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The Synthesis of a New Class of Chiral Pincer Ligands and Their Applications in Enantioselective Catalytic Fluorinations and the Nozaki–Hiyama–Kishi Reaction

Qing-Hai Deng, Hubert Wadepohl, and Lutz H. Gade*[a]

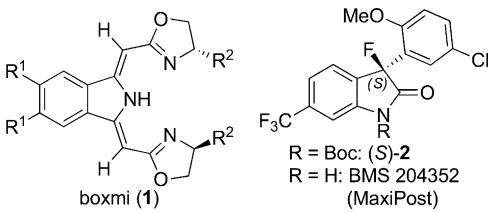
Abstract: A new class of chiral tridentate N-donor pincer ligands, bis(oxazolinylmethylidene)isoindolines (boxmi), was synthesized in three steps starting from readily available phthalimides. Their reaction with ethyl (triphenylphosphoranylidene)acetate by means of a key-step Wittig reaction gave the ligand backbones, which were condensed with amino alcohols and then cyclized to obtain the corresponding ligands. These ligands were subsequently applied in the nickel(II)-catalyzed enantioselective fluorination of oxindoles and β-ketoesters to obtain the corresponding products with enantioselectivities of up to >99% *ee* and high yields. Application of the chiral pincer ligands in the chromium-catalyzed enantioselective Nozaki–Hiyama–Kishi reaction of aldehydes gave the corresponding alcohols with an optimal enantioselectivity of 93%.

Keywords: asymmetric catalysis · fluorination · ligand design · nickel · Nozaki–Hiyama–Kishi reaction

Introduction

Meridionally coordinating chiral tridentate ligands, frequently referred to as "pincers,"[1] provide the structural platform for the construction of efficient stereodirecting molecular environments. Although many of the known chiral systems of the pincer-type perform relatively poorly in enantioselective catalysis due to certain lack of control of substrate orientation, the assembly from rigid heterocyclic units recently has given rise to several highly enantioselective catalysts.[2] These ligand systems, such as bis(oxazolinyl)phenyl (phebox),[3] bis(oxazolinyl)carbazole,[4] and chiral bis(pyridylimino)isoindole (bpi) derivatives[5] have been proven to act as efficient stereodirecting ligands in a variety of applications in molecular catalysis.

Oxindoles possess structural motifs found in many natural products[6] and biologically active compounds.[7] In particular, 3-fluorooxindoles were found to have broad applications in medicinal chemistry. One such example is BMS 204352 (MaxiPost) (Scheme 1), an effective opener of maxi-K channels and a potential agent for the treatment of stroke.[7e,f] Whereas several catalytic systems for the asymmetric fluorination of other nucleophiles[8,9] have been developed, there are only few reports on catalytic asymmetric fluorination of oxindoles[10] to obtain chiral 3-fluorooxindoles. Notably, the only example of a catalytic enantioselective preparation of the *N*-Boc-protected (Boc = *t*-butyloxycarbonyl) Maxipost derivative in Scheme 1 was obtained with moderate selectivity (71% *ee*).[10a] Thus, the development of new catalyst systems for the asymmetric fluorination of oxindoles and other substrates continues to be of considerable interest.



Scheme 1. Structure of the protioligand boxmi **1** and the maxi-K channel opener BMS 204352.

The Nozaki–Hiyama–Kishi (NHK) reaction, first reported in the late 1970s,[11] has become a powerful synthetic tool for the formation of carbon–carbon bonds under mild conditions.[12] In 1996, Fürstner et al. reported a catalytic redox system that used manganese as the reducing agent, which successfully reduced the quantity of Cr^{II} species, thereby making these reactions more valuable and environmentally benign.[13] Since the first catalytic enantioselective NHK reaction using a commercially available salen (salen = (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) ligand was reported by Cozzi and co-workers,[14] several new chiral ligands for the NHK reaction have been developed.[4,15]

Herein we report the synthesis of a new class of chiral N_3 pincer ligands, bis(oxazolinylmethylidene)isoindolines (boxmi, **1**), which are readily accessible in a modular three-step synthesis. In an evaluation of their potential in enantioselective catalysis, these were found to induce very high stereoselectivity in Ni-catalyzed enantioselective fluorination

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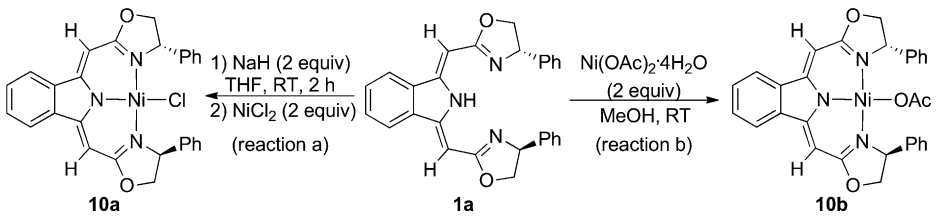
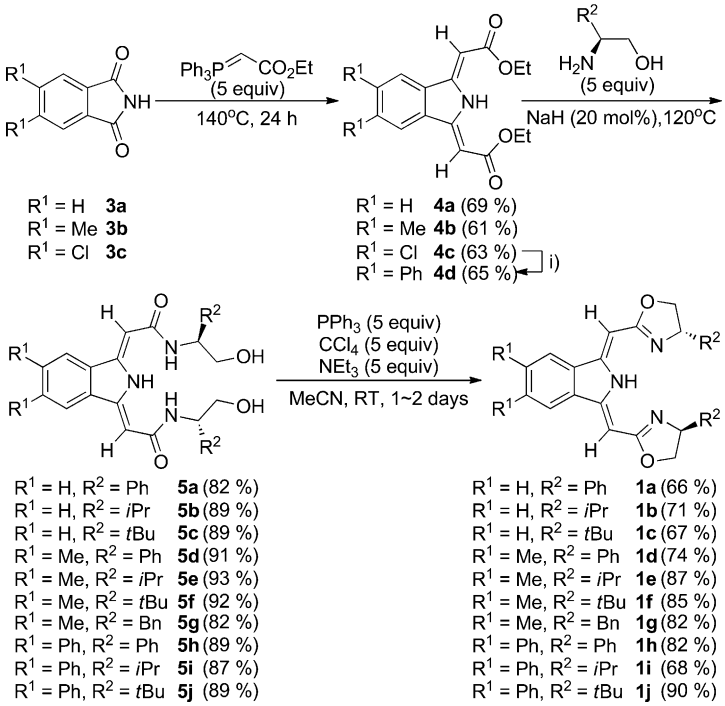
of oxindoles and β-ketoesters, and Cr-catalyzed enantioselective NHK reactions of aldehydes.

Results and Discussion



Scheme 3. Synthesis of the nickel complexes **10a** and **10b**.

