JOC The Journal of Organic Chemistry

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Rhodium-Catalyzed Direct C−H Amidation of Azobenzenes with Sulfonyl Azides: A Synthetic Route to Sterically Hindered *ortho*-Substituted Aromatic Azo Compounds

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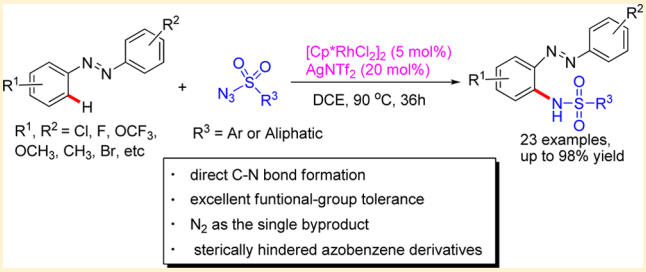
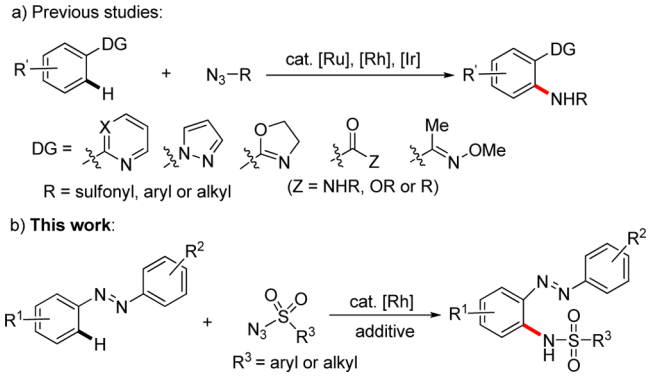
Supporting Information

ABSTRACT: A rhodium(III)-catalyzed direct *ortho*-amidation of azobenzenes with sulfonyl azides as the amino source is disclosed. This reaction exhibits a broad substrate scope, high functional group tolerance, and regioselectivity, providing a variety of sterically hindered *ortho*-substituted azobenzene derivatives in good to excellent yield.



It is well-known that aromatic azo compounds are important materials and have been broadly applied in many fields due to their unique properties. They can be used as light-triggered switches in surface-modified materials,[1] polymers,[2] molecular machines,[3] protein probes,[4] organic dyes,[5] nonlinear optical devices,[6] chemosensors,[7] and so forth. Recently, significant attention has been focused on direct C−H functionalization of azobenzenes using the azo group as a directing group. Wang et al. and Zeng et al. reported palladium-catalyzed *ortho*-acylation of azobenzenes with α-oxocarboxylic acids,[8] aldehydes,[9] and aryl methanes.[10] The palladium-catalyzed *ortho*-alkoxylation and halogenation of aromatic azo compounds were reported by Sun et al.[11] and Ma and Tian,[12] respectively. A rhodium(III)-catalyzed C−H bond addition of azobenzenes to aldehydes was also developed.[13] Despite the achievements that have been made with respect to direct C−H functionalization of azobenzenes, the formation of a C−N bond is rarely studied in the C−H activation process. To the best of our knowledge, the direct C−H amidation of azobenzenes with sulfonyl azides has never been reported. Very recently, transition-metal-catalyzed direct C−H amidation using sulfonyl azides as the amino source has attracted a great deal of attention.[14] Herein, we report a highly efficient strategy for the synthesis of sterically hindered aromatic azo compounds through Rh(III)-catalyzed *ortho*-amidation of azobenzenes with sulfonyl azides via azo-directed C−H activation (Scheme 1).

Scheme 1. Transition-Metal-Catalyzed Direct C−H Amidation with Azides

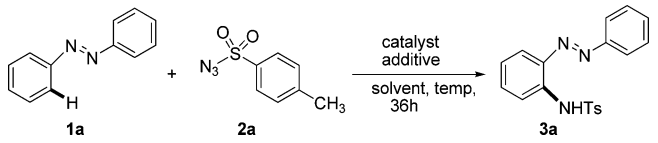


We started to optimize the reaction conditions by using azobenzene (**1a**) and *p*-toluenesulfonyl azide (**2a**) as the substrate (Table 1). The activities of different metal catalysts in combination with $AgSbF_6$ were first examined in 1,2-dichloroethane (DCE) at 80 °C for 36 h. Unfortunately, the use of $[Ru(p\text{-cymene})Cl_2]_2$ and $[Cp^*IrCl_2]_2$ proved unsuccessful in catalyzing this amidation reaction (entries 1 and 2). However, a trace amount of desired product **3a** was isolated when $[Cp^*RhCl_2]_2$ was employed (entry 3). Gratifyingly, the reaction activity of azobenzene (**1a**) with *p*-toluenesulfonyl azide (**2a**) could be enhanced by the use of $AgNTf_2$ as additive, leading to the formation of **3a** in 63% yield (entry 4). Screening of a range of solvents revealed that DCE was found to be the best solvent of choice compared with THF, toluene, and DMSO (entries 5−7). The critical improvement of reactivity was achieved by the use of a slight excess of azobenzene (**1a**). The amidation reaction proceeded smoothly at 90 °C in DCE to give the desired product **3a** in 75% yield when the ratio of **1a**/**2a** was switched to 1.5:1 (entry 8). There was no obvious promotion with an increase in the ratio of **1a**/**2a** to 2:1 (entry 9). Some additives, such as $AgBF_4$, $AgNO_3$, and Ag_2O, were also tested. In the presence of $AgBF_4$, the yield of product **3a** had a slight decrease (entry 10), but the presence of $AgNO_3$ and Ag_2O was obviously not favorable for this reaction (entries

