### SUPPORTING INFORMATION

#### Substrates, Reagents and Catalysts.

Potassium phthalimide, saccharin, sodium methoxide, (PIFA) Phenyliodine bis(trifluoroacetate), (PIDA) Iodobenzene diacetate, methanol, (ACN) acetonitrile, (DCM) dichloromethane, (DCE) dichloroethane, copper triflate, palladium acetate and other copper catalysts were purchased from Sigma Aldrich and Fisher Scientific. Flash chromatography was performed on Silicycle silica gel (60Å, 40-63 µm). All reagents were stored under an inert atmosphere before use.

Preparation of 2- arylpyridine derivatives by literature procedures.



Substrates **6**, **9** and **9f** were purchased from Sigma Aldrich. The other remaining substrates (**9a**, **9b**, **9c**, **9d**, **9g** and **9h**) were prepared via Suzuki coupling using a known procedure.<sup>1</sup> Substrate **9e** was prepared by literature procedure.<sup>2</sup> **9i** was prepared via Suzuki coupling using a literature procedure.<sup>3</sup> Substrate **6-d** was prepared by a known procedure.<sup>4</sup>

### Instrumentation

Microwave reactions were carried out in a CEM Discover microwave. Flash chromatography was performed using CombiFlash<sup>®</sup> Rf 200. GC/MS analysis was carried out on an Agilent Technologies 6890 GC system fixed with a 5973 mass selective detector. NMR spectrum were acquired using a Bruker Avance 300MHz spectrometer.



## Synthesis of phenyliodine(III) bis(phthalimidate) Iodane (3)

A mixture of (4.5 g, 1.04 mmol) phenyliodine(III) bis(trifluoroacetate) and potassium phthalimide (3.7 g, 2.0 mmol) in 100 mL of acetonitrile was stirred at 40  $^{\circ}$ C in an oil bath for 12 h. The off white precipitate was collected, washed with acetonitrile and dried under vaccum to obtain (3.6 g, 70 %) of the phenyliodine (III) bis(phthalimidate), Iodane **3**. The NMR matched with the

one published in literature.<sup>5</sup>

<sup>1</sup>**H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):** 7.84 (s, 5H), 7.76 (s, 3H), 7.69 – 7.64 (m, 1H), 7.53 – 7.32 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 169.21, 137.08, 134.29, 132.57, 130.64, 127.67, 122.90.

LRMS EI (m/z): [M+] calc'd for C<sub>14</sub>H<sub>9</sub>INO<sub>2</sub> [M–Phthalimidate] <sup>+</sup> 349.9672, 349.1 observed m/z



### Synthesis of sodium-saccharin

In a dry round bottom flask, a mixture of saccharin (0.25 g, 1.36 mmol) and sodium methoxide (0.073 g, 1.36 mmol) in 10 mL of methanol under nitrogen

atmosphere was refluxed for 25 minutes in an oil bath. After the reflux, the flask was allowed to cool and then the excess solvent was removed under pressure to get white solid product. (0.26 g, 92.83 %)

LRMS EI (m/z): [M+] calc'd for C<sub>7</sub>H<sub>4</sub>NNa<sub>3</sub>O<sub>3</sub>S 205.1663, observed 206.0 m/z.



### Synthesis of phenyliodine(III) bis(saccharin)Iodane (4)

A mixture of (0.27 g, 0.633 mmol) phenyliodine(III) bis(trifluoroacetate) and sodium saccharin (0.26 g, 1.267 mmol) in 100 mL of acetonitrile was stirred at 40  $^{\circ}$ C in an oil bath for 12 h. The white precipitate was

collected, washed with acetonitrile and dried under vaccum to obtain (0.234 g, 65%) of the phenyliodine(III) bis(saccharin) iodane **4**.

<sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 8.00 – 7.95 (m, 1H), 7.68 – 7.64 (m, 3H), 7.62 – 7.57 (m, 9H).