Synthesis of bis(oxazolinylmethylidene)isoindolines and their coordination to nickel(II): The bis(oxazolinylmethylidene)isoindoline protioligands were prepared in three steps starting from easily available phthalimides **3** (Scheme 2). The backbones of the pincer ligands



R^1 = H **3a**
R^1 = Me **3b**
R^1 = Cl **3c**

R^1 = H **4a** (69 %)
R^1 = Me **4b** (61 %)
R^1 = Cl **4c** (63 %)
R^1 = Ph **4d** (65 %)

R^1 = H, R^2 = Ph	**5a** (82 %)
R^1 = H, R^2 = *i*Pr	**5b** (89 %)
R^1 = H, R^2 = *t*Bu	**5c** (89 %)
R^1 = Me, R^2 = Ph	**5d** (91 %)
R^1 = Me, R^2 = *i*Pr	**5e** (93 %)
R^1 = Me, R^2 = *t*Bu	**5f** (92 %)
R^1 = Me, R^2 = Bn	**5g** (82 %)
R^1 = Ph, R^2 = Ph	**5h** (89 %)
R^1 = Ph, R^2 = *i*Pr	**5i** (87 %)
R^1 = Ph, R^2 = *t*Bu	**5j** (89 %)

R^1 = H, R^2 = Ph	**1a** (66 %)
R^1 = H, R^2 = *i*Pr	**1b** (71 %)
R^1 = H, R^2 = *t*Bu	**1c** (67 %)
R^1 = Me, R^2 = Ph	**1d** (74 %)
R^1 = Me, R^2 = *i*Pr	**1e** (87 %)
R^1 = Me, R^2 = *t*Bu	**1f** (85 %)
R^1 = Me, R^2 = Bn	**1g** (82 %)
R^1 = Ph, R^2 = Ph	**1h** (82 %)
R^1 = Ph, R^2 = *i*Pr	**1i** (68 %)
R^1 = Ph, R^2 = *t*Bu	**1j** (90 %)

Scheme 2. Synthesis of ligands **1**. i) $PhB(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, DME, H_2O, reflux.

(**4a–d**) were prepared according to improved Wittig procedures[16] (combined with a subsequent Suzuki coupling[17] for **4d**). Compounds **5a–j** were synthesized in high yields by melting **4** with the corresponding amino alcohols in the presence of a catalytic amount of NaH,[18] and the desired ligands **1a–j** were obtained from **5** using a $Ph_3P/CCl_4/Et_3N$ cyclization protocol[19] (for the detailed screening conditions of the ligand synthesis, see the Supporting Information)

Deprotonation of **1a** with two molar equivalents of NaH and subsequent stirring with $NiCl_2$ yielded the nickel(II) complex **10a** as a black red solid (Scheme 3, reaction a). The alternative methods to obtain nickel complex, direct complexation of **1a** with $Ni(OAc)_2$ in methanol at room temperature, gave the corresponding nickel(II)–acetato complex **10b** (Scheme 3, reaction b).

To establish the structural details of this new class of stereodirecting ligands, single-crystal X-ray structure analyses of the protioligand **1i** (Figure 1a) and the chloronickel complex [Ni(**L**)Cl] (**10a**) (Figure 1b) were carried out. The well-defined C_2-chiral molecular shape and preorganized orientation of the N-donor functions is apparent in the molecular structure of **1i**, the gross features of which are retained in its metalated form as evidenced by the almost ideally square-planar nickel complex **10a**. It is notable that the usually observed difference in N–metal bond lengths for neutral and anionic N donors appears to be evened out in the structure of **10a** (the isoindolato Ni–N(1) is 1.904(1) Å, whereas

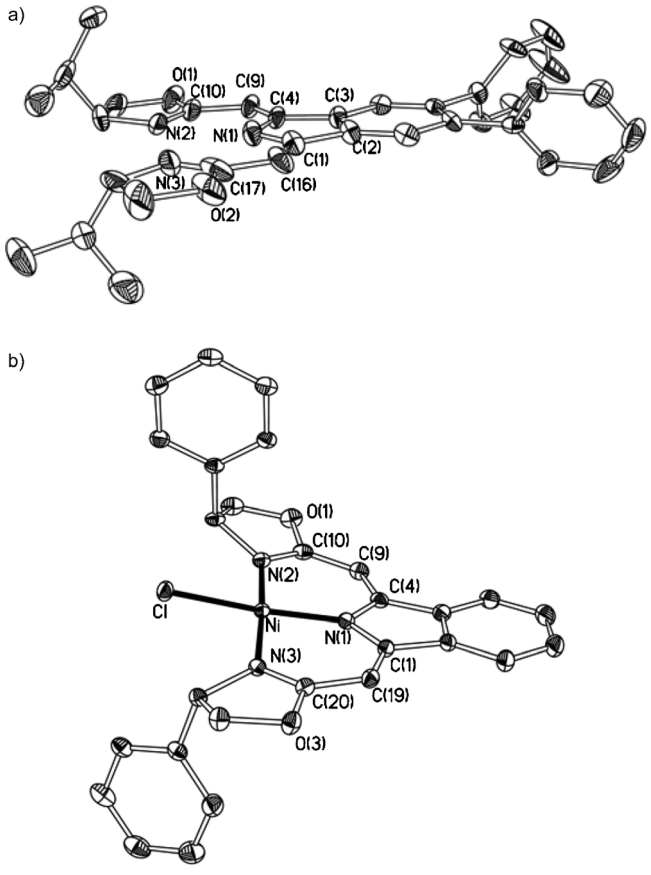


Figure 1. Molecular structure of a) ligand **1i** and b) [Ni(**L**)Cl] (**10a**); hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°] of [Ni(**L**)Cl] (**10a**): Ni–N(1) 1.904(1), Ni–N(2) 1.911(1), Ni–N(3) 1.911(1), Ni–Cl 2.1927(9); N(1)-Ni-N(2), 91.34(5), N(1)-Ni-N(3), 91.78(5), N(2)-Ni-N(3) 176.64(5), N(1)-Ni-Cl 174.33(4), N(2)-Ni-Cl 88.52(4), N(3)-Ni-Cl 88.49(4).

Ni–N(2) 1.911(1), Ni–N(3) 1.911(1) Å were found for the two oxazoline donors). This is thought to be a consequence of the delocalized π system that connects the donor atoms in this type of pincer ligand.

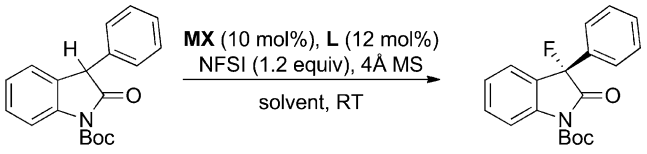
Enantioselective catalytic fluorination: The fluorination of oxindole **6a** was initially carried out using boxmi derivative **1a** as stereodirecting ligand and *N*-fluorobenzenesulfonamide (NFSI) as fluorinating agent.[10b] Solvent screening showed ethyl ether to be the most suitable solvent; it raised the enantioselectivity for this transformation to >99% *ee* (Table 1, entries 1–4). Other Lewis acidic metals were also screened (entries 5–7), and Ni and Zn complexes prepared in situ were found to give the fluorination product with high enantioselectivity (entries 4 and 5), whereas cobalt and magnesium complexes proved to be less efficient (entries 6 and 7). Finally, a screening of a series of boxmi ligands was carried out and, in general, the highest selectivities were obtained with derivatives that contained 4-phenyloxazolinyl units at the "wing tips" of the pincer ligand (ligands **1a**, **1d**, and **1h**; entries 4, 10, and 14).

With the optimized conditions in hand, we focused on the substrate scope and generality of the reaction. The introduction of electron-donating and -withdrawing groups on both the oxindole core and the 3-aryl group provided products with excellent enantioselectivity toward the *S* enantiomer (Table 2, **7a**–**j**). With a 3-methyl-substituted oxindole as a substrate, the reaction affords the product with 91% yield and 95% *ee* (Table 2, **7k**). It is notable that the *R* isomer of **2** was obtained in 90% yield with 99% *ee* when **1a** was employed as stereodirecting ligand. Compound **7l** would be converted into *R* enantiomer of MaxiPost by cleavage of the *N*-Boc group.[10a] To the best of our knowledge, this is the highest enantioselectivity for catalytic preparation of *N*-Boc-protected Maxipost.

