# **Supporting Information**

# **Copper(I)-Catalyzed Amidation Reaction of Organoboronic Esters and Isocyanates**

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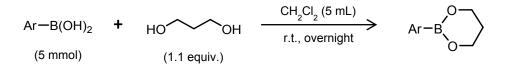
# **Table of Contents**

General information	S2
General procedures for arylboronate esters synthesis and amidation reaction	S2
Table S1 - Organoboron substrate scope	S3
Characterization data for amide products	S3
NMR Spectra	<b>S</b> 8

#### **General Information**

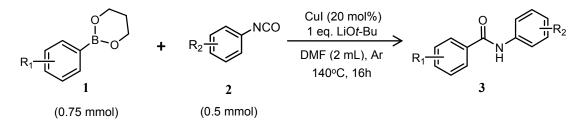
All anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Arylboronate esters were prepared from the corresponding arylboronic acids according to reported procedures<sup>1,2</sup> and other reagents were purchased and used as received. All reactions were carried out under argon atmosphere unless otherwise stated. Analytical thin layer chromatography (TLC) was performed using Merck 60 F-254 silica gel plates. Gas chromatography-mass spectrometry (GC-MS) analyses were performed with Shimadzu GC-2010 coupled with GCMS-QP2010. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF-QII spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AV-400 (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) with the residual solvent peak of tetramethylsilane used as the internal standard at 0.00 ppm. <sup>1</sup>H NMR data are reported in the following order: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constants (*J*, Hz), integration and assignment. NMR yields were determined by using 1,3,5-trimethoxybenzene as internal standard. Isolated yields were determined after purification of the crude product by flash column chromatography.

#### General procedure for the preparation of arylboronate esters<sup>1,2</sup>



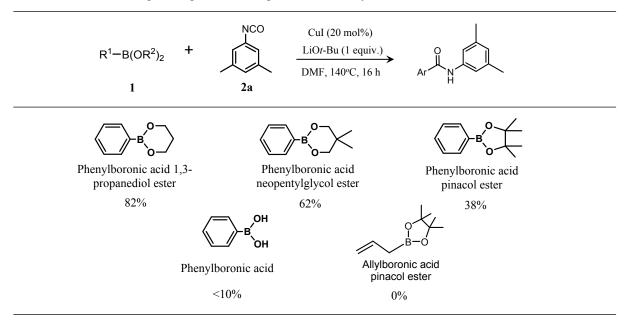
A 20 mL headspace vial was charged with arylboronic acid (5 mmol), 1,3-propanediol (5.5 mmol) and  $CH_2Cl_2$  (5 mL). The reaction mixture was stirred overnight at room temperature and the progress of the reaction was monitored by TLC. The crude reaction mixture was dried over anhydrous  $Na_2SO_4$ , filtered and evaporated to dryness. The residue was then purified by flash column chromatography (hexane/EtOAc) to give the pure product.

#### General procedure for amidation reaction



To a 20 mL headspace vial was added arylboronate ester 1 (0.75 mmol, 1.5 equiv.), CuI (19 mg, 20 mol% Cu), LiOt-Bu (40 mg, 0.5 mmol, 1 equiv.) and anhydrous DMF (2.0 mL) under an argon atmosphere. After the reaction vial was sealed with PTFE/silicone septa, a solution of isocyanate 2 (0.5 mmol, 1 quiv.) was injected using a microsyringe and the reaction mixture was stirred at 140°C for 16 hours. The progress of the reaction was monitored by GC-MS. Upon completion, the reaction was allowed to cool to room temperature before a saturated solution of NH<sub>4</sub>Cl (10 mL) was added. The mixture was then extracted with diethyl ether (3 x 15 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to afford the corresponding amide product **3**.

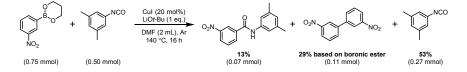
Table S1: Substrate scope of organoboron reagents for Cu-catalyzed amidation reaction.<sup>[a,b]</sup>



[a] Conditions: **1** (0.75 mmol), **2a** (0.5 mmol), CuI (20 mol%), LiO*t*-Bu (0.5 mmol), DMF (2 mL), 140°C, 16 h, Ar atmosphere, unless otherwise noted. [b] Yields determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

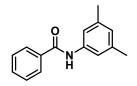
**Gram scale synthesis:** The reaction between organoboronic ester 1a and isocyanate 2a was also scaled up to investigate the scalability of our protocol. Under the optimized reaction conditions, amide 3a was furnished in excellent yield on a 6 mmol scale, demonstrating the synthetic utility and efficiency of our method for the gram-scale synthesis of secondary amides.