Received: February 15, 2014
Published: March 31, 2014

dx.doi.org/10.1021/jo500372d | J. Org. Chem. 2014, 79, 4180−4185

Table 1. Optimization of Reaction Conditions[a]



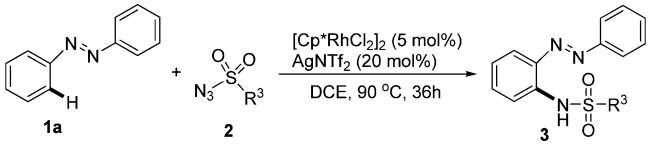
entry	catalyst	additive	solvent	T (°C)	yield[d] (%)
1	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	DCE	80	n. d.[e]
2	$[Cp^*IrCl_2]_2$	$AgSbF_6$	DCE	80	n. d.[e]
3	$[Cp^*RhCl_2]_2$	$AgSbF_6$	DCE	80	<10
4	$[Cp^*RhCl_2]_2$	$AgNTf_2$	DCE	80	63
5	$[Cp^*RhCl_2]_2$	$AgNTf_2$	THF	80	19
6	$[Cp^*RhCl_2]_2$	$AgNTf_2$	Toulene	110	n. d.[e]
7	$[Cp^*RhCl_2]_2$	$AgNTf_2$	DMSO	110	n. d.[e]
8[b]	**$[Cp^*RhCl_2]_2$**	**$AgNTf_2$**	**DCE**	**90**	**75(72)**[h]
9[c]	$[Cp^*RhCl_2]_2$	$AgNTf_2$	DCE	90	78(63)[f]
10[b]	$[Cp^*RhCl_2]_2$	$AgBF_4$	DCE	90	50
11[b]	$[Cp^*RhCl_2]_2$	$AgNO_3$	DCE	90	n. d.[e]
12[b]	$[Cp^*RhCl_2]_2$	Ag_2O	DCE	90	n. d.[e]
13[b]	$[Cp^*RhCl_2]_2$	$AgNTf_2$	DCE	100	68
14[b]	$[Cp^*RhCl_2]_2$	$AgNTf_2$	DCE	120	63
15	$[Cp^*RhCl_2]_2$	$AgNTf_2$	DCE	90	68[g]
16	$[Cp^*RhCl_2]_2$	$AgNTf_2$	DCE	90	78[g]

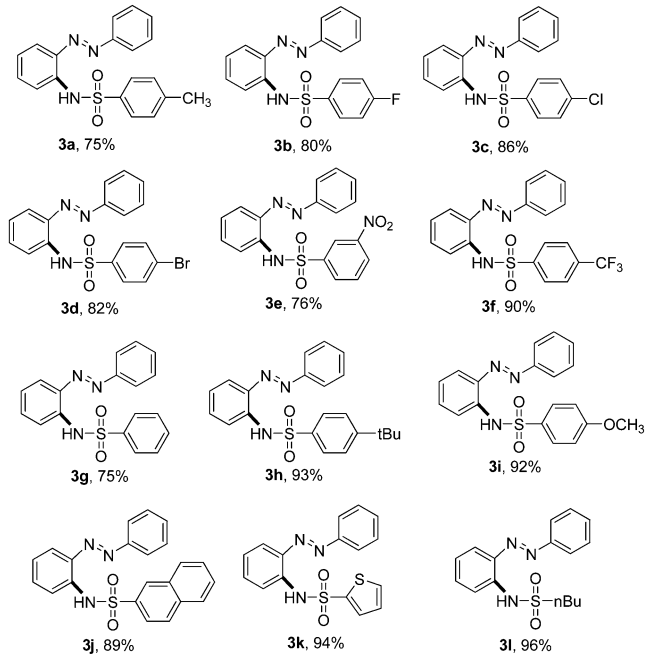
[a]Reaction conditions: **1a** (0.15 mmol), **2a** (2.0 equiv), catalyst (5 mol %), additive (20 mol %) in solvent (1.0 mL) at the indicated temperature for 36 h. [b]Reaction conditions: **1a** (1.5 equiv), **2a** (0.1 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), additive (20 mol %) in DCE at 90 °C for 36 h. [c]The reaction was carried out with **1a** (2.0 equiv) and **2a** (0.1 mmol). [d]Isolated yield. [e]The formation of product was not detected. [f]**1a** (0.15 mmol) and **2a** (1.0 equiv) were used as substrate. [g]$[Cp^*RhCl_2]_2$ (2.5 and 10 mol %) was used. [h]The reaction was carried out on a 10 mmol scale.

11 and 12). Different reaction temperatures were further investigated. Raising the temperature diminished the yield of the product **3a** (entries 13 and 14). Finally, the lower yield of **3a** was obtained when 2.5 mol % $[Cp^*RhCl_2]_2$ was used (entry 15), while utilizing $[Cp^*RhCl_2]_2$ (10 mol %) as the catalyst did not show higher catalytic activity (entry 16). After screening several parameters, eventually, the following conditions were chosen for examination of the reaction scope: $[Cp^*RhCl_2]_2$ (5 mol %), $AgNTf_2$ (20 mol %), and **1a**/**2a** = 1.5:1 in DCE at 90 °C for 36 h.

