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Synthesis of New Axially Chiral Iodoarenes

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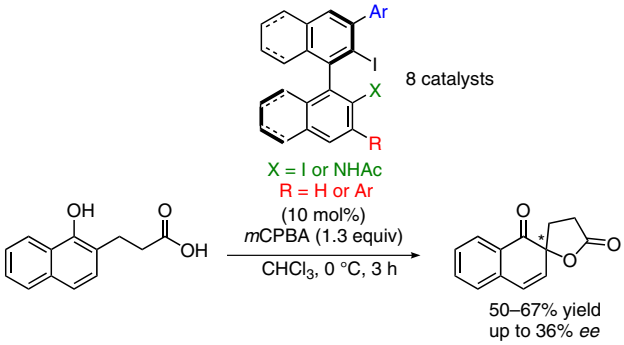

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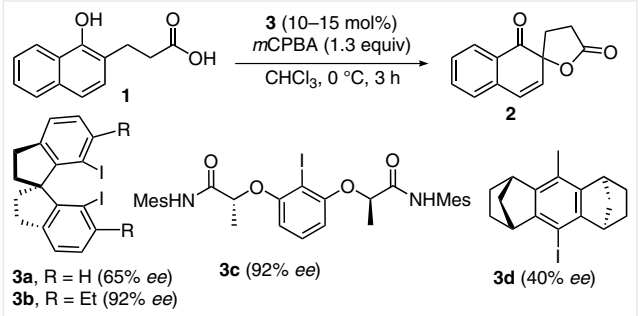
Abstract A new family of axially chiral iodoarenes derived from commercially available (*R*)-1,1′-binaphthyl-2,2′-diamine have been synthesized and employed as catalysts in Kita's enantioselective oxidative spirolactonization of propanoic acid tethered 1-naphthol. Through this study, we explored the relationship between the hypervalent iodoarene geometry and enantioselectivity, contributing to the current understanding of axial-to-central chirality transfer in organoiodine(III) catalysis.

Key words chiral iodane, hypervalent iodine, dearomatization, stereoselective synthesis, spirolactonization

The construction of complex molecules from simple and easily available aromatic compounds using a dearomatization strategy has been extensively explored by organic chemists. Among these strategies, enantioselective dearomatization of phenol derivatives[1] mediated by chiral hypervalent iodine reagents (iodanes) has drawn significant attention due to their low toxicity, stability towards moisture, and ease of handling.[2] Moreover, these oxidants can be selectively generated in situ,[3] thus minimizing the accumulation of unwanted waste. In spite of significant advances over the years, the development of catalytic enantioselective dearomatizations still remains one of the most challenging areas in asymmetric hypervalent iodine catalysis.[2f,m] In 2008, Kita et al. disclosed the first example of a highly enantioselective oxidative spirolactonization of propanoic acid tethered 1-naphthols with a novel rigid chiral iodane(III) compound based on the spirobiindane backbone **3a** (Scheme 1).[4a] While stoichiometric amounts of precatalyst **3a** were required for high enantiomeric excess (86%), moderate enantioselectivity was obtained with catalytic loading. Subsequently, the same group found that substituting the *ortho* position provided the best enantioselectivity (up to 92%, for **3b**).[4b] Later, Ishihara et al. reported that a new flexible C_2-symmetric iodoarene **3c** was an efficient precatalyst for the same reaction, producing spirolactones with high enantioselectivity (up to 92%).[4c,d] In 2015, Ibrahim et al. identified a new *anti*-dimethanoanthracene scaffold-based chiral iodoarene **3d** that induced moderate enantioselectivity in the spirolactonization.[4e] Also in 2015, Ishihara et al. developed highly enantioselective oxidative spirolactonization of 1-naphthol derivatives using chiral ammonium hypoiodite catalysis.[4f] Despite these achievements,[4,5] the development of new, efficient chiral hypervalent iodine precursors and a better understanding of the factors controlling the enantioselectivity in iodine(III) catalysis is still highly desirable.[2,4–6]



Scheme 1 Previous work on enantioselective oxidative spirolactonization of 1-naphthol **1**

Based on our experience in organocatalysis[7] and motivated by our recent interest in hypervalent iodine chemistry,[8] we have initiated a research project oriented toward the development of a catalyst family displaying tunable structural properties based on an axially chiral backbone. Wirth et al. first reported, in 2007, the use of 2,2′-diiodo-1,1′-binaphthyl (BINI) as a chiral iodine(III) precursor for the enantioselective α-oxytosylation of ketones.[9] In 2008

Kita et al.[4a] employed this oxidant precursor in stoichiometric amounts for enantioselective spirocyclization. In both studies, the enantioselectivities achieved were low (<10% ee). Due to poor enantioselectivity in both reactions, these structures were overlooked until the Quideau group reintroduced BINOL-derived iodoarenes as a promising backbone in asymmetric hypervalent iodine organocatalysis.[10] In 2013, Berthiol et al. also demonstrated that 3,3′-diiodo-BINOL-fused maleimide derivatives could mediate the α-functionalization of ketones with enantioselectivities comparable to the best results reported to date (46%[5c] vs 54% ee by Legault et al.[5a]). Despite the potential of axial-to-central chirality transfer in iodide(III) catalysis, existing scaffolds are limited in their tunability and/or synthetically challenging.[11] Taking into account the above-mentioned considerations, we designed a family of 2,2′-diiodo-1,1′-binaphthyls containing two main adjustable features: (i) modulation of the steric hindrance surrounding the hypervalent iodine center by introducing 3,3′-diaryl substituents on the binaphthyl **4**, (ii) modulation of the rigidity by additional noncovalent interactions between the group **X** and the iodine center (Figure 1). We report our initial efforts toward the development of novel chiral iodoarenes and their evaluation in the enantioselective Kita's spirolactonization.

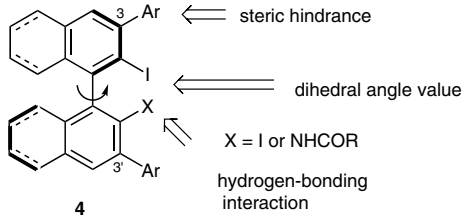
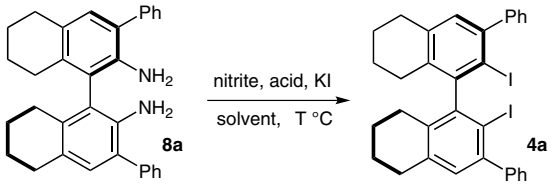


Figure 1 Targeted structures

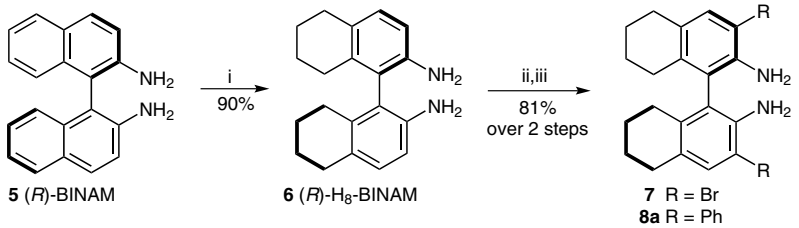
After designing an appropriately modular scaffold starting from commercially available (*R*)-1,1′-binaphthyl-2,2′-diamine [(*R*)-BINAM, **5**], a late-stage Sandmeyer reaction was chosen to introduce the iodine atoms (Scheme 2), despite the difficulties of such a reaction with hindered substrates.[12] This challenging system provided a platform to develop a highly efficient protocol for the Sandmeyer reaction with various 3,3′-diaryl (*R*)-BINAMs. First, **5** was reduced to (*R*)-H_8-BINAM (**6**) with Ni/Al alloy in good yield (Scheme 2).[13a] Compound **6** was then halogenated selectively at the 3,3′-positions with *N*-bromosuccinimide allowing subsequent arylation by Suzuki–Miyaura coupling.[13b] Due to the moderate yield for the rearomatization of **8a** (<50%), we decided to continue the synthesis with the octahydrogenated structure.[14] With the desired 3,3′-diphenyl-H_8-BINAM (**8a**) in hand, the stage was set for the proposed Sandmeyer reaction. At this step, we were particularly concerned about partial racemization of **8a** during the reaction.[15] Although stepwise methods involving the isolation of diazonium mercurate salts have been developed to overcome this issue,[15c] we wanted to develop a one-pot diazotization–iodination of the 3,3′-diphenyl (*R*)-H_8-BINAM (**8a**) without the use of toxic heavy metals (Table 1). Our first attempts under classical conditions were unsuccessful (entries 1–3). However, when the reaction was carried out with sodium nitrite, potassium iodide, and trifluoroacetic acid in water, the desired 3,3′-diphenyl-H_8-BINI (**4a**) was isolated in 11% yield without noticeable loss of enantiopurity. With this result in hand, a number of experiments were

