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Rhodium-catalyzed arylation of α-amido sulfones with arylboronic acids in a water–toluene biphasic system

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ABSTRACT

An efficient method for the synthesis of *N*-protected diaryl-methyl-amines was developed through a rhodium-catalyzed arylation of α-amido sulfones with arylboronic acids in a water–toluene biphasic system. The use of a base combined with a surfactant played a key role in this biphasic reaction. A diverse range of α-branched amine derivatives bearing different functional groups were obtained within 10 min under the present conditions.

1. Introduction

The addition reactions of various organometallic reagents to the C=N bond of imines and their derivatives have attracted considerable attention of organic chemists [1,2]. Such reactions can provide practical methods for the synthesis of α-branched amines and their derivatives, which are prevalent and important building blocks of many biological and pharmaceutical agents. However, most imines are unstable and prone to decomposition during workup. Furthermore, many functional groups are not tolerated with the classical organometallic reagents and need to be protected. Thus, methods involving the generation of the imine in situ are highly desirable. α-Amido sulfones are stable precursors of reactive imino derivatives, which can be easily synthesized by the three-components coupling of carbamate, aldehyde, and sodium sulfinates under acidic conditions [3]. Subsequent elimination of sulfinic acid leads to the in situ generation of reactive *N*-acylimines, which can react with nucleophilic reagents to give the corresponding addition products [3–6]. Recently, Ollevier's group developed a $Bi(OTf)_3$ catalyzed addition of allylsilanes and silyl enolates to *N*-alkoxycarbonylamino sulfones [7–9].

With the advances in organic chemistry, many stable organometallic compounds are developed as substitutes for Grignard and organolithium reagents. Such alternative reagents can tolerate an array of sensitive functional groups and can even work well in water and air. Among them, arylboronic acids are extremely powerful organometallic reagents in organic synthesis because they are moisture-stable, easy to handle, commercially available and compatible with many functional groups. Additions of arylboronic acids to imines have already been intensively studied recently; however, they generally suffer from harsh reaction conditions, a long reaction time and poor functional group compatibility [10–23]. Such restrictions undoubtedly limited the application of these reactions.

Due to the abundance of water as well as the inherent advantages of using water as a solvent, recent interest has been growing in studying organic reactions in water [24–26]. Many reactions that are traditionally carried out in organic solvent can be conducted in water with additional beneficial features: (1) water-soluble substrates such as carbohydrates can be used directly without derivatization, (2) the aqueous catalyst solution can be recycled easily, and (3) water-insoluble products can be separated conveniently by simple phase separations. Among them, we and others have reported that organometallic reagents including organoboron, organotin, organobismuth and organolead reagents were effective for carbonyl addition and conjugated addition reactions in air and water [27–39]. In addition, we also reported the copper-mediated or catalyzed direct nucleophilic additions of alkynes to reactive *N*-acylimines and *N*-acyliminium ions (generated in situ from α-amido sulfones or methoxyl groups as stable precursors), affording propargylamine derivatives in aqueous media [40].

Based on our intensive interest in organic reactions in aqueous media and the excellent properties of boronic acids, we envisioned

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that arylation of α-amido sulfones with arylboronic acids in aqueous media will be a direct and practical method for the synthesis of α-branched amines and their derivatives. To the best of our knowledge, such a reaction has not been achieved. Herein, we reported our results on the rapid arylation of α-amido sulfones with arylboronic acids in a water–toluene biphasic system.

2. Experimental

2.1. General

All work-up and purification procedures were carried out with reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) or Sorbent silica gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh) or Sorbent silica gel 30–60 μm. High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ACPI). Nuclear magnetic resonance (NMR) spectra were recorded on Varian MERCURY plus-300 spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz), a Varian MERCURY plus-400 spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz), or a Varian MERCURY plus-500 spectrometer (^{1}H 500 MHz, ^{13}C 125 MHz). Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. Unless stated otherwise, commercial reagents were used without further purification. All reagents were weighed and handled in air at room temperature. α-Amido sulfones were prepared according to the literature method [41].

2.2. A representative experimental procedure

A reaction vessel was charged with benzenesulfonyl-phenyl-methyl-carbamic acid benzyl ester **1a** (38.1 mg, 0.1 mmol), phenylboronic acid (18.3 mg, 0.15 mmol), sodium dodecyl sulfate (20 mg), $Rh(COD)_2BF_4$ (2.1 mg, 5 mmol%), water (0.3 mL), and toluene (0.5 mL); sealed and the resulting solution was stirred at 150 °C for 10 min. The resulting mixture was cooled to room temperature and the residue was extracted with ethyl acetate (3 × 5 mL). The combined organic extract was dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography on silica gel (eluent: hexane/diethyl ether = 10:1) to give benzyl benzhydrylcarbamate **3a**.

