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Stereoselective Synthesis of Optically Pure 2-Amino-2′-hydroxy-1,1′-binaphthyls

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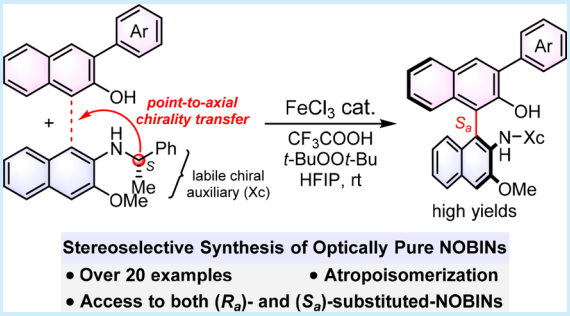
Supporting Information

ABSTRACT: Direct entry to optically pure 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) derivatives by an iron-catalyzed stereoselective oxidative cross-coupling reaction between 2-naphthol and 2-aminonaphthalene with a labile chiral auxiliary is reported. This efficient method offers entry to tailor-designed (R_a)- and (S_a)-NOBINs that are not accessible by any other means.



Axially chiral binaphthyls,[1] such as 1,1′-bi-2-naphthol (BINOL, **1**),[2] 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN, **2**),[3] and 1,1′-bi-2-naphthylamine (BINAM, **3**, Figure 1),[4] serve as privileged chiral entities for ligands and catalysts

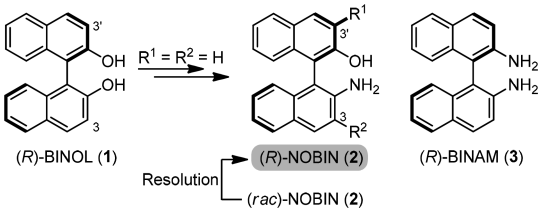


Figure 1. Chiral binaphthyl compounds.

used in stereoselective transformations.[5] The metal-catalyzed oxidative coupling reaction is the most attractive method in terms of step- and atom-economy in their preparation. However, although enantioselective conditions for the synthesis of enantioenriched *C*-1 and *C*-2 symmetric BINOLs, based on chiral iron,[6] copper,[7] and vanadium[8] catalysts have been formulated, direct access to enantiopure NOBINs by direct oxidative coupling methods remains elusive.[9] As a result, the synthesis of optically pure NOBINs is limited to enzymatic and chemical resolution of a racemate[10] and multistep syntheses starting from BINOL (Figure 1).[11] Unfortunately, these methods are mainly confined to NOBINs that lack substitutions at the C-3 and C-3′ positions. These sites are important for projecting the axial chirality around the catalyst's active site and for increasing the barrier for rotation around the biaryl bond (vide supra). Therefore, a general approach to produce optically pure 3,3′-disubstituted-NOBIN derivatives (R^1 and $R^2 \neq$ H) that will afford novel axial chirality compounds is an emerging synthetic challenge that needs to be addressed.

Reported herein is a general solution for preparing optically pure polysubstituted-NOBINs by an iron-catalyzed stereoselective oxidative coupling reaction between 2-naphthols and 2-aminonaphthalenes with a labile chiral auxiliary (Xc, Scheme 1). This scalable transformation is a rare example of a point-to-axial chirality transfer[12] in oxidative coupling reactions, therefore enabling access to optically pure tailor-designed (R_a)- and (S_a)-NOBINs that are not accessible by any other means.

This study commenced by examining the iron-catalyzed oxidative coupling reaction between 2-naphthol (**4a**) and (*S*)-*N*-(1-phenylethyl)naphthalen-2-amine (**5a**, Scheme 1). The latter amine is prepared in a single step on a multigram scale from either 2-bromonaphthalene[13] or 2-naphthol[14] and an inexpensive (*S*)-α-methylbenzylamine compound. Traditionally, synthesis of racemic NOBIN **2** by direct oxidative coupling of naphthol **4a** and 2-aminonaphthalene has been achieved using stoichiometric amounts of copper(II) amine[10b,e,15] or iron(III) complexes.[16] Taking into account environmental considerations, our group developed chemoselective oxidative phenol−phenol[17] and phenol−arene[18] cross-coupling reactions mediated by an $FeCl_3$ catalyst [(10 mol %), *t*-BuOO*t*-Bu (1.5 equiv), HFIP, room temperature]. Under these conditions, the coupling between 2-naphthol **4a** (1.5 equiv) and the free base of **5a** (1 equiv) was inefficient. However, the addition of CF_3COOH (1.25 equiv) was found to be essential for gaining complete consumption of the aminonaphthalene coupling partner (see the Supporting Information), affording the desired NOBIN diastereoisomers **6a** and **7a** (dr = 1.5:1 HPLC ratio) as a separable mixture in 57% and 38% isolated yields, respectively (Scheme 1). The reaction exhibited a high degree of chemoselectivity, with BINOL **1** being the only byproduct.

