herein, we report on the first synthesis of 2,8′-disubstituted-1,1′-binaphthyls (**3**; X = OMe, OH, Y = PPh_2, NH_2) and demonstrate their configurational stability.

Abstract in Czech: *2,8′-Disubstituované-1,1′-binaftyly, zejména polohové isomery MOPu (**19**) a NOBINu (**26**), byly syntetizovány s použitím Suzukiho reakce jako klíčového kroku (**10** + **15** → **18**), po němž následovala transformace funkčních skupin, zahrnující tvorbu C-P a C-N vazeb (**18** → **19** a **18** → **23**). Racemický meziprodukt **22** byl rozštěpen na enantiomery krystalizací s N-benzylcinchonidinium chloridem a jeho absolutní konfigurace byla stanovena pomocí rentgenostrukturní krystalografie. Tyto nové binaftyly jsou konfiguračně stabilní a tudíž potenciálně využitelné jako chirální ligandy v asymetrických reakcích. Michaelova adice enolátu **40**, odvozeného z glycinu, na methyl metakrylát, prováděná v přítomnosti (R)-(−)-**27** jako chirálního katalyzátoru fázového přenosu, poskytla* L*-glutamovou kyselinu (S)-(+)-**43** s 92 % ee (po hydrolýze primárního produktu).*

Results and Discussion

Construction of 2,8′-disubstituted 1,1′-binaphthyls by Suzuki coupling: The synthesis of the 2,8′-disubstituted 1,1′-binaphthyls **3** can be envisaged by the Suzuki[16] or related coupling (Scheme 1) as the key step to construct the 1,1′-bond. This approach would require two building blocks, namely a 1,2-disubstituted naphthalene and its 1,8-disubstituted partner. The substituents at the 1-position in each block would have to be suitable for the intended coupling, for example, a halogen and boron, with the choice of polarity (**A** or **B**). Availability of the starting materials appeared to favor the alternative **A**, since the naphthalene derivative with an electron-rich 2-substituent can be brominated at the 1-position (note that 1-bromo-2-naphthol is commercially available) and the synthesis of the boronic partner can be envisaged through the chelation-controlled deprotonation of a 1-substituted naphthalene in 8-position.

1-Methoxynaphthalene is known to be deprotonated by *n*BuLi at 2-position,[17–20] whereas *t*BuLi prefers the 8-position (though the conversion seems rather low and the primary product tends to equilibrate to the more thermodynamically stable 2-Li isomer).[20, 21] By contrast, 1-(dimethylamino)naphthalene (**4**) is selectively deprotonated at 8-position both with *n*BuLi and *t*BuLi.[21, 22] Therefore, we have first focused on **4** as a precursor.

Deprotonation of 1-(dimethylamino)naphthalene (**4**)[22] occurred at room temperature over a period of three days (Scheme 2) and was evidenced by a gradual precipitation of the yellow lithiated species, commencing about 18 – 24 hours after the setup of the reaction. The latter, in situ generated species was treated with $(MeO)_3B$ and the resulting borate was hydrolyzed under the standard acidic conditions (HCl) to afford the corresponding boronic acid **6** (44 %). However, the attempted Suzuki coupling of **6** with either 1-bromo-2-naphthol or its methyl ether **9** (vide infra), under a variety of conditions, was unsuccessful. Only the starting boronic acid and the dehalogenated 2-naphthol and 2-methoxynaphthalene were isolated after a prolonged reaction time. Apparently, this failure to react is associated with the B – N interaction (acid – base), evidenced by ^{11}B NMR spectroscopy, which showed the boron signal in **6** at $\delta = 10.56$ ppm, that is,

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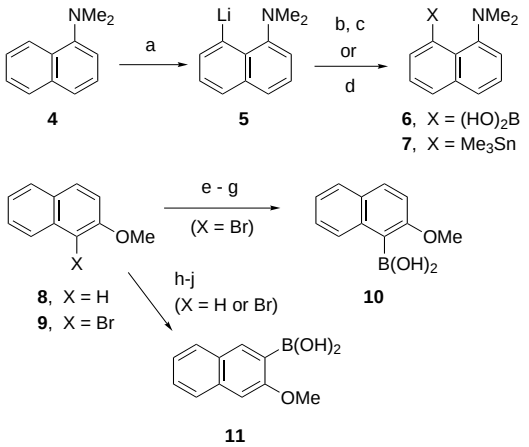
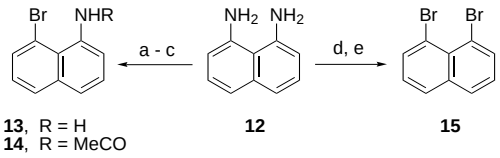


Scheme 2. a) *n*BuLi, Et_2O, RT, 3 d; b) $(MeO)_3B$, RT, overnight; c) HCl, H_2O, RT, 2 h, 44% overall; d) Me_3SnCl, RT, overnight, 53%; e) from **9**, Mg, THF, 30 min; f) $(iPrO)_3B$ (1.5 equiv), −78 °C, 1 h, then RT, 12 h; g) HCl, H_2O, RT, 30 min, 67% overall; h) from **9**, *n*BuLi, THF, −78 °C, 2 h; i) $(iPrO)_3B$, −78 °C to RT, 18 h; j) dil. HCl, RT, 30 min.

~8 ppm upfield relative to other boronic acids, such as $PhB(OH)_2$, whose ^{11}B signal appears at $\delta = 2.36$ ppm.[23, 24] Attempted Stille coupling of **9** with the tin analogue **7**,[25] obtained on quenching of the organolithium derivative **5** with Me_3SnCl, proved equally unsuccessful.

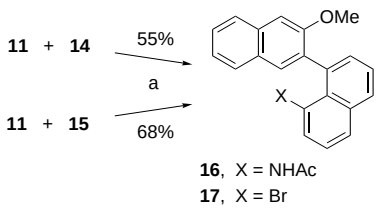
Since strategy **A** (Scheme 1) failed, we turned to the partners with swapped polarity (**B**). To this end, boronic acid[26] **10** was prepared as the nucleophilic partner from 1-bromo-2-methoxynaphthalene (**9**) from the corresponding Grignard reagent[26–28] (Scheme 2) and borate ester.[27] It is pertinent to note that **10** cannot be prepared directly from 2-methoxynaphthalene (**8**) through *ortho*-directed metallation or from **9** by lithiation, since these routes lead to the "wrong" boronic acid **11**.[29]

As an electrophilic partner, 1-amino-8-bromonaphthalene[30] (**13**) was synthesized from the commercially available 1,8-diamine **12** by the Sandmeyer reaction (Scheme 3). However, the attempted coupling of **13** with boronic acid **10**[27] also failed.



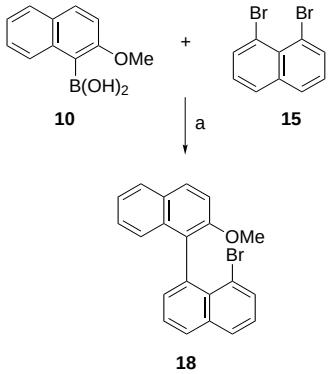
Scheme 3. a) $NaNO_2$ (1 equiv), HCl, −5 °C, 2 h, 10 °C, 18 h; b) HBr (excess), Cu bronze (0.66 equiv), 60 °C; 27%; c) Ac_2O, pyridine, 100 °C, 1 h, 80%; d) $NaNO_2$ (2.3 equiv), conc. H_2SO_4, 0 °C; e) HBr (excess), CuBr (1.3 equiv), RT; 25%.

Since the presence of an electron-rich substituent in the *peri*-position proved detrimental to the Suzuki coupling, we set out to explore the possibility of using a less Lewis basic group. To this end, bromoacetamide[31] **14** was prepared by acetylation of **13** and subjected to the coupling with **10**, but, again, was found to be inert. On the other hand, amide **14** did couple with the isomeric boronic acid **11** (unlike the amine **13**, which was still inert) to produce 1,2′-binaphthyl **16** (Scheme 4).



Scheme 4. a) $[Pd(PPh_3)_4]$ (5 mol%), DME, H_2O, Na_2CO_3, reflux 18 h.

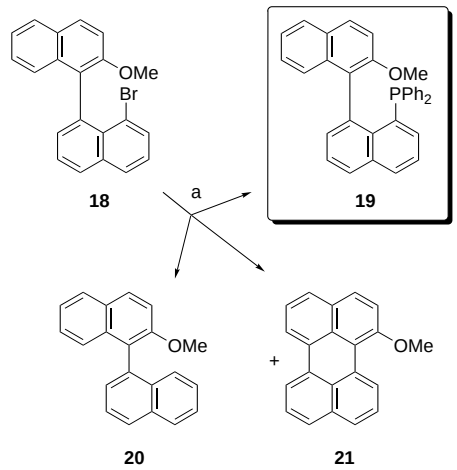
This last result suggested that, indeed, lowering the Lewis basicity of the neighboring group improved the reactivity in the 8-position. However, the reaction also required that steric hindrance be minimized, as in boronic acid **11**, which lacks the interference of the *peri*-hydrogen, characteristic of its isomer **10**. Apparently, the combined steric hindrance in **10** and **14** (particularly the *peri*-proton in **10**) is prohibitive. Since the steric architecture of the boronic acid cannot be altered (boron must be located in 1-position), any alteration can only be attempted in the electrophilic partner. Therefore, 1,8-dibromide[32] **15** was prepared from diamine **12** by a double Sandmeyer-type transformation and subjected to the coupling with **10**. On this occasion, the Suzuki reaction was successful (Scheme 5), affording the desired 1,1′-binaphthyl **18** (76%), whose structure was confirmed by X-ray crystallography (vide infra). However, a fair amount of optimization was required here; the highest yield (76%) of the desired product was obtained when the coupling was carried out with $[Pd(Ph_3P)_4]$ as the catalyst (3.5–5 mol%) and K_2CO_3 as a base in a 2:1 DME/H_2O mixture at reflux temperature for 24 hours.[33]



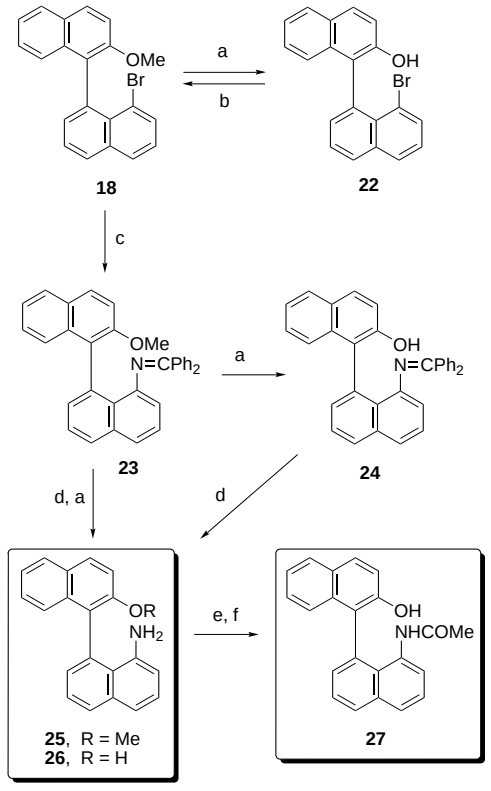
Scheme 5. a) $[Pd(PPh_3)_4]$ (3.5–5.0 mol%), Na_2CO_3, DME, H_2O, reflux, 24 h; 76%.

A control experiment showed that, as expected, dibromide **15** also coupled with the isomeric boronic acid **11** to afford 1,2′-binaphthyl **17** (Scheme 4).

Substituent variation in 2,8′-disubstituted 1,1′-binaphthyls: We envisaged that the availability of bromide **18** would open the routes to methoxyphosphine **19**, which can be regarded as the 2,8′-isomer of MOP[7] (Scheme 6), and to amino alcohol **26**, an isomer of NOBIN[5, 6] (Scheme 7). Indeed, replacement of bromine in **18** with the PPh_2 group did occur as expected by using the Ager protocol,[34] affording **19**, though in a modest yield (32%), owing to the competing reduction to 2-meth-



Scheme 6. a) Ph_2PCl, Zn, DMF, $(dppe)NiCl_2$ (5 mol%), 105 °C, 48 h.

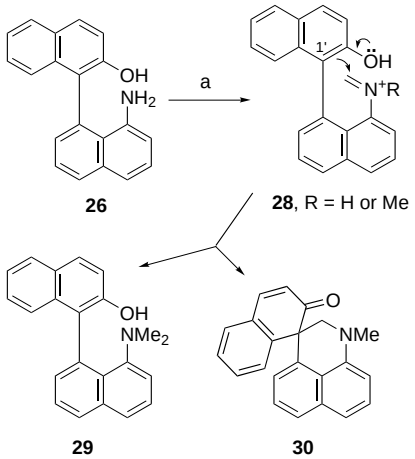


Scheme 7. a) BBr_3, CH_2Cl_2, RT, overnight; b) MeI, K_2CO_3, Me_2CO, reflux, 24 h, 97%; c) $Ph_2C{=}NH$, $[Pd(dba)_2]$, $(2\text{-}Ph_2P\text{-}C_6H_4)_2O$, *t*BuONa, toluene, 100 °C, 24 h; d) 35% aq HCl, CH_2Cl_2, RT, overnight; e) AcCl, C_5H_5N, CH_2Cl_2, RT, overnight; f) MeONa (cat.), MeOH, RT, overnight.

oxy-1,1′-binaphthyl (**20**, 6%)[35] and an insertion reaction resulting in the formation of 1-methoxyperylene (**21**, 26%),[36, 37] whose structure was proved by single-crystal X-ray analysis. Other attempts, such as the lithiation of **18** using *t*BuLi, followed by addition of Ph_2PCl,[8d] the Pd^0-catalyzed coupling of **18** with $Ph_2P(O)H$,[8a, 38] and the Ni^0-catalyzed coupling with Ph_2PH[34, 39] were entirely unsuccessful.