<sup>13</sup>C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 166.80, 144.13, 133.62, 130.43, 130.30, 129.87, 127.85, 125.35, 121.36, 117.97, 116.95.



Spectrum 1. <sup>1</sup>H NMR of Compound 4



Spectrum 2. <sup>13</sup>C NMR of Compound 4



### Synthesis of Iodonium Triflate salt (5)

A mixture of *m*-chloroperoxybenzoic acid (0.25 g, 1.495 mmol) and iodobenzene (0.3 g, 1.495 mmol) were dissolved in 2 mL dichloromethane in a vial and stirred at room temperature for 5 minutes. Phathalimide (0.2 g,

1.359 mmol) was added to this vial and the vial was cooled to 0  $^{\circ}$ C. This was followed by dropwise addition of triflic acid (0.6 g, 4.078 mmol) to the reaction mixture to give a colored solution. The reaction mixture was later stirred for at room temperature for 30 mins and subsequently concentrated under vacuum. Diethyl ether (2 mL) was added to the vial and the mixture was stirred at room temperature for 10 mins to precipitate out an off-white solid. The solid was filtered off, washed with ether and dried under vacuum to obtain (0.42 g, 61 %) of **5**.

<sup>1</sup>**H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):** δ 8.24 (d, *J* = 7.8 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H)

<sup>13</sup>C NMR (**75** MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 169.22, 140.33, 136.74, 135.14, 134.31, 132.07, 131.74,

127.04, 122.91, 122.77, 118.50, 116.77, 115.95, 114.23, 100.21

**LRMS EI (m/z):** [M+] calc'd for C<sub>14</sub>H<sub>9</sub>INO<sub>2</sub>  $[M-TfO^-]^+$  349.9672, 349.1 observed m/z.



Spectrum 3. <sup>1</sup>H NMR of Compound 5



Spectrum 4. <sup>13</sup>C NMR of Compound 5

## **Initial Optimization Studies**



Entry	R	Conditions	Yield 7/10 (%)
1	Н	<b>3</b> (1 equiv), PIDA (2.5 equiv), ACN, 145 $^{0}$ C (MW), 3h	-
2	Н	<b>3</b> (1 equiv), PIFA (2.5 equiv), ACN, 145 $^{\circ}$ C (MW), 3h	-
3	Η	<b>3</b> (1 equiv), $Pd(OAc)_2$ (25 mol %), ACN, 145 $^{0}C$ (MW), 3h	13
4	Η	<b>3</b> (1 equiv), Cu(OTf) <sub>2</sub> (25 mol %) , DCM, 70 <sup>o</sup> C , 5 h	9
5	Η	<b>3</b> (2.5 equiv), Cu(OTf) <sub>2</sub> (25 mol %) , DCM, 70 $^{0}$ C , 48 h	63
6	Η	<b>3</b> (1 equiv), Cu(OTf) <sub>2</sub> (1 equiv), DCM, 70 $^{0}$ C , 48 h	80
7	Η	<b>3</b> (2.5 equiv), Cu(OTf) <sub>2</sub> (1 equiv) , DCE, 70 $^{0}$ C , 48 h	87
8	Me	<b>3</b> (2.5 equiv), $CuF_2$ (1 equiv), DCE, 80 $^{0}C$ , 48 h	5
9	Me	<b>3</b> (2.5 equiv), CuCl (1 equiv) , DCE, 80 $^{0}$ C , 48 h	6
10	Me	<b>3</b> (2.5 equiv), CuBr (1 equiv) , DCE, 80 $^{0}$ C , 48 h	9
11	Me	<b>3</b> (2.5 equiv), CuBr <sub>2</sub> (1 equiv) , DCE, 80 $^{0}$ C , 48 h	5
12	Me	<b>3</b> (2.5 equiv), CuSO <sub>4</sub> (1 equiv) , DCE, 80 $^{0}$ C , 48 h	5
13	Me	<b>3</b> (2.5 equiv), Cu(NO <sub>3</sub> ) <sub>2</sub> (1 equiv), DCE, 80 $^{0}$ C , 48 h	5
14	Me	<b>3</b> (2.5 equiv), CuCN (1 equiv), DCE, 80 $^{0}$ C , 48 h	5