Table 1 Survey of Conditions for the Sandmeyer Reaction[a]



Entry	Nitrite	Acid	Solvent	T (°C)	Yield[b] (%)
1	*t*-BuONO	–	MeCN	0 to 60	–
2	$NaNO_2$	TFA	MeCN	0	–
3	$NaNO_2$	TFA	H_2O	0	11
4	$NaNO_2$	H_2SO_4	H_2O	0	–
5	$NaNO_2$	6 M aq HCl	H_2O	0	36
6	$NaNO_2$	48% aq HBr	H_2O	0	41
7	$NaNO_2$	33% HBr in AcOH	DMSO	r.t.	50[c]
8	$NaNO_2$	33% HBr in AcOH	DMSO	0 to r.t.	45
9	$NaNO_2$	33% HBr in AcOH	DMF	0 to r.t.	48

[a] General conditions: amine **7a** (0.05 mmol), nitrile (0.40 mmol), KI (0.80 mmol), solvent (1.0 mL).
[b] Yields refer to chromatographically pure product.
[c] Undesired rearomatization was observed.[16]

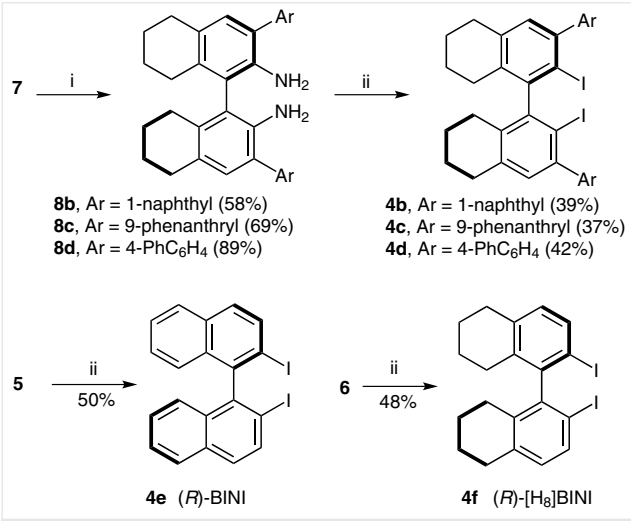


Scheme 2 Synthesis of 3,3′-diphenyl (*R*)-H_8-BINAM (**8a**). *Reagents and conditions*: (i) Ni/Al alloy, *i*-PrOH–H_2O, 90 °C, 120 h; (ii) NBS (2.2 equiv), THF, 0 °C, 1 min; (iii) $Pd(OAc)_2$ (0.1 equiv), Ph_3P (0.4 equiv), $Ba(OH)_2·8H_2O$ (4 equiv), $PhB(OH)_2$ (3 equiv), DME–H_2O, reflux, 24 h.

conducted to improve the yield. First, it was observed that the reaction is significantly affected by the acid used, with hydrobromic acid providing the best yield (entries 3–6). We were pleased to see that when 33% hydrobromic acid in acetic acid was employed, the desired product was isolated in higher yield albeit with the formation of a rearomatized side product (entry 7).[16] This side reaction was completely depressed by a modification of the reaction conditions, with only a slight decrease in the yield of **4a** (entry 8). We obtained very similar results when *N*,*N*-dimethylformamide was used as the solvent (entry 9).

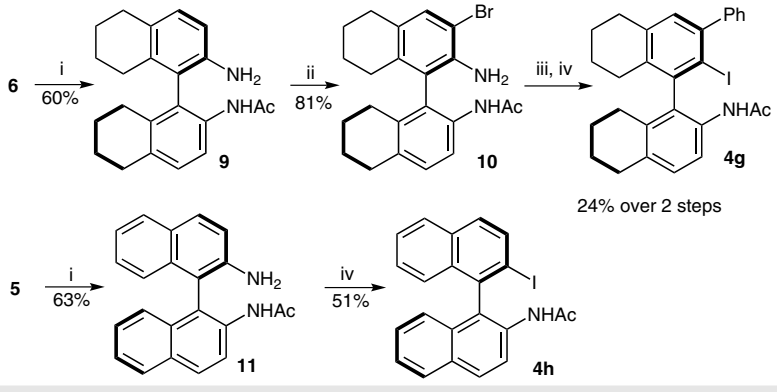
With these results in hands, we next synthesized three representative iodoarene precursors **4b**–**d** possessing different steric environments at the 3,3′-positions in modest yields (Scheme 3). A pair of unsubstituted catalysts **4e**[15e,16] and **4f**[16] were also synthesized to investigate the full range of steric environments (Scheme 3). Next, we focused on the synthesis of non-C_2-symmetric hypervalent iodine precursors. To that end, (*R*)-BINAM (**5**) and (*R*)-H_8-BINAM (**6**) were monoacylated with acetic anhydride in the presence of acetic acid (Scheme 4). Disappointingly, the monoacylation of 3,3′-diphenyl-H_8-BINAM (**8a**), resulted in an unsatisfactory yield (<20%),[17] so the synthesis was continued with only unsubstituted BINAMs.

Product **9** was subjected to the bromination conditions described above, but a mixture of mono- and dibrominated products were isolated with a combined yield of 24%. Fortunately, with a solution of bromine in acetic acid, the monobrominated H_8-BINAM **10** could be isolated in 81% yield. Despite all of our attempts to introduce a second bromine on the more electron-poor acetanilide ring of **10**, only degradation was observed. The Suzuki–Miyaura coupling of phenylboronic acid with monobrominated H_8-BINAM **10** led to the desired coupling product in a good yield, which was carried into a one-pot diazotization–iodination reaction to afford the expected non-C_2-symmetric product (*R*)-**4g**. The unsubstituted iodoarene precatalyst **4h** was prepared from **5** by monoacylation and Sandmeyer reaction (Scheme 4).



Scheme 3 Synthesis of new 3,3′-disubstituted H_8-BINIs **4**. *Reagents and conditions*: (i) $Pd(OAc)_2$ (0.1 equiv), Ph_3P (0.4 equiv), $Ba(OH)_2{\cdot}8H_2O$ (4 equiv), $ArB(OH)_2$ (3 equiv), DME–H_2O (10:1), reflux, 24 h; (ii) $NaNO_2$ (8 equiv), KI (10 equiv), DMSO, 0 °C to r.t.

