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### **Supplementary Information**

# Practical Direct Synthesis of N-Aryl-Substituted Azacycles from

### **N-Alkyl Protected Arylamines Using TiCl<sub>4</sub> and DBU**

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$ \begin{array}{c} & H \\ & H $								
1a	2a	3a						
Entry	Aniline	THF	TiCl <sub>4</sub>	DBU	Temp.	Yield <sup>b</sup>		
	(equiv.)	(equiv.)	(equiv.)	(equiv.)		(%)		
1	1	20	1.5	2.0	140 °C	93		
2	1	20	1.5	2.0	130 °C	93		
3	1	20	1.5	2.0	120 °C	93		
4	1	20	1.5	2.0	110 °C	54		
5	1	20	1.5	2.0	100 °C	8		

Table S1. Screening of temperature for preparation of azacycles<sup>a</sup>

<sup>a</sup> Reaction conditions: compound 1a (2.0 mmol), THF 2a (40 mmol), TiCl<sub>4</sub> (3.0 mmol), DBU (4.0 mmol), 14 h
<sup>b</sup> Isolated yield after purification by flash column chromatography.

#### 1-phenylpyrrolidine (3a)



#### <sup>1</sup>H NMR spectrum of 1-phenylpyrrolidine (**3a**)



<sup>13</sup>C NMR spectrum of 1-phenylpyrrolidine (**3a**)

#### 1-*p*-tolylpyrrolidine (3b)



## <sup>1</sup>H NMR spectrum of 1-*p*-tolylpyrrolidine (**3b**)



<sup>13</sup>C NMR spectrum of 1-*p*-tolylpyrrolidine (**3b**)

#### 1-*m*-tolylpyrrolidine (3c)



### <sup>1</sup>H NMR spectrum of 1-*m*-tolylpyrrolidine (3c)





1-(4-methoxyphenyl)pyrrolidine (3d)



<sup>1</sup>H NMR spectrum of 1-(4-methoxyphenyl)pyrrolidine (3d)



<sup>13</sup>C NMR spectrum of 1-(4-methoxyphenyl)pyrrolidine (3d)

1-(4-*tert*-butylphenyl)pyrrolidine (3e)



<sup>1</sup>H NMR spectrum of 1-(4-*tert*-butylphenyl)pyrrolidine (3e)



<sup>13</sup>C NMR spectrum of 1-(4-*tert*-butylphenyl)pyrrolidine (3e)

1-(3,5-dimethylphenyl)pyrrolidine (3f)



<sup>1</sup>H NMR spectrum of 1-(3,5-dimethylphenyl)pyrrolidine (3f)



<sup>13</sup>C NMR spectrum of 1-(3,5-dimethylphenyl)pyrrolidine (3f)

1-(2,6-dimethylphenyl)pyrrolidine (3g)



<sup>1</sup>H NMR spectrum of 1-(2,6-dimethylphenyl)pyrrolidine (**3g**)



<sup>13</sup>C NMR spectrum of 1-(2,6-dimethylphenyl)pyrrolidine (**3g**)

1-(4-chlorophenyl)pyrrolidine (3h)



<sup>1</sup>H NMR spectrum of 1-(4-chlorophenyl)pyrrolidine (3h)



<sup>13</sup>C NMR spectrum of 1-(4-chlorophenyl)pyrrolidine (**3h**)

1-(3-chlorophenyl)pyrrolidine (3i)



## <sup>1</sup>H NMR spectrum of 1-(3-chlorophenyl)pyrrolidine (3i)



<sup>13</sup>C NMR spectrum of 1-(3-chlorophenyl)pyrrolidine (3i)

1-(4-fluorophenyl)pyrrolidine (3j)



### <sup>1</sup>H NMR spectrum of 1-(4-fluorophenyl)pyrrolidine (3j)



<sup>13</sup>C NMR spectrum of 1-(4-fluorophenyl)pyrrolidine (3j)

1-(2,4-difluorophenyl)pyrrolidine (3k)



<sup>1</sup>H NMR spectrum of 1-(2,4-difluorophenyl)pyrrolidine (3k)



<sup>13</sup>C NMR spectrum of 1-(2,4-difluorophenyl)pyrrolidine (3k)

4-(pyrrolidin-1-yl)benzonitrile (3l)



<sup>1</sup>H NMR spectrum of 4-(pyrrolidin-1-yl)benzonitrile (31)



<sup>13</sup>C NMR spectrum of 4-(pyrrolidin-1-yl)benzonitrile (31)

1-(4-nitrophenyl)pyrrolidine (3m)



<sup>1</sup>H NMR spectrum of 1-(4-nitrophenyl)pyrrolidine (3m)



<sup>13</sup>C NMR spectrum of 1-(4-nitrophenyl)pyrrolidine (3m)

