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Pd-Catalyzed Enantioselective C−H Iodination: Asymmetric Synthesis of Chiral Diarylmethylamines

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Supporting Information

ABSTRACT: An enantioselective C−H iodination reaction using a mono-*N*-benzoyl-protected amino acid has been developed for the synthesis of chiral diarylmethylamines. The reaction uses iodine as the sole oxidant and proceeds at ambient temperature and under air.

Enantiopure diarylmethylamine is an important motif in bioactive compounds, as exemplified by the antihistamine drug, Certirizine hydrochloride, and the promising drug candidate, SNC-80, which contain a stereogenic diarylmethylamine core (Figure 1).[1] Extensive efforts have led to the development of two key strategies for the enantioselective synthesis of diarylmethylamines (Scheme 1).[2,3] The first approach involves the asymmetric addition of an arylmetal or arylboron species to aldimines using either a chiral ligand[4] or an auxiliary.[5] The Ellman auxiliary has found extensive applications due to its ready availability and reliability.[5a−h] Alternatively, asymmetric hydrogenation has been employed for the enantioselective synthesis of this important scaffold.[6] Unfortunately, an *ortho*-substitution is often required on at least one of the arenes to achieve high levels of enantioselection, except for a few examples relying on the use of a high pressure of hydrogen.[6c]

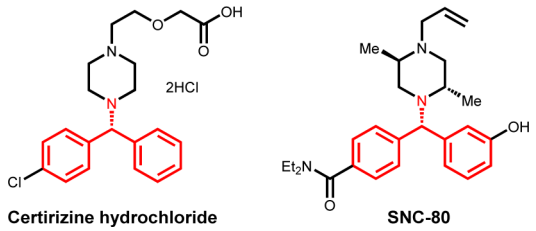
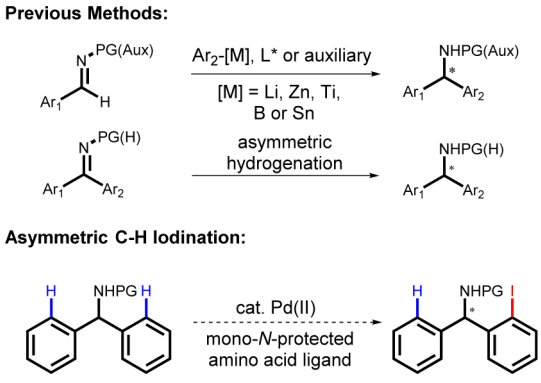


Figure 1. Biologically active diarylmethylamine compounds.

We have previously reported several examples of Pd(II)-catalyzed enantioselective C−H activation reactions in which a mono-*N*-protected amino acid (MPAA) ligand is used to control the stereochemistry during the asymmetric cleavage of a prochiral C−H bond.[7−10] While the majority of these reactions proceed via a Pd(II)/Pd(0) catalytic cycle, MPAA has also been shown to be an effective ligand in an intramolecular enantioselective C−H activation/C−O bond-forming reaction based on Pd(II)/Pd(IV) catalysis.[8f] Although an early example of asymmetric C−H iodination using a chiral auxiliary was reported, enantioselective iodination remains to be demonstrated.[11] Herein we report the first example of an enantioselective C−H iodination to provide a new route for the synthesis of diarylmethylamines. The use of inexpensive molecular iodine as the sole oxidant and a readily available chiral amino acid-derived ligand renders this reaction potentially practical for a large-scale production of enantiopure diarylmethylamines.

Scheme 1. Strategies Toward Chiral Diarylmethylamines



Recently, we developed a Pd-catalyzed C−H iodination of benzamides using inexpensive I_2 as the sole oxidant.[12] We found that product separation with this catalytic system is much simpler as there are no byproducts from the oxidants and the inert reactivity of I_2, relative to other commonly used highly electrophilic halogenating reagents, largely prevents background reactions. Therefore, we surmised that this catalytic system may be suitable for the development of an enantioselective C−H iodination reaction. In light of the importance of the chiral diarylmethylamine scaffolds, we embarked on the development of enantioselective C−H iodination of trifluoromethanesulfonyl-protected diarylmethylamines. The superior reactivity of triflamide compared to other protected amines (NHAc, NHTFA, NHBoc) was previously demonstrated.[13]