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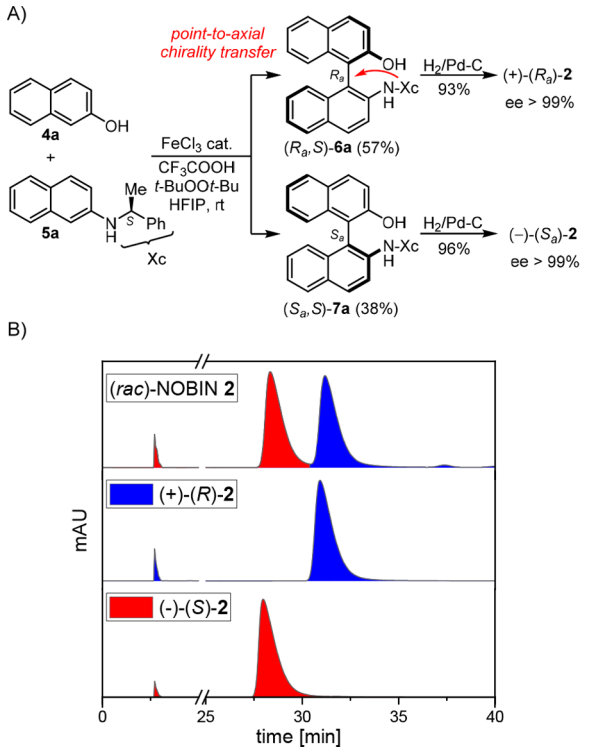
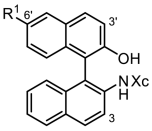
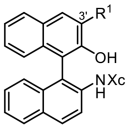
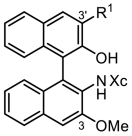
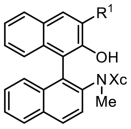
Scheme 1. (A) Asymmetric Synthesis of (R_a)- and (S_a)-NOBIN Enantiomers (2) and (B) Their Chiral-HPLC Chromatograms



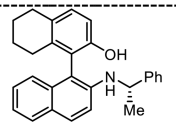
This observation implies that the coupling involves selective oxidation of 2-naphthol to a highly reactive naphthoxyl radical intermediate that reacts with nucleophilic aminonaphthalene.[19] The fact that BINAM is not formed under the reaction conditions emphasizes the mechanistic distinction between Shindo's Rh−C-catalyzed oxidative homo- and cross-coupling of *N*,*N*-dialkylaminonaphthalene.[20] To determine the absolute configuration of NOBINs **6a** and **7a**, the auxiliary benzylic group was hydrogenolyzed from each of the binaphthyls using 10% Pd−C [H_2 (1 atm), ethyl acetate, rt], affording optically pure NOBINs (+)-**2** (from **6a**) and (−)-**2** (from **7a**) with the known absolute configurations of R_a and S_a, respectively (Scheme 1).[3a,10f]

The efficiency of this method was examined for preparing optically pure NOBIN derivatives by coupling various 3- or 6-substituted 2-naphthols with (*S*)-*N*-(1-arylethyl)naphthalen-2-amine derivatives. The reaction was found to be general and highly practical, affording a long list of optically pure diastereoisomeric NOBIN pairs (R_a)-**6** and (S_a)-**7** with good to excellent combined yields (Table 1). Since methods to obtain optically pure substituted NOBINs were not available, a technique to establish the absolute configuration of the NOBIN products was developed.[21] In general, the doublet benzylic-CH_3 peak in the ^{1}H NMR spectrum of the NOBIN **6** serial resonates downfield with respect to the same peak in the NOBIN **7** partners. For example, the benzylic-CH_3 protons in (R_a,*S*)-**6a** resonate at δ = 1.29 ppm, whereas in (S_a,*S*)-**7a** these protons resonate at δ = 1.22 ppm. This assignment was supported by X-ray diffraction of compound (R_a,*S*)-**6f** (Figure 2B). However, in some cases, esterification of the naphtholic unit with pivaloyl chloride was needed to obtain selective NOE correlations between the *t*-Bu group of the pivaloyl group and either, the phenyl protons in the *R*-isomers (e.g., (R_a,*S*)-piv-**6a**, Figure 2A)