2.3. ^{1}H, ^{13}C NMR spectra and HR/MS data

Compound **3a** was obtained as a white solid [42]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.12 (s, 2H), 5.41 (bs, 1H), 6.00 (d, J = 7.6 Hz, 1H), 7.24–7.29 (m, 6H), 7.31–7.35 (m, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 58.8, 67.0, 127.2, 127.5, 128.2, 128.5, 128.6, 136.2, 141.6, 155.5.

Compound **3b** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (bs, 3H), 1.38 (bs, 2H), 1.61 (bs, 2H), 4.08 (t, J = 6.4 Hz, 2H), 5.31 (bs, 1H), 5.98 (d, J = 6.0 Hz, 1H), 7.24–7.28 (m, 6H), 7.31–7.35 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 19.0, 31.0, 58.6, 65.0, 127.2, 127.4, 128.6, 141.8, 155.9. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{18}H_{22}O_2N$, 284.16451; found, 284.16441.

Compound **3c** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.44 (s, 9H), 5.16 (bs, 1H), 5.91 (bs, 1H), 7.23–7.27 (m, 6H), 7.30–7.34 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.3, 58.4, 79.8, 127.2, 127.3, 128.6, 142.0, 155.0. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{18}H_{22}O_2N$, 284.16451; found, 284.16457.

Compound **3d** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25 (bs, 3H), 4.10–4.16 (q, J = 7.2 Hz, 2H), 5.28 (bs, 1H), 5.97 (d, J = 6.8 Hz, 1H), 7.23–7.28 (m, 6H), 7.31–7.35 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.5, 58.6, 61.1, 127.2, 127.4, 128.6, 141.8, 155.8. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{16}H_{18}O_2N$, 256.13321; found, 256.13323.

Compound **3e** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.69 (s, 3H), 5.32 (bs, 1H), 5.98 (d, J = 6.8 Hz, 1H), 7.23–7.28 (m, 6H), 7.31–7.35 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.3, 58.8, 127.2, 127.5, 128.6, 141.6, 156.2. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{15}H_{16}O_2N$, 242.11756; found, 242.11779.

Compound **3f** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (bs, 3H), 1.36 (bs, 2H), 1.57 (bs, 2H), 2.32 (s, 3H), 4.07 (t, J = 6.4 Hz, 2H), 5.25 (bs, 1H), 5.92 (bs, 1H), 7.13 (s, 4H), 7.23–7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 19.0, 21.0, 31.0, 58.4, 65.0, 127.1, 127.3, 128.5, 129.3, 137.1, 138.9, 142.0, 155.9. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{19}H_{24}O_2N$, 298.18016; found, 298.18022.

Compound **3g** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (bs, 3H), 1.36 (bs, 2H), 1.56 (bs, 2H), 4.07 (t, J = 6.4 Hz, 2H), 5.24 (bs, 1H), 5.92 (bs, 1H), 7.18–7.20 (m, 4H), 7.25–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 19.0, 30.9, 58.2, 65.1, 127.2, 127.7, 128.5, 128.7, 128.8, 133.2, 140.3, 141.2, 155.8. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{18}H_{21}O_2NCl$, 318.12553; found, 318.12548.

Compound **3h** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (bs, 3H), 1.36 (bs, 2H), 1.58 (bs, 2H), 4.07 (t, J = 6.4 Hz, 2H), 5.25 (bs, 1H, 5.90 (bs, 1H), 7.13(d, J = 8.4 Hz, 2H), 7.21 (d, J = 6.8 Hz, 2H),7.26–7.35 (m, 3H), 7.43–7.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.6, 18.09, 30.9, 58.2, 65.1, 121.3, 127.2, 127.7, 128.7, 128.8, 131.6, 140.9, 141.1, 155.8. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{18}H_{21}O_2NBr$, 362.07502; found, 362.07573.

Compound **3i** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, J = 6.8 Hz, 3H), 1.37–1.39 (m, 2H), 1.58–1.59 (m, 2H), 2.31 (s, 3H), 4.08 (t, J = 6.8 Hz, 2H), 5.26 (d, J = 6.4 Hz, 1H), 6.15 (d, J = 7.6 Hz, 1H), 7.14–7.23 (m, 6H), 7.25–7.33 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 19.0, 19.4, 31.0, 55.5, 65.0, 126.2, 126.5, 127.3, 127.4, 128.6, 130.7, 136.0, 139.8, 140.9, 141.2, 155.8. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{19}H_{24}O_2N$, 298.18016; found, 298.17998.