With the optimized conditions for the amidation of azobenzene in hand, we next examined the scope of this methodology. As summarized in Table 2, the C−H amidation of azobenzene (**1a**) with various sulfonyl azides could proceed smoothly and furnish the corresponding *ortho*-substituted products. The substituent on the benzene ring of sulfonyl azides showed obvious electronic effects on reaction activity. The substrates with a *para*-electron-withdrawing group (such as 4-F, 4-Cl, 4-Br) afforded the products **3b**−**3d** in good yields (80−86%), while the substrates with a strong *meta*-electron-withdrawing group (−NO_2) provided the corresponding product **3e** in 76% yield. Interestingly, the reaction of azobenzene (**1a**) with *p*-trifluoromethylphenylsulfonyl azide led to the desired azo compound **3f** in 90% yield. When the substrates with a *para*-electron-donating group (4-*t*-Bu, 4-OMe) were used, the *ortho*-substituted azobenzene derivatives **3h** and **3i** were obtained with 93% and 92% yields, respectively. To our delight, this catalytic system could be further extended to other sulfonyl azides. The 2-naphthyl sulfonyl azide could give the product **3j** in 89% yield under the same conditions. The 2-thienyl- and *n*-butyl-substituted sulfonyl azides could react well with azobenzene to facilitate the desired products **3k** and **3l** in excellent yields (94% and 96%, respectively).

Table 2. Rh-Catalyzed *ortho*-Amidation of Azobenzene with Different Sulfonyl Azides[a,b]



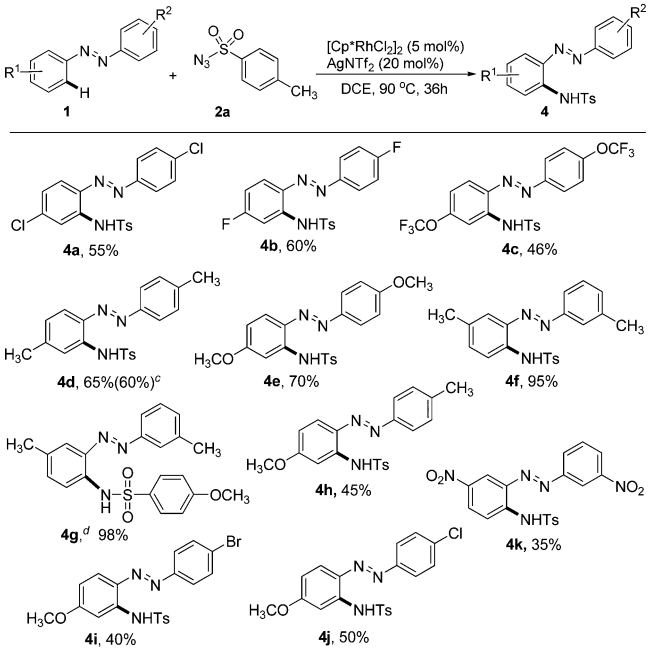


[a]Reaction conditions: **1a** (1.5 equiv), **2** (0.1 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgNTf_2$ (20 mol %) in 1,2-dichloroethane (1 mL) at 90 °C for 36 h. [b]Isolated yield.

dx.doi.org/10.1021/jo500372d | J. Org. Chem. 2014, 79, 4180−4185

After screening of different sulfonyl azides, the scope of substituted azobenzenes was then explored with *p*-toluenesulfonyl azide (**2a**). As can be seen from Table 3, the catalytic

Table 3. Rh-Catalyzed *ortho*-Amidation of Substituted Azobenzenes with *p*-Toluenesulfonyl Azide[a,b,c,d]

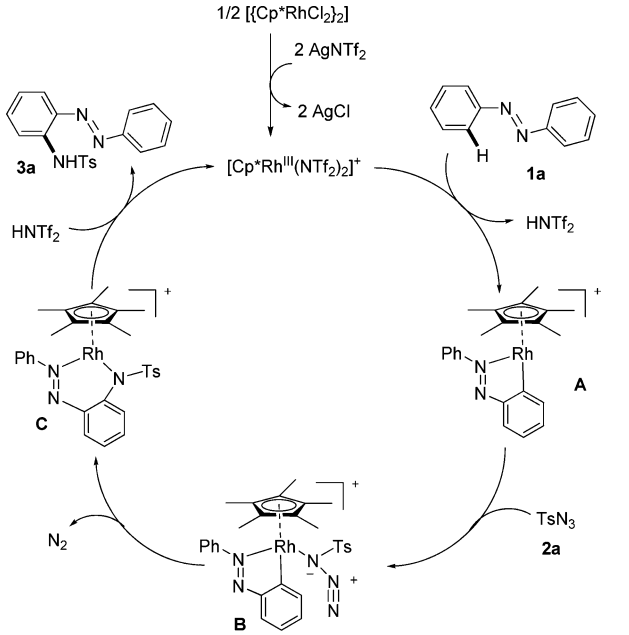


[a]Reaction conditions: **1** (1.5 equiv), **2a** (0.1 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgNTf_2$ (20 mol %) in 1,2-dichloroethane (1 mL) at 90 °C for 36 h. [b]Isolated yield. [c]The reaction was carried out by using **1** (1.5 equiv) and **2a** (10 mmol). [d]The *meta*-methyl substituted azobenene and *p*-methoxysulfonyl azide were used as substrate.