 Table 1. Initial Optimization Studies

### **General procedure for Substrate Library**

To a solution of the appropriate 2-arylpyridine (1 equiv) in 1,2-dichloroethane (4 mL) was added the appropriate iodane (2.5 equiv) and  $Cu(OTf)_2$  (1 equiv). The reaction was stirred for the 48 h at 80 ° C in an oil bath before dilution with DCM (30 mL) and washing with saturated sodium bicarbonate solution (30 mL). The aqueous phase was extracted further with DCM (25 mL) and the combined organic layers were dried over sodium sulphate and the excess solvent was removed under pressure. The crude residue was purified by flash column chromatography to obtain the pure aminated product.

This general procedure was followed for synthesis of 7, 10, 11, 12, 14, 15, 16, 17, 18, 19 and 20



### Synthesis of 2-(2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (7)

Substrate **6** was subjected to the general procedure. After purification by column chromatography, **7** was obtained (91 mg, 87%). The NMR matched with the one published in literature.<sup>6</sup>

 $R_f$ -Value: Hexane/Ethyl acetate (3:2 v/v) = 0.29.

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.29 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.76 – 7.71 (m, 3H), 7.65 (td, *J* = 7.9, 2.1 Hz, 1H), 7.59-7.54 (m, 2H), 7.47 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.44-7.40 (m, 1H), 7.07 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H).

LRMS EI (m/z): [M+] calc'd for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> 300.0899, 300.11 observed m/z.



## Synthesis of 2-(5-methyl-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (10)

Substrate 9 was subjected to the general procedure. After purification by column chromatography, 10 was obtained (40.2 mg, 88 %). The NMR matched with the one published in literature.<sup>6</sup>

 $R_f$ -Value: Hexane/Ethyl acetate (7:3 v/v) = 0.29.

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.26 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.62 (td, *J* = 7.8, 1.7 Hz, 2H), 7.48 – 7.35 (m, 2H), 7.22 (d, *J* = 1.1 Hz, 1H), 7.03 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 2.46 (s, 3H).

**LRMS EI (m/z):** [M+] calc'd for  $C_{20}H_{14}N_2O_2$  314.1055, 314.19 observed m/z.



Synthesis of 2-(3-methyl-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (11)

Substrate **9a** was subjected to the general procedure. After purification by column chromatography, **11** was obtained (13.1 mg, 40 %). The NMR matched with the one published in literature.<sup>6</sup>

 $R_f$ -Value: Hexane/Ethyl acetate (7:3 v/v) = 0.3.

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.38 (ddd, J = 4.8, 1.7, 1.0 Hz, 1H), 7.83-7.75 (m, 4H), 7.68 (td, J = 7.7, 1.8 Hz, 1H), 7.5 -7.45 (m, 2H), 7.37-7.33 (m, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.14 (ddd, J = 7.6, 4.9, 1.0 Hz, 1H), 2.06 (s, 3H)

LRMS EI (m/z): [M+] calc'd for  $C_{20}H_{14}N_2O_2$  314.1055, 314.19 observed m/z.



# Synthesis of 2-(5-methoxy-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (12)

Substrate **9b** was subjected to the general procedure. After purification by column chromatography, **12** was obtained (22.1 mg, 50%). The NMR matched with the one published in literature.  $^{6}$ 

 $R_f$ -Value: Hexane/Ethyl acetate (7:3v/v) = 0.24.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.49 (d, J = 4.9 Hz, 1H), 8.33 – 8.29 (m, 1H), 8.04 – 7.67 (m,

4H), 7.60 – 7.48 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.05 – 6.99 (m, 2H), 3.82 (s, 3H).