In the synthesis of *iso*-NOBIN (**26**), Hartwig–Buchwald amination[40] was employed as the key step (Scheme 7). Thus, following the protocol developed by Buchwald for an alternative synthesis of NOBIN,[40] methoxy bromide **18** was converted into imine **23** (97%). Interestingly, the analogous hydroxy bromide **22**, obtained on the BBr_3-mediated deprotection of **18** (96%), proved inert under the same conditions, demonstrating the importance of the protecting group. Hydrolysis of imine **23** afforded methoxy amine **25** (92%), whose deprotection with BBr_3 furnished the desired *iso*-NOBIN (**26**, 95%). Alternatively, oxygen deprotection of **23** resulted in the formation of hydroxy imine **24** (95%), demonstrating the stability of the imine functionality to Lewis acids in the absence of water; the structure of **24** was confirmed by X-ray crystallography (vide infra). Subsequent hydrolysis of **24** with Brønsted acid gave rise to **26** (89%), identical with the compound obtained from the first route. The overall yields of these two routes were practically identical. A two-step *N*-acetylation[5g] of **26** afforded acetamide **27** (94%).

The *N*,*N*-dimethylation of NOBIN (**1d**) by reductive amination with formaldehyde and $NaBH_4$ has been shown by us to occur uneventfully and with high yield.[5g,i] Interestingly, under the same conditions, *iso*-NOBIN (**26**) afforded a mixture (Scheme 8) of the expected dimethylamino derivative **29** (33%) and the *ipso*-product **30** (59%), whose structure was determined by the NMR spectroscopy with the full assignment of all protons and carbons. The spirocycle **30** apparently results from an electrophilic attack of the intermediate immonium ion **28** at C-1′.



Scheme 8. a) 35% aq CH_2O, $NaBH_4$, H_2SO_4, THF, RT, 15 min.

The electrophilic *ipso*-attack is not confined to this series. Thus, tosylate **31** is known to produce the tetrahydropyrane derivative **32** in alkaline medium rather than the expected eight-membered crown ether (Scheme 9).[41, 42] Similarly, MAP (**1f**) reacts with the electrophilic $PdCl_2$ to generate the five-membered P,C-chelate **33** rather than the seven-membered P,N-complex,[8c,g,h] and analogous results were reported for reactions of Pd^{II} with bisphenanthrol[43] and Pt^{II} with Me_2BINOL.[44]

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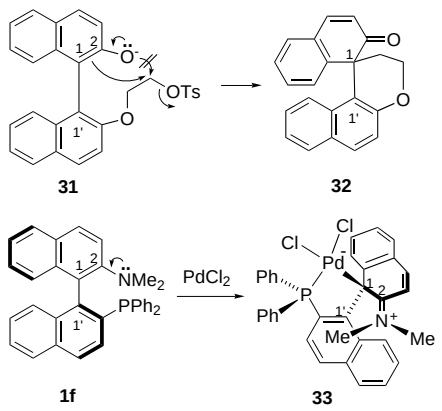
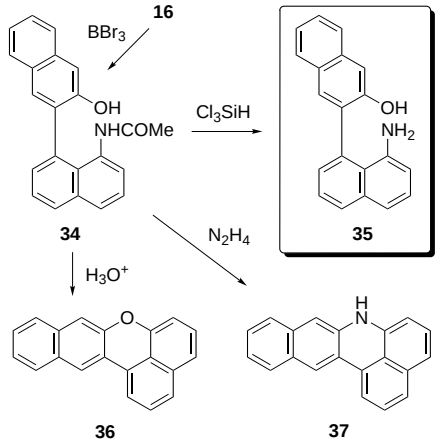


Scheme 9. Reaction scheme for the formation of compounds **32** and **33**.

Substituent variation in 8,3′-disubstituted 1,2′-binaphthyls: The straightforward synthesis of methoxy acetamide **16** by Suzuki coupling (Scheme 4) prompted us to establish a suitable deprotection of both heterosubstituents, aiming at the synthesis of another isomer of NOBIN. However, in contrast to the straightforward deprotection of **23**, this molecule proved to be more difficult to deal with. Thus, although the initial demethylation afforded the expected hydroxy acetamide **34** in 92% yield (Scheme 10), the subsequent attempt at hydrolysis of the *N*-acetyl group gave rise to dibenzoxanthene **36** (50%) as the only isolable product. Hydrazinolysis[45] of **34** was equally unsuccessful, furnishing dibenzoacridine **37** (78%). Finally, reaction of **34** with trichlorosilane produced the desired amino alcohol **35**, though in mere 16% yield.



Scheme 10. a) BBr_3, CH_2Cl_2, 0 °C, 14 h, 92%; b) aq. HCl, EtOH, reflux, 16 h, 50%; c) N_2H_4, amyl alcohol, reflux, 40 h, 78%; d) Cl_3SiH, Et_3N, xylene, 120 °C, 15 h, 16%.

Configurational stability of 2,2′- and 8,8′-disubstituted 1,1′-binaphthyls 1 and 2: Scalemic 2,2′-disubstituted 1,1′-binaphthyls are known to be configurationally more stable than their 8,8′-disubstituted counterparts. Selected data are summarized in Tables 1 and 2.

Interestingly, the 8,8′-disubstituted 1,1′-binaphthyls (**2**) with the substituents possessing an sp^2-hybridized carbon adjacent to the 8-position (and 8′) (Table 2, entries 1–3) appear to have the racemization barrier at the level of unsubstituted 1,1′-binaphthyl (Table 1, entry 6). By contrast, sp^3-substituents (Table 2, entries 4 and 6) increase the barrier by $\sim$6 kcal mol^{-1}.[11e]

Table 1. Racemization of selected 2,2′-disubstituted 1,1′-binaphthyls (**1**).

Entry	X	Y	T [°C]	Solvent	$\tau_{1/2(rac)}$ [min]	$\Delta G^{\ddagger}_{rac}$ [kcal mol^{-1}]	Ref.
1	CO_2H	CO_2H	208	tetralin	> 900	> 39.4	[46]
2	OH	OH	195	naphthalene	270	37.1	[41, 47]
3	NH_2	NH_2	220	caprolactam	240	38.7	[47]
4	I	I	315	caprolactam	77	45.5	[47]
5	OH	H	80	benzene	2600	29.4	[48]
6	H	H	40	benzene	102	24.0	[49]

Table 2. Racemization of selected 8,8′-disubstituted 1,1′-binaphthyls (**2**).

Entry	X	Y	T [°C]	Solvent	$\tau_{1/2(rac)}$ [min]	$\Delta G^{\ddagger}_{rac}$ [kcal mol^{-1}]	Ref.
1	CO_2H	CO_2H	50	DMF	51.5	24.4	[50]
2	CO_2Me	CO_2Me	50	DMF	23	23.8	[50]
3	CO_2H	CO_2Me	50	DMF	18.3	23.7	[51]
4	CH_2OH	CH_2OH	100	DMF	395	29.7	[51]
5	CO_2Me	CH_2OH	100	DMF	14.1	27.3	[51]
6	CH_3	CH_3	100	DMF	679	30.4	[51]
7	CO_2H	H	50	DMF	15.4	23.4	[50]
8	H	H	50	DMF	14.5	23.4	[50]

Configurational stability of 2,8′-disubstituted 1,1′-binaphthyls 18, 25, and 26 and 8,3′-disubstituted 1,2′-binaphthyls 16, 17, and 35: Racemic binaphthyl derivatives **16**, **17**, and **35** were resolved into enantiomers by means of analytical HPLC on Daicel Chiralpak AD; the quantities thus obtained were sufficient for the racemization experiments. Preparative resolution has been achieved for hydroxy bromide (±)-**22** (vide infra),[52, 53] from which enantiopure **18**, **25**, and **26** were synthesized (vide infra).

Racemization of the individual derivatives was monitored at the given temperature (Tables 3 and 4) by chiral HPLC. The racemization barriers were calculated from the rate constants by using Eyring equation.[54] The data obtained indicate that the 2,8′-disubstituted 1,1′-binaphthyls (Table 3) are sufficiently stable (as demonstrated for **18**, **25**, and **26**) to be employed as chiral ligands in asymmetric catalysis. Note that their barriers ($\sim$40 kcal mol^{-1}) are comparable with those reported for BINOL and other 2,2′-disubstituted binaphthyls (Table 1), which should allow their application in asymmetric catalysis at temperatures $\leq$150 °C.[15] By contrast, 1,2′-bi-

Table 3. Racemization of 2,8′-disubstituted 1,1′-binaphthyls **18**, **25**, and **26**.[a]

Entry	Compound	T [°C]	Solvent	k_{rac} [10^{-6} s^{-1}]	$\tau_{1/2(rac)}$ [min]	$\Delta G^{\ddagger}_{rac}$ [kcal mol^{-1}]
1	**18**	250	Ph_2O	59	200	41.3
2	**25**	225	Ph_2O	12	960	40.9
3	**26**[b]	190	Ph_2O	< 9.7	> 1200	> 38.1

[a] The accuracy of the measurement of $\Delta G^{\ddagger}_{rac}$ is ±0.2 kcal mol^{-1}. [b] Compound **26** undergoes gradual decomposition at high temperature, which precludes a more accurate measurement.

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Table 4. Racemization of 8,3′-disubstituted 1,2′-binaphthyls **16**, **17**, and **35**.[a]

Entry	Compound	T [°C]	Solvent	k_{rac} [10^{-6} s^{-1}]	$\tau_{1/2(rac)}$ [min]	$\Delta G^{\ddagger}_{rac}$ [kcal mol^{-1}]
1	**16**	22	DME	2.1	5400	24.8
2	**17**	22	DME	2.4	4800	24.8
3	**35**	20	DME	66	180	22.7
4	**35**	30	DME	300	38	22.7
5	**35**	40	DME	700	17	22.8

[a] The accuracy of the measurement of $\Delta G^{\ddagger}_{rac}$ is ± 0.1 kcal mol^{-1}.

naphthyls have their barriers around 23 kcal mol^{-1}, as shown for **16**, **17**, and **35** (Table 4), which is comparable with 8,8′-disubstituted-1,1′-binaphthyls with sp^2 substituents (Table 2, entries 1–3) and unsubstituted 1,1′-binaphthyl (Table 1, entry 6).

Quantum chemistry calculations, carried out for **18** (DFT-B3LYP with 6-31G** basis set), gave the racemization barrier of 39.2 kcal mol^{-1} (expressed as an energy difference between ground and transition state); the less accurate calculation (DFT-B3LYP at 6-31G level) gave 40.4 kcal mol^{-1}.[55] In both cases, the calculations are in an excellent agreement with the experimental value of $\Delta G^{\ddagger}_{rac}$ (41.3 kcal mol^{-1}; Table 3, entry 1).

Crystallographic characterization of racemic binaphthyls 18 and 24: A single-crystal X-ray analysis showed the bond lengths and angles in **18** (Figure 1) to be rather standard, with

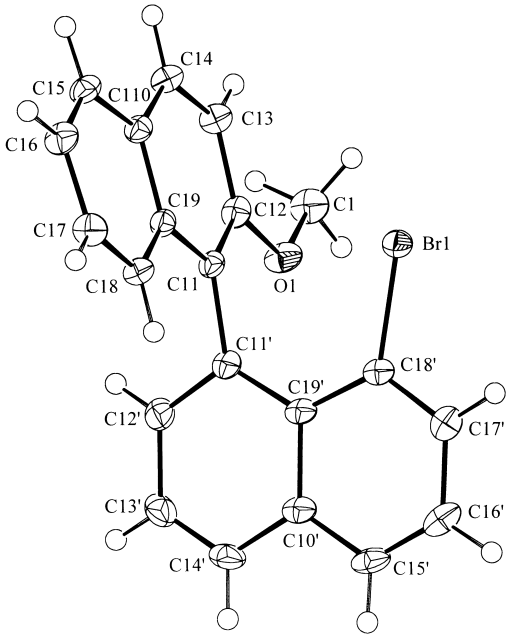

Figure 1. ORTEP diagram of (±)-**18** showing the atom labeling scheme. Displacement parameters are shown at the 50% probability level.

a notable deformation about the C–Br bond imposed by the bulky bromine atom that is repulsed by the naphthalene unit.[56] In both **18** and **24**, the two naphthalene units are almost perpendicular. Interesting characteristics were noted for imine **24** (Figure 2), in which one of the phenyl rings adjacent to the imine group is roughly parallel to the ring