Screening of our chiral MPAA ligands and various reaction parameters using **1a** as the model substrate led to an encouraging finding. The use of the Boc-Leu-OH ligand with CsOAc as a base in DMF provided the chiral diarylmethyl-

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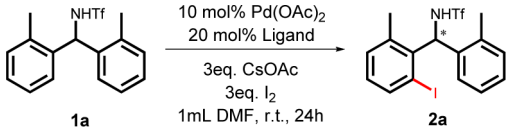
Table 1. Ligand Screening[a]



1a 2a

entry	ligand	yield (%)[b]	ee (%)[c]
1	Boc-Leu-OH	25	25
2	Boc-Val-OH	20	33
3	Boc-Ala-OH	11	23
4	Boc-Ile-OH	30	26
5	Boc-Phe-OH	26	25
6	Boc-D-Val-OH	18	−33
7	Boc-Nle-OH	20	15
8	Boc-Try(tBu)-OH	20	35
9	Boc-Asn-OH	n.r.	n.r.
10	Boc-MeAla-OH	34	2
11	Form-Leu-OH	10	30
12	Ac-Leu-OH	n.r.	n.r.
13	TFA-Leu-OH	10	3
14	TcBoc-Leu-OH	13	8
15	Me-Leu-OH	n.r.	n.r.
16	Bn-Leu-OH	n.r.	n.r.
17	MeO_2C-Leu-OH	43	15
18	Piv-Leu-OH	30	0
19	Bz-Leu-OH	20	67
20[d]	**Bz-Leu-OH**	**18 (47)** [e]	**89 (78)**[e]

[a]Conducted on 0.1 mmol scale. [b]Determined by ^{1}H NMR analysis using CH_2Br_2 as the internal standard. [c]Determined by chiral HPLC analysis. [d]*t*-Amyl-OH used as solvent with 15 equiv of DMF as an additive. [e]Conducted at 50 °C, 12 h.

Table 2. Base Screening[a]

1a 2a

entry	base	yield (%)[b]	ee (%)[c]
1	none	n.r.	n.r.
2	CsOAc	47	78
3	LiOAc	n.r.	n.r.
4	NaOAc	12	53
5	KOAc	40	60
6	$NaHCO_3$	n.r.	n.r.
7	$KHCO_3$	n.r.	n.r.
8	Li_2CO_3	n.r.	n.r.
9	Na_2CO_3	6	77
10	K_2CO_3	38	99
11	Cs_2CO_3	40	98
12	Na_2HPO_4	n.r.	n.r.
13	K_2HPO_4	20	83
14	K_3PO_4	33	97
15	LiH_2PO_4	58	75
16	CsOAc + Na_2CO_3[d]	82	89
17[e]	**CsOAc + Na_2CO_3**[d]	**81 (80)**[f]	**98 (98)**[f]
18[e]	CsOAc	45	90

[a]Conducted on 0.1 mmol scale. [b]Determined by ^{1}H NMR analysis using CH_2Br_2 as the internal standard. [c]By chiral HPLC analysis. [d]3 equiv of CsOAc and 3 equiv of Na_2CO_3. [e]15 equiv of DMSO as an additive instead of DMF. [f]Conducted at 30 °C, 48 h.

amine **2a** in 25% yield with 25% ee (Table 1, entry 1). Encouraged by this result, we screened a variety of Boc protected amino acid ligands with different backbones (entries 2−10). Unfortunately, no significant improvement was observed with these ligands, and the best enantioselectivity obtained was 33% ee when Boc-Val-OH was used (entry 2). The low yield observed in general is also a major concern at this stage.

Since we have shown previously that the *N*-protecting group on the MPAA ligand exerts significant influence on the enantioselectivity, we tested leucine ligands protected with various protecting groups that are available from our library (entries 11−20) and found that the use of benzoyl-protected leucine improved the enantioselectivity to 67% ee, albeit in low yield (entry 19). Through further optimization, however, we discovered that the use of a binary solvent system, *t*-amyl-OH, as the main solvent with 15 equiv of DMF as the additive provides a significant improvement in enantioselectivity in this transformation, affording the desired product in 89% ee, albeit in low yield (entry 20). Raising the reaction temperature to 50 °C increased the yield to 47%, with the enantioselectivity dropping to 78% ee (entry 20). Based on this finding, we also reexamined other amino acids protected with a benzoyl group and found that leucine backbone appeared to be the optimal. We also modified the benzoyl protecting group on the leucine ligand, attempting to improve the yields and enantioselectivity but without further success (see SI for a detailed study). In summary, Bz-Leu-OH was identified as the optimal ligand at this stage (Table 1).