LRMS EI (m/z): [M+] calc'd for C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> 330.1005, observed 330 m/z.



Synthesis of 2-(5-fluoro-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (14)

Substrate **9d** was subjected to the general procedure. After purification by column chromatography, **14** was obtained (16 mg, 37 %). The NMR matched with the one published in literature.<sup>6</sup>

 $R_f$ -Value: Hexane/Ethyl acetate (7:3 v/v) = 0.23

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.28 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.78 – 7.61 (m, 4 H), 7.44 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.31 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.17 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.08 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H).

LRMS EI (m/z): [M+] calc'd for C<sub>19</sub>H<sub>11</sub>F N<sub>2</sub>O<sub>2</sub> 318.0805, 318.01 observed m/z.



## Synthesis of 2-(5-chloro-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (15)

Substrate **9e** was subjected to the general procedure. After purification by column chromatography, **15** was obtained (106.5 mg, 41 %).

 $R_f$  -Value: Hexane/Ethyl acetate (7:3 v/v) = 0.26

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.27 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 – 7.72 (m, 2H), 7.70 – 7.62 (m, 2H), 7.55 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.45 (dd, *J* = 7.3, 1.5 Hz, 2H), 7.08 (ddd, *J* = 7.7, 4.9, 1.2 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 167.3, 156.0, 149.4, 137.0, 136.8, 134.9, 134.2, 131.9, 131.4, 130.8, 130.4, 129.7, 123.7, 122.7, 122.4.

LRMS EI (m/z): [M+] calc'd for  $C_{19}H_{11}Cl N_2O_2$  334.0509, 334.15 observed m/z.



**Spectrum 7.** <sup>1</sup>H NMR of Compound **15** 



Spectrum 8. <sup>13</sup>C NMR of Compound 15



Synthesis of 3-(1,3-dioxoisoindolin-2-yl)-4-(pyridin-2-yl)benzaldehyde (16)

Substrate **9f** was subjected to the general procedure. After purification by column chromatography, **16** was obtained (69.3 mg, 40 %).

 $R_f$ -Value: Hexane/Ethyl acetate (7:3 v/v) = 0.2

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 10.11 (s, 1H), 8.35 – 8.30 (m, 1H), 8.10 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.69 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.14 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 190.7, 167.3, 155.8, 149.5, 143.9, 137.0, 134.3, 131.9, 131.7, 131.4, 130.7, 130.0, 127.9, 123.8, 123.0, 122.9.

LRMS EI (m/z): [M+] calc'd for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub> 328.0848, 328.04 observed m/z.



Spectrum 9. <sup>1</sup>H NMR of Compound 16



**Spectrum 10.** <sup>13</sup>C NMR of Compound **16** 



## Synthesis of 2-(2-(5-nitropyridin-2-yl)phenyl)isoindoline-1,3-dione (17)

Substrate **9i** was subjected to the general procedure as described above. After purification by column chromatography, **17** was obtained (36.3 mg, 27%).  $R_f$ -Value: Dichloromethane = 0.69

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 9.11 (d, *J* = 2.7 Hz, 1H), 8.47 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.87 (dd, *J* = 5.4, 2.9 Hz, 2H), 7.80 – 7.76 (m, 3H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.65 (td, *J* = 6.7, 1.9 Hz, 2H), 7.48 (dd, *J* = 7.3, 1.9 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 167.4, 162.7, 144.6, 136.3, 134.5, 134.4, 132.05, 131.8, 131.0, 130.7, 130.4, 129.9, 129.7, 123.9, 123.6, 123.0.

LRMS EI (m/z): [M+] calc'd for  $C_{19}H_{11}N_3O_4$  345.075, 345.02 observed m/z.