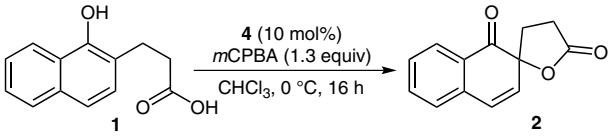
To test the potential application of these new chiral iodoarenes as hypervalent iodine organocatalysts, we used Kita's spirolactonization as a model reaction (Table 2).[4] On the basis of previous work,[4a,b] 10 mol% of (*R*)-BINI **4e** and 1.3 equivalents of 3-chloroperbenzoic acid were premixed for 10 minutes at 0 °C to preform the active hypervalent species,[18] then propanoic acid tethered 1-naphthol **1** was added. Chloroform was selected as a non-coordinating apolar solvent to favor an associative mechanism for the spirocyclization.[19] Precatalyst **4e** afforded the desired spirolactone **7** in 55% yield with <5% ee (entry 1) which is consistent with previous observations reported by Kita's group.[4a] Interestingly, non-C_2-symmetric iodoarene precatalyst **4h** gave better enantioselectivity (23% ee) than C_2-symmetric (*R*)-BINI **4e** (entry 1 vs 2). Similarly, substituting H_8-BINI **4f** for BINI **4e** in the spirolactonization reaction afforded an increase in enantioselectivity, presumably due to variation in

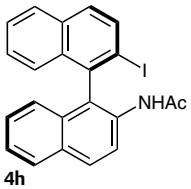
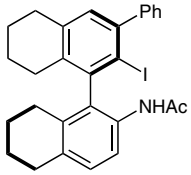
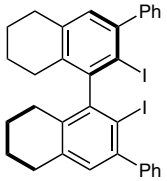
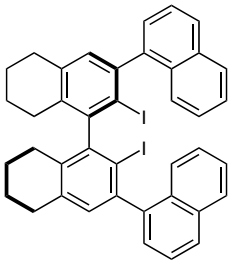
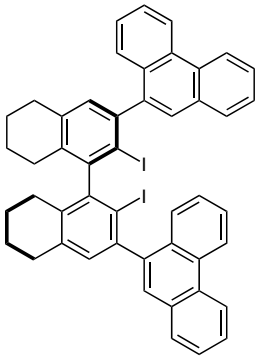
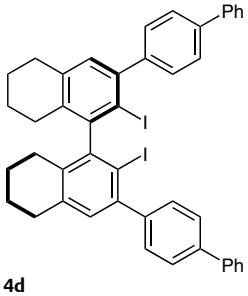


Scheme 4 Synthesis of non-C_2-symmetric BINIs **4**. *Reagents and conditions*: (i) AcOH (10.0 equiv) Ac_2O (1.1 equiv), CH_2Cl_2, 0 °C to r.t., 12 h; (ii) Br_2 (20 equiv), AcOH, r.t., 20 min; (iii) $Pd(OAc)_2$ (0.1 equiv), Ph_3P (0.4 equiv), $Ba(OH)_2{\cdot}8H_2O$ (4 equiv), $PhB(OH)_2$ (3 equiv), DME–H_2O, reflux, 24 h; (iv) $NaNO_2$ (8 equiv), KI (10 equiv), DMSO, 0 °C to r.t., 6 h.

the dihedral angle of **4**. Strikingly, a reversal of enantioselectivity was observed that is directly related to the presence of the amide function. Indeed, the combination of both features (non-C_2-symmetric and partially hydrogenated backbone) in **4a** provided the opposite enantiomer as the major product with similar enantioselectivity (entry 4). The introduction of aryl groups at the 3,3′-positions exerted a beneficial effect on the enantioselectivity with the 1-naphthyl-substituted catalyst **4b** performing slightly better than the other catalysts (entries 5–8). Finally, lowering the temperature to –30 °C did not improve the enantioselectivity and gave lower yields (entry 10).

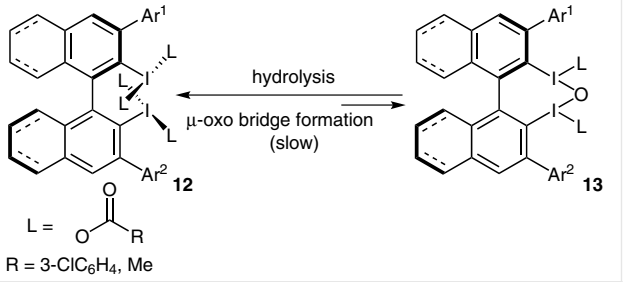
Table 2 Evaluation of Precatalysts in the Spirolactonization of **1**[a]



Entry	4	Yield[b] (%)	ee[c] (%)	Config[d]
1	BINI **4e**	55	2	*S*
2	 **4h**	61	23	*R*
3	H_8-BINI **4f**	67	22	*S*
4	 **4g**	62	24	*R*
5	 **4a**	64	31	*S*
6	 **4b**	63	36	*S*
7	 **4c**	59	30	*S*
8	 **4d**	53	33	*S*
9[e]	**4a**	60	30	*S*
10[f]	**4a**	50	31	*S*
11[g]	**4a**	61	1	*S*

[a] General conditions: **1** (0.05 mmol), $CHCl_3$ (1.0 mL).
[b] Yields refer to chromatographically pure product.
[c] Determined by HPLC analysis on chiral stationary phase.
[d] Absolute stereochemistry by comparing the optical rotation.[4]
[e] AcOH (5 equiv) was added.
[f] Reaction conducted at –30 °C.
[g] MeCN was used as the solvent.

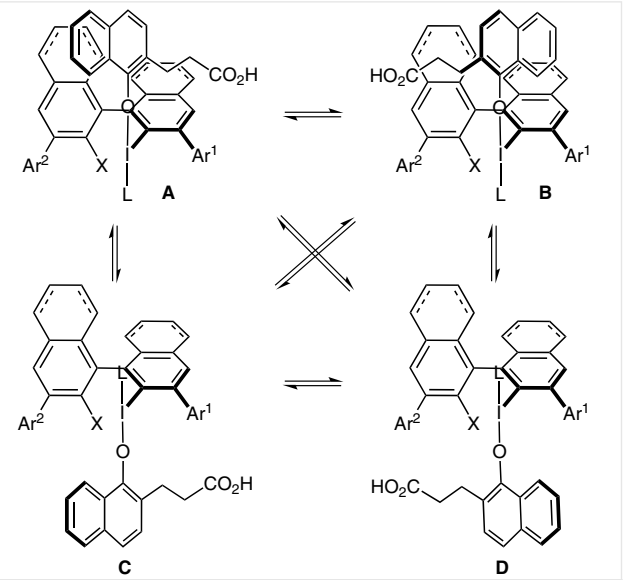
Since iodanes generally adopt a T-shaped conformation[20] with elongated I–O bonds,[21] the hypervalent form of **4** can exist as an iodine(III) tetracarboxylate **12** or a μ-oxo-bridged diodine(III) **13**, the latter being demonstrated by the group of Ochiai with the X-ray crystal structure of diacetoxy-λ³-iodobinaphthyl (Ar^1 = Ar^2 = H, L = OAc, Scheme 5).[6d] In addition, other, X-ray crystallographic studies have shown that aryl-λ³-iodanes free of acid can exist in an oligomeric state where they are linked by μ-oxo bridges.[21] On the other hand, aryl-λ³-iodanes mainly adopt an unbridged structure where two carboxylate groups are attached to the same iodine in the presence of an external acid source. This difference in structure is mainly due to the lability of μ-oxo-bridged iodine(III) under acidic conditions.[6d,22] Thus, the generation of 3-chlorobenzoic acid in the course of the spirolactonization should favor the formation of iodine(III) tetracarboxylate **12** (Scheme 5).[6d] As a result, the active catalyst could be **12** rather than μ-oxo-bridged species **13**. To support this, a control experiment was performed in which the oxidative lactonization was



Scheme 5 Possible of active catalyst form

carried out in the presence of excess acetic acid (Table 2, entry 9). As expected, the desired spirolactone **2** was isolated with similar yield and enantioselectivity, indicating the possibility of an unbridged active catalyst.[22a]

To rationalize the moderate enantiomeric excess obtained for this new series of chiral precatalysts **4**, we hypothesize that the iodine(III) tetracarboxylate **12** may interconvert between four transient intermediates **A**–**D** through ligand-exchange reactions between the phenol and iodine(III) carboxylate (Scheme 6). Accordingly, two subunits of **4** (i.e., 1,1′-binaphthyl moiety and 3,3′-diaryl-substituents) could govern the stereocontrol of the spirocyclization. Of the four transition state models, **A** and/or **B** are expected to be favored for the catalyst bearing substituents on the 3,3′-positions of BINI **4a**–**d** because **C** and **D** exhibit a destabilizing interaction between the aryl group of **4a**–**d** and naphthol derivative **1**. This could explain the better enantioselectivities observed with disubstituted precatalysts **4a**–**d**. Alternatively, the unsubstituted C_2-symmetric precatalyst **4e** could coexist in the four transition states leading



Scheme 6 Putative intermediates **4**

to the formation of racemic product **1**. By analogy with Ishihara's catalyst,[4c,d] two possible conformations are conceivable for the iodane precatalysts **4g**,**h** containing an amide group. The first conformer **14** would form a hydrogen bond between the amide and the ligands attached to the iodine atom, while the second one **15** could be stabilized by n–σ* interactions between the iodine(III) center and carbonyl oxygen (Figure 2). These additional non-covalent interactions may favor the transition states leading to the opposite enantiomer of **1** with the same enantioselectivity as obtained with **4a**–**d**.