We subsequently investigated the effect of the base on this transformation (Table 2). The identity of the metal counterion proved critical in this transformation with Cs^+ and K^+ being generally superior to Na^+ and Li^+ (entries 2−5). Both the conversions and ees were also significantly influenced by the anions of the base present (entries 6−15). The use of either sodium or potassium bicarbonate resulted in no reaction (entries 6 and 7) whereas sodium, potassium or cesium acetates and carbonates promoted the reaction to various extents (entries 2, 4, 5, 9, 10, and 11). Tripotassium phosphate was more effective than dipotassium phosphate in terms of both yield and enantioselectivity (entries 13 and 14). Surprisingly, monolithium phosphate gave moderate yields and enantioselectivity (entry 15). None of these conditions, however, provided synthetically useful yields. Ultimately we discovered that combination of Na_2CO_3 and CsOAc effectively promotes the iodination reaction, affording the desired product **2a** in 82% yield and 89% ee (entry 16). Replacing the 15 equiv of DMF with the same amount of DMSO improved the enantioselectivity to 98% ee while yield remained as high as 81% (entry 17).[14] DMF or DMSO could sequester the small amount of free Pd(II) species not coordinated to chiral ligand thereby avoiding racemic iodination. Removal of Na_2CO_3 from the reaction under these new conditions decreased the yield to 45%, while maintaining the high enantioselectivity (entry 18). These combined experimental results suggest that the use of mixed bases CsOAc and Na_2CO_3, and DMSO as an additive has significant beneficial effect on both the yield and enantioselectivity.

The iodination reaction also proceeded at 30 °C to give high yield and enantioselectivity (Table 2, entry 17). The excellent reactivity of this reaction at low temperature is a significant advantage when enantioselection of certain substrates become

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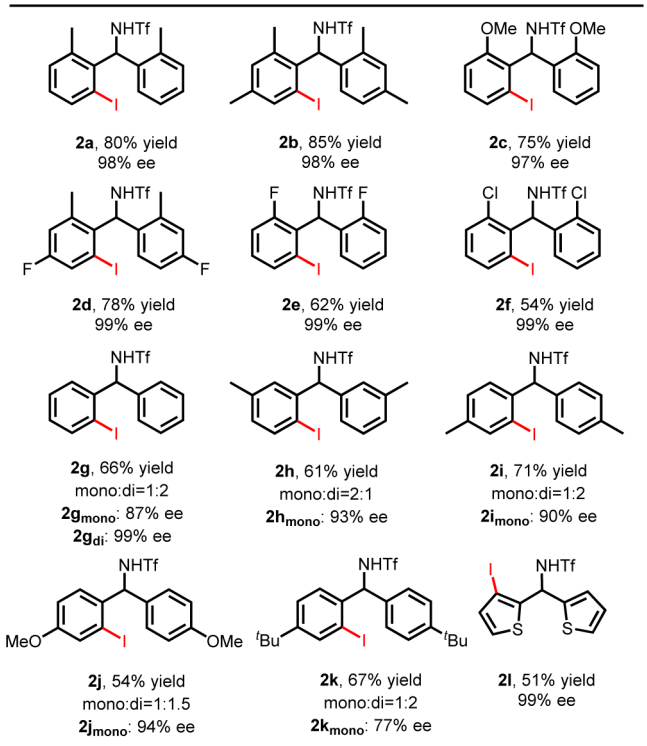
challenging. Tolerance of air also simplifies the experimental operation of this reaction.

With these optimized conditions in hand, we began to examine the substrate scope of this reaction. The achiral starting materials are readily prepared on gram-scale following literature procedures.[15] While the conditions for enantioselective iodination are effective with majority of the substrates, we found that the use of 40 mol% ligand gave slightly improved enantioselectivity overall (Table 3). Iodination of the *ortho*-

Table 3. Substrate Scope[a]