To further demonstrate the synthetic utility of the boxmi/Ni fluorination system, we also investigated the catalytic enantioselective fluorination of several cyclic β-ketoesters. The pharmaceutically important fluorinated β-ketoesters **9a**–**e**[7g] were obtained with high enantioselectivity (Table 3).

Enantioselective catalytic Nozaki–Hiyama–Kishi reaction: The Nozaki–Hiyama–Kishi allylation of benzaldehyde **11a** with allylic halide catalyzed by **1a**/$CrCl_2$ was selected as the initial test reaction. A variety of solvents, bases, allylic halides, and chlorosilanes were tested in the model reaction

Table 1. Optimization of the fluorination reaction conditions.[a]

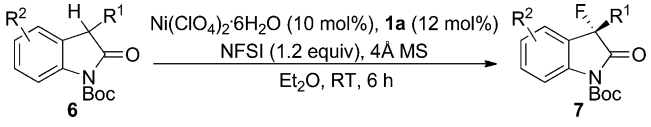


6a **7a**

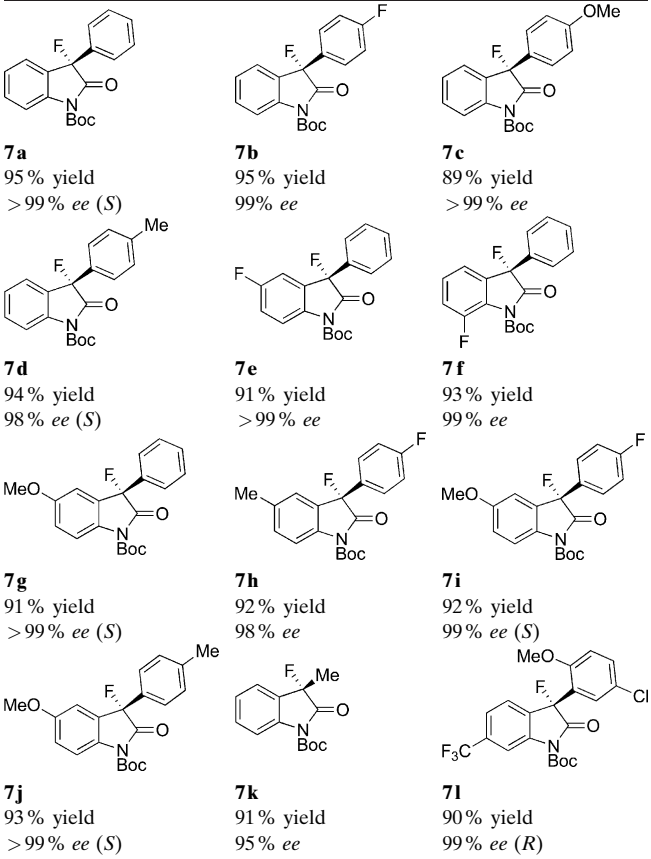
Entry	Metal(II) salt	L	Solvent	*t* [h]	Yield [%][b]	*ee* [%][c]
1	$Ni(ClO_4)_2{\cdot}6H_2O$	**1a**	CH_2Cl_2	4	94	97 (*S*)
2	$Ni(ClO_4)_2{\cdot}6H_2O$	**1a**	toluene	6	85	87 (*S*)
3	$Ni(ClO_4)_2{\cdot}6H_2O$	**1a**	THF	10	83	78 (*S*)
4	$Ni(ClO_4)_2{\cdot}6H_2O$	**1a**	Et_2O	6	95	>99 (*S*)
5	$Zn(NTf_2)_2$[d]	**1a**	Et_2O	5	91	87 (*S*)
6	$Co(OAc)_2{\cdot}4H_2O$	**1a**	Et_2O	8	91	29 (*S*)
7	$Mg(ClO_4)_2$	**1a**	Et_2O	8	88	11 (*S*)
8	$Ni(ClO_4)_2{\cdot}6H_2O$	**1b**	Et_2O	6	95	42 (*S*)
9	$Ni(ClO_4)_2{\cdot}6H_2O$	**1c**	Et_2O	6	90	21 (*S*)
10	$Ni(ClO_4)_2{\cdot}6H_2O$	**1d**	Et_2O	6	91	>99 (*S*)
11	$Ni(ClO_4)_2{\cdot}6H_2O$	**1e**	Et_2O	6	93	47 (*S*)
12	$Ni(ClO_4)_2{\cdot}6H_2O$	**1f**	Et_2O	6	92	25 (*S*)
13	$Ni(ClO_4)_2{\cdot}6H_2O$	**1g**	Et_2O	6	89	30 (*S*)
14	$Ni(ClO_4)_2{\cdot}6H_2O$	**1h**	Et_2O	6	90	99 (*S*)
15	$Ni(ClO_4)_2{\cdot}6H_2O$	**1i**	Et_2O	6	91	48 (*S*)
16	$Ni(ClO_4)_2{\cdot}6H_2O$	**1j**	Et_2O	6	89	28 (*S*)

[a] Reaction conditions: **6a** (0.1 mmol, 1.0 equiv), NFSI (1.2 equiv), ligand (12 mol%), MX (10 mol%), 4 Å molecular sieves (MS) (50 mg), solvent (2 mL) at room temperature under argon. [b] Yield of isolated products. [c] Determined by chiral HPLC analysis; absolute configuration of the product was determined by comparison with literature. [d] Tf = triflate.

Table 2. Substrate scope for the enantioselective fluorination of oxindoles.[a]



6 **7**



7a
95% yield
>99% *ee* (*S*)

7b
95% yield
99% *ee*

7c
89% yield
>99% *ee*

7d
94% yield
98% *ee* (*S*)

7e
91% yield
>99% *ee*

7f
93% yield
99% *ee*

7g
91% yield
>99% *ee* (*S*)

7h
92% yield
98% *ee*

7i
92% yield
99% *ee* (*S*)

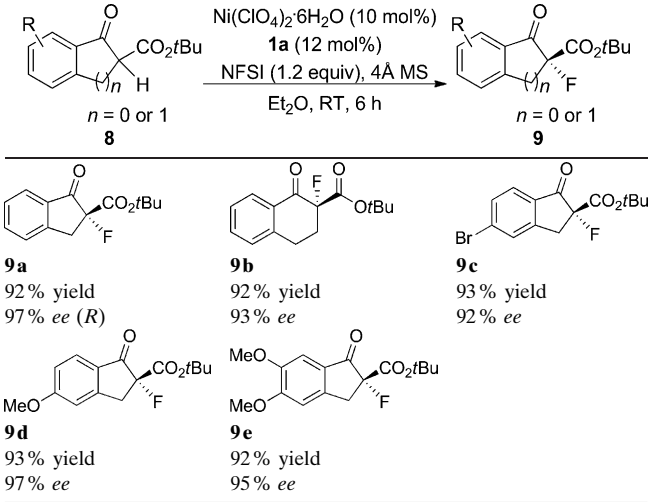
7j
93% yield
>99% *ee* (*S*)

7k
91% yield
95% *ee*

7l
90% yield
99% *ee* (*R*)

[a] Reaction conditions: **6** (0.1 mmol, 1.0 equiv), NFSI (1.2 equiv), **1a** (12 mol%), $Ni(ClO_4)_2{\cdot}6H_2O$ (10 mol%), 4 Å MS (50 mg), Et_2O (2 mL) at room temperature under argon. Yields refer to isolated products. Enantiomeric excess was determined by chiral HPLC analysis. Absolute configuration of the product was determined by comparison with literature.