Compound **3j** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (t, J = 6.8 Hz, 3H), 1.36–1.38 (m, 2H), 1.59 (bs, 2H), 3.77 (s, 3H), 4.07 (t, J = 6.8 Hz, 2H), 5.29 (bs, 1H), 5.93 (d, J = 6.8 Hz, 1H), 6.79–6.84 (m, 3H), 7.22–7.34 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 19.0, 31.0, 55.2, 58.6, 65.0, 112.5, 113.1, 119.5, 127.2, 127.4, 128.6, 129.6, 141.6, 143.4, 155.9, 159.7. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{19}H_{24}O_3N$, 314.17507; found, 314.17558.

Compound **3k** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (bs, 3H), 1.38 (bs, 2H), 1.59 (bs, 2H), 4.08 (t, J = 6.4 Hz, 2H), 5.29 (bs, 1H), 6.00 (bs, 1H), 7.20–7.22 (m, 2H), 7.27–7.40 (m, 5H), 7.59 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 19.0, 30.9, 58.5, 65.2, 125.5, 125.6, 127.3, 127.9, 128.9, 129.4, 140.8, 145.8, 155.8. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{19}H_{21}O_2NF_3$, 352.15189; found, 352.15213.

Compound **3l** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (bs, 3H), 1.39 (bs, 2H), 1.61 (bs, 2H), 4.10 (t, J = 6.8 Hz, 2H), 5.42 (bs, 1H), 6.14 (bs, 1H), 7.26–7.36 (m, 6H), 7.45–7.50 (m, 2H), 7.73 (s, 1H), 7.79–7.83 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 19.0, 31.0, 58.8, 65.1, 125.4, 125.7, 126.0, 126.3, 127.4, 127.5, 127.6, 128.0, 128.5, 128.7, 132.7, 133.2, 139.1, 141.6, 156.0. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{22}H_{24}O_2N$, 334.18016; found, 334.18052.

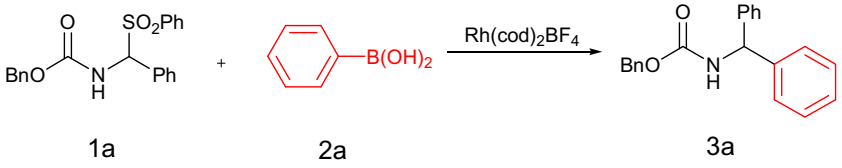
Compound **3m** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (bs, 3H), 1.38 (bs, 2H), 1.60 (bs, 2H), 4.07 (t, J = 6.4 Hz, 2H), 5.23 (d, J = 10.8 Hz, 1H), 5.28 (bs, 1H), 5.73 (d, J = 19.2 Hz, 1H), 5.95 (bs, 1H), 6.65–6.73 (dd, J = 17.6 Hz, J = 10.8 Hz, 1H), 7.20–7.28 (m, 5H), 7.31–7.38 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 19.0, 31.0, 58.4, 65.0, 114.0, 126.4, 127.2, 127.4, 127.5, 128.6, 136.2, 136.7, 141.3, 141.6, 155.9. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{20}H_{24}O_2N$, 310.18016; found, 310.18022.

Compound **3n** was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (bs, 3H), 1.37 (bs, 2H), 1.60 (bs, 2H), 2.58 (s, 1H), 4.08 (t, J = 6.8 Hz, 2H), 5.30 (bs, 1H), 5.99 (bs, 1H), 7.20–7.22 (m, 2H), 7.26–7.38 (m, 5H), 7.93 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.6, 18.9, 26.2, 30.9, 58.6, 65.2, 127.2, 127.3, 127.8, 128.7, 128.8, 136.2, 140.9, 147.1, 155.8, 197.6. HRMS APCI (m/z): $[M+H]^+$ calcd for $C_{20}H_{24}O_3N$, 326.17507; found, 326.17516.