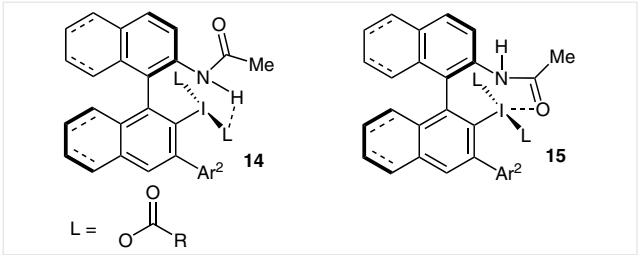


Figure 2 Two possible conformations of the active catalyst derived from **4g**,**h**

In summary, we have developed a suitable pathway to access a new family of axially chiral iodoarenes derived from commercially available (*R*)-BINAM. We have demonstrated the efficiency of these new iodoarenes as catalysts in Kita's spirolactonization of propanoic acid tethered 1-naphthol. Both the 3,3′-diaryl substituents and the H-bond amide donor in the octahydrogenated BINI backbone were key structural features for controlling stereoselectivity. The highly versatile synthetic approach should allow for modulation and optimization of the catalytic behavior of these precatalysts. Efforts towards achieving this goal are underway in our laboratory and will be reported in due course.

All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Analytical TLC was performed on plates precoated with silica gel layers. NMR spectra (^{1}H, ^{13}C) were recorded with 500 and 300 MHz spectrometers. Flash column chromatography was carried out using Merck Geduran 40–63 μm particle size silica gel. Preparative TLC was performed using Merck silica gel 60 F254. HRMS were recorded using ESI and a TOF analyzer, in positive-ion or negative-ion detection mode.

(*R*)-5,5′,6,6′,7,7′,8,8′-Octahydro-1,1′-binaphthyl-2,2′-diamine (6)

(*R*)-BINAM (**5**, 1 g, 3.52 mmol) and Ni–Al alloy (1:1, 7.04 g) were suspended in H_2O–*i*-PrOH (1:1, 800 mL). The mixture was heated to reflux with intensive stirring, and then 1% aq NaOH solution (800 mL) was added dropwise via an addition funnel over 1 h. When the addition was complete, the mixture was stirred vigorously at reflux for 5 d. The mixture was then cooled to r.t., filtered through a pad of Celite and the Celite was washed with EtOAc. The resulting biphasic solution was transferred into a separatory funnel, the layers were separated, and the aqueous layer was extracted with EtOAc (3 ×). The combined organic extracts were washed with water (2 ×) and brine, and

dried (Na_2SO_4). The inorganic salts were removed by filtration, and the organic layer was concentrated under reduced pressure with silica gel to afford a crude residue that was purified by chromatography (silica gel, heptane–EtOAc, gradient from 95:5 to 90:10) to afford the product as a white solid; yield: 999 mg (90%); mp 209–211 °C.

IR (neat): 3446, 3360, 3008, 2950, 2937, 2911, 1561, 1473, 1410, 1362, 1251, 1189, 1141, 1080, 1010, 805, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.91 (d, *J* = 8.0 Hz, 2 H), 6.60 (d, *J* = 8.0 Hz, 2 H), 3.32 (br s, 4 H), 2.73–2.69 (m, 4 H), 2.32–2.11 (m, 4 H), 1.76–1.61 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6 (2 Cq), 136.2 (2 Cq), 129.3 (2 CH), 127.7 (2 Cq), 122.0 (2 Cq), 113.1 (2 CH), 29.4 (2 CH_2), 27.0 (2 CH_2), 23.5 (2 CH_2), 23.3 (2 CH_2).

HRMS (ES^+): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{24}N_2Na$: 315.1832; found: 315.1837.

(*R*)-3,3′-Dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diamine (7)

To a stirred suspension of (*R*)-H_8-BINAM **6** (537 mg, 1.84 mmol) in THF, cooled to approx. 0 °C with an NaCl/ice-water bath, was added NBS (720 mg, 4.04 mmol, 2.2 equiv) in one portion. The mixture was stirred vigorously at 0 °C for 1 min, during which time the solution progressively turned dark brown. The mixture was then quenched with sat. $NaHCO_3$ and sat. Na_2SO_3 at 0 °C, and stirred vigorously for several minutes. The mixture was then diluted with EtOAc and H_2O and poured into a separatory funnel, the layers were separated, and the aqueous layer was extracted with EtOAc (3 ×). The combined organic extracts were washed with brine and dried (Na_2SO_4). The inorganic salt was removed by filtration, and the organic layer was concentrated under reduced pressure with silica gel to afford crude residue that was purified by chromatography (silica gel, heptane–EtOAc, gradient from 99:1 to 90:10) to afford the product as a brownish solid; yield: 780 mg (90%); mp 170–172 °C.

IR (neat): 3468, 3376, 2926, 2854, 1602, 1457, 1276, 1260, 762, 751 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.21 (s, 2 H), 3.69 (br s, 4 H), 2.70 (t, *J* = 6.0 Hz, 4 H), 2.30–2.01 (m, 4 H), 1.77–1.58 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2 (2 Cq), 135.7 (2 Cq), 132.3 (2 CH), 129.0 (2 Cq), 122.4 (2 Cq), 107.0 (2 CH), 29.0 (2 CH_2), 26.7 (2 CH_2), 23.2 (2 CH_2), 23.0 (2 CH_2).

HRMS (ES^+): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{22}Br_2N_2Na$: 471.0042; found: 471.0046.

(*R*)-3,3′-Diphenyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diamine (8a); Typical Procedure

This compound was prepared according to the procedure of Maruoka et al.:[13b] In an oven-dried flask, equipped with a stir bar and a reflux condenser, were placed (*R*)-3,3′-dibromo-H_8-BINAM **7** (177 mg, 395 µmol), $Pd(OAc)_2$ (9 mg, 39.5 µmol, 0.1 equiv), phenylboronic acid (144.6 mg, 1185 µmol, 3 equiv), Ph_3P (42 mg, 160 µmol, 0.4 equiv), and $Ba(OH)_2{\cdot}8H_2O$ (498 mg, 1580 µmol, 4 equiv), and the flask was purged with argon. Then, a degassed mixture of DME–H_2O (10:1, 10 mL) was added through the condenser. The resulting mixture was stirred vigorously and refluxed for 24 h under argon. The brown mixture was cooled to r.t., diluted with brine and EtOAc, and transferred to a separatory funnel; the layers were separated and the aqueous layer was extracted with EtOAc (3 ×). The combined organic extracts were washed with brine and dried (Na_2SO_4). The inorganic salts were removed by filtration through a short pad of Celite. The filtrate was concentrated under reduced pressure with silica gel to afford a crude residue that was purified by chromatography (silica gel, heptane–EtOAc, gradient from 99:1 to 95:5) to afford the product as a white solid; yield: 166 mg (90%); mp 228–230 °C.

$[\alpha]_D^{25}$ –40.0 (*c* 0.8, $CHCl_3$).

IR (neat): 3469, 3374, 3055, 2927, 2854, 2834, 1606, 1495, 1458, 1414, 1264, 776, 738, 703 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.46 (m, 4 H), 7.46–7.36 (m, 4 H), 7.35–7.27 (m, 2 H), 6.92 (s, 2 H), 3.37 (br s, 4 H), 2.86–2.66 (m, 4 H), 2.48–2.18 (m, 4 H), 1.84–1.64 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1 (2 C_{Ar}), 138.8 (2 C_{Ar}), 135.6 (2 C_{Ar}), 130.3 (2 C_{Ar}), 129.2 (4 C_{Ar}), 128.6 (4 C_{Ar}), 127.4 (2 C_{Ar}), 126.8 (2 C_{Ar}), 125.7 (2 C_{Ar}), 122.3 (2 C_{Ar}), 29.3 (2 CH_2), 27.0 (2 CH_2), 23.5 (2 CH_2), 23.3 (2 CH_2).

