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Synthesis of 2-Aryl-2*H*-benzotrizoles from Azobenzenes and *N*-Sulfonyl Azides through Sequential Rhodium-Catalyzed Amidation and Oxidation in One Pot

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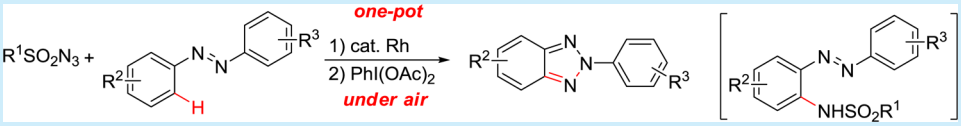
Supporting Information



ABSTRACT: An efficient synthetic method of 2-aryl-2*H*-benzotriazoles from nonprefunctionalized azobenzenes and *N*-sulfonyl azides via sequential Rh-catalyzed amidation (C−N bond formation) and oxidation (N−N bond formation) with $PhI(OAc)_2$ in one pot is reported.

Development of synthetic methods of 2-aryl-2*H*-benzotriazole derivatives from easily accessible reactants is highly significant because it is an essential component of pharmaceuticals, UV stabilizers, and organic electronic materials (Figure 1).[1] Because benzotriazoles exist as N^1-, N^2-, and N^3-substituted isomers, the selective preparation of benzotriazole represents an important synthetic challenge.[2] Although a variety of synthetic methods for N^1-arylation of benzotriazole have been reported,[3] a selective N^2-arylation of benzotriazole is still needed. To date, thermal decomposition of *o*-azidoazobenzenes,[4] reduction of 2-[(2-nitrophenyl)azo]-phenols with thiourea *S*,*S*-dioxide,[5] SmI_2,[6] or Zn[7] and Cu-catalyzed oxidative cyclization of azoanilines[8] were reported for N^2-arylation of benzotriazoles. However, these methods required prefunctionalized azobenzenes having an azido, nitro, or amino group on the aryl ring before cyclization. In addition, Pd-catalyzed arylation of benzotriazoles[9] and *N*-arylation of benzotriazole with benzyne[10] gave a mixture of N^1- and N^2-arylation products.

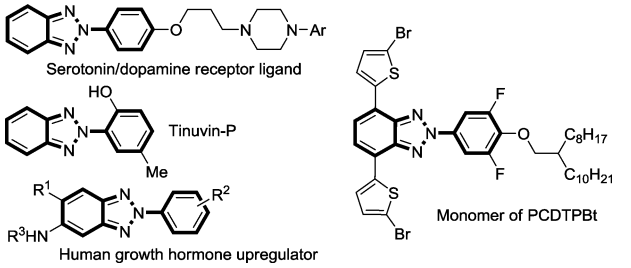
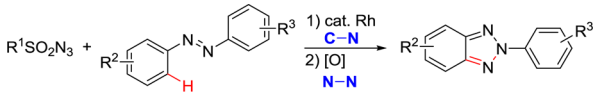


Figure 1. Important compounds containing 2-aryl-2*H*-benzotriazole moiety.

For this reason, the selective synthesis of 2-aryl-2*H*-benzotriazoles has been continuously in demand. In our continuing efforts to develop efficient C−H activations,[11] we report herein an efficient synthetic method for 2-aryl-2*H*-benzotriazoles from azobenzenes and *N*-sulfonyl azides through sequential Rh-catalyzed amidation (C−N bond formation) and oxidation (N−N bond formation) in one pot (Scheme 1).[12]

Scheme 1. Synthesis of 2-Aryl-2*H*-benzotrizoles from Azobenzenes and *N*-Sulfonyl Azides in One Pot