3. Results and discussion

Duo to the high catalytic activity of $Rh(cod)_2BF_4$ in the aqueous reaction in our initial studies, a model reaction employing benzenesulfonyl-phenylmethyl-carbamic acid benzyl ester **1a** and phenylboronic acid **2a** as substrates in water was examined (Scheme 1). However, no corresponding arylation product was detected (Table 1, entry 1). When an inorganic base was added, a low yield of benzyl benzhydrylcarbamate **3a** was obtained (Table 1, entries 2–4); and a better yield (30%) of **3a** was obtained when one equivalent of K_2CO_3 was added (Table 1, entry 2). Lowering the amount of K_2CO_3 decreased the yield, whereas further increasing the amount of K_2CO_3 above one equivalent did not give significant improvement of the yield (Table 1, entries 5 and 6). These results can be rationalized that the addition of bases facilitate the formation of the reactive *N*-acylimines that readily reacted with nucleophilic reagents to give the corresponding addition products; in addition, phenylboronic acid could also be activated under basic conditions [28].

There are two competitive reactions related to α-amido sulfones in water: (1) hydrolysis under basic conditions and (2) the tandem elimination–addition reaction with phenylboronic acid. In order to overcome hydrolysis of α-amido sulfones in water, we hypothesized that the use of a surfactant and an aqueous two-phase system would decrease the kinetics of hydrolysis by preventing and/or diminishing the *N*-acylimines from encountering water molecules. The use of a water–toluene biphasic system together with a catalytic amount of sodium laurylsulfate as a surfactant and one equivalent of K_2CO_3 provided the desired product in 60% yield (Table 1, entry 8). The use of a surfactant together with a biphasic system is very critical for the success of the reaction. After further optimization of the reaction conditions, 77% yield of the arylation product **3a** was obtained in a water (0.3 mL)–toluene (0.5 mL) biphasic system at 70 °C together with sodium laurylsulfate (20 mg) (Table 1, entry 12). It is interesting to note that only a trace amount of the corresponding product was detected when toluene alone was employed as the solvent (Table 1, entry 14 versus entry 2). Water is an essential co-solvent in the reaction, possibly by dissolving the K_2CO_3 that can neutralize the sulfinic acid generated from the coupling reaction and further driving the



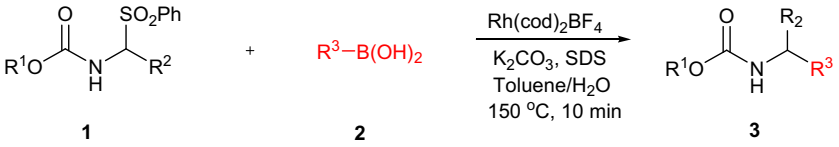
1a 2a 3a

Scheme 1. Arylation of benzenesulfonyl-phenylmethyl-carbamic acid benzyl ester.

Table 1
Optimization of the reaction conditions.[a]

Entry	Time	T (°C)	Solvent	Additive	Yield (%)
1	4 h	70	H_2O (0.2 mL)	/	0
2	4 h	70	H_2O (0.2 mL)	K_2CO_3 1 equiv	30
3	4 h	70	H_2O (0.2 mL)	KOH 1 equiv	26
4	4 h	70	H_2O (0.2 mL)	Cs_2CO_3 1 equiv	23
5	4 h	70	H_2O (0.2 mL)	K_2CO_3 0.4 equiv	19
6	4 h	70	H_2O (0.2 mL)	K_2CO_3 2 equiv	31
7	4 h	70	H_2O (0.2 mL)/toluene (0.2 mL)	K_2CO_3 1 equiv	38
8	4 h	70	H_2O (0.2 mL)/toluene (0.2 mL)	K_2CO_3 1 equiv, 10 mg SDS	60
9	4 h	70	H_2O (0.2 mL)/toluene (0.2 mL)	K_2CO_3 1 equiv, 20 mg SDS	65
10	4 h	70	H_2O (0.1 mL)/toluene (0.3 mL)	K_2CO_3 1 equiv, 20 mg SDS	34
11	4 h	70	H_2O (0.3 mL)/toluene (0.3 mL)	K_2CO_3 1 equiv, 20 mg SDS	64
12	4 h	70	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg SDS	77
13	4 h	70	H_2O (0.3 mL)/toluene (1.0 mL)	K_2CO_3 1 equiv, 20 mg SDS	75
14	4 h	70	toluene (0.2 mL)	K_2CO_3 1 equiv	trace
15	4 h	100	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg SDS	80
16	4 h	135	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg SDS	94
17	4 h	150	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg SDS	96
18	0.5 h	150	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg SDS	96
19	10 min	150	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg SDS	94
20[b]	10 min	150	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg TW40	60
21[c]	10 min	150	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg *N*-dodecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate	74
22[d]	10 min	150	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg cetyltrimethylammonium bromide	51
23[e]	10 min	150	H_2O (0.3 mL)/toluene (0.5 mL)	K_2CO_3 1 equiv, 20 mg cetyltrimethylammonium hydrogensulfate	37

[a] Benzyl phenyl(tosyl)methylcarbamate (0.1 mmol), arylboronic acids (0.15 mmol, 150 mol%), sodium dodecyl sulfonate (20 mg), and $Rh(cod)_2BF_4$ (0.005 mol, 5 mol%).
[b] Tween 40 (20 mg) as the surfactant.
[c] *N*-Dodecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate (20 mg) as the surfactant.
[d] Cetyltrimethylammonium bromide (20 mg) as the surfactant.
[e] Cetyltrimethylammonium hydrogensulfate (20 mg) as the surfactant.