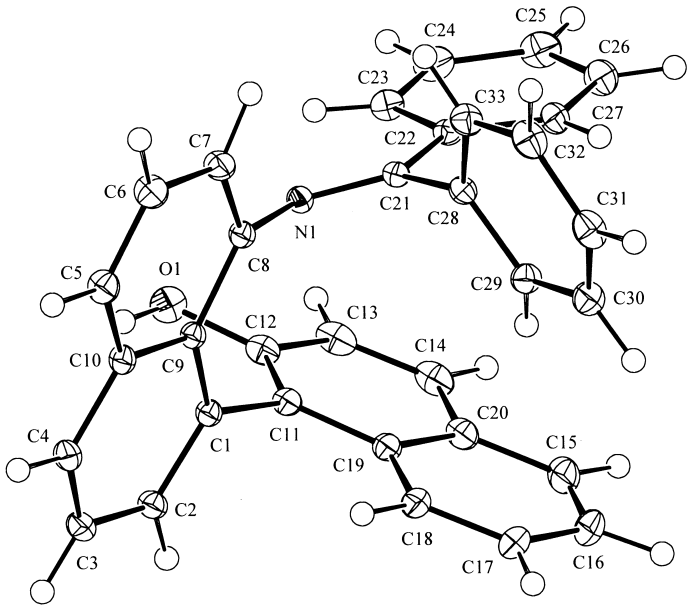

Figure 2. ORTEP diagram of (±)-**24** showing the atom labeling scheme. Displacement parameters are shown at the 50% probability level.

carrying the hydroxy group, whereas the other phenyl is practically perpendicular to the remaining ring of the same naphthalene unit. The latter orientation suggests a T-type H–π interaction of the *ortho* proton of the phenyl group with the π-system of the distal naphthalene ring.[57, 58]

Enantiomerically pure 2,8′-disubstituted 1,1′-binaphthyls: The key compound of this novel series to be successfully resolved on a preparative scale (~10 g) was hydroxy bromide (±)-**22**. Its single co-crystallization with *N*-benzylcinchonidinium chloride in acetonitrile[52, 53] afforded a crystalline inclusion complex that contained (+)-**22** (99.4% *ee*), while the mother liquor was enriched in the (−)-enantiomer (84% *ee*). The pure (+)-enantiomer was released by chromatography on silica gel using dichloromethane as eluent. Although we failed to purify the enriched (−)-enantiomer directly by crystallization of this material, we have found that, after its transformation into (+)-**26** (84% *ee*), this material could be crystallized from toluene to give racemic crystalline product, leaving (+)-**26** (94% *ee*) in the solution. Crystallization of the mother liquor from a dichloromethane-hexane mixture produced (+)-**26** (>99% *ee*). Even more efficient is the crystallization of the enantiomerically enriched amide (−)-**27** (~84% *ee*) from toluene, which gives an enantiopure product in a single operation.

The absolute configuration of **22** was established by a single-crystal X-ray analysis as (*S*)-(+)-**22** (Figure 3).[59] Methylation of (*S*)-(+)-**22** (>99% *ee*, MeI, K_2CO_3, acetone, reflux) produced (+)-**18** (95%), for which the absolute configuration was confirmed by X-ray crystallography as (*S*)-(+)-**18** (Figure 4).[60] The remaining members of the series were then synthesized by using the protocols developed for their racemic counterparts.[61]

From the absolute configuration of **18** and **22**, established by X-ray crystallography, the whole series of the generically related 2,8′-disubstituted 1,1′-binaphthyls can be inferred as

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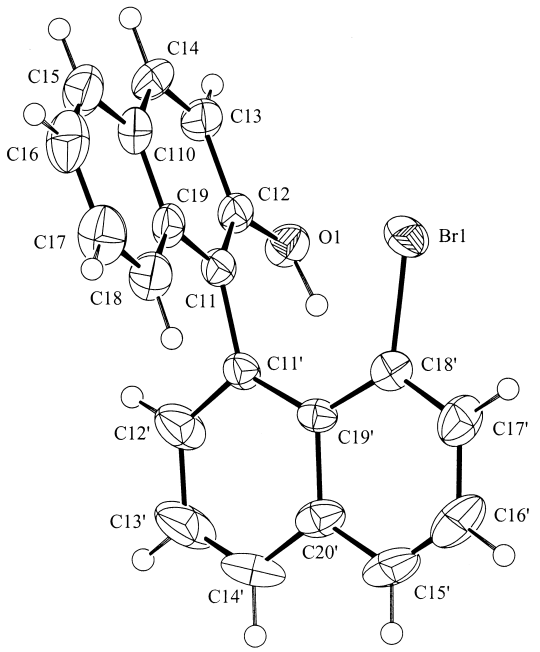


Figure 3. ORTEP diagram of (*S*)-(+)-**22** showing the atom labeling scheme. Displacement parameters are shown at the 50% probability level.

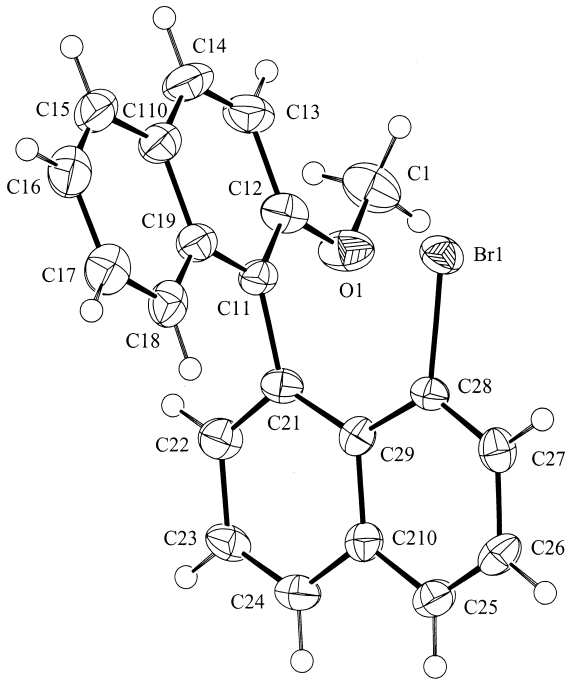
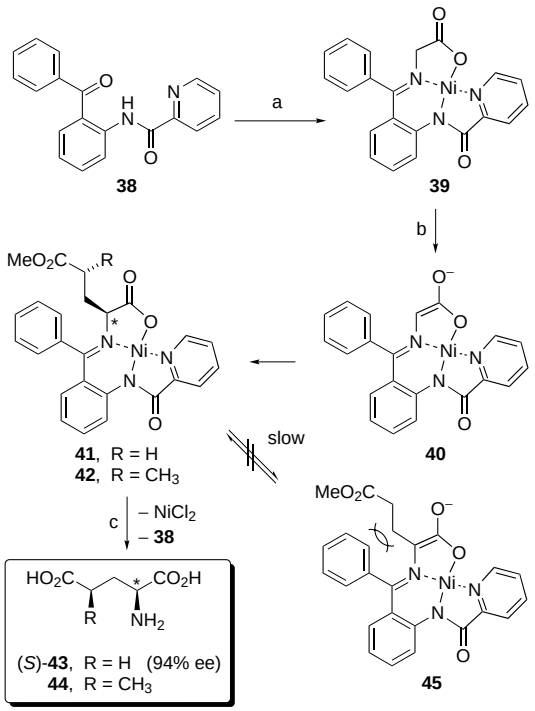


Figure 4. ORTEP diagram of (*S*)-(+)-**18** showing the atom labeling scheme. Displacement parameters are shown at the 50% probability level.

follows: (*S*)-(+)-**18**, (*S*)-(+)-**19**, (*S*)-(+)-**22**, (*S*)-(−)-**23**, (*S*)-(−)-**24**, (*S*)-(+)-**25**, (*S*)-(−)-**26**, and (*S*)-(+)-**27**.

***iso*-NOBIN-derived acetamide as an asymmetric phase-transfer catalyst**: The Ni^{II}-complex **39**,[62] derived from **38**, glycine, and Ni^{II} (Scheme 11), can be alkylated by good electrophiles, such as $PhCH_2Br$, in the presence of solid NaOH as a base and NOBIN (**1d**) as the phase-transfer catalyst, to give, after hydrolysis, amino acids with very high enantioselectivity (up to 99% *ee*).[6k, 63] The crucial role of Na^+ ion and a strong



Scheme 11. a) $Ni(NO_3)_2$, MeONa, MeOH, reflux 20 min, 91%; b) solid NaH, catalyst (10–15 mol%), CH_2=C(R)CO_2Me, CH_2Cl_2, RT, 2–3 min; c) 6 M HCl, MeOH, reflux for several min.

positive nonlinear effect have also been demonstrated for this reaction.[6k, 64] As an extension of this methodology, we elected to briefly study asymmetric Michael addition of **39** to methyl acrylate and methyl methacrylate CH_2=C(R)CO_2Me (Scheme 11 and Table 5). To this end, nonchiral ligand **38**, obtained from *o*-aminobenzophenone and *α*-picolinic acid chloride (Et_3N, CH_2Cl_2, RT, overnight; 85%),[6k] was condensed with glycine and to afford complex **39** (91%).[6k] The Michael addition of **39** to methyl acrylate (solid NaH, catalyst (10-15 mol%), in CH_2Cl_2, RT, 2–3 min), furnished the expected adduct **41** (for yields and enantioselectivities, see

Table 5. Michael addition of glycine complex **39** to methyl acrylate and methyl methacrylate catalyzed by 1,1′-binaphthyls (Scheme 11).[a]

Entry	R	Base [mol%]	Catalyst [mol%]	*T* [°C]	Time [min]	Yield[b] [%]	% *ee*[c] (configuration[d])
1	H	NaH (10)	(*R*)-**1d** (10)	18	3	40	26 (*S*)
2	H	NaH (100)	(*R*)-**1i** (10)	18	3	50	55 (*S*)
3	H	NaH (100)	(*S*)-**22** (10)	20	2.5	75	13 (*S*)
4	H	NaH (100)	(*R*)-**26** (10)	20	3	40	18 (*S*)
5	H	NaH (100)	(*R*)-**27** (10)	20	2	60	90 (*S*)
6[e]	H	NaH (100)	(*R*)-**27** (10)	20	2	65	92 (*S*)
7[f]	H	NaH (200)	(*R*)-**27** (10)	20	3	70	92 (*S*)
8	Me	NaH (100)	(*R*)-**27** (15)	20	9	50	81 (2*S*,4*R*)[g]

[a] The reaction was carried out at 1.0–4.0 mmol scale in CH_2Cl_2 with six equivalents of methyl acrylate. The crude product was hydrolyzed with 6 M HCl and **43**/**44** was isolated by ionex chromatography. [b] Isolated yield. [c] Determined by chiral GLC for the *n*-propyl ester of *N*-trifluoroacetyl derivative. [d] Determined by chiral GLC (by comparison with the known sample). [e] A fourfold increase in the concentration of the substrate, as compared with entry 4. [f] The experiment was carried out with (*R*)-**27** recovered from the reaction mixture (previous batch) in 60% yield. [g] Two diastereoisomers of **44** were formed: (2*S*,4*R*):(2*S*,4*S*) = 86:14. The minor diastereoisomer was of 66% *ee*.

Table 5), whose hydrolysis produced glutamic acid (*S*)-**43**. While (*R*)-**1d** gave only 26% *ee* (Table 5, entry 1), improvement to 55% *ee* has been attained with the corresponding acetamide (*R*)-**1i**[5g] (entry 2). When the *iso*-NOBIN-derived acetamide (*R*)-(−)-**27** was employed, substantial increase in asymmetric induction was observed (90% *ee*; entry 5), and further improvement (to 92% *ee*) was attained with a four-fold increase in the concentration of **39** (entry 6). No erosion of enantioselectivity was observed when **27**, regenerated from a previous batch, was re-employed as catalyst (entry 7). Both hydroxy bromide (*S*)-**22** and *iso*-NOBIN (*R*)-(+)-**26** also proved to catalyze the reaction, but the enantioselectivity was low (entries 3 and 4), demonstrating the key role played by the amide group.[65] With methyl methacrylate (R = Me) as the Michael acceptor, two diastereoisomers of **44** were formed in a 6:1 ratio; the major product, identified as the (2*S*,4*R*)-stereoisomer, was obtained in 81% *ee* (entry 8).

The salient feature of the present protocol is that a second alkylation of the primary product **41** has not been detected under the reaction conditions. This selectivity can be understood in terms of steric congestion, which the enolization of **41** to **45** would impose: here, by changing the hybridization at C_α, the new substituent would be brought into the plane of the chelate, which is apparently prohibited by the bulky phenyl group of the imine moiety.[66, 67] The less enantioselective Michael addition to methyl methacrylate can be attributed to the effect of the additional methyl group that renders the transition states less different in energy. The formation of the second chiral center in **42** (C-4) occurs through protonation of the corresponding enolate intermediate, arising by Michael addition. This step is notably diastereoselective (6:1), suggesting an effective 1,3-induction, exercised by the C-2 center.

Another notable feature of the Michael addition is the strong nonlinear effect[68] (Figure 5)—a behavior that is in line with the similar effect previously observed for the S_N2 alkylation of **39** with $PhCH_2Br$.[6k] In the present case, the catalyst of only 40% *ee* still exhibits an impressively high asymmetric induction (75% *ee*).