First, we examined the amidation of azobenzene **2a** (0.2 mmol, 1.0 equiv) with tosyl azide **1a** (1.2 equiv) in the presence of $[Cp^*RhCl_2]_2$ (4 mol %) with a multidude of additives (16 mol %) and solvents (Table 1 and see the Supporting Information (SI)). DCE was the solvent of choice (entry 5); other reaction media such as *tert*-amyl alcohol, 1,4-dioxane, chlorobenzene, and THF were less effective (entries 1−4). Among the additives such as $AgSbF_6$, $AgNTf_2$, $AgBF_4$, $AgPF_6$, and AgOTf, $AgNTf_2$ gave the amidated azobenzene **3a** in 66% yield (entry 6). However, formation of diamidated azobenzene **4a** was unavoidable. To increase the selectivity, the stoichiometry of azobenzene (1.0, 1.2, 1.5, and 2.0 equiv) was screened (entries 10−13). Use of an increased amount of azobenzene gave improved results. Eventually, the amidation of azobenzene **1a** (2.0 equiv) with tosyl azide **1a** (1.0 equiv) in the presence of $[Cp^*RhCl_2]_2$ (4 mol %) with $AgNTf_2$ (16 mol %) gave the best result in DCE at 90 °C under aerobic conditions, producing **3a** in 85% yield (entry 13).

A number of azobenzenes **2** were examined to expand the scope of azobenzenes in Rh-catalyzed amidation using tosyl azide (Table 2). Azobenzene **2b** having a 2-methyl group on the phenyl ring was selectively converted to the monoamidated

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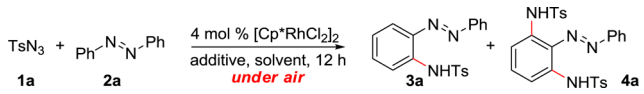
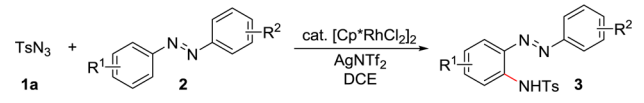
Table 1. Optimization of Amidation of Azobenzene[a]



entry	additive (mol %)	1a:2a (equiv)	solvent	temp (°C)	yield[b] (%)
1	$AgSbF_6$ (16)	1.2:1	*t*-AmOH	110	7
2	$AgSbF_6$ (16)	1.2:1	dioxane	110	34 (5)
3	$AgSbF_6$ (16)	1.2:1	PhCl	110	11
4	$AgSbF_6$ (16)	1.2:1	THF	110	39 (11)
5	$AgSbF_6$ (16)	1.2:1	DCE	110	60 (18)
6	$AgNTf_2$ (16)	1.2:1	DCE	110	66 (18)
7	$AgBF_4$ (16)	1.2:1	DCE	110	45 (6)
8	$AgPF_6$ (16)	1.2:1	DCE	110	35
9	AgOTf (16)	1.2:1	DCE	110	17
10	$AgNTf_2$ (16)	1:1	DCE	110	55 (19)
11	$AgNTf_2$ (16)	1:1.2	DCE	110	71 (14)
12	$AgNTf_2$ (16)	1:1.5	DCE	110	72 (10)
13	**$AgNTf_2$ (16)**	**1:2**	**DCE**	**90**	**85**[c] **(3)**[c]

[a]**2a** (0.2 mmol, entries 1−10), **1a** (0.2 mmol, entries 11−13) in solvent (1.0 mL) for 12 h. [b]^{1}H NMR yields using CH_2Br_2 as an internal standard. Numbers in parentheses are ^{1}H NMR yields of **4a**. [c]Isolated yield.

Table 2. Scope of Azobenzenes[a]



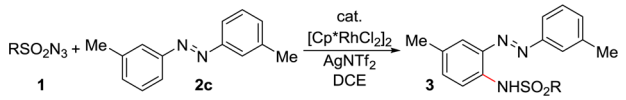
entry	R^1	R^2	method	product	yield[b] (%)
1	2-Me	2-Me	B	**3b**	82
2	3-Me	3-Me	B	**3c**	92
3	4-Me	4-Me	A	**3d**	87
4	2-Et	2-Et	B	**3e**	83
5	4-MeO	4-MeO	A	**3f**	84
6	4-Cl	4-Cl	A	**3g**	77
7	3-Br	3-Br	B	**3h**	79
8	3-Ac	3-Ac	B	**3i**	87
9	4-CO_2Et	4-CO_2Et	A	**3j**	79
10	H	3,5-$(Me)_2$	A	**3k**	65
11	H	3,5-$(CF_3)_2$	A	**3l**	56

[a]Method A: **1a** (0.2 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), and $AgNTf_2$ (16 mol %) in DCE (1.0 mL) at 90 °C for 12 h. Method B: **1a** (0.2 mmol), **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), and $AgNTf_2$ (16 mol %) in DCE (1.0 mL) at 110 °C for 12 h. [b]Isolated yields.