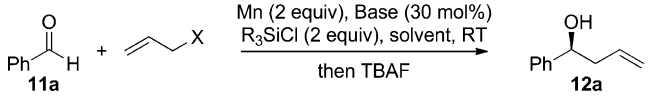
Table 3. Substrate scope for the enantioselective fluorination of β-ketoesters.[a]



[a] Reaction conditions: **8** (0.1 mmol, 1.0 equiv), NFSI (1.2 equiv), **1a** (12 mol%), $Ni(ClO_4)_2{\cdot}6H_2O$ (10 mol%), 4 Å MS (50 mg), Et_2O (2 mL) at room temperature under argon. Yields refer to isolated products. Enantiomeric excess was determined by chiral HPLC analysis. Absolute configuration of the product was determined by comparison with literature.

and the results are summarized in Table 4. Among a number of solvents examined, THF was found to be the optimal one (Table 4, entries 1–7). In addition, the yield and *ee* values depended on the bases and *N*,*N*-diisopropylethylamine (DIPEA) turned out to be the best base (entries 1 and 8–11). The use of allyl bromide gave highest enantioselectivity and yield compared to allyl chloride or allyl iodide (entries 1, 12, and 13). Finally, we found that the choice of the chlorosilane affected the results slightly, and trimethylsilyl chloride (TMSCl) was found to give the best results (entries 1, 14 and 15).

Table 4. Optimization of the Nozaki–Hiyama–Kishi reaction conditions.

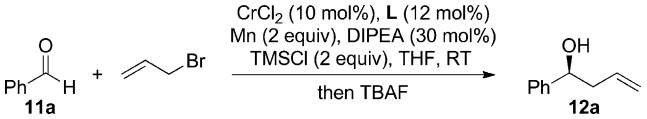


Entry	X	Base	R_3SiCl	Solvent	*t* [h]	Yield [%][a]	*ee* [%][b]
1	Br	DIPEA	TMSCl	THF	12	91	84 (*S*)
2	Br	DIPEA	TMSCl	MeCN	16	89	69 (*S*)
3	Br	DIPEA	TMSCl	EtCN	16	86	62 (*S*)
4	Br	DIPEA	TMSCl	DMSO	24	67	49 (*S*)
5	Br	DIPEA	TMSCl	DMF	24	51	7 (*S*)
6	Br	DIPEA	TMSCl	DME[c]	16	47	27 (*S*)
7	Br	DIPEA	TMSCl	CH_2Cl_2	24	32	12 (*S*)
8	Br	–	TMSCl	THF	24	87	45 (*S*)
9	Br	K_2CO_3	TMSCl	THF	24	91	59 (*S*)
10	Br	Et_3N	TMSCl	THF	24	89	49 (*S*)
11	Br	pyridine	TMSCl	THF	9	86	55 (*S*)
12	Cl	DIPEA	TMSCl	THF	12	80	43 (*S*)
13	I	DIPEA	TMSCl	THF	12	85	69 (*S*)
14	Br	DIPEA	TESCl[c]	THF	12	92	82 (*S*)
15	Br	DIPEA	TIPSCl[c]	THF	12	90	84 (*S*)

[a] Yield of isolated products. [b] Determined by chiral HPLC analysis; absolute configuration of the product was determined by comparison with literature. [c] DME = dimethoxyethane, TESCl = triethylsilyl chloride, TIPSCl = triisopropylsilyl chloride.

The reaction was further optimized by screening the whole series of ligands (Table 5). As shown, all catalysts that bore ligands **1a–j** exhibited high catalytic activity to afford the desired product **12a** with high yield. Ligand **1e**, which contained 4-isopropyloxazolinyl units and methyl groups in the backbone, gave the best enantioselectivity (86% *ee*) (Table 5, entry 5).

Table 5. Screening the ligands for the Nozaki–Hiyama–Kishi reaction.



Entry	**L**	*t* [h]	Yield [%][a]	*ee* [%][b]
1	**1a**	12	91	84 (*S*)
2	**1b**	12	92	83 (*S*)
3	**1c**	10	91	73 (*S*)
4	**1d**	10	89	54 (*S*)
5	**1e**	10	92	86 (*S*)
6	**1f**	10	93	68 (*S*)
7	**1g**	12	92	73 (*S*)
8	**1h**	12	93	79 (*S*)
9	**1i**	12	91	83 (*S*)
10	**1j**	12	92	63 (*S*)

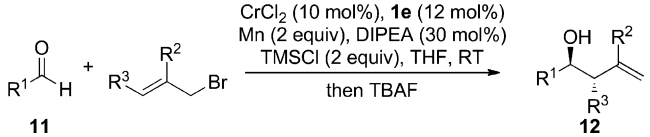
[a] Yield of isolated products. [b] Determined by chiral HPLC analysis; absolute configuration of the product was determined by comparison with literature.

With the optimal conditions in hand, the substrate scope was next explored with different aldehydes and bromides (Table 6). Aromatic and aliphatic aldehydes were all allylated with 86–88% *ee* in high yields (Table 6, entry 1–6). This system also catalyzed methallylation of aldehydes by the use of methallylbromide to obtain the corresponding products with 75–90% *ee* (entry 7–10). Furthermore, this enantioselective reaction was successfully extended to crotylations of aldehydes by the use of crotyl bromide. The crotylation of benzaldehyde gave the product with a 3.7:1 ratio of *anti* to *syn* in 90% yield with 86% *ee* (*anti* form) (entry 11). Notably, the observed diastereoselectivity of the crotylation of hydrocinnamaldehyde was high with a 10:1 ratio that favored the *anti* product obtained with 93% *ee* (entry 12).

Conclusion

The convenient synthetic access to this new class of tridentate ligands boxmi and the stability of their transition-metal complexes will allow their application in enantioselective catalysis. Their potential has been demonstrated in Ni-catalyzed enantioselective fluorinations of oxindoles and β-ketoesters and the Cr-catalyzed enantioselective NHK reaction of aldehydes. Further applications are currently being investigated in our laboratory.

Table 6. Substrate scope for the Nozaki–Hiyama–Kishi reaction.



Entry	R^1	R^2	R^3	t [h]	Product	Yield [%][a]	*ee* [%][b]
1	Ph	H	H	10	**12a**	92	86 (*S*)
2	*p*-MePh	H	H	11	**12b**	91	88 (*S*)
3	*p*-MeOPh	H	H	11	**12c**	93	88 (*S*)
4	*p*-ClPh	H	H	12	**12d**	92	86 (*S*)
5	*p*-BrPh	H	H	12	**12e**	91	86 (*S*)
6	$PhCH_2CH_2$	H	H	12	**12f**	90	87 (*R*)
7	Ph	Me	H	12	**12g**	93	86 (*S*)
8	*p*-MePh	Me	H	12	**12h**	90	90
9	*p*-ClPh	Me	H	12	**12i**	94	79 (*S*)
10	$PhCH_2CH_2$	Me	H	12	**12j**	91	75 (*R*)
11	Ph	H	Me	12	**12k**	90[c,d]	86 (*anti*)[e] 35 (*syn*)[f]
12	$PhCH_2CH_2$	H	Me	12	**12l**	89[c,g]	93 (*anti*)[h] 40 (*syn*)[i]