system proved to be broadly applicable and was found to be tolerant of electron-withdrawing (F, Cl, OCF_3) or electron-donating (4-OMe, 4-Me, 3-Me) functional groups. Substituents on the aromatic moiety of the aromatic azo compounds influenced the efficiency of this amidation reaction significantly. Substrates with a halogen atom (Cl or F) at the *para* position of the phenyl ring proceeded smoothly to give the corresponding products **4a** and **4b** in moderate yields (55% and 60%, respectively). The direct amidation of aromatic azo compounds bearing a strong electron-withdrawing group (OCF_3) was less efficient compared to those derivatives having a weak electron-withdrawing group at the *para* position of the phenyl ring. To our surprise, substrates bearing an electron-donating group, such as methyl or methoxy, at the *para* position of the phenyl ring furnished the desired product in moderate to good yield (65% for **4d**; 70% for **4e**). It should be noted that the yield of product had a sharp increase when azobenzene derivatives with a methyl group at the *meta* position of the phenyl ring was used as the substrate. The reaction of *meta*-methyl-substituted azobenzene with *para*-methoxysulfonyl azide led to the product **4g** in almost quantitative yield (98%) probably due to the "electron-donating" effect from methyl and methoxy groups. We also investigated the electronic effect of substituents on the regioselectivity of the *ortho*-amidation of unsymmetric azoarenes and found that these amidation reactions mainly took place on the electron-rich azo aromatic rings, and a trace amount of another regioisomer was observed by TLC. When unsymmetrical azobenzenes were employed as the substrates, the primary regioisomers, which could be determined by ^1H NMR, were obtained in lower yields (45% for **4h**; 40% for **4i**; 50% for **4j**, respectively). Finally, azobenzene with a nitro group at the *meta* position reacted with *p*-toluenesulfonyl azide (**2a**) to give the corresponding product **4k** in 35% yield, which further showed that a substrate with an electron-withdrawing group on the phenyl ring of azobenzene was unfavorable to the reaction.

On the basis of our experimental results and the previous literature,[14] a plausible mechanism for this direct amidation reaction is proposed in Scheme 2. First, this transformation

Scheme 2. Plausible Reaction Mechanism



may begin with formation of the cyclorhodium intermediate **A** through the reaction of azobenzene (**1a**) with the $[Cp^*Rh^{III}(NTf_2)_2]^+$ species generated from $[Cp^*RhCl_2]_2$ and $AgNTf_2$, which was treated with sulfonyl azide (**2a**) to provide intermediate **B**. Subsequent concerted migratory insertion led to the formation of a rhodium(III) amido species **C**. Finally, the desired product (**3a**) was obtained and the $[Cp^*Rh^{III}(NTf_2)_2]^+$ species was regenerated to complete the catalytic cycle by protonolysis of intermediate **C**.

In summary, a rhodium(III)-catalyzed direct *ortho*-amidation of aromatic azo compounds via C−H bond activation with sulfonyl azides as the amino source has been developed. This protocol provided a convenient method for synthesis of sterically hindered *ortho*-substituted symmetrical and unsymmetrical azobenzene derivatives, which could tolerate a wide range of functional groups, such as chloro, bromo, nitro, methyl, and methoxy groups, on the phenyl ring. The method was also applicable to heteroaromatic and aliphatic sulfonyl azides.

EXPERIMENTAL SECTION

General Methods. Unless otherwise stated, all manipulations were performed in a sealed tube with a Teflon-lined cap under an air atmosphere. Chemicals were commercially available and used without purification. Sulfonyl azide substrates[14e] and aromatic azo compounds[15] were prepared according to the literature procedure. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 or 300

dx.doi.org/10.1021/jo500372d | J. Org. Chem. 2014, 79, 4180−4185

spectrometer, and chemical shifts are reported in parts per million (ppm) using $(CH_3)_4Si$ (for ^1H, δ = 0.00; for ^{13}C, δ = 77.00) as the internal standard. The following abbreviations are used to denote the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (J) were reported in hertz unit (Hz). Melting points are uncorrected. C, H, and N analyses were measured on an elemental analyzer. HRMS data were obtained by ESI on a TOF mass analyzer. IR spectra were recorded as KBr pellets on an FTIR-8500 spectrometer.

General Procedure for Rhodium(III)-Catalyzed Direct *ortho*-Amidation of Azobenzenes with Sulfonyl Azides. To a 25 mL sealed tube with a Teflon-lined cap were added azobenzene **1** (1.5 equiv), sulfonyl azide **2** (0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), $AgNTf_2$ (7.76 mg, 20 mol %), and 1,2-dichloroethane (1 mL) under atmospheric conditions. The reaction mixture was stirred in a preheated oil bath at 90 °C for 36 h. After the mixture was cooled to room temperature, the volatiles were removed under reduced pressure, and the residue was purified by preparative thin layer chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as the eluent to give the desired product **3** or **4**.

*2-(4-Methylphenylsulfonamido)azobenzene (**3a**).* Yield 75% (26.3 mg); pale yellow solid, mp 129−130 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.82−7.80 (m, 2H), 7.75−7.70 (m, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.54−7.51 (m, 3H), 7.39 (t, J = 8.4 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 144.0, 140.0, 136.2, 134.5, 132.5, 131.7, 129.7, 129.3, 127.2, 124.3, 122.8, 122.7, 120.2, 21.5. Anal. Calcd for $C_{19}H_{17}N_3O_2S$: C, 64.94; H, 4.88; N, 11.96. Found: C, 64.85; H, 4.91; N, 12.02. IR (KBr, cm^{-1}): 3253, 3055, 2915, 1580, 1453, 1300, 1150, 1072, 925, 775, 691, 525.