azobenzene **3b** in 82% yield under the modified conditions (use of 1.2 equiv of **2**) (entry 1). Gratifyingly, the diamidated products were not observed. 3-Methyl-substituted azobenzene **2c** was selectively transformed to the amidated products **3c** having a tosylamino group at the 6-position in 92% yield due to steric hindrance (entry 2). It is noteworthy that 4-methyl-azobenzene underwent the selective monoamidation (entry 3). In the case of 4-methoxy azobenzene **2f**, the desired product **3f** was regioselectively obtained in 84% yield without diamidation (entry 5). Functional groups commonly used in synthetic chemistry were totally inert. For example, azobenzenes possessing a chloro, bromo, ketone, and ester group were selectively amidated to produce the amidated azobenzenes in good to excellent yields (entries 6−9). Next, the challenging amidation of unsymmetric substrates was investigated. Unsymmetric azobenzenes **2k** and **2l** were selectively amidated on an unsubstituted phenyl ring (entries 10 and 11).

Next, the variation of the substituent at the S of sulfonyl azides **1** was investigated in the reaction with **2c** using $[Cp^*RhCl_2]_2$ (4 mol %) as the catalyst (Table 3). Phenyl, 4-

Table 3. Scope of Sulfonyl Azides[a]



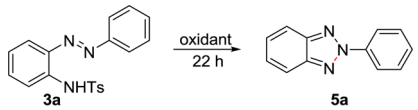
entry	R		product	yield (%)
1	Ph	**1b**	**3m**	89
2	4-MeC_6H_4	**1a**	**3c**	92
3	4-$MeOC_6H_4$	**1c**	**3n**	93
4	4-$CF_3C_6H_4$	**1d**	**3o**	91
5	4-$NO_2C_6H_4$	**1e**	**3p**	56
6	Me	**1f**	**3q**	54
7	*n*-Bu	**1g**	**3r**	60
8	Bn	**1h**	**3s**	61

[a]Reaction conditions: **1** (0.2 mmol), **2c** (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (4 mol %), and $AgNTf_2$ (16 mol %) in DCE (1.0 mL) at 110 °C for 12 h.

methoxyphenyl, and 4-trifluoromethylphenylsulfonyl azides **1b−d** were all suitable substrates in the amidation reaction (entries 1, 3, and 4). However, 4-nitrophenylsulfonyl azide **1e** gave the amidated product **3p** in 56% yield (entry 5). Although alkylsulfonyl azides were less reactive than arylsulfonyl azides in the amidation reaction, the amidated azobenzenes were obtained in acceptable yields (entries 6−8).

We next carried out the oxidative cyclization of tosylamino azobenzene **3a** to obtain 2-phenyl-2*H*-benzotrizole **5a** (Table 4). Among the oxidants tested, $PhI(OAc)_2$ (2.0 equiv) gave the best result (entry 3). Under the optimal conditions, **5a** was obtained in 95% yield in toluene at 40 °C after 22 h.

Table 4. Optimization of Cyclization



entry	oxidant (equiv)	solvent	temp (°C)	yield (%)
1	$PhI(OAc)_2$ (1.1)	toluene	40	70
2	$PhI(OAc)_2$ (1.5)	toluene	40	85
3	$PhI(OAc)_2$ (2.0)	toluene	40	95
4	$Cu(OAc)_2{\cdot}H_2O$ (3.0)	CH_3CN	80	50

Encouraged by these results, the substrate scope of a range of substituents to cyclize with $PhI(OAc)_2$ was studied (Scheme 2). Electronic variation of substituents at the arene moiety of azobenzenes **3** did not have an effect on the reaction efficiency. 3- and 4-Methyl-6-tosylamino azobenzenes **3c** and **3d** were smoothly oxidized to provide the corresponding 2-aryl-2*H*-benzotrizoles **5c** and **5d** in high yields. Azobenzenes **3b** and **3e** having a 2-methyl- and 2-ethyl-5-tosylamino group underwent the oxidative cyclization to produce **5b** (95%) and **5e** (99%). 2-(4′-Methoxyphenyl)-2*H*-benzotrizole **5f** having an electron-donating methoxy group was obtained in good yield. The reaction was highly chemoselective in that chloro, bromo, ketone, and ester groups were tolerated. The present method worked equally well even though with unsymmetric azoben-