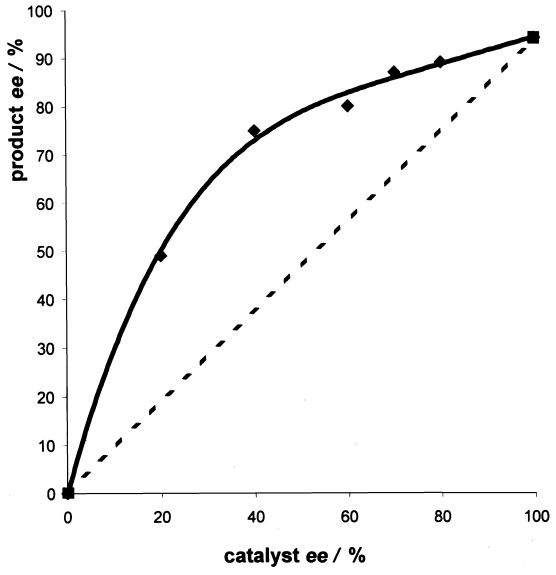


Figure 5. Nonlinear effect of (*R*)-**27** as catalyst in the Michael addition of **39** to methyl acrylate.

The present experiments show that this chemistry is not limited to S_N2 reactions with reactive electrophiles, as reported earlier.[6k] Further extensions can be anticipated, for example, for Michael additions generating two chiral centers at the newly-formed C–C bond, aldol condensations, etc. Moreover, these very fast and mild reactions may be amenable to the syntheses, for which speed is crucial, such as those involving ^{11}C and ^{18}F labeling.

Conclusion

In conclusion, we have synthesized a novel class of 1,1′-binaphthyls with substituents in 2,8′-positions (**3**), namely, the methoxy phosphine **19** (*iso*-MOP) and amino alcohol **26** (*iso*-NOBIN), using Suzuki coupling as the key step to construct the aryl–aryl bond (**10** + **15** → **18**). This coupling turned out to be sensitive to the nature of the 8-substituent and the overall steric congestion in the transition state.

Intermediate **22** was resolved into enantiomers and the absolute configuration of **18** and **22** was determined by X-ray crystallography. The new 2,8′-disubstituted binaphthyls **18**, **25**, and **26** proved to be as configurationally stable as their 2,2′-disubstituted counterparts **1** (both experimentally and by quantum chemistry calculations) and, therefore, suitable for asymmetric catalysis. By contrast, the 8,3′-disubstituted 1,2′-binaphthyls **16**, **17**, and **35** have low racemization barriers, comparable with that of unsubstituted 1,1′-binaphthyl **1g**.

iso-NOBIN **26** and, in particular, its acetamido derivative **27**, have been identified as efficient, chiral phase-transfer catalyst for the Michael addition of the enolate **40**, derived from the Ni^{II} complex of glycine-imine, to methyl acrylate, affording glutamic acid **43** in up to 92% *ee*.

Experimental Section

General methods: Melting points were determined on a Kofler block and are uncorrected. The optical rotations were measured in THF with an error of $< \pm 0.1$. The ^1H NMR spectra were recorded on 400 MHz instruments (FT mode) for solutions in $CDCl_3$ at 25 °C with TMS as internal reference. The ^{13}C NMR spectra were recorded on a 101 MHz instruments (FT mode) for solutions in $CDCl_3$ at 25 °C. The individual protons and carbon atoms were assigned by using DEPT, COSY, NOESY, HSQC, and HMBC techniques. The ^{31}P NMR spectra were recorded at 162 MHz (FT mode) for solutions in $CDCl_3$ at 25 °C with H_3PO_4 as external reference. The IR spectra were measured in dichloromethane or chloroform. The high-resolution mass spectra were measured on a ZAB2-SEQ double-focusing spectrometer (70 eV, 8 kV) with direct inlet and the lowest temperature enabling evaporation; the accuracy was ≤5 ppm. Yields are given in milligrams of isolated product, showing one spot on a chromatographic plate and no impurities detectable in the NMR spectrum. 2,2′-Bis(diphenylphosphino)diphenyl ether (dpePhos) was purchased from Strem. The syntheses of **38** and **39** were carried out as described earlier.[6k]

1-Dimethylamino-8-naphthaleneboronic acid (6): *n*BuLi (22 mL of a 2.5M solution in hexanes) was added to a solution of 1-(*N*,*N*-dimethylamino)-naphthalene (**4**: 1.92 mL, 11.6mmol) in anhydrous diethyl ether (5 mL). The yellow precipitate of the organolithium species **5** was observed after approximately 18–24 h, and the reaction was complete within 2–3 days. Aryllithium **5** thus generated was then added by means of a cannula to a solution of trimethylborate (6.17 mL, 55.0 mmol) in THF (8 mL) cooled to −78 °C and stirred at room temperature overnight. The reaction mixture was then poured into 10% aqueous HCl and stirred at room temperature

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for 2 h. The product was extracted with diethyl ether and sequentially washed with 10% aqueous HCl, water, and brine, and dried over $MgSO_4$. Flash chromatography on silica gel (30 g) using petroleum ether as eluent afforded pure, amorphous **6** (1.097 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.91$ (s, 6H), 7.21 (d, $J = 7.3$ Hz, 1H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.53 (t, $J = 7.3$ Hz, 1H), 7.61 (dd, $J = 8.2$, 0.9 Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 112.06$ (d), 119.99 (s), 121.93 (d), 125.61 (d), 126.02 (d), 126.14 (d), 128.97 (d), 132.55 (s), 134.17 (s), 153.64 (s); ^{11}B NMR (acetone): $\delta = 10.56$ (s).

1-Dimethylamino-8-(trimethyltin)naphthalene (7): The aryllithium **5** was generated from **4** (0.96 mL, 5.84 mmol) and *n*BuLi (16.8 mL of 1.6M solution in hexanes) in diethyl ether (5 mL) as described in the preparation of **6**. Trimethyltin chloride (28 mL of a 1.0 M solution in hexanes) was added at $-78\,^\circ$C, and the mixture was stirred at room temperature overnight. The mixture was poured into water, extracted with diethyl ether and the resulting solution was dried over $MgSO_4$ and the solvent was evaporated. Flash column chromatography on silica gel (20 g) using petroleum ether as eluent afforded pure **7** (1.04 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.26$ (s, 9H), 2.66 (s, 6H), 7.32 (ddd, $J = 7.4$, 1.3, 1.0 Hz, 1H), 7.50–7.42 (m, 2H), 7.66 (dd, $J = 8.0$, 1.1 Hz, 1H), 7.79 (dd, $J = 7.7$, 1.3 Hz, 2H); ^{13}C NMR NMR (100 MHz, $CDCl_3$): $\delta = 10.9$ (3q), 47.5 (2q), 115.9 (d), 125.5 (d), 125.6 (d), 125.7 (d), 128.3 (d), 134.3 (s), 134.8 (s), 135.8 (d), 138.7 (s), 153.0 (s).

1-Bromo-2-methoxynaphthalene (9):[26] A solution of bromine (12.9 mL, 0.25 mol) in acetic acid (100 mL) was added to a solution of 2-methoxynaphthalene (**8**: 39.5 g, 0.25 mol) in acetic acid (350 mL) over the period of 30 min. The mixture was stirred at room temperature for 30 min, the resulting suspension was poured into water (1.5 L), and the precipitated product was isolated with suction and washed with water. The crude product was dried and crystallized from ethanol with charcoal to afford **9** (50.5 g, 85%) as colorless plates. M.p. 85–86 °C (in accordance with the literature[26]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.03$ (s, 3H), 7.28 (d, $J = 9.0$ Hz, 1H), 7.37–7.42 (m, 1H), 7.54–7.59 (m, 1H), 7.76–7.84 (m, 2H), 8.20–8.24 (m, 1H).

2-Methoxy-1-naphthaleneboronic acid (10):[27] Magnesium (2.2 g, 91 mmol), activated by stirring for 24 h under argon was covered with THF (30 mL) and then a solution of **9** (20 g, 84 mmol) in THF (150 mL) was slowly added under argon. The formation of the Grignard reagent was accompanied by spontaneous heating of the mixture to the boiling point. After stirring for 30 min, the mixture was cooled to room temperature and added by means of a cannula to a solution of $(i\mathrm{PrO})_3$B (29 mL, 126 mmol, 1.5 equiv) in THF (40 mL) at $-78\,^\circ$C. The mixture was then stirred at $-78\,^\circ$C for 1 h and at room temperature for 12 h. Water (30 mL) was then added and the solvent was evaporated in vacuum. The residue was treated with water (150 mL) and acidified with HCl (1M, 200 mL) to precipitate the product. Dichloromethane (30 mL) was added and the resulting heterogeneous mixture was vigorously stirred for 10 min to dissolve 2-methoxynaphthalene, the undesired byproduct. The solid crude product was isolated with suction and washed with CH_2Cl_2 (2×10 mL). Crystallization from aqueous ethanol (1:1, 60 mL) gave boronic acid **10** (11.5 g, 67%) as a white solid: m.p. 140–144 °C (literature[29] reports 143–5 °C). The IR spectrum is in accordance with the literature data.[27] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.03$ (s, 3H), 6.11 (s, 2H), 7.28 (d, $J = 9.2$ Hz, 1H), 7.37 (ddd, $J = 8.0$, 6.7, 1.3 Hz, 1H), 7.51 (ddd, $J = 8.5$, 6.9, 1.6 Hz, 1H), 7.78 (dm, $J = 8.2$ Hz, 1H), 7.94 (d, $J = 9.0$ Hz, 1H), 8.83 (dm, $J = 8.7$ Hz, 1H).

2-Methoxy-3-naphthaleneboronic Acid (11):[29] A solution of *n*-butyllithium (1.6M in hexanes, 15.6 mL, 25 mmol) was added to a solution of **9** (5.69 g, 24 mmol) in THF (30 mL) under argon at $-78\,^\circ$C. The mixture was stirred at $-78\,^\circ$C for 2 h and then added by means of a cannula to a solution of $(i\mathrm{PrO})_3$B (8.3 mL, 36 mmol, 1.5 equiv) in THF (20 mL), cooled to $-78\,^\circ$C. The resulting mixture was stirred at $-78\,^\circ$C for 1 h and then at room temperature for 18 h. The mixture was then poured into HCl (1M, 250 mL) and vigorously stirred for 30 min. NaOH (5M, excess) was then added and the mixture was extracted with dichloromethane (2×50 mL). The aqueous layer was acidified with Hcl (5M) and the product was extracted into dichloromethane (3×30 mL). The extract was washed with water and dried with Na_2SO_4, and the solvent was evaporated in vacuum to furnish crude product **15** (2.62 g, 54%) as light brown crystalline material that was not further purified: m.p. 173–174 °C (dichloromethane; literature[29] reports 153–155 °C). The IR spectrum is in accordance with the literature data.[29] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.03$ (s, 3H), 6.07 (s, 2H), 7.16 (s, 1H), 7.37 (ddd, $J = 8.2$, 6.9, 1.3 Hz, 1H), 7.49 (ddd, $J = 8.2$, 6.9, 1.4 Hz, 1H), 7.74 (dd, $J = 8.2$, 1.0 Hz, 1H), 7.84 (dd, $J = 8.2$, 1.0 Hz, 1H), 8.41 (s, 1H).

1-Amino-8-bromonaphthalene (13):[30] A solution of $NaNO_2$ (6.70 g, 97.1 mmol, 1.02 equiv) in water (150 mL) was added to a solution of 1,8-diaminonaphthalene (15.0 g, 94.8 mmol) in HCl (0.4 M, 1.0 L) at $-5\,^\circ$C. The mixture was then stirred at $-5\,^\circ$C for 2 h and at 10 °C for 18 h. The black precipitate was filtered off, washed with water, dried at room temperature for 1 h, and then dissolved in aqueous HBr (48%, 100 mL). Copper bronze (4.0 g, 63 mmol), first activated by heating with flame for 10 min under argon, was added to the resulting solution at 60 °C. The mixture was stirred for 18 h, water (220 mL) was then added, and the mixture was heated to the boiling point. The precipitate was filtered off with suction and boiled with additional water. The combined filtrate was neutralized with ammonium carbonate and extracted with dichloromethane (3×40 mL); the extract was dried with Na_2SO_4 and evaporated. Chromatography of the crude product on silica gel (100 g) with toluene afforded **13** (5.66 g, 27%) as pink crystals: m.p. 90–91 °C (toluene) and IR are in accord with the literature.[30] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.14$ (br s, 2H), 6.71–6.76 (m, 1H), 7.11–7.16 (m, 1H), 7.23–7.25 (m, 2H), 7.62 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.68 (dd, $J = 8.2$, 1.2 Hz, 1H).

1-Acetamido-8-bromonaphthalene (14):[31] A mixture of **13** (3.10 g, 14 mmol), acetic anhydride (1.4 mL, 15 mmol, 1.07 equiv), and pyridine (8 mL) was heated at 100 °C for 1 h and then evaporated in vacuum. The oily residue was treated with cold, diluted hydrochloric acid (50 mL), and the resulting crystalline material was isolated with suction, washed with water, and dried on the air. The crude product was recrystallized from 50% aqueous acetic acid (8 mL) to furnish pure **14** (2.87 g, 80%) as colorless crystals: m.p. 143–144 °C agrees with the literature.[31] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.28$ (s, 3H), 7.23 (t, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 8.79 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.83$ (q), 115.73 (s), 124.56 (s), 124.82 (d), 125.91 (d), 126.29 (d), 127.00 (d), 129.57 (d), 131.98 (s), 133.68 (d), 136.57 (s), 168.36 (s); IR ($CHCl_3$): $\tilde{\nu} = 3438$ (NH), 1690 (C=O), 1530 (arom), 1490 (arom), 1272 (C–N) cm^{-1}.