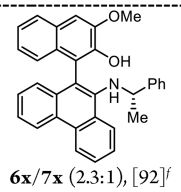
Table 1. Reaction Scope

NOBIN		R^1	Ar	*dr* [**6**:**7**][b]	**6** [%][c]	**7** [%][c]
	**a**	H	Ph	1.5:1	57	38
	b	Br	Ph	1.7:1	58	34
	c	CO2Me	Ph	1.6:1	47	25
	d	CO2i-Pr	Ph	1.9:1	51	31
	e	(4-t-Bu)C6H4	Ph	1.5:1	55	34
	**f**[d]	CO_2Me	Ph	2.3:1	57	35
	g	CO_2i-Pr	Ph	2.3:1	71	24
	h	CO_2i-Pr	2-Nf	2.5:1	66	25
	i[e]	OMe	Ph	1.6:1	55	35
	j	Br	Ph	1:1.1	42	49
	k	I	Ph	1:1.1	41	52
	l	(4-*t*-Bu)C_6H_4	Ph	1:3.0	16	47
	m	(4-*t*-Bu)C_6H_4	2-Nf	1:3.0	22	57
	n	(2-Me)C_6H_4	Ph	1:1.6	29	36
	o	(2-Me)C_6H_4	2-Nf	1:1.5	30	44
	**p**	H	Ph	1:4.0		77
	q	(4-*t*-Bu)C_6H_4	Ph	0:1.0		84
	r	(4-*t*-Bu)C_6H_4	2-Nf	1:5.0		67
	s	(3,5-diCF_3)C_6H_3	Ph	1:8.6		82
	t	(3,5-diCF_3)C_6H_3	2-Nf	1:30		66
	**u**	CO_2Me	Ph	1.9:1	[58][f]	
	v	(4-*t*-Bu)C_6H_4	Ph	0:1		50

Xc = -CH(CH_3)Ar



6w/**7w** (1.27:1), [90][f]



6x/**7x** (2.3:1), [92][f]

[a]Reaction conditions: 2-aminonaphthalene (1 equiv), 2-naphthol (1.5 equiv), $FeCl_3$ (10 mol %), *t*-BuOO*t*-Bu (1.5 equiv), CF_3COOH (1.25 equiv), HFIP, rt. [b]The diastereoselectivity ratios were determined by HPLC analysis or by ^{1}H NMR spectroscopy. [c]Isolated yield of pure products. [d]The reaction was performed on a 3 mmol scale. [e]The reaction was performed on a 4 mmol scale. [f]Combined yield of an inseparable mixture of products.

or the methyl protons in the *S*-isomer (e.g., (S_a,*S*)-piv-**7a**) of the chiral auxiliary group.

The basic factors that determine the observed stereoselectivity were investigated. Rotation around the biaryl bond, a consequence of BINOL-to-metal charge transfer, results in a rapid loss of optical purity in 3,3′-unsubstituted BINOLs.[6a,17a,c,22] Similarly, (R_a)-NOBIN-**2** underwent complete racemization within 5 h in the presence of $FeCl_3$ (10 mol %, Figure 3A, black circles); this phenomenon was utilized by Kočovsky for the kinetic resolution of **2** by a stoichiometric amount of chiral copper amine complexes.[10b] Furthermore, a rapid atropoisomerization process took place when NOBINs **6a** and **7a** were treated in two separate vials under the reaction conditions, leading to the formation of thermodynamic mixtures with similar diatereoisomeric ratios (**6a**:**7a**, 1.5:1,