HRMS (ES^+): *m*/*z* $[M + Na]^+$ calcd for $C_{32}H_{32}N_2Na$: 467.2458; found: 467.2464.

(*R*)-3,3′-Di(1-naphthyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diamine (8b)

Following the typical procedure for **8a** using (*R*)-3,3′-dibromo-H_8-BINAM **7** (177 mg, 395 µmol) with naphthalen-1-ylboronic acid (204 mg, 1185 µmol, 3 equiv) afforded the product as a white solid; yield: 125 mg (58%).

$[\alpha]_D^{25}$ –50.0 (*c* 0.4, $CHCl_3$).

IR (neat): 3465, 3372, 2922, 2853, 1604, 1506, 1452, 1418, 1391, 1353, 1336, 1313, 1263, 1242, 1212, 1084, 976, 913, 879, 822, 801, 776, 733, 666 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.99–7.28 (m, 14 H), 6.94 and 6.93 (br s, 2 H), 2.98 (br s, 4 H), 2.87–2.65 (m, 4 H), 2.62–2.31 (m, 4 H), 1.93–1.69 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6 (2 C_{Ar}), 137.6 (2 C_{Ar}), 135.9 (2 C_{Ar}), 133.9 (2 C_{Ar}), 131.9 (2 C_{Ar}), 131.0 (2 C_{Ar}), 131.0 (2 C_{Ar}), 128.3 (2 C_{Ar}), 127.7 (2 C_{Ar}), 127.2 (2 C_{Ar}), 126.3 (2 C_{Ar}), 126.1 (2 C_{Ar}), 126.0 (2 C_{Ar}), 125.8 (2 C_{Ar}), 124.0 (2 C_{Ar}), 122.0 (2 C_{Ar}), 29.3 (2 CH_2), 27.1 (2 CH_2), 23.7 (2 CH_2), 23.4 (2 CH_2).

HRMS (ES^+): *m*/*z* $[M + H]^+$ calcd for $C_{40}H_{37}N_2$: 545.2951; found: 545.2952.

(*R*)-3,3′-Di(phenanthren-9-yl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diamine (8c)

Following the typical procedure for **8a** using (*R*)-3,3′-dibromo-H_8-BINAM **7** (177 mg, 395 µmol) with phenanthren-9-ylboronic acid (263.2 mg, 1185 µmol, 3 equiv) afforded the product as a white solid; yield: 176 mg (69%).

$[\alpha]_D^{25}$ –63.0 (*c* 1.0, $CHCl_3$).

IR (neat): 3464, 3375, 2923, 2853, 1602, 1527, 1492, 1461, 1447, 1422, 1354, 1314, 1244, 1212, 1164, 1134, 1115, 1097, 1040, 967, 948, 894, 769, 745, 724, 676 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.84–8.64 (m, 4 H), 7.97–7.52 and 7.51–7.38 (m, 14 H), 7.02 and 7.00 (br s, 2 H), 3.11 (br s, 4 H), 2.90–2.68 (m, 4 H), 2.66–2.33 (m, 4 H), 1.96–1.70 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (2 C_{Ar}), 136.1 (2 C_{Ar}), 136.1 (2 C_{Ar}), 135.9 (2 C_{Ar}), 131.9 (2 C_{Ar}), 131.1 (2 C_{Ar}), 130.7 (2 C_{Ar}), 130.1 (2 C_{Ar}), 128.7 (2 C_{Ar}), 128.3 (2 C_{Ar}), 127.3 (2 C_{Ar}), 127.0 (2 C_{Ar}), 126.8 (4 C_{Ar}), 126.6 (4 C_{Ar}), 123.9 (2 C_{Ar}), 122.9 (2 C_{Ar}), 122.5 (2 C_{Ar}), 122.0 (2 C_{Ar}), 29.3 (2 CH_2), 27.2 (2 CH_2), 23.7 and 23.6 (2 CH_2), 23.4 (2 CH_2).

HRMS (ES$^+$): m/z [M + H]$^+$ calcd for $C_{48}H_{41}N_2$: 645.3264; found: 645.3269.

(*R*)-3,3′-Di(biphenyl-4-yl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diamine (8d)

Following the typical procedure for **8a** using (*R*)-3,3′-dibromo-H_8-BINAM **7** (177 mg, 395 µmol) with biphenyl-4-ylboronic acid (234.5 mg, 1185 µmol, 3 equiv) afforded the product as a brownish solid; yield: 210 mg (89%).

$[\alpha]_D^{25}$ –340.0 (*c* 1.0, $CHCl_3$).

IR (neat): 3450, 3366, 3027, 2923, 1602, 1519, 1486, 1436, 1394, 1355, 1308, 1263, 1242, 1075, 1007, 842, 825, 769, 734, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.53 and 7.52–7.40 and 7.40–7.31 (m, 18 H), 6.98 (s, 2 H), 2.85–2.73 (m, 4 H), 2.50–2.21 (m, 4 H), 1.85 (br s, 4 H), 1.90–1.62 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.9 (2 C_{Ar}), 139.7 (2 C_{Ar}), 139.1 (2 C_{Ar}), 138.8 (2 C_{Ar}), 135.8 (2 C_{Ar}), 130.4 (4 C_{Ar}), 129.6 (4 C_{Ar}), 128.9 (4 C_{Ar}), 127.6 (2 C_{Ar}), 127.4 (4 C_{Ar}), 127.3 (2 C_{Ar}), 127.1 (2 C_{Ar}), 125.2 (2 C_{Ar}), 122.5 (2 C_{Ar}), 29.4 (2 CH_2), 27.1 (2 CH_2), 23.6 (2 CH_2), 23.4 (2 CH_2).

HRMS (ES$^+$): m/z [M + H]$^+$ calcd for $C_{44}H_{41}N_2$: 597.3264; found: 597.3269.

(*R*)-2,2′-Diiodo-3,3′-diphenyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (4a); Typical Procedure

In an oven-dried flask equipped with a stir bar, were placed (*R*)-3,3′-diphenyl-H_8-BINAM **8a** (223 mg, 500 µmol), $NaNO_2$ (276 mg, 4 mmol, 8 equiv), and KI (830 mg, 5 mmol, 10 equiv). Then, DMSO (10 mL) was added, and the suspension was gently stirred at r.t. to allow complete dissolution of the solids. The solution was then cooled to approx. 0 °C with an NaCl/ice-water bath, and stirred vigorously to avoid solidification of the solvent. 33% HBr in AcOH (1 mL) was added dropwise quickly, but carefully, leading to a visible gas evolution. The resulting black solution was stirred for several hours, monitoring the reaction by TLC. The solution was then poured into sat. aq $NaHCO_3$ solution, and diluted with CH_2Cl_2. The resulting biphasic solution was transferred to a separatory funnel and the layers were separated; the aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic extracts were washed with $NaHSO_3$ and brine, and dried (Na_2SO_4). The inorganic salts were removed by filtration, and the organic layer was concentrated under reduced pressure with silica gel to afford a crude residue that was purified by chromatography (silica gel, heptane–CH_2Cl_2, gradient from 100:0 to 85:15) to afford the product as a yellowish solid; yield: 150 mg (45%).

$[\alpha]_D^{25}$ –31.0 (*c* 10.0, $CHCl_3$).

IR (neat): 3055, 3026, 2929, 1495, 1443, 1432, 1420, 1373, 1352, 1308, 1279, 1170, 1028, 910, 874, 822, 766, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.30 (m, 10 H), 7.07 (s, 2 H), 2.91–2.72 (m, 4 H), 2.53–2.33 and 2.30–2.11 (m, 4 H), 1.88–1.65 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.9 (2 C_{Ar}), 145.4 (2 C_{Ar}), 145.2 (2 C_{Ar}), 137.8 (2 C_{Ar}), 135.3 (2 C_{Ar}), 131.3 (C_{Ar}), 129.8 (2 C_{Ar}), 129.6 (2 C_{Ar}), 129.6 (2 C_{Ar}), 127.9 (C_{Ar}), 127.8 (2 C_{Ar}), 127.3 (2 C_{Ar}), 102.2 (2 C_{Ar}), 29.6 (2 CH_2), 29.1 (2 CH_2), 23.5 (2 CH_2), 22.7 (2 CH_2).