## Example of a 3-nitrophenylboronic ester substrate:



#### Characterization data for amide products

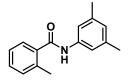
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N-(3,5-Dimethylphenyl)benzamide (3a)<sup>3</sup>
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This compound was prepared according to the general procedure and isolated by column chromatography (hexanes:Et<sub>2</sub>O = 9:1-3:1 gradient elution) to give the product as a white solid (90 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (br s, 1H, NH), 7.83 (d, *J* = 7.5 Hz, 2H, ArH), 7.49 (t, *J* = 7.5 Hz, 1H, ArH), 7.40 (t, *J* = 7.5 Hz, 2H, ArH), 7.27 (s, 2H, ArH), 6.76 (s, 1H, ArH), 2.27 (s,

6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 138.7, 137.8, 135.1, 131.7, 128.7, 127.1, 126.3, 118.2, 21.4. GC-MS: m/z = 225.

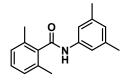
#### N-(3,5-Dimethylphenyl)-2-methylbenzamide (3b)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 4:1$ ) to give the product as a white solid (96 mg, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45-7.43 (m, 2H, ArH + NH), 7.35 (t, *J* = 7.5 Hz, 1H, ArH), 7.25-7.22 (m, 4H, ArH), 6.80 (s, 1H, ArH), 2.49 (s, 3H, CH<sub>3</sub>), 2.32 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.1,

138.9, 137.8, 136.6, 136.4, 131.3, 130.2, 126.6, 126.3, 125.9, 117.6, 21.4, 19.9. HRMS (ESI) m/z 240.1379 (240.1383 calcd for  $C_{16}H_{18}NO [M+H]^+$ ).

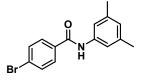
#### *N*-(3,5-Dimethylphenyl)-2,6-dimethylbenzamide (3c)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes:  $Et_2O = 9:1$ ) to give the product as a white solid (82 mg, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28-7.25 (m, 3H, ArH + NH), 7.20 (t, J = 7.5 Hz, 1H, ArH), 7.06 (d, J = 7.5 Hz, 2H, ArH), 6.81 (s, 1H, ArH), 2.38 (s, 6H, CH<sub>3</sub>), 2.33 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 

168.5, 139.0, 137.8, 137.6, 134.4, 129.1, 127.7, 126.5, 117.6, 21.4, 19.3. HRMS (ESI) m/z 254.1531 (254.1539 calcd for  $C_{17}H_{20}NO\ [M+H]^+).$ 

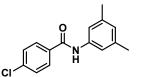
#### *N*-(3,5-Dimethylphenyl)-4-bromobenzamide (3d)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 9:1$ ) to give the product as a white solid (121 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (br s, 1H, NH), 7.68 (d, J = 8.5 Hz, 2H, ArH), 7.51 (d, J = 8.5 Hz, 2H, ArH), 7.24 (s, 2H, ArH), 6.78 (s, 1H, ArH), 2.27 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

 $\delta \ 165.0, \ 138.8, \ 137.5, \ 133.9, \ 131.9, \ 128.8, \ 126.6, \ 126.4, \ 118.3, \ 21.4. \ HRMS \ (ESI) \ m/z \ 304.0335 \ (304.0332 \ calcd \ for \ C_{15}H_{15}BrNO \ [M+H]^+).$ 

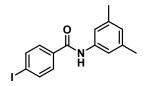
#### N-(3,5-Dimethylphenyl)-4-chlorobenzamide (3e)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 9:1$ ) to give the product as a white solid (96 mg, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (br s, 1H, NH), 7.75 (d, J = 8.5 Hz, 2H, ArH), 7.36 (d, J = 8.5 Hz, 2H, ArH), 7.24 (s, 2H,

ArH), 6.78 (s, 1H, ArH), 2.27 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.9, 138.8, 138.0, 137.5, 133.4, 128.9, 128.6, 126.6, 118.3, 21.4. HRMS (ESI) m/z 260.0828 (260.0837 calcd for C<sub>15</sub>H<sub>15</sub>ClNO [M+H]<sup>+</sup>).

