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Catalytic asymmetric addition of arylboronic acids to *N*-Boc imines generated in situ using C_2-symmetric cationic *N*-heterocyclic carbenes (NHCs) Pd^{2+} diaquo complexes

Zhen Liu, Min Shi *

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

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ABSTRACT

The catalytic asymmetric addition of arylboronic acids to *N*-Boc imines generated in situ from stable and easily prepared α-carbamoyl sulfones was realized by using chiral cationic C_2-symmetric *N*-heterocyclic carbene (NHC) Pd^{2+} diaquo complexes **1a–c** as the catalysts, producing the corresponding adducts in good to high yields (up to 89%) and good to high enantioselectivities (up to 90% ee).

1. Introduction

Recently, *N*-heterocyclic carbenes (NHCs) have been widely used as ancillary ligands in organometallic chemistry and catalysis since they have several significant advantages over their phosphine counterparts such as stronger σ-donor and weaker π-acceptor properties than phosphine ligands and their air/moisture stabilities, which make them to be handled easily and conveniently.[1,2] Even though the chiral NHC–metal complexes have been applied in some catalytic asymmetric transformations[1b,3] such as enolate arylation,[4] π-allyl alkylation,[5] and various ring-closing reactions with carbopalladation,[6] the fully successful examples are still limited. Thus, further exploration of novel catalytic asymmetric system using chiral NHC–metal complexes is still highly desirable at the present stage.

The asymmetric addition of nucleophiles to ^{t}BuOC(O)-protected imines (*N*-Boc imine) has provided a straightforward synthetic approach to chiral amines because its precursor (Boc_2O) is easily available and N-protected group (*N*-Boc) can be cleaved under several convenient acidic conditions (HCl or TFA).[7] Thus far, although asymmetric additions of nucleophiles such as arylboronic acids to activated imine derivatives catalyzed by Rh complexes have made great progress,[8] the asymmetric addition of arylboronic acids to *N*-Boc imines was missing until Ellman and co-workers first reported on the Rh-catalyzed asymmetric addition of arylboronic acids to *N*-Boc imines generated in situ from stable and easily prepared α-carbamoyl sulfones in the presence of Et_3N and K_2CO_3, affording a particularly efficient and straightforward synthetic method for the preparation of various chiral amines.[9] On the other hand, previously, we reported the catalytic enantioselective arylation of *N*-tosylarylimines with arylboronic acids using C_2-symmetric cationic *N*-heterocyclic carbenes (NHCs) Pd^{2+} diaquo complexes, derived from 1,1′-binaphthalenyl-2,2′-diamine (BINAM) or H_8-BINAM, to afford the corresponding adducts in excellent yields (up to 99%) and good to excellent enantioselectivities (up to 94% ee).[3f,10] In this paper, we wish to report the extension on the utilization of these chiral C_2-symmetric cationic NHC–Pd^{2+} diaquo complexes as the catalysts for the enantioselective arylation of *N*-Boc imines generated in situ similarly from α-carbamoyl sulfones with arylboronic acids under mild conditions.

2. Results and discussion

2.1. Synthesis of chiral cationic C_2-symmetric *N*-heterocyclic carbene (NHC) Pd^{2+} diaquo complexes 1a–c

As shown in Figure 1, a series of the chiral cationic NHC–Pd^{2+} diaquo complexes **1a–c** were designed and synthesized in a six-step pathway starting from optically active 1,1′-binaphthyl-2,2′-diamine (BINAM) or H_8-BINAM according to our previously reported procedure.[3f,10]

2.2. Catalytic enantioselective addition of arylboronic acids to *N*-Boc imines generated in situ

At first, we examined the catalytic ability of chiral NHC–Pd catalyst **1a** in the reactions of α-carbamoyl sulfone **2a** (1.0 equiv) with phenylboronic acid (2.0 equiv, the formation of the homo-coupling products (Ar–Ar) of arylboronic acids was also observed in this reaction) to develop the optimal conditions and the results of these experiments are summarized in Table 1. 4 Å molecular sieves

* Corresponding author.
E-mail address: mshi@mail.sioc.ac.cn (M. Shi).