*2-(4-Fluorophenylsulfonamido)azobenzene (**3b**).* Yield 80% (28.4 mg); pale yellow solid, mp 117−118 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.83−7.75 (m, 5H), 7.71 (dd, J = 1.2, 8.4 Hz, 1H), 7.55−7.53 (m, 3H), 7.42 (dt, J = 1.6, 8.4 Hz, 1H), 7.20 (dt, J = 1.2, 8.4 Hz, 1H), 6.99 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 163.9, 151.9, 140.3, 133.9, 132.6, 131.9, 129.9, 129.4, 124.8, 122.8, 120.5, 116.4, 116.2. Anal. Calcd for $C_{18}H_{14}FN_3O_2S$: C, 60.83; H, 3.97; N, 11.82. Found: C, 60.68; H, 4.05; N, 11.59. IR (KBr, cm^{-1}): 3275, 3094, 2932, 1587, 1455, 1325, 1165, 1092, 931, 780, 692, 536.

*2-(4-Chlorophenylsulfonamido)azobenzene (**3c**).* Yield 86% (31.9 mg); pale yellow solid, mp 94−95 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.81 (dd, J = 2.4, 8.0 Hz, 2H), 7.76 (dd, J = 1.6, 8.0 Hz, 1H), 7.72−7.69 (m, 3H), 7.55−7.53 (m, 3H), 7.41 (dt, J = 1.6, 8.4 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.20 (dt, J = 1.2, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 140.3, 139.7, 137.5, 133.9, 132.6, 131.9, 129.4, 128.5, 124.9, 123.0, 122.8, 120.6. Anal. Calcd for $C_{18}H_{14}ClN_3O_2S$: C, 58.14; H, 3.79; N, 11.30. Found: C, 58.43; H, 3.65; N, 11.52. IR (KBr, cm^{-1}): 3258, 3062, 2917, 1575, 1495, 1332, 1160, 1088, 920, 795, 693, 530.

*2-(4-Bromophenylsulfonamido)azobenzene (**3d**).* Yield 82% (34.1 mg); pale yellow solid, mp 143−144 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.82−7.76 (m, 3H), 7.70 (dd, J = 1.2, 8.4 Hz, 1H), 7.62 (dd, J = 2.0, 7.2 Hz, 2H), 7.63−7.54 (m, 3H), 7.49−7.39 (m, 3H), 7.21 (dt, J = 1.2, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 140.3, 138.0, 133.8, 132.6, 132.3, 131.9, 129.4, 128.6, 124.8, 123.1, 122.8, 120.5. Anal. Calcd for $C_{18}H_{14}BrN_3O_2S$: C, 51.93; H, 3.39; N, 10.09. Found: C, 52.11; H, 3.25; N, 9.88. IR (KBr, cm^{-1}): 3265, 3097, 2915, 1578, 1501, 1376, 1330, 1164, 1091, 745, 648, 528.

*2-(3-Nitrophenylsulfonamido)azobenzene (**3e**).* Yield 76% (29.1 mg); pale yellow solid, mp 102−104 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 8.63−8.61 (m, 1H), 8.26−8.23 (m, 1H), 8.01−7.98 (m, 1H), 7.78−7.72 (m, 4H), 7.54−7.51 (m, 4H), 7.49−7.44 (m, 1H), 7.27−7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 148.1, 141.0, 140.8, 133.2, 132.7, 132.4, 132.2, 130.8, 130.3, 129.5, 127.5, 125.7, 122.8, 122.7, 122.4, 121.5. Anal. Calcd for $C_{18}H_{14}N_4O_4S$: C, 56.54; H, 3.69; N, 14.65. Found: C, 56.75; H, 3.87; N, 14.37. IR (KBr, cm^{-1}): 3282, 3075, 2940, 1588, 1344, 1172, 1094, 834, 671, 534.

*2-(4-Trifluoromethylphenylsulfonamido)azobenzene (**3f**).* Yield 90% (36.5 mg); pale yellow solid, mp 107−108 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.80−7.76 (m, 3H), 7.73 (dd, J = 1.2, 8.4 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.55 (dd, J = 1.6, 4.8 Hz, 3H), 7.43 (dt, J = 1.6, 8.4 Hz, 1H), 7.23 (t, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 140.4, 134.5, 133.5, 132.6, 132.0, 129.4, 127.6, 126.2, 126.1, 125.1, 124.4, 123.3, 122.8, 120.7. HRMS (ESI) m/z: Calcd for $C_{19}H_{14}F_3N_3O_2S$: $[M + H]^+$ 406.0832, found 406.0835. IR (KBr, cm^{-1}): 3265, 2920, 1584, 1328, 1174, 1065, 925, 718, 688, 532.