[a] Yield of isolated products. [b] Determined by chiral HPLC analysis; absolute configuration of the product was determined by comparison with literature. [c] Isolated yield of a mixture of *anti* and *syn* product after chromatographic purification; *anti*/*syn* ratio determined by ^{1}H NMR spectroscopy of crude product. [d] *anti*/*syn* = 3.7:1. [e] The absolute configuration was determined to be (1*S*,2*S*) by comparison with the literature.[15g,20] [f] The absolute configuration was determined to be (1*S*,2*R*) by comparison with the literature.[15g,20] [g] *anti*/*syn* = 10:1. [h] The absolute configuration was determined to be (1*R*,2*S*) by comparison with the literature.[15g,21] [i] The absolute configuration was determined to be (1*R*,2*R*) by comparison with the literature.[15g,21]

Experimental Section

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were pre-dried over activated 4 Å molecular sieves and were heated to reflux over magnesium (methanol), sodium (toluene), potassium (hexane), sodium–potassium alloy (tetrahydrofurane, diethyl ether), or calcium hydride (dichloromethane) under an argon atmosphere and collected by distillation. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using a Bruker Avance III 600, Bruker Avance II 400, and Bruker DRX 200 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane. ^{19}F NMR spectroscopy was measured at 376 MHz, and $CFCl_3$ (δ = 0 ppm) was used as an external standard. HPLC analyses using a Thermo Electron Surveyor chromatograph. Infrared spectra were prepared as KBr pellets and were recorded using a Varian Excalibur 3100 series FTIR spectrometer. Optical rotations were measured using a Perkin–Elmer 241 polarimeter in a 1 dm cuvette. Mass spectra were recorded by the mass spectrometry service of the University of Heidelberg Organic Chemistry Laboratory, and the elemental analyses were measured by the analytical services of the University of Heidelberg. Compounds **3b**,[22] **6**,[10a,c] and **8**[23] were synthesized according to the literature procedures. All other reagents were commercially available and used as received.

General procedure for the synthesis of 4a–c: Phthalimides (20–30 mmol) and (carbethoxymethylene)triphenylphosphorane (5 equiv) were mixed in a Schlenk tube under argon. Then the solid mixture was stirred in 140 °C for 24 h. The crude product was directly purified by column chromatography (*n*-hexane/ethyl acetate 4:1) to obtain the desired product. For characterization data, see the Supporting Information.

Procedure for the synthesis of 4d: Compound **4c** (950 mg, 2.67 mmol, 1 equiv), Cs_2CO_3 (8.70 g, 26.7 mmol, 10 equiv), and phenylboronic acid (2.73 g, 21.36 mmol, 8 equiv) were dissolved in a mixture of dimethoxyethane (200 mL) and H_2O (60 mL). After degassing the mixture, [Pd(PPh_3)$_4$] (711 mg, 0.67 mmol, 0.25 equiv) was added. The resulting suspension was heated at refluxing temperature for two days. After removing dimethoxyethane under vacuum, the mixture was diluted in dichloromethane and washed with water (3 × 100 mL), and the separated organic phase was dried over anhydrous sodium sulfate. Evaporation of the solvent under vacuum and purification by column chromatography (hexane/ethyl acetate 4:1) to afford **4d** (763 mg, 1.74 mmol) in 65 % yield. For characterization data, see the Supporting Information.

General procedure for the synthesis of 5: Compound **4** (1 equiv) and (*S*)-amino alcohol (5 equiv) were mixed and melted in a Schlenk tube under argon. The solid mixture was then rapidly heated to 120 °C in a preheated oil bath. NaH (60 %, 20 mol %) was added to the resulting mixture, and the reaction mixture was stirred under slightly reduced pressure for 7 h. The reaction mixture turned brown and became highly viscous. After subsequent cooling to ambient temperature, the crude product was directly purified by column chromatography (dichloromethane/methanol from 40:1 to 10:1) to obtain the desired product **5**. For characterization data, see the Supporting Information.

General procedure for the synthesis of 1: PPh_3 (12.5 mmol, 5 equiv), Et_3N (12.5 mmol, 5 equiv), and CCl_4 (12.5 mmol, 5 equiv) were added to a solution of **5** (2.5 mmol, 1 equiv) in MeCN (300 mL). The reaction mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), water (500 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (300 mL × 5). The combined organic phase was dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate 4:1) to give **1** as yellow solid.

*(1Z,3Z)-1,3-Bis{[(S)-4-phenyl-4,5-dihydrooxazol-2-yl]methylene}isoindoline (**1a**)*: Yield: 66 %; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.90 (br s, 1H), 7.72–7.70 (m, 2H), 7.51–7.50 (m, 2H), 7.31–7.27 (m, 8H), 7.24–7.20 (m, 2H), 5.72 (s, 2H), 5.30 (t, J = 8.0 Hz, 2H), 4.65 (t, J = 8.0 Hz, 2H), 4.06 ppm (t, J = 7.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.2, 147.9, 143.0, 135.0, 130.0, 128.6, 127.3, 126.7, 121.2, 83.1, 73.8, 69.7 ppm; IR (KBr): $\tilde{\nu}$ = 1643, 1607, 1475, 1167, 1116, 1065, 993, 755 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{24}N_3O_2$+H [M^++H]: 434.18630; found: 434.18618; elemental analysis calcd (%) for $C_{28}H_{23}N_3O_2$: C 77.58, H 5.35, N 9.69; found: C 77.30, H 5.29, N 9.73.

Characterization data for 1b–j: See the Supporting Information.

Procedure for the synthesis of nickel complex 10a: Compound **1a** (86.6 mg, 0.20 mmol) and sodium hydride (98 %, 24 mg, 1 mmol, 5 equiv) were suspended in THF (10 mL) and stirred at room temperature for two hours. It was then added through a cannula to a suspension of $NiCl_2$ (51.9 mg, 0.40 mmol, 2 equiv) in THF (10 mL). After stirring the reaction mixture for 8 h, the solvent was removed under vacuum, and the residue was redissolved in dichloromethane and filtered. The crude reaction product was recrystallized from dichloromethane/hexane to obtain pure product (93.7 mg, 0.18 mmol) as a dark-red solid in 89 % yield. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.76 (dd, J = 3.0, 5.4 Hz, 2H), 7.52 (dd, J = 3.0, 5.4 Hz, 2H), 7.37 (t, J = 7.2 Hz, 4H), 7.30 (t, J = 7.2 Hz, 2H), 7.16 (d, J = 7.2 Hz, 4H), 5.86 (s, 2H), 5.72 (dd, J = 3.0, 8.4 Hz, 2H), 4.48 (t, J = 8.4 Hz, 2H), 4.08 ppm (dd, J = 3.0, 8.4 Hz, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 164.4, 158.6, 144.4, 137.7, 130.1, 128.9, 127.7, 126.6, 120.6, 82.3, 74.8, 67.5 ppm; IR (KBr): $\tilde{\nu}$ = 1614, 1566, 1532, 1301, 1215, 1116, 1036, 761 cm^{-1}; HRMS (FAB): *m*/*z* calcd for $C_{28}H_{22}N_3O_2{}^{35}L^{58}Ni^{+1}$ [M^+]: 525.0754; found: 525.0729; elemental analysis calcd (%) for $C_{28}H_{22}N_3O_2ClNi$: C 63.86, H 4.21, N 7.98; found: C 63.89, H 4.05, N 7.92.