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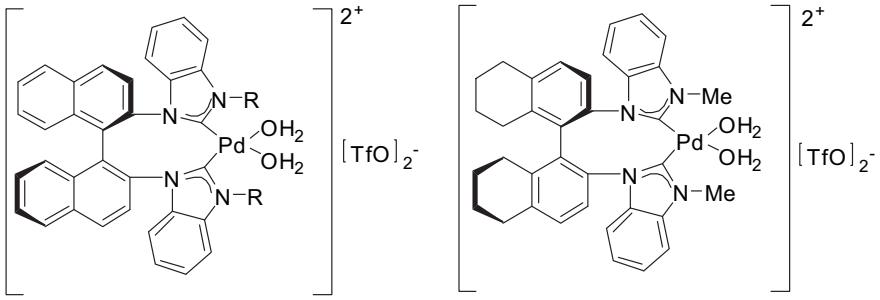
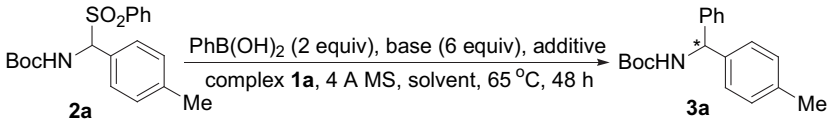


(*R*)-*N*-Me-NHC-Pd^{2+} **1a** (R = Me)
(*R*)-*N*-Bn-NHC-Pd^{2+} **1b** (R = Bn)

(*R*)-H_8-*N*-Me-NHC-Pd^{2+} **1c** (R = Me)

Figure 1. Chiral cationic NHC–Pd^{2+} diaquo complexes **1a–c**.

Table 1
Optimization of the reaction condition for catalytic enantioselective addition of arylboronic acids to *N*-Boc imines generated in situ using C_2-symmetric cationic *N*-heterocyclic carbene Pd^{2+} diaquo complexes **1a–c**

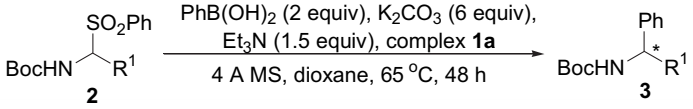


Entry	Base	Additive[a]	Solvent	Yield (%)[b]	ee (%)[c]
1	KOH	—	Dioxane	<5	—
2	K_2CO_3	—	Dioxane	<5	—
3	Et_3N	—	Dioxane	<5	—
4	K_2CO_3	Et_3N	Dioxane	69	86 (−)
5[d]	K_2CO_3	Et_3N	Dioxane	21	82 (−)
6[e]	K_2CO_3	Et_3N	Dioxane	67	68 (−)
7[f]	K_2CO_3	Et_3N	Dioxane	83	72 (−)
8[g]	K_2CO_3	Et_3N	Dioxane	<5	—
9	Na_2CO_3	Et_3N	Dioxane	<5	—
10	Cs_2CO_3	Et_3N	Dioxane	<5	—
11	KOH	Et_3N	Dioxane	<5	—
12	$K_3PO_4 \cdot 3H_2O$	Et_3N	Dioxane	17	72 (−)
13	K_2CO_3	Et_2NH	Dioxane	20	84 (−)
14	K_2CO_3	Propylamine	Dioxane	<5	—
15	K_2CO_3	DIPEA	Dioxane	72	84 (−)
16	K_2CO_3	DBU	Dioxane	<5	—
17	K_2CO_3	DMAP	Dioxane	<5	—
18	K_2CO_3	Et_3N	THF	63	56 (−)
19	K_2CO_3	Et_3N	DMF	<5	—
20	K_2CO_3	Et_3N	IPA	<5	—
21	K_2CO_3	Et_3N	CH_3CN	<5	—

[a] 1.5 equiv of additive was added.
[b] Isolated yields.
[c] Determined by chiral HPLC.
[d] 4.0 equiv K_2CO_3 was added.
[e] Complex **1b** was used.
[f] Complex **1c** was used.
[g] The counter anion of complex **1a** was replaced with BF_4^-.