Spectrum 11. <sup>1</sup>H NMR of Compound 17



Spectrum 12. <sup>13</sup>C NMR of Compound 17



## Synthesis of 2-(2-(5-fluoropyridin-2-yl)phenyl)isoindoline-1,3-dione (18)

Substrate **9g** was subjected to the general procedure. After purification by column chromatography, **18** was obtained (152.1 mg, 83 %).

 $R_f$ -Value: Hexane/Ethyl acetate (7:3 v/v) = 0.2.

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.14 (d, *J* = 2.8 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.76 – 7.73 (m, 2H), 7.69 (dd, *J* = 5.7, 3.4 Hz, 1H), 7.57 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.41 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.36 (dd, *J* = 8.5, 2.8 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  167.6, 153.2 (d,  $J_{C-F} = 4.3$  Hz), 137.6 (d,  $J_{C-F} = 4.2$  Hz), 135.8 (d,  $J_{C-F} = 223.7$  Hz), 134.17, 132.7, 132.0, 130.3 (d,  $J_{C-F} = 17.8$  Hz), 129.6, 123.9 (br), 123.8, 123.7, 123.6, 123.5.

LRMS EI (m/z): [M+] calc'd for C<sub>19</sub>H<sub>11</sub>FN<sub>2</sub>O<sub>2</sub> 318.0805, 318.11 observed m/z.



Spectrum 13. <sup>1</sup>H NMR of Compound 18



Spectrum 14. <sup>13</sup>C NMR of Compound 18



## Synthesis of 2-(2-(5-fluoropyridin-2-yl)-5-methylphenyl)isoindoline-1,3dione (19)

Substrate **9h** was subjected to the general procedure as described above. After purification by column chromatography, **19** was obtained (66.6 mg, 34 %).

 $R_f$ -Value: Dichloromethane = 0.81.

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.11 (d, *J* = 2.9 Hz, 1H), 7.87 (td, *J* = 5.6, 3.0 Hz, 4H), 7.76 (td, *J* = 5.3, 3.0 Hz, 4H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 8.7, 2.6 Hz, 2H), 7.22 (d, *J* = 1.8 Hz, 1H), 2.46 (s, 3H).

<sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  168.0, 156.7, 138.6 (d,  $J_{C-F} = 210.6$  Hz), 137.5, 134.66, 134.34, 134.2 (d,  $J_{C-F} = 16.2$  Hz), 132.6, 132.0, 130.6 (d,  $J_{C-F} = 17.3$  Hz), 130.2, 129.3, 123.7, 123.6 (br), 21.1.

LRMS EI (m/z): [M+] calc'd for C<sub>20</sub>H<sub>13</sub>FN<sub>2</sub>O<sub>2</sub> 332.0961, 332 observed m/z.



Spectrum 15. <sup>1</sup>H NMR of Compound 19

0000006-	800000	-700000	-600000	500000	400000	300000	-200000	100000	Ģ	
									N/H/H/H	
									MANAN	
		INPhi								
		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	-п б							5 -
									Ministry (1940	- 8
									NO. NO.	- 6
									Priling In	- 5
									-	
									urine in the	
									, when the	
										- 8
										- 6 (mdd
24'8ZT1									And the second se	- 01
29'221- 29'221- 223'20										- 11
-123'22 -126'30									Milanopala	- 12
91 021 92 021 02 021										- 8
10'221-2 +9'221-7 10'221-7										
+134'34 -134'99 -134'10									Ni-united	14
05'ZET- 86'6ET-									ant (	150 -
29 931-									-	160
66'291										170
									-	180
									and the second	- 6
									-	

**Spectrum 16.** <sup>13</sup>C NMR of Compound **19** 



### Synthesis of 20

Substrate 4 was subjected to the general procedure as described above. After purification by column chromatography, **20** was obtained (10.5 mg, 88 %).  $R_f$ -Value: Hexane/Ethyl acetate (7:3 v/v) = 0.14.