Procedure for the synthesis of nickel complex 10b: Compound **1a** (65 mg, 0.15 mmol) was added to a solution of Ni^{II} acetate tetrahydrate (74.6 mg, 0.30 mmol) in methanol (10 mL) and stirred over night. The deep-red solution was concentrated under vacuum, then the residue dissolved in CH_2Cl_2 (10 mL) and filtered. The crude reaction product was recrystallized from dichloromethane/hexane to obtain pure product (70 mg, 0.13 mmol) as a red solid in 85 % yield. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.81 (dd, J = 3.0, 5.4 Hz, 2H), 7.61 (dd, J = 3.0, 5.4 Hz, 2H), 7.38 (t, J = 7.2 Hz, 4H), 7.32 (t, J = 7.2 Hz, 2H), 7.23 (d, J = 7.2 Hz, 4H), 5.62 (d, J = 7.2 Hz, 2H), 5.53 (s, 2H), 4.48 (t, J = 8.4 Hz, 2H), 4.29 (d, J = 8.4 Hz, 2H), 1.81 ppm (s, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 170.6,

165.7, 161.5, 146.4, 144.7, 130.6, 129.1, 127.9, 126.0, 121.6, 84.5, 79.4, 71.4, 29.7 ppm; IR (KBr): $\tilde{\nu}$ = 1612, 1569, 1535, 1314, 1223, 1115, 952, 738 cm^{-1}; HRMS (FAB): *m*/*z* calcd for $C_{30}H_{25}N_3O_4{}^{58}Ni^{+1}$ [M^+]: 549.1199; found: 549.1195; elemental analysis calcd (%) for $C_{30}H_{25}N_3O_4Ni$: C 65.49, H 4.58, N 7.64; found: C 65.68, H 4.73, N 7.94.

General procedure for enantioselective catalytic fluorination: $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol%) and ligand **1a** (12 mol%) were stirred under vacuum for 2 h at room temperature, then 4 Å molecular sieves (50 mg) and dry Et_2O (2 mL) were added under argon atmosphere and stirred for 1 h. Then substrate **6** or **8** (0.10 mmol) was added to the catalyst solution. After stirring for another 30 min, *N*-fluorobenzenesulfonimide (NFSI; 1.2 equiv) was added directly to the mixture. The reaction was stirred at room temperature for 6 h, then stopped by the addition of water (0.5 mL). The reaction mixture was diluted with CH_2Cl_2, filtered through Celite and anhydrous Na_2SO_4. After removal of solvent, the residue was purified by column chromatography on silica gel (eluent: hexane/AcOEt 10:1 or CH_2Cl_2 directly) to afford pure product **7** or **9**. For further data, see the Supporting Information.

General procedure for enantioselective catalytic NHK reaction: Anhydrous chromium(II) chloride (6.1 mg, 0.05 mmol), ligand **1e** (23.6 mg, 0.06 mmol), and manganese (54.9 mg, 1.00 mmol) were added into a flame-dried Schlenk tube. Dry THF (2 mL) was added under argon atmosphere and stirred for 1 h. DIPEA (26.2 μL, 0.15 mmol) was added. The mixture was then stirred at room temperature for 30 min prior to the addition of allyl bromide (1.00 mmol) with the resulting solution being stirred for a further 1 h. The reaction was then initiated by the addition of aldehyde (0.50 mmol) and chlorotrimethylsilane (130 μL, 1.00 mmol) and stirred under an atmosphere of argon at room temperature until the disappearance of aldehyde (monitored by TLC). The resulting suspension was quenched with saturated aqueous $NaHCO_3$ (1 mL) and filtered over a pad of Celite using Et_2O as eluent (15 mL). The aqueous phase was extracted with Et_2O (2×5 mL) and the combined organic layers were then dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum to give a red residue. The red oil was then dissolved in THF (2 mL) and tetra-*n*-butylammonium fluoride (TBAF; 1 M in THF, 1.0 mL) was added. After stirring for another 30 min, the resulting solution was quenched with saturated aqueous NH_4Cl (1 mL), and the resulting aqueous phase was extracted with Et_2O (3×5 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give an oil. The crude mixture was then purified by flash column chromatography on silica gel using CH_2Cl_2 as the eluent to give the desired alcohols **13**. For further data, see the Supporting Information.

X-ray diffraction study of 1i and 10a: Data collection: Bruker AXS Smart 1000 CCD diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator, λ = 0.71073 Å, T = 100(2) K. Lorentz, polarization, and semiempirical absorption correction.[24a,b] Structure solution: charge flip.[24c] Refinement: full-matrix least squares based on F^2;[24d] all non-hydrogen atoms anisotropic. Hydrogen atoms: NH hydrogen in **1i** located and refined, all others at calculated positions (refined riding). Crystals of **1i** were 1:1 merohedral twins (apparent space group $P4_122$). In the structure of **10a**, electron density attributed to disordered *n*-pentane was removed from the structure (and the corresponding F_{obsd}) with the BYPASS procedure.[24e] Crystal data for **1i**: $C_{34}H_{34}N_3O_2$; tetragonal, space group $P4_1$; a = 11.863(1), c = 20.149(2) Å; V = 2835.7(4) $Å^3$; Z = 4; μ = 0.076 mm^{-1}; F_{000} = 1100; θ range 1.0 to 29.7°; reflections measured: 65364, independent: 4120 (R_{int} = 0.0812), observed ($I > 2\sigma(I)$): 3245; final R indices ($F_o > 4\sigma(F_o)$): $R(F)$ = 0.0593, $wR(F^2)$ = 0.1433; GOF = 1.028. Crystal data for **10a**: $C_{33}H_{34}ClN_3NiO_2$; monoclinic, space group $P2_1$; a = 14.999(7), b = 6.393(3), c = 15.423(6) Å; β = 109.328(8)°; V = 1395.4(10) $Å^3$; Z = 2; μ = 0.827 mm^{-1}; F_{000} = 628; θ range 2.3 to 32.2°; reflections measured: 35221, independent: 9240 (R_{int} = 0.0328), observed ($I > 2\sigma(I)$): 8937; final R indices ($F_o > 4\sigma(F_o)$): $R(F)$ = 0.0284, $wR(F^2)$ = 0.0776; GOF = 1.099; Flack x = −0.003(6).

CCDC-830007 (**1i**) and -830008 (**10a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] Reviews covering "pincer" complex chemistry: a) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866–3898; *Angew. Chem. Int. Ed.* **2001**, 40, 3750–3781; b) M. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792; Selected references for chiral pincer-based catalysts: c) B. S. Williams, P. Dani, M. Lutz, A. L. Spek, G. Van Koten, *Helv. Chim. Acta* **2001**, *84*, 3519–3530; d) B. Soro, S. Stoccoro, G. Minghetti, A. Zucca, M. A. Cinellu, M. Manassero, S. Gladiali, *Inorg. Chim. Acta* **2006**, *359*, 1879–1888; e) J. Aydin, K. S. Kumar, M. J. Sayah, O. A. Wallner, K. J. Szabo, *J. Org. Chem.* **2007**, *72*, 4689–4697.

[2] a) *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**; b) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, **1994**; c) *Transition Metals for Organic Synthesis*, 2nd ed. (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**; d) *New Frontiers in Asymmetric Catalysis*, (Eds.: K. Mikami, M. Lautens), Wiley: Hoboken, NJ, **2007**; e) *Catalysis in Asymmetric Synthesis*, 2nd ed. (Eds.: V. Caprio, J. M. J. Williams), Wiley: Hoboken, NJ, **2009**; f) *Catalytic Asymmetric Synthesis*, 3rd ed. (Ed.: I. Ojima), Wiley: Hoboken, NJ, **2010**.

[3] a) H. Nishiyama, J.-i. Ito, *Chem. Commun.* **2010**, *46*, 203–212; b) H. Nishiyama, J.-i. Ito, *Chem. Rec.* **2007**, *7*, 159–166; c) H. Nishiyama, *Chem. Soc. Rev.* **2007**, *36*, 1133–1141.