(240 mg for 0.15 mmol boronic acid) were added into this reaction since *N*-Boc imines could be hydrolyzed by ambient moisture in the reaction system. It was found that the reaction was sluggish without the formation of the desired product **3a** (Table 1, entries 1–3) if only base (KOH, K_2CO_3 or Et_3N, 6.0 equiv) was used. Similarly as that reported by Ellman, it was found that using Et_3N (1.5 equiv) as the additive and K_2CO_3 (6.0 equiv) as the base led to the corresponding adduct **3a** in 69% yield and 86% ee in dioxane at 65 °C (Table 1, entry 4). The yield and the achieved ee value were lower when 4.0 equiv of K_2CO_3 was used as the base under identical conditions (Table 1, entry 5). On the basis of these tentatively optimized conditions, we next examined chiral NHC–Pd complexes **1b** and **1c** in this reaction. We found that when chiral NHC–Pd complex **1b** was used as the catalyst, **3a** was obtained in 67% yield and 68% ee (Table 1, entry 6), presumably due to that the sterically more bulky Pd catalysts did not favor the catalytic process. In addition, using chiral NHC–Pd complex **1c** as the catalyst afforded **3a** in 83% yield and 72% ee under otherwise identical conditions. Poor conversion was obtained when the counter anion of complex **1a** was replaced by BF_4^- (Table 1, entry 8). These results suggested that in order to obtain superior ee value complex **1a** is the best catalyst in this asymmetric reaction, although higher yield of **3a** could be realized in the presence of chiral NHC–Pd complex **1c**. The examination of various inorganic bases in combination with additive Et_3N as well as inorganic base K_2CO_3 in combination with many other amine additives revealed that K_2CO_3 and Et_3N are still the best combination for this asymmetric addition reaction, which are very similar as that of Ellman's report (Table 1, entries 9–17). Moreover, the examination of the solvent effect disclosed that dioxane is the solvent of choice in the combination with K_2CO_3 (base) and Et_3N

Table 2
Catalytic asymmetric arylation of *N*-Boc Imines with phenylboronic acid



Entry	R^1	Yield (%)[a]	ee (%)[b]
1	4-ClC_6H_4 (**2b**)	75	83 (*S*)[c]
2	4-$CF_3C_6H_4$ (**2c**)	83	87 (*S*)[c]
3	4-FC_6H_4 (**2d**)	89	86 (+)[c]
4	4-$MeOC_6H_4$ (**2e**)	52	86 (*S*)[c]
5	3-ClC_6H_4 (**2f**)	87	73 (+)
6	3-MeC_6H_4 (**2g**)	71	82 (−)
7	3-$MeOC_6H_4$ (**2h**)	88	82 (+)
8	2-Thienyl (**2i**)	84	84 (−)
9	Cyclohexyl (**2j**)	<5	—

[a] Isolated yields.
[b] Determined by chiral HPLC.
[c] Determined by comparison of the sign of optical rotation to the literature values.[5]

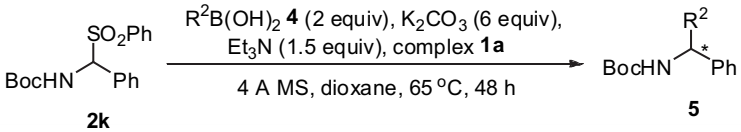
(additive) if using NHC–Pd complex **1a** as the catalyst and other solvents such as tetrahydrofuran (THF), leading to the formation of **3a** in 63% yield and 56% ee (Table 1, entry 18), dimethylformamide (DMF), isopropyl alcohol (IPA), and CH_3CN usually gave poorer results under the standard conditions (Table 1, entries 18–21).