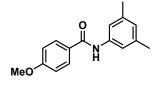
#### *N*-(3,5-Dimethylphenyl)-4-iodobenzamide (3f)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 9:1$ ) to give the product as a white solid (96 mg, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, J = 8.5 Hz, 2H, ArH), 7.76 (br s, 1H, NH), 7.57 (d, J = 8.5 Hz, 2H, ArH), 7.26 (s, 2H, ArH), 6.81 (s, 1H, ArH), 2.32 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 

164.9, 138.9, 138.0, 137.5, 134.5, 128.6, 126.6, 118.3, 98.8, 21.4. HRMS (ESI) m/z 352.0194 (352.0193 calcd for  $C_{15}H_{15}INO [M+H]^+$ ).

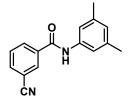
#### *N*-(3,5-Dimethylphenyl)-4-methoxybenzamide (3g)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes:EtOAc = 4:1) to give the product as a white solid (89 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 9.0 Hz, 2H, ArH), 7.75 (br s, 1H, NH), 7.27 (s, 2H, ArH), 6.95 (d, *J* = 9.0 Hz, 2H, ArH), 6.78 (s, 1H, ArH), 3.86 (s, 3H, OCH<sub>3</sub>), 2.31 (s, 6H,

CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.2, 162.4, 138.8, 137.9, 128.9, 127.3, 126.1, 117.9, 113.9, 55.5, 21.4. HRMS (ESI) m/z 256.1330 (256.1332 calcd for C<sub>16</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>).

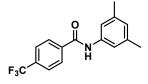
#### *N*-(3,5-Dimethylphenyl)-3-cyanobenzamide (3h)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 2:1$ ) to give the product as a white solid (77 mg, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (br s, 1H, NH), 8.15 (s, 1H, ArH), 8.10 (d, J = 8.0 Hz, 1H, ArH), 7.78 (d, J = 8.0 Hz, 1H, ArH), 7.57 (t, J = 8.0 Hz, 1H, ArH), 7.25 (s, 2H, ArH), 6.80 (s, 1H, ArH), 2.28 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.8, 138.9, 137.2, 136.3, 134.8, 131.7, 130.9,

129.7, 127.0, 118.5, 118.1, 112.8, 21.4. HRMS (ESI) m/z 251.1172 (251.1179 calcd for  $C_{16}H_{15}N_2O$  [M+H]<sup>+</sup>).

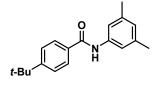
#### *N*-(3,5-Dimethylphenyl)-4-trifluoromethyl-benzamide (3i)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes:EtOAc = 4:1) to give the product as a white solid (102 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (br s, 1H, NH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.67 (d, *J* = 8.5 Hz, 2H, ArH), 7.26 (s, 2H, ArH), 6.81 (s, 1H, ArH), 2.29 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101

MHz, CDCl<sub>3</sub>)  $\delta$  164.6, 138.9, 138.3, 137.3, 133.4 (q, *J* = 33.0 Hz) ,127.5, 126.8, 125.7 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 272.5 Hz), 118.3, 21.4. HRMS (ESI) m/z 294.1105 (294.1100 calcd for C<sub>16</sub>H<sub>15</sub>F<sub>3</sub>NO [M+H]<sup>+</sup>).

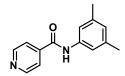
#### *N*-(3,5-Dimethylphenyl)-4-tert-butyl-benzamide (3j)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes:  $Et_2O = 9:1$ ) to give the product as a white solid (116 mg, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80-7.78 (m, 3H, ArH + NH), 7.48 (d, J = 8.5 Hz, 2H, ArH), 7.28 (s, 2H, ArH), 6.78 (s, 1H, ArH), 2.31 (s, 6H, CH<sub>3</sub>), 1.35 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C

NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.6, 155.3, 138.8, 137.9, 132.2, 126.9, 126.2, 125.7, 117.9, 35.0, 31.2, 21.4. HRMS (ESI) m/z 282.1862 (282.1852 calcd for C<sub>19</sub>H<sub>24</sub>NO [M+H]<sup>+</sup>).