[4] a) M. Inoue, T. Suzuki, M. Nakada, *J. Am. Chem. Soc.* **2003**, *125*, 1140–1141; b) M. Inoue, M. Nakada, *Org. Lett.* **2004**, *6*, 2977–2980; c) M. Inoue, M. Nakada, *Angew. Chem.* **2005**, *117*, 258–261; *Angew. Chem. Int. Ed.* **2005**, *44*, 253–257; d) M. Inoue, M. Nakada, *J. Am. Chem. Soc.* **2007**, *129*, 4164–4165; e) M. Inoue, T. Suzuki, A. Kinoshita, M. Nakada, *Chem. Rec.* **2008**, *8*, 169–181.

[5] B. K. Langlotz, H. Wadepohl, L. H. Gade, *Angew. Chem.* **2008**, *120*, 4748–4752; *Angew. Chem. Int. Ed.* **2008**, *47*, 4670–4674.

[6] a) S. E. Reisman, J. M. Ready, M. M. Weiss, A. Hasuoka, M. Hirata, K. Tamaki, T. V. Ovaska, C. J. Smith, J. L. Wood, *J. Am. Chem. Soc.* **2008**, *130*, 2087–2100; b) Y. Yamada, M. Kitajima, N. Kogure, H. Takayama, *Tetrahedron* **2008**, *64*, 7690–7694; c) C. V. Galliford, K. A. Scheidt, *Angew. Chem.* **2007**, *119*, 8902–8912; *Angew. Chem. Int. Ed.* **2007**, *46*, 8748–8758; d) T. Kagata, S. Saito, H. Shigemori, A. Ohsaki, H. Ishiyama, T. Kubota, J. I. Kobayashi, *J. Nat. Prod.* **2006**, *69*, 1517–1521.

[7] a) B. Volk, J. Barkóczy, E. Hegedus, S. Udvari, I. Gacsályi, T. Mezei, K. Pallagi, H. Kompagne, G. Lévay, A. Egyed, J. L. G. Hársing, M. Spedding, G. Simig, *J. Med. Chem.* **2008**, *51*, 2522–2532; b) A. Fensome, W. R. Adams, A. L. Adams, T. J. Berrodin, J. Cohen, C. Huselton, A. Illenberger, J. C. Kern, V. A. Hudak, M. A. Marella, E. G. Melenski, C. C. McComas, C. A. Mugford, O. D. Slayden, M. Yudt, Z. Zhang, P. Zhang, Y. Zhu, R. C. Winneker, J. E. Wrobel, *J. Med. Chem.* **2008**, *51*, 1861–1873; c) F. C. Stevens, W. E. Bloomquist, A. G. Borel, M. L. Cohen, C. A. Droste, M. L. Heiman, A. Kriauciunas, D. J. Sall, F. C. Tinsley, C. D. Jesudason, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6270–6273; d) T. Jiang, K. L. Kuhen, K. Wolff, H. Yin, K. Bieza, J. Caldwell, B. Bursulaya, T. Y.-H. Wu, Y. He, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 2105–2108; e) P. Hewawasam, V. K. Gribkoff, Y. Pendri, S. I. Dworetzky, N. A. Meanwell, E. Martinez, C. G. Boissard, D. J. Post-Munson, J. T. Trojnacki, K. Yeleswaram, L. M. Pajor, J. Knipe, Q. Gao, R. Perrone, J. E. Starrett, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1023–1026; f) V. K. Gribkoff, J. E. Starrett, S. I. Dworetzky, P. Hewawasam, C. G. Boissard, D. A. Cook, S. W. Frantz, K. Heman, J. R. Hibbard, K. Huston, G. Johnson, B. S. Krishnan, G. G. Kinney, L. A. Lombardo, N. A. Meanwell, P. B. Molinoff, R. A. Myers, S. L. Moon, A. Ortiz, L. Pajor, R. L. Pieschl, D. J. Post-Munson, L. J. Signor, N. Srinivas, M. T. Taber, G. Thalody, J. T. Trojnacki, H. Wiener, K. Yeleswaram, S. W. Yeola, *Nat. Med.*

2001, *7*, 471–477; g) A. Denis, F. Bretin, C. Fromentin, A. Bonnet, A. Bonnefoy, C. Agouridas, G. Piltan, *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2019–2022.

[8] For reviews of enantioselective fluorination reactions, see: a) K. Muñiz, *Angew. Chem.* **2001**, *113*, 1701–1704; *Angew. Chem. Int. Ed.* **2001**, *40*, 1653–1656; b) J.-A. Ma, D. Cahard, *Chem. Rev.* **2004**, *104*, 6119–6146; c) P. M. Pihko, *Angew. Chem.* **2006**, *118*, 558–561; *Angew. Chem. Int. Ed.* **2006**, *45*, 544–547; d) G. K. S. Prakash, P. Beier, *Angew. Chem.* **2006**, *118*, 2228–2230; *Angew. Chem. Int. Ed.* **2006**, *45*, 2172–2174; e) V. A. Brunet, D. O'Hagan, *Angew. Chem.* **2008**, *120*, 1198–1201; *Angew. Chem. Int. Ed.* **2008**, *47*, 1179–1182; f) K. L. Kirk, *Org. Process Res. Dev.* **2008**, *12*, 305–321; g) M. Ueda, T. Kano, K. Maruoka, *Org. Biomol. Chem.* **2009**, *7*, 2005–2012; h) A. M. R. Smith, K. K. Hii, *Chem. Rev.* **2010**, *111*, 1637–1656; i) S. Lectard, Y. Hamashima, M. Sodeoka, *Adv. Synth. Catal.* **2010**, *352*, 2708–2732.

[9] Selected examples for catalytic enantioselective fluorination, see: a) L. Hintermann, A. Togni, *Angew. Chem.* **2000**, *112*, 4530–4533; *Angew. Chem. Int. Ed.* **2000**, *39*, 4359–4362; b) D. Y. Kim, E. J. Park, *Org. Lett.* **2002**, *4*, 545–547; c) Y. Hamashima, K. Yagi, H. Takano, L. Tamás, M. Sodeoka, *J. Am. Chem. Soc.* **2002**, *124*, 14530–14531; d) M. Marigo, D. Fielenbach, A. Braunton, A. Kjærsgaard, K. A. Jørgensen, *Angew. Chem.* **2005**, *117*, 3769–3772; *Angew. Chem. Int. Ed.* **2005**, *44*, 3703–3706; e) D. D. Steiner, N. Mase, C. F. Barbas III, *Angew. Chem.* **2005**, *117*, 3772–3776; *Angew. Chem. Int. Ed.* **2005**, *44*, 3706–3710; f) L. Bernardi, K. A. Jørgensen, *Chem. Commun.* **2005**, 1324–1326; g) T. D. Beeson, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2005**, *127*, 8826–8828; h) J. Franzén, M. Marigo, D. Fielenbach, T. C. Wabnitz, K. A. Jørgensen, *J. Am. Chem. Soc.* **2005**, *127*, 18296–18304; i) M. Althaus, C. Becker, A. Togni, A. Mezzetti, *Organometallics* **2007**, *26*, 5902–5911; j) T. Suzuki, Y. Hamashima, M. Sodeoka, *Angew. Chem.* **2007**, *119*, 5531–5535; *Angew. Chem. Int. Ed.* **2007**, *46*, 5435–5439; k) D. S. Reddy, N. Shibata, J. Nagai, S. Nakamura, T. Toru, S. Kanemasa, *Angew. Chem.* **2008**, *120*, 170–174; *Angew. Chem. Int. Ed.* **2008**, *47*, 164–168; l) D. H. Paull, M. T. Scerba, E. Alden-Danforth, L. R. Widger, T. Lectka, *J. Am. Chem. Soc.* **2008**, *130*, 17260–17261; m) M. Frings, C. Bolm, *Eur. J. Org. Chem.* **2009**, *2009*, 4085–4090; n) X. Wang, Q. Lan, S. Shirakawa, K. Maruoka, *Chem. Commun.* **2010**, *46*, 321–323.