*2-(Phenylsulfonamido)azobenzene (**3g**).* Yield 75% (25.3 mg); pale yellow solid, mp 108−109 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 9.81 (s, 1H, NH), 7.82−7.79 (m, 4H), 7.74 (dt, J = 0.9, 7.2 Hz, 2H), 7.55−7.51 (m, 3H), 7.46−7.39 (m, 2H), 7.34 (t, J = 6.0 Hz, 2H), 7.16 (dt, J = 0.9, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9, 140.1, 139.1, 134.3, 133.1, 132.5, 131.8, 129.3, 129.0, 127.1, 124.4, 122.8, 122.8, 120.3. HRMS (ESI) m/z: Calcd for $C_{18}H_{16}N_3O_2S$ $[M + H]^+$ 338.0958, found 338.0962. IR (KBr, cm^{-1}): 3248, 1580, 1453, 1335, 1154, 1068, 918, 775, 693, 550.

*2-(4-tert-Butylphenylsulfonamido)azobenzene (**3h**).* Yield 93% (36.5 mg); pale yellow solid, mp 132−133 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.81−7.78 (m, 3H), 7.76−7.71 (m, 3H), 7.55−7.51 (m, 3H), 7.41 (dt, J = 1.6, 8.4 Hz, 1H), 7.35 (d, J = 1.6 Hz, 2H), 7.16 (dt, J = 1.2, 8.4 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 151.9, 140.0, 136.2, 134.6, 132.6, 131.7, 129.3, 127.0, 126.1, 124.2, 122.8, 122.6, 120.2, 35.1, 30.9. HRMS (ESI) m/z: Calcd for $C_{22}H_{24}N_3O_2S$ $[M + H]^+$ 394.1584, found 394.1588. IR (KBr, cm^{-1}): 3249, 2961, 1502, 1338, 1164, 1092, 910, 768, 685, 520.

*2-(4-Methoxyphenylsulfonamido)azobenzene (**3i**).* Yield 92% (33.8 mg); pale yellow solid, mp 108−109 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.82 (t, J = 2.4 Hz, 2H), 7.74−7.69 (m, 4H), 7.52 (dd, J = 1.2, 4.4 Hz, 3H), 7.38 (t, J = 8.4 Hz, 1H), 7.15 (t, J = 8.4 Hz, 1H), 6.77 (dd, J = 2.0, 6.8 Hz, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 151.9, 140.1, 134.6, 132.5, 131.7, 130.6, 129.3, 128.2, 124.3, 122.8, 122.6, 120.2, 114.2, 55.5. HRMS (ESI) m/z: Calcd for $C_{19}H_{18}N_3O_3S$ $[M + H]^+$ 368.1063, found 368.1068. IR (KBr, cm^{-1}): 3315, 2925, 2840, 1594, 1495, 1332, 1268, 1152, 1097, 893, 792, 685, 537.

*2-(2-Naphthylsulfonamido)azobenzene (**3j**).* Yield 89% (34.4 mg); pale yellow solid, mp 93−94 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.42 (s, 1H), 7.82−7.69 (m, 8H), 7.56−7.49 (m, 5H), 7.37 (t, J = 8.4 Hz, 1H), 7.12 (t, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 140.0, 136.0, 134.9, 134.2, 132.6, 131.9, 131.7, 129.4, 129.3, 129.2, 128.9, 128.8, 127.9, 127.5, 124.4, 123.0, 122.8, 122.0, 120.2. Anal. Calcd for $C_{22}H_{17}N_3O_2S$: C, 68.20; H, 4.42; N, 10.85. Found: C, 67.98; H, 4.51; N, 10.77. IR (KBr, cm^{-1}): 3263, 3062, 2922, 2853, 1586, 1464, 1295, 1152, 1092, 927, 767, 684, 543.

*2-(2-Thienylsulfonamido)azobenzene (**3k**).* Yield 94% (32.2 mg); pale yellow solid, mp 132−134 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 9.83 (s, 1H, NH), 7.86−7.79 (m, 4H), 7.56 (dd, J = 4.2, 9.6 Hz, 4H), 7.46 (dd, J = 4.8, 7.2 Hz, 1H), 7.27−7.19 (m, 1H), 6.92 (t, J = 3.6 Hz, 1H), 4.12 (dd, J = 7.2, 14.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9, 140.4, 139.6, 134.2, 132.8, 132.6, 131.8, 129.3, 127.3, 124.8, 122.9, 122.6, 120.6. Anal. Calcd for $C_{16}H_{13}N_3O_2S_2$: C, 55.96; H, 3.82; N, 12.24. Found: C, 56.05; H, 3.94; N, 12.05. IR (KBr, cm^{-1}): 3255, 3105, 3075, 1586, 1407, 1253, 1083, 927, 834, 714, 683.

*2-(Butylsulfonamido)azobenzene (**3l**).* Yield 96% (30.4 mg); pale yellow solid, mp 72−74 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.92−7.87 (m, 3H), 7.78 (dd, J = 1.2, 8.4 Hz, 1H), 7.57−7.51 (m, 3H), 7.47 (dt, J = 1.2, 8.4 Hz, 1H), 7.23 (t, J = 8.4 Hz, 1H), 3.17−3.14 (m, 2H), 1.81−1.73 (m, 2H), 1.36 (q, J = 7.2 Hz, 2H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 139.2, 134.9, 132.9, 131.8, 129.4, 123.9, 123.2, 122.8, 118.6, 51.7, 25.4, 21.3, 13.4. Anal. Calcd for $C_{16}H_{19}N_3O_2S$: C, 60.54; H, 6.04; N, 13.24. Found: C, 60.73; H, 6.18; N, 13.05. IR (KBr, cm^{-1}): 3264, 2953, 2865, 1502, 1378, 1335, 1154, 923, 782, 648, 531.