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  8.49 (dt, J = 4.9, 1.4 Hz, 1H), 8.07 (dd, J = 6.8, 1.7 Hz, 1H),

7.94 – 7.81 (m, 4H), 7.70 – 7.58 (m, 5H), 7.14 (ddd, *J* = 6.7, 4.8, 2.1 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 156.3, 149.5, 141.0, 137.8, 136.4, 134.8, 134.3, 131.6, 131.1, 131.0, 129.9, 126.0, 125.6, 123.0, 122.4, 121.2.

**LRMS EI (m/z):** [M+] calc'd for C<sub>19</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub> 336.0569, 336.11 observed m/z.



Spectrum 17. <sup>1</sup>H NMR of Compound 20



**Spectrum 18.** <sup>13</sup>C NMR of Compound **20** 

### **Kinetic Isotope Effect**



To a solution of **6-d** (0.0179 g, 0.114 mmol) in 1,2-dichloroethane (4 mL) was added the iodane **3** (0.142 g, 0.286 mmol) and Cu(OTf)<sub>2</sub> (0.041 g, 0.114 mmol). The reaction mixture was stirred for 48 h at 80  $^{\circ}$ C in an oil bath. The reaction was then cooled, and an aliquot was removed and analyzed by GC/MS.

**GC/MS Conditions:** J & W Scientific DB-1, capillary 25.0m x 200μm x 0.33μm, 1.3 mL/min, 40 °C, hold 0.50min, 12 °C/min to 320 °C, hold 6.0 min.

 $k_{\rm H}/k_{\rm D} = 1.15$ 

## **Competition experiment**



To a solution of equimolar amounts of Py-Ar<sub>1</sub>-H (lequiv) and Py-Ar<sub>2</sub>-H (lequiv) in 1,2dichloroethane (4 mL) was added the iodane **3** (2.5 equiv) and Cu(OTf)<sub>2</sub> (1 equiv). The reaction was mixture was stirred for the 48 h at 80  $^{\circ}$ C in an oil bath. The reaction was then cooled, and an aliquot was removed and analyzed by GC/MS.

Py-Ar <sub>1</sub> -H	Py-Ar <sub>2</sub> -H	Py-Ar <sub>1</sub> -NPhth (%) <sup>[a]</sup>	Py-Ar <sub>2</sub> -NPhth (%) <sup>[a]</sup>
<b>R</b> <sub>1</sub>	<b>R</b> <sub>2</sub>		
Н	Me	42	58
Н	F	92	8
Me	F	94	6
	<b>Ру-Аг<sub>1</sub>-Н</b> <b>R</b> 1 Н Н Ме	Ру-Аг₁-Н         Ру-Аг₂-Н           R₁         R₂           H         Me           H         F           Me         F	Py-Ar <sub>1</sub> -H         Py-Ar <sub>2</sub> -H         Py-Ar <sub>1</sub> -NPhth (%) <sup>[a]</sup> R <sub>1</sub> R <sub>2</sub> $42$ H         Me         42           H         F         92           Me         F         94

[a] Mole fractions determined by GC/MS

### **Calibration Curve**



The pure product **10** was isolated by column chromatography. Known Concentrations in ppm for (1-100% yield) were prepared in DCE. The plot of various concentrations against their area under the curve from GC-MS spectrum generates the calibration curve.



### **References**

- [1] C. Liu, W. Yang, *Chemical Communications* **2009**, 6267-6269.
- [2] S.-H. Kim, R. D. Rieke, *Tetrahedron Letters* 2009, *50*, 5329-5331.
- [3] C. Liu, N. Han, X. Song, J. Qiu, European Journal of Organic Chemistry 2010, 2010, 5548-5551.
- [4] X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *Journal of the American Chemical Society* 2006, *128*, 6790-6791.
- [5] K. Moriyama, K. Ishida, H. Togo, *Organic Letters* **2012**, *14*, 946-949.
- [6] S. Yu, B. Wan, X. Li, Organic Letters 2013, 15, 3706-3709.