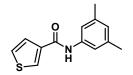
#### *N*-(3,5-Dimethylphenyl)-isonicotinamide (3k)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes:EtOAc = 1:1) to give the product as a white solid (81 mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.77 (d, J = 6.0 Hz, 2H, NCHCH), 8.08 (br s, 1H, NH), 7.71 (d, *J* = 6.0 Hz, 2H, NCH), 7.29 (s, 2H,

ArH), 6.85 (s, 1H, ArH), 2.34 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.7, 150.7, 142.2, 139.0, 137.1, 127.0, 120.9, 118.2, 21.4. HRMS (ESI) m/z 227.1178 (227.1179 calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O  $[M+H]^{+}).$ 

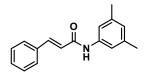
#### *N*-(3,5-Dimethylphenyl)-3-thiophenecarboxamide (31)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 4:1$ ) to give the product as a white solid (67 mg, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (dd, J = 3.0, 1.5 Hz, 1H, SCH), 7.85 (br s, 1H, NH), 7.48 (dd, J = 5.0, 1.5 Hz, 1H, SCH), 7.35 (dd, J

= 5.0, 3.0 Hz, 1H, SCH), 7.24 (s, 2H, ArH), 6.77 (s, 1H, ArH), 2.28 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.3, 138.8, 137.9, 137.6, 129.7, 126.7, 126.3, 126.2, 118.2, 21.4. HRMS (ESI) m/z 232.0788 (232.0791 calcd for C<sub>13</sub>H<sub>14</sub>NOS [M+H]<sup>+</sup>).

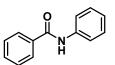
#### *N*-(3,5-Dimethylphenyl)-3-phenyl-(E)-2-propenamide (3m)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 3:1$ ) to give the product as a white solid (50 mg, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d, J = 15.5 Hz, 1H, CH), 7.61 (br s, 1H, NH), 7.50-7.48 (m, 2H, ArH), 7.36-7.34 (m,

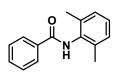
3H, ArH), 7.27-7.26 (m, 2H, ArH), 6.76 (s, 1H, ArH), 6.57 (d, J = 15.5 Hz, 1H, CH), 2.28 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) & 164.1, 142.2, 138.8, 137.9, 134.7, 129.9, 128.9, 128.0, 126.2, 121.1, 117.8, 21.4. HRMS (ESI) m/z 252.1382 (252.1383 calcd for  $C_{17}H_{18}NO [M+H]^+$ ).

#### N-Phenylbenzamide (3n)<sup>4</sup>



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 9:1-4:1$  gradient elution) to give the product as a white solid (76 mg, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.84 (m, 3H, ArH + NH), 7.65 (d, J = 8.0 Hz, 2H, ArH), 7.56 (t, J = 7.5 Hz, 1H, ArH), 7.49 (t, J = 7.5 Hz, 2H, ArH), 7.38 (t, J = 7.5 Hz, 2H, ArH), 7.16 (t, J = 8.0 Hz, 1H, ArH); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.8, 137.9, 135.0, 131.9, 129.2, 128.8, 127.0, 124.6, 120.2. GC-MS: m/z 197.

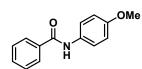
N-(2,6-Dimethylphenyl)benzamide (30)<sup>4</sup>



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 4:1$ ) to give the product as a white solid (92 mg, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90-7.88 (d, J = 7.5 Hz, 2H, ArH), 7.57-7.53 (m, 2H, ArH + NH), 7.46 (t, J = 7.5 Hz, 2H, ArH), 7.16-7.09

(m, 3H, ArH), 2.25 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.0, 135.6, 134.4, 133.9, 131.8, 128.8, 128.3, 127.5, 127.3, 18.5. GC-MS: m/z 225.

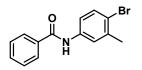
## *N*-(4-Methoxyphenyl)benzamide (3p)<sup>5</sup>



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 3:1$ ) to give the product as a white solid (96 mg, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) & 7.86-7.84 (m, 3H, ArH + NH), 7.55-7.51 (m, 3H, ArH), 7.46 (t, J = 7.0 Hz, 2H, ArH), 6.89 (d, J = 9.0 Hz, 2H, ArH), 3.81 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.7, 156.6, 135.0,

131.7, 131.0, 128.8, 127.0, 122.2, 114.2, 55.5. GC-MS: m/z 227.