*2-(4-Methylphenylsulfonamido)-4,4′-dichloroazobenzene (**4a**).* Yield 55% (23.1 mg); pale yellow solid, mp 165−167 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.78−7.69 (m, 6H), 7.52 (dd, J = 2.1, 6.6 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.12 (dd, J = 2.1, 8.4 Hz,

dx.doi.org/10.1021/jo500372d | J. Org. Chem. 2014, 79, 4180−4185

1H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2, 144.5, 138.9, 138.0, 135.9, 135.4, 129.9, 129.8, 129.7, 127.2, 124.4, 124.2, 124.0, 119.5, 21.5. Anal. Calcd for $C_{19}H_{15}Cl_2N_3O_2S$: C, 54.29; H, 3.60; N, 10.00. Found: C, 54.45; H, 3.38; N, 10.12. IR (KBr, cm^{-1}): 3248, 3086, 2926, 1578, 1534, 1356, 1143, 1085, 978, 834, 650.

*2-(4-Methylphenylsulfonamido)-4,4′-difluoroazobenzene (**4b**).* Yield 60% (29.2 mg); pale yellow solid, mp 160−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 7.84 (dt, J = 2.0, 6.8 Hz, 2H), 7.79−7.73 (m, 3H), 7.42 (dd, J = 2.4, 7.5 Hz, 1H), 7.26−7.20 (m, 4H), 6.85−6.80 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 163.5, 148.2, 144.4, 136.0, 129.9, 127.2, 126.1, 125.9, 124.8, 124.7, 116.5, 111.4, 106.4, 21.6. Anal. Calcd for $C_{19}H_{15}F_2N_3O_2S$: C, 58.91; H, 3.90; N, 10.85. Found: C, 59.05; H, 3.81; N, 10.92. IR (KBr, cm^{-1}): 3284, 3095, 2924, 1598, 1535, 1178, 1092, 972, 848, 735, 645.

*2-(4-Methylphenylsulfonamido)-4,4′-di(trifluoromethoxy)azobenzene (**4c**).* Yield 46% (23.9 mg); pale yellow solid, mp 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 7.78 (d, J = 9.2 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.4 Hz, 3H), 7.40 (d, J = 8.4 Hz, 1H), 7.31 (dd, J = 1.2, 8.8 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 150.0, 145.7, 144.5, 140.7, 135.8, 134.1, 130.6, 129.8, 127.1, 125.5, 124.2, 122.2, 119.1, 114.5, 113.1, 21.5. Anal. Calcd for $C_{21}H_{15}F_6N_3O_4S$: C, 48.56; H, 2.91; N, 8.09. Found: C, 48.69; H, 3.02; N, 7.94. IR (KBr, cm^{-1}): 3252, 3107, 2895, 1580, 1364, 1258, 1092, 854, 738, 640, 551.

*2-(4-Methylphenylsulfonamido)-4,4′-dimethylazobenzene (**4d**).* Yield 65% (24.6 mg); pale yellow solid, mp 161−162 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.73−7.63 (m, 5H), 7.53 (s, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 6.99 (dd, J = 1.2, 8.1 Hz, 1H), 2.47 (s, 3H), 2.39 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.0, 143.9, 143.2, 142.1, 138.1, 136.3, 133.9, 129.9, 129.6, 127.1, 125.2, 123.3, 122.6, 120.3, 21.9, 21.6, 21.5. Anal. Calcd for $C_{21}H_{21}N_3O_2S$: C, 66.47; H, 5.58; N, 11.07. Found: C, 66.58; H, 5.45; N, 11.24. IR (KBr, cm^{-1}): 2963, 2856, 1665, 1605, 1582, 1499, 1330, 1154, 1085, 905, 825, 658.

*2-(4-Methylphenylsulfonamido)-4,4′-dimethoxyazobenzene (**4e**).* Yield 45% (28.8 mg); pale yellow solid, mp 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.54 (s, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.70 (dd, J = 5.6, 8.8 Hz, 3H), 7.19 (d, J = 2.4 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.65 (dd, J = 2.4, 8.8 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 162.0, 146.1, 143.9, 136.3, 135.3, 134.2, 129.7, 127.2, 126.4, 124.2, 114.4, 110.6, 103.6, 55.7, 55.6, 21.5. HRMS (ESI) m/z: Calcd for $C_{21}H_{22}N_3O_4S$ $[M + H]^+$ 412.1326, found 412.1327. IR (KBr, cm^{-1}): 3265, 3098, 2954, 1592, 1248, 1175, 1086, 945, 832, 740, 652, 539.

*2-(4-Methylphenylsulfonamido)-5,5′-dimethylazobenzene (**4f**).* Yield 95% (36.0 mg); pale yellow solid, mp 107−108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.49 (s, 1H), 7.66−7.59 (m, 5H), 7.54 (d, J = 1.5 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.22 (dd, J = 1.5, 8.1 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 2.49 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1, 143.8, 140.3, 139.2, 136.1, 134.4, 133.2, 132.4, 132.0, 129.6, 129.1, 127.1, 123.2, 122.4, 120.8, 120.1, 29.7, 21.5, 20.8. HRMS (ESI) m/z: Calcd for $C_{21}H_{22}N_3O_2S$ $[M + H]^+$ 380.1427, found 380.1432. IR (KBr, cm^{-1}): 3278, 2923, 2854, 1512, 1385, 1165, 1082, 812, 642.