Having established the optimal reaction conditions, the arylation of a variety of α-carbamoyl sulfones **2** having diverse substituents on the benzene rings and [(benzenesulfonyl)cyclohexylmethyl]carbamic acid *tert*-butyl ester **2j** were evaluated for the reaction with phenylboronic acid. The results are summarized in Table 2. The corresponding adducts **3** were obtained in high yields (up to 89%) and good enantiomeric excesses (up to 86%) whether they have electron-donating or electron-withdrawing substituents on the benzene rings (Table 2, entries 1–4). Furthermore, the position of substituents on the benzene rings is also not restrictive for obtaining high enantioselectivities (Table 2, entries 1 and 5, and 4 and 7). It should be noted that the asymmetric addition of phenylboronic acid to *N*-Boc 2-thiophenyl carboxaldimine also proceeded smoothly, giving the corresponding adduct **3i** in 84% yield and 84% ee (Table 2, entry 8). Unfortunately, the examination of the asymmetric addition of phenylboronic acid to aliphatic substrate **2j** failed to give the desired product after 48 h (Table 2, entry 9). In addition, only a trace amount of product was detected when the straightforward addition of phenylboronic acid to the isolated pure *N*-Boc cyclohexyl imine was carried out under the standard conditions.

Encouraged by the above results, we next studied the asymmetric addition reaction of a variety of arylboronic acids **4a–g** with α-carbamoyl sulfone **2k** under the standard conditions. The results are summarized in Table 3. It was found that the corresponding adducts **5** were produced in good to excellent yields (62–87%) and good enantiomeric excesses (70–90%), whether they have electron-donating or electron-withdrawing substituents on their benzene rings (Table 3, entries 1–7).

Although the mechanism of this interesting asymmetric addition reaction has not been unequivocally established, a plausible mechanism for this reaction has been shown in our previous paper.[3f] A Pd hydroxo-complex might be the active species in this asymmetric reaction.[3f,11]

Table 3
Catalytic asymmetric arylation of *N*-Boc imine **2k** with various arylboronic acids



Entry	R^2	Yield (%)[a]	ee (%)[b]
1	4-ClC_6H_4 (**4a**)	72	90 (*R*)[c]
2	4-$CF_3C_6H_4$ (**4b**)	65	88 (*R*)[c]
3	4-FC_6H_4 (**4c**)	87	86 (−)
4	4-$MeOC_6H_4$ (**4d**)	77	76 (*R*)[c]
5	4-MeC_6H_4 (**4e**)	77	70 (+)
6	3-ClC_6H_4 (**4f**)	79	78 (−)
7	3-$MeOC_6H_4$ (**4g**)	62	82 (−)

[a] Isolated yields.
[b] Determined by chiral HPLC.
[c] Determined by comparison of the sign of optical rotation to the literature values.[5]

3. Conclusion

In conclusion, we have successfully established an efficient catalytic system for the enantioselective arylation of *N*-Boc imines generated in situ with arylboronic acids using a series of novel chiral C_2-symmetric cationic NHC–Pd^{2+} diaquo complex catalysts using K_2CO_3 as a base and Et_3N as an additive under mild conditions. This system provides easy access to chiral diarylmethylamides **3** or **5** in good yields and good to high enantioselectivities. This interesting asymmetric addition reaction also shows a broad substrate scope, which enables the use of a variety of easily available α-carbamoyl sulfones and arylboronic acids as the starting materials.

Development of other reactions using these NHC–Pd^{2+} diaquo complex catalysts and probing the detailed mechanism are in progress in our group.

4. Experimental section

4.1. General methods

Mp was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Optical rotations were determined in a solution of $CHCl_3$ or CH_2Cl_2 at 20 °C by using a Perkin–Elmer-241 MC polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Infrared spectra were measured on a spectrometer. Unless noted, ^1H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; ^{19}F NMR spectra were recorded at 376 MHz for a solution in $CDCl_3$ with $CFCl_3$ as the external reference. *J*-values are in hertz (Hz). Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai $60F_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. The optical purities of adducts were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. Chiralcel AD and OD) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation.