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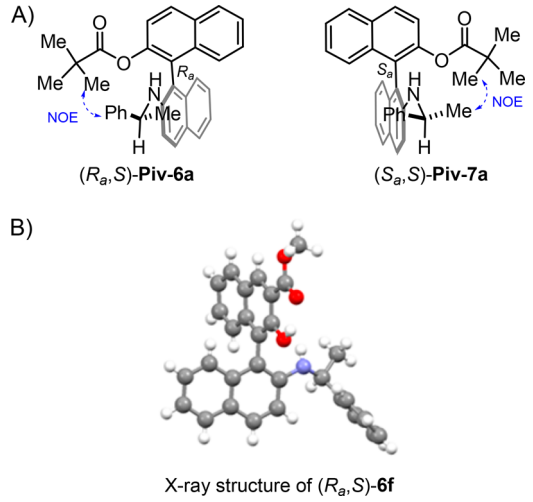

Figure 2. (A) Key NOE correlations that aid in the assignment of the absolute configuration of NOBINs **6** and **7** serials and (B) ORTEP diagram of compound **6f**.

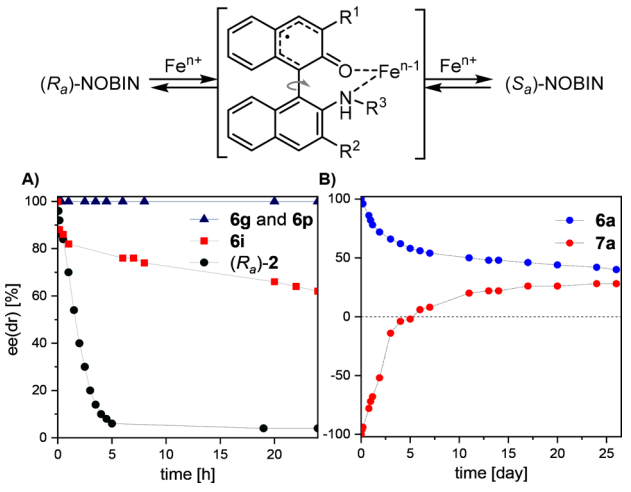

Figure 3. Atropoisomerization studies of (A) NOBINs (R_a)-**2** (black circles), (R_a,S)-**6g** and (R_a,S)-**6p** (blue triangles), and (R_a,S)-**6i** (red squares). (B) NOBINs (R_a,S)-**6a** (blue circles) and (S_a,S)-**7a** (red circles). Conditions: NOBIN (1 equiv), $FeCl_3$ (10 mol %), *t*-BuOO*t*-Bu (1.5 equiv), CF_3COOH (1.25 equiv), HFIP, rt.

Figure 3B, red and blue circles). The fact that the oxidative coupling between reactants **4a** and **5a** afforded NOBINs **6a** and **7a** with similar selectivity (Scheme 1 and Table 1, entry 1) implies that an atropodiastereomeric equilibrium exists during the oxidative coupling. It is suspected that 6′-substituted-3,3′-unsubstituted NOBIN products (R_a,S)-**6a−e** and (S_a,S)-**7a−e** (Table 1), which were obtained with low stereoselectivity (dr = 1.5:1−1.9:1), are also optically unstable under the coupling conditions. Interestingly, whereas 3′-methoxy-NOBIN **6i** underwent racemization at room temperature (Figure 3A, red squares), its constitutional isomer 3-methoxy-NOBIN **6p** is stable under the reaction conditions (Figure 3A, blue triangles). It is possible that the latter NOBIN adopts a conformation, in which the benzylic group points away from the neighboring methoxy group at a location that prevents the rotation. Furthermore, NOBINs with bulky groups *meta* to the biaryl bond have high rotation barriers; therefore, they are not prone to isomerization at room temperature (see **6g**, Figure 3A, blue triangles).

On the basis of this study, it is suggested that the degree of stereoselectivity obtained during the formation of 3′-substituted-NOBINs, such as **6f**/**7f−6o**/**7o**, results from face selection during the biaryl bond-forming step. The coupling of 3-aryl-2-naphthols with 3-methoxy-2-aminonaphthalene (**5b**) afforded (S_a,S)-NOBINs **7p−t** with high efficiency and excellent S_a-selectivity. To rationalize the S_a-selectivity in NOBIN **7q**, which was isolated as a single compound in 84% yield, we postulated a transition state that involves inner-sphere coupling between a ligated naphthoxyl radical and chelated aminonaphthalene **5** from the opposite face of the bulky phenyl group of the chiral auxiliary (see TS-1, Figure 4). Chiral tertiary

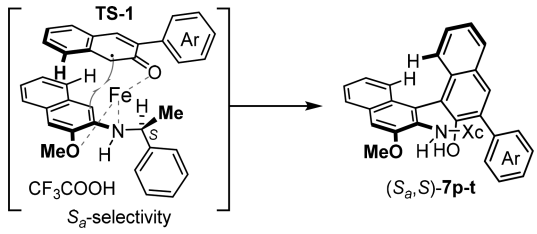

Figure 4. Postulated TS for explaining the *S*-selectivity observed in NOBINs **7p−t**.