1-(naphthalen-1-yl) pyrrolidine (3n)



<sup>1</sup>H NMR spectrum of 1-(naphthalen-1-yl)pyrrolidine (**3n**)



<sup>13</sup>C NMR spectrum of 1-(naphthalen-1-yl)pyrrolidine (**3n**)

2-methyl-1-phenylpyrrolidine (4a)



#### <sup>1</sup>H NMR spectrum of 2-methyl-1-phenylpyrrolidine (4a)



<sup>13</sup>C NMR spectrum of 2-methyl-1-phenylpyrrolidine (4a)

2-methyl-1-m-tolylpyrrolidine (4b)



<sup>1</sup>H NMR spectrum of 2-methyl-1-m-tolylpyrrolidine (4b)



<sup>13</sup>C NMR spectrum of 2-methyl-1-m-tolylpyrrolidine (4b)

1-(3,5-dimethylphenyl)-2-methylpyrrolidine (4c)



<sup>1</sup>H NMR spectrum of 1-(3,5-dimethylphenyl)-2-methylpyrrolidine (**4c**)



<sup>13</sup>C NMR spectrum of 1-(3,5-dimethylphenyl)-2-methylpyrrolidine (4c)

1-(4-fluorophenyl)-2-methylpyrrolidine (4d)



<sup>1</sup>H NMR spectrum of 1-(4-fluorophenyl)-2-methylpyrrolidine (4d)



<sup>13</sup>C NMR spectrum of 1-(4-fluorophenyl)-2-methylpyrrolidine (4d)

#### 1-phenylpiperidine (4e)



### <sup>1</sup>H NMR spectrum of 1-phenylpiperidine (4e)



<sup>13</sup>C NMR spectrum of 1-phenylpiperidine (4e)

#### 2-phenylisoindoline (4f)



<sup>1</sup>H NMR spectrum of 2-phenylisoindoline (4f)



<sup>13</sup>C NMR spectrum of <sup>1</sup>H NMR spectrum of 2-phenylisoindoline (4f)

#### 2-p-tolylisoindoline (4g)



## <sup>1</sup>H NMR spectrum of 2-*p*-tolylisoindoline (**4g**)



<sup>13</sup>C NMR spectrum of 2-*p*-tolylisoindoline (**4g**)

#### 2-(4-ethylphenyl)isoindoline (4h)



<sup>1</sup>H NMR spectrum of 2-(4-ethylphenyl)isoindoline (**4h**)



<sup>13</sup>C NMR spectrum of 2-(4-ethylphenyl)isoindoline (**4h**)

#### 2-(4-chlorophenyl)isoindoline (4i)



<sup>1</sup>H NMR spectrum of 2-(4-chlorophenyl)isoindoline (4i)



<sup>13</sup>C NMR spectrum of 2-(4-chlorophenyl)isoindoline (4i)

2-phenyl-1,2,3,4-tetrahydroisoquinoline (4j)



<sup>1</sup>H NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (4j)



<sup>13</sup>C NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (4j)



2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (4k)

<sup>1</sup>H NMR spectrum of 2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (4k)



<sup>13</sup>C NMR spectrum of 2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (4k)

#### 2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (4l)



<sup>1</sup>H NMR spectrum of 2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (41)



<sup>13</sup>C NMR spectrum of 2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (41)

#### 4-(3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile (4m)



<sup>1</sup>H NMR spectrum of 4-(3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile (**4m**)



<sup>13</sup>C NMR spectrum of 4-(3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile (4m)

#### 1-benzylpyrrolidine (8)



<sup>1</sup>H NMR spectrum of 1-benzylpyrrolidine (8)



<sup>13</sup>C NMR spectrum of 1-benzylpyrrolidine (8)

(1,4-di(pyrrolidin-1-yl)benzene) (11)



<sup>1</sup>H NMR spectrum of (1,4-di(pyrrolidin-1-yl)benzene) (11)



<sup>13</sup>C NMR spectrum of (1,4-di(pyrrolidin-1-yl)benzene) (11)

N-isopropyl-4-(pyrrolidin-1-yl)anilin (12)



<sup>1</sup>H NMR spectrum of *N*-isopropyl-4-(pyrrolidin-1-yl)aniline (12)



<sup>13</sup>C NMR spectrum of *N*-isopropyl-4-(pyrrolidin-1-yl)aniline (12)

1-(4-(pyrrolidin-1-yl)phenyl)piperidine (13)



<sup>1</sup>H NMR spectrum of 1-(4-(pyrrolidin-1-yl)phenyl)piperidine (13)



<sup>13</sup>C NMR spectrum of 1-(4-(pyrrolidin-1-yl)phenyl)piperidine (13)