1,8-Dibromonaphthalene (15):[32] Solid $NaNO_2$ (10.0 g, 0.145 mol, 2.3 equiv) was cautiously added to a stirred concentrated H_2SO_4 (100 mL) at 0 °C. Then, a solution of 1,8-diaminonaphthalene (10.0 g, 63.2 mmol) in acetic acid (100 mL) was added at 0 °C over a period of 3 h with vigorous stirring with a mechanical stirrer. The mixture was stirred at 0 °C for an additional 30 min and then slowly poured onto ice (200 g). Free HNO_2 was decomposed by adding a saturated aqueous solution of urea (2.0 g). The resulting mixture was poured into a solution of CuBr (25.0 g, 0.174 mol) in aqueous HBr (48%, 375 mL) and stirred at room temperature for 18 h. Toluene (150 mL) was then added and the solution was filtered with suction and the black solid was washed with dichloromethane and the filtrate was treated with water (1 L). The aqueous layer was extracted with dichloromethane (2×50 mL) and the combined extracts were dried with Na_2SO_4 and evaporated in vacuum to produce crude **15**. Flash chromatography on silica gel (100 g) with toluene gave pure **15** (4.48 g, 25%) as yellow crystals: m.p. 104–106 °C (toluene) and IR are in accord with the literature.[32] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.26$ (dd, $J = 8.2$, 7.6 Hz, 2H), 7.80 (dd, $J = 8.2$, 1.2 Hz, 2H), 7.92 (dd, $J = 7.6$, 1.2 Hz, 2H).

(±)-8-Acetamido-3′-methoxy-1,2′-binaphthyl (16): A solution of Na_2CO_3 (1.40 g) in water (6.5 mL), which was previously purged with argon for 10 min, was added to a solution of **14** (660 mg, 2.50 mmol), boronic acid **11** (505 mg, 2.50 mmol), and $(Ph_3P)_4Pd$ (144 mg, 125 μmol, 5 mol%) in DME (14 mL) under argon. The mixture was refluxed for 18 h and then the solvent was evaporated in vacuum. Water (8 mL) was added to the residue and the product was taken up into dichloromethane (2×5 mL). The extract was dried with Na_2SO_4 and evaporated. Chromatography of the crude product on silica gel (50 g) with a petroleum ether/ethyl acetate mixture (1:1) followed by crystallization from ethyl acetate afforded pure **16** (471 mg, 55%) as colorless crystals. M.p. 150–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.17$ (s, 3H), 3.78 (s, 3H), 7.14 (br s, 1H), 7.25 (dd, $J = 6.7$, 1.2 Hz, 1H), 7.40–7.46 (m, 1H), 7.48–7.56 (m, 4H), 7.76–7.88 (m, 5H), 7.92 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 23.50$ (q), 55.72 (q), 105.16 (d), 122.77 (d), 124.55 (d), 124.95 (d), 125.66 (d), 125.93 (s), 126.40 (d), 126.55 (d), 126.93 (d), 127.64 (d), 128.41 (s), 129.14 (d), 129.27 (d), 130.00 (d), 133.05 (s), 133.08 (s), 134.23 (s), 134.27 (s), 134.88 (s), 155.65 (s), 167.86 (s); IR ($CHCl_3$): $\tilde{\nu} = 3429$ (NH), 1685 (C=O), 1523 (arom), 1495 (arom), 1255 cm^{-1} (C–O); MS: m/z (%): 341 (74) [M^+], 299 (18), 283 (12),

268 (100), 267 (78), 254 (19), 43 (21); HRMS for $C_{23}H_{19}NO_2$: calcd 341.1416; found 341.1392. The small-scale enantiomeric separation was performed on a Daicel Chiralpak AD column using a hexane-methanol-isopropyl alcohol mixture (67:30:3); the retention times were 7.0 and 8.8 min.

(±)-8-Bromo-3′-methoxy-1,2′-binaphthyl (17): A solution of Na_2CO_3 (810 mg) in water (3.8 mL), which was previously purged with argon for 10 min, was added to a solution of 1,8-dibromonaphthalene **15** (418 mg, 1.46 mmol), boronic acid **11** (294 mg, 1.46 mmol), and $(Ph_3P)_4Pd$ (84 mg, 73 μmol, 5 mol %) in DME (8.0 mL) under argon. The mixture was refluxed for 18 h and then the solvent was evaporated in vacuum. Water (5 mL) was added to the residue and the product was taken up into dichloromethane (2 × 3 mL). The extract was dried with Na_2SO_4 and evaporated. Chromatography of the crude product on silica gel (50 g) with a toluene/petroleum ether mixture (7:3) afforded pure **17** (359 mg, 68 %). M.p. 118–119 °C (ethyl acetate/methanol); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.80$ (s, 3H), 7.15 (s, 1H), 7.27 (dd, $J = 8.1$, 7.3 Hz, 1H), 7.37 (ddd, $J = 8.1$, 6.9, 1.2 Hz, 1H), 7.45 (dd, $J = 7.2$, 1.5 Hz, 1H), 7.47 (ddd, $J = 8.2$, 6.9, 1.4 Hz, 1H), 7.53 (dd, $J = 8.1$, 7.0 Hz, 1H), 7.69 (s, 1H), 7.75 (dd, $J = 7.5$, 1.4 Hz, 1H), 7.77 (dm, $J = 8.1$ Hz, 1H), 7.81 (dm, $J = 8.1$ Hz, 1H), 7.89 (dd, $J = 8.6$, 1.4 Hz, 1H), 7.91 (dd, $J = 8.4$, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.55$ (q), 104.47 (d), 120.60 (s), 123.72 (d), 125.52 (d), 125.81 (d), 126.16 (d), 126.41 (d), 127.70 (d), 128.51 (s), 129.05 (d), 129.37 (d), 129.88 (d), 130.49 (s), 131.46 (d), 133.18 (d), 134.31 (s), 134.45 (s), 135.73 (s), 136.53 (s), 157.11 (s); IR ($CHCl_3$): $\tilde{\nu} = 1632$ (arom), 1503 (arom), 1475 (arom), 1253 (C–O), 1171 cm^{-1} (arom); MS: m/z (%): 364 (23) [M^+] (^{81}Br), 362 (23) [M^+] (^{79}Br), 283 (78), 268 (100), 252 (46), 239 (53), 141.5 (18), 134 (41), 126 (16), 119.5 (44), 118.5 (17), 106.5 (11); HRMS for $C_{21}H_{15}{}^{79}BrO$: calcd 362.0306; found 362.0311. The small-scale enantiomeric separation was performed on a Daicel Chiralpak AD column using a hexane-methanol-isopropyl alcohol mixture (79:18:3); the retention times were 4.7 and 5.3 min.

(±)-8-Bromo-2′-methoxy-1,1′-binaphthyl (18): A solution of Na_2CO_3 (3.2 g) in water (15 mL), which was previously purged with argon for 10 min, was added to a solution of **15** (2.0 g, 7.0 mmol), boronic acid **10** (1.41 g, 7.0 mmol), and $[Pd(Ph_3P)_4]$ (290 mg, 0.25 mmol, 3.5 mol %) in DME (32 mL) under argon. The mixture was refluxed for 24 h and then the solvent was evaporated in vacuum. Water (40 mL) was added to the residue and the product was taken up into dichloromethane (2 × 10 mL). The extract was dried with Na_2SO_4 and evaporated. Chromatography of the crude product on silica gel (50 g) with a toluene-petroleum ether mixture (1:1) afforded pure **18** (1.94 g, 76 %) as yellow crystals. M.p. 121–122 °C (ethyl acetate/methanol); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.80$ (s, 3H), 7.08 (d, $J = 8.4$ Hz, 1H), 7.24 (ddd, $J = 8.2$, 6.9, 1.5 Hz, 1H), 7.28 (dd, $J = 8.4$, 7.6 Hz, 1H), 7.31 (ddd, $J = 8.1$, 6.7, 1.2 Hz, 1H), 7.35 (d, $J = 9.2$ Hz, 1H), 7.42 (dd, $J = 7.0$, 1.4 Hz, 1H), 7.59 (dd, $J = 8.2$, 7.0 Hz, 1H), 7.69 (dd, $J = 7.5$, 1.4 Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.93 (dd, $J = 8.2$, 1.4 Hz, 1H), 7.95 (d, $J = 9.0$ Hz, 1H), 7.97 (dd, $J = 8.2$, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 56.52$ (q), 113.54 (d), 119.81 (s), 123.29 (d), 125.54 (d), 125.67 (s), 125.81 (d), 125.87 (d), 126.22 (d), 127.66 (d), 128.74 (s), 129.29 (3d), 130.75 (s), 131.98 (d), 133.39 (d), 134.19 (s), 135.04 (s), 136.04 (s), 154.54 (s); IR ($CHCl_3$): $\tilde{\nu} = 3015$, 1623 (C=C arom), 1595 (arom), 1510 (arom), 1274 (C–O), 1085 cm^{-1} (arom); MS: m/z (%): 364 (21) [M^+] (^{81}Br), 362 (21) [M^+] (^{79}Br), 283 (13), 268 (29), 252 (100), 239 (38); HRMS for $C_{21}H_{15}{}^{79}BrO$: calcd 362.0306; found 362.0312. Crystallographic data for (±)-**18**: $C_{21}H_{15}BrO$, $M_r = 362.03$. Crystals were obtained from ethyl acetate by slow diffusion of methanol vapors at room temperature. System: triclinic; space group $P\bar{1}$, $a = 9.8350(2)$, $b = 15.2530(2)$, $c = 17.0760(3)$ Å, $\alpha = 108.084(1)°$, $\beta = 91.353(1)°$, $\gamma = 99.355(1)°$. Data were collected at 105(2) K on a Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and ω scan mode at five different crystal orientations, covering thus the entire reciprocal sphere up to 0.84 Å resolution. A total of 34246 reflections were measured, from which 8418 were unique ($R_{int} = 0.059$), with 7525 observed data with $I > 2\sigma(I)$. The structure was solved by direct methods (SIR92). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97). The hydrogen atoms were found on difference Fourier map and refined isotropically. Absorption correction ($\mu = 2.576$ mm^{-1}) was carried on, using multiscan procedure (SORTAV): min/max transmission = 0.415/0.598. Final R factors: $R_1 = 0.0335$ for the observed data and 0.0397 for all data; $wR_2 = 0.0900$, $S = 0.993$. The estimated error in the bond lengths for non-hydrogen atoms is in the interval 0.002 to 0.004 Å.

Isolation of enantiopure (*S*)-(+)-18: Solid K_2CO_3 (6.9 g, 50 mmol) and methyl iodide (3.2 mL, 50 mmol) were added to a solution of (*S*)-(+)-**22** (1.81 g, 5 mmol) in acetone (25 mL), and the mixture was refluxed for 24 h. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (50 g) with toluene as eluent to give (*S*)-(+)-**18** (1.75 g, 97 %) as a white powder. M.p. 160–161 °C (dichloromethane/hexane); $[\alpha]_D = +150.9$ ($c = 1.0$ in THF). Chiral chromatography on Daicel Chiralpak AD with a hexane/isopropyl alcohol mixture (98:2) gave > 99 % *ee* for this product ($t_R = 4.8$ min, $t_S = 5.8$ min). Crystallographic data for (*S*)-(+)-**18**: $C_{21}H_{15}BrO$, $M_r = 362.03$. Crystals were obtained from a dichloromethane solution by slow diffusion of hexane vapors at room temperature. Orthorhombic; space group $P2_12_12_1$; $a = 14.6360(4)$, $b = 14.6340(3)$, $c = 14.9980(3)$ Å. Data were collected at 150(2) K on a Nonius KappaCCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and ω scan mode at five different crystal orientations up to 0.8106 Å resolution. A total of 47446 reflections were measured, from which 6311 were unique ($R_{int} = 0.071$), with 6078 observed data with $I > 2\sigma(I)$. The structure was solved by direct methods (SIR92). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97) with hydrogen atoms calculated into theoretical positions, riding during refinement on the respective pivot atom (418 parameters). The symmetry of the lattice is close to tetragonal and crystals suffered by pseudomerohedric twinning with twin matrix.

$$\begin{pmatrix} h' & 0 & 1 & 0 & h \\ k' & -1 & 0 & 0 & k \\ l' & 0 & 0 & 1 & l \end{pmatrix}$$

The correction for this effect was included into refinement, which yielded fractional contribution of twin components 0.6991(8):0.3009. Absorption correction ($\mu = 2.561$ mm^{-1}) was carried out, by using Gaussian methods (Coppens, 1970): min/max transmission = 0.558/0.753. The absolute structure was determined clearly since the absolute structure parameter is equal 0.000(9). Final R factors: $R_1 = 0.030$ for the observed data and 0.032 for all data; $wR_2 = 0.0765$, $S = 0.925$. The estimated error in the bond lengths for non-hydrogen atoms is in the interval 0.004 to 0.007 Å.