### *N*-(4-Bromo-3-methylphenyl)benzamide (3q)



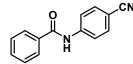
This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 4:1$ ) to give the product as a white solid (106 mg, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (br s, 1H, NH), 7.83 (d, *J* = 7.5 Hz, 2H, ArH), 7.57-7.52 (m, 2H, ArH), 7.47-7.43 (m, 3H,

ArH), 7.32 (dd, *J* = 9.0, 2.5 Hz, 1H, ArH), 2.36 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 138.7, 137.1, 134.7, 132.7, 132.0, 128.8, 127.1, 122.5, 119.8, 119.3, 23.1. HRMS (ESI) m/z 290.0178  $(290.0175 \text{ calcd for } C_{14}H_{13}BrNO [M+H]^+).$ 

#### N-(4-Chlorophenyl)benzamide (3r)<sup>4</sup>

This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: EtOAc = 4:1) to give the product as a white solid (81 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) & 7.87-7.84 (m, 3H, ArH + NH), 7.60 (d, J = 9.0 Hz, 2H, ArH), 7.57 (t, J = 7.5 Hz, 1H, ArH), 7.50  $(t, J = 7.5 \text{ Hz}, 2H, \text{ArH}), 7.34 (d, J = 9.0 \text{ Hz}, 2H, \text{ArH}); {}^{13}\text{C} \text{ NMR} (101 \text{ MHz}, \text{CDCl}_3) \delta 165.7, 136.5,$ 134.6, 132.1, 129.6, 129.2, 128.9, 127.1, 121.4. GC-MS: m/z 231.

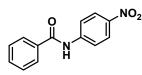
#### N-(4-Cyanophenyl)benzamide (3s)<sup>6</sup>



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 1:1$ ) to give the product as a white solid (73 mg, 66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (br s, 1H, NH), 7.87 (d, J = 7.5 Hz, 2H, ArH), 7.81 (d, J = 9.0 Hz, 2H, ArH), 7.65 (d, J = 9.0

Hz, 2H, ArH), 7.60 (t, J = 7.5 Hz, 1H, ArH), 7.51 (t, J = 7.5 Hz, 2H, ArH); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.0, 142.1, 134.1, 133.4, 132.5, 129.0, 127.2, 120.0, 118.9, 107.3. GC-MS: m/z 222.

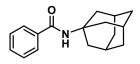
#### *N*-(4-Nitrophenyl)benzamide (3t)<sup>7</sup>



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 3:1$ ) to give the product as a pale yellow solid (64 mg, 53%). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$  10.84 (br s, 1H, NH), 8.28 (d, J = 9.5 Hz, 2H, ArH), 8.08 (d, J =

9.5 Hz, 2H, ArH), 7.99 (d, J = 8.0 Hz, 2H, ArH), 7.63 (t, J = 8.0 Hz, 1H, ArH), 7.57 (t, J = 8.0 Hz, 2H, ArH); <sup>13</sup>C NMR (101 MHz, d<sub>6</sub>-DMSO) δ 166.8, 146.0, 142.9, 134.7, 132.7, 129.0, 128.4, 125.3, 120.3. GC-MS: m/z 242.

#### N-(Adamantan-1-yl)benzamide (3u)



This compound was prepared according to the general procedure and isolated by column chromatography (hexanes: $Et_2O = 4:1$ ) to give the product as a

white solid (99 mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (d, *J* = 8.0 Hz, 2H, ArH), 7.46 (t, *J* = 8.0 Hz, 1H, ArH), 7.40 (t, *J* = 8.0 Hz, 2H, ArH), 5.85 (br s, 1H, NH), 2.13 (s, 9H), 1.72 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.7, 136.0, 131.1, 128.5, 126.7, 52.3, 41.7, 36.4, 29.5. HRMS (ESI) m/z 256.1689 (256.1696 calcd for C<sub>17</sub>H<sub>22</sub>NO [M+H]<sup>+</sup>).

# References

- 1. N. Dastbaravardeh, M. Schnurch and M. D. Mihovilovic, Org. Lett., 2012, 14, 1930-1933.
- 2. S. Oda and H. Yamamoto, Angew. Chem. Int. Ed., 2013, 52, 8165-8168.
- S. M. Johnson, S. Connelly, I. A. Wilson and J. W. Kelly, J. Med. Chem., 2008, 51, 6348-6358.
- 4. L. J. Zhang, S. P. Su, H. P. Wu and S. W. Wang, *Tetrahedron*, 2009, 65, 10022-10024.
- 5. C. A. Faler and M. M. Joullie, *Tetrahedron Lett.*, **2006**, 47, 7229-7231.
- 6. Sasaki, K.; Crich, D., Org. Lett., 2011, 13 (9), 2256-2259.
- Y. Wang, D. P. Zhu, L. Tang, S. J. Wang and Z. Y. Wang, *Angew. Chem. Int. Ed.*, 2011, 50, 8917-8921.