HRMS (ES$^+$): m/z [M]$^+$ calcd for $C_{32}H_{28}I_2$: 666.0275; found: 666.0275.

(*R*)-2,2′-Diiodo-3,3′-di(1-naphthyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (4b)

Following the typical procedure for **4a** using (*R*)-3,3′-di(1-naphthyl)-H_8-BINAM **8b** (150 mg, 276 µmol) afforded the product as a yellowish solid; yield: 149 mg (39%).

$[\alpha]_D^{25}$ – 78.0 (*c* 1.0, $CHCl_3$).

IR (neat): 2922, 2854, 1507, 1486, 1440, 1392, 1353, 820, 799, 773, 733 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99–7.83 (m, 4 H), 7.75–7.27 (m, 10 H), 7.17–7.07 (m, 2 H), 2.91–2.75 (m, 4 H), 2.69–2.23 (m, 4 H), 1.95–1.73 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.7, 143.7, 143.6, 143.4, 143.2, 141.5, 140.1, 139.8, 139.4, 139.2, 139.0, 138.0, 137.8, 137.7, 137.1, 137.0, 136.8, 136.7, 136.2, 136.1, 135.6, 135.5, 133.5, 133.4, 131.9, 131.8, 131.7, 130.7, 130.6, 128.3, 128.0, 127.9, 127.8, 127.4, 127.3, 126.8, 126.6, 126.5, 126.1, 126.0, 125.8, 125.7, 125.3, 125.1, 122.7, 60.4, 60.0, 59.8, 29.1, 28.9, 28.4, 28.2, 23.6, 23.5, 23.4, 23.3 (mixture of rotamers/atropoisomers).

HRMS (ES$^+$): m/z [M]$^+$ calcd for $C_{40}H_{32}I_2$: 766.0588; found: 766.0590.

(*R*)-2,2′-Diiodo-3,3′-di(phenanthren-9-yl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (4c)

Following the typical procedure for **4a** using (*R*)-3,3′-di(phenanthren-9-yl)-H_8-BINAM **8c** (150 mg, 276 µmol) afforded the product as a yellowish solid; yield: 88 mg (37%).

IR (neat): 3469, 3374, 3055, 2927, 2854, 2834, 1606, 1495, 1458, 1414, 1264, 776, 738, 703 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86–8.70 (m, 4 H), 8.00–7.81, 7.78–7.52, 7.49–7.35, and 7.24–7.10 (m, 16 H), 2.92–2.76 (m, 4 H), 2.73–2.26 (m, 4 H), 1.97–1.72 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.5, 145.6, 145.4, 144.7, 143.7, 143.6, 142.3, 141.9, 141.7, 141.5, 139.4, 139.2, 138.8, 138.4, 138.0, 138.0, 137.1, 136.9, 136.4, 136.3, 136.3, 135.7, 132.0, 131.8, 131.6, 131.4, 131.4, 131.2, 131.1, 131.1, 130.9, 130.8, 130.8, 130.5, 130.4, 130.3, 130.1, 129.9, 128.9, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 127.1, 127.0, 126.9, 126.8, 126.8, 126.5, 126.4, 122.9, 122.7, 122.6, 30.2, 29.7, 29.7, 29.2, 28.9, 28.4, 28.4, 28.2, 23.6, 23.5, 23.5, 23.4, 23.3, 23.3, 23.2, 22.7, 22.7 (mixture of rotamers/atropoisomers).

HRMS (ES$^+$): m/z [M]$^+$ calcd for $C_{48}H_{36}I_2$: 866.0901; found: 866.0901.

(*R*)-3,3′-Di(biphenyl-4-yl)-2,2′-diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (4d)

Following the typical procedure for **4a** using (*R*)-3,3′-di(biphenyl-4-yl)-H_8-BINAM **8d** (300 mg, 500 µmol) afforded the product as a brownish solid; yield: 172 mg (42%).

IR (neat): 2960, 2847, 2828, 1451, 1430, 765, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.30 (m, 18 H), 7.12 (s, 2 H), 2.91–2.73 (m, 4 H), 2.57–2.37 and 2.32–2.13 (m, 4 H), 1.92–1.67 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0 (2 C_{Ar}), 144.8 (2 C_{Ar}), 144.3 (2 C_{Ar}), 140.9 (2 C_{Ar}), 140.0 (2 C_{Ar}), 137.9 (2 C_{Ar}), 135.4 (4 C_{Ar}), 130.0 (2 C_{Ar}), 129.9 (2 C_{Ar}), 128.8 (2 C_{Ar}), 127.4 (2 C_{Ar}), 127.3 (4 C_{Ar}), 127.1 (2 C_{Ar}), 126.6 (2 C_{Ar}), 126.5 (2 C_{Ar}), 102.1 (2 C_{Ar}), 29.7 (2 CH_2), 29.1 (2 CH_2), 23.5 (2 CH_2), 22.7 (2 CH_2).

HRMS (ES$^+$): m/z [M]$^+$ calcd for $C_{44}H_{36}I_2$: 818.0901; found: 818.0906.

(*R*)-2,2′-Diiodo-1,1′-binaphthyl (4e)

This compound was prepared according to the procedure of Quideau et al.:[10b] To a solution of concd H_2SO_4 (65 mL) at –10 °C was added portionwise $NaNO_2$ (1.9 g, 275 mmol). The resulting suspension was allowed to warm up to r.t. until complete dissolution was observed and then it was cooled down again to –10 °C. A solution of commercial (*R*)-BINAM (**5**, 1.65 g, 5.81 mmol) in pyridine (10 mL) was slowly added and the resulting mixture was stirred at –10 °C for 2 h. The mixture was transferred to a large Erlenmeyer flask at 0 °C and ice was regularly added to the mixture over 1 h and, 30 min later, an ice-cooled aq urea solution (1.65 g, 41 mL, 0.0165 mol) was slowly added. This addition of urea caused abundant foam formation. To this mixture was added an aqueous solution of ZnI_2 (5.2 g, 0.0165 mol) and KI (8.75 g, 0.0495 mmol) (16 mL). After filtration of the resulting brownish suspension, the brown solid was triturated with Et_2O and the resulting red filtrate was discolored by washing with sat. aq $NaHSO_3$ solution and dried (Na_2SO_4). The inorganic salts were removed by filtration, and the organic layer was concentrated under reduced pressure with silica gel to afford a crude residue that was purified by column chromatography (silica gel, heptane–CH_2Cl_2, gradient from 100:0 to 85:15) to afford the product as a yellowish solid; yield: 1.47 g (50%); mp 206–208 °C.

IR (neat): 2970, 1459, 812 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.0 Hz, 2 H), 7.94 (d, *J* = 8.0 Hz, 2 H), 7.72 (d, *J* = 8.0 Hz, 2 H), 7.54–7.48 (m, 2 H), 7.33–7.26 (m, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.7 (2 Cq), 135.6 (2 CH), 133.0 (2 Cq), 129.6 (2 CH), 128.2 (2 CH), 127.9 (2 CH), 127.3 (2 CH), 126.6 (2 CH), 126.4 (2 CH), 99.7 (2 Cq).

HRMS (ES$^+$): *m*/*z* [M]$^+$ calcd for $C_{20}H_{12}I_2$: 505.9023; found: 505.9026.