(±)-8-Diphenylphosphino-2′-methoxy-1,1′-binaphthyl (19): Zinc powder (130 mg, 2.0 mmol) was added to a solution of binaphthyl **18** (363 mg, 1.0 mmol), $[NiCl_2(dppe)]$ (26 mg, 50 μmol, 5 mol %), and chlorodiphenylphosphine (285 μL, 1.5 mmol) in DMF (2 mL) under argon and the mixture was heated at 105 °C for 48 h. The mixture was cooled, water (10 mL) added, and acidified with diluted hydrochloric acid. The product was extracted with dichloromethane (2 × 3 mL), and the organic phase was dried with Na_2SO_4 and evaporated. The crude product was purified by chromatography on silica gel (20 g) with a toluene/petroleum ether mixture (1:1) to consecutively elute **21** (73 mg, 26 %), **20** (17 mg, 6 %), and **19** (150 mg, 32 %) as the most polar compound. (±)-**19** (a beige powder): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.28$ (s, 3H), 6.42–6.48 (m, 2H), 6.80–6.86 (m, 2H), 6.89 (dm, $J = 8.4$ Hz, 1H), 6.91–6.96 (m, 2H), 7.00–7.05 (m, 2H), 7.07 (d, $J = 9.0$ Hz, 1H), 7.10 (ddd, $J = 7.2$, 4.0, 1.4 Hz, 1H), 7.14–7.21 (m, 4H), 7.33 (dd, $J = 7.0$, 1.5 Hz, 1H), 7.35 (dd, $J = 8.1$, 7.2 Hz, 1H), 7.58 (dd, $J = 8.2$, 7.0 Hz, 1H), 7.75 (dm, $J = 8.1$ Hz, 1H), 7.91 (d, $J = 9.0$ Hz, 1H), 7.97 (dd, $J = 8.2$, 1.5 Hz, 1H), 7.98 (dt, $J = 8.2$, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.04$ (q), 112.81 (d), 122.89 (d), 125.04 (d), 125.36 (d), 125.55 (d), 125.95 (d), 127.49 (2d), 127.69 (d), 127.77 (d, J(C,P) = 6 Hz, 2d), 127.93 (d, J(C,P) = 6 Hz), 128.78 (s), 129.28 (d), 129.54 (d), 130.89 (d), 131.46 (d), 133.04 (d, J(C,P) = 21 Hz), 133.44 (d, J(C,P) = 21 Hz), 134.71–135.10 (3s), 135.72 (s), 135.80 (s), 136.12 (d, J(C,P) = 21 Hz), 136.93 (d), 139.19 (d, J(C,P) = 18 Hz), 139.40 (d, J(C,P) = 20 Hz), 154.81 (d, J(C,P) = 6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -9.36$ (s); IR (CCl_4): $\tilde{\nu} = 1623$ and 1594 (C=C arom), 1510 and 1434 (arom), 1263 (C–O); MS: m/z (%): 468 (5) [M^+], 453 (7), 437 (100), 283 (4), 239 (3), 218.5 (3), 183 (2); HRMS for $C_{33}H_{25}OP$: calcd 468.1643; found 468.1651.

Isolation of enantiopure (*S*)-(+)-19: Enantiopure **19** was prepared from (*S*)-(+)-**18** (363 mg) in 32 % yield by using the same procedure as that for (±)-**19**. $[\alpha]_D = +23$ ($c = 0.5$ in CH_2Cl_2). Chromatography on Daicel Chiralpak AD with a hexane/isopropyl alcohol mixture (98:2) showed > 99 % *ee* for this product ($t_R = 4.2$ min, $t_S = 4.6$ min).

(±)-2-Methoxy-1,1′-binaphthyl (20): Compound **20** was obtained along with **19** and **21** from the Ni^0-catalyzed coupling of **18** with Ph_2PCl. M.p. 107–108 °C (aqueous MeOH) (ref. [35f] gives 107–108 °C from aqueous

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MeOH). The ^{1}H NMR data were in agreement with the published values.[35f] An authentic sample was prepared by Suzuki coupling of 1-naphthaleneboronic acid with 1-bromo-2-methoxynaphthalene.[35f]

1-Methoxyperylene (21): Compound **21** was obtained along with **19** and **20** from the Ni^0-catalyzed coupling of **18** with Ph_2PCl. M.p. 111–113 °C (toluene, ref. [37] gives 111 °C); MS: *m*/*z* (%): 282 (100) [M^+], 268 (78), 239 (47), 141 (11), 119.5 (19); HRMS for $C_{21}H_{14}O$: calcd 282.1045; found 282.1053. Crystallographic data for **21**: $C_{21}H_{14}O$, $M = 282.34$. Crystals were obtained from dichloromethane by a slow diffusion of hexane at room temperature. Monoclinic; space group $P2_1/c$; $a = 18.2280(2)$, $b = 15.2280(3)$, $c = 10.2160(4)$ Å, $\beta = 104.4240(12)°$. Data were collected at 150(2) K on a Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and ω scan mode at five different crystal orientations up to 0.7696 Å resolution. A total of 43800 reflections were measured, from which 6287 were unique ($R_{int} = 0.030$), with 4753 observed data with $I > 2\sigma(I)$. The structure was solved by direct methods (SIR92). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97), all hydrogen atoms were found on difference Fourier map and refined isotropically (508 parameters). Absorption was neglected ($\mu = 0.082\,mm^{-1}$). Final *R* factors: $R_1 = 0.050$ for the observed data and 0.075 for all data; $wR_2 = 0.135$, $S = 1.051$. The estimated error in the bond lengths for non-hydrogen atoms is 0.002 Å.

(±)-8-Bromo-2′-hydroxy-1,1′-binaphthyl (22): Boron tribromide (15 mL, 1M solution in dichloromethane, 15 mmol) was added to a cooled solution (0 °C) of **18** (3.62 g, 10 mmol) in dichloromethane (40 mL) and the solution was slowly warmed to room temperature and stirred overnight. The reaction was quenched by adding water (30 mL) and satd. $NaHCO_3$ (10 mL), the dichloromethane phase was separated, and the water phase was extracted with dichloromethane (2×5 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated in vacuum. The residue was purified by chromatography on silica gel (50 g) with toluene as eluent to give **22** (3.34 g, 96%). M.p. 145–146 °C (toluene); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.77$ (s, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 7.21–7.35 (m, 4H), 7.54 (dd, $J = 6.8$, 0.8 Hz, 1H), 7.64 (dd, $J = 7.6$, 7.6 Hz, 1H), 7.75 (dd, $J = 7.6$ Hz, 0.8 Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.8$ Hz, 1H), 7.96 (dd, $J = 8.0$, 0.8 Hz, 1H), 8.05 (dd, $J = 8.4$, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 117.30$ (d), 119.44 (s), 121.65 (s), 123.15 (d), 124.90 (d), 126.37 (d), 126.40 (d), 126.60 (d), 127.83 (d), 128.64 (s), 129.39 (d), 129.70 (d), 130.81 (d), 130.86 (s), 131.22 (s), 133.29 (d), 134.21 (d), 135.06 (s), 136.43 (s), 150.74 (s); IR (CCl_4): $\tilde{\nu} = 3607$ (OH), 3560 (OH associated to an aromatic π-orbital), 1623 and 1598 (C=C arom), 1518 and 1469 cm^{-1} (arom); MS: *m*/*z* (%): 350 (36) [M^+] (^{81}Br), 348 (36) [M^+] (^{79}Br), 269 (100), 268 (53), 252 (44), 251 (30), 239 (56), 134 (9), 119.5 (16); HRMS for $C_{20}H_{13}{}^{79}BrO$: calcd 348.0150; found 348.0156.

Resolution of (±)-22: Racemic **22** (3.5 g, 10 mmol) and (−)-*N*-benzylcinchonidinium chloride (2.1 g, 5 mmol) were dissolved in MeCN (50 mL) at 70 °C. The mixture was heated during an additional 5 h, during which period a precipitate was formed. After cooling to room temperature, the precipitate was filtered off, washed with cold MeCN (5 mL), and dried in to give a white powder (3.5 g). The powder was suspended in dichloromethane (20 mL) and purified by chromatography on silica gel (50 g) with dichloromethane as eluent to give (*S*)-(+)-**22** (1.5 g, 43%). M.p. 121–123 °C (hexane/dichloromethane); $[\alpha]_D = +97.8$ ($c = 0.5$ in THF). Chromatography on Daicel Chiralpak AD using a hexane-isopropyl alcohol mixture (9:1) showed 99.4% *ee* for this product ($t_R = 10.8$ min, $t_S = 12.2$ min). The filtrate from the resolution process was evaporated under the reduced pressure and worked up in a similar manner to give (*R*)-(−)-**22** (1.9 g, 66%), which was of 84% *ee*. Crystallographic data for (*S*)-(+)-**22**: $C_{20}H_{13}BrO$, $M_r = 349.21$. Crystals were obtained from dichloromethane by a slow diffusion of hexane at room temperature. Tetragonal, space group $P4_1$; $a = 8.7450(1)$, $c = 40.0620(6)$ Å. Data were collected at 150(2) K on a Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and ω scan mode at three different crystal orientations up to 0.7696 Å resolution. A total of 15309 reflections were measured, from which 6463 were unique ($R_{int} = 0.029$), with 5858 observed data having $I > 2\sigma(I)$. The structure was solved by direct methods (SIR92). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97) with hydrogen atoms calculated into theoretical positions, riding during refinement on the respective pivot atom, except those of OH groups, which were found on difference Fourier map and refined isotropically (398 parameters). Absorption correction ($\mu = 2.682\,mm^{-1}$) was carried out, using multiscans procedure (SORTAV): min/max transmission = 0.447/0.518. The absolute structure was determined clearly, since the absolute structure parameter is equal −0.009(6). Final *R* factors: $R_1 = 0.030$ for the observed data and 0.037 for all data; $wR_2 = 0.0657$, $S = 1.050$. The estimated error in the bond lengths for non-hydrogen atoms is in the interval 0.003 to 0.006 Å.

(±)-8-Benzhydrylideneamino-2′-methoxy-1,1′-binaphthyl (23): Benzophenone imine[51] (2.34 g, 2.17 mL, 13 mmol) was added to a suspension of **18** (3.62 g, 10 mmol), [Pd(dba)$_2$] (229 mg, 0.5 mmol), 2,2′-bis(diphenylphosphino)diphenyl ether (268 mg, 0.5 mmol) and *t*BuONa (1.44 g, 15 mmol) in dry toluene (50 mL) and the mixture was heated at 100 °C for 24 h. The solvent was evaporated in vacuum and the residue was purified by chromatography on silica gel (50 g) with toluene as eluent to give **23** (4.49 g, 97%) as an amorphous solid: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.66$ (s, 3H), 6.01 (dd, $J = 7.4$, 0.8 Hz, 1H), 6.72–6.76 (m, 3H), 6.95–7.02 (m, 4H), 7.04–7.12 (m, 3H), 7.15–7.18 (m, 2H), 7.21–7.30 (m, 5H), 7.52–7.58 (m, 3H), 7.91 (dd, $J = 8.4$, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 56.00$ (q), 112.38 (d), 114.59 (d), 122.67 (d), 123.91 (d), 125.44 (d), 125.48 (d), 125.67 (d), 125.95 (d), 127.08 (2d), 127.32 (s), 127.48 (d), 127.69 (d), 128.11 (2d), 128.17 (s), 128.62 (s), 129.11 (d), 129.36 (d), 129.77 (d), 133.92 (s), 134.86 (s), 135.13 (s), 135.33 (s), 138.96 (s), 148.16 (s), 152.77 (s), 163.93 (s); IR (CCl_4): $\tilde{\nu} = 1622$ and 1596 (C=C arom), 1510, 1463 and 1446 (arom), 1261 cm^{-1} (C–O); MS: *m*/*z* (%): 463 (100) [M^+], 432 (9), 320 (14), 282 (20), 281 (25), 268 (25), 267 (16), 252 (20), 239 (20), 182 (11), 165 (13); HRMS for $C_{34}H_{25}NO$: calcd 463.1936; found 463.1929.

Isolation of enantiopure (*S*)-(−)-23: Enantiopure **23** was prepared from (*S*)-(+)-**18** (3.62 g) in 97% yield by using the same procedure as that for (±)-**23**. $[\alpha]_D = -603$ ($c = 0.8$ in THF). The enantiopurity was determined after the transformation into (*S*)-(+)-**25** (>99% *ee*).