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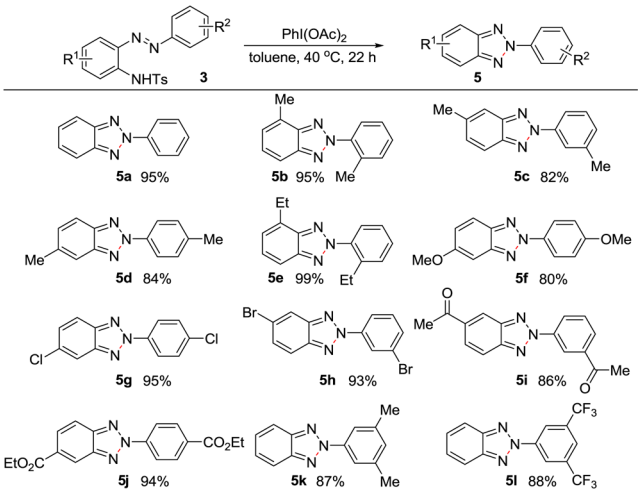
Scheme 2. Scope of Tosylamino Azobenzenes[a]

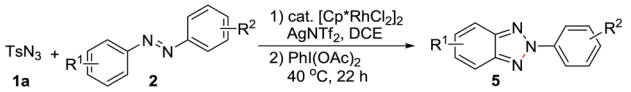


[a]**3** (0.1 mmol) and $PhI(OAc)_2$ (0.2 mmol) were used.

zenes. The oxidative cyclization of azobenzenes **3k** and **3l** having dimethylphenyl and di(trifluoromethyl)-phenyl group proceeded effectively to afford the desired 2-aryl-2*H*-benzotrizoles **5k** and **5l** in high yields.

As an extension of this work, we conducted a two-component one-pot synthesis of 2-aryl-2*H*-benzotrizole **5** from tosyl azide **1a** and azobenzenes **2** (Table 5). Azobenzene

Table 5. One-Pot Synthesis of Benzotriazoles Starting from Azobenzenes and Tosyl Azides[a,b]



entry	5	method	yield (%)	entry	5	method	yield (%)
1	**5a**	A	80 (80)[c]	7	**5g**	A	72
2	**5b**	B	76	8	**5h**	B	68
3	**5c**	B	73	9	**5i**	B	76
4	**5d**	A	76 (81)[c]	10	**5j**	A	76 (77)[c]
5	**5e**	B	70	11	**5k**	A	45
6	**5f**	A	77	12	**5l**	A	59

[a]Method A: **1a** (0.2 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), and $AgNTf_2$ (16 mol %) in DCE (1.0 mL) at 90 °C for 12 h. Method B: **1a** (0.2 mmol), **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), and $AgNTf_2$ (16 mol %) in DCE (1.0 mL) at 110 °C for 12 h. [b]$PhI(OAc)_2$ (0.4 mmol). [c]**1a** (2.0 mmol), **2** (4.0 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), and $AgNTf_2$ (16 mol %) in DCE (10 mL) at 90 °C for 12 h.

2a (0.40 mmol) was treated with tosyl azide **1a** (0.20 mmol) in the presence of $[Cp^*RhCl_2]_2$ (4 mol %) and $AgNTf_2$ (16 mol %) in DCE at 90 °C under aerobic conditions. After the consumption of **1a** for 12 h, $PhI(OAc)_2$ (0.4 mmol) was added to the reaction mixture and then the mixture was subsequently stirred at 40 °C for an additional 22 h, producing 2-phenyl-2*H*-benzotriazole **5a** in 80% yield. To demonstrate the applicability of the present method to larger scale processes, a reaction of a 2.0 mmol scale of **1a** was undertaken with **2a** (4.0 mmol). The semi-one-pot reaction smoothly proceeded, and the corresponding trizole **5a** was isolated in 80% yield (312.0 mg). Azobenzenes **2** having not only electron-donating groups such as methyl, ethyl, and methoxy but also electron-withdrawing groups such as chloro, bromo, trifuloromethyl, ketone, and ester on the phenyl ring underwent the sequential Rh-catalyzed amidation and oxidation, leading to a two-component one-pot synthesis of 2-aryl-2*H*-benzotrizoles **5** in reasonable yields.