(*R*)-2,2′-Diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (4f); Typical Procedure

This compound was prepared according to the procedure of Yamamoto et al.,[16] with slight modifications: In an oven-dried flask equipped with a stir bar, were placed (*R*)-H_8-BINAM **6** (146 mg, 500 µmol), $NaNO_2$ (276 mg, 4 mmol, 8 equiv), and KI (830 mg, 5 mmol, 10 equiv). Then, DMF (10 mL) was added, and the suspension was gently stirred at r.t. to allow complete dissolution of the solids. The solution was then cooled to approximately 0 °C with an NaCl/ice-water bath, and stirred vigorously to avoid solidification of the solvent. 33% HBr in AcOH (1 mL) was added dropwise quickly, but carefully, leading to visible gas evolution. The resulting black solution was stirred for several hours, monitoring the reaction by TLC. The solution was then poured in sat. aq $NaHCO_3$ solution and diluted with CH_2Cl_2. The resulting biphasic solution was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic extracts were washed with $NaHSO_3$ and brine, and dried (Na_2SO_4). The inorganic salts were removed by filtration, and the organic layer was concentrated under reduced pressure with silica gel to afford a crude residue that was purified by chromatography (silica gel, heptane–CH_2Cl_2, gradient from 100:0 to 85:15) to afford the product as a yellowish solid; yield: 123 mg (48%); slightly contaminated with an unknown compound.

IR (neat): 2980, 1450, 1236, 1070, 1030, 881 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.0 Hz, 2 H), 6.85 (d, *J* = 8.0 Hz, 2 H), 2.89–2.69 (m, 4 H), 2.41–2.00 (m, 4 H), 1.80–1.60 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.0 (2 Cq), 138.0 (2 Cq), 136.7 (2 CH), 135.8 (2 Cq, 130.4 (2 CH), 97.1 (2 Cq), 29.7 (2 CH_2), 28.9 (2 CH_2), 23.3 (2 CH_2), 22.5 (2 CH_2).

HRMS (ES$^+$): *m*/*z* [M]$^+$ calcd for $C_{20}H_{20}I_2$: 513.9649; found: 513.9649.

(*R*)-*N*-(2′-Amino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalen-2-yl)acetamide (9)

Following the typical procedure for **11** using (*R*)-H_8-BINAM **6** (292 mg, 1.0 mmol) afforded the product as a white foam; yield: 214 mg (60%).

$[\alpha]_D^{25}$ +27.0 (*c* 1.0, $CHCl_3$).

IR (neat): 3430, 3370, 1681, 1602, 1591, 1496, 1342, 1241, 1150, 1040, 966, 830, 747, 670 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.5 Hz, 1 H), 7.11 (d, *J* = 8.5 Hz, 1 H), 6.96 (d, *J* = 8.5 Hz, 1 H), 6.75 (br s, 1 H), 6.63 (d, *J* = 8.5 Hz, 1 H), 3.30 (br s, 2 H), 2.84–2.67 (m, 4 H), 2.36–2.01 (m, 4 H), 1.91 (s, 3 H), 1.81–1.43 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.3 (Cq), 141.4 (C_{Ar}), 134.9 (C_{Ar}), 132.2 (C_{Ar}), 131.3 (C_{Ar}), 130.1 (C_{Ar}), 129.5 (C_{Ar}), 129.3 (C_{Ar}), 127.9 (C_{Ar}), 127.2 (C_{Ar}), 124.3 (C_{Ar}), 118.3 (C_{Ar}), 113.2 (C_{Ar}), 29.6 (2 CH_2), 29.3 (2 CH_2), 27.2 (2 CH_2), 27.0 (2 CH_2), 23.2 and 22.9 (CH_3).

HRMS (ES$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{26}N_2ONa$: 357.1937; found: 357.1934.

(*R*)-*N*-(2′-Amino-3′-bromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalen-2-yl)acetamide (10); Typical Procedure

To a stirred suspension of (*R*)-*N*-(2′-amino-1,1′-binaphthalen-2-yl)acetamide **9** (150 mg, 449 µmol) in glacial AcOH, maintained at r.t. with a water bath, was added Br_2 (460 µL, 8.98 mmol, 20 equiv) dropwise. The resulting black suspension was stirred vigorously for several minutes, monitoring the reaction by TLC. Once all the starting material had been consumed, the solution was cooled to approx. 0 °C with an NaCl/ice-water bath, carefully quenched by slow addition of aq $NaHSO_3$ solution, and stirred vigorously until almost complete decoloration. AcOH was neutralized by slow addition of a non-sat. $NaHCO_3$ solution and diluted with CH_2Cl_2. The resulting biphasic solution was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic extracts were washed with H_2O and brine, and dried (Na_2SO_4). The inorganic salts were removed by filtration, and the organic layer was concentrated under reduced pressure with silica gel to afford a crude residue that was purified by chromatography (silica gel, heptane–EtOAc, gradient from 95:5 to 90:10) to afford the product as a white foam; yield: 150 mg (81%).

$[\alpha]_D^{25}$ –10.0 (*c* 0.8, $CHCl_3$).

IR (neat): 3432, 3367, 1690, 1599, 1540, 1430, 1397, 1312, 1267, 1221, 1170, 1039, 1018, 961, 832, 801 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.5 Hz, 1 H), 7.24 (s, 1 H), 7.13 (d, *J* = 8.5 Hz, 1 H), 6.66 (br s, 1 H), 3.70 (br s, 2 H), 2.85–2.63 (m, 4 H), 2.34–1.97 (m, 4 H), 1.91 (s, 3 H), 1.81–1.54 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.3 (Cq), 142.2 (C_{Ar}), 139.3 (C_{Ar}), 135.7 (C_{Ar}), 134.2 (C_{Ar}), 133.2 (C_{Ar}), 132.8 (C_{Ar}), 129.7 (C_{Ar}), 129.0 (C_{Ar}), 125.8 (C_{Ar}), 119.9 (C_{Ar}), 118.8 (C_{Ar}), 107.0 (C_{Ar}), 31.9 (2 CH_2), 29.5 (2 CH_2), 29.0 (2 CH_2), 27.0 and 26.9 (2 CH_2), 23.0 and 22.8 (CH_3).

HRMS (ES$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{26}BrN_2O$: 413.1223; found: 413.1221.

(*R*)-*N*-(2′-Iodo-3′-phenyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalen-2-yl)acetamide (4g)

Following the typical procedures for **8a** and **4a** using (*R*)-*N*-(2′-amino-3′-phenyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalen-2-yl)acetamide (**10**, 206 mg, 500 μmol) afforded the product as a white solid; yield: 93 mg (34%).

$[\alpha]_D^{25}$ –20.0 (*c* 1.0, $CHCl_3$).

IR (neat): 3411, 3293, 2927, 2856, 2833, 1676, 1595, 1506, 1433, 1413, 1371, 1310, 1288, 1241, 1146, 1028, 911, 813, 766, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.28 (m, 5 H), 7.21–7.05 (m, 3 H), 6.50 (br s, 1 H), 2.90–2.69 (m, 4 H), 2.44–1.87 (m, 4 H), 1.96 (s, 3 H), 1.86–1.59 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1 (Cq), 145.6 (C_{Ar}), 145.0 (C_{Ar}), 141.7 (C_{Ar}), 138.6 (C_{Ar}), 136.6 (C_{Ar}), 134.4 (C_{Ar}), 134.1 (C_{Ar}), 131.9 (C_{Ar}), 130.7 (C_{Ar}), 129.4 (2 C_{Ar}), 129.3 (C_{Ar}), 128.8 (C_{Ar}), 127.9 (2 C_{Ar}), 127.5 (2 C_{Ar}), 119.2 (C_{Ar}), 29.6 and 28.6 (2 CH_2), 27.5 and 27.3 (2 CH_2), 24.6 (CH_3), 23.3 and 23.2 (2 CH_2), 22.8 and 22.6 (2 CH_2).

HRMS (ES^+): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{28}INONa$: 544.1108; found: 544.1104.