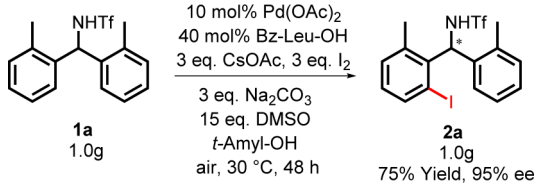


[a]Conducted on 0.2 mmol scale. Reaction conditions: 10 mol % $Pd(OAc)_2$, 40 mol % Bz-Leu-OH, 3 equiv of CsOAc, 3 equiv of Na_2CO_3, 3 equiv of I_2, 15 equiv of DMSO, 2 mL of *t*-amyl-OH, 30 °C, air, 48 h. Isolated yield are given; ee's were determined by chiral HPLC analysis.

substituted substrates **1a**–**1f** consistently affords the desired products **2a**–**2f** in moderate to good yields with excellent enantioselectivity (Table 3, 54–85% yield, 97–99% ee). Substitution of the aryl rings with electron-donating (OMe) or electron-withdrawing (F, Cl) substituents does not significantly affect the yield or enantioselectivity. In the absence of *ortho*-substitution, the iodination reaction proceeds to give a mixture of mono- and di-iodinated products **2g**–**2k** in 54–71% yields. Further ligand development will be required to suppress the di-iodination. The enantiomeric purity of the di-iodinated product $\mathbf{2g_{di}}$ is higher than that of the mono-iodinated product $\mathbf{2g_{mono}}$ (99% ee vs 87% ee), presumably due to a chiral Horeau's amplification during the second iodination.[16] The origin of low enantiomeric purity of **2k** (77% ee) remains to be understood at this stage. We were pleased to find that, under these conditions, di-(2-thiophenyl)methylamine **1l** can be selectively mono-iodinated to provide **2l** in 51% yield and 99% ee.

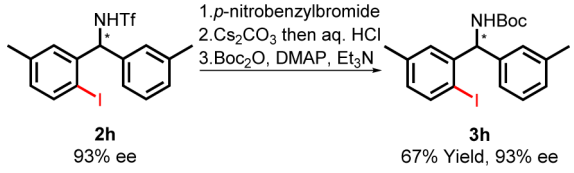
This new enantioselective iodination reaction was also performed on gram-scale using substrate **1a** to provide 1.0 g

Scheme 2. Gram-Scale Synthesis



of **2a** (75% yield) in 95% ee (Scheme 2). The minor decrease of the enantioselectivity in gram-scale could be due to the heterogeneity of this reaction and lack of highly efficient stirring. We were subsequently able to deprotect the trifluoromethylsulfonyl amine using a modification of conditions previously reported separately by Hendrickson, Danheiser, and Blakey.[17] Thus, activation of the triflamide with *p*-nitrobenzylbromide facilitated the deprotection of **2h**, as shown in Scheme 3.

Scheme 3. Deprotection



Finally, the coordination mode of the triflamide directing group is especially intriguing. Based on our previous stereochemical model with Pd(II)/MPAA catalysts, the directing group coordinates with Pd(II) as a neutral σ-donor similar to pyridine,[8a,d] carbonyl[8b] and imidate.[8c] These results have prompted us to invoke an unusual, weakly coordinating sulfonaimine structure **4** in the C–H activation step (Figure 2). The absolute configuration of the iodinated product **2a** (*R*,

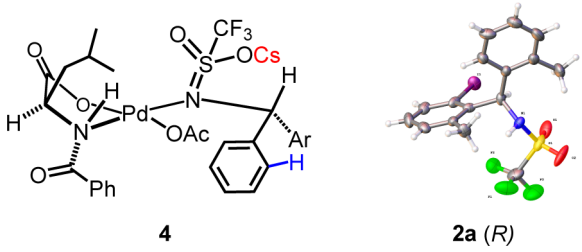


Figure 2. Proposed intermediate and X-ray structure of **2a** (*R*).

determined by X-ray) is also consistent with the structure of the proposed reactive intermediate **4**. We hope that further investigation into this coordination mode and the remarkable effects of the metal counterions will shed light onto enantioselective C–H activation reactions.

In summary, we have developed the first example of an enantioselective C–H iodination reaction, which provides a useful method for the preparation of chiral diarylmethylamines. The newly introduced iodides should be amenable to a variety of transformations leading to diarylmethylamine analogues. The use of a readily available mono-*N*-protected amino acid ligand in conjunction with the practical halogenating reagent I_2 should render this reaction practical for large-scale asymmetric iodination. Mechanistically, the ambient temperature and absence of strongly electron-donating ligands in this C–H

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iodination reaction begs further investigation whether Pd(IV) intermediate is involved in the functionalization step.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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