Scheme 2. $Rh(cod)_2BF_4$ catalyzed arylation of α-amido sulfones with arylboronic acids in water–toluene biphasic reaction system.

Table 2
Substrate scope.[a]

Entry	R^1	R^2	R^3	Product	Yield (%)[b]
1	Bn	Ph	Ph	**3a**	83
2	*n*-Bu	Ph	Ph	**3b**	84
3	*t*-Bu	Ph	Ph	**3c**	82
4	Et	Ph	Ph	**3d**	62
5	Mt	Ph	Ph	**3e**	57
6	*n*-Bu	4-Me–C_6H_4	Ph	**3f**	69
7	*n*-Bu	4-Cl–C_6H_4	Ph	**3g**	89
8	*n*-Bu	4-Br–C_6H_4	Ph	**3h**	86
9	*n*-Bu	Ph	2-Me–C_6H_4	**3i**	85
10	*n*-Bu	Ph	3-MeO–C_6H_4	**3j**	76
11	*n*-Bu	Ph	4-CF_3–C_6H_4	**3k**	28
12	*n*-Bu	Ph	2-naphthyl	**3k**	79
13	*n*-Bu	Ph	4-CH_2=CH–C_6H_4	**3m**	67
14	*n*-Bu	Ph	4-CH_3CO–C_6H_4	**3n**	51

[a] α-Amido sulfones (0.2 mmol), arylboronic acids (0.3 mmol, 150 mol%), sodium dodecyl sulfonate (40 mg), K_2CO_3 (0.2 mmol, 100 mol%) and $Rh(cod)_2BF_4$ (0.01 mol, 5 mol%) in water (0.6 mL), toluene (1.0 mL), 150 °C, 10 min.
[b] Isolated yield based on α-amido sulfones **1**.

reaction toward the formation of the desired product. The reaction temperature is another important factor for this reaction. The yield of **3a** increased as the reaction temperature was increased from 70 to 150 °C (entries 12, 15–17), and reached the maximum value of 96% at 150 °C. It is worth mentioning that the reaction proceeded very rapidly and could be completed within 10 min (Table 1, entry 19). Under the optimized reaction conditions, other surfactants available in our lab were also examined and gave relatively lower yields than sodium laurylsulfate under the same reaction conditions (Table 1, entries 20–23).

Subsequently, various α-amido sulfones were coupled with arylboronic acids under the optimized conditions (Scheme 2). The reaction was found to be highly sensitive to the carbamate structural motif of the starting material **1**. The α-phenylsulfonylamine with *n*-BOC, *n*-Bu and CBz groups could react smoothly to afford the desired coupling products in good yields (Table 2, entries 1–3). Relatively low yields of the corresponding products were obtained when using α-amido sulfones derived from methyl or ethyl carbamate (Table 2, entries 4 and 5). The electronic nature of the R^2 also has a significant effect on the reaction. The α-phenylsulfonylamine derived from aromatic aldehydes with electron-withdraw groups gave higher yields than the ones with electron-donating substituents (Table 2, entries 6–8). Various arylboronic acids were subjected to this reaction; and it was found that the nature of the R^3 also has a marked effect on the reactivity. Electron-rich arylboronic acids gave better yields than the electron-poor ones (Table 2, entries 9–11). Functional groups (e.g., carbonyl group and carbon–carbon double bond) are tolerated under the reaction conditions (Table 2, entries 13–14).

In conclusion, we have developed an effective arylation of α-amido sulfones with arylboronic acids catalyzed by $Rh(cod)_2BF_4$ in a water–toluene biphasic system. The uses of K_2CO_3 as a base and sodium dodecyl sulfate as a surfactant combined with a water–toluene biphasic system play a key role in the reaction. The reaction proceeds very rapidly and can be completed within 10 min. This method allows us to prepare a diverse range of α-branched amines derivatives, and can tolerate different functional groups.

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