(±)-8-Benzhydrylideneamino-2′-hydroxy-1,1′-binaphthyl (24): Boron tribromide (6 mL, 1M solution in dichloromethane, 6 mmol) was added to a cooled solution (0 °C) of **23** (1.85 g, 4 mmol) in dichloromethane (20 mL). The solution was slowly warmed to room temperature and stirred overnight. The reaction was quenched by adding water (20 mL) and satd $NaHCO_3$ (5 mL), the dichloromethane phase was separated and the water phase was extracted with dichloromethane (2×5 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated in vacuum. The residue was purified by chromatography on silica gel (20 g) with toluene as eluent to give **24** (1.71 mg, 95%). M.p. 226–229 °C (hexane/dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.22$ (br s, 1H), 6.15 (dd, $J = 7.3$, 1.2 Hz, 1H), 6.78 (d, $J = 8.9$ Hz, 1H), 6.80–6.87 (m, 4H), 7.02–7.26 (m, 10H), 7.30 (br t, $J = 7.3$ Hz, 1H), 7.38 (dd, $J = 7.0$, 1.4 Hz, 1H), 7.46 (m, 1H), 7.58 (dd, $J = 8.4$, 1.2 Hz, 1H), 7.60 (dd, $J = 8.2$, 7.0 Hz, 1H), 7.97 (dd, $J = 8.2$, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 115.67$ (d), 117.54 (d), 122.56 (d), 124.22 (d), 124.24 (s), 125.47 (d), 125.66 (d), 125.92 (d), 126.12 (d), 127.16 (2d), 127.53 (3d), 127.92 (d), 127.99 (s), 128.21 (d), 128.85 (s), 129.31 (2d), 129.51 (2d), 129.61 (d), 129.90 (d), 130.94 (s), 130.96 (d), 134.23 (s), 135.34 (s), 135.61 (2s), 138.72 (s), 147.65 (s), 149.88 (s), 164.91 (s); IR (CCl_4): $\tilde{\nu} = 3545$ (OH), 1621 and 1598 (C=C arom), 1570, 1517 and 1468 cm^{-1} (arom); MS: *m*/*z* (%): 449 (43) [M^+], 268 (100), 239 (15); HRMS for $C_{33}H_{23}NO$: calcd 449.1780; found 449.1781. Crystallographic data for (±)-**24**: $C_{33}H_{23}NO$, $M = 449.18$. Crystals (pale straw yellow) were obtained from an acetonitrile at room temperature. Monoclinic; space group $P2_1/c$, $a = 11.1055(1)$, $b = 11.6712(1)$, $c = 18.0627(1)$ Å, $\beta = 102.6753(3)$. Data were collected at 100 K on an Bruker-Nonius KappaCCD diffractometer, running under Nonius Collect software, and with graphite monochromated X-radiation ($\lambda = 0.71073$ Å). A total of 35 scan sets were measured. The low-angle scan sets were re-measured at one tenth the integration time to record the intense low-angle data more accurately. For these short scan sets, only those data with $\theta < 15°$ were used in the merging process. Precise unit cell dimensions were determined by post-refinement of the setting angles of 97904 reflections with $2.9 < \theta < 41.15°$ and data collection. The frame images were integrated with Denzo-SMN[69] and the resultant raw intensity files processed by using a locally modified version of DENZOX.[70] Data were then sorted and merged using SORTAV[70] after application of a semi-empirical absorption correction[71] to remove absorption anisotropy due to the crystal and the mounting medium. The structure was solved by direct methods (SHELXS-97).[72] All non-H atoms were allowed anisotropic thermal motion. Aromatic C–H hydrogen atoms were initially 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. In the final cycles of refinement, all these restraints were relaxed. The OH hydrogen position was obtained from a difference map and was refined without restraints. Refinement with SHELXL 97[72] with full-matrix least-squares on F^2, all the unique data, and with the weighting scheme $w=[\sigma(F_o)^2+(AP)^2+BP]^{-1}$, where $P=[F_o^2/3+2F_c^2/3]$, $A=0.0747$, and $B=0.1877$, converged to $R1=0.0421$. In the final residual map, peaks of $\sim 0.7-0.5\ e\ Å^{-3}$ were observed at the mid-points of all the covalent bonds, consistent with these being due to bonding density effects.

Isolation of enantiopure (*S*)-(−)-24: Enantiopure **24** was prepared from (*S*)-(−)-**23** (1.85 g) in 95% yield by using the same procedure as that for (±)-**23**. M.p. 196–199 °C (hexane/dichloromethane); $[\alpha]_D=-416$ ($c=0.6$ in THF). The enantiopurity was determined after the transformation into (*S*)-(+)-**25** (>99% *ee*).

(±)-8-Amino-2′-methoxy-1,1′-binaphthyl (25): A solution of **23** (2.3 g, 5 mmol) and conc HCl (1 mL, 10 mmol) in dichloromethane (30 mL) was stirred at room temperature overnight; NaOH (20 mL of 1M water solution, 20 mmol) was then added, the dichloromethane phase was separated, and the water phase was extracted with dichloromethane (2 × 5 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated in vacuum. The residue was purified by chromatography on silica gel (50 g) by using a 1:1 toluene/hexane mixture as eluent to give **25** (2.07 g, 92%). M.p. 159–160 °C (toluene); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.82$ (s, 3H), 6.53 (dd, $J=7.4$, 0.8 Hz, 1H), 7.12 (dd, $J=7.0$, 0.8 Hz, 1H), 7.22–7.38 (m, 5H), 7.41 (d, $J=8.8$ Hz, 1H), 7.48 (dd, $J=8.0$, 7.2 Hz, 1H), 7.82–7.88 (m, 2H), 7.96 (d, $J=8.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=56.82$ (q), 110.78 (d), 113.87 (d), 119.07 (d), 122.61 (s), 123.95 (d), 125.10 (d), 125.62 (d), 126.07 (s), 126.20 (d), 126.87 (d), 127.72 (d), 128.69 (s), 128.72 (d), 128.80 (d), 129.74 (d), 132.00 (s), 133.96 (s), 136.01 (s), 144.11 (s), 154.01 (s); IR (CCl_4): $\tilde{\nu}=3484$ and 3395 (NH_2), 1618 and 1594 (C=C arom), 1510 and 1460 (arom), 1260 cm^{-1} (C–O); MS: *m*/*z* (%): 299 (100) [M^+], 268 (35), 267 (70), 239 (4), 133.5 (7); HRMS for $C_{21}H_{17}NO$: calcd 299.1310; found 299.1307.

Isolation of enantiopure (*S*)-(+)-25: Enantiopure **25** was prepared from (*S*)-(−)-**23** (2.3 g) in 92% yield by using the same procedure as that for (±)-**25**. M.p. 130–133 °C (toluene); $[\alpha]_D=+86.2$; ($c=1$ in THF). Chiral chromatography on Daicel Chiralpak AD using a hexane/isopropyl alcohol mixture (9:1) showed >99% *ee* for this product ($t_R=12.0$ min, $t_S=16.6$ min).

(±)-8-Amino-2′-hydroxy-1,1′-binaphthyl (26) *Method A*: Boron tribromide (6 mL, 1M solution in dichloromethane, 6 mmol) was added to a cooled solution (0 °C) of **25** (1.20 g, 4 mmol) in dichloromethane (20 mL). The solution was slowly warmed to room temperature and stirred overnight. The reaction was quenched by adding water (20 mL) and satd $NaHCO_3$ (5 mL), the dichloromethane phase was separated, and the water phase was extracted with dichloromethane (2 × 5 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated in vacuum. The residue was purified by chromatography on silica gel (20 g) with toluene as eluent to give **26** (1.08 g, 95%). M.p. 153–154 °C (toluene); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.70$ (br s, 2H), 5.11 (s, 1H), 6.58 (dd, $J=7.6$, 1.2 Hz, 1H), 7.20 (dd, $J=8.0$, 0.8 Hz, 1H), 7.25 (dd, $J=7.2$, 1.2 Hz, 1H), 7.28–7.41 (m, 4H), 7.30 (d, $J=8.8$ Hz, 1H), 7.52 (dd, $J=7.8$, 7.2 Hz, 1H), 7.84 (dd, $J=7.6$, 1.2 Hz, 1H), 7.88 (d, $J=8.8$ Hz, 1H), 7.94 (dd, $J=8.2$, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=111.49$ (d), 117.46 (d), 119.09 (d), 121.66 (s), 122.23 (s), 123.77 (d), 125.03 (d), 125.61 (d), 127.04 (2d), 127.95 (d), 128.63 (s), 128.74 (s), 130.01 (d), 130.14 (d), 130.43 (d), 133.56 (s), 136.48 (s), 143.98 (s), 150.62 (s); IR (CCl_4): $\tilde{\nu}=3543$ (OH), 3490 and 3398 (NH_2), 1620 and 1599 (C=C arom), 1516 and 1467 cm^{-1} (arom); MS: *m*/*z* (%): 285 (100) [M^+], 268 (35), 267 (30), 254 (6), 239 (6), 119.5 (3); HRMS for $C_{20}H_{15}NO$: calcd 285.1154; found 285.1160.

Method B: A solution of **24** (449 mg, 1 mmol) and conc. HCl (0.2 mL, 2 mmol) in dichloromethane (10 mL) was stirred at room temperature overnight; NaOH (2 mL of 1M water solution, 2 mmol) was then added, the dichloromethane phase was separated, and the water phase was extracted with dichloromethane (2 × 2 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated in vacuum. The residue was purified by chromatography on silica gel (30 g) using a 1:1 toluene/hexane mixture as eluent to give **26** (254 mg, 89%).

Isolation of enantiopure (*S*)-(−)-26: Enantiopure (*S*)-(−)-**26** was prepared from (*S*)-(+)-**25** (1.20 g) in 95% yield by using the same procedure as that for (±)-**25**. M.p. 140–141 °C (dichloromethane/hexane); $[\alpha]_D=-25.9$ ($c=0.8$ in THF). Chiral chromatography on Daicel Chiralcel OD-H using a hexane/isopropyl alcohol mixture (4:1) showed >99% *ee* for this product ($t_S=8.0$ min, $t_R=10.3$ min).

Isolation of enantiopure (*R*)-(+)-26: Enantiopure (*R*)-(+)-**26** was obtained by enantiomeric enrichment of (*R*)-(+)-**26** as follows. (*R*)-(+)-(**25**) (285 mg, 1 mmol, 84% *ee*), prepared by using the same sequence as that employed for its enantiomer [commencing with (*R*)-(−)-**22** (84% *ee*)], was dissolved in hot toluene (5 mL), and the solution was allowed to crystallize overnight. The crystals were isolated by suction and dried to give (±)-(**26**) (41 mg). The mother liquor containing (*R*)-(+)-**26** (244 mg), enriched in 94% *ee*, as revealed by chiral HPLC, was evaporated and the residue was dissolved in dichloromethane (0.5 mL). The solution was over-layered with hexane (3 mL) and set aside at room temperature overnight. The crystals formed were collected to give of (*R*)-(+)-**26** (210 mg, 88%, >98% *ee*).

(±)-8-Acetamido-2′-hydroxy-1,1′-binaphthyl (27): Racemic (±)-**26** (285 mg, 1 mmol) was converted into racemic acetamide (±)-**27** in the same way as enantiopure (*S*)-(−)-**26** was transformed into acetamide (*S*)-(+)-**27**; the procedure afforded (±)-**27** (93%): m.p. 156–158 °C (toluene).

(*S*)-(+)-8-Acetimido-2′-hydroxy-1,1′-binaphthyl (27): Acetyl chloride (214 μL, 3 mmol) was added to a solution of (*S*)-(−)-**26** (285 mg, 1 mmol, 99% *ee*) in pyridine (5 mL), and the mixture was stirred at room temperature overnight. The reaction was quenched by adding 5% HCl (20 mL), the dichloromethane phase was separated and the water phase was extracted with dichloromethane (2 × 5 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated in vacuum. The residue was dissolved in dry methanol (20 mL), solid Na (20 mg) was added, and the mixture was stirred at room temperature for 3 h. The reaction was quenched by adding water (20 mL) and 5% HCl (10 mL) and the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated in vacuum. The residue was purified by chromatography on silica gel (10 g) using toluene as eluent to give (*S*)-(+)-**27** (307 mg, 94%). M.p. 213–215 °C (toluene); $[\alpha]_D=+2.6$ ($c=1.0$ in THF); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.03$ (s, 3H), 5.33 (br s, 1H), 7.09 (d, $J=8.4$ Hz, 1H), 7.22 (br s, 1H), 7.27–7.40 (m, 4H), 7.51–7.56 (m, 1H), 7.58–7.63 (m, 1H), 7.81–7.95 (m, 4H), 8.03 (dd, $J=8.2$, $J=0.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=23.28$ (q), 117.94 (d), 121.35 (s), 122.63 (d), 124.23 (d), 124.65 (d), 125.77 (d), 125.81 (s), 126.42 (d), 126.59 (d), 127.70 (d), 127.73 (s), 128.06 (d), 128.80 (s), 130.28 (d), 130.81 (d), 131.87 (d), 133.10 (s), 133.44 (s), 135.84 (s), 150.65 (s), 168.25 (s); IR ($CHCl_3$): $\tilde{\nu}=3530$ (OH), 3405 (NH), 1688 (C=O), 1619 and 1597 (C=C arom), 1521 and 1428 cm^{-1} (arom); MS: *m*/*z* (%): 327 (65) [M^+], 285 (49), 267 (100), 239 (10); HRMS for $C_{22}H_{17}NO_2$: calcd 327.1259; found 327.1256.

(*R*)-(−)-8-Acetimido-2′-hydroxy-1,1′-binaphthyl (27): (*R*)-(+)-**26** (84% *ee*) was acetylated using the same procedure as that employed for its enantiomer to give the crude (*R*)-(−)-**27** (327 mg, 1 mmol, 84% *ee*). The latter material was dissolved in hot toluene (5 mL) and the solution was allowed to crystallize overnight. The crystalline material was isolated by suction and dried to give (*R*)-(−)-**27** (247 mg, 90%). $[\alpha]_D=-2.5$ ($c=1.0$ in THF). Chiral chromatography on Daicel Chiralcel OD-H, with a hexane/isopropyl alcohol mixture (4:1), showed >99% *ee* for this product ($t_R=7.7$ min, $t_S=8.9$ min).

