



# Palladium-catalyzed annulation of 2-(aryldiazenyl) aniline with dimethyl sulfoxide to access *N*-aryl-1*H*-benzo[*d*]imidazol-1-amine



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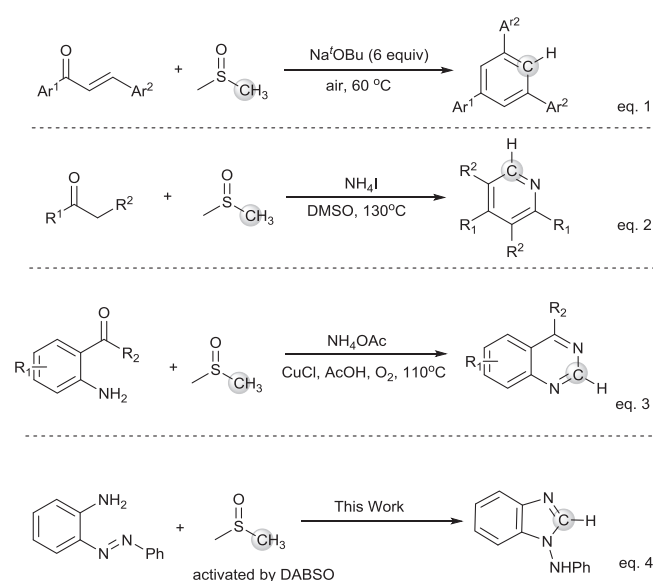
## ABSTRACT

A palladium-catalyzed annulation of 2-(aryldiazenyl) aniline and dimethyl sulfoxide was developed to access *N*-aryl-1*H*-benzo[*d*]imidazol-1-amine in moderate to good yields. Activated by 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO), DMSO served as a “=CH–” fragment during this procedure. It represents a facile pathway leading to benzimidazoles.

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Dimethyl sulfoxide (DMSO) is an aprotic polar solvent<sup>1</sup> as well as a versatile reagent in many well-known name reactions.<sup>2–5</sup> Pummerer reaction is one typical example employing DMSO as a building block in organic synthesis,<sup>6</sup> incorporating the fragment of “–CH<sub>2</sub>SMe” into the final product.<sup>7</sup> After proper activations, DMSO was widely employed in thiomethylation,<sup>8</sup> methylsulfonylation,<sup>9</sup> cyanation,<sup>10</sup> formylation,<sup>11</sup> methylation,<sup>12</sup> and methylenation.<sup>13</sup> Besides, DMSO also served as “=CH–” fragment in sequential annulation/aromatization reaction to construct heteroaromatic compounds. For example, recently, Cui developed an unprecedented protocol to access 1,3,5-triarylbenzenes from chalcones under metal-free and air-tolerant conditions (Scheme 1, Eq. (1)).<sup>14</sup> Yuan reported the access of symmetrical and unsymmetrical pyridines whereby ammonium iodide-promoted cyclization of ketones with DMSO and ammonium acetate (Scheme 1, Eq. (2)).<sup>15</sup> Ma demonstrated copper-catalyzed three-component procedure toward quinoxaline involving DMSO (Scheme 1, Eq. (3)).<sup>16</sup> We also demonstrated activation of DMSO by DABSO (DABSO = 1,4-diazabicyclo[2.2.2]octane-1,4-dium-1,4-disulfinate) leading to 4-aryl quinolines.<sup>17</sup>

Benzimidazoles are ubiquitous motifs in natural products and biologically active molecules,<sup>18</sup> serving as anti-inflammatory,




**Scheme 1.** DMSO serving as “=CH–” fragment in the construction of heterocycle.

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antimicrobial, antiviral reagents, antitubercular and analgesic.<sup>19</sup> Therefore, tremendous efforts have been devoted to access benzimidazoles, including condensation of benzene-1,2-diamine with

**Table 1**  
Screening the optimized reaction conditions.<sup>a</sup>



Entry	Catalyst	Additive (equiv)	Base	Yield (%)
1	–	–	Na <sup>t</sup> OBU	<10
2	–	–	K <sup>t</sup> OBU	23
3	–	DABSO (0.5)	–	42
4	Pd <sub>2</sub> (dba) <sub>3</sub>	DABSO (0.5)	–	58
5	Pd(dba) <sub>2</sub>	DABSO (0.5)	–	68
6	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DABSO (0.5)	–	67
7	Pd(OAc) <sub>2</sub>	DABSO (0.5)	–	73
8	Pd(CF <sub>3</sub> COO) <sub>2</sub>	DABSO (0.5)	–	65
9	Pd(acac) <sub>2</sub>	DABSO (0.5)	–	63
10	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	DABSO (0.5)	–	62
11	PdCl <sub>2</sub>	DABSO (0.5)	–	82, 36 <sup>b</sup> , 65 <sup>c</sup>
12	PdCl <sub>2</sub>	DABCO (0.5)	–	17
13	PdCl <sub>2</sub>	DABSO (0.2)	–	60
14	PdCl <sub>2</sub>	DABSO (1.0)	–	69
15	PdCl <sub>2</sub>	–	–	0
16	PdCl <sub>2</sub>	DABSO (0.5)	–	49 <sup>d</sup> , 64 <sup>e</sup> , 60 <sup>f</sup>
17 <sup>g</sup>	PdCl <sub>2</sub>	DABSO (0.5)	–	60

<sup>a</sup> Reaction conditions: 2-(phenyldiazenyl) aniline **1a** (0.2 mmol), Pd (10 mol%), additive (0.5 equiv), in DMSO (3 mL), under N<sub>2</sub>, 135 °C, 16 h, in sealed tube.