C_2-Symmetric cationic *N*-heterocyclic carbenes (NHCs) Pd^{2+} diaquo complexes **1a–c** were prepared according to our previously reported procedure.[3f,10]

4.2. General procedure for the enantioselective addition of arylboronic acids to *N*-Boc imines generated in situ

In a dried Schlenk tube, catalyst (0.0075 mmol), 4 Å molecular sieves (240 mg), arylboronic acids (0.3 mmol), *N*-Boc-α-(phenylsulfonyl)arylamine (0.15 mmol), K_2CO_3 (0.9 mmol), triethylamine (31.2 μL, 0.225 mmol) were dissolved in 1,4-dioxane (2 mL) under argon atmosphere. The solution was stirred at 65 °C. After the reaction was completed (monitored by TLC plates), the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel eluted with ethyl acetate:petroleum ether (1:20, v/v) to afford the products.

4.2.1. (Phenyl-p-tolylmethyl)carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-(phenylsulfonyl)benzylamine (52.1 mg, 0.15 mmol, 1.0 equiv) and 4-methylphenylboronic acid (40.8 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (32.6 mg, 77%, 70% ee, $[\alpha]_D^{20}$ +16.8 (*c* 0.7, $CHCl_3$), mp 129–130 °C) or with *N*-Boc-α-(phenylsulfonyl)-4-methylbenzylamine (54.2 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (29.1 mg, 69%, 86% ee, $[\alpha]_D^{20}$ −14.1 (*c* 0.95, $CHCl_3$), mp 130–131 °C). HPLC (Daicel AD column, hexane/ethanol=96:4, 1.0 mL/min, λ=222 nm): t_R=9.0 min, 10.8 min. This is a known compound.[9a] ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.44 (9H, s), 2.32 (3H, s), 5.14 (1H, m), 5.87 (1H, m), 7.12 (4H, m), 7.23–7.25 (3H, m), 7.29–7.33 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 21.1, 28.4, 58.1, 79.7, 127.12, 127.13, 127.2, 128.5, 129.3, 137.0, 139.2, 142.3, 155.0.

4.2.2. [(4-Chlorophenyl)-phenylmethyl]carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-(phenylsulfonyl)benzylamine (52.1 mg, 0.15 mmol, 1.0 equiv) and 4-chlorophenylboronic acid (46.9 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (34.5 mg, 72%, 90% ee, $[\alpha]_D^{20}$ −12.8 (*c* 0.4, $CHCl_3$), mp 124–125 °C) or with *N*-Boc-α-(phenylsulfonyl)-4-chlorobenzylamine (57.3 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (35.5 mg, 75%, 83% ee, $[\alpha]_D^{20}$ +9.5 (*c* 0.7, $CHCl_3$), mp 122–123 °C). HPLC (Daicel AD column, hexane/ethanol=96:4, 1.0 mL/min, λ=222 nm): t_R=10.7 min, 13.4 min. This is a known compound.[9a] ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.44 (9H, s), 5.12 (1H, m), 5.87 (1H, m), 7.17–7.22 (4H, m), 7.24–7.35 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 28.3, 57.9, 80.0, 127.3, 127.6, 128.5, 128.71, 128.75, 133.1, 140.7, 141.5, 154.9.

4.2.3. [Phenyl-(4-trifluoromethylphenyl)methyl]carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-(phenylsulfonyl)benzylamine (52.1 mg, 0.15 mmol, 1.0 equiv) and 4-(trifluoromethyl)phenylboronic acid (57.0 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (34.1 mg, 65%, 88% ee, $[\alpha]_D^{20}$ −54 (*c* 0.15, $CHCl_3$), mp 124–125 °C) or with *N*-Boc-α-(phenylsulfonyl)-4-(trifluoromethyl)benzylamine (62.3 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (44 mg, 83%, 87% ee, $[\alpha]_D^{20}$ +33.4 (*c* 0.75, $CHCl_3$), mp 125–126 °C). HPLC (Daicel AD column, hexane/^{i}PrOH=95:5, 0.7 mL/min, λ=214 nm): t_R=13.2 min, 14.3 min. This is a known compound.[9a] ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.44 (9H, s), 5.17 (1H, m), 5.95 (1H, m), 7.20–7.22 (2H, m), 7.26–7.35 (3H, m), 7.38–7.40 (2H, m), 7.58 (2H, d, *J*=8.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ −65.43. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 28.3, 58.2, 80.2, 124.1 (q, *J*=270.8 Hz), 125.5 (q, *J*=36 Hz), 127.3, 127.4, 127.8, 128.9, 141.1, 146.1, 154.9.