(*R*)-*N*-(2′-Amino-1,1′-binaphthalen-2-yl)acetamide (11)

Commercial (*R*)-BINAM **5** was mono-acylated according to the procedure reported by Shi et al. with slight modifications:[17] To a stirred suspension of (*R*)-BINAM (284 mg, 1.0 mmol) and glacial AcOH (600 μL, 10 equiv) in CH_2Cl_2 (10 mL), cooled to 5 °C with an ice/water bath, was added Ac_2O (104 μL, 1.1 mmol, 1.1 equiv) dropwise. The ice bath was removed and the solution was stirred overnight at r.t. The resulting mixture was then cooled with an ice/water bath and carefully quenched by slow addition of 2 M aq NaOH under vigorous stirring to reach pH 7. The resulting biphasic solution was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 ×). Combined organic extracts were washed with H_2O and brine, and dried (Na_2SO_4). The inorganic salts were removed by filtration, and the organic layer was concentrated under reduced pressure with silica gel to afford a crude residue that was purified by chromatography (silica gel, heptane–EtOAc, gradient from 80:20 to 50:50) to afford the product as a white solid; yield: 220 mg (63%).

$[\alpha]_D^{25}$ +27.0 (*c* 1.0, $CHCl_3$).

IR (neat): 3400, 1676, 1595, 1499, 1445, 1270, 1040, 965, 670 cm^{-1}.

^1H NMR(300 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 8.5 Hz, 1 H), 8.00 (d, *J* = 9.0 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.87 (d, *J* = 9.0 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 1 H), 7.31–7.18 (m, 4 H), 7.15 (d, *J* = 8.5 Hz, 1 H), 7.05 (br s, 1 H), 6.93 (d, *J* = 8.5 Hz, 1 H), 4.17 (br s, 2 H), 1.85 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7 (Cq), 142.7 (Cq), 135.1 (Cq), 133.6 (Cq), 130.4 (4 C_{Ar}), 129.3 (2 C_{Ar}), 128.2 (2 C_{Ar}), 127.3 (2 C_{Ar}), 126.8 (C_{Ar}), 125.4 (C_{Ar}), 125.1 (C_{Ar}), 123.7 (C_{Ar}), 122.8 (C_{Ar}), 120.9 (C_{Ar}), 118.1 (C_{Ar}), 24.8 (CH_3).

HRMS(ES^+): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{18}N_2ONa$: 349.1311; found: 349.1311.

(*R*)-*N*-(2′-Iodo-1,1′-binaphthalen-2-yl)acetamide (4h)

Following the typical procedure for **4a** using (*R*)-*N*-(2′-amino-1,1′-binaphthalen-2-yl)acetamide **11** (300 mg, 500 μmol) afforded the product as a white solid; yield: 117 mg (51%).

IR (neat): 3412, 3310, 3055, 2956, 2924, 1671, 1621, 1596, 1518, 1497, 1457, 1423, 1366, 1335, 1274, 1304, 1274, 1147, 1105, 1061, 827, 811, 773, 745, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 8.5 Hz, 1 H), 8.11 (d, *J* = 8.5 Hz, 1 H), 8.04 (d, *J* = 8.5 Hz, 1 H), 7.97–7.88 (m, 2 H), 7.75 (d, *J* = 8.5 Hz, 1 H), 7.53 (t, *J* = 8.5 Hz, 1 H), 7.42 (t, *J* = 8.5 Hz, 1 H), 7.33–7.21 (m, 2 H), 7.14 (d, *J* = 8.5 Hz, 1 H), 6.91 (d, *J* = 8.5 Hz, 1 H), 6.62 (br s, 1 H), 1.85 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 171.1 (Cq), 145.0 (C_{Ar}), 135.9 (2 C_{Ar}), 133.1 (C_{Ar}), 130.4 (2 C_{Ar}), 129.4 (2 C_{Ar}), 128.3 (2 C_{Ar}), 128.2 (2 C_{Ar}), 127.9 (2 C_{Ar}), 127.1 (C_{Ar}), 126.8 (C_{Ar}), 126.4 (C_{Ar}), 125.1 (2 C_{Ar}), 121.0 (C_{Ar}), 24.0 (CH_3).

HRMS (ES^+): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{16}INONa$: 460.0169; found: 460.0170.

3-(1-Hydroxynaphthalen-2-yl)propanoic Acid (1)

This compound was prepared according to the procedure reported by Kita et al. with slight modifications:[4a] To a stirred suspension of 3,4-dihydro-2*H*-benzo[*h*]chromen-2-one (1 g, 5 mmol) in anhyd THF (36 mL) was added dropwise 1 M aq LiOH solution (17.9 mL), during which the solution progressively turned green. After complete addition, the resulting brown solution was stirred vigorously at r.t. overnight. The pH was then adjusted to 3 with 2 M aq HCl. The mixture was diluted with EtOAc, the biphasic solution was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with EtOAc (3 ×). The combined organic extracts were washed with brine, and dried (Na_2SO_4). The inorganic salts were removed by filtration, and the organic layer was concentrated under reduced pressure with silica gel to afford a crude residue that was purified by chromatography (silica gel, heptane–EtOAc, gradient from 80:20 to 30:70) to afford the product as a white solid; yield: 992 mg (83%); mp 105–107 °C.

IR (neat): 3100, 1681, 1082, 808 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.25–8.22 (m, 1 H), 7.76–7.71 (m, 1 H), 7.47–7.42 (m, 2 H), 7.39 (d, *J* = 8.5 Hz, 1 H), 7.17 (d, *J* = 8.5 Hz, 1 H), 3.04 (t, *J* = 7.0 Hz, 2 H), 2.87 (t, *J* = 7.0 Hz, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ = 176.6 (Cq), 150.5 (Cq), 134.6 (C_{Ar}), 126.4 (C_{Ar}), 128.2 (C_{Ar}), 126.7 (C_{Ar}), 126.3 (C_{Ar}), 125.7 (C_{Ar}), 122.7 (C_{Ar}), 122.1 (C_{Ar}), 120.7 (C_{Ar}), 35.1 (CH_2), 25.7 (CH_2).

HRMS (ES^+): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{12}O_3Na$: 239.0679; found: 239.0684.

1′*H*,3*H*-Spiro[furan-2,2′-naphthalene]-1′,5(4*H*)-dione (2); General Procedure

To a stirred suspension of the iodoarene **4** (0.1 equiv, 5 μmol) in anhyd $CHCl_3$ (1 mL) was added wet *m*CPBA (77%, 14.5 mg, 65 μmol, 1.3 equiv). The solution was cooled to 0 °C with a cooler, and stirred for 10 min. Then, 3-(1-hydroxynaphthalen-2-yl)propanoic acid (**1**, 10.8 mg, 50 μmol, 1 equiv,) was added, and glassware was rinsed with $CHCl_3$ (1 mL); the solution was stirred at 0 °C for several hours, monitoring the reaction by TLC. When the reaction was complete, the mixture was carefully poured into sat. $NaHCO_3$ solution and diluted with CH_2Cl_2. The resulting biphasic solution was transferred into a separatory funnel and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic extracts were washed with $NaHCO_3$ and brine, and dried (Na_2SO_4). The inorganic salts were removed by filtration, and the organic layer was concentrated under reduced pressure to afford a crude residue that was puri-

fied by chromatography (silica gel, heptane–EtOAc, gradient from 95:5 to 80:20) to afford the product as a white solid, see Table 2; mp 103–105 °C.

HPLC (Daicel Chiralpak OD-H, hexane–*i*-PrOH, 85:15, flow rate 1.0 mL/min, 230 nm): t_R = 16.30, 21.51 min.

IR (neat): 1788, 1693, 1597, 1481, 1454, 1323, 1296, 1178, 1123, 1032, 930, 787 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 1 H), 7.26 (d, *J* = 7.5 Hz, 1 H), 6.66 (d, *J* = 10.0 Hz, 1 H), 6.20 (d, *J* = 10.0 Hz, 1 H), 2.98–2.85 and 2.65–2.55 and 2.47–2.39 and 2.25–2.13 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.5 (Cq), 176.5 (Cq), 136.7 (C_{Ar}), 135.6 (C_{Ar}), 132.1 (C_{Ar}), 128.8 (C_{Ar}), 127.9 (C_{Ar}), 127.8 (C_{Ar}), 127.5 (C_{Ar}), 127.1 (C_{Ar}), 83.4 (Cq), 31.0 (CH_2), 26.4 (CH_2).

HRMS (ES^+): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{11}O_3$: 215.0703; found: 215.0699.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560512.

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