## **Supporting Information**

for

## Synthesis of Aryl Iodides from Arylhydrazines and Iodine

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NHNH <sub>2</sub> ·	HCI I <sub>2</sub> (0.5 mmol), bas	e I	
cı	DMSO (1.5 mL)		
<b>1a</b> (0.5 mmol)	60 °C, 6 h	2a	
entry	base (mmol)	yield <sup><math>b</math></sup> (%)	
1	Li <sub>2</sub> CO <sub>3</sub> (0.5)	21	
2	Na <sub>2</sub> CO <sub>3</sub> (0.5)	62	
3	K <sub>2</sub> CO <sub>3</sub> (0.5)	59	
4	$Cs_2CO_3(0.5)$	63	
5	K <sub>3</sub> PO <sub>4</sub> (0.5)	63	
6	Et <sub>3</sub> N (0.5)	48	
7	DBU (0.5)	29	
8	K <sub>2</sub> HPO <sub>4</sub> (0.5)	45	
9	KOAc (1.0)	62	
10	KOH (1.0)	44	
11	KOH (0.5)	45	
12	NaHCO <sub>3</sub> (1.0)	46	
13	NaHCO <sub>3</sub> (0.5)	31	
<sup>a</sup> Conditions: 1a, I <sub>2</sub> , base, and solvent were stirred at			

 Table S1. Optimization of the Iodination of Arylhydrazines with Iodine Using

 Several Bases<sup>a</sup>

<sup>*a*</sup>Conditions: **1a**, I<sub>2</sub>, base, and solvent were stirred at 60 °C for 6 h. <sup>*b*</sup>Determined by <sup>1</sup>H NMR spectroscopy of the crude mixture using 1,3,5-trioxane as an internal standard.

The Procedure of Using *tert*-Butylhydrazine Hydrochloride as Substrate. *tert*-Butylhydrazine hydrochloride (62.3 mg, 0.5 mmol), I<sub>2</sub> (126.9 mg, 0.5 mmol), and DMSO (0.1 mL) were added to a round-bottomed flask, and the reaction mixture was stirred at 60 °C for 6 h under air. The resulting mixture was cooled to room temperature and directly analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>). As a result, the peak of 2-iodo-2-methlpropane (1.81 ppm) was not detected. Then, sat. Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (aq., 5 mL) and water (10 mL) were added into the combined reaction mixture. The mixture was extracted with CHCl<sub>3</sub> (4×5 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The residue was analyzed by GC-MS, and unfortunately, GC-MS spectra also indicated no formation of 2-iodo-2-methlpropane (184 *m/z*).

Figure S1: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2a



Figure S2: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2b



Figure S3: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2c





Figure S4: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2d

Figure S5: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2e



Figure S6: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2f



Figure S7: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2g







Figure S9: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2i











Figure S13: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2m



Figure S14: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2n

Figure S15: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 20





Figure S16: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2p





Figure S18: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2r

Figure S19: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2s



Figure S20: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2t



Figure S21: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2u







Figure S23: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2x

Figure S24: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2y





Figure S25: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2z



Figure S26: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Compound 2a'