<sup>b</sup> Under O<sub>2</sub>.

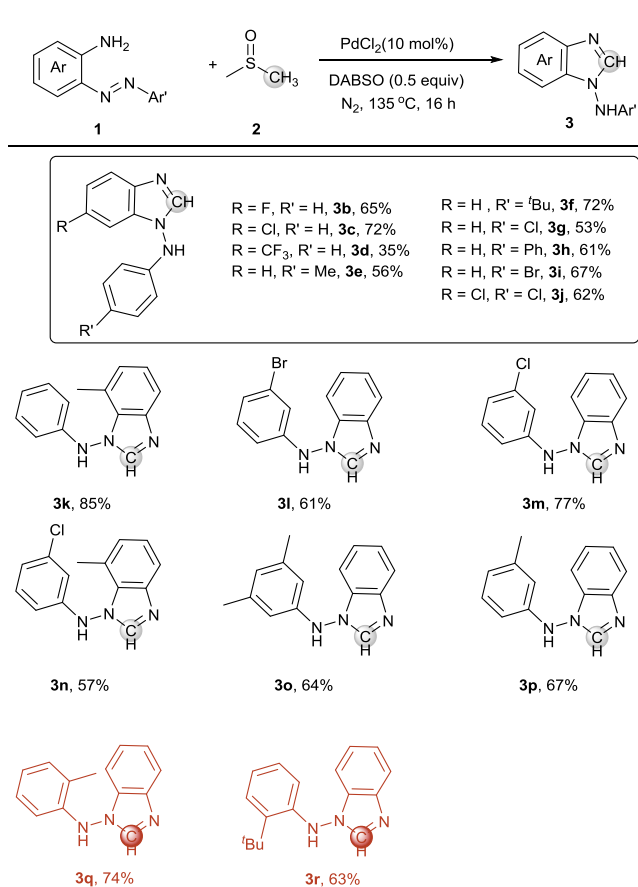
<sup>c</sup> Under air.

<sup>d</sup> 120 °C.

<sup>e</sup> 140 °C.

<sup>f</sup> 12 h.

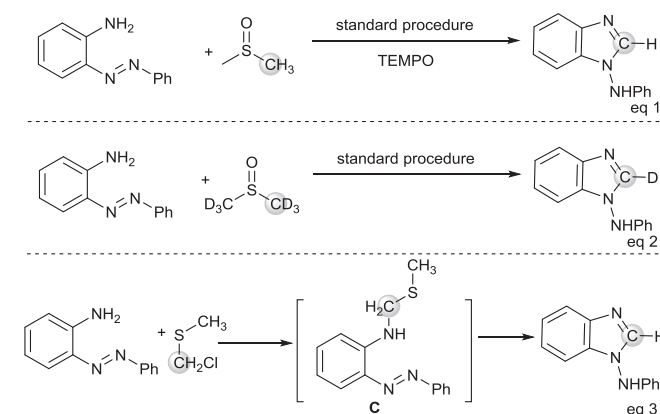
<sup>g</sup> Reaction performed on 1.0 mmol scale (**1a**).



**Scheme 2.** Substrate scope of 2-(aryldiazenyl) aniline.<sup>a</sup> <sup>a</sup>Reaction conditions: substituted 2-(aryldiazenyl) aniline **1** (0.2 mmol), PdCl<sub>2</sub> (10 mol%), DABSO (0.5 equiv), in DMSO (3 mL), under N<sub>2</sub>, 135 °C, 16 h, sealed tube.

carbonyl compounds synthon<sup>20</sup> and transition metal-catalyzed couplings of *ortho*-functionalized anilines.<sup>21</sup> However, they generally suffer from some limitations, such as the multiple steps, harsh conditions and availability of functionalized starting materials. Thus, the development of straightforward and eco-friendly processes to such frameworks remains highly desirable. Herein, we wish to report a palladium-catalyzed annulation of 2-(aryldiazenyl) aniline with DMSO, which serves as a “=CH–” fragment leading to *N*-aryl-1*H*-benzo[*d*]imidazol-1-amine (Scheme 1, Eq. (4)).

Initially, we tested the reaction of 2-(phenyldiazenyl) aniline **1a** in DMSO under N<sub>2</sub> at 135 °C in the presence of Na<sup>t</sup>OBU. After 16 h, the desired product *N*-phenyl-1*H*-benzo[*d*]imidazol-1-amine **3a** was isolated in less than 10% yield (Table 1, entry 1). Replacing Na<sup>t</sup>OBU with K<sup>t</sup>OBU resulted in 23% yield (Table 1, entry 2). To our delight, the yield dramatically increased to 42% by using DABSO



**Scheme 3.** Preliminary mechanism studies.

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