4.2.4. [(4-Fluorophenyl)phenylmethyl]carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-(phenylsulfonyl)benzylamine (52.1 mg, 0.15 mmol, 1.0 equiv) and 4-fluorophenylboronic acid (42.0 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (47.7 mg, 87%, 86% ee, $[\alpha]_D^{20}$ −12.9 (*c* 1.0, $CHCl_3$), mp 117–118 °C) or with *N*-Boc-α-(phenylsulfonyl)-4-fluorobenzylamine (54.8 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (48.9 mg, 89%, 86% ee, $[\alpha]_D^{20}$ +10.1 (*c* 1.0, $CHCl_3$), mp 118–119 °C). HPLC (Daicel AD column, hexane/^{i}PrOH=95:5, 0.7 mL/min, λ=214 nm): t_R=10.3 min, 11.6 min. IR (KBr) ν 3371, 2925, 2854, 1686, 1509, 1235, 1173, 1043, 846, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.43 (9H, s), 5.19 (1H, m), 5.88 (1H, m), 6.96–7.02 (2H, m), 7.18–7.24 (4H, m), 7.24–7.27 (1H, m), 7.29–7.34 (2H, m); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ −115.4; ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 28.3, 57.8, 79.9, 115.3 (d, *J*=22.0 Hz), 127.2, 127.4, 128.6, 128.7, 128.8, 137.9 (d, *J*=3.0 Hz), 141.8, 154.9, 161.9 (d, *J*=244.3 Hz). MS (ESI) *m/e* 324 (M^++23, 10.3); HRMS (ESI) calcd for $C_{18}H_{20}FNO_2Na^+$ requires 324.1376. Found 324.1370.

4.2.5. [(4-Methoxyphenyl)phenylmethyl]carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-(phenylsulfonyl)benzylamine (52.1 mg, 0.15 mmol, 1.0 equiv) and 4-methoxyphenylboronic acid (45.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (36.3 mg, 77%, 76% ee, $[\alpha]_D^{20}$ +15.2 (*c* 0.75, $CHCl_3$), mp 98–99 °C) or with *N*-Boc-α-(phenylsulfonyl)-4-methoxybenzylamine (56.6 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (24.5 mg, 52%, 86% ee, $[\alpha]_D^{20}$ −12.6 (*c* 0.5, $CHCl_3$), mp 101–102 °C). HPLC (Daicel AD column, hexane/ethanol=96:4, 1.0 mL/min, λ=222 nm): t_R=11.7 min, 18.7 min. This is a known compound.[9a] ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.43 (9H, s), 3.78 (3H, s), 5.12 (1H, m), 5.86 (1H, m), 6.84 (2H, d, *J*=8.4 Hz), 7.15 (2H, d, *J*=8.4 Hz), 7.23–7.25 (3H, m), 7.30–7.33 (2H, m). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 28.3, 55.2, 57.8, 79.7, 113.9, 127.1, 127.2, 128.4, 128.5, 134.3, 142.3, 155.0, 158.8.

4.2.6. [(3-Chlorophenyl)phenylmethyl]carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-

(phenylsulfonyl)benzylamine (52.1 mg, 0.15 mmol, 1.0 equiv) and 3-chlorophenylboronic acid (46.9 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (37.8 mg, 79%, 78% ee, $[\alpha]_D^{20}$ −29.0 (*c* 0.45, $CHCl_3$), mp 101–102 °C) or with *N*-Boc-α-(phenylsulfonyl)-3-chlorobenzylamine (57.3 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (41.6 mg, 87%, 73% ee, $[\alpha]_D^{20}$ +13.5 (*c* 0.5, $CHCl_3$), mp 103–104 °C). HPLC (Daicel OD column, hexane/^{i}PrOH=98:2, 0.7 mL/min, λ=230 nm): t_R=11.9 min, 13.2 min. This is a known compound.[9a] ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.44 (9H, s), 5.14 (1H, m), 5.87 (1H, m), 7.13–7.14 (1H, m), 7.20–7.29 (6H, m), 7.31–7.35 (2H, m). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 28.3, 58.1, 80.1, 125.3, 127.2, 127.3, 127.5, 127.7, 128.8, 129.8, 134.5, 141.3, 144.2, 154.9.