(±)-8-Dimethylamino-2′-hydroxy-1,1′-binaphthyl (29): A solution of the amino alcohol **26** (285 mg, 1 mmol) in THF (10 mL) and solid $NaBH_4$ (530 mg, 14 mmol) were slowly added (simultaneously) to a solution of the 40% aqueous formaldehyde (2 mL 24 mmol) and a 20% aqueous H_2SO_4 (2 mL) in THF (10 mL) over a period of 15 min at RT. The reaction mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH (200 mL). The resulting suspension was extracted with ethyl acetate (3 × 50 mL), and the extract was dried with $MgSO_4$ and evaporated. The residue was purified by flash chromatography on silica gel (50 g) with toluene to give the amino alcohol **29** (103 mg, 33%) as the faster moving product and **30** (184 mg, 59%) as the slower moving product. M.p. 119–120 °C (toluene); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.71$ (s, 3H), 2.22 (s, 3H), 5.07 (br s, 1H), 7.15 (dd, $J=7.5$, $J=1.4$ Hz, 1H), 7.17–7.19 (m, 2H), 7.23–7.26 (m, 1H), 7.26 (d, $J=8.7$ Hz, 1H), 7.44–7.50 (m, 2H), 7.59 (t, $J=8.2$ Hz, 1H), 7.72 (dd, $J=8.1$, $J=1.3$ Hz, 1H), 7.74 (d, $J=8.7$ Hz, 1H), 7.80 (td, $J=7.9$, 1.2 Hz, 1H), 7.98 (dd, $J=8.1$, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=45.02$ (q), 45.10 (q), 116.90 (d), 118.63 (d), 122.56 (d), 124.46 (s), 124.95 (2d), 125.64 (d), 125.84 (d), 126.33 (d), 127.78 (d), 127.88 (d), 128.47 (s), 129.20 (s), 129.97 (d), 130.14 (s), 131.71 (d), 133.93 (s), 136.70 (s),

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149.06 (s), 151.83 (s); IR (CCl_4): $\tilde{\nu}$ = 3551 (OH), 1621 and 1598 (C=C arom), 1576, 1517, and 1468 cm^{-1} (arom); MS: *m*/*z* (%): 313 (80) [M^+], 268 (100), 265 (42), 239 (28); HRMS for $C_{22}H_{19}NO$: calcd 313.1467; found 313.1466.

Compound (±)-30: Compound (±)-**30** was obtained as the major (polar) product along with **29** (vide supra) as an amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.98 (s, 3H; CH_3), 3.34 (d, *J* = 11.6 Hz, 1H; C*H*H), 3.55 (d, *J* = 11.6 Hz, 1H; CH*H*), 6.27 (d, *J* = 9.8 Hz, 1H; 3′-H), 6.69 (dd, *J* = 7.6, 1.2 Hz, 1H; 7-H), 6.78 (dd, *J* = 7.2, 1.2 Hz, 1H; 2-H), 6.90 (dm, *J* = 7.8 Hz, 1H; 8′-H), 7.21 (td, *J* = 7.8, 1.5 Hz, 1H; 7′-H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H; 6′-H), 7.34 (dd, *J* = 8.2, 7.2 Hz, 1H; 3-H), 7.34 (dd, *J* = 8.2, 1.2 Hz, 1H; 5-H), 7.41 (dd, *J* = 7.5, 1.5 Hz, 1H; 5′-H), 7.44 (dd, *J* = 8.1, 7.6 Hz, 1H; 6-H), 7.58 (br d, *J* = 9.9 Hz, 1H; 4′-H), 7.75 (dd, *J* = 8.2, 1.2 Hz, 1H; 4-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.61 (q, CH_3), 58.47 (s, C-1′), 61.80 (t, CH_2), 105.06 (d, C-7), 117.54 (d, C-5), 123.39 (s, C-9), 123.88 (d, C-2), 124.39 (d, C-3′), 125.77 (d, C-3), 126.42 (d, C-6), 127.29 (d, C-6′), 127.37 (d, C-4), 129.17 (s, C-10′), 129.48 (d, C-5′), 129.85 (d, C-7′), 129.96 (d, C-8′), 134.09 (s, C-1 or C-10), 134.18 (s, C-1 or C-10), 143.86 (s, C-9′), 144.08 (s, C-8), 144.72 (d, C-4′), 200.33 (s, C-2′). IR (CCl_4): $\tilde{\nu}$ = 1666 (C=O), 1621 and 1592 (C=C arom), 1566, 1514, and 1482 cm^{-1} (arom); MS: *m*/*z* (%): 311 (100) [M^+], 296 (22), 268 (31), 266 (19), 253 (14), 239 (11), 86 (40); HRMS for $C_{22}H_{17}NO$: calcd 311.1310; found 311.1310.

(±)-8-Acetamido-3′-hydroxy-1,2′-binaphthyl (34): Boron tribromide (1M in dichloromethane, 1.5 mL, 1.50 mmol) was added to a solution of **16** (341 mg, 1.0 mmol) in dichloromethane (4 mL) at 0 °C, and the mixture was stirred for 18 h at room temperature and then poured into water. Saturated $NaHCO_3$ was then added, and the product was extracted into ethyl acetate (2 × 3 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (20 g), with a 1:1 ethyl acetate/dichloromethane mixture as eluent to produce **34** as a white solid (301 mg, 92%). M.p. 208–211 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (s, 3H), 6.30 (br s, 1H), 7.17 (br s, 1H), 7.32–7.41 (m, 3H), 7.44–7.56 (m, 3H), 7.69–7.84 (m, 5H), 7.95 (dd, *J* = 8.3, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.32 (q), 110.03 (d), 123.94 (d), 124.28 (d), 125.30 (d), 125.95 (s), 126.03 (d), 126.21 (d), 126.86 (d), 127.12 (d), 127.65 (d), 128.44 (s), 128.87 (d), 130.08 (d), 130.99 (d), 131.36 (s), 132.50 (s), 132.75 (s), 134.55 (s), 135.25 (s), 151.85 (s), 168.99 (s); IR ($CHCl_3$): $\tilde{\nu}$ = 3547 (OH), 3426 (NH), 1684 (C–O), 1518, 1495 (arom), 1262 cm^{-1} (C–O); MS: *m*/*z* (%): 327 (26) [M^+], 285 (16), 284 (12), 268 (95), 267 (100), 254 (12), 239 (10), 43 (24); HRMS for $C_{22}H_{17}NO_2$: calcd 327.1259; found 327.1244.

(±)-8-Amino-3′-hydroxy-1,2′-binaphthyl (35): Trichlorosilane (0.75 mL, 7.2 mmol) was added to a mixture of **34** (200 mg, 0.61 mmol) and triethylamine (1.7 mL, 12 mmol) in xylene (14 mL) at 0 °C, and the mixture was stirred at 120 °C for 15 h. After being cooled to room temperature, the mixture was diluted with ethyl acetate (10 mL) and quenched with a small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (20 g) with a toluene-ethyl acetate mixture (9:1) to furnish **35** as a white solid (30 mg, 16%). M.p. 192–193 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.67 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.27–7.35 (m, 2H), 7.36–7.41 (m, 3H), 7.46–7.52 (m, 3H), 7.77–7.84 (m, 2H), 7.90 (dd, *J* = 8.2, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.24 (d), 111.85 (d), 119.42 (d), 121.37 (s), 124.20 (d), 125.22 (d), 126.54 (d), 126.78 (d), 127.08 (d), 127.80 (d), 128.39 (s), 128.88 (d), 129.57 (d), 130.24 (d), 131.17 (s), 132.39 (s), 134.81 (s), 136.02 (s), 143.71 (s), 151.56 (s); IR ($CHCl_3$): $\tilde{\nu}$ = 3549 (OH), 3496 (NH), 3402 (NH), 1597 (arom), 1500 (arom), 1449 (arom), 1263 cm^{-1} (C=O); MS: *m*/*z* (%): 285 (9) [M$^+$], 267 (100), 264 (10), 239 (5), 133.5 (16), 132.5 (11); HRMS for $C_{20}H_{15}NO$: calcd 285.1154; found 285.1162. The small-scale enantiomeric separation was performed on a Daicel Chiralpak AD column using a hexane-methanol-isopropyl alcohol mixture (77:20:3); the retention times were 11.0 and 14.1 min.

Dibenzo[*b*,*kl*]xanthene (36): A solution of **34** (80 mg, 0.24 mmol) in a mixture of ethanol (1.6 mL) and aqueous HCl (10%, 0.5 mL) was stirred under reflux for 16 h and then concentrated under reduced pressure. Water and saturated $NaHCO_3$ were added to the residue and the product was extracted into dichloromethane (2 × 2 mL). Combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure and the residue was purified by chromatography on silica gel (10 g) with toluene as eluent to produce **36** as a bright yellow solid (33 mg, 50%). M.p. 167–168 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97–7.02 (m, 1H), 7.32–7.49 (m, 6H), 7.65 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.86 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.52 (d), 112.24 (d), 115.66 (d), 120.10 (d), 120.71 (s), 121.28 (s), 121.92 (d), 124.81 (d), 126.46 (s), 126.52 (d), 126.70 (d), 126.84 (d), 127.18 (d), 127.23 (d), 128.03 (d), 130.33 (s), 134.49 (s), 134.78 (s), 149.94 (s), 150.51 (s); IR ($CHCl_3$): $\tilde{\nu}$ = 3016 (d), 1628 (C=C arom), 1450 (arom), 1402 (arom), 1276 cm^{-1} (C–O); MS: *m*/*z* (%): 268 (100) [M^+], 239 (17), 237 (7), 134 (19), 119.5 (10); HRMS for $C_{20}H_{12}O$: calcd 268.0888; found 268.0881.

7*H*-Dibenzo[*b*,*kl*]acridine (37): A solution of **34** (150 mg, 0.46 mmol) in a mixture of amyl alcohol (6.0 mL) and hydrazine hydrate (80%, 4.0 mL) was stirred under reflux for 40 h and then evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (15 g) with a 1:1 ethyl acetate/petroleum ether mixture as eluent to afford **37** as brown crystals (96 mg, 78%): m.p. 210–212 °C (toluene); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.46 (dd, *J* = 7.2, 1.0 Hz, 1H), 6.85 (br s, 1H), 6.94 (s, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.18–7.25 (m, 2H), 7.31–7.36 (m, 1H), 7.39–7.44 (m, 1H), 7.50–7.56 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 103.96 (d), 108.22 (d), 115.25 (d), 116.84 (d), 122.22 (d), 122.33 (s), 123.45 (d), 125.52 (d), 125.76 (d), 126.84 (d), 127.19 (d), 127.28 (d), 128.22 (d), 129.38 (s), 129.98 (s), 134.74 (s), 135.61 (s), 137.05 (s), 137.99 (s); IR ($CHCl_3$): $\tilde{\nu}$ = 3411 (NH), 1633 (C=C arom), 1587 (arom), 1478 (arom), 1463 cm^{-1} (arom); MS: *m*/*z* (%): 267 (100) [M^+], 266 (27), 264 (10), 239 (5), 135 (21), 133 (11), 132.5 (14); HRMS for $C_{20}H_{13}N$: calcd 267.1048; found 267.1043.

Asymmetric Michael addition of complex 39 to methyl acrylates: Sodium hydride (0.096 g, 2.4 mmol) was added to a solution of (*R*)-**27** (0.118 g, 0.36 mmol) in CH_2Cl_2, first thoroughly purged with Ar, and the mixture was stirred at room temperature for 3 min under argon. Complex **39** (1.00 g, 2.4 mmol) was then added while stirring, followed 5 min later by methyl acrylate or methyl methacrylate (13.7 mmol), and the reaction mixture was agitated for an additional 5 min [the course of the reaction was monitored by TLC ($CHCl_3$/Me_2CO 5:1)]. The reaction mixture was then quenched with aqueous acetic acid and the product was extracted into chloroform. The organic layer was separated and an aliquot was used to check the *ee* of the glutamic acid (Table 5). The remainder of the organic layer was evaporated and the residue was purified by chromatography on a silica gel column with a $CHCl_3$/Et_2O/AcOH mixture (3:1:1). The catalyst (*R*)-**27** was recovered from the first fraction and recrystallized from benzene (60%). The fraction containing **41** was decomposed with a 1:1 mixture of MeOH and conc. HCl by refluxing for 5 min (until the red color of the solution had disappeared). The resulting solution was evaporated, water was added to the residue, and the insoluble hydrochloride of **38** was removed by filtration. The pH of the filtrate was brought to 8 with aqueous NH_3, the solution was extracted with $CHCl_3$, and the aqueous solution was desalted on Dowex 50 in its H^+ form to give glutamic acid **43**. For yields and *ee*, see Table 5. The *ee* was determined by chiral GLC (Chirasil-Val phase).

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[56] Preliminary X-ray data indicate that the chiral axis in the 1,2′-isomer **17** is rather longer (1.570 Å) than that in **18** (1.496 Å). This structural feature is apparently reflected in the lower barriers to racemization of **16**, **17**, and **35** (Tables 3 and 4).
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[59] The crystallographically suitable crystals were obtained from a CH_2Cl_2 solution by a slow diffusion of hexane.
[60] Interestingly, the X-ray crystallography of (*S*)-(+)-**18** (Figure S4, Supporting Information) revealed the presence of two molecules in the cell, which differ slightly from each other. Thus, for instance, the dihedral angle about the chiral axis in the two molecules (C2-C1-C1′-C2′) differs by 7.9°, being 77.6° and 69.7°, respectively. Interestingly, this angle in the case of racemic (±)-**18** is 89.7°.
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