Because 2-aryl-2*H*-benzotrizoles were fluorescent, their optical properties in CH_2Cl_2 solution were examined (Table 6). The benzotrizole fluorophores showed large Stokes shifts

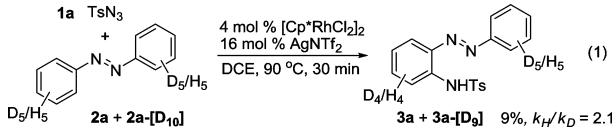
Table 6. Photophysical Properties of Benzotriazoles[a]

compd	$\lambda_{max,abs}$ (nm)	$\lambda_{max,em}$ (nm)	ε (M^{-1} cm^{-1})	ϕ
5a	309	365	26 929	0.47
5b	291	376	24 021	0.17
5c	313	361	27 232	0.55
5d	315	365	29 305	0.51
5e	290	372	18 179	0.17
5f	334	387	27 231	0.57
5g	318	368	29 382	0.37
5h	321	nd	30 310	–
5i	315	nd	36 471	–
5j	332	368	29 156	0.56
5k	312	361	26 629	0.45
5l	309	379	27 593	0.16

[a]Absorption peaks ($\lambda_{max,abs}$) and molar extinction coefficients (ε) were measured in CH_2Cl_2 (10^{-4} M). Full spectra are given in the SI.

(~60 nm) and high extinction coefficients (~3 × 10^4 M^{-1} cm^{-1}), which is an attractive property for biological probes (see SI).

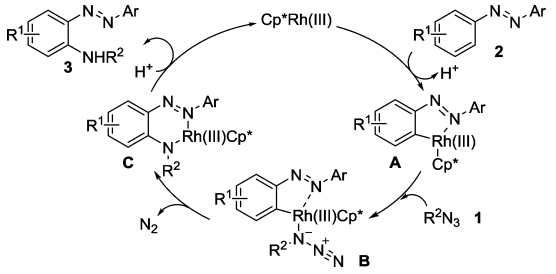
We carried out KIE studies to gain insight into the reaction mechanism (eq 1). A notable primary KIE was detected (k_H/k_D



= 2.1),[13] indicating that the C−H bond cleavage at the *ortho* position of azobenzene is most likely involved with the rate-determining step.

A plausible mechanism for the sequential Rh-catalyzed amidation and oxidation is described in Scheme 3.[14] First,

Scheme 3. A Plausible Mechanism of Amidation



exposure of $[Cp^*RhCl_2]_2$ to $AgNTf_2$ affords a cationic Rh(III) species, which assists the C−H activation to provide a five-membered rhodacycles **A**. Coordination of *N*-sulfonyl azide **1** to **A** followed by insertion of a sulfonamido moiety into the rhodacycle provides Rh(III) amido complex **C**. Finally, protonolysis of **C** produces the desired amidated product **3**.

Because the oxidation of tosylamino azobenzenes **3** to the corresponding 2-aryl-2*H*-benzotriazoles **5** could be quenched in the presence of TEMPO as a free radical scavenger, the

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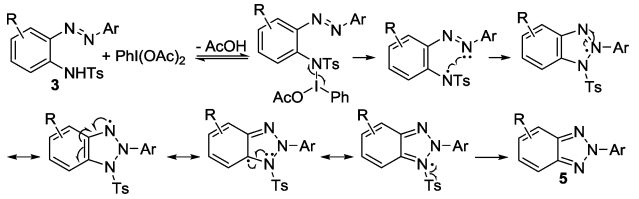
mechanism of the oxidative cyclization with $PhI(OAc)_2$ is proposed to involve the areneamino radical intermediate (Scheme 4).[8]

Scheme 4. A Plausible Mechanism of Oxidative Cyclization



In this paper, we have developed a selective synthetic method of 2-aryl-2*H*-benzotriazoles from nonprefunctionalized azobenzenes and *N*-sulfonyl azides through sequential rhodium-catalyzed amidation (C−N bond formation) and oxidation (N−N bond formation) in one pot. The present method enables the preparation of an array of 2-aryl-2*H*-benzotriazoles with varied substitution patterns for efficient optimization of photophysical properties.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and ^1H and ^{13}C NMR spectra for 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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