4.2.7. [(3-Methoxyphenyl)phenylmethyl]carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-(phenylsulfonyl)benzylamine (52.1 mg, 0.15 mmol, 1.0 equiv) and 3-methoxyphenylboronic acid (45.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (29.0 mg, 62%, 82% ee, $[\alpha]_D^{20}$ −3.3 (*c* 0.5, $CHCl_3$), mp 79–80 °C) or with *N*-Boc-α-(phenylsulfonyl)-3-methoxybenzylamine (56.6 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (41.3 mg, 88%, 82% ee, $[\alpha]_D^{20}$ +1.6 (*c* 1.15, $CHCl_3$), mp 77–78 °C). HPLC (Daicel AD column, hexane/ethanol=98:2, 1.0 mL/min, λ=222 nm): t_R=22.3 min, 26.1 min. IR (KBr) ν 2955, 2925, 2854, 1704, 1490, 1462, 1260, 1166, 1020, 764, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.44 (9H, s), 3.76 (3H, s), 5.16 (1H, m), 5.87 (1H, m), 6.78–6.84 (3H, m), 7.21–7.26 (4H, m), 7.29–7.33 (2H, m). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 28.3, 55.2, 58.4, 79.8, 112.5, 113.1, 119.5, 127.2, 127.3, 128.6, 129.6, 141.9, 143.7, 155.0, 159.8. MS (EI) *m*/*e* 313 (M^+, 1.90); HRMS (EI) calcd for $C_{19}H_{23}NO_3$ requires 313.1678. Found 313.1681.

4.2.8. (Phenylthiophen-2-yl-methyl)carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-(phenylsulfonyl)-α-(thiophen-2-yl)-methylamine (53.0 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (36.3 mg, 84%, 84% ee, $[\alpha]_D^{20}$ −3.4 (*c* 0.91, $CHCl_3$), mp 135–136 °C). HPLC (Daicel AD column, hexane/^{i}PrOH=95:5, 0.7 mL/min, λ=214 nm): t_R=19.7 min, 21.3 min. This is a known compound.[9a] ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.44 (9H, s), 5.27 (1H, m), 6.11 (1H, m), 6.79 (1H, d, *J*=3.2 Hz), 6.91 (1H, dd, *J*=3.2, 4.8 Hz), 7.20–7.22 (1H, m), 7.27–7.37 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 28.3, 54.4, 80.0, 125.0, 125.4, 126.8, 126.9, 127.7, 128.6, 141.7, 146.4, 154.7.

4.2.9. (Phenyl-m-tolylmethyl)carbamic acid tert-butyl ester. The general procedure was followed with *N*-Boc-α-(phenylsulfonyl)-3-methylbenzylamine (54.2 mg, 0.15 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 2.0 equiv) to provide the product as a white solid (31.8 mg, 71%, 82% ee, $[\alpha]_D^{20}$ −5.4 (*c* 0.75, $CHCl_3$), mp 99–100 °C). HPLC (Daicel AD column, hexane/ethanol=98:2, 1.0 mL/min, λ=222 nm): t_R=8.8 min, 10.3 min. This is a known compound.[9a] ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.44 (9H, s), 2.32 (3H, s), 5.13 (1H, m), 5.86 (1H, m), 7.02–7.07 (3H, m), 7.18–7.26 (4H, m), 7.30–7.34 (2H, m). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 21.5, 28.4, 58.4, 79.7, 124.2, 127.15, 127.24, 128.0, 128.1, 128.5, 128.6, 138.3, 142.0, 142.2, 155.0.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.02.037.

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