*2-(4-Methoxyphenylsulfonamido)-5,5′-dimethylazobenzene (**4g**).* Yield 98% (38.7 mg); pale yellow solid, mp 102−104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.46 (s, 1H), 7.68 (dd, J = 1.8, 7.8 Hz, 2H), 7.61 (t, J = 7.8 Hz, 3H), 7.53 (d, J = 0.9 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.22 (dd, J = 1.5, 8.4 Hz, 1H), 6.76 (dd, J = 1.8, 7.2 Hz, 2H), 3.73 (s, 3H), 2.48 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0, 152.1, 140.4, 139.2, 134.4, 133.2, 132.4, 132.1, 130.7, 129.3, 129.07, 123.2, 122.4, 120.9, 120.0, 114.1, 55.5, 21.4, 20.8. HRMS (ESI) m/z: Calcd for $C_{21}H_{22}N_3O_3S$ $[M + H]^+$ 396.1376, found 396.1378. IR (KBr, cm^{-1}): 3275, 2920, 2855, 1532, 1172, 1085, 940, 835, 742, 653, 540.

*2-(4-Methylphenylsulfonamido)-4-methoxy-4′-methylazobenzene (**4h**).* Yield 45% (17.7 mg); pale yellow solid, mp 126−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.64 (s, 1H), 7.75−7.69 (m, 5H), 7.32 (d, J = 8.1 Hz, 2H), 7.21 (t, J = 2.7 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 6.67 (dd, J = 2.7, 9.0 Hz, 1H), 3.86 (s, 3H), 2.45 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6, 149.9, 144.0, 141.5, 136.3, 135.54, 134.1, 129.9, 129.7, 127.2, 126.9, 122.3, 110.6, 103.5, 55.7, 29.7, 21.5. Anal. Calcd for $C_{21}H_{21}N_3O_3S$: C, 63.78; H, 5.35; N, 10.63. Found: C, 63.59; H, 5.44; N, 10.72. IR (KBr, cm^{-1}): 3278, 3062, 2922, 2849, 1508, 1378, 1142, 1087, 837, 698, 548.

*2-(4-Methylphenylsulfonamido)-4-methoxy-4′-bromoazobenzene (**4i**).* Yield 40% (18.4 mg); pale yellow solid, mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.48 (s, 1H), 7.74−7.71 (m, 3H), 7.64 (dt, J = 2.8, 8.8 Hz, 4H), 7.19−7.14 (m, 3H), 6.67 (dd, J = 2.8, 8.8 Hz, 1H), 3.86 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 150.6, 144.2, 136.3, 135.9, 134.0, 132.5, 129.7, 127.7, 127.2, 125.1, 123.8, 110.8, 103.4, 55.8, 21.5. Anal. Calcd for $C_{20}H_{18}BrN_3O_3S$: C, 52.18; H, 3.94; N, 9.13. Found: C, 52.32; H, 3.87; N, 9.02. IR (KBr, cm^{-1}): 3280, 3061, 2855, 1574, 1158, 1085, 968, 842, 647, 552.

*2-(4-Methylphenylsulfonamido)-4-methoxy-4′-chloroazobenzene (**4j**).* Yield 50% (20.7 mg); pale yellow solid, mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.48 (s, 1H), 7.74−7.71 (m, 5H), 7.47 (dd, J = 2.0, 6.8 Hz, 4H), 7.19 (s, 1H), 7.18 (d, J = 6.8 Hz, 2H), 6.67 (dd, J = 2.8, 8.8 Hz, 1H), 3.86 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 150.3, 144.2, 136.7, 136.3, 135.9, 134.0, 129.7, 129.6, 129.5, 127.2, 123.5, 110.8, 103.4, 55.8, 21.5. HRMS (ESI) m/z: Calcd for $C_{20}H_{19}ClN_3O_3S$ $[M + H]^+$ 416.0830, found 416.0836. IR (KBr, cm^{-1}): 3281, 3058, 2925, 1575, 1358, 1162, 1086, 975, 834, 658, 560.

*2-(4-Methylphenylsulfonamido)-5,5′-dinitroazobenzene (**4k**).* Yield 35% (15.4 mg); pale yellow solid, mp 213−215 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.70 (d, J = 2.4 Hz, 1H), 8.67 (t, J = 2.0 Hz, 1H), 8.45 (dd, J = 1.6, 6.0 Hz, 1H), 8.30 (dd, J = 2.8, 9.2 Hz, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.87−7.79 (m, 4H), 7.30 (d, J = 8.4 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 149.2, 145.3, 143.4, 140.3,137.8, 135.6, 130.6, 130.2, 129.2, 127.8, 127.3, 126.5, 118.6, 118.5, 117.3, 21.6. Anal. Calcd for $C_{19}H_{15}N_5O_6S$: C, 51.70; H, 3.43; N, 15.87. Found: C, 51.82; H, 3.51; N, 15.76. IR (KBr, cm^{-1}): 3295, 2948, 2871, 1532, 1389, 1165, 1089, 825, 654.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all products. 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.

■ ACKNOWLEDGMENTS

This work was financially supported by the Science Foundation (No. 872011, 872022) and the Startup Fund for Advanced Talents (No. 833158) of Shanxi Normal University.

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