2-aminonaphthalenes were also suitable coupling partners. Whereas NOBIN products **6u**/**7u** were obtained as inseparable mixtures, NOBIN **7v** was obtained as a single product in 50% yield. Other chiral auxiliaries were examined, and the coupling of *N*-(*S*)-(1-(2-naphthyl)ethyl)-2-aminonaphthalene (**5c**) instead of aminonaphthalene **5a** was not found to be beneficial with respect to both the selectivity and the efficiency (compare **6g**/**7g** with **6h**/**7h** and **6q**/**7q** with **6r**/**7r**). It is, therefore, suggested that the (R_a,S)-**6** diastereoisomers are formed as major isomers when atropodiastereomeric equilibrium is feasible during the coupling (NOBIN **6a-e** and **6i**) or for 3′-CO_2R-NOBIN derivatives such as **6f−h** and **6u**. On the other hand, NOBINs with bulky substituents at the C-3 or/and C-3′ positions that are formed under kinetic control showed a preference to the formation of (S_a,S)-NOBINs (see **7j−t** and **7v**).

The applicability of this method for supplementing sufficient quantities of optically pure NOBINs was proven by performing large-scale coupling, as demonstrated in the synthesis of NOBINs **6f**/**7f** and **6i**/**7i** on a multimmol scale without reduced coupling efficiency. The removal of the chiral auxiliary from NOBINs **6**/**7** was successfully achieved by simple hydrogenolysis (H_2, 10% Pd/C, ethyl acetate, rt), affording, for the first time, optically pure NOBINs **8−10** with different substituents on the binaphthalene backbone (Figure 5A). Finally, the novel NOBIN synthesis provides a new access to a class of chiral phosphoric acids[23] with tunable nitrogen atoms near the active phosphate site, thereby offering an additional dimension of modulation.[24] Indeed, *C*-1 symmetric NOBIN-based phosphoric acids **11a**, **11b**, **12**, and **13** (Figure 5B) were prepared with high yields by standard methods (see the Supporting Information).

In conclusion, a practical synthesis of optically pure NOBINs, based on an iron-catalyzed stereoselective oxidative cross-coupling reaction between substituted 2-naphthols and 2-aminonaphthalenes with labile chiral auxiliary, was developed. Evidence for the existence of an atropodiastereomeric equilibrium during the coupling was found, and the effect of

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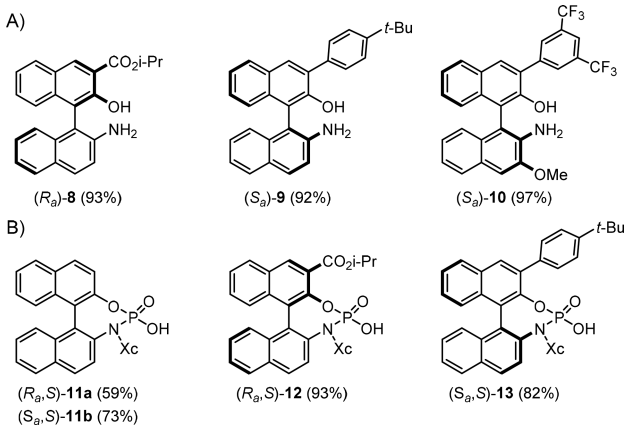

Figure 5. (A) Optically pure substituted NOBINs **8**–**10** and (B) NOBIN-based phosphoric acids **11a**, **11b**, **12**, and **13**.

bulky aryl groups *meta* to the biaryl bond on the level of stereoselectivity was evident. Finally, this work provides a synthetic strategy for preparing optically pure tailor-designed (R_a)- and (S_a)-NOBINs that are needed in asymmetric catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00800.

Full experimental procedures, characterization data, and NMR spectra (PDF)

Accession Codes

CCDC 1823309 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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