[10] For catalytic enantioselective fluorination of oxindoles, see: a) Y. Hamashima, T. Suzuki, H. Takano, Y. Shimura, M. Sodeoka, *J. Am. Chem. Soc.* **2005**, *127*, 10164–10165; b) N. Shibata, J. Kohno, K. Takai, T. Ishimaru, S. Nakamura, T. Toru, S. Kanemasa, *Angew. Chem.* **2005**, *117*, 4276–4279; *Angew. Chem. Int. Ed.* **2005**, *44*, 4204–4207; c) T. Ishimaru, N. Shibata, T. Horikawa, N. Yasuda, S. Nakamura, T. Toru, M. Shiro, *Angew. Chem.* **2008**, *120*, 4225–4229; *Angew. Chem. Int. Ed.* **2008**, *47*, 4157–4161.

[11] a) Y. Okude, S. Hirano, T. Hiyama, H. Nozaki, *J. Am. Chem. Soc.* **1977**, *99*, 3179–3181; b) K. Takai, K. Kimura, T. Kuroda, T. Hiyama, H. Nozaki, *Tetrahedron Lett.* **1983**, *24*, 5281–5284; c) H. Jin, J. Uenishi, W. J. Christ, Y. Kishi, *J. Am. Chem. Soc.* **1986**, *108*, 5644–5646.

[12] For reviews: a) M. Avalos, R. Babiano, P. Cintas, J. L. Jiménez, J. C. Palacios, *Chem. Soc. Rev.* **1999**, *28,* 169–177; b) A. Fürstner, *Chem. Rev.* **1999**, *99*, 991–1046; c) L. A. Wessjohann, G. Scheid, *Synthesis* **1999**, 1–36; d) K. Takai, H. Nozaki, *Proc. Jpn. Acad., Ser. B* **2000**, 76, 123–131; e) K. Takai, *Org. React.* **2004**, *64,* 253–612; f) G. C. Hargaden, P. J. Guiry, *Adv. Synth. Catal.* **2007**, *349*, 2407–2424.

[13] a) A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 2533–2534; b) A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 12349–12357.

[14] a) M. Bandini, P. G. Cozzi, P. Melchiorre, A. Umani-Ronchi, *Angew. Chem.* **1999**, *111*, 3558–3561; *Angew. Chem. Int. Ed.* **1999**, *38*, 3357–3359; b) M. Bandini, P. G. Cozzi, A. Umani-Ronchi, *Polyhedron* **2000**, *19*, 537–539; c) M. Bandini, P. G. Cozzi, A. Umani-Ronchi, *Angew. Chem.* **2000**, *112*, 2417–2420; *Angew. Chem. Int. Ed.* **2000**, *39*, 2327–2330; d) M. Bandini, P. G. Cozzi, P. Melchiorre, S. Morganti, A. Umani-Ronchi, *Org. Lett.* **2001**, *3*, 1153–1155.

[15] a) H.-w. Choi, K. Nakajima, D. Demeke, F.-A. Kang, H.-S. Jun, Z.-K. Wan, Y. Kishi, *Org. Lett.* **2002**, *4*, 4435–4438; b) M. Kurosu, M.-H. Lin, Y. Kishi, *J. Am. Chem. Soc.* **2004**, *126*, 12248–12249; c) A. Berkessel, D. Menche, C. A. Sklorz, M. Schröder, I. Paterson, *Angew. Chem.* **2003**, *115*, 1062–1065; *Angew. Chem. Int. Ed.* **2003**, *42*, 1032–1035; d) J.-Y. Lee, J. J. Miller, S. S. Hamilton, M. S. Sigman, *Org. Lett.* **2005**, *7*, 1837–1839; e) J. J. Miller, M. S. Sigman, *J. Am. Chem. Soc.* **2007**, *129*, 2752–2753; f) J. J. Miller, M. S. Sigman, *Angew. Chem.* **2008**, *120*, 783–786; *Angew. Chem. Int. Ed.* **2008**, *47*, 771–774; g) G. Xia, H. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 2554–2555; h) G. Xia, H. Yamamoto, *J. Am. Chem. Soc.* **2007**, *129*, 496–497; i) M. Naodovic, G. Xia, H. Yamamoto, *Org. Lett.* **2008**, *10*, 4053–4055; j) D. L. Usanov, H. Yamamoto, *Angew. Chem.* **2010**, *122*, 8345–8348; *Angew. Chem. Int. Ed.* **2010**, *49*, 8169–8172; k) D. L. Usanov, H. Yamamoto, *J. Am. Chem. Soc.* **2011**, *133*, 1286–1289; l) H. A. McManus, P. G. Cozzi, P. J. Guiry, *Adv. Synth. Catal.* **2006**, *348*, 551–558; m) G. C. Hargaden, H. A. McManus, P. G. Cozzi, P. J. Guiry, *Org. Biomol. Chem.* **2007**, *5*, 763–766; n) G. C. Hargaden, H. Müller-Bunz, P. J. Guiry, *Eur. J. Org. Chem.* **2007**, *2007*, 4235–4243; o) G. C. Hargaden, T. P. O'Sullivan, P. J. Guiry, *Org. Biomol. Chem.* **2008**, *6*, 562–566; p) V. Coeffard, M. Aylward, P. J. Guiry, *Angew. Chem.* **2009**, *121*, 9316–9319; *Angew. Chem. Int. Ed.* **2009**, *48*, 9152–9155.

[16] a) W. Flitsch, H. Peters, *Tetrahedron Lett.* **1969**, *10*, 1161–1162; b) W. Flitsch, H. Peters, *Chem. Ber.* **1970**, *103*, 805–817.

[17] a) N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **1979**, *20*, 3437–3440; b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.

[18] See for instance: a) F. Konrad, J. L. Fillol, H. Wadepohl, L. H. Gade, *Inorg. Chem.* **2009**, *48*, 8523–8535; b) F. Konrad, J. L. Fillol, C. Rettenmeier, H. Wadepohl, L. H. Gade, *Eur. J. Inorg. Chem.* **2009**, 4950–4961.

[19] H. Vorbrüggen, K. Krolikiewicz, *Tetrahedron Lett.* **1981**, *22*, 4471–4474.

[20] M. Wadamoto, N. Ozasa, A. Yanagisawa, H. Yamamoto, *J. Org. Chem.* **2003**, *68*, 5593–5601.

[21] V. Rauniyar, H. Zhai, D. G. Hall, *J. Am. Chem. Soc.* **2008**, *130*, 8481–8490.

[22] C. E. Godinez, G. Zepeda, C. J. Mortko, H. Dang, M. A. Garcia-Garibay, *J. Org. Chem.* **2004**, *69*, 1652–1662.

[23] T. A. Moss, D. R. Fenwick, D. J. Dixon, *J. Am. Chem. Soc.* **2008**, *130*, 10076–10077.

[24] a) *SAINT*, Bruker AXS, **1997–2008**; b) G. M. Sheldrick, *SADABS*, Bruker AXS, **2004–2008**; c) L. Palatinus, *SUPERFLIP*, EPF Lausanne, Switzerland, **2007**; d) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**; e) A. L. Spek, *PLATON*, Utrecht University, The Netherlands; f) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7.

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